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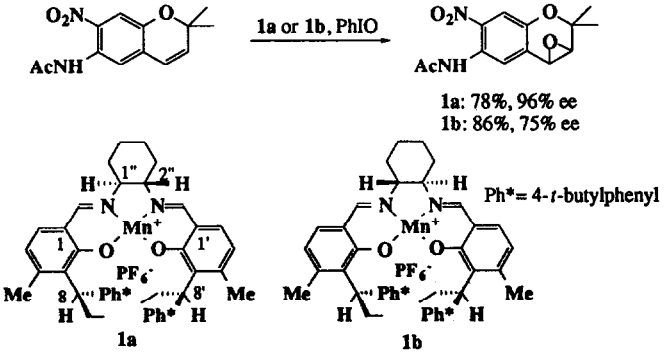
Catalytic Asymmetric Oxidation of Sulfides Using (Salen)manganese(III) Complex as a Catalyst

Kenji Noda†, Naoki Hosoya†, Ryo Irie, Yuji Yamashita, and Tsutomu Katsuki*

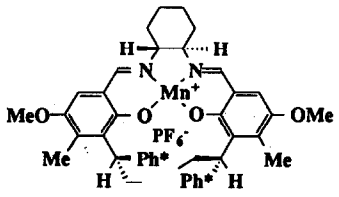
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812, Japan

Abstract: Asymmetric oxidation of sulfides was examined by using (salen)manganese(III) complexes as catalysts and (8*S*,8'*S*,1"*S*,2"*S*)-complex (**2b**) was found to show high asymmetric induction up to 90% ee. Its diastereomeric (8*R*,8'*R*,1"*S*,2"*S*)-complex (**1a**) that showed excellent asymmetric induction in the epoxidation of simple olefins, however, was a poor catalyst for the oxidation of sulfides. Kinetic resolution of racemic methyl phenyl sulfoxide with **2b** was not effective.

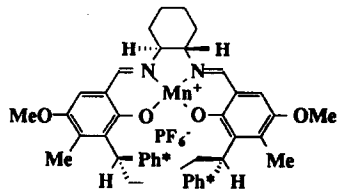
Asymmetric oxidation of sulfides is one of current topics, since optically active sulfoxides are of high synthetic use as chiral synthons or as chiral auxiliaries and many useful methodologies for this purpose have been reported to date.[1,2,3] For example, reactions using optically active oxaziridines as oxidants[1] or a *t*-butyl hydroperoxide/Ti(OPr-*i*)$_4$/dialkyl tartrate/H_2O system[2] show high enantioselectivity (>90% ee) but these reactions require a stoichiometric amount of chiral oxidant or catalyst. Recently Uemura et al. reported the catalytic formation of highly optically pure sulfoxides (up to 96% ee) by concomitantly performing enantioselective oxidation of sulfides and kinetic resolution of the resulting enantiomerically enriched sulfoxides with titanium-binaphthol complex as a catalyst.[3b] However, there is still no good methodology for yielding highly optically pure sulfoxides only by catalytic asymmetric oxidation of sulfides. On the other hand, it is well known that methodologies for asymmetric epoxidation are also useful ones for asymmetric oxidation of sulfides. Many optically active metalloporphyrins have, for example, been used as catalysts for asymmetric epoxidation and for asymmetric oxidation of sulfides.[2] Recently optically active



