

Selected Paper

Substituent-Control of Two Modes of Intramolecular Reactions of Allyloxy-Silyllithiums and Propargyloxy-Silyllithiums

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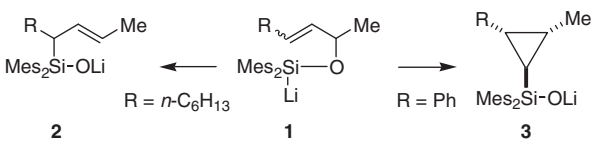
Intramolecular reactions of the [(allyloxy)silyl]lithiums and the [(propargyloxy)silyl]lithiums have been investigated. The [(allyloxy)silyl]lithiums proceed in two reaction modes depending on the electronic effect of the substituents at the terminus of the olefin. The [(allyloxy)silyl]lithiums bearing hydrogen, *n*-C_6H_{13}, or trimethylsilyl substituent undergo the [2,3]-sila-Wittig rearrangement to afford the lithium allylsilanolates, while those bearing the phenyl, thienyl, or triphenylsilyl substituent experience the 4-*exo-trig* cyclization and subsequent 1,3-cycloelimination to give the lithium cyclopropylsilanolates. On the other hand, the [(propargyloxy)silyl]lithiums preferentially undergo the 4-*exo-dig* cyclization over the [2,3]-sila-Wittig rearrangement in all cases.

The intramolecular reactions of organolithium reagents with olefins have been extensively studied in organic synthesis. One representative reaction is the Wittig rearrangement[1] of α-allyloxy organolithium compounds, which promises regio- and stereoselective C–C bond formation along with the allylic transposition. Another topic is the intramolecular carbolithiation[2] of olefins, which allows the regio- and stereoselective cyclization.

When we turn our attention to analogous reactions of silyllithium reagents,[3] we notice that there have been only a few examples of the corresponding reactions, despite the potential utility of the regio- and stereoselective Si–C bond formation. During the course of our studies on functionalized silyl anions,[4] we explored the preparation and reaction of [(allyloxy)silyl]lithiums and found two novel reaction modes, as shown in Scheme 1. One is the [2,3]-sila-Wittig rearrangement,[5] silicon analogues to the [2,3]-Wittig rearrangement. *prim*-, *sec*-, and *tert*-Allyloxy-silyllithiums[6] bearing an aliphatic substituent at the terminus of the olefin, such as **1** (R = *n*-C_6H_{13}), experienced the "[2,3]-Wittig" type rearrangement to afford the lithium allylsilanolates through a suprafacial concerted mechanism accompanied by the allylic transposition and the complete 1,3-chirality transfer.[5b] In contrast to this, the *sec*-allyloxy-silyllithium **1** (R = Ph) bearing a phenyl substituent at the terminus of the olefin undergoes the other type of reaction,[7,8] the 4-*exo-trig* cyclization via silyllithiation of the olefin followed by the 1,3-cycloelimination. This reaction proceeds in a stepwise manner to afford the lithium cyclopropylsilanolate **3** as a single diastereomer, regardless of the *E* or *Z* geometric isomer of the starting material, but keeping the original enantiopurity at the allylic position in **1**.[5b]



Scheme 1.

It was a surprise that just a change in the substituent at the terminus of the olefin caused such a dramatic change in the reaction modes of the [(allyloxy)silyl]lithiums. In order to clarify the origin of the substituent effect on the two reaction modes, we have carried out a detailed experimental study using several substituents at the terminus of the olefin. This report describes the results,[9] together with some aspects of the analogous [(propargyloxy)silyl]lithiums bearing substituents at the acetylenic carbon atom.

Results and Discussion

Throughout this paper, the three carbon atoms of the allyl and propargyl skeletons are numbered as shown in Chart 1.

Preparation of Substrates. The [(*sec*-allyloxy)silyl]stannanes **4** bearing substituents at the terminus of the olefin were prepared by the reaction of [(chloro)dimesitylsilyl]trimethylstannane (**5**) with a variety of substituted *sec*-allyl alcohols[10] **6** in the presence of triethylamine and 4-(dimethylamino)pyridine in refluxing THF, as shown in Scheme 2.[5b] The propargyloxy derivatives **7** were similarly prepared by the reaction of **5** with substituted *sec*-propargyl alcohols[10] **8** (Scheme 2). Based on these methods, we obtained the substrates containing the following substituents: H- (**a**), *n*-C_6H_{13}- (Hex-) (**b**), Ph- (**c**), 3-(trimethylsilyl)thienyl- (Th-) (**d**), Me_3Si- (**e**), and Ph_3Si- (**f**).

Intramolecular Reactions of Substituted [(*sec*-Allyloxy)-silyl]lithiums. The preparation and subsequent rearrangement of the [(*sec*-allyloxy)silyl]lithiums **1** were performed by treatment of the corresponding silylstannanes **4** with *n*-BuLi

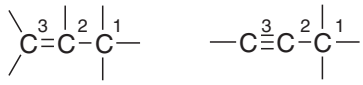


Chart 1.

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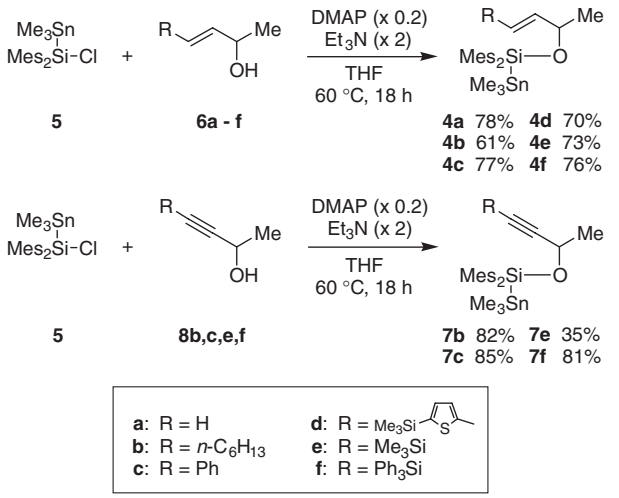
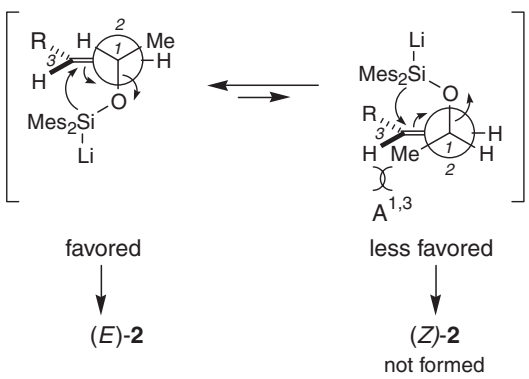
(1.2–2.0 molar amt.) in THF at 0 °C for 3 h, followed by quenching with a 5% aqueous solution of NH_4Cl, as shown in Scheme 3. The products were isolated by column chromatography. The Hex-substituted substrate **4b** afforded the (*E*)-allylsilanol **9b** in 74% yield via the [2,3]-sila-Wittig rearrangement, as previously reported.[5b] In addition to this, the non-substituted (**4a**) and the Me_3Si-substituted (**4e**) substrates also selectively gave (*E*)-allylsilanols **9a** and **9e** in 86% and 78% yields, respectively. Thus these three substituents induce the intramolecular nucleophilic attack of the silyl anion on the external carbon C(3) of the olefin in **1** (mode *a* in Scheme 3). The *E*-preference can be explained by the analogy to the transition states of the [2,3]-Wittig rearrangement.[1a,11] Thus, as shown in Scheme 4, the silyllithium **1** undergoes a suprafacial attack on the olefin in the lower-energy conformer around the C(1)–C(2) bond, which has a smaller 1,3-allylic strain ($A^{1,3}$).[5b]

