Supporting information for:

Unprecedented Highly Stereoselective α - and β -C-Glycosidation with Chiral Titanium Enolates

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1. Characterisation of adducts **2a–g** and **3a–g**

Pure samples of **2a–g** and **3a–g** were obtained by column chromatography or MPLC.

2a. Yellow oil; R_f (CH_2Cl_2) = 0.20; HPLC (hexanes/EtOAc 97:3) t_R = 17.1 min; $[\alpha]_D = +77.1$ ($c=0.75$ in CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ = 5.95 (1H, ddd, J = 10.4 Hz, J = 2.3 Hz, J = 1.2 Hz, $\text{CH}=\text{CHCHOAc}$), 5.87 (1H, ddd, J = 10.4 Hz, J = 3.0 Hz, J = 1.8 Hz, $\text{CH}=\text{CHCHOAc}$), 5.30–5.20 (1H, m, NCH), 5.15–5.10 (1H, m, CHOAc), 5.08 (1H, q, J = 6.8 Hz, COCHCH_3), 4.70–4.63 (1H, m, OCHCH), 4.21 (1H, dd, J = 11.7 Hz, J = 6.1 Hz, $\text{CH}_x\text{H}_y\text{OAc}$), 4.14 (1H, dd, J = 11.7 Hz, J = 4.0 Hz, $\text{CH}_x\text{H}_y\text{OAc}$), 3.93 (1H, dt, J = 6.1 Hz, J = 4.0 Hz, CHCH_2OAc), 3.49 (1H, dd, J = 11.6 Hz, J = 8.2 Hz, SCH_xH_y), 3.01 (1H, dd, J = 11.6 Hz, J = 1.2 Hz, SCH_xH_y), 2.40–2.25 (1H, m, $\text{CH}(\text{CH}_3)_2$), 2.08 (6H, s, Ac), 1.26 (3H, d, J = 6.8 Hz, COCHCH_3), 1.06 (3H, d, J = 7.0 Hz, CH_3), 0.98 (3H, d, J = 6.7 Hz, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3): δ = 202.9, 174.9, 170.7, 170.4, 131.2, 124.6, 71.8, 72.7, 70.8, 64.8, 62.9, 41.5, 30.8, 29.8, 21.0, 20.8, 19.1, 17.6, 13.6; IR (film): ν = 2945, 1735, 1680, 1360, 1230, 1160 cm^{-1} ; HRMS (+FAB): calcd. for $[\text{M}+\text{H}]^+$ $\text{C}_{19}\text{H}_{28}\text{NO}_6\text{S}_2$ 430.1358, found 430.1342.

3a. Yellow oil; R_f (CH_2Cl_2) = 0.20; HPLC (hexanes/EtOAc 90:10) t_R = 34.7 min; $[\alpha]_D = -98.0$ ($c=1.32$ in CHCl_3); ^1H NMR (500 MHz, C_6D_6): δ = 5.74–5.70 (1H, m, $\text{CH}=\text{CHCHOAc}$), 5.64–5.40 (1H, m, $\text{CH}=\text{CHCHOAc}$), 5.46–5.40 (1H, m, CHOAc), 5.00–4.90 (2H, m, NCH and COCHCH_3), 4.88–4.82 (1H, m, $\text{COCH}(\text{CH}_3)\text{CH}$), 4.25 (1H, dd, J = 12.0 Hz, J = 2.6 Hz,

CH_xH_yOAc), 4.10 (1H, dd, $J = 12.0$ Hz, $J = 5.2$ Hz, CH_xH_yOAc), 3.55–3.48 (1H, m, CHCH₂OAc), 2.39 (1H, dd, $J = 11.5$ Hz, $J = 8.9$ Hz, SCH_xH_y), 2.15–2.05 (1H, m, CH(CH₃)₂), 1.94 (1H, dd, $J = 11.5$ Hz, $J = 2.0$ Hz, SCH_xH_y), 1.62 (3H, s, Ac), 1.61 (3H, s, Ac), 1.20 (3H, d, $J = 6.9$ Hz, COCHCH₃), 0.68 (3H, d, $J = 6.7$ Hz, CH₃), 0.61 (3H, d, $J = 7.0$ Hz, CH₃); ¹³C NMR (75.4 MHz, CDCl₃): $\delta = 202.4, 174.3, 170.8, 170.3, 130.7, 126.6, 75.6, 74.2, 71.9, 65.3, 63.6, 43.1, 30.7, 29.4, 21.0, 20.8, 19.0, 17.2, 10.4$; IR (film): $\nu = 2965, 1744, 1713, 1240, 1123$ cm⁻¹; HRMS (+FAB): calcd. for [M+H]⁺ C₁₉H₂₈NO₆S₂ 430.1358, found 430.1348.

