1402 © *1990 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *63*, *1402—1408 (1990)* [Vol. 63, No. 5

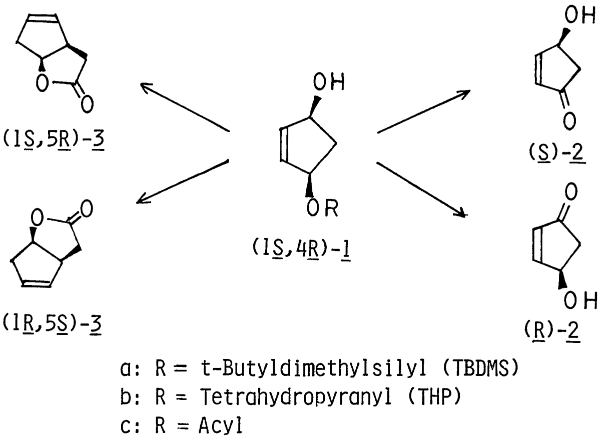
A Novel Asymmetric Synthesis of Chiral Cyclopentanoid Building Blocks by the Use of Chiral Lithium Amide

Masatoshi Asami
Department of Chemistry, Faculty of Education, Yokohama National University,
Tokiwadai, Hodogaya-ku, Yokohama 240

(Received December 13, 1989)

Enantioselective deprotonation of *meso*-epoxides, derived from 3-cyclopenten-1-ol, was examined using chiral lithium amide. Chiral *cis*-4-*t*-butyldimethylsiloxy-2-cyclopenten-1-ol, *cis*-4-tetrahydropyranyloxy-2-cyclopenten-1-ol, and their *trans*-isomers, which are useful chiral building blocks for the synthesis of cyclopentanoid natural compounds, were obtained with high enantiomeric excesses (72—90% ee). Both (*R*)- and (*S*)-4-hydroxy-2-cyclopenten-1-one were derived from (1*S*,4*R*)-4-*t*-butyldimethylsiloxy-2-cyclopenten-1-ol stereospecifically.

Chiral monoprotected *cis*-2-cyclopenten-1,4-diol (**1**) is known to be a useful chiral building block because it can be easily converted to both enantiomers of 4-hydroxy-2-cyclopenten-1-one (**2**)[1a] and 2-oxabicyclo[3.3.0]oct-6-en-3-one (**3**) (Scheme 1),[1a,b,d,f] pivotal intermediates in the total synthesis of optically active prostaglandins and other cyclopentanoids.[2—6] Therefore, considerable efforts have been made to develop an efficient method for the preparation of chiral **1** in recent years, and several methods have been devised.[1] Most of them employ enzymatic hydrolysis of *cis*-3,5-diacetoxy-1-cyclopentene[1b—h] and others employ enantioselective acylation of *cis*-2-cyclopentene-1,4-diol.[1a,i]



Scheme 1.

Recently we found that cyclic and acyclic *meso*-epoxides rearrange to chiral allylic alcohols with moderate to high stereoselectivity (41—92% enantiomeric excess (ee)) by enantioselective deprotonation by a chiral lithium amide, lithium (*S*)-2-(*N*,*N*-disubstituted aminomethyl)pyrrolidide (**4**).[7] This prompted us to develop a new and facile method for preparation of chiral *cis*-4-*t*-butyldimethylsiloxy-2-cyclopenten-1-ol (**1a**) and *cis*-4-tetrahydropyranyloxy-2-cyclopenten-1-ol (**1b**) starting from *meso*-epoxide, *cis*-4-*t*-butyldimethylsiloxy-1,2-epoxypentane (**5a**) and *cis*-4-tetrahydropyranyloxy-1,2-epoxycyclopentane(**5b**), using the asymmetric reaction. It was found that (1*S*,4*R*)-**1a** and (1*S*,4*R*)-**1b** were obtained in high ee as reported in a preliminary communication.[8]

At the same time, asymmetric transformation of *trans*-4-*t*-butyldimethylsiloxy-1,2-epoxycyclopentane (**6a**) and *trans*-4-tetrahydropyranyloxy-1,2-epoxycyclopentane (**6b**) was also examined. *trans*-4-*t*-Butyldimethylsiloxy-2-cyclopenten-1-ol (**7a**) and *trans*-4-tetrahydropyranyloxy-2-cyclopenten-1-ol (**7b**), which are also useful chiral intermediates in the synthesis of prostanoids,[9] were obtained in good ee under the different reaction conditions from that used in cases of *cis*-isomers **5a**, **b**.[10] Herein we wish to describe the results in detail.

Results and Discussion

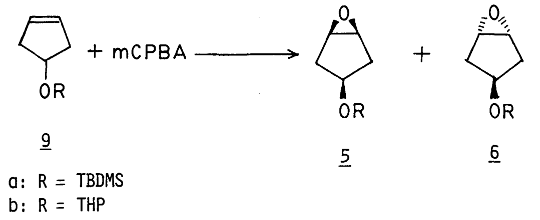
Preparation of Epoxides 5 and 6. All four epoxides **5a**, **b** and **6a**, **b** were prepared from 3-cyclopenten-1-ol (**8**).[11] Alcohol **8** was converted to 4-*t*-butyldimethylsiloxy-1-cyclopentene (**9a**) and 4-tetrahydropyranyloxy-1-cyclopentene (**9b**) in usual manners.[12,13] Epoxidation of **9a** was examined in various solvent with *m*-chloroperbenzoic acid (*m*CPBA) to afford a mixture of stereoisomers, that is, **5a** and **6a**. The isomers were easily separated by silica-gel column chromatography and the structures were determined by NMR spectra after transformation to **1a** or **7a**. In most of the solvents examined, *trans*-isomer **6a** was obtained predominantly, however, *cis*-isomer **5a** was obtained

Table 1. Epoxidation of **9a** and **9b** with *m*CPBA

Olefin	Solvent	Yield/%[a]	**5**:**6**
9a	Cyclohexane	82	20:80
9a	Cyclopentane	89	25:75
9a	Benzene	82	37:63
9a	CCl$_4$	53	22:78
9a	CH$_2$Cl$_2$	81	67:33
9a	Ether	64	19:81
9a	THF	73	17:83
9b	Cyclohexane	94	23:77
9b	CH$_2$Cl$_2$	67	40:60

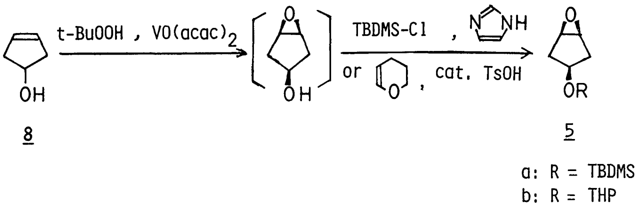
a) Isolated yield.

predominantly when the reaction was carried out in dichloromethane. Good yield and good selectivity was attained using cyclohexane as solvent. Epoxide **6b** was also obtained with good selectivity by the reaction of **9b** and *m*CPBA in cyclohexane. The results are summarized in Table 1.



