Optically Active *N,N'*-Bis(3-oxobutylidene)diaminatomanganese(III) Complexes as Novel and Efficient Catalysts for Aerobic Enantioselective Epoxidation of Simple Olefins

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A novel manganese(III) complex having an optically active *N,N'*-bis(3-oxobutylidene)diamine ligand with bulky substituents was prepared and characterized crystallographically. In the presence of a catalytic amount of the manganese(III) complex, unfunctionalized olefins were oxygenated to give optically active epoxides with molecular oxygen by the combined use of several aliphatic aldehydes. Cyclic and acyclic *cis*-β-substituted styrene derivatives, conjugated dienes, and enynes were converted into the corresponding epoxides with moderate-to-good enantioselectivities. The present aerobic and enantioselective epoxidation proceeded with the opposite enantioface selection from those obtained by using terminal oxidants, such as sodium hypochlorite and iodosylbenzene. The key intermediate of the aerobic asymmetric epoxidation is also discussed.

The development of a general method for the preparation of functionalized organic compounds from simple and readily available substrates is one of the most important propositions in organic synthesis. The oxidation of olefins catalyzed by transition-metal complexes is a fundamental synthetic tool, and many useful methods for the metal-catalyzed oxygenation of olefins have been studied during the last decade. An enantioselective nonenzymatic epoxidation of unfunctionalized olefins is one of the recent and important targets,[1] which contributes possible control of the stereochemistry of adjacent two-carbon centers. Several reactions have been reported which used artificial metalloporphyrins or manganese(III)–salen complexes together with terminal oxidants, such as iodosylbenzene,[2] sodium hypochlorite,[3] and hydrogen peroxide.[4] Progress in asymmetric epoxidation catalyzed by manganese(III)–salen-based complexes is especially worth of noticing.[5] However, few have successfully used molecular oxygen in the asymmetric epoxidation of unfunctionalized olefins.[6]

Recently, the oxidation–reduction hydration of olefins by the combined use of molecular oxygen and secondary alcohols catalyzed by cobalt(II) complexes having 1,3-diketone-type ligands with electron-withdrawing groups[7] and aerobic epoxidation of olefins catalyzed by a nickel(II) complex having 1,3-diketone-type ligands with electron-donating groups[8] were reported from our laboratory. Further, the effective aerobic epoxidation of olefins catalyzed by such metal complexes as iron(III),[9] vanadium(IV),[10] and manganese(II)[11] coordinated with the β-diketonato ligand in the coexistence of an aldehyde has been developed. During the course of the above-mentioned experiments, the stereoselective formation of β-epoxides by manganese(II)-catalyzed epoxidation of cholesterol derivatives was observed, while conventional methods using peroxyacids as oxidants gave α-epoxide, a reversal configuration.[11,12] These results suggest that the key intermediate generated from the manganese complex and molecular oxygen would participate directly during the oxidation step of olefin. Therefore, the aerobic enantioselective epoxidation of simple olefins could be achieved when manganese complexes having optically active ligands derived from β-diketone were used.

Then, new and effective kinds of optically active manganese(III) complexes having *N,N'*-bis(3-oxobutylidene)diamine ligands were designed.[13] After several experiments using these chiral catalysts, optically active *N,N'*-bis(3-oxobutylidene)diaminatomanganese(III) complexes (Fig. 1) having bulkier substituents proved to catalyze most effectively the aerobic enantioselective epoxidation of simple olefins.

This paper describes details concerning the aerobic and enantioselective epoxidation catalyzed by optically active *N,N'*-bis(3-oxobutylidene)diaminatomanganese(III) complexes, including the design of a catalyst based on a crystallographical analysis, and their preparative

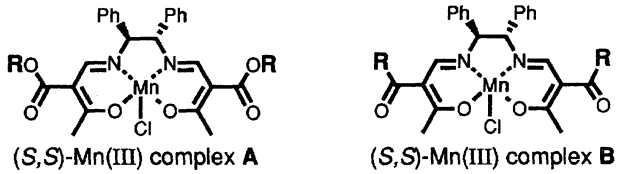
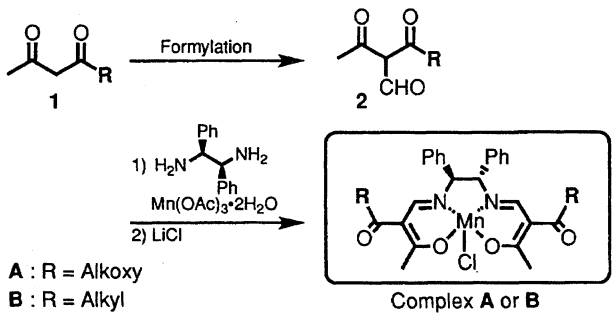


Fig. 1. Optically active [*N*,*N*′-bis(3-oxobutylidene)-diaminato]chloromanganese(III).

methods. Furthermore, a hypothetic consideration on the enantiofacial discrimination of olefins and the key intermediate of the epoxidation are also discussed.

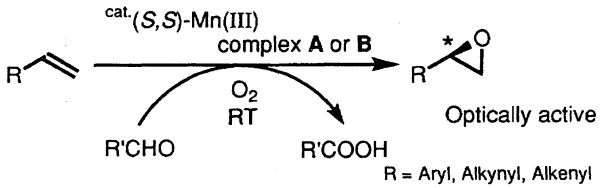
Results and Discussion

Preparation of Optically Active *N*,*N*′-Bis-(3-oxobutylidene)diaminatomanganese(III) Catalyst. Optically active chloro[*N*,*N*′-bis(3-oxobutylidene)diaminato]manganese(III) complexes, (*S*,*S*)-[*N*,*N*′-bis(2-alkoxycarbonyl-3-oxobutylidene)diaminato]chloromanganese(III) **A**, were prepared by the following procedure (Scheme 1). Alkyl acetoacetates **1** (R=alkoxy) were derived from the corresponding alcohols by the reported method,[14] and a treatment of **1** with *N*,*N*-dimethylformamide dimethylacetal[15] and subsequent hydrolysis afforded 2-formyl-3-oxobutyrate **2** (R=alkoxy). The formation of a manganese(III) complex from *N*,*N*′-bis(2-alkoxycarbonyl-3-oxobutylidene)diamine ligand were first tried using a template method,[2d] which was usually employed for the preparation of salen–manganese(III) complexes. For example, optically active manganese(III) complexes with salen-type ligands were prepared by mixing manganese(II) salt, such as manganese(II) acetate[16] and the ligand, followed by air oxidation. However, the above-mentioned procedure involving air oxidation afforded the desired manganese(III) complex in very low yield (<3%). Finally, it became evident that the use of manganese-(III) salt instead of manganese(II) salt was crucial; that is, the desired complex **A** was obtained by heating a mixture of **2** (R=alkoxy), (*S*,*S*)-1,2-diphenylethylenediamine, and manganese(III) acetate in a proper solvent, followed by the addition of lithium chloride.[17] The pure manganese(III) complex **A** was isolated as a dark-brown powder after purification by silica-gel column chromatography. In a similar manner, manganese(III) complex **B** was afforded from the corresponding *N*,*N*′-bis(2-acyl-3-oxobutylidene)ethylenediamine ligand derived from **2** (R=alkyl), prepared by the formylation of β-dicarbonyl compound **1**.



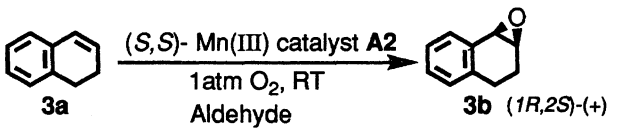
Scheme 1.

