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Palladium Catalyzed Reaction of Silacyclobutanes with Acetylenes

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Whereas the reaction of 1,1-dimethyl-1-silacyclobutane (**1a**) with dimethyl acetylenedicarboxylate in the presence of Pd catalyst provides dimethyl 1,1-dimethyl-1-sila-2-cyclohexene-2,3-dicarboxylate almost exclusively, the reaction of **1a** with phenylacetylene affords allyldimethylstyrylsilane as a major product. The reaction of silacyclobutane with phenylallene provided three isomeric products.

Strained small ring molecules are versatile building blocks and often provide short and elegant routes in organic synthesis. From the interest in the development of synthetic use of silacyclobutane, we have studied stereoselective formation of silacyclopentanes by the reaction of silacyclobutane with lithium carbenoids[1] and the base induced reaction of silacyclobutane with aldehyde to give oxasilacyclohexanes.[2] During the course of these studies, accidentally, it was found that the palladium catalyzed reaction of silacyclobutane with acetylenes provided a mixture of silacyclohexene derivatives and allylvinylsilane derivatives.

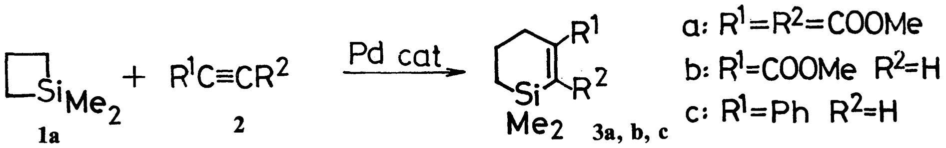
Sakurai and Imai have reported[3] that 1,1-dimethyl-1-silacyclobutane (**1a**) reacted smoothly with dimethyl acetylenedicarboxylate, methyl propiolate, or phenylacetylene to give dimethyl 1,1-dimethyl-1-sila-2-cyclohexene-2,3-dicarboxylate (**3a**), methyl 1,1-dimethyl-1-sila-2-cyclohexene-3-carboxylate (**3b**), or 1,1-dimethyl-3-phenyl-1-sila-2-cyclohexene (**3c**), respectively (Scheme 1).

Meanwhile, we have found that allylvinylsilane derivative **4** was formed in addition to the silacyclohexene derivative **3** in the reaction of **1** with acetylenic compounds. For instance, $PdCl_2(PPh_3)_2$ catalyzed reaction of 1,1-dimethyl-1-silacyclobutane (**1a**) with methyl propiolate in benzene under an argon atmosphere gave a mixture of methyl 1,1-dimethyl-1-sila-2-cyclohexene-3-carboxylate (**3b**) and methyl (*E*)-4,4-dimethyl-4-sila-2,6-heptadienoate (**4b**, **3b**/**4b**=4/6, Scheme 2). The representative results are summarized in Table 1.

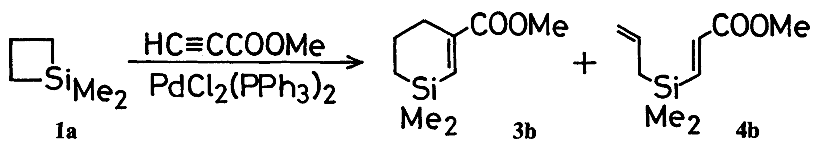
As shown in Table 1, the ratios of two types of the products, silacyclohexene **3** and allylvinylsilane derivative **4** heavily depend on the nature of acetylenic compounds. The reaction of silacyclobutane with dimethyl acetylenedicarboxylate provided the former product, silacyclohexene **3**, as a major product. In contrast, the reaction with phenylacetylene afforded the latter allylvinylsilane derivative **4** mainly. Whereas palladium complexes such as $Pd(PPh_3)_4$ and $PdCl_2(P(o\text{-tolyl})_3)_2$ were as effective as $PdCl_2(PPh_3)_2$, $PdCl_2(Ph_2PCH_2CH_2PPh_2)$ was not effective as a catalyst and phenylacetylene was recovered unchanged in the reaction with **1a**. The catalysts prepared in situ from $PdCl_2$ and PPh_3 or $PdCl_2(PPh_3)_2$ and pyridine were also ineffective. The ratios of two products were not affected by the ligand on palladium complex. Thus, the ratio of **3c** and **4c** was always 1/9—2/8 in the reaction of 1,1-dimethyl-1-silacyclobutane with phenylacetylene ($PdCl_2(PPh_3)_2$, 1/9; $PdCl_2(P(o\text{-tolyl})_3)_2$, 2/8; $PdCl_2$–$2P(OEt)_3$, 1/9). Tetrahydrofuran and dimethylformamide as well as benzene were suitable solvent for the reaction. Regioselective formation of single isomers **3** and **4** was observed for the reaction of methyl propiolate or phenylacetylene.

Prosaic acetylenic compound such as 1-dodecyne reacted very sluggishly to give the corresponding products in poor yield (17%, 3-decyl-1,1-dimethyl-1-sila-2-cyclohexene/(*E*)-allyl(1-dodecenyl)dimethylsilane=4/6).

Treatment of 3-deuterio-3-methyl-1,1-diphenyl-1-silacyclobutane **5**[4] with acetylenic compounds in the presence of $PdCl_2(PPh_3)_2$ gave the corresponding products

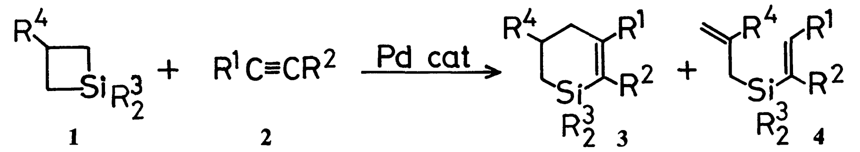


Scheme 1.



