Preparation of Optically Pure Propargylic and Allylic Alcohols from 2-(Trimethylsilyl)vinyl Sulfoxides as a Chiral Ethynyl Anion Synthon: Computational Studies on Elimination Reaction of 2-(Trimethylsilyl)vinyl Sulfoxides

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Received May 1, 2001

The reaction of the α-carbanion derived from (trimethylsilyl)vinyl sulfoxides with aldehydes afforded a diastereomeric mixture of the products. Each diastereomer was subjected to specific elimination reactions to give optically pure propargylic, trimethylsilylated propargylic, and allylic alcohols. Acceleration of the sulfenic acid-elimination from the *β*-silylvinyl sulfoxide was demonstrated by the ab initio calculation to be ascribed mainly to the *β*-effect of the silyl group.

Introduction

Optically active propargylic alcohols are important synthetic intermediates in the synthesis of natural products.[1] A number of asymmetric syntheses of propargylic alcohols have been reported, e.g., asymmetric reduction of ynones,[1e,j,2] addition of metalated acetylenes to aldehydes,[3] and reaction of alkynylaldehydes with nucleophiles.[4] However, these previously reported asymmetric syntheses appear to incur difficulty in the preparation of propargylic alcohols with high optical purity. Recently, we reported that the reaction of α-sulfinyl carbanions derived from *β*-(trimethylsilyl)ethyl sulfoxides with aldehydes proceeded with extremely high stereoselectivity on the face of the carbanion α to the sulfinyl group. This reaction provides a convenient method for the preparation of optically pure allylic alcohols via subsequent elimination of the sulfinyl and the silyl groups.[5] To develop a new chiral ethynyl anion equivalent, we studied the reaction of α-lithio (trimethylsilyl)-vinyl *p*-tolyl sulfoxide with aldehydes, followed by easy elimination of the sulfinyl group by the action of the adjacent trimethylsilyl group.[6] This methodology would provide the asymmetric synthesis of both enantiomers of propargylic alcohols. We now report in detail (1) the addition of (trialkylsilyl)vinyl sulfoxides with various aldehydes, (2) the transformation of the products into chiral propargylic and allylic alcohols, and (3) ab initio calculation of the elimination reaction of (trimethylsilyl)- and *tert*-butylvinyl sulfoxides.

Results and Discussion

Preparation of (*R*)-(*E*)-2-(Trialkylsilyl)vinyl Sulfoxides 3a−d. (*R*)-(*E*)-2-(Trialkylsilyl)vinyl sulfoxides **3a−d** were easily synthesized from readily obtainable (*R*)-*p*-tolyl 2-(trialkylsilyl)ethyl sulfoxides **1a−c** or (*R*)-*tert*-butyl 2-(trialkylsilyl)ethyl sulfoxide **1d**[7] in two steps as shown in Table 1. Treatment of a THF solution of **1a−d** with 1.1 equiv of LDA at −78 °C for 1 h and

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(3) (a) Mukaiyama, T.; Suzuki, K.; Soai, K.; Sato, T. *Chem. Lett.* **1979**, 447−448. (b) Niwa, S.; Soai, K. *J. Chem. Soc., Perkin Trans. 1* **1990**, 937−943. (c) Tombo, G. M. R.; Didier, E. *Synlett* **1990**, 547−548. (d) Corey. E. J.; Cimprich, K. A. *J. Am. Chem. Soc.* **1994**, *116*, 3151−3152. (e) Tan, L.; Chen, C.-Y.; Tillyer, R. D.; Grabowski, E. J. J.; Reider, P. J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 711−713. (f) Li, Z.; Upadhyay, V.; DeCamp, A. E.; DiMichele, L.; Reider, P. J. *Synthesis* **1999**, 1453−1458. (g) Frantz, D. E.; Fässler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 1806−1807. (h) Frantz, D. E.; Fässler, R.; Tomooka, C. S.; Carreira, E. M. *Acc. Chem. Res.* **2000**, *33*, 373−381. (i) Boyall, D.; Lopez, F.; Sasaki, H.; Frantz, D.; Carreira, E. M. *Org. Lett.* **2000**, *2*, 4233−4236. (j) Sasaki, H.; Boyall, D.; Carreira, E. M. *Helv. Chim. Acta* **2001**, *84*, 964−971.

(4) (a) Soai, K.; Niwa, S. *Chem. Lett.* **1989**, 481−484. (b) Kobayashi, S.; Furuya, M.; Ohtsubo, A.; Mukaiyama, T. *Tetrahedron: Asymmetry* **1991**, *2*, 635−638. (c) Weber, B.; Seebach. D. *Tetrahedron* **1994**, *50*, 7473−7484. (d) Singer, R. A.; Shepard, M. S.; Carreira, E. M. *Tetrahedron* **1998**, *54*, 7025−7032.

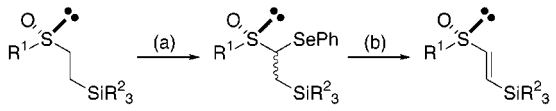
(5) (a) Kusuda, S.; Ueno, Y.; Toru, T. *Tetrahedron* **1994**, *50*, 1045−1062. (b) Toru, T.; Nakamura, S.; Takemoto, H.; Ueno, Y. *Synlett* **1997**, 449−450. (c) Nakamura, S.; Watanabe, Y.; Toru, T. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3403−3404. (d) Nakamura, S.; Takemoto, H.; Ueno, Y.; Toru, T.; Kakumoto, T.; Hagiwara, T. *J. Org. Chem.* **2000**, *65*, 469−474. (e) Nakamura, S.; Watanabe, Y.; Toru, T. *J. Org. Chem.* **2000**, *65*, 1758−1766.

(6) Kusuda, S.; Kawamura, K.; Ueno, Y. Toru, T. *Tetrahedron Lett.* **1993**, *34*, 6587−6590.

(7) (*R*)-*p*-tolyl 2-(trialkylsilyl)ethyl sulfoxides **1a−c** or (*R*)-*tert*-butyl 2-(trialkylsilyl)ethyl sulfoxide **1d** could be readily synthesized, see refs 5a, d.

10.1021/jo0157223 CCC: $22.00
Published on Web 01/04/2002

Table 1. Preparation of (*R*)-(*E*)-2-(Trialkylsilyl)vinyl Sulfoxides 3a−d and 2a−d



1a-d **2a-d** **3a-d**

a: R^1 = Tol, SiR^2_3 = $SiMe_3$
b: R^1 = Tol, SiR^2_3 = $SiPh_2Me$
c: R^1 = Tol, SiR^2_3 = $SiPh_3$
d: R^1 = *t*-Bu, SiR^2_3 = $SiMe_3$

product	yield (%)	diastereomer ratio[a]	product	yield (%)	ee (%)
2a	60	82:18	**3a**	94	>99[b]
2b	89	79:21	**3b**	92	>99[b]
2c	53	77:23	**3c**	80	>99[b]
2d	69	85:15	**3d**	97	>99[c]

[a] Determined by the ^{1}H NMR analysis. [b] Determined by the HPLC (Chiralcel OB−H) analysis. [c] Determined by the ^{1}H NMR analysis using (*R*)-(−)-(3,5-dinitrobenzoyl)-α-phenethylamine.

subsequently with 1.2 equiv of phenylselenenyl bromide gave α-(phenylseleno)ethyl sulfoxides **2a**−**d** which were selectively oxidized with *m*-CPBA in CH_2Cl_2 at 0 °C to give enantiomerically pure 2-(trialkylsilyl)vinyl sulfoxides **3a**−**d**. The geometry of the products **3a**−**d** was determined to be *E* by the coupling constants (J = 17.5−18.1 Hz) in their ^{1}H NMR spectra. The optical purities of **3a**−**d** were determined to be >99% ee by the HPLC analysis using Chiralcel OB−H or by the ^{1}H NMR analysis in the presence of (*R*)-(−)-(3,5-dinitrobenzoyl)-α-phenethylamine[8] as a chiral shift reagent.

Reaction of the α-Vinyl Anions Derived from Silylvinyl Sulfoxides 3a−d with Aldehydes. We first investigated the reaction of the α-vinyl anions derived from **3a**−**d** with various aldehydes. However, treatment of **3a**−**d** with 1.1 equiv of LDA in THF at −100 °C formed a number of undesired products, which consisted of oligomers probably formed from the partially lithiated **3a**−**d**. To avoid this oligomerization, the sulfoxides **3a**−**d** were treated with 2.0 equiv of LDA in THF at −100 °C for 20 min to generate the lithium carbanion completely, which was then reacted with an aldehyde at the same temperature for 5 min giving good yields of the products **4a**−**j**. The yields and the diastereomer ratios obtained in the reaction with benzaldehyde, acetaldehyde, hexanal, isobutyraldehyde, and 2,2-dimethylpropionaldehyde are shown in Table 2.

