Ring-Opening Reactions of Cyclic Acetals and 1,3-Oxazolidines with Halosilane Equivalents

Arihiro Iwata, Heqing Tang, Atsutaka Kunai,* Joji Ohshita, Yasushi Yamamoto, and
Chinami Matui

Supporting information

Detailed experimental procedures and spectral and analytical data for the products.

General Considerations. All reactions were carried out under an atmosphere of dry argon. ^1H and ^{13}C NMR spectra were recorded on a JEOL Model JNM-LA 400 spectrometer. Mass spectra were measured with a Hitachi M-80B spectrometer. IR spectra were measured on Perkin-Elmer FT-IR Model 1600 and Shimadzu FTIR-8700 spectrometers.

Materials. Methyl iodide and allyl bromide were dried over P_2O_5 and distilled just before use. Toluene was dried over sodium and distilled just before use.

Reaction of 2a with $\text{Me}_3\text{SiNEt}_2/\text{MeI}$. A solution of diethylaminotrimethylsilane (5.95 g, 41.0 mmol), **2a** (5.79 g, 40.8 mmol), and methyl iodide (12.2 g, 86.1 mmol) in 20 mL of toluene was stirred at 80–90 °C for 12 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give **3a** (6.63 g, 31.0 mmol, 76%), bp 73–75 °C/1 mmHg.

For **3a**: IR (neat) 2932, 2871, 1667, 1251, 1194, 1135, 1107, 900, 842 cm^{-1} ; ^1H NMR (δ in CDCl_3) 4.58 (s, 1H), 3.81 (t, $J = 5.1$ Hz, 2H), 3.69 (t, $J = 5.1$ Hz, 2H), 2.15–2.02 (m, 4H), 1.68–1.62 (m, 2H), 1.55–1.49 (m, 2H), 0.12 (s, 9H); ^{13}C NMR (δ in CDCl_3) 154.48, 93.85, 67.37, 61.46, 27.78, 23.49, 22.87, 22.72, –0.38; GC/MS m/z 214

(M^+), 199 ($M^+ - \text{Me}$), 141 ($M^+ - \text{SiMe}_3$). Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{O}_2\text{Si}$: C, 61.63; H, 10.34. Found: C, 61.51; H, 10.49.

Reaction of 2b with $\text{Me}_3\text{SiNEt}_2/\text{MeI}$. A solution of diethylaminotrimethylsilane (3.95 g, 27.2 mmol), **2b** (4.13 g, 26.5 mmol), and methyl iodide (8.16 g, 57.5 mmol) in 15 mL of toluene was stirred at 80–90 °C for 12 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give a 59/41 mixture of **3b-1** and **3b-2** (4.55 g, 20.0 mmol, 75%), bp 86–88 °C/1 mmHg. For the mixture: IR (neat) 2931, 2872, 1664, 1250, 1192, 1132, 1110, 899, 842 cm^{-1} ; ^{13}C NMR (δ in CDCl_3) 158.25 (C), 146.88 (C), 114.41 (C), 93.56 (CH), 69.40 (CH_2), 67.51 (CH_2), 61.96 (CH_2), 61.46 (CH_2), 31.99 (CH), 31.34 (CH_2), 30.25 (CH_2), 25.51 (CH_2), 24.05 (CH_2), 23.57 (CH_2), 22.81 (CH_2), 20.02 (CH_2), 19.01 (CH_3), 15.80 (CH_3), -0.42 (SiMe), -0.50 (SiMe); GC/MS m/z 228 (M^+), 213 ($M^+ - \text{Me}$), 155 ($M^+ - \text{SiMe}_3$). Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{O}_2\text{Si}$: C, 63.10; H, 10.59. Found: C, 63.19; H, 10.22.

For **3b-1**: ^1H NMR (δ in CDCl_3) 3.80–3.60 (m, 4H), 2.05–1.30 (m, 8H), 1.60 (s, 3H), 0.11 (s, 9H). For **3b-2**: ^1H NMR (δ in CDCl_3) 4.53 (t, $J = 4.0$ Hz, 1H), 3.80–3.60 (m, 4H), 2.05–1.30 (m, 7H), 1.65 (d, $J = 7.0$ Hz, 3H), 0.11 (s, 9H).

