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Catalytic Asymmetric Epoxidation of Unfunctionalized Olefins Using Chiral (Salen)manganese(III) Complexes[1)]

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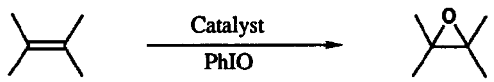
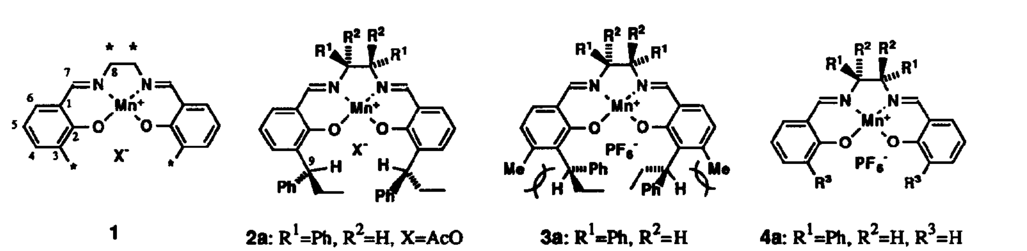
Abstract: Several kinds of chiral (salen)manganese(III) complexes (**2** and **3**) having chiral salicylaldehyde and chiral ethylenediamine moieties were prepared and used for catalytic asymmetric epoxidation of unfunctionalized olefins with iodosobenzene as a terminal oxidant. Catalysts **2** and **3** were found to show the characteristic substrate specificity for the enantiofacial selection of olefins, respectively. Furthermore, the addition of donor ligands such as pyridine *N*-oxide or 2-methylimidazole to the epoxidation reaction system was found to alter the enantioselectivity. As a result, the highest enantioselectivity for nonenzaymatic catalytic epoxidation was achieved for (*E*)-1-phenylpropene (56% ee, with **2c** in the presence of 2-methylimidazole), (*E*)-stilbene (48% ee, with **3a**), and dihydronaphthalene (83% ee, with **3a** in the presence of pyridine *N*-oxide).

Optically active epoxides occupy a very important position as versatile intermediary functionality in synthetic chemistry and many efforts have been directed toward the exploitation of highly enantioselective epoxidation reaction of olefins.[2)] In 1980, Sharpless and one of the authors (T.K.) reported highly enantioselective and practical epoxidation of allylic alcohols using a $Ti(O^iPr)_4$/diethyl tartrate/*t*-butyl hydroperoxide system,[3)] but enantioselective epoxidation of olefins which do not bear a specific adjacent functionality like a hydroxy group still remains unsettled.[4)]

In connection with the studies of developing model compounds for the cytochrome P-450 family, iron complexes of chiral porphyrins were found to be effective for the asymmetric epoxidation of unfunctionalized olefins showing up to 72% ee in the epoxidation of (Z)-1-phenylpropene.[4c)] On the other hand, it was reported that (salen)manganese(III) complex **1** was a useful catalyst for the epoxidation of olefins by Kochi *et al.*[5)] We assumed that replacement of carbons with asterisks in **1** by stereogenic carbons would provide the





1

2a: R^1=Ph, R^2=H, X=AcO
2b: R^1=H, R^2=Ph, X=AcO
2c: R^1=H, R^2=Ph, X=PF_6

3a: R^1=Ph, R^2=H
3b: R^1=H, R^2=Ph

4a: R^1=Ph, R^2=H, R^3=H
4b: R^1=H, R^2=Ph, R^3=Me_3C

better reaction site for enantioselective epoxidation, because there the asymmetric centers located closer to the metal center than those in porphyrin complexes. It was also considered that, in the epoxidation using this type of chiral salen complexes, the relative configuration of all the incorporated stereogenic carbons and conformational orientation of C-9 and C-9' stereogenic carbons would strongly affect the enantiofacial selectivity of olefins. In order to explore the potentiality of these chiral salen complexes as catalysts, we synthesized five chiral (salen)manganese(III) complexes (**2** and **3**) having C_2-symmetry, in which **2a** and **2b** and also **3a** and **3b** were diastereomeric to each other, respectively, and **2** and **3** have different C-9(C-9') conformational orientation, and studied the epoxidation of unfunctionalized olefins using them as catalysts.[6]

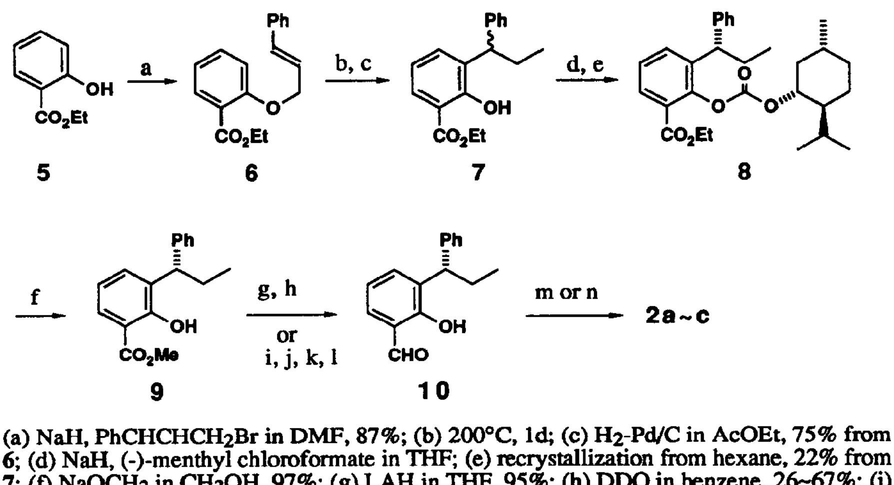
Recently Kochi *et al.* reported that donor ligands added to the reaction mixture coordinated to active oxo(salen)chromium(V) species at the axial site and brought about their conformational change resulting in the enhancement of the reaction rate.[7] Although enantiofacial selectivity of olefins in epoxidation reaction using above chiral salen complexes was anticipated to be primarily controlled by chiral centers incorporated into the salen skeleton, the conformational change of optically active oxo(salen)metal complexes owing to the coordination of donor ligands was also considered to alter their asymmetry-inducing ability. Therefore, we also examined the asymmetric epoxidation of unfunctionalized olefins catalyzed by **2** and **3** in the presence of various donor ligands and found that some donor ligands such as pyridine *N*-oxide and 2-methylimidazole enhanced the enantioselectivity to considerable extent.

In this paper, we describe synthesis of new chiral salen complexes (**2** and **3**) and enantioselective epoxidation of olefins catalyzed by them in full detail.

Synthesis of the Chiral (Salen)manganese(III) Complexes

Synthesis of 4-unsubstituted chiral (salen)manganese(III) complexes (**2a~c**) was commenced by cinnamylation of ethyl salicylate (**5**) to ethyl *O*-cinnnamylsalicylate (**6**) as shown in **Scheme 1**. Claisen rearrangement

