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Practical Asymmetric Synthesis of Both *erythro* and *threo* Aldols Based on the MABR-Promoted Selective Rearrangement of *erythro* and *threo* Epoxy Silyl Ethers: Unusual Effect of Silyl Substituents

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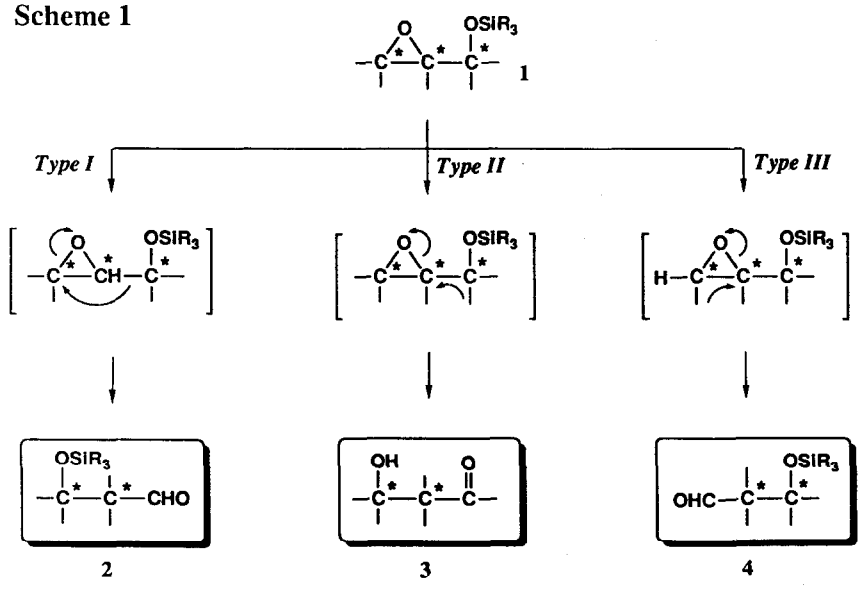
Abstract: A new asymmetric synthesis of both *erythro* and *threo* aldols (β-siloxy aldehydes) has been developed based on the respective stereocontrolled rearrangement of optically active *threo* and *erythro* epoxy silyl ethers with stoichiometric use of exceptionally bulky, oxygenophilic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) under mild conditions. The observed stereoselectivity varies with the electronic effect of silyl substituents rather than their steric effect, and the more electron-withdrawing triphenylsilyl group exhibits better selectivity than trialkylsilyl group. Since enantiomeric *erythro* and *threo* epoxy silyl ethers are readily accessible by Sharpless asymmetric epoxidation, this method allows the practical asymmetric synthesis of four possible aldol isomers with high selectivity.

Can epoxy alcohols become appropriate precursors of aldols ?

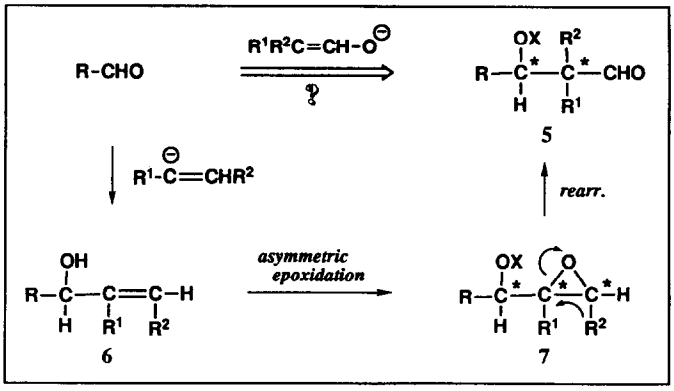
To answer this question we investigated the possibility of the stereoselective rearrangement of epoxy alcohols to β-hydroxy carbonyl compounds.[1-5] The rearrangement also represents an asymmetric approach to aldol synthesis by combining use of Sharpless asymmetric epoxidation of allylic alcohols.[6] As illustrated in Scheme 1, three types of site-specific rearrangements have, in principle, been conceivable for epoxy alcohol derivative **1** depending on the three possible migration patterns following C-O bond cleavage. The type-I and

Scheme 1

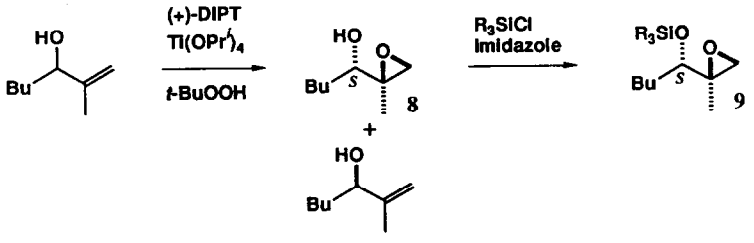


type-II rearrangements of epoxy silyl ethers **1** giving β-hydroxy carbonyl compounds **2** and **3** were recently realized in our laboratory and another.[2,3] The other unexplored type-III transformation, if successful in a stereoselective manner, would serve as a new and efficient access to the synthesis of various β-siloxy aldehydes **4**. Indeed, the β–hydroxy aldehyde unit is a valuable synthetic intermediate for further carbon-chain elongation leading to 1,3-dihydroxy functionality, which is a fundamental structural unit embedded in numerous natural products of acetate and propionate origin.[7] However, despite the recent extensive development of asymmetric aldol methodologies,[8] little is known of the asymmetric synthesis of parent aldols, *i.e.* β-hydroxy aldehydes **5** (X = H), because of the great difficulty of generating chiral aldehyde enolates (or their equivalents) for aldol condensations and the instability of the resulting β-hydroxy aldehydes **5** (X = H).[9] In this context, we set out to study a new asymmetric synthesis of *erythro* and *threo* aldols based on the Lewis acid-promoted rearrangement of optically active epoxy silyl ethers **7** (X = SiR_3), which is readily derivable by Sharpless asymmetric epoxidation[6] of allylic alcohols **6** followed by simple silylation as shown in Scheme 2. Since both *erythro* and *threo* epoxy silyl ethers are easily accessible in optically active forms, the only remaining problem is the stereoselectivity of the epoxide rearrangement. We report here the realization of the type-III transformation in a highly stereoselective manner, thereby permitting the practical asymmetric synthesis of both *erythro* and *threo* β-hydroxy aldehyde derivatives.

Scheme 2

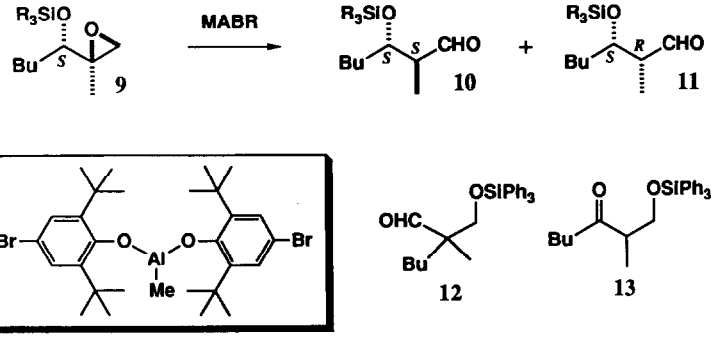


The starting optically active *erythro* epoxy silyl ether **9** was prepared by asymmetric epoxidation of 2-methyl-1-hepten-3-ol with (+)-DIPT, $Ti(OPr^i)_4$, and *t*-BuOOH in CH_2Cl_2 followed by silylation of optically active epoxy alcohol **8** with R_3SiCl and imidazole in DMF. Treatment of *erythro* epoxy silyl ether **9** (R_3 = *t*-



$BuMe_2$; >98% ee) with exceptionally bulky, oxygenophilic methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (abbreviated to MABR), recently developed in our laboratory as a highly effective epoxide-

rearrangement agent,[2] yielded a mixture of *threo* and *erythro* β-siloxy aldehydes **10** and **11** (R_3 = *t*-$BuMe_2$) in 75% yield, though the observed *threo*/*erythro* selectivity was quite disappointing (ratio, ~1:1.4). Even bulky triisopropylsilyl ether **9** (R = *i*-Pr) showed poor selectivity (**10**:**11** (R = *i*-Pr) = 1:2.7). In marked contrast, however, *erythro* epoxy triphenylsilyl ether **9** (R = Ph; >98% ee) on treatment with MABR gave *threo* β-siloxy aldehydes **10** (R = Ph; >98% ee) almost exclusively (**10**:**11** (R = Ph) = 40:1). It should be noted that attempted reaction of *erythro* epoxy silyl ether **9** (R = Ph) with conventional Lewis acid such as $TiCl_4$ and $BF_3{\cdot}OEt_2$ gave none of the desired β-siloxy aldehydes. For example, $TiCl_4$ showed totally different behavior for the substrate **9** (R = Ph) resulting in formation of 2-methyl-2-(triphenylsiloxymethyl)hexanal (**12**) and 2-methyl-1-(triphenylsiloxy)-3-heptanone (**13**) in 68% yield.



