

**SYNTHESIS OF TEDANOLIDE AND 13-DEOXYTEDANOLIDE.
ASSEMBLY OF A COMMON C(1)-C(11) SUBTARGET**

SUPPORTING INFORMATION

Amos B. Smith, III* and Stephanie A. Lodise

*Department of Chemistry, Laboratory for Research on the Structure of Matter, and Monell
Chemical Senses Center, University of Pennsylvania, Philadelphia, PA 19104, U. S. A.*

Oxazolidinone (+)-11. Colorless oil; $[\alpha]_D^{20} +52^\circ$ (*c* 0.42, CHCl_3); IR (CHCl_3) 3680 (w), 3540 (br), 3020 (m), 1780 (s), 1690 (m), 1380 (m), 1230 (m), 1210 (m), 910 (m), 690 (w) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.32 (m, 5 H), 4.66 (dd, *J* = 3.1, 3.1, 3.1, 6.9 Hz, 1 H), 4.22-4.11 (m, 3 H), 4.02 (dd, *J* = 6.7, 8.2 Hz, 1 H), 3.87-3.77 (m, 3 H), 3.25 (dd, *J* = 3.1, 13.4 Hz, 1 H), 2.76 (dd, *J* = 9.5, 13.4 Hz, 1 H), 2.46 (d, *J* = 6.6 Hz, 1 H), 1.41 (s, 3 H), 1.34 (s, 3 H), 1.31 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 175.2, 152.9, 135.1, 129.4, 128.9, 127.4, 109.6, 76.8, 71.6, 66.18, 66.16, 55.3, 41.2, 37.7, 26.4, 25.3, 12.2; high resolution mass spectrum (Cl, NH_3) *m/z* 364.1752 [(M+H) $^+$; calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_6$: 364.1759].

Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{O}_6\text{NO}_6$; C, 62.80; H, 6.93; N, 3.85. Found: C, 62.90; H, 7.20; N, 3.93.

Aldehyde (+)-12. Colorless oil; $[\alpha]_D^{20} +31^\circ$ (*c* 1.4, C_6H_6); IR (CHCl_3) 2940 (s), 2860 (s), 1730 (s), 1460 (m), 1380 (s), 1370 (s), 1260 (s), 1210 (m), 1150 (s), 1120 (s), 1060 (s), 940 (w), 830 (s), 780 (s) cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 9.4 (s, 1 H), 3.91 (m, 2 H), 3.57 (dd, *J* = 6.0, 8.0 Hz, 1 H), 3.34 (apparent t, *J* = 7.3 Hz, 1 H), 1.73 (dq, *J* = 3.0, 7.0 Hz, 1 H), 1.35 (s, 3 H), 1.24 (s, 3 H), 0.93 (m, 12 H), 0.11 (s, 3 H), 0.05 (s, 3 H); ^{13}C (125 MHz, C_6D_6) δ 201.5, 109.6, 77.8, 73.1, 65.7, 49.3, 26.5, 26.0, 25.5, 18.4, 8.1, -4.0, -4.8; high resolution mass spectrum (Cl, NH_3) *m/z* 320.2251 [(M+NH $_4$) $^+$; calcd for $\text{C}_{15}\text{H}_{34}\text{NO}_4\text{Si}$: 320.2257].

Acetal (+)-13. Colorless oil; $[\alpha]_D^{20} +21^\circ$ (*c* 0.44, CHCl_3); IR (CHCl_3) 3520 (s), 1620 (m), 1520 (m), 1460 (m), 1370 (m), 1360 (m), 1250 (s), 1220 (s), 1160 (m), 1130 (m), 1050 (s), 930 (m), 910 (m), 780 (s), 730 (s), 660 (s) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.39 (dd, *J* = 1.9, 8.6 Hz, 2 H), 6.86 (dd, *J* = 2.0, 8.8 Hz, 2 H), 5.41 (s, 1 H), 4.07 (m, 1 H), 4.00 (m, 2 H), 3.94 (dd, *J* = 5.9, 7.9 Hz, 1 H), 3.78 (m, 1 H), 3.77 (s, 3 H), 3.67 (dd, *J* = 1.4, 8.0 Hz, 1 H), 3.41 (dd, *J* = 8.2, 8.6 Hz, 1 H), 1.69 (m, 1 H), 1.45 (m, 1 H), 1.39 (s, 3 H), 1.33 (s, 3 H), 1.15 (d, *J* = 6.8 Hz, 3 H), 1.00 (d, *J* = 6.5 Hz, 3 H), 0.90 (s, 9 H), 0.12 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.8, 131.5, 127.2, 113.5, 109.1, 101.9, 81.3, 79.0, 73.5, 73.1, 66.0, 55.2, 37.4, 29.3, 26.7, 26.0, 25.7,