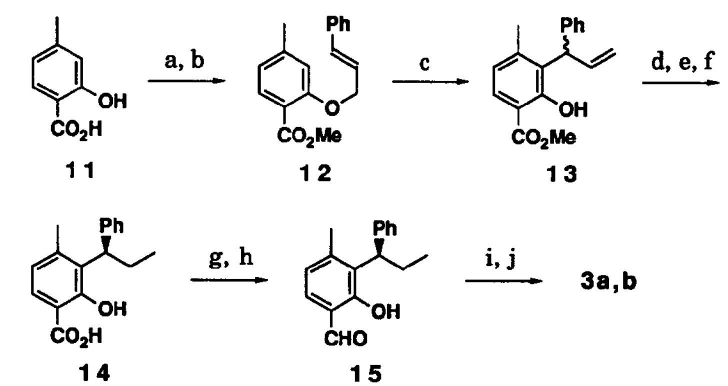
Scheme 1



(a) NaH, $PhCHCHCH_2Br$ in DMF, 87%; (b) 200°C, 1d; (c) H_2-Pd/C in AcOEt, 75% from **6**; (d) NaH, (-)-menthyl chloroformate in THF; (e) recrystallization from hexane, 22% from **7**; (f) $NaOCH_3$ in CH_3OH, 97%; (g) LAH in THF, 95%; (h) DDQ in benzene, 26~67%; (i) NaH, BnBr in DMF, quantitative; (j) LAH in THF, 87%; (k) MnO_2 in ether, 84%; (l) H_2-Pd/C in AcOEt, 85%; (m) (*S,S*)- or (*R,R*)-1,2-diphenylethylenediamine, $Mn(OAc)_2{\cdot}4H_2O$, O_2 in C_2H_5OH, 77% for **2a**, 69% for **2b**; (n) (*R,R*)-1,2-diphenylethylenediamine, $Mn(OAc)_2{\cdot}4H_2O$ in CH_3CN, then Cp_2FePF_6 in CH_3CN, 72% for **2c** of 6 followed by hydrogenation gave ethyl 3-[(*RS*)-(1-phenylpropyl)]salicylate (7). Menthyloxycarbonylation of 7 with (-)-menthyl chloroformate gave a mixture of diastereomeric carbonates which was converted to optically pure isomer **8**[8] by short column chromatography on silica gel and three recrystallizations from hexane. Treatment of **8** with sodium methoxide gave methyl ester **9**. Compound **9** was first converted into (*S*)-aldehyde **10** by reduction with lithium aluminium hydride (LAH) and subsequent oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). In the latter process, however, side reaction occurred with the formation of oxidatively dimerized product.[10] In order to suppress the side reaction, **9** was protected as a benzyl ether and, then, subjected to the sequence: i) LAH reduction, ii) MnO_2 oxidation, and iii) debenzylation, to give **10** in good yield. Successive treatments of **10** with (*R,R*)- or (*S,S*)-1,2-diphenylethylenediamine, and $Mn(OAc)_2 \cdot 4H_2O$ in air gave **2a,b** which were used for the following experiments after the recrystallization from hexane-dichloromethane. The cationic complex **2c** having hexafluorophosphate instead of acetate as a counter anion was prepared by treatment of **10** with (*R,R*)-1,2-diphenylethylenediamine and $Mn(OAc)_2 \cdot 4H_2O$ under nitrogen atmosphere followed by the oxidation with bis(cyclopentadienyl)iron(III) hexafluorophosphate.[5]

Another manganese complexes **3a,b** were prepared as follows (**Scheme 2**). Esterification of 4-methylsalicylic acid (**11**) by heating with trimethyl orthoformate and subsequent cinnamylation in basic conditions gave methyl *O*-cinnamyl-4-methylsalicylate (**12**). Heating **12** at 170~180°C in the presence of calcium carbonate[10] caused Claisen rearrangement to produce **13**. Hydrogenation of **13** followed by hydrolysis afforded 4-methyl-3-[(*RS*)-1-phenylpropyl]salicylic acid (*dl*-**14**) which could be resolved with the aid of (-)-brucine as a chiral base to give optically pure **14**. The absolute configuration of the optically active **14** thus obtained was determined to be *R* by its chemical correlation (see *Experimental*). LAH reduction of (*R*)-**8** and subsequent DDQ oxidation[11] of the resulting benzyl alcohol gave aldehyde **15**. Treatment of **15** with (*S,S*)- or (*R,R*)-1,2-diphenylethylenediamine and $Mn(OAc)_2 \cdot 4H_2O$ under nitrogen atmosphere gave yellowish manganese(II)

Scheme 2



(a) $(CH_3O)_3CH$, 120°C, 2d; (b) NaH, $PhCHCHCH_2Br$, in DMF, 77% (2 steps); (c) $CaCO_3$, 170~180°C, 1d, 71%; (d) H_2-Pd/C in AcOEt, quantitative; (e) 5N NaOH in C_2H_5OH, then HCl, quantitative; (f) (–)-Brucine·$2H_2O$, three repeated recrystallizations from acetone, then HCl, 22% from *dl*-**14**; (g) LAH in THF, 99%; (h) DDQ in AcOEt, 86%; (i) (*S,S*)- or (*R,R*)-1,2-diphenylethylenediamine, $Mn(OAc)_2 \cdot 4H_2O$, in C_2H_5OH or CH_3CN; (j) Cp_2FePF_6 in CH_3CN, 34% (2 steps) for **3a**, 72% (2 steps) for **3b**.

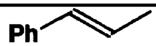
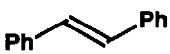
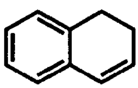
complexes which were further oxidized to manganese(III) complexes **3a,b** by treatment with bis(cyclopentadienyl)iron(III) hexafluorophosphate[7] with or without isolation of the divalent manganese complexes.

Asymmetric Epoxidation of Unfunctionalized Olefins Catalyzed by the Chiral (Salen)manganese(III) Complexes

The epoxidations catalyzed by **2** or **3** were examined with (*E*)-1-phenylpropene, (*E*)-stilbene, (*Z*)-1-phenylpropene, and dihydronaphthalene as substrates and iodosobenzene as a terminal oxidant in acetonitrile. The reaction in the absence of donor ligand in dichloromethane caused serious decomposition of some epoxides produced and the reaction in hexane was sluggish. All of the complexes showed catalytic activity and charactaristic enantioface selectivity as summerized in **Table 1**.

In the epoxidation of (*E*)-1-phenylstyrene and dihydronaphthalene using **2a,b**, it was found that **2b**

Table 1. Asymmetric Epoxidation of Unfunctionalized Olefins.[a]

Entry	Substrate	Catalyst	Yield (%)	% Ee	Abs. Confign.
1		**2a**	59	3 (20[b] 65[c])	(1*S*,2*S*)
2	"	**2b**	61	32	(1*R*,2*R*)
3	"	**2c**	28	18	(1*R*,2*R*)
4	"	**3a**	32[d]	7	(1*R*,2*R*)
5	"	**3b**	25[d]	17	(1*R*,2*R*)
6		**3a**	95	48 (33[b])	(1*R*,2*R*)
7	"	**3b**	16	6	(1*R*,2*R*)
8	 e)	**2b**	26[f]	44 (84[g])	(1*R*,2*S*)
9	"	**2c**	19[h]	46	(1*R*,2*S*)
10	"	**3a**	12[i]	68	(1*S*,2*R*)
11		**2a**	25	43 (78[g])	(1*S*,2*R*)
12	"	**2b**	93	49	(1*R*,2*S*)
13	"	**2c**	47	42	(1*R*,2*S*)
14	"	**3a**	65	72	(1*S*,2*R*)
15	"	**3b**	24	60	(1*R*,2*S*)

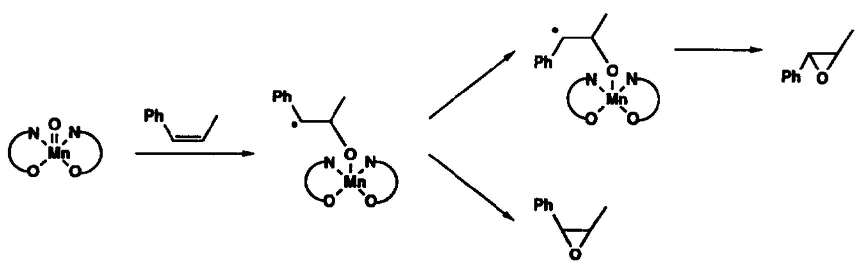
a) Reactions were conducted in acetonitrile at room temperature with molar ratio of substrate:catalyst:iodosobenzene=1:0.02:2~1:0.09:2.
b) Reported value using **4a** as a catalyst (reference 6).
c) The highest % ee previously reported for nonenzymatic stoichiometric epoxidation (reference 4d).
d) A trace amount of 1-phenyl-2-propanone was also produced.
e) The substrate contained 3% of (*E*)- isomer.
f) (1*S*,2*S*)-Epoxide of 47% ee (17%) and 1-phenyl-2-propanone (8%) were also obtained.
g) Reported value using **4b** as a catalyst (reference 6).
h) (1*R*,2*R*)-Epoxide of 6% ee (2%) and 1-phenyl-2-propanone (23%) were also obtained.
i) (1*R*,2*R*)-Epoxide of 38% ee (2%), 1-phenyl-2-propanone (12%), and 2-phenylpropanal (<5%) were also obtained.

exhibited a higher level of asymmetric induction (32 and 49% ee, entries 2 and 12) than **2a** (3 and 43% ee, entries 1 and 11) and that the sense of asymmetric induction by **2a** and **2b** were opposite to each other. These results suggested that the sense and degree of enantioface selection of olefins were affected by relative configuration between C-3 (C-3') and C-8 (C-8') stereogenic centers and that (*S*)-salicylaldehyde and (*R*,*R*)-diamine moieties constituted a matched pair in terms of double diastereoselection. Cationic complex **2c** showed the lower enantioselectivity as compared with **2b** in which only the counter anion was different from **2c**. This result may be explained by the donor ligand effect described in the following section.

