Supplementary Material (ESI) for Chemical Communications

Supplementary Information

on

Total syntheses of (+)-7-epi-goniofufurone, (+)-goniopypyrone and (+)-goniofufurone from a common precursor

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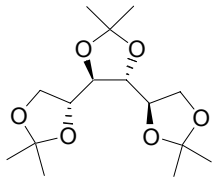
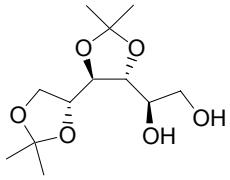
General. ^{1}H and ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ at 400 MHz and 100 MHz and referred, respectively, to the TMS signal used as an internal standard and the central line for $CDCl_3$. Chemical shifts are reported in ppm (δ) and the coupling constants in Hz. HRMS were recorded using a Q-Tof Premier Micromass machine. Column chromatographic separations were performed using silica gel (100-200 mesh). Routine monitoring of reactions was performed using silica gel-G LR and silica gel 60 PF_{254} in 3:1 ratio obtained from S.D.Fine and Merck, respectively. The radial chromatography was performed using plates coated with silica gel (60 PF_{254}). Reactions under anhydrous conditions were run under an atmosphere of nitrogen using flame-dried glasswares. The organic extracts were dried over anhydrous Na_2SO_4. Evaporation of the solvents was performed on a rotovap under reduced pressure. Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. CH_2Cl_2 and $CHCl_3$ were distilled from CaH_2. *tert*-Butyldiphenylsilyl chloride (TBDPSCl), Grubbs' catalyst (2nd generation), DMAP, *m*-CPBA, vinylacetic acid, TBAF, CBr_4 and DBU were obtained from Aldrich Chemical Company. Optical rotations were measured using Autopol III, Automatic Polarimeter at 25 ^{o}C.



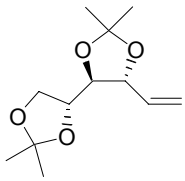
1,2:3,4:5,6-Tri-*O*-isopropylidene-D-mannitol, **4**

1,2:3,4:5,6-Tri-*O*-isopropylidene-D-mannitol 4. To a suspension of D-mannitol (30 g, 164.7 mmol) in dry acetone (1.5 l) was added conc. H_2SO_4 (98%, 9 mL) and stirred for 6 h at room temperature. Reaction was neutralized by saturated aqueous NaOH (150 mL) and the solvent was removed in vacuo. The resultant was diluted with EtOAc (200 mL) and saturated with NaCl (15 g). The organic layer was separated and the remaining aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic solution was washed with aqueous saturated NaOH (1 x 25 mL), H_2O (1 x 25 mL) and brine (1 x 25 mL) and dried. Removal of the solvent gave the crude product which was purified by column chromatography to isolate **4**, 42.30 g, 85%, white solid, mp 68-70 ^{o}C (lit.[1] mp 70 ^{o}C). ^{1}H NMR δ 4.20-4.17 (m, 2H), 4.10-4.07 (dd, J = 8.6, 6.4 Hz, 2H), 4.01-3.94 (m, 4H), 1.43 (s, 6H), 1.39 (s, 6H), 1.36 (s, 6H). ^{13}C NMR δ 110.2, 109.6, 79.4, 76.3, 66.2, 27.4, 26.5, 25.4. IR (KBr) ν_{max}/cm^{-1} 3054, 2986, 1261, 1067, 843, 740.



1,2:3,4-Di-*O*-isopropylidene-D-mannitol, **5**

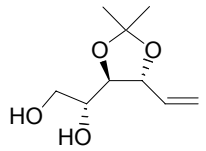
1,2:3,4-Di-*O*-isopropylidene-D-mannitol 5. Solid mannitol triacetonide **4** (30 g, 99.34 mmol) was taken in 684 mL of 70% aqueous ethanol at a steady temperature of 45 ^{o}C. Conc. HCl (2.1 mL) was added dropwise within 1 h while the temperature was maintained at 45 ^{o}C and the content was vigorously stirred. Immediately after the addition of HCl, the reaction was quenched by the addition of solid K_2CO_3 (10 g). The ethanol layer was separated and the aqueous phase was extracted with EtOAc (1 x 100 mL). The combined organic solution was concentrated and the residue was taken in cold H_2O when the unreacted starting material separated out as solid (16.27 g) and was filtered out. The aqueous layer was extracted with EtOAc (3 x 100 mL) to give the crude product **5**, 11.79 g, 99% based on the starting material recovered, low melting solid. The crude product was taken as such for the next step without further purification.



1,2:3,4-Di-*O*-isopropylidene-5,6-dideoxy-D-mannitol, **6**

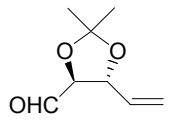
1,2:3,4-Di-*O*-isopropylidene-5,6-dideoxy-D-mannitol 6. To a solution of diol **5** (10 g, 38.17 mmol) in dry toluene (800 mL) was added triphenylphosphine (40 g, 152.67 mmol) followed by imidazole (10.4 g, 152.67 mmol) and stirred vigorously. To the resulting solution was added iodine (29 g, 114.5 mmol) and the mixture was refluxed at 110 ^{o}C for 3 h. The reaction mixture, after bringing to room temperature, was decanted into excess saturated aqueous $Na_2S_2O_3$ (100 mL) and saturated aqueous $NaHCO_3$ (100 mL) in a separatory funnel. The residue in the reaction flask was extracted with EtOAc (3 x 100 mL). These extracts were combined with the material in the separatory funnel and shaken until the iodine was consumed. The organic phase was washed with H_2O (1 x 100 mL), dried, and concentrated. The crude residue was chromatographed to obtain **6**, 7 g, 80.4%, viscous liquid. ^{1}H NMR δ 5.92-5.83 (1H, m), 5.38 (1H, d, J = 17.1 Hz),

5.18 (1H, d, *J* = 10.5 Hz), 4.32 (1H, t, *J* = 6.8 Hz), 4.12-4.04 (2H, m), 3.93-3.90 1H, (dd, *J* = 7.8, 4.4 Hz), 3.67 (1H, t, *J* = 7.4 Hz), 1.37 (9H, s), 1.31 (3H, s). ^{13}C NMR δ 135.8, 117.2, 109.6, 109.4, 81.1, 80.4, 76.6, 66.9, 26.9, 26.8, 26.6, 25.2. IR (neat) ν_{max}/cm^{-1} 2988, 2931, 2884, 1376, 1251, 1217, 1065, 925, 847. HRMS calcd for $C_{12}H_{20}O_4Na$ $(M+Na)^+$ 251.1259, found 251.1258.



