SUPPORTING INFORMATION

New Stereoselective β-Glycosylation by means of a Glycal-derived Vinyl Oxirane

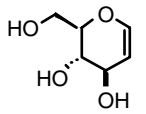
Valeria Di Bussolo, Micaela Caselli, Mauro Pineschi and Paolo Crotti*

Dipartimento di Chimica Bioorganica e Biofarmacia
Università di Pisa, Via Bonanno 33,
56126 Pisa, Italy

General Procedures. All reactions were performed in flame-dried modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper or rubber septa under a positive pressure of argon. Air/and moisture-sensitive liquids and solutions were transferred via syringe. Organic solutions were concentrated by rotary evaporator below 40°C at *ca.* 25 Torr. Flash column chromatography was performed employing 230-400 mesh silica gel. Analytical TLC were performed on Alugram SIL G/UV254 silica gel sheets (Macherey-Nagel) with detection by 0.5% phosphomolybdic acid solution in 95% EtOH.

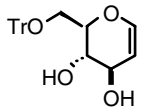
Materials. Isopropyl alcohol, methyl alcohol, *tert*-butyl alcohol and benzyl alcohol were distilled from calcium hydride at 760 Torr. Ethyl alcohol (absolute), anhydrous MeCN, phenol, sodium methantiolate, diacetone-D-glucose and *tert*-BuOK were purchased from Aldrich and used without purification. Benzene, benzene-d_6 and tetrahydrofuran were distilled from sodium/benzophenone.

Instrumentation. Infrared (IR) spectra were obtained using a Mattson 3000 FTIR spectrophotometer. Data are presented as frequency of absorption (cm^{-1}). Proton and carbon-13 nuclear magnetic resonance (^1H NMR and ^{13}C NMR) spectra were recorded on a Bruker AC 200 (50 MHz) spectrometer; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26, CHD_2OD: 3.31, C_6HD_5: δ 7.16. Data are presented as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, m=multiplet and/or multiple resonances), coupling constant (or $W_{1/2}$) in Hertz (Hz), integration. Optical rotation were acquired on a Perkin Elmer-341 Digital Polarimeter. Melting points were recorded with a Kofler melting point apparatus and are uncorrected.



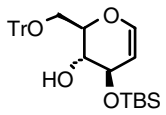
4

D-Glucal (4).[1] MeONa (0.050 g, 0.92 mmol) was added to a solution of tri-*O*-acetyl-D-glucal (**3**) (4.0 g, 14.7 mmol) in MeOH (40 mL) and the resulting reaction mixture was stirred at rt for 5 h under argon. Evaporation of the organic solvent afforded a product (2.0 g, 93% yield) consisting of **4**, practically pure as a syrup: R_f = 0.27 (9:1 CH_2Cl_2/MeOH) ^{1}H NMR (CD_3OD) δ 6.26 (dd, *J* = 6.0, 1.6 Hz, 1H), 4.60 (dd, *J* = 6.0, 2.2 Hz, 1H), 4.04 (dt, *J* = 7.0, 1.9 Hz, 1H), 3.85-3.58 (m, 3H), 3.48 (dd, *J* = 9.5, 7.0 Hz, 1H); ^{13}C NMR (CD_3OD) δ 146.49, 106.09, 81.86, 72.53, 72.13, 63.84; FTIR (neat film) 3398, 2926, 1645, 1413, 1230, 1074, 1015, 824, 735 cm^{-1}.



