Supporting Information for
Palladium-catalyzed silylation of alcohols with hexamethyldisilane

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General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL JNM LA-500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz) or a JEOL JNM FX-400 (^{1}H, 400 MHz) spectrometer using chloroform (^{1}H and ^{13}C) as an internal standard. GC spectra were taken on Shimadzu GC-14A. Elemental analyses were performed at the Microanalytical Center, Kyoto University. Unless otherwise noted, reagents are commercially available and were used without further purification. Anhydrous DMA was purchased from Aldrich Chemical Co. and was dried further with molecular sieves 3A, which was evacuated at 260 °C for 12 h prior to use. Hexamethyldisilane was purchased from Tokyo Kasei Kogyo Co., Ltd. or Shin-Etsu Chemical Co., Ltd., and was fractionally distilled. Triphenylphosphine was purchased from Wako Pure Chemical Industries Ltd. and was recrystallized from hexane. Activated Alumina (ca. 200 mesh) was purchased from Nacalai Tesque, Inc. $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (**3a**) [1] $[PdCl(\eta^3\text{-}PhCHCHCHPh)]_2$ (**3b**),[2] and *trans*-$PdH(Cl)(PPh_3)_2$ (**5**)[3] were prepared according to the literature methods.

Silylation of Alcohols with Hexamethyldisilane. A General Procedure. To a solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (**3a**: 7.4 mg, 0.040 mmol of Pd) and PPh_3 (21 mg, 0.080 mmol) in DMA (1.0 mL) were added successively an alcohol (**2**: 0.80 mmol) and hexamethyldisilane (**1a**: 70 mg, 0.48 mmol). After stirring at 80 °C for 3 h, the resulting mixture was diluted with diethyl ether (20 mL), washed with water (10 mL x 5) and brine (10 mL), and dried over anhydrous sodium sulfate. After filtration followed by evaporation of the solvent at atmospheric pressure, the resulting mixture was filtered through an alumina plug (10 mL) using hexane (30 mL) as an eluent. Evaporation of the solvent at atmospheric pressure followed by evacuation at 35 °C under ca. 20 mmHg gave trimethylsilyl ether **4**.

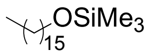

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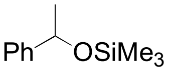
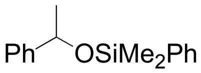
Table 1

1-(Trimethylsiloxy)hexadecane (4a).[4] A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 9 H), 0.87 (t, *J* = 7.0 Hz, 3 H), 1.19–1.28 (m, 26 H), 1.51 (quint, *J* = 6.9 Hz, 2 H), 3.55 (t, *J* = 6.7 Hz, 2 H).

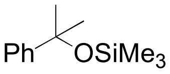


entry 2 of Table 1

1-Phenyl-1-(trimethylsiloxy)ethane (4b).[5] A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.02 (s, 9 H), 1.37 (d, *J* = 6.4 Hz, 3 H), 4.79 (q, *J* = 6.4 Hz, 1 H), 7.16 (tt, *J* = 6.7, 2.0 Hz, 1 H), 7.20–7.30 (m, 4 H).



1-[Dimethyl(phenyl)siloxy]-1-phenylethane (4'b).[6] A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.30 (s, 3 H), 0.35 (s, 3 H), 1.43 (d, *J* = 6.4 Hz, 3 H), 4.86 (q, *J* = 6.4 Hz, 1 H), 7.21–7.25 (m, 1 H), 7.27–7.33 (m, 4 H), 7.33–7.42 (m, 3 H), 7.56 (d, *J* = 7.5 Hz, 2 H).



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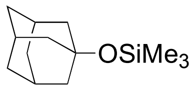
2-Phenyl-2-(trimethylsiloxy)propane (4c).[7] A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 1.53 (s, 6 H), 7.16 (t, *J* = 7.4 Hz, 1 H), 7.26 (t, *J* = 7.8 Hz, 2 H), 7.40 (d, *J* = 8.2 Hz, 2 H).



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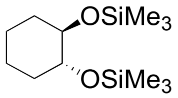
1-(Trimethylsiloxy)adamantane (4d).[8] A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.12 (s, 9 H), 1.58 (dt, *J* = 13.0, 3.1 Hz, 3 H), 1.61 (dt, *J* = 13.0, 3.1 Hz, 3 H), 1.76 (d, *J* = 3.1 Hz, 6 H), 2.07–2.13 (m, 3 H).



