Pergamon

Tetrahedron 54 (1998) 10339–10348

TETRAHEDRON

Asymmetric Desymmetrization of *meso*-Tetrahydrofuran Derivatives by Highly Enantiotopic Selective C-H Oxidation

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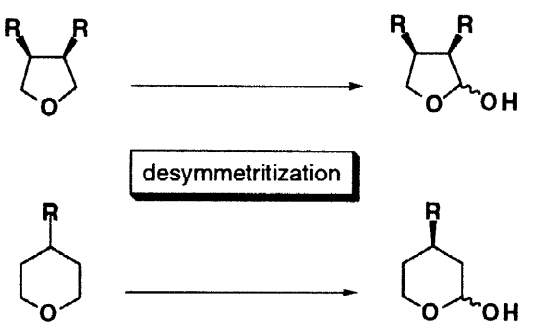
Received 5 January 1998; accepted 26 January 1998

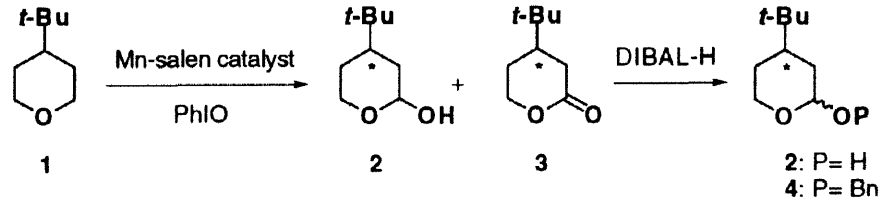
Abstract: Asymmetric desymmetrization of *meso*-tetrahydrofuran derivatives was successfully achieved by Mn-salen catalyzed enantiotopic selective C-H oxidation, giving optically active lactols (up to 90% ee) which serve as useful chiral building blocks for organic synthesis. © 1998 Elsevier Science Ltd. All rights reserved.

Recent development of asymmetric metal catalysis has realized highly enantioface-selective oxidation of carbon-carbon double bonds such as epoxidation, dihydroxylation, and aziridination.[1] On the other hand, enantiotopic selective C-H bond oxidation has so far been met with limited success: moderate to good enantioselectivity has been achieved in the oxidation of activated benzylic[2] and allylic C-H bonds.[3] This is mainly due to the high stability of C-H σ-bond which compels vigorous reaction conditions or use of highly reactive oxidants and makes realization of high enantioselectivity in C-H bond oxidation difficult. However, there are many biological C-H bond oxidations which proceed with high stereo- and regioselectivity. These oxidations are catalyzed by oxidizing enzymes which carry metallocomplex(es) as their active sites. For example, it is well known that an iron-porphyrin complex serves as the active site of oxidizing enzyme, cytochrome•P-450, and a dinuclear non-heme iron complex as the active site of methane monooxygenase. This suggests that a well-designed metal complex can be a good catalyst for enantiotopic selective oxidation of C-H bond. Recently, we and others have demonstrated that (salen)manganese(III) complexes (hereafter referred to as Mn-salen complexes) are excellent catalysts for asymmetric epoxidation of simple olefins.[4] We have also

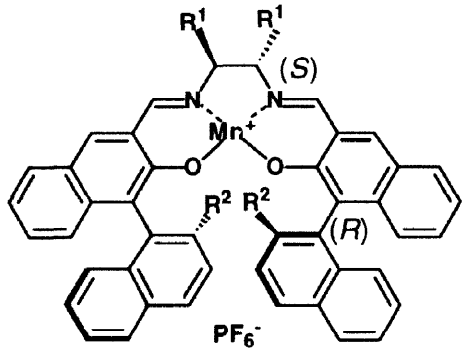


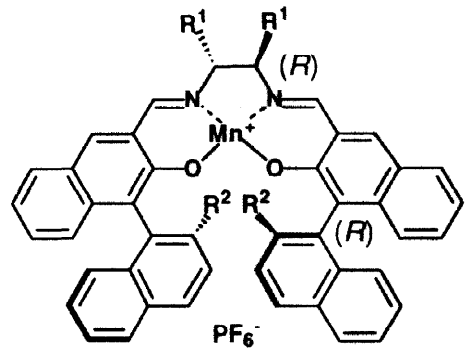
Scheme 1. Desymmetrzation of *meso*-tetrahydrofurans and prochiral tetrahydropyrans

