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Supporting Information

Allylic Sulfide 31. To a stirred solution of 1.0 g (2.60 mmol) of diene **32** in 20 mL of dry CH_2Cl_2 at 25°C was added 1.8 g (21.43 mmol) of solid sodium bicarbonate. The mixture was cooled to -78°C and a solution of freshly prepared phenylsulfenyl chloride (429 mg, 2.96 mmol) 5 mL of CH_2Cl_2 was added dropwise. After stirring for 3 h at -78°C the reaction was quenched by the addition of 20 mL of saturated sodium bicarbonate. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated. The residue was chromatographed (98:2 petroleum ether:EtOAc to provide 999 mg (78%) of sulfide **31** as a colorless oil. ^1H NMR ($CDCl_3$) δ 0.03 (6H, s), 0.17 (9H, 2), 0.87 (9H, s), 1.83 (3H, br s), 2.42 (1H, m), 3.82 (1H, d, J = 4.1 Hz), 3.95 (1H, dd, J = 10.3, 4.1 Hz), 3.98 (1H, d, J = 17.8 Hz), 4.16 (1H, d, J = 4.1 Hz),), 4.25 (1H, d, J = 17.8 Hz), 4.26 (dd, J = 19.2, 10.3 Hz), 5.53 (1H, d, J = 4.1 Hz), 7.10 - 7.30 (5H, band) . IR 3045, 2945, 2920, 2885, 1772, 1730, 1670, 1580, 1470, 1439, 1380, 1288, 1058 cm^{-1}. Anal: Calcd. for $C_{25}H_{40}O_4Si_2S$: C, 60.93; H, 8.18; Si, 11.40; S, 6.51. Found: C, 60.78; H, 8.58; Si, 10.65; S, 6.72.

Allylic Alcohol 47. To a stirred, cooled (-78°C) solution of 50 mg (0.10 mmol) of sulfide **31** in 5 mL of dry CH_2Cl_2 was added dropwise via syringe a solution of 29.2 mg (0.10 mmol) of 60% m-chloroperoxybenzoic acid in 1 mL of dry CH_2Cl_2. After 1 h the reaction mixture was warmed to room temperature and concentrated. The residue was chromatographed (9:1 hexanes:EtOAc) to provide 50.1 mg (100%) of the sulfoxide. ^1H NMR ($CDCl_3$) δ 0.07 (3H, s), 0.11 (3H, s), 0.19 (9H, 2), 0.91 (9H, s), 1.50 (3H, br s), 2.37 (1H, ddd, J = 1.2, 4.7, 4,7 Hz), 3.93 (1H, d, J = 4.7 Hz), 4.04 (1H, d, J = 18.6 Hz), 4.06 (1H, dd, J = 11.2, 3.7 Hz), 4.25 (1H, d, J = 18.6 Hz), 4.30 (d, J = 3.7 Hz), 4.36 (dd, J = 22.3, 11.2 Hz), 5.95 (1H, d, J = 3.7 Hz), 7.35 - 7.82 (5H, band) . IR

3045, 2945, 2920, 2885, 1772, 1730, 1670, 1580, 1470, 1439, 1380, 1288, 1058 cm^{-1}. A solution of 25 mg (0.05 mmol) of the sulfoxide from above and 58 μL (0.5 mmol) of trimethylphosphite in 6 mL of methanol was heated at reflux under argon for 3 h. The solvent was evaporated under vacuum and the residue was chromatographed (9:1 hexanes:EtOAc) to provide 19.7 mg (100%) of the allylic alcohol **47** as a colorless oil which was identical to that prepared by the oxidation of selenide **48** described above.