Scheme 1



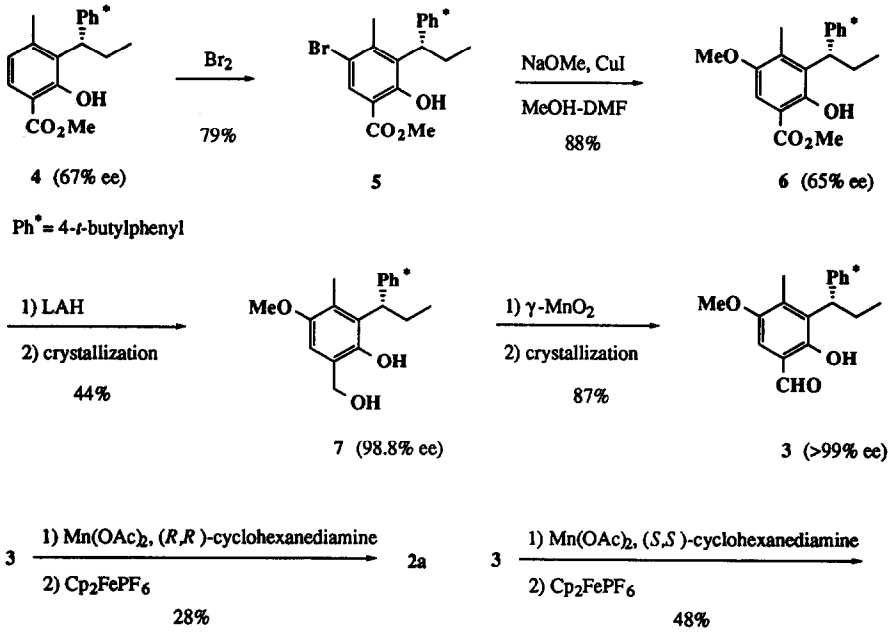
2a



2b

(salen)manganese(III) complexes have been found to be efficient catalysts for the asymmetric epoxidation of simple olefins (Scheme 1) by our[4] and Jacobsen's groups.[5] While some (salen)metal complexes have been applied to oxidation of sulfides by Fujita's and Jacobsen's groups, sufficient level of enantioselectivity has not been achieved to date.[6] We also examined oxidation of sulfides using our salen complexes as catalysts to extend the scope of salen-catalyzed asymmetric oxidation. In this paper, we describe highly enantioselective oxidation of sulfides by using our new (salen)manganese(III) complex bearing asymmetric carbons at C1", C2", C8 and C8' as a catalyst. Kinetic resolution of racemic methyl phenyl sulfoxide is also described.[7]

Synthesis of (Salen)manganese(III) Complexes



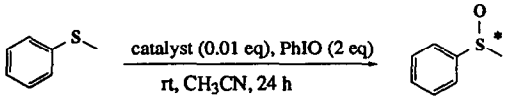
Scheme 2

For this study, we newly synthesized (salen)manganese(III) complexes (**2a** and **2b**) according to Scheme 2. Methoxy salicylaldehyde **3** requisite for the synthesis of complexes (**2a** and **2b**) was derived from salicylic acid methyl ester **4**[4c] of 67% ee which was an intermediate for the synthesis of complex **1**. Treatment of compound **4** with bromine in dichloromethane gave bromo salicylate **5** which was converted into the

corresponding methoxy derivative **6** by treatment with sodium methoxide in methanol-DMF at 110 °C (bath temperature). Compound **6** was reduced by lithium aluminum hydride to give alcohol **7** which was further enantiomerically enriched by crystallization from hexane. Although the resulting crystals showed the lowered optical purity, the component in the filtrate showed highly improved optical purity. The alcohol **7** of 98.8% ee thus obtained was treated with manganese dioxide to give aldehyde **3**. Optically pure **3** was obtained again from the filtrate upon its crystallization from hexane. Compound **3** was converted into (salen)manganese(III) complexes (**2a** and **2b**) according to the reported procedure.[4a)]

Asymmetric Oxidation of Sulfides

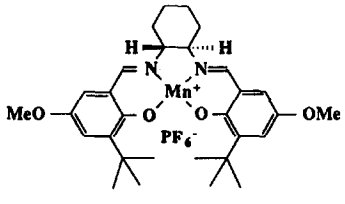
Since we had already found that (8*R*,8'*R*,1"*S*,2"*S*)-(salen)manganese(III) complexes such as **1a** showed higher asymmetric induction than diastereomeric (8*R*,8'*R*,1"*R*,2"*R*)-complexes such as **1b** in epoxidation (Scheme 1),[4)] we first examined the oxidation of methyl phenyl sulfide in the presence of various (8*R*,8'*R*,1"*S*,2"*S*)-complexes using iodosylbenzene as a terminal oxidant but all the complexes exhibited very poor asymmetric induction. For example, the epoxidation of 6-acetamido-2,2-dimethyl-7-nitrochromene with **1a** proceeded with 96% ee but the oxidation of methyl phenyl sulfide with the same catalyst showed only 3% ee (Scheme 3). However, the chemical yield of the desired sulfoxide was good (67%) and the undesired sulfone was a minor product (30%). Although Jacobsen recommended to use hydrogen peroxide as a terminal



1a: 67%, 3% ee
2a: 75%, 29% ee
1b: 54%, 20% ee
2b: 57%, 62% ee

Scheme 3

oxidant to prevent overoxidation to sulfone in the oxidation of sulfides using **8** as a catalyst,[6c)] it was not a good terminal oxidant for our system. Use of hydrogen peroxide led to a considerably lower chemical yield as compared with iodosylbenzene in all cases (cf. Table 1, entries 1 and 2). The origin of these differences between their and our reaction systems is unclear.



