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Enantioselective Activation of Ethers by Chiral Organoaluminum Reagents: Application to Asymmetric Claisen Rearrangement

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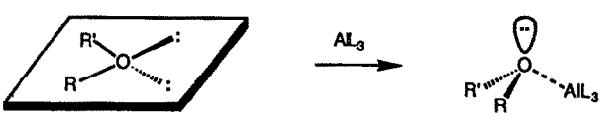
Abstract: The asymmetric Claisen rearrangement of allyl vinyl ethers has been effected with a chiral organoaluminum reagent, (*R*)-**1** or (*S*)-**1** as an example of the enantioselective activation of ether substrates. This method provides a facile asymmetric synthesis of various acylsilanes and acylgermanes with high optical purity. Among various trialkylsilyl substituents of chiral organoaluminum reagent **1**, use of the more bulky *t*-butyldiphenylsilyl group exhibits the highest enantioselectivity. The conformational analysis of two possible chairlike transition-state structures of an allyl vinyl ether substrate reveals that a chiral organoaluminum reagent **1** can discriminate between these two conformations only by a difference in the orientation of α-methylene groups of ethers.

The stereoselective activation of the ether moiety is the subject of our current interest. Oxygenophilic organoaluminum reagents are known to exhibit the great tendency to form stable ether-aluminum complexes,[1] it was our expectation that *an ethereal oxygen is stereoselectively activated by selective coordination of one of the oxygen lone pairs to aluminum reagent.* In an ether when R and R' are different, the ethereal oxygen is

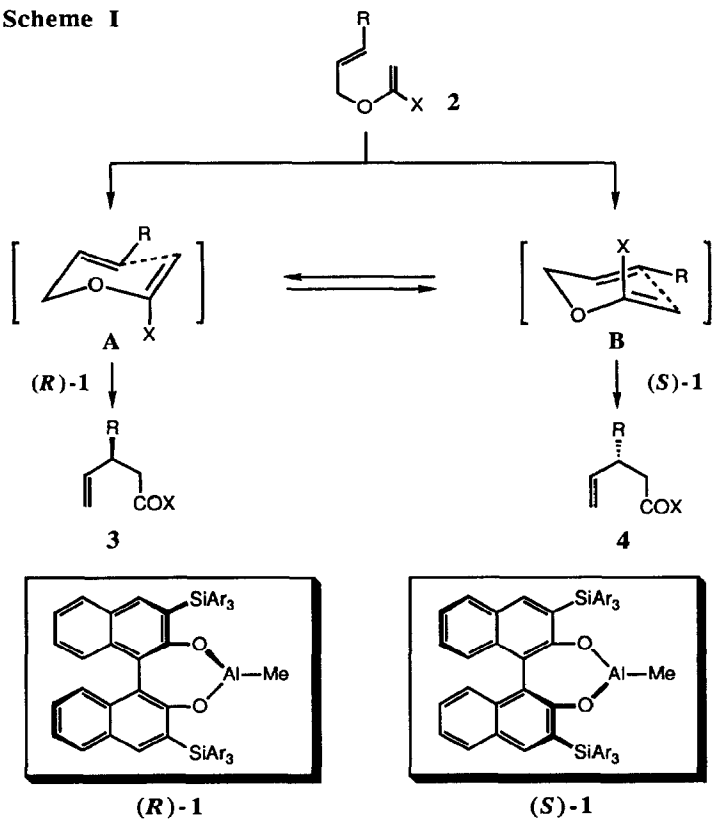


Chiral Substrates ⟹ ***Diastereoselective Activation***
Chiral Al Reagents ⟹ ***Enantioselective Activation***

prochiral, but by selective coordination to aluminum, this oxygen becomes chiral, assuming that there is no flipping at the ether oxygen. Hence, with chiral ethers diastereoselective activation of the ether oxygen would be possible using certain modified organoaluminum reagents, while combination of chiral organoaluminum reagents with prochiral ether substrates would enable the enantioselective activation of ethers.

We earlier succeeded in realizing the diastereoselective activation of the ether oxygen by applying it to the stereocontrolled Claisen rearrangement of allyl vinyl ethers with certain bulky organoaluminum reagents.[2] Thus, methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) can be utilized for obtaining (*Z*)-olefinic aldehydes with high selectivity, whereas (*E*)-olefinic aldehydes were produced in the presence of methylaluminum bis(2,6-diphenylphenoxide) (MAPH). In order to extend our concept on the stereoselective activation of ether moieties, we then examined the possibility of the enantioselective activation of the ether oxygen by applying it to the asymmetric Claisen rearrangement of allyl vinyl ethers.[3] This article describes our recent results on the enantioselective activation of ethers.

Scheme I

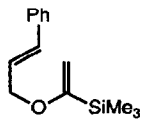
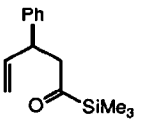
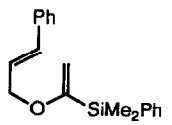
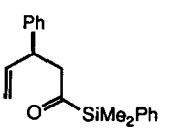
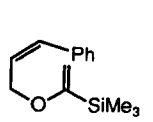
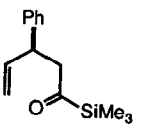
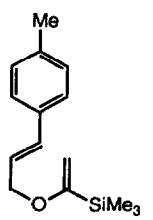
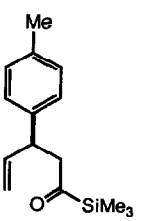
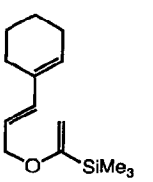
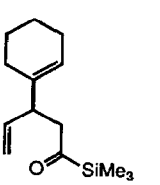


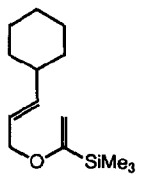
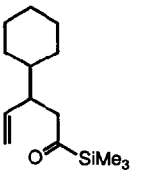
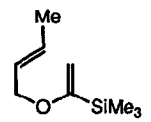
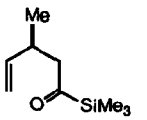
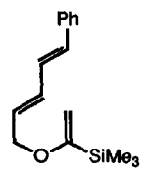
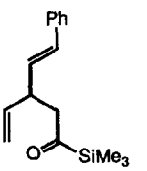
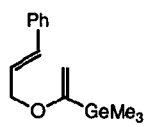
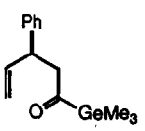
The Claisen rearrangement and its variants (Carroll, the ortho ester, Eschenmoser, and Ireland rearrangements)[4] provide an excellent stereoselective route to α,β-unsaturated carbonyl compounds (aldehydes, ketones, esters, amides, and acids) from allylic alcohols, and offer a crucial step in the stereo- and regiochemically defined synthesis of a wide variety of natural products.[5] The reactions involve a [3,3]-sigmatropic rearrangement and take place by a concerted mechanism through a cyclic six-membered chairlike transition state.[6] For the asymmetric rearrangement, two possible chairlike transition-state structures, **A** and **B** must be considered, each of which is readily interconvertible and produces enantiomers **3** and **4**, respectively as illustrated in Scheme I. Our interest is in the ability of chiral organoaluminum reagents of type (*R*)-**1** and (*S*)-**1** to discriminate between these two possible chairlike structures.[7]

