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Intramolecular allylation of the azo group of 2-(allylsilyl)azobenzenes and its photocontrol

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Abstract

Pentacoordinate allylsilanes bearing an azobenzene moiety were synthesized and their structures were elucidated. The reaction of allyldifluorosilane (*E*)-**7a** with $BF_3 \cdot OEt_2$ did not proceed, but (*E*)-**7a** was allowed to react with a fluoride ion to give tetrafluorosilicate **8a** via intramolecular allyl-migration from the silicon atom onto the azo group. Activation of both the nucleophilic and electrophilic parts by the Si···N interaction was found to be important for promotion of the allyl-migration reaction. The azobenzene moiety of the allylsilane was reversibly isomerized by photoirradiation. The (*Z*)-**7a** formed by photoirradiation of (*E*)-**7a** is in a tetracoordinate state in contrast to the (*E*)-**7a**, and it did not react with a fluoride ion at all under the conditions where (*E*)-**7a** reacted quantitatively. The reactivity was successfully controlled without changing any conditions other than the change of the coordination number of the silicon atom induced by photoirradiation.

Keywords: Azobenzene; Allylsilanes; Highly coordinate silicon compounds

1. Introduction

Reactions of allylsilanes with electrophiles result in both cleavage of the Si–C(allyl) bond and bond formation between carbon(allyl) and electrophiles [1]. The reactions of allylsilanes with imines and carbonyl compounds such as aldehydes, ketones and acid chlorides have been enthusiastically investigated. Penta- or hexacoordinate allylsilicon compounds work as reactive allylation reagents, because highly coordinate organosilicon compounds are known to exhibit higher nucleophilicity than those of ordinary organosilicon compounds with a tetracoordinate silicon atom (Chart 1) [2–4]. If the coordination number of the silicon atom of an allylsilane can be reversibly controlled by external stimuli such as light, with neither influencing the reaction conditions nor adding external reagents to the reaction system, the reactivities of the allylsilane can be altered by such stimuli. An azobenzene has been known as one of the photoswitching molecules, which change the structures and properties by photoirradiation. We have reported the synthesis and properties of azobenzenes bearing heteroatoms such as boron [5], silicon [6] and phosphorus [7] at the 2-position, and they feature the intramolecular coordination of the azo group to the silicon and the boron atom, or the nucleophilic addition of the phosphorus on the nitrogen atom. The nitrogen-heteroatom bonds induce large changes in properties and reactivities from unsubstituted azobenzene. The coordination numbers of the heteroatoms were successfully changed by photoirradiation of the azo group. Although a reversible change of the coordination number of silicon in response to heat and solvent had already been reported in some organosilicon compounds by taking advantage of equilibrated dissociation [8–10], this change was not applied to switching of the reactivities. Recently, the change of the coordination number of a silicon atom induced by photoirradiation was reported, but it was irreversible [11]. We previously reported the reactivity control of an allylsilane bearing a 2-(phenylazo)phenyl group by photoswitching

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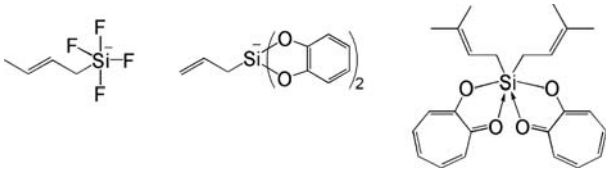


Chart 1. Highly coordinate allylsilanes.

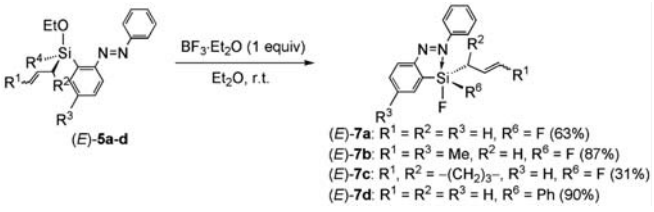
of the coordination number of the silicon atom in a preliminary communication [12]. In this paper, we report full details of the synthesis, structures and reactivities of various allylsilanes bearing a 2-(phenylazo)phenyl group and the change of the reactivity by switching of the coordination number of the silicon atom between four and five induced by photoirradiation. We also report the allylation reactions of azo compounds.

2. Results and discussion

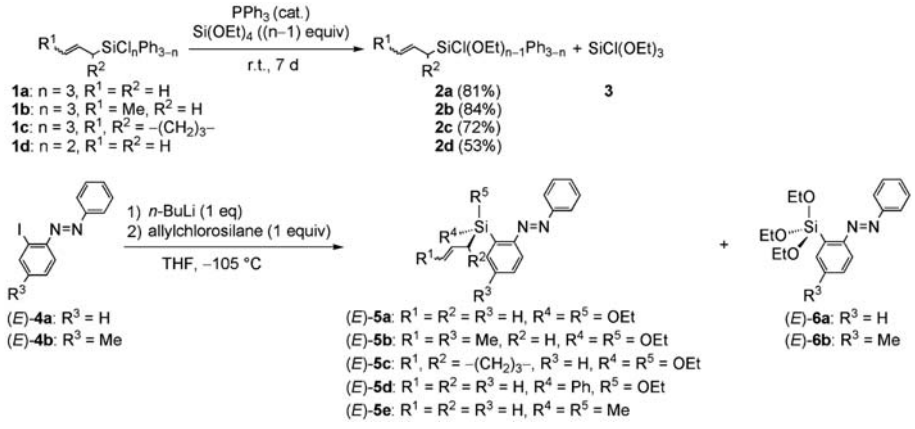
2.1. Synthesis

Allylsilanes bearing fluorine atoms besides an azobenzene moiety were selected as target molecules because the high Lewis acidity of the silicon center was required for pentacoordination of the silicon atom. Allylchlorodiethoxysilane (**2a**) was prepared as an inseparable mixture with chlorotriethoxysilane (**3**) by disproportionation of allyltrichlorosilane (**1a**) and tetraethoxysilane (Scheme 1) [13]. Treatment of the mixture with 2-lithioazobenzene gave a mixture of allyldiethoxysilane (*E*)-**5a** (35%) and triethoxysilane (*E*)-**6a** (58%), which were separated by silica gel chromatography (Table 1, entry 1). Fluorination of (*E*)-**5a** with $BF_3 \cdot OEt_2$ afforded allyldifluorosilane (*E*)-**7a** (63%) (Scheme 2). Difluorosilanes (*E*)-**7b** and (*E*)-**7c** bearing a crotyl and a 2-cyclohexenyl group instead of an allyl group, respectively, and allylfluorophenylsilane (*E*)-**7d** were synthesized similarly from (*E*)-**4a**,**b** via (*E*)-**5b**–**d** (Table 1, entries 2–4; Scheme 2). Allyldimethylsilane (*E*)-**5e** was obtained by the reaction of 2-lithioazobenzene with allylchlorodimethylsilane (entry 5). A direct reaction of 2-lithioazobenzene with allyltrichlorosilane gave a complex mixture, and 2-lithioazobenzene did not react with allyltriethoxysilane at all.

Reaction of (*E*)-**7a**–**c** with excess KF in the presence of 18-crown-6 in toluene at room temperature for 5 h followed by addition of water afforded white solids of tetrafluorosilicates **8a**–**c** (69%, 47% and 28%, respectively) (Scheme 3)



Scheme 2.

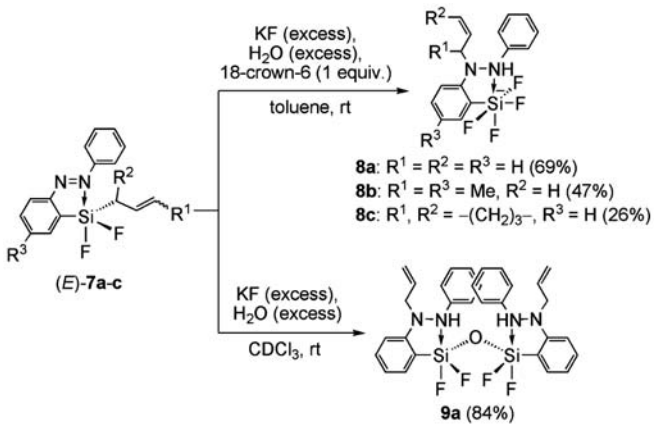


Scheme 1.

Table 1
Synthesis of tetracoordinate allylsilanes (*E*)-**5a**–**e**

Entry	(*E*)-**4**	Allylchlorosilane	Yield of (*E*)-**5** (%)[a]	Yield of (*E*)-**6** (%)[a]
1	(*E*)-**4a**	A 1:2 mixture of **2a** and **3**	(*E*)-**5a** (35)	(*E*)-**6a** (58)
2	(*E*)-**4b**	A 1:2 mixture of **2b** and **3**	(*E*)-**5b** (29)	(*E*)-**6b** (30)
3	(*E*)-**4a**	**2c**	(*E*)-**5c** (40)	–
4	(*E*)-**4a**	**2d**	(*E*)-**5d** (12)	–
5	(*E*)-**4a**	Allylchlorodimethylsilane	(*E*)-**5e** (73)	–

[a] Yields were based on (*E*)-**4a** or **4b**.



Scheme 3.

[12]. Reaction of (*E*)-**7a** with KF without 18-crown-6 in the presence of water in $CDCl_3$ at room temperature for 30 min gave not silicate **8a** but disiloxane **9a** (84%) as a main product [14].