18.5, 11.4, 9.6, -3.5, -5.2; high resolution mass spectrum (Cl, NH₃) *m/z* 481.2980 [(M+H)⁺; calcd for C₂₆H₄₅O₆Si: 481.2985].

(+)-**14**. Colorless oil; [α]_D²⁰ +4.8° (*c* 1.6, CHCl₃); IR (CHCl₃) 2980 (m), 1620 (m), 1590 (w), 1520 (m), 1470 (m), 1370 (m), 1300 (m), 1250 (s), 1170 (s), 1120 (m), 1110 (m), 1080 (s), 1050 (s), 1000 (m), 970 (m), 930 (m), 870 (w), 830 (m), 620 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.38 (dd, *J* = 1.9, 6.7 Hz, 2 H), 6.86 (dd, *J* = 1.9, 6.7 Hz, 2 H), 5.44 (s, 1 H), 4.25 (ddd, *J* = 6.0, 8.3, 8.3 Hz, 1 H), 4.07 (dd, *J* = 2.3, 11.2 Hz, 1 H), 4.01 (dd, *J* = 1.3, 11.2 Hz, 1 H), 3.97 (dd, *J* = 6.0, 8.1 Hz, 1 H), 3.82 (dd, *J* = 2.0, 9.7 Hz, 1 H), 3.77 (s, 3 H), 3.51 (s, 3 H), 3.46 (apparent t, *J* = 8.3 Hz, 1 H), 3.19 (dd, *J* = 1.8, 8.0 Hz, 1 H), 1.70 (m, 1 H), 1.55 (m, 1 H), 1.40 (s, 3 H), 1.36 (s, 3 H), 1.16 (d, *J* = 6.9 Hz, 3 H), 1.00 (d, *J* = 6.7 Hz, 3 H); ¹³C (125 MHz, CDCl₃) δ 159.8, 131.5, 127.1, 113.5, 109.4, 101.8, 81.2, 81.0, 79.4, 73.6, 66.2, 59.9, 55.2, 36.9, 30.0, 26.7, 25.8, 11.3, 10.1; high resolution mass spectrum (Cl, NH₃) *m/z* 381.2271 [(M+H)⁺; calcd for C₂₁H₃₃O₆: 381.2277].

Anal. Calcd. for C₂₁H₃₂O₆; C, 66.28; H, 8.48. Found: C, 65.88; H, 8.58.

(-)-**15**. A solution of (+)-**16** (992 mg, 2.60 mmol) in dichloromethane (26 mL) was cooled to -78 °C, treated dropwise with DIBAL-H (neat, 1.40 mL, 7.80 mmol) and warmed to -10 °C. The reaction mixture was stirred for 15 minutes then immediately diluted with MeOH (5 mL) and saturated aqueous Rochelle's salt (30 mL). The resultant mixture was stirred vigorously until two clear layers were obtained (1 h). The layers were separated and the aqueous layer was extracted with Et₂O (3 x 50 mL). The combined organic layers were washed with brine (75 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. Flash chromatography (20%→40% ethyl acetate/hexanes) provided 905 mg (91% yield) as a colorless oil: [α]_D²⁰ -18° (*c* 0.42, CHCl₃); IR (CHCl₃) 3640 (w), 3500 (br), 3000 (m), 1610 (m), 1520 (m), 1460 (m), 1380 (m), 1370 (m), 1300 (w), 1250 (br), 1040 (s), 920 (w), 840 (w), 820 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.24 (d, *J* = 8.5 Hz, 2 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 4.50 (q, *J*_{AB} = 10.8 Hz, Δ*v*_{AB} = 10.3 Hz, 2 H), 4.21 (m, 1 H), 3.95 (dd, *J* = 6.2, 8.0 Hz, 1 H), 3.77 (s, 3 H), 3.58 (m, 3 H), 3.51 (m, 4 H), 2.91 (dd, *J* = 2.9, 7.1 Hz, 1 H), 2.00 (m, 1 H),

