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Mn-Salen Catalyzed Nitrene Transfer Reaction: Enantioselective Imidation of Alkyl Aryl Sulfides

Hisashi Nishikori,† Chisa Ohta, Eva Oberlin, Ryo Irie, and Tsutomu Katsuki*

Department of Molecular Chemistry, Graduate School of Science, Kyushu University 33
Higashi-ku, Fukuoka 812-8581, Japan

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Abstract: Enantioselective imidation of alkyl aryl sulfides was achieved by using (*R,R*)- or (*R,S*)-Mn-salen complex [(*R,R*)-**3** or (*R,S*)-**3**] as a catalyst. The optimum reaction conditions are dependent upon the substrates examined. For example, the imidation of alkyl phenyl sulfides with PhI=NTs using Mn-salen complex (*R,R*)-**3** as a catalyst in the presence of *N*-methylmorpholine *N*-oxide showed high enantioselectivity (up to 89% ee). On the other hand, the reaction of methyl 2,4-dinitrophenyl sulfide was effected (97% ee) by using Mn-salen complex (*R,S*)-**3** as the catalyst in the absence of *N*-methylmorpholine *N*-oxide.

Introduction

Sulfimides are nitrogen equivalents of sulfoxides and optically active sulfimides are expected to be useful chiral auxiliaries as equally as optically active sulfoxides. However, their use in organic synthesis is very limited,[1] mainly because of the poor availability of optically active sulfimides. Optically active sulfimides have so far been prepared by the conversion from the corresponding optically active sulfoxides[2] and by kinetic resolution of racemic sulfimides using optically active base.[3] Recently, Uemura *et al.* reported enantioselective imidation of alkyl aryl sulfides using chiral copper(I)-bis(oxazoline) complex as a catalyst.[4] In this copper-mediated reaction, good enantioselectivity (71% ee) has been realized in the reaction of benzyl 1-naphthyl sulfide, while only modest enantioselectivity (13% ee) has been observed in the reaction of methyl tolyl sulfide.

Sulfimidation is a nitrene transfer reaction. We have recently found that a chiral (salen)manganese(III) complex is an efficient catalyst for enantioselective aziridination of styrenes, another nitrene transfer reaction.[5] We have also found that a slightly modified chiral (salen)manganese(III) complex is an excellent catalyst for enantioselective sulfoxidation of alkyl aryl sulfides.[6] These results strongly suggested that some appropriate chiral (salen)manganese(III) complex (hereafter referred to as Mn-salen complex) would catalyze sulfimidation in a highly enantioselective manner. Here we report our study on asymmetric imidation of alkyl aryl sulfides using Mn-salen complexes as catalysts.[7]

Results and Discussion

We first examined the imidation of methyl phenyl sulfide in chlorobenzene in the presence of 4-phenylpyridine *N*-oxide (PPNO) using *N*-(*p*-toluenesulfonyl)iminophenyliodinane as a nitrene precursor and

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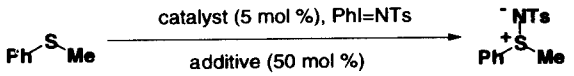


Table 1 Asymmetric imidation of methyl phenyl sulfide[a)]

entry	catalyst	solvent	additive[b)]	yield (%)[c)]	% ee[d)]	elution order[e)]
1	(*R*,*R*)-**1**	C_6H_5Cl	PPNO	65	32	-
2	(*R*,*S*)-**1**	"	"	55	32	+
3	(*R*,*R*)-**2**	"	"	53	15	-
4	(*R*,*S*)-**2**	"	"	41	29	+
5	(*R*,*R*)-**3**	"	"	50	64	+
6	(*R*,*S*)-**3**	"	"	57	50	+
7	(*R*,*R*)-**4**	"	"	57	0	
8	(*R*,*S*)-**4**	"	"	62	20	-
9	(*R*,*R*)-**3**	"	NMO	55	84	+
10[f)]	(*R*,*R*)-**3**	"	"	47	89	+
11	(*R*,*S*)-**3**	"	"	43	59	-
12[f)]	(*R*,*S*)-**3**	"	"	29	76	-
13	(*R*,*S*)-**3**	CH_2Cl_2	PPNO	60	31	+
14	(*R*,*R*)-**3**	C_6H_5CN	"	48	44	+
15	(*R*,*S*)-**3**	"	"	58	49	+
16[g)]	(*R*,*R*)-**3**	C_6H_5Cl	-	76	42	+
17[g)]	(*R*,*S*)-**3**	"	-	63	49	-
18[g)]	(*R*,*R*)-**3**	C_6H_5CN	-	68	19	+
19[g)]	(*R*,*S*)-**3**	"	-	70	39	-
20[g)]	(*R*,*R*)-**2**	C_6H_5Cl	-	66	37	-
21[g)]	(*R*,*S*)-**2**	"	-	52	24	-