(MABR)

Selected results of the rearrangement of *erythro* epoxy silyl ethers **9** with MABR to β-siloxy aldehydes **10** and **11** are summarized in Table 1, and show the following characteristic features. The observed stereoselectivity apparently reflects the marked electronic effect of silyl substituents rather than their steric effect (entries 1-9), and the more electron-withdrawing triphenylsilyl group exhibited better selectivity than the more sterically hindered *tert*-butyldiphenylsilyl group (entry 9 vs. 8).[10] The even more hindered triisopropylsilyl group did not significantly alter the selectivity (entry 2). The stereoselectivity of the phenylsilyl series (*i.e.*, $PhMe_2Si$, Ph_2MeSi, and Ph_3Si groups) increases with increasing electronegativity of the silyl groups (entries 4, 7, and 9). Furthermore, rearrangement of a dimethylphenylsilyl system bearing an electron-withdrawing fluoro group at the *p*-position exhibited higher selectivity than the unsubstituted system (entry 6 vs. 4). This rearrangement proceeded with the *anti* migration of the hydride to the epoxide moiety. Use of non-polar toluene showed higher selectivity than CH_2Cl_2. Notably, the stereoselectivity was markedly decreased with less bulky dimethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide or methylaluminum bis(4-bromo-2,6-diisopropylphenoxide). Similar electronic effect of silyl groups was observed in the rearrangement of optically active *threo* epoxy silyl ether **15** (entries 10-12), which can be prepared by the Mitsunobu inversion[11] of the hydroxy group of optically active *erythro* isomer **8** followed by silylation.

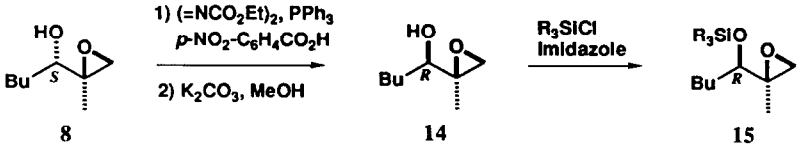
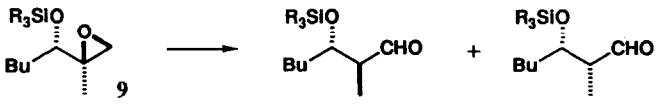
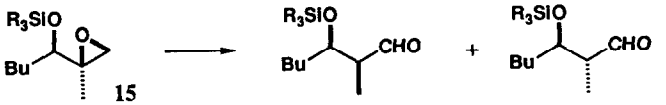


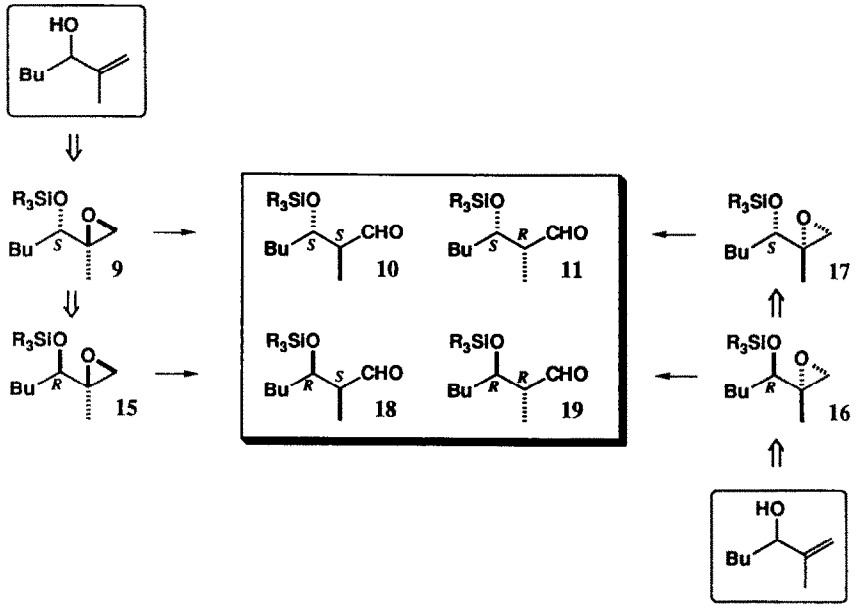
Table 1. Effect of Silyl Substituents of **9** and **15** on the Stereoselectivity [a]

entry	substrate	conditions (°C, h)	yield, % [b] (ratio) [c]
	 **9**		
1	R = Me	-40, 2; -20, 1	50 (1 : 2.2)
2	R = *i*-Pr	-78, 1; -40, 1	78 (1 : 2.7)
3	R_3 = *t*-BuMe$_2$	-78, 1; -40, 2	75 (1 : 1.4)
4	R_3 = PhMe$_2$	-78, 1; -40, 2	65 (1.5 : 1)
5		-40, 1.5; -20, 1.5 [d]	60 (3.5 : 1)
6	R_3 = (*p*-F-C$_6$H$_4$)Me$_2$	-78, 1; -40, 3	75 (2 : 1)
7	R_3 = Ph$_2$Me	-40, 2; -20, 1	77 (6 : 1)
8	R_3 = *t*-BuPh$_2$	-78, 2; -40, 2	72 (10 : 1)
9	R = Ph	-40, 1.5; -20, 0.5	73 (40 : 1)
	 **15**		
10	R_3 = *t*-BuMe$_2$	-78, 1; -40, 2	68 (1 : 2.2)
11	R_3 = PhMe$_2$	-40, 2; -20, 0.5	42 (1 : 2.6)
12	R = Ph	-40, 2; -20, 0.5	81 (1 : 12)

[a] Unless otherwise stated, the rearrangement of **9** and **15** was effected in CH_2Cl_2 with 2 equiv of MABR under the indicated conditions. [b] Isolated yield by column chromatography. [c] The *threo*/*erythro* ratios were determined by 200 MHz ^{1}H NMR or HPLC analysis. [d] Use of toluene as solvent.

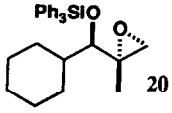
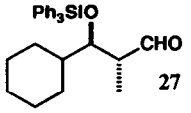
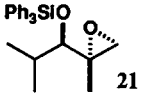
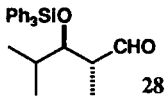
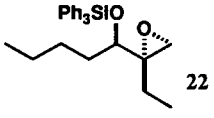
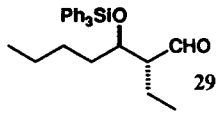
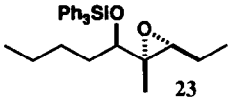
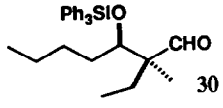
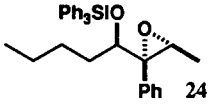
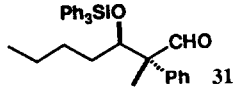
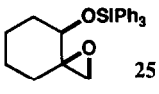
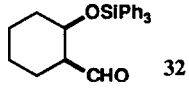
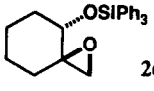
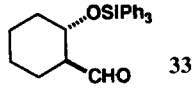
Since enantiomeric *erythro* epoxy silyl ether **16** and its *threo* isomer **17** are readily accessible by the Sharpless asymmetric epoxidation using (-)-DIPT as a chiral auxiliary,[6,11] the present method allows the practical asymmetric synthesis of four possible aldol isomers **10**, **11**, **18**, and **19** starting from the same allylic alcohol, 2-methyl-1-hepten-3-ol as depicted in Scheme 3. Other examples of triphenylsilyl substituents

Scheme 3



are illustrated in Table 2, and clearly indicate the generality of the present rearrangement. A profound solvent effect was again observed, and toluene as solvent was far superior to CH_2Cl_2 for obtaining high stereoselectivity (entries 2, 4, and 7). Notably, β-siloxy aldehydes possessing an asymmetric quartenary α-carbon, hitherto not obtainable by ordinary asymmetric aldol reactions, can be readily synthesized with virtually complete stereoselectivity (entries 7 and 8).

