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Dramatic Enhancement of Reactivity of Organosilicon Compounds Induced by Complexation of Bis(allyl)silanes with Fluoride Ion

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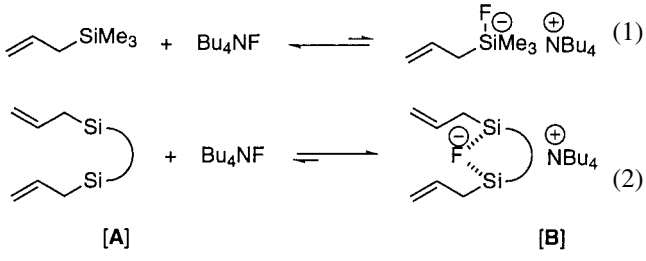
Abstract—New type of fluoride ion catalyzed allylation agent (**1a**, **1b**), allenylation agent (**9**, **10**), and alkynylation agent (**17**) can be successfully utilized for various carbonyl substrates. The rate acceleration is ascribable to the shift of equilibrium to the chelate complexes with Bu_4NF by the favorable chelation of bis(silyl) compounds toward the fluoride ion. The ^{19}F NMR spectrum (ethyl trifluoroacetate as external standard) of a mixture of **1a** and Bu_4NF in $CDCl_3$ showed two peaks at δ −81.75 and −77.67 (integration ratio~9:1). The large signal corresponds to the original peak of Bu_4NF and the small one might be ascribed to the chelate complex [**B**] between **1a** and Bu_4NF. The fluoride ion mediated reaction of bis(crotyldimethylsilyl)methane (**7**) with benzaldehyde was examined and the only γ-adduct **8** was obtained regioselectively.

Introduction

The fluoride ion-catalyzed reactions of reactive organosilicon compounds with carbonyl compounds have become one of the most general and efficient carbon–carbon bond formation methods under nearly neutral conditions available to the synthetic organic chemist.[1] The driving force of these reactions seems to be an extremely high affinity of fluoride ion toward silicon atoms in organosilicon compounds as expected from the high homolytic bond energy (132 kcal/mol) of the Si–F linkage.[2] The protonolysis of the Si–O bond was initially reported[3] and the fluoride-mediated generation of nucleophiles has been exploited by the desilylation of alkynylsilanes,[4] allylic silanes,[5,6] propargylsilanes,[7] benzylsilanes,[8] silyl enol ethers,[9,10] and silyl ketene acetals.[11] Among these, the desilylation condition of allylic silanes is not mild enough (THF reflux) for sensitive functional group compatibility within a molecule. This is mainly due to the mobile equilibrium between the parent allylic silanes and their unfavorable complexes with Bu_4NF (Eq. (1)). In this context, we have been interested for some time in the possibility of generating allyl anion species from certain allylic silanes with Bu_4NF catalyst under mild reaction conditions without affecting other sensitive functional groups. Recently we have communicated that some bis(allyl)silanes of type [**A**] are highly effective for generating allyl anion species via a chelate formation [**B**] with Bu_4NF (Eq. (2)), thereby allowing the hitherto unattainable mild allylation with carbonyl compounds.[12] In this paper we initially present a detailed study of the reactivity of bis(allyl)silanes. We then turn our attention to the extension of the present new activation method to other bis(silyl) compounds having propargyl and alkynyl group on silicon.



Results and Discussion

A. Preparation of bis(allylsilyl) compounds

o-Bis(allyldimethylsilyl)benzene (**1a**) was synthesized by treatment of *o*-bis(dimethylsilyl)benzene[13] with Br_2 (2 equiv.) followed by allylmagnesium bromide (2.2 equiv.) in 75% yield. Bis(allyldimethylsilyl)methane (**1b**) and 1,3-bis(allyldimethylsilyl)propane (**1d**) were prepared by aluminum chloride catalyzed double chlorination of the

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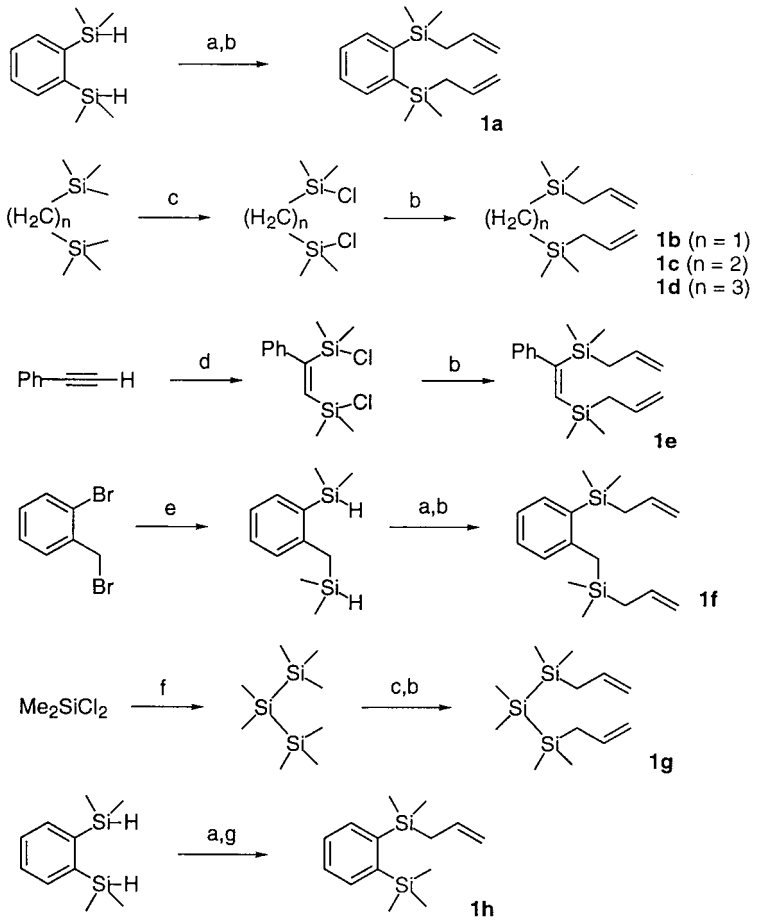


Scheme 1. (a) Br_2 (2 equiv.), CH_2Cl_2, −78°C→rt; (b) allylmagnesium bromide (2.2 equiv.), ether, −78°C; (c) cat. $AlCl_3$, TMSCl; (d) cat. $Pd(PPh_3)_4$, 1,2-dichlorotetramethyldisilane; (e) Me_2SiHCl (2 equiv.), Mg (2 equiv.); (f) TMSCl, Li; (g) (i) MeMgBr (1 equiv.), ether, −78°C, (ii) allylmagnesium bromide (1.2 equiv.), ether, −78°C.

