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Supporting Information

The Sila-Wittig Rearrangement

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Experimental Details

General Remarks. ^1H (200 MHz) and ^{13}C (50.29 MHz) NMR spectra were recorded on a Varian VXR-200 spectrometer, or ^1H (270 MHz) and ^{13}C (67.94 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer. ^1H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^1H δ 7.200 ppm and ^{13}C δ 128.00 ppm) or $CDCl_3$ (^{13}C δ 77.00 ppm). Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer equipped with a JMA-3500 data processing system. Melting points were measured with a Yanaco-MP-S3 apparatus and were uncorrected. The elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University: Analytical samples were purified by preparative GLC, preparative HPLC, or recycling reverse-phase liquid chromatography. Analytical and preparative GLC were performed on a Shimadzu GC-4B gas chromatography, equipped with a 3-m or 1-m column packed with 30% Silicone DC550 on Celite 545. Recycling reverse-phase liquid chromatography was performed with JAI LC-908 equipped with JAIGEL-ODS S-343-15 and P-15 columns. Reverse-phase column chromatography was performed by using Wakogel LP-40C18 (20–40 μm) (Wako Pure Chemical Industries). Reverse-phase thin layer chromatography was performed on plates of RP-18 F_{254}s (Merck). Column chromatography was performed by using Kieselgel 60 (70–230 mesh) (Merck). Thin layer chromatography was performed on plates of silica gel 60F-254 (Merck).

Trimethylchlorostannane was prepared by disproportionation between tetramethylstannane and dimethyldichlorostannane (Grant, D.; Wazer, J. R. *J. Organomet. Chem.* **1965**, *4*, 229): the last was kindly donated from Nitto Kasei Co.. Diphenyldichlorosilane was kindly donated from Shin-Etsu Chemical Co., Ltd.. Diphenylchlorosilane and silicon tetrachloride were purchased from Shin-Etsu Chemical Co., Ltd.. Trimethylchlorosilane was treated with small pieces of sodium under a nitrogen

atmosphere to remove the dissolved HCl and the supernatant was used. *n*-Butyllithium in hexane, *tert*-butyllithium in pentane, and granular lithium were purchased from Wako Pure Chemical Industries, Kanto Chemical Co., Inc., and Chemetall Gesellshaft, respectively. 4-(Dimethylamino)pyridine (DMAP) was purchased from Nacalai Tesque and used without purification. 12-crown-4 was purchased from Aldrich and dried over Molecular Sieves 3A before use. 2-Methyl-3-buten-2-ol and 1-octen-3-ol were purchased from Tokyo Chemical Industry. Spray-dried KF was purchased from Wako Pure Chemical Industries. THF and Et_2O were distilled under a nitrogen atmosphere from sodium benzophenone ketyl. Dichloromethane, triethylamine, and carbon tetrachloride were distilled from calcium hydride. All reactions were carried out under an argon atmosphere.

Preparation of Alcohols. 3,4-Dimethyl-1-penten-3-ol was obtained by reaction of 3-methyl-2-butanone with vinylmagnesium bromide in THF in 54% yield. 3,4,4-Trimethyl-1-penten-3-ol was obtained by reaction of 3,3-dimethyl-2-butanone with vinylmagnesium bromide in THF in 56% yield. 3-Phenyl-1-buten-3-ol was prepared by reaction of acetophenone with vinylmagnesium bromide in THF in 90% crude yield. This compound was decomposed by distillation, so that it was used in the next step without purification. 1-Vinyl-cyclohexanol was obtained by reaction of cyclohexanone with vinylmagnesium bromide in THF in 86% yield. 1-Propenyl-cyclohexanol was obtained by reaction of cyclohexanone with 1-propenylmagnesium bromide in THF in 25% yield as a 1:1 mixture of *E* and *Z* isomers. 1-(2'-Methyl-1'-propenyl)-cyclohexanol was obtained by reaction of cyclohexanone with 2-methyl-propenylmagnesium bromide in THF in only 14% yield, which was due to the poor separation by column chromatography on silica gel. 1-Methyl-1-(1'-cyclohexenyl)-ethanol was obtained by reaction of methyl 1-cyclohexene-1-carboxylate with methyllithium in Et_2O in 81% yield. 1-Vinyl-2-cyclohexenol was obtained by reaction of 2-cyclohexene-1-one with vinyllithium in Et_2O in 74% yield. 3-Ethyl-1-penten-3-ol was obtained by reaction of 3-pentanone with vinylmagnesium bromide in THF in 54% yield.

(Chlorodiphenylsilyl)trimethylstannane (3). To a solution of [(diethylamino)diphenylsilyl]trimethylstannane[4b] (18.8 g, 45.0 mmol) in dichloromethane (45.0 mL) was added dropwise acetyl chloride (3.50 mL, 49.2 mmol) at 0 °C and the reaction mixture was stirred at 0 °C for 1 h. The solvent was evaporated and the residue was distilled through a short column (123–149

°C/0.38 mmHg) to give **3** (15.5 g, 90% yield) as a colorless oil. ^{1}H NMR (C_6D_6): δ 0.27 (s, 9H, ^{2}J[Sn-H] = 51.3 and 49.1 Hz), 7.16–7.18 (m, 6H), 7.69–7.73 (m, 4H). ^{13}C NMR ($CDCl_3$): δ −10.65, 128.27, 130.23, 134.14, 135.72. MS: m/e 382 (M^+, 0.3), 367 (M^+–Me, 1), 217 ($ClPh_2Si^+$, 3), 199 (100), 165 (Me_3Sn^+, 1). Anal. Calcd for $C_{15}H_{19}SiClSn$: C, 47.22; H, 5.02. Found: C, 46.94; H, 4.92.

Typical Procedure for Preparation of (Allyloxysilyl)stannanes. [(2-Methyl-3-buten-2-oxy)diphenylsilyl]trimethylstannane (1). To a mixture of **3** (1.17 g, 3.07 mmol), triethylamine (0.47 mL, 3.4 mmol), and 4-(dimethylamino)pyridine (75 mg, 0.61 mmol) in Et_2O (9.0 mL) was added a solution of 2-methyl-3-buten-2-ol (**4**) (0.35 mL, 3.4 mmol) in Et_2O (2.0 mL) over 3 min at 0 °C. The reaction mixture was stirred at room temperature for 4 h. The mixture was diluted with hexane (ca. 20 mL) and the salts were filtered with suction. The filtrate was concentrated and the residue was distilled bulb-to-bulb to give **1** (1.16 g, 87% yield). bp: 145–165 °C/0.3 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.32 (s, 9H, ^{2}J[Sn-H] = 47.2 and 45.2 Hz), 1.34 (s, 6H), 4.92 (dd, J = 10.6 and 1.4 Hz, 1H), 5.21 (dd, J = 17.3 and 1.4 Hz, 1H), 5.97 (dd, 17.3 and 10.6 Hz, 1H), 7.23–7.25 (m, 6H), 7.75–7.80 (m, 4H). ^{13}C NMR (C_6D_6): δ −9.69, 30.20, 75.35, 111.98, 128.30, 129.78, 134.69, 139.67, 146.04. MS: *m/e* 432 (M^+, 0.3), 430 (0.2), 417 (M^+–Me, 3), 415 (3), 413 (2), 363 (19), 361 (14), 359 (8), 267 (34), 199 (100). Anal. Calcd for $C_{20}H_{28}OSiSn$: C, 55.70; H, 6.54. Found: C, 55.63; H, 6.54.

[(3,4-Dimethyl-1-penten-3-oxy)diphenyl]trimethylstannane (8a). This compound was obtained by reaction of **3** with 3,4-dimethyl-1-penten-3-ol in 74% yield as a colorless oil after reverse-phase column chromatography with CH_3CN as eluent (R_f = 0.40). ^{1}H NMR (C_6D_6): δ 0.33 (s, 9H, ^{2}J[Sn-H] = 47.5 and 45.4 Hz) 0.95 (d, J = 6.9 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H), 1.79 (septet, J = 6.9 Hz, 1H), 5.01 (dd, J = 10.8 and 1.4 Hz, 1H), 5.13 (dd, J = 17.5 and 1.4 Hz, 1H), 5.88 (dd, J = 17.5 and 10.8 Hz, 1H), 7.18–7.30 (m, 6H), 7.75–7.80 (m, 4H). ^{13}C NMR (C_6D_6): δ −9.48, 17.63, 17.71, 23.69, 39.43, 80.24, 114.31, 128.29, 129.73, 129.80, 134.70, 134.88, 139.72, 139.99, 143.54 (two phenyl groups on silicon are diastereotopic). MS: *m/e* 460 (M^+, 0.1), 445 (M^+–Me, 5), 415 (6), 363 (Me_3Sn-Ph_2Si-O^+, 18), 295 (M^+–Me_3Sn, 42), 199 (100). Anal. Calcd for $C_{22}H_{32}OSiSn$: C, 57.40; H, 7.04. Found: C, 57.53; H, 7.02.

