Supporting Information

Versatile Dehydrogenative Alcohol Silylation Catalyzed by Cu(I)–Phosphine Complex

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Materials.

All manipulations involving air- and moisture-sensitive compounds were carried out under argon or nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and purified by the standard procedure. Dry toluene and tetrahydrofuran (THF) were purchased from Tokyo Kasei Kogyo Co., Ltd. These solvents were degassed via three freeze-pump-thaw cycles and were further dried on MS 4A. Alcohols and hydrosilanes were distilled from CaH_2 and stored on MS 4A before use. Copper(I) *tert*-butoxide,¹ *tert*-butyldiphenylsilane,² $\text{Rh}_2(\text{OCOC}_4\text{F}_7)_4$,³ and 1-bromo-3,5-di-*tert*-butyl-4-methoxybenzene⁴ were prepared according to the reported procedure. Xantphos was purchased from Strem Chemical Co. or prepared according to the published procedure.⁵ Preparation of Cu(I) catalyst solutions was carried out under nitrogen atmosphere using a VAC Nexus 2000-M glove box system.

NMR spectra were recorded on Varian Gemini 2000 (^1H : 300 MHz; ^{13}C : 75.4 MHz; ^{31}P : 121.4 MHz) spectrometer or JEOL JNM EX-400 (^{13}C : 100.4 MHz) spectrometer. Tetramethylsilane (^1H), CDCl_3 (^{13}C), and 85 % phosphoric acid (^{31}P) were employed as internal and external standards, respectively. Gas chromatographic (GC) analyses were conducted on a Shimadzu GC-14B equipped with a flame ionization detector. Infrared spectra were recorded on a Perkin-Elmer Spectrum One. Elemental analyses were performed at the Center for Instrumental Analysis Hokkaido University. Low- and High-resolution mass spectra were recorded on a JEOL JMS-700TZ mass spectrometer.

Synthesis of 4,5-Bis[bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-9,9-dimethylxanthene (**1b**)⁵

A solution of *n*-BuLi (10 mL of a 1.56 M solution in hexane, 15.6 mmol) was added to the solution of 1.08 g (5.14 mmol) of 9,9-dimethylxanthene and 2.4 mL of TMEDA in 7.8 mL of dry ether at 0°C, and the mixture was stirred for overnight. The resulting orange colored solution was cooled to –78°C, and a solution of diethyl chlorophosphite (1.51 mL, 1.63 g, 10.4 mmol) in 10 mL of THF was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. After the solvent was removed *in vacuo*, 20 mL of degassed water and 20 mL of degassed dichloromethane were added to the residual oil. After vigorous stirring, the water layer was removed by a syringe. The organic layer was washed twice with degassed water (5 mL) and dried over MgSO₄ under argon. The solvents were removed *in vacuo* to afford a pale yellow oil. The formation of 4,5-bis(diethoxyphosphino)-9,9-dimethylxanthene was checked by ³¹P NMR (150.4 ppm). This compound was used without further purification. A solution of 3,5-di-*tert*-butyl-4-methoxyphenyllithium was prepared by addition of a solution of *n*-BuLi (16.7 mL of a 1.56 M solution in hexane, 26.0 mmol) to a solution of 1-bromo-3,5-di-*tert*-butyl-4-methoxybenzene (7.83 g, 26.0 mmol) in 50 mL of dry THF at –78°C. A solution of the crude oil containing 4,5-bis(diethoxyphosphino)-9,9-dimethylxanthene in 15 mL of THF was slowly added to the solution of 3,5-di-*tert*-butyl-4-methoxyphenyllithium at –78°C. The mixture was allowed to room temperature and stirred for overnight. After the solvent was removed *in vacuo*, 10 mL of degassed water and 40 mL of degassed dichloromethane were added to the residual oil. After vigorous stirring, the organic layer was separated and dried over MgSO₄ under argon. Evaporation of the solvent gave a yellow solid, which was purified by column chromatography using argon-bubbled solvents (SiO₂, hexane : diethyl ether = 99 : 1) to give **1b** as a white solid (1.23 g, 1.07 mmol, 21 %). ¹H NMR (300 MHz, CDCl₃, δ): 1.30 (br s, 72H, –C(CH₃)₃), 1.59 (s, 6H, –CH₃), 3.66 (s, 12H, –OCH₃), 6.48 (br d, *J* = 7.2 Hz, 2H, Ar), 6.92 (t, *J* = 7.7 Hz, 2H), 7.07–7.15 (m, 8H), 7.32 (br d, *J* = 7.8 Hz, 2H, Ar). ³¹P NMR (121.4 MHz, CDCl₃, δ): –15.97; ¹³C NMR (75.4 MHz, CDCl₃, δ): 32.02 (CH₃), 32.68 (CH₃), 33.99 (C), 35.64 (C), 64.13 (CH₃), 122.69 (CH), 125.99 (CH), 128.83 (m, C), 129.08 (C), 131.15 (C), 131.19 (dd, *J* = 4.6, 6.3 Hz, CH), 132.95 (m, CH), 142.76 (t, *J* = 3.4 Hz, C), 151.47 (t, *J* = 9.2 Hz, C), 159.9 (C). IR (neat, cm^{–1}): 2957 (s), 1406 (s). APCI–MS *m/z* (% relative intensity, ion): 1170 (100, M+Na⁺). Anal. Calcd for C₇₅H₁₀₄O₅P₂: C, 78.50; H, 9.13. Found: C, 78.67; H,

9.35.

