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Highly Enantioselective Benzylic Hydroxylation with Concave Type of (Salen)manganese(III) Complex

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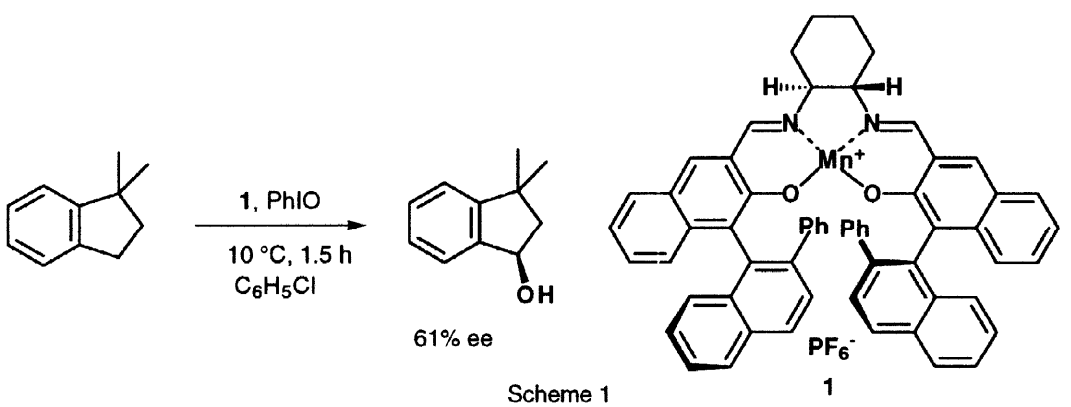
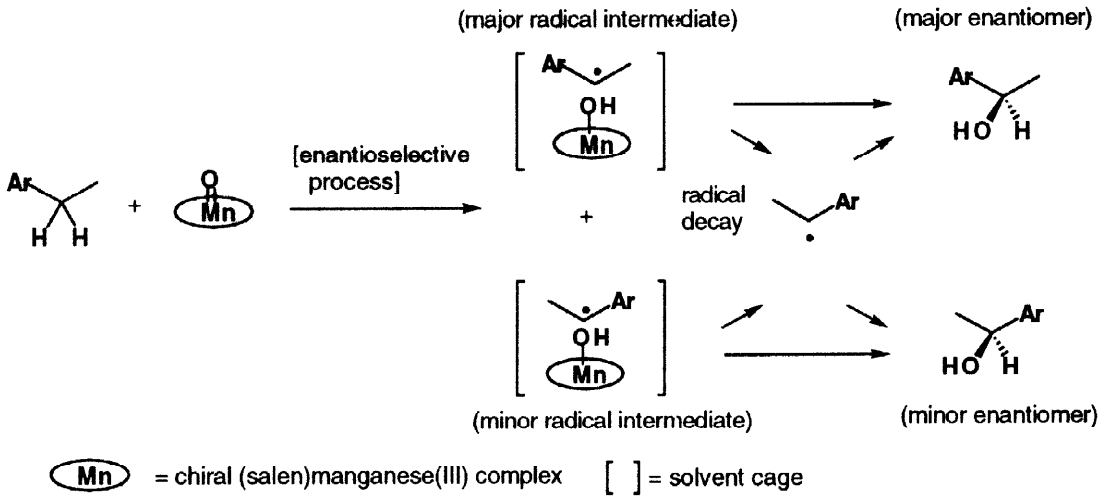
Abstract: Newly-designed optically active (salen)manganese(III) complexes (**5**) catalyze highly enantioselective benzylic hydroxylation and moderate level of enantiomer-differentiating oxidation (kinetic resolution) of the resulting benzylic alcohols. Thus, the enantiomeric excess of hydroxylation product was increased through kinetic resolution, as the reaction time was prolonged. For example, enantiomeric excess of 3,3-dimethylindan-1-ol, the hydroxylation product of 1,1-dimethylindan using **5a** as a catalyst in chlorobenzene, was 84% after 10 min and 90% after 20 h.

C-H oxidation takes part in a wide range of biological transformations and these biological C-H oxidations proceed with high stereoselectivity with aid of oxidizing enzymes. A group of cytochrome P-450's which are representative oxidizing enzymes and carry iron-porphyrin complex as the active site, catalyze highly stereoselective oxidations such as C-H oxidation and epoxidation.[1] An attempt to reproduce this hemenzyme-catalyzed C-H oxidation in flask has been carried out by Groves and Viski using an optically active iron-porphyrin complex as the catalyst and moderate enantioselectivity (up to 72% ee) has been achieved in benzylic oxidation.[2] On the other hand, we recently disclosed that (salen)manganese(III) complex **1** which has the structure similar to metalloporphyrin complexes also catalyzed benzylic hydroxylation with moderate enantioselectivity (Scheme 1).[3,4,5] In common with iron-porphyrin catalyzed benzylic hydroxylation,[6] this reaction has been proven to proceed stepwise via a radical intermediate. In the reaction using the iron-porphyrin catalyst which has a chiral bridge structure, decay of the radical intermediate occurs diastereoselectively and enhances the enantioselectivity achieved at the preceding hydrogen atom abstraction step.[2] In contrast to this, radical decay in the reaction using (salen)manganese(III) complex such as **1** as a catalyst was considered to be non- or low-diastereoselective process because **1** lacked the chiral bridge structure, and to deteriorate enantioselectivity of the reaction (Scheme 2). However, this undesired radical decay was expected to be suppressed by carrying out the reaction in the solvent of high viscosity which constitutes a stout solvent cage.[1] Actually, the reaction in a solvent of higher viscosity showed better enantioselectivity, except that the reactions in fluorobenzene and chlorobenzene showed equal level of enantioselectivity [viscosity coefficient (25 °C): CH_3CN, 0.341; ethyl acetate, 0.426; fluorobenzene, 0.598; chlorobenzene, 0.799] (Table 1, entries 1, 3, 5, and 7). Besides, enantiomeric excess of 3,3-dimethylindan-1-ol was found to increase as the reaction time was prolonged (entries 2, 4, 6, and 8).