corresponding 1,ω-bis(trimethylsilyl)alkane with chlorotrimethylsilane[14] followed by allylation with allylmagnesium bromide (2.2 equiv.) in 93 and 59%, respectively. As for 1,2-bis(allyldimethylsilyl)ethane (**1c**), the commercially available 1,2-bis(chlorodimethylsilyl)ethane was directly used (94% yield). *cis*-α,β-Bis(allyldimethylsilyl)-styrene (**1e**) was obtained from the palladium catalyzed double silylation of phenylacetylene using 1,2-dichlorotetramethyldisilane[15] followed by allylmagnesium bromide (3.6 equiv.) in 39% yield. For preparation of 1-allyldimethylsilyl-2-(allyldimethylsilylmethyl)benzene (**1f**), 1-dimethylsilyl-2-(dimethylsilylmethyl)benzene was produced by treatment of 2-bromobenzyl bromide with chlorodimethylsilane (2.1 equiv.) in the presence of magnesium (2.1 equiv.) in 91% yield. Then it was treated with Br_2 (2 equiv.) followed by allylmagnesium bromide (2.2 equiv.) to afford **1f** in 23% yield. To obtain 1,3-diallyl-1,1,2,2,3,3-hexamethyltrisilane (**1g**), octamethyltrisilane was prepared according to the literature (45% yield).[16] Then **1g** was synthesized by aluminum chloride catalyzed double chlorination of octamethyltrisilane,[14] followed by allylation using allylmagnesium bromide (2.2 equiv.) (45% yield). 1-Allyldimethylsilyl-2-trimethylsilylbenzene (**1h**) was prepared in 63% yield by treatment of *o*-bis(dimethylsilyl)benzene with Br_2 (2 equiv.) followed by methylmagnesium bromide (1 equiv.) and allylmagnesium bromide (1.2 equiv.) successively (Scheme 1). The monosilyl derivative, allyldimethylphenylsilane (**2**), was prepared by the standard method [chlorodimethylphenylsilane and allylmagnesium bromide] in high yield.

Table 1. Allylation of benzaldehyde with bis(silyl) compounds, **1a–h** in the presence of 5 mol% Bu_4NF (the reaction was carried out using bis(allyldimethylsilyl) compound (1.1 equiv.) and benzaldehyde (1.0 equiv.) at 0°C for 1 h)

Entry	Bis(silyl) compound	Yield of **3** (%)[a]
1	**1a**	100
2	**1b**	100
3	**1c**	53
4	**1d**	25
5	**1e**	53
6	**1f**	60
7	**1g**	0
8	**1h**	33

[a] Isolated yield.

B. Reactions of bis(allylsilyl) compounds

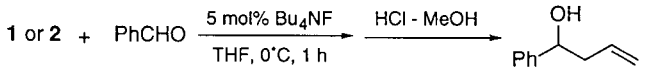
o-Bis(allyldimethylsilyl)benzene (**1a**) was initially selected to observe any chelation effect with Bu_4NF catalyst. Reaction of **1a** with benzaldehyde in the presence of 5 mol% Bu_4NF in THF at 0°C proceeded smoothly within 1 h to furnish allylation product **3** quantitatively (Eq. (3)). In contrast, 1 and 2 equiv. of allyldimethylphenylsilane (**2**)

Table 2. Allylation of various aldehydes **4** with bis(allyl)silane **1a** and **1b** in the presence of 5 mol% Bu_4NF in THF (the reaction was carried out using bis(allyldimethylsilyl) compound (**1a** or **1b**) (1.1 equiv.) and aldehydes **4** (1.0 equiv.))

Entry	Bis(allyl)silane R	Aldehyde **4**	Condition (°C, h)	Yield of **5** (%)[a]
1	**1a**	*p*-$MeOC_6H_4$	0, 4	85
2	**1a**	*p*-FC_6H_4	rt, 0.6	99
3	**1b**	*p*-FC_6H_4	0, 2	89
4	**1a**	β-naphtyl	rt, 0.3	98
5	**1a**	$CH_3(CH_2)_5$	rt, 4	32
6	**1b**	$CH_3(CH_2)_5$	rt, 3	34
7	**1a**	C_6H_{11}	0, 4	35
8	**1a**	PhCH=CH	0, 4	40
9	**1b**	PhCH=CH	rt, 3	49

[a] Isolated yield.

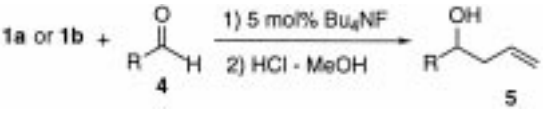
upon reaction with benzaldehyde under similar reaction conditions afforded **3** in only 4 and 7% yields, respectively.[17,18] Clearly, the rate acceleration with bis(silyl) compound **1a** is ascribable to the shift of equilibrium to the complex [**B**] with Bu_4NF by the favorable chelation of bis(silane) toward the fluoride ion as shown in Eq. (2).[19]



(3)

We then evaluated the chelation effect of **1b–h** with Bu_4NF catalyst by allylating benzaldehyde under the above conditions. The results, summarized in Table 1, showed bis-(allyl)silane **1a** and **1b** to be most satisfactory (entries 1 and 2). The reactions of **1c–f** were sluggish and allylation products were obtained in moderate yield (entries 3–6). No reaction occurred in the reaction of **1g** (entry 7). Notably, switching one allyldimethylsilyl group in **1a** by the trimethylsilyl group significantly lowered the yield of allylation product **3** (entry 8). Due to the relatively high electron-withdrawing property of allyl group compared to methyl, the allylsilyl moiety has stronger Lewis acidity than methylsilyl, and hence **1a** possessing two allylsilyl groups probably has higher affinity toward the fluoride ion than **1h**.

With this information at hand, the allylation reactions of *o*-bis(allyldimethylsilyl)benzene (**1a**) and bis(allyldimethylsilyl)methane (**1b**) with several aldehydes **4** were then carried out as listed in Table 2. Allylations of aromatic aldehydes proceeded smoothly at 0°C to room temperature to give the corresponding homoallyl alcohol **5** in high yields (entries 1–4). However, reactions of aliphatic and α,β-unsaturated aldehydes were sluggish under similar conditions (entries 5–9).

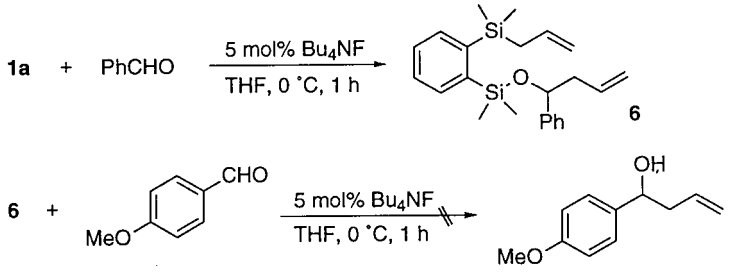


(4)

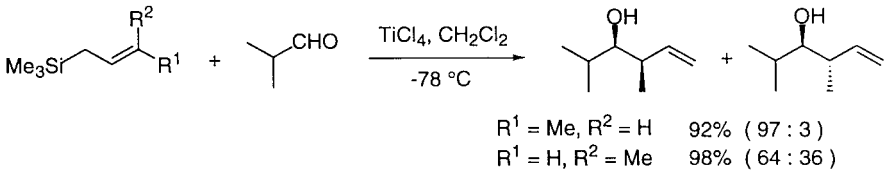
Before cleavage of the silicon–oxygen bond by HCl/MeOH, the allylation products have still one allyl group on silicon. To clarify the reactivity of allylation products, we prepared the allylation product **6** from the reaction of **1a** with benzaldehyde without cleavage of silicon–oxygen bond in 80% yield and examined the reaction of **6** with *p*-methoxybenzaldehyde in the presence of 5 mol% Bu_4NF. 1-*p*-Methoxylphenyl-3-buten-1-ol was not obtained at all but the small amount of 1-phenyl-3-buten-1-ol was produced by cleavage of silicon–oxygen bond of **6**. This result clearly showed that the reactivity of **6** was quite low under the above condition and only one of two allyl groups of **1** transferred to aldehydes in the reaction of **1** with aldehydes (Scheme 2).

