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# A carboxylate-bridged Mn(II) compound with 6-methylanthranilate/bipy: Oxidation of alcohols/alkenes and catalase-like activity

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A novel manganese compound,  $[Mn_2(\mu_{1,3}-6-CH_3-2-NH_2C_6H_4COO)_2(bipy)_4](ClO_4)_2$  (bipy = 2,2'bipyridine), was synthesized and used as a catalyst precursor in the oxidation of alkenes and primary alcohols to corresponding aldehydes, ketones, and acids. The six-coordinate compound has a binuclear structure in which two Mn(II) ions adopt a *syn-anti*  $\mu_{1,3}$ -bridging mode with two carboxylate groups and two chelated bipy ligands. The compound exhibits good activity in the oxidation of cyclohexene to 2-cyclohexene-1-one as the major product (93% conv. in 3 h, 79.3% selectivity) and of cinnamyl alcohol to cinnamaldehyde as the major product with 46% selectivity (100% conv. in 1.5 h) with *tert*-butyl hydroperoxide (TBHP) in acetonitrile at 70 °C. Furthermore, the catalase-like activity of the compound was studied in different solvents (acetonitrile, methanol, Tris-HCl buffer; TOF = 29910 h<sup>-1</sup> in Tris-HCl buffer).

Keywords: Manganese; Complex; Catalase; Oxidation; Catalysis

## 1. Introduction

Reactive oxygen species (ROS), such as superoxide anion, hydroxyl radical, and hydrogen peroxide, are generated during aerobic respiration. These ROS are associated with numerous pathological conditions, including atherosclerosis, ischemia, cancer, and Alzheimer's disease as

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well as aging [1]. All living cells, therefore, control ROS levels by using metalloenzymes such as the superoxide dismutases (SODs) and catalases (CATs) [2]. During the past two decades, a wide variety of binuclear manganese complexes has been synthesized to mimic structural features [3-9]. Mn(II) is one of the most interesting metals because of the biomimetic functional model of the catalase enzyme, which has a binuclear manganese compound. In addition, the use of inorganic-organic hybrid compounds as catalysts for the oxidation of alcohols and alkenes is of current interest, and the use of some efficient metal organic frameworks as catalysts has been reported [10-18]. One of the main purposes of catalytic chemistry is to develop new environmentally-friendly catalytic systems that show high atom efficiency without side-products and also replace low-cost first-row transition metal complexes instead of high-cost active platinum-group metal complexes. The coordination chemistry of manganese compound derivatives, especially with chelating neutral N-based and/or O-containing ligands, has been used as a catalyst in hydrocarbon oxidations because of the remarkably versatile redox chemistry of manganese [19-26]. Therefore, the multinuclear  $\mu$ -oxido- and  $\mu$ -carboxylato-bridged manganese complexes have attracted extensive interest in recent decades for selective catalytic oxidations and in bulk oxidation chemistry [27-31].

One of the challenges in this area, particularly from a green chemistry perspective, is the use of molecular oxygen ( $O_2$ ), *t*-BuOOH (*tert*-butylhydro-peroxide), and hydrogen peroxide ( $H_2O_2$ ), the most attractive oxidants because of their high active oxygen species content and coproduction of only water. Published examples of the TBHP and  $H_2O_2$  oxidation of alkenes and alcohols catalyzed with Mn[10] compounds have attracted much interest, but the search for a highly selective environmentally benign alkene oxidation with TBHP remains a challenge [32-36].

As a continuation of our catalytic research, the purpose of this work was to synthesize a new manganese compound with carboxylate and nitrogenous base ligands as oxidation catalysts. Here, we report the synthesis, crystallographic structure, and physical properties of the carboxylate-bridged homobinuclear compound of Mn(II),  $[Mn_2(\mu_{1,3}-6-CH_3-2-NH_2C_6H_4COO)_2(bipy)_4](ClO_4)_2$ , and its successful application as a catalyst precursor toward the disproportionation of  $H_2O_2$  in different solvents and in the oxidation of alkenes (ethylbenzene, cyclohexene, 1-hexene, 1-octene) and primary alcohols (benzyl alcohols, 1-heptanol, cyclohexanol, 1-octanol, cinnamyl alcohol) with TBHP as an oxidant in acetonitrile.

