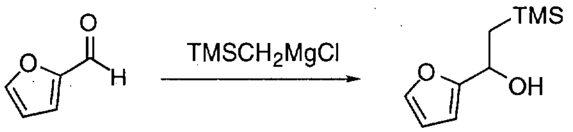
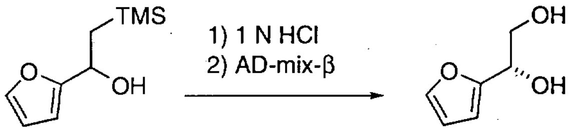
Supporting Information

Enantioselective Synthesis of Isoaltholactone, 3-*Epi*-Altholactone and 5-Hydroxy Goniothalamin

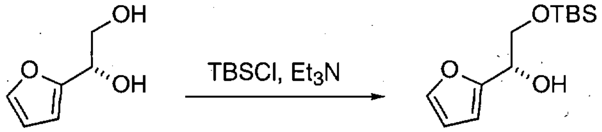
General Methods. Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen using oven-dried glassware and standard syringe/septa techniques. Analytical TLC was performed using precoated glass-backed plates (Whatman K6F 60A, F_{254}) that were analyzed by fluorescence upon 254 nm irradiation or by staining with with *p*-anisaldehyde, potassium permanganate, or phosphomolybdic acid stains. Liquid chromatography was performed using (flash chromatography) of the indicated solvent system on ICN reagent silica gel 60 (60-200 mesh). Ether and tetrahydrofuran were distilled from benzophenone and sodium metal. Dichloromethane and triethylamine were distilled from calcium hydride. Hexanes refers to the petroleum fraction bp 40-60 °C. Commercial reagents were used without purification unless otherwise noted. ^{1}H and ^{13}C spectra were recorded on Varian 300 and 500 MHz spectrometers. Chemical shifts are reported relative to $CDCl_3$ (δ 7.26 ppm) or internal tetramethylsilane (δ 0.00 ppm) for ^{1}H and $CDCl_3$ (δ 77.0 ppm) for ^{13}C. Melting points are uncorrected. Optical rotations were measured with a Jasco DIP-370 digital polarimeter. Infrared (IR) spectra were obtained on a Prospect MIDAC FT-IR spectrometer. High resolution mass spectrometric data was performed by the University of Minnesota Mass Spectrometry Laboratory. Combustion analyses were performed by M-H-W Laboratories, Phoenix, AZ.



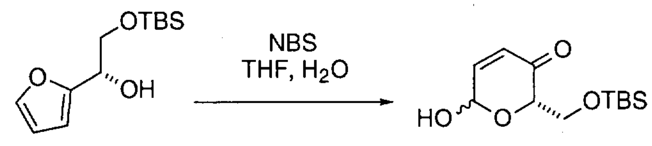
1-(2′-*Furyl*)-2-*trimethylsilanylethan*-1-*ol* (not shown). Magnesium turnings (10.1 g, 0.415 mol) were placed in a 1 L-3-neck round bottom flask and a condenser along with a side arm addition funnel were attached. The apparatus was flame dried (3x), each time flushing with nitrogen. Chloromethyltrimethylsilane (42.4 g, 0.346 mol) in 200 mL of Et_2O were added slowly to the dry magnesium. After the addition, the solution was refluxed for 1 h. Freshly distilled furfural (25.0 mL, 0.302 mol) and 300 mL of Et_2O were added slowly to the Grignard reagent at 0 °C and the solution was stirred for 3 h at 0 °C and 9 h at room temp. The reaction was quenched with 200 mL of sat. aq. NH_4Cl and extracted (3 x 100 mL) with Et_2O. The organic layer was washed with satd aq $NaHCO_3$ (2 x 50 mL), brine (2 x 50 mL), dried (Na_2SO_4), and concentrated under reduced pressure to give the β-hydroxy silane in a 90% yield, 50.1 g (0.272 mol): R_f (30% Et_2O/hexanes) = 0.58; IR (thin film, cm^{-1}) 3390, 2950, 2895, 1655, 1505, 1250; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (dd, J = 1.8, 0.7 Hz, 1H), 6.24 (dd, J = 3.1, 1.8 Hz, 1H), 6.13 (d, J = 3.3 Hz, 1H), 4.77 (dd, J = 8.8, 6.9 Hz, 1H), 3.13 (bs, 1H), 1.28 (dd, J = 14.1, 8.8 Hz, 1H), 1.23 (dd, J = 14.1, 6.8 Hz, 1H), -0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 141.6, 110.1, 105.5, 65.6, 24.8, -1.4; CIHRMS Calcd for $[C_9H_{16}O_2Si]^+$: 184.0920. Found 184.0905.



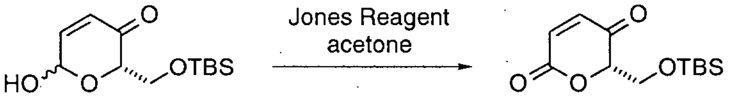
1-(2′-*Furyl*)*ethan*-1S,2-*diol* (not shown). The β-hydroxy silane (44.2 g, 0.240 mol) and 120 mL of Et_2O were added to a 500 mL round bottom flask followed by addition of 120 mL of 1 M HCl and the solution was stirred for 1 h. Phases were separated and the aq layer was extracted (2 x 50 mL) with Et_2O and combined with the organic layer. The organic layer was washed (2 x 50 mL) with sat. aq. $NaHCO_3$ and added to a solution of 300 mL of *t*-BuOH, 750 mL of H_2O, 50 g of AD-mix-β, 133 g of $K_3Fe(CN)_6$, and 56 g of K_2CO_3 at 0 °C. The solution was vigorously stirred with a mechanical stirrer for 12 h at 0 °C. The reaction was slowly quenched with (500 mL) satd aq Na_2SO_3. The phases were separated and the aqueous layer was extracted (6 x 100 mL) with EtOAc. The organic layer was washed with satd aq $NaHCO_3$ (2 x 100 mL), brine (2 x 100 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography eluting with 40% Et_2O/hexanes to yield 25.0 g (0.195 mol, 85%) of diol: R_f (50% Et_2O/hexanes) = 0.37; $[\alpha]^{21}_D$ = -30.0 (c 1.82, CH_2Cl_2); IR (thin film, cm^{-1}) 3390, 2933, 2881, 1684, 1505, 1464, 1228; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (dd, J = 1.8, 0.8 Hz, 1H), 6.34 (dd, J = 3.1, 1.8 Hz, 1H), 6.30 (dd, J = 3.2, 0.8 Hz, 1H), 4.78 (t, J = 5.7 Hz, 1H), 3.84 (d, J = 5.7 Hz, 2H), 3.82 (bs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 142.4, 110.5, 107.1, 68.5, 65.2; CIHRMS Calcd for $[C_6H_8O_3 + NH_4]^+$: 146.0817. Found 146.0822; Anal. Calcd for $C_6H_8O_3$: C, 56.23; H, 6.30. Found: C, 56.04; H, 6.20.