5

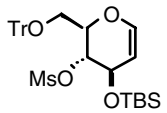
6-*O*-(Trityl)-D-glucal (5). A solution of D-glucal (**4**) (2.0 g, 13.7 mmol) in anhydrous pyridine (8 mL) was treated at 0°C with Ph_3CCl (4.20 g, 15.1 mmol). The reaction mixture was stirred 18 h at rt, diluted with Et_2O (30 mL) and washed sequentially with water (2 x 10 mL) and saturated aqueous sodium chloride (2 x 10 mL). The organic layer was dried ($MgSO_4$) and concentrated to afford a crude product which was purified by flash chromatography (1:1 hexane/EtOAc) to afford diol **5** (4.50 g, 85% yield), pure as a white solid: mp 51-53 °C; R_f = 0.33 (1:1 hexane/EtOAc) ^{1}H NMR δ 7.50-7.22 (m, 15H), 6.39 (dd,, *J* = 6.0, 1.6 Hz, 1H), 4.75 (dd, *J* = 6.0, 2.1 Hz, 1H), 4.27-4.19 (m, 1H), 3.95-3.77 (m, 2H), 3.56 (dd, *J* = 10.6, 3.2 Hz, 1H), 3.33 (dd, *J* = 10.5, 3.4 Hz, 1H), 2.44-2.17 (m, 2H); ^{13}C NMR δ 145.07, 144.12, 129.13, 128.55, 127.77, 103.11, 87.52, 78.25, 72.01, 70.08, 63.46; FTIR (neat film) 3356, 2924, 1645, 1448, 1228, 1074, 1015, 824, 735 cm^{-1}; Anal.Calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.24; H, 6.18.



6

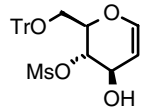
[1] Brimacombe, J. S.; Da'Aboul, I.; Tucker, L .C. N. *Carbohyd.Res.* **1971**, *19*, 276.

3-*O*-(*t*-Butyldimethylsilyl)-6-*O*-(trityl)-D-glucal (6). A solution of diol **5** (4.15 g, 10.7 mmol) in anhydrous THF (15 mL) containing imidazole (1.45 g, 21.3 mmol) was treated at 0°C with TBDMS-Cl (1.60 g, 10.7 mmol). The reaction mixture was stirred 18 h at rt, diluted with Et_2O (80 mL) and washed sequentially with water (2 x 20 mL) and saturated aqueous sodium chloride (2 x 20 mL). The organic layer was dried ($MgSO_4$) and concentrated to afford a crude product which was purified by flash chromatography (1:1 hexane/EtOAc) to afford alcohol **6** (5.20 g, 97% yield), pure as a syrup: R_f = 0.34 (9:1 hexane/EtOAc); ^{1}H NMR δ 7.51-7.17 (m, 15H), 6.34 (dd, *J* = 6.1, 1.3 Hz, 1H), 4.62 (dd, *J* = 6.1, 2.4 Hz, 1H), 4.20-4.13 (m, 1H), 3.96-3.76 (m, 2H), 3.54-3.36 (m, 2H), 0.86 (s, 9H), 0.06 (s, 6H); ^{13}C NMR δ 144.02, 143.79, 128.86, 128.05, 127.21, 103.62, 86.40, 77.66, 70.75, 69.92, 62.84, 26.02, 18.31, -4.37; FTIR (neat film) 3452, 3063, 2926, 1645, 1450, 1225, 1070, 698 cm^{-1}; Anal. Calcd $C_{31}H_{38}O_4Si$: C, 74.06; H, 7.62. Found: C, 74.00; H, 7.57.



7

3-*O*-(*t*-Butyldimethylsilyl)-4-*O*-mesyl-6-*O*-(trityl)-D-glucal (7). A solution of alcohol **6** (5.20 g, 10.3 mmol) in anhydrous pyridine (25 mL) was treated at 0°C with MsCl (1.64 ml, 21.2 mmol). The reaction mixture was stirred 18 h at rt, then diluted with Et_2O (80 mL) and washed with water (2 x 30 mL). The organic layer was dried ($MgSO_4$) and concentrated and the residue was purified by flash chromatography (8:2 hexane/EtOAc) to afford mesylate **7** (4.30 g, 72% yield), pure as a solid: mp 53-55°C; R_f = 0.49 (7:3 hexane/EtOAc): ^{1}H NMR δ 7.53-7.17 (m, 15H), 6.41 (d, *J* = 6.2 Hz, 1H), 4.80-4.70 (m, 1H), 4.69-4.61 (m, 1H), 4.40-4.29 (m, 1H), 4.19-4.10 (m, 1H), 3.69 (dd, *J* = 10.8, 8.0 Hz, 1H), 3.23 (dd, *J* = 11.0, 2.3 Hz, 1H), 2.93 (s, 3H), 0.98 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR δ 143.91, 143.57, 128.95, 128.03, 127.25, 101.35, 87.09, 77.21, 75.85, 64.04, 62.13, 39.00, 25.89, 18.06, -4.09, -4.30; FTIR (neat film) 3418, 2930, 2856, 1647, 1445, 1361, 1225, 1072, 700 cm^{-1}; Anal. Calcd $C_{32}H_{40}O_6SSi$: C, 66.18; H, 6.94. Found: C, 66.02; H, 6.73.