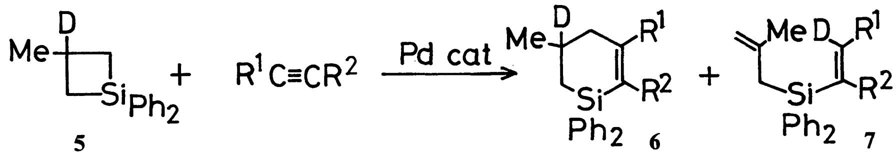
Scheme 2.

Table 1. Palladium Catalyzed Reaction of Silacyclobutanes with Acetylenes[a)]

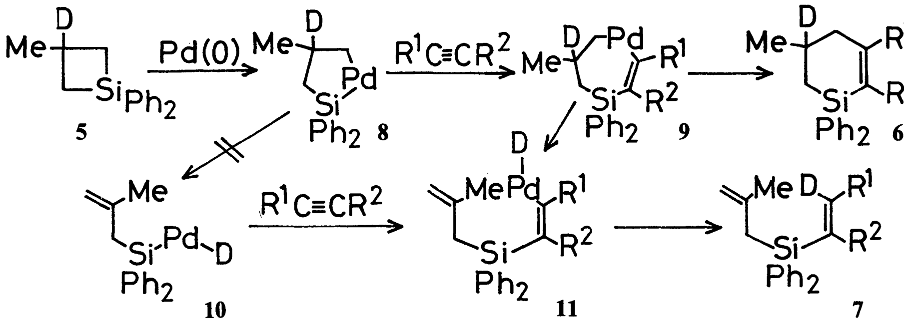


Entry	Silacyclobutane 1		Acetylene 2		Yield/%	
	R^3	R^4	R^1	R^2	**3**	**4**
1	Me	H (**1a**)	COOMe	COOMe	50 (**3a**)	18 (**4a**)
2	Me	H (**1a**)	COOMe	H	27 (**3b**)	41 (**4b**)
3	Me	H (**1a**)	Ph	H	6 (**3c**)	51 (**4c**)
4	Ph	H (**1b**)	COOMe	COOMe	86 (**3d**)	7 (**4d**)
5	Ph	H (**1b**)	COOMe	H	50 (**3e**)	26 (**4e**)
6	Ph	H (**1b**)	Ph	H	16 (**3f**)	60 (**4f**)
7	Me	Me (**1c**)	COOMe	COOMe	61 (**3g**)	13 (**4g**)
8	Me	Me (**1c**)	COOMe	H	43 (**3h**)	32 (**4h**)
9	Me	Me (**1c**)	Ph	H	12 (**3i**)	29 (**4i**)
10	Ph	Me (**1d**)	COOMe	COOMe	82 (**3j**)	4 (**4j**)
11	Ph	Me (**1d**)	COOMe	H	71 (**3k**)	26 (**4k**)
12	Ph	Me (**1d**)	Ph	H	50 (**3l**)	36 (**4l**)

a) One mmol of silacyclobutane, 1 mmol of acetylene, and a catalytic amount of $PdCl_2(PPh_3)_2$ were employed. The reaction mixture was refluxed for 2 h.



Scheme 3.

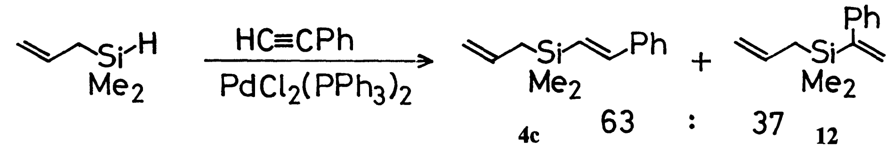


Scheme 4.

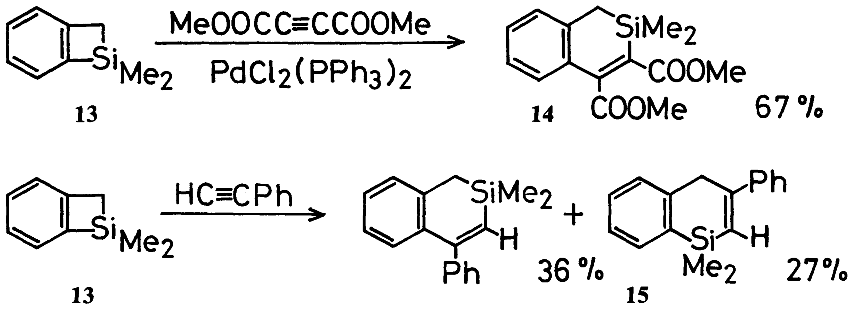
6 and **7**. In the case of the reaction with methyl propiolate, methyl (*E*)-2-deuterio-6-methyl-4,4-diphenyl- 4-sila-2,6-heptadienoate **7b** (R^1=COOMe, R^2=H) was obtained (12% yield) along with methyl 5-deuterio-5-methyl-1-sila-2-cyclohexene-3-carboxylate **6b** (R^1=COOMe, R^2=H, 76% yield). Deuterium occupied 2-position of 4-sila-2,6-heptadienoate **7b**. The ^{1}H NMR signal of δ=6.30 for the corresponding compound **4k** (methyl 6-methyl-4,4-diphenyl-4-sila-2,6-heptadienoate) completely disappeared in the product **7b**. The reaction with phenylacetylene or dimethyl acetylenedicarboxylate also provided the corresponding deuterated compounds **6** and **7** (Scheme 3)

Based on these results, we are tempted to assume the following reaction mechanism: (1) Insertion of Pd(0) into silacyclobutane leading to ring-expanded compound **8**,[5] (2) regioselective silylpalladation of acetylenic compounds to provide seven-membered ring intermediate **9**, and (3) reductive elimination of Pd(0) to afford silacyclohexene **6** or β-elimination of Pd–D followed by reductive elimination of Pd(0) to give allylvinylsilane derivative **7** (Scheme 4).[10]

