Synthesis of Various Silacycles via the Lewis Acid-Catalyzed Intramolecular *Trans*-Hydrosilylation of Unactivated Alkynes

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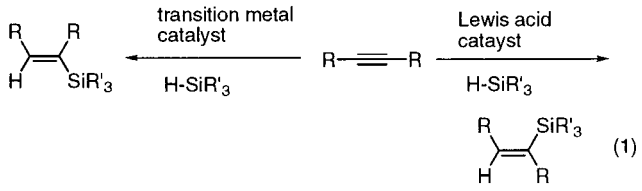
Various silacycles with vinylsilane framework are synthesized via the Lewis acid-catalyzed intramolecular hydrosilylation of alkynes. The cyclization proceeds in an *endo-trans* or/and in an *exo-trans* manner, depending on the substrate structure. This methodology is applicable to the synthesis of five-, six-, seven-, and eight-membered medium-sized silacycles. Furthermore, it is possible to obtain a silole derivative via the intramolecular hydrosilylation of the ortho-alkynyl-substituted phenylsilane **10**.

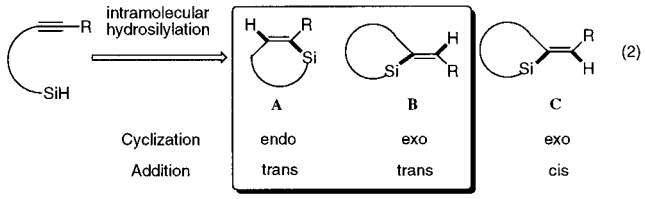
Introduction

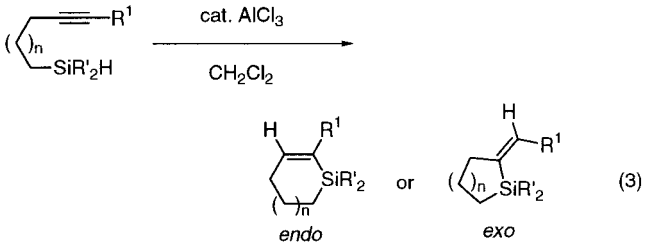
Hydrosilylation of alkynes is a widely used and general method for the synthesis of alkenylsilanes.[1] It has been known for many years that transition metal-catalyzed intermolecular hydrosilylation of alkynes proceeds in *cis*-manner to give the corresponding *cis*-hydrosilylation products (eq 1).[2] More recently, we found that the Lewis acid-catalyzed hydrosilylation proceeds in *trans*-manner to afford the *trans*-hydrosilylation products (eq 1).[3] Now, we are in a position to synthesize both stereoisomers independently from alkynes by choosing the catalyst. Compared to the intermolecular hydrosilylation, its intramolecular version has scarcely been studied.



It is considered that the intramolecular hydrosilylation of alkynes provides three different types of silacycles depending on the mode of the cyclization and addition of Si−H bond (eq 2).

The *endo-trans* and *exo-trans* mode give **A** and **B**, respectively, and the *exo-cis* mode produces **C**.[4] The intramolecular cyclization studied previously,[5] in which a transition metal catalyst such as hexachloroplatinic acid was used, proceeded exclusively via *cis*-hydrosilylation of alkynes leading to an *exo*-cyclized heterocycle. Since the transition metal-catalyzed hydrosilylation of alkynes proceeds in *cis*-manner, it is inevitable to produce the **C**-type silacycle. It occurred to us that the Lewis acid-catalyzed intramolecular hydrosilylation could produce the **A** and/or **B** type silacycles which are not easily available via the previous methodologies.[6] In this paper, we report that $AlCl_3$-catalyzed intramolecular *trans*-hydrosilylation of unactivated alkynes proceeds either in the *endo*- or *exo*-mode, depending on the substrates, to give five-, six-, seven-, and eight-membered silacycles in moderate to high yields (eq 3).





Results and Discussion

To find an optimum catalyst system, the reaction of **1b** was investigated, and we found that the best catalyst system for the intramolecular hydrosilylation was 20 mol % $AlCl_3$ in CH_2Cl_2 (1.0 M solution of $AlCl_3$). Although $EtAlCl_2$ and $GaCl_3$ were also effective for the intramolecular reaction, $AlCl_3$ was more easy to handle and cheaper than $EtAlCl_2$ and $GaCl_3$.[7] The optimal catalyst system was applied to the intramolecular hydrosilylation

(1) (a) Murata, M.; Watanabe, S.; Masuda, Y. *Tetrahedron Lett.* **1999**, *40*, 9255. (b) Pietraszuck, C.; Marciniec, B.; Fisher, H. *Organometallics* **2000**, *19*, 913. (c) Takai, K.; Hikasa, S.; Ichiguchi, T.; Sumino, N. *Synlett* **1999**, 1769 and references therein.

(2) (a) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 763. (b) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1998; Vol. 2, Chapter 29, p 1479.

(3) (a) Asao, N.; Sudo, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 7654. (b) Sudo, T.; Asao, N.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 2494.