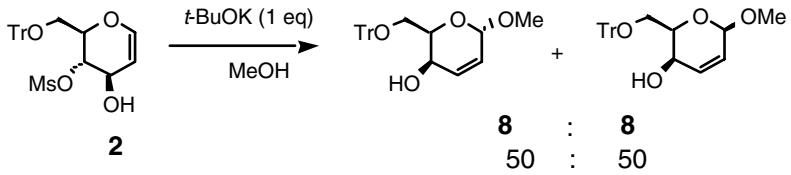


2

4-*O*-Mesyl-6-*O*-(trityl)-D-glucal (2). A solution of mesylate **7** (0.50 g, 0.86 mmol) in anhydrous THF (30 mL) was treated dropwise at 0°C with 1M TBAF in THF (0.86 mL, 0.86 mmol) and the reaction mixture was stirred for 20 min at the same temperature. The reaction

was diluted with water (20 mL) and the aqueous layer was extracted with Et_2O (2 x 60 mL). The combined organic layers were dried ($MgSO_4$) and concentrated.The residue was purified by flash chromatography (6:4 hexane/EtOAc) to afford hydroxy mesylate **2** (0.26 g, 65% yield), pure as a solid: mp 100-102°C; R_f = 0.22 (6:4 hexane/EtOAc): ^{1}H NMR δ 7.55-7.20 (m, 15H), 6.57 (dd, *J* = 6.0, 1.4 Hz, 1H), 4.99-4.87 (m, 2H), 4.53-4.33 (m, 1H), 4.19-4.07 (m, 1H), 3.64 (dd, *J* = 10.6, 2.6 Hz, 1H), 3.29 (dd, *J* = 10.7, 3.9 Hz, 1H), 3.07 (d, *J* = 5.5 Hz, 1H), 2.87 (s, 3H); ^{13}C NMR δ 144.94, 143.46, 128.91, 128.04, 127.35, 101.88, 87.27, 79.18, 75.11, 67.31, 62.06, 38.38; FTIR (neat film) 3420, 2926, 2854, 1714, 1647, 1452, 1359, 1103, 1071, 698 cm^{-1}; Anal. Calcd for $C_{26}H_{26}O_6S$: C, 66.94; H, 5.62. Found: C, 66.82; H, 5.57.

Reaction of Hydroxy Mesylate 2 in the Presence of *t*-BuOK with Methanol as the Solvent/Nucleophile.



A solution of hydroxy mesylate **2** (0.056 g, 0.12 mmol) in MeOH (4 mL) was treated with *t*-BuOK (0.014 g, 0.12 mmol, 1 equiv) and the reaction mixture was stirred at rt for 30 min. The solution was partitioned between CH_2Cl_2 (15 mL) and water (10 mL), and the aqueous layer was further extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated to afford a crude consisting of an 1:1 mixture of practically pure methyl glycosides **8α** and **8β** (^{1}H NMR) (0.043 g, 90% yield). Separation of the diasteroisomers was accomplished by flash chromatography (6:4 hexane/EtOAc) to afford pure:

Methyl-6-*O*-(trityl)-2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (8β)

