

# Bis( $\mu$ -hydroxo) bridged di-vanadium-catalyzed selective epoxidation of alkenes with $\text{H}_2\text{O}_2$

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## Abstract

The Keggin-type di-vanadium-substituted silicotungstate  $[\gamma\text{-}1,2\text{-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{4-}$  with the  $\{\text{VO}(\mu\text{-OH})_2\text{-VO}\}$  core catalyzes the epoxidation of various alkenes using only 1 equiv.  $\text{H}_2\text{O}_2$  with the high epoxide yield and high efficiency of  $\text{H}_2\text{O}_2$  utilization under very mild reaction conditions. Notably, this system shows unique stereospecificity, diastereoselectivity, and regioselectivity, which are quite different from those reported for the epoxidation systems including  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ .

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**Keywords:** Alkene; Epoxidation; Hydrogen peroxide; Polyoxometalate; Vanadium

## 1. Introduction

Vanadium is an important element in biology, inorganic chemistry and organic syntheses [1–7], and can heterogeneously or homogeneously catalyze selective oxidation reactions of alkanes, alkenes, aromatics, alcohols, halides, etc. [1–3,6–12]. While the homogeneous oxidation catalysis by mono- and di-vanadium complexes has extensively been studied, scarcely is known of the oxidation catalysis by bis( $\mu$ -hydroxo) bridged di-vanadium compounds [1,2,6,7,13,14]. In addition, even mono-vanadium complexes could not efficiently catalyze the epoxidation of alkenes with a green oxidant of  $\text{H}_2\text{O}_2$  because of the contribution of the radical mechanism; for example, the oxidation of cyclohexene with  $\text{H}_2\text{O}_2$  catalyzed by vanadium-based catalysts proceeded mainly at the allylic position to give the corresponding enol and enone (allylic oxidation) [8–12] and the efficiency of  $\text{H}_2\text{O}_2$  utilization is intrinsically low. Therefore, vanadium-catalyzed  $\text{H}_2\text{O}_2$ -based epoxidation of alkenes with high selectivity to the epoxide and high efficiency of  $\text{H}_2\text{O}_2$  utilization is previously unknown while it is well known that other transition metals such as tungsten, manganese, and iron show relatively high activity, selectivity, and efficiency of  $\text{H}_2\text{O}_2$  utilization [15].

Here, we report that the  $[\gamma\text{-}1,2\text{-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{4-}$  (**I**) with the  $\{\text{VO}(\mu\text{-OH})_2\text{-VO}\}$  core can efficiently catalyze epoxidation of alkenes using only 1 equiv.  $\text{H}_2\text{O}_2$  with the high epoxide yield and high efficiency of  $\text{H}_2\text{O}_2$  utilization [16]. Notably, this system shows unique stereospecificity, diastereoselectivity, and regioselectivity, which are quite different from those reported for the epoxidation systems [16].

## 2. Results and discussion

The scope of the present epoxidation by tetra-*n*-butylammonium salt of **I** (TBA-**I**) with regard to various kinds of mono-alkenes using 1 equiv.  $\text{H}_2\text{O}_2$  (except for gaseous alkenes such as propene and 1-butene) was examined. The results are summarized in Table 1. Under the present reaction conditions, neither allylic oxidation nor hydrolysis of epoxides proceeded in all cases. The epoxidation did not proceed at all in the absence of catalyst (entry 8). Mono- and tri-vanadium substituted compounds and fully occupied silicotungstate were completely inactive under the present conditions (entries 5–7). By using TBA-**I**, non-activated aliphatic terminal alkenes including propene could be transformed to the corresponding epoxide with high selectivity and efficiency of  $\text{H}_2\text{O}_2$  utilization (entries 1–4, and 11). A larger-scale reaction (50-fold scaled up) for 1-octene showed the same results as those for the small-scale experiments in Table 1 (99% selectivity to 1,2-epoxyoctane,

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Table 1  
Epoxidation of various alkenes with H<sub>2</sub>O<sub>2</sub><sup>a</sup>

