REVISED 2-15-00

Supplementary Material

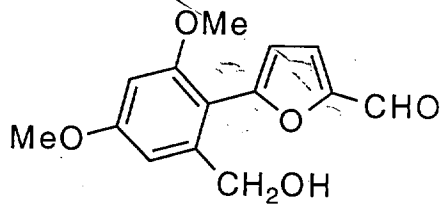
Experimental Section:

General Experimental: Low reaction temperatures were recorded as bath temperatures unless otherwise stated. Column chromatography was carried out on E.Merck silica gel 230-400 mesh ASTM using flash chromatography techniques. Analytical thin-layer chromatography (TLC) was performed on E.Merck or precoated silica gel 60 F254 plates. Hexanes, dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), and diethyl ether (Et_2O) used as eluants were ACS reagent grade solvent. The following reaction solvents were purified by distillation: dimethylformamide (DMF) (from calcium hydride, N_2), dichloromethane (from CaH_2, N_2), diethyl ether (Et_2O) (from Ph_2CONa, N_2), toluene (from CaH_2, N_2), dichloroethane (from P_2O_5, N_2) and tetrahydrofuran (THF) (from Ph_2CO-Na, N_2). Organic extracts were dried over anhydrous sodium sulfate (Na_2SO_4) or anhydrous magnesium sulfate ($MgSO_4$), filtered and rotary evaporated at <40 °C bath temperature; involatile oils were further evaporated at <1mm Hg. NBS was recrystallized prior to use. $Pd_2(dba)_3.CHCl_3$ was prepared by the reported procedure. ^1H NMR and ^{13}C NMR spectra were acquired on Varian 200, 300 and 500 MHz spectrometers. Chemical shifts and coupling constants are reported in parts per million (ppm) and hertz (Hz) respectively. Chemical shifts are reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^1H and $CDCl_3$ (δ 77.0 ppm) for ^{13}C. Melting Points are uncorrected. Combustion analysis was performed by M-H-W Laboratories, Phoenix, AZ.

General procedure for Stille coupling: To a round bottomed flask (10 ml) equipped with condenser, magnetic stir bar and nitrogen inlet was charged with tributylstannyl furanacetal (200 mg, 0.46 mmol), substituted bromobenzene(126 mg, 0.5 mmol), $Pd_2(dba)_3.CHCl_3$ (24 mg, 5 mol %) and triphenylphospine (30 mg, 25 mol %). Vacuum was applied for 10 min to remove moisture and oxygen and flushed with nitrogen gas. Toluene (3 ml) was added and stirred for 30 min, and the solution was heated slowly to reflux for 3h. A black color was produced indicating a reduced palladium which precipitated on the bottom of the flask and the solution was refluxed overnight. The reaction mixture was cooled to room temp, diluted with ether (5 ml) and saturated KF solution (1 ml) was added. The organic layer was separated, washed with water (5 ml), HCl (1 ml, 1 M), water (5 ml), brine (5 ml), and dried over Na_2SO_4 and the solvent was removed at reduced pressure to give a dark brown crude oil. The crude product is used as it is for the deprotection step.

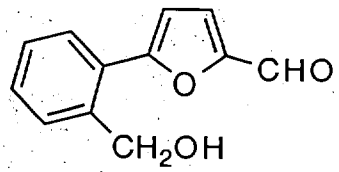
General procedure for deprotection of acetal: The crude product from above was dissolved in acetone (5 ml) then 1M HCl (0.2 ml) was added and stirred at room temp overnight. $NaHCO_3$ (5%, 0.2 ml) was added until reaction was neutralized and the solvent was evaporated. The crude product was extracted with CH_2Cl_2 (10 ml) washed with water, $NaHCO_3$ (5%, 2 ml), water (5 ml), brine and dried (Na_2SO_4). Evaporation of the solvent at reduced pressure and flash chromatography over silica gel resulted in the furfural aldehyde derivative as a pale yellow solid.

Compound 8: 5-(3,5-Dimethoxy-2-hydroxymethylphenyl)-furan-2-aldehyde



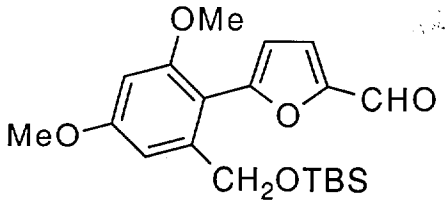
m.p: 89-90 °C. Yield: 60 %. R_f = 0.5 [Hexane/EtOAc (1:1)]. IR (thin film, cm^{-1}) 3400, 2943, 2834, 1660, 1600, 1583, 1512, 1501, 1463, 1452, 1431, 1387, 1354, 1316, 1284, 1240, 1202, 1153. ^1H NMR (300 MHz, $CDCl_3$): δ 9.56 (s, 1H). 7.31 (d, *J*=3.8 Hz, 1H), 6.79 (d, *J*=3.6 Hz, 1H), 6.76 (d, *J*=2.4 Hz, 1H), 6.45 (d, *J*=2.4 Hz, 1H), 4.68 (s, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 2.84 (1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.0, 161.9, 159.1, 156.1, 151.3, 143.4, 123.5, 113.6, 109.4, 105.3, 97.7, 63.6, 55.8, 55.4. HRMS (CI^+) calcd for $(M+H)^+$ $C_{14}H_{15}O_5$: 263.0919, found: 263.0908. Anal. Calcd for C = 64.1 %, H = 5.38 %; Anal. found C = 64.05 %, H = 5.29 %.

Compound 5a: 5-(2-Hydroxymethyl)-furan-2-aldehyde



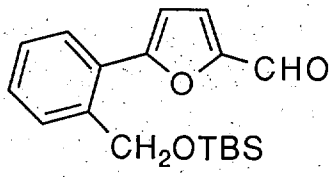
m.p: 51 °C. Yield: 66 %. R_f = 0.5 [Hexane/EtOAc (6:4)]. IR (thin film, cm^{-1}) 3424, 2870, 1667, 1563, 1514, 1482, 1463, 1442, 1389, 1285, 1243, 1196, 1032. ^1H NMR (200 MHz, $CDCl_3$) δ 9.6 (s, 1H), 7.76-7.81 (m, 1H), 7.54-7.59 (m, 1H), 7.39-7.45 (m, 2H), 7.34 (d, *J*=3.6 Hz, 1H), 6.94 (d, *J*=3.6 Hz, 1H), 4.85 (d, *J*=4.2 Hz, 2H), 2.28 (1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 158.7, 152.1, 138.3, 129.9, 129.7, 128.5, 128.1, 127.8, 123.7, 111.4, 63.6. HRMS (CI^+) calcd for $(M+H)^+$ $C_{12}H_{11}O_3$: 203.0708, found: 203.0714. Anal. Calcd for C = 71.26 %, H = 4.99 %; Anal. found C = 71.12 %, H = 4.80 %.

