



Supporting Information

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Regioselective Aliphatic Retro-[1,4]-Brook Rearrangements.

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Experimental

General: IR spectra were recorded in CHCl_3 solution on a JASCO FTIR-420 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL GX-270 or A-400 spectrometer in CDCl_3 solution using TMS and CDCl_3 (77.0 ppm) as internal standards, respectively. FAB mass spectra were obtained on a JEOL HX-110 mass spectrometer with 3-nitrobenzyl alcohol as the matrix. Optical rotations were determined on a JASCO DIP-370 digital polarimeter. All air- and moisture-sensitive reactions were carried out under an argon atmosphere in dry, freshly distilled solvents under anhydrous conditions. Flash chromatography was carried out with E. Merck silica gel 60 (230-400 mesh).

General procedure for retro-Brook rearrangement. 1,3-Bis(trialkylsilyloxy)-1-(tributylstannyl)butane (0.5 mmol) was dissolved in 4 mL of dry THF and cooled to -78°C under argon. A hexane solution of $n\text{BuLi}$ (5.0 equiv) was added. The reaction mixture was stirred for 30 min and then quenched with saturated aqueous NH_4Cl . The reaction mixture was extracted with diethyl ether, and the extract was washed with water and brine, dried with MgSO_4 , filtered, and evaporated. The crude products were purified by flash chromatography (4–8% ether-hexane) to give the [1,2]- and [1,4]-rearranged products.

Spectral data of 1,3-bis(trialkylsilyloxy)-1-(tributylstannyl)butanes 4a-g and 5a-g

(1S,3R)-1-Tributylstannyl-3-triethylsilyloxy-1-(trimethylsilyloxy)butane (4a): $[\alpha]_{\text{D}}^{25} +33.4^\circ$ (c 0.83, CHCl_3); IR (CHCl_3) 1250, 1170, 990, 840 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.12 (1H, dd, $J = 9.8, 4.0$ Hz), 3.89 (1H, m), 2.11 (1H, ddd, $J = 13.4, 9.8, 4.2$ Hz), 1.69 (1H, ddd, $J = 13.4, 8.6, 4.0$ Hz), 1.51–1.26 (12H, m), 1.16 (3H, d, $J = 6.1$ Hz), 1.02–0.78 (24H, m), 0.63–0.57 (6H, m), 0.08 (9H, s). Anal. Calcd for $\text{C}_{25}\text{H}_{58}\text{O}_2\text{Si}_2\text{Sn}$: C, 53.09; H, 10.34, found: C, 53.42; H, 10.65.

(1R,3R)-1-Tributylstannyl-3-triethylsilyloxy-1-(trimethylsilyloxy)butane (5a): $[\alpha]_{\text{D}}^{25} -10.8^\circ$ (c 0.86, CHCl_3); IR (CHCl_3) 1250, 1010, 840 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 4.20 (1H, dd, $J = 8.3, 6.6$ Hz), 3.84 (1H, m), 1.91 (2H, m), 1.53–1.27 (12H, m), 1.16 (3H, d, $J = 6.1$ Hz), 1.05–0.85 (24H, m), 0.63–0.57 (6H, m), 0.09 (9H, s). Anal. Calcd for $\text{C}_{25}\text{H}_{58}\text{O}_2\text{Si}_2\text{Sn}$: C, 53.09; H, 10.34, found: C, 53.26; H, 10.71.

(1S,3R)-1-Tributylstannyl-1,3-bis(triethylsilyloxy)butane (4b): $[\alpha]_{\text{D}}^{25} +22.1^\circ$ (c 0.66, CHCl_3); IR (CHCl_3) 1070, 1010 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 4.20 (1H, dd, $J = 8.4, 5.7$ Hz), 3.85 (1H, m), 2.08 (1H, ddd, $J = 13.8, 8.4, 5.0$ Hz), 1.76 (1H, ddd, $J = 13.8, 7.4, 5.7$ Hz), 1.57–1.24 (12H, m), 1.31 (3H, d, $J = 6.7$ Hz), 1.18–0.81 (33H, m), 0.64–0.53 (12H, m). Anal. Calcd for $\text{C}_{28}\text{H}_{64}\text{O}_2\text{Si}_2\text{Sn}$: C, 55.34; H, 10.62, found: C, 55.19; H, 10.77.

(1R,3R)-1-Tributylstannyl-1,3-bis(triethylsilyloxy)butane (5b): $[\alpha]_{\text{D}}^{25} +3.33^\circ$ (c 0.83, CHCl_3); IR (CHCl_3) 1380, 1070, 1010 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 4.13 (1H, t, $J = 7.7$ Hz), 3.78 (1H, m), 1.97 (2H, m), 1.55–1.24 (12H, m), 1.13 (3H, d, $J = 6.7$ Hz), 0.99–0.81 (33H, m), 0.64–0.54 (12H, m). Anal. Calcd for $\text{C}_{28}\text{H}_{64}\text{O}_2\text{Si}_2\text{Sn}$: C, 55.34; H, 10.62, found: C, 55.26; H, 10.35.

(1S,3R)-3-(tert-Butyldimethylsilyloxy)-1-tributylstannyl-1-(trimethylsilyloxy)butane (4c): $[\alpha]_D^{25} +27.2^\circ$ (c 0.88, CHCl₃); IR (CHCl₃) 1460, 1380, 1260, 1070, 1010, 840 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 4.14 (1H, dd, *J* = 9.1, 5.6 Hz), 3.85 (1H, m), 2.09 (1H, ddd, *J* = 13.8, 9.1, 5.0 Hz), 1.72 (1H, ddd, *J* = 13.8, 7.7, 5.6 Hz), 1.55–1.24 (12H, m), 1.15 (3H, d, *J* = 6.1 Hz), 0.92–0.83 (15H, m), 0.89 (9H, s), 0.10–0.06 (15H). Anal. Calcd for C₂₅H₅₈O₂Si₂Sn: C, 53.09; H, 10.34, found: C, 52.81; H, 10.49.