The reaction of lithiated **3a**−**c** with aldehydes gave the products **4b**−**h** with moderate selectivity (entries 2−8), favoring the formation of the (*S*)-isomer except for the reaction with benzaldehyde (entry 1). The stereoselective outcome appears to be irrespective of the steric bulkiness of the aldehydes and the silyl groups (entries 1−8). These results are not in accord with the previously reported results of the reaction of α-lithiated vinyl sulfoxides with aldehydes, in which bulky aldehydes afford highly stereoselective adducts.[9] Notably, replacement of the *p*-tolyl group with the *tert*-butyl group reversed the stereoselectivity, favoring the (*R*)-isomer (entries 9 and 10).[9d] A similar stereoselectivity was obtained in the reaction of *p*-tolyl sulfoxides **1a**,**b** in the presence of HMPA (2 equiv) (entries 11 and 12).[9d]

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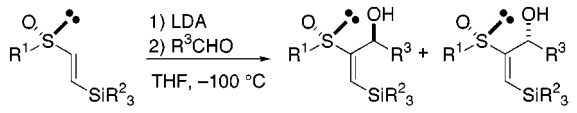
Table 2. Reaction of Silylvinyl Sulfoxides 3a−d with Various Aldehydes



3a-d (*S*)-**4** (*R*)-**4**

entry		sulfoxide R^1	sulfoxide SiR^2_3	aldehyde R^3	product	yield (%)	ratio[a] (*S*)-**4**:(*R*)-**4**
1	**3a**	Tol	$SiMe_3$	Ph	**4a**	88	45:55
2	**3a**	Tol	$SiMe_3$	Me	**4b**	82	68:32
3	**3a**	Tol	$SiMe_3$	n-C_5H_{11}	**4c**	93	73:27
4	**3a**	Tol	$SiMe_3$	*i*-Pr	**4d**	92	68:32
5	**3a**	Tol	$SiMe_3$	*t*-Bu	**4e**	71	76:24
6	**3b**	Tol	$SiPh_2Me$	n-C_5H_{11}	**4f**	77	69:31
7	**3c**	Tol	$SiPh_3$	n-C_5H_{11}	**4g**	70	66:34
8	**3c**	Tol	$SiPh_3$	*t*-Bu	**4h**	74	67:33
9	**3d**	*t*-Bu	$SiMe_3$	Ph	**4i**	88	34:66
10	**3d**	*t*-Bu	$SiMe_3$	n-C_5H_{11}	**4j**	82	29:71
11[b]	**3a**	Tol	$SiMe_3$	n-C_5H_{11}	**4c**	70	37:63
12[b]	**3b**	Tol	$SiPh_2Me$	n-C_5H_{11}	**4f**	65	32:68

[a] Isolated ratio. [b] HMPA (2.0 equiv) was added.

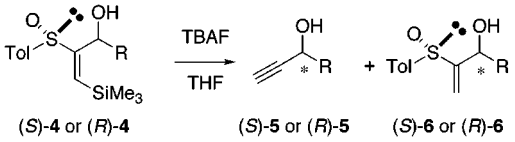
Desilylsulfinylation, Desilylation, and Desulfinylation from (*S*)-4 and (*R*)-4. Preparation of Optically Pure Propargylic Alcohols. The resulted diastereomers (*S*)-**4** and (*R*)-**4** could be easily separated by silica gel column chromatography, and they were separately subjected to the following transformations. Treatment of (*S*)-**4a**,**c** and (*R*)-**4** with tetrabutylammonium fluoride (TBAF) in THF at room temperature afforded the desilylated allylic alcohols (*S*)-**6** and (*R*)-**6**, respectively, as major products in moderate yields together with the formation of the propargylic alcohols **5** as minor products (Table 3). These results are in sharp contrast with those obtained in a similar treatment of the products from the *β*-silylethyl sulfoxides resulting in the simultaneous elimination of the sulfinyl and the trimethylsilyl groups. Interestingly, the addition of water was found to be effective for the selective desilylation to obtain **6** probably due to the rapid protonation of the vinyl anion formed during the reaction.

Thus, reaction of (*S*)-**4a** and (*R*)-**4a** with TBAF in the presence of water almost exclusively afforded (*S*)-**6a** and (*R*)-**6a**, respectively (entries 5 and 6), although it took longer to complete the reaction. To clarify the role of the hydroxyl group for desilylation, reaction of the THP-protected (*R*)-**4a** with TBAF was examined. It gave propargylic alcohol (*R*)-**5a** in higher yield than that of (*R*)-**4a** without protection (entry 7). In addition, desilylation of *p*-tolyl 2-(trimethylsilyl)vinyl sulfoxide **3a** with TBAF at 0 °C in THF for 3 h did not smoothly proceed and gave the desilylated product **7** in low yield (Scheme 1).

These results indicate that the hydroxyl group in **4** plays a significant role in effecting desilylation. Protonation of the vinyl anion by the hydroxyl group would suppress the subsequent desulfinylation and lead to the

(9) Reaction of α-lithiated vinyl sulfoxides with aldehydes give the products generally with low diastereoselectivity, see (a) Posner, G. H.; Mallamo, J. P.; Miura, K.; Hulce, M. *Pure Appl. Chem.* **1981**, *53*, 2307−2314. (b) Solladié, G.; Moine, G. *J. Am. Chem. Soc.* **1984**, *106*, 6097−6098. (c) House, S.; Jenkins, P., R.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1844−1845. (d) Fawcett, J.; House, S.; Jenkins, P. R.; Lawrence, N. J.; Russell, D. R. *J. Chem. Soc., Perkin Trans. 1* **1993**, 67−73. (e) Bonfand, E.; Gosselin, P.; Maignan, C. *Tetrahedron: Asymmetry* **1993**, *4*, 1667−1676.

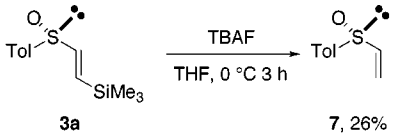
Table 3. Selective Conversion of 4 into Allylic Alcohols 6 on Treatment with Tetrabutylammonium Fluoride



entry		substrate, R	additive	reaction temp	reaction time	**5** yield (%)		**6** yield (%)	de (%)[a]
1	(*S*)-**4a**	Ph		rt	5 min	25	(*S*)-**6a**	57	>99
2	(*R*)-**4a**	Ph		rt	5 min	28	(*R*)-**6a**	63	>99
3	(*S*)-**4c**	n-C_5H_{11}		rt	5 min	31	(*S*)-**6c**	65	>99
4	(*R*)-**4a**	Ph		0	30 min	13	(*R*)-**6a**	84	>99
5	(*S*)-**4a**	Ph	H_2O (10 equiv)	0→rt	12 h	3	(*S*)-**6a**	96	>99
6	(*R*)-**4a**	Ph	H_2O (10 equiv)	0→rt	12 h	8	(*R*)-**6a**	90	>99
7	THP−(*R*)-**4a**[b]	Ph		rt	5 min	42[c]	THP−(*R*)-**6a**	23	>99

[a] Determined by ^{1}H NMR and HPLC analyses of the corresponding MTPA ester. [b] The THP-protected (*R*)-**4a** was used. [c] The THP-protected product was obtained.

Scheme 1



Scheme 2

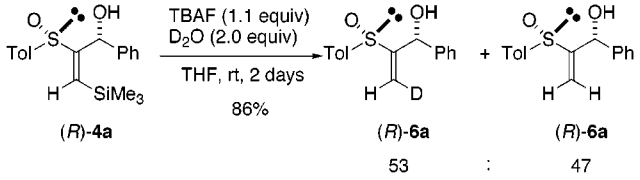
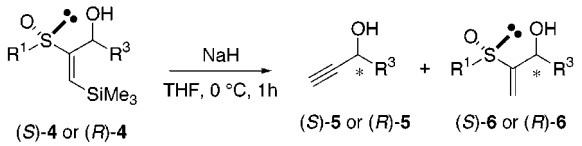


Table 4. Treatment of 4 with NaH into Propargylic Alcohols 5 and Allylic Alcohols 6



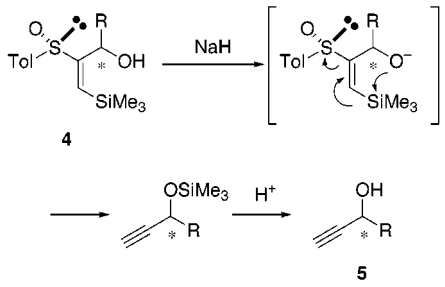
entry		substrate R^1	substrate R^3	product[a]	**5** yield (%)	ee (%)[b]	**6** yield (%)
1	(*S*)-**4a**	Tol	Ph	(*R*)-**5a**	83	>99	5
2	(*R*)-**4a**	Tol	Ph	(*S*)-**5a**	79	>99	8
3	(*S*)-**4c**	Tol	n-C_5H_{11}	(*S*)-**5c**	65	>99	10
4	(*R*)-**4c**	Tol	n-C_5H_{11}	(*R*)-**5c**	64	>99	14
5	(*R*)-**4j**	*t*-Bu	n-C_5H_{11}	(*R*)-**5c**	36	>99	63

[a] The absolute configuration was determined by comparison of the specific rotation with the reported value. [b] Determined by ^{1}H NMR and HPLC analyses of the corresponding MTPA ester.

desilylated allylic alcohols **6**. Indeed, deuteration occurred stereospecifically at the *E* position (Scheme 2).