(4) It has not been observed yet that the intramolecular hydrosilylation proceeds through the *endo-cis* mode.

(5) (a) Steinmetz, M. G.; Udayakumar, B. S.; *J. Organomet. Chem.* **1989**, *378*, 1. (b) Tamao, K.; Maeda, K.; Tanaka, T.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 6955. (c) Sashida, H.; Kudoda, A. *Synthesis* **1999**, 921.

(6) For reviews, see: (a) Hermanns, J.; Schmidt, B. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2209. (b) Hermanns, J.; Schmidt, B. *J. Chem. Soc., Perkin Trans. 1* **1999**, 81.

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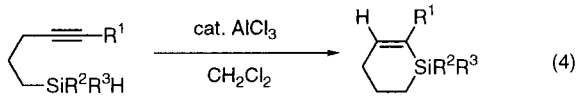
Table 1. $AlCl_3$-Catalyzed Intramolecular *Trans*-Hydrosilylation of 1[a]

entry	substr	R^1	R^2	R^3	reaction temp, °C	time	product	yield,[b] %
1	**1a**	H	Me	Me	0	10 min	**2a**	70[c]
2	**1b**	*n*-Hex	Me	Me	0	10 min	**2b**	78
3	**1c**	*t*-Bu	Me	Me	0	10 min	**2c**	72
4	**1d**	Ph	Me	Me	0	10 min	**2d**	78
5	**1e**	$SiMe_3$	Me	Me	0	10 min	**2e**	96
6	**1f**	$SiMe_3$	*i*-Pr	*i*-Pr	0	30 min	**2f**	89
7	**1g**	$SiMe_3$	Me	Ph	0 to rt	1 h	**2g**	86
8	**1h**	$SiMe_3$	Ph	Ph	0 to rt	5 h	**2h**	30(35)[d]

[a] The reaction was carried out in CH_2Cl_2 (1.0 M). [b] Isolated yield. [c] NMR yield. [d] Yield in parentheses means recovery of the starting material **1h**.

of **1** having a tether of three methylene groups between alkyne and hydrosilane moiety (eq 4). The results are summarized in Table 1.

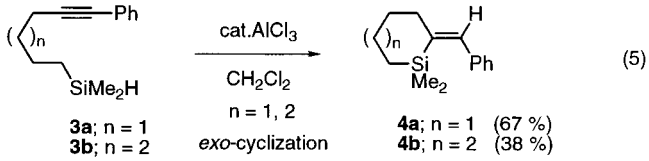


1 **2** (4)

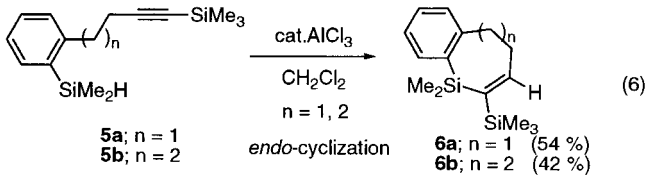
The cyclization of H-, alkyl-, phenyl-, and TMS-substituted alkynyldimethylhydrosilanes **1a**−**e** proceeded smoothly producing the six-membered silacycles **2a**−**e**, respectively, in good to nearly quantitative yields (entries 1−5). Next, the cyclization of TMS-substituted alkynylalkyl- and alkynylaryl-hydrosilanes **1f**−**h** was examined (entries 6−8). Except for the diphenylhydrosilane **1h**, even if the bulky substrates **1f** and **1g** were utilized, the *endo*-products **2f** and **2g** were obtained exclusively in 89 and 86% isolated yield, respectively. In the case of **1h**, the reaction was sluggish, and the starting material **1h** was recovered in 35% yield even after 5 h. In all cases, we could not detect the regio- and stereoisomers of **2**, the corresponding *exo*-cyclization products, in the crude reaction mixture.[8]

Analogously, the $AlCl_3$-catalyzed intramolecular hydrosilylation of the phenyl-substituted alkynes **3a** and **3b**, having a tether of four and five methylene groups (n = 1 and 2), was carried out. In contrast to the *endo*-mode cyclization of **1**, the *exo*-mode cyclization took place to give the six- and seven-membered silacycles **4a** and **4b** in moderate yields (eq 5). Here also, the regio- and stereoisomers of **4** were not obtained. The cyclization of the TMS-substituted alkynes bearing a benzene ring spacer, **5a** and **5b**, proceeded smoothly to give the corresponding *endo*-cyclization products **6a** and **6b** (eq 6).

The above results indicate that the reaction of alkynylsilanes having a longer tether, such as **3**, proceeds in the *exo-trans* mode **B**, whereas that having a shorter tether, such as **1**, proceeds in the *endo-trans* mode **A**. However, the alkynylsilanes having a benzene spacer **5**, despite a longer tether, gives the *endo-trans* products **6** through mode **A**.

