Formal [3 + 2] and [3 + 3] Additions of Acceptor-Substituted Cyclopropylmethylsilanes to Allenylsilanes

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SUPPLEMENTARY INFORMATION

Experimental details and characterization data (14 pages).

General. ^1H and ^{13}C spectra were recorded on JEOL JNM-LA400 instrument using solutions in CDCl_3 . The ^1H and ^{13}C spectra are referred, respectively, to TMS used as an internal standard and the central line for CDCl_3 respectively. Elemental (C and H) analyses were performed on a Perkin-Elmer 240-C automatic elemental analyzer. All the reactions were carried out using freshly distilled dry solvents. Column chromatography was performed over silica gel (100-200 mesh) obtained from Acme Chemicals using mixtures of hexanes and EtOAc. The separation of isomers was achieved by radial chromatography using plates coated with silica gel 60 PF₂₅₄ (E-Merck). Solvents were removed under reduced pressure on a rotovap. Organic extracts were dried with anhydrous Na_2SO_4 .

Materials. The allenylsilane **2a** was purchased from Sigma-Aldrich and the allenylsilane **2b** was prepared according to a literature procedure.¹

General procedure for cyclopropanation of allyl *tert*-butyldiphenylsilane with diazo compounds. The solution of a diazo compound (2 mmol) in CHCl_3 (2 mL) was added to a stirred solution of allyl *tert*-butyldiphenylsilane (1.120 g, 4 mmol) and $\text{Rh}_2(\text{OAc})_4$ (43 mg, 0.01 mmol) in anhydrous CHCl_3 (0.5 mL) under nitrogen over 10 h using a syringe pump. The reaction mixture was stirred further for 5 h and the solvent was removed. Purification of the residue by silica gel column chromatography (EtOAc/hexanes) furnished a mixture of the *cis*- and *trans*-products. The separation of the *cis*- and *trans*-isomers was achieved by radial chromatography (EtOAc/hexanes).

1a. Following the general procedure outlined above, cyclopropanation of allyl *tert*-butyldiphenylsilane with phenyl diazomethyl ketone afforded **1a** (*trans/cis* = 2.4:1) as a colorless liquid, 597 mg, 75%.

***trans*-1a.** ^1H NMR (400 MHz, CDCl_3): δ 7.71-7.69 (2H, m), 7.61-7.55 (4H, m), 7.51-7.47 (1H, m), 7.38-7.23 (8H, m), 2.31-2.27 (1H, m), 1.67-1.58 (1H, m), 1.45-1.39 (1H, dd, J = 15.0, 6.5 Hz), 1.37-1.31 (2H, m), 1.05 (9H, s), 0.78-0.73 (1H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 199.3, 137.6, 135.8, 135.7, 134.2, 134.0, 132.1, 129.0, 128.9, 128.0, 127.7, 127.4, 27.7, 27.3, 23.2, 21.7, 17.8, 15.6. Anal Calcd for $\text{C}_{27}\text{H}_{30}\text{OSi}$: C, 81.35; H, 7.59. Found: C, 81.22; H, 7.45.

cis-1a. ¹H NMR (400 MHz, CDCl₃): δ 7.94-7.91 (2H, m), 7.69-7.67 (2H, m), 7.69-7.28 (11H, m), 2.67-2.62 (1H, m), 1.60-1.50 (1H, m), 1.42-1.35 (1H, dd, *J* = 15.1, 9.8 Hz), 1.31-1.26 (1H, dd, *J* = 15.1, 3.9 Hz), 1.23-1.17 (1H, m), 1.02 (9H, s), 0.95-0.90 (1H, dt, *J* = 7.8, 4.4 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 198.8, 139.0, 136.1, 135.9, 134.6, 134.5, 132.3, 129.0, 128.9, 128.3, 127.9, 127.5, 27.7, 24.8, 22.5, 18.1, 16.7, 7.4. Anal Calcd for C₂₇H₃₀OSi: C, 81.35; H, 7.59. Found: C, 81.25; H, 7.50.

1b. Following the general procedure outlined above, cyclopropanation of allyl tert-butyl diphenylsilane with *n*-butyl diazomethyl ketone afforded **1b** (*trans/cis* = 2.1:1) as a colorless liquid, 454 mg, 60%.

trans-1b. ¹H NMR (400 MHz, CDCl₃): δ 7.62-7.56 (4H, m), 7.41-7.31 (6H, m), 2.21-2.13 (1H, ddd, *J* = 16.4, 8.3, 6.6 Hz), 2.06-1.98 (1H, ddd, *J* = 16.4, 8.3, 6.6 Hz), 1.52-1.48 (1H, m), 1.43-1.16 (7H, m), 1.11-1.07 (1H, m), 1.04 (9H, s), 0.84 (3H, t, *J* = 7.3 Hz), 0.59-0.54 (1H, m). ¹³C NMR (100 MHz, CDCl₃): δ 210.3, 136.0, 135.9, 134.6, 134.2, 129.1, 129.08, 127.6, 43.0, 30.9, 27.8, 25.9, 22.2, 21.5, 20.4, 18.0, 15.5, 13.8. Anal Calcd for C₂₅H₃₄OSi: C, 79.31; H, 9.05. Found: C, 79.20; H, 8.90.

