Supporting Information

Gold(I)–Phosphine Catalyst for the Highly Chemoselective Dehydrogenative Silylation of Alcohols

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Materials.

All reactions were carried out under argon or nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and purified by the standard procedure. Dry toluene, tetrahydrofuran (THF), dichloromethane were purchased from Tokyo Kasei Kogyo Co. Other solvents were distilled from CaH₂ and further dried on MS4A under argon atmosphere.

Alcohols and hydrosilanes were distilled from CaH₂ and stored on MS 4A before use. AuCl(SMe₂) was prepared according to the published procedure.¹ Xantphos was purchased from Strem Chemical Co. or prepared according to the published procedure.² Triphenylphosphine, bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)propane (dppp), bis(diphenylphosphino)butane (dppb), bis(diphenylphosphino)ferrocene (dppf) were purchased from commercial suppliers. Bis[2-(diphenylphosphino)phenyl] ether (DPEphos)² and 1,8-bis(diphenylphosphino)dibenzofuran (DBFphos)^{2,3} were prepared according to the published procedure.

NMR spectra were recorded on Varian Gemini 2000 (¹H: 300 MHz; ¹³C: 75.4 MHz; ³¹P: 121.4 MHz) spectrometer or JEOL JNM EX-400 (¹³C: 100.4 MHz) spectrometer. Tetramethylsilane (¹H), C₆D₆ (³¹C), CDCl₃ (³¹C), and 85 % phosphoric acid (³¹P) 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 and mass spectrometry were performed at the Center for Instrumental Analysis Hokkaido University.

General Procedure for Silylation of Alcohols with *in situ* Prepared Au(I) complexes (for Table 1).

AuCl(SMe₂) (0.005 mmol, 2.9 mg) and a ligand (0.005 mmol) were placed in the reaction vial connected with argon line. The flask was vacuumed and filled with argon. Then, dry dichloroethane (0.5 mL) was added with stirring. After stirring for 1 h at room temperature, the solvent was removed under reduced pressure and filled with argon again. Dry dichloroethane (0.5 mL) was added the vial to solve the resultant solid. 2-Phenylethanol (0.5 mmol, 61 mg), triethylsilane (1.0 mmol, 116.3 mg) were added dropwise by a syringe with stirring. The yield of silyl ether was determined by GC using 1,4-diisopropylbenzene as an internal standard.

Preparation of AuCl(xantphos).

AuCl(SMe₂) (0.30 mmol, 88.2 mg) and Xantphos (0.3 mmol, 173.5 mg) was placed in 20 mL round bottomed flask. The flask was vacuumed and filled with argon and dry THF (3.0 mL) was added with stirring. After stirring for 1 h, hexane (3.0 mL) was added to the reaction mixture and resultant white suspension was collected by filtration. The crude white solid was dissolved in hot benzonitrile. The solution was cooled to room temperature and then to -5°C. The resultant crystal was collected and washed by cold ether, dried under vacuum. To remove remaining benzonitrile in the crystal, it was dissolved in chloroform and precipitated by dropping into cold ether. After stirring for 1 h, the resultant white solid was collected by filtration, washed with cold ether (2 mL x 2) and dried under vacuum for 16 h to give the product as a white solid (211.2 mg, 87 %).

¹H NMR (300 MHz, CDCl₃, δ): 1.66 (s, 6 H), 6.57–6.65 (m, 2H), 7.11 (t, $J = 7.7$ Hz, 2H), 7.21–7.37 (m, 12H), 7.41–7.51 (m, 8H), 7.56 (dd, $J = 1.3, 7.7$ Hz, 2H). Pseudo-triplets due to AXX' spin system were observed in ¹³C NMR. ¹³C NMR (75.4 MHz, CDCl₃, δ): 28.0 (CH₃), 35.7 (C) 119.3 (t, $^2J_{P-C} + ^4J_{P'-C} = 40.0$ Hz, C), 124.7 (t, $^2J_{P-C} + ^4J_{P'-C} = 6.3$ Hz, CH), 127.0 (CH), 128.7 (t, $^2J_{P-C} + ^4J_{P'-C} = 11.3$ Hz, CH), 130.3 (CH), 131.7 (CH), 133.0 (t, $^2J_{P-C} + ^4J_{P'-C} = 46.4$ Hz, C), 133.9 (t, $^2J_{P-C} + ^4J_{P'-C} = 17.2$ Hz, CH), 134.1 (t, $^2J_{P-C} + ^4J_{P'-C} = 3.4$ Hz, C), 155.1 (t, $^2J_{P-C} + ^4J_{P'-C} = 10.3$ Hz, C). ³¹P NMR (121.4 MHz, CDCl₃, δ): 28.8. HRMS (m/z): [M-Cl]⁺ calcd for C₃₉H₃₂OP₂Au, 775.15939, found, 775.15682.

General Procedure for Silylation.