[(3-Phenyl-1-buten-3-oxy)diphenylsilyl]trimethylstannane (8c). This compound was obtained by reaction of **3** with 3-phenyl-1-buten-3-ol in 66% yield as a colorless oil after reverse-phase column chromatography with CH_3CN as eluent (R_f = 0.45). ^1H NMR (C_6D_6): δ 0.25 (s, 9H, ^2J[Sn-H] = 48.1 and 45.6 Hz), 1.65 (s, 3H), 4.98 (dd, J = 10.5 and 1.1 Hz, 1H), 5.26 (dd, J = 17.1 and 1.1 Hz, 1H), 6.10 (dd, J = 17.1 and 10.5 Hz, 1H), 7.10–7.30 (m, 9H), 7.56–7.59 (m, 2H), 7.77–7.82 (m, 4H). ^{13}C NMR (C_6D_6): δ -9.57, 29.24, 79.11, 113.19, 125.84, 127.16, 128.34, 128.45, 129.83, 134.72, 139.45, 139.48, 145.14, 147.14 (two phenyl groups on silicon are diastereotopic). MS: *m/e* 479 (M^+–Me, 7), 363 (Me_3Sn-Ph_2Si-O^+, 38), 329 (M^+–Me_3Sn, 50), 199 (100). Anal. Calcd for $C_{25}H_{30}OSi$: C, 60.87; H, 6.13. Found: C, 60.71; H, 6.12.

[(1-Vinyl-cyclohexanoxy)diphenylsilyl]trimethylstannane (11a). This compound was obtained by reaction of **3** with 1-vinyl-cyclohexanol in 83% yield as a colorless oil after reverse-phase column chromatography with CH_3CN as eluent (R_f = 0.35). ^1H NMR (C_6D_6): δ 0.33 (s, 9H, ^2J[Sn-H] = 47.5 and 45.1 Hz), 1.05–1.24 (m, 1H), 1.33–1.58 (m, 5H), 1.70–1.93 (m, 4H), 4.95 (dd, J = 10.8 and 1.1 Hz, 1H), 5.10 (dd, J = 17.7 and 1.1 Hz, 1H), 6.02 (dd, J = 17.7 and 10.8 Hz, 1H), 7.18–7.32 (m, 6H), 7.77–7.81 (m, 4H). ^{13}C NMR (C_6D_6): δ –9.48, 22.49, 25.92, 38.10, 76.05, 113.93, 128.25, 129.76, 134.81, 139.84, 145.20. MS: *m/e* 472 (M^+, 0.2), 457 (M^+–Me, 5), 363 (Me_3Sn-Ph_2Si-O^+, 25), 307 (M^+–Me_3Sn, 53), 199 (100). Anal. Calcd for $C_{28}H_{32}OSiSn$: C, 58.62; H, 6.84. Found: C, 58.37; H, 6.91.

{[1-Propenyl-cyclohexanoxy]diphenylsilyl}trimethylstannane (11b). This compound was obtained by reaction of **3** with 1-propenyl-cyclohexanol in 74% yield as a 1:1 mixture of *E* and *Z* isomers as a colorless oil after reverse-phase column chromatography with CH_3CN as eluent (R_f = 0.38). The isomeric ratio was determined by ^1H NMR. ^1H NMR (C_6D_6): A mixture of *E* and *Z* isomers; δ 0.34 (s, 9H, ^2J[Sn-H] = 47.3 and 45.1 Hz, one isomer) and 0.37 (s, 9H, ^2J[Sn-H] = 47.3 and 45.1 Hz, another isomer), 1.18–1.95 (m, 13H), 5.37–5.52 (m, 1H), 5.57–5.67 (m, 1H), 7.17–7.32 (m, 6H), 7.77–7.83 (m, 4H). ^{13}C NMR (C_6D_6): A mixture of *E* and *Z* isomers; δ –9.77, 9.28, 15.19, 18.05, 22.63, 23.10, 25.70, 26.10, 38.59, 40.37, 75.53, 76.90, 124.82, 127.84, 128.22 (2C), 129.67, 134.86, 134.94, 135.01, 136.36, 138.89, 139.91, 140.06. MS: *m/e* 486 (M^+, 0.2), 471 (M^+–Me, 25), 363 (Me_3Sn-Ph_2Si-O^+, 109), 321 (M^+–Me_3Sn, 88), 200 (100). Anal. Calcd for $C_{24}H_{34}OSiSn$: C, 59.40; H, 7.06. Found: C, 59.05; H, 7.05.

{[1-(2'-Methyl-1'-propenyl)-cyclohexanoxy]diphenylsilyl}trimethylstannane (11c). This compound was obtained by reaction of **3** with 1-(2'-methyl-1'-propenyl)-cyclohexanol in 74% yield as a colorless oil after reverse-phase column chromatography with CH_3CN as eluent (R_f = 0.28). ^1H NMR (C_6D_6): δ 0.36 (s, 9H, ^2J[Sn-H] = 46.7 and 45.1 Hz), 1.22–1.45 (m, 4H), 1.59 (d, J = 1.4 Hz, 3H), 1.64 (d, J = 0.8 Hz, 3H), 1.64–1.78 (m, 2H), 1.80–1.98 (m, 4H), 5.40–5.47 (m, 1H), 7.18–7.33 (m, 6H), 7.77–7.82 (m, 4H). ^{13}C NMR (C6D6): δ –9.54, 19.83, 23.26, 25.77, 27.45, 40.71, 76.27, 128.14, 129.60, 131.13, 135.04, 136.36, 139.93. MS: *m/e* 485 (M^+–Me, 6), 363 (Me_3Sn-Ph_2Si-O^+, 59), 335 (M^+–Me_3Sn, 67), 199 (100). Anal. Calcd for $C_{25}H_{36}OSiSn$: C, 60.13; H, 7.27. Found: C, 60.03; H, 7.29.

{[1-methyl-1-(1'-cyclohexenyl)-ethoxy]diphenylsilyl}trimethylstannane (13). This compound was obtained by reaction of **3** with 1-methyl-1-(1'-cyclohexenyl)-ethanol in 87% yield as a colorless oil after reverse-phase column chromatography with CH_3CN as eluent (R_f = 0.30). ^1H NMR (C_6D_6): δ 0.35 (s, 9H, ^2J[Sn-H] = 47.3 and 44.8 Hz), 1.43 (s, 6H), 1.46–1.58 (m, 4H), 1.87–2.02 (m, 2H), 2.03–2.08 (m, 2H), 5.78–5.84 (m, 1H), 7.17–7.33 (m, 6H), 7.78–7.81 (m, 4H). ^{13}C NMR (C_6D_6): δ –9.77, 22.59, 23.26, 24.77, 25.34, 29.91, 77.44, 119.72, 128.27, 129.73, 134.79, 139.77, 143.44. MS: *m/e* 471 (M^+–Me, 0.6), 363 (Me_3Sn-Ph_2Si-O^+, 10), 321 (M^+-Me_3Sn, 14), 199 (100). Anal. Calcd for $C_{24}H_{34}OSiSn$: C, 59.40; H, 7.06. Found: C, 59.04; H, 7.06.