In contrast, the Ph-substituted substrate **4c** afforded the cyclopropylsilanol **10c** in 68% yield under a similar reaction condition[5b,7] (Scheme 3). The Th-substituted (**4d**) and the Ph_3Si-substituted (**4f**) substrates also selectively gave the cyclopropylsilanols **10d** and **10f** in 64% and 71% yields, respectively. These substituents selectively cause the intramolecular nucleophilic attack of the silyl anion on the internal carbon C(2) in the olefin in **1** (mode *b* in Scheme 3). This 4-*exo-trig* cyclization, a favored process in Baldwin's rules,[12] affords the organolithium species **11** bearing the oxasilacyclobutane moiety, which subsequently undergoes 1,3-cycloelimination[13] to give the cyclopropylsilanolates **3** (**10** after hydrolysis).

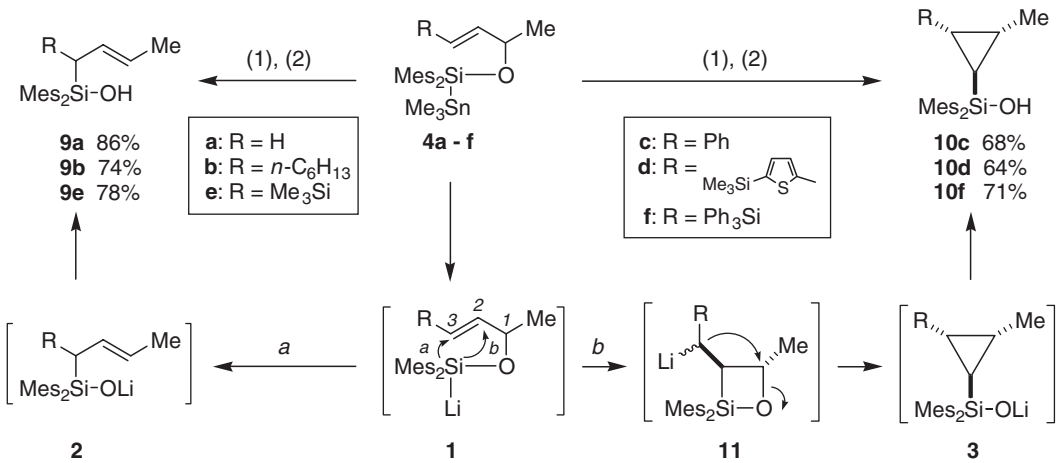
The stereochemistry of **10c** was previously determined as (*r-Si-trans,trans*) by its X-ray crystallographic analysis.[7] The stereochemistry of **10d** and **10f** were also determined to be (*r-Si-trans,trans*) by the NOE experiments and the coupling constants in the ^1H NMR spectra (see: Experimental section). The stereochemical courses of **10d** and **10f** can be similarly rationalized to that of **10c**, as shown in Scheme 5.[5b,7] The intramolecular *syn*-silyllithiation via the favorable conformer having a smaller $A^{1,3}$ strain proceeds in the initial step, facilitated by the electron-withdrawing group, to give **11(i)**. The intermediate **11(i)** is expected to be equilibrated with its epimer **11(ii)** due to the configurationally labile carbanion bearing the R group (R = Ph, Th, and Ph_3Si[14] in Scheme 5). Subsequently, 1,3-cycloelimination involving the oxasilacyclobutanes **11(i)** and **11(ii)** may take place with inversion or retention of the carbanion center C(3) and with inversion at the



Scheme 2.



Scheme 4.



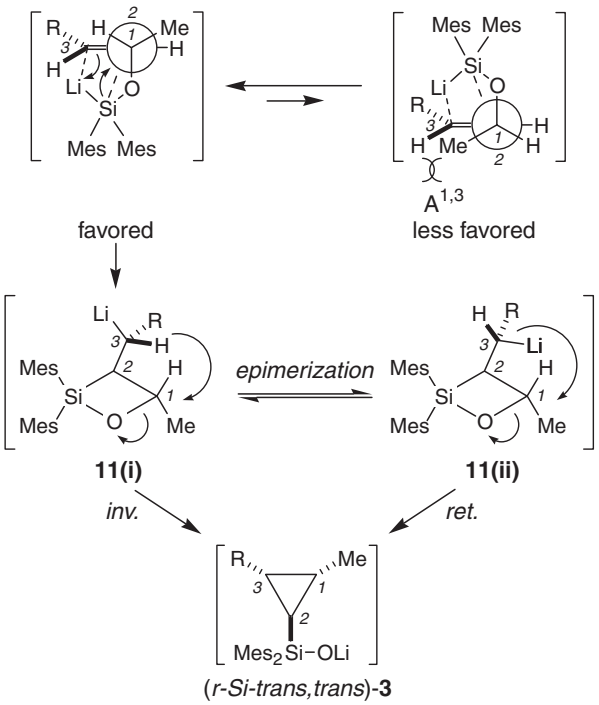
(1) *n*-BuLi (x 2.0 (for **4a**, **b**, **e**) or x 1.2 (for **4c**, **d**, **f**)) / THF / 0 °C, 3 h
(2) 5% NH_4Cl aq.

Scheme 3.

C(1) center.

In our preliminary communication,[7] the regioselectivity of the reaction of the silyllithium to the olefin (mode *a* vs mode *b*) was rationalized in terms of orbital control: ab initio molecular orbital calculations of allyloxysilanes bearing a propyl (instead of hexyl) or a phenyl substituent at the terminus of the olefin revealed that the propyl substituent maximizes the molecular orbital coefficient on C(3) in the LUMO, whereas the phenyl substituent maximizes the molecular orbital coefficient on C(2) in the LUMO.