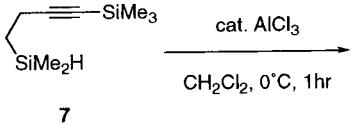


3a; n = 1 **3b**; n = 2 **4a**; n = 1 (67 %) **4b**; n = 2 (38 %) (5)



5a; n = 1 **5b**; n = 2 **6a**; n = 1 (54 %) **6b**; n = 2 (42 %) (6)

The intramolecular hydrosilylation of **7**, having a tether of two methylene groups, gave a mixture of the *endo*- (**8**) and *exo*-product (**9**) in 23 and 10% yield, respectively (eq 7). Interestingly, the intramolecular reaction of the substrate **10**, in which the tether is a part of benzene ring, gave the silole (silacyclobutadiene) derivative **11** in a moderate yield (eq 8). The difference of the cyclization mode between **7** and **10** is interesting. Although the difference is whether the tether is the ordinary carbon chain or a part of benzene ring, the former reaction proceeds both in the **A** and in the **B** mode, whereas the latter cyclization proceeds only in the **A** mode. Recently, much attention has been paid to siloles, since those compounds have potential as functional materials.[9] Accordingly, the Lewis acid-catalyzed intramolecular hydrosilylation of certain alkynes may be applicable to the synthesis of siloles, not easily available via the previous synthetic methods, which may be used for material science.



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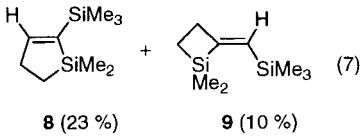
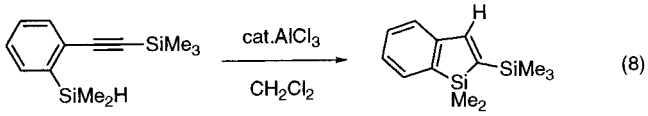


8 (23 %) **9** (10 %) (7)



10 **11** (36 %) (8)

The following mechanistic rational can explain the observed $AlCl_3$-catalyzed intramolecular *trans*-hydrosilylation of unactivated alkynes (Scheme 1). As previously being proposed for the Lewis acid-catalyzed hydro-[10] and allylstannation[11] and hydro-[3] and allylsilylation[12] and

(7) Other Lewis acids such as $TiCl_4$, $ZrCl_4$, and $HfCl_4$ also catalyzed the mentioned hydrosilylation, with lower chemical yields. No reaction took place when Et_2AlCl, BCl_3, $BF_3{\cdot}Et_2O$, and $InCl_3$ were used as a catalyst.

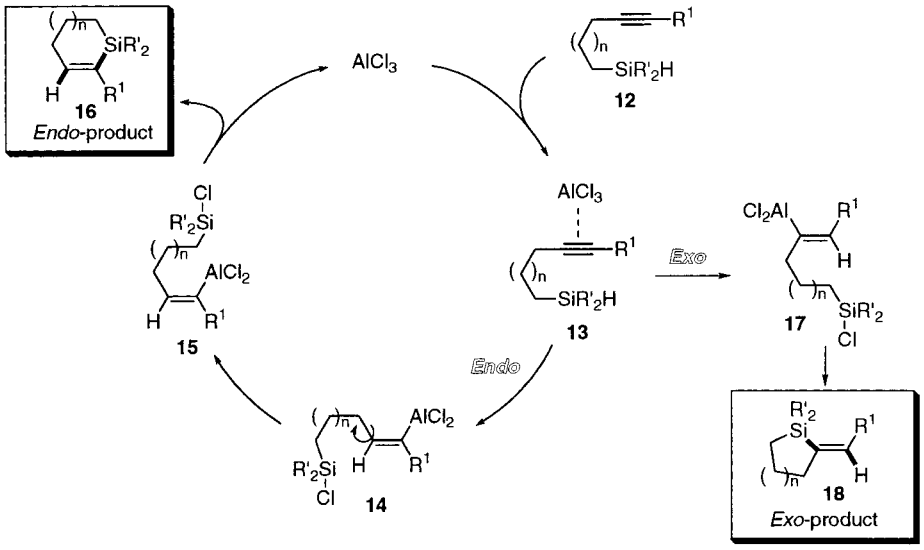
(8) Possible regio- and stereoisomers are shown below. These isomers were not detected.

(9) For recent reviews of siloles, see: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (b) Colomer, E.; Corriu, R. J. P.; Lheureux, M. *Chem. Rev.* **1990**, *90*, 265. (c) Tamao, K.; Yamaguchi, S. *Pure Appl. Chem.* **1996**, *68*, 139. (d) Dubac, J.; Guérin, C,; Manuel, G. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z.; Apeloig, Y., Eds.; J. Wiley & Sons: Chichester, 1998; Vol. 2, Chapter 34, p 1961. (e) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans. 1* **1998**, 3693.

(10) (a) Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 2405. (b) Asao, N.; Liu, J.-X.; Sudoh, T.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4568.

(11) Asao, N.; Matsukawa, Y.; Yamamoto, Y. *Chem. Commun.* **1996**, 1513.