2.2. NMR spectra

In the ^{29}Si NMR spectrum of (*E*)-**7a** in $CDCl_3$ at 20 °C, a triplet coupled with two fluorine nuclei was observed at δ_{Si} −38.5, which shifted up-field by 18 ppm compared with allyldifluorophenylsilane (**10**: δ_{Si} −20.4), indicating that the silicon atom of (*E*)-**7a** is a pentacoordinate structure in the solution state. In contrast, all the chemical shifts of diethoxysilanes (*E*)-**5a–c** ((*E*)-**5a**: δ_{Si} −24.5; (*E*)-**5b**: δ_{Si} −24.6; (*E*)-**5c**: δ_{Si} −24.5) are similar to that of allyldiethoxyphenylsilane (**11**: δ_{Si} −24.4) in $CDCl_3$, indicating that the tetracoordination states. The coupling constant of (*E*)-**7a** ($^1J_{SiF} = 278$ Hz) was smaller than that of **10** ($^1J_{SiF} = 299$ Hz) because one fluorine atom of (*E*)-**7a** should be located at the apical position that has less s-character than usual sp^3 hybridized orbital and two fluorine atoms exchange their positions too fast to be distinguished by the pseudorotation at 20 °C. Crotylsilane (*E*)-**7b** and 2-cyclohexenylsilane (*E*)-**7c**, which showed almost the same chemical shifts and coupling constants in the ^{19}F NMR and ^{29}Si NMR spectra as those of (*E*)-**7a**, are considered to have the similar structures. In the ^{19}F NMR spectrum of (*E*)-**7a**, a singlet at δ_F −140.4 with satellite peaks ($^1J_{SiF} = 278$ Hz) at 20 °C was split into two broad peaks at δ_F −141.27 (1F) and −127.17 (1F) at −90 °C in CD_2Cl_2. Such patterns and chemical shifts, which are similar to those of pentacoordinate 2-(dimethylaminomethyl)phenylsilanes [9,15], indicate nonequivalency of fluorine nuclei due to a trigonal bipyramidal (TBP) geometry around the silicon atom constructed by the coordination of a lone pair of a nitrogen atom of the azo group in the solution state. In the ^{19}F NMR spectrum of (*E*)-**7c**, two doublets were observed at 20 °C due to the nonequivalence of two fluorine atoms caused by a chirality of the carbon atom of the 1-position of the 2-cyclohexenyl group.

In the ^1H NMR spectrum of silicate **8a**, two broad signals of methylene protons of the allyl group were observed at a lower field (δ_H 3.56 (1H), 4.32 (1H)) than the multiplet of (*E*)-**7a** (δ_H 1.87–1.94 (2H)). These signals split into two doublets at −60 °C and all other signals also split similarly due to freezing of the inversion of the nitrogen atom attached to the allyl group. As the temperature raises, the signals become more broadened. In the ^{19}F NMR spectra, one broad signal at 60 °C split into four signals that show the same integral at −60 °C, indicating nonequivalence of four fluorine nuclei due to an octahedral geometry around the silicon atom. Two diastereomers were hardly distinguishable by the ^{19}F NMR spectroscopy. In the ^{29}Si NMR spectrum, signals could not be observed because of its low solubility and multiple coupling patterns.

Tetrafluorodisiloxane **9a** bearing two hydrazobenzene moieties showed the similar signals to **8a** in the ^1H NMR spectrum. In the ^{19}F NMR spectrum, **9a** showed one singlet (δ_F −136.78) at 60 °C, which split into two sets (1:1) of two doublets at −60 °C. Although four diastereomers should be observed separately in principle by freezing of both the pseudorotation around the silicon atom and the inversion at the nitrogen atoms, the signals due to two diastereomers were observed, suggesting that the circumstance of the two silicon atoms separated through two Si–O bonds was almost same and two silicon atoms could not be distinguished from each other. In the ^{29}Si NMR spectrum, **9a** showed one triplet (δ_{Si} −87.3 ($^1J_{Si-F} = 231.3$ Hz)), whose chemical shift and coupling constant are almost the same as those of pentacoordinate 1,1,3,3-tetrafluoro-1,3-bis[2-(phenylazo)phenyl]-disiloxane (δ_{Si} −88.0 ($^1J_{Si-F} = 233.2$ Hz)) [6c]. These spectral results suggest the formation of disiloxane **9a** despite failure of its isolation by the decomposition.

2.3. UV/Vis spectra

In the UV/Vis spectra of (*E*)-**7a** in $CHCl_3$, an absorption maximum (π–π*) was observed at 339 nm. In the UV/Vis spectra of (*E*)-**5a** and (*E*)-**5c** in $CHCl_3$, two absorption maxima were observed ((*E*)-**5a**; 324, 444 nm, (*E*)-**5c**; 324, 448 nm), which were almost the same as those of absorption maxima ascribed to the π–π* (320 nm) and n–π* (440 nm) transitions of unsubstituted azobenzene, respectively. Conversely, (*E*)-**7a** and (*E*)-**7c** showed only one red-shifted π–π* absorption maximum ((*E*)-**7a**; 339 nm, (*E*)-**7c**; 338 nm) due to π–π* transitions in the region over 300 nm, suggesting the perturbation of the electronic structure of the azo moiety. All the other azobenzenes coordinating to silicon atoms showed similar red shifts of the π–π* transitions of the azo groups [6].

2.4. X-ray crystallographic analyses

The pentacoordinate state of the silicon atom of (*E*)-**7a** in the crystalline state was clearly revealed by the X-ray crystallographic analysis (Fig. 1). The N2 atom of the azo moiety is directed to the Si1 atom despite the steric repul-

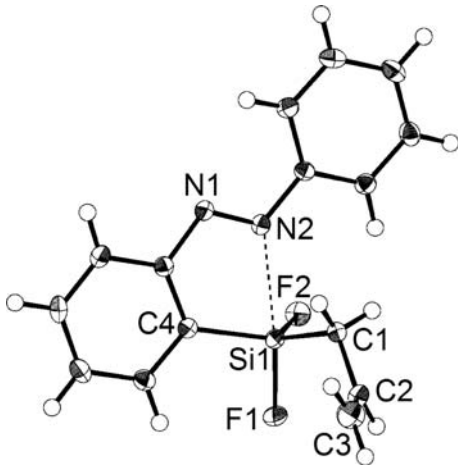


Fig. 1. ORTEP drawing of (*E*)-**7a** with thermal ellipsoid plots (50% probability).

Table 2
Selected bond lengths (Å) and angles (°) of (*E*)-**7a**

Bond lengths (Å)			
Si1···N2	2.389(2)	Si1–C4	1.858(2)
Si1–F1	1.622(2)	C1–C2	1.499(2)
Si1–F2	1.595(2)	C2–C3	1.308(3)
Si1–C1	1.864(2)	N1–N2	1.261(2)
Bond angles (°)			
F1–Si1–F2	97.29(7)	N2···Si1–F1	172.02(5)
F1–Si1–C1	102.89(7)	N2···Si1–F2	80.72(6)
F1–Si1–C4	99.83(7)	N2···Si1–C1	84.89(7)
F2–Si1–C1	115.35(8)	N2···Si1–C4	74.58(7)
F2–Si1–C4	117.79(7)	Si1–C1–C2	114.18(12)
C1–Si1–C4	117.99(8)	C1–C2–C3	125.46(18)

sion of a bulky silyl group. The intramolecular N2···Si1 distance (2.389(2) Å), which is almost similar to those of difluorophenyl[2-(phenylazo)phenyl]silane (2.419(2) Å) [6d] and difluoro[2-(dimethylaminomethyl)phenyl](methyl) silane (2.346(3) Å) [16], is much shorter than the sum of the corresponding van der Waals radii (3.65 Å) (Table 2). The crystal structure of (*E*)-**7a** is most likely interpreted as a distorted TBP structure with N2 and F1 atoms at apical positions and C1, C4, and F2 atoms at equatorial positions. The pentacoordination characters, $\%TBP_a$ and $\%TBP_e$ are defined by Eqs. (1) and (2), where θ_n and φ_n are the angles L_{ap}–Si–L_{eq} and L_{eq}–Si–L_{eq}, respectively [17]. For the pentacoordination characters of Si1 atom, L_{ap} is F1 atom and L_{eq} are C1, C4 and F2 atoms. For (*E*)-**7a**, $\%TBP_a$ and $\%TBP_e$ are 49% and 72%, respectively. These values are the almost same as those of difluorophenyl[2-(phenylazo)phenyl]silane (48% and 71%, respectively).

$$\%TBP_a = \left\{109.5^\circ - \frac{1}{3}\left(\sum_{n=1}^{3}\theta_n\right)\right\} \Big/ 109.5^\circ - 90^\circ \times 100 \quad (1)$$

$$\%TBP_e = \left\{\frac{1}{3}\left(\sum_{n=1}^{3}\varphi_n\right) - 109.5^\circ\right\} \Big/ 120^\circ - 109.5^\circ \times 100 \quad (2)$$

The octahedral structures of **8a** and **8b** with a hexacoordinate silicon atom were determined by X-ray crystallographic analyses (Fig. 2). The bond angles around the silicon atoms are almost 90° (Table 3). The intramolecular N2···Si1 distances (**8a**: 2.167(2) Å; **8b**: 2.211(3) Å) are very short for a dative N-Si bond and similar to those of tetrafluoro[2-(phenylazo)phenyl]silicate (2.257(3) Å) [6b] and tetrafluoro[8-(dimethylamino)naphthyl]silicate (2.213(6) Å) [18]. The similar compounds bearing hydrazinophenyl groups as intramolecular ligands, diethoxybis[2-(*N*,*N*,*N*′-trimethylhydrazino)phenyl]silane and dichloro[2-(dimethylaminomethyl)phenyl][2-(*N*,*N*,*N*′-trimethylhydrazino)phenyl]-silane show fairly longer N···Si interatomic distances (2.687(2), 2.772(2) and 2.564(2) Å, respectively) [19] than **8a** and **8b**.

