Aerobic Enantioselective Epoxidation of Unfunctionalized Olefins Catalyzed by Optically Active Salen–Manganese (III) Complexes

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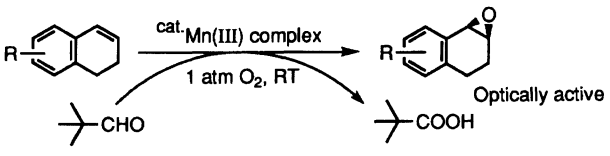
Enantioselective epoxidation of unfunctionalized olefins is achieved by the combined use of molecular oxygen and pivalaldehyde in the presence of a catalytic amount of optically active Mn(III)–salen complexes. *N*-Alkylimidazoles are effective axial ligands to produce optically active epoxides with high enantioselectivities in the present procedure; that is, 1,2-dihydronaphthalene derivatives and 2,2-dialkyl-2*H*-chromene derivatives are converted into the corresponding optically active epoxides with 60—92% enantiomeric excess. The key intermediates in the present aerobic epoxidation are also discussed.

Optically active epoxides have attracted much attention as versatile intermediates[1] for the synthesis of a wide variety of chiral compounds, for example, biologically active compounds[2] such as precocene II derivatives as selective cytotoxic agent to insects[3] or medicinal compounds for the remedy of hypertension and asthma,[4] and functional organic materials such as ferroelectric liquid crystals,[5] etc. The reliable enantioselective titanium-catalyzed epoxidation of allylic alcohols was developed by Sharpless and Katsuki using *t*-butyl hydroperoxide as an oxidant affording optically active 2,3-epoxy alcohols in good yields with very high enantiomeric excesses,[6] and has been successfully applied to the synthesis of a number of natural products. Concerning an efficient and widely applicable enantioselective epoxidation of simple olefins other than allyl alcohols, many efforts have been made; for example, several biological systems have been employed in the enantioselective epoxidation of terminal alkenes by using of an enzymatic catalyst such as *Pseudomonas oleovorans*,[7] hydrocarbon-assimilating microorganisms such as *Nocardia corallina* B-276[8] or *Corynebacterium equi* (IFO 3730).[9] In the nonbiological system, artificial metalporphyrin-type catalysts have been designed as cytochrome P-450 model systems for enantioselective epoxidation of styrene analogues.[10,11] Recently, Jacobsen[12] and Katsuki[13] independently reported that manganese (III)–salen complexes are effective catalysts for enantioselective epoxidation[14] of unfunctionalized olefins by using terminal oxidants such as iodosylbenzene or sodium hypochlorite.[15] Except for the epoxidation catalyzed by artificial bleomycin,[16] few have been reported on the utilization of molecular oxygen for preparing the optically active epoxide from simple olefins.

Recently, an efficient method for the aerobic epoxidation of olefins catalyzed by metal complexes such as nickel(II),[17] iron(III),[18] vanadium(IV),[19] and manganese(II)[20] coordinated by 1,3-diketone-type ligand with combined use of aldehyde under mild reaction conditions have been reported from our laboratory. It is also observed that β-epoxides are stereoselectively obtained by manganses(II)-catalyzed epoxidation of cholesterol derivatives[21] while peroxy acid oxidations afford α-epoxides of reversal configurations. Similar β-selection was reported in the aerobic epoxidation of cholesterol derivatives catalyzed by rutheniumn(II) tetramesitylporphyrin. These results suggest that the above-mentioned metal complex catalysts could participate directly in the oxidation step and reactive intermediates of the present epoxidation is expected to keep the ligand systems during the oxidation. In this report, we would like to fully disclose an aerobic enantioselective epoxidation of unfunctinalized olefins catalyzed by optically active salen-type manganese(III) complex in the coexistence of aldehyde (Scheme 1).

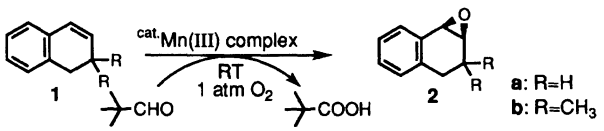
Results and Discussion

Asymmetric Epoxidation of 1,2-Dihydronaphthalenes. Optically active manganese(III) complexes **A** and **B** were prepared by Jacobsen's method,[22] and purified by column chromatography on silica gel or washing the benzene solution with aqueous lithium chloride solution. Purities of manganese(III) complex catalysts were quite influential to the optical yield in the present epoxidation procedure. As a result of screening the optically active manganese(III)–salen type complexes by taking the epoxidation of 1,2-dihydronaphthalene (**1a**) as a model reaction, *t*-butyl group on C_3 position of salicylaldehyde in the chiral ligand was essential to realize enantioselection,[15] and pivalaldehyde was the most effective reductant in respect of both enantioselectivity and chemical yield. An aromatic hydrocarbon such as toluene or benzene was suitable as a solvent and it should be noted that fluorobenzene is the most



Scheme 1.

Table 1. Asymmetric Epoxidation of 1,2-Dihydronaphthalenes



Entry	Catalyst	Olefin	Additive	Yield/%[c]	Optical yield/%ee[d]
1[a]	**A1**	**1a**	—	42	12 (1*R*,2*S*)-(+)
2[a]	**A1**	**1b**	—	51	6[e]
3[a]	**B1**	**1a**	—	37	6
4[b]	**A1**	**1a**	*N*-Me-Imd	62	52 (1*S*,2*R*)-(−)
5[b]	**A1**	**1b**	*N*-Me-Imd	67	56[e]
6[b]	**B1**	**1a**	*N*-Me-Imd	78	63
7[b]	**B1**	**1b**	*N*-Me-Imd	67	72[e]

a) Reaction conditions; olefin 1.15 mmol, pivalaldehyde 3.5 mmol, Mn(III) catalyst 0.138 mmol (12 mol%) in benzene 4 ml, RT, 1 atm O_2, overnight. b) Reaction conditions; olefin 1.15 mmol, pivalaldehyde 3.5 mmol, Mn(III) catalyst 0.138 mmol (12 mol%), *N*-methylimidazole (*N*-Me-Imd) 0.55 mmol in fluorobenzene 4 ml, RT, 1 atm O_2, overnight. c) Isolated yield. d) Determined by GC analysis (Chiraldex B-DA, ASTEC Co.). e) Absolute configuration were presumed from retention times of GC analysis and optical rotations.

