Supporting Information

Nickel-Catalyzed Regio- and Stereoselective Silylation of Terminal Alkenes with Silacyclobutanes: Facile Access to Vinylsilanes from Alkenes

Koji Hirano, Hideki Yorimitsu,* and Koichiro Oshima*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University,

Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Contents

Instrumentation and Chemicals	S2
Experimental Procedure for the Nickel-Catalyzed Silylation	S4
Optimization Studies	S5
Detailed Discussion on the Formations of 6d and 6i	S7
Characterization Data	S8
¹H NMR and ²H NMR Spectra for <i>deuterio</i>-3f	S15

Instrumentation and Chemicals

^1H NMR (300 MHz), ^2H NMR (46 MHz), and ^{13}C NMR (75.3 MHz) spectra were taken on Varian Mercury 300 spectrometers and were recorded in CDCl_3 . Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^1H and relative to CDCl_3 at 77.0 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene and triphenylphosphine were purchased from Wako Pure Chemical Co. and toluene was stored over slices of sodium. Bis(1,5-cyclooctadiene)nickel and tricyclohexylphosphine were obtained from Strem. Tricyclohexylphosphine was diluted to prepare 0.5 M toluene solution, which was stored strictly under argon. 1,1-Dimethylsilacyclobutane and 1,1-dichlorosilacyclobutane were available from Shinetsu Silicone Chemicals. All reactions were carried out under argon atmosphere. 1,1-Diphenylsilacyclobutane¹ and 2,3-benzo-1,1-dimethylsilacyclobutene² were prepared according to the reported procedures. *Deuterio-1f* was prepared by Wittig olefination of 4-methoxybenzaldehyde with (trideuteriomethyl)triphenylphosphonium

¹ Sunderhaus, J. D.; Lam, H.; Dudley, B. *Org. Lett.* **2003**, 5, 4571–4573.

iodide.³

² Eaborn, C.; Walton, D. R. M.; Chan, M. *J. Organomet. Chem.* **1967**, 9, 251–257.

³ Schlosser, M. *Chem. Ber.* **1964**, 97, 3219–3233.

Typical Procedure for Nickel-Catalyzed Silylation of Terminal Alkenes with Silacyclobutanes

With a glovebox filled with argon, Ni(cod)₂ (6.9 mg, 0.025 mmol) was placed in a reaction flask. Toluene (3.0 mL) and P(*c*-C₆H₁₁)₃ (0.50 M toluene solution, 0.10 mL, 0.050 mmol) were added dropwise. The solution was stirred for 10 min at 0 °C. A solution of benzyl acrylate (**1a**, 81 mg, 0.50 mmol) in toluene (2.0 mL) and 1,1-dimethylsilacyclobutane (**2**, 60 mg, 0.60 mmol) were then added and the resulting solution was heated at 100 °C. After being stirred for 12 h at the same temperature, the mixture was cooled to room temperature and filtered off. Concentration in vacuo followed by column chromatography on silica gel afforded benzyl (*E*)-3-(dimethylpropylsilyl)acrylate (**3a**, 125 mg, 0.475 mmol) in 95% yield.

Optimization Studies

Benzyl acrylate (**1a**) and 1,1-dimethylsilacyclobutane (**2**) were chosen as model substrates and the ligand effects were examined (Table S1).

Table S1. Optimization for the silylation of benzyl acrylate (**1a**) with 1,1-dimethylsilacyclobutane (**2**)^a

Reaction scheme: Benzyl acrylate (**1a**) + 1,1-dimethylsilacyclobutane (**2**) $\xrightarrow[\text{toluene, 100 } ^\circ\text{C, 12 h}]{\text{Ni(cod)}_2 \text{ (5 mol\%), ligand (10 mol\%)}}$ *n*-PrMe₂Si-CH=CH-CO₂CH₂Ph (**3a**)

entry	ligand	yield of 3a (%) ^b
1	P(<i>t</i> -Bu) ₃	0
2	P(<i>c</i> -C ₆ H ₁₁) ₃	95 ^c
3	P(<i>n</i> -Bu) ₃	22
4	PMe ₃	20
5	PPh ₃	81
6	P(<i>o</i> -tolyl) ₃	0
7	IMes ^d	11

^a A mixture of Ni(cod)₂ (0.025 mmol), ligand (0.050 mmol), **1a** (0.50 mmol), and **2** (0.60 mmol) was heated at 100 °C in toluene (5.1 mL) for 12 h. ^b ¹H NMR yields. ^c Isolated yield. ^d Generated in situ from 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride with *n*-BuLi.

