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Syntheses of substituted benzosiloles and siloles by diisobutylaluminium hydride-promoted cyclization of 1-silyl-2-(2-silylethynyl)benzenes and 1,4-disilylalk-3-en-1-ynes

Hidenori Kinoshita*, Hiroki Fukumoto, Akihiro Ueda, Katsukiyo Miura**

Department of Applied Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-ohkubo, Sakura-ku, Saitama 338-8570, Japan

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ABSTRACT

An efficient method for preparing substituted benzosiloles and unsymmetrically substituted siloles by intramolecular C-Si bond formation has been developed. The reaction of 1-methoxysilyl-2-[2-(trimethylsilyl)ethynyl]benzenes with 1.5 equiv of diisobutylaluminium hydride (DIBAL-H) gave benzosiloles in good to high yields. Similarly 4-methoxysilyl-1-silylalk-3-en-1-ynes were cyclized to multisubstituted siloles. Mechanistic study of this transformation uncovered that the methoxysilyl group was initially converted into the corresponding hydrosilyl group by the action of DIBAL-H, and that the resultant hydrosilanes underwent the DIBAL-H-promoted cyclization to benzosiloles. When 1-hydrosilyl-2-[2-(trimethylsilyl)ethynyl]benzenes were used as substrates, a substoichiometric amount of DIBAL-H was enough for the cyclization. The DIBAL-H-promoted transformation could be applied to regio-defined synthesis of unsymmetrically substituted siloles from 4-hydrosilyl-1-silylalk-3-en-1-ynes. This pre-installation approach provides a straightforward access to multisubstituted siloles with complete regioselection.

1. Introduction

Siloles and benzosiloles are cyclic organosilicon compounds having a silicon-bridged π-electron system. Their physical and chemical properties are intriguingly different from their carbon analogues, cyclopentadienes and indenes. Especially, they show beneficial photo- and electro-physical properties due to their unique electronic structures.[1,2] Therefore much attention has been paid for their use as electroluminescence and electron-transporting materials.[3] In this context, synthetic methods for siloles[4] and benzosiloles[5] have also been investigated intensively so far. The main approaches for silole ring construction can be classified into four types (Scheme 1): (a) intermolecular double C-Si bond formation, (b) intermolecular C-Si and C-C bond formation, (c) intramolecular C-Si bond formation, and (d) intramolecular C-C bond formation. The reaction of dichlorosilanes with 1,4-dimetallated π-conjugated compounds (eq. (1)) is a conventional method categorized as type (a).[6,7] A variety of silole rings are accessible by this method. As another example of type (a), the Ru–catalyzed double *trans*-hydrosilylation of 1,3-dienynes with dihydrosilanes is useful for the synthesis of 2,5-disubstituted siloles (eq. (2)).[8] The approach of type (b) is represented by catalytic cycloadditions between alkynes and organosilicon reagents. For instance, the Rh-[9] and Pd-catalyzed[10] reactions of internal alkynes with *o*-functionalized (trimethylsilyl)benzenes via sp^3-C-Si bond activation provide a convenient access to 2,3-disubstituted benzosiloles (eq. (3)). The transition metal-catalyzed [2 + 2+1] cycloadditions of silylene equivalents to alkynes also yield substituted siloles (eq. (4)).[11] The silole construction of type (c), which is frequently used for the synthesis of benzosiloles and dibenzosiloles, includes intramolecular hydrosilylation,[8] KH-promoted cyclization,[12] and tin-mediated cyclization[13] of alkynylated hydrosilanes (eq. (5)) and dehydrogenative coupling between Si-H and aryl C-H bonds[14,15] (eq. (6)). For the silole ring construction of type (d), reductive coupling of diynes (eq. (7))[16] and intramolecular coupling of 2-(arylsilyl)aryl triflates (eq. (8))[17] can be effectively utilized. Additionally, benzosilole syntheses by ring-closing alkene metathesis[18] and *anti*-hydroarylation via ortho-C-H activation[19] are known as an

* Corresponding author.
** Corresponding author.
E-mail addresses: hkino@mail.saitama-u.ac.jp (H. Kinoshita), kmiura@apc.saitama-u.ac.jp (K. Miura).

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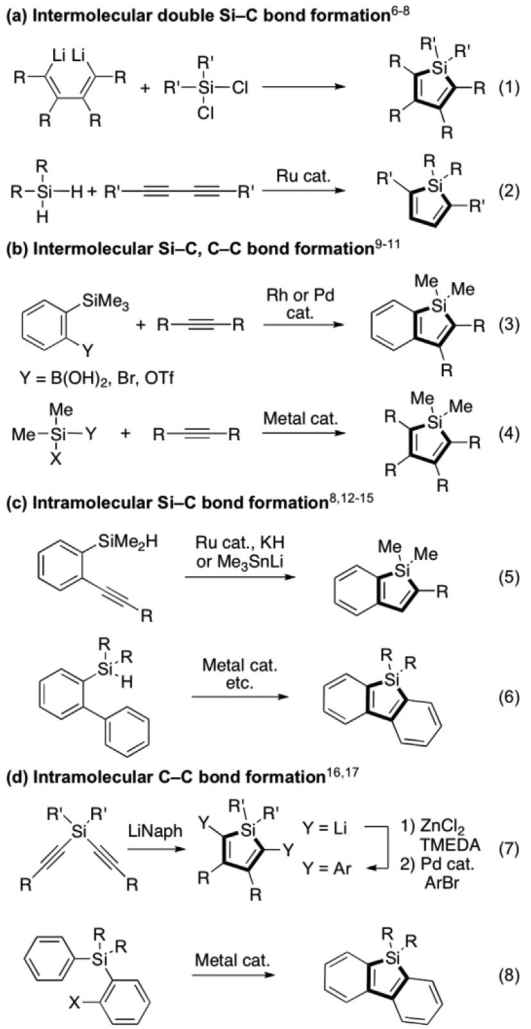


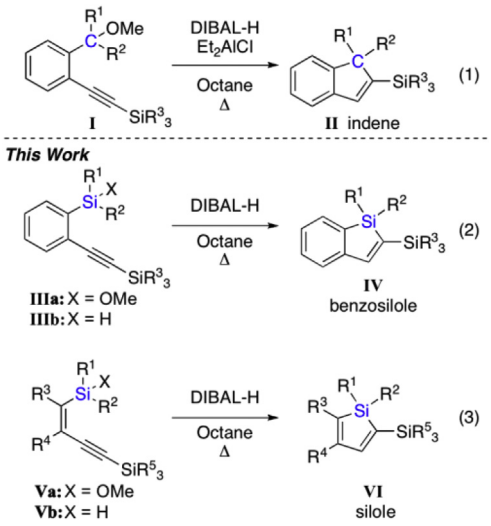
Scheme 1. Syntheses of benzosiloles and siloles.

examples of type (d).

In the view of the known methods for silole ring construction, there are many options for regio-controlled synthesis of substituted benzosiloles including dibenzosiloles. Contrary to the matured route to benzosiloles, the method for preparing substituted non-fused siloles still has much room for improvement. Regio-defined synthesis of unsymmetrically substituted siloles bearing different substituents remains unsolved although the approaches of types (c) and (d), which can be called pre-installation approaches, seem fruitful in solving this subject. Therefore, a versatile method, which enables to synthesize both multisubstituted benzosiloles and unsymmetrically substituted siloles with complete regioselection, is ideal for synthesizing silole derivatives.

We recently reported the DIBAL-H-promoted cyclization of *o*-(2-silylethynyl)benzyl ethers **I** to indenes **II** (Scheme 2, eq. (1)).[20] It was also found that several benzosiloles **IV** were successfully obtained from **IIIa** (eq. 2, X = OMe), which is the silicon analogue of **I**.[20]

In the course of our studies on mechanistic studies on the DIBAL-H-promoted benzosilole construction, we revealed that a methoxysilane **IIIa** was initially reduced to the corresponding hydrosilane **IIIb**, which was converted into **IV** by the action of DIBAL-H. With these findings, the DIBAL-H-promoted cyclization of hydrosilanes **IIIb** and **Vb** was examined (eqs. 2 and 3, X = H). Consequently, various substituted benzosiloles **IV** and



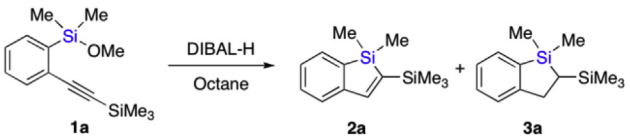
Scheme 2. Our previous work and this work.

unsymmetrically substituted siloles **VI**[21] were successfully obtained with complete regioselection by the pre-installation approach categorized as type (c). We herein report full investigation of the DIBAL-H-promoted cyclization of the silylethynylated methoxysilanes (**IIIa** and **Va**) and hydrosilanes (**IIIb** and **Vb**).

2. Results and discussion

Methoxysilane **1a** was used as a model substrate to optimize the reaction conditions for the DIBAL-H-promoted cyclization. The reaction conditions for the synthesis of indenes **II** [DIBAL-H (2.0 equiv), Et_2AlCl (1 equiv), 100 °C, 14 h][20] were initially adopted to the cyclization of **1a**. In the indene synthesis, Et_2AlCl serves as Lewis acid to promote nucleophilic substitution at the benzylic carbon by C-O bond activation (Scheme 2, eq. (1)). The reaction of **1a** using both DIBAL-H and Et_2AlCl gave the desired silole **2a** in 14% yield along with the reduced product **3a** in 19% yield (Table 1, entry 1). The cyclization to **2a** proceeded without Et_2AlCl and in an increased yield (entry 2). When the amount of DIBAL-H was decreased to 1.5

Table 1
Optimization for benzosilole synthesis.[a]



entry	DIBAL-H (equiv)	temp. (°C)	time (h)	isolated yield (%)	
				2a	3a
1[b]	2.0	100	14	14	19
2	2.0	100	14	40	12
3	1.5	100	14	49	13
4	1.5	80	14	80	2
5	1.5	75	14	88	0
6	1.5	70	14	81	0
7	1.5	75	6	89	0
8	1.5	75	3	86	0
9	1.3	75	6	86	0

[a] All reactions were carried out with **1a** (0.25 mmol) in octane (0.75 mL).
[b] Et_2AlCl (0.25 mmol) was used.

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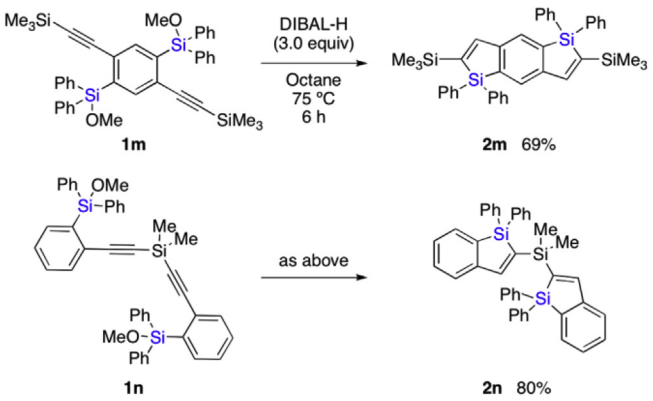
equiv, **2a** was obtained in 49% yield, and **3a** was still formed (entry 3). Lowering the reaction temperature was quite effective in improving the yield of **2a** (entries 4–6). The reaction at 75 °C provided **2a** in 88% yield as a sole product (entry 5). Variation of the reaction time revealed that the reaction was completed in 6 h (entry 7). Since further adjustment of the reaction conditions was unsuccessful in achieving more favourable results (entries 8 and 9), the conditions of entry 7 were determined as the optimized conditions for the cyclization of **1a** to **2a**.

With the optimized reaction conditions in hand, the scope of the benzosilole synthesis was investigated (Table 2). Methoxysilanes **1b** and **1c**, bearing a phenyl group as R^1, were cyclized to benzosiloles **2b** and **2c** in excellent yields. The reaction site of **1d** ($R^1 = R^2 = i$Pr) is sterically more hindered by the isopropyl groups. As anticipated, **1d** hardly underwent the transformation into **2d** under the standard conditions. However, the yield of **2d** was dramatically improved by both elevating the reaction temperature and elongating the reaction time (100 °C, 14 h). The cyclization of **1e** (*Si* = $SiMe_2t$Bu) and **1f** (*Si* = $SiMe_2$Ph), possessing a bulky silyl group at the alkyne terminus, proceeded smoothly. In the case of **1g** (*Si* = $Sii Pr_3$), where the silyl group is sterically more demanding, only a trace amount of **2g** was detected with nearly quantitative recovery of **1g**. Methoxysilanes **1h**–**k**, having a substituent on the *o*-phenylene tether, successfully reacted with DIBAL-H to give the corresponding benzosiloles **2h**–**k**. Naphthosilole **2l** was also prepared from methoxy(naphthyl)silane **1l** in an excellent yield.

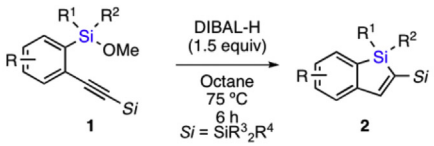
This transformation could be applied to the synthesis of bissiloles (Scheme 3). The reactions of bis(methoxysilyl)diynes **1m** and **1n** with 3.0 equiv of DIBAL-H gave the corresponding bissiloles **2m** and **2n** in good yields.

We next attempted the synthesis of multi-substituted siloles by the DIBAL-H-promoted cyclization of 1,4-disilylalk-3-en-1-ynes **4**. In contrast with the case of **1a**, the reaction of **4a** at 75 °C for 14 h resulted in a moderate yield (52%) of the desired silole **5a**. Elongating the reaction time to 24 h was effective, and **5a** was obtained in 80% isolated yield (Scheme 4). Further prolonged time merely led to the decrease of **5a**. When 1,3-enynes **4b** and **4c** were submitted to the reaction conditions, multi-substituted siloles **5b** and **5c** were



Scheme 3. Synthesis of bissiloles.

Table 2
Synthesis of benzosiloles **2**.[a]



product **2**, isolated yield		
2a 89%	**2b** 92%	**2c** 95%
2d 6% (76%)[b] (91%)[b,c]	**2e** 80% (86%)[b,c]	**2f** 84%
2g trace	**2h** 97%	**2i** 87%
2j 96%	**2k** 90%	**2l** 93%

[a] Unless otherwise noted, all reactions were carried out with **1** (0.25 mmol) and DIBAL-H (0.375 mmol) in octane (0.75 mL) at 75 °C for 6 h.