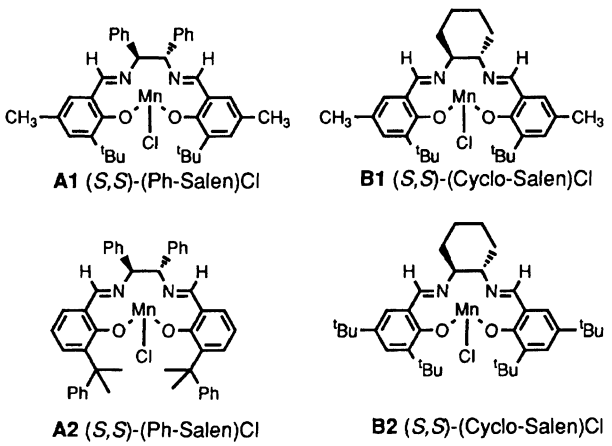


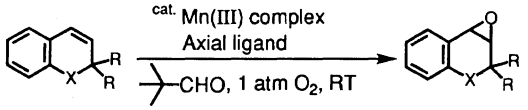
Fig. 1.

effective solvent to improve the enantiomeric excess.

When optically active Mn(III)–salen complex **A1** derived from (*S*,*S*)-1,2-diphenylethylenediamine was employed as a catalyst with combined use of molecular oxygen and pivalaldehyde, 1,2-dihydronaphthalene (**1a**) was converted into the corresponding epoxide in 42% yield, whose enantiomeric excess was determined by GC analysis (Chiraldex B-DA) to be 12%ee (Entry 1 in Table 1). (Cyclo-Salen)Cl **B** derived from (*S*,*S*)-1,2-cyclohexanediamine was also an effective catalyst to realize enantioselective epoxidation of simple olefins; for example, in the presence of catalytic amount of *N*-methylimidazole and Mn(III)–salen complex **B1**, 1,2-dihydronaphthalene (**1a**) and 2,2-dimethyl-1,2-dihydronaphthalene (**1b**) were converted with molecular oxygen into the corresponding optically active epoxides with good enantioselectivities, 63 and 72%ee, respectively (Entries 6 and 7)(Fig. 1). Recently, it was reported that a donor ligand, such as 2-methylimidazole or pyridine *N*-oxide improved enantioselection in manganese(III)-catalyzed epoxidation when iodosylbenzene was used as a terminal oxidant.[23]

***N*-Alkylimidazoles as Effective Axial Ligands.** These results clearly suggest that imidazole derivatives play important roles in the formation of reactive intermediates of the epoxidation reactions. Concerning the similar effect of imidazole derivatives in oxidation reaction, detailed structural studies of bonito ferrocytochrome *c* revealed that imidazole ring of histidine 18 in polypeptide coordinates the heme iron as the 5th ligand to activate molecular oxygen.[24] Myeloperoxidase also contains histidine coordinating the heme iron atom with the imidazole ring.[25] Bleomycin also contains imidazole moiety as the ligand of the central iron atom.[26] Although the effects of imidazole derivatives as donor ligands have been studied in cytochrome P-450 model reactions by several groups,[27] few were reported on the stereochemistry of olefin-epoxidation.[23] Then several nitrogen-containing ring compounds were screened as axial ligands in the present epoxidation, and imidazole and pyridine derivatives were found to enhance the enantiometic excess of the formed epoxide. The epoxidation of 2,2-dimethyl-1,2-dihydronaphthalene (**1b**), 6,7-dihydro-5*H*-benzocycloheptene (**1f**), and 2,2-dimethyl-2*H*-chromene (**3a**) afforded the optically active epoxides in good to high enantioselectivities by the addition of imidazole (**5a**) or *N*-methylimidazole (**5b**) (55—91%ee, Entries 1 and 2 in Table 2). While, the optical yields of the epoxides were much lower when 2-methyl-1*H*-imidazole (**7a**)[23] or 4-methyl-1*H*-imidazole (**7b**) was added (26—51%ee, Entries 4 and 5). Similar results were observed in the cases of using pyridine (**6**) or 2,6-lutidine (**8**) as an axial ligand; that is,

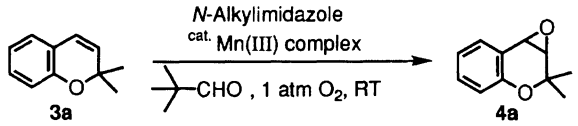
Table 2. Effective Axial Ligands on Enantioselection

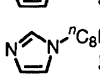


Entry[a]	Axial ligand		Optical yield/%ee[b] 2b	2g	4a
1		**5a**	55	63	91[c]
2		**5b**	71	83	91[c]
3		**6**	51	27	76[c]
4		**7a**	45	32	26[c]
5		**7b**	48	30	51[c]
6		**8**	7	1	22[c]

a) Reaction conditions; olefin 1.15 mmol, pivalaldehyde 3.5 mmol, axial ligand 0.55 mmol, Salen–Mn(III) complex **B1** 0.138 mmol (12 mol%) in fluorobenzene 4 ml, RT, 1 atm O_2. b) Determined by GC analysis (Chiraldex B-DA, ASTEC Co.). c) Salen(^{t}Bu)–Mn(III) complex **B2** was used as catalyst, and benzene as solvent.

