Synthesis of π-Extended Siloles Using Intramolecular Chain Hydrosilylation

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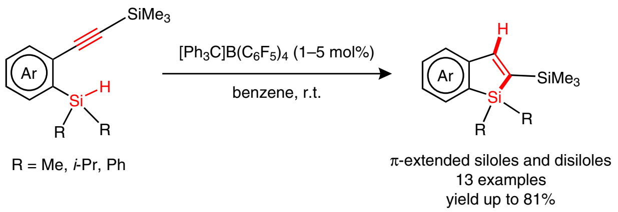
This paper is dedicated to Professor Marian Mikolajczyk on the occasion of his 80th birthday.



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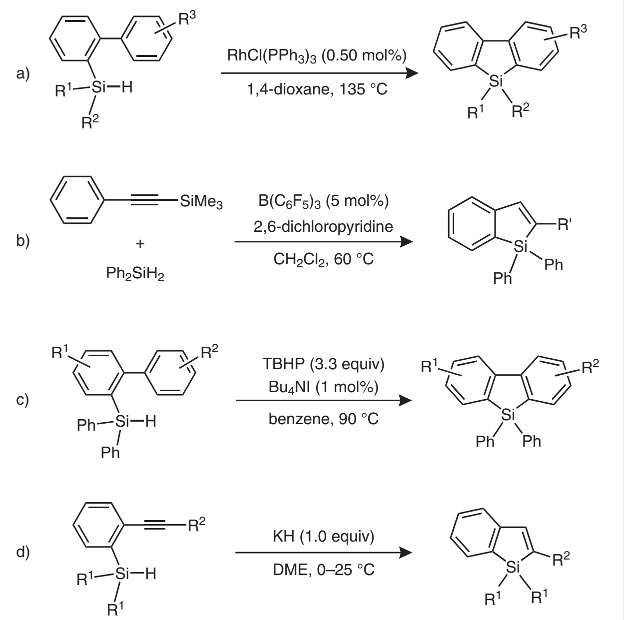
Abstract Intramolecular chain hydrosilylation afforded benzo- and naphtho-fused siloles in 20–81% yields from the corresponding hydrosilanes in the presence of a small amount of trityl tetrakis(pentafluorophenyl)borate as an initiator. This hydrosilylation can be applied for the synthesis of disiloles such as 1,5-disila-1,5-dihydro-*s*-indacene and naphthodisiloles.

Key words silole, silyl cation, chain hydrosilylation, cyclization, metal-free



Scheme 1 Selected syntheses of benzo- or dibenzosiloles

Siloles have attracted much attention because of their optical and electronic properties, which are useful for materials such as emission components and semiconductors.[1] These properties are due to the low-lying LUMO derived from the orbital interaction between the σ* orbital of the silylene moiety and the π* orbital of butadiene in the silole framework, which indicates that the siloles have HOMO-LUMO gaps that are smaller than their carbon analogues.[2] An aromatic ring-fused silole can have a decreased gap via π-conjugation between the silole moiety and the aromatic ring. Silole derivatives have been synthesized using various methods, including catalytic and stoichiometric reactions.[3,4] Si–C bond formation through C–H activation catalyzed by a transition metal[5] is a direct and powerful route to dibenzosilole and does not require a preliminary preparation such as functionalization of an aromatic ring (Scheme 1, a).[5b] Recently, a Lewis acid catalyst was found to induce intra- or intermolecular Si–C bond formation accompanied by H_2 evolution to give benzosiloles Scheme 1, b).[6] The chain reaction promoted by a small amount of an initiator is also one of the transition-metal-free systems. The three-coordinated silyl radical and five-coordinated silicate generated by the reactions of the corresponding hydrosilane with *tert*-butyl hydroperoxide (TBHP) and KH, respectively, act as a chain carrier to yield the siloles (Scheme 1, c and d).[7,8] The driving force of these reactions seems to be the formation of unusual coordination numbers 3 and 5 at the silicon atom, which make the species highly reactive. We have been investigating the reaction, which originates from the three-coordinated silyl cation with high Lewis acidity, and reported the syntheses of trisilasumanene as well as dibenzosiloles via the sila-Friedel–Crafts reaction, which involves the generation of silyl cations by hydride abstraction from the corresponding hydrosilanes with a triphenylmethyl cation and electrophilic attack on the intramolecular arene moiety followed by deprotonation with a base (Scheme 2).[9]

The sila-Friedel–Crafts reaction led us to develop a novel synthetic route to siloles. We hypothesized that the vinyl cation generated by the addition of the silyl cation to the neighboring C≡C bond[10] abstracts the hydride from the Si–H bond of a starting hydrosilane to regenerate the silyl cation, which may act as a chain carrier to undergo intramolecular chain hydrosilylation. It was reported as a preliminary communication that dialkyl[2-(trimethylsilylethynyl)phenyl]silanes were converted into the corresponding benzosiloles in the presence of a small amount of trityl tetrakis(pentafluorophenyl)borate (TTPFPB) as an initiator