General Procedure for Dehydrogenative Silylation Catalyzed by Copper(I)-Phosphine Catalysts.

In a glove box, a solution of *t*-BuOCu (0.01 M) in toluene and a solution of a phosphine (0.01 M) were prepared in a vial tube under nitrogen. Into a Schlenk tube equipped with a magnetic stirrer bar, a two-way stop cock on its side-arm, the solution of *t*-BuOCu (0.25 mL, 0.25×10^{-2} mmol) and 0.5 mL of dry toluene was added to the solution of the phosphine (0.25 mL, 0.25×10^{-2} mmol). After being sealed with a rubber septum, the Schlenk tube was removed from the glove box and connected to an argon line. Hydrosilane **3** (1.0 mmol) was added to the catalyst solution. After the mixture was stirred for 30 min, alcohol **2** (0.5 mmol) was added to the mixture. Conversion of the reaction was checked by GLC. After the reaction was completed, the mixture subjected to column chromatography (SiO₂, hexane : ethyl acetate = 99:1~90:10) to give the corresponding silyl ether (**4**).

Spectroscopic Data for Silyl Ethers

Full spectral data of **4ba**, **4ca**, **4bb**, **4eb**, **4fc**, **4ac**, **4fd**, **4ga**, **4ha**, **4ia** and **4ka** are provided. The ¹H and ¹³C NMR spectra of **4aa**, **4ad** and **4jb** were identical with those in the literature.

1-(Triethylsilyloxy)-1-phenylethane (**4aa**).

¹H NMR (300 MHz, CDCl₃, Δ): 0.45–0.66 (m, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.91 (t, $J = 8.0$ Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 1.43 (d, $J = 6.3$ Hz, 3H, $\text{PhCH}(\text{OSi})\text{CH}_3$), 4.86 (q, $J = 6.4$ Hz, 1H, $\text{PhCH}(\text{OSi})\text{CH}_3$), 7.17–7.37 (m, 5 H, *ArH*). ¹³C NMR (75.4 MHz, CDCl₃, Δ): 4.65 (SiCH_2CH_3), 6.64 (SiCH_2CH_3), 27.14 ($\text{PhCH}(\text{OSi})\text{CH}_3$), 70.54 ($\text{PhCH}(\text{OSi})\text{CH}_3$), 125.27 (CH), 126.81 (CH), 128.14 (CH), 146.98 (C).

¹H and ¹³C NMR spectral data were in agreement with those in the literature.⁶

1-(Triethylsiloxy)decane (**4ba**).

¹H NMR (300 MHz, CDCl₃, Δ): 0.60 (q, $J = 7.9$ Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.88 (t, $J = 6.8$ Hz, 3H,

CH_2CH_2-), 0.96 (t, $J = 7.8$ Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 1.10–1.18 (br s, 14H), 1.53 (qn, $J = 6.8$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 3.59 (t, $J = 6.8$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{O}-$). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.27 ($\text{CH}_3\text{CH}_2\text{Si}$), 6.64 ($\text{CH}_3\text{CH}_2\text{Si}$), 13.98 (CH_3), 22.59 (CH_2), 25.74 (CH_2), 29.25 (CH_2), 29.40 (CH_2), 29.49 (CH_2), 29.56 (CH_2), 31.83 (CH_2), 32.85 (CH_2), 62.97 ($\text{CH}_3\text{CH}_2\text{OSi}$). IR (neat, cm^{-1}): 2955 (m), 2876 (m), 1098 (s). HRMS (m/z): $[\text{M}-\text{Et}]^+$ calcd for $\text{C}_{14}\text{H}_{31}\text{OSi}$, 243.2144; found, 243.2139.

2-(Triethylsiloxy)decane (4ca).

^1H NMR (300 MHz, CDCl_3 , Δ): 0.59 (q, $J = 7.8$ Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.88 (t, $J = 6.6$ Hz, 3H, $-\text{CH}_3$), 0.96 (t, $J = 7.8$ Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 1.13 (d, $J = 6.0$ Hz, 3H, $-\text{CH}(\text{OSi})\text{CH}_3$), 1.19–1.55 (m, 14H, $-\text{CH}_2-$), 3.77 (sxt, $J = 6.0$ Hz, 1H, $-\text{CH}_2\text{CH}(\text{OSi})\text{CH}_3$). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.78 ($-\text{SiCH}_2\text{CH}_3$), 6.75 ($-\text{SiCH}_2\text{CH}_3$), 13.98 (CH_3), 22.57 (CH_2), 23.73 (CH_2), 25.74 (CH_2), 29.20 (CH_2), 29.53 (CH_2), 29.63 (CH_2), 31.80 (CH_2), 39.75 (CH_2), 68.51 (CH_2CHOSi). IR (neat, cm^{-1}): 2926 (s), 1006 (s). HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_{36}\text{OSi}$, 272.2535; found, 272.2536.