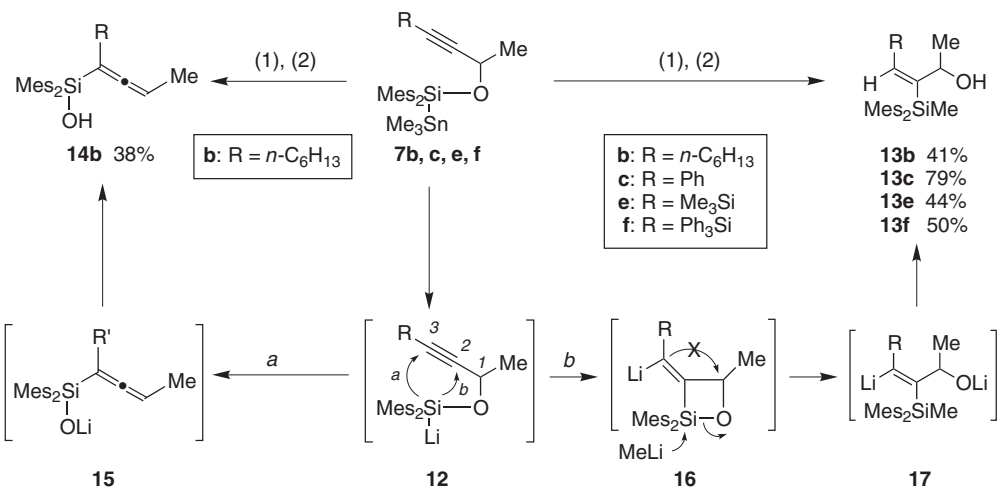
To our knowledge, there has been no example of the silyllithiation of olefins,[15] while the silylcupration to C–C multiple bonds has been extensively studied.[16,17] In contrast, it has been well demonstrated that the silylmetallation to intramolecular olefins catalyzed by transition metals undergoes 4-*exo*-*trig* cyclization to afford oxasilacyclobutanes.[18] The efficiency of the silyllithiation in the present case may be attributed to the activation of the olefins by the electron-withdrawing R groups (R = Ph, Th, and Ph_3Si[19] in Scheme 3) as well as to the intramolecular fashion of the reaction. These electron-withdrawing substituents may also effectively stabilize the negative charge generated on the R-bearing carbon atom C(3) in **11**. The cyclopropane formation by 1,3-cycloelimination, in which the lithiated carbon attacks the electrophilic carbon bearing the leaving group, has been established by several research groups in the last decade.[13] The present reaction is essentially the same when the silanolate anion is regarded as the leaving group.



Scheme 5.

Intramolecular Reactions of [(*sec*-Propargyloxy)silyl]-lithiums. Since the carbon–carbon triple bond is also receptive toward a silyl anion nucleophile,[16c,f] we next examined the reaction modes of analogous [(*sec*-propargyloxy)silyl]lithiums **12** bearing substituents at the acetylenic carbon atom, as shown in Scheme 6. The treatment of [(*sec*-propargyloxy)-silyl]stannane **7** with *n*-BuLi gave rise to a complex mixture, perhaps due to the high reactivity of *n*-BuLi toward the acetylene. Alternatively, MeLi was found to be effective for the Sn–Li exchange of **7** by keeping the acetylene moiety intact. Thus, the silylstannane **7** was treated with MeLi (2.0 molar amt.)[20] in THF at 0 °C for 3 h, followed by quenching with a 5% aqueous solution of NH_4Cl. These results are summarized in Scheme 6. The products were isolated by column chromatography.

It was found that the major product for each substituent was a vinylsilane **13**, in which the silicon group, attached to the C(2) atom of an allyl alcohol moiety, contains a methyl group arising from the MeLi used in excess for the Sn–Li exchange reaction. Thus, the Ph-substituted (**7c**), the Me_3Si-substituted (**7e**), and the Ph_3Si-substituted (**7f**) substrates afforded **13c**, **13e**, and **13f** in 79%, 44%, and 50% yields, respectively. Only the Hex-substituted substrate **7b** gave the allenylsilanol **14b** in addition to the vinylsilane **13b** in a 1:1 ratio.



Scheme 6.

Analogous to the reaction modes of the [(allyloxy)silyl]lithiums **1**, two reaction modes would also be expected for the silyllithium **12**. If **12** undergoes the intramolecular nucleophilic attack on the external carbon C(3) in the acetylene (mode *a* in Scheme 6), the [2,3]-sila-Wittig rearrangement[21] would proceed to give the lithium allenylsilanolate **15** and eventually **14**. This is the case of the Hex-substituted substrate (**7b**). On the other hand, if the silyllithium **12** experiences the intramolecular nucleophilic attack on the internal carbon C(2) in the acetylene (mode *b* in Scheme 6), the 4-*exo-dig* cyclization would produce a vinyllithium containing an oxasilacyclobutylidene moiety **16** as the most probable intermediate.[22] Although the 4-*exo-dig* cyclization is less favored according to the Baldwin rules,[12] the longer Si–C and Si–O bonds may reduce the steric strain in the transition state and/or the product and may allow the cyclization.[23] In the next step, contrary to the behavior of **11**, **16** cannot easily cyclize to the three-membered ring via the 1,3-cycloelimination due to the rigidity of the exocyclic C–C double bond skeleton. Alternatively, the nucleophilic attack by another molecule of MeLi on the electrophilic silicon atom cleaves the Si–O bond in **16**, resulting in the formation of **17** that contains the methyl-silylated vinyllithium and allyloxylithium moieties.

In the propargyloxy system, the silyl anion in **12** generally prefers the nucleophilic attack on C(2) rather than on C(3), which induces the 4-*exo-dig* cyclization. This regioselectivity is rationalized by considering that the approach of the anionic silicon center to the near carbon C(2) of the linear triple bond may be more energetically favored than the approach to the distant carbon C(3). To the best of our knowledge, no analogous 4-*exo-dig* cyclization has been reported for the carbanion counterparts, i.e., the propargyloxy-alkyllithiums. The unique reaction mode in our silicon case may be due to the flexibility of the silicon compounds with longer Si–C (1.87 Å) and Si–O (1.51 Å) bonds compared to the C–C (1.54 Å) and C–O (1.43 Å) bonds.[24]

Conclusion

The [(allyloxy)silyl]lithiums bearing the H, Hex, or Me_3Si substituent undergo the [2,3]-sila-Wittig rearrangement to afford the allylsilanols. On the other hand, the [(allyloxy)silyl]lithiums bearing the Ph, Th, or Ph_3Si substituent experience the 4-*exo-trig* cyclization, followed by the 1,3-cycloelimination, to give the cyclopropylsilanols. Thus two different types of compounds can be prepared from similar [(allyloxy)silyl]lithiums only by changing the substituent at the terminus of the olefin. The two different reaction modes were determined by the regioselection in the intramolecular reaction of the silyllithium with the olefin during the initial step. In the [(propargyloxy)silyl]lithiums, the unique 4-*exo-dig* cyclization is favored over the [2,3]-sila-Wittig rearrangement in all cases. This may depend on the distance between the silyl anion center and the reaction sites in the acetylenes.