[b] The reaction temperature was 100 °C.

[c] The reaction time was 14 h.

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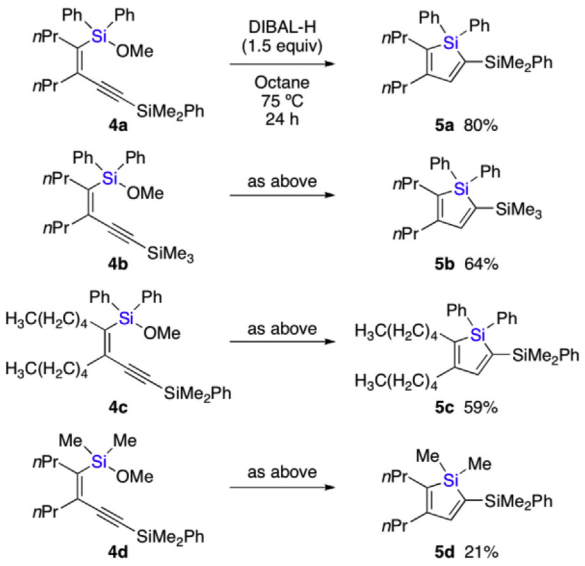
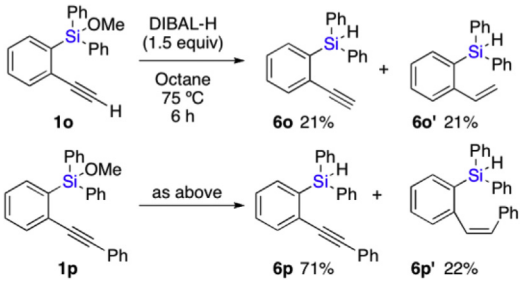


Scheme 4. Synthesis of multi-substituted siloles.

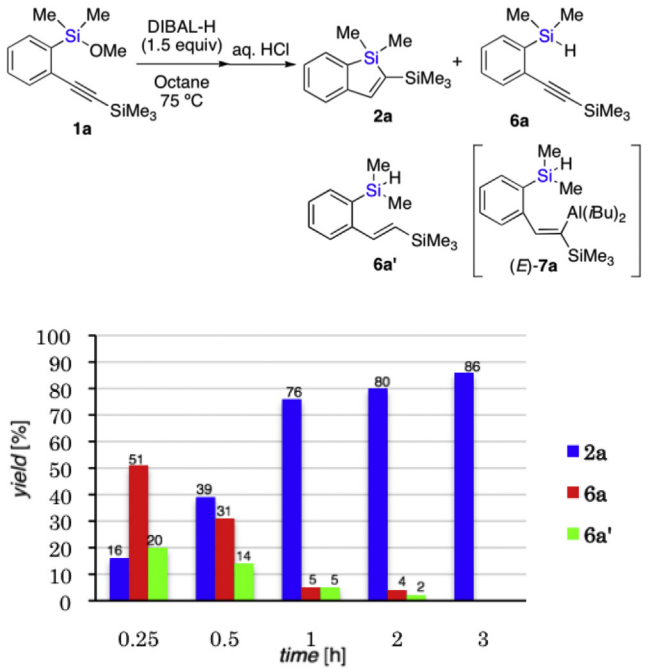
formed in moderate yields (Scheme 4). However, the reaction of **4d**, bearing a methoxy(dimethyl)silyl group, gave **5d** in a low yield despite complete conversion of **4d**. This is probably because **5d** is less stable under the reaction conditions than **5a**-**c**. Unfortunately, any side reactions consuming **5d** could not be identified. Generally, the synthesis of multisubstituted siloles **5** from **4** was not effective under the reaction conditions.

To ascertain the role of the silyl group at the alkyne terminus, methoxysilanes **1o** and **1p**, bearing a non-silylated alkyne part, were treated with DIBAL-H (Scheme 5). The reaction of **1o** gave hydrosilanes **6o** and **6o'** by hydride attack to the silicon center and further reduction of the alkyne moiety. Alkyne **1p** also underwent the reduction to form similar products **6p** and **6p'**. The minor stilbene product **6p'** was assigned to be *Z*-configurated. Thus, no silole products were obtained in both reactions. This fact clearly indicates that the silyl group at the sp-carbon is pivotal to promoting the present cyclization (*vide infra*).

To gain a mechanistic insight, the time course of the DIBAL-H-promoted reaction was investigated by using **1a** as a probe (Scheme 6). The reaction of **1a** was carried out while changing the reaction time (0.25, 0.5, 1, 2, and 3 h). After quenching with 1 M aq. HCl, the products were purified and identified. The reaction for 0.25 h provided hydrosilane **6a** in preference to **2a** and the doubly reduced product **6a'**. The methoxysilane product formed by simple reduction of the alkyne part was not detected. These results suggest that reduction of the methoxysilane part with DIBAL-H[22] is rather fast and occurs prior to that of the alkyne part. The perfect *E*-configuration of **6a'** can be rationalized by highly regioselective



Scheme 5. Reactions of methoxysilanes bearing a non-silylated alkyne moiety.

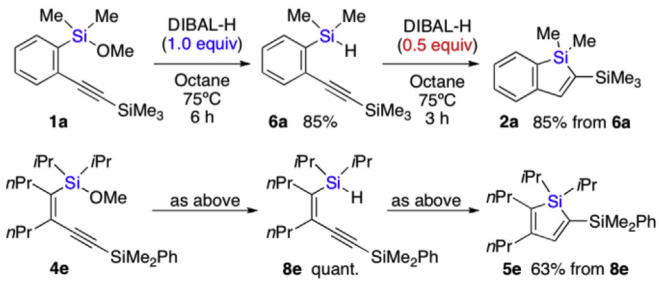


Scheme 6. Variation of product yields with reaction time. All reactions were carried out with **1a** (0.25 mmol) and DIBAL-H (0.375 mmol) in octane (0.75 mL) at 75 °C.

hydroalumination of **6a** and subsequent rapid geometrical isomerization of the initially formed *Z*-alkenylalane to the *E*-isomer (*E*)-**7a** (*vide infra*). The yields of **6a** and **6a'** decreased with reaction time. In contrast, the yield of **2a** increased with the decrease of **6a** and **6a'**. On the basis of these observations, it is highly probable that the formation of **2a** proceeds via hydrosilane **6a** and alkenylalane (*E*)-**7a**.

To make sure that the present cyclization starts with the selective formation of hydrosilane **6a**, the reaction of **1a** with an equimolar amount of DIBAL-H was first conducted (Scheme 7). Expectedly, **6a** was obtained exclusively without the formation of silole **2a**. Next, the isolated hydrosilane **6a** was treated with a substoichiometric amount (0.5 equiv) of DIBAL-H. The cyclization of **6a** to **2a** proceeded successfully in accordance with the mechanistic consideration. A similar examination was conducted using **4e**. As a result, selective formation of hydrosilane **8e** and its conversion into silole **5e** could be observed.

The efficient cyclization of hydrosilanes **6a** and **8e** with a substoichiometric amount of DIBAL-H (0.5 equiv) implies the regeneration of DIBAL-H in the C-Si bond-forming step. To prove the unprecedented process, deuterium-labelling experiments were performed with **6a**-*d* and **8b**-*d* (Scheme 8). When a substoichiometric amount of DIBAL-H acted on these deuterium-



Scheme 7. Stepwise cyclization of methoxysilanes **1a** and **4e** with DIBAL-H.

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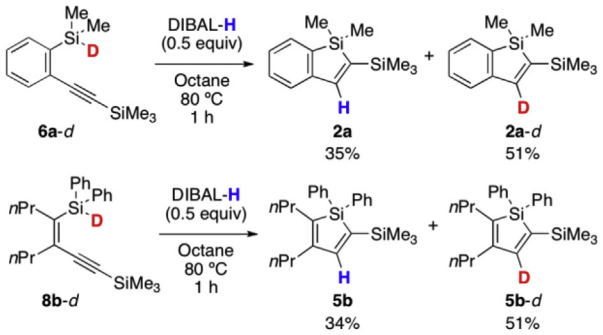
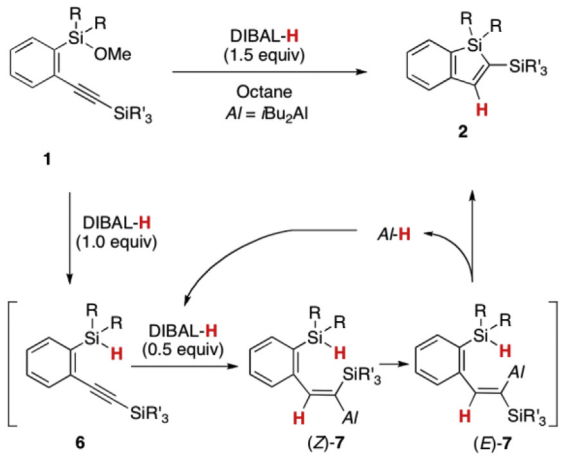


Scheme 8. Deuterium-labelling experiments.

labelled substrates, the cyclized products were obtained in good yields. The characterization of each product by NMR analysis revealed that it was partially deuterated at C(3), that is, a mixture of **2a** and **2a**-*d* or a mixture of **5b** and **5b**-*d*. In other words, deuterium transfer from the Si center to the C(3) center occurred. This result can be rationalized by the generation of DIBAL-D in the ring-closing step. DIBAL-D as well as DIBAL-H should promote the cyclization of **6a**-*d* and **8b**-*d* via highly regioselective deuterioalumination of the alkyne part, which should lead to the deuteration at C(3) (*vide infra*).

Taking all the observations into consideration, we propose a plausible mechanism for the DIBAL-H-promoted cyclization of a methoxysilane **1** (Scheme 9). The first step is hydride substitution of the methoxysilane part with DIBAL-H.[22] The resultant hydrosilane **6** undergoes highly regioselective hydroalumination of the alkyne part with DIBAL-H.[23] Then the initially formed alkenylalane (*Z*)-**7** is isomerized to (*E*)-**7**, the thermodynamically favored isomer.[23] Intramolecular nucleophilic substitution of (*E*)-**7** between the hydrosilane part[24] and the sp^2-C bound to Al forms the cyclized product **2** to regenerate DIBAL-H. The in situ generated DIBAL-H promotes the cyclization of hydrosilane **6** again. As mentioned above, the silyl group at the alkyne terminus is essential to the present cyclization. Its roles certainly consist of promoting the site selective hydroalumination step and facilitating the subsequent geometrical isomerization of (*Z*)-**7**.[23] The former role can be explained by α-effect of the silyl group, which lowers π* level of the C-C triple bond and stabilizes the newly formed C-Al bond α to silicon by hyperconjugation with σ* orbital of the C-Si bond. In addition, the α-effect and cooperative interaction with unoccupied p orbital of the Al metal can polarize the C-C double bond of (*Z*)-**7** to lower its rotation barrier.



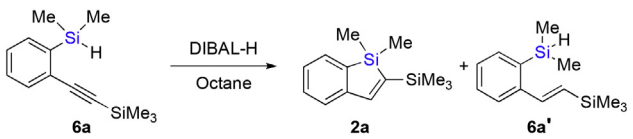
Scheme 9. A plausible mechanism for the DIBAL-H-promoted cyclization of **1**.

Generally, hydrotriorganosilanes are more stable and easily handled than the corresponding methoxytriorganosilanes. In addition, the DIBAL-H-promoted cyclization of methoxysilanes **1** or **4** proceeds via the formation of hydrosilanes **6** or **8**. We therefore took on the cyclization of **6** and **8** for efficient syntheses of benzosiloles **2** and siloles **5**. The optimization of the reaction conditions was initially conducted using hydrosilane **6a** as a probe (Table 3). As described above (Scheme 7), the cyclization of **6a** with 0.5 equiv of DIBAL-H gave benzosilole **2a** in 85% isolated yield as a sole product (entry 1). A less amount (0.3 equiv) of DIBAL-H was enough for the cyclization, but with a slight decrease in yield (entry 2). Further decrease of DIBAL-H (0.2 equiv) caused an incomplete conversion of **6a** (entry 3). The low catalytic turnover of DIBAL-H is likely due to its thermal instability. Shortening the reaction time to 1 h allowed an efficient cyclization even though small amounts of **6a'** and **6a** were detected (entry 4). When the reaction temperature was elevated to 80 °C, the cyclization was completed in 1 h to afford **2a** in 86% yield (entry 5). Use of an equimolar or more amount of DIBAL-H hardly affected the yield of **2a** (entries 6 and 7). However, when the reaction using 1.2 equiv of DIBAL-H was conducted for 0.5 h, the yield of **2a** reached 87% (entry 9).

Based on the results shown in Table 3, two sets of reaction conditions (methods A and B) were applied to the cyclization of various hydrosilanes **6** (Table 4). In the reactions using 1.2 equiv of DIBAL-H at 80 °C for 0.5 h (method A), benzosiloles **2** except **2d** and **2e** were obtained in excellent yields. The reactions of **6d** and **6e**, sterically hindered around the reaction centers, needed a prolonged time and an elevated temperature. It is noteworthy that large-scale reactions of **6j** (1.01 mmol) and **6l** (1.14 mmol) under the conditions of method A also gave the desired benzosiloles **2j** and **2l** in 84% and 91% yields, respectively. When selected substrates **6** were treated with 0.5 equiv of DIBAL-H at 80 °C for 1 h (method B), the cyclization to benzosiloles **2** proceeded smoothly. The substoichiometric use of DIBAL-H was also effective although the yields by method B were generally lower than those by method A.

Contrary to the benzosilole synthesis from methoxysilane **1**, the DIBAL-H-promoted cyclization of methoxysilanes **4** was not so efficient for the synthesis of unsymmetrically substituted siloles **5** (Scheme 4). To overcome the difficulty, the cyclization of hydrosilanes **8** was conducted by method A and B (Table 5). Upon the treatment with DIBAL-H (1.2 equiv) for 0.5 h (method A), various

Table 3
Optimization for benzosilole synthesis using hydrosilane **6**.[a]



entry	DIBAL-H (equiv)	temp (°C)	time (h)	yield (%)[b]		
				2a	6a'	6a
1	0.5	75	3	85	0	0
2	0.3	75	3	(84)	(0)	(1)
3	0.2	75	3	(76)	(0)	(10)
4	0.5	75	1	(82)	(2)	(1)
5	0.5	80	1	86	0	0
6	1.0	80	1	85	0	0
7	1.2	80	1	85	0	0
8	1.0	80	0.5	(82)	(11)	(2)
9	1.2	80	0.5	87	0	0

[a] All reactions were carried out with **6a** (0.25 mmol) in octane (0.75 mL).
[b] Isolated yield. ^{1}H NMR yield is shown in parentheses.