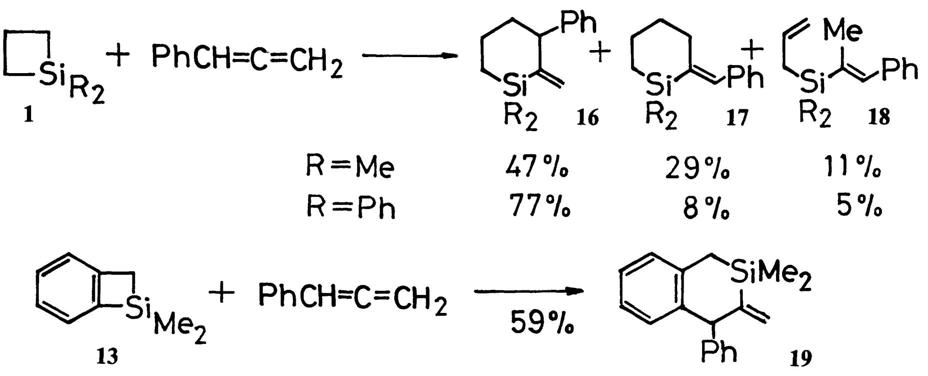
Alternatively, the formation of allylvinylsilane derivatives **7** might be explained by the addition of CH_2=$CMeCH_2SiPh_2$–Pd–D (**10**), which is derived by β-elimination of Pd–D from **8**, to acetylenic compounds providing **11** and successive reductive elimination of Pd(0) from **11**. However, this route was ruled out by



Scheme 5.



Scheme 6.



Scheme 7.

the following fact. Treatment of phenylacetylene with allyldimethylsilane in the presence of $PdCl_2(PPh_3)_2$ gave a regioisomeric mixture of allyldimethylstyrylsilane **4c** and allyldimethyl(1-phenylvinyl)silane **12** in low yield (<15% combined yield, **4c**/**12**=63/37) as depicted in Scheme 5.

The reaction of 1,2-dihydro-1,1-dimethyl-1-silabenzocyclobutene (**13**), which has no β-hydrogen, with dimethyl acetylenedicarboxylate or phenylacetylene under similar conditions gave the corresponding dihydrosilanaphthalenes, **14** or **15**, respectively (Scheme 6).

Phenylallene also easily reacted with silacyclobutanes in the presence of $PdCl_2(PPh_3)_2$ catalyst to give a mixture of three components, **16**, **17**, and **18**. On the other hand, 1,2-dihydro-1-silabenzocyclobutene **13** provided 1,2,3,4-tetrahydro-2-silanaphthalene **19** in 59% yield as a single product (Scheme 7).

Experimental

Distillations of the products were performed by use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. ^{1}H NMR and ^{13}C NMR spectra were taken on a Varian XL-200 spectrometer, $CDCl_3$ was used as solvent, and chemical shifts being given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The elemental analyses were carried out at the Elemental Analyses Center of Kyoto University.

Preparation of Silacyclobutane Derivatives. 1,1-Dimethyl-1-silacyclobutane (**1a**) was purchased from Shinetsu Silicone Chemicals and used as delivered. 1,1-Diphenyl-1-silacyclobutane (**1b**) was prepared in 86% yield by treatment of 1,1-dichloro-1-silacyclobutane (obtained from Petrarch Systems) with phenylmagnesium bromide in ether. 1,1,3-Trimethyl-1-silacyclobutane (**1c**) and 3-methyl-1,1-diphenyl-1-silacyclobutane (**1d**) were obtained from 2-methylallyl chloride. Hexachloroplatinic(IV) acid catalyzed hydrosilylation with $HSiClMe_2$ or $HSiClPh_2$ followed by treatment of the resulting $ClSiMe_2CH_2CH(Me)CH_2Cl$ or $ClSiPh_2CH_2CH(Me)CH_2Cl$ with Mg provided **1c** or **1d** in 26% or 35% overall yield, respectively.[4] 1,2-Dihydro-1-silabenzocyclobutene (**13**) was prepared following the reported procedure.[11]

General Procedure for the Reaction of Silacyclobutane with Acetylenic Compounds or Phenylallene in the Presence of Pd Catalyst. The reaction of 1,1-dimethyl-1-silacyclobutane with methyl propiolate is representative. A catalytic amount of $PdCl_2(PPh_3)_2$ (115 mg, 0.02 mmol) was added to a solution of 1,1-dimethyl-1-silacyclobutane (**1a**, 0.20 g, 2.0 mmol) and methyl propiolate (0.17 g, 2.0 mmol) in benzene (5 ml) under an argon atmosphere. The pale yellow mixture was heated at reflux for 2 h. The resulting dark brown mixture was concentrated in vacuo and the residual oil was submitted to silica-gel column chromatography to give a mixture of methyl 1,1-dimethyl-1-sila-2-cyclohexene-3-carboxylate (**3b**[3], 0.10 g, 27% yield) and methyl (*E*)-4,4-dimethyl-4-sila-2,6-heptadienoate (**4b**, 0.15 g, 41% yield). **4b:** Bp 65 °C (1.0 Torr, 1 Torr=133.322 Pa, bath temp); IR(neat) 2948, 1730, 1308, 1271, 1250, 1227, 1168, 995, 846 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.13 (s, 6H), 1.62 (d, *J*=8.0 Hz, 2H), 3.75 (s, 3H), 4.86 (bd, *J*=9.5 Hz, 1H), 4.87 (bd, *J*=17.6 Hz, 1H), 5.74 (ddt, *J*=9.5, 17.6, 8.0 Hz, 1H), 6.25 (d, *J*=18.9 Hz, 1H), 7.23 (d, *J*=18.9 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=−4.03, 22.69, 51.17, 114.0, 133.7, 134.4, 148.1, 166.2. Found: C, 58.38; H, 9.05%. Calcd for $C_9H_{16}O_2Si$: C, 58.65; H, 8.75%.