(1R,3R)-3-(tert-Butyldimethylsilyloxy)-1-tributylstannyl-1-(trimethylsilyloxy)butane (5c): $[\alpha]_D^{25} -16.3^\circ$ (c 1.0, CHCl₃); IR (CHCl₃) 1470, 1380, 1260, 1010, 840 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 4.22 (1H, dd, *J* = 8.9, 5.9 Hz), 3.86 (1H, m), 1.87 (2H, m), 1.55–1.24 (12H, m), 1.14 (3H, d, *J* = 6.1 Hz), 0.92–0.75 (15H, m), 0.88 (9H, s), 0.11–0.06 (15H). Anal. Calcd for C₂₅H₅₈O₂Si₂Sn: C, 53.09; H, 10.34, found: C, 52.75; H, 10.53.

(1S,3R)-3-(tert-Butyldimethylsilyloxy)-1-tributylstannyl-1-(triethylsilyloxy)butane (4d): $[\alpha]_D^{25} +16.0^\circ$ (c 1.33, CHCl₃); IR (CHCl₃) 1470, 1380, 1260, 1070, 1010, 840 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 4.21 (1H, t, *J* = 7.4 Hz), 3.80 (1H, m), 2.06 (1H, ddd, *J* = 13.8, 7.4, 6.1 Hz), 1.79 (1H, dt, *J* = 13.8, 6.7 Hz), 1.55–1.24 (12H, m), 1.15 (3H, d, *J* = 6.1 Hz), 1.11–0.83 (24H, m), 0.89 (9H, s), 0.62–0.53 (6H, m), 0.06 (3H, s), 0.05 (3H, s). Anal. Calcd for C₂₈H₆₄O₂Si₂Sn: C, 55.34; H, 10.62, found: C, 55.18; H, 10.88.

(1R,3R)-3-(tert-Butyldimethylsilyloxy)-1-tributylstannyl-1-(triethylsilyloxy)butane (5d): $[\alpha]_D^{25} -0.78^\circ$ (c 0.68, CHCl₃); IR (CHCl₃) 1470, 1380, 1260, 1070, 1010, 840 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 4.16 (1H, t, *J* = 7.7 Hz), 3.80 (1H, m), 2.04 (2H, m), 1.49–1.13 (12H, m), 1.12 (3H, d, *J* = 6.1 Hz), 0.98–0.83 (24H, m), 0.88 (9H, s), 0.63–0.54 (6H, m), 0.063 (3H, s), 0.061 (3H, s). Anal. Calcd for C₂₈H₆₄O₂Si₂Sn: C, 55.34; H, 10.62, found: C, 55.75; H, 10.26.

(1S,3R)-3-(tert-Butyldiphenylsilyloxy)-1-tributylstannyl-1-(trimethylsilyloxy)butane (4e): $[\alpha]_D^{25} +2.13^\circ$ (c 0.34, CHCl₃); IR (CHCl₃) 1430, 1120, 1070, 1000, 850, 710 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.69–7.33 (10H, m), 4.12 (1H, dd, *J* = 9.8, 4.4 Hz), 3.90 (1H, m), 2.23 (1H, ddd, *J* = 13.5, 9.8, 4.0 Hz), 1.72 (1H, ddd, *J* = 13.5, 8.1, 4.4 Hz), 1.49–1.20 (12H, m), 1.052 (3H, d, *J* = 6.1 Hz), 1.050 (9H, s), 0.95–0.81 (15H, m), –0.48 (9H, s). Anal. Calcd for C₃₅H₆₂O₂Si₂Sn: C, 60.95; H, 9.06, found: C, 60.47; H, 9.22.

(1R,3R)-3-(tert-Butyldiphenylsilyloxy)-1-tributylstannyl-1-(trimethylsilyloxy)butane (5e): $[\alpha]_D^{25} +26.9^\circ$ (c 0.43, CHCl₃); IR (CHCl₃) 1250, 1110, 1010, 850 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.70–7.26 (10H, m), 4.12 (1H, dd, *J* = 8.7, 6.4 Hz), 3.85 (1H, m), 2.00 (2H, m), 1.47–1.22 (12H, m), 1.03 (9H, s), 1.02 (3H, d, *J* = 6.1 Hz), 0.89–0.77 (15H, m), 0.02 (9H, s). Anal. Calcd for C₃₅H₆₂O₂Si₂Sn: C, 60.95; H, 9.06, found: C, 60.81; H, 9.37.

(1S,3R)-3-(tert-Butyldiphenylsilyloxy)-1-tributylstannyl-1-(triethylsilyloxy)butane (4f): $[\alpha]_D^{25} +22.1^\circ$ (c 0.68, CHCl₃); IR (CHCl₃) 1430, 1380, 1110, 1070, 1010, 710 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.70–7.33 (10H, m), 4.24 (1H, dd, *J* = 8.1, 6.1 Hz), 3.90 (1H, m), 2.21 (1H, ddd, *J* = 13.8, 8.1, 5.7 Hz), 1.81 (1H, dt, *J* = 13.8, 6.1 Hz), 1.47–1.20 (12H, m), 1.08 (9H, s), 1.06 (3H, d, *J* = 6.1 Hz), 0.92–0.74 (24H, m), 0.55–0.46 (6H, m). Anal. Calcd for C₃₈H₆₈O₂Si₂Sn: C, 62.37; H, 9.37, found: C, 62.06; H, 9.45.

(1R,3R)-3-(tert-Butyldiphenylsilyloxy)-1-tributylstannyl-1-(triethylsilyloxy)butane (5f): $[\alpha]_D^{25} +12.5^\circ$ (c 0.35, CHCl₃); IR (CHCl₃) 1430, 1380, 1010, 700 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.71–7.33 (10H, m), 4.09 (1H, t, *J* = 7.7 Hz), 3.78 (1H, m), 2.13 (1H, ddd, *J* = 13.1, 8.1, 5.1 Hz), 2.01 (1H, dt, *J* = 13.1, 7.7 Hz), 1.45–1.18 (12H, m), 1.04 (9H, s), 1.02 (3H, d, *J* = 6.1 Hz), 0.94–0.67 (24H, m), 0.57–0.48 (6H, m). Anal. Calcd for C₃₈H₆₈O₂Si₂Sn: C, 62.37; H, 9.37, found: C, 62.31; H, 9.68.