Regardless of the yields, high regio- and stereoselectivities were observed. P(*t*-Bu)₃ and P(*o*-tolyl)₃ showed no activity (entries 1 and 6) while P(*c*-C₆H₁₁)₃ led to the formation of the desired product in 95% yield (entry 2). P(*n*-Bu)₃, PMe₃, and an *N*-heterocyclic carbene ligand, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), had similar activities (entries 3, 4, and 7). Notably, in the case of PPh₃, **3a** was obtained in 81% yield (entry 5). These results indicate that the cone angles of the ligands play an

important role in the reaction as well as their ability of σ -donation. Nevertheless, the effects of several other factors involving electronic ones could not be completely excluded.

NiCl₂ instead of Ni(cod)₂ did not catalyze the reaction even in the presence of P(*c*-C₆H₁₁)₃ and 1,5-cyclooctadiene (COD). This is probably because the divalent nickel was not reduced to the zerovalent one under the reaction conditions so that the initial oxidative addition did not proceed. The catalysts prepared from NiCl₂, P(*c*-C₆H₁₁)₃, and DIBAL-H failed to catalyze the reaction. The aluminum salt generated in situ would prevent the reaction. Although the exact role of COD is not clear at this stage, COD was known to work as an effective ligand in other nickel-catalyzed reactions.⁴

⁴ (a) Vettel, S.; Vaupel, A.; Knochel, P. *Tetrahedron Lett.* **1995**, 36, 1023–1026. (b) Vettel, S.; Vaupel, A.; Knochel, P. *J. Org. Chem.* **1996**, 61, 7473–7481. (c) Pérez, I.; Sestelo, J. P.; Maestro, M. A.; Mouriño, A.; Sarandeses, L. A. *J. Org. Chem.* **1998**, 63, 10074–10076.

Detailed Discussion on the Formations of **6d** and **6i**

The formations of **6d** and **6i** (Table 2, entries 1 and 2) would proceed as follows (See the following scheme). Oxidative addition of the benzylic sp^3C-Si bond of **4** to Ni(0) followed by insertion of **1d** or **1i** gives the nickelasilacycloheptane **11**. Subsequent β -H elimination and reductive elimination produces **6d** or **6i** and regenerates the zerovalent nickel species. Nevertheless, in the reactions of dienes **1m** and **1n** with the benzene-fused silacyclobutane **4**, the byproducts corresponding to **6d** or **6i** were not detected (Table 2, entries 3 and 4). The finding suggests that the oxidative addition of the benzylic sp^3C-Si bond of **4** to Ni(0) would be reversible. Indeed, the oxidative addition of silacyclobutanes to palladium complexes is known to be in equilibrium.⁵

⁵ Tanaka, Y.; Yamashita, H.; Shimada, S.; Tanaka, M. *Organometallics* **1997**, *16*, 3246–3248.

Characterization Data

Benzyl (*E*)-3-(dimethylpropylsilyl)acrylate (3a): IR (neat) 2957, 2927, 2869, 1725, 1305, 1250, 1221, 1189, 1161, 997, 840, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.12 (s, 6H), 0.63 (t, J = 8.0 Hz, 2H), 0.97 (t, J = 7.5 Hz, 3H), 1.32–1.40 (m, 2H), 5.21 (s, 2H), 6.30 (d, J = 18.5 Hz, 1H), 7.32 (d, J = 18.5 Hz, 1H), 7.33–7.42 (m, 5H); ^{13}C NMR (CDCl_3) δ –3.60, 17.17, 17.48, 18.10, 66.35, 128.22, 128.30, 128.55, 133.83, 135.98, 149.82, 165.62. Found: C, 68.43; H, 8.29%. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Si}$: C, 68.66; H, 8.45%.

