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Vinyl Anion Equivalent V.[1] Asymmetric Synthesis of Allylic Alcohols Using Chiral 2-(Trialkylsilyl)ethyl Sulfoxides

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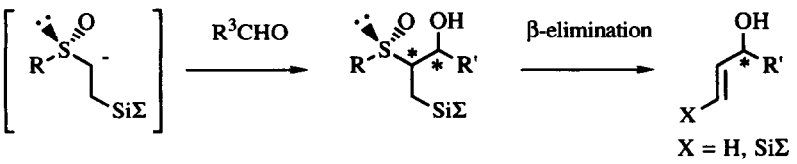
Abstract: Both enantiomers of optically pure secondary allylic alcohols can be conveniently prepared by the diastereoselective reaction of the α-sulfinyl carbanion of *p*-tolyl 2-(trialkylsilyl)ethyl sulfoxides or *tert*-butyl 2-(trimethylsilyl)ethyl sulfoxide with aldehydes followed by either fluoride-induced desilylsulfinylation or thermal elimination of the sulfinyl group.

Optically active secondary allylic alcohols are important compounds in organic syntheses because of their usefulness in a variety of organic transformations,[2] and the development of new routes to enantiomerically pure secondary allylic alcohols has attracted much attention in recent years.[2a,3] Recently, we have reported a synthetic methodology using an α-keto vinyl anion equivalent, in which the phenylseleno or phenylthio group, together with the vicinally positioned tributylstannyl or trialkylsilyl group, efficiently works as an olefin masking group.[1,4,5] We found that the methodology could be extended to an asymmetric synthesis of propargyl alcohols by using a vinyl anion having both an optically active sulfinyl group and a silyl group.[6] Herein, we report a novel asymmetric synthesis of optically pure secondary allylic alcohols starting with a chiral β-(trialkylsilyl)ethyl sulfoxide synthon.



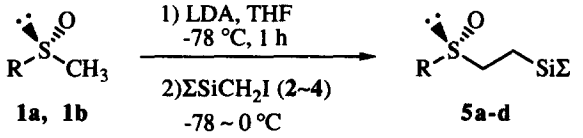
Scheme 1.

The sequence, as shown in Scheme 1, comprises reactions of α-sulfinyl carbanions with aldehydes and subsequent either β-elimination of the sulfinyl and trialkylsilyl groups or thermal elimination of the sulfenic acid. The overall transformation, therefore, provides a convenient preparation of chiral secondary allylic alcohols.

RESULTS AND DISCUSSION

Preparation of (*R*)-2-(Trialkylsilyl)ethyl Sulfoxide 5

The starting materials, *p*-tolyl 2-(trialkylsilyl)ethyl sulfoxides (**5a–c**) and *tert*-butyl 2-(trimethylsilyl)ethyl sulfoxide (**5d**) were prepared in a single step from readily obtainable (*R*)-methyl *p*-tolyl sulfoxide[7] (**1a**) and (*R*)-*tert*-butyl methyl sulfoxide[8] (**1b**) respectively as shown in Eq. 1. A tetrahydrofuran (THF) solution of **1a** was treated with 1.1 equiv of lithium diisopropylamide (LDA) at -78 °C for 1 h and subsequently with (iodomethyl)trimethylsilane (**2**), (iodomethyl)methyldiphenylsilane (**3**), or (iodomethyl)triphenylsilane (**4**) to give (*R*)-*p*-tolyl 2-(trimethylsilyl)ethyl sulfoxide (**5a**), (*R*)-2-(methyldiphenylsilyl)ethyl *p*-tolyl sulfoxide (**5b**), and (*R*)-*p*-tolyl 2-(triphenylsilyl)ethyl sulfoxide (**5c**) in 87, 68, and 99% yield, respectively (Table 1, Entries 1-3). (*R*)-*tert*-Butyl 2-(trimethylsilyl)ethyl sulfoxide (**5d**) was prepared in a similar manner from the corresponding (*R*)-*tert*-butyl sulfoxide **1b** in 85% yield on treatment with **2** (Table 1, Entry 4). The optical purities of **5a-d** were determined to be >99% ee by HPLC analyses using a chiral stationary phase (column, Daicel OB-H) through comparison with the racemic sulfoxides. The absolute configurations of sulfoxides **5a-d** were reasonably assigned as *R* since the above reactions should proceed with retention of the configuration.[9]



1a, 1b **5a-d** **Eq. 1**

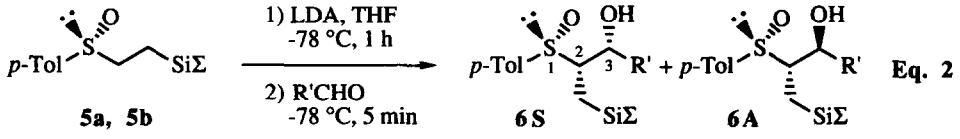
Table 1. Preparation of the 2-(Trialkylsilyl)ethyl Sulfoxides **5**

Entry	Substr.	R	$\Sigma SiCH_2I$ (No.)	Product	Yield, %	% ee[a]	$[\alpha]_D$[b]
1	**1a**	*p*-Tol	Me_3SiCH_2I (**2**)	**5a**	87	>99	+173.4 ° (c 0.98)
2	**1a**	*p*-Tol	$MePh_2SiCH_2I$ (**3**)	**5b**	68	>99	+122.0 ° (c 1.00)
3	**1a**	*p*-Tol	Ph_3SiCH_2I (**4**)	**5c**	99	>99	+60.0 ° (c 0.40)
4	**1b**	*t*-Bu	Me_3SiCH_2I (**2**)	**5d**	85	>99	-123.0 ° (c 0.66)

[a] Determined by HPLC (Chiralcel OB-H) analysis. [b] Optical rotation recorded in acetone.

Reaction of the α-Sulfinyl Carbanion of 5 with Aldehydes

We first studied the reaction of the α-sulfinyl carbanion derived from chiral β-(trialkylsilyl)ethyl sulfoxides **5** with various aldehydes.[10] (*R*)-*p*-Tolyl 2-(trimethylsilyl)ethyl sulfoxide (**5a**) was treated with 1.1 equiv of LDA in THF at -78 °C for 1 h to generate the lithium carbanion of **5a** which was then reacted with benzaldehyde at -78 °C for 5 min. The reaction mixture was quenched with aqueous NH_4Cl and the crude product was purified by silica gel column chromatography to give a high yield of the adduct **6a** (Table 2, Entry 1), which comprises two diastereoisomers **6a-S** and **6a-A** in a ratio of 69:31. The other two possible diastereoisomers were not found. The reaction of the lithium carbanion of **5a** with hexanal or isobutyraldehyde also afforded the corresponding adducts **6b** and **6c** respectively in high yields. Again, two diastereoisomers out of four possible stereoisomers were formed in these reactions. However, the stereoselectivity with respect to the aldehyde carbonyl, that is, 2,3-stereoselection was not satisfactory even in the reaction using sterically bulky isobutyraldehyde[11] (Table 2, Entries 2 and 3). Transmetallation sometimes improves the diastereoselectivity[12] and sometimes not[13]. Treatment of the lithium carbanion of **5a** with $ZnCl_2$ or $MgCl_2$ at -20 °C for 2 h followed by the addition of benzaldehyde resulted in recovery of the starting sulfoxide, and the use of $TiCl_4$ gave a complex mixture of unidentified decomposed products.



Eq. 2

Table 2. The Reactions of the Lithiated Sulfoxides **5** with Aldehydes

Entry	Substr.	SiΣ	R' of R'CHO	Product	Yield[a], %	6S : 6A[b]
1	**5a**	$SiMe_3$	Ph	**6a**	90	69 : 31
2	**5a**	$SiMe_3$	n-C_5H_{11}	**6b**	92	50 : 50
3	**5a**	$SiMe_3$	i-Pr	**6c**	83	53 : 47
4	**5b**	$SiMePh_2$	Ph	**6d**	80	53 : 47[c]
5	**5b**	$SiMePh_2$	n-C_5H_{11}	**6e**	86	54 : 46[c]

[a] Combined yields of **6S** and **6A**. [b] Isolated ratios unless otherwise noted.
[c] Determined by ^1H NMR analysis.

The absolute configurations of adducts **6S** and **6A** were determined as follows. The two diastereoisomers could be readily separated by column chromatography, and each diastereoisomer was separately subjected to β-elimination to form the corresponding allylic alcohol (see below), whose absolute configuration is known. Thus, the absolute configurations at C-3 of both diastereoisomers were assigned to be *S* and *R*, respectively, as shown in Eq. 2. The ^1H NMR spectra of these compounds shows that the coupling constants between the H^2 and H^3 protons (J_{23})[14] were 3.3 Hz and 5.9 Hz, respectively. The diastereoisomer showing the smaller *J* was tentatively assigned to **6a-S** and the larger *J* to **6a-A** according to the assignments

previously reported; the 2,3-*syn* diastereoisomer has smaller J_{23} than the 2,3-*anti*.[14,15] Since the difference between these *J* values is not so large as to be reported, we attempted to carry out single-crystal X-ray analysis in order to determine unambiguously their configurations. Unfortunately, it was extremely difficult to make a single crystal of the sulfoxide **6** because **6** decomposed on standing at room temperature in solution. A suitable single crystal for X-ray analysis could be obtained from the sulfone **7b-S** which was prepared by the oxidation of **6b-S** with *m*-CPBA at 0 °C. The diagram of the X-ray structure of the sulfone **7b-S** is shown in Figure 1. Since the stereochemistry of the sulfinyl center is *R*, the absolute configuration of **6b-S** was unambiguously determined to be (2*R*,3*R*), that is, 1,2-*syn*; 2,3-*syn*. Another diasteromer **6b-A** was also converted to the sulfone **7b-A**, which turned out to be a different compound from **7b-S**. This fact, in addition to the unambiguous assignment of the C-3 configuration by the transformation to the known allylic alcohol, allows us to assign the configurations of **6b-A** as (2*R*,3*S*), that is, 1,2-*syn*; 2,3-*anti*. As a result, the J_{23} values in the NMR spectra of these two diastereoisomers were in accord with the data reported[14] (see above). We deduced the configurations of the other sulfoxides **6a**, **6c**, **6d**, and **6e** listed in Table 2 from these assignments.

