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A Facile Preparation and Cyclopropanation of 1-Alkenylsilanols

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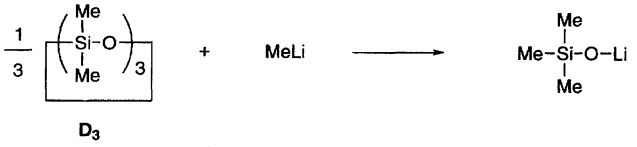
Alkenylsilanols are prepared by the reaction of hexamethyltrisiloxane (D_3) with alkenyllithiums or alternatively by the reaction of cyclic siloxanes substituted by an alkenyl group with organolithiums and transformed to the corresponding cyclopropylsilanols using diiodomethane and diethylzinc. Lithium alkenylsilanolates, primary products of the preparation, also undergo cyclopropanation. As in the case of allylic alcohols, the silanol functionality is found to enhance the rate of cyclopropanation compared with that of alkenyltrialkylsilane or alkoxydialkylsilane. The obtained cyclopropylsilanols are further converted into the corresponding cyclopropanols by the Tamao oxidation.

Despite numerous uses of organosilicon compounds in recent synthetic organic chemistry,[1] silanols that bear a hydroxy group on organosilanes have not been utilized as synthetic tools due to the instability to moisture, heat, acid, and base.[2] Silanols have been considered to be easily converted to the corresponding siloxanes via self-condensation (Eq. 1). Hence, to avoid undesirable condensation, synthetic applications of the silanols to organic synthesis have, in general, been limited to those with bulky substituents.[3]

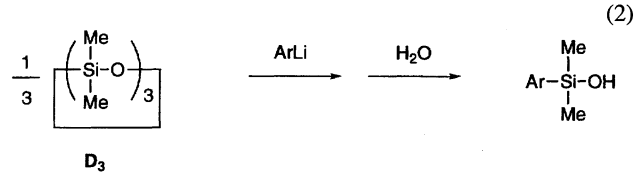
$$R_3Si{-}OH \xrightarrow[-H_2O]{H^+,\ OH^-\ \text{or}\ \Delta} R_3Si{-}O{-}SiR_3 \qquad (1)$$

The preparation of silanols has been made via careful hydrolysis of the corresponding chlorosilanes[4] and alkoxysilanes.[5] Rigorous control of pH during hydrolysis is important to obtain silanols in good yields. On the other hand, we have recently reported that an alkylative cleavage of cyclic siloxanes with an organolithium reagent forms lithium silanolates, which upon further reaction with a chlorosilane lead to unsymmetrical disiloxanes.[6] This process has been demonstrated to be a facile method for preparing siloxanes with functional group(s), provided that the functional group can be incorporated into the organolithium reagent and/or into the cyclic siloxanes (Scheme 1).

We thus envisaged that the alkylative cleavage of cyclic siloxanes can be a practical process[7] for a facile synthesis of silanols when the reaction is terminated by an aqueous work-up to hydrolyze the intermediate lithium silanolates. Indeed, a preparation of lithium trimethylsilanolate by the reaction of cyclic dimethylsiloxanes with methyllithium was briefly reported by Rudisch and Schmidt (Eq. 2).[8] Sieburth and Mu also reported that the reaction of a cyclic siloxane with an aryllithium formed the corresponding aryl(dimethyl)silanol in good yield (Eq. 3).[9]



(2)



(3)

We considered that it would be possible to introduce functional groups using a functionalized organolithium reagent or cyclic siloxanes substituted by the functional group. We thus focused on the preparation of 1-alkenylsilanols, since the olefinic group is easily transformed to a variety of functionalities. In these transformations, the hydroxy group of the silanol would play a significant role, since the alkenylsilanols serve as sila-analog of allylic alcohols[10] (Chart 1), whose olefins are known to react with various electrophiles or nucleophiles by support of the neighboring hydroxy groups.[11]

The Simmons–Smith cyclopropanation[12] is a typical example of the rate acceleration by the hydroxy group of an allylic alcohol. The reaction is arguably the most important application of an organozinc reagent in organic synthesis.[13] The reaction proceeds under mild conditions and is characterized by broad generality, olefin stereospecificity, and a high degree of relative stereoselectivity with allylic alcohols. Indeed, a strong directing effect of a hydroxy group has been recognized and shown to have preparative and mechanistic significance.[12,14] We thereby considered that a similar effect of the hydroxy group of allylic alcohol would also be possible for the cyclopropanation of alkenylsilanols.

We report herewith on a facile preparation of alkenylsilanols via the alkylative cleavage of cyclic siloxanes using organolithium reagents. The cyclopropanation of the

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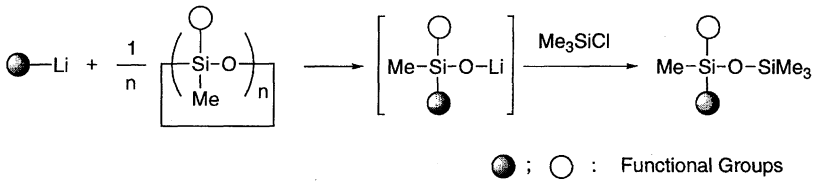


Scheme 1.

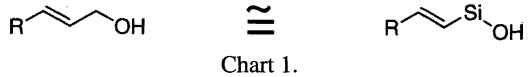


Chart 1.

alkenylsilanols, where the silanol hydroxy group plays a significant role to enhance the rate of cyclopropanation, is also described.[15]

Results and Discussion

Synthesis of Alkenylsilanols. Since silanols are accessible by an alkylative cleavage of a cyclic siloxane with an organolithium reagent, the synthesis of alkenylsilanols can be accessible by either of the following methods: i) the cleavage of a cyclic dimethylsiloxane, such as hexamethylcyclotrisiloxane (D_3) with an alkenyllithium, or ii) the cleavage of a cyclic siloxane with an alkenyl group by an alkyllithium (Scheme 2).

Table 1 gives the results of method i) using D_3 as a cyclic siloxane. The corresponding alkenyllithiums were prepared in situ by a halogen–lithium exchange or by proton abstraction with *n*- or *t*-butyllithium. The thus-generated alkenyllithiums were subjected to a reaction with D_3 in diethyl ether at −78 or 0 °C, and the corresponding silanols were obtained in 61—85% yields after stirring at room temperature for 10—24 h. The silanols were isolated by the usual aqueous work-up followed by bulb-to-bulb distillation under reduced pressure. We were pleased to observe that condensation to the corresponding disiloxane did not take place during the reaction, work-up or distillation. Flush chromatography on silica gel was also accessible when the procedure was carried out within a short period. The silanols showed infrared absorption at 953—848 cm^{-1}, which is characterized as Si–OH stretching (the corresponding disiloxane 1130—1000 cm^{-1}). A measurement of the ^1H NMR spectra indicated the characteristic CH_3 signals on the silicon atoms at 0.19—0.48 ppm, e.g. $\delta = 0.31$ for **1a** (the corresponding disiloxane **1c** at $\delta = 0.11, 0.22$).

