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Note

Stereospecific synthesis of β-D-allopyranosides by dihydroxylation of β-D-*erythro*-2,3-dideoxyhex-2-enopyranosides

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Abstract

The synthesis of 4,6-*O*-benzylidene-β-D-*erythro*-2-3-dideoxyhex-2-enopyranosides and their osmium and ruthenium catalysed dihydroxylation reactions have been investigated. These reactions have been shown, for a range of monosaccharides and a disaccharide, to proceed stereospecifically to give β-D-allopyranosides in moderate to excellent yield. © 2001 Published by Elsevier Science Ltd.

Keywords: Stereospecific synthesis; β-D-Allopyranoside; Dihydroxylation; β-D-*erythro*-2,3-Dideoxyhex-2-enopyranosides; Inversion of configuration

The stereospecific synthesis of glycosides is of interest due to the biological and medical importance of oligosaccharides, glycoproteins and glycolipids and also because of interest in carbohydrates as peptidomimetics[1] and as scaffolds for the synthesis of pharmacophore mapping libraries.[2] Methodology that can be used for inversion of configuration at a particular stereogenic centre of a pyranose or furanose is also of interest. These methods facilitate the synthesis of carbohydrates for evaluation as substrates of enzymes, as well as for other structure activity studies that could lead to the discovery of more selective enzyme inhibitors.[3]

Studies on the biological activity of β-D-mannopyranoside derivatives have been of interest to us as part of a project on the design and synthesis of novel carbohydrate based enzyme inhibitors. Difficulties in the stereoselective synthesis of β-D-mannopyranosides are well documented and progress in this area has recently been reviewed.[4] There have been reports in the literature describing the dihydroxylation reactions of some 2,3-dideoxyhex-2-enopyranosides[12–16] that give α-D-mannopyranosides but none that we could find on the corresponding reactions of the β-D-*erythro*-2,3-dideoxyhex-2-enopyranosides which could yield the β-D-mannose or β-D-allose derivatives as products. Herein we describe the results of dihydroxylation reactions of these compounds that stereospecifically gave β-D-allopyranosides.

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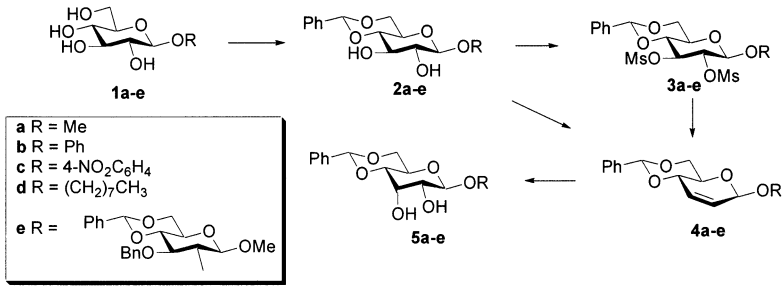
Methods that have been used previously for syntheses of the β-D-allopyranosides include reduction of ketosucroses,[5] epoxidation-ring closure of open-chain hydroxyenol ethers,[6] S_N2 displacement of leaving groups at C-3 of β-D-glucopyranose derivatives[7–10] and by chemical manipulation of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose.[11] The β-D-*erythro*-2,3-dideoxyhex-2-enopyranosides **4** used herein were synthesised as shown in Scheme 1. The benzylidene protected derivatives **2** were conveniently obtained from reaction of β-D-glucose derivatives **1** in the presence of camphorsulfonic acid and benzaldehyde dimethyl acetal in acetonitrile. The syntheses of the alkenes **4** from diols **2** were explored by a number of different methods (Table 1). It was found that, in general, the use of triphenylphosphine, iodine and imidazole in toluene was the most satisfactory method for this transformation.[17] The synthesis of **4a** was carried out via the dimesylate **3a**.

The osmium catalysed dihydroxylation of alkenes **4** proceeded in moderate to excellent yield and for all reactions examined were stereospecific (Scheme 1, Table 1) i.e., the β-D-mannopyranosides, possible products in these reactions, were not detected by ^{1}H NMR analysis of the crude reaction mixture in any case. The ^{1}H NMR spectra of **5a**–**e** showed signals for their anomeric protons from δ 4.50–5.50 as doublets with coupling constants of 7.5–8.0 Hz. Hydroxylation reactions of the *n*-octyl derivative **4d** and the disaccharide **4e** were sluggish using osmium, possibly due to decreased solubility of these alkenes under these conditions. This led to lower isolated yields in the case of the disaccharide. However, this problem could be overcome by carrying out the dihydroxylation reaction with $RuCl_3$–$NaIO_4$ as reported previously by Shing;[18] the reaction proceeded in good yield with no loss in stereoselectivity for the two cases examined (Table 1).

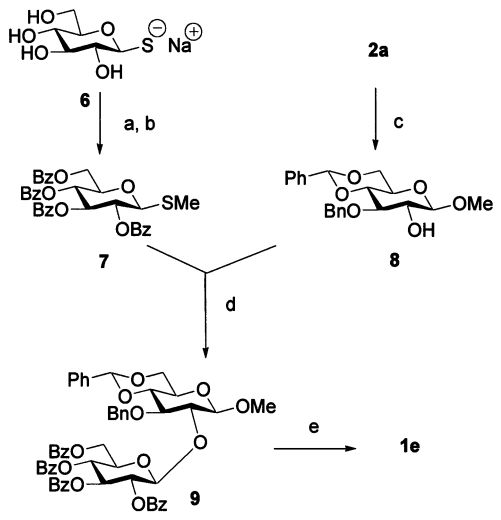


Scheme 1.

Table 1

Compound no.	% yield of **2** from **1** [a]	% yield of **4** from **2**	% yield of **5** from **4**
a	80	47 [b]	92 [e] 89 [f]
b	88	62 [c] 53 [d]	95 [e]
c	100	67 [c]	95 [e]
d	81	46 [c]	79 [e]
e	71	85 [c]	32 [e] 70 [f]

Reagents and conditions:
[a] $PhCH(OMe)_2$, camphorsulfonic acid, MeCN, rt.
[b] $ClPPh_2$, I_2, Im., toluene, then Zn, EtOH.
[c] PPh_3, I_2, Im., toluene.
[d] MsCl, Py then NaI, Zn dust, DMF, microwave oven, 3 min.
[e] $K_2OsO_2(H_2O)_2$, NMO, DABCO, *t*-BuOH, H_2O, 60 °C.
[f] $RuCl_3$, $NaIO_4$, CH_2Cl_2, rt.