Entry	Catalyst	Alkene	Yield (%)	Product (selectivity (%))	H <sub>2</sub> O <sub>2</sub> efficiency <sup>b</sup> (%)
1 <sup>c</sup>	TBA-I	Propene	87	1,2-Epoxypropane (99)	87
2 <sup>c</sup>	TBA-I	1-Butene	91	1,2-Epoxybutane (99)	91
3	TBA-I	1-Hexene	92	1,2-Epoxyhexane (99)	92
4	TBA-I	1-Octene	93	1,2-Epoxyoctane (99)	93
5 <sup>d</sup>	[ $\alpha$ -SiVW <sub>11</sub> O <sub>40</sub> ] <sup>5-</sup>	1-Octene	<1	–	–
6 <sup>d</sup>	[ $\alpha$ -1,2,3-SiV <sub>3</sub> W <sub>9</sub> O <sub>40</sub> ] <sup>7-</sup>	1-Octene	<1	–	–
7 <sup>d</sup>	[ $\gamma$ -SiW <sub>12</sub> O <sub>40</sub> ] <sup>4-</sup>	1-Octene	<1	–	–
8	None	1-Octene	<1	–	–
9	TBA-I	<i>cis</i> -2-Octene	90	<i>cis</i> -2,3-Epoxyoctane (99, only <i>cis</i> )	90
10	TBA-I	2-Methyl-1-heptene	88	1,2-Epoxy-2-methylheptane (98)	90
11	TBA-I	1-Decene	93	1,2-Epoxydecane (99)	93
12	TBA-I	Styrene	88	Styrene oxide (99)	88
13	TBA-I	Cyclohexene	90	1,2-Epoxy cyclohexane (99)	92
14	TBA-I	Cyclooctene	93	1,2-Epoxy cyclooctane (99)	93

<sup>a</sup> Reaction conditions: alkene (33.3 mM), catalyst (1.67 mM), H<sub>2</sub>O<sub>2</sub> (30% aq., 33.3 mM), CH<sub>3</sub>CN/*t*-BuOH (1.5/1.5 mL), 293 K, 24 h. Yields and selectivities were determined by gas chromatography or <sup>1</sup>H NMR using an internal standard technique and were based on alkenes.

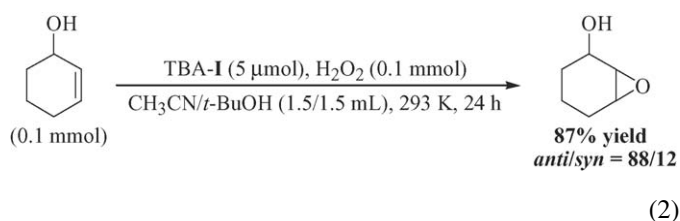
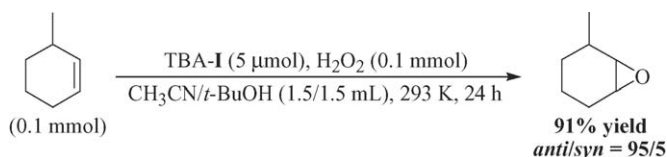
<sup>b</sup> H<sub>2</sub>O<sub>2</sub> efficiency (%) = [products (mol)/consumed H<sub>2</sub>O<sub>2</sub> (mol)] × 100.

<sup>c</sup> Propene (6 atm), 1-butene (3 atm).

<sup>d</sup> Tetra-*n*-butylammonium salts were used.

93% GC yield, and 86% isolated yield). The reaction rate increased with increase in the reaction temperature, and the TOF reached up to 38 h<sup>-1</sup> at 313 K, keeping the selectivity to 1,2-epoxyoctane as high as >99%, while the efficiency of H<sub>2</sub>O<sub>2</sub> utilization was a little decreased from 93% (293 K) to 85% (313 K). The catalytic epoxidation of cyclic alkenes such as cyclohexene and cyclooctene also efficiently proceeded to afford the corresponding epoxides in high yields (entries 13 and 14). The interesting point is that styrene (both styrene and styrene oxide are unstable under acidic conditions) was highly selectively epoxidized to styrene oxide without any by-products (entry 12).

