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Photopromoted Ru-Catalyzed Asymmetric Aerobic Sulfide Oxidation and Epoxidation Using Water as a Proton Transfer Mediator

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Abstract: Ru(NO)−salen complexes were found to catalyze asymmetric aerobic oxygen atom transfer reactions such as sulfide oxidation and epoxidation in the presence of water under visible light irradiation at room temperature. Oxidation of sulfides including alkyl aryl sulfides and 2-substituted 1,3-dithianes using complex **2** as the catalyst proceeded with moderate to high enantioselectivity of up to 98% ee, and epoxidation of conjugated olefins using complex **3** as the catalyst proceeded with good to high enantioselectivity of 76−92% ee. Unlike biological oxygen atom transfer reactions that need a proton and electron transfer system, this aerobic oxygen atom transfer reaction requires neither such a system nor a sacrificial reductant. Although the mechanism of this oxidation has not been completely clarified, some experimental results support the notion that an aqua ligand coordinated with the ruthenium ion serves as a proton transfer agent for the oxygen activation process, and it is recycled and used as the proton transfer mediator during the process. Thus, we have achieved catalytic asymmetric oxygen atom transfer reaction using molecular oxygen that can be carried out under ambient conditions.

1. Introduction

Oxidation and reduction are two fundamental chemical reactions, and both reactions have been extensively studied for many years. Today, asymmetric hydrogenation of olefins and carbonyl compounds can be carried out with almost complete enantioselectivity in quantitative yield. Two hydrogen atoms are incorporated into substrates without any byproducts. Asymmetric oxygen atom transfer reactions such as epoxidation and sulfide oxidation can also be carried out with high enantioselectivity, but the atom efficiency of the reactions is still mostly unsatisfactory because of the use of oxidants of low active oxygen content, except for a few examples.[1] On the other hand, it is well-known that most biological oxygen atom transfer reactions are highly, often completely, enantioselective and ecologically sustainable, because they use molecular oxygen in the air as an oxidant at body temperature and the only coproduct is water. However, biological reactions include sophisticated electron and proton transfer steps to activate molecular oxygen and are currently difficult to implement with a synthetic catalyst.[2] Thus, development of a simple oxidation catalyst that promotes asymmetric aerobic oxygen atom transfer reactions at room temperature without using a complicated electron and proton transfer system has long been a challenge in oxidation chemistry.

In 1993, Mukaiyama and co-workers developed an asymmetric oxygen atom transfer process using a Mn−salen/O_2/aldehyde system, in which the aldehyde serves as a sacrificial reductant, and achieved moderate to good enantioselective aerobic epoxidation (up to 92% ee) and sulfide oxidation.[3] In 1985, Groves and Quinn reported that a dioxo ruthenium(VI)−porphyrin complex catalyzed epoxidation in the absence of a sacrificial reductant. This epoxidation catalysis by the ruthenium complex was explained by a unique mechanism; an oxo ruthenium(IV) species resulting from epoxidation undergoes disproportionation to give the starting dioxo ruthenium(VI) species and a Ru(II) species that can be reoxidized by oxygen at room temperature to the oxo ruthenium(IV) species.[4] Later, Che et al. reported the asymmetric version of this epoxidation using 8 atm pressure of oxygen, albeit with moderate enanti-

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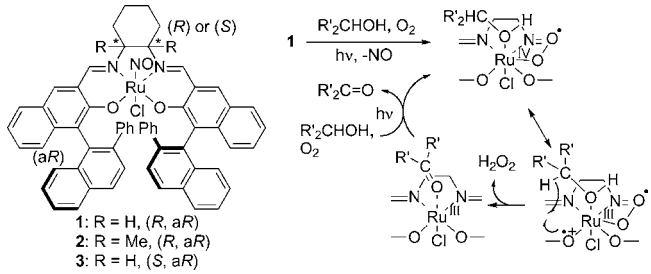
10.1021/ja104184r

Scheme 1. The Proposed Mechanism for Asymmetric Aerobic Oxidation of Alcohols Catalyzed by Ru−salen Complexes[a]



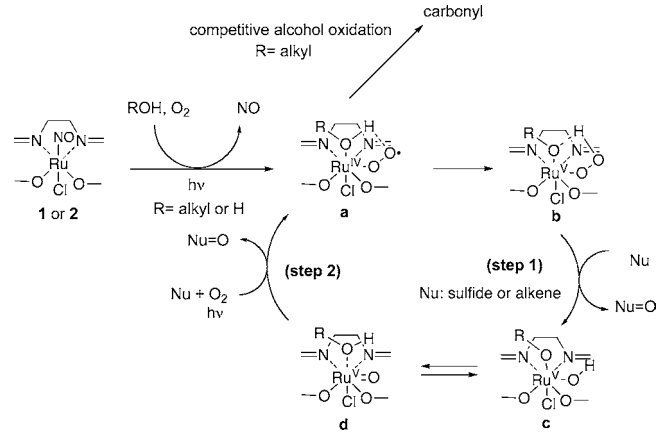
[a] The salen ligand is omitted for clarity, except for donor atoms.

oselectivity (up to 73% ee).[5] Subsequently, Beller et al. reported the modified version of Sharpless asymmetric dihydroxylation, another oxygen atom transfer reaction, using molecular oxygen at 50 °C as the terminal oxidant.[6] Realization of asymmetric aerobic oxygen atom transfer reactions under ambient conditions is still a challenging target.

In the aforementioned biological oxidation, the transferred proton for molecular oxygen activation is discarded as water, the byproduct of the oxygen activation process. This fact poses a question whether oxygen atom transfer reaction can be performed without any proton and electron transfer system, if the byproduced water is recycled as the proton source. In this paper, we describe a new method for asymmetric aerobic oxidation of sulfides and epoxidation under ambient conditions in which water serves as a proton transfer mediator.

There have been recent studies of aerobic oxidations such as alcohol oxidation and oxidative coupling of 2-naphthol that involve asymmetric catalysis of dehydrogenation using molecular oxygen.[7] We discovered that Ru(NO)−salen(X) complexes (X = Cl or OH) catalyze aerobic oxidative kinetic resolution of racemic alcohols, coupling of 2-naphthol and desymmetrization of *meso*-diols under ambient and visible light irradiation conditions (Scheme 1).[8] Irradiation promotes the dissociation of the nitrosyl group to give a Ru(solvent)−salen(X) species,[8e] and the Ru(ROH)−salen(X) species generated in the presence of alcohol catalyzes aerobic alcohol oxidation under irradiation.[8d] Moreover, the kinetic study of these alcohol oxidations disclosed that the rate laws of these oxidation reactions depend on the apical ligand of the catalyst; the rate of the reaction catalyzed by Ru(NO)−salen(Cl) complexes (**1** and **2**) shows the first order dependence on the concentration of molecular oxygen, while the reaction catalyzed by Ru(NO)−salen(OH) complexes shows fractional order dependence on the