Benzyl (*E*)-3-(diphenylpropylsilyl)acrylate (3a’): IR (neat) 3069, 2956, 2927, 2869, 1725, 1456, 1428, 1304, 1265, 1222, 1187, 1163, 1113, 998, 732, 699 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.01 (t, J = 7.0 Hz, 3H), 1.21 (t, J = 8.5 Hz, 2H), 1.44–1.53 (m, 2H), 5.21 (s, 2H), 6.34 (d, J = 18.5 Hz, 1H), 7.33–7.45 (m, 11H), 7.50–7.52 (m, 4H), 7.64 (d, J = 18.5 Hz, 1H); ^{13}C NMR (CDCl_3) δ 15.32, 17.33, 18.33, 66.55, 128.02, 128.30, 128.42, 128.57, 129.74, 133.67, 135.18, 135.76, 137.01, 145.42, 165.40. Found: C, 77.72; H, 6.92%. Calcd for $\text{C}_{25}\text{H}_{26}\text{O}_2\text{Si}$: C, 77.68; H, 6.78%.

***tert*-Butyl (*E*)-3-(diphenylpropylsilyl)acrylate (3b’):** IR (neat) 2957, 1708, 1428, 1367, 1310, 1238, 1152, 1113, 998, 730, 700, 688 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.01 (t, J = 7.0 Hz, 3H), 1.21 (t, J = 8.5 Hz, 2H), 1.46–1.51 (m, 2H), 1.50 (s, 9H), 6.22 (d, J = 18.5 Hz, 1H), 7.34–7.44 (m, 6H), 7.46 (d, J = 18.5 Hz, 1H), 7.51–7.53 (m, 4H); ^{13}C NMR (CDCl_3) δ 15.46, 17.35, 18.34, 28.09, 80.66, 127.98, 129.64, 134.09, 135.22, 139.32, 142.82, 164.96. Found: C, 75.02; H, 7.96%. Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_2\text{Si}$: C, 74.95; H, 8.01%.

***N,N*-Diethyl-(*E*)-3-(dimethylpropylsilyl)acrylamide [(*E*)-3c]:** IR (neat) 2957, 2932, 2908, 2871, 1638, 1597, 1445, 1426, 1379, 1264, 1249, 1138, 992, 853, 834 cm^{-1} ; ^1H NMR

(CDCl₃) δ 0.12 (s, 6H), 0.63 (t, J = 8.0 Hz, 2H), 0.97 (t, J = 7.0 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H), 1.22 (t, J = 7.0 Hz, 3H), 1.34–1.41 (m, 2H), 3.42 (q, J = 7.0 Hz, 2H), 3.45 (q, J = 7.0 Hz, 2H), 6.65 (d, J = 18.5 Hz, 1H), 7.16 (d, J = 18.5 Hz, 1H); ¹³C NMR (CDCl₃) δ –3.33, 13.10, 14.85, 17.27, 17.77, 18.17, 41.01, 42.16, 133.83, 144.56, 165.56. Found: C, 63.19; H, 11.28%. Calcd for C₁₂H₂₅NOSi: C, 63.38; H, 11.08%.

***N,N*-Diethyl-(*Z*)-3-(dimethylpropylsilyl)acrylamide [(*Z*)-3c]:** IR (neat) 2955, 2933, 2902, 2869, 1642, 1459, 1448, 1431, 1264, 1241, 1143, 841, 831, 810 cm^{–1}; ¹H NMR (CDCl₃) δ 0.15 (s, 6H), 0.70 (t, J = 8.0 Hz, 2H), 0.96 (t, J = 7.5 Hz, 3H), 1.16 (t, J = 7.0 Hz, 3H), 1.18 (t, J = 7.0 Hz, 3H), 1.34–1.39 (m, 2H), 3.36 (q, J = 7.0 Hz, 2H), 3.41 (q, J = 7.0 Hz, 2H), 6.20 (d, J = 14.5 Hz, 1H), 6.90 (d, J = 14.5 Hz, 1H); ¹³C NMR (CDCl₃) δ –2.29, 13.06, 14.39, 17.49, 18.26, 18.66, 40.07, 42.36, 137.42, 143.74, 167.22. Found: C, 63.53; H, 11.32%. Calcd for C₁₂H₂₅NOSi: C, 63.38; H, 11.08%.