(1S,3R)-1-(tert-Butyldimethylsilyloxy)-3-(tert-Butyldiphenylsilyloxy)-1-(tributylstannyl)butane (4g): $[\alpha]_D^{25} +23.7^\circ$ (c 0.42, CHCl₃); IR (CHCl₃) 1470, 1430, 1380, 1110, 1070, 1000, 710 cm⁻¹; ¹H NMR (270

MHz, CDCl₃) δ 7.69–7.32 (10H, m), 4.19 (1H, dd, J = 8.4, 5.4 Hz), 3.92 (1H, m), 2.22 (1H, ddd, J = 13.8, 8.4, 5.0 Hz), 1.79 (1H, ddd, J = 13.8, 8.1, 5.4 Hz), 1.50–1.20 (12H, m), 1.25 (9H, s), 1.08 (9H, s), 1.05 (3H, d, J = 6.1 Hz), 0.92–0.74 (18H, m), –0.02 (3H, s), –0.07 (3H, s). Anal. Calcd for C₃₈H₆₈O₂Si₂Sn: C, 62.37; H, 9.37, found: C, 62.49; H, 9.46.

(1R,3R)-1-(tert-Butyldimethylsilyloxy)-3-(tert-Butyldiphenylsilyloxy)-1-(tributylstannyl)butane (5g): $[\alpha]_D^{25}$ +9.84° (c 0.58, CHCl₃); IR (CHCl₃) 1470, 1260, 1110, 1020, 840, 770, 700 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 7.70–7.33 (10H, m), 4.04 (1H, t, J = 7.7 Hz), 3.80 (1H, m), 2.12 (1H, ddd, J = 13.1, 7.7, 5.0 Hz), 1.79 (1H, dt, J = 13.1, 7.7 Hz), 1.45–1.18 (12H, m), 1.04 (9H, s), 1.02 (3H, d, J = 6.1 Hz), 0.84 (9H, s), 0.88–0.67 (15H, m), –0.02 (3H, s). Anal. Calcd for C₃₈H₆₈O₂Si₂Sn: C, 62.37; H, 9.37, found: C, 62.69; H, 9.13.

Spectral data of compounds 6a-g, 7a-g, 8-10 in Table 1 and Scheme 3

(1S,3R)-3-Triethylsilyloxy-1-(trimethylsilyl)butanol (6a): $[\alpha]_D^{25}$ +30.4° (c 0.68, CHCl₃); IR (CHCl₃) 3480, 1250, 1130, 1070, 980, 840, 710 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 4.10 (1H, m), 3.51 (1H, dd, J = 11.4, 4.0 Hz), 3.42 (1H, br, OH), 1.63 (2H, m), 1.20 (3H, d, J = 6.1 Hz), 1.00–0.95 (9H, m), 0.68–0.59 (6H, m), 0.02 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 73.0, 66.1, 41.5, 24.5, 6.8 (3xC), 5.1 (3xC), –4.2 (3xC); HRFABMS m/z calcd for C₁₃H₃₃O₂Si₂ (MH⁺) 277.2019, found 277.2025.

(2R,4S)-4-Triethylsilyl-4-trimethylsilyoxy-2-butanol (7a): $[\alpha]_D^{25}$ +1.09° (c 0.94, CHCl₃); IR (CHCl₃) 3520, 1260, 1060, 990, 840, 710 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 3.94 (1H, m), 3.75 (1H, dd, J = 11.4, 4.0 Hz), 2.58 (1H, br, OH), 1.82 (1H, ddd, J = 14.5, 11.4, 7.4 Hz), 1.51 (1H, dt, J = 14.5, 4.0 Hz), 1.17 (3H, d, J = 6.4 Hz), 0.99–0.93 (9H, m), 0.62–0.53 (6H, m), 0.13 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 68.3, 65.1, 42.9, 23.2, 7.5 (3xC), 1.8 (3xC), 0.6 (3xC); HRFABMS m/z calcd for C₁₃H₃₃O₂Si₂ (MH⁺) 277.2019, found 277.2031.

(1S,3R)-1-Triethylsilyl-3-(triethylsilyloxy)butanol (6b): $[\alpha]_D^{25}$ +32.1° (c 1.0, CHCl₃); IR (CHCl₃) 3480, 1130, 1070, 1010, 980, 710 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 4.08 (1H, m), 3.68 (1H, dd, J = 11.4, 1.4 Hz), 3.23 (1H, br, OH), 1.74 (1H, ddd, J = 14.8, 11.4, 9.1 Hz), 1.52 (1H, ddd, J = 14.8, 4.4, 1.4 Hz), 1.19 (3H, d, J = 6.1 Hz), 1.01–0.94 (18H, m), 0.68–0.54 (12H, m); ¹³C NMR (100 MHz, CDCl₃) δ 72.8, 64.2, 42.2, 24.4, 7.5 (3xC), 6.8 (3xC), 5.1 (3xC), 1.5 (3xC); HRFABMS m/z calcd for C₁₆H₃₉O₂Si₂ (MH⁺) 319.2489, found 319.2472.

(2R,4S)-4-Triethylsilyl-4-triethylsilyoxy-2-butanol (7b): $[\alpha]_D^{25}$ –0.16° (c 1.0, CHCl₃); IR (CHCl₃) 3480, 1230, 1070, 1010, 710 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 3.94 (1H, m), 3.76 (1H, dd, J = 9.7, 4.7 Hz), 2.35 (1H, br, OH), 1.80 (1H, ddd, J = 14.1, 9.7, 7.4 Hz), 1.58 (1H, dt, J = 14.1, 4.7 Hz), 1.17 (3H, d, J = 6.1 Hz), 0.99–0.93 (18H, m), 0.66–0.54 (12H, m); ¹³C NMR (100 MHz, CDCl₃) δ 67.8, 64.5, 43.6, 23.6, 7.5 (3xC), 7.0 (3xC), 5.3 (3xC), 1.9 (3xC); HRFABMS m/z calcd for C₁₆H₃₉O₂Si₂ (MH⁺) 319.2489, found 319.2481.