3,4-*O*-isopropylidene-5,6-dideoxy-D-mannitol, **7**

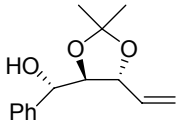
3,4-*O*-isopropylidene-5,6-dideoxy-D-mannitol 7. To a solution of the diacetonide **6** (10 g, 43.86 mmol) in CH_3CN (100 mL) was added $CuCl_2.2H_2O$ (7.48 g, 43.86 mmol) at 0 ^oC and stirred at the same temperature for 40 min. The reaction was quenched by aqueous saturated $NaHCO_3$ (20 mL) and filtered through celite. The aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic extract was dried and concentrated to obtain a residue that was purified by column chromatography to isolate 2.5 g of the starting material and 6.18 g of the desired product **7**, 99.9% based on the starting material recovered, yellow oil. $[\alpha]_D$ +6.7 (*c* 0.58, CH_2Cl_2) [lit.[2] $[\alpha]_D$ +6.4 (*c* 0.47, CH_2Cl_2)]. ^{1}H NMR δ 5.94-5.85 (m, 1H), 5.46-5.41 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.29-5.26 (dt, *J* = 10.3, 1.0 Hz, 1H), 4.43-4.39 (dd, *J* = 8.0, 7.1 Hz, 1H), 3.88-3.87 (m, 1H), 3.81-3.78 (dd, *J* = 8.0, 5.4 Hz, 1H), 3.75-3.68 (m, 2H), 2.64 (bs, 1H, OH), 2.28 (bs, 1H, OH), 1.44 (s, 3H), 1.43 (s, 3H). ^{13}C NMR δ 135.8, 118.8, 109.3, 81.1, 79.2, 71.9, 63.4, 26.9, 26.8. IR (neat) ν_{max}/cm^{-1} 3401, 2988, 2933, 1644, 1378, 1054, 874.



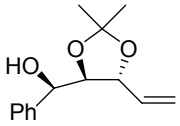
2,3-*O*-isopropylidene-4-pentenal, **8**

2,3-*O*-isopropylidene-4-pentenal 8. To a solution of diol **7** (5 g, 26.6 mmol) in DCM (100 mL), $Pb(OAc)_4$ (14.15 g, 31.9 mmol) was added at 0 ^oC and the reaction was allowed to proceed with gradual warming to room temperature. After 3 h, when all the diol had been consumed, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (20 mL). The solids

were removed by filtration through celite and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic solution was washed with H_2O (1 x 20 mL) and brine (1 x 20 mL), dried, and concentrated to give the requisite aldehyde **8**, 4.1 g, 99%, viscous liquid. The crude material was used as such in the next step.



3,4-*O*-isopropylidene-5-*C*-phenyl-L-*xylo*-pent-1-en-5-ol, **9**

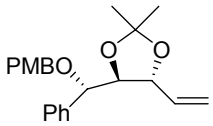


3,4-*O*-isopropylidene-5-*C*-phenyl-D-*arabino*-pent-1-en-5-ol, **10**

3,4-*O*-isopropylidene-5-*C*-phenyl-L-*xylo*-pent-1-en-5-ol 9 and 3,4-*O*-isopropylidene-5-*C*-phenyl-D-*arabino*-pent-1-en-5-ol 10. In a flame-dried 500 mL 2-neck round bottom flask were taken activated Mg turnings (2.06 g, 84.6 mmol), a few crystals of iodine and 10 mL THF at 0 ^oC. To the suspension was added bromobenzene (0.6 mL, 5.7 mmol), dropwise, and stirred vigorously until the disappearance of iodine color. The reaction mixture was diluted with THF (70 mL) and a solution of bromobenzene (7.5 mL, 71.2 mmol) in THF (80 mL) was added to it dropwise. The mixture was stirred for 1 h with gradual warming until the consumption of Mg was complete. The reaction mixture was cooled to 0 ^oC and a solution of the aldehyde **8** (4 g, 25.6 mmol) in THF (80 mL) was added to it dropwise. The stirring was continued for 8 h with gradual warming to room temperature. The reaction was quenched by saturated aq NH_4Cl (30 mL) and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic extract was washed with brine (1 x 50 mL), dried, and concentrated. Purification by column chromatography afforded the two isomers **9** and **10** in the ratio of 1.5:1; 77.3% yield, viscous liquid.

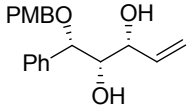
3,4-*O*-isopropylidene-5-*C*-phenyl-L-*xylo*-pent-1-en-5-ol 9. $[\alpha]_D$ +14.9 (*c* 0.21, CH_2Cl_2) [lit.[2] $[\alpha]_D$ +14.4 (*c* 0.25, CH_2Cl_2)]. ^1H NMR δ 7.38-7.28 (m, 5H), 5.48-5.39 (m, 1H), 5.09 (d, *J* = 17.1 Hz, 1H), 5.00 (d, *J* = 10.5 Hz, 1H), 4.63 (t, *J* = 5.4 Hz, 1H), 4.32 (t, *J* = 7.1 Hz, 1H), 3.95-3.92 (dd, *J* = 8.0, 5.1 Hz, 1H), 2.79 (d, *J* = 5.4 Hz, 1H), 1.49 (s, 3H), 1.44 (s, 3H). ^{13}C NMR δ 139.9, 134.7, 128.4, 128.3, 126.9, 118.2, 109.7, 84.4, 79.0, 74.1, 27.0. IR (neat) ν_{max}/cm^{-1} 3444, 2987, 2931, 1376, 1250, 1052, 703.

3,4-*O*-isopropylidene-5-*C*-phenyl-D-*arabino*-pent-1-en-5-ol 10. $[\alpha]_D$ +4.6 (*c* 0.32, CH_2Cl_2) [lit.[2] $[\alpha]_D$ +4.4 (*c* 0.21, CH_2Cl_2)]. ^{1}H NMR δ 7.37-7.25 (m, 5H), 5.31-5.23 (m, 1H), 5.01 (d, *J* = 3.9 Hz, 1H), 4.96 (d, *J* = 4.9 Hz, 1H), 4.88 (d, *J* = 5.8 Hz, 1H), 4.40 (t, *J* = 7.1 Hz, 1H), 4.01-3.98 (dd, *J* = 8.1, 3.9 Hz, 1H), 2.71 (d, *J* = 2.2 Hz, 1H), 1.44 (s, 3H), 1.42 (s, 3H). ^{13}C NMR δ 138.6, 135.6, 128.2, 127.8, 126.0, 116.9, 109.2, 84.1, 76.9, 71.7, 26.9. IR (neat) ν_{max}/cm^{-1} 3458, 2988, 2889, 1376, 1249, 1054, 705.