The chiral organoaluminum reagent (*R*)-**1** was prepared from trimethylaluminum and (*R*)-(+)- or (*S*)-(-)-3,3'-bis(triarylsilyl)binaphthol in CH_2Cl_2 as described previously.[8,9] Attempted reaction of cinnamyl vinyl ether **2** (R = Ph, X = H) with (*R*)-**1** (Ar = Ph) resulted only in C-O bond cleavage without any rearrangement. This result implies the difficulty of forming a six-membered cyclic transition-state for the substrate **2** (R = Ph, X = H) under the influence of the organoaluminum reagent (*R*)-**1** (Ar = Ph). Accordingly, introduction of the methyl substituent into substrate **2** (*i.e.*, R = Ph, X = Me) should achieve the desired cyclic transition-state, thereby yielding a rearranged ketone, 4-phenyl-5-hexen-2-one in 43% yield; the optical yield, however, was disappointingly low (13% ee). Use of more hindered alkyl substituent X for substrate **2** could, in principle, enhance the enantioselectivity of the rearrangement, though such substrates seem to be synthetically difficult. In fact, attempted synthesis of *tert*-butyl derivative **2** (R = Ph; X = *t*-Bu) failed completely. In marked contrast, preparation of the trimethylsilyl and trimethylgermyl derivatives **2** (R = Ph; X = $SiMe_3$, $GeMe_3$) was found to be rather easy,[10] and yet these substrates were successfully transformed in the presence of (*R*)-**1** (Ar = Ph) to the corresponding acylsilane and acylgermane **3** (R = Ph; X = $SiMe_3$, $GeMe_3$), respectively, with high optical purity (80-90% ee), demonstrating the effectiveness for both steric and enantioselective requirements of substrate **2** (R = Ph; X = $SiMe_3$, $GeMe_3$). The optical yield of the acylsilane product **3** (R = Ph; X = $SiMe_3$) was determined by GLC analysis using a capillary PEG-HT column after conversion to the acetal of (-)-(2*R*,3*R*)-butanediol with triethyl orthoformate and catalytic *p*-TsOH in benzene under reflux. The absolute configuration of **3** (R = Ph; X = $SiMe_3$) was determined by correlation to the known (*R*)-3-phenyl-4-pentenal.[11] This was accomplished by desilylation of the acylsilane **3** (R = Ph; X = $SiMe_3$) with HF·Py in THF. Other selected examples are listed in Table 1.

Several characteristic features of the reaction have been noted. (1) First, the ligand effect of various chiral organoaluminum reagents was studied in detail in the rearrangement of **2** (R = Ph; X = $SiMe_3$). No rearrangement was observed with 3,3'-diphenylbinaphthol as ligand. Among various trialkylsilyl substituents in (*R*)-**1**, use of the more bulky *t*-butyldiphenylsilyl group exhibited the highest enantioselectivity (entry 3 vs. 2).[9] The less bulky *t*-butyldimethylsilyl group significantly lowered the enantioselectivity (entry 1). Introduction of alkyl substituents at the remote para position of the triphenylsilyl groups also decreased the selectivity. For example, rearrangement of **2** (R = Ph; X = $SiMe_3$) with (*R*)-**1** (Ar = p-Tolyl and *p*-$(C_6H_4)Bu^t$) in CH_2Cl_2 at -25 ~ 25 °C gave rise to **3** (R = Ph; X = $SiMe_3$) in 62% ee and 48% ee, respectively, with the *S* configuration. (2) The observed enantioselectivity appeared to increase when the trimethylsilyl substituent was changed to more hindered dimethylphenylsilyl substituent in **2** (R = Ph; X = SiR_3) (entries 5-6 vs. 2-3). (3) The present asymmetric Claisen rearrangement is best carried out in CH_2Cl_2 solvent. Use of other solvents such as toluene, ether, and THF significantly retarded the rate of the rearrangement. Attempted reaction of **2** (R = Ph; X = $SiMe_3$) with (*R*)-**1** (Ar = Ph) in these solvents at temperatures between -40 ~ 0 °C resulted in recovery of most of the starting **2**. (4) Use of *cis*-cinnamyl 1-(trimethylsilyl)vinyl ether yielded (*S*)-Claisen product **3** (R = Ph; X = $SiMe_3$) (entry 7). (5) Dienyl ether substrate **2** (R = *trans*-PhCH=CH; X = $SiMe_3$) gave the normal [3.3]-rearrangement product **3** (R = *trans*-PhCH=CH; X = $SiMe_3$) (entry 14). (6) Trimethylgermyl derivative **2** (R = Ph; X = $GeMe_3$) exhibited higher enantioselectivity than the trimethylsilyl analogue **2** (R = Ph; X = $SiMe_3$) (entries 15-16 vs. 2-3). (7) The present method is chirally flexible and allows the synthesis of both antipodal Claisen products, **3** and **4** by selection of the appropriate handedness of the chiral aluminum reagents (entry 4 vs. 2).[8]

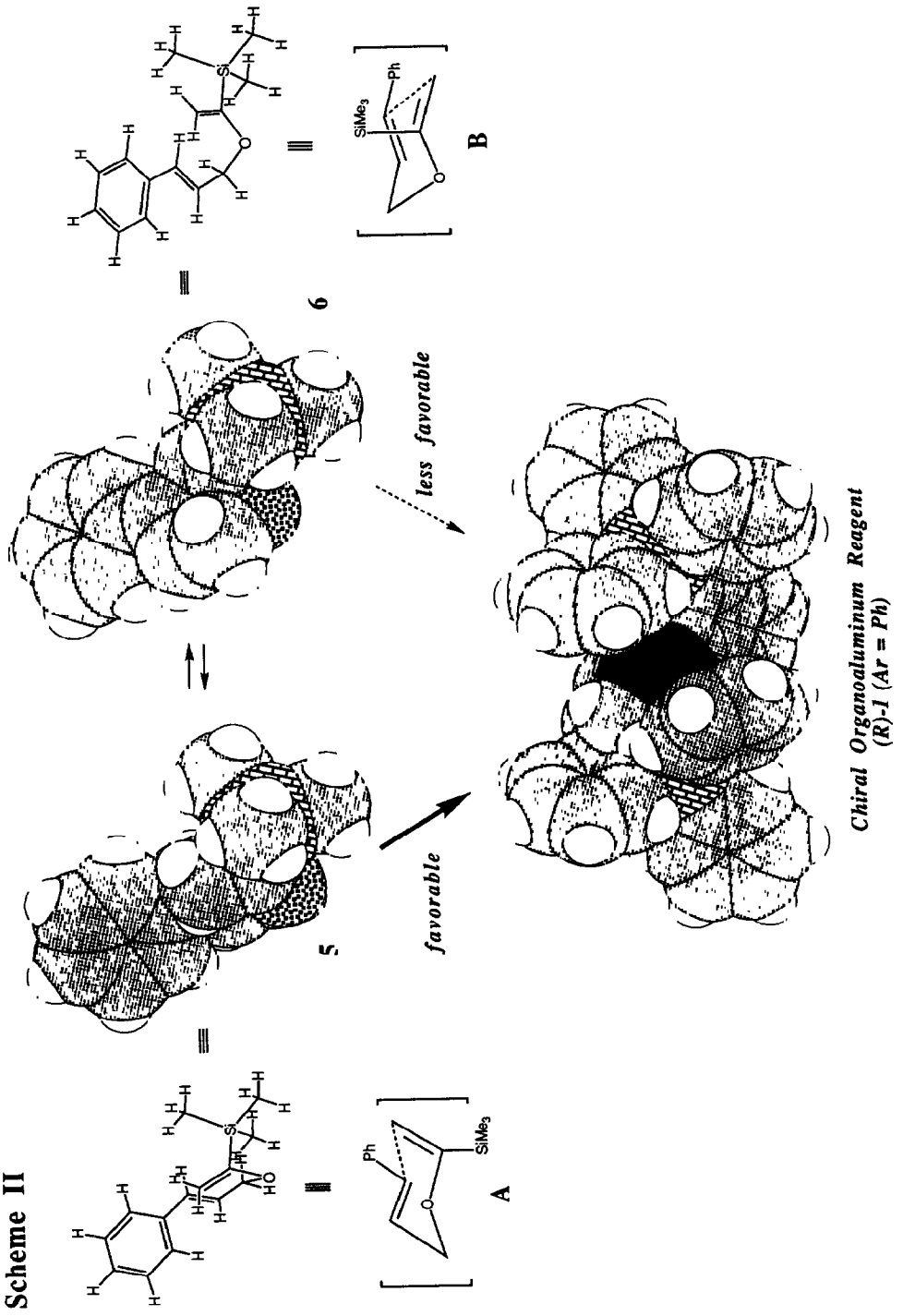
Table I. Asymmetric Claisen Rearrangement [a]

