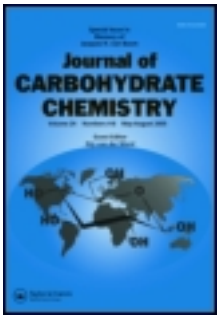

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SELECTIVELY DEOXYGENATED DERIVATIVES OF β-MALTOSYL-(1→4)-TREHALOSE AS BIOLOGICAL PROBES

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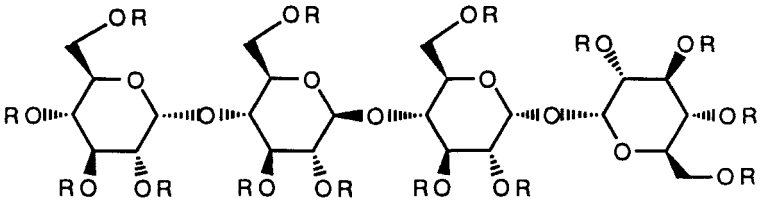
ABSTRACT

The four derivatives of β-maltosyl-(1→4)-trehalose have been synthesized, which are monodeoxygenated at the site of one of the primary hydroxyl groups. The tetrasaccharides were constructed in [2+2] block syntheses. Thus, 6'''-deoxy-β-maltosyl-(1→4)-trehalose was prepared by selective iodination of allyl 2,3,6,2',3'-penta-*O*-acetyl-β-maltoside (**3**) followed by catalytic hydrogenolysis and coupling with 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl 2',3',6'-tri-*O*-benzyl-α-D-glucopyranoside (**9**), and 6''-deoxy-β-maltosyl-(1→4)-trehalose by selective iodination of allyl 4',6'-*O*-isopropylidene-β-maltoside (**14**), coupling with **9**, and one-step hydrogenolysis at the tetrasaccharide level. For the synthesis of 6'-deoxy-β-maltosyl-(1→4)-trehalose, the diol 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl 2',3'-di-*O*-benzyl-α-D-glucopyranoside (**22**) was selectively iodinated and glycosylated with acetobromomaltose followed by catalytic hydrogenolysis. The 6-deoxy-β-maltosyl-(1→4)-trehalose was obtained upon selective iodination of a tetrasaccharide diol.

INTRODUCTION

Sulfated β-maltosyl-(1→4)-trehalose (**1**) has been found[1] to effectively inhibit the proliferation of smooth muscle cells (SMC), a pivotal process in the development of arteriosclerotic lesions.[2,3] The endogenous regulator of



1 R = SO_3Na or H, DS ≈ 2.8[4]

2 R = H

Scheme 1

SMC growth is thought to be heparan sulfate, a sulfated glucosaminoglycan, and it is this activity which seems to be mimicked by **1** (Scheme 1). The inhibitory effect of **1** is as high as for the related glucosaminoglycan heparin.[1]

Sulfated β-maltosyl-(1→4)-trehalose is distinctly more active than sulfated α-maltosyl-(1→4)-trehalose and than analogous equatorially linked tetrasaccharides in which the maltose moiety is replaced by other disaccharides.[1,5] In this group of analogues only sulfated β-isomaltosyl-(1→4)-trehalose has a comparable antiproliferative effect, probably due to similar conformations of the maltosyl and isomaltosyl moieties.

The activity loss upon modification of **1** demonstrates that a specific activity was found. Moreover, **1** is the smallest saccharide with high SMC antiproliferative activity detected so far, so that this sulfated tetrasaccharide was regarded worth further investigation. Since it was not possible to completely sulfate β-maltosyl-(1→4)-trehalose (**2**), **1** was obtained as a mixture of derivatives sulfated at different positions. To arrive at chemically defined compounds it was of interest to investigate which of the sulfates are essential for biological activity. Towards this end we have synthesized selectively deoxygenated derivatives of **2**, and here we describe those analogues that are deoxygenated at the primary positions.

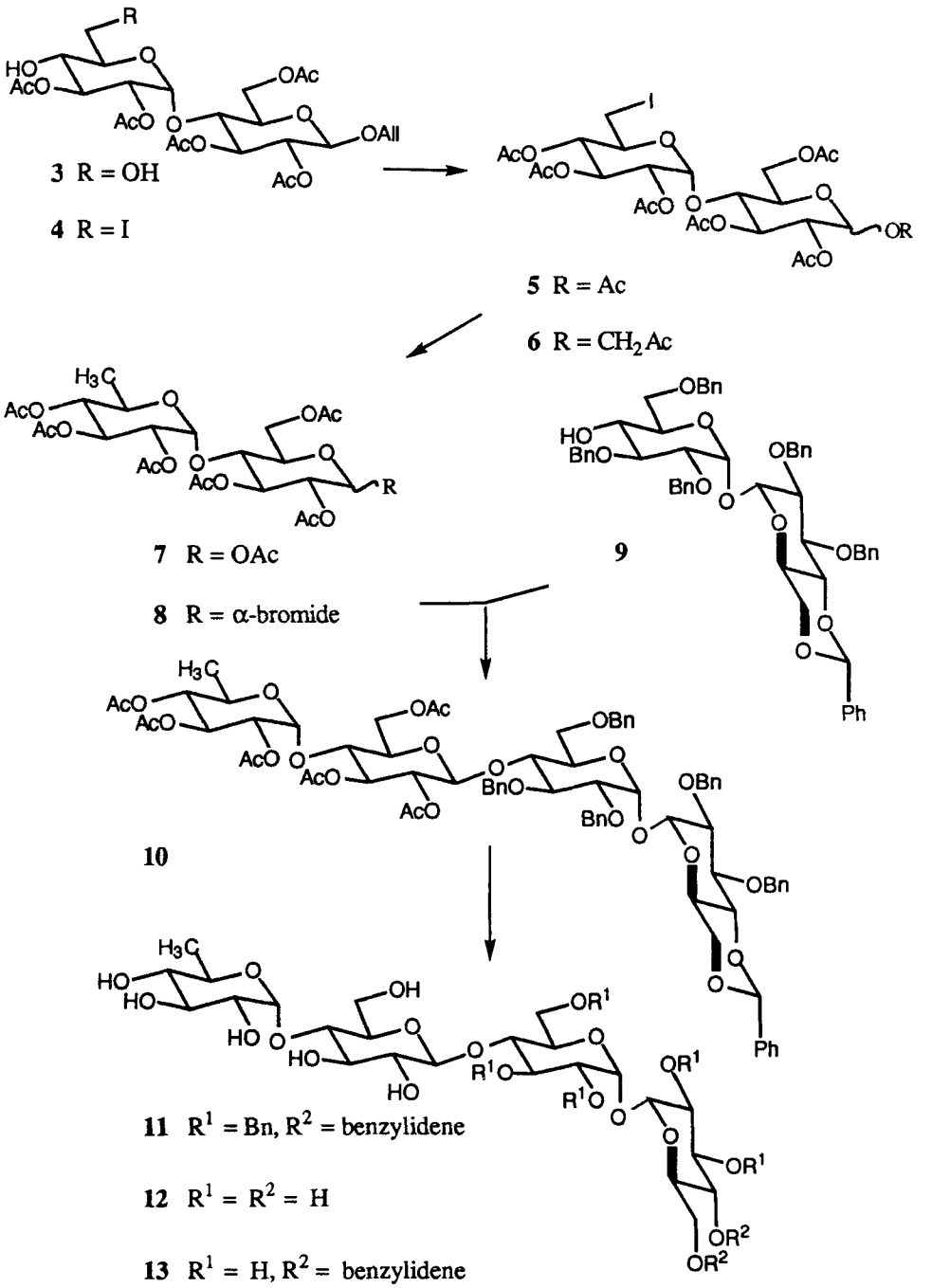
RESULTS AND DISCUSSION

Pioneered by the work of Lemieux and colleagues,[6,7] saccharides have been modified at specific positions to investigate the interaction with biomolecules. For this purpose, hydroxyl functions were replaced by deoxy-, deoxy-halogeno, methylated, or *nor*- analogues. For the investigation of

sulfated compounds, however, this approach has not been employed yet. We have chosen to prepare deoxygenated analogues to i) rule out the presence of a sulfate at this position, to ii) avoid additional hydrophobic interactions due to groups bigger than a hydroxyl group, and iii) for reasons of synthetic simplicity.

β-Maltosyl-(1→4)-trehalose (**2**) has been synthesized in a [2+2] block synthesis from suitable maltosyl and trehalose precursors.[8] Since maltose as well as trehalose are readily available saccharides we decided to introduce the deoxy functions, wherever possible, on a disaccharide level to avoid additional glycoside syntheses. Most reactions were not optimized, but carried out to obtain small amounts of deoxygenated tetrasaccharide as biological probe.[9]

For the reduction of the 6'-hydroxyl group of maltose we started from the selectively acylated allyl 2,3,6,2',3'-penta-*O*-acetyl-β-maltoside (**3**),[10] which is readily prepared from allyl 4',6'-*O*-isopropylidene-β-maltoside[11] by acetylation followed by acetal hydrolysis. This compound was chosen as a common starting material for a number of compounds of interest to us and was made available in quantity. Regioselective iodination of crude **3** using the triphenylphosphine, imidazole/iodine system in toluene according to Garegg and Samuelsson[12] furnished the 6'-iodinated product **4** in a yield of 60 % (Scheme 2). The anomeric allyl protective group was removed with palladium chloride - sodium acetate - aqueous acetic acid;[13] as described earlier by us,[10] this reaction was advantageously carried out under sonication. The crude product mixture was acetylated to afford **5** as a mixture of anomeric acetates (79 %) along with some oxopropyl β-maltoside **6** (20 %). Analogous oxopropyl glycosides were observed as by-products before,[10,14,15] interestingly, also being β-configurated;[10] they can be cleaved by photolysis in the presence of triethylamine.[16] Both acetates, **5α** and **5β**, could be separated by chromatography, which is, however, not necessary for further processing. The iodo derivative **5** has been prepared before[17] via the 6'-tosylate of 1,6-anhydro-maltose, and **5β** has been synthesized in a similar fashion[18,19] or, in a very efficient approach, from the 6'-tosylate of an ester protected maltose.[20] These disaccharides gave ^{1}H NMR spectra well interpretable by first order analysis. The iodide **5** was reduced to the 6'-deoxy derivative **7** by catalytic hydrogenolysis using palladium on carbon in 90 % yield; dioxane proved to be the superior solvent over tetrahydrofuran, Takeo and Shinmitsu[20] have