(1S,3R)-3-(tert-Butyldimethylsilyloxy)-1-(trimethylsilyl)butanol (6c): $[\alpha]_D^{25}$ –44.3° (c 0.28, CHCl₃); IR (CHCl₃) 3500, 1380, 1250, 1130, 1070, 880, 840 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 4.08 (1H, m), 3.49 (1H, d, J = 10.8 Hz), 3.22 (1H, br, OH), 1.59 (2H, m), 1.18 (3H, d, J = 6.1 Hz), 0.90 (9H, s), 0.13 (3H, s), 0.11 (3H, s), 0.03 (9H, s); HRFABMS m/z calcd for C₁₃H₃₃O₂Si₂ (MH⁺) 277.2019, found 277.2032.

(2R,4S)-4-(tert-Butyldimethylsilyl)-4-trimethylsilyoxy-2-butanol (7c): $[\alpha]_D^{25}$ +7.05° (c 1.1, CHCl₃); IR (CHCl₃) 3500, 1470, 1250, 1060, 990, 910, 840 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.94 (1H, m), 3.49 (1H, dd, J = 10.8, 3.7 Hz), 2.42 (1H, br, OH), 1.85 (1H, ddd, J = 14.5, 10.8, 6.7 Hz), 1.56 (1H, ddd, J =

14.5, 5.0, 3.7 Hz), 1.17 (3H, d, $J = 6.1$ Hz), 0.91 (9H, s), 0.12 (9H, s), -0.01 (3H, s), -0.03 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 67.8, 65.2, 44.1, 27.3 (3xC), 23.1, 17.1, 0.8 (3xC), -6.6 , -7.3 ; HRFABMS m/z calcd for $\text{C}_{13}\text{H}_{33}\text{O}_2\text{Si}_2$ (MH^+) 277.2019, found 277.2002.

(1S,3R)-3-(tert-Butyldimethylsilyloxy)-1-(triethylsilyl)butanol (6d): $[\alpha]_D^{25} -31.7^\circ$ (c 0.72, CHCl_3); IR (CHCl_3) 3500, 1260, 1130, 1070, 980, 890, 840 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 4.06 (1H, m), 3.65 (1H, dd, $J = 11.1, 1.5$ Hz), 3.04 (1H, br, OH), 1.74 (1H, ddd, $J = 14.8, 11.1, 9.1$ Hz), 1.54 (1H, ddd, $J = 14.8, 7.7, 1.5$ Hz), 1.18 (3H, d, $J = 6.1$ Hz), 0.98–0.95 (9H, m), 0.90 (9H, s), 0.67–0.54 (6H, m), 0.12 (3H, s), 0.10 (3H, s); HRFABMS m/z calcd for $\text{C}_{16}\text{H}_{39}\text{O}_2\text{Si}_2$ (MH^+) 319.2489, found 319.2453.

(2R,4S)-4-(tert-Butyldimethylsilyl)-4-triethylsilyloxy-2-butanol (7d): $[\alpha]_D^{25} +0.68^\circ$ (c 0.92, CHCl_3); IR (CHCl_3) 3500, 1460, 1250, 1070, 1010, 830 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 3.94 (1H, m), 3.74 (1H, dd, $J = 9.1, 5.4$ Hz), 2.05 (1H, br, OH), 1.80 (1H, ddd, $J = 14.1, 9.1, 7.1$ Hz), 1.66 (1H, dt, $J = 14.1, 5.0$ Hz), 1.18 (3H, d, $J = 6.1$ Hz), 0.99–0.87 (9H, m), 0.92 (9H, s), 0.67–0.58 (6H, m), 0.12 (9H, m), 0.01 (3H, s), -0.01 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 67.3, 64.9, 44.6, 27.4 (3xC), 23.5, 17.1, 7.1 (3xC), 5.4 (3xC), -6.5 (3xC), -7.1 (3xC); HRFABMS m/z calcd for $\text{C}_{16}\text{H}_{39}\text{O}_2\text{Si}_2$ (MH^+) 319.2489, found 319.2467.

(1S,3R)-3-(tert-Butyldiphenylsilyloxy)-1-(trimethylsilyl)butanol (6e): $[\alpha]_D^{25} -1.52^\circ$ (c 0.07, CHCl_3); IR (CHCl_3) 3500, 1430, 1260, 1100, 820, 700 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 7.76–7.38 (10H, m), 4.15 (1H, m), 3.48 (1H, dd, $J = 11.4, 1.5$ Hz), 2.43 (1H, br, OH), 1.70 (1H, ddd, $J = 14.5, 11.4, 7.4$ Hz), 1.52 (1H, ddd, $J = 14.5, 6.4, 1.5$ Hz), 1.05 (9H, s), 1.00 (3H, d, $J = 6.4$ Hz), 0.01 (3H, s); HRFABMS m/z calcd for $\text{C}_{23}\text{H}_{37}\text{O}_2\text{Si}_2$ (MH^+) 401.2332, found 401.2329.

(2R,4S)-4-(tert-Butyldiphenylsilyl)-4-trimethylsilyloxy-2-butanol (7e): $[\alpha]_D^{25} +4.62^\circ$ (c 0.81, CHCl_3); IR (CHCl_3) 3500, 1430, 1250, 1100, 1060, 900, 700 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 7.76–7.32 (10H, m), 4.33 (1H, dd, $J = 7.4, 6.1$ Hz), 3.59 (1H, m), 1.91 (2H, m), 1.28 (1H, br, OH), 1.11 (9H, s), 0.98 (3H, d, $J = 6.4$ Hz), 0.03 (9H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 136.4 (2xC), 136.3 (2xC), 134.1, 134.0, 129.2, 129.1, 127.6 (2xC), 127.5 (2xC), 66.6, 64.8, 44.9, 28.7 (3xC), 23.2, 18.5, 0.8 (3xC); HRFABMS m/z calcd for $\text{C}_{23}\text{H}_{37}\text{O}_2\text{Si}_2$ (MH^+) 401.2332, found 401.2337.