Influence of an Aldehyde on the Optical Yields in the Aerobic and Asymmetric Epoxidation of Unfunctionalized Olefins. In order to examine the effect of aldehyde on the enantiomeric excess, 1,2-dihydronaphthalene (**3a**) was chosen as a model substrate (Table 1). The reaction was carried out in benzene[18] at room temperature[19] under an atmospheric pressure of oxygen in the coexistence of the optically active (*S*,*S*)-[*N*,*N*′-bis(2-alkoxycarbonyl-3-oxobutylidene)diaminato]chloromanganese(III) **A2** (R=methyl) using various aliphatic aldehydes. It was noted that the enantioselectivities were influenced by the structure of an aldehyde; that is, in the presence of butyraldehyde, 1,2-dihydronaphthalene was converted into the corresponding (1*R*,2*S*)-(+)-epoxide **3b** in 48% yield with molecular oxygen, whose enantiomeric excess was determined by a GC analysis to be 14% ee. When isobutyraldehyde and isovaleraldehyde were used, the optical yields of epoxide **3b** were 15 and 26% ee, respectively. The use of 2,2-dimethylpropanal was proved to be the most effective in respect of enantioselection (33% ee).



Scheme 2.

Table 1. Aldehydes as Reductant in Aerobic Asymmetric Epoxidation

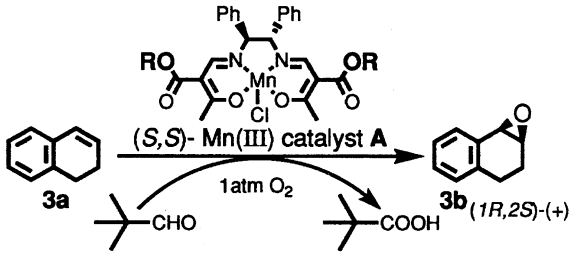


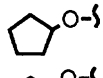
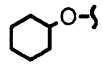
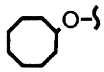
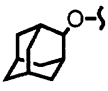
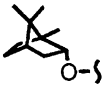
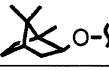
Entry[a]	Aldehyde	Yield/%[b]	Optical yield/%ee[c]
1	CHO	48	14
2	CHO	82	15
3	CHO	51	26
4	CHO	64	33

a) Reaction conditions; 1,2-dihydronaphthalene 0.8 mmol, aldehyde 2.8 mmol (3.5 molar amounts), Mn(III) catalyst **A2** (R=methyl) 0.104 mmol in benzene 2 ml, RT, 1 atm O_2, 1 h. b) Isolated yield. c) Determined by GC analysis (Chiraldex B-DA(20 m×0.25 mm ID×0.125 μm film)).

Steric Effect of the Ester Moiety in *N,N'*-Bis(2-alkoxycarbonyl-3-oxobutylidene)diamine Ligand on the Enantioselectivities of the Aerobic Epoxidation. The steric effect of alkyl groups (**R**) contained in complex **A** upon enantioselection was examined (Table 2); (*S,S*)-[*N,N'*-bis(2-alkoxycarbonyl-3-oxobutylidene)diaminato]chloromanganese(III) catalyst **A** derived from a bulkier alcohol improved the enantiomeric excess of epoxide **3b**. Compared with the cases of using (*S,S*)-**A2** (33% ee) derived from methyl acetoacetate, optically active epoxide **3b** was obtained with better enantioselections when (*S,S*)-[*N,N'*-bis(2-alkoxycarbonyl-3-oxobutylidene)diaminato]chloromanganese(III) catalysts **A3**, **A4**, **A5**, and **A6**, with bulkier substituents such as cyclopentyl, cyclohexyl, cyclooctyl, and 2-adamantyl groups were used (37, 42, 43, and 44% ee, respectively). In the cases of (*S,S*)-catalyst **A7** and (*R,R*)-catalyst **A7** derived from chiral (−)-borneol and optically active (*S,S*) or (*R,R*)-1,2-diphenylethylenediamine, the absolute configurations and optical yields of epoxide **3b** were (1*R*,2*S*)-(+) (50% ee) (Entry 7) and (1*S*,2*R*)-(−) (45% ee), respectively. These results indicate that the enantioface selection in the present asymmetric reaction is dominated by the absolute configuration of optically active diamine unit and that the chirality of ester moiety had little influence.

Table 2. Correlation between Steric Bulkiness of Type **A** Catalyst and Optical Yield of Epoxide **3b**



Entry[a]	OR		Yield/%[b]	Optical yield/%ee[c]
1	CH_3O-	**A2**	64	33
2		**A3**	45	37
3		**A4**	42	42
4		**A5**	39	43
5		**A6**	46	44
7[d]		**A7**	47	50
8[e]		**A1**	51	52

a) Reaction conditions; 1,2-dihydronaphthalene 0.8 mmol, 2,2-dimethylpropanal 2.8 mmol, Mn(III) catalyst 0.104 mmol (13 mol%) in benzene 2 ml, RT, 1 atm O_2, 1 h. b) Isolated yield. c) Determined by GC analysis (Chiraldex B-DA (20 m×0.25 mm ID×0.125 μm film)). d) (*S,S*)-Diamine/(−)-borneol-catalyst was used. e) (*S,S*)-Diamine/DL-isoborneol-catalyst.

In the case of the manganese(III) complex **A1**, having bulky alkoxycarbonyl moieties derived from DL-isoborneol, the optical yield was improved up to 52% ee (Entry 8).

Designing of [*N,N'*-Bis(2-acyl-3-oxobutylidene)ethylenediaminato]chloromanganese(III) B Based on an X-Ray Analysis. The crystal of (*R,R*)-[*N,N'*-bis(2-cyclopentyloxycarbonyl-3-oxobutylidene)ethylenediaminato]chloromanganese(III) **A3** (R= cyclopentyl) was obtained as dark-brown needles by slowly evaporating the solvent (dichloromethane/hexane=1/2) at room temperature for 3 d. The crystallographical analysis was performed by using the above-mentioned crystal.[13b] Contrary to our expectations, the X-ray analysis revealed that the bulky alkoxycarbonyl moiety on the ligand of catalyst **A** was located in the neighborhood of the aromatic ring of the optically active diamine part, as illustrated in Fig. 2(b); cyclopentyl group of the alkoxycarbonyl moiety was adjacent to the phenyl group of the diamine unit. Consequently, a sterically more hindered site was constructed on the square base of the manganese complex (site **b** in (Fig. 2 (b)). It is noted that the bulkiness of the alkoxycarbonyl substituent may only serve to control the approach of olefins to the chiral 1,2-diphenylethylenediamine unit.

Based on the above observation, [*N,N'*-bis(2-acyl-3-oxobutylidene)ethylenediaminato]chloromanganese(III) **B** was designed with the expectation that the bulky ketone function would be more effective to establish enantioselective epoxidation; the distance between the bulky substituent of the ketone moiety and the reaction site, manganese atom, would be shortened by one bond in length compared to that of ester-type catalyst **A**. It was therefore expected that the ketone function served to create a more sterically controlled configuration, which would improve the enantioselection. Then, several manganese(III) catalysts **B** were prepared and examined in the aerobic enantioselective epoxidation of 6,7-dihydro-5*H*-benzocycloheptene (**4a**). As expected, the manganese(III) complexes, **B3** and **B4**, having bulky substituents, such as 2-naphthyl and 1-naphthyl groups, were found to catalyze the aerobic epoxidation with moderate enantioselectivities (53 and 63% ee, respectively) (Entries 2 and 3 in Table 3). Finally, the enantiomeric excess of the corresponding epoxide **4b** increased up to 76% ee (Entry 4) by using catalyst **B1** derived from 2,4,6-trimethylacetophenone.

