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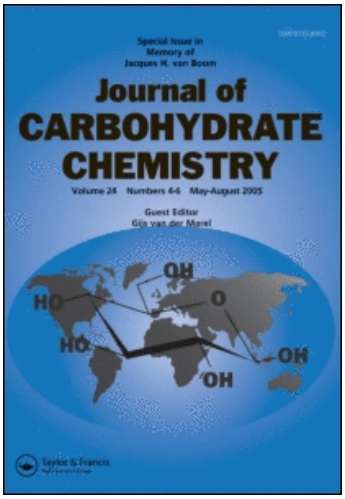

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Selectively Deoxygenated Derivatives of β-Maltosyl-(1→4)-Trehalose as Biological Probes. II. the Synthesis of the 4- and 4'''-Monodeoxygenated Analogues

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SELECTIVELY DEOXYGENATED DERIVATIVES OF β-MALTOSYL-(1→4)-TREHALOSE AS BIOLOGICAL PROBES. II. THE SYNTHESIS OF THE 4- AND 4'''-MONODEOXYGENATED ANALOGUES

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ABSTRACT

Two derivatives of β-maltosyl-(1→4)-trehalose monodeoxygenated at positions 4 or 4''' have been synthesized in [2+2] block syntheses. After the preparation of precursors with only one free hydroxyl group the deoxy function was introduced by a Barton-McCombie reaction. Thus, glycosylation of 2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**4**) with octa-*O*-acetyl-β-maltose (**3**) gave tetrasaccharide **5** with only one free hydroxyl group at the 4-position. The 4'-position of an allyl maltoside was available selectively after removal of a 4',6'-cyclic acetal and selective benzoylation of the 6'-position. Reduction of this derivative **11** afforded allyl *O*-(2,3-di-*O*-acetyl-6-*O*-benzoyl-4-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (**14**), which was deallylated, activated as an trichloroacetimidate, and coupled to 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl 2',3',6'-tri-*O*-benzyl-α-D-glucopyranoside (**20**). Several compounds were fully characterized by ^{1}H NMR spectroscopy. Deprotection furnished the monodeoxygenated tetrasaccharides **9** and **23**.

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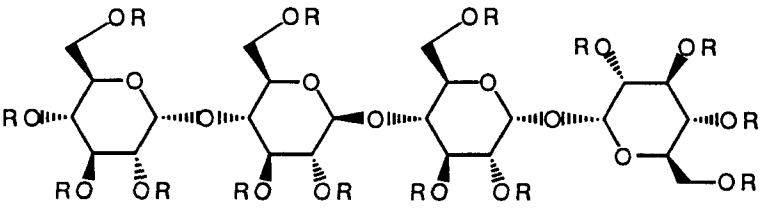