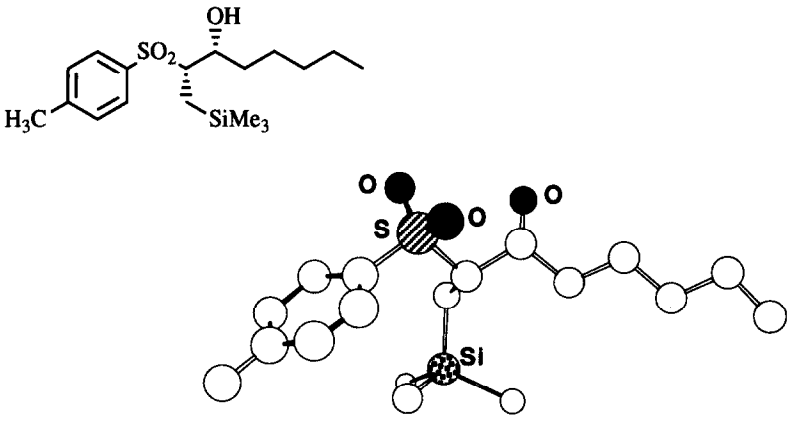
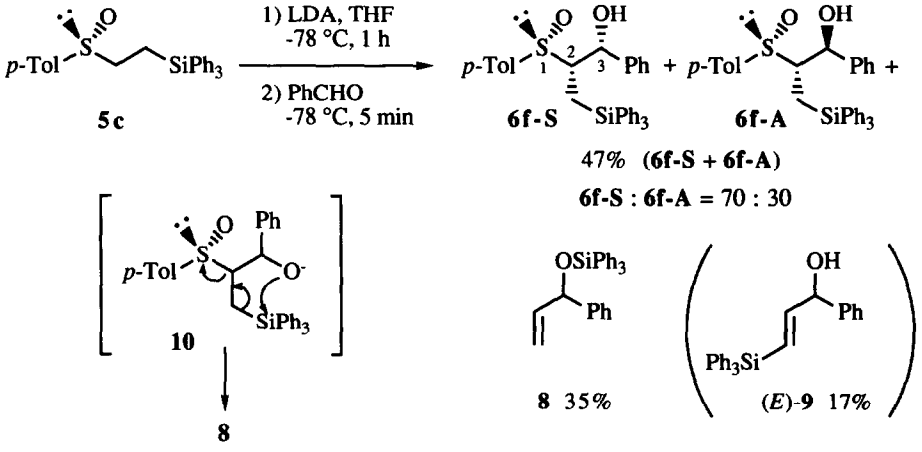


Figure 1. The Diagram of the X-Ray Structure of the Sulfone **7b-S**

We next studied the reactions of sulfoxides having a bulky silyl group. The reaction of the α-sulfinyl carbanion of **5b** (SiΣ=SiMePh$_2$) with benzaldehyde or hexanal afforded the corresponding adducts **6d** and **6e** in high yields, respectively (Table 2, Entries 4 and 5). The reaction proceeded with a 100% face-selection with respect to the carbanion with aldehydes, albeit poor selectivity with respect to the face of the aldehyde carbonyl as in the reactions of **5a** described above. On the other hand, treatment of the α-sulfinyl carbanion of **5c** (SiΣ=SiPh$_3$) with benzaldehyde afforded somewhat different results from those of **5a** or **5b**, giving a mixture of two diastereoisomeric adducts **6f-S** and **6f-A** in 47% yield in a diastereoisomeric ratio of 70:30 (**6h-S/6h-A**). In addition to **6f**, the (*E*)-γ-(triphenylsilyl)allyl alcohol **9** and the allyl ether **8** were also isolated in 17 and 35% yields, respectively (Scheme 2). Formation of the adducts **6f-S** and **6f-A**, and the allyl ether **8** was observed by the TLC analysis of the reaction mixture at -78 °C, but the allyl alcohol **9** was not detected at this

stage. The allyl alcohol **9** was found to be formed after work-up of the reaction mixture, namely, it was assumed that **9** was the product derived from the adducts **6** on warming the reaction mixture. This assumption was verified by a NMR study: in each ^1H NMR spectrum of the isolated adducts **6f-S** and **6f-A**, the signals decreased on standing in $CDCl_3$ at room temperature. Interestingly, **6f-A** was less stable than **6f-S**, namely, the signals due to **6f-A** completely disappeared on standing for 3 days, whereas the initial intensity of the signals due to **6f-S** decreased only to half, and the γ-silyl allylic alcohol **9** was the only product formed. Thus, the compound **9** was reasonably formed from the adducts **6f**, mainly from **6f-A**, through a smooth elimination of sulfenic acid assisted by the electron-withdrawing triphenylsilyl group. On the other hand, the allyl ether **8** was obtained exclusively when the carbanion of **5c** and benzaldehyde were reacted at -78 °C, the reaction temperature was allowed to increase to 0 °C, and the mixture was stirred for 1 h at that temperature. Thus, the allyl ether **8** was formed possibly from the intermediate anion **10** through an intramolecular alkoxide-promoted β-elimination of the triphenylsilyl and *p*-tolyl sulfinyl groups.



Scheme 2.

It has been reported that the *tert*-butyl sulfoxides give the adducts with high stereoselection in the reaction with aldehydes.[12,13] (*R*)-*tert*-Butyl 2-(trimethylsilyl)ethyl sulfoxide (**5d**) was reacted with benzaldehyde or hexanal in a similar manner to the reaction of *p*-tolylsulfoxides as shown in Eq. 3. The crude product was purified by silica gel column chromatography to give two sets of a mixture of two diastereoisomers (**6g-AA** + **6g-AS**) and (**6g-SA** + **6g-SS**) in a ratio of 90:10. The ^1H NMR spectra of each mixture showed two sets of the coupling constants between H^2 and H^3 protons (J_{23}): 9.3 and 1.8 Hz for the major mixture and 6.0 and 2.4 Hz for the minor mixture. The larger J_{23} was reasonably assigned to 2,3-*anti* and the smaller J_{23} to 2,3-*syn*.[14,15] Fortunately, a single crystal of a diastereoisomer having 2,3-*anti* could be obtained from the major mixture. The diagram of the X-ray structure is shown in Fig. 2, showing the structure of 1,2-*anti*-2,3-*anti* (**6g-AA**). These results, coupled with those obtained by the transformation of each mixture to the allylic

alcohols, allowed us to assign sulfoxides in the major mixture as **6g-AA** and **6g-AS**, and those in the minor mixture as **6g-SA** and **6g-SS**.

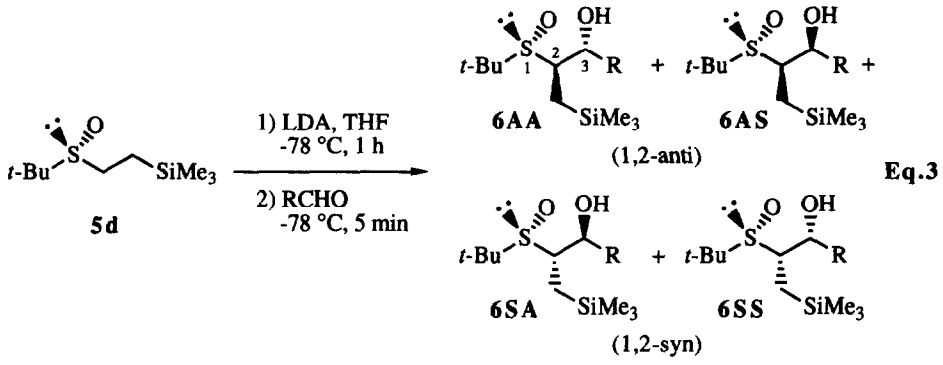


Table 3. Reactions of the Lithiated **5d** with Aldehydes

Entry	R of RCHO	Product	Yield[a], %	AA : AS : SA : SS[b, c]
1	Ph	**6g**	94	50 : 40 : 7 : 3
2	n-C_5H_{11}	**6h**	89	48 : 41 : 6 : 5

[a] Combined yields of (**6AA** + **6AS**) and (**6SA** + **6SS**). [b] Determined by ^{1}H NMR.

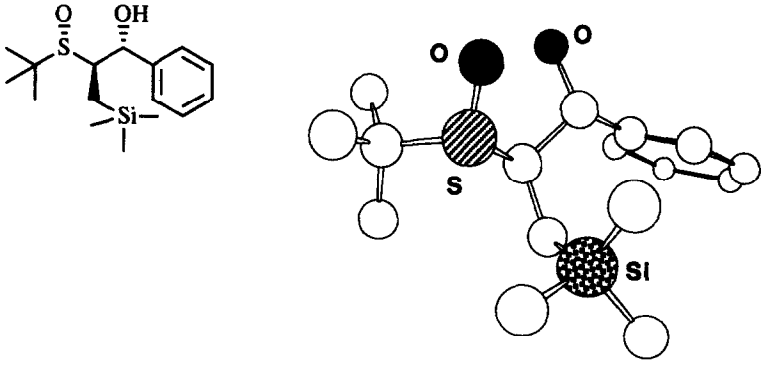
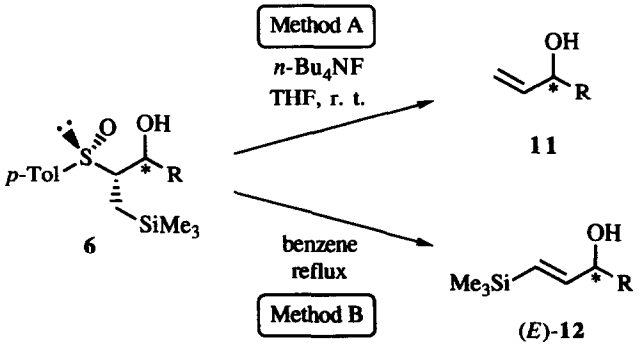