C. ^{19}F NMR study

The possibility of the chelate complex formation of **1a** with fluoride ion like [**B**] was also examined by ^{19}F NMR analysis. The spectra of Bu_4NF and a mixture of Bu_4NF and **2** in $CDCl_3$ did not show any noticeable difference in chemical shifts. The original F signal in Bu_4NF appeared at δ −81.98 and, upon addition of 1 equiv. of **2**, the signal shifted slightly to δ −82.01 (ethyl trifluoroacetate as external standard). However, the spectrum of the mixture of **1a** and Bu_4NF showed two peaks at δ −81.75 and −77.67, respectively (integration ratio~9:1). The large signal corresponds to the original peak of Bu_4NF and the small one might be ascribed to the complex formation



Scheme 2.



Scheme 3.

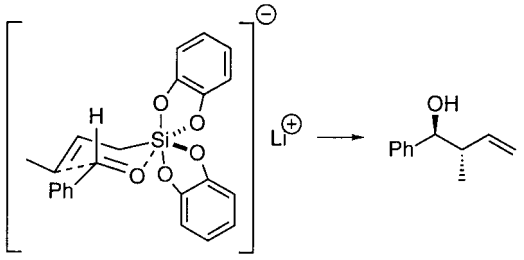
between **1a** and Bu_4NF. The small peak at δ −77.67 also implies that the equilibrium in Eq. (2) largely shifts to the decomplexation at room temperature, and a small quantity (~10%) of the Bu_4NF/**1a** complex participates in the allylation reaction.

D. Preparation and reaction of bis(crotylsilyl) compounds

The Lewis acid mediated reactions of allylic silanes with aldehydes were known to proceed through an acyclic transition state and the mechanism was confirmed from the stereochemical outcome of the reaction using crotylsilanes. For example, (*E*)-crotyltrimethylsilanes produces the syn-alcohol in 97% diastereoselectivity upon treatment with isobutyraldehyde–$TiCl_4$ complex, and (*Z*)-crotyltrimethylsilane also affords the *syn*-alcohol as a major product (64% selectivity) (Scheme 3).[20]

On the other hand, the pentacoordinate allylsilicates react with aldehydes via a six-membered cyclic transition state, and (*E*)-crotylsiliconates give *anti*-homoallyl alcohols, whereas (*Z*)-isomers afford *syn*-homoallyl alcohols (Scheme 4).[21]

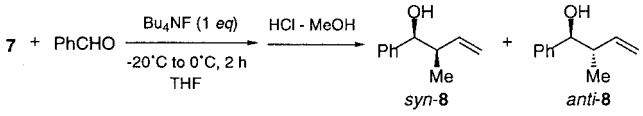
Additionally, the fluoride ion catalyzed reactions of crotyltrifluorosilanes were reported to proceed via the cyclic transition state.[22] On the other hand, the reactions of crotyltrimethylsilane with aldehyde are known to be not regiospecific and the linear allylation product, which was produced by bonding between aldehyde-carbon and γ-carbon of crotylsilane, was obtained predominantly over the branched one, which was produced by bonding between aldehyde-carbon and γ-carbon of crotylsilane, probably because the hypervalent intermediate is no longer stable with respect to [1,3] sigmatropic shift of the silyl group under the severe reaction conditions as mentioned above (Scheme 5).[5]



Scheme 4.

We decided to examine the reaction of bis(crotylsilyl) compound with benzaldehyde and clarify the regio- and stereoselectivity of bis(silanes). The synthesis of desired bis((*E*)-crotyldimethylsilyl)methane (**7**) follows: Cuprous chloride-catalyzed condensation of trichlorosilane with (*E*)-crotyl chloride, and subsequent treatment with methyllithium (2 equiv.) gave (*E*)-crotyldimethylsilyl chloride (46% yield), which was reacted with Mg and dibromomethane to afford **7** as a sole product in 49% yield (Scheme 6).

Since the reaction of **7** with benzaldehyde in the presence of 5 mol% Bu_4NF was sluggish even at room temperature, the reaction was carried out using stoichiometric amount of Bu_4NF at 0°C and only the branched product **8** was obtained in 40% yield. This result implied that the [1,3] sigmatropic shift of the silyl group was suppressed in the reaction of **7**. The diastereomeric ratio of *syn* and *anti* was found to be 54:46 and this result showed that the reaction proceeded through both the acyclic transition state (for example [**C**]) and the cyclic transition state (for example [**D**]) at random.[23,24]



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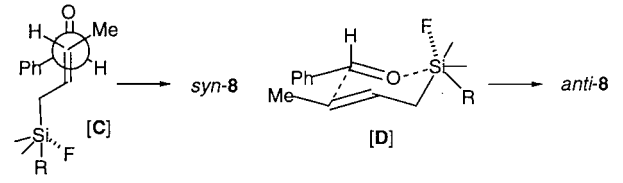
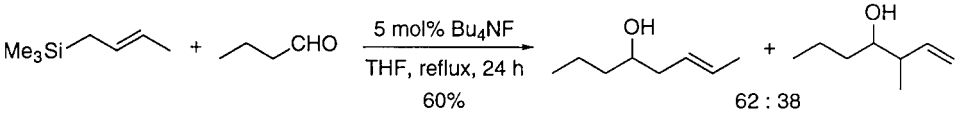


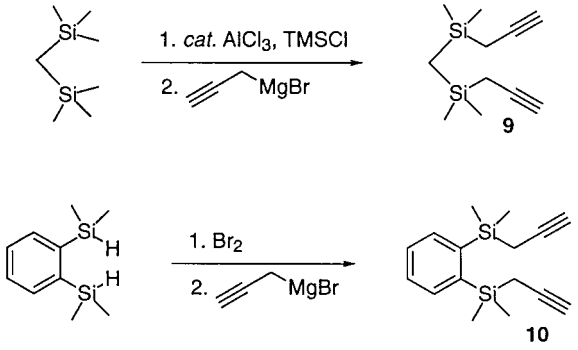
Preparation and reactions of bis(propargylsilyl) compounds

These results encouraged us to extend this activation method to other reactive organosilicon compounds. Propargylsilanes are known to react with carbonyl compounds

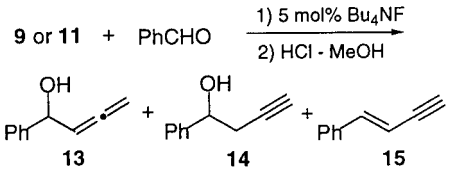


Scheme 5.

in the presence of catalytic amounts of fluoride ion.[7] Based on the results of bis(allylsilyl) compound, bis(propargylsilyl)methane (**9**) and 1,2-bis(propargylsilyl)benzene (**10**) were synthesized in analogy to **1b** and **1a** in 48 and 54% yields, respectively. The corresponding monosilyl derivatives, propargyltrimethylsilane (**11**) and dimethylphenylpropargylsilane (**12**), were prepared by the standard method in 18 and 63% yields, respectively.