Diol 51. To 634 mg (1.29 mmol) of sulfide **31** was added 10 mL of a freshly prepared mixture of acetonitrile and 40% aqueous HF (ratio 95:5). The resulting solution was stirred at room temperature for 20 min. The reaction was then quenched by adding solid sodium bicarbonate in small batches until the carbon dioxide evolution stopped. The mixture was then filtered through a pad of Celite / $MgSO_4$ and concentrated to provide 394 mg (100%) of diol **51** as a white solid. R_f (50% EtOAc/hexanes): 0.24. ^1H NMR $CDCl_3$) δ 1.92 (3H, br. s), 2.37 (1H, dt, J = 5.26, 3.76 Hz), 3.77 (1H, d, J = 5.26 Hz), 3.95-4.17 (2H, band, 2 H), 4.03 (1H, d, J = 18.05 Hz), 4.21 (1H, d, J = 4.51 Hz), 4.30 (1H, d, J = 18.05 Hz), 5.69 (1H, br. d, J = 4.51 Hz), 7.19-7.37 and 7.47-7.57 (5H, band). IR (film) 3420, 3060, 2975, 2945, 2920, 2880, 1772, 1672, 1590, 1485, 1383, 1296, 1171, 1114, 1084, 1037, 952 cm^{-1}. Anal. Calcd. for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.92; S, 10.47. Found: C, 63.08; H, 6.05; S, 10.12.

Alcohol 52 To a stirred solution of 64.2 mg (0.21 mmol) of diol **51** in 5 mL of CH_2Cl_2 at room temperature under argon was added 0.195 mL (1.68 mmol) of 2,6-lutidine dropwise *via* syringe, followed by 0.16 mL (0.84 mmol) trimethylsilyl trifluoromethanesulfonate *via* syringe. The solution was for 12 h. The reaction was then quenched with a saturated aqueous sodium bicarbonate solution (5 mL) and brine. The aqueous layers were extracted twice with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under high vacuum (<1 mm. Hg). The

residue was chromatographed on a silica gel column over 2 hours (2 to 5% EtOAc / petroleum ether) to provide 71.4 mg (90%) of alcohol **52** as an oil. R_f (25% EtOAc/hexanes): 0.09. ^{1}H NMR ($CDCl_3$) δ 0.15 (9H, s), 1.84 (3 H,br. s), 2.50 (1H, dt, J = 7.43, 5.58 Hz), 3.76 (1H, d, J = 5.58 Hz,), 3.98 (1H, d, J = 18.59 Hz), 4.06-4.22 (3H, band), 4.27 (1H, d, J = 18.59 Hz), 5.57 (1H, br. d, J = 4.65 Hz), 7.14-7.30 and 7.49-7.55 (5H, band). Anal. Calcd. for $C_{18}H_{26}O_4SSi$: C, 58.98; H, 7.15. Found: C, 58.97; H, 7.10.

Aldehyde 54. Method A: To a stirred solution of 39.93 μL (0.08 mmol) of oxalyl chloride (2.0 M in CH_2Cl_2) in 5 mL of CH_2Cl_2 at -78 °C under argon was added dropwise 11.33 μL (0.16 mmol) of DMSO in 0.5 mL of CH_2Cl_2 *via* syringe, while maintaining the temperature below -65 °C. The solution was allowed to stir 5 min and then 30 mg (0.07 mmol) of alcohol **52** 0.5 mL of CH_2Cl_2 was added dropwise. After stirring for 35 min at -78 °C, neat triethylamine (46.38 μL, 0.33 mmol) was added slowly and dropwise *via* syringe so as to maintain a temperature below -65 °C. After the reaction was stirred for 15 min at -78 °C, it was slowly warmed to room temperature by removing the cooling bath. The mixture was then extracted with water (5 mL) and the aqueous layer was back extracted twice with fresh CH_2Cl_2 (5 mL). The combined organic layers were then washed with brine, dried on $MgSO_4$, filtered and concentrated. The residue was chromatographed (5% EtOAc/petroleum ether) to provide aldehyde **54** (25.4 mg, 85%) as an oil.

Method B: Solid tetra-*n*-propylammonium perruthenate (2.5 mg, 7 mmol) was added in one portion to a stirred solution of 32 mg of alcohol **52** (0.07 mmol) and powdered 4Å molecular sieves (433 mg) in CH_2Cl_2 (4 mL) at room temperature under argon. A solution of *N*-methylmorpholine *N*-oxide (12.5 mg, 0.11 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise. The solution was stirred for 3 hours. Upon completion, the reaction mixture was filtered through a pad of silica, eluting with CH_2Cl_2. The filtrate was condensed and the residue was chromatographed (5% EtOAc/petroleum ether) to provide

aldehyde **54** (29 mg, 91%) as an oil. R_f(25% EtOAc/hexanes): 0.48. ^{1}H NMR ($CDCl_3$) δ 0.13 (9H, s), 1.78 (3H, br. s), 2.80 (1H, dd, J = 5.41, 2.70 Hz), 3.72 (1H, d, J = 5.41 Hz), 3.98 (1H, d, J = 18.02 Hz), 4.17 (1H, d J = 18.02 Hz), 5.35 (1H, m), 7.16-7.30 and 7.37-7.44 (5H, band), 10.05 (1H, d, J = 2.7 Hz).