Scheme 2. Reagents and conditions: (a) MeI_2, DMF; (b) BzCl, Py, 0 °C; (c) Bu_2SnO, benzene then Bu_4NI, BnBr; (d) NIS, AgOTf, CH_2Cl_2; (e) NaOMe, MeOH.

The disaccharide **1e**, used for the synthesis of allose containing disaccharide **5e**, was synthesised by AgOTf–NIS promoted coupling of the thioglycoside donor **7** with acceptor **8**[19] and subsequent removal of the benzoyl groups using NaOMe–MeOH (Scheme 2). The thioglycoside donor was first prepared by methylation and subsequent benzoylation of commercially available sodium 1-thio-β-D-glucopyranose. The acceptor **8** was prepared by regioselective benzylation of the 3-OH group of **2a**.

In summary, osmium or ruthenium catalysed dihydroxylation of 4,6-di-*O*-benzylidene-β-D-*erythro*-2,3-dideoxyhex-2-enopyranosides can be used for the stereospecific synthesis of β-D-allopyranosides and the sequence described is convenient for preparing these carbohydrates.

1. Experimental

Optical rotations were determined with a Perkin–Elmer 241 model polarimeter at the sodium D line at 23 °C. NMR spectra were recorded with JEOL JNM-GX270 and Varian Inova 300 spectrometers. Chemical shifts are reported relative to internal Me_4Si in $CDCl_3$ (δ 0.0), Me_2SO-d_6 (δ 2.50) or acetone-d_6 (δ 2.20) for ^1H and either $CDCl_3$ (δ 77.0), Me_2SO-d_6 (δ 43.5) or acetone-d_6 (δ 205.1) for ^{13}C. Coupling constants are reported in hertz. IR spectra were recorded with a Mattson Galaxy Series FTIR 3000 using either thin film between NaCl plates or KBr discs, as specified. Melting points were measured on a Gallenkamp melting point apparatus. Elemental analysis was performed on an Exeter Analytical CE440 elemental analyser. Low and high resolution mass spectra were measured on either a micromass VG 70/70H or VG ZAB-E or autospec spectrometers and were measured in ES positive mode unless otherwise indicated. TLC was performed on aluminium sheets precoated with Silica Gel 60 (HF_{254}, E. Merck) and spots visualised by UV and charring with 1:20 H_2SO_4–EtOH. Flash-column chromatography was carried out with Silica Gel 60 (0.040–0.630 mm, E. Merck) and using a stepwise solvent polarity gradient correlated with TLC mobility. Chromatography solvents used were EtOAc (Riedel–deHaen) and petroleum ether (bp 40–60 °C, BDH laboratory supplies). Acetonitrile, toluene, benzene and CH_2Cl_2 reaction solvents were freshly distilled from CaH_2 and anhyd DMF was used as purchased from Sigma–Aldrich. The β-D-glucopyranosides **1a**–**d** were purchased from Sigma–Aldrich.

Phenyl 4,6-O-benzylidene-β-D-glucopyranoside (**2a**).—A solution of **1a** (10 g, 39 mmol), camphorsulphonic acid (50 mg) and benzaldehyde dimethylacetal (11.8 mL, 78.8 mmol) in MeCN (300 mL) was stirred for 12 h at rt. Triethylamine (5 mL) was added and the solution was allowed to stir for a further 1 h. The product was then filtered off as a white solid, washed with petroleum ether and dried under diminished pressure (11.8 g, 88%); mp 163–165 °C, $[\alpha]_D$ −51.5° (*c* 2.0, acetone) (lit.:[20] mp 179–181 °C (EtOH); $[\alpha]_D$ −66.5° (*c* 2.0, acetone)); ^1H NMR (270 MHz, $CDCl_3$): δ 7.52–7.04 (ms, 10 H, aromatic H), 5.54 (s, 1 H, C*H*Ph), 5.04 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.39 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 10.5 Hz, H-6), 3.90 (apt t, 1 H, $J_{2,3}$ 9.0, $J_{3,4}$ 9.0 Hz, H-3), 3.84–3.77 (overlapping signals, 2 H, H-2, H-6), 3.63 (apt t, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 3.57 (m, 1 H, H-5), 2.81 (br s, 1 H, OH), 2.70 (br s, 1 H, OH); ^{13}C NMR (270 MHz, $CDCl_3$): δ 156.7, 137.2 (each s, each aromatic C) 129.7, 129.4, 128.4, 126.3, 123.3, 116.8 (each d, each aro-

matic CH), 102.0, 101.1, 80.3, 74.3, 73.2 (each d), 68.6 (t, C-6), 66.6 (d); IR (KBr): 3584, 3371, 2925, 2885, 1634, 1592, 1497, 1386, 1228, 1082, 1031, 751, 698 cm^{-1}. ESHRMS: Found 345.1338, required 345.1338 $[M + H]^+$.

Methyl 4,6-O-benzylidene-β-D-glucopyranoside (**2b**).—Treatment of **1b** (10.0 g, 49 mmol) as described for **1a** gave **2b** (11.0 g, 80%); mp 169–172 °C; $[\alpha]_D$ −61.5° (*c* 0.2, $CHCl_3$) (lit.:[21] mp 198–200 °C; $[\alpha]_D$ −65.2° (*c* 1.0, $CHCl_3$)); ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.26 (ms, 5 H, aromatic H), 5.55 (s, 1 H, C*H*Ph), 4.36 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$10.5 Hz, H-6a), 4.33 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.82 (apt t, 1 H, $J_{2,3}$ 9.0, $J_{3,4}$ 9.0 Hz, H-3), 3.80 (apt t, 1 H, $J_{5,6b}$ 10.5 Hz, H-6b), 3.59 (s, 3 H, OCH_3), 3.48 (overlapping signals, 3 H, H-2,4,5); ^{13}C NMR (300 MHz, 1:10 Me_2SO-d_6-$CDCl_3$): δ 137.5 (s, aromatic C), 129.2, 128.2, 126.6 (each d, each aromatic CH), 104.6, 101.9, 80.6, 74.9, 73.6 (each d), 68.9 (t, C-6), 66.5 (d), 57.4 (q, OCH_3); IR (KBr): 3385, 3241, 2981, 2942, 2882, 1452, 1388, 1227, 1087, 1038, 997, 694 cm^{-1}.