Table 3. *N*-Alkylimidazoles as Effective Axial Ligands



Entry[a]	Imidazole	Yield/%[b]	Optical yield/%ee[c]
1	 **5f**	23	71
2	 **5b**	12	91
3	 **5c**	31	91
4	 **5d**	26	92
5	 **5e**	37	92

a) Reaction conditions; olefin 1.15 mmol, pivalaldehyde 3.5 mmol, imidazole 0.55 mmol, Mn(III) complex **B2** 0.138 mmol (12 mol%) in benzene 4 ml, RT, 1 atm O_2. b) Isolated yield. c) Determined by GC analysis (Chiradex B-DA, ASTEC Co.).

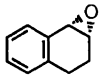
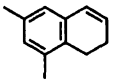
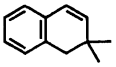
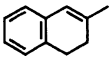
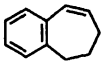
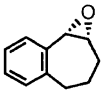
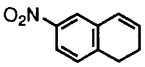
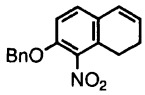
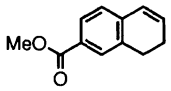
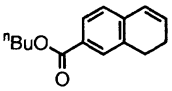
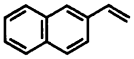
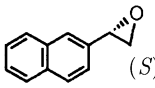
when pyridine (**6**) was added, the optically active epoxide was obtained with better enantioselection compared with that by adding 2,6-lutidine (**8**), 51 vs. 7%ee, 27 vs. 1%ee, and 76 vs. 22%ee, respectively (Entries 3 and 6). The results suggested that alkyl groups attached to the carbon next to nitrogen would prevent the coordination to manganese(III) complexes because of their steric hindrance during oxidation. Since the highest optical yields were observed in all cases when *N*-alkylimidazole was added, a variety of *N*-alkyl imidazoles[28] was examined by taking 2,2-dimethyl-2*H*-chromene (**3**) as a model olefin. The optical yields of the corresponding epoxides were improved up to more than 90%ee by the addition of imidazole derivatives having *N*-alkyl groups (see Table 3), whereas 71%ee in case of using *N*-phenylimidazole (**5f**). When longer alkyl groups were attached to the imidazole rings, chromene oxide was formed in higher chemical yield. Then it was noted that *N*-octylimidazole (**5e**) was suitable axial ligand with respect to both chemical and optical yields (Entry 5).

Aerobic Enantioselective Epoxidation of Various Olefins. The present system was applied to the enantioselective epoxidations of various olefins (Table 4). Dihydronaphthalenes **1a**—**1e** were converted into the corresponding optically active epoxides in good yields with moderate to good enantioselectivities (49—72%ee, Entries 1—5). The enantioselective aerobic epoxidation of 7-membered cyclic olefin (**1f**) afforded the corresponding epoxide with high enantiomeric excess in the presence of manganese(III) complex ((Cyclo-Salen)Cl **B1**) (Entry 6). Dihydronaphthalene derivatives having nitro and/or benzyloxy groups (**1g** and **1h**) or alkoxycarbonyl group (**1i** and **1j**) were also oxygenated into the corresponding optically active epoxides with 43—66% enantioselectivities (Entries 7—10). Also in the case of acyclic olefin such as 2-vinylnaphthalene (**1k**), the optically active epoxide was afforded in 52%ee (Entry 11). The absolute configurations of the formed epoxides were determined to be (1*S*,2*R*) (**2a** and **2f**)[29] and (*S*) (**2k**),[30] respectively, corresponding to (*S*,*S*)-salen complex **B1** and imidazole system by comparing the sign of optical rotations with reported values.

As optically active chromene oxides have attracted much attention as intermediates for the synthesis of biologically active compounds,[31] enantioselective epoxidation of chromene derivatives by using optically active salen–manganese(III)-type complex catalysts were already studied by using sodium hypochlorite or iodosylbenzene as terminal oxidants.[32] Then, the present aerobic system was applied to the enantioselective epoxidation of various chromene derivatives (see Table 5). In all cases of chromene derivatives, the corresponding optically active epoxides were obtained with more than 90% enantiomeric excess.

Reversal of Absolute Configuration by Using of *N*-Alkylimidazole as an Additive. The absolute configuration of epoxide **2a** was determined to be (1*R*,2*S*) by comparing the sign of optical rotation with the reported value[33] when (*S*,*S*)-complex was em-

Table 4. Examples of Asymmetric Epoxidation

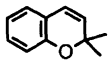
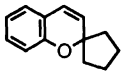
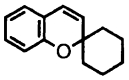
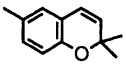
Entry[a]	Olefin[b]		Yield/%[c]	Optical yield/%ee[d]	Note
1		**1a**	78	63	 (1*S*,2*R*) **2a**
2		**1c**	73	52	
3		**1b**	80	72	
4		**1d**	35	63	
5		**1e**	55	49[e]	
6		**1f**	52	83	 (1*S*,2*R*)[g] **2f**
7		**1g**	43	43[e]	
8		**1h**	38	66[f]	
9		**1i**	38	57[e]	
10		**1j**	48	57[e]	
11		**1k**	34	52[e]	 (*S*)[h] **2k**

a) Reaction conditions; olefin 1.15 mmol, pivalaldehyde 3.5 mmol, *N*-methylimidazole 0.55 mmol, [$Mn^{III}Cl$\{(*S*,*S*)-Cyclo-Salen\}] **B1** 0.138 mmol (12 mol%) in fluorobenzene 4 ml, RT, 1 atm O_2, overnight. b) Olefins were prepared from the corresponding tetralone derivatives. c) Isolated yield. d) Determined by GC analysis unless otherwise stated. ASTEC Co. Chiraldex B-DA (20 m×0.25 mm i.d.×0.125μm film). e) Determined by NMR analysis. Eu(hfc)$_3$ was used as a shift reagent in $CDCl_3$. f) Determined by HPLC analysis. Daicel Chiralcel OD(+) (Hexane : 2-propanol). g) Absolute configuration was determined by optical rotation, see Ref. 29. h) Absolute configuration was determined by optical rotation, see Ref. 30.