5-[3,5-Dimethoxy-2-(*tert*-butyl)dimethylsilyloxymethyl-phenyl]-furan-2-aldehyde



To the 5-(3,5-dimethoxy-2-hydroxymethyl-phenyl)-furan-2-aldehyde **8** (1 g, 3.8 mmol) in DMF (10 ml) was added imidazole (0.52 g, 7.6 mmol) and DMAP (50 mg) at room temperature under nitrogen atmosphere, then TBSCl (0.57 g, 3.8 mmol) was added and the stirring continued overnight. The reaction was worked up by pouring it into water (75 ml) and extract with ether (2 x 30 ml). The organic layer was washed with water (5 ml), aqueous hydrochloric acid (1 M, 2 ml), water (5 ml), brine (5 ml) and dried (Na_2SO_4). Evaporation of solvent under reduced pressure and flash chromatography over silica gel using hexanes:ethylacetate (20%) resulted in the viscous liquid of TBS protected alcohol. yield: 1.05 g (73 %), m.p: 69-70 °C. R_f= 0.6 [hexanes:EtOAc (8:2)]. IR (thin film, cm^{-1}) 2926, 1675, 1604, 1461, 1383, 1323, 1250, 1202, 1157, 1116, 1062. ^1H NMR (300 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.31 (d, *J*=3.6 Hz, 1H), 6.92 (dd, *J*=1.65, 0.6 Hz, 1H), 6.72 (d, *J*=3.6 Hz, 1H), 6.42 (d, *J*=2.4 Hz, 1H), 4.81 (s, 2H), 3.86 (s, 3H), 3.8 (s, 3H), 0.92 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 161.8, 159.0, 156.1, 151.6, 144.3, 122.5, 113.4, 108.6, 103.4, 97.2, 63.2, 55.8, 55.4, 25.9, 18.4, -5.3. HRMS (CI^+) calcd for $(M+H)^+$ $C_{20}H_{29}O_5Si$: 377.1784, found: 377.1796. Anal. Calcd for C = 63.8 %, H = 7.5 %; Anal. found C = 63.68 %, H = 7.41%.

Compound 5b: 5-[2-(*tert*-butyl)dimethylsilyloxymethyl-phenyl]-furan-2-aldehyde



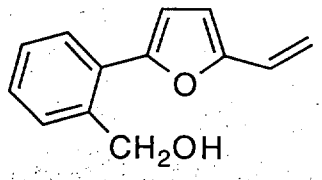
The preparation procedure was similar to that of above. Yield: 73 %. R_f = 0.6 [Hexane/EtOAc (8:2)]. IR (thin film, cm^{-1}) 2928, 2855, 1676, 1512, 1461, 1389, 1196, 1126, 1085. ^1H NMR (300 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.8 (dd, *J*=7.6, 1.5 Hz, 1H), 7.62 (d, *J*=7.5 Hz, 1H), 7.34-7.45 (m, 2H), 7.33 (d, *J*=3.9 Hz, 1H), 6.87 (d, *J*=3.9 Hz, 1H), 4.9 (s, 2H), 0.9 (s, 9H), 0.1 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.4, 158.5, 152.1, 138.9, 129.6, 128.2, 128.1, 127.5, 127.1, 123.0, 111.4, 63.6, 25.9,

18.4, -5.1. FAB HRMS calcd for $(M+H)^+$ $C_{18}H_{25}O_3Si$: 317.1573, found: 317.1584. Anal. Calcd for C = 68.32 %, H = 7.65 %; Anal. found C = 68.40 %, H = 7.59 %.

General procedure for Wittig reaction.

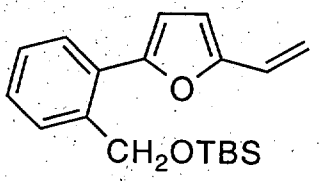
To the triphenylphosphoniummethylbromide (dry) (1.5 eq) in THF (0.1 molar) under N_2 atmosphere at 0 °C, was added n-BuLi in hexane drop by drop (1.2 eq) then the reaction allowed to stirr at this temperature for 1hr. Then the reaction flask brought to -78 °C and the aldehyde **5b** (1 eq) in THF was added dropwise. The solution was stirred at -78 °C for 3 h, then allowed to come to room temperature. The reaction was diluted with ether (100 ml) and filtered through celite, and the solvent removed under reduced pressure and purified by flash chromatography through silica gel using Hexane-ethyl acetate (20 %) gave the pure product.

Compound 4a: 5-(2-Hydroxymethyl-phenyl)-2-vinyl-furan



Yield: 65 %. R_f = 0.4 [Hexane/EtOAc (8:2)]. IR (thin film, cm^{-1}) 3431, 2932, 2876, 1675, 1601, 1514, 1482, 1463, 1443, 1390, 1359, 1267, 1006. ^1H NMR (300 MHz, $CDCl_3$) δ 7.67-7.72 (m, 1H), 7.49-7.54 (m, 1H), 7.31-7.37 (m, 2H), 6.68 (d, *J*=3.4 Hz, 1H), 6.54 (dd, *J*=17.6, 11.2 Hz, 1H), 6.38 (d, *J*=3.4 Hz, 1H), 5.72 (dd, *J*=17.5, 1 Hz, 1H), 5.22 (dd, *J*=11.2, 1 Hz, 1H), 4.85(d, *J*=6.2 Hz, 2H), 2.19 (t, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 152.5, 137.0, 129.4, 129.3, 128.1, 128.0, 127.5, 124.8, 112.6, 110.4, 110.3, 64.3.

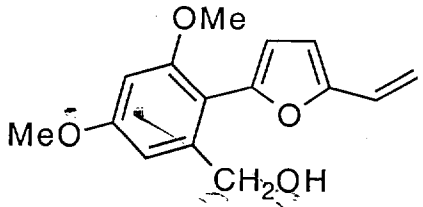
Compound 4b: 5-[2-(*tert*-butyl)dimethylsilyloxymethyl-phenyl]-2-vinyl-furan



Yield: 95 %. R_f = 0.9 [Hexane/EtOAc (8:2)]. IR (thin film, cm^{-1}) 3064, 2955, 2928, 2856, 1638, 1603, 1518, 1470, 1462, 1380, 1360, 1255, 1196, 1125, 1085, 1059, 1007. ^1H NMR (300 MHz, $CDCl_3$) δ 7.65-7.72 (m, 2H), 7.30-7.34 (m, 2H), 6.60 (d, *J*=3.3 Hz, 1H), 6.54 (dd, *J*=17.5, 11.1 Hz, 1H), 6.36 (d, *J*=3.6 Hz, 1H), 5.73 (dd, *J*=17.4, 1.2

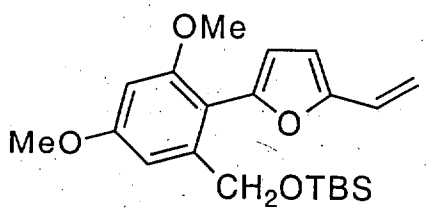
Hz, 1H), 5.2 (dd, *J*=11.25, 1.2 Hz, 1H), 4.96 (s, 2H), 0.96 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7, 152.4, 137.7, 128.0, 127.7, 127.2, 126.9, 126.8, 124.9, 112.2, 110.3, 110.2, 63.6, 26.0, 18.5, -5.2. FAB HRMS calcd for $(M)^+$ $C_{19}H_{26}O_2Si$: 314.1702, found: 314.1729.

Compound 4c: 5-(3,5-Dimethoxy-2-hydroxymethyl-phenyl)-2-vinyl furan



m.p: 103 °C. Yield: 62 %. R_f = 0.3 [Hexane/EtOAc (8:2)]. IR (thin film, cm^{-1}) 3390, 2943, 2834, 1605, 1583, 1463, 1316, 1196, 1153, 1071, 1033, 902, 837, 799. ^1H NMR (300 MHz, $CDCl_3$) δ 6.73 (d, *J*=2.1 Hz, 1H), 6.57 (d, *J*=3.3 Hz, 1H), 6.49 (m, 1H), 6.47 (d, *J*=2.4 Hz, 1H), 6.36 (d, *J*=3.3 Hz, 1H), 5.59 (dd, *J*=17.4, 0.6 Hz, 1H), 5.14 (dd, *J*=11.4, 1.2 Hz, 1H), 4.67 (d, *J*=6.6 Hz, 2H), 3.85 (s, 3H), 3.8 (s, 3H), 2.26 (t, *J*=6.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 158.6, 152.1, 148.5, 142.2, 124.9, 112.5, 111.7, 109.9, 105.1, 105.0, 98.2, 64.5, 55.9, 55.5. HRMS (CI^+) calcd for $(M+H)^+$ $C_{15}H_{17}O_4$: 261.1126, found: 261.1122.