(1S,3R)-3-(tert-Butyldiphenylsilyloxy)-1-(triethylsilyl)butanol (6f): $[\alpha]_D^{25} -1.27^\circ$ (c 1.0, CHCl_3); IR (CHCl_3) 3500, 1430, 1240, 1100, 820, 700 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 7.76–7.37 (10H, m), 4.14 (1H, m), 3.64 (1H, dd, $J = 11.4, 1.5$ Hz), 2.27 (1H, br, OH), 1.81 (1H, ddd, $J = 14.5, 11.4, 7.4$ Hz), 1.53 (1H, ddd, $J = 14.5, 6.1, 1.5$ Hz), 1.06 (9H, s), 1.02 (3H, d, $J = 6.1$ Hz), 1.00–0.94 (9H, m), 0.61–0.52 (6H, m); HRFABMS m/z calcd for $\text{C}_{26}\text{H}_{43}\text{O}_2\text{Si}_2$ (MH^+) 443.2802, found 401.2793.

(2R,4S)-4-(tert-Butyldiphenylsilyl)-4-triethylsilyloxy-2-butanol (7f): $[\alpha]_D^{25} -4.76^\circ$ (c 0.34, CHCl_3); IR (CHCl_3) 3600, 1430, 1100, 1060, 1010, 700 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 7.79–7.31 (10H, m), 4.37 (1H, t, $J = 6.7$ Hz), 3.45 (1H, m), 1.91 (2H, m), 1.49 (1H, br, OH), 1.11 (9H, s), 0.97–0.91 (9H, m), 0.92 (3H, d, $J = 6.4$ Hz), 0.61–0.52 (6H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 136.4 (2xC), 136.3 (2xC), 134.2, 134.1, 129.2, 129.1, 127.6 (2xC), 127.5 (2xC), 66.1, 64.5, 45.3, 28.7 (3xC), 23.5, 18.6, 7.1 (3xC), 5.5 (3xC); HRFABMS m/z calcd for $\text{C}_{26}\text{H}_{43}\text{O}_2\text{Si}_2$ (MH^+) 443.2802, found 401.2817.

(1S,3R)-1-(tert-Butyldimethylsilyl)-3-(tert-butylphenylsilyloxy)butanol (8): $[\alpha]_D^{25} -0.66^\circ$ (c 0.53, CHCl_3); IR (CHCl_3) 3500, 1430, 1110, 820, 700 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 7.77–7.37 (10H, m), 4.15 (1H, m), 3.65 (1H, dd, $J = 11.4, 1.5$ Hz), 2.25 (1H, br, OH), 1.78 (1H, ddd, $J = 14.5, 11.4, 7.4$ Hz), 1.57 (1H, ddd, $J = 14.5, 5.7, 1.5$ Hz), 1.07 (9H, s), 1.03 (3H, d, $J = 6.1$ Hz), 0.94 (9H, m), -0.02 (3H, s), -0.10 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 135.9 (2xC), 134.4 (2xC), 133.8, 129.7, 129.6, 127.7 (2xC),

127.5 (2xC), 72.0, 63.3, 43.1, 27.1 (3xC), 27.0 (3xC), 23.8, 19.1, 16.8, -7.6, -8.8; HRFABMS m/z calcd for $C_{26}H_{43}O_2Si_2$ (MH^+) 443.2802, found 401.2793.

(2R,4S)-4-(tert-Butyldimethylsilyloxy)-4-(tert-butyldiphenylsilyl)-2-butanol (9): $[\alpha]_D^{25}$ -4.09° (c 0.55, $CHCl_3$); IR ($CHCl_3$) 3500, 1430, 1110, 1060, 840, 710 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 7.80–7.32 (10H, m), 4.35 (1H, dd, J = 7.4, 5.4 Hz), 3.36 (1H, m), 2.03 (1H, ddd, J = 14.8, 7.4, 4.7 Hz), 1.90 (1H, ddd, J = 14.8, 8.1, 5.4 Hz), 1.53 (1H, br, OH), 1.13 (9H, s), 0.90 (3H, d, J = 6.1 Hz), 0.87 (9H, s), 0.15 (3H, s), -0.11 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5 (2xC), 136.3 (2xC), 134.3 (2xC), 129.3, 129.1, 127.7 (2xC), 127.5 (2xC), 65.7, 63.8, 45.5, 28.8 (3xC), 26.1 (3xC), 23.6, 18.5, 18.2, -3.6, -4.4; HRFABMS m/z calcd for $C_{26}H_{43}O_2Si_2$ (MH^+) 443.2802, found 401.2733.

(2R,4S)-4-(tert-Butyldimethylsilyl)-4-(tert-butyldiphenylsilyloxy)-2-butanol (10): $[\alpha]_D^{25}$ -10.8° (c 0.55, $CHCl_3$); IR ($CHCl_3$) 3500, 1110, 1050, 830, 710 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 7.78–7.40 (10H, m), 3.66 (1H, t, J = 6.4 Hz), 3.40 (1H, m), 1.71 (2H, m), 1.58 (1H, br, OH), 1.00 (9H, s), 0.97 (9H, s), 0.63 (3H, d, J = 6.1 Hz), 0.06 (3H, s), 0.01 (3H, s); HRFABMS m/z calcd for $C_{26}H_{43}O_2Si_2$ (MH^+) 443.2802, found 401.2786.

