Supporting Information

Stereoselective Preparation of 1-Siloxy-1-Alkenylcopper Species by 1,2 C^{sp2}-to-O Silyl Migration of Acylsilane

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General. *N,N*-Dimethylformamide (DMF) was distilled from calcium hydride under reduced pressure. Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in CDCl_3 and chemical shifts (δ) were quoted in parts per million from tetramethylsilane for ^1H and CDCl_3 for ^{13}C spectroscopy. IR absorptions are reported in cm^{-1} .

Preparation of acylsilanes 1. According to the literature procedure,¹ the acylsilanes **1** were prepared by triphenylsilylation of 1,3-dithianes, followed by the hydrolysis of the resulting 2-triphenylsilyl-1,3-dithianes with chloramine T.

Triphenyl(3-phenylpropanoyl)silane (1a): mp 86.5-89.5 °C; IR (KBr) 3069, 3045, 3023, 1637, 1428, 1389, 1110, 758, 745, 736, 699; ^1H NMR 2.83 (t, $J = 7.4$ Hz, 2H), 3.05 (t, $J = 7.5$ Hz, 2H), 7.04 (d, $J = 6.6$ Hz, 2H), 7.11-7.27 (m, 3H), 7.33-7.50 (m, 9H), 7.52-7.59 (m, 6H); ^{13}C NMR 28.3, 52.1, 125.9, 128.2, 128.3, 128.4, 130.3, 131.1, 136.1, 141.3, 242.1. Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{OSi}$: C, 82.61; H, 6.16. Found: C, 82.39; H, 6.24.

Butanoyltriphenylsilane (1b): mp 106-109.5 °C; IR (KBr) 3066, 3053, 2961, 2929, 2871, 1641, 1427, 1111, 746, 699, 677; ^1H NMR 0.80 (t, $J = 7.4$ Hz, 3H), 1.52 (tq, $J = 7.3, 7.3$ Hz, 2H), 2.71 (t, $J = 7.1$ Hz, 2H), 7.32-7.54 (m, 9H), 7.56-7.62 (m, 6H); ^{13}C NMR 13.7, 15.6, 52.6, 128.2, 130.2, 131.4, 136.1, 243.3. Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{OSi}$: C, 79.95; H, 6.71. Found: C, 79.97; H, 6.79.

Triphenylpropanoylsilane (1c): mp 111-115 °C; IR (KBr) 3067, 2971, 2932, 1644, 1428, 1110, 1091, 745, 699; ^1H NMR 0.96 (t, $J = 7.1$ Hz, 3H), 2.75 (q, $J = 7.1$ Hz, 2H), 7.32-7.54 (m, 9H), 7.55-7.65 (m, 6H); ^{13}C NMR 6.2, 44.0, 128.2, 130.2, 131.4, 136.1, 243.2. Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{OSi}$: C, 79.70; H, 6.37. Found: C, 79.38; H, 6.49.

Acetyltriphenylsilane (1d): mp 125-127 °C (lit.² 125-126 °C); IR (KBr) 3065, 3006, 2997, 1646, 1483, 1427, 1340, 1111, 749, 739, 712, 699; ^1H NMR 2.40 (s, 3H), 7.35-7.51

(m, 9H), 7.55-7.63 (m, 6H); ^{13}C NMR 38.0, 128.2, 130.3, 131.1, 136.1, 242.2. Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{OSi}$: C, 79.42; H, 6.00. Found: C, 79.19; H, 6.16.

(3-Phenethyl-4-phenylbutanoyl)triphenylsilane (1e): IR (neat) 3067, 3025, 2923, 2854, 1643, 1428, 1111, 738, 698; ^1H NMR 2.51 (d, $J = 4.8$ Hz, 4H), 2.54-2.63 (m, 1H), 2.67 (d, $J = 4.9$ Hz, 2H), 6.96-7.50 (m, 25H); ^{13}C NMR 36.2, 40.0, 53.7, 125.9, 128.1, 128.2, 129.2, 130.2, 131.2, 136.1, 140.3, 242.9. Anal. Calcd for $\text{C}_{35}\text{H}_{32}\text{OSi}$: C, 84.63; H, 6.49. Found: C, 84.22; H, 6.54.