cis-1b. ¹H NMR (400 MHz, CDCl₃): δ 7.66-7.59 (4H, m), 7.40-7.32 (6H, m), 2.43-2.35 (1H, ddd, *J* = 16.4, 8.3, 6.6 Hz), 2.28-2.20 (1H, ddd, *J* = 16.4, 8.3, 6.6 Hz), 1.91-1.86 (1H, m), 1.57-1.22 (8H, m), 1.03 (9H, s), 0.90 (3H, t, *J* = 7.3 Hz), 0.81-0.76 (1H, m). ¹³C NMR (100 MHz, CDCl₃): δ 209.0, 136.2, 136.1, 134.9, 134.6, 129.0, 128.97, 127.5, 127.46, 44.6, 27.8, 27.1, 26.1, 22.4, 21.4, 18.1, 16.9, 13.9, 7.2. Anal Calcd for C₂₅H₃₄OSi: C, 79.31; H, 9.05. Found: C, 79.15; H, 8.90.

1c. Following the general procedure outlined above, cyclopropanation of allyl tert-butyl diphenylsilane with *t*-butyl diazomethyl ketone afforded **1c** (*trans/cis* = 2:1) as a colorless liquid, 454 mg, 60%.

trans-1c. ¹H NMR (400 MHz, CDCl₃): δ 7.64-7.58 (4H, m), 7.39-7.32 (6H, m), 1.89-1.85 (1H, m), 1.59-1.54 (1H, dd, *J* = 14.9, 4.6 Hz), 1.40-1.33 (2H, m), 1.27-1.21 (1H, m), 1.07 (9H, s), 1.06 (9H, s), 0.57-0.53 (1H, m). ¹³C NMR (100 MHz, CDCl₃): δ 214.5, 136.0, 135.9, 134.5, 134.47, 129.1, 127.6, 127.5, 43.6, 27.8, 26.8, 26.2, 21.6, 21.0, 18.0, 15.7. Anal Calcd for C₂₅H₃₄OSi: C, 79.31; H, 9.05. Found: C, 79.23; H, 8.94.

cis-1c. ^1H NMR (400 MHz, CDCl_3): δ 7.68-7.66 (2H, m), 7.63-7.60 (2H, m), 7.41-7.32 (6H, m), 2.21-2.16 (1H, m), 1.37-1.25 (2H, m), 1.21-1.02 (1H, m), 1.17 (9H, s), 1.04 (9H, s), 0.95-0.88 (1H, m), 0.76-0.71 (1H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 213.3, 136.2, 136.0, 134.9, 134.6, 129.0, 128.97, 127.5, 127.4, 44.2, 27.8, 26.3, 23.1, 21.5, 18.1, 16.5, 7.3. Anal Calcd for $\text{C}_{25}\text{H}_{34}\text{OSi}$: C, 79.31; H, 9.05. Found: C, 79.16; H, 8.94.

16. Following the general procedure outlined above, cyclopropanation of allyl tert-butylidiphenylsilane with 2-diazocyclohexanone afforded **16** (*trans/cis* = 3:1) as a colorless liquid, 226 mg, 30%.

trans-16. ^1H NMR (400 MHz, CDCl_3): δ 7.62-7.56 (4H, m), 7.40-7.32 (6H, m), 2.30-2.15 (2H, m), 1.78-1.64 (7H, m), 1.49-1.33 (3H, m), 1.07(9H, s), 0.09-0.07 (1H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 211.5, 136.0, 135.9, 134.5, 134.4, 129.1, 127.6, 127.5, 39.7, 33.6, 28.1, 27.9, 26.1, 26.0, 23.8, 23.6, 18.2, 10.0. Anal Calcd for $\text{C}_{25}\text{H}_{32}\text{OSi}$: C, 79.73; H, 8.56. Found: C, 79.60; H, 8.45.

cis-16. ^1H NMR (400 MHz, CDCl_3): δ 7.66-7.56 (4H, m), 7.40-7.32 (6H, m), 2.04-1.88 (2H, m), 1.76-1.65 (3H, m), 1.25-0.98 (7H, m), 1.02 (9H, s), 0.41-0.35 (1H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 209.8, 136.1, 136.0, 134.8, 134.4, 129.0, 127.6, 127.5, 42.0, 36.0, 35.8, 29.3, 27.8, 25.1, 23.9, 20.3, 18.1, 8.6. Anal Calcd for $\text{C}_{25}\text{H}_{32}\text{OSi}$: C, 79.73; H, 8.56. Found: C, 79.56; H, 8.46.