Scheme 1

PII: S0040-4020(98)00603-6



Scheme 2

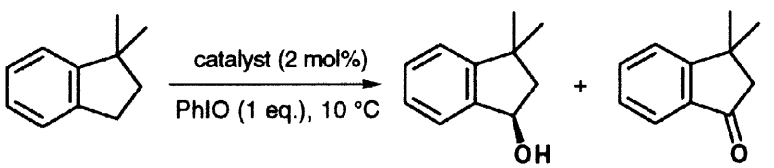
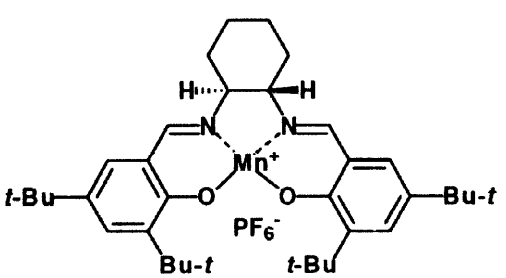


Table 1. Asymmetric hydroxylation of 1,1-dimethylindan using optically active (salen)manganese(III) complex as a catalyst[a)]

entry	complex	solvent	time	ee (%)	yield (%)	alcohol/ketone
1	**1**	CH_3CN	5 min	31	7	26
2	"	"	1.5 h	39	18	4
3	"	AcOEt	5 min	44	8	16
4	"	"	1.5 h	50	17	4
5	"	C_6H_5F	5 min	54	3	11
6	"	"	1.5 h	60	10	3
7	"	C_6H_5Cl	5 min	53	2	11
8	"	"	1.5 h	61	7	3
9	**2**	CH_3CN	5 min	5	4	18
10	"	"	1.5 h	3	5	4
11	"	C_6H_5Cl	5 min	10	1	23
12	"	"	1.5 h	9	1	3

a) Enantiomeric excess of alcohol, yields of alcohol and ketone and their ratio were determined by capillary GLC equipped with optically active column (SUPELCO β-DEX™ 120 fused silica capillary column, 30 m x 0.25 mm ID, 0.25 μm film), using *p*-dichlorobenzene as an internal standard.



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This suggested that oxidation of the produced alcohol to ketone occurred in an enantiomer-differentiating manner. Thus, we explored the possibility of kinetic resolution of racemic 3,3-dimethylindan-1-ol using **1** as a catalyst. As expected, the (*S*)-isomer was oxidized faster than the (*R*)-isomer, though the values of relative rate constant (k_S/k_R) were small (Table 2). The maximum value (4.2) was observed when chlorobenzene was used as solvent.

Oxidation of 1,1-dimethylindan was also examined with complex **2**. Complex **2**, however, showed poor enantioselectivity and the yield of the alcohol was low (Table 1, entries 9 and 11).[7] Kinetic resolution with complex **2** was also less effective (Table 2, entries 2 and 6).

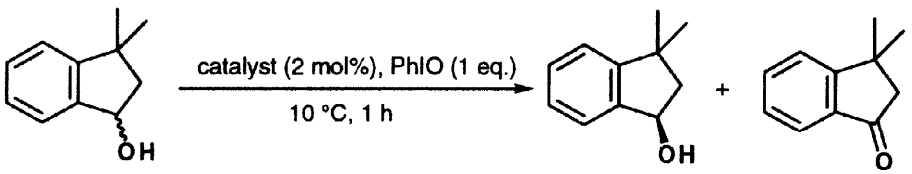
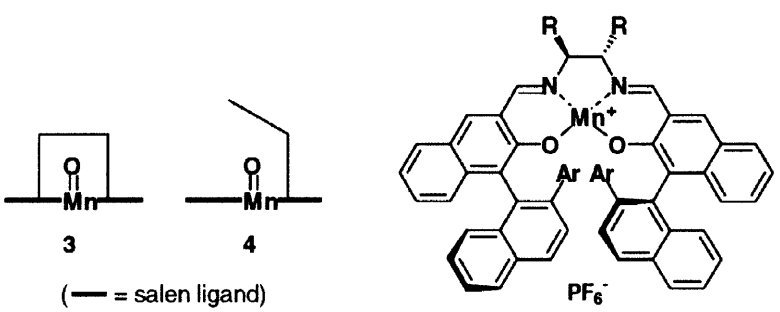


Table 2. Kinetic resolution of racemic 3,3-dimethylindan-1-ol using (salen)manganese(III) complex as a catalyst

entry	complex	solvent	conversion (%)	ee (%)	k_{rel}
1	**1**	CH_3CN	56	38	2.6
2	**2**	"	52	8	1.3
3	**1**	AcOEt	43	28	2.9
4	"	C_6H_5F	51	38	3.1
5	"	C_6H_5Cl	45	40	4.2
6	**2**	"	34	<2	1.0

The above experiments suggested that the choice of solvent was important for achieving higher enantioselectivity. However, they also indicated that it was difficult to achieve sufficient level of enantioselectivity only by choosing the solvent and that appropriate modification of the salen ligand structure was necessary for the further improvement of enantioselectivity. At first, a bridged (salen)manganese(III) complex like **3** was considered to be a good candidate in order to prevent the undesired radical decay effectively (Fig. 1). We recently, however, found that high asymmetry-inducing ability of (salen)manganese(III) complexes was strongly related to the flexibility of salen ligands[8] and it was apprehended that introduction of a bridge structure into the salen ligand would reduce the flexibility of the salen ligand and deteriorate its asymmetric induction. We considered that this dilemma would be solved by introduction of a new (salen)manganese(III) complex of concave type. This type of complex **4** was expected to be flexible but to suppress the undesired radical dissociation effectively. As this type of (salen)manganese(III) complex, we synthesized complexes (**5a** and **5b**) in which the bulky silyl substituent hangs over the manganese ion (Fig. 2).