Methyl (*E*)-3-Methoxycarbonyl-4,4-dimethyl-4-sila-2,6-heptadienoate (4a): Bp 95 °C (1.0 Torr, bath temp); IR(neat) 2952, 1728, 1436, 1341, 1238, 1198, 1174, 1039, 890 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.19 (s, 6H), 1.69 (d, *J*=8.0 Hz, 2H), 3.73 (s, 3H), 3.81 (s, 3H), 4.90 (d, *J*=17.5 Hz, 1H), 4.91 (d, *J*=8.0 Hz, 1H), 5.73 (ddt, *J*=17.5, 8.0, 8.0 Hz, 1H), 6.08 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=−4.45, 21.98, 52.02, 114.8, 129.5, 132.8, 154.0, 164.4, 170.8. Found: C, 54.37; H, 7.43%. Calcd for $C_{11}H_{18}O_4Si$: C, 54.52; H, 7.49%.

(*E*)-Allyldimethylstyrylsilane (4c): Bp 90 °C (1.0 Torr, bath temp); IR(neat) 3074, 2954, 1629, 1604, 1572, 1493, 1248, 1154, 988, 851, 687, 645 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.16 (s, 6H), 1.66 (d, *J*=8.0 Hz, 2H), 4.87 (d, *J*=10.2 Hz, 1H), 4.89 (d, *J*=16.9 Hz, 1H), 5.83 (ddt, *J*=10.2 Hz, 1H), 6.50 (d, *J*=19.3 Hz, 1H), 6.91 (d, *J*=19.3 Hz, 1H), 7.15—7.45 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=−3.46, 23.66, 113.2, 126.4, 127.4, 128.1, 128.5, 134.8, 138.2, 144.5. Found: C, 76.95; H, 9.09%. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.96%.

Dimethyl 1,1-Diphenyl-1-sila-2-cyclohexene-2,3-dicarboxylate (3d): Bp 200 °C (1.0 Torr, bath temp); IR(neat) 2946, 1719, 1600, 1430, 1280, 1236, 1191, 1145, 1114, 1050, 1029, 776, 730, 698, 661 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.18—1.33 (m, 2H), 1.88—2.08 (m, 2H), 2.62 (t, *J*=5.8 Hz, 2H), 3.48 (s, 3H), 3.79 (s, 3H), 7.33—7.70 (m, 10H); ^{13}C NMR (CDCl$_3$) δ=9.62, 19.83, 31.64, 51.52, 52.30, 127.8, 129.8, 132.6, 133.3, 135.4, 155.3, 169.4. Found: C, 68.56; H, 6.00%. Calcd for $C_{21}H_{22}O_4Si$: C, 68.82; H, 6.05%.

Methyl (*E*)-3-Methoxycarbonyl-4,4-diphenyl-4-sila-2,6-heptadienoate (4d): Bp 200 °C (1.0 Torr, bath temp); IR(neat) 2948, 1726, 1430, 1339, 1239, 1197, 1173, 1112, 1036, 897, 770, 736, 699 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.32 (d, *J*=7.8 Hz, 2H), 3.66 (s, 3H), 3.72 (s, 3H), 4.93—5.10 (m, 2H), 5.84 (ddt, *J*=17.6, 9.8, 7.8 Hz, 1H), 6.10 (s, 1H), 7.35—7.68 (m, 10H); ^{13}C NMR (CDCl$_3$) δ=19.97, 51.97, 52.06, 116.2, 128.1, 130.3, 131.2, 132.2, 133.5, 135.6, 150.6, 164.4, 170.3. Found: C, 68.59; H, 6.25%. Calcd for $C_{21}H_{22}O_4Si$: C, 68.82; H, 6.05%.

Methyl 1,1-Diphenyl-1-sila-2-cyclohexene-3-carboxylate (3e): Bp 150 °C (0.3 Torr, bath temp); IR(neat) 3066, 3000, 2922, 1715, 1590, 1428, 1293, 1221, 1112, 776, 734, 698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.18—1.33 (m, 2H), 1.88—2.08 (m, 2H), 2.56 (t, *J*=5.8 Hz, 2H), 3.76 (s, 3H), 7.30—7.70 (m, 11H); ^{13}C NMR (CDCl$_3$) δ=9.07, 20.96, 29.32, 52.02, 128.0, 129.7, 133.7, 134.9, 135.3, 150.1, 167.3. Found: *m*/*z* 308.1227. Calcd for $C_{19}H_{20}O_2Si$: M, 308.1233.

Methyl (*E*)-3-(Allyldiphenylsilyl)acrylate (4e): Bp 150 °C (0.3 Torr, bath temp); ^{1}H NMR (CDCl$_3$) δ=2.25 (d, *J*=1.1 Hz, 2H), 3.75 (s, 3H), 4.90—5.08 (m, 2H), 5.82 (ddt, *J*=17.0, 10.1, 7.9 Hz, 1H), 6.31 (d, *J*=18.9 Hz, 1H), 7.30—7.70 (m, 11H); ^{13}C NMR (CDCl$_3$) δ=20.43, 51.68, 115.5, 128.0, 129.9, 132.7, 132.8, 135.8, 137.6, 143.8, 165.8.

1,1,3-Triphenyl-1-sila-2-cyclohexene (3f): Bp 145 °C (0.2 Torr, bath temp); IR(neat) 3064, 2918, 1589, 1565, 1493, 1427, 1110, 794, 729, 697 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.28 (m, 2H), 2.10 (m, 2H), 2.74 (t, *J*=5.5 Hz, 2H), 6.42 (s, 1H), 7.25—7.75 (m, 15H); ^{13}C NMR (CDCl$_3$) δ=20.00, 21.29, 33.10, 119.7, 125.6, 127.6, 128.2, 129.3, 129.9, 134.9, 136.7, 138.8, 144.9. Found: C, 84.56; H, 6.73%. Calcd for $C_{23}H_{22}Si$: C, 84.61; H, 6.79%.