Also, the *N,N'*-bis-(3-oxobutylidene)diaminatomanganese(III) complex catalysts, **A1** and **B1**, were examined in the aerobic epoxidation of *cis*-β-methylstyrene as a model reaction of an acyclic olefin. The type **B** catalyst proved to achieve a good enantiomeric ex-

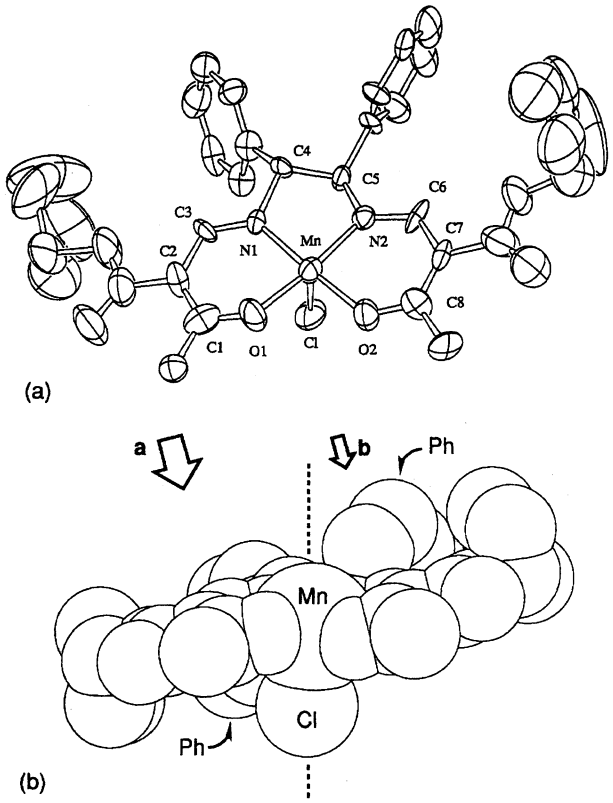
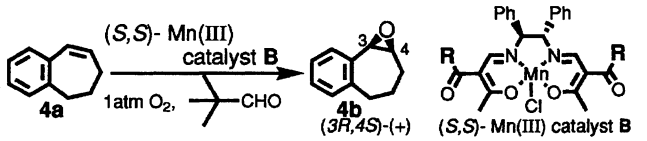


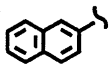
Fig. 2. Crystal structure of (*R*,*R*)-[*N*,*N*′-bis(2-cyclopentyloxycarbonyl-3-oxobutylidene)-1,2-diphenylethylenediaminato]chloromanganese(III) **A3** (R=cyclopentyl): (a) ORTEP view. Selected bond lengths (Å) and bond angles (°) are as follows: Mn–Cl, 2.574(9); Mn–O(1), 1.92(1); Mn–O(2), 1.91(1); Mn–N(1), 1.94(1); Mn–N(2), 1.95(1); Cl–Mn–O(1), 95.0(5); Cl–Mn–O(2), 95.5(5); Cl–Mn–N(1), 84.2(5); Cl–Mn–N(2), 88.2(5); O(1)–Mn–N(2), 173.8(7); O(2)–Mn–N(1), 176.9(6); O(1)–Mn–O(2), 93.5(5); O(1)–Mn–N(1), 89.7(6); O(2)–Mn–N(2), 91.5(6); N(1)–Mn–N(2), 85.4(6); (b) Side view (Space filling model based on the X-ray crystal structure).

cess; that is, complex **B1** afforded the corresponding optically active *cis*-epoxide with 80% ee, while complex **A1** did so with 67% ee (Table 4).

Aerobic Enantioselective Epoxidation of Various Simple Olefins. An asymmetric aerobic epoxidation catalyzed by optically active [*N*,*N*′-bis (2-alkoxycarbonyl-3-oxobutylidene)diaminato]chloromanganese(III) **A1** was sucessfully applied to several 1,2-dihydronaphthalene derivatives. Dihydronaphthalenes without having any functional groups, **3a**, **6a**, and **7a**, were converted into the corresponding epoxides at 30 °C[19] in good yields with good enantioselections, 64, 53, and 70% ee, respectively, by the combined use of molecular oxygen and 2,2-dimethylpropanal (Entries 1, 2, and 3 in Table 5). In the case of an enantioselective epoxidation of 6,7-dihydro-5*H*-benzocycloheptene (**4a**), the optically active (3*R*,4*S*)-(+)-epoxide was obtained with good enantiomeric excess (84% ee, Entry 6).[20]

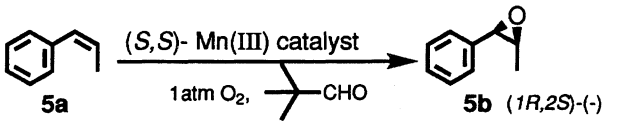
Table 3. Correlation between Steric Bulkiness of Type **B** Catalyst and Optical Yield of Epoxide **4b**

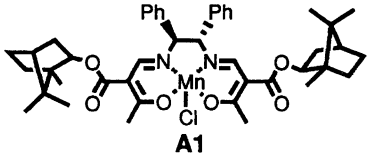
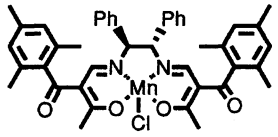


Entry[a]	R		Yield/%[b]	Optical yield/%ee[c]
1	CH_3	**B2**	53	52
2		**B3**	56	53
3		**B4**	37	63
4		**B1**	43	76

a) Reaction conditions; 6,7-dihydro-5*H*-benzocycloheptene 0.8 mmol, 2,2-dimethylpropanal 2.8 mmol, Mn(III) catalyst 0.104 mmol (13 mol%) in benzene 2 ml, RT, 1 atm O_2, 1 h. b) Isolated yield. c) Determined by GC analysis (Chiraldex B-DA (20 m×0.25 mm ID×0.125 μm film)).

Table 4. Comparison between Catalyst **A** and **B** in Aerobic Asymmetric Epoxidation of β-Methylstyrene

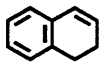
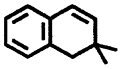
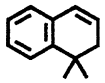
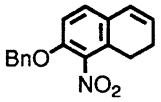
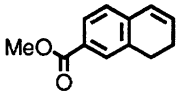
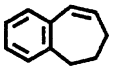
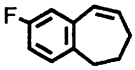
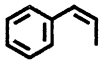
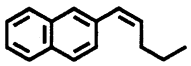
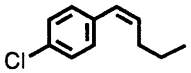
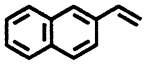


Entry[a]	Catalyst	Optical yield/%ee[b]
1	 **A1**	67
2	 **B1**	80

a) Reaction conditions; olefin 0.8 mmol, aldehyde 2.0 mmol (2.5 molar amounts), Mn(III) catalyst 0.104 mmol in benzene 2 ml, RT, 1 atm O_2, 1 h. b) Determined by GC analysis (Chiraldex B-PH (30 m×0.32 mm ID×0.125 μm film)).