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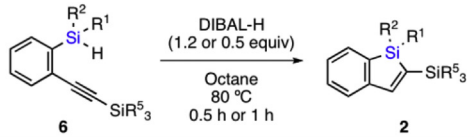
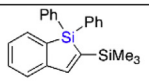
Table 4
Synthesis of benzosiloles **2** from hydrosilanes **6**.[a]

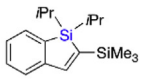
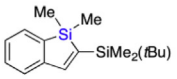
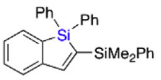


6 **2**

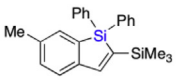
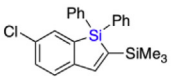
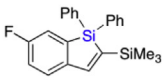
product **2**, isolated yield[b]

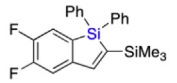
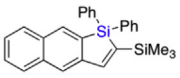
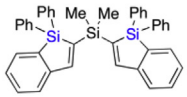

2a 87% (86%) **2b** 92% **2c** 99%

2d 88%[c] **2e** 78%[d] **2q** 91% (84%)

2h 97% (89%) **2i** 91% (88%) **2j** 97% (92%)

2k 90% **2l** 93% (94%) **2n** 86% (82%)

[a] Unless otherwise noted, all reactions were carried out with **6** (0.25 mmol) and DIBAL-H (0.30 mmol for method A or 0.125 mmol for method B) in octane (0.75 mL) at 80 °C for 0.5 h (method A) or 1 h (method B).

[b] The yield by method B is shown in parentheses.

[c] The reaction was carried out at 100 °C for 14 h.

[d] The reaction time was 6 h.

unsymmetrically substituted siloles were obtained in good to excellent yields, except for sterically hindered silole **5e**. A prolonged reaction improved the yield of **5e** to 63%. Compared with 1,1-diphenyl-substituted siloles, 1,1-dimethyl-substituted silole **5d** was inferior in isolated yield probably due to its instability under these conditions. It is noteworthy that four or five different substituents could be introduced on the silole ring in **5k**-**o**. The present reaction was scalable, and a large-scale reaction of **8b** (1 mmol) gave **5b** in 83% isolated yield. The reaction of several substrates **8** with a substoichiometric amount of DIBAL-H (0.5 equiv) for 1 h at 80 °C (method B) was conducted and the results are shown in parentheses. The corresponding siloles were obtained in satisfied yields although, in most cases, the yields were slightly lower than those by method A.

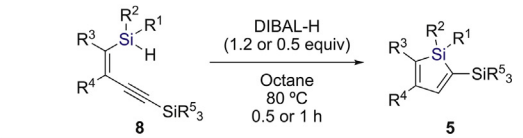
To expand synthetic utility of the products of the present reaction, halodesilylation of the cyclized products **2** and **5** were attempted (Scheme 10). Bromodesilylation of **2l** with bromine proceeded successfully to form 2-bromonaphthosilole **9** in 72% yield. The reaction of **2j** with ICl afforded 2-iodobenzosilole **10** in 85% yield. Contrary to the case of silylated benzosiloles, halodesilylation of silylated siloles is known to be cumbersome.[25] Indeed, iododesilylation of silole **5b** by the reported method[26] resulted in a low yield of the desired 2-iodosilole **11** although **5b** was consumed completely. However, these halogenated siloles can be potential building blocks for further transformations including transition metal-catalyzed coupling reactions.

3. Conclusions

We developed the DIBAL-H-promoted cyclization of 1-methoxysilyl-2-[2-(trimethylsilyl)ethynyl]benzenes **1** and 4-methoxysilyl-1-(trimethylsilyl)alk-3-en-1-ynes **4** to substituted benzosiloles **2** and siloles **5**. The cyclization of **1** was quite valuable for benzosilole synthesis. The reaction mechanism involves the formation of hydrosilanes **6** and **8** by hydride substitution of the methoxysilane part with DIBAL-H. When hydrosilanes **6** and **8** were used as substrates, substituted benzosiloles **2** and siloles **5** were obtained efficiently. Particularly, the cyclization of **8** enabled the synthesis of unsymmetrically substituted siloles bearing four or five different groups on the ring, which are inaccessible by the known methods. In addition, a substoichiometric amount of DIBAL-H (0.5 equiv) allowed efficient cyclization to **2** and **5**. As shown in eq. (5) of Scheme 1, intramolecular reaction between Si-H bond and C-C triple bond is known to be useful for silole construction. However, unlike the known methods, the present method is practicable with DIBAL-H, or a readily accessible and handling, common reagent.

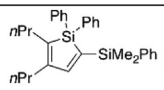
Please cite this article in press as: Kinoshita H, et al., Syntheses of substituted benzosiloles and siloles by diisobutylaluminium hydride-promoted cyclization of 1-silyl-2-(2-silylethynyl)benzenes and 1,4-disilylalk-3-en-1-ynes, Tetrahedron (2018), https://doi.org/10.1016/j.tet.2018.02.011

Table 5
Synthesis of siloles **5** from hydrosilanes **8**.[a]

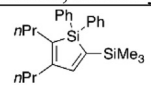


8 **5**

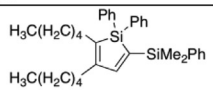
product **5**, isolate yield[b]



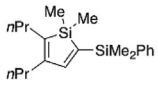
5a 96% (81%)



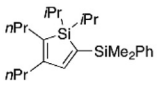
5b 89% (85%)



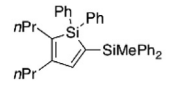
5c 93%



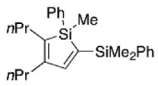
5d 70%



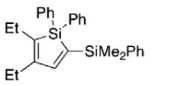
5e 21%, 63%[c]



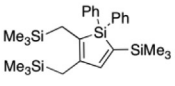
5f 93%



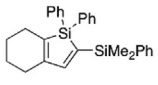
5g 97% (92%)



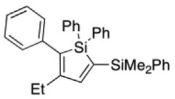
5h 83% (76%)



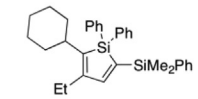
5i 82% (85%)



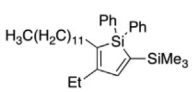
5j 88%



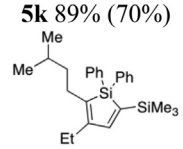
5k 89% (70%)



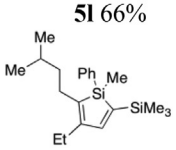
5l 66%



5m 91% (85%)



5n 95% (92%)

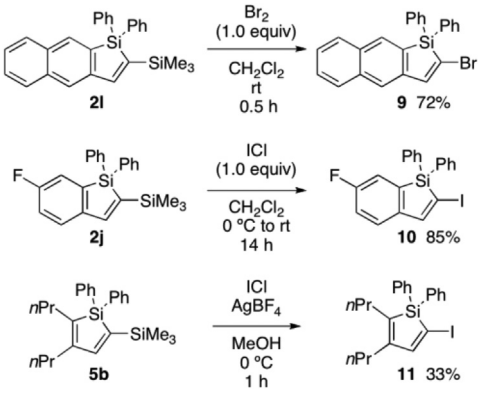


5o 89% (81%)

[a] All reactions were carried out with **8** (0.25 mmol) and DIBAL-H (0.30 mmol for method A or 0.125 mmol for method B) in octane (0.75 mL) at 80 °C for 0.5 h (method A) or 1 h (method B).

[b] The yield by method B is shown in parentheses.

[c] The reaction time was 24 h.



Scheme 10. Halodesilylation of 2-(trimethylsilyl)siloles.

Additionally, it enables efficient synthesis of unsymmetrically poly-substituted siloles as well as substituted benzosiloles. The silylated products could be converted to halogenated benzosiloles and siloles useful for further modifications. Consequently, we succeeded in providing not only an inclusive regio-defined, efficient approach to both multi-substituted benzosiloles and siloles but also synthetically valuable, novel information on the reactivity of organoalanes.

4. Experimental section

4.1. General experimental

Unless otherwise noted, all reactions were carried out under argon atmosphere. All reagents were purchased from common suppliers and used as received. Analytical thin layer chromatography was performed using 0.25 mm silica gel 60 F_{254} plates. Chromatography was performed using silica gel 60 N (spherical, neutral, 63–210 mm). NMR spectra were recorded on a 300, 400, or 500 MHz NMR spectrometer. The chemical shifts are reported with reference at 7.26 ppm ($CHCl_3$) for the proton and at 77.0 ppm

Please cite this article in press as: Kinoshita H, et al., Syntheses of substituted benzosiloles and siloles by diisobutylaluminium hydride-promoted cyclization of 1-silyl-2-(2-silylethynyl)benzenes and 1,4-disilylalk-3-en-1-ynes, Tetrahedron (2018), https://doi.org/10.1016/j.tet.2018.02.011

(centered on the signal of $CDCl_3$) for the carbon. Data for ^1H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept. = septet, m = multiplet), coupling constants (*J*, reported as values in hertz (Hz)), and integration. Infrared spectra and high-resolution mass spectra were obtained for all new compounds. The high-resolution mass analysis was conducted by a double focusing magnetic sector mass spectrometer. Melting points were measured for solid compounds.

4.1.1. Synthesis of methoxysilanes 1 (typical procedure)

Et_2NH (20 mL), THF (20 mL), 1-bromo-2-iodobenzene (2.2 mL g, 18 mmol), and trimethylsilylacetylene (2.9 mL, 21 mmol) were successively added to a flask containing $PdCl_2(PPh_3)_2$ (0.25 g, 0.35 mmol) and CuI (0.067 g, 0.35 mmol). The mixture was stirred at room temperature for 12 h and then evaporated. The residue was diluted with hexane/AcOEt (5:1) and washed with 1 M aqueous HCl. The organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica-gel column (hexane) gave 1-bromo-2-[2-(trimethylsilyl)ethynyl]benzene [38274-16-7] (**1a'**) as a pale yellow clear liquid (4.12 g, 16.3 mmol, 92% yield).

*n*BuLi (2.65 M in hexane, 701 mL, 1.86 mmol) was added to a stirred solution of **1a'** (472 mg, 1.86 mmol) in THF (4 mL) at −78 °C. After 0.5 h, Me_2SiCl_2 (223 mL, 1.86 mmol) was added to the mixture at that temperature. Then the mixture was warmed to room temperature and stirred for 2 h. MeOH (0.5 mL) and Et_3N (290 mL, 2.08 mmol) were successively added to the reaction mixture at −78 °C. After removing the cooling bath, the resultant mixture was stirred at room temperature for 1 h. The mixture was quenched with water and extracted with hexane/AcOEt (30:1) three times. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography (hexane/AcOEt = 40:1). The title compound, 1-(methoxydimethylsilyl)-2-[2-(trimethylsilyl)ethynyl]benzene (**1a**), was obtained as a pale yellow liquid (0.721 g, 2.75 mmol, 71% yield). ^1H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.25 (s, 9H), 0.47 (s, 6H), 3.56 (s, 3H), 7.30–7.34 (m, 2H), 7.48–7.50 (m, 1H), 7.59–7.61 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −1.8, −0.3, 50.9, 96.9, 106.4, 127.7, 127.7, 129.2, 132.8, 134.0, 140.8; IR (neat) 3073, 3052, 2959, 2831, 2155, 1429 cm^{-1}; HRMS (EI^+) calcd for $C_{14}H_{22}OSi_2$ [M^+] 262.1209, found 262.1209.

The substrates **1b-l**, and **1p** were synthesized by the same manner as described for the preparation of **1a**.

*4.1.1.1. 1-(Methoxydiphenylsilyl)-2-[2-(trimethylsilyl)ethynyl]benzene (**1b**).* Pale yellow powder (1.58 g, 4.09 mmol, 74% yield from **1a'**); m.p. 89–90 °C; ^1H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ −0.10 (s, 9H), 3.63 (s, 3H), 7.32–7.44 (m, 8H), 7.54 (d, J = 7.5 Hz, 1H), 7.65–7.69 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.7, 52.0, 98.3, 106.1, 127.6, 127.8, 129.1, 129.8, 133.3, 133.8, 135.5, 136.3, 136.7; IR (nujol) 3069, 2854, 2156, 1249, 1118 cm^{-1}; HRMS (EI^+) calcd for $C_{24}H_{26}OSi_2$ [M^+] 386.1522, found 386.1511.

*4.1.1.2. 1-[Methoxy(methyl)(phenyl)silyl]-2-[2-(trimethylsilyl)ethynyl]benzene (**1c**).* Pale yellow liquid (1.69 g, 5.21 mmol, 84% yield from **1a'**); ^1H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.08 (s, 9H), 0.76 (s, 3H), 3.56 (s, 3H), 7.32–7.36 (m, 3H), 7.36–7.41 (m, 2H), 7.49–7.52 (m, 1H), 7.57–7.60 (m, 2H), 7.63–7.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −3.4, −0.5, 51.4, 97.6, 106.1, 127.7, 127.7, 128.4, 129.5, 129.6, 133.0, 134.4, 135.1, 135.6, 138.6; IR (neat) 3069, 3050, 3001, 2899, 2155, 1582, 1250 cm^{-1}; HRMS (EI^+) calcd for $C_{19}H_{24}OSi_2$ [M^+] 324.1366, found 324.1360.

*4.1.1.3. 1-(Methoxydiisopropylsilyl)-2-[2-(trimethylsilyl)ethynyl]benzene (**1d**).* Pale yellow liquid (886.8 mg, 2.78 mmol, 47% yield from **1a'**); ^1H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.23 (s, 9H), 1.05 (d, J = 7.6 Hz, 6H), 1.09 (d, J = 7.6 Hz, 6H), 1.56 (sept, J = 7.6 Hz, 2H), 3.68 (s, 3H), 7.29–7.34 (m, 2H), 7.49–7.52 (m, 1H), 7.60–7.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.4, 13.1, 17.4, 18.0, 52.4, 95.6, 107.2, 127.4, 128.1, 128.8, 133.4, 135.6, 138.1; IR (neat) 3052, 2155, 1098 cm^{-1}; HRMS (EI^+) calcd for $C_{18}H_{30}OSi_2$ [M^+] 318.1835, found 318.1843.