For the competitive epoxidation of *cis*- and *trans*-2-octenes (100  $\mu$ mol each, the other conditions were the same as those in Table 1), the initial rates for the epoxidation of *cis*- and *trans*-2-octene were 0.32 and 0.001 mM min<sup>-1</sup>, respectively. The ratio of the formation rate of *cis*-2,3-epoxyoctane to that of the *trans* isomer was >300 and the value is much larger than those (1.3–11.5) reported for the other stereospecific epoxidation systems [17]. In this case, the configuration around the C=C moieties was completely retained in the corresponding epoxides. The epoxidation of 3-substituted cyclohexenes such as 3-methyl-1-cyclohexene and 2-cyclohexen-1-ol showed unusual diastereoselectivities; the epoxidation was highly diastereoselective and gave the corresponding epoxides with oxirane ring *trans* to the substituents (*anti* configuration) [Eqs. (1) and (2)].



Further, it is noted that more accessible, but less nucleophilic double bonds in non-conjugated dienes such as *trans*-1,4-hexadiene, *R*-(+)-limonene, 7-methyl-1,6-octadiene, and 1-methyl-1,4-cyclohexadiene were highly regioselectively epoxidized. The results for the epoxidation of dienes with H<sub>2</sub>O<sub>2</sub> catalyzed by TBA-I are shown in Table 2. For the *trans*-1,4-hexadiene epoxidation (entry 1), the [terminal epoxide]/[total epoxide] ratio was >0.99 and much higher than those reported for the epoxidation with NaOCl or PhIO; Mn(TTPPP)(OAc)/NaOCl (0.35) [18], Mn(T(2',6'-G1Ph)P)Cl/PhIO (0.20) [19], Mo(CO)<sub>6</sub>/CHP (0.14) [20], Mn(TPP)(OAc)/NaOCl (0.03) [18], and Mn(T(3',5'-G2Ph)P)Cl/PhIO (0.03) [21]. In addition, for the (*R*)-(+)-limonene epoxidation (entry 2), the [8,9-epoxide]/[total epoxide] ratio was 0.99 and the value was much higher than those reported for the epoxidation with H<sub>2</sub>O<sub>2</sub> by PhCN/KHCO<sub>3</sub> (0.37) [22], and Ti-beta zeolite (0.55) [23]. The comparison with sterically hindered porphyrin systems with NaOCl or PhIO shows that the regioselectivity for TBA-I is higher than the values reported (0.62–0.75) [18,24–26]. Similarly, in the case of 7-methyl-1,6-octadiene (entry 3), the [terminal epoxide]/[total epoxide] was 0.93 and the value was much higher than those for the H<sub>2</sub>O<sub>2</sub>-based epoxidation systems of Al<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (<0.01) [27], CF<sub>3</sub>CH<sub>2</sub>OH/Na<sub>2</sub>HPO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (<0.01) [28], and (CF<sub>3</sub>)<sub>2</sub>CO/C<sub>2</sub>F<sub>5</sub>OH/NaHPO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (<0.01) [29].

Next, the regioselectivity for the epoxidation of dienes by TBA-I is compared with those by various tungstate

Table 2  
Epoxidation of various dienes with H<sub>2</sub>O<sub>2</sub> catalyzed by TBA-I<sup>a</sup>

Entry	Diene	Product (yield (%))	[Less substituted epoxide]/[total epoxide]	H <sub>2</sub> O <sub>2</sub> efficiency <sup>b</sup> (%)
1	<i>trans</i> -1,4-Hexadiene	1,2-Epoxy- <i>trans</i> -4-hexene (91)	>0.99	91
2	( <i>R</i> )-(+)-Limonene	8,9-Epoxy- <i>limonene</i> (89) Diepoxide (1)	0.99	91
3	7-Methyl-1,6-octadiene	7-Methyl-1,2-epoxy-6-octene (77) 7-Methyl-6,7-epoxy-1-octene (5) Diepoxide (4)	0.93	87
4	1-Methyl-1,4-cyclohexadiene	1-Methyl-4,5-epoxy-1-cyclohexene (71) 1-Methyl-1,2-epoxy-4-cyclohexene (5)	0.88	81