1 R = SO_3Na or H, DS ≈ 2.8[4]

2 R = H

Scheme 1

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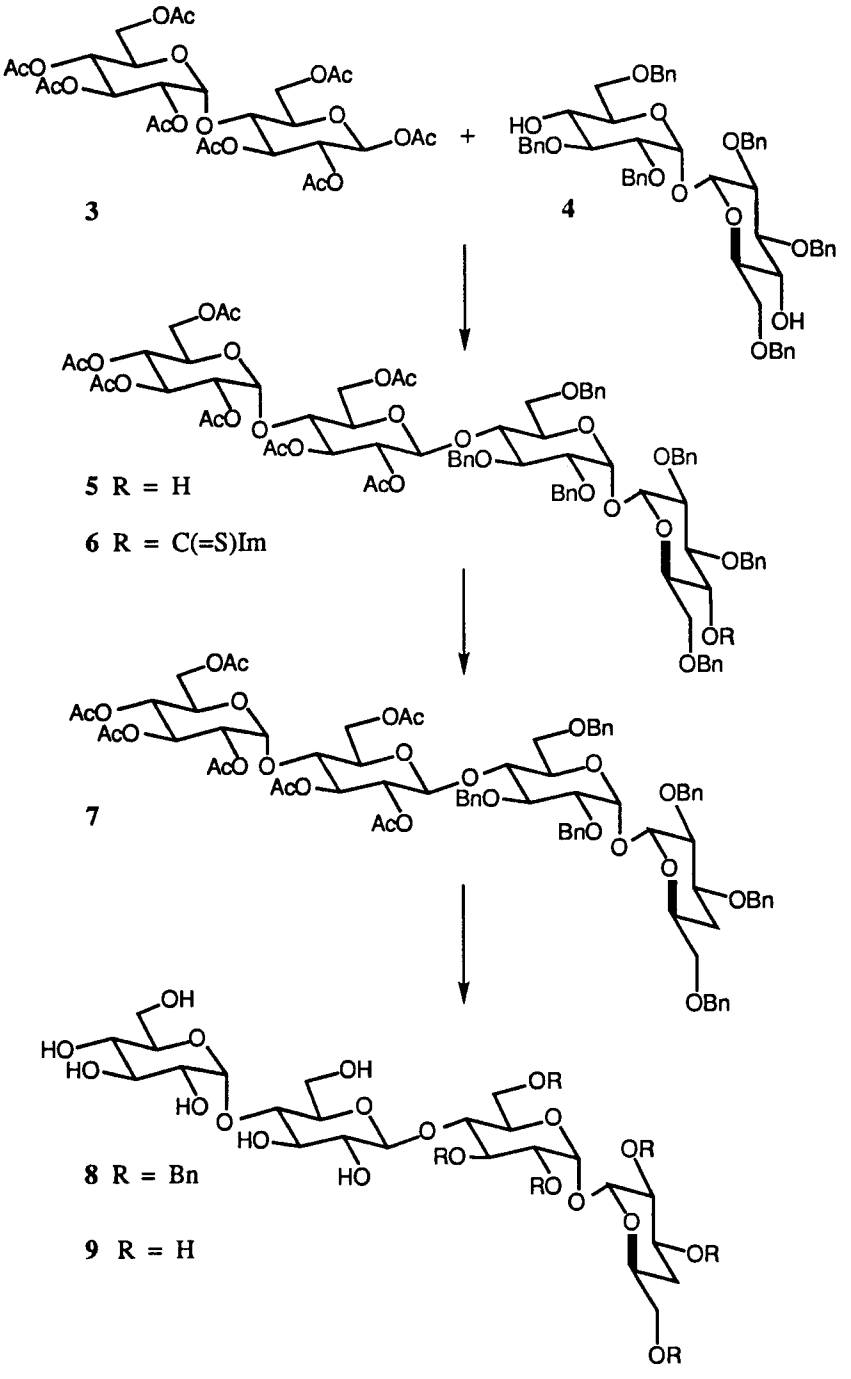
INTRODUCTION

We have reported that sulfated β-maltosyl-(1→4)-α,α-trehalose (**1**)[1] effectively inhibits the proliferation of smooth muscle cells (SMC), a pivotal process in the development of arteriosclerotic lesions.[2,3] The inhibitory effect of **1** is approximately as high as for heparin[1] and thus seems to mimic the action of heparan sulfate, an endogenous regulator of SMC growth.

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] It was therefore of interest to investigate which of the sulfates are essential for biological activity. As detailed in a recent publication,[6] we have synthesized selectively deoxygenated derivatives of **2** towards this end. The analogues deoxygenated at the primary positions have been obtained in block syntheses via the respective iodinated derivatives.[6] Here we describe the synthesis of the tetrasaccharide analogues deoxygenated in positions 4 and 4'''.

RESULTS AND DISCUSSION

The synthetic strategy, starting with suitably protected maltose and trehalose building blocks, aimed at intermediates with only one free hydroxyl group to facilitate deoxygenation. While the parent tetrasaccharide β-maltosyl-(1→4)-trehalose (**2**) has been prepared in a [2+2] block synthesis from hepta-*O*-acetyl-maltosyl bromide and 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside as glycosyl acceptor,[7] we envisaged for the synthesis of the analogous tetrasaccharide deoxygenated



Scheme 2

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in the 4-position 2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**4**)[8] as an acceptor to arrive at a tetrasaccharide with the 4-hydroxyl group ready for further manipulation. We have described before that this symmetrical glycosyl acceptor is suitable for glycosylation since, after one glycosylation, the reactivity of the remaining hydroxyl group seems to be reduced so that glycosylation is a good 'symmetry breaking' reaction.[8] And indeed, with two equivalents of octa-*O*-acetyl-β-maltose (**3**) as glycosyl donor and catalysis of trimethylsilyl triflate,[9] a 53 % yield of tetrasaccharide **5** was obtained (cf. Scheme 2). This example demonstrates that also block syntheses with unreactive glycosyl acceptors can be carried out with 1-*O*-acyl-sugars as glycosyl donors.