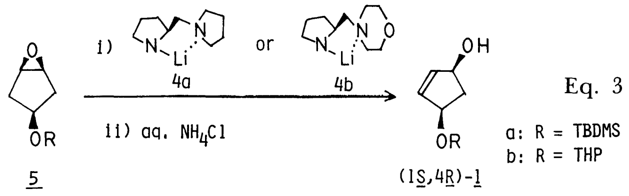
Eq. 1

Next, a stereoselective preparation of *cis*-epoxide **5** was examined. Only *cis*-epoxide **5a** was obtained in 65%[14] employing hydroxy directed epoxidation of **8** with *t*-butyl hydroperoxide and oxobis(2,4-pentanedionato)vanadium(IV) (VO(acac)$_2$) in benzene[15] followed by treatment of the reaction mixture with *t*-butyldimethylchlorosilane and imidazole in DMF. *cis*-Epoxide **5b** was also prepared stereoselectively in 49%[14] from **8** by the epoxidation and tetrahydropyranylation.



Eq. 2

Asymmetric Transformation of *cis*-Epoxide 5a and 5b. In the first place, asymmetric transformation of **5a** was examined using lithium (*S*)-2-(1-pyrrolidinylmethyl)pyrrolidide **4a** in THF. The reaction was carried out as follows: To a THF solution of (*S*)-2-(1-pyrrolidinylmethyl)pyrrolidine (**10a**) (1.65 mmol) was added a hexane solution of butyllithium (1.5 mmol) at 0 °C. After 30 min, a THF solution of **5a** (1.0 mmol) was added at 0 °C and stirring was continued for 3 h. Workup of the reaction mixture afforded (1*S*,4*R*)-**1a** ([α]$^{20}_{D}$ +16.5° (*c* 1.17, CHCl$_3$)) in 76% (66% ee). The absolute configuration and the optical purity was determined by comparing the optical rotation with the reported value after conversion to (1*S*,4*R*)-4-hydroxy-2-cyclopentenyl benzoate ([α]$^{21}_{D}$ −87.8° (*c* 2.40, CHCl$_3$); lit,[1a] [α]$^{20}_{D}$ +133° (*c* 1.7, CHCl$_3$) for (1*R*,4*S*)-4-hydroxy-2-cyclopentenyl benzoate). It was surprising that good selectivity was obtained for **4a**, because the selectivity was low for cyclopentene oxide.[7b,c] Then we examined the effect of reaction solvent to improve the optical purity of the resulting alcohol **1a**. The results are shown in Table 2 (Entries 1—5). High selectivity was attained by employment of solvent which did not coordinate to lithium atom of lithium amide **4a** while THF was the best solvent in the reaction of simple epoxides.[7c] Ee was increased to 90% by using benzene as reaction solvent. It is assumed that in non-coordinating solvent the reaction proceeded more preferentially via transition state A (Fig. 1) in which a tight complex (**11**) was formed effectively by coordination by two oxygen atoms in epoxide **5a** to lithium atom of lithium amide **4a** to yield (1*S*,4*R*)-**1a**. Disadvantages of transition state B (Fig. 1), which leads to (1*R*,4*S*)-**1a**, are due to lack of coordination by oxygen atom on a substituent of epoxide **5a** and steric repulsion between lithium amide **4a** and epoxide **5a**.



Eq. 3

The selectivity was not improved by introduction of one more oxygen atom into epoxide part (epoxide **5b**) or lithium amide part (lithium (*S*)-2-(morpholinomethyl)pyrrolidide **4b**) (Table 2, Entries 6—9). The absolute configuration and optical purity of **1b** was also determined based on the optical rotation after the

Table 2. Asymmetric Transformation of **5** with **4**

Entry	Epoxide	Lithium amide	Solvent	Yield/%[a]	[α]$_D$/° (temp(°C), *c*(CHCl$_3$))	Ee/%[b,c]
1	**5a**	**4a**	THF	76	+16.5 (20, 1.17)	66
2	**5a**	**4a**	Ether	83	+16.9 (22, 0.88)	70
3	**5a**	**4a**	Benzene	92	+21.5 (22, 0.94)	90(86)[d]
4	**5a**	**4a**	Toluene	84	+20.0 (22, 0.89)	84
5	**5a**	**4a**	Hexane	91	+21.0 (22, 0.82)	88
6	**5a**	**4b**	THF	65	+5.7 (22, 0.69)	26
7	**5a**	**4b**	Benzene	78	+19.7 (16, 0.68)	89
8	**5b**	**4a**	THF	89	+23.2 (19, 0.82)	62
9	**5b**	**4a**	Benzene	77	+27.3 (18, 0.77)	89

a) Isolated yield. b) Determined by comparing the optical rotation with the reported value after conversion to (1*S*,4*R*)-4-hydroxy-2-cyclopentenyl benzoate.[1a] c) In every case, (1*S*,4*R*)-**1** was obtained. d) Determined by ^{1}H NMR spectra of (*R*)- and (*S*)-4-acetoxy-2-cyclopenten-1-one derived from **1a** using Eu(hfbc)$_3$ as chiral shift reagent.[20]

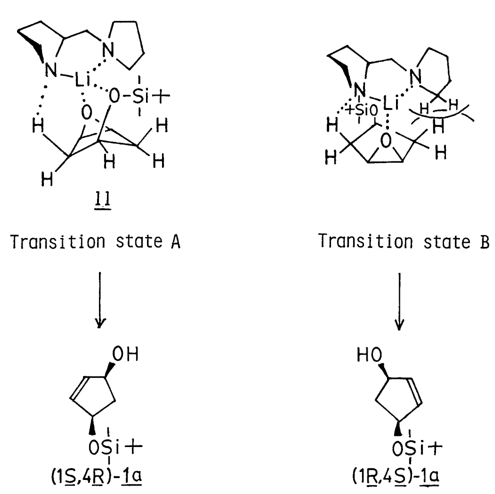


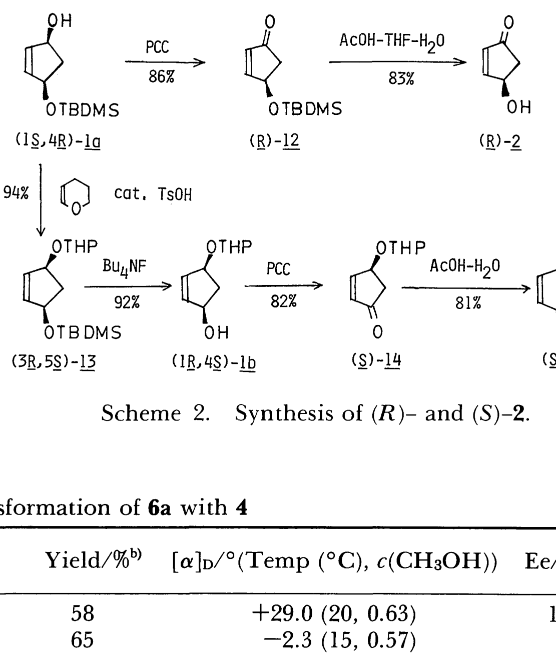
Fig. 1. Transition state models for the reaction of **4a** and **5a**.