#### 2. Experimental

#### 2.1. Synthesis of compound

A solution of manganese(II) perchlorate hydrate (Mn(ClO<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O) (347.0 mg, 0.96 mmol) in methanol (10 mL) was added to a neutralized solution of 2-amino-6-methylbenzoic acid (145.0 mg, 0.96 mmol) with NaOH (3.0 mL, 0.306 M). After a 1-hour mixing of the solution at 50 °C, bipy (150.0 mg, 0.96 mmol) in methanol (2 mL) was added to the reaction mixture. The final solution was refluxed for five hours, and then the solution was filtered over celite. After solvent evaporation, the product was washed with diethyl ether and then dried under vacuum. The single crystals of the yellow compound were obtained by diethylether diffusion to methanol. The compound is soluble in polar solvents and slightly soluble in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>. Yield 182.0 mg, 61.5%; m.p. 252 °C. Anal. Found (%): C, 54.48; H, 3.46; N, 11.56. Calcd. for C<sub>32</sub>H<sub>27</sub>ClMnN<sub>4</sub>O<sub>8</sub> (%): C, 54.51; H, 3.92; N, 11.35. IR bands (KBr pellet, cm<sup>-1</sup>): 3384 (s), 3071 (s), 1588 (vs), 1468 (vs), 1439 (vs), 1161 (vs), 1079(vs).  $\Delta_M = 318.1$  S cm<sup>2</sup> mol<sup>-1</sup>.

#### 2.2. Materials and measurements

All chemicals were purchased from commercial sources and used as received. IR spectra were measured with a Jasco FT/IR-300 E spectrometer from 4000-400 cm<sup>-1</sup>. UV-vis spectra of compound were recorded on a Shimadzu UV-2450 spectrophotometer. Crystallographic data were collected at room temperature with a Bruker APEX II CCD using Mo-K $\alpha$  radiation and corrected for absorption with SADABS. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F<sup>2</sup>.

### 2.3. Crystallographic analyses

Diffraction data for the compound were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 296(2) K, by using graphite monochromated Mo K $\alpha$  radiation at  $\lambda = 0.71073$  Å. The data reduction was performed with the Bruker SMART program package [37]. The structure was solved by direct methods and the non-hydrogen atoms were located through subsequent difference Fourier syntheses. The SHELXS-97 package was used for structure solution and was refined with SHELXL-97 against F<sup>2</sup> using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms [38]. Hydrogens were added to the

structure model at calculated positions. The molecular drawing was obtained using MERCURY [39]. PLATON program was used for geometric calculations [40].

#### 2.4. Catalase activity

The catalase activity studies were performed by volumetric determination of the oxygen evolved with a gas-volumetric burette (with a precision of 0.1 mL). The  $H_2O_2$ /catalyst ratio was used as 2.500. The catalyst concentration in the reaction mixture is  $6.47 \times 10^{-4}$  M. In a typical experiment, a 30%  $H_2O_2$  aqueous solution ( $9.7 \times 10^{-3}$  mol, 1 mL) was added to closed vessels through the rubber septum using a syringe containing acetonitrile (5.0 mL) solutions of the compound ( $3.88 \times 10^{-6}$  mol). After 10 min of stirring to get a stable temperature, 1 mL of  $H_2O_2$  solution was injected and the volume of evolved dioxygen was measured at time intervals of 1 min. The volume of oxygen gas was calculated using the ideal-gas equation.

### 2.5. General procedure of the catalytic oxidation experiments

The study of catalytic reactions was performed in 50-mL flasks with a temperature controller unit. An oxidant solution of 2 mL was added dropwise to a solution of catalyst and substrate at 70 °C. The substrate-catalyst ratio was kept constant at 265. The reaction mixture was analyzed at certain time intervals with a GC (HP-5) quartz capillary column (30 m  $\times$  0.32 mm  $\times$  0.25 µm) and a FID detector.

#### 3. Results and discussion

#### 3.1. Spectral characterization

The FT-IR spectrum of the compound was recorded by preparing KBr pellets. The bands observed at 1439 and 1588 cm<sup>-1</sup> indicate symmetric and asymmetric vibrations of the carboxylate group. The value of  $\Delta$  (=  $v_{as}$ (COO) -  $v_{s}$ (COO)) = 150 cm<sup>-1</sup> indicates that the carboxylate ligand is coordinated in a bidentate bridging mode [41]. The bipy ligand generates characteristic bands at 1500, 1474 and 1439 cm<sup>-1</sup>. A weak band at 3071 cm<sup>-1</sup> indicates the aromatic C-H stretch vibrations of the bipy ligand. The N-H stretching vibration of the 6-methylanthranilate ligand is observed around 3384 cm<sup>-1</sup>. In the compound spectrum, the observed bands at 1120 cm<sup>-1</sup> and 623 cm<sup>-1</sup> are assigned to the perchlorate anion.