4-Nitrophenyl 4,6-O-benzylidene-β-D-glucopyranoside (**2c**).—Treatment of **1c** (2.0 g, 6.6 mmol) as described for **1a** gave **2c** (2.1 g, 81%); mp 180–182 °C; $[\alpha]_D$ −116.7° (*c* 0.04, $CHCl_3$) (lit.:[22] mp 184–85 °C; $[\alpha]_D$ −44.9° (*c* 2.0, acetone); ^1H NMR (300 MHz, Me_2SO-d_6:$CDCl_3$, 1:10): δ 8.20 (d, 2 H, *J* 9.5 Hz, aromatic H), 7.54–7.33 (ms, 5 H, aromatic H), 7.17 (d, 2 H, *J* 9.5 Hz, aromatic H), 5.56 (s, 1 H, C*H*Ph), 5.18 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.36 (dd, 1 H, $J_{5,6a}$ 4.0, $J_{6a,6b}$ 10.0 Hz, H-6a), 3.86–3.58 (overlapping signals, 5 H, H-2,3,4,5,6b); ^{13}C NMR (300 MHz, $CDCl_3$): δ 161.4, 142.0 (each s, each aromatic C), 136.6, 128.5, 127.5, 125.9, 125.0, 116.1 (each d, each aromatic CH), 102.2, 101.1, 79.7, 73.7, 72.8 (each d), 67.9 (t, C-6), 66.0 (d); IR (KBr): 3500, 1595, 1515, 1350, 1250, 1087 cm^{-1}. Anal. Calcd for $C_{19}H_{19}NO_8$: C, 58.61; H, 4.92; N, 3.60. Found: C, 57.86; H, 4.96; N, 3.51. ESHRMS: Found 424.0797, required 424.0799 $[M + Cl]^-$.

Octyl 4,6-O-benzylidene-β-D-glucopyranoside (**2d**).—Treatment of **1d** (1.0 g, 3.4 mmol) as described for **1a** gave **2d** (1.2 g, 100%); mp 149–152 °C; $[\alpha]_D$ −55° (*c* 0.02, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.52–7.32 (ms, 5 H, aromatic H), 5.53 (s, 1 H, C*H*Ph), 4.39 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.33 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.90 (m, 1 H, OC(*H*)HCH_2), 3.82 (apt t, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 9.5 Hz, H-3), 3.79 (apt t, 1 H, $J_{5,6b}$ 10.5 Hz, H-6b), 3.59–3.41 (overlapping signals, 4 H, H-2,4,5 and OC(H)*H*CH_2), 2.16 (br s, 1 H, OH), 2.04 (br s, 1 H, OH), 1.66 (m, 2 H, OCH_2CH_2), 1.37–1.23 (m, 10 H, octyl CH_2), 0.89 (t, 3 H, *J* 6.5 Hz, CH_3); ^{13}C NMR (300 MHz, $CDCl_3$) δ 137.3 (s, aromatic C), 129.1, 128.2, 126.4 (each d, each aromatic CH), 103.4, 101.8, 80.7, 74.8, 73.4 (each d), 70.4 (t, O*C*H_2CH_2), 68.8 (t, C-6), 66.4 (d), 31.8, 29.7, 29.3, 29.2, 25.9, 22.6 (each t, octyl-CH_2), 14.1 (q, CH_3); IR (KBr) 3501, 3206, 2924, 2853, 1450, 1376, 1084, 1001, 747, 698 cm^{-1} Anal. Calcd for $C_{21}H_{32}O_6$: C, 66.29; H, 8.48. Found: C, 66.33; H, 8.43. ESHRMS: Found 381.2293, required 381.2277 $[M + H]^+$.

Methyl (4,6-O-benzylidene-β-D-glucopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (**2e**).—Treatment of **1e** (0.41 g, 0.77 mmol) as described for **1a** gave **2e** (0.34 g, 71%); mp >250 °C; $[\alpha]_D$ −72.5° (*c* 0.12, 1:1 MeOH–$CHCl_3$); ^1H NMR (300 MHz, Me_2SO-d_6): δ 7.39–7.22 (ms, 15 H, aromatic H), 5.64 (s, 1 H, C*H*Ph), 5.53 (s, 1 H, C*H*Ph), 5.28 (2 H, overlapping signals), 4.83 and 4.70 (AB d, 2 H, *J* 11.0 Hz, O*C*H_2Ph), 4.75 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.46 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1′), 4.22 (dd, 1 H, $J_{5',6a'}$ 5.0, $J_{6a',6b'}$ 10.5 Hz, H-6a′), 4.21 (dd, 1 H, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 10.0 Hz, H-6a), 3.81-3.64 (4 H, overlapping signals), 3.60 (apt t, 1 H, $J_{2',3'}$ 7.5 Hz, H-2′), 3.45 (m, 1 H, H-5), 3.36 (s, 3 H, O*C*H_3), 3.20 (overlapping signals, 2 H, H-5 and H-5′); ^{13}C NMR (300 MHz, Me_2SO-d_6): δ 139.3, 138.4, 138.3 (each s, each aromatic C), 129.5, 129.4, 128.8, 128.7, 128.7, 128.1, 127.0, 126.6, 103.6, 103.0, 101.29, 100.8, 81.5, 81.1, 81.0, 79.7, 75.3 (each d), 74.2 (t), 73.8 (d), 68.6 (t), 66.7, 65.6 (each d), 56.7 (q, O*C*H_3); IR (KBr): 3481, 2921, 1752, 1378, 1238, 1101, 1069 cm^{-1}. ESHRMS: Found 645.2310, required 645.2312 $[M + Na]^+$.

