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Synthesis of 1-Silabenzo[*d*,*e*]isochromanes via Electrophilic Aromatic Substitution of Aldehydes Activated by Silylium Ion

Hidekazu Arii, Kenichi Nakao, Hideki Masuda, and Takayuki Kawashima*

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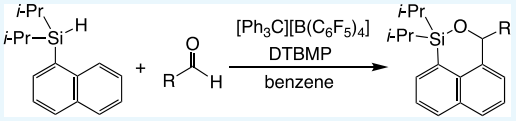
ABSTRACT: A strong Lewis acid silylium ion was utilized for dehydrogenative annulation between dialkyl(1-naphthyl)silanes **1** and aldehydes **2**. Silane **1a** was reacted with $[Ph_3C][B(C_6F_5)_4]$ in the presence of 2,6-di-*tert*-butyl-4-methylpyridine and aldehydes **2** to afford the annulation product, 1-silabenzo[*d*,*e*]isochromanes **3**, in moderate isolated yields. The annulation occurred only at the 8-position on the 1-naphthyl group. The silylium ion-promoted hydrosilylation proceeded competitively to afford silyl ethers **4** via the same intermediates, silylcarboxonium ions, in the dehydrogenative annulation. The ratio of **3** and **4** was affected by solvents and the electronic properties of aromatic aldehydes; for example, the use of less polar solvents and that of benzaldehydes with an electron-withdrawing group at the *para*-position predominantly yielded **3**. This annulation reaction was applicable to aldehydes bearing a heteroaromatic group and aliphatic alkyl groups. Judging from these results, both the formation of silylcarboxonium ions by *in situ*-generated silylium ions and the electrophilic aromatic substitution are important for this annulation reaction.



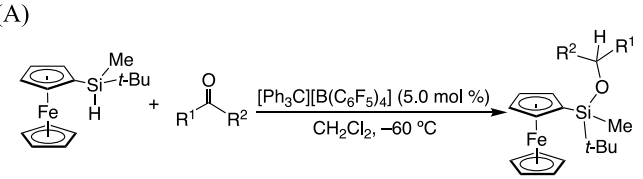
INTRODUCTION

A silylium ion known as a Lewis acid has received much attention due to the activation of substrates in organic syntheses as reactants or catalysts.[1] The vacant p orbital on the silylium ion can interact with unsaturated hydrocarbons as well as hetero-double-bonded compounds such as carbonyl compounds and imines.[2] The high Lewis acidity generates active reaction intermediates, which undergo the desired reactions in both the stoichiometric and catalytic systems.[3−7] Sakurai et al. achieved the reduction of ketones associated with silylcarboxonium ions formed by the reaction of trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate with Et_3SiH in the presence of ketones.[8] The silylium ion generated by a catalytic amount of trityl cation functions as a chain carrier in the hydrosilylation of carbonyl compounds reported by Oestreich et al. (Scheme 1A).[9] $B(C_6F_5)_3$ is one of the most popular catalysts for hydrosilylation in the absence of transition metals, and Piers et al. established the effective hydrosilylation of aromatic aldehydes, ketones, and esters in the catalytic amount of $B(C_6F_5)_3$ (Scheme 1B).[10] The reaction mechanism was investigated in detail using silanes with a chiral silicon center where a Walden-type inversion occurred in the hydride transfer process of the silane to $B(C_6F_5)_3$.[11] The silylium ion is employed as a Lewis acid catalyst as well as a chain carrier, and Mukaiyama aldol reaction and Diels−Alder reaction are carried out.[12,13] Understanding the behavior of a silylium ion toward carbonyl compounds allows the development of various reactions based on the silylium ion; however, an electrophilic substitution reaction of a generated silylcarboxonium ion species is limited in both stoichiometric and catalytic systems.

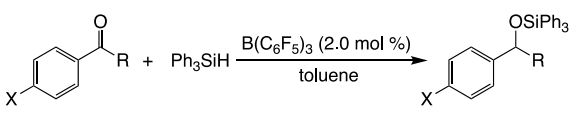
We were interested in the reactivity of tricoordinate heavier group 14 element cations and have studied the dehydrogenative annulation reactions between dialkylbenzylsilanes or dialkyl(1-naphthyl)silanes and unsaturated hydrocarbons through the formation of the corresponding silylalkenylium or silylalkylium ions, followed by their electrophilic substitution on the intramolecular aromatic ring (Scheme 2).[14] In this paper, we investigate the reactions of dialkyl(1-naphthyl)-silanes with aldehydes to obtain 1-silabenzo[*d*,*e*]isochromane derivatives and describe about the steric and electronic effects

Scheme 1. Hydrosilylation of Carbonyl Compounds using Trityl Cation (A) and Borane as a Catalyst (B).

(A)



(B)



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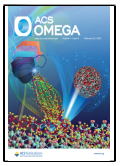

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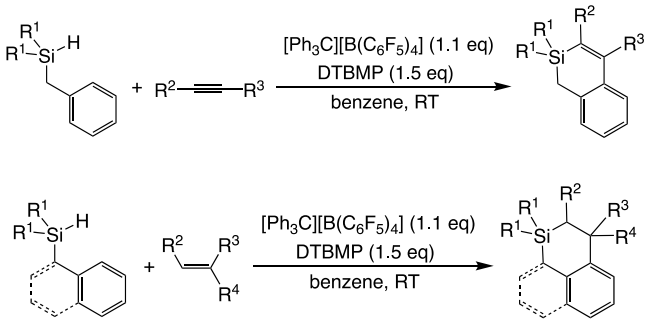
Scheme 2. Silylium Ion-Promoted Dehydrogenative Annulation.



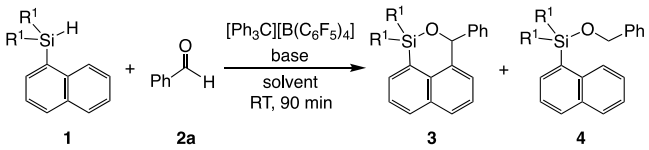
of the substituent groups on aromatic aldehydes and the reaction mechanism for dehydrogenative annulation.

RESULTS AND DISCUSSION

The dehydrogenative annulation via an *in situ*-generated silylium ion requires bases and solvents with poor coordinating properties. Among the bases explored in the annulation between diisopropyl(1-naphthyl)silane (**1a**) and benzaldehyde (**2a**) (Table 1, entries 1−4), only 2,6-di-*tert*-butyl-4-methyl-pyridine (DTBMP) afforded the desired cyclic product, that is, 1,1-diisopropyl-3-phenyl-1-silabenzo[*d*,*e*]isochromane (**3aa**), in 50% isolated yield, accompanied by benzyloxydiisopropyl(1-naphthyl)silane (**4aa**) as a hydrosilylation product in 10% yield.[15] The bases other than DTBMP can bind to the silylium ion to some extent, while DTBMP has a sterically bulky substituent such as a *tert*-butyl group, resulting in the inhibition of the interaction with the silylium ion. The annulation occurred not at the 2-position on the naphthyl group but at the 8-position to give **3aa** because of the higher reactivity of the latter position based on electron density. The hydrosilylation of carbonyl compounds initiated by the prepared or *in situ*-generated silylium ions has been reported previously and is a potential competing reaction for annulation.[8,9] A change from benzene to CH_2Cl_2 as a solvent affected the product distribution to cause the ratio of **3aa** to **4aa** to be approximately 1:1 (Table 1, entry 6), while the yields and ratio in toluene were similar to those in benzene (Table 1, entries 2 and 5). In the aromatic solvents, more stable silylium−arene complexes are readily formed through hydride abstraction by Ph_3C^+, resulting in the rapid consumption of **1a**. Therefore, hydride abstraction of the intermediary silylcarboxonium ion from **1a** becomes slow because only a small amount of unreacted **1a** remains. On the other hand, the hydride abstraction step is slow in CH_2Cl_2 because the silylium−CH_2Cl_2 complex is less stable, and consequently the residual starting material **1a** can work as a hydride donor to give the hydrosilylation product. In addition, in CH_2Cl_2 which is a more polar solvent, silylcarboxonium borate exists as a solvent-separated ion pair rather than a contact ion pair. Its bimolecular reaction with **1a** becomes more favored sterically and can compete with the intramolecular aromatic substitution reaction, which decreases the ratio of **3aa** to **4aa**.

The scope and limitations were studied in the dehydrogenative annulation reactions between silanes **1** and aldehydes **2**. Upon using **1b** with methyl groups, neither cyclic nor hydrosilylated products were obtained, but the reaction using **1c** with phenyl groups gave the hydrosilylation product **4ca** in 31% yield together with the annulation product **3ca** (6% yield) (Table 2, entries 2 and 3). Aromatic groups on the silicon center are known to lead to the effective hydrosilylation of ketones relative to isopropyl groups.[16] In the reaction using **1b**, a complex of the generated silylium ion with an arene or a base seems stable and not reactive with an aldehyde. Therefore, we decided to use silane **1a** as a substrate because **1a** among **1a−c** affords the annulation products in moderate yields. The

Table 1. Dehydrogenative Annulation between Silanes 1 and Benzaldehyde (2a)[a]

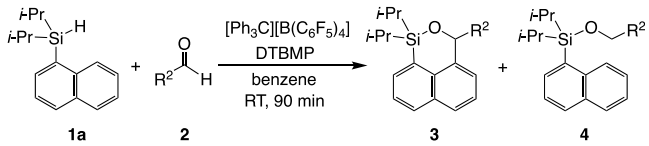


1 2a 3 4

				yield (%)[b]	
entry	base	solvent	R^1	3	4
1	2,6-lutidine	benzene	*i*-Pr	[c]	[c]
2	DTBMP	benzene	*i*-Pr	50 (**3aa**)	10 (**4aa**)
3	K_2CO_3	benzene	*i*-Pr	[c]	[c]
4	DBU[d]	benzene	*i*-Pr	[e]	[e]
5	DTBMP	toluene	*i*-Pr	48 (**3aa**)	8 (**4aa**)
6	DTBMP	CH_2Cl_2	*i*-Pr	28 (**3aa**)	27 (**4aa**)
7	DTBMP	benzene	Me	[c]	[c]
8	DTBMP	benzene	Ph	6 (**3ca**)	31 (**4ca**)

[a]Reaction conditions: **1** (0.10 mmol), **2a** (3.0 equiv), $[Ph_3C][B(C_6F_5)_4]$ (1.1 equiv), and base (1.5 equiv). [b]Isolated yields based on **1**. [c]Not obtained. [d]1,8-Diazabicyclo[5.4.0]-7-undecene. [e]No reaction.

