Stereoselective Intramolecular Bis-Silylation of Alkenes Promoted by a Palladium–Isocyanide Catalyst Leading to Polyol Synthesis

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Abstract: Details of a study on the intramolecular bis-silylation of terminal alkenes promoted by a palladium–*tert*-alkyl isocyanide catalyst are described. With a disilanyl ether derived from a homoallylic alcohol, intramolecular regioselective addition of the Si–Si linkage to the C=C bond took place to furnish an *exo*-ring closure product, *i.e.*, 1,2-oxasilolane. The bis-silylation of alkenes having substituents α to the C=C bond gave *trans*-3,4-disubstituted oxasilolanes, while substitution β to the C=C bond favored *cis*-3,5-disubstituted oxasilolanes. The stereoselectivity trends are formulated as arising from a preference for a chairlike transition state over a boatlike one. A substituent, either α or β to the C=C bond, prefers the equatorial position in a chairlike transition state. The 1,2-oxasilolanes thus produced stereoselectively were oxidatively converted to the corresponding 1,2,4-triols. The present methodology for the synthesis of 1,2,4-triols was successfully extended to the stereoselective synthesis of 1,2,4,5,7- and 1,2,4,6,7-pentaols through a sequence of intramolecular bis-silylations. The bis-silylation was also performed with alkenes linked to disilanyl groups through a three-carbon chain and through an amide linkage. Stereoselections analogous to those of the ether substrates were observed. Alkenes tethered to disilanyl groups through chains of two atoms underwent similar intramolecular bis-silylation. In conclusion, the intramolecular bis-silylation of C=C bonds followed by oxidation constitutes a new synthetic transformation equivalent to the stereoselective dihydroxylation of olefins.

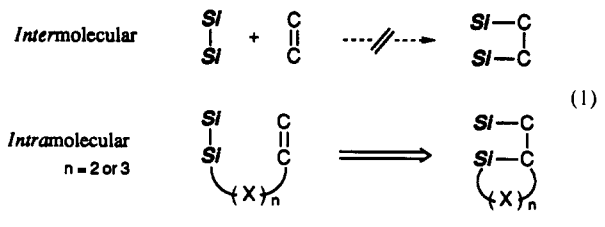
Introduction

The addition of organosilicon compounds to unsaturated organic substrates is a fundamental process in organosilicon chemistry. The utility of hydrosilylation as a synthetic tool has even been extended into the area of enantioselective reactions.[1] Although less attention has been paid to bis-silylation than to hydrosilylation, the addition of Si–Si bonds across C–C multiple bonds to give 1,2-bis(organosilyl)alkanes (or -alkenes), i.e., *bis-silylation*, is a particularly attractive transformation in that two Si–C bonds are created at once. The bis-silylation of C–C triple bonds with disilanes has been achieved by use of palladium catalysts.[2,3] In contrast, difficulties were encountered with C–C double bonds. While the catalytic bis-silylation of ethene using a platinum complex was recently reported, the synthetic utilities were limited.[4]

We have been studying the reactions of polysilanes with unsaturated organic molecules[5] and have disclosed a bis-silylation of C–C triple bonds catalyzed by a new catalyst system, palladium(II) acetate–*tert*-alkyl isocyanide.[3] Although this new catalyst failed to promote the intermolecular bis-silylation of alkenes, application to the *intra*molecular variant found wide synthetic usefulness. The present paper describes the details of our study on the stereoselective intramolecular bis-silylation of C–C double bonds which provides a new method for polyol synthesis.[6]

Results and Discussion

Intramolecular bis-silylation of alkenes tethered to disilanyl groups with chains of two and three atoms was examined. With alkenes tethered to disilanyl groups by chains of more than four atoms, bis-silylation did not occur at all, even with use of the present catalyst system. Consequently, appropriate juxtaposition with a disilanyl group is required for bis-silylation of a C=C bond to take place.



(1)

† Research visitor (in 1990) from the Department of Organic Chemistry, University of Uppsala, Sweden.

(1) (a) Kagan, H. B. *Pure Appl. Chem.* **1975**, *43*, 401. (b) Ojima, I.; Hirai, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: Orlando, FL, 1985; Vol. 5, pp 104–125. (c) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley Interscience: Chichester, U.K., 1989; Chapter 25. (d) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090. (e) Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712. (f) Tamao, K.; Tohma, T.; Inui, N.; Nakayama, O.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 7333. (g) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2121 and references cited therein.

(2) (a) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931. (c) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51. (d) Yamashita, H.; Catellani, M.; Tanaka, M. *Chem. Lett.* **1991**, 241 and references cited therein.

(3) (a) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948. (b) Murakami, M.; Oike, H.; Sugawara, M.; Suginome, M.; Ito, Y. *Tetrahedron* **1993**, *49*, 3933.

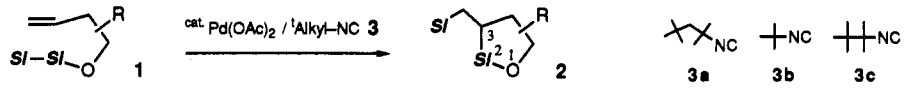
(4) Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280.

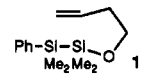
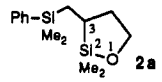
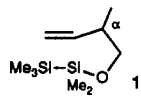
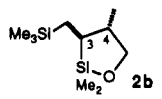
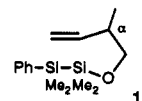
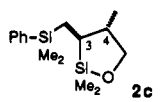
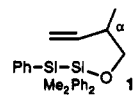
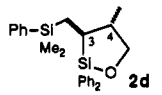
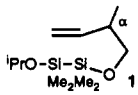
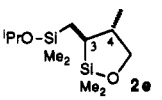
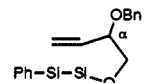
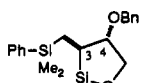
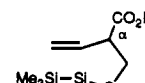
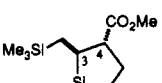
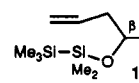
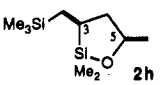
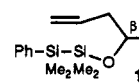
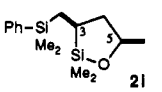
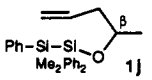
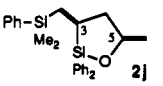
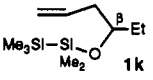
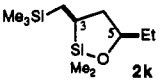
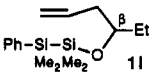
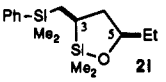
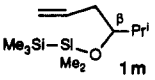
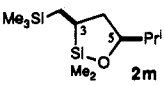
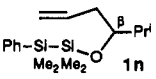
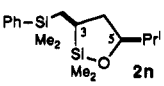
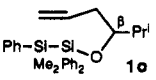
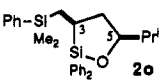
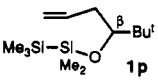
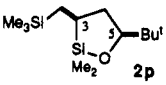
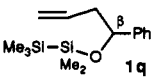
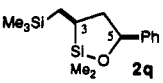
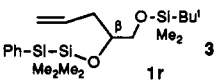
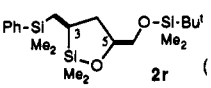
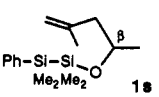
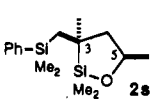
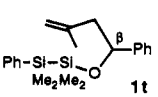
(5) (a) Ito, Y.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1988**, *110*, 3692. (b) Ito, Y.; Suginome, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899.

(6) A preliminary communication: Murakami, M.; Anderson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987.

0002-7863/93/1515-6487$04.00/0

Table I. Intramolecular Bis-Silylation of C=C Bonds



entry	1	3	conditions	product 2	yield, % (cis : trans)
1	 1a	3b	rt 10 h	 2a	94 (—)
2	 1b	3a	rt 6 h	 2b	90 (7:93)
3	 1c	3a	rt 1 h	 2c	95 (7:93)
4		3a	111 °C 0.5 h		88 (10:90)
5		3b	rt 3 h		97 (11:89)
6		3c	rt 9 h		77 (8:92)
7		3a	rt 2 h		84 (3:97)
8	1d	3b	rt 2 h	2d	95 (4:96)
9	 1e	3a	35 °C 4 h	 2e	90 (5:95)
10	 1f	3a	rt 12 h	 2f	92 (3:97)
11	 1g	3a	rt 8 h	 2g	85 (1:>99)
12	 1h	3a	35 °C 10 h	 2h	91 (92:8)
13	 1i	3a	rt 2 h	 2i	90 (93:7)
14		3a	111 °C 0.5 h		91 (90:10)
15		3b	rt 2 h		90 (90:10)
16	1i	3c	rt 6 h	2i	86 (92:8)
17	 1j	3b	rt 6 h	 2j	90 (96:4)
18	 1k	3a	rt 8 h	 2k	88 (92:8)
19	 1l	3a	rt 2 h	 2l	93 (91:9)
20	 1m	3a	35 °C 10 h	 2m	97 (93:7)
21	 1n	3a	rt 2 h	 2n	98 (93:7)
22	 1o	3a	rt 1 h	 2o	92 (96:4)
23	 1p	3a	rt 10 h	 2p	92 (93:7)
24	 1q	3a	75 °C 6 h	 2q	95 (97:3)
25	 1r	3a	rt 6 h	 2r	96 (93:7)
26	 1s	3a	80 °C 2 h	 2s	97 (96:4)
27	 1t	3a	80 °C 2 h	2t	99 (96:4)

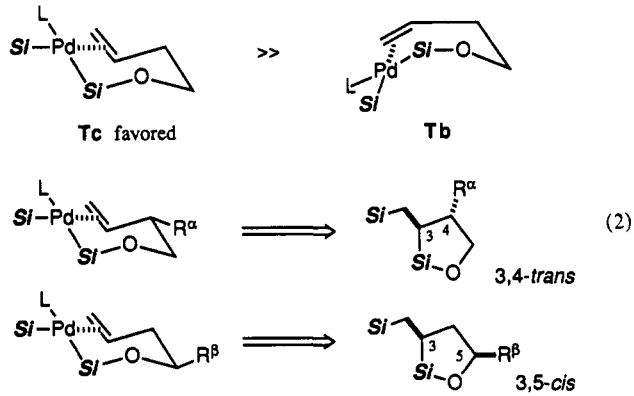
Intramolecular Bis-Silylation of Alkenes Tethered to a Disilanyl Group by a Chain of Three Atoms through an Ether Linkage (1). Disilanyl alkenes **1** were prepared in good yield by the reaction of homoallylic alcohols with chlorodisilanes in the presence of an amine. The bis-silylation of **1** was carried out in the presence of catalytic amounts of palladium(II) acetate (0.01–0.05 equiv) and *tert*-alkyl isocyanide **3** (0.15–0.75 equiv) in toluene under the conditions specified in Table I. Intramolecular regioselective addition of the Si–Si linkage across the C=C bond took place to furnish the *exo*-ring closure product, *i.e.*, 1,2-oxasilolane **2**, in good yield. Tertiary alkyl carbon–silicon bonds were readily formed by the bis-silylation of geminally disubstituted olefins, although heating at 80 °C was required (entries 26 and 27). In contrast, vicinally disubstituted olefins were found to not undergo the bis-silylation. Ester and allylic benzyloxy groups did not encumber the desired bis-silylation reaction (entries 10 and 11).

It is noteworthy that the bis-silylation of an alkene having an asymmetric center in the tether proceeds with high diastereoselection. Alkenes having substituents in allylic positions, *i.e.*, α to the C=C bond, gave *trans*-3,4-disubstituted **2** (entries 2–11). On the other hand, the *cis*-3,5-disubstituted **2** were favored in the reaction of β-substituted alkenes (entries 12–27). Very similar selectivities in the vicinity of 92:8–93:7 were observed with β-substituents of varying bulkiness ranging from methyl to *tert*-butyl groups (entries 12, 18, 20, and 23). Geminal disubstitution of the C=C bond improved the selectivity slightly (entries 13 and 26). The reaction at reflux in toluene resulted in only a little decrease in the selectivity (entries 3, 4, 13, and 14). Use of THF as solvent gave similar chemical yield and stereoselectivity. Among the *tert*-alkyl isocyanides examined, 1,1,3,3-tetramethylbutyl isocyanide (**3a**) was the isocyanide of choice in terms of reaction rate and stereoselectivity (entries 3, 5, 6, 13, 15, and 16).

The influence of the silicon substituents on stereoselectivity was examined; no significant difference in selectivity was observed among pentamethyldisilanyl, 2-phenyl-1,1,2,2-tetramethyldisilanyl, and 2-isopropoxy-1,1,2,2-tetramethyldisilanyl groups, in-

dicating that the stereochemical outcome was not affected by the substituents on the silicon atom distal to the ether oxygen (entries 2, 3, and 9). In contrast, the two phenyl groups on the silicon atom proximal to the ether oxygen increased the selectivity slightly (entries 7, 17, and 22).[7]

The stereoselectivity trends observed are formulated as arising from a preference for the chairlike transition state (T_c) over the boatlike one (T_b). In the chairlike transition state (T_c), a substituent, either α or β to the C=C bond, prefers the equatorial position. Consequently, the α-substitution of the C=C bond leads to *trans*-3,4-disubstituted oxasilolane and β-substitution to *cis*-3,5-disubstituted oxasilolane.



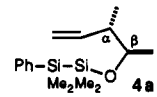
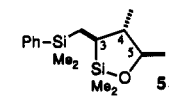
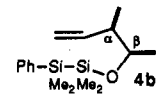
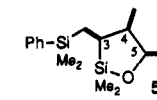
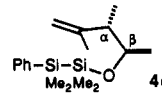
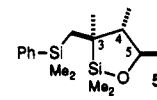
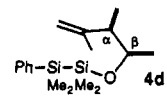
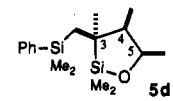
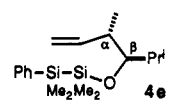
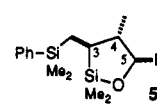
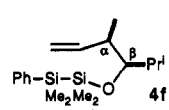
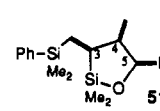
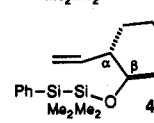
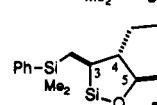
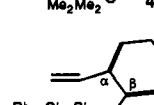
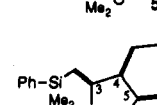
(2)

The bis-silylation reaction of the pairs of diastereomers **4**, with two substituents in the tether, is interesting in terms of stereodifferentiation (Table II): In the case of one diastereomer (**4a,c,e,g**), both substituents in the tether can occupy equatorial positions in the proposed chairlike transition state, reinforcing the inherent stereochemical preferences. In the case of the other diastereomer (**4b,d,f,h**), it is impossible for the two substituents to be equatorial concurrently, and in consequence, the stereochemical preferences of the two substituents are in conflict. A series of those substrates were prepared and subjected to the protocol for the bis-silylation mentioned above. In the reactions of **4a,c,e,g**, the two substituents in the tether both favored the (3*R**,4*R**,5*R**) configuration and improved the selectivity. In the particular case of **4g**, the C=C bond and the disilanyl group are fixed on a cyclohexane ring by *trans*-1,2-substitution, which results in a rigid conformation of the tether. The fact that complete diastereoselection was attained with **4g** supports the strong preference for the chairlike transition state (T_c) over the boat-like one (T_b) (entry 7). In the reaction of **4b,d,f,h**, the substituent β to the C=C bond predominantly governed the stereochemistry at the new stereocenter (5-position) favoring the (3*R**,4*S**,5*R**) configuration, although the other substituent α to the C=C bond worked adversely, decreasing the selectivity.

The Palladium Catalyst. Stirring a mixture of palladium(II) acetate and *tert*-alkyl isocyanide resulted in a dramatic change in color from orange to dark red in 1 min, probably due to the formation of a palladium(0) isocyanide complex. An excess of the isocyanide (*tert*-alkyl isocyanide/$Pd(OAc)_2$ = 6–15) was required. Use of less than 6 equiv of isocyanide to $Pd(OAc)_2$ did not bring the reaction to completion. A catalyst prepared from $Pd(acac)_2$ and *tert*-alkyl isocyanide exhibited similar catalytic activity. In the absence of *tert*-alkyl isocyanide, none of the palladium compounds examined [$Pd(OAc)_2$, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $Pd(OAc)_2/PPh_3$ (1:2), Pd_2{dibenzylideneacetone (dba)}$_3$·$CHCl_3$/PPh_3 (1:4), $Pd_2(dba)_3$·$CHCl_3$/$P(OEt)_3$ (1:4), and $Pd_2(dba)_3$·$CHCl_3$/2,2′-bipyridine (1:4)] afforded the intramolecular bis-silylation product at all. Palladium species prepared by mixing $Pd(OAc)_2$ with other isocyanides shown in Chart I exhibited no catalytic activity.

(7) The reactions of phenyl-substituted disilanyl ethers such as **1c,d** were generally faster than those of pentamethyldisilanyl ethers like **1b**.