8

Recently Fujita et al. reported that (salen)vanadium complexes having an electron-donating group in its salicylaldehyde part showed better asymmetric induction than the corresponding salen complex having no such group.[6a,8)] According to this paper, we examined the oxidation using the salen complex **2a** having methoxy group at C5 and C5', as a catalyst. However, asymmetric induction by **2a** was only moderate (29% ee, Scheme 3). After many trials for years, we incidentally found that the diastereomeric (8*R*,8'*R*,1"*R*,2"*R*)-**1b** showed

much higher asymmetric induction than **1a**, though insufficient level (Scheme 3). With this result in hand, we further examined the oxidation using complex **2b** which is diastereomeric to **2a** and found that **2b** showed the remarkably enhanced asymmetric induction (62% ee) and that the ratio of sulfoxide to sulfone was also improved to 7.1:1. Since we had found that addition of donor ligand such as pyridine *N*-oxide to salen-catalyzed epoxidation system improved its enantioselectivity,[4a] we also examined oxidation of methyl phenyl sulfide in the presence of various donor ligands. However, all the ligands examined showed the negative effect on enantioselectivity, though the ratio of sulfoxide to sulfone was further improved to 47:1 when pyridine *N*-oxide was used. To explore the temperature effect on enantioselectivity, the reaction at -20 °C was next examined and slightly improved enantioselectivity (63% ee) was observed. The reaction at -20 °C also suppressed the formation of undesired sulfone (cf. Table 1, entries 1 and 3). Accordingly, oxidation of various other sulfides was examined at -20 °C. Sulfides bearing an electron-withdrawing group such as bromo or nitro group in its aryl group showed higher enantioselectivity (entries 4-7) than the sulfide bearing an electron-donating group (entry 8), suggesting that the reaction proceeded via formation of charge transfer complex.[9] Oxidation of methyl *o*-nitrophenyl sulfide exhibited the highest enantioselectivity of 90% ee. We further examined the oxidation of ethyl *o*-nitrophenyl sulfide. In contrast to methyl aryl sulfides, however, the reaction was slow and enantioselectivity was poor (entry 9).

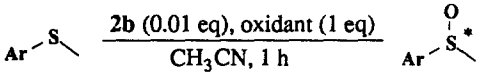


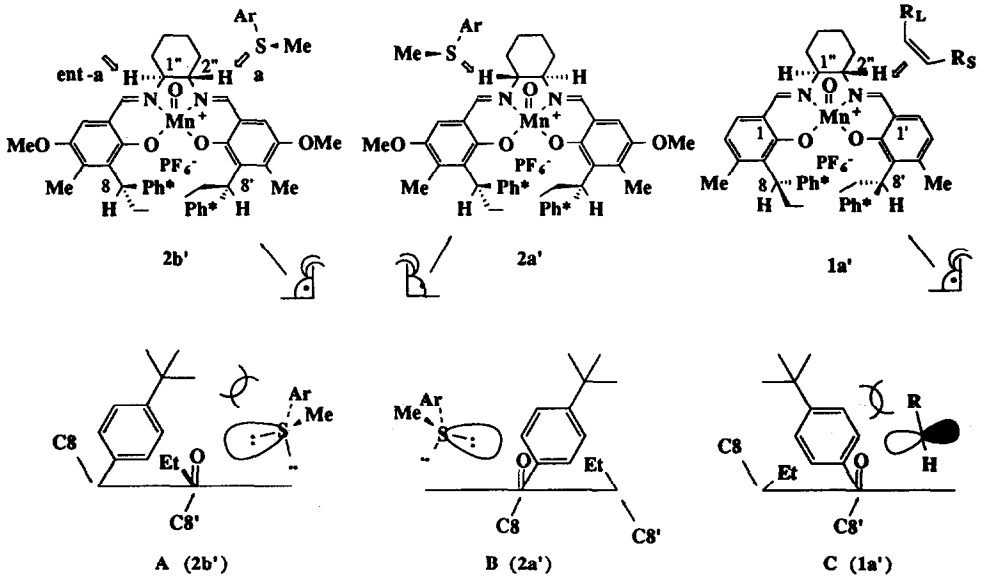
Table 1. Asymmetric oxidation of sulfides with (salen)manganese(III) complex as a catalyst