20. Following the general procedure outlined above, cyclopropanation of allyl tert-butylidiphenylsilane with 2-diazocyclopentanone afforded **20** (*trans/cis* = 1.1:1) as a colorless liquid, 232 mg, 32%.

trans-20 (colorless dense liquid). ^1H NMR: δ 7.61-7.55 (4H, m), 7.40-7.31 (6H, m), 2.24-2.16 (1H, m), 2.12-2.04 (1H, m), 1.94-1.86 (2H, m), 1.79-1.72 (2H, m), 1.47-1.41 (1H, m), 1.38-1.33 (1H, dd, J = 14.6, 4.9 Hz), 1.21-1.18 (1H, m), 1.07 (9H, s), 0.97-0.94 (1H, dd, J = 14.6, 9.0 Hz), 0.34-0.31 (1H, m). ^{13}C NMR: δ 219.3, 136.0, 135.9, 134.3, 129.1, 127.6, 127.5, 38.7, 35.3, 27.9, 27.8, 27.3, 25.4, 20.7, 18.1, 11.4. Anal. Calcd. for $\text{C}_{24}\text{H}_{30}\text{OSi}$: C, 79.50; H, 8.34. Found: C, 79.38; H, 8.24.

cis-20 (colorless dense liquid). ^1H NMR: δ 7.66-7.57 (4H, m), 7.42-7.31 (6H, m), 2.18-2.09 (1H, m), 2.03-1.95 (1H, m), 1.82-1.75 (2H, m), 1.61-1.50 (4H, m), 1.30-1.23 (1H, m), 1.01

(9H, s), 0.99-0.91 (2H, m). ^{13}C NMR: δ 218.5, 136.2, 136.1, 134.7, 134.5, 129.0, 127.53, 127.5, 40.1, 34.7, 34.0, 30.0, 27.8, 25.6, 20.7, 18.1, 7.6. Anal. Calcd. for $\text{C}_{24}\text{H}_{30}\text{OSi}$: C, 79.50; H, 8.34. Found: C, 79.35; H, 8.25.

Preparation of *tert*-Butyldiphenylsilyllallene 2c: An oven-dried 50 mL round bottom flask was charged with 1.712 g (6.53 mmol) of Ph_3P under nitrogen atmosphere and 14 mL of THF was added. The solution was cooled to $-15\text{ }^\circ\text{C}$ and a solution of 1.264 g (6.26 mmol) of diisopropylazodicarboxylate in 2 mL THF was added over 2 min, followed immediately by the addition of a solution of 1.6 g (5.44 mmol) of 3-*tert*-butyldiphenylsilyl-2-propyn-1-ol in 4 mL THF over 2 min. After stirring the contents for 5 min, a solution of 1.77 g (6.53 mmol) of *o*-nitrobenzenesulfonyl hydrazide in 8 mL THF was added to the reaction mixture over 5 min. The resultant orange-red solution was stirred at $-15\text{ }^\circ\text{C}$ for 45 min, allowed to warm up to $25\text{ }^\circ\text{C}$ and held at that temperature for 5h. The reaction mixture was poured into a separatory funnel containing 50 mL hexane and washed with water (4 x 10 mL) and brine (1 x 10 mL). The organic layer was dried and concentrated. Purification of the residue by column chromatography gave the pure product, 912 mg, 61%, colorless liquid. ^1H NMR: δ 7.66-7.64 (4H, m), 7.40-7.32 (6H, m), 5.31-5.27 (1H, dd, $J = 7.3, 7.3\text{ Hz}$), 4.38 (2H, d, $J = 7.3\text{ Hz}$), 1.09 (9H, s). ^{13}C NMR: δ 215.1, 135.9, 134.2, 129.2, 127.5, 75.8, 68.0, 27.4, 18.9. Anal. Calcd. for $\text{C}_{19}\text{H}_{22}\text{Si}$: C, 81.95; H, 7.96. Found: C, 81.80; H, 7.84.

General procedure for the TiCl_4 -assisted reaction. A solution of freshly distilled TiCl_4 (61 mg, 0.326 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added slowly under N_2 to the stirred solution of a cyclopropylmethylsilane (0.251 mmol) and an allenylsilane (0.326 mmol) in anhydrous CH_2Cl_2 (0.8 mL) at $-78\text{ }^\circ\text{C}$. The reaction mixture turned deep red. After stirring for 3 h at $-78\text{ }^\circ\text{C}$, it was warmed slowly over 1 h to $-40\text{ }^\circ\text{C}$. The stirring was continued at this temperature for 2 h and the reaction mixture was taken in Et_2O (10 mL). The ethereal solution was washed with water (1 x 7 mL). The aqueous washing was extracted with Et_2O (2 x 5 mL). The combined organic extracts were washed with brine, dried, and concentrated. Purification of the residue by silica gel column chromatography (EtOAc /hexanes) furnished the pure product(s). The separation of the *cis*- and *trans*-isomers was achieved by radial chromatography over silica gel (EtOAc /hexanes).