5a: Ar= 4-[*t*-Bu(C_6H_5)$_2$]SiC_6H_4
R= 3,5-$(CH_3)_2C_6H_3$
5b: Ar= 4-[*t*-Bu(C_6H_5)$_2$]SiC_6H_4
R,R= $(CH_2)_4$

Fig. 1

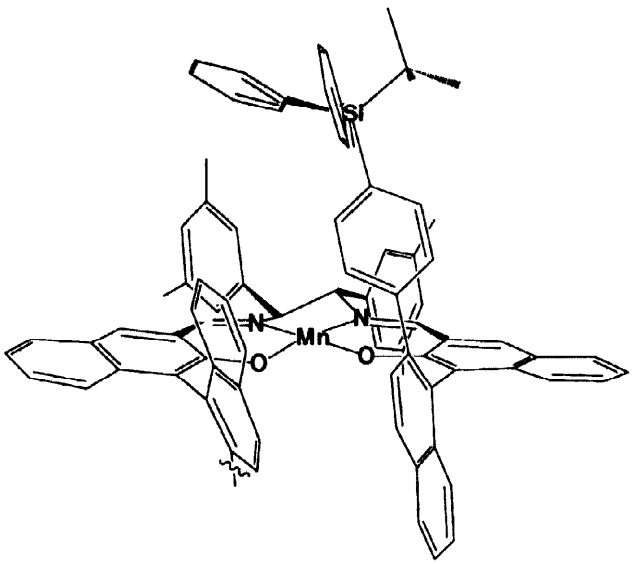
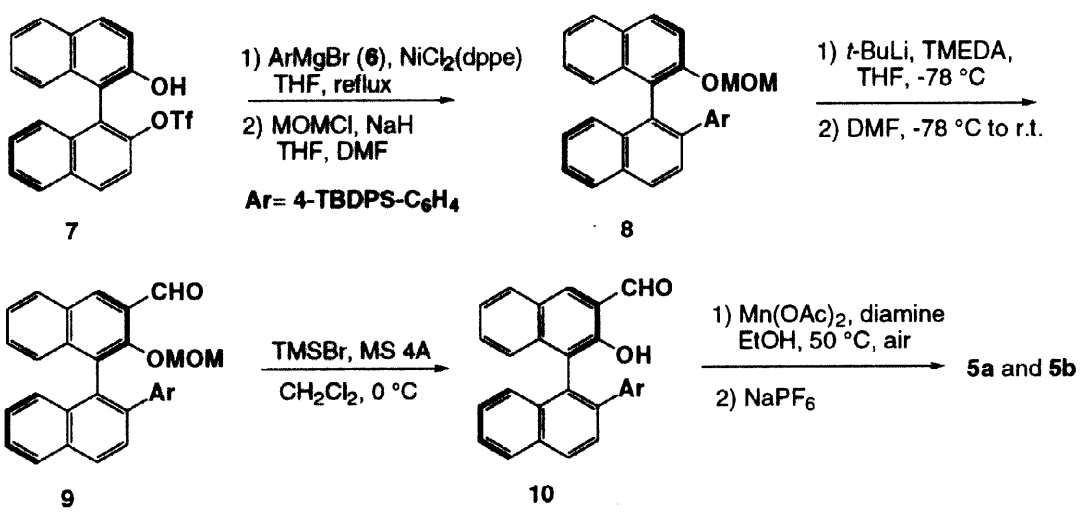


Fig. 2. The structure of **5a** drawn on the basis of the X-ray structure of the related Mn-salen complex I (see, reference 9). All the hydrogen atoms, counter anion, and the left bottom part of the ligand were omitted for clarification. The conformation of *t*-butyldiphenylsilyl moiety was optimized by using TRIPOS-SYBYL on an IRIS Indigo 2. The structure of the other part of the complex was kept fixed during the calculation.

The synthesis of complexes (**5a** and **5b**) started with coupling[10] of Grignard reagent **6**[11] and triflate **7**[12] and subsequent protection as MOM ether (Scheme 3). The resulting MOM ether **8** was converted into aldehyde **10** by the sequence: i) *ortho*-lithiation[13] and subsequent formylation giving **9** and ii) deprotection. Aldehyde **10** was converted into (salen)manganese(III) complexes (**5a** and **5b**) in a conventional manner.



Scheme 3

In order to compare the asymmetry-inducing ability of complexes (**1**, **5a**, and **5b**), we first examined the hydroxylation of 1,1-dimethylindan with these complexes as catalysts under the identical conditions. To estimate enantioselectivity in the hydroxylation step correctly, the reaction must be performed under the conditions that the further oxidation of the generated alcohol is suppressed. Thus the reaction was carried out at -20 °C and stopped at 10 min (Table 3, entries 1-3). As expected, the reaction using **5a** or **5b** as a catalyst showed better enantioselectivity than that using **1** as a catalyst. When **5a** was used as a catalyst, high enantioselectivity of 84% ee was observed (entry 2).

Table 3. Asymmetric benzylic hydroxylation of 1,1-dimethylindan using (salen)manganese(III) complexes (**1**, **5a** and **5b**) as catalysts[a)]

entry	catalyst	time	% ee[b)]	yield (%)[c)]	confign[d)]
1	**1**	10 min	56	1.5 (0.1)	*R*
2	**5a**	10 min	84	4.8 (trace[e)])	*R*
3	**5b**	10 min	70	4.0 (0.15)	*R*
4	**5a**	20 h	90	24.5 (10.2)	*R*
5	**5b**	20 h	81	16.6 (11.9)	*R*
6	**2**	10 min	14	0.7 (0.2)	*R*

a) Reaction was carried out in chlorobenzene at - 20 °C by using 2 mol% of catalyst and iodosylbenzene as a terminal oxidant.

b) Determined by capillary GLC using optically active column (SUPELCO β-DEX™ 120 fused silica capillary column, 30 m x 0.25 mm ID, 0.25 μm film).

c) Yield was determined by GLC analysis using *p*-dichlorobenzene as an internal standard. The number in parentheses is the yield of ketone.

d) Determined by modified Mosher's method; Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092-4096 (see Experimental).

e) GLC analysis indicated the formation of a trace amount of ketone.

