Supporting Information

(+)-Rimocidin Synthetic Studies: Construction of the C(1-27) Aglycone Skeleton

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Experimental Section

I. Material and Methods

Reactions were carried out in oven-dried or flame-dried glassware under argon unless otherwise specified. Anhydrous tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone under argon or obtained from a commercial solvent purification system. Dichloromethane was distilled from calcium hydride under argon or obtained from a commercial solvent purification system. Triethylamine, 2,6-lutidine, diisopropylethylamine, pyridine, and hexamethylphosphoramide were freshly distilled from calcium hydride under argon. All commercially available reagents were used without purification unless otherwise noted. Alkyllithium reagents were titrated using *N*-benzylbenzamide[1] Reactions were magnetically stirred unless otherwise stated and monitored by thin layer chromatography (TLC) with 0.25 mm E. pre-coated silica gel plates. Silica gel chromatography was performed using ACS grade solvents. Deactivated silica gel was prepared by adding triethylamine to a slurry of silica gel in hexanes.

Melting points are uncorrected. Infrared spectra were obtained using an FT/IR spectrometer. Rotations were measured at the sodium line at ambient temperature. Proton, carbon and 2D (COSY, NOESY, HSQC, HMQC) NMR spectra were obtained on a 500 MHz spectrometer. Chemical shifts are reported relative to chloroform (δ 7.26) or benzene (δ 7.16) for ^{1}H NMR and chloroform (δ 77.0) or benzene (δ 128.0) for ^{13}C NMR. High resolution mass spectra were obtained using ESI or CI. Single X-ray structures were obtained using automated diffractometer.

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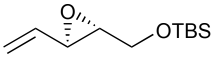
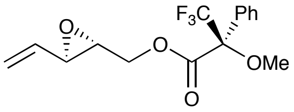
[1] Burchat, A. F.; Chong, J, M.; Nielsen, N. *J. Organomet. Chem.*, **1997**, *542*, 281.

II. Procedure



(+)-**14**

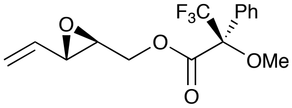
Vinyl Epoxide (+)-14: $[\alpha]_D^{23}$ +14.80° (c = 1.10, $CHCl_3$); IR (film) 2955, 2931, 2890, 2858, 1468, 1255, 1139, 1109, 838, 779 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.60 (ddd, *J* = 7.5, 10.3, 17.3 Hz, 1H), 5.48 (dd, *J* = 2.2, 17.8 Hz, 1H), 5.29 (dd, *J* = 1.5, 10.6 Hz, 1H), 3.86 (dd, *J* = 3.2, 12.0 Hz, 1H), 3.72 (dd, *J* = 4.5, 12.0 Hz, 1H), 3.28 (dd, *J* = 2.1 7.5 Hz, 1H), 3.00 (ddd, *J* = 2.2, 3.3, 4.5 Hz, 1H), 0.90 (s, 9H), 0.083 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.2, 119.4, 63.0, 60.3, 56.1, 25.8 (3C), 18.4, -5.3 (2C); high resolution mass spectrum (CI+) m/z 215.1464 [(MH^+); calculated for $C_{11}H_{22}OSi$+H: 215.1467]. The proton and carbon NMR spectra are identical to those shown for the enantiomer (-)-**14**.



(-)-**S1**

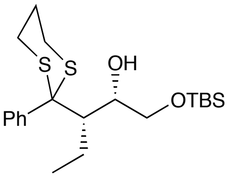
Mosher Ester (-)-S1: In the preparation of (+)- and (-)-**14**, prior to addition of trimethyl phosphite a small aliquot of the asymmetric epoxidation reaction mixture (~9 mg) was placed in a 1 dram vial containing CH_2Cl_2 (300 μL), Et_3N (100 μL), catalytic DMAP and R)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (20 μL). After vigorous shaking the solution turned orange. Following an additional 15 min of standing the reaction mixture was loaded onto a 500 μm preparative TLC plate and eluted with 4:1 hexanes:EtOAc. Ester (-)-**S1** was isolated in approximately 60% yield in 94% d.e.: $[\alpha]_D^{23}$ -31.16° (c = 0.84, CH_2Cl_2); IR (film) 3066, 2991, 2953, 2850, 1754, 1452, 1273, 1243, 1170, 1123, 1023, 932, 880, 720 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.68 (m, 2H), 7.10 (m, 2H), 7.04 (m, 1H), 5.21 (ddd, *J* = 7.3, 10.1, 17.1 Hz, 1H), 5.13 (dd, *J* = 1.6, 17.2 Hz, 1H), 4.93 (dd, *J* = 1.6, 10.1 Hz, 1H), 4.02 (dd, *J* = 3.2, 12.1 Hz, 1H), 3.76 (dd, *J* = 6.2, 12.1 Hz, 1H), 3.41 (s, 3H), 2.78 (dd, *J* = 1.9, 7.2

1H), 2.57 (ddd, *J* = 2.1, 3.0, 5.9 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 166.4, 134.7, 132.8, 129.8 (2C), 128.6 (2C), 127.7, 125.3, 122.9, 119.5, 65.6, 56.1, 56.0, 55.4; high resolution mass spectrum (CI+) m/z 317.1006 [(MH$^+$); calculated for $C_{15}H_{15}F_3O_4$+H: 317.1001].



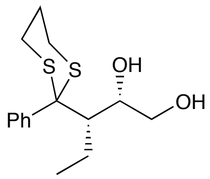
(-)-**S2**

Mosher Ester (-)-**S2:** $[\alpha]_D^{23}$ -71.08° (c = 1.18, C_6H_6); IR (film) 3056, 2990, 2953, 2850, 1754, 1452, 1273, 1173, 1124, 1022, 998, 765, 720 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.67 (m, 2H), 7.09 (m, 2H), 7.03 (m, 1H), 5.23 (ddd, *J* = 7.6, 10.5, 17.6 Hz, 1H), 5.15 (d, *J* = 17.5, 1H), 4.93 (d, *J* = 10.2 Hz, 1H), 4,17 (dd, *J* = 2.9, 21.1 Hz, 1H), 3.64 (dd, *J* = 5.5, 12.2 Hz, 1H), 3.41 (s, 3H), 2.85 (d, *J* = 7.3 Hz, 1H), 2.63 (ddd, *J* = 2.2, 2.2, 4.9 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 166.4, 134.7, 132.7, 129.8 (2C), 128.7 (2C), 128.3, 125.3, 124.0, 119.5, 65.0, 56.2, 55.9, 55.4; high resolution mass spectrum (CI+) m/z 317.1006 [(MH$^+$); calculated for $C_{15}H_{15}F_3O_4$+H: 317.1001].



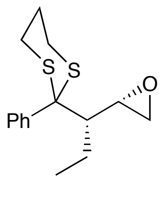
(+)-**S3**

Alcohol (+)-S3: Alcohol (+)-**19** (8.34 g, 20.4 mmol) was dissolved in reagent grade MeOH (60 mL) and cannulated into a 2-necked flask equipped with a reflux condenser. Triethylamine (6.25 mL, 44.9 mmol) and tosylhydrazide (7.60 g, 40.81mmol) were added to the flask and the reaction was heated to 55 °C for 14 h. Tosylhydrazide (1-2 equiv.) and 1.2-2.2 equivalents of Et_3N were added every 6 h until the reaction was judged to be complete by TLC. The flask was cooled to room temperature, the reaction mixture was transferred to a one-necked flask and the MeOH was removed under reduced pressure. The resulting residue was dissolved in EtOAc and washed with distilled water, dried over $MgSO_4$ and concentrated. Column chromatography (98:2 hexanes:EtOAc) afforded the desired product, (+)-**S3** (6.87 g, 16.6 mmol) as a pale yellow oil in 81% yield: $[\alpha]^{23}_{D}$ +1.06° (c = 2.16, $CHCl_3$); IR (film) 3468, 2929, 2857, 1466, 1253, 1112, 1009, 839, 776, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.38 (m, 2H), 7.26 (m, 1H), 4.26 (app t, *J* = 6.6 Hz, 1H), 3.47 (dd, *J* = 7.7, 9.9 Hz 1H), 3.34 (dd, *J* = 6.2, 9.9 Hz, 1H), 2.72-2.60 (m, 4H), 1.91 (m, 2H), 1.77 (m, 1H), 1.65 (m, 2H), 0.87 (s, 9H), 0.69 (dd, *J* = 7.5, 7.5 Hz, 3H), 0.057 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 129.8 (2C), 128.5 (2C), 126.9, 71.2, 65.8, 65.6, 54.8, 27.5, 27.4, 25.9 (3C), 25.1, 18.2, 17.0, 15.6, -5.38, -5.41; high resolution mass spectrum (ES+) *m/z* 435.1805 [(M+Na^+); calculated for: $C_{21}H_{36}O_2S_2Si$+Na 435.1824].



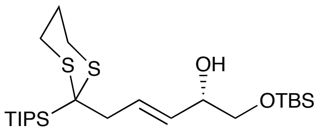
(+)-**10**

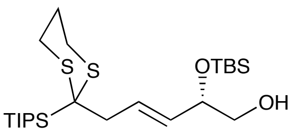
Diol (+)-10: Alcohol (+)-**S3** was dissolved in methanolic HCl (2.7% HCl, 100 mL) and the reaction was allowed to stir at room temperature until the starting material was completely consumed as judged by TLC. The solution was then carefully basified with solid $NaHCO_3$. The MeOH was removed under reduced pressure and the resulting slurry was taken up in Et_2O, filtered though Celite and concentrated. Following flash chromatography (1:1 hexanes:EtOAc) diol (+)-**10** was isolated as a colorless oil in 96% yield (4.58 g, 15.5 mmol): $[\alpha]^{23}_{D}$ +15.70° (c = 1.72, $CHCl_3$); IR (film) 3420, 2932, 1441, 1274, 1047, 896, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (m, 2H), 7.40 (m, 2H), 7.28 (m,1H), 4.46 (dd, *J* = 4.0, 9,2 Hz, 1H), 3.57 (dd, *J* = 9.3, 10.9 Hz, 1H), 3.36 (dd, *J* = 6.9, 10.9 Hz, 1H), 2.78-2.66 (m, 1H), 2.63 (m, 3H), 1.95-1.90 (m, 3H), 1.65 (m, 4H), 0.65 (dd, *J* = 7.3, 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 129.6 (2C), 128.7 (2C), 127.2, 72.1, 65.7, 65.6, 55.9, 27.5, 27.3, 25.0, 17.1, 15.5; high resolution mass spectrum (ES+) *m/z* 321.0944 [(M+Na$^+$); calculated for: $C_{15}H_{22}O_2S_2$+Na 321.0959].



(+)-**20**

Epoxide (+)-20: A round bottom flask was charged with 95% NaH (1.38 g, 54.6 mmol), dry THF (80 mL) and was cooled to 0 °C in an ice water bath. Diol (+)-**10** (5.31 g, 17.9 mmol) was dissolved in dry THF (80 mL) and added to the NaH slurry via cannula. The reaction stirred for 1 h prior to addition of trisylimidazole via cannula (6.59 g, 19.71 mmol) in dry THF (45 mL). The reaction warmed to room temperature over the course of 2 h at which point it was quenched by addition of saturated NH_4Cl (18 mL) and diluted with Et_2O (200 mL). The layers were separated and the aqueous phase was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with saturated $NaHCO_3$ (20 mL), brine (50 mL), dried over $MgSO_4$ and concentrated. The crude material was purified using flash chromatography (97:2:1 hexanes:EtOAc:Et_3N) to afford epoxide (+)-**20** as an amorphous solid in 84% yield (4.22 g, 15.05 mmol). X-Ray quality crystals were obtained via vapor diffusion from hexanes, melting point 46-50 °C: $[\alpha]_D^{23}$ +20.35° (c = 1.14, $CHCl_3$); IR (film) 3494, 3053, 2930,. 1482, 1442, 1256, 1106, 1034, 895, 842, 703 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (m, 2H), 7.39 (m, 2H), 7.27 (m, 1H), 2.90 (ddd, *J* = 2.7, 3.8, 8.6 Hz, 1H), 2.74-2.60 (m, 4H), 2.59 (dd, *J* = 4.0, 4.7 Hz, 1H), 2.22 (dd, *J* = 2.8, 4.7 Hz, 1H), 2.00 (m, 1H), 1.93-1.87 (m, 2H), 1.58-1.52 (m, 1H), 1.40 (ddd, *J* = 3.1, 8.9, 8.9 Hz, 1H), 0.94 (dd, *J* = 7.5, 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 129.9 (2C), 128.4 (2C), 127.1, 64.0, 55.9, 53.8, 47.4, 27.5, 27.4, 25.1, 23.2, 13.3; high resolution mass spectrum (ES+) *m/z* 281.1033 [(MH$^+$); calculated for: $C_{15}H_{20}OS_2$+H 281.1034].[2]


(+)-**22**


(+)-**23**

Alkenes (+)-22 and (+)-23: 2-Triisopropylsilyl-1,3-dithiane (**21**) (7.84 g, 28.4 mmol) was azeotroped three times with benzene and placed under high vacuum for 2 h. Vinyl epoxide (+)-**14** (4.87 g, 22.7 mmol) was dissolved in dry THF (18 mL) and the solution was allowed to stand over CaH_2 for 30 min to remove trace water. The dithiane (**21**) was dissolved in dry THF (104 mL) and HMPA (7.90 mL, 45.4 mmol) was added. The solution was cooled to -78 °C in a dry ice/acetone bath and *t*-BuLi (1.38M, 19.75 mL, 27.26mmol) was added. After 5 min the reaction was placed in a -40 °C bath (dry ice/CH_3CN) and allowed to stir for 1 h. The flask was re-cooled to -78 °C and the epoxide was added via cannula. The reaction warmed slowly in the bath for 1.5 h, then stirred at room temperature for an additional 1.5 h, turning from yellow to dark red over the course of the reaction. The reaction was quenched with saturated NH_4Cl (9 mL) and diluted with Et_2O (200 mL) and distilled water (20 mL). The layers were separated and the aqueous layer was extracted twice with Et_2O then water was run through the combined organic layers to remove the HMPA. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. Flash chromatography (95:5 to 4:1 hexanes:EtOAc) afforded a mixture of (+)-**22** (major) and (+)-**23** (minor) in a total of 9.29 g (18.9 mmol, 83% yield): (+)-**22** $[\alpha]_D^{23}$ +10.88° (c = 0.91, $CHCl_3$); IR (film) 3456, 2951, 2870, 1462, 1257, 1095, 1026, 802 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.15

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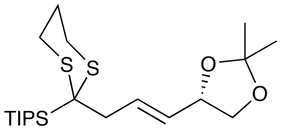
[2] CCDC 727530 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

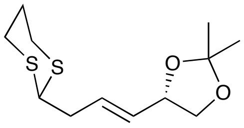
(dddd, *J* = 1.1, 7.4, 7.4, 15.4 Hz, 1H), 5.59 (dddd, *J* = 1.4, 1.4, 6.4, 15.5 Hz, 1H), 4.18 (bs, 1H), 3.66 (dd, *J* = 3.5, 10.0 Hz, 1H), 3.46 (dd, *J* = 8.0, 10.0 Hz, 1H), 3.19-3.07 (m, 4H), 2.54 (bs, 1H), 2.40 (ddd, *J* = 3.7, 3.7, 14.1 Hz, 2H), 2.07-2.05 (m, 1H), 1.95 (ddddd, *J* = 3.1, 3.1, 12.6, 12.6, 12.6, 1H), 1.48 (septet, *J* = 7.3 Hz, 3H), 1.23 (d, 7.4 Hz, 18H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.0, 129.8, 72.8, 67.0, 43.1, 40.18, 25.9 (3C), 24.6, 24.5 (2C) 20.0 (6C), 18.3, 12.1 (3C), -5.3, -5.4; high resolution mass spectrum (ES+) *m/z* 513.2680 [(M+Na$^+$); calculated for: $C_{24}H_{50}O_2S_2Si_2$+Na 513.2688]: (+)-**23** $[\alpha]_D^{23}$ +2.69° (c = 0.26, $CHCl_3$); IR (film) 3456, 2943, 2870, 1462, 1381, 1254, 1095, 833, 775, 660 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.99 (ddd, *J* = 0.9, 7.1, 7.1, 16.3 Hz, 1H), 5.57 (dddd, *J* = 1.2, 1.2, 7.7, 16.6 Hz, 1H), 4.24 (ddd, *J* = 6.0, 6.0, 6.0 Hz, 1H), 3.54-3.46 (m, 2H), 3.17 (ddddd, *J* = 1.1, 8.6, 15.4, 15.4, 15.4 Hz, 2H), 3.06 (dddd, *J* = 1.1, 2.6, 13.8, 13.8 2H), 2.37 (ddd, *J* = 3.4, 3.4, 7.4 HZ, 2H), 2.06-1.91 (m, 3H), 1.45 (septet, *J* = 7.6 Hz, 3H), 1.23 (d, *J* = 7.4 Hz, 18H), 0.91 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ 131.5, 130.9, 74.1, 66.9, 42.4, 40.2, 25.9 (3C), 24.6, 24.4 (2C), 20.0 (6C), 18.2, 12.2 (3C), -4.3, -4.8; high resolution mass spectrum (ES+) *m/z* 513.2699 [(M+Na$^+$); calculated for: $C_{24}H_{50}O_2S_2Si_2$+Na 513.2689].



(+)-**S4**

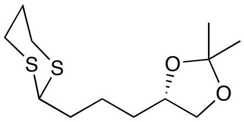
Acetonide (+)-S4: A mixture of (+)-**22** and (+)-**23** (3.08 g, 6.37 mmol) was dissolved in of MeOH (35 mL) and *p*-toluenesulfonic acid (0.36 g, 1.88 mmol) was added. After 20 min the MeOH was removed under reduced pressure and 2,2-dimethoxypropane (28 mL, 228.0 mmol) was added. After 1 h TLC showed complete conversion of starting material to product. The reaction was diluted with CH_2Cl_2, washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated. The unpurified material was carried forward to the next step, although a small sample was purified for characterization purposes: $[\alpha]_D^{23}$ +29.87° (c = 1.51, C_6H_6); IR (film) 2943, 2867, 1463, 1371, 1244, 1156, 1062, 881, 658 cm $^{-1}$; ^{1}H

NMR (500 MHz, $CDCl_3$) δ 6.15 (ddd, *J* = 7.0, 7.0, 14.6 Hz, 1H), 5.62 (dd, *J* = 7.5, 15.4 Hz, 1H), 4.53 (ddd, *J* = 7.3, 7.3, 7.3 Hz, 1H), 4.08 (dd, *J* = 6.2, 8.0 Hz, 1H), 3.59 (dd, *J* = 8.0, 8.0 Hz, 1H), 3.23 (dd, *J* = 7.8, 15.4 Hz, 1H), 3.13 (d, *J* = 7.8, 17.0 Hz, 1H), 3.06 (m, 2H), 2.40 (m, 2H), 2.05 (m, 1H), 1.95 (ddddd, *J* = 3.2, 3.2, 12.9, 12.9, 12.9 1H), 1.47 (septet, *J* = 7.5 Hz, 3H), 1.43 (s, 3H), 1.39 (s, 3H), 1.22 (d, J = 7.4 Hz, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.4, 129.1, 109.2, 77.1, 69.2, 42.7, 40.1, 26.8, 25.9, 24.60, 24.57, 24.5, 20.00 (6C), 12.1 (3C).



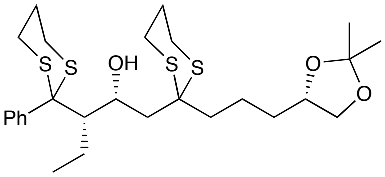
(+)-**24**

Dithiane (+)-24: Unpurified acetonide (+)-**S4** was dissolved in THF (20 mL) and a solution of TBAF in THF (1 M, 12.5 mL, 12.5 mmol) was added. The reaction stirred at room temperature for 1 h at which point saturated NH_4Cl (8 mL) and Et_2O (30 mL) were added. The layers were separated and the organic layer was washed with distilled H_2O and brine. The organic material was dried over $MgSO_4$ and concentrated under reduced pressure. Flash column chromatography (9:1 hexanes : EtOAc) afforded (+)-**24** in 73% yield (1.19 g, 4.57 mmol) over three steps: $[\alpha]_D^{23}$ +41.33° (c = 0.38, $CHCl_3$); IR (film) 2983, 2896, 1422, 1369, 1214, 1155, 1058, 968, 861 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (ddd, *J* = 7.3, 7.3, 15.0 Hz, 1H), 5.57 (dddd, *J* = 1.2, 1.2, 7.6, 15.2 Hz, 1H), 4.47 (ddd, *J* = 7.4, 7.4, 7.4 Hz, 1H), 4.07 (m, 2H), 3.58 (dd, *J* = 7.9, 7.9 Hz, 1H), 2.85 (m, 4H), 2.51 (m, 2H), 2.11 (m, 1H), 1.85 (ddddd, *J* = 3.2, 3.2, 12.9, 12.9, 12.9 Hz, 1H), 1.42 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.9, 130.0. 109.2, 78.6, 69.3, 46.9, 38.1, 30.4, 30.3, 26.7, 25.8, 25.7; high resolution mass spectrum (CI+) *m/z* 260.0903 [(M^+); calculated for: $C_{12}H_{20}O_2S_2$ 260.0905].



(+)-**11**

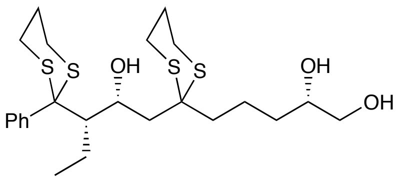
Dithiane (+)-11: Dithiane (+)-**24** (1.19 g, 4.57 mmol) was dissolved in anhydrous CH_2Cl_2 (25 mL) and the Wilkinson catalyst (0.211 g, 0.228 mmol) was added. A large balloon filled with H_2 (g) was bubbled through the reaction mixture prior to stirring under an atmosphere of hydrogen for 30 h. The reaction was judged to be complete when the TLC shows complete conversion from a spot that stains blue/purple in anisaldehyde stain to a spot that stains bright yellow. The reaction mixture was filtered through a short plug of silica and Celite and concentrated to afford a brown oil. The desired saturated dithiane was further purified using flash chromatography (9:1 hexanes:EtOAc) to afford the product as a yellow oil in 84% yield (1.01 g, 3.85 mmol): $[\alpha]_D^{23}$ +15.3° (c = 1.74, $CHCl_3$); IR (film) 2983, 2935, 1455, 1422, 1368, 1214, 1155, 1058, 909, 861 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.06 (m, 1H), 4.03 (m, 2H), 3.49 (dd, *J* = 7.2 Hz, 1H), 2.84 (m, 4H), 2.10 (ddddd, *J* = 2.4, 2.4, 4.8, 7.3, 7.3, Hz, 1H), 1.84 (ddddd, *J* = 3.8, 3.8, 11.3, 11.3, 11.3 Hz, 1H), 1.76 (m, 2H), 1.63 (m, 2H), 1.52 (m, 2H), 1.39 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.7, 75.7, 69.3, 47.3, 35.3, 33.0, 30.4 (2C), 26.9, 26.0, 25.7, 22.9; high resolution mass spectrum (CI+) *m/z* 262.1052 [(M^+); calculated for: $C_{12}H_{22}O_2S_2$ 262.1061].



(-)-**25**

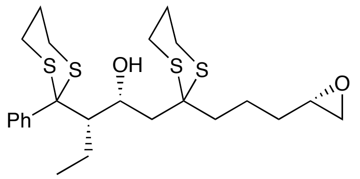
Alcohol (-)-25: Dithiane (+)-**11** (557 mg, 2.12 mmol) and epoxide (+)-**20** (295 mg, 1.05 mmol) were both azeotroped three times with benzene and dried under high vacuum for 45 min. Dithiane (+)-**11** was dissolved in dry THF (5 mL) and cooled to -78 °C in a dry ice/acetone bath.

Hexamethylphosphoramide (0.73 mL, 4.20 mmol) was added followed by *n*-BuLi (2.78 M, 0.81 mL, 2.17 mmol). The reaction mixture stirred at -78 °C for 45 min at which point (+)-**20** in dry THF (6 mL) was added via cannula. The dry ice bath was removed and the reaction warmed to room temperature and stirred for 3 h. The reaction was quenched with saturated NH_4Cl (3 mL) and diluted with Et_2O (20 mL). The layers were separated and the organic layer was washed with distilled H_2O (6 x 3 mL) and brine, dried over $MgSO_4$ and concentrated to give an orange oil. The desired adduct (-)-**25** was isolated in 68% yield (392 mg, 0.722 mmol) following column chromatography (9:1 to 3:1 hexanes:EtOAc): $[\alpha]_D^{23}$ -14.54° (c = 0.055, $CHCl_3$); IR (film) 3463, 2931, 2869, 1491, 1445, 1368, 1217, 1156, 1054, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.31 (m, 2H), 7.22 (m, 1H), 4.04 (m, 2H), 3.50 (dd, *J* = 7.2, 7.2 Hz, 1H), 3.37 (dd, *J* = 6.0, 11.6 Hz, 1H), 3.24 (m, 3H), 2.60 (ddd, *J* =4.0, 4.0, 7.5 Hz, 2H), 2.52-2.33 (m, 4H), 2.08 (m, 1H), 1.97 (m, 1H), 1.91 (m, 1H), 1.80 (m, 2H), 1.66 (m, 5H), 1.50 (m, 3H), 1.40 (s, 3H), 1.34 (s, 3H), 1.27 (ddd, *J* = 5.9, 5.9, 7.5 Hz, 1H), 1.13 (dd, *J* = 7.4, 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 130.1 (2C), 128.4 (2C), 126.9, 108.7, 75.8, 69.4, 63.3, 62.4, 42.8, 39.5, 34.3, 33.4, 31.9, 30.9, 30.7, 28.5, 27.3, 27.0 (2C), 25.7, 25.0, 22.5, 20.7, 14.2; high resolution mass spectrum (ES+) *m/z* 565.1904 [(M+Na^+); calculated for: $C_{27}H_{42}O_3S_4$+Na 565.1915].



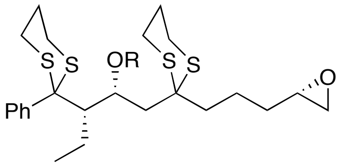
(+)-**26**

Triol (+)-26: Acetonide (-)-**25** (321 mg, 0.592 mmol) was dissolved in MeOH (10 mL), pyridinium *p*-toluenesulfonate (181 mg, 0.720 mmol) was added and the reaction stirred at room temperature overnight. The reaction was quenched slowly with Et_3N (1 mL), the solvent was removed under reduced pressure and triol (+)-**26** was isolated in 76% yield (225 mg, 0.447 mmol) following column chromatography (99:1 CH_2Cl_2:MeOH): $[\alpha]_D^{23}$ +8.72° (c = 0.94, $CHCl_3$); IR (film) 3374, 2916, 1861, 1444, 1105, 1030, 754, 703 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.31 (m, 2H), 7.22 (m, 1H), 3.73 (m, 1H), 3.46 (dd, *J* = 7.4, 11.1 Hz, 1H), 3.40 (dd, *J* = 5.9, 11.6 Hz, 1H), 3.24 (m, 3H), 2.60 (m, 2H), 2.53-2.36 (m, 4H), 2.09 (m, 1H), 1.97 (dd, *J* = 1.9, 6.4 Hz, 1H), 1.96 (d, *J* = 8.3 Hz, 1H), 0.89 (m, 1H), 1.79 (m, 2H), 1.69 (m, 5H), 1.46 (m, 2H), 1.30 (m, 2H), 1.13 (dd, *J* = 7.4, 7.4 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 142.1, 130.8 (2C), 128.6 (2C), 127.0, 72.1, 66.9, 63.3, 63.2, 43.5, 39.9, 35.4, 33.2, 32.3, 31.4, 31.2, 28.9, 27.5 (2C), 25.3, 23.0, 21.0, 14.4; high resolution mass spectrum (ES+) *m/z* 525.1620 [(M+Na^{+}); calculated for: $C_{24}H_{38}O_3S_4$+Na 525.1602].



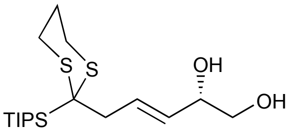
(+)-**S5**

Epoxide (+)-S5: Triol (+)-**26** (13 mg, 0.026 mmol) was azeotroped three times with benzene and dried under high vacuum for 3 h before being dissolved in anhydrous THF (0.40 mL). Sodium hydride (95%) (3.3 mg, 0.13 mmol) was placed in a round bottom flask, dry THF (0.25 mL) was added and the flask was placed in an ice bath. Triol (+)-**26** was added to the NaH suspension via cannula and the reaction stirred for 30 min at 0 °C before being cooled to -78 °C. Trisylimidazole (8.5 mg, 0.028 mmol) was dissolved in dry THF (0.20 mL) and added to the reaction slurry via cannula. The reaction warmed to 0 °C over 2 h and was quenched with saturated NH_4Cl (0.30 mL). The reaction was diluted with Et_2O (5 mL) and following separation the aqueous layer was extracted with Et_2O (2 x 3 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Following purification by column chromatography (4:1 hexanes:EtOAc) epoxide (+)-**S5** was isolated in 38% yield (6 mg, 0.012 mmol): $[\alpha]_{\mathrm{D}}^{23}$ +4.36° (c = 1.01, C_6H_6); IR (film) 3435, 2921, 1457, 1257, 1027, 906, 841 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.30 (m, 2H), 7.21 (m, 1H), 3.36 (dd, *J* = 6.1, 11.6 Hz, 1H), 3.23 (m, 3H), 2.91 (m, 1H), 2.74 (dd, *J* = 4.1, 4.9 Hz, 1H), 2.59 (ddd, *J* = 3.2, 3.2, 7.3 Hz, 2H), 2.45 (m, 4H), 2.36 (ddd, *J* = 7.1, 7.1, 12.5 Hz, 1H), 2.08 (m, 1H), 1.99 (dd, *J* = 2.9, 6.2 Hz, 1H), 1.97 (m, 1H), 1.89 (m, 1H), 1.81 (m, 3H), 1.67 (m, 3H), 1.59 (m, 2H), 1.33 (m, 1H), 1.27 (m, 1H), 1.13 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.6, 130.1 (2C), 128.4 (2C), 126.9, 63.3, 62.3, 52.0, 47.0, 42.6, 39.5, 34.3, 32.3, 31.9, 30.9, 30.7, 28.4, 27.3 (2C), 25.0, 22.5, 20.8, 14.2; high resolution mass spectrum (ES+) *m/z* 507.1490 [(M+Na$^+$); calculated for: $C_{24}H_{36}O_2S_4$+Na 507.1496].



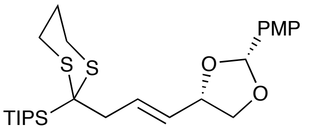
(-)-**7** R = TBS

Linchpin Epoxide (-)-7: Epoxide (+)-**S5** (22 mg, 0.046 mmol) was dissolved in anhydrous CH$_2$Cl$_2$ (0.50 mL) and 2,6-lutidine (30 μL, 0.28 mmol) was added. The flask was placed in a 0 °C ice bath prior to addition of TBSOTf (30 μL, 0.14 mmol). After 2 h the reaction was quenched with saturated NH$_4$Cl (0.30 mL). The mixture was diluted with CH$_2$Cl$_2$ (3 mL) and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 2 mL). The combined organic layers were washed with brine, dried over MgSO$_4$ and concentrated. Column chromatography afforded epoxide (-)-**7** as a colorless oil in 67% yield (18.5 mg, 0.031 mmol): $[\alpha]_D^{23}$ -0.73° (c = 0.15, CHCl$_3$); IR (film) 2953, 2927, 2855, 2360, 1461, 1253, 1076, 908, 838, 775, 702 cm^{-1}; ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 7.50 (m, 2H), 7.18 (m, 2H), 7.06 (m, 1H), 3.42 (dd, *J* = 5.7, 10.9 Hz, 1H), 3.18 (dd, *J* = 8.2, 10.9 Hz, 1H), 3.05 (app. ddd, *J* = 2.6, 12.2, 16.8 Hz, 1H), 2.59-2.46 (m, 5H), 2.29 (dd, *J* = 3.9, 5.3 Hz, 1H), 2.17-2.12 (m, 2H), 2.09-2.03 (m, 3H), 1.98-1.89 (m, 3H), 1.81-1.70 (m, 3H), 1.56-1.46 (m, 3H), 1.42 (ddd, *J* = 6.0, 6.0, 8.2 Hz, 1H), 1.31-1.23 (m, 2H), 1.20-1.17 (m, 1H), 1.16 (dd, *J* = 7.6, 7.6 Hz, 3H), 0.97 (s, 9H), -0.045 (s, 3H), -0.055 (s, 3H); ^{13}C NMR (125 Hz, C$_6$D$_6$) δ 142.1, 131.0 (2C), 128.3 (2C), 127.0, 63.8, 63.2, 51.5, 46.2, 43.1, 40.0, 35.4, 32.5, 32.3, 31.3, 31.2, 28.9, 27.5 (2C), 26.1 (3C), 25.2, 23.1, 21.4, 18.3, 14.4, -5.33 (2C); high resolution mass spectrum (ES+) *m/z* 621.2371 [(M+Na$^+$); calculated for: $C_{30}H_{50}O_2S_4Si$+Na 621.2361].

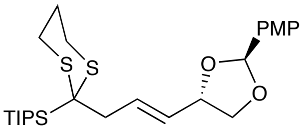


(+)-**27**

Diol (+)-27: The mixture of alcohols (+)-**22** and (+)-**23** (3.01 g, 6.13 mmol) was dissolved in methanolic HCl (2% HCl, 50 mL) and stirred for 2 h. Solid $NaHCO_3$ was added until the pH was between 7 and 8 and then MeOH was removed under reduced pressure. The resulting slurry was dissolved in Et_2O and filtered through Celite. Flash chromatography (1:1 hexanes:EtOAc) afforded diol (+)-**27** in 99% yield (2.31 g, 6.13 mmol): $[\alpha]_D^{23}$ +4.78° (c = 0.33, $CHCl_3$); IR (film) 3371, 2943, 2870, 1462, 1068, 1014, 879 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.14 (ddd, *J* = 7.0, 7.0, 14.4 Hz, 1H), 5.64 (dd, *J* = 6.3, 15.5 Hz, 1H), 4.27 (m, 1H), 3.68 (m, 1H), 3.54 (m, 1H), 3.28 (m, 2H), 3.07 (m, 2H), 2.41 (m, 2H), 2.05 (m, 2H), 1.99-1.91 (m, 2H), 1.47 (septet, *J* = 7.5 Hz, 3H), 1.23 (d, *J* = 7.5 Hz, 18H); ^{13}C NMR (125 MHZ, $CDCl_3$) δ 132.1, 130.1, 72.9, 66.3, 42.6, 40.1, 24.5, 24.4 (2C), 19.9 (6C), 12.1 (3C); high resolution mass spectrum (ES+) *m/z* 399.1821 [(M+Na$^+$); calculated for: $C_{18}H_{36}O_2S_2Si$+Na 399.1824].



