Supporting information for :
Chemo- and Stereoselective Palladium-catalyzed Allylic Alkylations Controlled
by Silicon.

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General Remarks. All reactions requiring anhydrous conditions were performed under a positive nitrogen or argon atmosphere using oven-dried glassware. All solvents were purified and distilled according to standard methods. Final product solutions were dried over MgSO_4 or Na_2SO_4 , filtered and evaporated under reduced pressure on a rotary evaporator. Thin layer chromatography (TLC) was performed on silica gel 60 F₂₅₄. Chromatographic purifications were conducted using 40-63 μm or 15-40 μm silica gel. All compounds were isolated as oils unless otherwise specified. ^1H NMR and ^{13}C NMR spectra were recorded on 200 MHz and 400 MHz spectrometers. Chemical shifts are given in ppm, referenced to the residual proton resonances of the solvents (7.25/77.16 ppm for CDCl_3). Coupling constants (*J*) are given in Hertz (Hz). The letters m, s, d, t, q, mean respectively multiplet, singlet, doublet, triplet, quartet. The letters br mean the signal is broad.

(E)-Acetic acid 4-acetoxy-2-(tert-butyldimethylsilyl)but-2-enyl ester (2b). Following the general method A, **2b** was isolated as a colorless oil (2.435 g, 85%). ¹H NMR (CDCl₃, 200 MHz): δ 5.95 (dt, 1H, *J* = 5.9 and 1 Hz); 4.69 (d, 2H, *J* = 5.9 Hz); 4.65 (s br, 2H); 2.03 (s, 3H); 2.00 (s, 3H); 0.83 (s, 9H); 0.06 (s, 6H); ¹³C NMR (CDCl₃, 50 MHz): δ 170.8; 170.7; 140.2; 137.5; 62.6; 61.6; 26.7; 21.0; 20.9; 17.1; -5.8. IR (ATR), cm⁻¹ : 2928; 2856; 1741; 1464; 1362; 1220; 1025; 824; 771. Anal. Calcd for C₁₄H₂₆O₄Si: C, 58.70; H, 9.15. Found: C, 58.65; H, 9.22.

(E)-Acetic acid 4-acetoxy-2-(dimethylphenylsilyl)but-2-enyl ester (2c). Following the general method A, **2c** was isolated as a colorless oil (3.05 g, 98%). ¹H NMR (CDCl₃, 400 MHz): δ 7.49 (m, 2H); 7.34 (m, 3H); 6.01 (tt, 1H, *J* = 5.6 and 1.5 Hz); 4.75 (d, 2H, *J* = 5.6 Hz); 4.73 (d, 2H, *J* = 1.5 Hz); 2.07 (s, 3H); 1.83 (s, 3H); 0.42 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.9; 170.7; 138.8; 138.5; 137.4; 133.9; 129.3; 127.9; 62.8; 61.5; 21.0 and 20.7: (2CH₃); -2.7. IR (ATR), cm⁻¹ : 2956; 1739; 1428; 1362; 1220; 1112; 1026; 817; 774; 733; 700. Anal. Calcd for C₁₆H₂₂O₄Si: C, 62.71; H, 7.24. Found: C, 63.04; H, 7.59.

(E)-Acetic acid 4-acetoxy-2-(methyldiphenylsilyl)-but-2-enyl ester (2d). Following the general method A, **2d** was isolated as a colorless oil (3.68 g, 98%). ¹H NMR (CDCl₃, 400 MHz): δ 7.52 (m, 4H); 7.38 (m, 2H); 7.36 (m, 4H); 5.99 (tt, 1H, *J* = 5.6 and 1.5 Hz); 4.82 (s br, 2H); 4.80 (d, 2H, *J* = 5.6 Hz); 2.05 (s, 3H); 1.67 (s, 3H); 0.73 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.8; 170.6; 141.0; 137.1; 135.1; 134.0; 129.6; 128.0; 62.8; 61.6; 21.0; 20.5; -3.7. IR (ATR), cm⁻¹ : 3069; 1739; 1428; 1376; 1361; 1220; 1111; 1026; 787; 726; 698. Anal. Calcd for C₂₁H₂₄O₄Si: C, 68.45; H, 6.56. Found: C, 68.38; H, 6.46.