Phenyl 4,6-O-benzylidene-β-D-erythro-2,3-dideoxyhex-2-enopyranoside (**4a**).—To a stirred solution of **2a** (0.1 g, 0.3 mmol), imidazole (80 mg, 1 mmol) and triphenylphosphine (0.27 g, 1 mmol) in toluene (10 mL) at 80 °C

was added iodine (0.25 g, 1 mmol), portion wise over 20 min. The reaction mixture was heated at reflux and was complete after 1 h. The toluene was decanted off and the residue was dissolved in aq NaOH (1 M, 20 mL) and the product extracted into EtOAc, which was combined with the toluene layer, washed with aq $NaHCO_3$ (2×20 mL), water (1×20 mL), dried over $MgSO_4$ and concentrated. The resulting residue was purified by chromatography (petroleum ether–EtOAc) to give **4a** (55 mg, 62%); mp 136–138 °C (EtOAc); $[\alpha]_D$ −28° (*c* 0.25, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 7.51–7.00 (ms, 10 H, aromatic H), 6.24 (br d, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 5.93 (apt dt, 1 H, $J_{1,2}$ 1.5, $J_{1,3}$ 1.5, $J_{1,4}$ 3.0 Hz, H-1), 5.82 (1 H, ddd, $J_{3,4}$ 2.5 Hz, H-3), 5.60 (s, 1 H, CHPh), 4.44 (m, 1 H, H-4), 4.34 (m, 1 H, H-6), 3.91 (overlapping signals, 2 H, H-5, H-6); ^{13}C NMR (270 MHz, $CDCl_3$): δ 156.7, 137.2 (each s, each aromatic C), 132.0, 129.5, 129.2, 128.3, 127.2, 126.2, 122.6, 116.7 (each d), 102.1 (d, *C*HPh), 96.5 (d, C-1), 74.7, 70.9 (each d), 69.0 (t, C-6); IR (KBr): 1598, 1493, 1380, 1229, 1082 cm^{-1}. Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.43; H, 5.91.

Compound **4a** was also prepared by two methods from **3a**. Thus to a solution of **2a** (0.50 g, 1.52 mmol) in pyridine (1.5 mL) at 0 °C was added a solution of methanesulfonyl chloride (0.52 g, 4.6 mmol) also in pyridine (2.8 mL), dropwise over 0.5 h. After stirring for 1 h the solution was allowed to warm to rt and was stirred for a further 1 h. The pyridine was then removed under diminished pressure and the resulting white foam recrystallised from toluene–EtOH to provide the white solid **3a** (0.62 g, 85%); $[\alpha]_D$ −56° (*c* 0.25, $CHCl_3$); mp 202–203 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.48–7.08 (ms, 10 H, aromatic H), 5.59 (s, 1 H, C*H*Ph), 5.15 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.97 (apt t, $J_{2,3}$ 8.5, $J_{3,4}$ 8.5 Hz, H-3), 4.94 (apt t, H-2), 4.45 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.86 (apt t, $J_{4,5}$ 8.5 Hz, H-4), 3.86 (apt t, $J_{5,6b}$ 10.5 Hz, H-6b), 3.67–3.65 (m, 1 H, H-5), 3.24 (s, 3 H, SO_2CH_3), 3.09 (s, 3 H, SO_2CH_3); ^{13}C NMR (270 MHz, $CDCl_3$): δ 156.4, 136.2 (each s, each aromatic C), 129.8 (2d), 129.5, 128.5, 126.0, 124.0, 117.4 (each d, aromatic CH), 101.7 (d, C*H*Ph), 99.6 (d, C-1), 78.9, 77.1, 76.7 (each d), 68.2 (t, C-6), 66.0 (d), 39.8, 39.2 (each q, each SO_2CH_3); IR (KBr) 1593, 1489, 1372, 1228, 1094, 972, 826 cm^{-1}. Anal. Calcd for $C_{21}H_{24}O_{10}S_2$: C, 50.39; H, 4.83; S, 12.81. Found: C, 50.32; H, 4.76; S, 13.15. ESLRMS: Found 523.1, required 523.1 $[M + Na]^+$.

Sodium iodide (0.68 g, 4.6 mmol), zinc dust (0.30 g) and **3a** (0.5 g, 1 mmol) in DMF (10 mL) were heated and stirred at reflux for 16 h. The mixture was diluted with CH_2Cl_2 (20 mL) and filtered through celite. It was then washed with aq $NaHCO_3$ (2×20 mL), dried over $MgSO_4$ and concentrated. The product **4a** (34 mg, 11%) was isolated by chromatography (petroleum ether–EtOAc). Alkene **4a** was obtained in higher yield from **3a** using a microwave method. Thus to an open 100 mL Erlenmeyer flask was added sodium iodide (0.68 g, 4.6 mmol), zinc dust (0.3 g) and **3a** (0.5 g, 1 mmol) in DMF (30 mL). The mixture was stirred and then heated in a standard microwave oven for 3 min at 350 W power. The product **4a** (0.16 g, 53%) was obtained as described above.

*Methyl 4,6-*O*-benzylidene-β-*D*-erythro-2,3-dideoxyhex-2-enopyranoside* (**4b**).—To a stirred solution of **2b** (1.0 g, 3.55 mmol), imidazole (1.1 g, 15.5 mmol) and chlorodiphenylphosphine (1.9 g, 1.5 mL, 8.5 mmol) in toluene (90 mL) at 80 °C was added iodine (2.2 g, 8.5 mmol), portion wise over 0.5 h. The solution was heated and stirred at reflux until **1b** had been converted into an iododiphenylphosphonate intermediate (16 h).[23] The toluene layer was washed with aq sodium thiosulfate (3×100 mL), aq NaOH (2×100 mL) and water (1×100 mL). It was dried over $MgSO_4$, concentrated and the intermediate (1.3 g) was isolated by chromatography (petroleum ether–EtOAc). It was then dissolved in EtOH (120 mL) and zinc dust (1.2 g) was added and the mixture stirred and heated at reflux for 5 h. It was then filtered through celite, concentrated and passed through a bed of silica to provide **4b** (0.38 g, 47% over two steps); mp 86–87 °C (EtOAc) $[\alpha]_D$ +31° (*c* 0.1, $CHCl_3$) (lit.:[24] mp 94–95 °C; $[\alpha]_D$ +43° (*c* 1.0, $CHCl_3$); ^1H NMR[25] (300 MHz, $CDCl_3$): δ 7.51–7.24 (ms, 5 H, aromatic H), 6.15 (br d, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 5.66 (1