[(1-Vinyl-2-cyclohexenoxy)diphenylsilyl]trimethylstannane (15). This compound was obtained by reaction of **3** with 1-vinyl-2-cyclohexenol in 70% yield as a colorless oil after reverse-phase column chromatography with CH_3CN as eluent (R_f = 0.40). ^1H NMR (C_6D_6): δ 0.34 (s, 9H, ^2J[Sn-H] = 47.5 and 45.4 Hz), 1.34–1.50 (m, 1H), 1.52–1.85 (m, 4H), 1.94–2.06 (m, 1H), 5.03 (dd, J = 10.5 and 1.4 Hz, 1H), 5.25 (dd, J = 17.3 and 1.4 Hz, 1H), 5.67 (dt, J = 10.0 and 3.5 Hz, 1H), 5.80 (d, J = 10.0 Hz, 1H), 6.07 (dd, J = 17.3 and 10.5 Hz, 1H), 7.18–7.32 (m, 6H), 7.76–7.85 (m, 4H). ^{13}C NMR (C_6D_6): δ –9.49, 19.10, 24.96, 37.29, 75.35, 113.64, 127.73, 127.78, 129.22, 129.27, 130.80, 131.02, 134.30, 139.30, 139.35, 144.26 (two phenyl groups on silicon are diastereotopic). MS: m/e 470 (M^+, 0.1), 455 (M^+–Me, 23), 359 (100), 333 (53), 289 (34), 255 (33), 200 (99), 197 (94). Anal. Calcd for $C_{23}H_{30}OSiSn$: C, 58.87; H, 6.44. Found: C, 58.80; H, 6.49.

[(3,4,4-Trimethyl-1-penten-3-oxy)diphenylsilyl]trimethylstannane (8b). (1) (3,4,4-Trimethyl-1-penten-3-oxy)diphenylchlorosilane was prepared from diphenyldichlorosilane (2.10 mL,

10.1 mmol) and 3,4,4-trimethyl-1-penten-3-ol (1.41g, 11.0 mmol) in the presence of triethylamine (1.80 mL, 12.9 mmol) and 4-(dimethylamino)pyridine (245 mg, 2.00 mmol) in THF (12.0 mL) by refluxing for 44 h in 60% yield.[4c] bp: 166–183 °C/0.60 mmHg (bath temperature). **(3,4,4-Trimethyl-1-penten-3-oxy)diphenylchlorosilane:** ^{1}H NMR (C_6D_6): δ 1.02 (s, 9H), 1.38 (s, 3H), 4.97 (dd, J = 17.3 and 1.4 Hz, 1H), 5.10 (dd, J = 10.8 and 1.4 Hz, 1H), 6.03 (dd, J = 17.3 and 10.8 Hz, 1H), 7.16–7.23 (m, 6H), 7.82–7.96 (m, 4H). (2) (Trimethylstannyl)lithium was prepared from Me_3SnCl (463 mg, 2.33 mmol) with granular lithium (74 mg, 11 mg-atom) in THF (3.0 mL) by the literature method (Ritter, K. *Synthesis* **1989**, 218). The resulting green solution was used in the next step without titration after removal of the unreacted lithium. (3) To a solution of (3,4,4-trimethyl-1-penten-3-oxy)diphenylchlorosilane (681 mg, 1.97 mmol) in THF (1.5 mL) was added over 3 min the solution of (trimethylstannyl)lithium in THF at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 3 h. The reaction mixture was diluted with hexane (ca. 10 mL) and filtered. The filtrate was concentrated and the residue was subjected to reverse-phase column chromatography (Wakogel LP-40C18, 50 mL) with CH_3CN as eluent to give **8b** (541 mg, 58% yield) (R_f = 0.40) as a colorless oil. **8b:** ^{1}H NMR (C_6D_6): δ 0.33 (s, 9H, ^{2}J[Sn-H] = 47.5 and 45.4 Hz), 1.02 (s, 9H), 1.26 (s, 3H), 5.01 (dd, J = 11.1 and 1.4 Hz, 1H), 5.05 (dd, J = 17.4 and 1.4 Hz, 1H), 6.02 (dd, J = 17.4 and 11.1 Hz, 1H), 7.18–7.30 (m, 6H), 7.75–7.80 (m, 4H). ^{13}C NMR (C_6D_6): δ −9.32, 22.14, 25.68, 38.69, 82.07, 114.88, 128.25, 128.29, 129.69, 129.83, 134.72, 135.08, 139.64, 140.06, 143.11 (two phenyl groups on silicon are diastereotopic). MS: *m/e* 474 (M^+, 0.8), 459 (M^+–Me, 30), 417 (M^+–*t*-Bu, 4), 363 (Me_3Sn-Ph_2Si-O^+, 44), 309 (M^+–Me_3Sn, 69), 267 (93), 199 (100). Anal. Calcd for $C_{23}H_{34}OSiSn$: C, 58.36; H, 7.24. Found: C, 58.28; H, 7.34.

Reaction of 1 with *n*-Butyllithium: Synthesis of [(2-Methyl-3-buten-2-oxy)diphenylsilyl]lithium (2) and Trapping as 1-(2'-Methyl-3'-buten-2'-oxy)-1,1-diphenyl-2,2,2-trimethyldisilane (6). To a solution of **1** (227 mg, 0.526 mmol) in THF (2.0 mL) was added dropwise over 1 min *n*-butyllithium in hexane (1.64 M, 0.64 mL, 1.1 mmol) at −78 °C and the reaction mixture was stirred for 3 h to give a yellow solution of **2**. To the solution was added Me_3SiCl (0.15 mL, 1.2 mmol) at −78 °C. After being stirred for 30 min, the reaction mixture was warmed to ambient temperature. The mixture was evaporated, diluted with hexane (ca. 20 mL), and filtered. The filtrate was concentrated and the residue was subjected to column chromatography on silica

gel (20 mL) eluted with hexane/AcOEt (30/1) to give a mixture (148 mg) (R_f = ca. 0.55) of **5** (21% yield), **6** (51% yield), and 1,2-di(2'-methyl-3'-buten-2'-oxy)-1,1,2,2-tetraphenyldisilane (13% yield). The yields were estimated by ^{1}H NMR. **6:** The authentic sample was obtained by reaction of 1-chloro-1,1-diphenyl-2,2,2-trimethyldisilane with 2-methyl-3-buten-2-ol in the presence of triethylamine and 4-(dimethylamino)pyridine in a similar way for **1** and purified by column chromatography on silica gel eluted with hexane/AcOEt (60/1) (47% yield) (R_f = 0.28). ^{1}H NMR (C_6D_6): δ 0.27 (s, 9H), 1.31 (s, 6H), 4.91 (dd, J = 10.6 and 1.6 Hz, 1H), 5.25 (dd, J = 17.2 and 1.6 Hz, 1H), 5.98 (dd, 17.2 and 10.6 Hz, 1H), 7.23–7.27 (m, 6H), 7.77–7.82 (m, 4H). ^{13}C NMR ($CDCl_3$): δ −1.20, 30.26, 74.75, 110.98, 127.60, 129.09, 134.91, 138.65, 146.51. MS: *m/e* 340 (M^+, 0.2), 325 (M^+–Me, 3), 272 (66), 271 (76), 267 (25), 255 (25), 199 (67), 193 (100). Anal. Calcd for $C_{20}H_{28}OSi_2$: C, 70.53; H, 8.29. Found: C, 70.43; H, 8.28. **1,2-Di(2'-methyl-3'-buten-2'-oxy)-1,1,2,2-tetraphenyldisilane:** The pure sample was obtained as colorless crystals by recrystallization from hexane. mp: 166–167 °C. ^{1}H NMR (C_6D_6): δ 1.35 (s, 12H), 4.88 (dd, J = 10.7 and 1.6 Hz, 2H), 5.19 (dd, J = 17.3 and 1.6 Hz, 2H), 6.03 (dd, 17.3 and 10.7 Hz, 2H), 7.19–7.20 (m, 12H), 7.88–7.92 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 30.08, 75.92, 110.80, 127.28, 129.16, 135.89, 137.38, 146.38. MS: *m/e* 534 (M^+, 0.1), 519 (M^+–Me, 1), 465 (0.3), 397 (100), 319 (99), 267 (52), 199 (99). Anal. Calcd for $C_{34}H_{38}O_2Si_2$: C, 76.35; H, 7.16. Found: C, 76.48; H, 7.00.