Reaction of 2c with $\text{Me}_3\text{SiNEt}_2/\text{MeI}$. A solution of diethylaminotrimethylsilane (4.68 g, 32.3 mmol), **2c** (4.09 g, 32.0 mmol), and methyl iodide (9.85 g, 69.4 mmol) in 20 mL of toluene was stirred at 80–90 °C for 12 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give **3c** (4.78 g, 23.9 mmol, 75%), bp 74 °C/1 mmHg.

For **3c**: IR (neat) 2930, 2875, 1670, 1250, 1191, 1136, 902, 841 cm^{-1} ; ^1H NMR (δ in CDCl_3) 4.42 (brs, 1H), 3.81 (t, $J = 3.9$ Hz, 2H), 3.80 (t, $J = 3.9$ Hz, 2H), 2.40–2.26 (m, 4H), 1.85 (p, 2H), 0.12 (s, 9H); ^{13}C NMR (δ in CDCl_3) 159.83, 93.76, 70.41, 61.25, 31.85, 28.95, 21.25, -0.43 ; GC/MS m/z 200 (M^+), 185 ($\text{M}^+ - \text{Me}$), 127 ($\text{M}^+ - \text{SiMe}_3$). Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{O}_2\text{Si}$: C, 59.95; H, 10.06. Found: C, 59.77; H, 9.89.

Reaction of 2d with $\text{Me}_3\text{SiNEt}_2/\text{MeI}$. A solution of diethylaminotrimethylsilane (2.82 g, 19.4 mmol), **2d** (2.55 g, 19.6 mmol), and methyl iodide (6.10 g, 43.0 mmol) in 10 mL of toluene was stirred at 80–90 $^\circ\text{C}$ for 12 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give an 80/20 *E/Z* mixture of **3d** (1.90 g, 12.0 mmol, 62%), bp 90–95 $^\circ\text{C}/20$ mmHg. For the mixture: IR (neat) 2930, 2875, 1670, 1250, 1191, 1136, 902, 841 cm^{-1} ; GC/MS m/z 202 (M^+), 187 ($\text{M}^+ - \text{Me}$). Anal. Calcd for $\text{C}_{10}\text{H}_{22}\text{O}_2\text{Si}$: C, 59.35; H, 10.96. Found: C, 59.01; H, 10.64.

For (*E*)-**3d**: ^1H NMR (δ in CDCl_3) 4.32 (q, $J = 6.8$ Hz, 1H), 3.81 (t, $J = 5.3$ Hz, 2H), 3.63 (t, $J = 5.3$ Hz, 2H), 2.14 (q, $J = 7.5$ Hz, 2H), 1.56 (d, $J = 6.8$ Hz, 3H), 1.03 (t, $J = 7.5$ Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (δ in CDCl_3) 157.90, 90.00, 67.63, 61.47, 23.21, 12.10, 11.41, -0.48 . For (*Z*)-**3d**: ^1H NMR (δ in CDCl_3) 4.47 (q, $J = 6.8$ Hz, 1H), 3.69 (t, $J = 5.7$ Hz, 2H), 3.45 (t, $J = 5.7$ Hz, 2H), 2.41 (q, $J = 7.5$ Hz, 2H), 1.66 (d, $J = 6.8$ Hz, 3H), 0.81 (t, $J = 7.5$ Hz, 3H), 0.11 (s, 9H); ^{13}C NMR (δ in CDCl_3) 156.37, 103.27, 69.52, 62.13, 25.09, 10.15, 7.84, -0.42 .

Reaction of 2e with $\text{Me}_3\text{SiNEt}_2/\text{MeI}$. A solution of diethylaminotrimethylsilane (7.56 g, 52.1 mmol), **2e** (7.43 g, 51.6 mmol), and methyl iodide (14.8 g, 104 mmol) in

20 mL of toluene was stirred at 80–90 °C for 12 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give a 60/30/10 mixture of **3e-1**, (*E*)-**3e-2**, and (*Z*)-**3e-2** (8.02 g, 37.1 mmol, 72%), bp 98–100 °C/20 mmHg. For the mixture: IR (neat) 2956, 1655, 1301, 1251, 1141, 842 cm^{-1} ; GC/MS m/z 216 (M^+), 201 ($M^+ - \text{Me}$), 173 ($M^+ - i\text{-Pr}$); HRMS calcd for $\text{C}_{11}\text{H}_{24}\text{O}_2\text{Si}$ (M^+) 216.1546, found 216.1561.