entry	catalyst (*R*)-**1**	two stage reaction conditions (°C, h)	yield [b] (%)	$[\alpha]_D$ (deg) [c]	% ee [d] (confign)
					
1	$Ar_3 = Bu^tMe_2$	-40, 0.1; -20, 24	22		14 (*S*)
2	Ar = Ph	-40, 0.1; -20, 8	86	-32.6	80 (*S*)
3	$Ar_3 = Bu^tPh_2$	-40, 0.1; -20, 3	99	-38.5	88 (*S*)
4	Ar = Ph [e]	-40, 0.1; -20, 5	85	+34.6	80 (*R*)
					
5	Ar = Ph	-78, 0.1; -40, 16	65	-19.4	85 (*S*)
6	$Ar_3 = Bu^tPh_2$	-78, 0.1; -40, 8	76	-20.6	90 (*S*)
					
7	Ar = Ph	-20, 0.1; 0, 2	77	-28.7	67 (*S*)
					
8	Ar = Ph	-78, 0.1; -40, 8	69	-26.4	78 (*S*)
					
9	Ar = Ph	-78, 0.1; -40, 6	83	+7.5	72 (*S*)
10	$Ar_3 = Bu^tPh_2$	-40, 0.1; -20, 1.5	96	+6.6	60 (*S*)

entry	catalyst (*R*)-**1**	two stage reaction conditions (°C, h)	yield [b] (%)	$[\alpha]_D$ (deg) [c]	% ee [d] (confign)
					
11	Ar = Ph	-40, 0.1; -20, 4	79	+3.4	61 (*S*)
12	Ar_3 = Bu^tPh_2	-40, 0.1; -20, 4	84	+4.0	71 (*S*)
					
13	Ar = Ph	-20, 0.1; 0, 0.7	80	-1.4	43 [f] (*S*)
					
14	Ar = Ph	-40, 0.1; -20, 10	40	-3.4	60 (*S*)
					
15	Ar = Ph	-78, 0.1; -40, 15	73	-23.7	91 (*S*)
16	Ar_3 = Bu^tPh_2	-78, 0.1; -40, 16	68		93 (*S*)

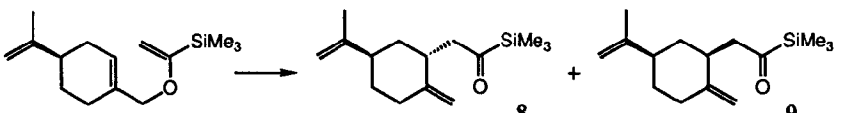
[a] Unless otherwise noted, the rearrangement of **2** was carried out with 1.1~2 equiv of (*R*)-**1** in CH_2Cl_2 solvent. [b] Isolated yield. [c] In $CHCl_3$ (*c* 0.5). [d] Determined by capillary GLC analysis after conversion to the acetals of (2*R*,3*R*)-butanediol with $HC(OEt)_3$ and catalytic *p*-TsOH in benzene. [e] Use of (*S*)-**1** as catalyst. [f] Determined by capillary GLC analysis after conversion to the alcohol with $NaBH_4$ followed by its (+)-MTPA ester.

Scheme II


favorable
less favorable
A
B
Chiral Organoaluminum Reagent
(R)-1 (Ar = Ph)

Based on these experimental findings, the transition state in the asymmetric Claisen rearrangement can be visualized as shown in Scheme II. The space-filling models **5** and **6** of cinnamyl vinyl ether **2** (R = Ph; X = $SiMe_3$) are derived by appropriate rotation of the two possible chairlike structures **A** and **B** (R = Ph; X = $SiMe_3$), respectively. In this rearrangement the orientation of α-methylene groups of **2** (R = Ph; X = $SiMe_3$) is of the utmost importance for achieving high enantioselection, and the chiral aluminum reagent (*R*)-**1** (Ar = Ph) can discriminate between these two conformations only by a difference in orientation of α-methylene groups. The conformation **5** makes a good match for the molecular cleft of the chiral aluminum reagent, producing the *S*-isomer **3** (R = Ph; X = $SiMe_3$) in accord with the experimental findings. In contrast, the conformation **6**, because of the projecting α-methylene substituent, is prevented from approaching the cleft of the aluminum reagent.

The importance of acylsilanes and acylgermanes in organic synthesis has already been demonstrated.[12] The present method, in addition to its asymmetric character, should provide a facile route to the general synthesis of such valuable compounds as shown below. Again, the organoaluminum-promoted Claisen rearrangement exhibited far better stereoselectivity than the thermal rearrangement.



7 *trans isomer* **8** *cis isomer* **9**

Heat (200 °C) : 91 % (85:15)
(±)-1 at -20 °C : 75 % (97: 3)

Experimental Section

General. Infrared (IR) spectra were recorded on a Hitachi 260-10 spectrometer. ^1H NMR spectra were measured on a Varian Gemini-200 spectrometer. Chemical shifts of ^1H NMR are expressed in parts per million downfield relative to internal tetramethylsilane (δ = 0). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. Analytical gas-liquid phase chromatograpy (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. Optical rotations were measured on a JASCO DIP-140 digital polarimeter. 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 60 E. Merck Art 9385. Microanalyses were accomplished by the Faculty of Agriculture, Nagoya University. Reaction involving air- or moisture-sensitive compounds were conducted in appropriate round-bottomed flasks with magnetic stirring bars under an atmosphere of dry argon.

In experiments requiring dry solvents, ether and tetrahydrofuran (THF) were freshly distilled from sodium metal using benzophenone ketyl as indicator. Benzene, hexane, and toluene were dried over sodium metal. Methylene chloride and DMF were stored over 4A molecular sieves. In the asymmetric Claisen process, methylene chloride as solvent was freshly distilled before use. Pyridine and triethylamine were stored over

KOH pellets. Trimethylaluminum was obtained from Toso-Akzo Chem. Co. Ltd., Japan. Other simple chemicals were purchased and used as such.