a) Reactions were carried out in a molar ratio of substrate : PhI=NTs : catalyst : additive = 2 : 1 : 0.05 : 0.5 at room temperature unless otherwise mentioned.

b) PPNO= 4-phenylpyridine *N*-oxide, NMO= *N*-methylmorpholine *N*-oxide.

c) Isolated yield based on the amount of PhI=NTs used.

d) Determined by HPLC analysis using DAICEL CHIRALCEL OJ column (hexane/2-propanol= 1 : 1).

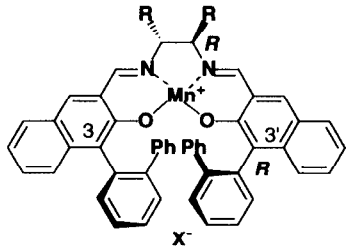
e) Plus sign indicates that the major enantiomer was eluted prior to the minor enantiomer and minus sign stands for the reversed elution order.

f) Reaction was carried out at 0 °C.

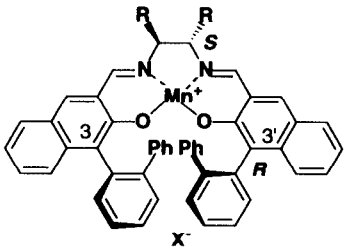
g) Reaction was carried out in the absence of additive.

Mn-salen complexes [(*R*,*R*)- and (*R*,*S*)-**1**-**4**] as catalysts (Table 1, entries 1-8).

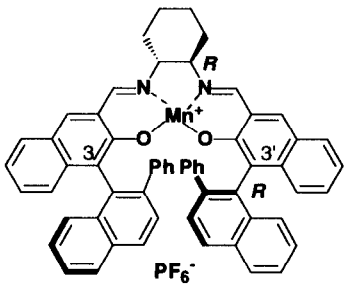
The degree of enantioselectivity was found to depend on the substituent on the salen ligand, its relative configuration, the presence or absence of apical ligand and its structure. In accord with aziridination,[5)] complexes [(*R*,*R*)- and (*R*,*S*)-**1**-**3**] bearing biphenyl group as C3 and C3' substituents (entries 1-6) are also



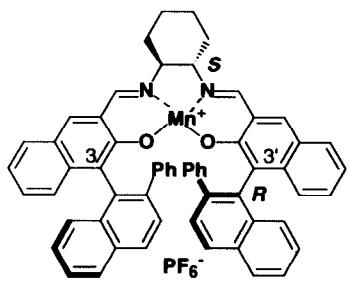
(*R,R*)-**1**: R= Me, X= OAc
(*R,R*)-**2**: R= Ph, X= OAc
(*R,R*)-**3**: R,R= -$(CH_2)_4$-, X= PF_6