For **3e-1**: ^1H NMR (δ in CDCl_3) 3.82 (t, $J = 5.2$ Hz, 2H), 3.81 (br s, 2H, $=\text{CH}_2$), 3.70 (t, $J = 5.2$ Hz, 2H), 1.95 (d, $J = 7.0$ Hz, 2H), 1.91–1.81 (m, 1H), 0.87 (d, $J = 6.5$ Hz, 6H), 0.12 (s, 9H); ^{13}C NMR (δ in CDCl_3) 162.44 (C=), 81.87 ($=\text{CH}_2$), 68.38, 61.21, 44.42 ($\text{CH}_2\text{C=}$), 23.41, 22.30, -0.42 . For (*E*)-**3e-2**: ^1H NMR (δ in CDCl_3) 4.18 (d, $J = 8.9$ Hz, 1H), 3.82 (t, $J = 5.2$ Hz, 2H), 3.65 (t, $J = 5.2$ Hz, 2H), 2.41–2.32 (m, 1H), 1.81 (s, 3H), 1.03 (d, $J = 5.8$ Hz, 6H), 0.12 (s, 9H); ^{13}C NMR (δ in CDCl_3) 150.74 (C=), 105.77 ($=\text{CH}$), 67.56, 61.45, 26.83, 26.21, 16.22, -0.39 (SiMe). For (*Z*)-**3e-2**: ^1H NMR (δ in CDCl_3) 4.29 (d, $J = 8.9$ Hz, 1H), 3.82 (t, $J = 5.2$ Hz, 2H), 3.70 (t, $J = 5.2$ Hz, 2H), 2.79–2.73 (m, 1H), 1.94 (s, 3H), 0.92 (d, $J = 5.8$ Hz, 6H), 0.12 (s, 9H); ^{13}C NMR (δ in CDCl_3) 150.74 (C=), 117.77 ($=\text{CH}$), 69.19, 61.87, 28.83, 23.33, 17.97, -0.50 (SiMe).

Reaction of 2f with $\text{Me}_3\text{SiNEt}_2/\text{MeI}$. A solution of diethylaminotrimethylsilane (7.86 g, 54.2 mmol), **2f** (8.33 g, 53.4 mmol), and methyl iodide (16.1 g, 113 mmol) in 25 mL of toluene was stirred at 80–90 °C for 12 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give an 87/13 mixture of **3f-1** and **3f-2** (10.2 g, 44.8 mmol, 84%), bp 50–53 °C/1 mmHg. For the mixture: IR (neat) 2931, 1666, 1251, 1186, 1098,

842 cm^{-1} ; GC/MS m/z 228 (M^+), 213 ($\text{M}^+ - \text{Me}$), 155 ($\text{M}^+ - \text{SiMe}_3$); HRMS calcd for $\text{C}_{12}\text{H}_{24}\text{O}_2\text{Si}$ (M^+) 228.1546, found 228.1515.

For **3f-1**: ^1H NMR (δ in CDCl_3) 4.65 (s, 1H), 4.13–4.08 (m, 1H), 3.67–3.63 (m, 1H), 3.54–3.44 (m, 1H), 2.03–2.01 (m, 4H), 1.65 (br s, 2H), 1.57–1.52 (m, 2H), 1.17 (d, $J = 6.0$ Hz, 3H), 0.11 (s, 9H); ^{13}C NMR (δ in CDCl_3) 152.79, 95.10, 71.55, 65.74, 28.11, 23.55, 22.95, 22.72, 16.50, -0.43 . For **3f-2**: ^1H NMR (δ in CDCl_3) 4.56 (s, 1H), 4.08–3.98 (m, 1H), 3.54–3.44 (m, 2H), Other signals were overlapped with **3f-1**; ^{13}C NMR (δ in CDCl_3) 154.42, 93.64, 71.60, 66.95, 27.76, 23.46, 22.86, 20.86, 0.15.

Reaction of 2g with $\text{Me}_3\text{SiNEt}_2/\text{MeI}$. A solution of diethylaminotrimethylsilane (4.63 g, 31.9 mmol), **2g** (4.87 g, 31.2 mmol), and methyl iodide (8.89 g, 62.6 mmol) in 15 mL of toluene was stirred at 80–90 $^\circ\text{C}$ for 12 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give a 40/60 mixture of **3g-1** and **3g-2** (4.82 g, 20.7 mmol, 64%), bp 89–92 $^\circ\text{C}/20$ mmHg.

