

Regiochemically and Stereochemically Defined Synthesis of Allylsilanes

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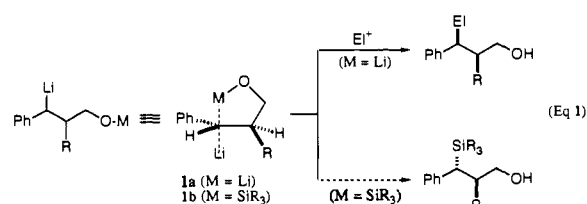
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Abstract: Allyl sulfides containing a siloxy or hydroxy group at appropriate positions were successfully converted by two methods into two types of allylsilanes with almost complete stereo- and regiocontrol. In one method, an allyllithium was generated from the siloxy compound after which the silyl group migrated from oxygen to the carbanionic site. The reaction of 4-[[trimethylsilyloxy]methyl]-3-methyl-2-cyclohexenyl phenyl sulfide with lithium di-*tert*-butylbiphenylide (LDBB) led to an exclusive formation of (1*R**,2*R**)-2-methyl-2-(trimethylsilyl)-3-cyclohexene-1-methanol. The second method involved the silylation of an oxyanion–carbanion. Using this method, (1*R**,4*R**)-1-methyl-4-(trimethylsilyl)-2-cyclohexene-1-methanol was obtained by treating its lithium alkoxide with LDBB followed by silylation with chlorotrimethylsilane.

The stereochemical outcome of several organic transformations using organosilicon compounds depends on the stereochemistry of organosilicon reactants.¹ Nevertheless, few reports have described the stereochemically defined synthesis of carbon–silicon bonds.² The most commonly used method for preparing organosilicon compounds involves silylation of the corresponding carbanionic species which are rapidly epimerizable under usual reaction conditions.³ Silylation of allylanionic species⁴ has also been widely employed for the preparation of synthetically useful allylsilanes, but that method usually results in the formation of stereo- and regioisomeric mixtures.

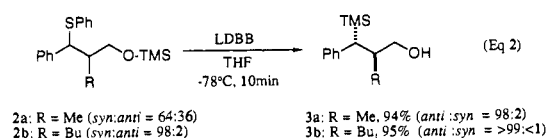
In the previous paper, we described stereoselective carbon–carbon bond formation using dilithiated species as reactants.⁵ This remarkable property may be attributable to the formation of a cyclic dilithiated species⁶ in which the steric repulsion between the phenyl and the alkyl group favors **1a**. Such a dilithiated species would selectively react with electrophiles from the opposite site of the O–Li substituent (eq 1).



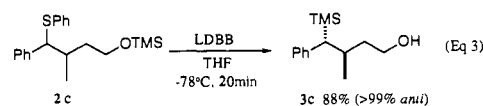
On the basis of the facile migratory aptitude of the silyl group⁷ and the stereoselective reactivity of the dilithiated species,⁸ we assumed that silylated alkanols could be prepared with high selectivity *via* a pentavalent silicon species, **1b**, as shown in eq 1.

Results and Discussion

We attempted to generate lithiated species from the corresponding sulfides using lithium di-*tert*-butylbiphenylide (LDBB).⁹ Expecting general applicability, 2-substituted 3-phenyl-3-(phenylthio)alkyl silyl ethers **2** were treated with LDBB at –78 °C. The corresponding 3-silylated alcohols **3** were formed in good yield. As expected from **1b**, the reaction proceeded with high *anti* selectivity (eq 2). The configuration of **3b** was



determined by the stereochemically defined elimination reaction of 2-silyl alkanol as shown in Scheme I. Interestingly, 1,5-migration could also be achieved with high diastereoselectivity (eq 3).¹⁰



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(10) The stereochemistry of **3c** was determined by comparison with the authentic sample prepared from **3a**.

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(1) (a) Fleming, I. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1992; Vol. 2, pp 563–593. (b) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React. (NY)* **1989**, *37*, 57. (c) Colvin, E. *Silicon Reagents in Organic Synthesis*; Academic Press, London, 1988. (d) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer Verlag, Berlin, 1983. (e) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981. On stereoselective conversion of the C–Si bond to the C–OH bond; see: Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983.

(2) (a) Sparks, M. A.; Panek, J. S. *J. Org. Chem.* **1991**, *56*, 3431. (b) Panek, J. S.; Yang, M. *J. Am. Chem. Soc.* **1991**, *113*, 6594. (c) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090. (d) Bernhard, W.; Fleming, I.; Waterson, D. *J. Chem. Soc., Chem. Commun.* **1984**, 28.