Unsaturated ester 55. Carbethoxymethylenetriphenylphosphine (7.67 g, 22 mmol) was added in one portion to a stirred solution of 1.089 g (2.2 mmol) of ketone **31** in 25 mL of toluene at room temperature under argon. The reaction mixture was heated to reflux and allowed to stir for 4 days. The mixture was then cooled and the solvent removed at reduced pressure. The crude residue was taken up in a minimum amount of CH_2Cl_2 and this diluted with methyl butane until precipitation ceased. This mixture was cooled to 0 °C, filtered and the residue washed with ice cold methyl butane (30 mL). This process was repeated once more and the filtrate was reduced under vacuum and chromatographed (5% EtOAc/petroleum ether) to provide 1.04 g (84%) of ester **55** as an oil. ^{1}H NMR ($CDCl_3$) δ 0.02 (3H, s), 0.04 (3H, s), 0.16 (9H, s), 0.90 (9H, s), 1.34 (3H, t, J = 7.4 Hz), 1.83 (3H, s), 2.26 (1H, m), 3.84 (1H, d, J = 4.6 Hz), 4.03 (1H, dd, J = 9.3, 3.7 Hz), 4.07 (1H, d, J = 5.6 Hz, 1 H), 4.23 (2H, m), 4.35 (1H, dd, J = 9.3, 9.3 Hz), 4.88 (1H, d, J = 1.9 Hz), 5.53 (1H, br. d, J = 5.6 Hz), 5.87 (1H, t, J = 3.7 Hz), 7.13-7.45 and 7.40-7.64 (5H, band). Anal. Calcd. for $C_{29}H_{46}O_5SSi_2$: C, 61.88; H, 8.24. Found: C, 61.75; H, 8.31.

Allylic alcohol 56. To a stirred suspension of 310 mg (10 mmol) lithium aluminum hydride in 20 mL of diethyl ether at -78 °C under argon was added dropwise 2.56 g (4.55 mmol) of ester **55** in 5 mL of diethyl ether so as to maintain the temperature below -70°C. After the addition was complete, the suspension was stirred for 8 hours at -78 °C, overnight at room temperature and then quenched by cautious addition of 5% NaOH until only a flocculent white salt remained in suspension. The reaction mixture was then filtered

and the salts rinsed with fresh diethyl ether (2 X 10 mL). The filtrate was washed with water (10 mL) and brine, then dried over $MgSO_4$ and filtered. The solvents were concentrated and the residue was chromatographed (5 to 10 to 30% EtOAc/petroleum ether) to provide 2.01 g (85%) of alcohol **56** as an oil. R_f (50% EtOAc/hexanes): 0.57. ^1H NMR ($CDCl_3$) δ 0.03 (3H, s), 0.04 (3H, s), 0.17 (9H, s), 0.9 (9H, s), 1.7 (1H, br. s,), 1.8 (3H, br. s), 2.14 (1H, ddd, J = 9.8, 4.5, 3.8 Hz), 3.82 (1H, d, J = 4.5 Hz), 4.02 (1H, br. d, J = 3.8 Hz), 4.10 (1H, dd, J = 9.8, 3.8 Hz), 4.18 (2H, d, J = 6.0 Hz), 4.39 (1H, dd, J = 9.8, 9.8 Hz), 4.52 (2H, br. s), 5.5 (1H, br. d, J = 3.8 Hz), 5.60 (1H, m), 7.15-7.29 and 7.61-7.65 (5H, band). Anal. Calcd. for $C_{27}H_{44}O_4SSi_2$: C, 62.26; H, 8.52. Found: C, 62.02; H, 8.19.