[*N*,*N*′-Bis(2-acyl-3-oxobutylidene)ethylenediaminato]-chloromanganese(III) **B1** was effective for the aerobic epoxidation of several acyclic unfunctionalized olefins. By using complex **B1**, *Z*-2-(1-pentenyl)naphthalene (**11a**) was converted into the corresponding optically active *cis*-epoxide with good enantioselection (76% ee) along with *trans*-epoxide.[21] When an atmospheric pressure of air was used instead of oxygen, the formation of *trans*-epoxide was suppressed. The ratio of *cis*/*trans*

Table 5. Aerobic Enantioselective Epoxidation of Various Simple Olefins

Entry	Olefin[a]		Catalyst[b]	Yield/%[c] (*cis*/*trans* ratio[d])	Optical yield/%ee[e]
1		**3a**	**A1**	70	64
2		**6a**	**A1**	40	53
3		**7a**	**A1**	43	70
4		**8a**	**A1**	73	43
5		**9a**	**A1**	67	59
6		**4a**	**A1**	52	84
7		**10a**	**A1**	32	79
8		**5a**	**B1**	28(63/37)	*cis* 80[f] *trans* 47[g]
9		**11a**	**B1**	40(88/12)	*cis* 80[h]
10			**B1**[i]	57(79/21)	*cis* 76[h] *trans* 31[h]
11		**12a**	**B1**	31(69/31)	*cis* 79[f] *trans* 24[f]
12		**13a**	**B1**[j]	49	48[k]
13		**14a**[l]	**B1**	53(63/37)	*cis* 75[h] *trans* 87[h]
14		**15a**	**B1**	47	57[m]

a) Dihydronaphthalene derivatives were prepared from the corresponding tetralone derivatives. b) Catalyst **A1**; olefin 0.8 mmol, 2,2-dimethylpropanal 2.8 mmol, Mn(III) catalyst **A1** 0.104 mmol (13 mol%) in benzene 2 ml, 30 °C, 1 atm O_2, 1 h: Catalyst **B1**; Mn(III) catalyst **B1** 0.104 mmol (13 mol%) in benzene 2 ml, RT, 1 atm air, 1 h. c) Isolated yield. d) *cis*/*trans* ratio of formed epoxides. Determined by ^{1}H NMR analysis. e) Determined by GC analysis (Chiraldex B-DA) unless otherwise noted. f) Determined by GC analysis (Chiraldex B-PH). g) Determined by GC analysis (Chiraldex G-TA). h) Determined by HPLC analysis (Chiralpak AD). i) 2,2-Dimethylpropanal 4.0 mmol (5.0 molar amounts) was used in two portions. j) Atmospheric pressure of oxygen was used. k) Determined by HPLC analysis (Chiralcel OB, Daicel, Ltd.). l) Prepared by the literature procedure. See Ref. 24. m) Determined by ^{1}H NMR using Eu(hfc)$_3$ as a shift reagent.

isomers improved from 65/35 to 88/12, and the chemical yield of *cis*-epoxide increased (Entry 9). These results were reasonably explained by assuming the initial generation of a radical intermediate formed from *cis*-olefin. The intermediate readily cyclized to produce *cis*-epoxide along with *trans*-epoxide in the manganese(III)-catalyzed epoxidation when a terminal oxidant, such as sodium hypochlorite or iodosylbenzene, was used.[22] It is also reported that the radical intermediate mentioned above could capture molecular oxygen to generate dioxyl species, which induces the conversion of *cis*-olefin into *trans*-epoxide to result in the formation of a mixture of *cis*- and *trans*-epoxides.[23] When an atmospheric pressure of air was used as an oxygen source, the trap-

ping of the radical intermediate by molecular oxygen was controlled, and the ratio of the formation of *cis*-epoxide against *trans*-epoxide was improved. In general, 2,2-dimethylpropanal was properly employed as a reductant in the present aerobic enantioselective epoxidation; for example, *cis*-β-alkylstyrene derivatives **5a** and **12a** were converted into the corresponding *cis*-epoxides with good enantioselections, 80 and 79% ee, by means of an atmospheric pressure of air at room temperature (Entries 8 and 11). Terminal olefin **13a** was also led to the corresponding optically active epoxide with moderate enantioselection (Entry 12).

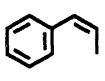
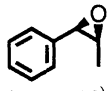
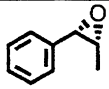
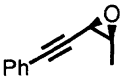
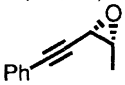
The present aerobic enantioselective epoxidation was applicable not only to styrene derivatives, but also to aliphatic olefins conjugated to a π-electron system, such as alkynyl and alkenyl groups (Entries 13 and 14). It is noted that *cis*-enyne **14a** was converted into the corresponding *cis*-epoxide as a major product in 75% ee along with *trans*-epoxide, a minor product, with higher enantioselectivity (87% ee) than that of *cis*-epoxide.[24]

Reversal of the Absolute Configuration by Using Terminal Oxidant. It is particularly important to note that the present enantiofacial selection is opposite to those of reported methods in which oxidants other than molecular oxygen were used; that is, by using a terminal oxidant, such as sodium hypochlorite,[3b] (*S,S*)-[*N,N'*-bis(2-acyl-3-oxobutylidene)ethylenediaminato]chloromanganese(III) **B1** afforded (1*S*,2*R*)-(+)-*cis*-epoxide with only 29% ee. On the contrary, (1*R*,2*S*)-(−)-epoxide (80% ee) was obtained by the present aerobic epoxidation catalyzed by (*S,S*)-[*N,N'*-bis(2-acyl-3-oxobutylidene)ethylenediaminato]chloromanganese(III) **B1** with the combined use of molecular oxygen and 2,2-dimethylpropanal (Entry 1 in Table 6).[25] A reversal of the absolute configuration by using sodium hypochlorite as an oxidant was observed in cases of the asymmetric epoxidation of enyne **14a** (Entry 2) and 1,3-cyclooctadiene (**15a**).[26] The face selections in the asymmetric epoxidation of *cis*-1,2-disubstituted olefins conjugated to a π-electron system, such as aryl, alkynyl, and alkenyl groups, are also shown in Fig. 3.

Reactive Intermediates in Aerobic Epoxidation Catalyzed by Optically Active [*N,N'*-Bis(3-oxobutylidene)diaminato]chloromanganese(III) Catalyst. The above results clearly indicate that the active species of the present aerobic epoxidation is different from the oxo-manganese complex **II** (Fig. 4), which has been widely accepted as an intermediate when terminal oxidants, such as sodium hypochlorite and iodosylbenzene, were used.[22]

(1*R*,2*S*)-(−)-Epoxide was also formed in 67% ee corresponding to (*S,S*)-[*N,N'*-bis(2-acyl-3-oxobutylidene)ethylenediaminato]chloromanganese(III) **B1** (Fig. 4) when peracetic acid was used as an oxidant instead of the combination of molecular oxygen and 2,2-dimethylpropanal. Recently, it was reported that similar

Table 6. Reversion of Absolute Configuration of Epoxides by the Use of Terminal Oxidant

Entry	Substrate	Oxidant	Major product (ee/%)	
			O_2, CHO[a]	NaClO[b]
1		**5a**	 (80) (1*R*,2*S*)[c]	 (29) (1*S*,2*R*)
2		**14a**	 (75) (3*R*,4*S*)[d]	 (16) (3*S*,4*R*)

a) The present procedure. (*S,S*)-**B1** catalyst was used. b) Jacobsen's procedure with (*S,S*)-**B1** as a catalyst. Ref. 3b. c) Absolute configuration was identified from the retention times of GC analysis comparing with the authentic sample prepared by the reported method. (Ref. 3b). d) Absolute configuration was determined by GC analysis compared with reported results (Refs. 24 and 25b).

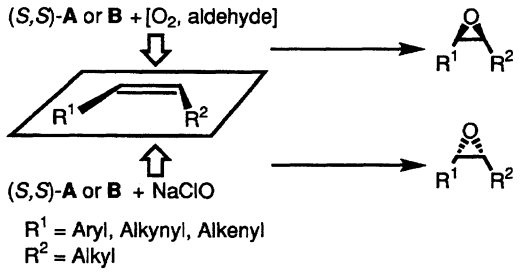


Fig. 3. Absolute configuration in epoxidation catalyzed by (*S,S*)-[*N,N'*-bis(3-oxobutylidene)diaminato]chloromanganese(III) **A** or **B**.