Figure 2. The Diagram of the X-Ray Structure of **6g-AA**

It is noteworthy that the reaction of the lithium carbanion of *p*-tolyl 2-(trialkylsilyl)ethyl sulfoxides **5a-c** with aldehydes proceeded stereoselectively to give two diastereoisomers out of four possible diastereoisomers with 100% diastereofacial selectivity with respect to attack of the aldehyde on the carbanion, though without diastereofacial selectivity with respect to the aldehyde carbonyl. The exclusive formation of the 1,2-*syn* compounds in the reaction of **5a-c** is noteworthy, since reactions of the lithium carbanion of *p*-tolyl sulfoxides with aldehydes are known to proceed with low 1,2-stereoselection, giving all four possible diastereoisomers with poor selectivity.[13] The reaction of *tert*-butyl sulfoxides with aldehydes results in the exclusive formation of 1,2-*anti* diastereoisomers with the predominance of 2,3-*anti* stereoisomers.[12,13] Our results of the reaction of *tert*-butyl sulfoxide seem to be in accord with those previously reported, except that our reaction did not proceed with complete 1,2-*anti* selectivity but with predominance of formation of 1,2-*anti* diastereoisomers. Several transition states have previously proposed such as the six-membered transition state derived from the four-membered lithium carbanion,[16] the six-membered chair-like transition state,[17,18] or the boat-like transition state for the high stereoselection in the reaction of *tert*-butyl sulfoxides.[12,13] However, these transition states proposed so far may not account for the reaction of *p*-tolyl 2-(trialkylsilyl)ethyl sulfoxides **5a-c**, and the discrepancy between the stereochemical outcomes derived from the reactions of **5a-c** and *p*-tolyl sulfoxides remains to be solved.

Preparation of Optically Pure Allylic Alcohols 11 and 12

Each diastereoisomer of compound **6** obtained from β-(trimethylsilyl)ethyl *p*-tolyl sulfoxides **5a** could be easily isolated by column chromatography. Optically active allyl alcohols **11** and trimethylsilyl-substituted allylic alcohols **12** were conveniently prepared as shown in Eq. 4. Treatment of each diastereoisomer of **6a** and **6b** with 1.1 equiv of tetrabutylammonium fluoride (TBAF) in THF at room temperature afforded the allylic alcohol **11a** or **11b** in high yield through β-elimination of the trimethylsilyl and *p*-tolyl sulfinyl groups starting with an initial attack of fluoride ion on the silicon (Method A; Table 4, Entries 1–4).[19] β-Elimination of the 2,3-*syn* compound **6S** proceeded much faster than that of the 2,3-*anti* **6A**. In ^{1}H NMR spectra of highly diluted $CDCl_3$ solutions of isolated diastereoisomers **6**, the signals due to the hydroxyl proton appeared at 2.90, 4.65, 2.20, and 3.37 ppm for **6a-S**, **6a-A**, **6b-S**, and **6b-A**, respectively. The signal due to the hydroxyl proton at



Eq. 4

Table 4. Conversion of the Adduct **6** into Allylic Alcohols **11** and **12**

Entry	Substrate	R	Method[a]	React. time	Allylic alcohol	% yield[b]	% ee[c]	Config.[d]	$[\alpha]_D$
1	**6a-S**	Ph	A	1 min	**11a**	97	>99	*S*	-8.4 ° (c 2.87)[e]
2	**6a-A**	Ph	A	1 h	**11a**	94	>99	*R*	+8.3 ° (c 3.11)[e]
3	**6b-S**	n-C_5H_{11}	A	45 min	**11b**	91	>99	*R*	-10.0 ° (c 1.67)[f]
4	**6b-A**	n-C_5H_{11}	A	3.5 h	**11b**	91	>99	*S*	+10.1 ° (c 0.67)[f]
5	**6b-S**	n-C_5H_{11}	B	30 min	**12**	80	>99	*R*	-10.9 ° (c 1.10)[f]
6	**6b-A**	n-C_5H_{11}	B	30 min	**12**	89	>99	*S*	+10.9 ° (c 1.11)[f]

[a] Method A: TBAF, THF, room temperature. Method B: benzene, reflux. [b] Isolated yields.
[c] Determined by ^1H NMR analysis of corresponding MTPA esters.
[d] Determined by chiroptic comparison with published values (see refs. 25–30).
[e] Optical rotation recorded in benzene. [f] Optical rotation recorded in $CHCl_3$.

the low field shows the presence of the intramolecular hydrogen bonding in 2,3-*anti* diastereoisomers **6a-A** and **6b-A**, which forms a chair-like six-membered ring. On the other hand, the 2,3-*syn* isomers **6a-S** and **6b-S** would be conformationally so flexible as to take the antiperiplanar conformation with respect to S-C and C-Si bonds which makes the β-elimination of the sulfinyl and silyl group easier.

On the other hand, thermal treatment of a benzene solution of each isomer of **6b** at reflux for 30 min resulted in the exclusive formation of the (*E*)-γ-trimethylsilyl-substituted allylic alcohol **12** (Method B; Table 4, Entries 5, 6).[20] Easy elimination of the sulfinyl group is apparently due to the effect of the silyl group, which has been pointed out by Fleming[21] and Ochiai.[20] There was no racemization during the conversion of the adduct **6** into allylic alcohols **11** and **12**, and the optical purities of **11** and **12** thus obtained were found to be >99% ee by ^1H NMR analysis of the corresponding MTPA esters.

In conclusion, the present process has several unique features such as (1) ready availablity of starting chiral sulfoxides, (2) extremely high diastereoselectivity in the reaction of the α-sulfinyl carbanions **5** with aldehydes, (3) easy separation of each diastereoisomer of the adducts **6**, and (4) flexible preparation of both enantiomers of either trialkylsilyl-substituted or unsubstituted secondary allylic alcohols **11** and **12**. In addition, the high yield of allylic alcohols by the fluoride-induced desilylsulfinylation which is facilitated by the silyl group shows the outstanding functioning of vicinally positioned phenylsulfinyl and trialkylsilyl groups as an olefin masking group. Thus, the present method provides a convenient route for the synthesis of optically pure secondary allylic alcohols.

EXPERIMENTAL

General

The melting points were measured on a Yanaco micro melting-point apparatus and are uncorrected. The ^1H NMR spectra were recorded on a Varian XL-200 (200 MHz) or Varian Gemini-200BB (200 MHz) spectrometer, and are reported in δ from Me_4Si. The IR spectra were recorded on a JASCO A-102 spectrometer, and the reported IR figures are ν_{max} in cm^{-1}. The mass spectra were recorded on a Hitachi M-2000 spectrometer, and optical rotations were measured on a JASCO DIP-4 polarimeter.

All reactions were performed in oven- and flame-dried glassware under a positive pressure of argon. Air- and moisture-sensitive reagents and solvents were transferred *via* syringe or cannula, and were introduced into the reaction vessels through a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25-mm E. Merck silica-gel plates (60F-254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid in ethanol / heat. Column chromatography was carried out with a Michel Miller column packed with Fuji Davison silica gel (BW-200) equipped with an FMI Lab Pump (RP-G150) and an FMI Pulse Dampener (PD-60-LF), normally at a pressure of 1–2 kg cm^{-2}.

Materials

Unless otherwise noted, the materials were obtained from commercial suppliers and were used without purification. Tetrahydrofuran (THF) was freshly distilled from sodium diphenylketyl under argon before use. Diisopropylamine was distilled from potassium hydroxide. The aldehydes were freshly distilled before use. (*R*)-Methyl *p*-tolyl sulfoxide[7] (**1a**) and (*R*)-*tert*-butyl methyl sulfoxide[8] (**1b**) were prepared according to procedures described in the literature. (Iodomethyl)trimethylsilane (**2**) was distilled before use. Two organosilicon compounds **3** and **4** were synthesized by modification of published procedures: $MePh_2SiCH_2I$ (**3**) (bp 130–131 °C / 0.3 mmHg, lit.[22] 159–161 °C / 25 mmHg) was prepared in 80% yield by refluxing $MePh_2SiCH_2Cl$[22] and NaI (1:10) in dry acetone; Ph_3SiCH_2I (**4**) (mp 114–116 °C, lit.[23] 114–115 °C) was prepared by the iodomethylation of Ph_3SiCl with CH_2I_2 and butyllithium as described in the literature.[24]

Representative Procedure for the Preparation of β-(Trialkylsilyl)ethyl Sulfoxides. (*R*)-*p*-Tolyl 2-(Trimethylsilyl)ethyl Sulfoxide (5a)

To a solution of diisopropylamine (303 mg, 3.0 mmol) in THF (3.0 ml) was added butyllithium (1.59 mol dm^{-3} in hexane; 1.8 ml, 2.9 mmol) at 0 °C and the mixture was stirred for 15 min. The reaction mixture was then cooled to -78 °C and a solution of (*R*)-methyl *p*-tolyl sulfoxide (**1a**) (400 mg, 2.6 mmol) in THF (4.0 ml) was added and the mixture was stirred for 1 h. (Iodomethyl)trimethylsilane (**2**) (620 mg, 2.9 mmol) was then added and the bath temperature was allowed to rise to ambient temperature over a period of 2 h. Saturated aq. NH_4Cl (5 ml) was added under vigorous stirring and the organic layer was separated. The water layer was extracted with CH_2Cl_2 (3 x 20 ml) and the combined organic extracts were washed with brine (20 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure to leave a residue which was purified by column chromatography (silica gel 40 g, 75:25 hexane/ethyl acetate) to give **5a** (543 mg, 87% yield) as a colorless solid: mp 37 °C (acetone); TLC R_f 0.50 (60:40 hexane/ethyl acetate); $[\alpha]^{19}_D$ +173.4 ° (c 0.98, acetone); IR (KBr) 3010, 2950, 1490, 1400, 1245, 1150, 1080, 1040, 1010, 860, 840, 810, 750, 690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ –0.01 (9 H, s, $SiMe_3$), 0.70–0.88 (2 H, m, CH_2), 2.42 (3 H, s, CH_3), 2.59–

2.88 (2 H, m, CH_2), 7.32 (2 H, d, J = 8.4 Hz, arom), 7.49 (2 H, d, J = 8.4 Hz, arom); MS m/z (rel) 212 ($M^+-C_2H_4$, 24), 197 (5), 181 (4), 140 (2), 139 (15), 123 (4), 101 (4), 91 (6), 73 (100). Anal. Calcd for $C_{12}H_{20}OSSi$: C, 59.95; H, 8.38. Found: C, 59.86; H, 8.42.