Attempted reaction of propargyltrimethylsilane (**11**) with benzaldehyde in the presence of 5 mol% Bu_4NF in THF at −45°C for 10 min gave no products. In contrast, **9** upon reaction with benzaldehyde under similar conditions afforded the mixture of allenylation product **13**, propargylation product **14**, and enyne compound **15** in the ratio of 71:22:7 and the chemical yield was quantitative (Eq. (6)). Product **15** was probably formed by dehydration reaction of propargylation product **14**. The regioselectivity in the reaction of propargylsilanes have been reported to depend on the kinds of aldehydes, i.e. allenylation products were obtained from aliphatic aldehydes and mixture of allenylation and propargylation products were produced from aromatic aldehydes.[7] The similar results were obtained in the reactions using **10** and **12**. The reaction of **10** with heptanal catalyzed by Bu_4NF in THF at −25°C for 7 min gave allenylation product **16** in 55% yield. On the other hand, allenylation product **16** was obtained in lower yield (12%) in the reaction of the corresponding monosilyl reagent, dimethylphenylpropargylsilane (**12**), under similar reaction conditions (Eq. (7)). Interestingly, the reactivities of these compounds somewhat depended on the fluoride ion source. The reaction of **10** with heptanal catalyzed by 5 mol% $Bu_4N(Ph_3SnF_2)$ in THF at rt for 11 h gave **16** in 43% yield.[25] On the contrary, allenylation product was not obtained at all with **12** under similar reaction conditions. Thus, the dramatic differences in chemical yield between bis(propargylsilyl) reagents and monosilyl reagents provide strong evidence for the existence of the chelate complex [**B**] not only in the reactions of bis(allylsilyl) compounds but also in the reactions of bis(propargylsilyl) reagents.



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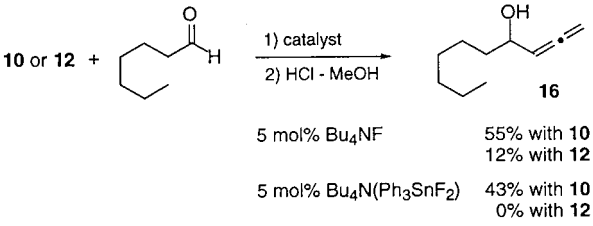

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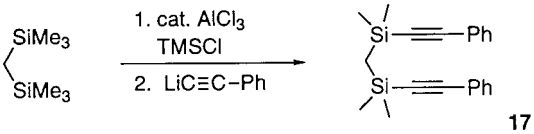
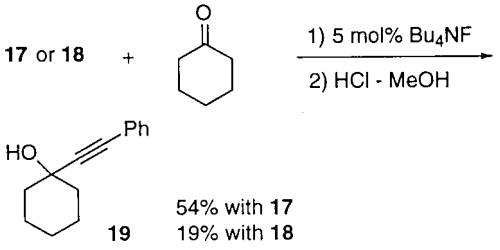
Preparation and reactions of bis(alkynylsilyl) compounds

In order to apply the present methodology to alkynylsilanes, we next prepared bis[dimethyl(phenylethynyl)silyl]methane (**17**) from bis(trimethylsilyl)methane in analogy to **1b** in 64% yield and the monosilyl analog, 1-phenyl-2-(trimethylsilyl)acetylene (**18**), by the standard method, and examined the reactions of **17** and **18** with cyclohexanone, respectively, in the presence of 5 mol% Bu_4NF at −78°C for 4 h. The bis(silyl) compound **17** showed moderate reactivity and the alkynylation product **19** was obtained in 54% yield. On the other hand, the monosilyl reagent **18** gave **19** in only 19% yield under similar reaction conditions. These results clarified that the reactivity of alkynylsilanes could be increased by using bis(silyl) compound **17**.

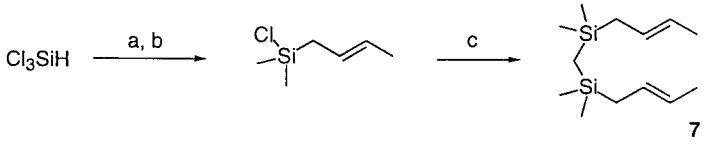




(8)

Conclusions

In summary, we have developed new types of fluoride



Scheme 6. (a) Crotyl chloride, Et_3N, cat. CuCl, ether, rt. (b) MeLi, ether, −78°C. (c) Mg, dibromomethane, THF, rt.

ion-catalyzed allylation agents, *o*-bis(allyldimethylsilyl)-benzene (**1a**) and bis(allyldimethylsilyl)methane (**1b**), allenylation agent, bis(dimethylpropargylsilyl)methane (**9**) and *o*-bis(dimethylpropargylsilyl)benzene (**10**), and alkynylation agent, bis[dimethyl(phenylethynyl)silyl]methane (**17**). The reactions using such bis(silyl) compounds proceed much faster than those with monosilyl counterparts due to the preferable formation of the chelate complex [**B**] (Eq. (2)) by the chelation effect of two neighboring silicon atoms and various data presented in this article imply the high synthetic potential of our new methodology in organosilicon chemistry.

Experimental

General

Infrared (IR) spectra were recorded on a Shimazu FT-IR 8100A spectrometer. ^{1}H, ^{13}C and ^{19}F spectra were measured on a Varian Gemini-300 (300 MHz). All experiments were carried out under an atmosphere of dry argon. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel (E. Merck 9385). Microanalyses were accomplished at the Center of Instrumental Analysis, Hokkaido University. The high-resolution mass spectra (HRMS) were conducted at the School of Agriculture, Hokkaido University.

In experiments requiring dry solvents, ether and tetrahydrofuran (THF) were purchased from Kanto Chemical Co. Ltd as 'Dehydrated'. A 1 M THF solution of Bu_4NF was stored over 4 Å molecular sieves.