1-(*tert*-Butyldimethylsiloxy)decane (4bb).

^1H NMR (300 MHz, CDCl_3 , Δ): 0.04 (s, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.85–0.93 (m, 12H, $-\text{C}(\text{CH}_3)_3 + -\text{CH}_2\text{CH}_3$), 1.10–1.19 (br s, 14H, $-\text{CH}_2-$), 1.49 (qn, $J = 6.6$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 3.59 (t, $J = 6.7$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{OSi}$). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): -5.43 ($-\text{OSiCH}_3$), 14.0 (CH_3), 18.27 ($-\text{C}(\text{CH}_3)_3$), 22.60 (CH_2), 25.73 (CH_2), 25.89 ($-\text{C}(\text{CH}_3)_3$), 29.27 (CH_2), 29.38 (CH_2), 29.52 (CH_2), 29.58 (CH_2), 31.85 (CH_2), 32.83 (CH_2), 63.32 (CH_2OSi). IR (neat, cm^{-1}): 2956 (m), 2926 (m), 2856 (m), 1254 (m), 1100 (s). HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_{36}\text{OSi}$, 272.2535; found, 272.2529.

1-(*tert*-Butyldimethylsiloxy)cyclohexane (4eb).

^1H NMR (300 MHz, CDCl_3 , Δ): 0.05 (s, 6H, $-\text{SiCH}_3$), 0.89 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.11–1.38 (m, 5H), 1.41–1.57 (m, 1H), 1.64–1.80 (m, 4H) 3.54–3.64 (m, 1H, CHOSi). ^{13}C NMR (100.4 MHz, CDCl_3 , Δ): -4.54 (OSiCH_3), 18.30 ($\text{C}(\text{CH}_3)_3$), 24.16 (CH_2), 25.75 (CH_2), 25.98 (CH_2), 35.95 (CH_2), 70.79 (CHOSi). IR (neat, cm^{-1}): 2930 (s), 2857 (s), 1094 (s). HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$, 214.1753; found, 214.1763.

1-(*tert*-Butyldiphenylsiloxy)-2-phenylethane (4fc).

^1H NMR (300 MHz, CDCl_3 , Δ): 1.02 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 2.85 (t, $J = 7.0$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{O}$), 3.84 (t, $J = 7.0$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{O}$), 7.12–7.44 (m, 11H, ArH), 7.56–7.62 (m, 4H, ArH). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 19.03 ($\text{C}(\text{CH}_3)_3$), 26.71 ($\text{C}(\text{CH}_3)_3$), 39.22 (PhCH_2-), 65.11 ($-\text{CH}_2\text{OSi}$), 126.16 (CH), 127.68 (CH), 128.25 (CH), 129.33 (CH), 129.62 (CH), 133.87 (C), 135.66 (CH), 139.19 (C). IR (neat, cm^{-1}): 3070 (m), 2857 (m), 1428 (m), 1105 (s), 1092 (s), 1079 (s). HRMS (m/z): $[\text{M}-^t\text{Bu}]^+$ calcd for $\text{C}_{20}\text{H}_{19}\text{OSi}$, 303.1205; found, 303.1207. Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{OSi}$: C, 79.95; H, 7.83. Found: C, 80.13; H, 8.02.

1-(*tert*-Butyldiphenylsiloxy)-1-phenylethane (4ac).

^1H NMR (300 MHz, CDCl_3 , Δ): 1.05 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.33 (d, $J = 6.3$ Hz, 3H, $-\text{CH}(\text{OSi})\text{CH}_3$), 4.84 (q, $J = 6.3$ Hz, 1H, $-\text{CH}(\text{OSi})\text{CH}_3$), 7.18–7.48 (m, 11H, ArH), 7.48–7.52 (m, 2 H, ArH), 7.69–7.76 (m, 2H, ArH). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 19.18 ($\text{C}(\text{CH}_3)_3$), 26.86 ($\text{C}(\text{CH}_3)_3$), 27.03 (CH_3), 71.80 ($-\text{CH}(\text{OSi})\text{CH}_3$), 125.45 (CH), 126.81 (CH), 127.48 (CH), 127.61 (CH), 128.14 (CH), 129.54 (CH), 129.65 (CH), 133.82 (C), 134.60 (C), 135.94 (CH), 146.61 (C). IR (neat, cm^{-1}): 3071 (w), 2857 (m), 1427 (m), 1105 (s), 1086 (s). HRMS (m/z): $[\text{M}-^t\text{Bu}]^+$ calcd for $\text{C}_{20}\text{H}_{19}\text{OSi}$, 303.1205; found, 303.1213. Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{OSi}$: C, 79.95; H, 7.83. Found: C, 80.01; H, 7.86.

1-(Triphenylsiloxy)-2-phenylethane (4fd).