Table 2. Stereoselective Rearrangement of Various Epoxy Silyl Ethers with MABR [a]

entry	substrate	conditions (°C, h)	major isomer of siloxy aldehyde	yield, % [b] (*erythro*/*threo*) [c]
1	 **20**	-78, 1; -40, 1.5	 **27**	92 (1 : 6)
2		-78, 1; -40, 2 [d]		88 (1 : 100)
3	 **21**	-78, 1; -40, 0.5	 **28**	86 (1 : 6)
4		-78, 2; -40, 2 [d]		82 (1 : 30)
5	 **22**	-40, 2; -20, 0.5	 **29**	67 (1 : 100)
6	 **23**	-40, 2; -20, 2	 **30**	47 (4 : 1)
7		-40, 2; -20, 2 [d]		64 (200 : 1)
8	 **24**	-78, 0.5	 **31**	83 (0 : 1)
9	 **25**	-40, 2; -20, 2 [d]	 **32**	85 (1 : 0)
10	 **26**	-40, 1; -20, 2.5 [d]	 **33**	50 (1 : 13) [e]

[a] Unless otherwise stated, the rearrangement was carried out in CH_2Cl_2 using 2 equiv of MABR under the indicated conditions. [b] Isolated yield. [c] Determined by 200 MHz ^1H NMR or HPLC analysis. [d] Use of toluene as solvent. [e] A ring-contracted α-(triphenylsiloxymethyl)cyclopentanecarboxaldehyde is also formed in 10% yield.

Experimental Section

General. Infrared (IR) spectra were recorded on a Hitachi 260-10 spectrometer. ^{1}H NMR spectra were measured on a Varian Gemini-200 spectrometer. Analytical gas-liquid phase chromatography (GLC) was performed on Gasukuro Kogyo Model 370 and Shimadzu GC-8A instruments equipped with a flame ionization detector and a capillary column of PEG-HT (0.25 X 25,000 mm) using nitrogen as carrier gas. High-performance liquid chromatography (HPLC) analyses were carried out on a Shimadzu LC-6A instrument with a SPD-6A UV detector. Optical rotations were measured on a JASCO DIP-140 digital polarimeter. All experiments were carried out under an atmosphere of dry argon. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel E. Merck 9385. Microanalyses were accomplished in the Faculty of Agriculture, Nagoya University.

In experiments requiring dry solvents, ether was freshly distilled from sodium metal using benzophenone ketyl as indicator. Hexane, benzene, and toluene were dried over sodium metal. Methylene chloride and DMF were stored over 4A molecular sieves. Pyridine was stored over KOH pellets. Trimethylaluminum was obtained from Toso-Akzo Chem. Co. Ltd., Japan. Other simple chemicals were purchased and used as such.

Preparation of *erythro* Epoxy Alcohols. A variety of *erythro* epoxy alcohols were prepared by Sharpless asymmetric epoxidation of allylic alcohols according to the literature procedures.[6]

Preparation of *threo* Epoxy Alcohol 14: Diethyl azodicarboxylate (6.3 mL, 40 mmol) was added at 0 °C to a solution of *erythro* epoxy alcohol **8** (1 g, 7 mmol), *p*-nitrobenzoic acid (6.7 g, 40 mmol), and triphenylphosphine (10 g, 40 mmol) in benzene (15 mL).[11] The mixture was stirred at room temperature overnight, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (ether/hexane = 1:3) to furnish *threo* epoxy *p*-nitrobenzoate (880 mg, 43% yield): ^{1}H NMR ($CDCl_3$) δ 8.22-8.36 (4H, m, *p*-NO_2-C_6H_4), 4.93 (1H, dd, *J* = 8, 6 Hz, CH-OCO), 2.81 (1H, d, *J* = 4 Hz, CH-O), 2.73 (1H, d, *J* = 4 Hz, CH-O), 1.77-1.84 (2H, m, CH_2C-O), 1.48 (3H, s, CH_3C-O), 1.33-1.44 (4H, m, $(CH_2)_2$), 0.92 (3H, t, *J* = 7 Hz, CH_3C-C); IR (liquid film) 2940, 1715, 1520, 1345, 1320, 1270, 1115, 1100, 870, 845 cm^{-1}. Anal. Calcd for $C_{15}H_{19}NO_5$: C, 61.42; H, 6.53. Found: C, 61.48; H, 6.52.

This *p*-nitrobenzoate was hydrolyzed with K_2CO_3 (150 mg) in MeOH (5 mL) at 25 °C for 10 min. After usual workup, the crude material was purified by column chromatography on silica gel (ether/hexane = 1:2) to furnish the title alcohol **14** (412 mg, 96% yield): $[\alpha]_D^{24}$ +18.1° (*c* 1.00, $CHCl_3$), >98% ee; ^{1}H NMR ($CDCl_3$) δ 3.31 (1H, m, CH-O), 2.79 (1H, d, *J* = 5 Hz, CH-O), 2.69 (1H, d, *J* = 5 Hz, CH-O), 2.01 (1H, d, *J* = 3Hz, OH), 1.34 (3H, s, CH_3C-O), 1.28-1.56 (6H, m, $(CH_2)_3$), 0.93 (3H, t, *J* = 7 Hz, CH_3C-C); IR (liquid film) 3440, 2960, 2930, 2870, 1450, 1395, 1105, 1065, 1015, 870 cm^{-1}. Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.79; H, 11.51.

Preparation of *erythro* and *threo* Epoxy Silyl Ethers. Various *erythro* and *threo* epoxy silyl ethers were obtained in a usual manner by treatment of the corresponding *erythro* and *threo* epoxy alcohols with trialkylsilyl chloride or triflate (1.1~1.5 equiv) and imidazole (2 equiv) in DMF at 0 ~ 25°C for several hours.

***erythro* Epoxy *tert*-Butyldimethylsilyl Ether 9 (R_3 = *t*-BuMe$_2$):** $[\alpha]_D^{22}$ -6.80° (*c* 1.00, $CHCl_3$), >98% ee; ^{1}H NMR ($CDCl_3$) δ 3.25 (1H, dd, *J* = 7, 4 Hz, CH-OSi), 2.67 (1H, d, *J* = 5 Hz, CH-O), 2.57 (1H, d, *J* = 5 Hz, CH-O), 1.25-1.57 (6H, m, $(CH_2)_3$), 1.28 (3H, s, CH_3C-O), 0.90 (3H, t, *J* = 6 Hz, CH_3C-C), 0.88 (9H, s, $SiC(CH_3)_3$), 0.04 (3H, s, $SiCH_3$), 0.03 (3H, s, $SiCH_3$); IR (liquid film) 2940,

2860, 1455, 1350, 1245, 995, 930, 830, 765 cm^{-1}. Anal. Calcd for $C_{14}H_{30}O_2Si$: C, 65.04; H, 11.72. Found: C, 64.96; H, 11.98.

***erythro* Epoxy Triphenylsilyl Ether 9 (R = Ph):** $[\alpha]_D^{23}$ +10.0° (*c* 1.02, $CHCl_3$), >98% ee; ^1H NMR ($CDCl_3$) δ 7.33–7.65 (15H, m, $SiPh_3$), 3.34 (1H, t, *J* = 6 Hz, CH-OSi), 2.34 (1H, d, *J* = 5 Hz, CH-O), 2.19 (1H, d, *J* = 5 Hz, CH-O), 1.63 (2H, m, CH_2C-OSi), 1.36 (3H, s, CH_3C-O), 1.10-1.33 (4H, m, $(CH_2)_2$), 0.78 (3H, t, *J* = 7 Hz, CH_3C-C); IR (liquid film) 2955, 2935, 1420, 1105, 1080, 1065, 730, 700, 685 cm^{-1}. Anal. Calcd for $C_{26}H_{30}O_2Si$: C, 77.57; H, 7.51. Found: C, 77.62; H, 7.48.

***erythro* Epoxy Trimethylsilyl Ether 9 (R = Me):** ^1H NMR ($CDCl_3$) δ 3.30 (1H, dd, *J* = 8, 4 Hz, CH-OSi), 2.70 (1H, d, *J* = 5 Hz, CH-O), 2.58 (1H, d, *J* = 5 Hz, CH-O), 1.26-1.57 (6H, m, $(CH_2)_3$), 1.30 (3H, s, CH_3C-O), 0.92 (3H, t, *J* = 7 Hz, CH_3C-C), 0.12 (9H, s, $Si(CH_3)_3$); IR (liquid film) 2955, 2865, 1250, 1135, 1120, 1095, 1075, 940, 865, 835 cm^{-1}. Anal. Calcd for $C_{11}H_{24}O_2Si$: C, 61.04; H, 11.20. Found: C, 60.71; H, 11.71.