General procedure for the Et₂AlCl-assisted reaction. A solution of Et₂AlCl (54 mg, 0.375 mmol) in toluene (208 μ L) was added slowly under N₂ to the stirred solution of a cyclopropylmethylsilane (0.251 mmol) and an allenylsilane (0.326 mmol) in anhydrous CH₂Cl₂ (1.3 mL) at 25 °C when the reaction mixture turned pale yellow. After stirring for 6 h, the reaction mixture was quenched with water at 0 °C and diluted with Et₂O (10 mL). The ethereal solution was washed with water (7 mL). The aqueous washing was extracted with Et₂O (2 x 5 mL). The combined organic extracts were washed with brine, dried, and concentrated. Purification of the residue by silica gel column chromatography (EtOAc/hexanes) furnished the pure product.

5. Following the general procedure for the TiCl₄-assisted reaction outlined above, reaction of cyclopropylmethylsilane **1a** with the allenylsilane **2a** afforded **5** (*cis/trans* = 3.2:1) as a colorless liquid, 102 mg, 90%.

¹H NMR: δ 7.87-7.85 (2H, m), 7.65-7.60 (4H, m), 7.55-7.52 (1H, m), 7.44-7.31 (8H, m), 5.33-5.27 (1H, m), 4.14-4.10 (1H, m), 2.13-1.93 (4H, m), 1.35-1.29 (3H, m), 1.25 (3H, d, *J* = 6.3 Hz). 0.99 (9H, s). ¹³C NMR: δ 201.6, 142.4, 136.8, 136.1, 136.0, 134.9, 134.8, 132.8, 129.1, 129.0, 128.5, 128.4, 127.5, 117.3, 49.0, 45.1, 43.0, 36.2, 27.8, 18.1, 15.7, 14.9. Anal. Calcd. for C₃₁H₃₆OSi: C, 82.25; H, 8.02. Found: C, 82.14; H, 7.94.

¹H NMR: δ 7.78-7.76 (2H, m), 7.60-7.50 (5H, m), 7.41-7.26 (8H, m), 5.45-5.40 (1H, m), 4.29-4.25 (1H, m), 2.46-2.39 (1H, m), 2.27-2.20 (1H, m), 1.93-1.87 (1H, m), 1.71-1.63 (1H, m), 1.60-1.53 (1H, m), 1.37-1.35 (3H, dd, *J* = 6.8, 1.0 Hz), 1.30-1.25 (1H, dd, *J* = 15.1, 6.6 Hz), 1.20-1.14 (1H, dd, *J* = 15.1, 7.8 Hz), 1.01 (9H, s). ¹³C NMR: δ 200.9, 141.7, 136.5, 136.0, 135.96, 135.2, 134.9, 132.6, 129.0, 128.97, 128.4, 128.38, 127.5, 118.4, 47.9, 43.8,

41.2, 34.2, 27.9, 18.1, 15.7, 15.4. Anal. Calcd. for C₃₁H₃₆OSi: C, 82.25; H, 8.02. Found: C, 82.15; H, 7.90.

6. Following the general procedure for the TiCl₄-assisted reaction outlined above, reaction of the cyclopropylmethylsilane **1a** with the allenylsilane **2a** in presence of 1.3 equiv of Et₂AlCl afforded **6** (*cis/trans* = 7:1) as a colorless liquid, 76 mg, 58%.

Mixture of the *trans*- and *cis*-isomers. ¹H NMR: 7.91-7.88 (m), 7.81-7.78 (m), 7.74-7.52 (m), 7.46-7.30 (m), 4.39-4.36 (m), 4.28-4.24 (m), 2.31-2.14 (m), 1.97-1.94 (m), 1.64-1.55 (m), 1.43-1.24 (m), 1.38 (s), 1.29 (s), 1.02 (s), 1.01 (s), 0.01 (s), -0.1 (s). ¹³C NMR: δ 201.7, 152.1, 137.0, 136.1, 136.0, 134.9, 134.7, 132.7, 132.6, 129.1, 129.0, 128.5, 128.4, 128.3, 127.6, 127.58, 127.4, 51.8, 51.0, 44.9, 44.0, 43.1, 40.6, 27.9, 27.0, 19.6, 18.1, 16.0, 15.9, -0.6, -0.63. Anal. Calcd. for C₃₄H₄₄OSi₂: C, 77.80; H, 8.45. Found: C, 77.67; H, 8.35.