PII: S0040-4020(98)00489-X



Scheme 2





(*R,S*)-**5**: R^1= -$(CH_2)_4$-
R^2= C_6H_5

(*R,S*)-**6**: R^1= -$(CH_2)_4$-
R^2= 4-(TBDPS)C_6H_4

(*R,S*)-**7**: R^1= C_6H_5
R^2= 4-(TBDPS)C_6H_4

(*R,R*)-**5**: R^1= -$(CH_2)_4$-
R^2= C_6H_5

(*R,R*)-**6**: R^1= -$(CH_2)_4$-
R^2= 4-(TBDPS)C_6H_4

(*R,R*)-**7**: R^1= C_6H_5
R^2= 4-(TBDPS)C_6H_4

disclosed that Mn-salen complexes are effective catalysts for enantioselective hydroxylation of a prochiral benzylic carbon.[2b] There is, however, no successful example of desymmetrization of *meso*- or prochiral-compounds through enantiotopic selective oxidation performed by molecular catalyst, though oxidative desymmetrization of these classes of compounds is a useful synthetic tool. For example, oxidative desymmetrization of *meso*-tetrahydrofurans and prochiral tetrahydropyrans provides the corresponding optically active lactols (Scheme 1) which can be readily oxidized to butyrolactones and varelolactones, respectively. Both the lactols and lactones are useful building blocks in organic synthesis. Furthermore, the easy availability of many *meso*- or prochiral cyclic ethers enhances the synthetic utility of oxidative desymmetrization. To realize highly effective desymmetrization and to expand the scope of enantioselective C-H oxidation, we examined Mn-salen catalyzed oxidation of prochiral cyclic ethers.[5]

At first, we examined the oxidation of 4-(*t*-butyl)tetrahydropyran **1**[6] as a test material in chlorobenzene[7] using iodosylbenzene as a terminal oxidant in the presence of catalytic amount of Mn-salen complex (*R,S*-**5**-**7** or *R,R*-**5**)[8] as a catalyst which has asymmetric centers both at ethylenediamine and salicyl aldehyde moieties (Scheme 2). We have already demonstrated that the relative configuration of these asymmetric moieties affects enantioselectivity of the oxidation examined and that the best combination of these moieties varies with the type of reactions.[4a,b] For example, (*R,S*)-complexes generally show higher enantioselectivity in epoxidation of olefins and benzylic hydroxylation than the corresponding (*R,R*)-complexes, while (*R,R*)-complexes show higher enantioselectivity in oxidation of sulfides than (*R,S*)-complexes. Thus, oxidation of **1** was studied with

Table 1. Oxidative desymmetrization of **1** using Mn-salen complexes as catalysts[a)]

entry	catalyst	temp. (°C)	time (h)	yield(%)[b)]	% ee[c)]
1	(*R*,*S*)-**5**	10	2	12	3
2	(*R*,*S*)-**6**	10	1	12	3
3	(*R*,*S*)-**7**	10	2	2	3
4	(*R*,*R*)-**5**	10	2	12	22
5	"	-10	4	14	36
6	"	-40	71	13	48

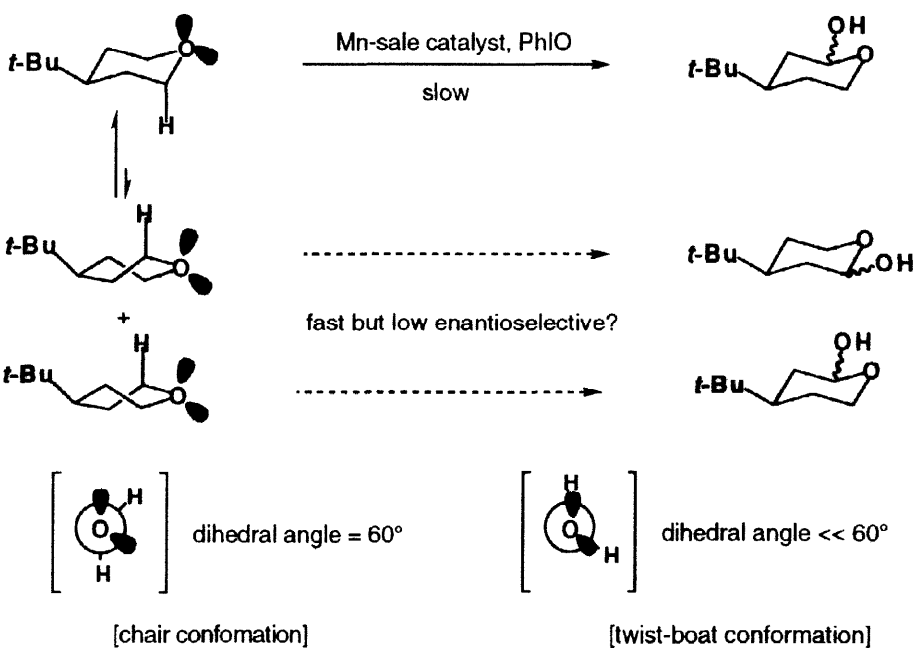
a) The reaction was carried out in chlorobenzene by using 1 equivalent of iodosylbenzene as an oxidant.