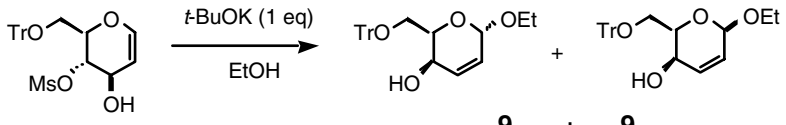
a liquid, R_f = 0.38 (6:4 hexane/EtOAc): ^{1}H NMR δ 7.53-7.13 (m, 15H), 6.13 (ddd, *J* = 11.3, 5.2, 1.3 Hz, 1H), 5.82 (d, *J* = 11.0 Hz, 1H), 5.01 (bs, $W_{1/2}$ = 4.3 Hz, 1H, H-1), 4.01-3.87 (m, 1H), 3.80 (dt, *J* = 6.2, 2.0 Hz, 1H), 3.56-3.40 (m, 1H), 3.53 (s, 3H), 3.28 (dd, *J* = 9.6, 5.9 Hz, 1H); ^{13}C NMR δ 144.10, 131.11, 130.98, 128.91, 128.04, 127.26, 99.05, 86.95, 74.97, 63.45, 63.01, 55.94; FTIR (neat film) 3418, 2928, 1629, 1615, 1448, 1051, 696 cm^{-1}; Anal. Calcd for $C_{26}H_{26}O_4$: C, 77.59 H, 6.51. Found: C, 77.45; H, 6.42.

Methyl-6-*O*-(trityl)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (8α)

a solid: mp 138-140°C; R_f = 0.29 (6:4 hexane/EtOAc); ^{1}H NMR δ 7.55-7.16 (m, 15H), 6.12 (dd, *J* = 10.0, 5.4 Hz, 1H), 5.90 (dd, *J* =10.0, 3.0 Hz, 1H), 4.92 (d, *J* = 2.9 Hz, 1H, H-1), 4.20-4.09 (m, 1H), 3.86-3.79 (m, 1H), 3.53-3.44 (m, 1H), 3.49 (s, 3H), 3.29 (dd, *J* = 10.3, 5.9 Hz, 1H); ^{13}C NMR δ 144.12, 129.77, 128.88, 128.65, 128.07, 127.26, 95.45, 87.06, 70.02, 63.70,

62.34, 55.67; FTIR (neat film) 3448, 2926, 1714, 1454, 1280, 1101, 698 cm^{-1}; Anal. Calcd for $C_{26}H_{26}O_4$: C, 77.59 H, 6.51. Found: C, 77.48; H, 6.35

Reaction of Hydroxy Mesylate 2 in the Presence of *t*-BuOK with Ethanol as the Solvent/Nucleophile.



2 **9** : **9**
25 : 75

The same procedure described above for **8α** and **8β** was followed to prepare **9α** and **9β** using EtOH as the solvent/nucleophile. The practically pure crude obtained (0.041 g, 83% yield) consisting in a 25:75 mixture of ethyl glycosides **9α** and **9β** (^{1}H NMR) was subjected to flash chromatography (7:3 hexane/EtOAc) to afford pure:

Ethyl-6-*O*-(trityl)-2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (9β)
a liquid R_f = 0.43 (7:3 hexane/EtOAc): ^{1}H NMR δ 7.50-7.10 (m, 15H), 6.12 (dd, *J* = 10.3, 4.8 Hz, 1H), 5.83 (d, *J* = 10.3 Hz, 1H), 5.09 (bs, $W_{1/2}$ = 4.4 Hz, 1H, H-1), 4.04-3.85 (m, 2H), 3.85-3.73 (m, 1H), 3.73-3.55 (m, 1H), 3.46 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.28 (dd, *J* = 9.6, 5.8 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR δ 144.16, 131.39, 130.91, 128.94, 128.02, 127.22, 98.10, 86.94, 75.04, 64.36, 63.55, 63.07, 15.48; FTIR (neat film) 3422, 2925, 1623, 1618, 1450, 1063, 698 cm^{-1}; Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86 H, 6.78. Found: C, 77.69; H, 6.67.

Ehyl-6-*O*-(trityl)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (9α)[2]
a solid: mp 145°C (lit[2]:147 °C); R_f = 0.34 (7:3 hexane/EtOAc); $[\alpha]_D^{20}$=-58.4 (*c* = 0.98, $CHCl_3$) [(lit[2]: $[\alpha]_D^{20}$ = -62, c = 1, $CHCl_3$)]: ^{1}H NMR δ 7.52-7.12 (m, 15H), 6.12 (dd, *J* = 10.1, 5.3 Hz, 1H), 5.91 (dd, *J* = 10.1, 2.8 Hz, 1H), 5.03 (d, *J* = 2.9 Hz, 1H, H-1), 4.21 (ddd, *J* = 6.9, 5.2, 1.9 Hz, 1H), 3.96 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.87-3.77 (m, 1H), 3.65-3.41 (m, 2H), 3.28 (dd, *J* = 9.8, 5.3 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR δ 144.18, 129.71, 128.90, 128.04, 127.26, 94.17, 87.03, 77.85, 77.21, 76.58, 70.11, 63.76, 63.69, 62.46, 15.45; FTIR (neat film) 3420, 2925, 1618, 1602, 1445, 1053, 698 cm^{-1}; Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86 H, 6.78. Found: C, 77.51; H, 6.94.