7. Following the general procedure for the Et₂AlCl-assisted reaction outlined above, reaction of the cyclopropylmethylsilane **1a** with the allenylsilane **2a** afforded **7** as a colorless liquid, 85 mg, 65%.

¹H NMR: δ 7.94-7.91 (2H, m), 7.54-7.52 (4H, m), 7.45-7.29 (9H, m), 4.08 (1H, d, *J* = 5.6 Hz), 2.75-2.68 (1H, tdd, *J* = 15.8, 8.1, 1.9 Hz), 2.55-2.47 (1H, m), 2.14-2.07 (1H, m), 1.63 (3H, s), 1.49-1.41 (2H, m), 1.14-1.01 (2H, m), 0.94 (9H, s), 0.13 (9H, s). ¹³C NMR: δ 203.2, 146.5, 137.9, 137.8, 135.8, 134.7, 134.6, 132.8, 128.9, 128.5, 128.4, 127.5, 66.7, 47.9, 43.1, 30.2, 27.8, 18.0, 16.5, 9.0, -0.6. Anal. Calcd. for C₃₄H₄₄OSi₂: C, 77.80; H, 8.45. Found: C, 77.64; H, 8.36.

8, 9. Following the general procedure for the TiCl_4 -assisted reaction outlined above, reaction of the cyclopropylmethylsilane **1a** with the allenylsilane **2b** afforded a mixture of **8** and **9** (**8/9** = 1.7:1), 147 mg, 85%.

^1H NMR: δ 7.86-7.83 (2H, m), 7.73-7.71 (2H, m), 7.58-7.51 (3H, m), 7.46-7.20 (18H, m), 4.36-4.31 (1H, m), 2.06-2.01 (1H, m), 1.83-1.67 (1H, m), 1.64 (3H, s), 1.57-1.50 (2H, m), 1.32-1.24 (2H, m), 1.08-1.02 (1H, m), 1.00 (9H, s), 0.83 (9H, s). ^{13}C NMR: δ 201.1, 157.2, 136.7, 136.1, 136.0, 135.9, 135.8, 135.7, 135.57, 135.1, 134.2, 132.7, 128.84, 128.8, 128.7, 128.56, 128.5, 128.3, 127.5, 127.4, 52.5, 47.4, 41.5, 36.1, 28.6, 27.7, 21.9, 19.1, 17.9, 15.7. Anal. Calcd. for $\text{C}_{47}\text{H}_{54}\text{OSi}_2$: C, 81.68; H, 7.88. Found: C, 81.55; H, 7.75.

^1H NMR: δ 7.92-7.90 (2H, m), 7.72-7.71 (2H, m), 7.62-7.53 (7H, m), 7.44-7.30 (14H, m), 4.08 (1H, broad s), 3.00-2.98 (1H, m), 2.56-2.47 (2H, m), 1.63-1.52 (4H, m), 1.20 (3H, s), 1.10 (9H, s), 0.97 (9H, s). ^{13}C NMR: δ 202.2, 151.9, 137.5, 136.1, 135.9, 135.8, 135.6, 135.1, 134.52, 134.5, 132.9, 132.8, 129.0, 128.9, 128.8, 128.6, 128.4, 127.63, 127.6, 66.5, 47.4, 45.1, 30.4, 28.2, 27.8, 19.0, 18.4, 18.1, 8.6. Anal. Calcd. for $\text{C}_{47}\text{H}_{54}\text{OSi}_2$: C, 81.68; H, 7.88. Found: C, 81.50; H, 7.74.

10. Following the general procedure for the TiCl_4 -assisted reaction outlined above, reaction of the cyclopropylmethylsilane **1b** with the allenylsilane **2a** afforded **10** (*cis/trans* = 1.9:1) as a colorless liquid, 82 mg, 75%.

^1H NMR: δ 7.63-7.61 (4H, m), 7.40-7.33 (6H, m), 5.27-5.22 (1H, m), 3.28-3.23 (1H, m), 2.34-2.29 (2H, m), 2.07-2.03 (1H, m), 1.90-1.85 (2H, m), 1.53-1.44 (2H, m), 1.35 (3H, d, J = 6.6 Hz), 1.32-1.20 (6H, m), 1.00 (9H, s), 0.88 (3H, t, J = 7.3 Hz). ^{13}C NMR: δ 212.1, 141.6, 136.0, 134.8, 129.1, 127.5, 118.1, 54.5, 45.3, 40.6, 39.3, 35.7, 27.8, 26.0, 22.4, 18.1, 15.8, 14.4, 13.9. Anal. Calcd. for $\text{C}_{29}\text{H}_{40}\text{OSi}$: C, 80.49; H, 9.32. Found: C, 80.35; H, 9.24.