Typical Procedure for Reaction of (Allyloxysilyl)stannane with *n*-Butyllithium and Subsequent Rearrangement: Synthesis of 1-(3'-Methyl-2'-butenyl)-1,1-diphenyl-3,3,3-trimethyldisiloxane (5). To a solution of **1** (216 mg, 0.501 mmol) in THF (1.0 mL) was added dropwise over 1 min *n*-butyllithium in hexane (1.76 M, 0.57 mL, 1.0 mmol) at –78 °C. The reaction mixture was stirred for 3 h, warmed to room temperature, and stirred for 2 h. To the reaction mixture was added Me_3SiCl (0.14 mL, 1.1 mmol). After being stirred for 30 min, the reaction mixture was evaporated and the residue was diluted with hexane (ca. 10 mL) and filtered. The filtrate was concentrated and the residue was subjected to column chromatography on silica gel (20 mL) eluted with hexane to give **5** (116 mg, 68% yield) (R_f = 0.28) as a colorless oil. ^{1}H NMR (C_6D_6): δ 0.18 (s, 9H), 1.48 (s, 3H), 1.67 (d, J = 1.0 Hz, 3H), 2.13 (d, J = 8.2 Hz, 2H), 5.40–5.51 (m, 1H), 7.23–7.27 (m, 6H), 7.71–7.75 (m, 4H). ^{13}C NMR (C_6D_6): δ 2.03, 17.76, 18.30, 25.90, 118.58, 130.54, 128.00,

129.85, 134.63, 137.35. MS: *m/e* 340 (M^+, 4), 325 (M^+–Me, 2), 271 (100), 255 (9), 193 (39). Anal. Calcd for $C_{20}H_{28}OSi_2$: C, 70.53; H, 8.29. Found: C, 70.28; H, 8.26.

Reaction of 1 with *n*-Butyllithium and Subsequent Rearrangement in the Presence of 12-Crown-4. To a solution of **1** (216 mg, 0.501 mmol) in THF (2.0 mL) was added dropwise over 1 min *n*-butyllithium in hexane (1.68 M, 0.60 mL, 1.0 mmol) at –78 °C and the reaction mixture was stirred for 3 h. To the resulting yellow solution was added 12-crown-4 (0.16 mL, 1.0 mmol) at –78 °C and the reaction mixture was stirred for another 1 h. To the reaction mixture was added Me_3SiCl (0.14 mL, 1.1 mmol). After being stirred for 10 min, the reaction mixture was warmed to room temperature. Water (10 mL) was added to the reaction mixture, which was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over $MgSO_4$. The solution was concentrated and the residue was subjected to bulb-to-bulb distillation (110–130 °C/0.90 mmHg, bath temperature) and column chromatography on silica gel (20 mL) eluted with hexane to give **5** (94 mg, 55% yield) (R_f = 0.28).

1-(3',4'-Dimethyl-2'-pentenyl)-1,1-diphenyl-3,3,3-trimethyldisiloxane (9a and 10a). This compound was obtained in 83% yield as a mixture of **9a** (*E*) and **10a** (*Z*) (**9a/10a** = 62/38) as a colorless oil after column chromatography on silica gel eluted with hexane (R_f = 0.33). The isomeric ratio was determined by ^1H NMR and the stereochemistry was determined by NOE experiments. The mixture was separated into **9a** and **10a** by means of recycling reverse-phase liquid chromatography with CH_3CN as eluent. ^1H NMR (C_6D_6): **9a**; δ 0.19 (s, 9H), 1.00 (d, J = 6.8 Hz, 6H), 1.43 (d, J = 0.8 Hz, 3H), 2.13 (d, J = 8.1 Hz, 2H), 2.24 (septet, J = 6.8 Hz, 1H), 5.50 (tq, J = 8.1 and 0.8 Hz, 1H), 7.20–7.30 (m, 6H), 7.68–7.75 (m, 4H). **10a**; δ 0.18 (s, 9H), 0.87 (d, J = 6.8 Hz, 6H), 1.60 (d, J = 1.1 Hz, 3H), 2.17 (dd, J = 8.0 and 1.0 (*homoallylic*) Hz, 2H), 2.79 (septet, J = 6.8 Hz, 1H), 5.39 (tq, J = 8.0 and 1.1 Hz, 1H), 7.20–7.32 (m, 6H), 7.70–7.95 (m, 4H). ^{13}C NMR ($CDCl_3$): **9a**; δ 2.00, 13.16, 17.68, 21.40, 37.04, 115.60, 127.55, 129.43, 134.25, 137.11, 140.09. **10a**; δ 2.02, 17.04, 18.10, 20.38, 28.14, 116.89, 127.58, 129.47, 134.29, 137.05, 139.68. MS: *m/e* 368 (M^+, 3), 353 (M^+–Me, 4), 273 (100), 198 (98). Anal. Calcd for $C_{22}H_{32}OSi_2$: C, 71.67; H, 8.75. Found: C, 71.58; H, 8.78.

1-(3',4',4'-Timethyl-2'-pentenyl)-1,1-diphenyl-3,3,3-trimethyldisiloxane (9b and 10b). This compound was obtained in 73% yield as a mixture of **9b** (*E*) and **10b** (*Z*) (**9b/10b** = 89/11) as a colorless oil after column chromatography on silica gel eluted with hexane (R_f = 0.41) and

HPLC eluted with hexane/AcOEt (100/1). The isomeric ratio was determined by ^{1}H NMR and the stereochemistry was determined by NOE experiments. The mixture was separated into **9b** and **10b** by means of recycling reverse-phase liquid chromatography with CH_3CN as eluent. ^{1}H NMR (C_6D_6): **9b**; δ 0.19 (s, 9H), 1.07 (s, 9H), 1.48 (d, J = 1.4 Hz, 3H), 2.14 (dd, J = 8.4 and 0.5 (*homoallylic*) Hz, 2H), 5.57 (tq, J = 8.4 and 1.4 Hz, 1H), 7.20–7.28 (m, 6H), 7.69–7.77 (m, 4H). **10b**; δ 0.19 (s, 9H), 1.15 (s, 9H), 1.73 (d, J = 1.4 Hz, 3H), 2.40 (dd, J = 8.5 and 0.9 (*homoallylic*) Hz, 2H), 5.52 (tq, J = 8.5 and 1.4 Hz, 1H), 7.20–7.34 (m, 6H), 7.75–7.80 (m, 4H). ^{13}C NMR ($CDCl_3$): **9b**; δ 2.03, 12.72, 18.17, 29.06, 36.26, 114.57, 127.55, 129.43, 134.27, 137.11, 142.12. **10b**; δ 2.02, 19.63, 24.14, 30.28, 35.37, 118.87, 127.58, 129.47, 134.30, 136.95, 141.67. MS: *m/e* 382 (M^+, 3), 272 (100), 255 (50), 241 (24), 193 (77). Anal. Calcd for $C_{23}H_{34}OSi_2$: C, 72.19; H, 8.96. Found: C, 72.26; H, 9.08.

1-(3'-Phenyl-2'-butenyl)-1,1-diphenyl-3,3,3-trimethyldisiloxane (9c and 10c). This compound was obtained in 77% yield as a mixture of **9c** (*E*) and **10c** (*Z*) (**9c/10c** = 29/71) as a colorless oil after column chromatography on silica gel eluted with hexane (R_f = 0.10–0.15) and reverse-phase column chromatography eluted with CH_3CN (R_f = 0.48). The isomeric ratio was determined by ^{1}H NMR and the stereochemistry was determined by NOE experiments. The mixture was separated into **9c** and **10c** by means of recycling reverse-phase liquid chromatography with CH_3CN as eluent. ^{1}H NMR (C_6D_6): **9c**; δ 0.16 (s, 9H), 1.83 (d, J = 1.4 Hz, 3H), 2.30 (d, J = 8.5 Hz, 2H), 6.12 (tq, J = 8.5 and 1.4 Hz, 1H), 7.05–7.13 (m, 1H), 7.15–7.28 (m, 8H), 7.33–7.40 (m, 2H), 7.68–7.77 (m, 4H). **10c**; δ 0.15 (s, 9H), 1.99 (d, J = 1.4 Hz, 3H), 2.26 (dq, J = 8.1 and 1.4 (*homoallylic*) Hz, 2H), 5.76 (tq, J = 8.1 and 1.4 Hz, 1H), 7.06–7.26 (m, 11H), 7.61–7.69 (m, 4H). ^{13}C NMR ($CDCl_3$): **9c**; δ 2.02, 15.78, 19.73, 122.66, 125.46, 126.07, 127.71, 128.07, 129.65, 133.89, 134.23, 136.66, 144.40. **10c**; δ 1.98, 18.67, 25.72, 121.11, 126.81, 127.64, 127.98, 128.12, 129.52, 134.25, 135.65, 136.73, 142.01. MS: *m/e* 402 (M^+, 5), 387 (M^+–Me, 10), 271 (Me_3Si-O-Ph_2Si^+, 100), 193 (46). Anal. Calcd for $C_{25}H_{30}OSi_2$: C, 74.57; H, 7.51. Found: C, 74.33; H, 7.46.