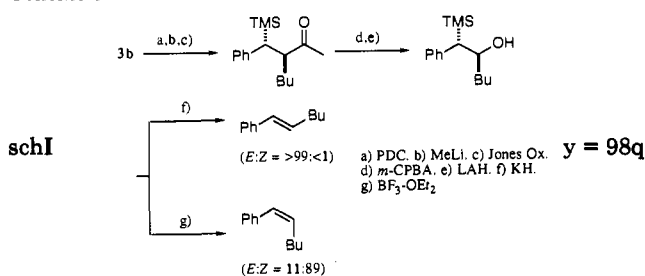
(3) For the effects of heteroatoms to retain the configuration of allyllithium species, see: (a) Hoffmann, R. W.; Bewersdorf, M. *Tetrahedron Lett.* **1990**, *31*, 67. (b) Cong, J. M.; Mar, E. K. *Ibid.* **1990**, *31*, 1981. Chan, P. C.-M.; Chong, J. M. *Ibid.* **1990**, *31*, 1985. (c) Tanaka, K.; Minami, K.; Funaki, I.; Suzuki, H. *Ibid.* **1990**, *31*, 2727. (d) Reich, H. J.; Bowe, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 8004. (e) Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152. Cohen, T.; Lin, M.-T. *J. Am. Chem. Soc.* **1984**, *106*, 1130. (f) Rychnovsky, S. D.; Mickus, D. E. *Tetrahedron Lett.* **1989**, *30*, 3011. (g) McDougal, P. G.; Condon, B. D.; Laffosse, M. D., Jr.; Lauro, A. M.; VanDerveer, D. *Ibid.* **1988**, *29*, 2547. (h) Beak, P.; Hunter, J. E.; Jun, Y. M.; Wallin, A. P. *J. Am. Chem. Soc.* **1987**, *109*, 5403.

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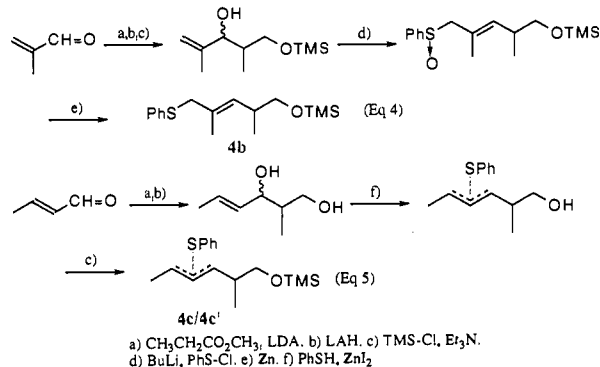
(5) Kato, T.; Marumoto, S.; Sato, T.; Kuwajima, I. *Synlett.* **1990**, 671.

(6) Benzylpotassium has been proven to have an sp²-like configuration; see: Peoples, P. R.; Grutzner, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 4709. In a species such as **1**, assumption of an sp² configuration coordinated by two metal species accounts for the characteristic feature of this species.

Scheme I



Next, we attempted to extend the silyl transfer to the preparation of synthetically useful allylsilanes. The requisite allyl sulfides were prepared by either of the following methods. In one method, sulfenylation of siloxy-substituted allylic alcohols followed by sigmatropic rearrangement¹¹ produced allyl sulfides which were reduced with zinc.¹² In the other method, allylic alcohols were treated with benzenethiol in the presence of ZnI_2 .¹³ The latter procedure often produces regioisomeric mixtures, but we used the resulting allyl sulfides as substrates without separation. Typical examples are shown in eqs 4 and 5. The [4 +



2]-cycloaddition of 1-(phenylthio)butadiene derivatives was used for the preparation of six-membered ring substrates.

Acyclic as well as cyclic allyl sulfides were converted to the corresponding allylsilanes in good yield on exposure to LDBB at low reaction temperature. Further, the allylsilanes thus obtained were proven to be regio- and stereochemically pure in most cases. The results are shown in Table I. Migratory aptitude is highly dependent on the bulk of the substituent on the silicon. As shown in entry 5, the trimethylsilyl group exhibits the highest migratory tendency, whereas the triisopropylsilyl group did not migrate to the carbanionic center under the present reaction conditions.

From a synthetic viewpoint, the following characteristic features attract much attention. (1) 1,4-Silyl group migration to give 3-silylated 4-alkenols **5** was observed both for 1-(silyloxy)-5-(phenylthio) 3-enes and for 1-(silyloxy)-3-(phenylthio) 4-enes. (2) The reactions of cyclic substrates **4d** and **4d'** as well as the acyclic substrate **4b** that included a methylallyl substituent proceeded with excellent regio- and stereoselectivities to afford the corresponding allylsilanes as single isomers (Table I). (3) The *cis*-substituted products **5d-n** were obtained exclusively in reactions of cyclic derivatives **4d-n**. (4) Use of optically active substrates allowed us to prepare the corresponding optically active allylsilanes. Thus, **4b**-(2*S*)^{14,15} (92% ee) gave **5b** (2*R*,3*R*)¹⁶ in 88% yield without any decrease of enantiomeric excess. (5) As shown in entry 7 of Table I, the migratory aptitudes of trimethylsilyl and triisopropylsilyl differ markedly.