2b. Yellow oil; R_f (CH₂Cl₂) = 0.20; HPLC (hexanes/EtOAc 90:10) t_R = 40.0 min; [α]_D = +98.5 ($c=0.85$ in CHCl₃); ¹H NMR (300 MHz, CDCl₃): $\delta = 6.10$ – 6.05 (1H, m, CHCH=CHCHOAc), 6.01 (1H, ddd, $J = 10.3$ Hz, $J = 4.8$ Hz, $J = 1.8$ Hz, CHCH=CHCHOAc), 5.25–5.05 (3H, m, NCH, COCHCH₃ and CHOAc), 4.70–4.60 (1H, m, CHCH=CHCHOAc), 4.25–4.15 (2H, m, CH₂OAc), 4.10–4.00 (1H, m, OCHCH₂OAc), 3.48 (1H, dd, $J = 11.5$ Hz, $J = 8.1$ Hz, SCH_xH_y), 3.01 (1H, dd, $J = 11.5$ Hz, $J = 1.2$ Hz, SCH_xH_y), 2.45–2.25 (1H, m, CH(CH₃)₂), 2.08 (3H, s, Ac), 2.07 (3H, s, Ac), 1.29 (3H, d, $J = 6.9$ Hz, COCHCH₃), 1.07 (3H, d, $J = 6.9$ Hz, CH₃), 0.99 (3H, d, $J = 6.9$ Hz, CH₃); ¹³C NMR (75.4 MHz, CDCl₃): $\delta = 203.1, 175.0, 170.6, 170.4, 132.7, 123.1, 73.7, 71.8, 69.3, 63.7, 62.9, 40.4, 30.8, 30.0, 20.9, 20.8, 19.1, 17.6, 14.7$; IR (film): $\nu = 2945, 1735, 1680, 1360, 1230, 1160$ cm⁻¹; HRMS (+FAB): calcd. for [M+H]⁺ C₁₉H₂₈NO₆S₂ 430.1358, found 430.1354.

3b. Yellow oil; R_f (CH₂Cl₂) = 0.15; HPLC (hexanes/EtOAc 97:3) t_R = 28.3 min; [α]_D = -319.1 ($c=1.2$ in CHCl₃); ¹H NMR (300 MHz, CDCl₃): $\delta = 6.09$ (1H, ddd, $J = 10.2$ Hz, $J = 5.3$ Hz, $J = 2.0$ Hz, CH=CH), 6.01 (1H, dd, $J = 10.2$ Hz, $J = 1.4$ Hz, CH=CH), 5.38 (1H, ddd, $J = 8.6$ Hz, $J = 5.6$ Hz, $J = 1.8$ Hz, NCH), 5.05–5.00 (1H, m, CHOAc), 4.91 (1H, qd, $J = 6.7$ Hz, $J = 4.0$ Hz, COCHCH₃), 4.80–4.70 (1H, m, OCHCH=CH), 4.18 (1H, dd, $J = 11.4$ Hz, $J = 6.3$ Hz, CH_xH_yOAc), 4.11 (1H, dd, $J = 11.4$ Hz, $J = 6.6$ Hz, CH_xH_yOAc), 3.90–3.83 (1H, m, CHCH₂OAc), 3.50 (1H, dd, $J = 11.5$ Hz, $J = 8.6$ Hz, SCH_xH_y), 3.01 (1H, dd, $J = 11.5$ Hz, $J = 1.8$ Hz, SCH_xH_y), 2.40–2.20 (1H, m, CH(CH₃)₂), 2.06 (3H, s, Ac), 2.03 (3H, s, Ac), 1.17 (3H, d, $J = 6.7$ Hz, COCHCH₃), 1.06 (3H, d,

$J = 6.9$ Hz, CH₃), 0.98 (3H, d, $J = 7.0$ Hz, CH₃); ¹³C NMR (75.4 MHz, CDCl₃): $\delta = 202.4, 174.4, 170.6 (\times 2), 133.9, 123.7, 75.8, 73.4, 71.9, 63.5, 62.9, 42.8, 30.7, 29.4, 20.9, 20.7, 19.0, 17.2, 10.7$; IR (film): $\nu = 2965, 1740, 1700, 1370, 1242, 1160$ cm⁻¹; HRMS (+FAB): calcd. for [M+H]⁺ C₁₉H₂₈NO₆S₂ 430.1358, found 430.1363.

2c. Yellow oil; R_f (CH₂Cl₂) = 0.25; HPLC (hexanes/EtOAc 89:11) t_R = 10.7 min; $[\alpha]_D = -36.6$ ($c=0.68$ in CHCl₃); ¹H NMR (500 MHz, CDCl₃): $\delta = 8.10\text{--}8.00$ (4H, m, ArH), 7.58–7.52 (2H, m, ArH), 7.45–7.40 (4H, m, ArH), 6.20–6.10 (2H, m, CH=CH), 5.45–5.40 (1H, m, CHOBz), 5.24 (1H, dq, $J = 8.1$ Hz, $J = 6.9$ Hz, COCHCH₃), 5.25–5.20 (1H, m, NCH), 4.75–4.70 (1H, m, CHOCHCH₂), 4.62 (1H, dd, $J = 11.6$ Hz, $J = 7.9$ Hz, CH_xH_yOBz), 4.47 (1H, dd, $J = 11.6$ Hz, $J = 4.3$ Hz, CH_xH_yOBz), 4.40–4.35 (1H, m, OCHCH₂OBz), 3.47 (1H, dd, $J = 11.6$ Hz, $J = 8.1$ Hz, SCH_xH_y), 3.00 (1H, dd, $J = 11.6$ Hz, $J = 1.3$ Hz, SCH_xH_y), 2.38–2.28 (1H, m, CH(CH₃)₂), 1.32 (3H, d, $J = 6.9$ Hz, COCHCH₃), 1.04 (3H, d, $J = 6.8$ Hz, CH₃), 0.94 (3H, d, $J = 6.9$ Hz, CH₃); ¹³C NMR (75.4 MHz, CDCl₃): $\delta = 203.1, 175.0, 166.2, 165.9, 133.2, 133.0, 132.9, 129.8, 129.7, 128.4, 128.3, 123.4, 73.8, 71.8, 69.8, 64.5, 63.7, 40.8, 30.8, 29.8, 19.1, 17.5, 14.5$; IR (film): $\nu = 2966, 1719, 1654, 1451, 1316, 1266, 1158$ cm⁻¹; HRMS (+FAB): calcd. for [M+H]⁺ C₂₃H₄₀NO₅SiS₂ 554.1671, found 554.1673.