Spectral data of 11a-g and 12a-g in Table 2

(1R,3R)-3-Triethylsilyloxy-1-(trimethylsilyl)butanol (11a): $[\alpha]_D^{25}$ -4.76° (c 1.0, $CHCl_3$); IR ($CHCl_3$) 3480, 1250, 1070, 1110, 980, 840, 710 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 4.26 (1H, m), 3.79 (1H, dd, J = 12.1, 2.0 Hz), 3.20 (1H, br, OH), 1.85 (1H, ddd, J = 14.5, 12.1, 3.7 Hz), 1.39 (1H, ddd, J = 14.5, 4.4, 2.0 Hz), 1.24 (3H, d, J = 6.4 Hz), 0.95–0.93 (9H, m), 0.65–0.56 (6H, m), 0.03 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.6, 61.7, 39.6, 22.2, 6.8 (3xC), 4.7 (3xC), -4.3 (3xC); HRFABMS m/z calcd for $C_{13}H_{33}O_2Si_2$ (MH^+) 277.2019, found 277.2035.

(2R,4R)-4-Triethylsilyl-4-trimethylsilyoxy-2-butanol (12a): $[\alpha]_D^{25}$ +5.02° (c 1.0, $CHCl_3$); IR ($CHCl_3$) 3480, 1260, 1070, 990, 850, 710 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 4.05 (1H, m), 3.89 (1H, t, J = 4.7 Hz), 3.12 (1H, br, OH), 1.66 (2H, m), 1.16 (3H, d, J = 6.1 Hz), 1.00–0.94 (9H, m), 0.66–0.56 (6H, m), 0.12 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.0, 64.7, 42.4, 24.0, 7.5 (3xC), 2.3 (3xC), 0.35 (3xC); HRFABMS m/z calcd for $C_{13}H_{33}O_2Si_2$ (MH^+) 277.2019, found 277.2028.

(1R,3R)-1-Triethylsilyl-3-(triethylsilyloxy)butanol (11b): $[\alpha]_D^{25}$ -1.93° (c 1.0, $CHCl_3$); IR ($CHCl_3$) 3470, 1380, 1240, 1130, 1070, 1010, 990, 710 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 4.26 (1H, m), 3.97 (1H, dd, J = 12.2, 1.5 Hz), 2.90 (1H, br, OH), 1.92 (1H, ddd, J = 14.4, 12.2, 3.7 Hz), 1.40 (1H, ddd, J = 14.4, 4.6, 1.5 Hz), 1.23 (3H, d, J = 6.1 Hz), 1.00–0.94 (18H, m), 0.65–0.56 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.4, 59.9, 40.4, 22.3, 7.5 (3xC), 6.8 (3xC), 4.7 (3xC), 1.5 (3xC); HRFABMS m/z calcd for $C_{16}H_{39}O_2Si_2$ (MH^+) 319.2489, found 319.2477.

(2R,4R)-4-Triethylsilyl-4-triethylsilyoxy-2-butanol (12b): $[\alpha]_D^{25}$ +5.10° (c 0.88, $CHCl_3$); IR ($CHCl_3$) 3470, 1420, 1250, 1070, 1010, 990, 710 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 4.07 (1H, m), 3.91 (1H, t, J = 4.7 Hz), 3.50 (1H, br, OH), 1.78 (1H, ddd, J = 14.8, 10.4, 4.7 Hz), 1.60 (1H, ddd, J = 14.8, 4.7, 2.0 Hz), 1.15 (3H, d, J = 6.1 Hz), 1.00–0.94 (18H, m), 0.67–0.58 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.7, 65.6, 42.5, 24.1, 7.6 (3xC), 6.9 (3xC), 5.1 (3xC), 2.5 (3xC); HRFABMS m/z calcd for $C_{16}H_{39}O_2Si_2$ (MH^+) 319.2489, found 319.2521.

(1R,3R)-3-(tert-Butyldimethylsilyloxy)-1-(trimethylsilyl)butanol (11c): $[\alpha]_D^{25}$ -3.47° (c 0.3, $CHCl_3$); IR ($CHCl_3$) 3470, 1260, 1070, 990, 840 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 4.28 (1H, m), 3.79 (1H, d, J = 12.1 Hz), 3.07 (1H, br, OH), 1.85 (1H, ddd, J = 14.9, 11.4, 3.7 Hz), 1.39 (1H, dd, J = 14.9, 4.7 Hz),

1.23 (3H, d, $J = 6.4$ Hz), 0.89 (9H, s), 0.09 (3H, s), 0.08 (3H, s), 0.03 (9H, s); HRFABMS m/z calcd for $C_{13}H_{33}O_2Si_2$ (MH^+) 277.2019, found 277.1993.

(2R,4R)-4-(tert-Butyldimethylsilyl)-4-trimethylsilyloxy-2-butanol (12c): $[\alpha]_D^{25} +0.91^\circ$ (c 1.1, $CHCl_3$); IR ($CHCl_3$) 3470, 1250, 1070, 990, 900, 840 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 4.05 (1H, m), 3.92 (1H, dd, $J = 5.4, 4.7$ Hz), 2.93 (1H, br, OH), 1.70 (2H, m), 1.15 (3H, d, $J = 6.1$ Hz), 0.91 (9H, s), 0.14 (9H, s), 0.03 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.6, 64.6, 43.2, 27.1 (3xC), 24.1, 16.9, 0.6 (3xC), -6.4 (3xC), -7.1 (3xC); HRFABMS m/z calcd for $C_{13}H_{33}O_2Si_2$ (MH^+) 277.2019, found 277.2041.

(1R,3R)-3-(tert-Butyldimethylsilyloxy)-1-(triethylsilyl)butanol (11d): $[\alpha]_D^{25} -5.14^\circ$ (c 0.44, $CHCl_3$); IR ($CHCl_3$) 3470, 1470, 1260, 1130, 1070, 990, 840 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 4.24 (1H, m), 3.97 (1H, d, $J = 12.4$ Hz), 2.80 (1H, br, OH), 1.91 (1H, ddd, $J = 14.5, 12.4, 3.7$ Hz), 1.40 (1H, ddd, $J = 14.5, 4.8, 1.5$ Hz), 1.22 (3H, d, $J = 6.4$ Hz), 1.01–0.95 (9H, m), 0.89 (9H, s), 0.64–0.55 (6H, m), 0.08 (3H, s), 0.07 (3H, s); HRFABMS m/z calcd for $C_{16}H_{39}O_2Si_2$ (MH^+) 319.2489, found 319.2497.