ployed as a catalyst in the present aerobic epoxidation (Entry 1 in Table 6). It should be noted here that thus formed (1*R*,2*S*)-epoxide by using (*S*,*S*)-catalyst is reversal to the results reported by Jacobsen[12] or Katsuki[34] in term of enantioselection (Entries 2 and 3). The addition of silylating reagents, *N*,*O*-bis(trimethylsilyl)trifluoroacetamide, in the present reaction mixture improved optical yield of (1*R*,2*S*)-(+)-epoxide from 12 upto 33%ee (Entries 1 and 2 in Table 7). When (*S*,*S*)-salen–manganese(III) complex **A2** derived from more hindered substituents on C_3 positions of salicylaldehyde moiety was employed as catalyst, (1*R*,2*S*)-(+)-epoxide was also obtained in 54%ee (Entry 3). Furthermore, it is interesting to point out that in the coexistence of a catalytic amount of *N*-methylimidazole, the absolute configuration of the epoxide formed by (*S*,*S*)-complex **A1** or **B1**-catalyzed epoxidation is completely reversed to give the epoxide of (1*S*,2*R*)-configuration and the enantiomeric excess is also improved upto 63%ee (Entry 5 in Table 7).

Reactive Intermediates in the Aerobic Epoxidation Catalyzed by Manganese(III)–Salen Complexes. In the presence of a catalytic amount of (*S*,*S*)-salen–Mn(III) complex **A1**, the epoxidation using peracetic acid as an oxidant instead of molecular oxygen and pivalaldehyde gave (1*R*,2*S*)-(+)-epoxide with 22%ee (Entry 3 in Table 8). By addition of *N*-methylimidazole both in the present aerobic procedure and the above peracid system, absolute configurations of the formed epoxide were reversed into (1*S*,2*R*)-(−) with 51 and 49%ee, respectively (Entries 4 and 5). It was recently reported that (acylperoxo)-porphyrinatoiron complexes were converted into the corresponding oxo-iron complexes by coordination of imidazole derivatives[35] (Scheme 2). Reversal of the absolute configuration of the epoxides suggested that the

Table 5. Aerobic Asymmetric Epoxidation of Various Chromenes

Entry[a]	Chromene	Yield/%[b]	Optical yield/%ee
1	 **3a**	37	92[c]
2	 **3b**	32	90[d]
3	 **3c**	34	91[d]
4	 **3d**	24	91[e]

a) Reaction conditions; olefin 1.15 mmol, pivalaldehyde 3.5 mmol, *N*-octylimidazole 0.55 mmol, Mn(III) complex **B2** 0.138 (12 mol%) in benzene 4 ml, RT, 1 atm O_2. b) Isolated yield. c) Determined by GC analysis (Chiraldex B-DA, ASTEC Co.). d) Determined by ^{1}H NMR analysis. Eu(hfc)$_3$ was used as a chiral shift reagent in $CDCl_3$. e) Determined by GC analysis (Chiraldex G-TA, ASTEC Co.).

similar phenomenon is observed in the present epoxidation by combined use of molecular oxygen and aldehyde; that is, acylperoxo-manganese complex **I** would be formed from molecular oxygen, pivalaldehyde, and original manganese(III) complex in the first step. In the absence of *N*-alkyl imidazole, acylperoxo-manganese (*S,S*)-salen complex **I** itself[36] would react with olefin to afford (1*R*,2*S*)-(+)-epoxide. In the presence of *N*-alkylimidazole, acylperoxo-manganese complex **I** was converted into oxo-manganese complex **II** by the coordination of donor axial ligand, *N*-alkylimidazole (Fig. 2). Oxo-manganese complex **II** has been widely accepted[37] as reactive intermediates for epoxidations by using terminal oxidants such as iodosylbenzene[38] and sodium hypochlorite.[39]

It is noted that *N*-alkylimidazoles was quite effective as an axial donor ligand to improve optical yield whereas 2-alkyl- or 4-alkylimidazole and 2,6-lutidine were not (Table 2). The difference of the effects between two kinds of axial donor ligands, *N*-alkyl- and 2-alkylimidazoles, could be reasonably explained as following considerations; that is, *N*-alkylimidazole or pyridine could strongly coordinate onto the central manganese atom to form oxo-manganese complex **II** leading to selective formation of (1*S*,2*R*)-epoxide corresponding to (*S,S*)-salen complex. On the other hand, 2-alkyl- or 4-alkylimidazole and 2,6-lutidine do not completely coordinate onto the central manganese atom because of their steric hindrance. Therefore, the total optical yield of the epoxide was offset and lowered as a result of competitive pathways catalyzed by oxo-manganese **II** (affording (1*S*,2*R*)-epoxide, see Table 8) and imidazole-free complex **I** (affording (1*R*,2*S*)-epoxide).