AuCl(xantphos) (4.1 mg, 0.005 mmol) was placed in the reaction vial connected with vacuum line. The flask was vacuumed and filled with argon and a solvent (0.5 mL) was added with stirring. An

alcohol (0.5 mmol), a hydrosilane (1.0 mmol) were added to the vial at the reaction temperature. After the reaction was complete, the reaction mixture was directly subjected to column chromatography (SiO₂, Hexane/EtOAc (100:0–95:5) to give the corresponding silyl ether. Purity of the product was checked by GC and NMR.

Spectroscopic Data for Silyl Ethers

Full spectral data of all unknown compounds are described. ¹H and/or ¹³C NMR spectra of known compounds were identical with those in the literature. ¹H and ¹³C NMR spectra of all compounds and ³¹P NMR of AuCl(xantphos) are provided (S9–S28).

1-(Triethylsiloxy)-2-phenylethane.

¹H NMR (300 MHz, CDCl₃, δ): 0.57 (q, J = 7.9 Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.93 (t, J = 7.8 Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 2.84 (t, J = 7.4 Hz, 2H), 3.80 (t, J = 7.4 Hz, 2H), 7.15–7.32 (m, 5H). ¹³C NMR (75.4 MHz, CDCl₃, δ): 4.2 (CH₂), 6.6 (CH₃), 39.6 (CH₂), 64.2 (CH₂), 126.2 (CH), 128.3 (CH), 129.2 (CH), 139.1 (C).

¹³C NMR spectral data were in agreement with those in the literature.⁴

1-(Triethylsiloxy)decane.

¹H NMR (300 MHz, CDCl₃, δ): 0.60 (q, J = 8.0 Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.88 (t, J = 6.9 Hz, 3H, CH_3CH_2-), 0.96 (t, J = 8.0 Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 1.20–1.38 (br s, 14H), 1.53 (quintet, J = 6.9 Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$), 3.59 (t, J = 6.9 Hz, 2H, $-\text{CH}_2\text{CH}_2\text{O}-$). ¹³C NMR (75.4 MHz, CDCl₃, δ): 4.3 (CH₃CH₂Si), 6.6 (CH₃CH₂Si), 14.0 (CH₃), 22.6 (CH₂), 25.7 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 31.8 (CH₂), 32.8 (CH₂), 63.0 (CH₃CH₂OSi).

¹H and ¹³C NMR spectral data were in agreement with those in the literature.⁵

2-(Triethylsiloxy)decane.

¹H NMR (300 MHz, CDCl₃, δ): 0.59 (q, J = 8.0 Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.88 (t, J = 6.7 Hz, 3H,

CH_3CH_2-), 0.96 (t, $J = 8.0$ Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 1.13 (d, $J = 6.0$ Hz, 3H, $-\text{CH}(\text{OSi})\text{CH}_3$), 1.20-1.52 (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): 4.8 ($-\text{SiCH}_2\text{CH}_3$), 6.7 ($-\text{SiCH}_2\text{CH}_3$), 14.0 (CH_3), 22.6 (CH_2), 23.7 (CH_2), 25.8 (CH_2), 29.2 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 39.8 (CH_2), 68.5 (CH_2CHOSi).

^1H and ^{13}C NMR spectral data were in agreement with those in the literature.⁵

2-Methyl-1-phenyl-2-(triethylsiloxy)propane

^1H NMR (300 MHz, CDCl_3 , Δ): 0.54 (q, $J = 8.0$ Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.90 (t, $J = 7.8$ Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 1.20 (s, 6H), 2.72 (s, 2H), 7.18–7.28 (m, 5H). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 6.6 (CH_2), 6.9 (CH_3), 29.6 (CH_2), 51.2 (CH_2), 73.6 (C), 126.0 (CH), 127.6 (CH), 130.8 (CH), 139.0 (C). IR (neat, cm^{-1}): 3030 (w), 2955 (m), 1040 (s). HRMS (m/z): $[\text{M}-\text{Et}]^+$ calcd for $\text{C}_{14}\text{H}_{23}\text{OSi}$, 235.1518; found, 235.1516.

1-(Triethylsiloxy)-4-methylbenzene.

^1H NMR (300 MHz, CDCl_3 , Δ): 0.72 (q, 6H, $J = 8.0$ Hz, $-\text{SiCH}_2\text{CH}_3$), 0.99 (t, 9H, $J = 7.8$ Hz, $-\text{SiCH}_2\text{CH}_3$), 2.27 (s, 3H, ArCH_3), 6.75 (d, 2H, $J = 8.4$ Hz ArH), 7.02 (d, 2H, $J = 8.4$ Hz ArH). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.8 (CH_2), 6.5 (CH_3), 20.4 (CH_3), 119.7 (CH), 129.9 (CH), 130.5 (C), 153.3 (C). IR (neat, cm^{-1}): 2956 (m), 2878 (m), 1508 (s), 1255 (s). HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{13}\text{H}_{22}\text{OSi}$, 222.1440; found, 222.1443.