1-(2'-Cyclohexylidene-ethyl)-1,1-diphenyl-3,3,3-trimethyldisiloxane (12a). This compound was obtained in 80% yield as a colorless oil after column chromatography on silica gel eluted with hexane (R_f = 0.35). ^{1}H NMR (C_6D_6): δ 0.19 (s, 9H), 1.22–1.38 (m, 2H), 1.39–1.54 (m, 4H), 1.98–2.13 (m, 4H), 2.16 (d, J = 8.2 Hz, 2H), 5.42 (t, J = 8.2 Hz, 1H), 7.22–7.28 (m, 6H), 7.70–

7.77 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 2.00, 16.95, 26.88, 27.10, 28.39, 28.43, 37.31, 114.65, 127.57, 129.43, 134.29, 137.00, 138.56. MS: *m/e* 380 (M^+, 3), 365 (M^+–Me, 1), 271 (Me_3Si-O-Ph_2Si^+, 100), 193 (81). Anal. Calcd for $C_{23}H_{32}OSi_2$: C, 72.57; H, 8.47. Found: C, 72.44; H, 8.45.

1-(1'-Methyl-2'-cyclohexylidene-ethyl)-1,1-diphenyl-3,3,3-trimethyldisiloxane (12b). This compound was obtained in 77% yield as a colorless oil after column chromatography on silica gel eluted with hexane (R_f = 0.30). ^1H NMR (C_6D_6): δ 0.21 (s, 9H), 1.16–1.59 (m, 6H), 1.32 (d, J = 7.3 Hz, 3H), 1.92–2.05 (m, 1H), 2.07–2.23 (m, 3H), 2.56 (dq, J = 10.8 and 7.3 Hz, 1H), 5.30 (d, J = 10.8 Hz, 1H), 7.22–7.35 (m, 6H), 7.76–7.81 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 2.09, 15.76, 20.97, 26.88, 27.26, 28.41, 28.88, 37.43, 122.98, 127.37, 127.49, 129.54, 129.29, 134.52, 134.70, 136.35, 137.30 (two phenyl groups on silicon are diastereotopic). MS: *m/e* 394 (M^+, 0.9), 379 (M^+–Me, 4), 297 (16), 273 (100), 193 (95). Anal. Calcd for $C_{24}H_{34}OSi_2$: C, 73.03; H, 8.68. Found: C, 72.88; H, 8.77.

1-(1',1'-Dimethyl-2'-cyclohexylidene-ethyl)-1,1-diphenyl-3,3,3-trimethyldisiloxane (12c). This compound was obtained in 84% yield as a colorless oil after column chromatography on silica gel eluted with hexane (R_f = 0.48). ^1H NMR (C_6D_6): δ 0.21 (s, 9H), 1.31–1.63 (m, 6H), 1.45 (s, 6H), 2.12–2.19 (m, 4H), 5.43 (s, 1H), 7.22–7.38 (m, 6H), 7.86–7.94 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 2.14, 25.88, 26.70, 26.78, 27.69, 28.92, 29.83, 39.59, 127.33, 128.73, 129.22, 135.15, 136.06, 138.62. MS: *m/e* 408 (M^+, 0.3), 393 (M^+–Me, 0.3), 311 (43), 273 (100), 193 (94). Anal. Calcd for $C_{25}H_{36}OSi_2$: C, 73.47; H, 8.88. Found: C, 73.30; H, 8.84.

1-(2'-Isopropylidene-cyclohexyl)-1,1-diphenyl-3,3,3-trimethyldisiloxane (14). This compound was obtained in 79% yield as a colorless oil after column chromatography on silica gel eluted with hexane (R_f = 0.35). ^1H NMR (C_6D_6): δ 0.19 (s, 9H), 1.28–1.42 (m, 1H), 1.44 (s, 3H), 1.55–1.68 (m, 1H), 1.72 (s, 3H), 1.75–1.92 (m, 3H), 2.05–2.30 (m, 2H), 2.74–2.86 (m, 1H), 2.97–3.05 (m, 1H), 7.20–7.39 (m, 6H), 7.65–7.74 (m, 2H), 7.79–7.89 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 2.14, 20.07, 20.45, 24.10, 27.51, 27.96, 28.68, 29.80, 120.34, 127.17, 127.66, 129.15, 129.29, 131.36, 134.48, 134.57, 137.05, 137.36 (two phenyl groups on silicon are diastereotopic). MS: *m/e* 394 (M^+, 3), 379 (M^+–Me, 1), 271 (Me_3Si-O-Ph_2Si^+, 100), 93(35). Anal. Calcd for $C_{24}H_{34}OSi_2$: C, 73.03; H, 8.68. Found: C, 72.69; H, 8.82.

1-[2-(2'-Cyclohexene)-ethyl]-1,1-diphenyl-3,3,3-trimethyldisiloxane (16). This compound was obtained in 65% yield as a mixture of *E* and *Z* isomers (*E*/*Z* = 35/65) as a colorless oil after column chromatography on silica gel eluted with hexane (R_f = 0.28). The isomeric ratio was determined by ^{1}H NMR and the stereochemistry was determined by ^{1}H-^{1}H COSY and NOE experiments. ^{1}H NMR (C_6D_6): δ 0.18 (s, 9H, *E*), 0.20 (s, 9H, *Z*), 1.46–1.56 (m, 2H, *E*), 1.56–1.66 (m, 2H, *Z*), 1.95–2.03 (m, 2H, *E* and *Z*), 2.13–2.21 (m, 4H, *E*) 2.22–2.30 (m, 4H, *Z*), 5.39 (t, J = 8.2 Hz, 1H, *Z*), 5.54–5.65 (m, 2H, *E*), 5.72 (ddt, J = 10.0, 4.1, and 2.0 Hz, 1H, *Z*), 6.17 (dt, J = 8.1 and 1.9 Hz, 1H, *E*), 6.49 (ddt, J = 10.0, 1.9, and 1.1 Hz, 1H, *Z*), 7.24–7.27 (m, 6H, *E* and *Z*), 7.70–7.75 (m, 4H, *E* and *Z*). ^{13}C NMR ($CDCl_3$) (Two isomers are named arbitrary A and B): δ 1.98 (A and B), 17.13 (A), 18.13 (B), 22.27 (B), 23.25 (A), 25.20 (A or B), 25.54 (A or B), 26.22 (A or B), 32.58 (A or B), 119.07 (A), 121.22 (B), 124.53 (A), 125.80 (B), 127.66 (A and B), 128.75 (B), 129.49 (A and B), 129.56 (A), 131.30 (A or B), 132.83 (A or B), 134.21 (A and B), 136.82 (B), 136.95 (A). MS: *m/e* 378 (M^+, 3), 345 (16), 271 (Me_3Si-O-Ph_2Si^+, 83), 193 (56), 144 (100). Anal. Calcd for $C_{23}H_{30}OSi_2$: C, 72.96; H, 7.99. Found: C, 72.89; H, 8.03.