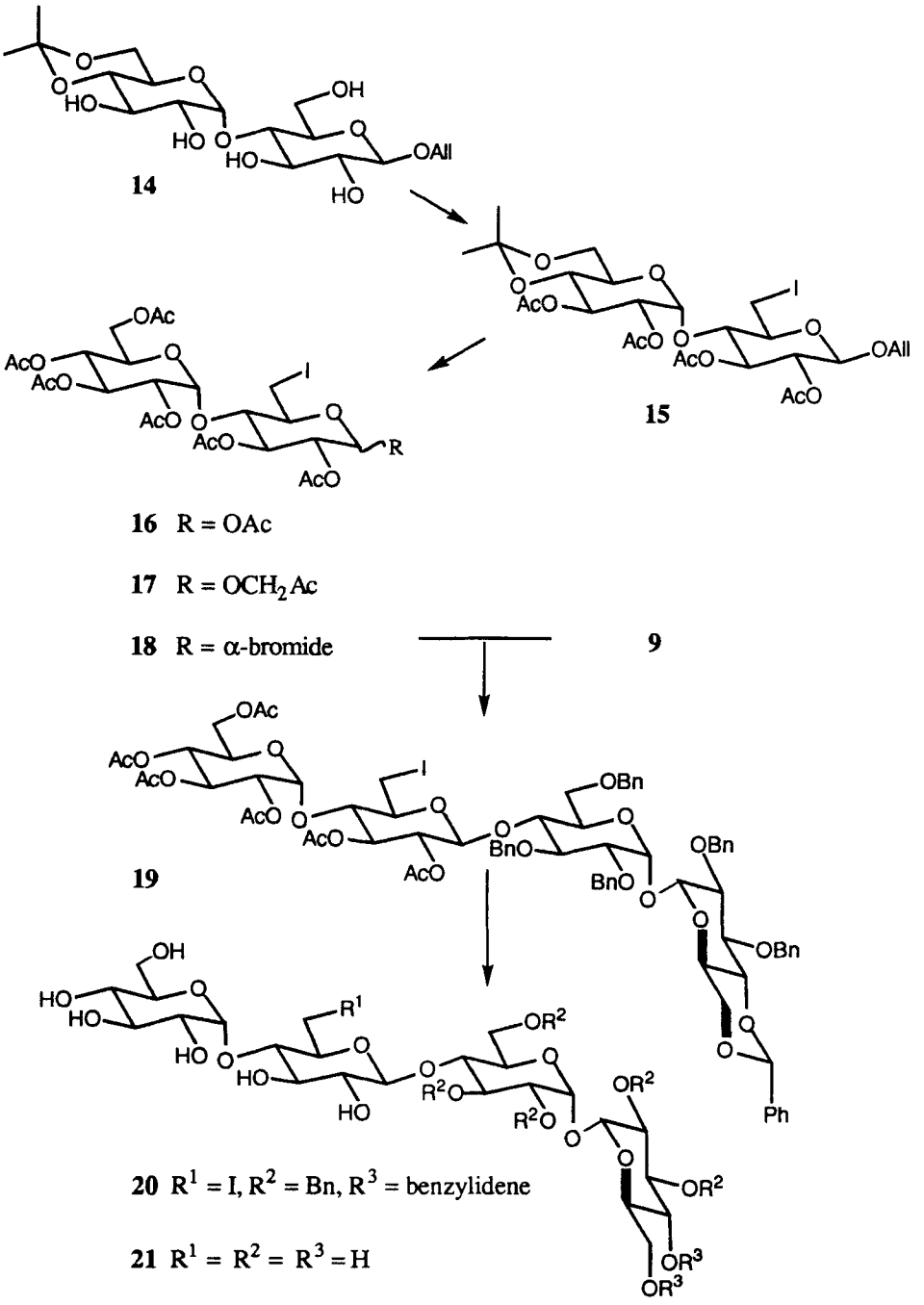
Scheme 2

employed a methanol/dioxane mixture for the same reaction. The anomeric acetate **7** was transformed to α-bromide **8** with HBr/HOAc.

This glycosyl donor, activated with silver triflate,[21] was reacted with our well-established[8,22-25] glycosyl acceptor 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl 2',3',6'-tri-*O*-benzyl-α-D-glucopyranoside (**9**) to afford tetrasaccharide **10** in 50 % yield in a Koenigs-Knorr glycosylation. As a by-product, we isolated the hydrolysis product (42 %) of bromide **8**, which could be converted to **7** by standard acetylation. Deacetylation of **10** gave tetrasaccharide **11** in 85 % yield, which was quantitatively deblocked by hydrogenolysis to **12**, the 6'''-deoxygenated analogue[26] of tetrasaccharide **2**.

It is interesting to note that the benzyl groups could be removed with high selectivity (93 % yield) to afford the benzylidene protected tetrasaccharide **13** when the reaction time was shortened from two days to 18 hours. This compound was fully analyzed by NMR spectroscopy; since the anomeric protons were sufficiently separated, the carbohydrate protons could be readily assigned by a series of 1D TOCSY experiments. The assignment of the sub-spectra to the individual pyranose rings was straightforward: one maltosyl ring could be assigned due the presence of the 6'''-deoxy group, the other maltosyl ring due to the axial position of H-1'', and the first trehalose ring due to the diaxial position of H-5/ H-6a typical for the condensed 4,6-*O*-acetal ring. These assignments were supported by an inter-ring H-1''-H-4' ROE.

For the reduction of the 6-hydroxyl group of maltose we started from allyl 4',6'-*O*-isopropylidene-β-maltoside (**14**),[11] as described above, the synthetic precursor of **3**. In a slight modification of the procedure by Garegg et al.,[27] **14** was iodinated using the triphenylphosphine, imidazole/iodine system in tetrahydrofuran/ toluene 1:1 instead of toluene/ acetonitrile 2:1 to furnish, after acetylation, crystalline **15** in 92 % yield (Scheme 3). This compound was deallylated with palladium chloride as described above; under the acidic reaction conditions the 4',6'-*O*-isopropylidene acetal was cleaved concomitantly. The crude product was acetylated to afford **16** (56 %) as a mixture of anomers, which were separable by chromatography, along with the oxopropyl β-maltoside **17**. The β-anomer of **16** has been prepared before starting from 1,6-anhydromaltose derivatives.[18,28-30] The catalytic hydrogenolysis of iodide **16** proceeded sluggishly so that we preferred to hydrogenate at a later stage. Thus, **16** was converted to the anomeric bromide **18** with HBr in acetic acid. This glycosyl donor was coupled to acceptor **9** as described above for **10** to afford tetrasaccharide **19** (54 %) in a silver triflate



Scheme 3

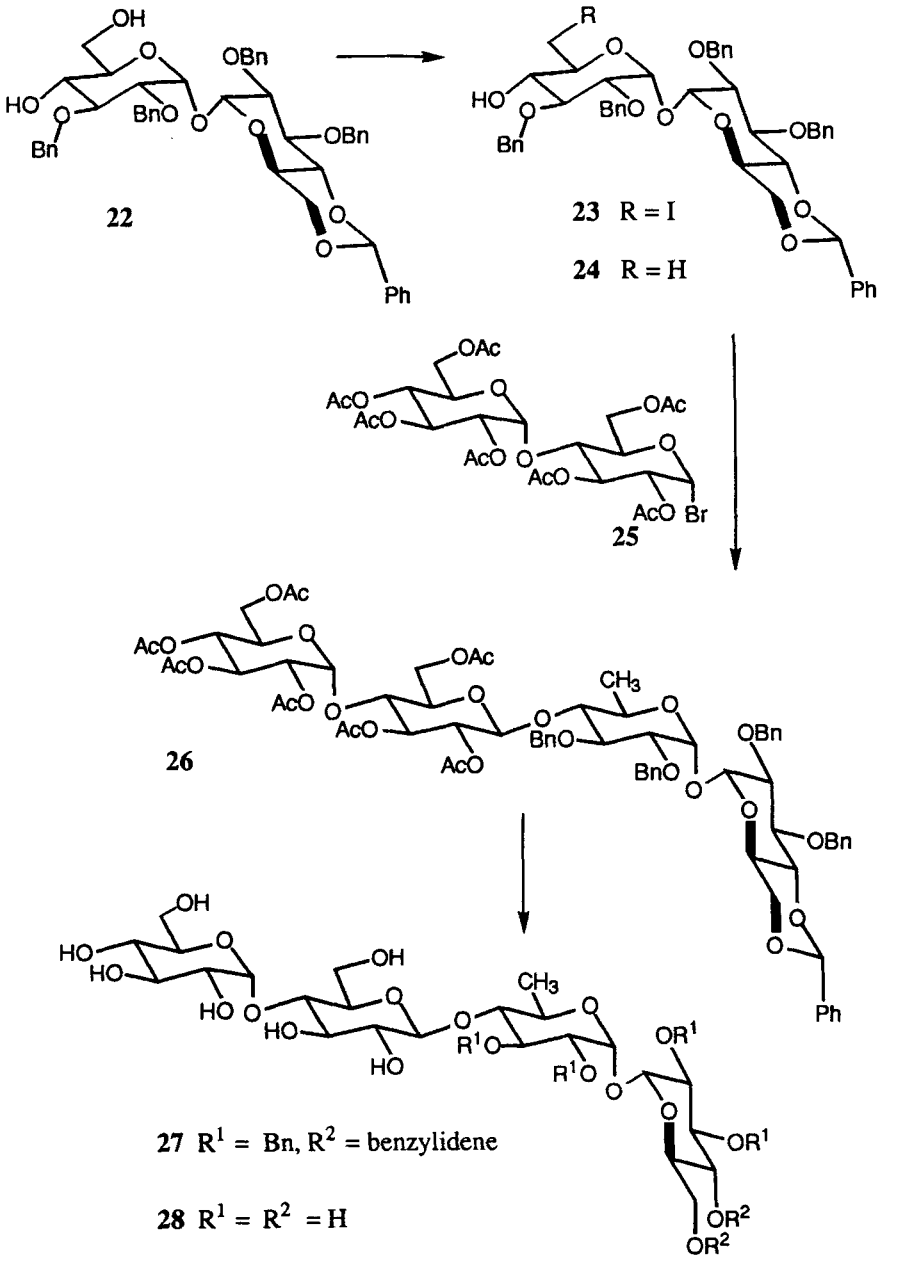
mediated glycosylation reaction. After quantitative deacetylation of **19** to give **20**, catalytic hydrogenolysis removed the iodo, benzyl, and benzylidene groups in one step to result in **21** quantitatively. This fully deblocked tetrasaccharide is the 6''-deoxygenated analogue of tetrasaccharide **2**.

A remarkable feature of the ^{1}H NMR spectra of the fully protected tetrasaccharides is the pronounced up-field shift of one of the acetate signals (**19**: δ 1.72 ppm, **10**: δ 1.71 ppm, analogous non-deoxygenated tetrasaccharide: δ 1.71 ppm, **30** and **31**: δ 1.72 ppm, **32**: δ 1.71 ppm) which is in the range of orthoester protons. These signals disappear after deacetylation so that they can be clearly assigned to an acetate. The effect is obviously caused by a neighbouring benzyl group interacting with 6''-OAc or 2''-OAc. From the occurrence of this effect in **19**, with an iodo substituent in the 6''-position, we conclude that the up-field shifted acetate is 2''-OAc. Also H-5'', in **19** and **20**, appears at unusually high field (δ 2.54 - 2.63 ppm).

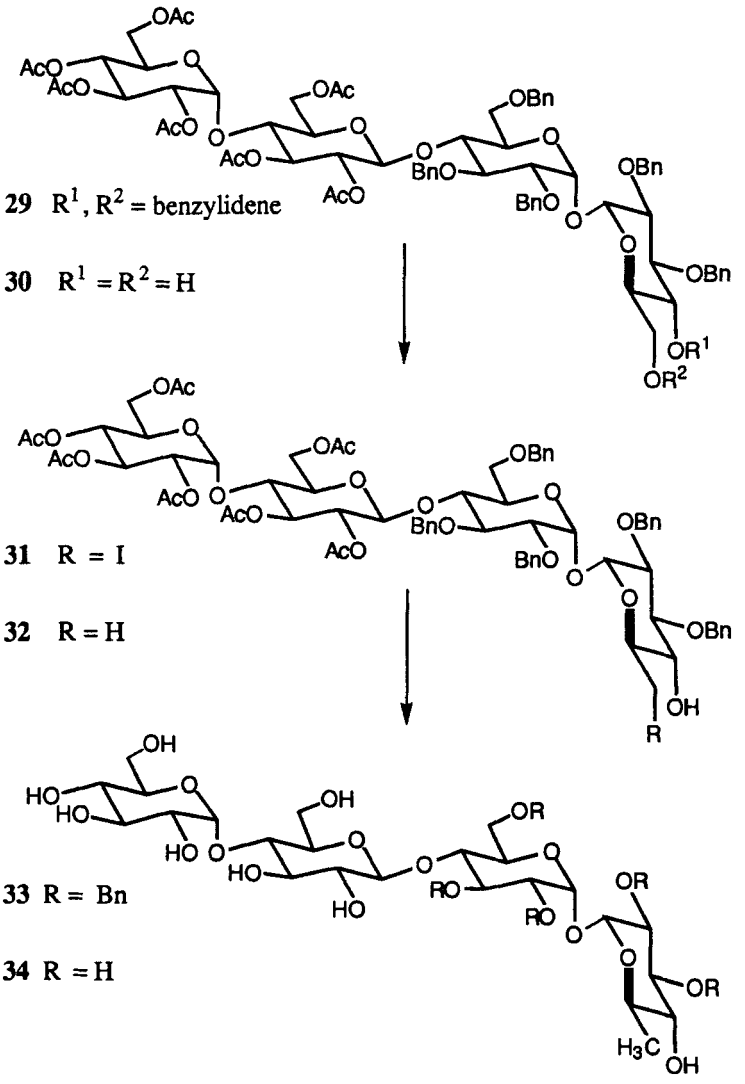
Our starting material for the introduction of the 6'-deoxy function was the diol **22** described before[23] which was iodinated regioselectively at the primary position according to Garegg et al.[27] to afford iodide **23** in 83 % yield (Scheme 4). The iodide was then removed selectively by catalytic hydrogenolysis in the presence of triethylamine to afford the deoxygenated glycosyl acceptor **24**. Upon Koenigs-Knorr glycosylation with acetobromomaltose **25**[31] we obtained tetrasaccharide **26** which was deprotected in the usual way to give **27** after deacetylation and, after catalytic hydrogenolysis, tetrasaccharide **28**, the 6'-deoxygenated analogue of tetrasaccharide **2**.