3c. Yellow oil; R_f (CH₂Cl₂) = 0.40; HPLC (hexanes/EtOAc 91:9) t_R = 15.8 min; $[\alpha]_D = -419.0$ ($c=1.03$ in CHCl₃); ¹H NMR (500 MHz, CDCl₃): $\delta = 8.08\text{--}8.04$ (2H, m, ArH), 8.00–7.96 (2H, m, ArH), 7.60–7.52 (2H, m, ArH), 7.48–7.38 (4H, m, ArH), 6.27 (1H, ddd, $J = 10.1$ Hz, $J = 5.7$ Hz, $J = 2.0$ Hz, CH=CHCHOBz), 6.08–6.05 (1H, m, CH=CHCHOBz), 5.42–5.38 (2H, m, NCH and CHOBz), 4.95–4.89 (2H, m, COCH(CH₃)CH), 4.56 (1H, dd, $J = 11.3$ Hz, $J = 6.6$ Hz, CH_xH_yOBz), 4.42 (1H, dd, $J = 11.3$ Hz, $J = 6.4$ Hz, CH_xH_yOBz), 4.17–4.13 (1H, m, CHCH₂OBz), 3.49 (1H, dd, $J = 11.4$ Hz, $J = 8.7$ Hz, SCH_xH_y), 3.00 (1H, dd, $J = 11.4$ Hz, $J = 1.8$ Hz, SCH_xH_y), 2.34–2.23 (1H, m, CH(CH₃)₂), 1.23 (3H, d, $J = 6.6$ Hz, COCHCH₃), 1.00 (3H, d, $J = 6.8$ Hz, CH₃), 0.90 (3H, d, $J = 7.1$ Hz, CH₃); ¹³C NMR (75.4 MHz, CDCl₃): $\delta = 202.4, 174.2, 166.1, 165.9, 134.2, 133.1, 133.0, 129.9, 129.8, 129.7, 129.6, 128.4, 128.3, 123.9, 75.6, 73.5, 71.9, 64.0, 63.4, 42.8, 30.8, 29.3, 18.8, 17.0$,

10.4; IR (film): ν = 2966, 1719, 1266, 1160, 1110 cm^{-1} ; HRMS (+FAB): calcd. for $[\text{M}+\text{H}]^+$ $\text{C}_{29}\text{H}_{32}\text{NO}_6\text{S}_2$ 554.1671, found 554.1687.

2d. Yellow oil; R_f (CH_2Cl_2) = 0.15; HPLC (hexanes/EtOAc 93:7) t_R = 26.4 min; $[\alpha]_D = +96.3$ ($c=0.7$ in CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ = 5.90–5.84 (1H, m, $\text{OCHCH}=\text{CH}$), 5.78–5.73 (1H, m, $\text{OCHCH}=\text{CH}$), 5.23 (1H, ddd, J = 8.2 Hz, J = 6.0 Hz, J = 1.4 Hz, NCH), 5.11 (1H, dq, J = 8.1 Hz, J = 6.9 Hz, COCHCH_3), 4.58–4.54 (1H, m, $\text{OCHCH}=\text{CH}$), 4.11 (2H, d, J = 5.3 Hz, CH_2OAc), 3.95–3.85 (1H, m, CHCH_2OAc), 3.47 (1H, dd, J = 11.4 Hz, J = 8.2 Hz, SCH_xH_y), 2.99 (1H, dd, J = 11.4 Hz, J = 1.4 Hz, SCH_xH_y), 2.40–2.25 (1H, m, $\text{CH}(\text{CH}_3)_2$), 2.08 (3H, s, Ac), 2.05–1.95 (2H, m, $\text{CH}=\text{CHCH}_2$), 1.26 (3H, d, J = 6.9 Hz, COCHCH_3), 1.05 (3H, d, J = 6.7 Hz, CH_3), 0.98 (3H, d, J = 6.9 Hz, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3): δ = 202.9, 175.5, 170.9, 127.3, 124.5, 73.7, 71.8, 67.1, 66.1, 42.0, 30.7, 29.7, 26.3, 20.9, 19.1, 17.5, 14.2; IR (film): ν = 2966, 1740, 1688, 1368, 1241, 1156 cm^{-1} ; HRMS (+FAB): calcd. for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{26}\text{NO}_4\text{S}_2$ 372.1303, found 372.1320.