Scheme 2. An Expected Mechanism for Asymmetric Aerobic Oxygen Atom Transfer Catalyzed by Ru−salen Complexes



oxygen concentration.[8d] This indicates that an oxygen molecule participates in the transition state of this oxidation by complex **1** or **2**. With these results and hypothesis, we further inferred that molecular oxygen coordinates with the ruthenium(III) ion prior to the single electron transfer event and the resulting superoxide is also bound to the oxidized ruthenium(IV) ion. When an alcohol substrate exists in the reaction mixture, it is oxidized.[8] Superoxide is nucleophilic and is relatively nonreactive with nucleophilic substrates. In most biological oxidation reactions, an umpolung step, conversion of a superoxo to an electrophilic hydroperoxo or oxo species, is included, but it requires a sophisticated electron and proton transfer system.[2] The oxidation with **1** or **2** also shows the first order dependence on alcohol concentration,[8d] and the alcohol should be coordinated with the ruthenium ion and be acidic. On the other hand, it is known that superoxo species can undergo proton coupled electron transfer to give hydroperoxo species, if a proton donor exists nearby it.[9,10] Thus, the superoxo species **a** is likely to undergo proton coupled electron transfer to generate a more electrophilic hydroperoxo species **b**. Based on these considerations, we expected that aerobic oxygen atom transfer would occur in a pathway via **b** competitively with the alcohol oxidation, if the reaction mixture includes an appropriate nucleophile such as a sulfide or an alkene (Scheme 2). Moreover, oxygen atom transfer by species **b** generates an (alkoxo)(hydroxo)Ru species **c** that could tautomerize to an (alcohol)(oxo)Ru species **d**.[11] An alcohol is regenerated by this tautomerization process and the alcohol can serve as a proton transfer mediator. Moreover, if the oxo species **d** undergoes another oxo transfer reaction, it produces a Ru(III)−salen species

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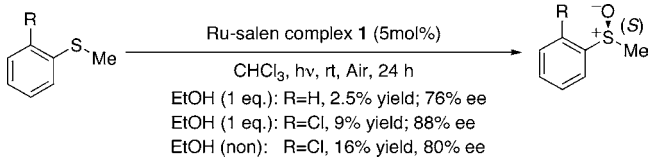
Scheme 3. A Preliminary Experiment on Asymmetric Aerobic Oxidation Catalyzed by Ru−salen Complex **1**



that can undergo single electron transfer upon irradiation[8d] under aerobic conditions, regenerating the starting ruthenium(IV) species **a**. Based on this mechanistic consideration, the aerobic oxygen atom transfer reaction was expected to occur via this catalytic pathway. However, this catalytic pathway includes two different oxygen atom transfer steps, and it is preferred that the two different active species would show the same asymmetric catalysis. Recently, we discovered that the complexes of salen ligands bearing a binaphthyl moiety show excellent enantioselectivity in an identical sense, irrespective of their configuration.[12] Thus, we expected that the above oxidation could be realized in a highly enantioselective manner by using a ruthenium−salen complex.

2. Results and Discussion

2.1. Asymmetric Aerobic Oxidation of Sulfides. We first examined the oxidation of methyl phenyl sulfide and *o*-chlorophenyl methyl sulfide in chloroform with **1** in the presence of 1 equiv of ethanol under ambient air (Scheme 3). The reactions had good enantioselectivity (76 and 88% ee, respectively); however, the oxidation of sulfides and the alcohol oxidation almost stopped after a short time and the yields of the sulfoxides were low, though the yield (9%) of *o*-chlorophenyl methyl sulfoxide was nearly four times better than that (2.5%) of methyl phenyl sulfoxide. These results suggested that catalyst poisoning by the product is responsible for the low yield. During the study, we found that the reaction proceeded in a better yield (16%) even in the absence of ethanol, albeit with a slightly reduced selectivity (80% ee) (Scheme 3). According to the elementary analysis of complex **1** prepared based on the literature,[13] it contains water molecule. The water should be lattice water, but it can coordinate at the apical position of the resulting denitrosylated Ru complex upon irradiation and serve as the hydrogen bond donor. Similar alcohol coordination has been observed in aerobic alcohol oxidation (Scheme 1).[8d] These results were reminiscent of the following advantages of water as a proton transfer mediator: (i) water is less oxidizable than alcohol, (ii) water could be a better H-bond donor than alcohols,[14] and (iii) it has two protons. Thus, water has the specific advantage of proton coupled electron transfer from the aqua ligand generating (hydroperoxo)(hydroxo) species (**b**, R = H). The hydroxo group can then form a hydrogen bond with the distal oxygen atom of the hydroperoxo group to the metal ion (Scheme 4). This type of hydrogen bond cannot be formed when the hydrogen bond donor is an alcohol. Sharpless and co-workers have proposed that, in a metal catalyzed epoxidation using alkyl hydroperoxide as the terminal oxidant, the hydrogen bond formation between a hydroxo group and the distal oxygen atom of an alkylperoxo group facilitates O−O bond cleavage and epoxidation.[15] Moreover, in biological system catalyzed cytochrome P-450, a superoxo species is converted to a hydroperoxo species via a proton and electron transfer, and the resulting hydroperoxo species is converted into an oxo species via protonation at the oxygen atom distal to the ferric ion.[2b] The nature of species **e** should be similar to that of the protonated or hydrogen-bonded hydroperoxo species, which might undergo O−O bond fission[16] or the desired oxygen atom transfer directly (Scheme 4). We were intrigued by the hypothesis that water supplies two protons which are retrieved during the catalytic cycle.

Scheme 4. A Possible Reaction Pathway in the Presence of an Aqua Ligand

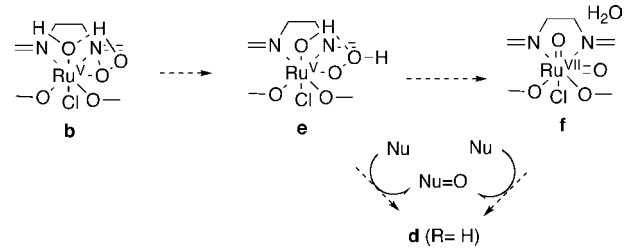
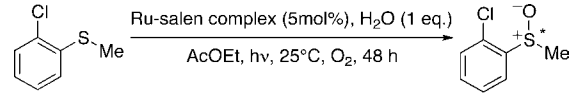


Table 1. Aerobic Oxidation of 2-Chlorophenyl Methyl Sulfide with Ru(NO)−salen Complexes as the Catalyst[a]



run	cat.	solvent	time (h)	yield[b] (%)	ee[c] (%)
1	**1**	$CHCl_3$	24	3	75 (*S*)
2	**1**	toluene	24	4	78 (*S*)
3	**1**	acetone	24	7	72 (*S*)
4	**1**	AcOEt	24	18	80 (*S*)
5[d]	**1**	AcOEt	48	59	82 (*S*)
6[e]	**1**	AcOEt	24	nr	
7[d]	**2**	AcOEt	48	56[f]	93 (*S*)
8[d]	**2**	AcOEt	72	99[f]	92 (*S*)
9	**2**	AcOEt	48	99[d,f](89)[f,g]	94 (94)[g] (*S*)
10[h]	**2**	AcOEt	48	34[d,f]	94 (*S*)
11	**3**	AcOEt	48	18[f]	15 (*R*)

[a] Reactions were run at 25 °C on a 0.1 mmol scale with Ru−salen complex (5 mol %) as a catalyst in the presence of H_2O (1 equiv) in 1.0 mL of solvent under air and visible light irradiation with a halogen lamp, unless otherwise noted. [b] Determined by HPLC analysis using phenanthrene as an internal standard. [c] Determined by HPLC analysis using a chiral stationary phase. [d] The reaction was run in 0.5 mL of AcOEt. [e] The reaction was carried out in the dark. [f] Isolated yield. [g] The reaction was run in 2.5 mL of AcOEt on a 0.5 mmol scale. [h] The reaction was performed without addition of water.