(*E*)-1,1,3-Triphenyl-3-sila-1,5-hexadiene (4f): Bp 145 °C (0.2 Torr, bath temp); IR(neat) 3064, 2918, 1428, 1110, 794, 731, 697 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.26 (d, *J*=7.9 Hz, 2H), 4.91 (d, *J*=9.9 Hz, 1H), 4.98 (d, *J*=17.2 Hz, 1H), 5.89 (ddt, *J*=17.2, 9.9, 7.9 Hz, 1H), 6.75 (d, *J*=19.4 Hz, 1H), 6.98 (d, *J*=19.4 Hz, 1H), 7.25—7.88 (m, 15H); ^{13}C NMR (CDCl$_3$) δ=21.30, 114.8, 122.9, 126.7, 127.7, 127.9, 128.45, 128.54, 129.5, 133.8, 134.8, 135.4, 148.3. Found: C, 84.83; H, 6.79%. Calcd for $C_{23}H_{22}Si$: C, 84.61; H, 6.79%.

Dimethyl 1,1,5-Trimethyl-1-sila-2-cyclohexene-2,3-dicarboxylate (3g): Bp 90 °C (1.0 Torr, bath temp); IR(neat) 2950, 1719, 1604, 1432, 1229, 1144, 830, 801 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.19 (s, 3H), 0.21 (s, 3H), 0.45 (dd, *J*=14.3, 12.8 Hz, 1H), 0.87 (d, *J*=14.3 Hz, 1H), 1.08 (d, *J*=6.2 Hz, 3H), 1.80—2.03 (m, 1H), 2.04 (dd, *J*=18.1, 10.8 Hz, 1H), 2.53 (d, *J*=18.1 Hz, 1H), 3.75 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (CDCl$_3$) δ=−2.75, −2.54, 20.25, 25.91, 27.53, 38.96, 51.57, 52.02, 136.4, 151.0, 169.0, 170.1. Found: C, 56.36; H, 8.12%. Calcd for $C_{12}H_{20}O_4Si$: C, 56.22; H, 7.86%.

Methyl (*E*)-3-Methoxycarbonyl-4,4,6-trimethyl-4-sila-2,6-heptadienoate (4g): Bp 90 °C (1.0 Torr, bath temp); IR(neat) 2950, 1725, 1637, 1434, 1338, 1235, 1195, 1172, 1037, 843 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.23 (s, 6H), 1.719 (s, 3H), 1.723 (s, 2H), 3.75 (s, 3H), 3.83 (s, 3H), 4.54—4.60 (m, 1H), 4.68—4.73 (m, 1H), 6.11 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=−3.88, 25.12, 25.75, 51.95, 110.1, 129.3, 141.5, 154.4, 164.4, 170.8. Found: C, 56.27; H, 8.01%. Calcd for $C_{12}H_{20}O_4Si$: C, 56.22; H, 7.86%.

Methyl 1,1,5-Trimethyl-1-sila-2-cyclohexene-3-carboxylate (3h): Bp 70 °C (1.0 Torr, bath temp); IR(neat) 2950, 1717, 1434, 1272, 1249, 1219, 1059, 1048, 850, 801 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.110 (s, 3H), 0.114 (s, 3H), 0.37 (dd, *J*=14.3, 12.8 Hz, 1H), 0.81 (d, *J*=14.3 Hz, 1H), 1.08 (d, *J*=6.2 Hz, 3H), 1.60—1.93 (m, 2H), 2.50—2.73 (m, 1H), 3.75 (s, 3H), 7.00 (s, 1H); ^{13}C NMR (CDCl$_3$) δ=−2.27 −2.20, 20.38, 26.42, 28.56, 37.27, 51.78, 138.0, 147.2, 167.5. Found: C, 60.46; H, 9.33%. Calcd for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15%.

Methyl (*E*)-4,4,6-Trimethyl-4-sila-2,6-heptadienoate (4h): Bp 70 °C (1.0 Torr, bath temp); IR(neat) 2952, 1732, 1436, 1306, 1271, 1251, 1227, 1195, 1168, 997, 843, 803 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.17 (s, 6H), 1.65 (s, 2H), 1.70 (s, 3H), 3.76 (s, 3H), 4.49—4.53 (m, 1H), 4.62—4.65 (m, 1H), 6.27 (d, *J*=18.9 Hz, 1H), 7.27 (d, *J*=18.9 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ=−3.49, 25.18, 26.71, 51.63, 109.3, 134.1, 142.3, 148.5, 166.1. Found: C, 60.49; H, 9.30%. Calcd for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15%.

1,1,5-Trimethyl-3-phenyl-1-sila-2-cyclohexene (3i): Bp 100 °C (1.0 Torr, bath temp); IR(neat) 2950, 2902, 2876, 1589, 1568, 1492, 1453, 1442, 1206, 847, 787, 693 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.10 (s, 3H), 0.12 (s, 3H), 0.42 (dd, *J*=14.0, 12.8 Hz, 1H), 0.84 (d, *J*=14.0 Hz, 1H), 1.11 (d, *J*=6.4 Hz, 3H), 1.83—2.10 (m, 1H), 2.18 (ddd, *J*=16.9, 10.5, 2.4 Hz, 1H), 2.57 (ddd, *J*=16.9, 3.1, 1.6 Hz, 1H), 6.01 (s, 1H), 7.20—7.53 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=−1.47, −1.37, 20.75, 26.79, 29.23, 41.47, 124.2, 125.5, 127.1, 128.1, 145.2, 156.6. Found:

C, 77.50; H, 9.54%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

(*E*)-3,3,5-Trimethyl-1-phenyl-3-sila-1,5-hexadiene (4i): Bp 95 °C (1.0 Torr, bath temp); IR(neat) 2956, 1636, 1604, 1493, 1447, 1247, 987, 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.19 (s, 6H), 1.67 (s, 2H), 1.73 (s, 3H), 4.53—4.58 (m, 1H), 4.60—4.68 (m, 1H), 6.47 (d, J=19.2 Hz, 1H), 6.90 (d, J=19.2 Hz, 1H), 7.25—7.53 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−2.87, 25.29, 27.73, 108.6, 126.4, 128.0, 128.5, 138.3, 143.4, 144.3. Found: C, 77.97; H, 9.58%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

Dimethyl 5-Methyl-1,1-diphenyl-1-sila-2-cyclohexene-2,3-dicarboxylate (3j): Bp 180 °C (0.3 Torr, bath temp); IR(neat) 2948, 2918, 1719, 1601, 1429, 1236, 1191, 1144, 1111, 1039, 779, 730, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.00 (dd, J=14.5, 13.0 Hz, 1H), 1.11 (d, J=6.3 Hz, 3H), 1.30 (d, J=14.5 Hz, 1H), 1.95—2.20 (m, 1H), 2.27 (dd, J=18.5, 10.9 Hz, 1H), 2.66 (d, J=18.5 Hz, 1H), 3.49 (s, 3H), 3.79 (s, 3H), 7.30—7.78 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=18.99, 26.11, 27.40, 39.72, 51.51, 52.28, 127.8, 127.9, 129.77, 129.85, 132.3, 133.2, 135.3, 135.4, 155.1, 169.3. Found: C, 69.18; H, 6.43%. Calcd for $C_{22}H_{24}O_4Si$: C, 69.44; H, 6.36%.