The following compounds were prepared according to the representative procedure described above. (*R*)-methyl *p*-tolyl sulfoxide (**1a**) or (*R*)-*t*-butyl methyl sulfoxide (**1b**) (amount), (iodomethyl)trialkylsilane (amount), reaction time, eluent for column chromatography, product yield, and product property are given in this abbreviated format.

(*R*)-2-(Methyldiphenylsilyl)ethyl *p*-Tolyl Sulfoxide (5b): 1a (990 mg, 6.42 mmol), (iodomethyl)methyldiphenylsilane (**3**) (3.25 g, 9.61 mmol), 6 h, 75:25 hexane / ethyl acetate, 1.59 g (68% yield), a colorless solid: mp 94 °C (hexane/diethyl ether); TLC R_f 0.42 (60:40 hexane/ethyl acetate); $[\alpha]^{23}_D$ +122.0 ° (c 1.00, acetone); IR (KBr) 3040, 3010, 2950, 2900, 1730, 1580, 1485, 1420, 1300, 1247, 1150, 1105, 1090, 1040, 1010, 865, 800, 785, 728, 695 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.52 (3 H, s, SiMe), 1.26 (1 H, ddd, J = 5.0, 13.0, 13.0 Hz, CH_2), 1.38 (1 H, ddd, J = 5.0, 13.0, 13.0 Hz, CH_2), 2.41 (3 H, s, CH_3), 2.68 (1 H, ddd, J = 5.0, 13.0, 13.0 Hz, CH_2), 2.86 (1 H, ddd, J = 5.0, 13.0, 13.0 Hz, CH_2), 7.25–7.47 (14 H, m, arom); MS m/z (rel) 336 ($M^+-C_2H_4$, 60), 224 (34), 209 (43), 197 (100), 183 (24), 146 (26), 139 (20), 121 (22), 120 (23), 105 (59), 91(50). Anal. Calcd for $C_{22}H_{24}OSSi$: C, 72.48; H, 6.63. Found: C, 72.42; H, 6.69.

(*R*)-*p*-Tolyl 2-(Triphenylsilyl)ethyl Sulfoxide (5c): 1a (1.18 g, 7.65 mmol), (iodomethyl)triphenylsilane (**4**) (4.00 g, 9.99 mmol), 10 h, 95:5 and 80:20 CH_2Cl_2/ethyl acetate, 3.25 g (99% yield), a colorless solid: mp 136 °C (acetone); TLC R_f 0.55 (50:50 hexane/ethyl acetate); $[\alpha]^{19}_D$ +60.0 ° (c 0.40, acetone); IR (KBr) 3000, 1620, 1590, 1425, 1110, 1095, 1035, 825, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.52 (1 H, ddd, J = 4.6, 13.1, 13.1 Hz, CH_2), 1.68 (1 H, ddd, J = 4.6, 13.1, 13.1 Hz, CH_2), 2.42 (3 H, s, CH_3), 2.77 (1 H, ddd, J = 4.6, 13.1, 13.1 Hz, CH_2), 2.98 (1 H, ddd, J = 4.6, 13.1, 13.1 Hz, CH_2), 7.20–7.51 (19 H, m, arom); MS m/z (rel) 286 ($M^+-C_7H_8OS$, 77), 259 (78), 208 (49), 182 (100), 140 (22), 139 (27), 123 (26), 105 (64), 91 (60). Anal. Calcd for $C_{27}H_{26}OSSi$: C, 76.01; H, 6.14. Found: C, 76.13; H, 6.02.

(*R*)-*tert*-Butyl 2-(Trimethylsilyl)ethyl Sulfoxide (5d): 1b (800 mg, 6.65 mmol), (iodomethyl)trimethylsilane (**2**) (2.16 g, 10.11 mmol), 5 h, 60:40 hexane/ethyl acetate, 1.17 g (85% yield), a colorless paste: TLC R_f 0.36 (50:50 hexane/ethyl acetate); $[\alpha]^{19}_D$ −123.0 ° (c 0.66, acetone); IR (neat) 2950, 1460, 1360, 1250, 1170, 1030, 890, 860, 840, 760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.06 (9 H, s, $SiMe_3$), 0.78 (1 H, ddd, J = 6.0, 12.6, 14.2 Hz, CH_2), 1.21 (1 H, ddd, J = 5.6, 12.6, 14.2 Hz, CH_2), 1.25 (9 H, s, *t*-Bu), 2.37 (1 H, ddd, J = 5.6, 12.6, 12.6 Hz, CH_2), 2.47 (1 H, ddd, J = 6.0, 12.6, 12.6 Hz, CH_2); MS m/z (rel) 207 (M^++1, 1.7), 206 (M^+, 77), 191 (1.5), 178 (60), 163 (16), 150 (5), 135 (54), 122 (85), 107 (70), 106 (59), 101 (59), 73 (100). Anal. Calcd for $C_9H_{22}OSSi$: C, 52.37; H, 10.74. Found: C, 51.99; H, 11.08.

Representative Procedure for the Reaction of 2-(Trialkylsilyl)ethyl Sulfoxides with Aldehydes. (1*R*,2*R*)-1-Phenyl-2-[(*R*)-*p*-tolylsulfinyl]-3-(trimethylsilyl)-1-propanol (6a-S) and (1*S*,2*R*)-1-Phenyl-2-[(*R*)-*p*-tolylsulfinyl]-3-(trimethylsilyl)-1-propanol (6a-A)

To a solution of diisopropylamine (35 mg, 0.34 mmol) in THF (0.4 ml) was added butyllithium (1.57 mol dm^{-3} in hexane; 0.21 ml, 0.33 mmol) at 0 °C and the mixture was stirred for 15 min. After the reaction

mixture was cooled to -78 °C, a solution of **5a** (72 mg, 0.30 mmol) in THF (0.5 ml) was added dropwise over a period of 5 min and the mixture was stirried for 1 h. Benzaldehyde (35 mg, 0.33 mmol) was then added. After 5 min, the solution was quenched rapidly with saturated aq. NH_4Cl (3 ml) under vigorous stirring and the organic layer was separated. The water layer was extracted with CH_2Cl_2 (3 x 5 ml) and the combined organic extracts were washed with brine (5 ml), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel 20 g, hexane/ethyl acetate) to give **6a-S** (64 mg, 62% yield) and **6a-A** (29 mg, 28% yield) as a colorless solid. **6a-S**: mp 100–102 °C (diethyl ether); TLC R_f 0.41 (60:40 hexane/ethyl acetate); $[\alpha]^{21}_D$ +26.8 ° (c 0.69, acetone); IR (KBr) 3360, 2950, 2880, 1610, 1430, 1245, 1050, 840, 700 cm^{-1}; ^1H NMR (200 MHz, 4 mM/$CDCl_3$) δ –0.55 (9 H, s, $SiMe_3$), 0.80 (1 H, dd, *J* = 4.4, 16.2 Hz, H-3), 0.94 (1 H, dd, *J* = 6.6, 16.2 Hz, H-3), 2.41 (3 H, s, CH_3), 2.86 (1 H, ddd, *J* = 3.3, 4.4, 16.2 Hz, H-2), 2.90 (1 H, d, *J* = 2.2 Hz, OH), 5.50 (1 H, dd, *J* = 2.2, 3.3 Hz, H-1), 7.29–7.49 (9 H, m, arom); MS m/z (rel) 212 (6), 206 (85), 205 (88), 191 (88), 140 (94), 139 (92), 116 (100), 107 (62), 91 (97). Anal. Calcd for $C_{19}H_{26}O_2SSi$: C, 65.85; H, 7.56. Found: C, 65.67; H, 7.73. **6a-A**: mp 109–110 °C (diethyl ether); TLC R_f 0.27 (60:40 hexane/ethyl acetate); $[\alpha]^{21}_D$ +16.4 ° (c 0.55, acetone); IR (KBr) 3230, 2950, 2890, 1610, 1410, 1245, 1050, 840, 690 cm^{-1}; ^1H NMR (200 MHz, 4 mM/$CDCl_3$) δ –0.18 (9 H, s, $SiMe_3$), 0.49 (1 H, dd, *J* = 5.3, 15.6 Hz, H-3), 0.83 (1 H, dd, *J* = 8.1, 15.6 Hz, H-3), 2.43 (3 H, s, CH_3), 2.98 (1 H, ddd, *J* = 5.3, 5.9, 15.6 Hz, H-2), 4.65 (1 H, d, *J* = 4.8 Hz, OH), 4.95 (1 H, dd, *J* = 4.8, 5.9 Hz, H-1), 7.29–7.43 (9 H, m, arom); MS m/z (rel) 212 (3), 206 (12), 205 (18), 191 (17), 140 (28), 139 (34), 116 (100), 91 (51). Anal. Calcd for $C_{19}H_{26}O_2SSi$: C, 65.85; H, 7.56. Found: C, 65.71; H, 7.67.

The following compounds were prepared according to the representative procedure described above. The 2-(trialkylsilyl)ethyl sulfoxide **5** (amount), aldehyde (amount), eluent for column choromatography, product yield, and product property are given in this abbreviated format.