***erythro* Epoxy Triisopropylsilyl Ether 9 (R = *i*-Pr):** ^1H NMR ($CDCl_3$) δ 3.44 (1H, t, *J* = 6 Hz, CH-OSi), 2.72 (1H, d, *J* = 5 Hz, CH-O), 2.59 (1H, d, *J* = 5 Hz, CH-O), 1.63 (2H, m, CH_2C-OSi), 1.37 (4H, m, $(CH_2)_2$), 1.32 (3H, s, CH_3C-O), 1.02-1.20 (21H, m, $Si(CH(CH_3)_2)_3$),0.92 (3H, t, *J* = 7 Hz, CH_3C-C); IR (liquid film) 2950, 2875, 1465, 1383, 1120, 1100, 1075, 890, 835, 680 cm^{-1}. Anal. Calcd for $C_{17}H_{36}O_2Si$: C, 67.92; H,12.10. Found: C, 67.81; H, 12.32.

***erythro* Epoxy Dimethylphenylsilyl Ether 9 (R_3 = $PhMe_2$):** ^1H NMR ($CDCl_3$) δ 7.37–7.61 (5H, m, SiPh), 3.24 (1H, dd, *J* = 7, 5 Hz, CH-OSi), 2.39 (1H, d, *J* = 5 Hz, CH-O), 2.37 (1H, d, *J* = 5 Hz, CH-O), 1.21-1.56 (6H, m, $(CH_2)_3$), 1.27 (3H, s, CH_3C-O), 0.88 (3H, t, *J* = 7 Hz, CH_3C-C), 0.39 (6H, s, $Si(CH_3)_2$); IR (liquid film) 2955, 2865, 1425, 1250, 1115, 1090, 1070, 845, 825, 780, 695 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.00; H, 9.43. Found: C, 69.20; H, 9.83.

***erythro* Epoxy Dimethyl(*p*-fluorophenyl)silyl Ether 9 (R_3 = (p-F-C_6H_4)Me_2):** ^1H NMR ($CDCl_3$) δ 7.03–7.60 (4H, m, *p*-F-C_6H_4), 3.27 (1H, dd, *J* = 8, 4 Hz, CH-OSi), 2.42 (2H, s, CH_2-O), 1.26 (3H, s, CH_3C-O), 1.21-1.60 (6H, m, $(CH_2)_3$), 0.88 (3H, t, *J* = 7 Hz, CH_3C-C), 0.37 (6H, s, $Si(CH_3)_2$); IR (liquid film) 2955, 2885, 1580, 1490, 1245, 1225, 1095, 1055, 830, 775 cm^{-1}. Anal. Calcd for $C_{16}H_{25}O_2SiF$: C, 64.82; H, 8.50. Found: C, 64.80; H, 8.65.

***erythro* Epoxy Diphenylmethylsilyl Ether 9 (R_3 = Ph_2Me):** ^1H NMR ($CDCl_3$) δ 7.35–7.62 (10H, m, $SiPh_2$), 3.30 (1H, t, *J* = 6 Hz, CH-OSi), 2.35 (1H, d, *J* = 5 Hz, CH-O), 2.27 (1H, d, *J* = 5 Hz, CH-O), 1.60 (2H, m, CH_2C-O), 1.23-1.53 (4H, m, $(CH_2)_2$), 1.31 (3H, s, CH_3C-O), 0.90 (3H, t, *J* = 6 Hz, CH_3C-C), 0.66 (3H, s, $SiCH_3$); IR (liquid film) 2960, 2875, 1420, 1240, 1110, 1080, 1060, 780, 725, 685 cm^{-1}. Anal. Calcd for $C_{21}H_{28}O_2Si$: C, 74.05; H, 8.30. Found: C, 74.31; H, 8.69.

***erythro* Epoxy *tert*-Butyldiphenylsilyl Ether 9 (R_3 = *t*-$BuPh_2$):** ^1H NMR ($CDCl_3$) δ 7.34–7.69 (10H, m, $SiPh_2$), 3.17 (1H, t, *J* = 6 Hz, CH-OSi), 2.32 (1H, d, *J* = 5 Hz, CH-O), 2.19 (1H, d, *J* = 5 Hz, CH-O), 1.58 (2H, m, CH_2C-O), 1.35 (3H, s, CH_3C-O), 1.14-1.33 (4H, m, $(CH_2)_2$), 1.08 (9H, s, $SiC(CH_3)_3$), 0.82 (3H, t, *J* = 7 Hz, CH_3C-C); IR (liquid film) 2955, 2935, 2865, 1425, 1115, 1090, 1070, 825, 740, 700 cm^{-1}. Anal. Calcd for $C_{24}H_{34}O_2Si$: C, 75.32; H, 8.97. Found: C, 75.50; H, 9.27.

***threo* Epoxy Triphenylsilyl Ether 15 (R = Ph):** $[\alpha]_D^{22}$ -4.64° (*c* 1.00, $CHCl_3$), >98% ee; ^1H NMR ($CDCl_3$) δ 7.33–7.71 (15H, m, $SiPh_3$), 3.34 (1H, t, *J* = 7 Hz, CH-OSi), 2.58 (1H, d, *J* = 5 Hz, CH-O), 2.49 (1H, d, *J* = 5 Hz, CH-O), 1.56 (2H, m, CH_2C-O), 1.41 (3H, s, CH_3C-O), 1.07-1.26 (4H, m, $(CH_2)_2$), 0.75 (3H, t, *J* = 7 Hz, CH_3C-C); IR (liquid film) 3045, 2955, 2935, 2865, 1425, 1105, 1080, 1025, 725, 700, 690 cm^{-1}. Anal. Calcd for $C_{26}H_{30}O_2Si$: C, 77.57; H, 7.51. Found: C, 77.61; H, 7.64.

***threo* Epoxy *tert*-Butyldimethylsilyl Ether 15 (R_3 = *t*-BuMe$_2$):** ^{1}H NMR ($CDCl_3$) δ 3.12 (1H, dd, *J* = 8, 5 Hz, CH-OSi), 2.62 (1H, d, *J* = 5 Hz, CH-O), 2.57 (1H, d, *J* = 5 Hz, CH-O), 1.22-1.51 (6H, m, $(CH_2)_3$), 1.28 (3H, s, CH_3C-O), 0.92 (9H, s, $SiC(CH_3)_3$), 0.90 (3H, t, *J* = 6 Hz, CH_3C-C), 0.11 (3H, s, $SiCH_3$), 0.05 (3H, s, $SiCH_3$); IR (liquid film) 2945, 2870, 1460, 1245, 1120, 1085, 935, 885, 830, 770 cm^{-1}. Anal. Calcd for $C_{14}H_{30}O_2Si$: C, 65.04; H, 11.72. Found: C, 64.96; H, 11.96.

***threo* Epoxy Dimethylphenylsilyl Ether 15 (R_3 = PhMe$_2$):** ^{1}H NMR ($CDCl_3$) δ 7.34–7.64 (5H, m, SiPh), 3.18 (1H, dd, *J* = 8, 5 Hz, CH-OSi), 2.60 (1H, d, *J* = 5 Hz, CH-O), 2.55 (1H, d, *J* = 5 Hz, CH-O), 1.16-1.52 (6H, m, $(CH_2)_3$), 1.28 (3H, s, CH_3C-O), 0.85 (3H, t, *J* = 7 Hz, CH_3C-C), 0.42 (3H, s, $SiCH_3$), 0.41 (3H, s, $SiCH_3$); IR (liquid film) 2970, 2950, 1250, 1120, 1090, 940, 830, 785, 735, 690 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.00; H, 9.43. Found: C, 69.01; H, 9.61.

***erythro* Epoxy Triphenylsilyl Ether 20:** ^{1}H NMR ($CDCl_3$) δ 7.30–7.78 (15H, m, $SiPh_3$), 3.05 (1H, d, *J* = 7 Hz, CH-OSi), 2.21 (1H, d, *J* = 5 Hz, CH-O), 2.17 (1H, d, *J* = 5 Hz, CH-O), 0.75-1.98 (11H, m, cyclohexyl), 1.38 (3H, s, CH_3C-O); IR (liquid film) 2940, 2850, 1435, 1415, 1100, 1050, 1025, 885, 825, 725, 690 cm^{-1}. Anal. Calcd for $C_{28}H_{32}O_2Si$: C, 78.46; H, 7.52. Found: C, 78.60; H, 7.35.

***erythro* Epoxy Triphenylsilyl Ether 21:** ^{1}H NMR ($CDCl_3$) δ 7.34–7.67 (15H, m, $SiPh_3$), 3.04 (1H, d, *J* = 7 Hz, CH-OSi), 2.27 (1H, d, *J* = 5 Hz, CH-O), 2.23 (1H, d, *J* = 5 Hz, CH-O), 2.01 (1H, octet, *J* = 7 Hz, C-CH-C), 1.40 (3H, s, CH_3C-O), 0.91 (6H, d, *J* = 7 Hz, $(CH_3)_2C$-C); IR (liquid film) 3060, 2970, 1470, 1425, 1110, 1055, 845, 735, 700, 690 cm^{-1}. Anal. Calcd for $C_{25}H_{28}O_2Si$: C, 77.27; H, 7.26. Found: C, 77.20; H, 7.36.