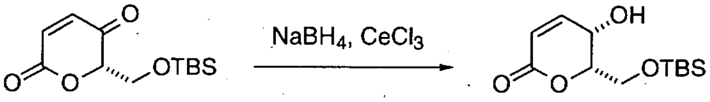
1-(2′-*Furyl*)-2-tert-*butyldimethylsilanyloxyethan*-1S-*ol* (3). Diol from AD-mix-β (0.986 g, 7.70 mmol), 15 mL of CH_2Cl_2, and 5.5 mL of Et_3N were added to a round bottom flask and cooled to 0 °C. A catalytic amount (50 mg, 0.41 mmol) of DMAP was added followed by addition of *tert*-butyldimethylsilyl chloride (1.19 g, 7.89 mmol) and the solution was stirred at 0 °C for 6 h. The reaction was quenched with 1 M $NaHSO_4$ and extracted (3 x 25 mL) with Et_2O, washed with satd aq $NaHCO_3$ (2 x 20 mL), and dried (Na_2SO_4). The crude product was purified by silica gel flash chromatography eluting with 25% Et_2O/hexanes to yield 1.69 g (6.97 mmol, 91%) of **3**: R_f (30% Et_2O/hexanes) = 0.55; $[\alpha]^{21}_D = -14.6$ (*c* 0.99, CH_2Cl_2); IR (thin film, cm^{-1}) 3447, 2954, 2930, 2884, 2857, 1471, 1463, 1361, 1148, 1119, 1006; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.36 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.34 (dd, *J* = 3.0, 0.8 Hz, 1H), 4.78 (dd, *J* = 6.9, 4.8 Hz, 1H), 3.90 (dd, *J* = 9.9, 4.5 Hz, 1H), 3.86 (dd, *J* = 9.9, 6.9 Hz, 1H), 2.89 (bs, 1H), 0.92 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 142.1, 110.3, 107.1, 68.5, 65.8, 25.9, 18.4, -5.3; CIHRMS Calcd for $[(C_{12}H_{22}O_3Si)-H_20]^+$: 225.1310. Found 225.1296; Anal. Calcd for C, 59.47; H, 9.16. Found C, 59.80; H, 9.37.



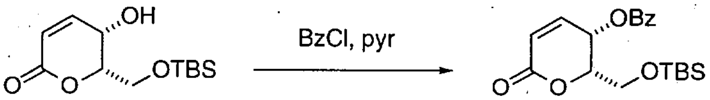
6-*Hydroxy*-(2S)-2-tert-*butyldimethylsilanyloxymethyl*-2H-*pyran*-3-(6H)-*one* (not shown). Compound **3** (1.69 g, 6.97 mmol), 12 mL of THF, and 3 mL of H_2O were added to a round bottom flask and cooled to 0 °C. Solid $NaHCO_3$ (1.17 g, 13.9 mmol), $NaOAc{\bullet}3H_20$ (0.950 g, 6.98 mmol), and NBS (1.24 g, 6.97 mmol) were added to the solution and the mixture was stirred for 1 h at 0 °C. The reaction was quenched with satd aq $NaHCO_3$ (15 mL), extracted (3 x 25 mL) with Et_2O, dried (Na_2SO_4), concentrated under reduced pressure and purified by silica gel chromatography eluting with 20% EtOAc/hexanes to give 1.71 g (6.62 mmol, 95%) of **6-*hydroxy*-(2S)-2-tert-*butyldimethylsilanyloxymethyl*-2H-*pyran*-3-(6H)-*one***: R_f (20% EtOAc/hexanes) = 0.25; IR (thin film, cm^{-1})3389, 2942, 2867, 1692, 1460, 1256, 1125, 1088; ^1H NMR (500 MHz, $CDCl_3$) major isomer δ 6.89 (dd, *J* = 10.0, 3.0 Hz, 1H), 6.08 (dd, *J* = 10.0 Hz, 1H), 5.75 (dd, *J* = 5.5, 3.0 Hz, 1H), 4.54 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.03 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.98 (dd, *J* = 11.5, 5.0 Hz, 1H), 0.83 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) major isomer δ 194.7, 147.0, 127.8, 87.8, 79.6, 63.2, 25.8, 18.3, -5.4, -5.5.; CIHRMS Calcd for $[(C_{12}H_{22}O_4Si)+H]^+$: 259.1366. Found 259.1366; Anal. Calcd for C, 55.79; H, 8.59. Found C, 55.86; H, 8.45.



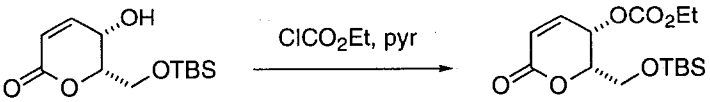
(6S)-6-tert-*Butyldimethylsilanyloxymethylpyran*-2,5-*dione* (not shown). Compound **6-*hydroxy*-(2S)-2-tert-*butyldimethylsilanyloxymethyl*-2H-*pyran*-3-(6H)-*one*** (460 mg, 1.79 mmol) was dissolved in 15 mL of acetone and Jones reagent (2.5 M) was dripped in at room temp until a yellow color persisted. After 15 min the starting material was no longer visible by TLC and the solution was filtered through a pad a celite and washed with 150 mL of Et_2O. The Et_2O filtrate was washed with satd aq $NaHCO_3$ (50 mL) and the phases were separated. The organic layer was dried ($MgSO_4$) and concentrated to yield 367 mg (1.43mmol, 80%) of pure dione **(6S)-6-tert-*Butyldimethylsilanyloxymethylpyran*-2,5-*dione***: R_f (20% EtOAc/hexanes) = 0.40; $[\alpha]^{21}{}_D = -58.0$ (*c* 0.81, CH_2Cl_2); IR (thin film, cm^{-1}) 2949, 2928, 2892, 2857, 1721, 1697, 1461, 1360, 1306, 1261, 1128, 1111, 1083; ^1H NMR (500 MHz, $CDCl_3$) δ 6.92 (d, *J* = 10.0 Hz, 1H), 6.77 (d, *J* = 10.0 Hz, 1H), 4.88 (dd, *J* = 3.5, 3.5 Hz, 1H), 4.08 (dd, *J* = 17.5, 3.5 Hz, 1H), 4.03 (dd, *J* = 17.5, 4.5 Hz, 1H), 0.81 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.6, 160.5, 138.8, 136.2, 84.3, 65.2, 25.5, 18.0, -5.8, -5.9; CIHRMS Calcd for $[C_{12}H_{20}O_4Si + NH_4]^+$: 274.1475. Found: 274.1456; Anal. Calcd for C, 56.23; H, 7.87. Found C, 56.10; H, 7.68.