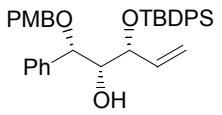
3,4-*O*-isopropylidene-5-*C*-phenyl-5-*O*-(p-methoxy-pbenzyl)-L-*xylo*-pent-1-ene, **11**

3,4-*O*-isopropylidene-5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-L-*xylo*-pent-1-ene 11. A solution of the alcohol **9** (3 g, 12.8 mmol) in THF (30 mL) was added to a 0 ^oC cooled suspension of NaH (55% dispersion in mineral oil, 840 mg, 19.23 mmol) in THF (30 mL). After stirring at 0 ^oC for 15 min, *p*-methoxybenzyl bromide (3.1 g, 15.38 mmol) dissolved in THF (30 mL) was added dropwise, at the same temperature, followed by the addition of tetrabutylammonium iodide (94.7 mg, 0.26 mmol). The reaction mixture was stirred for 6 h with gradual warming to room temperature. After completion of the reaction, it was quenched by the addition of H_2O (20 mL). The aqueous solution was extracted with EtOAc (3 x 10 mL). The combined organic extract was dried and concentrated. Purification by column chromatography afforded the PMB-ether **11**, 4.2 g, 92.5%, viscous liquid. $[\alpha]_D$ +92.6 (*c* 0.81, $CHCl_3$). ^{1}H NMR δ 7.38-7.29 (m, 5H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.89-6.85 (dd, *J* = 11.5, 9.5 Hz, 2H), 5.30-5.21 (m, 1H), 4.84 (d, *J* = 1.02 Hz, 1H), 4.81-4.80 (m, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 6.3 Hz, 1H), 4.26 (d, *J* = 12.0 Hz, 1H), 4.14 (t, *J* = 6.8 Hz, 1H), 3.99-3.96 (dd, J = 8.0, 6.3 Hz, 1H), 3.80 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H). ^{13}C NMR δ 159.1, 137.5, 135.1, 130.0, 129.4, 128.5, 128.4, 128.2, 117.1, 113.6, 109.4, 83.8, 80.9, 78.7, 69.6, 55.2, 27.0, 26.9. IR (neat) ν_{max}/cm^{-1} 3410, 2930, 1612, 1513, 1248, 1062, 702.



5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-L-*xylo*-pent-1-en-3,4-diol, **12**

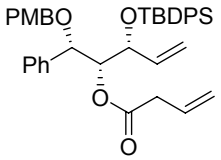
5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-L-*xylo*-pent-1-en-3,4-diol 12. AcOH (50 mL) and H_2O (20 mL) were mixed with **11** (4 g, 11.3 mmol) and the resultant was stirred for 4 h at 50 ^oC. After completion of the reaction, solvent was removed under reduced pressure and the crude was purified by column chromatography to obtain the diol **12**, 3.5 g, 99%, viscous oil. $[\alpha]_D$ +56.4 (*c* 3.41, $CHCl_3$). ^1H NMR δ 7.42-7.34 (m, 5H), 7.21 (d, J = 2.0 Hz, 1H), 7.19 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 1.9 Hz, 1H), 5.87-5.79 (m, 1H), 5.23-5.18 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.16-5.12 (dt, *J* = 10.7, 1.5 Hz, 1H), 4.53 (d, *J* = 6.8 Hz, 1H), 4.45 (d, *J* = 11.0 Hz, 1H), 4.21 (d, *J* = 11.2 Hz, 1H), 3.88 (bs, 1H), 3.81 (s, 3H), 3.63-3.62 (m, 1H), 3.01 (bs, 1H, OH), 2.62 (bs, 1H, OH). ^{13}C NMR δ 159.4, 138.1, 138.0, 129.7, 129.6, 128.7, 128.4, 127.7, 116.0, 113.9, 81.4, 77.3, 71.4, 70.4, 55.3. IR (neat) ν_{max}/cm^{-1} 3415, 2919, 1612, 1513, 1248, 1033, 822, 702. HRMS calcd for $C_{19}H_{22}O_4Na$ $(M+Na)^+$ 337.1416, found 337.1414.



5-*C*-phenyl-5-*O*-(*p*-methoxybenzyl)-3-*O*-*t*-butyldiphenylsilyl-L-*xylo*-pent-1-en-4-ol, **13**

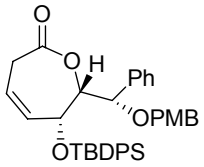
5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-3-*O*-*t*-butyldiphenylsilyl-L-*xylo*-pent-1-en-4-ol 13. To a solution of the diol **12** (3.5 g, 11.15 mmol) in anhydrous DCM (70 mL) was added a solution of *t*-butyldiphenyl silane (3.06 g, 11.15 mmol) in dry DCM (30 mL). The reaction mixture was cooled to 0 ^oC and imidazole (2.3 g, 33.45 mmol) was added. The reaction mixture was stirred for 12 h with gradual warming to room temperature. The reaction mixture was transferred to a separatory funnel and washed with water (1 x 30 mL). The aqueous solution was separated and extracted with DCM (3 x 20 mL). The combined organic extract was dried and concentrated. Purification of the residue by column chromatography afforded 540 mg of bis-protected and 4.3 g of the terminally mono-protected compound **13** along with the recovery of 700 mg of the starting diol **12**. The cleavage of the O-Si bond in the bis-protected compound using 2.0 equivalents of TBAF at 0 ^oC, 0.5 h, afforded 215 mg of the starting diol **12**, making the total starting material recovered to 915 mg. The desired mono-protected compound **13** was obtained in 95% yield (based on the starting diol recovered and also the conversion of the bis-protected compound to the diol) as viscous oil. $[\alpha]_D$ +68.8 (*c* 4.11, $CHCl_3$). ^1H NMR δ 7.61 (t, *J* = 7.1 Hz,

4H), 7.41-7.30 (m, 11H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.90-5.81 (m, 1H), 4.90 (d, *J* = 10.5 Hz, 1H), 4.71 (d, *J* = 17.1 Hz, 1H), 4.55 (d, *J* = 3.7 Hz, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 4.21-4.14 (m, 2H), 3.79 (s, 3H), 3.60-3.56 (dd, *J* = 9.8, 5.1 Hz, 1H), 2.76 (d, *J* = 6.1 Hz, 1H, OH), 1.03 (s, 9H). ^{13}C NMR δ 159.2, 139.6, 137.1, 136.0, 135.9, 133.7, 133.6, 130.0, 129.7, 129.5, 128.3, 127.7, 127.5, 127.3, 117.1, 113.7, 78.5, 78.1, 76.1, 70.0, 55.2, 27.0, 19.3. IR (neat) ν_{max}/cm^{-1} 3559, 3070, 2931, 2857, 1612, 1513, 1426, 1249, 1111, 704. HRMS calcd for $C_{35}H_{40}O_4Si$ Na $(M+Na)^+$ 575.2594, found 575.2590.



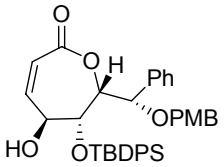
5-*C*-phenyl-5-*O*-(*p*-methoxybenzyl)-3-*t*-butyldiphenylsilyloxy-L-*xylo*-pent-1-en-4-yl-3-butenoate, **14**

