# Enantioselective Aerobic Oxidation of Sulfides Catalyzed by Optically Active β-Oxo Aldiminatomanganese(III) Complexes

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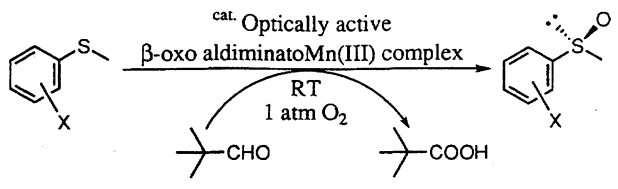
Enantioselective aerobic oxidation of sulfides into optically active sulfoxides was achieved by using pivalaldehyde in the presence of a catalytic amount of optically active β-oxo aldiminatomanganese(III) complexes. An acylperoxomanganese complex, formed from the original manganese complex, molecular oxygen, and pivalaldehyde, was supposed to be a key intermediate in the present oxidation. The crystal structure of chloro-{*N*,*N*′-bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-(1*S*,2*S*)-1,2-diphenylethylenediaminato}manganese(III) was determined by X-ray diffraction methods, which suggested that the bulkiness of the substituents in β-oxo aldimine ligand had played an important role in controlling the approach of sulfides to the manganese complex. Kinetic resolution took place during the subsequent oxidation process of sulfoxide into the corresponding sulfone, and the optical purity of the remaining sulfoxide increased.

As optically active sulfoxide is one of the most reliable building blocks to construct new chiral centers in organic compounds,[1] much effort has been made to develop efficient methods for the preparation of optically active sulfoxides.[2] Andersen's method[3] of diastereoselective recrystalization, for example, is a typical procedure to prepare optically active tolyl sulfoxide and has been widely applied to organic synthesis.[4] In order to obtain various kinds of optically active sulfoxides, direct enantioselective oxidations of the corresponding sulfides attracted much attention in the last decade as titanium/diethyl tartrate/water/hydroperoxide system[5] or stoichiometric amount of chiral *N*-sulfonyloxaziridine[6] afforded optically active sulfoxides in good-to-excellent enantioselection. Optically active porphyrinatoiron(III) complexes[7] or (salen)manganese(III) complexes[8] were reported to be effective catalysts for enantioselective oxidation of sulfides with terminal oxidant such as iodosylbenzene or hydrogen peroxide, etc.[9] However, few examples are known as yet to utilize molecular oxygen as an oxidant in asymmetric oxidation of sulfides.[10]

Recently, it was reported that β-oxo aldiminatomanganese(III) complexes were successfully employed as effective catalysts in aerobic enantioselective epoxidation of unfunctionalized olefins in coexistence of aldehyde.[11] These complexes were prepared from the corresponding β-diketone, and their steric and electronic characters could be controlled by designing the β-oxo aldimine ligand which contributed to improve optical yields of epoxides. The above aerobic enantioselective reaction was applied to oxidation of sulfides into optically active sulfoxides.[12] In this report, we would like to disclose detailed results of the aerobic enantioselective oxidation of sulfides catalyzed by optically active β-oxo aldiminatomanganese(III) complexes (Scheme 1).

## Results and Discussion

**Effect of Aldehydes on Aerobic and Enantioselective Oxidation of Aryl Methyl Sulfide.** Since an aldehyde is an essential reagent in the present aerobic oxidation, various aldehydes were screened in the enantioselective oxidation of sulfide catalyzed by manganese(III) complex **A** (Fig. 1) by taking 2-bromophenyl methyl sulfide (**1a**) as a model compound. When pivalaldehyde was used together with molecular oxygen, asymmetric oxidation of sulfide **1a** proceeded to afford the corresponding optically active sulfoxide **2a** in 73% yield whose optical yield was determined by HPLC analysis to be 52% ee (Entry 1 in Table 1). In cases of




Scheme 1.