Based on this hypothesis, we next examined the oxidation of *o*-chlorophenyl methyl sulfide with **1** in the presence of 1 equiv of water under ambient air (Table 1). The reactions in chloroform, toluene and acetone were slow, and the yields of the sulfoxide were less than 7% (runs 1−3). A better yield was obtained in ethyl acetate (AcOEt) without eroding the enantioselectivity (run 4), and the yield was further improved to 59% as the substrate concentration was increased and the reaction time was elongated (run 5). No reaction occurred without irradiation (run 6). We expected that the yield might be improved if catalyst poisoning by the sulfoxide could be

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Table 2. Aerobic Oxidation of Sulfides with Ru(NO)−salen Complex **2** as the Catalyst[a]

run	sulfide	yield[b] (%)	ee[c] (%)	config [d]
1	PhSMe	74	94	*S*
2	*p*-ClPhSMe	69	84	*S*
3	*p*-MePhSMe	61	91	*S*
4	*o*-MePhSMe	86	96	*S*
5	mesityl methyl sulfide	18	72	*S*
6[e]	BnSMe	26	75	*S*
7[e]	2-phenyl-1,3-dithiane	57	98	1*S*,2*S*
8	2-(*t*-butyl)-1,3-dithiane	98	91	1*S*,2*S*

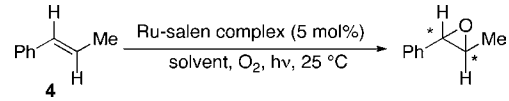
[a] Reactions were carried out at 25 °C in the presence of water (1 equiv) in 2.5 mL of ethyl acetate for 48 h on a 0.5 mmol scale under oxygen and visible light irradiation with a halogen lamp, unless otherwise noted. [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase, as described in the Experimental Section. [d] Absolute configuration was determined by chiroptical comparison. [e] Sulfide was added dropwise.

suppressed by using a complex possessing a sterically congested coordination sphere, which allows the coordination of molecular oxygen in preference to a more bulky sulfoxide. Thus, we examined oxidation using complex **2** that carries two methyl groups near the ruthenium ion[8d] as the catalyst. To our delight, a remarkably improved enantioselectivity of 93% ee was obtained, though the yield was still moderate (run 7). Eventually, a satisfactory yield was obtained by extending the reaction time (run 8) or by performing the reaction under oxygen atmosphere (run 9). The reaction was also performed without adding water under oxygen atmosphere (run 10). The reaction proceeded with the same enantioselectivity, albeit slowly. The reaction with complex **3**, a diastereomer of **1**, was of low enantioselectivity (run 11). Overoxidation is often observed in oxidation of sulfides.[17] It is, however, noteworthy that no overoxidation to sulfone was observed in the present oxidation.

Under oxygen atmosphere, oxidation of other aryl methyl sulfides using **2** as the catalyst also proceeded with high enantioselectivity (up to 96%) (Table 2, runs 1−4). However, bulky sulfides such as mesityl methyl sulfide were more slowly oxidized, and the enantioselectivity was moderate (run 5). The reaction of benzyl methyl sulfide was slow, and the enantioselectivity was moderate (75% ee) (run 6). The reactions of 2-substituted 1,3-dithianes proceeded with high diastereo- and enantioselectivity (runs 7 and 8). No overoxidation to sulfone or disulfoxide was also observed in this oxidation.[17]

2.2. Asymmetric Aerobic Epoxidation of Conjugated Olefins. The successful results of asymmetric aerobic oxidation of sulfides prompted us to further explore the epoxidation of olefins, which are weaker nucleophiles than sulfides. The epoxidation of *trans*-*β*-methylstyrene **4** using Ru(NO)−salen complexes (**1**−**3**) as catalysts was examined in chloroform at room temperature in the presence of water (1 equiv) under oxygen atmosphere. The reactions were carried out under irradiated conditions (Table 3). The epoxidation using complex **1** as the catalyst occurred slowly with modest enantioselectivity (run 1). Complex **2** showed excellent enantioselectivity, but its catalytic activity for epoxidation was poor (run 2). However, complex **3**, a poor catalyst for oxidation of sulfides, was found to show high enantioselectivity, albeit with modest yield (run 3). Thus, the reaction was further optimized with respect to

Table 3. Aerobic Epoxidation of *trans*-*β*-Methylstyrene with Ru(NO)−salen Complexes as Catalyst[a]



run	cat.	solvent	yield[b] (%)	ee[c] (%)	config [d]
1[e,f]	**1**	$CHCl_3$	14[g]	27	1*R*,2*R*
2[e,f]	**2**	$CHCl_3$	trace[g]	>99	1*R*,2*R*
3[e]	**3**	$CHCl_3$	28	90	1*S*,2*S*
4[e,f]	**3**	$(CHCl_2)_2$	46[g]	89	1*S*,2*S*
5[e]	**3**	ClC_6H_5	58	86	1*S*,2*S*
6	**3**	$CH_3C_6H_5$	26[g]	83	1*S*,2*S*
7	**3**	AcOEt	28[g]	77	1*S*,2*S*
8	**3**	ClC_6H_5	59 (58)[h]	87 (88)[h]	1*S*,2*S*
9[i]	**3**	ClC_6H_5	nr		
10[j]	**3**	ClC_6H_5	nr		

[a] Reactions were carried out at 25 °C in 2.5 mL of solvent for 36 h on a 0.5 mmol scale without adding water under oxygen and visible light irradiation with a halogen lamp, unless otherwise noted. [b] Isolated yield. [c] Determined by HPLC or GLC analysis using a chiral stationary phase as described in the Experimental Section. [d] Determined by chiroptical comparison. [e] 1.0 equiv of water was added. [f] Reaction was run on a 0.1 mmol scale. [g] Determined by GLC analysis using bicyclohexyl as an internal standard. [h] For 48 h. [i] Carried out in the dark. [j] Carried out in nitrogen atmosphere.

solvent by using **3** as the catalyst, and better yield (58%) was obtained in chlorobenzene, albeit with slightly reduced enantioselectivity (run 5). The reactions in toluene and ethyl acetate were slower and less selective (runs 6 and 7). Although the best enantioselectivity was obtained in the reaction in chloroform, chlorobenzene was chosen in consideration of yield for the solvent of the following reactions. The catalytic activities of complex **3**[13] pretreated with 1 equiv of water and complex **3** were almost identical, supporting the observation that water molecule is recycled during the oxidation process (*vide infra*) (runs 5 and 8). Epoxidation did not occur without irradiation or in nitrogen atmosphere under otherwise identical conditions, suggesting that irradiation and the presence of oxygen are essential for this oxidation (runs 9 and 10).