Entry	Ar	R	Oxidant	Temp.	Yield (%)[a]		% ee	Abs. Confign.
1	Ph	Me	PhIO	r.t.	57[b]	(8)	62[c]	R[d]
2	Ph	Me	H_2O_2	r.t.	9	(-)[e]	50[c]	R[d]
3	Ph	Me	PhIO	-20 °C	76	(-)[e]	63[c]	R[d]
4	*o*-NO_2Ph	Me	PhIO	-20 °C	51	(-)[e]	90[f]	-
5	*p*-NO_2Ph	Me	PhIO	-20 °C	67	(5)	86[g]	-
6	*o*-BrPh	Me	PhIO	-20 °C	74	(-)[e]	88[h]	-
7	*p*-BrPh	Me	PhIO	-20 °C	63	(2)	75[h]	-
8	*p*-MeOPh	Me	PhIO	-20 °C	45	(4)	40[f]	-
9	*o*-NO_2Ph	Et	PhIO	-20 °C	21	(-)[e]	8.5[g]	-

a) Isolated yield. The number in parentheses is the yield of the corresponding sulfone.
b) Two equivalents of iodosylbenzene was used.
c) Determined by HPLC analysis (Daicel Chiralcel OD, hexane-*i*-PrOH 9:1).
d) Determined by comparison of optical rotation with reported value (reference 5b).
e) Formation of sulfone was not detected by TLC analysis.
f) Determined by HPLC analysis (Daicel Chiralcel OD, hexane-*i*-PrOH 30:1).
g) Determined by ^{1}H NMR (400 MHz) analysis using (*R*)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol as a shift reagent.
h) Determined by ^{1}H NMR (400 MHz) analysis using (*R*)-(+)-2,2'-dihydroxy-1,1'-binaphthyl as a shift reagent.

Recently we proposed that olefins approach the metal-oxo bond along the pathway a in salen-catalyzed epoxidation reaction (Fig. 1).[10] This proposal also leads to a reasonable explanation about the difference in stereochemistry of the epoxidation of simple olefins and of the oxidation of sulfides. In the case of the

epoxidation with **1a**, C8'-*t*-butylphenyl group interacts with the substituent of the oncoming olefin so that **1a** can discriminate olefin's enantioface efficiently (Fig. 1, C). In the case of sulfide oxidation with **2a**, however, C8-*t*-butylphenyl group can not interact with the oncoming sulfide, because the sulfur atom takes sp^3 configuration and, therefore, substituents of the sulfide stay behind the sulfur atom. Accordingly, high enantioselectivity was not realized in the oxidation of sulfide with **2a** as a catalyst (**B**). On the other hand, C8-*t*-butylphenyl group in **2b** protrudes toward the oncoming sulfide and interacts with the sulfide's substituent (**A**).[11] This model correctly predicts the stereochemistry of methyl phenyl sulfoxide obtained with **2b** to be *R*.



The views of oxo species (**1a'**, **2a'**, and **2b'**) derived from **1a**, **2a** and **2b**, from C3' or C3 substituent side

Fig. 1

Kinetic Resolution of Racemic Methyl Phenyl Sulfoxide

As mentioned at the beginning of this paper, Uemura et al. reported that asymmetric oxidation of sulfides using titanium-binaphthol complex as a catalyst was accompanied by the oxidation of the resulting sulfoxides to sulfones, in which process further enhancement of the optical purity of the sulfoxide was caused by the enantiomer-differentiating oxidation (kinetic resolution) of the sulfoxide.[3b] We also observed that the oxidation of methyl phenyl sulfide using **2b** as a catalyst at room temperature gave a considerable amount of sulfone (Table 1, entry 1). Accordingly we examined the oxidation of racemic methyl phenyl sulfoxide with **2b** as a catalyst at 0 °C. As expected, the optical purity of the sulfoxide increased as it was consumed (Fig. 2), but the efficiency of the kinetic resolution was poor. The relative rate of oxidation of enantiomers was determined to be only ca. 2 by using Kagan's equation.[12] Accordingly it is not expected in our system that a combination of asymmetric oxidation and kinetic resolution gives the sulfoxide of high optical purity without consuming a bulk of the sulfoxide, though asymmetric oxidation and kinetic resolution show the same sense of enantioselectivity.