Typical experimental procedure for the copper(I) *tert*-butoxide-promoted reaction of acylsilanes 1 with allylic, methyl, benzyl, and tributylstannyl halides 5. CuI (76 mg, 0.40 mmol) and DMF (0.6 mL) were placed in a flask under argon and cooled to 0 °C. After addition of lithium *tert*-butoxide (0.1 M in THF, 0.44 mL, 0.44 mmol), the mixture was stirred at 25 °C for 30 min. A DMF (0.7 mL) solution of the acylsilane **1a** (79 mg, 0.20 mmol) was added and the mixture was stirred for 30 min. A DMF (0.7 mL) solution of methallyl chloride **5a** (36 mg, 0.40 mmol) was added to the reaction mixture, which was further stirred for 30 min at 25 °C. The mixture was diluted with hexane and applied to a filter pad of Celite to remove copper salts. The pad was washed with hexane and CH_2Cl_2 . The organic solvent was removed under reduced pressure and residue was purified by PTLC (hexane : AcOEt = 9 : 1, v/v) to give **6a** (56 mg, 63%).

Typical Experimental Procedure for the Pd(0) catalyzed coupling of the alkenylcopper species with aryl and alkenyl halides 7. Lithium *tert*-butoxide (0.1 M in THF, 0.44 mL, 0.44 mmol) was added to a DMF (0.6 mL) suspension of CuI (76 mg, 0.40 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (7 mg, 0.006 mmol) at 0 °C under argon. After stirring for 30 min at 25 °C, a DMF (0.7 mL) solution of the acylsilane **1a** (79 mg, 0.20 mmol) was added and the mixture was stirred for 30 min. A DMF (0.7 mL) solution of iodobenzene **7a** (82 mg, 0.40 mmol) was added to the reaction mixture, which was further stirred for 30 min at 25 °C. Similar workup described above gave **6k** (67 mg, 71%).

Characterization data for the enol silyl ethers 6.

(Z)-2-Methyl-6-phenyl-4-(triphenylsilyloxy)-1,4-hexadiene (6a): IR (neat) 3069, 3050, 3026, 3001, 2908, 1672, 1428, 1352, 1188, 1158, 1117, 1012, 997, 736, 712, 698; ^1H NMR 1.54 (s, 3H), 2.68 (s, 2H), 3.33 (d, $J = 7.1$ Hz, 2H), 4.64 (s, 1H), 4.70 (dt, $J = 0.7$, 7.1 Hz, 1H), 4.74 (s, 1H), 7.00 (d, $J = 7.1$ Hz, 2H), 7.09-7.24 (m, 3H), 7.31-7.49 (m, 9H), 7.59-7.71 (m, 6H); ^{13}C NMR 22.1, 31.8, 44.9, 109.4, 113.1, 125.5, 127.8, 128.2, 128.3, 130.1, 134.2, 135.5, 141.8, 141.9, 148.5. Anal. Calcd for $\text{C}_{31}\text{H}_{30}\text{OSi}$: C, 83.36; H, 6.77. Found: C, 83.55; H, 6.85.