The epoxidation catalyzed by **3a,b** in which stereogenic centers in the C-3 and C-3' substituents were considered to take the hydrogen in plane conformation to the aromatic ring in order to minimize the allylic strain between the C-3 and C-4 aromatic substituents in **3**, was next examined. Epoxidation of (*E*)-stilbene underwent smoothly and 48% ee was realized by using **3a** as a catalyst (entry 6). This is the highest one to date observed for the metal-catalyzed epoxidation of (*E*)-stilbene. Although another chiral catalyst **3b** was not effective for the epoxidation in terms of chemical yield and enantioselectivity (entry 7), it was note worthy that the sense of asymmetric induction was the same as that catalyzed by **3a**. This was also observed for the epoxidation of (*E*)-1-phenylpropene (entries 4 and 5). These results suggest that the chirality of C-3 and C-3' substituents has stronger influence upon the sense of asymmetric induction than that of ethylenediamine moiety. It is also interesting note that **3a** showed higher ee for the epoxidation of (*E*)-stilbene than for that of (*E*)-1-phenylpropene while **3b** showed higher ee for the epoxidation of (*E*)-1-phenylpropene, suggesting that the best conformation of C-3 and C-3' substituents changed with substrates for the epoxidation of (*E*)-olefins.

On the other hand, in the epoxidation of (*Z*)-olefins such as (*Z*)-1-phenylpropene and dihydronaphthalene, the enantiofacial selection was found to be mainly controlled by the chirality of the diamine moiety (entries 10, 14, and 15) as observed for the reaction catalyzed by **2a,b**. In another words, the chirality of C-3 and C-3' substituents had only small influence, differing from the epoxidation of (*E*)-olefins (*vide supra*). This result may explain why the high asymmetric inducing ability of Jacobsen's complex **4b** is confined to epoxidation of (*Z*)-olefins.[6] Although the enantioselectivity was slightly decreased as compared with **4b**, **3** showed superior asymmetric induction to **2** having the same C-3 and C-3' substituents. These results also implied that C-3 and C-3' substituents in **4b** and **3** have similar conformations to each other in which C-9 alkyl group (methyl group for **4b** or ethyl group for **3**) is synclinal to (C-2)-(C-3) bond of aromatic ring but those in **2** have a different conformation. Therefore, the bulkiness and conformation of C-3 and C-3' substituents are important in affecting the degree of enantiofacial selection of this type of olefins.

Interestingly, epoxidation of (*Z*)-1-phenylpropene gave a mixture of (1*R*,2*S*)- (44% ee) and (1*S*,2*S*)-epoxides (47% ee) together with a small amount of 1-phenylpropan-2-one (entry 8). That the optical yields of



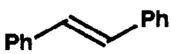
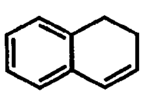
Scheme 3

(1*R*,2*S*)- and (1*S*,2*S*)-epoxides were almost the same and that their absolute configurations at C-2 were both *S* suggested the intervention of a radical intermediate in the course of the reaction as shown in the following **Scheme 3**, in agreement with Kochi's proposal.[12] But the precise reaction mechanism is unclear at present.

Donor Ligand Effect in the Asymmetric Epoxidation.

Effects of addition of a donor ligand to the epoxidation reaction system using **2** and **3** were next examined. Several kinds of donor ligands were examined with (*E*)-1-phenylpropene as a test olefin. As described in **Table 2** (entries 1~7), improvement of asymmetric yield was observed by addition of 2-methylimidazole, pyridine *N*-oxide, and lutidine *N*-oxide though addition of *N*,*N*-dimethylformamide (DMF) was not effective so much. To be interested, addition of donor ligands suppressed decomposition of epoxides even when dichloromethane was used as a solvent, and the reaction in dichloromethane showed slightly better stereoselectivity than that in acetonitrile (entries 1 to 2 and 3 to 4). Therefore dichloromethane was employed as a solvent hereafter. In addition, larger donor ligand effect was observed for the epoxidation catalyzed by cationic catalyst **2c** wherein coordination of donor ligands was considered to occur with ease, and finally the highest enantioselectivity of 56% ee for the nonenzymatic catalytic epoxidation of (*E*)-1-phenylpropene was achieved as shown in entry 4.

Table 2. Effects of Donor Ligands on Enantioselectivity in the Epoxidation.[a)]

Entry	Olefin	Catalyst	Solvent	Donor Ligand[b)]	Yield (%)	% Ee[c)]	Abs. Confign.
1		**2b**	CH_3CN	2-Me-ImH	37	44 (32)	(1*R*,2*R*)
2	"	**2b**	CH_2Cl_2	2-Me-ImH	37	50	(1*R*,2*R*)
3	"	**2c**	CH_3CN	2-Me-ImH	37	42 (18)	(1*R*,2*R*)
4	"	**2c**	CH_2Cl_2	2-Me-ImH	32	56	(1*R*,2*R*)
5	"	**2c**	CH_2Cl_2	DMF	31[d)]	23	(1*R*,2*R*)
6	"	**2c**	CH_2Cl_2	Py-N-oxide	93	46	(1*R*,2*R*)
7	"	**2c**	CH_2Cl_2	Lu-N-oxide	82[d)]	43	(1*R*,2*R*)
8		**3a**	CH_2Cl_2	2-Me-ImH	20	10 (48)	(1*R*,2*R*)
9	"	**3a**	CH_2Cl_2	Py-N-oxide	36	36	(1*R*,2*R*)
10		**2c**	CH_2Cl_2	2-Me-ImH	59[d,e)]	47 (46)	(1*R*,2*S*)
11	"	**2c**	CH_2Cl_2	Py-N-oxide	49[d,f)]	65	(1*R*,2*S*)
12	"	**3a**	CH_2Cl_2	Py-N-oxide	24[d,g)]	68 (68)	(1*S*,2*R*)
13		**2c**	CH_2Cl_2	Py-N-oxide	71	66 (42)	(1*R*,2*S*)
14	"	**3a**	CH_2Cl_2	Py-N-oxide	71	83 (72)	(1*S*,2*R*)

a) Reactions were conducted in acetonitrile at room temperature with molar ratio of substrate:catalyst:iodosobenzene:donor ligand=1:0.02:2:0.5~1:0.05:0.5
b) 2-Me-ImH = 2-methylimidazole, Py-N-oxide = pyridine *N*-oxide, Lu-N-oxide = lutidine *N*-oxide.
c) The results obtained in the absence of donor ligand were referred in parentheses.
d) A trace amount of 1-phenyl-2-propanone was also produced.
e) (1*S*,2*S*)-Epoxide of 29% ee (4%) was also obtained.
f) (1*S*,2*S*)-Epoxide of 42% ee (5%) was also obtained.
g) (1*R*,2*R*)-Epoxide of 14% ee (9%) was also obtained.

On the other hand, the reversed donor ligand effect was observed for the epoxidation of (*E*)-stilbene catalyzed by **3a** (entries 8 and 9). For the epoxidation of (*Z*)-olefins such as (*Z*)-1-phenylpropene and dihydronaphthalene, pyridine *N*-oxide was found to be the best donor ligand (entries 10~14) and the highest asymmetric yield of 83% ee for the nonenzymatic catalytic epoxidation of dihydronaphthalene was achieved (entry 14).