Stereochemistries of **5a**, **5e**, **5g**, and **5l** were determined. Claisen-Ireland rearrangement^{2a,b,17} of 3-silylallyl propionate

(11) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

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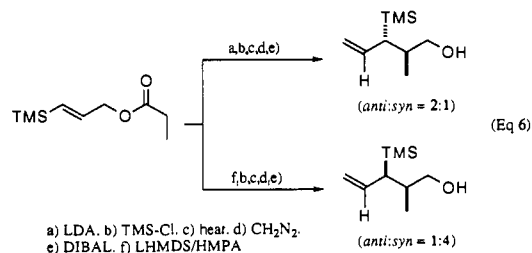
(14) The optically active **4b**-(2*S*) was prepared from (*R*)-(-)-methyl 3-hydroxy-2-methylpropionate. See the supplementary material.

Table I. Stereochemically and Regiochemically Defined Preparation of Allylsilanes, Migration of a Silyl Group

entry	starting material	product	yield ^a (%) (diastereomeric ratio)
1	 4a (R = H) 4b (R = Me)	 5a (R = H) 80 ^b (96:4) 5b (R = Me) 97 (>99:<1)	88 (98:2) (<i>E:Z</i> = 76:24)
2	 4c 4c'	 5c	82 (>99:<1)
3	 4d 4d'	 5d	82 (>99:<1)
4	 4e (R = H) 4f (R = Me)	 5e (R = H) 93 ^b (>99:<1) 5f (R = Me) 99 (>99:<1)	
5	 4g (R = Me) 4h (R = Et) 4i (R = <i>i</i> Pr) 4j (R = <i>i</i> Pr)	 5g (R = Me) 83 ^b (>99:<1) 5h (R = Et) 70 (>99:<1) 5i (R = <i>i</i> Pr) 49 (>99:<1) 5j (R = <i>i</i> Pr) 0	
6	 4k	 5k	99 (>99:<1)
7	 4l (R = H) 4m (R = Me)	 5l (R = H) 95 ^b (>99:<1) 5m (R = Me) 89 (>99:<1)	
8	 4n	 5n	89 (>99:<1)

^a Isolated yield. ^b For structure determination, see the text.

followed by DIBAL reduction gave the authentic sample of **5a** as a mixture of *syn* and *anti* isomers (eq 6). The products **5e** and



5l were confirmed by ¹H NMR coupling constants or NOE of

(15) The enantiomeric excess of the starting material was determined as follows. Desulfurization with Raney nickel followed by hydrogenation of the parent alcohol gave 2,4-dimethyl-1-pentanol which was then converted to the (*R*)-MTPA ester. ¹H NMR signals of the $\text{CH}_2\text{-O}$ group of each (*R*)-MTPA ester appear as follows. (2*S*): 4.12 (dd, *J* = 10.6 Hz, 5.8 Hz, 1H), 4.17 (dd, *J* = 10.6 Hz, 5.8 Hz, 1H). (2*R*): 4.06 (dd, *J* = 10.6 Hz, 6.8 Hz, 1H), and 4.23 (dd, *J* = 10.6 Hz, 5.4 Hz, 1H). Comparison of the integral ratio showed it to be 92% ee (*S*).

(16) The enantiomeric excess of the product was determined by comparison of the integral ratio of $\text{CH}_2\text{-O}$ signals of (2*R*,3*R*) and (2*S*,3*S*) of each (*R*)-MTPA ester. ¹H NMR signals of the $\text{CH}_2\text{-O}$ group of each (*R*)-MTPA ester appear as follows. (2*R*,3*R*): 4.10 (dd, *J* = 10.8 Hz, 7.0 Hz, 1H), 4.38 (dd, *J* = 10.8 Hz, 4.6 Hz, 1H). (2*S*,3*S*): 3.97 (dd, *J* = 10.4 Hz, 7.4 Hz, 1H), 4.51 (dd, *J* = 10.4 Hz, 4.6 Hz, 1H).

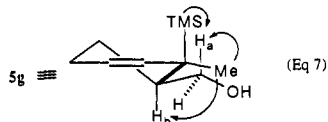
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Table II. Stereochemically and Regiochemically Defined Preparation of Allylsilanes, Silylation of Dilithiated Species

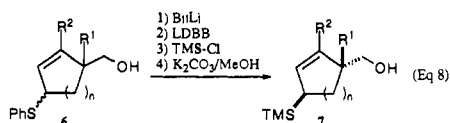
entry	starting material	product	yield ^a (%) (diastereomeric ratio)
1			75 (7a:7a' = 75:23) ^b
2			53 (>99:<1)
3			83 (>99:<1)
4			7d (R = H) 62 ^c (>99:<1)
			7e (R = Me) 82 (>99:<1)
5			7f (R = H) 77 ^c (99:1)
			7g (R = Me) 90 (99:1)

^a Isolated yield. ^b Other isomers (2%) were also formed. ^c For structure determination, see the text.

each hydrogenation product.¹⁸ NOE of **5g** indicated that it has an axial TMS and an equatorial hydroxymethyl group (eq 7).



For the preparation of other allylsilanes, silylation of the dilithiated species was also attempted. Alcohol **6** was treated with butyllithium and then with lithium di-*tert*-butylbiphenylide at $-78\text{ }^{\circ}\text{C}$. The reaction was quenched with chlorotrimethylsilane. After removal of the silyl group from oxygen, the resulting alcohols **7** were isolated by column chromatography. Applying this silylation procedure to the simple cyclohexyl derivative **6a** gave a mixture of two regioisomers **7a** and **7a'**. But introduction of substituent, especially at the 1- or 2-position, enhanced both regio- and stereoselectivities to yield a single product in each case. As shown in Table II, the hydroxy group greatly influences the regio- and stereochemical outcome with an almost single product yielded in each case.