(*R,S*)-**1**: R= Me, X= OAc
(*R,S*)-**2**: R= Ph, X= OAc
(*R,S*)-**3**: R,R= -$(CH_2)_4$-, X= PF_6



(*R,R*)-**4**



(*R,S*)-**4**

superior to complexes [(*R,R*)- and (*R,S*)-**4**] bearing (2"-phenyl)naphthyl group (entries 7 and 8) for the present reaction. It is noteworthy that the sense of enantioselection by these complexes (**1-4**) was dictated not only by the chirality of the ethylenediamine moiety but also by the presence or absence of an apical ligand and its varieties. For example, complexes (*R,R*)-**3** and (*R,S*)-**3** showed the opposite sense of enantiotopic selectivity to each other in the absence or in the presence of *N*-methylmorpholine *N*-oxide (NMO) as the apical ligand (entries 9-11 and 16-19), while they exhibited the same sense of enantioselectivity in the presence of PPNO (entries 5 and 6). On the other hand, complexes (*R,R*)-**2** and (*R,S*)-**2** showed the same sense of enantioselectivity to each other in the absence of NMO (entries 20 and 21) but they showed the opposite sense of enantioselectivity in the presence of PPNO as the apical ligand (entries 3 and 4), though enantioselectivity was only modest. These results indicate that enantioselection by Mn-salen complex was affected by the chirality of ethylenediamine unit as well as coordination of an apical ligand. Among the reaction conditions examined, a combination of (*R,R*)-**3** and NMO in chlorobenzene showed the highest enantioselectivity of 84% ee (entry 9). Lowering the reaction temperature to 0 °C improved enantioselectivity to 89% ee (entry 10).

Although the mechanism of enantiotopic selection by Mn-salen complexes is unclear at present, we believe that it is strongly related to the conformation of the intermediary imino Mn-salen complexes. We recently disclosed that the ligand-conformation of Mn-salen complexes which are catalysts for asymmetric oxidation is mainly dictated by the two factors: i) the chirality of the five-membered chelate ring including manganese ion and ethylenediamine unit and ii) the OH-π interaction between the C3 and C3' substituents and apical aqua ligands. Furthermore, it was also disclosed that replacement of an apical aqua ligand with other donor ligand causes the change in the ligand-conformation and affects enantioselection by Mn-salen complexes.[8] We could

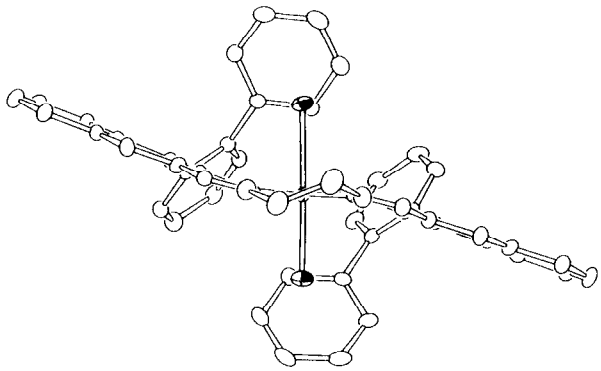
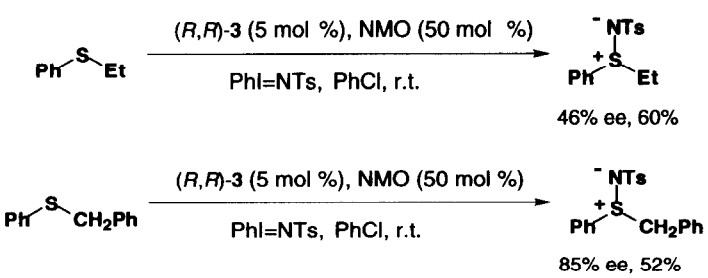


Figure 1. An ORTEP drawing for the cation part of (*R,R*)-**3** (the side view from the cyclohexane ring). All hydrogen atoms have been omitted for clarity.

determine the structure of (*R,R*)-**3** bearing two apical aqua ligands unambiguously (Figure 1). From the analysis of the structure, the ligand-conformation of (*R,R*)-**3** was found to be also dictated by the above two factors: OH-π interaction (the distance between the apical aqua ligand and 2"-phenyl group is as short as *ca.* 3.4 Å) and the five membered chelate ring of a half-chair conformation. Two factors work cooperatively[8] and the salen ligand takes a deeply folded stepped conformation. Therefore it is expected that addition of donor ligand replaces the apical aqua ligand and causes some change in the conformations of the basal salen ligand and of C3- and C3'-substituents, giving some influence on the enantioselectivity of the reaction. However, differing from the oxo Mn-salen complex [O=Mn(salen)] which is the active species in asymmetric oxidation, the imino complex [RN=Mn(salen)] that is active species for the present reaction bears *p*-toluenesulfonyl group (R= *p*-Ts) on the imino nitrogen atom and its orientation also gives an influence on enantioselectivity. The orientation of the *N*-substituent should also be affected by the presence or absence of apical ligand and its varieties. These apical ligand effects should be related to the above-described stereochemistry but further study is required for the detailed discussion of the mechanism of enantioselection in the present reaction.