b) Isolated yield of the lactol after DIBAL-H reduction.

c) Determined by HPLC using optically active column (DAICEL CHIRALCEL OD, hexane/*i*-PrOH 100:1).

both (*R*,*S*)- and (*R*,*R*)-complexes. All the reactions afforded a mixture of the corresponding lactol **2** and lactone **3** as the products. To determine enantiotopic selectivity of the reaction, the mixture was directly treated with diisobutylaluminum hydride (DIBAL-H) to give the lactol **2** which was in turn converted into the corresponding *trans*- and *cis*-benzyl acetals **4**. These isomeric acetals were separated by silica gel chromatography (pentane-ether = 30 : 1) and their enantiomeric excesses were determined by HPLC analysis. Enantiomeric excesses of both the *trans*- and *cis*-acetals were identical. The results are summarized in Table 1. (*R*,*S*)-Complexes showed very poor enantioselectivity (entries 1-3), while (*R*,*R*)-complex **5** showed modest but considerably improved enantioselectivity of 22% ee (entry 4). Enantioselectivity enhanced up to 48% ee by lowering the reaction temperature (entries 5 and 6). In all cases, however, the reaction rates were slow.

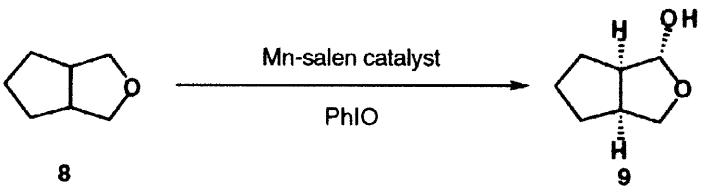
Recently, Koga and the co-worker have reported highly enantiotopic selective proton abstraction.[9] In this study, they reported that enantioselectivity of the reactions using cyclohexanone derivatives as substrates was affected by the participation of a boat conformer. The substrate of the present reaction, 4-(*t*-



Scheme 3

butyl)tetrahydropyran, also exists in an equilibrium mixture of chair and enantiomeric twist-boat conformers, though the chair conformer is far most stable than the twist-boat conformers. It was, however, considered that the reaction via the enantiomeric twist boat-conformers participated in the present reaction to a considerable extent and caused deterioration of enantioselectivity, for the following reason (Scheme 3). Ether oxidation starts with α-hydrogen atom abstraction, and the interaction of the resulting incipient SOMO orbital with vicinal *n*-orbital is expected to stabilize the transition state of the reaction and to accelerate hydrogen abstraction.[10] Therefore, the conformer having a smaller dihedral angle between these two orbitals (C-H σ- and *n*-orbitals) is expected to react faster than the conformer having the larger dihedral angle. In the chair conformer, the dihedral angle is 60° but, in twist-boat conformers, the dihedral angle is much smaller. Thus, the enantiomeric twist-boat conformers were considered to react faster than the chair conformer, but to show low enantioselectivity.