In contrast to the other protected tetrasaccharides, no up-field shifted acetate signal was observed in the ^{1}H NMR spectrum of **26**; since this tetrasaccharide has no 6'-*O*-benzyl group, this may mean that the up-field shift described above is due to an interaction of 2''-OAc with 6'-OBn.

For the synthesis of the tetrasaccharide deoxygenated in position 6 we could start from tetrasaccharide **29**,[8] the benzylidene protected synthetic precursor of **2**. The benzylidene group was cleaved by hydrolysis to furnish the tetrasaccharide diol **30** in 91 % yield (Scheme 5). Again, selective iodination following the Garegg procedure[27] gave an excellent yield of primary iodide **31** (95 %). The 6-deoxy function was introduced by selective hydrogenolysis (85 %) of the iodo group to give **32** without affecting the benzyl groups. The tetrasaccharide was then deprotected by deacetylation to



Scheme 4



Scheme 5

afford **33** (86 %) followed by catalytic hydrogenolysis to the free saccharide **34** (95 %), the 6-deoxy analogue of tetrasaccharide **2**.

In summary, four analogues of the maltosyl trehalose **2** deoxygenated at the primary position have been prepared in [2+2] block syntheses. Intermediates were made available effectively by regioselective iodination of

a partially protected di- or tetrasaccharide with triphenylphosphine, imidazole, and iodine. An investigation of the antiproliferative activities of the highly sulfated derivatives of the deoxygenated tetrasaccharides **12**, **21**, **28**, and **34** has shown that the sulfate in position 6''' is one of the critical sulfates for this biological effect.[9]

EXPERIMENTAL

General Procedures. Solvents and reagents were bought from Fluka. Evaporation: *in vacuo*, conducted with a Büchi rotary evaporator. TLC: precoated silica gel 60F-254 plates (Merck), detection by UV light (254 nm) and spraying with a 10% soln of concd sulfuric acid in methanol followed by heating. Medium pressure liquid chromatography (MPLC): Lobar column, LiChroprep Si 60 (40 - 63 μm, Merck) at 2 -5 bar (Labomatic MD 80/100 pump). Sonication was performed with TEC-15, 33 kHz. Specific rotations: Perkin-Elmer Polarimeter 241, measured at 20 °C. MS: FAB: MS 902 with data system DS 2050 (VG); thermospray: CSP 46 Finnigan MAT, Bremen; ionspray: API III Sciex, Perkin Elmer; MALDI: Vision 2000, Finnigan, with 2,5-dihydroxybenzoic acid matrix. ^{1}H NMR: Bruker AM-400 (400 MHz) with Aspect 3000, ARX-400 with ASPECT station 1 and z-gradient accessory kit with 10 Amps power amplifier for pulsed field z-gradient (PFG) experiments; chemical shifts in ppm relative to tetramethylsilane or sodium 2,2,3,3-tetradeutero-3-(trimethylsilyl)-propionate as internal standard. Pulse sequence and experimental conditions for the 1D TOCSY and 1D T-ROESY experiments with $(180°_x - 180°_{-x})_n$ spin-lock of 0.6 s duration (n = 2400) and selective excitation by a sequence of DANTE pulses were essentially as described before.[23,32]

Allyl *O*-(2,3-Di-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (4). To a soln of crude (not crystallized after hydrolysis of the isopropylidene acetal) **3**[10] (6.4 g, 10.8 mmol) in toluene (170 mL) was added imidazole (2.20 g, 32.4 mmol), triphenylphosphine (4.28 g, 16.3 mmol), and iodine (3.87 g, 15.2 mmol). The reaction mixture was stirred at 80 °C for 90 min and then poured into water. The organic phase was separated and washed with water twice. The combined organic phases were dried over sodium sulfate and concentrated. The residue was purified by MPLC using ethyl acetate/ hexane 1:1 as eluent to furnish **4** (4.53 g, 60 %) as a colourless foam: $[\alpha]_D$ +27.5 ° (*c* 0.4, dioxane); MS (thermospray) *m*/z 720

(100 %, $[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.85 (dddd ~ ddt, 1H, allyl), 5.37 (d, 1H, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.27, 5.20 (2 dddd ~ dq, 2H, allyl), 5.25 (dd ~ t, 1H, H-3), 5.20 (dd ~ t, 1H, $J_{3',4'}$ = 9.2 Hz, H-3'), 4.87 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-2), 4.81 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 4.57 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.54 (dd, 1H, $J_{5,6a}$ = 2.7 Hz, H-6a), 4.32, 4.10 (2 dddd ~ ddt, 2H, allyl), 4.26 (dd, 1H, $J_{5,6b}$ = 5.0, $J_{6a,6b}$ = 12.0 Hz, H-6b), 4.01 (dd ~ t, 1H, $J_{3,4}$ = 8.9 Hz, H-4), 3.66 (ddd, 1H, $J_{4,5}$ = 9.5 Hz, H-5), 3.52 (dd ~ t, 1H, $J_{4',5'}$ = 9.2 Hz, H-4'), 3.50 (dd, 1H, $J_{5',6a'}$ = 2.7, $J_{6a',6b'}$ = 11.1 Hz, H-6a'), 3.45 (dd, 1H, $J_{5',6b'}$ = 5.0 Hz, H-6b'), 3.39 (ddd, 1H, H-5'), 2.14, 2.10, 2.06, 2.03, 2.01 (5 s, 15H, OAc).

Anal. Calcd for $C_{25}H_{35}IO_{15}$: C, 42.75; H, 5.02; I, 18.07. Found: C, 42.50; H, 5.09; I, 18.87.

***O*-(2,3,4-Tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranosyl)-(1→4)-1,2,3,6-tetra-*O*-acetyl-D-glucopyranose (5) and Oxopropyl *O*-(2,3,4-Tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (6).** To a soln of **4** (4.45 g, 6.33 mmol) in 90 % aqueous acetic acid (300 mL) was added palladium chloride (4.49 g) and sodium acetate (4.49 g). The reaction mixture was sonicated for 3 h and filtered over Speedex, and the residue was washed with ethyl acetate. The combined filtrates were concentrated. The residue was co-evaporated with toluene and acetylated with acetic anhydride (75 mL) in pyridine (150 mL) for 16 h at rt. The reaction mixture was filtered over Speedex, and the residue was washed with ethyl acetate. The filtrates were combined and concentrated. The residue was taken up in ethyl acetate, washed with 2n sulfuric acid/ice, saturated sodium bicarbonate soln/ice and ice water, dried over sodium sulfate, and concentrated. The residue was purified by MPLC using ethyl acetate/ hexane 1:1 as eluent to afford pure **5β** (670 mg, 14 %), α/β-mixture **5** (670 mg, 21 %), and pure **5α** (2.08 g, 44 %) followed by **6** (970 mg, 20 %).

Data for **5β**: $[\alpha]_D$ +62.7 ° (*c* 0.15, dioxane), $[\alpha]_D$ +55.5 ° (*c* 0.2, methanol), ref 20: $[\alpha]_D$ +64.1 ° (*c* 1.3, chloroform), ref 18: $[\alpha]_D^{24}$ +82.4 ° (*c* 0.73, methanol);[19] MS (thermospray) *m/z* 764 (30 %, $[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.75 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 5.42 (d, 1H, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.37 (dd, 1H, $J_{3',4'}$ = 9.5 Hz, H-3'), 5.30 (dd ~ t, 1H, $J_{3,4}$ = 8.8 Hz, H-3), 4.99 (dd, 1H, $J_{2,3}$ = 9.1 Hz, H-2), 4.90 (dd ~ t, 1H, $J_{4',5'}$ = 9.6 Hz, H-4'), 4.83 (dd, 1H, $J_{2',3'}$ = 10.9 Hz, H-2'), 4.48 (dd, 1H, $J_{5,6a}$ = 2.3, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.32 (dd, 1H, $J_{5,6b}$ = 5.0 Hz, H-6b), 4.04 (dd ~ t, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 3.85 (ddd, 1H, H-5), 3.67 (ddd, 1H, H-5'), 3.28 (dd, 1H, $J_{5',6a'}$ = 2.9, $J_{6a',6b'}$ = 11.2 Hz, H-6a'), 3.15 (dd, 1H, $J_{5',6b'}$ = 6.1 Hz, H-6b'), 2.15, 2.10 (2 s, 6H, OAc), 2.06 (s, 6H, OAc), 2.04, 2.03, 2.02 (3 s, 9H, OAc).

Data for **5α**: $[\alpha]_D$ +104.0 ° (*c* 0.2, dioxane); MS (FAB, xenon) *m/z* 785 (35 %, $[M + K]^+$), 769 (55 %, $[M + Na]^+$), 687 (50 %, $[M + H - AcOH]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 6.25 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.51 (dd, 1H, $J_{3,4}$ = 8.7 Hz, H-3), 5.44 (d, 1H, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.40 (dd, 1H, $J_{3',4'}$ = 9.2 Hz, H-3'), 4.98 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 4.93 (dd ~ t, 1H, $J_{4',5'}$ = 10.0 Hz, H-4'), 4.84 (dd, 1H, $J_{2',3'}$ = 10.8 Hz, H-2'), 4.49 (dd, 1H, $J_{5,6a}$ = 2.8, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.30 (dd, 1H, $J_{5,6b}$ = 4.0 Hz, H-6b), 4.12 (ddd, 1H, H-5), 4.04 (dd ~ t, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 3.67 (ddd, 1H, H-5'), 3.29 (dd, 1H, $J_{5',6a'}$ = 2.9, $J_{6a',6b'}$ = 11.2 Hz, H-6a'), 3.16 (dd, 1H, $J_{5',6b'}$ = 5.8 Hz, H-6b'), 2.22, 2.15, 2.10, 2.08, 2.05, 2.01, 2.00 (7 s, 21H, OAc).

Anal. Calcd for $C_{26}H_{35}IO_{17}$: C, 41.84; H, 4.73. Found: C, 41.82; H, 4.76.