The following two features of this silylation procedure are of potential value. (1) Selective silylation takes place on the allylic site remote from the alcohol moiety. (2) Selective silylation occurs at the *anti* face of the hydroxymethyl group. Thus, one can prepare two types of allylsilanes with almost complete selectivity. (Compare **5g**, **5l**, and **5n** with **7c**, **7f**, and **7e**, respectively.) Stereochemistries of **7d** and **7f** were confirmed by NOE of their hydrogenation products.¹⁸

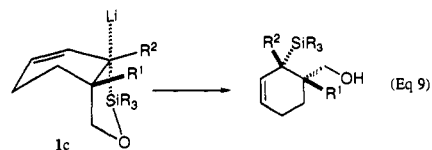
Conclusion

It has been reported that benzylic potassium has an sp^2 -like configuration.⁵ To explain the results obtained above, we propose

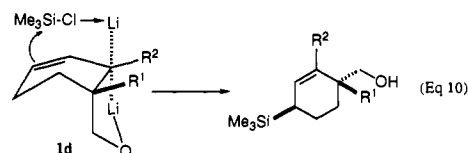
(18) On details, see the supplementary material.

that benzyl- and allyllithiums containing metal alkoxide moieties on appropriate positions have sp^2 -like configurations shown in **1a-d**. Utilizing these oxygen functional substituents as directing groups, regio- and stereochemically pure allylsilanes were prepared from **2**, **4**, and **6** as described above.

In the case of a cyclic substrate having a siloxy group, axial-oriented $\text{CH}_2\text{-OTMS}$ coordinates with allyllithium to form **1c**, through which the silyl group migrates from oxygen to carbon to produce the cyclic allylsilane **5**, *cis*-substituted by the silyl and the hydroxymethyl group (eq 9). Similarly, treatment of the



lithium alkoxide with LDBB generates the dilithiated species **1d**, which reacts with chlorosilane at the opposite face of OLi. Steric hindrance around the OLi moiety may favor a *syn*- Se_1 process to yield the *trans*-substituted allylsilanes **7** (eq 10). Thus, the present



procedures broaden the synthetic utilities of allylsilane by providing a valuable platform for further stereoselective transformations.

Experimental Section

General. ¹H NMR spectra were taken on a JEOL GSX-270 (270 MHz) and are reported in parts per million from internal tetramethylsilane. IR spectra were recorded on a JACSO IR-810 spectrometer. GLC analysis was performed on a Shimadzu GC-14A instrument equipped with a Nihon Chromato capillary column OV-1 (0.25 mm \times 25 m) or PEG-20M (0.25 mm \times 25 m) using nitrogen as the carrier gas. The area of a peak was calculated automatically by Chromatopack Shimadzu CR-6A. Microanalyses were performed on a Perkin-Elmer 2400 or a Yanaco MT-3 instrument. All reactions were performed under a nitrogen atmosphere.

Preparation of 3 and 5. To a lithium dispersion (1 mmol) suspended in THF (1 mL) was added a THF (2 mL) solution of 4,4'-di-*tert*-butylbiphenyl (0.240 g, 0.9 mmol) at $0\text{ }^{\circ}\text{C}$, and the solution was stirred for 3 h. To the resulting LDBB solution was added the silyl ether **2** or **4** (0.3 mmol) at $-78\text{ }^{\circ}\text{C}$. After the solution was stirred for 0.5–1 h at $-78\text{ }^{\circ}\text{C}$, the reaction was quenched with saturated aqueous NaHCO_3 . Usual workup followed by separation with silica gel column chromatography gave the corresponding allylsilane **3** or **5**. The spectral and analytical data of **3** and **5** are as follows.

(2R*,3R*)-2-Methyl-3-phenyl-3-(trimethylsilyl)-1-propanol (3a): IR 3330, 2950, 2880, 1600, 1490, 1450, 1240, 1030, 860, 840, 750, 700 cm^{-1} ; ¹H NMR (CDCl_3) δ -0.04 (s, 9 H), 0.90 (d, $J = 6.2$ Hz, 3 H), 1.39 (br s, 1 H), 2.07 (d, $J = 8.0$ Hz, 1 H), 2.1–2.3 (m, 1 H), 3.43 (dd, $J = 10.2$ Hz, 6.0 Hz, 1 H), 3.60 (dd, $J = 10.2$ Hz, 5.4 Hz, 1 H), 6.9–7.3 (m, 5 H). Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{OSi}$: C, 70.21; H, 9.97. Found: C, 70.49; H, 9.70.