Preparation of bis(allylsilyl) compounds

***o*-Bis(allyldimethylsilyl)benzene (1a).**[26] To a solution of 1,2-bis(dimethylsilyl)benzene (3.89 g, 20 mmol) in CH_2Cl_2 (40 mL) was added Br_2 (2.06 mL, 40 mmol) at −78°C under argon and the mixture was stirred for 30 min at −78°C. CH_2Cl_2 was evaporated in vacuo and the residue was diluted with THF (40 mL). The solution was cooled to −78°C. Then a 1.0 M ethereal solution of allylmagnesium bromide (44.0 mL, 44 mmol) was added, and the mixture was stirred at −78°C for 30 min and at room temperature for additional 30 min. The solution was quenched with saturated NH_4Cl and extracted with ether. The organic extracts were dried over Na_2SO_4. Evaporation of solvent and purification of the residual oil by column chromatography on silica gel (hexane as eluent) gave *o*-bis(allyldimethylsilyl)benzene (**1a**) (4.12 g, 15 mmol, 75% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.30–7.38 and 7.61–7.69 (4H, m, C_6H_4), 5.71–5.86 (2H, m, 2C*H*=CH_2), 4.86–4.93 (4H, m, 2CH=CH_2), 1.85 (4H, d, J=7.8 Hz, $2CH_2Si$), 0.38 (12H, s, $4CH_3$).

Bis(allyldimethylsilyl)methane (1b). A mixture of bis(trimethylsilyl)methane (3.20 mL, 15 mmol), chlorotrimethylsilane (16.5 mL, 130 mmol) and anhydrous aluminum chloride (200 mg, 1.5 mmol) under argon was heated to gentle reflux. After ca. 4 h, the temperature of the flask was increased to distill unreacted chlorotrimethylsilane. The residue was diluted with THF (45 mL) and the solution was cooled to −78°C. A 1.0 M ethereal solution of allylmagnesium bromide (33.0 mL, 33 mmol) was added, and the mixture was stirred at −78°C for 30 min and at room temperature for additional 30 min. The solution was quenched with saturated NH_4Cl and extracted with ether. The organic extract was dried over Na_2SO_4. Evaporation of solvent and purification of the residual oil by column chromatography on silica gel (hexane as eluent) gave bis(allyldimethylsilyl)methane (**1b**) (2.96 g, 14 mmol, 93% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.70–5.86 (2H, m, 2C*H*=CH_2), 4.80–4.86 (4H, m, 2CH=CH_2), 1.51 (4H, d, J=8.1 Hz, $2CH_2C$=C), 0.03 (12H, s, $4CH_3$), −0.25 (2H, s, $SiCH_2Si$); IR (liquid film) 3078, 2955, 2897, 1632, 1254, 1155, 1057, 893, 933 cm^{-1}; MS: *m*/*z* 197 (M^+−Me), 171 (100%), 155, 131, 129, 73. Anal. Calcd for $C_{11}H_{24}Si_2$: C, 62.17; H, 11.38. Found: C, 61.91; H, 11.27.

1,2-Bis(allyldimethylsilyl)ethane (1c).[27] To a solution of 1,2-bis(chlorodimethylsilyl)ethane (2.15 g, 10 mmol) in THF (20 mL) was added a 1.0 M ethereal solution of allylmagnesium bromide (22.0 mL, 22 mmol) at −78°C under argon. The mixture was stirred at −78°C for 30 min and at room temperature for additional 30 min. The solution was quenched with saturated NH_4Cl and extracted with ether. The organic extract was dried over Na_2SO_4. Evaporation of solvent and purification of the residual oil by column chromatography on silica gel (hexane as eluent) gave 1,2-bis(allyldimethylsilyl)ethane (**1c**) (2.14 g, 9.4 mmol, 94% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.70–5.85 (2H, m, 2C*H*=CH_2), 4.79–4.89 (4H, m, 2CH=CH_2), 1.52 (4H, d, J=8.4 Hz, $2CH_2C$=C), 0.41 (4H, s, $SiCH_2CH_2Si$), −0.03 (12H, s, $4CH_3$).

1,3-Bis(allyldimethylsilyl)propane (1d). Following the same procedure for **1b**, the double chlorination of 1,3-bis(trimethylsilyl)propane (1.37 g, 7.3 mmol) with catalytic aluminum chloride (0.097 g, 0.73 mmol) and chlorotrimethylsilane (8.00 mL, 63 mmol), followed by allylation with a 1.0 M ethereal solution of allylmagnesium bromide (16.0 mL, 16 mmol) gave 1,3-bis(allyldimethylsilyl)propane (**1d**) (1.03 g, 4.3 mmol, 59% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.70–5.86 (2H, m, 2C*H*=CH_2), 4.78–4.89 (4H, m, 2CH=CH_2), 1.51 (4H, d, J=8.1 Hz, $2CH_2C$=C), 1.29–1.40 (2H, m, CH_2C–Si), 0.58 (4H, t, J=8.4 Hz, $2CH_2Si$), −0.02 (12H, s, $4CH_3$); IR (liquid film) 3078, 2955, 2912, 1630, 1252, 1155, 905, 837 cm^{-1}; MS: *m*/*z* 240 (M^+), 225, 212, 199, 157, 125, 99 (100 %), 73. Anal. Calcd for $C_{13}H_{28}Si_2$: C, 64.91; H, 11.73. Found: C, 64.80; H, 11.76.

***cis*-α,β-Bis(allyldimethylsilyl)styrene (1e).** A mixture of 1,2-dichlorotetramethyldisilane (0.97 mL, 6 mmol), phenylacetylene (0.55 mL, 5 mmol), and tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol) was heated at 110°C (oil bath) with magnetic stirring for 1.5 h. The resulting mixture was diluted with THF (10 mL) and the solution was cooled to −78°C. A 1.0 M ethereal solution of allylmagnesium bromide (18 mL, 18 mmol) was added, and the mixture was stirred at −78°C for 30 min and at room temperature for additional 30 min. The solution was

quenched with saturated NH_4Cl and extracted with ether. The organic extract was dried over Na_2SO_4. Evaporation of solvent and purification of the residual oil by column chromatography on silica gel (hexane as eluent) gave *cis*-α,β-bis(allyldimethylsilyl)styrene (**1e**) (0.56 g, 1.9 mmol, 39% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.23–7.31 (2H, m, 2Ph–H), 7.15–7.22 (1H, m, Ph–H), 6.99–7.05 (2H, m, 2Ph–H), 6.44 (1H, s, =CH–Si), 5.58–5.89 (2H, m, 2C*H*=CH_2), 4.77–4.91 (4H, m, 2CH=C*H*$_2$), 1.68 (2H, d, *J*=8.1 Hz, CH_2Si), 1.61 (2H, d, *J*=7.8 Hz, CH_2Si), 0.23 (6H, s, $2CH_3$), 0.17 (6H, s, $2CH_3$); IR (liquid film) 3076, 2957, 2897, 1630, 1256, 1153, 895, 820, 700 cm^{-1}; MS: *m*/*z* 300 (M^+), 285, 259 (100 %), 217, 185, 159, 135, 99. Anal. Calcd for $C_{18}H_{28}Si_2$: C, 71.92; H, 9.38. Found: C, 71.71; H, 9.46.