Reaction of Hydroxy Mesylate 2 in the Presence of *t*-BuOK with Isopropanol as the Solvent/Nucleophile.

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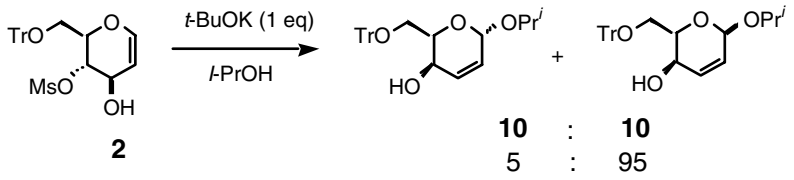
[2]Moufid, N.; Chapleur, Y.; Mayon, P. *J. Chem. Soc. Perkin Trans. 1* **1992**, 991.

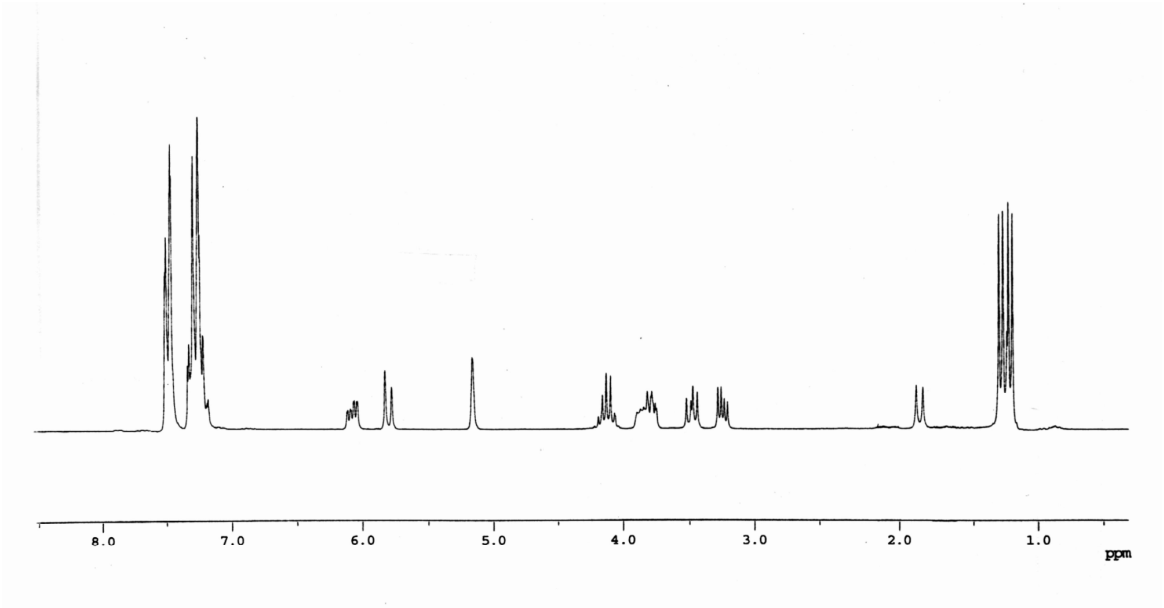


The same procedure described above for **8α** and **8β** was followed to prepare **10α** and **10β** using *i*-PrOH as the solvent/nucleophile. The practically pure crude obtained (0.048 g, 93% yield) consisting in a 5:95 mixture of isopropyl glycosides **10α** and **10β** (^{1}H NMR) was subjected to flash chromatography (8:2 hexane/EtOAc) to afford pure:

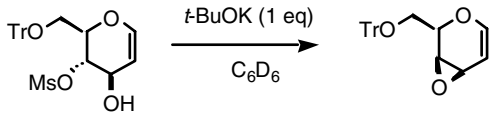
Isopropyl-6-*O*-(trityl)-2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (10β)