3d. Yellow oil; R_f (CH_2Cl_2) = 0.55; HPLC (hexanes/EtOAc 90:10) t_R = 15.0 min; $[\alpha]_D = -211.4$ ($c=1.35$ in CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ = 5.95–5.87 (1H, m, $\text{OCHCH}=\text{CH}$), 5.70–5.65 (1H, m, $\text{OCHCH}=\text{CH}$), 5.40 (1H, ddd, J = 8.8 Hz, J = 5.5 Hz, J = 1.9 Hz, NCH), 4.84 (1H, qd, J = 6.6 Hz, J = 3.6 Hz, COCHCH_3), 4.80–4.75 (1H, m, $\text{OCHCH}=\text{CH}$), 4.07 (1H, dd, J = 11.5 Hz, J = 4.6 Hz, $\text{CH}_x\text{H}_y\text{OAc}$), 4.03 (1H, dd, J = 11.5 Hz, J = 6.1 Hz, $\text{CH}_x\text{H}_y\text{OAc}$), 3.85–3.75 (1H, m, CHCH_2OAc), 3.49 (1H, dd, J = 11.4 Hz, J = 8.8 Hz, SCH_xH_y), 3.01 (1H, dd, J = 11.4 Hz, J = 1.9 Hz, SCH_xH_y), 2.40–2.25 (1H, m, $\text{CH}(\text{CH}_3)_2$), 2.05 (3H, s, Ac), 2.05–1.90 (2H, m, $\text{CH}=\text{CHCH}_2$), 1.13 (3H, d, J = 6.6 Hz, COCHCH_3), 1.05 (3H, d, J = 6.7 Hz, CH_3), 0.98 (3H, d, J = 6.9 Hz, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3): δ = 202.2, 175.0, 170.9, 128.0, 125.3, 75.5, 71.9, 71.5, 66.7, 43.5, 30.7, 29.2, 27.0, 20.8, 19.0, 17.1, 10.2; IR (film): ν = 2966, 1742, 1713, 1370, 1243, 1158 cm^{-1} ; HRMS (+FAB): calcd. for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{26}\text{NO}_4\text{S}_2$ 372.1303, found 372.1314.

2e. Yellow oil; R_f (CH_2Cl_2) = 0.30; HPLC (hexanes/EtOAc 93:7) t_R = 12.7 min; $[\alpha]_D = +209.9$ ($c=1.07$ in CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ = 5.93 (1H,

ddd, $J = 10.4$ Hz, $J = 2.3$ Hz, $J = 1.1$ Hz, $\text{CH}=\text{CHCHOAc}$), 5.88 (1H, ddd, $J = 10.4$ Hz, $J = 3.4$ Hz, $J = 1.9$ Hz, $\text{CH}=\text{CHCHOAc}$), 5.28 (1H, ddd, $J = 8.3$ Hz, $J = 5.9$ Hz, $J = 1.4$ Hz, NCH), 5.15–5.10 (1H, m, CHOAc), 5.04 (1H, pent, $J = 6.7$ Hz, COCHCH_3), 4.66–4.63 (1H, m, CHOCHCH_2), 3.80–3.75 (1H, m, CHOCHCH_2), 3.75–3.65 (2H, m, CH_2OTBS), 3.48 (1H, dd, $J = 11.5$ Hz, $J = 8.3$ Hz, SCH_xH_y), 3.00 (1H, dd, $J = 11.5$ Hz, $J = 1.4$ Hz, SCH_xH_y), 2.38–2.27 (1H, m, $\text{CH}(\text{CH}_3)_2$), 2.06 (3H, s, Ac), 1.25 (3H, d, $J = 6.7$ Hz, COCHCH_3), 1.06 (3H, d, $J = 6.9$ Hz, CH_3), 0.98 (3H, d, $J = 7.0$ Hz, CH_3), 0.88 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.04 (6H, br s, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (75.4 MHz, CDCl_3): $\delta = 202.7, 175.2, 170.6, 131.5, 124.4, 73.9, 72.5, 71.8, 65.1, 62.9, 41.8, 30.8, 29.7, 25.9, 21.1, 19.1, 18.3, 17.5, 13.2, -5.4, -5.5$; IR (film): $\nu = 2960, 1735, 1696, 1372, 1239, 1162, 1121\text{ cm}^{-1}$; HRMS (+FAB): calcd. for $[\text{M}+\text{H}]^+ \text{C}_{23}\text{H}_{40}\text{NO}_5\text{Si}_2$ 502.2117, found 502.2110.