Table II. Intramolecular Bis-Silylation of Disubstituted Disilanyl Alkenes **4**

entry	4	conditions	product **5**	yield, % (cis : trans) [a]
1	 **4a**	rt 70 min	 **5a**	94 (96 : 4)
2	 **4b**	rt 70 min	 **5b**	96 (82 : 18)
3	 **4c**	80 °C 2 h	 **5c**	90 (99 : 1)
4	 **4d**	80 °C 2 h	 **5d**	90 (92 : 8)
5	 **4e**	rt 2 h	 **5e**	93 (97 : 3)
6	 **4f**	rt 3.5 h	 **5f**	91 (91 : 9)
7	 **4g**	rt 2 h	 **5g**	99 (100 : 0)
8	 **4h**	rt 12 h	 **5h**	99 (82 : 18)

[a] Referring to the relationship between the 3- and 5-substituents of **5**

Chart I

Although the precise mechanism is not clear, we assume that palladium(II) acetate is initially reduced by *tert*-alkyl isocyanide[8] to form the palladium(0) species ligated by *tert*-alkyl isocyanide. Next the oxidative insertion of the palladium(0) species into the Si–Si linkage takes place to give a bis(organosilyl)palladium(II) complex.[9] Insertion of the C=C bond into the Pd–Si bond followed by reductive elimination of the palladium(0) species would complete the catalytic cycle.

It has been reported that $Pd(CNBu^t)_2$, the most likely precursor of the active catalyst species, can be prepared by the reaction of (η^3-allyl)(η^5-cyclopentadienyl)palladium(II) with *tert*-butyl isocyanide.[8] However, the isolated complex was insoluble in toluene and consequently exhibited no catalytic activity. Addition of 4 equiv of *tert*-alkyl isocyanide **3a** to (η^3-allyl)(η^5-cyclopentadienyl)-palladium(II) in toluene afforded a dark red solution, which promoted the intramolecular bis-silylation. Nevertheless, the dark red color gradually faded away into pale yellow and the reaction did not lead to completion. Finally, it was found that (η^3-allyl)-(η^5-cyclopentadienyl)palladium(II) together with 15 equiv of *tert*-alkyl isocyanide **3a** was as effective as the catalyst prepared from $Pd(OAc)_2$ and **3a**. On the basis of these results, it is presumed

(8) (a) Fischer, E. O.; Werner, H. *Chem. Ber.* **1962**, *95*, 703. (b) Otsuka, S.; Nakamura, A.; Tatsuno, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6994.

(9) Recently, the synthesis of thermally stable bis(organosilyl)palladium-(II) complexes and the reaction with an alkyne have been reported: Pan, Y.; Mague, J. T.; Fink, M. J. *Organometallics* **1992**, *11*, 3495.

that palladium(0) isocyanide complex is the precursor of the active catalyst species for the present bis-silylation reaction. Excess *tert*-alkyl isocyanide might be required to hinder the palladium(0) isocyanide complex from decomposing during the reaction course.

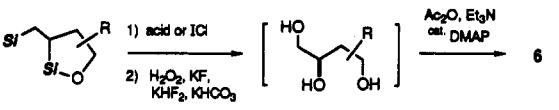
Oxidative Transformations of the 1,2-Oxasilolanes into 1,2,4-Triols. It has been reported that the oxidative cleavage of a Si–C bond furnishing a hydroxyl group proceeds with retention of configuration at the cleaved carbon atom and that at least one functional group bound to the silicon such as an alkoxy group or a halogen is required for the oxidation to proceed.[10] A phenyl-substituted silicon also undergoes oxidation via prior cleavage of the Ph–Si bond.[10d-f]

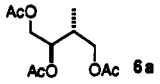
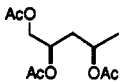
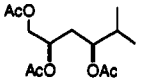
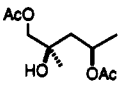
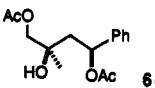
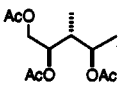
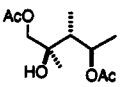
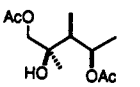
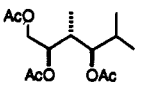
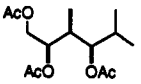
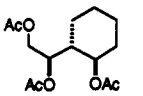
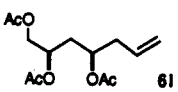
The 1,2-oxasilolanes **2** and **5** have two Si–C bonds, and in particular, those derived from 2-phenyldisilanyl ethers are possible precursors of 1,2,4-triols because both Si–C bonds fulfill the requirement for the oxidation mentioned above. The Si–Ph bonds were cleaved in the following ways prior to the oxidation by hydrogen peroxide (Table III). For **2c,d,i,j,n,s, 5a,c,e,g,** and **8**, the cleavage was carried out by treatment with an acid as reported.[10d,e] Subsequent treatment with hydrogen peroxide accomplished the oxidative transformation to the corresponding 1,2,4-triols, which were isolated as di- or triacetates **6** in moderate to good yield. When **2t** was reacted with trifluoroacetic acid, intramolecular migration of the phenyl group from the silicon to the benzylic carbon occurred to give 2-methyl-4,4-diphenylbutan-1,2-diol after oxidation.[10d] In order to prevent this Friedel–Crafts type reaction, ICl was used instead of an acid for cleavage of the Si–Ph bond (entry 7).[11] An alternative method for cleavage of the Si–Ph bond of the 1,2-oxasilolane has also been devised. Treatment of the 1,2-oxasilolane with potassium *tert*-butoxide in dimethyl sulfoxide (DMSO) successfully cleaved the Si–Ph bond presumably via a ring-opening reaction (entries 8, 11, and 13).[12] For **5d,f**, cleavage with potassium *tert*-butoxide gave a much better yield of 1,2,4-triols than with trifluoroacetic acid. Thus, the stereoselective bis-silylation of C≡C bonds followed by oxidation constitutes a new synthetic transformation equivalent to the stereoselective dihydroxylation of olefins.[13]

Synthesis of Pentaols. This new method for the synthesis of 1,2,4-triols was extended to the stereoselective synthesis of pentaols through a sequence of intramolecular bis-silylation procedures (Scheme I). On treatment with palladium(II) acetate–*tert*-alkyl isocyanide, a disilanyl ether (**7**) derived from 1,6-heptadien-4-ol produced 3,5-*cis*-disubstituted oxasilolane **8** selectively (*cis*:*trans* = 93:7). The ring opening of **8** with phenyllithium in ether gave a homoallylic alcohol (**9**), which was separated from the minor isomer by HPLC. Introduction of a disilanyl group followed by the second bis-silylation reaction afforded 3,5-*cis*-disubstituted oxasilolane **11** selectively (*cis*:*trans* = 92:8). Finally, oxidative transformation of all C–Si bonds into C–OH bonds gave rise to a 1,2,4,6,7-pentaol, which was isolated as a pentaacetate (**12**).

Another example is presented for the synthesis of a 1,2,4,5,7-pentaol, which involves elongation of the carbon chain (Scheme II). A triacetate (**6d**), obtained from a homoallylic alcohol via 3,5-*cis*-disubstituted oxasilolane **2o** as mentioned above, was

Table III. Oxidation of 1,2-Oxasilolanes into 1,2,4-Triols



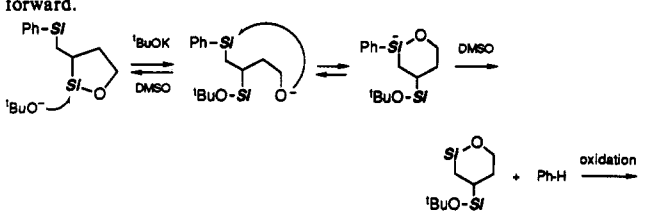
entry	oxasilolane	reagent[a]	6	yield, %
1	**2c**	CF_3CO_2H	 **6a**	77
2	**2d**	CF_3CO_2H	**6a**	76
3	**2i**	CF_3CO_2H	 **6b**	74
4	**2j**	CF_3CO_2H	**6b**	64
5	**2n**	HBF_4	 **6c**	81
6	**2s**	CF_3CO_2H	 **6d**	82
7	**2t**	ICl	 **6e**	67
8	**2t**	$KOBu^t$	**6e**	78
9	**5a**	CF_3CO_2H	 **6f**	91
10	**5c**	CF_3CO_2H	 **6g**	90
11	**5d**	$KOBu^t$	 **6h**	78
12	**5e**	CF_3CO_2H	 **6i**	91
13	**5f**	$KOBu^t$	 **6j**	78
14	**5g**	CF_3CO_2H	 **6k**	83
15	**8**	CF_3CO_2H	 **6l**	80

[a] Reagent used for cleavage of the Si–Ph bond.

(10) (a) Colvin, E. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 7, pp 641–651. (b) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983. (c) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. (d) Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29. (e) Tamao, K.; Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C37. (f) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229.

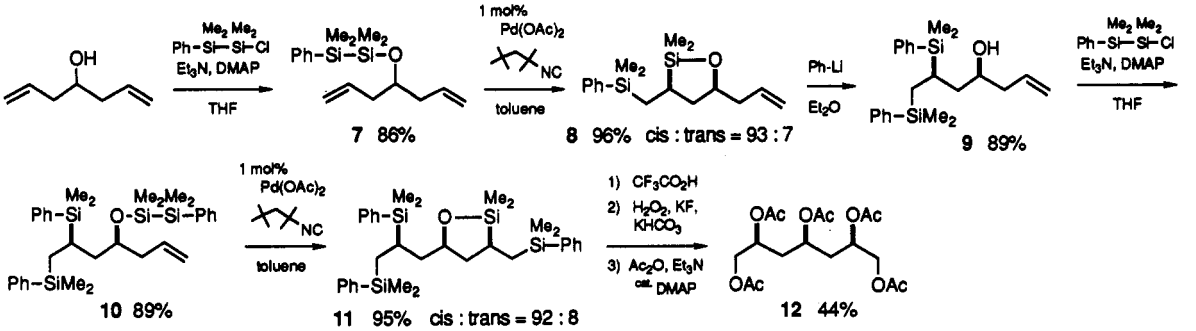
(11) Stock, L. M.; Spector, A. R. *J. Org. Chem.* **1963**, *28*, 3272.

(12) The cleavage failed in aprotic ether solvents. It has been reported that the Si–Me bond of tetramethylsilane is cleaved by treatment with ^{t}BuOK in DMSO: Price, C. C.; Sowa, J. R. *J. Org. Chem.* **1967**, *32*, 4126. However, cleavage of the Ph–Si bond of $PhSiMe_2Bu^n$ mediated intermolecularly by ^{t}BuOK in DMSO was found to be much slower than that of the Ph–Si bonds of 1,2-oxasilolanes. It has been also reported that an alkoxide anion assists intramolecularly to cleave an unactivated C–Si bond: Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809. Hudrlik, P. F.; Abdallah, Y. M.; Hudrlik, A. M. *Tetrahedron Lett.* **1992**, *33*, 6743, 6747. On the basis of these reports, we propose the following mechanism to account for the present facile cleavage of the Ph–Si bonds of 1,2-oxasilolanes: ^{t}BuOK causes a ring-opening reaction of the 1,2-oxasilolane to produce an alkoxide anion, which intramolecularly assists cleavage of the Ph–Si bond via a pentacoordinated silicate. DMSO provides a proton to shift the reaction forward.

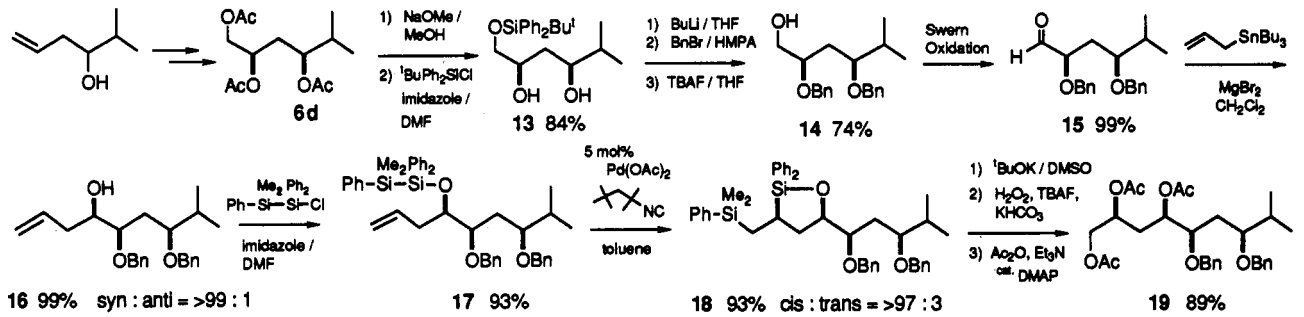


(13) For a review of dihydroxylation of olefins, see: Hudlicky, M. *Oxidation in Organic Chemistry*; American Chemical Society: Washington, DC, 1990; pp 67–73.

Scheme I



Scheme II

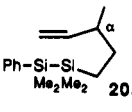
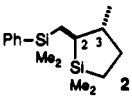
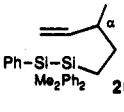
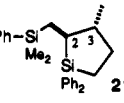
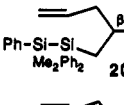
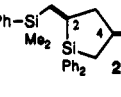
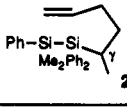
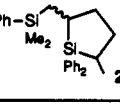


hydrolyzed to the corresponding 1,2,4-triol. After selective protection of the primary hydroxyl group with *tert*-butyldiphenylsilyl chloride, the two secondary hydroxyl groups of **13** were benzylated. The Si–O bond was cleaved by tetrabutylammonium fluoride (TBAF), giving the primary alcohol **14**, which was separated from the minor isomer by HPLC. Swern oxidation of **14** produced α-benzyloxy aldehyde **15**. Notably, allylation of **15** with an allyltin reagent[14] afforded a homoallylic alcohol (**16**) as a single stereoisomer in 99% yield. This selectivity is accounted for by the chelation model. Introduction of a disilanyl group and the subsequent intramolecular bis-silylation gave 3,5-*cis*-disubstituted oxasilolane **18** selectively. The following oxidative transformation of C–Si bonds into C–OH bonds furnished 1,2,4,5,7-pentaol derivative **19**. In the course of the transformation from **6d** to **19**, an elongation of the skeleton by a three-carbon chain as well as a stereoselective introduction of two hydroxyl groups has been achieved. The repetition of this sequence would provide an access to stereoselective construction of highly polyoxygenated skeletons.

Intramolecular Bis-Silylation of Alkenes Tethered to a Disilanyl Group by a Chain of Three Carbon Atoms (20). In most of the bis-silylations of C–C multiple bonds reported so far,[2,4] disilanes bearing electron-withdrawing substituents such as fluoro and alkoxy groups gave much better yields of bis-silylated products than did ordinary hexaalkyldisilanes. In contrast, the present intramolecular bis-silylation promoted by a palladium–*tert*-alkyl isocyanide catalyst requires no electron-withdrawing group on the silicon atom and, hence, was successfully performed with hexaorganyldisilanes **20** (Table IV). Such an alkene linked to a disilanyl group through a three-carbon chain (**20**) was prepared by the reaction of an olefinic Grignard reagent with a chlorodisilane in THF. The intramolecular bis-silylation of **20** led to the formation of silolane **21**. Stereoselections analogous to those of the ether substrates **1** were observed; alkenes having substituents α to the C=C bond gave *trans*-2,3-disubstituted silolanes (entries 1 and 2), while substitution β to the C=C bond led to *cis*-2,4-disubstituted silolane **21c** (entry 3). However, poor selectivity was obtained with a disilanyl alkene (**20d**) possessing a substituent γ to the C=C bond, the reason being unclear so far (entry 4).

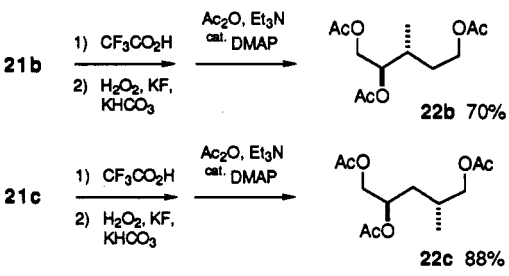
(14) Keck, G. E.; Boden, E. P. *Tetrahedron Lett.* **1984**, *25*, 265.

Table IV. Intramolecular Bis-Silylation of Alkenes Tethered to a Disilanyl Group through Chains of Three Carbon Atoms (**20**)

entry	20	conditions	product 21	yield, % (cis : trans)
1		50 °C 2 h		87 (14 : 86)
2		30 °C 4 h		99 (1 : >99)
3		rt 1 h		92 (96 : 4)
4		40 °C 2 h		89 (40 : 60)[a]

[a] The assignment of the stereochemistry is tentative.