conversion to (1*S*,4*R*)-4-hydroxy-2-cyclopentenyl benzoate.[1a,16)]

Syntheses of (*R*)- and (*S*)-4-Hydroxy-2-cyclopenten-1-one 2. The conversion of (1*R*,4*R*)-4-hydroxy-2-cyclopentenyl acetate,[9a)] (1*R*,4*S*)-**1b**,[1a)] or (1*S*,4*R*)-**1b**[1a)] to optically active **2** has already been reported. Therefore, we examined the transformation of (1*S*,4*R*)-**1a** to both (*R*)- and (*S*)-**2** employing similar reaction sequence. (Scheme 2)

(*R*)-4-Hydroxy-2-cyclopenten-1-one **2** ($[\alpha]_D^{25}$ +81.3° (*c* 1.55, $CHCl_3$); lit,[1a)] $[\alpha]_D^{20}$ −94.1° (*c* 3.4, $CHCl_3$) for (*S*)-**2**) was easily derived from (1*S*,4*R*)-**1a** ($[\alpha]_D^{22}$ +21.5° (*c* 0.94, $CHCl_3$)) via (*R*)-4-*t*-butyldimethylsiloxy-2-cyclopenten-1-one (**12**) ($[\alpha]_D^{25}$ +58.1° (*c* 1.13, CH_3OH); lit,[17)] $[\alpha]_D^{20}$ +67.4° (*c* 0.4, CH_3OH) for (*R*)-**12**), namely the oxidation with pyridinium chlorochromate (PCC)[18)] (86%) followed by deprotection in AcOH–THF–H_2O[9a,12)] (83%). Both *R*-**2** and *R*-**12** are key intermediates for the synthesis of naturally occurring prostaglandins.[2–5)]

Longer reaction sequence was required for the transformation to (*S*)-**2**. Alcohol (1*S*,4*R*)-**1a** ($[\alpha]_D^{22}$ +21.5° (*c* 0.94, $CHCl_3$)) was converted to (3*R*,5*S*)-3-*t*-butyldimethylsiloxy-5-tetrahydropyranyloxy-1-cyclopentene (**13**) ($[\alpha]_D^{24}$ +2.04° (*c* 1.08, $CHCl_3$)) with 3,4-dihydro-2*H*-pyran in 94%.[13)] Then *t*-butyldimethylsilyl group was removed selectively with tetrabutylammonium fluoride[12)] to afford (1*R*,4*S*)-**1b** ($[\alpha]_D^{27}$ −22.3° (*c* 1.25, $CHCl_3$)) in 92%. Alcohol (1*R*,4*S*)-**1b** was oxidized to (*S*)-4-tetrahydropyranyloxy-2-cyclopen-



Scheme 2. Synthesis of (*R*)- and (*S*)-**2**.

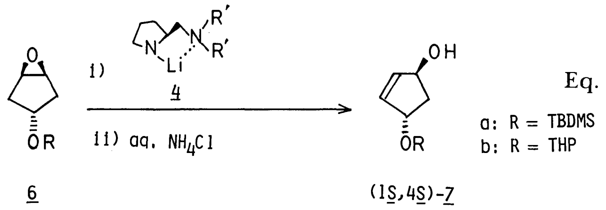
Table 3. Asymmetric Transformation of **6a** with **4**

Entry	Lithium amide	Solvent	Additive	Reaction conditions[a)]	Yield/%[b)]	$[\alpha]_D$/°(Temp (°C), *c*(CH_3OH))	Ee/%[c,d)]
1	**4a**	Hexane	—	Refl, 3.5 h	58	+29.0 (20, 0.63)	17
2	**4a**	Benzene	—	Rt, on	65	−2.3 (15, 0.57)	1
3	**4a**	Ether	—	Refl, 3.5 h	73	−47.3 (20, 0.78)	27
4	**4a**	DMM[e)]	—	Refl, 1 h	75	−72.2 (20, 0.81)	42
5	**4a**	DME[f)]	—	Refl, 2 h	57	−85.6 (17, 0.48)	49
6	**4a**	THF	—	Refl, 2 h	78	−100.3 (16, 0.66)	58
7	**4a**	THF	Pyridine	Refl, 1 h	93	−99.1 (15, 0.99)	57
8	**4a**	THF	$(C_2H_5)_3N$	Rt, 2 h	78	−106.8 (16, 0.83)	62
9	**4a**	THF	TMEDA[g)]	Rt, on	82	−104.8 (14, 0.62)	61
10	**4a**	THF	HMPA[h)]	Rt, 1 h	91	−107.9 (20, 0.90)	62
11	**4a**	THF	DBN[i)]	Rt, on	59	−118.4 (16, 0.61)	68
12	**4a**	THF	DBU[j)]	Rt, on	97	−129.0 (20, 0.69)	74[k)]
13	**4a**	Hexane	DBU	Rt, on	93	−126.1 (30, 0.92)	73
14	**4b**	THF	DBU	Rt, on	86	−122.7 (18, 0.66)	71
15	**4c**[l)]	THF	DBU	Rt, 3 h	64	−92.4 (20, 0.68)	53
16	**4d**[m)]	THF	—	Rt, on	81	−90.4 (21, 0.69)	52

a) Refl, rt, and on refer reflux, room temperature, and overnight respectively. b) Isolated yield. c) Determined by comparing the optical rotation with that obtained in Entry 12 ($[\alpha]_D^{16}$ −129° (*c* 0.69, CH_3OH) for 74% ee of (1*S*,4*S*)-**7a**). d) Except for Entry 1 (1*S*,4*S*)-**7a** was obtained. e) Dimethoxymethane. f) 1,2-Dimethoxyethane. g) *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine. h) Hexamethylphosphoric triamide. i) 1,5-Diazabicyclo[4.3.0]non-5-ene. j) 1,8-Diazabicyclo[5.4.0]undec-7-ene. k) Determined by comparing the optical rotation after conversion to (*S*)-4-*t*-butyldimethylsiloxy-2-cyclopenten-1-one.[17)] l) Lithium (*S*)-2-(piperidinomethyl)pyrrolidide.[7a,c)] m) Lithium (*S*)-2-[(4-methyl-1-piperazinyl)methyl]pyrrolidide.[7a,c)] ten-1-one (**14**) ($[\alpha]_D^{29}$ −54.9° (*c* 0.97, $CHCl_3$); lit,[1a] $[\alpha]_D^{20}$ −70.5° (*c* 1.3, $CHCl_3$)) with PCC[18] (82%), and then hydrolyzed with AcOH–H_2O[1a] to afford (*S*)-**2** ($[\alpha]_D^{24}$ −79.3° (*c* 1.5, $CHCl_3$)) in 81%. Compound (*S*)-**2** was employed as an important starting material in the synthesis of novel marine prostanoids clavulone II and 12-*O*-deacetylclavulone II.[19]