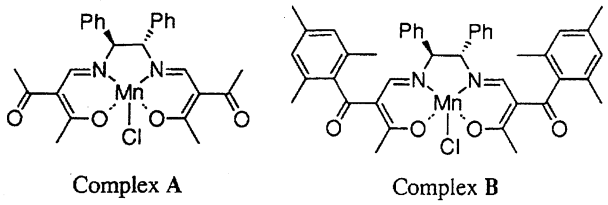
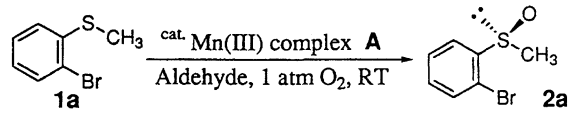
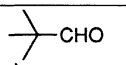
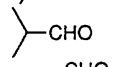
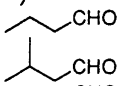
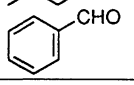



Fig. 1. Optically active β-oxo aldiminatomanganese-(III) complexes.

Table 1. Effect of Aldehydes on Optical Yield of Sulfoxide




| Entry[a] | Aldehyde | Yield/% | Optical yield/%ee[b] |
|---|---|---|---|
| 1 |  | 73 | 52 |
| 2 |  | 39 | 46 |
| 3 |  | 38 | 42 |
| 4 |  | 23 | 44 |
| 5 |  | Trace | — |

a) Reaction conditions; sulfide **1a** 0.25 mmol, aldehyde 0.75 mmol, Mn(III) complex **A** 0.03 mmol in toluene 2 ml, RT, 1 atm $O_2$. b) Determined by HPLC analysis (Daicel Chiralcel OB).

using isobutyraldehyde, butyraldehyde and isovaleraldehyde, both chemical and optical yields of the sulfoxide were lower than 39% and 46% ee, respectively (Entries 2, 3, and 4). It is noted that the above yields were improved by using an aldehyde with a bulky alkyl group such as *t*-butyl group. Benzaldehyde was not effective in the present oxidation (Entry 5). This tendency was also observed in the aerobic enantioselective epoxidation of unfunctionalized olefins catalyzed by β-oxo aldiminatomanganese(III) complexes[11c] and (salen)manganese(III) complexes.[13] The observed correlation between structure of aldehyde and enantioselection indicates that the aldehyde participated in the improvement of optical yields. Therefore, the key intermediate in the oxidation of sulfide would be an acylperoxomanganese complex[14] (Fig. 2) which was similar to that proposed in the aerobic and enantioselective epoxidation.[11c]

**Absolute Configuration of Sulfoxide.** In the present oxidation catalyzed by optically active β-oxo aldiminatomanganese(III) complex, (*S*)-sulfoxides were

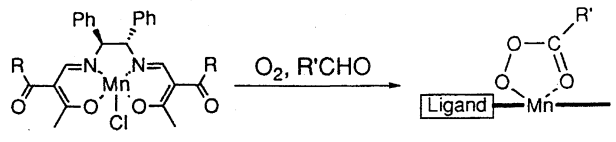



Fig. 2. Formation of acylperoxomanganese complex.

afforded from sulfides corresponding to (*S*,*S*)-complex catalyst. The enantiofacial selection was explained as follows: Sulfur atom, conjugated with aryl group, was attacked from the top face by the above-mentioned intermediate as depicted in Fig. 3. In cases of enantioselective epoxidation of olefins, (1*R*,2*S*)-epoxides were obtained by using the same (*S*,*S*)-complex catalyst. The enantioselection in the epoxidation indicated that the oxidant approached from the top face to the olefin conjugated with aryl group (Fig. 3). These observations concerning the enantiofacial selection suggested that the oxidation would proceed via the identical reactive intermediates, acylperoxomanganese complexes, in the oxidations of both sulfide and olefin.[15]

**Influence of Substituent in β-Oxo Aldimine Ligand on Optical Yield of Sulfoxide.** Optically active β-oxo aldiminatomanganese(III) complexes were prepared by the method reported in our previous paper,[11c] and the effect of the substituents (**R** in Table 2) in the β-oxo aldimine ligand on optical yield of sulfoxide **2a** was examined. When β-oxo aldiminatomanganese(III) complex **A** (**R**=methyl) was employed as the catalyst, sulfide **1a** was converted into the corresponding sulfoxide in 52% ee (Entry 1). When manganese(III) complex catalysts with bulkier substituents such as ethoxy, cyclopentyloxy, and isobornyloxy were used, the optical yields of the sulfoxide increased to 60% ee over (Entries 2, 3, and 4). In case of using complex **B** (**R**=mesityl) as the catalyst, optically active sulfoxide **2a** was afforded in 66% ee (Entry 5). Similar results were obtained in the aerobic epoxidation of 1,2-dihydronaphthalene (**4**): The manganese(III) complex **B** containing mesityl group was an effective catalyst for the enantioselective olefin-epoxidation.[11c]