***Cis-trans* diene 57Z.** A solution of 0.85 mL (1.28 mmol) of methyllithium-lithium bromide complex (1.5 M solution in diethyl ether) was added dropwise to a stirred solution of 1.12 g (1.16 mmol) phosphonium salt **4** in 10 mL of tetrahydrofuran at -78 °C under argon. The solution was stirred 1 h at -78 °C and 602 mg (1.16 mmol) of the freshly chromatographed aldehyde **5** in 2 mL of tetrahydrofuran was added dropwise. The mixture was stirred 3.5 h at -78 °C and warmed to 25 °C. The reaction was then quenched with a solution of saturated ammonium chloride (10 mL), extracted with diethyl ether (15 mL), brine, dried over $MgSO_4$ and filtered. The solvent was concentrated and the residue was chromatographed (5% EtOAc/petroleum ether) to afford the 1.04 g (83%) of *cis-trans* diene **61Z**. R_f (25% EtOAc/hexanes): 0.75. IR ($CDCl_3$) 2960, 2933, 2859, 1462, 1385, 1254, 1107, 1084. ^1H NMR (400 MHz, $CDCl_3$) δ 0.03 (3H, s), 0.04 (3H, s), 0.14 (9H, s, 9 H), 0.69 (3H, d, J = 5.20 Hz), 0.70 (3H, d, J = 5.20 H), 0.76 (3H, d, J = 6.3 Hz), 0.90 (9H, s, 9 H), 0.98 (3H, d, J = 6.30 H), 1.08 (9H, s, 9 H), 1.22-2.22 (15H, band), 1.59 (3H, s), 1.82 (3H, s), 2.85 (1H, m), 2.92 (1H, dd, J = 10.00, 2.00 Hz), 3.32 (1H, m), 3.84 (1H, d, J = 4.80 Hz), 4.03 (1H, br. s), 4.13 (1H, m), 4.44 (1H, t, J = 10.00 Hz), 4.55 (b1H, r. s), 5.17 (1H, t, J = 6.8 Hz), 5.33 (1H, t, J = 10.4, 10.0 Hz), 5.51

(1H, br. s), 5.74 (1H, dd, J = 11.6, 10.8 Hz), 6.24 (1H, br. d, J = 12.0 Hz), 7.14-7.44 and 7.64-7.92 (15H, band). ^{13}C NMR (400 MHz, $CDCl_3$) d 2.28, 13.95, 16.02, 17.40, 18.33, 19.14, 20.60, 20.76, 22.57, 25.97, 26.98, 28.14, 30.07, 31.46, 34.38, 35.61, 41.03, 44.53, 45.25, 47.84, 51.11, 59.91, 66.72, 67.67, 67.99, 76.70, 78.56, 79.28, 97.06, 118.63, 121.78, 122.94, 125.72, 127.45, 128.50, 129.41, 130.71, 134.60, 134.47, 134.54, 135.65, 139.45, 141.55. Anal. Calcd. for $C_{64}H_{96}O_6SSi_3$: C,71.13; H, 8.98. Found: C, 71.45; H, 9.06.