(E)-Acetic acid 4-acetoxy-2-triphenylsilyl-but-2-enyl ester (2e). Following the general method A, **2e** was isolated as a white solid (3.28 g, 72%). M.p. = 66 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.59 (m, 3_2H); 7.43 (m, 3_3H); 6.17 (t, 1H, *J* = 5.6 Hz); 4.90 (s, 2H); 4.88 (s, 2H); 2.08 (s, 3H); 1.60 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7; 170.5; 143.4; 136.2; 135.3; 133.4; 129.8; 128.0; 62.6; 61.7; 20.9; 20.4. IR (ATR), cm⁻¹ : 3055; 1739; 1427; 1360; 1224 (br); 1109; 1029; 698. Anal. Calcd for C₂₆H₂₆O₄Si: C, 72.53; H, 6.09. Found: C, 72.45; H, 6.03

(E)-Acetic acid 4-acetoxy-2-[(4-methoxyphenyl)-dimethylsilyl]-but-2-enyl ester (2f). Following the general method A, **2f** was isolated as a white solid (1.34 g, 98%). ¹H NMR (CDCl₃, 400

MHz): δ 7.40 (d, 2H, J = 8.6 Hz); 6.89 (d, 2H, J = 8.6 Hz); 5.97 (tt, 1H, J = 5.6 and 1.5 Hz); 4.73 (d, 2H, J = 5.6 Hz); 4.71 (s br, 2H); 3.79 (s, 3H); 2.06 (s, 3H); 1.87 (s, 3H); 0.38 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.8; 170.6; 160.6; 139.1; 138.3; 135.4; 128.0; 113.7; 62.8; 61.5; 55.1; 21.0; 20.8; -2.6. IR (neat), cm^{-1} : 2956; 1743; 1594; 1504; 1278; 1248; 1183; 1113; 1030; 824; 774. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_5\text{Si}$: C, 60.69; H, 7.19. Found : C, 60.58; H, 7.33.

(E)-Acetic acid 4-acetoxy-2-[dimethyl-(4-trifluoromethylphenyl)-silanyl]-but-2-enyl ester (2g). Following the general method A, **2g** was isolated as a white solid (1.50 g, 98%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.60 (d, 2H, J = 8.1 Hz); 7.57 (d, 2H, J = 8.1 Hz); 6.01 (t, 1H, J = 5.6 Hz); 4.74 (d, 2H, J = 5.6 Hz); 4.72 (s, 2H); 2.06 (s, 3H); 1.79 (s, 3H); 0.42 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.8; 170.5; 142.7; 139.2; 137.9; 134.2; 129.6: (q, $^2J_{\text{C-F}}$ = 128 Hz); 122.7: (q, $^1J_{\text{C-F}}$ = 1082 Hz); 124.4; 62.8; 61.4; 20.9; 20.6; -2.9; ^{19}F NMR (CDCl_3 , 367 MHz): δ -63.39. IR (neat), cm^{-1} : 2958; 1747; 1379; 1326; 1224; 1164; 1127; 1060; 1029; 831; 779; 700. Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{F}_3\text{O}_4\text{Si}$: C, 54.53; H, 5.65. Found: C, 54.38; H, 5.84

(Z)-2-(4-acetoxy-2-triethylsilanyl-but-2-enyl)-malonic acid dimethyl ester [(Z)-6a]. Following the general method B, from **(Z)-2a**, **(Z)-6a** was isolated as a 90/10 mixture of *Z* and *E* isomers as a colorless oil (259 mg, 72%). ^1H NMR (CDCl_3 , 400 MHz): δ 6.08 (t, 1H, J = 6.6 Hz); 4.53 (d, 2H, J = 6.6 Hz); 3.69 (s, 6H); 3.48 (t, 1H, J = 7.6 Hz); 2.67 (d, 2H, J = 7.6 Hz); 2.01 (s, 3H); 0.91 (t, 9H, J = 7.6 Hz); 0.67 (q, 6H, J = 7.6 Hz); ^{13}C NMR (CDCl_3 , 100 MHz): δ 169.42; 169.39; 139.3; 138.4; 63.6; 52.6; 51.7; 36.5; 21.1; 7.4; 4.1. IR (ATR), cm^{-1} : 2954; 2876; 1736; 1435; 1378; 1225; 1152; 1021; 962; 720. Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{O}_6\text{Si}$: C, 56.95; H, 8.43. Found: C, 57.02; H, 8.60.