**Crystal Structure of Optically Active β-Oxo Aldiminatomanganese(III) Complex.** The crystal structure of manganese(III) complex **B** containing bulky substituents (mesityl groups) was determined by X-ray diffraction methods, and a view of the molecule is shown in Fig. 4. The complex has a nearly square planar geometry with two oxygen atoms and two nitrogen atoms coordinating to manganese(III) ion. Similar to the case of chloro-{*N*,*N*′-bis[2-(cyclopentyloxycarbonyl)-3-oxobutylidene]-1,2-diphenylethylenediaminato}manganese-(III) (**D**),[11b] it was shown there that the bulky sub-

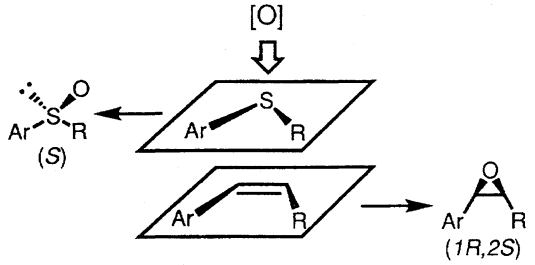
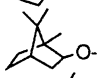



Fig. 3. Enantiofacial selection in oxidation catalyzed by (*S*,*S*)-β-oxo aldiminatomanganese(III) complex.

Table 2. Asymmetric Oxidation of Sulfide **1a** and Olefin **4** Catalyzed by Various Optically Active $\beta$-Oxo Aldiminatomanganese(III) Complexes

| Entry | R | | Sulfide[a] **1a** Optical yield/%ee[c] (Yield/%ee[e]) | Olefin[b] **4** Optical yield/%ee[d] |
|---|---|---|---|---|
| 1 | Me- | **A** | 52 (73) | 45 |
| 2 | EtO- | **C** | 60 (95) | 36 |
| 3 |  | **D** | 60 (88) | 37 |
| 4 |  | **E** | 62 (94) | 52 |
| 5 |  | **B** | 66 (91) | 60 |

a) Reaction conditions; methyl 2-bromophenyl sulfide (**1a**) 0.25 mmol, Mn(III) complex 0.03 mmol, pivalaldehyde 0.75 mmol, toluene 2.0 ml, RT, 1 atm $O_2$. b) Reaction conditions; 1,2-dihydronaphthalene (**4**) 0.8 mmol, Mn(III) complex 0.104 mmol, pivalaldehyde 2.8 mmol, benzene 2.0 ml, RT, 1 atm $O_2$. See Ref. 10c. c) Determined by HPLC analysis (Chiralcel OB). d) Determined by GC analysis (Chiraldex B-DA). e) Isolated yield.

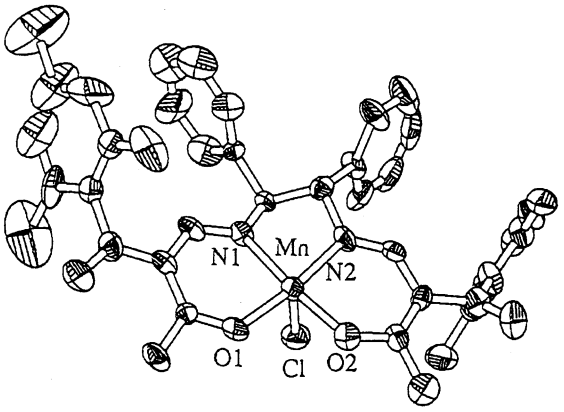
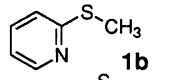
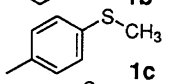
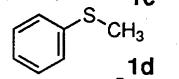
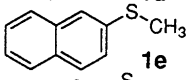
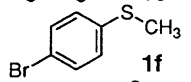
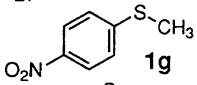
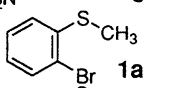
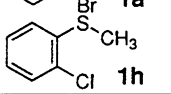