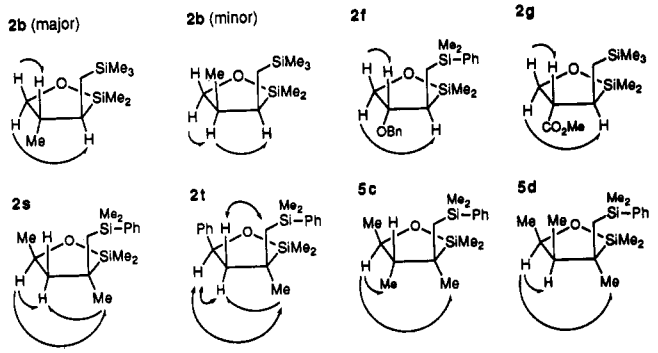
The two phenyl groups on the silicon atom proximal to the C=C bond improved the selectivity, being analogous to the improvement seen in the ether substrates **1** (entries 1 and 2). Oxidative elaboration of the silolanes **21b,c** furnished the corresponding 1,2,5-triols **22**.



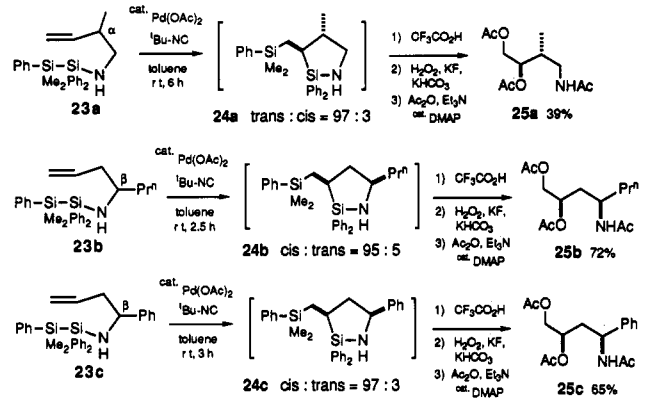
(3)

Intramolecular Bis-Silylation of Alkenes Tethered to a Disilanyl Group by a Chain of Three Atoms through an Amide Linkage (23). The present method of polyol synthesis was next applied

Chart II



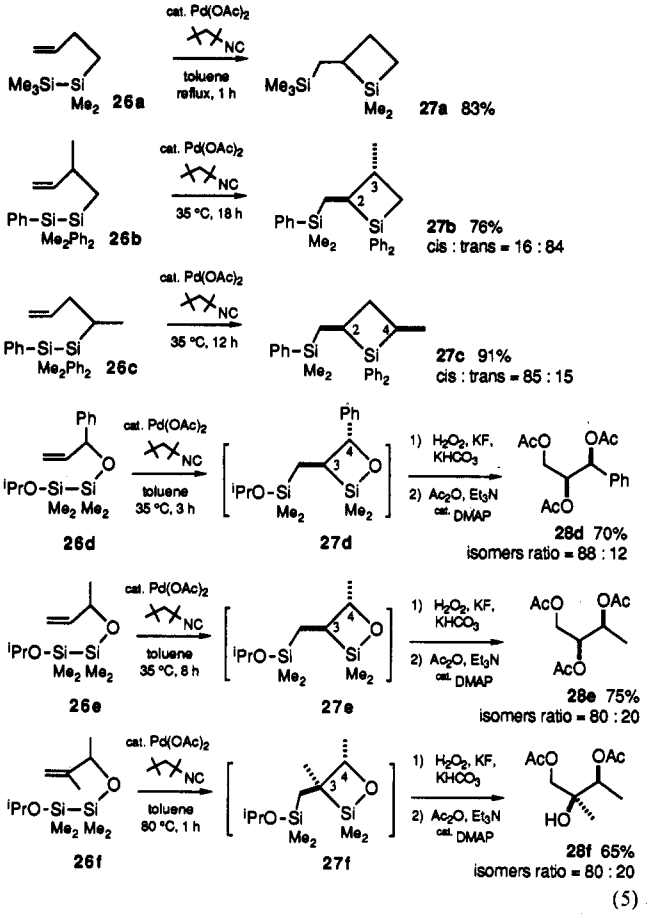
to the synthesis of amino diols. Disilanyl amides **23** were readily prepared by the reaction of primary homoallylic amines with 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane in the presence of triethylamine, and Kugelrohr distillation allowed their isolation.[15] The intramolecular bis-silylation of the disilanyl amide **23** also took place on treatment with a palladium–*tert*-alkyl isocyanide catalyst. After removal of the catalyst by filtration, the crude cyclic silyl amide **24** was subjected to the oxidation procedure without purification since the silyl–amide linkage is generally unstable. 4-Acetamido-1,2-diol diacetates **25** were produced, and their stereoselectivity trends were analogous to that observed with disilanyl alkenes **1** and **20**. Protection of the remaining amide hydrogen of **23** with a trimethylsilyl group resulted in a loss of stereoselectivity in the bis-silylation reaction, which might be in line with the poor selectivity observed with the disilanyl alkene **20d** bearing a γ-substituent.



(4)

Intramolecular Bis-Silylation of Alkenes Tethered to a Disilanyl Group by a Chain of Two Atoms (26). Next, the bis-silylation of alkenes tethered to disilanyl groups through chains of two atoms (**26**) was examined. A disilanyl alkene (**26a**) underwent the intramolecular bis-silylation analogous to that of alkenes tethered to disilanyl groups through chains of three atoms, affording a 4-membered *exo*-ring closure product **27a**. An alkene (**26b**) having a substituent α to the C=C bond gave *trans*-2,3-disubstituted siletane **27b** predominantly. On the other hand, substitution β to the C=C bond favored *cis*-2,4-disubstituted siletane **27c**. Although the bis-silylation took place also with the disilanyl ethers **26d–f**, the products were difficult to isolate. Therefore, the reaction mixtures were directly oxidized after removal of the catalyst by filtration, giving the corresponding triol triacetates **28d–f** with moderate stereoselection. On the basis of the formation of the 4-membered siletanes **27a–c** from **26a–c** and the stereochemistry of the oxidized products **28d–f**, it is likely that 4-membered and *trans*-3,4-disubstituted 1,2-oxasiletanes **27d–f** are the primary bis-silylation products.

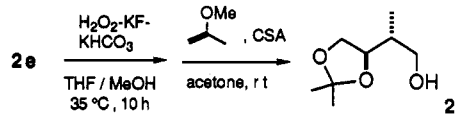
(15) Pentamethyldisilanyl or 2-phenyl-1,1,2,2-tetramethyldisilanyl groups were not suitable for a disilanyl group of **23** because serious decomposition of those disilanyl amides took place during the bis-silylation reaction.



(5)

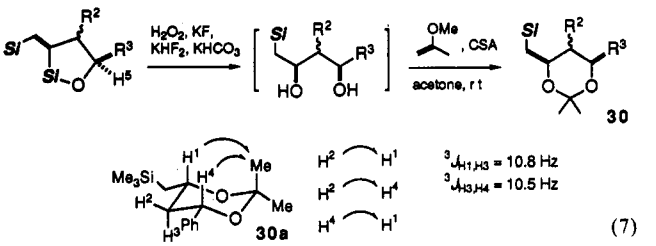
Stereochemical Assignments. The stereochemistries of the 1,2-oxasilolanes **2b,f,g,s,t**, **5c**, and **5d** were deduced by NOE experiments, the results shown in Chart II. For **2b**, an NOE experiment was also carried out on the minor isomer to ascertain the assignment.

The 1,2-oxasilolanes **2c–e** were converted to the 1,3-dioxolane **29** through a triol, and comparison with the literature data[16] established the stereochemistry of **2c–e**.



(6)

The 1,2-oxasilolanes **2h,m,q**, **5e–h**, **8**, and **11** were converted to 1,3-dioxanes **30** via 1,3-diols formed by partial oxidation of the Si–C bonds in the oxasilolane rings with the Me_3Si–C or $PhMe_2$-Si–C bonds on the side chains retained. For **30a** obtained from **2q**, the NOE experiment together with the coupling constants ($^3J_{H1,H3}$ and $^3J_{H3,H4}$) in the ^1H NMR clearly showed a *cis* relationship between the 4- and 6-substituents.



(7)

For 4,6-disubstituted 1,3-dioxanes **30b–e**, a *cis* relationship between the 4- and 6-substituents was elucidated according to the ^{13}C NMR chemical shift correlation method reported

(16) Mori, K.; Iwasawa, H. *Tetrahedron* **1980**, *36*, 87.

Table V. ^{13}C NMR Chemical Shifts of the Three Acetonide Carbons of **30**

		^{13}C NMR chemical shifts (δ)		
		acetonide Me carbons		
30	1,2-oxasilolane[a]			ketal carbon
30b	**2h**	19.7	30.3	98.2
30c	**2m**	19.7	30.3	98.1
30d	**8**	19.6	30.2	98.4
30e	**11**	19.7	30.1	98.1
30f	**5e**	19.2	30.0	97.6
30g	**5f**	19.5	30.0	98.6
30h	**5g**	19.2	30.0	97.6
30i	**5h**	19.5	30.0	98.9

[a] The parent 1,2-oxasilolane from which **30** was prepared.

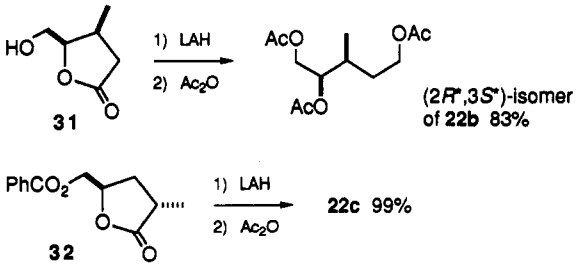
Table VI. ^1H NMR Chemical Shifts of H5 of 1,2-Oxasilolanes

	^1H NMR chemical shifts (δ)	
1,2-oxasilolane	*cis*-isomer	*trans*-isomer
2h	3.81–4.00	4.10–4.27
2m	3.48–3.60	3.64–3.80
2q	4.83	5.10
8	3.72–3.88	3.97–4.12
11	3.34–3.56	3.61–3.86
5e	3.24	3.35
5f	3.14	3.42
5g	3.16	
5h	3.84–3.93	3.95–4.04

recently.[17a] The ^{13}C NMR chemical shifts of the three acetonide carbons fall adequately within the distinguished ranges of 4,6-*cis*-disubstitution [δ (ppm): axial acetonide Me = 19.5 ± 0.2, equatorial acetonide Me = 30.1 ± 0.2, ketal carbon = 98.3 ± 0.7]. The stereochemistries of 4,5,6-trisubstituted 1,3-dioxanes **30f–i** were determined in a similar manner.[17b]

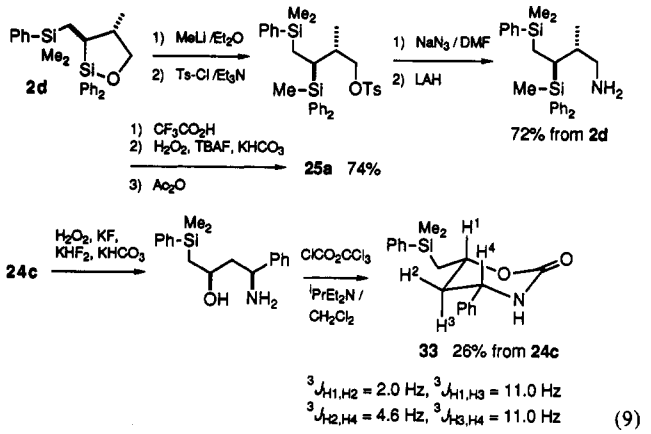
Thus, the *cis* relationship between the 3- and 5-substituents has been established for 3,5-disubstituted and 3,4,5-trisubstituted 1,2-oxasilolanes (**2h,m,q, 5e–h, 8,** and **11**). Listed in Table VI are ^1H NMR chemical shifts of the proton at the 5-position (H5) of those 3,5-*cis*-disubstituted 1,2-oxasilolanes and of the corresponding 3,5-*trans*-disubstituted 1,2-oxasilolanes obtained as minor isomers. Inspection of the chemical shifts in Table VI demonstrates a stereoregular pattern that a 3,5-*cis*-disubstituted 1,2-oxasilolane resonates at higher field than its *trans*-isomer. Application of this correlation to 1,2-oxasilolanes **2i–l,n–p,r, 5a,** and **5b** revealed that all the major isomers have a *cis* relationship between the 3- and 5-substituents without exception.

Reduction of γ-lactone **31**[18] afforded the (2*R**,3*S**)-isomer of **22b**. Similarly, an authentic sample of **22c** was prepared from γ-lactone **32**. Comparison of **22b,c** with those samples established the stereochemistry of the parent silolanes **21b,c**.



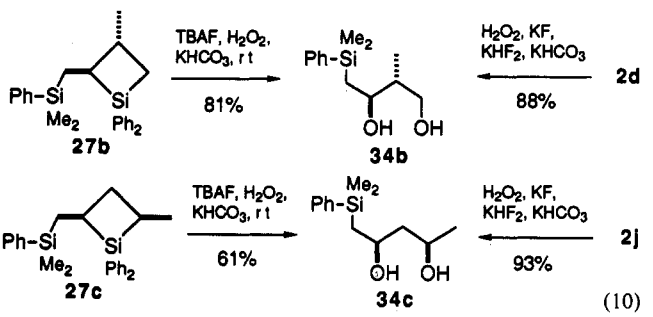
(8)

The 4-acetamido-1,2-diol diacetate **25a** was found to be identical with an authentic sample synthesized from 1,2-oxasilolane **2d** via the route shown in the following scheme. The stereochemistry of the 4-acetamido-1,2-diol diacetate **25c** was elucidated from coupling constants in the ^1H NMR of a 6-membered cyclic carbamate (**33**) derived from the intermediary amide **24c**.



(9)

Oxidation of the siletanes **27b,c** with alkaline hydrogen peroxide led to a facile cleavage of the strained 4-membered rings to afford diols **34b,c**, which have the same configuration as those obtained by partial oxidation of **2d** and **2j**, respectively. The stereochemistries of 1,2,3-triol triacetates **28d–f** were determined by comparison with samples prepared by OsO_4-catalyzed *cis*-dihydroxylation of allylic alcohol derivatives.[13]



(10)

Conclusion

The diastereoselective introduction of silicons into a carbon framework was accomplished in a predictable manner by the intramolecular bis-silylation of C=C bonds. With subsequent oxidation of C–Si bonds, this reaction constitutes a new synthetic transformation equivalent to the stereoselective dihydroxylation of olefins.[13] The present method provides an access to the stereoselective construction of highly polyoxygenated skeletons.

Experimental Section

General Procedure. Column chromatography was performed with silica gel (Wakogel C-200). Preparative thin-layer chromatography (TLC) was performed with silica gel 60 PF_{254} (E. Merck, Darmstadt). ^1H and ^{13}C NMR spectra were acquired in chloroform-*d* unless otherwise noted. Where appropriate, NMR data only for the major stereoisomer were described. Na_2SO_4 was used to dry organic layers after extraction. All reactions were performed under a dry nitrogen atmosphere.

Unless otherwise noted, materials were obtained from commercial sources. THF and ether were distilled from sodium diphenyl ketyl, toluene from $LiAlH_4$, MeOH from $Mg(OMe)_2$, and CH_2Cl_2, DMF, DMSO, and HMPA from CaH_2. 1,1,2,2-Tetramethylpropyl isocyanide (**3c**) was prepared according to the procedure in the literature.[19]

Chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane were prepared according to the procedure in the literature.[20] 1-Chloro-1,1,2,2-tetramethyl-2-phenyldisilane[21] was prepared as follows. To a solution of

(17) (a) Rychnovsky, S. D.; Skalitzky, D. J. *Tetrahedron Lett.* **1990**, *31*, 945. (b) Evans, D. A.; Rieger, D. L.; Gage, J. R. *Ibid.* **1990**, *31*, 7099.

(18) Collum, D. B.; McDonald, J. H.; Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2118.

(19) Ugi, I.; Meyer, R. In *Organic Synthesis*; Baumgarten, H. E., Ed.; Wiley: New York, 1973; Collective Vol. 5, p 1060.

(20) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, 5493.

(21) Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478.

$ClMe_2SiNEt_2$ (39 g, 0.23 mol) in THF (100 mL) in a flask immersed in a water bath was added a solution of $PhMe_2SiLi$, prepared from $PhMe_2SiCl$ (40 g, 0.23 mol) and lithium (6.5 g, 0.94 mol) in THF (200 mL). After the mixture was stirred for 4 h, acetyl chloride (22 g, 0.28 mol) was added and stirring was continued for an additional 2 h. THF was removed under reduced pressure and the residue was diluted with hexane. Filtration through Celite followed by distillation (114–118 °C/17 mmHg) afforded 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane (32 g, 60%). 1-Chloro-2,2-dimethyl-1,1,2-triphenyldisilane[22] was prepared by a similar procedure (180–200 °C/0.1 mmHg, 59%).