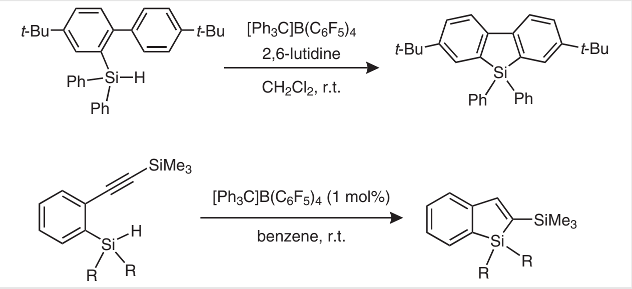
Biographical Sketches

Hidekazu Arii received his Ph.D. in 2003 from Nagoya Institute of Technology under the direction of Professor Hideki Masuda. He moved to Chuo University as a Research Associate in 2004 under Professor Makoto Chikira. In 2006, he worked as a postdoctoral research fellow at the laboratory of Professor Hiroyuki Kawaguchi in Institute for Molecular Science. He moved to Faculty of Science, Gakushuin University as a Research Associate in 2007 and researched under the direction of Professor Kunio Mochida. He moved to University of Miyazaki as an Associate Professor in 2014. His research interest is the chemistry of low-coordinated heavier group 14 elements.

Kenichi Nakabayashi received his Ph.D. in 1993 from Osaka University under the direction of Professor Setsuo Takamuku. He accepted positions as a Lecturer, an Associate Professor, and a Professor at the University of Miyazaki. He did research with Professor W. Schnabel at Hahn Meitner Institute Berlin from 1990 to 1991. His research interest involves organic photochemistry and chemical education.

Kunio Mochida received his D. Sci. degree in 1976 from Tohoku University under the supervision of Professor Hideki Sakurai. After he worked as a research fellow of JSPS (Japan Society for the Promotion of Science) in 1976, he moved to Indiana University as a postdoctoral research fellow under the direction of Professor J. K. Kochi in 1977. He moved to Faculty of Science, Gakushuin University as a Lecturer in 1978, where he was promoted to Professor in 1986. His research interest is not only the chemistry of germanium compounds but also transition-metal chemistry.

Takayuki Kawashima received his D. Sci. degree in 1974 from the University of Tokyo under the supervision of Professor Naoki Inamoto. He was a Research Associate, a Lecturer, and an Associate Professor of Department of Chemistry, Faculty of Science, The University of Tokyo from 1974 to 1998 and became a Professor of Department of Chemistry, Graduate School of Science, The University of Tokyo in 1998. From 1976 to 1978, he did postdoctoral research with Professor J. G. Verkade at Iowa State University and with Professor W. G. Bentrude at the University of Utah. In 2010, he retired from the University of Tokyo and became Professor Emeritus at the University of Tokyo. He was a Visiting Professor of Gakushuin University from 2010 to 2013 and he joined the Graduate School of Science and Technology, Gunma University as a Visiting Professor in 2013. His research interest is centered on organoheteroatom chemistry.

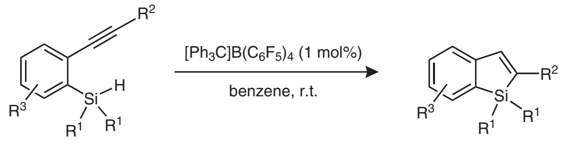


Scheme 2 Our previous work on the synthesis of siloles utilizing a silyl cation

(Scheme 2).[11] Herein, we further describe the scope and limitation of this intramolecular chain hydrosilylation, including its application for the synthesis of π-extended disiloles.

Dimethyl[2-(trimethylsilylethynyl)phenyl]silane (**1a**) was reacted with 1 mol% TTPFPB in benzene to afford the corresponding benzosilole **2a** in 34% isolated yield (Table 1, entry 1). The low yield is attributable to the formation of unidentified oligomers by the intermolecular addition of the silyl cation to the alkyne moiety. The sterically bulkier substituent on the silicon atom improved the yields of **2b** and **2c** to 55 and 77%, respectively (entries 2 and 3).

Table 1 Intramolecular Chain Hydrosilylation of Silanes **1** to Benzosiloles **2a–h**, **2h′**