Tetrasaccharide **5** was fully analyzed by NMR spectroscopy. With the anomeric protons being sufficiently separated, the carbohydrate protons could be readily assigned by a series of 1D TOCSY experiments. The assignment of the four sub-spectra to the individual pyranose rings was straightforward: one maltosyl ring could be assigned because H-1'' is the only axial anomeric proton, the other maltosyl ring due to the low field shifted protons caused by the acetates. The first trehalose ring is characterized by the presence of the 4-OH group resonating at high field. These ring assignments were supported by an inter-ring H-1''→H-4' ROE. As observed with other maltosyl trehalose derivatives, one of the acetate signals is characteristically shifted to high field (δ 1.71 ppm), probably due to an interaction of 2''-OAc with 6'-OBn.[6,7]

The free secondary hydroxyl group in **5** was subjected to a Barton-McCombie reaction sequence:[10] reaction with 1,1'-thiocarbonyldiimidazole in refluxing acetonitrile gave the thiocarbonylimidazole derivative **6** (85 %), which was reduced with tributyltin hydride in toluene in the presence of azoisobutyronitrile (AIBN) as a radical starter to furnish tetrasaccharide **7** in 72 % yield. For this compound no mass peak was obtained with ionspray mass spectroscopy, but the presence of the 4-deoxy group was evident in the ^{1}H NMR spectrum. After the introduction of the deoxy function on the tetrasaccharide level, the protective groups were removed in classical manner. Deacetylation of **7** with sodium methoxide in methanol to give **8** was followed by catalytic hydrogenolysis to afford in 90 % yield the deblocked tetrasaccharide **9**, the 4-deoxygenated analogue of tetrasaccharide **2**.

Starting point for the reduction of the 4'-hydroxyl group of maltose was the selectively acylated allyl 2,3,6,2',3'-penta-*O*-acetyl-β-maltoside (**10**),[11] which has been employed as a common precursor for a number of syntheses

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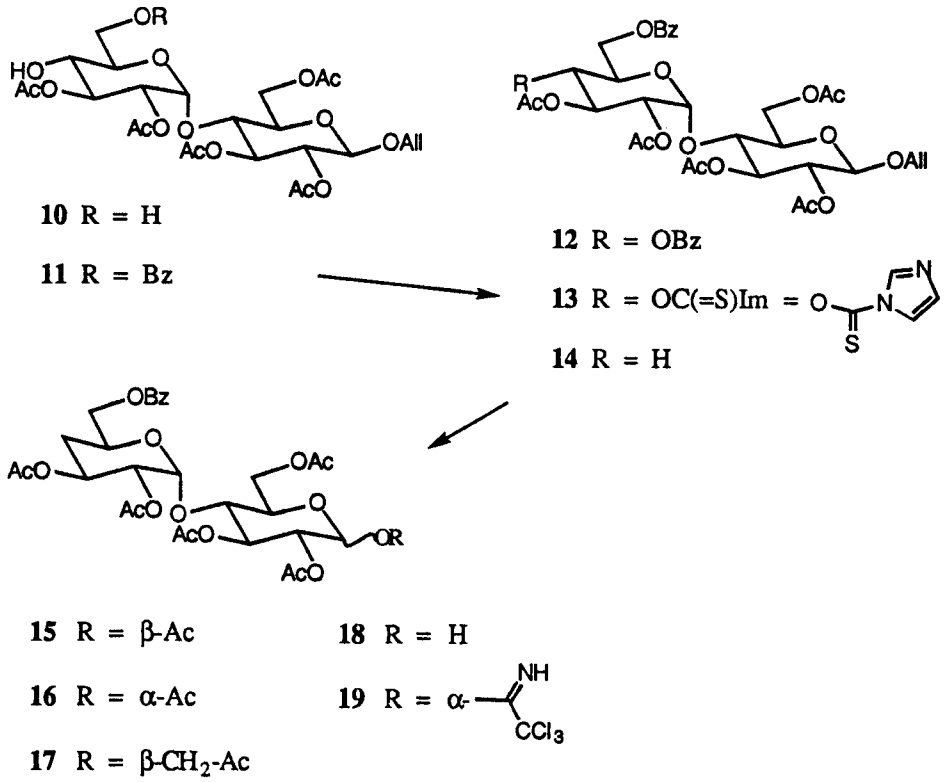

Scheme 3

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and was available in quantity.[6] Regioselective benzoylation of the primary hydroxyl group was achieved with benzoyl cyanide in acetonitrile in the presence of triethylamine, a method which has been successfully applied in the chemistry of nucleosides,[12] carbohydrates,[13] and other oligohydroxy compounds.[14] Thus, benzoylation of diol **10** gave 84 % of monobenzoate **11** along with 10 % of dibenzoate **12** (Scheme 3). In the Barton-McCombie reaction of **11** with thiocarbonyldiimidazole in tetrahydrofuran/1,2-dichloroethane, the formation of thioimidazolide **13** proceeded in excellent yield (98 %).