(E)-2-[4-acetoxy-2-(tert-butyldimethylsilanyl)but-2-enyl]-malonic acid dimethylester (6b). Following the general method B, **6b** was isolated as a colorless oil (357 mg, 98%). ^1H NMR (CDCl_3 , 200 MHz): δ 5.80 (t, 1H, J = 5.9 Hz); 4.60 (d, 2H, J = 5.9 Hz); 3.61 (s, 6H); 3.35 (t, 1H, J = 7.9 Hz); 2.73 (d, 2H, J = 7.9 Hz); 1.95 (s, 3H); 0.77 (s, 9H); -0.01 (s, 6H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 170.7; 169.2; 139.0; 138.9; 61.2; 52.5; 51.4; 29.9; 26.7; 20.9; 17.2; -5.6. IR (neat), cm^{-1} : 2940; 2840; 1740; 1430; 1355; 1230; 1145; 1020; 820; 680. Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{O}_6\text{Si}$: C, 56.95; H, 8.43. Found: C, 56.96; H, 8.51.

(E)-2-[4-Acetoxy-2-(dimethylphenylsilanyl)-but-2-enyl]-malonic acid dimethyl ester (6c).

Following the general method B, **6c** was isolated as a colorless oil (358 mg, 94%). ¹H NMR (CDCl₃, 200 MHz): δ 7.46 (m, 2H); 7.32 (m, 3H); 5.97 (t, 1H, *J* = 6.4 Hz); 4.73 (d, 2H, *J* = 6.4 Hz); 3.69 (s, 6H); 3.24 (t, 1H, *J* = 7.9 Hz); 2.76 (d, 2H, *J* = 7.9 Hz); 2.04 (s, 3H); 0.38 (s, 6H); ¹³C NMR (CDCl₃, 50 MHz): δ 170.8; 169.1; 139.7; 138.9; 137.3; 133.9; 129.3; 127.9; 61.4; 52.5; 51.0; 29.3; 21.0; -2.7. IR (neat), cm⁻¹: 3069; 3009; 2955; 1740; 1436; 1378; 1234; 1111; 1029; 835; 818; 777; 736; 703. Anal. Calcd. for C₁₉H₂₆O₆Si: C, 60.29; H, 6.92. Found: C, 60.14; H, 7.06.

(E)-2-[4-acetoxy-2-(methyldiphenylsilanyl)-but-2-enyl]-malonic acid dimethyl ester (6d).

Following the general method B, **6d** was isolated as a colorless oil (440 mg, 98%). ¹H NMR (CDCl₃, 400 MHz): δ 7.49-7.47 (m, 4H); 7.39-7.33 (m, 6H); 5.96 (t, 1H, *J* = 6.0 Hz); 4.78 (d, 2H, *J* = 6.0 Hz); 3.60 (s, 6H); 3.17 (t, 1H, *J* = 7.6 Hz); 2.85 (d, 2H, *J* = 7.6 Hz); 2.03 (s, 3H); 0.69 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.9; 169.2; 141.7; 137.7; 135.2; 129.7; 128.1; 61.6; 52.6; 51.1; 29.7; 21.1; -3.5. IR (ATR), cm⁻¹: 2953; 1734; 1429; 1361; 1228; 1026; 787; 725; 700. Anal. Calcd for C₂₄H₂₈O₆Si: C, 65.43; H, 6.41. Found: C, 65.25; H, 6.54.

(E)-2-{4-Acetoxy-2-[(4-methoxyphenyl)-dimethylsilanyl]-but-2-enyl}-malonic acid dimethyl ester (6f). Following the general method B, **6f** was isolated as a colorless oil (337 mg, 82%). ¹H NMR (CDCl₃, 400 MHz): δ 7.38 (d, 2H, *J* = 8.6 Hz); 6.88 (d, 2H, *J* = 8.6 Hz); 5.95 (t, 1H, *J* = 6.1 Hz); 4.72 (d, 2H, *J* = 6.1 Hz); 3.79 (s, 3H); 3.62 (s, 6H); 3.26 (t, 1H, *J* = 7.6 Hz); 2.76 (d, 2H, *J* = 7.6 Hz); 2.04 (s, 3H); 0.36 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ 171.1; 169.5; 160.9; 140.3; 138.9; 135.7; 128.2; 114.0; 61.7; 55.3; 52.8; 51.3; 29.6; 21.3; -2.2. IR (neat), cm⁻¹: 2954; 1735; 1593; 1503; 1436; 1276; 1228; 1182; 1109; 1027; 812; 772. Anal. Calcd for C₂₀H₂₈O₇Si: C, 58.80; H, 6.91. Found: C, 58.70; H, 7.08.