Scheme 1



vinylsilylation[13] of alkynes, the coordination of $AlCl_3$ to the acetylenic bond of **12** forms the π-complex **13**. A hydride of the hydrosilane would attack intramolecularly the sp carbon substituted by the methylene tether from the side opposite to $AlCl_3$ to produce the alkenyl aluminum **14**.[14] The C−C bond rotation in the intermediate **14** makes the silyl moiety close to the Al atom (**15**). The intermediate **15** would undergo coupling between the silyl group and vinyl group with retention of geometry to give the *endo*-product **16** and $AlCl_3$. If a hydride of SiR'_2H of **13** attacks alternative sp carbon attached with R^1 group, the regioisomeric alkenyl aluminum intermediate **17** is produced. In a similar manner described above, the *exo*-product **18** is produced from **17**.

In conclusion, we have provided a new and useful method for the preparation of medium-sized silacycles with vinylsilane framework.

Experimental Section

General Information. All manipulations were conducted under an argon atmosphere using standard Schlenk techniques or the Wheaton microreactors. Anhydrous solvents were purchased from Kanto Chemicals. $AlCl_3$ was used after sublimation.

Dimethylpent-4-ynylsilane (1a). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (septet, J = 3.6 Hz, 1H), 2.21 (dt, J = 2.7, 6.9 Hz, 2H), 1.95 (t, J = 2.7 Hz, 1H), 1.55 (tt, J = 7.2, 7.2 Hz, 2H), 0.70 (m2H), 0.075 (d, J = 3.6 Hz, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 84.5, 68.4, 28.3, 24.2, 21.8, 13.6, −4.58. IR (neat) 2935, 2360, 2116, 1251 cm^{-1}.

Dimethyl(undec-4-ynyl)silane (1b). The preparation of the compound **1b** is representative. (1) To a solution of 1-octyne (3.11 mL, 10 mmol) in THF (10 mL) was added at 0 °C, dropwise via syringe, n-BuLi in hexane (7.4 mL, 1.50 M, 11 mmol). The solution was stirred for 30 min and then cooled to −78 °C and stirred further at this temperature for 10 min. To this solution was added at −78 °C, via cannula, 1,3-dibromopropane (1.6 mL, 15 mmol) in THF (10 mL). The solution was gradually warmed to room temperature and then stirred at this temperature for 5 h. The reaction mixture was quenched with a saturated solution of NH_4Cl (20 mL) and extracted with ether (2 × 50 mL). The extracts were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was subjected to Kugelrohr distillation to give 1-bromo-4-undecyne (1.20 g, 5.2 mmol, 52% yield) as a colorless oil: (2) A 50 mL two-necked flask with reflux condenser containing Mg tuning (243 mg, 10 mmol) was used under argon atmosphere. THF (1.0 mL) was added, and then a few drops of 1,2-dibromoethane were added to activate Mg tuning. After thermodynamic reaction finished, THF (5.0 mL) was added further. A mixture of 1-bromo-4-undecyne (1.15 g, 5 mmol) and $ClSiMe_2H$ (0.83 mL, 7.5 mmol) was added very slowly, dropwise via cannula. The reaction mixture was stirred for 10 h and the quenched at 0 °C with a saturated solution of NH_4Cl (20 mL). The product was extracted with ether (2 × 50 mL). The extracts were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane as an eluent to yield **1b** as a colorless oil (666 mg, 3.2 mmol, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (septet, J = 3.6 Hz, 1H), 2.17 (tt, J = 7.2, 2.5 Hz, 2H), 2.15 (tt, J = 7.2, 2.5 Hz, 2H), 1.58−1.27 (m, 10H), 0.89 (t, J = 6.6 Hz, 3H), 0.68 (m, 2H), 0.069 (d, J = 3.6 Hz, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 80.6, 80.0, 31.4, 29.1, 28.5, 24.4, 22.6, 22.2, 18.8, 14.0, 13.7, −4.52. IR (neat) 3000, 2858, 2112, 1250, 887 cm^{-1}. HRMS calcd for $C_{13}H_{26}Si$ 210.1802, found 210.1784.

Dimethyl(6,6-dimethylhex-4-ynyl)silane (1c). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (septet, J = 3.6 Hz, 1H), 2.15 (t, J = 7.2 Hz, 2H), 1.50 (tt, J = 7.2, 7.2 Hz, 2H), 1.19 (s, 9H), 0.66 (m2 H), 0.07 (d, J = 3.6 Hz, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 89.3, 78.3, 31.4, 31.4, 27.3, 24.5, 22.1, 13.6, −4.5. IR (neat) 2968, 2866, 2114, 1250, 889 cm^{-1}. HRMS calcd for $C_{11}H_{22}Si$ 182.1490, found 182.1490.

Dimethyl(5-phenylpent-4-ynyl)silane (1d). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.38 (m, 2H), 7.29−7.26 (m, 2H), 3.89 (septet, J = 3.6 Hz, 1H), 2.44 (t, J = 7.2 Hz, 2H), 0.76 (m, 2H), 0.10 (d, J = 3.9 Hz, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 131.5, 128.2, 127.5, 124.0, 90.2, 80.9, 24.0, 22.8,

(12) (a) Asao, N.; Yoshikawa, E.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4784. (b) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781. (c) Imamura, K.-i.; Yoshikawa, E.; Gevorgyan, V.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5339.