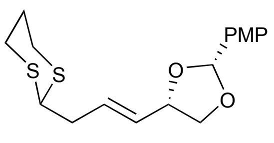
(-)-**28**



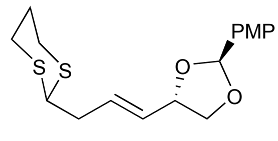
(+)-**29**

PMP Acetals (-)-28 and (+)-29: Diol (+)-**27** (32.30 g, 85.75 mmol) was dissolved in dry CH_2Cl_2 (350 mL) and PPTS (4.31 g, 17.15 mmol) and 4-methoxybenzaldehyde dimethyl acetal (55.7 mL, 342.9 mmol) were added. The reaction stirred at room temperature overnight. The following morning Et_3N (50 mL) was added and the solution was washed once with distilled water, once with brine, dried over $MgSO_4$

and concentrated to afford the desired acetals as a 2:1 mixture of diastereomers. In practice this material was carried forward without further purification however, a small amount was purified using preparative TLC for characterization purposes: (-)-**28** (major) $[\alpha]_D^{23}$ -38.97° (c = 0.91, C_6H_6); IR (film) 2944, 2867, 1615, 1516, 1462, 1391, 1303, 1249, 1171, 1076, 1034, 978, 883, 828 cm^{-1}; ^1H NMR (500 MHz, C_6H_6) 7.58 (m, 2H), 6.81 (m, 2H), 6.25 (ddd, *J* = 6.9, 6.9 14.8 Hz, 1H), 5.87 (s, 1H), 5.69 (dddd, *J* = 2.2, 2.2, 1.7, 15.6 Hz, 1H), 4.46 (ddd, *J* = 6.9, 6.9, 6.9 Hz, 1H), 3.88 (dd, *J* = 7.4, 7.4 Hz, 1H), 3.70 (dd, *J* = 6.8, 7.4 Hz, 1H), 3.27 (s, 3H), 3.15 (d, *J* = 7.1 Hz, 2H), 2.74 (dddd, *J* = 2.6, 13.1, 14.6, 15.6 Hz, 2H), 1.97 (m, 2H), 1.68 (ddddd, *J* = 3.2, 3.2, 6.3, 13.1, 13.1 Hz, 1H), 1.61 (septet, *J* = 7.4 Hz, 3H), 1.40 (s, 1H). 1.34 (d, *J* = 7.4 Hz, 18H); ^{13}C NMR (125 MHz, C_6H_6) 160.6, 133.1, 130.8, 129.5, 128.2 (2C), 113.7 (2C), 104.4, 77.9, 69.8, 54.5, 43.2, 40.0, 24.4, 24.3, 24.2, 20.1 (6C), 12.3 (3C); (+)-**29** (minor) $[\alpha]_D^{23}$ +13.24° (c = 0.36, C_6H_6); IR (film) 2943, 2867, 1615, 1515, 1463, 1389, 1303, 1249, 1172, 1084, 1034, 975, 883, 828 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) 7.55 (m, 2H), 6.81 (m, 2H), 6.24 (dddd, *J* = 1.1, 7.1, 7.1, 15.3 Hz, 1H), 6.09 (s, 1H), 5.63 (dddd, *J* = 1.6, 1.6, 7.1, 15.7 Hz, 1H), 4.57 (ddd, *J* = 7.1, 7.1, 7.1 Hz, 1), 4.07 (dd, *J* = 6.4, 8.0 Hz, 1H), 3.57 (dd, *J* = 7.5, 7.5, Hz, 1H), 3.30 (s, 3H), 3.17 (m, 2H), 2.75 (m, 2H), 1.97 (m, 2H), 1.67 (ddddd, *J* = 3.2, 3.2, 6.3, 13.1, 13.1 Hz, 1H), 1.59 (septet, *J* = 7.3 Hz, 3H), 1.40 (s, 1H), 1.36 (dd, *J* = 1.2, 7.5 Hz, 18H); ^{13}C NMR (125 MHz, C_6H_6) 160.5, 133.0, 131.3, 129.7, 128.2 (2C), 114.0 (2C), 104.2, 77.2, 70.5, 54.7, 43.5, 40.07, 24.7, 24.6, 24.5, 20.4 (6C), 12.5 (3C); high resolution mass spectrum (ES+) *m/z* 517.2244[(M+Na$^+$); calculated for: $C_{26}H_{42}O_3S_2Si$+Na 517.2242].

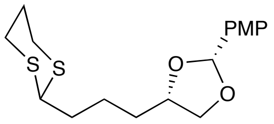


(-)-**S6**

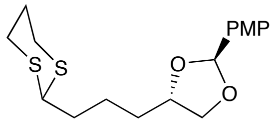


(+)-**S7**

Dithianes (-)-S6 and (+)-S7: The unpurified mixture of acetals from the previous step was dissolved in THF (200 mL) and a solution of TBAF (35.87 g in 100 mL THF) was added. The flask containing the TBAF was rinsed with additional THF (50 mL) which was added to the reaction. The reaction stirred at room temperature for 1 h after which saturated NH_4Cl (100 mL) and Et_2O (600 mL) were added. The layers were separated and the aqueous layer was extracted once with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to give an orange oil. Following column chromatography (98:2 to 4:1 hexanes:EtOAc) the acetals were isolated as a 2:1 mixture of diastereomers in 80% yield over the two steps. A small amount of the mixture was further purified using preparative TLC for characterization purposes: (-)-**S6** (major) $[\alpha]_D^{23}$ -36.81° (c = 0.24, C_6H_6); IR (film) 2895, 1613, 1516, 1428, 1303, 1248, 1172, 1075, 1031, 971, 830 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) 7.56 (m, 2H), 6.81 (m, 2H), 5.81 (s, 1H), 5.81 (dddd, *J* = 0.7, 7.1, 7.1, 15.3 Hz, 1H), 5.52 (dddd, *J* = 1.3, 1.3, 7.2, 15.3 Hz, 1H), 4.33 (ddd, *J* = 6.9, 6.9 Hz, 1H), 3.78 (dd, *J* = 6.9, 6.9 Hz, 1H), 3.77 (dd, *J* = 7.7, 7.7 Hz, 1H), 3.60 (dd, *J* = 6.7, 7.6 Hz, 1H), 3.26 (s, 3H), 2.43 (m, 2H), 2.31 (m, 4H), 1.54 (m, 1H), 1.40 (m, 1H); ^{13}C NMR (125 MHz, C_6D_6) 160.8, 131.3, 131.1, 129.7, 128.6 (2C), 113.9 (2C), 104.6, 77.8, 70.1, 54.7, 47.2, 38.5, 30.22, 30.18, 25.8; high resolution mass spectrum (ES+) *m/z* 339.1078 [(M+H$^+$); calculated for: $C_{17}H_{23}O_3S_2$ 339.1089]. (+)-**S7** (minor) $[\alpha]_D^{23}$ +34.23° (c = 0.13, C_6H_6); IR (film) 2896, 1652, 1614, 1516, 1422, 1392, 1302, 1247, 1170, 1080, 1031, 967, 828 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) 7.51 (m, 2H), 6.80 (m, 2H), 6.02 (s, 1H), 5.78 (dddd, *J* = 1.1, 7.0, 7.0, 15.2 Hz, 1H), 5.47 (dddd, *J* = 1.3, 1.3, 7.0, 15.3 Hz, 1H), 4.44 (ddd, *J* = 7.0, 7.0, 7.0 Hz, 1H), 3.96 (dd, *J* = 6.4, 8.1 Hz, 1H), 3.81 (dd, *J* = 6.9, 6.9 Hz, 1H), 3.47 (dd, *J* = 7.5, 8.2 Hz, 1H), 3.27 (s, 3H), 2.46 (m, 2H), 2.33 (m, 4H), 1.54 (m, 1H), 1.41 (m, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.4, 131.2, 130.9, 129.0, 128.0 (2C), 113.7 (2C), 103.8, 76.5, 70.3, 54.5, 47.0, 38.3, 30.00, 29.97, 25.6; high resolution mass spectrum (ES+) *m/z* 339.1082 [(M+H$^+$); calculated for: $C_{17}H_{23}O_3S_2$ 339.1089].

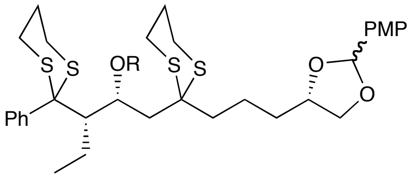


(-)-**30**



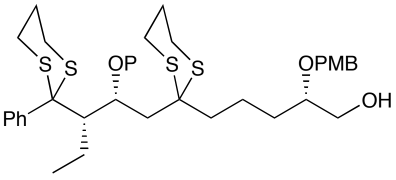
(+)-**S8**

Saturated Acetals (-)-30 and (+)-S8: A mixture of acetals (-)-**S6** and (+)-**S7** (4.97 g, 14.68 mmol) was placed in a flask with $Rh(PPh_3)_3Cl$ (679 mg, 0.734 mmol) and CH_2Cl_2 (80 mL) was added. A balloon filled with H_2 was bubbled through the reaction mixture and was refilled. The reaction stirred under an atmosphere of hydrogen for 36 h. The balloon was removed and silica gel was added to the flask. The solvent was evaporated and the silica gel was loaded onto a column. The product was eluted using 30% EtOAc in hexanes to give the saturated acetals in 91% yield (4.55 g, 13.34 mmol). The diastereomers were isolated for characterization purposes, the high resolution mass spectrum was obtained using the 2:1 mixture of diastereomers: (-)-**30** (major) $[\alpha]_D^{23}$ -25.44° (c = 0.845, C_6H_6); IR (film) 2936, 2901, 1614, 1515, 1434, 1379, 1304, 1248, 1172, 1077, 1032, 830 cm $^{-1}$; ^1H NMR (C_6D_6, 500 MHz) δ 7.53 (m, 2H), 6.80 (m, 2H), 5.77 (s, 1H), 3.83 (dd, J = 6.8, 6.8 Hz, 1H), 3.81 (m, 1H), 3.70 (dd, J = 6.9, 7.4 Hz, 1H), 3.42 (dd, J = 6.7, 7.3 Hz, 1H), 3.26 (s, 3H), 2.36 (m, 4H), 1.75 (m, 2H), 1.60 (m, 1H), 1.64-1.42 (m, 4H), 1.25 (m, 1H); ^{13}C NMR (C_6D_6, 125 MHz) δ 160.8, 131.2, 128.5 (2C), 113.9 (2C), 104.3, 76.9, 70.0, 54.7, 47.7, 35.7, 33.3, 30.2 (2C), 26.2, 23.4: (+)-**S8** (minor) $[\alpha]_D^{23}$ +35.73° (c = 0.69, C_6H_6); IR (film) 2936, 2901, 1614, 1518, 1461, 1434, 1381, 1302, 1248, 1170, 1078, 1034, 828 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 7.50 (m, 2H), 6.80 (m, 2H), 5.95 (s, 1H), 3.89 (m, 3H), 3.28 (dd, J = 3.6, 4.4 Hz, 1H), 3.27 (s, 3H), 2.38 (m, 4H), 1.77 (m, 2H), 1.71-1.56 (m, 2H), 1.48 (m, 3H), 1.13 (m, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.4, 131.6, 128.3 (2C), 113.6 (2C), 103.2, 75.8, 70.3, 54.5, 47.5, 35.5, 32.9, 30.1 (2C), 25.9, 23.2; high resolution mass spectrum (ES+) m/z 363.1069 [(M+Na$^+$); calculated for: $C_{17}H_{24}O_3S_2$+Na 363.1065].



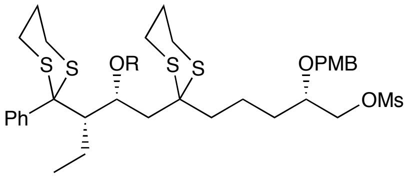
R = TBS, **S9**

Bis-dithiane S9: Alcohol **31** (216 mg, 0.348 mmol) was dissolved in dry CH_2Cl_2 (2 mL) and cooled in an ice bath. 2,6-Lutidine (80 μL, 0.70 mmol) was added followed by TBSOTf (95 μL, 0.42 mmol). The reaction stirred at 0 °C for 40 min at which time it was quenched with saturated NH_4Cl (1 mL) and diluted with CH_2Cl_2 (5 mL). The layers were separated and the aqueous layer was extracted once with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Flash chromatography (9:1 hexanes:EtOAc) afforded the desired TBS ether, **S9** as a 2:1 mixture of diastereomers at the acetal carbon, in 90% yield (231 mg, 0.314 mmol): IR (film) 2952, 1617, 1519, 1464, 1249, 1077, 836, 776, 701 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.54 (m, 1H), 7.50 (m, 2H), 7.19 (m, 6H), 7.07 (m, 1.5H), 6.81 (m, 3H), 5.97 (s, 0.5H), 5.78 (s, 1H), 3.95 (m, 0.5H), 3.91 (dd, *J* = 6.2, 6.2Hz, .5H), 3.85 (m, 1H), 3.73 (dd, *J* = 7.4, 7.4 Hz, 1H), 3.44 (m, 2.5H), 3.31 (dd, *J* = 7.5, 7.5 Hz, .5H), 3.29 (s, 1.5H), 3.28 (s, 3H), 3.27 (m, 0.5H), 3.19 (dd, *J* = 8.2, 10.9 Hz, 1.5H), 3.05 (m, 3H), 2.51 (m, 6H), 2.14 (m, 3H), 2.06 (m, 4.5H), 1.93 (m, 3H), 1.76 (m, 4.5H), 1.57-1.45 (m, 4.5H), 1.42 (m, 1.5H), 1.31 (m, 1H), 1.19 (m, 0.5H), 1.05 (dd, *J* = 7.4, 7.4 Hz, 4.5H), .0.97 (s, 13.5H), -0.045 (s, 4.5H), -0.055 (s, 4.5H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.7, 160.6, 142.1, 131.9, 131.2, 131.0, 128.5, 128.34, 128.28, 127.0, 113.9, 104.3, 103.5, 77.0, 76.1, 70.6, 70.0, 63.8, 63.2, 54.7, 43.4, 43.3, 40.0, 35.4, 33.7, 33.5, 32.3, 31.0, 31.2, 28.9, 27.5, 26.1, 25.2, 23.1, 21.39, 21.37, 18.3, 14.3, -5.3; high resolution mass spectrum (ES+) *m/z* 757.2920 [(M+Na$^+$); calculated for: $C_{38}H_{58}O_4S_4Si$+Na 757.2885].



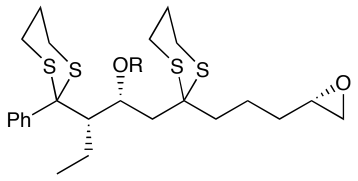
R = TBS (-)-**32**

PMB Ether (-)-32: Acetal **S9** (193 mg, 0.262 mmol) was dissolved in dry CH_2Cl_2 (2.8 mL) and cooled to -78 °C in a dry ice/acetone bath. Diisobutylaluminum hydride (1M, 1.05 mL, 1.05 mmol) was added dropwise and the reaction stirred at -78 °C for 1 h and then warmed to -20 °C over 1 h. The reaction stirred an additional 30 min at 0 °C. An excess of MeOH (0.50 mL) was added followed by Et_2O (10 mL) and a saturated solution of Rochelle's salts (5 mL). The reaction stirred at room temperature until both layers were clear. Flash chromatography afforded desired primary alcohol (-)-**32** in 70% yield (135 mg, 0.183 mmol) along with the secondary alcohol (42 mg, 0.057 mmol, 21%): $[\alpha]_D^{23}$ -1.23° (c = 0.325, C_6H_6); IR (film) 3433, 2927, 2857, 1611, 1514, 1462, 1428, 1076, 837, 776, 701 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.51 (m, 2H), 7.24-7.17 (m, 4H), 7.06 (m, 1H), 6.82 (m, 2H), 4.39 (d, *J* = 10.8 Hz, 1H), 4.31 (d, J = 11.3 Hz, 1H), 3.52 (ddd, *J* = 3.9, 6.4, 11.5 Hz, 1H), 3.42 (dd, *J* = 5.8, 10.9 Hz, 1H), 3.43-3.38 (m, 1H), 3.32 (s, 3H), 3.27 (m, 1H), 3.19 (dd, *J* = 8.2, 10.8 Hz, 1H), 3.17 (m, 2H), 2.60-2.46 (m, 4H), 2.17-2.13 (m, 2H), 2.10-2.06 (m, 2H), 2.00-1.92 (m, 3H), 1.81-1.73 (m, 3H), 1.57-1.48 (m, 2H), 1.46-1.34 (m, 3H), 1.19-1.15 (m, 1H), 1.15 (dd, *J*= 7.4, 7.4 Hz, 3H), 0.97 (s, 9H), -0.044 (s, 3H), -0.53 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 159.7, 142.1, 131.4, 131.0 (2C), 129.5 (2C), 128.3 (2C), 127.0, 114.1 (2C), 79.5, 71.4, 64.3, 68.8, 63.3, 54.8, 43.7, 40.0, 35.4, 32.3, 31.35, 31.32, 31.2 29.0, 27.5 (2C), 26.1 (3C), 25.2, 23.1, 20.8, 18.3, 14.4, -5.3 (2C); high resolution mass spectrum (ES+) *m/z* 759.3058 [(M+Na$^+$); calculated for: $C_{38}H_{60}O_4S_4Si$+Na 759.3041].



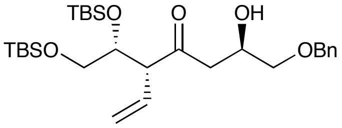
R = TBS (-)-**S10**

Mesylate (-)-S10: Alcohol (-)-**32** (134 mg, 0.182 mmol) was dissolved in dry CH_2Cl_2 (1.8 mL) and DMAP (4.3 mg, 0.035 mmol) and Et_3N (70 μL, 0.55 mmol) were added. The solution was cooled to 0 °C and methanesulfonyl chloride (20 μL, 0.24 mmol) was added. The reaction stirred for 30 min and then the solution was loaded onto a silica gel column. Elution with 4:1 hexanes:EtOAc afforded mesylate (-)-**S10** (142 mg, 0.174 mmol) in 95% yield: $[\alpha]_D^{23}$ -4.11° (c = .805 C_6H_6); IR (film) 2953, 2856, 1614, 1514, 1460, 1358, 1247, 1178, 1077, 958, 837, 774, 703 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.50 (m, 2H), 7.25 (m, 2H), 7.19 (m, 2H) 7.06 (m, 1H), 6.81 (m, 2H), 4.37 (d, *J* = 11.1 Hz, 1H), 4.27 (d, *J* = 11.1 Hz, 1H), 4.04 (dd, *J* = 3.6, 11.1 Hz, 1H), 3.87 (dd, *J* = 5.3, 11.0 Hz, 1H), 3.42 (dd, *J* = 5.7, 10.9 Hz, 1H), 3.32 (s, 3H), 3.26 (m, 1H), 3.18 (dd, *J* = 8.2, 10.9 Hz, 1H), 3.06 (m, 1H), 2.60-2.45 (m, 4H), 2.26 (s, 3H), 2.15 (m, 2H), 2.02 (m, 1H), 2.01 (d, *J* = 8.2 Hz, 1H), 1.98-1.91 (m, 2H), 1.89-1.81 (m, 1H), 1.80-1.72 (m, 4H), 1.59-1.36 (m, 5H), 1.24 (m, 1H), 1.16 (ddd, *J* = 6.7, 6.7, 13.9 Hz, 1H), 1.14 (dd, *J* = 7.4, 7.4 Hz, 3H), 0.94 (s, 9H), -0.047 (s, 3H), -0.56 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 159.8, 142.1, 131.0 (2C), 130.7, 129.7 (2C), 128.5 (2C), 127.0, 114.1 (2C), 76.4, 71.9, 70.7, 63.8, 63.2, 54.8, 43.4, 40.0, 37.0, 35.4, 32.3, 31.4, 31.3, 31.2, 30.2, 28.9, 27.5, 26.1 (3C), 25.2, 23.1, 20.6, 18.3, 14.4, -5.3 (2C); high resolution mass spectrum (ES+) *m/z* 837.3837 [(M+Na^+); calculated for: $C_{39}H_{63}O_6S_5Si$+Na 837.3817].



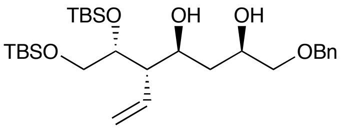
R = TBS (-)-**7**

Linchpin Epoxide (-)-7: Mesylate (-)-**S10** (522 mg, 0.677 mmol) was dissolved in CH_2Cl_2 (7.2 mL) and pH 8 phosphate buffer (1.8 mL) and cooled to 0 °C in an ice bath. Following the addition of DDQ (461 mg, 2.03 mmol) the reaction stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2 and washed twice with saturated $NaHCO_3$ and once with brine. The organic layer was dried, concentrated and passed through a quick plug of silica gel (2:1 hexanes:EtOAc). The resulting alcohol was taken on without further purification. The alcohol (464 mg, 0.677 mmol) was dissolved in MeOH (7 mL) and K_2CO_3 (467 mg, 3.38 mmol) was added. After 30 min the reaction was diluted with Et_2O and filtered through Celite. The resulting epoxide was purified on a silica gel column that had been neutralized with 99:1 hexanes:EtOAc and 1% Et_3N. The desired compound was eluted using 9:1 hexanes:EtOAc (301 mg, 0.502 mmol, 74% over 2 steps. The analytical data for this compound was identical to the data described previously for (-)-**7** on page S13 of this supporting information.



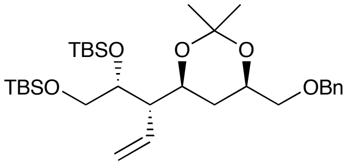
(+)-**S11**

Ketone (+)-S11: Dithiane (-)-**34** (9.43 g, 15.38 mmol) was dissolved in a THF : H_2O solution (4:1, 100 mL) and cooled to 0 °C in an ice bath. 2,6-Lutidine (8.0 mL, 69.2 mmol) was added followed by addition of $Hg(ClO_4)_2$ (13.52 g, 33.84 mmol) in three portions. A yellow solid formed almost immediately. After 10 min the reaction mixture was diluted with EtOAc, filtered through Celite, rinsing with EtOAc bringing the total volume of EtOAc used to 250 mL. The filtrate was added to a separatory funnel containing saturated NH_4Cl (100 mL). The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered through Celite and concentrated under reduced pressure to provide a yellow oil. The desired ketone was purified using silica gel chromatography (9:1 hexanes:EtOAc) affording 5.71 g of ketone (+)-**S11** (71%, 10.91 mmol): $[\alpha]_D^{23}$ +67.4° (c = 0.33, $CHCl_3$); IR (film) 3454, 2929, 1709, 1470, 1362, 1254, 1107, 835, 777 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.35-7.26 (m, 5H), 5.92 (ddd, *J* = 10.0, 10.0, 17.3 Hz, 1H), 5.29 (dd, *J* = 1.8, 10.2 Hz, 1H), 5.17 (dd, *J* = 1.3, 17.0 Hz, 1H), 4.55 (m, 2H), 4.25 (m, 1H), 4.16 (ddd, *J* = 4.7, 4.7, 7.4 Hz, 1H), 3.51-3.28 (m, 4H), 3.28 (dd, *J* = 4.2, 9.7 Hz, 1H), 2.99 (s, 1H), 2.77 (dd, *J* = 8.2, 18.0 Hz, 1H), 2.67 (dd, *J* = 4.0, 18.0 Hz, 1H), 0.88 (s, 9H), 0.83 (s, 9H), 0.049 (s, 3H), 0.029 (s, 6H), 0.019 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 210.7, 138.3, 132.6, 128.3 (2C), 127.6 (3C), 120.4, 73.3, 73.2, 72.9, 66.6, 64.8, 60.8, 45.8, 25.9 (3C), 25.7 (3C), 18.3, 18.0, -4.4, -4.9 -5.48, -5.51; high resolution mass spectrum(ES+) *m/z* 545.3086 [(M+Na$^+$) calculated for: $C_{28}H_{50}O_5Si_2$+Na 545.3095].



(+)-**35**

Diol (+)-35: Ketone (+)-**S11** (5.58 g, 10.67 mmol) was dissolved in dry THF (50 mL) and anhydrous MeOH (24 mL, 50 equiv.) and cooled to -78 °C in a dry ice/acetone bath. To this solution was added a 1 M solution of diethylmethoxy borane in THF (11.74 mL, 11.74 mmol) dropwise. After 30 min. $NaBH_4$ (807 mg, 21.3 mmol) was added in one portion. The reaction continued to stir at -78 °C for 2.5 h at which time it was quenched with distilled water and warmed to room temperature. The reaction was diluted with Et_2O and water and the layers were separated. The aqueous layer was extracted once with Et_2O and then the combined organic layers were concentrated to a total volume of 100 mL. Methanol (15 mL) and pH 7 phosphate buffer (15 mL) were added and the solution was cooled to 0 °C in an ice bath. A solution of MeOH and 30% H_2O_2 (2:1, 30 mL) was added slowly and the solution stirred until TLC indicated complete oxidation of the boron intermediate. The solution was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted with Et_2O until the product was removed as determined by TLC. Solid Na_2SO_3 was added to quench any remaining peroxide. The mixture was poured through a plug of cotton to remove the solids and the filtrate was washed twice with a saturated solution of Na_2SO_3, once with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification using flash chromatography afforded the desired *syn* diol (+)-**35** in 85% yield (4.81 g, 9.16 mmol). The relative stereochemistry of the diol was verified using the Rychnovsky acetonide analysis[3] (see compound (+)-**36**): $[\alpha]_D^{23}$ +23.80° (c = 0.35, $CHCl_3$); IR (film) 3443, 2953, 2929, 2857, 1470, 1254, 1106, 836, 777, 668 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.36-7.27 (m, 5H), 5.62 (ddd, *J* = 10.1, 10.1, 17,3 Hz, 1H), 5.13 (dd, *J* = 2.1, 10.3, Hz, 1H), 5.08 (dd, *J* = 2.1, 17.2 Hz, 1H), 4.57 (s, 2H), 4.05 (m, 2H), 4.00 (d, *J* = 2.1 Hz, 1H), 3.96 (m, 1H), 3.54 (dd, *J* = 10.0, 20.9 Hz, 1H), 3.53 (dd, *J* = 10.0, 21.4 Hz, 1H), 3.46 (d, *J* = 1.6 Hz, 1H), 3.42 (dd, *J* = 9.5, 19.3 Hz, 1H), 3.41 (dd, *J* = 9.5, 21.7 Hz, 1H), 2.28 (ddd, *J* = 2.4, 9.5, 9.5 Hz, 1H), 1.74 (ddd, *J* = 21., 2.1, 14.4 Hz, 1H), 1.40 (ddd, *J* = 10.0, 10.0, 14.4 Hz, 1H), 0.89 (s, 18H), 0.12 (s, 3H), 0.087 (s, 3H), 0.037 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.1, 135.4, 128.3 (2C), 127.7 (2C), 127.6, 118.5, 74.3, 73.5, 73.3 71.7, 71.4, 64.9, 54.0, 38.4, 25.9 (3C), 25.8 (3C), 18.3, 18.0, -4.3, -5.1, -5.4, -5.5; high resolution mass spectrum (ES+) *m/z* 547.3235 [(M+Na$^+$) calculated for: $C_{28}H_{52}O_5Si_2$+Na 547.3251].



(+)-**36**

Acetonide (+)-36: Diol (+)-**35** (5.60 g, 10.68 mmol) was dissolved in DMF (43 mL) and PPTS (134 mg, 0.534 mmol) was added followed by the addition of 2,2-dimethoxypropane (13.1 mL, 106.8 mmol). After stirring overnight at room temperature the reaction was partitioned between EtOAc (200

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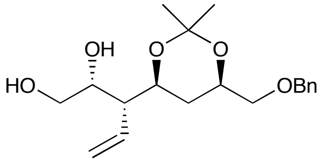
[3] Rychnovsky, S. D; Rogers, B. N. Richardson, T. F. *Acc. Chem. Res.* **1998**, *31*, 9.

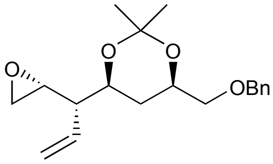
mL) and H_2O (50 mL). The organic layer was washed with distilled H_2O (3 x 50 mL), once with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography (95:5 hexanes:EtOAc) afforded (+)-**36** as a colorless oil in 78% yield (4.78 g, 8.46 mmol): $[\alpha]_D^{23}$ +9.06° (c = 1.22, $CHCl_3$); IR (film) 2954, 2929, 2857, 1472, 1379, 1255, 1104, 836, 776 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.27 (m, 5H), 5.63 (ddd, *J* = 10.2, 10.2, 17.3 Hz, 1H), 5.13 (dd, *J* = 2.4, 10.3 Hz, 1H), 5.06 (dd, *J* = 2.4, 17.3 Hz, 1H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 12.3 Hz, 1H), 4.12 (ddd, *J* = 1.0, 4.7, 6.2 Hz, 1H), 4.05 (m, 1H), 3.91 (ddd, *J* = 2.6, 9.5, 14.1 Hz, 1H), 3.47 (m, 2H), 3.37 (m, 2H), 2.23 (dd, *J* = 10.0, 10.0 Hz, 1H), 1.52 (m, 1H), 1.46 (s, 3H), 1.40 (s, 3H), 1.06 (app q, *J* = 11.8 Hz, 1H), 0.89 (s, 9H), 0.88 (s, 9H), 0.071 (s, 3H), 0.067 (s, 3H), 0.039 (s, 3H), 0.033 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz), δ 138.4, 133.9, 127.84 (2C), 127.79 (2C), 127.6, 119.0, 98.6, 73.9, 73.4, 70.0, 68.7, 66.4, 65.4, 53.5, 33.2, 30.2, 26.0 (3C), 25.9 (3C), 20.4, 18.3, 18.2, -3.5, -4.9, -5.2, -5,3; high resolution mass spectrum (ES+) *m/z* 587.3588 [(M+Na^+) calculated for: $C_{31}H_{56}O_5Si_2$+Na 587.3564].



(+)-**S12**

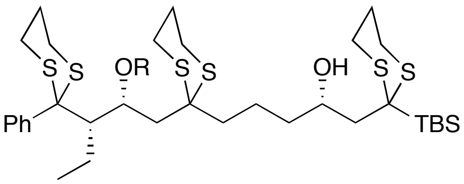
Diol (+)-S12: Acetonide (+)-**36** (3.89 g, 6.88 mmol) was dissolved in THF (80 mL) and a solution of TBAF in THF (1.0 M, 34.5 mL, 34.5 mmol) was added. After 2 h the reaction mixture was diluted with Et_2O (100 mL) and saturated NH_4Cl (6 mL) was added. The aqueous layer was extracted twice with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to afford an orange oil. Flash chromatography (1:1 hexanes:EtOAc) provided diol (+)-**S12** as a yellow oil in 96% yield (2.07 g, 6.25 mmol): $[\alpha]_D^{23}$ +20.9° (c = 0.56, $CHCl_3$); IR (film) 3421, 2991, 2910, 2360, 1454, 1381, 1262, 1202, 1173, 1107, 1003, 922, 848, 744, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.35-7.26 (m, 5H), 5.72 (ddd, *J* = 10.0, 10.0, 17.2 Hz, 1H), 5.20 (dd, *J* =

1.8, 10.3 Hz, 1H), 5.14 (dd, *J* = 1.7, 17.2 Hz, 1H), 4.59 (d, *J* = 12.5 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.06 (m, 2H), 3.97 (s, 1H), 3.60 (m, 2H), 3.50 (dd, *J* = 5.7, 10.0 Hz, 1H), 3.34 (dd, *J* = 4.8, 10.0 Hz, 1H), 2.21 (ddd, *J* = 2.8, 10.1, 10.1 Hz, 1H), 1.54 (m, 1H), 1.45 (s, 3H), 1.43 (s, 3H), 1.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.2, 134.2, 128.4 (2C), 127.8 (2C), 127.7, 119.3, 99.0, 73.50, 73,48, 71.8, 69.6, 68.7, 65.1, 52.6, 32.5, 30.1, 19.6; high resolution mass spectrum (ES+) *m/z* 359.1821 [(M+Na$^+$) calculated for: $C_{19}H_{28}O_5$+Na 359.1834].



(+)-**9**

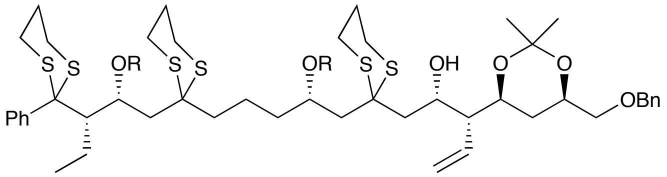
Epoxide (+)-9: Diol (+)-**S12** (1.30 g, 3.88 mmol) was dissolved in THF (20 mL) and added, via cannula, to a flask containing THF (10 mL) and NaH (300 mg, 11.87 mmol), pre-cooled to 0 °C. After 1 h, trisylimidazole (1.29 g, 3.88 mmol) in THF (20 mL) was added to the reaction. A thick white solid formed within 30 min. After 1 h the reaction was quenched with saturated NH_4Cl and diluted with Et_2O. The aqueous layer was extracted twice with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to afford a sticky, white oil. The oil was dissolved in Et_2O and adsorbed onto silica gel prior to isolation via flash chromatography (9:1 hexanes:EtOAc). The desired epoxide was obtained as a colorless oil in 93% yield (1.15 g, 3.61 mmol): $[\alpha]_D^{23}$ +22.72° (c = 0.79, $CHCl_3$); IR (film) 2992, 2865, 1454, 1380, 1263, 1201, 1175, 1106, 997, 923, 863, 739, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34 (m, 4H), 7.28 (m, 1H), 5.56 (ddd, *J* = 9.0, 10.5, 17.1 Hz, 1H), 5.20-5.24 (m, 2H), 4.60 (d, *J* = 12.5 Hz, 1H), 4.54 (d, *J* = 12.2 Hz, 1H), 4.12-4.05 (m, 1H), 3.96 (ddd, *J* = 2.4, 8.3, 14.1 Hz, 1H), 3.50 (dd, *J* = 5.8, 10.0 Hz, 1H), 3.37 (dd, *J* = 4.8, 10.0 Hz, 1H), 3.19 (ddd, *J* = 2.8, 4.0, 4.9 Hz, 1H), 2.76 (dd, *J* = 4.0, 5.1 Hz, 1H), 2.58 (dd, *J* = 2.8, 5.0 Hz, 1H), 2.10 (ddd, *J* = 5.1, 8.7, 8.7 Hz, 1H), 1.56 (m, 1H), 1.47 (s, 3H), 1.41 (s, 3H), 1.25 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.2, 133.2, 128.4 (2C), 127.8 (2C), 127.6, 119.5, 98.8, 73.6, 73.5, 69.2, 68.6, 51.8, 51.7, 46.1, 32.3, 30.0, 19.8; high resolution mass spectrum (ES+) *m/z* 341.1736 [(M+Na$^+$) calculated for: $C_{19}H_{26}O_4$+Na 341.1729].



(-)-**37** R = TBS

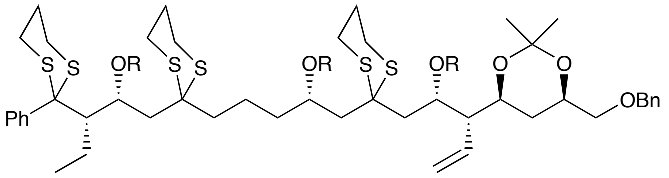
Alcohol (-)-37: Epoxide (-)-**7** (300 mg, 0.501 mmol) and 2-*tert*-butyldimethylsilyl-1,3-dithiane (**8**) (142 mg, 0.607 mmol) were each azeotroped three times with benzene and placed under high vacuum with a cannula needle connecting the two flasks. After 5 h the flasks were backfilled with argon and the dithiane was dissolved in dry Et_2O (2.7 mL) and cooled to -78 °C in a dry ice/acetone bath. *t*-Butyllithium (1.44 M, 0.45 mL, 0.66 mmol) was added and after 5 min the flask was placed in a -45 °C bath (dry ice/acetonitrile) for 1 h. The solution remained clear and colorless. The dithiane solution was re-cooled to -78 °C and the epoxide (-)-**7** in dry Et_2O (3 mL) was added via cannula with a 1 mL Et_2O rinse. The reaction was warmed to between -30 and -20 °C (dry ice/acetone) and was allowed to stir for 45 min. Saturated NH_4Cl (2 mL) was added to quench the reaction and the layers were separated. The aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Flash chromatography (95:5 to 85:15 hexanes:EtOAc) afforded (-)-**37** in 72% yield (301 mg, 0.361 mmol): $[\alpha]_D^{23}$ -6.63° (c = 1.63, C_6H_6); IR (film) 3430, 2929, 2856, 2360, 1464, 1253, 1076, 837, 775, 702 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.51 (m, 2H), 7.20 (m, 2H), 7.05 (m, 1H), 4.21 (s, 1H), 4.19 (m, 1H), 3.42 (dd, *J* = 5.8, 10.8 Hz, 1H), 3.21 (dd, *J* = 8.2, 10.8 Hz, 1H), 3.08 (m, 2H), 2.87 (ddd, *J* = 2.3, 12.7, 14.1 Hz, 1H), 2.77 (dd, *J* = 9.9, 15.2 Hz, 1H), 2.72 (dd, *J* = 12.6, 14.8 Hz, 1H), 2.57 (m, 3H), 2.48 (m, 1H), 2.31 (m, 4H), 2.16 (m, 2H), 1.94 (m, 3H), 1.79 (m, 3H), 1.62 (m, 1H), 1.55 (m, 2H), 1.47 (m, 2H), 1.42 (ddd, *J* = 6.1, 6.1, 8.1 Hz, 1H), 1.33 (m, 2H), 1.17 (m, 1H), 1.16 (dd, *J* = 7.4, 7.4 Hz, 3H), 1.14 (s, 9H), 0.96 (s, 9H), 0.46 (s, 3H), 0.28 (s, 3H), -0.041 (s, 3H), -

0.050 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 142.1, 131.1 (2C), 128.4 (2C), 127.0, 70.5, 63.9, 63.5, 44.7, 43.8, 40.04, 40.00, 38.5, 35.4, 32.4, 31.4, 31.2, 29.0, 28.7 (3C), 27.5, 26.1 (3C), 25.3, 24.5 (2C), 24.0, 23.4, 23.1, 21.0, 20.1, 18.4, 14.5, -4.6, -5.3 (2C), -5.4; high resolution mass spectrum (ES+) *m/z* 855.3327 [(M+Na$^+$); calculated for: $C_{40}H_{72}O_2S_6Si_2$+Na 855.3293].