^1H NMR: δ 7.61-7.59 (4H, m), 7.41-7.33 (6H, m), 5.36-5.30 (1H, m), 2.34-2.29 (2H, m), 2.22-2.10 (1H, m), 1.90-1.79 (2H, m), 1.50-1.41 (5H, m), 1.39 (3H, d, J = 6.6 Hz), 1.24-1.10 (4H, m), 1.00 (9H, s), 0.83 (3H, t, J = 7.3 Hz). ^{13}C NMR: δ 212.1, 141.1, 136.0, 134.9, 129.0, 127.5, 118.9, 53.6, 43.4, 39.8, 39.6, 34.1, 27.8, 25.8, 22.3, 18.1, 15.7, 15.0, 13.9. Anal. Calcd. for $\text{C}_{29}\text{H}_{40}\text{OSi}$: C, 80.49; H, 9.32. Found: C, 80.38; H, 9.22.

11. Following the general procedure for the Et_2AlCl -assisted reaction outlined above, reaction of the cyclopropylmethylsilane **1b** with the allenylsilane **2a** afforded **11** as a colorless liquid, 82 mg, 65%.

^1H NMR: δ 7.60-7.56 (4H, m), 7.39-7.32 (6H, m), 3.14-3.12 (1H, m), 2.73-2.65 (1H, tdd, J = 16.1, 8.0, 2.2 Hz), 2.36-2.30 (2H, m), 2.28-2.24 (1H, m), 2.09-2.04 (1H, m), 1.64 (3H, s), 1.54-1.47 (2H, m), 1.41-1.22 (4H, s), 1.12-1.05 (2H, m), 1.02 (9H, s), 0.88 (3H, t, J = 7.3 Hz), 0.11 (9H, s). ^{13}C NMR: δ 213.2, 145.7, 137.0, 135.9, 135.8, 134.7, 134.6, 128.9, 127.6,

72.9, 45.6, 43.6, 40.2, 30.5, 27.8, 25.8, 22.4, 18.1, 16.2, 13.9, 8.5, -0.7. Anal. Calcd. for $C_{32}H_{48}OSi_2$: C, 76.12; H, 9.58. Found: C, 75.95; H, 9.45.

12. Following the general procedure for the Et_2AlCl -assisted reaction outlined above, reaction of the cyclopropylmethylsilane **1b** with the allenylsilane **2b** afforded **12** as a colorless liquid, 93 mg, 55%.

1H NMR: δ 7.62-7.54 (8H, m), 7.40-7.25 (12H, m), 3.19 (1H, broad s), 3.03-2.97 (1H, tdd, J = 16.1, 8.0, 2.1 Hz), 2.45-2.31 (4H, m), 1.56-1.40 (5H, m), 1.33-1.24 (2H, sextet, J = 7.3 Hz), 1.19 (3H, s), 1.17-1.12 (1H, m), 1.07 (9H, s), 1.03 (9H, s), 0.89 (3H, t, J = 7.3 Hz). ^{13}C NMR: δ 212.4, 151.1, 137.0, 135.9, 135.8, 135.3, 134.6, 129.0, 128.9, 127.6, 72.6, 46.0, 45.4, 40.5, 30.8, 28.2, 27.9, 25.8, 22.5, 19.0, 18.1, 18.15, 13.9, 8.2. Anal. Calcd. for $C_{45}H_{58}OSi_2$: C, 80.54; H, 8.71. Found: C, 80.44; H, 8.60.

13. Following the general procedure for the $TiCl_4$ -assisted reaction outlined above, reaction of the cyclopropylmethylsilane **1c** with the allenylsilane **2b** afforded **13** as a colorless liquid, 109 mg, 65%.

1H NMR: δ 7.75-7.73 (2H, m), 7.61-7.58 (7H, m), 7.39-7.25 (11H, m), 3.50 (1H, broad s), 2.98-2.92 (1H, tdd, J = 15.6, 7.6, 2.2 Hz), 2.53-2.50 (1H, m), 2.13-2.11 (1H, m), 1.53-1.39 (2H, m), 1.30-1.22 (2H, m), 1.12 (3H, s), 1.10 (9H, s), 1.07 (9H, s), 1.02 (9H, s). ^{13}C NMR: δ 216.4, 152.2, 136.2, 135.9, 135.8, 135.2, 134.6, 132.8, 129.0, 128.8, 128.7, 127.7, 127.6, 127.5, 65.5, 47.0, 44.7, 44.6, 30.6, 28.2, 27.9, 26.1, 18.9, 18.3, 18.2, 8.0. Anal. Calcd. for $C_{45}H_{58}OSi_2$: C, 80.54; H, 8.71. Found: C, 80.45; H, 8.63.