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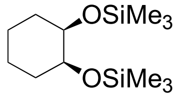
***trans*-1,2-Bis(trimethylsiloxy)cyclohexane (4e).**[9] A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 18 H), 1.12–1.33 (m, 4 H), 1.52–1.66 (m, 2 H), 1.73–1.84 (m, 2 H), 3.28–3.36 (m, 2 H).



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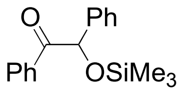
***cis*-1,2-Bis(trimethylsiloxy)cyclohexane (4f).** A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 18 H), 1.16–1.32 (m, 2 H), 1.33–1.44 (m, 2 H), 1.55–1.67 (m, 2 H), 1.67–1.76 (m, 2 H), 3.59–3.67 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.7, 22.0, 31.2, 72.5. Anal. Calcd for $C_{12}H_{28}O_2Si_2$: C, 55.32; H, 10.83. Found: C, 55.61; H, 10.93.



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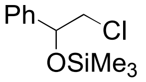
1,2-Diphenyl-2-(trimethylsiloxy)ethanone (4g).[10] A white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.10 (s, 9 H), 5.84 (s, 1 H), 7.19 (t, *J* = 7.4 Hz, 1 H), 7.23–7.32 (m, 4 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.48 (d, *J* = 7.7 Hz, 2 H), 7.98 (d, *J* = 8.1 Hz, 2 H).



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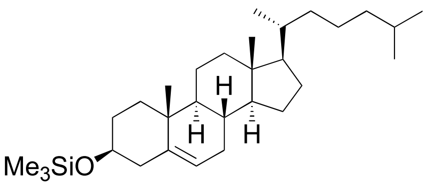
1-Chloro-2-phenyl-2-(trimethylsiloxy)ethane (4h).[11] A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 9 H), 3.58 (d, *J* = 6.3 Hz, 2 H), 4.81 (t, *J* = 6.3 Hz, 1 H), 7.27–7.37 (m, 5 H); (500Mhz, C_6D_6) δ 0.07 (s, 9 H), 3.31 (dd, *J* = 11.2, 4.0 Hz, 1 H), 3.42 (dd, *J* = 11.2, 8.2 Hz, 1 H), 4.69 (dd, *J* = 8.2, 4.0 Hz, 1 H), 7.04 (td, *J* = 7.3, 2.5 Hz, 1 H), 7.09 (t, *J* = 7.3 Hz, 2 H), 7.12–7.18 (m, 2 H).



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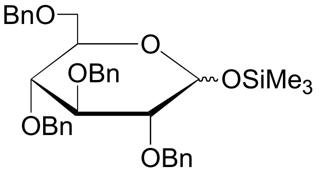
Cholesterol trimethylsilyl ether (4i). A white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.11 (s, 9 H), 0.67 (s, 3 H), 0.85 (d, *J* = 6.6 Hz, 3 H), 0.87 (d, *J* = 6.6 Hz, 3 H), 0.91 (d, *J* = 6.5 Hz, 3 H), 0.99 (s, 3 H), 0.87–1.61 (m, 21 H), 1.65–1.75 (m, 1 H), 1.76–1.88 (m, 2 H), 1.91–2.06 (m, 2 H), 2.16 (ddd, *J* = 13.4, 4.9, 2.2 Hz, 1 H), 2.29 (t, *J* = 13.4 Hz, 1 H), 3.47 (tt, *J* = 11.1, 4.8 Hz, 1 H), 5.28–5.35 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.4, 12.0, 18.9, 19.5, 21.2, 22.7, 23.0, 24.0, 24.4, 28.1, 28.4, 32.0, 32.1, 32.1, 36.0, 36.4, 36.7, 37.6, 40.0, 40.0, 42.5, 42.8, 50.4, 56.3, 56.9, 72.5, 121.4, 141.5. Anal. Calcd for $C_{30}H_{54}OSi$: C, 78.53; H, 11.86. Found: C, 78.56; H, 11.82.