Data for **6**: $[\alpha]_D$ +42.5 ° (*c* 0.2, dioxane); MS (FAB, xenon) *m/z* 799 (20 %, $[M + K]^+$), 783 (30 %, $[M + Na]^+$), 761 (5 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.42 (d, 1H, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.37 (dd, 1H, $J_{3',4'}$ = 9.3 Hz, H-3'), 5.28 (dd ~ t, 1H, $J_{3,4}$ = 9.1 Hz, H-3), 4.93 (dd, 1H, $J_{2,3}$ = 9.4 Hz, H-2), 4.89 (dd ~ t, 1H, $J_{4',5'}$ = 9.9 Hz, H-4'), 4.82 (dd, 1H, $J_{2',3'}$ = 10.6 Hz, H-2'), 4.59 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.50 (dd, 1H, $J_{5,6a}$ = 3.0, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.33 (dd, 1H, $J_{5,6b}$ = 5.0 Hz, H-6b), 4.22, 4.15 (2 d, 2H, J_{gem} = 16.8 Hz, OCH_2Ac), 4.02 (dd ~ t, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 3.73 - 3.67 (m, 2H, H-5, H-5'), 3.29 (dd, 1H, $J_{5',6a'}$ = 2.9, $J_{6a',6b'}$ = 11.2 Hz, H-6a'), 3.15 (dd, 1H, $J_{5',6b'}$ = 6.5 Hz, H-6b'), 2.16, 2.15, 2.08, 2.06, 2.05, 2.04, 2.02 (7 s, 21H, OAc).

Anal. Calcd for $C_{27}H_{37}IO_{17}$: C, 42.64; H, 4.90. Found: C, 42.44; H, 5.02.

***O*-(2,3,4-Tri-*O*-acetyl-6-deoxy-α-D-glucopyranosyl)-(1→4)-1,2,3,6-tetra-*O*-acetyl-D-glucopyranose (7).** A soln of **5** (1.86 g, 2.49 mmol) in dioxane (10 mL) and triethylamine (0.1 mL) was hydrogenated in the presence of 10 % palladium on charcoal (1.0 g) at 1.1 bar for 3 days. The reaction mixture was filtered through a pad of filter aid and washed with dioxane, and the filtrate was concentrated. The residue was filtered over silica gel using acetone/hexane 2:3 as eluent to afford pure **7** (1.40 g, 90 %) as a colourless foam: MS (FAB) *m/z* 659 (2 %, $[M + K]^+$), 643 (5 %, $[M + Na]^+$), 561 (5 %, $[M + H]^+$ - AcOH); ^1H NMR ($CDCl_3$, 400 MHz) δ 6.24 (d, $J_{1,2}$ = 3.8 Hz, H-1α), 5.75 (d, $J_{1,2}$ = 8.2 Hz, H-1β), 1.15 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6').

Anal. Calcd for $C_{26}H_{36}O_{17}$: C, 50.32; H, 5.85. Found: C, 49.86; H, 6.96.

***O*-(2,3,4-Tri-*O*-acetyl-6-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl bromide (8).** To a soln of dry **7** (1.3 g, 2.09 mmol) in abs dichloromethane (2 mL) was added a soln of HBr in acetic acid (3 mL) at 0 °C. After 15 min at this temperature, the reaction mixture was allowed to reach rt and was diluted with dichloromethane after a total of 30 min, poured into

ice/ bicarbonate soln and washed with water. The organic phase was dried over magnesium sulfate, concentrated, and purified by chromatography on silica gel using dichloromethane/ ether 95:5 as eluent to give pure **8** (890 mg, 66 %), MS (FAB) *m/z* 681 (35 %, $[M + K]^+$), 665 (50 %, $[M + Na]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 6.51 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 5.62 (dd ~ t, 1H, $J_{3',4'}$ = 9.0 Hz, H-3'), 5.35 (d, 1H, H-1'), 5.33 (dd ~ t, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 4.83 (dd, 1H, $J_{2,3}$ = 10.5 Hz, H-2), 4.77 (dd ~ t, 1H, $J_{4',5'}$ = 10.5 Hz, H-4'), 4.72 (dd, 1H, $J_{1',2'}$ = 4.0 , $J_{2',3'}$ = 9.9 Hz, H-2'), 4.52 (m_c, 1H, H-6a), 4.29 - 4.24 (m, 2H, H-5, H-6b), 4.12 (dd ~ t, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 3.80 (dq, 1H, H-5'), 2.14 (s, 3H, OAc), 2.07 (s, 6H, OAc), 2.04 (s, 6H, OAc), 2.01 (s, 3H, OAc), 1.16 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6').

Anal. Calcd for $C_{24}H_{33}BrO_{15}$: C, 44.94; H, 5.19. Found: C, 44.75; H, 5.24.

***O*-(2,3,4-Tri-*O*-acetyl-6-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (10).** To a soln of dried glycosyl acceptor **9** (221 mg, 0.25 mmol), dried silver triflate (64 mg, 0.25 mmol), and tetramethylurea (32 μL, 0.27 mmol) in abs dichloromethane (2 mL) was added glycosyl donor **8** (160 mg, 0.25 mmol) in abs dichloromethane (2 mL) at 0 °C. The reaction mixture was stirred at this temperature for 15 min, poured into ice/ sodium bicarbonate soln, and extracted with ethyl acetate. The organic phases were dried over sodium sulfate and concentrated. The residue was purified by MPLC using toluene/ ethyl acetate 4:1 as eluents to furnish **10** (179 mg, 50 %) as a colourless foam along with hydrolysis product from **8** (60 mg, 42 %).

Data for **10**: $[\alpha]_D$ +90.0 ° (*c* 0.1, dioxane); MS (FAB) *m/z* 1479 (2 %, $[M + K]^+$), 1463 (3 %, $[M + Na]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.48 - 7.19 (m, 30H, aromat), 5.53 (s, 1H, PhCHO), 5.33 (dd ~ t, 1H, ΣJ = 19.5 Hz, H-3'''), 5.23 (d, 1H, $J_{1''',2'''}$ = 4.0 Hz, H-1'''), 5.13, 5.12 (2d ≈ t, 2H, $J_{1,2} \approx J_{1',2'} \approx 4$ Hz, H-1, H-1'), 4.49 (dd, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 4.26 (ddd ~ dt, 1H, ΣJ = 24.8, $J_{5,6a}$ = 5.0 Hz, H-5), 3.71 (dq, 1H, $J_{4''',5'''}$ = 9.7 Hz, H-5'''), 3.12 (ddd ~ dt, 1H, $J_{5'',6a''} \approx J_{5'',6b''} \approx 3$, $J_{4'',5''}$ = 9.7 Hz, H-5), 2.09, 2.07, 2.01, 1.97, 1.87 (5s, 15H, OAc), 1.71 (s, 3H, 2''-OAc), 1.09 (d, 3H, $J_{5''',6'''}$ = 6.2 Hz, H-6''').

Anal. Calcd for $C_{78}H_{88}O_{26}$: C, 64.99; H, 6.15. Found: C, 64.82; H, 6.24.

***O* - (6-Deoxy-α-D-glucopyranosyl) - (1→4) - *O*-β-D-glucopyranosyl- (1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (11).** To a soln of **10** (160 mg, 0.111 mmol) in methanol (1 mL) and cyclohexane (0.2 mL) was a added a soln of sodium methanolate (2 drops of 2.0 g Na/ 100 mL methanol) at rt. The reaction mixture was kept

for 16 h at rt, neutralized with Amberlite IR 120 (H^+) and filtered. After addition of a few drops of triethylamine, the filtrate and methanol washings were concentrated. The residue was chromatographed on silica gel using ethyl acetate/ methanol/ water 85 : 1 : 1 as eluent to obtain pure **11** (110 mg, 85 %) as a colourless foam: $[\alpha]_D$ +109.0 ° (*c* 0.2, dioxane); MS (FAB) *m/z* 1227 (3 %, $[M + K]^+$), 1211.4 (5 %, $[M + Na]^+$); ^1H NMR ($(CD_3)_2SO$, 400 MHz) δ 7.50 - 7.48 (m, 2H, aromat), 7.39 - 7.23 (m, 28H, aromat), 5.55 (s, 1H, PhCHO), 5.13, 5.11 (2d, 2H, $J_{1,2} = J_{1',2'} = 3.7$ Hz, H-1, H-1'), 4.91 (d, 1H, $J_{1''',2'''} \approx 4$ Hz, H-1'''), 4.38 (dd, 1H, $J_{1'',2''} = 7.8$ Hz, H-1''), 4.25 (ddd ~ dt, 1H, ΣJ = 24.6, $J_{5,6a} = 5.0$ Hz, H-5), 3.08, 2.04 (2 t, 2H, J = 9.1, J = 4.5 Hz, 6-OH, 6'-OH), 1.21 (d, 3H, $J_{5''',6'''} = 6.2$ Hz, H-6''').

Anal. Calcd for $C_{66}H_{76}O_{20}$: C, 66.65; H, 6.44. Found: C, 66.46; H, 6.48.

***O*-(6-Deoxy-α-D-glucopyranosyl)-(1→4)-*O*-β-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl α-D-Glucopyranoside (12).** A soln of **11** (20 mg, 0.017 mmol) in ethanol/water 3:1 (0.5 mL) was hydrogenated in the presence of 10 % palladium on charcoal (10 mg) at 1.1 bar for 48 h. The reaction mixture was filtered through a pad of filter aid and washed with ethanol water 1:1. After addition of a few drops of triethylamine the filtrate was concentrated. The residue was chromatographed on Sephadex LH 20 using water as eluent to obtain pure **12** (11 mg) quantitatively as a colourless solid: $[\alpha]_D$ +140.0 ° (*c* 0.2, water); MS (MALDI, pos.) *m/z* 673 (15 %, $[M + Na]^+$); ^1H NMR (D_2O, 400 MHz) δ 5.35 (d, 1H, $J_{1''',2'''} = 3.4$ Hz, H-1'''), 5.19, 5.18 (2d, 2H, $J_{1,2} \approx J_{1',2'} \approx$ 3.6 Hz, H-1, H-1'), 4.53 (dd, 1H, $J_{1'',2''} = 7.9$ Hz, H-1''), 1.28 (d, 3H, $J_{5''',6'''} = 6.3$ Hz, H-6''').

Anal. Calcd for $C_{24}H_{42}O_{20}$: C, 44.31; H, 6.51. Found: C, 44.22; H, 6.56.