Methyl (*E*)-3-Methoxycarbonyl-6-methyl-4,4-diphenyl-4-sila-2,6-heptadienoate (4j): ^{1}H NMR ($CDCl_3$) δ=1.60 (s, 3H), 2.30 (s, 2H), 3.65 (s, 3H), 3.72 (s, 3H), 4.62 (s, 1H), 4.70 (s, 1H), 6.15 (s, 1H), 7.30—7.80 (m, 10H). Analytically pure sample could not be obtained because of its small yield.

Methyl 5-Methyl-1,1-diphenyl-1-sila-2-cyclohexene-3-carboxylate (3k): Bp 155 °C (0.3 Torr, bath temp); IR(neat) 2948, 2918, 1715, 1597, 1454, 1429, 1271, 1219, 1113, 1057, 790, 776, 732, 712, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.92 (dd, J=14.0, 12.0 Hz, 1H), 1.14 (d, J=5.8 Hz, 3H), 1.37 (d, J=12.0 Hz, 1H), 1.80—2.20 (m, 2H), 2.67—2.92 (m, 1H), 3.77 (s, 3H), 7.25—7.70 (m, 11H); ^{13}C NMR ($CDCl_3$) δ=18.34, 26.52, 28.51, 37.50, 52.04, 128.0, 129.7, 133.6, 134.8, 134.9, 135.1, 149.6, 167.2. Found: C, 74.20; H, 6.91%. Calcd for $C_{20}H_{22}O_2Si$: C, 74.49; H, 6.88%.

Methyl (*E*)-6-Methyl-4,4-diphenyl-4-sila-2,6-heptadienoate (4k): Bp 155 °C (0.3 Torr, bath temp); IR(neat) 2948, 1720, 1429, 1271, 1224, 1190, 1169, 1112, 789, 777, 732, 712, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.58 (s, 3H), 2.25 (s, 2H), 3.76 (s, 3H), 4.60 (bs, 1H), 4.70 (bs, 1H), 6.30 (d, J=19.0 Hz, 1H), 7.25—7.75 (m, 11H); ^{13}C NMR ($CDCl_3$) δ=24.66, 25.50, 51.78, 111.2, 129.9, 133.3, 135.3, 137.5, 141.5, 144.4, 165.9. Found: C, 74.63; H, 6.90%. Calcd for $C_{20}H_{22}O_2Si$: C, 74.49; H, 6.88%.

5-Methyl-1,1,3-triphenyl-1-sila-2-cyclohexene (3l): Bp 175 °C (0.3 Torr, bath temp); IR(neat) 3064, 3016, 2948, 2916, 2864, 1591, 1565, 1492, 1444, 1428, 1264, 1207, 1187, 1111, 843, 793, 758, 730, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.93 (dd, J=13.3, 14.1 Hz, 1H), 1.16 (d, J=6.4 Hz, 3H), 1.39 (d, J=14.1 Hz, 1H), 2.00—2.26 (m, 1H), 2.35 (ddd, J=17.1, 10.7, 2.4 Hz, 1H), 2.73 (d, J=17.1 Hz, 1H), 6.38 (s, 1H), 7.24—7.75 (m, 15H); ^{13}C NMR ($CDCl_3$) δ=18.75, 26.80, 29.10, 41.65, 119.6, 125.7, 127.6, 127.8, 128.2, 129.3, 134.8, 135.0, 145.0, 159.7. Found: C, 84.53; H, 7.04%. Calcd for $C_{24}H_{24}Si$: C, 84.65; H, 7.10%.

(*E*)-5-Methyl-1,3,3-triphenyl-3-sila-1,5-hexadiene (4l): Bp 170 °C (0.3 Torr, bath temp); IR(neat) 3064, 3018, 2960, 2914, 1638, 1599, 1570, 1493, 1446, 1428, 1277, 1263, 1110, 1028, 997, 873, 795, 733, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.62 (s, 3H), 2.26 (s, 2H), 4.61 (s, 1H), 4.67 (s, 1H), 6.79 (d, J=19.1 Hz, 1H), 6.96 (d, J=19.1 Hz, 1H), 7.24—7.75 (m, 15H); ^{13}C NMR ($CDCl_3$) δ=25.30,25.60, 110.5, 123.4, 126.7, 127.8, 128.4, 128.5, 129.5, 135.1, 135.5, 138.1, 142.4, 148.2. Found: C, 84.48; H, 7.04%. Calcd for $C_{24}H_{24}Si$: C, 84.65; H, 7.10%.