Preparation of Disilanyl Ethers 1 and 7. The following describes the general procedure for the synthesis of disilanyl ethers **1** and **7** except **1d,e,j,o**. To a mixture of a homoallylic alcohol (4.3 mmol), Et_3N (6.4 mmol), and a catalytic amount of 4-(dimethylamino)pyridine in THF (10 mL) was added chlorodisilane (4.3 mmol) at room temperature. The reaction was monitored by GC and/or TLC, and after completion, hexane (10 mL) was added to the mixture, which was filtered to remove salts. Kugelrohr distillation or column chromatography (silica gel) of the filtrate afforded a disilanyl ether.

Disilanyl alkenes **1d,j,o** were prepared according to the following procedure. To a mixture of a homoallylic alcohol (5.7 mmol) and 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane (5.7 mmol) in DMF (3.5 mL) was added imidazole (11.4 mmol), which was stirred at room temperature. After completion, the mixture was purified by column chromatography to afford **1**.

Disilanyl alkene **1e** was prepared as follows. To a mixture of 1,2-dichlorotetramethyldisilane (2.0 g, 10.7 mmol) and Et_3N (2.2 g, 22 mmol) in THF (15 mL) at −10 °C was added 2-propanol (0.64 g, 10.7 mmol) in THF (5 mL). After the mixture was stirred for 4.5 h, 2-methyl-3-buten-1-ol (0.92 g, 10.7 mmol) was added and stirring was continued for 1.5 h at −10 °C. Resulting insoluble materials were filtered off, and distillation of the filtrate afforded a crude **1e** (2.6 g, 80% purity by GLC analysis), which was subjected to preparative GLC providing a pure sample of **1e**.

3-[(Dimethylphenylsilyl)methyl]-2,2-dimethyl-1,2-oxasilolane (2a). To a mixture of palladium(II) acetate (25 mg, 0.11 mmol) and *tert*-butyl isocyanide (142 mg, 1.71 mmol) in toluene (3.8 mL) was added **1a** (1.50 g, 5.70 mmol). The mixture was stirred at room temperature for 10 h. Kugelrohr distillation afforded **2a** (1.41 g, 94%) as a colorless liquid: ^{1}H NMR δ 0.06 (s, 3 H), 0.09 (s, 3 H), 0.30 (s, 6 H), 0.76–0.97 (m, 2 H), 1.00–1.15 (m, 1 H), 1.44–1.65 (m, 1 H), 1.93–2.10 (m, 1 H), 3.65 (dt, J = 4.8, 9.5 Hz, 1 H), 3.92 (ddd, J = 3.3, 6.3, 9.5 Hz, 1 H), 7.31–7.40 (m, 3 H), 7.48–7.55 (m, 2 H); ^{13}C NMR δ −3.0, −2.6, −2.4, −1.0, 15.6, 19.4, 36.8, 65.9, 127.8, 129.0, 133.6, 139.4; IR (neat) 2968, 1430, 1252, 1114, 1042, 834 cm^{-1}. Anal. Calcd for $C_{14}H_{24}OSi_2$: C, 63.57; H, 9.14. Found: C, 63.48; H, 9.16.

The following intramolecular bis-silylation reactions producing **2** and **5** were carried out according to the preceding procedure for **2a**. 1,2-Oxasilolanes **2d,j,o** were isolated by column chromatography.

(3*R,4*R**)-2,2,4-Trimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2b)**: ^{1}H NMR δ 0.00 (s, 9 H), 0.12 (s, 3 H), 0.24 (s, 3 H), 0.49–0.60 (m, 2 H), 0.67–0.85 (m, 1 H), 0.94 (d, J = 6.4 Hz, 3 H), 1.61–1.84 (m, 1 H), 3.26 (dd, J = 9.4, 10.4 Hz, 1 H), 3.98 (dd, J = 6.3, 9.4 Hz, 1 H); ^{13}C NMR δ −2.4, −1.2, −0.2, 14.6, 15.5, 28.3, 43.2, 72.7; IR (neat) 2968, 2876, 1252, 1038, 856, 820 cm^{-1}. Anal. Calcd for $C_{10}H_{24}OSi_2$: C, 55.49; H, 11.18. Found: C, 55.61; H, 11.40.

(3*R,4*R**)-3-[(Dimethylphenylsilyl)methyl]-2,2,4-trimethyl-1,2-oxasilolane (2c)**: ^{1}H NMR δ 0.028 (s, 3 H), 0.035 (s, 3 H), 0.30 (s, 3 H), 0.32 (s, 3 H), 0.50 (dt, J = 2.8, 11.3 Hz, 1 H), 0.81 (dd, J = 11.3, 14.7 Hz, 1 H), 0.93 (d, J = 6.5 Hz, 3 H), 1.04 (dd, J = 2.8, 14.7 Hz, 1 H), 1.60–1.88 (m, 1 H), 3.24 (dd, J = 9.4, 10.5 Hz, 1 H), 3.97 (dd, J = 6.2, 9.4 Hz, 1 H), 7.32–7.60 (m, 5 H); ^{13}C NMR δ −2.8, −2.6, −0.5, 13.9, 15.5, 28.1, 43.2, 72.6, 127.8, 129.0, 133.7, 139.0; IR (neat) 2968, 2876, 1430, 1252, 1114, 1036, 838 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.42; H, 9.67.

(3*R,4*R**)-3-[(Dimethylphenylsilyl)methyl]-4-methyl-2,2-diphenyl-1,2-oxasilolane (2d)**: ^{1}H NMR δ 0.16 (s, 3 H), 0.19 (s, 3 H), 0.78–1.08 (m, 2 H), 1.02 (d, J = 6.5 Hz, 3 H), 1.18 (dt, J = 3.5, 10.0 Hz, 1 H), 1.90–2.14 (m, 1 H), 3.53 (dd, J = 9.4, 10.3 Hz, 1 H), 4.28 (dd, J = 6.3, 9.4 Hz, 1 H), 7.26–7.70 (m, 15 H); ^{13}C NMR δ −2.7, −2.2, 13.8, 15.8, 26.6, 43.4, 73.3, 127.7, 127.8, 128.9, 130.0, 130.2, 132.7, 133.6, 134.2, 135.0, 135.5, 139.0; IR (neat) 3076, 2964, 2876, 1592, 1432, 1252, 1118, 1026, 836, 796, 734, 700 cm^{-1}. Anal. Calcd for $C_{25}H_{30}OSi_2$: C, 74.57; H, 7.51. Found: C, 74.50; H, 7.56.

(22) Gilman, H.; Tomasi, R. A. *Chem. Ind. (London)* **1963**, 954.

(3*R,4*R**)-3-[(Isopropoxydimethylsilyl)methyl]-2,2,4-trimethyl-1,2-oxasilolane (2e)**: ($Pd(OAc)_2$ (12.9 mg, 0.058 mmol), **3a** (120 mg, 0.86 mmol), toluene (2.3 mL), **1e** (460 mg, 1.8 mmol)): ^{1}H NMR δ 0.08 (s, 3 H), 0.09 (s, 3 H), 0.14 (s, 3 H), 0.24 (s, 3 H), 0.48–0.56 (m, 2 H), 0.75–0.83 (m, 1 H), 0.93 (d, J = 6.5 Hz, 3 H), 1.13 (d, J = 6.1 Hz, 6 H), 1.58–1.82 (m, 1 H), 3.24 (dd, J = 9.5, 10.5 Hz, 1 H), 3.84–4.04 (m, 2 H); ^{13}C NMR δ −2.4, −1.2, −1.1, −0.2, 15.2, 15.4, 25.8, 27.6, 43.0, 64.9, 72.7; IR (neat) 2974, 2880, 1252, 1126, 1038, 838, 782 cm^{-1}. Anal. Calcd for $C_{12}H_{28}O_2Si_2$: C, 55.32; H, 10.83. Found: C, 55.33; H, 11.06.

(3*R,4*R**)-4-(Benzyloxy)-2,2-dimethyl-3-[(dimethylphenylsilyl)methyl]-1,2-oxasilolane (2f)**: ^{1}H NMR δ 0.05 (s, 3 H), 0.12 (s, 3 H), 0.297 (s, 3 H), 0.300 (s, 3 H), 0.83 (dd, J = 9.8, 14.8 Hz, 1 H), 0.97 (dd, J = 4.9, 14.8 Hz, 1 H), 1.26 (ddd, J = 4.9, 6.5, 9.8 Hz, 1 H), 3.60 (ddd, J = 4.4, 5.6, 6.5 Hz, 1 H), 3.69 (dd, J = 5.6, 9.9 Hz, 1 H), 3.98 (dd, J = 4.4, 9.9 Hz, 1 H), 4.46 (s, 2 H), 7.27–7.40 (m, 8 H), 7.48–7.53 (m, 2 H); ^{13}C NMR δ −2.8, −2.7, −2.4, 0.0, 13.3, 25.8, 68.4, 71.3, 86.0, 127.4, 127.8, 128.17, 128.24, 129.0, 133.6, 138.6, 138.9; IR (neat) 2964, 2872, 1252, 1114, 1046, 836, 732, 700 cm^{-1}. Anal. Calcd for $C_{21}H_{30}O_2Si_2$: C, 68.05; H, 8.16. Found: C, 67.78; H, 8.39.

(3*R,4*S**)-4-(Methoxycarbonyl)-2,2-dimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2g)**: ^{1}H NMR δ −0.01 (s, 9 H), 0.15 (s, 3 H), 0.29 (s, 3 H), 0.65 (dd, J = 11.6, 14.7 Hz, 1 H), 0.78 (dd, J = 3.3, 14.7 Hz, 1 H), 1.41 (ddd, J = 3.3, 11.1, 11.6 Hz, 1 H), 2.69 (ddd, J = 6.9, 10.5, 11.1 Hz, 1 H), 3.69 (s, 3 H), 3.74 (dd, J = 9.4, 10.5 Hz, 1 H), 4.12 (dd, J = 6.9, 9.4 Hz, 1 H); ^{13}C NMR δ −2.4, −1.3, −0.5, 15.6, 24.8, 51.7, 54.1, 67.4, 174.2; IR (neat) 2964, 2900, 1740, 1254, 1198, 1040, 858 cm^{-1}. Anal. Calcd for $C_{11}H_{24}O_3Si_2$: C, 50.72; H, 9.29. Found: C, 50.55; H, 9.51.

(3*R,5*R**)-2,2,5-Trimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2h)**: ^{1}H NMR δ 0.01 (s, 9 H), 0.10 (s, 3 H), 0.20 (s, 3 H), 0.51–0.76 (m, 2 H), 1.07–1.20 (m, 2 H), 1.23 (d, J = 6.0 Hz, 3 H), 1.99–2.23 (m, 1 H), 3.81–4.00 (m, 1 H); ^{13}C NMR δ −2.7, −1.3, −1.0, 16.5, 21.3, 23.3, 45.2, 73.2; IR (neat) 2968, 2864, 1252, 1100, 1048, 940 cm^{-1}; MS m/z 216 (M^+). Anal. Calcd for $C_{10}H_{24}OSi_2$: C, 55.49; H, 11.18. Found: C, 55.46; H, 11.03.

(3*R,5*R**)-3-[(Dimethylphenylsilyl)methyl]-2,2,5-trimethyl-1,2-oxasilolane (2i)**: ^{1}H NMR δ 0.06 (s, 3 H), 0.10 (s, 3 H), 0.30 (s, 3 H), 0.31 (s, 3 H), 0.80–1.28 (m, 4 H), 1.23 (d, J = 6.0 Hz, 3 H), 2.00–2.21 (m, 1 H), 3.75–4.00 (m, 1 H), 7.32–7.60 (m, 5 H); ^{13}C NMR δ −2.7, −2.5, −2.2, −0.9, 16.0, 21.3, 23.4, 45.4, 73.1, 127.8, 129.0, 133.6, 139.3; IR (neat) 2968, 2860, 1252, 1116, 940, 824 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.42; H, 9.53.

(3*R,5*R**)-3-[(Dimethylphenylsilyl)methyl]-5-methyl-2,2-diphenyl-1,2-oxasilolane (2j)**: ^{1}H NMR δ 0.31 (s, 3 H), 0.32 (s, 3 H), 0.75 (dd, J = 9.5, 15.2 Hz, 1 H), 1.13 (dd, J = 4.8, 15.2 Hz, 1 H), 1.22–1.42 (m, 1 H), 1.47 (d, J = 6.0 Hz, 3 H), 1.74–1.94 (m, 1 H), 2.31 (ddd, J = 3.7, 7.3, 12.4 Hz, 1 H), 4.06–4.30 (m, 1 H), 7.30–7.80 (m, 15 H); ^{13}C NMR δ −2.5, −2.2, 15.7, 20.2, 23.3, 44.4, 74.2, 127.67, 127.72, 127.9, 128.9, 130.0, 130.2, 133.1, 133.6, 134.4, 134.7, 135.3, 139.3; IR (neat) 3076, 2972, 2864, 1592, 1432, 1250, 1120, 938, 832, 700 cm^{-1}. Anal. Calcd for $C_{25}H_{30}OSi_2$: C, 74.57; H, 7.51. Found: C, 74.45; H, 7.61.

(3*R,5*R**)-5-Ethyl-2,2-dimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2k)**: ^{1}H NMR δ 0.01 (s, 9 H), 0.10 (s, 3 H), 0.22 (s, 3 H), 0.54–0.77 (m, 2 H), 0.91 (t, J = 7.4 Hz, 3 H), 1.00–1.26 (m, 2 H), 1.37–1.70 (m, 2 H), 2.07–2.20 (m, 1 H), 3.63–3.79 (m, 1 H); ^{13}C NMR δ −2.6, −1.0, −0.8, 9.9, 16.8, 20.9, 30.6, 42.5, 78.4; IR (neat) 2968, 1252, 876, 864, 840 cm^{-1}. Anal. Calcd for $C_{11}H_{26}OSi_2$: C, 57.32; H, 11.37. Found: C, 57.05; H, 11.52.

(3*R,5*R**)-3-[(Dimethylphenylsilyl)methyl]-5-ethyl-2,2-dimethyl-1,2-oxasilolane (2l)**: ^{1}H NMR δ 0.04 (s, 3 H), 0.09 (s, 3 H), 0.29 (s, 3 H), 0.31 (s, 3 H), 0.78–0.97 (m, 5 H), 1.07–1.23 (m, 2 H), 1.31–1.70 (m, 2 H), 2.04–2.17 (m, 1 H), 3.60–3.76 (m, 1 H), 7.30–7.41 (m, 3 H), 7.45–7.56 (m, 2 H); ^{13}C NMR δ −2.7, −2.6, −2.3, −0.9, 9.8, 16.0, 20.8, 30.6, 42.6, 78.3, 127.8, 128.9, 133.6, 139.4; IR (neat) 2968, 1430, 1252, 1116, 878, 832, 780 cm^{-1}. Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.69; H, 9.65. Found: C, 65.56; H, 9.77.

(3*R,5*S**)-5-Isopropyl-2,2-dimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2m)**: ^{1}H NMR δ 0.00 (s, 9 H), 0.08 (s, 3 H), 0.22 (s, 3 H), 0.52–0.76 (m, 2 H), 0.86 (d, J = 6.7 Hz, 3 H), 0.92 (d, J = 6.7 Hz, 3 H), 1.06–1.30 (m, 2 H), 1.54–1.76 (m, 1 H), 1.98–2.10 (m, 1 H), 3.48–3.60 (m, 1 H); ^{13}C NMR δ −2.7, −1.1, −0.8, 16.7, 17.8, 18.7, 20.9, 34.2, 39.5, 82.1; IR (neat) 2968, 2856, 1252, 1038, 864, 840 cm^{-1}; MS m/z 230 (M^+). Anal. Calcd for $C_{12}H_{28}Si_2O$: C, 58.94; H, 11.54. Found: C, 58.75; H, 11.47.

(3*R,5*S**)-3-[(Dimethylphenylsilyl)methyl]-5-isopropyl-2,2-dimethyl-1,2-oxasilolane (2n)**: ^{1}H NMR δ 0.03 (s, 3 H), 0.09 (s, 3 H), 0.30 (s, 3 H), 0.31 (s, 3 H), 0.84 (d, J = 6.7 Hz, 3 H), 0.90 (d, J = 6.8 Hz, 3

H), 0.70–1.38 (m, 4 H), 1.50–1.80 (m, 1 H), 1.95–2.09 (m, 1 H), 3.46–3.58 (m, 1 H), 7.32–7.64 (m, 5 H); ^{13}C NMR δ –2.7, –2.3, –0.9, 16.0, 17.8, 18.7, 20.7, 34.1, 39.5, 81.9, 127.8, 128.9, 133.6, 139.4; IR (neat) 2968, 1472, 1430, 1252, 1114, 1038, 834 cm^{-1}. Anal. Calcd for $C_{17}H_{30}OSi_2$: C, 66.60; H, 9.86. Found: C, 66.50; H, 9.92.