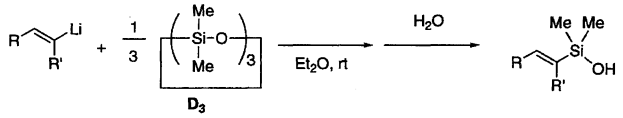
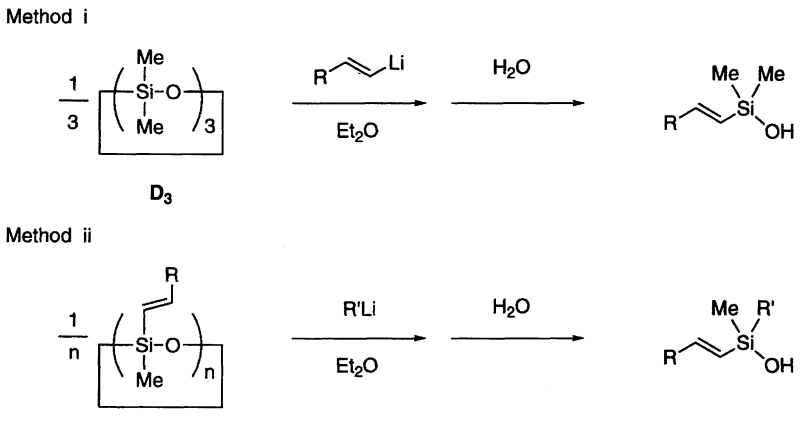


Table 1. Reaction of D_3 with Alkenyllithium

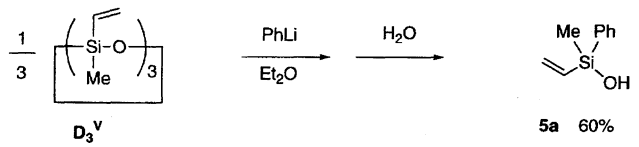
Entry		Time (h)	Product	Isolated yield (%)
1		24	**1a**	85
2		24	**2**	65
3		12	**3a**	65[a]
4		10	**4**	61

a) $E:Z = 3:1$.

Method ii) is representative by the reaction of commercially available 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (D_3^V) with organolithium reagents. As shown in Eq. 4, **5a** was prepared in 60% yield by the reaction of D_3^V with phenyllithium.



Scheme 2.



(4)

Cyclic siloxanes with an alkenyl group were synthesized by the hydrosilylation of alkynes[16] with 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H). For the reaction of symmetric 4-octyne using a catalytic amount of platinum complex ($(Bu_4N)_2[PtCl_6]$)[17] followed by alkylative cleavages of the resulting cyclic siloxane with the alkenyl group by methyllithium or phenyllithium, as shown in Scheme 3, afforded the corresponding silanols in 41% (R = Me) and 48% (R = Ph) yields, respectively.[18]

However, hydrosilylation of 1-alkynes caused regio- and stereochemical problems to yield the silanols as a mixture of *trans*-(*β*-adduct), *cis*-(*β*-adduct), and 1,1-disubstituted-(*α*-adduct) products. Table 2 gives the results of the hydrosilylation of 1-phenylethyne and 1-hexyne followed by alkylative cleavages with methyllithium. Since the regio- and stereoisomeric ratio of hydrosilylation was not identified by measurements of the intermediate cyclic siloxanes by ^{1}H NMR, the isomer ratio was determined after alkylative cleavages were carried out. Although several catalysts were preliminary examined, no catalyst was found to be regio- and stereoselective to give a mixture of *trans*-(*β*-adduct), *cis*-(*β*-adduct), and *α*-products.

Thus, a survey of the regio- and stereoselective catalyst for hydrosilylation was carried out using 1-phenylethyne and pentamethyldisiloxane as a model reaction; we found that the addition of sodium iodide to the Wilkinson's complex [RhCl(PPh$_3$)$_3$][19] resulted in high selectivity. The corresponding pentamethyl[(*E*)-2-phenylethenyl]disiloxane was formed by a reaction in the presence of 0.1 mol% of [RhCl(PPh$_3$)$_3$], 5.3 mol% of NaI at 60 °C for 18 h.[20] The reaction with D_4^H was also selective to give the corresponding alkenylsilanols after an alkylative cleavage with methyllithium, as shown in Scheme 4.

The attempted alternative method, which involves the alkylative cleavage of D_3 with an alkynyllithium followed by a stereoselective reduction of the corresponding alkynylsilanol using Lindlar catalyst (*cis*-silanol),[21] lithium aluminum hydride (lithium tetrahydridoaluminate)[22] or diisobutylaluminum hydride,[23] has not yet been successful (Scheme 5).

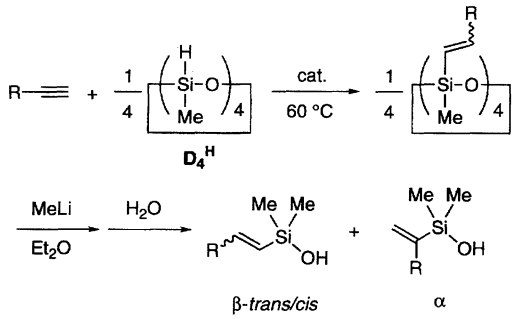


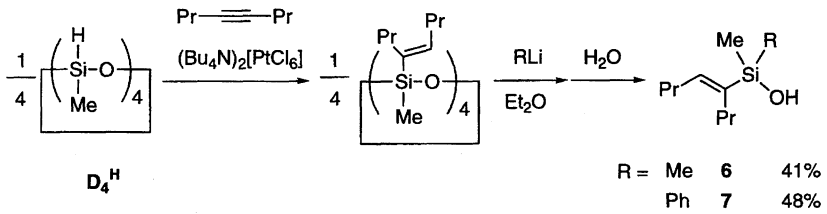
Table 2. Hydrosilylation of Cyclic Siloxane

Entry	R	Cat.	Time (h)	*t* : *c* : *α*	Yield (%)
1	Ph	$(Bu_4N)_2[PtCl_6]$	20	69 : 0 : 31	60
2		$[RhCl(PPh_3)_3]$	18	95 : 0 : 5	>10
3	Bu	$(Bu_4N)_2[PtCl_6]$	48	70 : 0 : 30	66
4		$[RhCl(PPh_3)_3]$	72	62 : 15 : 23	70

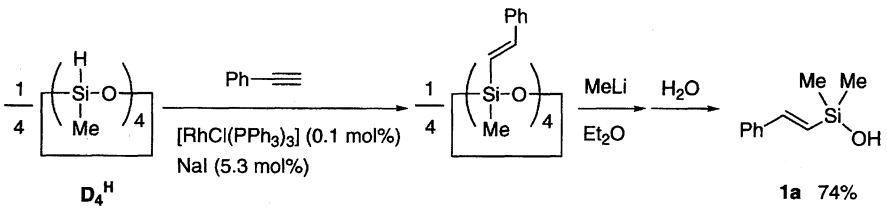
t: *β-trans*, *c*: *β-cis*.

Cyclopropanation of Alkenylsilanols. Since we have in hand several methods for the facile preparation of alkenylsilanols, as mentioned above, we focused on cyclopropanation using diiodomethane and diethylzinc, which is a representative transformation of the alkenyl group meditated by the neighboring hydroxy group. The reaction, whose details were recently studied by Denmark[24] and Charette[25] independently, with diiodomethane (2 mol) and diethylzinc (1 mol) was reported to form $Zn(CH_2I)_2$, which was characterized by X-ray crystallography and NMR spectroscopy.[26] We, thus, followed the above reaction conditions for the reaction of alkenylsilanols.