(E)-2-{4-Acetoxy-2-[dimethyl-(4-trifluoromethyl)phenylsilanyl]-but-2-enyl}-malonic acid dimethyl ester (6g). Following the general method B, **6g** was isolated as a colorless oil (287 mg, 64%). ¹H NMR (CDCl₃, 400 MHz): δ 7.57 (s, 4H); 5.98 (t, 1H, *J* = 6.1 Hz); 4.74 (d, 2H, *J* = 6.1 Hz); 3.59 (s, 6H); 3.21 (t, 1H, *J* = 7.6 Hz); 2.76 (d, 2H, *J* = 7.6 Hz); 2.04 (s, 3H); 0.40 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ: 170.9; 169.1; 142.6; 139.9; 138.9; 134.4; 134.3; 131.3 (q, ¹*J*_{C-F} = 128 Hz); 124.5 (q, ²*J*_{C-F} = 15 Hz); 61.5; 52.7; 51.2; 29.4; 21.1; -2.7. IR (ATR), cm⁻¹: 2956; 1736; 1436; 1324; 1229; 1161; 1122; 1059; 1019; 815; 777; 699. Anal. Calcd for C₂₀H₂₅F₃O₆Si: C, 53.80; H, 5.64. Found: C, 54.22; H, 6.07.

(Z) and (E)-2-(4-acetoxy-2-tert-butyl-but-2-enyl)-malonic acid dimethyl ester (10a). Following method B, (Z) and (E)-**10a** were purified by flash chromatography and isolated as a 1/1 mixture of colorless oil in 25% yield. **(Z)-10a** : ^1H NMR (CDCl_3 , 200 MHz): δ 5.47 (t, 1H, $J = 6.9$ Hz); 4.51 (d, 2H, $J = 6.9$ Hz); 3.66 (s, 6H); 3.45 (t, 1H, $J = 7.3$ Hz); 2.75 (d, 2H, $J = 7.3$ Hz); 1.98 (s, 3H); 1.10 (s, 9H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 170.8; 169.4; 148.6; 120.8; 61.7; 53.3; 52.5; 36.8; 29.7; 26.9; 21.0. **(E)-10a** : ^1H NMR(CDCl_3 , 200 MHz): δ 5.07 (t, 1H, $J = 6.2$ Hz); 4.67 (d, 2H, $J = 6.2$ Hz); 3.66 (s, 6H); 3.53 (t, 1H, $J = 7.8$ Hz); 2.61 (d, 2H, $J = 7.8$ Hz); 1.98 (s, 3H); 1.10 (s, 9H); ^{13}C NMR (CDCl_3 , 50 MHz): δ : 170.8; 169.4; 146.2; 122.5; 62.1; 51.2; 51.8; 35.9; 34.8; 30.4; 21.0.

(E) and (Z)-2-(2-tert-butyl-4-methoxycarbonyloxy-but-2-enyl)-malonic acid dimethyl ester (10b). Following method B without addition of base, (E) and (Z)-**10b** were separated by flash chromatography and isolated as colorless oil in 8% and 11% yield respectively. **(E)-10b** : ^1H NMR (CDCl_3 , 200 MHz): δ 5.55 (t, 1H, $J = 6.0$ Hz); 4.62 (d, 2H, $J = 6.0$ Hz); 3.75 (s, 6H); 3.45 (t, 1H, $J = 7.7$ Hz); 2.80 (d, 2H, $J = 7.7$ Hz); 1.05 (s, 9H); ^{13}C NMR (CDCl_3 , 50 MHz): δ : 169.3; 155.7; 146.8; 121.8; 65.4; 54.7; 52.6; 51.7; 36.0; 34.6; 30.4. **(Z)-10b** : ^1H NMR (CDCl_3 , 200 MHz): δ 5.13 (t, 1H, $J = 6.0$ Hz); 4.79 (d, 2H, $J = 6.0$ Hz); 3.70 (s, 6H); 3.56 (t, 1H, $J = 7.7$ Hz); 2.65 (d, 2H, $J = 7.7$ Hz); 1.14 (s, 9H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 169.4; 155.7; 149.2; 120.3; 65.0; 54.7; 52.6; 52.0; 36.8; 29.7; 26.8. IR (neat), cm^{-1} : 2956; 1736; 1337; 1346; 1258 (br); 1152; 950; 792. Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{O}_7$: C, 56.95; H, 7.65. Found: C, 56.96; H, 7.62.