(1-Octen-3-oxy)diphenylchlorosilane (17). (1) To a mixture of diphenylchlorosilane (4.40 mL, 25.0 mmol) and triethylamine (3.80 mL, 27.0 mmol) in hexane (100 mL) was added dropwise a solution of 1-octen-3-ol (4.20 mL, 27.0 mmol) in hexane (6.0 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h. The salts were filtered with suction. The filtrate was concentrated and the residue was distilled to give (1-octen-3-oxy)diphenylsilane (6.22 g, 80% yield) as a colorless oil. **(1-Octen-3-oxy)diphenylsilane:** bp: 146–147 °C/0.80 mmHg. ^{1}H NMR (C_6D_6): δ 0.88 (t, J = 6.8 Hz, 3H), 1.13–1.29 (m, 4H), 1.30–1.48 (m, 2H), 1.49–1.64 (m, 1H), 1.65–1.78 (m, 1H), 4.33 (dt, J = 6.8 and 6.2 Hz, 1H), 5.03 (ddd, J = 10.4, 1.4, and 1.4 Hz, 1H), 5.23 (ddd, J = 17.0, 1.4, and 1.4 Hz, 1H), 5.82 (s, 1H), 5.86 (ddd, J = 17.0, 10.4, and 6.2 Hz, 1H), 7.18–7.28 (m, 6H), 7.75–7.78 (m, 4H). (2) To a suspension of palladium chloride (128 mg, 0.724 mmol) in carbon tetrachloride (5.0 mL) was added over 13 min a solution of (1-octen-3-oxy)diphenylsilane (4.26 g, 13.7 mmol) in carbon tetrachloride (6.0 mL) at room temperature and the reaction mixture was stirred for 1 h. The reaction mixture was filtered and the filtrate was concentrated. The residue was distilled through short column to give **17** (3.03 g, 64% yield) as a colorless oil. **17:** bp: 124–139 °C/0.25 mmHg. ^{1}H NMR (C_6D_6): δ 0.87 (t, J = 6.8 Hz, 3H), 1.12–1.28 (m, 4H), 1.28–1.42 (m, 2H), 1.53–1.80 (m, 2H), 4.57

(ddd, J = 6.1, 1.5, and 1.5 Hz, 1H), 4.99 (ddd, J = 10.3, 1.5 and 1.5 Hz, 1H), 5.19 (ddd, J = 17.0, 1.5, and 1.5 Hz, 1H), 5.84 (ddd, J = 17.0, 10.3, and 6.1 Hz, 1H), 7.17–7.22 (m, 6H), 7.86–7.90 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 14.00, 22.52, 24.49, 31.61, 37.20, 75.65, 115.08, 127.91, 127.96, 130.89, 132.79, 132.99, 134.47, 134.57, 139.64 (two phenyl groups on silicon are diastereotopic). MS: *m/e* 344 (M^+, 9), 317 (7), 273 (82), 217 ($ClPh_2Si^+$, 100). Anal. Calcd for $C_{20}H_{25}OSiCl$: C, 69.64; H, 7.30. Found: C, 69.25; H, 7.59.

Reaction of 17 with Lithium Naphthalenide and Subsequent Rearrangement: Synthesis of 1-(2'-Octenyl)-1,1-diphenyl-3,3,3-trimethyldisiloxane (18). To a THF solution of lithium naphthalenide, prepared from naphthalene (442 mg, 3.45 mmol) and granular lithium (24 mg, 3.5 mmol) in THF (7.0 mL), was added over 1 min a solution of **17** (409 mg, 1.19 mmol) in THF (1.2 mL) at –45 °C.[4d] The reaction mixture was stirred at –45 °C for 1 h and at 0 °C for 1 h. To the reaction mixture was added Me_3SiCl (0.45 mL, 3.6 mmol) at 0 °C. After being stirred at room temperature for 15 min, the reaction mixture was diluted with hexane (ca. 15 mL) and filtered. The filtrate was evaporated and the residue was subjected to sublimination at 50 °C in vacuo to remove the regenerated naphthalene. The obtained residue was sebjected to column chromatography on silica gel (30 mL) eluted with hexane to give **18** (171 mg, 38% yield) (R_f = 0.28) as a 1:1 mixture of *E* and *Z* isomers as a colorless oil. The isomeric ratio was determined by ^1H NMR. Two isomers are named arbitrary A and B for the spectral assignment. ^1H NMR (C_6D_6): δ 0.18 (s, 9H, A), 0.20 (s, 9H, B), 0.91 (t, J = 6.8 Hz, 3H, A and B), 1.17–1.40 (m, 6H, A and B), 1.95–2.06 (m, 2H, A and B), 2.16 (dd, J = 7.6 and 1.1 Hz, 2H, B), 2.22 (d, J = 8.1 Hz, 2H, A), 5.37–5.78 (m, 2H, A and B), 7.23–7.28 (m, 6H, A and B), 7.71–7.76 (m, 4H, A and B). ^{13}C NMR ($CDCl_3$): δ 2.02 (A and B), 14.04 (A or B), 14.07 (A or B), 21.80 (A or B), 22.54 (A or B), 27.14 (A or B), 29.18 (A or B), 29.38 (A or B), 31.27 (A or B), 31.61 (A or B), 32.78 (A or B), 123.09 (A or B), 123.88 (A or B), 127.60 (A and B), 129.45 (A or B), 129.52 (A or B), 129.61 (A or B), 131.11 (A or B), 134.23 (A and B), 136.80 (A or B), 136.93 (A or B). MS: *m/e* 382 (M^+, 3), 367 (2), 271 (Me_3Si-O-Ph_2Si^+, 100), 193 (30). Anal. Calcd for $C_{23}H_{34}OSi_2$: C, 72.19; H, 8.95. Found: C, 72.31; H, 9.22.

{*N*-Trimethylsilyl-*N*-(2-propenyl)-amino]diphenylsilyl}trimethylstannane (19). (1) To a solution of allylamine (2.30 mL, 30.7 mmol) in Et_2O (10.0 mL) was added over 10 min a solution of **3** (3.79 g, 9.93 mmol) in Et_2O (6.0 mL) at 0 °C and the reaction mixture was stirred for 1 h.

Then the solvent was evaporated and the residue was diluted with hexane (ca. 30 mL) and filtered. The filtrate was concentrated and the residue was distilled bulb-to-bulb to give [(2-propenyl-amino)diphenylsilyl]trimethylstannane (3.36 g, 84% yield) as a colorless oil. **{[*N*-(2-propenyl)-amino]diphenylsilyl}trimethylstannane:** bp: 145–160 °C/0.70 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.30 (s, 9H, ^{2}J[Sn-H] = 47.5 and 45.4 Hz), 3.41 (ddd, J = 5.1, 1.6, and 1.6 Hz, 2H), 4.99 (ddt, J = 10.3, 1.6, and 1.6 Hz, 1H), 5.17 (ddt, J = 17.3, 1.6, and 1.6 Hz, 1H), 5.84 (ddt, J = 17.3, 10.3, and 5.1 Hz, 1H), 7.23–7.30 (m, 6H), 7.65–7.69 (m, 4H). (2) To a solution of {[*N*-(2-propenyl)amino]diphenylsilyl}trimethylstannane (3.36 g, 8.35 mmol) in THF (15.0 mL) was added over 20 min *tert*-butyllithium in pentane (1.54 M, 6.00 mL, 9.24 mmol) at –78 °C over 20 min and the reaction mixture was stirred for 1 h. To the solution was added Me_3SiCl (1.30 mL, 10.3 mmol) at –78 °C. The reaction mixture was stirred for 15 min at that temperature and warmed to ambient temperature. After being stirred for 15 min, the solvent was evaporated. The residue was diluted with hexane (ca. 30 mL) and filtered. The filtrate was concentrated and the residue was distilled bulb-to-bulb to give **19** (3.62 g, 92% yield) as a colorless oil. **19:** bp: 184–197 °C/0.50 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.11 (s, 9H), 0.28 (s, 9H, ^{2}J[Sn-H] = 46.4 and 44.8 Hz), 3.72 (ddd, J = 5.3, 1.6, and 1.6 Hz, 2H), 4.98 (ddt, J = 10.3, 1.6, and 1.6 Hz, 1H), 5.14 (ddt, J = 17.0, 1.6, and 1.6, 1H), 5.83 (ddt, J = 17.0, 10.3, and 5.3 Hz, 1H), 7.18–7.35 (m, 6H), 7.70–7.78 (m, 4H). ^{13}C NMR (C_6D_6): δ –9.14, 2.23, 50.98, 114.78, 128.23, 129.53, 135.33, 138.75, 140.13. MS: *m/e* 460 (M^+–Me, 4), 434 (M^+–(CH_2=CH-CH_2-), 1), 310 (M^+–Me_3Sn, 100) 197 (34), 135 (57). Anal. Calcd for $C_{21}H_{33}NSi_2Sn$: C, 53.17; H, 7.01; N, 2.95. Found: C, 52.90; H, 7.11; N, 2.95.