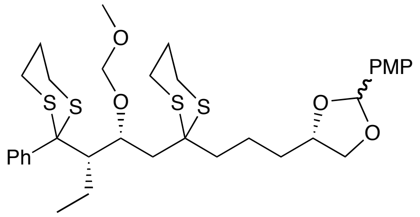
(-)-**40** R = TBS

Linchpin Product (-)-40: Dithiane (-)-**37** (300 mg, 0.360 mmol) and epoxide (+)-**9** (183 mg, 0.567 mmol) were each azeotroped three times with benzene and place under high vacuum overnight. Dithiane (-)-**37** was dissolved in dry Et_2O (7 mL) and epoxide (+)-**9** was dissolved in dry Et_2O (4 mL) and HMPA (0.19 mL, 1.08 mmol). The dithiane solution was cooled to -78 °C in a dry ice/acetone bath and *n*-BuLi (2.35 M, 0.17 mL, 0.40 mmol) was added. After 10 min the epoxide solution was added to the reaction mixture via cannula turning the solution pale orange. After warming slowly in the dry ice bath over 5 h the solution became yellow. After an additional 2 h saturated NH_4Cl (3 mL) and Et_2O (10 mL) were added. The layers were separated and the organic layer was washed with brine, dried over $MgSO_4$ and concentrated. Flash chromatography (95:5 to 9:1 to 4:1 hexanes:EtOAc) afforded the desired addition product, (-)-**40**, in 35% yield (147 mg, 0.128 mmol): $[\alpha]_D^{23}$ -3.33° (c = 0.21, C_6H_6); IR (film) 3503, 2928, 2857, 1460, 1380, 1256, 1200, 1096, 837, 776 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.51 (m, 2H), 7.30 (m, 2H), 7.20 (m, 4H), 7.08 (m, 2H), 5.93 (dd, *J* = 10.1, 10.1, 17.4 Hz, 1H), 5.17 (dd, *J* = 2.2, 10.3 Hz, 1H), 5.05 (dd, *J* = 2.2, 17.3 Hz, 1H), 4.87 (d, *J* = 8.4 Hz, 1H), 4.42-4.39 (m, 3H), 4.20 (ddd, *J* = 2.2, 8.4, 11.2 Hz, 1H), 4.02 (m, 1H), 3.51 (dd, *J* = 5.5, 9.8 Hz, 1H), 3.42 (dd, *J* = 5.8, 10.8 Hz, 1H), 3.41 (m, 1H), 3.33 (dd, *J* = 5.0, 9.7 Hz, 1H), 3.20 (dd, *J* = 8.2, 10.8 Hz, 1H), 3.10-3.03 (m, 2H), 2.63-2.44 (m, 8H), 2.36 (dd, *J* = 5.1, 15.0 Hz, 1H), 2.36-2.30 (m, 2H), 2.20-2.07 (m, 7H), 2.02 (d, *J* = 14.3 Hz, 1H), 2.00-1.95 (m, 1H), 1.79 (m, 4H), 1.66 (m, 1H), 1.56 (m, 1H), 1.55 (s, 3H), 1.53-1.40 (m, 5H), 1.40 (s, 3H), 1.36 (m, 2H), 1.16 (dd, *J* = 7.4, 7.4 Hz, 3H), 1.10 (s, 9H), 0.98 (s, 9H), 0.33 (s, 3H), 0.28 (s, 3H), -0.040 (s, 3H), -0.050 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 141.8, 138.9, 134.8, 130.7 (2C), 128.3 (2C), 128.2 (2C), 128.1 (2C), 127.2, 126.7, 118.7, 98.7, 74.0, 73.2, 69.7, 69.0, 68.3, 66.2, 63.6, 63.1, 57.2, 52.1, 47.5, 45.3, 43.6, 39.7, 39.3, 35.1, 32.9, 32.1, 31.1, 30.9, 30.2, 29.9, 28.7, 26.5, 26.2 (3C), 26.0, 25.8 (3C), 25.7, 25.0, 24.6, 22.8, 20.1, 19.5, 18.2, 18.1, 14.2, -3.6, -4.0, -4.3, -5.6; high resolution mass spectrum (ES+) *m/z* 1173.5168 [(M+Na$^+$); calculated for: $C_{59}H_{98}O_6S_6Si_2$+Na 1173.5124].



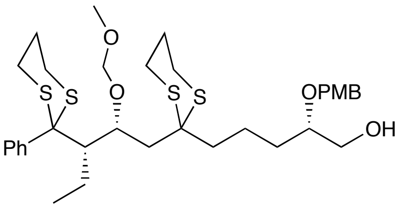
(+)-**6** R = TBS

Silyl Ether (+)-6: Tris-dithiane (-)-**40** (21 mg, 0.018 mmol) was dissolved in CH_2Cl_2 (500 μL) and cooled to 0 °C in an ice bath. 2,6-Lutidine (6.6 μL, 0.057 mmol) and TBSOTf (6.6 μL, 0.029 mmol) were added. After 1 h the reaction was diluted with CH_2Cl_2 (5 mL) and quenched with saturated NH_4Cl (1 mL). The layers were separated and the organic layer was washed once with saturated $CuSO_4$, once with brine, dried over $MgSO_4$ and concentrated. Flash chromatography (95:5 hexanes:EtOAc) afforded the desired TBS ether (+)-**6** in 66% yield (15 mg, 0.012 mmol): $[\alpha]^{23}_{D}$ +4.18° (c = 0.94, C_6H_6); IR (film) 2955, 2926, 2854, 1461, 1378, 1255, 1074, 835, 774 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.51 (m, 2H), 7.28 (m, 2H), 7.22-7.15 (m, 4H), 7.08 (m, 2H), 5.95 (ddd, *J* = 10.2, 10.2, 17.4 Hz, 1H), 5.30 (dd, *J* = 2.2, 16.7 Hz, 1H), 5.28 (dd, *J* = 2.8, 10.3 Hz, 1H), 4.95 (d, *J* = 8.7 Hz, 1H), 4.44 (d, *J* = 12.3 Hz, 1H), 4.39 (d, *J* = 12.3 Hz, 1H), 4.36 (dd, *J* = 3.8, 8.8 Hz, 1H), 4.07 (m, 2H), 3.52 (dd, *J* = 5.8, 9.8 Hz, 1H), 3.42 (dd, *J* = 5.8, 10.8 Hz, 1H), 3.30 (dd, *J* = 4.8, 5.8 Hz, 1H), 3.20 (dd, *J* = 8.2, 10.8 Hz, 1H), 3.06 (m, 2H), 2.83 (dd, *J* = 9.7, 9.7 Hz, 1H), 2.76 (dd, *J* = 8.8, 15.5 Hz, 1H), 2.60-2.42 (m, 10H), 2.20-2.11 (m, 7H), 1.97 (m, 1H), 1.90-1.69 (m, 5H), 1.64 (s, 3H), 1.63 (m, 1H), 1.56-5.45 (m, 4H), 1.50 (s, 3H), 1.42 (ddd, *J* = 5.8, 5.8, 8.2 Hz, 1H), 1.31 (ddd, *J* = 11.9, 11.9, 11.9 Hz, 1H), 1.17 (m, 1H), 1.16 (dd, *J* = 7.3, 7.3 Hz, 3H), 1.10 (s, 9H), 1.07 (s, 9H), 0.97 (s, 9H), 0.41 (s, 3H), 0.35 (s, 3H), 0.33 (s, 3H), 0.30 (s, 3H), -0.039 (s, 3H), -0.049 (s, 3H); ^{13}C NMR (125 MHz, C_6H_6) δ 142.1, 138.9, 135.1, 131.0 (2C), 128.7 (2C), 128.3 (2C), 128.1 (2C), 127.2, 126.9, 120.3, 98.7, 74.4, 73.5, 70.2, 69.0, 67.6, 67.5, 63.8, 63.4, 58.6, 52.3, 49.2, 47.1, 43.9, 40.0, 39.8, 35.3, 34.0, 32.4, 31.3, 31.2, 30.7 (2C), 29.0, 27.5, 26.7, 26.6, 26.5 (3C) 26.4 (3C), 26.1 (3C), 25.2, 24.8, 23.1, 20.6, 20.3, 18.6, 18.5, 18.3, 14.5, -2.5, -3.458, -3.462, -4.3, -5.3 (2C); high resolution mass spectrum (ES+) *m/z* 1287.6015 [(M+Na$^+$); calculated for $C_{65}H_{112}O_6S_6Si_3$+Na 1287.5989].



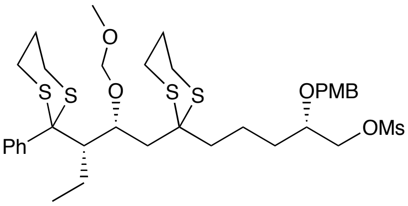
S13

MOM Ether S13: Bis-dithiane **31** (974 mg, 1.57 mmol) was dissolved in anhydrous CH_2Cl_2 (7 mL) and diisopropylethylamine (1.1 mL 6.27 mmol) was added followed by MOMCl (0.24 mL, 3.14 mmol). The reaction stirred at room temperature until judged complete by TLC. Saturated NH_4Cl was added and the organic layer was washed with saturated $CuSO_4$ and brine, dried over $MgSO_4$ and concentrated. Flash chromatography (3:1 hexanes:EtOAc) afforded protected bis-dithiane **S13** as a 2:1 mixture of diastereomers at the acetal carbon in 88% yield (919 mg, 1.38 mmol): IR (film) 2930, 1615, 1517, 1249, 1032, 831, 702 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.54 (m, 2H), 7.49 (m, 1H), 7.46 (m, 3H), 7.19 (m, 3H), 7.04 (m, 1.5H), 6.81 (m, 3H), 5.97 (s, 0.5H), 5.78 (s, 1H), 4.39 (AB q, *J* = 6.4 Hz, 3H), 3.95 (m, 0.5H), 3.91 (m, 0.5H), 3.84 (m, 1H), 3.72 (dd, *J* = 7.5, 7.5 Hz, 1H), 3.45 (dd, *J* = 7.4, 7.4 Hz, 1H), 3.31 (dd, *J* = 7.5, 7.5 Hz, 0.5H), 3.29 (s, 1.5H), 3.28 (m, 0.5H), 3.27 (s, 3H), 3.25 (m, 1H), 3.11 (m, 1.5H), 3.11 (s, 4.5H), 3.05 (m, 3H), 2.57-2.42 (m, 6H), 2.14 (m, 3H), 2.04 (m, 4.5H), 1.90 (m, 3H), 1.79-1.68 (m, 4.5H), 1.51 (m, 4.5H), 1.44 (m, 1.5H), 1.31 (m, 1H), 1.21 (m, 0.5H), 1.16 (m, 1.5H), 1.11 (dd, *J* = 7.4, 7.4 Hz, 4.5H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.5, 141.7, 131.6, 130.9, 130.7, 128.3, 128.1, 126.8, 113.6, 104.1, 103.2, 96.3, 76.8, 75.9, 70.4, 69.8, 68.4, 62.9, 54.7, 54.5, 43.1, 43.1, 39.7, 33.5, 33.2, 32.3, 32.0, 31.3, 30.9, 28.7, 27.2, 25.0, 22.8, 21.1, 14.1; high resolution mass spectrum (ES+) *m/z* 687.2289 [(M+Na$^+$); calculated for $C_{34}H_{48}O_5S_4$+Na 687.2282].



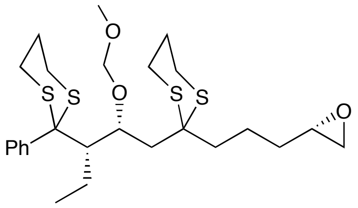
(+)-**S14**

PMB Ether (+)-S14: Protected bis-dithiane **S13** (400 mg, 0.602 mmol) was dissolved in dry CH_2Cl_2 (6.6 mL) and cooled to -78 °C in a dry ice/acetone bath. A solution of DIBAL-H in hexanes (1 M, 2.4 mL, 2.4 mmol) was added dropwise and the reaction stirred for 1 h at -78 °C and 2 h at 0 °C. The reaction was quenched with excess MeOH, diluted with Et_2O (14 mL) and stirred with saturated Rochelle's salt overnight. The layers were separated and the aqueous layer was extracted twice with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Flash chromatography (3:1 to 2:1 hexanes:EtOAc) afforded desired primary alcohol (+)-**S14** in 80% yield (321 mg, 481 mmol): $[\alpha]_D^{23}$ +6.74° (c = 0.37 CH_2Cl_2); IR (film) 3465, 2927, 1612, 1513, 1444, 1248, 1106, 1034, 918, 822, 754, 702 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.47 (m, 2H), 7.23 (m, 2H), 7.16 (m, 2H), 7.05 (m, 1H), 6.82 (m, 2H), 4.44 (d, *J* = 6.4 Hz, 1H), 4.38 (d, *J* = 11.4 Hz, 1H), 4.36 (d, *J* = 6.4 Hz, 1H), 4.32 (d, *J* = 11.3 Hz, 1H), 3.52 (ddd, *J* = 3.8, 6.1, 11.1 Hz, 1H), 3.42 (m, 1H), 3.32 (s, 3H), 3.27 (m, 1H), 3.26 (dd, *J* = 5.8, 10.4 Hz, 1H), 3.11 (dd, *J* = 8.4, 10.6 Hz, 1H), 3.11 (s, 3H), 3.06 (m, 2H), 2.58-2.41 (m, 4H), 2.15 (m, 2H), 2.07 (m, 2H), 2.01-1.89 (m, 3H), 1.77 (m, 1H), 1.71 (m, 2H), 1.54-1.46 (m, 4H), 1.44 (ddd, *J* = 6.1, 8.1, 8.1 Hz, 1H), 1.40-1.33 (m, 1H), 1.16 (ddd, *J* = 6.9, 6.9, 6.9 Hz, 1H), 1.11 (dd, *J* = 7.3, 7.3 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 159.5, 141.7, 131.2, 130.7 (2C), 129.2 (2C), 128.1 (2C), 126.8, 113.9 (2C), 96.3, 79.2, 71.2, 68.4, 64.0, 63.0, 54.7, 54.5, 43.4, 39.7, 32.3, 32.1, 31.3, 31.1, 30.9, 28.8, 27.2 (2C), 25.0, 22.8, 20.6, 14.0; high resolution mass spectrum (ES+) *m/z* 689.2446 [(M+Na$^+$); calculated for $C_{34}H_{50}O_5S_4$+Na 689.2439].



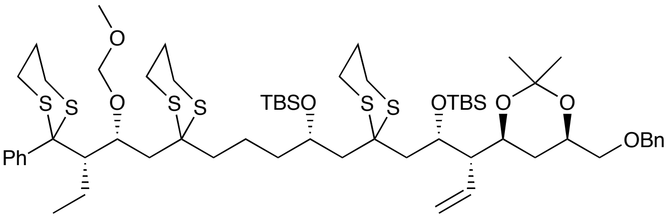
(+)-**S15**

Mesylate (+)-S15: Alcohol (+)-**S14** (320 mg, 0.479 mmol) was dissolved in CH_2Cl_2 (4.8 mL) and, following addition of Et_3N (0.22 mL, 1.53 mmol), was cooled to 0 °C in an ice bath. Methanesulfonyl chloride (60 μL, 0.62 mmol) was added and the reaction stirred at 0 °C until judged complete by TLC. The reaction solution was then loaded onto a silica gel column and eluted (4:1 hexanes:EtOAc) to afford mesylate (+)-**S15** in 91% yield (324 mg, 0.434 mmol) and was carried forward without purification: $[\alpha]_D^{23}$ +4.64° (c = 0.27, CH_2Cl_2); IR (film) 2930, 1612, 1514, 1444, 1358, 1249, 1176, 1107, 1023, 956, 918, 824, 753, 702 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.47 (m, 2H), 7.25 (m, 2H), 7.17 (m, 2H), 7.06 (m, 1H), 6.82 (m, 2H), 4.44 (d, *J* = 7.0 Hz, 1H), 4.37 (d, *J* = 11.1 Hz, 1H), 4.36 (d, *J* = 7.0 Hz, 1H), 4.27 (11.1 Hz, 1H), 4.04 (dd, *J* = 3.6, 11.0 Hz, 1H), 3.85 (dd. *J* = 5.3, 11.0 Hz, 1H), 3.31 (s, 3H), 3.26 (dd, *J* = 6.0, 11.0 Hz, 1H), 3.11 (s, 3H), 3.11 (dd, *J* = 8.8, 10.4 Hz, 1H), 3.05 (m, 2H), 2.57-2.42 (m, 4H), 2.26 (s, 3H), 2.15 (m, 2H), 2.02 (m, 1H), 2.01 (d, *J* = 8.0 Hz, 1H), 1.93 (m, 2H), 1.85 (m, 1H), 1.78 (m, 1H), 1.72 (m, 2H), 1.53 (m, 1H), 1.49-1.38 (m, 2H), 1.44 (ddd, *J* = 6.0, 6.0, 8.1 Hz, 1H), 1.23 (m, 2H), 1.17 (ddd, *J* = 6.8, 6.8, 6.8 Hz, 1H), 1.12 (dd, *J* = 7.4, 7.4 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 159.8, 141.9, 131.0 (2C), 130.7, 129.7 (2C), 128.5 (2C), 127.0, 114.1 (2C), 96.6, 76.4, 71.9, 70.7, 68.7, 63.1, 54.9, 54.8, 43.4, 40.0, 36.9, 32.6, 32.3, 31.6, 31.4, 31.1, 29.0, 27.5 (2C), 25.2, 23.0, 20.6, 14.3; high resolution mass spectrum (ES+) *m/z* 767.2180 [(M+Na$^+$); calculated for: $C_{35}H_{52}O_7S_5$+Na 767.2214].



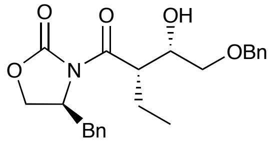
(-)-**41**

Epoxide (-)-41: Mesylate (+)-**S15** (323 mg, 0.433 mmol) was dissolved in CH_2Cl_2 (5 mL) and pH 8 phosphate buffer (1 mL). The solution was cooled to 0 °C in an ice bath and DDQ (137 mg, 0.606 mmol) was added. After 4 h the reaction was diluted with CH_2Cl_2 and the organic layer was extracted three times with half-saturated $NaHCO_3$. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated. Flash chromatography (2:1 to 3:7 hexanes:EtOAc) afforded the secondary alcohol in 85% yield (230 mg, 368 mmol). This compound was immediately carried forward without full characterization. The alcohol (230 mg, 0.368 mmol) was dissolved in MeOH (5 mL) and stirred at room temperature with K_2CO_3 (254 mg, 1.84 mmol) for 30 min. The reaction was then diluted with Et_2O and washed twice with distilled H_2O. The aqueous layer was extracted twice with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Flash chromatography (97:2:1 to 94:5:1 hexanes:EtOAc:Et_3N) afforded the desired epoxide (-)-**41** in 90% yield (174 mg, .329 mmol): $[\alpha]_D^{23}$ -1.64° (c = 0.56, C_6H_6); IR (film) 2924, 1492, 1445, 1381, 1277, 1214, 1149, 1134, 1106, 1067, 1048, 918, 844, 754, 702 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.46 (m, 2H), 7.16 (m, 2H), 7.05 (m, 1H), 4.41 (d, *J* = 6.5 Hz, 1H), 4.36 (d, *J* = 6.5 Hz, 1H), 3.25 (dd, *J* = 5.9, 10.7 Hz, 1H), 3.11 (s, 3H), 3.10 (dd, *J* = 8.3, 10.6 Hz, 1H), 3.04 (m, 2H), 2.56-2.39 (m, 5H), 3.91 (dd, *J* = 3.9, 5.2 Hz, 1H), 2.18-2.13 (m, 2H), 2.05 (m, 3H), 1.92 (m, 3H), 1.76 (m, 1H), 1.72-1.66 (m, 2H), 1.55-1.47 (m, 2H), 1.43 (ddd, *J* = 6.2, 6.2, 8.2 Hz, 1H), 1.26 (m, 2H), 1.16 (ddd, *J* = 6.8, 6.8, 6.8 Hz, 1H), 1.11 (dd, *J* = 7.3, 7.3 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 141.9, 131.0 (2C), 128.4 (2C), 127.0, 96.6, 68.7, 63.1, 54.9, 51.4, 46.2, 43.1, 40.0, 32.6, 32.5, 32.3, 31.6, 31.1, 29.0 27.4 (2C), 25.2, 23.0, 21.4, 14.3; high resolution mass spectrum (ES+) *m/z* 529.1957 [(MH^+); calculated for: $C_{26}H_{40}O_3S_4$+H 529.1939].



(+)-**43**

Tris-dithiane Silyl Ether (+)-43: Linchpin product (-)-**42** (29 mg, 0.027 mmol) was dissolved in CH_2Cl_2 (200 μL) and cooled to 0 °C in an ice bath. 2,6-Lutidine (10 μL, .086 mmol) and TBSOTf, (9 μL, .04 mmol) were added and the reaction stirred for 45 min. The reaction mixture was applied directly onto a silica gel column and the product was eluted using 95:5 hexanes:EtOAc. The desired product was isolated in 81% yield (26 mg, 0.22 mmol): $[\alpha]_D^{23}$ +3.61° (c = 0.21, C_6H_6); IR (film) 2953, 2928, 2855, 1471, 1378, 1254, 1105, 1070, 1048, 919, 835, 774, 699 cm^{-1}; ^{1}H NMR (550 MHz, C_6D_6) δ 7.48 (m, 2H), 7.30 (m, 1H), 7.16 (m, 5H), 7.05 (m, 2H), 5.95 (ddd, *J* = 10.2, 10.2, 17.4 Hz, 1H), 5.31 (dd, *J* = 2.3, 17.4 Hz, 1H), 5.28 (dd, *J* = 2.3, 10.3 Hz, 1H), 4.95 (d, *J* = 8.7 Hz, 1H), 4.46 (d, *J* = 6.5 Hz, 1H), 4.38 (d, *J* = 7.8 Hz, 2H), 4.37 (m, 1H), 4.33 (d, *J* = 6.1 Hz, 1H), 4.07 (m, 2H), 3.52 (dd, *J* = 5.7, 9.8 Hz, 1H), 3.32 (dd, *J* = 4.8, 9.8 Hz, 1H), 3.26 (dd, *J* = 6.0, 10.6 Hz, 1H), 3.13 (dd, *J* = 8.2, 10.7 Hz, 1H), 3.11 (s, 3H), 3.05 (m, 2H), 2.84 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.73 (dd, *J* = 8.8, 15.5 Hz, 1H), 2.58-2.39 (m, 10H), 2.21-2.11 (m, 7H), 1.94 (m, 1H), 1.88 (m, 1H), 1.79 (m, 1H), 1.73 (m, 3H), 1.65 (s, 3H), 1.64 (m, 1H), 1.58-1.42 (m, 5H), 1.50 (s, 3H), 1.32 (m, 1H), 1.18 (ddd, *J* = 6.7, 6.7, 6.7 Hz, 1H), 1.13 (dd, *J* = 7.3, 7.3 Hz, 3H), 1.10 (s, 9H), 1.07 (s, 9H), 0.41 (s, 3H), 0.35 (s, 3H), 0.33 (s, 3H), 0.31 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 141.7, 138.9, 134.8, 130.7 (2C), 128.3 (2C), 128.2 (2C), 128.0 (2C), 127.4, 126.8, 120.4, 98.4, 96.3, 74.2, 73.2, 69.9, 68.8, 68.4, 67.3, 67.2, 63.2, 58.3, 54.4, 52.0, 48.9, 46.8, 43.7, 39.7, 39.5, 33.7, 32.3, 32.1, 31.3, 30.9, 30.5, 28.8, 27.2 (2C), 26.5, 26.4, 26.25 (3C), 26.16 (3C), 25.0, 24.5, 22.8, 20.3, 20.0, 18.4, 18.2, 14.1, -2.7, -3.70, -3,74, -4.6; high resolution mass spectrum (ES+) *m/z* 1217.5435 [(M+Na$^+$); calculated for: $C_{61}H_{102}O_7S_6Si_2$+Na 1217.5386].



(+)-**48**

Aldol Adduct (+)-**48:** A 250 mL 3-necked flask was fitted with an addition funnel and charged with dry CH_2Cl_2 (100 mL). The flask was placed in a water bath and Et_3B (13.0 mL, 90.0 mmol) was added followed by the dropwise addition of trifluoromethane sulfonic acid[4] (8.0 mL, 90.0 mmol). Following addition of TfOH the reaction was allowed to stir for 30 min. Oxazolidinone (+)-**46** (18.53 g, 75.0 mmol) was placed in a 1 L 2-necked flask, dry CH_2Cl_2 (200 mL) was added and the flask was cooled to 0 °C in an ice bath. To this was added the freshly prepared solution of diethylboron triflate via cannula followed by Et_3N (13.6 mL, 97.5 mmol) which was added dropwise so that the internal temperature remained below +2 °C. After the addition of the Et_3N the reaction stirred for 10 min before the temperature was lowered to -72 °C. Freshly prepared and distilled benzyloxyacetaldehyde[5] (**47**) was added in dry CH_2Cl_2 (30 mL). The reaction stirred for 20 min at -72 °C before being warmed to 0 °C for 2 h. Phosphate buffer (pH 7, 90 mL) and MeOH (100 mL) were added and the flask was fitted with an addition funnel. A MeOH:30% H_2O_2 solution (2:1, 300 mL) was added dropwise via the addition funnel. The rate of addition was such that the internal temperature remained below +10 °C. Following addition of the peroxide solution the reaction stirred and warmed for 1 h. The layers were separated and the aqueous layer was extracted once with CH_2Cl_2. The organic layer was treated with solid sodium sulfite until starch iodide paper indicated that the peroxides had been quenched. The salts were filtered off and the organic layer was washed with saturated brine, dried over $MgSO_4$ and concentrated. Aldol product (+)-**48** was isolated in 82% yield (24.38 g, 61.36 mmol) following flash chromatography (4:1 hexanes :

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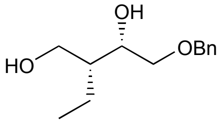
[4] Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R.; *J. Am. Chem. Soc.* **1981**, *103*, 3099.

[5] Benzyloxy acetaldehyde was prepared from *cis*-2-butene-1,-diol via benzylation, followed by dihydroxylation and sodium periodate mediated oxidative cleavage. The aldehyde was then purified via Kugelrorh distillation. For the benzylation procedure please see a) Thurner, A.; Faigl, F.; Toke, L.; Mordini, A.; Valacchi, M.; Reginato, G.; Czira, G. *Tetrahedron* **2001**, *57*, 8173. For the dihydroxylation procedure please see b) Pappo, R.; Allen, D. S., Jr.; Lemieux, R. U.; Johnson, W. S. *J. Org. Chem.* **1956**, *21*, 478.

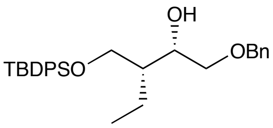
EtOAc): $[\alpha]_D^{23}$ +48.97° (c = 0.15, $CHCl_3$); IR (film) 3480, 3028, 2926, 1780, 1692, 1497, 1454, 1387, 1350, 1209, 1114, 745, 700 cm $^{-1}$; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 6H), 7.28 (m, 2H), 7.20 (m, 2H), 4.57 (m, 1H), 4.53 (d, *J* = 4.8 Hz, 2H), 4.11 (m, 2H), 4.07 (dd *J* = 2.7, 9.1 Hz, 1H), 3.95 (dd, *J* = 8.5, 8.5 Hz, 1H), 3.59 (dd, *J* = 3.8, 9.6 Hz, 1H), 3.55 (dd, *J* = 6.1, 9.6 Hz, 1H), 3.33 (dd, *J* = 3.4, 13.3 Hz, 1H), 2.66 (dd, *J* = 10.3, 13.3 Hz, 1H), 2.48 (d, *J* = 3.4 Hz, 1H), 1.89 (m, 1H), 1.81 (m, 1H), 0.98 (dd, *J* = 7.5, 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.8, 153.3, 137.9, 135.3, 129.3 (2C), 128.9 (2C), 128.4 (2C), 127.7 (3C), 127.3, 73.4, 72.2, 70.9, 65.8, 55.5, 46.7, 38.1, 21.5, 11.3; high resolution mass spectrum (ES+) *m/z* 420.1786 [(M+Na)$^+$; calculated for $C_{23}H_{27}NO_5Na$: 420.1787].



(+)-**S16**

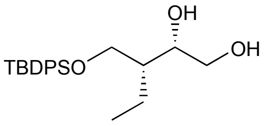
Diol (+)-**S16:** Oxazolidinone (+)-**48** (19.87 g, 50.0 mmol) was dissolved in Et_2O (450 mL) and MeOH (4.44 mL, 100.0 mmol). The solution was cooled to 0 °C in an ice bath and a solution of $LiBH_4$ in THF (2 M, 100.0 mmol) was added dropwise. The ice bath was removed and the reaction stirred at room temperature for 2 h. Half saturated $NaHCO_3$ (100 mL) was added to the reaction and it stirred vigorously until both layers were clear. The layers were separated and the aqueous layer was extracted with Et_2O until all the product was removed as judged by TLC (2:1 hexanes : EtOAc). The organic extracts were combined, washed with brine, dried over $MgSO_4$ and concentrated. The majority of the reaction mixture was carried forward without further purification as it was contaminated by the auxiliary byproduct. A small amount of (+)-**S16** was purified for analytical purposes: $[\alpha]_D^{23}$ +2.53° (c = 0.87, $CHCl_3$); IR (film) 3397, 2966, 2931, 2875, 1455, 1101, 1025, 736, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (m, 5H), 4.58 (d, *J* = 2.3 Hz, 2H), 4.05 (m, 1H), 3.73 (d, *J* = 5.3 Hz, 2H), 3.58 (m, 2H), 2.58 (bs, 2H), 1.68 (dddd, *J* = 4.5, 4.5, 13.5, 13.5 Hz, 1H), 1.39 (m, 2H), 0.95 (dd, *J* = 7.4, 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 137.7, 129.3 (2C), 128.6, 128.5 (2C), 74.0, 73.6, 72.4, 63.7, 44.7, 19.0, 12.2; high resolution mass spectrum (CI+) *m/z* 225.1490 [(M+H)$^+$; calculated for $C_{13}H_{21}O_3$: 225.1491].



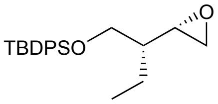
(-)-**49**

Benzyl Ether (-)-**49:** The mmols of unpurified diol used in this reaction were estimated using the weight of the unpurified mixture from the previous step and the ratio of diol (+)-**S16** to auxiliary as determined by the ^{1}H NMR. The mixture of diol (+)-**S16** (10.17 g, 45.35 mmol) and auxiliary was placed in a flask with DMAP (4.53 g, 0.55 mmol) and anhydrous CH_2Cl_2 (250 mL) was added. The flask was cooled in an ice bath followed by the addition of Et_3N (12.6 mL, 90.71 mmol) and TBDPSCl (12.8 mL, 49.9 mmol). The reaction warmed to room temperature over 4 h and was quenched with saturated NH_4Cl. The reaction mixture was diluted with CH_2Cl_2 and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 until no product remained in the aqueous layer as judged by TLC (3:1 hexanes : EtOAc). Alcohol (-)-**49** was isolated in 70% yield for the two steps (18.40 g, 39.78 mmol) using flash chromatography (95:5 hexanes : EtOAc). The auxiliary could be recovered by flushing the column with 100% EtOAc: $[\alpha]_D^{23}$ -3.88° (c = 0.33, $CHCl_3$); IR (film) 3465, 3058, 2931, 1461, 1425, 1109, 739, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (m, 5H), 7.43 (m, 2H), 7.38 (m, 5H), 7.34 (m, 3H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.07 (ddd, *J* = 4.4, 7.6 Hz, 1H), 3.71 (d, *J* = 4.7 Hz, 2H), 3.58 (dd, *J* = 4.1, 9.6 Hz, 1H), 3.53 (dd, *J* = 7.6, 9.6 Hz, 1H), 2.93 (bs, 1H), 1.57 (m, 1H), 1.49 (m, 1H), 1.42 (m, 1H), 1.05 (s, 9H), 0.80 (dd, *J* = 7.4, 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 135.6 (2C), 135.5 (2C), 133.2, 133.1, 129.7 (2C), 128.3 (2C), 127.7 (5C), 127.6 (2C), 73.3, 72.7, 72.4, 64.1, 44.8, 26.8 (3C), 19.1, 18.6, 11.9; high resolution mass spectrum (ES+) *m/z* 485.2504 [(M+Na)$^+$; calculated for $C_{29}H_{38}O_3SiNa$: 485.2480].



(-)-**S17**

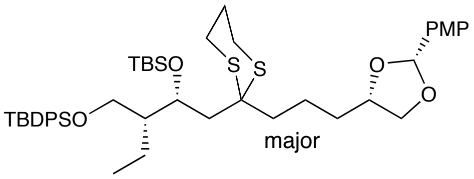
Diol (-)-**S17:** Alcohol (-)-**49** (4.27 g, 9.23 mmol) was dissolved in MeOH (40 mL). The flask was evacuated and backfilled with argon three times before addition of $Pd(OH)_2$ on carbon (20 wt.%, 648 mg). The flask was evacuated and backfilled with argon an additional two times before being evacuated and backfilled with hydrogen gas. The reaction stirred under an atmosphere of hydrogen for 2 d. The flask was evacuated and backfilled with argon and the reaction mixture was filtered through Celite to remove the $Pd(OH)_2/C$. Diol (-)-**S17** was isolated in 96% yield (3.32 g, 8.91 mmol) using flash chromatography (3:1 to 2:1 hexanes : EtOAc): $[\alpha]_D^{23}$ -5.29° (c = 0.37, $CHCl_3$); IR (film) 3391, 3073, 2962, 2928, 2856, 1472, 1428, 1113, 1052, 823, 787, 739, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (m, 4H), 7.43 (m, 6H), 3.87 (ddd, *J* = 3.9, 3.9, 7.4 Hz, 1H), 3.78-3.63 (m, 4H), 3.09 (bs, 1H), 2.39 (bs, 1H), 1.67 (m, 1H), 1.37 (m, 1H), 1.33 (m, 1H), 1.07 (m, 9H), 0.79 (dd, *J* = 7.5, 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6 (2C), 135.5 (2C), 132.7, 132.6, 129.92, 129.88, 127.8 (4C), 74.5, 64.6, 64.3, 44.9, 26.8 (3C), 19.3, 19.1, 11.9; high resolution mass spectrum (ES+) *m/z* 395.2030 [$(M+Na)^+$; calculated for $C_{22}H_{32}O_3SiNa$: 395.2018].