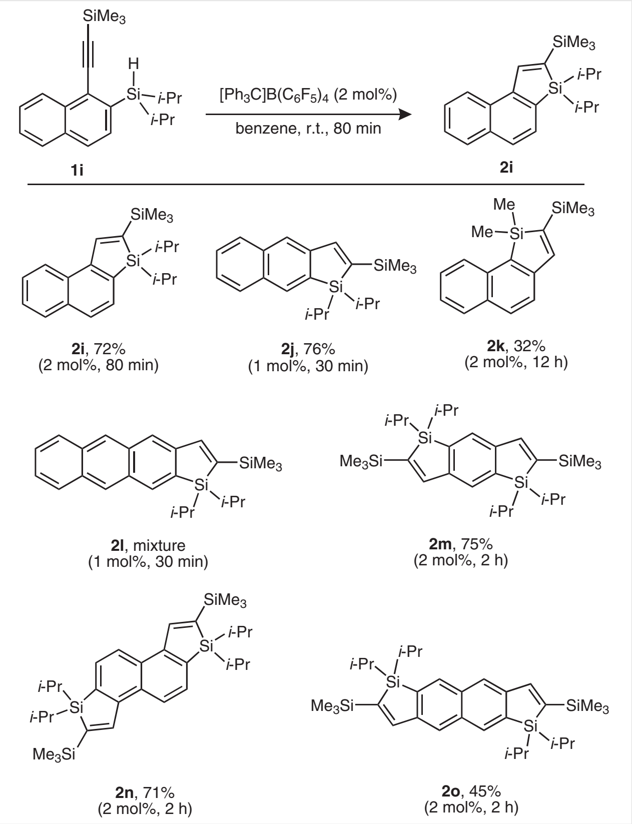
1a–h **2a–h, 2h′**

Entry	Silane **1**	R^1	R^2	R^3	Time (min)	Yield of **2** (%)[a]
1	**1a**	Me	TMS	H	30	34 (**2a**)[b]
2	**1b**	Ph	TMS	H	30	55 (**2b**)[b]
3	**1c**	*i*-Pr	TMS	H	30	77 (**2c**)[b]
4	**1d**	*i*-Pr	*n*-Bu	H	720	–[c] (**2d**)[b]
5	**1e**	*i*-Pr	TBDMS	H	720	–[c] (**2e**)
6	**1f**	*i*-Pr	TMS	4-Me	30	71 (**2f**)[b]
7	**1g**	*i*-Pr	TMS	5-Me	50	81 (**2g**)[b]
8[d]	**1h**	*i*-Pr	TMS	4-MeO	720	34 (**2h**)[e]
9[d]	**1h**	*i*-Pr	TMS	4-MeO	2880	20 (**2h′**)[f]

[a] Isolated yield based on **1**.
[b] Ref. 11.
[c] Not obtained.
[d] TTPFPB used: 5 mol%.
[e] Ratio of **1h**/**2h** = 1:10 estimated by ^{1}H NMR analysis.
[f] **2h′** = R^1 = *i*-Pr, R^2 = TMS, R^3 = 7-OMe.

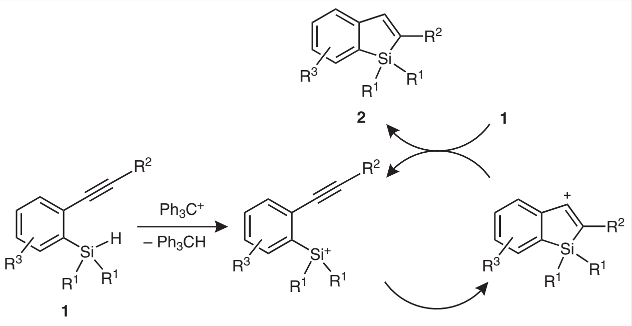
The substituent of the ethynyl group was limited to the trimethylsilyl group. Specifically, the aliphatic *n*-butyl or bulky *tert*-butyldimethylsilyl groups prevented the desired hydrosilylation, in which case the corresponding starting materials were recovered (Table 1, entries 4 and 5). This implies that the trimethylsilyl group is associated with the stability of the reaction intermediate, that is, the ethenyl carbocation is stabilized by additional β-silyl effect of the trimethylsilyl group, and such double β-silyl effects were also effective for stable vinyl cations.[10] Benzosiloles **2f** and **2g** bearing a methyl group on the aromatic ring were obtained in yields similar to that of **2c** (Table 1, entries 6 and 7). The best yield of **2g** seems to be attributable to stabilization by the inductive effect of the electron-rich carbon emerging from hyperconjugation of the 6-methyl group on the electron deficient carbon of an intermediary ethenyl carbocation. The methoxy derivative **2h** was formed in 34% yield from **1h** upon using 5 mol% TPFPB, although the reaction needed more TTPFPB and a longer time than those required for reactions using **1a**–**g** (Table 1, entry 8). The significantly slower conversion causes intermolecular interaction of the silyl cation with the methoxy group to compete with its electrophilic addition to the ethynyl moiety. Interestingly, the extension of the reaction time to 2 days resulted in the formation of regioisomer, 1,1-diisopropyl-7-methoxy-2-trimethylsilylbenzo[*b*]silole (**2h′**) in 20% yield with consumption of **2h** (Table 1, entry 9). The rearrangement from **2h** to **2h′** is considered to have taken place through the protodesilylation of **2h** followed by the sila-Friedel–Crafts reaction at the *ortho*-position to the methoxy group (see the Supporting Information, Scheme S1).