On the other hand, optically pure propargylic alcohols could be selectively prepared as shown in Table 4. The (*S*)- and (*R*)-isomers of **4a**,**c** were separately treated with sodium hydride (1.2 equiv) in THF at 0 °C for 1 h to give the optically active propargylic alcohols **5a**,**c** in good yields accompanied with a small amount of the desilylated allylic alcohols **6** (entries 1−4). A similar treatment of the *tert*-butyl vinyl sulfoxide **4j** predominantly gave the allylic alcohol **6j**, showing the *tert*-butyl sulfoxide is not an appropriate substrate for the preparation of the propargylic alcohols (entry 5). The obtained propargylic alcohols **5a**,**c** were determined to be enantiomerically

Scheme 3



pure (>99% ee) by ^{1}H NMR and HPLC analyses after conversion to the corresponding MTPA esters.[10]

The predominant formation of the propargylic alcohols **5** can be ascribed to the β-elimination initiated by an intramolecular attack of the alkoxide ion on the silicon as shown in Scheme 3.

On the other hand, thermal treatment of each diastereomer of **4** readily induced the elimination of the sulfenic acid, and the elimination was complete within 1 h under reflux in toluene to give the trimethylsilylpropargylic alcohols **8** in excellent yields as shown in Table 5.

Transformation of the vinyl sulfoxides without any accelerating groups into the acetylenic linkage is known to be unsuccessful[11,12] and only the more reactive vinyl selenoxides can undergo elimination to give triple bonds, although strong basic conditions are needed.[13] Thus, the present easy formation of **8** from the trimethylsilyl sulfoxides **4** is noteworthy, apparently owing to the α-carbanion or β-carbocation stabilizing effect of the silyl group.[14,15] The *tert*-butyl sulfoxide **4j** again showed inap-

(10) (a) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543−2549. (b) Dale, J. A.; Mosher, S. H. *J. Am. Chem. Soc.* **1973**, *95*, 512−519. (c) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370−2374.

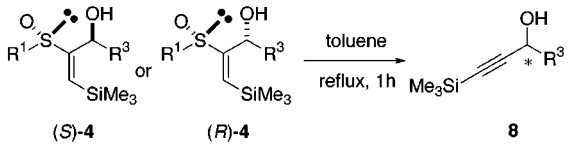
(11) Thermal desilylsulfinylation of the (*Z*)-β-silyl-α-sulfinyl-α,β-unsaturated ketone has been reported to give the acetylenic ketone, whereas thermal treatment of (*E*)-isomer hardly induces the elimination, see Fleming, I.; Goldhill, J.; Perry, D. A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1563−1569.

(12) We confirmed thermal treatment of a toluene solution of nonsilylated sulfoxide **6** under reflux gave no acetylenic compound.

(13) Reich, H.-J.; Willis, W. W. *J. Am. Chem. Soc.* **1980**, *102*, 5967−5968.

(14) The effect of the silyl group on the thermal elimination of the sulfinyl group to a double bond has been reported, see Ochiai, M.; Tada, S.; Sumi, K.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1982**, 281−282, and see also refs 5 and 10.

Table 5. Thermal Treatment of 4 into Trimethylsilylpropargylic Alcohols 8



(*S*)-**4** (*R*)-**4** **8**

entry		R^1	R^3	product[a]	yield (%)	ee (%)[b]
1	(*S*)-**4a**	Tol	Ph	(*S*)-**8a**	87	>99
2	(*R*)-**4a**	Tol	Ph	(*R*)-**8a**	95	>99
3	(*S*)-**4b**	Tol	Me	(*S*)-**8b**	71	>99
4	(*R*)-**4b**	Tol	Me	(*R*)-**8b**	71	>99
5	(*S*)-**4c**	Tol	*n*-C_5H_{11}	(*S*)-**8c**	80	>99
6	(*R*)-**4c**	Tol	*n*-C_5H_{11}	(*R*)-**8c**	66	>99
7	(*R*)-**4j**	*t*-Bu	*n*-C_5H_{11}	(*R*)-**8d**	23	>99

[a] The absolute configuration was determined by comparison of the specific rotation with the reported value. [b] Determined by ^{1}H NMR and HPLC analyses of the corresponding MTPA ester.

propriate reactivity for the preparation of the silyl propargylic alcohols, giving **8d** in low yield probably due to the desulfinylation occurring toward the *tert*-butyl group.[16]

To gain more quantitative information on the effect of the silyl group in the elimination reaction, the activation energies of the elimination reaction from 2-(*tert*-butyl)-vinyl sulfoxide **9** and 2-(trimethylsilyl)vinyl sulfoxide **10** were estimated by ab initio calculation. First, the relative stabilities of conformers of **9** and **10** were calculated with Gaussian 98[17] HF/3-21+G*. These optimized structures were confirmed to have no negative frequency by the frequency calculations. The thermal correction from 0 to 384 K, including the correction of zero-point energies, was obtained from HF/3-21+G* calculations of vibrational frequencies scaled by 0.9409. The relative energies of the optimized structures of **9** and **10** obtained by these calculations are depicted in Figure 1.

The optimized conformers **9** and **10** were structurally similar, and their dihedral angles (O−S−C_β-C_α) were 127.2° and 132.7°, respectively. Next, we calculated the transition states for the elimination reaction from the sulfoxides **9** and **10**. It is well-known that the thermal elimination reaction of the sulfenic acid from the sulfoxide proceeds through a five-membered cyclic transition state.[11,13,18] The five-membered cyclic transition structures were fully optimized without any constraint and characterized by vibrational-frequency calculations, leading to the transition states **TS-9** and **TS-10** with a negative frequency corresponding to the elimination of

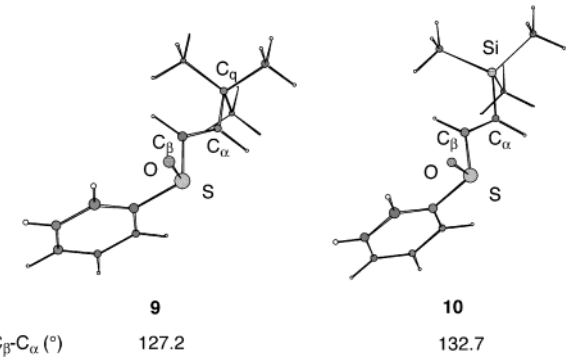


Figure 1. relative energies of the optimized structures of **9** and **10**.

the sulfenic acid. The intrinsic reaction coordination (IRC) calculation starting from **TS-9** and **TS-10** confirmed the formation of the starting sulfoxides **9** and **10** and the products, the alkyne and the sulfenic acid. Figure 2 shows the relative energies of the optimized transition states **TS-9** and **TS-10** to those of the respective optimized ground states **9** and **10**.

The structure of the transition state **TS-10** was also similar to **TS-9**, and the activation energy from **10** (34.7 kcal/mol) was apparently lower than that from **9** (53.6 kcal/mol). We also calculated stabilizing effects of the silicon in transition states using the NPA[19] and the NBO analyses.[20] These analyses showed that the stabilizing effect of the silicon on the cationic C_β-carbon was larger in comparison with that on the anionic C_α-carbon.[21,22] Thus, the acceleration of the sulfenic acid-elimination reaction from the β-silylvinyl sulfoxide **10** can be ascribed mainly to the stabilizing effect of the silicon on the cationic C_β-carbon.

Summary

The reaction of the vinyl anion α to the chiral sulfinyl group with aldehydes, separation of diastereomers, and specific elimination reactions provide reliable routes for the selective synthesis of optically pure propargylic alcohols, trimethylsilylpropargylic alcohols, and sulfinyl-substituted allylic alcohols. The MO calculations revealed that acceleration of the sulfenic acid-elimination from the β-(trimethylsilyl)vinyl sulfoxide could be ascribed mainly to the β-effect of the silyl group.

Experimental Section

Representative Procedure for the Preparation of the α-Selenosulfoxide. 1-Phenylseleno-1-[(*S*)-*p*-tolylsulfinyl]-2-(trimethylsilyl)ethane (2a). To a solution of diisopropylamine (0.028 mL, 0.21 mmol) in THF (0.28 mL) was added *n*-butyllithium (1.57 mol dm^{-3} in hexane, 0.135 mL, 0.21 mmol)

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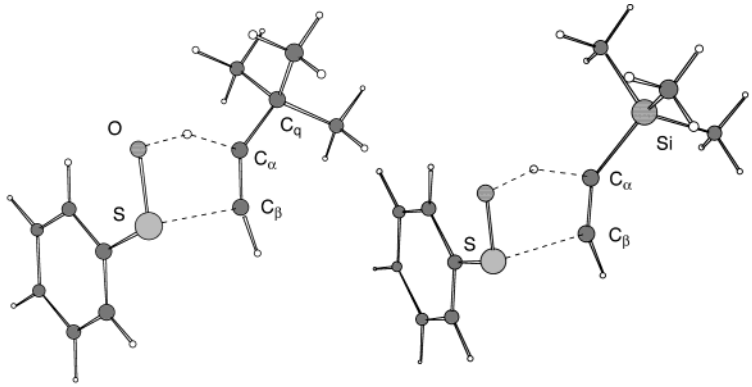
(20) NBO Ver. 3.1: Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. See also ref 18b.

(21) See Supporting Information.

(22) A similar calculation result was obtained in the elimination reaction from β-(trimethylsilyl)ethyl sulfoxide.