Compound 4c: 5-[3,5-Dimethoxy-2-(*tert*-butyl)dimethylsilyloxymethyl-phenyl]-2-vinyl-furan



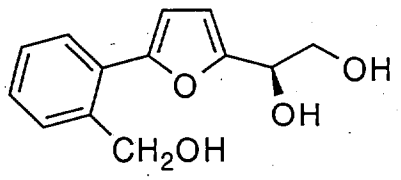
m.p: 32 °C. Yield: 99 %. R_f = 0.8 [Hexane/EtOAc (8:2)]. IR (thin film, cm^{-1}) 2943, 2921, 2856, 1605, 1583, 1463, 1430, 1370, 1316, 1251, 1196, 1158, 1114, 1065, 1060. ^1H NMR (300 MHz, $CDCl_3$): δ 6.95 (d, *J*=2.4 Hz, 1H), 6.52 (d, *J*=3.3 Hz, 1H), 6.51 (dd, *J*=17.5, 11.1 Hz, 1H), 6.43 (d, *J*=2.4 Hz, 1H), 6.34 (d, *J*=3.3 Hz, 1H), 5.62 (dd, *J*=17.55, 1.5 Hz, 1H), 5.14 (dd, *J*=11.1, 1.5 Hz, 1H), 4.86 (s, 2H), 3.86 (s, 3H), 3.8 (s, 3H), 0.95 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.6, 158.3, 151.9, 148.7, 143.5, 125.2, 112.1, 111.1, 110.1, 109.7, 102.7, 97.2, 63.2(CH_2), 55.8, 55.3, 26.0, 18.4, -5.3. HRMS (CI^+) calcd for $(M)^+$ $C_{21}H_{30}O_4Si$: 374.1913, found: 374.1921.

General Procedure

Asymmetric Dihydroxylation using AD-mix-α

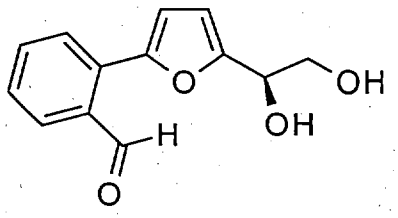
To a solution of *t*-butyl alcohol (30 ml) and water (75 ml) a solution of vinyl furan (4 mmol) in ether (5 ml) was added at 0 °C, then AD-mix-α (6 g), potassium ferricyanide (13.3 g) and potassium carbonate (5.6 g) were added. The solution was vigorously stirred for 12 h at 0 °C and monitored by TLC until the absence of starting material. The solution was quenched with 1M sodium bisulfite (10 ml) then ethyl acetate (50 ml) was added. The phases were separated and the aqueous layer was extracted with ethyl acetate (2 x 25 ml). The organic layers were combined and washed with saturated sodium bicarbonate (10 ml), brine (20 ml) and dried (Na_2SO_4). Concentration under reduced pressure and flash column chromatography over silica gel using hexane-ethyl acetate yielded the dihydroxylated compound.

Compound 3a: 5-(2-Hydroxymethyl-phenyl)-2-furan-ethanediol



m.p: 86 °C. Yield: 71 %. R_f = 0.4 [EtOAc (100 %)]. $[\alpha]_D$ = +32.0 in CH_3CN (1.1%). IR (thin film, cm^{-1}) 3397, 1555, 1441, 1364, 1316, 1199, 1112, 1017. ^1H NMR (200 MHz, $CDCl_3$): δ 7.57-7.62 (m, 1H), 7.42-7.46 (m, 1H), 7.29-7.35 (m, 2H), 6.6 (d, *J*=3.4 Hz, 1H), 6.41 (d, *J*=3.4 Hz, 1H), 4.77-4.84 (m, 3H), 3.92 (br.t, 2H), 3.19 (d, *J*=5.4 Hz, 1H), 2.84 (br.t, 1H), 2.67 (br.t, 1H). ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6) δ 154.7, 152.3, 137.6, 129.2, 127.6, 127.4, 127.1, 109.2, 108.5, 68.3, 65.2, 63.4. HRMS (CI^+) calcd for $(M)^+$ $C_{13}H_{14}O_4$: 234.0892, found: 234.0894. Anal. Calcd for C = 73.66 %, H = 5.3 %; Anal. found C = 73.46 %, H = 5.56 %.

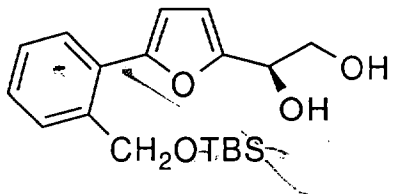
5-(2-carboxaldehyde-phenyl)-2-furan-ethandiol



Yield: 10 %. R_f = 0.4 [Hexane/EtOAc (1:1)]. IR (thin film, cm^{-1}) 3408, 2924, 1765, 1681, 1595, 1514, 1463, 1443, 1402, 1254, 1197, 1028. ^1H NMR (300 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.85 (dd, *J*=7.8, 0.9 Hz, 1H), 7.48-7.57 (m, 2H), 7.28-7.38 (m, 1H), 6.49 (d,

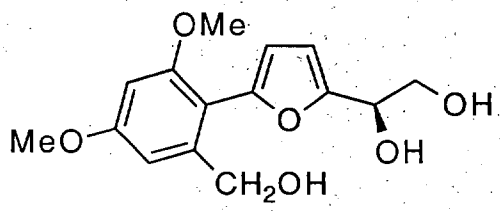
J=3.3 Hz, 1H), 6.41 (d, *J*=3.3 Hz, 1H), 4.83 (t, *J*=5.7 Hz, 1H), 3.86 (d, *J*=12.6 Hz, 2H), 3.0 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.6, 155.5, 150.8, 133.7, 132.9, 128.4, 128.3, 128.2, 111.9, 109.4, 98.6, 68.4, 65.0. FAB HRMS calcd for $(M+Na)^+$ $C_{13}H_{12}O_4Na$: 255.0633, found: 255.0646.

Compound 3b: 5-[2-(*tert*-butyl)dimethylsilyoxymethyl-phenyl]-2-furan-ethanediol



Yield: 93 %. R_f = 0.6 [Hexane/EtOAc (1:1)]. $[\alpha]_D$ = +23.7 in CH_2Cl_2 (1%). IR (thin film, cm^{-1}) 3339, 2951, 2922, 2854, 1600, 1540, 1467, 1461, 1442, 1384, 1360, 1253, 1200, 1122, 1083. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.64 (m, 2H), 7.29-7.33 (m, 2H), 6.54 (d, *J*=3.3 Hz, 1H), 6.42 (dd, *J*=3.3, 0.6 Hz, 1H), 4.87 (br.s, 3H), 3.93 (br.d, *J*=4.2 Hz, 2H), 2.75 (br.d, 1H), 2.4 (br.s, 1H), 0.91 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 152.7, 137.5, 128.4, 127.8, 127.7, 127.2, 127.0, 109.4, 109.1, 68.5, 65.2(CH_2), 63.8(CH_2), 25.9, 18.4, -5.1. FAB HRMS calcd for $(M+Na)^+$ $C_{19}H_{28}O_4SiNa$: 371.1654, found: 371.1662. Anal. Calcd for C = 65.48 %, H = 8.1 %; Anal. found C = 65.62 %, H = 7.93 %.

