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Stereoselective Synthesis of 1,2,4-Triols via Intramolecular Bis-silylation of Carbon–Carbon Triple Bonds Followed by Hydrogenation

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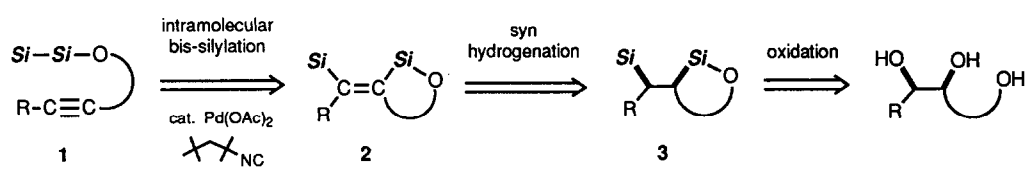
Abstract: A new strategy for the stereoselective synthesis of 1,2,4-triols has been developed. An alkyne tethered to a disilanyl group, upon treatment with palladium acetate and *tert*-alkyl isocyanide, furnished an exocyclic bis-silylated olefin. Subsequent hydrogenation took place from the less-hindered side of the ring producing *cis*-disubstituted oxasilolane. Oxidation of the two C–Si bonds of the hydrogenated oxasilolane led to the stereo- and regio-defined synthesis of 1,2,4-triol.

INTRODUCTION

The development of new synthetic strategies for stereoselective construction of polyol skeletons has been an active area of research in recent years. Stereoselective formation of C–Si bonds is one of the promising approaches to the polyol synthesis,[1] since oxidation of C–Si bonds gives rise to hydroxyl groups with retention of stereochemistry.[2] We have been studying bis-silylation of unsaturated organic molecules,[3,4] and developed a highly efficient catalyst system, palladium(II) acetate / *tert*-alkyl isocyanide, for the inter- and/or intramolecular bis-silylation of C–C triple[3c] and double[3d] bonds. Intramolecular regioselective bis-silylation reaction of an alkyne tethered to a disilanyl group **1** produces an exocyclic olefin **2**, which is derived from *syn* addition of the two silicon atoms across the triple bond. The following *syn* addition of hydrogen to the C–C double bond of **2** would stereoselectively create two asymmetric centers each having a silicon atom, which constitute a potential precursor for a vicinal diol unit. Herein, we report the details of the stereoselective synthesis of 1,2,4-triols by intramolecular bis-silylation of C–C triple bonds and subsequent hydrogenation as envisioned in Scheme 1.



Scheme 1.

RESULTS AND DISCUSSION

Synthesis of Alkynes Tethered to Disilanyl Groups 1

Alkynes tethered to disilanyl groups through silyl ether linkage **1** were readily prepared in good yield by the reaction of acetylenic alcohols with chlorodisilanes in the presence of amines in tetrahydrofuran (THF) or in *N,N*-dimethylformamide (DMF). An alkyne linked to a disilanyl group through a carbon chain **1h** was prepared by the reaction of an acetylenic Grignard reagent with a chlorodisilane in THF.

Intramolecular Bis-silylation of C–C Triple Bonds

A mixture of a disilanyl alkyne **1**, palladium(II) acetate (0.007–0.02 equiv), and 1,1,3,3-tetramethylbutyl isocyanide (0.1–0.3 equiv) in toluene was heated under the conditions specified in Table 1. The Si–Si linkage added intramolecularly to the C–C triple bond and, except entry 15, this addition was totally exo and *syn*,[5] as is the case with an intermolecular variant,[3c,4] to afford a bis-silylated exocyclic olefin **2** in good yield. Although the catalyst is potentially effective for the intermolecular bis-silylation of terminal alkynes,[3c] those **1a–e** reacted only intramolecularly giving the corresponding cyclic 1,2-oxasilolanes **2a–e** (entries 1–5). Furthermore, the high activity of the present catalyst system, combined with an advantage of intramolecular reaction, rendered it possible to insert an *internal* C–C triple bond into Si–Si linkage (entries 6–14), whereas only terminal alkynes have been bis-silylated in an intermolecular reaction so far.[4] The internal C–C triple bonds in conjugation with an ester or an olefin underwent the chemoselective bis-silylation (entries 9, 10). The intramolecular bis-silylations of alkynes **1** bearing various substituents in the tether worked as well, affording the corresponding oxasilolanes **2** with an asymmetric center in the ring. It may be remarked that a propargylic hydroxyl group does not encumber the desired bis-silylation (entry 14). Reaction employing a terminal alkyne tethered to a disilanyl group by a chain of 4 atoms produced a mixture of (*Z*)- and (*E*)-isomers (88 : 12) of 6-membered adducts (entry 15). However, bis-silylation failed to proceed with an internal alkyne tethered to a disilanyl group by a chain of 4 atoms.

Table 1. Intramolecular Bis-silylation of **1** Catalyzed by $Pd(OAc)_2$ / *tert*-Alkyl Isocyanide.

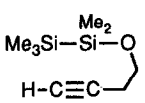
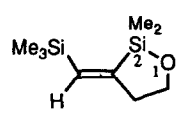
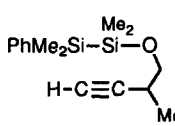
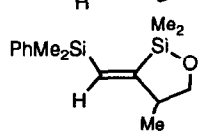
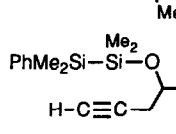
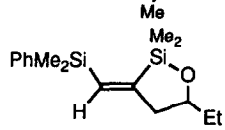
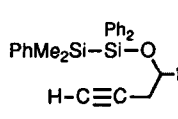
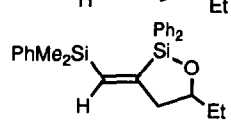
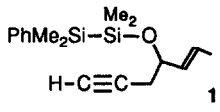
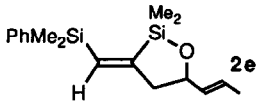
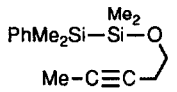
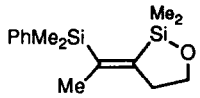
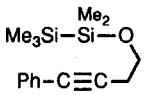
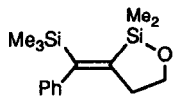
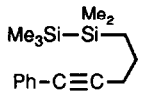
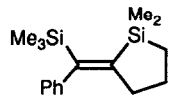
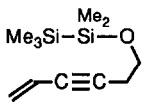
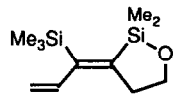
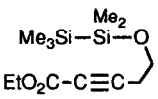
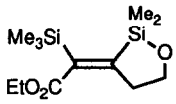
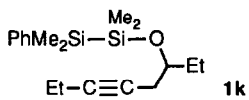
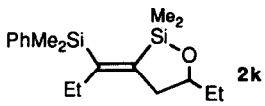
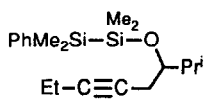
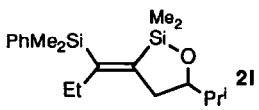
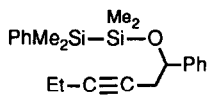
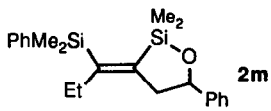
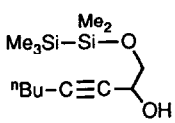
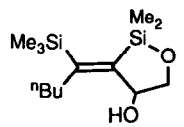
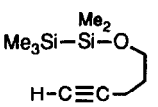
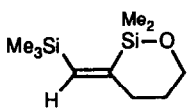
entry	1	conditions	product **2**	yield, %
1	 **1a**	80 °C 6 h	 **2a**	91
2	 **1b**	80 °C 2.5 h	 **2b**	56
3	 **1c**	60 °C 13 h	 **2c**	96
4	 **1d**	70 °C 12 h	 **2d**	99