Experimental

The ^{1}H (270 MHz), ^{13}C (67.94 MHz), and ^{29}Si (53.67 MHz) NMR spectra were recorded using a JEOL EX-270 spectrometer. The ^{1}H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to the internal benzene-d_6 (^{1}H 7.200 ppm; ^{13}C 128.0 ppm) and $CDCl_3$ (^{13}C 77.00 ppm). The mass spectra were measured at 70 eV using a JEOL JMS-DX300 mass spectrometer. The elemental analyses were performed at the Microanalysis Division of the Institute for Chemical Research, Kyoto University. The analytical samples were purified by recycling reverse-phase liquid chromatography or recrystallization. Column chromatography was performed using Kieselgel 60 (70–230 mesh) (Merck). Thin layer chromatography was performed on plates of silica gel 60F-254 (Merck). Trimethylchlorostannane was prepared by disproportionation between the tetramethylstannane and dimethyldichlorostannane; the latter was kindly donated from Nitto Kasei Co. 3-Butyn-2-ol (**8a**) and sodium dihydrobis(2-methoxyethoxy)aluminate (Red-Al) were purchased from the Aldrich Co., and used as received. 3-Buten-2-ol (**6a**) and 4-(dimethylamino)pyridine were purchased from Nacalai Tesque and used as received. Butyllithium in hexane was purchased from Wako Pure Chemical Industries. Granular lithium was purchased from Chemetall Gesellshaft. Methyllithium in diethyl ether was purchased from Kanto Chemical Co., Inc. Triethylamine, carbon tetrachloride, and dichloromethane were distilled under a nitrogen atmosphere over calcium hydride. THF and Et_2O were distilled under a nitrogen atmosphere over sodium diphenylketyl. All reactions were carried out under an inert atmosphere.

Preparation of Propargyl Alcohols 8. 3-Decyn-2-ol (**8b**), 4-phenyl-3-butyn-2-ol (**8c**), 4-(5-trimethylsilyl-2-thienyl)-3-butyn-2-ol (**8d**), 4-trimethylsilyl-3-butyn-2-ol (**8e**), and 4-triphenylsilyl-3-butyn-2-ol (**8f**) were prepared from 3-butyn-2-ol (**8a**) according to the literature procedures.[10]

Preparation of Allyl Alcohols 6. (*E*)-3-decen-2-ol (**6b**), (*E*)-4-(5-trimethylsilyl-2-thienyl)-3-buten-2-ol (**6d**), (*E*)-4-trimethylsilyl-3-buten-2-ol (**6e**), and (*E*)-4-triphenylsilyl-3-buten-2-ol (**6f**) were prepared by reduction of the corresponding propargyl alcohols **8** (see above) with Red-Al according to the literature procedures.[10] (*E*)-4-phenyl-3-buten-2-ol (**6c**) was prepared by the reaction of (*E*)-3-phenyl-2-propenal with methyllithium.

A Typical Procedure for Preparation of [(Allyloxy)silyl]-stannanes 4 and [(Propargyloxy)silyl]stannanes 7. Synthesis of (*E*)-[(3-Buten-2-oxy)dimesitylsilyl]trimethylstannane (4a): 3-Buten-2-ol (**6a**) (0.35 mL, 2.5 mmol), 4-(dimethylamino)pyridine (98 mg, 0.80 mmol), and triethylamine (1.1 mL, 8.0 mmol) were added to a THF (8 mL) solution of (chlorodimesitylsilyl)trimethylstannane (**5**), prepared by the reaction of (dimesitylsilyl)trimethylstannane (1.86 g, 4.0 mmol) and carbon tetrachloride (8 mL). The reaction mixture was stirred at 60 °C for 18 h. The volatile materials were evaporated and the residue was diluted with hexane (20 mL). The resulting salts were removed by filtration and the filter cake was washed with hexane (30 mL). The filtrate was concentrated and the residue (2.32 g) was subjected to column chromatography on silica gel eluted with hexane/AcOEt (100/1) ($R_f = 0.52$) to give **4a** (1.04 g, 78% yield) as a colorless oil. **4a**; ^{1}H NMR ($CDCl_3$): δ 0.06 (s, 9H), 1.14 (d, $J = 6.0$ Hz, 3H), 2.23 (s, 3H), 2.24 (s, 3H), 2.27 (s, 6H), 2.30 (s, 6H), 4.10 (dq, $J = 6.0$ and 6.0 Hz, 1H), 4.92 (dq, $J = 10.5$ and 1.2 Hz, 1H), 4.95 (dt, $J = 17.1$ and 1.2 Hz, 1H), 5.79 (ddd, $J = 17.1$, 10.5, and 6.0 Hz, 1H), 6.72 (s, 2H), 6.74 (s, 2H). ^{13}C NMR ($CDCl_3$): δ −8.42, 21.17, 23.88, 23.97, 72.10, 113.43, 128.83, 128.90, 128.93, 133.11, 133.29, 138.36, 138.67, 142.15, 142.72, 142.79, 143.05. MS (EI): m/z 502 (M^+), 487, 447, 445, 373, 371, 337, 283, 217, 163. Anal. Calcd for $C_{25}H_{38}OSiSn$: C, 59.89; H, 7.64%. Found: C, 59.61; H, 7.79%.

(*E*)-[(3-Decen-2-oxy)dimesitylsilyl]trimethylstannane (4b):

^{1}H NMR (C_6D_6): δ 0.35 (s, 9H), 0.94 (t, $J = 6.6$ Hz, 3H), 1.22–1.27 (m, 8H), 1.29 (d, $J = 6.0$ Hz, 3H), 1.89–2.00 (m, 2H), 2.16 (s, 6H), 2.54 (s, 12H), 4.31 (dq, $J = 6.6$ and 6.3 Hz, 1H), 5.40 (dt, $J = 15.0$ and 6.3 Hz, 1H), 5.55 (dd, $J = 15.0$ and 7.2 Hz, 1H), 6.77 (s, 4H). ^{13}C NMR (C_6D_6): δ −8.44, 14.29, 21.07, 22.99, 24.17, 24.62, 29.24, 29.37, 32.06, 32.48, 72.58, 129.69, 130.55, 133.77, 134.15, 134.43, 138.84, 139.09, 143.06, 143.35 (Although there should be 10 peaks of the sp^2 carbons, only 9 peaks were observed). MS (EI): m/z 586 (M^+), 571, 451, 447, 421, 283. Anal. Calcd for $C_{31}H_{50}OSiSn$: C, 63.53; H, 8.71%. Found: C, 63.59; H, 8.61%.