This intramolecular chain hydrosilylation was applied to the synthesis of π-extended benzosiloles. Specifically, the treatment of 2-diisopropylsilyl-1-trimethylsilylethynylnaphthalene (**1i**) with 2 mol% TTPFPB in benzene afforded 3,3-diisopropyl-2-trimethylsilylnaphtho[2,1-*b*]silole (**2i**) in 72% yield (Scheme 3). The regioisomer of **1j** was also converted into the corresponding naphthosilole **2j** in 76% yield. On the other hand, **1k**, which has a dimethylsilyl group at the 1-position of 2-trimethylsilylethynylnaphthalene, must be used because a diisopropylsilyl group cannot be introduced. The reaction using **1k** required more time than the reactions using **1i** and **1j** to give **2k** in 32% yield despite a less bulky methyl group on the silicon atom. The 1-position of naphthalene has a kinetic disadvantage for approaching the other molecules, which causes the slow hydride abstraction from the Si–H bond by the trityl cation and an unsuccessful introduction of a bulkier diisopropylsilyl group to the 1-position of 2-trimethylsilylethynylnaphthalene. However, the reaction that uses **1l** with an anthracene backbone afforded a complex mixture rather than the desired product, probably because the 9- and 10-positions of **1l** are very reactive toward electrophiles, which results in intermolecular reactions with an intermediary silyl cation at these positions.



Scheme 3 Scope and limitation of π-extended siloles by the chain hydrosilylation

Next, double hydrosilylation was examined for synthesizing π-extended disiloles. The reactions using **1m–o** were carried out in the presence of 2 mol% TTPFPB, which has the same mol% against a silyl group as that used for the single hydrosilylation. The reactions needed a longer reaction time (2 h) and gave the desired products **2m–o** in 75, 71, 45% yield, respectively. Although the polymerization proceeded partially, the yields were similar to those of the single hydrosilylation products.



Scheme 4 Plausible reaction mechanism for intramolecular chain hydrosilylation of **1**

The postulated mechanism of intramolecular chain hydrosilylation is described for benzosiloles as typical examples in Scheme 4. Trityl cation, as an initiator, abstracts the hydride from the Si–H bond of **1** to generate the corresponding silyl cation. Subsequently, the intramolecular electrophilic addition of the silyl cation moiety to the neighboring C≡C bond produces an alkenyl carbocation, which is stabilized via the additional β-silyl effect of the trimethylsilyl group. Finally, the intermolecular hydride abstraction of the alkenyl carbocation from another **1** affords benzosiloles **2** with regeneration of the silyl cation, which works as a chain carrier.

In summary, we have synthesized various π-extended siloles, such as benzosiloles, naphthosiloles, 1,5-disila-1,5-dihydro-*s*-indacene, and naphthodisiloles, via intramolecular chain hydrosilylation in low to moderate yields up to 81%. The steric bulkiness on the silyl group affects the yield of benzosiloles to prevent the undesired alkyne polymerization based on the silyl cation. Although the intramolecular chain hydrosilylation requires the trimethylsilyl group on the ethynyl moiety to stabilize the intermediary ethenyl carbocation via the β-silyl effect, the reaction can be carried out under mild conditions without any metal. The present chain hydrosilylation is one of the available methods for the synthesis of π-extended siloles to reduce waste.

All experiments were carried out using standard vacuum line and Schlenk techniques in an argon atmosphere or dry box. All the reagents were of the highest grade available and were used without further purification. All solvents used for the synthesis were distilled according to the general procedure. $[Ph_3C]B(C_6F_5)_4$,[12] **1a**,[13] **1b**,[8] **1c**,**d**,**f**,**g**,[11] and aryl bromides bearing trimethylsilylethynyl group[14] were synthesized according to the previously reported methods. The ^1H and ^{13}C NMR spectral measurements were performed on a Varian 400-MR NMR or a Bruker AV 400M spectrometers. The ^{29}Si NMR spectra were measured on a JEOL ECA-600 spectrometer using TMS as an external standard. The ^1H and ^{13}C chemical shifts are reported relative to the residual protonated solvent and the solvent, respectively, according to the literature.[15] High-resolution mass spectra were measured by a JEOL GCMATE II or JMS-700N operating by electron impact ionization (EI). Gel permeation liquid chromatography (GPLC) was performed by a Japan Analytical Industry LC-918 using $CHCl_3$ as an eluent.

Silanes 1e,h–l; General Procedure

To the corresponding bromo compound (1.3 mmol) in hexane (8 mL) were added 1.6 M pentane solution of *t*-BuLi (0.84 mL, 1.4 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.23 g, 2.0 mmol) at –80 °C, and the solution was stirred for 20 min at the temperatures below –70 °C. To the solution was added *i*-Pr_2SiHCl (0.20 g, 1.4 mmol) at –70 °C, the solution was stirred, and slowly warmed to r.t. The reaction mixture was quenched with 5% aq NH_4Cl. The mixture was extracted with hexane (2 × 20 mL), and the combined organic layers were dried (anhyd Na_2SO_4). The filtrate was concentrated under reduced pressure to remove volatiles, and the residue was purified by chromatography over a silica gel column (eluent: hexane). Further purification was carried out by GPLC to obtain **1e**,**h–l**.