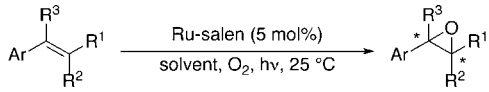
Under the optimized conditions, we examined the epoxidation of several other olefins (Table 4). Epoxidation of 2-[(*E*)-1-propenyl]naphthalene **5** and *m*-methyl[(*E*)-1-propenyl]benzene **6** also proceeded with high enantioselectivity (runs 1 and 2). Epoxidation of *p*-methyl[(*E*)-1-propenyl]benzene **7** proceeded with good enantioselectivity (run 3); however, as the reaction time extended the enantiomeric excess of the epoxide decreased to some extent. This is because the epoxide slowly rearranged to a ketone, and the rearrangement of the major enantiomer of the epoxide to the ketone is faster than that of the minor enantiomer (runs 4 and 5).[18] The epoxidations of (*E*)-α,*β*-dimethylstyrene **8** and *cis*-*β*-methylstyrene **9** were highly enantioselective, albeit with modest yields (runs 6 and 7). It is of note that the epoxidation is stereospecific; *trans*- and *cis*-*β*-methystyrenes gave the corresponding *trans*- and *cis*-epoxides, respectively.[18,19]

2.3. Validation of the Working Hypothesis on the Role of Water as a Proton Transfer Mediator in Aerobic Oxygen Atom Transfer Reaction. Based on the working hypothesis that water could serve as a proton transfer mediator, we examined

(17) For reviews on asymmetric sulfoxidation, see: (a) Legros, J.; Dehli, J. R.; Bolm, C. *Adv. Synth. Catal.* **2005**, *347*, 19–31. (b) Kagan, H. B.; Luukas, T. O. Catalytic Asymmetric sulfide Oxidations. In *Transition Metals for Organic Synthesis*, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. 2, pp 479−495.

(18) For the enantiomer-differentiating epoxide-rearrangement using complex **3** as the catalyst, see: (a) Takeda, T.; Irie, R.; Shinoda, Y.; Katsiki, T. *Synlett* **1999**, 1157–1159. (b) Nakata, K.; Takeda, T.; Mihara, J.; Hamada, T.; Irie, R.; Katsuki, T. *Chem.—Eur. J.* **2001**, *7*, 3776–3782.

Table 4. Asymmetric Aerobic Epoxidation with Ru(NO)−salen Complex **3** as the Catalyst[a]

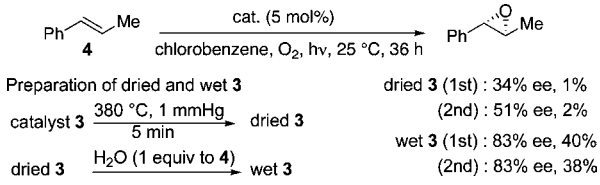


5: Ar=2-Naphthyl, R^1=Me, R^2, R^3=H
6: Ar=*m*-MeC_6H_4, R^1=Me, R^2, R^3=H
7: Ar=*p*-MeC_6H_4, R^1=Me, R^2, R^3=H
8: Ar=Ph, R^1, R^3=Me, R^2=H
9: Ar=Ph, R^2=Me, R^1, R^3=H

run	substrate	yield[b] (%)	ee[c] (%)	config [d]
1	**5**	75	92	
2	**6**	67	90	
3[e]	**7**	52 (1)[f,g]	77	
4[h,i]	**7**	44[f]	78	
5[h]	**7**	58 (3)[f,g]	76	
6	**8**	55	88	2*R*,3*R*
7[e]	**9**	34 (3)[f,g]	90	1*S*,2*R*

[a] Reactions were carried out using **3** as the catalyst at 25 °C in 2.5 mL of chlorobenzene for 48 h on a 0.5 mmol scale without adding water under oxygen and visible light irradiation with a halogen lamp, unless otherwise noted. [b] Isolated yield. [c] Determined by HPLC or GLC analysis using a chiral stationary phase as described in the Experimental Section. [d] Determined by chiroptical comparison. [e] For 36 h. [f] Determined by ^{1}H NMR analysis using phenanthrene as an internal standard. [g] The number in parentheses is the yield of ketone. [h] Reaction was run on a 0.1 mmol scale. [i] For 12 h.

Scheme 5. Epoxidation under Anhydrous or Hydrous Conditions

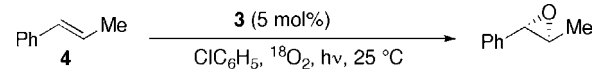


Ru-catalyzed asymmetric aerobic oxidation in the absence of sacrificial reductant and achieved highly enantioselective oxidation of sulfides and epoxidation. To explore the feasibility of the hypothesis, we performed several experiments.

2.3.1. Study of the Effect of Water on Epoxidation Rate: Asymmetric Epoxidation of *trans*-*β*-Methylstyrene Using 3 as the Catalyst under Anhydrous and Hydrous Conditions. In the hypothesis, a metal-bound water molecule plays a crucial role in the activation of a putative superoxo or hydroperoxo species. Complex **3** prepared according to the literature[13] contains a water molecule. Thus, complex **3** was dehydrated in vacuo at ca. 380 °C and used as catalyst for the epoxidation of *trans*-*β*-methylstyrene under two different conditions, anhydrous and hydrous, to study the effect of water on epoxidation (Scheme 5). Epoxidation using dried **3** was sluggish, and the enantioselectivity was lower and its reproducibility was poor. The epoxidation catalysis of **3** was restored by adding water (wet **3**) (*cf.* Table 3, run 5), supporting the hypothesis on the role of water.

2.3.2. ^{18}O Incorporation Experiment: Epoxidation of *trans*-*β*-Methylstyrene with 3 as the Catalyst in $^{18}O_2$. To verify that molecular oxygen is the terminal oxidant of this oxidation, the ^{18}O incorporation experiment was performed. The epoxidation of *trans*-*β*-methylstyrene in $^{18}O_2$ atmosphere revealed that ^{18}O incorporation increased from 76 to 82% as the reaction proceeded (Table 5). This result suggests that most of the incorporated oxygen atom originates from molecular oxygen but some originates from another oxygen source.

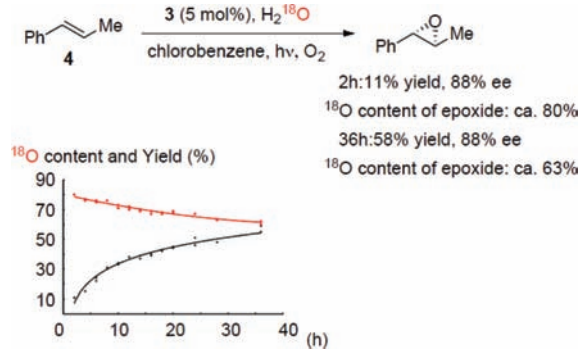
Table 5. Epoxidation of *trans*-*β*-Methylstyrene in $^{18}O_2$ Atmosphere[a]



run	time (h)	yield[b] (%)	^{18}O content[c] (%)	% ee[d]
1	6	39	76	85
2	12	46	79	84
3	24	49	81	85
4	36	53	82	85

[a] Reactions were carried out using **3** as the catalyst at 25 °C in 0.5 mL of chlorobenzene on a 0.1 mmol scale without adding water under oxygen ($^{18}O_2$) and visible light irradiation with a halogen lamp, unless otherwise noted. [b] Determined by ^{1}H NMR analysis using phenanthrene as an internal standard. [c] Determined by ESI-TOF-MS analysis (average of three runs). [d] Determined by HPLC analysis using a chiral stationary phase as described in the Experimental Section.