The UV-vis spectrum of the compound was recorded in acetonitrile solution. No

absorption bands exist in the visible region of the spectrum because of the d<sup>5</sup> configuration of the Mn(II) ion. The observed bands at 230 and 294 nm are related to the ligand-centered  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  transitions in the bipy ligands.

Molar conductivity measurements allowed the verification of the compound's stability and the dissociation degree of the compounds in studied solutions. The compound has an  $\Lambda_M$ value of 318.1 S cm<sup>2</sup> mol<sup>-1</sup>, close to the expected value for 1:2 electrolyte in acetonitrile. Thus, in solution, the compound retained its binuclear structure, and the perchlorate anions are not coordinated to the manganese ions.

#### 3.2. Crystal structure

The crystallographic data and corresponding selected bond lengths and angles of the compound are given in tables 1 and 2. The crystal structure of the compound consists of a binuclear cation,  $[Mn_2(\mu_{1,3}-6-CH_3-2-NH_2C_6H_4COO)_2(bipy)_4]^{2+}$ , as shown in figure 1. Two perchlorate anions are outside the complex cation as counterions. Two chemically equivalent units crystallize in a unit structure. Each structure has a center of symmetry. The carboxylate group of the 6-methylanthranilate ligand acts as the  $\mu_{1,3}$ -bidentate bridging mode in a *syn-anti* fashion. Each Mn(II) ion is coordinated by four nitrogen atoms of two bipy ligands and two oxygen atoms of two carboxylate groups. The geometry around the Mn(II) centers is distorted octahedral with coordination angles within the range of 71.5(1)° to 105.6(9)° deviating from 90° and 159.9(1)° to 167.7(1)° deviating from 180°. The bite angles of bipy ligands are 71.5(1)° and 72.0(1)°. The bipy ligand is closer to planarity, as indicated by the C7-C1-C2-C6 torsion angle at 0.51° and the C12-C11-C16-C20 torsion angle at 8.63°.

The Mn-O bond length is similar (2.121(2) Å) and comparable to that of analogous compounds [42-44]. The Mn-N bond lengths are within the range of 2.229(3) to 2.283(3) Å, with an average value of 2.271 Å. The Mn...Mn distance (= 4.825 Å) is significantly longer than those of analogous compounds found in [Mn<sub>2</sub>(OAc)<sub>2</sub>(4-aba)<sub>2</sub>(2,2'-bipy)<sub>2</sub>] (4.081 Å) and [Mn<sub>3</sub>(4-aba)<sub>6</sub>]<sub>n</sub> (3.452(2) Å). The intermolecular weak hydrogen bonds are observed among the oxygen atoms of the perchlorate ion, the carboxylate group, and the hydrogen atom of the amine group.

#### 3.3. Alcohol and alkene oxidation

The Mn(II) compound has been tested for the oxidation of primary alcohols and alkenes to the

corresponding aldehyde, ketones, and carboxylic acids as a homogeneous catalyst precursor. The catalytic reactions were performed under mild conditions (70 °C) in acetonitrile with TBHP as an oxidant. The subs./cat. ratio (265) was kept constant in all catalytic reactions (tables 3 and 4).

In the Mn(II)/TBHP/olefin/CH<sub>3</sub>CN catalytic system, we observed that the most effective among the studied alcohols is cinnamyl alcohol, while cyclohexene is the most reactive among the studied alkenes. The compound has the highest activity for the oxidation of cyclohexene, which is an electron-rich alkene; on the other hand, the catalyst has relatively low activity for the electron-deficient alkene, ethylbenzene. The compound oxidized cyclohexene to cyclohexanone (79.3%) (total conv. 92.8% in 3 h) and other products - 2-cyclohexen-1-ol (1.7%), cyclohexene oxide (4.9%), and 1,2-cyclohexanediol (6.9%) - based on the total yield of products (total conv. 92.8% in 3 h, table 3). The rapid reaction reached a total conversion of 22.2% at 1 minute (TOF: 3556 h<sup>-1</sup>) and a total conversion of 92.8% within 3 h (TOF = 243 h<sup>-1</sup>) (figure 2). Ethyl benzene oxidation shows the slowest kinetic profile among the other olefins (figure 2). Acetophenone was detected in the oxidation of ethylbenzene (18.9% total conv. in 6 h).