(*E*)-[(4-Phenyl-3-buten-2-oxy)dimesitylsilyl]trimethylstannane (4c): ^{1}H NMR (C_6D_6): δ 0.30 (s, 9H), 1.32 (d, $J = 6.3$ Hz, 3H), 2.13 (s, 3H), 2.16 (s, 3H), 2.51 (s, 6H), 2.52 (s, 6H), 4.42 (dq, $J = 6.3$ and 6.3 Hz, 1H), 6.15 (dd, $J = 16.2$ and 6.3 Hz, 1H), 6.25 (d, $J = 16.2$ Hz, 1H), 6.73 (s, 2H), 6.78 (s, 2H), 7.07–7.22 (m, 5H). ^{13}C NMR ($CDCl_3$): δ −8.70, 21.01, 21.06, 23.79, 23.83, 24.21, 72.08, 126.38, 127.30, 128.34, 129.00, 129.06, 133.15, 133.52, 133.71, 136.82, 138.53, 138.72, 142.80, 143.07, 143.13. MS (EI): m/z 578 (M^+), 563, 447, 413, 283, 163, 131. Anal. Calcd for $C_{31}H_{42}OSiSn$: C, 64.48; H, 7.33%. Found: C, 64.32; H, 7.40%.

(*E*)-{[(5-Trimethylsilyl-2-thienyl)-3-buten-2-oxy]dimesitylsilyl}trimethylstannane (4d): ^{1}H NMR (C_6D_6): δ 0.27 (s, 9H), 0.32 (s, 9H), 1.27 (d, $J = 6.4$ Hz, 3H), 1.58 (s, 3H), 2.14 (s, 6H), 2.52 (s, 12H), 4.36 (dq, $J = 6.4$ and 6.4 Hz, 1H), 6.17 (dd, $J = 15.6$ and 6.4 Hz, 1H), 6.43 (d, $J = 15.6$ Hz, 1H), 6.74 (s, 2H), 6.77 (s, 2H), 6.89 (d, $J = 3.3$ Hz, 1H), 7.03 (d, $J = 3.3$ Hz, 1H). ^{13}C NMR (C_6D_6): δ −8.22, 0.04, 21.27, 24.35, 24.40, 72.32, 122.93, 127.23, 129.70, 129.76, 133.50, 133.66, 133.96, 134.66, 138.91, 139.12, 139.34, 142.97, 143.34, 147.55. MS (EI): m/z 656 (M^+), 491, 447, 407, 283, 73. Anal. Calcd for $C_{32}H_{48}OSSi_2Sn$: C, 58.62; H, 7.38%. Found: C, 58.69; H, 7.37%.

(*E*)-[(4-Trimethylsilyl-3-buten-2-oxy)dimesitylsilyl]trimethylstannane (4e): ^{1}H NMR (C_6D_6): δ 0.10 (s, 9H), 0.33 (s, 9H), 1.24 (d, $J = 6.3$, 3H), 2.14 (s, 6H), 2.52 (s, 12H), 4.34 (dq, $J = 6.3$ and 1.2 Hz, 1H), 5.74 (dd, $J = 19.0$ and 1.2 Hz, 1H), 6.11 (dd, $J = 19.0$ and 6.7 Hz, 1H), 6.75 (s, 2H), 6.76 (s, 2H). ^{13}C NMR ($CDCl_3$): δ −8.52, −0.01, 21.14, 21.17, 23.92, 23.95, 24.20, 71.67, 121.99, 126.51, 128.95, 129.00, 133.08, 133.44, 133.49, 134.05, 138.44, 138.64, 139.17, 142.69, 143.00, 147.03. MS (EI): m/z 574 (M^+), 559, 409, 283, 217, 163, 119. Anal. Calcd for $C_{28}H_{46}OSi_2Sn$: C, 58.64; H, 8.08%. Found: C, 58.72; H, 8.11%.

(*E*)-[(4-Triphenylsilyl-3-buten-2-oxy)dimesitylsilyl]trimethylstannane (4f): ^{1}H NMR (C_6D_6): δ 0.28 (s, 9H), 1.18 (d, $J = 6.3$ Hz, 3H), 2.12 (s, 3H), 2.13 (s, 3H), 2.47 (s, 6H), 2.48 (s, 6H), 4.45 (dt, $J = 6.3$ and 4.2 Hz, 1H), 6.33 (dd, $J = 18.6$ and 4.2 Hz, 1H), 6.41 (d, $J = 18.6$ Hz, 1H), 6.70 (s, 2H), 6.74 (s, 2H), 7.22–7.26 (m, 9H), 7.61–7.65 (m, 6H). ^{13}C NMR ($CDCl_3$): δ −8.50, 21.15, 23.57, 23.97, 24.00, 74.10, 121.10, 127.63, 128.93, 128.97, 129.30, 133.34, 133.44, 134.36, 135.81, 138.48, 142.71, 142.76, 155.21. MS (EI): m/z 758 (M^+), 744, 595, 549, 283, 259. Anal. Calcd for $C_{43}H_{52}OSi_2Sn$: C, 67.98; H, 6.90%. Found: C, 68.15; H, 6.97%.

[(3-Decyn-2-oxy)dimesitylsilyl]trimethylstannane (7b): ^{1}H NMR (C_6D_6): δ 0.40 (s, 9H), 0.91 (t, $J = 6.3$ Hz, 3H), 1.15–1.44 (m, 8H), 1.46 (d, $J = 6.3$ Hz, 3H), 2.07 (dt, $J = 7.2$ and 1.2 Hz, 2H), 2.14 (s, 3H), 2.15 (s, 3H), 2.56 (s, 12H), 4.60 (q, $J = 6.3$ Hz, 1H), 6.77 (s, 2H), 6.78 (s, 2H). ^{13}C NMR ($CDCl_3$): δ −8.46, 14.18, 18.93, 21.15, 22.66, 23.90, 23.95, 25.63, 28.64, 31.45, 60.53, 82.24, 84.24, 128.91, 132.91, 133.04, 138.35, 138.68, 142.90, 143.17. MS (EI): m/z 584 (M^+), 569, 567, 487, 447, 419, 376, 375, 283, 273, 163, 119. Anal. Calcd for $C_{31}H_{48}OSiSn$: C, 63.81; H, 8.29%. Found: C, 63.75; H, 8.28%.