Reaction of 23 with *tert*-Butyllithium: Synthesis of {[*N*-Trimethylsilyl-*N*-(2'-propenyl)-amino]diphenylsilyl}lithium (20) and Trapping as 1-[*N*-Trimethylsilyl-*N*-(2'-propenyl)-amino]-1,1-diphenyl-2,2,2-trimethyldisilane (21). To a solution of **19** (256 mg, 0.539 mmol) in THF (1.1 mL) was added over 1 min *tert*-butyllithium in pentane (1.54 M, 0.70 mL, 1.1 mmol) at –45 °C and the reaction mixture was stirred for 2 h to give a yellow solution of **20**. To the solution was added Me_3SiCl (0.15 mL, 1.2 mmol) at –45 °C. The reaction mixture was warmed to ambient temperature. After being stirred for 15 min, the reaction mixture was diluted with hexane (ca. 5 mL) and filtered. The filtrate was concentrated and the residue was distilled bulb-to-bulb to give **21** (177 mg, 86% yield) as a colorless oil. bp: 174–211 °C/0.70 mmHg. ^{1}H NMR (C_6D_6): δ 0.10 (s, 9H),

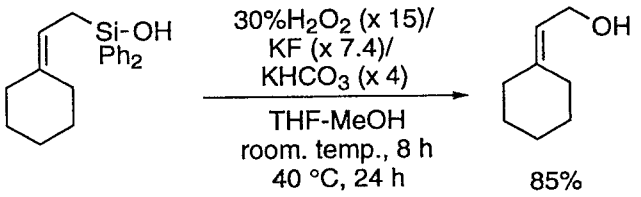
0.21 (s, 9H), 3.80 (ddd, J = 5.4, 1.6, and 1.6 Hz, 2H), 4.99 (ddt, J = 10.0, 1.6, and 1.6 Hz, 1H), 5.15 (ddt, J = 17.0, 1.6, and 1.6 Hz, 1H), 5.96 (ddt, J = 17.0, 10.0, and 5.4 Hz, 1H), 7.20–7.36 (m, 6H), 7.76–7.83(m, 4H). ^{13}C NMR ($CDCl_3$): δ –0.38, 2.18, 50.68, 114.27, 127.60, 128.77, 135.17, 138.28, 140.93.MS: *m/e* 383 (M^+, 1), 368 (M^+–Me, 1), 342 (M^+–(CH_2=CH-CH_2-), 0.3), 310 (M^+–$SiMe_3$, 19), 254 (1), 233(2), 84 (100). Anal. Calcd for $C_{21}H_{33}NSi_3$: C, 65.73; H, 8.67; N, 3.65. Found: C, 65.43; H, 8.77; N, 3.66.

Reaction of 23 with *tert*-Butyllithium and Subsequent Rearrangement: Synthesis of [*N*,*N*-Bis(trimethylsilyl)amino](2-propenyl)diphenylsilane (23). To a solution of **19** (440 mg, 0.928 mmol) in THF (2.0 mL) was added over 1 min *tert*-butyllithium in pentane (1.64 M, 1.89 mL, 1.15 mmol) at –45 °C and the reaction mixture was stirred for 2 h. To the solution was added a solution of 12-crown-4 (0.31 mL, 1.9 mmol) in THF (0.8 mL) at –45 °C and the reaction mixure was stirred for another 2 h. To the reaction mixture was added Me_3SiCl (0.26 mL, 2.1 mmol) at –45 °C. The reaction mixture was warmed to ambient temperature. After being stirred for 15 min, the reaction mixture was diluted with hexane (ca. 5 mL) and filtered. The filtrate was concentrated and the residue was distilled bulb-to-bulb to give **23** (307 mg, 86% yield) as a colorless oil. bp: 191–201 °C/0.38 mmHg. ^1H NMR (C_6D_6): δ 0.22 (s, 18H), 2.34 (ddd, J = 6.5, 1.4, and 1.4 Hz, 2H), 4.95–5.08 (m, 2H), 5.91–6.08 (m, 1H), 7.20–7.28 (m, 6H), 7.77–7.90 (m, 4H). ^{13}C NMR (C_6D_6): δ 5.65, 26.65, 114.88, 127.39, 129.08, 134.97, 135.27, 139.16. MS: *m/e* 368 (M^+–Me, 8), 343 (100), 326 (58), 264 (61) 192 (54). Anal. Calcd for $C_{21}H_{33}NSi_3$: C, 65.73; H, 8.67; N, 3.65. Found: C, 65.43; H, 8.66; N, 3.56.

Reaction of 15a with *n*-Butyllithium, Subsequent Rearrangement, and Trapping as 1-(2'-Cyclohexylidene-ethyl)-1,1-diphenylsilanol. To a solution of **11a** (1.42 g, 3.01 mmol) in THF (6.0 mL) was added *n*-butyllithium in hexane (1.76 M, 3.50 mL, 6.16 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 3 h, warmed to room temperature, and stirred for 2 h. A 5% aq. solution of NH_4Cl (7.5 mL) was added to the reaction mixture at 0 °C, which was warmed to ambient temperature with stirring. The mixture was extracted with Et_2O (20 mL x 3) and the combined organic layer was washed with water (20 mL) and brine (20 mL), and dried over $MgSO_4$. The solution was evaporated. The residue was subjected to colum chromathography on silica gel (80 mL) eluted with hexane/AcoEt (10/1) to give the title compound (806 mg, 89% yield) (R_f = 0.23) as a colorless oil. ^1H

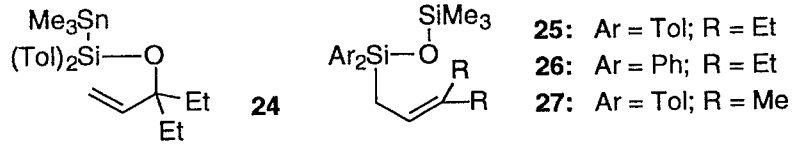
NMR (C_6D_6): δ 1.23–1.36 (m, 2H), 1.37–1.53 (m, 4H), 1.73 (s, 1H), 1.96–2.15 (m, 6H), 5.33 (t, J = 8.4 Hz, 1H), 7.20–7.32 (m, 6H), 7.64–7.77 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 12.26, 26.83, 27.33, 28.48, 28.56, 37.23, 113.95, 127.80, 129.87, 134.30, 135.94, 139.55. Anal. Calcd for $C_{20}H_{24}OSi$: C, 77.87; H, 7.84. Found: C, 77.67; H, 7.84. MS: *m/e* 308 (M^+, 72), 230 (9), 200 (100), 199 ($Ph_2(HO)Si^+$, 81), 181 (25).

Hydrogen Peroxide Oxidation of 1-(2'-Cyclohexylidene-ethyl)-1,1-diphenylsilanol: Synthesis of 2-(Cyclohexylidene)ethyl alcohol. To a solution of 1-(2'-Cyclohexylidene-ethyl)-1,1-diphenylsilanol (173 mg, 0.560 mmol) in THF (0.6 mL) and MeOH (0.6 mL) was added successively KF (239 mg, 4.12 mmol), $KHCO_3$ (223 mg, 2.23 mmol), and 30% H_2O_2 (0.63 mL, 5.6 mmol) at room temperature and the reaction mixture was stirred for 8 h. Then 30% H_2O_2 (0.32 mL, 2.8 mmol) was added to the reaction mixture, which was stirred at 40 °C for 24 h. The reaction mixture was poured into H_2O (10 mL) and the mixture was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with a 10% aq. solution of $Na_2S_2O_3$ (10 mL), a 1 M solution of NaOH (10 mL x 3), water (10 mL), and brine (10 mL), and dried over $MgSO_4$. The solution was concentrated and the residue was subjected to column chromatography on silica gel (15 mL) eluted with hexane/AcoEt (7/1) to give the title compound (60 mg, 85% yield) (R_f = 0.13) as a colorless oil. The spectral data were identical with the reported data.[16b]



Crossover Experiments

The intramolecular fashion of the rearrangement was confirmed by the following crossover experiment. An equimolar mixture of (allyloxysilyl)stannanes **1** and **24** was treated with *n*-butyllithium (4 equiv) under the same condition employed for **1** to give only the intramolecular rearrangement products **5** and **25** in 81% and 82% yields, respectively. No cross-over products **26** and **27** were detected at all.