Fig. 4. Crystal structure of chloro-{*N*,*N*′-bis-[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-(1*S*,2*S*)-1,2-diphenylethylenediaminato}manganese(III) (**B**) (ORTEP View); selected bond lengths (Å) and bond angles (°) are as follows: Mn–Cl, 2.603(6); Mn–O(1), 1.897(11); Mn–O(2), 1.904(11); Mn–N(1), 1.980(12); Mn–N(2), 1.963(13); Cl–Mn–O(1), 97.6(4); Cl–Mn–O(2), 90.2(4); Cl–Mn–N(1), 90.7(5); Cl–Mn–N(2), 85.0(5); O(1)–Mn–N(2), 172.8(6); O(2)–Mn–N(1), 174.5(6); O(1)–Mn–O(2), 94.6(5); O(1)–Mn–N(1), 90.7(5); O(2)–Mn–N(2), 92.0(6); N(1)–Mn–N(2), 82.6(6).

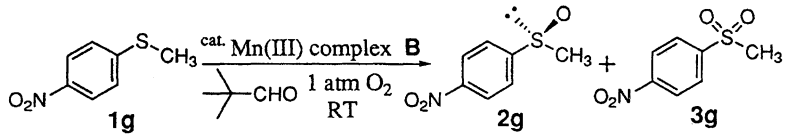
stituents on $\beta$-oxo aldimine ligand (mesityl groups in complex **B**) was oriented in the neighborhood of phenyl group in chiral diphenylethylenediamine and they occupied large space symmetrically around the central metal. It was confirmed by the molecular view that the distance between bulky substituent in ligand and reaction site, manganese atom, would be shortened by one bond length compared to that of ester type catalyst **D**. Consequently, the reaction site around manganese(III) ion was sterically hindered and a possible direction of approach to the catalyst of sulfide and/or olefin would be appropriately controlled by groups of mesityl in $\beta$-oxo aldimine and phenyl in chiral diamine to achieve

Table 3. Examples of Aerobic Asymmetric Oxidation of Sulfides

| Entry[a] | Sulfide | Yield/% | Optical yield/%ee |
|---|---|---|---|
| 1[b] |  **1b** | 55 | 24[e] |
| 2[b] |  **1c** | 58 | 44[f] |
| 3[b] |  **1d** | 66 | 51[f] |
| 4[b] |  **1e** | 57 | 51[e] |
| 5[b] |  **1f** | 55(30)[c] | 61[e] |
| 6 |  **1g** | 44(10)[c] | 69[e] |
| 7[b] |  **1a** | 93[d] | 70[e] |
| 8 |  **1h** | 72[d] | 72[e] |

a) Reaction conditions; sulfide 0.125 mmol, pivalaldehyde 0.375 mmol, Mn(III) complex **B** 0.0225 mmol in *m*-xylene 5 ml, RT, 1 atm $O_2$. b) Another portion of pivalaldehyde (0.375 mmol) was added during reaction. c) Sulfone was also obtained. Yields are in parentheses. d) Sulfone was not detected. e) Determined by HPLC analysis (Chiralcel OB). f) Determined by HPLC analysis (Chiralcel OD).

Table 4. Kinetic Resolution of Sulfoxides




| Entry[a)] | Amount of aldehyde /molar amounts | Yield of **2g**/% | Optical yield of **2g**/%ee[b)] | Yield of **3g**/% |
|---|---|---|---|---|
| 1[c)] | 3.0 | 44 | 69 | 10 |
| 2[d)] | 2.0+(2.0×3) | 16 | 79 | 84 |

a) Reaction conditions; sulfide **1g** 0.125 mmol, Mn(III) complex **B** 0.0225 mmol in *m*-xylene 5 ml, RT, 1 atm $O_2$. b) Determined by HPLC analysis (Chiralcel OB). c) Pivalaldehyde (0.375 mmol) was added at the start of the reaction. d) Pivalaldehyde (0.25 mmol) was added at the start of the reaction and three additional portions of 0.25 mmol each were added during the reaction.

good-to-high enantioselection in the aerobic oxidation.