Ethyl 1-(trimethylsilyl)vinyl ether and ethyl 1-(trimethylgermyl)vinyl ether were synthesized according to the literature procedure.[10]

Preparation of Allylic Alcohols. (*Z*)-Cinnamyl alcohol was prepared by the partial hydrogenation of 3-phenyl-2-propyn-1-ol with P-2 Nickel and ethylenediamine in EtOH under a hydrogen atmosphere.[13] (*E*)-3-(*p*-Tolyl)-2-propen-1-ol, (*E*)-3-(1-cyclohexenyl)-2-propen-1-ol, (*E*)-3-cyclohexyl-2-propen-1-ol, and (*2E,4E*)-5-phenyl-2,4-pentadien-1-ol were prepared by reaction of aldehydes [*p*-tolylaldehyde, 1-(cyclohexene)carbaldehyde, cyclohexanecarbaldehyde, and (*E*)-cinnamaldehyde] with the sodium enolate of ethyl diethylphosphonoacetate in THF followed by reduction of the resulting α,β-unsaturated esters with AlH_3.

Preparation of (*E*)-Cinnamyl Vinyl Ether.[14] A mixture of (*E*)-cinnamyl alcohol (15 mmol), mercury(II) acetate (3.2 g, 10 mmol), and ethyl vinyl ether (37.5 mL) was stirred at room temperature for 3 h. The mixture was then poured into 5% potassium hydroxide solution (15 mL) and extracted with hexane. After drying over Na_2SO_4, the hexane extracts were concentrated. The residual crude product was purified by column chromatography using hexane as eluant to afford (*E*)-cinnamyl vinyl ether[15] (1.492 g, 62% yield): ^1H NMR ($CDCl_3$) δ 7.25-7.43 (5H, m, C_6H_5), 6.66 (1H, d, J = 16 Hz, Ph-CH=C), 6.52 (1H, dd, J = 7, 14 Hz, C=CH-O), 6.32 (1H, dt, J = 16, 6 Hz, Ph-C=CH), 4.40 (2H, d, J = 6 Hz, CH_2-O), 4.28 (1H, dd, J = 2, 14 Hz, *cis* CH=C-O), 4.07 (1H, dd, J = 2, 7 Hz, *trans* CH=C-O); IR (liqiud film) 3025, 2900, 1635, 1610, 1450, 1370, 1315, 1190, 1150, 1055, 960, 815, 735, 685 cm^{-1}.

(*E*)-Cinnamyl Isopropenyl Ether. 38% yield: ^1H NMR ($CDCl_3$) δ 7.24-7.44 (5H, m, C_6H_5), 6.67 (1H, d, J = 16Hz, Ph-CH=C), 6.36 (1H, dt, J = 16, 6 Hz, Ph-C=CH), 4.38 (2H, d, J = 6 Hz, CH_2-O), 3.91 (2H, s, CH_2=C-O), 1.88 (3H, s,CH_3); IR (liqiud film) 3030, 2920, 1660, 1600, 1495, 1450, 1365, 1275, 1115, 1060, 985, 965, 800, 745, 690 cm^{-1}.

General Method for Preparation of Allylic 1-(Trimethylsilyl)vinyl Ethers.[14] A mixture of allylic alcohol (10 mmol), mercury(II) acetate (637 mg, 2 mmol), and ethyl 1-(trimethylsilyl)vinyl ether (1.5 g, 10 mmol) was stirred at room temperature for 8-12 h. The mixture was then poured into 5% potassium hydroxide solution and extracted with hexane. After drying over Na_2SO_4, the hexane extracts were concentrated. The residual crude product was purified by column chromatography (hexane or ether/hexane = 1:50 as eluent).

(*E*)-Cinnamyl 1-(Trimethylsilyl)vinyl Ether. 34% yield: ^1H NMR ($CDCl_3$) δ 7.20-7.44 (5H, m, C_6H_5), 6.64 (1H, d, J = 16Hz, Ph-CH=C), 6.35 (1H, dt, J = 16, 5 Hz, Ph-C=CH), 4.65 (1H, d, J = 2 Hz, CH=C-O), 4.38 (2H, d, J = 5 Hz, CH_2-O), 4.36 (1H, d, J = 2 Hz, CH=C-O), 0.15 (9H, s, $Si(CH_3)_3$); IR (CCl_4 solution) 3025, 2960, 2900, 1590, 1495, 1450, 1365, 1250, 1210, 1015, 960, 850, 840, 685 cm^{-1}.

(*E*)-Cinnamyl 1-(Dimethylphenylsilyl)vinyl Ether. 19% yield: ^1H NMR ($CDCl_3$) δ 7.20-7.64 (10H, m, C_6H_5), 6.60 (1H, d, J = 16Hz, Ph-CH=C), 6.33 (1H, dt, J = 16, 6 Hz, Ph-C=CH), 4.75 (1H, d,

J = 2 Hz, CH=C-O), 4.39-4.42 (3H, m, CH=C-O and CH_2-O), 0.43 (6H, s, $Si(CH_3)_2$); IR (liquid film) 3025, 2960, 1585, 1425, 1240, 1205, 1110, 1015, 965, 880, 815, 775, 725, 685 cm^{-1}.

(*Z*)-Cinnamyl 1-(Trimethylsilyl)vinyl Ether. 43% yield: ^1H NMR ($CDCl_3$) δ 7.20-7.41 (5H, m, C_6H_5), 6.62 (1H, d, J = 12Hz, Ph-CH=C), 5.91 (1H, dt, J = 12, 6 Hz, Ph-C=CH), 4.54 (1H, d, J = 2 Hz, CH=C-O), 4.48 (2H, d, J = 6 Hz, CH_2-O), 4.32 (1H, d, J = 2 Hz, CH=C-O), 0.14 (9H, s, $Si(CH_3)_3$); IR (liqiud film) 3040, 2970, 1590, 1500, 1250, 1215, 1030, 935, 840, 775, 760, 700 cm^{-1}.

(*E*)-3-(*p*-Tolyl)-2-propenyl 1-(Trimethylsilyl)vinyl Ether. 35% yield: ^1H NMR ($CDCl_3$) δ 7.13 and 7.30 (4H, d, J = 8 Hz, C_6H_4), 6.60 (1H, d, J = 16Hz, Ar-CH=C), 6.30 (1H, dt, J = 16, 6 Hz, Ar-C=CH), 4.64 (1H, d, J = 2 Hz, CH=C-O), 4.36 (2H, d, J = 6 Hz, CH_2-O), 4.35 (1H, d, J = 2 Hz, CH=C-O), 2.34 (3H, s, Ar-CH_3), 0.15 (9H, s, $Si(CH_3)_3$); IR (CCl_4 solution) 3040, 2970, 1590, 1520, 1365, 1250, 1210, 1020, 965, 855, 840, 700 cm^{-1}.

(*E*)-3-(1-Cyclohexenyl)-2-propenyl 1-(Trimethylsilyl)vinyl Ether. 22% yield: ^1H NMR ($CDCl_3$) δ 6.25 (1H, d, J = 16Hz, cyclohexenyl-CH=C), 5.75 (1H, br s, cyclic C=CH), 5.68 (1H, dt, J = 16, 6 Hz, cyclohexenyl-C=CH), 4.31 and 4.60 (2H, d, J = 2 Hz, CH_2=C-O), 4.25 (2H, d, J = 6 Hz, CH_2-O), 2.06-2.22 (4H, m, CH_2-C=C-CH_2), 1.55-1.74 (4H, m, CH_2CH_2), 0.13 (9H, s, $Si(CH_3)_3$); IR (liqiud film) 2930, 2860, 1590, 1250, 1210, 1020, 965, 840, 760 cm^{-1}.