***erythro* Epoxy Triphenylsilyl Ether 22:** ^{1}H NMR ($CDCl_3$) δ 7.31–7.65 (15H, m, $SiPh_3$), 3.48 (1H, t, *J* = 6 Hz, CH-OSi), 2.47 (1H, d, *J* = 5 Hz, CH-O), 2.25 (1H, d, *J* = 5 Hz, CH-O), 1.52-2.00 (4H, m, CH_2C-O and CH_2C-OSi), 1.05-1.38 (4H, m, $(CH_2)_2$), 0.78 (3H, t, *J* = 8 Hz, CH_3), 0.77 (3H, t, *J* = 8 Hz, CH_3); IR (liquid film) 3060, 2970, 2950, 1420, 1110, 1070, 1020, 705, 685 cm^{-1}. Anal. Calcd for $C_{27}H_{32}O_2Si$: C, 77.84; H, 7.74. Found: C, 77.95; H, 7.40.

***erythro* Epoxy Triphenylsilyl Ether 23:** ^{1}H NMR ($CDCl_3$) δ 7.32–7.65 (15H, m, $SiPh_3$), 3.31 (1H, t, *J* = 6 Hz, CH-OSi), 2.30 (1H, t, *J* = 6 Hz, CH-O), 1.16-1.71 (8H, m, CH_2C-O and $(CH_2)_3$), 1.34 (3H, s, CH_3C-O), 0.87 (3H, t, *J* = 7 Hz, CH_3), 0.78 (3H, t, *J* = 7 Hz, CH_3); IR (liquid film) 2965, 2940, 2880, 1420, 1110, 1075, 1020, 730, 700, 690 cm^{-1}. Anal. Calcd for $C_{28}H_{34}O_2Si$: C, 78.09; H, 7.96. Found: C, 78.08; H, 7.77.

***erythro* Epoxy Triphenylsilyl Ether 24:** ^{1}H NMR ($CDCl_3$) δ 7.31–7.87 (20H, m, PhC-O and $SiPh_3$), 3.56 (1H, t, *J* = 6 Hz, CH-OSi), 2.81 (1H, q, *J* = 5 Hz, CH-O), 0.88-1.48 (6H, m, $(CH_2)_3$), 0.84 (3H, d, *J* = 5 Hz, CH_3), 0.65 (3H, t, *J* = 7 Hz, CH_3); IR (liquid film) 2970, 2940, 1425, 1110, 1080, 1020, 735, 700, 690 cm^{-1}. Anal. Calcd for $C_{32}H_{34}O_2Si$: C, 80.29; H, 7.16. Found: C, 80.35; H, 7.16.

***threo* Epoxy Triphenylsilyl Ether 25:** ^{1}H NMR ($CDCl_3$) δ 7.33–7.68 (15H, m, $SiPh_3$), 3.73 (1H, dd, *J* = 4, 3 Hz, CH-OSi), 2.72 (1H, d, *J* = 5 Hz, CH-O), 2.53 (1H, d, *J* = 5 Hz, CH-O), 1.26-2.16 (8H, m, $(CH_2)_4$); IR (liquid film) 3060, 2945, 1425, 1165, 1105, 1075, 1045, 1020, 895, 695, 685 cm^{-1}. Anal. Calcd for $C_{25}H_{26}O_2Si$: C, 77.68; H, 6.78. Found: C, 77.87; H, 7.24.

***erythro* Epoxy Triphenylsilyl Ether 26:** ^{1}H NMR ($CDCl_3$) δ 7.37–7.64 (15H, m, $SiPh_3$), 3.66 (1H, dd, *J* = 7, 3 Hz, CH-OSi), 2.55 (1H, d, *J* = 5 Hz, CH-O), 2.43 (1H, d, *J* = 5 Hz, CH-O), 1.35-1.97 (8H, m, $(CH_2)_4$); IR (liquid film) 2930, 1420, 1150, 1135, 1110, 1075, 1040, 1020, 905, 690 cm^{-1}. Anal. Calcd for $C_{25}H_{26}O_2Si$: C, 77.68; H, 6.78. Found: C, 77.70; H, 6.76.

Preparation of MABR. To a solution of 4-bromo-2,6-di-*tert*-butylphenol (2 equiv) in CH_2Cl_2 or toluene was added at room temperature a 2 M hexane solution of Me_3Al (1 equiv). The methane gas evolved

immediately. The resulting colorless solution was stirred at room temperature for 1 h and used as a solution of MABR in CH_2Cl_2 or toluene without any purification. Other modified organoaluminum reagents such as methylaluminum bis(4-bromo-2,6-diisopropylphenoxide), and dimethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide were prepared *in situ* from Me_3Al and the corresponding phenols in CH_2Cl_2 at room temperature for 1 h.

General Method for the Rearrangement of Epoxy Silyl Ethers with MABR. To a solution of MABR (1 mmol) in CH_2Cl_2 or toluene (5 mL) was added an epoxy silyl ether (0.5 mmol) at -78°C. The mixture was stirred at -78 ~ -20 °C for several hours. The solution was poured into diluted HCl and extracted with CH_2Cl_2 or ether. The combined extracts were dried over Na_2SO_4. Evaporation of solvents and purification of the residue by column chromatography (ether/hexane as eluant) gave β-siloxy aldehyde in the yields as shown in Table I and II. The *threo*/*erythro* ratios were determined by 200 MHz ^{1}H NMR or HPLC analysis.

2-Methyl-3-(*tert*-butyldimethylsiloxy)heptanal: IR (liquid film) 2935, 2860, 1720, 1455, 1245, 1095, 1070, 1030, 830, 765 cm^{-1}. Anal. Calcd for $C_{14}H_{30}O_2Si$: C, 65.04; H, 11.72. Found: C, 65.01; H, 12.08. ***threo*-Isomer 10 (R_3 = *t*-BuMe$_2$)**: ^{1}H NMR ($CDCl_3$) δ 9.74 (1H, d, J = 2 Hz, CHO), 3.91 (1H, q, J = 5 Hz, CH-OSi), 2.45 (1H, m, CH-C=O), 1.14-1.56 (6H, m, $(CH_2)_3$), 1.07 (3H, d, J = 7 Hz, CH_3C-C=O), 0.90 (3H, t, J = 7 Hz, CH_3), 0.86 (9H, s, $SiC(CH_3)_3$), 0.06 (3H, s, $SiCH_3$), 0.03 (3H, s, $SiCH_3$). ***erythro*-Isomer 11 (R_3 = *t*-BuMe$_2$)**: ^{1}H NMR ($CDCl_3$) δ 9.77 (1H, s, CHO), 4.10 (1H, dt, J = 6, 4 Hz, CH-OSi), 1.05 (3H, d, J = 7 Hz, CH_3).

(2*S*,3*S*)-2-Methyl-3-(triphenylsiloxy)heptanal 10 (R = Ph): $[\alpha]_D^{22}$ +38.5° (*c* 1.00, $CHCl_3$), >98% ee; ^{1}H NMR ($CDCl_3$) δ 9.73 (1H, d, J = 2 Hz, CHO), 7.34–7.65 (15H, m, $SiPh_3$), 4.10 (1H, td, J = 6, 5 Hz, CH-OSi), 2.55 (1H, qdd, J = 7, 5, 2 Hz, CH-C=O), 1.04-1.66 (6H, m, $(CH_2)_3$), 1.05 (3H, d, J = 7 Hz, CH_3C-C=O), 0.75 (3H, t, J = 7 Hz, CH_3); IR (liquid film) 2945, 2925, 1720, 1420, 1110, 1080, 1035, 1015, 735, 700, 690 cm^{-1}. Anal. Calcd for $C_{26}H_{30}O_2Si$: C, 77.57; H, 7.51. Found: C, 77.57; H, 7.85.