14. Following the general procedure for the TiCl_4 -assisted reaction outlined above, reaction of the cyclopropylmethylsilane **1a** with the allenylsilane **2c** afforded **14** (*cis/trans* = 2.8:1) as a colorless liquid, 105 mg , 62%.

^1H NMR: δ 7.94-7.91 (2H, m), 7.55-7.21 (21H, m), 7.14-7.10 (2H, m), 5.46 (1H, s), 4.33-4.28 (1H, m), 1.83-1.53 (5H, m), 1.21-1.07 (2H, m), 0.87 (9H, s), 0.75 (9H, s). ^{13}C NMR: δ 200.9, 165.0, 137.8, 136.0, 135.97, 135.9, 135.8, 134.8, 134.6, 134.4, 134.0, 132.8, 129.0, 128.9, 128.8, 128.5, 127.5, 127.4, 127.3, 116.1, 55.1, 44.5, 39.3, 35.6, 27.8, 27.1, 18.0, 16.0. Anal. Calcd. for $\text{C}_{46}\text{H}_{52}\text{OSi}_2$: C, 81.60; H, 7.74. Found: C, 81.47; H, 7.65.

^1H NMR: δ ^1H NMR: δ 7.85-7.83 (2H, m), 7.64-7.62 (2H, m), 7.55-7.21 (19H, m), 7.18-7.10 (2H, m), 5.63 (1H, bs), 4.49-4.45 (1H, m), 1.93-1.50 (5H, m), 1.27-1.11 (2H, m), 0.93 (9H, s), 0.80 (9H, s). ^{13}C NMR: δ 200.9, 164.7, 137.5, 136.0, 135.97, 135.9, 135.7, 134.8, 134.6, 134.4, 134.2, 132.6, 128.9, 128.87, 128.8, 128.4, 127.5, 127.4, 127.3, 117.2, 54.0, 44.7, 38.4, 34.6, 27.9, 27.1, 18.0, 17.99, 16.5. Anal. Calcd. for $\text{C}_{46}\text{H}_{52}\text{OSi}_2$: C, 81.60; H, 7.74. Found: C, 81.45; H, 7.50.

15. Following the general procedure for the TiCl_4 -assisted reaction outlined above, reaction of the cyclopropylmethylsilane **1c** with the allenylsilane **2c** afforded **15** (*cis/trans* = 5.8:1) as a colorless liquid, 99 mg , 60%.

^1H NMR: δ 7.65-7.63 (2H, m), 7.50-7.20 (16H, m), 7.13-7.09 (2H, m), 5.43-5.37 (1H, s), 3.88-3.83 (1H, m), 1.80-1.57 (4H, m), 1.32-1.06 (3H, m), 1.10 (9H, s), 0.87 (9H, s), 0.86 (9H, s). ^{13}C NMR: δ 218.0, 167.7, 136.1, 135.9, 135.8, 135.7, 134.9, 134.8, 134.2, 133.9, 128.8, 128.7, 127.5, 127.4, 127.3, 54.3, 45.2, 44.6, 42.6, 36.1, 27.7, 27.2, 26.9, 18.0, 17.9, 15.9. Anal. Calcd. for $\text{C}_{44}\text{H}_{56}\text{OSi}_2$: C, 80.43; H, 8.59. Found: C, 80.35; H, 8.50.

The *trans*-isomer could be fully separated from the *cis*-isomer. However, it was contaminated with another product (uncharacterized) that it could not be separated from. Some characteristic ^1H absorptions for the *trans*-isomer are: δ 5.54 (bs), 4.05-4.02 (m).

17, 18. Following the general procedure for the TiCl_4 -assisted reaction outlined above, reaction of the cyclopropylmethylsilane **16** with the allenylsilane **2b** afforded a mixture of **17** **18** (**17/18** = 2:1) as a colorless liquid, 151 mg, 90%.

^1H NMR: δ 7.79-7.77 (2H, m), 7.59-7.57 (2H, m), 7.41-7.22 (16H, m), 2.41-2.37 (1H, m), 2.01-1.95 (1H, m), 1.85-1.71 (4H, m), 1.57 (3H, s), 1.45-1.39 (3H, m), 1.32-1.18 (2H, m), 0.99 (9H, s), 0.92-0.74 (4H, m), 0.85 (9H, s). ^{13}C NMR: δ 212.5, 161.0, 136.7, 136.3, 136.0, 135.9, 135.5, 135.3, 134.4, 128.9, 128.8, 128.6, 128.5, 127.6, 127.4, 122.4, 61.9, 47.5, 47.2,

40.3, 34.6, 33.5, 28.5, 27.7, 24.5, 24.3, 22.2, 19.1, 17.9, 14.7. Anal. Calcd. for $C_{45}H_{56}OSi_2$: C, 80.78; H, 8.44. Found: C, 80.65; H, 8.36.