1-(Dimethylphenylsiloxy)-1-phenylethane.

^1H NMR (300 MHz, CDCl_3 , Δ): 0.28 (s, 3H, $-\text{SiCH}_3$), 0.33 (s, 3H, $-\text{SiCH}_3$), 1.42 (d, $J = 6.3$ Hz, CHCH_3), 4.85 (q, 6.3 Hz, $-\text{CHCH}_3$), 7.16–7.41 (m, 8H), 7.53–7.59 (m, 2H). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): -1.5 (CH_3), -1.0 (CH_3), 26.7 (CH_3), 71.0 (CH), 125.5 (CH), 127.0 (CH), 127.8 (CH), 128.2 (CH), 129.6 (CH), 133.6 (CH), 138.2 (C), 146.3 (C). IR (neat, cm^{-1}): 3069 (m), 2973 (m), 1088 (s). HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{16}\text{H}_{20}\text{OSi}$, 256.1283; found, 256.1286.

1-(*tert*-Butyldimethylsiloxy)-2-phenylethane.

^1H NMR (300 MHz, CDCl_3 , Δ): -0.02 (s, 6 H, $-\text{SiCH}_3$), 0.87 (s, 9 H), 2.82 (t, 2 H, $J = 7.2$ Hz), 3.80 (t, 2 H, $J = 7.2$ Hz), 7.19 – 7.35 (m, 5 H). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): -5.6 (CH_3), 18.2 (C), 25.8 (CH_3), 39.5 (CH_2), 64.6 (CH_2), 126.2 (CH), 128.3 (CH), 129.2 (CH), 139.2 (C). IR (neat, cm^{-1}): 3029 (s), 2929 (m), 2857 (m), 1096 (s). HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{13}\text{H}_{21}\text{OSi}$, 221.1362 ; found, 221.1364 .

(*tetr*-Butyldimethylsiloxy)cyclohexane.

^1H NMR (300 MHz, CDCl_3 , Δ): 0.05 (s, 6H, $-\text{SiCH}_3$), 0.89 (s, 9H, CCH_3), 1.10 – 1.39 (m, 5H), 1.40 – 1.48 (m, 1H), 1.65 – 1.80 (m, 4H), 3.59 (dt, 1H, $J = 3.6, 9.2$ Hz). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): -4.8 (CH_3), 18.1 (C), 24.0 (CH_2), 25.6 (CH_2), 25.8 (CH_2), 35.8 (CH_2), 70.8 (CH). IR (neat, cm^{-1}): 2930 (m), 2857 (m), 1094 (s). HRMS (m/z): $[\text{M}]^+$ calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$, 214.1753 ; found, 214.1748 .

1-(Triphenylsiloxy)-2-phenylethane.

^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): 39.1 (CH_2), 65.0 (CH_2), 126.2 (CH), 127.9 (CH), 128.3 (CH), 129.2 (CH), 130.1 (CH), 134.2 (C), 135.4 (CH), 138.9 (C).

^1H and ^{13}C NMR spectral data were in agreement with those in the literature.⁵

1-(*tetr*-Butyldiphenylsiloxy)-2-phenylethane.

^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): 19.0 ($\text{C}(\text{CH}_3)_3$), 26.7 ($\text{C}(\text{CH}_3)_3$), 39.2 (PhCH_2-), 65.1 ($-\text{CH}_2\text{OSi}$), 126.2 (CH), 127.7 (CH), 128.3 (CH), 129.3 (CH), 129.6 (CH), 133.9 (C), 135.7 (CH), 139.2 (C).

^1H and ^{13}C NMR spectral data were in agreement with those in the literature.⁵

1-(Triethylsiloxy)-9-decene.

^1H NMR (300 MHz, CDCl_3 , Δ): 0.60 (q, $J = 7.9$ Hz, 6H, $-\text{SiCH}_2\text{CH}_3$), 0.96 (t, $J = 8.0$ Hz, 9H, $-\text{SiCH}_2\text{CH}_3$), 1.22–1.42 (m, 10H, $-\text{CH}_2-$), 1.43–1.60 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OSi}$), 2.04 (br q, $J = 7.0$ Hz, 2H, $\text{CH}_2=\text{CHCH}_2\text{CH}_2-$), 3.59 (t, $J = 6.6$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{OSi}-$), 4.90–5.03 (m, 2H, $\text{CH}_2=\text{CH}-$), 5.73–5.89 (m, 1H, $\text{CH}_2=\text{CH}-$). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.3 ($\text{CH}_3\text{CH}_2\text{Si}$), 6.6 ($\text{CH}_3\text{CH}_2\text{Si}$), 25.7 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 32.8 (CH_2), 33.7 (CH_2), 63.0 (CH_2OSi), 114.2 (CH_2), 139.3 (CH).