(3*R,5*S**)-3-[(Dimethylphenylsilyl)methyl]-5-isopropyl-2,2-diphenyl-1,2-oxasilolane (2o)**: ^{1}H NMR δ 0.24 (s, 6 H), 0.71 (dd, *J* = 9.4, 15.1 Hz, 1 H), 0.91 (d, *J* = 6.8 Hz, 3 H), 1.04 (d, *J* = 6.8 Hz, 3 H), 0.90–1.14 (m, 1 H), 1.30 (dt, *J* = 11.1, 12.5 Hz, 1 H), 1.62–1.90 (m, 2 H), 2.19 (ddd, *J* = 3.9, 7.4, 12.5 Hz, 1 H), 3.65 (ddd, *J* = 3.9, 6.9, 11.1 Hz, 1 H), 7.30–7.60 (m, 15 H); ^{13}C NMR δ –2.4, –2.2, 15.9, 18.3, 19.4, 20.1, 34.9, 39.8, 83.3, 127.7, 127.8, 127.9, 128.9, 129.9, 130.1, 133.4, 133.6, 133.9, 134.8, 135.4, 139.5; IR (neat) 3144, 2964, 1592, 1432, 1250, 1120, 1032, 1000, 836, 700 cm^{-1}. Anal. Calcd for $C_{27}H_{34}OSi_2$: C, 75.29; H, 7.96. Found: C, 75.06; H, 8.05.

(3*R,5*S**)-5-*tert*-Butyl-2,2-dimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2p)**: ^{1}H NMR δ 0.00 (s, 9 H), 0.06 (s, 3 H), 0.23 (s, 3 H), 0.59 (dd, *J* = 7.0, 14.7 Hz, 1 H), 0.70 (dd, *J* = 7.7, 14.7 Hz, 1 H), 0.88 (s, 9 H), 0.97–1.16 (m, 1 H), 1.25 (dt, *J* = 10.9, 12.2 Hz, 1 H), 1.97 (ddd, *J* = 4.2, 7.0, 12.2 Hz, 1 H), 3.48 (dd, *J* = 4.2, 10.9 Hz, 1 H); ^{13}C NMR δ –2.8, –1.0, –0.7, 16.7, 21.1, 25.7, 34.3, 37.5, 84.8; IR (neat) 2964, 1252, 1028, 886, 862, 834 cm^{-1}. Anal. Calcd for $C_{13}H_{30}OSi_2$: C, 60.39; H, 11.69. Found: C, 60.38; H, 11.75.

(3*R,5*S**)-2,2-Dimethyl-5-phenyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2q)**: ^{1}H NMR δ 0.02 (s, 9 H), 0.24 (s, 3 H), 0.32 (s, 3 H), 0.56–0.81 (m, 2 H), 1.20–1.58 (m, 2 H), 2.33–2.47 (m, 1 H), 4.83 (dd, *J* = 4.1, 10.6 Hz, 1 H), 7.18–7.37 (m, 5 H); ^{13}C NMR δ –2.7, –1.0, –0.8, 16.4, 21.9, 46.5, 78.7, 125.2, 127.0, 128.2, 144.6; IR (neat) 3040, 2964, 2908, 2860, 1252, 1078, 1040, 864, 840 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.65; H, 9.59.

(3*R,5*S**)-5-[(*tert*-Butyldimethylsiloxy)methyl]-2,2-dimethyl-3-[(dimethylphenylsilyl)methyl]-1,2-oxasilolane (2r)**: ^{1}H NMR δ 0.03 (s, 3 H), 0.04 (s, 6 H), 0.09 (s, 3 H), 0.29 (s, 3 H), 0.30 (s, 3 H), 0.84–0.99 (m, 2 H), 0.89 (s, 9 H), 1.01–1.41 (m, 2 H), 2.08 (ddd, *J* = 4.5, 6.8, 12.2 Hz, 1 H), 3.52 (dd, *J* = 5.4, 10.3 Hz, 1 H), 3.64 (dd, *J* = 4.4, 10.3 Hz, 1 H), 3.71–3.87 (m, 1 H), 7.31–7.40 (m, 3 H), 7.47–7.56 (m, 2 H); ^{13}C NMR δ –5.3, –2.7, –2.3, –1.0, 16.0, 18.4, 20.4, 26.0, 39.4, 67.5, 77.2, 127.8, 129.0, 133.6, 139.3; IR (neat) 2964, 1254, 1114, 1092, 836 cm^{-1}. Anal. Calcd for $C_{21}H_{40}O_2Si_3$: C, 61.70; H, 9.86. Found: C, 61.70; H, 10.04.

(3*R,5*R**)-3-[(Dimethylphenylsilyl)methyl]-2,2,3,5-tetramethyl-1,2-oxasilolane (2s)**: ^{1}H NMR δ 0.02 (s, 3 H), 0.09 (s, 3 H), 0.34 (s, 3 H), 0.35 (s, 3 H), 1.00 (d, *J* = 15.1 Hz, 1 H), 1.05 (s, 3 H), 1.07 (d, *J* = 15.1 Hz, 1 H), 1.19 (d, *J* = 6.0 Hz, 3 H), 1.42 (dd, *J* = 10.9, 12.9 Hz, 1 H), 1.63 (dd, *J* = 2.2, 10.9 Hz, 1 H), 3.93–4.10 (m, 1 H), 7.32–7.39 (m, 3 H), 7.48–7.58 (m, 2 H); ^{13}C NMR δ –3.6, –1.1, –0.6, 23.2, 23.6, 25.8, 26.2, 53.3, 71.0, 127.8, 128.8, 133.6, 140.2; IR (neat) 2968, 2912, 1252, 1114, 824 cm^{-1}. Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.69; H, 9.65. Found: C, 65.49; H, 9.79.

(3*R,5*S**)-3-[(Dimethylphenylsilyl)methyl]-2,2,3-trimethyl-5-phenyl-1,2-oxasilolane (2t)**: ^{1}H NMR δ 0.12 (s, 3 H), 0.25 (s, 3 H), 0.37 (s, 3 H), 0.39 (s, 3 H), 0.99–1.44 (m, 2 H), 1.17 (s, 3 H), 1.74 (dd, *J* = 11.1, 13.2 Hz, 1 H), 1.92 (dd, *J* = 4.7, 13.2 Hz, 1 H), 4.95 (dd, *J* = 4.7, 11.1 Hz, 1 H), 7.20–7.65 (m, 10 H); ^{13}C NMR δ –3.7, –1.3, –0.7, –0.6, 23.0, 26.0, 26.2, 54.4, 76.7, 125.2, 126.9, 127.8, 128.2, 128.9, 133.6, 140.0, 144.8; IR (neat) 3076, 2964, 1256, 1114, 1044, 860, 832, 788 cm^{-1}. Anal. Calcd for $C_{21}H_{30}OSi_2$: C, 71.12; H, 8.53. Found: C, 70.98; H, 8.66.

(3*R,4*R**,5*R**)-3-[(Dimethylphenylsilyl)methyl]-2,2,4,5-tetramethyl-1,2-oxasilolane (5a)**: ^{1}H NMR δ –0.01 (s, 3 H), 0.01 (s, 3 H), 0.28 (s, 3 H), 0.29 (s, 3 H), 0.55 (dt, *J* = 2.2, 11.7 Hz, 1 H), 0.79 (dd, *J* = 11.7, 14.6 Hz, 1 H), 0.94 (d, *J* = 6.3 Hz, 3 H), 0.99 (dd, *J* = 2.2, 14.6 Hz, 1 H), 1.22 (d, *J* = 6.0 Hz, 3 H), 1.11–1.32 (m, 1 H), 3.42 (dq, *J* = 9.5, 6.0 Hz, 1 H), 7.31–7.40 (m, 3 H), 7.46–7.55 (m, 2 H); ^{13}C NMR δ –2.8, –2.6, –2.3, –0.6, 14.3, 15.7, 21.7, 29.0, 50.4, 78.9, 127.8, 129.0, 133.7, 139.1; IR (neat) 2968, 2872, 1430, 1378, 1252, 1114, 1042, 938, 834 cm^{-1}. Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.69; H, 9.65. Found: C, 65.57; H, 9.84.

(3*R,4*S**,5*R**)-3-[(Dimethylphenylsilyl)methyl]-2,2,4,5-tetramethyl-1,2-oxasilolane (5b)**: ^{1}H NMR δ 0.03 (s, 3 H), 0.08 (s, 3 H), 0.29 (s, 3 H), 0.31 (s, 3 H), 0.80 (d, *J* = 7.1 Hz, 3 H), 0.85–1.02 (m, 2 H), 1.18 (d, *J* = 6.4 Hz, 3 H), 1.20–1.33 (m, 1 H), 1.93 (d-quintet, *J* = 3.6, 7.1 Hz, 1 H), 3.93 (dq, *J* = 3.6, 6.4 Hz, 1 H), 7.30–7.40 (m, 3 H), 7.46–7.56 (m, 2 H); ^{13}C NMR δ –2.8, –2.4, –1.1, –0.1, 9.1, 12.5, 19.8, 27.2, 43.3, 75.9, 127.8, 129.0, 133.6, 139.2; IR (neat) 2976, 2896, 1430, 1380, 1252, 1114, 1010, 930, 830 cm^{-1}. Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.69; H, 9.65. Found: C, 65.58; H, 9.93.

(3*R,4*R**,5*R**)-3-[(Dimethylphenylsilyl)methyl]-2,2,3,4,5-pentamethyl-1,2-oxasilolane (5c)**: ^{1}H NMR δ –0.05 (s, 3 H), 0.07 (s, 3 H), 0.329 (s, 3 H), 0.335 (s, 3 H), 0.78 (d, *J* = 6.8 Hz, 3 H), 0.82 (d, *J* = 15.0 Hz, 1 H), 0.82 (s, 3 H), 1.08 (d, *J* = 15.0 Hz, 1 H), 1.20 (d, *J* = 6.0 Hz, 3 H), 1.26–1.42 (m, 1 H), 3.57 (dq, *J* = 9.9, 6.0 Hz, 1 H), 7.30–7.40 (m, 3 H), 7.47–7.57 (m, 2 H); ^{13}C NMR δ –3.1, –1.1, –0.8, 8.2, 16.9, 22.1, 24.2, 27.3, 53.1, 76.5, 127.8, 128.9, 133.8, 139.9; IR (neat) 2972, 1456, 1430, 1380, 1252, 1116, 1076, 936, 824 cm^{-1}. Anal. Calcd for $C_{17}H_{30}OSi_2$: C, 66.60; H, 9.86. Found: C, 66.64; H, 9.88.

(3*R,4*S**,5*R**)-3-[(Dimethylphenylsilyl)methyl]-2,2,3,4,5-pentamethyl-1,2-oxasilolane (5d)**: ^{1}H NMR δ –0.01 (s, 3 H), 0.16 (s, 3 H), 0.357 (s, 3 H), 0.363 (s, 3 H), 0.88 (d, *J* = 7.3 Hz, 3 H), 1.00–1.12 (m, 2 H), 1.13 (s, 3 H), 1.17 (d, *J* = 6.4 Hz, 3 H), 1.43 (dq, *J* = 3.9, 7.3 Hz, 1 H), 4.33 (dq, *J* = 3.9, 6.4 Hz, 1 H), 7.30–7.40 (m, 3 H), 7.49–7.60 (m, 2 H); ^{13}C NMR δ –2.7, –0.43, –0.38, 0.0, 10.6, 19.6, 22.5, 25.1, 29.5, 50.8, 73.1, 127.8, 128.8, 133.6, 140.4; IR (neat) 2976, 1456, 1430, 1380, 1254, 1114, 1072, 932, 832 cm^{-1}. Anal. Calcd for $C_{17}H_{30}OSi_2$: C, 66.60; H, 9.86. Found: C, 66.43; H, 9.96.

(3*R,4*R**,5*R**)-3-[(Dimethylphenylsilyl)methyl]-5-isopropyl-2,2,4-trimethyl-1,2-oxasilolane (5e)**: ^{1}H NMR δ –0.02 (s, 3 H), 0.00 (s, 3 H), 0.28 (s, 3 H), 0.29 (s, 3 H), 0.54 (dt, *J* = 2.2, 11.4 Hz, 1 H), 0.79 (d, *J* = 6.8 Hz, 3 H), 0.86 (d, *J* = 6.4 Hz, 3 H), 0.99 (d, *J* = 7.0 Hz, 3 H), 0.71–1.09 (m, 2 H), 1.32–1.56 (m, 1 H), 1.64–1.82 (m, 1 H), 3.24 (dd, *J* = 2.0, 9.6 Hz, 1 H), 7.32–7.40 (m, 3 H), 7.42–7.58 (m, 2 H); ^{13}C NMR δ –2.8, –2.5, –0.5, 14.2, 14.7, 16.3, 21.0, 28.9, 30.1, 44.5, 87.3, 127.8, 129.0, 133.7, 139.2; IR (neat) 2968, 2892, 1472, 1430, 1386, 1252, 1114, 1006, 834 cm^{-1}. Anal. Calcd for $C_{18}H_{32}OSi_2$: C, 67.43; H, 10.06. Found: C, 67.13; H, 10.09.

(3*R,4*S**,5*R**)-3-[(Dimethylphenylsilyl)methyl]-5-isopropyl-2,2,4-trimethyl-1,2-oxasilolane (5f)**: ^{1}H NMR δ 0.03 (s, 3 H), 0.08 (s, 3 H), 0.29 (s, 3 H), 0.31 (s, 3 H), 0.71–1.04 (m, 2 H), 0.77 (d, *J* = 7.1 Hz, 3 H), 0.79 (d, *J* = 6.7 Hz, 3 H), 0.99 (d, *J* = 6.5 Hz, 3 H), 1.21 (dt, *J* = 8.8, 6.6 Hz, 1 H), 1.52–1.79 (m, 1 H), 2.04 (ddq, *J* = 2.9, 6.6, 6.7 Hz, 1 H), 3.14 (dd, *J* = 2.9, 9.6 Hz, 1 H), 7.28–7.42 (m, 3 H), 7.43–7.60 (m, 2 H); ^{13}C NMR δ –2.8, –2.3, –1.0, 0.1, 8.7, 12.7, 18.5, 20.9, 27.5, 30.8, 40.7, 86.4, 127.8, 129.0, 133.7, 139.4; IR (neat) 2968, 2900, 1472, 1430, 1382, 1252, 1116, 988, 832 cm^{-1}. Anal. Calcd for $C_{18}H_{32}OSi_2$: C, 67.43; H, 10.06. Found: C, 67.20; H, 10.27.

(1*R,6*R**,9*R**)-9-[(Dimethylphenylsilyl)methyl]-8,8-dimethyl-7-oxa-8-silabicyclo[4.3.0]nonane (5g)**: ^{1}H NMR δ 0.02 (s, 3 H), 0.04 (s, 3 H), 0.28 (s, 3 H), 0.29 (s, 3 H), 0.54–0.91 (m, 3 H), 0.96–1.38 (m, 5 H), 1.65–1.85 (m, 2 H), 1.97–2.12 (m, 2 H), 3.16 (dt, *J* = 4.0, 10.2 Hz, 1 H), 7.31–7.41 (m, 3 H), 7.45–7.55 (m, 2 H); ^{13}C NMR δ –2.8, –2.7, –2.6, –0.6, 13.2, 24.8, 26.1, 26.7, 29.4, 34.4, 54.0, 80.7, 127.8, 129.0, 133.7, 139.1; IR (neat) 2940, 2864, 1450, 1430, 1252, 1114, 1016, 836 cm^{-1}. Anal. Calcd for $C_{18}H_{30}OSi_2$: C, 67.86; H, 9.49. Found: C, 67.63; H, 9.74.

(1*S,6*R**,9*R**)-9-[(Dimethylphenylsilyl)methyl]-8,8-dimethyl-7-oxa-8-silabicyclo[4.3.0]nonane (5h)**: ^{1}H NMR δ 0.05 (s, 3 H), 0.12 (s, 3 H), 0.29 (s, 3 H), 0.30 (s, 3 H), 0.82–2.10 (m, 12 H), 3.84–3.93 (m, 1 H), 7.31–7.45 (m, 3 H), 7.45–7.60 (m, 2 H); ^{13}C NMR δ –2.8, –2.4, –1.2, 0.1, 11.4, 20.0, 24.3, 25.5, 27.6, 31.3, 44.8, 75.5, 127.8, 129.0, 133.6, 139.3; IR (neat) 2940, 2864, 1450, 1430, 1252, 1114, 974, 834 cm^{-1}. Anal. Calcd for $C_{18}H_{30}OSi_2$: C, 67.86; H, 9.49. Found: C, 67.75; H, 9.76.