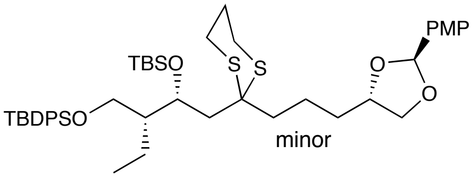
(+)-**45**

Epoxide (+)-**45**: Diol (-)-**S17** (1.53 g, 4.07 mmol) was azeotroped three times with toluene and placed under high vacuum overnight. Sodium hydride (247 mg, 9.78 mmol) was dissolved in THF (36 mL) and cooled to 0 °C. The diol was added to the suspension as a solution in THF (27 mL). The reaction stirred for 40 min followed by the addition of trisylimidazole (1.44g, 4.48 mmol) as a solution in

THF (40 mL). The reaction stirred at 0 °C for 2 h after which it was quenched with saturated NH_4Cl. The reaction was diluted with Et_2O, the layers were separated and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The resulting slurry was dissolved in ether and adsorbed onto silica gel. The mixture was purified using flash chromatography (95:5 hexanes:EtOAc) affording the desired epoxide in 84% yield (1.21 g, 3.41 mmol). $[\alpha]_D^{23}$ +1.00° (c = .13, $CHCl_3$); IR (film) 3049, 2964, 2931, 2856, 1472, 1428, 1113, 845, 823, 739, 701, 689 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.73 (m, 4H), 7.22 (m, 6H), 3.61 (dd, *J* = 4.8, 10.2 Hz, 1H), 3.56 (dd, *J* = 6.5, 10.2 Hz, 1H), 2.71 (ddd, *J* = 2.6, 3.9, 7.7 Hz, 1H), 2.45 (dd, *J* = 3.9, 5.3 Hz, 1H), 2.33 (dd, *J* = 2.6, 5.3 Hz, 1H), 1.53 (m, 1H), 1.46 (m, 1H), 1.18 (m, 1H), 1.15 (s, 9H), .89 (dd, *J* = 7.6, 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.5 (4C), 133.5 (2C), 129.7 (2C), 127.6 (4C), 64.2, 54.7, 46.4, 46.1, 26.8 (3C), 22.2, 19.2, 11.5; high resolution mass spectrum (CI+) *m/z* 395.2030 $[(M+H)^+]$; calculated for $C_{22}H_{30}O_2Si$+H: 395.2018].

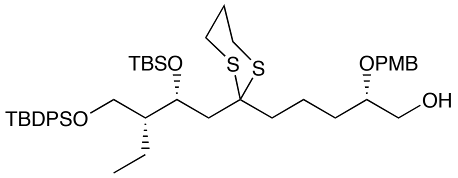


(-)-**51**



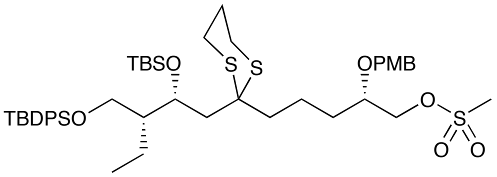
(+)-S18

TBS Ethers (-)-**51 and** (+)-**S18:** A mixture of dithianes (-)-**50** and the minor diastereomer (5.55 g, 7.99 mmol) was dissolved in dry CH_2Cl_2 (50 mL) and cooled to 0 °C in an ice bath. 2,6-Lutidine (3.8 mL, 32.0 mmol) was added followed by TBSOTf (3.7 mL, 16.0 mmol). The reaction slowly warmed to room temperature over the course of 2 h. Saturated NH_4Cl was added and the layers were separated. The aqueous layer was extracted three times with CH_2Cl_2 and the combined organic layers were washed with brine, dried $MgSO_4$ and concentrated. The yellow oil was dissolved in EtOAc and washed with a saturated solution of $CuSO_4$, followed by saturated sodium bicarbonate and brine to removed the excess 2,6-lutidine. Following flash chromatography (98:2 hexanes:EtOAc) the desired products were isolated as a colorless oil in 97% yield (6.28 g, 7.76 mmol). The diastereomers were separated on small scale for characterization purposes: (major) (-)-**51** $[\alpha]^{23}_{\mathrm{D}}$ -11.94° (c = 0.18, C_6H_6) IR (film) 2954, 2931, 2855, 1466, 1431, 1250, 1111, 1079, 831, 703 cm $^{-1}$; ^{1}H NMR (500 MHz, C_6D_6) δ 7.87 (m, 4H), 7.55 (m 2H), 7.27 (m, 6H), 6.81 (m, 2H), 5.82 (s, 1H), 4.70 (ddd, *J* = 2.2, 5.3, 5.3 Hz, 1H), 3.97 (m, 2H), 3.89 (dd, *J* = 6.8, 10.0 Hz, 1H), 3.81 (dd, *J* = 7.3, 7.3 Hz, 1H), 3.54 (dd, *J* = 6.9, 6.9 Hz, 1H), 3.26 (s, 3H), 2.53 (dd, *J* = 5.6, 15.3 Hz, 1H), 2.36 (m, 4H), 2.24 (dd, *J* = 5.3, 15.3 Hz, 1H), 2.13 (m, 2H), 1.96 (m, 1H), 1.89 (m, 1H), 1.76 (m, 2H), 1.53 (m, 5H), 1.26 (s, 9H), 0.98 (s, 9H), 0.94 (dd, *J* = 7.4, 7.4 Hz, 3H), 0.31 (s, 3H), 0.21 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.8, 136.1 (4C), 134.3, 134.2, 131.2, 129.9 (2C), 128.5 (2C), 127.9 (4C), 113.9 (2C), 104.4, 77.4, 70.2, 69.9, 63.23, 54.7, 53.4, 49.69, 43.2, 39.7, 34.1, 27.3 (3C), 26.43 (3C), 26.37, 26.1, 25.3, 22.0, 19.78, 19.5, 18.5, 12.9, -3.2, -3.90; (minor) (+)-**S18** $[\alpha]^{23}_{\mathrm{D}}$ +6.74° (c = 0.23, C_6H_6); IR (film) 2930, 2856, 1614, 1514, 1462, 1428, 1249, 1170, 1111, 8345, 702 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.87 (m, 4H), 7.51 (m, 2H), 7.27 (m, 6H), 6.80 (m, 2H), 6.03 (s, 1H), 4.70 (ddd, *J* = 2.3, 5.3, 5.3 Hz, 1H), 4.07 (m, 1H), 3.99 (m, 2H), 3.89 (dd, *J* = 6.7, 10.0 Hz, 1H), 3.42 (dd, *J* = 7.6, 7.6 Hz, 1H), 3.27 (s, 3H), 2.55 (dd, *J* = 5.5, 15.3 Hz, 1H), 2.43 (m, 4H), 2.25 (dd, *J* = 5.4, 15.3 Hz, 1H), 2.14 (m, 2H), 1.95 (m, 1H), 1.89 (m, 1H), 1.79 (m, 1H), 1.69 (m, 1H), 1.53 (m, 4H), 1.39 (dddd, *J* = 5.0, 5.0, 13.0, 15.6 Hz, 1H), 1.26 (s, 9H), 0.99 (s, 9H), 0.96 (dd, *J* = 7.5, 7.5 Hz, 3H), 0.32 (s, 3H), 0.22 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.6, 136.2 (2C), 136.1 (2C), 134.28, 134.2, 131.9, 130.0 (2C), 128.3 (2C), 127.9 (4C), 113.9 (2C), 103.5, 76.4, 70.8, 69.94, 63.17, 54.7, 53.4, 49.71, 43.2, 39.7, 33.9, 27.3 (3C), 26.45 (3C), 26.40, 26.2, 25.3, 21.9, 19.81, 19.5, 18.5, 12.9, -3.1, -3.89; high resolution mass spectrum (ES+) *m/z* 831.3957 [(M+Na$^+$) calculated for: $C_{45}H_{68}O_5S_2Si_2$+Na 831.3944].



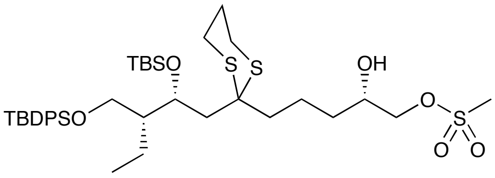
(+)-**S19**

PMB Alcohol (+)-**S19:** Dithianes (-)-**51** and (+)-**S18** (8.02 g, 9.91 mmol) were dissolved in anhydrous CH_2Cl_2 (70 mL) and cooled to -78 °C in a dry ice / acetone bath. A solution of DIBAL-H in hexanes (1 M, 48.0 mL, 48.0 mmol) was added dropwise and the reaction stirred for 1.5 h at -78 °C. The excess DIBAL-H was quenched with MeOH and the reaction was diluted with Et_2O (100 mL) and aqueous Rochelle's salt (40 mL) was added. The biphasic mixture stirred at room temperature until both layers were clear. The layers were separated and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The product was purified using silica gel chromatography (4:1 to 2:1 hexanes:EtOAc) to afford the desired primary alcohol (+)-**S19** in 89% yield (7.84 g, 9.66 mmol) along with 9% of the secondary alcohol. $[\alpha]_D^{23}$ +6.20° (c = 1.0, $CHCl_3$); IR (film) 3453, 2932, 2857, 1614, 1514, 1472, 1428, 1247, 1108, 833, 773, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.69 (m, 4H), 7.39 (m, 6H), 7.26 (m, 2H), 6.87 (m, 2H), 4.62 (d, *J* = 11.1 Hz, 1H), 4.40 (d, *J* = 1.11 Hz, 1H), 4.35 (m, 1H), 3.80 (s, 3H), 3.74 (dd, *J* = 4.9, 10.1 Hz, 1H), 3.68 (m, 1H), 3.67 (dd, *J* = 6.1, 10.0 Hz, 1H), 3.49 (m, 2H), 2.78 (m, 4H), 2.30 (dd, *J* = 4.7, 15.3 Hz, 1H), 1.93 (m, 5H), 1.73 (m, 1H), 1.58 (m, 4H), 1.48 (m, 1H), 1.42 (m, 1H), 1.35 (m, 1H), 1.07 (s, 9H), 0.87 (dd, *J* = 7.4, 7.4 Hz, 3H), 0.84 (s, 9H), 0.12 (s, 3H), 0.058 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.3, 135.7 (4C), 133.91, 133.87, 130.6, 129.5 (2C), 129.4 (2C), 127.5 (4C), 113.9 (2C), 79.6, 71.4, 69.8, 64.3, 62.4, 55.3, 53.0, 49.2, 42.0, 39.5, 31.1, 27.0 (3C), 26.4, 26.1 (4C), 25.1, 20.8, 19.7, 19.3, 18.1, 12.6, -3.5, -4.1; high resolution mass spectrum (ES+) *m/z* 833.4133 [(M+Na$^+$) calculated for: $C_{45}H_{70}O_5S_2Si_2$+Na 833.4101].



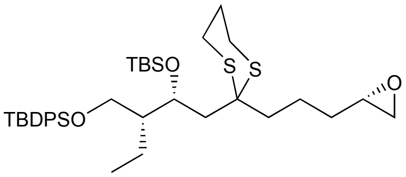
(+)-**S20**

Mesylate (+)-**S20:** Primary alcohol (+)-**S19** (4.96 g, 6.11 mmol) was dissolved in dry CH_2Cl_2 (45 mL) and Et_3N (2.70 mL, 19.6 mmol) was added. The flask was placed in an ice water bath and methanesulfonyl chloride (0.61 mL, 7.95 mmol) was added. After 45 min the reaction was quenched with saturated NH_4Cl (3 mL). The reaction mixture was poured into a separatory funnel and deionized water (10 mL) and CH_2Cl_2 (20 mL) were added. The layers were separated and the aqueous layer was extracted twice with CH_2Cl_2 (10 mL). The organic layers were washed with brine and dried over $MgSO_4$. Concentration under reduced pressure furnished mesylate (+)-**S20** in near quantitative yield: $[\alpha]_D^{23}$ +1.05° (c = 0.095, $CHCl_3$); IR (film) 2931, 1514, 1466, 1357, 1250, 1175, 1108, 832, 775 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.69 (m, 4H), 7.39 (m, 6H), 7.26 (m, 2H), 6.86 (m, 2H), 4.56 (d, *J* = 11.0 Hz, 1H), 4.49 (d, *J* = 11.0 Hz, 1H), 4.34 (m, 1H), 4.29 (dd, *J* = 3.5, 10.9 Hz, 1H), 4.15 (dd, *J* = 5.7, 10.9 Hz, 1H), 3.79 (s, 3H), 3.74 (dd, *J* = 4.9, 10.0 Hz, 1H), 3.66 (dd, *J* = 3.9, 10.0 Hz, 1H), 3.62 (m, 1H), 2.97 (s, 3H), 2.78 (m, 4H), 2.29 (dd, *J* = 4.7, 15.4 Hz, 1H), 1.94 (m, 4H), 1.72 (m, 1H), 1.66-1.53 (m, 4H), 1.51 (m, 1H), 1.42 (m, 1H), 1.34 (m, 1H), 1.10 (s, 9H), 0.87 (dd, *J* = 7.4, 7.4 Hz, 3H), 0.84 (s, 9H), 0.11 (s, 3H), 0.053 (s, 3H); ^{13}C NMR ($CDCl_3$,125 MHz) δ 159.3, 135.7 (4C), 133.9 (2C), 130.0, 129.5 (4C), 127.6 (4C), 113.9 (2C), 76.5, 72.0, 71.1, 69.8, 62.4, 55.2, 53.0, 49.2, 42.2, 39.3, 37.6, 31.5, 27.0 (3C), 26.3, 26.1 (4C), 25.1, 10.7, 19.8, 19.2, 18.1, 12.6, -3.5, -4.1; high resolution mass spectrum (ES+) *m/z* 911.3896 [(M+Na^+) calculated for: $C_{46}H_{72}O_7S_3Si_2$+Na 911.3876].



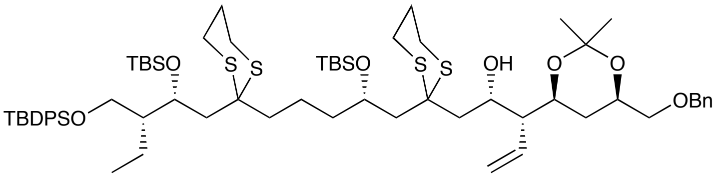
(-)-**S21**

Secondary Alcohol (-)**-S21:** Mesylate (+)-**S20** (5.37 g, 6.04 mmol) was dissolved in CH_2Cl_2 (40 mL) and pH 8 phosphate buffer (10 mL) and placed in an ice bath. DDQ (1.92 g, 8.45 mmol) was added in three portions at 30 min intervals. Following the third addition of DDQ the reaction was allowed to stir for one h at which point an additional portion of DDQ (200 mg) was added. When the reaction was complete the layers were separated and the organic layer was washed with saturated $NaHCO_3$ until the aqueous layer was no longer red. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated to give an orange oil, which was purified using column chromatography (4:1 to 3:1 to 3:2 hexanes:EtOAc). Secondary alcohol (-)-**S21** was obtained as a colorless oil and was immediately taken to the next reaction: $[\alpha]_D^{23}$ -1.11° (c = 0.09, $CHCl_3$); IR (film) 3435, 2955, 2930, 2856, 1468, 1427, 1357, 1254, 1175, 1108, 959, 835, 703 cm $^{-1}$; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73, (m, 4H), 7.44 (m, 6H), 4.38 (m, 1H), 4.25 (dd, *J* = 2.9, 10.5 Hz, 1H), 4.11 (dd, *J* = 7.1, 10.5 Hz, 1H), 3.93 (m, 1H), 3.79 (dd, *J* = 5.0, 10.1 Hz, 1H), 3.71 (dd, *J* = 6.1, 10.2 Hz, 1H), 3.09 (s, 3H), 2.82 (m, 4H), 2.34 (dd, *J* = 4.2, 15.3 Hz, 1H), 2.07 (d, *J* = 4.5 Hz, 1H), 1.99 (m, 4H), 1.71 (m, 2H), 1.63 (m, 1H), 1.50 (m, 3H), 1.38 (m, 2H), 1.11 (s, 9H), 0.93 (dd, *J* = 7.5, 7.5 Hz, 3H), 0.87 (s, 9H), 0.15 (s, 3H), 0.095 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.7 (4C), 133.94, 133.88, 129.6, 129.5, 127.6 (4C), 73.5, 70.0, 69.7, 62.4, 53.1, 49.3, 42.1, 39.1, 37.6, 32.9, 29.7, 27.0 (3C), 26.4, 26.1 (3C), 25.1, 20.7, 19.9, 18.3, 18.2, 12.6, -3.5, -4.0; high resolution mass spectrum (ES+) *m/z* 791.3276 [(M+Na$^+$) calculated for: $C_{38}H_{64}O_6S_3Si_2$+Na 791.3301].



(-)-**44**

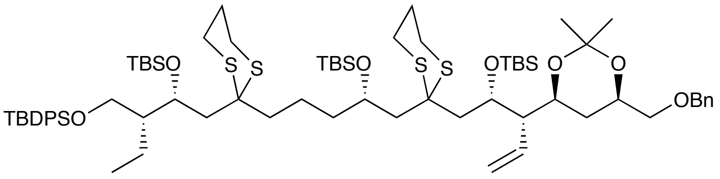
Epoxide (-)-**44**: Secondary alcohol (-)-**S21** from the previous step was dissolved in MeOH (50 mL) and approximately 5 equiv of K_2CO_3 was added. After 30 min water was added until the white solid was completely dissolved. The reaction mixture was extracted three times with EtOAc and the combined extracts were washed with brine, dried over $MgSO_4$ and concentrated. Purification using a buffered silica gel column (9:1 hexanes:EtOAc with 1% Et_3N) provided epoxide (-)-**44** in 72% for the two steps (2.92 g, 4.34 mmol): $[\alpha]_D^{23}$ -8.42° (c = 0.095, $CHCl_3$); IR (film) 2929, 1253, 1109, 835, 774, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (m, 4H), 7.38 (m, 6H), 4.35 (m, 1H), 3.74 (dd, *J* = 4.8, 10.0 Hz, 1H), 3.66 (dd, *J* = 6.1, 10.1 Hz, 1H), 2.89 (m, 1H), 2.77 (m, 5H), 2.45 (m, 1H), 2.29 (dd, *J* = 4.5, 15.3 Hz, 1H), 1.96 (m, 5H), 1.68 (m, 3 H), 1.57-1.42 (m, 2H), 1.36 (m, 1H), 1.26 (m, 1H), 1.07 (s, 9H), 0.88 (dd, *J* = 7.5, 7.5 Hz, 3H), 0.83 (s, 9H), 0.11 (s, 3H), 0.052 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.7 (4C), 133.83, 133.80, 129.4 (2C), 127.5 (4C), 69.8, 62.3, 53.0, 52.1, 49.2, 46.9, 41.8, 38.9, 32.3, 29.6, 26.9 (3C), 26.3, 26.0 (3C), 25.1, 21.2, 19.8, 19.2, 18.1, 12.5, -3.5, -4.1; high resolution mass spectrum (ES+) *m/z* 673.3586 [(M+Na$^+$) calculated for: $C_{37}H_{60}O_3S_2Si_2$+Na 673.3601].



(-)-**52**

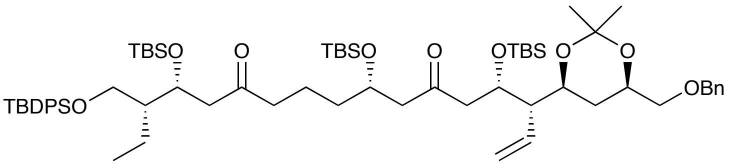
Linchpin Adduct (-)-**52:** Epoxide (-)-**44** (171 mg, 0.254 mmol) and epoxide (+)-**9** (139 mg, 0.436 mmol) were each azeotroped three times with toluene and placed under high vacuum overnight. 2-*tert*-Butyldimethylsilyl-1,3-dithiane (**8**) (81 mg, 0.34 mmol) was azeotroped three times with toluene and placed under high vacuum for 1.25 h after which it was dissolved in dry Et_2O (1.5 mL) and the solution was cooled to -78 °C in a dry ice / acetone bath. A solution of *t*-BuLi in hexanes (1.40 M, 0.22 mL, 0.32 mmol) was added dropwise and the solution stirred at -45 °C for 1 h. The reaction flask was re-cooled to -78 °C and epoxide (-)-**44** in dry Et_2O (1.8 mL) was added via cannula. The solution turned pale yellow and was allowed to stir at -20 °C for 1 h. Epoxide (+)-**9** was dissolved in anhydrous THF (3.3 mL) and HMPA (0.13 mL, 0.76 mmol) was added. This solution was added to a re-cooled (-78 °C) reaction mixture via cannula and the solution turned bright yellow. The reaction was allowed to warm to -20 °C and stir for 1 h before warming to room temperature over the course of an additional hour. The solution was then quenched with saturated NH_4Cl and diluted with Et_2O. The aqueous layer was extracted twice with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to afford and orange oil. The linchpin product (-)-**52** was isolated in 50% yield (157 mg, 0.128 mmol) using flash chromatography (95:5 to 4:1 hexanes:EtOAc). The product of addition into the first epoxide followed by Brook rearrangement was isolated in 25% yield (73 mg, 0.064 mmol): $[\alpha]^{23}_{D}$ -1.01° (c = 0.095, $CHCl_3$); IR (film) 3434, 2930, 2856, 1472, 1429, 1380, 1254, 1107, 836, 774, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.70 (m, 4H), 7.39 (m, 6H), 7.34 (m, 4H), 7.27 (m, 1H), 5.78 (ddd, *J* = 10.1, 10.1, 17.2 Hz, 1H), 5.19 (dd, *J* = 2.1, 10.3 Hz, 1H), 5.13 (dd, *J* = 2.1, 17.4 Hz, 1H), 4.60 (d, *J* = 12.3 Hz, 1H), 4.54 (d, *J* = 12.2 1H), 4.44 (d, *J* = 8.5 Hz, 1H), 4.36 (m, 1H), 4.07 (m, 3H), 3.68 (m, 2H), 3.49 (dd, *J* = 5.9, 10.1 Hz, 1H), 3.37 (dd, *J* = 4.6, 10.1 Hz, 1H), 3.27 (s, 1H), 2.90-2.70 (m, 9H), 2.32 (m, 1H), 2.28 (dd, *J* = 4.1, 10.5 Hz, 1H), 2.08 (dd, *J* = 5.5, 15.4 Hz, 1H), 2.00-1.83 (m, 9H), 1.76 (m, 1H), 1.67 (m, 1H), 1.60 (m, 2H), 1.53 (ddd, *J* = 2.3, 2.3, 12.9 Hz, 2H), 1.47 (s, 3H), 1.42 (s, 3H), 1.37 (m, 2H), 1.18 (q, *J* = 12.2 Hz, 1H), 1.07 (s, 9H), 0.881 (s, 9H), 0.879 (m, 3H), 0.84 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H), 0.083 (s, 3H), 0.055 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.3, 135.7 (2C), 135.6 (2C), 134.1, 134.0, 133.8, 129.4 (2C), 128.3 (2C), 127.7 (2C), 127.5 (5C), 119.2, 98.8, 73.7, 73.4, 69.7, 69.6, 68.8, 68.2, 66.3, 62,7, 56.5, 53.2, 51.7, 49.3, 47.0, 44.6, 42.6, 39.8, 39.3, 32.5, 30.1, 27.0 (3C), 26.7, 26.4, 26.3, 26.2 (3C), 26.1

(4C), 25.1, 24.7, 20.3, 19.72, 19.68, 19.2, 18.1, 18.0, 12.6, -3.5, -3.7, -4.1 (2C); high resolution mass spectrum (ES+) *m/z* 1247.6139 [(M+Na$^+$) calculated for: $C_{66}H_{108}O_7S_4Si_3$+Na 1247.6183].



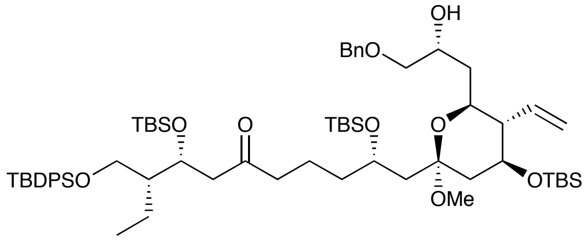
(+)-**53**

Bis-dithiane (+)-**53:** Linchpin product (-)-**52** (143 mg, 0.117 mmol) and catalytic DMAP were dissolved in pyridine (4 mL) and cooled to 0 °C in an ice bath. TBSOTf (0.13 mL, 0.59 mmol) was added and the flask sat in a 0 °C refrigerator for 18 h. The product was purified using flash chromatography (9:1 hexanes : EtOAc) to afford silyl ether (+)-**53** as a colorless oil in 93% yield (147 mg, 0.110 mmol): $[\alpha]_D^{23}$ +1.75° (c = 0.29, C_6D_6); ^{1}H NMR (500 MHz, C_6D_6) δ 7.90 (m, 4H), 7.23 (m, 10 H), 7.16 (m, 1H), 7.12 (m, 1H), 5.96 (ddd , *J* = 10.2, 10.2, 17.4 Hz, 1H), 5.30 (dd, *J* = 2.2, 17.3, Hz, 1H), 5.28 (dd, *J* = 2.2, 10.3 Hz, 1H), 4.96 (d, *J* = 8.4 Hz, 1H), 4.64 (m, 1H), 4.40 (d, *J* = 12.1 Hz, 1H), 4.38 (m, 1H), 4.36 (d, *J* = 12.3 Hz, 1H), 4.07 (m, 1H), 3.97 (dd, *J* = 5.1, 10.0 Hz, 1H), 3.92 (dd, *J* = 6.7, 9.8 Hz, 1H), 3.52 (dd, *J* = 5.6, 9.8 Hz, 1H), 3.30 (dd, *J* = 4.5, 9.8 Hz, 1H), 2.83 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.80 (dd, *J* = 8.8, 15.7 Hz, 1H), 2.58-2.40 (m, 13H), 2.21 (dd, *J* = 5.2, 15.3 Hz, 1H), 2.16 (m, 2H), 2.12 (d, *J* = 15.2 Hz, 1H), 2.04 (m, 2H), 1.97 (m, 2H), 1.78 (m, 1H), 1.64 (s, 3H), 1.58 (m, 5H), 1.50 (s, 3H), 1.29 (m, 1H), 1.28 (s, 9H), 1.10 (s, 9H), 1.06 (s, 9H), 1.02 (s, 9H), 0.99 (dd, *J* = 7.5, 7.5 Hz, 3H), 0.40 (s, 3H), 0.36 (s, 3H), 0.352 (s, 3H), 0.349 (s, 3H), 0.31 (s, 3H). 0.24 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 139.2, 136.2 (2C), 136.1 (2C), 135.2, 134.4, 134.3, 129.9 (2C), 128.5 (2C), 128.3 (2C), 127.8 (4C), 127.6, 120.3, 98.7, 74.4, 73.5, 70.6, 69.9, 69.0, 67.6, 67.5, 63.5, 58.7, 53.8, 52.4, 49.9, 49.6, 47.2, 44.0, 40.7, 40.3, 34.0, 30.7, 27.4 (3C), 26.8, 26.6, 26.52 (3C), 26.47 (3C), 26.4 (3C), 26.3, 26.2, 25.3, 24.8, 20.6, 19.8, 19.6, 18.7, 18.51, 18.47, 13.1, -2.4, -2.9, -3.1, -3.3, -3.4, -3.8, -4.3; high resolution mass spectrum (ES+) *m/z* 1361.7019 [(M+Na$^+$) calculated for $C_{72}H_{122}O_7S_4Si_4$+Na 1361.7048].



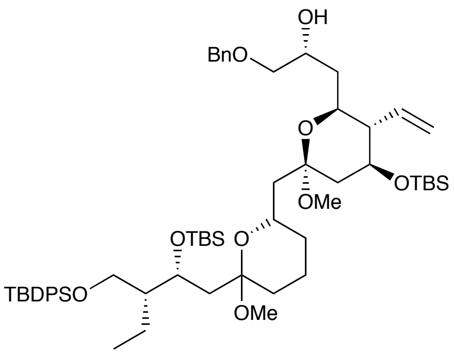
(-)-**54**

Diketone (-)-**54:** Bis-dithiane (+)-**53** (144 mg, 0.107 mmol) was dissolved in a THF:H_2O solution (4:1, 5 mL) and cooled in an ice bath. 2,6-Di-*t*-butyl-4-methylpyridine (154 mg, 0.752 mmol) was added followed by $Hg(ClO_4)_2$ (128 mg, 0.321 mmol). A white solid formed after several seconds and the slurry continued to stir at 0 °C for 1 h. The reaction was diluted with EtOAc and filtered through Celite. The filtrate was washed with saturated NH_4Cl and brine, dried over $MgSO_4$, filtered through Celite a second time and concentrated. Purification using flash chromatography (95:5 hexanes:EtOAc) afforded the diketone (-)-**54** in 59% yield (74 mg, 0.064 mmol): $[\alpha]_D^{23}$ -14.00° (c = 0.10, C_6D_6); IR (film) 2957, 2927, 2856, 1717, 1472, 1462, 1379, 1255, 1112, 836, 775, 701 cm^{-1}; ^1H NMR (C_6D_6) δ 7.84 (m, 4H), 7.29 (6H), 7.17 (m, 5H), 5.80 (ddd, *J* = 10.2, 10.2, 17.4 Hz, 1H), 5.14 (dd, *J* = 2.1, 10.3 Hz, 1H), 5.05 (m, 1H), 5.04 (dd, *J* = 1.7, 17.1 Hz, 1H), 4.71 (ddd, *J* = 3.6, 3.6, 7.6 Hz, 1H), 4.42 (d, *J* = 12.2 Hz, 1H), 4.37 (d, *J* = 12.3 Hz, 1H), 4.31 (dd, *J* = 5.7, 5.7 Hz, 1H), 4.02 (m, 2H), 3.90 (dd, *J* = 5.0, 10.2 Hz, 1H), 3.86 (dd, *J* = 5.3, 10.1 Hz, 1H), 3.52 (dd, *J* = 5.6, 9.8 Hz, 1H), 3.32 (dd, *J* = 4.9, 9.8 Hz, 1H), 2.63 (dd, *J* = 8.4, 16.2 Hz, 1H), 2.60 (m, 3H), 2.53 (dd, *J* = 5.6, 16.4 Hz, 1H), 2.40 (dd, *J* = 6.1, 16.5 Hz, 1H), 2.35 (dd, *J* = 3.7, 16.2 Hz, 1H), 2.17 (m, 3H), 1.64 (m, 3H), 1.56 (s, 3H), 1.51 (m, 2H), 1.45 (s, 3H), 1.34 (m, 2H), 1.24 (m, 1H), 1.24 (s, 9H), 1.01 (s, 9H), 1.00 (s, 9H), 0.96 (s, 9H), 0.88 (dd, *J* = 7.5, 7.5 Hz, 3H), 0.26 (s, 3H), 0.164, (s, 3H), 0.155 (s, 6H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 207.4, 205.7, 138.9, 135.8 (4C), 134.3, 133.9, 133.8, 129.7 (2C), 128.2 (2C), 128.0 (2C), 127.8 (4C), 127.4, 119.3, 98.5, 74.1, 73.3, 68.71, 68.67, 68.2, 66.8, 65.2, 62.6, 57.5, 51.0, 50.9, 48.7, 47.0, 44.0, 37.0, 33.4, 30.3, 26.9 (3C), 26.0 (3C), 25.92 (3C), 25.89 (3C), 20.2, 20.1, 19.2, 19.1, 18.3, 18.04, 17.98, 12.3, -3.7, -4.58, -4.62, -4.7, -4.9, -5.0; high resolution mass spectrum (ES+) *m/z* 1181.7115 [(M+Na^+) calculated for $C_{66}H_{110}O_9Si_4$+Na 1181.7125].



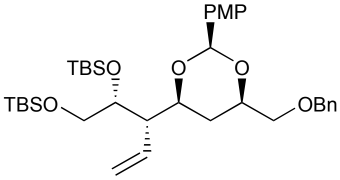
(-)-**55**

Acetal (-)-**55:** Diketone (-)-**54** (54 mg, 0.046 mmol) was dissolved in MeOH (2.5 mL) and PPTS (23 mg, 0.093 mmol) was added. The reaction stirred at room temperature until the bis-ketal product (-)-**56** began to stain on the TLC plate. The reaction was quenched with Et_3N and the MeOH was removed under reduced pressure. The resulting oil was dissolved in Et_2O, washed successively with saturated NH_4Cl, water and brine, dried over $MgSO_4$ and concentrated. The ketal product (-)-**55** was isolated in 43% yield (22 mg, 0.019 mmol) following preparative TLC (1000 μm, 9:1 hexanes:EtOAc). A small amount of starting material [(-)-**54**, 8 mg, 15%] was also recovered: $[\alpha]_D^{23}$ -4.19° (c = 0.43, toluene); IR (film) 3515, 2955, 2928, 2856, 1717, 1467, 1375, 1254, 1093, 836, 775, 739, 703 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 7.85 (m, 4H), 7.30 (m, 7H), 7.21 (m, 3H), 7.10 (m, 1H), 5.28 (ddd, *J* = 9.9, 9.9, 17.1 Hz, 1H), 5.10 (dd, *J* = 2.1, 17.1 Hz, 1H), 5.05 (dd, *J* = 2.1, 10.1 Hz, 1H), 4.72 (ddd, *J* = 3.6, 3.6, 7.8 Hz, 1H), 4.39 (s, 2H), 4.19 (m, 1H), 4.00 (m, 2H), 3.91 (dd, *J* = 5.0, 10.1 Hz, 1H), 3.87 (dd, *J* = 5.2, 10.1 Hz, 1H), 3.67 (dd, *J* = 2.4, 10.1 Hz, 1H), 3.56 (dd, *J* = 5.8, 9.3 Hz, 1H), 3.43 (dd, *J* = 6.3, 9.3 Hz, 1H), 3.31 (s, 1H), 3.07 (s, 3H), 2.67 (dd, *J* = 8.3, 16.1 Hz, 1H), 2.38 (dd, *J* = 3.7, 16.1 Hz, 1H), 2.34 (dd, *J* = 4.8, 13.1 Hz, 1H), 2.23 (apt t, *J* = 7.0 Hz, 2H), 2.13 (ddd, *J* = 2.6, 3.7, 14.6 Hz, 1H), 2.02 (m, 2H), 1.90 (dd, *J* = 5.5, 14.9 Hz, 1H), 1.79 (dd, *J* = 10.9, 13.1 Hz, 1H), 1.76-1.61 (m, 5H), 1.57-1.48 (m, 2H), 1.34 (m, 1H), 1.23 (s, 9H), 1.04 (s, 9H) 1.01 (s, 9H), 0.97 (s, 9H), 0.89 (dd, *J* = 7.5, 7.5 Hz, 3H), 0.19 (s, 3H), 0.175 (s, 3H), 0.166 (s, 6H), 0.15 (s, 3H), 0.068 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 138.2, 136.6, 135.6 (4C), 133.75, 133.67, 129.4 (2C), 128.3 (2C), 127.2 (2C), 127.54 (4C), 127.48, 119.3, 100.6, 74.1, 72.1, 70.4, 69.0, 68.4, 67.9, 62.1, 55.7, 48.4, 47.6, 47.0, 44.6, 43.1, 42.7, 37.1, 37.0, 26.93, 26.86 (3C), 26.1, 25.9 (3C), 25.8 (6C), 19.9, 19.2, 19.1, 18.0, 17.8, 12.3, -4.2 (4C), -4.7, -4.8; high resolution mass spectrum (ES+) *m/z* 1155.6967 [(M+Na$^+$) calculated for: $C_{64}H_{108}O_9Si_4$+Na 1155.6968].