^1H NMR (300 MHz, CDCl_3 , Δ): 2.88 (t, $J = 7.1$ Hz, 2H, $\text{PhCH}_2\text{CH}_2\text{O}-$), 3.98 (t, $J = 7.2$ Hz, 2H, $\text{PhCH}_2\text{CH}_2\text{O}-$), 7.12–7.60 (m, 20 H, ArH). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 39.12 (CH_2), 65.00 (CH_2), 126.21 (CH), 127.91 (CH), 128.31 (CH), 129.24 (CH), 130.06 (CH), 134.22 (C), 135.45 (CH), 138.85 (C). IR (neat, cm^{-1}): 3067 (m), 2867 (m), 1428 (m), 1114 (s), 1077 (s). HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{26}\text{H}_{24}\text{OSi}$, 380.1596; found, 380.1594. Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{OSi}$: C, 82.06; H, 6.36. Found: C, 82.18; H, 6.23.

1-(Triphenylsiloxy)-1-phenylethane (4ad).

^1H NMR (300 MHz, CDCl_3 , Δ): 1.42 (d, $J = 6.3$ Hz, 3H, $\text{ArCH}(\text{OSi})\text{CH}_3$), 5.03 (t, $J = 6.3$ Hz, 1H, $\text{ArCH}(\text{OSi})\text{CH}_3$), 7.18–7.46 (m, 14H, ArH), 7.57–7.63 (m, 6H, ArH). ^{13}C NMR (75 MHz, CDCl_3 , δ): 26.8 (ArCHCH_3), 72.00 (ArCHOSi), 125.51 (CH), 126.94 (CH), 127.84 (CH), 128.19 (CH), 130.00 (CH), 134.63 (C), 135.54 (CH), 146.03 (C).

^1H and ^{13}C NMR spectral data were in agreement with those in the literature.⁷

1-(Triethylsiloxy)-9-decene (4ga).

^1H NMR (300 MHz, CDCl_3 , Δ): 0.59 (q, $J = 7.9$ Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.95 (t, $J = 7.8$ Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 1.22–1.42 (m, 10H, $-\text{CH}_2-$), 1.52 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OSi}$), 2.03 (br q, $J = 6.9$ Hz, 2H, $\text{CH}_2=\text{CHCH}_2\text{CH}_2-$), 3.59 (t, $J = 6.8$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{OSi}-$), 4.90–5.03 (m, 2H, $\text{CH}_2=\text{CH}-$), 5.74–5.87 (m, 1H, $\text{CH}_2=\text{CH}-$). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.30 ($\text{CH}_3\text{CH}_2\text{Si}$), 6.63 ($\text{CH}_3\text{CH}_2\text{Si}$), 25.72 (CH_2), 28.83 (CH_2), 28.98 (CH_2), 29.32 (CH_2), 29.38 (CH_2), 32.84 (CH_2), 33.72 (CH_2), 62.94 (CH_2OSi), 114.14 ($\text{CH}_2=\text{CH}$), 139.30 ($\text{CH}_2=\text{CH}$). IR (neat, cm^{-1}): 2928 (s), 1641 (m), 1098 (s). HRMS (m/z): $[\text{M-Et}]^+$ calcd for $\text{C}_{14}\text{H}_{29}\text{OSi}$, 241.1988; found, 241.1984.

1-(Triethylsiloxy)-3-hexyne (4ha).

^1H NMR (300 MHz, CDCl_3 , Δ): 0.61 (q, $J = 8.0$ Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.97 (t, $J = 7.8$ Hz, 9H, SiCH_2CH_3), 1.11 (t, $J = 7.5$ Hz, 3H, $-\text{CH}_2\text{CH}_3$), 2.16 (tq, $J = 2.2, 7.5$ Hz, 2H, $\text{CH}_3\text{CH}_2\text{CC}-$), 2.38 (tt, $J = 2.3, 7.4$ Hz, 2H, $-\text{CCCH}_2\text{CH}_2\text{OSi}$), 3.69 (t, $J = 7.4$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{OSi}$). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.21 ($\text{CH}_3\text{CH}_2\text{Si}$), 6.55 ($\text{CH}_3\text{CH}_2\text{Si}$), 12.26 ($\text{CH}_3\text{CH}_2\text{CC}$), 14.02 ($\text{CH}_3\text{CH}_2\text{CC}$), 23.00 ($\text{CH}_2\text{CH}_2\text{O}-$), 62.00 ($-\text{CH}_2\text{CH}_2\text{OSi}$), 76.09 ($\text{CH}_3\text{CH}_2\text{CC}$), 82.84 ($-\text{CCCH}_2\text{CH}_2\text{O}-$). IR (neat, cm^{-1}): 2956 (s), 2877 (s), 1101 (s); Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{OSi}$: C, 67.86; H, 11.39. Found: C, 67.68; H, 11.32. HRMS (m/z): $[\text{M}-\text{Et}]^+$ calcd for $\text{C}_{10}\text{H}_{19}\text{OSi}$, 183.1205; found, 183.1191.

5-(Triethylsiloxy)pentan-2-one (4ia).

^1H NMR (300 MHz, CDCl_3 , Δ): 0.59 (q, $J = 7.9$ Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.95 (t, $J = 8.0$ Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 1.74–1.85 (m, 2H $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OSi}$), 2.16 (s, 3H, $\text{CH}_3\text{CO}-$), 2.53 (t, $J = 7.2$ Hz, 2H, $-\text{COCH}_2\text{CH}_2-$), 3.62 (t, $J = 6.3$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{OSi}$). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.09 (SiCH_2CH_3), 6.49 (SiCH_2CH_3), 26.66 (CH_2), 29.70 (CH_2), 39.87 (CH_2), 61.63 ($-\text{COCH}_2\text{CH}_2\text{OSi}$), 208.95 ($\text{CH}_3\text{COCH}_2-$). IR (neat, cm^{-1}): 2955 (s), 2877 (s), 1717 (s), 1096 (s). HRMS (m/z): $[\text{M}-\text{Et}]^+$ calcd for $\text{C}_9\text{H}_{19}\text{O}_2\text{Si}$, 187.1154; found, 187.1153.