Diisopropyl[2-(*tert*-butyldimethylsilylethynyl)phenyl]silane (1e)

Compound **1e** was obtained from 1-bromo-2-*tert*-butyldimethylsilylethynylbenzene (0.38 g, 1.3 mmol); yield: 0.26 g (60%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.51–7.48 (m, 2 H, ArH), 7.32–7.25 (m, 2 H, ArH), 4.06 (t, 1 H, *J* = 3.6 Hz, SiH), 1.50–1.41 [m, 2 H, 2 × $\mathit{CH}(CH_3)_2$], 1.10 [d, *J* = 7.6 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 1.00 (s, 9 H, *t*-C_4H_9), 0.99 [d, *J* = 8.0 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.18 [s, 6 H, $Si(CH_3)_2$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.0, 136.6, 133.2, 129.3, 128.9, 127.5, 107.4, 94.7, 26.3, 19.3, 19.2, 16.9, 11.3, –4.5.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{20}H_{34}Si_2$: 330.2199; found: 330.2199.

Diisopropyl[2-(trimethylsilylethynyl)-4-methoxyphenyl]silane (1h)

Compound **1h** was obtained from 1-bromo-4-methoxy-2-trimethylsilylethynylbenzene (0.73 g, 2.58 mmol); yield: 0.42 g (51%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.38 (d, *J* = 8.4 Hz, 1 H, ArH), 7.03 (d, *J* = 2.8 Hz, 1 H, ArH), 6.85 (dd, *J* = 8.0 Hz, *J* = 2.8 Hz, 1 H, ArH), 3.98 (t, *J* = 4.0 Hz, 1 H, SiH), 3.80 (s, 3 H, OCH_3), 1.45–1.36 [m, 2 H, 2 × $\mathit{CH}(CH_3)_2$], 1.09 [d, *J* = 7.2 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.98 [d, *J* = 7.2 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.25 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.1, 138.1 130.3, 129.2, 117.6, 114.6, 106.6, 96.0, 55.3, 19.3, 11.4, –0.07.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{18}H_{30}OSi_2$: 318.1835; found: 318.1835.

2-Diisopropylsilyl-1-trimethylsilylethynylnaphthalene (1i)

Compound **1i** was obtained from 2-bromo-1-trimethylsilylethynylnaphthalene (0.20 g, 0.86 mmol); yield: 0.12 g (54%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.43 (d, *J* = 8.4 Hz, 1 H, ArH), 7.82 (d, *J* = 7.6 Hz, 1 H, ArH), 7.78 (d, *J* = 8.4 Hz, 1 H, ArH), 7.61–7.49 (m, 3 H, ArH), 4.20 (t, *J* = 4.0 Hz, 1 H, SiH), 1.60–1.50 [m, 2 H, 2 × $\mathit{CH}(CH_3)_2$], 1.16 [d, *J* = 7.2 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 1.03 [d, *J* = 7.2 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.35 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.6, 133.7, 133.4, 132.5, 128.2, 127.6, 127.5, 126.9, 126.8, 126.5, 104.4, 102.5, 19.4, 19.3, 11.5, 0.06.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{21}H_{30}Si_2$: 338.1886; found: 338.1880.

2-Diisopropylsilyl-3-trimethylsilylethynylnaphthalene (1j)

Compound **1j** was obtained from 2-bromo-3-trimethylsilylethynylnaphthalene (0.26 g, 0.86 mmol); yield: 0.16 g (55%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.01 (d, *J* = 7.2 Hz, 2 H, ArH), 7.81–7.74 (m, 2 H, ArH), 7.51–7.46 (m, 2 H, ArH), 4.10 (t, *J* = 4.4 Hz, 1 H, SiH), 1.57–1.48 [m, 2 H, 2 × $\mathit{CH}(CH_3)_2$], 1.14 [d, *J* = 7.2 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 1.01 [d, *J* = 7.6 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.28 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.8, 134.7, 133.3, 132.5, 132.3, 128.0, 127.6, 127.1, 126.9, 125.1, 107.1, 96.1, 19.5, 19.4, 11.5, –0.03.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{21}H_{30}Si_2$: 338.1886; found: 338.1886.

1-Dimethylsilyl-2-trimethylsilylethynylnaphthalene (1k)

Compound **1k** (0.15 g, 62%) was obtained from 1-bromo-2-trimethylsilylethynylnaphthalene (0.26 g, 0.86 mmol) using Me_2SiHCl instead of *i*-Pr_2SiHCl; yield: 0.15 g (62%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.44 (d, *J* = 8.0 Hz, 1 H, ArH), 7.81–7.76 (m, 2 H, ArH), 7.54–7.45 (m, 3 H, ArH), 5.21 (sept, *J* = 3.6 Hz, 1 H, SiH), 0.58 (d, *J* = 3.6 Hz, 6 H, 2 × CH_3), 0.29 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 139.2, 137.0, 132.7, 129.9, 129.6, 128.9, 128.22, 128.15, 126.4, 126.3, 107.1, 99.3, –0.08, –2.82.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{17}H_{28}Si_2$: 282.1260; found: 282.1260.