	TS-9	TS-10
∠ O-S-C_β-C_α (°)	359.2	0.0
$\Delta G^\ddagger$ (kcal/mol)	53.6	34.7

Figure 2. optimized transition states **TS-9** and **TS-10** and their relative energies to the corresponding ground states.

at 0 °C, and the mixture was stirred for 30 min. The reaction mixture was cooled to −78 °C, and then a solution of **1a** (42 mg, 0.17 mmol) in THF (0.25 mL) was added dropwise over a period of 10 min. The mixture was stirred for an additional 1 h. Phenylselenenyl bromide (0.050 mg, 0.21 mmol) in THF (0.25 mL) was then added, and the mixture was stirred for 4 h, the solution was quenched with saturated aqueous NH_4Cl (5 mL) under vigorous stirring, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product which was purified by column chromatography (silica gel 9 g, hexane/ethyl acetate = 85:15) to give **2a** (41 mg, 60%). The diastereomer ratio was determined to be 82:18 by the ^{1}H NMR analysis of the crude product. ^{1}H NMR (for major) δ 0.07 (s, 9H), 0.31 (dd, 1H, J = 12.7, 15.0 Hz), 1.72 (dd, 1H, J = 2.8, 15.0 Hz), 2.41 (s, 3H), 3.67 (dd, 1H, J = 2.8, 12.7 Hz), 7.10−7.70 (m, 9H); (for minor) δ 0.04 (s, 9H), 0.95 (dd, 1H, J = 13.0, 15.0 Hz), 1.50 (dd, 1H, J = 2.6, 15.0 Hz), 2.41 (s, 3H), 3.67 (dd, 1H, J = 2.6, 13.0 Hz), 7.10−7.70 (m, 9H); IR (neat) 3050, 2950, 1570, 1470, 1430, 1240, 1030, 840, 780 cm^{-1}; EIMS m/z (rel intensity) 256 (M^+-C_7H_8OS, 55), 241 (10), 140 (60), 91 (100). Found: C, 54.79; H, 6.39. Calcd for $C_{18}H_{24}OSSeSi$: C, 54.67; H, 6.12%.

2-(Methyldiphenylsilyl)-1-phenylseleno-1-[(*S*)-*p*-tolylsulfinyl]ethane (2b). The reaction was carried out as described above except using **1b** (184 mg, 0.50 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 80:20) to afford **2b** (234 mg, 89%). The diastereomer ratio was determined to be 79:21 by the ^{1}H NMR analysis of the crude product. ^{1}H NMR (for major) δ 0.66 (s, 3H), 0.86 (dd, 1H, J = 12.3, 15.2 Hz), 2.28 (dd, 1H, J = 3.2, 15.2 Hz), 2.36 (s, 3H), 4.06 (dd, 1H, J = 3.2, 12.3 Hz), 7.03−7.59 (m, 19H); (for minor) δ 0.66 (s, 3H), 1.41 (dd, 1H, J = 12.3, 15.2 Hz), 1.50 (dd, 1H, J = 3.0, 15.2 Hz), 2.30 (s, 3H), 3.75 (dd, 1H, J = 3.0, 12.3 Hz), 7.03−7.59 (m, 19H); IR (neat) 3050, 1580, 1480, 1430, 1260, 1190, 1120, 1050, 820, 740, 700 cm^{-1}; EIMS m/z (rel intensity) 520 (M^+, 1), 380 (90), 197 (100). Found: C, 64.86; H, 5.70. Calcd for $C_{28}H_{28}OSSeSi$: C, 64.72; H, 5.43%.

1-Phenylseleno-1-[(*S*)-*p*-tolylsulfinyl]-2-(triphenylsilyl)-ethane (2c). The reaction was carried out as described above except using **1c** (1.02 g, 2.39 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 99:1) to afford **2c** (740 mg, 53%). The diastereomer ratio was determined to be 77:23 by the ^{1}H NMR analysis of the crude product. ^{1}H NMR (for major) δ 1.24 (dd, 1H, J = 11.5, 15.5 Hz), 2.36 (s, 3H), 2.60 (dd, 1H, J = 3.7, 15.5 Hz), 3.85 (dd, 1H, J = 3.7, 11.5 Hz), 6.95−7.55 (m, 24H); (for minor) δ 1.76 (dd, 1H, J = 12.7, 15.7 Hz), 2.28 (dd, 1H, J = 2.4, 15.7 Hz), 2.36 (s, 3H), 3.85 (dd, 1H, J = 2.4, 12.7 Hz), 6.95−7.55 (m, 24H); IR (neat) 3050, 1580, 1490, 1440, 1260, 1200, 1120, 1040, 810, 740, 710 cm^{-1}; EIMS m/z (rel intensity) 583 (M^+, 3), 424 (3), 398 (58), 259 (100). Found: C, 68.21; H, 5.38. Calcd for $C_{33}H_{30}OSSeSi$: C, 68.14; H, 5.20%.

1-[(*S*)-*tert*-Butylsulfinyl]-1-phenylseleno-2-(trimethylsilyl)ethane (2d). The reaction was carried out as described above except using **1d** (896 mg, 4.34 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 80:20) to afford **2d** (1.08 g, 69%). The diastereomer ratio was determined to be 85:15 by the ^{1}H NMR analysis of the crude product. Recrystallization from hexanes−ethyl acetate afforded diastereomerically pure **2d**; δ 0.18 (s, 9H), 0.87 (dd, 1H, J = 13.1, 16.0 Hz), 1.08 (s, 9H), 1.48 (dd, 1H, J = 2.2, 16.0 Hz), 4.00 (dd, 1H, J = 2.2, 13.1 Hz), 7.28−7.70 (m, 5H); IR (neat) 2950, 1460, 1430, 1400, 1360, 1250, 1170, 1030, 840, 740, 690 cm^{-1}; EIMS m/z (rel intensity) 255 (M^+-C_4H_9OS, 2), 105 (12), 73 (100). Found: C, 49.93; H, 7.47. Calcd for $C_{15}H_{16}OSSeSi$: C, 49.84; H, 7.25%.

Representative Procedure for the Preparation of the Vinylsulfoxide. (*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-2-(trimethylsilyl)ethylene (3a). To a solution of **2a** (52 mg, 0.13 mmol) in CH_2Cl_2 (1.0 mL) was added *m*-CPBA (29.4 mg, 0.14 mmol) in CH_2Cl_2 (0.5 mL) at −78 °C, and the mixture was stirred for 1 h. The solution was quenched with 10% aqueous Na_2SO_3 (4 mL). The aqueous layer was extracted with CH_2Cl_2 and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product which was purified by column chromatography (silica gel 7 g, hexane/ethyl acetate = 90:10) to give **3a** (29 mg, 94%). *E*/*Z* ratio was determined to be >98:2 by the ^{1}H NMR analysis of the crude product. $[\alpha]^{26}_D$ +344.0 (*c* 0.29 in EtOH); ^{1}H NMR δ 0.12 (s, 9H), 2.39 (s, 3H), 6.58 (d, 1H, 17.5 Hz), 6.94 (d, 1H, J = 17.5 Hz), 7.29 (d, 2H, J = 7.9 Hz), 7.46 (d, 2H, J = 7.9 Hz); IR (neat) 2950, 1570, 1240, 1140, 1080, 1040, 970, 860, 830, 720 cm^{-1}; EIMS m/z (rel intensity) 238 (M^+, 5), 212 (90), 140 (80), 73 (100). Found: C, 60.39; H, 7.67. Calcd for $C_{12}H_{18}OSSi$: C, 60.45; H, 7.61%. HPLC (Daicel Chiralcel OB−H, hexane/*i*-PrOH = 95:5, flow rate 0.50 mL/min) t_R 22.4 (*R*) min (>99% ee).

(*E*)-2-(Diphenylmethylsilyl)-1-[(*R*)-*p*-tolylsulfinyl]ethylene (3b). The reaction was carried out as described above except using **2b** (711 mg, 1.37 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 80:20) to afford **3b** (455 mg, 92%). *E*/*Z* ratio was determined to be >98:2 by the ^{1}H NMR analysis of the crude product. mp 96−97 °C; $[\alpha]^{20}_D$ +263.4 (*c* 0.34 in acetone); ^{1}H NMR δ 0.68 (s, 3H), 2.41 (s, 3H), 6.70 (d, 1H, 17.7 Hz), 7.27−7.51 (m, 15H); IR (KBr) 2950, 1570, 1420, 1250, 1110, 1080, 1040, 970, 810, 790, 765, 730, 700 cm^{-1}; EIMS m/z (rel intensity) 223 (M^+-C_7H_7OS, 66), 197 (100), 165 (18). Found: C, 72.67; H, 5.85. Calcd for $C_{22}H_{22}OSSi$: C, 72.88; H, 6.12%.

(*E*)-1-[(*R*)-*p*-Tolylsulfinyl]-2-(triphenylsilyl)ethylene (3c). The reaction was carried out as described above except using **2c** (435 mg, 0.87 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 99:1) to afford **3c** (288 mg, 80%). *E*/*Z* ratio was determined to be >98:2 by the ^{1}H NMR analysis of the crude product. mp 140−142 °C; $[\alpha]^{25}_D$ +179.6 (*c* 0.48 in EtOH); ^{1}H NMR δ 2.41 (s, 3H), 6.74 (d, 1H, *J* = 17.5 Hz), 7.25−7.58 (m, 20H); IR (KBr) 3050, 1580, 1490, 1430, 1260, 1140, 1120, 1060, 970, 810, 780, 740, 710 cm^{-1}; EIMS *m*/*z* (rel intensity) 424 (M^+, 2), 398 (62), 284 (58), 259 (100), 207 (68), 140 (18). Found: C, 76.31; H, 5.76. Calcd for $C_{27}H_{24}OSSi$: C, 76.37; H, 5.70%.