1.84 (apparent t, J = 5.1 Hz, 1 H), 1.71 (m, 1 H), 1.39 (s, 3 H), 1.35 (s, 3 H), 1.03 (d, J = 1.0 Hz, 3 H), 0.88 (d, J = 6.9, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.2, 130.8, 129.3, 113.8, 109.2, 83.0, 80.6, 78.6, 74.2, 66.2, 66.1, 60.1, 55.2, 38.1, 37.9, 26.6, 25.8, 10.9, 10.8; high resolution mass spectrum m/z 383.2433 [(M+H) $^+$; calcd for $\text{C}_{21}\text{H}_{35}\text{O}_6$: 383.2433].

Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{O}_6$: C, 65.94; H, 8.96. Found: C, 65.89; H, 8.86.

Aldehyde (+)-7. Colorless oil; $[\alpha]_D^{20} +23^\circ$ (c 0.50, C_6H_6); IR (C_6H_6) 2980 (s), 2700 (w), 1730 (s), 1610 (m), 1510 (s), 1455 (m), 1380 (m), 1250 (s), 1040 (s), 730 (m) cm^{-1} ; ^1H NMR (500 MHz, C_6H_6) δ 9.63 (s, 1 H), 7.15 (d, J = 8.1 Hz, 2 H), 6.76 (d, J = 8.6 Hz, 2 H), 4.26 (q, J_{AB} = 10.7 Hz, $\Delta\nu_{AB}$ = 33.1 Hz, 2 H), 4.17 (ddd, J = 6.3, 6.3, 8.5 Hz, 1 H), 3.93 (dd, J = 2.8, 7.7 Hz, 1 H), 3.70 (dd, J = 6.2, 8.0 Hz, 1 H), 3.39 (s, 3 H), 3.37 (apparent t, J = 8.2 Hz, 1 H), 3.27 (s, 3 H), 3.01 (dd, J = 2.6, 6.8 Hz, 1 H), 2.39 (dq, J = 2.8, 7.1 Hz, 1 H), 1.57 (m, 1 H), 1.38 (s, 3 H), 1.31 (s, 3 H), 1.05 (d, J = 7.0 Hz, 3 H), 0.99 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, C_6H_6) δ 202.9, 159.8, 129.5, 128.1, 114.0, 109.4, 82.7, 79.5, 79.0, 73.6, 66.4, 59.5, 54.7, 49.4, 38.6, 26.8, 26.0, 11.3, 7.9; high resolution mass spectrum (Cl, NH_3) m/z 398.2548 [(M+NH $_4$) $^+$; calcd for $\text{C}_{21}\text{H}_{36}\text{NO}_6$: 398.2542].

(-)-17. Colorless oil; $[\alpha]_D^{20} -20.9^\circ$ (c 1.35, CHCl_3); IR (CHCl_3) 2980 (m), 1620 (w), 1450 (w), 1430 (w), 1380 (w), 1280 (w), 710 (w) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.43 (d, J = 9.4 Hz, 1 H), 4.05 (d, J = 6.0 Hz, 1 H), 2.92-2.83 (m, 5 H), 2.11-2.05 (m, 1 H), 1.89-1.82 (m, 1 H), 1.18 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.8, 89.8, 52.4, 43.1, 30.5, 30.3, 25.8, 16.6; high resolution mass spectrum (Cl, NH_3) m/z 330.8782 [(M+H) $^+$; calcd for $\text{C}_8\text{H}_{13}\text{Br}_2\text{S}_2$: 330.8825].