Table 2. Scope for Dehydrogenative Annulation[a]



1a 2 3 4

entry	aldehydes 2	yield (%)[b]			
	R^2	3		4	
1	Ph	**3aa**	50 (59)	**4aa**	10 (14)
2	4-OMe-C_6H_4	**3ab**	13 (21)	**4ab**	4 (7)
3	4-Me-C_6H_4	**3ac**	32 (38)	**4ac**	14 (20)
4	4-Cl-C_6H_4	**3ad**	50 (60)	**4ad**	13 (16)
5	4-CN-C_6H_4	**3ae**	63 (71)	**4ae**	(2)[cd]
6	4-NO_2-C_6H_4	**3af**	51 (73)	**4af**	(3)[cd]
7	2-Me-C_6H_4	**3ag**	52 (57)	**4ag**	10 (12)
8	3-Me-C_6H_4	**3ah**	40 (46)	**4ah**	14 (18)
9	1-naphthyl	**3ai**	53 (64)	**4ai**	23 (25)
10	2-naphthyl	**3aj**	40 (47)	**4aj**	16 (24)
11	3-thienyl	**3ak**	12 (17)	**4ak**	(9)[cd]
12	*n*-Bu	**3al**	22 (24)	**4al**	[e]
13	*sec*-Bu	**3am**	31 (34)	**4am**	[f]
14	*tert*-Bu	**3an**	28 (30)	**4an**	15 (21)
15	cyclohexyl	**3ao**	26 (32)	**4ao**	[f]

[a]Reaction conditions: **1a** (0.10 mmol), **2** (3.0 equiv), $[Ph_3C][B(C_6F_5)_4]$ (1.1 equiv), and DTBMP (1.5 equiv). [b]Isolated yields based on **1a**. NMR yields based on the internal standard Me_2Ph_2Si in parentheses. [c]Not isolated. [d]Detection by the proton signals for NMR spectrum relative to the authentic sample. See Experimental Section in detail. [e]Not obtained. [f]Obtained silyl enol ether **5** instead of **4**.

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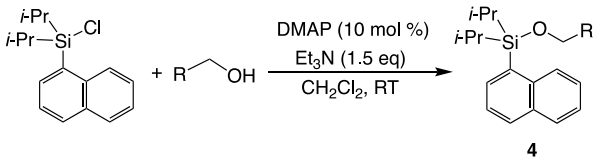
introduction of electron-donating substituents such as MeO and Me groups to the *para*-position on the benzene ring of aldehyde decreased the sum of yields of **3** and **4** (Table 1, entries 7 and 8).

The use of benzaldehydes with the electron-withdrawing substituents (Cl, CN, and NO_2) afforded **3** in the yields similar to that of benzaldehyde (Table 2, entries 4−6), and in the case of the cyano and nitro groups with a high Hammett constant, traces of hydrosilylation products (**4ae** and **4af**) were observed in the ^{1}H NMR spectra consistent with those synthesized by the alternative method (Scheme 3). The electronic substituent

Scheme 3. Alternative Synthesis of Silyl Ethers 4 from a Silyl Chloride and Corresponding Alcohols



effect indicates that dehydrogenative annulation is associated with the electron density on the intermediary silylcarboxonium carbon accessible to the 8-position on the naphthalene, that is, the increased electronic deficiency of the silylcarboxonium carbon caused by the cyano or nitro groups accelerates both electrophilic aromatic substitution giving the annulation products **3** and hydride abstraction from **1a** giving hydrosilylation products **4**, but the former, which is an intramolecular reaction, is accelerated more than the latter intermolecular reaction. Product **3ad** was obtained as single crystals suitable for X-ray diffraction analysis from Et_2O solution. The molecular structure of **3ad** revealed that the fused six-membered ring including a silicon atom involves the bond between the carbonyl carbon from *p*-chlorobenzaldehyde and the carbon at the 8-position on the 1-naphthyl group (Figure 1). The benzene ring is oriented perpendicular to

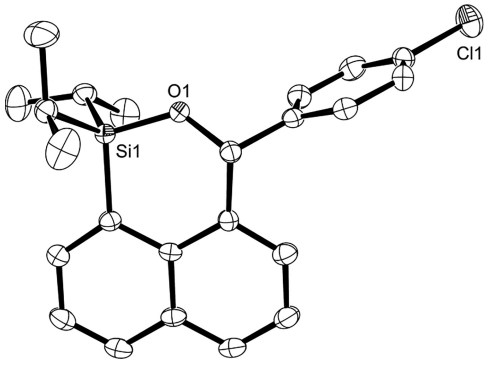
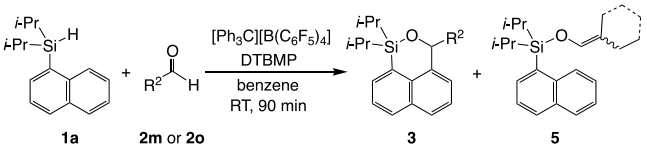


Figure 1. Crystal structure of **3ad**, showing 50% probability of thermal ellipsoid. The hydrogen atoms are omitted for clarity.

naphthalene to prevent the steric repulsion between them. The introduction of a methyl group to the *ortho*- or *meta*-position in benzaldehyde increased the yield of desired products **3** relative to that to the *para*-position (Table 2, entries 3, 7, and 8), implying that the electron-donating property of the methyl group depends on its substituent position. As the CO plane of the silylcarboxonium ion formed from *o*-methylbenzaldehyde is out of the plane of the benzene ring due to steric hindrance to the methyl group, the silylcarboxonium carbon does not accept effective electron donation from the methyl group. Similar behavior is found in the lower pK_a of *o*-methylbenzoic acid at 3.90 than that of *p*-methylbenzoic acid at 4.36.[17]

For other aromatic aldehydes, **3ai** and **3aj** from regioisomers of naphthaldehydes were obtained in moderate yields (Table 2, entries 9 and 10). The use of 1-naphthaldehyde afforded the sum of isolated yields for **3ai** and **4ai** up to 76%. The silylcarboxonium ion surrounded by sterically crowded 1-naphthyl group prohibits undesired intermolecular reactions except for hydrosilylation. 3-Thiophenecarbaldehyde with a heteroaromatic ring gave the annulation product **3ak** in 12% yield (Table 2, entry 11). The poor yield is attributed to the coordination of the thienyl group toward the generated silylium ion and/or the electron-donating property of the thienyl group to the silylcarboxonium carbon. Aliphatic aldehydes also afforded the annulation products **3al**−**ao** in low yields, independent of the branched alkyl group (Table 2, entries 12−15). Interestingly, the diastereomer ratio of **3am** that showed at 2.8:1 was attributed to the conformation preventing the steric repulsion between the silyloxy and the ethyl of *sec*-butyl group. Aldehydes with an α-proton did not give the corresponding hydrosilylation products **4** as a subproduct. The abstraction of α-proton accessible to DTBMP is sufficiently predicted, resulting in the isolation of the silyl enol ethers **5am** (14%) and **5ao** (8%) using 3-methylbutanal (**2m**) and cyclohexanecarbaldehyde (**2o**), respectively (Scheme 4).

Scheme 4. Dehydrogenative Annulation between 1a and Aldehydes with Secondary Alkyl Group



The reaction mechanism for the dehydrogenative annulation between silanes **1** and aldehydes **2** is shown in Scheme 5. The hydride abstraction from silanes **1** by Ph_3C^+ forms the silylium−arene complex. Exchange of the arene to an aldehyde affords an intermediate with two resonance structures, that is, an adduct of silylium ion to the oxygen of the aldehyde and a silyloxycarbenium ion. An aldehyde with a more basic C═O moiety is expected to form the silylcarboxonium intermediate rapidly, and the following electrophilic aromatic substitution produces **3** and/or hydrosilylation products **4** in higher yields. However, the results for 4-substituted benzaldehydes indicate that the higher yields were obtained in the cases of electron-withdrawing substituents. The increase in basicity on the carbonyl oxygen accelerates the oligomerization where the excess aldehyde reacts with the silylcarboxonium ion, although it has an advantage for the coordination toward the silylium ion. Therefore, aldehydes with an electron-withdrawing group effectively undergo the annulation reaction because of the low basicity of the carbonyl oxygen. The intramolecular electrophilic aromatic substitution of the silylcarboxonium carbon occurs only at the 8-position on the 1-naphthyl group and then the proton is abstracted by DTBMP to give the annulation products **3**. As a competing reaction with annulation, the silylcarboxonium carbon abstracts the hydride from silanes **1** to form the hydrosilylation products **4**. The ratio of **3** to **4** is attributed to the hydride property of Si−H. The substitution of

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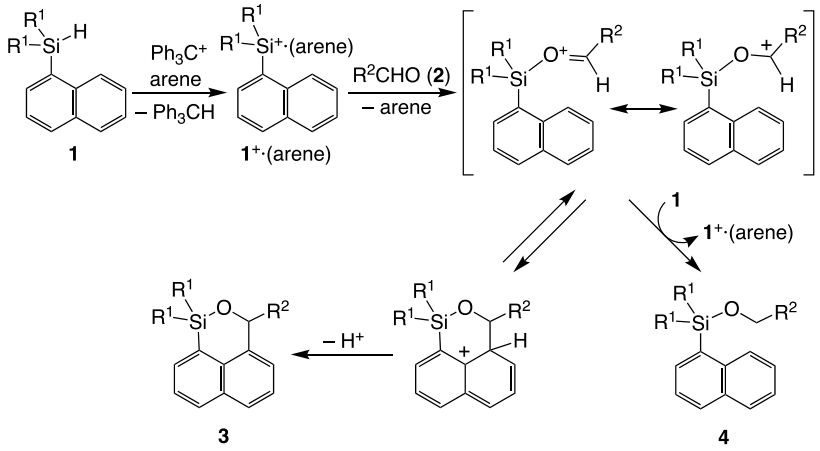
Scheme 5. Plausible Mechanism for Dehydrogenative Annulation and Hydrosilylation between 1 and Aldehydes 2



an aryl group on silicon generally facilitates hydride donation, and triarylsilanes in the $B(C_6F_5)_3$ catalysis system undergo effective hydrosilylation of carbonyl compounds.[16] In fact, the use of triarylsilane **1c** predominantly gave the hydrosilylation product in contrast to that of **1a**.

CONCLUSIONS

We described the dehydrogenative annulation of dialkyl(1-naphthyl)silanes **1** with various aldehydes **2** via the silylcarboxonium ion intermediate. The *in situ*-generated silylium ions bound to various aldehydes underwent intramolecular electrophilic aromatic substitution at the 8-position of the 1-naphthyl group to form 1-silabenzo[*d*,*e*]isochromane derivatives **3**, and no substitution at the 2-position was observed. The hydrosilylation of aldehydes competed with the annulation and afforded silyl ether derivatives **4**. The intrinsic activity of the carbonyl moiety in aldehydes affects the ratio of **3** and **4**, where benzaldehyde bearing an electron-withdrawing group at the para-position predominantly gave the annulation product with **1a**. On the other hand, the use of CH_2Cl_2 as a solvent and aldehydes with an electron-donating substituent accelerates the hydrosilylation reaction. The activation of carbonyl moiety by a silylium ion, followed by the electrophilic aromatic substitution has been demonstrated as a synthetic method for 1-silabenzo[*d*,*e*]isochromanes.