For **3g-1**: ^1H NMR (δ in CDCl_3) 3.65 (t, $J = 6.3$ Hz, 4H), 1.73 (p, $J = 6.3$ Hz, 2H), 0.10 (s, 9H); ^{13}C NMR (δ in CDCl_3) 59.16, 35.52, -0.53 ; GC/MS m/z 205 ($\text{M}^+ - \text{Me}$), 147 ($\text{M}^+ - \text{SiMe}_3$). Assignment for **3g-2** is shown later in an another experiment.

Reaction of 4a with 2 equiv of $\text{Me}_3\text{SiNEt}_2/\text{MeI}$. A solution of diethylaminotrimethylsilane (10.7 g, 73.8 mmol), **4a** (5.35 g, 35.7 mmol), and methyl iodide (21.2 g, 149 mmol) in 40 mL of toluene was stirred at 80–90 $^\circ\text{C}$ for 12 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the

residue was fractionally distilled under reduced pressure to give **5** (5.81 g, 28.2 mmol, 79%), bp 70–71 °C/25 mmHg.

For **5**: IR (neat) 2957, 1251, 1098, 842 cm^{-1} ; ^1H NMR (δ in CDCl_3) 3.66 (s, 4H), 0.11 (s, 18H); ^{13}C NMR (δ in CDCl_3) 63.87, –0.45; GC/MS m/z 206 (M^+), 191 ($\text{M}^+ - \text{Me}$), 133 ($\text{M}^+ - \text{SiMe}_3$). Anal. Calcd for $\text{C}_8\text{H}_{22}\text{O}_2\text{Si}_2$: C, 46.55; H, 10.74. Found: C, 46.56; H, 10.80.

Reaction of 4b with $\text{Me}_3\text{SiNEt}_2/\text{MeI}$. A solution of diethylaminotrimethylsilane (4.80 g, 33.1 mmol), **4b** (2.58 g, 15.7 mmol), and methyl iodide (10.2 g, 71.8 mmol) in 20 mL of toluene was stirred at 80–90 °C for 12 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give a 80/20 mixture of **5** and **6a** (2.04 g, 9.55 mmol, 61%), bp 69–75 °C/25 mmHg.

Reaction of 4c with $\text{Me}_3\text{SiNEt}_2/\text{MeI}$. A solution of diethylaminotrimethylsilane (5.95 g, 41.0 mmol), **4c** (5.79 g, 40.8 mmol), and methyl iodide (12.2 g, 86.1 mmol) in 20 mL of toluene was stirred at 80–90 °C for 12 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give benzophenone (2.57 g, 14.1 mmol, 67%) and **6a** (3.19 g, 13.1 mmol, 62%).

For **6a**: bp 70–71 °C/ 25 mmHg; IR (neat) 2955, 1251, 1103, 842 cm^{-1} ; ^1H NMR (δ in CDCl_3) 3.80 (t, $J = 6.8$ Hz, 2H), 3.18 (t, $J = 6.8$ Hz, 2H), 0.11 (s, 9H); ^{13}C NMR (δ in CDCl_3) 63.79, 6.55, –0.44; GC/MS m/z 229 ($\text{M}^+ - \text{Me}$). Anal. Calcd for $\text{C}_5\text{H}_{13}\text{IOSi}$: C, 24.60; H, 5.37. Found: C, 24.39; H, 5.33.

Reaction of 4d with Me₃SiNEt₂/MeI. A solution of diethylaminotrimethylsilane (3.20 g, 22.1 mmol), **4d** (4.82 g, 20.1 mmol), and methyl iodide (6.55 g, 46.1 mmol) in 20 mL of toluene was stirred at 80–90 °C for 48 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give benzophenone (2.74 g, 15.1 mmol, 75%) and **3g-2** (3.68 g, 14.3 mmol, 71%).

For **3g-2**: bp 70–71 °C/15 mmHg; IR (neat) 2957, 1250, 1098, 842 cm⁻¹; ¹H NMR (δ in CDCl₃) 3.63 (t, *J* = 5.8 Hz, 2H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.05–1.96 (m, 2H), 0.12 (s, 9H); ¹³C NMR (δ in CDCl₃) 61.82, 35.94, 3.56, –0.51; GC/MS *m/z* 243 (M⁺–Me). Anal. Calcd for C₆H₁₃IOSi: C, 27.91; H, 5.86. Found: C, 27.66; H, 5.87.