5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-3-*t*-butyldiphenylsilyloxy-L-*xylo*-pent-1-en-4-yl-3-butenoate 14. Vinylacetic acid (1.85 mL, 21.74 mmol) and DMAP (442 mg, 3.6 mmol) were added to a solution of the alcohol **13** (4 g, 7.25 mmol) in CH_3CN (100 mL). The reaction mixture was cooled to 0 ^oC and mixed, dropwise, with a solution of DCC (3.74 g, 18.12 mmol) in CH_3CN (60 mL). The reaction mixture was stirred for 10 h with gradual warming to room temperature. The white solid formed was removed by filtration through celite. The filtrate was concentrated and the residue passed through a short silica gel column before the final separation of the product from the starting material through radial chromatography. Purification afforded 1.8 g of the starting material and 1.89 g of the ester **14**; viscous oil, 76.49% yield based on the starting material recovered. $[\alpha]_D$ +35.7 (*c* 1.15, $CHCl_3$). ^{1}H NMR δ 7.64-7.60 (m, 4H), 7.41-7.24 (m, 11H), 7.11-7.09 (m, 2H), 6.83-6.81 (m, 2H), 5.75-5.71 (m, 2H), 5.11-4.98 (m, 3H), 4.86 (d, *J* = 10.5 Hz, 1H), 4.69 (d, *J* = 18.0 Hz, 1H), 4.62 (d, *J* = 3.9 Hz, 1H), 4.46-4.37 (m, 2H), 4.07 (d, *J* = 11.5 Hz, 1H), 3.80 (s, 3H), 2.88-2.86 (m, 2H), 1.00 (s, 9H). ^{13}C NMR δ 170.4, 159.0, 138.1, 136.6, 136.1, 135.9, 133.8, 130.3, 130.0, 129.5, 129.3, 128.3, 127.9, 127.4, 118.1, 113.6, 78.6, 78.4, 74.4, 70.0, 55.2, 38.9, 26.9, 19.3. IR (neat) ν_{max}/cm^{-1} 3369, 3070, 2932, 2858, 1744, 1513, 1248, 1110, 704. HRMS calcd for $C_{39}H_{44}O_5SiNa$ $(M+Na)^+$ 643.2850, found 643.2856.



7(*R*)-[(*S*)-(p-methoxybenzyloxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-4,5-didehydro-2-oxepanone, **15**

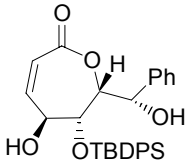
7(*R*)-[(*S*)-(p-methoxybenzyloxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-4,5-didehydro-2-oxepanone 15. To a stirred solution of the ester **14** (1.8 g, 2.9 mmol) in dry benzene (522 mL) at 80 ^{o}C was added, dropwise, a solution of Grubbs' second generation catalyst (123 mg, 0.145 mmol) in dry benzene (123 mL) over a period of 1 h through an addition funnel. The resulting solution was stirred further for 10 h at the same temperature. The reaction mixture was brought to room temperature and concentrated. Purification by column chromatography afforded the 7-membered ring lactone **15**, 1.1 g, 82% (based on 22% recovered starting material), viscous liquid. $[\alpha]_D$ +97.4 (*c* 0.25, $CHCl_3$). ^{1}H NMR δ 7.57-7.25 (m, 17H), 6.89-6.86 (m, 2H), 5.26-5.14 (m, 2H), 5.00 (d, *J* = 8.8 Hz, 1H), 4.60 (d, *J* = 9.0 Hz, 1H), 4.48-4.42 (m, 2H), 3.94-3.92 (dd, *J* = 4.6, 2.4 Hz, 1H), 3.79 (s, 3H), 3.52-3.47 (dd, *J* = 16.8, 2.4 Hz, 1H), 3.04-2.97 (dd, *J* = 16.8, 8.3 Hz, 1H), 1.02 (s, 9H). ^{13}C NMR δ 171.3, 159.2, 137.8, 135.8, 135.3, 133.8, 133.7, 131.5, 129.9, 129.8, 129.7, 128.7, 128.3, 127.7, 127.4, 120.4, 113.8, 83.0, 79.9, 71.0, 68.0, 55.2, 34.0, 26.9, 19.3. IR (neat) ν_{max}/cm^{-1} 3369, 2928, 2857, 1745, 1252, 1109, 1038, 823, 702.



7(*R*)-[(*S*)-(p-methoxybenzyloxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-5(*S*)-hydroxy-3,4-didehydro-2-oxepanone, **16**

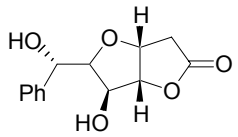
7(*R*)-[(*S*)-(p-methoxybenzyloxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-5(*S*)-hydroxy-3,4-didehydro-2-oxepanone 16. *m*-CPBA (77%, 568 mg, 2.53 mmol) and $NaHCO_3$ (212.5 mg, 2.53 mmol) were added to a solution of **15** (1g, 1.69 mmol) in dry DCM (50 mL) and the solvent was removed immediately on a rotovap with the water bath being held at 45 ^{o}C. The content was maintained at 45 ^{o}C in an oil bath for 24 h. The flask was cooled to room temperature and mixed with DCM (50 mL), *m*-CPBA (77%, 568 mg, 2.53 mmol) and $NaHCO_3$ (212.5 mg, 2.53 mmol).

The solvent was removed immediately, as above, and the content was maintained at 45 ^{o}C for another 24 h. It was cooled to room temperature followed by dilution with DCM (20 mL). Saturated aqueous Na_2SO_3 (20 mL) was added and the content was stirred for 30 min. This was transferred to a separatory funnel, solid $NaHCO_3$ was added and the content was shaken well. The organic solution was separated and aqueous solution was extracted with DCM (3 x 30 mL). The combined organic solution was dried, concentrated, and purified by column chromatography to obtain **16**, 321.5 mg, 77.34% (based on 40% starting material reacted), low melting solid. $[\alpha]_D$ +101.2 (*c* 0.41, $CHCl_3$). ^{1}H NMR δ 7.60-7.14 (m, 15H), 6.88 (t, *J* = 6.6 Hz, 4H), 6.07 (s, 2H), 4.69 (d, *J* = 9.3 Hz, 1H), 4.60 (d, *J* = 9.0 Hz, 1H), 4.38 (d, *J* = 11.0 Hz, 1H), 4.27 (d, *J* = 11.5 Hz, 1H), 4.02 (bs, 1H), 3.81 (s, 3H), 3.52 (d, *J* = 3.2 Hz, 1H), 1.03 (s, 9H). ^{13}C NMR δ 166.5, 159.2, 139.2, 137.1, 136.1, 135.7, 133.1, 132.4, 130.1, 129.6, 128.5, 127.9, 127.7, 122.4, 113.8, 80.1, 78.6, 73.1, 72.3, 70.5, 55.3, 26.7, 19.2.



7(*R*)-[(*S*)-(hydroxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-5(*S*)-hydroxy-3,4-didehydro-2-oxepanone, **17**

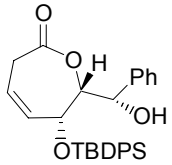
7(*R*)-[(*S*)-(hydroxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-5(*S*)-hydroxy-3,4-didehydro-2-oxepanone 17. The hydroxy olefin **16** (320 mg, 0.53 mmol) was taken with 5% HF in CH_3CN (3.2 mL) in an eppendorf tube and the content was stirred at room temperature for 24 h. The reaction mixture was diluted with EtOAc (10 mL) and washed with brine (1 x 5 mL). The aqueous solution was extracted with EtOAc (3 x 3 mL) and the combined organic extract was dried, concentrated, and purified by column chromatography to obtain the requisite diol **17**, 200.34 mg, 78%, low melting solid. $[\alpha]_D$ +47.3 (*c* 0.56, $CHCl_3$). ^{1}H NMR δ 7.65-7.61 (m, 4H), 7.48-7.09 (m, 12H), 5.99-5.97 (dd, *J* = 5.9, 2.0 Hz, 1H), 5.07-5.06 (m, 1H), 4.86 (d, *J* = 4.6 Hz, 1H), 3.99 (t, *J* = 3.4 Hz, 1H), 3.68 (bs, 1H), 3.09 (bs, 1H, OH), 2.89 (bs, 1H, OH), 1.10 (s, 9H). ^{13}C NMR δ 172.2, 154.3, 140.2, 136.0, 132.2, 132.1, 130.4, 128.5, 128.1, 128.0, 126.6, 122.0, 82.2, 73.8, 72.4, 72.3, 27.0, 19.4.