Trans-trans* diene 57*E A few drops of diluted solution of iodine in benzene-d_6 were added to a stirred solution of 1.04 g (0.96 mmol) of cis-trans diene **61Z** in 5 mL of benzene-d_6 at room temperature under argon. The reaction was followed by ^1H-NMR. Upon completion, the reaction was quenched with a solution of 10% sodium thiosulfate (10 mL), extracted with ether (10 mL), brine, dried over $MgSO_4$ and filtered. The solvent were concentrated and the residue was chromatographed (5% EtOAc/petroleum ether) to afford 1.04 g (100%) of the *trans-trans* diene **61*E*** R_f (25% EtOAc/hexanes): 0.71. IR ($CDCl_3$) 2956, 2933, 2859, 1466, 1385, 1254, 1107, 1073. ^1H NMR (400 MHz, $CDCl_3$) d 0.01 (3H, s, 3 H), 0.02 (3H, s), 0.10 (9H, s), 0.12 (9H, s), 0.67 (3H, d, J = 6.8 Hz), 0.69 (3H, d, J = 8.0 Hz), 0.72 (3H, d, J = 6.8 Hz), 0.87 (9H, s), 0.95 (3H, m), 1.06 (9H, s), 1.19-1.90 and 1.95-2.24 (15H, band), 1.56 (3H, s, 3 H), 1.80 (3H, s), 2.37 (1H, m), 2.90 (1H, dd, J = 9.7, 2.58 Hz), 3.31 (1H, m), 3.80 (1H, d, J = 4.6 Hz), 4.00 (1H, br. s), 4.11 (1H, m), 4.34 (1H, td, J = 9.84, 2.08 Hz), 4.54 (2H, br. s), 5.13 (1H, m), 5.47 (1H, br. d, J = 3.95 Hz), 5.63 (1H, m), 5.83 (1H, m), 5.86 (1H, m), 7.12-7.44 and 7.60-7.70 (15H, band). ^{13}C NMR (250 MHz, $CDCl_3$) d 2.22, 11.41, 13.95, 16.39, 17.38, 18.29, 19.14, 19.42, 19.54, 20.41, 20.59, 22.54, 22.59, 25.98, 28.97, 27.63, 28.16, 29.03, 31.48, 34.33, 35.10, 35.15, 35.84, 40.99, 44.91, 45.27, 47.35, 51.30, 60.00, 66.78, 67.79, 68.02, 77.88, 78.88, 79.09, 97.11, 122.88, 123.11, 123.82, 125.71, 127.45, 128.52, 129.41, 130.72, 134.47, 134.53, 134.81, 135.88,

140.33, 141.97, 142.05. Anal. Calcd. for $C_{64}H_{96}O_6SSi_3$: C,71.13; H, 8.98. Found: C, 71.27; H, 8.72.

Diol 58. To a stirred solution of 337 mg (0.3 mmol) of diene ***57E*** in 5 mL of methanol at room temperature under argon was added 4 mg (0.029 mmol) of potassium carbonate in one portion. The mixture was stirred for 5 days at 25 °C. The solvent was concentrated and the residue was then diluted with 10 mL of ether, washed with a solution of saturated ammonium chloride (2 X 5 mL) and brine. The organic layer was dried over $MgSO_4$, filtered, the solvent were and concentrated. The residue was chromatographed (5 to 20% EtOAc/petroleum ether) to provide 256 mg (89%) of diol **58** as an oil. R_f (25% EtOAc/hexanes): 0.2. IR ($CDCl_3$) 3426, 2959, 2930, 2859, 1732, 1460, 1439, 1385. ^1H NMR (400 MHz, $CDCl_3$) δ 0.64 (3H, d, J = 7.0 Hz), 0.66 (3H, d, J = 7.0 Hz), 0.70 (3H, d, J = 7.0 Hz), 0.90 (3H, d, J = 7.0 Hz), 1.04 (9H, s), 1.18-2.36 (18H, band), 1.53 (1H, s), 1.91 (1H, s), 2.88 (1H, dd, J = 9.8, 1.75 Hz, 1 H, 3.29 (1H, m), 3.50 (1H, d, J = 6.58 Hz), 3.82 (1H, d, J = 4.52 Hz), 3.95 (1H, d, J = 4.21 Hz), 4.11 (1H, m), 4.34 (1H, m), 4.53 (1H, d, J = 14.23 H), 4.61 (1H, d, J = 14.23 H), 5.11 (1H, t, J = 7.04 Hz), 5.66 (1H, br. d, J = 3.56 Hz), 5.71 (1H, m, 1 H), 5.83 (1H, m), 6.12 (1H, dd, J = 10.79, 1.1 Hz), 7.25-7.40 and 7.55-7.67 (15H, band). ^{13}C NMR (250 MHz, $CDCl_3$) δ 3.10, 13.93, 14.16, 16.28, 17.37, 19.12, 19.25, 19.39, 20.56, 21.01, 22.31, 26.96, 28.12, 31.46, 34.30, 34.81, 34.91, 35.60, 40.92, 42.29, 45.23, 47.16, 52.58, 57.02, 60.35, 61.41, 66.74, 68.01, 68.05, 76.62, 77.32, 77.66, 77.89, 79.79, 88.84, 97.10, 120.03, 122.82, 123.13, 123.17, 123.24, 127.40, 127.44, 129.32, 129.41, 131.21, 134.40, 134.45, 134.58, 135.66, 137.27, 140.83, 140.87, 141.08, 141.13, 142.98. Anal. Calcd. for $C_{55}H_{74}O_6SSi$: C, 74.12; H, 8.37. Found: C, 74.00; H, 8.62.