Dimethyl[(*E*)-2-phenylethenyl]propylsilane (3d): IR (neat) 2955, 2926, 2868, 1495, 1247, 989, 850, 803, 739, 724, 690 cm^{–1}; ¹H NMR (CDCl₃) δ 0.15 (s, 6H), 0.66 (t, J = 8.0 Hz, 2H), 0.99 (t, J = 7.0 Hz, 3H), 1.38–1.45 (m, 2H), 6.50 (d, J = 19.0 Hz, 1H), 6.89 (d, J = 19.0 Hz, 1H), 7.25–7.28 (m, 1H), 7.32–7.36 (m, 2H), 7.44–7.47 (m, 2H); ¹³C NMR (CDCl₃) δ –3.00, 17.41, 18.25, 18.35, 126.32, 127.87, 128.48, 128.73, 138.41, 143.86. Found: C, 76.34; H, 9.74%. Calcd for C₁₃H₂₀Si: C, 76.39; H, 9.86%.

Dimethyl[(*E*)-2-(2-methylphenyl)ethenyl]propylsilane (3e): IR (neat) 3017, 2955, 2926, 2868, 1599, 1479, 1461, 1247, 1208, 1066, 989, 846, 803, 743, 665 cm^{–1}; ¹H NMR (CDCl₃) δ 0.16 (s, 6H), 0.66 (t, J = 8.0 Hz, 2H), 1.00 (t, J = 7.5 Hz, 3H), 1.38–1.46 (m, 2H), 2.39 (s, 3H), 6.37 (d, J = 19.0 Hz, 1H), 7.13 (d, J = 19.0 Hz, 1H), 7.13–7.21 (m, 3H), 7.52

(dd, $J = 7.0, 2.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ -2.92, 17.44, 18.25, 18.39, 19.57, 125.28, 126.05, 127.63, 130.26, 130.59, 135.19, 137.78, 141.66. Found: C, 77.18; H, 10.37%. Calcd for $\text{C}_{14}\text{H}_{22}\text{Si}$: C, 76.99; H, 10.15%.

Dimethyl[(*E*)-2-(4-methoxyphenyl)ethenyl]propylsilane (3f): IR (neat) 2955, 2927, 2868, 1607, 1510, 1465, 1304, 1295, 1251, 1172, 1038, 986, 843, 794, 739 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.13 (s, 6H), 0.64 (t, $J = 8.5$ Hz, 2H), 0.98 (t, $J = 7.0$ Hz, 3H), 1.36–1.44 (m, 2H), 3.83 (s, 3H), 6.30 (d, $J = 19.0$ Hz, 1H), 6.82 (d, $J = 19.0$ Hz, 1H), 6.87 (d, $J = 9.0$ Hz, 2H), 7.39 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ -2.93, 17.42, 18.25, 18.45, 55.28, 113.87, 125.89, 127.53, 131.47, 143.26, 159.51. Found: C, 71.61; H, 9.41%. Calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}$: C, 71.73; H, 9.46%.

2-[(*E*)-2-(Dimethylpropylsilyl)ethenyl]pyridine (3h): IR (neat) 3003, 2956, 2926, 2868, 1587, 1562, 1463, 1427, 1247, 1066, 994, 843, 808, 753 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.17 (s, 6H), 0.67 (t, $J = 8.0$ Hz, 2H), 0.98 (t, $J = 7.5$ Hz, 3H), 1.38–1.45 (m, 2H), 6.99 (s, 2H), 7.16 (ddd, $J = 7.5, 5.0, 1.5$ Hz, 1H), 7.39 (dt, $J = 7.5, 1.0$ Hz, 1H), 7.66 (td, $J = 7.5, 1.5$ Hz, 1H), 8.59 (dq, $J = 5.0, 1.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ -3.10, 17.38, 18.15, 18.24, 121.30, 122.38, 134.14, 136.48, 143.67, 149.52, 156.04. Found: C, 70.13; H, 9.51%. Calcd for $\text{C}_{12}\text{H}_{19}\text{NSi}$: C, 70.18; H, 9.32%.