The maltoside ^{1}H NMR spectra (Tables 1 and 2) were conveniently interpreted by first order analysis. In the spectrum of **13**, the thiocarbonylimidazolyl residue causes a strong down-field shift of H-4' of nearly 2.5 ppm compared to the monohydroxyl derivative **11**, and a 0.6 ppm stronger down-field shift than the 4'-*O*-benzoate.

Table 1. ^{1}H NMR Chemical shifts and multiplicities for compounds **11 - 17**

	11	**12**	**13**	**14**	**15**	**16**	**17**
H-1, d	4.58	4.60	4.60	4.57	5.74	6.24	5.57
H-2, dd	4.86	4.87	4.87	4.85	4.97	4.96	4.84
H-3, dd	5.25, ~t	5.29, ~t	5.28, ~t	5.25, ~t	5.29, ~t	5.52, ~t	5.27, ~t
H-4, dd	4.03, ~t	4.08, ~t	4.04, ~t	4.02, ~t	4.04, ~t	4.06, ~t	4.01, ~t
H-5, ddd	3.68	3.72	3.71	3.65	3.81	4.08, m_c higher order	3.66
H-6a, dd	4.54	4.57[a]	4.59	4.53	4.49	4.48	4.51
H-6b, dd	4.21	4.29	4.21	4.21	4.21	4.18	4.20
H-1', d	5.38	5.47	5.47	5.42	5.41	5.44	5.41
H-2', dd	4.80	4.95	4.98	4.83	4.84	4.85	4.84
H-3', dd	5.26, ~t	5.61, ~t	5.64, ~t	5.23, ddd ~dt	5.23, ddd ~dt	5.27, ddd ~dt	5.23, ddd ~dt
H-4'$_{ax}$, dd	3.59 ddd ~dt	5.46, ~t	6.06, ~t	1.73, ddd~q	1.73, ddd~q	1.76, ddd~q	1.73, ddd~q
H-4'$_{eq}$, ddd	-	-	-	2.26	2.26	2.26	2.26
H-5', ddd	3.91, ~dt	4.24 ~dt	m	m_c	4.18, m	4.18, m_c	4.18
H-6a', dd	4.84	4.56[a]	4.56	4.37	4.35, d (2H)	4.36, d (2H)	4.38
H-6b', dd	4.42	4.33	m	4.34			4.34

a. Assignments may be interchanged.

Radical reduction of **13** with tributyltin hydride gave the protected allyl 4'-deoxymaltoside **14** in a yield of 92 %. The methyl 4'-deoxymaltoside has been prepared following a similar synthetic line.[15]

To allow the activation of the anomeric centre, the anomeric allyl protective group was removed with palladium chloride - sodium acetate -

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Table 2. ^{1}H NMR Coupling constants in Hz for compounds **11 - 17**

	11	**12**	**13**	**14**	**15**	**16**	**17**
$J_{1,2}$	8.0	8.0	7.9	8.0	8.2	3.8	8.2
$J_{2,3}$	9.0	9.0	9.3	9.0	9.2	10.3	9.2
$J_{3,4}$	9.0	9.0	9.3	9.0	8.9	8.1	8.8
$J_{4,5}$	9.5	9.5	9.4	9.6	9.7	-	9.5
$J_{5,6a}$	2.5	2.6	2.4	2.5	2.5	1.9	2.4
$J_{5,6b}$	4.3	3.8	4.2	4.5	4.3	3.4	4.5
$J_{6a,6b}$	12.0	12.0	12.0	12.1	12.0	12.0	12.0
$J_{1',2'}$	4.0	4.0	3.9	4.0	4.0	4.0	3.9
$J_{2',3'}$	10.5	10.1	10.5	10.4	10.0	10.6	10.5
$J_{3',4'ax}$	9.5	9.9	9.5	11.2	12.0	11.3	11.5
$J_{3',4'eq}$	-	-	-	5.0	5.0	5.0	4.8
$J_{4'ax,5'}$	9.8	9.8	9.8	≈11.9	≈12.7		
$J_{4'eq,5'}$	-	-	-	1.8	1.9	2.2	
$J_{5',6a'}$	2.8	3.0	3.0	2.8	4.1	4.0	4.5
$J_{5',6b'}$	2.0	3.6	-	3.8	4.1	4.0	4.0
$J_{6a',6b'}$	12.2	12.0	12.4	12.3	-	-	11.8

aqueous acetic acid[16] under sonication.[6,11] The crude product mixture was acetylated to afford the anomeric acetates **15** and **16** (64 %) along with oxopropyl β-maltoside **17** (20 %).[17] As noted before,[6] only the β-configured Wacker product **17** was formed. This by-product, which has also been observed in analogous reactions,[11,18,19] could in this case be avoided when oxygen was rigorously excluded, and the maltose derivative **18** was obtained in nearly quantitative yield (98 %) as mixture of anomers (α/β = 7:3). Reaction