Alcohol 59. To a stirred solution of 274 mg of diol (0.31 mmol) **58** in 10 mL of CH_2Cl_2at room temperature under argon was added 0.29 mL (2.46 mmol) of 2,6-lutidine dropwise followed by 0.24 mL (1.23 mmol) of trimethylsilyl trifluoromethanesulfonate . The solution was stirred for 2 hours at 25 °C. The reaction was then quenched with a saturated aqueous sodium bicarbonate solution (10 mL) and brine. The aqueous layer was extracted with CH_2Cl_2 (2 X 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under high vacuum (<1 mm. Hg). The residue was chromatographed over 2 hours (5 to 15% EtOAc/petroleum ether) to provide 258 mg (87%) of alcohol **59** as an oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.11 (9H, s), 0.64 (3H, d, J = 6.80 Hz), 0.66 (3H, d, J = 6.80 Hz), 0.70 (3H, d, J = 7.0 Hz), 0.90 (9H, d, J = 6.8 Hz), 1.04 (9H, s), 1.18-2.38 (18H, band), 1.54 (3H, s), 1.80 (3H, s), 2.88 (1 H, dd, J = 9.95, 1.94 Hz), 3.30 (1 H, m), 3.79 (1 H, d, J = 4.78 Hz), 4.00-4.18 (3H, band), 4.26 (1 H, m), 4.51 (1 H, br. s), 5.10 (1 H, m), 5.49 (1 H, br. d, J = 4.46 Hz), 5.66 (1 H, m), 5.79 (1 H, m), 5.94 (1 H, br. d, J = 10.82 Hz), 7.13-7.40 and 7.52-7.67 (15H, band). ^{13}C NMR (63 MHz, $CDCl_3$) δ 2.19, 14.00, 16.39, 17.44, 19.18, 19.37, 19.46, 20.62, 22.5, 27.03, 28.20, 31.53, 34.38, 34.91, 35.16, 35.67, 40.97, 44.33, 45.31, 47.25, 47.38, 51.39, 60.78, 66.80, 67.96, 68.06, 77.73, 79.10, 79.73, 118.17, 122.93, 123.11, 123.19, 123.57, 126.41, 127.51, 129.00, 129.48, 130.69, 130.75, 134.49, 134.64, 135.73, 139.68, 140.33, 142.64, 142.69, 142.99. Anal. Calcd. for $C_{58}H_{82}O_6SSi_2$: C,72.30; H, 8.58. Found: C, 72.66; H, 8.31.

Aldehyde 60. Solid tetra-*n*-propylammonium perruthenate (0.6 mg, 10%) was added in one portion to a stirred solution of 17 mg (0.02 mmol) of alcohol **59** and powdered 4Å molecular sieves (0.108 g) in 2 mL of CH_2Cl_2 at room temperature under argon. A solution of 2.56 mg (0.02 mmol) of *N*-methylmorpholine *N*-oxide in CH_2Cl_2 was added dropwise. The solution was stirred for 30 min. Upon completion the reaction mixture was filtered through a pad of silica, eluting with CH_2Cl_2 . The filtrate was condensed and the

residue was chromatographed (5% EtOAc/petroleum ether) to provide 12.7 mg (75%) of aldehyde **60** as an oil. R_f(25% EtOAc/hexanes): 0.48. IR ($CDCl_3$) 2959, 2958, 1717, 1385, 1111, 1085 1067, 1011. ^1H NMR (400 MHz, $CDCl_3$) d 0.27 (9H, s), 0.64 (3H, d, J = 6.79 Hz), 0.66 (3H, d, J = 6.47 Hz), 0.70 (3H, d, J = 7.00 Hz), 0.80-2.38 (17H, band),1.03 (9H, s), 1.52 (3H, s), 1.78 (3H, s), 2.75 (1H, d, J = 5.5 Hz, 1 H), 2.87 (1H, dd, J = 9.84, 1.94 Hz, 1 H), 3.28 (1H, m), 3.71 (1H, d, J = 5.5 Hz), 4.02-4.16 (2H, band), 4.51 (2H, br. s), 5.10 (1H, m), 5.52 (1H, br. d, J = 4.35 Hz), 5.69-5.80 (1H, band), 5.99 (1H, dd, J = 10.75, 1.11 Hz), 7.15-7.44 and 7.58-7.68 (15H, band).