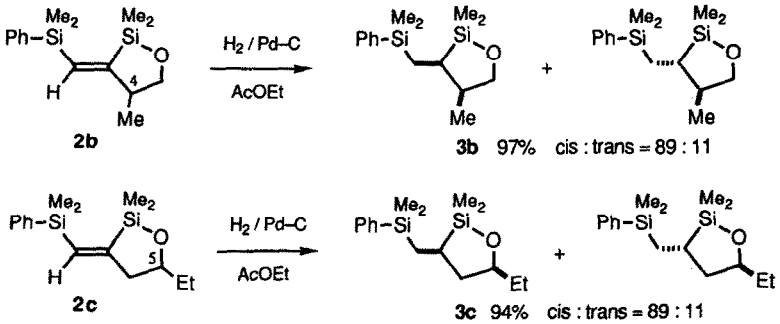
Table 1 (continued).

entry	1	conditions	product 2	yield, %
5	 1e	50 °C 23 h	 2e	75
6	 1f	80 °C 1 h	 2f	94
7	 1g	111 °C 2 h	 2g	85
8	 1h	111 °C 1 h	 2h	85
9	 1i	80 °C 2 h	 2i	81
10	 1j	80 °C 3 h	 2j	97
11	 1k	70 °C 15 h	 2k	93
12	 1l	100 °C 6 h	 2l	97
13	 1m	70 °C 8 h	 2m	82
14	 1n	60 °C 9 h	 2n	96
15	 1o	100 °C 10 h	 2o	71 [a]

[a] A mixture of (*Z*)- and (*E*)-isomers (88 : 12).

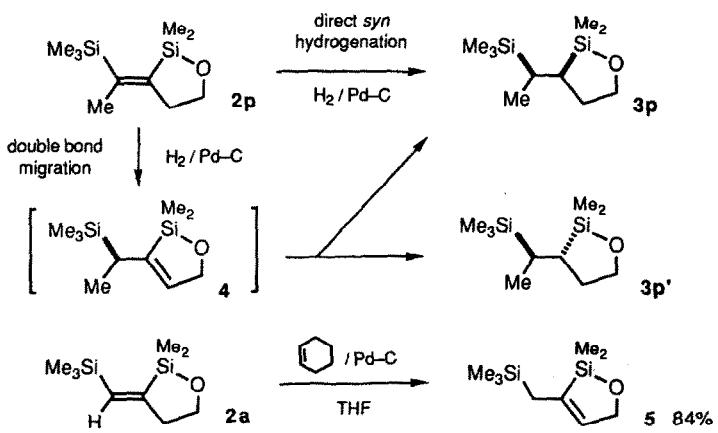
Hydrogenation of the Bis-silylated Products 2

Catalytic hydrogenation of the 1,2-oxasilolanes **2b** and **2c** having asymmetric centers on 4- and 5-positions of the rings, respectively, was carried out using Pd on carbon under an atmospheric pressure of hydrogen in AcOEt at room temperature (Scheme 2). In both cases, addition of hydrogen to the C–C double bond occurred from the less-hindered side of the ring to give *cis*-disubstituted oxasilolanes with fair diastereoselection.[6]



Scheme 2.

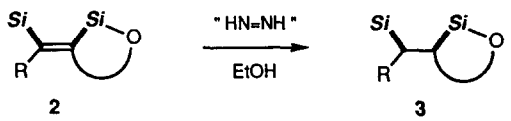
Next, a 1,2-oxasilolane **2p** prepared from an internal alkyne[3c] was hydrogenated, stereospecific formation of **3p** being expected from a *syn* hydrogenation mechanism. However, catalytic hydrogenation of the tetra-substituted olefin **2p** was slower than that of tri-substituted olefins **2b** and **2c**, and produced 1:1 mixture of **3p** and an unexpected isomer **3p'** (Scheme 3). It may be presumed that double bond migration of **2p** takes place prior to, or in competition with, direct hydrogenation and that hydrogenation of the resulting endocyclic olefin **4** proceeds non-stereoselectively affording a mixture of **3p** and its stereoisomer **3p'**. An analogous double bond migration to an endocyclic olefin **5** was observed when **2a** was treated with Pd on carbon in the presence of cyclohexene. This result supports the involvement of double bond migration in the catalytic hydrogenation process.



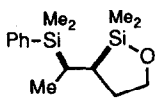
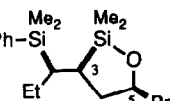
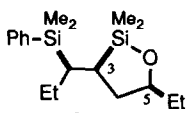
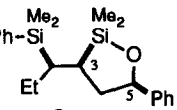
Scheme 3.

Stereospecific *syn* hydrogenation of tetra-substituted olefins **2f,k–m** could be achieved by means of diimide reduction (Table 2). Diimide, generated *in situ* by acid treatment of potassium azodicarboxylate, reduced **2f** to give the *syn*-hydrogenated product **3f** exclusively, presumably by a cyclic mechanism.[7] In the diimide reduction of **2k–m** having an asymmetric center in the oxasilolane ring, *syn* addition of hydrogen to the C–C double bond took place preferentially from the less-hindered side of the ring like the catalytic hydrogenation using Pd on carbon.[6] Of note was that two asymmetric centers were stereoselectively created in **3k–m** at once.

Table 2. Hydrogenation of Tetra-substituted Olefins with Diimide.

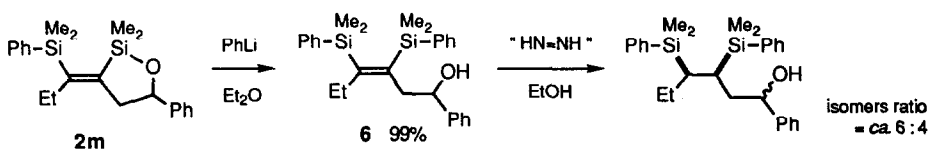


2 **3**

entry	2	major product	cis : trans [a] (yield, %)	entry	2	major product	cis : trans [a] (yield, %)
1	**2f**	 **3f**	— (99)	3	**2l**	 **3l**	88 : 12 (98)
2	**2k**	 **3k**	85 : 15 (97)	4	**2m**	 **3m**	92 : 8 (99)

[a] Referring to the relationship between the 3- and 5-substituents of the 1,2-oxasilolane.