Preparation of 3-Deuterio-3-methyl-1,1-diphenyl-1-silacyclobutane (5). The title compound was obtained following the procedure described for the preparation of **1d**. Hydrosilylation of 2-methylallyl chloride with diphenyldeuteriochlorosilane ($Ph_2Si(D)Cl$) in the presence of platinum catalyst gave 3-chloro-2-deuterio-2-methylpropyldiphenylchlorosilane in 36% yield: Bp 130—150 °C (0.2 Torr); IR(neat) 3068, 3048, 2998, 2962, 2870, 1457, 1429, 1378, 1283, 1246, 1115, 815, 766, 727, 697, 652 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.00 (s, 3H), 1.31 (d, J=15.1 Hz, 1H), 1.68 (d, J=15.1 Hz, 1H), 3.40 (d, J=10.7 Hz, 1H), 3.44 (d, J=10.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=20.27, 21.27, 31.18, (t, J=20.1 Hz), 53.11, 128.1, 130.5, 130.6, 134.1, 134.2. Treatment of 3-chloro-2-deuterio-3-methylpropyldiphenylchlorosilane with Mg gave **5** in 79% yield: Bp 100 °C (0.3 Torr, bath temp); IR(neat) 3064, 3046, 3010, 2946, 2912, 2854, 1450, 1428, 1196, 1151, 1114, 842, 789, 736, 717, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.13 (d, J=15.6 Hz, 2H), 1.23 (s, 3H), 1.69 (d, J=15.6 Hz, 2H), 7.38—7.78 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=22.25, 27.49, 129.6, 134.5, 134.7, 135.9, 137.1. The signal for the carbon bearing deuterium could not be observed even with high concentrated sample. Found: C, 80.48; H, 7.85%. Calcd for $C_{16}H_{17}DSi$: C, 80.27; H, 8.00%.

The Reaction of 5 with Dimethyl Acetylenedicarboxylate. Heating a benzene solution of **5** (0.23 g, 0.97 mmol), dimethyl acetylenedicarboxylate (0.14 g, 1.0 mmol), and $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) at 80 °C for 3 h under argon atmosphere. The resulting mixture was concentrated in vacuo and the residual oil was submitted to silica-gel column chromatography to give **6a** (0.31 g, 84%) and **7a** (12 mg, 3%). Methyl 5-deuterio-5-methyl-1,1-diphenyl-1-sila-2-cyclohexene-2,3-dicarboxylate (**6a**): Bp 180 °C (0.3 Torr, bath temp); IR(neat) 2948, 2916, 1719, 1602, 1450, 1429, 1238, 1205, 1192, 1145, 1113, 1040, 898, 779, 759, 733, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.99 (d, J=14.6 Hz, 1H), 1.10 (s, 3H), 1.29 (d, J=14.6 Hz, 1H), 2.26 (d, J=19.0 Hz, 1H), 2.65 (d, J=19.0 Hz, 1H), 3.49 (s, 3H), 3.79 (s, 3H), 7.36—7.75 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=18.86, 26.02, 39.65, 51.54, 52.31, 127.8, 127.9, 129.8, 129.9, 135.3, 135.4, 155.2, 169.4. The signal for the carbon bearing deuterium could not be observed. Found: C, 68.98; H, 6.40%. Calcd for $C_{22}H_{23}DO_4Si$: C, 69.26; H, 6.60%.

Reaction of Allyldimethylsilane with Phenylacetylene in the Presence of $PdCl_2(PPh_3)_2$ or H_2PtCl_6. A benzene solution of allyldimethylsilane (0.15 g, 1.5 mmol) and phenylacetylene (0.10 g, 1.0 mmol) was heated in the presence of catalytic amount of $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol) at reflux for 2 h. The resulting dark brown solution was concentrated and the residual oil was submitted to silica-gel column chromatography to give a mixture of allyldimethylstyrylsilane (**4c**) and allyldimethyl(1-phenylvinyl)silane (**12**, 30 mg, **4c**/**12**=63/37) in <15% combined yield. **12**: ^{1}H NMR ($CDCl_3$) δ=5.65 (d, J=2.9 Hz, 1H), 5.90 (d, J=2.9 Hz, 1H). Meanwhile, stirring a mixture of allyldimethylsilane (0.30 g, 3.0 mmol) and phenylacetylene (0.30 g, 3.0 mmol) in the presence of $H_2PtCl_6 \cdot 6H_2O$ (5 mg) at room temperature for 15 h gave a mixture of **4c** and **12** (0.31 g, **4c**/**12**=2.4/1) in 52% yield.[12)]

Dimethyl 1,2-Dihydro-2,2-dimethyl-2-silanaphthalene-3,4-dicarboxylate (14): Bp 119 °C (1.0 Torr, bath temp); IR(neat) 2950, 1734, 1715, 1584, 1554, 1435, 1302, 1231, 1208, 1070, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.20 (s, 6H); 2.19 (s, 2H), 3.77 (s, 3H), 3.91 (s, 3H), 7.10—7.24 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=−3.96, 20.77, 51.82, 52.40, 126.0, 129.1, 129.9, 131.4, 131.9, 137.5, 145.4, 153.3, 169.6, 169.9. Found: C, 61.89; H, 6.32%. Calcd for $C_{15}H_{18}O_4Si$: C, 62.04; H, 6.25%.

1,2-Dihydro-2,2-dimethyl-4-phenyl-2-silanaphthalene (15a): Mp 76.5—77.0 °C (hexane); IR(neat before crystallization) 3040, 2945, 2840, 1570, 1540, 1475, 1435, 1242, 1203, 822, 797, 761, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.13 (s, 6H), 2.22 (s, 2H), 6.14 (s, 1H), 6.98—7.30 (m, 4H), 7.37 (bs, 5H); ^{13}C NMR ($CDCl_3$) δ=−3.63, 21.41, 125.0, 127.1, 127.3, 128.0, 128.2, 129.4. Found: C, 81.52; H, 7.11%. Calcd for $C_{17}H_{18}Si$: C, 81.54; H, 7.24%.

1,4-Dihydro-1,1-dimethyl-3-phenyl-1-silanaphthalene (15b): Bp 120 °C (0.3 Torr, bath temp); IR(neat) 3052, 2952, 1595, 1492, 1436, 1247, 1136, 844, 772, 741, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.32 (s, 6H), 4.07 (s, 2H), 6.33 (s, 1H), 7.25—7.68 (m, 9H); ^{13}C NMR ($CDCl_3$) δ=−1.21, 38.78, 123.9, 125.7, 125.8, 127.5, 128.3, 128.6, 128.8, 133.1, 134.0, 144.7, 144.8, 155.1. Found: C, 81.38; H, 7.26%. Calcd for $C_{17}H_{18}Si$: C, 81.54; H, 7.24%.