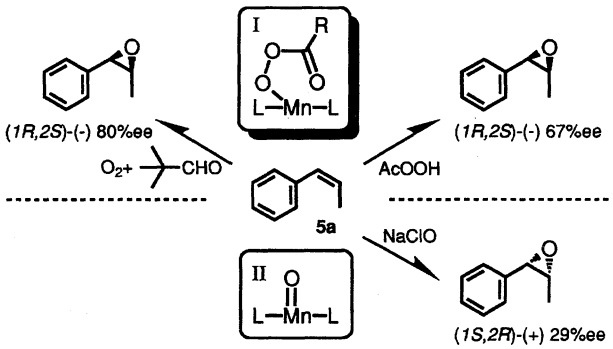


Fig. 4. Reactive intermediates of asymmetric epoxidation catalyzed by [*N,N'*-bis(3-oxobutylidene)-diaminato]chloromanganese(III) **B1** with combined use of various oxidants.

acylperoxo–metal porphyrin complexes directly participate in epoxidation where the oxo-intermediate is a less-favorable process.[27] Accordingly, it is reasonable to assume that the key intermediate in the present aerobic epoxidation is the acylperoxo–manganese complex **I** (Fig. 4), generated from an optically active manganese catalyst, molecular oxygen, and 2,2-dimethylpropanal. It is noted that the optically active *N,N'*-bis(3-oxobu-

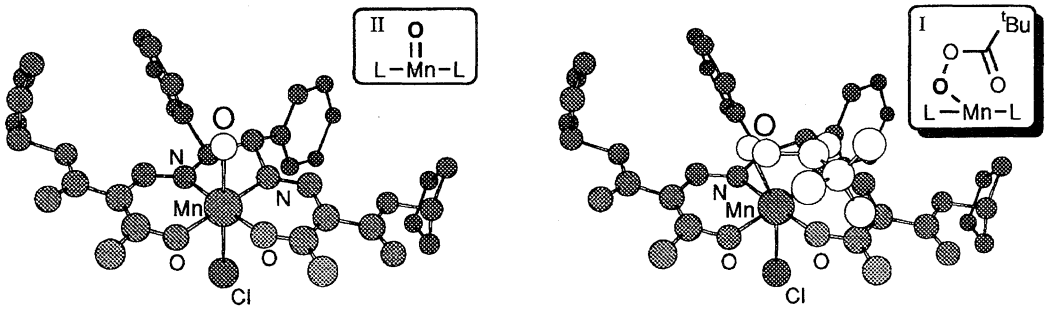


Fig. 5. Asymmetric environments of supposed reactive intermediates based on X-ray analysis of complex **A3**.

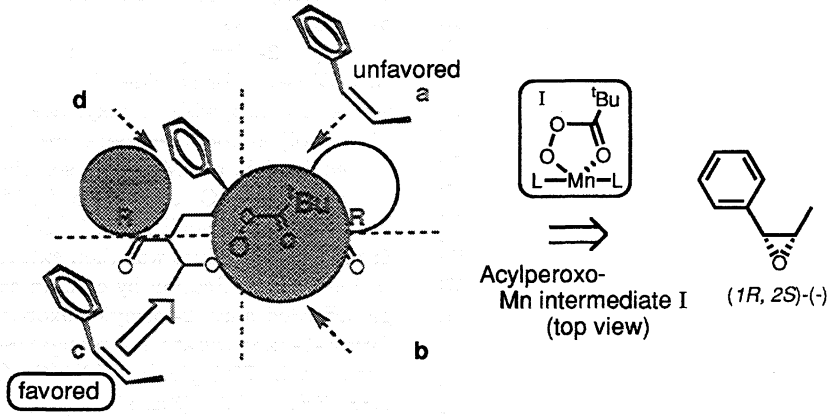


Fig. 6. Enantioface discrimination in epoxidation of β-methylstyrene catalyzed by (*S*,*S*)-**A** or **B**.

tylidene)diamine derivative is quite an effective ligand, leading to good enantioselection in manganese(III)-catalyzed aerobic epoxidation.

Sense of Asymmetric Induction. The aerobic epoxidation of *cis*-β-substituted styrene derivatives catalyzed by (*S*,*S*)-[*N*,*N*′-bis(3-oxobutylidene)-diaminato]manganese(III) complexes gives the corresponding *cis*-(1*R*,2*S*)-epoxide, while terminal oxidants, such as sodium hypochlorite and iodosylbenzene, afford the *cis*-(1*S*,2*R*)-epoxide as a major product. Although the mechanism of manganese(III)-catalyzed aerobic epoxidation of *cis*-1,2-disubstituted olefins has not yet been elucidated, the enantioface selection can be explained as follows. In contrast to the side-on approach of the oxo-metal intermediate, which has been proposed to account for the observed face selection of symmetric epoxidation catalyzed by porphyrin or salen complexes using the terminal oxidant,[2a,2c] asymmetric induction in epoxidation catalyzed by the *N*,*N*′-bis(3-oxobutylidene)diaminatomanganese(III) complex can be reasonably explained on the basis of this model. The following three interactions were supposed to be important factors for absolute enantioface selection: (1) the electrostatic interaction[28] between the aryl group (or alkynyl, alkenyl groups) conjugated to the reacting C–C double bond and the square plane containing the manganese atom in the *N*,*N*′-bis(3-oxobutylidene)diaminatomanganese(III) complex;[29] (2) the presence of bulky groups in the *N*,*N*′-bis(3-oxobutylidene)-diamine ligand of manganese(III) complex **A** or **B**; (3) the presence or absence of the bulky acylperoxy group in the key intermediates I or II.

(a) Oxo-Mn Intermediate II Generated from *N*,*N*′-Bis(3-oxobutylidene)diaminatomanganese(III) Complex A or B and Sodium Hypochlorite. The asymmetric environment created by (*S*,*S*)-*N*,*N*′-bis(3-oxobutylidene)diaminatomanganese(III) complex **A** or **B** and sodium hypochlorite is illustrated in Fig. 5(a)[30] based on an X-ray analysis of the manganese(III) complex **A3**. In the key intermediate II, olefin would approach the oxo–manganese bond along the manganese–nitrogen bond[31] (approach **a** in Fig. 6) because of (1) a π–π electronic repulsion[29] between the aryl group of the substrate and the square base containing the manganese atom and (2) a steric repulsion between the substrate and the 1,2-diphenyldiamine part of the manganese(III) complex. Accordingly, the major isomer (1*S*,2*R*)-(+) would be formed via approach **a** from β-methylstyrene. On the other hand, there may be few differences concerning asymmetric environments with respect to approaches **b** and **c** from the opposite site of the diamine part. Therefore, intermediate II could not discriminate the *re*-face from the *si*-face of the olefin when it approached the oxo-manganese intermediate II away from the optically active diamine unit. That is, a low enantioselectivity in the epoxidation by using sodium hypochlorite was observed (29% ee, Entry 1 in Table 6), because approaches

b and **c** were not so effectively limited.

(b) Acylperoxo-Mn Intermediate I Generated from *N,N'*-Bis(3-oxobutylidene)diaminatomanganese(III) Complex A or B, Molecular Oxygen, and 2,2-Dimethylpropanal. The asymmetric environment of the present epoxidation catalyzed by (*S,S*)-*N,N'*-bis(3-oxobutylidene)diaminatomanganese(III) complex **A** or **B** with the combined use of molecular oxygen and 2,2-dimethylpropanal is illustrated in Fig. 5(b). In this reaction, it is assumed that the acylperoxy group generated from molecular oxygen and aldehyde occupies the less hindered sites **a** and **b** on the square base of the manganese complex. Contrary to the former epoxidation, approach **a** is limited by the bulky *t*-butyl group, and approach **c** is presumably favored (Fig. 6); thus, (1*R*,2*S*)-(−)-epoxide **5b** was formed with good enantiomeric excess (80% ee) (Entry 1 in Table 6).