***O*-(6-Deoxy-α-D-glucopyranosyl)-(1→4)-*O*-β-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl 4,6-*O*-Benzylidene-α-D-glucopyranoside (13).** A soln of **11** (140 mg, 0.118 mmol) in ethanol (3 mL) and water (1 mL) was hydrogenated in the presence of 10 % palladium on charcoal (80 mg) at 1.1 bar for 18 h. The reaction mixture was filtered through a pad of filter aid and washed with ethanol water 1:1. After addition of a few drops of triethylamine the filtrate was concentrated. The residue was chromatographed on Sephadex LH 20 using water as eluent to obtain pure **13** (81 mg, 93 %) as a colourless solid: $[\alpha]_D$ +104.5 ° (*c* 0.2, water); MS (MALDI, pos.) *m/z* 761.4 (50 %, $[M + Na]^+$); ^1H NMR (D_2O, 400 MHz; 1D TOCSY, 1D T-ROESY) δ 7.58 - 7.55 (m, 2H, aromat), 7.50 - 7.47 (m, 3H, aromat), 5.77 (s, 1H, PhCHO), 5.35 (d, 1H, $J_{1''',2'''} =$ 3.4 Hz, H-1'''), 5.26 (d, 1H, $J_{1,2} = 3.9$ Hz, H-1), 5.22 (d, 1H, $J_{1',2'} = 3.7$ Hz, H-1'),

4.55 (dd, 1H, $J_{1'',2''}$ = 7.7 Hz, H-1''), 4.32 (dd, 1H, $J_{5,6a}$ = 5.3, $J_{6a,6b}$ = 10.2 Hz, H-6a), 4.10 (ddd ~ dt, 1H, $J_{4,5}$ = 10.0 Hz, H-5), 4.08 (dd ~ t, 1H, $J_{3,4}$ = 9.7 Hz, H-3), 4.00 (dd ~ t, 1H, $J_{3',4'}$ = 8.9 Hz, H-3'), 3.98 (ddd ~ dt, 1H, H-5'), 3.94 (dd, 1H, $J_{5'',6a''} \leq 2$, $J_{6a'',6b''}$ = 11.8 Hz, H-6a''), 3.93 (dd, 1H, $J_{5',6a'}$ = 2.5 Hz, H-6a'), 3.90 (dd ~ t, 1H, $J_{5,6b}$ = 10.0 Hz, H-6b), 3.87 (dd, 1H, $J_{5',6b'}$ = 4.5, $J_{6a',6b'}$ = 12.0 Hz, H-6b), 3.80 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 3.79 (dd ~ t, 1H, $J_{3'',4''}$ = 8.7 Hz, H-3''; dd, 1H, $J_{5'',6b''}$ = 5.4 Hz, H-6b''; dq, 1H, $J_{5''',6'''}$ = 9.8 Hz, H-5'''), 3.73 (dd ~ t, 1H, H-4), 3.72 (dd ~ t, 1H, $J_{2',3'}$ = 10.0 Hz, H-2'), 3.71 (dd ~ t, 1H, H-4'), 3.67 - 3.61 (m, 2H, H-4'', H-5''), 3.63 (dd ~ t, 1H, H-3'''), 3.37 (dd, 1H, $J_{2'',3''}$ = 9.5 Hz, H-2''), 3.17 (dd ~ t, 1H, $J_{2',3'}$ = 10.0 Hz, H-2'), 3.17 (dd ~ t, 1H, $J_{3''',4'''}$ = 8.4 Hz, H-4'''), 1.28 (d, 3H, $J_{5''',6'''}$ = 6.3 Hz, H-6''').

Anal. Calcd for $C_{31}H_{46}O_{20}$: C, 50.41; H, 6.28. Found: C, 50.29; H, 6.32.

Allyl *O*-(2,3-Di-*O*-acetyl-4,6-*O*-isopropylidene-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-acetyl-6-deoxy-6-iodo-β-D-glucopyranoside (15). To a soln of **14**[10] (6.42 g, 15.2 mmol) in tetrahydrofuran (40 mL) was added toluene (40 mL), imidazole (3.11 g, 45.6 mmol), triphenylphosphine (5.99 g, 22.8 mmol), and iodine (5.41 g, 21.3 mmol). During the addition the temperature rose to 36 °C. After stirring for 50 min at 80 °C the reaction mixture was concentrated. The residue was dissolved in pyridine (80 mL), and acetic anhydride (40 mL) was added slowly at 0 °C. After stirring for 16 h at rt the reaction mixture was poured on ice/ water and extracted with ethyl acetate three times. The organic phases were washed with water, dried over sodium sulfate, and concentrated. Crystallization from ethyl acetate gave pure **15** (5.12 g, 48 %). The mother liquor was purified by chromatography on silica gel using ethyl acetate/ hexane 1:2 as eluent to furnish another lot of **15** (4.65 g, 44 %): mp 217 °C; $[\alpha]_D$ +15.0 ° (*c* 0.2, dioxane); MS (thermospray) *m/z* 718 (100 %, $[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.86 (dddd ~ ddt, 1H, allyl), 5.34 (d, 1H, $J_{1',2'}$ = 4.1 Hz, H-1'), 5.30, 5.22 (2 dddd ~ dq, 2H, allyl), 5.26 (2 dd ~ t, 2H, H-3, H-3'), 4.86 (dd, 1H, $J_{2,3}$ = 9.1 Hz, H-2), 4.84 (dd, 1H, $J_{2',3'}$ = 10.2 Hz, H-2'), 4.64 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.35, 4.15 (2 dddd ~ ddt, 2H, allyl), 4.03 (dd, 1H, $J_{5',6a'}$ = 4.5 Hz, $J_{6a',6b'}$ = 10.5 Hz, H-6a'), 3.87 (dd ~ t, 1H, $J_{3,4}$ = 8.8 Hz, H-4), 3.73 and 3.70 - 3.63 (dd ~ t and m, 3H, H-4', H.5', H-6b'), 3.61 (dd, 1H, $J_{5,6a}$ = 2.7, $J_{6a,6b}$ = 10.6 Hz, H-6a), 4.39 (dd, 1H, $J_{5,6b}$ = 5.8, H-6b), 3.29 (ddd, 1H, $J_{4,5}$ = 9.3 Hz, H-5), 2.06, 2.04, 2.02, 1.99 (4 s, 12H, OAc), 1.47, 1.40 (2 s, 6H, CH_3).

Anal. Calcd for $C_{26}H_{37}IO_{14}$: C, 44.58; H, 5.32; I, 18.12. Found: C, 44.51; H, 5.31; I, 18.09.

O-(2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl)-(1→4)-1,2,3-tri-O-acetyl-6-deoxy-6-iodo-D-glucopyranose (16) and **Oxopropyl O-(2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl)-(1→4)-1,2,3-tri-O-acetyl-6-deoxy-6-iodo-β-D-glucopyranoside (17)**. To a soln of **15** (898 mg, 1.28 mmol) in 90 % aqueous acetic acid (50 mL) was added palladium chloride (0.91 g, 5.13 mmol) and sodium acetate (0.91 g). The reaction mixture was sonicated for 5 h, during this time the temperature rose to 49 °C. The mixture was then filtered over Speedex, and the residue was washed with ethyl acetate. The combined filtrates were concentrated. The residue was acetylated with acetic anhydride (11 mL) in pyridine (22 mL) for 17 h at rt. The reaction mixture was poured onto ice/ water and extracted with ethyl acetate. The organic solutions were washed with 2n sulfuric acid/ice, saturated sodium bicarbonate soln/ice and ice water, dried over sodium sulfate, and concentrated. The residue, which contained **16β**, **16α**, and **17** in ratio 2:5:1 by ^{1}H NMR, was chromatographed on silica gel using ethyl acetate/ hexane 1:1 as eluent to afford pure **16** (550 mg, 56 %) as a mixture of anomers. **16β/ 16α** and **16α /17** were separated on an analytical scale.

Data for **16β**: $[\alpha]_D$ +54.0 ° (*c* 0.2, dioxane), ref 28: $[\alpha]_D$ +50 °, ref 29: $[\alpha]_D^{14}$ +51 ° (*c* 1, chloroform); MS (thermospray) *m/z* 764 (40 %, $[M + NH_4]^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.82 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 5.47 (d, 1H, $J_{1',2'}$ = 3.9 Hz, H-1'), 5.36 (dd ~ t, 1H, $J_{3',4'}$ = 9.6 Hz, H-3'), 5.32 (dd ~ t, 1H, $J_{3,4}$ = 8.7 Hz, H-3), 5.09 (dd ~ t, 1H, $J_{4',5'}$ = 10.2 Hz, H-4'), 4.98 (dd , 1H, $J_{2,3}$ = 9.0 Hz, H-2), 4.88 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 4.33 (dd, 1H, $J_{5',6a'}$ = 3.5, $J_{6a',6b'}$ = 12.6 Hz, H-6a'), 4.23 (dd, 1H, $J_{5',6b'}$ = 2.2 Hz, H-6b'), 4.00 (dd ~ t, 1H, $J_{4,5}$ = 9.0 Hz, H-4), 3.85 (ddd ~ br d, 1H, H-5'), 3.60 (dd, 1H, $J_{5,6a}$ = 3.0, $J_{6a,6b}$ = 11.1 Hz, H-6a), 3.41 (dd, 1H, $J_{5,6b}$ = 3.9 Hz, H-6b), 3.36 (ddd, 1H, H-5), 2.11, 2.10, 2.05 2.04, 2.02, 2.015, 2.01 (7 s, 21H, OAc).

Data for **16α**: $[\alpha]_D$ +89.5 ° (*c* 0.2, dioxane); MS (thermospray) *m/z* 764 (100 %, $[M + NH_4]^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.26 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.55 (dd, 1H, $J_{3,4}$ = 8.9 Hz, H-3), 5.49 (d, 1H, $J_{1',2'}$ = 3.9 Hz, H-1'), 5.38 (dd, 1H, $J_{3',4'}$ = 9.7 Hz, H-3'), 5.10 (dd ~ t, 1H, $J_{4',5'}$ = 10.0 Hz, H-4'), 4.96 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 4.89 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 4.36 (dd, 1H, $J_{5',6a'}$ = 3.4, $J_{6a',6b'}$ = 12.6 Hz, H-6a'), 4.24 (dd, 1H, $J_{5',6b'}$ = 1.9 Hz, H-6b'), 3.99 (ddd ~ dt, 1H, H-5'), 3.97 (dd ~ t, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.63 (ddd ~ dt, 1H, H-5), 3.56 (dd, 1H, $J_{5,6a}$ = 2.9 Hz, H-6a), 3.41 (dd, 1H, $J_{5,6b}$ = 3.7, $J_{6a,6b}$ = 12.3 Hz, H-6b), 2.22, 2.12, 2.07, 2.04, 2.03, 2.02, 2.01 (7 s, 21H, OAc).

Anal. Calcd for $C_{26}H_{35}IO_{17}$: C, 41.84; H, 4.73. Found: C, 41.82; H, 4.76.

Data for **17**: MS (thermospray) *m/z* 778 (95 %, $[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 5.44 (d, 1H, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.35 (dd, 1H, $J_{3',4'}$ = 9.4 Hz, H-3'), 5.30 (dd ~ t, 1H, $J_{3,4}$ = 8.6 Hz, H-3), 5.06 (dd ~ t, 1H, $J_{4',5'}$ = 10.3 Hz, H-4'), 4.94 (dd , 1H, $J_{2,3}$ = 9.4 Hz, H-2), 4.86 (dd, 1H, $J_{2',3'}$ = 10.6 Hz, H-2'), 4.67 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.32 (dd, 1H, $J_{5',6a'}$ = 4.0, $J_{6a',6b'}$ = 12.5 Hz, H-6a'), 4.26, 4.20 (2 d, 2H, J_{gem} = 16.9 Hz, OCH_2O), 4.19 (dd, 1H, $J_{5',6b'}$ = 2.2 Hz, H-6b'), 3.97 (ddd, 1H, H-5'), 3.91 (dd ~ t, 1H, $J_{4,5}$ = 9.1 Hz, H-4), 3.59 (dd, 1H, $J_{5,6a}$ = 2.7, $J_{6a,6b}$ = 10.7 Hz, H-6a), 3.35 (dd, 1H, $J_{5,6b}$ = 5.7 Hz, H-6b), 3.36 (ddd, 1H, H-5), 2.21, 2.11, 2.06 (3 s, 9H, OAc), 2.05 (s, 6H, OAc), 2.01, 2.00 (2 s, 6H, OAc).

Anal. Calcd for $C_{27}H_{37}IO_{17}$: C, 42.64; H, 4.90. Found: C, 42.53; H, 4.94.