2-Methyl-3-(trimethylsiloxy)heptanal: IR (liquid film) 2960, 2885, 1725, 1245, 1090, 1070, 1030, 835, 745 cm^{-1}. Anal. Calcd for $C_{11}H_{24}O_2Si$: C, 61.04; H, 11.20. Found: C, 61.03; H, 11.46. ***threo*-Isomer 10 (R = Me)**: ^{1}H NMR ($CDCl_3$) δ 9.73 (1H, d, J = 2 Hz, CHO), 3.89 (1H, dt, J = 6, 5 Hz, CH-OSi), 2.34 (1H, m, CH-C=O), 1.16-1.56 (6H, m, $(CH_2)_3$), 1.06 (3H, d, J = 7 Hz, CH_3C-C=O), 0.89 (3H, t, J = 7 Hz, CH_3), 0.10 (9H, s, $Si(CH_3)_3$). ***erythro*-Isomer 11 (R = Me)**: ^{1}H NMR ($CDCl_3$) δ 9.74 (1H, s, CHO), 4.07 (1H, dt, J = 6, 4 Hz, CH-OSi).

2-Methyl-3-(triisopropylsiloxy)heptanal: IR (liquid film) 2940, 2870, 2710, 1720, 1450, 1090, 1030, 1000, 870, 660 cm^{-1}. Anal. Calcd for $C_{17}H_{36}O_2Si$: C, 67.92; H, 12.10. Found: C, 67.96; H, 12.48. ***threo*-Isomer 10 (R = *i*-Pr)**: ^{1}H NMR ($CDCl_3$) δ 9.82 (1H, d, J = 2 Hz, CHO), 4.14 (1H, q, J = 5 Hz, CH-OSi), 2.52 (1H, m, CH-C=O), 1.21-1.69 (6H, m, $(CH_2)_3$), 1.04-1.17(24H, m, CH_3C-C=O and $Si(CH(CH_32)_3$), 0.92 (3H, t, J = 7 Hz, CH_3). ***erythro*-Isomer 11 (R = *i*-Pr)**: ^{1}H NMR ($CDCl_3$) δ 9.86 (1H, s, CHO), 4.34 (1H, dt, J = 6, 3 Hz, CH-OSi).

2-Methyl-3-(dimethylphenylsiloxy)heptanal: IR (liquid film) 2935, 2860, 1715, 1240, 1105, 1085, 1060, 1020, 815, 770 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_2Si$: C, 69.00; H, 9.43. Found: C, 69.11; H, 9.73. ***threo*-Isomer 10 (R_3 = PhMe$_2$)**: ^{1}H NMR ($CDCl_3$) δ 9.69 (1H, d, J = 2 Hz, CHO), 7.35-7.60 (5H, m, SiPh), 3.93 (1H, q, J = 5 Hz, CH-OSi), 2.40 (1H, m, CH-C=O), 1.13-1.56 (6H, m, $(CH_2)_3$), 1.03 (3H, d, J = 7 Hz, CH_3C-C=O), 0.84 (3H, t, J = 7 Hz, CH_3), 0.40 (3H, s, $SiCH_3$), 0.38 (3H, s,

$SiCH_3$). ***erythro*-Isomer 11 (R_3 = $PhMe_2$)**: ^1H NMR ($CDCl_3$) δ 9.66 (1H, s, CHO), 4.10 (1H, dt, *J* = 6, 4 Hz, CH-OSi), 1.04 (3H, d, *J* = 7 Hz, CH_3).

2-Methyl-3-[dimethyl(*p*-fluorophenyl)]heptanal: IR (liquid film) 2970, 2950, 1725, 1590, 1250, 1160, 1100, 1030, 830, 780 cm^{-1}. Anal. Calcd for $C_{16}H_{25}O_2SiF$: C, 64.82; H, 8.50. Found: C, 64.71; H, 8.66. ***threo*-Isomer 10 (R_3 = (p-F-C_6H_4)Me_2)**: ^1H NMR ($CDCl_3$) δ 9.69 (1H, d, *J* = 3 Hz, CHO), 7.04-7.56 (4H, m, p-F-C_6H_4Si), 3.92 (1H, q, *J* = 5 Hz, CH-OSi), 2.44 (1H, m, CH-C=O), 1.13-1.56 (6H, m, $(CH_2)_3$), 1.03 (3H, d, *J* = 7 Hz, CH_3C-C=O), 0.85 (3H, t, *J* = 7 Hz, CH_3), 0.38 (3H, s, $SiCH_3$), 0.37 (3H, s, $SiCH_3$). ***erythro*-Isomer 11 (R_3 = (p-F-C_6H_4)Me_2)**: ^1H NMR ($CDCl_3$) δ 9.65 (1H, s, CHO), 4.11 (1H, dt, *J* = 7, 4 Hz, CH-OSi), 1.05 (3H, d, *J* = 7 Hz, CH_3).

2-Methyl-3-(diphenylmethylsiloxy)heptanal: IR (liquid film) 2935, 1720, 1420, 1110, 1080, 1030, 1020, 780, 730, 690 cm^{-1}. Anal. Calcd for $C_{21}H_{28}O_2Si$: C, 74.05; H, 8.30. Found: C, 74.00; H, 8.31. ***threo*-Isomer 10 (R_3 = Ph_2Me)**: ^1H NMR ($CDCl_3$) δ 9.72 (1H, d, *J* = 2 Hz, CHO), 7.32-7.61 (10H, m, $SiPh_2$), 4.03 (1H, q, *J* = 5 Hz, CH-OSi), 2.51 (1H, m, CH-C=O), 1.14-1.60 (6H, m, $(CH_2)_3$), 1.04 (3H, d, *J* = 7 Hz, CH_3C-C=O), 0.80 (3H, t, *J* = 7 Hz, CH_3), 0.67 (3H, s, $SiCH_3$). ***erythro*-Isomer 11 (R_3 = Ph_2Me)**: ^1H NMR ($CDCl_3$) δ 9.66 (1H, s, CHO), 4.20 (1H, dt, *J* = 6, 4 Hz, CH-OSi), 1.08 (3H, d, *J* = 7 Hz, CH_3).

2-Methyl-3-(*tert*-butyldiphenylsiloxy)heptanal: IR (liquid film) 2970, 2940, 2865, 1715, 1420, 1110, 1035, 1025, 735, 695 cm^{-1}. Anal. Calcd for $C_{24}H_{34}O_2Si$: C, 75.32; H, 8.97. Found: C, 75.32; H, 9.04. ***threo*-Isomer 10 (R = *t*-$BuPh_2$)**: ^1H NMR ($CDCl_3$) δ 9.72 (1H, d, *J* = 2 Hz, CHO), 7.31-7.70 (10H, m, $SiPh_2$), 4.01 (1H, dt, *J* = 6, 4 Hz, CH-OSi), 2.51 (1H, m, CH-C=O), 1.37-1.55 (2H, CH_2C-O), 1.08 (9H, s, $SiC(CH_3)_3$), 1.03-1.23 (7H, m, $(CH_2)_2$ and CH_3C-C=O), 0.76 (3H, t, *J* = 7 Hz, CH_3). ***erythro*-Isomer 11 (R = *t*-$BuPh_2$)**: ^1H NMR ($CDCl_3$) δ 9.75 (1H, s, CHO), 4.17 (1H, dt, *J* = 6, 3 Hz, CH-OSi).

(2*S*,3*R*)-2-Methyl-3-(triphenylsiloxy)heptanal (18): $[\alpha]_D^{23}$ +14.5° (*c* 1.00, $CHCl_3$), >98% ee; ^1H NMR ($CDCl_3$) δ 9.65 (1H, s, CHO), 7.35–7.77 (15H, m, $SiPh_3$), 4.27 (1H, td, *J* = 6, 3 Hz, CH-OSi), 2.46 (1H, qd, *J* = 7, 3 Hz, CH-C=O), 1.43-1.64 (2H, m, CH_2C-OSi), 0.89-1.29 (4H, m, $(CH_2)_2$), 1.13 (3H, d, *J* = 7 Hz, CH_3C-C=O), 0.75 (3H, t, *J* = 6 Hz, CH_3); IR (liquid film) 2950, 1720, 1415, 1105, 1025, 1015, 730, 695, 685 cm^{-1}. Anal. Calcd for $C_{26}H_{30}O_2Si$: C, 77.57; H, 7.51. Found: C, 77.57; H, 7.51.

3-Cyclohexyl-2-methyl-3-(triphenylsiloxy)propanal: IR (liquid film) 2950, 2880, 1720, 1445, 1420, 1110, 1060, 1030, 1015, 735, 695 cm^{-1}. Anal. Calcd for $C_{28}H_{32}O_2Si$: C, 78.46; H, 7.52. Found: C, 78.38; H, 7.42. ***threo*-Isomer** 27: ^1H NMR ($CDCl_3$) δ 9.78 (1H, d, *J* = 2 Hz, CHO), 7.34–7.80 (15H, m, $SiPh_3$), 3.84 (1H, t, *J* = 5 Hz, CH-OSi), 2.62 (1H, qdd, *J* = 7, 5, 2 Hz, CH-C=O), 0.85-1.79 (11H, m, cyclohexyl), 1.01 (3H, d, *J* = 7 Hz, CH_3C-C=O). ***erythro*-Isomer of 27**: ^1H NMR ($CDCl_3$) δ 9.53 (1H, s, CHO), 4.05 (1H, t, *J* = 5 Hz, CH-OSi).