Under the optimized conditions, the imidation of ethyl phenyl sulfides and benzyl phenyl sulfide was examined and the latter reaction also proceeded with high enantioselectivity of 85% ee (Scheme 1).



Scheme 1

Sulfimidation is considered to proceed through an electrophilic Mn-imino species [*p*-TsN=Mn(salen)] as described above.[6,9] Therefore, we expected that the less nucleophilic substrate bearing an electron-

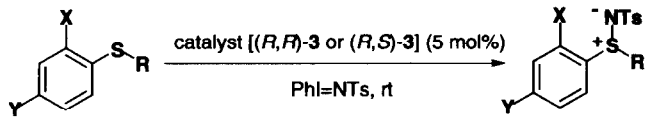


Table 2 Asymmetric imidation of alkyl aryl sulfides bearing an electron-withdrawing group[a]

entry	catalyst	substrate			solvent	yield (%)[b]	% ee	elution order[c]
		X	Y	R				
1	(*R*,*R*)-**3**	NO_2	H	Me	C_6H_5Cl	53	30	+
2	(*R*,*S*)-**3**	NO_2	H	Me	"	53	70[d]	-
3[e]	(*R*,*S*)-**3**	NO_2	H	Me	"	7	56	-
4[f]	(*R*,*R*)-**3**	NO_2	H	Me	"	61	56	+
5[f]	(*R*,*S*)-**3**	NO_2	H	Me	"	17	60	-
6	(*R*,*S*)-**3**	NO_2	H	Me	CH_3CN	53	67	-
7[e]	(*R*,*S*)-**3**	NO_2	H	Me	"	10	52	-
8	(*R*,*S*)-**3**	NO_2	H	Me	CH_3CO_2Et	22	74	-
9	(*R*,*S*)-**3**	NO_2	H	Me	C_6H_5CN	55	80	-
10[f]	(*R*,*S*)-**3**	NO_2	H	Me	"	-	-	
11[f,g]	(*R*,*R*)-**3**	NO_2	H	Me	"	trace	60	+
12[g]	(*R*,*R*)-**3**	NO_2	H	Me	"	80	64	+
13[g]	(*R*,*S*)-**3**	NO_2	H	Me	"	77	90	-
14	(*R*,*S*)-**3**	H	NO_2	Me	"	99	55[h]	-
15	(*R*,*S*)-**3**	Br	H	Me	"	71	66[i]	-
16[g]	(*R*,*S*)-**3**	NO_2	NO_2	Me	"	42	97[d]	-
17	(*R*,*S*)-**3**	NO_2	H	Et	"	62	72[d]	-
18[g]	(*R*,*S*)-**3**	NO_2	NO_2	Et	"	25	66[d]	-
19[g]	(*R*,*S*)-**3**	NO_2	H	Bn	"	26	36[j]	+

a) Reactions were carried out in a molar ratio of substrate : PhI=NTs : catalyst = 2 : 1 : 0.05 at room temperature unless otherwise mentioned.

b) Isolated yield based on the amount of PhI=NTs used.

c) Plus sign indicates that the major enantiomer was eluted prior to the minor enantiomer and minus sign stands for the reversed elution order.

d) Determined by HPLC analysis using DAICEL CHIRALCEL AD column (hexane/2-propanol= 1 : 1).

e) Reaction was carried out in the presence of 4-PPNO (10 mol equiv of the catalyst).

f) Reaction was carried out in the presence of NMO (10 mol equiv of the catalyst).

g) Reaction was carried out in the presence of MS 3A.

h) Determined by HPLC analysis using DAICEL CHIRALCEL OD column (hexane/2-propanol= 1 : 1).

i) Determined by HPLC analysis using DAICEL CHIRALCEL OJ column (hexane/2-propanol= 1 : 1).

j) Determined by HPLC analysis using DAICEL CHIRALCEL OT column (hexane/2-propanol= 7 : 3).

withdrawing group such as methyl *o*-nitrophenyl sulfide would give higher enantioselectivity than the parent methyl phenyl sulfide and examined its imidation in various solvents using complexes (*R,R*)-**3** and (*R,S*)-**3** as the catalysts (Table 2).