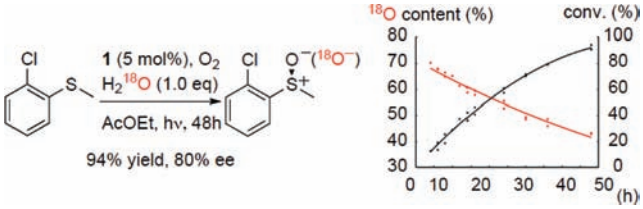
Scheme 6. The Yield of Epoxide (Black Line) and the ^{18}O Content of the Epoxide Product (Red Line) vs Reaction Time Plots for the Epoxidation of *β*-Methylstyrene with Complex **3** as a Catalyst in the Presence of $H_2{}^{18}O$ (1 equiv)



This result, in addition to the previous result that no epoxidation occurs in the absence of molecular oxygen (Table 3, run 10), proves that molecular oxygen is the terminal oxidant.

2.3.3. ^{18}O Incorporation Experiment: Asymmetric Epoxidation of *trans*-*β*-Methylstyrene Using 3 as the Catalyst in the Presence of ^{18}O-Labeled Water. The expected reaction pathway (Scheme 2) includes a dihydroxo species (**c**, R = H) that is in equilibrium with an aqua(oxo) species (**d**, R = H), and a water oxygen atom can be incorporated into epoxides via the dihydroxo and aqua(oxo) tautomerization.[11] To investigate the plausibility of the oxygen atom incorporation from water, we examined the epoxidation of *trans*-*β*-methylstyrene in the presence of 1 equiv of $H_2{}^{18}O$ under $^{16}O_2$ atmosphere. As expected, ^{18}O incorporation was observed, but the ^{18}O incorporation value of the epoxide product exceeded 50% (Scheme 6). We also examined the oxidation of *o*-chlorophenyl methyl sulfide in the presence of $H_2{}^{18}O$ under $^{16}O_2$ atmosphere. The ^{18}O incorporation value of the sulfoxide product was 70% at 11% conversion, and it diminished to 43% at 94% conversion (Scheme 7). These results support the assumed mechanism for incorporation of the water oxygen atom and regeneration of water. However, in the assumed reaction pathway for aerobic oxidation (Scheme 2), the oxygen atom incorporation from water occurs only in the second step, and the ^{18}O incorporation value must be ≤50%. Thus, these results suggested that ^{16}O/^{18}O exchange between $H_2{}^{18}O$ and an active species can occur also in the first step. Although more detailed experiments are required, the reaction pathway via dioxo species **f** (Scheme 4) may explain the experimental results.

Scheme 7. Conversion of Sulfide (Black Line) and the ^{18}O Content of the Sulfoxide Product (Red Line) vs Reaction Time Plots for Asymmetric Oxidation of *o*-Chlorophenyl Methyl Sulfide in the Presence of $H_2{}^{18}O$



All the above observations are consistent with the reaction pathway of asymmetric aerobic oxygen atom transfer using water as the proton transfer mediator described in Schemes 2 and 4.

3. Conclusion

In summary, we have demonstrated that Ru(NO)(salen) complexes **2** and **3** can catalyze aerobic oxygen atom transfer reactions such as oxidation of sulfides and epoxidation of conjugated olefins in the presence of water with good to high enantioselectivity at room temperature under irradiated conditions. The terminal oxidant is molecular oxygen. Water serves as a proton transfer mediator for these oxygen atom transfer reactions. That is, water is recycled during the oxidation process that includes two oxidation steps. These aerobic oxygen atom transfer reactions do not need a special proton and electron transfer system. The present results pave the way for ecologically sustainable oxygen atom transfer. The mechanism of these reactions is now under investigation.

4. Experimental Section

4.1. General. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz on a JEOL JNM-AL-400 instrument. All signals were expressed as ppm downfield from tetramethylsilane used as an internal standard (δ-value in $CDCl_3$). High-resolution electron spray ionization mass spectra (HRMS-ESI) were measured with a BRUKER DALTONICS MICRO TOF-KS1 focus. Optical rotations were measured with a JASCO P-1020 polarimeter. Enantiomeric excesses were determined by HPLC analysis using SHIMADZU LC-10AT-VP or GLC analysis using SHIMADZU GC-1700, equipped with a chiral stationary phase. All the reactions were carried out in a 5 mL Schlenk tube (∅: ca. 13 mm) placed in a cooling bath (25 °C), except the experiments for Table 1 which were carried out in an air-conditioned room (25 °C). The reaction mixtures were irradiated by the light (intensity: ca. 90 mW/cm^2) from a halogen lamp (6423 FO, fiber optic lamp, PHILIPS) at a distance of 0.5 cm through a vinyl covered optical fiber in water to keep the reaction temperature constant at 25 °C. Column chromatography was conducted on a silica gel 60N (spherical, neutral), 63−210 μm, available from Kanto Chemical Co., Inc., or a Chromatorex NH (spherical, basic), 100−200 μm, available from Fuji Silysia Chemical Ltd. Preparative thin layer chromatography was performed on 0.5 mm × 20 cm × 20 cm E. Merck silica gel plate (60 F-254). Ru(NO)−salen complexes **1**,[13] **2**[8d] and **3**[13] were prepared according to the literature. Commercial *trans*-β-methylstyrene and *cis*-β-methylstyrene were distilled before use. 2-[(*E*)-1-Propenyl]naphthalene and (*E*)-α,β-dimethylstyrene were prepared from the corresponding alkenylboronic acid and aryl bromide via Suzuki−Miyaura coupling.[20] $^{18}O_2$ and $H_2{}^{18}O$ (^{18}O content ≥ 98%) were purchased from Taiyo Nippon Sanso Corporation.

4.2. Experimental Procedures for Asymmetric Oxidation of Sulfides and Epoxidation.

4.2.1. Typical Procedure for Asymmetric Aerobic Oxidation of Sulfides Using 2 as the Catalyst under Oxygen Atmosphere. Complex **2** (25.5 mg, 25 μmol) and water (9.0 μL, 0.5 mmol) were placed in a Schlenk tube, which was previously purged with oxygen, and AcOEt (2.5 mL) was added to the mixture. The resultant solution was stirred under irradiation with a halogen lamp at room temperature. After 30 min, sulfide (0.5 mmol) was added to the solution and stirred for 48 h under oxygen and irradiation at room temperature in the closed tube. The mixture was concentrated and the residue was chromatographed on an NH-silica gel column to give the corresponding sulfoxide. All the fractions containing the sulfoxide were collected.[21] The enantiomeric excess of the sulfoxide was determined by HPLC analysis using a chiral stationary phase.

4.2.1.1. (*S*)-*o*-Chlorophenyl Methyl Sulfoxide (Table 1, Run 9). Colorless oil. Yield 99% (94% ee). $[\alpha]_D^{25}$ −257.5 (*c* 3.3, acetone). Lit.[22] [96% ee, (*S*)-isomer; $[\alpha]_D^{25}$ −266.5 (*c* 2.0, acetone)]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.97 (dd, J = 1.7, 7.8 Hz, 1H), 7.55 (ddd, J = 1.5, 7.3, 7.8 Hz, 1H), 7.45 (ddd, J = 1.7, 7.3, 7.8 Hz, 1H), 7.40 (dd, J = 1.5, 7.8 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.1, 131.6, 129.4, 129.4, 127.8, 124.9, 41.5 ppm. HPLC: t_R (*S*) =15.2 min, t_R (*R*) =22.4 min (DAICEL CHIRALCEL OB-H; flow rate, 0.5 mL/min; hexane/EtOH/*i*-PrOH = 90/5/5).