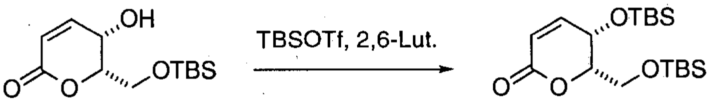
(6S)-6-tert-*Butyldimethylsilanyloxymethyl*-(5S)-5-*hydroxy*-5,6-*dihydro*-*pyran*-2-*one* (4). Compound **(6S)-6-tert-*butyldimethylsilanyloxymethylpyran*-2,5-*dione*** (870 mg, 3.39 mmol) was dissolved in 10 mL of CH_2Cl_2, cooled to -78 °C with a dry ice/acetone bath, and 17 mL of a 0.4 M solution of $CeCl_3$ in MeOH was added to the solution. $NaBH_4$ (193 mg, 5.09 mmol) was added and the solution was stirred for 1.5 h. The solution was warmed to room temp and 50 mL of Et_2O and 100 mL of H_2O were added. The phases were separated and the aq layer was extracted (5 x 50 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (20% EtOAc/hexanes) to give 840 mg (3.25 mmol, 96%) of compound **4**: R_f (20% EtOAc/hexanes) = 0.28; $[\alpha]^{21}{}_D = 94.1$ (*c* 0.58, CH_2Cl_2); IR (thin film, cm^{-1}) 3416, 2930, 2857, 1713, 1631, 1472, 1383, 1258, 1138, 1098, 1059; ^1H NMR (500 MHz, $CDCl_3$) δ 7.00 (dd, *J* = 9.5, 6.0 Hz, 1H), 6.12 (d, *J* = 10.0 Hz, 1H), 4.41 (ddd, *J* = 6.0, 6.0, 3.0 Hz, 1H), 4.37 (ddd, *J* = 7.0, 4.5, 3.0 Hz, 1H), 4.09 (dd, *J* = 10.5, 6.5 Hz, 1H), 4.03 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.10 (bs, 1H), 0.91 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 144.0, 123.0, 78.6, 62.1, 61.3, 25.7, 18.2, -5.5 (2C); CIHRMS Calcd for $[C_{12}H_{22}O_4Si + NH_4]^+$: 276.1631. Found: 276.1646; Anal. Calcd for C, 55.79; H, 8.59; Found C, 55.98; H, 8.39.



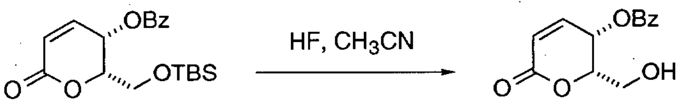
(6S)-6-tert-*Butyldimethylsilanyloxymethyl*-(5S)-5-*benzoyl*-5,6-*dihydro*-*pyran*-2-*one* (5a). Compound **4** (375 mg, 1.45 mmol) was dissolved in 5 mL of CH_2Cl_2 and (240 uL, 2.90 mmol) of pyridine was added to the solution. Benzoyl chloride (840 uL, 7.25 mmol) was added and the solution was stirred at room temp for 3 h. The reaction was quenched with (10 mL) of satd aq $NaHCO_3$ and 10 mL of Et_2O. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (10% EtOAc/hexanes) to give 415 mg (1.14 mmol, 80 %) of compound **5a**: R_f (10% EtOAc/hexanes) = 0.3; $[\alpha]^{21}_D$ = 218.3 (*c* 1.54, CH_2Cl_2); IR (thin film, cm^{-1}) 2955, 2929, 2884, 2856, 1724, 1452, 1266, 1136, 1095; ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.59 (dt, *J* = 8.5, 1.5, 1.5 Hz, 1H), 7.46 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.18 (dd, *J* = 9.5, 6.0 Hz, 1H), 6.25 (d, *J* = 10.0 Hz, 1H), 5.58 (dd, *J* = 6.0, 2.5 Hz, 1H), 4.67 (ddd, *J* = 8.5, 5.5, 2.5 Hz, 1H), 4.00 (dd, *J* = 10.0, 8.5 Hz, 1H), 3.96 (dd, *J* = 10.0, 5.5 Hz, 1H), 0.81 (s, 9H), 0.01 (s, 3H), -0.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 162.2, 140.5, 133.6, 129.8, 128.6, 125.3, 78.4, 61.4, 60.2, 25.6, 18.0, -5.6, -5.8; FABHRMS Calcd for $[C_{19}H_{26}O_5Si + H]^+$: 363.1628. Found: 363.1624.