(2*R*,3*R*)-2-[(*R*)-*p*-Tolylsulfinyl]-1-(trimethylsilyl)-3-octanol (6b-S) and (2*R*,3*S*)-2-[(*R*)-*p*-Tolylsulfinyl]-1-(trimethylsilyl)-3-octanol (6b-A): **5a** (72 mg, 0.30 mmol), hexanal (33 mg, 0.33 mmol), 93:7 $CHCl_3$/diethyl ether, **6b-S** (47 mg, 46% yield) and **6b-A** (47 mg, 46% yield) as a colorless solid. **6b-S**: mp 110–111 °C (diethyl ether); TLC R_f 0.49 (60:40 hexane/ethyl acetate); $[\alpha]^{25}_D$ +82.9 ° (c 0.55, acetone); IR (KBr) 3360, 2940, 2860, 1625, 1595, 1490,1250, 1140, 1080, 1020, 1010, 840 cm^{-1}; ^1H NMR (200 MHz, 4 mM/$CDCl_3$) δ –0.18 (9 H, s, $SiMe_3$), 0.72 (1 H, dd, *J* = 4.2, 15.7 Hz, H-1), 0.85 (1 H, dd, *J* = 8.9, 15.7 Hz, H-1), 0.90 (3 H, t, *J* = 6.5 Hz, H-8), 1.24–1.41 (6 H, m, H-5, 6, 7), 1.52–1.71 (2 H, m, H-4), 2.20 (1 H, d, *J* = 4.3 Hz, OH), 2.41 (3 H, s, CH_3), 2.69 (1 H, ddd, *J* = 2.8, 4.2, 8.9 Hz, H-2), 4.08–4.20 (1 H, m, H-3), 7.32 (2 H, d, *J* = 8.4 Hz, arom), 7.44 (2 H, d *J* = 8.4 Hz, arom); MS m/z (rel) 278 (92), 262 (46), 246 (87), 214 (79), 182 (10), 167 (8), 155 (83), 139 (98), 124 (93), 91 (100). Anal. Calcd for $C_{18}H_{32}O_2SSi$: C, 63.48; H, 9.47. Found: C, 63.35; H, 9.73. **6b-A**: mp 73–74 °C (diethyl ether); TLC R_f 0.41 (60:40 hexane/ethyl acetate); $[\alpha]^{25}_D$ +63.9 ° (c 0.31, acetone); IR (KBr) 3380, 2910, 1620, 1490, 1250, 1020, 1010, 840 cm^{-1}; ^1H NMR (200 MHz, 4 mM/$CDCl_3$) δ –0.12 (9 H, s, $SiMe_3$), 0.51 (1 H, dd, *J* = 3.8, 15.3 Hz, H-1), 0.91 (3 H, t, *J* = 6.4 Hz, H-8), 1.05 (1 H, dd, *J* = 10.1, 15.3 Hz, H-1), 1.24–2.02 (8 H, m, H-4, 5, 6, 7), 2.42 (3 H, s, CH_3), 2.62 (1 H, ddd, *J* = 3.8, 4.0, 10.1 Hz, H-2), 3.37 (1 H, d, *J* = 6.5 Hz, OH), 3.77–3.92 (1 H, m, H-3), 7.33 (2 H, d, *J* = 8.4 Hz, arom), 7.39 (2 H, d *J* = 8.4 Hz, arom); MS m/z (rel) 278 (33), 262 (37), 246 (63), 214 (53), 182 (7), 167 (24), 157 (84), 139 (92), 124 (90), 91 (100). Anal. Calcd for $C_{18}H_{32}O_2SSi$: C, 63.48; H, 9.47. Found: C, 63.53; H, 9.75.

Oxidation of each isomer **6b-S** (97 mg, 0.29 mmol) or **6b-A** (8 mg, 0.02 mmol) with *m*-CPBA in CH_2Cl_2 at 0 °C for 10 min gave (2*R*,3*R*)-2-(*p*-tolylsulfonyl)-1-(trimethylsilyl)-3-octanol (**7b-S**) (98 mg, 96% yield) or (2*R*,3*S*)-2-(*p*-tolylsulfonyl)-1-(trimethylsilyl)-3-octanol (**7b-A**) (7 mg, 86% yield), respectively. **7b-S**: a colorless solid; mp 73–74 °C (hexane); TLC R*f* 0.47 (80:20 hexane/ethyl acetate); $[\alpha]^{24}_D$ +4.3 ° (c 1.0, acetone); IR (KBr) 3470, 2930, 1590, 1410, 1285, 1250, 1140, 840 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.00 (9 H, s, $SiMe_3$), 0.84 (3 H, t, *J* = 7.0 Hz, CH_3), 1.03 (1 H, dd, *J* = 5.7, 15.0 Hz, H-1), 1.12 (1 H, dd, *J* = 6.7, 15.0 Hz, H-1), 1.11–1.68 (8 H, m), 2.47 (3 H, s, CH_3), 3.07 (1 H, ddd, *J* = 1.8, 5.7, 6.7 Hz, H-2), 3.19 (1 H, d, *J* = 4.5 Hz, OH), 3.87–3.99 (1 H, m, H-3), 7.38 (2 H, d, *J* = 8.0 Hz, arom), 7.77 (2 H, d, *J* = 8.0 Hz, arom); MS m/z (rel) 357 (M+1, 0.6), 341 (4.3), 256 (20), 228 (93), 213 (74), 201 (22), 185 (94), 180 (95), 149 (97), 139 (46), 91 (65), 73 (100). Anal. Calcd for $C_{18}H_{32}O_3SSi$: C, 60.63; H, 9.04. Found: C, 60.62; H, 9.16. **7b-A**: a colorless oil; TLC R*f* 0.36 (80:20 hexane/ethyl acetate); IR (neat) 3550, 2975, 2950, 1710, 1600, 1470, 1420, 1290, 1250, 1140, 850 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ -0.09 (9 H, s, $SiMe_3$), 0.80 (3 H, t, *J* = 6.5 Hz, CH_3), 0.87 (1 H, dd, *J* = 5.2, 14.2 Hz, H-1), 0.95 (1 H, dd, *J* = 8.2, 14.2 Hz, H-1), 1.11–1.58 (9 H, m), 2.38 (3 H, s, CH_3), 3.10 (1 H, ddd, *J* = 4.9, 5.2, 8.2 Hz, H-2), 3.72–3.83 (1 H, m, H-3), 7.25–7.72 (4 H, m, arom); MS m/z (rel) 341 (M^+-15, 4), 338 (2), 323 (1), 256 (12), 228 (93), 213 (52), 201 (10), 185 (55), 180 (98), 165 (10), 155 (14), 149 (99), 139 (56), 111 (57), 91 (75), 73 (100). Anal. Calcd for $C_{18}H_{32}O_3SSi$: C, 60.63; H, 9.04. Found: C, 60.59; H, 9.17.

(2*R*,3*R*)-4-Methyl-2-[(*R*)-*p*-tolylsulfinyl]-1-(trimethylsilyl)-3-pentanol (6c-S) and (2*R*,3*S*)-4-Methyl-2-[(*R*)-*p*-tolylsulfinyl]-1-(trimethylsilyl)-3-pentanol (6c-A): **5a** (72 mg, 0.30 mmol), isobutyraldehyde (24 mg, 0.33 mmol), 93:7 $CHCl_3$/diethyl ether, **6c-S** (41 mg, 44% yield) and **6c-A** (37 mg, 39% yield) as a colorless solid. **6c-S**: mp 93–94 °C (diethyl ether); TLC R_f 0.42 (80:20 $CHCl_3$/diethyl ether); $[\alpha]^{26}_D$ +60.1 ° (c 1.03, acetone); IR (KBr) 3340, 2960, 1495, 1250, 1020, 1010, 860, 845, 810 cm^{-1}; ^1H NMR (200 MHz, 4 mM/$CDCl_3$) δ –0.18 (9 H, s, $SiMe_3$), 0.79 (1 H, dd, *J* = 5.1, 16.2 Hz, H-1), 0.93 (3 H, d, *J* = 6.7 Hz, CH_3), 0.94 (1 H, dd, *J* = 6.5, 16.2 Hz, H-1), 1.03 (3 H, d, *J* = 6.7 Hz, CH_3), 1.86 (1 H, dqq, *J* = 6.7, 6.7, 7.6 Hz, H-4), 2.17 (1 H, br s, OH), 2.42 (3 H, s, CH_3), 2.82 (1 H, ddd, *J* = 3.2, 5.1, 6.5 Hz, H-2), 3.90 (1 H, dd, *J* = 3.2, 7.6 Hz, H-3), 7.33 (2 H, d, *J* = 8.5 Hz, arom), 7.45 (2 H, d *J* = 8.5 Hz, arom); MS m/z (rel) 293 (M^+-18, 0.01), 278 (0.01), 212 (16), 197 (2), 172 (8), 157 (45), 140 (86), 139 (66), 129 (92), 91 (98), 73 (100). Anal. Calcd for $C_{16}H_{27}O_2SSi$: C, 61.69; H, 8.74. Found: C, 61.58; H, 8.86. **6c-A**: mp 83–84 °C (diethyl ether); TLC R_f 0.32 (80:20 $CHCl_3$/diethyl ether); $[\alpha]^{26}_D$ +84.2 ° (c 1.19, acetone); IR (KBr) 3520, 2960, 1495, 1420, 1250, 1030, 1015, 995, 860, 845, 810 cm^{-1}; ^1H NMR (200 MHz, 4 mM/$CDCl_3$) δ –0.11 (9 H, s, $SiMe_3$), 0.45 (1 H, dd, *J* = 3.8, 15.1 Hz, H-1), 1.03 (3 H, d, *J* = 6.7 Hz, CH_3), 1.15 (3 H, d, *J* = 6.7 Hz, CH_3), 1.20 (1 H, dd, *J* = 10.3, 15.1 Hz, H-1), 2.36 (1 H, dqq, *J* = 6.7, 6.7, 7.5 Hz, H-4), 2.43 (3 H, s, CH_3), 2.81 (1 H, ddd, *J* = 3.6, 3.8, 10.3 Hz, H-2), 3.35 (1 H, d, *J* = 7.5 Hz, OH), 3.44 (1 H, ddd, *J* = 3.6, 7.5, 7.5 Hz, H-3), 7.30-7.41 (4 H, m, arom); MS m/z (rel) 293 (m^+-18, 0.2), 278 (4), 212 (18), 197 (2), 172 (10), 157 (48), 140 (80), 139 (92), 129 (88), 91 (95), 73 (100). Anal. Calcd for $C_{16}H_{27}O_2SSi$: C, 61.69; H, 8.74. Found: C, 61.54; H, 8.87.