Dimethylpropyl[(*E*)-1-tetradecenyl]silane (3i): IR (neat) 2956, 2925, 2855, 1617, 1462, 1247, 989, 837, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.03 (s, 6H), 0.54 (t, $J = 8.0$ Hz, 2H), 0.89 (t, $J = 7.0$ Hz, 3H), 0.96 (t, $J = 7.0$ Hz, 3H), 1.27–1.42 (m, 22H), 2.08–2.13 (m, 2H), 5.60 (dt, $J = 18.5, 1.5$ Hz, 1H), 6.02 (dt, $J = 18.5, 6.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ -2.90, 14.10, 17.41, 18.26, 18.51, 22.68, 28.74, 29.17, 29.35, 29.51, 29.61, 29.66 (Two signals

were overlapped), 29.69, 31.93, 36.82, 128.57, 147.78. Found: C, 76.86; H, 13.80%. Calcd for C₁₉H₄₀Si: C, 76.94; H, 13.59%.

(E)-2,6-Disila-2-phenyl-2,6,6-trimethyl-4-nonene (3j): IR (neat) 2955, 2869, 1605, 1427, 1249, 1142, 1114, 987, 839, 757, 729, 698, 665 cm⁻¹; ¹H NMR (CDCl₃) δ 0.00 (s, 6H), 0.28 (s, 6H), 0.51 (t, *J* = 8.5 Hz, 2H), 0.95 (t, *J* = 8.0 Hz, 3H), 1.28–1.36 (m, 2H), 1.87 (dd, *J* = 7.5, 1.5 Hz, 2H), 5.43 (dt, *J* = 18.5, 1.5 Hz, 1H), 6.00 (dt, *J* = 18.5, 7.5 Hz, 1H), 7.36–7.38 (m, 3H), 7.50–7.52 (m, 2H); ¹³C NMR (CDCl₃) δ –3.50, –2.80, 17.43, 18.29, 18.62, 27.49, 127.67, 128.05, 128.95, 133.63, 138.67, 143.24. Found: C, 69.46; H, 10.48%. Calcd for C₁₆H₂₈Si₂: C, 69.49; H, 10.20%.

[(E)-11-(tert-Butyldimethylsiloxy)-1-undecenyl]dimethylpropylsilane (3k): IR (neat) 2928, 2856, 1248, 1099, 836, 774, 665 cm⁻¹; ¹H NMR (CDCl₃) δ 0.03 (s, 6H), 0.06 (s, 6H), 0.56 (t, *J* = 8.0 Hz, 2H), 0.91 (s, 9H), 0.96 (t, *J* = 7.0 Hz, 3H), 1.29–1.42 (m, 14H), 1.49–1.54 (m, 2H), 2.08–2.13 (m, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 5.60 (dt, *J* = 18.5, 1.5 Hz, 1H), 6.02 (dt, *J* = 18.5, 6.0 Hz, 1H); ¹³C NMR (CDCl₃) δ –5.28, –2.92, 17.38, 18.24, 18.35, 18.48, 25.78, 25.97, 28.70, 29.13, 29.40, 29.41, 29.54, 32.78, 36.79, 63.31, 128.56, 147.72. Found: C, 68.81; H, 12.74%. Calcd for C₂₂H₄₈OSi₂: C, 68.67; H, 12.57%.

(E)-11-Dimethylpropylsilyl-10-undecenyl 2,2-dimethylpropanoate (3l): IR (neat) 2927, 2855, 1732, 1616, 1480, 1462, 1398, 1258, 1247, 1153, 1066, 989, 772 cm⁻¹; ¹H NMR (CDCl₃) δ 0.03 (s, 6H), 0.54 (t, *J* = 8.0 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H), 1.21 (s, 9H), 1.29–1.41 (m, 14H), 1.60–1.65 (m, 2H), 2.08–2.12 (m, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 5.60 (dt, *J* = 18.5, 1.5 Hz, 1H), 6.02 (dt, *J* = 18.5, 6.0 Hz, 1H); ¹³C NMR (CDCl₃) δ –2.90, 17.40, 18.26, 18.50, 25.91, 27.21, 28.62, 28.70, 29.11, 29.20, 29.38, 29.44, 36.79, 38.73,

64.45, 128.63, 147.68, 178.63. Found: C, 71.22; H, 12.13%. Calcd for C₂₁H₄₂O₂Si: C, 71.12; H, 11.94%.