(-)-18. Colorless oil; $[\alpha]_D^{20} -12^\circ$ (c 1.00, CHCl_3); IR (CHCl_3) 2900 (m), 2360 (w), 1450 (m), 1430 (m), 1380 (m), 1280 (m), 1250 (m), 1180 (m), 910 (w), 900 (w), 740 (m) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.04 (d, J = 5.8 Hz, 1 H), 2.84 (m, 4 H), 2.07 (m, 2 H), 1.86 (m, 1 H), 1.80 (d, J = 2.3 Hz, 3 H), 1.30 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 79.7, 78.6, 53.3, 32.0, 30.54, 30.51,

25.8, 19.2, 3.6; high resolution mass spectrum (Cl, NH₃) *m/z* 187.0606 [(M+H)⁺; calcd for C₉H₁₅S₂: 187.0615].

Vinyl Iodide (-)-8. Pale yellow oil; [α]_D²⁰ -30° (*c* 1.8, C₆H₆); IR (CCl₄) 2900 (s), 1630 (m), 1420 (m), 1380 (m), 1280 (m), 1180 (m), 1140 (m), 1090 (m), 1040 (m), 910 (m), 860 (m), 740 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 6.27 (dq, *J* = 1.4, 2.9 Hz, 1 H), 3.60 (d, *J* = 6.7 Hz, 1 H), 2.62 (m, 1 H), 2.34-2.26 (m, 4 H), 2.13 (d, *J* = 1.5 Hz, 3 H), 1.50 (m, 1 H), 1.38 (m, 1 H), 1.01 (d, *J* = 6.8 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 143.1, 95.2, 53.5, 40.7, 30.5, 30.3, 27.9, 26.0, 17.8; high resolution mass spectrum (Cl, NH₃) *m/z* 314.9738 [(M+H)⁺; calcd for C₉H₁₆IS₂: 314.9738].

(-)-20/(-)-21. To a solution of (-)-8 (181 mg, 0.576 mmol) in Et₂O/pentane (4:1, 3 mL) at -78 °C was added *t*-BuLi (1.7 M in pentane, 0.64 mL, 1.094 mmol). After stirring for 25 min, a white precipitate was observed. The solution was added via cannula to a solution of (+)-7 (109 mg, 0.288 mmol) in Et₂O/pentane (4:1, 3 mL) at -100 °C and stirred for 10 min before warming to -78 °C. After 15 min, the reaction mixture was quenched with MeOH (0.5 mL) and saturated aqueous NaHCO₃ (5 mL) and then diluted with Et₂O (15 mL). The layers were separated, and the aqueous layer was extracted with Et₂O (2 x 10 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated in vacuo. Flash chromatography (25% ethyl acetate/hexanes) afforded (-)-20 and (-)-21 as a 4:1 mixture of diastereomers (106 mg, 65% yield).

(-)-20. Colorless oil; [α]_D²⁰ -49° (*c* 0.90, CHCl₃); IR (CHCl₃) 3600 (w), 3560-3400 (br), 2989 (s), 1620 (m), 1510 (m), 1460 (m), 1380 (m), 1370 (m), 1250 (s), 1110 (s), 1040 (s), 830 (w) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.25 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 5.50 (d, *J* = 9.7 Hz, 1 H), 4.59 (q, *J_{AB}* = 10.8 Hz, Δ*v_{AB}* = 35.0 Hz, 2 H), 4.22 (ddd, *J* = 6.3, 7.4, 7.4 Hz, 1 H), 4.17 (d, *J* = 4.7 Hz, 1 H), 4.03 (d, *J* = 6.5 Hz, 1 H), 3.95 (dd, *J* = 6.1, 8.0 Hz, 1 H), 3.77 (s, 3 H), 3.58 (dd, *J* = 2.7, 7.5 Hz, 1 H), 3.51 (s, 3 H), 3.49-3.43 (m, 2 H), 3.13 (dd, *J* = 2.7, 7.4 Hz, 1 H), 2.85-2.78 (m, 4 H), 2.41 (broad s, 1 H), 2.06 (m, 1 H), 1.90 (m, 1 H), 1.80 (m, 1 H), 1.68 (m, 1 H), 1.64 (s, 3 H), 1.39