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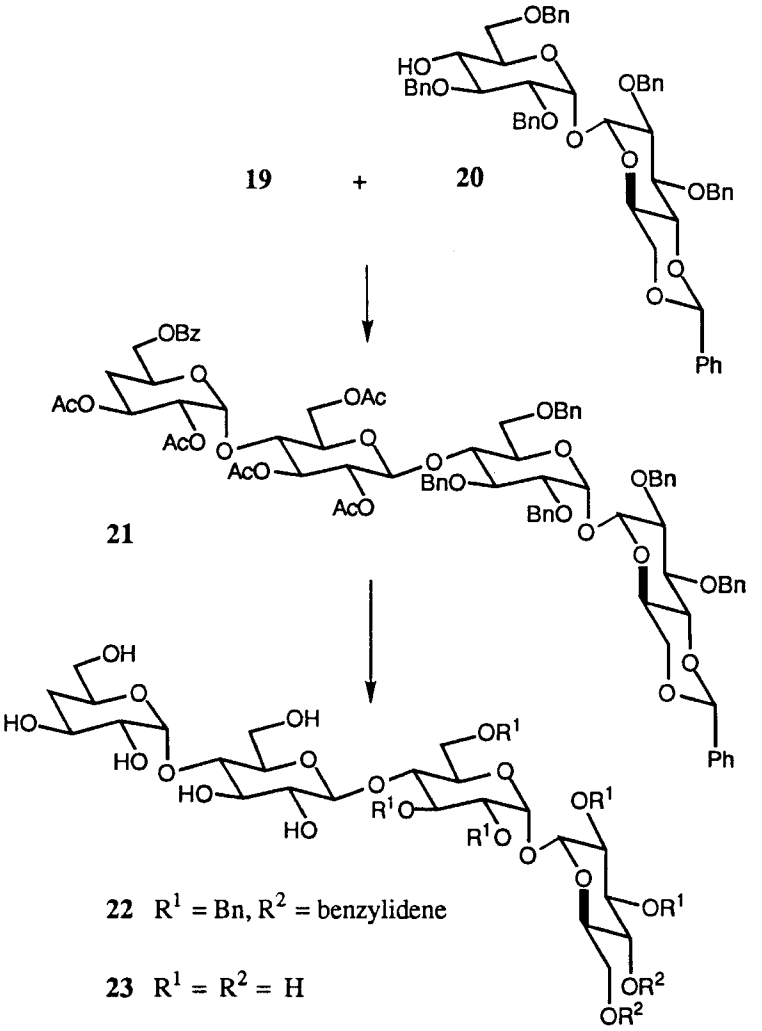

Scheme 4

of **18** with trichloroacetonitrile in dichloromethane, catalyzed by sodium hydride, furnished the α-trichloroacetimidate **19** (71 %).

This glycosyl donor was reacted with the standard trehalose glycosyl acceptor[7,8,20-22] 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**20**) to afford tetrasaccharide **21** in 71 % yield (Scheme 4). In contrast, employment of the anomeric acetate **15** as glycosyl donor gave, with catalysis of trimethylsilyl triflate, the tetrasaccharide in only

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26 % yield. The tetrasaccharide was then deprotected by transesterification with sodium methanolate to afford **22** followed by catalytic hydrogenolysis to the free saccharide **23** (96 % over 2 steps), the 4'''-deoxy analogue of tetrasaccharide **2**.

In summary, two analogues of the maltosyl trehalose **2** deoxygenated at the 4- and 4'''-position have been prepared in [2+2] block syntheses. Isolated secondary hydroxyl groups were reduced effectively using the Barton-McCombie reaction. The investigation of the antiproliferative activities of the highly sulfated derivatives of the deoxygenated tetrasaccharides **9** and **23** has shown that the sulfate in position 4 is critical for this biological effect, while removal of the sulfate in the 4'''-position leads only to a relatively small reduction in activity.[23]

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EXPERIMENTAL

General Procedures. Experimental conditions were essentially as described before.[6] MPLC = medium pressure liquid chromatography. Flash chromatography was conducted with silica gel (0.040 - 0.063 mm, Merck, Darmstadt). Specific rotations were measured at 20 °C. Mass spectra were recorded on API III Sciex, Perkin Elmer (ionspray) or MS 902 (FAB) with data system DS 2050 (VG).