Acid 62. To a solution of 15.2 mg (0.016 mmol) of aldehyde **60** in 0.5 mL of tert-butyl alcohol and 0.5 mL of water at 0 °C was added 0.5 mL of 2-methyl-2-butene. Solid sodium chlorite (80%) (8.9 mg, 0.079 mmol) and 13 mg (0.094 mmol) of sodium phosphate monobasic monohydrate were added sequentially. The resulting biphase mixture was raised to room temperature and stirred vigorously for 5 h. The reaction was poured into pH 4.0 buffer (2 mL) and extracted with ether (3 X 3 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated. The filtrate was condensed and the residue was chromatographed (5% to 20% EtOAc/petroleum ether) to provide 11.9 mg (83%) of acid **61**. R_f(100% EtOAc/hexanes): 0.61. IR ($CDCl_3$) 3250, 2930, 1725, 1380, 1089, 1011. ^1H NMR (400 MHz, $CDCl_3$) δ 0.62 (3H, d, J = 6.79 Hz), 0.65 (3H, d, J = 6.79 Hz), 0.78 (3H, d, J = 7.00 Hz), 0.80-2.38 (17H, band),1.03 (9H, s), 1.50 (3H, s), 1.88 (3H, s), 2.86 (1H, m), 3.29 (1H, m), 3.38 (1H, m), 3.80 (1H, d, J = 5.7 Hz), 4.02 (1H, m), 4.12 (1H, m), 4.52 (1H, AB, J = 14.81 Hz), 4.60 (1H, AB, J = 14.81 Hz), 5.10 (1H, m), 5.57-5.81 (3H, band), 6.24 (1H, m), 7.12-7.45 and 7.58-7.68 (15H, band).

Tetrabutylammonium fluoride (0.09 mL, 0.09 mmol), as a 1 M solution in THF, was added to a solution of acid from above (11.2 mg, 0.012 mmol) in 0.5 mL of THF. The resulting solution was stirred for 24 h at room temperature. The solution was concentrated

in vacuo and purified by column chromatography on silica gel (25-50% EtOAc/hexanes) then (10-30% MeOH/hexanes) to provide hydroxy acid **62** (8.0 mg, 97%) as a white foam. IR ($CDCl_3$) 3250, 2930, 1725, 1380, 1089, 1011. ^1H NMR (200 MHz, $CDCl_3$) δ 0.77 (3H, d, J = 6.8 Hz), 0.82 (3H, d, J = 6.8 Hz), 0.98 (3H, d, J = 7.00 Hz), 1.02 (3H, d, J = 7.00 Hz); 0.80-2.48 (17H, band), 1.56 (3H, s), 1.89 (3H, s), 2.86 (1H, m), 3.04 (1H, m), 3.19 (1H, m), 3.59 (1H, m), 3.78 (1H, m), 4.01 (1H, m), 4.28 (1H, m), 4.58 (2H, AB, J = 14.81 Hz), 4.93 (1H, m), 5.42-5.81 (3H, band), 6.26 (1H, m), 7.17-7.32 and 7.46-7.55 (5H, band). Anal. Calcd. for $C_{39}H_{54}O_7S$: C, 70.24; H, 8.16. Found: C, 69.90; H, 8.01.