3e. Yellow oil; R_f (hexanes/EtOAc 80:20) = 0.35; HPLC (hexanes/EtOAc 90:10) $t_R = 8.8$ min; $[\alpha]_D = -128.5$ ($c=1.0$ in CHCl_3); ^1H NMR (500 MHz, CDCl_3): $\delta = 6.03$ (1H, ddd, $J = 10.3$ Hz, $J = 2.4$ Hz, $J = 1.2$ Hz, $\text{OCHCH}=\text{CH}$), 5.94 (1H, ddd, $J = 10.3$ Hz, $J = 3.5$ Hz, $J = 2.0$ Hz, $\text{OCHCH}=\text{CH}$), 5.25–5.20 (2H, m, NCH and CHOAc), 5.13 (1H, dq, $J = 7.6$ Hz, $J = 6.9$ Hz, COCHCH_3), 4.68–4.63 (1H, m, $\text{OCHCH}=\text{CH}$), 3.90–3.85 (1H, m, CHCH_2OTBS), 3.76 (1H, dd, $J = 10.9$ Hz, $J = 4.5$ Hz, $\text{CH}_x\text{H}_y\text{OTBS}$), 3.67 (1H, dd, $J = 10.9$ Hz, $J = 4.7$ Hz, $\text{CH}_x\text{H}_y\text{OTBS}$), 3.48 (1H, dd, $J = 11.5$ Hz, $J = 8.3$ Hz, SCH_xH_y), 3.00 (1H, dd, $J = 11.5$ Hz, $J = 1.4$ Hz, SCH_xH_y), 2.40–2.30 (1H, m, $\text{CH}(\text{CH}_3)_2$), 2.07 (3H, s, Ac), 1.15 (3H, d, $J = 6.9$ Hz, COCHCH_3), 1.06 (3H, d, $J = 6.9$ Hz, CH_3), 0.98 (3H, d, $J = 6.9$ Hz, CH_3), 0.87 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.03 (3H, s, SiCH_3), 0.02 (3H, s, SiCH_3); ^{13}C NMR (75.4 MHz, CDCl_3): $\delta = 202.7, 175.7, 170.5, 130.2, 125.3, 73.7, 72.8, 71.9, 65.0, 62.4, 42.0, 30.7, 29.7, 25.9, 21.2, 19.2, 18.3, 17.5, 13.6, -5.5$ ($\times 2$); IR (film): $\nu = 2960, 1739, 1698, 1370, 1245, 1164, 1123\text{ cm}^{-1}$; HRMS (+FAB): calcd. for $[\text{M}+\text{H}]^+ \text{C}_{23}\text{H}_{40}\text{NO}_5\text{Si}_2$ 502.2117, found 502.2130.

2f was better characterised as its desilylated derivative.

Yellow oil; R_f (CH_2Cl_2) = 0.05; HPLC (hexanes/EtOAc 90:10) $t_R = 23.3$ min; $[\alpha]_D = +158.9$ ($c=0.5$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): $\delta = 5.95$ –5.87 (1H, m, $\text{OCHCH}=\text{CH}$), 5.79–5.71 (1H, m, $\text{OCHCH}=\text{CH}$), 5.24 (1H, ddd, $J =$

8.2 Hz, $J = 6.1$ Hz, $J = 1.4$ Hz, NCH), 5.11 (1H, pent, $J = 6.9$ Hz, COCHCH₃), 4.64–4.56 (1H, m, OCHCH=CH), 3.88–3.78 (1H, m, CHCH₂OH), 3.70–3.55 (2H, m, CH₂OH), 3.48 (1H, dd, $J = 11.5$ Hz, $J = 8.2$ Hz, SCH_xH_y), 3.00 (1H, dd, $J = 11.5$ Hz, $J = 1.4$ Hz, SCH_xH_y), 2.40–2.25 (1H, m, CH(CH₃)₂), 2.10–1.90 (2H, m, CH=CHCH₂), 1.27 (3H, d, $J = 6.9$ Hz, COCHCH₃), 1.07 (3H, d, $J = 6.9$ Hz, CH₃), 0.99 (3H, d, $J = 6.9$ Hz, CH₃); ¹³C NMR (75.4 MHz, CDCl₃): $\delta = 203.0, 175.6, 127.0, 125.2, 73.4, 71.8, 69.6, 65.3, 42.1, 30.8, 29.8, 25.9, 19.1, 17.6, 14.4$; IR (film): $\nu = 3600\text{--}3300$ (br), 2964, 1688, 1360, 1248, 1156 cm⁻¹; HRMS (+FAB): calcd. for [M+H]⁺ C₁₅H₂₄NO₃S₂ 330.1197, found 330.1199.