**Aerobic Enantioselective Oxidation of Various Sulfides.** The present aerobic asymmetric oxidation of various sulfides showed that aromatic hydrocarbon solvents such as benzene, toluene and *o*-, *m*- or *p*-xylene were suitable on the enantiomeric excess, and that *m*-xylene was the most effective. While the optical yields of the sulfoxides derived from methyl 4-methylphenyl sulfide (**1c**) and methyl phenyl sulfide (**1d**) were lower than 51% ee (Entries 2 and 3 in Table 3), the ones derived from 4-bromophenyl methyl sulfide (**1f**) and methyl 4-nitrophenyl sulfide (**1g**) gave 61% ee and 69% ee, respectively (Entries 5 and 6). Concerning the effect of substituents attached to aromatic ring of sulfides, the electron-withdrawing groups improved the optical yield. It was observed that the enantiofacial selection for *o*-halo-substituted aryl sulfides was more preferable than for *p*-halo-substituted ones (Entries 7 and 8 vs. 5).

**Kinetic Resolution of Sulfoxide.** The formation of the corresponding sulfones was detected in the above-mentioned oxidation of 4-bromophenyl methyl sulfide (**1f**) and methyl 4-nitrophenyl sulfide (**1g**) (Entries 5 and 6 in Table 3) while sulfones were not obtained from 2-bromophenyl methyl sulfide (**1a**) and 2-chlorophenyl methyl sulfide (**1h**) (Entries 7 and 8). In cases of using *o*-halo-substituted aryl sulfides, it was supposed that the sulfur atom of the obtained sulfoxide would be coordinated by the halogen atom[16)] substituted in *o*-position of the aromatic ring, causing steric hindrance around the sulfur atom. Therefore, approach of the oxidant, acylperoxomanganese complex, to the sulfur atom of the sulfoxide would be prevented and further oxidation into the sulfone would be interrupted.

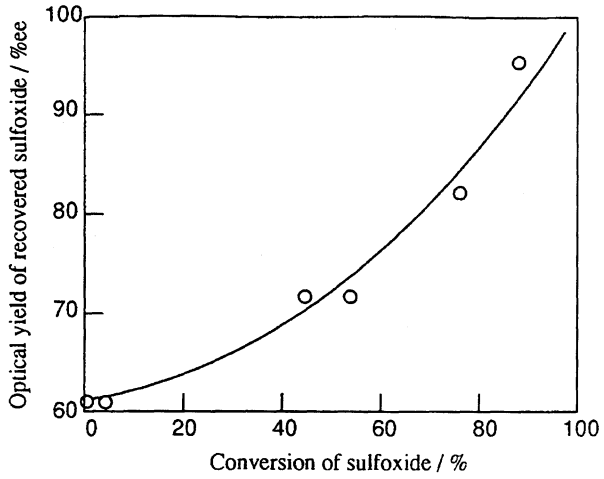



Fig. 5. Kinetic resolution of methyl 4-nitrophenyl sulfoxide.

Kinetic resolution was observed in the oxidation of sulfoxide **2** into the corresponding sulfone **3**.[17)] When three molar amounts of pivalaldehyde against sulfide were employed in the enantioselective oxidation, methyl 4-nitrophenyl sulfide (**1g**) was converted into the corresponding sulfoxide **2g** in 44% yield with 69% ee along with sulfone **3g** (10% yield) (Entry 1 in Table 4). In the case of adding two molar amounts of aldehyde each in four portions during the reaction (eight molar amounts of aldehyde was totally used, see Entry 2), chemical yield of sulfoxide **2g** decreased to 16% and the corresponding sulfone **3g** was obtained in 84% yield. It should be noted that the optical purity of sulfoxide **2g** was 79% ee in the latter case. This fact indicated that sulfide **1g** was enantioselectively oxidized into the corresponding sulfoxide **2g** in the first step and the minor enantiomer among the formed sulfoxide **2g** was further oxidized into sulfone **3g** preferably in the second step resulting in the increase of the optical purity of remaining sulfoxide **2g**.

When optically active sulfoxide **2g** with 61% ee, obtained by enantioselective oxidation of sulfide **1g**, was treated under the present reaction conditions, the increase of optical purity was observed according to the consumption of sulfoxide (Fig. 5). The optical yield of the sulfoxide, isolated at 88% conversion, was augmented up to 95% ee. Therefore, the relative rate of the oxidations of two enantiomers was estimated to be ca. 2, by the reported equation.[18)]

## 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 FX-270 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). HPLC analyses were performed on a Shimadzu LC-6A chromatograph using Chiralcel OB or Chiralcel OD column (Daicel Ltd., Co) and the peak areas were calculated on a Shimadzu chromatopack CR-4A.