4.2.1.2. (*S*)-Methyl Phenyl Sulfoxide (Table 2, Run 1). Colorless oil. Yield 74% (94% ee). $[\alpha]_D^{25}$ −136.3 (*c* 0.33, acetone). Lit.[22] [96% ee, (*S*)-isomer; $[\alpha]_D^{25}$ −141.0 (*c* 0.43, acetone)]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.67−7.65 (m, 2H), 7.56−7.48 (m, 3H), 2.73 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.4, 130.7, 129.0, 123.2, 44.0 ppm. HPLC: t_R (*S*) = 22.5 min, t_R (*R*) = 36.2 min (DAICEL CHIRALCEL OB-H; flow rate, 0.5 mL/min; hexane/EtOH/*i*-PrOH = 90/5/5).

4.2.1.3. (*S*)-*p*-Chlorophenyl Methyl Sulfoxide (Table 2, Run 2). Colorless oil. Yield 69% (84% ee). $[\alpha]_D^{25}$ −98.0 (*c* 2.0, acetone). Lit.[22] [94% ee (*S*)-isomer; $[\alpha]_D^{25}$ −114.9 (*c* 1.28, acetone)]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.61−7.59 (d, J = 8.4 Hz, 2H), 7.52−7.51 (d, J = 8.4 Hz, 2H), 2.73 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.0, 136.9, 129.3, 124.6, 44.1 ppm. HPLC: t_R (*S*) = 16.2 min, t_R (*R*) = 24.0 min (DAICEL CHIRALCEL OB-H; flow rate, 0.5 mL/min; hexane/*i*-PrOH = 80/20).

4.2.1.4. (*S*)-Methyl *p*-Methylphenyl Sulfoxide (Table 2, Run 3). Colorless oil. Yield 61% (91% ee). $[\alpha]_D^{25}$ −134.6 (*c* 0.22, acetone). Lit.[22] [96% ee (*S*)-isomer; $[\alpha]_D^{25}$ −140.3 (*c* 0.63, acetone)]. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55−7.53 (d, J = 8.0 Hz, 2H), 7.35−7.33 (d, J = 8.0 Hz, 2H), 2.73 (s, 3H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.1, 141.2, 129.7, 123.2, 43.9, 21.4 ppm. HPLC: t_R (*S*) = 9.4 min, t_R (*R*) = 15.3 min (DAICEL CHIRALCEL OB-H; flow rate, 0.5 mL/min; hexane/*i*-PrOH = 50/50).

(19) Stereospecific asymmetric epoxidation reactions using a Ru complex have been reported: (a) End, N.; Pfaltz, A. *Chem. Commun.* **1998**, 589–590. (b) Gross, Z.; Ini, S. *Org. Lett.* **1999**, 2077–2080. (c) Tes, M. K.; Döbler, C.; Bhor, S.; Klawonn, M.; Mägerlein, W.; Hugl, H.; Beller, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5255–5260. (d) Tes, M. K.; Bhor, S.; Klawonn, M.; Anilkumar, G.; Jiao, H.; Spannenberg, A.; Döbler, C.; Mägerlein, W.; Hugl, H.; Beller, M. *Chem.—Eur. J.* **2006**, *12*, 1875–1888.

(20) (a) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *36*, 3437–3440. (b) Uenishi, J.; Beau, J.-M.; Armstrong, R. W.; Kishi, Y. *J. Am. Chem. Soc.* **1987**, *109*, 4756–4758.

(21) Diter, P.; Taudien, S.; Samuel, O.; Kagan, H. B. *J. Org. Chem.* **1994**, *59*, 370–373.

(22) Egami, H.; Katsuki, T. *J. Am. Chem. Soc.* **2007**, *129*, 8940–8941.

4.2.1.5. (*S*)-Methyl *o*-Methylphenyl Sulfoxide (Table 2, Run 4). Colorless oil. Yield 86% (96% ee). $[\alpha]_D^{25}$ −211.8 (*c* 2.7, acetone). Lit.[23] [53% ee, (*S*)-isomer; $[\alpha]_D^{20}$ −122 (*c* 2.0, acetone)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (dd, J = 1.5, 7.8 Hz, 1H), 7.45 (ddd, J = 0.7, 7.6, 7.8 Hz, 1H), 7.39 (ddd, J = 1.5, 7.3, 7.6 Hz, 1H) 7.21 (dd, J = 0.7, 7.3 Hz, 1H), 2.69 (s, 3H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.8, 133.8, 130.5, 127.3, 122.9, 42.1, 18.2 ppm. HPLC: t_R (*R*) = 103.7 min, t_R (*S*) = 109.8 min (DAICEL CHIRALPAC IC; flow rate, 0.5 mL/min; hexane/*i*-PrOH = 90/10).

4.2.1.6. (*S*)-Mesityl Methyl Sulfoxide (Table 2, Run 5). Yellow oil. 18% (72% ee). $[\alpha]_D^{25}$ −179.2 (*c* 1.0, $CHCl_3$). Lit.[24] [98% ee, (*S*)-isomer; $[\alpha]_D$ −241 (*c* 1.0, $CHCl_3$)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.85 (s, 3H), 2.84 (s, 3H), 2.50 (s, 6H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 137.3, 130.7, 38.5, 20.8, 18.0 ppm. HPLC: t_R (*S*) = 10.0 min, t_R (*R*) = 11.1 min (DAICEL CHIRALCEL OJ-H; flow rate, 1.0 mL/min; hexane/*i*-PrOH = 95/5).

4.2.1.7. (*S*)-Benzyl Methyl Sulfoxide (Table 2, Run 6). Colorless solid. Yield 26% (75% ee). $[\alpha]_D^{24}$ +79.9 (*c* 0.56, EtOH). Lit.[22] [87% ee, (*S*)-isomer; $[\alpha]_D^{24}$ +97.9 (*c* 0.25, EtOH)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41−7.28 (m, 5H), 4.07 (d, J = 12.9 Hz, 1H), 3.93 (d, J = 12.9 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 129.9, 129.6, 128.9, 128.4, 60.4, 37.3 ppm. HPLC: t_R (*S*) = 20.1 min, t_R (*R*) = 25.1 min (DAICEL CHIRALCEL OB-H; flow rate, 0.5 mL/min; hexane/*i*-PrOH = 80/20).

4.2.1.8. (1*S*,2*S*)-2-Phenyl-1,3-dithiane 1-Oxide (Table 2, Run 7). Colorless solid. Yield 57% (98% ee). $[\alpha]_D^{24}$ +122.4 (*c* 0.86, $CHCl_3$). Lit.[25] [99% ee, (1*S*,2*S*)-isomer; $[\alpha]_D^{24}$ +106.48 (*c* 0.88, $CHCl_3$)]. ^{1}H NMR (400 MHz): δ 7.43−7.36 (m, 5H), 4.59 (s, 1H), 3.60−3.55 (m, 1H), 2.90 (ddd, J = 2.7, 12.4, 12.4 Hz, 1H), 2.79 (ddd, J = 2.9, 13.2, 13.2 Hz, 1H), 2.69 (dddd, J = 1.2, 2.4, 13.2, 13.2 Hz, 1H), 2.58−2.51 (m, 1H), 2.44−2.32 (m, 1H). ^{13}C NMR (100 MHz): δ 133.0, 129.1, 128.8, 128.4, 69.6, 54.7, 31.4, 29.5 ppm. HPLC: t_R (1*R*,2*R*) = 15.2 min, t_R (1*S*,2*S*) = 25.0 min (DAICEL CHIRALCEL AD-H; flow rate, 0.5 mL/min; hexane/*i*-PrOH = 75/25).