Since it was expected that in situ kinetic resolution of the generated alcohol would also occur in the reaction using **5a** or **5b**, we continued the reaction for 20 h and found that the enantiomeric excesses of the alcohols amounted to 90 (**5a**) and 81 % ee (**5b**) (entries 4 and 5). Accordingly, we next examined the oxidation of racemic 3,3-dimethylindan-1-ol using **5a**, **5b** or **1** and estimated the values of relative rate constants (k_{rel}, at -20 °C) to be 5.0±0.2, 4.4±0.3 and 4.2±0.3 respectively. However, if oxidation of the generated 3,3-dimethylindan-1-ol giving 10.2 and 11.9% of ketone had occurred with these relative rate constants, enantiomeric excesses of the remaining alcohol should have been much higher than 90 and 81%, respectively. This indicated that a part of the ketone was supplied by the reaction other than the oxidation of the alcohol. Although we did not examine about the mechanism of the formation of ketone in detail, we observed that the formation of the ketone increased when the reaction was carried out in air, suggesting that molecular oxygen reacted with radical intermediate to give ketone via hydroperoxide. However, even under the strictly deaerated conditions, the amount of the ketone was found to exceed the calculated one from the enantiomeric excess of the remaining alcohol, suggesting the presence of the reaction pathway of ketone formation other than alcohol oxidation.[14] Although the enantiomeric excess of the alcohol was expected to be improved to optical purity if the reaction could proceed enough, the reaction stopped at about 30 h probably due to the decomposition of the catalyst, without further improvement of enantioselectivity.[15]

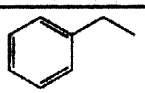
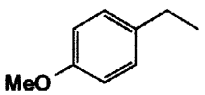
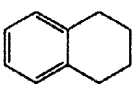
The chemical yield of hydroxylation product with **5** is insufficient but it is noteworthy that the initial oxidation rates of 3,3-dimethylindan with **5a** and **5b** were *ca.* 2-3 times faster than that with **1** and *ca.* 6-7 times faster than that with **2**, for all that coordination spheres of **5a** and **5b** are much more congested than those of **1** and **2** (entries 1, 2, 3, and 6). Since it is reasonable to consider that the mechanism of hydroxylation by these catalysts should be the same, these results suggest that there is some favorable interaction between substrates and the salen ligands in **5a** and **5b**, for hydroxylation.

In the case of other substrates such as ethylbenzene and *p*-methoxyethylbenzene, however, complex **5b** showed better asymmetric induction than **5a** (Table 4, entries 2, 3, 5, and 6). The relative rates in kinetic resolution of racemic phenethyl alcohol and *p*-methoxyphenethyl alcohol using **5b** as a catalyst were 7.6 and 1.8, respectively.

Although we already disclosed that the present reaction proceeds through a radical intermediate, it is still questionable whether hydrogen atom is directly abstracted by oxo species (path a) or one electron transfer occurs first (path b) (Scheme 4). To answer this question, we compared the reaction rate of oxidation of ethylbenzene and ethylbenzene-d_2 and found that k_H/k_D was 4.6±1, suggesting that hydrogen atom abstraction is the rate determining step.[16,17]

In conclusion, we were able to demonstrate that the concave type of (salen)manganese(III) complexes showed high asymmetric induction in benzylic oxidation.

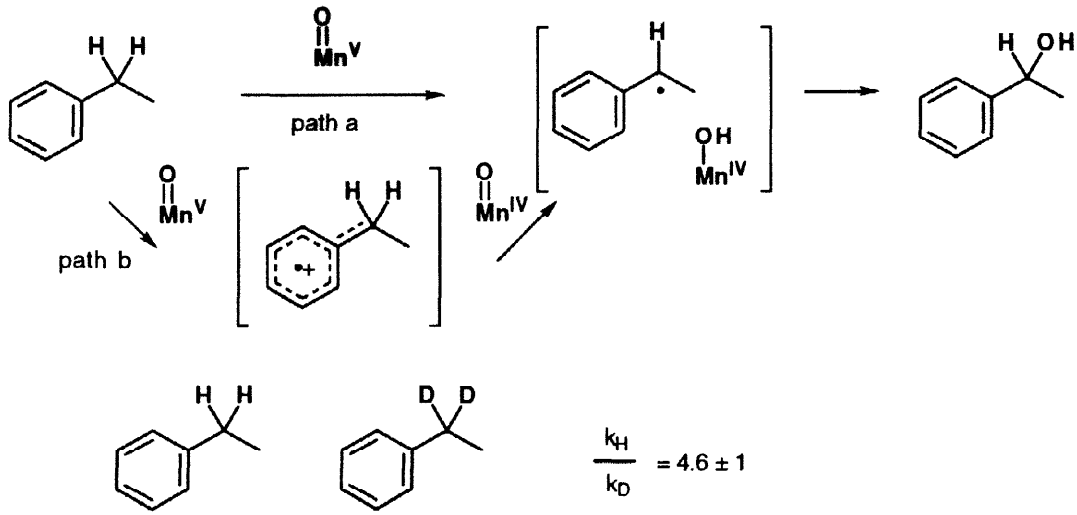
Table 4. Asymmetric benzylic hydroxylation using (salen)manganese(III) complexes (**5a** and **5b**) as catalysts[a)]