These analyses prompted us to use a conformationally fixed and planar cyclic ether such as 3-oxa-bicyclo[3.3.0]octane (**8**) which has a small dihedral angle, as a substrate for the present oxidation. Differing from the oxidation of 4-(*t*-butyl)tetrahydropyran, oxidation of **8** gave one lactol isomer **9** as a major product and the formation of the lactone was slow. This is probably because the lactol having *exo*-configuration is formed preferentially to minimize steric repulsion and oxidation of the sterically hindered *endo* C-H bond at



8 **9**

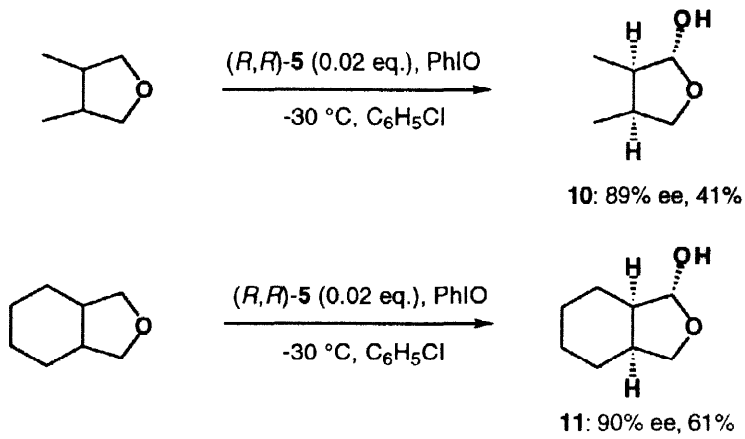
Table 2. Desymmetrization of **8** using Mn-salen complexes as catalysts[a)]

entry	catalyst	temp. (°C)	solvent	time (h)	yield (%)	% ee	Confign.[b)]
1	(*R,S*)-**5**	-10	C_6H_5Cl	1	26	3	(1*R*,5*S*)
2	(*R,S*)-**6**	-10	"	4	22	21	(1*R*,5*S*)
3	(*R,S*)-**7**	-10	"	2	28	19	(1*R*,5*S*)
4	(*R,R*)-**5**	-10	"	4	45	77	(1*R*,5*S*)
5	"	-10	C_6H_5F	4	29	73	(1*R*,5*S*)
6	"	-10	acetone	3.5	37	74	(1*R*,5*S*)
7	"	-10	CH_2Cl_2	4	9	69	(1*R*,5*S*)
8	"	-10	ethyl acetate	4	19	65	(1*R*,5*S*)
9	"	-30	C_6H_5Cl	65	59	82	(1*R*,5*S*)
10	(*R,R*)-**6**	-10	"	2	30	41	(1*R*,5*S*)
11	(*R,R*)-**7**	-10	"	3	27	42	(1*R*,5*S*)

a) The reaction was carried out by using 1 equivalent of iodosylbenzene as an oxidant.

b) The configuration of the major enantiomer of the product obtained in entry **9** was determined after its conversion to the corresponding lactone by comparison of specific rotation with that of the known compound (see text). The configurations of the products in other entries were determined by the elution order of enantiomers in HPLC analysis using optically active column (DAICEL CHIRALCEL OD, hexane/*i*-PrOH 1000/1).

the acetal carbon is slow. The enantiomeric excess of the lactol was determined by HPLC analysis after the lactol was converted into the corresponding benzyl acetal. The results are summarized in Table 2. (*R,S*)-Complexes **5-7** again showed poor enantioselectivity (entries 1-3), while (*R,R*)-complexes **5-7** showed moderate to good enantioselectivity. Especially oxidation with (*R,R*)-**5** gave the corresponding lactol of 77% ee (entry 4). We also examined oxidation of **8** with (*R,R*)-**5** in other solvents but the reaction in chlorobenzene gave the best result in terms of enantioselectivity and chemical yield (entries 5-8). The reaction at lower temperature (-30 °C) improved enantioselectivity up to 82% ee (entry 9) together with slightly better chemical yield. The reaction at -40 °C exhibited the same level of enantioselectivity (82% ee) but the yield of **9** decreased to 49%.



Scheme 4

We also examined oxidation of 3,4-dimethyltetrahydrofuran and 8-oxabicyclo[4,3,0]nonane under the optimized conditions (Scheme 4). Both the reactions proceeded with high enantiotopic selectivity of 89 and 90% ee, respectively, giving the corresponding lactols (**10** and **11**) in moderate to good yield.