[(4-Phenyl-3-butyn-2-oxy)dimesitylsilyl]trimethylstannane (7c): ^{1}H NMR (C_6D_6): δ 0.37 (s, 9H), 1.50 (d, $J = 6.3$ Hz, 3H), 2.13 (s, 3H), 2.15 (s, 3H), 2.56 (s, 12H), 4.76 (d, $J = 6.3$ Hz, 3H), 6.75 (s, 2H), 6.77 (s, 4H), 6.98–7.05 (m, 3H), 7.39–7.43 (m, 2H). ^{13}C NMR ($CDCl_3$): δ −8.45, 21.14, 21.17, 23.92, 23.95, 25.28, 60.78, 83.66, 91.38, 122.96, 127.93, 127.96, 131.58, 132.78, 132.92, 138.51, 138.79, 142.97, 143.18. MS (EI): m/z 576 (M^+), 561, 447, 411, 368, 367, 283, 265, 239, 163, 119. Anal. Calcd for $C_{31}H_{40}OSiSn$: C, 64.70; H, 7.01%. Found: C, 64.80; H, 7.11%.

[(5-Trimethylsilyl-3-butyn-2-oxy)dimesitylsilyl]trimethylstannane (7e): ^{1}H NMR (C_6D_6): δ 0.20 (s, 9H), 0.38 (s, 9H), 1.40 (d, $J = 6.3$ Hz, 3H), 2.13 (s, 3H), 2.14 (s, 3H), 2.53 (s, 6H), 2.54 (s, 6H), 4.54, (q, $J = 6.3$ Hz, 1H), 6.75 (s, 2H), 6.76 (s, 2H). ^{13}C NMR ($CDCl_3$): δ −8.45, −0.03, 21.15, 23.93, 23.97, 25.15, 60.71, 87.56, 107.71, 128.93, 132.68, 132.80, 138.51, 138.76, 142.92, 143.10. MS (EI): m/z 572 (M^+), 557, 447, 407, 363, 335, 283, 261. Anal. Calcd for $C_{28}H_{44}OSi_2Sn$: C, 58.84; H, 7.76%. Found: C, 59.07; H, 8.04%.

[(4-Triphenylsilyl-3-butyn-2-oxy)dimesitylsilyl]trimethylstannane (7f): ^{1}H NMR (C_6D_6): δ 0.29 (s, 9H), 1.40 (d, $J = 6.6$ Hz, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 2.50 (s, 6H), 2.51 (s, 6H), 4.63, (q, $J = 6.6$ Hz, 1H), 6.71 (s, 2H), 6.73 (s, 2H), 7.22–7.24 (m, 9H), 7.79–7.83 (m, 6H). ^{13}C NMR ($CDCl_3$): δ −8.63, 21.18, 23.92, 23.97, 25.20, 61.01, 82.66, 112.31, 127.73, 128.98, 129.69, 132.27, 133.31, 135.47, 138.71, 142.90, 143.05. MS (EI): m/z 742 (M^+), 641, 549, 447, 283, 209, 163, 73. Anal. Calcd for $C_{43}H_{50}OSi_2Sn$: C, 68.16; H, 6.65%. Found: C, 67.94; H, 6.67%.

Typical Procedure for the [2,3]-Sila-Wittig Rearrangement. Synthesis of (*E*)-(2-Buten-1-yl)dimesitylsilanol (9a): A solution of *n*-BuLi in hexane (1.6 M, 0.63 mL, 1.0 mmol) was added dropwise to a solution of **4a** (251 mg, 0.50 mmol) in THF (1.0 mL) at 0 °C and the reaction mixture was stirred for 3 h at 0 °C. A 5% aq solution of NH_4Cl (1.0 mL) was added to the reaction mixture at 0 °C. The mixture was extracted with Et_2O (10 mL × 3) and the combined organic layer was dried over anhydrous $MgSO_4$. The solution was concentrated in vacuo and the residue was subjected to column chromatography on silica gel (40 mL) eluted with hexane/AcOEt (20/1) ($R_f = 0.25$) to give **9a** (146 mg, 86% yield) as a colorless oil. **9a**; ^{1}H NMR (C_6D_6): δ 1.56 (d, $J = 6.9$ Hz, 3H), 1.84 (s, 1H), 2.14 (s, 6H), 2.18 (dd, $J = 5.7$ and 1.2 Hz, 2H), 2.43 (s, 12H), 5.22–5.53 (m, 2H), 6.75 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 18.17, 21.09, 23.67, 27.68, 125.72, 126.40, 129.02, 132.88, 138.81, 143.27. MS (EI): m/z 338 (M^+), 283, 163. Anal. Calcd for $C_{22}H_{30}OSi$: C, 78.05; H, 8.93%. Found: C, 78.13; H, 9.04%.

(*E*)-(2-Decen-4-yl)dimesitylsilanol (9b): ^{1}H NMR (C_6D_6): δ 0.92 (t, $J = 6.6$ Hz, 3H), 1.22–1.42 (m, 7H), 1.59 (d, $J = 6.0$ Hz, 3H), 1.60–1.76 (m, 3H), 1.84–1.96 (m, 1H), 2.15 (s, 6H), 2.34 (t, $J = 9.9$ Hz, 1H), 2.51 (s, 6H), 2.52 (s, 6H), 5.34 (dq, $J = 15.3$ and 6.0 Hz, 1H), 5.49 (dd, $J = 15.3$ and 9.0 Hz, 1H), 6.77 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 14.18, 18.32, 21.04, 22.75, 23.69, 23.82, 28.90, 29.20, 29.32, 31.87, 36.72, 42.30, 124.59, 128.97, 129.15, 131.89, 132.92, 133.24, 138.50, 138.55, 143.31, 143.53. MS (EI): m/z 421 (M^+), 283, 163. Anal. Calcd for $C_{28}H_{42}OSi$: C, 79.56; H, 10.01%. Found: C, 79.47; H, 10.06%.

(*E*)-(4-Trimethylsilyl-2-buten-4-yl)dimesitylsilanol (9e): ^{1}H NMR (C_6D_6): δ 0.19 (s, 9H), 1.59 (d, $J = 6.0$ Hz, 3H), 1.60–1.76 (m, 3H), 1.61 (d, $J = 6.3$ Hz, 3H), 1.74 (brs, 1H), 1.84–1.96 (m, 1H), 2.15 (s, 6H), 2.34 (t, $J = 9.9$ Hz, 1H), 2.51

(s, 6H), 2.52 (s, 6H), 5.34 (dq, $J = 15.3$ and 6.0 Hz, 1H), 5.49 (dd, $J = 15.3$ and 9.0 Hz, 1H), 6.77 (s, 4H). ^{13}C NMR ($CDCl_3$): δ −0.13, 18.37, 21.00, 21.04, 23.55, 24.01, 27.88, 124.11, 127.98, 129.13, 129.43, 134.03, 134.13, 138.38, 138.61, 143.33, 143.45. MS (EI): m/z 410 (M^+), 395, 320, 283, 163. Anal. Calcd for $C_{25}H_{38}OSi_2$: C, 73.10; H, 9.33%. Found: C, 73.15; H, 9.33%.