Macrolactone 3 A solution of *N,N*-dicyclohexylcarbodiimide (62 mg, 0.30 mmol), 4-dimethylaminopyridine (32 mg, .26 mmol) and DMAP·HCl (45 mg, 0.28 mmol) in 35 mL of dry (ethanol-free) $CHCl_3$ was heated to reflux. Hydroxy acid **62** (8.0 mg, 0.012 mmol) in 6 mL of dry (ethanol-free) $CHCl_3$ was added to the refluxing solution via a syringe pump over a period of 16 h. The long needle was inserted through the condenser and placed right over the refluxing solution such that the refluxing chloroform washed the substrate droplets forming at its tip. Upon completion of the addition, the flask and syringe containing the substrate were washed by more chloroform (2 x 2 mL) and these solutions were delivered by syringe pump over a period of 1 h. The reaction mixture was cooled to room temperature and excess DCC was consumed by adding MeOH (0.6 mL) and acetic acid (0.05 mL). The resulting solution was stirred at room temperature for 2 h, concentrated in vacuo and purified by column chromatography on silica gel (0-5-10% EtOAc/hexanes) to afford macrolactone **3** (4.0 mg, 57%) as a white foam: ^1H NMR (200 MHz, $CDCl_3$) δ 0.79 (3H, d, J = 6.8 Hz), 0.92 (3H, d, J = 6.8 Hz), 0.97 (3H, d, J = 7.00 Hz), 1.07 (3H, d, J = 7.00 Hz); 0.80-2.42 (17H, band), 1.48 (3H, s), 2.08 (3H, s), 2.92 (1H, d, J = 5.5 Hz), 3.04 (1H, m), 3.58 (1H, m), 3.61 (1H, d, J = 5.5 Hz), 3.97 (1H, m), 4.52 (2H, AB, J = 14.8 Hz), 4.92 (1H, m), 5.08 (1H, m), 5.37-5.76 (3H,

band), 6.09 (1H, m), 7.17-7.45 (5H, band). Anal. Calcd. for $C_{39}H_{52}O_6S$: C, 72.19; H, 8.08. Found: C, 71.92; H, 8.36.

Sulfoxide 63 To a stirred, cooled (-78°C) solution of 13 mg (0.02 mmol) of sulfide **62** in 1.5 mL of dry CH_2Cl_2 was added dropwise via syringe 0.7 mL (0.021 mmol) of a 0.03 M solution of 60% m-chloroperoxybenzoic acid in of dry CH_2Cl_2. After 2 h an additional 0.15 mL of m-CPBA solution was added. After an additional 1h the reaction mixture was warmed to room temperature and concentrated. The residue was chromatographed (9:1 hexanes:EtOAc) to provide 6.0 mg (45%) of the sulfoxide. ^1H NMR (200 MHz, $CDCl_3$) δ 0.79 (3H, d, J = 6.8 Hz), 0.95 (3H, d, J = 6.8 Hz), 0.98 (3H, d, J = 7.00 Hz), 1.07 (3H, d, J = 7.00 Hz); 0.80-2.42 (17H, band), 1.49 (3H, s), 1.68 (3H, s), 3.06 (1H, d, J = 5.5 Hz), 3.13 (1H, m), 3.48 (1H, m), 4.03 (1H, m), 4.55 (2H, AB, J = 14.8 Hz), 4.92 (1H, m), 5.33-5.72 (3H, band), 5.88 (1H, m), 6.13 (1H, m), 7.43-7.71 (5H, band). Anal. Calcd. for $C_{39}H_{52}O_7S$: C, 70.45; H, 7.89. Found: C, 70.41; H, 7.69.

Diene 64 A solution of 6 mg (0.009 mmol) of the sulfoxide **63** from above and 10 μL (0.09 mmol) of trimethylphosphite in 2 mL of methanol was heated at reflux under argon for 3 h. The solvent was evaporated under vacuum and the residue was chromatographed (9:1 hexanes:EtOAc) to provide 3 mg (62%) of the elimination product **64** as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$) δ 0.82 (3H, d, J = 6.8 Hz), 0.87 (3H, d, J = 6.8 Hz), 1.03 (3H, d, J = 7.00 Hz), 1.08 (3H, d, J = 7.00 Hz); 0.80-2.45 (17H, band), 1.48 (3H, s), 1.94 (3H, s), 3.11 (1H, m), 3.63 (1H, m), 4.14 (1H, s), 4.29 (1H, d, J = 4 Hz), 4.39 (1H, AB, J = 15, 2 Hz), 4.54 (1H, AB, J = 15, 2 Hz), 4.95 (1H, m), 5.36 (1H,m), 5.48 (1H, dd, J = 10, 15 Hz), 5.77 (1H, dd, J = 11, 15 Hz), 6.02 (1H, m), 6.34 (2H, m). Anal. Calcd. for $C_{33}H_{46}O_6$: C, 73.40; H, 8.59. Found: C, 73.81; H, 8.50.