EXPERIMENTAL SECTION

General Procedure. All experiments were carried out using standard vacuum line and Schlenk techniques under Ar atmosphere or in the drybox. All the reagents were of the highest grade available and were used without further purification. All solvents used for the syntheses were distilled according to the general procedure. Trityl tetrakis(pentafluorophenyl)borate[18] and diisopropyl(1-naphthyl)silane (**1a**)[14b] were synthesized according to the previously reported method. ^{1}H NMR and ^{13}C NMR spectral measurements were performed on Bruker AV400M spectrometers. ^{1}H and ^{13}C chemical shifts are reported relative to the residual protonated solvent, respectively, according to the literature.[19] High-resolution mass spectra were measured by a JEOL JMS-700N mass spectrometer operated by electron impact ionization (EI). Gel permeation liquid chromatography (GPLC) was performed by a Japan Analytical Industry LC-918 using chloroform as an eluent.

X-ray Crystallography. The crystal of **3ad** was mounted on a glass fiber, and the diffraction data were collected at −100 °C on a Rigaku R-AXIS RAPID II large-area curved imaging plate detector using graphite monochromated Mo Kα radiation. The structure was solved by the direct method using SHELXT-2014/5.[20] All nonhydrogen atoms were anisotropically refined by full-matrix least-squares calculation on F^2 using SHELXL-2016/6.[21] All hydrogen atoms were placed at geometrically calculated positions.

Preparation of Compounds. *Dimethyl(1-naphthyl)-silane (**1b**).* To 1-bromonaphthalene (0.30 g, 1.4 mmol) in Et_2O (3 mL) was added 1.6 M *t*-BuLi pentane solution (1.8 mL, 2.9 mmol) at −80 °C, and the solution was warmed to room temperature. After chlorodimethylsilane (0.13 g, 1.4 mmol) was added to the reaction mixture at −80 °C, it was gradually warmed to room temperature and stirred for a day. The reaction was quenched by aq. NH_4Cl, and the organic layer was extracted twice by Et_2O. The combined organic layers dried over Na_2SO_4 were filtrated. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 20/1). Further purification was carried out by GPLC to obtain **1b** (0.18 g, 67%) as an oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13 (d, J = 8.4 Hz, 1H, Ar), 7.90−7.86 (m, 2H, Ar), 7.74 (dd, J = 6.4 Hz, J = 1.2 Hz, 1H, Ar), 7.56−7.45 (m, 3H, Ar), 4.88 (sept, J = 4.0 Hz, 1H, SiH), 0.51 (d, J = 4.0 Hz, 6H, $SiMe_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.1, 135.8, 133.8, 133.3, 130.1, 129.1, 127.8, 126.1, 125.7, 125.3, −3.1. HRMS (EI) m/z: $[M]^+$ calcd for $C_{12}H_{14}Si$, 186.0865; found, 186.0865.

*1-Naphthyldiphenylsilane (**1c**).* Silane **1c** was synthesized similar to **1b**, except for using chlorodiphenylsilane (0.31 g, 1.4 mmol) instead of chlorodimethylsilane, to obtain as a white powder (0.40 g, 89%). mp: 89−90 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.14 (d, J = 8.4 Hz, 1H, Ar), 7.99 (d, J = 8.0 Hz, 1H, Ar), 7.93 (d, J = 7.2 Hz, 1H, Ar), 7.70−7.64 (m, 5H, Ar), 7.55−7.39 (m, 9H, Ar), 5.98 (s, 1H, SiH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.5, 137.0, 136.1, 133.4, 133.3, 131.5, 130.9, 130.0, 129.0, 128.4, 128.2, 126.3, 125.9, 125.4. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{18}Si$, 310.1178; found, 310.1178.

Reaction Using Silanes 1 and Aldehydes 2. To $[Ph_3C][B(C_6F_5)_4]$ (101 mg, 0.11 mmol), an aldehyde (0.30 mmol), and DTBMP (31 mg, 0.15 mmol) in benzene (2 mL) was slowly added a benzene solution (1 mL) of silanes **1** (0.10 mmol) at room temperature under Ar atmosphere, and the

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resulting solution was stirred for 90 min. The reaction mixture was quenched with H_2O and then the organic layer was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure to remove the volatiles. The crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 10/1). Further purification was carried out by Preparative thin-layer chromatography and/or GPLC to obtain each of the products.

*1,1-Diisopropyl-3-phenyl-1-silabenzo[d,e]isochromane (**3aa**).* **3aa** (17.2 mg, 50%) was obtained as a white powder accompanied by **4aa** (3.6 mg, 10%) as a colorless oil from the reaction using **1a** (24.1 mg, 99.4 μmol) and benzaldehyde (**2a**). mp: 51−53 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H, Ar), 7.77 (d, *J* = 8.4 Hz, 1H, Ar), 7.68 (dd, *J* = 6.4 Hz, *J* = 1.2 Hz, 1H, Ar), 7.54 (dd, *J* = 8.0 Hz, *J* = 6.4 Hz, 1H, Ar), 7.39−7.29 (m, 6H, Ar), 6.84 (dt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H, Ar), 6.39 (s, 1H, OC*H*Ar), 1.37 (sept, *J* = 7.2 Hz, 1H, C*H*(CH_3)$_2$), 1.18 (sept, *J* = 7.2 Hz, 1H, C*H*(CH_3)$_2$), 1.115 (d, *J* = 7.6 Hz, 3H, CH(CH_3)$_2$), 1.108 (d, *J* = 7.6 Hz, 3H, CH(CH_3)$_2$), 0.99 (d, *J* = 7.2 Hz, 3H, CH(CH_3)$_2$), 0.90 (d, *J* = 7.2 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.7, 138.7, 136.1, 133.3, 131.8, 130.3, 129.5, 128.44, 128.43, 128.3, 127.8, 125.6, 125.08, 125.00, 78.3, 18.8, 17.6, 17.4, 17.2, 14.1, 13.2. HRMS (EI) *m*/*z*: $[M]^+$ calcd for $C_{23}H_{26}OSi$, 346.1753; found, 346.1753.

*Benzyloxydiisopropyl(1-naphthyl)silane (**4aa**).* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, *J* = 8.0 Hz, 1H, Ar), 7.89 (d, *J* = 8.0 Hz, 1H, Ar), 7.85 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H, Ar), 7.79 (dd, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H, Ar), 7.50−7.34 (m, 7H, Ar), 7.29 (d, *J* = 7.2 Hz, 1H, Ar), 4.93 (s, 2H, CH_2Ph), 1.56 (sept, *J* = 7.6 Hz, 2H overlapped by H_2O, C*H*(CH_3)$_2$), 1.16 (d, *J* = 7.6 Hz, 6H, CH(CH_3)$_2$), 1.09 (d, *J* = 7.6 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 137.9, 135.2, 133.6, 133.0, 130.3, 129.0, 128.9, 128.4, 127.0, 126.2, 125.9, 125.5, 125.0, 65.7, 18.2, 18.0, 13.7. HRMS (EI) *m*/*z*: $[M]^+$ calcd for $C_{23}H_{28}OSi$, 348.1909; found, 348.1903.

*1,1,3-Triphenyl-1-silabenzo[d,e]isochromane (**3ca**).* **3ca** (2.5 mg, 6.1%) was obtained as a white powder accompanied by **4ca** (12.7 mg, 31%) as a colorless oil from the reaction using **1c** (30.6 mg, 98.6 μmol) and benzaldehyde (**2a**). mp: 176−178 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H, Ar), 7.82−7.77 (m, 2H, Ar), 7.73−7.69 (m, 2H, Ar), 7.59−7.53 (m, 3H, Ar), 7.45−7.42 (m, 1H, Ar), 7.40−7.25 (m, 11H overlapped by residual protonated $CDCl_3$, Ar), 6.90 (dt, *J* = 7.2 Hz, *J* = 1.6 Hz, 1H, Ar), 6.46 (s, 1H, OC*H*Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.3, 138.7, 136.0, 135.6, 135.5, 134.4, 134.0, 133.52, 133.46, 131.0, 130.5, 130.4, 128.8, 128.5, 128.44, 128.41, 128.2, 128.0, 127.8, 125.9, 125.4, 125.3, 78.1. HRMS (EI) *m*/*z*: $[M]^+$ calcd for $C_{29}H_{22}OSi$, 414.1440; found, 414.1426.

*Benzyloxydiphenyl(1-naphthyl)silane (**4ca**).* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, *J* = 8.4 Hz, 1H, Ar), 7.96 (d, *J* = 8.0 Hz, 1H, Ar), 7.88 (d, *J* = 8.8 Hz, 1H, Ar), 7.80 (dd, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H, Ar), 7.69−7.66 (m, 4H, Ar), 7.49−7.42 (m, 4H, Ar), 7.40−7.29 (m, 9H, Ar), 7.27−7.22 (m, 1H, Ar), 4.95 (s, 2H, OCH_2Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.7, 137.6, 137.0, 135.6, 134.7, 133.6, 132.1, 131.3, 130.2, 129.3, 128.9, 128.4, 128.1, 127.2, 126.6, 126.2, 125.8, 125.2, 66.0. HRMS (EI) *m*/*z*: $[M]^+$ calcd for $C_{29}H_{24}OSi$, 416.1596; found, 416.1596.

*3,3-Diisopropyl-1-phenyl-3-silaisochromane (**3da**).* **3da** (2.5 mg, 8.0%) was obtained as a colorless oil accompanied by **4da** (13.6 mg, 44%) as a colorless oil from the reaction using **1d** (20.3 mg, 98.4 μmol) and benzaldehyde (**2a**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38−7.28 (m, 5H, Ar), 7.21−7.19 (m, 2H, Ar), 7.06−7.02 (m, 1H, Ar), 6.70 (d, *J* = 8.0 Hz, 1H, Ar), 5.94 (s, 1H, OC*H*Ar), 2.15 (d, *J* = 15.6 Hz, 1H, $SiCH_2$Ar), 2.04 (d, *J* = 15.2 Hz, 1H, $SiCH_2$Ar), 1.05−1.01 (m, 1H, C*H*(CH_3)$_2$), 0.98−0.94 (m, 6H, CH(C*H*$_3$)$_2$), 0.91−0.83 (m, 7H, C*H*(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.9, 141.3, 137.1, 130.8, 128.3, 128.0, 127.6, 127.5, 127.4, 124.8, 77.9, 17.6, 17.4, 17.3, 17.2, 14.6, 13.3, 13.2. HRMS (EI) *m*/*z*: $[M]^+$ calcd for $C_{20}H_{26}OSi$, 310.1753; found, 310.1753.

*Benzyl(benzyloxy)diisopropylsilane (**4da**).* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36−7.29 (m, 4H, Ar), 7.27−7.24 (m, 1H overlapped by residual protonated $CDCl_3$, Ar), 7.21−7.17 (m, 2H, Ar), 7.15−7.12 (m, 2H, Ar), 7.07 (tt, *J* = 7.2 Hz, *J* = 1.6 Hz, 1H, Ar), 4.75 (s, 2H, OCH_2Ph), 2.30 (s, 2H, $SiCH_2$Ph), 1.15−1.07 (m, 2H, C*H*(CH_3)$_2$), 1.05−1.01 (m, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.4, 139.5, 128.9, 128.4, 128.3, 127.0, 126.0, 124.3, 65.2, 20.8, 17.71, 17.68, 12.5. HRMS (EI) *m*/*z*: $[M]^+$ calcd for $C_{20}H_{28}OSi$, 312.1909; found, 312.1909.