*4.1.1.4. 1-Bromo-2-[2-[(1,1-dimethylethyl)dimethyl-silyl]ethynyl] benzene (**1e'**).* For the synthesis of **1e**, the title compound **1e'** was prepared as follows. A solution of LDA, prepared from *i*Pr_2NH (0.93 mL, 6.5 mmol) and *n*BuLi (2.7 M in hexane, 2.4 mL, 6.5 mmol) in THF (6 mL) at 0 °C, was added to a solution of 1-bromo-2-ethynylbenzene [766-46-1] (1.1 g, 5.9 mmol) in THF (6 mL) at −78 °C for 30 min *tert*-Butyldimetylsilyl chloride [18162-48-6] (1.1 g, 7.1 mmol) was added to the mixture at that temperature. The reaction mixture was warmed to room temperature and stirred for 12 h. After adding aqueous NH_4Cl, the aqueous mixture was extracted with hexane three times. The combined organic phase was dried over Na_2SO_4 and evaporated. Purification of the residue by silica-gel column chromatography gave 1-bromo-2-[2-[(1,1-dimethylethyl)dimethyl-silyl]ethynyl]benzene in (1.6 g, 5.4 mmol, 92%) as a pale yellow liquid. ^1H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.21 (s, 6H), 1.02 (s, 9H), 7.15 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 7.24 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 7.50 (dd, J = 7.6, 1.6 Hz, 1H), 7.57 (dd, J = 8.0, 1.2 Hz, 1H).

*4.1.1.5. 1-(Methoxydimethylsilyl)-2-[2-(tert-butyldimethylsilyl)ethynyl]benzene (**1e**).* Colorless liquid (1.1 g, 3.5 mmol, 54% yield from **1e'**); ^1H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.19 (s, 6H), 0.47 (s, 6H), 1.00 (s, 9H), 3.55 (s, 3H), 7.29–7.34 (m, 2H), 7.48–7.52 (m, 1H), 7.57–7.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −4.7, −1.8, 16.8, 26.2, 50.8, 95.4, 107.0, 127.7, 127.9, 129.2, 133.3, 134.0, 140.5; IR (neat) 3052, 2930, 2153, 1250, 1092 cm^{-1}; HRMS (EI^+) calcd for $C_{17}H_{28}OSi_2$ [M^+] 304.1679, found 304.1685.

*4.1.1.6. 1-(Methoxydimethylsilyl)-2-[2-(dimethylphenylsilyl)ethynyl] benzene (**1f**).* Pale yellow liquid (1.1 g, 3.2 mmol, 71% yield from 1-bromo-2-[2-(dimethylphenylsilyl)ethynyl]benzene [935221-20-8] instead of **1a'**); ^1H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ 0.44 (s, 6H), 0.50 (s, 6H), 3.53 (s, 3H), 7.31–7.35 (m, 2H), 7.36–7.41 (m, 3H), 7.51–7.55 (m, 1H), 7.59–7.62 (m, 1H), 7.66–7.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −1.8, −1.1, 50.8, 94.9, 107.9, 127.5, 127.9, 127.9, 129.2, 129.5, 133.1, 133.8, 134.1, 136.7, 140.9; IR (neat) 3051, 2959, 2154, 1428, 1250 cm^{-1}; HRMS (EI^+) calcd for $C_{19}H_{24}OSi_2$ [M^+] 324.1366, found 324.1373.

*4.1.1.7. 1-(Methoxydimethylsilyl)-2-[2-(triisopropylsilyl)ethynyl]benzene (**1g**).* Pale yellow liquid (932 mg, 2.66 mmol, 79% yield from 1-bromo-2-[2-[tris(1-methylethyl)silyl]ethynyl]benzene [261713-83-1] instead of **1a'**); ^1H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.49 (s, 6H), 1.13–1.15 (m, 21H), 3.54 (s, 3H), 7.29–7.35 (m, 2H), 7.51–7.55 (m 1H), 7.58–7.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −1.6, 11.5, 18.6, 50.8, 93.8, 108.1, 127.5, 128.2, 129.2, 134.0, 134.0, 139.9; IR (neat) 3052, 2943, 2866, 2148, 1250, 1129 cm^{-1}; HRMS (EI^+) calcd for $C_{20}H_{34}OSi_2$ [M^+] 346.2148, found 346.2151.

*4.1.1.8. 2-(Methoxydiphenylsilyl)-4-methyl-1-[2-(trimethylsilyl)ethynyl]benzene (**1h**).* White powder (1.01 g, 2.51 mmol, 52% yield form 2-bromo-4-methyl-1-[2-(trimethylsilyl)ethynyl]benzene [935223-82-8] instead of **1a'**); m.p. 91–92 °C; ^1H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ −0.12 (s, 9H), 2.34 (s, 3H), 3.61 (s, 3H), 7.18–7.21 (m, 1H), 7.34–7.38 (m, 4H), 7.40–7.45 (m, 3H), 7.49–7.51 (m, 1H), 7.67–7.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.6, 21.6, 51.9, 97.5, 106.4, 126.1, 127.6, 129.8, 130.6, 133.3, 133.9, 135.5, 136.5, 136.8, 137.7; IR (nujol) 3054, 2152, 1250, 1117, 1080 cm^{-1};

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HRMS (EI$^+$) calcd for $C_{25}H_{28}OSi_2$ [M$^+$] 400.1679, found 400.1674.

*4.1.1.9. 4-Chloro-2-(methoxydiphenylsilyl)-1-[2-(trimethylsilyl)ethynyl]benzene (**1i**).* Pale yellow liquid (1.13 g, 2.69 mmol, 55% yield from 2-bromo-4-chloro-1-[2-(trimethylsilyl)ethynyl]benzene [935222-84-7] instead of **1a'**); ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ −0.11 (s, 9H), 3.60 (s, 3H), 7.32–7.47 (m, 8H), 7.65–7.69 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.8, 51.9, 99.5, 105.0, 127.4, 127.8, 130.0, 130.1, 133.0, 134.5, 134.7, 135.5, 135.9, 139.5; IR (neat) 3070, 3050, 2835, 2156, 1450, 1117 cm^{-1}; HRMS (EI$^+$) calcd for $C_{24}H_{25}ClOSi_2$ [M$^+$] 420.1132, found 420.1131.

*4.1.1.10. 4-Fluoro-2-(methoxydiphenylsilyl)-1-[2-(trimethylsilyl)ethynyl]benzene (**1j**).* White powder (942 mg, 2.33 mmol, 48% yield from 2-bromo-4-fluoro-1-[2-(trimethylsilyl)ethynyl]benzene [1609556-12-8] instead of **1a'**); m.p. 107–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ −0.11 (s, 9H), 3.61 (s, 3H), 7.05 (ddd, J = 8.4, 8.4, 2.8 Hz, 1H), 7.35–7.40 (m, 5H), 7.41–7.46 (m, 2H), 7.51 (dd, J = 8.4, 8.4 Hz, 1H), 7.66–7.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.7, 52.0, 97.9, 105.1, 117.0 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 122.9 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 125.1 (d, $^3J_{C\text{-}F}$ = 4.0 Hz), 127.8, 130.1, 133.0, 135.5, 135.5, 140.4 (d, $^3J_{C\text{-}F}$ = 5.0 Hz), 162.2 (d, $^1J_{C\text{-}F}$ = 251.5 Hz); IR (nujol) 3068, 2156, 1250, 1117, 1081 cm^{-1}; HRMS (EI$^+$) calcd for $C_{24}H_{25}FOSi_2$ [M$^+$] 404.1428, found 404.1428.

*4.1.1.11. 4,5-Difluoro-1-(methoxydiphenylsilyl)-2-[2-(trimethylsilyl)ethynyl]benzene (**1k**).* Pale yellow liquid (1.5 g, 3.6 mmol, 50% yield from 1-bromo-4,5-difluoro-2-[2-(trimethylsilyl)ethynyl]benzene [2073117-80-1] instead of **1a'**); ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ −0.10 (s, 9H), 3.61 (s, 3H), 7.31–7.51 (m, 8H), 7.64–7.67 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.8, 52.0, 99.1, 103.9, 122.5 (d, $^2J_{C\text{-}F}$ = 17.0 Hz), 125.1 (d, $^2J_{C\text{-}F}$ = 16.0 Hz), 126.1 (m), 127.8, 130.2, 132.8, 135.1 (d, $^3J_{C\text{-}F}$ = 4.0 Hz), 135.4, 150.3 (dd, $^1J_{C\text{-}F}$ = 252.0 Hz, $^2J_{C\text{-}F}$ = 12.0 Hz), 150.8 (dd, $^1J_{C\text{-}F}$ = 250.0 Hz, $^2J_{C\text{-}F}$ = 13.0 Hz); IR (neat) 3071, 2960, 2838, 2155, 1587, 1483, 1293, 1118, 845 cm^{-1}; HRMS (EI$^+$) calcd for $C_{24}H_{24}F_2OSi_2$ [M$^+$] 422.1334, found 422.1328.

*4.1.1.12. 2-Bromo-3-[2-(trimethylsilyl)ethynyl]naphthalene (**1l'**).* For the synthesis of **1l**, the title compound **1l'** was prepared from 3-bromonaphthalen-2-yl trifluoromethanesulfonate [1245602-31-6] and trimethylsilylacetylene according to the method for the synthesis of **1a'**. The triflate was obtained from 3-bromonaphthalen-2-ol [30478-88-7][27] by treatment with trifluoromethanesulfonic anhydride and pyridine in CH_2Cl_2. Yellow powder (1.30 g, 4.30 mmol, 65% yield from 3-bromonaphthalen-2-yl trifluoromethanesulfonate); m.p. 64–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.31 (s, 9H), 7.46–7.52 (m, 2H), 7.70–7.77 (m, 2H), 8.03 (s, 1H), 8.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.1, 99.3, 103.3, 121.9, 122.5, 126.8, 127.6, 127.6, 130.9, 131.6, 133.6, 133.7; IR (nujol) 3056, 2898, 2156, 1425, 1250, 1132 cm^{-1}; HRMS (EI$^+$) calcd for $C_{15}H_{15}BrSi_2$ [M$^+$] 302.0126, found 302.0122.

*4.1.1.13. 2-(Methoxydiphenylsilyl)-3-[2-(trimethylsilyl)ethynyl]naphthalene (**1l**).* Pale yellow liquid (1.12 g, 2.57 mmol, 65% yield from **1l'**); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ −0.08 (s, 9H), 3.68 (s, 3H), 7.35–7.40 (m, 4H), 7.41–7.45 (m, 2H), 7.46–7.54 (m, 2H), 7.72 (dd, J = 6.4, 0.8 Hz, 4H), 7.79 (dd, J = 7.6, 7.6 Hz, 2H), 8.07 (s, 1H), 8.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.6, 52.1, 97.9, 106.4, 124.8, 126.8, 127.4, 127.5, 127.7, 128.4, 129.8, 132.2, 133.0, 133.2, 133.7, 134.0, 135.6, 138.0; IR (neat) 3051, 2958, 2149, 1250, 1116 cm^{-1}; HRMS (EI$^+$) calcd for $C_{28}H_{28}OSi_2$ [M$^+$] 436.1679, found 436.1672.

*4.1.1.14. 1,4-Bis(methoxydiphenylsilyl)-2,5-bis[2-(trimethylsilyl)ethynyl]benzene (**1m**).* The title compound **1m** was prepared from 1,4-dibromo-2,5-bis[2-(trimethylsilyl)ethynyl]benzene (**1m'**) and Ph_2SiCl_2 according to the method for the synthesis of **1a**. Dibromobenzene **1m'** was obtained by the method reported by Liu's group.[28] White powder (214 mg, 0.308 mmol, 31% yield); m.p. 156–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ −0.12 (s, 18H), 3.59 (s, 6H), 7.34–7.45 (m, 12H), 7.68–7.71 (m, 8H), 7.90 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.7, 51.9, 100.7, 106.2, 127.7, 128.1, 130.0, 133.2, 135.6, 138.6, 140.6; IR (nujol) 3069, 2834, 2151, 1249, 1116 cm^{-1}; HRMS (EI$^+$) calcd for $C_{42}H_{46}O_2Si_4$ [M$^+$] 694.2575, found 694.2553.

*4.1.1.15. Bis[(2-(methoxydiphenylsilyl)phenyl)ethynyl]dimethylsilane (**1n**).* A solution of LDA, prepared from iPr$_2$NH (0.29 mL, 2.0 mmol) and nBuLi (2.6 M in hexane, 0.77 mL, 2.0 mmol) in THF (2 mL) at 0 °C, was added to a solution of (2-ethynylphenyl)(methoxy)diphenylsilane (**1o**) (0.58 g, 1.8 mmol) in THF (2 mL) at −78 °C. After 30 min of stirring, Me_2SiCl_2 (0.11 mL, 0.9 mmol) was added to the mixture. The reaction mixture was gradually warmed to room temperature and stirred for 12 h. After adding MeOH (10 mL), the resultant mixture was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane/AcOEt = 20:1). Pale yellow liquid (45 mg, 0.65 mmol, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ −0.31 (s, 6H), 3.61 (s, 6H), 7.31–7.41 (m, 16H), 7.51–7.54 (m, 2H), 7.64–7.67 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.9, 52.0, 94.6, 106.5, 127.7, 128.0, 128.8, 129.8, 129.8, 133.5, 133.7, 135.5, 136.3, 137.0; IR (neat) 3050, 3010, 2835, 2158, 1117 cm^{-1}; HRMS (EI$^+$) calcd for $C_{44}H_{40}O_2Si_3$ [M$^+$] 684.2336, found 684.2336.

*4.1.1.16. (2-Ethynylphenyl)(methoxy)diphenylsilane (**1o**).* A solution of methoxysilane **1b** (2.6 g, 6.7 mmol) and K_2CO_3 (0.28 mg, 2.0 mmol) in MeOH (7 mL)/THF (7 mL) was stirred at room temperature for 14 h under the atmosphere. After the solvent was evaporated, the residue was purified by silica-gel column chromatography (hexane/AcOEt = 20:1). Pale yellow liquid (1.28 g, 4.08 mmol, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 2.84 (s, 1H), 3.66 (s, 3H), 7.34–7.41 (m, 6H), 7.41–7.46 (m, 2H), 7.54–7.57 (m, 1H), 7.65–7.68 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ 52.1, 81.1, 84.5, 127.7, 127.9, 128.0, 128.1, 129.9, 133.5, 133.7, 135.5, 136.4, 137.2; IR (neat) 3283, 3049, 1116 cm^{-1}; HRMS (EI$^+$) calcd for $C_{21}H_{18}OSi$ [M$^+$] 314.1127, found 314.1126.