Observed relationship between the sense of asymmetric induction and configurations of (salen)manganese(III) complexes was consistent with the discussion in the previous section. Although the origin of donor ligand effect is not clear at present, the change in asymmetric induction was considered to be attributable to the conformational change of the skeleton of (salen)manganese(III) complexes and of C-3 and C-3' substituents brought about by coordination of a donor ligand.[13)]

These results described here shed some light on the mechanistic consideration of the epoxidation catalyzed by oxo(salen)metal complexes and provide a basis for the introduction of more effective chiral (salen)metal catalyst.

Experimental

All melting points are uncorrected. Measurements of optical rotations were performed with a JASCO DIP-360 automatic digital polarimeter. IR spectral measurements were carried out with a JASCO IR-700 diffraction grating infrared spectrometer. ^{1}H NMR spectra were measured with a JEOL JNM FX-90Q FT-NMR spectrometer (90 MHz) or a JEOL JNM GX-400 FT-NMR spectrometer (400 MHz). All signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ-value in $CDCl_3$). Kieselgel 60 (Merck 6670) and Wakogel C-300 were used as an adsorbent for column chromatography. Kieselgel 60F254 (Merck 5715) was used for preparative TLC.

Ethyl *O*-Cinnamylsalicylate (6). A solution of ethyl salicylate (1.00 g, 6.0 mol) in THF (3.0 ml) was added to a suspension of sodium hydride (0.173 g, 7.2 mmol) in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (3.0 ml) at 0°C. The mixture was stirred until evolution of hydrogen ceased. A solution of cinnamyl bromide (1.18 g, 6.0 mmol) in THF (3.0 ml) was added to the reaction mixture at room temperature. After stirring at room temperature for 4h, the mixture was diluted with 5% H_3PO_4 (1.0 ml), ether (30 ml), and water (30ml). The aqueous phase was extracted with ether. The combined extracts were washed with saturated aqueous NaCl. The organic phase was dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and purified with column chromatography (SiO_2, hexane-AcOEt 15:1) to give **6** as colorless crystals (1.48 g, 87%). An analytical sample was obtained by recrystallization from methanol. Mp 61.7~62.7°C. IR (KBr): 1713 (CO) cm^{-1}. ^{1}H NMR (90 MHz): 1.38 (3H, t, J=7.1 Hz, CH_3), 4.37 (2H, q, J=7.1 Hz, $CH_3\underline{CH_2}$), 4.78 (2H, dd, J=1.1, 5.3 Hz, $CH\underline{CH_2}$), 6.40 (1H, dt, J=5.3, 16.2 Hz, $OCH_2\underline{CH}$), 6.81 (1H, dt, J=1.1, 16.2 Hz, Ph$\underline{CH}$), 7.00 (1H, d, J=7.3 Hz, C_3-H), 7.10~7.70 (7H, m, other aromatic protons), 7.80 (1H, dd, J=1.8, 8.1 Hz, C_6-H). Found: C, 76.46; H, 6.32%. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43%.

Ethyl 3-[(*RS*)-1-Phenyl-2-propyl]salicylate (7). **6** (63.9 g, 0.23 mol) was heated at 190~200°C for 3h, cooled, and diluted with AcOEt (150 ml). 10% Pd-C (3.5 g) was added to the solution and stirred at room temperature for 10 h under hydrogen atmosphere. The catalyst was filtered off and the filtrate was concentrated *in vacuo*. The residue was dissolved in hexane (135 ml) by heating. The solution was cooled and allowed to stand for a day at room temperature to give **7** as colorless crystals (29.9 g). A second crop (18.2 g) was obtained by the concentration of the filtrate and centrifugal filtration. The combined yield was 75%. An analytical sample was obtained by recrystallization from hexane. Mp 49.8~50.8°C. IR (KBr): 1664 (CO) cm^{-1}. ^1H NMR (90 MHz): 0.91 (3H, t, J=7.4 Hz, $CHCH_2\underline{CH_3}$), 1.37 (3H, t, J=7.0 Hz, $OCH_2\underline{CH_3}$), 2.04 (2H, quint, J=7.4 Hz, $CH\underline{CH_2}CH_3$), 4.33 (1H, t, J=7.4 Hz, $CH_2\underline{CH}$), 4.36 (2H, q, J=7.0 Hz, $CH_3\underline{CH_2}O$), 6.82 (1H, t, J=7.9 Hz, C_5-H), 7.11~7.45 (6H, m, other aromatic protons), 7.70 (1H, dd, J=1.8, 7.9 Hz, C_6-H), 11.19 (1H, s, OH). Found: C, 75.93; H, 6.89%. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

Ethyl *O*-(*l*-Menthyloxycarbonyl)-3-[(*S*)-1-phenylpropyl]salicylate (8). A solution of **7** (24.4 g, 86 mmol) in THF (300 ml) was added to a suspension of sodium hydride (3.12 g, 0.13 mol) in THF (200 ml) at 0°C. The mixture was stirred until evolution of hydrogen ceased. To the reaction mixture was added (-)-menthyl chloroformate (18.4 ml, 86 mmol) at 0°C. After stirring at room temperature for 1.5 h, the mixture was diluted with 5% H_3PO_4 (10 ml), ether (500 ml), and water (500 ml). The organic phase was washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The product contained in the residue was isolated by a centrifugal filtration and recrystallized from hexane three times affording **8** as colorless crystals (8.51 g, 21%). The ^1H NMR spectrum (400 MHz) of this sample showed C_6-H as a double doublet at 7.86 ppm. Since the diastereomeric mixture exhibited two double doublets of equal integration ratio at 7.86 and 8.00 ppm, the diasteromeric excess of this sample was estimated to be >99%. Mp 110.1~111.1°C. $[\alpha]_D^{27}$ -146 (c 1.12, $CHCl_3$). IR (KBr): 1754 (CO), 1719(CO) cm^{-1}. ^1H NMR (400 MHz): 0.88 (3H, d, J=6.8 Hz, $CH\underline{CH_3}$), 0.92 (3H, t, J=7.3 Hz, $CH_2\underline{CH_3}$), 0.95 (1H, m), 0.97 (3H, d, J=6.4 Hz, $\underline{CH_3}(CH_3)CH$), 0.99 (3H, d, J=6.8 Hz, $CH_3(\underline{CH_3})CH$), 1.05~1.21 (2H, m), 1.36 (3H, t, J=7.1 Hz, $OCH_2\underline{CH_3}$), 1.51~1.58 (2H, m), 1.71~1.76 (2H, m), 1.99~2.14 (3H, m), 2.18~2.23 (1H, m), 4.19 (1H, t, J=7.6 Hz, $Ph\underline{CH}$), 4.33 (2H, q, J=7.1 Hz, OCH_2), 4.59 (1H, dt, J=4.4, 10.7 Hz, OCH), 7.17~7.30 (6H, m, other aromatic protons), 7.51 (1H, dd, J=1.5, 7.8 Hz, C_4-H), 7.86 (1H, dd, J=1.5, 7.8 Hz, C_6-H). Found: C, 74.66; H, 8.21%. Calcd for $C_{29}H_{38}O_5$: C, 74.65; H, 8.21%.