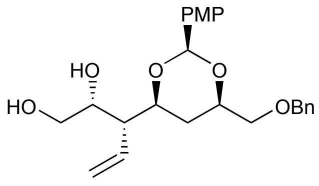
(-)-**56**

Bis-ketal (-)-56: $[\alpha]_D^{23}$ -8.70° (c = 0.38, $CHCl_3$); IR (film) 3471, 2930, 2856, 1471, 1361, 1253, 1090, 861, 836, 774, 739, 701 cm $^{-1}$; ^{1}H NMR (500 MHz, C_6D_6) δ 7.85 (m, 4H), 7.28 (m, 6H), 7.18 (m, 4H), 7.04 (m, 1H), 5.26 (ddd, *J* = 9.9, 9.9, 17.1 Hz, 1H), 5.07 (dd, *J* = 2.0, 17.1 Hz, 1H), 5.03 (dd, *J* = 2.1, 10.1 Hz, 1H) 4.53 (dd, *J* = 6.0, 6.0 Hz,1H), 4.39 (s, 2H), 4.19 (m, 1H), 3.97 (ddd, *J* = 4.8, 10.6, 10.6 Hz, 1H), 3.87 (m, 3H), 3.68 (ddd, *J* = 2.33, 10.3, 10.3 Hz, 1H), 3.59 (dd, *J* = 5.6, 9.3 Hz, 1H), 3.55 (bs, 1H), 3.42 (s, 3H), 3.41 (dd, *J* = 5.8, 9.2 Hz, 1H) 3.01 (s, 3H), 2.66 (dd, *J* = 4.6, 13.4 Hz, 1H), 2.25 (dd, *J* = 7.9, 14.1 Hz, 1H), 2.15 (ddd, *J* = 2.8, 2.8, 14.7 Hz, 1H), 2.04 (m, 3H), 1.90 (m, 1H), 1.88 (m, 1H), 1.81 (d, *J* = 1.5 Hz, 1H), 1.70 (m, 5H), 1.49 (m, 1H), 1.39 (m, 1H), 1.29 (m, 1H), 1.22 (s, 9H), 1.16 (m, 1H), 1.00 (s, 9H), 0.99 (m, 9H), 0.94 (dd, *J* = 7.5, 7.5 Hz, 3H), 0.21 (s, 3H), 0.20 (s, 3H), 0.096 (s, 3H), 0.049 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 136.6, 135.6 (2C), 135.5 (2C), 134.0, 133.9, 129.5, 129.4, 128.3 (2C), 127.7 (2C), 127.52 (2C), 127.49 (3C), 119.2, 100.6, 98.8, 74.1, 73.3, 72.6, 70.8, 67.8, 67.7, 66.1, 63.1, 55.7, 47.7, 47.2, 43.3, 43.0, 40.3, 37.1, 31.51, 31.46, 26.9 (3C), 25.8 (3C), 25.7 (3C), 19.1, 18.7, 18.0, 17.9, 12.6, -3.9 (4C), -4.3, -4.5; high resolution mass spectrum (ES+) *m/z* 1055.6225 [(M+Na$^+$) calculated for: $C_{59}H_{96}O_9Si_3$+Na 1055.6260].



(-)-S22

PMP-Acetal (-)-**S22:** Diol (+)-**35** (10.02 g, 19.09 mmol) and PPTS (239 mg, 0.954 mg) were placed in a flask equipped with a short path distillation apparatus. Toluene (125 mL) and 4-methoxybenzaldehyde dimethyl acetal (4.22 mL, 24.8 mmol) were added. The reaction was heated to 80 °C and the methanol was removed as it formed via distillation. After 40 min the reaction was quenched by addition of excess Et_3N. After cooling to room temperature the toluene was washed with water and brine, dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography (95:5 hexanes:EtOAc) afforded acetal (-)-**S22** in 91% yield (11.26 g, 17.51 mmol): $[\alpha]_D^{23}$ -25.49° (c = 0.97, C_6H_6); IR (film) 2931, 2858, 1616, 1517, 1465, 1390, 1251, 1152, 1107, 1034, 1010, 918, 834, 778 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.33 (m, 4H), 7.29 (m, 1H), 6.89 (m, 2H), 5.66 (ddd, *J* = 10.2, 10.2, 17.3 Hz, 1H), 5.51 (s, 1H), 5.18 (dd, *J* = 2.3, 10.3 Hz, 1H), 5.11 (dd, *J* = 2.2, 17.3 Hz, 1H), 4.61 (d, *J* = 12.4 Hz, 1H), 4.56 (d, *J* = 12.3 Hz, 1H), 4.22 (ddd, *J* = 1.4, 5.9, 7.4 Hz, 1H), 4.04 (dddd, *J* = 2.3, 5.0, 6.6, 11.4 Hz, 1H), 3.88 (m, 1H), 3.82 (s, 3H), 3.63 (dd, *J* = 6.07, 10.3 Hz, 1H), 3.50 (dd, *J* = 4.6, 10.3 Hz, 1H), 3.44 (dd, *J* = 5.9, 9.8 Hz, 1H), 3.34 (dd, *J* = 7.7, 9.8 Hz, 1H), 2.41 (ddd, *J* = 1.2, 10.0, 10.0 Hz, 1H), 1.66 (ddd, *J* = 2.3, 2.3, 13.3 Hz, 1H), 1.32 (ddd, *J* = 11.4, 11.4, 13.2 Hz, 1H), 0.882 (s, 9H), 0.878 (s, 9H), 0.031 (s, 3H), 0.017 (s, 6H), 0.013 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 138.3, 133.4, 131.3, 128.3 (2C), 127.8 (2C), 127.6, 127.5 (2C), 119.4, 113.4 (2C), 100.4, 76.3, 74.0, 73.5, 73.1, 69.6, 65.3, 55.2, 52.6, 32.9, 26.0 (3C), 25.9 (3C), 18.3, 18.1, -4.0, -5.0, -5.3, -5.4; high resolution mass spectrum (ES+) *m/z* 643.3864 [(MH^+) calculated for: $C_{36}H_{58}O_6$+H 643.3850].



(-)-**S23**

Diol (-)-**S23:** Acetal (-)-**S22** (12.84 g, 19.98 mmol) was dissolved in dry THF (100 mL) and TBAF (15.67 g, 59.93 mmol) was added. The reaction stirred for 2 h after which a saturated solution of NH_4Cl was added. The organic solvent was removed under reduced pressure and the resulting slurry was dissolved in EtOAc and distilled water and the layers were separated. The aqueous layer was extracted twice with EtOAc and the combined organic material was washed with brine, dried over $MgSO_4$ and concentrated to afford an orange oil. Flash chromatography (4:1 to 3:1 hexanes:EtOAc) provided diol (-)-**S23** as a white solid in 87% yield (7.20 g, 17.37 mmol). X-Ray quality crystals were obtained via vapor diffusion from hexanes/EtOAc, melting point 104-106 °C: $[\alpha]_D^{23}$ -7.03° (c = 0.37, C_6H_6); IR (film) 3435, 2917, 2861, 1617, 1517, 1455, 1248, 1146, 1110, 1025, 1007, 830 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (m, 2H), 7.30 (m, 2H), 7.18 (m, 2H), 7.09 (m, 1H), 6.82 (m, 2H), 5.74 (ddd, J = 10.2, 10.2, 17.3 Hz, 1H), 5.43 (s, 1H), 4.98 (dd, J = 2.0, 10.3 Hz, 1H), 4.87 (dd, J = 2.1, 17.3 Hz, 1H), 4.40 (s, 2H), 4.13 (ddd, J = 3.3, 3.3, 7.3 Hz, 1H), 3.86 (m, 2H), 3.54 (dd, J = 5.6, 10.1 Hz, 1H), 3.45 (dd, J = 8.3, 10.9 Hz, 1H), 3.64 (dd, J = 4.8, 10.2 Hz, 1H), 3.35 (m, 1H), 3.27 (s, 3H), 2.37 (bs, 1H), 2.12 (m, 1H), 1.42 (m, 2H), 1.31 (bs, 1H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 160.0, 138.1, 133.6, 130.7, 128.3 (2C), 127.7 (2C), 127.6, 127.3 (2C), 119.6, 113.6 (2C), 100.7, 76.3, 76.1, 73.5, 72.8, 70.8, 65.3, 55.2, 52.3, 32.3; high resolution mass spectrum (ES+) *m/z* 415.2115 [(MH^+) calculated for: $C_{24}H_{30}O_6$+H 415.2121].[6]

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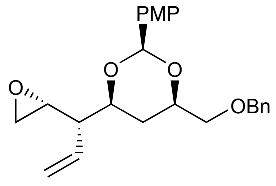
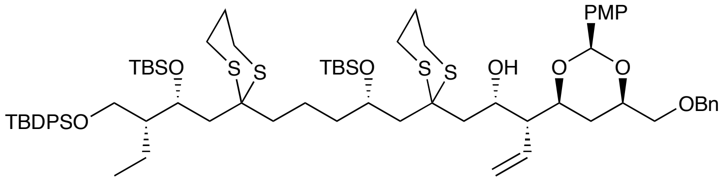
[6] CCDC 7275131contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



(-)-**57**

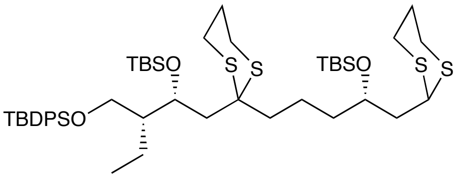
PMP Acetal Epoxide (-)-**57**: Sodium hydride (1.40 g, 55.4 mmol) was placed in a flask, THF (100 mL) was added and the flask was cooled to 0 °C in an ice bath. Diol (-)-**S23** (5.90 g, 14.2 mmol) was dissolved in THF (75 mL) and added to the NaH slurry via cannula. After 30 min trisylimidazole (5.00 g, 14.9 mmol) was added as a solution in THF (75 mL). The reaction stirred and additional 30 min at 0 °C. When judged complete by TLC, MeOH was added until the white solid was completely dissolved. The reaction mixture was diluted with Et_2O (300 mL), washed with saturated NH_4Cl and brine, dried over $MgSO_4$ and concentrated. The white oil was purified using flash column chromatography (4:1 hexanes:EtOAc) to furnish desired epoxide (-)-**57** as an amorphous solid in 95% yield (5.63 g, 14.2 mmol): $[\alpha]_D^{23}$ -0.83° (c = 0.37, C_6H_6); IR (film) 2954, 2907, 2854, 1247, 1171, 1102, 1028, 919, 828, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.30 (m, 2H), 7.18 (m, 2H), 7.10 (m, 1H), 6.85 (m, 2H), 5.55 (ddd, *J* = 9.0, 9.6, 17.8 Hz, 1H), 5.43 (s, 1H), 5.04 (m, 2H), 4.43 (d, *J* = 12.3 Hz, 1H), 4.40 (d, *J* = 12.3 Hz, 1H), 3.83 (dddd, *J* = 4.8, 4.8, 6.7, 10.4 Hz, 1H), 3.69 (ddd, *J* = 4.3, 7.1, 8.5 Hz, 1H), 3.55 (dd, *J* = 5.6, 10.1 Hz, 1H), 3.37 (dd, *J* = 4.8, 10.1 Hz, 1H), 3.29 (s, 3H), 3.18 (ddd, *J* = 2.6, 4.1, 4.7 Hz, 1H), 2.43 (dd, *J* = 3.8, 5.3 Hz, 1H), 2.39 (dd, *J* = 2.6, 5.3 Hz, 1H), 2.13 (ddd, *J* = 4.8, 8.6, 8.6 Hz, 1H), 1.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 138.1, 132.8, 131.0 128.3 (2C), 127.7 (2C), 127.6, 127.3 (2C), 119.8, 113.5 (2C), 100.4, 76.0, 73.5, 72.9, 55.2, 51.8, 51.4, 46.2, 32.8 an additional carbon is visible at 76.9 ppm in the benzene spectra of (-)-**57**; high resolution mass spectrum (ES+) *m/z* 397.1999 [(MH^+) calculated for: $C_{24}H_{28}O_5$+H 397.2015].



58

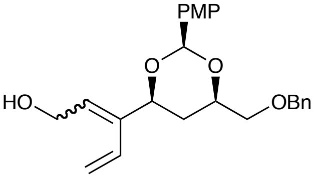
Bis-dithiane 58: 2-*tert*-Butyldimethylsilyl-1,3-dithiane (**8**), epoxide (-)-**44** and epoxide (-)-**57** were placed in separate flasks and each azeotroped three times with toluene and further dried under high vacuum overnight. Dithiane **8** (84 mg, 0.36 mmol) was then dissolved in Et_2O (3.2 mL) and cooled to -78 °C in a dry ice/acetone bath. The dithiane was treated with *t*-BuLi (1.4 M, 0.25 mL, 0.36 mmol) and the flask was placed in a -45 °C bath for 50 min. Epoxide (-)-**44** (200 mg, 0.30 mmol) was dissolved in Et_2O (2.5 mL) and added via cannula to the dithiane solution. The reaction was removed from the -78 °C bath and warmed to -25 °C over 35 min. The reaction then stirred an additional 40 min at -25 °C before being re-cooled to -78 °C. Epoxide (-)-**57** (159 mg, 0.40 mmol) was dissolved in THF (4 mL) and HMPA (0.51 mL, 3.0 mmol) was added to the flask. The epoxide mixture was added to the reaction via cannula and the solution turned yellow. The reaction stirred at -78 °C for 10 min before being warmed to -45 °C for 1.5 h. The flask was then warmed to room temperature over the course of 2 h after which the reaction was quenched with NH_4Cl and diluted with EtOAc. The aqueous layer was extracted twice with EtOAc and the combined organic layers were washed with brine and dried over $MgSO_4$. The desired adduct **58** was isolated following column chromatography (95:5 to 9:1 to 4:1 hexanes:EtOAc) in 6% yield (24 mg, 0.018 mmol) along with (+)-**59** (107 mg, 0.12 mmol, 40%) and diene (+)-**60** (37 mg, 0.093, 24%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (m, 4H), 7.45 (m, 2H), 7.36 (m, 11 H), 6.87 (m, 2H), 5.75 (ddd, *J* = 10.2, 10.2, 17.4 Hz, 1H), 5.55 (s, 1H), 5.23 (dd, *J* = 2.0, 10.4 Hz, 1H), 5.18 (dd, *J* = 2.0, 17.2 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.59 (m, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.34 (m 1H), 4.07 (m, 3H), 3.79 (s, 3H), 3.69 (m, 2H), 3.63 (m, 1H), 3.52 (m, 1H), 2.76 (m, 9H), 2.39-2.22 (m, 4H), 2.14 (m, 1H), 1.88 (m, 7H), 1.75

(m, 1H), 1.64 (m, 2H), 1.60-1.37 (m, 7H), 1.10 (s, 9H), 0.88 (dd, *J* = 7.4, 7.4 Hz, 3H), 0.86 (s, 9H), 0.83 (s, 9H), 0.11 (s, 3H), 0.064 (s, 3H), 0.057 (s, 3H), 0.051 (s, 3H), 0.031 (s, 3H).[7]



(+)-**59**

Bis-dithiane (+)-59: $[\alpha]_D^{23}$ +7.2° (c = 0.68, C_6D_6); IR (film) 2930, 2854, 1472, 1254, 1107, 836, 774, 701 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz) δ 7.88 (m, 4H), 7.30 (m, 6H), 4.70 (ddd, *J* = 2.3, 5.2, 5.2 Hz, 1H), 4.27 (dd, *J* = 5.4, 8.9 Hz, 1H), 4.21 (m, 1H), 3.98 (dd, *J* = 4.8, 10.0 Hz, 1H), 3.90 (dd, *J* = 6.8, 10.0 Hz, 1H), 2.52-2.44 (m, 6H), 2.38 (m, 3H), 2.22 (dd, *J* = 5.3, 15.3 Hz, 1H), 2.16 (ddd, *J* = 2.5, 8.1, 8,1 Hz, 1H), 2.13-2.04 (m, 3H), 1.98 (m, 1H), 1.82 (m, 2H), 1.66-1.45 (m, 9H), 1.27 (s, 9H), 1.05 (s, 9H), 1.00 (s, 9H), 0.97 (dd, *J* = 7.4, 7.4 Hz, 3H), 0.33 (s, 3H), 0.24 (s, 3H), 0.23 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.68 (2C), 135.67 (2C), 133.9, 133.8, 129.4 (2C), 128.3 (benzene), 127.53 (2C), 127.50 (2C), 69.6, 68.6, 62.5, 53.1, 49.2, 44.1, 42.7, 42.3, 39.5, 37.8, 31.5, 30.5, 30.3, 30.0, 27.0 (3C), 26.3, 26.1 (3C), 25.9 (3C), 25.1, 20.4, 19.7, 19.2, 18.1, 18.0, 12.6, -3.5, -4.1, -4.3, -4.5; high resolution mass spectrum (ES+) *m/z* 929.4406 [(M+Na$^+$) calculated for: $C_{47}H_{83}O_3S_4Si_3$+Na 929.4352].



(+)-**60**

Diene (+)-60: Diene (+)-**60** was isolated as a single olefin isomer of unknown geometry about the C(2-3) olefin: $[\alpha]_D^{23}$ +7.39° (c = 0.115, $CHCl_3$); IR (film) 3411, 2920, 2858, 1614, 1517, 1452, 1368,

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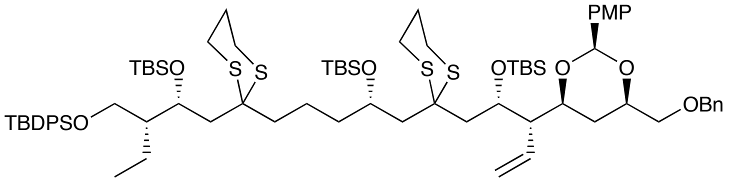
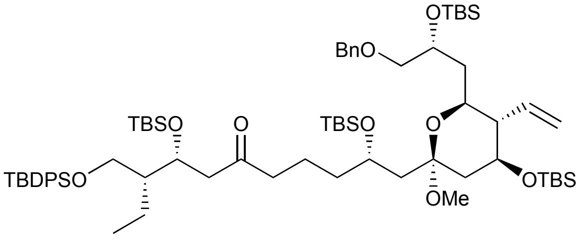
[7] Owing to the poor yield of the reaction used to prepare compound **58** (~6%) only a few milligrams of material was obtained. The structure was assigned using ^1H NMR. The major products derived from this reaction are fully characterized [see (+)-**59** and (+)-**60**].

1304, 1249, 1173, 1121, 1008, 913, 830 cm $^{-1}$; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 (m, 2 H), 7.34 (m, 4H), 7.28 (m, 1H), 6.89 (m, 2H), 6.30 (dd, *J* = 11.2, 17.7 Hz, 1H), 5.85 (dd, *J* = 6.9, 6.9 Hz, 1H), 5.57 (s, 1H), 5.33 (d, *J* = 17.7 Hz, 1H), 5.09 (d, *J* = 11.5 Hz, 1H), 4.82 (dd, *J* = 2.9, 11.8 Hz, 1H), 4.60 (d, *J* = 12.3 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.43 (m, 1H), 4.29 (m, 1H), 4.15 (m, 1H), 3.80 (s, 3H), 3.67 (dd, *J* = 5.7, 10.2 Hz, 1H), 3.53 (dd, *J* = 4.9, 10.2 Hz, 1H), 1.93 (bs, 1H), 1.80 (m, 2H); ^{13}C NMR (125 MHz, CDC$_3$) δ 160.0, 139.8, 138.1, 137.1, 131.9, 130.6, 128.5 (2C), 127.72 (2C), 127.66, 127.5 (2C), 113.7 (2C), 113.6, 101.7, 76.3, 75.0, 73.5, 72.7, 58.8, 55.2, 33.1; high resolution mass spectrum (ES+) *m/z* 419.1854 [(M+Na$^+$) calculated for $C_{24}H_{28}O_5$ +Na 419.1834].



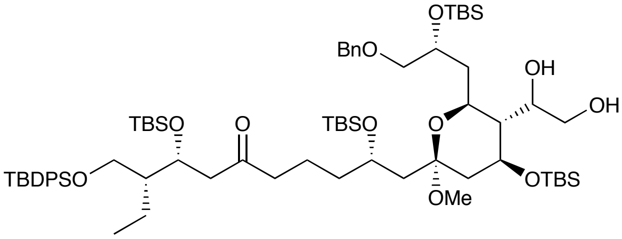
(-)-**S24**

Bis-dithiane (-)-**S24:** Linchpin adduct (-)-**61** (2.48 g, 1.90 mmol) was dissolved in dry CH$_2$Cl$_2$ (12.5 mL) and cooled to 0 °C in an ice bath. 2,6-Lutidine (1.33 mL, 11.4 mmol) was added followed by TBSOTf (0.88 mL, 3.80 mmol). After 1 h the reaction was quenched with saturated NH$_4$Cl (4 mL) and diluted with CH$_2$Cl$_2$. The layers were separated and the aqueous layer was extracted twice with CH$_2$Cl$_2$. The combined organic layers were washed with brine, dried over MgSO$_4$ and concentrated. The resulting colorless oil was purified using flash column chromatography (95:5 to 9:1 hexanes:EtOAc) to provide (-)-**S24** as a white foam in 93% yield (2.51 g, 1.77 mmol): $[\alpha]_D^{23}$ -13.57° (c = 0.76, C$_6$H$_6$); IR (film) 2948, 2930, 2861, 1600, 1466, 1431, 1105, 833, 774 cm $^{-1}$; ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 7.89 (m, 4H), 7.85 (m, 2H), 7.29 (m, 8H), 7.18 (m, 2H), 7.10 (m, 1H), 6.94 (m, 2H), 5.98 (ddd, *J* = 10.2, 10.2, 17.4 Hz, 1H), 5.70 (s, 1H), 5.32 (dd, *J* = 2.1, 17.4 Hz, 1H), 5.30 (dd, *J* = 2.2, 10.3 Hz, 1H), 5.21 (d, *J* = 8.6 Hz, 1H), 4.74 (ddd, *J* = 2.2, 5.0, 5.0 Hz, 1H), 4.43 (d, *J* = 12.3 Hz, 1H), 4.40 (d, *J* = 12.3 Hz, 1H), 4.34 (m, 1H), 4.04 (m, 2H), 3.97 (dd, *J* = 5.0, 10.6 Hz, 1H), 3.92 (dd, *J* = 6.7, 10.0 Hz, 1H), 3.58 (dd, *J* = 6.0, 10.2 Hz, 1H), 3.37 (dd, *J* = 4.6 10.2 Hz, 1H), 3.33 (s, 3H), 3.02 (dd, *J* = 9.8, 9.8 Hz, 1H), 2.76 (dd, *J* = 8.7, 15.6 Hz, 1H), 2.59-2.38 (m, 11H), 2.21 (m, 2H), 2.16 (m, 1H), 2.13 (d, *J* = 15.2 Hz, 1H), 2.03 (m, 1H), 1.94 (m, 3H), 1.73 (m, 1H), 1.68 (ddd, *J* = 2.2, 2.2, 13.2 Hz, 1H), 1.60-1.45 (m, 7 H), 1.28 (s, 9H), 1.08 (s, 9H), 1.07 (s, 9H), 1.02 (s, 9H), 0.99 (dd, *J* = 7.5, 7.5, Hz, 3H), 0.40 (s, 3H), 0.35 (s, 3H), 0.299 (s, 3H), 0.295 (s, 3H), 0.29 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 138.2, 135.7 (2C), 135.6 (2C), 134.0, 133.84, 133.78, 131.5, 129.4 (2C), 128.3 (2C), 127.7 (2C), 127.55, 127.53 (2C), 127.49 (4C), 120.4, 113.2 (2C), 99.8, 76.2, 74.5, 73.5, 73.2, 70.0, 69.5, 66.7, 62.7, 57.6, 55.2, 53.3, 52.3, 49.3, 48.8, 46.5, 42.7, 39.8, 39.4, 32.9, 26.9 (3C), 26.6, 26.41, 26.37, 26.1 (9C), 25.6, 25.1, 24.7, 20.2, 19.6, 19.2, 18.2, 18.1, 18.0, 12.7, -3.2, -3.5, -3.7, -4.0, -4.1, -4.9; high resolution mass spectrum (ES+) *m/z* 1439.7115 [(M+Na$^+$) calculated for $C_{77}H_{124}O_8S_4Si_4$+Na 1439.7154].



(-)-**63**

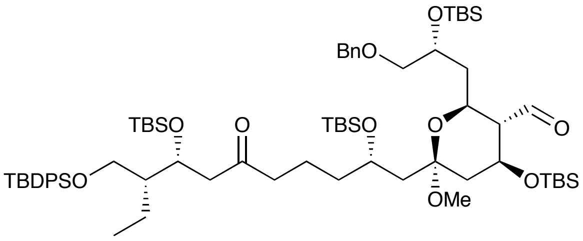
TBS Ether (-)-**63:** Ketal (-)-**55** (533, 0.470 mmol) and DMAP (57 mg, 0.47 mmol) were dissolved in dry pyridine (4 mL) and cooled to 0 °C in an ice bath. TBSOTf (0.21 mL, 0.94 mmol) was added and the reaction stirred for 1.5 h. The reaction was then diluted with CH_2Cl_2 and washed with NH_4Cl and brine, dried over $MgSO_4$ and concentrated to give a yellow oil. Column chromatography provided ether (-)-**63** as a colorless oil in 91% yield (538 mg, 0.431 mmol): $[\alpha]_D^{23}$ -10.94° (c = 0.16, $CHCl_3$); IR (film) 2955, 2929, 2887, 2856, 1717, 1471, 1428, 1361, 1254, 1093, 836, 775, 701 cm $^{-1}$; ^{1}H NMR (500 MHz, C_6D_6) δ 7.85 (m, 4H), 7.36 (m, 2H), 7.30 (m, 6H), 7.24 (m, 2H), 7.12 (m, 1H), 5.44 (ddd, *J* = 9.7, 9.7, 17.3 Hz, 1H), 5.12 (dd, *J* = 1.6, 17.6 Hz, 1H), 5.05 (dd, *J* = 1.5, 10.2 Hz, 1H), 4.72 (ddd, *J* = 3.5, 3.5, 7.9 Hz, 1H), 4.47 (s, 2H), 4.31 (m, 1H), 4.05 (m, 2H), 3.90 (dd, *J* = 5.1, 10.1 Hz, 1H), 3.86 (dd, J = 5.3, 10.1 Hz, 1H), 3.78 (dd, J = 10.2, 10.2 Hz, 1H), 3.67 (dd, J = 7.0, 9.7 Hz, 1H), 3.57 (dd, J = 3.4, 9.7 Hz, 1H), 3.14 (s, 3H), 2.66 (dd, J = 8.3, 16.1 Hz, 1H), 2.37 (m, 2H), 2.25 (app t, J = 6.8 Hz, 2H), 2.13 (m, 2H), 2.00 (ddd, J = 9.7, 9.7, 9.7 Hz, 1H), 1.92 (dd, J = 5.4, 14.9 Hz, 1H), 1.83 (m, 1H), 1.74 (m, 3H), 1.61 (m, 1H), 1.54 (m, 2H), 1.35 (m, 2H), 1.23 (s, 9H), 1.053 (s, 9H), 1.050 (s, 9H), 1.02 (s, 9H), 0.97 (s, 9H), 0.89 (dd, J = 7.4, 7.4 Hz, 3H), 0.24 (s, 3H), 0.23 (s, 3H), 0.21 (s, 3H), 0.19 (s, 3H), 0.16 (s, 6H), 0.15 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 138.7, 137.2, 135.6 (4C), 133.75, 133.67, 129.5 (2C), 128.1 (2C), 127.6 (4C), 127.5 (2C), 127.3, 118.8, 100.0, 74.8, 73.1, 69.2, 69.0, 68.5, 68.3, 67.9, 62.1, 55.6, 48.4, 47.7, 47.0, 44.8, 43.2, 42.8, 38.8, 36.9, 26.9 (3C), 26.0 (3C), 25.9 (3C), 25.0 (6C), 19.9, 19.18, 19.16, 18.1, 18.0, 17.9 (2C),12.3, -4.2 (4C), -4.4, -4.6, -4.7, -4.8; high resolution mass spectrum (ES+) m/z 1269.7821 [(M+Na$^+$) calculated for $C_{70}H_{122}O_9Si_5$+Na 1269.7833].



(-)-**S25**

Diol (-)-**S25:** Alkene (-)-**63** (287 mg, 0.230 mmol) was dissolved in THF (4 mL) and water (1 mL) was added. 4-Methylmorpholine *N*-oxide (67.0 mg, 0.575 mmol) was added followed by 5 drops of a 4% solution of OsO_4 in water. The flask was capped tightly with a yellow cap and allowed to stir at room temperature for 5 days. The reaction mixture was quenched with solid Na_2SO_3 and diluted with EtOAc. The aqueous layer was extracted three times with EtOAc, the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to give a yellow oil. Purification via flash chromatography (95:5 to 3:1 hexanes:EtOAc) afforded diol (-)-**S25** as a colorless oil in 73% yield (215 mg, 0.168 mmol). The starting material was recovered (19%) and recycled: $[\alpha]^{23}_{D}$ -4.13° (c = 1.49, C_6H_6); IR (film) 3434, 2932, 2861, 1718, 1591, 1467, 1254, 1101, 836, 776, 702 cm $^{-1}$; ^{1}H NMR (500 MHz,

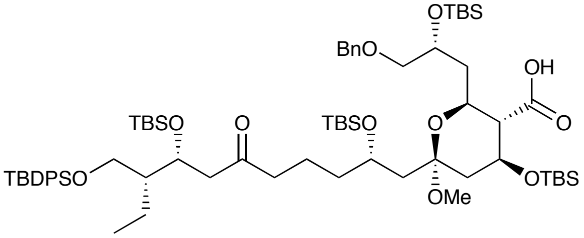
C_6D_6) δ 7.85 (4H), 7.32 (8H), 7.20 (m, 2H), 7.10 (1H), 4.71 (ddd, *J* = 3.5, 3.5, 7.5 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.43 (m, 2H), 4.41 (d, *J* = 12.2 Hz, 1H), 4.05 (m, 2H), 3.89 (m, 3H), 3.76 (dd, *J* = 8.2, 10.8 Hz, 1H) 3.64 (dd, *J* = 6.0, 9.9 Hz, 1H), 3.56 (dd, *J* = 3.8, 9.8 Hz, 1H), 3.52 (dd, *J* = 3.3, 11.0 Hz, 1H), 3.07 (s, 3H), 2.66 (dd, *J* = 8.3, 16.0 Hz, 1H), 2.34 (m, 3H), 2.27 (app dd, *J* = 7.1, 7.1 Hz, 2H), 2.19 (bs, 1H), 2.15 (dd, *J* = 7.9, 14.9 Hz, 1H), 1.91 (m, 3H), 1.80 (m, 2H), 1.70 (dd, *J* = 11.0, 12.3 Hz, 1H), 1.57 (m, 4H), 1.34 (m, 2H), 1.23 (s, 9H), 1.07 (s, 9H), 1.05 (s, 9H), 1.01 (s, 9H), 0.96 (s, 9H), 0.89 (dd, *J* = 7.5, 7.5 Hz, 3H), 0.27 (s, 3H), 0.24 (s, 3H), 0.21 (s, 6H), 0.20 (s, 3H), 0.17 (s, 3H), 0.161 (s, 3H), 0.159 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.8, 138.3, 135.6 (4C), 133.75, 133.65, 129.5 (2C), 128.3 (2C), 127.7 (2C), 127.6 (4C), 127.5, 99.3, 74.5, 73.3, 70.7, 69.1, 69.0, 68.7, 67.3, 66.1, 65.3, 62.1, 50.3, 48.4, 47.7, 46.9, 44.7, 43.1, 43.0, 38.4, 36.4, 26.9 (3C), 25.9 (6C), 25.82 (3C), 25.80 (3C), 20.0, 19.5, 19.2, 18.1, 18.0, 17.92, 17.89, 12.3, -3.5, -4.2, -4.3, -4.4, -4.5, -4.6, -4.7, -4.8; high resolution mass spectrum (ES+) *m/z* 1303.7894 [(M+Na$^+$) calculated for $C_{70}H_{124}O_{11}Si_5$+Na 1303.7888].



(-)-**64**

Aldehyde (-)-**64:** Diol (-)-**S25** (123 mg, 0.096 mmol) was dissolved in benzene (1.5 mL) and $Pb(OAc)_4$ (85 mg, 0.19 mmol) was added. After 10 min H_2O (2 mL) and CH_2Cl_2 (2 mL) were added to the reaction and a brown solid formed. The reaction mixture was filtered through Celite and rinsed with CH_2Cl_2. The layers were separated and the aqueous layer was extracted once with CH_2Cl_2. The organic layers were combined and washed once with half saturated $NaHCO_3$, once with H_2O and once with brine. The organic layer was dried over $MgSO_4$ and concentrated to afford aldehyde (-)-**64** as a colorless oil in 95% yield (114 mg, 0.91 mmol). The aldehyde was used without further purification: $[\alpha]_D^{23}$ -1.18° (c =

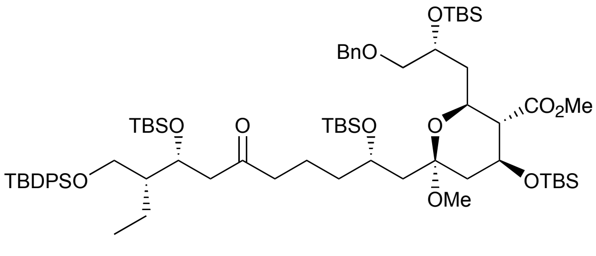
0.26, $CHCl_3$); IR (film) 2956, 2929, 2857, 1739, 1718, 1472, 1362, 1256, 1112, 836, 776, 701 cm $^{-1}$; ^1H NMR (500 MHz, C_6D_6) δ 9.78 (d, *J* = 3.4 Hz, 1H), 7.85 (m, 4H), 7.28 (m, 10H), 7.12 (m, 1H), 4.71 (ddd, *J* = 3.7, 3.7, 11.4 Hz, 1H), 4.61 (ddd, *J* = 4.8, 10.8, 10.8 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 11.9 Hz, 1H), 4.25 (m, 1H), 4.16 (m, 1H), 4.01 (m, 1H), 3.91 (dd, *J* = 5.2, 10.4 Hz, 1H), 3.86 (dd, *J* = 5.2, 10.0 Hz, 1H), 3.61 (dd, *J* = 6.1, 9.9 Hz, 1H), 3.50 (dd, *J* = 4.1, 9.7 Hz, 1H), 3.08 (s, 3H), 2.67 (dd, *J* = 8.4, 16.5 Hz,1 H), 2.50 (ddd, *J* = 3.0, 10.0, 10.0 Hz, 1H), 2.37 (m, 2H), 2.24 (app t, *J* = 7.5 Hz, 2H), 2.09 (dd, *J* = 5.2, 14.5 Hz, 1H), 1.88 (m, 2H), 1.77 (m, 2H), 1.71 (m, 2H), 1.62 (m, 1H), 1.54 (m, 2H), 1.35 (m, 2H), 1.23 (s, 9H), 1.04 (s, 18H), 0.97 (s, 9H), 0.95 (s, 9H), 0.89 (dd, *J* = 7.6, 7.6 Hz, 3H), 0.22 (s, 3H), 0.20 (s, 3H), 0.19 (s, 3H), 0.18 (s, 3H), 0.16 (s, 6H), 0.12 (s, 3H), 0.034 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 203.4, 138.5, 135.6 (4C), 133.7, 133.6, 129.51, 129.48, 128.2 (2C), 127.6 (6C), 127.4, 100.2, 74.7, 73.2, 69.0, 68.6, 68.4, 66.2, 64.5, 62.6, 62.1, 48.4, 47.9, 47.0, 44.7, 42.9, 42.3, 39.0, 36.9, 26.9 (3C), 25.9 (3C), 25.82 (3C), 25.79 (3C), 25.6 (3C), 20.0, 19.2, 19.0, 18.1, 18.0, 17.9, 17.7, 12.3, -4.1, -4.2 (2C), -4.6, -4.75, -4.83 (2C), -4.9; high resolution mass spectrum (ES+) *m/z* 1271.7710 [(M+Na$^+$) calculated for $C_{69}H_{120}O_{10}Si_5$+Na 1271.7626].