R_f = 0.48 (7:3 hexane/EtOAc): ^{1}H NMR δ 7.56-7.14 (m, 15H), 6.09 (ddd, *J* = 10.0, 5.0, 1.3 Hz, 1H), 5.81 (d, *J* = 10.0 Hz, 1H), 5.16 (d, *J* = 0.8 Hz, 1H, H-1), 4.13 (hept, *J* = 6.2 Hz, 1H), 3.92-3.74 (m, 2H), 3.49 (dd, *J* = 9.7, 6.7 Hz, 2H), 3.25 (dd, *J* = 9.8, 5.1 Hz, 1H), 1.30 (d, *J* = 6.2 Hz, 3H) 1.23 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR δ 144.22, 131.97, 130.76, 128.97, 128.02, 127.21, 96.80 86.89, 75.20, 71.18, 63.79, 63.21, 23.91, 22.67; FTIR (neat film) 3429, 2918, 1589, 1602, 1420, 1165, 1061, 696 cm^{-1}; Anal. Calcd for $C_{28}H_{30}O_4$: C, 78.11 H, 7.02. Found: C, 78.02; H, 6.93.

^{1}H NMR spectrum of compound **10β**.



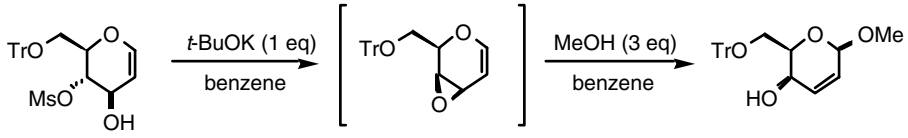
^{1}H NMR confirmation of the formation of epoxide 1



2 **1**

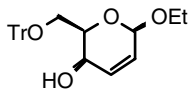
A solution of hydroxy mesylate **2** (0.020 g, 0.042 mmol) in C_6D_6 (0.7 mL) was treated, in the NMR tube, with *t*-BuOK (0.005 g, 0.045 mmol). After 5 min at rt, the ^{1}H NMR analysis showed pure epoxide **1**: δ 7.70-6.98 (m, 15H), 6.11 (d, *J* = 5.7 Hz, 1H), 4.78 (dd, *J* = 5.7, 4.3 Hz, 1H), 4.00 (t, *J* = 6.2 Hz, 1H), 3.68-3.49 (m, 2H), 3.20 (d, *J* = 4.4 Hz, 1H), 2.81 (t, *J* = 3.7 Hz, 1H).

Typical Procedure for Glycosylation of the *in situ* formed Epoxide 1 in Benzene with Alcohol as the Nucleophile.



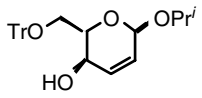
2 **1** **8**

A solution of hydroxy mesylate **2** (0.112 g, 0.24 mmol) in anydrous benzene (4 mL) was treated with *t*-BuOK (0.027 g, 0.24 mmol, 1 equiv) and the reaction mixture was stirred at rt for 10 min. Methyl alcohol (30 μL, 0.74 mmol, 3 equiv) was added and the solution was stirred at rt for 30 min. The solution was partitioned between CH_2Cl_2 (15 mL) and water (10 mL), and the aqueous layer was further extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated to afford a crude mostly consisting of **8β** (the α anomer, detected by ^{1}H NMR, was less than 3%) which was purified by flash chromatography (6:4 hexane/EtOAc) to afford pure **8β** (0.089 g, 92% yield).



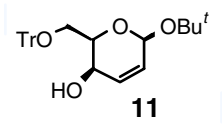
9

The same reaction carried out with EtOH (3 equiv), afforded a crude product (only β anomer was detected by ^{1}H NMR) which was purified by flash chromatography (7:3 hexane/EtOAc) to afford pure **9β** (0.085 g, 85% yield).



10

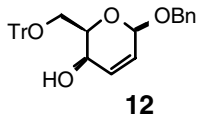
The same reaction carried out with *i*-PrOH (3 equiv), afforded a crude product (only β anomer was detected by ^{1}H NMR) which was purified by flash chromatography (8:2 hexane/EtOAc) to afford pure **10β** (0.094 g, 91% yield).