*1,1-Diisopropyl-3-(4-methoxyphenyl)-1-silabenzo[d,e]-isochromane (**3ab**).* **3ab** (4.7 mg, 13%) was obtained as a white powder accompanied by **4ab** (1.7 mg, 4.5%) as a white powder from the reaction using **1a** (24.2 mg, 99.8 μmol) and *p*-anisaldehyde (**2b**). mp: 125−126 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H, Ar), 7.76 (d, *J* = 8.0 Hz, 1H, Ar), 7.66 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 1H, Ar), 7.52 (dd, *J* = 8.4 Hz, *J* = 6.8 Hz, 1H, Ar), 7.31 (dd, *J* = 8.0 Hz, *J* = 6.8 Hz, 1H, Ar), 7.25−7.21 (m, 2H, Ar), 6.90−6.84 (m, 3H, Ar), 6.35 (s, 1H, OC*H*Ar), 3.82 (s, 3H, OCH_3), 1.35 (sept, *J* = 8.0 Hz, 1H, C*H*(CH_3)$_2$), 1.16 (sept, *J* = 7.6 Hz, 1H, C*H*(CH_3)$_2$), 1.095 (d, *J* = 7.6 Hz, 3H, CH(C*H*$_3$)$_2$), 1.087 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$), 0.98 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$), 0.89 (d, *J* = 7.6 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 139.0, 137.2, 136.1, 133.3, 131.7, 130.3, 129.6, 128.2, 125.6, 125.1, 125.0, 113.8, 77.9, 55.4, 18.1, 17.6, 17.5, 17.2, 14.1, 13.2. HRMS (EI) *m*/*z*: $[M]^+$ calcd for $C_{24}H_{28}O_2Si$, 376.1859; found, 376.1858.

*Diisopropyl((4-methoxyphenyl)methoxy)(1-naphthyl)-silane (**4ab**).* mp: 76−77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, *J* = 8.4 Hz, 1H, Ar), 7.88 (d, *J* = 8.4 Hz, 1H, Ar), 7.85 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H, Ar), 7.78 (dd, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H, Ar), 7.49−7.38 (m, 3H, Ar), 7.32 (d, *J* = 8.4 Hz, 2H, Ar), 6.90 (d, *J* = 8.4 Hz, 2H, Ar), 4.85 (s, 2H, OCH_2Ar), 3.82 (s, 3H, OCH_3), 1.54 (sept, *J* = 7.6 Hz, 2H overlapped by H_2O, C*H*(CH_3)$_2$), 1.14 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.08 (d, *J* = 7.6 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.9, 137.9, 135.7, 135.2, 133.6, 133.1, 130.3, 129.0, 128.9, 127.7, 125.9, 125.5, 125.0, 113.8, 65.5, 55.4, 18.2, 18.0, 13.7. HRMS (EI) *m*/*z*: $[M]^+$ calcd for $C_{24}H_{30}O_2Si$, 378.2015; found, 378.2015.

*1,1-Diisopropyl-3-(4-methylphenyl)-1-silabenzo[d,e]-isochromane (**3ac**).* **3ac** (11.5 mg, 32%) was obtained as a white powder accompanied by **4ac** (5.0 mg, 14%) as a colorless oil from the reaction using **1a** (24.2 mg, 99.8 μmol) and *p*-methylbenzaldehyde (**2c**). mp: 134−135 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H, Ar), 7.76 (d, *J* = 8.0 Hz, 1H, Ar), 7.67 (dd, *J* = 6.8 Hz, *J* = 1.6 Hz, 1H, Ar), 7.53 (dd, *J* = 8.0 Hz, *J* = 6.8 Hz, 1H, Ar), 7.30 (dd, *J* = 8.0 Hz, *J* = 7.2 Hz, 1H, Ar), 7.22 (d, *J* = 8.0 Hz, 2H, Ar), 7.17 (d, *J* = 7.6 Hz, 2H, Ar), 6.85 (dt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H, Ar), 6.35 (s, 1H, OC*H*Ar), 2.37 (s, 3H, $ArCH_3$), 1.36

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(sept, J = 7.6 Hz, 1H, CH(CH$_3$)$_2$), 1.18 (sept, J = 7.2 Hz, 1H, CH(CH$_3$)$_2$), 1.106 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$), 1.100 (d, J = 7.2 Hz, 3H, CH(CH_3)$_2$), 0.99 (d, J = 7.2 Hz, 3H, CH(CH_3)$_2$), 0.90 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 141.8, 138.9, 137.5, 136.1, 133.3, 131.7, 130.3, 129.6, 129.1, 128.4, 128.2, 125.6, 125.1, 125.0, 78.1, 21.4, 18.1, 17.6, 17.5, 17.3, 14.1, 13.2. HRMS (EI) m/z: [M]$^+$ calcd for $C_{24}H_{28}OSi$, 360.1909; found, 360.1913.

*Diisopropyl((4-methylphenyl)methoxy)(1-naphthyl)silane (**4ac**).* ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.33 (d, J = 8.4 Hz, 1H, Ar), 7.89 (d, J = 8.4 Hz, 1H, Ar), 7.85 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H, Ar), 7.78 (dd, J = 6.8 Hz, J = 1.2 Hz, 1H, Ar), 7.49−7.38 (m, 3H, Ar), 7.30 (d, J = 8.4 Hz, 2H, Ar), 7.17 (d, J = 7.2 Hz, 2H, Ar), 4.89 (s, 2H, OCH$_2$Ar), 1.55 (sept, J = 7.6 Hz, 2H overlapped by H$_2$O, CH(CH$_3$)$_2$), 1.15 (d, J = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.08 (d, J = 7.6 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 138.3, 137.9, 136.6, 135.2, 133.6, 133.1, 130.2, 129.06, 129.02, 128.9, 126.3, 125.9, 125.5, 125.0, 65.7, 21.3, 18.2, 18.0, 13.7. HRMS (EI) m/z: [M]$^+$ calcd for $C_{24}H_{30}OSi$, 362.2066; found, 362.2066.

*3-(4-Chlorophenyl)-1,1-diisopropyl-1-silabenzo[d,e]-isochromane (**3ad**).* **3ad** (19.1 mg, 50%) was obtained as a white powder accompanied by **4ad** (5.1 mg, 13%) as a colorless oil from the reaction using **1a** (24.3 mg, 0.100 mmol) and *p*-chlorobenzaldehyde (**2d**). mp: 144−146 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.95 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H, Ar), 7.78 (d, J = 8.4 Hz, 1H, Ar), 7.67 (dd, J = 6.8 Hz, J = 1.6 Hz, 1H, Ar), 7.54 (dd, J = 8.4 Hz, J = 6.8 Hz, 1H, Ar), 7.35−7.29 (m, 3H, Ar), 7.28−7.25 (m, 2H, Ar), 6.81 (dt, J = 7.2 Hz, J = 1.2 Hz, 1H, Ar), 6.36 (s, 1H, OCHAr), 1.36 (sept, J = 7.6 Hz, 1H, CH(CH$_3$)$_2$), 1.18 (sept, J = 7.6 Hz, 1H, CH(CH$_3$)$_2$), 1.102 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$), 1.094 (d, J = 7.2 Hz, 3H, CH(CH_3)$_2$), 0.99 (d, J = 7.2 Hz, 3H, CH(CH_3)$_2$), 0.90 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 143.3, 138.1, 136.0, 133.6, 133.4, 131.9, 130.4, 129.8, 129.3, 128.6, 128.5, 125.5, 125.11, 125.05, 77.6, 18.0, 17.51, 17.46, 17.2, 14.1, 13.2. HRMS (EI) m/z: [M]$^+$ calcd for $C_{23}H_{25}ClOSi$, 380.1363; found, 380.1364.

*(4-Chlorophenylmethoxy)diisopropyl(1-naphthyl)silane (**4ad**).* ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.27 (d, J = 8.4 Hz, 1H, Ar), 7.90 (d, J = 8.4 Hz, 1H, Ar), 7.85 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 7.76 (dd, J = 6.8 Hz, J = 1.2 Hz, 1H, Ar), 7.50−7.37 (m, 3H, Ar), 7.33 (s, 4H, Ar), 4.87 (s, 2H, OCH$_2$Ar), 1.55 (sept, J = 7.6 Hz, 2H overlapped by H$_2$O, CH(CH$_3$)$_2$), 1.15 (d, J = 7.6 Hz, 6H, CH(CH_3)$_2$), 1.08 (d, J = 7.6 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 139.8, 137.9, 135.2, 133.6, 132.8, 130.4, 129.0, 128.8, 128.5, 127.5, 126.0, 125.6, 125.1, 65.1, 18.1, 18.0, 13.7. HRMS (EI) m/z: [M]$^+$ calcd for $C_{23}H_{27}ClOSi$, 382.1520; found, 382.1519.

*3-(4-Cyanophenyl)-1,1-diisopropyl-1-silabenzo[d,e]-isochromane (**3ae**).* **3ae** (23.4 mg, 63%) was obtained as a white powder from the reaction using **1a** (24.1 mg, 99.4 μmol) and 4-formylbenzonitrile (**2e**). Mp: 146−147 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.96 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H, Ar), 7.80 (d, J = 8.0 Hz, 1H, Ar), 7.70−7.64 (m, 3H, Ar), 7.56 (dd, J = 8.0 Hz, J = 6.4 Hz, 1H, Ar), 7.46−7.43 (m, 2H, Ar), 7.32 (dd, J = 8.0 Hz, J = 7.2 Hz, 1H, Ar), 6.75 (dt, J = 7.2 Hz, J = 1.2 Hz, 1H, Ar), 6.42 (s, 1H, OCHAr), 1.37 (sept, J = 7.6 Hz, 1H, CH(CH$_3$)$_2$), 1.18 (sept, J = 7.6 Hz, 1H, CH(CH$_3$)$_2$), 1.098 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$), 1.090 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$), 0.99 (d, J = 7.2 Hz, 3H, CH(CH_3)$_2$), 0.89 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 150.0, 137.1, 135.8, 133.4, 132.3, 130.5, 129.1, 129.0, 128.8, 125.4, 125.3, 125.0, 119.0, 111.7, 77.6, 18.0, 17.5, 17.4, 17.2, 14.0, 13.1. HRMS (EI) m/z: [M]$^+$ calcd for $C_{24}H_{25}NOSi$, 371.1705; found, 371.1705.