(s, 3 H), 1.35 (s, 3 H), 1.15 (d, J = 6.7 Hz, 3 H), 1.03 (d, J = 6.9 Hz, 3 H), 0.90 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.1, 136.5, 130.9, 129.0, 113.8, 109.3, 83.7, 82.8, 79.1, 74.3, 66.2, 60.1, 55.2, 54.8, 39.3, 38.0, 37.4, 30.8, 30.6, 26.7, 26.1, 25.8, 18.4, 13.2, 10.6, 7.4; high resolution mass spectrum (ESI) m/z 591.2831 [(M+Na) $^+$; calcd for $\text{C}_{30}\text{H}_{48}\text{O}_6\text{S}_2\text{Na}$: 591.2790].

(-)•21. Colorless oil; $[\alpha]_D^{20}$ -31° (c 0.90, CHCl_3); IR (CHCl_3) 3500-3400 (br), 2980 (s), 1620 (m), 1520 (m), 1450 (m), 1380 (m), 1370 (m), 1250 (m), 1110 (m), 840 (m) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.27 (d, J = 8.6 Hz, 2 H), 6.85 (d, J = 8.7 Hz, 2 H), 5.42 (d, J = 9.8 Hz, 1 H), 4.60 (q, J_{AB} = 10.9 Hz, $\Delta\nu_{AB}$ = 35.0 Hz, 2 H), 4.21 (ddd, J = 6.2, 8.3, 8.3 Hz, 1 H), 4.05 (d, J = 6.4 Hz, 1 H), 3.95 (dd, J = 6.1, 8.0 Hz, 1 H), 3.92 (dd, J = 3.3, 8.8 Hz, 1 H), 3.87 (dd, J = 1.7, 7.8 Hz, 1 H), 3.78 (s, 3 H), 3.53 (s, 3 H), 3.46 (apparent t, J = 8.2 Hz, 1 H), 3.08 (dd, J = 2.3, 7.4 Hz, 1 H), 2.88-2.80 (m, 5 H), 2.32 (d, J = 3.1 Hz, 1 H), 2.07 (m, 1 H), 1.94 (m, 1 H), 1.82 (m, 1 H), 1.67 (m, 1 H), 1.64 (s, 3 H), 1.40 (s, 3 H), 1.35 (s, 3 H), 1.13 (d, J = 6.7 Hz, 3 H), 1.03 (d, J = 6.9 Hz, 3 H), 0.73 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.2, 137.3, 130.0, 129.1, 113.8, 109.4, 83.3, 80.1, 79.7, 78.8, 76.3, 73.9, 66.4, 60.0, 55.2, 54.8, 38.4, 37.5, 37.4, 30.9, 30.7, 26.7, 26.1, 25.8, 18.3, 11.4, 11.1, 10.7; high resolution mass spectrum (ESI) m/z 591.2786 [(M+Na) $^+$; calcd for $\text{C}_{30}\text{H}_{48}\text{O}_6\text{S}_2\text{Na}$: 591.2790].

(-)•3: Colorless oil; $[\alpha]_D^{20}$ -39° (c 1.3, CHCl_3); IR (CHCl_3) 2940 (s), 1610 (m), 1510 (m), 1460 (m), 1380 (m), 1370 (m), 1240 (s), 1040 (s), 870 (m) cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, J = 8.6 Hz, 2 H), 6.83 (d, J = 8.6 Hz, 2 H), 5.31 (d, J = 9.5 Hz, 1 H), 4.72 (d, J = 11.3 Hz, 1 H), 4.57 (d, J = 11.3 Hz, 1 H), 4.20 (m, 1 H), 4.18 (d, J = 9.8 Hz, 1 H), 4.03 (d, J = 5.7 Hz, 1 H), 3.94 (dd, J = 6.0, 7.9 Hz, 1 H), 3.77 (s, 3 H), 3.56 (apparent d, J = 8.1 Hz, 1 H), 3.50 (s, 3 H), 3.43 (apparent t, J = 8.3 Hz, 1 H), 3.13 (dd, J = 1.9, 7.7 Hz, 1 H), 2.86-2.80 (m, 5 H), 2.06 (m, 1 H), 1.86-1.80 (m, 2 H), 1.65 (s, 3 H), 1.55 (m, 1 H), 1.39 (s, 3 H), 1.34 (s, 3 H), 1.11 (d, J = 6.7 Hz, 3 H), 1.05-1.01 (m, 27 H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.7, 138.2, 132.1, 131.3, 128.5, 113.6, 109.3, 82.7, 81.4, 80.3, 79.6, 74.2, 66.4, 59.8, 55.2, 40.2, 39.9, 37.5, 30.8, 30.6, 26.8, 26.2, 25.9, 18.4, 18.38, 18.31,