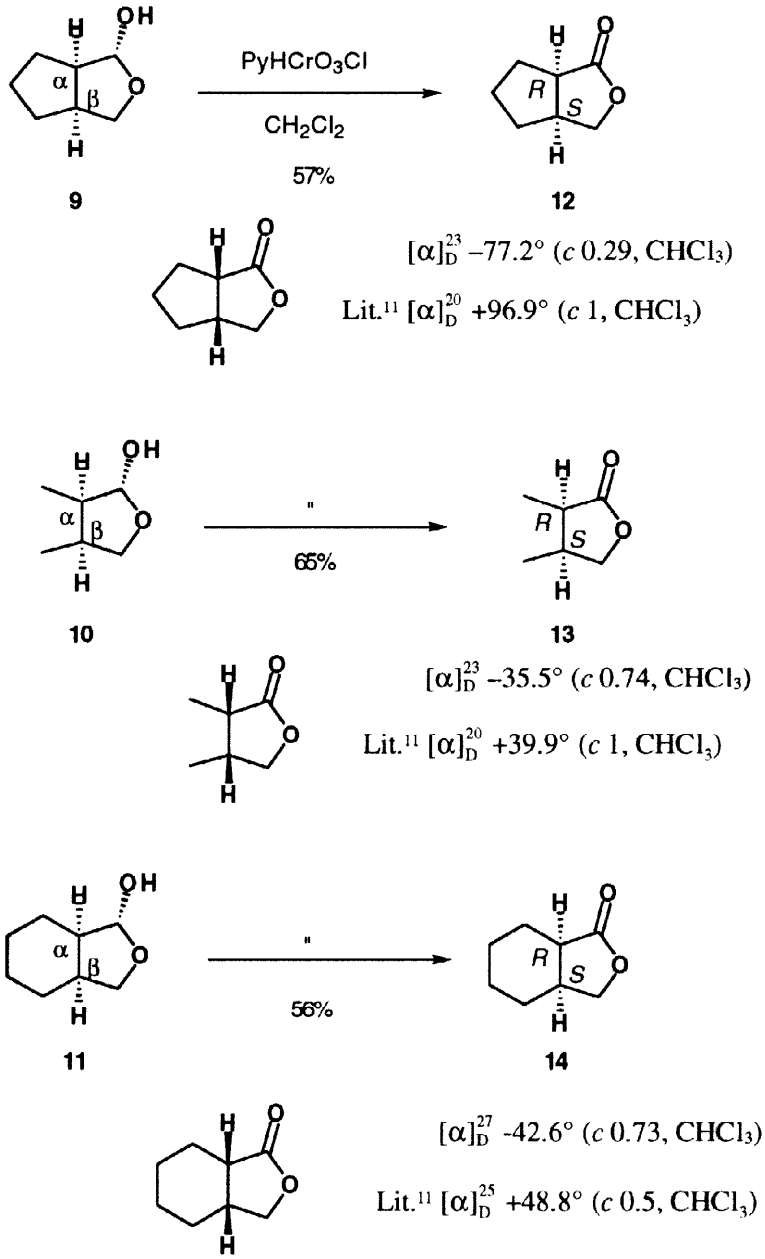
Absolute configurations of the lactols **9**, **10**, and **11** were determined to be $\alpha R,\beta S$ by the comparison of the specific rotation with the reported ones,[11] after they were converted into the corresponding lactones **12**, **13**, and **14** by oxidation using pyridinium chlorochromate (PCC) (Scheme 5).

In conclusion, we were able to demonstrate that Mn-salen complex (*R,R*)-**5** was an efficient catalyst for desymmetrization of *meso*-tetrahydrofuran derivatives. This is the first example of metal-catalyzed oxidative desymmetrization of *meso*-compounds.

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 CDCl3), unless otherwise noted. IR spectra were obtained with a JASCO IR-700 instrument. Optical rotation was measured with a JASCO DIP-360 automatic digital polarimeter. Column chromatography was conducted on Silica Gel 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) and experimental section. 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.