H, ddd, $J_{1,3}$ 1.5, $J_{3,4}$ 2.5 Hz, H-3), 5.59 (s, 1 H, C*H*Ph), 5.27 (apt dt, 1 H, $J_{1,2}$ 1.5, $J_{1,4}$ 3.0 Hz, H-1), 4.29–4.35 (overlapping signals, 2 H, H-4 and H-6a), 3.89 (apt t, 1 H, $J_{5,6b}$ 10.0, $J_{6a,6b}$ 10.0 Hz, H-6b), 3.89 (s, 3 H, O*C*H$_3$), 3.75 (ddd, 1 H, $J_{4,5}$ 8.0, $J_{5,6a}$ 4.5 Hz, H-5); ^{13}C NMR (270 MHz, $CDCl_3$): δ 137.3 (s, aromatic C), 131.5, 129.1, 128.3, 128.1, 126.2 (each d), 102.0 (d, *C*HPh), 99.2 (d, C-1), 75.0, 70.4 (each d), 69.0 (t, C-6), 55.0 (q, O*C*H$_3$); IR (KBr): 2934, 1744, 1453, 1378, 1378, 1206, 1096, 1001, 750, 693, 654 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.46; H, 6.46.

*4-Nitrophenyl 4,6-*O*-benzylidene-β-*D*-erythro-2,3-dideoxyhex-2-enopyranoside* (**4c**).—Treatment of **2c** (0.55 g, 1.41 mmol) with imidazole, triphenylphosphine and iodine as described for **2b** gave **4c** (0.23 g, 46%); mp 163–164 °C (EtOAc); $[\alpha]_D$ −102.5° (*c* 0.04, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, 2 H, *J* 9.0 Hz, aromatic H), 7.52–7.35 (ms, 5 H, aromatic H), 7.17 (d, 2 H, aromatic H), 6.35 (br d, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 6.05 (apt dt, 1 H, $J_{1,2}$ 1.5, $J_{1,3}$ 1.5, $J_{1,4}$ 3.0 Hz, H-1), 5.85 (1 H, dt, $J_{3,4}$ 1.5 Hz, H-3), 5.63 (s, 1 H, C*H*Ph), 4.40 (dd, 1 H, $J_{5,6a}$ 4.0, $J_{6a,6b}$ 10.0 Hz, H-6a) 4.43 (d, 1 H, $J_{4,5}$ 8.5 Hz, H-4), 3.97–3.86 (overlapping signals, 2 H, H-5, H-6b); ^{13}C NMR (300 MHz, $CDCl_3$): δ 161.6, 137.0 (each s, each aromatic C), 133.2, 129.3, 128.4, 126.2, 125.9, 125.8, 116.6 (each d), 102.3 (d, *C*HPh), 96.1 (d, C-1), 74.5, 71.3 (each d), 68.9 (t, C-6); IR (KBr): 1594, 1519, 1340, 1244, 1111 cm^{-1}. ESHRMS: Found 356.1134, required 356.1134 $[M+H]^+$.

*Octyl 4,6-*O*-benzylidene-β-*D*-erythro-2,3-dideoxyhex-2-enopyranoside* (**4d**).—Treatment of **2d** (1.2 g, 3.4 mmol) with imidazole, triphenylphosphine and iodine as described for **2b** gave **4d** (0.73 g, 67%); $[\alpha]_D$ +40.9° (*c* 1.3, acetone); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.25 (ms, 5 H, aromatic H), 6.13 (br d, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 5.70 (1 H, ddd, $J_{1,3}$ 1.5, $J_{3,4}$ 2.5 Hz, H-3), 5.60 (s, 1 H, C*H*Ph), 5.33 (apt dt, 1 H, $J_{1,2}$ 1.5, $J_{1,4}$ 3.0 Hz, H-1), 4.35–4.27 (overlapping signals, 2 H, H-4, H-6a), 3.71–3.91 (overlapping signals, 3 H, H-6b, OCH_2), 3.51 (apt dt, 1 H, $J_{5,6a}$ 7.0, $J_{5,6b}$ 9.5, $J_{4,5}$ 9.5 Hz, H-5); 1.50–1.66 (m, 2 H, octyl CH_2), 1.37–1.23 (m, 10 H, octyl CH_2), 0.88 (t, 3 H, *J* 6.5 Hz, CH_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ 137.6 (s, aromatic CH), 131.4, 129.4, 128.9, 128.6, 126.5, (each d), 102.4 (d, *C*HPh), 99.0 (d, C-1), 75.4, 70.7 (each d), 69.4, 68.7 (each t), 32.1, 30.0, 29.6, 29.5, 26.3, 22.9 (each t, each octyl-CH_2), 14.3 (q, CH_3); IR (KBr) 2956, 2919, 2854, 1378, 1298, 1100, 1001 cm^{-1}. ESHRMS: Found 347.2222, required 347.2221 $[M+H]^+$.

*Methyl (4,6-*O*-benzylidene-β-*D*-erythro-2,3-dideoxyhex-2-enopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**4e**).—Treatment of **2e** (0.3 g, 0.48 mmol) with imidazole, triphenylphosphine and iodine as described for **2b** gave **4e** (0.24 g, 85%); mp 171–173 °C (EtOAc); $[\alpha]_D$ −8.3° (*c* 0.05, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49–7.26 (ms, 15 H, aromatic H), 6.09 (br d, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 5.68 (1 H, dt, $J_{3,4}$ 2.5, $J_{1,3}$ 2.5 Hz, H-3), 5.58 (3 H, overlapping signals, 2 × C*H*Ph, H-1), 4.93 and 4.75 (AB d, 2 H, *J* 11.5 Hz, OCH_2Ph), 4.43 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1′), 4.40-4.34 (overlapping signals, 2 H, H-4,4′), 4.27 (dd, 1 H, $J_{5',6a'}$ 4.5, $J_{6a',6b'}$ 10.0 Hz, H-6a′), 3.85 (apt t, 1 H, $J_{5a',6b'}$ 10.0 Hz, H-6b′), 3.82–3.65 (overlapping signals, 5 H, H-2,6a,5′,2′,3′), 3.56 (s, 3 H, OCH_3), 3.44 (m, 1 H, H-5); ^{13}C NMR (300 MHz, $CDCl_3$): δ 138.5, 137.6, 137.5 (each s, each aromatic C), 131.2, 129.4, 129.2, 128.7, 128.6, 128.5, 128.3, 128.1, 126.5, 126.2, 103.9, 102.3, 101.4, 100.0, 81.8, 81.2, 80.4 (each d), 75.4 (t, CH_2), 75.1, 71.1 (each d), 69.4, 69.1 (each t), 66.1 (d), 57.4 (q, O*C*H$_3$); IR (KBr): 2922, 1452, 1370, 1093, 1003, 697 cm^{-1} ESHRMS: Found 589.2434, required 589.2438 $[M+H]^+$.