(-)-**S26**

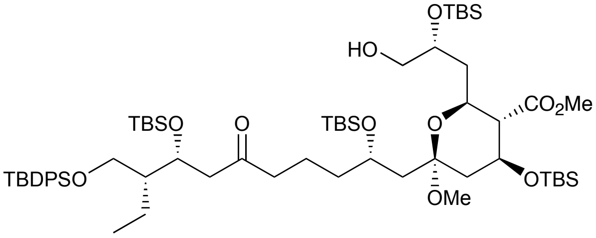
Acid (-)-**S26:** Aldehyde (-)-**64** (360 mg, 0288 mmol) was placed in a flask with THF (3 mL), *tert*-butyl alcohol (3 mL) and H_2O (1.5 mL). The flask was placed in an ice bath and 2-methyl-2-butene (3 mL) was added followed by NaH_2PO_4 (539 mg, 3.46 mmol) and $NaClO_2$ 80% (391 mg, 3.46 mmol). After 2 h the reaction was judged complete by TLC and saturated NH_4Cl and EtOAc were added to the flask. The aqueous layer was extracted three times with EtOAc and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Acid (-)-**S26** was obtained as a colorless oil in

86% yield (315 mg, 0.249 mmol) following column chromatography (4:1 hexanes:EtOAc): $[\alpha]_D^{23}$ -2.50° (c = 0.26, $CHCl_3$); IR (film) 3390, 2959, 2930, 2857, 1708, 1471, 1362, 1255, 1107, 836, 776, 702 cm $^{-1}$; ^{1}H NMR (500 MHz, C_6H_6) δ 7.85 (m, 4H), 7.37 (m, 2H), 7.26 (m, 9H), 4.71 (ddd, *J* = 4.5, 4.5, 7.6 Hz, 1H), 4.66 (ddd, *J* = 4.7, 10.4, 10.4 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 4.42 (d, *J* = 12.2 Hz, 1H), 4.30 (m, 1H), 4.20 (ddd, *J* = 1.9, 10.4, 10.4 Hz, 1H), 4.00 (m, 1H), 3.90 (dd, *J* = 5.0, 10.1 Hz, 1H), 3.87 (dd, *J* = 5.2, 10.0 Hz, 1H), 3.66 (dd, *J* = 6.9, 9.7 Hz, 1H), 3.55 (dd, *J* = 3.7, 9.8 Hz, 1H), 3.09 (s, 3H), 2.67 (dd, *J* = 8.4, 16.0 Hz, 1H), 2.50 (dd, *J* = 10.3, 10.3 Hz, 1H), 2.37 (m, 2H), 2.23 (app t, *J* = 7.1 Hz, 2H), 2.08 (dd, *J* = 5.6, 15.0 Hz, 1H), 1.88 (m, 1H), 1.86 (m, 2H), 1.76 (m, 2H), 1.63 (m, 2H), 1.61 (m, 1H), 1.52 (m, 2H), 1.35 (m, 2H), 1.23 (s, 9H), 1.06 (s, 9H), 1.04 (s, 9H), 1.03 (s, 9H), 0.96 (s, 9H), 0.89 (dd, *J* = 7.4, 7.4 Hz, 3H), 0.24 (s, 3H), 0.22 (s, 3H), 0.19 (s, 3H), 0.182 (s, 3H), 0.177 (s, 6H), 0.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.5, 177.8, 138.5, 135.6 (4C), 133.7, 133.6, 129.5 (2C), 128.2 (2C), 127.6 (6C), 127.3, 100.2, 74.9, 73.1, 69.0, 68.7, 68.4, 67.6, 66.4, 62.1, 57.1, 48.4, 47.9, 47.0, 44.7, 42.9, 42.4, 38.9, 36.9, 26.9 (3C), 26.0 (3C), 25.8 (6C), 25.6 (3C), 20.0, 19.3, 19.1, 18.1, 18.0, 17.9, 17.7, 12.3, -4.1, -4.2, -4.3, -4.6, -4.7, -4.80, -4.83, -5.0; high resolution mass spectrum (ES+) *m/z* 1287.7530 [(M+Na$^+$) calculated for $C_{69}H_{120}O_{11}Si_5$+Na 1287.7575].



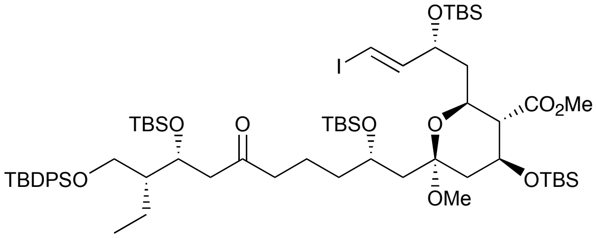
(-)-**65**

Methyl Ester (-)-**65:** Carboxylic acid (-)-**S26** (198 mg, 0.156 mmol) was dissolved in a toluene:MeOH solution (1:1, 4 mL)) and a 0.5 M solution of $TMSCHN_2$ in Et_2O was added dropwise until the reaction solution remained yellow. A stream of argon was then bubbled through the reaction for 30 min before concentrating under reduced pressure. Methyl ester (-)-**65** was obtained in 98% yield (196 mg, 0.153 mmol) and was used without further purification: $[\alpha]_D^{23}$ -3.52° (c = 0.36, $CHCl_3$); IR (film) 2948, 2928, 2856, 1734, 1716, 1472, 1361, 1256, 1105, 836, 776, 701 cm $^{-1}$; ^{1}H NMR (500 MHz, C_6D_6) δ 7.85 (m, 4H), 7.37 m, 2H), 7.30 (m, 6H), 7.26 (m, 2H), 7.12 (m 1H), 4.70 (m, 2H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.41 (d, *J* = 12.1 Hz, 1H), 4.23 (m, 1H), 4.02 (m, 1H), 3.91 (dd, *J* = 5.0, 10.1 Hz, 1H), 3.87 (d, *J* = 5.2, 10.1 Hz, 1H), 3.66 (dd, *J* = 6.8, 9.8 Hz, 1H), 3.54 (dd, *J* = 3.7, 9.8 Hz, 1H), 3.43 (s, 3H), 3.10 (s, 3H), 2.67 (dd, *J* = 8.4, 16.0 Hz, 1H), 2.55 (dd, *J* = 10.3, 10.3 Hz, 1H), 2.38 (m, 2H), 2.23 (app t, *J* = 6.8 Hz, 2H), 2.09 (dd, *J* = 5.6, 15.0 Hz, 1H), 1.89 (m, 3H), 1.73 (m, 3H), 1.71 (dd, *J* = 10.9, 13.0 Hz, 1H), 1.61 (m, 1H), 1.53 (m, 2H), 1.35 (m, 2H), 1.23 (s, 9H), 1.044 (s, 9H), 1.041 (s, 9H), 0.99 (s, 9H), 0.97 (s, 9H), 0.89 (dd, *J* = 7.5, 7.5 Hz, 3H), 0.221 (s, 3H), 0.215 (s, 3H), 0.19 (s, 3H), 0.18 (s, 3H), 0.17 (s, 3H), 0.16 (s, 6H), 0.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 173.0, 138.6, 135.6 (4C), 133.7, 133.6, 129.50, 129.49, 128.2 (2C), 127.6 (4C), 127.5 (2C), 127.3, 100.2, 74.6, 73.1, 69.0, 68.8, 68.5, 67.6, 66.7, 62.1, 57.4, 51.4, 48.4, 47.8, 46.9, 44.7, 42.9, 42.4, 39.0, 36.9, 26.9 (3C), 25.9 (3C), 25.83 (3C), 25.79 (3C), 25.5 (3C), 20.0, 19.2, 19.1, 18.1, 18.0, 17.9, 17.7, 12.3, -4.1, -4.2 (2C), -4.67, -4.74, -4.8, -4.9, -5.2; high resolution mass spectrum (ES+) *m/z* 1301.7754 [(M+Na$^+$) calculated for $C_{70}H_{122}O_{11}Si_5$+Na 1301.7731].



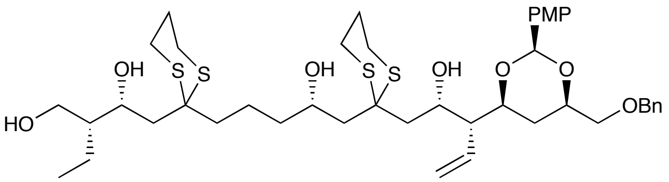
(-)-**66**

Alcohol (-)-**66:** Methyl ester (-)-**65** (30 mg, 0.024 mmol) was dissolved in a EtOAc:MeOH solution (1:1, 3 mL) and D*t*BMP (25 mg, 0.12 mmol) was added. The solvent was placed under vacuum and backfilled with argon three times before addition of $Pd(OH)_2$ 20 wt% on carbon (37 mg). The solution was placed under vacuum and backfilled with argon an additional three times. The flask was placed under vacuum a fourth time and a H_2 filled balloon was inserted through the septa. The reaction stirred overnight under 1 atm of hydrogen. The reaction mixture was filtered through Celite, rinsed with EtOAc and concentrated. The desired alcohol (-)-**66** was isolated as a colorless oil in 71% yield (20 mg, 0.017 mmol) following column chromatography (9:1 hexanes:EtOAc): $[\alpha]_D^{23}$ -6.25° (c = 0.16, $CHCl_3$); IR (film) 3460, 2955, 2930, 2887, 2857, 1736, 1718, 1472, 1430, 1361, 1255, 1110, 837, 776, 703 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.85 (m, 4H), 7.29 (m, 6H), 4.70 (m, 2H), 4.16 (ddd, *J* = 4.8, 7.1, 11.1 Hz, 1H), 4.07 (m, 1H), 4.00 (m, 1H), 3.91 (dd, *J* = 4.5, 9.8 Hz, 1H), 3.86 (dd, *J* = 5.2, 9.8 Hz, 1H), 3.71 (m, 2H), 3.45 (s, 3H), 3.10 (s, 3H), 2.67 (dd, *J* = 8.4, 16.0 Hz, 1H), 2.55 (dd, *J* = 10.3, 10.3 Hz, 1H), 2.37 (m, 2H), 2.21 (app dd, *J* = 7.2, 7.2 Hz, 2H), 2.08 (dd, *J* = 5.2, 15.0 Hz, 1H), 1.96 (dd, *J* = 6.4, 6.4 Hz, 1H), 1.89 (m, 2H), 1.71 (dd, *J* = 11.2, 13.1 Hz, 1H), 1.68 (m, 3H), 1.53 (m, 2H), 1.35 (m, 2H), 1.23 (s, 9H), 1.04 (s, 9H), 0.99 (s, 9H), 0.97 (s, 18H), 0.89 (dd, *J* = 7.1, 7.1 Hz, 3H), 0.19 (s, 3H), 0.18 (s, 3H), 0.17 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H), 0.099 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 172.9, 135.6 (4C), 133.7, 133.6, 129.5 (2C), 127.6 (4C), 100.6, 69.7, 69.0, 68.4, 67.5, 66.6, 65.9, 62.0, 57.0, 51.6, 48.4, 48.0. 47.0, 44.6, 42.9, 42.4, 37.9, 37.1, 26.9 (3C), 26.0 (3C), 25.79 (3C), 25.52 (3C), 25.5 (3C), 20.0, 19.2, 19.0, 18.0 (2C), 17.9, 17.7, 12.3, -4.1, -4.16, -4.22, -4.7, -4.75, -4.83, -4.9, -5.2; high resolution mass spectrum (ES+) *m/z* 1211.7277 [(M+Na^+) calculated for $C_{63}H_{116}O_{11}Si_5$+Na 1211.7262].



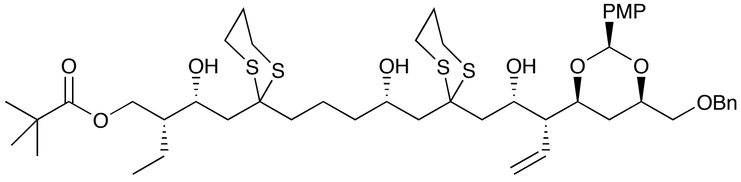
(-)-**67**

Vinyl Iodide (-)-**67:** Alcohol (-)-**66** (30 mg, 0.025 mmol) and SO_3•pyridine (20 mg, 0.13 mmol) were dissolved in CH_2Cl_2 (1 mL) and cooled to 0 °C in an ice bath. Diisopropylethylamine (3 drops) was added followed by DMSO (3 drops). After 1.5 h the reaction was quenched with saturated $NaHCO_3$ and extracted three times with CH_2Cl_2, dried over $MgSO_4$ and concentrated. The unpurified aldehyde was placed in a flask with CHI_3 (16 mg, 0.042 mmol) and D*t*BMP (10 mg, 0.050 mmol) and the mixture was azeotroped three times with benzene. The aldehyde was dried under high vacuum for 2 h. Anhydrous 1,4-dioxane and THF were further dried over activated 4 Å molecular sieves. Chromium (II) chloride (14 mg, 0.12 mmol) was placed in a flask and gently flamed-dried under vacuum. After cooling, THF (0.5 mL) was added to the $CrCl_2$ and the flask was wrapped in foil. The aldehyde with CHI_3 and D*t*BMP was then dissolved in 1,4-dioxane (1.6 mL) and added to the flask containing $CrCl_2$ over 1.5 h using a syringe pump. The $CrCl_2$ solution turned dark red upon addition of the aldehyde solution. The reaction stirred an additional 3 h before being quenched by the addition of H_2O and Et_2O. The aqueous layer was extracted three times with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$. Concentration under reduced pressure afforded a yellow oil which was purified on silica gel (95:5 hexanes:EtOAc) to afford vinyl iodide (-)-**67** as a colorless oil in 54% yield over two steps (12 mg, 0.0091 mmol): $[\alpha]_D^{23}$ -4.53° (c = 0.155, C_6H_6); IR (film) 2955, 2928, 2856, 1736, 1722, 1463, 1430, 1361, 1257, 1107, 1034, 837, 776, 702 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.85 (m, 4H), 7.29 (m, 6H), 6.72 (dd, J = 5.6, 14.3 Hz, 1H), 6.24 (dd, J = 1.4, 14.3 Hz, 1H), 4.72 (m, 1H), 4.68 (ddd, J = 5.1, 11.0, 11.0 Hz, 1H), 4.23 (m, 1H), 4.13 (m, 1H), 4.03 (m, 1H), 3.90 (dd, J = 4.2, 9.6 Hz, 1H), 3.86 (dd, J = 5.4, 10.6 Hz, 1H), 3.42 (s, 3H), 3.14 (s, 3H), 2.67 (dd, J = 8.2, 15.5 Hz, 1H), 2.53 (dd, J = 10.8, 10.8 Hz, 1H), 2.39 (m, 2H), 2.26 (dd, J = 7.5, 7.5, Hz, 2H), 2.18 (dd, J = 5.2, 15.0 Hz, 1H), 1.93 (dd, J = 6.8, 15.2 Hz, 1H), 1.81 (m, 3H), 1.71 (m, 3H), 1.59 (m, 4H), 1.23 (s, 9H), 1.05 (s, 9H), 0.99 (s, 9H), 0.97 (s, 9H), 0.93 (s, 9H), 0.89 (dd, J = 7.5, 7.5, Hz, 3H), 0.21 (s, 3H), 0.19 (s, 3H), 0.17 (s, 9H), 0.084 (s, 3H), 0.045 (s, 3H). 0.0075 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 172.9, 148.6, 135.7 (2C), 135.6 (2C), 133.8, 133.7, 129.57, 129.55, 127.6 (2C),127.6 (2C), 100.5, 75.8, 71.8, 69.1, 68.6, 67.6, 66.3, 62.1, 57.3, 51,6, 48.5, 48.0, 47.0, 44.8, 43.0, 42.5, 41.9, 37.2, 26.9 (3C), 26.0 (3C), 25.9 (3C), 25.8 (3C), 25.6 (3C), 20.0, 19.3, 19.1, 18.2, 18.03, 17.99, 17.7, 12.3, -4.0, -4.1, -4.2, -4.7, -4.76, -4.77, -4.9, -5.1; high resolution mass spectrum (ES+) *m/z* 1333.6278 [(M+Na$^+$) calculated for $C_{64}H_{115}O_{11}ISi_5$+Na 1333.6279].



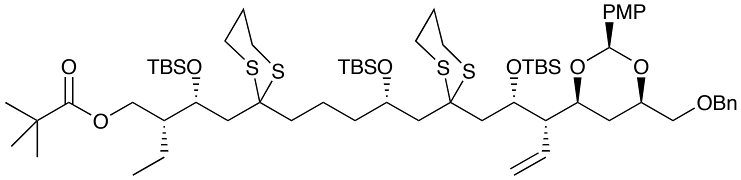
(-)-**S27**

Tetraol (-)-**S27:** Linchpin adduct (-)-**61** (749 mg, 0.574 mmol) was dissolved in THF (18 mL) and solid TBAF (1.05 g, 4.02 mmol) was added. The solution was heated to 40 °C for 18 h at which point the heating bath was removed and the flask cooled to room temperature. A solution of saturated NH_4Cl was added followed by EtOAc (50 mL). The layers were separated and the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to give a yellow oil. Following column chromatography (1:1 to 1:3 hexanes:EtOAc) the desired tetraol (-)-**S27** was isolated as a white foam in 92% yield (441 mg, 0.528 mg): $[\alpha]_D^{23}$ -1.38° (c = 0.32, $CHCl_3$); IR (film) 3408, 2910, 1298, 1248, 1105, 1024, 915, 827, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.34 (m, 4H), 7.29 (m, 1H), 6.89 (m, 2H), 5.81 (ddd, *J* = 10.0, 10.0, 17.2 Hz, 1H), 5.54 (s, 1H), 5.26 (dd, *J* = 2.2, 10.1 Hz, 1H), 5.18 (dd, *J* = 1.6, 17.5 Hz, 1H), 4.61 (d, *J* = 12.3 Hz, 1H), 4.57 (d, *J* = 12.3 Hz, 1H), 4.53 (m, 1H), 4.19 (m, 1H), 4.04 (m, 3H), 3.82 (m, 1H), 3.81 (s, 3H), 3.69 (m, 2H), 3.63 (dd, *J* = 5.4, 9.9 Hz, 1H), 3.52 (dd, *J* = 5.1, 10.5 Hz, 1H), 3.28 (m, 1H), 3.07 (bs, 2H), 2.90 (m, 5H), 2.79 (m, 3H), 2.38 (dd, *J* = 8.9, 14.6 Hz, 1H), 2.22 (m, 3H), 1.98 (m, 9H), 1.65 (m, 1H), 1.57 (m, 3H), 1.44 (m, 3H), 1.37 (m, 2H), 0.94 (dd, *J* = 7.5, 7.5, Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 138.1, 133.4, 130.9, 128.4 (2C), 127.8 (2C), 127.6, 127.3 (2C), 119.8, 113.5 (2C), 100.4, 76.3, 76.1, 73.5, 72.9, 71.5, 67.7, 66.4, 63.8, 56.2, 55.3, 52.3, 51.7, 47.2, 45.9, 44.5, 40.7, 38.9, 37.5, 32.6, 26.5, 26.3, 26.2, 26.0, 25.0, 24.8, 19.8, 18.7, 12.3; high resolution mass spectrum (ES+) *m/z* 859.3399 [(M+Na$^+$) calculated for $C_{43}H_{64}O_8S_4$+Na 859.3382].



(-)-**S28**

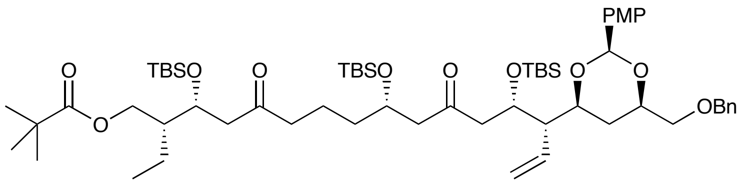
Pivalate Ester (-)-**S28:** Tetraol (-)-**S27** (1.18 g, 1.33 mmol) was dissolved in CH_2Cl_2 (13 mL) and cooled to 0 °C in an ice bath. Triethylamine (0.55 mL, 3.99 mmol) was added followed by trimethylacetyl chloride (0.20 mL, 1.60 mmol). The reaction warmed to room temperature overnight and an additional 0.05 mL of acetyl chloride was added the next morning. After stirring at room temperature for an additional 8 h the reaction was quenched via addition of a saturated solution of NH_4Cl. The aqueous layer was extracted four times with CH_2Cl_2 and the combined organic layers were washed once with saturated $NaHCO_3$, once with brine, dried over $MgSO_4$ and concentrated to give a yellow oil. Flash chromatography (2:1 hexanes:EtOAc) furnished pivalate (-)-**S28** in 87% yield (1.07 g, 1.16 mmol) A small amount of tetraol (-)-**S27** was also recovered (51 mg, 4%): $[\alpha]_D^{23}$ -3.66° (c = 0.30, $CHCl_3$); IR (film) 3443, 2957, 2932, 2911, 1718, 1650, 1616, 1558, 1540, 1518, 1457, 1420, 1248, 1166, 1107, 1031, 912, 828, 754 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.33 (m, 4H), 7.27 (m, 1H), 6.88 (m, 2H), 5.81 (dd, *J* = 10.1, 10.1, 17.3 Hz, 1H), 5.53 (s, 1H), 5.24 (dd, *J* = 2.0, 10.5 Hz, 1H), 5.18 (dd, *J* = 2.0, 17.3 Hz, 1H), 4.61 (d, *J* = 12.3 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.55 (m, 1H), 4.17 (dd, *J* = 7.0, 11.4 Hz 1H), 4.10 (dd, *J* = 4.8, 11.2 Hz, 1H), 4.03 (m, 4H), 3.79 (s, 3H), 3.63 (dd, *J* = 5.8, 10.1 Hz, 1H), 3.51 (dd, *J* = 4.7, 10.8 Hz, 1H), 3.24 (bs, 2H), 2.85 (m, 8H), 2.22 (m, 4H), 1.96 (m, 9H), 1.62 (m, 4H), 1.39 (m, 5H), 1.20 (s, 9H), 0.96 (dd, *J* = 7.7, 7.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.6, 159.8, 138.1, 133.4, 130.9, 128.3 (2C), 127.7 (2C), 127.6, 127.3 (2C), 119.7, 113.5 (2C), 100.4, 76.13, 76.06, 73.4, 72.9, 68.2, 67.7, 66.3, 63.7, 56.2, 55.2, 52.5, 51.7, 46.1, 46.0, 44.6, 41.7, 39.1, 38.8, 37.6, 32.3, 27.2 (3C), 26.5, 26.2, 26.1, 26.0, 24.9, 24.7, 19.9, 19.3, 12.2; high resolution mass spectrum (ES+) *m/z* 943.3967 [(M+Na$^+$) calculated for $C_{48}H_{72}O_9S_4$+Na 943.3957].



(-)-**69**

TBS Ether (-)-**69:** Pivalate ester (-)-**S28** (500 mg, 0.542 mmol) and DMAP (280 mg, 2.18 mmol) were dissolved in pyridine (9 mL) and cooled to 0 °C. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (1.25 mL, 5.43 mmol, 10 equiv.) was added and the reaction stirred at 0 °C for 18 h at which point an additional 3 equivalents of TBSOTf was added. After stirring an additional 12 h the reaction was quenched with NH_4Cl and diluted with CH_2Cl_2. The aqueous layer was extracted three times with CH_2Cl_2 and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to give a colorless oil. Purification via column chromatography (98:2 to 95:5 to 9:1 hexanes:EtOAc) afforded tris-TBS ether (-)-**69** as a white foam in 90% yield (617 mg, 0.488 mmol): $[\alpha]_D^{23}$ -1.22° (c = 0.41, $CHCl_3$); IR (film) 2955, 2930, 2856, 1730, 1518, 1471, 1460, 1251, 1154, 1104, 1038, 834, 774 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (m, 2H), 7.34 (m, 4H), 7.29 (m, 1H), 6.87 (m, 2H), 5.74 (ddd, *J* = 10.0, 10.0, 17.1 Hz, 1H), 5.52 (s, 1H), 5.26 (dd, *J* = 2.0, 10.2 Hz, 1H), 5.20 (dd, *J* = 2.5, 17.5 Hz, 1H), 4.83 (m, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.6 Hz, 1H), 4.27 (m, 1H), 4.14 (dd, *J* = 5.4, 11.1 Hz, 1H), 4.04 (m, 2H), 3.97 (m, 1H), 3.89 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.81 (s, 3H), 3.62 (dd, *J* = 6.3, 10.0 Hz, 1H), 3.49 (dd, *J* = 4.0, 10.0 Hz, 1H), 2.85 (m, 4H), 2.71 (m, 4H), 2.64 (dd, *J* = 9.8, 9.8 Hz, 1H), 2.40 (dd, *J* = 9.0, 16.0 Hz, 1H), 2.18 (m, 3H), 1.89 (m, 8H), 1.77 (d, *J* = 14.6 Hz, 1H), 1.63 (m, 3H), 1.45 (m, 2H), 1.31 (m, 3H), 1.22 (s, 9H), 0.99 (dd, *J* = 7.7, 7.7 Hz, 3H), 0.881 (s, 9H), 0.877 (s, 9H), 0.87 (s, 9H), 0.13 (s, 6H), 0.081 (s, 3H), 0.078 (s, 3H), 0.067 (s, 3H), 0.040 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.5, 159.6, 138.3, 133.8, 131.5, 128.4 (2C), 127.8 (2C), 127.61, 127.57 (2C), 120.5, 113.3 (2C), 99.9, 76.2, 74.5, 73.5, 73.2, 70.0, 69.3, 66.8, 63.8, 57.6, 55.3, 53.0, 52.3, 48.9, 46.5, 46.3, 42.4, 39.9, 39.3, 38.8, 33.0, 27.3 (3C), 26.7, 26.5, 26.12 (7C), 26.08 (4C), 25.1, 24.8, 20.2, 19.9, 18.3, 18.2, 18.1, 12.5, -3.2, -3.5, -3.7, -

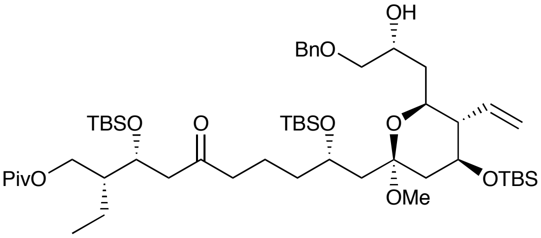
3.9, -4.3, -4.9; high resolution mass spectrum (ES+) *m/z* 1285.6522 [(M+Na$^+$) calculated for $C_{66}H_{114}O_9Si_3$+Na 1285.6551].



(+)-**S29**

Diketone (+)-**S29**: Bis-dithiane (-)-**69** (389 mg, 0.308 mmol) and D*t*BMP (474 mg, 2.31 mmol) were dissolved in THF (8 mL) and distilled water (2 mL). The solution was cooled in an ice bath and $Hg(ClO_4)_2$ (430 mg, 1.08 mmol) was added in one portion. A white solid formed immediately and the reaction stirred at 0 °C for 1 h. The white slurry was quenched with saturated NH_4Cl, diluted with EtOAc and filtered through Celite to give a pale yellow biphasic filtrate. The layers were separated and the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to provide a pale yellow oil. The oil was purified using silica gel chromatography (95:5 to 9:1 hexanes:EtOAc) to afford diketone (+)-**S29** as a colorless oil in 82% yield (264 mg, 0.254 mmol): $[\alpha]_D^{23}$ +2.98° (c = 0.52, $CHCl_3$); IR (film) 2955, 2930, 2856, 1720, 1616, 1518, 1462, 1251, 1154, 1101, 1037, 1007, 835, 776 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.75 (m, 2H), 7.30 (m, 2H), 7.18 (m, 2H), 7.10 (m, 1H), 6.83 (m, 2H), 5.80 (ddd, *J* = 10.1, 10.1, 167.7 Hz, 1H), 5.64 (s, 1H), 5.14 (m, 2H), 5.06 (dd, *J* = 2.1, 17.0 Hz, 1H), 4.58 (ddd, *J* = 4.0, 4.0, 7.6 Hz, 1H), 4.44 (d, *J* = 12.4 Hz, 1H), 4.41 (d, *J* = 12.2 Hz, 1H), 4.30 (m, 2H), 4.24 (dd, *J* = 5.5, 10.6 Hz, 1H), 3.97 (m, 2H), 3.59 (dd, *J* = 5.8, 10.0 Hz, 1H), 3.39 (dd, *J* = 5.2, 10.0 Hz, 1H), 3.26 (s, 3H), 2.62 (m, 2H), 2.53 (dd, *J* = 5.8, 16.7 Hz, 1H), 2.40 (m, 3H), 2.18 (dd, *J* = 4.9, 16.7 Hz, 1H), 2.11 (app t, *J* = 7.0 Hz, 2H), 1.66 (m, 4H), 1.46 (m, 3H), 1.28 (m, 2H), 1.23 (s, 9H), 1.02 (s, 9H), 0.99 (s, 9H), 0.96 (s, 9H), 0.88 (dd, *J* = 7.6, 7.6, Hz, 3H), 0.20 (s, 3H), 0.16 (s, 3H), 0.14 (s, 3H), 0.12 (s, 3H), 0.114 (s, 3H), 0.110 (s 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.9, 207.2, 178.5, 159.7, 138.2, 133.6, 131.2, 128.4 (2C), 127.8 (2C), 127.63, 127.60

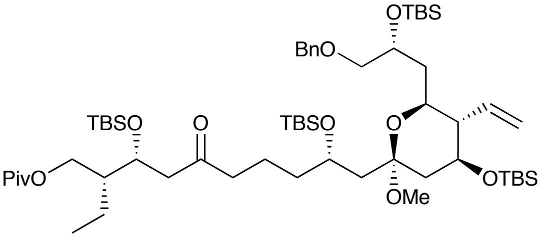
(2C), 120.0, 113.4 (2C), 100.5, 76.2, 74.1, 73.5, 73.1, 68.5, 68.2, 64.9. 63.4, 55.7, 55.2, 51.1, 50.6, 46.6, 45.5, 44.5, 38.8, 36.8, 32.8, 27.2 (3C), 26.0 (3C), 25.9 (3C), 25.8 (3C), 20.2, 19.0, 18.1, 18.0 (2C), 12.2, -4.2, -4.62, -4.64 (3C), -4.9; high resolution mass spectrum (ES+) *m/z* 1105.6654 [(M+Na$^+$) calculated for $C_{60}H_{102}O_{11}Si_3$+Na 1105.6628].



(-)-**70**

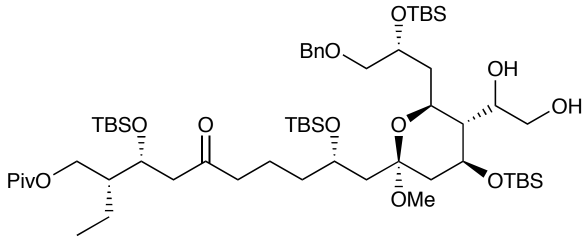
Methyl Ketal (-)-**70:** Diketone (+)-**S29** (264 mg, 0.244 mmol) was dissolved THF (3 mL) and MeOH (12 mL) was added. The solution was cooled to 10 °C before addition of PPTS (113 mg, 0.487 mmol). The reaction was allowed to stir at 10 °C for 14 h at which point it was quenched by the addition of a saturated solution of $NaHCO_3$. The reaction mixture was poured into a separatory funnel containing water and EtOAc. The layers were separated and the aqueous layer was extracted four times with EtOAc. The combined organic layers were then washed with brine and dried over $MgSO_4$. Concentration under reduced pressure provided a yellow oil. Column chromatography on silica gel deactivated with Et_3N (95:5 to 9:1 hexanes:EtOAc) furnished ketal (-)-**70** as a colorless oil in 44% yield (105 mg, 0.101 mmol). Diketone (+)-**S29** was recovered in 37% (99 mg, 0.091mmol): $[\alpha]_D^{23}$ -7.57° (c = 0.39, $CHCl_3$); IR (film), 3520, 2956, 2930, 2857, 1729, 1462, 1364, 1281, 1254, 1151, 1092, 836, 774 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.38 (m, 2H), 7.19 (m, 2H), 7.10 (m, 1H), 5.26 (ddd, *J* = 10.0, 10.0, 17.3 Hz, 1H), 5.09 (dd, *J* = 2.2, 17.1 Hz, 1H), 5.04 (dd, *J* = 2.2, 10.3 Hz, 1H), 4.59 (ddd, *J* = 3.9, 3.9, 11.6 Hz, 1H), 4.38 (s, 2H), 4.31 (dd, *J* = 6.1, 11.0 Hz, 1H), 4.25 (dd, *J* = 5.9, 11.2 Hz, 1H), 4.19 (m, 1H), 4.00 (m, 2H), 3.67 (ddd, *J* = 2.4, 105, 10.5 Hz, 1H), 3.56 (dd, *J* = 5.9, 9.3 Hz, 1H), 3.43 (dd, *J* = 5.4, 9.5 Hz, 1H), 3.33 (d, *J* = 1.5 Hz, 1H), 3.06 (s, 3H), 2.47 (dd, *J* = 8.0, 16.1 Hz, 1H), 2.34 (dd, *J* = 5.4, 13.7 Hz, 1H), 2.21 (m, 3H), 2.13 (ddd, *J* =

2.9, 2.9, 13.9 Hz, 1H), 2.02 (m, 2H), 1.90 (dd, *J* = 5.1, 14.9 Hz, 1H), 1.81 (dd, *J* = 10.7, 12.9 Hz, 1H), 1.70 (m, 4H), 1.51 (m, 1H), 1.30 (m, 3H), 1.24 (s, 9H), 1.04 (s, 9H), 1.01 (s, 9H), 0.97 (s, 9H), 0.90 (dd, *J* = 7.4, 74 Hz, 3H), 0.18 (s, 3H), 0.17 (s, 6H), 0.14 (s, 3H), 0.13 (s, 3H), 0.064 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.9 178.5, 138.3, 136.6, 128.4 (2C), 127.7 (2C), 127.6, 119.4, 100.7, 74.1, 73.3, 72.3, 70.5, 68.5, 68.4, 67.9, 63.4, 55.7, 47.7, 46.6, 45.5, 44.7, 43.1, 42.7, 38.8, 37.1, 37.0, 27.2 (3C), 26.0 (3C), 25.84 (3C), 25.82 (3C), 20.2, 19.2, 18.01, 17.99 (2C), 12.2, -4.1 (4C), -4.6, -4.9; high resolution mass spectrum (ES+) *m/z* 1001.6351 [(M+Na$^+$) calculated for $C_{53}H_{98}O_{10}Si_3$+Na 1001.6366].