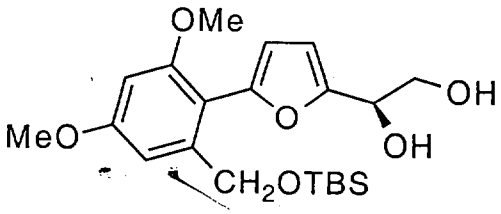
Compound 3c: 5-(3,5-Dimethoxy-2-hydroxymethyl-phenyl)-2-furan-ethandiol



m.p: 71 °C. Yield: 62 %. R_f = 0.3 [EtOAc (100 %)]. $[\alpha]_D$ = +18.1 in CH_3CN (1.1 %). IR (thin film, cm^{-1}) 3357, 2943, 1600, 1583, 1463, 1430, 1322, 1284, 1202, 1153, 1087, 1065, 1033. ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.66 (d, *J*=2.4 Hz, 1H), 6.49 (m, 2H), 6.42 (d, *J*=3.4 Hz, 1H), 4.81 (q, *J*=5.4 Hz, 1H), 4.58 (d, *J*=6.4 Hz, 2H), 3.93 (t, *J*=6.4, 5 Hz, 2H), 3.85 (s, 3H), 3.8 (s, 3H), 2.8 (d, *J*=5.8 Hz, 1H), 2.54 (q, *J*=12.4, 5.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 158.2, 152.6, 148.5, 142.0, 111.7, 111.1, 108.4, 105.5, 98.1, 68.1, 64.9, 63.9, 55.7, 55.4. HRMS (CI^+) calcd for $(M)^+$ $C_{15}H_{18}O_6$:

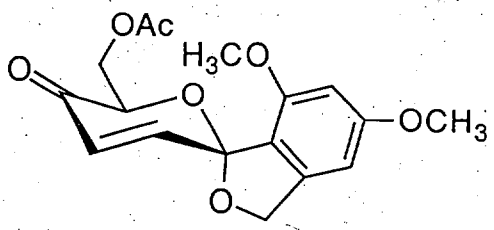
294.1103, found: 294.1109. Anal. Calcd for C = 61.2 %, H = 6.17 %; Anal. found C = 60.96 %, H = 5.99 %.

Compound 3d: 5-[3,5-Dimethoxy-2-(*tert*-butyl)dimethylsilyloxymethyl-phenyl)-2-furan-ethanediol



Yield: 77 %. R_f = 0.5 [Hexane/EtOAc (4:6)]. $[\alpha]_D$ = +14.5 in CH_2Cl_2 (0.8 %). IR (thin film, cm^{-1}) 3390, 2953, 2932, 2856, 1600, 1583, 1463, 1376, 1316, 1251, 1196, 1153, 1109, 1065. ^1H NMR (300 MHz, $CDCl_3$) δ 6.83 (d, *J*=2.4 Hz, 1H), 6.38-6.41(m, 3H), 4.8(br.q, 1H), 4.7 (s, 2H), 3.88 (br.d, 2H), 3.84 (s, 3H), 3.76 (s, 3H), 2.69 (d, *J*=1.8 Hz, 1H), 2.4(br.t, 1H), 0.9(s, 9H), 0.04(s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 158.4, 152.5, 148.7, 143.4, 110.9, 110.2, 108.3, 103.1, 97.3, 68.5, 65.4, 63.3, 55.8, 55.3, 25.9, 18.4, -5.2. HRMS (CI^+) calcd for $(M)^+$ $C_{21}H_{32}O_6Si$: 408.1968, found: 408.1967.

Compound 7a: Oxidative ring enlargement: Preparation of spiro enone ester



To the triol **3c** (75 mg, 0.25 mmol) in THF/H_2O (4:1) (1.2 ml:0.3 ml), $NaHCO_3$ (42.8 mg, 0.5 mmol) and NaOAc.$3H_2O$ (34.7 mg, 0.25 mmol) at 0 °C was added NBS (45.4 mg, 0.25 mmol) in 3 portions. The solution was stirred at 0 °C for 2h until TLC analysis showed the absence of starting material. The solution was quenched with saturated $NaHCO_3$ (0.2 ml). More ethyl acetate (5 ml) was added, and the organic layer was separated. The organic layer was washed with brine (5 ml) and dried (Na_2SO_4). Solvent evaporated under reduced pressure followed by column chromatography over silica gel resulted in light yellow liquid.

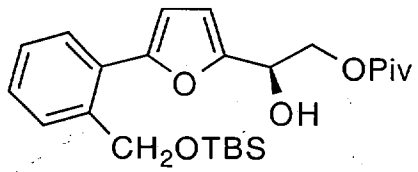
To the solution acetic anhydride (2 ml) and pyridine (2 ml) were added and stirred at room temperature over night. After 12 h stirring, the reaction mixture was poured into ice-water (5ml) and the compound extracted with ether (3x10 ml). The organic layer was

washed with water, brine and dried ($MgSO_4$). Concentration and column chromatography purification gave 25 % yield of the spiroproduct . Rf: 0.9 [hexane:EtOAc (8:2)]. ^1H NMR (300 MHz, $CDCl_3$) δ 6.92 (d, *J*=10.2 Hz, 1H), 6.35(s, 2H), 6.17 (d, *J*=10.2 Hz, 1H), 5.08 (dd, *J*=49.8, 12.6 Hz, 2H), 4.82 (dd, *J*=3.75, 2.7 Hz, 1H), 4.46 [d(q), *J*=27.6, 11.7, 3.9 Hz, 2H], 3.81 (s, 3H), 3.75 (s, 3H), 1.13(s, 9H).

General procedure for Pivaloyl protection.

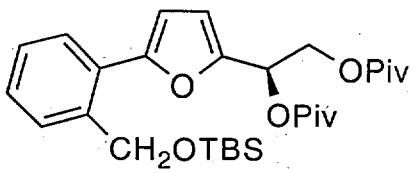
Synthesis of Compound 3e: To a solution diol **3b** (7.48 g, 21 mmol) in CH_2Cl_2 (150 ml) under N_2 atmosphere at -78 °C was added Et_3N (11 ml, 5 eq) then pivaloylchloride (2.64 ml, 1.3 mmol) in CH_2Cl_2 (10 ml). After stirring for 3h at -78 °C allowed to come to room temperature and stirred overnight. The solution was diluted with more CH_2Cl_2 (100 ml) and quenched with sodium bisulfate (1M, 25 ml) then washed with water, brine and dried (Na_2SO_4) and flash chromatographed over silica gel using hexane ethylacetate (10 %) as eluent.

Compound 3e: Major Fraction (mono protected).



Yield: 65 %. R_f = 0.5 [Hexane/EtOAc (8:2)]. $[\alpha]_D$ = +17.9 in CH_2Cl_2 (1%). IR(thin film, cm^{-1}) 3448, 2954, 2931, 2872, 1731, 1478, 1461, 1396, 1361, 1284, 1249, 1155, 1125, 1079. ^1H NMR (300 MHz, $CDCl_3$) δ 7.6-7.67 (m, 2H), 7.27-7.35 (m, 2H), 6.54 (d, *J*=3.6 Hz, 1H), 6.43 (dd, *J*=3.3, 0.6 Hz, 1H), 5.02 (t, *J*=5.7 Hz, 1H), 4.86 (s, 2H), 4.43 (dd, *J*=6.3, 1.2 Hz, 2H), 1.19 (s, 9H), 0.94 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 152.6, 152.5, 137.6, 128.2, 127.8, 127.6, 127.4, 127.1, 126.9, 111.2, 109.5, 109.3, 66.7, 66.5, 63.5, 38.9, 27.2, 26.0, 18.4, -5.2. HRMS (CI^+) calcd for $(M-H)^+$ $C_{24}H_{35}O_5Si$: 431.2254, found: 431.2261. Anal. Calcd for C = 66.63 %, H = 8.39 %; Anal. found C = 66.81 %, H = 8.12 %.