1-Allyldimethylsilyl-2-(allyldimethylsilylmethyl)benzene (1f). To a mixture of Mg (1.02 g, 42 mmol) and chlorodimethylsilane (5.33 mL, 42 mmol) in THF (20 mL) was added a solution of 2-bromobenzyl bromide (5.00 g, 20 mmol) in THF (20 mL) dropwise at 0°C under argon. The mixture was stirred for 2 h at room temperature. The solution was then quenched with saturated NH_4Cl and extracted with ether. The organic extract was dried over Na_2SO_4. Evaporation of solvent and purification of the residual oil by column chromatography on silica gel (hexane as eluent) gave 1-dimethylsilyl-2-(dimethylsilylmethyl)-benzene as a precursor of **1f** (3.78 g, 18 mmol, 91% yield as a colorless oil). Following the same procedure for **1a**, 1-dimethylsilyl-2-(dimethylsilylmethyl)benzene was treated with Br_2 (1.85 mL, 36.0 mmol) followed by a 1.0 M ethereal solution of allylmagnesium bromide (39.6 mL, 39.6 mmol) to afford **1f** (1.19 g, 4.1 mmol, 23% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.41 (1H, dd, *J*=1.5, 7.5 Hz, Ar–H), 7.24 (1H, dt, *J*=1.5, 7.5 Hz, Ar–H), 7.03–7.11 (2H, m, 2Ar–H), 5.70–5.85 (2H, m, 2C*H*=CH_2), 4.83–4.91 (4H, m, 2CH=C*H*$_2$), 2.30 (2H, s, Ar–CH_2Si), 1.81 (2H, d, *J*=8.1 Hz, CH_2C=C), 1.59 (2H, d, *J*=8.1 Hz, CH_2C=C), 0.32 (6H, s, $2CH_3$), 0.01 (6H, s, $2CH_3$); IR (liquid film) 3076, 3057, 2957, 1630, 1587, 1250, 1155, 895 cm^{-1}; MS: *m*/*z*, 259, 247 (100 %), 231, 205, 173, 159, 145, 133, 99, 73. Anal. Calcd for $C_{17}H_{28}Si_2$: C, 70.76; H, 9.08. Found: C, 70.41; H, 9.46.

1,3-Diallyl-1,1,2,2,3,3-hexamethyltrisilane (1g).[28] Following the same procedure for **1b**, the double chlorination of 1,1,1,2,2,3,3,3-octamethyltrisilane (2.04 g, 10 mmol) with catalytic aluminum chloride (133 mg, 1 mmol) and chlorotrimethylsilane (11.9 mL, 93.8 mmol), followed by allylation with a 1.0 M ethereal solution of allylmagnesium bromide (22.0 mL, 22 mmol) gave 1,3-diallyl-1,1,2,2,3,3-hexamethyltrisilane (**1g**) (1.14 g, 4.4 mmol, 45% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.70–5.86 (2H, m, 2C*H*=CH_2), 4.80–4.89 (4H, m, 2CH=C*H*$_2$), 1.61 (4H, d, *J*=9.0 Hz, $2CH_2C$=C), 0.12 (6H, s, $2CH_3$), 0.08 (12H, s, $4CH_3$).

1-Allyldimethylsilyl-2-trimethylsilylbenzene (1h). Following the same procedure for **1a**, the title compound was prepared in 63% yield (1.56 g, 6.3 mmol) as a colorless oil by treatment of *o*-bis(dimethylsilyl)benzene (1.94 g, 10 mmol) with Br_2 (1.03 mL, 20 mmol), followed by a 1.0 M THF solution of methylmagnesium bromide (10.0 mL, 10 mmol) and then a 1.0 M ethereal solution of allylmagnesium bromide (12.0 mL, 12 mmol): ^{1}H NMR ($CDCl_3$) δ 7.61–7.70 (2H, m, 2Ar–H), 7.29–7.36 (2H, m, 2Ar–H), 5.72–5.87 (1H, m, C*H*=CH_2), 4.85–4.93 (2H, m, CH=C*H*$_2$), 1.85 (2H, d, *J*=8.1 Hz, CH_2Si), 0.37 (15H, s, $5CH_3$); IR (liquid film) 3854, 3649, 2953, 1717, 1684, 1558, 1508, 1250, 1155, 1119, 839, 737 cm^{-1}. MS: *m*/*z* 248 (M^+), 233, 217, 207, 191 (100%), 159, 135, 73. Anal. Calcd for $C_{14}H_{24}Si_2$: C, 67.66; H, 9.73. Found: C, 67.29; H, 9.77.

Preparation of bis(crotylsilyl) compound

Bis(crotyldimethylsilyl)methane (7). To a mixture of cuprous chloride (107 mg, 1.08 mmol) and triethylamine (5.36 mL, 38.5 mmol) in ether (22 mL) were added crotyl chloride (2.95 g, 32.5 mmol) and trichlorosilane (4.71 mL, 46.7 mmol) at room temperature under argon. The mixture was stirred at room temperature for 4 h. Then, this mixture was filtered with Celite and washed with ether. Distillation of the concentrated filtrate gave trichlorocrotylsilane (2.83 g, 14.9 mmol, 46% yield) as a colorless oil (bp 67°C at 62 mmHg).

To a solution of trichlorocrotylsilane (2.83 g, 14.9 mmol) in ether (30 mL) was added a 1.14 M ethereal solution of methyllithium (24.9 mL, 28.4 mmol) at −78°C under argon. The mixture was stirred at −78°C for 2.5 h. Then, this mixture was filtered with Celite and washed with ether. Distillation of the concentrated filtrate gave chlorocrotyldimethylsilane (1.16 g, 7.89 mmol, 53% yield) as a colorless oil (bp 71°C at 80 mmHg).

To a suspension of magnesium (102 mg, 4.2 mmol) in THF (2 mL) was added chlorocrotyldimethylsilane (624 mg, 4.2 mmol) at room temperature under argon. Dibromomethane (140 μL, 2 mmol) was added dropwise at room temperature and the whole mixture was stirred at room temperature for 2 h and 70°C for 19 h. The solution was then quenched with saturated NH_4Cl and extracted with ether. The organic extract was dried over Na_2SO_4. Evaporation of solvent and purification of the residual oil by column chromatography on silica gel (hexane as eluant) gave bis(crotyldimethylsilyl)methane (**7**) (235 mg, 2.1 mmol, 49% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.32–5.44 (2H, m, 2CH=C*H*CH_3), 5.18–5.29 (2H, m, $2CH_2C$*H*=CH), 1.64 (6H, dq, *J*=1.2, 6.3 Hz, 2C=CHC*H*$_3$), 1.38 (4H, dt, *J*=1.2, 7.5 Hz, 2C*H*$_2$CH=C), 0.00 (12H, s, $4SiCH_3$), −0.29 (2H, s, $SiCH_2Si$); IR (liquid film) 3012, 2956, 2929, 2856, 2362, 2341, 1508, 1400, 1377, 1305, 1251, 1161, 1055, 964, 837 cm^{-1}; MS(EI) *m*/*z* 185 ($M-CH_2CH$=$CHCH_3$)$^+$; HRMS(EI) Calcd for $C_9H_{21}Si_2$: 185.4367 ($M-CH_2CH$=$CHCH_3$)$^+$. Found: 185.4341 ($M-CH_2CH$=$CHCH_3$)$^+$.