11

***t*-Butyl-6-*O*-(trityl)-2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (11β)**

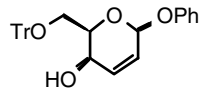
The same reaction carried out with *t*-BuOH (3 equiv), afforded a crude product (only β anomer was detected by ^{1}H NMR) which was purified by flash chromatography (8:2 hexane/EtOAc) to afford pure **11β** (0.083 g, 78% yield); R_f = 0.48 (7:3 hexane/EtOAc); ^{1}H NMR δ 7.61-7.02 (m, 15H), 6.04 (ddd, *J* = 9.8, 4.9, 1.3 Hz, 1H), 5.75 (d, *J* = 9.9 Hz, 1H), 5.27 (bs, $W_{1/2}$ = 4.3 Hz, 1H, H-1), 3.84-3.70 (m, 2H), 3.51 (dd, *J* = 9.7, 7.4 Hz, 2H), 3.18 (dd, *J* = 9.9, 4.3 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR δ 144.29, 133.29, 130.54, 128.96, 128.00, 127.16, 93.35, 86.82, 75.59, 68.86, 63.98, 63.10, 29.00; FTIR (neat film) 3452, 2918, 1615, 1434, 1265, 1108, 685 cm^{-1}; Anal. Calcd for $C_{29}H_{32}O_4$: C, 78.35 H, 7.25. Found: C, 78.28; H, 7.19.



12

Benzyl-6-*O*-(trityl)-2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (12β)

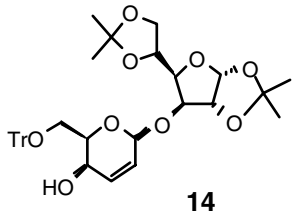
The same reaction carried out with BnOH (3 equiv), afforded a crude product (only β anomer was detected by ^{1}H NMR) which was purified by flash chromatography (8:2 hexane/EtOAc) to afford pure **12β** (0.104 g, 91% yield); R_f = 0.25 (8:2 hexane/EtOAc); ^{1}H NMR δ 7.55-7.18 (m, 20H), 6.11 (ddd, *J* = 10.1, 5.0, 1.3 Hz, 1H), 5.86 (d, *J* = 10.1 Hz, 1H), 5.15 (d, *J* = 0.9 Hz, 1H, H-1), 4.93 (d, *J* = 11.8 Hz, 1H), 4.72 (d, *J* = 11.8 Hz, 1H), 3.98-3.86 (m, 1H), 3.85-3.75 (m, 1H), 3.53 (dd, *J* = 9.8, 6.6 Hz, 2H), 3.30 (dd, *J* = 9.8, 5.4 Hz, 1H); ^{13}C NMR δ 144.15, 137.52, 131.13, 131.07, 128.93, 128.64, 128.44, 128.20, 128.07, 127.29, 96.85, 86.91, 75.19, 70.00, 63.98, 63.80, 63.33; FTIR (neat film) 3435, 3059, 2931, 2877, 1639, 1597, 1491, 1448,1248, 1051, 698 cm^{-1}; Anal. Calcd for $C_{32}H_{30}O_4$: C, 80.31 H, 6.32. Found: C, 80.26; H, 6.28.



13

Phenyl-6-*O*-(trityl)-2,3-dideoxy-β-D-*threo*-hex-2-enopyranoside (13β)