*Phenyl 4,6-*O*-benzylidene-β-*D*-allopyranoside* (**5b**).—To a solution of **4b** (0.22 g, 0.74 mmol) in *tert*-butanol and water (1:1, 16 mL) at 60 °C was added 4-methylmorpholine-*N*-oxide (0.8 g, 0.7 mL, 0.54 mmol), K_2CO_3 (0.9 g, 6.55 mmol), potassium osmate dihydrate (2 mg, 8 μmol), and DABCO (80 mg, 0.74 mmol). The mixture was stirred and heated at 80 °C for 16 h until complete. 4,5-Dihydroxy-1,3-benzenedisulfonic acid disodium salt (5 mg, 15 μmol) was added and the reaction was stirred for further 1 h. It was then diluted with EtOAc (30 mL), washed with water (50 mL), dried over $MgSO_4$ and concentrated to provide **5b** as a white solid (0.24 g, quantita-

tive); mp 155–157 °C (water); $[\alpha]_D$ −40° (*c* 0.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.52–7.04 (ms, 10 H, aromatic H), 5.60 (s, 1 H, C*H*Ph), 5.35 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.49 (apt t, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 2.5 Hz, H-3), 4.43 (dd, 1 H, $J_{5,6a}$ 5.5, $J_{6a,6b}$ 10.0 Hz, H-6), 4.15 (dt, 1 H, $J_{4,5}$ 10.0, $J_{5,6b}$ 10.0 Hz, H-5), 3.80 (overlapping signals, 2 H, H-2, H-6b) 3.70 (dd, 1 H, H-4), 2.72 (br s, 1 H, OH), 2.54 (br s, 1 H, OH); ^{13}C NMR (270 MHz, $CDCl_3$): δ 157.0, 136.9 (each s, each aromatic C), 129.6, 129.4, 128.4, 126.3, 122.9, 116.7 (each d, each aromatic CH), 102.0 (d, CHPh), 99.3 (d, C-1), 78.5, 70.9 (each d), 69.0 (t, C-6), 69.0, 63.2 (each d); IR (KBr): 3415, 2919, 1597, 1491, 1391, 1228, 1076, 1011, 761 cm^{-1}. Anal. Calcd for $C_{19}H_{20}O_6$: C, 66.27; H, 5.85. Found: C, 65.97; H, 5.55.

*Methyl 4,6-*O*-benzylidene-β-*D*-allopyranoside* (**5a**).—Treatment of **4a** (0.25 g, 1 mmol) as described for **4b** gave **5b** (0.26 g, 92% yield); mp 157–158 °C (water); $[\alpha]_D$ −63° (*c* 0.88, $CHCl_3$) (lit.:[26] $[\alpha]_D$ −45.1° (*c* 0.48, $CHCl_3$)); ^1H NMR (300 MHz, 1:10 Me_2SO-d_6-$CDCl_3$): δ 7.53–7.32 (ms, 5 H, aromatic H), 5.55 (s, 1 H, C*H*Ph), 4.58 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.38 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 10.5 Hz, H-6), 4.31 (br s, 1 H, H-3), 4.11 (br s, 1 H, OH), 4.00 (m, 1 H, H-5), 3.83 (br d, 1 H, *J* 6.0 Hz, OH), 3.74 (apt t, 1 H, $J_{5,6b}$ 10.5 Hz, H-6b), 3.56 (s, 3 H, OCH_3), 3.54 (dd, 1 H, $J_{3,4}$ 2.5, $J_{4,5}$ 9.5 Hz, H-4), 3.46 (br s, 1 H, H-2); ^{13}C NMR (270 MHz, $CDCl_3$): δ 137.4 (s, aromatic C), 129.1, 128.2, 126.4 (each d, each aromatic CH), 102.6, 101.8, 79.1, 71.1 (each d), 69.2 (t, C-6), 68.9, 62.9 (each d), 57.3 (OCH_3); IR (KBr): 3490, 3403, 2923, 2862, 1451, 1385, 1209, 1109, 1014, 757, 701 cm^{-1}; Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.32; H, 6.46.

*4-Nitrophenyl 4,6-*O*-benzylidene-β-*D*-allopyranoside* (**5c**).—Treatment of **4c** (0.15 g, 0.42 mmol) as described for **4b** gave **5c** (0.13 g, 79%); mp 203–205 °C (water); $[\alpha]_D$ −294° (*c* 0.02, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$:Me_2SO-d_6, 10:1): δ 8.25–8.21 (d, 2 H, *J* 9.0 Hz, aromatic H), 7.98–7.29 (ms, 5 H, aromatic H), 7.18 (d, 2 H, *J* 9.0 Hz, aromatic H), 5.67 (s, 1 H, C*H*Ph), 5.52 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.42 (apt t, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 2.5 Hz, H-3), 4.21 (apt dt, 1 H, $J_{4,5}$ 10.0, $J_{5,6a}$ 5.0, $J_{5,6b}$ 10.0 Hz, H-5), 4.39 (dd, 1 H, $J_{6a,6b}$ 10.0 Hz, H-6a), 3.77 (br s, 1 H, H-2), 3.75 (apt t, 1 H, H-6b), 3.66 (dd, 1 H, H-4); ^{13}C NMR (300 MHz, $CDCl_3$) δ 162.3, 142.4 (each s, each aromatic C) 138.5, 128.9, 128.2, 126.7, 125.8, 116.8 (each d, each aromatic CH), 101.7, 99.6, 78.9, 71.1 (each d), 69.6 (t, C-6), 68.8, 63.6 (each d); IR (KBr): 3491, 1593, 1511, 1346, 1247, 1081, 971 cm^{-1}. Anal. Calcd for $C_{19}H_{19}O_8N$: C, 58.61; H, 4.92; N, 3.60. Found: C, 58.45; H, 4.78; N, 3.83.