entry	catalyst	substrate	time	% ee	yield (%)[b)]	confign	% ee[c)]
1	**5b**		10 min	65[d)]	2.1 (trace[e)])	*R*[f)]	40
2	"	"	12 h	78	6.4 (3.3)	*R*	
3	**5a**	"	12 h	64	2.0 (4.4)	*R*	
4	**5b**		10 min	83[g)]	1.8 (trace[e)])	*R*[h)]	66
5	"	"	24 h	87	13.0 (10.5)	*R*	
6	**5a**	"	12 h	77	7.2 (11.1)	*R*	
7[i)]	**5b**		12 h	77[j)]	22.0 (6.2)	*R*[k)]	72

a) Reaction was carried out in chlorobenzene at -30 °C by using 2 mol% of catalyst and iodosylbenzene as a terminal oxidant unless otherwise noted.
b) Yield was determined by GLC analysis using *p*-dichlorobenzene as an internal standard. The number in parentheses is the yield of ketone.
c) Reported value with optically active iron-porphyrin complex as catalyst (ref. 2).
d) Determined by HPLC analysis of 3,5-dinitrobenzoate derivative using optically active column (DAICEL CHIRALPAK AD, hexane/2-propanol= 15/1, flow rate= 0.5 ml/min).
e) GLC analysis indicated the formation of a trace amount of ketone.
f) Determined by comparing the retention times of the enantiomers of the product (DAICEL CHIRALCEL OB-H, hexane/2-propanol= 9/1, flow rate= 0.5 ml/min) with that of commercial (*R*)-1-phenylethanol (Tokyo Chemical Industry Co., Ltd.).
g) Determined by HPLC analysis using optically active column (DAICEL CHIRALPAK OB-H, hexane/2-propanol= 9/1, flow rate= 0.5 ml/min).
h) Determined by chiroptical comparison; Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 601-612.
i) Reaction was carried out with 3 mol % of catalyst.
j) Determined by HPLC analysis of 3,5-dinitrobenzoate derivative using optically active column (DAICEL CHIRALPAK AD, hexane/2-propanol= 100/1, flow rate= 0.5 ml/min).
k) Determined by chiroptical comparison; Kabuto, K.; Imuta, M.; Kempner, E. S.; Ziffer, H. *J. Org. Chem.* **1978**, *43*, 2357-2361.

Experimental

^{1}H NMR spectra were recorded at 270 MHz on a JEOL EX-270 or at 400 MHz on a JEOL GX-400 instrument. All signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ-value in $CDCl_3$). IR spectra were obtained with a JASCO IR-700 instrument. High resolution mass spectra were recorded on a JEOL JMS-SX/SX 102A instrument. FAB mass spectra were obtained by using *m*-nitrobenzyl alcohol as a matrix. Optical rotation was measured with a JASCO DIP-360 automatic digital polarimeter. 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 Table 4. GC analysis of enantiomeric excess was carried out using SHIMADZU GC-17A with SUPELCO β-DEX^{TM} 120 fused silica capillary column, as described in the footnote of each Table. 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. Iodosylbenzene was purchased from Tokyo Chemical Industry Co., Ltd. Manganese(II) acetate tetrahydrate was purchased from Nacalai Tesque Inc. (*1S,2S*)-1,2-Diaminocyclohexane and sodium hexafluorophosphate were purchased from Aldrich Chemical Co., Inc. Compound **7** was prepared according to the reported procedure.[12] 1,1-Dimethylindan was prepared according to the literature procedures.[18] Ethylbenzene and tetrahydronaphthalene were purchased from Nacalai Tesque Inc. 4-Methoxyethylbenzene was purchased from Tokyo Chemical Industry Co., Ltd. All the substrates for asymmetric oxidation were distilled prior to use.



Scheme 4

N,N'-Bis(3,5-di-*t*-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) hexafluorophosphate (2)

To a suspension of (*1S,2S*)-*N,N'*-bis(3,5-di-*t*-butylsalicylidene)-1,2-cyclohexanediamine[19] (65.0 mg, 119 μmol) in deaerated CH_3CN (6.0 ml) was added $Mn(OAc)_2 \cdot 4H_2O$ (29.2 mg, 119 μmol) in deaerated CH_3OH (1.0 ml) under argon atmosphere and the mixture was stirred for 30 min at room temperature. The mixture was warmed up to 50 °C, stirred for 3 h at the temperature, and allowed to cool to room temperature. To this mixture was added fericenium hexafluorophosphate (39.4 mg, 119 μmol) in deaerated CH_3CN (2.0 ml) and the whole mixture was stirred for another 3 h at room temperature. The mixture was concentrated *in vacuo*. The residue was chromatographed on a short silica gel (hexane/CH_2Cl_2= 1/0 to 19/1) and recrystallized from CH_2Cl_2-hexane to give **2** (62.1 mg, 70%) as dark brown crystals. M.p. (dec) 235-237 °C. IR (KBr): 3449, 2955, 1612, 1537, 1433, 1340, 1312, 1271, 1252, 1177, 845, 577, 559 cm^{-1}. Anal. Calcd for $C_{36}H_{52}F_6MnN_2O_2P \cdot 2CH_3OH$: C, 56.43; H, 7.48; N, 3.46%. Found: C, 56.58; H, 7.74; N, 3.31%. The complex was moisture-sensitive and stored under argon atmosphere.