The reversal of the enantiofacial selection can also be reasonably explained based on the above consideration. Further, it was supported by the observation that the enantioselectivity was considerably influenced by the structure of the aldehyde used as a reductant; in the epoxidation of 1,2-dihydronaphthalene catalyzed by (*S,S*)-manganese(III) complex **A2**, the corresponding optically active epoxide was formed with 14, 15, 26, and 33% ee, by using butyraldehyde, isobutyraldehyde, isovaleraldehyde, and 2,2-dimethylpropanal, respectively (Table 1).

Conclusion

Optically active *N,N'*-bis(3-oxobutylidene)diaminatomanganese(III) complexes efficiently catalyzed the aerobic enantioselective epoxidation of simple olefins. Several unfunctionalized olefins, such as *cis*-*β*-substituted styrene derivatives, aliphatic conjugated diene, and enyne, were led to the corresponding epoxides with moderate-to-good enantioselectivities.

Experimental

General: The melting points were measured on a Mettler FP62 apparatus or a Seiko Denshi Kogyo Ltd. DSC-100 apparatus and were uncorrected.

(a) Spectrometers: Infrared (IR) spectra were recorded on a JASCO Model IR-700 spectrometer on KBr pellets or liquid film on KBr. ^{1}H NMR spectra were measured on a JEOL Model FX-270 spectrometer using $CDCl_3$ as a solvent and with tetramethylsilane as an internal standard.

(b) Chromatography: For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel (Daiso gel IR-60). High-performance liquid chromatography (HPLC) analyses were performed with a Shimadzu LC-6A chromatograph using an optically active column (Chiralcel OB and Chiralpak AD columns, Daicel Ltd., Co.); the peak areas were obtained with a Shimadzu chromatopack CR-4A. Analytical gas-liquid phase chromatography (GC) for a determination of the optical yields were performed on a Shimadzu GC-15A or GC-14A instrument equipped with a flame-ionization detector and an optically active glass capillary column (Chiraldex B-DA, 0.25 mm i.d., 20 m, 0.125 μm film, Chiraldex B-PH, 0.32 mm i.d., 30 m, 0.125 μm film, Chiraldex G-TA, 0.25 mm i.d., 20 m, 0.125 μm film, ASTEC Co.). The peak areas were obtained with a Shimadzu chromatopack CR-5A.

(c) Optical Rotations: Optical rotations were measured with a JASCO DIP-360 digital polarimeter.

General Procedure for Preparation of Optically Active [*N,N'*-Bis(2-alkoxycarbonyl-3-oxobutylidene)diaminato]chloromanganese(III) A (Scheme 1, R=Alkoxy): Manganese(III) complexes type-**A** were prepared as follows.

Alkyl 2-Formyl-3-oxobutyrate (2, R=Alkoxy): *N,N*-Dimethylformamide dimethylacetal (7.14 g, 60 mmol) was added dropwise to alkyl acetoacetate (**1**, R=Alkoxy) (30 mmol) at room temperature.[15] After the mixtuxe was stirred for 2 h, a 1 M NaOH solution (MeOH–H_2O, 50 ml) was added at 0 °C (1 M=1 mol dm^{-3}). After stirring for 2 h, the mixture was acidified at 0 °C with 1 M HCl into pH 3—4; the crude product was then extracted with ether. Evaporation and purification by column chromatography on silica gel afforded alkyl 2-formyl-3-oxobutyrate (**2**). Isobornyl 2-formyl-3-oxobutyrate for manganese(III) complex **A1** was obtained in 75% yield: ^{1}H NMR ($CDCl_3$) δ=0.86 (3H s), 0.88 (3H, s), 1.00 (3H, s), 1.1—1.3 (2H, m), 1.5—1.9 (5H, m), 2.56 (3H, s), 4.80 (1H, m), 9.16 (1H, d, J=5.9 Hz); IR 1715, 1636, 1573, 1455, 1412, 1357, 1265, 1184, 1069, 768 cm^{-1}.

[*N,N'*-Bis(2-alkoxycarbonyl-3-oxobutylidene)-(1*S*,2*S*)-diphenylethylenediaminato]chloromanganese(III) (A) (Templete Method): A mixture of alkyl 2-formyl-3-oxobutyrate (**2**, R=Alkyl) (6.6 mmol) and (*S,S*)-(−)-1,2-diphenylethylenediamine (0.64 g, 3.0 mmol) in 1,2-dicholoroethane (10 ml) was added to a suspension of manganese(III) acetate ($Mn(OAc)_3 \cdot 2H_2O$) (1.63 g, 6.0 mmol) in ethanol-1,2-dichloroethane (5 ml/15 ml). The resulting mixture was refluxed for 3 h; then, lithium chloride (0.32 g, 7.6 mmol) was added as a powder. After 1 h, the solvent was removed under reduced pressure. The residue was extracted with dichloromethane, and dried over sodium sulfate. Concentration in vacuo gave a crude manganese(III) complex. A pure manganese(III) complex was obtained as a dark-brown powder after purification by column chromatography on silica gel (dichloromethane/acetone) and reprecipitation (dicholoromethane/ether). Complexation of isobornyl 2-formyl-3-oxobutyrate gave the desired manganese(III) complex as a dark-brown powder (**A1**, 45% yield). Mp 230 °C (DSC). Found: C, 65.08; H, 6.38; N, 3.66%. Calcd for $C_{44}H_{54}N_2O_6ClMn$: C, 66.28; H, 6.83; N, 3.51%.

General Procedure for Preparation of Optically Active [*N,N'*-Bis(2-acyl-3-oxobutylidene)ethylenediaminato]chloromanganese(III) B (Scheme 1, R=Alkyl): Manganese(III) Complexes type-**B** were prepared as follows.

Formylation of 1,3-Diketone 1 (R=Alkyl): A mixture of 1,3-diketone **1**[32] (20 mmol) and trimethyl orthoformate (3.7 g, 35 mmol) in acetic anhydride (6.1 g, 60 mmol) was heated at 120 °C for 5 h. After acetic anhy-

dride was removed off under reduced pressure, distillation or column chromatography on silica gel afforded 2-formyl-1,3-dione **2**. The formylation of (2,4,6-trimethylbenzoyl)acetone (R=mesityl) provided 2-formyl-1-(2,4,6-trimethylphenyl)-1,3-dioxobutane (82% yield) for the manganese complex **B1**: ^{1}H NMR ($CDCl_3$) δ=2.20 (9H, s), 2.29 (3H, s), 6.92 (2H, s), 9.25 (1H, s); IR 1681, 1613, 1412, 1030, 850, 748 cm^{-1}.

***N,N'*-Bis(2-acyl-3-oxobutylidene)-(1*S*,2*S*)-1,2-diphenylethylenediamine:** A mixture of (*S,S*)-(−)-diphenylethylenediamine (2.12 g, 10 mmol) and 2-formyl-1,3-dione **2** (22 mmol) in ethanol/1,2-dichloroethane (50 ml/100 ml) was heated at 70 °C for 2 h under argon. Evaporation gave a crude product, which was purified by recrystallization (dichloromethane/hexane) to afford the ligand of the manganese(III) catalyst **B1**, *N,N'*-bis[2-(2,4,6-trimethylbenzoyl)-3-oxobutylidene]-1,2-diphenylethylenediamine in 94 % yield: Mp 203—208 °C; ^{1}H NMR ($CDCl_3$) δ=1.64 (3H, s), 1.92 (6H, s), 1.97 (6H, s), 2.26 (6H, s), 4.41 (2H, d, J=8.2 Hz), 6.70 —7.25 (16H, m); IR 3028, 2968, 2916, 2856, 1614, 1589, 1454, 1404, 1352, 1299, 1251 cm^{-1}. Found: C, 78.72; H, 6.92; N, 4.37%. Calcd for $C_{42}H_{44}N_2O_4$: C, 77.76; H, 6.85, N, 4.27%.