Both (*R*)- and (*S*)-**2** were derived to (*R*)- and (*S*)-4-acetoxy-2-cyclopenten-1-one, and ee of those were 86% by ^{1}H NMR spectra taken with tris(heptafluorobutyryl-*d*-camphorato)europium (III) (Eu(hfbc)$_3$).[20]

Asymmetric Transformation of *trans*-Epoxides 6a and 6b. Asymmetric transformation of **6a** to chiral **7a** was also examined using chiral lithium amide **4a** under a variety of reaction conditions. As shown in Table 3, THF was found to be best for reaction solvent to yield (1*S*,4*S*)-**7a** ($[\alpha]_D^{16}$ −100.3° (*c* 0.66, CH_3OH)) in 58% ee[21] (78%) (Entries 1—6). The selectivity was enhanced to 74% ee employing 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) as an additive (Entry 12) as observed in cases of simple epoxides.[7b,c] Similar selectivity (93%, 73% ee) was also obtained even in hexane in the presence of DBU (Entry 13), which indicated that DBU played a significant role in the reaction. Little selectivity was obtained in benzene (Entry 2) and low and opposite selectivity was obtained in hexane (Entry 1) though high selectivity was achieved in those solvents in case of *cis*-epoxide **5a**. These results support our assumption that the high selectivity achieved for *cis*-epoxide **5a** is due to the formation of complex **11** by two oxygen atoms in **5a**.



Eq. 4

The absolute configuration and ee were determined based on optical rotation of (*S*)-**12** ($[\alpha]_D^{18}$ −50.2° (*c* 1.02, CH_3OH)) obtained by oxidation of (1*S*,4*S*)-**7a** ($[\alpha]_D^{20}$ −129.0° (*c* 0.69, CH_3OH)).

Alcohol (1*S*,4*S*)-**7b** ($[\alpha]_D^{20}$ −129.0° (*c* 0.59, CH_3OH)) was also obtained in 78% with 72% ee by the reaction of **6b** and **4a** in THF in the presence of DBU (rt, 2.5 h).

It is noteworthy that good selectivity was also achieved for *trans*-epoxide **6** though the selectivity was low for cyclopentene oxide (41% ee) under similar reaction conditions.[7b,c]

Experimental

General. Melting and boiling points are uncorrected. ^{1}H NMR spectra were recorded on a Hitachi R-24B spectrometer or a JEOL FX-90Q spectrometer with tetramethylsilane as internal standard. IR spectra were taken on a Shimadzu IR-440 spectrometer. High resolution mass spectra were obtained on a Hitachi M-80 GC-MC spectrometer operating with an ionization energy (70 eV). Optical rotations were measured on a JASCO DIP-SL or a JASCO DIP-181 polarimeter. All solvents used were purified according to the standard procedure.

4-*t*-Butyldimethylsiloxy-1-cyclopentene 9a. To a DMF (5 ml) solution of 3-cyclopenten-1-ol **8** (0.50 g, 6.0 mmol) and imidazole (0.89 g, 13.1 mmol) was added *t*-butyldimethylchlorosilane (1.09 g, 7.2 mmol) at 0 °C under a nitrogen atmosphere and the reaction mixture was stirred at room temperature overnight. Hexane and water were added to the reaction mixture and the organic layer was washed with water and brine. After drying over anhydrous Na_2SO_4, the solvent was removed in vacuo. The crude product was purified by bulb-to-bulb distillation (150—160 °C (oven temperature)/90 mmHg 1 mmHg=133.322 Pa) to yield **9a** (1.09 g) in 92%. IR (neat): 3070, 2960, 2940, 2860, 1460, 1410, 1360, 1255, 1195, 1075, 960, 870, 835, and 775 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.05 (s, 6H), 0.9 (s, 9H), 1.9—3.0 (m, 4H), 4.3—4.8 (m, 1H), and 5.63 (s, 2H). Found: *m/z* 183.1210. Calcd for $C_{10}H_{19}OSi$: (M−15) 183.1204.

4-Tetrahydropyranyloxy-1-cyclopentene 9b. A mixture of **8** (0.42 g, 5 mmol), 3,4-dihydro-2*H*-pyran (2.5 g, 30 mmol), and *p*-toluenesulfonic acid (10 mg) in dichloromethane (25 ml) was stirred at 0 °C for 15 min. After addition of ether, the mixture was washed successively with brine, saturated $NaHCO_3$ solution, water, and brine. After drying over anhydrous Na_2SO_4, the organic layer was concentrated in vacuo. The crude product was purified by column chromatography (silica-gel/hexane–ether) followed by bulb-to-bulb distillation (100 °C (oven temperature)/0.15 mmHg; lit,[22] 54—55 °C/1.2 mmHg) to yield **9b** in 87%.

4-t-Butyldimethylsiloxy-1,2-epoxycyclopentane 5a and 6a. To **9a** (294 mg, 1.5 mmol) in solvent (6 ml) was added *m*-chloroperbenzoic acid (363 mg, 2.1 mmol) in several portions at 0 °C and the reaction mixture was stirred at room temperature overnight. Ether and water were added to the reaction mixture and the organic layer was washed with 10% $NaHSO_3$ solution until *m*CPBA was not detected any more. Then the organic layer was further washed with saturated $NaHCO_3$ solution, water, and brine, successively, and dried over anhydrous Na_2SO_4. After removal of solvent, *cis*-epoxide **5a** and *trans*-epoxide **6a** were separated by column chromatography (silica-gel/hexane–ether) (**6a** moved faster than **5a**). Epoxides **5a** and **6a** were further purified by bulb-to-bulb distillation. **5a**: bp 150 °C (oven temperature)/20 mmHg; IR (neat): 3030, 2970, 2940, 2900, 2860, 1460, 1400, 1370, 1255, 1210, 1100, 1035, 1015, 890, 840, and 780 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.05 (s, 6H), 0.9 (s, 9H), 1.8—2.3 (m, 4H), 3.33 (s, 2H), and 4.2—4.6 (m, 1H). Found: *m/z* 214.1413. Calcd for $C_{11}H_{22}O_2Si$: M, 214.1388. **6a**: bp 160 °C(oven temperature)/30 mmHg; IR (neat): 3050, 2980, 2960, 2920, 2880, 1475, 1465, 1375, 1285, 1260, 1120, 1075, 1020, 895, 840, and 780 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.05 (s, 6H), 0.9 (s, 9H), 1.56, and 2.40 (ABX, 4H, *J*=14 Hz and 7 Hz), 3.33 (s, 2H), and 4.05 (qui, 1H). Found: *m/z* 214.1389. Calcd for $C_{11}H_{22}O_2Si$: M, 214.1388.