Preparation of bis(propargylsilyl) compounds

Bis(dimethylpropargylsilyl)methane (9). Following the procedure for **1b**, the double chlorination of bis(trimethylsilyl)methane (6.41 mL, 30 mmol) with catalytic aluminum chloride (400 mg, 3 mmol) and chlorotrimethylsilane (33.0 mL, 260 mmol), and subsequent addition of a 1.0 M ethereal solution of propargylmagnesium bromide (66.0 mL, 66 mmol) gave bis(propargylsilyl)methane (**9**)

(2.92 g, 14 mmol, 48% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.84–1.86 (2H, t, J=3.0 Hz, 2CCH), 1.50–1.51 (4H, d, J=3.0 Hz, $2SiCH_2CC$), 0.169 (12H, s, $4SiCH_3$), 0.169 (2H, s, $SiCH_2Si$); IR (liquid film) 3313, 2956, 2895, 2115, 1398, 1255, 1155, 1058, 952, 837, 696 cm^{-1}; MS(EI) m/z 193 $(M-CH_3)^+$; HRMS(EI) Calcd for $C_{10}H_{17}Si_2$: 193.4159 $(M-CH_3)^+$. Found: 193.4120 $(M-CH_3)^+$.

***o*-Bis(propargyldimethylsilyl)benzene (10).** To a solution of 1,2-bis(dimethylsilyl)benzene (5.83 g, 30 mmol) in CH_2Cl_2 (60 mL) was added Br_2 (3.09 mL, 60 mmol) at −78°C under argon. The mixture was stirred at −78°C for 30 min, and CH_2Cl_2 was evaporated in vacuo. The residue was diluted with ether (50 mL), and cooled to −78°C. Then a 1.0 M ethereal solution of propargylmagnesium bromide (66.0 mL, 66 mmol) was added, and the mixture was stirred at −78°C for 30 min and at room temperature for additional 30 min. The solution was quenched with saturated NH_4Cl and extracted with ether. The organic extract was dried over Na_2SO_4. Evaporation of solvent and purification of the residual oil by column chromatography on silica gel (hexane as eluent) gave *o*-bis(propargyldimethylsilyl)benzene (**10**) (4.42 g, 16.3 mmol, 54% yield) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.67–7.73 (2H, m, 2Ar–H), 7.35–7.41 (2H, m, 2Ar–H), 1.88 (2H, t, J=3.0 Hz, 2C≡CH), 1.82 (4H, d, J=3.0 Hz, $2CH_2Si$); 0.51 (12H, s, $4CH_3$); IR (liquid film) 3294, 2957, 2116, 1414, 1254, 1150, 1121, 953, 841, 816, 745, 631, 451 cm^{-1}; MS: m/z 270 (M^+), 255, 231 (100%), 215, 191, 177, 145, 133, 97, 73. Anal. Calcd for $C_{16}H_{22}Si_2$: C, 71.03; H, 8.19. Found: C, 70.81; H, 7.82.

Bis((phenylethynyl)dimethylsilyl)methane (17). A mixture of bis(trimethylsilyl)methane (1.06 mL, 5 mmol) and chlorotrimethylsilane (635 μL, 5 mmol) was heated to gentle reflux in the presence of anhydrous aluminum chloride (66.7 mg, 0.5 mmol) under argon. After ca. 4 h, the temperature of the flask was increased to distill chlorotrimethylsilane. The residue was diluted with THF (15 mL) and the solution was cooled to −78°C. A 0.5 M THF solution of lithium phenylacetylide (22.0 mL, 11 mmol) was added, and the mixture was stirred at −78°C for 30 min and at room temperature for additional 30 min. The solution was quenched with saturated NH_4Cl and extracted with ether. The organic extract was dried over Na_2SO_4. Evaporation of solvent and purification of the residual oil by column chromatography on silica gel (hexane as eluent) gave bis((phenylethynyl)dimethylsilyl)methane (**17**) (1.07 g, 3.2 mmol, 64% yield) as an orange oil: ^{1}H NMR ($CDCl_3$) δ 7.43–7.48 (4H, m, Ph–H), 7.27–7.32 (6H, m, Ph–H), 0.35 (12H, s, $4CH_3$), 0.17 (2H, s, CH_2); IR (liquid film) 3080, 2959, 2901, 2158, 1489, 1443, 1250, 1221, 1055, 1028, 853, 823, 756, 691, 536 cm^{-1}; MS: m/z 332 (M^+), 317, 245, 215, 159 (100%), 143, 129, 105, 73. Anal. Calcd for $C_{21}H_{24}Si_2$: C, 75.83; H, 7.27. Found: C, 75.67; H, 7.40.

Reactions of bis(allylsilyl) compounds

General procedure for the allylation of aldehydes with bis(allylsilyl) compounds. To a solution of **1a** (0.32 mL, 1.1 mmol) and benzaldehyde (0.10 mL, 1.0 mmol) in THF (2 mL) was added a 1 M THF solution of Bu_4NF (0.05 mL, 0.05 mmol) at 0°C under argon. After stirring for 1 h at this temperature, the reaction was quenched by a mixture of conc. HCl and MeOH (1:100) at 0°C. Ether was added and the mixture was washed with saturated $NaHCO_3$ and brine. The organic layer was dried, filtered, and concentrated. The residue was purified by column chromatography on silica gel using a mixture of hexane and EtOAc (6:1) as eluent to give 1-phenyl-3-buten-1-ol (**3**) (148 mg, 100% yield) as a colorless oil.

1-Phenyl-3-buten-1-ol (3).[29] ^{1}H NMR ($CDCl_3$) δ 7.25–7.39 (5H, m, Ph), 5.75–5.89 (1H, m, C*H*=CH_2), 5.13–5.21 (2H, m, CH=CH_2), 4.71–4.77 (1H, m, CH–O), 2.43–2.59 (2H, m, CH_2C=C), 2.08 (1H, br s, OH).

1-(*p*-Methoxyphenyl)-3-buten-1-ol.[29] ^{1}H NMR ($CDCl_3$) δ 7.28 (2H, d, J=8.7 Hz, 2Ar–H), 6.89 (2H, d, J=8.7 Hz, 2Ar–H), 5.74–5.87 (1H, m, C*H*=CH_2), 5.12–5.20 (2H, m, CH=CH_2), 4.69 (1H, t, J=6.3 Hz, CH–O), 3.81 (3H, s, OCH_3), 2.52 (2H, t, J=6.3 Hz, CH_2C=C), 2.00 (1H, br s, OH).

1-(*p*-Fluorophenyl)-3-buten-1-ol.[29] ^{1}H NMR ($CDCl_3$) δ 7.30–7.38 (2H, m, 2Ar–H), 7.00–7.08 (2H, m, 2Ar–H), 5.73–5.86 (1H, m, C*H*=CH_2), 5.14–5.21 (2H, m, CH=CH_2). 4.73 (1H, t, J=6.0 Hz, CH–O), 2.14–2.56 (2H, m, CH_2C=C), 2.08 (1H, br s, OH).