Differing from imidation of methyl phenyl sulfide, complex (*R,S*)-**3** was found to be a catalyst for the present reaction, superior to complex (*R,R*)-**3** (Table 2, *c.f.* entries 1, 4, 12 and 2, 5, 13). Although special trend was not observed in the solvent effect, the reaction in benzonitrile showed the highest enantioselectivity of 80% ee (entry 9). Addition of MS 3Å further increased enantioselectivity up to 90% ee (entry 13). Effect of donor ligand was also examined. Addition of donor ligand such as NMO and PPNO decreased both the chemical yield and enantioselectivity when (*R,S*)-**3** was used as a catalyst (entries 3, 5, and 7), but enantioselectivity was improved when (*R,R*)-**3** was used (entry 4). Despite this description, complex (*R,S*)-**3** afforded higher enantioselectivity than complex (*R,R*)-**3** under all the identical reaction conditions.

Excellent enantioselectivity (97% ee) was attained in the imidation of methyl dinitrophenyl sulfide, though chemical yield was moderate (entry 16). On the other hand, imidation of methyl *p*-nitrophenyl sulfide showed moderate enantioselectivity of 55% ee (entry 14). Imidation of *o*-bromophenyl methyl sulfide also gave moderate but slightly better enantioselectivity of 66% ee (entry 15). These results suggest that effect of *o*-nitro group on enantioselectivity is attributed not only to its electronic but also to steric and/or coordinating natures. Enantioselectivity decreased as the size of alkyl group (R) increased. Imidation of ethyl *o*-nitrophenyl sulfide in benzonitrile showed good enantioselectivity of 72% ee, while the reaction of benzyl *o*-nitrophenyl sulfide exhibited only modest enantioselectivity of 36% ee (entries 17 and 19).

In conclusion, we found that enantioselectivity of Mn-salen catalyzed asymmetric sulfimidation is dependent upon several factors; the configuration of the salen ligand, apical ligand, solvent, nucleophilicity of sulfides, and so on. By choosing a suitable combination of these factors, we were able to achieve high enantioselectivity in sulfimidation of alkyl aryl sulfides. This new knowledge will contribute to the further development of asymmetric sulfimidation.

Experimental

^{1}H NMR spectra were recorded at 270 MHz on a JEOL EX-270 instrument. All signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ value in $CDCl_3$), unless otherwise noted. IR spectra were obtained with a JASCO IR-700 instrument. Optical rotation was measured with a JASCO P-1020-GT automatic digital polarimeter. High-resolution mass spectra were recorded on a JEOL JMS-SX/SX 102A instrument. Column chromatography was conducted on Silica Gel BW-820MH, 70-200 mesh ASTM, available from FUJI SILYSIA CHEMICAL LTD. HPLC analysis of enantiomeric excess was carried out using Hitachi L-4000 equipped with an appropriate optically active column, as described in the footnotes of Tables 1 and 2. The reaction temperature was controlled with EYELA COOL ECS 50. Solvents were dried and distilled shortly before use. Reactions were carried out under an atmosphere of nitrogen if necessary. [*N*-(*p*-Toluenesulfonyl)imino]phenyliodinane was prepared according to the reported procedure[10] and recrystallized from methanol before use. Complex **1** was prepared according to the reported procedure.[5]

Mn-salen complex [(*R,R*)-2]

To a solution of (1*R*,2*R*)-1,2-diphenylethylenediamine (13.1 mg, 0.062 mmol) in ethanol (4 ml) was added $Mn(OAc)_2 \cdot 4H_2O$ (15.2 mg, 0.062 mmol) and the mixture was stirred for 1 h at room temperature. To this

solution was added (*R*)-3-formyl-2-hydroxy-1-[(2-phenyl)phenyl]naphthalene (40.0 mg, 0.12 mmol), and the mixture was stirred for 18 h at the same temperature in air. The reaction mixture was concentrated *in vacuo* to give Mn-salen complex (*R,R*)-**2** in a quantitative yield. IR (KBr): 3055, 3028, 1603, 1555, 1340, 1223, 1151, 1009, 959, 702 cm^{-1}. Anal. Calcd for $C_{62}H_{45}N_2O_4Mn{\cdot}2.5H_2O$: C, 75.83; H, 5.13 N, 2.85%. Found: C, 75.97; H, 4.92; N, 2.83%.