The yields and the products ratios are summarized in Table 1.

4-Tetrahydropyranyloxy-1,2-epoxycyclopentane 5b and 6b. Epoxides **5b** and **6b** were prepared from **9b** in a similar manner as above. **5b**: bp 130 °C (oven temperature)/0.15 mmHg; IR (neat): 3040, 2950, 2880, 1455, 1440, 1420, 1350, 1240, 1200, 1140, 1120, 1080, 1035, 1025, 1005, 845, 790, and 765 cm^{-1}; ^{1}H NMR (CCl$_4$) δ=1.2—2.5 (m, 10H), 3.28 (s, 2H), 3.2—4.0 (m, 1H), and 4.45 (bs, 1H). Found: *m/z* 185.1150. Calcd for $C_{10}H_{17}O_3$: (M+1), 185.1175. **6b**: bp 130 °C(oven temperature)/0.15 mmHg; IR (neat): 3040, 2960, 2880, 2860, 1455, 1440, 1400, 1345, 1140, 1125, 1080, 1040, 1025, 980, and 835 cm^{-1}; ^{1}H NMR (CCl$_4$) δ=1.1—2.0 (m, 8H), 2.38 (ABX, 2H, *J*=7 and 2 Hz), 3.27 (s, 2H), and 3.0—4.2 (m, 3H), and 4.40 (bs, 1H). Found: *m/z* 185.1155. Calcd for $C_{10}H_{17}O_3$: (M+1), 185.1175.

The yields and the products ratios are shown in Table 1.

Stereoselective Synthesis of 5a. To a benzene (4 ml) solution of **8** (168 mg, 2.0 mmol) was added a catalytic amount of VO(acac)$_2$ and a benzene (2 ml) solution of *t*-butyl hydroperoxide (the solution was prepared by mixing *t*-butyl hydroperoxide (0.4 ml of 70% aqueous solution) and benzene (2 ml) and standing the mixture for 30 min with anhydrous MgSO$_4$) at room temperature and the reaction mixture was stirred overnight. The reaction mixture was directly separated by column chromatography (silica-gel/ether) to afford 3,4-epoxycyclopentanol. To a DMF (4 ml) solution of 3,4-epoxycyclopentanol thus obtained and imidazole (340 mg, 5.0 mmol) was added *t*-butyldimethylchlorosilane (354 mg, 2.4 mmol) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 7 h, then ether and water were added. The organic layer was washed with water and brine, and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent, crude product was purified by column chromatography (silica-gel/hexane–ether) to afford **5a** (138 mg) in 65% (**6a** was not detected by TLC).

Stereoselective Synthesis of 5b. A mixture of 3,4-epoxycyclopentanol, obtained in a similar manner as above from **8** (168 mg, 2.0 mmol), 3,4-dihydro-2*H*-pyran (572 mg, 6.8 mmol), and a catalytic amount of *p*-toluenesulfonic acid in dichloromethane (10 ml) was stirred at 0 °C for 15 min. After addition of ether, the mixture was washed successively with brine, saturated NaHCO$_3$, water and brine. After drying over anhydrous Na$_2$SO$_4$, the organic layer was concentrated in vacuo. The crude product was purified by column chromatography (silica-gel/hexane–ether) to afford **5b** (180mg) in 49% (**6b** was not detected by TLC).

Asymmetric Transformation of 5a. Under a nitrogen atmosphere, a hexane (1 ml) solution of butyllithium (1.5 mmol) was added to a solution of (*S*)-2-(1-pyrrolidinylmethyl)pyrrolidine **10a** (254 mg, 1.65 mmol) in solvent (5 ml) at 0 °C. After 30 min at 0 °C, **5a** (214 mg, 1.0 mmol) in solvent (4 ml) was added at 0 °C and stirring was continued for 3 h. Then, NH$_4$Cl solution and ether were added to the reaction mixture and the organic layer was washed with water and brine. After drying over anhydrous Na$_2$SO$_4$ and removal of the solvent in vacuo, the oily substance was purified by column chromatography (silica-gel/hexane–ether) to afford **1a**. IR (neat): 3300, 3040, 2920, 2840, 1460, 1360, 1250, 1120, 1095, 1065, 1015, 900, 835, 770, and 660 cm^{-1}; ^{1}H NMR (CCl$_4$) δ=0.05 (s, 6H), 0.9 (s, 9H), 1.50 (dt, 1H, *J*=15 and 5 Hz), 2.63 (dt, 1H, *J*=15 and 6 Hz), 3.50 (bs, 1H), 4.2—4.8 (m, 2H), and 5.6—6.0 (m, 2H). Found: *m/z* 196.1272. Calcd for $C_{11}H_{20}OSi$: (M−18), 196.1282.

The yields, optical rotations, and ee's are summarized in Table 2.

Asymmetric Transformation of 5b. The reaction was carried out in a similar manner as above to afford **1b**.[1a,d,f]

The results are shown in Table 2.

(1*S*,4*R*)-4-*t*-Butyldimethylsiloxy-2-cyclopentenyl Benzoate. To a dichloromethane (3 ml) solution of (1*S*,4*R*)-**1a** (94 mg, 0.44 mmol) ($[\alpha]^{22}_{D}$ +21.5° (*c* 0.94, CHCl$_3$)) and pyridine (139 mg, 1.76 mmol) was added a dichloromethane (3 ml) solution of benzoyl chloride (124 mg, 0.88 mmol) and a catalytic amount of 4-dimethylaminopyridine, and the reaction mixture was stirred at room temperature for several hours. After addition of ether and water, the organic layer was washed successively with 2% HCl solution, water, 4% NaHCO$_3$ solution, water, and brine, and dried over anhyd Na$_2$SO$_4$. The solvent was evaporated in vacuo and the resulting viscous oil was purified by preparative TLC (silica-gel/hexane–ether) to afford (1*S*,4*R*)-4-*t*-butyldimethylsiloxy-2-cyclopentenyl benzoate (129 mg) in 93%. $[\alpha]^{29}_{D}$ −60.8° (*c* 1.83, hexane). IR (neat): 3040, 2920, 2850, 1720, 1450, 1260, 1110, 1065, 1045, 905, 835, 775, and 710 cm^{-1}; ^{1}H NMR (CCl$_4$) δ=0.08 (s, 6H), 0.88 (s, 9H), 1.70 (dt, 1H, *J*=15 and 5 Hz), 2.85(dt, 1H, *J*=14 and 6 Hz), 4.73 (t, 1H, *J*=6 Hz), 5.5—5.9 (m, 1H), 5.97 (s, 2H), 7.1—7.7 (m, 3H), and 7.8—8.2 (m, 2H). Found: *m/z* 317.1554. Calcd for $C_{18}H_{25}O_3Si$: (M−1), 317.1571.