(*E*)-3-Cyclohexyl-2-propenyl 1-(Trimethylsilyl)vinyl Ether. 32% yield: ^1H NMR ($CDCl_3$) δ 5.48-5.73 (2H, m, CH=CH), 4.30 and 4.58 (2H, d, J = 2 Hz, CH_2=C-O), 4.15 (2H, d, J = 5 Hz, CH_2-O), 1.90-2.08 (1H, m, CH-C=C-C-O), 0.97-1.82 (10H, m, $(CH_2)_5$), 0.13 (9H, s, $Si(CH_3)_3$); IR (liqiud film) 2930, 2860, 1590, 1450, 1245, 1220, 1025, 975, 845, 760 cm^{-1}.

(*E*)-Crotyl 1-(Trimethylsilyl)vinyl Ether. 24% yield: ^1H NMR ($CDCl_3$) δ 5.56-5.84 (2H, m, CH=CH), 4.30 and 4.58 (2H, d, J = 2 Hz, CH_2=C-O), 4.13 (2H, d, J = 5 Hz, CH_2-O), 1.73 (3H, d, J = 5 Hz, C=C-CH_3), 0.12 (9H, s, $Si(CH_3)_3$); IR (liqiud film) 2970, 2910, 2870, 1585, 1450, 1365, 1250, 1215, 1090, 1015, 965, 845, 760 cm^{-1}.

(*2E,4E*)-5-Phenyl-2,4-pentadienyl 1-(Trimethylsilyl)vinyl Ether. 17% yield: ^1H NMR ($CDCl_3$) δ 7.17-7.41 (5H, m, C_6H_5), 6.80 (1H, dd, J = 10, 16 Hz, Ph-C=CH), 6.54 (1H, d, J = 16 Hz, Ph-CH=C), 6.43 (1H, dd, J = 10, 15 Hz, Ph-C=C-CH=C), 5.94 (1H, dt, J = 15, 6 Hz, Ph-C=C-C=CH), 4.34 and 4.61 (2H, d, J = 2 Hz, CH_2=C-O), 4.30 (2H, d, J = 6 Hz, CH_2-O), 0.14 (9H, s, $Si(CH_3)_3$).

(*E*)-Cinnamyl 1-(Trimethylgermyl)vinyl Ether. 31% yield: ^1H NMR ($CDCl_3$) δ 7.20-7.44 (5H, m, C_6H_5), 6.64 (1H, d, J = 16Hz, Ph-CH=C), 6.35 (1H, dt, J = 16, 6 Hz, Ph-C=CH), 4.60 (1H, d, J = 2 Hz, CH=C-O), 4.39 (2H, d, J = 6 Hz, CH_2-O), 4.22 (1H, d, J = 2 Hz, CH=C-O), 0.29 (9H, s, $Ge(CH_3)_3$); IR (CCl_4 solution) 3030, 2980, 2910, 2860, 1585, 1360, 1240, 1195, 1015, 965, 830, 690 cm^{-1}.

(*R*)-Perillyl 1-(Trimethylsilyl)vinyl Ether. 37% yield: ^1H NMR ($CDCl_3$) δ 5.69-5.78 (1H, m, cyclic C=CH), 4.73 (2H, s, CH_2=C-C), 4.30 and 4.59 (2H, d, J = 2 Hz, CH_2=C-O), 4.07 (2H, s, CH_2-O),

1.40-2.27 (7H, m, $CH_2CHCH_2CH_2$), 1.75 (3H, s, C=C-CH_3), 0.13 (9H, s, $Si(CH_3)_3$); IR (liquid film) 2970, 2925, 1650, 1590, 1450, 1435, 1245, 1210, 1050, 1010, 890, 840, 755 cm^{-1}.

Preparation of Chiral Organoaluminum Reagent (*R*)-1 or (*S*)-1.[8a] To a degassed solution of (*R*)-(+)- or (*S*)-(-)-3,3'-bis(triarylsilyl)binaphthol (0.2 mmol)[9] in CH_2Cl_2 (3 mL) was added a 0.5 M hexane solution of Me_3Al (0.4 mL, 0.2 mmol). Methane gas evolved immediately, the resulting wine-red solution was stirred at room temperature for 1.5 h and used as a solution of chiral organoaluminum reagent (*R*)-**1** or (*S*)-**1** in CH_2Cl_2 without any purification.

General Method for the Asymmetric Claisen Rearrangement of Allylic Vinyl Ethers with Chiral Organoaluminum Reagent (*R*)-1 or (*S*)-1 (Ar = Ph). To a solution of the chiral organoaluminum reagent (*R*)-**1** or (*S*)-**1** (Ar = Ph) (0.2 mmol) in degassed CH_2Cl_2 (3 mL) was added an allylic vinyl ether (0.1 mmol) in CH_2Cl_2 (0.3 mL) at -78 ~ -40 °C. The mixture was stirred under the conditions indicated in Table 1. The reaction mixture was poured into 1*N* HCl, extracted with CH_2Cl_2, and dried over Na_2SO_4 Evaporation of solvents and purification of the residue by column chromatography (ether/hexane as eluant) gave a Claisen product in the yields shown in Table I. The Claisen product was converted to the acetal of (-)-(2*R*,3*R*)-butanediol with triethyl orthoformate (2 equiv) and catalytic *p*-TsOH in benzene under reflux for 1-3 h. Its optical purity was established by capillary GLC analysis based on separated two peaks.

(*S*)-4-Phenyl-5-hexen-2-one. 43% yield; 13% ee by capillary GLC after conversion to the acetal of (-)-(2*R*,3*R*)-butanediol (t_R ((*R*)-isomer) = 40.7 min and t_R ((*S*)-isomer) = 40.1 min at the column temperature of 130 °C); ^1H NMR ($CDCl_3$) δ 7.17-7.36 (5H, m, C_6H_5), 5.97 (1H, ddd, *J* = 7, 10, 17 Hz, Ph-C-CH=), 5.06 (1H, d, *J* = 10 Hz, CH=C-C), 5.02 (1H, d, *J* = 17 Hz, CH=C-C), 3.92 (1H, q, *J* = 7 Hz, Ph-CH), 2.86 (2H, dd, *J* = 7, 3 Hz, CH_2-C=O), 2.09 (3H, s, CH_3); IR (liquid film) 3040, 1715, 1635, 1495, 1455, 1410, 1360, 1160, 995, 920, 745, 695 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O$: C, 82.70; H, 8.10. Found: C, 82.70; H, 8.08.

(*S*)-3-Phenyl-1-(trimethylsilyl)-4-penten-1-one. 86% yield; 80% ee by capillary GLC after conversion to the acetal of (-)-(2*R*,3*R*)-butanediol (t_R ((*R*)-isomer) = 16.0 min and t_R ((*S*)-isomer) = 15.8 min at the column temperature of 140 °C); $[\alpha]_D^{24}$ -32.6 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.16–7.34 (5H, m, C_6H_5), 5.95 (1H, ddd, *J* = 7, 10, 17 Hz, Ph-C-CH=), 5.03 (1H, d, *J* = 10 Hz, CH=C-C), 4.94 (1H, d, *J* = 17 Hz, CH=C-C), 4.01 (1H, q, *J* = 7 Hz, Ph-CH), 3.03 (2H, d, *J* ≠ 7 Hz, CH_2-C=O), 0.14 (9H, s, $Si(CH_3)_3$); IR (liquid film) 3035, 2970, 1645, 1495, 1455, 1250, 910, 840, 750, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.43; H, 8.92.