***O* - (2,3,4,6-Tetra-*O* -acetyl-α-D-glucopyranosyl) - (1→4) - 2,3-di-*O* -acetyl-6-deoxy-6-iodo-α-D-glucopyranosyl Bromide (18).** To a soln of **16** (875 mg, 1.17 mmol) in dichloromethane (10 mL) at 0 °C was added dropwise a soln of HBr (33 %) in acetic acid (2 mL). After 15 min the reaction mixture was poured into ice/ water, the aqueous phase was extracted twice with dichloromethane. The organic phase was washed with bicarbonate soln and water, dried over magnesium sulfate, concentrated, and purified by flash chromatography on silica gel using toluene/ ethyl acetate 78:22 as eluent to give pure **18** (678 mg, 76 %): MS (thermospray) *m/z* 704 (100 %, $[M - Br + OH + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 6.54 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 5.66 (dd ~ t, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 5.49 (d, 1H, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.38 (dd, 1H, $J_{3',4'}$ = 9.9 Hz, H-3'), 5.11 (dd ~ t, 1H, $J_{4',5'}$ = 9.9 Hz, H-4'), 4.89 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 4.70 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 4.36 (dd, 1H, $J_{5',6a'}$ = 3.3, $J_{6a',6b'}$ = 12.6 Hz, H-6a'), 4.25 (dd, 1H, $J_{5',6b'}$ = 2.2 Hz, H-6b'), 4.02 (dd ~ t, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 4.00 (ddd ~ dt, 1H, H-5'), 3.82 (ddd ~ dt, 1H, H-5), 3.59 (dd, 1H, $J_{5,6a}$ = 3.1 Hz, H-6a), 3.48 (dd, 1H, $J_{5,6b}$ = 3.4, $J_{6a,6b}$ = 11.5 Hz, H-6b), 2.11, 2.08, 2.07 (3 s, 9H, OAc), 2.04 (s, 6H, OAc), 2.02 (s, 3H, OAc).

***O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3-di-*O*-acetyl-6-deoxy-6-iodo-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (19).** To a soln of dried glycosyl acceptor **9** (510 mg, 0.58 mmol), dried silver triflate (222 mg, 0.86 mmol), and tetramethylurea (153 μL, 1.28 mmol) in abs dichloromethane (0.6 mL) was added dropwise a soln of glycosyl donor **18** (657 mg, 0.86 mmol) in abs dichloromethane (5 mL) at -30 °C. The reaction mixture was allowed to reach rt and was continued to stir for 4 days. Then it was filtered and concentrated. The residue was purified by flash chromatography using

toluene/ ethyl acetate 4:1 as eluents to furnish **19** (490 mg, 54 %) as a colourless foam along with unchanged acceptor **9** (132 mg, 26 %) and the hydrolysis product from **18** (370 mg).

Data for **17**: $[\alpha]_D$ +74.0 ° (*c* 0.3, chloroform); MS (FAB) *m/z* 1605 (3 %, [M + K]$^+$, 1589 (4%, [M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz; H,H-COSY) δ 7.53 - 7.17 (m, 30H, aromat), 5.53 (s, 1H, CHPh), 5.38 (dd, 1H, $J_{3''',4'''}$ = 9.4 Hz, H-3'''), 5.36 (d, 1H, H-1'''), 5.13 (d, 1H, $J_{1,2}$ ≈ 3.8 Hz, H-1), 5.12 (d, 1H, $J_{1',2'}$ = 3.8 Hz, H-1'), 5.08 (dd ~ t, 1H, $J_{4''',5'''}$ = 10.2 Hz, H-4'''), 5.07, 4.79 (2 d, 2H, CH_2Ph), 5.03 (dd ~ t, 1H, H-3''), 5.00, 4.89 (2 d, 2H, J_{gem} = 11.1 Hz, CH_2Ph), 4.87 (dd, 1H, $J_{1''',2'''}$ = 4.0 Hz, $J_{2''',3'''}$ = 10.6 Hz, H-2'''), 4.76, 4.37 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.74, 4.68 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.71 (dd ~ t, 1H, $J_{2'',3''}$ = 9.2 Hz, H-2''), 4.70, 4.64 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.52 (d, 1H, $J_{1'',2''}$ = 8.1 Hz, H-1''), 4.31 (dd, 1H, $J_{5''',6a'''}$ = 3.7 Hz, $J_{6a''',6b'''}$ = 12.1 Hz, H-6a'''), 4.25 (ddd ~ dt, 1H, $J_{5,6a}$ = 5.0, $J_{4,5}$ = 10.0 Hz, H-5), 4.17 (dd, 1H, $J_{5''',6b'''}$ = 2.0 Hz, H-6b'''), 4.13 (dd ~ t, 1H, $J_{3,4}$ ≈ 9 Hz, H-3), 4.06 (dd, 1H, $J_{5,6a}$ = 4.9, $J_{6a,6b}$ = 10.2 Hz, H-6a), 4.02 (ddd ~ br d, 1H, $J_{4',5'}$ = 9.7 Hz, H-5'), 3.95 (dd ~ t, 1H, H-3'), 3.91 (ddd ~ dt, 1H, H-5'''), 3.89 (dd ~ t, 1H, H-4'), 3.75 (dd ~ t, 1H, ΣJ = 17.6 Hz, H-4''), 3.63 (dd, 1H, $J_{5',6a'}$ ≈ 2.5 Hz, H-6a'), 3.62 (dd ~ t, 1H, $J_{5,6b}$ = 10.0 Hz, H-6b), 3.61 (dd ~ t, 1H, H-4), 3.57 (dd, 1H, $J_{2,3}$ ≈ 9 Hz, H-2), 3.52 (dd, 1H, $J_{2',3'}$ ≈ 9 Hz, H-2'), 3.48 (dd, 1H, $J_{5',6b'}$ ≈ 1.2 Hz, $J_{6a',6b'}$ ≈ 10.5 Hz, H-6b'), 3.33 (dd, 1H, $J_{5'',6b''}$ = 2.5, $J_{6a'',6b''}$ = 11.0 Hz, H-6a''), 3.02 (dd, 1H, $J_{5'',6b''}$ = 4.8 Hz, H-6b''), 2.63 (ddd, 1H, $J_{4'',5''}$ = 9.4 Hz, H-5''), 2.09, 2.08, 2.05, 2.02, 1.97 (6 s, 18H, OAc), 1.72 (s, 3H, 2''-OAc).

Anal. Calcd for $C_{78}H_{87}IO_{26}$: C, 59.77; H, 5.59. Found: C, 59.91; H, 5.71.

***O*-α-D-Glucopyranosyl-(1→4)-*O*-(6-deoxy-6-iodo-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (20).** To a soln of **19** (270 mg, 0.172 mmol) in abs methanol (25 mL) and tetrahydrofuran (5 mL) was a added a catalytic amount of sodium. The reaction mixture was kept for 25 min at rt, neutralized with Amberlite IR 120 (H$^+$) and filtered. The filtrate and methanol washings were concentrated, and the residue was filtered over silica gel using chloroform/ methanol 85 : 15 as eluent to obtain pure **20** (226 mg) quantitatively as a hygroscopic colourless foam: $[\alpha]_D$ +91.3 ° (*c* 0.3, chloroform); MS (FAB) *m/z* 1353 (65 %, [M + K]$^+$), 1337 (100 %, [M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 - 7.48 (m, 2H, aromat), 7.39 - 7.20 (m, 28H, aromat), 5.54 (s, 1H, PhCHO), 5.10, 5.07 (2d, 2H, $J_{1,2} = J_{1',2'}$ = 3.7 Hz, H-1, H-1'), 4.23 (ddd ~ dt, 1H, ΣJ = 24.8, $J_{5,6a}$ = 5.0 Hz, H-5), 2.54 (ddd ~ br d, 1H, H-5'').

Anal. Calcd for $C_{66}H_{76}O_{20}$: C, 60.27; H, 5.75. Found: C, 60.06; H, 5.83.

***O*-α-D-Glucopyranosyl-(1→4)-*O*-(6-deoxy-β-D-glucopyranosyl)-(1→4)-α-D-glucopyranosyl α-D-Glucopyranoside (21).** A soln of **20** (182 mg, 0.138 mmol) in ethanol/water 4:1 (20 mL) was hydrogenated in the presence of 10 % palladium on charcoal (200 mg) at 1.1 bar. The reaction mixture was filtered through a pad of filter aid and washed with ethanol/ water 1:1. A few drops of triethylamine were added, and the filtrates were concentrated and reacted again as described above. This procedure was repeated several times. After a total reaction time of 72 h the worked-up reaction mixture was chromatographed on Sephadex LH 20 using water as eluent to obtain pure **21** (90 mg) quantitatively as a colourless solid: MS (MALDI, pos.) *m/z* 673 (45 %, $[M + Na]^+$); ^1H NMR (D_2O, 400 MHz) δ 5.43 (d, 1H, $J_{1''',2'''}$ = 3.7 Hz, H-1'''), 5.18 (2d, 2H, $J_{1,2} \approx J_{1',2'} \approx$ 3.6 Hz, H-1, H-1'), 4.49 (dd, 1H, $J_{1'',2''}$ = 7.9 Hz, H-1''), 1.36 (d, 3H, $J_{5'',6''}$ = 6.1 Hz, H-6'').

Anal. Calcd for $C_{24}H_{42}O_{20}$: C, 44.31; H, 6.51. Found: C, 44.24; H, 6.58.

2,3-Di-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (23). To a soln of diol **22** (6.68 g, 8.42 mmol) in acetonitrile (33 mL) and toluene (66 mL) were added triphenylphosphine (4.94 g, 18.8 mmol) and imidazole (2.6 g, 38.2 mmol); the reaction mixture was then heated to 70 °C, and iodine (4.45 g, 17.5 mmol) was added in one portion. The reaction temperature was then reduced to 50 °C and held at this temperature for 1 h. The dark brown reaction mixture was then cooled and, after addition of ice water, extracted twice with ethyl acetate. The combined organic layers were washed with ice water and brine, dried over magnesium sulfate, and concentrated. The residue was chromatographed on silica gel with ethyl acetate/ hexane 1:4 as eluent to furnish **23** (6.31 g, 83%) as a colourless foam: $[\alpha]_D$ + 76.6 ° (*c* 0.5, chloroform); MS (FAB) *m/z* 939 (25 %, $[M + K]^+$), 901 (75 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.52 - 7.50 (m, 2H, aromat), 7.42 - 7.25 (m, 23H, aromat), 5.57 (s, 1H, CHPh), 5.24 (d, 1H, $J_{1',2'}$ = 3.7 Hz, H-1'), 5.19 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 5.03, 4.73 (2 d, 2H, J_{gem} = 11.3 Hz, CH_2Ph), 4.98, 4.85 (2 d, 2H, J_{gem} = 11.2 Hz, CH_2Ph), 4.86, 4.75 (2 d, 2H, J_{gem} = 11.8 Hz, CH_2Ph), 4.73, 4.69 (2 d, 2H, J_{gem} = 11.9 Hz, CH_2Ph), 4.23 (ddd ~ dt, 1H, $J_{5,6a}$ = 4.9, $J_{4,5}$ = 10.1 Hz, H-5), 4.13 (dd ~ t, 1H, $J_{3,4}$ = 8.9 Hz, H-3), 4.12 (dd, 1H, $J_{6a,6b}$ = 10.2 Hz, H-6a), 3.89 (dd ~ t, 1H, $J_{3',4'}$ = 9.2 Hz, H-3'), 3.69 (dd ~ t, 1H, $J_{5,6b}$ = 10.0 Hz, H-6b), 3.66 (dd ~ t, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 3.64 (dd, 1H, $J_{2',3'}$ = 9.2 Hz, H-2'), 3.61 (ddd, 1H, $J_{4',5'}$ = 9.4 Hz, H-5'), 3.57 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 3.38 (ddd ~ dt, 1H, H-4'), 3.19 (dd, 1H, $J_{5',6a'}$ = 4.8, $J_{6a',6b'}$ =

11.0 Hz , H-6a'), 3.15 (dd, 1H, $J_{5',6b'}$ = 3.0 Hz, H-6b'), 2.11 (d, 1H, $J_{4',4'\text{-OH}}$ = 3.0 Hz, 4'-OH).

Anal. Calcd for $C_{47}H_{49}IO_{10}$: C, 62.67; H, 5.48. Found: C, 62.59; H, 5.56.