Typical Procedure for Cyclopropylsilane Synthesis. Synthesis of (2-Triphenylsilyl-3-methylcyclopropan-1-yl)dimesitylsilanol (10f): A solution of *n*-BuLi in hexane (1.6 M, 0.38 mL, 0.60 mmol) was added dropwise to a solution of **7f** (380 mg, 0.50 mmol) in THF (1.0 mL) at 0 °C and the reaction mixture was stirred for 3 h. A 5% aq solution of NH_4Cl (1.0 mL) was added to the reaction mixture at 0 °C. The mixture was extracted with Et_2O (10 mL × 3) and the combined organic layer was dried over $MgSO_4$. The solution was concentrated in vacuo and the residue was subjected to column chromatography on silica gel (50 mL) eluted with hexane/AcOEt (20/1) ($R_f = 0.23$) to give **10f** (210 mg, 71% yield) as a colorless oil. **10f**: ^{1}H NMR (C_6D_6): δ 0.54 (dd, $J_{ab} = 7.8$ and $J_{ac} = 7.8$ Hz, 1H), 0.92 (dd, $J_{bc} = 8.7$ and $J_{ab} = 7.8$ Hz, 1H), 1.17 (d, $J_{cd} = 6.0$ Hz, 3H), 1.44 (s, 1H), 1.54–1.61 (m, 1H), 2.13 (s, 3H), 2.18 (s, 3H), 2.43 (s, 6H), 2.45 (s, 6H), 6.72 (s, 2H), 6.76 (s, 2H), 7.18–7.22 (m, 9H), 7.67–7.70 (m, 6H) (Chart 2). ^{13}C NMR ($CDCl_3$): δ 6.52, 16.21, 17.58, 21.07, 21.15, 127.57, 128.95, 129.06, 131.76, 133.00, 135.40, 135.88, 138.53, 138.91, 143.17, 143.78. MS (EI): m/z 596 (M^+), 541, 476, 421, 283, 259. Anal. Calcd for $C_{44}H_{44}OSi_2$: C, 80.48; H, 7.43%. Found: C, 80.41; H, 7.65%.

(3-Methyl-2-phenylcyclopropan-1-yl)dimesitylsilanol (10c): ^{1}H NMR (C_6D_6): δ 0.68 (dd, $J_{ab} = 7.1$ and $J_{ac} = 7.1$ Hz, 1H), 0.98 (d, $J_{cd} = 6.0$ Hz, 3H), 1.32–1.41 (m, 1H), 1.49 (s, 1H), 2.15 (s, 3H), 2.16 (s, 3H), 2.41 (dd, $J_{bc} = 8.7$ and $J_{ab} = 7.1$ Hz, 1H), 2.50 (s, 6H), 2.52 (s, 6H), 6.76 (s, 2H), 6.78 (s, 2H), 7.08–7.17 (m, 5H) (Chart 3). ^{13}C NMR ($CDCl_3$): δ 14.27, 16.34, 18.44, 21.01, 23.78, 26.60, 125.62, 127.82, 129.06, 129.09, 132.20, 132.79, 138.90, 139.01, 139.48, 143.49, 143.68 (Although there should be 12 peaks of the sp^2 carbons, only 11 peaks were observed). MS (EI): m/z 414 (M^+), 323, 296, 283, 163. Anal. Calcd for $C_{28}H_{34}OSi$: C, 81.10; H, 8.26%. Found: C, 81.04; H, 8.49%.

[3-Methyl-2-(5-trimethylsilyl-2-thienyl)cyclopropan-1-yl]dimesitylsilanol (10d): ^{1}H NMR (C_6D_6): δ 0.28 (s, 9H), 0.74 (dd, $J_{ab} = 7.2$ and $J_{ac} = 7.2$ Hz, 1H), 1.13 (d, $J_{cd} = 6.0$ Hz, 3H), 1.32–1.42 (m, 1H), 1.58 (s, 1H), 2.14 (s, 3H), 2.15 (s, 3H), 2.42–2.57 (m, 1H), 2.49 (s, 6H), 2.51 (s, 6H), 6.74 (s, 2H), 6.75 (s, 2H), 6.83 (d, $J = 3.0$ Hz, 1H), 7.08 (d, $J = 3.0$ Hz, 1H) (Chart 4). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 0.11, 14.55, 19.42, 20.33, 21.14, 21.65, 23.92, 23.97, 126.40, 129.03, 131.68, 132.29, 133.59, 137.80, 138.92, 138.99, 143.41, 143.55, 149.63. MS (EI): m/z 492 (M^+), 477, 283. HRMS (EI): Calcd for $C_{29}H_{40}OSSi_2$: m/z 492.2338. Found: m/z 492.2338.

Typical Procedure for Intramolecular Reaction of (Propargyloxysilyl)stannanes. Reaction of 7b with MeLi: A solution of MeLi in Et_2O (1.14 M, 0.88 mL, 1.0 mmol) was added dropwise to a solution of **7b** (292 mg, 0.50 mmol) in THF (1.0 mL) at 0 °C and the reaction mixture was stirred for 3 h. A 5% aq solution of NH_4Cl (1.0 mL) was added to the reaction mixture at 0 °C. The mixture was extracted with Et_2O (10 mL × 3) and the combined organic layer was dried over anhydrous $MgSO_4$. The solution was concentrated in vacuo and the residue was subjected to column chromatography on silica gel (40 mL) eluted with hexane/AcOEt (40/1) to give **13b** (90 mg, 41% yield) ($R_f = 0.12$) and **14b** (80 mg, 38% yield) ($R_f = 0.27$) as colorless oils.

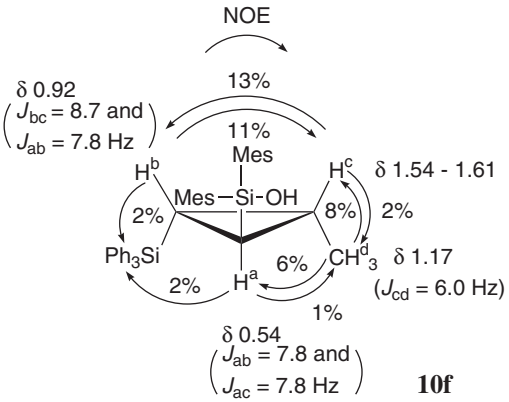


Chart 2.