(+)-7-*epi*-goniofufurone, **2**

(+)-7-*epi*-Goniofufurone 2. A solution of the hydroxyl olefin **17** (200 mg, 0.41 mmol) in $CHCl_3$ (30 mL) containing DBU (68.63 mg, 0.45 mmol) was stirred at room temperature for 24 h. After the reaction was complete, the solvent was removed and the residue was purified by column chromatography to obtain the requisite bicyclic skeleton, 140 mg, 70%, viscous oil. $[\alpha]_D$ +79.4 (*c* 0.23, $CHCl_3$). ^{1}H NMR δ 7.70 (d, *J* = 7.3 Hz, 2H), 7.45-7.20 (m, 13H), 4.92 (bs, 1H), 4.87 (d, *J* = 7. 6 Hz, 1H), 4.72 (d, *J* = 4.4 Hz, 1H), 4.20 (d, *J* = 7.3 Hz, 1H), 3.86 (bs, 1H), 2.74-2.68 (dd, *J* = 19.0, 6.4 Hz, 1H), 2.60 (d, *J* = 18.3 Hz, 1H), 1.00 (s, 9H).

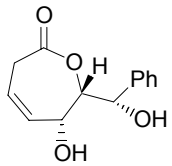
AcOH (1.32 mg, 0.022 mmol) and TBAF (1M in THF, 0.22 mL, 0.22 mmol) were added to a solution of the above bicyclic material (100 mg, 0.20 mmol) in anhydrous THF (3.5 mL) at 0 ^{o}C and stirred for 5 min. The reaction mixture was diluted with EtOAc (5 mL) and washed with brine (1 x 5 mL). The aqueous solution was extracted with EtOAc (3 x 3 mL) and the combined organic extract was dried and concentrated to obtain a residue that was filtered through a short silica gel column to obtain (+)-7-*epi*-Goniofufurone **2**, 50.2 mg, 98%, white solid, mp 192-194 ^{o}C; $[\alpha]_D$ +104.0 (*c* 0.7, EtOH) [lit.[3] mp 190-192 ^{o}C; $[\alpha]_D$ +108.0 (*c* 0.2, EtOH)]. ^{1}H NMR δ 7.44-7.34 (m, 5H), 5.13-5.07 (m, 2H), 4.90 (d, *J* = 4.1 Hz, 1H), 4.42 (t, *J* = 3.7 Hz, 1H), 4.24 (t, *J* = 3.7 Hz, 1H), 3.54 (d, *J* = 4.9 Hz, 1H), 2.80-2.68 (m, 3H). ^{13}C NMR δ 174.9, 139.9, 128.8, 128.5, 126.5, 87.8, 82.9, 77.2, 75.7, 72.8, 36.1. IR (KBr) ν_{max}/cm^{-1} 3359, 2923, 1743, 1602, 1457, 1020, 761. HRMS calcd for $C_{13}H_{13}O_5$ $(M-H)^+$ 249.0763, found 249.0762.



7(*R*)-[(*S*)-hydroxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-4,5-didehydro-2-oxepanone, **18**

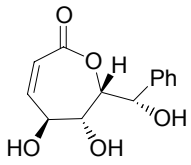
7(*R*)-[(*S*)-hydroxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-4,5-didehydro-2-oxepanone 18. Ph_3CBF_4 (415.8 mg, 1.26 mmol, prepared according to a literature procedure[4]) was added to a

solution of **15** (500 mg, 0.84 mmol) in DCM (40 mL) and stirred for 30 s. The reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic extract was dried and concentrated. The residue was purified by filtration through a short silica gel column to afford the alcohol **18**, 378.72 mg, 95%, viscous oil. $[\alpha]_D$ +33.0 (*c* 0.45, $CHCl_3$). ^1H NMR δ 7.54-7.51 (m, 4H), 7.36-7.20 (m, 11H), 5.25 (d, *J* = 8.6 Hz, 1H), 5.21-5.18 (m, 2H), 4.35 (d, *J* = 8.5 Hz, 1H), 4.02 (d, *J* = 4.2 Hz, 1H), 3.39 (d, *J* = 17.1 Hz, 1H), 3.04 (bs, 1H), 3.01-2.95 (m, 1H), 0.99 (s, 9H).

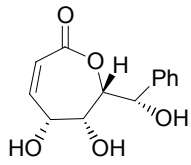


7(*R*)-[(*S*)-hydroxy)benzyl]-6(*R*)-hydroxy-4,5-didehydro-2-oxepanone, **19**

7(*R*)-[(*S*)-hydroxy)benzyl]-6(*R*)-hydroxy-4,5-didehydro-2-oxepanone 19. A solution of the alcohol **18** (300 mg, 0.64 mmol) and CBr_4 (85 mg, 0.26 mmol) in anhydrous MeOH (6.5 mL) was refluxed for 12 h. After completion of the reaction, the solvent was removed and the residue was purified by column chromatography to obtain the diol **19**, 125.34 mg, 85%, viscous oil. $[\alpha]_D$ +9.6 (*c* 0.14, $CHCl_3$). ^1H NMR δ 7.48-7.32 (m, 5H), 5.96 (d, *J* = 9.8 Hz, 1H), 5.73 (d, *J* = 10.0 Hz, 1H), 4.97 (d, *J* = 8.3 Hz, 1H), 4.68 (bs, 1H), 3.75 (d, *J* = 8.0 Hz, 1H), 3.24-3.17 (dd, *J* = 22.0, 2.9 Hz, 1H), 3.04 (d, *J* = 22.0 Hz, 1H). HRMS calcd for $C_{13}H_{14}O_4Na$ $(M+Na)^+$ 257.0790, found 257.0793.



7(*R*)-[(*S*)-hydroxy)benzyl]-6(*R*)-hydroxy-5(*S*)-hydroxy-3,4-didehydro-2-oxepanone, **20**



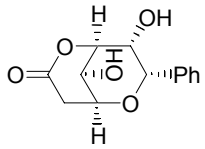
7(*R*)-[(*S*)-hydroxy)benzyl]-6(*R*)-hydroxy-5(*R*)-hydroxy-3,4-didehydro-2-oxepanone, **21**

7(*R*)-[(*S*)-hydroxy)benzyl]-6(*R*)-hydroxy-5(*S*)-hydroxy-3,4-didehydro-2-oxepanone 20 and 7(*R*)-[(*S*)-hydroxy)benzyl]-6(*R*)-hydroxy-5(*R*)-hydroxy-3,4-didehydro-2-oxepanone 21. To a solution of the above diol **19** (100 mg, 0.43 mmol) in anhydrous benzene (35 mL) at 0 ^oC were

added $VO(acac)_2$ (17.14 mg, 0.065 mmol) and t-BuOOH (0.58 mL, 4.43 M in anhydrous benzene) and the resultant was stirred at room temperature for 10 h. The solvent was evaporated and the residue was purified by column chromatography to afford **20** and **21** in the ratio 5:1 in 80% overall yield (based on 66% starting material reacted), both as white sticky solids.