(Z)- 6-Phenyl-4-(triphenylsilyloxy)-1,4-hexadiene (6b): IR (neat) 3069, 3026, 2897, 1672, 1494, 1428, 1351, 1158, 1118, 996, 912, 734, 698; ^1H NMR 2.74 (d, $J = 6.6$ Hz, 2H), 3.33 (d, $J = 7.0$ Hz, 2H), 4.68 (t, $J = 7.1$ Hz, 1H), 4.89 (d, $J = 17.0$ Hz, 1H), 4.94 (d, $J = 11.0$ Hz, 1H), 5.69 (ddt, $J = 10.2$, 17.0, 6.8 Hz, 1H), 7.00 (d, $J = 7.1$ Hz, 2H), 7.08-7.24 (m, 3H), 7.30-7.49 (m, 9H), 7.58-7.73 (m, 6H); ^{13}C NMR 31.7, 40.8, 108.5, 116.9, 125.5, 127.9, 128.2, 128.3, 130.2, 134.1, 134.3, 135.4, 141.7, 149.3. Anal. Calcd for $\text{C}_{30}\text{H}_{28}\text{OSi}$: C, 83.29; H, 6.52. Found: C, 82.90; H, 6.49.

A mixture of (Z)-6-methyl-1-phenyl-3-(triphenylsiloxy)-2,5-heptadiene and (Z)-3,3-dimethyl-6-phenyl-4-(triphenylsiloxy)-1,4-hexadiene (85 : 15) (6c): IR (neat) 3068, 3025, 3000, 2911, 1672, 1590, 1494, 1452, 1428, 1357, 1331, 1147, 1118, 996, 711; ^1H NMR 1.14 (s, 0.9H), 1.32 (s, 2.55H), 1.60 (s, 2.55H), 2.68 (d, $J = 7.0$ Hz, 1.7H), 3.06 (d, $J = 7.1$ Hz, 0.3H), 3.35 (d, $J = 7.1$ Hz, 1.7H), 4.66 (t, $J = 7.1$ Hz, 0.85H), 4.72 (t, $J = 7.1$ Hz, 0.15H), 4.89 (dd, $J = 1.2$, 10.7 Hz, 0.15H), 4.95 (dd, $J = 1.2$, 17.5 Hz, 0.15H), 5.06 (t, $J = 7.1$ Hz, 0.85H), 5.88 (dd, $J = 10.6$, 17.6 Hz, 0.15H), 6.84 (d, $J = 6.8$ Hz, 0.3H), 7.01 (d, $J = 6.8$ Hz, 1.7H), 7.08-7.23 (m, 3H), 7.31-7.46 (m, 9H), 7.60-7.70 (m, 6H); ^{13}C NMR 17.5, 25.6, 25.9, 31.7, 32.7, 35.3, 43.0, 105.0, 107.3, 111.6, 119.9, 125.5, 127.7, 127.8, 128.0, 128.1, 128.4, 129.9, 130.1, 133.8, 134.2, 134.7, 135.4, 135.5, 141.9, 145.9, 150.0. Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{OSi}$: C, 83.43; H, 7.00. Found: C, 83.70; H, 6.97.

(Z)-1-Phenyl-3-(triphenylsiloxy)-2-butene (6d): mp 68.5-69.0 °C; IR (neat) 3067, 3050, 3022, 2997, 2912, 1678, 1427, 1380, 1332, 1281, 1218, 1149, 1118, 1068, 1011, 996, 745, 698 ; ¹H NMR 1.73 (s, 3H), 3.39 (d, *J* = 7.1 Hz, 2H), 4.65 (t, *J* = 7.2 Hz, 1H), 7.03-7.27 (m, 5H), 7.33-7.49 (m, 9H), 7.62-7.71 (m, 6H); ¹³C NMR 23.1, 31.8, 108.2, 125.5, 127.9, 128.2, 128.4, 130.2, 134.3, 135.4, 142.0, 147.2. Anal. Calcd for C₂₈H₂₆OSi: C, 82.71; H, 6.45. Found: C, 82.88; H, 6.36.