(R*)-2-[(R*)-Phenyl(trimethylsilyl)methyl]-1-hexanol (3b): IR 3350, 2950, 1600, 1490, 1450, 1250, 1040, 860, 830, 700 cm^{-1} ; ¹H NMR (CDCl_3) δ 0.00 (s, 9 H), 0.85 (t, $J = 6.0$ Hz, 3 H), 1.1–1.7 (m, 7 H), 2.0–2.2 (m, 1 H), 2.27 (d, $J = 8.9$ Hz, 1 H), 3.6–3.8 (m, 2 H), 7.0–7.4 (m, 5 H). Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{OSi}$: C, 72.66; H, 10.67. Found: C, 72.96; H, 10.97.

(3R*,4R*)-3-Methyl-4-phenyl-4-(trimethylsilyl)-1-butanol (3c): IR 3330, 2950, 1600, 1490, 1450, 1250, 1050, 840, 700 cm^{-1} ; ¹H NMR (CDCl_3) δ -0.04 (s, 9 H), 0.85 (d, $J = 6.6$ Hz, 3 H), 1.2–1.4 (m, 1 H), 1.5–1.7 (m, 1 H), 1.7–1.9 (m, 1 H), 1.90 (d, $J = 8.2$ Hz, 1 H), 2.1–2.3 (m, 1 H), 3.6–3.8 (m, 2 H), 6.9–7.3 (m, 5 H). Anal. Calcd for $\text{C}_{14}\text{H}_{24}\text{OSi}$: C, 71.12; H, 10.23. Found: C, 71.32; H, 9.93.

(2R*,3S*)-2-Methyl-3-(trimethylsilyl)-4-penten-1-ol (5a): IR 3320, 2950, 1620, 1460, 1410, 1380, 1240, 1030, 900, 860, 830 cm^{-1} ; ¹H NMR

(CDCl₃) δ 0.02 (s, 9 H), 0.95 (d, $J = 7.0$ Hz, 3 H), 1.5–1.7 (m, 1 H), 1.81 (dd, $J = 11.0$ Hz, 3.4 Hz, 1 H), 1.8–2.0 (m, 1 H), 3.41 (dd, $J = 10.0$ Hz, 6.4 Hz, 1 H), 3.46 (dd, $J = 10.0$ Hz, 7.2 Hz, 1 H), 4.8–5.0 (m, 2 H), 5.77 (dt, $J = 16.6$ Hz, 10.2 Hz, 1 H). Anal. Calcd for C₉H₂₀OSi: C, 62.72; H, 11.70. Found: C, 62.87; H, 11.92.

(2*R**,3*R**)-2,4-Dimethyl-3-(trimethylsilyl)-4-penten-1-ol (**5b**): IR 3320, 2950, 1630, 1450, 1370, 1250, 1030, 870, 830 cm⁻¹; ¹H NMR (CDCl₃) δ 0.11 (s, 9 H), 0.99 (d, $J = 6.4$ Hz, 3 H), 1.39 (br s, 1 H), 1.48 (d, $J = 9.8$ Hz, 1 H), 1.68 (s, 3 H), 1.8–2.1 (m, 1 H), 3.42 (dd, $J = 10.2$ Hz, 7.2 Hz, 1 H), 3.72 (dd, $J = 10.2$ Hz, 4.6 Hz, 1 H), 4.56 (s, 1 H), 4.73 (s, 1 H). Anal. Calcd for C₁₀H₂₂O₂Si: C, 64.45; H, 11.90. Found: C, 64.68; H, 12.18.

(*E*)- and (*Z*)-(2*R**,3*S**)-2-Methyl-3-(trimethylsilyl)-4-hexen-1-ol (**5c-E** and **5c-Z**): IR 3330, 2950, 2920, 1460, 1380, 1250, 1030, 860, 830 cm⁻¹; ¹H NMR (CDCl₃) (**5c-E**) δ -0.01 (s, 9 H), 0.92 (d, $J = 7.0$ Hz, 3 H), 1.66 (d, $J = 4.8$ Hz, 3 H), 1.71 (dd, $J = 6.8$ Hz, 3.0 Hz, 1 H), 1.8–2.0 (m, 2 H), 3.3–3.5 (m, 2 H), 5.2–5.6 (m, 2 H); (**5c-Z**) δ 0.01 (s, 9 H), 0.94 (d, $J = 6.8$ Hz, 3 H), 1.59 (d, $J = 6.0$ Hz, 3 H), 1.8–2.0 (m, 2 H), 2.14 (dd, $J = 10.0$ Hz, 2.8 Hz, 1 H), 3.3–3.5 (m, 1 H), 3.60 (dd, $J = 10.8$ Hz, 4.4 Hz, 1 H), 5.2–5.6 (m, 2 H).

(1*R**,2*R**)-2-(Trimethylsilyl)-3-cyclopentene-1-methanol (**5d**): IR 3330, 2950, 1250, 1020, 830, 710 cm⁻¹; ¹H NMR (CDCl₃) δ 0.02 (s, 9 H), 1.52 (br s, 1 H), 2.03 (d, $J = 9.7$ Hz, 1 H), 2.0–2.2 (m, 1 H), 2.4–2.6 (m, 1 H), 2.6–2.8 (m, 1 H), 3.68 (dd, $J = 10.2$ Hz, 8.8 Hz, 1 H), 3.85 (dd, $J = 10.2$ Hz, 6.2 Hz, 1 H), 5.6–5.7 (m, 1 H), 5.7–5.8 (m, 1 H). Anal. Calcd for C₉H₁₈O₂Si: C, 63.47; H, 10.65. Found: C, 63.46; H, 10.95.