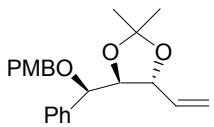
7(*R*)-[(*S*)-hydroxy)benzyl]-6(*R*)-hydroxy-5(*S*)-hydroxy-3,4-didehydro-2-oxepanone 20. $[\alpha]_D$ +62.9 (*c* 0.31, $CHCl_3$). ^{1}H NMR δ 7.44-7.31 (m, 5H), 6.95-6.92 (dd, *J* = 9.5, 5.8 Hz, 1H), 6.08 (d, *J* = 9.8 Hz, 1H), 5.03 (d, *J* = 5.9 Hz, 1H), 4.32 (d, *J* = 5.8 Hz, 1H), 4.22 (d, *J* = 5.1 Hz, 1H), 4.12 (s, 1H). HRMS calcd for $C_{13}H_{13}O_5$ $(M-H)^+$ 249.0763, found 249.0766.

7(*R*)-[(*S*)-hydroxy)benzyl]-6(*R*)-hydroxy-5(*R*)-hydroxy-3,4-didehydro-2-oxepanone 21. ^{1}H NMR δ 7.42-7.35 (m, 5H), 6.83 (d, *J* = 10.0 Hz, 1H), 5.89 (d, *J* = 9.8 Hz, 1H), 5.02 (d, *J* = 5.9 Hz, 1H), 4.85 (bs, 1H), 4.06 (bs, 1H), 3.88 (d, *J* = 10.7 Hz, 1H). HRMS calcd for $C_{13}H_{13}O_5$ $(M-H)^+$ 249.0763, found 249.0765.



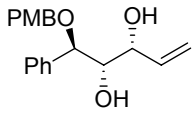
(+)-goniopypyrone, **3**

(+)-Goniopypyrone 3. A solution of **20** (20 mg, 0.08 mmol) in $CHCl_3$ (5mL) containing DBU (13.4 mg, 0.088 mmol) was stirred at room temperature for 0.5 h. After the reaction was complete, the solvent was removed and the residue filtered through a small silica gel column to obtain **3**, 16.8 mg, 84%, crystalline solid. mp 180-182 ^{o}C; $[\alpha]_D$ +55.0 (*c* 0.9, EtOH) [lit.[5] mp 182-184 ^{o}C; $[\alpha]_D$ +54.0 (*c* 0.4, EtOH)]. ^{1}H NMR δ 7.46-7.36 (m, 5H), 5.03 (s, 1H), 4.83-4.81 (dd, *J* = 5.8, 3.4 Hz, 1H), 4.49-4.47 (dd, *J* = 4.6, 2.0 Hz, 1H), 4.13-4.03 (m, 3H), 3.12-3.07 (dd, *J* = 19.8, 2.0 Hz, 1H), 3.04-2.98 (dd, *J* = 19.3, 4.9 Hz, 1H), 2.16 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR δ 167.8, 135.9, 129.0, 128.7, 126.2, 72.7, 71.0, 70.4, 70.2, 64.5, 35.2. IR (KBr) ν_{max}/cm^{-1} 3355, 2924, 1744, 1452, 1221, 1058, 735. HRMS calcd for $C_{13}H_{13}O_5$ $(M-H)^+$ 249.0763, found 249.0761.



3,4-*O*-isopropylidene-5-*C*-phenyl-5-*O*-(*p*-methoxybenzyl)-D-*arabino*-pent-1-ene, **22**

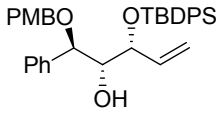
3,4-*O*-isopropylidene-5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-D-*arabino*-pent-1-ene 22. In a flame-dried 2-neck round bottom flask was placed a suspension of NaH (55% dispersion in mineral oil, 560 mg, 12.82 mmol) in THF (20 mL) and cooled to 0 ^{o}C. To it was added, dropwise, a solution of the alcohol **10** (2 g, 8.54 mmol) in THF (20 mL). After stirring at 0 ^{o}C for 15 min, *p*-methoxybenzyl bromide (2.1 g, 10.25 mmol) dissolved in THF (20 mL) was added, dropwise, at the same temperature followed by the addition of tetrabutylammonium iodide (63.1 mg, 0.17 mmol). The reaction mixture was stirred for 6 h with gradual warming to room temperature and quenched by addition of H_2O (10 mL). The aqueous layer was extracted with EtOAc (3 x 10 mL) and the combined organic extract was dried and concentrated. Purification by column chromatography afforded the PMB-ether **22**, 2.74 g, 90.5%, viscous liquid. $[\alpha]_D$ -97.8 (*c* 0.72, $CHCl_3$). ^{1}H NMR δ 7.46-7.32 (m, 5H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.86-5.78 (m, 1H), 5.36-5.31 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.16 (d, *J* = 9.3 Hz, 1H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.45 (d, *J* = 5.6 Hz, 1H), 4.39 (t, J = 7.3 Hz, 1H), 4.29 (d, *J* = 11.5 Hz, 1H), 4.03-3.99 (dd, J = 7.6, 5.6 Hz, 1H), 3.83 (s, 3H), 1.41 (s, 3H), 1.35 (s, 3H). ^{13}C NMR δ 159.2, 138.2, 136.3, 130.1, 129.5, 128.2, 128.1, 128.0, 117.1, 113.7, 109.4, 83.8, 81.0, 79.7, 70.4, 55.2, 27.1, 26.8. IR (neat) ν_{max}/cm^{-1} 3444, 2987, 2872, 1612, 1513, 1249, 1069, 702.



5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-D-*arabino*-pent-1-en-3,4-diol, **23**

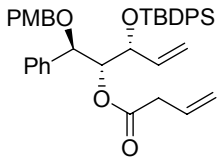
5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-D-*arabino*-pent-1-en-3,4-diol 23. The PMB ether **22** (2.5 g, 7.06 mmol) was mixed with AcOH (30 mL) and H_2O (12.5 mL) and stirred for 4 h at 50 ^{o}C. The solvents were removed and the residue filtered through a short silica gel column to afford the diol **23**, 2.2 g, 99%, viscous oil. $[\alpha]_D$ -58.7 (*c* 0.97, $CHCl_3$). ^{1}H NMR δ 7.47-7.36 (m, 5H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.96-5.87 (m, 1H), 5.39-5.34 (dt, *J* = 17.1, 1.7 Hz, 1H), 5.25-5.21 (dt, *J* = 10.5, 1.4 Hz, 1H), 4.62 (d, *J* = 6.1 Hz, 1H), 4.48 (d, *J* = 11.0 Hz, 1H), 4.45-4.43 (m, 1H), 4.29 (d, *J* = 11.0 Hz, 1H), 3.83 (s, 3H), 3.71-3.69 (dd, *J* = 6.1, 2.2 Hz, 1H). ^{13}C NMR δ 159.4, 138.3, 137.6, 129.6, 128.7, 128.3, 127.5, 116.0, 113.9, 82.8, 75.9, 71.0, 70.9,

55.2. IR (neat) ν_{max}/cm^{-1} 3459, 2909, 1612, 1514, 1249, 1062, 1033, 702. HRMS calcd for $C_{19}H_{22}O_4Na$ $(M+Na)^+$ 337.1416, found 337.1417.