Scheme 5

Manganese(II) acetate tetrahydrate was purchased from Nacalai Tesque Inc. (*1R,2R*)-1,2-Diaminocyclohexane was purchased from Wako Pure Chemical Industries, Ltd. (*1S,2S*)-1,2-Diaminocyclohexane and sodium hexafluorophosphate were purchased from Aldrich Chemical Co., Inc. (*S,S*)- and (*R,R*)-1,2-diphenylethylenediamine were purchased from Environmental Research Center Co., Ltd. (*R*)-3-Formyl-2-hydroxy-2'-phenyl-1,1'-binaphthyl was prepared according to the reported procedure.[12] 8-Oxabicyclo[4.3.0]nonane was prepared according to the literature procedure.[13] 3-Oxabicyclo[3.3.0]octane is a known compound[14] but it was prepared from cyclopentene-1,2-dicarboxylic acid which was prepared according to the reported procedure,[15] by the sequence: i) catalytic hydrogenation with Pd-C, ii) LAH reduction of the resulting *cis*-cyclopentane-1,2-dicarboxylic acid, and iii) heating the resulting diol in DMSO.[13]

meso-3,4-Dimethyltetrahydrofuran is also a known compound,[16] but it was prepared according to the reported procedure.[17] Their spectroscopic data (^{1}H NMR and IR) are given below.

Mn-salen complex [(*R,R*)-5]

To a solution of (*1R,2R*)-1,2-diaminocyclohexane (23.8 mg, 210 μmol) in EtOH (15 ml) was added $Mn(OAc)_2$•$4H_2O$ (51 mg, 210 μmol) and the mixture was stirred for 1 h at room temperature. To this solution was added (a*R*)-3-formyl-2-hydroxy-2'-phenyl-1,1'-binaphthyl (157 mg, 420 μmol), and the whole mixture was stirred for 8 h at 60 °C in air. To this solution was added $NaPF_6$ (353 mg, 2.1 mmol), and the mixture was further stirred for 23 h at the same temperature, then allowed to cool to room temperature, and concentrated to dryness. The residue was chromatographed on silica gel (dichloromethane/methanol= 1/0 to 19/1) to give Mn-salen complex (*R,R*)-**5** (211 mg) as dark brown crystals in 98% yield. (*R,R*)-**5**: IR (KBr): 3568, 3051, 2936, 1611, 1583, 1350, 1327, 845 cm^{-1}. Anal. Calcd for $C_{60}H_{44}F_6MnN_2O_2P$•$2H_2O$: C, 67.93; H, 4.56; N, 2.64%. Found: C, 68.02; H, 4.62; N, 2.73%.

3-Oxabicyclo[3.3.0]octane (8)

^{1}H NMR: δ 3.81 (dd, *J*= 7.3, 8.9 Hz, 2H), 3.43 (dd, *J*= 3.6, 8.9 Hz, 2H), 2.67-2.62 (m, 2H), 1.76-1.39 (m, 6H). IR (neat): 2947, 2862, 2841, 1088, 1076, 918 cm^{-1}. Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78%. Found: C, 74.83; H, 10.74%.

8-Oxabicyclo[4.3.0]nonane

^{1}H NMR: δ 3.79 (dd, *J*= 6.6, 7.9 Hz, 2H), 3.63 (dd, *J*= 5.6, 7.9 Hz, 2H), 2.25-2.17 (m, 2H), 1.73-1.34 (m, 8H). IR (neat): 2924, 2856, 1448, 1084, 1063, 1032, 1007, 928, 895 cm^{-1}.

***meso*-3,4-Dimethyltetrahydrofuran**

^{1}H NMR: δ 3.92 (dd, *J*= 6.6, 8.3 Hz, 2H), 3.42 (dd, *J*= 5.9, 8.3 Hz, 2H), 2.21-2.32 (m, 2H), 0.93 (d, *J*= 6.9 Hz, 6H). ^{1}H NMR (C_6D_6): δ 3.83 (dd, *J*= 6.6, 8.3 Hz, 2H), 3.33 (dd, *J*= 5.9, 8.3 Hz, 2H), 1.87-1.94 (m, 2H), 0.68 (d, *J*= 6.6 Hz, 6H). ^{13}C NMR (C_6D_6): δ 74.8 (OCH_2), 36.8 (CH), 12.7 (CH_3). IR (neat): 2966, 2924, 2878, 2855, 1458, 1385, 1119, 1061, 1015, 999, 916 cm^{-1}.

General procedure for oxidative desymmetrization of *meso*-tetrahydrofuran derivatives using Mn-salen complex (*R,R*)-5 as a catalyst.