Diimide reduction was also conducted with the acyclic substrate alkene **6** prepared by ring opening reaction of the oxasilolane **2m** with phenyllithium (Scheme 4). In marked contrast to the cyclic substrate **2m**, the acyclic **6** resulted in poor selectivity together with poor yield, suggesting the advantages of the cyclic system of the oxasilolane.

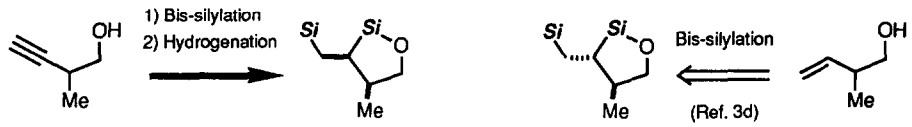


2m **6** 99%

Scheme 4.

As reported in our previous paper,[3d] the intramolecular bis-silylation of ***alkenes*** also stereoselectively furnishes oxasilolanes and the alkene having an allylic substituent leads to the ***trans***-3,4-disubstituted oxasilolane. On the other hand, the present intramolecular bis-silylation of an ***alkyne*** bearing a propargylic

substituent followed by hydrogenation gave rise to the corresponding ***cis***-3,4-disubstituted oxasilolane (Scheme 5). Furthermore, the intramolecular bis-silylation of internal alkenes is intrinsically unsuccessful and, hence, can provide no synthetic access to those oxasilolanes **3f,k–m**. Thus, the present stereoselective synthesis of oxasilolanes gives synthetically useful features complementary to the intramolecular bis-silylation of alkenes.[3d]

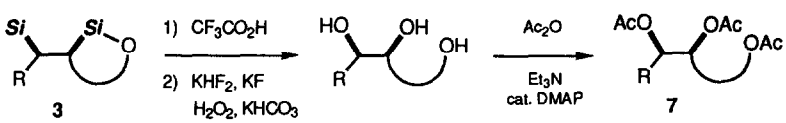


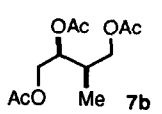
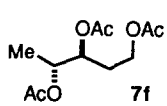
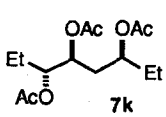
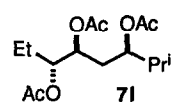
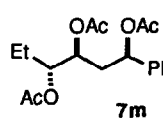
Scheme 5.

Oxidation of the Hydrogenated Products 3 into 1,2,4-Triols

The oxasilolanes **3b,f,k–m**, bearing dimethylphenylsilyl groups feasible for the oxidative transformation into hydroxyl groups,[2d,e] were subjected to the oxidation procedure (Table 3). The Ph–Si bonds of **3b,f,k,l** were cleaved by treatment with trifluoroacetic acid[2e] and subsequent hydrogen peroxide oxidation in the presence of fluoride anion[2c] afforded the corresponding 1,2,4-triols with retention of stereochemistry. With **3m**, the Ph–Si bond was cleaved by treatment with potassium *tert*-butoxide in dimethyl sulfoxide (DMSO)[8,9] to prevent Friedel-Crafts type migration of the phenyl group on the silicon (entry 5).[2d,10] The 1,2,4-triols thus produced were acetylated to allow an isolation affording the triacetates **7** in moderate to good yield.

Table 3. Synthesis of 1,2,4-Triols by Oxidation of Oxasilolanes **3**.



entry	3	product[a]	yield, %
1	**3b**	 **7b**	97
2	**3f**	 **7f**	86
3	**3k**	 **7k**	57
4	**3l**	 **7l**	56
5	**3m**	 **7m**	78[b]

[a] A mixture of stereoisomers of **3** was oxidized and the produced major isomer is shown.

[b] Oxidation: 1) $KOBu^t$ / DMSO. 2) TBAF, $KHCO_3$, H_2O_2.

CONCLUSIONS

A carbon–carbon triple bond was stereoselectively transformed to a vicinal diol unit through the intramolecular bis-silylation, hydrogenation, and oxidation. This procedure, creating two asymmetric centers, provides a novel method for stereoselective synthesis of 1,2,4-triols. Of note is that the present method offers a new synthetic means complementary to the intramolecular bis-silylation of carbon–carbon double bonds.[3d]

EXPERIMENTAL

General. Column chromatography was performed with silica gel (Wakogel C-200). ^1H and ^{13}C NMR spectra were acquired in chloroform-*d* unless otherwise noted. Carbon chemical shifts were recorded relative to chloroform-*d* (δ 77.0). Where appropriate, NMR data only for the major stereoisomer were described. Toluene was distilled from $LiAlH_4$, THF from sodium diphenylketyl, DMF, AcOEt and DMSO from CaH_2, and methanol from magnesium methoxide. Unless otherwise noted, materials were obtained from commercial sources. 2-Methylbut-3-yn-1-ol was prepared by the reaction of a propargylic titanium reagent with formaldehyde.[11] Hept-5-en-1-yn-4-ol was prepared by zinc mediated reaction of propargyl bromide with crotonaldehyde.[12] 4-Phenylbut-3-yn-1-ol and hex-5-en-3-yn-1-ol were prepared using Sonogashira procedure.[13] Ethyl 5-hydroxypent-2-ynoate was prepared by the reaction of a lithium acetylide with oxirane.[14]

Preparation of Disilanyl Alkynes 1. The following describes the general procedure for the synthesis of disilanyl alkynes **1a–c,e–g,i–k,n,o**. To a mixture of an acetylenic alcohol (4.3 mmol), Et_3N (6.4 mmol), and a catalytic amount of 4-(dimethylamino)pyridine in THF (10 mL) at rt was added a chlorodisilane (4.3 mmol). Progress of the reaction was monitored by GC and/or TLC and, after completion, the mixture was diluted with hexane (10 mL). Filtration to remove salts and Kugelrohr distillation of the filtrate afforded **1**.

Disilanyl alkynes **1d,l,m** were prepared according to the following procedure. To a mixture of an acetylenic alcohol (5.7 mmol) and a chlorodisilane (5.7 mmol) in DMF (3.5 mL) at rt was added imidazole (11.4 mmol). The mixture was stirred at rt and, after completion, subjected to column chromatography to afford **1**.

A disilanyl alkyne **1h** was prepared as follows. To a solution of (5-phenyl-4-pentynyl)magnesium chloride (18.5 mmol) in THF (19 mL) at 0 °C was added chloropentamethyldisilane (3.3 g, 20 mmol). The mixture was stirred at rt for 2 h and at 50 °C for 1.5 h, cooled, and then slowly poured into aqueous HCl (1 N) at 0 °C. Extraction with ether followed by Kugelrohr distillation afforded **1h** (1.5 g, 30%).