<sup>a</sup> Reaction conditions: diene (33.3 mM), TBA-I (1.67 mM), H<sub>2</sub>O<sub>2</sub> (30% aq., 33.3 mM), CH<sub>3</sub>CN/*t*-BuOH (1.5/1.5 mL), 293 K, 24 h. Yields and selectivities were determined by gas chromatography or <sup>1</sup>H NMR using an internal standard technique and were based on diene.

<sup>b</sup> H<sub>2</sub>O<sub>2</sub> efficiency (%) = [products (mol)/consumed H<sub>2</sub>O<sub>2</sub> (mol)] × 100.

compounds (Fig. 1). For example, the regioselectivity for (*R*)-(+)-limonene with H<sub>2</sub>O<sub>2</sub> was much higher than those with [γ-SiW<sub>10</sub>O<sub>34</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>4-</sup> ([8,9-epoxide]/[total epoxide] = 0.37), [W(=O)(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>(μ-PO<sub>4</sub>)<sup>3-</sup> (0.03), and [W(=O)(O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sub>2</sub>(μ-O)<sup>2-</sup> (0.18), which are reported to be active for the epoxidation with H<sub>2</sub>O<sub>2</sub> [30–32]. Similarly, the regioselectivities for the epoxidation of *trans*-1,4-hexadiene, 1-methyl-1,4-cyclohexadiene, and 7-methyl-1,6-octadiene were much different from those for the other tungstate compounds.

The relative reactivity (rate) of a series of C<sub>8</sub>-alkenes decreased in the order of 2-methyl-1-heptene (1.1) > 1-octene (1.0 taken as unity) > *cis*-2-octene (0.87) > 2-methyl-2-heptene (0.03) > *trans*-2-octene (<0.01) (Table 3). This order is not consistent with that of the π(C=C) HOMO energies of C<sub>8</sub>-olefins because the π(C=C) HOMO energies decreased with increase in numbers of the alkyl substituents in alkenes [33]. Therefore, the inconsistency of the orders between the π(C=C) HOMO energy and the reactivity would be caused by the steric constraints of the active site of **I**, that is, an active oxygen species formed by the reaction of **I** with H<sub>2</sub>O<sub>2</sub> is embedded in the polyoxometalate framework.

Table 3  
Initial and relative rates for the epoxidation of a series of C<sub>8</sub>-alkenes with H<sub>2</sub>O<sub>2</sub> catalyzed by TBA-I<sup>a</sup>

Entry	Alkene	R <sub>0</sub> (μM min <sup>-1</sup> )	Relative rate <sup>b</sup>
1	2-Methyl-1-heptene	420	1.1
2	1-Octene	384	1.0
3	<i>cis</i> -2-Octene	334	0.87
4	2-Methyl-2-heptene	10	0.03
5	<i>trans</i> -2-Octene	<1.4	<0.01

<sup>a</sup> Reaction conditions: alkene (33.3 mM), **I** (tetrabutylammonium salt, 1.67 mM), H<sub>2</sub>O<sub>2</sub> (30% aq., 33.3 mM), CH<sub>3</sub>CN/*t*-BuOH (1.5/1.5 mL), 293 K. Initial rates (R<sub>0</sub>) were determined from the reaction profiles at low conversion (<10%) of hydrogen peroxide.

<sup>b</sup> The R<sub>0</sub> value obtained with 1-octene was taken as unity.