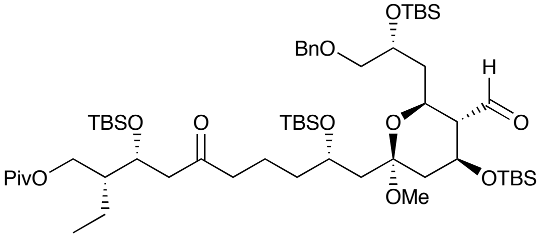
(-)-**S30**

TBS Ether (-)-**S30**: Alcohol (-)-**70** (154 mg, 0.157 mmol) and DMAP (19 mg, 0.16 mmol) were dissolved in pyridine (1 mL) and cooled to 0 °C in an ice bath. To this solution was added TBSOTf (0.60 mL, 0.24 mmol). After 1 h the reaction was quenched with saturated NH_4Cl and diluted with CH_2Cl_2. The aqueous layer was extracted three times with CH_2Cl_{2-}, the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to afford a viscous oil. Column chromatography on silica gel deactivated with Et_3N (98:2 hexanes:EtOAc) furnished TBS ether (-)-**S30** as a colorless oil in 92% yield (159 mg, 0.145 mmol): $[\alpha]_D^{23}$ -24.86° (c = 0.14, $CHCl_3$); IR (film) 2955, 2929, 2856, 1731, 1471, 1362, 1254, 1146, 1092, 1037, 836, 775, 669 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.36 (m, 2H), 7.23 (m, 2H), 7.10 (m, 1H), 5.44 (ddd, *J* = 9.9, 9.9, 17.2 Hz, 1H), 5.11 (m, 2H), 4.60 (ddd, *J* = 3.7, 3.7, 11.6 Hz, 1H), 4.47 (s, 2H), 4.32 (m, 2H), 4.35 (dd, *J* = 5.6, 10.8 Hz, 1H), 4.06 (m, 2H), 3.79 (ddd, *J* = 2.0, 10.6, 10.6 Hz, 1H), 3.67 (dd, *J* = 7.3, 10.1 Hz, 1H), 3.57 (dd, *J* = 3.9, 10.2 Hz, 1H), 3.14 (s, 3H), 2.48 (dd, *J* = 8.0, 16.5 Hz, 1H), 2.38 (dd, *J* = 4.8, 13.1 Hz, 1H), 2.19 (m, 3 H), 2.11 (m, 2H), 2.00 (ddd, *J* = 9.4, 9.4, 9,4 Hz, 1H), 1.93 (dd, *J* = 5.6, 15.0 Hz, 1H), 1.70 (m, 5H), 1.30 (m, 1H), 1.13 (m, 3H), 1.23 (s, 9H), 1.059 (s, 9H), 1.056 (s, 9H), 1.02 (s, 9H), 0.97 (s, 9H), 0.90 (dd, *J* = 7.6, 7.6, 3H), 0.24 (2, 3H), 0.23 (s, 3H). 0.21 (s, 3H), 0.19 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H), 0.13 (s, 3H), 0.064 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 207.3, 177.6, 139.2, 137.8, 128.5 (2C), 127.7, 119.0, 100.5, 75.5, 73.4, 69.8, 69.2, 68.8, 68.6, 68.4, 63.7, 56.1, 48.0, 46.8, 46.1, 44.5, 43.7, 39.6, 38.8, 37.4, 31.9, 27.4 (3C), 26.3 (3C), 26.2 (3C), 26.15 (3C), 26.11 (3C), 20.6, 19.6, 18.4, 18.29, 18.27, 18.2, 12.4, -3.90, -3.91, -3.93, -4.0, -4.2, -4.3, -4.5, -4.8 note: (the phenyl protons are clearly visible at 138.7, 128.2 (2C), 127.6 (2C) 127.4 ppm when the spectrum is taken in $CDCl_3$); high resolution mass spectrum (ES+) *m/z* 1115.7247 [(M+Na$^+$) calculated for $C_{59}H_{112}O_{10}Si_4$+Na 1115.7230].



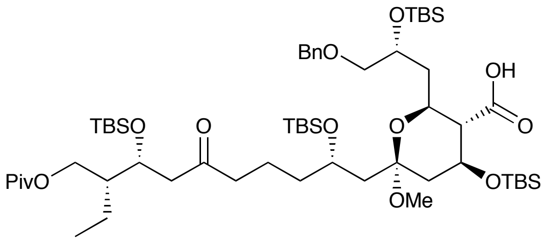
(-)-**S31**

Diol (-)-**S31**: Alkene (-)-**S30** (85 mg, 0.078 mmol) was dissolved THF (4 mL) and H_2O (1 mL) and NMO (23 mg, 0.19 mmol) was added followed by a catalytic amount of OsO_4 (4% wt. solution in H_2O). The reaction was capped with a plastic cap and allowed to stir at room temperature for 48 h. A few more drops of OsO_4 solution was added and the reaction continued to stir for a total of six days. The reaction was quenched with solid Na_2SO_3 and diluted with water and EtOAc. The layers were separated and the aqueous layer was extracted three times with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated. Purification on silica gel deactivated with Et_3N (9:1 to 3:1) afforded diol (-)-**S31** as a light yellow oil in 75% yield (66 mg, 0.056 mmol): $[\alpha]_D^{23}$ -15.60° (c = 0.13, $CHCl_3$); IR (film) 3446, 2955, 2927, 2855, 1731, 1718, 1462, 1262, 1254, 1096, 836, 775 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.33 (m, 2H), 7.21 (m, 2H), 7.11 (m, 1H), 4.55 (ddd, *J* = 3.6, 3.6, 11.6 Hz, 1H), 4.45 (d, *J* = 12.8 Hz, 1H), 4.41 (d, *J* = 11.6 Hz, 1H), 4.38 (m, 2H), 4.27 (dd, *J* = 6.2, 11.1 Hz, 1H), 4.21 (dd, *J* = 5.2, 10.6 Hz, 1H), 4.10 (m, 1H), 4.01 (m, 1H), 3.87 (dd, *J* = 9.7, 9.7 Hz, 1H), 3.80 (dd, *J* = 10.3, 10.3 Hz, 1H), 3.62 (dd, *J* = 5.7, 9.2 Hz, 1H), 3.55 (m, 2H), 3.04 (s, 3H), 2.64 (bs, 1H), 2.45 (dd, *J* = 8.5, 16.4 Hz, 1H), 2.36 (dd, *J* = 9.0, 14.1 Hz, 1H), 2.29 (dd, *J* = 4.9, 12.8 Hz, 1H), 2.19 (m, 4H), 2.11 (dd, *J* = 7.9, 15.1 Hz, 1H), 1.87 (m, 3H), 1.73 (m, 4H), 1.59 (dd, *J* = 10.4, 10.4 Hz, 1H), 1.50 (m, 1H), 1.27 (m, 2H), 1.21 (s, 9H), 1.05 (s, 9H), 1.02 (s, 9H), 1.01 (s, 9H), 0.94 (s, 9H), 0.88 (dd, *J* = 7.5, 7.5, Hz, 3H), 0.25 (s, 3H). 0.22 (s, 3H), 0.19 (s, 3H), 0.18 (s, 6H), 0.17 (s, 3H), 0.14 (s, 3H), 0.098 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 210.3, 177.7, 139.0, 128.6 (2C), 99.8, 75.3, 73.6, 71.0, 69.8, 69.3, 68.6, 67.9, 66.2, 65.3, 63.7, 51.3, 47.9, 46.7, 46.0, 44.5, 44.0, 43.7, 39.7, 38.8, 36.9, 27.4 (3C), 26.22 (6C), 26.20 (3C), 26.1 (3C), 20.6, 19.9, 18.5, 18.31, 18.25, 18.2, 12.4, -3.5, -3.9, -4.07, -4.15 (2C), -4.29, -4.33, -4.8 note: (the aromatic peaks are clearly visible at 128.3 (2C), 127.7 (2C), 127.5 ppm when the spectrum is taken in $CDCl_3$); high resolution mass spectrum (ES+) *m/z* 1149.7324 [(M+Na$^+$) calculated for $C_{59}H_{114}O_{12}Si_4$+Na 1149.7285].



(-)-**71**

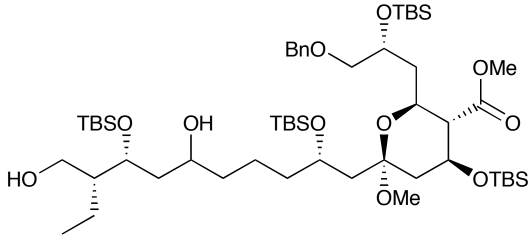
Aldehyde (-)-**71**: Diol (-)-**S31** (94 mg, 0.083 mmol) was dissolved in benzene (1.5 mL) and $Pb(OAc)_4$ (74 mg, 0.17 mmol) was added in one portion. After 20 min the reaction was quenched with water and diluted with CH_2Cl_2. A brown solid formed instantly and was removed by filtration through Celite. The filtrate was separated and the aqueous layer was extracted twice with CH_2Cl_2. The organic layer was washed once with saturated $NaHCO_3$ and once with brine, dried over $MgSO_4$ and concentrated to provide a colorless oil. Aldehyde (-)-**71** was isolated in 95% yield (87 mg, 0.079 mmol) and used in the next step without further purification: $[\alpha]^{23}_{\mathrm{D}}$ -7.74° (c = 0.26, $CHCl_3$); IR (film) 2956, 2930, 2857, 1731, 1472, 1463, 1362, 1283, 1255, 1092, 1034, 1006, 837, 776 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 9.78 (d, *J* = 3.3 Hz, 1H), 7.35 (m, 2H), 7.23 (m, 2H), 7.12 (m, 1H), 4.61 (m, 2H), 4.43 (d, *J* = 12.1 Hz, 1H), 4.40 (d, *J* = 12.4 Hz, 1H), 4.32 (dd, *J* = 6.3, 11.4 Hz, 1H), 4.25 (dd, *J* = 5.3, 11.1 Hz, 1H), 4.25 (m, 1H), 4.17 (m, 1H), 4.00 (dddd, *J* = 5.1, 5.1, 5.1, 5.1 Hz, 1H), 3.60 (dd, *J* = 6.9, 9.2 Hz, 1H), 3.49 (dd, *J* = 4.3, 9.5 Hz, 1H), 3.08 (s, 3H), 2.49 (m, 2H), 2.36 (dd, *J* = 5.3, 12.9 Hz, 1H), 2.20 (m, 3H), 2.09 (dd, *J* = 5.8, 15.5 Hz, 1H), 1.87 (m, 2H), 1.73 (m, 6H), 1.52 (m, 1H), 1.30 (m, 2H), 1.24 (s, 9H), 1.05 (s, 18H), 0.97 (s, 9H), 0.96 (s, 9H), 0.90 (dd, *J* = 7.7, 7.7 Hz, 3H), 0.22 (s, 3H), 0.21 (s, 3H). 0.19 (s, 3H), 0.18 (s, 3H), 0.17 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.034 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.0, 203.5, 178.5, 138.5, 128.3 (2C), 127.6 (2C), 127.5, 100.3, 74.7, 73.2, 68.7, 68.6, 68.5, 66.2, 64.6, 63.4, 62.6, 47.9, 46.6, 45.5, 44.8, 42.9, 42.4, 39.1, 38.8, 36.9, 27.2 (3C), 26.0 (3C), 25.9 (3C), 25.8 (3C), 25.6 (3C), 20.2, 19.1, 18.1, 18.03, 17.98, 17.8, 12.2, -4.0, -4.10, -4.14, -4.5, -4.6, -4.77, -4.81, -4.9; high resolution mass spectrum (ES+) *m/z* 1117.7003 [(M+Na$^+$) calculated for $C_{58}H_{110}O_{11}Si_4$+Na 1117.7023].



(-)-**S32**

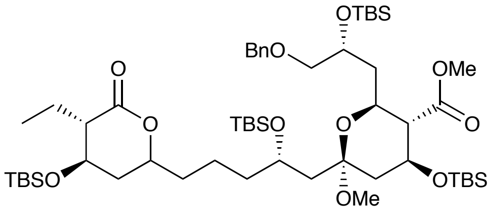
Acid (-)-**S32**: Aldehyde (-)-**71** (108 mg, 0.099 mmol) was dissolved in THF (1.6 mL), *t*-BuOH (1.6 mL), H_2O (0.8 mL) and cooled to 0 °C in an ice bath. 2-Methyl-2-butene (1.6 mL) was added followed by $NaH_2PO_4{\cdot}2H_2O$ (195 mg, 1.25 mmol) and $NaClO_2$ (141 mg, 1.25 mmol). After 1 h the reaction was quenched by the addition of saturated NH_4Cl and diluted with EtOAc. The aqueous layer was extracted three times with EtOAc and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Acid (-)-**S32** was characterized without further purification: $[\alpha]^{23}_{\mathrm{D}}$ -

35.13° (c = 0.06, $CHCl_3$); IR (film) 2956, 2930, 2857, 1731, 1708, 1472, 1462, 1362, 1254, 1149, 1100, 1033, 836, 776 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.38 (m, 2H), 7.25 (m, 2H), 7.10 (m, 1H), 4.67 (ddd, *J* = 4.6, 10.0, 10.0 Hz, 1H), 4.59 (ddd, *J* = 4.2, 4.2, 74 Hz, 1H), 4.48 (d, *J* = 12.8 Hz, 1H), 4.43 (d, *J* = 12.4 Hz, 1H), 4.31 (m, 2H), 4.24 (m, 2H), 4.00 (m, 1H), 3.68 (dd, *J* = 7.4, 10.1 Hz, 1H), 3.56 (dd, *J* = 3.7, 9.6 Hz, 1H), 3.10 (s, 3H), 2.45 (dd, *J* = 10.1, 10.1 Hz, 1H), 2.48 (dd, *J* = 7.8, 16.1 Hz, 1H), 2.38 (dd, *J* = 5.1, 13.3 Hz, 1H), 2.20 (m, 3H), 2.09 (dd, *J* = 6.0, 15.2 Hz, 1H), 1.98 (m, 1H), 1.88 (m, 2H), 1.73 (m, 4H), 1.52 (m, 1H), 1.30 (m, 3H), 1.24 (s, 9H), 1.07 (s, 9H), 1.05 (s, 18H), 0.97 (s, 9H), 0.90 (dd, *J* = 7.7, 7.7 Hz, 3H), 0.25 (s, 3H), 0.24 (s, 3H), 0.193 (s, 3H), 0.189 (s, 6H), 0.18 (s, 3H), 0.17 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 207.4, 179.3, 178.8, 139.1, 128.5 (2C), 128.3 (2C), 127.7, 100.8, 75.5, 73.4, 69.5, 69.1, 68.6, 68.4, 67.1, 63.7, 57.8, 48.1, 46.8, 46.1, 44.4, 43.4, 43.2, 39.8, 38.9, 37.4, 27.4 (3C), 26.3 (3C), 26.2 (3C), 26.09(3C), 26.01 (3C), 20.6, 19.5, 18.4, 18.29, 18.27, 18.1, 12.4, -3.90, -3.92, -4.0, -4.2, -4.3, -4.5, -4.6, -4.8; high resolution mass spectrum (ES+) *m/z* 1133.6956 [(M+Na$^+$) calculated for $C_{58}H_{110}O_{12}Si_4$+Na 1133.6972].



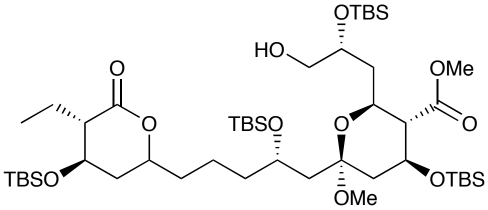
(-)-**72**

Diol (-)-**72:** Acid (-)-**S32** (assume 0.099 mmol) was dissolved in CH_2Cl_2 (2 mL) and cooled to -78 °C. A solution of DIBAL-H (1 M, 0.60 mL, 0.60 mmol) in hexanes was added dropwise. A solid formed so an additional 2 mL of CH_2Cl_2 was added. After 30 min the reaction was quenched by the addition of MeOH. Ether (10 mL) and 10 mL of a saturated solution of Rochelle's salt were added. The biphasic mixture stirred vigorously until both layers were clear. The layers were separated and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The unpurified diastereomeric mixture of diols (3:1) was dissolved in a solution of toluene:MeOH (1:1, 2 mL). A solution of $TMSCHN_2$ in Et_2O was added until the reaction mixture turned yellow and evolution of H_2 (g) was no longer observed. After stirring for 10 min the solvent was removed under reduced pressure and the resulting yellow oil was purified using flash chromatography. The diol diastereomers could be separated (9:1 to 4:1 hexanes:EtOAc) and were isolated in a combined 64% yield over three steps. [(major) 51 mg 0.049 mmol, (minor) 15.5 mg, 0.015 mmol]. The major diastereomer (more polar) (-)-**72** was fully characterized: $[\alpha]_D^{23}$ -16.86° (c = 0.24, $CHCl_3$); IR (film) 3409, 2957, 2930, 2857, 1739, 1465, 1442, 1409, 1381, 1327, 1254, 1100, 1035, 836, 775 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 7.36 (m, 2H), 7.23 (m, 2H), 7.12 (m, 1H), 4.70 (ddd, *J* = 4.6, 10.8, 10.8 Hz, 1H), 4.44 (d, *J* = 12.4 Hz, 1H), 4.39 (d, *J* = 12.4 Hz, 1H), 4.23 (m, 2H), 4.14 (m, 1H), 4.04 (m, 1H), 3.76 (m, 1H), 3.65 (m, 2H), 3.57 (dd, *J* = 4.1, 9.3 Hz, 1H), 3.54 (dd, *J* = 3.6, 9.8 Hz, 1H), 3.43 (s, 3H), 3.10 (s, 3H), 2.54 (dd, *J* = 10.3, 10.3 Hz, 1H), 2.39 (dd, *J* = 4.6, 12.4 Hz, 1H), 2.10 (dd, *J* = 4.6, 14.9 Hz, 1H), 1.89 (m, 3H), 1.70 (m, 6H), 1.54 (m, 4H), 1.23 (m, 2 H), 1.05 (s, 9H), 1.04 (s, 9H), 0.99 (s, 9H), 0.98 (s, 9H), 0.89 (dd, *J* = 7.3, 7.3 Hz, 3H), 0.22 (s, 3H), 0.21 (s, 3H), 0.20 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H) 0.15 (s, 3H), 0.13 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$,) δ 173.0, 138.6, 128.2 (2C), 127.6 (2C), 127.4, 100.3, 75.5, 74.6, 73.2, 70.9, 68.9, 68.5, 67.7, 66.7, 63.4, 57.4, 51.5, 47.9, 47.2, 43.0, 42.5, 39.0, 38.3, 37.8, 37.5, 26.0 (3C), 25.9 (3C), 25.8 (3C), 25.6 (3C), 21.0, 20.8, 18.2, 18.1, 17.8, 17.7, 12.4, -4.0, -4.08, 4.11, -4.14, -4.6, -4.7, -4.8, -5.1; high resolution mass spectrum (ES+) *m/z* 1065.6736 [(M+Na$^+$) calculated for $C_{54}H_{106}O_{11}Si_4$+Na 1065.6812].



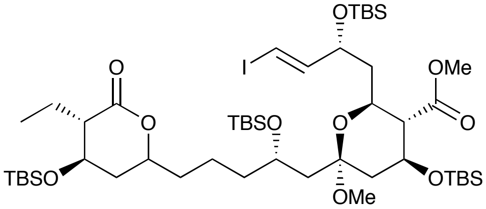
(-)-**74**

Lactone (-)-**74**: Diol (-)-**72** (59 mg, 0.057 mmol) and NMO (20 mg, 0.17 mmol) were placed in a round bottom flask with 60 mg of activated 4Å powered molecular sieves. Dichloromethane (1 mL) was added to the flask and the solution stirred for 15 min before addition of catalytic TPAP (less than 1 mg). After 1.5 h neither the starting material nor the lactol could be observed by TLC. The reaction mixture was filtered through a short plug of silica gel that had been deactivated with Et_3N using CH_2Cl_2 as the eluent. Concentration under reduced pressure cleanly afforded lactone (-)-**74** in 94% yield: $[\alpha]_D^{23}$ -30.53° (c = 0.15, $CHCl_3$); IR (film) 2953, 2929, 2857, 1739, 1585, 1463, 1361, 1255, 1098, 1034, 836 cm $^{-1}$; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 5H), 4.58 (m, 1H), 4.53 (d, *J* = 12.4 Hz, 1H), 4.49 (d, *J* = 12.4 Hz, 1H), 4.25 (dd, *J* = 4,9, 10.7, 10.7 Hz, 1H), 4.05 (m, 1H), 3.98 (ddd, *J* = 3.5, 3.5, 3.5 Hz, 1H), 3.79 (m, 2H), 3.64 (s, 3H), 3.46 (m, 2H), 3.00 (m, 3H), 2.41 (ddd, *J* = 4.5, 6.6, 6.6 Hz, 1H), 2.24 (dd, *J* = 10.4, 10.4 Hz, 1H), 2.02 (dd, *J* = 4.9, 12.8 Hz, 1H), 1.87 (dd, *J* = 6.2, 15.2 Hz, 1H), 1.77 (m, 2H), 1.74-1.58 (m, 8H), 1.39 (m, 4H), 1.04 (dd, *J* = 7.3, 7.3 Hz, 3H), 0.883 (s, 18H), 0.877 (s, 9H), 0.83 (s, 9H), 0.077 (s, 3H), 0.067 (s, 3H), 0.062 (s, 3H), 0.055 (s, 3H), 0.054 (s, 3H), 0.047 (s, 3H), 0.039 (s, 3H), -0.015 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 173.0, 138.6, 128.2 (2C), 127.6 (2C), 127.4, 100.2, 75.3, 74.6, 73.1, 68.8, 68.4, 67.7 (2C), 66.7, 57.4, 51.5, 50.4, 47.9, 43.1, 42.5, 39.1, 37.2, 35.5 (2C), 26.0 (3C), 25.9 (3C), 25.7 (3C), 25.6 (3C), 23.2, 20.5, 18.2, 18.0, 17.9, 17.7, 12.3, -4.0, -4.1 (2C), -4.6 (2C), -4.8 (2C), -5.1; high resolution mass spectrum (ES+) *m/z* 1061.6383 [(M+Na$^+$) calculated for $C_{54}H_{102}O_{11}Si_4$+Na 1061.6397].



(-)-**S33**

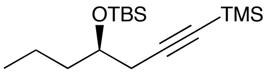
Alcohol (-)-**S33:** Benzyl ether (-)-**74** (78 mg, 0.075 mmol) and D*t*BMP (77 mg, 0.38 mmol) were placed in a round bottom flask with a solution of MeOH:EtOAc (1:1, 10 mL). The flask was evacuated and backfilled with argon three times before addition of 20% $Pd(OH)_2$ on carbon (156 mg, 2 wt. equiv.). The flask was evacuated and backfilled with argon an additional three times before being evacuated and backfilled one time with H_2 (g). The reaction stirred for 14 h under an atmosphere of hydrogen. The reaction mixture was then filtered through a pad of Celite and rinsed with EtOAc. Concentration afforded an oily solid which was purified using silica gel deactivated with Et_3N (95:5 to 4:1 hexanes:EtOAc). The desired primary alcohol (-)-**S33** was isolated in 80% yield (57 mg, 0.060 mmol): $[\alpha]_D^{23}$ -22.91° (c = 0.14, $CHCl_3$); IR (film) 3489, 2953, 2930, 2894, 2857, 1738, 1464, 1362, 1255, 1099, 1037, 938, 837, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.59 (m, 1H), 4.27 (ddd, *J* = 5.4, 10.7, 10.7 Hz, 1H) 3.98 (m, 2H), 3.80 (m, 2H), 3.67 (s, 3H), 3.56 (m, 2H), 3.12 (s, 3H), 2.41 (ddd, *J* = 4.1, 6.6, 6.6 Hz, 1H), 2.27 (dd, *J* = 10.7, 10.7 Hz, 1H), 2.20 (m, 1H), 2.06 (dd, *J* = 4.5, 13.1 Hz, 1H), 1.93 (dd, *J* = 5.8, 15.3 Hz, 1H), 1.68 (m, 2H), 1.74-1.54 (m, 9 H), 1.42 (m, 3H), 1.04 (dd, *J* = 7.0, 7.0 Hz, 3H), 0.89 (s, 9H), 0.882 (s, 9H), 0.876 (s, 9H), 0.83 (s, 9H), 0.076 (s, 3H), 0.067 (s, 9H), 0.063 (s, 3H), 0.053 (s, 3H), 0.040 (s, 3H), -0.020 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 172.9, 100.6, 75.3, 69.8, 68.3, 67.7, 67.6, 66.6, 66.0, 57.1, 51.6, 50.4, 48.1, 43.0, 42.4, 38.0, 37.4, 35.6, 35.5, 26.0 (3C), 25.8 (3C), 25.7 (3C), 25.6 (3C), 23.2, 20.4, 18.0 (2C), 17.9, 17.7, 12.2, -4.0, -4.1, -4.2, -4.61, -4.62 (2C), -4.8, -5.2; high resolution mass spectrum (ES-) *m/z* 983.5761 [(M+Cl^-) calculated for $C_{47}H_{96}O_{11}Si_4$+Cl 983.5718].



(-)-**75**

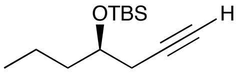
Vinyl Iodide (-)-**75:** Alcohol (-)-**S33** (90 mg, 0.095 mmol) was placed in flask with SO_3•pyridine (75 mg, 0.47 mmol) and CH_2Cl_2 (3 mL) was added. The flask was cooled to 0 °C before the addition of Hunig's base (80 μL) and DMSO (50 μL). After 1 h the reaction was quenched with saturated $NaHCO_3$ and the aqueous layer was extracted three times with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated to afford a yellow oil. The aldehyde was isolated in 77% yield (69 mg, 0.073 mmol) following flash chromatography using high quality silica gel (9:1 to

4:1 hexanes:EtOAc). The aldehyde, CHI_3 (86 mg, 0.022 mmol) and D*t*BMP (90 mg, 0.044 mmol) were placed in a flask and azeotroped six times with benzene. This mixture then dried under vacuum for 15 h. A flask containing freshly activated 4 Å molecular sieves was charged with anhydrous 1,4-dioxane. The flask was placed under vacuum and back-filled with argon three times after which the 1,4-dioxane dried for 1 h over the sieves. An argon-filled, flame-dried flask was charged with $CrCl_2$ (125 mg, 1.00 mmol) and gently flame-dried. After addition of THF (2 mL) the flask was wrapped in foil. The aldehyde mixture was dissolved in 1,4-dioxane (2.4 mL) and the solution was added to the $CrCl_2$ slurry using a syringe pump (1.5 mL/h), the reaction solution turned red upon addition of the aldehyde solution. After the addition the reaction stirred an additional 3 h before being quenched with pH 8 buffer. The solution was diluted with Et_2O and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to afford a yellow oil. Purification using high quality silica gel (98:2 to 95:5 hexanes:EtOAc) afforded vinyl iodide (-)-**75** in 63% yield over the two steps (64 mg, 0.060 mmol). The *E*/*Z* selectivity was greater than 20:1: $[\alpha]_D^{23}$ -31.67° (c = 0.075, $CHCl_3$); IR (film) 2928, 2856, 1738, 1462, 1258, 1098, 837, 775 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 6.82 (dd, *J* = 5.4 14.4 Hz, 1H), 6.35 (dd, *J* = 1.4, 14.3 Hz, 1H), 4.79 (ddd, *J* = 4.7, 10.6, 10.6 Hz, 1H), 4.56 (m, 1H), 4.33 (m, 1H), 4.26 (m, 1H), 4.13 (m, 1H), 3.77 (m, 1H), 3.52 (s, 3H), 3.25 (s, 3H), 2.63 (dd, *J* = 10.3, 10.3 Hz, 1H), 2.51 (dd, *J* = 4.7, 13.0 Hz, 1H), 2.46 (ddd, *J* = 5.4, 5.4, 7.3 Hz, 1H), 2.27 (dd, *J* = 4.8, 15.1 Hz, 1H), 2.02 (dd, *J* = 5.9, 15.0 Hz, 1H), 1.91-1.79 (m, 6H), 1.69-1.57 (m, 7H), 1.15 (s, 9H), 1.14 (dd, *J* = 7.4, 7.4 Hz, 3H), 1.09 (s, 9H), 1.04 (s, 9H), 1.01 (s, 9H), 0.31 (s, 3H), 0.27 (s, 3H), 0.26 (s, 3H), 0.18 (s, 3H), 0.14 (s, 3H), 0.11 (s, 3H), 0.070 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 172.8, 171.7, 149.6, 100.9, 75.3, 74.3, 72.3, 69.0, 68.3 (2C), 66.7, 57.7, 51.2, 50.5, 48.2, 43.6, 43.3, 42.0, 38.1, 37.2, 36.0, 26.3 (3C), 26.0 (3C), 25.88 (3C), 25.86 (3C), 22.8, 21.0, 18.32, 18.31, 18.0 (2C), 12.4, -3.79, -3.80, -4.0, -4.5, -4.76, -4.83, -4.84, -4.9; high resolution mass spectrum (ES-) *m/z* 1093.4950 [(M+Na^+) calculated for $C_{48}H_{95}IO_{10}Si_4$+Na 1093.4945].



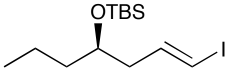
(+)-**S34**

Silyl Ether (+)-S34: A solution of (*R*)-1-(trimethylsilyl)hept-1-yne-4-ol (2.10 g, 11.4 mmol) in methylene chloride (57 mL) at 0 °C was treated with imidazole (2.30 g, 34.2 mmol) and TBSCl (2.60 g, 17.1 mmol). The reaction was allowed to warm to room temperature and stir for 48 h. The reaction mixture was washed with water (60 mL), and the aqueous layer was extracted with methylene chloride (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed *in vacuo*. The resulting yellow oil was purified by column chromatography (99:1 hexanes:EtOAc) to give (+)-**S34** as a colorless oil in 85% yield (2.9 g, 9.7 mmol): $[\alpha]_D^{23}$ +5.83 (c = 0.205, $CHCl_3$); IR (film) 2958, 2857, 2178, 1463, 1362, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80-3.77 (m, 1H), 2.34 (d, *J* = 6 Hz, 2H), 1.59-1.43 (m, 2H), 1.41-1.26 (m, 2H), 0.91 (t, *J* = 7 Hz, 3H), 0.89 (s, 9H), 0.14 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 105.1, 86.1, 71.1, 39.4, 29.0, 26.0 (3C), 18.5, 18.2, 14.3, 0.21 (3C), -4.2, -4.5; high resolution mass spectrum (CI) *m/z* 283.1927 [(M–Me$^+$) calculated for $C_{15}H_{31}OSi_2$ 283.1913].



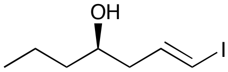
(-)-**78**

Alkyne (-)-78: A solution of (+)-**S34** (410 mg, 1.4 mmol) in methanol (7 mL) was treated with K_2CO_3 (580 mg, 5.2 mmol) and stirred at room temperature for 3 h. The methanol was removed *in vacuo*, and the reaction mixture was redissolved in ether (10 mL) and washed with water (10 mL). The aqueous layer was extracted with ether (2 x 10 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed *in vacuo*. The resulting oil was purified by column chromatography (99:1 hexanes:EtOAc) to provide (-)-**78** as a colorless oil in 93% yield (300 mg, 1.3 mmol): $[\alpha]_D^{23}$ -14.0 (c = 0.235, $CHCl_3$); IR (film) 3315, 2958, 2929, 2857, 1463, 1362, 1255, 1111, 1093, 1042, 1006, 991, 837, 808, 775 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80-3.78 (m, 1H), 2.32 (dd, *J* = 5.5, 2.5 Hz, 2H), 1.97 (t, *J* = 3 Hz, 1H), 1.56-1.27 (m, 4H), 0.92 (t, *J* = 7 Hz, 3H), 0.89 (s, 9H), 0.07 (d, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.1, 71.0, 70.0, 39.2, 27.6, 26.1 (3C), 18.6, 18.2, 14.4, -4.3, -4.4; high resolution mass spectrum (CI) *m/z* 211.1528 [(M–Me^{+}) calculated for $C_{12}H_{23}OSi$ 211.1518].



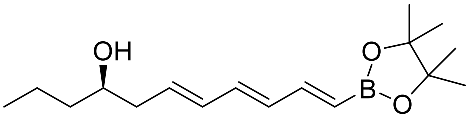
(-)-**S35**

Vinyl Iodide (-)-S35: A solution of $LiHBEt_3$ (2.46 mL, 1.0 M in THF, 2.46 mmol) was added dropwise to a solution of Cp_2ZrCl_2 (719 mg, 2.46 mmol) in THF (12.3 mL, dried over molecular sieves), which was covered in foil. The solution was stirred at room temperature for 1 h, after which a solution of (-)-**78** (280 mg, 1.23 mmol) in THF (7.2 mL) was added dropwise and the reaction mixture stirred for 0.5 h at room temperature. The mixture was cooled to 0 °C and a solution of I_2 (312 mg, 1.23 mmol) in methylene chloride (6.8 mL) was added dropwise. The solution maintained its yellow color, so additional I_2 crystals (~20 mg) were added until a deep red color persisted. The reaction mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$ (30 mL), which was extracted with ether (3 x 30 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed *in vacuo*. The resulting oil was purified by column chromatography (95:5 hexanes:EtOAc) to provide (-)-**S35** as a colorless oil in 87% yield (380 mg, 1.07 mmol): $[\alpha]_D^{23}$ = -3.82 (c = 0.19, $CHCl_3$); IR (film) 2956, 2929, 2857, 1462, 1254 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.56-6.49 (m, 1H), 6.01 (dt, *J* = 14.5, 1.5 Hz, 1H), 3.69-3.67 (m, 1H), 2.21-2.15 (m, 2H), 1.43-1.26 (m, 4H), 0.91 (m, 3H) 0.87 (2, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 76.4, 71.2, 43.9, 39.5, 26.1, 18.7, 18.3, 14.4, -4.2, -4.3; high resolution mass spectrum (CI) *m/z* 339.0674 [(M–Me^{+}) calculated for $C_{12}H_{24}IOSi$ 339.0641].



(-)-**79**

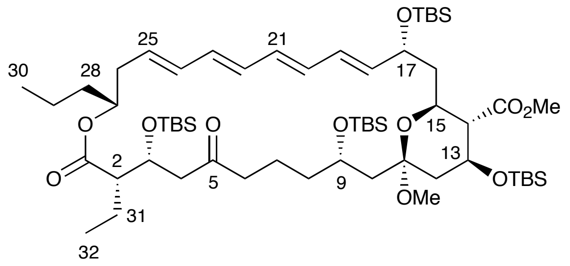
Alcohol (-)-79: A solution of (-)-**S35** (44 mg, 0.12 mmol) in THF (3.3 mL) was treated with TBAF (0.37 mL, 1.0 M in THF, 0.37 mmol) and stirred at room temperature for 1 h, after which time additional TBAF was added (0.25 mL). The reaction mixture was stirred for an additional 1 h and then poured into water (5 mL). The aqueous layer was extracted with ether (3 x 5 mL), and the combined organic layers were dried over Na_2SO_4. The solvent was removed *in vacuo*, and the resulting oil was purified by column chromatography (98:2 to 9:1 hexanes:EtOAc) to afford (-)-**79** as a colorless oil in 92% yield (26 mg, 0.11 mmol): $[\alpha]_D^{23}$ –3.82 (c = 0.19, $CHCl_3$); IR (film) 3376, 2957, 2925, 2870, 1605, 1463, 1214, 1163, 1122, 1076, 1021 cm^{-1}; ^1H NMR (500 MHz, $CHCl_3$) δ 6.58-6.54 (m, 1H), 6.13 (dt, *J* = 14.5, 1.5 Hz, 1H), 3.70-3.67 (m, 1H), 2.29-2.24 (m, 1H), 2.20-2.13 (m, 1H), 1.48-1.43 (m, 4H), 0.93 (t, *J* = 7 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 143.7, 77.3, 70.1, 44.4, 39.5, 19.3, 14.5; high resolution mass spectrum (CI) *m/z* 240.00106 [(M^+) calculated for $C_7H_{13}IOSi$ 240.00111].