Methyl 3-[(*S*)-1-Phenylpropyl]salicylate (9). A solution of **8** (5.43 g, 12 mmol) in THF was added to a solution of sodium methoxide in methanol (3.5M, 20 ml, 70 mmol) at 0°C. After stirring at room temperature for 11h, the mixture was concentrated *in vacuo*. The residue was neutralized with 1N HCl (70 ml) and extracted with ether. The combined extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified with column chromatography (SiO_2, hexane-AcOEt 100:1) to give **9** as colorless crystals (3.04 g, 97%). An analytical sample was obtained by recrystallization from hexane. Mp 75.0~76.0°C. $[\alpha]_D^{25}$ -180 (c 1.19, CH_3OH). IR (KBr): 1664 (CO) cm^{-1}. ^1H NMR (400 MHz): 0.91 (3H, t, J=7.8 Hz, $CH_2\underline{CH_3}$), 2.04 (2H, quint, J=7.8 Hz, $CH_3\underline{CH_2}$), 3.90 (3H, s, OCH_3), 4.34 (1H, t, J=7.8 Hz, $CH_2\underline{CH}$), 6.83 (1H, t, J=7.8 Hz, C_5-H), 7.13~7.31 (5H, m, Ph), 7.41 (1H, dd, J=2.0, 7.8 Hz, C_4-H), 7.69 (1H, dd, J=2.0, 7.8 Hz, C_6-H), 11.11 (1H, s, OH). Found: C, 75.48; H, 6.71%. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

3-[(*S*)-1-Phenylpropyl]salicylaldehyde (10). A solution of **9** (3.04 g, 11 mmol) in *N,N*-dimethylformamide (DMF) (35 ml) was added to a suspension of sodium hydride (0.297 g, 12 mmol) in DMF (10 ml) at 0°C. The mixture was stirred until evolution of hydrogen ceased. Benzyl bromide (1.5 ml, 12 mmol) was added to the reaction mixture at room temperature. After stirring for 1d, the mixture was diluted with 5% H_3PO_4 (2.0 ml), ether (100 ml), and water (100 ml). The aqueous phase was extracted with ether. The combined extracts were washed with saturated aqueous NaCl. The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified with column chromatography (SiO_2, hexane-AcOEt 100:1) to give methyl *O*-benzyl-3-[(*S*)-1-phenylpropyl]salicylate as a colorless oil (3.95 g, quantitative yield). $[\alpha]_D^{20}$ -125 (c 1.01, $CHCl_3$). IR (neat): 1725 (CO) cm^{-1}. ^1H NMR (90 MHz): 0.84 (3H, t, J=7.2 Hz, $CH_2\underline{CH_3}$), 1.98 (2H, m, J=7.8 Hz, $CH_3\underline{CH_2}$), 3.83 (3H, S, OCH_3), 4.36 (1H, t, J=7.9 Hz, $CH_2\underline{CH}$), 4.74 (2H, ABq, J=11.2 Hz, $Ph\underline{CH_2}$), 7.06~7.54 (12H, m, other aromatic protons), 7.70 (1H, dd, J=2.0, 7.4 Hz, C_6-H). Found: C, 79.82; H, 6.77%. Calcd for $C_{24}H_{24}O_3$: C, 79.97; H, 6.71%. To a solution of methyl *O*-benzyl-3-[(*S*)-1-phenylpropyl]salicylate (4.11 g, 11 mmol) in THF (45 ml) was added LAH (0.443 g, 11 mmol) at 0°C. After stirring at room temperature for a day, the mixture was diluted with water (5.0 ml) and saturated aqueous Roschelle's salt (25 ml). After stirring for additional 3.5 h, the mixture was extracted with ether. The combined extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give 2-benzyloxy-3-[(*S*)-1-phenylpropyl]benzyl alcohol as a colorless oil (3.31 g, 87%). $[\alpha]_D^{24}$ -88.2 (c 1.12, C_2H_5OH). ^1H NMR (90 MHz): 0.88 (3H, t, J=7.2 Hz, $CH_2\underline{CH_3}$), 1.84~2.20 (3H, m, OH, $CH_3\underline{CH_2}$), 4.33 (1H, t, J=7.9 Hz, $CH_2\underline{CH}$), 4.70 (2H, s, $Ph\underline{CH_2}$), 4.82 (2H, ABq, J=13.0 Hz, $\underline{CH_2}OH$), 7.14~7.68 (13H, m, aromatic protons). Found: C, 82.81; H, 7.20%. Calcd for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28%. To a solution of 2-benzyloxy-3-[(*S*)-1-phenylpropyl]benzyl alcohol (1.37 g, 4.1 mmol) in ether (16 ml) was added activated γ-MnO_2 (14.0 g, 0.16 mol) at room temperature. After stirring for 4 h, the mixture was diluted with ether (16 ml) and stirred for additional 14 h at room temperature. The reaction mixture was filtered, concentrated *in vacuo*, and purified with column chromatography (SiO_2, hexane-AcOEt 100:1) to give *O*-benzyl-3-[(*S*)-1-phenylpropyl]salicylaldehyde as a colorless oil (1.14 g, 84%). $[\alpha]_D^{25}$ -101 (c 1.15, $CHCl_3$). IR (neat): 1686 (CO) cm^{-1}. ^1H NMR (90 MHz): 0.87 (3H, t, J=7.4 Hz, $CH_2\underline{CH_3}$), 2.02 (2H, m, $CH_3\underline{CH_2}$), 4.33 (1H, t, J=7.9 Hz, $CH_2\underline{CH}$), 4.82 (2H, s, $Ph\underline{CH_2}$), 7.02~7.38 (11H, m, other aromatic protons), 7.62 (1H, dd, J=2.0, 7.7 Hz, C_4-H), 7.73 (1H, dd, J=2.0, 7.7 Hz, C_6-H), 10.26 (1H, s, CHO). Found: C, 83.49; H, 6.73%. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71%. A mixture of *O*-benzyl-3-[(*S*)-1-phenylpropyl]salicylaldehyde (1.14 g, 3.5 mmol), 10% Pd-C (0.114 g), and triethylamine (0.475 ml, 3.4 mmol) in benzene (14 ml) was stirred at room temperature for 20 min under hydrogen atmosphere. The catalyst was filtered off and the filtrate was concentrated *in vacuo*. The residue was purified with column chromatography (SiO_2, hexane-AcOEt 100:1) to give **10** (0.700 g, 85%). $[\alpha]_D^{21}$ -257 (c 1.12, C_2H_5OH). IR (neat): 1654 (CO) cm^{-1}. ^1H NMR (400 MHz): 0.92 (3H, t, J=7.3 Hz, $CH_2\underline{CH_3}$), 2.06 (2H, quint, J=7.3 Hz, $CH_3\underline{CH_2}$), 4.34 (1H, t, J=7.3 Hz, $CH_2\underline{CH}$), 6.98 (1H, t, J=7.3 Hz, C_5-H), 7.15~7.32 (5H, m, Ph), 7.39 (1H, dd, J=1.5, 7.3 Hz, C_4-H), 7.49 (1H, dd, J=1.5, 7.3 Hz, C_6-H), 9.85 (1H, s, CHO), 11.37 (1H, s, OH). Found: C, 79.85; H, 6.75%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

Methyl *O*-Cinnamyl-4-methylsalicylate (12). A mixture of 4-methylsalicylic acid (**11**) (25.6 g, 0.17 mol) and trimethyl orthoformate (300ml, 2.7 mol) was refluxed (120°C) for 2 days. Resulting methyl formate and excess trimethyl orthoformate were removed by a fractional distillation. The residue was distilled under reduced pressure (bp 124~140°C/20 mmHg) to give almost pure methyl 4-methylsalicylate as a colorless oil (28.7 g) which was used for the following reaction without further purification. Sodium hydride (4.00g, 0.17 mol) was added to a solution of methyl 4-methylsalicylate (25.4 g, 0.15 mol) in DMF (75 ml) at <10°C. The mixture was stirred until evolution of hydrogen ceased. Cinnamyl bromide (31.7 g, 0.16 mol) was added to the reaction mixture. After stirring overnight at room temperature, the mixture was diluted with 1N HCl (50 ml) and extracted with AcOEt . The combined extracts were washed successively with saturated aqueous $NaHCO_3$, water, and saturated aqueous NaCl. The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified with column chromatography (SiO_2, hexane-AcOEt 19:1~9:1) to give **12** as a colorless oil (32.8 g, 77% from 4-methylsalicylic acid). IR (neat): 1724 (CO) cm^{-1}. ^1H NMR

(400 MHz): 2.38 (3H, s, C_4-CH_3), 3.90 (3H, s, OCH_3), 4.78 (2H, d, J=4.9 Hz, OCH_2), 6.43 (1H, dt, J=4.9, 15.6 Hz, $CH_2\underline{CH}$), 6.81 (1H, d, J= 7.8 Hz, C_5-H), 6.82 (1H, d, J= 15.6 Hz, Ph$\underline{CH}$), 6.83 (1H, s, C_3-H), 7.26 (1H, t, J=7.8 Hz), 7.33 (2H, t, J=7.8 Hz), 7.42 (2H, d, J=7.8 Hz), 7.75 (1H, d, J=7.8 Hz, C_6-H). Found: C, 76.53; H, 6.38%. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43%.