In a 10 ml round-bottom flask were placed 3-oxabicyclo[3.3.0]octane (**8**, 11.7 mg, 0.10 mmol), complex (*R,R*)-**5** (2.1 mg, 2.0 μmol), and chlorobenzene (1.0 ml) under nitrogen atmosphere. The mixture was cooled to -30 °C and transferred by using a cannula under nitrogen atmosphere, to another flask containing iodosylbenzene (22.0 mg, 0.10 mmol). The mixture was stirred for 65 h at the same temperature and quenched by adding several drops of dimethyl sulfide. The mixture was directly chromatographed on silica gel (hexane/ethyl acetate= 1/0 to 7/3) to give the corresponding lactol **9** (7.6 mg) in 59% yield. The lactol was used for the next reaction without further purification.

Typical procedure for the preparation of benzyl acetals

To a solution of 2-hydroxy-3-oxabicyclo[3.3.0]octane (**9**, 4.0 mg, 31 μmol) in dichloromethane (300 μl)

was added several drops of benzyl alcohol and catalytic amount of camphorsulfonic acid in air. After stirring for 2 h, the mixture was concentrated and chromatographed on silica gel (pentane/ether= 30/1) to give (1*R*,5*S*)-2-benzyloxy-3-oxabicyclo[3.3.0]octane (5.3 mg) in 79% yield. The enantiomeric excess of the product was determined to be 82% by HPLC analysis. $[\alpha]_D^{27}$ -112.9° (*c* 0.72, $CHCl_3$). ^1H NMR: δ 7.45-7.06 (m, 5H), 4.89 (s, 1H), 4.74 (d, *J*= 11.9 Hz, 1H), 4.41 (d, *J*= 11.9 Hz, 1H), 4.02 (dd, *J*= 8.6, 8.6 Hz, 1H), 3.51 (dd, *J*= 1.7, 8.6 Hz, 1H), 2.68-2.60 (m, 1H), 2.47 (m, 1H), 1.53-1.45 (m, 3H), 1.35-1.21 (m, 3H). IR (neat): 2949, 2868, 1497, 1454, 1350, 1094, 1063, 1016, 961, 930, 733, 698 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%. Found: C, 77.19; H, 8.44%. Configuration of the C2-acetal carbon is unknown.

trans-2-Benzyloxy-4-(*t*-butyl)tetrahydropyran (*trans*-4)

Relative configuration of the product was determined to be *trans*, based on the coupling constant of the proton at the acetal carbon. The enantiomeric excess was determined to be 48% ee by HPLC analysis. $[\alpha]_D^{27}$ -53.04° (*c* 1.15, $CHCl_3$, 48% ee). ^1H NMR: δ 7.37-7.09 (m, 5H), 4.96 (br d, *J*= 3.3, 1H), 4.75 (d, *J*= 12.2 Hz, 1H), 4.43 (d, *J*= 12.2 Hz, 1H), 3.81 (ddd, *J*= 4.3, 10.9, 10.9 Hz, 1H), 3.63 (ddd, *J*= 2.0, 4.3, 10.9 Hz, 1H), 1.77-1.70 (m, 2H), 1.32-1.21 (m, 3H), 0.73 (s, 9H). IR (neat): 2959, 2872, 1456, 1394, 1366, 1128, 1115, 1051, 982, 880, 733 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74%. Found: C, 77.39; H, 9.66%.

cis-2-Benzyloxy-4-(*t*-butyl)tetrahydropyran (*cis*-4)

Relative configuration of the product was determined to be *cis*, based on the coupling constant of the proton at the acetal carbon. The enantiomeric excess was determined to be 48% ee by HPLC analysis. $[\alpha]_D^{27}$ +33.6° (*c* 0.91, $CHCl_3$). ^1H NMR: δ 7.42-7.09 (m, 5H), 5.04 (d, *J*= 12.2 Hz, 1H), 4.61 (d, *J*= 12.2, 1H), 4.31 (dd, *J*= 2.3, 9.2 Hz, 1H), 3.95 (ddd, *J*= 3.2, 3.2, 11.6 Hz, 1H), 3.13 (ddd, *J*= 4.6, 6.9, 11.6, 1H), 1.86-1.81 (m, 1H), 1.45-0.87 (m, 4H), 0.70 (s, 9H). IR (neat): 2959, 2849, 1366, 1261, 1148, 1119, 1074, 951, 733, 698 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74%. Found: C, 77.34; H, 9.68%.