(Z)-2,2-Dimethyl-3-[(trimethylsilyl)methylene]-1,2-oxasilolane (2a). A toluene solution (3.5 mL) of $Pd(OAc)_2$ (6.6 mg, 29 μmol), 1,1,3,3-tetramethylbutyl isocyanide (62 mg, 0.45 mmol), and 4-[(pentamethyldisilanyl)oxy]-1-butyne (**1a**, 542 mg, 2.7 mmol) was heated at 80 °C for 6 h. Kugelrohr distillation [130–140 °C (20 mmHg)] of the cooled reaction mixture afforded **2a** (493 mg, 91%). IR (neat) 2964, 2908, 2868, 1252, 1068, 1030 cm^{-1}; ^1H NMR δ 0.11 (s, 9 H), 0.32 (s, 6 H), 2.65 (dt, J = 2.2, 6.5 Hz,

2 H), 3.94 (t, J = 6.5 Hz, 2 H), 6.57 (t, J = 2.2 Hz, 1 H); ^{13}C NMR δ -0.18, 0.30, 43.67, 64.83, 141.70, 159.81. Anal. Calcd for $C_9H_{20}OSi_2$: C, 53.93; H, 10.06. Found: C, 53.72; H, 10.18.

The following reactions for the synthesis of **2** were carried out according to the preceding procedure for **2a** under the conditions specified in Table 1.

*(Z)-3-[(Dimethylphenylsilyl)methylene]-2,2,4-trimethyl-1,2-oxasilolane (**2b**).* IR (neat) 2968, 1252, 1114, 1036, 850 cm^{-1}; ^{1}H NMR δ 0.10 (s, 3 H), 0.13 (s, 3 H), 0.40 (s, 6 H), 1.07 (d, J = 6.8 Hz, 3 H), 2.57–2.78 (m, 1 H), 3.47 (dd, J = 7.8, 9.2 Hz, 1 H), 4.09 (dd, J = 6.6, 9.2 Hz, 1 H), 6.59 (d, J = 2.3 Hz, 1 H), 7.32–7.40 (m, 3 H), 7.50–7.59 (m, 2 H); ^{13}C NMR δ -0.63, -0.49, 0.70, 1.00, 16.74, 46.29, 72.01, 128.33, 129.62, 134.70, 137.71, 139.39, 167.21. Anal. Calcd for $C_{15}H_{24}OSi_2$: C, 65.15; H, 8.75. Found: C, 65.10; H, 8.95.

*(Z)-3-[(Dimethylphenylsilyl)methylene]-5-ethyl-2,2-dimethyl-1,2-oxasilolane (**2c**).* IR (neat) 2968, 1252, 1111, 836 cm^{-1}; ^{1}H NMR δ 0.11 (s, 6 H), 0.38 (s, 3 H), 0.39 (s, 3 H), 0.94 (t, J = 7.4 Hz, 3 H), 1.36–1.74 (m, 2 H), 2.43 (ddd, J = 2.4, 8.0, 15.0 Hz, 1 H), 2.73 (ddd, J = 1.8, 5.2, 15.0 Hz, 1 H), 3.82–3.98 (m, 1 H), 6.68 (dd, J = 1.8, 2.4 Hz, 1 H), 7.28–7.65 (m, 5 H); ^{13}C NMR δ -1.29, -1.12, 0.24, 0.55, 9.86, 30.61, 49.26, 76.76, 127.78, 129.08, 134.15, 138.83, 139.27, 162.85. Anal. Calcd for $C_{16}H_{26}OSi_2$: C, 66.14; H, 9.02. Found: C, 66.14; H, 9.22.

*(Z)-3-[(Dimethylphenylsilyl)methylene]-5-ethyl-2,2-diphenyl-1,2-oxasilolane (**2d**).* IR (neat) 3076, 2968, 1432, 1252, 1118, 840 cm^{-1}; ^{1}H NMR δ 0.01 (s, 3 H), 0.02 (s, 3 H), 0.94 (t, J = 7.4 Hz, 3 H), 1.45–1.85 (m, 2 H), 2.64 (ddd, J = 2.5, 8.4, 15.5 Hz, 1 H), 2.93 (ddd, J = 1.7, 5.3, 15.5 Hz, 1 H), 4.05–4.22 (m, 1 H), 6.92 (dd, J = 1.7, 2.5 Hz, 1 H), 7.19–7.69 (m, 15 H); ^{13}C NMR δ -1.71, -1.59, 9.87, 30.81, 49.99, 77.55, 127.64, 127.83, 128.78, 130.35, 133.22, 133.77, 135.63, 135.76, 138.96, 142.89, 158.12. Anal. Calcd for $C_{26}H_{30}OSi_2$: C, 75.31; H, 7.29. Found: C, 75.46; H, 7.37.

*(Z)-3-[(Dimethylphenylsilyl)methylene]-2,2-dimethyl-5-(1-propenyl)-1,2-oxasilolane (**2e**).* IR (neat) 2968, 1438, 1254, 1116, 842 cm^{-1}; ^{1}H NMR δ 0.09 (s, 3 H), 0.10 (s, 3 H), 0.36 (s, 3 H), 0.37 (s, 3 H), 1.69 (dd, J = 1.4, 6.4 Hz, 3 H), 2.53 (ddd, J = 2.6, 8.6, 15.4 Hz, 1 H), 2.69 (ddd, J = 1.6, 5.2, 15.4 Hz, 1 H), 4.27–4.41 (m, 1 H), 5.49 (ddd, J = 1.4, 6.8, 15.2 Hz, 1 H), 5.70 (dq, J = 15.2, 6.4 Hz, 1 H), 6.66 (dd, J = 1.6, 2.6 Hz, 1 H), 7.30–7.66 (m, 5 H); ^{13}C NMR δ -1.30, -1.12, -0.29, 0.41, 17.69, 50.33, 76.06, 127.04, 127.83, 129.15, 133.50, 134.20, 138.77, 139.51, 162.39. Anal. Calcd for $C_{17}H_{26}OSi_2$: C, 67.49; H, 8.66. Found: C, 67.23; H, 8.76.

*(Z)-3-[1-(Dimethylphenylsilyl)ethylidene]-2,2-dimethyl-1,2-oxasilolane (**2f**).* IR (neat) 2964, 1435, 1252, 1066, 1036, 934, 810 cm^{-1}; ^{1}H NMR δ 0.16 (s, 6 H), 0.40 (s, 6 H), 1.83 (t, J = 1.4 Hz, 3 H), 2.63 (tq, J = 6.6, 1.4 Hz, 2 H), 3.99 (t, J = 6.6 Hz, 2 H), 7.29–7.54 (m, 5 H); ^{13}C NMR δ -1.11, 0.56, 21.39, 36.11, 64.17, 127.35, 128.99, 134.17, 138.69, 146.21, 153.30. Anal. Calcd for $C_{15}H_{24}OSi_2$: C, 65.15; H, 8.75. Found: C, 65.10; H, 8.97.