2,4-Dimethyl-3-(triphenylsiloxy)pentanal: IR (liquid film) 2970, 1720, 1420, 1110, 1030, 700, 690 cm^{-1}. Anal. Calcd for $C_{25}H_{28}O_2Si$: C, 77.27; H, 7.26. Found: C, 77.28; H, 7.23. ***threo*-Isomer 28**: ^1H NMR ($CDCl_3$) δ 9.77 (1H, d, *J* = 2 Hz, CHO), 7.34–7.65 (15H, m, $SiPh_3$), 3.81 (1H, dd, *J* = 5, 4 Hz, CH-OSi), 2.61 (1H, qdd, *J* = 7, 4, 2 Hz, CH-C=O), 1.90 (1H, qd, *J* = 7, 5 Hz, CHC-OSi), 0.99 (3H, d, *J* = 7 Hz, CH_3C-C=O), 0.90 (3H, d, *J* = 7 Hz, CH_3), 0.82 (3H, d, *J* = 7 Hz, CH_3). ***erythro*-Isomer of 28**: ^1H NMR ($CDCl_3$) δ 9.52 (1H, s, CHO), 4.03 (1H, dd, *J* = 5, 4 Hz, CH-OSi).

2-Ethyl-3-(triphenylsiloxy)heptanal: IR (liquid film) 2955, 2925, 2865, 1720, 1415, 1105, 1080, 1035, 730, 695, 685 cm^{-1}. Anal. Calcd for $C_{27}H_{32}O_2Si$: C, 77.84; H, 7.74. Found: C, 77.78; H,

7.67. ***threo*-Isomer 29**: ^{1}H NMR ($CDCl_3$) δ 9.76 (1H, d, *J* = 3 Hz, CHO), 7.34–7.80 (15H, m, $SiPh_3$), 4.07 (1H, td, *J* = 6, 4 Hz, CH-OSi), 2.24 (1H, tdd, *J* = 9, 4, 2 Hz, CH-C=O), 0.98-1.82 (8H, m, CH_2C-C=O and $(CH_2)_3$), 0.77 (3H, t, *J* = 6 Hz, CH_3), 0.75 (3H, t, *J* = 7 Hz, CH_3). ***erythro*-Isomer of 29**: ^{1}H NMR ($CDCl_3$) δ 9.50 (1H, s, CHO), 4.16 (1H, td, *J* = 6, 4 Hz, CH-OSi).

***erythro*-2-Ethyl-2-methyl-3-(triphenylsiloxy)heptanal (30)**: ^{1}H NMR ($CDCl_3$) δ 9.57 (1H, s, CHO), 7.34–7.76 (15H, m, $SiPh_3$), 3.83 (1H, dd, *J* = 8, 3 Hz, CH-OSi), 0.82-1.72 (8H, m, CH_2C-C=O and $(CH_2)_3$), 1.05 (3H, s, CH_3C-C=O), 0.71 (3H, t, *J* = 8 Hz, CH_3), 0.68 (3H, t, *J* = 6 Hz, CH_3); IR (liquid film) 2960, 2880, 1715, 1415, 1105, 1075, 1040, 725, 695, 685 cm^{-1}. Anal. Calcd for $C_{28}H_{34}O_2Si$: C, 78.09; H, 7.96. Found: C, 78.11; H, 7.97.

***threo*-2-Methyl-2-phenyl-3-(triphenylsiloxy)heptanal (31)**: ^{1}H NMR ($CDCl_3$) δ 9.43 (1H, s, CHO), 7.10–7.66 (20H, m, PhC-C=O and $SiPh_3$), 4.63 (1H, dd, *J* = 8, 2 Hz, CH-OSi), 1.67 (3H, s, CH_3C-C=O), 0.73-1.64 (6H, m, $(CH_2)_3$), 0.50 (3H, t, *J* = 6 Hz, CH_3); IR (liquid film) 3060, 2960, 2880, 1720, 1425, 1110, 1085, 1065, 1020, 700, 690 cm^{-1}. Anal. Calcd for $C_{32}H_{34}O_2Si$: C, 80.29; H, 7.16. Found: C, 80.43; H, 7.50.

***erythro*-2-(Triphenylsiloxy)cyclohexanecarbaldehyde (32)**: ^{1}H NMR ($CDCl_3$) δ 9.67 (1H, s, CHO), 7.32–7.63 (15H, m, $SiPh_3$), 4.54 (1H, td, *J* = 6, 3 Hz, CH-OSi), 2.28 (1H, dt, *J* = 9, 3 Hz, CHC=O), 1.18-2.11 (8H, m, $(CH_2)_4$); IR (liquid film) 2930, 1720, 1420, 1110, 1080, 1025, 1010, 730, 700, 690 cm^{-1}. Anal. Calcd for $C_{25}H_{26}O_2Si$: C, 77.68; H, 6.78. Found: C, 77.78; H, 6.86.

***threo*-2-(Triphenylsiloxy)cyclohexanecarbaldehyde (33)**: ^{1}H NMR ($CDCl_3$) δ 9.56 (1H, d, *J* = 3 Hz, CHO), 7.33–7.64 (15H, m, $SiPh_3$), 4.03 (1H, td, *J* = 9, 4 Hz, CH-OSi), 2.45 (1H, m, CHC=O), 1.06-1.91 (8H, m, $(CH_2)_4$); IR (liquid film) 3069, 2936, 2861, 1728, 1449, 1152, 1117, 870, 743, 700, 712 cm^{-1}. Anal. Calcd for $C_{25}H_{26}O_2Si$: C, 77.68; H, 6.78. Found: C, 77.66; H, 6.85.

Rearrangement of *erythro* Epoxy Triphenylsilyl Ether 9 (R = Ph) with $TiCl_4$. Treatment of **9** (R = Ph) (140 mg, 0.35 mmol) in CH_2Cl_2 (5 mL) with a 1 M CH_2Cl_2 solution of $TiCl_4$ (0.35 mmol) at -78 °C for 10 min afforded a mixture of 2-methyl-2-(triphenylsiloxymethyl)hexanal (**12**) and 2-methyl-1-(triphenylsiloxy)-3-heptanone (**13**) in 68% yield.

2-Methyl-2-(triphenylsiloxymethyl)hexanal (**12**): ^{1}H NMR ($CDCl_3$) δ 9.56 (1H, s, CHO), 7.29–7.64 (15H, m, $SiPh_3$), 3.87 (1H, d, *J* = 10 Hz, CH-OSi), 3.73 (1H, d, *J* = 10 Hz, CH-OSi), 1.02-1.65 (6H, m, $(CH_2)_3$), 1.06 (3H, s, CH_3), 0.85 (3H, t, *J* = 7 Hz, CH_3).

2-Methyl-1-(triphenylsiloxy)-3-heptanone (**13**): ^{1}H NMR ($CDCl_3$) δ 7.28–7.65 (15H, m, $SiPh_3$), 3.95 (1H, dd, *J* = 10, 8 Hz, CH-OSi), 3.77 (1H, dd, *J* = 10, 5 Hz, CH-OSi), 2.82 (1H, m, CH-C=O), 2.45 (2H, t, *J* = 7 Hz, CH_2-C=O), 1.16-1.62 (4H, m, $(CH_2)_2$), 1.02 (3H, d, *J* = 7 Hz, CH_3), 0.86 (3H, t, *J* = 7 Hz, CH_3).

Determination of the Optical Purity of *erythro* and *threo* β-Siloxy Aldehydes. The determination of the optical purity of (2*S*,3*S*)-2-methyl-3-(triphenylsiloxy)heptanal **10** (R = Ph) is representative.

To a solution of the aldehyde **10** (R = Ph) (35 mg, 0.087 mmol) in MeOH (1 mL) was added $NaBH_4$ (0.1 mmol) at room temperature. The mixture was stirred at room temperature for 10 min, poured into brine, and extracted with ether. The concentrated crude material was purified by column chromatography on silica gel (ether/hexane = 1:2) to furnish (2*S*,3*S*)-2-methyl-3-(triphenylsiloxy)-1-heptanol (34.4 mg, 98% yield): $[\alpha]_D^{19}$ +24.9° (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.34–7.77 (15H, m, $SiPh_3$), 3.86 (1H, td, *J* = 6, 5 Hz, CH-OSi), 3.78 (1H, dd, *J* = 11, 4 Hz, CH-O), 3.56 (1H, dd, *J* = 11, 5 Hz, CH-O), 2.08 (1H, br s,

OH), 1.79 (1H, m, C<u>H</u>-Me), 1.54 (2H, m, CH_2C-OSi), 1.12 (4H, m, $(CH_2)_2$), 0.96 (3H, d, J = 7 Hz, CH_3), 0.74 (3H, t, J = 7 Hz, CH_3).