In contrast to reported Mn(II) compounds, good results have been obtained for terminal olefins 1-hexene (79.7%) and 1-octene (31.4%). Although 1-hexene is a substrate that is rather hard to oxidize, the compound exhibits very high activity for the oxidation of 1-hexene, affording 35.8% 2,5-hexenedione as a major product with the formation of other products; 15.2% 1-hexene-3-one and 28.7% 2-hexanal. The oxidation of 1-octene was catalyzed by the compound to yield hexanoic acid (19.9%) and 1-octen-3-one (11.5%) after 24 h. The TOF value of the compound is 212 h<sup>-1</sup> for 1-hexene oxidation and 83 h<sup>-1</sup> for 1-octene oxidation after a 24-h reaction time (table 3).

The Mn(II)/TBHP/alcohol/CH<sub>3</sub>CN catalytic system exhibits very high activity for the oxidation of cinnamyl alcohol, moderate activity for benzyl alcohol and cyclohexanol, and very low activity for 1-octanol and 1-heptanol. The time-dependent catalytic activity results are shown in figure 3 and table 4. Among the studied alcohols, the catalytic oxidation of cinnamyl alcohol resulted in ~100% conversion in 90 min (TON ~ 266 h<sup>-1</sup>). The catalytic rate of cinnamyl alcohol oxidation is extremely high: TOF = 11057 h<sup>-1</sup> in the first minute of the reaction. Other reaction products of cinnamyl alcohol are benzaldehyde (46.3%), cinnamyl aldehyde (15.9%), styrene (14.2%), benzoic acid (14.0%), and 3-phenylglycidol (5.9%). Primary aliphatic alcohols (1-heptanol and 1-octanol) were oxidized to carboxylic acids as their secondary oxidation

products, whereas secondary alcohol (cyclohexanol) was oxidized to cyclohexanone (43.6% in 6 h) without a carbon-carbon chain cleavage (table 4). These results support the reports that the compound is more reactive in the oxidation of benzylic alcohols than that of aliphatic alcohols [45]. Benzaldehyde and benzoic acid were detected during the catalytic oxidation of benzyl alcohol. After a 24-h reaction, the total conversion was recorded at 80.2% for benzyl alcohol oxidation with an aldehyde selectivity of 46.6% (table 4).

#### 3.4. Catalase activity

The disproportionation of hydrogen peroxide to water and oxygen (catalase activity) was studied with a Mn(II) compound at 25 °C (table 5). The catalase activity was studied in a solvent (5 mL) with the compound  $(3.88 \times 10^{-6} \text{ mol})$  and  $9.7 \times 10^{-3}$  mol of H<sub>2</sub>O<sub>2</sub>. The same procedure was repeated in different solvents. The blank experiment, performed without the catalyst, showed a negligible decomposition of H<sub>2</sub>O<sub>2</sub>. The initial solution of the compound was colorless, and after H<sub>2</sub>O<sub>2</sub> was added, it became yellow, and an immediate evolution of oxygen was observed. The catalytic activity of Mn(ClO<sub>4</sub>)<sub>2</sub> toward H<sub>2</sub>O<sub>2</sub> decomposition was tested under similar conditions used for compound synthesis; ~1% of the H<sub>2</sub>O<sub>2</sub> decomposition was observed. Observed initial rates were expressed as mL s<sup>-1</sup>, taking the volume of the evolved oxygen into account and calculated from the maximum curve slope describing the evolution of O<sub>2</sub> *vs*. the time graph (table 5). The initial rates are strongly dependent on the solvent. The induction period was not observed in any of the studied solvents.

The catalytic activities of the compound toward  $H_2O_2$  disproportionation were investigated in acetonitrile, methanol, and a Tris-HCl buffer (table 5 and figure 4). The highest activity was observed with 87.5% disproportionation (23×10<sup>-4</sup> mL s<sup>-1</sup> and TOF = 29910 h<sup>-1</sup>) in the Tris-HCl buffer, which corresponds to the physiological conditions of the cell environment. This result suggests that the compound would also be an active catalyst *in vitro*. The rate of decomposition is almost 16 times and 49 times faster in the Tris-HCl buffer than in the acetonitrile and methanol solutions, respectively.