(1*R*,2*R*)-3-(Methyldiphenylsilyl)-1-phenyl-2-[(*R*)-*p*-tolylsulfinyl]-1-propanol (6d-S) and (1*S*,2*R*)-3-(Methyldiphenylsilyl)-1-phenyl-2-[(*R*)-*p*-tolylsulfinyl]-1-propanol (6d-A): **5b** (182 mg, 0.50 mmol), benzaldehyde (58 mg, 0.55 mmol), 75:25 hexane/ethyl acetate, a mixture of **6d-S** and **6d-A** (188 mg, 80% yield, **S:A** = 53:47) as a biscose oil. Recrystallization of the mixture from acetone afforded pure **6d-S** as colorless needles. **6d-S**: mp 107–108 °C (acetone); TLC R_f 0.49 (60:40 hexane/ethyl

acetate); $[\alpha]^{23}_D$ +59.4 ° (c 0.16, acetone); IR (KBr) 3370, 3070, 1490, 1445, 1425, 1250, 1110, 1025, 1015, 815, 795, 775, 755, 730, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.20 (3 H, s, SiMe), 1.36 (1 H, dd, *J* = 4.8, 16.2 Hz, H-3), 1.47 (1 H, dd, *J* = 7.6, 16.2 Hz, H-3), 2.32 (1 H, br s, OH), 2.40 (3 H, s, CH_3), 3.02 (1 H, ddd, *J* = 4.8, 4.9, 7.6 Hz, H-2), 5.20 (1 H, d, *J* = 4.2 Hz, H-1), 7.06–7.38 (19 H, m, arom); MS m/z (rel) 455 (M^+-15, 0.1), 336 (12), 331 (9), 330 (5), 321 (7), 316 (23), 197 (100), 183 (21), 140 (56), 139 (71), 107 (4), 91 (63). Anal. Calcd for $C_{29}H_{30}O_2SSi$: C, 74.00; H, 6.42. Found: C, 73.85; H, 6.64. **6d-A**: TLC R_f 0.49 (60:40 hexane/ethyl acetate); IR (neat) 3370, 3070, 1490, 1445, 1425, 1250, 1110, 1025, 1015, 815, 795, 775, 755, 730, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.44 (3 H, s, SiMe), 1.06 (1 H, dd, *J* = 4.3, 15.6 Hz, H-3), 1.69 (1 H, dd, *J* = 9.4, 15.6 Hz, H-3), 2.42 (3 H, s, CH_3), 2.85 (1 H, ddd, *J* = 4.2, 4.3, 9.4 Hz, H-2), 4.47 (1 H, d, J = 5.2 Hz, OH), 4.86 (1 H, dd, *J* = 4.9, 5.2 Hz, H-1), 7.06–7.38 (19 H, m, arom); MS m/z (rel) 455 (M^+-15, 0.1), 336 (21), 331 (7), 330 (6), 321 (9), 316 (18), 197 (100), 183 (25), 140 (60), 139 (78), 107 (5), 91 (72). Anal. Calcd for $C_{29}H_{30}O_2SSi$: C, 74.00; H, 6.42. Found: C, 73.91; H, 6.61.

(2*R*)-1-(Methyldiphenylsilyl)-2-[(*R*)-*p*-tolylsulfinyl]-3-octanol (6e): **5b** (200 mg, 0.55 mmol), hexanal (61 mg, 0.61 mmol), 75:25 hexane/ethyl acetate, a mixture of two diastereoisomers **6e-S** and **6e-A** (219 mg, 86% yield) as a colorless oil: TLC R_f 0.46 (60:40 hexane/ethyl acetate); IR (neat) 3470, 2970, 2950, 1495, 1425, 1250, 1110, 1030, 910, 810, 730, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) for **6e-S** δ 0.36 (3 H, s, SiMe), 0.85 (3 H, t, *J* = 6.3 Hz, CH_3), 1.02–1.58 (10 H, m), 2.43 (3 H, s, CH_3), 2.77 (1 H, ddd, *J* = 3.1, 3.4, 10.1 Hz, H-2), 3.80 (1 H, br s, OH), 3.85 (1 H, ddd, *J* = 3.1, 3.6, 8.9 Hz, H-3), 7.20-7.44 (14 H, m, arom); for **6e-A** δ 0.41 (3 H, s, SiMe), 0.86 (3 H, t, *J* = 6.3 Hz, CH_3), 1.08–1.92 (10 H, m), 2.43 (3 H, s, CH_3), 2.56 (1 H, ddd, *J* = 2.4, 3.5, 11.3 Hz, H-2), 3.10 (1 H, br s, OH), 3.59–3.71 (1 H, m, H-3), 7.20-7.38 (14 H, m, arom); MS m/z (rel) 449 (M^+-15, 0.07), 431 (0.3), 336 (11), 325 (3), 324 (6), 321 (8), 307 (9), 292 (7), 197 (87), 183 (19), 140 (89), 139 (100), 91 (78). Anal. Calcd for $C_{28}H_{36}O_2SSi$: C, 72.37; H, 7.81. Found: C, 72.39; H, 7.97.

(2*R*)-1-Phenyl-2-[(*R*)-*p*-tolylsulfinyl]-3-(triphenylsilyl)-1-propanol (6f): **5c** (132 mg, 0.31 mmol), benzaldehyde (37 mg, 0.35 mmol), 30:70 hexane/CH_2Cl_2 and 95:5 CH_2Cl_2/ethyl acetate, a mixture of two diastereoisomers **6f-S** and **6f-A** (78 mg, 47% yield). In this reaction, 1-phenyl-1-(triphenylsilyl)oxy-2-propene (**8**) (43 mg, 35% yield) and (*E*)-1-phenyl-3-(triphenylsilyl)-2-propen-1-ol (**9**) (21 mg, 17% yield) and were also obtained. **6f**: ^1H NMR (200 MHz $CDCl_3$) for **6f-S**, δ 1.40 (1 H, dd, *J* = 3.4, 15.7 Hz, H-3), 2.22 (1 H, dd, *J* = 11.6, 15.7 Hz, H-3), 2.42 (3 H, s, CH_3), 2.86 (1 H, ddd, *J* = 3.0, 3.4, 11.6 Hz, H-2), 4.36 (1 H, d, *J* = 7.1 Hz, OH), 4.78–4.88 (1 H, m, H-1), 7.19–7.42 (24 H, m, arom); for **6f-A**, δ 1.66 (2 H, d, *J* = 6.2 Hz, H-3), 2.10 (1 H, br s, OH), 2.40 (3 H, s, CH_3), 3.13 (1 H, dt, *J* = 5.8, 6.2 Hz, H-2), 5.06 (1 H, d, *J* = 5.8 Hz, H-1), 7.19–7.42 (24 H, m, arom). **8**: IR (neat) 3075, 1820, 1590, 1490, 1430, 1110, 1030, 1000, 920, 740, 710, 700 cm^{-1}; ^1H NMR (200 MHz $CDCl_3$) δ 5.01 (1 H, ddd, *J* = 1.4, 1.4, 10.0 Hz, H-1), 5.15 (1 H, ddd, *J* = 1.4, 1.4, 17.1 Hz, H-1), 5.31 (1 H, ddd, *J* = 1.4, 1.4, 5.6 Hz, H-3), 5.96 (1 H, ddd, *J* = 5.6, 10.0, 17.1 Hz, H-2), 7.20–7.62 (20 H, m, 4 x Ph); MS m/z (rel) 392 (M^+, 15), 314 (19), 276 (6), 259 (47), 246 (100), 199 (37), 123 (68). Anal. Calcd for $C_{27}H_{24}OSi$: C, 82.61; H, 6.16. Found: C, 82.76; H, 6.32. **9**: IR (neat) 3430, 3075, 1620, 1595, 1490, 1430, 1110, 1000, 910, 810, 740, 700 cm^{-1}; ^1H NMR (200 MHz $CDCl_3$) δ 2.01 (1 H, br s, OH), 5.31 (1 H, dd, *J* = 1.2, 4.5 Hz, H-1), 6.35 (1 H, dd, *J* = 4.5, 18.6 Hz, H-2), 6.59 (1 H, dd, *J* = 1.2, 18.6 Hz, H-3), 7.15–7.67 (20 H, m, 4 x Ph); MS m/z (rel) 392 (M^+, 0.6), 314 (1.2), 276 (25), 259 (21), 246 (78), 199 (89), 123 (100). Anal. Calcd for $C_{27}H_{24}OSi$: C, 82.61; H, 6.16. Found: C, 82.53; H, 6.14.