5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-3-*O*-*t*-butyldiphenylsilyl-D-*arabino*-pent-1-en-4-ol, **24**

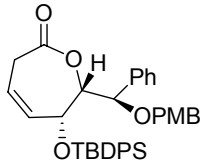
5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-3-*O*-*t*-butyldiphenylsilyl-D-*arabino*-pent-1-en-4-ol 24. *t*-Butyldiphenyl silane (1.93 g, 7.00 mmol) in dry DCM (20 mL) was mixed with a solution of the above diol **23** (2.2 g, 7.00 mmol) in DCM (45 mL). The resultant was cooled to 0 ^oC, mixed further with imidazole (1.43 g, 21.00 mmol), and stirred for 12 h with gradual warming to room temperature. The reaction mixture was transferred to a separatory funnel and washed with water (1 x 20 mL). The aqueous solution was separated and extracted with DCM (3 x 10 mL). The combined organic extract was dried and concentrated to furnish a residue that was purified by column chromatography to afford an inseparable 1:2 (by weight) mixture of the bis- and mono-protected compounds in an overall yield of 97.56%, the yield of the desired mono-silylated compound **24** being 72.3% (based on the starting material recovered), viscous liquid.



5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-3-*t*-butyldiphenylsilyloxy-D-*arabino*-pent-1-en-4-yl-3-butenoate, **25**

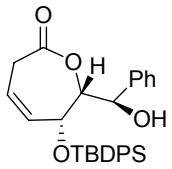
5-*C*-phenyl-5-*O*-(p-methoxybenzyl)-3-*t*-butyldiphenylsilyloxy-D-*arabino*-pent-1-en-4-yl-3-butenoate 25. To a solution of the above mixture of the mono- and bis-silylated compounds (4.2 g, containing 5.1 mmol of the required mono-silylated alcohol **24**) in CH_3CN (100 mL) was added vinylacetic acid (1.3 mL, 15.3 mmol) and DMAP (311.5 mg, 2.55 mmol). The reaction mixture was cooled to 0 ^oC and mixed with a solution of DCC (2.63 g, 12.75 mmol) in CH_3CN (60 mL) dropwise. The reaction mixture was stirred for 8 h with gradual warming to room temperature. The white solid formed was filtered off through celite. The filtrate was concentrated and the residue filtered through a short silica gel column. Purification by radial chromatography

afforded the ester **25**; 1.4 g, 78% yield (based on **57**% mono-silylated compound reacted), viscous oil and 2.6 g of starting material was recovered (containing 1.4 g of bisilylated material). $[\alpha]_D$ -21.2 (*c* 0.85, $CHCl_3$). ^{1}H NMR δ 7.72-7.70 (dd, *J* = 7.6, 1.7 Hz, 5H), 7.43-7.27 (m, 10H), 7.06-7.03 (dd, *J* = 8.6, 2.4 Hz, 2H), 6.81 (d, *J* = 7.3 Hz, 2H), 5.67-5.59 (m, 2H), 5.21 (bs, 1H), 5.05-4.96 (m, 2H), 4.84 (d, *J* = 2.2 Hz, 1H), 4.81 (d, *J* = 2.4 Hz, 1H), 4.66-4.64 (m, 2H), 4.18 (d, *J* = 11.0 Hz, 1H), 3.96 (d, *J* = 10.7 Hz, 1H), 3.79 (s, 3H), 2.72 (t, *J* = 6.1 Hz, 2H), 1.07 (s, 9H). ^{13}C NMR δ 169.9, 159.0, 138.2, 136.7, 136.0, 135.9, 134.7, 134.0, 133.9, 130.2, 130.1, 129.5, 129.2, 128.3, 128.0, 127.6, 127.4, 127.3, 118.2, 117.5, 113.6, 79.2, 77.7, 74.0, 69.9, 55.2, 38.9, 27.0, 19.5. IR (neat) ν_{max}/cm^{-1} 3509, 3071, 2931, 2857, 1745, 1514, 1249, 1112, 703.



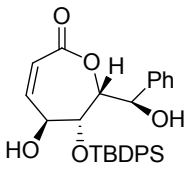
7(*R*)-[(*R*)-(p-methoxybenzyloxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-4,5-didehydro-2-oxepanone, **26**

7(*R*)-[(*R*)-(p-methoxybenzyloxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-4,5-didehydro-2-oxepanone 26. To a stirred solution of the ester **25** (1.4 g, 2.26 mmol) in dry benzene (404 mL) at 80 ^{o}C was added a solution of Grubbs' second generation catalyst (96 mg, 0.113 mmol) in dry benzene (96 mL), dropwise, within a period of 1 h using an addition funnel. The resulting solution was stirred further for 10 h at the same temperature. The reaction mixture was brought to room temperature and the solvent was removed. Purification by column chromatography afforded the 7-membered ring lactone **26**, 1.0 g, 85% (based on 88% starting material reacted), white solid, mp 190-192 ^{o}C. $[\alpha]_D$ -116.4 (*c* 0.45, $CHCl_3$). ^{1}H NMR δ 7.77 (d, *J* = 6.8 Hz, 2H), 7.67 (d, *J* = 7.1 Hz, 2H), 7.51-7.29 (m, 11H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 5.42-5.36 (m, 2H), 5.00 (bs, 2H), 4.43 (d, *J* = 8.8 Hz, 1H), 4.26 (d, *J* = 9.8 Hz, 1H), 4.07 (d, *J* = 10.2 Hz, 1H), 3.81 (s, 3H), 3.23 (d, *J* = 16.1 Hz, 1H), 2.94-2.88 (dd, *J* = 16.8, 7.8 Hz, 1H), 1.09 (s, 9H). ^{13}C NMR δ 170.8, 159.3, 138.8, 136.0, 135.7, 133.6, 132.2, 130.0, 129.9, 129.7, 129.4, 128.6, 128.4, 127.9, 127.8, 127.5, 119.9, 113.8, 82.0, 78.6, 70.3, 67.3, 55.3, 33.8, 26.9, 19.5. IR (KBr) ν_{max}/cm^{-1} 3031, 2930, 2856, 1748, 1514, 1249, 1110, 1065, 822, 701. HRMS calcd for $C_{37}H_{40}O_5SiNa$ $(M+Na)^+$ 615.2543, found 615.2544.