4.2.1.9. (1*S*,2*S*)-2-*tert*-Butyl-1,3-dithiane 1-Oxide (Table 2, Run 8). Colorless solid. Yield 98% (91% ee). $[\alpha]_D^{25}$ −51.5 (*c* 0.87, EtOH). Lit.[26] [35% ee, (1*S*,2*S*)-isomer]; $[\alpha]_D$ −13 (EtOH). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.52 (s, 1H), 3.39 (ddd, J = 3.7, 3.7, 12.7 Hz, 1H), 2.70 (ddd, J = 2.9, 12.7, 13.0 Hz, 1H), 2.63 (pseudodd, J = 2.9, 8.54 Hz, 2H), 2.45−2.38 (m, 1H), 2.32−2.18 (m, 1H), 1.25 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 77.2, 55.7, 36.3, 30.7, 30.3, 28.8 ppm. HPLC: t_R (1*R*,2*R*) = 18.1 min, t_R (1*S*,2*S*) = 24.6 min (DAICEL CHIRALCEL OD-H; flow rate, 0.5 mL/min; hexane/*i*-PrOH = 90/10).

4.2.2. Typical procedure for Asymmetric Aerobic Epoxidation Using 3 as the Catalyst under Oxygen Atmosphere. Complex **3** (24.8 mg, 25 μmol) and chlorobenzene (2.5 mL) were placed in a Schlenk tube, which was previously purged with oxygen. Alkene (0.5 mmol) was added to the solution and stirred for 36 h under oxygen and irradiation in the closed tube. The mixture was chromatographed on an NH-silica gel column with pentane and Et_2O (1:0 to 20:1) to give the corresponding epoxide. The enantiomeric excess of the epoxide was determined by GLC or HPLC analysis using a chiral stationary phase.

4.2.2.1. *trans*-1-Phenyl-1,2-epoxypropane (Table 3, Run 8). Colorless oil. Yield 58% (88% ee). $[\alpha]_D^{24}$ −41.7 (*c* 0.88, $CHCl_3$). Lit.[27] [95.7% ee, (1*S*,2*S*)-isomer; $[\alpha]_D^{25}$ −46.9 (*c* 0.88, $CHCl_3$)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.24 (m, 5H), 3.57 (d, J = 2.2 Hz, 1H), 3.04 (dq, J = 2.2, 5.1 Hz, 1H), 1.45 (d, J = 5.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 137.6, 128.3, 127.9, 125.4, 59.5, 59.0, 17.9 ppm. GLC: t_R (1*S*,2*S*) = 23.8 min, t_R (1*R*,2*R*) = 25.9 min [InertCap CHIRAMIX: 70 °C (5.5 min) to 110 °C (46 °C/min) then 110 to 133 °C (1 °C/min)].

4.2.2.2. *trans*-1-(2-Naphthyl)-1,2-epoxypropane (Table 4, Run 1). White solid. Yield 75% (92% ee). $[\alpha]_D^{25}$ −42.4 (*c* 0.90,$CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83−7.76 (m, 4H), 7.51−7.30 (m, 3H), 3.74 (d, J = 2.0 Hz, 1H), 3.14 (dq, J = 2.0, 5.3 Hz,1H), 1.50 (d, J = 5.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.2, 133.2, 133.2, 128.2, 127.7, 126.3, 125.9, 125.0, 123.0, 59.8, 59.1, 12.9 ppm. HPLC: t_R (minor) = 16.5 min, t_R (major) = 18.2 min (DAICEL CHIRALCEL OB-H; flow rate, 1.0 mL/min; hexane/*i*-PrOH = 99.9/0.1; at 30 °C).

4.2.2.3. *trans*-1-(*m*-Methylphenyl)-1,2-epoxypropane (Table 4, Run 2). Colorless oil. Yield 67% (90% ee). $[\alpha]_D^{25}$ −44.6 (*c* 0.35, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26−7.06 (m, 4H), 3.54 (d, J = 2.2 Hz, 1H), 3.1−3.0 (dq, J = 5.1, 2.2 Hz, 1H), 2.34 (s, 3H), 1.45 (d, J = 5.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 138.0, 137.5, 128.6, 128.2, 125.9, 122.6, 59.6, 58.9, 21.5, 18.0 ppm. HPLC: t_R (minor) = 8.8 min, t_R (major) = 13.3 min (DAICEL CHIRALPAC AS-H; flow rate, 0.5 mL/min; hexane/*i*-PrOH = 95/5).

4.2.2.4. *trans*-1-(*p*-Methylphenyl)-1,2-epoxypropane (Table 4, Run 5). Colorless oil. Yield 58% (76% ee). $[\alpha]_D^{24}$ −30.3 (*c* 0.59, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26−7.06 (m, 4H), 3.54 (d, J = 2.0 Hz, 1H), 3.03 (dq, J = 5.1, 2.0 Hz, 1H), 2.34 (s, 3H), 1.44 (d, J = 5.1 Hz, 3H). ^{13}C NMR (100 MHz): δ 137.6, 134.5, 129.0, 125.4, 59.6, 58.9, 21.3, 18.0 ppm. HPLC: t_R (minor) = 8.6 min, t_R (major) = 10.3 min (DAICEL CHIRALPAC AS-H; flow rate, 0.5 mL/min; hexane/*i*-PrOH = 90/10).

4.2.2.5. (2*R*,3*R*)-2-Phenyl-2,3-epoxybutane (Table 4, Run 6). Colorless oil. Yield 55% (88% ee). $[\alpha]_D^{25}$ +14.8 (*c* 0.88, $CHCl_3$). Lit.[28] [99% ee, (2*S*,3*S*)-isomer; $[\alpha]_D^{20}$ −16.0 (*c* 1.0, $CHCl_3$)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36−7.24 (m, 5H), 2.95 (q, J = 5.4 Hz, 1H), 1.66 (s, 3 H), 1.43 (d, J = 5.4 Hz, 3H). ^{13}C NMR (100 MHz): δ 143.0, 128.3, 127.1, 125.0, 62.3, 60.3, 17.4, 14.4 ppm. HPLC: t_R (1*R*,2*R*) = 16.5 min, t_R (1*S*,2*S*) = 20.0 min (DAICEL CHIRALPAC AS-H; flow rate, 0.5 mL/min; hexane).

4.2.2.6. (1*S*,2*R*)-*cis*-β-Methylstyrene Oxide (Table 4, Run 7). Colorless oil. Yield 34% (90% ee). $[\alpha]_D^{25}$ +43.8 (*c* 0.15, $CHCl_3$). Lit.[29] [>99% ee, (1*S*,2*R*)-isomer; $[\alpha]_D^{20}$ +47.5 (*c* 1.17, $CHCl_3$)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37−7.25 (m, 5H), 4.06 (d, J = 4.4 Hz, 1H), 3.34 (dq, J = 4.4, 5.4 Hz, 1H), 1.08 (d, J = 5.4 Hz, 3H). ^{13}C NMR (100 MHz): δ 135.3, 127.8, 127.3, 126.4, 57.5, 55.2, 12.7 ppm. GLC: t_R (1*S*,2*R*) = 24.1 min, t_R (1*R*,2*S*) = 25.6 min [InertCap CHIRAMIX: 70 °C (5.5 min) to 110 °C (46 °C/min) then 110 to 133 °C (1 °C/min)].