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

**Sulfides:** Sulfides **1a**, **1f**, and **1g** were purchased from Aldrich Chemical Company, Inc., and **1c** and **1d** from Tokyo Kasei Kogyo Co., Ltd., respectively. Sulfide **1b**,[19] **1e**,[20] and **1h**[19] were prepared from the corresponding thiols by the literature methods, respectively.

**Preparation of Optically Active β-Oxo Aldiminatomanganese(III) Complexes:** Catalysts **A**—**E** were prepared by the reported method[11c] from the corresponding β-ketocarbonyl compounds and optically active 1,2-diphenyl-1,2-ethylenediamine.

**General Procedure for Aerobic and Enantioselective Oxidation of Sulfide into Sulfoxide (2a, Entry 7 in Table 3).** To a mixture of (*S*,*S*)-β-oxo aldiminatoMn(III) complex **B** (16.4 mg, 0.0225 mmol) in *m*-xylene (4.0 ml) was added a solution of 2-bromophenyl methyl sulfide (25.4 mg, 0.125 mmol) and pivalaldehyde (32.3 mg, 0.375 mmol) in *m*-xylene (1.0 ml). After stirred for 8 h at room temperature under an oxygen atmosphere, another portion of pivalaldehyde (32.3 mg, 0.375 mmol) in *m*-xylene (1.0 ml) was then added and the solution was stirred for another 12 h. The evaporation of solvent and purification by silica-gel column chromatography (hexane/ethyl acetate, 2/1) afforded the corresponding sulfoxide in 93% yield (25.5 mg). The enantiomeric excess was determined to be 70% ee by HPLC analysis (Daicel Chiralcel OB).

**$^1$H NMR and IR Spectra of the Sulfoxide (Table 3).**

**2-Bromophenyl Methyl Sulfoxide (2a):** $^1$H NMR ($CDCl_3$) $\delta$=2.81 (3H, s), 7.33—7.41 (1H, m), 7.55—7.62 (2H, m), 7.93—7.97 (1H, m). IR (neat) 3058, 2996, 1092, 1058, 758, 516 cm$^{-1}$. $[\alpha]_D^{30}$ −144.9° (*c* 0.18, acetone, 58%ee). Optical yield was determined by HPLC analysis (Chiralcel OB).

**Methyl 2-Pyridyl Sulfoxide (2b):** $^1$H NMR ($CDCl_3$) $\delta$=2.86 (3H, s), 7.36—7.41 (1H, m), 7.92—8.06 (2H, m), 8.62 (1H, d, *J*=3.96 Hz). IR (neat) 3048, 1086, 1037, 774, 507 cm$^{-1}$. $[\alpha]_D^{29}$ −11.4° (*c* 0.23, acetone, 24%ee). Optical yield was determined by HPLC analysis (Chiralcel OB).

**Methyl 4-Methylphenyl Sulfoxide (2c):** $^1$H NMR ($CDCl_3$) $\delta$=2.42 (3H, s), 2.70 (3H, s), 7.33 (2H, d, *J*=8.24 Hz), 7.54 (2H, d, *J*=8.24 Hz). IR (neat) 3044, 2996, 1087, 1044, 809 cm$^{-1}$. $[\alpha]_D^{33}$ −49.0° (*c* 0.34, acetone, 35%ee). Optical yield was determined by HPLC analysis (Chiralcel OD).

**Methyl Phenyl Sulfoxide (2d):** $^1$H NMR ($CDCl_3$) $\delta$=2.73 (3H, s), 7.50—7.56 (3H, m), 7.64—7.67 (2H, m). IR (neat) 3054, 2996, 1089, 1047, 750, 693 cm$^{-1}$. $[\alpha]_D^{30}$ −38.9° (*c* 0.39, acetone, 30%ee). Optical yield was determined by HPLC analysis (Chiralcel OD).