Benzyltrimethyl[(E)-2-phenylethenyl]silane (5d, contaminated with 6d): IR (neat) 3059, 3023, 2956, 1601, 1574, 1493, 1447, 1248, 1206, 1154, 989, 833, 813, 791, 761, 739, 699, 690 cm⁻¹; ¹H NMR (CDCl₃) δ 0.16 (s, 0.89 × 6H, for **5d**), 0.51 (s, 0.11 × 6H, for **6d**), 2.24 (s, 0.89 × 2H, for **5d**), 2.49 (s, 0.11 × 3H, for **6d**), 6.45 (d, *J* = 19.0 Hz, 0.89 × 1H, for **5d**), 6.66 (d, *J* = 19.0 Hz, 0.11 × 1H, for **6d**), 6.87 (d, *J* = 19.0 Hz, 0.89 × 1H, for **5d**), 6.95 (d, *J* = 19.0 Hz, 0.11 × 1H, for **6d**), 7.06 (d, *J* = 7.5 Hz, 0.89 × 2H, for **5d**), 7.11 (t, *J* = 7.5 Hz, 0.89 × 1H, for **5d**), 7.17–7.32 (m, 0.11 × 3H, for **6d**), 7.24 (t, *J* = 7.5 Hz, 0.89 × 2H, for **5d**), 7.28 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.46–7.48 (m, 0.11 × 1H, for **6d**); ¹³C NMR (CDCl₃) For **5d**: δ –3.36, 26.12, 124.01, 126.39, 126.45, 127.36, 128.07, 128.13, 128.27, 128.51, 139.87, 144.69 Found: C, 81.11; H, 8.04%. Calcd for C₁₇H₂₀Si: C, 80.89; H, 7.99%.

A mixture of benzyltrimethyl[(E)-1-tetradecenyl]silane [(E)-5i], benzyltrimethyl[(Z)-1-tetradecenyl]silane [(Z)-5i], and dimethyl(2-methylphenyl) [(E)-1-tetradecenyl]silane (6i): IR (neat) 3024, 2956, 2925, 2854, 1617, 1602, 1494, 1452, 1247, 1206, 831, 817, 795, 698 cm⁻¹; ¹H NMR (CDCl₃) For **(E)-5i**: δ 0.03 (s, 6H), 0.90 (t, *J* = 7.0 Hz, 3H), 1.27–1.42 (m, 20H), 2.08–2.17 (m, 2H), 2.19 (s, 2H), 5.59 (dt, *J* = 19.0, 1.5 Hz, 1H), 6.01 (dt, *J* = 19.0, 6.0 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.5, 1H), 7.21 (t, *J* = 7.5 Hz, 2H), For **(Z)-5i**: δ 0.10 (s, 6H), 0.90 (t, *J* = 7.0 Hz, 3H), 1.27–1.42 (m, 20H), 2.08–2.17 (m, 2H), 2.17 (s, 2H), 5.44 (dt, *J* = 14.0, 1.5 Hz, 1H), 6.35 (dt, *J* = 14.0, 7.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.5, 1H), 7.21 (t, *J* = 7.5 Hz, 2H), For **6i**: δ 0.38 (s, 6H), 0.90 (t, *J* = 7.0 Hz, 3H), 1.27–1.42 (m, 20H), 2.08–2.17 (m, 2H), 2.44 (s,

3H), 5.80 (dt, $J = 19.0, 1.5$ Hz, 1H), 6.10 (dt, $J = 19.0, 6.0$ Hz, 1H), 7.15–7.35 (m, 3H), 7.47–7.56 (m, 1H); ^{13}C NMR (CDCl_3) For (*E*)-**5i**: δ –3.31, 14.08, 22.66, 26.26, 28.63, 29.14, 29.33, 29.49, 29.59, 29.62, 29.66, 29.67, 31.90, 36.78, 123.80, 127.37, 127.98, 128.24, 140.25, 148.77. Found: C, 80.39; H, 11.58%. Calcd for $\text{C}_{23}\text{H}_{40}\text{Si}$: C, 80.15; H, 11.70%.