(-)-**3**

Borate Ester (-)-3: A solution of 2-((1*E*,3*E*)-4-(tributylstannyl)buta-1,3-dienyl)-4,4,5,5-tetramethyl-1,3,-dioxaborolane (**77**) (336 mg, 0.716 mmol) and (-)-**79** (86 mg, 0.358 mmol) in DMF (3.5 mL) was covered in foil and then evacuated and refilled with argon three times. $PdCl_2(CH_3CN)_2$ (5 mg, 0.018 mmol) was added, and the flask was evacuated and refilled with argon twice. The reaction mixture was stirred at room temperature for 30 min until all vinyl iodide was consumed (verified by TLC). The mixture was poured into a saturated aqueous solution of NH_4Cl (10 mL). The aqueous layer was extracted with ether (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4. The solvent was removed *in vacuo*, and the resulting yellow oil was purified by column chromatography (96:4 to 9:1

hexanes:EtOAc) to furnish (-)-**3** as a yellow oil in 54% yield (57 mg, 0.195 mmol): $[\alpha]_D^{23}$ = -11.00 (c = 0.07, $CHCl_3$); IR (film) 3404, 2927, 1616, 1584, 1365, 1145 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.91 (dd, *J* = 17.5, 10.5 Hz, 1H), 6.24 (dd, *J* = 14.5, 10.5 Hz, 1H), 6.12 (dd, *J* = 14.5, 10.5 Hz, 1H), 6.07 (dd, *J* = 15, 10.5 Hz, 1H), 5.71 (dt, *J* = 15, 7.5 Hz, 1H), 5.44 (d, *J* = 18 Hz, 1H), 3.60-3.56 (m, 1H), 2.27-2.22 (m, 1H), 2.15-2.09 (m, 1H), 1.36-1.33 (m, 4H), 1.17 (s, 12H), 0.83 (t, *J* = 7 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 150.9, 137.0, 134.0, 133.9, 133.6, 83.5 (2C), 71.0, 42.0, 40.0, 25.3 (4C), 19.5, 14.6; high resolution mass spectrum (ESI) *m/z* 315.2110 [(M+Na^+) calculated for $C_{17}H_{29}BO_3$+Na 315.2107].

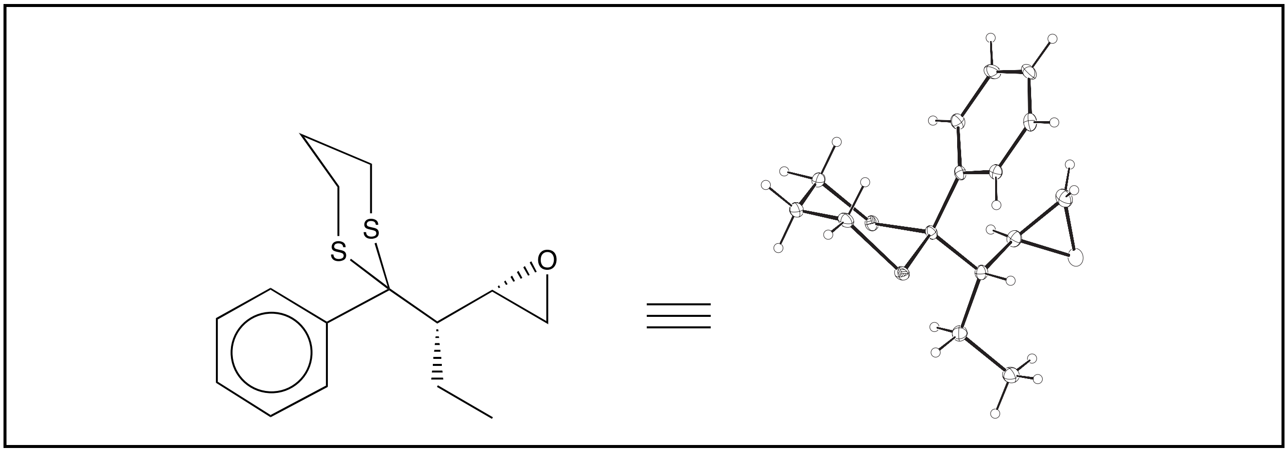


Macrolide (-)-**80**

Macrolide (-)-80: ^1H NMR (500 MHz, C_6D_6) δ 6.39-6.14 (m, 6H, H19, H24, H21, H22, H23, H20), 5.77 (dd, *J* = 3.3, 14.0 Hz, 1H, H18), 5.67 (ddd, *J* = 5.3, 9.2, 14.9 Hz, 1H, H25), 5.10-5.06 (m, 1H, H27), 4.73 (ddd, *J* = 4.7, 10.5, 10.5 Hz, 1H, H13), 4.50 (ddd, *J* = 1.8, 6.2, 9.6 Hz, 1H, H3), 4.38 (br s, 1H, H17), 4.30 (ddd, *J* = 1.6, 10.3, 10.3 Hz, 1H, H15), 4.09-4.06 (m, 1H, H9), 3.50 (s, 3H, COOMe), 3.24 (s, 3H, OMe), 2.97 (dd, *J* = 9.8, 16.0, Hz, 1H, H4), 2.73 (dt, *J* = 4.9, 11.5 Hz, 1H, H2), 2.64 (ddd, *J* = 3.1, 9.1, 15.7 Hz, 1H, H26), 2.56-2.50 (m, 2H, H12, H14), 2.41 (dt, *J* = 6.2, 18.9 Hz, 1H, H6), 2.32 (dd, *J* = 1.7, 16.0 Hz, 1H, H4′), 2.28-2.22 (m, 1H, H6′), 2.18-2.12 (m, 1H, H26′), 2.01 (dd, *J* = 1.2, 15.4 Hz, 1H, H10), 1.86-1.14 (series of m, 14H, H7, H16, H10′, H16′, H8, H12′, H28, H7′, H8′, H31, H31′, H29, H28′, H29′), 1.10 (s, 9H, TBS-*t*-Bu), 1.07 (s, 9H, TBS-*t*-Bu), 1.02 (s, 9H, TBS-*t*-Bu), 1.01 (s, 9H, TBS-*t*-Bu), 0.87 (t, *J* = 7.4 Hz, 3H, H32), 0.82 (t, *J* = 7.0 Hz, 3H, H30), 0.30 (s, 3H, TBS-Me), 0.28 (s, 3H, TBS-Me), 0.27 (s, 3H, TBS-Me), 0.21 (s, 3H, TBS-Me), 0.18 (s, 3H, TBS-Me), 0.082 (s, 3H, TBS-Me), 0.078 (s, 3H, TBS-Me), 0.073 (s, 3H, TBS-Me); ^{13}C NMR (125 MHz, C_6D_6) δ 207.8 (C5), 173.2 (ester), 171.8

(ester), 140.3 (C18), 134.5 (one of C19-C24), 134.0 (one of C19-C24), 132.8(one of C19-C24), 132.3(one of C19-C24), 130.7(one of C19-C24), 128.9 (C25), 125.6(one of C19-C24), 101.0 (C11), 73.2 (C27), 70.1 (C3), 69.5 (C17), 68.7 (C13), 68.5 (C9), 66.0 (C15), 57.9 (C14), 56.6 (C2), 51.2 (COOMe), 48.5 (OMe), 46.6 (C4), 45.7 (C6), 44.0 (C10), 43.7 (C12), 41.0 (C16), 39.2 (C8), 36.8 (C26), 35.2 (C28), 30.2 (C29), 26.5 (3C, TBS-*t*-Bu), 26.3 (3C, TBS-*t*-Bu), 26.1 (3C, TBS-*t*-Bu), 26.0 (3C, TBS-*t*-Bu), 22.9 (C31), 19.4 (TBS-*t*-Bu), 18.6 (TBS-*t*-Bu), 18.5 (TBS-*t*-Bu), 18.4 (TBS-*t*-Bu), 18.1 (C7), 14.0 (C30), 12.4 (C32), -3.3 (TBS-Me), -3.8 (TBS-Me), -4.0 (TBS-Me), -4.1 (TBS-Me), -4.5 (TBS-Me), -4.8 (TBS-Me), -4.9 (TBS-Me), -5.0 (TBS-Me);

X-ray Structure Determination of Compound (+)-20



Compound (+)-**20**, $C_{15}H_{20}S_2O$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences h00: h=odd, 0k0: k=odd, and 00l: l=odd) with a=7.2254(9)Å, b=12.631(2)Å, c=15.299(2)Å, V=1396.2(3)$Å^3$, Z=4 and d_{calc}=1.334 g/cm^3. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K_α radiation (λ=0.71069 Å) at a temperature of 143K. Preliminary indexing was performed from a series of twelve 0.5° rotation images with exposures of 30 seconds. A total of 548 rotation images were collected with a crystal to detector distance of 35 mm, a 2θ swing angle of -12°, rotation widths of 0.5° and exposures of 40 seconds: scan no. 1 was a ϕ-scan from 52.5° to 262.5° at ω = 10° and χ = 20°; scan no. 2 was an ω-scan from -20° to 20° at χ = -90° and ϕ = 135°; scan no. 3 was an ω-scan from -14° to 10° at χ = -90° and ϕ = 0°. Rotation images were processed using CrystalClear[i], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the CrystalStructure[ii] program package for further processing and structure solution on a Dell Pentium III computer. A total of 9714 reflections were measured over the ranges $5.32 \le 2\theta \le 50.06$ °, $-7 \le h \le 8$, $-14 \le k \le 15$, $-18 \le l \le 17$ yielding 2458 unique reflections (R_{int} = 0.0157). The intensity data were corrected for Lorentz and polarization effects and for absorption. using REQAB[iii] (minimum and maximum transmission 0.852, 1.000).

The structure was solved by direct methods (SIR97[iv]). Refinement was by full-matrix least squares based on F^2 using SHELXL-97[v]. All reflections were used during refinement (F^2 's that were experimentally negative were replaced by F^2 = 0). The weighting scheme used was $w=1/[\sigma^2(F_o^2)+$

$0.0380P^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to R_1=0.0200 and wR_2=0.0547 for 2384 reflections for which $F > 4\sigma(F)$ and R_1=0.0206, wR_2=0.0549 and GOF = 1.078 for all 2458 unique, non-zero reflections and 165 variables[vi]. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.171 and -0.159 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Table 2. Anisotropic thermal parameters are in Table 3. Tables 4. and 5. list bond distances and bond angles. Figure 1. is an ORTEP[vii] representation of the molecule with 30% probability thermal ellipsoids displayed.

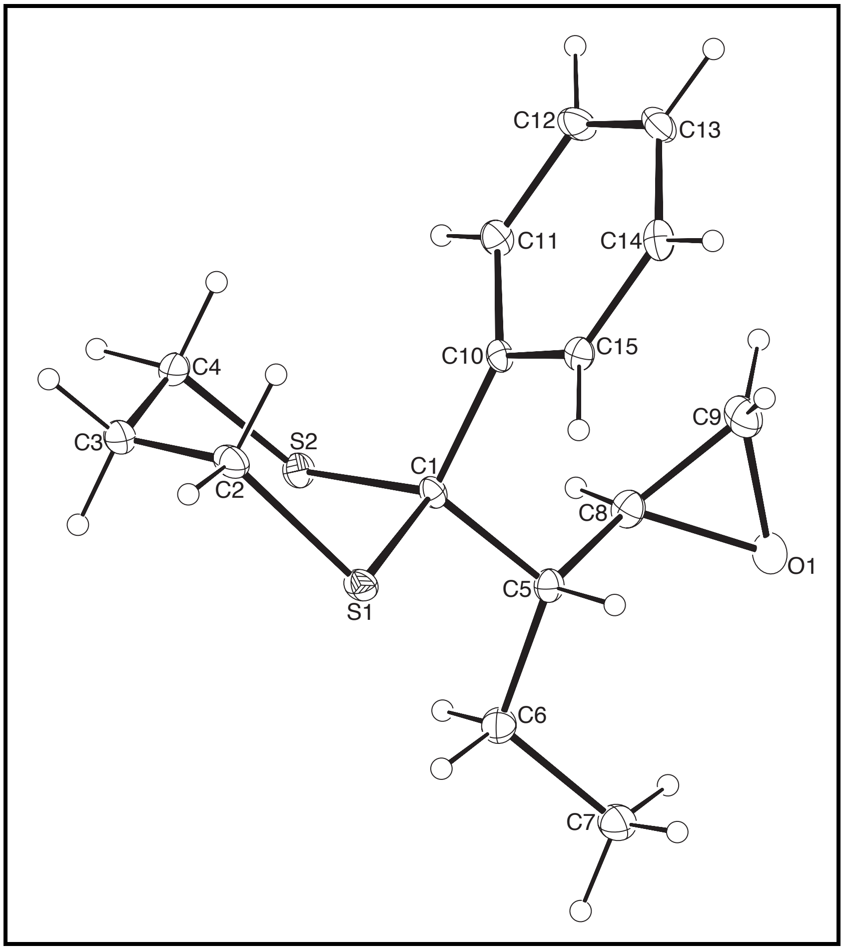


Figure 1. ORTEP drawing of (+)-**20** with 30% probability thermal ellipsoids

Table 1. Summary of Structure Determination of Compound (+)-20

Formula:	$C_{15}H_{20}S_2O$
Formula weight:	280.43
Crystal class:	orthorhombic
Space group:	$P2_12_12_1$ (#19)
Z	4
Cell constants:	
a	7.2254(9)Å
b	12.631(2)Å
c	15.299(2)Å
V	1396.2(3)$Å^3$
μ	3.67 cm^{-1}
crystal size, mm	0.32 x 0.22 x 0.20
D_{calc}	1.334 g/cm^3
F(000)	600
Radiation:	Mo-K_α (λ=0.71069Å)
2θ range	5.32 – 50.06 °
hkl collected:	$-7 \leq h \leq 8$; $-14 \leq k \leq 15$; $-18 \leq l \leq 17$
No. reflections measured:	9714
No. unique reflections:	2458 (R_{int}=0.0157)
No. observed reflections	2384 ($F>4\sigma$)
No. reflections used in refinement	2458
No. parameters	165
R indices ($F>4\sigma$)	R_1=0.0200
	wR_2=0.0547
R indices (all data)	R_1=0.0206
	wR_2=0.0549
GOF:	1.078
Final Difference Peaks, e/$Å^3$	+0.171, -0.159

Table 2. Refined Positional Parameters for Compound (+)-20

Atom	x	y	z	U_{eq}, Å^2
S1	0.57154(5)	0.50718(3)	0.62135(2)	0.01826(10)
S2	0.25945(5)	0.35391(3)	0.64615(2)	0.01913(10)
O1	0.0766(2)	0.60470(8)	0.85371(6)	0.0266(2)
C1	0.4007(2)	0.45562(11)	0.69955(8)	0.0143(3)
C2	0.7028(2)	0.38727(12)	0.60131(8)	0.0232(3)
H2a	0.8067	0.4040	0.5636	0.031
H2b	0.7522	0.3618	0.6564	0.031
C3	0.5902(2)	0.29964(12)	0.55934(9)	0.0261(4)
H3a	0.6721	0.2416	0.5442	0.035
H3b	0.5356	0.3261	0.5057	0.035
C4	0.4368(2)	0.25806(11)	0.61836(9)	0.0238(3)
H4a	0.4922	0.2323	0.6720	0.032
H4b	0.3783	0.1983	0.5897	0.032
C5	0.2698(2)	0.54975(10)	0.72474(8)	0.0162(3)
H5	0.3490	0.6066	0.7471	0.021
C6	0.1594(2)	0.59633(12)	0.64816(9)	0.0215(3)
H6a	0.2429	0.6095	0.5997	0.029
H6b	0.0683	0.5449	0.6290	0.029
C7	0.0611(2)	0.69919(12)	0.67187(9)	0.0256(3)
H7a	-0.0323	0.6851	0.7150	0.038
H7b	0.0044	0.7285	0.6205	0.038
H7c	0.1492	0.7487	0.6950	0.038
C8	0.1410(2)	0.51868(12)	0.79861(9)	0.0200(3)
H8	0.0482	0.4649	0.7841	0.027
C9	0.1939(2)	0.52435(12)	0.89066(9)	0.0267(4)
H9a	0.1381	0.4739	0.9306	0.035
H9b	0.3207	0.5434	0.9042	0.035
C10	0.4970(2)	0.41687(11)	0.78354(8)	0.0145(3)
C11	0.4325(2)	0.33038(11)	0.83094(8)	0.0188(3)
H11	0.3411	0.2871	0.8073	0.025
C12	0.5037(2)	0.30824(12)	0.91345(8)	0.0222(3)
H12	0.4584	0.2507	0.9448	0.029
C13	0.6405(2)	0.37048(12)	0.94929(9)	0.0222(3)
H13	0.6859	0.3561	1.0049	0.030
C14	0.7097(2)	0.45474(12)	0.90138(8)	0.0197(3)
H14	0.8035	0.4965	0.9247	0.026
C15	0.6402(2)	0.47722(11)	0.81900(8)	0.0159(3)
H15	0.6895	0.5331	0.7870	0.021

$U_{eq}={}^{1}/{}_{3}[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$

Table 3. Refined Thermal Parameters (U's) for Compound (+)-20

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0190(2)	0.0203(2)	0.0154(2)	0.00320(13)	0.00386(14)	0.0006(2)
S2	0.0208(2)	0.0181(2)	0.0184(2)	-0.00276(12)	-0.0055(2)	-0.0025(2)
O1	0.0270(6)	0.0319(6)	0.0210(5)	-0.0028(4)	0.0060(5)	0.0091(5)
C1	0.0155(7)	0.0159(7)	0.0117(6)	-0.0008(5)	0.0000(5)	-0.0043(6)
C2	0.0242(8)	0.0301(8)	0.0153(6)	0.0034(6)	0.0043(6)	0.0108(7)
C3	0.0373(10)	0.0251(7)	0.0160(7)	-0.0002(6)	0.0020(7)	0.0116(8)
C4	0.0351(9)	0.0166(7)	0.0199(7)	-0.0038(6)	-0.0078(7)	0.0046(7)
C5	0.0160(7)	0.0157(7)	0.0167(6)	-0.0019(5)	-0.0004(6)	-0.0022(6)
C6	0.0213(8)	0.0220(8)	0.0212(7)	-0.0020(6)	-0.0027(7)	0.0033(6)
C7	0.0267(9)	0.0278(8)	0.0224(7)	0.0015(6)	0.0001(7)	0.0068(7)
C8	0.0168(8)	0.0214(8)	0.0219(7)	-0.0014(6)	0.0043(6)	0.0005(6)
C9	0.0241(9)	0.0353(9)	0.0206(7)	-0.0001(7)	0.0056(6)	0.0049(7)
C10	0.0131(7)	0.0180(7)	0.0123(6)	-0.0022(5)	0.0013(5)	0.0009(6)
C11	0.0189(7)	0.0201(7)	0.0173(7)	-0.0008(5)	-0.0003(6)	-0.0042(6)
C12	0.0262(8)	0.0233(7)	0.0170(7)	0.0058(6)	0.0026(6)	-0.0026(7)
C13	0.0230(8)	0.0306(8)	0.0131(6)	0.0005(6)	-0.0025(6)	0.0055(7)
C14	0.0144(8)	0.0257(7)	0.0192(7)	-0.0064(6)	0.0002(6)	0.0001(6)
C15	0.0138(7)	0.0172(7)	0.0167(6)	-0.0010(5)	0.0031(5)	-0.0006(6)

The form of the anisotropic displacement parameter is:
$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+ 2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$.

Table 4. Bond Distances in Compound (+)-20, Å

S1-C2	1.813(2)	S1-C1	1.8380(14)	S2-C4	1.813(2)
S2-C1	1.8330(14)	O1-C9	1.438(2)	O1-C8	1.452(2)
C1-C10	1.541(2)	C1-C5	1.568(2)	C2-C3	1.517(2)
C3-C4	1.523(2)	C5-C8	1.515(2)	C5-C6	1.534(2)
C6-C7	1.525(2)	C8-C9	1.461(2)	C10-C11	1.392(2)
C10-C15	1.395(2)	C11-C12	1.392(2)	C12-C13	1.377(2)
C13-C14	1.385(2)	C14-C15	1.386(2)		

Table 5. Bond Angles in Compound (+)-20, °

C2-S1-C1	99.51(7)	C4-S2-C1	100.30(7)	C9-O1-C8	60.73(9)
C10-C1-C5	107.96(10)	C10-C1-S2	113.61(9)	C5-C1-S2	107.75(9)
C10-C1-S1	110.62(10)	C5-C1-S1	107.25(9)	S2-C1-S1	109.40(6)
C3-C2-S1	113.61(11)	C2-C3-C4	113.04(11)	C3-C4-S2	115.02(10)
C8-C5-C6	110.48(12)	C8-C5-C1	110.94(11)	C6-C5-C1	114.63(10)
C7-C6-C5	112.78(11)	O1-C8-C9	59.17(9)	O1-C8-C5	115.85(12)
C9-C8-C5	123.06(13)	O1-C9-C8	60.10(9)	C11-C10-C15	118.36(12)
C11-C10-C1	122.17(13)	C15-C10-C1	119.05(12)	C12-C11-C10	120.41(14)
C13-C12-C11	120.81(13)	C12-C13-C14	119.14(12)	C13-C14-C15	120.50(14)
C14-C15-C10	120.69(13)				

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[i]. CrystalClear: Rigaku Corporation, 1999.

[ii]. CrystalStructure: Crystal Structure Analysis Package, Rigaku Corp. Rigaku/MSC (2002).

[iii]. REQAB4: R.A. Jacobsen, (1994). Private Communication.

[iv]. SIR97: Altomare, A., M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori & R. Spagna (1999). *J. Appl. Cryst.*, **32**, 115-119.

[v]. SHELXL-97: Program for the Refinement of Crystal Structures, Sheldrick, G.M. (1997), University of Göttingen, Germany.

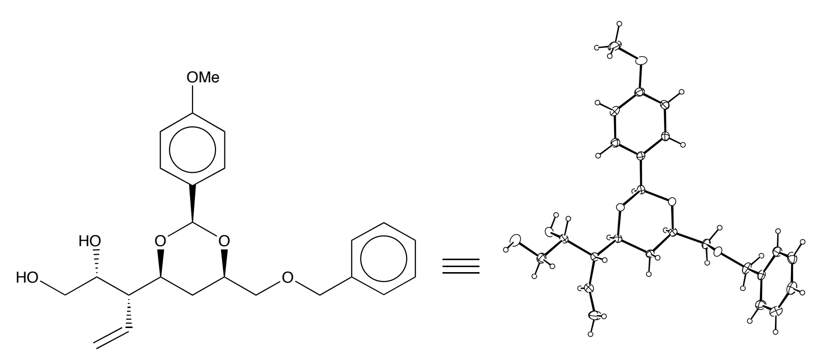
[vi]. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

$wR_2 = \{ \sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$

$GOF = \{ \sum w (F_o^2 - F_c^2)^2 / (n - p)\}^{1/2}$
where n = the number of reflections and p = the number of parameters refined.

[vii]. "ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations". C.K. Johnson (1976) ORNL-5138.

X-ray Structure Determination of Compound (-)-S23



Compound (-)-**S23**, $C_{24}H_{30}O_6$, crystallizes in the monoclinic space group $P2_1$ (systematic absences 0k0: k=odd) with a=10.8151(12)Å, b=7.9505(9)Å, c=12.684(2)Å, β=97.330(3)°, V=1081.8(2)Å^3, Z=2 and d_{calc}=1.272 g/cm^3. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K_α radiation (λ=0.71073 Å) at a temperature of 143K. Preliminary indexing was performed from a series of twelve 0.5° rotation images with exposures of 30 seconds. A total of 522 rotation images were collected with a crystal to detector distance of 35 mm, a 2θ swing angle of -12°, rotation widths of 0.5° and exposures of 15 seconds: scan no. 1 was a ϕ-scan from 37.5° to 187.5° at ω = 10° and χ = 20°; scan no. 2 was an ω-scan from -20° to 5° at χ = -90° and ϕ = 135°; scan no. 3 was an ω-scan from -20° to 4° at χ = -90° and ϕ = 45°; scan no. 4 was an ω-scan from -9° to 13° at χ = -90° and ϕ = 225°; scan no. 5 was an ω-scan from -20° to 20° at χ = -90° and ϕ = 0°. Rotation images were processed using CrystalClear[viii], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the CrystalStructure[ix] program package for further processing and structure solution on a Dell Pentium III computer. A total of 7206 reflections were measured over the ranges $5.3 \leq 2\theta \leq 50.04$ °, $-11 \leq h \leq 12$, $-9 \leq k \leq 8$, $-13 \leq l \leq 15$ yielding 3370 unique reflections (R_{int} = 0.0127). The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB[x] (minimum and maximum transmission 0.853, 1.000).

The structure was solved by direct methods (SIR97[xi]). Refinement was by full-matrix least squares based on F^2 using SHELXL-97[xii]. All reflections were used during refinement (F^2 's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w=1/[\sigma^2(F_o^2)+$

$0.0526P^2 + 0.1130P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to R_1=0.0297 and wR_2=0.0768 for 3297 reflections for which $F > 4\sigma(F)$ and R_1=0.0303, wR_2=0.0775 and GOF = 1.052 for all 3370 unique, non-zero reflections and 275 variables[xiii]. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.263 and -0.154 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Table 2. Anisotropic thermal parameters are in Table 3. Tables 4. and 5. list bond distances and bond angles. Figure 1. is an ORTEP[xiv] representation of the molecule with 30% probability thermal ellipsoids displayed.

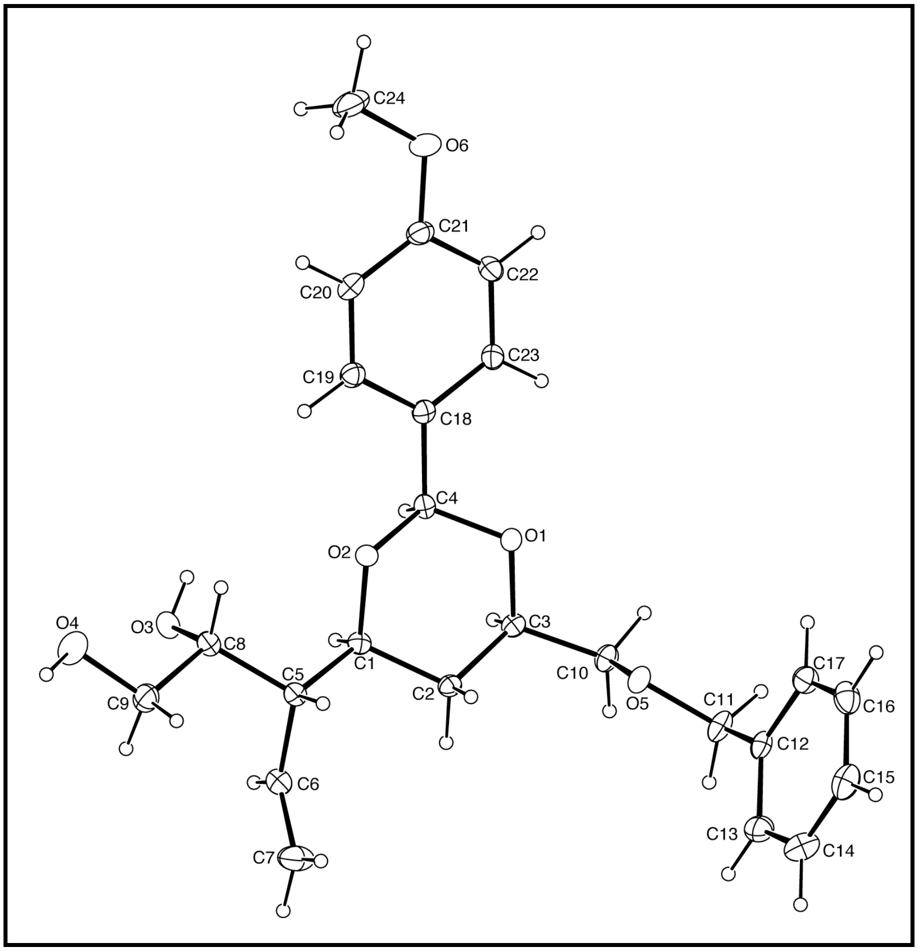


Figure 1. ORTEP drawing of (-)-**S23** with 30% probability thermal ellipsoids

Table 1. Summary of Structure Determination of Compound (-)-S23

Formula:	$C_{15}H_{20}S_2O$
Formula weight:	280.43
Crystal class:	orthorhombic
Space group:	$P2_12_12_1$ (#19)
Z	4
Cell constants:	
a	7.2254(9)Å
b	12.631(2)Å
c	15.299(2)Å
V	1396.2(3)$Å^3$
μ	3.67 cm^{-1}
crystal size, mm	0.32 x 0.22 x 0.20
D_{calc}	1.334 g/cm^3
F(000)	600
Radiation:	Mo-K_α (λ=0.71069Å)
2θ range	5.32 – 50.06 °
hkl collected:	$-7\leq h \leq 8$; $-14\leq k \leq 15$; $-18\leq l \leq 17$
No. reflections measured:	9714
No. unique reflections:	2458 (R_{int}=0.0157)
No. observed reflections	2384 (F>4σ)
No. reflections used in refinement	2458
No. parameters	165
R indices (F>4σ)	R_1=0.0200
	wR_2=0.0547
R indices (all data)	R_1=0.0206
	wR_2=0.0549
GOF:	1.078
Final Difference Peaks, $e/Å^3$	+0.171, -0.159

Table 2. Refined Positional Parameters for Compound (-)-S23

Atom	x	y	z	U_{eq}, Å^2
S1	0.57154(5)	0.50718(3)	0.62135(2)	0.01826(10)
S2	0.25945(5)	0.35391(3)	0.64615(2)	0.01913(10)
O1	0.0766(2)	0.60470(8)	0.85371(6)	0.0266(2)
C1	0.4007(2)	0.45562(11)	0.69955(8)	0.0143(3)
C2	0.7028(2)	0.38727(12)	0.60131(8)	0.0232(3)
H2a	0.8067	0.4040	0.5636	0.031
H2b	0.7522	0.3618	0.6564	0.031
C3	0.5902(2)	0.29964(12)	0.55934(9)	0.0261(4)
H3a	0.6721	0.2416	0.5442	0.035
H3b	0.5356	0.3261	0.5057	0.035
C4	0.4368(2)	0.25806(11)	0.61836(9)	0.0238(3)
H4a	0.4922	0.2323	0.6720	0.032
H4b	0.3783	0.1983	0.5897	0.032
C5	0.2698(2)	0.54975(10)	0.72474(8)	0.0162(3)
H5	0.3490	0.6066	0.7471	0.021
C6	0.1594(2)	0.59633(12)	0.64816(9)	0.0215(3)
H6a	0.2429	0.6095	0.5997	0.029
H6b	0.0683	0.5449	0.6290	0.029
C7	0.0611(2)	0.69919(12)	0.67187(9)	0.0256(3)
H7a	-0.0323	0.6851	0.7150	0.038
H7b	0.0044	0.7285	0.6205	0.038
H7c	0.1492	0.7487	0.6950	0.038
C8	0.1410(2)	0.51868(12)	0.79861(9)	0.0200(3)
H8	0.0482	0.4649	0.7841	0.027
C9	0.1939(2)	0.52435(12)	0.89066(9)	0.0267(4)
H9a	0.1381	0.4739	0.9306	0.035
H9b	0.3207	0.5434	0.9042	0.035
C10	0.4970(2)	0.41687(11)	0.78354(8)	0.0145(3)
C11	0.4325(2)	0.33038(11)	0.83094(8)	0.0188(3)
H11	0.3411	0.2871	0.8073	0.025
C12	0.5037(2)	0.30824(12)	0.91345(8)	0.0222(3)
H12	0.4584	0.2507	0.9448	0.029
C13	0.6405(2)	0.37048(12)	0.94929(9)	0.0222(3)
H13	0.6859	0.3561	1.0049	0.030
C14	0.7097(2)	0.45474(12)	0.90138(8)	0.0197(3)
H14	0.8035	0.4965	0.9247	0.026
C15	0.6402(2)	0.47722(11)	0.81900(8)	0.0159(3)
H15	0.6895	0.5331	0.7870	0.021

$U_{eq}={}^1/_3[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha]$

Table 3. Refined Thermal Parameters (U's) for Compound (-)-S23

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0190(2)	0.0203(2)	0.0154(2)	0.00320(13)	0.00386(14)	0.0006(2)
S2	0.0208(2)	0.0181(2)	0.0184(2)	-0.00276(12)	-0.0055(2)	-0.0025(2)
O1	0.0270(6)	0.0319(6)	0.0210(5)	-0.0028(4)	0.0060(5)	0.0091(5)
C1	0.0155(7)	0.0159(7)	0.0117(6)	-0.0008(5)	0.0000(5)	-0.0043(6)
C2	0.0242(8)	0.0301(8)	0.0153(6)	0.0034(6)	0.0043(6)	0.0108(7)
C3	0.0373(10)	0.0251(7)	0.0160(7)	-0.0002(6)	0.0020(7)	0.0116(8)
C4	0.0351(9)	0.0166(7)	0.0199(7)	-0.0038(6)	-0.0078(7)	0.0046(7)
C5	0.0160(7)	0.0157(7)	0.0167(6)	-0.0019(5)	-0.0004(6)	-0.0022(6)
C6	0.0213(8)	0.0220(8)	0.0212(7)	-0.0020(6)	-0.0027(7)	0.0033(6)
C7	0.0267(9)	0.0278(8)	0.0224(7)	0.0015(6)	0.0001(7)	0.0068(7)
C8	0.0168(8)	0.0214(8)	0.0219(7)	-0.0014(6)	0.0043(6)	0.0005(6)
C9	0.0241(9)	0.0353(9)	0.0206(7)	-0.0001(7)	0.0056(6)	0.0049(7)
C10	0.0131(7)	0.0180(7)	0.0123(6)	-0.0022(5)	0.0013(5)	0.0009(6)
C11	0.0189(7)	0.0201(7)	0.0173(7)	-0.0008(5)	-0.0003(6)	-0.0042(6)
C12	0.0262(8)	0.0233(7)	0.0170(7)	0.0058(6)	0.0026(6)	-0.0026(7)
C13	0.0230(8)	0.0306(8)	0.0131(6)	0.0005(6)	-0.0025(6)	0.0055(7)
C14	0.0144(8)	0.0257(7)	0.0192(7)	-0.0064(6)	0.0002(6)	0.0001(6)
C15	0.0138(7)	0.0172(7)	0.0167(6)	-0.0010(5)	0.0031(5)	-0.0006(6)

The form of the anisotropic displacement parameter is:
$\exp[-2\pi^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+ 2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$.

Table 4. Bond Distances in Compound (-)-S23, Å

S1-C2	1.813(2)	S1-C1	1.8380(14)	S2-C4	1.813(2)
S2-C1	1.8330(14)	O1-C9	1.438(2)	O1-C8	1.452(2)
C1-C10	1.541(2)	C1-C5	1.568(2)	C2-C3	1.517(2)
C3-C4	1.523(2)	C5-C8	1.515(2)	C5-C6	1.534(2)
C6-C7	1.525(2)	C8-C9	1.461(2)	C10-C11	1.392(2)
C10-C15	1.395(2)	C11-C12	1.392(2)	C12-C13	1.377(2)
C13-C14	1.385(2)	C14-C15	1.386(2)		

Table 5. Bond Angles in Compound (-)-S23, °

C2-S1-C1	99.51(7)	C4-S2-C1	100.30(7)	C9-O1-C8	60.73(9)
C10-C1-C5	107.96(10)	C10-C1-S2	113.61(9)	C5-C1-S2	107.75(9)
C10-C1-S1	110.62(10)	C5-C1-S1	107.25(9)	S2-C1-S1	109.40(6)
C3-C2-S1	113.61(11)	C2-C3-C4	113.04(11)	C3-C4-S2	115.02(10)
C8-C5-C6	110.48(12)	C8-C5-C1	110.94(11)	C6-C5-C1	114.63(10)
C7-C6-C5	112.78(11)	O1-C8-C9	59.17(9)	O1-C8-C5	115.85(12)
C9-C8-C5	123.06(13)	O1-C9-C8	60.10(9)	C11-C10-C15	118.36(12)
C11-C10-C1	122.17(13)	C15-C10-C1	119.05(12)	C12-C11-C10	120.41(14)
C13-C12-C11	120.81(13)	C12-C13-C14	119.14(12)	C13-C14-C15	120.50(14)
C14-C15-C10	120.69(13)				

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[xiii]. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

$wR_2 = \{ \sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$

$GOF = \{ \sum w (F_o^2 - F_c^2)^2 / (n - p) \}^{1/2}$
where n = the number of reflections and p = the number of parameters refined.

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