2-Diisopropylsilyl-3-trimethylsilylethynylanthracene (1l)

Compound **1l** was obtained from 2-bromo-3-trimethylsilylethynylanthracene (70 mg, 0.20 mmol); yield: 25 mg (33%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.38 (s, 1 H, ArH), 8.33 (s, 1 H, ArH), 8.19 (s, 2 H, ArH), 8.01–7.98 (m, 2 H, ArH), 7.49–7.46 (m, 2 H, ArH), 4.14 (t, *J* = 4.0 Hz, 1 H, SiH), 1.60–1.51 [m, 2 H, 2 × $\mathit{CH}(CH_3)_2$], 1.17 [d, *J* = 7.6 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 1.05 [d, *J* = 7.6 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.30 [s, 9 H, Si(CH3)$_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.6, 133.8, 133.0, 132.50, 132.45, 131.2, 130.3, 128.5, 128.4, 126.6, 126.1, 126.0, 125.9, 123.9, 107.3, 96.6, 19.5, 19.4, 11.6, 0.0.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{25}H_{32}Si_2$: 388.2043; found: 388.2044.

Disilanes 1m–o; General Procedure

To bis(trimethylsilylethynyl)aryl dibromide (0.66 mmol) in Et_2O (12 mL) were added 1.6 M pentane solution of *t*-BuLi (1.6 mL, 2.6 mmol) and at –80 °C, and the solution was stirred, and warmed to r.t. gradually. To the solution was added *i*-Pr_2SiHCl (0.22 g, 1.44 mmol) at –70 °C, the solution was stirred, and slowly warmed to r.t. The reaction mixture was quenched with 5% aq NH_4Cl. The mixture was extracted with Et_2O (2 × 20 mL), and the combined organic layers were dried (anhyd Na_2SO_4). The filtrate was concentrated under reduced pressure to remove volatiles, and the residue was purified by chromatography over a silica gel column (eluent: hexane). Further purification was carried out by GPLC to obtain **1m**–**o**.

1,4-Bis(diisopropylsilyl)-2,5-bis(trimethylsilylethynyl)benzene (1m)

Compound **1m** was obtained from 1,4-dibromo-2,5-bis(trimethylsilylethynyl)benzene (0.32 g, 0.66 mmol); yield: 0.16 g (49%); colorless solid; mp 126.8–128.5 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.59 (s, 2 H, ArH), 3.97 (t, *J* = 4.0 Hz, 2 H, SiH), 1.48–1.40 [m, 4 H, 4 × $\mathit{CH}(CH_3)_2$], 1.10 [d, *J* = 7.6 Hz, 12 H, 2 × $CH(\mathit{CH}_3)_2$], 0.98 [d, *J* = 7.2 Hz, 12 H, 2 × $CH(\mathit{CH}_3)_2$], 0.25 [s, 18 H, 2 × $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.4, 139.0, 127.8, 106.8, 98.1, 19.4, 19.2, 11.3, –0.09.

Anal. Calcd for $C_{28}H_{50}Si_4$: C, 67.39; H, 10.10. Found: C, 67.20; H, 10.25.

2,6-Bis(diisopropylsilyl)-1,5-bis(trimethylsilylethynyl)naphthalene (1n)

Compound **1n** was obtained from 2,6-dibromo-1,5-bis(trimethylsilylethynyl)naphthalene (0.21 g, 0.44 mmol); yield: 0.12 g (50%); colorless solid; mp 163.8–165.2 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.37 (d, *J* = 8.4 Hz, 2 H, ArH), 7.67 (d, *J* = 8.4 Hz, 2 H, ArH), 4.20 (t, *J* = 3.6 Hz, 2 H, SiH), 1.58–1.50 [m, 4 H, 4 × $\mathit{CH}(CH_3)_2$], 1.15 [d, *J* = 7.6 Hz, 12 H, 2 × $CH(\mathit{CH}_3)_2$], 1.02 [d, *J* = 7.6 Hz, 12 H, 2 × $CH(\mathit{CH}_3)_2$], 0.33 [s, 18 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.6, 133.6, 133.4, 127.9, 125.7, 104.1, 102.8, 19.30, 19.29, 11.4, 0.03.

Anal. Calcd for $C_{32}H_{52}Si_4$: C, 70.00; H, 9.55. Found: C, 70.10; H, 9.70.

2,6-Bis(diisopropylsilyl)-3,7-bis(trimethylsilylethynyl)naphthalene (1o)

Compound **1o** was obtained from 2,6-dibromo-3,7-bis(trimethylsilylethynyl)naphthalene (0.18 g, 0.38 mmol); yield: 0.12 g (58%); colorless solid; mp 137.3–138.2 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (s, 2 H, ArH), 7.92 (s, 2 H, ArH), 4.11 (t, *J* = 4.0 Hz, 2 H, SiH), 1.55–1.47 [m, 4 H, 4 × $\mathit{CH}(CH_3)_2$], 1.14 [d, *J* = 7.6 Hz, 12 H, 2 × $CH(\mathit{CH}_3)_2$], 1.01 [d, *J* = 7.2 Hz, 12 H, 2 × $CH(\mathit{CH}_3)_2$], 0.28 [s, 18 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.2, 136.1, 132.4, 132.0, 126.1, 106.9, 97.0, 19.4, 19.3, 11.5, –0.05.

Anal. Calcd for $C_{32}H_{52}Si_4$: C, 70.00; H, 9.55. Found: C, 70.06; H, 9.74.