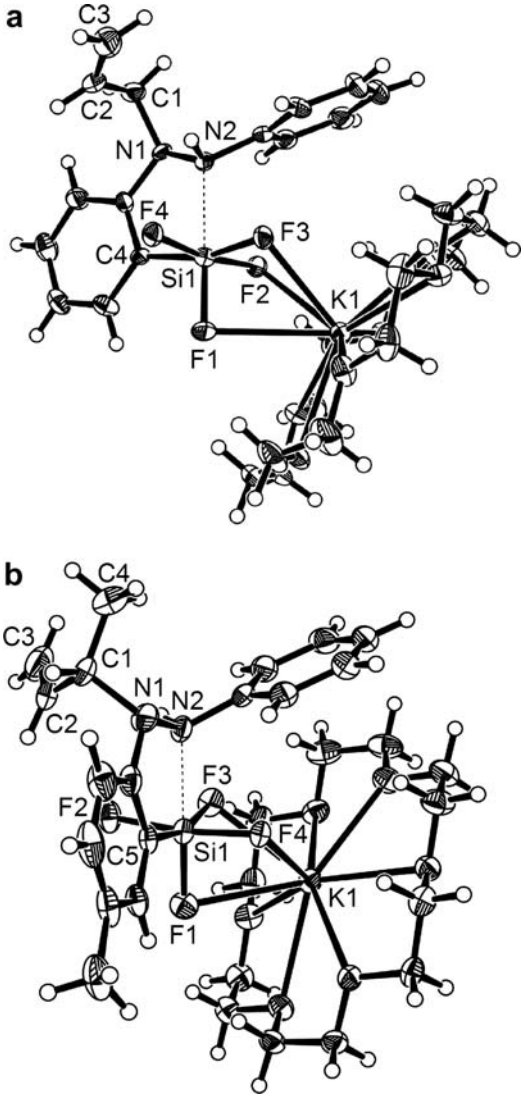


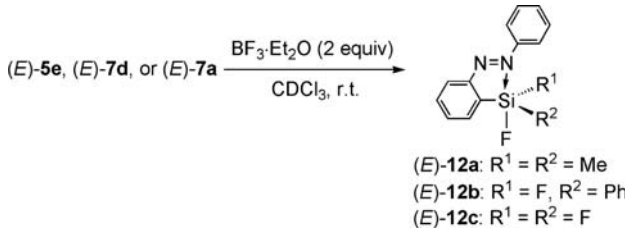
Fig. 2. ORTEP drawings of **8a** (a) and **8b** (b) with thermal ellipsoid plots (50% probability).

Table 3
Selected bond lengths (Å) and angles (°) of **8a** and **8b**

*Compound **8a***			
Bond lengths (Å)			
Si1···N2	2.164(2)	Si1–C4	1.898(2)
Si1–F1	1.647(2)	N1–N2	1.441(2)
Si1–F2	1.682(2)	N1–C1	1.479(2)
Si1–F3	1.676(2)	C1–C2	1.497(3)
Si1–F4	1.701(2)	C2–C3	1.313(3)
Bond angles (°)			
F1–Si1–F2	94.25(6)	F4–Si1–C4	89.31(7)
F1–Si1–F3	94.57(6)	N2···Si1–F1	178.37(6)
F1–Si1–F4	94.58(6)	N2···Si1–F2	87.13(6)
F1–Si1–C4	100.14(7)	N2···Si1–F3	84.59(6)
F2–Si1–F3	88.39(6)	N2···Si1–F4	84.00(6)
F2–Si1–F4	170.54(6)	N2···Si1–C4	80.65(7)
F2–Si1–C4	92.49(7)	N1–C1–C2	112.66(15)
F3–Si1–F4	87.51(6)	C1–C2–C3	123.6(2)
F3–Si1–C4	165.15(7)		
*Compound **8b***			
Bond lengths (Å)			
Si1···N2	2.211(3)	N1–N2	1.434(4)
Si1–F1	1.642(2)	N1–C1	1.507(5)
Si1–F2	1.692(2)	C1–C2	1.528(7)
Si1–F3	1.662(2)	C2–C3	1.383(7)
Si1–F4	1.682(2)	C1–C4	1.526(6)
Si1–C5	1.897(3)		
Bond angles (°)			
F1–Si1–F2	94.58(11)	F4–Si1–C5	92.34(12)
F1–Si1–F3	96.08(10)	N2···Si1–F1	178.60(11)
F1–Si1–F4	93.41(10)	N2···Si1–F2	84.28(11)
F1–Si1–C5	101.11(13)	N2···Si1–F3	83.07(10)
F2–Si1–F3	87.33(10)	N2···Si1–F4	87.67(10)
F2–Si1–F4	171.23(11)	N2···Si1–C5	79.71(13)
F2–Si1–C5	89.66(12)	N1–C1–C2	110.9(4)
F3–Si1–F4	88.25(10)	C1–C2–C3	126.8(5)
F3–Si1–C5	162.73(13)		

2.5. Reactions with $BF_3 \cdot OEt_2$

The allylation reaction upon using an allylsilane needs a catalyst such as a Lewis acid, a Lewis base or both of them. Upon using a Lewis acid as a catalyst, an allylsilane bearing electron-donating groups such as a methyl group is more reactive than that bearing electron-withdrawing groups such as a fluorine atom [20]. Reactions of allylsilanes bearing an azobenzene moiety with $BF_3 \cdot OEt_2$ were examined to investigate their reactivities as an allylation reagent. In the reaction of (*E*)-**5e** with $BF_3 \cdot OEt_2$ in $CDCl_3$ at room temperature for 1 h, the allyl group was eliminated to give fluorodimethylsilane (*E*)-**12a** quantitatively (Scheme 4, Table 4, entry 1) [6d,14]. Allyltrifluoroborate as a by-product was observed in the ^1H, ^{11}B and ^{19}F NMR spectra. Allylfluorosilane (*E*)-**7d** hardly reacted with $BF_3 \cdot OEt_2$ under the same conditions (entry 2), however, the reaction was continued for 24 h to give difluorosilane (*E*)-**12b** quantitatively (entry 3) [6d]. Treatment of allyldifluorosilane (*E*)-**7a** with $BF_3 \cdot OEt_2$ for 48 h resulted in no reaction (entry 4). The reactions of tetracoordinate allylsilanes with electrophiles proceed less efficiently as the silyl groups are more electronegative because of a decreased β effect of electronegative silyl groups [1,21]. Contrary, highly coordinate allylsilanes have high reactivity toward electrophiles even if the silyl groups have electronegative substituents [20]. Allylsilanes bearing an azo group showed reactivities similar to tetracoordinate allylsilanes despite pentacoordination states of (*E*)-**7a** and (*E*)-**7d**, indicating that the coordination of the azo group is not strong enough to make the allyl group active despite the pentacoordinate silicon atom.



Scheme 4.

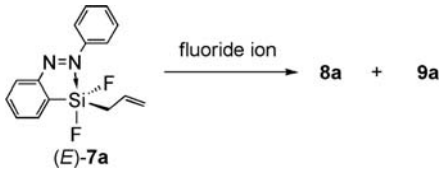
Table 4
Reaction of allylsilanes (*E*)-**5e**, (*E*)-**7d** and (*E*)-**7a** with $BF_3 \cdot OEt_2$

Entry	Allylsilane	Reaction time (h)	Product	Yield (%)
1	(*E*)-**5e**	1	(*E*)-**12a**	Quantitative
2	(*E*)-**7d**	2	(*E*)-**12b**	10
3	(*E*)-**7d**	24	(*E*)-**12b**	Quantitative
4	(*E*)-**7a**	48	(*E*)-**12c**	0

Contrary to the reactions with $BF_3 \cdot OEt_2$, neither tetracoordinate allylsilane (*E*)-**5a** nor (*E*)-**5e** reacted with a fluoride ion. The reaction mechanism of the allylation reaction catalyzed by a Lewis base is much different from that of the allylation using Lewis acid and thought to proceed via the highly coordinate allylsilanes. The silicon atom of allylsilanes needs to have very electronegative substituents to form a high coordinate state in the reaction with a Lewis base, and their reactivities catalyzed by a Lewis base become higher as the number of electron-withdrawing groups on the silicon atom increases in contrast to the reactions catalyzed by a Lewis acid [22]. Electron-donating substituents such as methyl group and less electron-withdrawing ones such as ethoxy groups could not make the silicon atom electronegative enough to react with a fluoride ion.

2.6. Reaction mechanisms of allylation of azobenzenes

As shown in Scheme 3, the reaction of (*E*)-**7a** with excess KF in the presence of 18-crown-6 in toluene at room temperature for 5 h in the presence of water afforded colorless solid of tetrafluorosilicate **8a** (69%, Scheme 5, Table 5, entry 1) [12]. A similar reaction in benzene-d_6 in the presence of water at room temperature for 30 min gave 98% yield of **8a** (entry 2). The yield is higher than that in $CDCl_3$ (82%) despite the shorter reaction time, 10 min (entry 3).



Scheme 5.

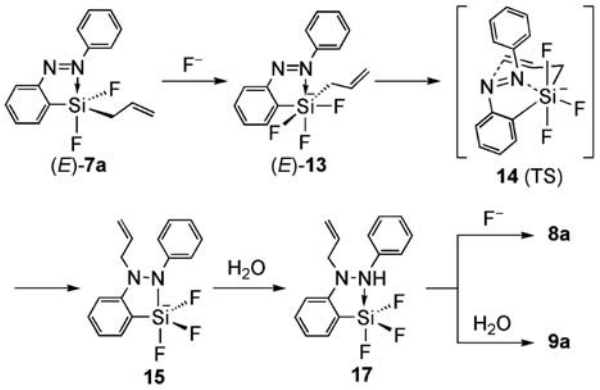
Monitoring the reaction in both benzene-d_6 and $CDCl_3$ by UV/Vis spectroscopy revealed complete disappearance of the absorbance due to the azo unit, indicating that the migration of the allyl group from the silicon to the nitrogen atom proceeded completely in both solutions. The lower yield of **8a** in the reaction in $CDCl_3$ is most reasonably explained by hydrolysis of intermediates. The yield rose up to 96% in $CDCl_3$ upon using tetrabutylammonium fluoride (TBAF) instead of KF and 18-crown-6 because of higher nucleophilicity of TBAF than KF and 18-crown-6 (entry 4). These results lead to a speculation that hydrolysis takes priority over fluorination when a less nucleophilic fluoride source was used. The reaction under an absolute condition resulted in a complex mixture, but the complete allyl-migration was confirmed by UV/Vis spectroscopy (entry 5). Water is needed not for allyl-migration but for quenching. Reaction of (*E*)-**7a** with KF without 18-crown-6 in the presence of water in benzene-d_6 or $CDCl_3$ at room temperature for 30 min gave not silicate **8a** but disiloxane **9a** as a main product (89% or 84%, respectively, entries 6 and 7).