(3*R*,4*S*)-2-Benzyloxy-3,4-dimethyltetrahydrofuran

Absolute configuration of the acetal carbon has not been determined. The enantiomeric excess was determined to be 89% ee by HPLC analysis using optically active column (DAICEL CHIRALCEL OD, hexane/*i*-PrOH 1000/1). $[\alpha]_D^{25}$ -84.0° (*c* 0.64, $CHCl_3$). ^1H NMR: δ 7.35-7.26 (m, 5H), 4.82 (d, *J*= 1.3 Hz, 1H), 4.73 (d, *J*= 11.9 Hz, 1H), 4.46 (d, *J*= 11.9 Hz, 1H), 4.08 (dd, *J*= 7.9, 7.9 Hz, 1H), 3.53 (dd, *J*= 7.9, 7.9 Hz, 1H), 2.65-2.55 (m, 1H), 2.27-2.18 (m, 1H), 0.95 (d, *J*= 6.9 Hz, 3H), 0.91 (d, *J*= 7.3 Hz, 3H). IR (neat): 2966, 2934, 2878, 1454, 1385, 1356, 1094, 1043, 984, 916, 735, 696 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. Found: C, 75.66; H, 8.77%.

(1*R*,6*S*)-7-Benzyloxy-8-oxabicyclo[4.3.0]nonane

Absolute configuration of the C7-acetal carbon has not been determined. The enantiomeric excess was determined to be 90% ee by HPLC analysis using optically active column (DAICEL CHIRALCEL OD, hexane/*i*-PrOH 1000/1). $[\alpha]_D^{27}$ -82.9° (*c* 1.41, $CHCl_3$, 90% ee), ^1H NMR: δ 7.34-7.24 (m, 5H), 4.86 (d, *J*= 1.7 Hz, 1H), 4.74 (d, *J*= 11.9 Hz, 1H), 4.47 (d, *J*= 11.9 Hz, 1H), 4.00 (dd, *J*= 7.9, 7.9 Hz, 1H), 3.73 (dd, *J*= 7.9, 7.9 Hz, 1H), 2.57-2.53 (m, 1H), 2.14-2.10 (m, 1H), 1.65-1.28 (m, 8H). IR (neat) 2928, 2856, 1452, 1055, 1020, 1007, 914, 733, 696 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%. Found: C, 77.48; H, 8.62%.

2-Oxo-4-(*t*-butyl)tetrahydropyran (3)

In the oxidation of 4-(*t*-butyl)tetrahydropyran, the resulting lacol **2** and lactone **3** could not be separated chromatographycally. To identify the lactone **3**, the lactol **2** of 48% ee was oxidized to **3**.

To a stirred suspension of PCC (140 mg, 0.65 mmol) and celite (200 mg) in 4.5 ml of dichrolomethane was added a solution of **2** (21 mg, 0.13 mmol) in 0.5 ml of dichrolomethane. After the suspension had been stirred at 15°C for 5 h, this suspension was filtrated and the solvent was removed under reduced pressure. The residual mixture was subjected to column chromatography on silica gel (hexane/ethyl acetate= 7/3) to give 2-oxo-4-(*t*-butyl)tetrahydropyran (12.4 mg, 62%). $[\alpha]_D^{25}$ +13.8° (*c* 0.98, $CHCl_3$). ^1H NMR: δ 4.40 (ddd, *J*= 4.0, 4,0, 11.1 Hz, 1H), 4.22 (ddd, *J*= 3.3, 11.1, 11.1 Hz, 1H), 2.63 (dd, *J*= 5.9, 17.2 Hz, 1H), 2.28 (dd, *J*= 10.9, 17.2 Hz, 1H), 1.93-1.87 (m, 1H), 1.86-1.70 (m, 1H), 1.65-1.51 (m, 1H), 0.90 (s, 9H). IR (neat) 2963, 2872, 1740, 1477, 1400, 1369, 1292, 1261, 1238, 1202, 1080, 964, 839, 793 cm^{-1}. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32%. Found: C, 69.19; H, 10.25%.

Acknowledgment Financial support from a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan, and Asahi Glass Foundation is gratefully acknowledged.

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