Methyl 4-Methyl-3-[(*RS*)-1-phenyl-2-propenyl]salicylate (13). A mixture of **12** (32.6 g, 0.12 mol) and calcium carbonate (12.1 g, 0.12 mol) was heated at 170~180°C with stirring for a day.[10] After cooling, the mixture was filtered through a pad of Celite, rinsing with AcOEt, and the combined filtrates were concentrated *in vacuo*. The residue was separated to two fractions with column chromatography (SiO_2, hexane-CH_2Cl_2 1:0~9:1 then hexane-AcOEt 9:1). From the less polar fraction, **13** was obtained as a colorless oil (23.3 g, 71%). IR (neat): 1669 (CO) cm^{-1}. ^1H NMR (400 MHz): 2.25 (3H, s, C_4-CH_3), 3.91 (3H, s, OCH_3), 5.18 (1H, d, J=17.6 Hz, $C\underline{H}H$=CH), 5.22 (1H, d, J=10.3 Hz, $CH\underline{H}$=CH), 5.31 (1H, d, J= 8.1 Hz, Ph$\underline{CH}$), 6.60 (1H, ddd, J= 8.1, 10.3, 17.6 Hz, CH_2=$\underline{CH}$), 6.72 (1H, d, J=8.1 Hz, C_5-H), 7.16~7.28 (5H, m, Ph), 7.67 (1H, d, J=8.1 Hz, C_6-H),11.13 (1H, s, OH). Found: C, 76.42; H, 6.32%. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43%. Concentration of the more polar fraction gave undesired methyl 4-methyl-5-(3-phenyl-2-propenyl)salicylate (7.50 g, 23%) ^1H NMR (400 MHz) 2.32 (3H, s, C_4-CH_3), 3.46 (2H, m, CH_2), 3.92 (3H, s, OCH_3), 6.26 (2H, m, Ph$\underline{CHCH}$), 6.81 (1H, s, C_3-H), 7.18~7.35 (5H, m, Ph), 7.62 (1H, s, C_6-H), 10.57 (1H, s, OH).

4-Methyl-3-[(*R*)-1-phenylpropyl]salicylic Acid (14). A mixture of **13** (20.3 g, 72 mmol) and 10% Pd-C (60 mg) in AcOEt (150 ml) was stirred overnight at room temperature under hydrogen atmosphere. The mixture was filtered through a pad of Celite and concentrated *in vacuo* to give methyl 4-methyl-3-[(*RS*)-1-phenylpropyl]salicylate as colorless crystals (20.7 g, quantitative yield). Mp 53.0~55.0°C. IR (KBr): 1664 (CO) cm^{-1}. ^1H NMR (400 MHz): 0.89 (3H, t, J=7.3 Hz, $CH_2\underline{CH_3}$), 2.30 (3H, s, C_4-CH_3), 2.24~2.34 (2H, m, $CH_3\underline{CH_2}$), 3.90 (3H, s, OCH_3), 4.45 (1H, m, CH), 6.67 (1H, d, J=7.8 Hz, C_5-H), 7.14 (1H, t, J=7.8 Hz), 7.24 (2H, t, J=7.8 Hz), 7.30 (2H, d, J=7.8 Hz), 7.62 (1H, d, J=7.8 Hz, C_6-H),11.12 (1H, s, OH). Found: C, 76.09; H, 7.00%. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%. A part of this sample (11.1 g, 37 mmol) was dissolved in ethanol (50 ml) and 5N NaOH (22.3 ml, 0.112 mol) was added to the solution at room temperature. After stirring at room temperature for 12h and at 60°C for 30 min, the mixture was cooled and diluted with 1N HCl (37 ml). Concentration *in vacuo* to half volume, dilution with 1N HCl (80 ml), and filtration of resulting precipitate gave 4-methyl-3-[(*RS*)-1-phenylpropyl]salicylic acid as colorless crystals (10.6 g, quantitative yield). This was purified by a single recrystallization from methanol. Resolution of 4-methyl-3-[(*RS*)-1-phenylpropyl]salicylic acid was effected as follows. 4-Methyl-3-[(*RS*)-1-phenylpropyl]salicylic acid (8.05 g, 30 mmol) and (-)-brucin·$2H_2O$ (12.8 g, 30 mmol) were dissolved in hot acetone (70 ml), filtered, allowed to cool, seeded with crystals of previously prepared authentic sample, and allowed to stand for a day at room temperature. The colorless crystalline precipitate (10.3 g) was separated by filtration and recrystallized twice from acetone affording optically pure salt as an acetone adduct (4.78 g). Mp 107~108°C. $[\alpha]_D^{25}$ +14.3 (c 1.36, $(CH_3)_2HOH$) A part of the above salt (2.95 g) was decomposed by adding 1N HCl (8 ml) and the resulting mixture was extracted with AcOEt. The combined extracts were washed with saturated aqueous NaCl and dried over anhydrous $MgSO_4$. Filtration and concentration *in vacuo* gave optically pure **14** as colorless crystals (1.07 g, 22% from *dl*-**14**). Mp 183.5~184.5°C. $[\alpha]_D^{24}$ +33.6 (c 1.01, C_2H_5OH). IR (KBr): 1642 (CO) cm^{-1}. ^1H NMR (400 MHz): 0.90 (3H, t, J=7.3 Hz, $CH_2\underline{CH_3}$), 2.25~2.34 (3H, m, $CH_3\underline{CH_2}$, COOH), 2.34 (3H, s, CH_3), 4.45 (1H, m, CH), 6.73 (1H, d, J=7.8 Hz, C_5-H), 7.15 (1H, t, J=6.8 Hz), 7.25 (2H, t, J=6.8 Hz),7.30 (2H, d, J=6.8 Hz), 7.70 (1H, d, J=7.8 Hz, C_6-H),10.78 (1H, s, OH). Found: C, 75.73; H, 6.66%. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%. The absolute configuration of **14** was determined to be *R* by the following correlation. A solution of trimethylsilyldiazomethane in hexane (10%) was added to a solution of **14** (57.2 mg, 0.21 mmol) in a mixed solvent of ether (1.0 ml) and methanol (0.5 ml) until the solution turned yellow. After stirring at room temperature for 0.5 h, the mixture was concentrated *in vacuo*. The residue was dissolved in a mixture of acetonitlile (3.0 ml), CCl_4 (3.0 ml), and water (4.5 ml). To the solution were added $RuCl_3 \cdot nH_2O$ (ca. 2 mg) and $NaIO_4$ (0.679 g, 3.2 mmol). After stirring vigorously at room temperature for 2 h, the reaction mixture was extracted with CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was purified with column chromatography (SiO_2, hexane-AcOEt 5:1) affording (*R*)-2-phenylbutyric acid (18.0 mg, 52% from **14**) This acid showed a specific rotation of $[\alpha]_D^{26}$ -76.1 (c 0.74, C_2H_5OH). Since (*S*)-2-phenylbutyric acid has been reported to exhibit $[\alpha]_D^{25}$ +78.5 (C_2H_5OH), the absolute configuration of (-)-**14** was determined to be *R*.