Reaction of 4e with Me₃SiNEt₂/MeI. A solution of diethylaminotrimethylsilane (5.46 g, 37.7 mmol), **4e** (8.92 g, 37.2 mmol), and methyl iodide (10.9 g, 76.8 mmol) in 20 mL of toluene was stirred at 80–90 °C for 48 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give benzophenone (4.73 g, 26.0 mmol, 70%) and an 83/17 mixture of **6b** and **6c** (7.00 g, 27.1 mmol, 73%). For the mixture of **6**: bp 70 °C/20 mmHg; GC/MS *m/z* 243 (M⁺–Me). Anal. Calcd for C₆H₁₃IOSi: C, 27.91; H, 5.86. Found: C, 27.69; H, 6.03.

For **6b**: ¹H NMR (δ in CDCl₃) 4.13–4.05 (m, 1H), 3.82–3.55 (m, 2H), 1.86 (d, *J* = 7.0 Hz, 3H), 0.12 (s, 9H); ¹³C NMR (δ in CDCl₃) 70.04, 28.05, 24.30, –0.43. For **6c**: ¹H NMR (δ in CDCl₃) 3.88–3.78 (m, 1H), 3.17–3.10 (m, 2H), 1.26 (d, *J* = 6.0 Hz, 3H), 0.13 (s, 9H); ¹³C NMR (δ in CDCl₃) 68.45, 23.38, 14.56, 0.18.

Reaction of 7a with Me₃SiNEt₂/MeI. A solution of diethylaminotrimethylsilane (21.2 g, 146 mmol), **7a** (19.0 g, 135 mmol), and methyl iodide (20.8 g, 146 mmol) in 100 mL of toluene was stirred at 80–90 °C for 5 h. Triethylamine (16.0 g, 158 mmol) was added to the reaction mixture. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give **8a** (23.9 g, 112 mmol, 83%), bp 65–68 °C/1 mmHg.

For **8a**: IR (neat) 2932, 2861, 1717, 1665, 1448, 1250, 1108, 879, 842 cm⁻¹; ¹H NMR (δ in CDCl₃) 3.77 (t, *J* = 6.5 Hz, 2H), 3.43 (t, *J* = 6.5 Hz, 2H), 2.27–2.26 (m, 4H), 1.78–1.60 (m, 6H), 0.09 (s, 9H); ¹³C NMR (δ in CDCl₃) 174.53, 62.91, 52.49, 39.94, 29.14, 27.66, 26.94, 26.00, -0.47; GC/MS *m/z* 213 (M⁺), 198 (M⁺-Me), 140 (M⁺-SiMe₃). Anal. Calcd for C₁₁H₂₃NOSi: C, 61.91; H, 10.86; N, 6.56. Found: C, 61.52; H, 10.85; N, 6.51.

Reaction of 7b with Me₃SiNEt₂/MeI. A solution of diethylaminotrimethylsilane (5.38 g, 37.1 mmol), **7b** (4.70 g, 36.4 mmol), and methyl iodide (10.6 g, 74.6 mmol) in 20 mL of toluene was stirred at room temperature for 2 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give **8b** (5.87 g, 29.8 mmol, 82%), bp 70 °C/15 mmHg.

For **8b**: IR (neat) 2969, 2937, 1660, 1442, 1251, 1113, 879, 841 cm⁻¹; ¹H NMR (δ in CDCl₃) 3.78 (t, *J* = 6.8 Hz, 2H), 3.43 (t, *J* = 6.8 Hz, 2H), 2.27–2.19 (m, 4H), 1.05 (t, *J* = 7.5 Hz, 3H), 1.02 (t, *J* = 7.7 Hz, 3H), 0.09 (s, 9H); ¹³C NMR (δ in CDCl₃) 176.69, 63.09, 52.85, 32.65, 24.05, 10.99, 10.83, -0.48; GC/MS *m/z* 201 (M⁺), 186 (M⁺-Me), 128 (M⁺-SiMe₃). Anal. Calcd for C₁₀H₂₃NOSi: C, 59.64; H, 11.51; N, 6.96. Found: C, 60.01; H, 11.85; N, 6.81.

Reaction of 7c with Me₃SiNEt₂/MeI. A solution of diethylaminotrimethylsilane (5.71 g, 39.4 mmol), 7c (5.57 g, 39.0 mmol), and methyl iodide (5.85 g, 41.2 mmol) in 20 mL of toluene was stirred at room temperature for 2 h. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give an isomeric mixture of 8c (6.12 g, 28.5 mmol, 73%): bp 105–107 °C/20 mmHg.