We observed the systematic correlation between compound activity and the relative dielectric constants of solvents; the activity increases in the order of the relative dielectric constants: Tris-HCl buffer (TOF = 29910 h<sup>-1</sup>,  $v_i$  = 383×10<sup>-3</sup> mL s<sup>-1</sup>) > acetonitrile (TOF = 773 h<sup>-1</sup>,  $v_i$  = 23.5×10<sup>-3</sup> mL s<sup>-1</sup> > methanol (TOF = 577 h<sup>-1</sup>,  $v_i$  = 4.3×10<sup>-3</sup> mL s<sup>-1</sup>). The observed

activity in different solvents indicates that Mn(II) solvent coordination is necessary for the catalytic cycle.

#### 4. Conclusion

A novel Mn(II) compound,  $[Mn_2(\mu_{1,3}-6-CH_3-2-NH_2C_6H_4COO)_2(bipy)_4](ClO_4)_2$ , with 6-methylanthranilate and bipy has been synthesized, and the solid-state structure was characterized through X-ray crystallography. The Mn(II) compound exhibited catalytic activity as a homogeneous catalyst precursor for the oxidation of various alkenes and primary alcohols, with a low-to-good yield under mild reaction conditions (70 °C) in acetonitrile and with TBHP as an oxygen source. All studied primary alcohols were selectively oxidized to corresponding aldehydes and overoxidized product carboxylic acids. Linear secondary alcohols were converted into corresponding ketones in a very low yield, whereas the complex showed higher activity in the oxidation of benzylic alcohol (1-phenylethanol) to acetophenone in a very good yield (73% in 6 h). Moreover, the homobinuclear Mn(II) compound exhibited remarkable activity (383×10<sup>-3</sup> mL s<sup>-1</sup> and TOF up to 29910 h<sup>-1</sup>) in the Tris-HCI buffer at room temperature.

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CCDC 993362 contains the supplementary crystallographic data for compound. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: <a href="mailto:deposit@ccdc.cam.ac.uk">deposit@ccdc.cam.ac.uk</a>.

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Figure 2. Alkene oxidation of Mn(II) compound with TBHP at 70 °C in acetonitrile.



Figure 3. Primary alcohol oxidation of Mn(II) compound with TBHP at 70 °C in acetonitrile.



Figure 4. Time dependence of  $O_2$  evolution upon reaction of the compound with  $H_2O_2$  in different solvents.

Empirical formula	$C_{56}H_{48}Cl_2Mn_2N_{10}O_{12}$
MW	1233.82
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Color	Yellow
Crystal system	Triclinic
Space group	P-1
a (Å)	12.840(5)
b (Å)	14.794(5)
c (Å)	15.839(6)
α (°)	87.245(6)
β (°)	70.002(5)
γ (°)	87.716(6)
Volume, V (Å <sup>3</sup> )	2823.3(18)
Z	2
Density (mg m <sup>-3</sup> )	1.456
Absorption coefficient (mm <sup>-1</sup> )	0.613
$\theta$ range for data collection (°)	1.69 to 28.21
Goodness-of-fit on F <sup>2</sup>	0.982
R indices (all data)	R1 = 0.0928, $wR2 = 0.0619$
Largest diff. peak and hole	1.093 and -0.550 e A <sup>-3</sup>
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0619, wR_2 = 0.1798$

Table 1. Crystal data and structure refinement parameters of compound.