In conclusion, aerobic enantioselective epoxidation of simple olefins was successfully performed by using optically active salen–manganese(III) complex catalyst in the coexistence of pivalaldehyde. *N*-Alkylimidazole derivatives were effective axial donor ligands in the present epoxidation with regard to both chemical and optical yields. Several unfunctionalized olefins, 1,2-dihydronaphthalene derivatives or 2,2-dialkyl-2*H*-chromene derivatives were converted into the corresponding optically active epoxides with 60—92% enantiomeric excess.

Table 6. Absolute Configuration of Epoxide Catalyzed by (*S,S*)-Salen–Manganese(III)-Type Complex **A**

Entry	Oxidant	Major product
1	O_2, [a]	 (1*R*,2*S*)-(+)
2	NaClO[b]	 (1*S*,2*R*)-(−)
3	PhIO[c]	

a) The present procedure. b) Jacobsen's procedure. Ref. 15 c) Jacobsen's and Katsuki's procedure. Refs. 12 and 13, respectively.

Experimental

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

(a) Spectrometers: IR spectra were obtained by using a JASCO Model IR-700 infrared spectrometer on KBr pellets or liquid film on KBr. ^{1}H NMR spectra were recorded with a JEOL Model FX270 spectrometer using $CDCl_3$ as solvent and with tetramethylsilane as internal standard.

(b) Chromatography: Column chromatography was conducted under silica gel (Daiso gel IR-60). Preparative TLC was carried out on silica gel (E. Merck, 5714). HPLC analyses were performed on a Shimadzu LC-6A chromatograph using Chiralcel OD column (Daicel Ltd., Co) and the peak areas were calculated on a Shimadzu chromatopack CR-4A. GC-analyses for determination of optical yields were performed on a Shimadzu GC-15A or GC-14A chromatograph using a glass capillary column (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, and Chiraldex B-DA, 0.25 mm i.d., 20 m, 0.125 μm film, ASTEC Co.), and the peak areas were obtained with a Shimadzu chromatopack CR-5A.

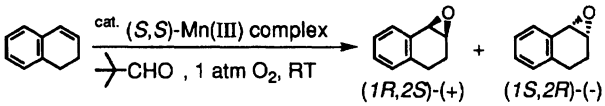
(c) Optical rotations: Optical rotations were measured with a JASCO DIP-360 digital polarimeter.

Preparation of Optically Active Salen–Manganese(III) Complexes: Catalysts **A1**, **A2**, **B1**, and **B2** were prepared by the reported method[22] from the corresponding salicylaldehyde and optically active diamine, respectively. (*S,S*)-1,2-Cyclohexanediamine was purchased from Wako pure chemical industries, Ltd., and (*S,S*)-1,2-diphenylethylenediamine was prepared by the reported method.[40]

[(*S,S*)-*N,N'*-Bis(5-methyl-3-*t*-butylsalicylidene)-1,2-diphenylethylenediamine]chloromanganese(III) (A1): Mp 258 °C (DSC).

[(*S,S*)-*N,N'*-Bis[3-(1-methyl-1-phenylethyl)sali-

Table 7. Reversion of Absolute Configuration of Obtained Epoxide by Addition of *N*-Methylimidazole



Entry[a]	Mn(III) complex	Additive	Yield/%[b]	Optical yield/%ee[c]	
				(1*R*,2*S*)-(+)[d]	(1*S*,2*R*)-(−)
1	**A1**	—	42	12	
2	**A1**	*N*,*O*-BSA[e]	60	33	
3	**A2**	*N*,*O*-BSA	55	54	
4	**A1**	*N*-Me-Imd[f]	62		52
5	**B1**	*N*-Me-Imd	78		63

a) Reaction conditions were described in Experimental part. b) Isolated yield. c) Determined by GC analysis (Chiraldex B-DA). d) Absolute configurations were presumed from retention times of GC analysis and optical rotations. e) *N*,*O*-Bis(trimethylsilyl)-trifluoroacetamide. f) *N*-Methylimidazole.

Table 8. Asymmetric Epoxidation of 1,2-Dihydronaphthalene by Using Peracetic Acid

Entry[a]	Oxidant	Catalyst	Additive	Optical yield/%ee[b]	
				(1*R*,2*S*)-(+)	(1*S*,2*R*)-(−)
1	O_2, CHO	**A1**	—	12	
2	O_2, CHO	**A2**	*N*,*O*-BSA	54	
3	CH_3CO_3H[c]	**A1**	—	22	
4	O_2, CHO	**B1**	*N*-Me-Imd		51
5	CH_3CO_3H[c]	**B1**	*N*-Me-Imd		49

a) Reaction conditions was described in Experimental part. b) Determined by GC analysis. c) 32 wt% in dilute acetic acid (Aldrich Co.).

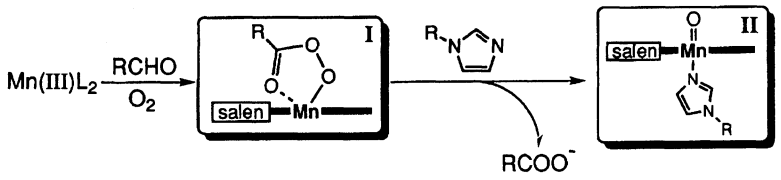
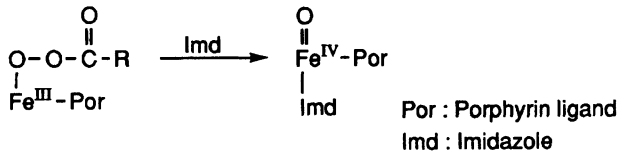


Fig. 2.