*1,1-Diisopropyl-3-(4-nitrophenyl)-1-silabenzo[d,e]-isochromane (**3af**).* **3af** (19.5 mg, 51%) was obtained as a white powder from the reaction using **1a** (24.0 mg, 99.0 μmol) and 4-nitrobenzaldehyde (**2f**). mp: 130−132 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.25−8.21 (m, 2H, Ar), 7.96 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H, Ar), 7.81 (d, J = 8.8 Hz, 1H, Ar), 7.69 (dd, J = 6.8 Hz, J = 1.6 Hz, 1H, Ar), 7.56 (dd, J = 8.0 Hz, J = 6.4 Hz, 1H, Ar), 7.53−7.49 (m, 2H, Ar), 7.32 (dd, J = 8.4 Hz, J = 7.2 Hz, 1H, Ar), 6.76 (dt, J = 7.2 Hz, J = 1.2 Hz, 1H, Ar), 6.47 (s, 1H, OCHAr), 1.38 (sept, J = 7.6 Hz, 1H, CH(CH$_3$)$_2$), 1.19 (sept, J = 7.6 Hz, 1H, CH(CH$_3$)$_2$), 1.103 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$), 1.095 (d, J = 7.2 Hz, 3H, CH(CH_3)$_2$), 0.99 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$), 0.90 (d, J = 7.2 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 151.8, 147.6, 137.0, 135.8, 133.5, 132.1, 130.5, 129.3, 128.91, 128.87, 125.36, 125.33, 125.0, 123.8, 77.3, 17.98, 17.46, 17.2, 14.0, 13.1. HRMS (EI) m/z: [M]$^+$ calcd for $C_{23}H_{25}NO_3Si$, 391.1604; found, 391.1603.

*1,1-Diisopropyl-3-(2-methylphenyl)-1-silabenzo[d,e]-isochromane (**3ag**).* **3ag** (18.5 mg, 52%) was obtained as a colorless oil accompanied by **4ag** (3.6 mg, 10%) as a white powder from the reaction using **1a** (24.0 mg, 99.0 μmol) and *o*-methylbenzaldehyde (**2g**). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.95 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H, Ar), 7.77 (d, J = 8.0 Hz, 1H, Ar), 7.69 (dd, J = 6.4 Hz, J = 1.2 Hz, 1H, Ar), 7.55 (dd, J = 8.0 Hz, J = 6.4 Hz, 1H, Ar), 7.29 (dd, J = 8.4 Hz, J = 7.2 Hz, 1H, Ar), 7.26−7.24 (m, 2H, Ar), 7.19−7.16 (m, 2H, Ar), 6.76 (dt, J = 7.2 Hz, J = 1.2 Hz, 1H, Ar), 6.56 (s, 1H, OCHAr), 2.38 (s, 3H, ArCH$_3$), 1.41 (sept, J = 7.2 Hz, 1H, CH(CH$_3$)$_2$), 1.19 (sept, J = 7.6 Hz, 1H, CH(CH$_3$)$_2$), 1.165 (d, J = 7.2 Hz, 3H, CH(CH_3)$_2$), 1.158 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$), 1.00 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$), 0.90 (d, J = 7.6 Hz, 3H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 142.2, 138.3, 137.0, 136.4, 133.4, 131.8, 130.7, 130.3, 129.8, 129.0, 128.3, 127.8, 126.2, 125.2, 125.0, 124.7, 19.8, 18.3, 17.7, 17.6, 17.3, 14.2, 13.2. HRMS (EI) m/z: [M]$^+$ calcd for $C_{24}H_{28}OSi$, 360.1909; found, 360.1912.

*Diisopropyl((2-methylphenyl)methoxy)(1-naphthyl)silane (**4ag**).* mp: 44−46 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.32 (d, J = 8.4 Hz, 1H, Ar), 7.90 (d, J = 8.4 Hz, 1H, Ar), 7.85 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 7.79 (dd, J = 6.8 Hz, J = 1.2 Hz, 1H, Ar), 7.60 (d, J = 8.0 Hz, 1H, Ar), 7.50−7.37 (m, 3H, Ar), 7.28−7.23 (m, 1H overlapped by residual protonated CDCl$_3$, Ar), 7.21 (dt, J = 7.6 Hz, J = 1.6 Hz, 1H, Ar), 7.15 (d, J = 6.8 Hz, 1H, Ar), 4.90 (s, 2H, OCH$_2$Ar), 2.24 (s, 3H, ArCH$_3$), 1.57 (sept, J = 7.6 Hz, 2H overlapped by H$_2$O, CH(CH$_3$)$_2$), 1.17 (d, J = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.10 (d, J = 7.2 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 139.1, 138.0, 135.14, 135.11, 133.6, 133.1, 130.3, 129.9, 129.0, 128.9, 127.0, 126.6, 126.0, 125.9, 125.5, 125.1, 64.0, 18.8, 18.2, 18.1, 13.8. HRMS (EI) m/z: [M]$^+$ calcd for $C_{24}H_{30}OSi$, 362.2066; found, 362.2066.

*1,1-Diisopropyl-3-(3-methylphenyl)-1-silabenzo[d,e]-isochromane (**3ah**).* **3ah** (14.4 mg, 40%) was obtained as a white powder accompanied by **4ah** (5.0 mg, 14%) as a white powder from the reaction using **1a** (24.3 mg, 0.100 mmol) and *m*-methylbenzaldehyde (**2h**). mp: 39−40 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.94 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H, Ar), 7.76 (d, J = 8.0 Hz, 1H, Ar), 7.68 (dd, J = 6.8 Hz, J = 1.6 Hz, 1H, Ar), 7.53 (dd, J = 8.4 Hz, J = 6.8 Hz, 1H, Ar), 7.30

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(dd, J = 8.4 Hz, J = 7.2 Hz, 1H, Ar), 7.25 (t, J = 7.6 Hz, 1H, Ar), 7.21 (s, 1H, Ar), 7.14 (d, J = 7.2 Hz, 1H, Ar), 7.10 (d, J = 7.2 Hz, 1H, Ar), 6.83 (dt, J = 7.2 Hz, J = 1.2 Hz, 1H, Ar), 6.35 (s, 1H, OC*H*Ar), 2.36 (s, 3H, $ArCH_3$), 1.37 (sept, J = 7.6 Hz, 1H, $CH(CH_3)_2$), 1.19 (sept, J = 7.6 Hz, 1H, $CH(CH_3)_2$), 1.120 (d, J = 7.6 Hz, 3H, $CH(CH_3)_2$), 1.116 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$), 0.99 (d, J = 7.6 Hz, 3H, $CH(CH_3)_2$), 0.92 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.6, 138.9, 138.0, 136.1, 133.3, 131.7, 130.3, 129.5, 129.2, 128.6, 128.3, 128.2, 125.6, 125.5, 125.1, 125.0, 78.3, 21.6, 18.1, 17.6, 17.5, 17.3, 14.2, 13.2. HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{28}OSi$, 360.1909; found, 360.1909.

*Diisopropyl((3-methylphenyl)methoxy)(1-naphthyl)silane (**4ah**).* mp: 39−40 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.34 (d, J = 8.4 Hz, 1H, Ar), 7.89 (d, J = 8.0 Hz, 1H, Ar), 7.85 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 7.79 (dd, J = 7.2 Hz, J = 1.6 Hz, 1H, Ar), 7.50−7.38 (m, 3H, Ar), 7.28−7.21 (m, 3H overlapped by residual protonated $CDCl_3$, Ar), 7.09 (d, J = 7.6 Hz, 1H, Ar), 4.90 (s, 2H, OCH_2Ar), 2.37 (s, 3H, $ArCH_3$), 1.56 (sept, J = 7.2 Hz, 2H overlapped by H_2O, $CH(CH_3)_2$), 1.16 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$), 1.09 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.2, 137.9, 135.2, 133.6, 133.1, 130.3, 129.1, 128.9, 128.3, 127.8, 127.0, 125.9, 125.5, 125.0, 123.3, 65.8, 21.6, 18.1, 18.0, 13.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{30}OSi$, 362.2066; found, 362.2067.

*1,1-Diisopropyl-3-(1-naphthyl)-1-silabenzo[d,e]-isochromane (**3ai**).* **3ai** (20.8 mg, 53%) was obtained as a colorless oil accompanied by **4ai** (9.1 mg, 23%) as a colorless oil from the reaction using **1a** (24.0 mg, 99.0 μmol) and 1-naphthaldehyde (**2i**). ^1H NMR (C_6D_6, 373 K, 400 MHz): δ 8.42−8.38 (m, 1H, Ar), 7.77 (d, J = 8.0 Hz, 1H, Ar), 7.70−7.56 (m, 4H, Ar), 7.37 (dd, J = 8.0 Hz, J = 6.4 Hz, 1H, Ar), 7.28−7.24 (m, 2H, Ar), 7.13−7.09 (m, 3H, Ar), 7.01 (t, J = 7.6 Hz, 1H, Ar), 6.87 (d, J = 7.2 Hz, 1H, Ar), 1.33 (sept, J = 7.6 Hz, 1H, $CH(CH_3)_2$), 1.16 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$), 1.12 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$), 1.04 (sept, J = 7.2 Hz, 1H, $CH(CH_3)_2$), 0.95 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 0.82 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR (C_6D_6, 373 K, 100 MHz): δ 140.8, 138.8, 137.1, 135.0, 134.2, 132.8, 132.1, 130.7, 130.5, 128.92, 128.89, 128.6, 127.0, 126.4, 126.1, 126.0, 125.8, 125.5, 125.4, 125.2, 18.2, 17.6, 17.3, 14.5, 13.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{28}OSi$, 396.1909; found, 396.1909.

*Diisopropyl((1-naphthyl)methoxy)(1-naphthyl)silane (**4ai**).* ^1H NMR ($CDCl_3$, 400 MHz): δ 8.35 (d, J = 8.4 Hz, 1H, Ar), 7.97−7.94 (m, 1H, Ar), 7.91−7.79 (m, 5H), 7.75 (dd, J = 6.8 Hz, J = 1.2 Hz, 1H, Ar), 7.53−7.42 (m, 5H, Ar), 7.38−7.33 (m, 1H, Ar), 5.40 (s, 2H, OCH_2Ar), 1.62 (sept, J = 7.6 Hz, 2H, $CH(CH_3)_2$), 1.19 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$), 1.13 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.0, 136.5, 135.2, 133.64, 133.61, 133.1, 130.8, 130.3, 129.0, 128.9, 128.7, 127.7, 125.99, 125.96, 125.70, 125.67, 125.5, 125.1, 124.0, 123.4, 64.2, 18.2, 18.1, 13.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{30}OSi$, 398.2066; found, 398.2066.