4-Methyl-3-[(*R*)-1-phenylpropyl]salicylaldehyde (15). LAH (0.270 g, 7.1 mmol) was added to a solution of **14** (1.01 g, 3.7 mmol) in THF (20 ml) at 0°C. After stirring at room temperature for 1 h and at 50°C for 1 h, the mixture was successively treated with methanol (1.0 ml) and 1N HCl (30 ml). The reaction mixture was extracted with AcOEt. The combined extracts were washed with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified with column chromatography (SiO_2, hexane-AcOEt 19:1~9:1) affording 6-hydroxymethyl-3-methyl-2-[(*R*)-1-phenylpropyl]phenol as a colorless oil (0.941 g, 99%). $[\alpha]_D^{23}$ +60.8 (c 1.04, C_2H_5OH). ^{1}H NMR (400 MHz): 0.92 (3H, t, J=7.3 Hz, $CH_2\underline{CH_3}$), 2.07 (1H, t, J=5.9 Hz, $CH_2\underline{OH}$), 2.21~2.37 (2H, m, $CH_3\underline{CH_2}$), 2.32 (3H, s, C_4-CH_3), 4.39 (1H, m, CH), 4.73 (2H, d, J=5.9 Hz, $\underline{CH_2}OH$), 6.68 (1H, d, J=7.8 Hz, C_5-H), 6.81 (1H, br s, C_2-OH), 6.84 (1H, d, J=7.8 Hz, C_6-H), 7.17 (1H, t, J=7.8 Hz), 7.27 (2H, t, J=7.8 Hz), 7.33 (2H, d, J=7.8 Hz). Found: C, 79.62; H, 7.83%. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86%. A solution of 6-hydroxymethyl-3-methyl-2-[(*R*)-1-phenylpropyl]phenol (0.629 g, 2.5 mmol) in AcOEt (4.9 ml) was added to a solution of DDQ (0.586 g, 2.6 mmol) in AcOEt (4.9 ml) at 0°C. After stirring at room temperature for 2 d, the precipitate was filtered off. The filtrate was concentrated and purified with column chromatography (SiO_2, hexane-AcOEt 1:0~19:1) to give **15** as colorless crystals (0.534 g, 86%). An analytical sample was obtained by recrystallization from methanol. Mp 43~44°C. $[\alpha]_D^{24}$ -3.62 (c 1.19, C_2H_5OH). IR (KBr): 1640 (CO) cm-1. ^{1}H NMR (400 MHz): 0.90 (3H, t, J=7.3 Hz, $CH_2\underline{CH_3}$), 2.24~2.39 (2H, m, $CH_3\underline{CH_2}$), 2.34 (3H, s, CH_3), 4.44 (1H, m, CH), 6.81 (1H, d, J=7.8 Hz, C_5-H), 7.13~7.31 (6H, m, C_6-H, Ph), 9.78 (1H, s, CHO), 11.49 (1H, s, OH). Found: C, 80.39; H, 7.03%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%.

[(8*S*,8'*S*)-3,3'-Bis[(*S*)-1-phenylpropyl]-8,8'-diphenylsalen]manganese(III) Acetate (2a). $Mn(OAc)_2 \cdot 4H_2O$ (27.0 mg, 0.11 mmol) and (1*S*,2*S*)-1,2-diphenylethylenediamine (23.4 mg, 0.11 mmol) were added to a solution of **10** (53.0 mg, 0.22 mmol) in ethanol (11 ml) in air. After stirring at room temperature for 1.5 h, the mixture was concentrated *in vacuo* to give **2a** as dark brown crystals. Recrystallization from the mixed solvent of CH_2Cl_2 and hexane gave analytically pure sample (65.3 mg, 77%). IR (KBr): 1594 (s), 1544 (s), 1491(m), 1450 (m), 1419 (s), 1382 (m), 1310 (s), 1210 (m), 1163 (w), 1088 (w), 1006 (m), 869 (m), 749 (m), 698 (s), 663 (w). Found: C, 73.32; H, 5.83; N, 3.45%. Calcd for $C_{48}H_{45}N_2O_4Mn \cdot H_2O$: C, 73.27; H, 6.02; N, 3.56%

[(8*R*,8'*R*)-3,3'-Bis[(*S*)-1-phenylpropyl]-8,8'-diphenylsalen]manganese(III) Acetate (2b). $Mn(OAc)_2 \cdot 4H_2O$ (24.6 mg, 0.10 mmol) and (1*R*,2*R*)-1,2-diphenylethylenediamine (21.3 mg, 0.10 mmol) were added to a solution of **10** (48.4 mg, 0.20 mmol) in (10 ml) in air. After stirring at room temperature for 1.5 h, the mixture was concentrated *in vacuo* to give **2b** as dark brown crystals. Recrystallization from the mixed solvent of CH_2Cl_2 and hexane gave analytically pure sample (53.3 mg, 69%). IR (KBr): 1595 (s), 1544 (s), 1491(w), 1450 (m), 1419 (s), 1310 (m), 1209 (m), 1310 (m), 1209 (m), 1089 (w), 1006 (w), 868 (w), 749 (m), 699 (m), 648 (w). Found: C, 73.73; H, 5.82; N, 3.58%. Calcd for $C_{48}H_{45}N_2O_4Mn{\bullet}0.7H_2O$: C, 73.78; H, 5.98; N, 3.58%

[(8*R*,8'*R*)-3,3'-Bis[(*S*)-1-phenylpropyl]-8,8'-diphenylsalen]manganese(III) Hexafluorophosphate (2c). A solution of (1*R*,2*R*)-1,2-diphenylethylenediamine (0.111 g, 0.52 mmol) and **10** (0.251 g, 1.0 mmol) in acetonitrile (5.0 ml) was added to $Mn(OAc)_2{\cdot}4H_2O$ (0.128 g, 0.52 mmol) and the mixture was stirred for 1.5 h at room temperature. To this mixture was added a solution of ferricenium hexafluorophosphate (0.173 g, 0.52 mmol) in acetonitrile (2.5 ml) at room temperature. After stirring for 11 h, the mixture was concentrated *in vacuo*. The crystalline residue was washed with hexane to remove ferrocene produced and recrystallized from a mixed solvent of acetone and ethanol to afford **2c** as dark brown crystals (0.321 g, 72%). IR (KBr): 1597 (s), 1544 (s), 1515 (w), 1491 (w), 1450 (w), 1419 (m), 1383 (w), 1308 (m), 1005 (w), 845 (s), 751 (m), 699 (m), 664 (w). Found: C, 63.78; H, 5.74; N, 3.05%. Calcd for $C_{46}H_{42}N_2O_2MnPF_6{\cdot}1.5C_2H_5OH$: C, 63.70; H, 5.56; N, 3.03%.

[(8*S*,8'*S*)-3,3'-Bis[(*R*)-1-phenylpropyl]-4,4'-dimethyl-8,8'-diphenylsalen]manganese(III) Hexafluorophosphate (3a). Solutions of (1*S*,2*S*)-1,2-diphenylethylenediamine (83.5 mg, 0.39 mmol) in ethanol (1.0 ml) and **15** (0.200 g, 0.79 mmol) in ethanol (1.0 ml) were successively added to a solution of $Mn(AcO)_2{\cdot}4H_2O$ (0.101 g, 0.41 mmol) in ethanol (1.0 ml). After stirring overnight at room temperature, the mixture was filtered to isolate yellowish crystals (0.239 g). A part of this sample (21 mg) was added to a solution of ferricenium hexafluorophosphate (8.9 mg, 0.027 mmol) in acetonitrile (0.9 ml). After stirring at room temperature for 1 h, the mixture was concentrated *in vacuo*. The crystalline residue was suspended in ether (2 ml) and insoluble material was filtered off, then the filtrate was concentrated *in vacuo*. The residue (21.0 mg) was washed with hexane and recrystallized from a mixed solvent of methanol and water affording **3a** as dark brown crystals (8.0 mg, 34% from **15**). IR (KBr): 1585 (s), 1524 (m), 1491(w), 1450 (w), 1380 (w), 1295 (w), 1215 (w), 1007 (w), 845 (s), 703 (m), 664 (w). Found: C, 63.51; H, 5.31; N, 3.02%. Calcd for $C_{48}H_{46}N_2O_2MnPF_6{\bullet}1.5H_2O$: C, 63.37; H, 5.43; N, 3.08%.