(2*S*)-2-[(*R*)-*tert*-Butylsulfinyl]-1-phenyl-3-(trimethylsilyl)-1-propanol (6g-AA, and 6g-AS) and (2*R*)-2-[(*R*)-*tert*-Butylsulfinyl]-1-phenyl-3-(trimethylsilyl)-1-propanol (6g-SA, and 6g-SS): **5e** (77 mg, 0.37 mmol), benzaldehyde (44 mg, 0.42 mmol), 70:30 and 50:50 hexane/ethyl acetate, a mixture of **6g-AA** and **6g-AS** (99 mg, 85% yield, **AA:AS** = 55:45) and a mixture of **6g-SA** and **6g-SS** (10 mg, 9% yield, **SA:SS** = 70:30). Diastereoisomeric ratios were determined by ^{1}H NMR analysis. **6g-AA, AS**: IR (neat) 3330, 2950, 1445, 1410, 1360, 1320, 1250, 1170, 1085, 1060, 1035, 1015, 995, 840, 760, 750, 710, 695 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) for **6g-AA**, δ –0.13 (9 H, s, $SiMe_3$), 0.62 (1 H, dd, *J* = 1.7, 16.2 Hz, H-3), 0.77 (1 H, dd, *J* = 8.2, 16.2 Hz, H-3), 1.43 (9 H, s, *t*-Bu), 3.36 (1 H, ddd, *J* = 1.7, 8.2, 9.3 Hz, H-2), 4.98 (1 H, dd, *J* = 2.3, 9.3 Hz, H-1), 5.68 (1 H, d, *J* = 2.3 Hz, OH), 7.23–7.44 (5 H, m, Ph); for **6g-AS**, δ –0.13 (9 H, s, $SiMe_3$), 1.04 (1 H, dd, *J* = 5.0, 16.2 Hz, H-3), 0.77 (1 H, dd, *J* = 8.6, 16.2 Hz, H-3), 1.35 (9 H, s, *t*-Bu), 3.08 (1 H, ddd, *J* = 1.8, 5.0, 8.6 Hz, H-2), 4.76 (1 H, d, *J* = 3.1 Hz, OH), 5.63 (1 H, dd, *J* = 1.8, 3.1 Hz, H-1), 7.23–7.44 (5 H, m, Ph); MS m/z (rel) 297 (M^+-15, 0.4), 279 (0.3), 256 (0.3), 205 (35), 191 (60), 178 (45), 116 (100), 107 (32), 106 (56), 91 (43), 73, (94). Anal. Calcd for $C_{16}H_{28}O_2SSi$: C, 61.49; H, 9.03. Found: C, 61.36; H, 9.10. On standing of a solution of a mixture of **6g-AA** and **6g-AS** at -30 °C for 3 months, **6g-AA** was obtained as colorless needles: mp 94–95 °C (diethyl ether); $[\alpha]^{23}_D$ +89.0 ° (c 0.51, acetone). **6g-SA, SS**: IR (KBr) 3360, 2950, 1450, 1245, 1035, 1005, 840, 750, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) for **6g-SA**, δ 0.06 (9 H, s, $SiMe_3$), 0.51 (1 H, dd, *J* = 12.0, 16.3 Hz, H-3), 1.13 (9 H, s, *t*-Bu), 1.15 (1 H, dd, *J* = 1.7, 16.3 Hz, H-3), 2.35 (1 H, br s, OH), 3.24 (1 H, ddd, *J* = 1.7, 6.0, 12.0 Hz, H-2), 4.93 (1 H, d, *J* = 6.0 Hz, H-1), 7.29–7.46 (5 H, m, Ph); for **6g-SS**, δ 0.14 (9 H, s, $SiMe_3$), 0.88 (9 H, s, *t*-Bu), 1.03 (1 H, dd, *J* = 9.5, 15.8 Hz, H-3), 1.12 (1 H, dd, *J* = 5.3, 15.8 Hz, H-3), 2.63 (1 H, br s, OH), 3.05 (1 H, ddd, *J* = 2.4, 5.3, 9.5 Hz, H-2), 5.10 (1 H, d, *J* = 2.4 Hz, H-1), 7.22–7.42 (5 H, m, Ph); MS m/z (rel) 297 (M^+-15, 0.1), 279 (0.5), 256 (0.4), 205 (31), 191 (30), 178 (9), 116 (948), 107 (24), 106 (37), 91 (15), 73, (100). Anal. Calcd for $C_{16}H_{28}O_2SSi$: C, 61.49; H, 9.03. Found: C, 61.23; H, 9.05.

(2*R*)-2-[(*R*)-*t*-Butylsulfinyl]-1-(trimethylsilyl)-3-octanol (6h-AA, and 6h-AS) and (2*S*)-2-[(*R*)-*t*-Butylsulfinyl]-1-(trimethylsilyl)-3-octanol (6h-SA, and 6h-SS): **5e** (81 mg, 0.39 mmol), hexanal (43 mg, 0.43 mmol), 80:20 and 40:60 hexane/ethyl acetate, a mixture of **6h-AA** and **6h-AS** (96 mg, 80% yield, **AA:AS** = 54:46) and a mixture of **6h-SA** and **6h-SS** (11 mg, 9% yield, **SA:SS** = 51:49). Diastereoisomeric ratios were determined by ^{1}H NMR analysis. **6h-AA, AS**: IR (neat) 3360, 2950, 1460, 1360, 1250, 1030, 1000, 840 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) for **6h-AA**, δ 0.13 (9 H, s, $SiMe_3$), 0.77–0.97 (5 H, m, H-1 and CH_3), 1.24–1.67 (8 H, m), 1.29 (9 H, s, *t*-Bu), 3.02 (1 H, ddd, *J* = 4.0, 7.6, 7.6 Hz, H-2), 3.88–4.02 (1 H, m, H-3), 4.83 (1 H, d, *J* = 4.0 Hz, OH); for **6h-AS**, δ 0.09 (9 H, s, $SiMe_3$), 0.85–1.14 (5 H, m, H-1 and CH_3), 1.24–1.67 (8 H, m), 1.31 (9 H, s, *t*-Bu), 3.11 (1 H, ddd, *J* = 2.7, 6.3, 9.1 Hz, H-2), 4.02–4.15 (1 H, m, H-3), 4.27 (1 H, d, *J* = 6.9 Hz, OH); MS m/z (rel) 306 (M^+, 0.1), 291 (0.9), 273 (0.4), 250 (5), 201 (17), 185 (96), 178 (77), 167 (2), 157 (41), 149 (66), 144 (67), 129 (72), 122 (99), 111 (93), 106 (50), 73 (100). Anal. Calcd for $C_{15}H_{34}O_2SSi$: C, 58.77; H, 11.18. Found: C, 58.85; H, 11.32. **6h-SA, SS**: IR (KBr) 3300, 2960, 2940, 1460, 1250, 1005, 850 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) for **6h-SA**, δ 0.10 (9 H, s, $SiMe_3$), 0.66 (1 H, dd, *J* = 12.9, 15.7 Hz, H-1), 0.89 (3 H, t, *J* = 6.3 Hz, CH_3), 0.95 (1 H, dd, *J* = 2.8, 15.7 Hz, H-1), 1.22 (9 H, s, *t*-Bu), 1.19–1.38 (6 H, m), 1.56–1.79 (2 H, m), 1.66 (1 H, d, *J* = 6.4 Hz, OH), 3.10 (1 H, ddd, *J* = 2.8, 3.0, 12.9 Hz, H-2), 3.78–3.91 (1 H, m, H-3); for **6h-SS**, δ 0.11 (9 H, s, $SiMe_3$), 0.90 (3 H, t, *J* = 7.4 Hz, CH_3), 0.92 (1 H, dd, *J* = 10.6, 15.6 Hz, H-1), 1.02 (1 H, dd,

J = 4.0, 15.6 Hz, H-1), 1.21 (9 H, s, t-Bu), 1.24–1.77 (8 H, m), 2.84 (1 H, ddd, J = 2.1, 4.0, 10.6 Hz, H-2), 3.72–3.94 (1 H, m, H-3); MS m/z (rel) 306 (M^+, 0.5), 291 (0.2), 273 (0.1), 250 (0.2), 201 (3), 185 (30), 178 (15), 167 (24), 157 (52), 149 (63), 144 (98), 129 (87), 122 (18), 111 (46), 106 (57), 73 (100).
Anal. Calcd for $C_{15}H_{34}O_2SSi$: C, 58.77; H, 11.18. Found: C, 58.93; H, 11.21.

Representative Procedure for the Conversion of Compounds 6 into the Allylic Alcohols 11 with Tetrabutylammonium Fluoride (TBAF)

(*S*)-1-Phenyl-2-propen-1-ol[25] [(*S*)-11a]: To a solution of **6a-S** (48 mg, 0.14 mmol) in THF (1.5 ml) was added a THF solution of tetrabutylammonium fluoride (TBAF) (1.0 mol dm^{-3}, 0.16 ml, 0.16 mmol), and the mixture was stirred for 1 min. THF was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel 10 g, 90:10 hexane/ethyl acetate) to give (*S*)-**11a** (18 mg, 97% yield) as a colorless oil. Optical purity was confirmed as >99% ee by ^1H NMR analysis of the corresponding MTPA ester, and absolute configuration was determined by chiroptic comparison with published values: $[\alpha]^{10}_D$ -8.4 ° (c 2.87, benzene) [lit.[25] $[\alpha]^{25}_D$ -7.8 ° (c 5, benzene) for a 95% ee sample]; ^1H NMR (200 MHz, $CDCl_3$) δ 1.95 (1 H, br s, OH), 5.20 (1 H, d, J = 10.0 Hz, CH=CH_2), 5.22 (1 H, d, J = 6.0 Hz, CHOH), 5.36 (1 H, d, J = 10.0 Hz, CH=CH_2), 6.05 (1 H, ddd, J = 6.0, 10.0, 17.0 Hz, CH=CH_2), 7.26–7.40 (5 H, m, Ph).

The following compounds were prepared according to the representative procedure described above. The compound **6** (amount), reaction time, product yield, and optical purity are given in this abbreviated format.

(*R*)-1-Phenyl-2-propen-1-ol[26] [(*R*)-11a]: **6a-A** (48 mg, 0.14 mmol), 1 h, 17 mg (94% yield) as a colorless oil, >99% ee: $[\alpha]^{10}_D$ +8.3 ° (c 3.11, benzene) [lit.[26] $[\alpha]_D$ +8.2 ° (c 5.2, benzene)]

(*R*)-1-Octen-3-ol[27] [(*R*)-11b]: **6b-S** (117 mg, 0.34 mmol), 45 min, 40 mg (91% yield) as a colorless oil, >99% ee: $[\alpha]^{15}_D$ -10.0 ° (c 1.67, $CHCl_3$) [lit.[27] $[\alpha]^{20}_D$ -17.1 ° (neat)]; ^1H NMR (200 MHz, $CDCl_3$) δ 1.89 (3 H, t, J = 6.8 Hz, CH_3), 1.22–1.60 (8 H, m, 4 x CH_2), 1.44 (1 H, d, J = 4.5 Hz, OH), 4.03–4.17 (1 H, m, CHOH), 5.10 (1 H, ddd, J = 1.4, 1.4, 10.3 Hz, CH=CH_2), 5.22 (1 H, ddd, J = 1.4, 1.4, 17.2 Hz, CH=CH_2), 5.87 (1 H, ddd, J = 6.1, 10.3, 17.2 Hz, CH=CH_2).

(*S*)-1-Octen-3-ol[28] [(*S*)-11b]: **6b-A** (82 mg, 0.24 mmol), 3.5 h, 28 mg (91% yield) as a colorless oil, >99% ee: $[\alpha]^{19}_D$ +10.1 ° (c 0.67, $CHCl_3$) [lit.[28] $[\alpha]_D$ +16.9 ° (neat)].