*1,1-Diisopropyl-3-(2-naphthyl)-1-silabenzo[d,e]-isochromane (**3aj**).* **3aj** (15.8 mg, 40%) was obtained as a white powder accompanied by **4aj** (6.5 mg, 16%) as a colorless oil from the reaction using **1a** (24.1 mg, 99.4 μmol) and 2-naphthaldehyde (**2j**). mp: 150−152 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.96 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H, Ar), 7.87−7.80 (m, 3H, Ar), 7.78 (d, J = 8.0 Hz, 1H, Ar), 7.75 (s, 1H, Ar), 7.70 (dd, J = 7.4 Hz, J = 1.2 Hz, 1H, Ar), 7.58−7.53 (m, 2H, Ar), 7.51−7.46 (m, 2H, Ar), 7.28 (dd, J = 8.4 Hz, J = 7.6 Hz, 1H overlapped by residual protonated $CDCl_3$, Ar), 6.84 (dt, J = 7.6 Hz, J = 1.6 Hz, 1H, Ar), 6.42 (s, 1H, OC*H*Ar), 1.41 (sept, J = 7.6 Hz, 1H, $CH(CH_3)_2$), 1.22 (sept, J = 7.6 Hz, 1H, $CH(CH_3)_2$), 1.15 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$), 1.01 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$), 0.94 (d, J = 7.6 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.0, 138.6, 136.1, 133.4, 133.25, 133.24, 131.8, 130.4, 129.4, 128.5, 128.3, 128.2, 127.9, 127.2, 126.5, 126.2, 126.1, 125.8, 125.1, 125.0, 78.5, 18.1, 17.59, 17.52, 17.3, 14.2, 13.2. HRMS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{28}OSi$, 396.1909; found, 396.1909.

*Diisopropyl((2-naphthyl)methoxy)(1-naphthyl)silane (**4aj**).* ^1H NMR ($CDCl_3$, 400 MHz): δ 8.37 (d, J = 8.4 Hz, 1H, Ar), 7.92−7.80 (m, 7H, Ar), 7.52−7.43 (m, 5H, Ar), 7.41−7.36 (m, 1H, Ar), 5.09 (s, 2H, OCH_2Ar), 1.60 (sept, J = 7.6 Hz, 2H, $CH(CH_3)_2$), 1.19 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$), 1.12 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.8, 137.9, 135.2, 133.62, 133.57, 133.0, 132.9, 130.3, 129.0, 128.9, 128.1, 128.0, 127.8, 126.1, 126.0, 125.7, 125.6, 125.1, 124.8, 124.6, 66.0, 18.2, 18.1, 13.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{30}OSi$, 398.2066; found, 398.2066.

*1,1-Diisopropyl-3-thiophenyl-1-silabenzo[d,e]-isochromane (**3ak**).* **3ak** (4.2 mg, 12%) was obtained as a white powder from the reaction using **1a** (23.9 mg, 98.6 μmol) and 3-thiophenecarbaldehyde (**2k**). mp: 50−51 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.94 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H, Ar), 7.79 (d, J = 8.0 Hz, 1H, Ar), 7.63 (dd, J = 6.4 Hz, J = 1.2 Hz, 1H, Ar), 7.52 (dd, J = 8.0 Hz, J = 6.4 Hz, 1H, Ar), 7.38 (dd, J = 8.0 Hz, J = 7.2 Hz, 1H, Ar), 7.27 (dd, J = 4.8 Hz, J = 2.8 Hz, 1H, Ar), 7.12 (dd, J = 4.8 Hz, J = 1.2 Hz, 1H, Ar), 7.07 (dt, J = 7.2 Hz, J = 1.2 Hz, 1H, Ar), 6.79 (dt, J = 2.8 Hz, J = 1.2 Hz, 1H, Ar), 6.49 (s, 1H, OC*H*Ar), 1.30 (sept, J = 7.2 Hz, 1H, $CH(CH_3)_2$), 1.07 (sept, J = 7.2 Hz, 1H, $CH(CH_3)_2$), 1.04 (d, J = 7.6 Hz, 3H, $CH(CH_3)_2$), 1.01 (d, J = 7.6 Hz, 3H, $CH(CH_3)_2$), 0.98 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 0.83 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8, 135.7, 133.4, 131.7, 130.2, 129.4, 128.4, 128.0, 125.9, 125.1, 125.0, 123.1, 74.3, 17.9, 17.5, 17.3, 17.1, 13.9, 13.3. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{24}OSSi$, 352.1317; found, 352.1313.

*3-n-Butyl-1,1-diisopropyl-1-silabenzo[d,e]isochromane (**3al**).* **3al** (7.2 mg, 22%) was obtained as a colorless oil from the reaction using **1a** (24.0 mg, 99.0 μmol) and pentanal (**2l**). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H, Ar), 7.73 (d, J = 8.0 Hz, 1H, Ar), 7.59 (dd, J = 6.8 Hz, J = 1.6 Hz, 1H, Ar), 7.48 (dd, J = 8.4 Hz, J = 6.8 Hz, 1H, Ar), 7.41 (dd, J = 8.4 Hz, J = 7.2 Hz, 1H, Ar), 7.26−7.23 (m, 1H overlapped by residual protonated $CDCl_3$, Ar), 5.29 (dd, J = 8.8 Hz, J = 4.4 Hz, 1H, OC*H*Ar), 1.88−1.73 (m, 2H, *n*-Bu), 1.62−1.58 (m, 1H overlapped by H_2O, *n*-Bu), 1.48−1.16 (m, 5H, *n*-Bu and *i*-Pr), 1.19 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$), 1.13 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$), 0.92 (d, J = 7.6 Hz, 3H, $CH(CH_3)_2$), 0.90 (t, J = 7.2 Hz, 3H, *n*-Bu), 0.84 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.0, 135.2, 133.4, 131.4, 130.1, 129.0, 127.6, 125.1, 124.9, 123.3, 76.8, 41.4, 28.6, 22.7, 17.8, 17.6, 17.31, 17.27, 14.3, 13.9, 13.5. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{30}OSi$, 326.2066; found, 326.2064.

*3-sec-Butyl-1,1-diisopropyl-1-silabenzo[d,e]isochromane (**3am**).* **3am** (10.2 mg, 31%) was obtained with d.r. = 2.8:1 as a colorless oil accompanied by **5am** (4.7 mg, 14%) with d.r. = 1.6:1 as a colorless oil from the reaction using **1a** (24.2 mg, 99.8 μmol) and 3-methylbutanal (**2m**). HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{30}OSi$, 326.2066; found, 326.2066. Major

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diastereomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 7.73 (d, J = 8.0 Hz, 1H, Ar), 7.58 (dd, J = 6.8 Hz, J = 1.6 Hz, 1H, Ar), 7.49−7.39 (m, 2H, Ar), 7.29 (dt, J = 7.2 Hz, J = 1.2 Hz, 1H, Ar), 5.34 (d, J = 3.6 Hz, 1H, OC*H*Ar), 2.04−1.98 (m, 1H, *sec*-Bu), 1.62−1.51 (m, 1H overlapped by H_2O, *sec*-Bu), 1.45−1.25 (m, 3H, *sec*-Bu and *i*-Pr), 1.15 (d, J = 7.6 Hz, 3H, *i*-Pr), 1.10 (d, J = 7.2 Hz, 3H, *i*-Pr), 0.97 (t, J = 7.2 Hz, 3H, *sec*-Bu), 0.94 (d, J = 7.6 Hz, 3H, *i*-Pr), 0.91 (d, J = 7.6 Hz, 3H, *i*-Pr), 0.82 (d, J = 6.4 Hz, 3H, *sec*-Bu). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.8, 136.6, 133.42, 131.2, 130.2, 129.49, 127.6, 125.0, 124.7, 123.3, 78.1, 42.6, 27.2, 17.93, 17.88, 17.43, 17.39, 14.3, 13.6, 13.1, 12.3. Minor diastereomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 7.73 (d, J = 8.0 Hz, 1H, Ar), 7.58 (dd, J = 6.8 Hz, J = 1.6 Hz, 1H, Ar), 7.49−7.39 (m, 2H, Ar), 7.26−7.23 (m, 1H overlapped by residual protonated $CDCl_3$, Ar), 5.12 (d, J = 5.2 Hz, 1H, OC*H*Ar), 1.92−1.85 (m, 1H, *sec*-Bu), 1.62−1.51 (m, 1H overlapped by H_2O, *sec*-Bu), 1.40−1.18 (m, 3H, *sec*-Bu and *i*-Pr), 1.21 (d, J = 7.2 Hz, 3H, *i*-Pr), 1.14 (d, J = 7.2 Hz, 3H, *i*-Pr), 0.89 (d, J = 7.2 Hz, 3H, *i*-Pr), 0.85 (t, J = 7.6 Hz, 3H, *sec*-Bu), 0.85 (d, J = 6.8 Hz, 3H, *sec*-Bu), 0.80 (d, J = 7.6 Hz, 3H, *i*-Pr). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.4, 136.2, 133.38, 131.3, 130.1, 129.40, 127.7, 124.85, 124.79, 123.8, 80.9, 43.1, 23.8, 17.9, 17.7, 17.43, 17.33, 16.8, 14.2, 13.3, 11.9.

1-(Diisopropyl(1-naphthyl)silyloxy)-3-methyl-1-butene (***5am***). HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{30}OSi$, 326.2066; found, 326.2065. Major diastereomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21−8.18 (m, 1H, Ar), 7.89 (d, J = 8.4 Hz, 1H, Ar), 7.86−7.83 (m, 1H, Ar), 7.79−7.75 (m, 1H, Ar), 7.50−7.44 (m, 3H, Ar), 6.24−6.22 (m, 1H, C═CH), 1.89 (q, J = 7.2 Hz, 2H, CH_2CH_3), 1.75 (d, J = 1.2 Hz, 3H, C═CCH_3), 1.56−1.47 (m, 2H, *i*-Pr), 1.132 (d, J = 7.2 Hz, 6H, *i*-Pr), 1.041 (d, J = 7.2 Hz, 6H, *i*-Pr), 0.95 (t, J = 7.6 Hz, 3H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 135.13, 134.0, 133.6, 132.8, 130.4, 129.0, 128.9, 125.89, 125.5, 125.0, 118.9, 27.0, 17.91, 17.7, 13.82, 13.4, 12.8. Minor diastereomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21−8.18 (m, 1H, Ar), 7.89 (d, J = 8.4 Hz, 1H, Ar), 7.86−7.83 (m, 1H, Ar), 7.79−7.75 (m, 1H, Ar), 7.50−7.44 (m, 3H, Ar), 6.17−6.16 (m, 1H, C═CH), 2.27 (q, J = 7.6 Hz, 2H, CH_2CH_3), 1.56−1.47 (m, 5H, C═CCH_3 and *i*-Pr), 1.127 (d, J = 7.2 Hz, 6H, *i*-Pr), 1.08−1.02 (m, 9H, *i*-Pr and CH_2CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 135.11, 133.6, 133.5, 132.8, 130.4, 129.0, 128.9, 125.91, 125.5, 125.0, 118.5, 22.0, 17.89, 17.7, 16.7, 13.77, 12.3.