4-(*t*-Butyldiphenylsilyl)phenylmagnesium bromide (6)

To a solution of 1,4-dibromobenzene (5.00 g, 21.2 mmol) in Et_2O (74 ml) was added a *n*-hexane solution of *n*-butyllithium (1.60 M, 12.9 ml, 20.6 mmol) at -20 °C and the mixture was stirred for 30 min at the temperature. To this solution was added *t*-butylchlorodiphenylsilane (5.0 ml, 19.1 mmol) in Et_2O (10 ml) dropwise over a period of 50 min. After stirring for 30 min at the same temperature, the cooling bath was removed, and the mixture was stirred for 2.5 h at room temperature, and refluxed for another 1 h. The reaction mixture was quenched with aqueous NH_4Cl, extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was diluted with pentane (30 ml) and Et_2O (15 ml) and the insoluble 1,4-bis(*t*-butyldiphenylsilyl)benzene was removed by filtration. The filtrate was concentrated *in vacuo*, and the resulting precipitate was collected by filtration and washed with MeOH to give 1-bromo-4-(*t*-butyldiphenylsilyl)benzene (3.78 g, 50 %) as colorless crystals. M.p. 110-111 °C. ^1H NMR: δ 7.56-7.32 (m, 14H), 1.17 (s, 9H). IR (KBr): 3044, 2966, 1568, 1479, 1427, 1107, 1009, 810, 741, 725, 700, 606, 530, 525 cm^{-1}. Anal. Calcd for $C_{22}H_{23}BrSi$: C, 66.83; H, 5.86%. Found: C, 66.95; H, 5.88%.

To a suspension of Mg (172 mg, 7.06 mmol) and 1,2-dibromoethane (cat. amount) in tetrahydrofuran (THF) (2.1 ml) was added 1-bromo-4-(*t*-butyldiphenylsilyl)benzene (2.54 g, 6.42 mmol) in THF (19.3 ml) dropwise over a period of 1 h. The mixture was refluxed for 2 h and allowed to cool to room temperature. This THF solution of 4-(*t*-butyldiphenylsilyl)phenylmagnesium bromide (**6**, ca 0.2 M) was used for the next reaction.

(a*R*)-2-Methoxymethoxy-2'-(4-*t*-butyldiphenylsilylphenyl)-1,1'-binaphthyl (8)

To a mixture of **7** (680 mg, 1.63 mmol) and $NiCl_2$(dppe) (42.9 mg, 81.3 μmol) was slowly added **6** (ca 0.2 M THF solution, 19.0 ml, 3.80 mmol) at room temperature and the mixture was refluxed for 2 h. After cooled to room temperature, the mixture was quenched with aqueous NH_4Cl and extracted with Et_2O. The extract was washed successively with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was submitted to column chromatography (SiO_2, hexane/CH_2Cl_2= 1/0 to 4/1 to 2/1) to give the coupling product (820 mg) which was contaminated with a small amount of (a*R*)-2-hydroxy-1,1'-binaphthyl, as colorless crystals. The crude product was used for the next reaction without further purification.

To sodium hydride (60% dispersion in mineral oil, 77.6 mg, 1.94 mmol) was added a solution of the crude coupling product (815 mg) in THF/*N*,*N*-dimethylformamide (5.2 ml, 1/1) at 0 °C and the mixture was stirred for 2 h at the temperature. To the mixture was added chloromethyl methyl ether (147 μl, 1.94 mmol) and the whole mixture was stirred for another 12 h at room temperature. The reaction mixture was quenched with water, extracted with Et_2O, washed three times with water, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexane/CH_2Cl_2= 1/0 to 4/1) to give **8** (808 mg, 79% for two steps) as colorless crystals. M.p. 88-89 °C. $[\alpha]_D^{29}$ +92.4° (*c* 0.26, $CHCl_3$). ^1H NMR: δ 8.03 (d, *J*= 8.6 Hz, 1H), 7.95 (d, *J*= 8.3 Hz, 1H), 7.82 (d, *J*= 9.2 Hz, 1H), 7.79 (d, *J*= 9.2 Hz, 1H), 7.72 (d, *J*= 8.3 Hz, 1H), 7.48-7.04 (m, 21H), 4.83 (ABq, *J*=7.6 Hz, 2H), 3.09 (s, 3H), 1.04 (s, 9H). IR (KBr): 3051, 2928, 2856, 1593, 1508, 1427, 1242, 1148, 1105, 1053, 1032, 814, 702, 509 cm^{-1}. Anal. Calcd for $C_{44}H_{40}O_2Si$: C, 84.03; H, 6.41%. Found: C, 83.76; H, 6.45%.

(a*R*)-3-Formyl-2-methoxymethoxy-2'-(4-*t*-butyldiphenylsilylphenyl)-1,1'-binaphthyl (9)

t-Butyllithium (1.7 M in pentane, 1.5 ml, 2.6 mmol) was added to a solution of **8** (803 mg, 1.28 mmol) and *N*,*N*-tetramethylethylenediamine (424 μl, 2.81 mmol) in THF (5.1 ml) at -78 °C and the mixture was stirred for 3 h at the temperature. After *N*,*N*-dimethylformamide (495 μl, 6.39 mmol) was added, the mixture was allowed to warm to room temperature and stirred for another 1 h. The reaction mixture was quenched with aqueous NH_4Cl, extracted with Et_2O, washed successively with aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexane/toluene= 1/0 to 1/1 to 0/1) to give **9** (773 mg, 92%) as colorless crystals. M.p. 90-91 °C. $[\alpha]_D^{27}$ -4.46° (*c* 0.22, $CHCl_3$). ^1H NMR: δ 10.33 (s, 1H), 8.43 (s, 1H), 8.07 (d, *J*= 8.3 Hz, 1H), 7.98 (d, *J*= 7.6 Hz, 2H), 7.73 (d, *J*= 8.3 Hz, 1H), 7.51-7.15 (m, 18H), 7.01 (d, *J*= 7.9 Hz, 2H), 4.51 (ABq, *J*= 5.9 Hz, 2H), 2.84 (s, 3H), 1.03 (s, 9H). IR (KBr): 3449, 3069, 2961, 2930, 2856, 1692, 1618, 1587, 1427, 1157, 1105, 1034, 966, 816, 702, 509 cm^{-1}. Anal. Calcd for $C_{45}H_{40}O_3Si$: C, 82.28; H, 6.14%. Found: C, 82.10; H, 6.18%.