(13) Asao, N.; Shimada, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3797.

(14) In our previous papers about the Lewis acid-catalyzed hydrosilylation of alkyne compounds,[3] we proposed a mechanism involving a silylcation species. However, both referees suggested that if free silyl cations would be formed under the conditions, chlorosilanes could be the products since free silyl cations would be very unstable. On the other hand, a stable triarylsilicenium ion has been known.[15] Taken together, we propose **14** as a nonionic intermediate in the intramolecular hydrosilylation reaction although this is still highly speculative.

(15) Lambert, J. B.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 400.

(16) Conlin, R. T.; Namavari, M. *J. Am. Chem. Soc.* **1988**, *110*, 3639. The spectral data of **2a** was reported in this paper.

13.8, −4.5. IR (neat) 3080, 2929, 2110, 1488, 1250, 878 cm^{-1}. Anal., Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97. Found: C, 76.76; H, 8.98.

Dimethyl(5-trimethylsilylpent-4-ynyl)silane (1e). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 3.85 (septet, J = 3.6 Hz, 1H), 2.24 (t, J = 7.2 Hz, 2H), 1.58 (tt, J = 7.2, 7.2 Hz, 2H), 0.67 (s, 2H), 0.15 (s, 9H), 0.08 (d, J = 3.6 Hz, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 107.5, 84.6, 23.9, 23.3, 13.7, 0.17, −4.5. IR (neat) 2958, 2933, 2176, 2114, 1745, 1250 cm^{-1}. HRMS calcd for $C_{10}H_{22}Si_2$ 198.1260, found 198.1188.

Diisopropyl(5-trimethylsilylpent-4-ynyl)silane (1f). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 3.41 (bs, 1H), 2.25 (t, J = 7.2 Hz, 2H), 1.61 (tt, J = 7.2, 7.2 Hz, 2H), 1.02 (bs, 14H), 0.73 (m, 2H), 0.15 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 107.4, 84.7, 24.7, 23.5, 19.0, 18.6, 10.5, 7.7, 0.15. IR (neat) 2940, 2864, 2176, 2093, 1464, 1250 cm^{-1}. Anal. Calcd for $C_{14}H_{30}Si_2$: C, 66.06; H, 11.88. Found: C, 66.06; H, 11.71.

Methylphenyl(5-trimethylsilylpent-4-ynyl)silane (1g). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.56−7.53 (m, 2H), 7.42−7.33 (m, 3H), 4.36 (septet, J = 3.6 Hz, 1H), 2.25 (t, J = 7.2 Hz, 2H), 1.60 (tt, J = 7.2, 7.2 Hz, 2H), 0.96 (m, 2H), 0.35 (d, J = 3.6 Hz, 3H), 0.15 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.1, 134.3, 129.3, 127.9, 107.3, 84.7, 23.8, 23.2, 12.8, 0.16, −5.7. IR (neat) 3069, 2959, 2174, 2116, 1428, 1250, 1115, 1020 cm^{-1}. Anal. Calcd for $C_{15}H_{24}Si_2$: C, 69.15; H, 9.29. Found: C, 69.45; H, 9.12.

Diphenyl(5-trimethylsilylpent-4-ynyl)silane (1h). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.71−7.69 (m, 4H), 7.54−7.46 (m, 6H), 5.04 (t, J = 3.6 Hz, 1H), 2.14 (t, J = 7.2 Hz, 2H), 1.82 (t, J = 7.2 Hz, 2H), 1.42 (m, 2H), 0.31 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 135.1, 134.0, 129.6, 128.0, 107.1, 84.9, 23.7, 23.1, 11.5, 0.18. IR (neat) 3067, 2933, 2898, 2174, 2120, 1429, 1250, 1117, 1020 cm^{-1}. HRMS calcd for $C_{20}H_{26}Si_2$ 322.1573, found 322.1577.

1,1-Dimethyl-2-silacyclohexene (2a).[16] Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 6.71 (dt, J = 14.1, 3.6 Hz, 1H), 5.68 (d, J = 14.1 Hz, 1H), 2.19 (dt, J = 6.9, 3.6 Hz, 2H), 1.79 (tt, J = 6.9, 6.9 Hz, 2H), 0.66 (m, 2H).

1,1-Dimethyl-2-hexyl-2-silacyclohexene (2b). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 6.28 (t, J = 3.9 Hz, 1H), 2.13−2.02 (m, *8*H), 1.73 (tt, J = 6.3, 6.3 Hz, 2H), 1.28 (bs, 8H), 0.89 (t, J = 6.6 Hz, 3H), 0.64 (m, 2H), 0.07 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 141.2, 138.5, 36.6, 31.8, 30.6, 29.8, 29.3, 22.7, 21.3, 14.1, 12.5, −2.1. IR (neat) 2357, 1609, 1456, 1246, 1150, 1119 cm^{-1}. Anal. Calcd for $C_{13}H_{26}Si$: C, 74.20; H, 12.45. Found: C, 73.85; H, 12.43.