Mn-salen complex [(*R,S*)-2]

Mn-salen complex [(*R,S*)-**2**] was synthesized from (*R*)-3-formyl-2-hydroxy-1-[(2-phenyl)phenyl]-naphthalene and (1*S*,2*S*)-1,2-diphenylethylenediamine in the same manner as described for the synthesis of Mn-salen complex [(*R,R*)-**2**]. IR (KBr): 3053, 3026, 1603, 1555, 1308, 1223, 1150, 1009, 959, 702 cm^{-1}. Anal. Calcd for $C_{62}H_{45}N_2O_4Mn{\cdot}3H_2O$: C, 75.14; H, 5.19; N, 2.83%. Found: C, 75.39; H, 4.89; N, 2.66%.

Mn-salen complex [(*R,R*)-3]

To a solution of (1*R*,2*R*)-1,2-diaminocyclohexane (26.3 mg, 0.23 mmol) in ethanol (5 ml) was added $Mn(OAc)_2{\cdot}4H_2O$ (60.9 mg, 0.23 mmol) and the mixture was stirred for 1 h at room temperature. To this solution was added (*R*)-3-formyl-2-hydroxy-1-[(2-phenyl)phenyl]naphthalene (162 mg, 0.46 mmol), and the mixture was stirred for 18 h at the same temperature in air. To this solution was added $NaPF_6$ (386.3 mg, 2.3 mmol), and the mixture was further stirred for 10 h at the temperature, then concentrated to dryness. The residue was chromatographed on silica gel (dichloromethane/methanol= 1/0 to 20/1) to give Mn-salen complex (*R,R*)-**3** (202 mg) as dark brown crystals in 95% yield. IR (KBr): 3057, 2937, 2862, 1612, 1585, 1312, 1028, 960, 843 cm^{-1}. Anal. Calcd for $C_{52}H_{40}N_2O_2MnPF_6{\cdot}2H_2O{\cdot}CH_2Cl_2$: C, 60.87; H, 4.43; N, 2.68%. Found: C 61.11; H, 4.65; N, 2.55%.

Mn-salen complex [(*R,S*)-3]

Mn-salen complex [(*R,S*)-**3**] was synthesized from (*R*)-3-formyl-2-hydroxy-1-[(2-phenyl)phenyl]-naphthalene and (1*S*,2*S*)-1,2-diaminocyclohexane in the same manner as described for the synthesis of Mn-salen complex [(*R,R*)-**3**]. IR (KBr): 3053, 2937, 2862, 1609, 1585, 1312, 1028, 960, 843 cm^{-1}. Anal. Calcd for $C_{52}H_{40}N_2O_2MnPF_6{\cdot}2H_2O$: C, 65.00; H, 4.62; N, 2.92%. Found: C, 64.77; H, 4.81; N, 2.74%.

X-ray crystal structure determination of Mn-salen complex [(*R,R*)-3]

Mn-salen complex (*R,R*)-**3** was dissolved in toluene on heating and the hot mixture was filtered through a pad of Celite. The filtrate was allowed to stand at room temperature to grow single crystals of (*R,R*)-**3**·$(H_2O)_2$·$(toluene)_3$ suitable for x-ray structure analysis. A crystal with dimensions of 0.10 X 0.20 X 0.20 mm^3 was mounted on a glass fiber and diffraction measurement was made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα (λ= 0.71069 Å) at -90 °C. Indexing was performed from 2 oscillation images which were exposed for 100 sec. The crystal-to-detector distance was 127.4 mm. The data were collected over 44 oscillation images with the detector swing angle of 5° and the exposed time of 100 sec per degree for each image. Readout was performed with the pixel size of 100 μm x 100 μm. The structural analysis was carried out on an IRIS O2 computer using teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan. Neutral scattering factors were obtained from the standard source.[11] In the reduction of data, Lorentz and polarization corrections were made. A collection