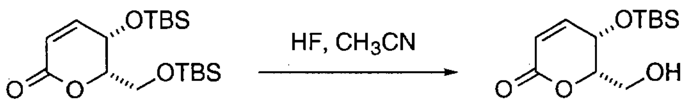
(6S)-6-tert-*Butyldimethylsilanyloxymethyl*-(5S)-5-*ethoxycarbonyl*-5,6-*dihydro-pyran*-2-*one* (5b). Compound **4** (32 mg, 0.12 mmol) was dissolved in 1.5 mL of CH_2Cl_2 and 100 uL of pyridine was added to the solution. Ethyl chloroformate (118 uL, 1.2 mmol) was added and the solution was stirred at room temp for 8 h. The reaction was quenched with (10 mL) of satd aq $NaHCO_3$ and 10 mL of Et_2O. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (10% EtOAc/hexanes) to give 37 mg (0.11 mmol, 92%) of compound **5b**: R_f (10% EtOAc/hexanes) = 0.28; $[\alpha]^{21}_D$ = 189.9 (*c* 0.67, CH_2Cl_2); IR (thin film, cm^{-1}) 2958, 2931, 2886, 2857, 1747, 1472, 1372, 1341, 1256, 1136; ^1H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, *J* = 9.5, 6.0 Hz, 1H), 6.20 (d, *J* = 9.5 Hz, 1H), 5.19 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.53 (ddd, *J* = 8.5, 5.5, 2.5 Hz, 1H), 4.17 (dq, *J* = 14.0, 7.0, 1.0 Hz, 2H), 3.91 (dd, *J* = 10.0, 9.0 Hz, 1H), 3.86 (dd, *J* = 10.0, 6.0 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 3H), 0.85 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 154.1, 139.6, 125.6, 77.9, 64.6, 63.7, 59.8, 25.6, 18.0, 14.1, -5.7, -5.9; FABHRMS Calcd for $[C_{15}H_{26}O_6Si + H]^+$: 331.1577. Found: 331.1580; Anal. Calcd for C, 54.52; H, 7.94; Found C, 54.72; H, 8.04.



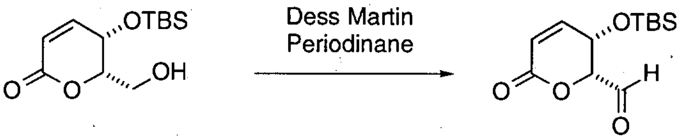
(6S)-6-tert-*Butyldimethylsilanyloxymethyl*-(5S)-5-tert-*butyldimethylsilanyloxy* -5,6-*dihydro-pyran*-2-*one* (5c). Compound **4** (70 mg, 0.27 mmol) was dissolved in 1.5 mL of CH_2Cl_2 and 125 uL (1.1 mmol) of 2,6-lutidine was added to the solution. TBSOTf (125 uL, 0.54 mmol) was added and the solution was stirred at 0 °C for 0.5 h. The reaction was quenched with (10 mL) of satd aq $NaHCO_3$ and 10 mL of Et_2O. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (10% EtOAc/hexanes) to give 86 mg (0.23 mmol, 85%) of compound **5c**: R_f (10% EtOAc/hexanes) = 0.25; $[\alpha]^{21}{}_D$ = 124.0 (*c* 0.60, CH_2Cl_2); IR (thin film, cm^{-1}) 2954, 2929, 2886, 2857, 1715, 1472, 1383, 1253, 1115, 1069; ^1H NMR (500 MHz, $CDCl_3$) δ 6.87 (dd, *J* = 10.0, 5.5 Hz, 1H), 6.06 (d, *J* = 9.5 Hz, 1H), 4.30 (dd, *J* = 5.5, 2.5 Hz, 1H), 4.26 (ddd, *J* = 8.0, 5.5, 3.0 Hz, 1H), 3.94 (dd, *J* = 10.5, 8.0 Hz, 1H), 3.83 (dd, *J* = 10.0, 5.0 Hz, 1H), 0.88 (s, 9H), 0.86 (s, 9H), 0.07 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 144.5, 122.6, 80.7, 60.4, 60.2, 25.8, 25.6, 18.2, 18.0, -4.2, -4.9, -5.43, -5.44; FABHRMS Calcd for $[C_{18}H_{36}O_4Si_2 + Na]^+$: 395.2045. Found: 395.2045; Anal. Calcd for C, 58.03; H, 9.75; Found C, 57.99; H, 9.64.



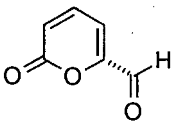
(5S)-5-*benzoyl*-(6S)-6-hydroxymethyl-5,6-*dihydro-pyran*-2-*one* (6a). Compound **5a** (29 mg, 0.080 mmol) was dissolved in 0.4 mL of CH_3CN and (270 uL, 0.23 mmol) of a 5 % solution of HF (48 %) in CH_3CN was added to the solution. The solution was stirred at room temp for 4 hours. The reaction was quenched with (10 mL) of satd aq $NaHCO_3$ and 10 mL of Et_2O. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (50% EtOAc/hexanes) to give 19 mg (0.077 mmol, 96 %) of compound **6a**: M. pt. = 116-117 °C; R_f (50% EtOAc/hexanes) = 0.2; $[\alpha]^{21}{}_D$ = 358.5 (*c* 0.40, CH_2Cl_2); IR (thin film, cm^{-1}) 3518, 3077, 2944, 2859, 1716, 1641, 1451, 1380, 1263, 1101, 1058; ^1H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.62 (dt, *J* = 9.0, 1.5, 1.5 Hz, 1H), 7.47 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.11 (dd, *J* = 10.0, 6.0 Hz, 1H), 6.32 (d, *J* = 10.0 Hz, 1H), 5.63 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.73 (ddd, *J* = 9.0, 6.5, 2.5 Hz, 1H), 4.04 (ddd, *J* = 12.5, 6.5, 6.0 Hz, 1H), 3.85 (ddd, *J* = 12.0, 7.5, 6.5 Hz, 1H), 2.38 (dd, J = 7.5, 6.0, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 162.1, 139.9, 134.0, 130.0, 128.7, 125.7, 79.1, 61.8, 60.6; FABHRMS Calcd for $[C_{13}H_{12}O_5 + H]^+$: 249.0763. Found: 249.0774.