(2*R,3*R**)-3-Methylbutane-1,2,4-triol Triacetate (6a).** A mixture of **2c** (112 mg, 0.40 mmol) and trifluoroacetic acid (917 mg, 8.0 mmol) was stirred at 50 °C for 2.5 h. After removal of trifluoroacetic acid under reduced pressure, KHF_2 (125 mg, 1.6 mmol), MeOH (0.7 mL), KF (47 mg, 0.80 mmol), THF (0.7 mL), H_2O_2 (30% in water, 0.48 mL), and $KHCO_3$ (322 mg, 3.2 mmol) were added, and the mixture was stirred at 40 °C for 4 h. Excess $Na_2S_2O_3$ was added and abolition of H_2O_2 was ascertained by test paper. After evaporation of volatiles, THF (2 mL), Et_3N (609 mg, 6.0 mmol), acetic anhydride (410 mg, 4.0 mmol), and a catalytic amount of 4-(dimethylamino)pyridine were added and the mixture was stirred for 10 h. Column chromatography (hexane:ether = 2:1–1:1) afforded **6a** (76 mg, 77%).[23]

The following oxidative transformations producing **6b,d,f,g,i,k,l** were carried out according to the preceding procedure for **6a**.

(2*R,4*R**)-Pentane-1,2,4-triol Triacetate (6b)**: ^{1}H NMR δ 1.25 (d, *J* = 6.3 Hz, 3 H), 1.77 (dt, *J* = 5.8, 14.4 Hz, 1 H), 1.88–2.04 (m, 1 H), 2.03 (s, 3 H), 2.06 (s, 6 H), 4.02 (dd, *J* = 6.1, 12.0 Hz, 1 H), 4.27 (dd, *J* = 3.5, 12.0 Hz, 1 H), 4.88–5.04 (m, 1 H), 5.08–5.20 (m, 1 H); ^{13}C NMR δ 19.9, 20.7, 21.0, 21.3, 36.6, 64.8, 67.5, 68.6, 170.3, 170.4, 170.7;

(23) Bhat, K. S.; Dixit, K. N.; Rao, A. S. *Indian J. Chem., Sect. B* **1985**, *24B*, 509.

IR (neat) 2988, 1738, 1442, 1376, 1240, 1086, 1050 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.56; H, 7.48.

(2*R,4*R**)-1,4-Diacetoxy-2-methylpentan-2-ol (6d)**: ^{1}H NMR δ 1.23 (s, 3 H), 1.28 (d, J = 6.2 Hz, 3 H), 1.66 (dd, J = 3.3, 15.1 Hz, 1 H), 1.94 (dd, J = 8.7, 15.1 Hz, 1 H), 2.04 (s, 3 H), 2.11 (s, 3 H), 2.12–2.60 (br, 1 H), 3.95 (s, 2 H), 5.08–5.27 (m, 1 H); ^{13}C NMR δ 20.8, 21.5, 21.6, 24.5, 44.5, 67.8, 70.8, 70.9, 170.7, 171.0; IR (neat) 3504, 2988, 1740, 1378, 1256, 1048 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.97; H, 8.48.

(2*R,3*R**,4*R**)-3-Methylpentane-1,2,4-triol Triacetate (6f)**: ^{1}H NMR δ 0.96 (d, J = 7.1 Hz, 3 H), 1.17 (d, J = 6.5 Hz, 3 H), 2.04 (s, 3 H), 2.05 (s, 3 H), 2.08 (s, 3 H), 2.00–2.22 (m, 1 H), 4.03 (dd, J = 7.0, 12.2 Hz, 1 H), 4.35 (dd, J = 2.9, 12.2 Hz, 1 H), 4.94 (m, 1 H), 5.07 (dt, J = 2.9, 7.0 Hz, 1 H); ^{13}C NMR δ 19.7, 24.1, 28.2, 28.4, 28.6, 43.5, 65.2, 71.4, 72.7, 157.9, 158.0, 158.2; IR (neat) 2992, 1740, 1444, 1378, 1252, 1050, 1028 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.49; H, 8.02.

(2*R,3*R**,4*R**)-1,4-Diacetoxy-2,3-dimethylpentan-2-ol (6g)**: ^{1}H NMR δ 0.92 (d, J = 7.1 Hz, 3 H), 1.12 (s, 3 H), 1.25 (d, J = 6.4 Hz, 3 H), 1.95–2.12 (m, 1 H), 2.04 (s, 3 H), 2.11 (s, 3 H), 2.15–2.55 (br, 1 H), 3.96 (d, J = 11.4 Hz, 1 H), 4.04 (d, J = 11.4 Hz, 1 H), 5.15 (quintet, J = 6.4 Hz, 1 H); ^{13}C NMR δ 10.6, 17.5, 20.8, 21.5, 43.2, 70.2, 71.6, 73.4, 170.3, 171.0; IR (neat) 3508, 2992, 1740, 1380, 1250, 1046 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.73; H, 8.89.

(2*R,3*R**,4*R**)-3,5-Dimethylhexane-1,2,4-triol Triacetate (6i)**: ^{1}H NMR δ 0.83 (d, J = 6.7 Hz, 3 H), 0.91 (d, J = 6.7 Hz, 3 H), 0.92 (d, J = 7.3 Hz, 3 H), 1.82–2.28 (m, 2 H), 2.01 (s, 3 H), 2.04 (s, 3 H), 2.08 (s, 3 H), 4.05 (dd, J = 8.6, 12.0 Hz, 1 H), 4.33 (dd, J = 2.7, 12.0 Hz, 1 H), 4.71 (t, J = 6.5 Hz, 1 H), 5.16 (ddd, J = 2.7, 4.3, 8.6 Hz, 1 H); ^{13}C NMR δ 12.1, 17.0, 19.4, 20.7, 20.8, 21.0, 29.5, 36.5, 63.2, 71.5, 78.8, 170.2, 170.68, 170.71; IR (neat) 2980, 1754, 1468, 1442, 1376, 1240, 1088, 1048 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.04; H, 8.62.

(1*R,2*R**,1′*R**)-2-(1′,2′-Diacetoxyethyl)cyclohexanol Acetate (6k)**: ^{1}H NMR δ 1.03–1.40 (m, 4 H), 1.55–1.75 (m, 2 H), 1.75–1.91 (m, 2 H), 1.91–2.12 (m, 1 H), 1.98 (s, 3 H), 2.03 (s, 3 H), 2.04 (s, 3 H), 4.02 (dd, J = 8.3, 11.9 Hz, 1 H), 4.21 (dd, J = 3.5, 11.9 Hz, 1 H), 4.65 (dt, J = 4.5, 10.1 Hz, 1 H), 5.17 (dt, J = 8.3, 3.5 Hz, 1 H); ^{13}C NMR δ 20.7, 20.9, 21.3, 23.9, 24.7, 26.6, 31.7, 43.5, 63.8, 71.7, 72.7, 170.3, 170.7; IR (neat) 2948, 2872, 1740, 1454, 1372, 1236, 1040 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.73; H, 7.74. Found: C, 58.57; H, 7.96.

(2*R,4*R**)-Hept-6-ene-1,2,4-triol Triacetate (6l)**: ^{1}H NMR δ 1.80–1.91 (m, 2 H), 2.01 (s, 3 H), 2.026 (s, 3 H), 2.031 (s, 3 H), 2.18–2.44 (m, 2 H), 4.00 (dd, J = 6.0, 12.1 Hz, 1 H), 4.23 (dd, J = 3.4, 12.1 Hz, 1 H), 4.86–5.18 (m, 4 H), 5.58–5.81 (m, 1 H); ^{13}C NMR δ 20.6, 21.0, 21.1, 34.3, 38.4, 64.6, 68.6, 69.7, 118.4, 132.8, 170.2, 170.3, 170.5; IR (neat) 2984, 1740, 1442, 1376, 1240, 1048, 1026 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.36; H, 7.49.

(2*R,4*S**)-5-Methylhexane-1,2,4-triol Triacetate (6c).** To a solution of **2n** (717 mg, 2.34 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added HBF_4·OEt_2 (85%, 1.1 g, 5.7 mmol), and the mixture was stirred for 1 h. After evaporation of volatiles, THF (10 mL), MeOH (10 mL), KF (273 mg, 4.7 mmol), $KHCO_3$ (1.17 g, 11.7 mmol), and H_2O_2 (30% in water, 2.34 mL) were added, and the mixture was stirred at 40 °C for 4 h. Excess $Na_2S_2O_3$ was added and abolition of H_2O_2 was ascertained by test paper. After evaporation of volatiles, the residue was acetylated by a procedure similar to that used for **6a** to give **6c** (519 mg, 81%): ^{1}H NMR δ 0.87 (d, J = 6.8 Hz, 3 H), 0.88 (d, J = 6.9 Hz, 3 H), 1.70–1.95 (m, 3 H), 2.037 (s, 3 H), 2.043 (s, 3 H), 2.05 (s, 3 H), 4.05 (dd, J = 5.9, 12.1 Hz, 1 H), 4.27 (dd, J = 3.2, 12.1 Hz, 1 H), 4.78 (q, J = 5.9 Hz, 1 H), 5.00–5.13 (m, 1 H); ^{13}C NMR δ 17.4, 18.1, 20.7, 21.0, 31.4, 32.0, 64.5, 69.1, 74.6, 170.3, 170.6, 170.7; IR (neat) 2980, 1740, 1376, 1240 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 56.70; H, 8.31.

(2*R,4*S**)-1,4-Diacetoxy-2-methyl-4-phenylbutan-2-ol (6e). Method A.** To a solution of **2t** (100 mg, 0.282 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C was added ICl (1 M in CH_2Cl_2, 0.3 mmol), and the mixture was stirred for 3 h. After evaporation of volatiles, THF (1 mL), 2-propanol (51 mg, 0.85 mmol), and Et_3N (86 mg, 0.85 mmol) were added. The mixture was stirred at room temperature for 10 h and then passed through a short column of silica gel. After evaporation, TBAF (1 M in THF, 1.1 mmol), MeOH (1 mL), H_2O_2 (30% in water, 0.34 mL), and $KHCO_3$ (56 mg, 0.56 mmol) were added to the residue, which was stirred at 40 °C for 4 h. Excess $Na_2S_2O_3$ was added and abolition of H_2O_2 was ascertained by test paper. After evaporation of volatiles, the residue was acetylated by a procedure similar to that used for **6a** to give **6e** (53 mg, 67%).

Method B. To a solution of **2t** (100 mg, 0.282 mmol) in DMSO (0.5 mL) at room temperature was added KOBu^t (35 mg, 0.31 mmol). The mixture was stirred for 4 h, then diluted with ether (10 mL) and phosphate buffer solution (pH 7), and extracted with ether. After evaporation, oxidation and acetylation of the residue were carried out by a procedure similar to that of method A to give **6e** (62 mg, 78%): ^{1}H NMR (C_6D_6) δ 1.09 (s, 3 H), 1.68 (s, 3 H), 1.69 (s, 3 H), 1.79 (dd, J = 3.5, 14.9 Hz, 1 H), 2.20 (dd, J = 9.2, 14.9 Hz, 1 H), 2.30–2.70 (br, 1 H), 3.94–4.06 (m, 2 H), 6.29 (dd, J = 3.5, 9.2 Hz, 1 H), 7.02–7.40 (m, 5 H); ^{13}C NMR (C_6D_6) δ 19.3, 19.9, 24.1, 44.6, 69.7, 70.0, 71.7, 125.9, 126.8, 127.3, 141.2, 168.7, 169.4; IR (neat) 3492, 2984, 1740, 1378, 1248, 1046 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.26; H, 7.15.

(2*R,3*S**,4*R**)-1,4-Diacetoxy-2,3-dimethylpentan-2-ol (6h)**: ^{1}H NMR δ 1.04 (d, J = 7.2 Hz, 3 H), 1.18 (s, 3 H), 1.22 (d, J = 6.5 Hz, 3 H), 1.70 (dq, J = 1.6, 7.2 Hz, 1 H), 2.01 (s, 3 H), 2.07 (s, 3 H), 3.95 (d, J = 11.4 Hz, 1 H), 4.05 (d, J = 11.4 Hz, 1 H), 5.29 (dq, J = 1.6, 6.5 Hz, 1 H); ^{13}C NMR δ 7.8, 19.3, 20.8, 21.4, 23.0, 44.9, 69.2, 69.3, 73.3, 170.6, 171.1; IR (neat) 3504, 2988, 1740, 1378, 1248 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.70; H, 8.82.

(2*R,3*S**,4*R**)-3,5-Dimethylhexane-1,2,4-triol Triacetate (6j)**: ^{1}H NMR δ 0.87 (d, J = 6.6 Hz, 3 H), 0.89 (d, J = 6.8 Hz, 3 H), 0.95 (d, J = 7.0 Hz, 3 H), 1.85–2.20 (m, 2 H), 2.05 (s, 3 H), 2.07 (s, 3 H), 2.09 (s, 3 H), 4.11 (dd, J = 6.5, 12.1 Hz, 1 H), 4.34 (dd, J = 3.3, 12.1, Hz, 1 H), 4.75 (dd, J = 4.4, 7.4 Hz, 1 H), 4.99 (dt, J = 3.3, 6.5 Hz, 1 H); ^{13}C NMR δ 9.6, 17.8, 19.1, 20.6, 20.8, 29.7, 35.2, 63.4, 72.5, 77.4, 170.3, 170.5, 170.7; IR (neat) 2988, 1746, 1374, 1240, 1048, 1022 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.25; H, 8.54.

(3*S,5*S**)-5-Allyl-3-[(dimethylphenylsilyl)methyl]-2,2-dimethyl-1,2-oxasilolane (8).** By a procedure similar to that used to prepare **2a**, the intramolecular bis-silylation of **7** was carried out using 1,1,3,3-tetramethylbutyl isocyanide (**3a**) to give **8** (96%): ^{1}H NMR δ 0.05 (s, 3 H), 0.09 (s, 3 H), 0.29 (s, 3 H), 0.30 (s, 3 H), 0.76–1.30 (m, 4 H), 2.02–2.12 (m, 1 H), 2.12–2.40 (m, 2 H), 3.72–3.88 (m, 1 H), 4.99–5.11 (m, 2 H), 5.69–5.91 (m, 1 H), 7.32–7.40 (m, 3 H), 7.46–7.60 (m, 2 H); ^{13}C NMR δ –2.8, –2.7, –2.3, –0.9, 16.0, 20.7, 42.1, 42.7, 76.2, 116.7, 127.8, 129.0, 133.6, 135.0, 139.2; IR (neat) 3076, 2964, 2856, 1646, 1430, 1252, 1116, 828 cm^{-1}. Anal. Calcd for $C_{17}H_{28}OSi_2$: C, 67.04; H, 9.27. Found: C, 66.85; H, 9.51.

(4*S,6*S**)-6,7-Bis(dimethylphenylsilyl)hept-1-en-4-ol (9).** To a solution of **8** (263 mg, 0.863 mmol) in ether (3 mL) at room temperature was added PhLi (0.56 M, 1.9 mL, 1.0 mmol). The mixture was stirred for 2 h and then diluted with water. Extraction with ether followed by column chromatography on silica gel (ether:hexane = 1:9) afforded **9** (290 mg, 88%) as a mixture of diastereomers. The major isomer was isolated by HPLC: ^{1}H NMR δ 0.23 (s, 3 H), 0.26 (s, 6 H), 0.30 (s, 3 H), 0.60 (dd, J = 7.4, 15.4 Hz, 1 H), 0.90–1.38 (m, 4 H), 1.47–1.61 (m, 1 H), 1.78–2.10 (m, 2 H), 3.22–3.38 (m, 1 H), 4.95–5.09 (m, 2 H), 5.44–5.66 (m, 1 H), 7.34–7.60 (m, 10 H); ^{13}C NMR δ –4.8, –4.3, –3.0, –2.2, 15.2, 16.0, 40.7, 42.2, 68.8, 117.6, 127.2, 127.8, 128.9, 129.0, 133.7, 134.1, 135.1, 138.7, 139.7; IR (neat) 3592, 3484, 3076, 2964, 2908, 1644, 1430, 1250, 1114, 818, 700 cm^{-1}. Anal. Calcd for $C_{23}H_{34}OSi_2$: C, 72.19; H, 8.95. Found: C, 72.25; H, 9.03.