(1*S*,4*R*)-4-Hydroxy-2-cyclopentenyl Benzoate. (1*S*,4*R*)-4-*t*-Butyldimethylsiloxy-2-cyclopentenyl benzoate (129 mg, 0.41 mmol) ($[\alpha]^{29}_{D}$ −60.8°(*c* 1.83, hexane)) in 10 ml of AcOH–THF–H$_2$O (3:1:1) was stirred at room temperature for 14 h. Toluene was added to the reaction mixture and the mixture was concentrated azeotropically in vacuo below 30 °C.[9a,12] The residue was separated by preparative TLC (silica-gel/hexane–ether) to afford (1*S*,4*R*)-4-hydroxy-2-cyclopentenyl benzoate (70 mg) in 84% as white solid (mp 58—60 °C; lit,[1a] 62—63 °C). $[\alpha]^{17}_{D}$ −120.2° (*c* 1.73, CHCl$_3$) (lit,[1a] $[\alpha]^{20}_{D}$ +133° (*c* 1.7, CHCl$_3$) for (1*R*,4*S*)-4-hydroxy-2-cyclopentenyl benzoate).

(1*S*,4*R*)-4-Hydroxy-2-cyclopentenyl Benzoate from (1*S*,4*R*)-1b. Alcohol (1*S*,4*R*)-**1b** (77 mg, 0.42 mmol) ($[\alpha]^{18}_{D}$ +27.3° (*c* 0.77, CHCl$_3$)) was converted to the corresponding benzoate according to a procedure similar to that used for (1*S*,4*R*)-**1a** (2% HCl solution treatment was not done) in a quatitative yield (121 mg) after purification by preparative TLC (silica-gel/hexane–ether). IR (neat): 3050, 2940, 2860, 1710, 1600, 1580, 1445, 1270, 1140, 1065, 1020, and 710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.2—2.2 (m, 7H), 2.93 (dt, 1H, *J*=15 and 2 Hz), 3.3—4.2 (m, 2H), 4.5—5.0 (m, 2H), 5.5—5.9 (m, 2H), 5.9—6.3 (m, 2H), 7.0—7.7 (m, 3H), and 7.7—8.3 (m, 2H). The benzoate (121 mg) was then converted to (1*S*,4*R*)-4-hydroxy-2-cyclopentenyl benzoate by stirring in methanol in the presence of a catalytic amount of *p*-toluenesulfonic acid at room temperature for 1 h. Ether and water were added to the reaction mixture, and the organic layer was successively washed with saturated NaHCO$_3$ solution, water, and brine. After drying over anhydrous Na$_2$SO$_4$, the solvent was removed in vacuo and the residue was purified by preparative TLC (silica-gel/hexane–ethyl acetate) to afford (1*S*,4*R*)-4-hydroxy-2-cyclopentenyl benzoate (56 mg) in 65%. $[\alpha]^{16}_{D}$ −118.8° (*c* 1.7, CHCl$_3$).

(*R*)-4-*t*-Butyldimethylsiloxy-2-cyclopenten-1-one 12. To a dichloromethane (2 ml) suspension of pyridinium chlorochromate (244 mg, 1.13 ml) was added a dichloromethane (2 ml) solution of (1*S*,4*R*)-**1a** (133 mg, 0.63 mmol) ($[\alpha]^{22}_{D}$ +21.5° (*c* 1.01, CHCl$_3$)) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 2 h at room temperature and dry ether (20 ml) was added to it. The supernatant was decanted and the residue was washed three times with ether. The supernatant and washings were passed through a short silica-gel column (ether) and then concentrated in vacuo. The residue was purified by column chromatography (silica-gel/hexane–ether) to afford (*R*)-**12**[9a,17)] (132 mg) in 86%. $[\alpha]_D^{25}$ +58.1° (*c* 1.13, CH$_3$OH) (lit,[17)] $[\alpha]_D^{22}$ +67.4° (*c* 0.4, CH$_3$OH) for (*R*)-**12**).

(*R*)-4-Hydroxy-2-cyclopenten-1-one 2. Compound (*R*)-**12** (113 mg, 0.54 mmol) ($[\alpha]_D^{25}$ +58.1° (*c* 1.13, CH$_3$OH)) in 5 ml of AcOH–THF–H$_2$O (3:1:1) was stirred at room temperature for 21 h. Toluene was added to the reaction mixture and the mixture was concentrated in vacuo below 30 °C. The residue was purified by column chromatography (silica-gel/ether) to afford (*R*)-**2** (43.7 mg) in 83%. $[\alpha]_D^{25}$ +81.3° (*c* 1.55,CHCl$_3$), $[\alpha]_D^{26}$ +83.5° (*c* 2.00, CH$_3$OH) (lit, $[\alpha]_D^{20}$ −94.1° (*c* 3.4, CHCl$_3$) for (S)-**2**,[1a)] $[\alpha]_D^{24}$ +83.1° (*c* 1.70, CH$_3$OH) for 94% ee of (*R*)-**2**[20)]).

Acetylation of (*R*)-**2** (38 mg, 0.39 mmol) was conducted with acetic anhydride (48 mg, 0.47 mmol), pyridine (86 mg, 1.09 mmol), and a catalytic amount of 4-dimethylaminopyridine in dichloromethane (1 ml) at 0 °C for 30 min. Ether and water were added to the reaction mixture, and the organic layer was washed successively with 2% HCl solution, saturated NaHCO$_3$ solution, water, and brine, and dried over anhydrous Na$_2$SO$_4$. After evaporation of the solvent, the residue was purified by preparative TLC (silica-gel/hexane–ether) to afford (*R*)-4-acetoxy-2-cyclopenten-1-one (31 mg) in 57%. $[\alpha]_D^{22}$ +84.1° (*c* 1.48, CH$_3$OH) (lit,[20)] $[\alpha]_D^{22}$ +86.5° (*c* 3.00, CH$_3$OH) for 94% ee of (*R*)-4-acetoxy-2-cyclopenten-1-one). The ee was determined to be 86% on the basis of ^{1}H NMR taken with Eu(hfbc)$_3$ which exhibited the acetoxyl methyl signals at the different chemical shifts depending upon the enantiomers.[20)]

(3*R*,5*S*)-3-*t*-Butyldimethylsiloxy-5-tetrahydropyranyloxy-1-cyclopentene 13. A mixture of (1*S*,4*R*)-**1a** (166 mg, 0.78 mmol) ($[\alpha]_D^{22}$ +21.5° (*c* 0.94, CHCl$_3$)), 3,4-dihydro-2*H*-pyran (200 mg, 2.38 mmol), and a catalytic amount of *p*-toluenesulfonic acid in dichloromethane (2.5 ml) was stirred at 0 °C for 10 min. After addition of ether, the mixture was washed successively with saturated NaHCO$_3$ solution, water, and brine. After drying over anhydrous Na$_2$SO$_4$, the solvent was removed and the residue was purified by column chromatography (silica-gel/hexane–ether) to afford (3*R*,5*S*)-**13** (219 mg) in 94%. $[\alpha]_D^{24}$ +2.04° (*c* 1.08, CHCl$_3$). IR (neat): 3060, 2960, 2880, 1460, 1440, 1365, 1250, 1100, 1070, 1020, 840, and 780 cm^{-1}; ^{1}H NMR (CCl$_4$) δ=0.06(s, 6H), 0.90(s, 9H), 1.3—1.9 (m, 7H), 2.71 (dt, 1H, *J*=14 and 2 Hz), 3.2—4.2 (m, 2H), 4.4—4.9 (m, 3H), and 5.8—6.1 m, 2H).