for secondary extinction was also applied. The function minimized was $\Sigma w(|F_O| - |F_C|)^2$, where $w = [\sigma^2(F_O)]^{-1} = [\sigma_c^2(F_O)+p^2F_O^2/4]^{-1}$, $\sigma_c(F_O)$ = e.s.d. based on counting statistics, and p = p-factor. The schemes for unweighted and weighted agreement factors were $R = \Sigma||F_O| - |F_C|| / \Sigma|F_O|$ and $R_w = [(\Sigma w(|F_O| - |F_C|)^2 / \Sigma wF_O^2]^{1/2}$, respectively. Crystallographic data, as well as other information pertinent to structural solution and refinement, are as follows: $C_{73}H_{68}N_2O_4MnPF_6$, M = 1237.25, monoclinic, space group $P2_1$, a = 9.6217(5) Å, b = 18.986(1) Å, c = 17.389(1) Å, V = 3104.7(3) Å^3; Z = 2; D_C = 1.323 g cm^{-3}, μ(Mo-Kα) = 3.08 cm^{-1}, R = 0.058, Rw= 0.050 for 5760 reflections [I > 1.00σ(I)] and 784 variables, GOF = 1.35. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF94). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Atomic coordinates, bond lengths and angles, and thermal parameters of the complex (*R*,*R*)-**3** are available on request from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, U.K.

General procedures for sulfimidation

General procedures for sulfimidation of alkyl aryl sulfides and of sulfides bearing an electron-withdrawing group are exemplified by the imidation of methyl phenyl sulfide with (*R*,*R*)-**3** and that of methyl *o*-nitrophenyl sulfide with (*R*,*S*)-**3**, respectively.

Sulfimidation of methyl phenyl sulfide: Complex (*R*,*R*)-**3** (4.6 mg, 5 μmol) and *N*-methylmorpholine *N*-oxide (5.9 mg, 50 μmol) were suspended in dry toluene (1 ml), azeotropically concentrated *in vacuo*, and re-suspended in chlorobenzene (0.5 ml). To this suspension was added methyl phenyl sulfide (23.4 μl, 0.2 mmol) and cooled to 0 °C. [*N*-(*p*-Toluenesulfonyl)imino]phenyliodinane (35.7 mg, 0.1 mmol) was added to the mixture which was allowed to warm to room temperature and stirred for 6 h at the temperature. The reaction mixture was directly subjected to silica-gel column chromatography (hexane : ethyl acetate= 7 : 3 to 3 : 7) to give *S*-methyl *S*-phenyl *N*-(*p*-toluenesulfonyl)sulfimide of 89% ee (13.8 mg, 47 %). The enantiomeric excess of the product was determined by HPLC analysis under the conditions described in the footnote of Table 1.

Sulfimidation of methyl o-nitrophenyl sulfide: Complex (*R*,*S*)-**3** (4.6 mg, 5 μmol) was dissolved in dry toluene (1 ml), azeotropically concentrated *in vacuo*, and re-dissolved in benzonitrile (0.5 ml). To this solution were added methyl *o*-nitrophenyl sulfide (33.8 μl, 0.2 mmol) and MS-3A (50 mg) and stirred for half an hour at room temperature. [*N*-(*p*-Toluenesulfonyl)imino]phenyliodinane (35.7 mg, 0.1 mmol) was added to this suspension and stirred for 3 h at the temperature. The reaction mixture was directly subjected to silica gel column chromatography (hexane : ethyl acetate= 7 : 3 to 3 : 7) to give *S*-methyl *S*-*o*-nitrophenyl *N*-(*p*-toluenesulfonyl)sulfimide (26.0 mg, 77%). The enantiomeric excess of the product was determined by HPLC analysis under the conditions described in the footnote of Table 2.

***S*-Methyl *S*-phenyl *N*-(*p*-toluenesulfonyl)sulfimide**

The enantiomeric excess was determined to be 89% ee by HPLC analysis. $[\alpha]_D^{24}$ -237° (*c* 1.20, $CHCl_3$). ^1H NMR: δ 7.72 (d *J*= 8.3 Hz, 2H), 7.68 (dd, *J*= 8.3 and 1.7 Hz, 2H), 7.56-7.44 (m, 3H), 7.15 (d *J*= 8.3 Hz, 2H), 2.83 (s, 3H), 2.34 (s, 3H). IR (KBr): 3084, 3026, 2926, 1596, 1446, 1281, 1141, 1087, 934, 764, 652, 577 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_2S_2$: C, 57.31; H, 5.15; N, 4.77%. Found: C, 57.27; H, 5.22; N, 4.81%.