3f. Yellow oil; R_f (CH₂Cl₂) = 0.50; HPLC (hexanes/EtOAc 93:7) t_R = 20.2 min; [α]_D = -203.7 ($c=1.82$ in CHCl₃); ¹H NMR (500 MHz, CDCl₃): $\delta = 6.00\text{--}5.95$ (1H, m, OCHCH=CH), 5.85–5.80 (1H, m, OCHCH=CH), 5.29 (1H, ddd, $J = 8.4$ Hz, $J = 5.9$ Hz, $J = 1.3$ Hz, NCH), 5.27 (1H, dq, $J = 9.2$ Hz, $J = 6.9$ Hz, COCHCH₃), 4.65–4.60 (1H, m, OCHCH=CH), 3.90–3.83 (1H, m, CHCH₂OTBS), 3.68 (1H, dd, $J = 10.0$ Hz, $J = 4.5$ Hz, CH_xH_yOTBS), 3.49 (1H, dd, $J = 10.0$ Hz, $J = 7.0$ Hz, CH_xH_yOTBS), 3.46 (1H, dd, $J = 11.5$ Hz, $J = 8.4$ Hz, SCH_xH_y), 2.98 (1H, dd, $J = 11.5$ Hz, $J = 1.3$ Hz, SCH_xH_y), 2.40–2.30 (1H, m, CH(CH₃)₂), 2.16–2.09 (1H, m, CH=CHCH_xH_y), 2.08–2.00 (1H, m, CH=CHCH_xH_y), 1.13 (3H, d, $J = 6.9$ Hz, COCHCH₃), 1.08 (3H, d, $J = 6.9$ Hz, CH₃), 1.00 (3H, d, $J = 7.0$ Hz, CH₃), 0.88 (9H, s, SiC(CH₃)₃), 0.03 (6H, s, SiCH₃); ¹³C NMR (75.4 MHz, CDCl₃): $\delta = 202.8, 176.3, 126.2, 125.7, 74.3, 71.9, 69.4, 65.7, 42.4, 30.8, 29.4, 27.2, 25.9, 19.2, 18.4, 17.5, 14.2, -5.3$ ($\times 2$); IR (film): $\nu = 2931, 1698, 1360, 1252, 1154$ cm⁻¹; HRMS (+FAB): calcd. for [M+H]⁺ C₂₁H₃₈NO₃SiS₂ 444.2062, found 444.2046.

2g. Yellow solid; m.p. 136.0–136.5 °C; R_f (CH₂Cl₂) = 0.10; HPLC (hexanes/EtOAc 89:11) t_R = 11.5 min; [α]_D = +244.3 ($c=1.0$ in CHCl₃); ¹H NMR (500 MHz, CDCl₃): $\delta = 6.02$ (1H, ddd, $J = 10.4$ Hz, $J = 2.5$ Hz, $J = 1.5$ Hz, CHCH=CHCHOAc), 5.85 (1H, ddd, $J = 10.4$ Hz, $J = 3.1$ Hz, $J = 2.1$ Hz, CHCH=CHCHOAc), 5.27 (1H, ddd, $J = 8.2$ Hz, $J = 6.0$ Hz, $J = 1.3$ Hz, NCH), 5.22 (1H, dq, $J = 8.3$ Hz, $J = 6.9$ Hz, COCHCH₃), 4.92–4.88 (1H, m, CHOAc), 4.65–4.60 (1H, m, CHCH=CHCHOAc), 3.95–3.90 (1H, m, OCHCH₃), 3.47

(1H, dd, $J = 11.5$ Hz, $J = 8.2$ Hz, SCH_xH_y), 2.99 (1H, dd, $J = 11.5$ Hz, $J = 1.3$ Hz, SCH_xH_y), 2.40–2.30 (1H, m, $\text{CH}(\text{CH}_3)_2$), 2.08 (3H, s, Ac), 1.17 (3H, d, $J = 6.5$ Hz, OCHCH_3), 1.15 (3H, d, $J = 6.9$ Hz, COCHCH_3), 1.06 (3H, d, $J = 6.8$ Hz, CH_3), 0.98 (3H, d, $J = 6.9$ Hz, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3): $\delta = 202.9, 175.8, 170.7, 130.0, 125.6, 72.8, 71.9, 69.7, 68.8, 41.6, 30.7, 29.6, 21.2, 19.1, 17.6, 17.2, 13.9$; IR (film): $\nu = 2971, 1735, 1700, 1372, 1240, 1158\text{ cm}^{-1}$; HRMS (+FAB): calcd. for $[\text{M}+\text{H}]^+ \text{C}_{17}\text{H}_{26}\text{NO}_4\text{S}_2$ 372.1303, found 372.1298.

3g. Yellow oil; R_f (CH_2Cl_2) = 0.25; HPLC (hexanes/EtOAc 90:10) $t_R = 10.0$ min; $[\alpha]_D = -281.0$ ($c=1.07$ in CHCl_3); ^1H NMR (500 MHz, CDCl_3): $\delta = 5.94$ (1H, ddd, $J = 10.3$ Hz, $J = 2.0$ Hz, $J = 0.9$ Hz, $\text{CH}=\text{CHCHOAc}$), 5.90–5.85 (1H, m, $\text{CH}=\text{CHCHOAc}$), 5.34 (1H, ddd, $J = 8.5$ Hz, $J = 5.6$ Hz, $J = 1.5$ Hz, NCH), 5.01 (1H, qd, $J = 6.8$ Hz, $J = 5.4$ Hz, COCHCH_3), 4.85–4.80 (1H, m, CHOAc), 4.70–4.65 (1H, m, $\text{CHCH}=\text{CHCHOAc}$), 3.96 (1H, qd, $J = 6.7$ Hz, $J = 3.8$ Hz, OCHCH_3), 3.49 (1H, dd, $J = 11.5$ Hz, $J = 8.5$ Hz, SCH_xH_y), 3.00 (1H, dd, $J = 11.5$ Hz, $J = 1.5$ Hz, SCH_xH_y), 2.37–2.25 (1H, m, $\text{CH}(\text{CH}_3)_2$), 2.07 (3H, s, Ac), 1.21 (3H, d, $J = 6.7$ Hz, CH_3), 1.20 (3H, d, $J = 6.8$ Hz, CH_3), 1.06 (3H, d, $J = 6.7$ Hz, CH_3), 0.98 (3H, d, $J = 7.0$ Hz, CH_3); ^{13}C NMR (75.4 MHz, CDCl_3): $\delta = 202.7, 175.0, 170.8, 132.1, 123.6, 71.8, 70.3, 69.7, 68.8, 41.9, 30.8, 29.5, 21.1, 19.0, 17.4, 16.6, 12.3$; IR (film): $\nu = 2968, 1734, 1700, 1372, 1240, 1160, 1023\text{ cm}^{-1}$; HRMS (+FAB): calcd. for $[\text{M}+\text{H}]^+ \text{C}_{17}\text{H}_{26}\text{NO}_4\text{S}_2$ 372.1303, found 372.1308.