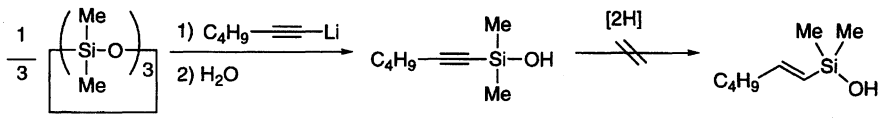
The reactions of alkenylsilanols with diethylzinc and diiodomethane were carried out under several conditions, as given in Tables 3, 4, and 5. The reaction of dimethyl[(*E*)-2-phenylethenyl]silanol (**1a**) was carried out using 2 molar



Scheme 3.

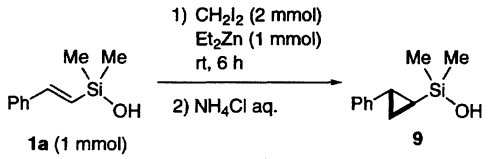


Scheme 4.



D$_3$ **8**

Scheme 5.

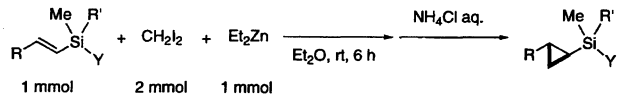


1a (1 mmol) **9**

Table 3. Solvent Effect

Entry	Solvent	Yield (%)[a]
1	CH_2Cl_2	73
2	Et_2O	71
3	Hexane	50
4	THF	0
5	DMF	0

a) Yield was calculated based on the ratio in ^{1}H NMR.



1 mmol 2 mmol 1 mmol

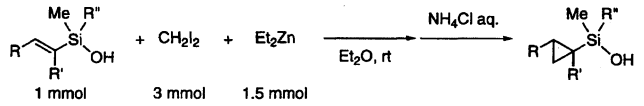
Table 4. Effect of a Hydroxyl Protective Group

Entry	R	R′	Y		Yield (%)[a]
1	Ph	Me	OH	**1a**	71
2			OCH_2CH_2Ph	**1b**	50
3			$OSiMe_3$	**1c**	0
4	C_6H_{13}	Me	OH	**3a**[b]	100
5			OCH_2CH_2Ph	**3b**	81
6			$OSiMe_3$	**3c**[b]	0
7	H	Ph	OH	**5a**	72
8			OCH_2CH_2Ph	**5b**	Trace
9			$OSiMe_3$	**5c**	0

a) Yield was based on the ratio in ^{1}H NMR. b) $E:Z=3:1$.

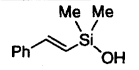
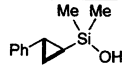
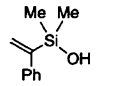
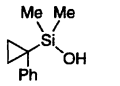
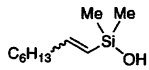
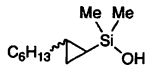
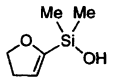
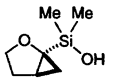
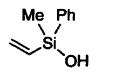
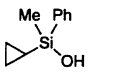
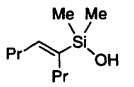
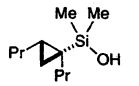
amounts of diiodomethane and 1 mol amount of diethylzinc in dichloromethane at room temperature for 6 h. The cyclopropanation proceeded to yield the corresponding product in 73% yield.[27] Several solvents were examined, as shown in Table 3. The use of diethyl ether or hexane as a solvent was similarly found to be effective for cyclopropanation in moderate-to-good yields. In contrast, polar aprotic solvents, such as THF and DMF, resulted in no reaction.

The effect of the hydroxy group on silicon in the cyclopropanation was confirmed by comparing with the reactions of silanols (**1a**, **3a**, and **5a**), alkoxysilanes (**1b**, **3b**, and **5b**) and disiloxanes (**1c**, **3c**, and **5c**). Table 4 summarizes the results on the effect of the hydroxy group. The reactions of alkenylsilanes with an alkoxy group and trimethylsiloxy group as well as the silanol were studied using three kinds of compounds: **1**, **3**, and **5**. The reactions of alkenylsilanols proceeded smoothly. On the other hand, only a trace amount of cyclopropanation was observed when alkoxysilane **5b** was



1 mmol 3 mmol 1.5 mmol

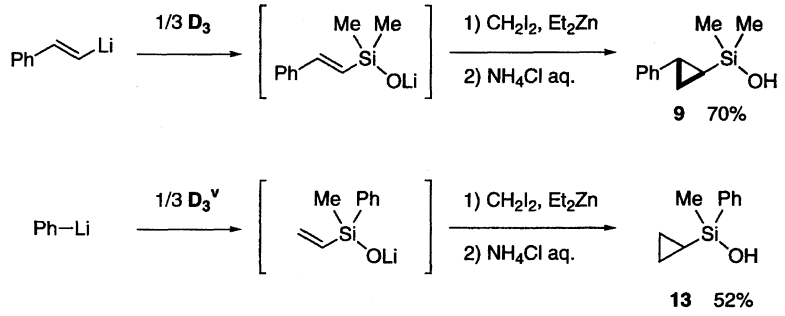
Table 5. Cyclopropanation of Alkenylsilanols

Entry	Substrate	Product	Time (h)	Isolated yield (%)[a]
1	 **1a**	 **9**[b]	6	70
2	 **2**	 **10**	6	78
3	 **3a**[b]	 **11**[b]	6	85
4	 **4**	 **12**[b]	2	63
5	 **5a**	 **13**	6	60
6	 **6**	 **14**[b]	6	80

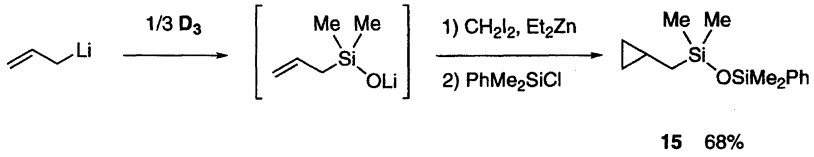
a) Products were purified by column chromatography on silica gel. b) Diastereoisomers can not be detected in ^{1}H NMR. c) $E:Z=3:1$.

employed as a substrate. Although the cyclopropanation of other alkoxysilanes **1b** and **3b** proceeded in slightly lower yields compared with those of the corresponding silanols, sterically congested disiloxanes (substituted with trimethylsilyl group) **1c**, **3c**, and **5c**, which inhibited the coordination of the zinc reagent to the oxygen on silicon, resulted in no reaction. In addition, trimethylvinylsilane was also reported to react more slowly with the zinc–copper couple and diiodomethane in di-*n*-butyl ether at 60 °C for 26 h to yield the corresponding product in 50%.[28]

The reactions of a variety of alkenylsilanols, such as monosubstituted, *trans*- and/or *cis* disubstituted, 1,1-disubstituted,



Scheme 6.



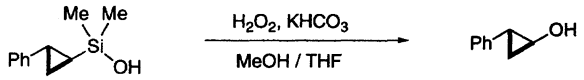
Scheme 7.

and trisubstituted ones, proceeded in good yields. The results are given in Table 5.

Cyclopropanation of Alkenylsilanolates. We also envisioned the cyclopropanation of alkenyl silanolates. Since the lithium alkenylsilanolates are considered to be generated by the reaction of a cyclic siloxane and an organolithium reagent, the addition of diethylzinc and diiodomethane to the mixture would result in a one-pot synthesis of the cyclopropylsilanol from an organolithium reagent, cyclic siloxane, and cyclopropanation reagents. Scheme 6 is illustrative as one-pot cyclopropanation reactions. When D_3 was subjected to in situ generated (*E*)-2-phenylethenyllithium at 0 °C, followed by a treatment of diiodomethane and diethylzinc, it afforded the corresponding cyclopropylsilanol **7** in 70% yield after hydrolysis. In addition, cyclopropyl(methyl)phenylsilanol (**11**) was also obtained in 52% yield in a similar manner. The yields were higher than those of subsequent two-step reactions including alkylative cleavage and cyclopropanation.