(2R,4R)-4-(tert-Butyldimethylsilyl)-4-triethylsilyloxy-2-butanol (12d): $[\alpha]_D^{25} +6.77^\circ$ (c 1.0, $CHCl_3$); IR ($CHCl_3$) 3480, 1260, 1070, 1010, 830 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 4.07 (1H, m), 3.93 (1H, t, $J = 4.7$ Hz), 3.34 (1H, br, OH), 1.83 (1H, ddd, $J = 14.9, 10.4, 4.4$ Hz), 1.66 (1H, ddd, $J = 14.9, 4.7, 2.4$ Hz), 1.14 (3H, d, $J = 6.4$ Hz), 1.00–0.94 (9H, m), 0.90 (9H, s), 0.69–0.59 (6H, m), 0.05 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 67.4, 65.7, 43.2, 27.2 (3xC), 24.0, 16.9, 7.0 (3xC), 5.3 (3xC), -6.21, -7.0; HRFABMS m/z calcd for $C_{16}H_{39}O_2Si_2$ (MH^+) 319.2489, found 319.2481.

(1R,3R)-3-(tert-Butyldiphenylsilyloxy)-1-(trimethylsilyl)butanol (11e): $[\alpha]_D^{25} +14.8^\circ$ (c 0.04, $CHCl_3$); IR ($CHCl_3$) 3430, 1430, 1250, 1110, 840, 700 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 7.73–7.38 (10H, m), 4.20 (1H, m), 3.72 (1H, d, $J = 13.1$ Hz), 2.64 (1H, br, OH), 1.84 (1H, m), 1.38 (1H, m), 1.21 (9H, s), 1.19 (3H, d, $J = 6.4$ Hz), 0.01 (9H, s); HRFABMS m/z calcd for $C_{23}H_{37}O_2Si_2$ (MH^+) 401.2332, found 401.2361.

(2R,4R)-4-(tert-Butyldiphenylsilyl)-4-trimethylsilyloxy-2-butanol (12e): $[\alpha]_D^{25} -5.93^\circ$ (c 1.0, $CHCl_3$); IR ($CHCl_3$) 3450, 1430, 1250, 1110, 1070, 1000, 845, 710 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 7.76–7.32 (10H, m), 4.55 (1H, dd, $J = 7.1, 3.7$ Hz), 3.89 (1H, m), 1.76 (2H, m), 1.30 (1H, br, OH), 1.13 (9H, s), 1.03 (3H, d, $J = 6.1$ Hz), 0.06 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4 (4xC), 134.4, 134.1, 129.2, 129.1, 127.6 (2xC), 127.4 (2xC), 65.9, 64.4, 44.0, 28.6 (3xC), 24.1, 18.4, 0.7 (3xC); HRFABMS m/z calcd for $C_{23}H_{37}O_2Si_2$ (MH^+) 401.2332, found 401.2337.

(1R,3R)-3-(tert-Butyldiphenylsilyloxy)-1-(triethylsilyl)butanol (11f): $[\alpha]_D^{25} +13.4^\circ$ (c 0.14, $CHCl_3$); IR ($CHCl_3$) 3500, 1470, 1380, 1110, 1060, 1000, 820, 700 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 7.74–7.35 (10H, m), 4.17 (1H, m), 3.86 (1H, d, $J = 11.8$ Hz), 2.17 (1H, br, OH), 1.87 (1H, ddd, $J = 14.5, 11.8, 2.5$ Hz), 1.38 (1H, ddd, $J = 14.5, 7.2, 1.5$ Hz), 1.16 (3H, d, $J = 6.4$ Hz), 1.06 (9H, s), 0.99–0.93 (9H, m), 0.57–0.54 (6H, m); HRFABMS m/z calcd for $C_{26}H_{43}O_2Si_2$ (MH^+) 443.2802, found 443.2814.

(2R,4R)-4-(tert-Butyldiphenylsilyl)-4-triethylsilyloxy-2-butanol (12f): $[\alpha]_D^{25} -7.71^\circ$ (c 0.34, $CHCl_3$); IR ($CHCl_3$) 3520, 1420, 1100, 1000, 700 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 7.79–7.29 (10H, m), 4.56 (1H, t, $J = 5.2$ Hz), 3.86 (1H, m), 1.80 (2H, m), 1.60 (1H, br, OH), 1.11 (9H, s), 1.01 (3H, d, $J = 6.4$ Hz), 0.93–0.87 (9H, m), 0.61–0.52 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4 (2xC), 136.3 (2xC), 134.5, 134.0, 129.2, 129.1, 127.6 (2xC), 127.4 (2xC), 66.3, 64.8, 44.4, 28.6 (3xC), 24.0, 18.4, 7.0 (3xC), 5.4 (3xC); HRFABMS m/z calcd for $C_{26}H_{43}O_2Si_2$ (MH^+) 443.2802, found 443.2785.

(1R,3R)-1-(tert-Butyldimethylsilyl)-3-(tert-butyldiphenylsilyloxy)butanol (11g): $[\alpha]_D^{25} +10.6^\circ$ (c 0.98, $CHCl_3$); IR ($CHCl_3$) 3460, 1480, 1430, 1250, 1120, 830, 710 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$) δ 7.77–

7.39 (10H, m), 4.17 (1H, m), 3.77 (1H, d, $J = 12.4$ Hz), 1.90 (1H, br, OH), 1.80 (1H, ddd, $J = 14.7, 12.4, 3.0$ Hz), 1.44 (1H, ddd, $J = 14.7, 13.1, 1.5$ Hz), 1.19 (3H, d, $J = 6.1$ Hz), 1.06 (9H, s), 0.90 (9H, s), -0.25 (3H, s), -0.89 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 136.0 (2xC), 135.9 (2xC), 134.0, 133.7, 129.8, 129.7, 127.7 (2xC), 127.5 (2xC), 68.2, 59.8, 41.7, 27.0 (6xC), 22.8, 19.2, 16.8, -7.7, -8.8 (3xC); HRFABMS m/z calcd for $\text{C}_{26}\text{H}_{43}\text{O}_2\text{Si}_2$ (MH^+) 443.2802, found 443.2779.