1-(β-Naphthyl)-3-buten-1-ol. ^{1}H NMR ($CDCl_2$) δ 7.79–7.87 (4H, m, 4Ar–H), 7.45–7.51 (3H, m, 3Ar–H), 5.76–5.90 (1H, m, C*H*=CH_2), 5.13–5.23 (2H, m, CH=CH_2), 4.88–4.93 (1H, m, CH–O), 2.51–2.68 (2H, m, CH_2C=C), 2.20 (1H, br s, OH). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.69; H, 7.21.

1-Decen-3-ol.[30] ^{1}H NMR ($CDCl_3$) δ 5.77–5.91 (1H, m, C*H*=CH_2), 5.11–5.18 (2H, m, CH=CH_2), 3.61–3.69 (1H, m, CH–O), 2.09–2.35 (2H, m, CH_2C=C), 1.61 (1H, br s, OH), 1.16–1.48 (10H, m, $5CH_2$), 0.89 (3H, t, J=6.9 Hz, CH_3).

1-Cyclohexyl-3-buten-1-ol.[30] ^{1}H NMR ($CDCl_3$) δ 5.78–5.92 (1H, m, C*H*=CH_2), 5.12–5.19 (2H, m, CH=CH_2), 3.36–3.43 (1H, m, CH–O), 2.07–2.38 (2H, m, CH_2C=C), 1.61–1.90 (5H, m, CH+$2CH_2$), 1.58 (1H, br s, OH), 0.95–1.42 (6H, m, $3CH_2$).

(*E*)-1-Phenyl-1,5-hexadien-3-ol.[29] ^{1}H NMR ($CDCl_3$) δ 7.22–7.41 (5H, m, Ph), 6.61 (1H, d, J=15.6 Hz, PhCH), 6.25 (1H, dd, J=15.9 Hz, PhC=CH), 5.79–5.93 (1H, m, C*H*=CH_2), 5.15–5.23 (2H, m, CH=CH_2), 4.35–4.38 (1H, m, CH–O), 2.33–2.50 (2H, m, CH_2C=C), 1.85 (1H, br s, OH).

Allylation product 6. ^{1}H NMR ($CDCl_3$) δ 7.63–7.68 (2H, m, 2Ar–H), 7.22–7.36 (7H, m, 2Ar–H+Ph), 5.55–5.86 (2H, m, 2C*H*=CH_2), 4.82–5.01 (4H, m, 2CH=CH_2), 4.76 (1H, t, J=6.9 Hz, PhCH), 2.49–2.71 (2H, dd, CH_2C=C), 1.92 (2H, d, J=7.8 Hz, CH_2C=C), 0.35–0.42 (9H, m, $3CH_3$), 0.18 (3H, s, CH_3); IR (liquid film) 3074, 3045, 2955, 2903, 2361, 1630, 1454, 1418, 1252, 1119, 1080, 1059, 1042, 930, 835, 764, 700 cm^{-1}; MS: m/z, 332, 317, 265, 233, 209, 193, 149, 131 (100 %), 91, 73.

Anal. Calcd for $C_{23}H_{32}OSi_2$: C, 72.56; H, 8.47. Found: C, 72.24; H, 8.56.

^{19}F NMR study

The ^{19}F NMR analysis of Bu_4NF in $CDCl_3$/THF in the absence or presence of allylic silanes (**1a** or **2**) was carried out using ethyl trifluoroacetate (δ=0) as external standard.

Bu_4NF: ^{19}F NMR ($CDCl_3$) δ −81.98.

An equimolar mixture of Bu_4NF and allyldimethylphenylsilane (**2**): ^{19}F NMR ($CDCl_3$) δ −82.01.

An equimolar mixture of Bu_4NF and *o*-bis(allyldimethylsilyl)benzene (**1a**): ^{19}F NMR ($CDCl_3$) δ −77.67 (chelate complex [**B**]), −81.75 (integration ratio∼1:9).

Reaction of bis(crotylsilyl) compounds

***syn*-1-Phenyl-2-methyl-3-buten-1-ol (*syn*-8).**[24] ^{1}H NMR ($CDCl_3$) δ 7.20–7.39 (5H, m, Ph), 5.52–5.72 (1H, m, C*H*=CH_2), 5.00–5.10 (2H, m, CH=CH_2), 4.62 (1H, d, *J*=8.5 Hz, PhCH), 2.35–2.57 (1H, m, CH–C=C), 1.68 (1H, s, OH), 0.98 (3H, d, *J*=8 Hz, CH_3).

***anti*-1-Phenyl-2-methyl-3-buten-1-ol (*anti*-8).**[24] ^{1}H NMR ($CDCl_3$) δ 7.21–7.40 (5H, m, Ph), 5.66–5.86 (1H, m, C*H*=CH_2), 5.15–5.26 (2H, m, CH=CH_2), 4.34 (1H, d, *J*=8.5 Hz, PhCH), 2.35–2.53 (1H, m, CH–C=C), 1.62 (1H, s, OH), 0.86 (3H, d, *J*=8 Hz, CH_3).

Reaction of bis(propargylsilyl) compounds

1-Phenyl-2,3-butadien-1-ol (13).[30] ^{1}H NMR ($CDCl_3$) δ 7.28–7.44 (5H, m, Ph), 5.45 (1H, td, *J*=6.6, 6.6 Hz, CH=C), 5.25–5.30 (1H, m, CH–O), 4.88–4.99 (2H, m, CH_2=C), 2.46 (1H, br s, OH).

1-Phenyl-3-butyn-1-ol (14).[30] ^{1}H NMR ($CDCl_3$) δ 7.28–7.42 (5H, m, Ph), 4.89 (1H, dt, *J*=3.3, 6.6 Hz, PhCH), 2.65 (2H, dd, *J*=2.7, 6.6 Hz, CH_2), 2.40 (1H, br d, *J*=3.3 Hz, OH), 2.08 (1H, t, *J*=2.7 Hz, C≡CH).

1-Phenyl-1-buten-3-yne (15).[31] ^{1}H NMR ($CDCl_3$) δ 7.28–7.41 (5H, m, Ph), 7.05 (1H, d, *J*=16.5 Hz, PhCH), 6.14 (1H, dd, *J*=2.4, 16.5 Hz, CH=C*H*C), 3.06 (1H, d, *J*=2.4 Hz, C≡CH).

1,2-Decadien-4-ol (16).[30] ^{1}H NMR ($CDCl_3$) δ 5.24 (1H, dt, *J*=6.6, 6.6 Hz, =CH), 4.86 (2H, dd, *J*=2.5, 6.6 Hz, =CH_2), 4.12–4.22 (1H, m, CH–O), 1.87 (1H, br s, OH), 1.16–1.62 (10H, m, 5CH_2), 0.87 (3H, t, *J*=6.9 Hz, CH_3).

1-(Phenylethynyl)-1-cyclohexanol (19). ^{1}H NMR ($CDCl_3$) δ 7.41–7.46 (2H, m, Ph–H), 7.29–7.33 (3H, m, Ph–H), 2.09 (1H, br s, OH), 1.21–2.06 (10H, m, 5CH_2). The authentic sample was independently prepared by treatment of cyclohexanone with phenylethynyllithium in THF at 0°C.

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