In addition, we performed a one-pot reaction of allyllithium and D_3, and then the cyclopropanation, to give the corresponding (cyclopropylmethyl)dimethylsilanol (Scheme 7). The product was isolated as the corresponding disiloxane **15** after a treatment with $PhMe_2SiCl$ and Et_3N, because of the low boiling point of the silanol. Since isolation of allyldimethylsilanol is considered to be difficult due to the sensitivity of the allylic carbon–silicon bond toward moisture,[1] a one-pot reaction using allyllithium should be of great synthetic utility.

A transformation of the carbon–silicon bond of the obtained cyclopropylsilanol was performed. The carbon–silicon bond is successfully transformed to a carbon–oxygen bond, the process being representative as the Tamao oxidation.[29] The cyclopropylsilanol **7** was treated with 30% H_2O_2 and $NaHCO_3$ in MeOH/THF to give alcohol **16** in 48% yield (Eq. 5).



7 **16** 48% (5)

Conclusion

In conclusion, alkylative cleavages of cyclic siloxanes with organolithium reagents were demonstrated as a facile preparative method for the alkenylsilanols. The procedure afforded the silanols in good yields, and can avoid any undersirable formation of the disiloxane via self-condensation. The alkenyl groups were readily accessible to a transformation leading to cyclopropanes via the Simmons–Smith reaction using diiodomethane and diethylzinc. In these reactions, the hydroxy group on the silicon played significant roles to enhance the rate of cyclopropanation. A one-pot synthesis of the cyclopropylsilanol from cyclic siloxanes and organolithium reagents has also been demonstrated.

Experimental

General. All temperatures are uncorrected. The melting points were measured with a Yanagimoto micro melting-point apparatus. All NMR spectra were measured in a $CDCl_3$ solution, the chemical shifts being given in ppm. ^1H NMR spectra ($CHCl_3$; 7.26 ppm as an internal standard) and ^{13}C NMR spectra ($CDCl_3$; 77.0 ppm as an internal standard) were measured on a Bruker AC-200 spectrometer. The IR spectra were recorded with a Shimadzu FTIR-8000A spectrometer in neat liquid or KBr. The mass spectra were recorded with a Shimadzu QP-5000 GC-MS system. Elemental analyses were carried out by Elemental Analysis Center, Tokyo Institute of Technology, using Yanako MT2 CHN CORDER. High-resolution mass spectra were obtained on a JEOL MStation. For thin-layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Flush column chromatography was performed using Merck Kieselgel 60 (70—230 mesh and 230—400 mesh) or Wakogel C-200.

All of the reactions were carried out under an argon atmosphere unless otherwise noted. Diethyl ether, THF, and hexane were distilled from sodium/benzophenone prior to use. Dichloromethane

was distilled from CaH_2 prior to use. DMF was distilled from CaH_2 and stored over MS-4A under an argon atmosphere. Cyclic siloxanes (D_3, D_4^H, and D_3^V) were kindly donated by Shin-Etsu Chemical Co., Ltd and used as such. Et_2Zn, BuLi, *t*-BuLi, and PhLi were purchased from Kanto Chemical Inc. and used without further purification.

(*E*)-1-[Hydroxy(dimethyl)silyl]-2-phenylethene (1a)[10] **(Method i):** To a solution of (*E*)-1-bromo-2-phenylethene (2.75 g, 15 mmol) in dry diethyl ether (15 mL) was slowly added *t*-BuLi (21.4 mL, 30 mmol, 1.4 M in pentane, 1 M = 1 mol dm^{-3}) at −78 °C. After the mixture was stirred at −78°C for 1 h, D_3 (1.11 g, 5.0 mmol) was added at −78 °C. The resulting solution was allowed to warm to room temperature, stirred for an additional 24 h, quenched with H_2O (20 mL) at 0 °C, and the organic phase was separated. The aqueous phase was extracted with diethyl ether (50 mL×3). The combined extracts were washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was distilled with a bulb-to-bulb distillation apparatus under reduced pressure to give **1a** (2.30 g, 86% yield) as a colorless oil: Bp 150 °C/1 mmHg (1 mmHg = 133.322 Pa) (bath temp). IR (neat) 3300, 2992, 2959, 1605, 1574, 1495, 1446, 1252, 991, 848, 779 cm^{-1}; ^1H NMR (200 MHz) δ = 0.31 (s, 6H), 1.71 (br, 1H), 6.46 (d, J = 19.4 Hz, 1H), 7.01 (d, J = 19.4 Hz, 1H), 7.26—7.47 (m, 5H); ^{13}C NMR (50.3 MHz) δ = 0.2, 126.7, 127.5, 128.5, 128.7, 137.9, 145.3; MS (70 eV) *m/z* (%) 178 (M^+; 21), 163 (69), 145 (100), 104 (49).

1-[Hydroxy(dimethyl)silyl]-1-phenylethene (2): Method i procedure with 1-bromo-1-phenylethene (2.75 g, 15 mmol), *t*-BuLi (21.4 mL, 30 mmol, 1.4 M in pentane), and D_3 (1.11 g, 5.0 mmol) gave **2** (1.74 g, 65% yield) as a colorless oil: Bp 150 °C/1 mmHg (bath temp). IR (neat) 3300, 2961, 2903, 1878, 1597, 1491, 1253, 1101, 937, 848, 785 cm^{-1}; ^1H NMR (200 MHz) δ = 0.31 (s, 6H), 1.80 (br, 1H), 5.73 (d, J = 2.7 Hz, 1H), 5.93 (d, J = 2.7 Hz, 1H), 7.23—7.34 (m, 5H); ^{13}C NMR (50.3 MHz) δ = 0.3, 126.8, 126.8, 128.1, 128.4, 143.4, 152.2; MS (70 eV) *m/z* (%) 178 (M^+; 21), 163 (69), 145 (100), 104 (49). Found: *m/z* 178.0815. Calcd for $C_{10}H_{14}OSi$: M^+, 178.0814.

A Mixture of (*E*)-1-[Hydroxy(dimethyl)silyl]-1-octene and (*Z*)-1-[Hydroxy(dimethyl)silyl]-1-octene ((*E*) : (*Z*) = 3 : 1) (3a): The procedure of Method i with 1-bromo-1-octene (0.45 g, 2.2 mmol, (*E*) : (*Z*) = 3 : 1), *t*-BuLi (2.74 mL, 4.4 mmol, 1.57 M in pentane), and D_3 (0.16 g, 0.7 mmol) gave **3a** (0.26 g, 65% yield) as a colorless oil: Bp 115 °C/0.9 mmHg (bath temp). IR (neat) 3316, 2959, 2928, 1609, 1468, 1379, 1252, 1069, 868 cm^{-1}; ^1H NMR (200 MHz) δ = 0.20; 0.25 (s, 6H), 0.89 (m, 3H), 1.26—1.37 (m, 8H), 2.16 (m, 2H), 5.47 (dt, J = 1.2, 14.1 Hz, (*E*)); 5.65 (dt, J = 1.4, 18.6 Hz, (*Z*)), 6.20 (dt, J = 6.2, 18.6 Hz, (*Z*)); 6.37 (dt, J = 7.2, 14.1 Hz, (*E*)); ^{13}C NMR (50.3 MHz) δ = 0.1, 1.8, 14.1, 22.7, 28.6, 29.0, 29.1, 29.7, 31.8, 31.9, 33.8, 36.7, 127.7, 128.3, 149.6, 151.0; MS (70 eV) *m/z* (%) 186 (M^+; 2), 171 (23), 149 (12), 116 (12), 75 (100). Found: *m/z* 186.1440. Calcd for $C_{10}H_{22}OSi$: M^+, 186.1440.