(*R*)-3-Phenyl-1-(trimethylsilyl)-4-penten-1-one. 85% yield; 80% ee by capillary GLC : $[\alpha]_D^{24}$ +34.6 (*c* 0.5, $CHCl_3$).

(*S*)-3-Phenyl-1-(dimethylphenylsilyl)-4-penten-1-one. 65% yield; 85% ee by capillary GLC after conversion to the acetal of (-)-(2*R*,3*R*)-butanediol (t_R ((*R*)-isomer) = 34.0 min and t_R ((*S*)-isomer) = 33.4 min at the column temperature of 180 °C): $[\alpha]_D^{24}$ -19.4 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.04–

7.52 (10H, m, C_6H_5), 5.85 (1H, ddd, J = 7, 10, 17 Hz, Ph-C-CH=), 4.95 (1H, d, J = 10 Hz, CH=C-C), 4.83 (1H, d, J = 17 Hz, CH=C-C), 3.94 (1H, q, J = 7 Hz, Ph-CH), 2.98 (2H, d, J = 7 Hz, CH_2-C=O), 0.41 and 0.45 (6H, s, $Si(CH_3)_2$); IR (liquid film) 3080, 3040, 1650, 1500, 1430, 1250, 1110, 920, 835, 820, 780, 730, 695 cm^{-1}. Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53. Found: C, 77.51; H, 7.46.

(*S*)-3-(*p*-Tolyl)-1-(trimethylsilyl)-4-penten-1-one. 69% yield; 78% ee by capillary GLC after conversion to the acetal of (-)-(2*R*,3*R*)-butanediol (t_R ((*R*)-isomer) = 51.1 min and t_R ((*S*)-isomer) = 49.7 min at the column temperature of 120 °C): $[\alpha]_D^{24}$ -26.4 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.04–7.14 (4H, m, C_6H_4), 5.93 (1H, ddd, J = 7, 10, 17 Hz, Ar-C-CH=), 5.01 (1H, d, J = 10 Hz, CH=C-C), 4.93 (1H, d, J = 17 Hz, CH=C-C), 3.97 (1H, q, J = 7 Hz, Ar-CH), 3.01 (2H, dd, J = 7, 4 Hz, CH_2-C=O), 2.31 (3H, s, Ar-CH_3), 0.15 (9H, s, $Si(CH_3)_3$); IR (liquid film) 2970, 2925, 1645, 1515, 1415, 1245, 915, 845, 820, 755 cm^{-1}. Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 73.16; H, 8.85.

(*S*)-3-(1-Cyclohexenyl)-1-(trimethylsilyl)-4-penten-1-one. 83% yield; 72% ee by capillary GLC after conversion to the acetal of (-)-(2*R*,3*R*)-butanediol (t_R ((*R*)-isomer) = 19.8 min and t_R ((*S*)-isomer) = 20.6 min at the column temperature of 120 °C): $[\alpha]_D^{24}$ +7.5 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.69 (1H, ddd, J = 7, 10, 17 Hz, cyclohexenyl-C-CH=), 5.43 (1H, br s, cyclic C=CH), 4.95 (1H, d, J = 10 Hz, CH=C-C), 4.92 (1H, d, J = 17 Hz, CH=C-C), 3.25 (1H, q, J = 7 Hz, cyclohexenyl-CH), 2.77 (2H, d, J = 7 Hz, CH_2-C=O), 1.85-2.04 (4H, m, CH_2-C=C-CH_2), 1.47-1.65 (4H, m, -CH_2CH_2-), 0.20 (9H, s, $Si(CH_3)_3$); IR (liquid film) 2930, 2855, 2840, 1640, 1450, 1440, 1410, 1245, 910, 840, 750 cm^{-1}. Anal. Calcd for $C_{14}H_{24}OSi$: C, 71.11; H, 10.24. Found: C, 71.20; H, 10.50.

(*S*)-3-Cyclohexyl-1-(trimethylsilyl)-4-penten-1-one. 79% yield; 61% ee by capillary GLC after conversion to the acetal of (-)-(2*R*,3*R*)-butanediol (t_R ((*R*)-isomer) = 19.4 min and t_R ((*S*)-isomer) = 18.2 min at the column temperature of 120 °C): $[\alpha]_D^{24}$ +3.4 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.61 (1H, ddd, J = 7, 10, 17 Hz, cyclohexyl-C-CH=), 4.95 (1H, d, J = 10 Hz, CH=C-C), 4.88 (1H, d, J = 17 Hz, CH=C-C), 2.66 (2H, d, J = 7 Hz, CH_2-C=O), 2.47-2.61 (1H, m, cyclohexyl-CH), 0.79-1.80 (11H, m, cyclohexyl), 0.18 (9H, s, $Si(CH_3)_3$); IR (liquid film) 2930, 2870, 1645, 1455, 1415, 1250, 1000, 915, 845, 755 cm^{-1}. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.53; H, 11.16.

(*S*)-3-Methyl-1-(trimethylsilyl)-4-penten-1-one. 80% yield; 43% ee by capillary GLC after conversion to the alcohol with $NaBH_4$ followed by its (+)-MTPA ester (t_R ((*R*)-isomer) = 23.0 and 25.1 min and t_R ((*S*)-isomer) = 23.5 and 24.5 min at the column temperature of 170 °C): $[\alpha]_D^{24}$ -1.4 (*c* 0.5, $CHCl_3$); ^1H-NMR ($CDCl_3$) δ 5.76 (1H, ddd, J = 7, 10, 17 Hz, C-CH=C), 4.96 (1H, d, J = 17 Hz, CH=C-C), 4.91 (1H, d, J = 10 Hz, CH=C-C), 2.71-2.87 (1H, m, Me-CH), 2.48-2.73 (2H, m, CH_2-C=O), 0.97 (3H, d, J = 7 Hz, CH_3), 0.20 (9H, s, $Si(CH_3)_3$); IR (liquid film) 3090, 2970, 2930, 2900, 1645, 1460, 1420, 1400, 1245, 1000, 910, 845, 750 cm^{-1}. Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.36; H, 10.97.

(*S*)-(*E*)-5-Phenyl-1-(trimethylsilyl)-3-vinyl-4-penten-1-one. 40% yield; 60% ee by capillary GLC after conversion to the acetal of (-)-(2*R*,3*R*)-butanediol (t_R ((*R*)-isomer) = 68.8 min and t_R ((*S*)-isomer) = 70.7 min at the column temperature of 140 °C): $[\alpha]_D^{24}$ -3.4 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.12–

7.39 (5H, m, C_6H_5), 6.35 (1H, d, J = 16 Hz, Ph-CH=C), 6.09 (1H, dd, J = 7, 16 Hz, Ph-C=CH), 5.80 (1H, ddd, J = 7, 10, 17 Hz, C=CH-C), 5.03 (1H, d, J = 17 Hz, CH=C-C), 5.02 (1H, d, J = 10 Hz, CH=C-C), 3.56 (1H, quintet, J = 7 Hz, C=C-CH), 0.18 (9H, s, $Si(CH_3)_3$).