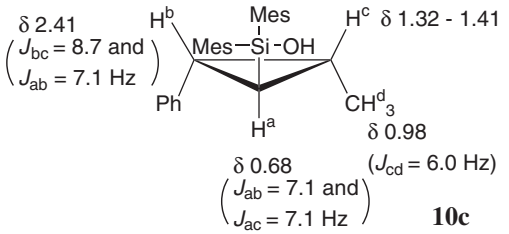


Chart 3.

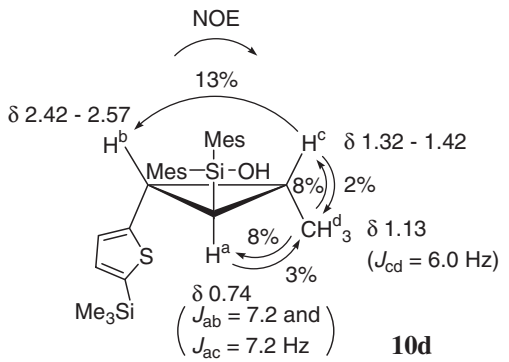


Chart 4.

(*E*)-(2-Hydroxy-3-decen-3-yl)dimesitylmethylsilane (13b): ^{1}H NMR (C_6D_6): δ 0.89 (t, $J = 6.7$ Hz, 3H), 0.99 (s, 3H), 1.18–1.25 (m, 10H), 1.31 (d, $J = 6.5$ Hz, 3H), 2.16 (s, 6H + 1H), 2.42 (s, 6H), 2.46 (s, 6H), 4.42–4.50 (m, 1H), 6.50 (t, $J = 7.0$ Hz, 1H), 7.28 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 14.14, 21.00, 22.65, 23.93, 24.76, 24.85, 29.28, 29.31, 31.77, 32.92, 70.48, 129.28, 129.31, 134.19, 134.26, 138.16, 138.20, 143.73, 144.20, 144.24, 145.09. MS (EI): m/z 436 (M^+), 421, 418, 316, 281, 179. HRMS (EI): Calcd for $C_{29}H_{44}OSi$: m/z 436.3136. Found: m/z 436.3150.

(1-Hexyl-3-methylallen-1-yl)dimesitylsilanol (14b): ^{1}H NMR (C_6D_6): δ 0.91 (t, $J = 7.2$ Hz, 3H), 1.20–1.50 (m, 9H), 1.60–1.75 (m, 2H), 2.16 (s, 6H), 2.20–2.35 (m, 2H), 2.54 (s, 6H), 2.55 (s, 6H), 4.70–4.83 (m, 1H), 6.79 (s, 4H). ^{13}C NMR (C_6D_6): δ 13.10, 14.51, 21.28, 23.24, 24.30, 24.36, 29.62, 29.81, 29.95, 32.34, 82.33, 99.31, 129.53, 129.54, 133.49, 133.52, 138.88, 138.97, 144.08, 144.11, 208.82. MS (EI): m/z 420 (M^+), 283, 163. HRMS (EI): Calcd for $C_{28}H_{40}OSi$: m/z 420.2848. Found: m/z 420.2852.

(*E*)-(2-Hydroxy-4-phenyl-3-buten-3-yl)dimesitylmethylsilane

(13c): ^{1}H NMR (C_6D_6): δ 0.58 (s, 3H), 1.32 (d, $J = 6.9$ Hz, 3H), 1.46 (d, $J = 5.4$ Hz, 1H), 2.15 (s, 6H), 2.35 (s, 6H), 2.50 (s, 6H), 4.64 (dq, $J = 6.9$ and 5.4 Hz, 1H), 6.78 (s, 2H), 6.80 (s, 2H), 6.97–7.00 (m, 3H), 7.37–7.40 (m, 2H), 7.69 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 6.85, 21.07, 24.01, 24.79, 70.86, 127.16, 127.81, 128.60, 129.41, 129.59, 134.21, 135.00, 138.39, 138.53, 139.07, 141.87, 143.97, 144.09, 149.42. MS (EI): m/z 428 (M^+), 410, 395, 383, 308, 281. HRMS (EI): Calcd for $C_{29}H_{36}OSi$: m/z 428.2535. Found, m/z 428.2507.

(*E*)-(2-Hydroxy-4-trimethylsilyl-3-buten-3-yl)dimesitylmethylsilane (13e): ^{1}H NMR (C_6D_6): δ 0.19 (s, 9H), 1.03 (s, 3H), 1.21 (d, $J = 6.3$ Hz, 3H), 1.38 (d, $J = 5.7$ Hz, 1H), 2.14 (s, 3H), 2.15 (s, 3H), 2.38 (s, 6H), 2.44 (s, 6H), 4.53 (dq, $J = 6.3$ and 5.7 Hz, 1H), 6.78 (s, 4H), 7.03 (s, 1H). ^{13}C NMR (C_6D_6): δ 0.95, 8.85, 21.18, 24.47, 25.52, 25.79, 73.04, 129.94, 129.98, 134.73, 135.17, 138.59, 138.62, 143.26, 144.57, 144.62, 168.92. MS (EI): m/z 424 (M^+), 408, 281, 179. HRMS (EI): Calcd for $C_{26}H_{40}OSi_2$: m/z 424.2618. Found: m/z 424.2638.

(*E*)-(2-Hydroxy-4-triphenylsilyl-3-buten-3-yl)dimesitylmethylsilane (13f): ^{1}H NMR (C_6D_6): δ 0.33 (s, 3H), 1.25 (d, $J = 6.3$ Hz, 3H), 1.54 (d, $J = 5.4$ Hz, 1H), 2.14 (s, 3H), 2.15 (s, 3H), 2.34 (s, 6H), 2.37 (s, 6H), 4.72 (dq, $J = 6.3$ and 5.4 Hz, 1H), 6.70 (s, 2H), 6.73 (s, 2H), 7.09–7.27 (m, 9H), 7.77–7.80 (m, 6H), 7.85 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 7.41, 21.04, 24.57, 25.12, 25.27, 73.53, 127.55, 129.13, 129.26, 129.33, 133.72, 134.86, 135.07, 135.84, 138.07, 138.27, 143.89, 144.20, 172.75. MS (EI): m/z 608 (M^+), 592, 281, 259. Anal. Calcd for $C_{41}H_{46}OSi_2$: C, 80.60; H, 7.59%. Found: C, 80.41; H, 7.65%.

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Supporting Information

Summary schemes of the preparation of *sec*-allyl alcohols (**6a–f**) and *sec*-propargyl alcohols (**8b**, **c**, **e**, and **f**). This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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