2-[Hydroxy(dimethyl)silyl]-4,5-dihydrofuran (4): To a solution of 2,3-dihydrofuran (1.13 mL, 15 mmol) in dry THF was slowly added BuLi (10.1 mL, 15 mmol, 1.4 M in hexane) at −78 °C, and mixture was stirred at −78 °C for 1 h. The temperature was gradually raised to room temperature, and the reaction mixture was stirred for 30 min before recooling to −78 °C; D_3 (1.11 g, 5.0 mmol) was then added. The resulting solution was allowed to warm to room temperature, stirred for 10 h, quenched with H_2O (20 mL) at 0 °C, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (50 mL×3). The combined extracts were washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was subjected to bulb-to-bulb distillation under reduced pressure to furnish **4** (1.32 g, 61% yield) as a colorless oil: Bp 110 °C/0.6 mmHg (bath temp). IR (neat) 3384, 2961, 2859, 1597, 1448, 1404, 1253, 1099, 928, 785 cm^{-1}; ^1H NMR (200 MHz) δ = 0.29 (s, 6H), 1.65 (br, 1H), 2.61 (dt, J = 2.5, 9.6 Hz, 2H), 4.29 (t, J = 9.6 Hz, 2H), 5.32 (t, J = 2.5 Hz, 1H); ^{13}C NMR (50.3 MHz) δ = 0.8, 30.6, 70.4, 112.5, 160.9. Found: C, 49.79; H, 8.41%. Calcd for $C_6H_{12}O_2Si$: C, 49.96; H, 8.39%.

1-[Hydroxy(methyl)phenyl]silylethene (5a) (Method ii): Phenyllithium (5.56 mL, 10 mmol, 1.8 M in cyclohexane/diethyl ether) was slowly added to a solution of D_3^V (0.85 g, 3.3 mmol) in dry diethyl ether (5 mL) at 0 °C. The mixture was stirred at room temperature for an additional 24 h and then was quenched with H_2O (20 mL) at 0 °C. The organic layer was separated and the aqueous layer was extracted with diethyl ether (50 mL×3). The combined extracts were washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was subjected to bulb-to-bulb distillation under reduced pressure to give **5a** (0.98 g, 60% yield) as a colorless oil: Bp 115 °C/0.6 mmHg (bath temp). IR (neat) 3280, 3071, 1593, 1429, 1406, 1253, 1118, 1008, 960, 858, 796, 729 cm^{-1}; ^1H NMR (200 MHz) δ = 0.48 (s, 3H), 2.04 (s, 1H), 5.91 (dd, J = 4.7, 19.5 Hz, 1H), 6.12 (dd, J = 4.7, 14.9 Hz, 1H), 6.32 (dd, J = 14.9, 19.5 Hz, 1H), 7.36—7.43 (m, 3H), 7.57—7.59 (m, 2H); ^{13}C NMR (50.3 MHz) δ = −1.7, 128.0, 129.9, 133.7, 134.6, 136.6, 137.3; MS (70 eV) *m/z* (%) 164 (M^+; 17), 149 (100), 137 (46), 123 (54), 91 (14). Found: C, 65.66; H, 7.26%. Calcd for $C_9H_{12}OSi$: C, 65.80; H, 7.36%.

4-[Hydroxy(dimethyl)silyl]-4-octene (6a): A mixture of 4-octyne (3.67 mL, 25 mmol), $(Bu_4N)_2[PtCl_6]$ (23.0 mg, 0.003 mmol), and D_4^H (1.46 mL, 6 mmol) was stirred in a sealed screw-capped glass tube at 60 °C for 2 d. The reaction was monitored by taking an aliquot of the mixture and measuring with ^1H NMR. After completion of the reaction, this material was used directly for the next reaction.

To a solution of the crude product (0.88 g) in dry diethyl ether (10 mL) was slowly added MeLi (7.33 mL, 11 mmol, 1.5 M in diethyl ether) at 0 °C. The reaction mixture was stirred at room temperature for 12 h before quenching with H_2O (20 mL) at 0 °C. The organic layer was separated, and an aqueous layer was extracted with diethyl ether (50 mL×3). The combined extracts were washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was subjected to bulb-to-bulb distillation under reduced pressure to give **6a** (0.75 g, 41% yield) as a colorless oil: Bp 145 °C/0.4 mmHg (bath temp). IR (neat) 3285, 2959, 2932, 2872, 1613, 1377, 1252, 1163, 1019, 864 cm^{-1}; ^1H NMR (200 MHz) δ = 0.19 (s, 6H), 0.91 (t, J = 7.2 Hz, 6H), 1.26—1.46 (m, 4H), 1.62 (br, 1H), 2.09 (dt, J = 6.9, 14.5 Hz, 2H), 2.13 (t, J = 8.4 Hz, 2H), 5.87 (t, J = 6.9 Hz, 1H); ^{13}C NMR (50.3 MHz) δ = 0.0, 14.0, 14.5, 22.7, 23.6, 30.5, 31.4, 140.6, 142.0; MS (70 eV) *m/z* (%) 186 (M^+; 3), 171 (5), 110 (14), 75 (100). Found: *m/z* 186.1434. Calcd for $C_{10}H_{22}OSi$: M^+, 186.1439.

4-[Hydroxy(methyl)phenylsilyl]-4-octene (7): Following the procedure of Method ii using PhLi (6.1 mL, 11 mmol, 1.8 M in cyclohexane/diethyl ether), **7** (0.88 g) was obtained in 48% yield as a colorless oil: Bp 150 °C/0.4 mmHg (bath temp). IR (neat) 3312, 2959, 2930, 2872, 1613, 1429, 1254, 1115, 1019, 853 cm^{-1}; ^1H NMR (200 MHz) δ = 0.46 (s, 3H), 0.86 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H), 1.15—1.22 (m, 4H), 1.89 (br, 1H), 2.08—2.19 (m, 4H), 5.97 (t, J = 7.0 Hz, 1H), 7.33—7.41 (m, 3H), 7.56—7.63 (m, 2H); ^{13}C NMR (50.3 MHz) δ = −1.3, 14.0, 14.5, 22.7, 23.5, 30.7, 31.6, 127.8, 129.5, 133.8, 138.3, 138.6, 144.2; MS (70 eV) *m/z* (%) 248 (M^+; 38), 233 (13), 191 (18), 135 (20), 71 (100).

Found: *m/z* 248.1596. Calcd for $C_{15}H_{24}OSi$: M^+, 248.1595.