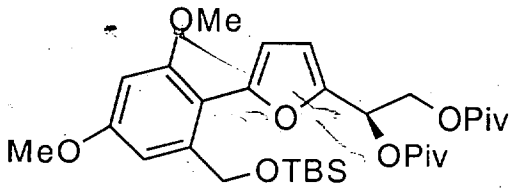
Minor Fraction (di protected)



Yield: 10 %. R_f = 0.9 [Hexane/EtOAc (8:2)]. IR (thin film, cm^{-1}) 2956, 2929, 2856, 1736, 1678, 1601, 1572, 1480, 1462, 1368, 1256, 12228, 1196, 1136, 1083, 1006. ^1H NMR

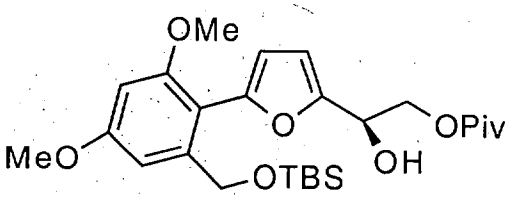
(300 MHz, $CDCl_3$) δ 7.61-7.65 (m, 2H), 7.27-7.36 (m, 2H), 6.55 (d, *J*=3.3 Hz, 1H), 6.46 (dd, *J*=3.3, 0.6 Hz, 1H), 6.14 (dd, *J*=7.5, 4.2 Hz, 1H), 4.87 (s, 2H), 4.5 (dq, *J*=22.2, 11.7 Hz, 2H), 1.21 (s, 9H), 1.17 (s, 9H), 0.93 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 177.3, 153.1, 149.1, 137.8, 128.0, 127.9, 127.3, 127.1, 127.0, 110.9, 109.4, 66.5, 63.5, 38.9, 38.8, 27.1, 26.5, 25.9, 18.4, -5.2. FAB HRMS calcd for $(M+Na)^+$ $C_{29}H_{44}O_6SiNa$: 539.2804, found: 539.2799.

Pivaloyl protection of diol 3d (Minor Fraction):



m.p: 54 °C. Yield: 8 %. R_f = 0.8 [Hexane/EtOAc (8:2)]. $[\alpha]_D$ = +63.9 in CH_2Cl_2 (1.6%). IR (thin film, cm^{-1}) 2960, 2864, 1735, 1609, 1582, 1473, 1460, 1433, 1394, 1367, 1319, 1280, 1253, 1218, 1197, 1157, 1135, 1065, 1030. ^1H NMR (300 MHz, $CDCl_3$) δ 6.89 (d, *J*=2.4 Hz, 1H), 6.44 (d, *J*=3.3 Hz, 1H), 6.40 (d, *J*=2.7 Hz, 1H), 6.39 (d, *J*=3.3 Hz, 1H), 6.12 (dd, *J*=7.95, 4.2 Hz, 1H), 4.69 (s, 2H), 4.39-4.51 (m, 2H), 3.84 (s, 3H), 3.75 (s, 3H), 1.2 (s, 9H), 1.16 (s, 9H), 0.92 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 177.2, 160.9, 158.5, 149.3, 148.3, 143.8, 110.9, 110.4, 109.9, 102.6, 97.2, 66.5, 63.6, 62.9, 55.8, 55.3, 38.8, 38.7, 27.1, 27.0, 25.9, 18.3, -5.3. HRMS (CI^+) calcd for $(M)^+$ $C_{31}H_{48}O_8Si$: 576.3118 , found: 576.3129. Anal. Calcd for C = 64.55 %, H = 8.39 %; Anal. found C = 64.73 %, H = 8.17 %.

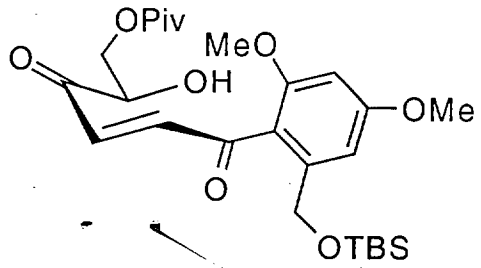
Compound 9 (Major Fraction):



m.p: 46 °C. Yield: 69 %. R_f = 0.5 [Hexane/EtOAc (8:2)]. $[\alpha]_D$ = +9.1 in CH_2Cl_2 (1%). IR (thin film, cm^{-1}) 3446, 2953, 2851, 1728, 1600, 1584, 1461, 1323, 1282, 1251, 1200, 1154, 1067. ^1H NMR (300 MHz, $CDCl_3$) δ 6.87 (d, *J*=2.4Hz, 1H), 6.37-6.41 (m, 3H), 4.96 (t, *J*=6 Hz, 1H), 4.7 (s, 2H), 4.39 (d, *J*=2.1 Hz, 1H), 4.37 (d, *J*=0.9 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 1.18 (s, 9H), 0.92 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.7, 160.9, 158.5, 151.7, 148.8, 143.7, 110.9, 110.1, 108.5, 102.7, 97.2,

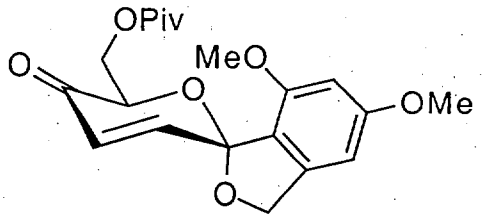
66.6, 66.5, 63.0, 55.8, 55.3, 38.8, 27.2, 25.9, 18.4, -5.3. HRMS (CI^+) calcd for $(M)^+$ $C_{26}H_{40}O_7Si$: 492.254, found: 492.255.

Oxidative ring expansion of mono pivaloyl protected furan carbinol



To a solution of compound **9** (1.74 g, 3.53 mmol) in THF/H_2O (4:1) (14.6 ml:3.6 ml) was added $NaHCO_3$ (0.6 g, 7.6 mmol), $NaOAc.3H_2O$ (0.48 g, 3.53 mmol) at 0 °C and then added NBS (0.69 g, 3.8 mmol) in 3 portions. The solution was stirred at 0 °C for 2 h. TLC showed the absence of starting material. The reaction was quenched with saturated $NaHCO_3$ (1 ml) and more hexane (50 ml). The organic layer was separated and washed with brine and dried (Na_2SO_4). Solvent evaporated under reduced pressure followed by column chromatography over silica gel resulted in light yellow viscous liquid. Yield. 1.3 g (74 %). R_f = 0.4 [Hexane/ EtOAc (7:3)]. IR (thin film, cm^{-1}) 3463, 2956, 2856, 1732, 1602, 1462, 1424, 1370, 1325, 1284, 1255, 1201, 1156, 1067. ^1H NMR (300 MHz, $CDCl_3$) δ 7.02 (d, *J*=2.2 Hz, 1H), 6.9 (d, *J*=11.8 Hz, 1H), 6.33 (d, *J*=2.2 Hz, 1H), 6.29 (d, *J*=12 Hz, 1H), 4.93 (d, *J*=2.8 Hz, 2H), 4.53 (q, 1H), 4.35 (d, *J*=0.6 Hz, 1H), 4.35 (d, *J*=1.4 Hz, 1H), 3.81 (s, 3H), 3.85 (s, 3H), 3.63 (d, 1H), 1.14 (s, 9H), 0.95 (s, 9H), 0.11 (s, 3H), 0.1 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.9, 193.3, 178.3, 163.8, 161.1, 148.2, 142.4, 127.6, 117.3, 103.4, 96.8, 75.1, 64.9, 62.9, 55.8, 55.4, 38.8, 27.1, 26.0, 18.4, -5.3. HRMS (CI^+) calcd for $(M+H)^+$ $C_{26}H_{41}O_8Si$: 509.2571, found: 509.2583.