(1*R*,4*S*)-4-Tetrahydropyranyloxy-2-cyclopenten-1-ol 1b. To a THF (0.5 ml) solution of tetrabutylammonium fluoride (427 mg, 1.48 mmol) was added a THF (3 ml) solution of (3*R*,5*S*)-**13** (219 mg, 0.74 mmol) ($[\alpha]_D^{24}$ +2.04° (*c* 1.08, CHCl$_3$)) at 0 °C under a nitrogen atmosphere. After stirring for 1 h at 0 °C, ether and saturated NH$_4$Cl solution was added to the reaction mixture. The organic layer was washed with water and brine, and dried over anhyd Na$_2$SO$_4$. The solvent was removed in vacuo and the residue was purified by column chromatography (silica-gel/ether) to afford (1*R*,4*S*)-**1b** (125 mg) in 92%. $[\alpha]_D^{27}$ −22.3° (*c* 1.25, CHCl$_3$).

(*S*)-4-Tetrahydropyranyloxy-2-cyclopenten-1-one 14. To a dichloromethane (1.5 ml) suspension of PCC (264 mg, 1.23 mmol) was added a dichloromethane (3.5 ml) solution of (1*R*,4*S*)-**1b** (125 mg, 0.68 mmol) ($[\alpha]_D^{27}$−22.3 ° (*c* 1.25, CHCl$_3$)) at 0 °C under a nitrogen atmosphere. The mixture was stirred for 16 h at room temperature and dry ether (20 ml) was added to it. The mixture was treated in a similar manner as used for the preparation of (*R*)-**12** to afford (*S*)-**14** (101 mg) in 82%. $[\alpha]_D^{29}$ −54.9° (*c* 0.97, CHCl$_3$) (lit,[1a)] $[\alpha]_D^{20}$ −70.5° (*c* 1.3, CHCl$_3$)).

(*S*)-4-Hydroxy-2-cyclopenten-1-one 2. Compound (*S*)-**14** (97 mg, 0.53 mmol) ($[\alpha]_D^{29}$ −54.9° (c 0.97, CHCl$_3$)) in 10 ml of AcOH–H$_2$O (7:3) was stirred at room temperature for 17 h. Toluene was added to the reaction mixture and the mixture was concentrated in vacuo below 30 °C. The residue was purified by column chromatography (silica-gel/ether) to afford (*S*)-**2** (42 mg) in 81% ($[\alpha]_D^{25}$ −79.3° (*c* 1.50, CHCl$_3$)), which was converted to (*S*)-4-acetoxy-2-cyclopenten-1-one ($[\alpha]_D^{26}$ −87.2° (*c* 1.49, CH$_3$OH)) in a similar manner as used for (*R*)-**2**. The ee was determined to be 86% on the basis of ^{1}H NMR taken in the presence of Eu(hfbc)$_3$.

Asymmetric Transformation of 6a and 6b. A representative reaction procedure is described for the reaction using chiral lithium amide **4a** in THF in the presence of DBU (Entry 12); To a THF (2 ml) solution of **10a** (254 mg, 1.65 mmol) was added a hexane (1 ml) solution of butyllithium (1.5 mmol) at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 30 min and a THF (1.5 ml) solution of DBU (251 mg, 1.65 mmol) was added at the temperature. After 30 min, a THF (2 ml) solution of **6a** (210 mg, 1.0 mmol) was added and the reaction mixture was stirred overnight at room temperature. Saturated NH$_4$Cl solution was added to the reaction mixture and it was extracted with ether. The organic layer was washed with water and brine, and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent, the residue was purified by column chromatography (silica-gel/hexane–ether) to afford (1*S*,4*S*)-**7a** (204 mg) in 97%. $[\alpha]_D^{20}$ −129.0° (*c* 0.69, CH$_3$OH) (lit,[9a)] $[\alpha]_D^{20}$ +81° (*c* 0.059, CH$_3$OH) for 56% ee of (1*R*,4*R*)-**7a**).

Spectral data for **7b** are as follows: IR (neat): 3350, 3040, 2930, 2860, 1445, 1430, 1355, 1195, 1125, 1110, 1050, 1015, 985, and 790 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.1—1.9 (m, 6H), 1.9—2.3 (m, 4H), 2.77 (bs, 1H), 3.2—4.1 (m, 2H), 4.63 (s, 1H), 4.97 (t, 2H, *J*=5 Hz), and 6.00 (s, 2H). Found: *m/z* 185.1206. Calcd for C$_{10}$H$_{17}$O$_3$: (M+1), 185.1177.

The yields, the optical rotations, and ee's are summarized in Table 3.

(*S*)-4-*t*-Butyldimethylsiloxy-2-cyclopenten-1-one 12. Alcohol (1*S*,4*S*)-**7a** ($[\alpha]_D^{20}$−129.0 ° (*c* 0.69, CH$_3$OH)) was converted to (*S*)-**12** in a similar manner as described for (1*S*,4*R*)-**1a** in 87%. $[\alpha]_D^{18}$ −50.2° (*c* 1.02, CH$_3$OH).

(1*S*,4*S*)-4-Hydroxy-2-cyclopentenyl Acetate. A mixture of (1*S*,4*S*)-**7b** (59 mg, 0.32 mmol) ($[\alpha]_D^{20}$ −129.0° (*c* 0.59, CHCl$_3$), acetic anhydride (65 mg, 0.64 mmol), pyridine (101 mg, 1.28 mmol), and a catalytic amount of 4-dimethylaminopyridine in dichloromethane (3 ml) was stirred at room temperature overnight. After addition of ether and water, the organic layer was washed successively with 4% NaHCO$_3$ solution, water, and brine, and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography (silica-gel/hexane–ether) to afford (1*S*,4*S*)-4-tetrahydropyranyloxy-2-cyclopentenyl acetate (68 mg) in 93%. IR (neat): 3060, 2950, 2880, 1735, 1440, 1360, 1240, 1130, 1030, and 975 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.2—1.9 (m, 6H), 1.90 (s, 3H), 1.9—2.3 (m, 2H), 3.0—4.0 (m, 2H), 4.5—5.0 (m, 2H), and 5.4—6.2 (m, 2H). Then a mixture of (1*S*,4*S*)-4-tetrahydropyranyloxy-2-cyclopentenyl acetate (68 mg, 0.3 mmol), AcOH (3.5 ml), and water (1.5 ml) was stirred at room temperature overnight. Toluene was added to the reaction mixture and the mixture was concentrated in vacuo. The residue was purified by column chromatography (silica-gel/hexane–ether) to afford (1*S*,4*S*)-4-hydroxy-2-cyclopentenyl acetate (31 mg) in 74%. ($[\alpha]^{14}_{D}$ −205.4° (*c* 1.49, CH_3OH) (lit,[9a] $[\alpha]^{20}_{D}$ +229° (*c* 0.027, CH_3OH) for 90% ee of (1*R*,4*R*)-4-hydroxy-2-cyclopentenyl acetate).