(Z)-1,4-Diphenyl-2-(triphenylsiloxy)-2-butene (6e): IR (neat) 3063, 3028, 2917, 1670, 1428, 1147, 1118, 1106, 1010, 997, 755, 740, 714, 698; ¹H NMR 3.29 (s, 2H), 3.34 (d, *J* = 7.3 Hz, 2H), 4.54 (t, *J* = 7.1 Hz, 1H), 6.93-7.00 (m, 4H), 7.08-7.23 (m, 6H), 7.30-7.50 (m, 9H), 7.56-7.64 (m, 6H); ¹³C NMR 31.7, 42.8, 110.1, 125.5, 126.1, 127.85, 127.89, 128.1, 128.3, 129.2, 130.2, 134.0, 135.5, 137.8, 141.6, 150.2. Anal. Calcd for C₃₄H₃₀OSi: C, 84.60; H, 6.26. Found: C, 84.48; H, 6.47.

(Z)-3-Phenyl-1-(tributylstannyl)-1-(triphenylsiloxy)-1-propene (6f): IR (neat) 3069, 3026, 2955, 2924, 2870, 2852, 1604, 1454, 1428, 1117, 1072, 1025, 739, 712, 699; ¹H NMR 0.62 (m, 6H), 0.81 (t, *J* = 7.1 Hz, 9H), 1.12-1.45 (m, 12H), 3.28 (d, *J* = 6.8 Hz, 2H), 4.91 (t, *J* = 6.8 Hz, 1H, ³*J*_{Sn-H} = 24.1 Hz), 6.96 (d, *J* = 6.8 Hz, 2H), 7.08-7.23 (m, 3H), 7.23-7.47 (m, 9H), 7.58-7.67 (m, 6H); ¹³C NMR 10.1, 13.7, 27.2, 28.9, 32.0, 125.4, 126.4, 127.8, 128.1, 128.4, 130.0, 134.4, 135.7, 141.6, 157.7. Anal. Calcd for C₃₉H₅₀OSiSn: C, 68.72; H, 7.39. Found: C, 68.49; H, 7.56

(Z)-2-Methyl-4-(triphenylsiloxy)-1,4-heptadiene (6g): IR (neat) 3070, 3050, 2963, 2931, 2871, 1676, 1428, 1353, 1186, 1117, 1073, 1047, 738, 711, 698; ¹H NMR 0.75 (t, *J* = 7.5 Hz, 3H), 1.55 (s, 3H), 1.97 (dq, *J* = 7.4, 7.4 Hz, 2H), 2.62 (s, 2H), 4.47 (t, *J* = 7.1 Hz, 1H), 4.63 (s, 1H), 4.74 (s, 1H), 7.30-7.47 (m, 9H), 7.60-7.68 (m, 6H); ¹³C NMR 14.1, 18.9, 22.0, 44.9, 112.6, 112.8, 127.7, 130.0, 134.4, 135.5, 142.2, 147.2. Anal. Calcd for C₂₆H₂₈OSi: C, 81.20; H, 7.34. Found: C, 81.16; H, 7.35.

(Z)-2-Methyl-4-(triphenylsiloxy)-1,4-hexadiene (6h): IR (neat) 3069, 3049, 2915, 1679, 1428, 1329, 1187, 1116, 1047, 893, 739, 699; ^1H NMR 1.45 (d, $J = 6.6$ Hz, 3H), 1.53 (s, 3H), 2.62 (s, 2H), 4.54 (q, $J = 6.7$ Hz, 1H), 4.62 (s, 1H), 4.74 (s, 1H), 7.31-7.48 (m, 9H), 7.62-7.71 (m, 6H); ^{13}C NMR 11.0, 22.0, 45.0, 104.6, 112.8, 127.7, 130.0, 134.4, 135.4, 142.2, 148.9. Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{OSi}$: C, 81.03; H, 7.07. Found: C, 80.65; H, 7.04.

2-Methyl-4-(triphenylsiloxy)-1,4-pentadiene (6i): IR (neat) 3070, 3050, 2972, 2913, 1631, 1429, 1298, 1254, 1186, 1117, 1044, 893, 698; ^1H MNR 1.65 (s, 3H), 2.80 (s, 2H), 4.10 (s, 1H), 4.14 (d, $J = 1.1$ Hz, 1H), 4.82 (s, 2H), 7.31-7.47 (m, 9H), 7.60-7.71 (m, 6H); ^{13}C NMR 21.8, 45.5, 93.6, 113.1, 127.8, 130.1, 133.8, 135.5, 142.1, 156.5. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{OSi}$: C, 80.85; H, 6.78. Found: C, 80.47; H, 6.98.