***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 2,3,6-Tri-*O*-benzyl-α-D-glucopyranoside** (**5**). A soln of dried maltose peracetate **3** (157 mg, 0.231 mmol) and dried glycosyl acceptor **4**[8] (102 mg, 0.115 mmol) in abs dichloromethane (8 mL) was stirred in the presence of 4 Å molecular sieves for 1 h. After cooling to -20 °C trimethylsilyl triflate (42 μL) was added. The reaction mixture was allowed to reach rt, and stirring was continued for 2 h. Then triethylamine (1 mL) was added, and the reaction mixture was filtered through a pad of celite. After washing with dichloromethane the filtrates were evaporated, and the residue was purified by flash chromatography using toluene/ ethyl acetate 7:3 as eluents to furnish **5** (91 mg, 53 %) as a colourless solid which was crystallized from hexane: mp 68 °C; $[\alpha]_D$ +84.7 ° (*c* 0.3, chloroform); MS (FAB) *m/z* 1539.7 (45 %, [M + K]$^+$), 1523.7 (70 %, [M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz; 1D TOCSY, 1D T-ROESY) δ 7.46 - 7.14 (m, 30H, aromat), 5.38 (dd, 1H, $J_{3''',4'''}$ = 9.3 Hz, H-3'''), 5.32 (d, 1H, $J_{1''',2'''}$ = 4.0 Hz,

H-1'''), 5.19 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 5.16 (d, 1H, $J_{1',2'}$ = 3.7 Hz, H-1'), 5.06 (dd ~ t, 1H, $J_{4''',5'''}$ = 10.2 Hz, H-4'''), 5.05, 4.86 (2 d, 2H, J_{gem} = 11.5 Hz, CH_2Ph), 5.01 (dd ~ t, 1H, $J_{3'',4''}$ = 9.1 Hz, H-3''), 5.01, 4.72 (2 d, 2H, J_{gem} = 11.5 Hz, CH_2Ph), 4.86 (dd, 1H, $J_{2''',3'''}$ = 10.7 Hz, H-2'''), 4.74, 4.37 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.73 (dd ~ t, 1H, $J_{1'',2''}$ = 8.3 Hz, $J_{2'',3''}$ = 8.9 Hz, H-2''), 4.66, 4.62 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.60, 4.57 (2 d, 2H, J_{gem} = 12.5 Hz, CH_2Ph), 4.48 (d, 1H, H-1''), 4.21 (dd, 1H, $J_{5''',6a'''}$ = 3.6 Hz, $J_{6a''',6b'''}$ = 12.6 Hz, H-6a'''), 4.11 (dd, 1H, $J_{5'',6a''}$ = 3.0 Hz, $J_{6a'',6b''}$ = 12.5 Hz, H-6a''), 4.09 (ddd ~ dt, 1H, $J_{5,6a}$ = 4.0 Hz, H-5), 4.04 (dd, 1H, $J_{5'',6b''}$ = 4.0 Hz, H-6b''), 3.99 (ddd ~ br d, 1H, H-5'), 3.97 (dd, 1H, $J_{5''',6b'''}$ = 2.2 Hz, H-6b'''), 3.88 (dd ~ t, 1H, $J_{4',5'}$ = 9.8 Hz, H-4'), 3.87 (3H; ddd ~ br d, H-5'''; dd ~ t, $J_{3,4}$ = 8.7 Hz, H-3; dd ~ t, H-4''), 3.83 (dd ~ t, 1H, $J_{3',4'}$ = 8.2 Hz, H-3'), 3.68 (dd ~ t, 1H, $J_{4,5}$ = 9.9 Hz, H-4), 3.62 (dd, 1H, $J_{5',6a'}$ = 2.8 Hz, $J_{6a',6b'}$ = 11.0 Hz, H-6a'), 3.56 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 3.50 (dd, 1H, $J_{2',3'}$ = 9.4 Hz, H-2'), 3.48 (dd, 1H, H-6a), 3.45 (dd, 1H, $J_{5',6b'}$ ≈ 1.5 Hz, H-6b'), 3.42 (dd, 1H, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 10.4 Hz, H-6b), 3.13 (ddd ~ dt, 1H, $J_{4'',5''}$ = 10.0 Hz, H-5''), 2.30 (d, 1H, $J_{4,\ 4\text{-OH}}$ = 2.9 Hz, 4-OH), 2.10, 2.07, 2.04, 2.02, 1.96, 1.92, 1.71 (7 s, 21H, OAc); NMR ($CDCl_3$, 100 MHz; DEPT, H,C-COSY) δ 99.60 (C-1''), 95.72 (C-1'''), 94.86 (C-1), 94.75 (C-1'), 80.86 (C-3), 79.93 (C-3'), 79.48 (C-2), 78.23 (C-2'), 77.26 (C-4'), 7'5.94 (C-3'), 75.22 , 74.87, 73.80, 73.61, 73.04 (5 CH_2Ph), 73.03 (C-2''), 72.83 (CH_2Ph), 72.73 (C-4''), 71.67 (C-5''), 70.86 (C-4), 70.58 (C-5), 70.48 (C-5'), 70.09 (C-2'''), 69.30 (C-3'''), 69.09 (C-6), 68.54(C-5'''), 67.94 (C-4'''), 67.61 (C-6'), 63.11 (C-6''), 61.38 (C-6'''), 20.96, 20.68 (2 Ac), 20.65 (4 Ac), 20.56 (Ac).