(1*R**,2*R**)-2-(Trimethylsilyl)-3-cyclohexene-1-methanol (**5e**): IR 3330, 3020, 2950, 2890, 1620, 1250, 1040, 1020, 830, 710, 650 cm⁻¹; ¹H NMR (CDCl₃) δ 0.04 (s, 9 H), 1.4–1.6 (m, 1 H), 1.6–1.8 (m, 3 H), 2.0–2.2 (m, 3 H), 3.54 (dd, $J = 10.4$ Hz, 8.4 Hz, 1 H), 3.64 (dd, $J = 10.4$ Hz, 6.2 Hz, 1 H), 5.5–5.7 (m, 2 H). Anal. Calcd for C₁₀H₂₀O₂Si: C, 65.15; H, 10.93. Found: C, 64.94; H, 10.63.

(1*R**,2*R**)-4-Methyl-2-(trimethylsilyl)-3-cyclohexene-1-methanol (**5f**): IR 3320, 2950, 2920, 1450, 1250, 1050, 1020, 1000, 840, 750, 680 cm⁻¹; ¹H NMR (CDCl₃) δ 0.04 (s, 9 H), 1.3–1.8 (m, 5 H), 1.66 (s, 3 H), 1.9–2.1 (m, 2 H), 3.54 (dd, $J = 10.0$ Hz, 8.2 Hz, 1 H), 3.64 (dd, $J = 10.0$ Hz, 6.2 Hz, 1 H), 5.3–5.4 (m, 1 H). Anal. Calcd for C₁₁H₂₂O₂Si: C, 66.60; H, 11.18. Found: C, 66.48; H, 10.99.

(1*R**,2*R**)-2-Methyl-2-(trimethylsilyl)-3-cyclohexene-1-methanol (**5g**): IR 3320, 2940, 1640, 1450, 1250, 1020, 1000, 850, 830, 700, 640 cm⁻¹; ¹H NMR (CDCl₃) δ 0.03 (s, 9 H), 1.09 (s, 3 H), 1.4–1.6 (m, 3 H), 1.8–1.9 (m, 1 H), 2.0–2.1 (m, 2 H), 3.45 (dd, $J = 10.4$ Hz, 9.0 Hz, 1 H), 3.89 (dd, $J = 10.4$ Hz, 3.2 Hz, 1 H), 5.34 (dt, $J = 10.0$ Hz, 2.2 Hz, 1 H), 5.61 (dt, $J = 10.0$ Hz, 3.2 Hz, 1 H). Anal. Calcd for C₁₁H₂₂O₂Si: C, 66.60; H, 11.18. Found: C, 66.90; H, 10.88.

(1*R**,2*R**)-2-Methyl-2-(triethylsilyl)-3-cyclohexene-1-methanol (**5h**): IR 3430, 2950, 2880, 1460, 1250, 1090, 1020, 1000, 730, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 0.66 (q, $J = 7.6$ Hz, 6 H), 0.98 (t, $J = 7.6$ Hz, 9 H), 1.11 (s, 3 H), 1.2–1.6 (m, 3 H), 1.8–2.1 (m, 3 H), 3.48 (t, $J = 9.6$ Hz, 1 H), 3.87 (dd, $J = 9.6$ Hz, 3.0 Hz, 1 H), 5.44 (dt, $J = 10.0$ Hz, 1.6 Hz, 1 H), 5.54 (dt, $J = 10.0$ Hz, 3.2 Hz, 1 H). Anal. Calcd for C₁₄H₂₈O₂Si: C, 69.93; H, 11.74. Found: C, 69.70; H, 11.44.

(1*R**,2*R**)-2-Methyl-2-(tripropylsilyl)-3-cyclohexene-1-methanol (**5i**): IR 3330, 3020, 2950, 2930, 2870, 1460, 1420, 1380, 1330, 1210, 1060, 1030, 1000, 740, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 0.5–0.7 (m, 6 H), 0.9–1.0 (m, 9 H), 1.10 (s, 3 H), 1.2–1.6 (m, 9 H), 1.8–2.2 (m, 3 H), 3.48 (t, $J = 9.6$ Hz, 1 H), 3.88 (dd, $J = 9.6$ Hz, 1.8 Hz, 1 H), 5.42 (d, $J = 9.8$ Hz, 1 H), 5.54 (dt, $J = 9.8$ Hz, 3.6 Hz, 1 H). Anal. Calcd for C₁₇H₃₄O₂Si: C, 72.27; H, 12.13. Found: C, 72.09; H, 11.83.

(1*R**,2*R**)-1-Methyl-2-(trimethylsilyl)-3-cyclohexene-1-methanol (**5k**): IR 3360, 3020, 2950, 2870, 1640, 1450, 1250, 1030, 840, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 0.04 (s, 9 H), 1.03 (s, 3 H), 1.2–1.4 (m, 2 H), 1.4–1.7 (m, 2 H), 2.0–2.1 (m, 2 H), 3.47 (s, 2 H), 5.5–5.7 (m, 2 H).