2,3-Di-*O*-benzyl-6-deoxy-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (24). A soln of iodide **23** (5.61 g, 6.23 mmol) in ethanol (140 mL) and triethylamine (3 mL) was hydrogenated in the presence of 5% palladium on charcoal (6.0 g) at 1.1 bar and rt for 3.5 h. The reaction mixture was filtered through a pad of filter aid and washed with ethanol. The filtrate was concentrated under diminished pressure, and the residue was chromatographed on silica gel using ethyl acetate/ hexane 1:4 and 1:3 as eluent to obtain **24** (3.0 g, 57 %) as a colourless foam; $[\alpha]_D$ +72.2 ° (*c* 0.4, chloroform); MS (ionspray) *m/z* 793.0 (95 %, $[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.52 - 7.50 (m, 2H, aromat), 7.41 - 7.24 (m, 23H, aromat), 5.56 (s, 1H, CHPh), 5.16 (d, 1H, $J_{1',2'}$ = 3.7 Hz, H-1'), 5.12 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.03, 4.74 (2 d, 2H, J_{gem} = 11.4 Hz, CH_2Ph), 4.96, 4.86 (2 d, 2H, J_{gem} = 11.2 Hz, CH_2Ph), 4.80, 4.72 (2 d, 2H, J_{gem} = 12.1 Hz, CH_2Ph), 4.74, 4.69 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.25 (ddd ~ dt, 1H, $J_{5,6a}$ = 4.9, $J_{4,5}$ = 9.9 Hz, H-5), 4.12 (dd ~ t, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 4.11 (dd, 1H, $J_{6a,6b}$ = 10.0 Hz, H-6a), 4.09 (dq, 1H, H-5'), 3.82 (dd ~ t, 1H, $J_{3',4'}$ = 9.2 Hz, H-3'), 3.66 (dd ~ t, 1H, $J_{5,6b}$ = 10.0 Hz, H-6b), 3.64 (dd ~ t, 1H, H-4), 3.61 (dd, 1H, $J_{2',3'}$ = 9.3 Hz, H-2'), 3.56 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.19 (ddd ~ dt, 1H, $J_{4',5'}$ = 9.3 Hz, H-4'), 2.13 (d, 1H, $J_{4',4'\text{-OH}}$ = 2.9 Hz, 4'-OH), 1.16 (dd, 1H, $J_{5',6'}$ = 6.2 Hz, H-6').

Anal. Calcd for $C_{47}H_{50}O_{10}$: C, 72.85; H, 6.50. Found: C, 72.79; H, 6.52.

***O* - (2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl) - (1—>4) - *O* - (2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl) - (1—>4) - 2,3-di-*O* -benzyl-6-deoxy-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (26).** To a soln of **24** (2.86 g, 3.7 mmol) and acetobromomaltose **25** (3.90 g, 5.55 mmol) in abs dichloromethane (15 mL) was added tetramethylurea (1.33 mL, 11.1 mmol) and silver triflate (1.44 g, 5.6 mmol) at -10 °C. The reaction mixture was stirred at 0 - 5 °C for 1 h, then at rt over night. The reaction mixture was filtered through a pad of filter aid and washed with dichloromethane, and the filtrate was washed twice with saturated sodium bicarbonate soln. The organic layers were dried over magnesium sulfate and concentrated. The residue was chromatographed on silica gel using ethyl acetate/ hexane 1:1 and 2:1 as eluents to produce **26** (2.55 g, 50%) as a colourless foam: $[\alpha]_D$ +84.6 ° (*c* 0.5, chloroform); MS (ionspray) *m/z* 1411.6 (95 %, $[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.51 - 7.48 (m, 2H, aromat), 7.43 - 7.22 (m, 23H, aromat),

5.54 (s, 1H, CHPh), 5.36 (d, 1H, $J_{1''',2'''}$ = 4.0 Hz, H-1'''), 5.30 (dd ~ t, 1H, $J_{3''',4'''}$ = 9.4 Hz, H-3'''), 5.17 (dd ~ t, 1H, $J_{3'',4''}$ = 9.0 Hz, H-3''), 5.09, 5.05 (2 d, 2H, $J_{1,2}$ = $J_{1',2'}$ = 3.7 Hz, H-1, H-1'), 5.04 (dd ~ t, 1H, $J_{4''',5'''}$ = 10.3 Hz, H-4'''), 5.00, 4.96 (2 d, 2H, J_{gem} = 11.8 Hz, CH_2Ph), 4.99, 4.90 (2 d, 2H, J_{gem} = 11.0 Hz, CH_2Ph), 4.88 (d, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 4.83 (dd, 1H, $J_{2''',3'''}$ = 10.6 Hz, H-2'''), 4.80 (dd ~ t, 1H, $J_{2'',3''}$ = 9.2 Hz, H-2''), 4.76, 4.69 (2 d, 2H, J_{gem} = 12.5 Hz, CH_2Ph), 4.64, 4.60 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.23 (ddd ~ dt, 1H, $J_{5,6a}$ = 5.0, $J_{4,5}$ = 10.0 Hz, H-5), 4.21 (dd, 1H, $J_{5''',6a'''}$ = 3.5 Hz, $J_{6a''',6b'''}$ = 12.5 Hz, H-6a'''), 4.13 (dd ~ t, 1H, H-3), 4.12 (dq, 1H, H-5'), 4.08 (dd, 1H, $J_{5'',6b''}$ ≈ 4, $J_{6a'',6b''}$ ≈ 11 Hz, H-6a''), ~4.05 (dd, 1H, $J_{5''',6b'''}$ = 2.0 Hz, H-6b'''), 3.99 - 3.93 (m, 4H, H-6a, H-3', H-4'', H-6b''), 3.82 (ddd ~ dt, 1H, $J_{4''',5'''}$ = 10.0 Hz, H-5'''), 3.62 (dd ~ t, 1H, $J_{5,6b}$ ≈ 10 Hz, H-6b), 3.61 (dd ~ t, 1H, H-4), 3.57, 3.51 (2 d, 2H, J = 9.3 Hz, J = 9.5 Hz, H-2, H-2'), 2.63 (ddd ~ dt, 1H, $J_{4'',5''}$ = 9.4 Hz, H-5''), 3.34 (dd ~ t, 1H, H-4'), 2.07, 2.03, 2.02, 2.00, 1.98, 1.97, 1.89 (7s, 21H, OAc), 1.15 (dd, 1H, $J_{5',6'}$ = 6.3 Hz, H-6').

Anal. Calcd for $C_{73}H_{84}O_{27}$: C, 62.92; H, 6.08. Found: C, 62.81; H, 6.12.

***O*-α-D-Glucopyranosyl - (1—>4) -*O*-β-D-glucopyranosyl - (1—>4)-2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (27).** To a soln of **26** (2.43 g, 1.75 mmol) in diethyl ether (5 mL) and methanol (25 mL) was added a soln of sodium methanolate (5 mL of 2 g Na/ 100 mL methanol) at rt. The reaction mixture was stirred for 4 h at rt, neutralized with Amberlite IR 120 (H^+), and filtered. After addition of a few drops of triethylamine, the filtrate and methanol washings were concentrated. The residue was chromatographed on silica gel using ethyl acetate/ methanol/ water 96:2:2 as eluent to obtain **27** (1.85 g, 96%) as a colourless foam: $[\alpha]_D$ +112.4 ° (*c* 0.5, chloroform); MS (FAB) *m/z* 1137.3 (60 %, $[M + K]^+$), 1121.3 (42 %, $[M + Na]^+$); ^1H NMR ($(CD_3)_2SO$, 400 MHz) δ 7.42 - 7.21 (m, 3H, aromat), 5.68 (s, 1H, PhCHO), 5.49 (d, 1H, J = 3.0 Hz, OH), 5.44 (d, 1H, J = 6.0 Hz, OH), 5.24 (d, 1H, J ≈ 5.8 Hz, OH), 5.25, 5.18, 5.02 (3 d, 3H, H-1''', H-1, H-1'), 4.97, 4.71 (2 d, 2H, J_{gem} = 11.0 Hz, CH_2Ph), 4.92 (d, 1H, J = 5.8 Hz, OH), 4.90 (d, 1H, J = 5.0 Hz, OH), 4.80, 4.76 (2 d, 2H, J_{gem} = 11.7 Hz, CH_2Ph), 4.71 (s, 2H, CH_2Ph), 4.68, 4.63 (2 d, 2H, J_{gem} = 11.9 Hz, CH_2Ph), 4.55 (t, 1H, J = 5.4 Hz, OH), 4.47 (d, 1H, $J_{1'',2''}$ = 7.7 Hz, H-1''), 4.20 (t, 1H, J = 5.5 Hz, OH), 1.28 (d, 3H, $J_{5',6'}$ = 6.2 Hz, H-6').

Anal. Calcd for $C_{59}H_{70}O_{20}$: C, 64.47; H, 6.42. Found: C, 64.33; H, 6.46.

***O*-α-D-Glucopyranosyl-(1—>4)-*O*-β-D-glucopyranosyl-(1—>4)-6-deoxy-α-D-glucopyranosyl α-D-Glucopyranoside (28).** A soln of **27** (1.80 g, 1.64 mmol) in ethanol (45 mL) and water (15 mL) was hydrogenated in the presence of

10 % palladium on charcoal at 1.1 bar and rt for 6 h. The reaction mixture was filtered through a pad of filter aid and washed with ethanol/water 1:1. The filtrate was concentrated and the aqueous residue was lyophilized to obtain **28** (1.07 g, 99 %): $[\alpha]_D$ +139.6 ° (*c* 0.5, water); MS (FAB) *m/z* 759.1 (100 %, [M + K]$^+$), 743.0 (70 %, [M + Na]$^+$), 721 (72 %, [M + H]$^+$); ^{1}H NMR (D_2O, 400 MHz) δ 5.42 (d, 1H, $J_{1''',2'''}$ = 3.9 Hz, H-1'''), 5.17, 5.14 (2 d, 2H, J = 3.8, J = 3.8 Hz, H-1, H-1'), 4.59 (dd, 1H, $J_{1'',2''}$ = 7.9 Hz, H-1''), 1.35 (d, 3H, $J_{5',6'}$ = 6.3 Hz, H-6').

Anal. Calcd for $C_{24}H_{42}O_{20}$: C, 44.31; H, 6.51. Found: C, 44.26; H, 6.54.