**Methyl 2-Naphthyl Sulfoxide (2e):** $^1$H NMR ($CDCl_3$) $\delta$=2.80 (3H, s), 7.56—7.62 (3H, m), 7.89—8.00 (3H, m), 8.22 (1H, s). IR (KBr) 3054, 2988, 1068, 1043, 822 cm$^{-1}$. $[\alpha]_D^{30}$ −25.9° (*c* 0.39, acetone, 32%ee). Optical yield was determined by HPLC analysis (Chiralcel OB).

**4-Bromophenyl Methyl Sulfoxide (2f):** Mp 85.2—85.6 °C; $^1$H NMR ($CDCl_3$) $\delta$=2.72 (3H, s), 7.52 (2H, d, *J*=8.57 Hz), 7.67 (2H, d, *J*=8.57 Hz). IR (KBr) 2990, 2910, 1083, 1041, 815, 512 cm$^{-1}$. $[\alpha]_D^{31}$ −47.6° (*c* 0.24, acetone, 48%ee). Optical yield was determined by HPLC analysis (Chiralcel OB).

**Methyl 4-Nitrophenyl Sulfoxide (2g):** Mp 150.4—152.6 °C; $^1$H NMR ($CDCl_3$) $\delta$=2.80 (3H, s), 7.85 (2H, d, *J*=8.57 Hz), 8.40 (2H, d, *J*=8.91 Hz). IR (KBr) 3100, 3018, 1519, 1344, 1086, 1048, 851 cm$^{-1}$. $[\alpha]_D^{30}$ −55.1° (*c* 0.37, acetone, 55%ee). Optical yield was determined by HPLC analysis (Chiralcel OB).

**2-Chlorophenyl Methyl Sulfoxide (2h);** $^1$H NMR ($CDCl_3$) $\delta$=2.83 (3H, s), 7.38—7.48 (2H, m), 7.51—7.67 (1H, m), 7.97 (1H, dd, $J_1$=1.65 Hz, $J_2$=7.91 Hz). IR (neat) 3062, 2998, 1100, 1067, 761, 730 cm$^{-1}$. $[\alpha]_D^{22}$ −189.0° (*c* 0.20, acetone, 69%ee). Optical yield was determined by HPLC analysis (Chiralcel OB).

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## References

1) G. Solladié, "Asymmetric Synthesis," ed by J. D. Morrison, Academic Press, New York (1983), Vol. 2, Part A, Chap. 6; M. Shimizu, Y. Kooriyama, and T. Fujisawa, *Chem. Lett.*, **1994**, 2419; G. Solladié and N. Huser, *Tetrahedron Lett.*, **35**, 5297 (1994).

2) For example: D. A. Evans, M. M. Faul, L. Colombo, J. J. Bisaha, J. Clardy, and D. Cherry, *J. Am. Chem. Soc.*, **114**, 5977 (1992).

3) K. K. Andersen, *Tetrahedron Lett.*, **1962**, 93.

4) D. H. Hua, S. N. Bharathi, F. Takusagawa, A. Tsujimoto, J. A. K. Panangadan, M. H. Hung, A. A. Bravo, and A. M. Erpelding, *J. Org. Chem.*, **54**, 5659 (1989); S. G. Pyne, P. Bloem, S. L. Chapman, C. E. Dixon, and R. Griffith, *J. Org. Chem.*, **55**, 1086 (1990); G. Solladié, A. Almario, and C. Dominguez, *Pure Appl. Chem.*, **10/11**, 2159 (1994).

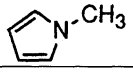
5) P. Pitchen, E. Duñach, M. N. Deshmukh, and H. B. Kagan, *J. Am. Chem. Soc.*, **106**, 8188 (1984).

6) F. A. Davis, J. P. McCauley, S. Chattopadhyay, M. E. Harakal, J. C. Towson, W. H. Watson, and I. Tavanaiepour, *J. Am. Chem. Soc.*, **109**, 3370 (1987).

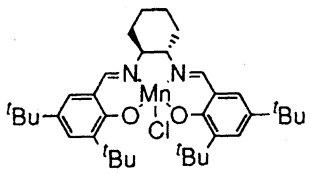
7) J. T. Groves and P. Viski, *J. Org. Chem.*, **55**, 3628 (1990); Y. Naruta, F. Tani, and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, **1990**, 1378; L.-C. Chiang, K. Konishi, T. Aida, and S. Inoue, *J. Chem. Soc., Chem. Commun.*, **1992**, 254.