(Z)-2,2-Dimethyl-3-[phenyl(trimethylsilyl)methylene]-1,2-oxasilolane (2g). IR (neat) 3064, 2964, 2868, 1252, 1088, 1030 cm^{-1}; ^1H NMR δ 0.06 (s, 9 H), 0.42 (s, 6 H), 2.30 (t, J = 6.6 Hz, 2 H), 3.82 (t, J = 6.6 Hz, 2 H), 6.87–6.92 (m, 2 H), 7.12–7.21 (m, 1 H), 7.26–7.35 (m, 2 H); ^{13}C NMR δ -0.01, 0.69, 37.71, 64.64, 125.36, 126.69, 128.36, 146.77, 153.30, 156.57. Anal. Calcd for $C_{15}H_{24}OSi_2$: C, 65.15; H, 8.75. Found: C, 65.13; H, 8.93.

(Z)-1,1-Dimethyl-2-[phenyl(trimethylsilyl)methylene]silolane (2h). IR (neat) 2948, 1598, 1250 cm^{-1}; ^1H NMR δ 0.04 (s, 9 H), 0.33 (s, 6 H), 0.70 (t, J = 7.0 Hz, 2 H), 1.53 (quintet, J = 7.0 Hz, 2 H), 1.99 (t, J = 7.0 Hz, 2 H), 6.82–6.89 (m, 2 H), 7.09–7.18 (m, 1 H), 7.23–7.32 (m, 2 H); ^{13}C NMR δ -0.27, 0.63, 15.86, 23.69, 39.54, 124.73, 126.87, 128.00, 147.52, 154.93, 157.81. Anal. Calcd for $C_{16}H_{26}Si_2$: C, 70.00; H, 9.54. Found: C, 70.09; H, 9.76.

(Z)-2,2-Dimethyl-3-[1-(trimethylsilyl)prop-2-enylene]-1,2-oxasilolane (2i). IR (neat) 2964, 1616, 1252, 1032 cm^{-1}; ^1H NMR δ 0.16 (s, 9 H), 0.35 (s, 6 H), 2.66 (dt, J = 1.4, 6.5 Hz, 2 H), 3.92 (t, J = 6.5 Hz, 2 H), 4.93 (dd, J = 2.0, 18.0 Hz, 1 H), 5.14 (dd, J = 2.0, 11.6 Hz, 1 H), 6.42 (ddt, J = 11.6, 18.0, 1.4 Hz, 1 H); ^{13}C NMR δ 0.70, 0.92, 37.03, 64.49, 114.83, 140.53, 151.97, 152.92. Anal. Calcd for $C_{11}H_{22}OSi_2$: C, 58.34; H, 9.79. Found: C, 58.08; H, 10.00.

(Z)-3-[(Ethoxycarbonyl)(trimethylsilyl)methylene]-2,2-dimethyl-1,2-oxasilolane (2j). IR (neat) 2968, 1716, 1254, 1200, 1094, 1032, 864 cm^{-1}; ^1H NMR δ 0.19 (s, 9 H), 0.37 (s, 6 H), 1.32 (t, J = 7.2 Hz, 3 H), 2.69 (t, J = 6.5 Hz, 2 H), 3.95 (t, J = 6.5 Hz, 2 H), 4.22 (q, J = 7.2 Hz, 2 H); ^{13}C NMR δ 10.05, 10.64, 22.75, 43.56, 62.49, 66.22, 137.78, 147.41, 159.49. Anal. Calcd for $C_{12}H_{24}O_3Si_2$: C, 52.89; H, 8.88. Found: C, 53.04; H, 9.17.

(Z)-3-[1-(Dimethylphenylsilyl)propylidene]-5-ethyl-2,2-dimethyl-1,2-oxasilolane (2k). IR (neat) 2972, 1432, 1252, 1112, 832 cm^{-1}; ^1H NMR δ 0.05 (s, 3 H), 0.07 (s, 3 H), 0.40 (s, 6 H), 0.90 (t, J = 7.6 Hz, 3 H), 0.94 (t, J = 7.2 Hz, 3 H), 1.38–1.72 (m, 2 H), 2.16–2.40 (m, 3 H), 2.83 (dd, J = 5.5, 16.0 Hz, 1 H), 3.80–3.95 (m, 1 H), 7.28–7.56 (m, 5 H); ^{13}C NMR (C_6D_6) δ -1.39, -1.31, 0.29, 0.58, 9.42, 12.75, 27.55, 30.64, 40.21, 75.46, 127.30, 128.36, 133.82, 138.37, 151.25, 154.09. Anal. Calcd for $C_{18}H_{30}OSi_2$: C, 67.85; H, 9.49. Found: C, 67.65; H, 9.65.

(Z)-3-[1-(Dimethylphenylsilyl)propylidene]-5-isopropyl-2,2-dimethyl-1,2-oxasilolane (2l). IR (neat) 2968, 1472, 1432, 1252, 1112, 864, 810 cm^{-1}; ^1H NMR δ 0.04 (s, 3 H), 0.05 (s, 3 H), 0.38 (s, 6 H), 0.89 (d, J = 6.4 Hz, 3 H), 0.90 (t, J = 7.4 Hz, 3 H), 0.95 (d, J = 6.8 Hz, 3 H), 1.56–1.78 (m, 1 H), 2.28 (q, J = 7.4 Hz, 2 H), 2.34 (dd, J = 8.4, 16.0 Hz, 1 H), 2.76 (dd, J = 5.8, 16.0 Hz, 1 H), 3.65 (ddd, J = 5.8, 6.8, 8.4 Hz, 1 H), 7.27–7.63 (m, 5 H); ^{13}C NMR δ -0.56, -0.48, 0.96, 1.05, 13.50, 18.06, 18.65, 28.15, 34.49, 37.51, 80.13, 127.69, 128.97, 134.48, 139.20, 152.02, 154.07. Anal. Calcd for $C_{19}H_{32}OSi_2$: C, 68.60; H, 9.70. Found: C, 68.58; H, 9.94.

*(Z)-3-[1-(Dimethylphenylsilyl)propylidene]-2,2-dimethyl-5-phenyl-1,2-oxasilolane (**2m**).* IR (neat) 2972, 1456, 1432, 1252, 1058, 1032, 864, 808 cm^{-1}; ^1H NMR δ 0.15 (s, 3 H), 0.16 (s, 3 H), 0.42 (s, 3 H), 0.43 (s, 3 H), 0.89 (t, *J* = 7.6 Hz, 3 H), 2.28 (q, *J* = 7.6 Hz, 2 H), 2.48 (dd, *J* = 9.7, 16.0 Hz, 1 H), 3.18 (dd, *J* = 5.2, 16.0 Hz, 1 H), 4.94 (dd, *J* = 5.2, 9.7 Hz, 1 H), 7.20–7.6 (m, 10 H); ^{13}C NMR δ -0.70, -0.48, 0.88, 0.99, 13.49, 28.26, 44.07, 76.65, 125.39, 127.15, 127.77, 128.30, 129.09, 134.53, 138.91, 144.72, 152.94, 153.35. Anal. Calcd for $C_{22}H_{30}OSi_2$: C, 72.07; H, 8.25. Found: C, 71.83; H, 8.22.