***O* - (2,3,4,6-Tetra-*O* -acetyl-α-D-glucopyranosyl) - (1—>4) - *O* - (2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1—>4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-α-D-glucopyranoside (30).** A soln of tetrasaccharide **29** (10.5 g, 7.5 mmol) in 80 % aqueous acetic acid (105 mL) was heated to 80 °C for 1 h and then concentrated under diminished pressure. The oily residue was taken up in ethyl acetate, washed three times with saturated sodium bicarbonate soln and once with brine, dried over magnesium sulfate, and concentrated. The residue was chromatographed on silica gel using ethyl acetate/ hexane 1:1 and 2:1 as eluent to furnish **30** (9.05 g, 92 %) as a foam; $[\alpha]_D$ +91.4 ° (*c* 0.5, chloroform); MS (FAB) *m/ z* 1433.4 (70 % , [M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 - 7.19 (m, 25H, aromat), 5.38 (dd ~ t, 1H, H-3'''), 5.32 (d, 1H, $J_{1''',2'''}$ = 3.9 Hz, H-1'''), 5.17, 5.14 (2 d, 2H, J = 3.4, J = 3.8 Hz, H-1, H-1'), 5.06 (dd ~ t, 1H, H-4'''), 5.06, 4.73 (2 d, 2H, CH_2Ph), 5.03, 4.83 (2 d, 2H, J_{gem} = 11.0 Hz, CH_2Ph), 5.02 (dd ~ t, 1H, H-3''), 4.86 (dd, 1H, $J_{2''',3'''}$ = 10.5 Hz, H-2'''), 4.75 (d, 1H, J_{gem} = 11.5 Hz, CH_2Ph), 4.74 (dd, 1H, $J_{2'',3''}$ ≈ 9.2 Hz, H-2''), 4.68 - 4.63 (m, 3H, CH_2Ph), 4.59 (d, 1H, J_{gem} = 12.0 Hz, CH_2Ph), 4.48 (d, 1H, $J_{1'',2''}$ = 8.1 Hz, H-1''), 4.38 (d, 1H, J_{gem} = 11.8 Hz, CH_2Ph), 4.21 (dd, 1H, $J_{5''',6a'''}$ = 3.6 Hz, $J_{6a''',6b'''}$ = 12.5 Hz, H-6a'''), 4.13 (dd, 1H, $J_{5'',6b''}$ = 2.7, $J_{6a'',6b''}$ = 12.2 Hz, H-6a''), 4.06 (dd, 1H, $J_{5'',6b''}$ = 3.9 Hz, H-6b''), 4.00 - 3.96 (m, 3H), 3.92 - 3.82 (m, 5H), 3.64 - 3.55 (m, 4H), 3.53, 3.51 (2 d, 2H, J = 9.1 Hz, J = 9.5 Hz, H-2, H-2'), 3.46 (dd, 1H, $J_{5',6b'}$ ≈ 1.4, $J_{6a',6b'}$ = 10.8 Hz, H-6b'), 3.15 (ddd ~ dt, 1H, $J_{4'',5''}$ = 9.6 Hz, H-5''), 2.32 (d, 1H, $J_{4,4\text{-OH}}$ = 3.2 Hz, 4-OH), 2.10, 2.07, 2.04, 2.02, 1.96, 1.92 (6s, 18H, OAc), 1.72 (s, 3H, 2''-OAc), 1.59 (t, 1H, $J_{6,6\text{-OH}}$ = 6.3 Hz, 6-OH).

Anal. Calcd for $C_{73}H_{86}O_{28}$: C, 62.12; H, 6.14. Found: C, 62.08; H, 6.18.

***O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1—>4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1—>4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside (31).** To a soln of **30** (8.5 g, 6.0 mmol) in acetonitrile/ toluene 1:2 (72 mL) was added triphenylphosphine (3.6 g, 13.8 mmol) and imidazole (1.91 g, 28 mmol); the reaction mixture was

then heated to 70 °C and iodine (3.27 g, 12.8 mmol) was added in one portion. The reaction temperature rose to 80 °C. The mixture was further stirred at 70 °C for 1 h, then cooled, and, after addition of ice water, extracted twice with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate and concentrated. The residue was chromatographed on silica gel using ethyl acetate/ hexane 2:3 as eluent to furnish **31** (8.7 g, 95%) as a colourless foam: $[\alpha]_D$ + 90.6 ° (*c* 0.5, chloroform); MS (FAB) *m/z* 1543.2 (58 %, $[M + Na]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.48 - 7.19 (m, 25H, aromat), 5.38 (dd ~ t, 1H, H-3'''), 5.32 (d, 1H, $J_{1''',2'''}$ = 3.9 Hz, H-1'''), 5.22, 5.20 (2 d, 2H, J = 3.7, J = 3.4 Hz, H-1, H-1'), 5.06 (dd ~ t, 1H, H-4'''), 5.06, 4.79 (2 d, 2H, J_{gem} = 11.5 Hz, CH_2Ph), 5.03 (d, 1H, CH_2Ph), 5.02 (dd ~ t, 1H, H-3''), 4.86 (dd, 1H, $J_{2''',3'''}$ = 10.5 Hz, H-2'''), 4.75 (d, 1H, CH_2Ph), 4.74 (dd, 1H, $J_{2'',3''}$ = 9.2 Hz, H-2''), 4.73 - 4.60 (m, 5H, CH_2Ph), 4.49 (d, 1H, $J_{1'',2''}$ = 8.2 Hz, H-1''), 4.39 (d, 1H, J_{gem} = 12.0 Hz, CH_2Ph), 4.21 (dd, 1H, $J_{5''',6a'''}$ = 3.5 Hz, $J_{6a''',6b'''}$ = 12.5 Hz, H-6a'''), 4.13 (dd, 1H, $J_{5'',6b''}$ = 2.5, $J_{6a'',6b''}$ = 12.0 Hz, H-6a''), 4.05 (dd, 1H, $J_{5'',6b''}$ = 3.9 Hz, H-6b''), 4.00 -3.82 (m, 5H), 3.62 (dd, 1H, $J_{5',6a'}$ = 2.5, $J_{6a',6b'}$ = 10.9 Hz, H-6a'), 3.57 - 3.52 (m, 3H), 3.46 (dd, 1H, $J_{5',6b'}$ ≈ 1 Hz, H-6b'), 3.37 (ddd ~ dt, 1H, $J_{4,4\text{-OH}}$ = 3.4 Hz, H-4), 3.19 (dd, 1H, $J_{5,6a}$ = 4.5, $J_{6a,6b}$ = 11.0 Hz, H-6a), 3.16 (ddd ~ dt, 1H, H-5''), 3.08 (dd, 1H, $J_{5,6b}$ = 2.8 Hz, H-6b), ~2.10 (d, 1H, 4-OH), 2.10, 2.07, 2.04, 2.02, 1.96, 1.93 (7s, 21H, OAc), 1.72 (s, 3H, 2''-OAc).

Anal. Calcd for $C_{73}H_{85}IO_{27}$: C, 57.63; H, 5.63. Found: C, 57.53; H, 5.66.

***O* - (2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl) - (1—>4) - *O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1—>4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-6-deoxy-α–D-glucopyranoside (32).** A soln of **31** (8.5 g, 5.6 mmol) in dimethoxyethane (17 mL), ethanol (170 mL), and triethylamine (8.5 mL) was hydrogenated in the presence of 5% palladium on charcoal (5.0 g) at 1.1 bar and rt for 4 h. The reaction mixture was filtered through a pad of filter aid and washed with ethanol. The filtrate was then concentrated under diminished pressure. The residue was chromatographed on silica gel using ethyl acetate/ hexane 1:1 and 2:1 as eluents to obtain **32** (6.63 g, 85%) as a colourless foam: $[\alpha]_D$ + 85.4 ° (*c* 0.5, chloroform); MS (FAB) *m/ z* 1433.3 (45%, $[M + K]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.44 - 7.22 (m, 25H, aromat), 5.39 (dd ~ t, 1H, H-3'''), 5.32 (d, 1H, $J_{1''',2'''}$ = 3.9 Hz, H-1'''), 5.15, 5.13 (2 d, 2H, J = 3.7, J = 3.4 Hz, H-1, H-1'), 5.07, 4.81 (2 d, 2H, J_{gem} = 11.4 Hz, CH_2Ph), 5.06 (dd ~ t, 1H, H-4'''), 5.02, 4.74 (2 d, 2H, J_{gem} = 11.5 Hz, CH_2Ph), 5.01 (dd ~ t, 1H, H-3''), 4.86 (dd, 1H, $J_{2''',3'''}$ = 10.6 Hz, H-2'''), 4.74, 4.37 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.73 (dd ~ t, 1H, H-2''), 4.67, 4.62 (2 d, 2H, J_{gem} = 12.2 Hz, CH_2Ph), 4.64, 4.60 (2 d, 2H,

J_{gem} = 12.2 Hz, CH_2Ph), 4.48 (d, 1H, $J_{1'',2''}$ = 8.1 Hz, H-1''), 4.21 (dd, 1H, $J_{5''',6a'''}$ = 3.5 Hz, $J_{6a''',6b'''}$ = 12.5 Hz, H-6a'''), 4.13 (dd, 1H, $J_{5'',6b''}$ = 2.4, $J_{6a'',6b''}$ = 12.0 Hz, H-6a''), 4.09 - 4.03 (m, 2H), 3.99 - 3.96 (m, 2H), 3.91 - 3.79 (m, 5H), 3.62 (dd, 1H, $J_{5',6a'}$ = 2.5, $J_{6a',6b'}$ = 10.9 Hz, H-6a'), 3.53, 3.51 (2 d, 2H, H-2, H-2'), 3.44 (dd ~ br d, 1H, $J_{5',6b'} \leq$ 1.5 Hz, H-6b'), 3.18 (dd ~ t, 1H, H-4), 3.14 (ddd ~ dt, 1H, H-5''), 2.10, 2.07, 2.04, 2.02, 1.96, 1.92 (7s, 21H, OAc), 1.71 (s, 3H, 2''-OAc), 1.13 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6).

Anal. Calcd for $C_{73}H_{86}O_{27}$: C, 62.83; H, 6.21. Found: C, 62.78; H, 6.24.

***O*-α-D-Glucopyranosyl-(1—>4)-*O*-β-D-glucopyranosyl-(1—>4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3-Di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (33).** To a soln of **32** (6.3 g, 4.52 mmol) in diethyl ether (15 mL) and methanol (75 mL) was added a soln of sodium methanolate (12 mL of 2 g Na/100 mL methanol) at rt. The reaction mixture was stirred for 4 h at rt, neutralized with Amberlite IR 120 (H^+), and filtered. After addition of a few drops of triethylamine, the filtrate and methanol washings were concentrated. The residue was chromatographed on silica gel using ethyl acetate/ methanol/ water 96:2:2 and 92:4:4 as eluents to obtain **33** (4.31 g, 86%) as a colourless foam: $[\alpha]_D$ +123.0 ° (*c* 0.4, chloroform); MS (ionspray) *m/ z* 1118.8 (95 %, $[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.33 - 7.20 (m, 25H, aromat), 5.14, 5.07 (2 d, 2H, J = 3.2, J = 3.1 Hz, H-1, H-1'), 5.01 (d ~ br s, 1H, H-1'''), 4.97, 4.71 (2 d, 2H, J_{gem} = 11.3 Hz, CH_2Ph), 4.91, 4.87 (2 d, 2H, J_{gem} = 12.4 Hz, CH_2Ph), 4.63, 4.59 (2 s, 4H, CH_2Ph), 4.51, 4.43 (2 d, 2H, J_{gem} = 12.1 Hz, CH_2Ph), 4.38 (d, 1H, $J_{1'',2''}$ = 7.3 Hz, H-1''), 1.12 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6).

Anal. Calcd for $C_{59}H_{72}O_{20}$: C, 64.35; H, 6.59. Found: C, 64.31; H, 6.61.

***O* -α-D-Glucopyranosyl - (1—>4) - *O* -β-D-glucopyranosyl - (1—>4) - α-D-glucopyranosyl 6-Deoxy-α-D-glucopyranoside (34).** A soln of **33** (3.93 g 3.5 mmol) in ethanol (90 mL) and water (30 mL) was hydrogenated in the presence of 10% palladium on charcoal (2.0 g) at 1.1 bar and rt for 6 h. The reaction mixture was filtered through a pad of filter aid and washed with ethanol/ water. After addition of a few drops of triethylamine, the filtrate was concentrated. The residue was chromatographed on silica gel using ethyl acetate/ methanol/ water 6:2:2 and 3:2:1 as eluents. The product containing fractions were concentrated and the residue was lyophilized to obtain **34** (2.17 g, 95 %) as an amorphous powder; $[\alpha]_D$ + 154.6 ° (*c* 0.5, water); MS (ionspray) *m/z* 668.2 (100 % , $[M + NH_4]^+$); ^1H NMR (D_2O, 400 MHz) δ 5.42 (d, 1H, $J_{1''',2'''}$ = 3.8 Hz, H-1'''), 5.17, 5.13 (2 d, 2H, $J_{1,2} = J_{1',2'}$ = 3.8 Hz, H-1, H-1'), 4.54 (dd, 1H, $J_{1'',2''}$ = 7.9 Hz, H-1''), 1.28 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6).

Anal. Calcd for $C_{24}H_{42}O_{20}$: C, 44.31; H,6.51. Found: C, 44.27; H,6.55.

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