4.3. Confirmation of the Effect of Water on Asymmetric Aerobic Oxidation: Asymmetric Epoxidation of *trans*-β-Methylstyrene Using Dried or Wet 3 as the Catalyst. Epoxidation with dried **3** as the catalyst: Complex **3** (4.9 mg, 5.0 μmol) was placed in a Schlenk tube. The Schlenk tube was heated at 380 °C with a heat gun for 5 min in vacuo followed by cooling at room temperature and purging with O_2 gas. After that, chlorobenzene (0.5 mL), *trans*-β-methylstyrene (13 μL, 0.1 mmol), and a small amount of phenanthrene as an internal standard for ^{1}H NMR analysis were added to the Schlenk tube. An aliquot (40 μL) of this solution was taken out of the Schlenk tube as the zero point. The aliquot was diluted by $CDCl_3$ and submitted to ^{1}H NMR analysis. The reaction mixture was stirred at room temperature for 36 h under visible light irradiation in the closed tube. A small quantity of the samples were taken out for ^{1}H NMR analysis and GLC analysis with InertCap CHIRAMIX [70 °C

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(5.5 min) to 110 °C (46 °C/min) then 110 to 133 °C (1 °C/min)], respectively. The results are shown in Scheme 5.

Epoxidation with wet **3** as the catalyst: The epoxidation was carried out in the same manner as that with dried **3**, except that water (1.8 μL, 0.1 mmol) was added to the tube together with *trans*-β-methylstyrene.

ESI-TOF-MS analysis of **3** and dried **3** gave the ion peak [M^+] at *m*/*z* 956.2428 and 956.2436, respectively (*m*/*z* calcd for [M^+] $C_{60}H_{44}N_3O_3Ru$, 956.2437).

4.4. Proof of the Necessity of Irradiation for Aerobic Oxidation: The Reaction of *trans*-β-Methylstyrene Using 3 as the Catalyst in the Dark. Complex **3** (4.9 mg, 5 μmol) and chlorobenzene (0.5 mL) were placed in a Schlenk tube, which was previously purged with oxygen. To the solution were added *trans*-β-methylstyrene (13.0 μL, 0.1 mmol) and a small amount of phenanthrene as an internal standard for ^{1}H NMR analysis. An aliquot (20 μL) of this solution was taken out of the Schlenk tube as the zero point. The aliquot was diluted by $CDCl_3$ and submitted to ^{1}H NMR analysis. The Schlenk tube was light-shielded, and the mixture was stirred for 36 h under irradiation in the closed tube. No formation of the epoxide was detected by ^{1}H NMR analysis.

4.5. Confirmation of the Stoichiometric Oxidant of the Present Asymmetric Oxidation.

4.5.1. The Reaction of *trans*-β-Methylstyrene Using 3 as the Catalyst under Nitrogen Atmosphere. Under nitrogen atmosphere, Ru−salen complex **3** (4.9 mg, 5 μmol) and chlorobenzene (0.5 mL) were placed in a Schlenk tube. To the solution were added *trans*-β-methylstyrene (13.0 μL, 0.1 mmol) and a small amount of phenanthrene as an internal standard for ^{1}H NMR analysis. An aliquot (20 μL) of this solution was taken out of the Schlenk tube as the zero point. The aliquot was diluted by $CDCl_3$ and submitted to ^{1}H NMR analysis. The reaction mixture was stirred under visible light irradiation for 36 h in the closed tube. No formation of the epoxide was detected by ^{1}H NMR analysis.

4.5.2. ^{18}O Incorporation Experiment: Asymmetric Epoxidation of *trans*-β-Methylstyrene Using 3 as the Catalyst in $^{18}O_2$. Complex **3** (4.9 mg, 5 μmol) and chlorobenzene (0.5 mL) were placed in a Schlenk tube, which was previously purged with $^{18}O_2$. To the solution were added *trans*-β-methylstyrene (13.0 μL, 0.1 mmol) and a small amount of phenanthrene as an internal standard for ^{1}H NMR analysis. An aliquot (40 μL) of this solution was taken out of the Schlenk tube as the zero point. The aliquot was diluted by $CDCl_3$ and submitted to ^{1}H NMR analysis. The reaction mixture was stirred at room temperature under visible light irradiation in the closed tube. A small quantity of the sample was taken out at an appropriate interval for ^{1}H NMR analysis, GLC analysis with InertCap CHIRAMIX [70 °C (5.5 min) to 110 °C (46 °C/min) then 110 to 133 °C (1 °C/min)], and ESI-TOF-MS analysis. The results are shown in Table 5.

4.6. Confirmation of the Incorporation of the Oxygen Atom from Water to the Product.

4.6.1. Asymmetric Epoxidation of *trans*-β-Methylstyrene Using 3 as the Catalyst in the Presence of ^{18}O-Labeled Water. A solution of complex **3** in chlorobenzene (0.05 M, 0.1 mL, 5 μmol) and $H_2{}^{18}O$ (2.0 μL, 0.1 mmol) was added to 0.3 mL of chlorobenzene under O_2 atmosphere in a 5 mL Schlenk tube and stirred for 1 h at room temperature under visible light irradiation. A solution of *trans*-β-methylstyrene in chlorobenzene (1 M, 0.1 mL, 0.1 mmol) with a small amount of phenanthrene as an internal standard was added to the mixture. The reaction was carried out under irradiation in the closed tube. Samples (10 μL) were taken out at an appropriate interval for ^{1}H NMR, GLC with InertCap CHIRAMIX [70 °C (5.5 min) to 110 °C (46 °C/min), then 110 to 133 °C (1 °C/min)], and ES-TOF-MS analyses. The results are described in Scheme 6.

4.6.2. Asymmetric Oxidation of *o*-Chlorophenyl Methyl Sulfide Using 1 in the Presence of ^{18}O-Labeled Water. Complex **1** (5.0 mg, 5.0 μmol) and dry AcOEt (0.5 mL) were placed in a 5 mL Schlenk tube under oxygen atmosphere. $H_2{}^{18}O$ (1.8 μL, 0.1 mmol, content of $^{18}O > 98\%$) and a small amount of phenanthrene as an internal standard for HPLC analysis were added to the suspension. The mixture was stirred for 30 min under irradiation with a halogen lamp. Then, *o*-chlorophenyl methyl sulfide (13 μL, 0.1 mmol) was added to the mixture. An aliquot (10 μL) of this suspension was taken out of the Schlenk tube as the zero point. The aliquot was diluted by EtOH and submitted to HPLC analysis. The reaction was carried out for 48 h under irradiation and oxygen atmosphere, and traced by HPLC analysis. Yield and enantiomeric excess of *o*-chlorophenyl methyl sulfoxide were determined by HPLC analysis using chiral stationary phase [DAICEL CHIRALCEL OB-H (hexane/*i*-PrOH/EtOH = 90/5/5)], and the ^{18}O content of each sulfoxide was determined by ESI-TOF-MS analysis. The results are shown in Scheme 7.

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Supporting Information Available: GLC and HPLC conditions and ESI-TOF-MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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