No significant changes of in situ IR spectra were observed during the catalytic epoxidation by TBA-I with H<sub>2</sub>O<sub>2</sub>. On the other hand, a H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/H<sub>2</sub>O<sub>2</sub>/alkene mixture exhibited a drastic change of the spectral pattern due to the conversion of [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> to [W(=O)<sub>2</sub>(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>(μ-PO<sub>4</sub>)<sup>3-</sup> and [W(=O)(O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sub>2</sub>(μ-O)<sup>2-</sup>. The first-order dependence of the reaction rate on the concentration of TBA-I

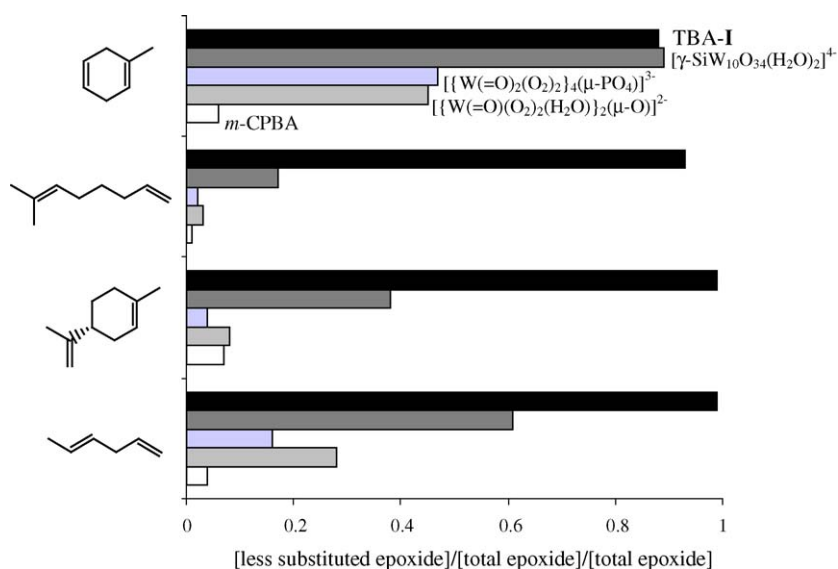


Fig. 1. Ratio of less substituted epoxides to total epoxides formed by the epoxidation of various dienes.

and the fact that the regioselectivity for TBA-I was much different from those for the other tungstates show that the fragmentation of TBA-I does not occur during the catalytic process. In addition, it was confirmed by *in situ* IR and NMR measurements that the tungstate compounds such as  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$  and  $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$  were not formed during the catalysis. The  $^{51}\text{V}$  NMR spectrum of the catalyst recovered after completion of the epoxidation in  $\text{CD}_3\text{CN}$  showed a line at  $-564$  ppm ( $\Delta\nu_{1/2} = 125$  Hz) and the  $^{183}\text{W}$  NMR spectrum in  $\text{CD}_3\text{CN}$  showed three lines at  $\delta = -84$  ppm ( $\Delta\nu_{1/2} = 9.9$  Hz),  $-97$  ppm ( $\Delta\nu_{1/2} = 2.3$  Hz), and  $-131$  ppm ( $\Delta\nu_{1/2} = 1.6$  Hz) with an integrated intensity ratio of 2:1:2, respectively, in agreement with the  $\gamma$ -Keggin framework. The lines due to the tungstate compounds such as  $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ ,  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ ,  $[\{\text{W}(\text{=O})(\text{O}_2)_2(\text{H}_2\text{O})_2\}_2(\mu\text{-O})]^{2-}$ , and  $[\text{H}_n\text{WO}_2(\text{O}_2)_2]^{(2-n)-}$  were not observed. IR and UV–vis spectra of the catalyst recovered after the completion of the epoxidation were the same as those of the fresh one, also suggesting the maintenance of the  $\gamma$ -Keggin framework of **I**. All these facts strongly show that the  $\{\text{VO}(\mu\text{-OH})_2\text{-VO}\}$  core is preserved in the cluster framework of **I** during the catalytic process.

As above mentioned, mono- and tri-vanadium-substituted compounds of  $[\alpha\text{-SiVW}_{11}\text{O}_{40}]^{5-}$  and  $[\alpha\text{-1,2,3-SiV}_3\text{W}_9\text{O}_{40}]^{7-}$  were completely inactive for the epoxidation under the present conditions, suggesting that the V–O–W and V=O centers are not the active sites. The fully occupied silicotungstates of  $[\gamma\text{-SiW}_{12}\text{O}_{40}]^{4-}$  with the same structure of **I** was inactive, suggesting that the tungsten atoms in **I** are inactive. These results show that  $\{\text{VO}(\mu\text{-OH})_2\text{-VO}\}$  core in **I** would act as an active site for the present epoxidation [34].