The formation mechanisms of **8a** and **9a** are described as follows: the silicon atom of (*E*)-**7a** is fluorinated by a fluoride ion to generate intermediary silicate (*E*)-**13**. The nitrogen of (*E*)-**13** is allylated to give **15** via six-membered ring transition state **14** similarly to the intramolecular allylation of allylsilanes bearing tropolonato ligands (Scheme 6) [4]. Aminosilicate **15**, which has a polar Si–N bond, gives a complex mixture via the cleavage of the Si–N bond in the absence of water. When there is water in the reaction mixture, protonation at the nitrogen of **15** with water proceeds faster than the decomposition. Additional fluorination at the silicon of trifluorosilane **17** with a fluoride ion resulted in the formation of **8a**, or hydrolysis of **17** succeeded by dehydrative condensation gave **9a**. Trifluorosilane (*E*)-**12c** bearing an azo group showed similar reactivity for the formation of silicate and disiloxane [6b–d].

Table 5
Intramolecular allylation reactions of (*E*)-**7a** with a fluoride ion[a]

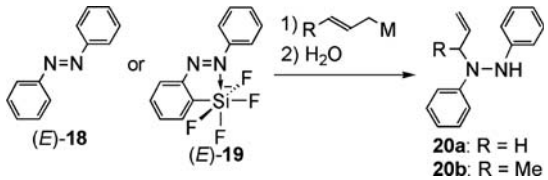
Entry	Fluoride sources	Additive	Solvent	Product	Yield (%)
1	KF, 18-crown-6	Water	Toluene	**8a**	69[b]
2	KF, 18-crown-6	Water	C_6D_6	**8a**	98[c]
3	KF, 18-crown-6	Water	$CDCl_3$	**8a**	82[c]
4	$^nBu_4N^+F^-$	Water	$CDCl_3$	**8a**	96[c]
5	KF, 18-crown-6	None	$CDCl_3$	Complex mixture	–
6	KF	Water	C_6D_6	**9a**	89[c]
7	KF	Water	$CDCl_3$	**9a**	84[c]

[a] Excess KF and water and an excess of 18-crown-6 was used at room temperature.
[b] An isolated yield.
[c] Yields were estimated by ^1H and ^{19}F NMR spectra after 30 min at room temperature.



Scheme 6.

Intermolecular allylation reactions of aldehydes and imines with allyltrifluorosilane and a fluoride ion were reported to proceed in good yields under mild conditions [4], and allylation of azobenzene with allylmagnesium chloride [23] is also known. The modified reaction of azobenzene with allylmagnesium chloride as well as intermolecular allylation using in situ generated cesium allyl- and crotylsilicates from the corresponding allyl and crotylsilane and CsF were carried out and the results are summarized in Scheme 7 and Table 6. The intermolecular allylation of azobenzene with allylmagnesium chloride proceeded under the mild condition (entry 1), but similar allylation of azobenzene with crotyltrifluorosilane and cesium fluoride did not proceed at all even under the stronger condition (entry 2). The nucleophilicity of a crotyl group in the crotylsilicates is considered to be low for the allylation of azobenzene. The reaction needs activation of not only the nucleophilicity of the allyl group but also the electrophilicity of the azo group by coordination of the azo group to the silicon atom similarly to the activation of carbonyl compounds. The importance of this activation was further revealed by the following experiments: allylation of hexacoordinate potassium (*E*)-tetrafluorosilicate (*E*)-**19** with the crotylsilicate from crotyltrifluorosilane and CsF in refluxing THF for 24 h and successive hydrolysis yielded *N*-(1-methyl-2-propenyl)hydrazobenzene **20b** (59%) (entry 4). The similar reactions using allyldifluorophenylsilane and CsF proceeded (entries 5 and 6). It was found that



Scheme 7.

Table 6
Intermolecular allylation reactions of azobenzenes with allyl and crotyl reagents

Entry	Azobenzene	Allylmetal compound	Condition	Product	Yield (%)
1	(*E*)-**18**	AllylMgCl	0 °C, 1 h	**20a**	89
2	(*E*)-**18**	$CrotylSiF_3$, CsF	70 °C, 4 days	No reaction	–
3	(*E*)-**19**	$CrotylSiF_3$, CsF	r.t., 60 h	**20b**	17
4	(*E*)-**19**	$CrotylSiF_3$, CsF	70 °C, 24 h	**20b**	59
5	(*E*)-**19**	$AllylSiPhF_2$, CsF	r.t., 60 h	No reaction	–
6	(*E*)-**19**	$AllylSiPhF_2$, CsF	70 °C, 24 h	**20a**	36

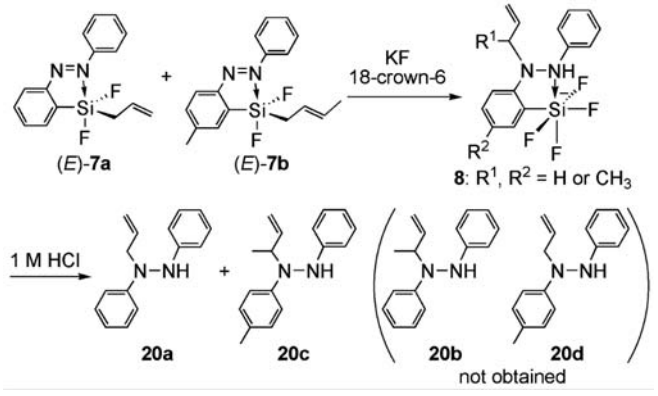
intermolecular allylation of azo group proceeds when both allyl and azo groups were activated.

As described above, the formation of **8b** from crotyldifluorosilane (*E*)-**7b** reveals that the allylic rearrangement reaction proceeds regiospecifically at the γ-position of its allyl group. A crossover experiment using a mixture of (*E*)-**7a** and (*E*)-**7b** yielded an inseparable mixture of silicates **8a** and **8b** (Scheme 8), which was hydrolyzed by aqueous HCl to give only hydrazobenzenes **20a** and **20c**. Formation of **20a** and **20c** was confirmed by mass spectroscopy and that of **20b** and **20d** was not. This result shows the intramolecular allylation of an azo group via the six-membered ring transition state where the carbon atom at the γ-position of the allyl group has to approach the intramolecular nitrogen atom. It is interesting that the similar silicate **8c** was formed under the same condition though a 2-cyclohexenyl group of (*E*)-**7c** appears to be difficult to approach intramolecularly to nitrogen atom due to the rigid cyclic structure.

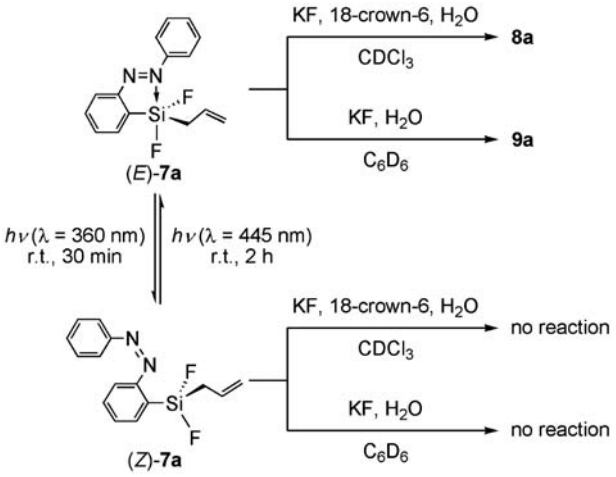
Reactions of (*E*)-**7d** with a fluoride ion were monitored by ^1H and ^{19}F NMR and UV/Vis spectroscopy. Allylfluorosilane (*E*)-**7d** immediately reacted with TBAF to show no absorption of the azo group in the UV/Vis spectra due to the conversion to the hydrazobenzene. Compound (*E*)-**7d** disappeared more slowly in the reaction with KF and 18-crown-6, and the intramolecular allylation of (*E*)-**7d** hardly proceeded upon using KF without 18-crown-6 while allyldifluorosilane (*E*)-**7a** reacted more easily with these fluoride sources. Monofluorosilane (*E*)-**7d** is less electronegative than difluorosilane (*E*)-**7a** because the latter has less number of fluorine atoms. Unfortunately, reaction products have not been identified.

2.7. Photoisomerization

Isomerization of (*E*)-**7a** to (*Z*)-**7a** in $CDCl_3$ was carried out quantitatively by irradiation ($\lambda = 360$ nm) for 40 min (Scheme 9) [12]. The solution of (*Z*)-**7a** showed its absorption maximum (n–π^*) at 443 nm. Irradiation ($\lambda = 445$ nm) of the solution of (*Z*)-**7a** at room temperature for 2 h caused regeneration of (*E*)-**7a** (72%). Compound (*Z*)-**7a** was thermally isomerized to (*E*)-**7a** quantitatively in $CDCl_3$ after 11 days, during which it was maintained at room temperature in the dark. In the ^{29}Si NMR spectrum of (*Z*)-**7a** in $CDCl_3$ at −70 °C, a triplet ($^1J_{SiF} = 299$ Hz) was observed at δ_{Si} −20.0, which significantly shifted downfield compared to (*E*)-**7a**, suggesting that (*Z*)-**7a** possessed a tetracoordinate silicon atom without Si···N interaction. The absence of the coordination due to the configuration of the lone pair of the nitrogen atom, which is far from the silicon atom, is responsible for these spectral features of (*Z*)-**7a**. Conversely, no change was observed on treatment of (*Z*)-**7a** with excess KF in the presence of 18-crown-6 in $CDCl_3$ and upon standing at room temperature for 30 min in the dark, which is in contrast to the case of (*E*)-**7a**. Silicate **8a** was obtained in 36% yield after a period of 2 days. However, photoirradiation ($\lambda = 445$ nm) of tetracoordinate (*Z*)-**7a** with an excess amount of KF in the



Scheme 8.