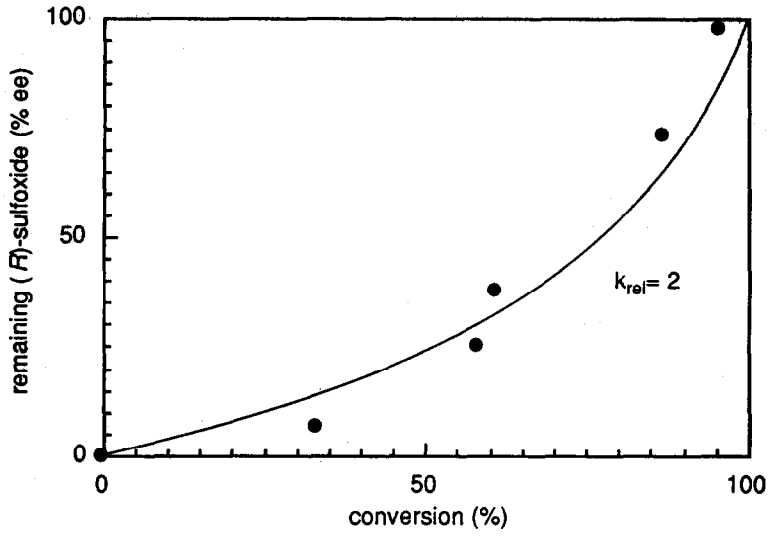


Fig. 2 Kinetic resolution of racemic methyl phenyl sulfoxide

Experimental

NMR spectra were recorded in $CDCl_3$ at 400 MHz on a JEOL GX-400 instrument, unless otherwise mentioned. All signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ-value). IR spectra were obtained with a JASCO IR-700 instrument. Optical rotation was measured with a JASCO DIP-360 automatic digital polarimeter. Column chromatography was conducted on Silica Gel 60, 70-230 mesh ASTM, available from E. Merck. Preparative thin layer chromatography was performed on 0.5 mm x 20 cm x 20 cm E. Merck silica gel plate (60 F-254). Solvents were dried and distilled shortly before use. Reactions were carried out under an atmosphere of nitrogen if necessary.

Methyl (*S*)-3-[1-(4-*t*-butylphenyl)propyl]-4-methylsalicylate (4). When (*dl*)-3-[1-(4-*t*-butylphenyl)-propyl]-4-methylsalicylic acid was treated with (-)-brucine•$2H_2O$ in acetone, (*R*)-acid made a crystalline salt with the base.[4c] Concentration of the filtrate after collecting (*R*)-salt gave the salt enriched in (*S*)-isomer. This concentrate was used for this study. The concentrate was treated with 1N HCl and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The resulting acid was refluxed for 17 h in trimethyl orthoformate. After cooled to room temperature, the mixture was concentrated *in vacuo* and chromatographed on silica gel (hexane-ethyl acetate = 40:1) to give **4** (64%) as an oil. The optical purity of **4** was determined to be 68% ee by HPLC analysis using Daicel Chiralcel OD (hexane). **4**; IR (KBr): 3088, 2956, 2862, 1670, 1665, 1607, 1450, 1355, 1318, 1292, 1237, 1195, 1151, 944, 779 cm^{-1}. ^1H NMR (400 MHz): 11.12 (s, 1H), 7.61 (d, J = 8.30 Hz, 1H), 7.29-7.21 (m, 4H), 6.67 (d, J = 8.30 Hz, 1H), 4.40 (br s, 1H), 3.90 (s, 3H), 2.31-2.23 (m, 5H), 1.28 (s, 9H), 0.88 (t, J = 7.33 Hz, 3H). Calcd. for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29%. Found: C, 77.63; H, 8.31%.