2. Stereochemical proof for **2a**.

2.1. Reduction of **2a**.

A solution of **2a** (172 mg, 0.4 mmol) in THF (2 mL) was added to a suspension of NaBH₄ (75 mg, 2.0 mmol) in THF–H₂O 10:1 (3.3 mL) under N₂ at 0 °C. The mixture was stirred for 10 min, warmed to room temperature and stirred for 2 h. It was quenched with saturated aqueous NH₄Cl (4 mL), extracted with CH₂Cl₂ (3 × 20 mL), and the organic layers were washed with saturated aqueous NaHCO₃ (50 mL) and brine (50 mL). The organic extracts were dried (Na₂SO₄), filtered, and concentrated *in vacuo*. Purification by column chromatography on silica gel (CH₂Cl₂/EtOAc 80:20) afforded the alcohol **10** as a colourless oil (85 mg, 78%).

R_f (CH₂Cl₂/EtOAc 80:20) = 0.25; [α]_D = +96.1 (*c*=2.6 in CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ = 6.03–5.95 (2H, m, CH=CH), 5.00–4.95 (1H, m, CHOAc), 4.40–4.35 (1H, m, OCHCH=CH), 4.33 (1H, dd, *J* = 12.7 Hz, *J* = 9.0 Hz, CH_xH_yOAc), 4.13–4.07 (2H, m, CHCH₂OAc and CH_xH_yOAc), 3.68–3.58 (2H, m, CH₂OH), 2.45 (1H, br s, CH₂OH), 2.10 (3H, s, Ac), 2.09 (3H, s, Ac), 2.05–1.95 (1H, m, CHCH₃), 0.97 (3H, d, *J* = 7.0 Hz, CHCH₃); ¹³C NMR (75.4 MHz, CDCl₃): δ = 170.8, 170.5, 133.0, 122.8, 72.3, 72.1, 65.5, 64.5, 61.9, 39.1, 21.0, 20.7, 11.7; IR (film): ν = 3463 (br), 2967, 1742, 1654, 1457, 1372, 1235 cm⁻¹.

2.2. Cyclisation of **10**.

Hg(OOCCF₃)₂ (115 mg, 0.27 mmol) was added to a mixture of **10** (63 mg, 0.23 mmol) and CaCO₃ anh. (50 mg, 0.5 mmol) in THF (1.5 mL) under N₂ at 0 °C. The mixture was stirred for 1 h, quenched with saturated aqueous KBr (2 mL) and stirred for 5 min. The resulting mixture was poured into a mixture of Et₂O (20 mL) and saturated aqueous KBr (15 mL). The layers were separated and the aqueous phase was extracted with Et₂O (3 × 20 mL). The organic layers were dried (MgSO₄), filtered and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (CH₂Cl₂/EtOAc 80:20) to afford **11** as a colourless oil (27 mg, 56%). The structure and stereochemistry of **11** was established by NMR studies.

R_f (CH₂Cl₂/EtOAc 80:20) = 0.45; [α]_D = −122.9 (*c*=1.4 in CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ = 6.15–6.10 (1H, m, CHCH=CH), 5.96–5.90 (1H, m, OCHCH=CH), 4.42–4.38 (1H, m, OCHCH₂OAc), 4.30 (1H, dd, *J* = 11.9 Hz, *J* = 8.1 Hz, CH_xH_yOAc), 4.18 (1H, dd, *J* = 8.3 Hz, *J* = 6.5 Hz, OCH_xH_y), 4.05–4.02 (2H, m, OCHCHO), 4.00 (1H, dd, *J* = 11.9 Hz, *J* = 3.4 Hz, CH_xH_yOAc), 3.42 (1H, dd, *J* = 8.3 Hz, *J* = 4.7 Hz, OCH_xH_y), 2.40–2.35 (1H, m, CHCH₃), 2.07 (3H, s, Ac), 1.10 (3H, d, *J* = 7.1 Hz, CHCH₃); ¹³C NMR (75.4 MHz, CDCl₃): δ = 170.8, 128.7, 125.4, 77.9, 73.4, 70.3, 70.1, 63.1, 40.0, 20.9, 16.4; IR (film): ν = 2966, 2877, 1744, 1381, 1233, 1113 cm^{−1}.