2-Methylene-1,1-dimethyl-3-phenyl-1-silacyclohexane (16a): Bp 100 °C (1.0 Torr, bath temp); IR(neat) 2954, 2920, 2852, 1729, 1630, 1599, 1491, 1447, 1250, 1154, 1121, 1073, 1032, 961, 892, 835, 758, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.12 (s, 3H), 0.17 (s, 3H), 0.50—0.80 (m, 1H), 0.80—1.00 (m, 1H), 1.60—1.90 (m, 2H), 1.90—2.03 (m, 1H), 2.03—2.13 (m, 1H), 3.40—3.60 (m, 1H), 4.84 (t, J=2.5 Hz, 1H), 5.24 (t, J=2.5 Hz, 1H), 7.10—7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−3.05, 15.19, 23.61, 36.77, 52.50, 122.0, 125.9, 128.1, 128.5, 143.8, 155.7. Found: C, 77.82; H, 9.50%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

2-Benzylidene-1,1-dimethyl-1-silacyclohexane (17a): Bp 100 °C (1.0 Torr, bath temp); IR(neat) 2950, 2916, 2848, 1729, 1598, 1492, 1445, 1429, 1249, 1139, 1111, 900, 871, 828, 776, 751, 732, 712, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 6H), 0.65—0.80 (m, 2H), 1.40—1.70 (m, 2H), 1.75—1.95 (m, 2H), 2.55—2.70 (m, 2H), 6.68 (s, 1H), 7.10—7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−3.49, 15.36, 24.37, 30.70, 31.60, 126.3, 128.0, 128.9, 134.1, 138.1, 145.5. Found: C, 77.75; H, 9.47%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

Allyldimethyl(α-methylstyryl)silane (18a): Bp 90 °C (1.0 Torr, bath temp); IR(neat) 2954, 2922, 2852, 1630, 1598, 1490, 1447, 1250, 1153, 1120, 1072, 1031, 961, 930, 892, 835, 758, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.15 (s, 6H), 1.66 (d, J=8.0 Hz, 2H), 1.94 (d, J=1.8 Hz, 3H), 4.80—5.00 (m, 2H), 5.83 (ddt, J=17.0, 10.0, 8.0 Hz, 1H), 6.77 (s, 1H), 7.10—7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=−4.26, 16.57, 22.74, 113.1, 122.0, 126.5, 128.0, 128.5, 129.0, 135.0, 137.8, 138.2, 138.6. Found: C, 77.77; H, 9.56%. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32%.

2-Methylene-1,1,3-triphenyl-1-silacyclohexane (16b): Bp 175 °C (0.25 Torr, bath temp); IR(neat) 3062, 3048, 3020, 2916, 2850, 1491, 1451, 1429, 1111, 938, 814, 732, 711, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.15—1.45 (m, 1H), 1.45—2.12 (m, 4H), 2.18—2.35 (m, 1H), 3.52 (d, J=10.0 Hz, 1H), 5.06 (s, 1H), 5.20 (s, 1H), 7.10—7.80 (m, 15H); ^{13}C NMR ($CDCl_3$) δ=12.45, 23.88, 36.87, 52.81, 126.0, 127.0, 127.7, 128.2, 128.5, 129.47, 129.52, 134.0, 134.7, 135.2, 135.5, 143.7, 151.2. Found: C, 84.56; H, 7.20%. Calcd for $C_{24}H_{24}Si$: C, 84.65; H, 7.10%.

2-Benzylidene-1,1-diphenyl-1-silacyclohexane (17b): Bp 175 °C (0.4 Torr, bath temp); ^{1}H NMR ($CDCl_3$) δ=1.25—2.20 (m, 6H), 2.65—2.80 (m, 2H), 6.67 (s, 1H), 7.20—7.80 (m, 15H); ^{13}C NMR ($CDCl_3$) δ=12.64, 24.14, 30.42, 32.15, 126.6, 127.9, 128.0, 129.0, 135.5, 139.3, 141.2. Found: C, 84.36; H, 6.98%. Calcd for $C_{24}H_{24}Si$: C, 84.65; H, 7.10%.

Allyldiphenyl(α-methylstyryl)silane (18b): Bp 175 °C (0.3 Torr, bath temp); ^{1}H NMR ($CDCl_3$) δ=2.07 (s, 3H), 2.35 (d, J=8.0 Hz, 2H), 4.85—5.03 (m, 2H), 5.80—6.15 (m, 1H), 6.90 (s, 1H), 7.20—7.80 (m, 15H); ^{13}C NMR ($CDCl_3$) δ=17.65, 20.53, 114.8, 126.9, 127.8, 128.1, 129.1, 134.1, 134.4, 135.6, 142.4. Found: C, 84.57; H, 6.96%. Calcd for $C_{24}H_{24}Si$: C, 84.65; H, 7.10%.

1,2,3,4-Tetrahydro-2,2-dimethyl-3-methylene-4-phenyl-2-silanaphthalene (19): Mp 85—86 °C (hexane); IR(neat before crystallization) 3058, 3026, 2944, 1491, 1481, 1447, 1246, 922, 834, 805, 776, 754, 736, 697, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.04 (s, 3H), 0.06 (s, 3H), 1.65 (d, J=14.8 Hz, 1H), 1.84 (d, J=14.8 Hz, 1H), 4.72 (s, 1H), 5.59 (d, J=2.6 Hz, 1H), 5.91 (d, J=2.6 Hz, 1H), 7.05—7.38 (m, 9H); ^{13}C NMR ($CDCl_3$) δ=−2.42, −0.80, 20.87, 60.58, 125.5, 125.9, 126.5, 127.1, 127.5, 128.1, 130.0, 130.9, 138.0, 140.8, 141.7, 151.3. Found: C, 81.72; H, 7.57%. Calcd for $C_{18}H_{20}Si$: C, 81.76; H, 7.62%.

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