Methyl (*S*)-5-bromo-3-[1-(4-*t*-butylphenyl)propyl]-4-methylsalicylate (5). Bromine (0.38 ml, 7.38 mmol) was added to a solution of compound **4** (2.24 g, 6.58 mmol) in dichloromethane (16 ml). After stirring for 160 min at room temperature, the mixture was washed with aqueous $Na_2S_2O_3$. The aqueous layer was extracted with ether. The combined organic layers were successively washed with water, saturated aqueous ammonium chloride, and brine, and dried over anhydrous $MgSO_4$. The solution was concentrated under reduced pressure and submitted to silica gel column chromatography (hexane-ethyl acetate = 16:1) to give **5** (2.17 g, 79%) as crystals. **5**; m.p. 64.5-65.5 °C. IR (KBr): 2952, 1668, 1600, 1440, 1341, 1263, 1224, 1194, 1157, 992, 791 cm^{-1}. ^1H NMR (400 MHz): 11.07 (s, 1H), 7.96 (s, 1H), 7.27-7.16 (m, 4H), 4.61 (br s, 1H), 3.93 (s, 3H), 2.29 (m, 5H), 1.29 (s, 9H), 0.88 (t, J = 7.36 Hz, 3H). Calcd. for $C_{22}H_{27}BrO_3$: C, 63.01; H, 6.49%. Found: C, 63.13; H, 6.63%.

Methyl (*S*)-5-methoxy-4-methyl-3-[1-(4-*t*-butylphenyl)propyl]salicylate (6). To a suspension of copper(I) iodide (1.91 g, 10.0 mmol) and **5** (2.17 g, 5.03 mmol) in *N,N*-dimethylformamide (9 ml) was added a solution of sodium methoxide (1.81 g, 33.5 mmol) in methanol (11 ml) dropwise and the whole mixture was stirred for 3 h at 110 °C (bath temperature). The mixture was allowed to cool to room temperature, diluted with ether (50 ml) and saturated aqueous ammonium chloride (50 ml), and stirred for 30 min at room temperature. The mixture was filtered and the aqueous layer was separated. The organic layer was washed with aqueous sodium hydrogen carbonate and brine, and concentrated *in vacuo*. Silica gel chromatography (hexane-ethyl acetate = 30:1) gave **6** (1.70 g, 88%) as an oil. The optical purity of **6** was determined to be 65% ee by HPLC analysis using Daicel Chiralcel OD (hexane-2-propanol = 400:1). **6**; IR (KBr): 3447, 3153, 2963, 2872, 1670, 1616, 1508, 1458, 1360, 1339, 1269, 1232, 1200, 1173, 1134, 1121, 1078, 1018, 793, 762 cm^{-1}. ^1H NMR (400 MHz): 10.82 (s, 1H), 7.26-7.19 (m, 4H), 7.14 (s, 1H), 4.52 (br s, 1H), 3.91 (s, 3H), 3.78 (s, 3H), 2.33-2.18 (m, 5H), 1.28 (s, 9H), 0.87 (t, J = 7.44 Hz, 3H). Calcd. for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16%. Found : C, 74.54; H, 8.15%.

(*S*)-3-[1-(4-*t*-Butylphenyl)propyl]-2-hydroxy-5-methoxy-4-methylbenzylalcohol (7). Lithium aluminum hydride (300 mg, 7.9 mmol) was added to a solution of **6** (2.67 g, 7.21 mmol) in tetrahydrofuran (25 ml) and stirred for 24 h at room temperature. The mixture was quenched with 1N HCl (20 ml) and extracted with ether. The ethereal solution was washed with brine, concentrated, and chromatographed on silica gel (hexane-ethyl acetate = 9:1~4:1) to give the crystalline **7** (2.33 g, 94%), which was recrystallized from hexane. The optical purity of the precipitated crystals (1.24 g) was 51% ee but that of the crystals (1.10 g) obtained by concentration of the filtrate was 98.8% ee. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OF (hexane-2-propanol = 100:1). The crystals of 51% ee was recrystallized again and concentration of the filtrate gavè another **7** (0.49 g) of 98.8% ee. **7**; $[\alpha]_D^{21}$ -88.6° (c 1.20, $CHCl_3$). m.p. 99.5-100.5 °C. IR (KBr): 3526, 3334, 2952, 1606, 1454, 1371, 1304, 1246, 1129, 1080, 830, 559 cm^{-1}. ^1H NMR (400 MHz): 7.30 (ABq, J_{AB} = 9.27 Hz, 4H), 6.56 (s, 1H), 4.68 (d, J = 4.88 Hz, 2H), 4.42 (br s, 1H), 3.76 (s, 3H), 2.34-2.14 (m, 5H), 1.29 (s, 9H), 0.93 (t, J = 7.32 Hz, 3H). Calcd. for $C_{22}H_{30}O_3$: C, 77.16; H, 8.83%. Found: C, 77.16; H, 8.87%.