1-(*tert*-Butyldimethylsiloxy)-2-methoxyethane (4jb).

^1H NMR (300 MHz, CDCl_3 , Δ): 0.08 (s, 6H, $-\text{SiCH}_3$), 0.90 (s, 9H, $-\text{SiC}(\text{CH}_3)_3$), 3.38 (s, 3H, $\text{CH}_3\text{O}-$), 3.47 (t, $J = 5.1$ Hz, 2H, $\text{CH}_3\text{OCH}_2\text{CH}_2-$), 3.77 (t, $J = 5.4$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{OSi}$). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): -5.43 ($-\text{SiCH}_3$), 18.31 ($-\text{SiC}(\text{CH}_3)_3$), 25.86 ($-\text{SiC}(\text{CH}_3)_3$), 59.05 ($\text{CH}_3\text{O}-$), 62.62 (CH_2), 74.12 (CH_2).

^1H and ^{13}C NMR spectral data were in agreement with those in the literature.⁸

Silylation of Geraniol (2k) with Triethylsilane (3a) on a Large Scale

A Schlenk tube equipped with a magnetic stirrer bar, a two-way stop cock on its side-arm, was charged with *t*-BuOCu (6.8 mg, 0.050 mmol) and Xantphos (28.9 mg, 0.050 mmol). After the reaction tube was sealed with a rubber septum, it was removed from the glove box and connected with a argon line. Triethylsilane (6.44 g 55.3 mmol) was injected in the Schlenk tube and the resultant mixture was stirred for 30 min to give yellow solution. Geraniol (7.73 g, 50.1 mmol) was added to the mixture by syringe over 30 min. Vigorous hydrogen gas evolution was occurred during the addition of the alcohol. The reaction tube was kept in a water bath at 24 °C, as the reaction is exothermic. After the addition was completed, the reaction mixture further stirred for 30 min. The reaction mixture was distilled under reduced pressure to give a desired product (90 Pa, 45°C, 12.55 g, 93 %). A fore-running portion of the distillate was purified with column chromatography (SiO_2 , hexane : ethyl acetate = 97 : 3) to give a additional amount of the silyl ether (0.544 g, 4 %).

Geranyl Triethylsilyl Ether (4ka).

^1H NMR (300 MHz, CDCl_3 , Δ): 0.62 (t, J = 8.0 Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.97 (t, J = 8.0 Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 1.60 (s, 3H, $-\text{CH}_3$), 1.63 (s, 3H, $-\text{CH}_3$), 1.68 (s, 3H, $-\text{CH}_3$), 1.96–2.15 (m, 4H, $-\text{CH}_2\text{CH}_2-$), 4.18 (d, J = 6.6 Hz, 2H, $\text{C}=\text{CHCH}_2\text{OSi}$), 5.10 (br t, J = 6.9 Hz, 1H, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2-$), 5.33 (br t, J = 6.5 Hz, 1H, $-(\text{CH}_3)\text{C}=\text{CHCH}_2\text{OSi}-$). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.33 ($-\text{SiCH}_2\text{CH}_3$), 6.60 ($-\text{SiCH}_2\text{CH}_3$), 16.13 (CH_3), 17.48 (CH_3), 25.52 (CH_3), 26.21 (CH_2), 39.45 (CH_2), 59.73 (CH_2), 124.15 (CH), 124.22 (CH), 131.57 (C), 137.21 (C); IR (neat, cm^{-1}): 2877 (s), 1062 (s). HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_{32}\text{OSi}$, 268.2222; found, 268.2230. Anal. Calcd for $\text{C}_{16}\text{H}_{32}\text{OSi}$: C, 71.57; H, 12.01. Found: C, 71.45; H, 11.86.

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4,5-Bis[bis (3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-9,9-dimethylxanthene (1b)

Original File: Sep 28 04
Date: Sep 28 04
Comments: STANDARD IN OBSERVE
ObsNuc: 1H
ExMode: NMR
ObsFreq: 299.99 MHz
ObsSet: 1.0 MHz
ObsTime: 995.0017 Hz
Point: 16384
Frequency(Span): 4500.45 Hz
Scan: 128
AcqTime: 3.4983 s
PD: 1.502 s
Pulse1: 0.0 µs
Temperature: 29.0 °C
Solvent: CDCl₃
Reference: 0.0 ppm
Broad Factor: 0.1312 Hz
RinIn: 18
Printed: 2004/Sep/29 20:28:08
Operator:

Original File: Oct 15 04
Date: Oct 15 04
Comments: C13 Standard Observe
Stick+none Tune=0.4 Match=0.4
ObsNuc: 13C
ExMode: NMR
ObsFreq: 76.43 MHz
ObsSet: 1.0 MHz
ObsTime: 996.3672 Hz
Point: 32768
Frequency(Span): 18751.73 Hz
Scan: 12544
AcqTime: 1.5992 s
PD: 1.501 s
Pulse1: 0.0 µs
Temperature: 29.0 °C
Solvent: CDCl₃
Reference: 77.0 ppm
Broad Factor: 0.2863 Hz
RinIn: 30
Printed: 2004/Oct/24 10:03:52
Operator:

```

Comment
      STANDARD IN OBSERVE

ObsMod      HI
ExMod       NONE
ObsFreq      299.96 MHz
ObsSet      -1.0 kHz
ObsFine      995.0017 Hz
Point        16384
Frequency(Span) 4500.45 Hz
Scan         16
AcqTime      3.4983 s
PD           1.502 A
Puls1        6.0 μs
Temperature   29.0 °C
Solvent      CDCl3
Reference     0.0 ppm
Broad. Factor 0.25 Hz
RGain         24
Printed      2004/Sep/29 17:06:09
Operator

```

1-(Triethylsiloxy)decane (4ba)

2-(Triethylsiloxy)decane (4ca)

1-(*tert*-Butyldimethylsiloxy)decane (4bb)

STANDARD IN OBSERVE

ObsNuc ¹H
ExMode NON
ObsFreq 299.99 MHz
ObsSet -1.0 Hz
ObsFine 995.0047 Hz
Point 16364
Frequency(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse 6.0 μs
Temperature 28.0 °C
Reference CDCl₃
Broad Factor 7.25 ppm
Min 12
Printed 2004/Jul/31 13:27:13
Operator

Comment
C13 Standard Observe
Stick=none Tune=6.4 Match=0.4

ObsNuc ¹³C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 Hz
ObsFine 995.2672 Hz
Point 32768
Frequency(Span) 16761.72 Hz
Scan 64
AcqTime 1.4992 s
PD 1.501 s
Pulse 6.0 μs
Temperature 29.0 °C
Reference CDCl₃
Broad Factor 77.0 ppm
Min 30
Printed 2004/Jul/31 13:09:55
Operator

1-(*tert*-Butyldimethylsiloxy)cyclohexane (4b)

2-53

STANDARD IN OBSERVE

ObsMod: 1H
ExMode: WDR
ObsFreq: 299.96 MHz
ObsSet: -1.0 Hz
ObsPine: 996.0047 Hz
Point: 16384
Frequency (Span): 4950.45 Hz
Scan: 16
AcqTime: 3.4983 s
PD: 1.562 s
Pulse1: 6.0 μs
IrrMod: 1H
Probed: 1H
Instrument: Varian UNITY
Pulse Program:
Gradient Program:
Temperature: 25.0 °C
Solvent: CDCl3
Reference: 0.0 ppm
Broad Factor: 0.25 Hz
Window: Exponential
RGain: 24
Operator: _____