*(Z)-4-Hydroxy-2,2-dimethyl-3-[1-(trimethylsilyl)pentylidene]-1,2-oxasilolane (**2n**).* IR (neat) 3432, 2968, 2880, 1252, 1092, 1064, 952, 858, 828, 788 cm^{-1}; ^1H NMR δ 0.15 (s, 9 H), 0.32 (s, 3 H), 0.41 (s, 3 H), 0.91 (t, *J* = 7.1 Hz, 3 H), 1.14–1.58 (m, 5 H), 2.22–2.56 (m, 2 H), 3.81 (dd, *J* = 2.9, 11.0 Hz, 1 H), 4.06 (d, *J* = 11.0 Hz, 1 H), 4.76 (d, *J* = 2.9 Hz, 1 H); ^{13}C NMR δ 0.54, 1.18, 1.89, 13.95, 23.14, 33.37, 34.85, 71.82, 72.20, 152.30, 160.00. Anal. Calcd for $C_{13}H_{28}O_2Si_2$: C, 57.29; H, 10.35. Found: C, 57.13; H, 10.60.

*(Z)-2,2-Dimethyl-3-[(trimethylsilyl)methylene]perhydro-1,2-oxasilin (**2o**).* IR (neat) 2968, 2928, 1434, 1252, 824 cm^{-1}; ^1H NMR δ 0.11 (s, 9 H), 0.29 (s, 6 H), 1.68–1.81 (m, 2 H), 2.49–2.59 (m, 2 H), 3.92 (t, *J* = 5.3 Hz, 2 H), 6.19 (t, *J* = 1.7 Hz, 1 H); ^{13}C NMR δ 0.59, 0.65, 30.69, 44.21, 64.77, 142.35, 159.88. *(E)-2,2-Dimethyl-3-[(trimethylsilyl)methylene]perhydro-1,2-oxasilin.* ^1H NMR δ 0.07 (s, 9 H), 0.19 (s, 6 H), 1.73–1.85 (m, 2 H), 2.43–2.51 (m, 2 H), 3.86 (t, *J* = 5.7 Hz, 2 H), 6.10 (s, 1 H). Anal. Calcd for $C_{10}H_{22}OSi_2$: C, 56.01; H, 10.34. Found: C, 55.80; H, 10.55.

*cis-3-[(Dimethylphenylsilyl)methyl]-2,2,4-trimethyl-1,2-oxasilolane (**3b**).* Palladium on carbon (5% w/w, 115 mg) was activated by stirring in AcOEt (2 mL) under an atmospheric pressure of hydrogen at rt for 10 h, to which **2b** (300 mg, 1.1 mmol) was added. The mixture was stirred at rt for 7 h, filtered through Celite, and concentrated to give **3b** (293 mg, 97%) as a mixture of diastereomers. IR (neat) 2968, 1252, 1114, 1030, 982, 832 cm^{-1}; ^1H NMR (major isomer) δ 0.06 (s, 3 H), 0.08 (s, 3 H), 0.31 (s, 6 H), 0.74–1.04 (m, 2 H), 0.95 (d, *J* = 7.1 Hz, 3 H), 1.10–1.22 (m, 1 H), 2.03–2.23 (m, 1 H), 3.62 (dd, *J* = 4.1, 9.2 Hz, 1 H), 3.76 (dd, *J* = 4.6, 9.2 Hz, 1 H), 7.32–7.44 (m, 3 H), 7.46–7.58 (m, 2 H); (minor isomer) δ 3.24 (dd, H-5), 3.97 (dd, H-5);[9] ^{13}C NMR (major isomer) δ -2.82, -2.63, -1.58, -0.26, 10.36, 14.35, 24.17, 38.78, 72.21, 127.76, 128.98, 133.64, 139.14. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.76; H, 9.64.

*cis-3-[(Dimethylphenylsilyl)methyl]-5-ethyl-2,2-dimethyl-1,2-oxasilolane (**3c**).* By a procedure similar to that used to reduce **2b** (rt, 5 h), the title compound was obtained from **2c** as a mixture of diastereomers (94%). IR (neat) 2968, 1252, 1114, 830 cm^{-1}; ^1H NMR (major isomer) δ 0.04 (s, 3 H), 0.09 (s, 3 H), 0.29 (s, 3 H), 0.30 (s, 3 H), 0.70–1.90 (m, 9 H), 2.00–2.22 (m, 1 H), 3.60–3.78 (m, 1 H), 7.30–7.66 (m, 5 H); (minor isomer) δ 3.86–4.02 (m, H-5); ^{13}C NMR (major isomer) δ -2.75, -2.65, -2.31, -0.94, 9.85, 16.01, 20.72, 30.56, 42.59, 78.23, 127.73, 128.91, 133.58, 139.29. Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.68; H, 9.65. Found: C, 65.57; H, 9.76.

(3S)-3-[(1R*)-1-(Dimethylphenylsilyl)ethyl]-2,2-dimethyl-1,2-oxasilolane (3f).* To a mixture of potassium azodicarboxylate (1.40 g, 7.2 mmol) and **2f** (200 mg, 0.72 mmol) in ethanol (4 mL) at 0 °C was added over 20 min AcOH (2.17 g, 36 mmol) in EtOH (1 mL). The mixture was gradually warmed to rt overnight with stirring, then diluted with saturated aqueous $NaHCO_3$, and extracted with ether. The organic layer was washed with saturated aqueous $NaHCO_3$, dried over K_2CO_3, and concentrated to afford **3f** (200 mg, 99%). IR (neat) 2968, 2868, 1430, 1252, 1112, 1042, 814 cm^{-1}; ^1H NMR δ 0.15 (s, 3 H), 0.22 (s, 3 H), 0.30 (s, 3 H), 0.33 (s, 3 H), 0.88–1.10 (m, 5 H), 1.34–1.58 (m, 1 H), 1.82–1.96 (m, 1 H), 3.57 (ddd, *J* = 4.3, 9.3, 11.8 Hz, 1 H), 3.89–4.03 (m, 1 H), 7.32–7.40 (m, 3 H), 7.48–7.59 (m, 2 H); ^{13}C NMR δ -3.74, -3.68, -2.65, 0.63, 17.58, 20.31, 30.47, 33.69, 66.55, 127.68, 128.75, 133.76, 139.32. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.79; H, 9.63.

(3S,5S*)-3-[(1R*)-1-(Dimethylphenylsilyl)propyl]-5-ethyl-2,2-dimethyl-1,2-oxasilolane (3k).* By a procedure similar to that used to reduce **2f** (-40 °C, 8 h), the title compound was obtained from **2k** as a mixture of diastereomers (97%). IR (neat) 2968, 1252, 1114, 830 cm^{-1}; ^1H NMR (major isomer) δ 0.11 (s, 3 H), 0.24 (s, 3 H), 0.32 (s, 3 H), 0.35 (s, 3 H), 0.72–0.88 (m, 6 H), 0.90–1.65 (m, 7 H), 1.92 (ddd, *J* = 3.9, 6.8, 12.3 Hz, 1 H), 3.57–3.73 (m, 1 H), 7.28–7.60 (m, 5 H); (minor isomer) δ 3.82–3.98 (m, H-5); ^{13}C NMR (major isomer) δ -2.50, -2.35, -2.13, 0.72, 9.70, 12.87, 26.04, 27.76, 28.62, 30.65, 39.12, 78.53, 127.60, 128.56, 133.64, 140.24. Anal. Calcd for $C_{18}H_{32}OSi_2$: C, 67.43; H, 10.06. Found: C, 67.41; H, 10.24.