1-[Hydroxy(dimethyl)silyl]-1-hexyne (8): Butyllithium (6.75 mL, 11 mmol, 1.6 M in hexane) was slowly added to a solution of 1-hexyne (1.22 mL, 10 mmol) in dry THF (15 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 1 h, and again cooled to 0 °C. To the reaction mixture was added D_3 (0.73 g, 3.3 mmol). The resulting solution was allowed to warm to room temperature, stirred for 12 h, quenched with H_2O (20 mL) at 0 °C, and the organic layer was separated. The aqueous layer was extracted with diethyl ether (50 mL×3). The combined extracts were washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was subjected to bulb-to-bulb distillation under reduced pressure to give **8** (0.75 g, 48% yield) as a colorless oil: Bp 110 °C/0.5 mmHg (bath temp). IR (neat) 3300, 2961, 2936, 2178, 1323, 1258, 1067, 953 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ = 0.28 (s, 6H), 0.92 (t, J = 6.8 Hz, 3H), 1.35—1.59 (m, 4H), 1.75 (br 1H), 2.24 (t, J = 7.0 Hz, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 1.7, 13.6, 19.5, 22.0, 30.6, 83.5, 107.8; MS (70 eV) *m/z* (%) 156 (M^+; 12), 99 (22), 85 (72), 75 (100), 61 (33). Found: *m/z* 156.0964. Calcd for $C_8H_{16}OSi$: M^+, 156.0970.

General Procedure for the Cyclopropanation. To a solution of alkenylsilanol (0.5 mmol) in dry diethyl ether (2 mL) were slowly added Et_2Zn (0.76 mL, 0.75 mmol, 0.99 M in hexane) and CH_2I_2 (0.12 mL, 0.40 g, 1.5 mmol) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and for 5 h at room temperature, then quenched with aqueous NH_4Cl (5 mL); the organic layer was then separated. The aqueous layer was extracted with diethyl ether (20 mL×3). The combined extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography and/or bulb-to-bulb distillation to give the corresponding cyclopropylsilanol. The stereochemistry of **9** was confirmed after leading to **16** by the Tamao oxidation. The stereochemistries of other products **11**, **12**, and **14** were deduced from the result of **9**.

***trans*-1-[Hydroxy(dimethyl)silyl]-2-phenylcyclopropane (9):** This compound was obtained in 74% yield as a colorless oil. R_f 0.40 (Hexane/AcOEt = 5/1). Bp 140 °C/0.8 mmHg (bath temp). IR (neat) 3300, 3068, 2959, 1605, 1498, 1253, 981, 908, 779 cm^{-1}; ^1H NMR (500 MHz) δ = 0.17 (s, 6H), 0.16 (m, 1H), 1.00 (ddd, J = 4.5, 7.0, 17.0 Hz, 2H), 1.91 (dd, J = 7.0, 11.0 Hz, 1H), 7.06—7.30 (m, 5H); ^{13}C NMR (50.3 MHz) δ = −1.1, 11.0, 12.8, 19.6, 125.6, 125.7, 128.4, 144.0; MS (70 eV) *m/z* (%) 192 (M^+; 4), 159 (4), 115 (9), 91 (5), 75 (100). Found: C, 68.87; H, 8.45%. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.38%.

1-[Hydroxy(dimethyl)silyl]-1-phenylcyclopropane (10): Obtained in 78% yield as a white solid. R_f 0.30 (Hexane/AcOEt = 5/1). Bp 140 °C/0.8 mmHg (bath temp). Mp 48—49 °C. IR (neat) 3300, 3069, 1959, 1599, 1489, 1252, 1215, 1026, 925, 835, 777, 700 cm^{-1}; ^1H NMR (200 MHz) δ = 0.07 (s, 6H), 0.87 (dt, J = 2.1, 10.0 Hz, 4H), 1.55 (br, 1H), 7.09—7.30 (m, 5H); ^{13}C NMR (50.3 MHz) δ = −2.3, 9.6, 16.4, 125.4, 128.2, 130.4, 145.4; MS (70 eV) *m/z* (%) 192 (M^+; 4), 159 (6), 137 (5), 115 (11), 91 (5), 75 (100). Found 192.0974. Calcd for $C_{11}H_{16}OSi$: M^+, 192.0970.

***trans*- and *cis*-1-[Hydroxy(dimethyl)silyl]-2-hexylcyclopropane (11) (Used Mixture of (*E*)- and (*Z*)-3a):** Obtained in 85% yield as a colorless oil. Bp 115 °C/0.9 mmHg (bath temp). IR (neat) 3300, 3060, 2957, 2926, 2855, 1379, 1252, 1057, 936, 860 cm^{-1}; ^1H NMR (200 MHz) δ = 0.16 (m, 1H), 0.17 (s, 6H), 0.85—0.92 (m, 5H), 1.29—1.40 (m, 11H); ^{13}C NMR (50.3 MHz) δ = −1.3, −1.0, 1.2, 1.3, 3.5, 8.9, 9.0, 14.1, 17.1, 22.8, 29.3, 30.4, 32.0, 32.4; MS (70 eV) *m/z* (%) 200 (M^+; 7), 185 (5), 115 (4), 75 (100). Found: *m/z* 200.1602. Calcd for $C_{11}H_{24}OSi$: M^+, 200.1595.

1-[Hydroxy(dimethyl)silyl]-*cis*-2-oxabicyclo[3.1.0]hexane (12): Obtained in 63% yield as a colorless oil. R_f0.20 (Hexane/AcOEt = 5/1). Bp 110 °C/0.8 mmHg (bath temp). IR (neat) 3400, 2959, 2874, 1253, 1147, 1062, 1010, 983, 889, 781 cm^{-1}; ^1H NMR (200 MHz) δ = 0.18 (s, 3H), 0.19 (s, 3H), 0.47 (dd, J = 6.3, 8.5 Hz, 1H), 0.81 (dd, J = 5.0, 6.4 Hz, 1H), 1.50 (m, 1H), 2.03 (m, 2H), 2.11 (br, 1H), 3.54 (dd, J = 8.9, 17.2 Hz, 1H), 3.97 (dt, J = 5.6, 8.9 Hz, 1H); ^{13}C NMR (50.3 MHz) δ = −2.1, −2.0, 0.4, 12.0, 20.2, 29.0, 67.0; MS (70 eV) *m/z* (%) 158 (M^+; 4), 143 (4), 125 (6), 75 (100). Found: *m/z* 158.0764. Calcd for $C_7H_{14}O_2Si$: M^+, 158.0762.

[(Hydroxy)(methyl)phenylsilyl]cyclopropane (13): Obtained in 60% yield as a colorless oil. R_f 0.34 (Hexane/AcOEt = 5/1). Bp 130 °C/0.6 mmHg (bath temp). IR (neat) 3300, 3071, 2999, 1429, 1288, 1255, 1115, 1035, 900, 854, 736, 721, 698 cm^{-1}; ^1H NMR (200 MHz) δ = −0.13 (tt, J = 6.8, 9.8 Hz, 1H), 0.31 (s, 3H), 0.38 (m, 2H), 1.68 (ddd, J = 4.5, 6.1, 9.4 Hz, 2H), 1.81 (br, 1H), 7.35—7.43 (m, 3H), 7.61—7.67 (m, 2H); ^{13}C NMR (50.3 MHz) δ = −4.7, −3.1, 1.2, 1.3, 127.9, 129.7, 133.6, 137.9. Found: C, 67.27; H, 8.15%. Calcd for $C_{10}H_{14}OSi$: C, 67.36; H, 7.91%.