*4.1.1.17. Methoxydiphenyl[2-(phenylethynyl)phenyl]silane (**1p**).* Pale yellow powder (1.08 g, 2.77 mmol, 79% yield from 1-bromo-2-(2-phenylethynyl)benzene [21375-88-2] instead of **1a'**); m.p. 106–107 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 3.65 (s, 3H), 6.85–6.87 (m, 2H), 7.14–7.18 (m, 2H), 7.2–7.24 (m, 1H), 7.33–7.36 (m, 5H), 7.38–7.45 (m, 3H), 7.59 (d, J = 7.5 Hz, 1H), 7.68–7.72 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ 52.0, 91.1, 93.3, 123.1, 127.6, 127.7, 127.9, 128.0, 129.3, 129.8, 130.0, 131.2, 132.6, 133.9, 135.5, 136.4, 136.6; IR (nujol) 3050, 2834, 1117, 1087 cm^{-1}; HRMS (EI$^+$) calcd for $C_{27}H_{22}OSi$ [M$^+$] 390.1440, found 390.1438.

4.1.2. Synthesis of methoxysilanes 4 (typical procedure)

CH_3CN (15 mL), 4-octyne (1.6 mL, 6.3 mmol), and (2-bromoethynyl)dimethyl(phenyl)silane (1.8 g, 7.6 mmol) were successively added to a flask containing $Pd(OAc)_2$ (72 mg, 0.32 mmol). After 8 h stirring at 30 °C, the solution was filtered though a silica gel pad on a Na_2SO_4 column and evaporated. Purification of the residue by silica gel column chromatography (hexane) gave (*Z*)-4-bromo-7-[dimethyl(phenyl)silyl]-5-(propyl)hept-4-en-6-yne (**4a'**)[21,29] as a pale yellow liquid (2.0 g, 5.7 mmol, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.45 (s, 6H), 0.93 (t, J = 7.5 Hz, 3H), 0.94 (t,

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$J = 7.5$ Hz, 3H), 1.56–1.65 (m, 4H), 2.19–2.23 (m, 2H), 2.54 (t, $J = 7.0$ Hz, 2H), 7.35–7.38 (m, 3H), 7.67–7.70 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.8, 13.3, 13.6, 21.9, 21.9, 35.1, 39.0, 96.3, 107.0, 124.3, 127.8, 129.3, 133.8, 134.0, 137.2; IR (neat) 3070, 3023, 2962, 2872, 2146, 2068 cm^{-1}; HRMS (EI$^+$) calcd for $C_{18}H_{25}BrSi$ [M$^+$] 348.0909, found 348.0914.

*n*BuLi (2.7 M in hexane, 0.69 mL, 1.8 mmol) was added to a stirred solution of **4a'** (0.64 g, 1.8 mmol) in THF (2 mL) at −78 °C. After 0.5 h, Ph_2SiCl_2 (0.38 mL, 1.8 mmol) was added to the mixture. The mixture was warmed to room temperature and stirred for 2 h. MeOH (0.5 mL) and Et_3N (0,29 mL, 2.1 mmol) were successively added to the reaction mixture at −78 °C. After removing the cooling bath, the resultant mixture was stirred at room temperature for 1 h. The mixture was quenched with water and extracted with hexane/AcOEt (30:1) three times. The combined organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica-gel column chromatography (hexane/AcOEt = 40:1) gave (*Z*)-4-(methoxydiphenylsilyl)-7-[dimethyl(phenyl)silyl]-5-(propyl)hept-4-en-6-yne (**4a**) as a pale yellow liquid (0.48 g, 1.0 mmol, 55% yield); ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ 0.01 (s, 6H), 0.84 (t, $J = 7.5$ Hz, 3H), 0.96 (t, $J = 7.5$ Hz, 3H), 1.30–1.39 (m, 2H), 1.57–1.70 (m, 2H), 2.26–2.35 (m, 4H), 3.45 (s, 3H), 7.24–7.40 (m, 11H), 7.66–7.69 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −1.4, 13.9, 14.4, 21.8, 23.4, 33.5, 35.1, 51.8, 96.9, 109.0, 127.5, 127.6, 129.0, 129.5, 133.7, 134.6, 135.5, 136.4, 137.2, 146.0; IR (neat) 3068, 3049, 2959, 2871, 2138, 1115 cm^{-1}; HRMS (EI$^+$) calcd for $C_{31}H_{38}OSi_2$ [M$^+$] 482.2461, found 482.2477.

The 1,4-bissilyl-1,3-enynes **4b**-**e** were synthesized in the same manner as described for the preparation of **4a.**

*4.1.2.1. (Z)-4-(Methoxydiphenylsilyl)-7-(trimethylsilyl)-5-(propyl) hept-4-en-6-yne (**4b**).* Pale yellow liquid (664 mg, 1.58 mmol, 67% yield from (*Z*)-4-bromo-7-(trimethylsilyl)-5-(propyl)hept-4-en-6-yne [1231256-01-1]); ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ −0.21 (s, 9H), 0.83 (t, $J = 7.2$ Hz, 3H), 0.96 (t, $J = 7.5$ Hz, 3H), 1.26–1.35 (m, 2H), 1.56–1.67 (m, 2H), 2.25–2.31 (m, 4H), 3.47 (m, 3H), 7.31–7.39 (m 6H), 7.66–7.72 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.7, 13.9, 14.4, 21.8, 23.4, 33.5, 35.0, 51.8, 99.1, 107.5, 127.4, 129.4, 134.8, 135.4, 136.6, 145.4; IR (neat) 3069, 3050, 2871, 2138, 1250, 1115 cm^{-1}; HRMS (EI$^+$) calcd for $C_{26}H_{36}OSi_2$ [M$^+$] 420.2305, found 420.2294.

*4.1.2.2. (Z)-6-(Methoxydiphenylsilyl)-9-[dimethyl(phenyl)silyl]-7-(pentyl)non-6-en-8-yne (**4c**).* Colorless clear oil (only pure fraction, 142 mg, 0.263 mmol, 22% yield from (*Z*)-6-bromo-9-[dimethyl(phenyl)silyl)-7-(pentyl)non-6-en-8-yne); ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ 0.03 (s, 6H), 0.84 (t, $J = 6.9$ Hz, 3H), 0.92 (t, $J = 7.2$ Hz, 3H), 1.18–1.40 (m, 10H), 1.55–1.67 (m, 2H), 2.28–2.37 (m, 4H), 3.47 (s, 3H), 7.23–7.42 (m, 11H), 7.65–7.70 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −1.4, 14.0, 14.0, 22.3, 22.5, 28.3, 29.6, 31.4, 31.6, 32.1, 33.0, 51.8, 96.8, 109.1, 127.5, 127.6, 129.0, 129.5, 133.7, 134.6, 135.5, 136.5, 137.2, 145.9; IR (neat) 3069, 3051, 2960, 2830, 2136, 1116 cm^{-1}; HRMS (EI$^+$) calcd for $C_{35}H_{46}OSi_2$ [M$^+$] 538.3087, found 538.3073.

*4.1.2.3. (Z)-4-(Methoxydimethylsilyl)-7-[dimethyl(phenyl)silyl]-5-(propyl)hept-4-en-6-yne (**4d**).* Colorless clear oil (only pure fraction, 0.39 g, 1.1 mmol, 22% yield from (*Z*)-4-bromo-7-[dimethyl(phenyl) silyl]-5-(propyl)hept-4-en-6-yne); ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ 0.3 (s, 6H), 0.42 (s, 6H), 0.89–0.95 (m, 6H), 1.25–1.36 (m, 2H), 1.54–1.62 (m, 2H), 2.15–2.24 (m, 4H), 3.44 (s, 3H), 7.35–7.38 (m, 3H), 7.61–7.65 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −1.4, −1.0, 13.8, 14.4, 21.7, 23.4, 33.2, 34.6, 50.6, 94.5, 109.4, 127.8, 129.3, 133.1, 133.7, 137.2, 150.4; IR (neat) 3069, 3051, 2960, 2830, 2136, 1116 cm^{-1}; HRMS (EI$^+$) calcd for $C_{21}H_{34}OSi_2$ [M$^+$] 358.2148, found 358.2152.

*4.1.2.4. (Z)-4-(Diisopropylmethoxysilyl)-7-[dimethyl(phenyl)silyl]-5-(propyl)hept-4-en-6-yne (**4e**).* Colorless clear oil (only pure fraction, 111 mg, 0.268 mmol, 20% yield from (*Z*)-4-bromo-7-[dimethyl(-phenyl)silyl]-5-(propyl)hept-4-en-6-yne); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.39 (s, 6H), 0.89–0.95 (m, 6H), 1.02 (dd, $J = 7.5$, 7.5 Hz, 12H), 1.26–1.34 (m, 2H), 1.35–1.45 (m, 2H), 1.55–1.63 (m, 2H), 2.13–2.16 (m, 2H), 2.21–2.24 (m, 2H), 3.59 (s, 3H), 7.35–7.38 (m, 3H), 7.58–7.61 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −1.2, 13.5, 13.8, 14.7, 17.8, 18.4, 21.8, 23.2, 33.9, 34.9, 52.3, 93.6, 110.2, 127.8, 129.2, 132.8, 133.7, 137.2, 150.0; IR (neat) 3070, 2958, 2866, 2136, 2066, 1115 cm^{-1}; HRMS (EI$^+$) calcd for $C_{25}H_{42}OSi_2$ [M$^+$] 414.2774, found 414.2785.

4.1.3. Synthesis of hydrosilanes 6 (typical procedure)

A solution of methoxysilane **1a** (0.38 g, 1.5 mmol) in Et_2O (1 mL) was added to a suspension of $LiAlD_4$ (56 mg, 1.5 mmol) in Et_2O (2 mL) at 0 °C. After 18 h stirring at room temperature, MeOH (5 mL) and 1M aqueous HCl were successively added to the reaction mixture at 0 °C. The aqueous mixture was extracted with hexane three times. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica-gel column chromatography (hexane). [(2-(Deuteriodimethylsilyl)phenyl)ethynyl] trimethylsilane (**6a-*d***) was obtained as a colorless liquid (0.29 g, 0.87 mmol, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.25 (s, 9H), 0.41 (s, 6H), 7.27–7.33 (m, 2H), 7.46–7.49 (m, 1H), 7.50–7.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −4.1, −0.2, 97.2, 105.7, 127.7, 128.6, 129.0, 132.2, 134.7, 140.4; IR (neat) 3052, 2959, 2155, 1548, 1127 cm^{-1}; HRMS (EI$^+$) calcd for $C_{13}H_{19}DSi_2$ [M$^+$] 233.1166, found 233.1173.

Hydrosilanes **6a** and **6b** are known compounds.[12] Hydrosilanes **6c**, **6h**, **6j**, **6k**, and **6q** were prepared by the method reported by this group.[21] Other hydrosilanes **6** were obtained from methoxysilanes **4** and $LiAlH_4$ according to the same procedure used for the synthesis of **6a**-*d*.

*4.1.3.1. 1-(Diisopropylsilyl)-2-[2-(trimethylsilyl)ethynyl]benzene (**6d**).* Colorless clear liquid (0.20 g, 0.70 mmol, 92% yield from **1d**); ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.24 (s, 9H), 0.99 (d, $J = 7.6$ Hz, 6H), 1.10 (d, $J = 7.2$ Hz, 6H), 1.40–1.49 (m, 2H), 4.02 (t, $J = 4.0$ Hz, 1H), 7.24–7.32 (m, 2H), 7.47–7.48 (m, 1H), 7.49–7.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.2, 11.2, 19.1, 19.1, 96.1, 106.7, 127.4, 128.8, 128.9, 132.7, 136.6, 138.1; IR (neat) 3051, 2956, 2863, 2156, 1250 cm^{-1}; HRMS (EI$^+$) calcd for $C_{17}H_{28}Si_2$ [M$^+$] 288.1730, found 288.1720.

*4.1.3.2. 1-(Dimethylsilyl)-2-[2-(tert-butyldimethylsilyl)ethynyl]benzene (**6e**).* Pale yellow liquid (497 mg, 1.81 mmol, 83% yield from **1e**); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.19 (s, 6H), 0.41 (d, $J = 4.0$ Hz, 6H), 1.00 (s, 9H), 4.55 (sept, $J = 4.0$ Hz, 1H), 7.27–7.33 (m, 2H), 7.48–7.52 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −4.6, −4.0, 16.7, 26.2, 95.6, 106.3, 127.7, 128.8, 129.0, 132.6, 134.6, 140.1; IR (neat) 3053, 2929, 2857, 2153 cm^{-1}; HRMS (EI$^+$) calcd for $C_{16}H_{26}Si_2$ [M$^+$] 274.1573, found 274.1578.

*4.1.3.3. 5-Chloro-1-(diphenylsilyl)-2-[2-(trimethylsilyl)ethynyl]benzene (**6i**).* Colorless clear liquid (0.33 g, 0.85 mmol, 98% yield from **1i**); ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.01 (s, 9H), 5.59 (s, 1H), 7.30–7.47 (m, 9H), 7.54–7.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.6, 99.8, 104.2, 128.0, 128.1, 129.9, 129.9, 132.2, 133.7, 134.4, 135.9, 136.3, 139.1; IR (neat) 3069, 2959, 2156, 1251 cm^{-1}; HRMS (EI$^+$) calcd for $C_{23}H_{23}ClSi_2$ [M$^+$] 390.1027, found 390.1024.

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*4.1.3.4. 2-(Diphenylsilyl)-3-[2-(trimethylsilyl)ethynyl]naphthalene (**6l**).* Colorless clear gum (0.83 g, 2.1 mmol, 99% yield from **1l**); ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.03 (s, 9H), 5.73 (s, 1H), 7.35–7.53 (m, 9H), 7.60–7.63 (m, 3H), 7.71 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.87 (s, 1H), 8.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.5, 98.2, 105.6, 125.4, 126.8, 127.4, 127.5, 127.9, 128.2, 129.6, 132.2, 132.8, 133.3, 133.6, 136.0, 138.3; IR (neat) 3068, 2148, 1250 cm^{-1}; HRMS (EI$^+$) calcd for $C_{27}H_{26}Si_2$ [M$^+$] 406.1573, found 406.1571.