(3S,5R*)-3-[(1R*)-1-(Dimethylphenylsilyl)propyl]-5-isopropyl-2,2-dimethyl-1,2-oxasilolane (3l).* By a procedure similar to that used to reduce **2f** (-40 °C, 2 d), the title compound was obtained from **2l** as a mixture of diastereomers (98%). IR (neat) 2968, 1252, 1114, 1044, 834 cm^{-1}; ^1H NMR (major isomer) δ 0.12 (s, 3 H), 0.27 (s, 3 H), 0.34 (s, 3 H), 0.38 (s, 3 H), 0.73 (d, *J* = 6.7 Hz, 3 H), 0.85 (d, *J* = 6.2 Hz, 3 H), 0.86 (t, *J* = 7.2 Hz, 3 H), 0.92–1.68 (m, 6 H), 1.82 (ddd, *J* = 4.1, 6.9, 12.2 Hz, 1 H), 3.49 (ddd, *J* = 4.1, 6.1, 10.9 Hz, 1 H), 7.29–7.65 (m, 5 H); (minor isomer) δ 3.62 (ddd, H-5); ^{13}C NMR (major isomer) δ -2.61, -2.45, -2.27, 0.72, 12.88, 17.51, 18.72, 26.04, 27.86, 28.44, 34.25, 36.09, 82.25, 127.60, 128.55, 133.64, 140.24. Anal. Calcd for $C_{19}H_{34}OSi_2$: C, 68.19; H, 10.20. Found: C, 68.15; H, 10.41.

(3S,5R*)-3-[(1R*)-1-(Dimethylphenylsilyl)propyl]-2,2-dimethyl-5-phenyl-1,2-oxasilolane (3m).* By a procedure similar to that used to reduce **2f** (-40 °C, 2 d), the title compound was obtained from **2m** as a mixture of diastereomers (99%). IR (neat) 2968, 1252, 1112, 1046, 864, 838, 700 cm^{-1}; ^1H NMR (major isomer) δ 0.31 (s, 3 H), 0.385 (s, 3 H), 0.391 (s, 3 H), 0.40 (s, 3 H), 0.89 (t, *J* = 7.4 Hz, 3 H), 1.04–1.29 (m, 1 H), 1.30–1.70 (m, 4 H), 2.33 (ddd, *J* = 1.6, 4.2, 11.5 Hz, 1 H), 4.84 (dd, *J* = 4.2, 10.8, 1 H), 7.15–7.64 (m, 10 H); (minor isomer) δ 5.11 (dd, H-5); ^{13}C NMR (major isomer) δ -2.71, -2.05, -1.70, 0.71, 13.04, 26.12, 27.72, 29.67, 42.77, 78.77, 125.19, 126.97, 127.66, 128.17, 128.67, 133.68, 139.73, 144.44. Anal. Calcd for $C_{22}H_{32}OSi_2$: C, 71.68; H, 8.75. Found: C, 71.55; H, 8.71.

3-[1-(Trimethylsilyl)ethyl]-2,2-dimethyl-1,2-oxasilolane (3p and 3p'). The oxasilolane $\mathbf{2p^{3c}}$ was hydrogenated by a procedure similar to that used to reduce **2b**. Filtration through Celite followed by

preparative GC afforded a mixture of **3p** and **3p'** (*ca.* 1:1, 33%). ^{13}C NMR δ -2.68, -2.26, -2.02, -1.68, -0.16, 0.69, 14.25, 17.32, 18.58, 20.56, 27.03, 30.55, 31.74, 33.65, 66.26, 66.63.

3-[(Trimethylsilyl)methyl]-2,2-dimethyl-Δ^3-1,2-oxasilolene (5). A mixture of **2a** (100 mg, 0.50 mmol), cyclohexene (3.0 mL) and Pd on carbon (5% w/w, 75 mg) in THF (20 mL) was stirred at 70 °C for 30 h. Filtration through Celite followed by Kugelrohr distillation afforded **5** (84 mg, 84%). IR (neat) 2964, 1252, 1096, 856 cm^{-1}; ^1H NMR δ 0.02 (s, 9 H), 0.22 (s, 6 H), 1.65–1.71 (m, 2 H), 4.52–4.58 (m, 2 H), 6.23–6.28 (m, 1 H); ^{13}C NMR δ -1.27, 0.19, 20.26, 71.76, 137.69, 139.62. Anal. Calcd for $C_9H_{20}OSi_2$: C, 53.93; H, 10.06. Found: C, 53.71; H, 10.09.

(Z)-3,4-Bis(dimethylphenylsilyl)-1-phenylhex-3-en-1-ol (6). To a solution of **2m** (106 mg, 0.29 mmol) in ether (0.9 mL) at 0 °C was added PhLi (2.0 M in ether / cyclohexane, 0.43 mmol). The mixture was stirred at 0 °C for 15 min and at rt for 3.5 h, diluted with water, and extracted with ether. Evaporation of volatiles afforded **6** (127 mg, 99%). ^1H NMR δ 0.29 (s, 3 H), 0.33 (s, 3 H), 0.47 (s, 6 H), 0.99 (d, J = 7.4 Hz, 3 H), 2.13 (br s, 1 H), 2.21–2.45 (m, 1 H), 2.58–2.80 (m, 1 H), 2.80 (dd, J = 4.1, 13.6 Hz, 1 H), 3.06 (dd, J = 9.6, 13.6 Hz, 1 H), 4.74 (dd, J = 4.1, 9.6 Hz, 1 H), 7.27–7.80 (m, 15 H); ^{13}C NMR δ 0.72, 1.14, 1.61, 1.82, 14.88, 27.51, 43.74, 73.42, 125.50, 127.28, 127.67, 127.81, 128.30, 128.64, 128.81, 133.88, 134.01, 140.37, 140.97, 144.35, 148.04, 160.72.