Scheme 9.

presence of water and 18-crown-6 in $CDCl_3$ at room temperature for 30 min gave 91% yield of **8a** [12]. Isomerization of (*Z*)-**7a** to (*E*)-**7a** and the successive formation of **8a** should have occurred instead of direct formation of **8a** from (*Z*)-**7a**. These results clearly illustrate the change in the reactivities of **7a** induced by photoirradiation. Contrary to the behavior of (*E*)-**7a**, neither allyldifluorophenylsilane nor (*Z*)-**7a** reacted with a fluoride ion under the same reaction conditions. The tetracoordinate state of (*Z*)-**7a** is obviously responsible for the reluctant reactivities. Differences in the reactivity of (*E*)-**7a** and (*Z*)-**7a** toward a fluoride ion also indicate the importance of activation of the azo moiety induced by coordination to silicon in the *N*-allylation of the azo group. Similarly, (*Z*)-**7a** did not react with KF in the presence of water either in $CDCl_3$ with 18-crown-6 nor in benzene-d_6 without 18-crown-6 at room temperature for 30 min at all, while photoirradiation ($\lambda = 445$ nm) of the reaction mixture gave **8a** and **9a**, respectively, as well as (*E*)-**7a** did.

3. Conclusion

To summarize, we have achieved control of a series of reactions yielding silicate **8a** from allylsilane (*E*)-**7a** based on change of the coordination number of the silicon atom induced by photoirradiation. To promote the reaction, it is important that both the nucleophilic and electrophilic parts are activated by the Si···N interaction. More than one fluorine substituent is needed for the reaction with a fluoride ion, which causes the high nucleophilicity of an allyl group. In addition, the coordination of an azo group to silicon is needed to increase the electrophilicity of the azo group. The photoswitching of the Si···N interaction caused the photocontrol of an intramolecular allylation of the azo group. Such a type of reaction control can lead to new ways of starting or stopping a reaction without changing any other conditions that are suitable for the promotion of a certain reaction.

4. Experimental

All melting points are uncorrected. THF and ether were purified before use by reported methods. $CDCl_3$ and C_6D_6 were purchased from Wako Pure Chemical Industries and used without purification in most experiments. In the experiment without water as an additive (Table 5, entry 5), $CDCl_3$ was distilled from CaH_2 and further purified by using vacuum transfer technique from molecular sieves 4A. All reactions were carried out under argon atmosphere unless otherwise noted. The ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz), ^{29}Si NMR (99 MHz) spectra were measured with a JEOL A500 spectrometer using tetramethylsilane (TMS) as an internal standard. The ^{19}F NMR (254 MHz) spectra were taken with a JEOL EXcalibur270 spectrometer using Fleon® as an external standard. High-pressure liquid chromatography (HPLC) was performed by LC-918 with JAIGEL 1H and 2H columns (Japan Analytical Industry) with chloroform as the solvent. Elemental analyses were performed by the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo.

4.1. Preparation of allylchlorodiethoxysilane

A mixture of allyltrichlorosilane (3.8 g, 21 mmol), tetraethoxysilane (9.3 mL, 46 mmol) and triphenylphosphine (20 mg, 0.076 mmol) was stirred at room temperature for 7 days and distilled to give colorless liquid of a 1:2 mixture of allylchlorodiethoxysilane (**2a**) and chlorotriethoxysilane (10.1 g, 81%). The mixture was used in the following reaction without further purification. **2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (t, $^3J = 7.5$ Hz, 6H), 1.84 (dt, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 2H), 3.81 (q, $^3J = 7.5$ Hz, 4H), 4.96–5.07 (m, 2H), 5.69–5.82 (m, 1H). **2b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (t, $^3J = 7.5$ Hz, 6H), 1.65 (d, $^3J = 7.5$ Hz, 3H), 1.97 (d, $^3J = 7.5$ Hz, 2H), 3.82 (q, $^3J = 7.5$ Hz, 4H), 5.33–5.54 (m, 2H). **2c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, $^3J = 7.5$ Hz, 6H), 1.49–1.56 (m, 1H), 1.67–1.83 (m, 3H), 1.92–2.06 (m, 2H), 3.70–3.87 (m, 4H), 5.66–5.77 (m, 2H). **2d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, $^3J = 7.5$ Hz, 3H), 1.80 (d, $^3J = 7.5$ Hz, 2H), 3.80 (q, $^3J = 7.5$ Hz, 2H), 4.93–5.06 (m, 2H), 5.64–5.82 (m, 1H), 7.30–7.56 (m, 5H).

4.2. Synthesis of (*E*)-allyldiethoxy[2-(phenylazo)phenyl]silane ((*E*)-**5a**–**d**)

To a THF solution (80 mL) of 2-lithioazobenzene, which was prepared from 2-iodoazobenzene [24] (4.00 g, 12.9 mmol) and *n*-BuLi (1.62 M in hexane, 8.10 mL, 13.1 mmol) at −105 °C, a mixture of **2a** and chlorotriethoxysilane (2.8 mL, 13 mmol) was added. After the reaction mixture was stirred at −105 °C for 15 min and further at 0 °C for 22 h, the solvent was evaporated from the reaction mixture. The residue was dissolved in hexane, filtrated, and separated with silica gel column chromato- graphy to give a red oil of (*E*)-allyldiethoxy[2-(phenylazo)phenyl]silane ((*E*)-**5a**) (1.54 g, 35%) together with (*E*)-triethoxy[2-(phenylazo)phenyl]silane ((*E*)-**6a**) (2.52 g, 58%). (*E*)-**5a**: red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (t, $^3J = 7.0$ Hz, 6H), 2.01 (dt, $^3J = 7.0$ Hz, $^4J = 1.5$ Hz, 2H), 3.77–3.93 (m, 4H), 4.74 (dt, $^3J = 10.4$ Hz, $^4J = 1.5$ Hz, 1H), 4.82 (dt, $^3J = 17.2$ Hz, $^4J = 1.5$ Hz, 1H), 5.72 (ddt, $^3J = 17.2$ Hz, $^3J = 10.4$ Hz, $^3J = 7.0$ Hz, 1H), 7.42–7.55 (m, 5H), 7.80 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 7.97 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.23 (*C*H$_3$), 22.79 (*C*H$_2$), 58.74 (*C*H$_2$), 114.39 (*C*H$_2$), 114.93 (*C*H), 122.28 (*C*H), 128.78 (*C*H), 129.96 (*C*H), 130.28 (*C*H), 131.10 (*C*H), 133.08 (*C*H), 134.68 (*C*Si), 136.84 (*C*H), 152.50 (*C*N), 157.18 (*C*N); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −24.46 (s). Anal. Calc. for $C_{19}H_{24}N_2O_2Si$: C, 67.02; H, 7.10; N, 8.23. Found: C, 66.79; H, 7.12; N, 8.13%. (*E*)-**6b**: red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (t, $^3J =$

7.0 Hz, 9H), 2.26 (s, 3H), 3.84 (q, $^3J = 7.0$ Hz, 6H), 7.34 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 7.45 (tt, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 7.51 (t, $^3J = 7.5$ Hz, 2H), 7.74 (d, $^3J = 7.5$ Hz, 1H), 7.80 (d, $^4J = 1.5$ Hz, 1H), 7.99 (d, $^3J = 7.5$ Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 18.12 (*C*H_3), 21.47 (*C*H_3), 58.57 (O*C*H_2), 114.69 (*C*H), 123.23 (*C*H), 128.98 (*C*H), 130.71 (*C*H), 132.12 (*C*H), 132.84 (*C*Si), 137.88 (*C*H), 140.66 (*C*Me), 152.60 (*C*N), 155.48 (*C*N); ^{29}Si NMR (99 MHz, $CDCl_3$) δ 59.07 (s). Anal. Calc. for $C_{19}H_{26}N_2O_3Si$: C, 63.65; H, 7.31; N, 7.81. Found: C, 63.59; H, 7.26; N, 7.71. (*E*)-**5b**: red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (t, $^3J = 7.0$ Hz, 6H), 1.46 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 3H), 1.90 (d, $^3J = 7.5$ Hz, 2H), 2.40 (s, 3H), 3.77–3.93 (m, 4H), 5.20 (qd, $^3J = 15.0$ Hz, $^3J = 7.5$ Hz, 1H), 5.32 (qtd, $^3J = 15.0$ Hz, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 7.34 (td, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 7.46 (t, $^3J = 7.5$ Hz, 1H), 7.52 (t, $^3J = 7.5$ Hz, 2H), 7.76 (d, $^3J = 7.5$ Hz, 1H), 7.79 (t, $^4J = 1.5$ Hz, 1H), 7.98 (d, $^3J = 7.5$ Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 17.97 (*C*H_3), 18.25 (*C*H_3), 20.94 (CH=CH*C*H_2), 58.69 (O*C*H_2), 114.69 (*C*H), 123.18 (*C*H), 124.79 (*C*H), 124.90 (*C*H), 129.05 (*C*H), 130.68 (*C*H), 131.80 (*C*H), 135.15 (*C*Si), 137.20 (*C*H), 140.59 (*C*Me), 152.57 (*C*N), 155.73 (*C*N); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −24.55 (s). Anal. Calc. for $C_{21}H_{28}N_2O_2Si$: C, 68.44; H, 7.66; N, 7.60. Found: C, 68.38; H, 7.69; N, 7.40%. (*E*)-**5c**: red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (t, $^3J = 7.0$ Hz, 3H), 1.27 (t, $^3J = 7.0$ Hz, 3H), 1.40–1.47 (m, 1H), 1.64–1.76 (m, 3H), 1.93–1.98 (m, 2H), 2.15–2.21 (m, 1H), 3.84–3.87 (m, 2H), 3.91–3.98 (m, 2H), 5.58–5.63 (m, 1H), 5.87–5.92 (m, 1H), 7.47–7.57 (m, 5H), 7.85 (d, $^3J = 7.5$ Hz, 1H), 8.02 (d, $^3J = 7.8$ Hz, 2H), 8.06 (d, $^3J = 7.5$ Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 8.28 (*C*H_3), 18.41 (*C*H_3), 22.27 (*C*H_2), 22.90 (*C*H_2), 25.02 (*C*H_2), 26.24 (*C*H), 58.89 (O*C*H_2), 59.02 (O*C*H_2), 114.55 (*C*H), 123.42 (*C*H), 125.68 (*C*H), 126.91 (*C*H), 129.13 (*C*H), 130.92 (*C*H), 131.01 (*C*H), 131.04 (*C*H), 135.12 (*C*Si), 137.23 (*C*H), 152.58 (*C*N), 157.31 (*C*N); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −24.53 (s); UV/Vis ($CHCl_3$) λ_{max} (ε) 324 (1.9×0^4), 448 nm (1.0×0^4). Anal. Calc. for $C_{22}H_{28}N_2O_2Si$: C, 69.43; H, 7.42; N, 7.36. Found: C, 69.44; H, 7.45; N, 7.12%. (*E*)-**5d**: red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (t, $J = 7.5$ Hz, 3H), 2.19 (dd, $J = 13.0$ Hz, $J = 8.0$ Hz, 1H), 2.29 (dd, $J = 13.0$ Hz, $J = 8.0$ Hz, 1H), 3.80 (q, $J = 7.5$ Hz, 2H), 4.76 (d, $J = 10.7$ Hz, 1H), 4.82 (d, $J = 16.7$ Hz, 1H), 5.77 (ddt, $J = 16.7$ Hz, $J = 10.7$ Hz, $J = 8.0$ Hz, 1H), 7.26–7.32 (m, 4H), 7.33–7.35 (m, 2H), 7.45–7.49 (m, 3H), 7.52–7.56 (m, 3H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 7.5$ Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 8.31 (*C*H_3), 23.42 (*C*H_2), 59.34 (*C*H_2), 114.36 (*C*H_2), 116.08 (*C*H), 122.97 (*C*H), 127.54 (*C*H), 128.79 (*C*H), 129.35 (*C*H), 130.38 (*C*H), 130.75 (*C*H), 131.07 (*C*H), 131.90 (*C*H), 133.62 (*C*H), 135.66 (*C*Si), 136.17 (*C*Si), 136.55 (*C*H), 152.21 (*C*N), 156.87 (*C*N); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −8.25 (s). Anal. Calc. for $C_{23}H_{24}N_2OSi$: C, 74.15; H, 6.49; N, 7.52. Found: C, 74.06; H, 6.76; N, 7.30%.