***r*,1-[Hydroxy(dimethyl)silyl]-*t*-1,*t*-2-dipropylcyclopropane (14):** Obtained in 80% yield as a colorless oil. Bp 110 °C/0.6 mmHg (bath temp). IR (neat) 3310, 2959, 2872, 1466, 1377, 1252, 1194, 1009, 920, 860 cm^{-1}; ^1H NMR (200 MHz) δ = 0.07 (s, 3H), 0.08 (s, 3H), 0.61—0.74 (m, 2H), 0.85—0.99 (m, 7H), 0.23—1.50 (m, 8H), 1.56 (br, 1H); ^{13}C NMR (50.3 MHz) δ = −1.4, −1.3, 11.9, 14.2, 15.0, 15.5, 20.0, 23.2, 23.5, 30.6, 33.3; MS (70 eV) *m/z* (%) 200 (M^+; 1), 185 (1), 115 (3), 82 (2), 75 (100). Found: *m/z* 200.1589. Calcd for $C_{11}H_{24}OSi$: M^+, 200.1595.

One-Pot Procedure for the Synthesis of 9. *t*-Butyllithium (1.36 mL, 2.0 mmol, 1.47 M in pentane) was slowly added to a solution of (*E*)-1-bromo-2-phenylethene (0.13 mL, 1.0 mmol) in dry diethyl ether (1 mL) at −78 °C. After the mixture was stirred for 1 h at −78 °C, D_3 (73.4 mg, 0.3 mmol) was added at −78 °C. The resulting solution was allowed to warm to room temperature, stirred for 12 h, and treated with Et_2Zn (1.5 mL, 1.5 mmol, 1.0 M in hexane) and CH_2I_2 (0.24 mL, 3.0 mmol) at 0 °C; it was then stirred at room temperature for an additional 6 h, and quenched with aqueous NH_4Cl (5 mL), after which the organic layer was separated. The aqueous layer was extracted with diethyl ether (20 mL×3). The combined extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/AcOEt = 15/1, R_f 0.40 (Hexane/AcOEt = 5/1)) to give **9** (123.5 mg, 70% yield) as a colorless oil.

One-Pot Procedure for Synthesis of 13. Phenyllithium (1.8 mL, 1.0 mmol, 1.8 M in cyclohexane/diethyl ether) was slowly added to a solution of D_3^V (0.85 mg, 0.3 mmol) in dry diethyl ether (1 mL) at 0 °C. The reaction mixture was stirred at room temperature for 24 h. Et_2Zn (1.5 mL, 1.5 mmol, 1.0 M in hexane) and CH_2I_2 (0.24 mL, 3.0 mmol) were added to the mixture at 0 °C. The mixture was stirred at room temperature for an additional 6 h, quenched with aqueous NH_4Cl (5 mL), and the organic layer was separated. The aqueous layer was extracted with diethyl ether (20 mL×3). The combined extracts were washed with brine (5 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/AcOEt = 15/1, R_f 0.34 (Hexane/AcOEt = 5/1)) gave **13** (91.8 mg, 52% yield) as a colorless oil.

(*E*)-1-[Dimethyl(2-phenylethoxy)silyl]-2-phenylethene (1b): To a solution of 2-phenylethanol (0.23 mL, 2.0 mmol) in dry triethylamine (1.0 mL, 7.0 mmol) was slowly added (*E*)-1-[chloro(dimethyl)silyl]-2-phenylethene (0.38 mL, 2.0 mmol) at room

temperature. When the mixture was stirred vigorously for 2 h, white precipitates formed. The reaction mixture was diluted with dry hexane (10 mL), stirred for 10 min at room temperature, and filtered through a Celite® pad. The filtrate was concentrated in vacuo. The residue was subjected to bulb-to-bulb distillation under reduced pressure to give **1b** (0.54 g, 95% yield) as a colorless oil: Bp 210 °C/0.7 mmHg (bath temp). IR (neat) 3027, 2955, 1605, 1574, 1495, 1252, 1096, 1030, 992, 851 cm^{-1}; ^1H NMR (200 MHz) δ = 0.22 (s, 6H), 2.86 (t, J = 7.2 Hz, 2H), 3.84 (t, J = 7.2 Hz, 2H), 6.33 (d, J = 19.3 Hz, 1H), 6.94 (d, J = 19.3 Hz, 1H), 7.18—7.36 (m, 10H); ^{13}C NMR (50.3 MHz) δ = −1.7, 39.5, 64.2, 126.3, 126.4, 126.7, 128.3, 128.4, 128.6, 129.2, 138.0, 139.0, 145.7. Found: C, 76.34; H, 7.71%. Calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85%.

Pentamethyl[(*E*)-2-phenylethenyl]disiloxane (1c): Chlorotrimethylsilane (0.13 mL, 1.0 mmol) was slowly added to a solution of **1a** (0.18 mL, 1.0 mmol) in dry triethylamine (0.6 mL, 4.0 mmol) at room temperature. When the reaction mixture was stirred vigorously for 3 h, white precipitates formed. The mixture was diluted with dry hexane (10 mL), stirred for 10 min at room temperature, and filtered through a Celite® pad. The filtrate was concentrated in vacuo. The residue was subjected to bulb-to-bulb distillation under reduced pressure to give **1c** (151.2 mg, 60% yield) as a colorless oil: Bp 120 °C/0.6 mmHg (bath temp). IR (neat) 3027, 2957, 1607, 1574, 1495, 1447, 1254, 1196, 1055, 990, 847, 804, 781 cm^{-1}; ^1H NMR (200 MHz) δ = 0.11 (s, 9H), 0.22 (s, 6H), 6.41 (d, J = 19.1 Hz, 1H), 6.93 (d, J = 19.1 Hz, 1H), 7.25—7.47 (m, 5H); ^{13}C NMR (50.3 MHz) δ = 0.9, 2.1, 126.6, 128.2, 128.6, 128.9, 138.4, 144.3; MS (70 eV) *m/z* (%) 250 (M^+; 24), 235 (100), 149 (33), 134 (10), 73 (71). Found: *m/z* 250.1206. Calcd for $C_{13}H_{22}OSi_2$: M^+, 250.1208.

(*E*)-1-[Dimethyl(2-phenylethoxy)silyl]octene (3b): The procedure described for compound **1b** was followed using chloro(dimethyl)(1-octenyl)silane (1.17 mL, 5.0 mmol), and gave **3b** (1.23 g, 84% yield) as a colorless oil: Bp 180 °C/0.5 mmHg (bath temp). IR (neat) 2957, 2928, 2859, 1744, 1619, 1497, 1374, 1250, 1094, 1048, 994, 845 cm^{-1}; ^1H NMR (200 MHz) δ = 0.12 (s, 6H), 0.89 (t, J = 6.6 Hz, 3H), 1.28—1.42 (m, 8H), 2.11 (m, 2H), 2.80 (t, J = 7.3 Hz, 2H), 3.78 (t, J = 7.3 Hz, 2H), 5.55 (dt, J = 1.6, 18.8 Hz, 1H), 6.14 (dt, J = 6.2, 18.8 Hz, 1H), 7.16—7.22 (m, 5H); ^{13}C NMR (50.3 MHz) δ = −1.8, 14.4, 22.7, 28.6, 28.9, 31.8, 36.7, 39.6, 64.1, 126.2, 127.1, 128.3, 129.2, 139.1, 150.1; MS (70 eV) *m/z* (%) 290 (M^+; 3), 275 (43), 199 (10), 178 (78), 169 (41), 133 (100), 105 (29), 91 (10). Found: *m/z* 290.2058. Calcd for $C_{18}H_{30}OSi$: M^+, 290.2064.