(2R,3S*)-3-Methylbutan-1,2,4-triol Triacetate (7b).* A mixture of **3b** (cis : trans = 89 : 11, 100 mg, 0.36 mmol) and trifluoroacetic acid (818 mg, 7.2 mmol) was stirred at rt for 11 h. After removal of trifluoroacetic acid under reduced pressure, KHF_2 (112 mg, 1.4 mmol), MeOH (0.7 mL), KF (42 mg, 0.72 mmol), THF (0.7 mL), H_2O_2 (30% in water, 0.43 mL), and $KHCO_3$ (287 mg, 2.9 mmol) were added to the mixture, which was stirred at rt for 29 h. Aqueous $Na_2S_2O_3$ was added and then volatile compounds were thoroughly removed by evaporation. THF (2 mL), Et_3N (545 mg, 5.4 mmol), acetic anhydride (367 mg, 3.59 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 **7b** (84 mg, 95%), whose minor stereoisomer was found to be identical with an authentic sample.[3d] IR (neat) 2984, 1740, 1374, 1232, 1040 cm^{-1}; ^1H NMR δ 0.99 (d, J = 7.0 Hz, 3 H), 2.05 (s, 3 H), 2.06 (s, 3 H), 2.07 (s, 3 H), 2.10–2.30 (m, 1 H), 3.94 (dd, J = 5.9, 11.2 Hz, 1 H), 4.00 (dd, J = 6.9, 11.2 Hz, 1 H), 4.09 (dd, J = 7.2, 11.8 Hz, 1 H), 4.27 (dd, J = 3.9, 11.8 Hz, 1 H), 5.18 (ddd, J = 3.9, 4.6, 7.2 Hz, 1 H); ^{13}C NMR δ 11.71, 20.69, 20.78, 33.77, 63.52, 65.23, 71.15, 170.27, 170.60, 170.84. Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.44; H, 7.43.

(3R,4S*)-1,3,4-Pentantriol Triacetate (7f).* By a procedure similar to that used to prepare **7b**, the title compound was obtained from **3f** (86%). IR (neat) 2996, 1740, 1438, 1378, 1236, 1052 cm^{-1}; ^1H NMR δ 1.20 (d, J = 6.4 Hz, 3 H), 1.83–1.99 (m, 2 H), 2.03 (s, 6 H), 2.05 (s, 3 H), 3.99–4.20 (m, 2 H), 4.98–5.12 (m, 2 H); ^{13}C NMR δ 15.02, 20.81, 20.85, 21.04, 28.49, 60.41, 70.45, 71.29, 170.23, 170.34, 170.90. Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.36; H, 7.52.

(3S,4R*,6R*)-3,4,6-Octantriol Triacetate (7k).* By a procedure similar to that used to prepare **7b**, the title compound was obtained from **3k** (57%). IR (neat) 2980, 2948, 1744, 1374, 1240, 1024 cm^{-1}; ^1H NMR δ 0.85 (t, J = 7.4 Hz, 3 H), 0.87 (t, J = 7.4 Hz, 3 H), 1.47–1.66 (m, 4 H), 1.70–1.92 (m, 2 H), 2.01 (s, 6 H), 2.02 (s, 3 H), 4.74–4.96 (m, 2 H), 4.98–5.12 (m, 1 H); ^{13}C NMR δ 9.24, 9.81, 20.86, 20.93, 21.09, 22.34, 26.27, 32.83, 70.81, 72.29, 75.22, 170.31, 170.49, 170.56. Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.35; H, 8.57.

(3S,5R*,6S*)-2-Methyloctan-3,5,6-triol Triacetate (7l).* By a procedure similar to that used to prepare **7b**, the title compound was obtained from **3l** (56%). IR (neat) 2976, 1740, 1468, 1438, 1374, 1240, 1024 cm^{-1}; ^1H NMR δ 0.80–1.05 (m, 9 H), 1.48–1.62 (m, 2 H), 1.75–1.92 (m, 3 H), 2.01 (s, 3 H), 2.03 (s, 6 H), 4.70–4.82 (m, 1 H), 4.83–4.96 (m, 1 H), 5.04 (ddd, J = 3.3, 5.4, 7.4 Hz, 1 H); ^{13}C NMR δ 9.87, 17.09, 18.40, 20.90, 20.96, 21.06, 22.34, 30.74, 71.16, 75.18, 75.23, 170.30, 170.59. Anal. Calcd for $C_{15}H_{26}O_6$: C, 59.58; H, 8.67. Found: C, 59.41; H, 8.96.

(1S,3R*,4S*)-1-Phenylhexan-1,3,4-triol Triacetate (7m).* A mixture of **3m** (100 mg, 0.27 mmol) and potassium *tert*-butoxide (32 mg, 0.29 mmol) in DMSO (1 mL) was stirred at rt for 1 h. The mixture was diluted with phosphate buffer solution (pH 7), extracted with ether, washed with water, dried over Na_2SO_4, and evaporated. To the residual oil were added tetrabutylammonium fluoride (1 M in THF, 1.1 mL, 1.1 mmol), MeOH (1 mL), H_2O_2 (30% in water, 0.33 mL) and $KHCO_3$ (54 mg, 0.54 mmol), and the mixture was stirred at 40 °C for 12 h. Aqueous $Na_2S_2O_3$ was added and then volatile compounds were thoroughly removed by evaporation. The residue was acetylated by a procedure similar to that used for **7b** to give **7m** (71 mg, 78%). IR (neat) 2984, 1740, 1374, 1248, 1024 cm^{-1}; ^1H NMR δ 0.82 (t, J = 7.4 Hz, 3 H), 1.40–1.53 (m, 2 H), 1.98 (s, 3 H), 2.00–2.15 (m, 1 H), 2.06 (s, 3 H), 2.07 (s, 3 H), 2.29 (ddd, J = 5.9, 9.5, 14.4 Hz, 1 H), 4.80 (dt, J = 9.5, 3.1 Hz, 1 H), 4.93 (ddd, J = 3.1, 5.2, 8.3 Hz, 1 H), 5.78 (dd, J = 5.9, 8.1 Hz, 1 H), 7.25–7.40 (m, 5 H); ^{13}C NMR δ 9.72, 20.85, 20.90, 21.17, 22.83, 35.23, 70.84, 73.24, 74.96, 126.55, 128.31, 128.63, 139.23, 169.92, 170.17, 170.54. Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 63.99; H, 7.30.

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5. The *syn* addition of the Si–Si linkages in the produced 1,2-oxasilolanes **2a–c,e,f,m,o** was deduced from NOE experiments. The stereochemistry of the other bis-silylated products **2** was assigned by analogy.
6. The stereochemical assignment of **3b** was based on the oxidative transformation to **7b**. The relationship between the 3- and 5-substituents of **3c,k–m** was elucidated according to the ^{1}H NMR chemical shift correlation method.[9]
7. High degrees of regio- and stereospecificities have been observed in numerous examples of diimide reductions of C–C double bonds. This advantage of diimide reduction has been utilized to determine the positions of unsaturation in naturally derived fatty acids; Pasto, D. J.; Tailor, R. T. In *Organic Reactions*, Vol. 40; Paquette, L. A., Ed.; John Wiley and Sons Inc.; 1991, pp. 91–155, and references cited therein. The stereochemical assignment of the side chains of **3f,k–m** is based on the assumption that the direct *syn* addition of hydrogen to the C–C double bonds took place.
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9. The details will be provided in a forthcoming separate article on the intramolecular bis-silylation of C–C double bonds; Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. submitted to *J. Am. Chem. Soc.* for publication..
10. When **3m** was treated with trifluoroacetic acid, intramolecular migration of the phenyl group from the silicon to the benzylic carbon took place giving 1,1-diphenylhexan-3,4-diol after oxidation.
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