^1H and ^{13}C NMR spectral data were in agreement with those in the literature.⁵

1-(Triethylsiloxy)-10-undecyne.

^1H NMR (300 MHz, CDCl_3 , Δ): 0.60 (q, 6H, $J = 7.9$ Hz, $-\text{SiCH}_2\text{CH}_3$), 0.96 (t, 9H, $J = 8.0$ Hz, $-\text{SiCH}_2\text{CH}_3$), 1.24–1.34 (br, 8H), 1.34–1.45 (m, 2H), 1.47–1.58 (m, 4H), 1.94 (t, 1H, $J = 2.6$ Hz, HCCCH_2-), 2.18 (dt, 2H, $J = 2.5, 7.0$ Hz, $-\text{HCCCH}_2\text{CH}_2-$), 3.59 (t, 2H, $J = 6.6$ Hz, $-\text{CH}_2\text{CH}_2\text{OSi}$). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.2 (CH_2), 6.6 (CH_3), 18.2 (CH_2), 25.7 (CH_2), 28.4 (CH_2), 28.6 (CH_2), 28.9 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 32.8 (CH_2), 62.9 (CH_2), 68.0 (CH), 84.7 (C). IR (neat, cm^{-1}): 3315 (m), 2931 (m), 2120 (w), 1094 (s). HRMS (m/z): $[\text{M}-\text{C}_2\text{H}_5]^+$ calcd for $\text{C}_{15}\text{H}_{29}\text{OSi}$, 253.1988; found, 253.1983.

1-(Triethylsiloxy)-3-chloropropane.

^1H NMR (300 MHz, CDCl_3 , Δ): 0.61 (q, 6H, $J = 7.7$ Hz, $-\text{SiCH}_2\text{CH}_3$), 0.96 (t, 9H, $J = 8.0$ Hz, $-\text{SiCH}_2\text{CH}_3$), 1.97 (qui, 2H, $J = 6.1$ Hz, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 3.66 (q, 2H, $J = 6.5$ Hz, CH_2), 3.75 (q, 2H, $J = 5.8$ Hz, CH_2). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.2 (CH_2), 6.6 (CH_3), 35.4 (CH_2), 41.7 (CH_2), 59.1 (CH_2). IR (neat, cm^{-1}): 2956 (m), 2877 (m), 1100 (s). HRMS (m/z): $[\text{M}-\text{C}_2\text{H}_5]^+$ calcd for $\text{C}_7\text{H}_{16}\text{ClOSi}$, 179.0659; found, 179.0651.

1-(Triethylsiloxy)-3-bromopropane.

^1H NMR (300 MHz, CDCl_3 , Δ): 0.61 (q, 6H, $J = 7.8$ Hz, $-\text{SiCH}_2\text{CH}_3$), 0.97 (t, 9H, $J = 8.0$ Hz, $-\text{SiCH}_2\text{CH}_3$), 2.05 (qui, 2H, $J = 6.2$ Hz, $-\text{CH}_2\text{CH}_2\text{CH}_2-$), 3.52 (q, 2H, $J = 6.5$ Hz, CH_2), 3.74 (q, 2H, $J = 5.7$ Hz, CH_2). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.2 (CH_2), 6.6 (CH_3), 30.5 (CH_2), 35.5 (CH_2), 60.1 (CH_2). IR (neat, cm^{-1}): 2955 (m), 2876 (m), 1098 (s). HRMS (m/z): $[\text{M}-\text{C}_2\text{H}_5]^+$ calcd for $\text{C}_7\text{H}_{16}\text{BrOSi}$, 223.0153; found, 223.0155.

4-[(Triethylsiloxy)methyl]benzaldehyde.

^1H NMR (300 MHz, CDCl_3 , Δ): 0.67 (q, 6H, $J = 8.0$ Hz, $-\text{SiCH}_2\text{CH}_3$), 0.99 (t, 9H, $J = 8.0$ Hz, $-\text{SiCH}_2\text{CH}_3$), 4.82 (s, 2H, $\text{ArCH}_2\text{O}-$), 7.51 (d, 2H, $J = 7.8$ Hz, ArH), 7.86 (d, 2H, $J = 8.4$ Hz, ArH), 10.0 (s, 1H, ArCHO). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.3 (CH_2), 6.6 (CH_3), 64.1 (CH_2), 126.4 (CH), 129.9 (CH), 135.4 (C), 148.7 (C), 192.3 (CH). IR (neat, cm^{-1}): 2955 (m), 2876 (m), 1695 (s), 1089 (s). EI-MS m/z (relative intensity, ion): 250 (2.0%, M^+), 221 (100%, $\text{M}-\text{C}_2\text{H}_5$). Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2\text{Si}$: C, 67.15, H, 8.86. Found: C, 67.04, H, 8.83.