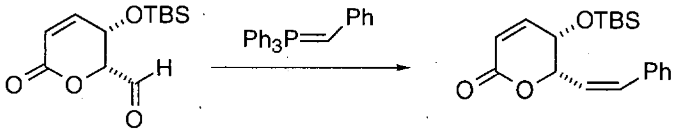
(5S)-5-tert-*butyldimethylsilanyloxy* -(6S)-6-*hydroxymethyl*-5,6-*dihydro-pyran*-2-*one* (6c). Compound **5c** (140 mg, 0.376 mmol) was dissolved in 0.6 mL of CH_3CN and (0.6 mL, 0.56 mmol) of a 5 % solution of HF (48 %) in CH_3CN was added to the solution. The solution was stirred at room temp for 6 hours. The reaction was quenched with (10 mL) of satd aq $NaHCO_3$ and 10 mL of Et_2O. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (50% EtOAc/hexanes) to give 88 mg (0.341 mmol, 91 %) of compound **6c**: M. pt. = 93-95 °C; R_f (50% EtOAc/hexanes) = 0.3; $[\alpha]^{21}_{D}$ = 149.4 (*c* 0.81, CH_2Cl_2); IR (thin film, cm^{-1}) 3367, 2957, 2928, 2856, 1710, 1462, 1385, 1257, 1117, 1070; ^1H NMR (500 MHz, $CDCl_3$) δ 6.83 (dd, *J* = 10.0, 5.5 Hz, 1H), 6.11 (d, *J* = 10.0 Hz, 1H), 4.44 (ddd, *J* = 8.0, 5.0, 3.0 Hz, 1H), 4.33 (dd, *J* = 5.5, 3.0 Hz, 1H), 4.02 (ddd, *J* = 12.0, 7.0 Hz, 1H), 3.85 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.14 (bs, 1H), 0.87 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 144.0, 122.6, 80.9, 61.6, 61.5, 25.5, 18.0, -4.2, -5.0; FABHRMS Calcd for $[C_{12}H_{22}O_4Si + H]^+$: 259.1366. Found: 259.1380; Anal. Calcd for C, 55.79; H, 8.42; Found C, 55.83; H, 8.42.



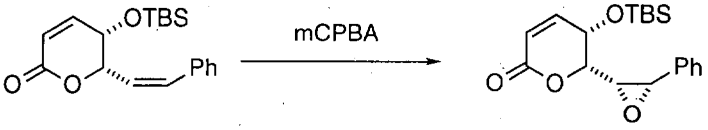
(3S)-3-tert-*butyldimethylsilanyloxy* -6-*oxo*-3,6-*dihydro*-2H-*pyran*-(2S)-2-*carbaldehyde* (7c). Compound **6c** (172 mg, 0.665 mmol) was dissolved in 3.0 mL of CH_2Cl_2 and (850, 10.1 mmol) of $NaHCO_3$ and (850 mg, 2.00 mmol) of Dess Martin reagent were added to the solution. The solution was stirred at room temp for 0.5 hours. The reaction was quenched with 20 mL of Et_2O. The solution was filtered through florisil and subsequent washing of the florisil with 100 ml of Et_2O. The organic fraction was concentrated to give crude **7c**, 140 mg (0.527 mmol, 79 %): R_f (100% Et_2O) = 0.3; IR (thin film, cm^{-1}) 2957, 2929, 2896, 2858, 1724, 1472, 1463, 1380,1255, 1123, 1084; ^1H NMR (300 MHz, $CDCl_3$) δ 9.75 (s, 1H), 6.80 (dd, *J* = 9.9, 4.5 Hz, 1H), 6.12 (d, *J* = 9.6 Hz, 1H), 4.71 (m, 2H), 0.84 (s, 9H), 0.09 (s, 3H), 0.086 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 161.3, 143.3, 122.5, 83.2, 62.8, 25.4, 17.9, -4.4, -5.1; CI HRMS Calcd for $[C_{12}H_{20}O_4Si + H]^+$: 257.1209. Found: 257.1218.



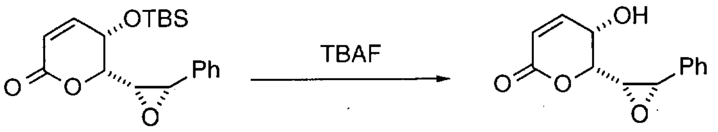
6-*oxo*-6H-*pyran*-2-*carbaldehyde* (8). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.47 (dd, *J* = 15.5, 10.5 Hz, 1H), 6.91 (dd, *J* = 10.5, 2.0 Hz, 1H), 6.61 (dd, J = 16.0, 2.0 Hz, 1H.



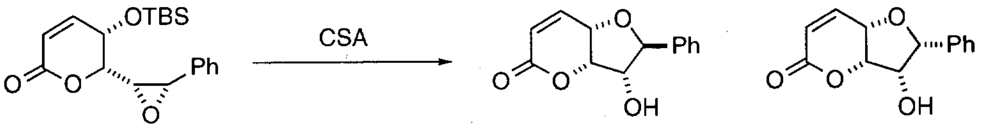
(5S)-5-tert-*butyldimethylsilanyloxy* -(6S)-6-cis-*styryl*-5,6-*dihydro*-*pyran*-2-*one* (2a). Benzyl triphenylphosphonium bromide (100 mg, 0.228 mmol) was dissolved in 0.5 mL of THF and (115 uL, 0.182 mmol) of *n*-BuLi was added to the solution at 0 °C. The solution was stirred at room temp for 20 min. The solution was cooled to -78 °C and compound **7c** (39 mg, 0.152 mmol) in 0.5 mL of THF was syringed into the benzylidene triphenyl phosphorane solution. The solution was stirred at -78 °C for 30 min. The reaction was warmed to room temp, quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (20% EtOAc/hexanes) to give **2a**, 21 mg (0.064 mmol, 42 % over two steps): M. pt. = 144-147 °C; R_f (20 % EtOAc/hexanes) = 0.25; $[\alpha]^{21}_D$ = -16.4 (*c* 0.97, CH_2Cl_2); IR (thin film, cm^{-1}) 2928, 2855, 1715, 1463, 1443, 1384, 1360, 1277, 1256, 1101, 1080; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.29 (m, 3H), 6.88 (d, *J* = 11.5 Hz, 1H), 6.81 (dd, *J* = 9.5, 5.0 Hz, 1H), 6.07 (d, *J* = 9.5 Hz, 1H), 6.04 (dd, *J* = 11.5, 9.5 Hz, 1H), 5.15 (dd, *J* = 9.5, 3.0 Hz, 1H), 4.25 (dd, *J* = 4.5, 3.0 Hz, 1H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 145.1, 135.9, 135.6, 128.53, 128.50, 127.8, 124.9, 122.1, 76.8, 63.7, 25.6, 18.1, -4.4, -4.8; FAB HRMS Calcd for $[C_{12}H_{20}O_3Si + H]^+$: 331.1729. Found: 331.1725; Anal. Calcd for C, 69.06; H, 7.94; Found C, 68.85; H, 7.76.