[*N,N'*-Bis(2-acyl-3-oxobutylidene)-(1*S*,2*S*)-1,2-diphenylethylenediaminato]chloromanganese(III) (B): To a suspension of manganese(III) acetate ($Mn(OAc)_3 \cdot 2H_2O$) (1.63 g, 6.0 mmol) in ethanol-1,2-dichloroethane (5 ml/15 ml) was added a solution of *N,N'*-bis(2-acyl-3-oxobutylidene)-(1*S*,2*S*)-1,2-diphenylethylenediamine (3.0 mmol) in 1, 2-dicholoroethane (10 ml). The resulting mixture was refluxed for 3 h, followed by the addition of lithium chloride (0.32 g, 7.6 mmol). After 1 h, the solvent was removed under reduced pressure. The residue was then extracted with dichloromethane, and dried over anhydrous sodium sulfate. Concentration in vacuo gave a crude manganese(III) complex. Analytically pure manganese(III) complex **B1**, chloro-*N,N'*-bis[2-(2,4,6-trimethylbenzoyl)-3-oxobutylidene-(1*S*, 2*S*)-1,2-diphenylethylenediaminato]manganese(III), was obtained as a dark-brown powder after purification by column chromatography on silica gel (dichloromethane/acetone=5/1) and reprecipitation (dicholoromethane/ether) in 45% yield: Mp 222 °C (DSC). Found: C, 67.59; H, 5.70; N, 3.72%. Calcd for $C_{42}H_{42}N_2O_4MnCl$: C, 69.18; H, 5.81, N, 3.84%.

Preparation of Olefins: 1,2-Dihydronaphthalene (**3a**) was purchased from Aldrich Co., and other dihydronaphthalene derivatives were prepared by reduction and dehydration from the corresponding tetralone derivatives, which were purchased from Tokyo Kasei Kogyo Co. (**4a**), Aldrich Co. (**10a**), or prepared by reported procedure, **6a**,[33] **7a**,[34] and **8a**,[35] respectively. *cis*-β-Substituted styrene derivatives were obtained from literature methods from the corresponding acetylene derivatives,[36] which were prepared by a reported procedure.[37] 2-Vinylnaphthalene (**13a**) and 1,3-cyclooctadiene (**15a**) were purchased from Aldrich Co. and Tokyo Kasei Kogyo Co., respectively. Enyne **14a** was prepared by a reported method.[38]

General Procedure for Aerobic Enantioselective Epoxidation of 1,2-Dihydronaphthalene Derivatives (Table 5). To a suspension of (*S,S*)-**A1** (83 mg, 0.104 mmol) in benzene (1.0 ml) was added a solution of olefin (0.8 mmol) and 2,2-dimethylpropanal (241 mg, 2.8 mmol) in benzene (1.0 ml); the resulting mixture was stirred at 30 °C for 1 h under an atmospheric pressure of oxygen. The crude product was poured into aqueous sodium hydrogencarbonate and extracted with ether. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by column chromatography on silica gel (hexane/ethyl acetate) gave the corresponding optically active epoxide. The aerobic and enantioselective epoxidation of 1,2-dihydronaphthalene (**3a**) provided 1,2-epoxy-1,2,3,4-tetrahydronaphthalene (**3b**) in 70% yield. The enantiomeric excess was determined by GC analysis (Chiraldex B-DA, ASTEC Co.) to be 64% ee. The absolute configuration of the eposide was assigned to be (1*R*,2*S*) by a polarimetry analysis compared with reported results (Ref. 19). $[\alpha]_D^{30}$ +81.8° (*c* 0.45, $CHCl_3$).

General Procedure for Aerobic Enantioselective Epoxidation of Acyclic *cis*-β-Substituted Styrene Derivatives and Alkynyl or Alkenyl Olefins (Table 5). An atmospheric pressure of air was used instead of 1 atm oxygen.

Epoxidation by Using Peracetic Acid as Terminal Oxidant (Fig. 4): To a mixture of (*S,S*)-manganese(III) complex **B1** (83 mg, 0.104 mmol) and 1-propenylbenzene (**5a**, 94 mg, 0.8 mmol) in benzene (2.0 ml) was added a solution of peracetic acid in acetic acid (32 wt%, Aldrich Co., 0.3 ml) at room temparature under an argon atmosphere. After being stirred for 15 min, the reaction was quenched by adding aqueous sodium hydrogencarbonate, extracted with ether, and washed with brine. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel to afford the corresponding optically active *cis*-epoxide **5b** along with *trans*-isomer (*cis*/*trans*=84/16, determined by ^{1}H NMR analysis) in 18% yield (19 mg). The enantiomeric excess of *cis*-epoxide was determined by a GC analysis (Chiraldex B-PH) to be 67%ee. The absolute configuration was assigned from the retention time of the GC analysis to be (1*R*,2*S*) by comparing it with an authentic sample prepared by the reported method (Ref. 3b).

^{1}H NMR and IR Spectra of the Epoxides (Table 5). 1,2-Epoxy-1,2,3,4-tetrahydronaphthalene (3b); NMR ($CDCl_3$) δ=1.77 (1H, ddd, J_1=5.61 Hz, J_2=13.85 Hz), 2.40 (1H, m), 2.53 (1H, ddd, J_1=5.61 Hz, J_2=15.50 Hz), 2.77 (1H, ddd, J_1=13.85 Hz, J_2=6.27 Hz, J_3=15.00 Hz), 3.69 (1H, m, J=4.29 Hz), 3.78 (1H, d, J=4.29 Hz), 7.05—7.42 (4H, m); IR (neat) 2930, 1492, 1433, 851, 747 cm^{-1}. Optical yield was determined by GC analysis (Chiraldex B-DA).

1,2-Epoxy-3,3-dimethyl-1,2,3,4-tetrahydronaphthalene (6b); ^{1}H NMR ($CDCl_3$) δ=0.82 (3H, s), 1.30 (3H, s), 2.20 (1H, d, J=15.2 Hz), 2.70 (1H, d, J=15.2 Hz), 3.23 (1H, d, J=4.29 Hz), 3.84 (1H, d, J=4.29 Hz), 7.00—7.40 (4H, m); IR (neat) 2958, 1494, 1468, 764, 750 cm^{-1}. Optical yield was determined by GC analysis (Chiraldex B-DA).

1,2-Epoxy-4,4-dimethyl-1,2,3,4-tetrahydronaphthalene (7b); ^{1}H NMR ($CDCl_3$) δ=1.31 (3H, s), 1.35 (3H, s), 1.86 (1H, dd, J_1=0.65 Hz, J_2=15.0 Hz), 2.22 (1H, dd, J_1=2.47 Hz, J_2=15.0 Hz), 3.72 (1H, m, J=4.29 Hz), 3.86 (1H, d, J=4.29 Hz), 7.16—7.50 (4H, m); IR (neat) 2960, 1492, 1463, 1361, 758 cm^{-1}. Optical yield was determined by GC analysis (Chiraldex B-DA).

6-Benzyloxy-1,2-epoxy-5-nitro-1,2,3,4-tetrahydro-

naphthalene (8b); ^{1}H NMR ($CDCl_3$) δ=1.65—1.80 (1H, m), 2.35—2.90 (3H, m), 3.72 (1H, d, J=4.29 Hz), 3.82 (1H, d, J=4.29 Hz), 5.15 (2H, s), 6.90 (1H, m), 7.22—7.45 (6H, m); IR (neat) 2918, 1697, 1534, 1373, 1280, 1056, 748 cm^{-1}. Optical yield was determined by HPLC analysis (Chiralcel OD).