A Mixture of Pentamethyl[(*E*)-1-octenyl]disiloxane and Pentamethyl[(*Z*)-1-octenyl]disiloxane ((*E*) : (*Z*)=3 : 1) (3c): The procedure described for **1c** using **3a** (a mixture of (*E*)- and (*Z*)-isomer) (0.10 mL, 0.5 mmol), gave **3c** (76.5 mg, 66% yield) as a colorless oil: Bp 80 °C/0.5 mmHg (bath temp). IR (neat) 2959, 2928, 2857, 2178, 1609, 1379, 1254, 1055, 843 cm^{-1}; ^1H NMR (200 MHz) δ = 0.07, 0.08 (s, 9H), 0.16, 0.19 (s, 6H), 0.88 (m, 3H), 1.25—1.50 (m, 8H), 2.15 (m, 2H), 5.42 (dt, J = 1.2, 14.2 Hz, (*E*)), 5.59 (dt, J = 1.6, 18.6 Hz, (*Z*)), 6.10 (dt, J = 6.3, 18.6 Hz, (*Z*)), 6.30 (dt, J = 7.4, 14.2 Hz, (*E*)); ^{13}C NMR (50.3 MHz) δ = 2.0, 2.1, 2.5, 2.6, 14.2, 22.7, 29.0, 29.2, 29.8, 31.9, 32.0, 33.6, 128.8, 129.5, 148.3, 149.8; MS (70 eV) *m/z* (%) 258 (M^+; 8), 149 (11), 132 (23), 111 (6), 85 (20), 75 (100), 73 (18). Found: *m/z* 258.1817. Calcd for $C_{13}H_{30}OSi_2$: M^+, 258.1834.

(Methyl)(phenyl)(2-phenylethoxy)vinylsilane (5b): The procedure for **1b** was applied starting with chloro(methyl)(phenyl)vinylsilane (1.1 mL, 6.0 mmol), and gave **5b** (1.3 g, 81%) as a colorless oil: Bp 160 °C/0.9 mmHg (bath temp). IR (neat) 3069, 3029, 2948, 1497, 1429, 1254, 1080, 961, 858 cm^{-1}; ^1H NMR (200 MHz) δ = 0.39 (s, 3H), 2.86 (t, J = 7.2 Hz, 2H), 3.86 (t, J = 7.2 Hz, 2H), 5.83 (dd, J = 5.7, 18.6 Hz, 1H), 6.11 (dd, J = 5.7, 14.9 Hz, 1H), 6.25 (dd, J = 14.9, 18.6 Hz, 1H), 7.14—7.40 (m, 8H), 7.49—7.57 (m, 2H); ^{13}C NMR (50.3 MHz) δ = −3.5, 39.4, 64.6, 126.2, 127.9, 128.3, 129.2, 129.8, 134.0, 135.0, 135.5, 136.2, 138.9. Found: C, 75.76; H, 7.78%. Calcd for $C_{10}H_{14}OSi$: C, 76.07; H, 7.51%.

Tetramethyl[1-phenyl-1-vinyl]disiloxane (5c): The experimental procedure for **1c** was applied to **5a** (0.6 mL, 3.6 mmol), and gave **5c** (195.9 mg, 26% yield) as a colorless oil: Bp 105 °C/0.6 mmHg (bath temp). IR (neat) 3071, 3054, 2959, 1483, 1429, 1404, 1254, 1119, 1059, 959, 841 cm^{-1}; ^1H NMR (200 MHz) δ = 0.10 (s, 9H), 0.39 (s, 3H), 6.05 (dd, J = 4.5, 19.5 Hz, 1H), 6.05 (dd, J = 4.5, 14.7 Hz, 1H), 6.25 (dd, J = 14.7, 19.5 Hz, 1H), 7.56—7.33 (m, 5H); ^{13}C NMR (50.3 MHz) δ = −0.8, 2.1, 127.8, 129.5, 133.4, 133.6, 137.9, 138.4. Found: C, 61.12; H, 8.53%. Calcd for $C_{10}H_{14}OSi$: C, 60.95; H, 8.53%.

One-Pot Procedure of 15. Phenyllithium (1.10 mL, 2.0 mmol, 1.8 M in cyclohexane/diethyl ether) was slowly added to a solution of tetraallyltin (0.12 mL, 0.5 mmol) in dry diethyl ether (1 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C. To the mixture was added D_3 (146.8 mg, 0.66 mmol) at 0 °C. After being stirred at room temperature for 12 h, the mixture was treated with Et_2Zn (3 mL, 3.0 mmol, 1.0 M in hexane) and CH_2I_2 (0.48 mL, 6.0 mmol) at 0 °C, stirred at room temperature for an additional 10 h, then treated with triethylamine (0.42 mL, 3.0 mmol) and chloro(dimethyl)phenylsilane (0.75 mL, 3.0 mmol) at 0 °C, again stirred at room temperature for 10 h, and finally quenched with aqueous NH_4Cl (5 mL). The organic layer was separated. The aqueous layer was extracted with diethyl ether (20 mL×3). The combined extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel, (hexane as an eluent) to give **15** (356 mg, 68% yield) as a colorless oil: R_f 0.70 (Hexane). Bp 120 °C/120 mmHg (bath temp). IR (neat) 3002, 2959, 2897, 1429, 1364, 1254, 1121, 1063, 1015, 999, 899 cm^{-1}; ^1H NMR (200 MHz) δ = −0.04 (m, 2H), 0.11 (s, 6H), 0.32 (s, 6H), 0.43 (m, 2H), 0.59 (m, 1H), 0.89 (m, 2H), 7.34—7.37 (m, 3H), 7.53—7.55 (m, 2H); ^{13}C NMR (50.3 MHz) δ = 0.8, 1.0, 5.6, 6.4, 23.9, 127.8, 129.2, 133.1, 140.3; MS (70 eV) *m/z* (%) 264 (M^+; 10), 189 (10), 149 (27), 115 (11), 74 (24), 68 (100). Found: *m/z* 264.1380. Calcd for $C_{14}H_{24}OSi_2$: M^+, 264.1364.

Tamao Oxidation of 7.[30] To a solution of **7** (96.1 mg, 0.5 mmol) and $KHCO_3$ (50 mg, 0.5 mmol) in MeOH/THF solution (0.5 mL/0.5 mL) was slowly added 30% H_2O_2 (1.02 mL, 9.0 mmol) at room temperature. The mixture was stirred for 6 h at room temperature. To the mixture were slowly added saturated aqueous $NaHSO_3$ (2 mL) and saturated aqueous $NaHCO_3$ (3 mL) at 0 °C successively. The mixture was stirred at 0 °C for 20 min and then extracted with diethyl ether (30 mL×3). The combined extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane : AcOEt = 5 : 1) to give 2-phenylcyclopropanol (**16**, 32.1 mg, 48% yield) as a colorless oil: R_f 0.44 (Hexane : AcOEt = 3 : 1). IR (neat) 3310, 3028, 1605, 1496, 1145, 1089, 1026, 958, 927, 875 cm^{-1}; ^1H NMR (200 MHz) δ = 1.04 (dd, J = 6.3, 12.5 Hz, 1H), 1.27 (ddd, J = 3.5, 6.1, 10.1 Hz, 1H), 2.11 (ddd, J = 2.4, 6.1, 10.1 Hz, 1H), 2.11 (br, 1H), 3.63 (ddd, J = 2.4, 3.5, 6.3 Hz, 1H), 6.99—7.03 (m, 2H), 7.11—7.37 (m, 3H); ^{13}C NMR (50.3 MHz) δ = 17.8, 25.5, 55.4, 125.8, 125.9, 128.4, 141.2.

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