*4.1.3.5. Bis[(2-(diphenylsilyl)phenyl)ethynyl]dimethylsilane (**6n**).* Colorless clear gum (0.21 g, 0.34 mmol, 86% yield from **1n**); ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ −0.04 (s, 6H), 5.64 (s, 2H), 7.27–7.40 (m, 18H), 7.53–7.59 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.5, 94.8, 105.9, 127.9, 128.1, 129.4, 129.6, 129.7, 132.6, 133.0, 136.0, 136.6, 136.8; IR (neat) 3063, 2855, 2197, 2154, 1455 cm^{-1}; HRMS (EI$^+$) calcd for $C_{42}H_{36}Si_3$ [M$^+$] 624.2125, found 624.2119.

*4.1.3.6. 1-(Diphenylsilyl)-2-[2-(dimethylphenylsilyl)ethynyl]benzene (**6q**).* Colorless clear liquid (195 mg, 0.465 mmol, quant from 2-bromo-1-[2-(dimethyl(phenyl)silyl)ethynyl]benzene [935221-20-8]);[21] ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.26 (s, 6H), 5.66 (s, 1H), 7.26–7.42 (m, 13H), 7.46–7.48 (m, 2H), 7.54–7.60 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −1.3, 96.3, 106.8, 127.8, 127.9, 128.0, 129.3, 129.6, 129.7, 132.7, 132.9, 133.7, 135.9, 136.5, 136.7; IR (neat) 3068, 3049, 3000, 2958, 2155, 1429, 1117 cm^{-1}; HRMS (EI$^+$) calcd for $C_{28}H_{26}Si_2$ [M$^+$] 418.1573, found 418.1576.

4.1.4. Synthesis of hydrosilanes 8 (typical procedure)

*n*BuLi (2.7 M in hexane, 2.2 mL, 5.9 mmol) was added to a solution of **4a'** (1.9 g, 5.6 mmol)[29] in THF (15 mL) at −78 °C. After 0.5 h stirring, Ph_2SiCl_2 (1.2 mL, 5.6 mmol) was added to the mixture. The resultant mixture was stirred for 1 h at −78 °C and then warmed to 0 °C. After adding $LiAlH_4$ (0.21 g, 5.6 mmol), the mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was quenched with water and extracted with hexane three times. The combined organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by silica-gel column chromatography (hexane) and then recycling preparative HPLC ($CHCl_3$) gave (*Z*)-4-(diphenylsilyl)-7-[dimethyl(phenyl)silyl]-5-(propyl) hept-4-en-6-yne (**8a**)[21] was obtained as a colorless clear liquid (only pure fraction, 0.99 g, 2.2 mmol, 39% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 6H), 0.73 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H), 1.15–1.28 (m, 2H), 1.61–1.72 (m, 2H), 2.14–2.20 (m, 2H), 2.30–2.35 (m, 2H), 5.33 (s, 1H), 7.24–7.40 (m, 11H), 7.56–7.7.59 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −1.3, 13.9, 14.2, 21.9, 23.1, 34.6, 96.1, 108.5, 127.6, 127.7, 129.1, 129.3, 133.7, 133.8, 135.9, 136.8, 137.2, 144.9; IR (neat) 3068, 3049, 2959, 2138 cm^{-1}; HRMS (EI$^+$) calcd for $C_{30}H_{36}Si_2$ [M$^+$] 452.2356, found 452.2358.

The substrates **8b**–**h** were prepared following our previous report.[21]

The alkenyl iodides **8k'**, **8l'**, **8m'**, and **8n'** were prepared by the reported methods,[30] and used for the synthesis of **8k**–**o** by the method reported by this group.[21]

*4.1.4.1. (Z)-14-Ethyl-13-iodo-16-(trimethylsilyl)hexadec-13-en-15-yne (**8m'**).* [21,30] Colorless liquid (558 mg, 1.25 mmol, 42% yield from hexadec-1-yne); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.22 (s, 9H), 0.88 (t, J = 7.5 Hz, 3H), 1.12 (t, J = 7.5 Hz, 3H), 1.25–1.31 (m, 18H), 1.45–1.51 (m, 2H), 2.27 (q, J = 7.5 Hz, 2H), 2.57 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.1, 13.5, 14.1, 22.7, 26.3, 28.6, 29.4, 29.5, 29.5, 29.6, 31.9, 40.8, 97.5, 109.1, 113.9, 132.4; IR (neat) 2925, 2143, 1249 cm^{-1}; HRMS (EI$^+$) calcd for $C_{21}H_{39}ISi$ [M$^+$] 446.1866, found 446.1872.

*4.1.4.2. (Z)-14-Ethyl-16-(trimethylsilyl)-13-(diphenylsilyl)hexadec-13-en-15-yne (**8m**).* Colorless liquid (270 m g, 0.54 mmol, 43% yield from **8m'**); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ −0.09 (s, 9H), 0.88 (t, J = 7.5 Hz, 3H), 1.05–1.34 (m, 23 H), 2.14–2.18 (m, 2H), 2.33 (q, J = 7.5 Hz, 2H), 5.29 (s, 1H), 7.31–7.39 (m, 6H), 7.57–7.60 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.5, 13.4, 14.1, 22.7, 25.8, 29.2, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 32.3, 98.5, 106.8, 127.7, 129.3, 134.0, 135.9, 138.2, 143.7; IR (neat) 3068, 2958, 2138, 1112 cm^{-1}; HRMS (EI$^+$) calcd for $C_{33}H_{50}Si_2$ [M$^+$] 502.3451, found 502.3453.

*4.1.4.3. (Z)-6-Ethyl-5-iodo-2-methyl-8-(trimethylsilyl)oct-5-en-7-yne (**8n'**).* [30] Colorless liquid (571 mg, 1.64 mmol, 55% yield from 5-methylhex-1-yne); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.22 (s, 9H), 0.91 (d, J = 6.5 Hz, 6H), 1.12 (t, J = 7.5 Hz, 3H), 1.38–1.43 (m, 2H), 1.58 (sept, J = 6.5 Hz, 1H), 2.26 (q, J = 7.5 Hz, 2H), 2.56–2.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.2, 13.5, 22.5, 26.1, 27.3, 38.6, 38.9, 97.5, 109.0, 113.9, 132.2; IR (neat) 2958, 2143, 1044 cm^{-1}; HRMS (EI$^+$) calcd for $C_{14}H_{25}ISi$ [M$^+$] 348.0770, found 348.0773.

*4.1.4.4. (Z)-6-Ethyl-2-methyl-8-(trimethylsilyl)-5-(diphenylsilyl)oct-5-en-7-yne (**8n**).* Colorless liquid (146 mg, 0.361 mmol, 45% yield from **8n'**); ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ −0.09 (s, 9H), 0.66 (d, J = 6.6 Hz, 6H), 0.99–1.08 (m, 2H), 1.17 (t, J = 7.5 Hz, 3H), 1.29 (sept, J = 6.5 Hz, 1H), 2.11–2.17 (m, 2H), 2.32 (q, J = 7.5 Hz, 2H), 5.30 (s, 1H), 7.30–7.41 (m, 6H), 7.55–7.62 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.5, 13.4, 22.1, 25.7, 28.3, 30.1, 38.6, 98.5, 106.7, 127.7, 129.3, 134.0, 135.9, 138.2, 143.7; IR (neat) 3068, 2957, 2139, 1112 cm^{-1}; HRMS (EI$^+$) calcd for $C_{26}H_{36}Si_2$ [M$^+$] 404.2356, found 404.2358.

*4.1.4.5. (Z)-6-Ethyl-2-methyl-8-(trimethylsilyl)-5-[methyl(phenyl)silyl]oct-5-en-7-yne (**8o**).* Colorless liquid (147 mg, 0.429 mmol, 39% yield from **8n'**); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.07 (s, 9H), 0.54 (d, J = 3.5 Hz, 3H), 0.79 (d, J = 7.0 Hz, 6H), 1.05–1.12 (m, 2H), 1.21 (t, J = 7.5 Hz, 3H), 1.43 (sept, J = 7.0 Hz, 1H), 2.16 (t, J = 8.0 Hz, 2H), 2.26 (q, J = 7.5 Hz, 2H), 4.75 (q, J = 3.5 Hz, 1H), 7.31–7.35 (m, 3H), 7.58–7.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −5.1, −0.3, 13.3, 22.3, 25.6, 28.4, 30.3, 38.7, 97.3, 107.0, 127.6, 129.0, 134.8, 136.1, 136.4, 145.7; IR (neat) 3068, 2958, 2138, 1112 cm^{-1}; HRMS (EI$^+$) calcd for $C_{21}H_{34}Si_2$ [M$^+$] 342.2199, found 342.2191.

4.1.5. Synthesis of benzosiloles 2 from Methyl silyl ethers 1 (general procedure)

DIBAL-H (1.0 M solution in hexane, 0.33 mL, 0.33 mmol) was added to a flask containing substrate **1** (0.25 mmol). After removing the hexane under reduced pressure, octane (0.75 mL) was added to the residue. The resultant mixture was stirred at 75 °C for 6 h. The mixture was cooled to room temperature. Then 1 M aqueous HCl (2.0 mL) was added to the mixture. The aqueous mixture was stirred vigorously and extracted with hexane three times. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica-gel column chromatography (hexane).

*4.1.5.1. 1,1-Dimethyl-2-(trimethylsilyl)-1H-benzo[b]silole (**2a**) [152554-94-4].* Colorless liquid (52 mg, 0.22 mmol, 89%); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.17 (s, 9H), 0.32 (s, 6H), 7.21 (ddd, J = 7.5, 7.0, 1.0 Hz, 1H), 7.27 (d, J = 7.0 Hz, 1H), 7.32 (ddd, J = 7.5, 7.0, 1.0 Hz, 1H), 7.50 (s, 1H), 7.53 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −3.2, −0.6, 124.0, 126.9, 129.7, 131.5, 140.7, 146.8, 150.0, 155.3; IR (neat) 3055, 2952, 1519, 1249 cm^{-1}; HRMS (EI$^+$) calcd for $C_{13}H_{20}Si_2$ [M$^+$] 232.1104, found 232.1093.

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*4.1.5.2. 1,1-Dimethyl-2-(trimethylsilyl)-1H-benzo[b]silole (**2a**-d).* Colorless liquid (29.8 mg, 0.128 mmol, 51% from **6a**-*d*). ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.17 (s, 9H), 0.32 (s, 6H), 7.20 (ddd, J = 7.5, 7.0, 1.0 Hz, 1H), 7.27–7.28 (m, 1H), 7.32 (ddd, J = 7.5, 7.0, 1.0 Hz, 1H), 7.53 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −3.2, −0.5, 124.0, 126.9, 129.7, 131.5, 140.7, 146.6, 149.9, 155.0 (t, J = 23.8 Hz); IR (neat) 3055, 2953, 2209, 1249 cm^{-1}; HRMS (EI$^+$) calcd for $C_{13}H_{19}DSi_2$ [M$^+$] 233.1166, found 233.1174.

*4.1.5.3. 1,1-Dimethyl-2-(trimethylsilyl)-2,3-dihydro-1H-benzo[b]silole (**3a**) [66535-02-2].* [31] Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.08 (s, 9H), 0.25 (s, 3H), 0.34 (s, 3H), 0.44 (dd, J = 10.0, 8.8 Hz, 1H), 2.98 (dd, J = 16.8, 10.0 Hz, 1H), 3.21 (dd, J = 16.8, Hz, 8.8 Hz, 1H), 7.17–7.32 (m, 3H), 7.50 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −1.0, −0.9, −0.3, 14.1, 34.3, 125.2, 125.6, 129.0, 131.6, 140.5, 153.5; IR (neat) 3055, 2952, 2120, 1250 cm^{-1}; HRMS (EI$^+$) calcd for $C_{13}H_{22}Si_2$ [M$^+$] 234.1260, found 234.1254.

*4.1.5.4. 1,1-Diphenyl-2-(trimethylsilyl)-1H-benzo[b]silole (**2b**).* Colorless liquid (82 mg, 0.23 mmol, 92%); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.06 (s, 9H), 7.22 (ddd, J = 7.0, 6.5, 2.0 Hz, 1H), 7.32–7.37 (m, 6H), 7.38–7.43 (m, 2H), 7.58 (d, J = 6.5 Hz, 1H), 7.60–7.62 (m, 4H), 7.74 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.1, 124.5, 127.6, 128.0, 129.9, 130.2, 132.7, 132.9, 135.6, 138.2, 144.0, 150.9, 158.7; IR (neat) 3052, 3023, 2953, 1515, 1113 cm^{-1}; HRMS (EI$^+$) calcd for $C_{23}H_{24}Si_2$ [M$^+$] 356.1417, found 356.1425.

*4.1.5.5. 1-Methyl-1-phenyl-2-(trimethylsilyl)-1H-benzo[b]silole (**2c**).* Pale yellow liquid (70.0 mg, 0.238 mmol, 95%); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.06 (s, 9H), 0.66 (s, 3H), 7.19–7.23 (m, 1H), 7.29–7.39 (m, 5H), 7.47–7.50 (m, 2H), 7.50–7.52 (m, 1H), 7.62 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −5.6, −0.5, 124.2, 127.3, 127.9, 129.6, 130.0, 132.2, 134.3, 134.5, 139.3, 145.7, 150.7, 156.7; IR (neat) 3053, 3000, 2953, 1519, 1123 cm^{-1}; HRMS (EI$^+$) calcd for $C_{18}H_{22}Si_2$ [M$^+$] 294.1260, found 294.1253.

*4.1.5.6. 1,1-Diisopropyl-2-(trimethylsilyl)-1H-benzo[b]silole (**2d**).* Colorless liquid (65.7 mg, 0.228 mmol, 91%); ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ 0.19 (s, 9H), 0.92 (d, J = 7.5 Hz, 6H), 1.06 (d, J = 7.5 Hz, 6H), 1.30 (sept, J = 7.5 Hz, 2H), 7.18 (ddd, J = 6.9, 6.9, 1.5 Hz, 1H), 7.24–7.27 (m, 1H), 7.31 (ddd, J = 7.2, 7.2, 1.2 Hz, 1H), 7.49–7.52 (m, 1H), 7.59 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.2, 11.2, 18.0, 123.9, 126.7, 129.5, 132.6, 137.4, 143.1, 151.2, 158.2; IR (neat) 3055, 2952, 1514, 1248, 966 cm^{-1}; HRMS (EI$^+$) calcd for $C_{17}H_{28}Si_2$ [M$^+$] 288.1730, found 288.1724.