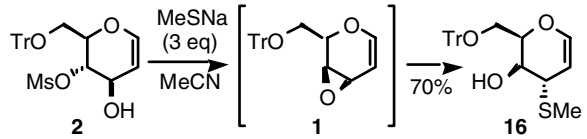
The same reaction carried out with PhOH (3 equiv), afforded a crude product (only β anomer was detected by ^{1}H NMR) which was purified by flash chromatography (8:2 hexane/EtOAc) to afford pure **13β** (0.099 g, 89% yield); R_f = 0.32 (8:2 hexane/EtOAc); ^{1}H NMR δ 7.56-7.13 (m, 20H), 6.20 (dd, *J* = 10.0, 4.8 Hz, 1H), 6.20 (d, *J* = 10.1 Hz, 1H), 5.75 (bs, $W_{1/2}$ = 4.3 Hz, 1H, H-1), 3.99-3.82 (m, 2H), 3.58 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.29 (dd, *J* = 10.0, 4.2 Hz, 1H); ^{13}C NMR δ 157.18, 144.07, 131.56, 130.24, 129.63, 128.91, 128.04, 127.23, 122.61, 116.81, 96.25, 87.06, 75.60, 63.98, 63.76 62.95; FTIR (neat film) 3442, 3063, 2994, 2885, 1620, 1594, 1495, 1320, 1245, 1158, 1085, 696 cm^{-1}; Anal. Calcd for $C_{31}H_{28}O_4$: C, 80.15 H, 6.07. Found: C, 80.03; H, 5.96.



14

3-*O*-(4-*O*-hydroxy-6-*O*-trityl-2,3-dideoxy-β-D-*threo*-hex-2-enopyranosyl)-1,2,5,6-di-*O*-isopropylidene-α-D-glucofuranose (14β)

The same reaction carried out with diacetone D-glucose (3 equiv), afforded a crude product (only β anomer was detected by ^{1}H NMR) which was purified by flash chromatography (6:4 hexane/EtOAc) to afford pure **14β** (0.115 g, 76% yield); R_f = 0.33 (6:4 hexane/EtOAc); ^{1}H NMR δ 7.55-7.15 (m, 15H), 6.23 (dd, *J* = 10.0, 5.4 Hz, 1H), 5.90 (d, *J* = 3.6 Hz, 1H), 5.83 (d, *J* = 10.1 Hz, 1H), 5.34 (bs, $W_{1/2}$ = 4.4 Hz, 1H, H-1), 4.68 (d, *J* = 3.6 Hz, 1H), 4.48 (dd, *J* = 16.2, 3.2 Hz, 1H), 4.37-3.85 (m, 5H), 3.83-3.73 (m, 1H), 3.47-3.25 (m, 2H), 1.47 (s, 3H) 1.34 (s, 3H), 1.28 (s, 3H), 1.24 (s, 3H); ^{13}C NMR δ 144.01, 132.46, 130.12, 128.88, 127.23, 111.93, 108.90, 105.32, 96.25, 86.89, 84.00, 80.70, 77.63, 75.55, 73.16, 67.13, 63.75, 62.94, 27.15, 27.00, 26.62, 25.61; FTIR (neat film) 3462, 2985, 2935, 1716, 1565, 1450, 1381, 1217, 1163, 1072, 910, 846, 732, 707 cm^{-1}; Anal. Calcd for $C_{37}H_{42}O_9$: C, 70.46 H, 6.71. Found: C, 70.38; H, 6.59.



2 **1** **16**

6-*O*-(trityl)-3-deoxy-3-methylthio-D-gulale (16). A solution of hydroxy mesylate **2** (0.10 g, 0.21 mmol) in anydrous MeCN (6 mL) was treated with CH_3SNa (0.044 g, 0.63 mmol, 3 equiv) and the reaction mixture was stirred at rt for 30 min. The solution was partitioned between CH_2Cl_2 (15 mL) and water (10 mL), and the aqueous layer was further extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated to afford a crude mostly consisting of **16** which was purified by flash chromatography (7:3 hexane/EtOAc) to afford the glycal **16** (0.065 g, 70% yield), pure as a liquid; R_f = 0.45 (7:3 hexane/EtOAc): ^{1}H NMR δ 7.55-7.16 (m, 15H), 6.55 (d, *J* = 6.0, 1H), 4.87-4.79 (m, 1H), 4.19-4.11 (m, 1H), 3.97-3.90 (m, 1H), 3.62 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.27 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.21 (d, *J* = 5.2, 1H), 3.13-3.06 (m, 1H), 2.11 (s, 3H) ^{13}C NMR δ 145.62, 143.71, 128.93, 128.27, 127.49, 98.81, 87.69, 72.04, 69.18, 65.02, 44.32, 14.95; Anal. Calcd for $C_{26}H_{26}O_3S$: C, 74.61 H, 6.26. Found: C, 74.49; H, 6.15.