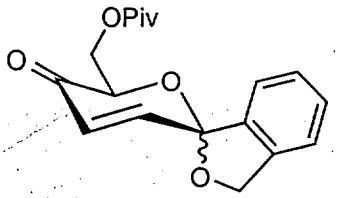
Compound 10: Spirocyclization using HCl/H_2O/THF condition



To a solution of the above intermediate (0.8 g, 1.57 mmol) in THF (10 ml) was added H_2O (1 ml) then aq. HCl (1M, 0.4 ml) at room temperature then stirred for 3 h. TLC analysis showed the disappearance of starting material and appearance of less polar

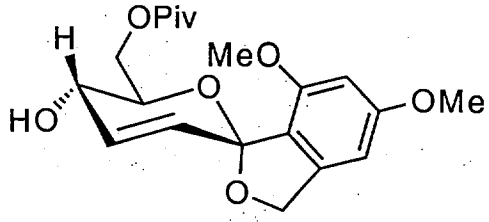
compound. The solution was quenched with saturated potassium carbonate (0.5 ml). The reaction mixture diluted with ether (20 ml) washed with brine and dried (Na_2SO_4). Filtration and evaporation under reduced pressure gave a crude product. Which was purified by flash chromatography over silica gel using hexanes: ethyl acetate (10 %) as eluent. Yield: 0.37 g (64 %). R_f: 0.4 [hexanes:EtOAc (75:25)]. $[\alpha]_D$ = +48.8 in CH_2Cl_2 (1.1%). IR (thin film, cm^{-1}) 2956, 1729, 1697, 1609, 1495, 1463, 1430, 1394, 1343, 1283, 1223, 1201, 1155, 1043, 1086, 1017. ^1H NMR (300 MHz, $CDCl_3$) δ 6.91 (d, *J*=10.2 Hz, 1H), 6.35 (s, 2H), 6.17 (d, *J*=10.2 Hz, 1H), 5.17 (d, *J*=12.6 Hz, 2H), 5.01(d, *J*=12.6Hz, 1H), 4.82 (dd, *J*=3.4, 2.7 Hz, 1H), 4.48 (dq, *J*=27.6, 11.7, 3.9 Hz, 2H), 3.81 (s, 3H), 3.75 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.2, 178.0, 163.4, 155.9, 147.6, 143.7, 126.6, 119.5, 104.3, 98.2, 96.9, 75.1, 72.5, 62.7, 55.7, 55.4, 39.0, 27.0. HRMS (CI^+) calcd for $(M+H)^+$ $C_{20}H_{25}O_7$: 377.1600 , found: 377.1598.

Compound 7b: Spiro enone



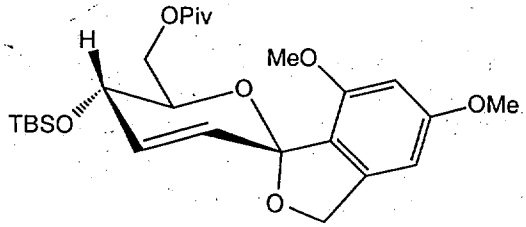
IR(thin film, cm^{-1}) 2966, 2872, 1725, 1696, 1572, 1478, 1461, 1390, 1278, 1231, 1155, 1114, 1084, 1026. **Isomer 1**. ^1H NMR (200 MHz, $CDCl_3$) δ 7.32 (m, 4H), 6.85 (d, *J*=10 Hz, 1H), 6.25 (d, *J*=10 Hz, 1H), 5.24 (d, *J*=12.6 Hz, 1H), 5.11(d, *J*=12.4 Hz, 1H), 4.86 (t, *J*=3.6 Hz, 1H), 4.46 (d, *J*=3.6 Hz, 2H), 1.13 (s, 9H). **Isomer 2**. ^1H NMR (200 MHz, $CDCl_3$) δ 7.32 (m, 4H), 6.88(d, *J*=10.4Hz, 1H), 6.28(d, *J*=10.4Hz, 1H), 5.27 (d, *J*=12.8 Hz, 1H), 5.07(d, *J*=12.8Hz, 1H), 4.93 (dd, *J*=20, 8 Hz, 1H), 4.52 (t, *J*=2.4 Hz, 2H), 1.15(s, 9H). HRMS (CI^+) calcd for $(M+H)^+$ $C_{18}H_{21}O_5$: 317.1388, found: 317.1387.

Compound 11: Reduction of Spiro enone into alcohol using $NaBH_4$



To a solution of sodium borohydride (4 mg, 0.1 mmol) in water (0.8 ml) was added dropwise a solution of enone **10** (27 mg, 0.085 mmol) in THF (0.4 ml) at 0 °C. The reaction mixture was stirred for 45 min at the same temperature, until TLC showed the absence of starting material a brine (5 ml) solution was added and the mixture was extracted with EtOAc (2x10 ml) and dried (Na_2SO_4). The organic phase after filtration and evaporation under reduced pressure and gave a crude product, which was purified by flash chromatography over silica gel using ethyl acetate:hexane (4:6) to yield the alcohol (24 mg, 88 %). R_f = 0.4 [Hexanes:EtOAc (6:4)]. $[\alpha]_D$ = +31.2 in CH_2Cl_2 (0.9%). IR (thin film, cm^{-1}) 3471, 2960, 1728, 1608, 1497, 1465, 1431, 1344, 1287, 1222, 1200, 1156, 1089, 1067, 1017. ^1H NMR (300 MHz, $CDCl_3$) δ 6.32 (s, 2H), 6.04 (dd, *J*=10.05,1.8 Hz, 1H), 5.71 (dd, *J*=10.05, 2.4 Hz, 1H), 5.09(d, *J*=12.6 Hz, 1H), 4.95(d, *J*=12.6Hz, 1H), 4.62 (dd, *J*=12.3, 3.6 Hz, 1H), 4.2 (dd, *J*=12.3, 2.4 Hz, 1H), 4.04 - 4.1 (br.m, 1H), 3.92 (dt, *J*=10.2, 2.7 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 2.68 (d, *J*=6 Hz, 1H), 1.2 (s, 9H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.6, 162.9, 156.1, 143.6, 132.0, 128.4, 120.1, 105.9, 98.3, 96.8, 74.1, 71.8, 63.5, 63.4, 55.7, 55.4, 39.0, 27.2. HRMS (CI^+) calcd for $(M+H)^+$ $C_{20}H_{27}O_7$: 379.1757, found: 379.1770.