Chain Hydrosilylation; General Procedure

To trityl tetrakis(pentafluorophenyl)borate (TTPFPB, 1.0 mg, 0.10 μmol) in benzene (0.5 mL) was added a benzene solution (1.5 mL) of the corresponding **1a–l** (0.10 mmol) or a benzene solution (0.5 mL) of the corresponding **1m–o** (50.0 μmol) at r.t. under argon atmosphere, and the resulting solution was stirred at r.t.. After quenching the reaction mixture with 2,6-lutidine (2 μL) and H_2O, the mixture was extracted with hexane (2 × 5 mL). The organic layers were combined and dried (anhyd Na_2SO_4), filtered, and the solvent was evaporated under reduced pressure. Purification was carried out by GPLC to remove polymeric materials.

1,1-Diisopropyl-5-methoxy-2-trimethylsilylbenzo[*b*]silole (2h)

Compound **2h** was obtained by the hydrosilylation of **1h** (30.8 mg, 96.7 μmol) for 12 h with 5 mol% TTPFPB; yield: 10.5 mg (34%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.54 (s, 1 H, CH=C), 7.40 (d, *J* = 7.6 Hz, 1 H, ArH), 6.85 (d, *J* = 2.4 Hz, 1 H, ArH), 6.75 (dd, *J* = 7.6, 2.4 Hz, 1 H, ArH), 3.82 (s, 3 H, OCH_3), 1.31–1.22 [m, 2 H, 2 × $\mathit{CH}(CH_3)_2$], 1.05 [d, *J* = 7.2 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.92 [d, *J* = 7.6 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.18 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 157.8, 153.2, 145.1, 133.6, 127.9, 112.3, 110.4, 55.2, 18.17, 18.15, 11.40, 11.38, –0.03.

^{29}Si DEPT NMR (119 MHz, $CDCl_3$): δ = 22.8, –6.5.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{30}OSi_2$: 318.1835; found: 318.1838.

1,1-Diisopropyl-7-methoxy-2-trimethylsilylbenzo[*b*]silole (2h′)

Compound **2h′** was obtained by the hydrosilylation of **1h** (62.6 mg, 0.196 mmol) for 2 days with 5 mol% TTPFPB; yield: 12.3 mg (20%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.55 (s, 1 H, CH=C), 7.29 (dd, *J* = 8.0 Hz, *J* = 7.2 Hz, 1 H, ArH), 6.90 (d, *J* = 7.6 Hz, 1 H, ArH), 6.72 (d, *J* = 7.6 Hz, 1 H, ArH), 3.79 (s, 3 H, OCH_3), 1.38 [sept, *J* = 7.6 Hz, 2 H, 2 × $\mathit{CH}(CH_3)_2$], 1.04 [d, *J* = 7.6 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.94 [d, *J* = 7.2 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.18 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 157.6, 153.0, 143.9, 131.7, 123.6, 117.4, 109.3, 55.1, 18.4, 18.2, 11.3, 0.04.

^{29}Si DEPT NMR (119 MHz, $CDCl_3$): δ = 28.0, –6.4.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{30}OSi_2$: 318.1835; found: 318.1866.

3,3-Diisopropyl-2-trimethylsilylnaphtho[2,1-*b*]silole (2i)

Compound **2i** was obtained by the hydrosilylation of **1i** (32.8 mg, 96.9 μmol) for 80 min; yield: 23.6 mg (72%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.43 (s, 1 H, CH=C), 8.31 (d, *J* = 8.4 Hz, 1 H, ArH), 7.85 (d, *J* = 7.6 Hz, 1 H, ArH), 7.71 (d, *J* = 7.6 Hz, 1 H, ArH), 7.64 (d, *J* = 8.0 Hz, 1 H, ArH), 7.53 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1 H, ArH), 7.47 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1 H, ArH), 1.39 [sept, 7.6 Hz, 2 H, 2 × $\mathit{CH}(CH_3)_2$], 1.09 [d, *J* = 7.2 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.95 [d, *J* = 7.2 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.25 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 147.4, 143.9, 136.0, 134.9, 129.2, 128.9, 128.7, 126.7, 125.9, 125.8, 123.3, 18.23, 18.17, 11.3, 0.10.

^{29}Si DEPT NMR (119 MHz, $CDCl_3$): δ = 24.6, –6.1.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{30}Si_2$: 338.1886; found: 338.1859.

1,1-Diisopropyl-2-trimethylsilylnaphtho[2,3-*b*]silole (2j)

Compound **2j** was obtained by the hydrosilylation of **1j** (32.8 mg, 96.9 μmol) for 30 min; yield: 24.8 mg (76%); colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.97 (s, 1 H, ArH), 7.84–7.78 (m, 2 H, ArH), 7.78 (s, 1 H, CH=C), 7.66 (s, 1 H, ArH), 7.48–7.41 (m, 2 H, ArH), 1.37 [sept, *J* = 7.2 Hz, 2 H, 2 × $\mathit{CH}(CH_3)_2$], 1.11 [d, *J* = 7.2 Hz, 6 H, $CH(\mathit{CH}_3)_2$], 0.96 [d, 6 H, *J* = 7.2 Hz, $CH(\mathit{CH}_3)_2$], 0.24 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.5, 148.3, 145.3, 135.5, 134.8, 133.3, 133.1, 128.5, 128.3, 126.4, 125.8, 122.2, 18.2, 18.1, 11.6, 0.04.