Compound part 1A		Compound part 1B*	
Mn(1)-O(1)	2.121(2)	Mn(2)-O(4)	2.113(2)
Mn(1)-O(2)	2.154(2)	Mn(2)-O(3)	2.145(2)
Mn(1)-N(2)	2.241(3)	Mn(2)-N(7)	2.229(3)
Mn(1)-N(1)	2.302(3)	Mn(2)-N(6)	2.280(3)
Mn(1)-N(4)	2.305(3)	Mn(2)-N(9)	2.261(3)
Mn(1)-N(3)	2.271(3)	Mn(2)-N(8)	2.283(3)
O(2)-Mn(1)-N(3)	95.67(10)	O(4)-Mn(2)-N(7)	100.57(10)
N(2)-Mn(1)-N(3)	160.13(10)	O(4)-Mn(2)-N(9)	91.67(10)
O(1)-Mn(1)-N(1)	97.79(9)	N(7)-Mn(2)-N(9)	163.13(11)
O(2)-Mn(1)-N(1)	167.74(10)	O(3)-Mn(2)-N(6)	167.36(11)
N(3)-Mn(1)-N(1)	93.19(10)	N(9)-Mn(2)-N(6)	94.84(11)
O(2)-Mn(1)-N(4)	85.58(10)	O(3)-Mn(2)-N(8)	80.91(10)
N(3)-Mn(1)-N(4)	71.54(10)	N(9)-Mn(2)-N(8)	71.86(10)
O(1)-Mn(1)-O(2)	90.82(9)	O(4)-Mn(2)-O(3)	95.57(9)
O(1)-Mn(1)-N(2)	105.63(9)	O(3)-Mn(2)-N(7)	98.56(10)
O(2)-Mn(1)-N(2)	97.28(10)	O(3)-Mn(2)-N(9)	91.70(10)
O(1)-Mn(1)-N(3)	89.15(9)	O(4)-Mn(2)-N(6)	95.04(10)
N(2)-Mn(1)-N(1)	72.03(10)	N(7)-Mn(2)-N(6)	72.71(10)
O(1)-Mn(1)-N(4)	159.85(9)	O(4)-Mn(2)-N(8)	162.94(9)
N(2)-Mn(1)-N(4)	94.49(10)	N(7)-Mn(2)-N(8)	96.46(10)
N(1)-Mn(1)-N(4)	89.21(10)	N(6)-Mn(2)-N(8)	90.85(11)

Table 2. Selected bond lengths (Å) and angles (°) of compound 1.

\*The second unit parameters

A CONTRACTOR

Substrate	Product distribution	Conv.	Time	Total conv.	TON
		(%)	(h)	(%)	(h <sup>-1</sup> )
Cyclohexene	Cyclohexene oxide	4.9			
	2-Cyclohexene-1-one	79.3	3	92.8	246
	2-Cyclohexene-1-ol	1.7			240
	1,2-Cyclohexanediol	6.9			$\mathcal{Q}$
Ethylbenzene	Acetophenone	18.9	6	18.9	50
	1-Hexen-3-one	15.2		$\mathcal{C}$	
1-Hexene	2-Hexenal	28.7	24	79.7	212
	2,5-Hexanedione	35.8		$\mathcal{O}^{-}$	
1-Octene	Hexanoic acid	19.9	2	31.4	83
	1-Octen-3-one	11.5		51.4	05

Table 3. Oxidation of alkenes with Mn(II)/TBHP/acetonitrile system.

Reaction conditions:  $1.46 \times 10^{-2}$  mol of oxidant,  $4.3 \times 10^{-3}$  mmol of catalyst, subst./cat. = 266, T = 70 °C, TON = number of moles of product per mole of catalyst.

Substrate	Products	Conv.	Time	Total conv.	TON
		(%)	(h)	(%)	$(h^{-1})$
	Cinnamyl aldehyde	15.9			
Cinnamyl alcohol	Benzaldehyde	46.3			$\square$
	Styrene	14.2	1.5	100	266
	Benzoic acid	14			2
	3-Phenylglycidol	5.9			$\rightarrow$
Cyclohexanol	Cyclohexanone	43.6	6	43.6	116
Hantanal	Heptanal	12.4	6 6	15.5	41
Heptanol	Heptanoic acid	3.1			
	Octanal	2.0	())		
1-Octanol	Octanoic acid	2.5		14.5	30
	Heptanal	7.2	0	14.5	39
	Heptanoic acid	2.8			
Benzyl alcohol	Benzaldehyde	37.4	24	80.2	213
	Benzoic acid	42.8	<b>∠न</b>	00.2	213

Table 4. Oxidation of alcohols with Mn(II)/TBHP/acetonitrile system.

Reaction conditions:  $1.46 \times 10^{-2}$  mol of oxidant,  $4.3 \times 10^{-3}$  mmol of catalyst, subst./cat. = 266, T = 70 °C, solvent = acetonitrile

Solvent	Total O <sub>2</sub> (mL)	$v_{i} \times 10^{-3} (mL s^{-1})$	TON (h <sup>-1</sup> )	TOF (h <sup>-1</sup> )
Methanol	34	4.3	346	577
Acetonitrile	76	23.5	773	3092
Tris-HCl Buffer	98	383	997	29910

Table 5.  $H_2O_2$  disproportionation with 1 in different solvents.

Reaction conditions: T = 25 °C,  $H_2O_2 = 9.7 \times 10^{-3}$  mol, catalyst =  $3.88 \times 10^{-6}$  mol, solvent = 5 mL

# **Graphical abstract**