Conversion of Compounds 6b into The β-Trialkylsilyl Allylic Alcohols 12 with Heat

(*R*)-(*E*)-1-Trimethylsilyl-1-octen-3-ol[29] [(*R*)-(*E*)-12]: A solution of compound **6b-S** (51 mg, 0.15 mmol) and pyridine (23 mg, 0.30 mmol) in benzene (1.0 ml) was heated under reflux for 30 min. After the mixture was cooled, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel 15 g, 93:7 hexane/ethyl acetate) to give (*R*)-(*E*)-**12** (24 mg, 80% yield) as a colorless oil. Optical purity was confirmed as >99%ee by ^1H NMR analysis of the corresponding MTPA ester, and absolute configuration was determined by chiroptic comparison with published values: $[\alpha]^{20}_D$ -10.9 ° (c 1.01, $CHCl_3$) [lit.[29] $[\alpha]^{25}_D$ -9.8 ° (c 1.10, $CHCl_3$)]; ^1H NMR (200 MHz, $CDCl_3$) δ 0.07 (9 H, s, $SiMe_3$), 0.88 (3 H, t, J = 6.4 Hz, CH_3), 1.23–1.58 (8 H, m, 4 x CH_2), 1.52 (1 H, d, J = 4.3 Hz, OH), 4.01–4.18 (1 H, m, CHOH), 5.82 (1 H, dd, J = 1.1, 18.7 Hz, CH=CHSiMe_3), 6.04 (1 H, dd, J = 5.1, 18.7 Hz, CH=CHSiMe_3).

(*S*)-(*E*)-1-Trimethylsilyl-1-octen-3-ol[30] **[(*S*)-(*E*)-12]**: In a similar fashion, compound **6b-A** (65 mg, 0.19 mmol) and pyridine (39 mg, 0.49 mmol) gave (*S*)-(*E*)-**12** (34 mg, 89% yield) as a colorless oil with >99% ee: $[\alpha]^{20}_{D}$ +10.9 ° (c 1.11, $CHCl_3$).

X-ray Structure Determinations of Compounds 7b-S and 6g-AA

Crystal data and experimental details for the compounds are summarized in Table 5. Diffraction data for **7b-S** and **6g-AA** were obtained with an Enraf Nonius CAD4 four-circle automated diffractometer. The reflection intensities were monitored by three standard reflections at every 2 h, and the decays of intensities two crystals were within 2%. Reflection data were corrected for Lorentz and polarization effects. Absorption corrections for the crystals were applied according to the DIFABS[31] procedure in both the cases.

The structure were solved by the direct method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. All refinements were continued until all shifts were smaller than one-third

Table 5. Crystal Data and Refinement Details for Compounds **7d-S** and **6g-AA**

	7d-S	**6g-AA**
formula	$C_{18}H_{32}O_3SSi$	$C_{16}H_{28}O_2SSi$
fw	356.60	312.55
color	colorless	colorless
crystal system	orthorhmbic	orthorhmbic
crystal size/mm	0.15 x 0.15 x 0.15	0.3 x 0.5 x 0.5
space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	5.9917(9)	10.1619(4)
b/Å	16.493(2)	11.6676(4)
c/Å	21.724(5)	15.3280(6)
β/deg	89.98(2)	89.994(3)
V/Å^3	2146.9(7)	1817.4(1)
Z	4	4
ρ/g cm^{-3}	1.103	1.142
μ/cm^{-1}	2.088	2.347
F(000)	776	680
scan method	ω-2θ	ω-2θ
$2\theta_{max}$/deg	52.64	52.64
λ(Mo Kα)/Å	0.7103	0.7103
total no. of reflcns	2521	2119
no. of reflcns used in refinement[a]	1051	1946
R[b]	0.049	0.039
R_w[c]	0.052	0.064

[a] $|F_o| > 3\sigma(F_o)$. [b] $R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from literature[32]. All hydrogen atoms for the two structures were included as isotropic in the structure factor calculations at the final stage of refinement; their positions were located on the positions obtained from the difference Fourier maps. The final R and R_w values were 0.049 and 0.052 for **7b-S**, 0.039 and 0.064 for **6g-AA**, respectively. The weighting scheme $w^{-1} = \{\sigma^2(|F_o|)+(0.02(|F_o|)^2\}$ was employed for both crystals. The final difference Fourier map did not show any significant features. The calculations were performed on a micro VAX-3100 computer by using the program system SDP-MolEN[33].

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REFERENCES AND NOTES

1. Part IV: Kusuda, S.; Ueno, Y.; Toru, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2720.
2. (a) Johnson, R. A.; Sharpless, K. B. *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, 1990; Vol. 7, Chapter 3.2. (b) Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841. (c) Ziegler, F. E. *Chem. Rev.* **1988**, *88*, 1423.
3. For some recent preparations of optically active secondary allylic alcohols; (a) Noyori, R.; Tomino, I.; Tamada, M.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, *106*, 6717; (b) Fujiwara, J.; Fukatani, Y.; Hasegawa, M.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1984**, *106*, 5004; (c) Kitano, Y.; Matsumoto, T.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1986**, 1323; (d) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765; (e) Kitamura, M.; Manabe, K.; Noyori, R.; Takaya, H. *Tetrahedron Lett.* **1987**, *28*, 4719; (f) Kitamura, M.; Kasahara, I.; Manabe, K.; Noyori, R.; Takaya, H. *J. Org. Chem.* **1988**, *53*, 708; (g) Satoh, T.; Oohara, T.; Ueda, Y.; Yamakawa, K. *J. Org. Chem.* **1989**, *54*, 3130; (h) Hayashi, M.; Kanako, T.; Oguni, N. *J. Chem. Soc., Perkin Trans. 1* **1991**, 25; (i) Okamoto, S.; Tani, K.; Sato, F.; Sharpless, K. B.; Zargarian, D. *Tetrahedron Lett.* **1993**, *34*, 2509 and references cited therein.
4. Kusuda, S.; Watanabe, Y.; Ueno, Y.; Toru, T. *J. Org. Chem.* **1992**, *57*, 3145.
5. Kusuda, S.; Ueno, Y.; Hagiwara, T.; Toru, T. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1981.
6. Kusuda, S.; Ueno, Y.; Toru, T. *Tetrahedron Lett.* in press.
7. Solladié, G.; Hutt, J.; Girardin, A. *Synthesis* **1987**, 173.
8. Fernández, I.; Khiar, N.; Llera, J. M.; Alcudia, F. *J. Org. Chem.* **1992**, *57*, 6789.
9. Solladié, G. *Synthesis* **1981**, 185.
10. For review of the reaction of α-sulfinyl carbanion of sulfoxides with aldehydes: (a) Oae, S.; Uchida, Y. Behavior of α-Sulfinyl Carbanions. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S.; Rappoport, Z.; Stirling, C. Eds.; John Wiley and Sons, 1988; pp. 583–664. (b) Walker, A. J. *Tetrahedron: Asymmetry* **1992**, *3*, 961.
11. Tentative numbering is used through the text as shown in equations.
12. Pyne, S. G.; Boche, G. *J. Org. Chem.* **1989**, *54*, 2663.

13. Casey, M.; Mukherjee, I.; Trabsa, H. *Tetrahedron Lett.* **1992**, *33*, 127.
14. The stereochemical assignment of the 2,3-*syn* and 2,3-*anti* diastereoisomers by the H^2, H^3 coupling constant has been established: Bravo, P.; Resnati, G.; Viani, F.; Arnone, A. *Tetrahedron* **1987**, *43*, 4635 and references cited therein.
15. We use the stereochemical descriptors *syn* and *anti* according to Masamune et al.: Masamune, S.; Ali, S. A.; Snitman, D. L.; Garvey, D. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1413.
16. Marsch, M.; Massa, W.; Harms, K.; Baum, G.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1011.
17. Kingsbury, C. A. *J. Org. Chem.* **1972**, *37*, 102.
18. Colombo, L.; Gennari, C.; Scolastico, C. *J. Chem. Soc., Chem. Commun.* **1979**, 591.
19. We have reported the fluoride-induced desilylselenenylation, destannylselenenylation, and destannylsulfenylation, see refs. 4 and 5. And also see: Kocienski, P. J. *Tetrahedron Lett.* **1979**, 2649.
20. The synthesis of vinylsilanes from thermonolysis of β-trimethylsilyl sulfoxides has been reported: Ochiai, M.; Tada, S.; Sumi, K.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1982**, 281.
21. The effect of the silyl group on the thermal elimination of the sulfinyl group has been reported: Fleming, I.; Goldhill, J.; Perry, D. A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1563 and see also ref. 15.
22. Huang, C.-T.; Wang, P.-J. *Hua Hsüeh Hsüeh pao* **1959**, *25*, 341; *Chem. Abstr.*, *54*, 16413e (1960).
23. Kauffmann, T.; Ilchmann, G.; König, R.; Wensing, M. *Chem. Ber.* **1985**, *118*, 391.
24. Kobayashi, T.; Pannell, K. H. *Organometallics* **1991**, *10*, 1960.
25. Claremon, D. A.; Lumma, P. K.; Phillips, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 8265.
26. Duveen, D. I.; Kenyon, J. *J. Chem. Soc.* **1939**, 1697.
27. Jeromin, G. E.; Scheidt, A. *Tetrahedron Lett.* **1991**, *32*, 7021.
28. Brown, E.; Penfornis, A.; Bayma, J.; Touet, J. *Tetrahedron: Asymmetry* **1991**, *2*, 339.
29. Kitano, Y.; Matsumoto, T.; Sato, F. *Tetrahedron* **1988**, *44*, 4073.
30. Matsumoto, T.; Kitano, Y.; Sato, F. *Tetrahedron Lett.* **1988**, *29*, 5685.
31. Walker, N. P. C.; Stuart, D. *Acta Crystallogr., Sect. A*, **1983**, *39*, 158.
32. Ibers, J. A.; Hamilton, W. C. *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, 1974; Vol. IV.
33. Frenz, B. A. "Enraf-Nonius Structure Determination Package; SDP User's Guide, Version 4, Enraf-Nonius, Delft, The Netherlands.

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