(*S*)-3-Phenyl-1-(trimethylgermyl)-4-penten-1-one. 73% yield; 91% ee by capillary GLC after conversion to the acetal of (-)-(2*R*,3*R*)-butanediol (t_R ((*R*)-isomer) = 48.6 min and t_R ((*S*)-isomer) = 48.2 min at the column temperature of 120 °C): $[\alpha]_D^{24}$ -23.7 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.14–7.35 (5H, m, C_6H_5), 5.95 (1H, ddd, J = 7, 10, 17 Hz, Ph-C-CH=), 5.04 (1H, d, J = 10 Hz, CH=C-C), 4.95 (1H, d, J = 17 Hz, CH=C-C), 4.00 (1H, q, J = 7 Hz, Ph-CH), 3.07 (2H, d, J = 7 Hz, CH_2-C=O), 0.29 (9H, s, $Ge(CH_3)_3$); IR (liquid film) 3030, 2970, 2910, 1665, 1495, 1450, 1415, 1215, 915, 825, 755, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{20}OGe$: C, 60.72; H, 7.28. Found: C, 60.60; H, 7.33.

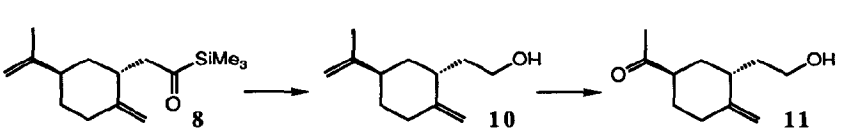
(*R,R*)-*trans*-Acylsilane 8. 75% yield; ^1H NMR ($CDCl_3$) δ 4.70 (2H, s, CH_2=C-Me), 4.61-4.68 (2H, m, CH_2=C), 3.03-3.15 (1H, m, C=C-CH), 2.78 (2H, d, J = 7 Hz, CH_2-C=O), 2.10-2.28 (3H, m, isopropenyl-CH and C=C-CH_2), 1.70 (3H, s, CH_3), 1.20-1.88 (4H, m, CH_2), 0.20 (9H, s, $Si(CH_3)_3$); IR (liquid film) 3080, 2930, 2870, 1645, 1440, 1415, 1380, 1250, 885, 840, 755 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSi$: C, 71.94; H, 10.46. Found: C, 72.12; H, 10.71. The *cis/trans* ratio of the Claisen products was established by capillary GLC analysis based on separated two peaks: t_R (*cis*- isomer **9**) = 9.2 min; t_R (*trans*-isomer **8**) = 8.0 min at the column temperature of 150 °C.

Stereochemical Assignment of the (*R,R*)-*trans*-Isomer 8. The Claisen product **8** (500 mg) in MeOH (5 mL) was reduced with excess $NaBH_4$ at 0 °C for 10 min. After usual work up and purification procedures, α-silyl alcohol was dissolved in DMF (5 mL) and treated with a 1 M THF solution of tetrabutylammonium fluoride (3.5 mL) at room temperature for 12 h. Aqueous work up and isolation by column chromatography on silica gel (ether/hexane = 1:1) produced (*R,R*)-alcohol **10** (311 mg, 87 % yield): ^1H NMR ($CDCl_3$) δ 4.70 (4H, br s, $2CH_2$=C), 3.65 (2H, t, J = 7 Hz, CH_2-O), 2.49-2.62 (1H, m, C=C-CH), 2.15-2.35 (3H, m, C=C-CH and C=C-CH_2), 1.70 (3H, s, CH_3), 1.20-2.01 (7H, m, $3CH_2$ and OH).

The isomeric ratio of the (*R,R*)-alcohol **10** was determined to be 97:3 by capillary GLC analysis based on the observation of two peaks: t_R (*cis*-isomer) = 17.5 min; t_R (*trans*-isomer **10**) = 13.4 min at the column temperature of 150 °C.

The (*R,R*)-alcohol **10** (300 mg) in CH_2Cl_2 (5 mL) was treated with MCPBA (431 mg, 2 mmol) at 0 °C for 1 h to give mono-epoxidation products (155 mg), which, without purification, were reacted with HIO_4 (228 mg, 1 mmol) in aqueous THF (3 mL) at 0 °C for 2.5 h to afford (*R,R*)-*trans*-ketoalcohol **11** (45 mg, 15% yield): ^1H NMR ($CDCl_3$) δ 4.72 (2H, s, CH_2=C), 3.66 (2H, t, J = 7 Hz, CH_2-O), 2.45-2.75 (2H, m, CH-C=O and C=C-CH), 2.22 (2H, dd, J = 4, 8 Hz, C=C-CH_2), 2.15 (3H, s, CH_3), 1.36-2.05 (7H, m, $3CH_2$ and OH).

This isomeric ratio was determined to be 97:3 by capillary GLC analysis based on the observation of two peaks:t_R (*trans*-isomer) = 18.0 min; t_R (*cis*- isomer) = 23.0 min at the column temperature of 180 °C.



The *trans*-ketoalcohol **11** was isomerized with NaOMe in MeOH under reflux for 6 h to furnish a 52:48 mixture of *trans*- and *cis*-ketoalcohol.

Determination of the Absolute Configuration of (*S*)-3-Phenyl-1-(trimethylsilyl)-4-penten-1-one and (*S*)-3-Phenyl-1-(dimethylphenylsilyl)-4-penten-1-one. To a solution of (*S*)-3-phenyl-1-(trimethylsilyl)-4-penten-1-one (46 mg, 0.2 mmol; $[\alpha]_D^{24}$ -32.6 (*c* 0.5, $CHCl_3$), 80% ee) in THF (3 mL) was added excess Py·HF (5 drops) at room temperature. The mixture was stirred at room temperature for 2 days, poured into sat. $NaHCO_3$, and extracted with ether. The concentrated crude material was purified by column chromatography on silica gel (ether/hexane = 1:7) to furnish (*S*)-3-phenyl-4-pentenal (4 mg, 13% yield): $[\alpha]_D$ +11.2 (*c* 0.1, EtOH); ^1H NMR ($CDCl_3$) δ 9.74 (1H, t, *J* = 2 Hz, CHO), 7.20–7.38 (5H, m, C_6H_5), 6.01 (1H, ddd, *J* = 7, 10, 17 Hz, Ph-C=CH), 5.13 (1H, d, *J* = 10 Hz, CH=C-C), 5.08 (1H, d, *J* = 17 Hz, CH=C-C), 3.97 (1H, q, *J* = 7 Hz, Ph-CH), 2.86 (2H, dt, *J* = 7, 2 Hz, CH_2-C=O).

Since the optical rotation value of the authentic (*R*)-3-phenyl-4-pentenal of 35% ee is reported to be $[\alpha]_D$ -5.0° (*c* 0.1, EtOH)[11], this Claisen product possesses the *S* configuration.

The absolute configuration of (*S*)-3-phenyl-1-(dimethylphenylsilyl)-4-penten-1-one was also established to be *S* in a similar manner as described above.