1,1-Dimethyl-2-*tert*-butyl-2-silacyclohexene (2c). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 6.44(t, J = 4.2 Hz, 1H), 2.15 (dt, J = 5.7, 5.7 Hz, 2H), 1.74−1.66 (m, 2H), 1.07 (s, 9H), 0.64 (m, 2H), 0.19 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 146.8, 139.2, 37.0, 31.5, 31.1, 21.0, 14.3, 1.2. IR (neat) 2953, 2869, 1591, 1364, 1250, 1146, 894 cm^{-1}. Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.27; H, 8.34.

1,1-Dimethyl-2-phenyl-2-silacyclohexene (2d). The preparation of **2d** is representative. A mixture of $AlCl_3$ (13 mg, 20 mol %) and CH_2Cl_2 (0.5 mL) was stirred at room temperature for 10 min and then cooled to 0 °C and followed by addition of **1d** (110 mg, 0.5 mmol). After 10 min, the reaction mixture was diluted with ether, quenched with aqueous $NaHCO_3$ solution (0.4 mL), filtered through basic Al_2O_3, and concentrated. Purification by column chromatography (silica gel, hexane eluent) gave **2d** (79 mg, 0.36 mmol) in 78% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.31−7.27 (m, 2H), 7.20−7.15 (m, 3H), 6.32 (t, J = 4.2 Hz, 1H), 2.30 (dt, J = 6.0, 4.2 Hz, 2H), 1.84 (m, 2H), 0.76 (m, 2H), 0.15 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.0, 144.8, 140.1, 126.6, 125.6, 31.0, 20.9, 12.5, −1.6. IR (neat) 3068, 2952, 1670, 1429, 1250, 1110 cm^{-1}. Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97. Found: C, 77.40; H, 8.85.

1,1-Dimethyl-2-trimethylsilyl-2-silacyclohexene (2e). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.00 (t, J = 3.9 Hz, 1H), 2.17 (dt, J = 6.0, 3.9 Hz, 2H), 1.73 (m, 2H), 0.63 (m, 2H), 0.09 (s, 6H), 0.05 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 156.8, 138.6, 33.3, 20.8, 20.8, 12.8, −0.04, −0.41. IR (neat) 3069, 2950, 1670, 1429, 1250, 1110 cm^{-1}. HRMS calcd for $C_{10}H_{22}Si_2$ 198.1259, found 198.1252.

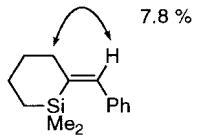


Figure 1. NOE experiment of **4a**.

1,1-Diisopropyl-2-trimethylsilyl-2-silacyclohexene (2f). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (t, J = 4.0 Hz, 1H), 2.12 (dt, J = 5.5, 4.0 Hz, 2H), 1.71−1.66 (m, 16H), 1.01−0.93 (m, 2H), 0.08 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 160.3, 135.9, 33.2, 21.7, 19.1, 18.2, 12.7, 4.6, 0.42. Anal. Calcd for $C_{14}H_{30}Si_2$: C, 66.06; H, 11.88. Found: C, 66.16; H, 11.46. Additionally, C−H COSY and COLOC (500 MHz, $CDCl_3$) spectra of **2f** are available in Supporting Information.

1-Phenyl-1-methyl-2-trimethylsilyl-2-silacyclohexene (2g). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.54−7.32 (m, 5H), 7.23 (t, J = 3.9 Hz, 1H), 2.30 (dt, J = 5.5, 3.9 Hz, 2H), 1.86−1.76 (m, 2H), 0.92−0.74 (m, 2H), 0.43 (s, 3H), −0.10 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 158.7, 139.5, 136.5, 134.4, 128.8, 127.5, 33.2, 20.6, 12.7, −0.2, −3.0. IR (neat) 3069, 2953, 2902, 1672, 1560, 1429, 1250, 1111, 959 cm^{-1}. HRMS calcd for $C_{15}H_{24}Si_2$ 260.1415, found 260.1389.

1,1-Diphenyl-2-trimethylsilyl-2-silacyclohexene (2h). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.68−7.65 (m, 4H), 7.45−7.40 (m, 7H), 2.44 (dt, J = 5.7, 4.2 Hz, 2H), 1.89−1.81 (m, 2H), 1.15 (m, 2H), 0.13 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 160.1, 136.7, 135.7, 134.5, 129.1, 127.6, 33.5, 20.0, 11.8, −0.08. IR (neat) 3068, 2952, 1558, 1429, 1245, 1112 cm^{-1}. Anal. Calcd for $C_{20}H_{26}Si_2$: C, 74.46; H, 8.12. Found: C, 74.26; H, 8.34.