(1*R**,2*R**)-1-[[Triisopropylsilyl]oxy]methyl-2-(trimethylsilyl)-3-cyclohexene-1-methanol (**5l**): IR 3450, 2930, 2860, 1640, 1460, 1380, 1250, 1090, 1060, 880, 840, 680, 660 cm⁻¹; ¹H NMR (CDCl₃) δ 0.08 (s, 9 H), 1.0–1.2 (m, 21 H), 1.47 (s, 1 H), 1.54 (dt, $J = 14.6$ Hz, 5.8 Hz, 1 H), 1.76 (ddd, $J = 14.6$ Hz, 8.0 Hz, 7.2 Hz, 1 H), 1.9–2.1 (m, 2 H), 3.27 (dd, $J = 7.0$ Hz, 4.2 Hz, 1 H), 3.60 (dd, $J = 10.6$ Hz, 7.0 Hz, 1 H), 3.65 (d, $J = 9.2$ Hz, 1 H), 3.69 (dd, $J = 10.6$ Hz, 4.2 Hz, 1 H), 3.87 (d, $J = 9.2$ Hz, 1 H), 5.5–5.7 (m, 2 H). Anal. Calcd for C₂₀H₄₂O₂Si₂: C, 64.80; H, 11.42. Found: C, 65.10; H, 11.23.

(1*R**,2*R**)-3-Methyl-1-[[triisopropylsilyl]oxy]methyl-2-(trimethylsilyl)-3-cyclohexene-1-methanol (**5m**): IR 3460, 2950, 2870, 1460, 1250, 1070, 890, 860, 840, 690 cm⁻¹; ¹H NMR (CDCl₃) δ 0.13 (s, 9 H), 1.0–1.1 (m, 21 H), 1.2–1.5 (m, 2 H), 1.69 (s, 3 H), 1.77 (s, 1 H), 1.8–2.2 (m,

1 H), 3.25 (br s, 1 H), 3.54 (d, $J = 9.0$ Hz, 1 H), 3.5–3.8 (m, 2 H), 3.89 (d, $J = 9.0$ Hz, 1 H), 5.27 (s, 1 H). Anal. Calcd for C₂₁H₄₄O₂Si₂: C, 65.56; H, 11.53. Found: C, 65.78; H, 11.71.

(1*R**,2*R**)-1,3-Dimethyl-2-(trimethylsilyl)-3-cyclohexene-1-methanol (**5n**): IR 3350, 2950, 2810, 1660, 1450, 1380, 1250, 1080, 1040, 850, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 0.10 (s, 9 H), 0.99 (s, 3 H), 1.1–1.3 (m, 1 H), 1.32 (s, 1 H), 1.3–1.4 (m, 1 H), 1.42 (dt, $J = 13.2$ Hz, 9.0 Hz, 1 H), 1.67 (d, $J = 1.4$ Hz, 3 H), 2.0–2.2 (m, 2 H), 3.42 (dd, $J = 10.0$ Hz, 4.8 Hz, 1 H), 3.56 (dd, $J = 10.0$ Hz, 4.8 Hz, 1 H), 5.28 (s, 1 H). Anal. Calcd for C₁₂H₂₄O₂Si: C, 67.86; H, 11.39. Found: C, 67.78; H, 11.62.

Preparation of Allylsilanes 7. A THF (0.5 mL) solution of alcohol **6** (0.20 mmol) was treated with a hexane solution of butyllithium (0.22 mmol) at -78 °C for 5 min, and it was added to a THF (1.5 mL) solution of LDBB (0.6 mmol). After the solution was stirred for 30 min at -78 °C, chlorotrimethylsilane (1 mmol) was added and the solution stirred for 10 min. Quenching with saturated aqueous NaHCO₃ followed by usual workup gave the crude bisilylated product. The resulting product was dissolved in methanol (2 mL) containing a catalytic amount of K₂CO₃ and was stirred overnight at room temperature. Usual workup followed by separation with silica gel column chromatography gave the corresponding **7**. The spectral and analytical data of **7** are as follows.

4-(Trimethylsilyl)-2-cyclohexene-1-methanol (**7a**) and 2-(Trimethylsilyl)-3-cyclohexene-1-methanol (**7a'**): IR 3230, 2950, 2920, 2850, 1630, 1440, 1240, 1060, 1030, 870, 830, 750 cm⁻¹; ¹H NMR (CDCl₃) (**7a**) δ 0.00 (s, 9 H), 1.2–2.4 (m, 7 H), 3.54 (t, $J = 5.8$ Hz, 2H), 5.54 (dt, $J = 10.0$ Hz, 1.8 Hz, 1 H), 5.77 (dt, $J = 10.0$ Hz, 1.8 Hz, 1 H); (**7a'**) δ 0.03 (s, 9 H), 1.2–2.4 (m, 7 H), 3.54 (t, $J = 5.8$ Hz, 2H), 5.5–5.7 (m, 2 H).