3-tert-Butyl-1,1-diisopropyl-1-silabenzo[d,e]isochromane (***3an***). **3an** (9.2 mg, 28%) was obtained as a colorless oil accompanied by **4an** (5.0 mg, 15%) as a colorless oil from the reaction using **1a** (24.2 mg, 99.8 μmol) and 2,2-dimethylpropanal (**2n**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H, Ar), 7.73 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H, Ar), 7.57 (dd, J = 6.4 Hz, J = 1.2 Hz, 1H, Ar), 7.44 (dd, J = 8.0 Hz, J = 6.4 Hz, 1H, Ar), 7.38 (dd, J = 8.0 Hz, J = 7.2 Hz, 1H, Ar), 6.76 (dt, J = 7.2 Hz, J = 1.2 Hz, 1H, Ar), 5.06 (s, 1H, OC*H*Ar), 1.51 (sept, J = 7.6 Hz, 1H, $CH(CH_3)_2$), 1.37 (d, J = 7.6 Hz, 3H, $CH(CH_3)_2$), 1.33 (d, J = 7.6 Hz, 3H, $CH(CH_3)_2$), 1.07 (sept, J = 7.6 Hz, 1H, $CH(CH_3)_2$), 0.79 (s, 9H, *t*-Bu), 0.66 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$), 0.57 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.8, 135.9, 132.8, 130.9, 129.7, 129.6, 127.8, 125.7, 124.6, 124.0, 86.0, 38.8, 27.0, 18.4, 18.0, 17.44, 17.40, 14.5, 13.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{30}OSi$, 326.2066; found, 326.2066.

Diisopropyl(2,2-dimethylpropoxy)(1-naphthyl)silane (***4an***). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38−8.34 (m, 1H, Ar), 7.88−7.82 (m, 2H, Ar), 7.76 (dd, J = 6.8 Hz, J = 1.2 Hz, 1H, Ar), 7.49−7.44 (m, 3H, Ar), 3.48 (s, 2H, OCH_2*t*-Bu), 1.49 (sept, J = 7.6 Hz, 2H, $CH(CH_3)_2$), 1.13 (d, J = 7.2 Hz, 6H, $CH(CH_3)_2$), 1.06 (d, J = 7.2 Hz, 6H, $CH(CH_3)_2$), 0.99 (s, 9H, *t*-Bu). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.0, 134.9, 133.9, 133.5, 130.0, 129.4, 128.8, 125.6, 125.4, 125.0, 74.1, 33.4, 26.6, 18.2, 18.0, 13.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{32}OSi$, 328.2222; found, 328.2222.

3-Cyclohexyl-1,1-diisopropyl-1-silabenzo[d,e]-isochromane (***3ao***). **3ao** (9.0 mg, 26%) was obtained as a colorless oil accompanied by **5ao** (2.7 mg, 7.7%) as a colorless oil from the reaction using **1a** (23.9 mg, 98.6 μmol) and cyclohexanecarbaldehyde (**2o**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H, Ar), 7.73 (d, J = 8.0 Hz, 1H, Ar), 7.58 (dd, J = 6.8 Hz, J = 1.6 Hz, 1H, Ar), 7.48 (dd, J = 8.0 Hz, J = 6.4 Hz, 1H, Ar), 7.40 (dd, J = 8.0 Hz, J = 6.8 Hz, 1H, Ar), 7.22 (dt, J = 7.2 Hz, J = 1.2 Hz, 1H, Ar), 5.00 (d, J = 6.0 Hz, 1H, OC*H*Ar), 1.91−1.87 (m, 1H, Cy), 1.72−1.60 (m, 4H, Cy), 1.36 (sept, J = 7.6 Hz, 1H, $CH(CH_3)_2$), 1.26−1.11 (m, 13H, Cy and *i*-Pr), 0.87 (d, J = 7.6 Hz, 3H, $CH(CH_3)_2$), 0.74 (d, J = 7.2 Hz, 3H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.8, 136.0, 133.3, 131.3, 130.1, 129.3, 127.7, 124.82, 124.76, 124.1, 81.3, 46.3, 30.8, 28.3, 26.63, 26.58, 26.3, 18.0, 17.6, 17.4, 17.3, 14.1, 13.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{32}OSi$, 352.2222; found, 352.2222.

(Cyclohexylidenemethoxy)(diisopropyl) (1-naphthyl)-silane (***5ao***). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21−8.18 (m, 1H, Ar), 7.89 (d, J = 8.4 Hz, 1H, Ar), 7.86−7.83 (m, 1H, Ar), 7.77 (dd, J = 7.2 Hz, J = 1.6 Hz, 1H, Ar), 7.50−7.45 (m, 3H, Ar), 6.19−6.17 (m, 1H, C═CH), 2.38−2.34 (m, 2H, Cy), 1.93−1.89 (m, 2H, Cy), 1.57−1.44 (m, 8H overlapped by H_2O, Cy and *i*-Pr), 1.13 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$), 1.04 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.7, 135.2, 133.6, 132.7, 131.5, 130.4, 129.1, 128.9, 125.9, 125.5, 125.0, 121.1, 30.7, 28.6, 27.22, 27.17, 25.7, 17.9, 17.7, 13.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{32}OSi$, 352.2222; found, 352.2222.

Alternative Synthesis of ***4ae, 4af,*** *and* ***4ak.*** To 1-bromonaphthalene (0.50 g, 2.4 mmol) in Et_2O (5 mL) was added 1.6 M *t*-BuLi pentane solution (3.0 mL, 4.8 mmol) at −80 °C, and the solution was warmed to room temperature. After dichlorodiisopropylsilane (0.44 g, 2.4 mmol) was added to the reaction mixture at −80 °C, it was gradually warmed to room temperature and stirred for a day. After filtration, volatiles were removed from the filtrate under reduced pressure to obtain chlorodiisopropyl(1-naphthyl)silane which was used for the following reactions without further purification. To chlorodiisopropyl(1-naphthyl)silane (0.20 mmol) in CH_2Cl_2 (3 mL) was added an alcohol (0.30 mmol), triethylamine (40 μL, 0.29 mmol), and 4-dimethylaminopyridine (DMAP, 2.4 mg, 20 μmol), and the solution was stirred overnight at room temperature. The reaction mixture was quenched with 1 M HCl and then the organic layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure to remove the volatiles. The crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 10/1). Further purification was carried out by GPLC to obtain each of the products.

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*((4-Cyanophenyl)methoxy)diisopropyl(1-naphthyl)silane (**4ae**).* **4ae** (35.8 mg, 50%) was obtained as a colorless oil from the reaction using chlorodiisopropyl(1-naphthyl)silane (52.8 mg, 0.191 mmol) and 4-hydroxymethylbenzonitrile. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (d, J = 8.4 Hz, 1H, Ar), 7.91 (d, J = 8.0 Hz, 1H, Ar), 7.86 (dd, J = 8.0 Hz, J = 1.2 Hz, 1H, Ar), 7.76 (dd, J = 6.8 Hz, J = 1.6 Hz, 1H, Ar), 7.66 (d, J = 8.4 Hz, 2H, Ar), 7.53−7.44 (m, 4H, Ar), 7.38 (ddd, J = 8.1 Hz, J = 6.8 Hz, J = 1.6 Hz, 1H, Ar), 4.95 (s, 2H, OCH_2Ar), 1.58 (sept, J = 7.6 Hz, 2H overlapped by H_2O, $CH(CH_3)_2$), 1.17 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$), 1.10 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.8, 137.8, 135.2, 133.6, 132.4, 132.3, 130.6, 129.1, 128.6, 126.5, 126.1, 125.6, 125.1, 119.2, 110.8, 65.1, 18.1, 18.0, 13.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{27}NOSi$, 373.1862; found, 373.1861.

*Diisopropyl(1-naphthyl)((4-nitrophenyl)methoxy)silane (**4af**).* **4af** (44.8 mg, 62%) was obtained as a colorless oil from the reaction using chlorodiisopropyl(1-naphthyl)silane (54.9 mg, 0.198 mmol) and (4-nitrophenyl)methanol. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25−8.21 (m, 3H, Ar), 7.92 (d, J = 8.0 Hz, 1H, Ar), 7.87 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 7.77 (dd, J = 7.2 Hz, J = 1.6 Hz, 1H, Ar), 7.57 (d, J = 8.8 Hz, 2H, Ar), 7.51−7.44 (m, 2H, Ar), 7.38 (ddd, J = 8.4 Hz, J = 6.4 Hz, J = 1.2 Hz, 1H, Ar), 4.99 (s, 2H, OCH_2Ar), 1.60 (sept, J = 7.6 Hz, 2H overlapped by H_2O, $CH(CH_3)_2$), 1.18 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$), 1.11 (d, J = 7.2 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.8, 147.2, 137.8, 135.2, 133.6, 132.3, 130.6, 129.1, 128.5, 126.5, 126.1, 125.7, 125.1, 123.7, 65.0, 18.1, 18.0, 13.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{27}NO_3Si$, 393.1760; found, 393.1761.

*Diisopropyl(1-naphthyl)((3-thienyl)methoxy)silane (**4ak**).* **4ak** (18.4 mg, 27%) was obtained as a colorless oil from the reaction using chlorodiisopropyl(1-naphthyl)silane (53.1 mg, 0.192 mmol) and 3-thienylmethanol. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.33 (d, J = 8.0 Hz, 1H, Ar), 7.90 (d, J = 8.4 Hz, 1H, Ar), 7.86 (dd, J = 7.6 Hz, J = 2.0 Hz, 1H, Ar), 7.79 (dd, J = 7.2 Hz, J = 1.6 Hz, 1H, Ar), 7.50−7.40 (m, 3H, Ar), 7.31 (dd, J = 5.2 Hz, J = 2.8 Hz, 1H, Ar), 7.26−7.24 (m, 1H, Ar), 7.09 (dd, J = 5.2 Hz, J = 1.6 Hz, 1H, Ar), 4.92 (d, J = 1.2 Hz, 2H, OCH_2Ar), 1.55 (sept, J = 7.6 Hz, 2H overlapped by H_2O, $CH(CH_3)_2$), 1.16 (d, J = 7.2 Hz, 6H, $CH(CH_3)_2$), 1.09 (d, J = 7.6 Hz, 6H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.7, 137.9, 135.2, 133.6, 133.0, 130.3, 129.0, 128.9, 126.4, 125.9, 125.8, 125.5, 125.0, 120.8, 62.4, 18.1, 18.0, 13.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{26}OSSi$, 354.1474; found, 354.1473.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06228.

Crystallographic data for **3ad** and NMR spectra of **1**, **3**, **4**, and **5** (PDF)

Accession Codes

CCDC 2112414 contains the supplementary crystallographic data for compound **3ad** in this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

■ AUTHOR INFORMATION

Corresponding Author

Takayuki Kawashima − *Graduate School of Science and Technology, Gunma University, Kiryu 376-8515 Gunma, Japan*; Email: kawashima.t@gunma-u.ac.jp

Authors

Hidekazu Arii − *Faculty of Education, University of Miyazaki, Miyazaki 889-2192, Japan*; orcid.org/0000-0003-3707-7565

Kenichi Nakao − *Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Nagoya 466-8555, Japan*

Hideki Masuda − *Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Nagoya 466-8555, Japan*; orcid.org/0000-0002-1235-1129

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c06228

Notes

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■ REFERENCES

(1) (a) Lambert, J. B.; Kania, L.; Zhang, S. Modern Approaches to Silylium Cations in Condensed Phase. *Chem. Rev.* **1995**, *95*, 1191−1201. (b) Reed, C. A. The Silylium Ion Problem, R_3Si^+. Bridging Organic and Inorganic Chemistry. *Acc. Chem. Res.* **1998**, *31*, 325−332. (c) Klare, H. F. T.; Albers, L.; Süsse, L.; Keess, S.; Müller, T.; Oestreich, M. Silylium Ions: From Elusive Reactive Intermediates to Potent Catalysts. *Chem. Rev.* **2021**, *121*, 5889−5985.