(a*R*)-3-Formyl-2-hydroxy-2'-(4-*t*-butyldiphenylsilylphenyl)-1,1'-binaphthyl (10)

Bromotrimethylsilane (916 μl, 6.94 mmol) was added to a mixture of **9** (760 mg, 1.16 mmol) and MS 4Å (46 mg) in CH_2Cl_2 (4.6 ml) at 0 °C and stirred for 3 h at the temperature. The mixture was quenched with aqueous NH_4Cl, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was crystallized from ligroin to give **10** (577 mg, 81%) as yellow crystals. M.p. 208-209 °C. $[\alpha]_D^{27}$ -85.4° (*c* 0.18, $CHCl_3$). ^1H NMR: δ 10.40 (s, 1H), 10.09 (s, 1H), 8.16 (s, 1H), 8.07 (d, *J*= 8.6 Hz, 1H), 7.98 (d, *J*= 8.2 Hz, 1H), 7.87-7.83 (m, 1H), 7.72 (d, *J*= 8.6 Hz, 1H), 7.52-7.45 (m, 1H), 7.36-7.08 (m, 19H), 1.01 (s, 9H). IR (KBr): 3449, 3179, 3045, 2849, 1655, 1632, 1506, 1427, 1182, 1105, 937, 822, 758, 729, 700, 509 cm^{-1}. Anal. Calcd for $C_{43}H_{36}O_2Si$: C, 84.27; H, 5.92%. Found: C, 84.25; H, 5.93%.

Typical procedure for preparing (salen)manganese(III) complex

Preparation of complex **5b**: To a solution of (*1S*,*2S*)-1,2-diaminocyclohexane (11.5 mg, 101 μmol) in EtOH (10.0 ml) was added $Mn(OAc)_2 \cdot 4H_2O$ (24.7 mg, 101 μmol) and the mixture was stirred for 1 h at room temperature. To this solution was added **10** (124 mg, 202 μmol), and the whole mixture was stirred for 6 h at

50 °C in air. To the solution was added $NaPF_6$ (170 mg, 1.01 mmol), and the mixture was further stirred for another 20 h at the same temperature, then allowed to cool to room temperature, and concentrated to dryness. The residue was recrystallized from CH_2Cl_2-hexane. The combined first and second crops of **5b** weighed 123 mg (81%). Dark brown crystals. M.p. (dec) 230-232 °C. IR (KBr): 3518, 3049, 2930, 2856, 1609, 1348, 1327, 1290, 1105, 847, 816, 748, 700, 557, 511 cm^{-1}. Anal. Calcd for $C_{92}H_{80}F_6MnN_2O_2PSi_2 \cdot 2C_2H_5OH$: C, 72.34; H, 5.82; N, 1.76%. Found: C, 72.13; H, 5.68; N, 1.85%. HRFABMS m/z. Calcd. for $C_{92}H_{80}MnN_2O_2Si_2$ (-F_6P): 1355.5139. Found: 1355.5134.

(Salen)manganese(III) complex (5a)

Dark brown crystals. (The crude complex was recrystallized from CH_2Cl_2-hexane.) M.p. (dec) 213-215 °C. IR (KBr) 3449, 3049, 2928, 2856, 1597, 1427, 1331, 1294, 1105, 847, 737, 702, 557, 511 cm^{-1}. Anal. Calcd for $C_{104}H_{90}F_6MnN_2O_2PSi_2 \cdot 7/2H_2O$: C, 72.67; H, 5.69; N, 1.63%. Found: C, 72.72; H, 5.72; N, 1.59%. HRFABMS m/z. Calcd. for $C_{104}H_{90}MnN_2O_2Si_2$ (-F_6P): 1509.5921. Found: 1509.5928.

General procedure for benzylic oxidation

Typical procedure was exemplified with the oxidation of 1,1-dimethylindan using complex **5a** as a catalyst: In a 5 ml round-bottom flask were placed 1,1-dimethylindan (16.2 μl, 0.1 mmol), (salen)manganese(III) complex (**5a**, 3.3 mg, 2.0 μmol), and chlorobenzene (1.0 ml) under an argon atmosphere. The mixture was cooled in a liquid nitrogen bath, degassed three times, and allowed to warm to -20 °C. This solution was transferred by using a canula under an argon atmosphere, to another flask containing iodosylbenzene (22.0 mg, 0.1 mmol) and stirred for 20 h at the same temperature. The reaction mixture was quenched by adding several drops of dimethylsulfide and directly chromatographed on short silica gel column (hexane/ethyl acetate= 1/1). The yield of 3,3-dimethylindan-1-ol (25 %) and 3,3-dimethylindan-1-one (10 %) were determined by GLC (optically active column: SUPELCO β-DEX™ 120 fused silica capillary column) analysis using *p*-dichlorobenzene as an internal standard. The optical purity of the alcohol was determined to be 90% ee by GLC analysis.

Isolation of the products was carried out as follows. The reaction mixture was quenched by adding several drops of dimethylsulfide and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane/ethyl acetate= 1/0 to 9/1 to 8/2) to give 3,3-dimethylindan-1-ol (3.3 mg, 20 %) and 3,3-dimethylindan-1-one (1.4 mg, 9 %).

NMR and chiroptical data of the benzylic alcohols obtained

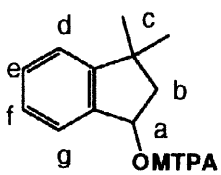
(*R*)-3,3-Dimethylindan-1-ol (90% ee); $[\alpha]_D^{25}$ -27.1° (*c* 0.11, $CHCl_3$). ^1H NMR: δ 7.41-7.37 (m, 1H), 7.33-7.18 (m, 3H), 5.30-5.24 (m, 1H), 2.39 (dd, *J*= 12.9 and 6.9 Hz, 1H), 1.84 (dd, *J*= 12.9 and 5.9 Hz, 1H), 1.72 (br s, 1H), 1.40 (s, 3H), 1.22 (s, 3H).