8) M. Palucki, P. Hanson, and E. N. Jacobsen, *Tetrahe-*

Table 5. Reversion of Absolute Configuration of Obtained Sulfoxide by Addition of *N*-Methylimidazole

| Entry[a)] | Additive | Optical yield/%ee[b)] |
|---|---|---|
| 1 | none | 18 (−)[c)] |
| 2[d)] |  | 25 (+)[c)] |

a) Reaction conditions; 2-bromophenyl methyl sulfide 0.25 mmol, pivalaldehyde 0.75 mmol, Mn(III) complex **F** 0.03 mmol in toluene 2 ml, RT, 1 atm $O_2$. b) Determined by HPLC analysis (Chiralcel OB). c) Signs of optical rotation are in parentheses. d) 0.12 mmol of *N*-methylimidazole was added.




(Salen)Mn(III) Complex **F**

*dron Lett.*, **33**, 7111 (1992); K. Noda, N. Hosoya, K. Yanai, R. Irie, and T. Katsuki, *Tetrahedron Lett.*, **35**, 1887 (1994).

9) K. Nakajima, M. Kojima, and J. Fujita, *Chem. Lett.*, **1993**, 1483.

10) H. L. Holland, F. M. Brown, and B. G. Larsen, *Tetrahedron: Asymmetry*, **5**, 1125 (1994); C. C. R. Allen, D. R. Boyd, H. Dalton, N. D. Sharma, S. A. Haughey, R. A. S. McMordie, B. T. McMurray, G. N. Sheldrake, and K. Sproule, *J. Chem. Soc., Chem. Commum.*, **1995**, 119.

11) a) T. Mukaiyama, T. Yamada, T. Nagata, and K. Imagawa, *Chem. Lett.*, **1993**, 327; T. Nagata, K. Imagawa, T. Yamada, and T. Mukaiyama, *Chem. Lett.*, **1994**, 1259; b) T. Nagata, K. Imagawa, T. Yamada, and T. Mukaiyama, *Inorg. Chim. Acta*, **220**, 1259 (1994); c) T. Nagata, K. Imagawa, T. Yamada, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **68**, 1455 (1995).

12) K. Imagawa, T. Nagata, T. Yamada, and T. Mukaiyama, *Chem. Lett.*, **1995**, 335.

13) T. Yamada, K. Imagawa, T. Nagata, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **67**, 2248 (1994).

14) Y. Watanabe, K. Yamaguchi, I. Morishima, K. Takehara, M. Shimizu, T. Hayakawa, and H. Orita, *Inorg. Chem.*, **30**, 2581 (1990).

15) Enantioselection was observed in the aerobic oxidation of sulfide catalyzed by optically active (salen)-manganese(III) complex **F**. When a catalytic amount of *N*-methylimidazole was added to the present oxidation, the absolute configuration of the obtained sulfoxide was reversed. The similar result in the aerobic asymmetric epoxidation of unfunctionalized olefins indicated that the acylperoxomanganese complex behaved as the reactive intermediate in the absence of *N*-methylimidazole, and oxomanganese complex by adding *N*-methylimidazole, respectively (Ref. 13. References are cited therein.) (Table 5).

16) For example, it was reported that *l*-menthyl *p*-toluenesulfinate was epimerized by back-side coordination of halogen atom against chiral sulfur atom (H. F. Herbrandson and R. T. Dickerson, Jr., *J. Am. Chem. Soc.*, **81**, 4102 (1959)).

17) N. Komatsu, M. Hashizume, T. Sugita, and S. Uemura, *J. Org. Chem.*, **58**, 4529 (1993); K. Noda, N. Hosoya, R. Irie, Y. Yamashita, and T. Katsuki, *Tetrahedron*, **50**, 9609 (1994).

18) H. B. Kagan and J. C. Fiaud, *Top. Stereochem.*, **18**, 249 (1988).

19) N. Furukawa, F. Takahashi, T. Kawai, K. Kishimoto, S. Ogawa, and S. Oae, *Phosphorus and Sulfur*, **16**, 167 (1983).

20) Y. Tamura, T. Saito, H. Ishibashi, and M. Ikeda, *Synthesis*, **1975**, 641.