(*E*)-1-[(*R*)-*tert*-Butylsulfinyl]-2-(trimethylsilyl)ethylene (3d). The reaction was carried out as described above except using **2d** (62 mg, 0.17 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 75:25) to afford **3d** (33 mg, 96%). *E*/*Z* ratio was determined to be >98:2 by the ^{1}H NMR analysis of the crude product. $[\alpha]^{26}_D$ +344.0 (*c* 0.29 in EtOH); ^{1}H NMR δ 0.14 (s, 9H), 1.20 (s, 9H), 6.60 (d, 1H, *J* = 18.0 Hz), 6.87 (d, 1H, *J* = 18.0 Hz); IR (neat) 2950, 1260, 1170, 1030, 980, 860, 840 cm^{-1}; EIMS *m*/*z* (rel intensity) 204 (M^+, 20), 189 (10), 105 (34), 73 (100). Found: C, 52.69; H, 9.72. Calcd for $C_9H_{20}OSSi$: C, 52.89; H, 9.86%.

Representative Procedure for the Reaction of Vinylsulfoxide with Aldehyde. (S_S,*S*)- and (S_S,*R*)-(*E*)-1-Phenyl-2-(*p*-tolylsulfinyl)-3-(trimethylsilyl)-2-propen-1-ol (4a). To a solution of diisopropylamine (0.069 mL, 0.49 mmol) in THF (0.50 mL) was added *n*-butyllithium (1.57 mol dm^{-3} in hexane, 0.31 mL, 0.49 mmol) at 0 °C, and the mixture was stirred for 30 min. The reaction mixture was cooled to −100 °C, and then a solution of **3a** (58.5 mg, 0.25 mmol) in THF (0.5 mL) was added dropwise over a period of 10 min. The mixture was stirred for an additional 10 min. Benzaldehyde (0.050 mL, 0.49 mmol) was then added, and the mixture was stirred for 20 min; the solution was quenched with saturated aqueous NH_4-Cl (3 mL) under vigorous stirring, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product which was purified by column chromatography (silica gel 10 g, hexane/ethyl acetate = 95:5) to give (S_S,*S*)-**4a** (33 mg, 40%) and (S_S,*R*)-**4a** (41 mg, 48%). (S_S,*S*)-**4a**: mp 124−125 °C; $[\alpha]^{27}_D$ +158.8 (*c* 0.37 in EtOH); ^{1}H NMR δ 0.15 (s, 9H), 2.35 (s, 3H), 2.93 (d, 1H, *J* = 5.2 Hz), 5.49 (d, 1H, *J* = 5.2 Hz), 6.70 (s, 1H), 7.10−7.38 (m, 9H); IR (KBr) 3300, 2950, 1600, 1490, 1440, 1390, 1320, 1250, 1180, 1080, 1030, 1000, 840, 800, 730, 690 cm^{-1}; EIMS *m*/*z* (rel intensity) 344 (M^+, 10), 204 (44), 189 (9), 140 (43), 73 (100). Found: C, 66.11; H, 7.14. Calcd for $C_{19}H_{24}O_2SSi$: C, 66.23; H, 7.02%. (S_S,*R*)-**4a**: mp 117−118 °C; $[\alpha]^{28}_D$ +192.8 (*c* 0.50 in EtOH); ^{1}H NMR δ 0.20 (s, 9H), 2.34 (s, 3H), 2.42 (d, 1H, *J* = 5.9 Hz), 5.82 (d, 1H, *J* = 5.9 Hz), 6.98 (s, 1H), 7.10−7.38 (m, 9H); IR (KBr) 3300, 3050, 2950, 1600, 1490, 1440, 1390, 1320, 1250, 1180, 1080, 1030, 1000, 840, 800, 780, 730, 690 cm^{-1}; EIMS *m*/*z* (rel intensity) 344 (M^+, 6), 204 (45), 140 (28), 73 (100). Found: C, 66.24; H, 7.13. Calcd for $C_{19}H_{24}O_2SSi$: C, 66.23; H, 7.02%.

(S_S,*S*)- and (S_S,*R*)-(*E*)-3-(*p*-Tolylsulfinyl)-4-(trimethylsilyl)-3-buten-2-ol (4b). The reaction was carried out as described above except using **3a** (60 mg, 0.25 mmol) and acetaldehyde (0.06 mL, 0.50 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 87:13) to afford (S_S,*S*)-**4b** (58 mg, 57%) and (S_S,*R*)-**4b** (21 mg, 25%). (S_S,*S*)-**4b**: $[\alpha]^{27}_D$ +195.9 (*c* 0.24 in acetone); ^{1}H NMR δ 0.20 (s, 9H), 1.06 (d, 3H, *J* = 6.6 Hz), 2.38 (s, 3H), 2.71 (d, 1H, *J* = 4.4 Hz), 4.64−4.70 (m, 1H), 6.54 (s, 1H), 7.25 (d, 2H, *J* = 7.9 Hz), 7.52 (d, 2H, *J* = 7.9 Hz); IR (neat) 3300, 2950, 1600, 1500, 1400, 1360, 1250, 1110, 950, 910, 850, 810, 730 cm^{-1}; EIMS *m*/*z* (rel intensity) 282 (M^+, 3), 140 (95), 73 (100). Anal. Calcd for $C_{14}H_{22}O_2SSi$: C, 59.53; H, 7.85. Found: C, 59.41; H, 7.95. (S_S,*R*)-**4b**: $[\alpha]^{20}_D$ +76.0 (*c* 0.50 in EtOH); ^{1}H NMR δ 0.22 (s, 9H), 1.34 (d, 3H, *J* = 6.7 Hz), 1.91 (d, 1H, *J* = 4.2 Hz), 2.37 (s, 3H), 4.79 (dq, 1H, *J* = 4.2, 6.7 Hz), 6.74 (s, 1H), 7.24 (d, 2H, *J* = 8.3 Hz), 7.52 (d, 2H, *J* = 8.3 Hz); IR (neat) 3300, 2950, 1600, 1500, 1400, 1360, 1250, 1110, 1030, 950, 910, 850, 810, 730 cm^{-1}; EIMS *m*/*z* (rel intensity) 282 (M^+, 3), 140 (90), 73 (100). Found: C, 59.41; H, 7.95. Calcd for $C_{14}H_{22}O_2SSi$: C, 59.53; H, 7.85%.

(S_S,*S*)- and (S_S,*R*)-(*E*)-2-(*p*-Tolylsulfinyl)-1-(trimethylsilyl)-1-octen-3-ol (4c). The reaction was carried out as described above except using **3a** (40 mg, 0.17 mmol) and hexanal (0.020 mL, 0.34 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 80:20) to afford (S_S,*S*)-**4c** (27 mg, 68%) and (S_S,*R*)-**4c** (12 mg, 25%). (S_S,*S*)-**4c**: $[\alpha]^{20}_D$ +100.7 (*c* 0.15 in acetone); ^{1}H NMR δ 0.19 (s, 9H), 0.82 (t, 3H, *J* = 6.5 Hz), 1.05−1.50 (m, 8H), 1.62 (br, 1H), 2.38 (s, 3H), 4.43 (br, 1H), 6.52 (s, 1H), 7.26 (d, 2H, *J* = 8.0 Hz), 7.51 (d, 2H, *J* = 8.0 Hz); IR (neat) 3350, 2920, 2850, 1590, 1490, 1450, 1240, 1080, 1030, 840, 800, 780, 760, 690 cm^{-1}; EIMS *m*/*z* (rel intensity) 212 (M^+-$C_8H_{14}O$, 9), 139 (45), 127 (100). Anal. Calcd for $C_{18}H_{30}O_2SSi$: C, 63.85; H, 8.93. Found: C, 63.63; H, 9.14. (S_S,*R*)-**4c**: $[\alpha]^{20}_D$ +78.5 (*c* 0.21 in acetone); δ 0.21 (s, 9H), 0.84 (t, 3H, *J* = 6.5 Hz), 1.05−1.60 (m, 8H), 1.75 (d, 1H, *J* = 4.9 Hz), 2.38 (s, 3H), 4.58 (dt, 1H, *J* = 4.9, 8.6 Hz), 6.77 (s, 1H), 7.25 (d, 2H, *J* = 8.0 Hz), 7.52 (d, 2H, *J* = 8.0 Hz); IR (neat) 3350, 2920, 2850, 1590, 1490, 1450, 1240, 1080, 1030, 840, 800, 780, 760, 690 cm^{-1}; EIMS *m*/*z* (rel intensity) 212 (M^+-$C_8H_{14}O$, 9), 139 (45), 127 (100). Found: C, 63.92; H, 8.72. Calcd for $C_{18}H_{30}O_2SSi$: C, 63.85; H, 8.93%.