(1*S*,4*S*)-4-Hydroxy-2-cyclopentenyl acetate thus obtained was converted to (*S*)-4-acetoxy-2-cyclopenten-1-one by a similar method described for (1*S*,4*R*)-**1a**. The ee was determined to be 72% on the basis of ^{1}H NMR taken with Eu(hfbc)$_3$.

The author would like to thank Dr. Keisuke Suzuki, Keio University, for high resolution mass spectra measurements. The partial contribution of Miss Toko Kawakami to the experimental work is appreciated.

References

1) a) M. Nara, S. Terashima, and S. Yamada, *Tetrahedron,* **36**, 3161 (1980); b) S. Takano, K. Tanigawa, and K. Ogasawara, *J. Chem. Soc., Chem. Commun.,* **1976**, 189; c) Y. -F. Wong, C. S. Chen, G. Girdaukas, and C. J. Sih, *J. Am. Chem. Soc.,* **106**, 3695 (1984); d) K. Laumen and M. Schneider, *Tetrahedron Lett.,* **25**, 5875 (1984); e) K. Laumen, E. H. Reimerdes, M. Schneider, and H. Görisch, *ibid.,* **26**, 407 (1985); f) K. Laumen and M. P. Schneider, *J. Chem. Soc., Chem, Commun.,* **1986**, 1298; g) D. R. Deardorff, A. J. Mattews, D. S. McMeeken, and C. L. Craney, *Tetrahedron Lett.,* **27**, 1255 (1986); h) T. Sugai and K. Mori, *Synthesis,* **1988**, 19; i) L. Duhamel and T. Herman, *Tetrahedron Lett.,* **26**, 3099 (1985).

2) A. Mitra, "The Synthesis of Prostaglandins," John Wiley & Sons, Inc., New York (1977).

3) J. S. Bindra, "The Synthesis of Prostaglandins," in "Total Synthesis of Natural Products," ed by L. ApSimon, John Wiley & Sons, Inc., New York (1981), Vol. 4, pp. 353—449.

4) S. M. Roberts and F. Scheinmann, "New Synthetic Routes to Prostaglandins and Thromboxanes," Academic Press, Inc., London (1982).

5) M. Harre, P. Raddatz, R. Walenta, and E. Winterfeldt, *Angew. Chem.,* **94**, 496 (1982); R. Noyori and M. Suzuki, *ibid.,* **96**, 854 (1984).

6) J. J. Partridge, N. K. Chada, and M. R. Uskokovic, *J. Am. Chem. Soc.,* **95**, 7171 (1973); L. Gruber, I. Tömösközi, E. Major, and G. Kovacs, *Tetrahedron Lett.,* **1974**, 3729; I. Tömösközi, L. Gruber, G. Kovacs, and V. Simonidesz, *ibid.,* **1976**, 4639.

7) a) M. Asami, *Chem. Lett.,* **1984**, 829; b) M. Asami and H. Kirihara, *ibid.,* **1987**, 389; c) M. Asami, *Bull. Chem. Soc. Jpn.,* **63**, 721 (1990).

8) M. Asami, *Tetrahedron Lett.,* **26**, 5803, (1985).

9) a) T. Tanaka, S. Kurozumi, T. Toru, S. Miura, M. Kobayashi, and S. Ishimoto, *Tetrahedron,* **32**, 1713 (1976); b) J. C. Saddler, R. E. Donaldson, and P. L. Fuchs, *J. Am. Chem. Soc.,* **103**, 2110 (1981).

10) M. Asami and T. Kawakami, Abstract, 52 nd Meeting of Chemical Society of Japan, Kyoto, April 1986, 4YO6. After we reported these results, the same transformation of **5a** and **6a** to **1a** and **7a** with chiral lithium amide **4a** was reported; S. K. Hendrie and J. Leonard, *Tetrahedron,* **43**, 3289 (1987).

11) H. M. Hess and H. C. Brown, *J. Org. Chem.,* **32**, 4138 (1967).

12) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.,* **94**, 6190 (1972).

13) K. F. Bernady, M. B. Floyd, J. F. Poletto, and M. J. Weiss, *J. Org. Chem.,* **44**, 1438 (1979).

14) No trans-isomer was detected by TLC.

15) K. B. Sharpless and R. C. Michaelson, *J. Am. Chem. Soc.,* **96**, 5254 (1974); G. Stork, I. Paterson, and F. K. C. Lee, *ibid.,* **104**, 4686 (1982). Epoxidation of **8** with peracid is known to afford a mixture of diastereomers (cis : trans≈10 : 1); A. C. Derby, H. B. Henbest, and I. McClenagham, *Chem. Ind. (London),* **1962**, 462; J. M. Hornback, *J. Org. Chem.,* **38**, 4122 (1973); F. David, *ibid.,* **46**, 3512 (1981).

16) The optical rotation values of diastereomers mixture of **1b** are reported. $[\alpha]^{20}_{D}$ −20.3° (*c* 1.3, $CHCl_3$) for (1*R*,4*S*)-**1b**,[1a] $[\alpha]^{20}_{D}$ +21.5° (*c* 3.12, $CHCl_3$) for (1*S*,4*R*)-**1b** (86% ee),[1d] $[\alpha]^{20}_{D}$ −25.7° (*c* 2.35, $CHCl_3$) for (1*R*,4*S*)-**1b** (97% ee).[1f]

17) M. Suzuki, A. Yanagisawa, and R. Noyori, *Tetrahedron Lett.,* **25**, 1383 (1984).

18) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.,* **1975**, 2647.

19) H. Nagaoka, T. Miyakoshi, and Y. Yamada, *Tetrahedron Lett.,* **25**, 3621 (1984).

20) R. Noyori, T. Tomino, M. Yamada, and M. Nishizawa, *J. Am. Chem. Soc.,* **106**, 6717 (1984).

21) Ee was determined based on $[\alpha]^{16}_{D}$ −129° (*c* 0.69, CH_3OH) for 74% ee of (1*S*,4*R*)-**7a** obtained in Entry 12 in Table 3, while $[\alpha]^{20}_{D}$ +81° (*c* 0.057, CH_3OH) is reported for (1*R*,4*R*)-**7a** (56% ee).[9a]