(4*S,6*S**)-6,7-Bis(dimethylphenylsilyl)-4-[(1′,1′,2′,2′-tetramethyl-2′-phenyldisilan-1′-yl)oxy]hept-1-ene (10).** According to the general procedure for the synthesis of disilanyl ethers **1**, the title compound **10** was obtained in 89% yield from **9**: ^{1}H NMR δ 0.10 (s, 3 H), 0.13 (s, 3 H), 0.22 (s, 3 H), 0.26 (s, 6 H), 0.29 (s, 3 H), 0.34 (s, 6 H), 0.59 (dd, J = 10.0, 15.1 Hz, 1 H), 0.85–1.11 (m, 2 H), 1.30–1.60 (m, 2 H), 1.72–1.90 (m, 1 H), 1.93–2.10 (m, 1 H), 3.38–3.53 (m, 1 H), 4.79–5.00 (m, 2 H), 5.38–5.59 (m, 1 H), 7.32–7.60 (m, 15 H); ^{13}C NMR δ –4.3, –3.8, –3.7, –2.3, –1.9, 0.3, 0.6, 16.2, 17.0, 41.0, 42.0, 72.0, 116.4, 127.7, 128.4, 128.8, 133.6, 133.9, 134.0, 135.4, 139.3, 139.8; IR (neat) 2964, 1430, 1250, 1112, 1062, 830, 814, 790, 700 cm^{-1}. Anal. Calcd for $C_{33}H_{50}OSi_4$: C, 68.92; H, 8.76. Found: C, 68.86; H, 8.85.

(3*R,5*R**,2′*S**)-5-[2′,3′-Bis(dimethylphenylsilyl)propyl]-3-[(dimethylphenylsilyl)methyl]-2,2-dimethyl-1,2-oxasilolane (11).** By a procedure similar to that used to prepare **2a**, the intramolecular bis-silylation of **10** was carried out using 1,1,3,3-tetramethylbutyl isocyanide (**3a**) to give **11** (95%): ^{1}H NMR δ –0.05 (s, 3 H), 0.02 (s, 3 H), 0.18 (s, 3 H), 0.20 (s, 3 H), 0.23 (s, 3 H), 0.25 (s, 3 H), 0.27 (s, 6 H), 0.54 (dd, J = 8.9, 15.3 Hz, 1 H), 0.65–0.99 (m, 5 H), 1.00–1.16 (m, 1 H), 1.17–1.33 (m, 1 H), 1.55–1.82 (m, 2 H), 3.38–3.53 (m, 1 H), 7.28–7.55 (m, 15 H); ^{13}C NMR δ –4.6, –4.3, –2.7, –2.6, –2.3, –1.0, 15.75, 15.84, 16.2, 20.7, 42.3, 43.3, 75.4, 127.6, 127.7, 127.8, 128.7, 128.9, 133.6, 134.0, 139.2, 139.5, 139.9; IR (neat) 2964, 1430, 1250, 1114, 832 cm^{-1}. Anal. Calcd for $C_{33}H_{50}OSi_4$: C, 68.92; H, 8.76. Found: C, 69.02; H, 8.96.

(2*S,4*R**,6*R**)-Heptane-1,2,4,6,7-pentanol Pentaacetate (12).** By a procedure similar to that used to prepare **6a**, the title compound **12** was obtained in 44% yield from **11**: ^{1}H NMR δ 1.81–1.99 (m, 4 H), 2.05 (s, 9 H), 2.06 (s, 6 H), 4.01 (dd, *J* = 5.9, 12.0 Hz, 2 H), 4.24 (dd, *J* = 3.5, 12.0 Hz, 2 H), 4.98 (quintet, *J* = 6.2 Hz, 1 H), 5.03–5.16 (m, 2 H); ^{13}C NMR δ 20.7, 21.0, 21.1, 34.8, 64.5, 67.5, 68.3, 170.3, 170.6; IR (neat) 2964, 1740, 1444, 1376, 1240, 1048 cm^{-1}. Anal. Calcd for $C_{17}H_{26}O_{10}$: C, 52.30; H, 6.71. Found: C, 52.01; H, 6.70.

(2*R,4*S**)-1-(*tert*-Butyldiphenylsiloxy)-5-methylhexane-2,4-diol (13).** To **6d** (443 mg, 1.61 mmol) in MeOH (10 mL) was added NaOMe (2.6 M in MeOH, 31 μL, 0.081 mmol), and the mixture was stirred for 5 h at room temperature. After the volatiles were evaporated, $ClSiPh_2Bu^t$ (531 mg, 1.93 mmol), DMF (3 mL), and imidazole (274 mg, 4.03 mmol) were added and the mixture was stirred at room temperature for 1 h. Column chromatography on silica gel (ether:hexane = 1:1) afforded **13** (524 mg, 84%): ^{1}H NMR δ 0.89 (d, *J* = 6.8 Hz, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H), 1.07 (s, 9 H), 1.30–1.78 (m, 3 H), 2.6–3.0 (br, 2 H), 3.49–3.68 (m, 3 H), 3.90–4.05 (m, 1 H), 7.35–7.50 (m, 6 H), 7.62–7.71 (m, 4 H); ^{13}C NMR δ 17.5, 18.2, 19.2, 26.8, 33.9, 35.4, 68.0, 73.3, 76.9, 127.8, 129.9, 133.0, 135.5; IR (neat) 3416, 2968, 2868, 1474, 1430, 1114, 1070, 702 cm^{-1}.

(2*R,4*S**)-2,4-Bis(benzyloxy)-5-methylhexan-1-ol (14).** To **13** (325 mg, 0.84 mmol) in THF (1.5 mL) at −78 °C was added butyllithium (1.62 M in hexane, 1.09 mL, 1.77 mmol). After the mixture was stirred for 1 h at −78 °C, benzyl bromide (431 mg, 2.52 mmol) in HMPA (1.5 mL) was added. The mixture was stirred for 30 min at 0 °C and for 2 d at room temperature, extracted with ether, dried over K_2CO_3, and evaporated. To the residue dissolved in THF (3 mL) was added TBAF (1.0 M in THF, 1.26 mL, 1.26 mmol), and the mixture was stirred at room temperature for 1 d. Column chromatography on silica gel (ether:hexane = 1:1) afforded **14** (204 mg, 74%): ^{1}H NMR δ 0.95 (d, *J* = 7.0 Hz, 6 H), 1.69–1.95 (m, 2 H), 1.98–2.18 (m, 1 H), 2.1–2.5 (br, 1 H), 3.31–3.43 (m, 1 H), 3.48–3.63 (m, 1 H), 3.64–3.76 (m, 2 H), 4.44 (d, *J* = 11.4 Hz, 1 H), 4.52 (d, *J* = 11.7 Hz, 1 H), 4.59 (d, *J* = 11.4 Hz, 1 H), 4.63 (d, *J* = 11.7 Hz, 1 H), 7.25–7.47 (m, 10 H); ^{13}C NMR δ 16.8, 18.5, 29.8, 30.6, 63.8, 71.0, 71.2, 77.0, 80.3, 127.6, 127.7, 127.8, 128.3, 128.4, 138.4, 138.5; IR (neat) 3448, 2968, 2880, 1458, 1070, 736, 698 cm^{-1}. Anal. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59. Found: C, 76.97; H, 8.66.

(2*R,4*S**)-2,4-Bis(benzyloxy)-5-methylhexanal (15).** To oxalyl chloride (121 mg, 0.95 mmol) in CH_2Cl_2 (2 mL) at −78 °C was slowly added DMSO (107 mg, 1.37 mmol) in CH_2Cl_2 (0.5 mL), and the mixture was stirred for 10 min. Then, **14** (195 mg, 0.59 mmol) in CH_2Cl_2 (1.5 mL) was added and stirring was continued for 10 min at −78 °C and for 50 min at −50 °C. Et_3N (481 mg, 4.8 mmol) was added, and the mixture was stirred at 0 °C for 20 min and then diluted with saturated aqueous NH_4Cl. Extraction with ether followed by column chromatography on silica gel (ether:hexane = 1:2) afforded **15** (192 mg, 99%): ^{1}H NMR δ 0.93 (d, *J* = 6.8 Hz, 3 H), 0.94 (d, *J* = 7.0 Hz, 3 H), 1.89–2.11 (m, 3 H), 3.52 (dt, *J* = 8.3, 4.6 Hz, 1 H), 3.94 (dt, *J* = 1.1, 5.2 Hz, 1 H), 4.45 (d, *J* = 11.2 Hz, 1 H), 4.52 (d, *J* = 11.2 Hz, 1 H), 4.58 (d, *J* = 11.9 Hz, 1 H), 4.73 (d, *J* = 11.9 Hz, 1 H), 7.20–7.45 (m, 10 H), 9.61 (d, *J* = 1.1 Hz, 1 H); ^{13}C NMR δ 16.9, 18.4, 30.0, 31.8, 71.3, 72.1, 79.0, 80.7, 127.4, 127.7, 127.8, 128.1, 128.2, 128.5, 137.5, 138.5, 202.5; IR (neat) 2968, 1736, 1092, 1072, 734 cm^{-1}. Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 76.99; H, 8.13.

(4*R,5*R**,7*S**)-5,7-Bis(benzyloxy)-8-methylnon-1-en-4-ol (16).** To a mixture of $MgBr_2$, prepared by the reaction of Mg (6.0 mg, 0.25 mmol) with excess 1,2-dibromoethane in ether, and **15** (54 mg, 0.17 mmol) in CH_2Cl_2 (0.7 mL) at −25 °C was added allyltributyltin (60 mg, 0.18 mmol). The mixture was allowed to warm up gradually to room temperature and stirred for 10 h at room temperature. Extraction with ether followed by column chromatography on silica gel (ether:hexane = 1:2) afforded **16** (60 mg, 99%): ^{1}H NMR δ 0.96 (d, *J* = 6.8 Hz, 6 H), 1.70–1.99 (m, 2 H), 2.00–2.20 (m, 1 H), 2.23–2.42 (m, 3 H), 3.36 (dt, *J* = 8.8, 4.0 Hz, 1 H), 3.50 (dt, *J* = 7.5, 4.1 Hz, 1 H), 3.51–3.70 (m, 1 H), 4.41 (d, *J* = 11.5 Hz, 1 H), 4.46 (d, *J* = 11.5 Hz, 1 H), 4.60 (d, *J* = 11.5 Hz, 1 H), 4.67 (d, *J* = 11.5 Hz, 1 H), 4.97–5.18 (m, 2 H), 5.66–5.88 (m, 1 H), 7.24–7.43 (m, 10 H); ^{13}C NMR δ 16.9, 18.4, 30.0, 30.1, 38.3, 71.2, 71.5, 71.8, 78.0, 80.2, 117.2, 127.5, 127.7, 127.8, 128.0, 128.29, 128.34, 135.1, 138.3, 138.7; IR (neat) 3464, 2968, 1644, 1068, 736, 698 cm^{-1}. Anal. Calcd for $C_{24}H_{32}O_3$: C, 78.22; H, 8.75. Found: C, 78.02; H, 8.71.

(4*R,5*R**,7*S**)-5,7-Bis(benzyloxy)-4-[(2′,2′-dimethyl-1′,1′,2′-triphenyldisilanyl)oxy]-8-methylnon-1-ene (17).** To a mixture of **16** (94 mg, 0.26 mmol) and $Me_2PhSiSiPh_2Cl$ (108 mg, 0.31 mmol) in DMF (1 mL) at room temperature was added imidazole (35 mg, 0.51 mmol), and the mixture was stirred for 6 h. Column chromatography on silica gel (ether:hexane = 1:4) afforded **17** (164 mg, 93%): ^{1}H NMR δ 0.46 (s, 3 H), 0.47 (s, 3 H), 0.80 (d, *J* = 6.7 Hz, 6 H), 1.49–1.67 (m, 1 H), 1.72 (ddd, *J* = 6.8, 8.3, 14.6 Hz, 1 H), 1.90 (ddd, *J* = 4.0, 6.8, 14.6 Hz, 1 H), 2.13–2.31 (m, 1 H), 2.36–2.53 (m, 1 H), 3.13 (dt, *J* = 3.8, 6.8 Hz, 1 H), 3.31 (dt, *J* = 8.3, 4.0 Hz, 1 H), 4.01 (dt, *J* = 4.0, 5.6 Hz, 1 H), 4.16 (d, *J* = 11.9 Hz, 1 H), 4.29 (d, *J* = 11.9 Hz, 1 H), 4.33 (d, *J* = 11.8 Hz, 1 H), 4.38 (d, *J* = 11.8 Hz, 1 H), 4.86–5.00 (m, 2 H), 5.55–5.78 (m, 1 H), 7.08–7.62 (m, 25 H); ^{13}C NMR δ −2.72, −2.67, 16.9, 18.9, 30.2, 30.4, 36.9, 71.1, 71.4, 73.7, 78.7, 81.0, 116.7, 127.1, 127.3, 127.5, 127.6, 127.7, 128.08, 128.13, 128.7, 129.5, 129.7, 134.4, 135.1, 135.4, 135.6, 136.3, 136.4, 138.2, 138.9, 139.3; IR (neat) 2968, 1430, 1108, 1070, 734, 700 cm^{-1}.

(3*S,5*R**)-3-[(Dimethylphenylsilyl)methyl]-5-[(1′*R**,3′*S**)-1′,3′-bis(benzyloxy)-4′-methylpentyl]-2,2-diphenyl-1,2-oxasilolane (18).** By a procedure similar to that used to prepare **2a**, the intramolecular bis-silylation of **17** was carried out using 1,1,3,3-tetramethylbutyl isocyanide (**3a**) to give **18** (93%): ^{1}H NMR δ 0.22 (s, 6 H), 0.66 (dd, *J* = 9.3, 15.1 Hz, 1 H), 0.90 (d, *J* = 6.8 Hz, 3 H), 0.92 (d, *J* = 6.8 Hz, 3 H), 1.03 (dd, *J* = 4.3, 15.1 Hz, 1 H), 1.43–2.07 (m, 6 H), 3.27–3.40 (m, 1 H), 3.41–3.52 (m, 1 H), 3.88–4.01 (m, 1 H), 4.43 (d, *J* = 11.7 Hz, 1 H), 4.52 (d, *J* = 11.7 Hz, 1 H), 4.65 (d, *J* = 11.7 Hz, 1 H), 4.72 (d, *J* = 11.7 Hz, 1 H), 7.20–7.62 (m, 25 H); ^{13}C NMR δ −2.4, −2.3, 15.8, 17.8, 17.9, 19.7, 30.3, 31.1, 38.0, 71.0, 72.3, 79.0, 79.3, 80.2, 127.3, 127.6, 127.7, 127.9, 128.0, 128.2, 128.9, 129.9, 130.1, 133.2, 133.6, 134.7, 135.5, 139.1, 139.4; IR (neat) 2968, 1458, 1120, 1068, 832, 724, 698 cm^{-1}. Anal. Calcd for $C_{44}H_{52}O_3Si_2$: C, 77.14; H, 7.65. Found: C, 77.11; H, 7.69.

(2*S,4*R**,5*R**,7*S**)-5,7-Bis(benzyloxy)-8-methylnonane-1,2,4-triol Triacetate (19).** By a procedure similar to that used to prepare **6e** by use of KOBu^t in DMSO, the title compound **19** was obtained in 89% yield from **18**: ^{1}H NMR δ 0.86 (d, *J* = 6.7 Hz, 3 H), 0.88 (d, *J* = 6.6 Hz, 3 H), 1.56–2.00 (m, 5 H), 2.00 (s, 3 H), 2.02 (s, 3 H), 2.06 (s, 3 H), 3.21 (dt, *J* = 7.4, 4.4 Hz, 1 H), 3.59 (dt, *J* = 3.4, 6.1 Hz, 1 H), 3.92 (dd, *J* = 5.8, 12.0 Hz, 1 H), 4.12 (dd, *J* = 3.3, 12.0 Hz, 1 H), 4.43 (d, *J* = 11.4 Hz, 1 H), 4.49 (d, *J* = 11.4 Hz, 1 H), 4.53 (d, *J* = 11.4 Hz, 1 H), 4.61 (d, *J* = 11.4 Hz, 1 H), 4.85–5.00 (m, 1 H), 5.04–5.16 (m, 1 H), 7.20–7.43 (m, 10 H); ^{13}C NMR δ 17.3, 17.9, 20.7, 21.0, 29.8, 30.1, 31.0, 64.5, 69.0, 70.0, 71.2, 71.4, 75.3, 80.1, 127.4, 127.7, 127.8, 128.3, 137.9, 138.9, 170.2, 170.4, 170.6; IR (neat) 2968, 1740, 1374, 1238, 1068, 736, 700 cm^{-1}. Anal. Calcd for $C_{30}H_{40}O_8$: C, 68.16; H, 7.63. Found: C, 68.28; H, 7.69.

Preparation of Disilanyl Alkenes 20. The following describes the general procedure for the synthesis of disilanyl alkenes **20a–c**. The solution of Grignard reagent (6 mmol) in THF (3 mL) at room temperature was added chlorodisilane (3.4 mmol). The mixture was stirred for 10 h, diluted with hexane, and filtered to remove insoluble materials. Column chromatography on silica gel (hexane) afforded the corresponding disilanyl alkene.