For 8c: IR (neat) 2957, 1664, 1251, 1109, 842 cm⁻¹; GC/MS *m/z* 215 (M⁺), 200 (M⁺-Me), 142 (M⁺-SiMe₃). Anal. Calcd for C₁₁H₂₅NOSi: C, 61.33; H, 11.70; N, 6.50. Found: C, 61.12; H, 11.65; N, 6.23. For major isomer of 8c: ¹H NMR (δ in CDCl₃) 3.81 (t, *J* = 6.8 Hz, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.12 (d, *J* = 7.1 Hz, 2H), 1.99–1.90 (m, 1H), 1.80 (s, 3H), 0.89 (d, *J* = 6.5 Hz, 6H), 0.10 (s, 9H); ¹³C NMR (δ in CDCl₃) 171.13, 62.86, 53.69, 51.89, 26.15, 22.44, 17.66, -0.50.

Reaction of 7d with Me₃SiNEt₂/MeI. A solution of diethylaminotrimethylsilane (14.7 g, 101 mmol), 7d (15.5 g, 100 mmol), and methyl iodide (14.6 g, 103 mmol) in 100 mL of toluene was stirred at 80–90 °C for 5 h. Triethylamine (21.0 g, 208 mmol) was added to the reaction mixture. After the resulting ammonium salts were filtered off, the solvent was evaporated and the residue was fractionally distilled under reduced pressure to give 8d (16.3 g, 72.0 mmol, 72%), bp 75 °C/1 mmHg.

For 8d: IR (neat) 2929, 2833, 1641, 1250, 1097, 879, 841 cm⁻¹; ¹H NMR (δ in CDCl₃) 4.41 (brs, 1H), 3.58 (t, *J* = 6.5 Hz, 2H), 3.08 (t, *J* = 6.5 Hz, 2H), 2.63 (s, 3H), 2.15–2.00 (m, 4H), 1.70–1.60 (m, 2H), 1.55–1.45 (m, 2H), 0.09 (s, 9H); ¹³C NMR (δ in CDCl₃) 143.99, 96.45, 59.93, 52.99, 38.32, 26.92, 24.63, 23.46, 22.86, -0.53; GC/MS

m/z 227 (M^+), 212 ($M^+ - \text{Me}$), 138 ($M^+ - \text{OSiMe}_3$). Anal. Calcd for $\text{C}_{12}\text{H}_{25}\text{NOSi}$: C, 63.38; H, 11.08; N, 6.16. Found: C, 63.32; H, 10.86; N, 6.14.

Reaction of 2a with $\text{Et}_3\text{SiH}/\text{MeI}(\text{Pd}(\text{acac})_2/\text{dppe})$. A mixture of triethylsilane (3.08 g, 26.6 mmol), **2a** (3.75 g, 26.4 mmol), methyl iodide (7.94 g, 55.9 mmol), palladium acetylacetonate (40 mg, 0.13 mmol), and 1,2-bis(diphenylphosphino)ethane (60 mg, 0.15 mmol) was stirred at 80–90 °C for 5 h. The reaction mixture was fractionally distilled by a Kügel-Rohr distillation apparatus to give hexaethyldisiloxane (2.68 g, 10.9 mmol, 82%) and **9a** (3.37 g, 9.64 mmol, 73%).

For **9a**: bp 170 °C/1 mmHg (oven temp.); IR (neat) 2926, 2855, 1740, 1167 cm^{-1} ; ^1H NMR (δ in CDCl_3) 5.36 (s, 1H), 4.31 (t, $J = 6.8$ Hz, 2H), 3.28 (t, $J = 6.8$ Hz, 2H), 2.32 (t, $J = 7.5$ Hz, 2H), 2.00–1.89 (m, 6H), 1.67–1.50 (m, 6H), 1.43–1.27 (m, 4H); ^{13}C NMR (δ in CDCl_3) 173.15, 137.67, 120.79, 64.31, 37.78, 34.13, 28.79, 28.23, 27.24, 25.22, 24.82, 23.01, 22.58, 0.50; GC/MS m/z 350 (M^+), 223 ($M^+ - \text{I}$), 195 ($M^+ - \text{CH}_2\text{CH}_2\text{I}$). Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{IO}_2$: C, 48.01; H, 6.62. Found: C, 48.31; H, 6.68.