(S_S,*S*)- and (S_S,*R*)-(*E*)-4-Methyl-2-(*p*-tolylsulfinyl)-1-(trimethylsilyl)-1-penten-3-ol (4d). The reaction was carried out as described above except using **3a** (61 mg, 0.27 mmol) and isobutyraldehyde (0.047 mL, 0.52 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, CH_2Cl_2/ethyl acetate = 99:1) to afford (S_S,*S*)-**4d** (50 mg, 47%) and (S_S,*R*)-**4d** (24 mg, 21%). (S_S,*S*)-**4d**: mp 122−123 °C; $[\alpha]^{24}_D$ +237.0 (*c* 0.29 in acetone); ^{1}H NMR δ 0.21 (s, 9H), 0.82 (d, 3H, *J* = 6.7 Hz), 0.97 (d, 3H, *J* = 6.7 Hz), 1.89−2.60 (m, 1H), 2.32 (d, 1H, *J* = 6.0 Hz), 2.40 (s, 3H), 3.89 (dd, 1H, *J* = 6.0, 7.2 Hz), 6.51 (s, 1H), 7.28 (d, 2H, *J* = 8.0 Hz), 7.53 (d, 2H, *J* = 8.0 Hz); IR (KBr) 3250, 2950, 1590, 1460, 1380, 1240, 1170, 1120, 1060, 1010, 1000, 920, 820, 810, 760, 740 cm^{-1}; EIMS *m*/*z* (rel intensity) 310 (M^+, 0.3), 212 (20), 140 (75), 73 (100). Found: C, 61.88; H, 8.42. Calcd for $C_{16}H_{26}O_2SSi$: C, 61.89; H, 8.44%. (S_S,*R*)-**4d**: mp 116−117 °C; $[\alpha]^{24}_D$ +131.0 (*c* 0.28 in acetone); ^{1}H NMR δ 0.21 (s, 9H), 0.79 (d, 3H, *J* = 6.8 Hz), 1.00 (d, 3H, *J* = 6.0 Hz), 1.50 (d, 1H, *J* = 6.0 Hz), 1.93−2.13 (m, 1H), 2.37 (s, 3H), 4.26 (dd, 1H, *J* = 6.0, 8.3 Hz), 6.88 (s, 1H), 7.25 (d, 2H, *J* = 8.0 Hz), 7.53 (d, 2H, *J* = 8.0 Hz); IR (KBr) 3250, 2950, 1590, 1460, 1380, 1240, 1170, 1120, 1060, 1010, 1000, 920, 820, 810, 760, 740 cm^{-1}; EIMS *m*/*z* (rel intensity) 310 (M^+, 1), 212 (20), 140 (75), 73 (100). Found: C, 61.88; H, 8.44. Calcd for $C_{16}H_{26}O_2SSi$: C, 61.89; H, 8.44%.

(S_S,*S*)- and (S_S,*R*)-(*E*)-4,4-Dimethyl-2-(*p*-tolylsulfinyl)-1-(trimethylsilyl)-1-penten-3-ol (4e). The reaction was carried out as described above except using **3a** (39 mg, 0.16 mmol) and 2,2-dimethylpropionaldehyde (0.035 mL, 0.32 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, CH_2Cl_2/ethyl acetate = 98:2) to afford (S_S,*S*)-**4e** (27 mg, 54%) and (S_S,*R*)-**4e** (8 mg, 17%). (S_S,*S*)-**4e**: mp 124−125 °C; $[\alpha]^{21}_D$ +205.7 (*c* 0.40 in acetone); ^{1}H NMR δ 0.19 (s, 9H), 1.02 (s, 9H), 2.39 (s, 3H), 2.52 (br, 1H), 3.86 (br, 1H), 6.53 (s, 1H), 7.27 (d, 2H, *J* = 8.3 Hz), 7.50 (d, 2H, *J* = 8.3 Hz); IR (KBr) 3200, 2950, 1590, 1460, 1380, 1360, 1290, 1245, 1180, 1060, 990, 890, 850, 810, 760 cm^{-1}; EIMS *m*/*z* (rel intensity) 324 (M^+, 0.5), 309 (0.4), 139 (95), 73 (100). Found: C, 63.07; H, 8.85. Calcd for $C_{17}H_{28}O_2SSi$: C, 62.91; H, 8.70%. (S_S,*R*)-**4e**: mp 95−96 °C; $[\alpha]^{24}_D$ +190.9 (*c* 0.15 in acetone); ^{1}H NMR δ 0.23 (s, 9H), 0.93 (d, 1H, *J* = 3.8 Hz), 1.05 (s, 9H), 2.37 (s, 3H), 4.50 (d, 1H, *J* = 3.6 Hz), 7.10 (s, 1H), 7.24 (d, 2H, *J* = 8.0 Hz), 7.54 (d, 2H, *J* = 8.0 Hz); IR (KBr) 3200, 2900, 1590, 1460, 1380, 1360, 1290, 1245, 1180, 1060, 990, 890, 850, 810, 760 cm^{-1}; EIMS *m*/*z* (rel intensity) 324 (M^+, 1), 309 (0.5), 139 (95), 73 (100). Found: C, 63.15; H, 8.94. Calcd for $C_{17}H_{28}O_2SSi$: C, 62.91; H, 8.70%.

(S_S,*S*)- and (S_S,*R*)-(*E*)-1-(Methyldiphenylsilyl)-2-(*p*-tolylsulfinyl)-1-octen-3-ol (4f). The reaction was carried out as described above except using **3b** (22 mg, 0.06 mmol) and hexanal (0.015 mL, 0.12 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, CH_2Cl_2/ethyl acetate = 99:1) to afford (S_S,*S*)-**4f** (15 mg, 53%) and (S_S,*R*)-**4f** (7 mg, 24%). (S_S,*S*)-**4f**: mp 112−113 °C; $[\alpha]^{18}_D$ +152.1 (*c* 0.15 in acetone); ^{1}H NMR δ 0.70 (s, 3H), 0.72−1.35 (m, 11H), 1.90 (d, 1H, *J* = 5.5 Hz), 2.34 (s, 3H), 4.10 (dt, 1H, *J* = 5.5, 6.8 Hz), 6.98 (s, 1H), 7.20−7.54 (m, 14H); IR (KBr) 3300, 2900, 1590, 1420, 1250, 1110, 1030, 910, 790, 730 cm^{-1}; EIMS *m*/*z* (rel intensity) 463 (M^+, 3), 444 (8), 265 (40), 197 (100). Found: C, 72.91; H, 7.25. Calcd for $C_{28}H_{34}O_2SSi$: C, 72.68; H, 7.41%. (S_S,*R*)-**4f**: $[\alpha]^{18}_D$ +93.6 (*c* 0.07 in acetone); ^{1}H NMR δ 0.70 (s, 3H), 0.72−1.65 (m, 11H), 1.27 (d, 1H, *J* = 8.0 Hz), 2.33 (s, 3H), 4.27 (dt, 1H, *J* = 4.8, 8.0 Hz), 7.10 (s, 1H), 7.18−7.52 (m, 14H); IR (neat) 3300, 2900, 1590, 1420, 1250, 1110, 1030, 910, 790, 730 cm^{-1}; EIMS *m*/*z* (rel intensity) 463 (M^+, 3), 444 (6), 265 (42), 197 (100). Found: C, 72.56; H, 7.52. Calcd for $C_{28}H_{34}O_2SSi$: C, 72.68; H, 7.41%.

(S_S,*S*)- and (S_S,*R*)-(*E*)-2-(*p*-Tolylsulfinyl)-1-(triphenylsilyl)-1-octen-3-ol (4g). The reaction was carried out as described above except using **3c** (113 mg, 0.27 mmol) and hexanal (0.065 mL, 0.54 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 90:10) to afford (S_S,*S*)-**4g** (65 mg, 46%) and (S_S,*R*)-**4g** (33 mg, 24%). (S_S,*S*)-**4g**: mp 120−121 °C; $[\alpha]^{23}_D$ +114.1 (*c* 0.16 in acetone); ^{1}H NMR δ 0.40−1.15 (m, 11H), 2.23 (d, 1H, *J* = 7.0 Hz), 2.41 (s, 3H), 4.12 (dt, 1H, *J* = 6.0, 7.0 Hz), 7.15 (s, 1H), 7.21−7.68 (m, 19H); IR (KBr) 3310, 3050, 2950, 2850, 1590, 1490, 1430, 1260, 1110, 910, 770, 730, 700 cm^{-1}; EIMS *m*/*z* (rel intensity) 524 (M^+, 0.5), 447 (3), 258 (38), 198 (100). Found: C, 75.81; H, 7.12. Calcd for $C_{33}H_{36}O_2SSi$: C, 75.53; H, 6.91%. (S_S,*R*)-**4g**: $[\alpha]^{23}_D$ +59.8 (*c* 0.08 in acetone); ^{1}H NMR δ 0.52−1.65 (m, 11H), 1.35 (br, 1H), 2.40 (s, 3H), 4.29 (t, 1H, *J* = 8.5 Hz), 7.21−7.64 (m, 20H); IR (neat) 3300, 3050, 2950, 2850, 1590, 1490, 1430, 1260, 1110, 910, 770, 730, 700 cm^{-1}; EIMS *m*/*z* (rel intensity) 524 (M^+, 0.4), 315 (22), 258 (42), 199 (100). Found: C, 75.68; H, 7.12. Calcd for $C_{33}H_{36}O_2SSi$: C, 75.53; H, 6.91%.