(*S*)-3-[1-(4-*t*-Butylphenyl)propyl]-5-methoxy-4-methylsalicylaldehyde (3). To a suspension of γ-MnO_2 (4.00 g, 46 mmol) in ether (20 ml) was added alcohol **7** (1.41 g, 4.12 mmol) and the mixture was stirred

for 19 h at room temperature. The mixture was filtered, concentrated in vacuo, and chromatographed on silica gel to give **3** (1.23 g, 88%). The resulting **3** was crystallized from hexane. After filtration, the filtrate was concentrated to give **8** of >99.5% ee (226 mg). The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OF (hexane-2-propanol = 100:1). **8**; $[\alpha]_D^{21}$ -16.9° (c 0.80, $CHCl_3$). m.p. 113.5-114 °C. IR (neat): 2950, 1636, 1448, 1321, 1119, 831, 763 cm^{-1}. ^1H NMR (400 MHz): 11.25 (s, 1H), 9,79 (s, 1H), 7.27-7.19 (m, 4H), 6.81 (s, 1H), 4.52 (br s, 1H), 3.82 (s, 3H), 2.30-2.21 (m, 5H), 1.28 (s, 9H), 0.88 (t, J = 7.57 Hz, 3H). Calcd. for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29%. Found: C, 77.51; H, 8.32%.

(Salen)manganese(III) complex (2b) A solution of (1*S*,2*S*)-cyclohexanediamine (5.5 mg, 48 μmol) in ethanol (1 ml) was added to a solution of aldehyde **8** (30.0 mg, 87.9 μmol) in ethanol (3 ml) and stirred for 8 h at room temperature. The mixture was concentrated to dryness *in vacuo* and diluted with deairated acetonitrile (8 ml). This solution was transferred by canula into the flask containing $Mn(OAc)_2 \cdot 4H_2O$ (10.8 mg, 44.1 μmol) and the resulting mixture was stirred for 3 h at room temperature. To this mixture was added a solution of ferricenium hexafluorophosphate (14.5 mg, 43.8 μmol) in deairated acetonitrile (2 ml) dropwise. The mixture was concentrated to dryness and washed with hexane to remove the side product, ferrocene. The residue was purified on silica gel column chromatography (dichloromethane-methanol = 10:1) to give **2b** (20.3 mg, 48%) as a solid. **2b**; IR (KBr): 2956, 2350, 2314, 1607, 1552, 1515, 1502, 1452, 1332, 843, 665, 557 cm^{-1}. Calcd. for $C_{50}H_{64}N_2O_4MnPF_6 \cdot 0.5CH_3CN$ (**2b**$\cdot 0.5CH_3CN$): C, 62.67; H, 6.75; N, 3.58%. Found: C, 62.62; H, 7.05; N, 3.40%.

(Salen)manganese(III) complex (2a) Salen complex **2a** was synthesized from **8** and (1*R*,2*R*)-cyclohexanediamine according to the same procedure as described above. **2a**; IR (KBr): 2961, 2868, 2368, 2345, 1616, 1522, 1458, 1339, 1138, 847, 559 cm^{-1}. Calcd. for $C_{50}H_{64}N_2O_4MnPF_6$: C, 62.76; H, 6.74; N, 2.93%. Found: C, 62.85; H, 6.96; N, 3.02%.

General procedure for asymmetric oxidation Methyl *o*-nitrophenyl sulfide (16.9 mg, 0.1 mmol) was added to a solution of **2b** (1.0 mg, 1 μmol) in acetonitrile (1 ml) and the mixture was cooled to -20 °C. To this solution was added iodosylbenzene (22.0 mg, 0.1 mmol) at the same temperature and the whole mixture was stirred for 1 h, then allowed to warm to room temperature, and filtrated through a pad of Celite. No sulfone formation was detected by TLC analysis of the filtrate. The filtrate was concentrated and purified by thin layer chromatography on silica gel (hexane-ethyl acetate = 1:1) to give methyl *o*-nitrophenyl sulfoxide (8.7 mg, 51%). The enantiomeric excess of the sulfoxide was determined to be 90% by HPLC analysis Daicel Chiralcel OD (hexane-*i*-PrOH = 30:1).

***(R)*-Methyl phenyl sulfoxide**; $[\alpha]_D^{21}$ +130.3° (c 0.49, $CHCl_3$). IR (neat): 3458, 1645, 1471, 1439, 1410, 1085, 1042, 953, 744, 687, 497 cm^{-1}. ^1H NMR (400 MHz): 7.67-7.64 (m, 2H), 7.56-7.49 (m, 3H), 2.73 (s, 3H).