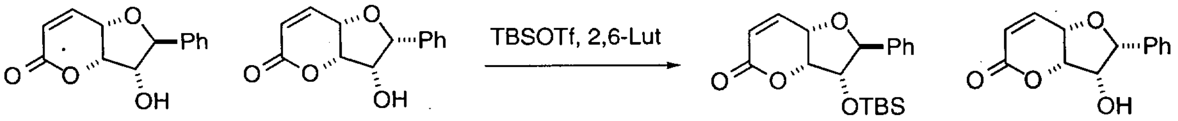


(5S)-5-tert-*butyldimethylsilanyloxy* -(6S)-6-((3S)-3-*phenyloxiranyl*)-5,6-*dihydro*-*pyran*-2-*one* (9). Compound **2a** (31 mg, 0.094 mmol) was dissolved in 0.4 mL of CH_2Cl_2, $NaHCO_3$ (47 mg, 0.56 mmol) and mCPBA (50 mg, 0.28 mmol) were added to the solution. The reaction was stirred for 8 hours at room temp. The reaction was quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (20% EtOAc/hexanes) to give **9**, 26 mg (0.075 mmol, 80 %): R_f (20 % EtOAc/hexanes) = 0.25; $[\alpha]^{21}_D$ = 98.6 (*c* 0.59, CH_2Cl_2); IR (thin film, cm^{-1}) 2952, 2927, 2855, 1722, 1462, 1379, 1254, 1158, 1104, 1061; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.31 (m, 5H), 6.83 (dd, *J* = 9.5, 6.0 Hz, 1H), 5.99 (d, *J* = 10 Hz, 1H), 4.32 (d, *J* = 4.0 Hz, 1H), 4.26 (dd, *J* = 5.5, 2.5 Hz, 1H), 3.65 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.62 (dd, *J* = 9.0, 2.5 Hz, 1H), 0.92 (s, 9H), 0.21 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 143.7, 133.9, 128.4, 128.2, 126.4, 122.7, 76.6, 61.5, 57.4, 55.0, 25.6, 18.1, -4.3, -5.0; FAB HRMS Calcd for $[C_{19}H_{26}O_4Si + H]^+$: 347.1679. Found: 347.1686.

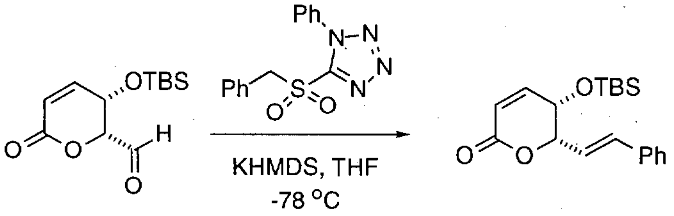


(5S)-5-*hydroxy* -(6S)-6-((3S)-3-*phenyloxiranyl*)-5,6-*dihydro-pyran*-2-*one* (not shown). Compound **9** (12 mg, 0.035 mmol) was dissolved in 0.3 mL of THF and 70 uL (0.07 mmol) of a 1.0 M solution of TBAF was added to the solution at room temp . The reaction was stirred for 0.5 h at room temp. The reaction was quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (100% Et_2O) to give **(5S)-5-*hydroxy* -(6S)-6-((3S)-3-*phenyloxiranyl*)-5,6-*dihydro-pyran*-2-*one***, 6.2 mg (0.026 mmol, 80 %): R_f (100 % Et_2O) = 0.25; $[\alpha]^{21}_D$ = 44.3 (*c* 0.14, CH_2Cl_2); IR (thin film, cm^{-1}) 3413, 2924, 2880, 1732, 1372, 1250, 1099, 1054; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46-7.32 (m, 5H), 6.96 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.06 (d, *J* = 9.6 Hz, 1H), 4.37 (d, *J* = 3.0 Hz, 1H), 4.32 (m, 1H), 3.76 (dd, *J* = 9.6, 2.4 Hz, 1H), 3.71 (dd, *J* = 9.9, 3.3 Hz, 1H), 2.24 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9, 143.3, 133.5, 128.6, 128.4, 126.3, 123.4, 75.9, 61.2, 57.6, 55.3; FAB HRMS Calcd for $[C_{13}H_{12}O_4 + H]^+$: 233.0814. Found: 233.0808.



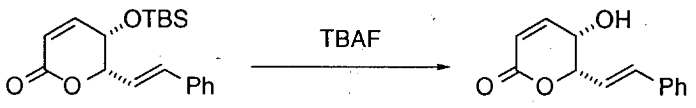


3-Epi-*Altholactone* (1a). (5S)-5-*hydroxy* -(6S)-6-((3S)-3-*phenyloxiranyl*)-5,6-*dihydro-pyran*-2-*one* (3.0 mg, 0.013 mmol) was dissolved in 0.15 mL of CH_2Cl_2 and a catalytic amount of CSA was added to the solution at room temp. The reaction was stirred for 1.5 h at room temp. The reaction was quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (100% Et_2O) to give **1a** and **1c** as a 1 : 1 mixture, 2.5 mg (0.011 mmol, 85 %). **3-Epi-*Altholactone* (1a)** and ***Isoaltholactone* (1c)** as a 1 : 1 mixture, 4.0 mg (0.017 mmol) was dissolved in 0.2 mL of CH_2Cl_2, 8 uL (0.07 mmol) of 2,6-lutidine, and 8 uL (0.03 mmol) of TBSOTf were added and stirred for 10 minutes. The reaction was quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (100% Et_2O) to give 1.5 mg (0.0065 mmol, 38 %) of **3-epi-*altholactone* (1a)** and 2.0 mg (0.0058 mmol, 34 %) of **3-tert-*butyldimethylsilanyloxy isoaltholactone* (12)**. **3-epi-*altholactone* (1a)**: R_f (100 % Et_2O) = 0.36; $[\alpha]^{21}_D = +30.7$ (*c* 0.06, EtOH); IR (thin film, cm^{-1}) 3376, 2922, 2852, 1714, 1455, 1398, 1246, 1159, 1118, 1042; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40-7.32 (m, 5H), 6.88 (dd, J = 10.0, 3.5 Hz, 1H), 6.15 (dd, J = 10.0, 1.0 Hz, 1H), 5.24 (dd, J = 8.0, 4.5 Hz, 1H), 5.10 (dd, J = 4.5, 4.5 Hz, 1H), 4.81 (ddd, J = 8.0, 3.5, 1.0 Hz, 1H), 4.56 (dd, J = 4.5, 4.5 Hz, 1H), 1.82 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0, 141.5, 135.1, 128.5, 128.4, 126.8, 121.7, 80.8, 79.6, 73.8, 67.3; FAB HRMS Calcd for $[C_{13}H_{12}O_4 + Na]^+$: 255.0633. Found: 255.0634.