[(3-Ethyl-1-penten-3-oxy)di(*p*-tolyl)silyl]trimethylstannane (24). (1) Di(*p*-tolyl)dichlorosilane was prepared by reaction of silicon tetrachloride with 2 equiv of (*p*-tolyl)magnesium bromide in THF-toluene in 85% yield. (2) (3-Ethyl-1-penten-3-oxy)di(*p*-tolyl)chlorosilane was prepared from di(*p*-tolyl)dichlorosilane (2.79 g, 9.93 mmol) and 3-ethyl-1-penten-3-ol (1.46 g, 12.8 mmol) in the presence of triethylamine (1.94 mL, 13.9 mmol) and 4-(dimethylamino)pyridine (123 mg, 0.990 mmol) in THF (12.0 mL) by essentially the same method as described in the literature.[4c] This compound decomposed during distillation, so that it was used in the next step without purification. **(3-Ethyl-1-penten-3-oxy)di(*p*-tolyl)chlorosilane:** ^{1}H NMR (C_6D_6): δ 0.91 (t, J = 7.4 Hz, 6H), 1.72 (q, J = 7.4 Hz, 2H), 1.76 (q, J = 7.4 Hz, 2H), 2.08 (s, 6H), 5.10 (dd, J = 10.7 and 1.8 Hz, 1H), 5.37 (dd, J = 17.3 and 1.8 Hz, 1H), 5.81 (dd, J = 17.3 and 10.7, 1H), 7.05 (d, J = 7.6 Hz, 4H), 7.88 (d, J = 7.6 Hz, 4H). (3) (Trimethylstannyl)lithium was prepared from Me_3SnCl (2.26 g, 11.3 mmol) with granular lithium (310 mg, 44.7 mg-atom) in THF (12.0 mL). The resulting solution was used in the next step without titration after removal of the unreacted lithium. (4) To a THF (10 mL) solution of (3-ethyl-1-penten-3-oxy)di(*p*-tolyl)chlorosilane prepared above was added over 10 min the solution of (trimethylstannyl)lithium in THF at 0 °C. The reaction mixture was stirred at 0 °C for 2.5 h and at room temperature for 10 h. The reaction mixture was evaporated, diluted with hexane (ca. 20 mL), and filtered. The filtrate was concentrated and the residue was subjected to reverse-phase column chromatography (Wakogel LP-40C18, 80 mL) with CH_3CN as eluent to give **24** as a colorless oil (70%

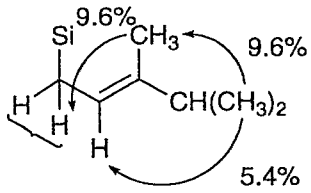
overall yield based on di(*p*-tolyl)dichlorosilane) (R_f = 0.35). **24:** ^{1}H NMR (C_6D_6): δ 0.38 (s, 9H, ^2J[Sn-H] = 46.8 and 44.8 Hz), 0.89 (t, J = 7.4 Hz, 6H), 1.76 (q, J = 7.4 Hz, 4H), 2.12 (s, 6H), 5.11 (dd, J = 10.8 and 1.6 Hz, 1H), 5.33 (dd, J = 17.4 and 1.6 Hz, 1H), 5.85 (dd, J = 17.4 and 10.8 Hz, 1H), 7.11 (d, J = 7.6 Hz, 4H), 7.77 (d, J = 7.6 Hz, 4H). ^{13}C NMR (C_6D_6): δ –9.49, 8.56, 21.44, 32.45, 80.67, 114.25, 129.14, 135.00, 136.42, 139.49, 143.19. MS: *m/e* 488 (M^+, 0.9), 473 (M^+–Me, 2), 391 (13), 323 (M^+–$SnMe_3$, 57), 227 (100). Anal. Calcd for $C_{24}H_{36}OSiSn$: C, 59.15; H, 7.45. Found: C, 58.91; H, 7.54.

Reaction of 24 with *n*-Butyllithium and Subsequent Rearrangement: Synthesis of 1-(3'-Ethyl-2'-pentenyl)-1,1-di(*p*-tolyl)-3,3,3-trimethyldisiloxane (25). To a solution of **24** (264 mg, 0.541 mmol) in THF (2.0 mL) was added dropwise over 1 min *n*-butyllithium in hexane (1.65 M, 0.66 mL, 1.1 mmol) at –78 °C. The reaction mixture was stirred for 3 h, warmed to room temperature, and stirred for 2 h. To the reaction mixture was added Me_3SiCl (0.15 mL, 1.2 mmol). After being stirred for 30 min, the reaction mixture was evaporated and the residue was diluted with hexane (ca. 10 mL) and filtered. The filtrate was concentrated and the residue was subjected to column chromatography on silica gel (25 mL) eluted with hexane to give **25** (175 mg, 81% yield) (R_f = 0.33) as a colorless oil. ^{1}H NMR (C_6D_6): δ 0.22 (s, 9H), 0.91 (t, J = 7.7 Hz, 3H), 1.03 (t, J = 7.4 Hz, 3H), 1.98–2.10 (m, 4H), 2.15 (s, 6H), 2.21 (d, J = 8.2 Hz, 2H), 5.45–5.54 (m, 1H), 7.13 (d, J = 7.8 Hz, 4H), 7.73 (d, J = 7.8 Hz, 4H). ^{13}C NMR ($CDCl_3$): δ 2.02, 12.51, 12.99, 17.49, 21.53, 22.73, 29.26, 116.35, 128.36, 133.71, 134.32, 139.21, 141.71. MS: *m/e* 396 (M^+, 4), 381 (M^+–Me, 0.9), 299 ($Me_3SiO(Tol)_2Si^+$, 100), 207 (31), 193 (4). Anal. Calcd for $C_{24}H_{36}OSi_2$: C, 72.66; H, 9.15. Found: C, 72.76; H, 9.26.

Crossover Experiment: Reaction of 1 and 24 with *n*-Butyllithium. To a mixture of **1** (227 mg, 0.526 mmol) and **24** (267 mg, 0.548 mmol) in THF (3.0 mL) was added *n*-butyllithium in hexane (1.57 M, 1.37 mL, 2.15 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 3 h, warmed to room temperature, and stirred for 2 h. To the reaction mixture was added Me_3SiCl (0.30 mL, 2.4 mmol). After being stirred for 30 min, the reaction mixture was evaporated, diluted with hexane (ca. 10 mL), and filtered. The filtrate was concentrated and the residue was subjected to column chromatography on silica gel (30 mL) eluted with hexane to give a mixture (324 mg) of **5** (81% yield) and **25** (82% yield) (R_f = ca. 0.3). The yields were estimated by ^{1}H NMR. The mixture was separated

by means of HPLC eluted with hexane/AcOEt (100/1) into **5** and **25**, which were characterized again by ^{1}H NMR, independently. ^{1}H NMR, GLC, and HPLC analyses of the reaction mixture revealed that **26** and **27** were not formed at all.

Results of NOE Experiments



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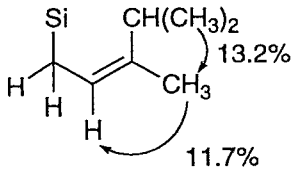

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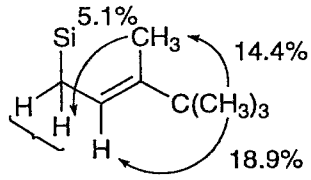

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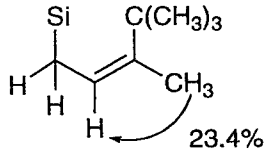

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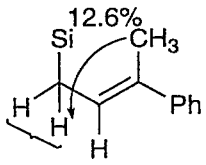

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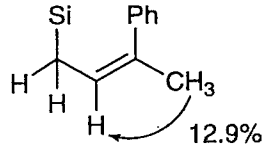

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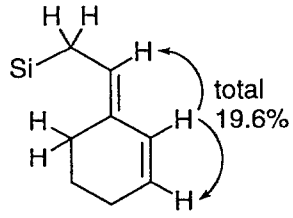
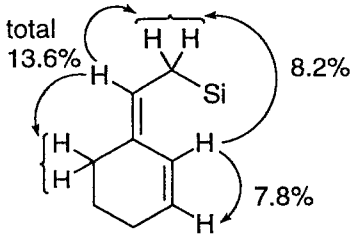


(*E*)-16



(*Z*)-16