(2) (a) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. Crystal Structure of a Silyl Cation with No Coordination to Anion and Distant Coordination to Solvent. *Science* **1993**, *260*, 1917−1918. (b) Ibad, M. F.; Langer, P.; Schulz, A.; Villinger, A. Silylium-Arene Adducts: An Experimental and Theoretical Study. *J. Am. Chem. Soc.* **2011**, *133*, 21016−21027. (c) Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. The Silylium Ion (R_3Si^+) Problem: Effect of Alkyl Substituents R. *Organometallics* **1995**, *14*, 3933−3941. (d) Müller, T.; Juhasz, M.; Reed, C. A. The X-ray Structure of a Vinyl Cation. *Angew. Chem., Int. Ed.* **2004**, *43*, 1543−1546. (e) Omann, L.; Qu, Z. W.; Irran, E.; Klare, H. F. T.; Grimme, S.; Oestreich, M. Electrophilic Formylation of Arenes by Silylium Ion Mediated Activation of Carbon Monoxide. *Angew. Chem., Int. Ed.* **2018**, *57*, 8301−8305.

(3) (a) Schäfer, A.; Saak, W.; Haase, D.; Müller, T. Silyl Cation Mediated Conversion of CO_2 into Benzoic Acid, Formic Acid, and Methanol. *Angew. Chem., Int. Ed.* **2012**, *51*, 2981−2984. (b) Konno, M.; Chiba, M.; Nemoto, K.; Hattori, T. Electrophilic Aromatic Substitution of Arenes with CO_2 Mediated by $R_3SiB(C_6F_5)_4$. *Chem. Lett.* **2012**, *41*, 913−914. (c) von Wolff, N.; Lefèvre, G.; Berthet, J.-C.; Thuéry, P.; Cantat, T. Implications of CO_2 Activation by Frustrated Lewis Pairs in the Catalytic Hydroboration of CO_2: A View Using N/Si^+ Frustrated Lewis Pairs. *ACS Catal.* **2016**, *6*, 4526−4535.

(4) (a) Roy, A.; Bonetti, V.; Wang, G.; Wu, Q.; Klare, H. F. T.; Oestreich, M. Silylium-Ion-Promoted Ring-Opening Hydrosilylation and Disilylation of Unactivated Cyclopropanes. *Org. Lett.* **2020**, *22*,

1213−1216. (b) He, T.; Wang, G.; Bonetti, V.; Klare, H. F. T.; Oestreich, M. Silylium-Ion-Promoted (5+1) Cycloaddition of Aryl-Substituted Vinylcyclopropanes and Hydrosilanes Involving Aryl Migration. *Angew. Chem., Int. Ed.* **2020**, *59*, 12186−12191. (c) He, T.; Wang, G.; Long, P.-W.; Kemper, S.; Irran, E.; Klare, H. F. T.; Oestreich, M. Intramolecular Friedel-Crafts alkylation with a silylium-ion-activated cyclopropyl group: formation of tricyclic ring systems from benzyl-substituted vinylcyclopropanes and hydrosilanes. *Chem. Sci.* **2021**, *12*, 569−575.

(5) Müther, K.; Mohr, J.; Oestreich, M. Silylium Ion Promoted Reduction of Imines with Hydrosilanes. *Organometallics* **2013**, *32*, 6643−6646.

(6) (a) Furukawa, S.; Kobayashi, J.; Kawashima, T. Development of a Sila-Friedel−Crafts Reaction and Its Application to the Synthesis of Dibenzosilole Derivatives. *J. Am. Chem. Soc.* **2009**, *131*, 14192−14193. (b) Chen, Q.-A.; Klare, H. F. T.; Oestreich, M. Brønsted Acid-Promoted Formation of Stabilized Silylium Ions for Catalytic Friedel-Crafts C-H Silylation. *J. Am. Chem. Soc.* **2016**, *138*, 7868−7871.

(7) (a) Douvris, C.; Ozerov, O. V. Hydrodefluorination of Perfluoroalkyl Groups Using Silylium-Carborane Catalysts. *Science* **2008**, *321*, 1188−1190. (b) Douvris, C.; Nagaraja, C. M.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. Hydrodefluorination and Other Hydrodehalogenation of Aliphatic Carbon−Halogen Bonds Using Silylium Catalysis. *J. Am. Chem. Soc.* **2010**, *132*, 4946−4953. (c) Allemann, O.; Duttwyler, S.; Romanato, P.; Baldridge, K. K.; Siegel, J. S. Proton-Catalyzed, Silane-Fueled Friedel-Crafts Coupling of Fluoroarenes. *Science* **2011**, *332*, 574−577. (d) Klare, H. F. T. Catalytic C-H Arylation of Unactivated C-H Bonds by Silylium Ion-Promoted C(sp^2)-F Bond Activation. *ACS Catal.* **2017**, *7*, 6999−7002.

(8) Kira, M.; Hino, T.; Sakurai, H. Siloxycarbenium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borates and Their Role in Reactions of Ketones with Nucleophiles. *Chem. Lett.* **1992**, *21*, 555−558.

(9) Müther, K.; Oestreich, M. Self-Regeneration of a Silylium Ion Catalyst in Carbonyl Reduction. *Chem. Commun.* **2011**, *47*, 334−336.

(10) (a) Parks, D. J.; Piers, W. E. Tris(pentafluorophenyl)boron-Catalyzed Hydrosilation of Aromatic Aldehydes, Ketones, and Esters. *J. Am. Chem. Soc.* **1996**, *118*, 9440−9441. (b) Parks, D. J.; Blackwell, J. M.; Piers, W. E. Studies on the Mechanism of $B(C_6F_5)_3$-Catalyzed Hydrosilation of Carbonyl Functions. *J. Org. Chem.* **2000**, *65*, 3090−3098.

(11) Rendler, S.; Oestreich, M. Conclusive Evidence for an S_N2-Si Mechanism in the $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Carbonyl Compounds: Implications for the Related Hydrogenation. *Angew. Chem., Int. Ed.* **2008**, *47*, 5997−6000.

(12) (a) Johannsen, M.; Jørgensen, K. A.; Helmchen, G. Synthesis and Application of the First Chiral and Highly Lewis Acidic Silyl Cationic Catalyst. *J. Am. Chem. Soc.* **1998**, *120*, 7637−7638. (b) Hara, K.; Akiyama, R.; Sawamura, M. Strong Counteranion Effects on the Catalytic Activity of Cationic Silicon Lewis Acids in Mukaiyama Aldol and Diels−Alder Reactions. *Org. Lett.* **2005**, *7*, 5621−5623. (c) Klare, H. F. T.; Bergander, K.; Oestreich, M. Taming the Silylium Ion for Low-Temperature Diels-Alder Reactions. *Angew. Chem., Int. Ed.* **2009**, *48*, 9077−9079. (d) Schmidt, R. K.; Müther, K.; Mück-Lichtenfeld, C.; Grimme, S.; Oestreich, M. Silylium Ion-Catalyzed Challenging Diels-Alder Reactions: The Danger of Hidden Proton Catalysis with Strong Lewis Acids. *J. Am. Chem. Soc.* **2012**, *134*, 4421−4428. (e) Sakaguchi, Y.; Iwade, Y.; Sekikawa, T.; Minami, T.; Hatanaka, Y. Chiral silicon Lewis acids having a pentacoordinate stereogenic silicon center: ^{29}Si NMR studies and application to asymmetric Diels-Alder reactions. *Chem. Commun.* **2013**, *49*, 11173−11175. (f) Gatzenmeier, T.; Turberg, M.; Yepes, D.; Xie, Y.; Neese, F.; Bistoni, G.; List, B. Scalable and Highly Diastereo- and Enantioselective Catalytic Diels-Alder Reaction of α,β-Unsaturated Methyl Esters. *J. Am. Chem. Soc.* **2018**, *140*, 12671−12676.

(13) (a) Tap, A.; Blond, A.; Wakchaure, V. N.; List, B. Chiral Allenes via Alkynylogous Mukaiyama Aldol Reaction. *Angew. Chem., Int. Ed.* **2016**, *55*, 8962−8965. (b) Bae, H. Y.; Höfler, D.; Kaib, P. S. J.; Kasaplar, P.; De, C. K.; Döhring, A.; Lee, S.; Kaupmees, K.; Leito, I.; List, B. Approaching sub-ppm-level asymmetric organocatalysis of a highly challenging and scalable carbon-carbon bond forming reaction. *Nat. Chem.* **2018**, *10*, 888−894.

(14) (a) Arii, H.; Kurihara, T.; Mochida, K.; Kawashima, T. Silylium Ion-promoted Dehydrogenative Cyclization: Synthesis of Silicon-containing Compounds Derived from Alkynes. *Chem. Commun.* **2014**, *50*, 6649−6652. (b) Arii, H.; Yano, Y.; Nakabayashi, K.; Yamaguchi, S.; Yamamura, M.; Mochida, K.; Kawashima, T. Regioselective and Stereospecific Dehydrogenative Annulation Utilizing Silylium Ion-Activated Alkenes. *J. Org. Chem.* **2016**, *81*, 6314−6319.

(15) Using benzyldiisopropylsilane (**1d**), which we used often in the previous papers,[14] instead of **1a** and benzaldehyde (**2a**), the corresponding annulation product, 3,3-diisopropyl-1-phenyl-3-silaisochromane (**3da**), was obtained in 8.0% isolated yield accompanied with the hydrosilylation product, benzyl(benzyloxy)diisopropylsilane (**4da**), in 44% yield.

(16) Rubin, M.; Schwier, T.; Gevorgyan, V. Highly Efficient $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Olefins. *J. Org. Chem.* **2002**, *67*, 1936−1940.

(17) Habibi-Yangjeh, A.; Danandeh-Jenagharad, M.; Nooshyar, M. Prediction Acidity Constant of Various Benzoic Acids and Phenols in Water Using Linear and Nonlinear QSPR Models. *Bull. Korean Chem. Soc.* **2005**, *26*, 2007−2016.

(18) Ihara, E.; Young, V. G., Jr.; Jordan, R. F. Cationic Aluminum Alkyl Complexes Incorporating Aminotroponiminate Ligands. *J. Am. Chem. Soc.* **1998**, *120*, 8277−8278.

(19) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176−2179.

(20) Sheldrick, G. M. SHELXT- Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3−8.

(21) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71*, 3−8.

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