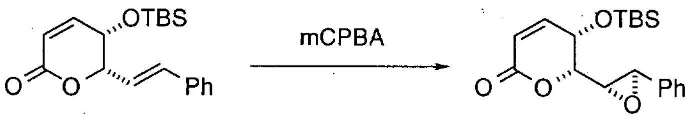


(5S)-5-tert-*butyldimethylsilanyloxy* -(6S)-6-trans-*styryl*-5,6-*dihydro-pyran*-2-*one* (2b). Sulfone tetrazole **10** (342 mg, 1.14 mmol) was dissolved in 1.0 mL of THF and (0.76 mL, 0.57 mmol) of 0.75 M KHMDS was added to the solution at 0 °C. The solution was stirred at room temp for 20 min. The solution was cooled to -78 °C and compound **7c** (146 mg, 0.57 mmol) in 2.5 mL of THF was syringed into the solution. The solution was stirred at -78 °C for 3 h and another 8 h at room temp. The reaction was quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (20% EtOAc/hexanes) to give **2b**, 75 mg (0.228 mmol, 40 % over two steps): R_f (20 % EtOAc/hexanes) =

0.18; $[\alpha]^{21}_D$ = 95.0 (*c* 1.85, CH_2Cl_2); IR (thin film, cm^{-1}) 3057, 2954, 2929, 2857, 1724, 1496, 1472, 1381, 1252, 1155, 1101, 1047; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5H), 6.83 (dd, *J* = 10.0, 5.0 Hz, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.37 (dd, *J* = 16.0, 7.0 Hz, 1H), 6.09 (d, *J* = 10.0, 9.5 Hz, 1H), 4.98 (ddd, *J* = 7.0, 4.5, 1.0 Hz, 1H), 4.37 (dd, *J* = 4.5 Hz, 1H), 0.88 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 145.3, 135.9, 134.4, 128.7, 128.2, 126.7, 122.9, 121.9, 81.4, 64.3, 25.6, 18.0, -4.5, -4.8; FAB HRMS Calcd for $[C_{12}H_{20}O_3Si + H]^+$: 331.1729. Found: 331.1758; Anal. Calcd for C, 69.06; H, 7.94; Found C, 69.25; H, 7.54.

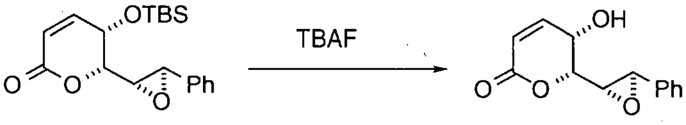


5-*hydroxy* -goniothalamin (14). Compound **2b** (5.5 mg, 0.017 mmol) was dissolved in 0.2 mL of THF and 30 uL (0.030 mmol) of a 1.0 M solution of TBAF was added to the solution at room temp . The reaction was stirred for 0.5 h at room temp. The reaction was quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (100% Et_2O) to give **14**, 2.8 mg (0.013 mmol, 75 %): R_f (100 % Et_2O) = 0.25; $[\alpha]^{21}_D$ = 62.4 (*c* 0.12, CH_2Cl_2); IR (thin film, cm^{-1}) 3386, 2924, 2854, 1712, 1450, 1377, 1253, 1085, 1037; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.32 (m, 5H), 7.04 (dd, *J* = 9.6, 5.4 Hz, 1H), 6.88 (dd, *J* = 15.3, 1.0 Hz, 1H), 6.37 (dd, *J* = 15.9, 6.3 Hz, 1H), 6.19 (d, *J* = 9.9 Hz, 1H), 5.08 (ddd, *J* = 6.6, 3.0, 1.5 Hz, 1H), 4.33 (dd, *J* = 5.7, 3.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 144.3, 135.3, 128.7, 128.6, 126.8, 125.5, 123.1, 121.4, 80.9, 63.1; FAB HRMS Calcd for $[C_{13}H_{12}O_3 + H]^+$: 217.0865. Found: 217.0880.

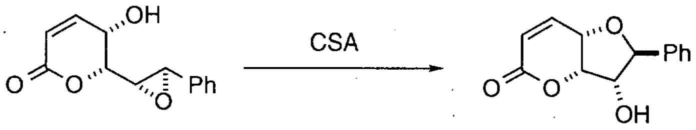


(5S)-5-tert-*butyldimethylsilanyloxy* -(6S)-6-((3R)-3-*phenyloxiranyl*)-5,6-*dihydro-pyran*-2-*one* (15). Compound **2b** (37 mg, 0.112 mmol) was dissolved in 1.1 mL of CH_2Cl_2, $NaHCO_3$ (60 mg, 0.67 mmol) and mCPBA (39 mg, 0.22 mmol) were added to the solution. The reaction was stirred for 8 hours at room temp. The reaction was quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (20% EtOAc/hexanes) to give **15**, 30 mg (0.087 mmol, 78 %): R_f (20 %

EtOAc/hexanes) = 0.15; $[\alpha]^{21}_{D}$ = 74.3 (*c* 0.70, CH_2Cl_2); IR (thin film, cm^{-1}) 2929, 2857, 1736, 1478, 1380, 1252, 1113, 1063; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.26 (m, 5H), 6.91 (dd, *J* = 10.0, 5.5 Hz, 1H), 6.13 (d, *J* = 9.5 Hz, 1H), 4.42 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.10 (dd, *J* = 7.0, 3.0 Hz, 1H), 3.96 (d, *J* = 2.0 Hz, 1H), 3.44 (dd, *J* = 6.5, 1.5 Hz, 1H), 0.89 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 144.0, 129.8, 128.6, 128.5, 125.7, 122.6, 80.9, 61.2, 58.8, 58.3, 25.6, 18.0, -4.4, -4.9; FAB HRMS Calcd for $[C_{19}H_{26}O_4Si + H]^+$: 347.1679. Found: 347.1686.