Scheme 2.

cylidene]-1,2-diphenylethylenediamine]chloromanganese(III) (A2): Mp 241 °C (DSC). Found: C, 75.47; H, 5.77; N, 3.16%. Calcd for $C_{46}H_{42}O_2N_2ClMn$: C, 74.14; H, 5.68; N, 3.76%.

[(*S*,*S*)-*N*,*N*′-Bis(5-methyl-3-*t*-butylsalicylidene)-1,2-cyclohexanediamine]chloromanganese(III) (B1): Mp 315 °C (DSC).

[(*S*,*S*)-*N*,*N*′-Bis(3,5-di-*t*-butylsalicylidene)-1,2-cyclohexanediamine]chloromanganese(III) (B2): Mp 313 °C (DSC).

Salicylaldehyde for salen–Mn(III) complex **A2** was prepared as follows.

2-(1-Methyl-1-phenylethyl)anisole: To dimethylzinc[41] (0.9 ml) in dichloromethane (5 ml) was added titanium tetrachloride (1.4 ml) in dichloromethane (20 ml) at −45 °C under argon atmosphere.[42] After stirring for 0.5 h, 2-methoxybenzophenone (1.06 g, 5 mmol) in dichloromethane (3 ml) was added at −45 °C. Reaction was monitored by TLC analysis, and quenched by adding methanol carefully and then water. Crude product was extracted with

ether and purified by distillation to afford 2-(1-methyl-1-phenylethyl)anisole (1.07 g, 95% yield) as oil. Bp 190 °C (2.1 mmHg, 1 mmHg=133.322 Pa, bath temp); ^{1}H NMR ($CDCl_3$) δ=1.68 (6H, s), 3.30 (3H, s), 6.75—7.48 (9H, m); IR (neat) 2964, 1599, 1490, 1243, 1029, 754, 700 cm^{-1}. Found: m/z 226.1351. Calcd for $C_{16}H_{18}O$: M, 226.1358.

2-Methoxy-3-(1-methyl-1-phenylethyl)benzaldehyde: Butyllithium solution in hexane (6.6 ml, 10.5 mmol) was added to *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1.82 g, 10.5 mmol) at 0 °C under argon atmosphere.[43] After 0.5 h, 2-(1-methyl-1-phenylethyl)anisole (2.16 g, 9.6 mmol) in dry benzene (3 ml) was added at 0 °C. After stirred for 30 min, dry *N*,*N*-dimethylformamide (1.2 ml) in dry benzene (10 ml) was added and reaction was monitored by TLC analysis, and quenched by adding water. Crude product was extracted with ether and purified silica-gel column chromatography to afford 2-methoxy-3-(1-methyl-1-phenylethyl)benzaldehyde (1.26 g, 52% yield) as oil. ^{1}H NMR ($CDCl_3$) δ=1.75 (6H, s), 2.85 (3H, s), 7.10—7.38 (6H, m), 7.70—7.81 (2H, m), 10.20 (1H, s); IR (neat) 2964, 1600, 1490, 1243, 1029, 754, 700 cm^{-1}. Found: m/z 254.1290. Calcd for $C_{17}H_{18}O_2$: M, 254.1307.

2-Hydroxy-3-(1-methyl-1-phenylethyl)benzaldehyde: To a solution of 2-methyoxy-3-(1-methyl-1-phenylethyl)benzaldehyde (400 mg, 1.57 mmol) in dichloromethane (3 ml) was added a boron trichloride (4 ml of 1 M solution 1 M=1 mol dm^{-3} in dichloromethane) at 0 °C under argon atmosphere.[44] After stirred for 4 h at 0 °C, reaction was quenched by adding water and crude product was extracted with ether and purified by silica-gel column chromatography to afford 2-hydroxy-3-(1-methyl-1-phenylethyl)benzaldehyde (374 mg, 99% yield) as colorless crystals. Mp 84—85.6 °C; ^{1}H NMR ($CDCl_3$) δ=1.93 (6H, s), 7.19—7.92 (8H, m), 9.80 (1H, s), 11.20 (1H, s); IR (neat) 3020, 1648, 1613, 1434, 1393, 1311, 1270, 1222, 1139, 758 cm^{-1}. Found: m/z 240.1159. Calcd for $C_{16}H_{16}O_2$: M, 240.1150.

Preparation of Olefins: 1,2-Dihydronaphthalene (**1a**) was purchased from Aldrich Co., and other olefins were prepared by reduction and dehydration from the corresponding tetralone derivatives, which were purchased from Aldrich Co. (**1c**), Lancaster Co. (**1g**), or Tokyo Kasei Kogyo Co. (**1f**), or prepared by reported methods, **1b**,[45] **1d**,[46] and **1h**.,[47] respectively. Chromene derivatives were prepared by the literature methods, **3a** and **3d**,[48] **3b** and **3c**.[49] The racemic chromene oxides were prepared from the corresponding chromene derivatives by using dimethyldioxirane as epoxidation reagent.[50]

General Procedure for Aerobic Enantioselective Epoxidation of 1,2-Dihydronaphthelene Derivatives (Entry 3 in Table 2). To a mixture of (*S*,*S*)-(Cyclo-Salen)Cl **B1** (76 mg, 0.138 mmol, 12 mol%[51]) and *N*-methylimidazole (**5b**, 45.3 mg, 0.552 mmol) in fluorobenzene (2.0 ml) was added a solution of 2,2-dimethyl-1,2-dihydronaphthalene (**1b**) (182 mg, 1.15 mmol) and pivalaldehyde (300 mg, 3.5 mmol) in fluorobenzene (2.0 ml) and stirred overnight at room temperature under an oxygen atmosphere. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate) to afford the corresponding optically active epoxide **2b** in 80% yield (160 mg). The enantiometic excess was determined by GC analysis (Chiraldex B-DA) to be 72%ee.