*4.1.5.7. 2-(tert-Butyldimethylsilyl)-1,1-dimethyl-1H-benzo[b]silole (**2e**).* Colorless liquid (59.0 mg, 0.215 mmol, 86%); ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.14 (s, 6H), 0.33 (s, 6H), 0.92 (s, 9H), 7.19–7.24 (m, 1H), 7.27–7.35 (m, 2H), 7.51–7.54 (m, 1H), 7.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −4.7, −2.7, 17.3, 26.8, 124.0, 127.0, 129.7, 131.4, 140.7, 143.9, 149.8, 157.7; IR (neat) 3055, 2953, 2855, 1514, 1252 cm^{-1}; HRMS (EI$^+$) calcd for $C_{16}H_{26}Si_2$ [M$^+$] 274.1573, found 274.1578.

*4.1.5.8. 2-[Dimethyl(phenyl)silyl]-1,1-dimethyl-1H-benzo[b]silole (**2f**).* Colorless liquid (62 mg, 0.21 mmol, 84%); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.19 (s, 6H), 0.45 (s, 6H), 7.21 (ddd, J = 7.0, 7.0, 1.0 Hz, 1H), 7.26–7.28 (m, 1H), 7.32 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.34–7.36 (m, 3H), 7.51–7.7.55 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −3.3, −2.0, 124.2, 127.1, 127.7, 128.9, 129.7, 131.5, 133.9, 139.0, 140.8, 144.5, 149.7, 157.0; IR (neat) 3052, 2954, 1518, 1110 cm^{-1}; HRMS (EI$^+$) calcd for $C_{18}H_{22}Si_2$ [M$^+$] 294.1260, found 294.1253.

*4.1.5.9. 6-Methyl-1,1-diphenyl-2-(trimethylsilyl)-1H-benzo[b]silole (**2h**).* White powder (89.9 mg, 0.243 mmol, 97%); m.p. 53.0–54.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.04 (s, 9H), 2.32 (s, 3H), 7.16 (dd, J = 7.8, 1.0 Hz, 1H), 7.24 (d. J = 7.5 Hz, 1H), 7.32–7.43 (m, 7H), 7.60–7.62 (m, 4H), 7.71 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1, 21.4, 124.2, 127.9, 129.9, 130.7, 132.9, 133.8, 135.6, 137.3, 138.4, 142.2, 148.4, 158.6; IR (nujol) 3067, 2953, 1510, 1248, 1114 cm^{-1}; HRMS (EI$^+$) calcd for $C_{24}H_{26}Si_2$ [M$^+$] 370.1573, found 370.1574.

*4.1.5.10. 6-Chloro-1,1-diphenyl-2-(trimethylsilyl)-1H-benzo[b]silole (**2i**).* White powder (85.1 mg, 0.218 mmol, 87%); m.p. 96–97 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.05 (s, 9H), 7.25–7.27 (m, 1H), 7.31–7.38 (m, 5H), 7.41–7.45 (m, 2H), 7.50 (d, J = 2.0 Hz, 1H), 7.58–7.60 (m, 4H), 7.68 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.2, 125.4, 128.1, 130.1, 130.2, 131.8, 132.7, 133.9, 135.5, 141.0, 144.8, 149.0, 157.4; IR (nujol) 3068, 3045, 1509, 1428, 1115 cm^{-1}; HRMS (EI$^+$) calcd for $C_{23}H_{23}ClSi_2$ [M$^+$] 390.1027, found 390.1030.

*4.1.5.11. 6-Fluoro-1,1-diphenyl-2-(trimethylsilyl)-1H-benzo[b]silole (**2j**).* White powder (90 mg, 0.24 mmol, 96%); m.p. 78.0–79.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05 (s, 9H), 7.03 (ddd, J = 8.5, 8.5, 2.5 Hz, 1H), 7.25 (dd, J = 7.5, 2.5 Hz, 1H), 7.30 (dd, J = 8.3, 5.0 Hz, 1H), 7.34–7.39 (m, 4H), 7.7.41–7.45 (m, 2H), 7.60 (dd, J = 8.0, 1.5 Hz, 4H), 7.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −0.1, 116.6 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 119.8 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 125.6 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 128.1, 130.2, 132.0, 135.5, 141.6, (d, $^3J_{C\text{-}F}$ = 6.3 Hz), 143.5, 146.7, 157.6, 162.8 (d, $^1J_{C\text{-}F}$ = 248.8 Hz); IR (nujol) 3068, 3024, 2954, 2895, 2155, 1116 cm^{-1}; HRMS (EI$^+$) calcd for $C_{23}H_{23}FSi_2$ [M$^+$] 374.1322, found 374.1318.

*4.1.5.12. 6-Chloro-1,1-diphenyl-2-(trimethylsilyl)-1H-benzo[b]silole (**2k**).* Pale yellow liquid (88.3 mg, 0.225 mmol, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 9H), 7.15 (dd, J = 10.6, 7.2 Hz, 1H), 7.29–7.47 (m, 7H), 7.56–7.60 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 113.4 (d, $J_{C\text{-}F}$ = 17.1 Hz), 121.4 (d, $J_{C\text{-}F}$ = 17.1 Hz), 128.2, 130.3, 131.6, 134.8 (dd, $J_{C\text{-}F}$ = 4.0, 4.0 Hz), 135.4, 146.3 (d, $J_{C\text{-}F}$ = 4.0 Hz), 147.5 (dd, $J_{C\text{-}F}$ = 5.0, 4.0 Hz), 150.3 (dd, $J_{C\text{-}F}$ = 251.0, 12.6 Hz), 152.0 (dd, $J_{C\text{-}F}$ = 250.0, 13.6 Hz), 156.3; IR (neat) 3069, 2955, 1597, 1520, 1322, 1116 cm^{-1}; HRMS (EI$^+$) calcd for $C_{23}H_{22}F_2Si_2$ [M$^+$] 392.1228, found 392.1227.

*4.1.5.13. 1,1-Diphenyl-2-(trimethylsilyl)-1H-naphtho[2,3-b]silole (**2l**).* White powder (94.6 mg, 0.233 mmol, 93%); m.p. 176–177 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.08 (s, 9H), 7.34–7.37 (m, 4H), 7.40–7.43 (m, 3H), 7.44–7.48 (m, 1H), 7.65–7.67 (m, 4H), 7.74 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 8.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.1, 122.9, 126.0, 126.7, 128.0, 128.4, 128.4, 130.0, 133.0, 133.4, 133.9, 134.9, 135.6, 135.9, 145.8, 147.6, 158.8; IR (nujol) 3055, 1516, 1427, 1245, 1117 cm^{-1}; HRMS (EI$^+$) calcd for $C_{27}H_{26}Si_2$ [M$^+$] 406.1573, found 406.1569.

*4.1.5.14. 1,5-Dihydro-1,1,5,5-tetraphenyl-2,6-bis(trimethylsilyl)-1,5-disila-s-indacene (**2m**).* White powder (110 mg, 0.173 mmol, 69%); m.p. 285–286 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.03 (s, 18H), 7.33–7.36 (m, 8H), 7.39–7.43 (m, 4H), 7.57 (s, 2H), 7.61–7.64 (m, 8H), 7.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −0.1, 128.0, 128.8, 130.0, 132.6, 135.6, 141.2, 144.0, 150.2, 159.0; IR (nujol) 3068, 3051, 1522, 1429, 1248, 1116 cm^{-1}; HRMS (EI$^+$) calcd for $C_{40}H_{42}Si_4$ [M$^+$] 634.2364, found 634.2353.

*4.1.5.15. Bis(1,1-diphenyl-1H-benzo[b]silol-2-yl)dimethylsilane (**2n**).* White powder (125 mg, 0.200 mmol, 80%); m.p. 169–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 7.26 ppm) δ 0.08 (s, 6H), 7.15 (d, J = 7.6 Hz,

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2H), 7.19–7.28 (m, 10H), 7.31–7.38 (m, 6H), 7.51–7.56 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ 0.1, 124.7, 127.6, 127.9, 129.9, 130.0, 132.6, 132.7, 135.6, 138.3, 141.8, 150.7, 160.6; IR (nujol) 3067, 3052, 1736, 1514, 1113 cm^{-1}; HRMS (EI$^+$) calcd for $C_{42}H_{36}Si_3$ [M$^+$] 624.2125, found 624.2119.

*4.1.5.16. (E)-1-(Dimethylsilyl)-2-[2-(trimethylsilyl)ethenyl]benzene (**6a'**).* Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ 0.16 (s, 9H), 0.37 (d, J = 3.9 Hz, 6H), 4.60 (sept, J = 3.9 Hz, 1H), 6.40 (d, J = 18.9 Hz, 1H), 7.21–7.27 (m, 2H), 7.37 (ddd, J = 7.2, 7.2, 1.2 Hz, 1H), 7.51 (dd, J = 7.2, 1.2 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ −3.2, −1.3, 124.7, 127.0, 129.7, 131.3, 134.8, 135.9, 144.3, 144.6; IR (neat) 3054, 2955, 2898, 2120, 1120 cm^{-1}; HRMS (EI$^+$) calcd for $C_{13}H_{22}Si_2$ [M$^+$] 234.1260, found 234.1255.

4.1.6. Synthesis of siloles 5 from Methyl silyl ethers 4 (general procedure)

DIBAL-H (1.0 M solution in hexane, 0.33 mL, 0.33 mmol) was added to a flask containing the substrate **4** (0.25 mmol). After removing the hexane under reduced pressure, octane (0.75 mL) was added to the residue. The resultant mixture was stirred at 75 °C for 24 h. The mixture was cooled to room temperature. Then 1 M aqueous HCl (2.0 mL) was added to the mixture. The aqueous mixture was stirred vigorously and extracted with hexane three times. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica-gel column chromatography (hexane).

4.1.7. Synthesis of benzosiloles 2 from hydrosilanes 6 (general procedure)

Method A: DIBAL-H (1.0 M solution in hexane, 0.30 mL, 0.30 mmol) was added to a flask containing the substrate **6** (0.25 mmol). **Method B:** DIBAL-H (1.0 M solution in hexane, 0.125 mL, 0.125 mmol) was added to a flask containing the substrate **6** (0.25 mmol). After removing the hexane under reduced pressure, octane (0.75 mL) was added to the residue. The resultant mixture was stirred at 80 °C for 0.5 h (method A) or 1 h (method B). The mixture was cooled to room temperature. Then 1 M aqueous HCl (2.0 mL) was added to the mixture. The aqueous mixture was stirred vigorously and extracted with hexane three times. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica-gel column chromatography (hexane).

*4.1.7.1. 2-[Dimethyl(phenyl)silyl]-1,1-diphenyl-1H-benzo[b]silole (**2q**).* Colorless liquid (95.2 mg, 0.228 mmol, 91%); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 0.32 (s, 6H), 7.21–7.42 (m, 14H), 7.48–7.50 (m, 4H), 7.59 (d, J = 7.0 Hz, 1H), 7.72 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −1.4, 124.7, 127.6, 127.8, 127.9, 128.8, 129.9, 130.2, 132.4, 132.9, 134.0, 135.5, 138.3, 138.7, 141.8, 150.7, 160.3; IR (neat) 3067, 3050, 2955, 1514, 1428, 1113 cm^{-1}; HRMS (EI$^+$) calcd for $C_{28}H_{26}Si_2$ [M$^+$] 418.1573, found 418.1580.

4.1.8. Synthesis of siloles 5 from hydrosilanes 8 (general procedure)

Method A: DIBAL-H (1.0 M solution in hexane, 0.30 mL, 0.30 mmol) was added to a flask containing the substrate **8** (0.25 mmol). **Method B:** DIBAL-H (1.0 M solution in hexane, 0.125 mL, 0.125 mmol) was added to a flask containing the substrate **8** (0.25 mmol). After removing the hexane under reduced pressure, octane (0.75 mL) was added to the residue. The resultant mixture was stirred at 80 °C for 0.5 h (method A) or 1 h (method B). The mixture was cooled to room temperature. Then 1 M aqueous HCl (2.0 mL) was added to the mixture. The aqueous mixture was stirred vigorously and then extracted with hexane three times. The combined organic layer was dried over Na_2SO_4 and evaporated. The residue was purified by silica-gel column chromatography (hexane).

*4.1.8.1. 5-[Dimethyl(phenyl)silyl]-1,1-diisopropyl-2,3-dipropyl-1H-silole (**5e**).* Colorless liquid (60.0 mg, 0.158 mmol, 21%); ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ 0.38 (s, 6H), 0.83–0.94 (m, 18H), 1.03–1.14 (m, 2H), 1.34–1.47 (m, 4H), 2.15–2.29 (m, 4H), 7.12 (s, 1H), 7.30–7.35 (m, 3H), 7.46–7.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −1.5, 11.0, 13.9, 14.8, 17.5, 17.7, 22.2, 23.3, 31.9, 32.5, 127.5, 128.6, 134.0, 135.2, 139.7, 140.4, 153.6, 162.3; IR (neat) 3068, 2956, 1246, 1112 cm^{-1}; HRMS (EI$^+$) calcd for $C_{24}H_{40}Si_2$ [M$^+$] 384.2669, found 384.2674.

*4.1.8.2. 2-Dodecyl-3-ethyl-1,1-diphenyl-5-(trimethylsilyl)-1H-silole (**5m**).* Colorless liquid (0.11 g, 0.23 mmol, 91%); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ −0.08 (s, 9H), 0.88 (t, J = 7.0 Hz, 3H), 0.94–1.32 (m, 20H), 1.11 (t, J = 7.5 Hz, 3H), 2.31 (t, J = 7.5 Hz, 2H), 2.35 (q, J = 7.5 Hz, 2H), 7.25 (s, 1H), 7.31–7.41 (m, 6H), 7.57–7.59 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.2, 13.5, 14.1, 22.7, 23.4, 29.1, 29.3, 29.3, 29.5, 29.6, 29.6, 29.7, 30.2, 31.9, 127.8, 129.5, 133.4, 135.5, 140.4, 140.6, 155.8, 160.1; IR (neat) 3068, 3050, 2925, 1112 cm^{-1}; HRMS (EI$^+$) calcd for $C_{33}H_{50}Si_2$ [M$^+$] 502.3451, found 502.3449.