7(*R*)-[(*R*)-hydroxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-4,5-didehydro-2-oxepanone, **27**

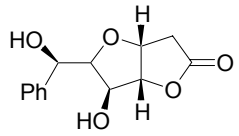
7(*R*)-[(*R*)-hydroxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-4,5-didehydro-2-oxepanone 27. To a solution of **26** (1.0 g, 1.69 mmol) in DCM (80 mL) at room temperature was added Ph_3CBF_4 (825 mg, 2.5 mmol) and the resultant was stirred for 5 min. The reaction was quenched by the addition of aqueous saturated $NaHCO_3$ (30 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic extract was dried and concentrated. Purification by filtration of the residue through a short silica gel column afforded **27**, 753.45 mg, 94.5%, white solid, mp 130±4 ^oC. $[\alpha]_D$ -20.7 (*c* 0.96, $CHCl_3$). ^1H NMR δ 7.76-7.74 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.66-7.64 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.40-7.18 (m, 11H), 5.52-5.47 (m, 1H), 5.42-5.37 (td, *J* = 8.5, 2.2 Hz, 1H), 5.01-4.98 (dd, *J* = 8.5, 2.4 Hz, 1H), 4.77-4.75 (dd, *J* = 4.6, 2.2 Hz, 1H), 4.25 (d, *J* = 8.5 Hz, 1H), 3.22-3.17 (dd, *J* = 16.6, 2.7 Hz, 1H), 2.92-2.85 (dd, *J* = 16.6, 8.3 Hz, 1H), 1.95 (d, *J* = 2.7 Hz, 1H), 1.03 (s, 3H). ^{13}C NMR δ 170.7, 141.1, 135.9, 135.7, 133.5, 133.2, 131.9, 130.1, 129.8, 128.5, 128.2, 127.9, 127.6, 126.8, 120.3, 82.1, 71.4, 67.2, 33.8, 26.9, 19.5. IR (KBr) ν_{max}/cm^{-1} 3453, 2930, 2856, 1736, 1428, 1267, 1112, 1041, 702. HRMS for $C_{29}H_{32}O_4SiNa$ $(M+Na)^+$ 495.1966, found 495.1968.



7(*R*)-[(*R*)-(hydroxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-5(*S*)-hydroxy-3,4-didehydro-2-oxepanone, **28**

7(*R*)-[(*R*)-(hydroxy)benzyl]-6(*R*)-*t*-butyldiphenylsilyloxy-5(*S*)-hydroxy-3,4-didehydro-2-oxepanone 28. To a solution of the alcohol **27** (750 mg, 1.6 mmol) in DCM (30 mL) was added *m*-CPBA (77%, 896.5 mg, 4 mmol) at 45 ^oC and the contents stirred at the same temperature for 24 h. The reaction vessel was cooled to room temperature followed by dilution with DCM (10 mL). Saturated aqueous Na_2SO_3 (10 mL) was added and the reaction mixture was stirred for 30

min. The contents were transferred to a separatory funnel, a little $NaHCO_3$ was added, and shaken well. The organic layer was separated and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic extract was dried and concentrated to obtain a residue that was purified by column chromatography to obtain **28**, 539 mg, 96.2% (based on 72.26% starting material reacted), low melting solid. $[\alpha]_D$ -41.6 (*c* 0.63, $CHCl_3$). ^{1}H NMR δ 7.75 (d, *J* = 6.1 Hz, 2H), 7.62 (d, *J* = 6.6 Hz, 2H), 7.43-7.19 (m, 11H), 6.13-6.09 (dd, *J* = 13.4, 3.7 Hz, 1H), 5.88 (d, *J* = 12.2 Hz, 1H), 4.85 (d, *J* = 7.3 Hz, 1H), 4.32 (d, *J* = 7.1 Hz, 1H), 4.25 (d, *J* = 3.9 Hz, 1H), 4.21 (bs, 1H), 1.02 (s, 9H). ^{13}C NMR δ 166.2, 140.8, 139.8, 136.1, 135.8, 133.3, 132.4, 130.3, 128.4, 128.1, 128.0, 127.9, 126.6, 121.8, 79.1, 73.3, 72.6, 72.2, 26.8, 19.4.



(+)-goniofufurone, **1**

(+)-Goniofufurone 1. A solution of the hydroxyl olefin **28** (200 mg, 0.41 mmol) in $CHCl_3$ (30 mL) containing DBU (68.66 mg, 0.45 mmol) was stirred at rt for 24 h. The solvent was removed and the residue purified by filtration through a short silica gel column to obtain the requisite bicyclic skeleton, 164 mg, 82%, viscous oil. $[\alpha]_D$ +3.2 (*c* 0.45, $CHCl_3$). ^{1}H NMR δ 7.76-7.71 (m, 4H), 7.50-7.32 (m, 11H), 5.01-4.98 (dd, *J* = 8.6, 3.4 Hz, 1H), 4.91 (t, *J* = 4.2 Hz, 1H), 4.76 (d, *J* = 2.4 Hz, 1H), 4.61 (d, *J* = 4.4 Hz, 1H), 4.06-4.03 (dd, *J* = 8.5, 2.7 Hz, 1H), 2.52-2.50 (m, 2H), 1.94 (d, *J* = 3.9 Hz, 1H), 1.15 (s, 9H).

To a solution of the above bicyclic material (100 mg, 0.20 mmol) in anhydrous THF (3.5 mL) at 0 ^{o}C was added AcOH (1.32 mg, 0.022 mmol) followed by TBAF (1M in THF, 0.22 mL, 0.22 mmol) and the contents stirred for 5 min. The reaction mixture was diluted with EtOAc (5 mL) and washed with brine (1 x 5 mL). The organic layer was separated and aqueous layer was extracted with EtOAc (3 x 3 mL). The combined organic extract was dried and concentrated, and the residue obtained was filtered through a short silica gel column to obtain (+)-Goniofufurone **1**, 50.5 mg, 98.6%, white solid, mp 148-150 ^{o}C; $[\alpha]_D$ +9.3 (*c* 0.27, EtOH) [lit.[5] mp 152-154 ^{o}C; $[\alpha]_D$ +9.0 (*c* 0.5, EtOH)]. ^{1}H NMR δ 7.44-7.33 (m, 5H), 5.19 (d, *J* = 4.6 Hz, 1H), 5.11 (t, *J* = 4.9 Hz, 1H), 4.86 (d, *J* = 4.2 Hz, 1H), 4.40 (bs, 1H), 4.26 (bs, 1H), 4.10-4.08 (dd, *J* = 4.6, 2.7 Hz, 1H), 3.00 (bs, 1H, OH), 2.78-2.72 (dd, *J* = 18.8, 5.8 Hz, 1H), 2.67 (d, *J* = 18.8 Hz, 1H). ^{13}C NMR δ

175.2, 138.9, 128.8, 128.5, 125.9, 87.5, 83.0, 77.4, 74.6, 73.6, 36.1. IR (KBr) ν_{max}/cm^{-1} 3412, 2924, 1783, 1454, 1191, 1047, 701. HRMS calcd for $C_{13}H_{13}O_5$ $(M-H)^+$ 249.0763, found 249.0764.

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