The absolute configuration of 3,3-dimethylindan-1-ol was determined after it was converted to the corresponding (*R*)- and (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetic acid esters (MTPA esters) by its treatment with (*R*)- or (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride and triethylamine. According to the Kusumi's procedure,[20] the relevant ^1H-NMR (600 MHz) spectroscopic data of MTPA esters were collected as described in Table 4. All the signals were reasonably assigned by analyzing the ^1H-^1H COSY spectra. Considering the sign of Δδ values, the absolute configuration of C1-carbon in the major enantiomer was determined to be *R*.

(*R*)-1-Phenyl-1-ethanol (78% ee); $[\alpha]_D^{30}$ +37.0° (*c* 0.06, CH_2Cl_2). [Lit.[21](96.2% ee) $[\alpha]_D^{23}$ +48.6° (*c* 1.0, CH_2Cl_2)] ^1H NMR: δ 7.47-7.27 (m, 5H), 4.91 (q, *J*= 6.6 Hz, 1H), 1.65 (br s, 1H), 1.50 (d, *J*= 6.6 Hz, 3H).

(*R*)-1-(4-Methoxyphenyl)-1-ethanol (87% ee); $[\alpha]_D^{25}$ +44.7° (*c* 0.13, $CHCl_3$). [Lit.[21](88.5% ee) $[\alpha]_D^{20}$ +47.2° (*c* 1.0, $CHCl_3$)] ^1H NMR: δ 7.31 (d, *J*= 8.8 Hz, 2H), 6.89 (d, *J*= 8.8 Hz, 2H), 4.87 (dq, *J*= 8.3 and 3.3 Hz, 1H), 3.81 (s, 3H), 1.70 (d, *J*= 3.3 Hz, 1H), 1.49 (d, *J*= 6.3 Hz, 3H).

Table 4. ^{1}H NMR data (chemical shifts and Δδ values) of (*R*)- and (*S*)-MTPA esters of 3,3-dimethylindan-1-ol[a)]

		δ*R* (ppm)	δ*S* (ppm)	Δδ (δ*R* -δ*S*)
	a	6.41	6.41	-0.00
	b	2.00	2.08	-0.08
		2.37	2.45	-0.08
	c	1.30	1.31	-0.01
		1.21	1.29	-0.08
	d	7.21	7.19	+0.02
	e	-[b)]	7.33	+[c)]
	f	7.24	7.20	+0.04
	g	7.40	7.30	+0.10

a) Data were obtained in $CDCl_3$ by using 600 MHz NMR.

b) Exact chemical shift could not be determined.

c) The sign of Δδ was positive but its exact value was not determined.

(*R*)-1,2,3,4-Tetrahydro-1-naphthol (77% ee); $[\alpha]_D^{24}$ -20.3° (*c* 0.08, $CHCl_3$). [Lit.[22] (>99.9% ee) $[\alpha]_D^{25}$ +26.8° (*c* 2.3, $CHCl_3$) reported for the (*S*)-enantiomer] ^{1}H NMR: δ 7.45-7.41 (m, 1H), 7.26-7.17 (m, 2H), 7.13-7.08 (m, 1H), 4.80 (br s, 1H), 2.87-2.69 (m, 2H), 2.04-1.68 (m, 5H).

General procedure for kinetic resolution of racemic benzylic alcohols

General procedure was exemplified with oxidation of (±)-phenethyl alcohol using complex **5b** as a catalyst: To a 5 ml round-bottom flask containing (salen)manganese(III) complex (**5b**, 3.0 mg, 2.0 μmol) was added a chlorobenzene solution (1.0 ml) of (±)-phenethyl alcohol and *p*-dichlorobenzene as an internal standard (concentration of each substrate was 0.1 M and 0.05 M, respectively) under an argon atmosphere. The mixture was cooled in a liquid nitrogen bath, degassed three times, and allowed to warm to room temperature. The 10 % of this solution was taken out of the flask as a zero point, directly chromatographed on a short silica gel (hexane/ethyl acetate= 1/1) and submitted to GLC analysis using optically active column (SUPELCO β-DEX™ 120 fused silica capillary column). The resultant solution was cooled to -30 °C and transferred by using a canula under an argon atmosphere to the pre-cooled (-30 °C) flask containing iodosylbenzene (19.8 mg, 0.09 mmol) and stirred for 12 h at -30 °C. The reaction mixture was quenched by adding several drops of dimethylsulfide and directly chromatographed on a short silica gel column (hexane/ethyl acetate= 1/1) to remove the catalyst. The eluate was submitted to GLC analysis to determine the amounts of resulting alcohol and ketone.

The optical purity of the unreacted alcohol was determined by HPLC analysis of 3,5-dinitrobenzoate derivative using optically active column (DAICEL CHIRALPAK AD, hexane/2-propanol= 15/1, flow rate= 0.5 ml/min).

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7. In the preliminary communication (ref. 3), we used commercially available Jacobsen catalyst (from Aldrich) bearing chloride as an axial ligand. In the present study, however, we used the cationic type of Jacobsen catalyst **2** to compare its catalytic activity with our Mn-salen catalysts (**1**, **5a**, and **5b**) that are cationic complexes. We appreciate the referee's comment to use the cationic Jacobsen catalyst for comparison, instead of neutral Jacobsen catalyst.
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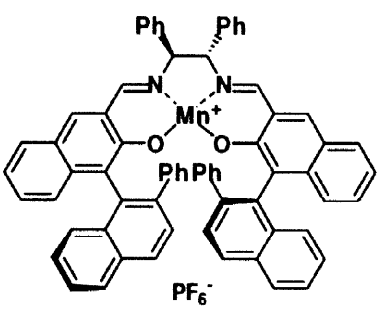

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