Ph-CH₂-OSiPh₂^tBu

7.694, 7.689, 7.684, 7.679, 7.674, 7.669, 7.664, 7.659, 7.654, 7.649, 7.644, 7.639, 7.634, 7.629, 7.624, 7.619, 7.614, 7.609, 7.604, 7.599, 7.594, 7.589, 7.584, 7.579, 7.574, 7.569, 7.564, 7.559, 7.554, 7.549, 7.544, 7.539, 7.534, 7.529, 7.524, 7.519, 7.514, 7.509, 7.504, 7.499, 7.494, 7.489, 7.484, 7.479, 7.474, 7.469, 7.464, 7.459, 7.454, 7.449, 7.444, 7.439, 7.434, 7.429, 7.424, 7.419, 7.414, 7.409, 7.404, 7.399, 7.394, 7.389, 7.384, 7.379, 7.374, 7.369, 7.364, 7.359, 7.354, 7.349, 7.344, 7.339, 7.334, 7.329, 7.324, 7.319, 7.314, 7.309, 7.304, 7.299, 7.294, 7.289, 7.284, 7.279, 7.274, 7.269, 7.264, 7.259, 7.254, 7.249, 7.244, 7.239, 7.234, 7.229, 7.224, 7.219, 7.214, 7.209, 7.204, 7.199, 7.194, 7.189, 7.184, 7.179, 7.174, 7.169, 7.164, 7.159, 7.154, 7.149, 7.144, 7.139, 7.134, 7.129, 7.124, 7.119, 7.114, 7.109, 7.104, 7.099, 7.094, 7.089, 7.084, 7.079, 7.074, 7.069, 7.064, 7.059, 7.054, 7.049, 7.044, 7.039, 7.034, 7.029, 7.024, 7.019, 7.014, 7.009, 7.004, 6.999, 6.994, 6.989, 6.984, 6.979, 6.974, 6.969, 6.964, 6.959, 6.954, 6.949, 6.944, 6.939, 6.934, 6.929, 6.924, 6.919, 6.914, 6.909, 6.904, 6.899, 6.894, 6.889, 6.884, 6.879, 6.874, 6.869, 6.864, 6.859, 6.854, 6.849, 6.844, 6.839, 6.834, 6.829, 6.824, 6.819, 6.814, 6.809, 6.804, 6.799, 6.794, 6.789, 6.784, 6.779, 6.774, 6.769, 6.764, 6.759, 6.754, 6.749, 6.744, 6.739, 6.734, 6.729, 6.724, 6.719, 6.714, 6.709, 6.704, 6.699, 6.694, 6.689, 6.684, 6.679, 6.674, 6.669, 6.664, 6.659, 6.654, 6.649, 6.644, 6.639, 6.634, 6.629, 6.624, 6.619, 6.614, 6.609, 6.604, 6.599, 6.594, 6.589, 6.584, 6.579, 6.574, 6.569, 6.564, 6.559, 6.554, 6.549, 6.544, 6.539, 6.534, 6.529, 6.524, 6.519, 6.514, 6.509, 6.504, 6.499, 6.494, 6.489, 6.484, 6.479, 6.474, 6.469, 6.464, 6.459, 6.454, 6.449, 6.444, 6.439, 6.434, 6.429, 6.424, 6.419, 6.414, 6.409, 6.404, 6.399, 6.394, 6.389, 6.384, 6.379, 6.374, 6.369, 6.364, 6.359, 6.354, 6.349, 6.344, 6.339, 6.334, 6.329, 6.324, 6.319, 6.314, 6.309, 6.304, 6.299, 6.294, 6.289, 6.284, 6.279, 6.274, 6.269, 6.264, 6.259, 6.254, 6.249, 6.244, 6.239, 6.234, 6.229, 6.224, 6.219, 6.214, 6.209, 6.204, 6.199, 6.194, 6.189, 6.184, 6.179, 6.174, 6.169, 6.164, 6.159, 6.154, 6.149, 6.144, 6.139, 6.134, 6.129, 6.124, 6.119, 6.114, 6.109, 6.104, 6.099, 6.094, 6.089, 6.084, 6.079, 6.074, 6.069, 6.064, 6.059, 6.054, 6.049, 6.044, 6.039, 6.034, 6.029, 6.024, 6.019, 6.014, 6.009, 6.004, 5.999, 5.994, 5.989, 5.984, 5.979, 5.974, 5.969, 5.964, 5.959, 5.954, 5.949, 5.944, 5.939, 5.934, 5.929, 5.924, 5.919, 5.914, 5.909, 5.904, 5.899, 5.894, 5.889, 5.884, 5.879, 5.874, 5.869, 5.864, 5.859, 5.854, 5.849, 5.844, 5.839, 5.834, 5.829, 5.824, 5.819, 5.814, 5.809, 5.804, 5.799, 5.794, 5.789, 5.784, 5.779, 5.774, 5.769, 5.764, 5.759, 5.754, 5.749, 5.744, 5.739, 5.734, 5.729, 5.724, 5.719, 5.714, 5.709, 5.704, 5.699, 5.694, 5.689, 5.684, 5.679, 5.674, 5.669, 5.664, 5.659, 5.654, 5.649, 5.644, 5.639, 5.634, 5.629, 5.624, 5.619, 5.614, 5.609, 5.604, 5.599, 5.594, 5.589, 5.584, 5.579, 5.574, 5.569, 5.564, 5.559, 5.554, 5.549, 5.544, 5.539, 5.534, 5.529, 5.524, 5.519, 5.514, 5.509, 5.504, 5.499, 5.494, 5.489, 5.484, 5.479, 5.474, 5.469, 5.464, 5.459, 5.454, 5.449, 5.444, 5.439, 5.434, 5.429, 5.424, 5.419, 5.414, 5.409, 5.404, 5.399, 5.394, 5.389, 5.384, 5.379, 5.374, 5.369, 5.364, 5.359, 5.354, 5.349, 5.344, 5.339, 5.334, 5.329, 5.324, 5.319, 5.314, 5.309, 5.304, 5.299, 5.294, 5.289, 5.284, 5.279, 5.274, 5.269, 5.264, 5.259, 5.254, 5.249, 5.244, 5.239, 5.234, 5.229, 5.224, 5.219, 5.214, 5.209, 5.204, 5.199, 5.194, 5.189, 5.184, 5.179, 5.174, 5.169, 5.164, 5.159, 5.154, 5.149, 5.144, 5.139, 5.134, 5.129, 5.124, 5.119, 5.114, 5.109, 5.104, 5.099, 5.094, 5.089, 5.084, 5.079, 5.074, 5.069, 5.064, 5.059, 5.054, 5.049, 5.044, 5.039, 5.034, 5.029, 5.02

1-(*tert*-Butyldiphenylsiloxy)-1-phenylethane (4ac)

1-(Triphenylsiloxy)-2-phenylethane (4fd)

Comment
STANDARD 1H OBSERVE

ObsNuc H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequency (Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse 6.0 μs
IrrNuc H
ProbeHead
Instrument Varian UNITY
Pulse Program
Gradient Program
Temperature 29.0 °C
Solvent CDCl₃
Reference 0.0 ppm
Broad Factor 0.25 Hz
Window Exponential
RGain 29
Operator

1-(Triphenylsiloxy)-1-phenylethane (4ad)

1-(Triethylsiloxy)-9-decene (4ga)