4-(Triethylsiloxy)-2-cyclohexenone.

^1H NMR (300 MHz, CDCl_3 , Δ): 0.66 (q, 6H, $J = 7.9$ Hz, $-\text{SiCH}_2\text{CH}_3$), 0.99 (t, 9H, $J = 7.8$ Hz, $-\text{SiCH}_2\text{CH}_3$), 2.02 (ddt, $J = 4.4, 9.1, 12.8$ Hz, 1H), 2.17–2.28 (m, 1H), 2.28–2.41 (m, 1H), 2.53–2.64 (m, 1H), 4.49–4.57 (m, 1H), 5.90–5.96 (m, 1H), 6.82–6.88 (m, 1H). ^{13}C NMR (75.4 MHz, CDCl_3 , Δ): 4.6 (CH_2), 6.6 (CH_3), 32.9 (CH_2), 35.5 (CH_2), 66.7 (CH), 128.8 (CH), 154.1 (CH), 199.1 (C). IR (neat, cm^{-1}): 2955 (m), 2877 (m), 1687 (s), 1095 (s). ESI-MS m/z (relative intensity, ion): 226 (0.2%, M^+), 197 (100%, $\text{M}-\text{C}_2\text{H}_5$). Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_2\text{Si}$: C, 63.66, H, 9.80. Found: C, 63.41, H, 9.76.

17-Hydroxy-21-(triethylsiloxy)pregn-4-ene-3,20-dione.

^1H NMR (300 MHz, CDCl_3 , δ): 0.66 (q, 6H, $J = 7.9$ Hz, $-\text{SiCH}_2\text{CH}_3$), 0.71 (s, 3H), 0.98 (t, 9H, $J = 7.8$ Hz, $-\text{SiCH}_2\text{CH}_3$), 1.04–1.18 (m, 1H), 1.19 (s, 3H, $-\text{CH}_3$), 1.21–1.93 (m, 12H), 1.99–2.09 (m, 1H), 2.30–2.51 (m, 4H), 2.60–2.73 (m, 1H), 3.71 (s, 1H, $-\text{CH}_3$), 4.42 (d, 1H, $J = 17.7$ Hz, one of $-\text{COCH}_2\text{OSi}$), 4.52 (d, 1H, $J = 17.7$ Hz, one of $-\text{COCH}_2\text{OSi}$), 5.74 (s, 1H, $-\text{COCH}=\text{C}$). ^{13}C NMR (75.4 MHz, C_6D_6 , δ): 5.2 (CH_2), 7.3 (CH_3), 15.6 (CH_3), 17.2 (CH_3), 21.1 (CH_2), 24.2 (CH_2), 31.4 (CH_2), 32.5 (CH_2), 32.9 (CH_2), 34.5 (CH_2), 35.1 (CH_2), 35.9 (CH), 36.1 (CH_2), 38.7 (C), 48.5 (C), 50.8 (CH), 53.7 (CH), 69.4 (CH_2), 91.0 (C), 124.8 (CH), 169.8 (C), 198.4 (C), 209.4 (C). IR (neat, cm^{-1}): 3464 (br), 2951 (m), 1714 (m), 1652 (s). HRMS–ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{44}\text{NaO}_4\text{Si}$, 483.2907; found, 483.2892.

***N*-[(1,1-Dimethylethoxy)carbonyl]-*O*-(triethylsilyl)-*D*-serine methyl ester**

Optical purity was determined by GC using a chiraldex G-TA chiral capillary column. No racemization occurred in silylation. ^1H NMR (300 MHz, CDCl_3 , δ): 0.57 (q, 6H, $J = 8.0$ Hz, $-\text{SiCH}_2\text{CH}_3$), 0.93 (t, 9H, $J = 7.8$ Hz, $-\text{SiCH}_2\text{CH}_3$), 1.46 (s, 9H), 3.75 (s, 3H), 3.83 (dd, 1H, $J = 3.0, 9.9$ Hz, $-\text{OCHHCHN}-$), 4.05 (dd, 1H, $J = 2.2, 9.9$ Hz, $-\text{OCHHCHN}-$), 4.31–4.42 (br d, 1H), 5.32–5.48 (br d, 1H). ^{13}C NMR (75.4 MHz, CDCl_3 , δ): 4.0 (CH_2), 6.4 (CH_3), 28.2 (CH_2), 52.2 (CH_3), 55.5 (CH), 63.4 (CH_2), 79.8 (C), 155.6 (C), 171.4 (C). IR (neat, cm^{-1}): 3452 (br), 2955 (m), 2878 (m), 1752 (m), 1717 (s), 1163 (s). HRMS–ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{31}\text{NO}_5\text{SiNa}$, 356.1869; found, 356.1866. Anal. Calcd for $\text{C}_{15}\text{H}_{31}\text{NO}_5\text{Si}$: C, 54.02, H, 9.37, N, 4.20. Found: C, 53.89, H, 9.37, N, 4.17.