(Z)-2-Methyl-6-phenethyl-7-phenyl-4-(triphenylsiloxy)-1,4-heptadiene (6j): mp 102.5-103 °C; IR (neat) 3069, 3026, 2915, 2851, 1673, 1495, 1452, 1428, 1364, 1265, 1148, 1117, 1018, 994, 908, 698; ^1H NMR 1.35 (s, 3H), 2.42 (dd, $J = 7.6, 13.5$ Hz, 2H), 2.44 (s, 2H), 2.53 (dd, $J = 6.6, 13.4$ Hz, 2H), 3.12-3.28 (m 1H), 4.36 (d, $J = 9.7$ Hz, 1H), 4.41 (s, 1H), 4.64 (s, 1H), 6.80-7.01 (m, 4H), 7.10-7.23 (m, 6H), 7.26-7.55 (m, 15H); ^{13}C NMR 21.9, 38.5, 41.2, 44.8, 112.9, 113.9, 125.5, 127.7, 127.9, 129.3, 130.0, 134.2, 135.5, 140.8, 142.0, 148.1. Anal. Calcd for $\text{C}_{39}\text{H}_{38}\text{OSi}$: C, 85.04; H, 6.95. Found: C, 85.20; H, 6.69.

(Z)-1,3-Diphenyl-1-(triphenylsiloxy)-1-propene (6k): IR (neat) 3069, 3027, 2976, 2869, 1649, 1493, 1429, 1330, 1284, 1117, 1073, 1043, 1024, 909, 766, 698; ^1H NMR 3.39 (d, $J = 7.1$ Hz, 2H), 5.28 (t, $J = 7.1$ Hz, 1H), 6.94-7.00 (m, 2H), 7.03-7.23 (m, 6H), 7.27-7.44 (m, 11H), 7.57-7.65 (m, 6H); ^{13}C NMR 32.6, 110.8, 125.7, 126.3, 127.5, 127.69, 127.73, 128.2, 128.4, 130.1, 133.7, 135.6, 138.4, 141.2, 149.8. Anal. Calcd for $\text{C}_{33}\text{H}_{28}\text{OSi}$: C, 84.57; H, 6.02. Found: C, 84.34; H, 5.70.

(Z)-1-(4-Methoxyphenyl)-3-phenyl-1-(triphenylsiloxy)-1-propene (6l): IR (neat) 3068, 2955, 2932, 2907, 2835, 1648, 1607, 1511, 1453, 1428, 1290, 1247, 1176, 1116, 1072, 1031, 834, 700; ^1H NMR 3.39 (d, $J = 7.1$ Hz, 2H), 3.70 (s, 3H), 5.17 (t, $J = 7.1$ Hz, 1H),

6.59 (d, $J = 8.8$ Hz, 2H), 6.97 (d, $J = 6.8$ Hz, 2H), 7.08-7.47 (m, 14H), 7.56-7.68 (m, 6H); ^{13}C NMR 32.6, 55.2, 109.3, 113.0, 125.6, 127.6, 127.7, 128.2, 128.3, 130.0, 131.0, 133.8, 135.6, 141.4, 149.5, 159.0. Anal. Calcd for $\text{C}_{34}\text{H}_{30}\text{O}_2\text{Si}$: C, 81.89; H, 6.06. Found: C, 81.62; H, 6.45.