4.3. Synthesis of (E)-allyldimethyl[2-(phenylazo)-phenyl]silane ((E)-5e)

Similarly to the synthesis of (*E*)-**5a**–**d**, (*E*)-**5e** was synthesized from 2-iodoazobenzene (500 mg, 1.62 mmol) and allylchlorodimethylsilane (0.30 mL, 2.05 mmol). Separation with HPLC gave a red oil of (*E*)-allyldimethyl[2-(phenylazo)phenyl]silane ((*E*)-**5e**) (332 mg, 73%). (*E*)-**5e**: red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.38 (s, 6H), 1.92 (d, $^3J = 7.0$ Hz, 2H), 4.79 (d, $^3J = 10.5$ Hz, 1H), 4.83 (d, $^3J = 15.0$ Hz, 1H), 5.77 (ddt, $^3J = 15.0$ Hz, $^3J = 10.5$ Hz, $^3J = 7.0$ Hz, 1H), 7.43 (td, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 7.50 (t, $^3J = 7.5$ Hz, 2H), 7.67 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 7.74 (t, $^3J = 7.5$ Hz, 2H), 7.75 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 7.92 (d, $^3J = 7.5$ Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −1.68 (*C*H_3), 24.82 (*C*H_2), 113.17 (*C*H_2), 114.69 (*C*H), 123.12 (*C*H), 129.08 (*C*H), 130.03 (*C*H), 130.05 (*C*H), 130.91 (*C*H), 134.95 (*C*H), 134.96 (*C*H), 140.13 (*C*Si), 152.33 (*C*N), 157.22 (*C*N); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −4.26 (s). Anal. Calc. for $C_{17}H_{20}N_2Si$: C, 72.81; H, 7.19; N, 9.99. Found: C, 72.77; H, 7.30; N, 9.71%.

4.4. Synthesis of (E)-allyldifluoro[2-(phenylazo)-phenyl]silane ((E)-7a–d)

To an ethereal solution of (*E*)-**5a** (81.5 mg, 0.240 mmol) was added $BF_3 \cdot Et_2O$ (25 μL, 0.20 mmol) and the reaction mixture was stirred at room temperature for 20 h. Removal of the solvent, addition of hexane, filtration of the insoluble materials and evaporation of the solvent gave a yellow viscous oil. Recrystallization of the oil from hexane gave yellow crystals of (*E*)-allyldifluoro[2-(phenylazo)phenyl]silane ((*E*)-**7a**) (13.8 mg, 63%). (*E*)-**7a**: yellow crystals (hexane); m.p. 38 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.87–1.94 (m, 2H), 4.72 (d, $^3J = 17.0$ Hz, 1H), 4.76 (d, $^3J = 10.2$ Hz, 1H), 5.57 (ddt, $^3J = 17.0$ Hz, $^3J = 10.2$ Hz, $^3J = 7.5$ Hz, 1H), 7.53–7.64 (m, 4H), 7.73 (dt, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 1H), 7.94 (dd, $^3J = 7.3$ Hz, $^4J = 1.6$ Hz, 1H), 8.04–8.07 (m, 2H), 8.14 (d, $^3J = 7.0$ Hz, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 22.92 (t, $^2J_{C-F} = 16.2$ Hz, *C*H_2), 116.07 (s, *C*H_2), 120.00 (t, $^2J_{C-F} = 18.0$ Hz, *C*Si), 123.12 (s, *C*H), 129.47 (s, *C*H), 129.52 (s, *C*H), 130.71 (s, *C*H), 132.11 (s, *C*H), 132.32 (s, *C*H), 132.90 (s, *C*H), 137.21 (t, $^3J_{C-F} = 2.5$ Hz), 149.11 (s, *C*N), 156.43 (t, $^3J_{C-F} = 3.1$ Hz, *C*N); ^{19}F NMR (254 MHz, $CDCl_3$, r.t.) δ 140.42 (s, $^1J_{Si-F} = 278$ Hz); ^{19}F NMR (254 MHz, CD_2Cl_2, −90 °C) δ −141.27 (br), −127.17 (br); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −38.53 (t, $^1J_{Si-F} = 277.6$ Hz). Anal. Calc. for $C_{15}H_{14}F_2N_2Si$: C, 62.48; H, 4.89; N, 9.71. Found: C, 62.24; H, 5.04; N, 9.62%. (*E*)-**7b**: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (dd, $^3J = 7.7$ Hz, $^4J = 1.5$ Hz, 3H), 1.78–1.81 (m, 2H), 2.47 (s, 3H), 5.12 (dq, $^3J = 15.0$ Hz, $^3J = 7.7$ Hz, 1H), 5.55 (dtq, $^3J = 15.0$ Hz, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 7.52–7.56 (m, 4H), 7.77 (s, 1H), 8.02 (d, $^3J = 8.0$ Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 17.96 (s, *C*H_3), 21.19 (t, $^2J_{C-F} = 15.3$ Hz, *C*H_2),

21.60 (s, CH_3), 120.31 (t, $^2J_{C-F} = 14.6$ Hz, CSi), 121.75 (s, CH), 122.91 (s, CH), 126.57 (s, CH), 129.30 (s, CH), 129.45 (s, CH), 131.67 (s, CH), 133.17 (s, CH), 137.17 (s, CH), 143.07 (s, CMe), 149.19 (s, CN), 154.73 (s, CN); ^{19}F NMR (254 MHz, $CDCl_3$) δ −140.49 (s, $^1J_{Si-F} = 279$ Hz, 1F); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −38.43 (t, $^1J_{Si-F} = 278.5$ Hz); MS (FAB) m/z 316 (M^+), 261 ($M^+ - CH_2CH{=}CHCH_3$). (*E*)-**7c**: yellow crystals; m.p. 70–71 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24–1.27 (m, 1H), 1.63–1.67 (m, 3H), 1.91 (br, 2H), 2.04 (m, 1H), 5.48 (ddt, $^3J = 10.5$ Hz, $^3J = 3.2$ Hz, $^4J = 2.0$ Hz, 1H), 5.62 (ddt, $^3J = 10.5$ Hz, $^3J = 6.4$ Hz, $^4J = 3.7$ Hz, 1H), 7.53–7.55 (m, 3H), 7.60 (t, $^3J = 7.5$ Hz, 1H), 7.72 (t, $^3J = 7.5$ Hz, 1H), 7.97 (d, $^3J = 7.5$ Hz, 1H), 8.01 (dd, $^3J = 7.5$ Hz, $^4J = 1.6$ Hz, 2H), 8.13 (d, $^3J = 7.5$ Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 21.77 (s, CH_2), 22.12 (s, CH_2), 24.62 (s, CH_2), 25.11 (t, $^2J_{C-F} = 19.6$ Hz, CH), 120.98 (t, $^2J_{C-F} = 17.0$ Hz, CSi), 123.01 (s, CH), 123.87 (s, CH), 127.80 (s, CH), 128.08 (s, CH), 129.37 (s, CH), 131.90 (s, CH), 132.08 (s, CH), 134.33 (s, CH), 137.21 (s, CH), 149.87 (s, CN), 156.70 (s, CN); ^{19}F NMR (254 MHz, $CDCl_3$) δ −145.07 (d, $^2J_{F-F} = 33.1$ Hz, $^1J_{Si-F} = 293$ Hz, 1F), −144.15 (d, $^2J_{F-F} = 32.4$ Hz, $^1J_{Si-F} = 284$ Hz, 1F); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −34.10 (t, $^1J_{Si-F} = 288$ Hz); UV/Vis ($CHCl_3$) λ_{max} (ε) 338 nm (2.0×10^4). Anal. Calc. for $C_{18}H_{18}F_2N_2Si$: C, 65.83; H, 5.52; N, 8.53. Found: C, 65.73; H, 5.72; N, 8.38%. (*E*)-**7d**: orange oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.03 (dddt, $^2J = 7.5$ Hz, $^3J = 7.5$ Hz, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 2.25 (dddt, $^2J = 7.5$ Hz, $^3J = 7.5$ Hz, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 4.72–4.78 (m, 2H), 5.73 (ddt, $^3J = 17.5$ Hz, $^3J = 9.2$ Hz, $^3J = 7.5$ Hz, 1H), 7.28 (d, $^3J = 7.5$ Hz, 1H), 7.31–7.39 (m, 5H), 7.41–7.48 (m, 4H), 7.61 (td, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 8.03 (td, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 1H), 8.15 (d, $^3J = 7.5$ Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 23.49 (d, $^2J_{C-F} = 18.1$ Hz, CH_2), 114.78 (s, CH_2), 122.55 (s, CH), 126.27 (d, $^2J_{C-F} = 17.4$ Hz, CSi), 126.98 (s, CH), 127.75 (s, CH), 128.90 (s, CH), 129.66 (s, CH), 131.14 (s, CH), 131.59 (s, CH), 131.60 (s, CH), 132.63 (s, CH), 133.53 (s, CH), 135.81 (d, $^2J_{C-F} = 20.6$ Hz, CSi), 136.71 (d, $J_{C-F} = 5.8$ Hz, CH), 150.02 (CN), 156.48 (CN); ^{19}F NMR (376 MHz, $CDCl_3$) δ −154.50 (t, $^3J_{F-H} = 7.5$ Hz, $^1J_{Si-F} = 277$ Hz); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −11.80 (d, $^1J_{Si-F} = 277$ Hz); HRMS (FAB) m/z calcd for $C_{21}H_{19}N_2FSi$: 346.1302; found: 346.1297 [M^+].