Determination of the Absolute Configuration of (*S*)-3-Cyclohexyl-1-(trimethylsilyl)-4-penten-1-one and (*S*)-3-(1-Cyclohexenyl)-1-(trimethylsilyl)-4-penten-1-one. A solution of (*S*)-3-cyclohexyl-1-(trimethylsilyl)-4-penten-1-one (12 mg, 0.05 mmol; $[\alpha]_D^{24}$ +3.4 (*c* 0.5, $CHCl_3$), 61% ee) in EtOH was hydrogenated with Raney Ni under H_2 at room temperature for 30 min. This mixture was filtered with the aid of EtOH. The combined filtrates were concentrated and applied to column chromatography (ether/hexane = 1:5 as eluant) to furnish (3*R*)-3-cyclohexyl-1-(trimethylsilyl)-1-pentanol (9 mg, 72% yield): ^1H NMR ($CDCl_3$) δ 3.32-3.45 (1H, m, CH-O), 0.82-1.82 (20H, m, C-H and OH), 0.04 (9H, s, $Si(CH_3)_3$).

This alcohol (9 mg) was dissolved in DMF (2 mL) and treated with a 1 M THF solution of tetrabutylammonium fluoride (0.1 mL) at room temperature for 3 h. Usual work up and purification of the residue by column chromatography (ether/hexane = 1:1 as eluant) gave (*R*)-3-cyclohexyl-1-pentanol (5 mg, 79% yield): ^1H NMR ($CDCl_3$) δ 3.65 (2H, dt, *J* = 2, 8 Hz, CH_2-O), 0.87 (3H, t, *J* = 7 Hz, CH_3), 0.81-1.82 (17H, m, C-H).

Dimethyl sulfoxide (16 mg, 0.2 mmol) was added dropwise to a solution of $(COCl)_2$ (9 μL, 0.1 mmol) in CH_2Cl_2 (1 mL) at -78 °C. After 20 min, (*R*)-3-cyclohexyl-1-pentanol (5 mg) dissolved in CH_2Cl_2 (1 mL) was added at -78 °C slowly. The resulting white suspension was stirred at -78 °C for 30 min and then treated with Et_3N (70 μL, 0.5 mmol) at this temperature. The whole mixture was stirred at -78 °C for 1 h and at 0 °C for 2 h, and worked up with water. The organic layer was extracted with CH_2Cl_2 and concentrated. The residue was purified by column chromatography (ether/hexane = 1:10 as eluant) to furnish (*R*)-3-cyclohexylpentanal (4.4 mg, 95% yield): ^1H NMR ($CDCl_3$) δ 9.77 (1H, t, *J* = 3 Hz, CHO), 2.24 and 2.42 (2H, ddd, *J* = 3, 6, 16 Hz, CH_2-C=O), 0.88 (3H, t, *J* = 7 Hz, CH_3), 0.84-1.85 (14H, m, C-H).

(*R*)-3–Cyclohexylpentanal, thus obtained, was converted to the acetal of (-)-(2*R*,4*R*)-pentanediol with triethyl orthoformate (2 equiv) and catalytic *p*-TsOH in benzene at room temperature for 2 h. The absolute configuration was established to be *R* by comparison with retention time of an authentic sample by capillary GLC analysis based on the observation of two peaks: t_R ((*R*)- isomer) = 52.1 min; t_R ((*S*)-isomer) = 50.0

min at the column temperature of 110 °C. The authentic (*R*)-3-cyclohexylpentanal was prepared by the Et_3Al-mediated ethylation to the (*E*)-3-cyclohexyl-2-pentenal acetal derived from (*R,R*)-(+)-*N,N,N',N'*-tetramethyltartaric acid diamide according to the literature procedure.[16]

The absolute configuration of (*S*)-3-(1-cyclohexenyl)-1-(trimethylsilyl)-4-penten-1-one was also established to be *S* in a similar manner as described above.

Determination of the Absolute Configuration of (*S*)-3-Phenyl-1-(trimethylgermyl)-4-penten-1-one. The absolute configuration of the optically active (*S*)-3-phenyl-1-(trimethyl-germyl)-4-penten-1-one was assigned to be *S* by comparison with an authentic specimen after conversion to the acetal of (-)-(2*R*,3*R*)-butanediol followed by its hydrogenation. The authentic (*R*)-3-phenyl-1-(trimethylgermyl)-pentan-1-one was synthesized as described below.

The optically active (*R*)-3-phenylpentanal was prepared by the Et_3Al-mediated ethylation to the (*E*)-cinnamaldehyde acetal derived from (*R,R*)-(+)-*N,N,N',N'*-tetramethyltartaric acid diamide in a similar manner as described in the synthesis of (*R*)-3-cyclohexylpentanal.[16]

A solution of trimethylgermyl chloride (62 μL, 0.5 mmol) in HMPA (1 mL) and ether (1 mL) was treated with lithium wire (17 mg, 2.5 mmol) at room temperature for 3 h to yield trimethylgermyllithium.[17] (*R*)-3-Phenylpentanal (41 mg, 0.25 mnol) was added to this mixture at 0 °C and the whole mixture was stirred at 0 °C for 40 min and at room temperature overnight. This was poured into aqueous NH_4Cl and extracted with ether. The concentrated crude material was purified by column chromatography (ether/hexane = 1:5 as eluant) to furnish diastereomeric (3*R*)-3-phenyl-1-trimethylgermyl-1-pentanol (33 mg, 47% yield): ^1H NMR ($CDCl_3$) δ 7.14–7.36 (5H, m, C_6H_5), 3.71 (1H, dd, *J* = 6, 9 Hz, diastereomeric CH-O), 3.29 (1H, dd, *J* = 2, 10 Hz, diastereomeric CH-O), 2.74-2.90 (1H, m, diastereomeric Ph-CH), 2.54-2.69 (1h, m, diastereomeric Ph-CH), 1.52-2.04 (4H, m, $2CH_2$), 0.92-1.14 (1H, m, OH), 0.79 (3H, t, *J* = 7 Hz, diastereomeric CH_3), 0.76 (3H, t, *J* = 7 Hz, diastereomeric CH_3), 0.15 (9H, s, diastereomeric $Ge(CH_3)_3$), 0.10 (9H, s, diastereomeric $Ge(CH_3)_3$).

Dimethyl sulfoxide (31 mg, 0.4 mmol) was added dropwise to a solution of $(COCl)_2$ (18 μL, 0.2 mmol) in CH_2Cl_2 (1 mL) at -78 °C. After 10 min, the diastereomeric (3*R*)-3-phenyl-1-trimethylgermyl-1-pentanol (22 mg) dissolved in CH_2Cl_2 (1 mL) was added at -78 °C slowly. The resulting white suspension was stirred at -78 °C for 30 min and then treated with Et_3N (0.14 mL, 1 mmol) at this temperature. The whole mixture was stirred at -78 °C for 2 h and worked up with water. The organic layer was extracted with CH_2Cl_2 and concentrated. The residue was purified by column chromatography (ether/hexane = 1/20 as eluant) to furnish (*R*)-3-phenyl-1-(trimethylgermyl)pentan-1-one (21 mg, 95% yield): ^1H NMR ($CDCl_3$) δ 7.13–7.34 (5H, m, C_6H_5), 3.01-3.18 (1H, m, Ph-CH), 2.99 (1H, dd, *J* = 7, 16 Hz, CH-C=O), 2.87 (1H, dd, *J* = 7, 16 Hz, CH-C=O), 1.40-1.77 (2H, m, CH_2), 0.75 (3H, t, *J* = 7 Hz, CH_3), 0.26 (9H, s, $Ge(CH_3)_3$).

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