*4.1.8.3. 3-Ethyl-2-isopentyl-1,1-diphenyl-5-(trimethylsilyl)-1H-silole (**5n**).* Colorless liquid (96 mg, 0.24 mmol, 95%); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ −0.08 (s, 9H), 0.65 (d, J = 6.5 Hz, 6H), 0.99–1.04 (m, 2H), 1.11 (t, J = 7.5 Hz, 3H), 1.29 (sept, J = 6.5 Hz, 1H), 2.29–2.38 (m, 4H), 7.25 (s, 1H), 7.32–7.35 (4H), 7.38–7.40 (m, 2H), 7.57–7.59 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −0.2, 13.6, 22.2, 23.4, 26.7, 27.8, 39.3, 127.8, 129.5, 133.4, 135.5, 140.4, 140.6, 155.6, 160.1; IR (neat) 3068, 2955, 1112 cm^{-1}; HRMS (EI$^+$) calcd for $C_{26}H_{36}Si_2$ [M$^+$] 404.2356, found 404.2362.

*4.1.8.4. 3-Ethyl-2-isopentyl-1-methyl-1-phenyl-5-(trimethylsilyl)-1H-silole (**5o**).* Colorless liquid (76 mg, 0.22 mmol, 89%); ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ −0.05 (s, 9H), 0.53 (s, 3H), 0.73 (d, J = 7.0 Hz, 3H), 0.81 (d, J = 6.5 Hz, 3H), 1.09 (t, J = 7.5 Hz, 3H), 1.09–1.17 (m, 2H), 1.40 (sept, J = 6.5 Hz, 1H), 2.13–2.19 (m, 1H), 2.26–2.36 (m, 3H), 7.13 (s, 1H), 7.26–7.35 (m, 3H), 7.42–7.45 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 77.0 ppm) δ −5.9, −0.5, 13.6, 22.3, 22.4, 23.2, 26.5, 27.8, 39.4, 127.7, 129.1, 134.1, 135.2, 141.4, 141.5, 154.4, 158.3; IR (neat) 3068, 2954, 1500, 1247, 1109 cm^{-1}; HRMS (EI$^+$) calcd for $C_{21}H_{34}Si_2$ [M$^+$] 342.2199, found 342.2187.

4.2. Derivatization of silylated products

Bromine (0.50 M solution in CH_2Cl_2 (0.25 mL), 20 mg, 0.12 mmol) was added to a solution of **2l** (51 mg, 0.12 mmol) in CH_2Cl_2 (1 mL) at room temperature. After 0.5 h stirring, the resultant mixture was quenched with saturated aqueous $Na_2S_2O_3$. The aqueous mixture was extracted with CH_2Cl_2 (20 mL) three times. The combined organic layer was dried over Na_2SO_4 and evaporated. Purification by silica-gel column chromatography (hexane/AcOEt = 20:1) gave 2-bromo-1,1-diphenyl-1*H*-naphtho[2,3-*b*]silole (**9**) as a colorless needle crystal (37 mg, 0.089 mmol, 72%). m.p. 179–180 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm) δ 7.38–7.51 (m, 8H), 7.65 (s, 1H), 7.72–7.74 (m, 4H), 7.78–7.82 (m, 3H), 8.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ 122.5, 126.2, 127.3, 127.8, 128.3, 128.3, 128.4, 130.2, 130.7, 132.1, 132.9, 134.8, 134.9, 135.6, 145.1, 150.5; IR (nujol) 3051, 1269, 1118 cm^{-1}; HRMS (EI$^+$) calcd for $C_{24}H_{17}BrSi$ [M$^+$] 412.0283, found 412.0280.

*4.2.1. 6-Fluoro-2-iodo-1,1-diphenyl-1H-benzo[b]silole (**10**)*

ICl (0.10 M in CH_2Cl_2, 1.5 mL, 0.15 mmol) was added to a solution

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of **2j** (57 mg, 0.15 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and then room temperature for 11 h. The resultant mixture was quenched with saturated aqueous $Na_2S_2O_3$. The aqueous mixture was extracted with CH_2Cl_2 (20 mL) three times. The combined organic layer was dried over Na_2SO_4 and evaporated. Purification by silica-gel column chromatography (hexane/AcOEt = 20:1) gave the title compound **10** as a white solid (56 mg, 0.13 mmol, 85%). m.p. 163–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ 6.80–7.05 (m, 1H), 7.20–7.25 (m, 1H), 7.32–7.36 (m, 1H), 7.37–7.43 (m, 4H), 7.46–7.52 (m, 2H), 7.64–7.67 (m, 4H), 7.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ 95.4, 116.9 (d, $^2J_{C\text{-}F}$ = 22.1 Hz), 120.6 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 125.0 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 128.4, 129.4, 130.9, 135.6, 138.1 (d, $^3J_{C\text{-}F}$ = 5.0 Hz), 146.7, 156.4, 162.5 (d, $^1J_{C\text{-}F}$ = 250.5 Hz); IR (nujol) 3070, 3050, 2854, 1195, 1117 cm^{-1}; HRMS (EI$^+$) calcd for $C_{20}H_{14}FISi$ [M$^+$] 427.9894, found 427.9891.

4.2.2. 5-Iodo-1,1-diphenyl-2,3-dipropyl-1H-silole (*11*)

2-Iodosilole **11** was derived from **5b** (86 mg, 0.22 mmol) by the reported method.[26] Pale orange liquid (32 mg, 0.072 mmol, 33%); ^{1}H NMR (300 MHz, $CDCl_3$, 7.26 ppm) δ 0.73 (t, J = 7.5 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H), 1.20–1.32 (m, 2H), 1.46–1.60 (m, 2H), 2.28–2.36 (m, 4H), 7.35–7.50 (m, 7H), 7.58–7.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 77.0 ppm) δ 13.9, 14.3, 21.7, 23.9, 32.0, 32.3, 92.6, 128.2, 130.3, 130.7, 135.6, 138.5, 155.3, 158.4; IR (neat) 3068, 2957, 2869, 1582, 1115 cm^{-1}; HRMS (EI$^+$) calcd for $C_{22}H_{25}ISi$ [M$^+$] 444.0770, found 444.0756.

References

1. Yamaguchi Y, S., Tamao K. In: Jones RG, Ando W, Chojnowski J, eds. *In Silicon-containing Polymers: The Science and Technology of Their Synthesis and Applications*. Dordrecht, The Netherlands: Kluwer Academic Publishers; 2000: 461–498.
2. (a) Yamaguchi S, Endo T, Uchida M, Izumizawa T, Furukawa K, Tamao K. *Chem Eur J*. 2000;6:1683–1692;
   (b) Yamaguchi S, Tamao K. *Chem Lett*. 2005;34:2–7;
   (c) Booker C, Wang X, Haroun S, et al. *Angew Chem Int Ed*. 2008;47:7731–7735;
   (d) Zhan, X.; Barlow, S.; Marder, S. R. Chem Commun 2009, 1948–1955.
3. (a) Yamaguchi S, Goto T, Tamao K. *Angew Chem Int Ed*. 2000;39:1695–1697;
   (b) Uchida M, Izumizawa T, Nakano T, Yamaguchi S, Tamao K, Furukawa K. *Chem Mater*. 2001;13:2680–2683;
   (c) Kim B-H, Woo H-G. *Organometallics*. 2002;21:2796–2798;
   (d) Liu MS, Luo J, Jen AK-Y. *Chem Mater*. 2003;15:3496–3500;
   (e) Wang F, Luo J, Yang K, Chen J, Huang F, Cao Y. *Macromolecules*. 2005;38: 2253–2260;
   (f) Yu G, Yin S, Liu Y, et al. *J Am Chem Soc*. 2005;127:6335–6346;
   (g) Peng L, Wang M, Zhang G, Zhang D, Zhu D. *Org Lett*. 2009;11:1943–1946;
   (h) Li Z, Dong YQ, Lam JWY, et al. *Adv Funct Mater*. 2009;19:905–917.
4. Selected examples of silole syntheses, see: (a) Wang Z, Fang H, Xi Z. *Tetrahedron Lett*. 2005;46:499–501;
   (b) Dierker G, Ugolotti J, Kehr G, Fröhlich R, Erker G. *Adv Synth Catal*. 2009;351: 1080–1088;
   (c) Ugolotti J, Kehr G, Fröhlich R, Erker G. *Chem Commun*. 2010;46:3016–3018.
5. Selected examples of recent benzosilole sytheses, see: (a) Sudo T, Asao N, Yamamoto YJ. *Org Chem*. 2000;65:8919–8923;
   (b) Mouri K, Wakamiya A, Yamada H, Kajiwara T, Yamaguchi S. *Org Lett*. 2007;9:93–96;
   (c) Li L, Xiang J, Xu C. *Org Lett*. 2007;9:4877–4879;
   (d) Matsuda T, Kadowaki S, Yamaguchi Y, Murakami M. *Chem Commun*. 2008: 2744–2746;
   (e) Shibata T, Uchiyama T, Yoshinami Y, Takayasu S, Tsuchikama K, Endo K. *Chem Commun*. 2012;48:1311–1313;
   (f) Ouyang K, Liang Y, Xi Z. *Org Lett*. 2012;14:4572–4575;
   (g) Xu L, Zhang S, Li P. *Org Chem Front*. 2015;2:459–463;
   (h) Zhang Q-W, An K, He W. *Synlett*. 2015;26:1145–1152.
6. For a review, see: Dubac J, Laporterie A, Manuel G *Chem Rev*. 1990;90:215–263.
7. (a) Curtis MD. *J Am Chem Soc*. 1969;91:6011–6018;
   (b) Chen J, Law CCW, Lam JWY, et al. *Chem Mater*. 2003;15:1535–1546;
   (c) Wang C, Luo Q, Sun H, Guo X, Xi Z. *J Am Chem Soc*. 2007;129:3094–3095.
8. Matsuda T, Kadowaki S, Murakami M. *Chem Commun*. 2007:2627–2629.
9. Onoe M, Baba K, Kim Y, Kita Y, Tobisu M, Chatani N. *J Am Chem Soc*. 2012;134: 19477–19488.
10. (a) Liang Y, Geng W, Wei J, Xi Z. *Angew Chem Int Ed*. 2012;51:1934–1937;
    (b) Meng T, Ouyang K, Xi Z. *RSC Adv*. 2013;3:14273–14276.
11. (a) Okinoshima H, Yamamoto K, Kumada M. *J Am Chem Soc*. 1972;94: 9263–9264;
    (b) Tamao K, Yamaguchi S, Shinozaki M, Nakagawa Y, Ito Y. *J Am Chem Soc*. 1992;114:5867–5869;
    (c) Ohmura T, Masuda K, Suginome M. *J Am Chem Soc*. 2008;130:1526–1527.
12. Ilies L, Tsuji H, Nakamura E. *Org Lett*. 2009;11:3966–3968.
13. Ilies L, Tsuji H, Sato Y, Nakamura E. *J Am Chem Soc*. 2008;130:4240–4241.
14. (a) Ureshino T, Yoshida T, Kuninobu Y, Takai K. *J Am Chem Soc*. 2010;132: 14324–14326;
    (b) Murata M, Takizawa M, Sasaki H, et al. *Chem Lett*. 2016;45:857–859.
15. (a) Furukawa S, Kobayashi J, Kawashima T. *J Am Chem Soc*. 2009;131: 14192–14193;
    (b) Curless LD, Ingleson MJ. *Organometallics*. 2014;33:7241–7246;
    (c) Omann L, Oestreich M. *Angew Chem Int Ed*. 2015;54:10276–10279.
16. (a) Tamao K, Yamaguchi S, Shiro M. *J Am Chem Soc*. 1994;116:11715–11722;
    (b) Tamao K, Uchida M, Izumizawa T, Furukawa K, Yamaguchi S. *J Am Chem Soc*. 1996;118:11974–11975;
    (c) Boydston AJ, Pagenkopf BL. *Angew Chem Int Ed*. 2004;43:6336–6338.
17. (a) Shimizu M, Mochida K, Hiyama T. *Angew Chem Int Ed*. 2008;47:9760–9764;
    (b) Yabusaki Y, Ohshima N, Kondo H, Kusamoto T, Yamanoi Y, Nishihara H. *Chem Eur J*. 2010;16:5581–5585;
    (c) Shimizu M, Hiyama T. *Synlett*. 2012;23:973–989.
18. Matsuda T, Yamaguchi Y, Murakami M. *Synlett*. 2008;4:561–564.
19. Minami Y, Noguchi Y, Hiyama T. *J Am Chem Soc*. 2017;139:14013–14016.
20. Kinoshita H, Fukumoto H, Tohjima T, Miura K. *Tetrahedron Lett*. 2016;57: 3571–3574.
21. For a preliminary study, see: Kinoshita H, Ueda A, Fukumoto H, Miura K *Org Lett*. 2017;19:882–885.
22. This reduction is known as the substitution reaction of alkoxysilane by hydride, see: Sommer LH, McLick J, Golino CM *J Am Chem Soc*. 1972;94:669–670.
23. (a) Eisch JJ, Foxton MW. *J Org Chem*. 1971;36:3520–3526;
    (b) Akiyama K, Gao F, Hoveyda AH. *Angew Chem Int Ed*. 2010;49:419–423.
24. For nucleophilic substitution of hydrosilanes with carbon nucleophiles at silicon, see: Corriu RJP, Guerin C, Moreau JJE (Chapter 4). In: Patai S, Rappoport Z, eds. *The Chemistry of Organic Silicon Compounds*. vol. 1. Chichester: Wiley; 1989:305–370.
25. Dubac J, Laporterie A, Manuel G. *Chem Rev*. 1990;90:215–263.
26. Yamaguchi S, Jin R-Z, Ohno S, Tamao K. *Organometallics*. 1998;17:5133–5138.
27. Shao J, Zhao X, Wang L, et al. *Tetrahedron Lett*. 2014;55:5663–5666.
28. Chen T-A, Lee T-J, Lin M-Y, et al. *Chem–A Eur J*. 2010;16:1826–1833.
29. Li Y, Liu X, Jiang H, Feng Z. *Angew Chem Int Ed*. 2010;49:3338–3341.
30. (a) Hara S, Satoh Y, Ishiguro H, Suzuki A. *Tetrahedron Lett*. 1983;24:735–738;
    (b) Martín R, Rivero MR, Buchwald SL. *Angew Chem Int Ed*. 2006;45: 7079–7082.
31. Ishikawa M, Fuchikami T, Kumada M. *J Organomet Chem*. 1978;149:37–48.

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