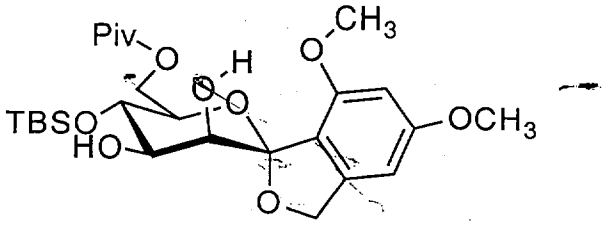
Compound 12



To the spiroenol **11** (54 mg, 0.14 mmol) in DMF (1ml) was added imidazole(19 mg, 0.28 mmol) and DMAP (5 mg) at room temperature under nitrogen atmosphere, then TBSCl (0.32 mg, 0.21 mmol). The solution was stirred overnight then pour into water (20 ml) and extract it with Et_2O (2x10 ml). The organic layer were washed with water, aqueous hydrochloric acid (1M), water, brine and dried (Na_2SO_4). Evaporation of solvent under reduced pressure and flash chromatography over silica gel using hexanes: ethyl acetate (10 %) resulted in the white crystalline solid of TBS protected alcohol. yield: 45 mg (64 %). m.p : 129-131 °C. R_f:0.6[hexanes:EtOAc (9:1)]. $[\alpha]_D$ = +137.2 in CH_2Cl_2 (0.7 %). IR (thin film, cm^{-1}) 2954, 2860, 1731, 1607, 1490, 1460, 1425, 1343, 1278, 1249, 1155, 1096, 1020. ^1H NMR (300 MHz, $CDCl_3$) δ 6.31 (br.s, 2H), 5.93 (dd, *J*=10.05, 1.8 Hz, 1H), 5.69 (dd, *J*=10.05, 2.1 Hz, 1H), 5.06 (d, *J*=12.9 Hz, 1H), 4.92(d, *J*=12.6 Hz, 1H), 4.4 (dd, *J*=11.7, 1.8 Hz, 1H), 4.33 (dt, *J*=9, 1.8 Hz, 1H), 4.09 (dd, *J*=11.7 Hz,

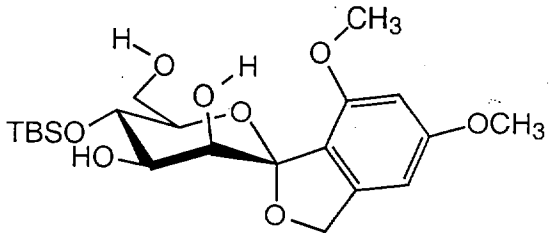
1H), 4.01 (m, *J*=1.8 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 1.16 (s, 9H), 0.89 (s, 9H), 0.13 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 162.7, 156.0, 143.8, 132.9, 127.8, 120.4, 105.6, 98.3, 96.8, 73.5, 71.7, 63.8, 63.1,55.7, 55.6, 38.8, 27.2, 25.7, 17.9, -4.1, -4.8. FAB HRMS calcd for $(M+H)^+$ $C_{26}H_{41}O_7Si$: 493.2621, found: 493.2633. Anal. Calcd for C = 63.38 %, H = 8.19 %; Anal. found C = 63.19 %, H = 7.91 %.

Compound 2



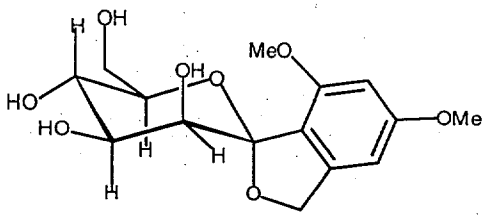
A round bottom flask containing a 0.1 M solution of protected alcohol **12** in *t*-butanol/H_2O (5:1) was stirred at room temperature. A molar excess of a 50 % w/w solution of 4-methyl morpholine-N-oxide in water was added to the solution. A catalytic amount (10 mol %) of OsO_4 was added to the reaction. The reaction was allowed to stirr at RT for 2 h. The temperature of the bath was slowly raised to 75 °C and the reaction was allowed to stirr at this temp for 20 hours. The solution was cooled to room temperature, 1M $NaHSO_3$ (1 ml) was added to the solution, after stirring 10 more minutes the mixture was extracted with ethyl acetate (10ml) and washed with brine. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Column chromatography on silica gel (40 % EtOAc/Hexanes) afforded the diol **2** as a major white solid in 69 % yield. R_f = 0.5 [hexanes:EtOAc (8:2)]. m.p : 55 °C. $[\alpha]_D$ = +37.5 in CH_2Cl_2 (0.9%). IR (thin film, cm^{-1}) 3460, 2942, 2860, 1731, 1607, 1601, 1490, 1466, 1461, 1431, 1396, 1343, 1284, 1249, 1219, 1202, 1155, 1108, 1090, 1026, 1008. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.41 (d, *J*=1.5 Hz, 1H), 6.39 (d, *J*=1.5 Hz, 1H), 5.09 (d, *J*=12.5 Hz, 1H), 5.01(d, *J*=13 Hz, 1H), 4.74 (d, *J*=2.5 Hz, 1H), 4.35 (dd, *J*=12, 2 Hz, 1H), 4.22 (dd, *J*=12, 3 Hz, 1H), 4.04 (t, *J*=9.5 Hz, 1H), 3.95 (q, *J*=4.75, 1.2 Hz, 1H), 3.91 (dt, *J*=16.5, 2.5 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 2.41 (d, *J*=10 Hz, 1H), 1.21 (s, 9H), 0.89 (s, 9H), 0.2 (s, 3H), 0.1 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.9, 162.9, 154.5, 143.9, 118.7, 110.8, 98.9, 98.0, 74.1, 73.6, 73.2, 72.3, 69.1, 62.6, 56.0, 55.7, 38.9, 27.2, 25.9, 18.3, -3.8, -4.9. HRMS (CI^+) calcd for $(M+H)^+$ $C_{26}H_{43}O_9Si$: 527.2676, found: 527.2683. Anal. Calcd for C = 59.29 %, H = 8.04 %; Anal. found C = 59.32 %, H = 7.94 %.

Compound 13.



