

The five-component coupling protocol illustrated for (+)-12. A solution of dithiane **6** (641 mg, 2.73 mmol) in anhydrous Et₂O (6 mL) was cooled to -78 °C. t-BuLi (1.50 M in pentane, 1.90 mL, 2.85 mmol) was added dropwise via syringe, and the reaction mixture was allowed to warm to -45 °C while stirring for 1 h. The mixture was recooled to -78 °C and a solution of epoxide (+)-**13** (409 mg, 2.49 mmol) in anhydrous Et₂O (2 mL) was added dropwise via cannula. The mixture was warmed to -25 °C over 1 h, recooled to -78 °C, and treated dropwise with a solution of diepoxypentane (-)-**14** (108 mg, 1.08 mmol) and HMPA (10% in THF, 2.50 mL, 1.43 mmol) via syringe. The reaction mixture was warmed to ambient temperature over 3 h, quenched with saturated aqueous NH₄Cl (1 mL), and diluted with EtOAc (5 mL). The layers were separated, the aqueous phase was extracted with EtOAc (3 x 5 mL), and the combined organic layers were dried over MgSO₄, filtered and concentrated. Flash chromatography (hexanes/ethyl acetate, 9:1 to 3:1) provided (+)-**12** (572 mg, 0.637 mmol, 59%) as a pale yellow oil: $[\alpha]_D^{23} +10.9$ (c = 1.8, CHCl₃); IR 3600-3300 (br), 2920, 1460, 1420, 1380, 1355, 1250, 1220, 1160, 1100, 910, 740 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.34 (s, 2 H), 7.33 (s, 2 H), 7.29-7.26 (m, 1 H), 4.53 (s, 2 H), 4.33 (m, 1 H), 4.25 (m, 1 H), 3.75 (d, *J* = 3.2 Hz, 1 H), 3.46 (dd, *J* = 9.5, 4.8 Hz, 1 H), 3.36 (dd, *J* = 9.5, 6.5 Hz, 1 H) 2.86-2.77 (m, 4 H), 2.49 (dd, *J* = 15.3, 3.1 Hz, 1 H), 2.23 (m, 2 H), 2.10 (dd, *J* = 15.0, 1.3 Hz, 1 H), 1.93-1.90 (m, 2 H), 1.55 (t, *J* = 6.0 Hz, 1 H), 0.88 (s, 9 H), 0.14 (s, 3 H), 0.08 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 138.2, 128.3, 127.6, 127.5, 74.7, 73.1, 69.5, 65.5, 51.7, 46.8, 45.9, 43.5, 26.3, 26.0, 24.9, 18.0, -3.7, -4.2. high resolution mass spectrum (FAB, NBA) *m/z* 919.3963 [(M+Na)⁺; calcd. for C₄₅H₇₆O₆S₄Si₂: 919.3961].

Bis-(β-hydroxy) ketone (+)-20. Pale yellow oil; $[\alpha]_D^{23} +3.3^\circ$ (c = 4.7, CHCl₃); IR 3600-3300 (br), 3010, 2940, 1710, 1510, 1420, 1385, 1370, 1225, 1205, 1110, 1050, 1030,

930, 910, 730 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.36–7.29 (m, 4 H), 4.54 (s, 2 H), 4.28–4.25 (m, 2 H), 3.49–3.42 (m, 2 H), 2.98 (br s, 1 H), 2.71 (dd, $J = 8.2, 16.2$, 1 H), 2.65 (d, $J = 2.7$, 1 H), 2.64 (s, 1 H), 2.46 (dd, $J = 4.7, 16.2$, 1 H), 1.65 (t, $J = 7.7$, 1 H), 1.29 (s, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 208.1, 137.9, 128.4, 127.7, 100.8, 73.4, 73.3, 66.7, 62.9, 49.1, 46.9, 37.5, 24.5; high resolution mass spectrum (FAB, NBA) m/z 551.2644 [(M+Na) $^+$; calcd for $\text{C}_{30}\text{H}_{40}\text{O}_8\text{Na}$: 551.2621].

Trisacetonide (+)-21. Pale yellow oil; $[\alpha]_{\text{D}}^{23} +7.14$ ($c = 0.70$, CHCl_3); IR 3000, 2950, 2920, 2880, 1460, 1385, 1255, 1230, 1205, 1180, 1140, 1110, 1030, 990, 940, 910, 870, 820 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.34–7.32 (m, 3 H), 7.29–7.26 (m, 1 H), 4.60 (d, $J = 12.2$, 1 H), 4.54 (d, $J = 12.2$, 1 H), 4.12–4.03 (m, 3 H), 3.50 (dd, $J = 5.8, 10.1$, 1 H), 1.57–1.47 (m, 4 H), 1.44 (s, 3 H), 1.40 (s, 3 H), 1.33 (s, 3 H), 1.21 (q, $J = 12.0$, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 138.3, 128.3, 127.6, 127.5, 100.4, 98.6, 73.7, 73.4, 68.7, 64.8, 62.4, 42.3, 39.0, 34.1, 30.2, 24.4, 19.7; high resolution mass spectrum (FAB, NBA) m/z 613.3752 [(M+H) $^+$; calcd. for $\text{C}_{36}\text{H}_{53}\text{O}_8$: 613.3740].

Trisacetonide Subtarget (+)-11. Pale yellow oil; $[\alpha]_{\text{D}}^{23} +8.0$ ($c = 0.90$, CHCl_3); IR 3600–3350 (br), 2990, 2940, 2860, 1460, 1380, 1245, 1190, 1170, 1105, 1025, 980, 935, 835, 805 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.10–4.03 (m, 4 H), 4.02–3.96 (m, 1 H), 3.93–3.88 (m, 1 H), 3.66–3.63 (dd, $J = 10.2, 5.2$ Hz, 1 H), 3.61–3.57 (m, 1 H), 3.51–3.47 (m, 1 H), 3.45 (dd, $J = 10.2, 6.2$ Hz, 1 H), 1.95–1.93 (bm, 1 H), 1.59–1.51 (m, 6 H), 1.44 (s, 3 H), 1.43–1.24 (m, 3 H), 1.42 (s, 3 H), 1.39 (s, 3 H), 1.36 (s, 3 H), 1.32 (s, 6 H), 1.12 (q, $J = 11.7$ Hz, 1 H), 0.88 (s, 9 H), 0.05 (s, 6 H), ^{13}C NMR (125 MHz, CDCl_3) δ 100.5, 98.8, 98.5, 70.1, 69.8, 66.9, 66.1, 65.0, 64.6, 62.5, 62.4, 42.5, 42.3, 39.1, 34.4,

32.7, 30.1, 25.9, 24.5, 19.9, 19.8, -5.2, -5.3; high resolution mass spectrum (FAB, NBA)
 m/z 547.3642 [(M+H)⁺; calcd. for C₂₈H₅₄O₈Si: 547.3666].