4.5. Synthesis of potassium tetrafluoro[2-(1-allyl-2-phenylhydrazino)phenyl]silicate, 18-crown-6 (**8a–c**)

To a toluene solution (10 mL) of (*E*)-**7a** (138 mg, 0.479 mmol) were added KF (60 mg, 1.0 mmol) and 18-crown-6 (0.15 g, 0.58 mmol) at room temperature and the reaction mixture was stirred for 5 h. Filtration of the yellow solid which was precipitated from the reaction mixture and successive washing with toluene and ether gave potassium tetrafluoro[2-(1-allyl-2-phenylhydrazino)-phenyl]silicate, 18-crown-6 (**8a**) (209 mg, 69%). Similarly, **8b** and **8c** were obtained from (*E*)-**7b** and (*E*)-**7c** in 47% and 26% yields, respectively. The decomposition point of **8a–c** could not be determined because their appearances did not change during heating of the crystals from room temperature to 500 °C, although they completely decomposed after the heating. **8a**: colorless crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.41 (brs, 24H), 4.32 (brs, 2H), 5.21 (d, $^3J = 17.0$ Hz, 1H), 5.28 (d, $^3J = 10.5$ Hz, 1H), 5.81 (tdd, $^3J = 17.0$ Hz, $^3J = 10.5$ Hz, $^3J = 6.0$ Hz, 1H), 6.23 (s, 1H), 6.71 (d, $^3J = 7.5$ Hz, 1H), 6.75 (t, $^3J = 7.0$ Hz, 1H), 6.99 (t, $^3J = 7.0$ Hz, 1H), 7.03 (t, $^3J = 7.5$ Hz, 1H), 7.13 (t, $^3J = 7.5$ Hz, 2H), 7.26 (d, $^3J = 7.5$ Hz, 2H), 7.56 (t, $^3J = 7.0$ Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 52.70 (CH_2), 69.89 (18-crown-6), 109.86 (CH), 119.86 (CH), 120.72 (CH_2), 122.13 (CH), 124.06 (CH), 126.29 (CH), 127.62 (CH), 131.08 (CH), 131.56 (CH), 144.93 (CN), 149.27 (CN); ^{19}F NMR (254 MHz, $CDCl_3$) δ (−60 °C) −145.71 (br, 1F), −124.74 (br, 1F), −110.54 (br, 1F), −92.61 (br, 1F); ^{19}F NMR (254 MHz, $CDCl_3$) δ (60 °C) −118.01 (br). Anal. Calc. for $C_{27}H_{39}N_2F_4KO_6Si \cdot 2.5H_2O$: C, 47.98; H, 6.56; N, 4.15. Found: C, 47.81; H, 6.32; N, 3.99%. **8b**: colorless crystals; ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C) δ 1.20 (d, $^3J = 6.8$, 3H), 2.27 (s, 3H), 3.50 (br, 24H), 4.56 (qddd, $^3J = 6.8$ Hz, $^3J = 6.7$ Hz, $^4J = 1.5$ Hz, $^4J = 1.0$ Hz, 1H), 5.16 (br, 1H), 5.22 (br, 1H), 6.00 (br, 1H), 6.11 (s, 1H), 6.70 (d, $^3J = 8.1$ Hz, 1H), 6.86–6.93 (m, 2H), 7.11 (t, $^3J = 7.7$ Hz, 2H), 7.26 (d, $^3J = 7.7$ Hz, 2H), 7.40 (s, 1H); ^{19}F NMR (254 MHz, $CDCl_3$) δ (60 °C) −118.03 (br). Anal. Calc. for $C_{29}H_{43}N_2F_4KO_6Si \cdot 2.5H_2O$: C, 49.48; H, 6.87; N, 3.98. Found: C, 49.63; H, 6.82; N, 3.77%. **8c**: colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C) δ 1.50–1.54 (m, 1H), 1.59–1.67 (m, 2H), 1.72–1.85 (m, 2H), 1.92–2.08 (m, 1H), 3.55 (br, 24H), 4.54 (br, 1H), 5.50 (d, $^3J = 10.0$ Hz, 1H), 5.87 (br, 1H), 6.00 (s, 1H), 6.90 (dt, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 1H), 6.95–6.98 (m, 2H), 7.04 (d, $^3J = 8.0$ Hz, 2H), 7.16 (dt, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 1H), 7.25 (dt, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 1H), 7.41 (tt, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 1H), 7.81 (dt, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz, 1H); ^{19}F NMR (254 MHz, $CDCl_3$, 60 °C) δ 118.67 (br).

4.6. X-ray crystallographic analyses of (*E*)-**7a**, **8a** and **8b**

All data were recorded on a Rigaku Mercury CCD diffractometer with monochromated Mo Kα radiation ($\lambda = 0.71070$ Å). Data were collected and processed using CrystalClear (Rigaku). The data were corrected for Lorentz polarization effects. The structures were solved by direct methods (SHELX-97) and expanded using Fourier techniques [25]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically with SHELX-97 [25]. The crystallographic data are summarized in Table 7. Coordinates and other crystallographic information were deposited with Cambridge Crystallographic Database Centre. CCDC Nos. 213638, 297947

Table 7
Crystallographic data of (*E*)-**7a**, **8a** · $2CHCl_3$ and **8b** · $CHCl_3$

Compound	(*E*)-**7a**	**8a** · $2CHCl_3$	**8b** · $CHCl_3$
Empirical formula	$C_{15}H_{14}N_2F_2Si$	$C_{27}H_{39}N_2O_6F_4SiK \cdot 2CHCl_3$	$C_{29}H_{43}N_2O_6F_4SiK \cdot CHCl_3$
Formula weight	288.37	869.53	778.21
Temperature (K)	120(2)	120(2)	120(2)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.192(4)	9.498(3)	9.787(3)
b (Å)	9.719(5)	11.145(4)	11.567(3)
c (Å)	10.504(6)	20.199(7)	18.490(5)
α (°)	74.20(2)	86.510(14)	75.297(13)
β (°)	87.53(3)	76.766(12)	79.002(14)
γ (°)	75.58(2)	67.754(11)	66.602(12)
V (Å^3)	684.0(7)	1925.9(11)	1848.6(9)
Z	2	2	2
ρ_{calc} (g cm^{-3})	1.400	1.499	1.398
μ (cm^{-1})	1.85	6.47	4.55
Crystal size (mm)	$0.45 \times 0.40 \times 0.30$	$0.60 \times 0.40 \times 0.15$	$0.50 \times 0.45 \times 0.45$
θ Limit (°)	3.40–25.00	3.47–25.00	3.06–25.00
Index ranges	$-8 \leqslant h \leqslant 6$, $-11 \leqslant k \leqslant 11$, $-12 \leqslant l \leqslant 12$	$-11 \leqslant k \leqslant 11$, $-13 \leqslant k \leqslant 13$, $-19 \leqslant l \leqslant 24$	$-11 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 13$, $-21 \leqslant l \leqslant 17$
Reflections collected	4394	11753	12006
Independent reflections	2325	6438	6337
Completeness to θ_{max} (%)	96.0	95.0	97.4
Parameters	223	446	426
Goodness-of-fit on F^2	1.062	1.050	1.048
R_1 [$I > 2\sigma(I)$]	0.0341	0.0328	0.0566
wR_2 (all data)	0.0833	0.0846	0.1804
Maximum peak and minimum hole (e Å^{-3})	0.380 and −0.237	0.884 and −0.807	1.244 and −0.649

and 297948 for (*E*)-**7a**, **8a** · $2CHCl_3$ and **8b** · $CHCl_3$, respectively.