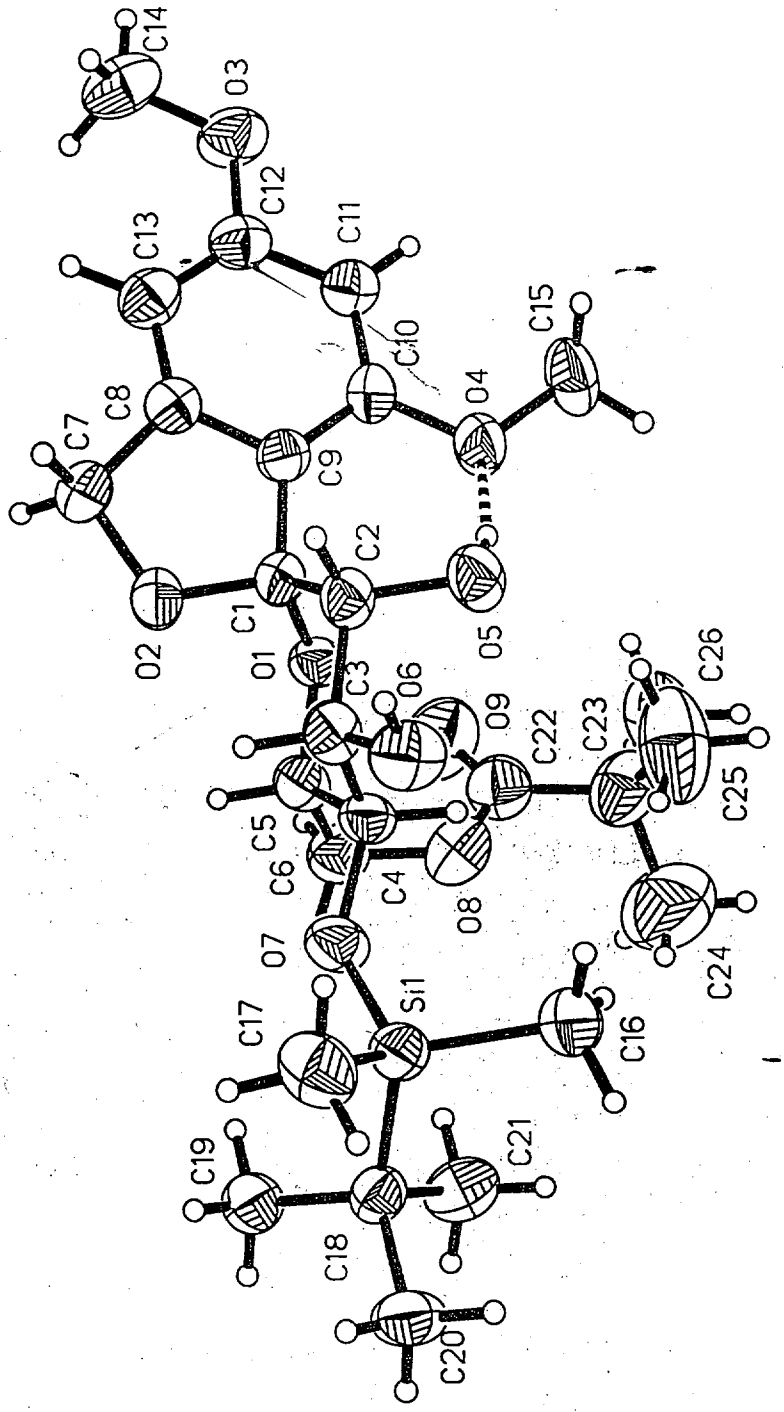
The ester **2** (64mg, 0.12 mmol) in ether (1.5 ml) was cooled to -78 °C , DIBAL-H (0.25ml, 1M in Hexane solution, 2equiv) was dropwise added over 5 min. The reaction was stirred for 3h at -78 °C before being quenched with 1mL of aq.ether(50%). The cooling bath was removed and was stirred at room temperature for 0.5h, diluted with ethyl acetate (5 ml) and filtered through plug of celite and silica gel using ethyl acetate as eluent. The organic filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (SiO_2, 50% EtOAc/Hexanes) affording 50mg (93%) of **13** as a white solid. R_f = 0.2 [hexanes:EtOAc (8:2)]. $[\alpha]_D$ = +32.1 in CH_2Cl_2 (0.76 %). IR (thin film, cm^{-1}): 3475, 2950, 2925, 2850, 1604, 1495, 1462, 1433, 1400, 1354, 1321, 1250, 1229, 1200, 1150, 1087, 1020, 975. ^1H NMR (300 MHz, $CDCl_3$) δ 6.42 (d, *J*=2.1 Hz, 1H), 6.4 (d, *J*=2.1 Hz, 1H), 5.1 (d, *J*=12.9 Hz, 1H), 4.99 (d, *J*=12.9 Hz, 1H), 4.69 (d, *J*=2.1 Hz, 1H), 3.97-3.75 (m, 5H), 3.9 (s, 3H), 3.8 (s, 3H), 2.4 (d, *J*=9.6 Hz, 1H), 1.9 (t, *J*=6.6 Hz, 1H), 1.6 (br s, 1H), 0.9 (s, 9H), 0.19 (s, 3H), 0.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 154.4, 144.0, 118.6, 110.8, 98.6, 97.9, 75.2, 73.9, 73.4, 72.1, 69.3, 62.1, 56.1, 55.7, 25.9, 18.3, -3.8, -4.9. HRFAB calcd for $(M+H)^+$ $C_{21}H_{35}O_8Si$: 443.2101, found: 443.2092.

Compound 14



A solution of compound **13** (9 mg, 0.02 mmol) in 0.3 mL of THF at room temperature was treated with tetrabutylammonium fluoride.$3H_2O$ (1.0M solution in THF, 40 μL, 0.04

mmol) under N_2 atmosphere. After 3h, the mixture was diluted with Et_2O (1 ml) and filtered through a plug of celite and florisil using methanol as eluent. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography [florisil, CH_2Cl_2/MeOH(8:2)] affording 6 mg (93%) of **14** as viscous oil. R_f = 0.5 [CH_2Cl_2/MeOH(8:2)]. $[\alpha]_D$ = +30.6 in CH_3OH (0.6 %). IR (thin film, cm^{-1}): 3389, 2931, 1613, 1601, 1490, 1461, 1431, 1337, 1296, 1225, 1196, 1155, 1090, 1067, 1026, 979, 908, 832. ^1H NMR (300 MHz, CD_3OD) δ 6.53 (s, 1H), 6.52 (s, 1H), 5.09 (d, *J*=12.9 Hz, 1H), 5.00 (d, *J*=12.9 Hz, 1H), 4.92 (s, 1H), 3.99-3.95 (m, 1H), 3.94-3.87 (m, 2H), 3.90 (s, 3H), 3.86 (m, 2H), 3.82 (s, 3H), 3.74-3.67 (m, 1H), 3.38-3.33 (m, 1H). ^{13}C NMR (75 MHz, CD_3OD) δ 164.7, 156.4, 145.7, 120.1, 112.5, 99.7, 99.3, 77.4, 75.7, 74.0, 73.2, 68.6, 63.4, 56.8, 56.3. HRFAB calcd for $(M+Na)^+$ $C_{15}H_{20}O_8Na$: 351.1055, found: 351.1053.


C14
O3
C12
C13
C11
C15
C10
O4
C8
C7
C9
C2
O2
C1
O1
O5
C3
O6
O9
C22
C23
C26
C5
C6
C4
O8
C25
O7
C24
Si1
C17
C16
C19
C21
C18
C20

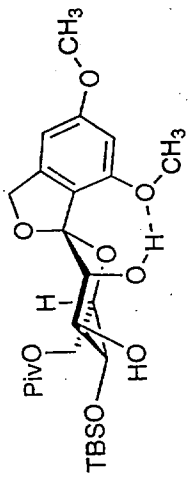

CH3
O
CH3
O
H
O
H
PivO
HO
TBSO

Table 1. Crystal data, data collection, and solution and refinement for 99275.

Crystal Data	
Empirical formula	$C_{26}H_{42}O_9Si$
Crystal Habit, color	plate, colouress
Crystal size	0.32 x 0.18 x 0.08 mm
Crystal system	Monoclinic
Space group	C2
	a = 17.067(3) Å α = 90.00)°
	b = 12.390(2) Å β = 107.172(3)°
	c = 15.389(2) Å γ = 90°
Volume	3109.0(8) $Å^3$
Z	4
Formula weight	526.69
Density (calculated)	1.125 Mg/m^3
Absorption coefficient	0.119 mm^{-1}
F(000)	1136
Data Collection	
Diffractometer	Bruker SMART Platform CCD
Wavelength	0.71073 Å
Temperature	173(2) K
θ range for data collection	2.06 to 27.52°
Index ranges	$-22 \le h \le 19$, $-16 \le k \le 14$, $-19 \le \ell \le 18$
Reflections collected	10224
Independent reflections	6264 (R_{int} = 0.0558)
Solution and Refinement	
System used	SHELXTL-V5.0
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2(F_o^2)+(AP)^2+(BP)]^{-1}$, where $P = (Fo^2+2Fc^2))/3$, A = 0.0553, and B = 0
Absorption correction	SADABS, G. Sheldrick (1999)
Max. and min. transmission	1.0000 and 0.7915
Absolute structure parameter	0.1(2)
Data / restraints / parameters	6264 / 20 / 368
R indices (I>2σ(I) = 2974)	R1 = 0.0546, wR2 = 0.1096
R indices (all data)	R1 = 0.1072, wR2 = 0.1297
Goodness-of-fit on F^2	0.813
Largest diff. peak and hole	0.247 and -0.190 $eÅ^{-3}$