Methyl 1,2-Epoxy-1,2,3,4-tetrahydronaphthalene-6-carboxylate (9b); ^{1}H NMR ($CDCl_3$) δ=1.70—1.83 (1H, m), 2.40—2.49 (1H, m), 2.57—2.65 (1H, m), 2.74—2.88 (1H, m), 3.76 (1H, m), 3.87 (1H, d, J=4.29 Hz), 3.91 (3H, s), 7.46 (1H, d, J=7.59 Hz), 7.77 (1H, s), 7.87 (1H, d, J=8.73 Hz); IR (neat) 2948, 2850, 1711, 1440 843, 778 cm^{-1}. Optical yield was determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as a chiral shift reagent.

5, 6- Epoxy- 6, 7, 8, 9- tetrahydro- 5*H*- benzocycloheptene (4b); ^{1}H NMR ($CDCl_3$) δ=1.53—2.18 (4H, m), 2.70—2.94 (2H, m), 3.40 (1H, m), 4.02 (1H, d, J=4.29 Hz), 7.07 (1H, m), 7.23 (2H, m), 7.49 (1H, m); IR (neat) 2934, 1468, 842, 793 cm^{-1}. Optical yield was determined by GC analysis (Chiraldex B-DA or B-PH).

3-Fluoro-5,6-epoxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (10b); ^{1}H NMR ($CDCl_3$) δ=1.44—1.80 (3H, m), 1.81—1.89 (1H, m), 2.11—2.20 (1H, m), 2.68—2.87 (2H, m), 3.37 (1H, m), 3.97 (1H, d, J=4.29 Hz), 6.91 (1H, m), 7.01 (1H, m), 7.21 (1H, m); IR (neat) 2936, 1493, 1453, 1232, 833 cm^{-1}. Optical yield was determined by GC analysis (Chiraldex B-DA).

(1,2-Epoxypropyl)benzene (5b); (*cis*/*trans*=63/37); ^{1}H NMR ($CDCl_3$) δ=1.09 (3H, d, J=5.28 Hz for *cis*), 1.45 (3H, d, J=5.28 Hz for *trans*), 3.04 (1H, dq, J_1=1.98 Hz, J_2=5.28 Hz for *trans*), 3.34 (1H, dq, J_1=4.29 Hz, J_2=5.28 Hz for *cis*), 3.57 (1H, d, J=1.98 Hz for *trans*), 4.06 (1H, d, J=4.29 Hz for *cis*), 7.20—7.36 (5H, m); IR (neat) 2968, 1496, 1452, 1259, 743, 700 cm^{-1}. Optical yields were determined by GC analysis (Chiraldex B-DA for *cis*-epoxide and Chiraldex G-TA for *trans*-epoxide).

2-(1,2-Epoxypentyl)naphthalene (11b); (*cis*/*trans*=88/12); ^{1}H NMR ($CDCl_3$) δ=0.83 (3H, t, J=7.3 Hz for *cis*), 1.02 (3H, t, J=7.3 Hz for *trans*), 1.15—1.80 (4H, m), 3.05 (1H, dt, J_1=2.3 Hz, J_2=5.2 Hz for *trans*), 3.29 (1H, dt, J_1=4.3 Hz, J_2=5.9 Hz for *cis*), 3.78 (1H, d, J=2.3 Hz for *trans*), 4.22 (1H, d, J=4.3 Hz for *cis*), 7.32 (1H, d, J=8.44 Hz), 7.43—7.53 (2H, m), 7.75—7.88 (4H, m); IR (neat) 2960, 1463, 1243, 818, 750 cm^{-1}. Optical yields were determined by HPLC analysis (Chiralpak AD).

4-(1,2-Epoxypentyl)chlorobenzene (12b); (*cis*/*trans*=69/31); ^{1}H NMR ($CDCl_3$) δ=0.84 (3H, t, J=8.44 Hz for *cis*), 0.98 (3H, t, J=8.44 Hz for *trans*) 1.20—1.73 (4H, m), 2.89 (1H, dt, J_1=2.0 Hz, J_2=5.3 Hz for *trans*), 3.19 (1H, dt, J_1=4.3 Hz, J_2=5.7 Hz for *cis*), 3.57 (1H, d, J=2.0 Hz for *trans*), 4.02 (1H, d, J=4.3 Hz for *cis*), 7.17—7.36 (4H, m); IR (neat) 2960, 1492, 1217, 1089, 778 cm^{-1}. Optical yields were determined by GC analysis for *cis*-epoxide (Chiraldex B-PH) and HPLC analysis for *trans*-epoxide (Chiralpak AD).

2-(1,2-Epoxyethyl)naphthalene (13b); ^{1}H NMR ($CDCl_3$) δ=2.89 (1H, m), 3.20 (1H, m), 4.01 (1H, m), 7.32 (1H, dd, J_1=1.65 Hz, J_2=8.58 Hz), 7.45—7.49 (2H, m), 7.78—7.83 (4H, m); IR (neat) 3052, 1508, 1335, 821, 742 cm^{-1}. Optical yield was determined by HPLC analysis (Chiralcel OB).

(3,4-Epoxy-1-pentynyl)benzene (14b); (*cis*/*trans*=63/37); ^{1}H NMR ($CDCl_3$) δ=1.38 (3H, d, J=4.94 Hz for *trans*), 1.50 (3H, d, J=4.94 Hz for *cis*), 3.25 (1H, dq, J_1=3.96 Hz, J_2=4.94 Hz for *cis*), 3.64 (1H, d, J=3.96 Hz for *cis*), 7.27—7.34 (3H, m), 7.42—7.49 (2H, m); IR (neat) 2994, 2226, 1491, 1236, 757, 691 cm^{-1}. Optical yields were determined by HPLC analysis (Chiralpak AD).

3,4-Epoxycyclooctene (15b); ^{1}H NMR ($CDCl_3$) δ=1.33—1.52 (2H, m), 1.53—1.83 (3H, m), 1.96—2.16 (2H, m), 2.24—2.39 (1H, m), 3.11 (1H, dtd, J_1=4.29 Hz, J_2=9.24 Hz, J_3=1.32 Hz), 3.46 (1H, dt, J_1=4.29 Hz, J_2=1.32 Hz), 5.59 (1H, dt, J_1=11.21 Hz, J_2=1.32 Hz), 5.77 (1H, dtd, J_1=11.21 Hz, J_2=5.61 Hz, J_3=1.32 Hz); IR (neat) 2930, 1453, 1241, 1045, 844, 812 cm^{-1}. Optical yield was determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as a chiral shift reagent.

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25) The absolute configuration of *cis*-epoxide was assigned to be (1*R*,2*S*) by polarimetry analysis by comparison with reported results (Ref. 3b). In addition, the minor *trans*-isomer was obtained in 47% ee with (1*S*,2*S*)-(−) configuration. Jacobsen et al. and Katsuki et al. independently pointed out the difference in the degree of enantioselectivities for both *cis*- and *trans*-isomers. a) W. Zhang, N. H. Lee, and E. N. Jacobsen, *J. Am. Chem. Soc.*, **116**, 425 (1994); b) T. Hamada, R. Irie, and T. Katsuki, *Synlett*, **1994**, 479.
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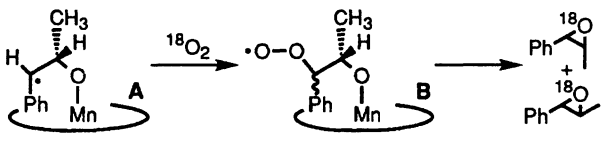

Chart 1.