^{29}Si DEPT NMR (119 MHz, $CDCl_3$): δ = 23.3, –6.2.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{30}Si_2$: 338.1886; found: 338.1886.

1,1-Dimethyl-2-trimethylsilylnaphtho[1,2-*b*]silole (2k)

Compound **2k** was obtained by the hydrosilylation of **1k** (28.3 mg, 100 μmol) with 2 mol% TTPFPB (1.9 mg, 2.0 μmol) for 12 h; yield: 9.0 mg (32%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 2 H, ArH), 7.80 (d, *J* = 8.4 Hz, 1 H, ArH), 7.63 (s, 1 H, CH=C), 7.50–7.40 (m, 3 H, ArH), 0.49 [s, 6 H, $Si(CH_3)_2$], 0.22 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.6, 148.7, 147.0, 139.1, 136.1, 132.9, 130.5, 129.0, 128.5, 126.5, 125.3, 123.3, –0.3, –2.5.

^{29}Si DEPT NMR (119 MHz, $CDCl_3$): δ = 11.8, –6.2.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{28}Si_2$: 282.1260; found: 282.1261.

1,1,5,5-Tetraisopropyl-2,6-bis(trimethylsilyl)-1,5-disila-1,5-dihydro-*s*-indacene (2m)

Compound **2m** was obtained by the double hydrosilylation of **1m** (24.7 mg, 49.5 μmol) for 2 h; yield: 18.6 mg (75%); colorless solid; mp 174.5–175.8 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.63 (s, 2 H, HC=C), 7.41 (s, 2 H, ArH), 1.30 [sept, *J* = 7.2 Hz, 4 H, 4 × $\mathit{CH}(CH_3)_2$], 1.07 [d, *J* = 7.2 Hz, 12 H, 2 × $CH(\mathit{CH}_3)_2$], 0.94 [d, *J* = 7.2 Hz, 12 H, 2 × $CH(\mathit{CH}_3)_2$], 0.18 [s, 18 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.8, 150.0, 142.9, 139.5, 128.5, 18.2, 11.4, 0.02.

^{9}Si DEPT NMR (119 MHz, $CDCl_3$): δ = 23.0, –6.6.

Anal. Calcd for $C_{28}H_{50}Si_4$: C, 67.39; H, 10.10. Found: C, 67.21; H, 10.17.

3,3,8,8-Tetraisopropyl-2,7-bis(trimethylsilyl)naphtho[2,1-*b*:6,5-*b*′]disilole (2n)

Compound **2n** was obtained by the double hydrosilylation of **1n** (27.3 mg, 49.7 μmol) as a starting material for 2 h; yield: 19.4 mg (71%); colorless solid; mp 183.5–184.1 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.45 (s, 2 H, HC=C), 8.23 (d, *J* = 8.0 Hz, 2 H, ArH), 7.70 (d, *J* = 8.0 Hz, 2 H, ArH), 1.40 [sept, 4 H, 7.2 Hz, 4 × $\mathit{CH}(CH_3)_2$], 1.10 [d, *J* = 7.6 Hz, 12 H, 2 × $CH(\mathit{CH}_3)_2$], 0.96 [d, *J* = 7.6 Hz, 12 H, 2 × $CH(\mathit{CH}_3)_2$], 0.26 [s, 18 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 154.3, 147.9, 143.9, 135.9, 130.2, 129.0, 121.7, 18.3, 18.2, 11.3, 0.11.

^{29}Si DEPT NMR (119 MHz, $CDCl_3$): δ = 25.0, –6.1.

Anal. Calcd for $C_{32}H_{52}Si_4$: C, 70.00; H, 9.55. Found: C, 70.40; H, 9.87.

1,1,6,6-Tetraisopropyl-2,7-bis(trimethylsilyl)naphtho[2,3-*b*:6,7-*b*′]disilole (2o)

Compound **2o** was obtained by the double hydrosilylation of **1o** (27.1 mg, 49.4 µmol) for 2 h; yield: 12.1 mg (45%); colorless solid; mp 220.7–221.7 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.91 (s, 2 H, ArH), 7.75 (s, 2 H, HC=C), 7.62 (s, 2H, ArH), 1.35 [sept, J = 7.6 Hz, 4 H, 4 × $CH(CH_3)_2$], 1.10 [d, J = 7.2 Hz, 12 H, 2 × $CH(CH_3)_2$], 0.95 [d, J = 7.6 Hz, 12 H, 2 × $CH(CH_3)_2$], 0.23 [s, 18 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.5, 148.5, 144.8, 136.0, 134.3, 133.7, 122.7, 18.2, 18.1, 11.6, 0.06.

^{29}Si DEPT NMR (119 MHz, $CDCl_3$): δ = 23.2, –6.3.

Anal. Calcd for $C_{32}H_{52.5}O_{0.25}Si_4$: C, 69.43; H, 9.56. Found: C, 69.58; H, 9.68.

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Supporting Information

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