This alcohol (34.4 mg, 0.085 mmol) was dissolved in THF (1 mL) and a 1 M THF solution of tetrabutylammonium fluoride (0.2 mL, 0.2 mmol) was added at 0°C. The mixture was stirred at 0°C for 10 min and poured into brine. The crude product was extracted with ether, concentrated, and purified by column chromatography on silica gel (AcOEt/hexane = 1:1) to furnish (2*S*,3*S*)-2-methyl-1,3-heptanediol (12 mg, 100% yield): ^{1}H NMR ($CDCl_3$) δ 3.79 (1H, dd, J = 11, 3.6 Hz, CH-O), 3.63 (1H, dd, J = 11, 7 Hz, CH-O), 3.56 (1H, m, CH-O), 2.72-3.02 (2H, br s, OH), 1.72 (1H, m, C<u>H</u>-Me), 1.16-1.62 (6H, m, $(CH_2)_3$), 0.93 (3H, t, J = 6 Hz, CH_3), 0.90 (3H, d, J = 7 Hz, CH_3).

The diol (12 mg, 0.085 mmol) was treated with (*R*)-(+)-MTPACl (107 mg, 0.43 mmol) and pyridine (52 μL, 0.65 mmol) in CH_2Cl_2 in the presence of catalytic DMAP at room temperature for 2 h. After usual workup, the crude material was purified by column chromatography on silica gel (ether/hexane = 1:100 to 1:50) to give di-MTPA ester of (2*S*,3*S*)-2-methyl-1,3-heptanediol (42 mg, 85% yield): ^{1}H NMR ($CDCl_3$) δ 7.36–7.55 (10H, m, Ph), 5.06 (1H, q, J = 6 Hz, CH-O), 4.06 and 4.20 (2H, dd, J = 11, 6 Hz, CH_2-O), 3.54 (3H, s, CH_3-O), 3.53 (1H, s, CH_3-O), 2.20 (1H, heptet, C<u>H</u>-Me), 1.57 (2H, m, CH_2C-O), 1.27 (4H, m, $(CH_2)_2$), 0.88 (3H, d, J = 7 Hz, CH_3), 0.85 (3H, d, J = 7 Hz, CH_3). Its optical purity was established to be >98% ee by HPLC analysis (JEOL Finepak SIL column; ether/hexane = 1:15 as eluant) based on separated two peaks: t_R ((2*S*,3*S*)-isomer) = 8.47 min; t_R ((2*R*,3*R*)-isomer) = 7.44 min.

The optical purity of other β-siloxy aldehydes were determined in a similar manner as described above.

Stereochemical Assignment of *erythro* and *threo* β-Siloxy Aldehydes. The stereochemical assignment of *erythro* and *threo* isomers was made by ^{1}H NMR analysis of the acetonides of diols, which was prepared as described above by the reduction-desilylation sequence of β-siloxy aldehydes.

To a solution of 2-methyl-1,3-heptanediol (9 mg, 0.06 mmol; derived from **9** (R = Me) in entry 1) in 2,2-dimethoxypropane (0.5 mL) was added catalytic *p*-TsOH at room temperature. The mixture was stirred at room temperature for 10 min. After usual workup and purification procedures, the isomeric acetonides were obtained in 76% yield. The ^{1}H NMR analysis revealed the *erythro*/*threo* ratio to be 1:2.2.

Threo isomer: ^{1}H NMR ($CDCl_3$) δ 3.69 (1H, dd, J = 11, 5 Hz, *equatorial* Me-C-C<u>H</u>-O), 3.49 (1H, t, J = 11 Hz, *axial* Me-C-C<u>H</u>-O), 3.41 (1H, m, *axial* Bu-C<u>H</u>-O), 1.18-1.50 (7H, m, MeC<u>H</u> and $(CH_2)_3$), 1.44 (3H, s, CH_3C-O), 1.40 (3H, s, CH_3C-O), 0.90 (3H, t, J = 7 Hz, CH_3), 0.74 (3H, d, J = 7 Hz, CH_3).

Erythro isomer: ^{1}H NMR ($CDCl_3$) δ 4.10 (1H, dd, J = 11, 3 Hz, *equatorial* Me-C-C<u>H</u>-O), 3.91 (1H, m, *axial* Bu-C<u>H</u>-O), 3.59 (1H, dd, J = 11, 2 Hz, *axial* Me-C-C<u>H</u>-O), 1.18-1.50 (7H, m, MeC<u>H</u> and $(CH_2)_3$), 1.44 (3H, s, CH_3C-O), 1.40 (3H, s, CH_3C-O), 1.05 (3H, d J = 7 Hz, CH_3), 0.90 (3H, t, J = 7 Hz, CH_3).

The stereochemistry of other β-siloxy aldehydes was determined in a similar manner as described above.

References and Notes

(1) Reviews of epoxide rearrangements: (a) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737. (b) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323. See also: Rickborn, B.; Gerkin, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 1693; Milstein, D.; Buchman, O.; Blum, J. *Tetrahedron Lett.* **1974**, 2257. For the transformation of 2,3-epoxy alcohols and their derivatives, see: Behrens, C. H.; Sharpless, K. B. *Aldrichimica Acta* **1983**, *16*, 67.

(2) Type-I rearrangement: (a) Maruoka, K.; Ooi, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 6431. (b) Maruoka, K.; Ooi, T.; Nagahara, S.; Yamamoto, H. *Tetrahedron* **1991**, *47*, 6983.

(3) Type-II rearrangement: (a) Maruoka, K.; Hasegawa, M.; Yamamoto, H.; Suzuki, K.; Shimazaki, M.; Tsuchihashi, G. *J. Am. Chem. Soc.* **1986**, *108*, 3827. See also: (b) Suzuki, K.; Miyazawa, M.; Tsuchihashi, G. *Tetrahedron Lett.* **1987**, *28*, 3515. (c) Shimazaki, M.; Hara, H.; Suzuki, K.; Tsuchihashi, G. *ibid.* **1987**, *28*, 5891.

(4) Epoxy alcohol rearrangement with $Ti(O\text{-}i\text{-}Pr)_4$: Morgans, D. J.; Sharpless, K. B.; Traynor, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 462.

(5) Certain *erythro* and *threo* epoxy alcohols are reported to rearrange stereospecifically with $BF_3{\cdot}OEt_2$ or alumina catalyst: Cheer, C. J.; Johnson, C. R. *J. Am. Chem. Soc.* **1968**, *90*, 178.

(6) (a) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237. (b) Hill, J. G.; Sharpless, K. B. *Org. Synth.* **1984**, *63*, 66. (c) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.

(7) (a) Masamune, S.; Choy, W. *Aldrich. Acta* **1982**, *15*, 47. (b) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1. (c) Danishefsky, S. J. *Aldrich. Acta* **1986**, *19*, 59.

(8) Reviews of aldol condensations: (a) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top Stereochem.* **1982**, *13*, 1. (b) Mukaiyama, T. *Org. React.* **1982**, *28*, 203. (c) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984, Vol.3B, Chapter 2. (d) Heathcock, C. H. In *Comprehensive Carbanion Chemistry*; Buncel, E.; Durst, T., Eds.; Elsevier: New York, 1984; Vol. 5B, p 177.

(9) For example, see: (a) Bianchi, D.; Cesti, P.; Golini, P. *Tetrahedron* **1989**, *45*, 869. (b) Ghiringhelli, D. *Tetrahedron Lett.* **1983**, *24*, 287. (c) Mukaiyama, T.; Iwasawa, N. *Chem. Lett.* **1982**, 1903.

(10) For steric and electronic nature of Si-O interactions, see: (a) Shambayati, S.; Blake, J. F.; Wierschke, S. G.; Jorgenson, W. L.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 697. (b) Stern, A. J.; Swenton, J. S. *J. Org. Chem.* **1989**, *54*, 2953. See also: Chen, X.; Hortelano, E. R.; Eliel, E. L.; Frye, S. V. *J. Am. Chem. Soc.* **1990**, *112*, 6130.

(11) Martin, S. F.; Dodge, J. A. *Tetrahedron Lett.* **1991**, *32*, 3017. For a review, see: Mitsunobu, O. *Synthesis*, **1981**, 1.