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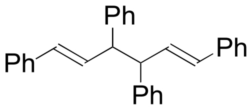
Mixture (67:33) of 1-*O*-trimethylsilyl-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside and 1-*O*-trimethylsilyl-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (4j).[12] A white solid. The data of ^{1}H and ^{13}C NMR are consistent with those reported in the literature.[11] Some peaks are assigned based on the literature.[11] ^{1}H NMR (α/β, 500 MHz, $CDCl_3$) δ 0.20/0.26 (s, 9 H), 3.42–4.08 (m, 6 H), 4.44–5.24 (m, 9 H), 7.16/7.21 (dd, *J* = 7.9/8.0, 2.0/1.9 Hz, 2 H), 7.24–7.41 (m, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.1 (α), 0.3 (β), 68.6 (α), 69.2 (β), 70.1

(α), 73.0 (α), 73.46 (α), 73.51 (β), 74.8 (β), 74.97 (β), 75.01 (β), 75.2 (α), 75.6 (α), 75.7 (β), 77.8 (α), 78.0 (β), 80.9 (α), 81.8 (α), 84.0 (β), 84.7 (β), 91.8 (α), 98.1 (β), 127.545, 127.554, 127.60, 127.66, 127.67, 127.69, 127.7, 127.8, 127.90, 127.93, 127.96, 128.00, 128.02, 128.2, 128.35, 128.37, 128.38, 128.41, 128.42, 128.43, 138.0, 138.28, 138.34, 138.4, 138.6, 138.7, 139.0. Anal. Calcd for $C_{37}H_{44}O_6Si$: C, 72.52; H, 7.24. Found as a 67:33 mixture of α- and β-isomers: C, 72.25; H, 7.41.

The Reaction of 1b with 2b in the Presence of a Stoichiometric Amount of 3b (eqn 2). To a solution of $[PdCl(\eta^3\text{-PhCHCHCHPh})]_2$ (**3b**: 134 mg, 0.400 mmol of Pd), PPh_3 (211 mg, 0.800 mmol) and 1,4-dimethoxybenzene (internal standard for GC analysis: 54.1 mg, 0.392 mmol) in DMA (10 mL) were added 1-phenylethanol (**2b**: 488 mg, 3.99 mmol) and 1,1,2,2-tetramethyl-1,2-diphenyldisilane (**1b**: 51.5 mg, 0.190 mmol). After stirring at 80 °C for 15 min, a part of the reaction mixture was subjected to ^{31}P NMR, and a broad singlet was observed at 28.1 ppm. GC analysis showed that the remaining reaction mixture after additional 45 min heating contained 1,3,4,6-tetraphenyl-1,5-hexadiene (**6b** as a mixture of diastereomers: 0.187 mmol, 94% yield based on **3b**) and 1-[dimethyl(phenyl)siloxy]-1-phenylethane (**4'b**: 0.352 mmol, 93% yield based on **1b**).



Mixture (48:52) of *dl-* and *meso-*1,3,4,6-Tetraphenyl-1,5-hexadiene (6b).[13] A colorless oil. ^{1}H NMR (*dl*/*meso*, 500 MHz, $CDCl_3$) δ 3.84–3.93 (m, 2 H), 6.39/6.20 (d, J = 15.8 Hz, 2 H), 6.53/6.31 (dd, J = 15.8, 8.1/7.8 Hz, 2 H), 7.03–7.31 (m, 20 H).

The Reaction of 1b with 2b in the Presence of a Stoichiometric Amount of 5 (eqn 3). To a solution of $PdH(Cl)(PPh_3)_2$ (**5**: 53.4 mg, 0.0800 mmol) and 1,4-dimethoxybenzene (internal standard for GC analysis: 12.0 mg, 0.0869 mmol) in DMA (2.0 mL) were added 1-phenylethanol (**2b**: 97.8 mg, 0.801 mmol) and 1,1,2,2-tetramethyl-1,2-diphenyldisilane (**1b**: 19.3 mg, 0.0713 mmol). After stirring at 0 °C for 1.5 h, the reaction mixture was analyzed by GC to contain dimethyl(phenyl)silane (**7b**: 0.0511 mmol, 72%), 1-[dimethyl(phenyl)siloxy]-1-phenylethane (**4'b**: 0.0715 mmol, 100%) and **1b** (0.00948 mmol, 13%). GC analysis of the reaction mixture after heating at 80 °C for 1 h showed that **7b** and **1b** had been completely consumed and the amount of **4'b** had increased to 0.130 mmol (182%).

References

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