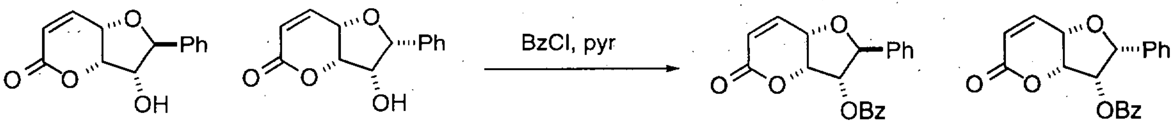


(5S)-5-*hydroxy* -(6S)-6-((3R)-3-*phenyloxiranyl*)-5,6-*dihydro-pyran*-2-*one* (16). Compound **15** (30 mg, 0.087 mmol) was dissolved in 0.5 mL of THF and 130 uL (0.13 mmol) of a 1.0 M solution of TBAF was added to the solution at room temp . The reaction was stirred for 0.5 h at room temp. The reaction was quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (100% Et_2O) to give **16**, 16.2 mg (0.07 mmol, 80 %): R_f (100 % Et_2O) = 0.22; $[\alpha]^{21}_{D}$ = +128.1(*c* 0.16, CH_2Cl_2); IR (thin film, cm^{-1}) 3422, 2958, 2926, 2855, 1729, 1465, 1379, 1257, 1158, 1100, 1072, 1047; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.26 (m, 5H), 7.04 (dd, *J* = 9.9, 6.0 Hz, 1H) 6.16 (d, *J* = 9.6 Hz, 1H), 4.43 (dd, *J* = 5.7, 2.7 Hz, 1H), 4.26 (dd, *J* = 6.0, 2.7 Hz, 1H), 4.01 (d, *J* = 1.8 Hz, 1H), 3.53 (dd, *J* = 6.0, 2.1 Hz, 1H), 2.68 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 143.6, 135.5, 128.7, 128.6, 125.8, 123.4, 79.8, 60.8, 58.9, 57.9; FAB HRMS Calcd for $[C_{13}H_{12}O_4 + Na]^+$: 255.0633. Found: 255.0627.



***IsoAltholactone* (1c).** Compound **16** (12.0 mg, 0.051 mmol) was dissolved in 0.5 mL of CH_2Cl_2 and a catalytic amount of CSA was added to the solution at room temp. The reaction was stirred for 1.5 h at room temp. The reaction was quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (100% Et_2O) to give **1c**, 11 mg (0.047 mmol, 93 %): R_f (100 % Et_2O) = 0.33; $[\alpha]^{21}_{D}$ = +26.1(*c* 0.56, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.31 (m, 5H), 6.90 (dd, *J* =

10.0, 4.5 Hz, 1H), 6.23 (d, J = 10.0 Hz, 1H), 5.08 (dd, J = 5.5, 5.5 Hz, 1H), 4.89 (dd, J = 5.5, 5.0 Hz, 1H), 4.79 (d, J = 7.5 Hz, 1H), 4.29 (dd, J = 7.5, 5.5 Hz, 1H), 2.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.06, 141.65, 138.35, 128.64, 128.30, 125.67, 122.96, 83.27, 78.51, 78.42, 67.67; FAB HRMS Calcd for $[C_{13}H_{12}O_4 + Na]^+$: 255.0633. Found: 255.0632.



3-Epi-3-*Benzoyl-altholactone* (10) and 3-*Benzoyl IsoAltholactone* (11). 3-Epi-*Altholactone* (1a) and ***Isoaltholactone* (1b)** as a 1 : 1 mixture, 6.0 mg (0.026 mmol) was dissolved in 0.3 mL of CH_2Cl_2,9.5 mg (0.078 mmol) of DMAP, and 9 uL (0.08 mmol) of benzoyl chloride were added and stirred for 6 h. The reaction was quenched with 10 mL of Et_2O and 10 mL of sat aq $NaHCO_3$. The phases were separated and the aq layer was extracted (5 x 10 mL) with Et_2O. The organic fractions were combined, dried ($MgSO_4$), concentrated, and the crude product was purified by silica gel chromatography eluting with (30 % EtOAc/hexanes) to give 3.5 mg (0.010 mmol, 38 %) of **3-epi-3-*benzoylaltholactone* (10)** and 3.5 mg (0.01 mmol, 38 %) of **3-*benzoylisoaltholactone* (11)**. **3-epi-3-*benzoylaltholactone* (10)**: R_f (30 % EtOAc/hexanes) = 0.15; $[\alpha]^{21}{}_D$ = +26.3(*c* 0.34, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12-8.10 (m, 1H), 7.50-7.46 (m, 2H), 7.34-7.19 (m, 5H), 6.98 (dd, J = 10.0, 3.0 Hz, 1H), 6.20 (dd, J = 10.0, 1.0 Hz, 1H), 5.99 (dd, J = 5.5, 4.0 Hz, 1H), 5.55 (dd, J = 8.0, 5.0 Hz, 1H), 5.27 (d, J = 4.5 Hz, 1H), 4.97 (ddd, J = 8.0, 3.5, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 160.2, 142.0, 134.6, 133.3, 129.4, 128.7, 128.4, 128.3, 128.1, 126.9, 121.2, 80.1, 78.1, 73.8, 67.4; FAB HRMS Calcd for $[C_{20}H_{16}O_5 + H]^+$: 337.1076. Found: 337.1085. **3-*benzoylisoaltholactone* (11)**: R_f (30 % EtOAc/hexanes) = 0.28; $[\alpha]^{21}{}_D$ = -36.5 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-7.99 (m, 1H), 7.61-7.58 (m, 1H), 7.50-7.33 (m, 8H), 6.91 (dd, J = 10.0, 3.5 Hz, 1H), 6.27 (dd, J = 10.0, 1.0 Hz, 1H), 5.44 (dd, J = 5.5, 5.5 Hz, 1H), 5.41 (dd, J = 5.5, 5.5 Hz, 1H), 5.24 (d, J = 5.0 Hz, 1H), 5.10 (ddd, J = 5.5, 4.0, 1.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 160.7, 142.0, 137.7, 133.7, 129.8, 128.8 (2C), 128.6 (2C), 125.6, 122.4, 81.6, 78.4, 76.2, 68.2; FAB HRMS Calcd for $[C_{20}H_{16}O_5 + H]^+$: 337.1076. Found: 337.1084.