(1*R**,4*R**)-1-Methyl-4-(trimethylsilyl)-2-cyclopentene-1-methanol (**7b**): IR 3350, 3040, 2950, 2860, 1460, 1250, 1040, 860, 840, 740, 700 cm⁻¹; ¹H NMR (CDCl₃) δ -0.02 (s, 9 H), 1.05 (s, 3 H), 1.3–2.2 (m, 6 H), 3.36 (d, $J = 4.2$ Hz, 2 H), 5.30 (dd, $J = 5.8$ Hz, 2.4 Hz, 1 H), 5.74 (dd, $J = 5.8$ Hz, 1.8 Hz, 1 H).

(1*R**,4*R**)-2-Methyl-4-(trimethylsilyl)-2-cyclohexene-1-methanol (**7c**): IR 3330, 2950, 2920, 2850, 1440, 1240, 1080, 1050, 1020, 890, 850, 830, 750, 690 cm⁻¹; ¹H NMR (CDCl₃) δ -0.02 (s, 9 H), 1.2–1.9 (m, 6 H), 1.72 (s, 3 H), 2.1–2.2 (m, 1 H), 3.69 (br s, 2 H), 5.53 (s, 1 H). Anal. Calcd for C₁₁H₂₂O₂Si: C, 66.60; H, 11.18. Found: C, 66.47; H, 11.11.

(1*R**,4*R**)-1-Methyl-4-(trimethylsilyl)-2-cyclohexene-1-methanol (**7d**): IR 3350, 2950, 2930, 2860, 1450, 1250, 1030, 870, 830, 740 cm⁻¹; ¹H NMR (CDCl₃) δ 0.01 (s, 9 H), 0.92 (s, 3 H), 1.2–1.7 (m, 5 H), 1.7–1.9 (m, 1 H), 3.30 (dd, $J = 9.8$ Hz, 7.4 Hz, 1 H), 3.40 (dd, $J = 9.8$ Hz, 3.8 Hz, 1 H), 5.36 (dd, $J = 9.8$ Hz, 1.6 Hz, 1 H), 5.77 (dd, $J = 9.8$ Hz, 2.8 Hz, 1 H).

(1*R**,4*R**)-1,3-Dimethyl-4-(trimethylsilyl)-2-cyclohexene-1-methanol (**7e**): IR 3350, 2950, 2860, 1660, 1450, 1380, 1250, 1090, 1040, 840, 750, 690 cm⁻¹; ¹H NMR (CDCl₃) δ 0.06 (s, 9 H), 0.92 (s, 3 H), 1.2–1.4 (m, 2 H), 1.47 (t, $J = 4.8$ Hz, 1 H), 1.5–1.9 (m, 3 H), 1.70 (s, 3 H), 3.27 (d, $J = 10.0$ Hz, 1 H), 3.36 (d, $J = 10.0$ Hz, 1 H), 5.01 (s, 1 H). Anal. Calcd for C₁₂H₂₄O₂Si: C, 67.86; H, 11.39. Found: C, 67.63; H, 11.09.

(1*S**,4*R**)-1-[[Triisopropylsilyl]oxy]methyl-4-(trimethylsilyl)-2-cyclohexene-1-methanol (**7f**): IR 3430, 2940, 2860, 1460, 1250, 1090, 1060, 880, 840, 730, 680, 660 cm⁻¹; ¹H NMR (CDCl₃) δ 0.00 (s, 9 H), 0.9–1.2 (m, 21 H), 1.4–1.6 (m, 3 H), 1.7–1.9 (m, 2 H), 2.90 (dd, $J = 6.6$ Hz, 5.0 Hz, 1 H), 3.53 (dd, $J = 10.4$ Hz, 6.6 Hz, 1 H), 3.64 (s, 2 H), 3.65 (dd, $J = 10.4$ Hz, 5.0 Hz, 1 H), 5.37 (dd, $J = 10.2$ Hz, 1.8 Hz, 1 H), 5.80 (dd, $J = 10.2$ Hz, 2.6 Hz, 1 H). Anal. Calcd for C₂₀H₄₂O₂Si₂: C, 64.80; H, 11.42. Found: C, 64.74; H, 11.32.

(1*S**,4*R**)-3-Methyl-1-[[triisopropylsilyl]oxy]methyl-4-(trimethylsilyl)-2-cyclohexene-1-methanol (**7g**): IR 3430, 2940, 2860, 1460, 1380, 1250, 1090, 1060, 880, 830, 680 cm⁻¹; ¹H NMR (CDCl₃) δ 0.05 (s, 9 H), 0.9–1.2 (m, 21 H), 1.2–1.9 (m, 5 H), 1.68 (s, 3 H), 3.00 (br s, 1 H), 3.4–3.7 (m, 4 H), 5.06 (s, 1 H). Anal. Calcd for C₂₁H₄₄O₂Si₂: C, 65.56; H, 11.53. Found: C, 65.73; H, 11.30.

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Supplementary Material Available: Preparative method of the starting materials, their spectral and analytical data, and determination of stereochemistries of **5e**, **5l**, **7d**, and **7f** (8 pages). Ordering information is given on any masthead page.