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Date: Apr 19 05
Comment: STANDARD III OBSERVE

Ch-Nuc	¹ H
ExMode	NOV
ObsFreq	299.96 MHz
ObsP1	-1.0 kHz
ObsP2	995.0047 Hz
Point	16384
Frequency (Span)	4560.45 Hz
Solvent	D ₂ O
AcqTime	3.4983 s
PD	1.502 A
PulseP	6.0 A/s
Temperature	29.0 °C
Solvent	D ₂ O
Reference	0.0 ppm
Recoupl. Factor	0.25 Hz
Gain	30
Printed	2005/Apr/19 16:19:53
Operator

Comment
P-31 STANDARD PARAMETERS
PHOSPHATE REGION

ObsNuc 31p
ExchNuc NMR
ObsFreq 121.42 MHz
ObsSet 0.9 kHz
ObsFwh 0.7709 Hz
Point 16384
Frequency (Span) 10000.01 Hz
Scan 200
AcqTime 1.6 s
PD 1.4 s
Pulse1 6.8 μ s
IrrNuc H
Preshifted
Instrument Varian UNITY
Pulse Program
Gradient Program
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad Factor 0.3052 Hz
Window Exponential
Ratio 30
Operator

³¹P NMR

AuCl(xatphos)

1-(Triethylsiloxy)-2-phenylethane.

Date: Apr 20 05
 Comment: STANDARD 1H OBSERVE
 ObsAcq: 41
 ExMode: NMR
 ObsFreq: 299.06 MHz
 ObsSet: -1.0 kHz
 ObsP1: 995.0017 Hz
 Point: 16384
 Frequency (Span): 1500.15 Hz
 Scan: 16
 AcqTime: 3.1983 s
 PD: 1.502 s
 Pulse1: 0.0 μs
 Temperature: 29.0 °C
 Solvent: CDCl₃
 Reference: 0.0 ppm
 Broad Factor: 0.25 Hz
 RGain: 18
 Printed: 2005/Apr/20 16:57:35
 Operator:

Date: Apr 20 05
 Comment: C13 Standard Observe
 S11-Kemone Tune-0.1 Match-0.1
 ObsAcq: 41
 ExMode: NMR
 ObsFreq: 75.43 MHz
 ObsSet: -1.0 kHz
 ObsP1: 996.3672 Hz
 Point: 32768
 Frequency (Span): 18761.73 Hz
 Scan: 181
 AcqTime: 1.1002 s
 PD: 1.501 s
 Pulse1: 0.0 μs
 Temperature: 29.0 °C
 Solvent: CDCl₃
 Reference: 77.0 ppm
 Broad Factor: 0.25 Hz
 RGain: 20
 Printed: 2005/Apr/20 22:24:02
 Operator:

2-(Triethylsiloxy)decane

Comment
STANDARD 1H OBSERVE

ObsNuc 1H
Etdole NMR
ObsFreq 299.96 MHz
ObsSet -1.0 Hz
ObsPine 996.0047 Hz
Point 16384
Frequency (Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse 6.0 μ s
IrrNuc 1H
ProbedNuc 1H
Instrument Varian UNITY
Pulse Program
Gradient Program
Solvent CDCl₃
Reference 0.0 ppm
Broad Factor 0.25 Hz
Window Exponential
Gain 13

Stick: none Tune=6.4 Match=0.4

ObsNuc 13C
Etdole NMR
ObsFreq 75.43 MHz
ObsSet -1.0 Hz
ObsPine 996.3672 Hz
Point 32768
Frequency (Span) 18761.73 Hz
Scan 544
AcqTime 1.4992 s
PD 1.501 s
Pulse 6.0 μ s
IrrNuc 13C
ProbedNuc 13C
Instrument Varian UNITY
Pulse Program
Gradient Program
Solvent CDCl₃
Reference 77.0 ppm
Broad Factor 0.2963 Hz
Window Exponential
Gain 30

Date: Apr 17 05
 Comment: STANDARD IN OBSERVE
 Name: 2
 Pulse: 220
 ObsFreq: 299.99 MHz
 ObsSel: 13C
 ObsPrg: 10000
 ObsTime: 4.000 s
 AcqTime: 1.000 s
 Temp: 29.0 C
 Solvent: CDCl3
 Reference: 0.0 ppm
 RelaxFactor: 0.25 Hz
 Scan: 14
 Process: 2005/04/13 21:49:05
 Operator:

2-Methyl-1-phenyl-2-(triethylsiloxy)propane

Date: Apr 12 05
 Comment: C13 Standard Reference
 Stickname: 2-methyl-1-phenyl-2-(triethylsiloxy)propane
 Name: 2
 Pulse: 220
 ObsFreq: 125.76 MHz
 ObsSel: 13C
 ObsPrg: 10000
 ObsTime: 4.000 s
 AcqTime: 1.000 s
 Temp: 29.0 C
 Solvent: CDCl3
 Reference: 0.0 ppm
 RelaxFactor: 0.25 Hz
 Scan: 20
 Process: 2005/04/13 09:21:13
 Operator:

1-(Triethylsiloxy)-4-methylbenzene

Comment
STANDARD 1H OBSERVE

ObsNuc	1H
LabDate	2008
ObsFreq	500.136 MHz
ObsSet	-1.0 kHz
ObsTime	955.0547 Hz
Point	16384
Frequency(Span)	4500.45 Hz
Scan	16
AcqTime	3.4983 s
P0	1.502 s
Pulse1	6.0 μs
Temperature	29.0 °C
Solvent	CDCl3
Reference	0.0 ppm
Broad Factor	0.25 Hz
Resin	12
Printed	2004/Nov/13 18:18:25
Operator

Comment
C13 Standard Observe
Stick-figure Tune=0.4 Match=0.4

ObsNuc	13C
LabDate	2008
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsTime	996.3672 Hz
Point	32768
Frequency(Span)	18751.73 Hz
Scan	64
AcqTime	1.4992 s
P0	1.501 s
Pulse1	6.0 μs
Temperature	29.0 °C
Solvent	CDCl3
Reference	77.0 ppm
Broad Factor	0.25 Hz
Resin	30
Printed	2004/Nov/13 18:35:51
Operator

CC(C)(c1ccccc1)OSi(C)(C)c2ccccc2

Date Jan 9 04
 Comment STANDARD 1H OBSERVE

ObsMod 1H
 ObsFreq 299.96 MHz
 ObsMod -1.0 kHz
 ObsPnt 996.0047 Hz
 Point 10584
 Frequency (Span) 4500.46 Hz
 Scan 18
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse 6.0 μs
 LyrPhs 0
 ProbeHead
 Instrument Varian UNITY
 Pulse Program
 Gradient Program 29.0 °C
 Temperature
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad Factor 0.25 Hz
 Window Exponential
 Rollin 19

Operator

1-(*tert*-Butyldimethylsiloxy)-2-phenylethane.

Date Rev 6 04
 Comment C13 Standard Observe
 StickName: Ima-6.1 Match-0.4

ObsMod 13C
 ObsFreq 125.76 MHz
 ObsMod -1.0 kHz
 ObsPnt 996.0047 Hz
 Point 32768
 Frequency (Span) 14076.73 Hz
 Scan 23520
 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
 Rollin 30
 Printed 2004/Dec/25 11:25:18
 Operator

(*tetr*-Butyldimethylsiloxy)cyclohexane.

c1ccccc1CCOSi(c2ccccc2)(c2ccccc2)c2ccccc2

CC(C)(C)Si(OCc1ccccc1)(c2ccccc2)c3ccccc3

Operator

```

Date          Apr 29 05
Comment
  C13 Standard Observed
  Stick/Noise Time=6.4 Match=0.4

ObsNuc      13C
ExpMode      NMR
ObsFreq      75.43 MHz
P1           1.0 kHz
ObsF1nu      990.3672 Hz
Point        32768
Freq (Spun)  18761.73 Hz
Solv         DMS
AcqTime      1.4692 s
PD           1.501 s
Pulse1       8.0 s
Temperature  29.9 °C
Solvent      CDCl3
Reference    77.0 ppm
Broad. Factor 0.25 Hz
29.99999999
Printed      2005/Apr/29 22:10:51
Operator

```

Date: Dec 25 04
 Comment: STANDARD 1H OBSERVE
 ObsRuc: HJ
 ExDate: MMH
 ObsPrg: 299.96 MHz
 ObsSet: -1.0 kHz
 ObsFlt: 996.0617 Hz
 Point: 10384
 Frequency (Span): 4000.45 Hz
 Scan: 10
 AcqTime: 3.4963 s
 PD: 1.562 s
 Pulse1: 6.0 μs
 Temperature: 29.0 °C
 Solvent: CDCl3
 Reference: 0.0 ppm
 Bond Factor: 0.25 Hz
 Blot: 18
 Printed: 2004/Dec/25 11:21:50
 Operator:

1-(Triethylsiloxy)-9-decene.