Anal. Calcd for $C_{80}H_{92}O_{28}$: C, 63.99; H, 6.18. Found: C, 63.82; H, 6.20.

***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 2,3,6-Tri-*O*-benzyl-4-*O*-(imidazol-1-ylthiocarbonyl)-α-D-glucopyranoside (6).** A soln of tetrasaccharide **5** (4.16 g, 2.77 mmol) and 1,1'-thiocarbonyldiimidazole (987 mg, 5.5 mmol) in acetonitrile (10 mL) was refluxed during 18 h. After evaporation of the solvent, the crude reaction mixture was purified by chromatography over silica gel using toluene/ ethyl acetate 2:1 as eluents to afford **6** (3.79 g, 85 %) as a colourless foam; $[\alpha]_D$ +96.5 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 1611.6 (45 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.02 (~s, 1H, imidazolyl), 7.50 - 7.08 (m, 31H, aromat), 7.00 (~s, 1H, imidazolyl), 5.88 (dd ~ t, 1H, ΣJ = 19.2 Hz, H-4), 5.39 (dd, 1H, $J_{3''',4'''}$ = 9.4 Hz, H-3'''), 5.33 (d, 1H, $J_{1''',2'''}$ = 3.9 Hz, H-1'''), 5.20, 5.19 (2 d, 2H, H-1, H-2), 5.07 (dd ~ t, 1H, $J_{4''',5'''}$ = 10.2 Hz, H-4'''), 5.05, 4.74 (2 d, 2H, J_{gem} = 11.5 Hz, CH_2Ph), 5.04 (dd ~ t, 1H, $J_{3'',4''}$ = 9.2 Hz, H-3''), 4.87 (d, 1H, J_{gem} = 11.3 Hz, CH_2Ph), 4.86 (dd, 1H, $J_{2''',3'''}$ = 10.7 Hz, H-2'''),

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4.78 (d, 1H, J_{gem} = 11.9 Hz, CH_2Ph), 4.77 (dd ~ t, 1H, $J_{2'',3''}$ = 9.8 Hz, H-2''), 4.69, 4.65 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.65 (d, 1H, CH_2Ph), 4.62 (d, 1H, CH_2Ph), 4.52 (d, 1H, J_{gem} = 11.5 Hz, CH_2Ph), 4.51 (d, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 4.42 (d, 1H, J_{gem} = 12.0 Hz, CH_2Ph), 4.34, 4.31 (2 d, 2H, J_{gem} = 11.8 Hz, CH_2Ph), 4.24 (ddd ~ dt, 1H, H-5), 4.21 (dd, 1H, $J_{5''',6a'''}$ = 3.4 Hz, H-6a'''), 4.16 (dd, 1H, $J_{5'',6a''}$ = 2.5 Hz, $J_{6a'',6b''}$ = 12.0 Hz, H-6a''), 4.10 (dd ~ t, $J_{3,4}$ = 9.3 Hz, H-3), 4.07 (dd, 1H, $J_{5'',6b''}$ = 3.7 Hz, H-6b''), 4.01 - 3.85 (m, 6H, H-3', H-4', H-5', H-4'', H-5''', H-6b'''), 3.70 (dd, 1H, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 9.3 Hz, H-2), 3.68 (dd, 1H, $J_{5',6a'}$ = 2.0 Hz, H-6a'), 3.52 (dd, 1H, $J_{5',6b'} \leq$ 1.5 Hz, $J_{6a',6b'}$ = 10.5 Hz, H-6b'), 3.24 (dd, 1H, $J_{5,6b}$ = 2.8 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6a), 3.16 (ddd ~ dt, 1H, $J_{4'',5''}$ = 9.6 Hz, H-5''), 3.03 (dd, 1H, $J_{5,6b}$ = 3.5 Hz, H-6b), 2.11, 2.07, 2.04, 2.02, 1.97, 1.92, 1.73 (7 s, 21H, OAc).