[(8*R*,8'*R*)-3,3'-Bis[(*R*)-1-phenylpropyl]-4,4'-dimethyl-8,8'-diphenylsalen]manganese(III) Hexafluorophosphate (3b). A solution of (1*R*,2*R*)-1,2-diphenylethylenediamine (53.3 mg, 0.25 mmol) and **15** (0.128 g, 0.50 mmol) in acetonitrile (2.5 ml) was added to $Mn(OAc)_2{\cdot}4H_2O$ (61.5 mg, 0.25 mmol) and stirred for 17 h at room temperature. To this mixture was added a solution of ferricenium hexafluorophosphate (83.0 mg, 0.25 mmol) in acetonitrile (2.5 ml) at room temperature. After stirring for 13 h, the mixture was concentrated *in vacuo*. The crystalline residue was washed with hexane to remove ferrocene produced and recrystallized from a mixed solvent of CH_2Cl_2 and hexane affording **3b** as dark brown crystals (0.160 g, 72%). An analytical sample was obtained by recrystallization with acetone-ethanol. IR (KBr): 1577 (s), 1525 (s), 1492 (s), 1449 (s), 1380 (s), 1295 (s), 1223 (s), 1102 (s), 1056 (s), 1008 (s), 949 (s), 834 (s), 756 (s), 699 (s), 651 (m). Found: C, 65.16; H, 5.21; N, 3.03%. Calcd for $C_{48}H_{46}N_2O_2MnPF_6$: C, 65.31; H, 5.25; N, 3.17%

Epoxidation of (*E*)-1-Phenylpropene Catalyzed by 2c in the Presence of 2-Methylimidazole (Table 2, Entry 4). Iodosobenzene (72.0 mg, 0.33 mmol) was added at once to a solution of (*E*)-1-

phenylpropene (19.4 mg, 0.16 mmol), **2c** (6.8 mg, 8 μmol), and 2-methylimidazole (6.7 mg, 0.08 mmol) in CH_2Cl_2 (4.1 ml) at room temperature. After stirring for 58 h, the mixture was carefully concentrated *in vacuo*. The residue was purified with column chromatography (SiO_2, pentane-Et_2O 60:1) to give (1*R*,2*R*)-1,2-epoxy-1-phenylpropane as a colorless oil (7.1 mg, 32%). The absolute configuration of this sample was determined to be 1*R*,2*R* by measuring the optical rotation. $[\alpha]_D^{25}$ +26 (c 0.56, $CHCl_3$) [*lit.*,[14] $[\alpha]_D^{20}$ +50.0 (c 1.17, $CHCl_3$) for (1*R*,2*R*)-isomer]. The optical purity of this sample was determined to be 56% ee by the ^1H NMR analysis (400 MHz) in the presence of chiral shift reagent, Eu(hfc)$_3$.

Epoxidation of (*E*)-Stilbene Catalyzed by 3a (Table 1, Entry 6). (*E*)-Stilbene (20.0 mg, 0.11 mmol) and iodosobenzene (48.8 mg, 0.22 mmol) were added to a solution of **3a** (6.0 mg, 6 μmol) in acetonitrile (1 ml) at room temperature. After stirring for 1 h, the mixture was concentrated *in vacuo* and purified with column chromatography (SiO_2, hexane-AcOEt 1:0~19:1) to give (1*R*,2*R*)-stilbene oxide as colorless crystals (20.0 mg, 95%). The absolute configuration of this sample was determined to be 1*R*,2*R* by measuring the optical rotation. $[\alpha]_D^{25}$ +126 (c 0.88, $CHCl_3$) [*lit.*,[15] $[\alpha]_D^{25}$ +342 (c 1.11, C_2H_5OH) for (1*R*,2*R*)-isomer]. The HPLC analysis (Daicel chiralcel OD, hexane-isopropanol 9:1, flow rate 0.6 ml/min) of this sample, clearly showed two peaks corresponding to (1*R*,2*R*)- and (1*S*,2*S*)-isomers at retention times of 13.9 min and 8.6 min, respectively. By comparing the integration of each peaks, the optical purity was estimated to be 48% ee.

Epoxidation of (*Z*)-1-Phenylpropene Catalyzed by 3a (Table 1, Entry 10). Iodosobenzene (0.112g, 0.53 mmol) was added at once to a solution of (*Z*)-1-phenylpropene (35.0 mg, 0.27 mmol) and **3a** (4.5 mg, 5 μmol) in acetonitrile (5.0 ml) at room temperature. After stirring for 12h, the mixture was carefully concentrated *in vacuo*. The residue was purified with column chromatography (SiO_2, hexane-AcOEt 1:0~30:1) to give (1*S*,2*R*)-1,2-epoxy-1-phenylpropane as a colorless oil (4.95 mg, 14%) from the first fraction which contained small amount of (1*R*, 2*R*)-1,2-epoxy-1-phenylpropane (2%). By considering the contaminant of (1*R*, 2*R*)-epoxide, the yield of (1*S*,2*R*)-epoxide could be calculated to be 12%. The rearranged products of 1-phenyl-2-propanone (4.10 mg, 12%) and 2-phenylpropanal (1.8 mg, <5%) together with a small amount of undefined product were obtained from second and third fractions, respectively. The absolute configuration of this epoxide was determined to be 1*S*,2*R* by measuring the optical rotation. $[\alpha]_D^{25}$ +28 (c 0.41, $CHCl_3$) [*lit.*,[14] $[\alpha]_D^{20}$ +47.5 (c 1.17, $CHCl_3$) for (1*S*,2*R*)-isomer]. The optical purity of this sample was determined to be 68% ee for (1*S*,2*R*)-epoxide and 38% ee for (1*R*,2*R*)-epoxide by the ^1H NMR analysis (400 MHz) in the presence of chiral shift reagent, Eu(hfc)$_3$.

Epoxidation of Dihydronaphthalene Catalyzed by 3a. a) In the absence of a donor ligand (**Table 1**, entry 14): Dihydronaphthalene (34.7 mg, 0.27 mmol) and iodosobenzene (0.118 g, 0.54 mmol) were added to a solution of **3a** (4.6 mg, 5 μmol) in acetonitrile (5 ml) at room temperature. After stirring at room temperature for 1.5 h, the mixture was concentrated *in vacuo* and purified with column chromatography (SiO_2, hexane-AcOEt 40:1) to give (1*S*,2*R*)-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (25.3 mg, 65%). The absolute configuration of this sample was determined to be 1*S*,2*R* by measuring the optical rotation. $[\alpha]_D^{25}$ -87.0 (c 1.33, $CHCl_3$) [*lit.*,[16] $[\alpha]_D^{25}$ +135 ($CHCl_3$) for (1*R*,2*S*)-isomer]. The optical purity of this sample was determined to be 72% ee by the ^1H NMR analysis (400 MHz) in the presence of chiral shift reagent, Eu(hfc)$_3$.
b) In the presence of a donor ligand (**Table 2**, entry 14): Iodosobenzene (76.0 mg, 0.35 mmol) was added at once to a solution of dihydronaphthalene (22.5 mg, 0.17 mmol), **3a** (3.1 mg, 3.5 μmol), and pyridine *N*-oxide (3.3 mg, 0.035 mmol) in CH_2Cl_2 (1.8 ml) at room temperature. After stirring for 12h, the mixture was carefully concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, pentane-Et_2O

30:1) to give (1*S*,2*R*)-1,2-epoxy-1,2,3,4-tetrahydronaphthalene as colorless crystals (18.0 mg, 71%). The optical purity of this sample was determined to be 83% ee by the ^{1}H NMR analysis (400 MHz, $CDCl_3$) in the presence of chiral shift reagent, $Eu(hfc)_3$.

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(9) In the DDQ oxidation of the benzylic alcohol to aldehyde **10**, the substrate should be added to a solution of DDQ slowly to minimize serious oxidative dimerization. In spite of this modification, the yield of **10** is unreproducible.
(10) Addition of one equivalent of calcium carbonate to the reaction was found to be effective for minimizing the side reaction of rearrangement of the cinnamyl moiety to C-5 position instead of C-3 position of the aromatic ring.
(11) The DDQ oxidation of the benzylic alcohol to aldehyde (**15**) was proceeded smoothly without serious oxidative dimerization which was observed for the oxidation to 4-unsubstituted aldehyde (**10**)
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