***S*-Benzyl *S*-phenyl *N*-(*p*-toluenesulfonyl)sulfimide**

The enantiomeric excess was determined to be 85% ee by HPLC analysis. $[\alpha]_D^{24}$ -59.8° (*c* 1.18, $CHCl_3$). ^1H

NMR: δ 7.61 (d, *J*= 8.3 Hz, 2H), 7.55-7.48 (m, 3H), 7.44-7.38 (m, 2H), 7.31-7.25 (m, 1H), 7.18 (dd, *J*= 8.3 and 7.6 Hz, 2H), 7.07 (d, *J*= 8.3 Hz, 2H), 6.97 (d, *J*= 7.3 Hz, 2H), 4.24 and 4.22 (ABq, J_{AB}= 12.5 Hz, 2H), 2.32 (s, 3H). IR (KBr): 3057, 2976, 2922, 1599, 1494, 1444, 1277, 1134, 1088, 989, 962, 752, 689, 571 cm^{-1}. Anal. Calcd for $C_{20}H_{19}NO_2S_2$: C, 65.01; H, 5.18, N, 3.79%. Found: C, 65.00; H, 5.20; N, 3.82%.

S-Methyl S-(2-nitrophenyl) N-(p-toluenesulfonyl)sulfimide

The enantiomeric excess was determined to be 90% ee by HPLC analysis. $[\alpha]_D^{25}$ +268° (*c* 2.20, $CHCl_3$). ^1H NMR: δ 8.64 (dd, *J*= 7.9 and 1.0 Hz, 1H), 8.34 (dd, *J*= 7.9 and 1.3 Hz, 1H), 7.96 (ddd, *J*= 7.9, 7.6, and 1.3 Hz, 1H), 7.75-7.81 (m, 3H), 7.23 (d, *J*= 7.9 Hz, 2H), 3.01 (s, 3H), 2.05 (s, 3H). IR (KBr): 3098, 3053, 2936, 2922, 1531, 1344, 1283, 1148, 1088, 998, 953, 758, 573 cm^{-1}. Anal. Calcd for $C_{14}H_{14}N_2O_4S_2$: C, 49.69; H, 4.17, N, 8.28%. Found: C, 49.51; H, 4.21; N, 8.34%.

S-Methyl S-(2,4-dinitrophenyl) N-(p-toluenesulfonyl)sulfimide

The enantiomeric excess was determined to be 97% ee by HPLC analysis. $[\alpha]_D^{24}$ +329° (*c* 0.117, $CHCl_3$). ^1H NMR: δ 9.13 (d, *J*= 2.0 Hz, 1H), 8.89 (d, *J*= 8.9 Hz, 1H), 8.73 (dd, *J*= 8.9 and 2.0 Hz, 1H), 7.78 (d, *J*= 8.3 Hz, 2H), 7.25 (*J*= 8.3 Hz, 2H), 3.07 (s, 3H), 2.41 (s, 3H). IR (KBr): 3087, 2934, 1607, 1541, 1339, 1300, 1142, 1082, 947, 756, 658, 575 cm^{-1}. HREIMS m/z. Calcd. for $C_{14}H_{13}N_3O_6S_2$: 383.0246. Found: 383.0249 (M^+).

S-Ethyl S-(2-nitrophenyl) N-(p-toluenesulfonyl)sulfimide

The enantiomeric excess was determined to be 72% ee by HPLC analysis. $[\alpha]_D^{25}$ +211° (*c* 0.160, $CHCl_3$). ^1H NMR: δ 8.61 (dd, *J*= 8.3 and 1.7 Hz, 1H), 8.35 (dd, *J*= 7.9 and 1.3 Hz, 1H), 7.95 (ddd, *J*= 8.3, 7.3, and 1.3 Hz, 1H), 7.74-7.80 (m, 3H), 7.23 (d, *J*= 7.9 Hz, 2H), 3.26 and 3.08 (qualtet of ABq, J_{AB}= 13.5 Hz and *J*= 7.3 Hz, 2H), 2.39 (s, 3H), 1.28 (t, *J*= 7.3 Hz, 3H). IR (KBr): 3097, 2976, 2870, 1570, 1530, 1342, 1300, 1148, 1090, 976, 739, 575 cm^{-1}. Anal. Calcd for $C_{15}H_{16}N_2O_4S_2$: C, 51.12; H, 4.58, N, 7.95%. Found: C, 50.89; H, 4.63; N, 7.83%.

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† Research Fellow of the Japan Society for the Promotion of Science.

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