Disilanyl alkene **20d** was prepared from a secondary Grignard reagent as follows. To a solution of Grignard reagent, prepared from 5-bromo-1-hexane (1.60 g, 10 mmol) and Mg (0.27 g, 11.0 mmol) in THF (5 mL) at 0 °C were successively added CuCN (70 mg, 1.0 mmol) and 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane (2.8 g, 8.0 mmol). The mixture was stirred at 0 °C for 3 h and at room temperature for 10 h, diluted with hexane, and filtered to remove insoluble materials. Column chromatography on silica gel (hexane) afforded **20d** (2.3 g, 70%).

(2*R,3*R**)-2-[(Dimethylphenylsilyl)methyl]-1,1,3-trimethylsilolane (21a).** To a mixture of palladium(II) acetate (2.2 mg, 10 μmol) and 1,1,3,3-tetramethylbutyl isocyanide (21 mg, 0.15 mmol) in toluene (0.5 mL) was added **20a** (100 mg, 0.36 mmol). The mixture was stirred at 50 °C for 2 h. Preparative TLC of silica gel (hexane) afforded **21a** (87 mg, 87%) as a colorless liquid: ^{1}H NMR δ −0.04 (s, 3 H), −0.01 (s, 3 H), 0.21 (dt, *J* = 2.9, 10.5 Hz, 1 H), 0.30 (s, 6 H), 0.42 (ddd, *J* = 8.2, 12.4, 14.4 Hz, 1 H), 0.67 (ddd, *J* = 2.0, 6.8, 14.4 Hz, 1 H), 0.73–1.10 (m, 3 H), 0.95 (d, *J* = 6.3 Hz, 3 H), 1.15–1.38 (m, 1 H), 1.80–1.95 (m, 1 H), 7.30–7.40 (m, 3 H), 7.49–7.60 (m, 2 H); ^{13}C NMR δ −3.4, −2.6, −2.5, −1.3, 12.4, 14.7, 19.9, 29.0, 34.1, 45.2, 127.6, 128.7, 133.6, 139.9; IR (neat) 2960, 1250, 1114, 836 cm^{-1}. Anal. Calcd for $C_{16}H_{28}Si_2$: C, 69.49; H, 10.20. Found: C, 69.32; H, 10.46.

The following intramolecular bis-silylation reactions of **20b–d** producing **21b–d** were carried out according to the preceding procedure for **21a**.

(2*R,3*R**)-2-[(Dimethylphenylsilyl)methyl]-3-methyl-1,1-diphenylsilolane (21b):** ^{1}H NMR δ 0.09 (s, 3 H), 0.14 (s, 3 H), 0.80–1.33 (m, 6 H), 1.01 (d, *J* = 6.6 Hz, 3 H), 1.51–1.70 (m, 1 H), 2.02–2.18 (m, 1 H), 7.20–7.60 (m, 15 H); ^{13}C NMR δ −2.6, −2.1, 12.0, 15.3, 20.3, 27.4, 33.9, 46.1, 127.6, 127.7, 128.7, 129.1, 129.2, 133.7, 134.9, 135.2, 135.9,

136.3, 139.7; IR (neat) 3076, 2960, 1440, 1258, 1110, 840, 738, 700 cm^{-1}. Anal. Calcd for $C_{26}H_{32}Si_2$: C, 77.93; H, 8.05. Found: C, 78.01; H, 7.96.

(2R*,4R*)-2-[(Dimethylphenylsilyl)methyl]-4-methyl-1,1-diphenylsilolane (21c): ^1H NMR δ 0.23 (s, 3 H), 0.25 (s, 3 H), 0.66 (dd, J = 10.3, 14.8 Hz, 1 H), 0.79 (dd, J = 12.0, 14.8 Hz, 1 H), 0.96–1.10 (m, 1 H), 0.99 (dd, J = 4.2, 8.3 Hz, 1 H), 1.12 (d, J = 6.4 Hz, 3 H), 1.35 (ddd, J = 2.2, 6.1, 15.1 Hz, 1 H), 1.45–1.65 (m, 1 H), 1.65–1.88 (m, 1 H), 2.05–2.20 (m, 1 H), 7.25–7.60 (m, 15 H); ^{13}C NMR δ –2.4, –1.9, 17.1, 21.7, 22.0, 23.7, 34.3, 47.1, 127.7, 127.8, 128.7, 129.2, 133.6, 134.9, 135.2, 135.6, 136.5, 139.9; IR (neat) 3050, 2940, 1450, 1260, 1135, 850, 750, 720 cm^{-1}. Anal. Calcd for $C_{26}H_{32}Si_2$: C, 77.93; H, 8.05. Found: C, 77.92; H, 8.03.

2-[(Dimethylphenylsilyl)methyl]-5-methyl-1,1-diphenylsilolane (21d): ^{13}C NMR (a mixture of isomers) δ –2.5, –2.3, –2.2, –2.1, 16.2, 16.8, 17.1, 17.4, 19.7, 20.4, 21.0, 35.1, 35.5, 35.9, 36.4, 127.5, 127.7, 127.8, 128.7, 129.1, 129.2, 133.6, 133.8, 134.76, 134.83, 135.7, 135.8, 139.9, 140.0. Anal. Calcd for $C_{26}H_{32}Si_2$: C, 77.93; H, 8.05. Found: C, 77.83; H, 8.17.

(2R*,3R*)-3-Methylpentane-1,2,5-triol Triacetate (22b). By a procedure similar to that used to prepare **6a**, the oxidation of **21b** was carried out to give **22b** (70%): ^1H NMR δ 0.97 (d, J = 6.9 Hz, 3 H), 1.34–1.58 (m, 1 H), 1.69–2.10 (m, 2 H), 2.04 (s, 6 H), 2.08 (s, 3 H), 3.98–4.19 (m, 3 H), 4.30 (dd, J = 3.1, 10.8 Hz, 1 H), 4.96 (dt, J = 3.1, 6.9 Hz, 1 H); ^{13}C NMR δ 15.2, 20.7, 20.9, 30.8, 31.2, 62.2, 63.3, 74.7, 170.5, 170.8, 171.0; IR (neat) 2976, 1740, 1374, 1248, 1052 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.16; H, 7.51.

(2R*,4R*)-4-Methylpentane-1,2,5-triol Triacetate (22c). By a procedure similar to that used to prepare **6a**, the oxidation of **21c** was carried out to give **22c** (88%): ^1H NMR δ 0.96 (d, J = 6.8 Hz, 3 H), 1.22–1.43 (m, 1 H), 1.68–1.97 (m, 2 H), 2.06 (s, 9 H), 3.94 (d, J = 5.9 Hz, 2 H), 4.01 (dd, J = 6.8, 11.8 Hz, 1 H), 4.24 (dd, J = 3.6, 11.8 Hz, 1 H), 5.22 (m, 1 H); ^{13}C NMR δ 16.3, 20.7, 20.8, 20.9, 29.0, 34.4, 65.5, 69.1, 170.5, 170.7, 171.0; IR (neat) 2972, 1738, 1376, 1240, 1040 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.24; H, 7.83.

Preparation of Disilanyl Amides 23. The following describes the general procedure for the preparation of disilanyl amides **23a–c**. To a mixture of chlorodisilane (3.0 mmol) and Et_3N (4.5 mmol) in MeCN (5 mL) at room temperature was added a homoallylic amine (3.0 mmol). The mixture was stirred for 3 h, diluted with ether, and filtered to remove insoluble materials. Kugelrohr distillation afforded the corresponding disilanyl amide **23**.

(2R*,3R*)-4-Acetamido-3-methylbutane-1,2-diol Diacetate (25a). To a mixture of palladium(II) acetate (4.5 mg, 20 μmol) and *tert*-butyl isocyanide (25 mg, 0.30 mmol) in toluene (0.7 mL) was added **23a** (400 mg, 1.00 mmol). The mixture was stirred at room temperature for 4 h, and then evaporated. The residue dissolved in hexane was treated with activated carbon, filtered through a pad of Celite, and evaporated. A mixture of the residue and trifluoroacetic acid (2.27 g, 20 mmol) was stirred at 45 °C for 10 h. After removal of trifluoroacetic acid under reduced pressure, KHF_2 (622 mg, 8.0 mmol), MeOH (1.5 mL), THF (1.5 mL), KF (116 mg, 2.0 mmol), H_2O_2 (30% in water, 1.0 mL), and $KHCO_3$ (800 mg, 8.0 mmol) were added, and the mixture was stirred at room temperature for 1 d. Excess $Na_2S_2O_3$ was added and abolition of H_2O_2 was ascertained by test paper. After evaporation of volatiles, the residue was acetylated by a procedure similar to that used for **6a**, and the title compound **25a** was isolated by column chromatography on silica gel ($CHCl_3$:MeOH:aqueous NH_3 = 250:15:1, 94 mg, 39%): ^1H NMR δ 0.96 (d, J = 7.1 Hz, 3 H), 1.95–2.10 (m, 1 H), 1.97 (s, 3 H), 2.05 (s, 3 H), 2.09 (s, 3 H), 3.08 (dt, J = 14.0, 5.5 Hz, 1 H), 3.43 (ddd, J = 5.3, 6.9, 14.0 Hz, 1 H), 4.05 (dd, J = 6.7, 12.1 Hz, 1 H), 4.33 (dd, J = 2.8, 12.1 Hz, 1 H), 4.95 (ddd, J = 2.8, 6.7, 7.8 Hz, 1 H), 5.75–6.00 (br, 1 H); ^{13}C NMR δ 13.8, 20.7, 21.0, 23.3, 34.5, 41.0, 63.5, 73.2, 170.3, 170.8, 171.0; IR (neat) 3304, 2980, 1740, 1660, 1558, 1442, 1376, 1230, 1050 cm^{-1}. Anal. Calcd for $C_{11}H_{19}NO_5$: C, 53.87; H, 7.81; N, 5.71. Found: C, 53.68; H, 7.54; N, 5.75.

The following syntheses of **25b,c** were carried out according to the preceding procedure for **25a**.

(2R*,4R*)-4-Acetamidoheptane-1,2-diol Diacetate (25b): ^1H NMR δ 0.80–0.93 (m, 3 H), 1.18–1.50 (m, 4 H), 1.57–1.82 (m, 2 H), 1.95 (s, 3 H), 2.02 (s, 6 H), 3.84–4.60 (m, 1 H), 4.08 (dd, J = 6.2, 12.2 Hz, 1 H), 4.24 (dd, J = 3.2, 12.2 Hz, 1 H), 4.93–5.07 (m, 1 H), 5.50–5.85 (br, 1 H); ^{13}C NMR δ 13.8, 18.9, 20.7, 21.1, 23.3, 35.8, 37.3, 45.9, 64.6, 69.5, 169.8, 170.7; IR (neat) 3288, 2968, 1740, 1658, 1548, 1446, 1376, 1244, 1048 cm^{-1}. Anal. Calcd for $C_{13}H_{23}NO_5$: C, 57.13; H, 8.48; N, 5.12. Found: C, 57.01; H, 8.35; N, 4.91.

(2R*,4S*)-4-Acetamido-4-phenylbutane-1,2-diol Diacetate (25c): ^1H NMR δ 1.92–2.23 (m, 2 H), 1.96 (s, 3 H), 1.97 (s, 3 H), 2.03 (s, 3 H), 4.09 (dd, J = 5.7, 12.1 Hz, 1 H), 4.24 (dd, J = 3.4, 12.1 Hz, 1 H), 4.84–4.98 (m, 1 H), 5.05 (q, J = 8.0 Hz, 1 H), 6.41 (d, J = 8.0 Hz, 1 H), 7.18–7.40 (m, 5 H); ^{13}C NMR δ 20.6, 20.9, 23.2, 36.9, 50.2, 64.5, 69.3, 126.3, 127.6, 128.7, 141.0, 169.4, 170.5, 170.6; IR (neat) 3304, 3024, 1740, 1660, 1546, 1374, 1220, 1050, 768 cm^{-1}. Anal. Calcd for $C_{16}H_{21}NO_5$: C, 62.53; H, 6.89; N, 4.56. Found: C, 62.25; H, 6.69; N, 4.51.

Preparation of Disilanyl Alkenes 26. Disilanyl alkenes **26a,b** were prepared from the corresponding Grignard reagents by a procedure similar to that used to prepare **20a–c**. Disilanyl alkene **26c** was prepared from 1-penten-4-ylmagnesium bromide by a procedure similar to that used to prepare **20d**. Disilanyl alkenes **26d–f** were prepared from the corresponding allylic alcohols and 1,2-dichlorotetramethyldisilane by a procedure similar to that used to prepare **1e**.

1,1-Dimethyl-2-[(trimethylsilyl)methyl]siletane (27a). By a procedure similar to that used to prepare **21a**, the intramolecular bis-silylation of **26a** was carried out to give **27a** (83%): ^1H NMR δ –0.06 (s, 9 H), 0.20 (s, 3 H), 0.25 (s, 3 H), 0.61–0.70 (m, 2 H), 0.75–0.86 (m, 2 H), 1.25–1.65 (m, 2 H), 2.34–2.52 (m, 1 H); ^{13}C NMR δ –5.1, –1.5, 1.0, 11.0, 18.8, 24.8, 29.5; IR (neat) 2964, 1250, 840 cm^{-1}; MS m/z: 186 (M^+). Anal. Calcd for $C_9H_{22}Si_2$: C, 57.98; H, 11.89. Found: C, 58.26; H, 12.05.

(2R*,3R*)-2-[(Dimethylphenylsilyl)methyl]-3-methyl-1,1-diphenylsiletane (27b). By a procedure similar to that used to prepare **21a**, the intramolecular bis-silylation of **26b** was carried out to give **27b** (76%): ^1H NMR δ 0.14 (s, 3 H), 0.18 (s, 3 H), 0.80–1.08 (m, 3 H), 1.20 (d, J = 6.3 Hz, 3 H), 1.39 (dt, J = 10.7, 3.3 Hz, 1 H), 1.69 (dd, J = 7.9, 14.1 Hz, 1 H), 1.94–2.20 (m, 1 H), 7.20–7.60 (m, 15 H); ^{13}C NMR δ –2.7, –2.5, 16.4, 20.1, 24.2, 33.0, 38.4, 127.6, 127.8, 128.7, 129.5, 133.7, 134.8, 135.5, 135.7, 136.4, 139.4; IR (neat) 3076, 2960, 1430, 1250, 1114, 838, 734, 700 cm^{-1}. Anal. Calcd for $C_{25}H_{30}Si_2$: C, 77.65; H, 7.82. Found: C, 77.78; H, 7.78.

(2R*,4R*)-2-[(Dimethylphenylsilyl)methyl]-4-methyl-1,1-diphenylsiletane (27c). By a procedure similar to that used to prepare **21a**, the intramolecular bis-silylation of **26c** was carried out to give **27c** (91%): ^1H NMR δ 0.22 (s, 6 H), 1.11 (dd, J = 7.8, 14.8 Hz, 1 H), 1.18 (d, J = 7.2 Hz, 3 H), 1.27 (dd, J = 7.8, 14.8 Hz, 1 H), 1.45–1.70 (m, 1 H), 1.72–1.95 (m, 2 H), 2.82 (dt, J = 10.6, 9.2 Hz, 1 H), 7.27–7.69 (m, 15 H); ^{13}C NMR δ –2.6, –2.4, 15.7, 17.8, 20.9, 22.2, 40.0, 127.7, 127.9, 128.7, 129.5, 133.6, 134.6, 135.7, 136.1, 137.1, 139.7; IR (neat) 3076, 2960, 1430, 1250, 1114, 834, 700 cm^{-1}. Anal. Calcd for $C_{25}H_{30}Si_2$: C, 77.65; H, 7.82. Found: C, 77.47; H, 7.61.

(1R*,2S*)-1-Phenyl-1,2,3-propanetriol Triacetate (28d). To a mixture of palladium(II) acetate (3.3 mg, 0.015 mmol) and 1,1,3,3-tetramethylbutyl isocyanide (31 mg, 0.22 mmol) in toluene (0.6 mL) was added **26d** (140 mg, 0.46 mmol). The mixture was stirred at 35 °C for 3 h, and then passed through Florisil. After evaporation of volatiles, THF (1 mL), MeOH (1 mL), KF (110 mg, 1.9 mmol), $KHCO_3$ (93 mg, 0.93 mmol), and H_2O_2 (30% in water, 0.47 mL) were added, and the mixture was stirred at 35 °C for 10 h. Excess $Na_2S_2O_3$ was added and abolition of H_2O_2 was ascertained by test paper. After evaporation of volatiles, the residue was acetylated by a procedure similar to that used for **6a** to give **28d** (95 mg, 70%).[24]

The syntheses of **28e**[10f] and **28f** were carried out according to the preceding procedure for **28d**. **28f**: ^1H NMR δ 1.20 (s, 3 H), 1.25 (d, J = 6.5 Hz, 3 H), 1.50–1.68 (br, 1 H), 2.09 (s, 3 H), 2.11 (s, 3 H), 4.03 (s, 2 H), 4.98 (q, J = 6.5 Hz, 1 H).

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