Dimethyl(6-phenylhex-5-ynyl)silane (3a). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.36−7.31 (m, 2H), 7.25−7.21(m, 3H), 3.82 (septet, J = 3.6 Hz, 1H), 2.37 (t, J = 7.2 Hz, 2H), 1.65−1.42 (m, 4H), 0.58 (m, 2H), 0.03 (d, J = 3.6 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 131.5, 128.1, 127.4, 124.1, 90.2, 80.6, 32.0, 23.7, 19.1, 13.6, −4.5. IR (neat) 2958, 2929, 2110, 1489, 1250, 887 cm^{-1}. HRMS calcd for $C_{14}H_{20}Si(M^+-2CH_3)$ 216.1333, found 216.1327.

Dimethyl(7-phenylhept-6-ynyl)silane (3b). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.31−7.27 (m, 2H), 7.24−7.19 (m, 3H), 3.82 (septet, J = 3.6 Hz, 1H), 2.37 (t, J = 7.2 Hz, 2H), 1.65−1.42 (m, 4H), 0.58 (m, 2H), 0.03 (d, J = 3.6 Hz, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 131.5, 128.1, 127.4, 124.1, 90.4, 80.6, 32.4, 28.4, 23.9, 19.3, 14.0, −4.5. IR (neat) 2930, 2856, 2108, 1489, 1250, 887 cm^{-1}. Anal. Calcd for $C_{15}H_{22}Si$: C, 78.19; H, 9.62. Found: C, 78.12; H, 9.83.

***E*-2-Benzylidene-1,1-dimethyl-1-silacyclohexane (4a).** Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.28−7.16 (m, 5H), 7.07 (bs, 1H), 2.45 (m, 2H), 1.77−1.72 (m, 2H), 1.60−1.58 (m, 2H), 0.62 (m, 2H), −0.1 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.4, 140.4, 13.0, 128.7, 127.6, 126.6, 41.5, 30.9, 24.5, 16.1, −1.6. IR (neat) 3061, 2914, 1705, 1452, 1252, 1057 cm^{-1}. Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 78.07; H, 9.49. NOE experiments were performed by irradiation of signals at 2.45 and 7.07 ppm. Signals showing NOE were indicated in Figure 1.

***E*-2-Benzylidene-1,1-dimethyl-1-silacycloheptane (4b).** Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.31−7.19 (m, 5H), 7.16 (bs, 1H), 2.45 (m, 2H), 1.70−1.55 (m, 4H), 0.70 (m, 2H), −0.1 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 147.1, 141.8, 140.5, 128.4, 127.7, 126.5, 40.7, 31.9, 31.4, 24.1, 16.7, −0.8. Anal. Calcd for $C_{15}H_{22}Si$: C, 78.19; H, 9.62. Found: C, 78.35; H, 9.86. NOE experiments were performed by irradiation of signals at 2.45 and 7.16 ppm. Signals showing NOE were indicated in Figure 2.

1-(Dimethylsilanyl)-2-[4-(trimethylsilyl)-but-3-ynyl]-benzene (5a). Colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J = 7.2 Hz, 1H), 7.37−7.21 (m, 3H), 4.60 (septet, J = 3.6 Hz, 1H), 2.98 (t, J = 7.8 Hz, 2H), 2.51 (t, J = 7.8 Hz, 2H), 0.39 (d, J = 3.6 Hz, 3H), 0.17 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 146.3, 135.9, 134.7, 129.5, 128.8, 125.8, 106.5, 85.1, 35.1, 22.5,

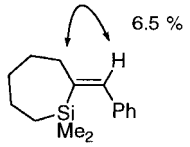


Figure 2. NOE experiment of **4b**.

0.10, −3.0. IR (neat) 3058, 2959, 2900, 2176, 2124, 1434, 1250, 1124 cm^{-1}. HRMS calcd for $C_{13}H_{18}Si_2$ 230.0946, found 230.0947.

1-(Dimethylsilanyl)-2-[5-(trimethylsilyl)-pent-4-ynyl]-benzene (5b). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 7.5 Hz, 1H), 7.35−7.17 (m, 3H), 4.58 (septet, J = 3.9 Hz, 1H), 2.85 (m, 2H), 2.30 (t, J = 6.9 Hz, 2H), 2.30 (tt, J = 7.8, 7.8 Hz, 2H), 0.37 (d, J = 3.9 Hz, 3H), 0.17 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 147.6, 135.9, 134.8, 129.5, 128.6, 125.4, 85.1, 35.1, 30.9, 19.8, 0.2, −2.9. IR (neat) 2957, 2174, 2122, 1250, 887 cm^{-1}. HRMS calcd for $C_{16}H_{26}Si_2$ 274.1572, found 274.1581.

5,5-Dimethyl-6-(trimethyl-silanyl)-8,9-dihydro-5*H*-5-sila-benzocycloheptene (6a). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (dd, J = 7.2, 1.8 Hz, 1H), 7.28 (dt, J = 7.5, 1.5 Hz, 1H), 7.19 (dt, J = 7.2, 1.2 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 6.95 (t, J = 4.5 Hz, 1H), 3.07 (m, 2H), 2.06 (m, 2H), 0.47 (s, 6H), 0.13 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 157.4, 149.0, 140.0, 137.5, 133.2, 129.5, 127.7, 125.2, 36.0, 35.0, 0.7, 0.5. Anal. Calcd for $C_{15}H_{24}Si_2$: C, 69.15; H, 9.29. Found: C, 69.28; H, 9.52.