2.3. Key relationships observed in nOe experiments of **2a** and **11**.

3. Stereochemical proof for **3a**.

3.1. Reduction of **3a**.

A solution of **3a** (248 mg, 0.6 mmol) in THF (2.5 mL) was added to a suspension of NaBH₄ (108 mg, 2.9 mmol) in THF–H₂O 10:1 (3.3 mL) under N₂ at 0 °C. The mixture was stirred for 10 min, warmed to room temperature, and stirred for 1 h. It was quenched with saturated aqueous NH₄Cl (4 mL), extracted with CH₂Cl₂ (3 × 20 mL), and the organic layers were washed with saturated aqueous NaHCO₃ (50 mL) and brine (50 mL). The organic extracts were dried (Na₂SO₄), filtered, and concentrated *in vacuo*. Purification by column chromatography on silica gel (CH₂Cl₂/EtOAc 80:20) afforded the alcohol **12** as a colourless oil (95 mg, 62%).

R_f ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 80:20) = 0.20; $[\alpha]_D = +92.2$ ($c=1.1$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ = 5.86–5.78 (2H, m, $\text{CH}=\text{CH}$), 5.32–5.27 (1H, m, CHOAc), 4.45–4.42 (1H, m, $\text{OCHCH}=\text{CH}$), 4.26 (1H, dd, $J = 12.1$ Hz, $J = 2.6$ Hz, $\text{CH}_x\text{H}_y\text{OAc}$), 4.14 (1H, dd, $J = 12.1$ Hz, $J = 5.2$ Hz, $\text{CH}_x\text{H}_y\text{OAc}$), 3.73 (1H, ddd, $J = 9.1$ Hz, $J = 5.2$ Hz, $J = 2.6$ Hz, CHCH_2OAc), 3.67–3.58 (2H, m, CH_2OH), 2.09 (6H, s, $2 \times \text{Ac}$), 2.04–1.94 (1H, m, CHCH_3), 0.90 (3H, d, $J = 7.0$ Hz, CHCH_3); ^{13}C NMR (75.4 MHz, CDCl_3): δ = 170.9, 170.3, 130.6, 126.5, 77.7, 74.0, 65.6, 65.4, 63.2, 39.2, 21.0, 20.7, 10.9; IR (film): ν = 3420 (br), 2965, 2364, 1742, 1372, 1233, 1042 cm^{-1} .

3.2. Cyclisation of **12**.

$\text{Hg}(\text{OOC}\text{CF}_3)_2$ (125 mg, 0.29 mmol) was added to a mixture of **12** (67 mg, 0.25 mmol) and CaCO_3 anh. (50 mg, 0.5 mmol) in THF (2 mL) under N_2 at 0 °C. The mixture was stirred for 2 h, quenched with saturated aqueous KBr (2 mL) and stirred for 5 min. The resulting mixture was poured into a mixture of Et_2O (20 mL) and saturated aqueous KBr (15 mL). The layers were separated and the aqueous phase was extracted with Et_2O (3×20 mL). The organic extracts were dried (MgSO_4), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 80:20) to afford **13** as a white solid (70 mg, 56%). The structure and stereochemistry of **13** was established by NMR studies.

R_f ($\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 80:20) = 0.40; $[\alpha]_D = +69.6$ ($c=0.99$ in CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ = 5.44 (1H, ddd, $J = 7.9$ Hz, $J = 4.5$ Hz, $J = 0.7$ Hz, CHOAc), 4.36 (1H, ddd, $J = 4.2$ Hz, $J = 2.8$ Hz, $J = 0.7$ Hz, CHCHHgBr), 4.23–4.15 (3H, m, CH_2OAc and OCH_xH_y), 3.82 (1H, dd, $J = 2.8$ Hz, $J = 1.4$ Hz, CHCH_3CHO), 3.53 (1H, ddd, $J = 7.9$ Hz, $J = 5.3$ Hz, $J = 2.9$ Hz, CHCH_2OAc), 3.54–3.46 (1H, m, CHHgBr), 3.44 (1H, dd, $J = 8.2$ Hz, $J = 3.5$

Hz, OCH_xH_y), 2.45–2.35 (1H, m, CHCH_3), 2.06 (3H, s, Ac), 2.05 (3H, s, Ac), 1.03 (3H, d, $J = 7.5$ Hz, CHCH_3); ^{13}C NMR (75.4 MHz, CDCl_3): $\delta = 170.6$, 169.6, 84.0, 78.1, 77.5, 74.1, 68.7, 63.3, 57.6, 40.6, 21.2, 20.8, 16.9; IR (film): $\nu = 2966, 2879, 1729, 1368, 1281, 1241, 1069, 1042\text{ cm}^{-1}$.

3.3. Key relationships observed in nOe experiments of **3a** and **13**.

4. ^1H NMR spectra for **2e**, **7**, **8**, and **9**.

CC(C)C(O)C1=CC=C(C(=C1)OC(C)C)OC(C)C

7

^1H NMR (300 MHz, CDCl_3)

8

^1H NMR (300 MHz, CDCl_3)

^1H NMR (300 MHz, CDCl_3)