Aerobic Enantioselective Epoxidation of Chromene Derivatives (Entry 1 in Table 4). To a mixture of (*S*,*S*)-salen–Mn(III)-type complex **B2** (87.7 mg, 0.138 mmol, 12 mol%) and *N*-octylimidazole (**5e**, 99.5 mg, 0.552 mmol) in benzene (3.0 ml) was added a solution of 2,2-dimethyl-2*H*-chromene (**3a**, 184 mg, 1.15 mmol) and pivalaldehyde (300 mg, 3.5 mmol) in benzene (1.0 ml). After stirred at room temperature under an oxygen atmosphere for 8 h, the reaction mixture was extracted with diethyl ether, washed with saturated solution of sodium hydrogencarbonate and brine, and then dried over anhydrous sodium sulfate. The solvent was removed under the reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate) to afford the corresponding optically active epoxide **4a** in 37% yield (65.4 mg). The enantiomeric excess was determined by GC analysis (Chiraldex B-DA) to be 92%ee.

Aerobic Enantioselective Epoxidation in the Presence of *N*,*O*-Silyl-Substituted Acetamide (Entry 3 in Table 7): To a mixture of (*S*,*S*)-salen–Mn(III) complex **A2** (100 mg, 0.134 mmol, 12 mol%) and *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (1.8 ml) in benzene (1.0 ml) was added a solution of 1,2-dihydronaphthalene (**1a**, 150 mg, 1.15 mmol) and pivalaldehyde (300 mg, 3.5 mmol) in benzene (2.0 ml) and stirred for 8 h at room temperature under an atmospheric pressure of oxygen. The crude product was purified by column chromatography on silica gel to afford the corresponding optically active epoxide **2a** in 55% yield (92.4 mg). The optical yield was determined by GC analysis (Chiraldex B-DA) to be 54%ee.

Epoxidation by Using Peracetic Acid as Terminal Oxidant (Entry 3 in Table 8): To a solution of (*S*,*S*)-salen–Mn(III) complex **A1** (33.6 mg, 0.060 mmol, 12 mol%) and 1,2-dihydronaphthalene (**1a**, 65.1 mg, 0.5 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 temperature under an argon atmosphere. After stirred for 10 min, reaction was quenched by adding aqueous sodium hydrogencarbonate, extracted with diethyl ether, and washed with brine. The solvent was removed under reduced pressure, and crude product was purified by column chromatography on silica gel to afford optically active epoxide **2a** in 14% yield (10.4 mg). Optically yield 22.4%ee.

Epoxidation by Using Peracetic Acid as Terminal Oxidant (Entry 5 in Table 8): To a solution of (*S*,*S*)-salen–Mn(III) complex **B1** (33.1 mg, 0.060 mmol, 12 mol%), *N*-methylimidazole (**5b**, 19.7 mg, 0.24 mmol, 4.0 equiv vs. Mn(III) complex), and 1,2-dihydronaphthalene (**1a**, 65.1 mg, 0.5 mmol) in benzene (2.0 ml) was added a solution of peracetic acid in acetic acid (32 wt%, 0.3 ml) at room temperature under an argon atmosphere. Quenching and purification were similar as described above. Yield 9.0% (6.3 mg), optical yield 49%ee.

^{1}H NMR and IR Spectra of the Epoxides (Tables 4 and 5). 1,2-Epoxy-1,2,3,4-tetrahydronaphthalene (2a); ^{1}H 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).

5,7-Dimethyl-1,2-epoxy-1,2,3,4-tetrahydronaph-

thalene (2c); ^{1}H NMR ($CDCl_3$) δ=1.65—1.80 (1H, m), 2.20 (3H, s), 2.30 (3H, s), 2.31—2.52 (2H, m), 2.60—2.70 (1H, m), 3.69 (1H, m, J=4.29 Hz), 3.78 (1H, d, J=4.29 Hz), 6.95 (1H, s), 7.05 (1H, s); IR (neat) 2974, 2930, 1483, 1459, 855, 827 cm^{-1}. Optical yield was determined by GC analysis (Chiraldex B-DA). $[\alpha]_D^{29}$ +43.6° (c 0.53, EtOH, 52%ee). Found: m/z 174.1033. Calcd for $C_{12}H_{14}O$: M, 174.1045.

3,3-Dimethyl-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (2b); ^{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 anaylsis (Chiraldex B-DA). $[\alpha]_D^{31}$ +46.6° (c 0.28, EtOH, 72%ee). Found: m/z 174.1066. Calcd for $C_{12}H_{14}O$: M, 174.1045.

4,4-Dimethyl-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (2d); ^{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 anaylsis (Chiraldex B-DA). $[\alpha]_D^{30}$ +50.8° (c 0.46, EtOH, 63%ee). Found: m/z 174.1049. Calcd for $C_{12}H_{14}O$: M, 174.1045.

2-Methyl-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (2e); ^{1}H NMR ($CDCl_3$) δ=1.55 (3H, s), 1.72—1.84 (1H, m), 2.15—2.24 (1H, m), 2.48—2.57 (1H, m), 2.76—2.90 (1H, m), 3.64 (1H, s), 7.08 (1H, d, J=6.93 Hz), 7.18—7.25 (1H, m), 7.35 (1H, dd, J_1=1.65 Hz J_2=6.93 Hz); IR (neat) 2990, 2934, 2910, 1497, 1410, 830, 767 cm^{-1}. Optical yield was determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as chiral shift reagent. $[\alpha]_D^{33}$ +50.5° (c 1.02, $CHCl_3$, 49%ee). Found: C, 82.39; H, 7.73%. Calcd for $C_{11}H_{12}O$: C, 82.47; H, 7.55%.