4.7. Reactions of (*E*)-*5e* and (*E*)-*7d* with $BF_3 \cdot OEt_2$

To a $CDCl_3$ solution (40 mM, 0.5 mL) of (*E*)-**5e** in a 5 mm∅ NMR tube, $BF_3 \cdot OEt_2$ (5 μL, 0.04 mmol) was added and the reaction solution was left alone at room temperature for 1 h. Quantitative conversion of (*E*)-**5e** to (*E*)-**12a** [6d] was confirmed by ^{1}H and ^{19}F NMR spectra. Similarly, reaction of (*E*)-**7d** with $BF_3 \cdot OEt_2$ for 24 h gave (*E*)-**12b** [6d] quantitatively.

4.8. Reaction of (*E*)-*7a* with potassium fluoride in the presence of 18-crown-6

To a $CDCl_3$ solution (5 mM, 0.5 mL) of (*E*)-**7a** were added KF (ca. 5 mg, 0.08 mmol) and 18-crown-6 (7.2 mg, 27 mmol) at room temperature. After the reaction mixture was stirred for 1 h, complete consumption of (*E*)-**7a** and formation of **8a** (82%) were confirmed by ^{19}F NMR spectra. The yield was determined by integral of ^{1}H NMR spectroscopy. Similar procedure without 18-crown-6 in $CDCl_3$ gave colorless solution of tetrafluorodisiloxane **9a** (84%). Evaporation of the solvent resulted in decomposition of **9a**. **9a**: ^{1}H NMR (500 MHz, C_6D_6) δ (60 °C) 3.64 (d, $^3J = 8.5$ Hz, 4H), 4.92 (d, $^3J = 17.0$ Hz, 2H), 5.04 (d, $^3J = 10.5$ Hz, 2H), 5.41–5.58 (m, 2H), 6.14 (s, 2H), 6.58 (d, $^3J = 7.5$ Hz, 2H), 6.88 (t, $^3J = 7.0$ Hz, 2H), 6.89 (t, $^3J = 7.5$ Hz, 4H), 6.93–7.05 (m, 8H), 8.08 (d, $^3J = 7.0$ Hz, 2H); ^{19}F NMR (254 MHz, C_6D_6) δ (60 °C) −136.78 (brs), ^{29}Si NMR (99 MHz, C_6D_6) δ −87.3 (t, $^1J_{Si-F} = 231.3$ Hz); UV/Vis (MeOH) λ_{max} (ε) 243 (8.7×10^3), 303 nm (2.6×10^3); MS (FAB) *m*/*z* 595 (M+H), 575 (M−F), 552 (M−$CH_2CH{=}CH_2$), 533 (M−$H_2CH{=}CH_2$).

4.9. Isomerization of (*E*)-*7a* to (*Z*)-allyldifluoro[2-(phenylazo)phenyl]silane ((*Z*)-*7a*)

A $CDCl_3$ solution (10 mM, 0.5 mL) of (*E*)-**7a** in a 5 mm∅ NMR tube was irradiated with high pressure mercury lamp through a colored glass filter ($\lambda = 360$ nm) for 40 min in the dark room. The color of the reaction solution was changed from yellow to red during the irradiation. In ^{19}F NMR spectra, a broad signal at δ_F −140.4 almost disappeared and a new sharp singlet was observed at δ_F −139.8 which was assigned as (*Z*)-allyldifluoro[2-(phenylazo)phenyl]silane, ((*Z*)-**7a**). Quantitative conversion of (*E*)-**7a** to (*Z*)-**7a** was confirmed by integral of ^{1}H NMR spectra. Due to the thermal instability of (*Z*)-**7a** at room temperature, the solution of (*Z*)-**7a** was used as such for further reactions. The reaction solution of (*Z*)-**7a** in a 5 mm∅ NMR tube was irradiated with a high-pressure mercury lamp through a colored glass filter ($\lambda = 445$ nm) for 2 h in the dark room, and then (*E*)-**7a** was regenerated in 72% yield. Otherwise, the reaction solution of (*Z*)-**7a** in a

5 mm∅ NMR tube was left alone at room temperature for 11 days in the dark to give (*E*)-**7a** quantitatively. (*Z*)-**7a**: red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.22–2.26 (m, 2H), 5.02 (d, $^3J = 10.1$ Hz, 1H), 5.11 (d, $^3J = 17.0$ Hz, 1H), 5.83 (ddt, $^3J = 17.0$ Hz, $^3J = 10.1$ Hz, $^3J = 7.8$ Hz, 1H), 6.18 (d, $^3J = 8.0$ Hz, 1H), 6.85 (dd, $^3J = 8.4$ Hz, $^4J = 1.2$ Hz, 2H), 7.16 (dd, $^3J = 7.8$ Hz, $^4J = 1.4$ Hz, 1H), 7.18 (td, $^3J = 7.5$ Hz, $^4J = 1.2$ Hz, 1H), 7.22 (t, $^3J = 7.2$ Hz, 1H), 7.27 (t, $^3J = 7.8$ Hz, 2H), 7.83 (dd, $^3J = 7.3$ Hz, $^4J = 1.3$ Hz, 1H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 20.34 (t, $^2J_{C-F} = 14.9$ Hz, *C*H$_2$), 116.07 (s, *C*H$_2$), 117.39 (s, *C*H), 118.97 (t, $^2J_{C-F} = 18.6$ Hz, *C*Si), 120.05 (s, *C*H), 123.11 (s, *C*H), 127.51 (s, *C*H), 127.77 (s, *C*H), 128.95 (s, *C*H), 131.54 (s, *C*H), 135.60 (s, *C*H), 153.57 (s, *C*N), 158.00 (s, *C*N); ^{19}F NMR (254 MHz, $CDCl_3$, −60 °C) δ −139.83 (s); ^{29}Si NMR (99 MHz, $CDCl_3$) δ −19.96 (t, $^1J_{SiF} = 298.6$ Hz).

4.10. Reaction of allylmagnesium chloride with azobenzene

To an ethereal solution (80 mL) of azobenzene (3.10 g, 17.0 mmol) was added an ethereal solution of allylmagnesium chloride (0.13 M, 200 mL) at 0 °C, and the reaction solution was further stirred at room temperature for 1 h. The reaction solution was quenched with water, extracted with chloroform, dried with $MgSO_4$, and separated by distillation in vacuo (0.5 mmHg, 132 °C) to give a pale yellow oil of 1-allyl-1,2-diphenylhydrazine (**20a**) (3.40 g, 89%). The spectral data accorded with those of the authentic sample reported in the literature [23].

4.11. Reaction of tetrafluoro[2-(phenylazo)phenyl]silicate with cesium fluoride and crotyltrifluorosilane

To a THF solution of potassium 2-(phenylazo)phenyltetrafluorosilicate · 18-crown-6 ((*E*)-**19**) (86.1 mg, 146 mmol) were added crotyltrifluorosilane (60 mL, 0.40 mmol) and cesium fluoride (71 mg, 0.47 mmol) at room temperature, and the reaction mixture was further stirred at 80 °C for 24 h. The reaction solution was quenched with water, extracted with chloroform, dried with $MgSO_4$. After evaporation of the solvent, the crude oil was subsequently subjected to silica gel column chromatography and HPLC to give a pale yellow oil of 1-(1-methyl-2-propenyl)-1,2-diphenylhydrazine (**20b**) (20.5 mg, 59%) [26]. **20b**: pale yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$, 60 °C) δ 1.35 (d, $^3J = 6.8$ Hz, 3H), 4.65 (qtd, $^3J = 6.8$ Hz, $^3J = 5.6$ Hz, $^4J = 1.5$ Hz, 1H), 5.17 (dt, $^3J = 10.8$ Hz, $^4J = 1.5$ Hz, 1H), 5.19 (dt, $^3J = 17.0$ Hz, $^4J = 1.5$ Hz, 1H), 5.41 (brs, 1H), 5.95 (ddd, $^3J = 17.0$ Hz, $^3J = 10.8$ Hz, $^3J = 5.5$ Hz, 1H), 6.75–6.86 (4H, m), 6.92–6.95 (2H, m), 7.14–7.25 (4H, m); ^{13}C NMR (68 MHz, $CDCl_3$, 60 °C) δ 58.20 (*C*H$_3$), 77.20 (*C*H), 112.12 (*C*H), 114.59 (*C*H), 116.19 (*C*H$_2$), 119.25 (*C*H), 119.46 (*C*H), 122.81 (*C*H), 128.99 (*C*H), 129.15 (*C*H), 149.23 (*C*N), 149.79 (*C*N); GC–MS (EI) *m*/*z* 238 (M^+), 183 (M^+−CH(CH$_3$)-CH=CH$_2$).

4.12. Photoswitching of the reaction of (*Z*)-7*a* with potassium fluoride in the presence of 18-crown-6 by photoirradiation

Treatment of (*Z*)-**7a** with KF (ca. 5 mg, 0.08 mmol) and 18-crown-6 (11 mg, 42 mmol) in $CDCl_3$ at room temperature in the dark and further stirring at room temperature for 20 min resulted in no change as judged by ^{1}H and ^{19}F NMR spectra. Photoirradiation ($\lambda = 445$ nm) with high pressure Hg lamp of the reaction solution at room temperature for 45 min gave **8a** (91%).

4.13. Control experiment of the reaction of (*E*)-7 with potassium fluoride in the presence of 18-crown-6 by photoirradiation

The 1:1 mixture (210 mg, 0.35 mmol) of (*E*)-**7a** and (*E*)-crotyldifluoro[3-methyl-6-(phenylazo)phenyl]silane ((*E*)-**7b**) was treated with KF (0.10 g, 1.7 mmol) and 18-crown-6 (0.20 g, 0.76 mmol) in toluene at room temperature in the dark. After the reaction mixture was stirred at room temperature for 8 h, formation of **8a** and **8b** was confirmed by ^{1}H NMR spectrum. The silicates **8a** and **8b** could not be separated. Treatment of the mixture of products with aqueous HCl gave pale brown oil, whose GC–MS spectra showed ion peaks of **20a** (*m*/*z* 224) and **20c** (*m*/*z* 252).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.045.

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