(2R,4R)-4-(tert-Butyldimethylsilyloxy)-4-(tert-butyldiphenylsilyl)-2-butanol (12g): $[\alpha]_D^{25} -6.65^\circ$ (c 1.1, CHCl_3); IR (CHCl_3) 3530, 1480, 1430, 1260, 1110, 1070, 840, 710 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 7.84–7.30 (10H, m), 4.56 (1H, dd, $J = 5.4, 4.4$ Hz), 3.90 (1H, m), 2.02 (1H, br, OH), 1.93 (1H, ddd, $J = 15.0, 9.8, 4.4$ Hz), 1.81 (1H, ddd, $J = 15.0, 5.4, 2.7$ Hz), 1.13 (9H, s), 1.00 (3H, d, $J = 6.1$ Hz), 0.82 (9H, s), 0.15 (3H, s), -0.11 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 136.5 (2xC), 136.4 (2xC), 134.7, 133.9, 129.3, 129.1, 127.6 (2xC), 127.5 (2xC), 66.6, 65.2, 44.1, 28.7 (3xC), 26.4 (3xC), 23.8, 18.5, 18.2, -3.6, -4.8; HRFABMS m/z calcd for $\text{C}_{26}\text{H}_{43}\text{O}_2\text{Si}_2$ (MH^+) 443.2802, found 443.2849.

Deprotection of the O-silyl group of the rearranged products

Typical procedure: Compounds **6a** and **7a** (each 0.1 mmol) were dissolved in 10% HCl-MeOH (0.5 mL), respectively. After stirring for 3 h at room temperature, each reaction mixture was concentrated under reduced pressure. Purification by flash chromatography (30 to 50% ethyl acetate in hexane) gave the corresponding 1-trialkylsilyl-1,3-butanediols.

(1S,3R)-1-Trimethylsilyl-1,3-butanediol obtained from **6a**: 90%; $[\alpha]_D^{25} -23.1^\circ$ (c 0.71, CHCl_3); IR (CHCl_3) 3600, 3480, 1250, 840 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 4.09 (1H, m), 3.63 (1H, dd, $J = 11.4, 2.4$ Hz), 1.91 (2H, br, OH), 1.64 (1H, ddd, $J = 14.8, 11.9, 9.1$ Hz), 1.53 (1H, dt, $J = 14.8, 2.4$ Hz), 1.23 (3H, d, $J = 6.1$ Hz), 0.04 (9H, s, SiMe_3); ^{13}C NMR (100 MHz, CDCl_3) δ 72.4, 67.8, 40.3, 24.3, -4.3 (3xC).

(1S,3R)-1-Triethylsilyl-1,3-butanediol obtained from **7a**: 85%; $[\alpha]_D^{25} -18.8^\circ$ (c 1.0, CHCl_3); IR (CHCl_3) 3610, 3490, 1240, 1020, 825 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 4.06 (1H, m), 3.79 (1H, dd, $J = 12.1, 2.0$ Hz), 2.80 (2H, br, OH), 1.71 (1H, ddd, $J = 14.6, 11.8, 9.4$ Hz), 1.51 (1H, dt, $J = 14.6, 2.2$ Hz), 1.20 (3H, d, $J = 6.1$ Hz), 0.98 (9H, t, $J = 7.7$ Hz, SiEt_3), 0.59 (6H, q, $J = 7.7$ Hz, SiEt_3); ^{13}C NMR (100 MHz, CDCl_3) δ 72.5, 66.2, 40.9, 24.2, 7.4 (3xC), 1.4 (3xC).

Acetylation of the rearranged products

Typical procedure: Compounds **6a** and **7a** (each 0.01 mmol) were dissolved in pyridine (0.2 mL) and acetic anhydride (0.2 mL), respectively. After stirring for 4 h at room temperature, each reaction mixture was concentrated under reduced pressure. Purification by flash chromatography (20 to 30% CH_2Cl_2 in hexane) gave the corresponding 1-acetoxy-3-triethylsilyloxy-1-trimethylsilylbutane and 3-acetoxy-1-trimethylsilyloxy-1-triethylsilylbutane.

(1S,3R)-1-Acetoxy-3-triethylsilyloxy-1-trimethylsilylbutane obtained from **6a**: 91%; IR (CHCl_3) 1725, 1240, 1005 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 4.93 (1H, dd, $J = 12.4, 1.7$ Hz), 3.71 (1H, m), 2.03 (3H, s), 1.98 (1H, ddd, $J = 14.5, 12.4, 2.7$ Hz), 1.55 (1H, ddd, $J = 14.5, 9.7, 1.7$ Hz), 1.18 (3H, d, $J = 6.1$ Hz), 0.96 (9H, t, $J = 7.7$ Hz, OSiEt_3), 0.59 (6H, q, $J = 7.7$ Hz, OSiEt_3); 0.03 (9H, s, SiMe_3).

(1S,3R)-3-Acetoxy-1-trimethylsilyloxy-1-triethylsilylbutane obtained from **7a**: 83%; IR (CHCl_3) 1730, 1255, 1010 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 4.92 (1H, m), 3.56 (1H, t, $J = 6.7$ Hz), 2.02 (3H, s), 1.92 (1H, dt, $J = 14.1, 7.1$ Hz), 1.75 (1H, dt, $J = 14.1, 6.7$ Hz), 1.23 (3H, d, $J = 6.4$ Hz), 0.96 (9H, t, $J = 7.9$ Hz, SiEt_3), 0.61 (6H, q, $J = 7.9$ Hz, SiEt_3); 0.13 (9H, s, OSiMe_3).