### 3. Experimental

Aqueous solution of  $[\gamma\text{-1,2-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{4-}$  was prepared according to ref. [35], and the anion was isolated as the tetra-*n*-butylammonium salt (TBA-I).  $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 12\text{H}_2\text{O}$  [36] (8 g, 2.7 mmol) was quickly dissolved in 1 M HCl (28 mL).  $\text{NaVO}_3$  (0.5 M, 11 mL, 5.5 mmol) was added, and the mixture was gently stirred for 5 min. The solution was filtered off followed by the addition of  $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$  (8 g, 25 mmol) in a single step. The resulting yellow precipitate was collected by the filtration and then washed with an excess amount of water (300 mL). The crude product was purified twice with the precipitation method (addition of 1 L of  $\text{H}_2\text{O}$  into acetonitrile solution of TBA-I (50 mL)). Analytically pure TBA-I was obtained as a pale yellow powder. Yield: 7.43 g (76%). Anal. calcd for  $[(\text{C}_4\text{H}_9)_4\text{N}]_4[\gamma\text{-1,2-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}] \cdot \text{H}_2\text{O}$ : C, 21.4; H, 4.15; N, 1.56; Si, 0.78; V, 2.83; W, 51.1;  $\text{H}_2\text{O}$ , 0.50. Found: C, 21.4; H, 3.91; N, 1.59; Si, 0.79; V, 2.88; W, 51.2;  $\text{H}_2\text{O}$ , 0.50.  $^{51}\text{V}$  NMR ( $\text{CD}_3\text{CN}$ ): An intense line at  $-563.6$  ppm ( $\Delta\nu_{1/2} = 133$  Hz) attributed to 2 equiv. vanadium atoms was observed.  $^{183}\text{W}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$ ,  $-82.2$  ppm ( $\Delta\nu_{1/2} = 9.6$  Hz),  $-95.6$  ppm ( $\Delta\nu_{1/2} = 2.5$  Hz) and  $-129.7$  ppm ( $\Delta\nu_{1/2} = 2.9$  Hz) with an integrated intensity ratio of 2:1:2, respectively.  $^{29}\text{Si}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$ ,  $-84.0$  ppm ( $\Delta\nu_{1/2} = 2.0$  Hz). UV–vis spectrum (in  $\text{CH}_3\text{CN}$ ) showed shoulder bands at 240 nm ( $\epsilon = 36,000 \text{ M}^{-1} \text{ cm}^{-1}$ ), 285 nm ( $\epsilon = 24,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and

350 nm ( $\epsilon = 5900 \text{ M}^{-1} \text{ cm}^{-1}$ ), characteristic of the  $\gamma$ -Keggin structure [37]. IR spectrum (KBr,  $\text{cm}^{-1}$ ): 1151, 1106, 1057, 1004, 995, 966, 915, 904, 875, 840, 790, 691, 550, 519, 482, 457, 405.

The epoxidation of gaseous substrates (propene and 1-butene) was carried out with Teflon coated autoclave. For the other substrates, glass tube reactor was used. The epoxidation was carried out as follows: catalyst (1.67 mM);  $\text{CH}_3\text{CN}/t\text{-BuOH}$  (1.5/1.5 mL);  $\text{H}_2\text{O}_2$  (30% aq., 33.3 mM), and substrates (propene, 6 atm; 1-butene, 3 atm; others, 33.3 mM) were charged in the reaction vessel. The reaction was carried out at  $293 \pm 0.2$  K. The reaction solution was periodically sampled and analyzed by GC in combination with mass spectroscopy. The products were identified by the comparison of mass and NMR spectra with those of authentic samples. Remaining  $\text{H}_2\text{O}_2$  after the reaction was analyzed by the  $\text{Ce}^{4+/3+}$  titration.

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