Benzyltrimethyl[(*E,E*)-4-phenyl-1,3-butadienyl]silane [(*E,E*)-5m**, contaminated with (*E,Z*)-**5m**]:** IR (neat) 3060, 3023, 2955, 1599, 1581, 1493, 1247, 1206, 1000, 857, 832, 818, 799, 748, 728, 699, 691 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.11 (s, $0.83 \times 6\text{H}$, for (*E,E*)-**5m**), 0.23 (s, $0.17 \times 6\text{H}$, for (*E,Z*)-**5m**), 2.19 (s, $0.83 \times 2\text{H}$, for (*E,E*)-**5m**), 2.27 (s, $0.17 \times 2\text{H}$, for (*E,Z*)-**5m**), 5.71 (d, $J = 13.5$ Hz, $0.17 \times 1\text{H}$, for (*E,Z*)-**5m**), 5.97 (d, $J = 18.5$ Hz, $0.83 \times 1\text{H}$, for (*E,E*)-**5m**), 6.54–6.58 (m, $0.17 \times 1\text{H}$, for (*E,Z*)-**5m**), 6.59 (d, $J = 16.0$ Hz, $0.83 \times 1\text{H}$, for (*E,E*)-**5m**), 6.64–6.70 (m, $0.17 \times 1\text{H}$, for (*E,Z*)-**5m**), 6.68 (ddd, $J = 18.5, 10.0, 0.5$ Hz, $0.83 \times 1\text{H}$, for (*E,E*)-**5m**), 6.80 (ddd, $J = 16.0, 10.0, 0.5$ Hz, $0.83 \times 1\text{H}$, for (*E,E*)-**5m**), 6.81–6.86 (m, $0.17 \times 1\text{H}$, for (*E,Z*)-**5m**), 7.02–7.04 (m, 2H), 7.08–7.11 (m, 1H), 7.22–7.25 (m, 2H), 7.25–7.27 (m, 1H), 7.32–7.35 (m, 2H), 7.42–7.43 (m, 2H); ^{13}C NMR (CDCl_3) For (*E,E*)-**5m**: δ –3.36, 26.09, 124.01, 126.57, 127.74, 128.13, 128.26, 128.61, 131.54, 132.63, 133.25, 137.13, 139.88, 145.16. Found: C, 81.93; H, 7.96%. Calcd for $\text{C}_{19}\text{H}_{22}\text{Si}$: C, 81.95; H, 7.96%.

Benzyltrimethyl[(*E,E*)-4-(1-naphthyl)-1,3-butadienyl]silane [(*E,E*)-5n**, contaminated with (*E,Z*)-**5n**]:** IR (neat) 3058, 3023, 2955, 2893, 1599, 1579, 1493, 1451, 1247, 1206, 1154, 1056, 1000, 831, 800, 774, 746, 699 cm^{-1} ; ^1H NMR (CDCl_3): δ 0.14 (s, $0.94 \times 6\text{H}$, for (*E,E*)-**5n**), 0.25 (s, $0.06 \times 6\text{H}$, for (*E,Z*)-**5n**), 2.22 (s, $0.94 \times 2\text{H}$, for (*E,E*)-**5n**), 2.29 (s, $0.06 \times 2\text{H}$, for (*E,Z*)-**5n**), 5.79 (d, $J = 14.0$ Hz, $0.06 \times 1\text{H}$, for (*E,Z*)-**5n**), 6.03 (d, $J = 17.5$ Hz, $0.94 \times 1\text{H}$, for (*E,E*)-**5n**), 6.50–6.62 (m, $0.06 \times 2\text{H}$, for (*E,Z*)-**5n**), 6.82 (dd, $J = 17.5,$

10.0 Hz, $0.94 \times 1\text{H}$, for (*E,E*)-**5n**), 6.87 (dd, $J = 15.0$, 10.0 Hz, $0.94 \times 1\text{H}$, for (*E,E*)-**5n**), 7.06 (d, $J = 7.5$ Hz, 2H), 7.11 (t, $J = 7.5$ Hz, 1H), 7.25 (t, $J = 7.5$ Hz, 2H), 7.38 (d, $J = 15.0$ Hz, 1H), 7.46–7.56 (m, 3H), 7.69 (d, $J = 7.0$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.86–7.88 (m, 1H), 8.17 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (CDCl_3) For (*E,E*)-**5n**: δ -3.35, 26.09, 123.43, 123.58, 124.03, 125.58, 125.78, 126.07, 128.14, 128.27, 128.43, 128.60, 129.98, 131.23, 132.97, 133.74, 134.30, 134.43, 139.87, 145.40. Found: C, 84.23; H, 7.44%. Calcd for $\text{C}_{23}\text{H}_{24}\text{Si}$: C, 84.09; H, 7.36%.

^1H NMR and ^2H NMR Spectra for *deuterio-3f*