*Octyl 4,6-*O*-benzylidene-β-*D*-allopyranoside* (**5d**).—Treatment of **4d** (0.46 g, 1.56 mmol) as described for **4b** gave **5d** (0.54 g, quantitative); mp 112–114 °C (water); $[\alpha]_D$ −42° (*c* 0.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.52–7.32 (ms, 5 H, aromatic H), 5.56 (s, 1 H, C*H*Ph), 4.69 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.39 (br s, 1 H, H-3), 4.38 (dd, 1 H, $J_{5,6a}$ 5.5, $J_{6a,6b}$ 10.0 Hz, H-6a) 3.96 (apt dt, 1 H, $J_{5,6b}$ 10.0, $J_{4,5}$ 10.0 Hz, H-5), 3.89 (m, 1 H, $OCH(H)CH_2$), 3.75 (apt t, 1 H, H-6b), 3.58 (dd, 1 H, $J_{3,4}$ 2.5 Hz, H-4), 3.51 (m, 2 H, H-2, $OCH(H)CH_2$), 2.57 (2 H, br s, OH), 1.65 (m, 2 H, octyl-CH_2), 1.28 (10 H, m, octyl-CH_2), 0.88 (3 H, t, *J* 6.5 Hz, CH_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ 137.3 (s, aromatic C), 129.5, 128.6, 126.5 (each d, each aromatic H), 102.2, 101.5, 79.1, 71.6 (each d), 70.8, 69.4 (each t), 69.2, 63.5 (each d), 32.0, 29.9, 29.6, 29.5, 26.2, 22.9 (each t, octyl-CH_2), 14.3 (q, CH_3); IR (KBr): 3501, 3206, 2924, 2853, 1450, 1376, 1085, 1001, 747, 698 cm^{-1} Anal. Calcd for $C_{21}H_{32}O_6$: C, 66.31; H, 8.48. Found: C, 66.08; H, 8.31. ESHRMS: Found 403.2079, required 403.2097 $[M+Na]^+$.

*Methyl (4,6-*O*-benzylidene-β-*D*-allopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**5e**).—Treatment of **4e** (90 mg, 0.15 mmol) as described for **4b** gave **5e** (30 mg, 32%); mp 194–196 °C (EtOAc); $[\alpha]_D$ −50.4° (*c* 0.25, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.25 (ms, 15 H, aromatic H), 5.57 and 5.54 (each s, each 1 H, each C*H*Ph), 4.79 and 4.99 (AB d, 2 H, OCH_2Ph, *J* 11.0 Hz), 4.93 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.41 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1′), 4.39–4.32 (overlapping signals, 3 H, H-3,6,6′), 4.05 (apt d, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 9.5 Hz, H-5), 3.88–3.70 (overlapping signals, 4 H, H-3′,4′,6′,6), 3.63 (apt t, 1 H, $J_{2,3}$ 7.5 Hz, H-2), 3.57 (dd, 1 H, $J_{3',4'}$ 2.5, $J_{4'5'}$ 9.5

Hz, H-4), 3.56 (s, 3 H, OCH_3), 3.38–3.46 (overlapping signals, 2 H, H-2′,5′); ^{13}C NMR (270 MHz, $CDCl_3$): δ 137.3, 137.1 (each s, aromatic C), 129.3, 129.1, 128.6, 128.5, 128.4, 128.2, 126.3, 126.0 (each d, each aromatic CH), 104.1, 103.4, 102.1, 101.2, 82.0, 81.8, 79.7, 78.8, 75.0, 72.5 (each d), 69.1 (t), 68.9 (d), 68.7 (t), 65.7, 63.9 (each d), 57.8 (q, OCH_3); IR (KBr) 3450, 2881, 1462, 1368, 1275, 1084, 1002, 764 cm^{-1}. ESHRMS: Found 645.2317, required 645.2312 $[M + Na]^+$.

Dihydroxylation using ruthenium trichloride.—To a stirred solution of **4b** (30 mg, 0.12 mmol) in 1:1 EtOAc–MeCN (2 mL) at 0 °C was added a solution of $RuCl_3$ (2.0 mg) and sodium periodate in distilled water (0.2 mL). The two-phase reaction was stirred vigorously for 2 min and was then diluted with EtOAc. The organic layer was washed with satd aq sodium thiosulfate (10 mL), then water (10 mL) and was dried over $MgSO_4$ and concentrated to give **5b** as a white solid (30 mg, 89%). Using this method **4e** gave **5e** (70%).

Methyl 2,3,4,6-tetra-O-*benzoyl-1-thio-β*-D-*glucopyranoside* (**7**).—To a solution of sodium thioglucose (20 g, 0.09 mol) in DMF at rt was added MeI (17.1 g, 7.5 mL, 0.12 mol, 1.3 equiv) and the reaction mixture was allowed to stir for 16 h after which BzCl (75 mL, 0.83 mol) and pyridine (100 mL) were added. The solution was stirred for a further 16 h and then washed with dilute HCl (3 × 200 mL). The organic layer was then concentrated and purified by chromatography to yield **7** as a brown oil (25 g, 0.04 mmol, 44%); mp 64–66 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.13–7.24 (ms, 20 H, aromatic H), 5.94 (apt t, 1 H, $J_{3,4}$ 9.5, $J_{4,5}$ 9.5 Hz, H-4), 5.68 (dd, 1 H, $J_{1,2}$ 9.5, $J_{2,3}$, 10.0 Hz, H-2), 5.60 (apt t, 1 H, H-3), 4.76 (d, 1 H, H-1), 4.64 (dd, 1 H, $J_{5,6a}$ 3.0, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.50 (dd, 1 H, $J_{5,6b}$ 5.0 Hz, H-6b), 4.19 (m, 1 H, H-5), 2.25 (3 H, SCH_3); ^{13}C NMR (270 MHz, $CDCl_3$): δ 166.1, 165.8, 165.2, 165.2 (each s, each C=O), 133.5, 133.4, 133.3, 133.1, 129.9, 129.8, 129.7, 129.0, 128.4, 128.3, 128.2 (each d, each aromatic CH), 83.3 (d, C-1), 76.3, 74.0, 69.8, 69.5 (each d), 63.2 (t, C-6), 21.5 (q, SCH_3); ESHRMS Found 649.1508, required 649.1529 $[M + Na]^+$.