1H NMR: δ 7.81-7.78 (2H, m), 7.63-7.58 (4H, m), 7.42-7.23 (14H, m), 2.57-2.31 (4H, m), 2.23-2.17 (1H, m), 1.88-1.82 (1H, m), 1.76-1.68 (1H, m), 1.62-1.48 (2H, m), 1.35-1.23 (3H, m), 1.11 (3H, s), 1.09 (9H, s), 1.03 (9H, s), 0.88-0.82 (3H, m). ^{13}C NMR: δ 213.0, 155.6, 136.0, 135.6, 135.2, 134.7, 134.4, 134.2, 130.2, 128.7, 128.5, 128.3, 127.3, 127.27, 127.1, 69.3, 49.4, 40.6, 40.0, 29.3, 27.9, 27.5, 25.8, 23.5, 21.6, 18.6, 17.8, 16.7, 8.7. Anal. Calcd. for $C_{45}H_{56}OSi_2$: C, 80.78; H, 8.44. Found: C, 80.65; H, 8.35.

19. Following the general procedure for the $TiCl_4$ -assisted reaction outlined above, reaction of the cyclopropylmethylsilane **16** with the allenylsilane **2c** afforded **19** as a colorless liquid, 90 mg, 55%.

1H NMR: δ 7.78-7.76 (2H, m), 7.56-7.54 (2H, m), 7.45-7.22 (14H, m), 7.20-7.15 (2H, m), 5.56 (1H, bs), 2.33-2.28 (1H, m), 2.18-2.10 (1H, m), 1.88-1.47 (9H, m), 1.34-1.26 (1H, m), 1.11-0.97 (3H, m), 0.92 (9H, s), 0.87 (9H, s). ^{13}C NMR: δ 212.3, 168.2, 136.2, 136.0, 135.9, 135.7, 135.14, 135.1, 134.33, 134.3, 128.9, 128.8, 128.78, 128.7, 127.5, 127.46, 127.4, 127.3, 114.3, 63.0, 45.9, 45.3, 40.1, 38.3, 33.4, 27.7, 27.2, 26.2, 22.1, 18.1, 17.9, 15.6. Anal. Calcd. for $C_{44}H_{54}OSi_2$: C, 80.67; H, 8.31. Found: C, 80.55; H, 8.20.

21, 22. Following the general procedure for the $TiCl_4$ -assisted reaction outlined above, reaction of the cyclopropylmethylsilane **20** with the allenylsilane **2b** afforded a mixture of **21** and **22** (**21/22** = 1:1.1) as a colorless liquid, 148 mg, 90%.

^1H NMR: δ 7.69-7.67 (2H, m), 7.56-7.54 (2H, m), 7.41-7.21 (16H, m), 2.43-2.31 (1H, m), 2.19-2.10 (1H, m), 2.04-1.86 (3H, m), 1.72 (3H, bs), 1.62-1.24 (6H, m), 1.13-1.01 (1H, m), 0.99 (9H, s), 0.93-0.78 (1H, m), 0.85 (9H, s). ^{13}C NMR: δ 222.0, 160.8, 136.1, 136.08, 136.0, 135.9, 135.7, 135.6, 135.3, 135.1, 134.5, 129.1, 128.9, 128.8, 128.7, 128.6, 127.6, 127.5, 127.4, 123.0, 63.2, 47.4, 47.1, 37.4, 35.8, 34.5, 28.6, 27.7, 23.2, 19.8, 19.0, 17.9, 14.2. Anal. Calcd. for $\text{C}_{44}\text{H}_{54}\text{OSi}_2$: C, 80.67; H, 8.31. Found: C, 80.58; H, 8.22.

^1H NMR: δ 7.68-7.66 (2H, m), 7.59-7.55 (6H, m), 7.40-7.28 (12H, m), 2.90-2.84 (1H, m), 2.42-2.36 (1H, m), 2.31-2.06 (3H, m), 2.01-1.95 (1H, m), 1.85-1.78 (1H, m), 1.71-1.49 (3H, m), 1.39-1.12 (2H, m), 1.10 (3H, bs), 1.07 (9H, s), 1.01 (9H, s), 0.97-0.83 (1H, m). ^{13}C NMR: δ 223.0, 156.4, 136.0, 135.9, 135.8, 135.7, 135.1, 134.6, 131.7, 129.0, 128.9, 128.8, 127.64, 127.62, 127.6, 127.5, 69.0, 50.8, 43.0, 38.6, 28.2, 28.0, 27.9, 24.7, 19.8, 18.9, 18.1, 16.3, 9.1. Anal. Calcd. for $\text{C}_{44}\text{H}_{54}\text{OSi}_2$: C, 80.67; H, 8.31. Found: C, 80.50; H, 8.25.

References:

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