Methyl *o*-nitrophenyl sulfoxide; $[\alpha]_D^{21}$ +116.5° (c 0.57, $CHCl_3$). IR (KBr): 3078, 3000, 1587, 1511, 1450, 1415, 1342, 1102, 1058, 1027, 968, 847, 784, 733, 675, 507 cm^{-1}. ^1H NMR (400 MHz, benzene-d_6):

8.21 (dd, J = 1.47 and 7.82 Hz, 1H), 7.57 (dd, J = 1.47 and 7.81 Hz, 1H), 6.95 (t, J = 7.57 Hz. 1H), 6.59 (t, J = 8.30 Hz. 1H), 2.19 (s, 3H).

Methyl *p*-nitrophenyl sulfoxide; $[\alpha]_D^{21}$ +135.9° (c 0.74, $CHCl_3$). IR (KBr): 3086, 2992, 2906, 1641, 1580, 1504, 1418, 1330, 1113, 1089, 964, 849, 828, 735, 676, 524, 464 cm^{-1}. ^1H NMR (400 MHz, benzene-d_6): 8.03 (dd, J = 1.46 and 7.81 Hz, 1H), 6.99 (dd, J = 0.98 and 7.81 Hz, 1H), 6.93 (t, J = 7.81 Hz, 1H), 6.60 (t, J = 7.81 Hz, 1H), 2.18 (s, 3H).

***o*-Bromophenyl methyl sulfoxide**; $[\alpha]_D^{21}$ +241.9° (c 0.48, $CHCl_3$). IR (neat): 3500, 2914, 1561, 1447, 1374, 1288, 1091, 1059, 1013, 955, 754, 713, 482, 440 cm^{-1}. ^1H NMR (400 MHz): 7.95 (dd, J = 1.71 and 7.57 Hz, 1H), 7.60-7.55 (m, 2H), 7.37 (dt, J = 1.30 and 7.57 Hz, 1H), 2.82 (s, 3H).

***p*-Bromophenyl methyl sulfoxide**; $[\alpha]_D^{21}$ +101.9° (c 0.73, $CHCl_3$). IR (KBr): 2982, 2904, 1567, 1467, 1416, 1381, 1303, 1170, 1081, 1065, 1040, 1003, 959, 942, 815, 718, 680, 512, 481 cm^{-1}. ^1H NMR (400 MHz, benzene-d_6): 7.09 (d, J =8.79 Hz, 2H), 6.96 (d, J =8.79 Hz, 2H), 1.89 (s, 3H).

***p*-Methoxyphenyl methyl sulfoxide**; $[\alpha]_D^{21}$ +66.7° (c 0.39, $CHCl_3$). IR (neat): 3458, 2996, 2832, 1589, 1491, 1299, 1249, 1175, 1086, 1025, 953, 829, 526 cm^{-1}. ^1H NMR (400 MHz): 7.60 (d, J = 9.28 Hz, 2H), 7.04 (d, J = 8.79 Hz, 2H), 3.86 (s, 3H), 2.70 (s, 3H).

Ethyl *o*-nitrophenyl sulfoxide; $[\alpha]_D^{24}$ +33.8° (c 0.15, $CHCl_3$). IR (KBr): 3596, 3090, 1513, 1448, 1341, 1304, 1103, 1061, 1016, 849, 790, 738, 675, 514 cm^{-1}. ^1H NMR (400 MHz): 8.34 (dd, J = 0.98 and 8.30 Hz, 1H), 8.29 (dd, J = 1.47 and 7.82 Hz, 1H), 7.96 (dt, J = 0.98 and 7.57 Hz, 1H), 7.71 (dt, J = 1.46 and 7.80 Hz, 1H), 3.31-3.22 (m, 1H), 2.89-2.80 (m, 1H), 1.34 (t, J = 7.33 Hz, 3H).

To get more information on the mechanism of salen-catalyzed oxidation of sulfides, further study is continuing in our laboratory.

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References and Notes

†) Present address: K. Noda; Mitsubishi Kasei Co. Ltd., 1 Toho-cho, Yokkaichi, Mie 510, Japan. N. Hosoya; Kao Co. Ltd., 20 Higashifukashiba, Kamisu-cho, Kashima-gun, Ibaraki 314-02, Japan.

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