Reaction of 2a with $\text{Et}_3\text{SiH}/\text{AllylBr}(\text{PdCl}_2)$. A mixture of triethylsilane (4.81 g, 41.5 mmol), **2a** (5.94 g, 41.8 mmol), allyl bromide (8.01 g, 66.2 mmol), and palladium dichloride (20 mg, 0.11 mmol) was stirred at 80–90 °C for 10 h. The reaction mixture was fractionally distilled by a Kügel-Rohr distillation apparatus to give hexaethyldisiloxane (4.13 g, 16.7 mmol, 81%) and an 80/20 mixture of **9b-1** and **9b-2** (4.95 g, 16.4 mmol, 79%), bp 150 °C/1 mmHg (oven temp.). Recycling GPC separation of the mixture eluting with benzene afforded **9b-1** and **9b-2** in pure forms.

For **9b-1**: IR (neat) 2928, 1738, 1167 cm^{-1} ; ^1H NMR (δ in CDCl_3) 5.36 (s, 1H), 4.36 (t, $J = 6.8$ Hz, 2H), 3.50 (t, $J = 6.8$ Hz, 2H), 2.33 (t, $J = 7.5$ Hz, 2H), 2.00–1.80 (m,

6H), 1.67–1.40 (m, 6H), 1.40–1.25 (m, 4H); ^{13}C NMR (δ in CDCl_3) 173.27, 137.62, 120.76, 63.53, 37.76, 34.03, 28.75, 28.75, 28.21, 27.21, 25.19, 24.77, 22.99, 22.56; GC/MS m/z 304 (M^+ for ^{81}Br), 302 (M^+ for ^{79}Br). Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{BrO}_2$: C, 55.45; H, 7.65. Found: C, 55.63; H, 7.81. For **9b-2**: IR (neat) 2934, 1738, 1453, 1168, 700 cm^{-1} ; ^1H NMR (δ in CDCl_3) 7.19–7.14 (m, 2H), 7.08–7.05 (m, 3H), 4.26 (t, $J = 6.3\text{ Hz}$, 2H), 3.38 (t, $J = 6.3\text{ Hz}$, 2H), 2.51 (t, $J = 7.7\text{ Hz}$, 2H), 2.24 (t, $J = 7.5\text{ Hz}$, 2H), 1.61–1.50 (m, 4H), 1.32–1.16 (m, 2H); ^{13}C NMR (δ in CDCl_3) 173.15, 142.37, 128.32, 128.21, 125.62, 63.53, 35.64, 33.93, 30.98, 28.73, 28.60, 24.69; GC/MS m/z 300 (M^+ for ^{81}Br), 298 (M^+ for ^{79}Br). Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{BrO}_2$: C, 56.20; H, 6.40. Found: C, 56.04; H, 6.55.

Reaction of 2b with $\text{Et}_3\text{SiH}/\text{MeI}(\text{PdCl}_2)$. A mixture of triethylsilane (3.52 g, 30.3 mmol), **2b** (4.56 g, 29.2 mmol), methyl iodide (6.74 g, 47.5 mmol), and palladium dichloride (20 mg, 0.11 mmol) was stirred at 80–90 °C for 5 h. The reaction mixture was fractionally distilled by a Kügel-Rohr distillation apparatus to give hexaethyldisiloxane (3.66 g, 14.9 mmol, 98%) and **9c** (4.20 g, 11.1 mmol, 76%).

For **9c**: bp 170–175 °C/1 mmHg (oven temp.); IR (neat) 2922, 2854, 1740, 1166 cm^{-1} ; ^1H NMR (δ in CDCl_3) 4.32 (t, $J = 6.8\text{ Hz}$, 2H), 3.28 (t, $J = 6.8\text{ Hz}$, 2H), 2.50–2.40 (m, 1H), 2.00–1.20 (m, 16H), 1.57 (s, 3H), 1.15 (d, $J = 7.0\text{ Hz}$, 3H); ^{13}C NMR (δ in CDCl_3) 176.20, 129.93, 125.92, 64.22, 39.46, 33.70, 33.24, 31.81, 29.51, 28.06, 27.28, 23.50, 23.40, 19.02, 17.03, 0.58; GC/MS m/z 378 (M^+), 251 ($\text{M}^+ - \text{I}$). Anal. Calcd for $\text{C}_{16}\text{H}_{27}\text{IO}_2$: C, 50.80; H, 7.19. Found: C, 50.60; H, 7.20.