(S_S,*S*)- and (S_S,*R*)-(*E*)-4,4-Dimethyl-2-(*p*-Tolylsulfinyl)-1-(triphenylsilyl)-1-penten-3-ol (4h). The reaction was carried out as described above except using **3c** (47 mg, 0.11 mmol) and 2,2-dimethylpropionaldehyde (0.024 mL, 0.22 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 95:5) to afford (S_S,*S*)-**4h** (28 mg, 50%) and (S_S,*R*)-**4h** (14 mg, 24%). (S_S,*S*)-**4h**: ^{1}H NMR δ 0.72 (s, 9H), 2.48 (s, 3H), 2.88 (d, 1H, *J* = 7.7 Hz), 3.94 (d, 1H, *J* = 7.7 Hz), 7.08 (s, 1H), 7.25−7.69 (m, 19H); IR (neat) 3250, 2900, 1660, 1490, 1450, 1260, 1120, 1060, 970, 800 cm^{-1}; EIMS *m*/*z* (rel intensity) 510 (M^+, 0.5), 198 (100). Found: C, 75.39; H, 6.98. Calcd for $C_{32}H_{34}O_2SSi$: C, 75.25; H, 6.71%. (S_S,*R*)-**4h**: δ 1.07 (s, 9H), 1.84 (d, 1H, *J* = 6.0 Hz), 2.41 (s, 3H), 4.16 (d, 1H, *J* = 6.0 Hz), 7.20−7.65 (m, 20H); IR (neat) 3200, 2910, 1600, 1480, 1460, 1260, 1120, 1050, 970, 810 cm^{-1}; EIMS *m*/*z* (rel intensity) 510 (M^+, 0.5), 198 (100). Found: C, 75.51; H, 6.94. Calcd for $C_{32}H_{34}O_2SSi$: C, 75.25; H, 6.71%.

(S_S,*S*)- and (S_S,*R*)-(*E*)-2-(*tert*-Butylsulfinyl)-1-phenyl-3-(trimethylsilyl)-2-propen-1-ol (4i). The reaction was carried out as described above except using **3d** (31 mg, 0.15 mmol) and benzaldehyde (0.031 mL, 0.30 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 95:5) to afford (S_S,*S*)-**4i** (14 mg, 30%) and (S_S,*R*)-**4i** (28 mg, 58%). (S_S,*S*)-**4i**: ^{1}H NMR δ 0.12 (s, 9H), 1.18 (s, 9H), 2.97 (d, 1H, *J* = 5.5 Hz), 5.82 (d, 1H, *J* = 5.5 Hz), 6.59 (s, 1H), 7.27−7.42 (m, 5H); IR (KBr) 3250, 2950, 1660, 1450, 1360, 1250, 1170, 1060, 1010, 960, 850, 740, 700 cm^{-1}; EIMS *m*/*z* (rel intensity) 310 (M^+, 5), 178 (24), 105 (100). Found: C, 62.11; H, 8.21. Calcd for $C_{16}H_{26}O_2SSi$: C, 61.89; H, 8.44%. (S_S,*R*)-**4i**: δ 0.13 (s, 9H), 1.28 (s, 9H), 4.02 (d, 1H, *J* = 7.9 Hz), 5.56 (d, 1H, *J* = 7.9 Hz), 6.33 (s, 1H), 7.26−7.45 (m, 5H); IR (KBr) 3250, 2950, 1600, 1450, 1360, 1250, 1170, 1060, 1010, 960, 850, 740, 700 cm^{-1}; EIMS *m*/*z* (rel intensity) 310 (M^+, 4), 178 (18), 105 (95), 73 (100). Found: C, 61.62; H, 8.51. Calcd for $C_{16}H_{26}O_2SSi$: C, 61.89; H, 8.44%.

(S_S,*S*)- and (S_S,*R*)-(*E*)-2-(*tert*-Butylsulfinyl)-1-trimethylsilyl-1-octen-3-ol (4j). The reaction was carried out as described above except using **3d** (116 mg, 0.57 mmol) and hexanal (0.137 mL, 1.14 mmol). Usual workup gave the crude product which was purified by column chromatography (silica gel, hexane/ethyl acetate = 95:5) to afford (S_S,*S*)-**4j** (41 mg, 24%) and (S_S,*R*)-**4j** (101 mg, 58%). (S_S,*S*)-**4j**: $[\alpha]^{20}_D$ −10.6 (*c* 0.10 in acetone); ^{1}H NMR δ 0.19 (s, 9H), 0.88 (t, 3H, *J* = 6.5 Hz), 1.28 (s, 9H), 1.29−1.99 (m, 8H), *3*.53 (d, 1H, *J* = 8.3 Hz), 4.40 (dt, 1H, *J* = 3.1, 8.3 Hz), 5.95 (s, 1H); IR (neat) 3300, 2900, 1580, 1450, 1360, 1250, 1180, 1010, 910, 850, 730 cm^{-1}; EIMS *m*/*z* (rel intensity) 304 (M^+, 1), 248 (24), 127 (90), 73 (100). Found: C, 58.93; H, 10.45. Calcd for $C_{15}H_{32}O_2SSi$: C, 59.16; H, 10.59%. (S_S,*R*)-**4j**: $[\alpha]^{22}_D$ +52.0 (*c* 0.46 in acetone); ^{1}H NMR δ 0.22 (s, 9H), 0.90 (br, 3H), 1.24 (s, 9H), 1.20−1.80 (m, 8H), 1.95 (d, 1H, *J* = 4.8 Hz), 4.64 (dt, 1H, *J* = 4.8, 6.8 Hz), 6.34 (s, 1H); IR (neat) 3300, 2900, 1580, 1450, 1360, 1250, 1180, 1010, 910, 850, 730 cm^{-1}; EIMS *m*/*z* (rel intensity) 248 (M^+-C_4H_8, 18), 199 (8), 127 (90), 73 (100). Found: C, 59.21; H, 10.67. Calcd for $C_{15}H_{32}O_2SSi$: C, 59.16; H, 10.59%.

Representative Procedure for the Conversion of (*R*)-4a into the Propargylic Alcohols 5a and Allylic Alcohols 6a with Tetrabutylammonium Fluoride. To a solution of (*R*)-**4a** (13 mg, 0.037 mmol) in THF (2.6 mL) was added a THF solution of tetrabutylammonium fluoride (1.0 mol L^{-1}, 0.039 mL, 0.039 mmol), which had been dried over molecular sieves 4A, at room temperature, and the mixture was stirred for 5 min. THF was then evaporated under reduced pressure and the residue was purified by column chromatography (silica gel 3 g, hexane/ethyl acetate = 99:1) to give (*R*)-**5a** (1.4 mg, 28%) and (*R*)-**6a** (6.5 mg, 63%).

Representative Procedure for the Conversion of 4a into the Propargylic Alcohol 5a and Allylic Alcohols 6a with NaH. To a suspension of sodium hydride (19 mg, 0.48 mmol) in THF (0.5 mL) was added a (*S*)-**4a** (129 mg, 0.40 mmol) in THF (0.8 mL) at 0 °C, and the mixture was stirred for 30 min, the solution was quenched with saturated aqueous NH_4Cl (3 mL) under vigorous stirring and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude product which was purified by column chromatography (silica gel 11 g, hexane/ethyl acetate = 99:1) to give (*R*)-**5a** (41 mg, 83%) and (*S*)-**6a** (5.8 mg, 5%).

Representative Procedure for the Conversion of 4a into the Trimethylsilylpropargylic Alcohol 8a under Thermal Conditions. A solution of (*S*)-**4a** (100 mg, 0.29 mmol) in toluene (2.0 mL) was heated under reflux for 1 h. After the mixture was cooled, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel 12 g, hexane/ethyl acetate = 95:5) to give (*S*)-**8a** (52 mg, 87%).

(*R*)-1-Phenyl-2-propyn-1-ol [(*R*)-5a]. $[\alpha]^{21}_D$ −26.7 (*c* 1.5 in $CHCl_3$) lit.[23] $[\alpha]^{22}_D$ −27.1 (*c* 2.4 in $CHCl_3$); ^{1}H NMR δ 2.15 (d, 1H, *J* = 6.3 Hz), 2.65 (d, 1H, *J* = 2.2 Hz), 5.45 (dd, 1H, *J* = 2.2, 6.3 Hz), 7.30−7.60 (m, 5H); IR (neat) 3300, 3270, 2110 cm^{-1}. MTPA ester of (*R*)-**5a**: ^{1}H NMR δ 2.69 (d, 1H, *J* = 2.1 Hz), 3.46 (s, 3H), 6.63 (d, 1H, *J* = 2.2 Hz), 7.25−7.68 (m, 10H).

(*S*)-1-Phenyl-2-propyn-1-ol [(*S*)-5a]. $[\alpha]^{22}_D$ +26.1 (*c* 1.6 in $CHCl_3$). MTPA ester of (*S*)-**5a**: ^{1}H NMR δ 2.73 (d, 1H, *J* = 2.2 Hz), 3.59 (s, 3H), 6.63 (d, 1H, *J* = 2.3 Hz), 7.25−7.49 (m, 10H).

(*R*)-1-Octyn-3-ol [(*R*)-5c]. $[\alpha]^{22}_D$ +20.5 (*c* 1.65 in Et_2O) lit.[1k] $[\alpha]^{21}_D$ −18.8 (*c* 1.30 in Et_2O) for (*S*)-isomer (84% ee); ^{1}H NMR δ 0.88−1.78 (m, 11H), 1.88 (d, 1H, *J* = 1.9 Hz), 2.45 (d, 1H, *J* = 1.9 Hz), 4.30−4.41 (br, 1H); IR (neat) 3400, 3350, 2950, 1040, 650 cm^{-1}. MTPA ester of (*R*)-**5c**: ^{1}H NMR δ 0.78−1.85 (m, 11H), 2.53 (d, 1H, *J* = 2.3 Hz), 3.60 (s, 3H), 5.54 (dt, 1H, *J* = 2.3, 6.5 Hz), 7.31−7.60 (m, 5H).