5,5-Dimethyl-6-(trimethylsilanyl)-5,8,9,10-dihydro-5-sila-benzocyclooctetene (6b). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 7.2 Hz, 1H), 7.30 (dd, J = 7.2, 7.2 Hz, 1H), 7.20 (dd, J = 7.2, 7.2 Hz, 1H), 7.11 (d, J = 7.2 Hz, 1H), 6.75 (t, J = 7.8 Hz, 1H), 2.79 (bs, 2H), 2.15 (dt, J = 7.2, 7.8 Hz, 2H), 1.58 (tt, J = 7.2,7.2 Hz, 2H), 0.36 (s, 6H), 0.19 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.1, 146.3, 145.5, 143.0, 132.8, 129.1, 129.1, 125.0, 31.5, 29.2, 28.0, 0.6. IR (neat) 3056, 2655, 2846, 1570, 1456, 1248, 1119 cm^{-1}. HRMS calcd for $C_{16}H_{26}Si_2$ 274.1572, found 260.1557.

Dimethyl(4-trimethylsilylbut-3-ynyl)silane (7). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.89 (septet, J = 3.6 Hz, 1H), 2.30 (t, J = 7.8 Hz, 2H), 0.88 (m, 2H), 0.14 (s, 9H), 0.11 (d, J = 3.6 Hz, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 109.1, 83.9, 14.9, 13.5, 0.09, −4.4. IR (neat) 2961, 2174, 2116, 1250, 881 cm^{-1}. HRMS calcd for $C_8H_{17}Si_2$ (M^+-CH_3) 169.0868, found 169.0863.

1,1-Dimethyl-2-trimethylsilyl-2-silacyclopentene (8): Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (t, J = 2.7 Hz, 1H), 2.54 (m, 2H), 0.67 (m, 2H), 0.15 (s, 6H), 0.07 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 160.2, 143.5, 34.6, 9.4, −0.21, −0.35. IR (neat) 2956, 5897, 1549, 1437, 1248, 1134 cm^{-1}. HRMS calcd for $C_9H_{20}Si_2$ 184.1102, found 184.1103. Additionally, C−H COSY and COLOC (500 MHz, $CDCl_3$) spectra of **8** are available in Supporting Information.

1,1-Dimethyl-2-(trimethyl-silanylmethylene)siletane (9). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.35 (t, J = 2.4 Hz, 1H), 2.57 (m, 2H), 0.70 (m, 2H), 0.12 (s, 6H), 0.08 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.2, 141.3, 34.6, 10.3, −1.2, −1.8. Additionally, C−H COSY and COLOC (500 MHz, $CDCl_3$) spectra of **9** are available in Supporting Information.

1-(Dimethylsilanyl)-2-(trimethylsilanylethynyl)benzene (10). To a solution of (2-bromophenylethynyl)trimethylsilane (2.5 g, 10 mmol) in hexane (10 mL) was added at −78 °C, dropwise via syringe, t-BuLi in pentane (12.3 mL, 1.63 M, 20 mmol). The solution was stirred for 1 h. To this solution was added tetramethylethylenediamine (3.0 mL, 20 mmol), and the mixture was stirred further at this temperature for 30 min. To this solution was added at −78 °C $ClSiMe_2H$ (1.3 mL, 20 mmol). The solution was gradually warmed to room temperature and then stirred at this temperature for 30 min. The reaction mixture was quenched with a saturated solution of NH_4Cl (20 mL) and extracted with ether (2 × 50 mL). The extracts were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel using hexane as an eluent to yield **7** as a colorless oil (1.75 g, 7.6 mmol, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51−7.44 (m, 2H), 7.32−7.24 (m, 2H), 4.50 (septet, J = 3.9 Hz, 1H), 0.40 (d, J = 3.9 Hz, 6H), 0.24 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 140.4, 134.7, 132.2, 129.0, 128.6, 127.8, 105.8, 97.2, −0.2, −4.0. IR (neat) 2961, 2156, 2124, 1460, 1250, 1126, 881 cm^{-1}. Anal. Calcd for $C_{13}H_{20}Si_2$: C, 67.166; H, 8.672. Found: C, 67.204; H, 8.611.

1,1-Dimethyl-2-(trimethylsilanyl)-1*H*-benzosilole (11). Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57−7.55 (m, 2H), 7.53 (s, 1H), 7.35−7.22 (m 2H), 0.35 (s, 6H), 0.20 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 155.4, 150.0, 146.7, 140.6, 131.5, 130.0, 127.0, 124.0, −0.6, −3.2. HRMS calcd for $C_{15}H_{20}Si_2$ 232.1104, found 232.1117.

Supporting Information Available: Spectroscopic and analytical data for compounds **1a**−**h**, **2b**−**h**, **3a, 3b, 4a, 4b**, **5a**, **5b**, **6a**, **6b**, **7**, **8**, **9**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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