Methyl 3-O-*benzyl-4,6*-O-*benzylidene-β*-D-*glucopyranoside* (**8**).—Compound **2b** (8.0 g, 28.4 mmol) and dibutyltin oxide (8.41 g, 34.6 mmol) were dissolved in benzene (400 mL) and stirred for 16 h, with azeotropic removal of water. The solution was concentrated to 200 mL and BnBr (7.81 mL, 30.4 mmol) and tetrabutylammonium iodide (11.85 g, 32.1 mmol) were added and it was again allowed to stir, heating at reflux, for a further 16 h. The solution was then concentrated and the resulting yellow solid recrystallised from MeOH to give **8** as a white solid (8.4 g, 85%); mp 119–121 °C (MeOH). The ^1H and ^{13}C NMR data is identical with that previously reported.[19] ESHRMS: Found 373.1654, required 373.1651 $[M + Na]^+$.

Methyl (2,3,4,6-tetra-O-*benzoyl-β*-D-*glucopyranosyl)-(1→2)-3*-O-*benzyl-4,6*-O-*benzylidene-β*-D-*glucopyranoside* (**9**).—Thioglycoside **7** (1.0 g, 1.6 mmol) and **8** (0.61 g, 1.8 mmol, 1.1 equiv) were stirred in CH_2Cl_2 (40 mL) containing 4 Å molecular sieves under an inert atmosphere. After 20 min *N*-iodosuccinimide (0.38 g, 2.1 mmol) was added and AgOTf (10 mg) was added after a further 20 min. The reaction was allowed to stir overnight and was then quenched with triethylamine (0.1 mL). The solution was filtered, concentrated and purified by chromatography using a petroleum ether and EtOAc gradient system as eluant to provide **9** as a white solid (0.87 g, 38%); mp 86–88 °C (EtOAc); $[\alpha]_D$ −6.3° (*c* 0.14, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 8.05–7.80 (ms, 10 H, aromatic H), 7.55–7.24 (ms, 20 H, aromatic H), 5.82 (dd, 1 H, $J_{2,3}$ 9.0, $J_{3,4}$ 9.5 Hz, H-3), 5.74 (dd, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 5.67 (dd, 1 H, $J_{1,2}$ 7.5 Hz, H-2), 5.55 (s, 1 H, C*H*Ph), 5.33 (d, 1 H, H-1), 4.65 (dd, 1 H, $J_{5,6a}$ 3.5, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.51 and 4.65 (AB d, 2 H, *J* 11.5 Hz, OCH_2Ph), 4.51 (dd, 1 H, $J_{5,6b}$ 7.5 Hz, H-6b), 4.46 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1′), 4.31 (dd, 1 H, $J_{5',6a'}$ 5.0, $J_{6a'6b'}$ 10.0 Hz, H-6a′), 4.10 (br s, 1 H, H-5), 3.78 (apt t, 1 H, $J_{2'3'}$ 7.5 Hz, H-2′), 3.71 (apt t, $J_{5',6b'}$ 10.0 Hz, H-6b′), 3.67 (dd, 1 H, $J_{3',4'}$ 10.0 Hz, H-3′), 3.60 (apt t, 1 H, $J_{4'5'}$ 10.0 Hz, H-4′), 3.53 (s, 3 H, OCH_3), 3.47–3.31 (apt dt, 1 H, H-5′); ^{13}C NMR (300 MHz, $CDCl_3$): δ 166.4, 166.0 (each C=O), 165.5 (2s, each C=O), 138.5, 137.4, 133.6, 133.4, 133.3, 130.1, 130.0, 129.9,

129.5, 129.2, 128.6, 128.4, 128.1, 127.8, 126.2 (aromatic C and CH), 103.4, 101.4, 100.9, 81.6, 81.0, 80.6 (each d), 74.9 (t), 73.5, 72.7, 72.4, 70.0 (each d), 69.0 (t), 65.8 (d), 63.5 (t), 57.3 (s, OCH_3); IR (KBr) 1734, 1601, 1452, 1266, 1094, 1070, 706 cm^{-1}. ESHRMS: Found 973.3048, required 973.3047 $[M+Na]^+$.

Methyl (β-D-glucopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (**1e**).—Disaccharide **9** was dissolved in MeOH (50 mL) and elemental sodium (30 mg) was added. The solution was stirred for 2 h and then amberlite IR-120 (H^+) ion exchange resin was added. After 10 min. the solution was filtered, concentrated and purified by chromatography (EtOAc and MeOH gradient system) to give **1e** as a white solid (0.45 g, 100%); mp 199–200 °C (MeOH); $[\alpha]_D$ −116.7° (*c* 0.06, MeOH); ^1H NMR (300 MHz, acetone-d_6): δ 7.55–7.28 (ms, 10 H, aromatic H), 5.71 (s, 1 H, C*H*Ph), 4.92 (2 H, s, CH_2Ph), 4.70 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.53 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1′), 4.31 (dd, 1 H, $J_{5',6a'}$ 5.0, $J_{6a',6b'}$ 10.5 Hz, H-6a′), 4.19 (2 H, br s, OH), 4.08 (br s, 1 H, OH), 3.91–3.70 (6 H, overlapping signals), 3.51 (s, 3 H, OCH_3), 3.57–3.11 (5 H, overlapping signals); ^{13}C NMR (300 MHz, acetone-d_6): δ 139.0, 138.4 (each s, each aromatic C), 128.9, 128.5, 128.5, 128.3, 128.2, 127.1, 126.4 (each d, each aromatic CH), 103.7, 103.65, 101.1, 81.7, 81.2, 80.3, 77.2, 76.9, 75.0, 74.4, 71.2, 68.7, 65.8, 62.4, 56.3; IR (KBr): 3388, 2913, 1451, 1369, 1094, 1067, 1031, 896 cm^{-1}. ESHRMS: Found 557.2005, required 557.1999 $[M+Na]^+$.

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