Solvent: CDCl₃
 Ambient temperature
 GEMINI-30088 "varian"
 PULSE SEQUENCE
 Relax: delay 1.502 sec
 Pulse 45.0 degrees
 Acq. time 3.498 sec
 Width 4500.5 Hz
 96 repetitions
 OBSERVE H1, 299.9534190 MHz
 DATA PROCESSING
 FT size 32768
 Total time 6 minutes

Solvent: CDCl₃
 Ambient temperature
 GEMINI-30088 "varian"
 PULSE SEQUENCE
 Relax: delay 1.501 sec
 Pulse 45.0 degrees
 Acq. time 1.499 sec
 Width 10761.7 Hz
 128 repetitions
 OBSERVE C13, 76.4233428 MHz
 DECOUPLE H1, 299.9544952 MHz
 Power 38 dB
 continuously on
 MULTIFID modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
 Total time 6 minutes

1-(Triethylsiloxy)-3-hexyne (4ha)

Comment
STANDARD 1H OBSERVE

ObsNuc 1H
ExMode NON
ObsFreq 298.96 MHz
ObsSet -1.0 kHz
ObsPine 995.0047 Hz
Point 16384
Frequency (Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse 6.0 μs
Temperature 29.0 °C
Solvent CDCl₃
Reference 0.0 ppm
Broad Factor 0.25 Hz
RGain 16
Printed 2004/Sep/28 15:28:43
Operator

Comment
C13 Standard Observe
StickName Tame6.4 Match=0.4

ObsNuc 13C
ExMode NON
ObsFreq 125.43 MHz
ObsSet -1.0 kHz
ObsPine 995.0047 Hz
Point 32768
Frequency (Span) 18701.73 Hz
Scan 256
AcqTime 1.4992 s
PD 1.501 s
Pulse 6.0 μs
Temperature 29.0 °C
Solvent CDCl₃
Reference 77.0 ppm
Broad Factor 0.2893 Hz
RGain 30
Printed 2004/Sep/30 14:57:01
Operator

5-(Triethylsiloxy)pentan-2-one (4ia)

Comment
STANDARD 1H OBSERVE

ObsNuc 1H
ExMode NMR
ObsFreq 299.95 MHz
ObsSet -1.0 MHz
ObsPine 996.0047 Hz
Point 16394
Frequency (Span) 4500.45 Hz
Scan 16
AcqTime 0.4983 s
PD 1.502 s
Pulse 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad Factor 0.25 Hz
RGain 18
Printed 2004/Nov/05 17:12:38
Operator

STANDARD 1H OBSERVE

Comment
C13 Standard Observe
Stick-none Tune=6.4 Match=0.4

ObsNuc 13C
ExMode NMR
ObsFreq 75.43 MHz
ObsSet -1.0 MHz
ObsPine 996.3672 Hz
Point 32758
Frequency (Span) 15761.73 Hz
Scan 208
AcqTime 1.4992 s
PD 1.501 s
Pulse 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 77.0 ppm
Broad Factor 0.25 Hz
RGain 30
Printed 2004/Nov/05 17:46:38
Operator

C13 Standard Observe

1-(*tert*-Butyldimethylsiloxy)-2-methoxyethane (4jb)

Comment
STANDARD 1H OBSERVE

ObsRuc 1H
ExMode 1H
ObsFreq 299.96 MHz
ObsSet -1.0 MHz
ObsFine 976.0247 Hz
Point 16384
Frequency (Span) 4590.45 Hz
Scan 16
AcqTime 3.5863 s
PD 1.502 s
Pulse 6.0 μ s
Temperature 29.0 °C
Solvent CDCl₃
Reference 0.0 ppm
Broad Factor 0.1373 Hz
RGain 19
Printed 2004/Oct/14 18:14:08
Operator

Comment
113 Standard Observe
Stickphone Tune=6.4 Match=0.4

ObsRuc 13C
ExMode 13C
ObsFreq 75.43 MHz
ObsSet -1.0 MHz
ObsFine 32768.3672 Hz
Point 16384
Frequency (Span) 18761.73 Hz
Scan 16384
AcqTime 1.4992 s
PD 1.501 s
Pulse 6.0 μ s
Temperature 29.0 °C
Solvent CDCl₃
Reference 77.0 ppm
Broad Factor 0.2053 Hz
RGain 30
Printed 2004/Oct/15 11:53:08
Operator

Geranyl triethylsilyl ether (4ka)

Comment
STANDARD 1H OBSERVE

ObsHuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 MHz
ObsFine 995.0047 Hz
Point 16384
Frequency (Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse 6.0 μs
Temperature 29.0 °C
Solvent CDCl₃
Reference 0.0 ppm
Broad Factor 0.25 Hz
RGain 18
Printed 2004/Nov/05 17:42:18
Operator

ObsHuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 MHz
ObsFine 995.3672 Hz
Point 32768
Frequency (Span) 18761.73 Hz
Scan 64
AcqTime 1.4992 s
PD 1.501 s
Pulse 6.0 μs
Temperature 29.0 °C
Solvent CDCl₃
Reference 77.0 ppm
Broad Factor 0.25 Hz
RGain 30
Printed 2004/Nov/04 18:37:04
Operator