5, 6- Epoxy- 6, 7, 8, 9- tetrahydro- 5*H*- benzocycloheptene (2f); ^{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, 1494, 1468, 842,793 cm^{-1}. Optical yield was determined by GC analysis (Chiraldex B-DA or B-PH).

7-Nitro-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (2g); Mp 71.6—72.4 °C; ^{1}H NMR ($CDCl_3$) δ=1.74—1.86 (1H, m), 2.44—2.54 (1H, m), 2.64—2.91 (2H, m), 3.79 (1H, m), 3.94 (1H, d, J=4.28 Hz), 7.26 (1H, d, J=7.91 Hz), 8.11 (1H, dd, J_1=2.31 Hz, J_2=8.25 Hz), 8.28 (1H, d, J=2.31 Hz); IR (KBr) 3000, 2950, 1614, 1593, 1517, 1356, 838, 740 cm^{-1}. Optical yield was determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as chiral shift reagent. $[\alpha]_D^{30}$ +58.7° (c 1.00, $CHCl_3$, 43%ee). Found: m/z 191.0602. Calcd for $C_{10}H_9O_3N$: M, 191.0582.

6-Benzyloxy-5-nitro-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (2h); ^{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). $[\alpha]_D^{29}$ +126° (c 0.32, $CHCl_3$, 57%ee). Found: m/z 297.1019. Calcd for $C_{17}H_{15}O_4N$: M, 297.1001.

Methyl 1,2-Epoxy-1,2,3,4-tetrahydronaphthalene-6-carboxylate (2i); ^{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 chiral shift reagent. $[\alpha]_D^{33}$ +66.4° (c 0.89, $CHCl_3$, 57%ee). Found: m/z 204.0795. Calcd for $C_{12}H_{12}O_3$: M, 204.0786.

Butyl 1,2-Epoxy-1,2,3,4-tetrahydronaphthalene-6-carboxylate (2j); ^{1}H NMR ($CDCl_3$) δ=0.98 (3H, t, J=7.42 Hz), 1.41—1.54 (2H, m), 1.70—1.83 (3H, m), 2.40—2.49 (1H, m), 2.58—2.66 (1H, m), 2.75—2.88 (1H, m), 3.77 (1H, d, J=4.29 Hz), 4.32 (2H, t, J=6.60 Hz), 7.46 (1H, d, J=7.92 Hz), 7.76 (1H, s), 7.88 (1H, m); IR (neat) 2960, 2930, 2860, 1721, 1463, 834 cm^{-1}. Optical yield was determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as chiral shift reagent. $[\alpha]_D^{32}$ +47.8° (c 1.35, $CHCl_3$, 57%ee). Found: m/z 246.1234. Calcd for $C_{15}H_{18}O_3$: M, 246.1256.

2-(2-Naphthyl)oxirane (2k); ^{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 ^{1}H NMR analysis using Eu(hfc)$_3$ as chiral shift reagent.

2,2-Dimethyl-3,4-epoxychroman (4a); ^{1}H NMR ($CDCl_3$) δ=1.25 (3H, s), 1.58 (3H, s), 3.50 (1H, d, J=4.29 Hz), 3.90 (1H, d, J=4.29 Hz), 6.79—6.95 (2H, m), 7.20—7.35 (2H, m); IR (neat) 2928, 2852, 1236, 752 cm^{-1}. Optical yield was determined by GC analysis (Chiraldex B-DA).

3,4-Epoxyspiro[chroman-2,1′-cyclopentane] (4b); ^{1}H NMR ($CDCl_3$) δ=1.22—1.88 (8H, m), 3.48 (1H, d, J=4.29 Hz), 3.86 (1H, d, J=4.29 Hz), 6.84—6.94 (2H, m), 7.21—7.34 (2H, m); IR (neat) 2928, 2854, 1481, 1241 cm^{-1}. Optical yield was determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as a chiral shift reagent. $[\alpha]_D^{26}$ −15.6° (c 0.62, EtOH, 91%ee). Found: C, 77.60; H, 7.48%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

3,4-Epoxyspiro[chroman-2,1′-cyclohexane] (4c); ^{1}H NMR ($CDCl_3$) δ=1.27—1.98 (10H, m), 3.40 (1H, d, J=4.29 Hz), 3.78 (1H, d, J=4.29 Hz), 6.76—6.87 (2H, m), 7.12—7.26 (2H, m); IR (neat) 2930, 2854, 1238, 752 cm^{-1}. Optical yield was determined by ^{1}H NMR analysis using Eu(hfc)$_3$ as a chiral shift reagent. $[\alpha]_D^{30}$ −10.9° (c 0.79, $CHCl_3$, 90%ee). Found: C, 78.10; H, 7.52%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

2,2,6-Trimethyl-3,4-epoxychroman (4d); ^{1}H NMR ($CDCl_3$) δ=1.23 (3H, s), 1.56 (3H, s), 2.28 (3H, s), 3.46 (1H, d, J=4.28 Hz), 3.85 (1H, d, J=4.28 Hz), 6.70 (1H, d, J=8.25 Hz), 7.02 (1H, m), 7.13 (1H, d, J=1.98 Hz); IR (neat) 2974, 2926, 1250, 818 cm^{-1}. Optical yield was determined by GC analysis (Chiraldex G-TA). $[\alpha]_D^{30}$ +10.1° (c 0.31, EtOH, 89%ee). Found: m/z 190.0989. Calcd for $C_{12}H_{14}O_2$: M, 190.0994.

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