Reaction of 4c with Et₃SiH/MeI(PdCl₂). A mixture of triethylsilane (1.31 g, 11.3 mmol), **4c** (2.36 g, 10.4 mmol), methyl iodide (4.58 g, 32.3 mmol), and palladium dichloride (20 mg, 0.11 mmol) was stirred at 80–90 °C for 24 h. The reaction mixture was fractionally distilled by a Kügel-Rohr distillation apparatus to give hexaethyldisiloxane (1.39 g, 5.65 mmol, 100%) and **10a** (1.65 g, 9.07 mmol, 87%).

For **10a**: bp 100–110 °C/1 mmHg (oven temp.); IR (neat) 1657, 1448, 1322, 1275, 765, 692 cm⁻¹; ¹H NMR (δ in CDCl₃) 7.82–7.79 (m, 4H), 7.61–7.56 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 2H); ¹³C NMR (δ in CDCl₃) 196.74, 137.61, 132.40, 130.05, 128.26; GC/MS *m/z* 182 (M⁺), 105 (M⁺–Ph).

Reaction of 4d with Et₃SiH/MeI(PdCl₂). A mixture of triethylsilane (1.20 g, 10.3 mmol), **4d** (2.41 g, 10.0 mmol), methyl iodide (4.22 g, 29.7 mmol), and palladium dichloride (17 mg, 0.096 mmol) was stirred at 80–90 °C for 24 h. The reaction mixture was fractionally distilled by a Kügel-Rohr distillation apparatus to give hexaethyldisiloxane (1.02 g, 4.16 mmol, 81%) and **10a** (1.49 g, 8.19 mmol, 82%).

Reaction of 4f with Et₃SiH/MeI(PdCl₂). A mixture of triethylsilane (1.24 g, 10.7 mmol), **4f** (2.52 g, 10.0 mmol), methyl iodide (3.54 g, 24.9 mmol), and palladium dichloride (20 mg, 0.11 mmol) was stirred at 80–90 °C for 24 h. The reaction mixture was fractionally distilled by a Kügel-Rohr distillation apparatus to give hexaethyldisiloxane (1.03 g, 3.91 mmol, 78%) and **10b** (1.54 g, 7.40 mmol, 74%).

For **10b**: bp 160 °C/1 mmHg (oven temp.); IR (neat) 1662, 1606, 1576, 1448, 1340, 1218, 1016, 979, 745 cm⁻¹; ¹H NMR (δ in CDCl₃) 8.04–8.01 (m, 2H), 7.82 (d, *J* = 16 Hz, 1H), 7.67–7.61 (m, 2H), 7.55 (d, *J* = 16 Hz, 1H), 7.52–7.39 (m, 6H); ¹³C NMR

(δ in CDCl_3) 190.54, 144.83, 138.21, 134.89, 132.76, 130.53, 128.94, 128.61, 128.49, 128.43, 122.10; GC/MS m/z 208 (M^+), 131 ($\text{M}^+ - \text{Ph}$).

Reaction of 4g with $\text{Et}_3\text{SiH}/\text{MeI}(\text{PdCl}_2)$. A mixture of triethylsilane (1.22 g, 10.5 mmol), **4g** (2.78 g, 10.0 mmol), methyl iodide (3.78 g, 26.6 mmol), and palladium dichloride (20 mg, 0.11 mmol) was stirred at 80–90 °C for 24 h. The reaction mixture was fractionally distilled by a K $\ddot{u}$ gel-Rohr distillation apparatus to give **10c** (1.87 g, 7.98 mmol, 80%).

For **10c**: bp 230–240 °C/1 mmHg (oven temp.); IR (neat) 1654, 1649, 1592, 1448, 1335, 1195, 984, 762, 694 cm^{-1} ; ^1H NMR (δ in CDCl_3) 7.74 (d, $J = 16$ Hz, 2H), 7.62–7.60 (m, 4H), 7.44–7.40 (m, 6H), 7.08 (d, $J = 16$ Hz, 2H); ^{13}C NMR (δ in CDCl_3) 188.92, 143.31, 134.81, 130.49, 128.96, 128.38, 125.43; GC/MS m/z 234 (M^+), 157 ($\text{M}^+ - \text{Ph}$).