17.5, 12.8, 11.5, 11.1, 10.0; high resolution mass spectrum (ESI) m/z 747.4153 [(M+Na)⁺; calcd for C₃₉H₆₈O₆S₂SiNa: 747.4124].

(-)-**23**. To a solution of (-)-**3** (8.5 mg, 0.0117 mmol) in 10% HMPA/THF (250 μ L) at -78 °C was added *t*-BuLi (1.5 M in pentane, 15 μ L, 0.0234 mmol) and the resulting yellow solution was stirred for 5 min before the addition of benzyl (S)-(+)glycidyl ether (5 μ L, 0.0351 mmol). After 10 min, the reaction mixture was quenched with saturated aqueous NaHCO₃ (5 mL) and diluted with Et₂O. The layers were separated, and the aqueous phase was extracted with Et₂O (2 x 5 mL). The organic layers were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. Flash chromatography (12% ethyl acetate/hexanes) provided 8.1 mg (78%) of (-)-**24** as a colorless oil. $[\alpha]_D^{20}$ -43° (*c* 0.40, CHCl₃); IR (CHCl₃) 3500 (w), 2920 (s), 1610 (w), 1510 (m), 1460 (m), 1450 (m), 1380 (m), 1370 (m), 1250 (s), 1040 (s) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.23 (m, 7 H), 6.81 (d, *J* = 8.6 Hz, 2 H), 5.59 (d, *J* = 9.8 Hz, 1 H), 4.82 (d, *J* = 11.0 Hz, 1 H), 4.59 (d, *J* = 11.0 Hz, 1 H), 4.50 (q, *J*_{AB} = 11.9 Hz, $\Delta\nu_{AB}$ = 21.4 Hz, 2 H), 4.25 (d, *J* = 9.8 Hz, 1 H), 4.25 (m, 1 H), 4.19 (ddd, *J* = 6.0, 8.6, 8.6 Hz, 1 H), 3.94 (dd, *J* = 6.0, 8.0 Hz, 1 H), 3.76 (s, 3 H), 3.65 (apparent d, *J* = 8.4 Hz, 1 H), 3.47 (s, 3 H), 3.43 (m, 2 H), 3.34 (dd, *J* = 7.2, 9.4 Hz, 1 H), 3.22 (m, 1 H), 3.15 (dd, *J* = 1.8, 7.7 Hz, 1 H), 2.88 (m, 1 H), 2.71 (m, 4 H), 2.13 (m, 2 H), 1.91 (m, 2 H), 1.78 (m, 1 H), 1.67 (d, *J* = 0.97 Hz, 3 H), 1.55 (m, 1 H), 1.39 (s, 3 H), 1.34 (s, 3 H), 1.15 (d, *J* = 6.8 Hz, 3 H), 1.05-0.99 (m, 27 H); ¹³C NMR (125 MHz, CDCl₃) δ 158.8, 138.0, 137.7, 132.0, 130.4, 128.6, 128.4, 127.7, 127.6, 113.6, 109.3, 82.5, 81.5, 80.3, 79.7, 74.7, 74.4, 73.2, 68.0, 66.5, 59.7, 57.5, 55.2, 39.9, 39.8, 39.4, 38.8, 29.6, 26.8, 26.0, 25.9, 25.0, 18.4, 18.3, 15.0, 12.8, 11.6, 11.4, 9.9; high resolution mass spectrum (ESI) m/z 911.4972 [(M+Na)⁺; calcd for C₄₉H₈₀O₈S₂SiNa: 911.4961].