Date: Dec 25 04
 Comment: C13 Standard Observe
 StickName: Toluene-2-Methyl-0.4
 ObsRuc: UC
 ExDate: MMH
 ObsPrg: 75.43 MHz
 ObsSet: -1.0 kHz
 ObsFlt: 996.3672 Hz
 Point: 32708
 Frequency (Span): 18761.73 Hz
 Scan: 698
 AcqTime: 1.4992 s
 PD: 1.561 s
 Pulse1: 6.0 μs
 Temperature: 29.0 °C
 Solvent: CDCl3
 Reference: 77.0 ppm
 Bond Factor: 0.25 Hz
 Blot: 30
 Printed: 2004/Dec/25 11:58:24
 Operator:

ClCCCCOSi(C)(C)C

STANDARD

OBSERVE

δ / ppm

Chemical Shift Range (δ , ppm)	Integration Value(s)
~7.8	1.00
3.8 - 3.6	3.7720, 3.7328, 3.7306, 2.0026, 3.6641, 3.6621, 3.6111, 2.0462
2.05 - 1.9	2.0065, 1.9952, 1.9451, 1.9449, 2.0
~1.0	2.0026, 2.0462
~0.0	2.0

```

Date          Jun 21 05
Comment       C13 Standard Observed
              Stickman TuneB.4 Match=0.4

ObsName      HIC
ExpName      NONE
ObsFreq      75.43 MHz
ObsRef       +1.0 kHz
ObsOffset     996.36172 Hz
Point         32768
Frequency (Spun) 18761.73 Hz
Scan         120
AcqTime      1.4992 s
PQ           1.501 s
PulseLen     6.0  $\mu$ s
Temperature   29.0 C
Solvent       CDCl3
Reference    77.0 ppm
Bromd.Factor 0.2863 Hz
Gain         32000
Printed      2005/Jun/21 20:18:19
Operator

```

BrCCCCOSi(C)(C)C

```

Date           Mar 12 05
Comment
  C13 Standard Observed
  Stick=none Tune=6.4 Match=0.4

ObsNuc      13C
ExpMode      NON
ObsFreq      75.43 MHz
ObsSet       -1.0 kHz
Offset       996.3672 Hz
Point        32768
Frequency (Span) 18761.73 Hz
Scan         45
AcqTime      1.4992 s
P1           1.501 s
P2           6.0 s
Temperature  29.0 C
Solvent      CDCl3
Reference    77.0 ppm
Broad Factor 0.25 Hz
Scan         30
Printed      2005/Mar/12 19:24:03
Operator

```

Date Sep 4 04
 Comment STANDARD 1H OBSERVE
 ObsNuc 1H
 ExMode NOM
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsLine 995.0047 Hz
 Point 16334
 Frequency (Span) 4500.45 Hz
 Scan 16
 AcqTime 3.4583 s
 PD 1.502 s
 Pulse 6.0 μs
 Temperature 25.0 °C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad Factor 0.1373 Hz
 RGain 12
 Printed 2004/Nov/18 12:34:05
 Operator

4-[(Triethylsiloxy)methyl]benzaldehyde.

Original File: Sep 4 04
 Date Sep 4 04
 Comment C13 Standard Observe
 Stick-nuclei Tune=6.4 Match=0.4
 ObsNuc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsLine 995.0047 Hz
 Point 32768
 Frequency (Span) 18761.73 Hz
 Scan 1024
 AcqTime 1.4962 s
 PD 1.502 s
 Pulse 6.0 μs
 Temperature 25.0 °C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad Factor 0.2853 Hz
 RGain 20
 Printed 2004/Nov/18 12:32:22
 Operator

CC(C)O[Si](C)(C)C1=CC=C(C(=O)O)C=C1

```
ObsNuc      1H
EdMode      NOM
ObsFreq      299.96 MHz
ObsSet      -1.0 kHz
ObsF1        995.0047
Point        16384
Frequency (Span) 4500.45 Hz
Scan         16
AcqTime      3.4983 s
PD           1.502 s
Pulse        6.0 p.s.
Temperature  29.0 °C
Solvent      CDCl3
Reference    0.0 ppm
Broad, Factor 0.25 Hz
RUnin        12
Printed      2004/Sep/04 19:48:12
Operator
```

```
ObsNuc      13C
ExMode      NON
ObsFreq      75.43 MHz
ObsRef      -1.0 kHz
ObsFine      996.3672 Hz
Point        32768
Frequency(Span) 18761.73 Hz
Scan         640
AcqTime      1.4992 s
FID          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/Sep/04 19:49:44
Operator
```

Chemical structure of compound 10: A steroid derivative with a ketone at C3, a double bond at C4, and a side chain at C17 consisting of a ketone, a hydroxyl group, and a triethylsilyl ether group.

Original File:
Date Apr 19 05
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4

ObsNuc	¹³ C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	0.0 kHz
ObsF1	3.1672 Hz
Point	32768
Frequency (Span)	18761.73 Hz
Scan	12000
AcqTime	1.4992 s
PD	1.501 s
Pulse1	6.0 μ s
Temperature	29.0 $^{\circ}$ C
Solvent	Benzene
Reference	128.5 ppm
Broad.Factor	0.2863 Hz
RGain	28
Printed	2005/Apr/30 14:26:33
Operator

N-[(1,1-Dimethylethoxy)carbonyl]-*O*-(triethylsilyl)-*D*-serine methyl ester