(Z)-1-Phenyl-3-(triphenylsiloxy)-2,4-undecadiene (6m): IR (neat) 3069, 3027, 2925, 2854, 1624, 1453, 1428, 1354, 1166, 1117, 1018, 997, 962, 699; ^1H NMR 0.86 (t, $J = 7.1$ Hz, 3H), 0.95-1.30 (m, 8H), 1.84 (dt, $J = 6.4, 6.4$ Hz, 2H), 3.22 (d, $J = 7.3$ Hz, 2H), 4.81 (t, $J = 7.2$ Hz, 1H), 5.67 (dt, $J = 15.4, 6.7$ Hz, 1H), 5.78 (d, $J = 15.6$ Hz, 1H), 6.85 (d, $J = 6.6$ Hz, 2H), 7.05-7.18 (m, 3H), 7.30-7.47 (m, 9H), 7.62-7.72 (m, 6H); ^{13}C NMR 14.1, 22.6, 28.7, 29.0, 31.7, 32.1, 32.3, 112.2, 125.6, 127.6, 127.8, 128.1, 128.3, 130.1, 131.4, 134.0, 135.6, 141.2, 148.8. Anal. Calcd for $\text{C}_{35}\text{H}_{38}\text{OSi}$: C, 83.61; H, 7.62. Found: C, 83.95; H, 7.34.

(Z)-1-Phenyl-1-(triphenylsiloxy)-1-butene (6n): IR (neat) 3069, 3050, 2963, 2930, 2871, 1650, 1428, 1338, 1298, 1282, 1117, 1074, 874, 765, 741, 697; ^1H NMR 0.74 (t, $J = 7.5$ Hz, 3H), 2.04 (dq, $J = 7.4, 7.4$ Hz, 2H), 5.08 (t, $J = 7.1$ Hz, 1H), 7.02-7.12 (m, 3H), 7.26-7.44 (m, 11H), 7.55-7.67 (m, 6H); ^{13}C NMR 13.9, 19.9, 114.0, 126.1, 127.2, 127.6, 127.7, 130.0, 133.9, 135.6, 138.6, 148.6. Anal. Calcd for $\text{C}_{28}\text{H}_{26}\text{OSi}$: C, 82.71; H, 6.45. Found: C, 82.97; H, 6.71.

(Z)-1-Phenyl-1-(triphenylsiloxy)-1-propene (6o): IR (neat) 3069, 2913, 2856, 1654, 1428, 1264, 1117, 1065, 998, 859, 764, 741, 697; ^1H NMR 1.53 (d, $J = 7.0$ Hz, 3H), 5.17 (q, $J = 6.9$ Hz, 1H), 7.03-7.13 (m, 3H), 7.23-7.45 (m, 11H), 7.56-7.67 (m, 6H); ^{13}C NMR 12.1, 106.2, 126.0, 127.2, 127.6, 127.7, 123.0, 134.0, 135.6, 138.7, 150.1. Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{OSi}$: C, 82.61; H, 6.16. Found: C, 82.42; H, 6.19.

(Z)-3-Phenethyl-1,4-diphenyl-1-(triphenylsiloxy)-1-butane (6p): mp 104.5-105.5 °C; IR (neat) 3054, 3023, 2917, 2848, 1656, 1494, 1453, 1428, 1355, 1303, 1117, 1073, 1059, 1024, 742, 724, 711; ^1H NMR 2.46 (dd, $J = 7.6, 13.5$ Hz, 2H), 2.57 (dd, $J = 6.2, 13.4$ Hz, 2H), 3.18-3.33 (m, 1H), 4.87 (d, $J = 9.7$ Hz, 1H), 6.90-7.48 (m, 30H); ^{13}C NMR 39.0,

41.0, 115.7, 125.6, 126.4, 127.1, 127.5, 127.6, 128.0, 129.4, 129.9, 133.8, 135.5, 139.1, 140.4, 149.9. Anal. Calcd for C₄₁H₃₆OSi: C, 85.97; H, 6.33. Found: C, 85.66; H, 6.60.

References

- (1) Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609.
- (2) Artamkina, G. A.; Kovalenko, S. V.; Beletskaya, I. P.; Reutov, O. A. *J. Organomet. Chem.* **1987**, *329*, 139.