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(*S*)-1-Octyn-3-ol [(*S*)-5c]. $[\alpha]^{22}_D$ −19.2 (*c* 1.50 in Et_2O). MTPA ester of (*S*)-**5c**: ^{1}H NMR δ 0.80−1.90 (m, 11H), 2.47 (d, 1H, *J* = 2.7 Hz), 3.54 (s, 3H), 5.50 (dt, 1H, *J* = 2.2, 6.7 Hz), 7.32−7.56 (m, 5H).

(S_S,*S*)-1-Phenyl-2-(*p*-tolylsulfinyl)-2-propen-1-ol [(*S*)-6a]. mp 129−130 °C; $[\alpha]^{21}_D$ +104.7 (*c* 0.48 in acetone); ^{1}H NMR δ 2.45 (s, 3H), 3.78 (d, 1H, *J* = 2.7 Hz), 5.30 (d, 1H, *J* = 2.7 Hz), 5.49 (s, 1H), 6.07 (s, 1H), 7.08−7.58 (m, 9H); IR (KBr) 3350, 2920, 2850, 1620, 1590, 1490, 1450, 1280, 1080, 1060, 1020, 920, 900, 840, 910, 760, 700 cm^{-1}; EIMS *m*/*z* (rel intensity) 272 (M^+, 1), 140 (95), 133 (100), 92 (58). Found: C, 70.48; H, 6.00. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92%.

(S_S,*R*)-1-Phenyl-2-(*p*-tolylsulfinyl)-2-propen-1-ol [(*R*)-6a]. $[\alpha]^{24}_D$ +205.7 (*c* 0.60 in acetone); ^{1}H NMR δ 2.43 (s, 3H), 3.12 (d, 1H, *J* = 5.0 Hz), 5.17 (d, 1H, *J* = 5.0 Hz), 5.40 (s, 1H), 6.04 (s, 1H), 7.17−7.30 (m, 7H), 7.58 (d, 2H, *J* = 6.5 Hz); IR (KBr) 3400, 2900, 1890, 1630, 1590, 1490, 1450, 1360, 1310, 1280, 1240, 1200, 1180, 1140, 1080, 1030, 1020, 950, 910, 840, 820, 770, 700 cm^{-1}; EIMS *m*/*z* (rel intensity) 272 (M^+, 15), 133 (100). Found: C, 70.58; H, 6.13. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92%.

(S_S,*S*)-2-(*p*-Tolylsulfinyl)-1-octen-3-ol [(*S*)-6c]. ^{1}H NMR δ 0.78−1.74 (m, 11H), 1.80−2.10 (br, 1H), 2.40 (s, 3H), 4.15 (t, 1H, *J* = 6.2 Hz), 5.84 (s, 1H), 6.06 (s, 1H), 7.29 (d, 2H, *J* = 8.2 Hz), 7.56 (d, 2H, *J* = 8.2 Hz); IR (neat) 3350, 2950, 1080, 1040, 780 cm^{-1}.

(S_S,*R*)-2-(*p*-Tolylsulfinyl)-1-octen-3-ol [(*R*)-6c]. $[\alpha]^{21}_D$ +134.9 (*c* 0.17 in acetone); ^{1}H NMR δ 0.80−1.65 (m, 11H), 2.39 (s, 3H), 2.86 (d, 1H, *J* = 3.4 Hz), 4.08−4.20 (m, 1H), 5.84 (s, 1H), 6.03 (s, 1H), 7.29 (d, 2H, *J* = 7.8 Hz), 7.56 (d, 2H, *J* = 7.8 Hz); IR (neat) 3400, 2950, 1080, 1040, 940, 780 cm^{-1}; EIMS *m*/*z* (rel intensity) 266 (M^+, 16), 249 (28), 140 (100). Anal. Calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32. Found: C, 67.75; H, 8.52.

(S_S,*R*)-2-(*tert*-Butylsulfinyl)-1-octen-3-ol [(*R*)-6j]. ^{1}H NMR δ 0.65−1.80 (m, 11H), 1.24 (s, 9H), 3.30 (d, 1H, *J* = 3.8 Hz), 4.40−4.50 (m, 1H), 5.63 (d, 1H, *J* = 1.1 Hz), 5.87 (d, 1H, *J* = 1.1 Hz); IR (neat) 3400, 3000, 1470, 1380, 1180, 1030, 940, 740 cm^{-1}; EIMS *m*/*z* (rel intensity) 176 (M^+-C_4H_8, 38), 158 (40), 57 (100). Anal. Calcd for $C_{12}H_{24}O_2S$: C, 62.02; H, 10.41. Found: C, 62.21; H, 10.34.

(*S*)-1-Phenyl-3-trimethylsilyl-2-propyn-1-ol [(*S*)-8a]. $[\alpha]^{21}_D$ −20.4 (*c* 1.05 in $CHCl_3$) lit.[3b] $[\alpha]^{25}_D$ +10.3 (*c* 3.39 in $CHCl_3$) for (*R*)-isomer (21% ee); ^{1}H NMR δ 0.21 (s, 9H), 2.18 (d, 1H, *J* = 7.1 Hz), 5.47 (d, 1H, *J* = 7.1 Hz), 7.31−7.61 (m, 5H); IR (neat) 3300, 2950, 2160, 1490, 1450, 1250, 1040, 980, 840, 760, 700 cm^{-1}. Anal. Calcd for $C_{12}H_{16}OSi$: C, 62.02; H, 10.41. Found: C, 62.21; H, 10.34. MTPA ester of (*S*)-**8a**: ^{1}H NMR δ 0.18 (s, 9H), 3.47 (s, 3H), 6.64 (s, 1H), 7.30−7.58 (m, 10H).

(*R*)-1-Phenyl-3-trimethylsilyl-2-propyn-1-ol [(*R*)-8a]. $[\alpha]^{21}_D$ +21.0 (*c* 1.11 in $CHCl_3$). MTPA ester of (*R*)-**8a**: ^{1}H NMR δ 0.20 (s, 9H), 3.60 (s, 3H), 6.66 (s, 1H), 7.28−7.52 (m, 10H).

(*S*)-4-Trimethylsilyl-3-butyn-2-ol [(*S*)-8b]. $[\alpha]^{22}_D$ −23.9 (*c* 0.64 in $CHCl_3$) lit.[24] $[\alpha]^{22}_D$ −25.9 (*c* 3.12 in $CHCl_3$); ^{1}H NMR δ 0.18 (s, 9H), 1.46 (d, 3H, *J* = 6.7 Hz), 1.87 (d, 1H, *J* = 5.2 Hz), 4.53 (dq, 1H, *J* = 5.2, 6.7 Hz); IR (neat) 3320, 2960, 2170, 1420, 1370, 1320, 1250, 1120, 1080, 1040, 940, 860, 840, 760 cm^{-1}. MTPA ester of (*S*)-**8b**: ^{1}H NMR δ 0.15 (s, 9H), 1.57 (d, 3H, *J* = 6.8 Hz), 3.56 (s, 3H), 5.63 (q, 1H, *J* = 6.8 Hz), 7.38−7.50 (m, 5H).

(*R*)-4-Trimethylsilyl-3-butyn-2-ol [(*R*)-8b]. $[\alpha]^{22}_D$ +24.7 (*c* 0.34 in $CHCl_3$). MTPA ester of (*R*)-**8b**: ^{1}H NMR δ 0.15 (s, 9H), 1.57 (d, 3H, *J* = 6.8 Hz), 3.56 (s, 3H), 5.63 (q, 1H, *J* = 6.8 Hz), 7.38−7.50 (m, 5H).

(*S*)-1-Trimethylsilyl-1-octyn-3-ol [(*S*)-8c]. $[\alpha]^{21}_D$ −14.3 (*c* 0.95 in $CHCl_3$); ^{1}H NMR δ 0.16 (s, 9H), 0.88 (t, 3H, *J* = 6.6 Hz), 1.20−1.75 (m, 8H), 1.76 (d, 1H, *J* = 5.6 Hz), 4.34 (dt, 1H, *J* = 5.6, 6.5 Hz); IR (neat) 3300, 2950, 2200, 1450, 1250, 1120, 1030, 840, 760 cm^{-1}; EIMS *m*/*z* (rel intensity) 183 (M^+-CH_3, 38), 125 (57), 73 (100). Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.49; H, 11.06. MTPA ester of (*S*)-**8c**: ^{1}H NMR δ 0.15 (s, 9H), 0.82−1.80 (m, 11H), 3.56 (s, 3H), 5.50 (t, 1H, *J* = 6.8 Hz), 7.35−7.60 (m, 5H).

(*R*)-1-Trimethylsilyl-1-octyn-3-ol [(*R*)-8c]. $[\alpha]^{21}_D$ +13.6 (*c* 1.10 in $CHCl_3$). MTPA ester of (*R*)-**8c**: ^{1}H NMR δ 0.14 (s, 9H), 0.80−1.80 (m, 11H), 3.59 (s, 3H), 5.53 (t, 1H, *J* = 6.7 Hz), 7.35−7.60 (m, 5H).

Supporting Information Available: Calculation results of **9** and **10**. The NPA and the NBO analyses of the stabilizing effects of the silicon in transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0157223

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