Anal. Calcd for $C_{84}H_{94}N_2O_{28}S$: C, 62.60; H, 5.88; N, 1.74; S, 1.99. Found: C, 62.74; H, 5.94; N, 1.70; S, 2.04.

***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 2,3,6-Tri-*O*-benzyl-4-deoxy-α-D-glucopyranoside** (7). A soln of thiocarbonylimidazole derivative **6** (1.0 g, 0.62 mmol) in toluene (8 mL) was refluxed in the presence of tributyltin hydride (0.64 mL, 2.48 mmol) and a catalytic amount of AIBN (ca. 15 mg). After 2 h more tributyltin hydride (0.32 mL, 1.24 mmol) was added. After another 30 min at reflux the solvent was evaporated. The crude reaction mixture was purified by chromatography over silica gel using toluene/ ethyl acetate 2:1 as eluents to afford **7** (660 mg, 72 %) as a colourless foam; $[\alpha]_D$ +93.2 ° (*c* 0.5, dioxane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 - 7.16 (m, 30H, aromat), 5.38 (dd, 1H, $J_{3''',4'''}$ = 9.7 Hz, H-3'''), 5.31 (d, 1H, $J_{1''',2'''}$ = 3.8 Hz, H-1'''), 5.22 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 5.20 (d, 1H, $J_{1',2'}$ = 3.9 Hz, H-1'), 5.06 (dd ~ t, 1H, $J_{4''',5'''}$ = 9.8 Hz, H-4'''), 5.01 (d, 1H, CH_2Ph), 5.00 (dd ~ t, 1H, ΣJ = 17.9 Hz, H-3''), 4.86 (dd, 1H, $J_{2''',3'''}$ = 10.3 Hz, H-2'''), 4.78 - 4.64 (m, 7H, 6 CH_2Ph, H-2''), 4.64, 4.57 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.50, 4.45 (2 d, 2H, J_{gem} = 12.1 Hz, CH_2Ph), 4.46 (d, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 4.30 (m_c, 1H, H-5), 4.21 (dd, 1H, $J_{5''',6a'''}$ = 3.4 Hz, $J_{6a''',6b'''}$ = 12.3 Hz, H-6a'''), 4.11 (dd, 1H, $J_{5'',6a''}$ = 2.6 Hz, $J_{6a'',6b''}$ = 12.0 Hz, H-6a''), 4.04 (ddd ~ dt, H-3), 4.02 (2H; dd, H-6b''; ddd ~ br d, H-5'), 3.97 (dd, 1H, $J_{5''',6b'''}$ = 2.0 Hz, H-6b'''), 3.88 (dd ~ t, 1H, H-4'), 3.86 (2H; ddd ~ br d, H-5'''; dd ~ t, H-4''), 3.81 (dd ~ t, 1H, H-3'), 3.63 (dd, 1H, $J_{5',6a'}$ = 2.5 Hz, $J_{6a',6b'}$ = 11.0 Hz, H-6a'), 3.51 (2 dd, 2H, H-2, H-2'), 3.47 (dd, 1H, $J_{5',6b'} \leq$ 1.2 Hz, H-6b'), 3.37 (dd, 1H, $J_{5,6b}$ = 3.7 Hz, H-6a), 3.29 (dd, 1H, $J_{5,6b}$ = 5.0 Hz, $J_{6a,6b}$ = 10.1 Hz, H-6b), 3.13 (ddd ~ dt, 1H, $J_{4'',5''}$ = 9.3 Hz, $J_{5'',6b''}$ = 3.6 Hz, H-5''), 2.08 (m, 1H,

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H-4_{eq}), 2.10, 2.07, 2.04, 2.02, 1.96, 1.90, 1.69 (7 s, 21H, OAc), 1.58 (ddd ~ q, 1H, H-4_{ax}).

Anal. Calcd for $C_{80}H_{92}O_{27}$: C, 64.68; H, 6.24. Found: C, 64.49; H, 6.34.

***O*- α-D-Glucopyranosyl- (1→4) -*O*--β-D-glucopyranosyl- (1→4) -2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl 2,3,6-Tri-*O*-benzyl-4-deoxy-α-D-glucopyranoside (8).** To a soln of **7** (760 mg, 0.512 mmol) in methanol (8 mL) was a added a soln of sodium methanolate (6 drops of 2.0 g Na/ 100 mL methanol) at rt. The reaction mixture was kept for 18 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 to obtain **8** (530 mg) quantitatively as a colourless foam: $[\alpha]_D$ +117.3 ° (*c* 0.3, dioxane); MS (ionspray) *m/z* 1208.8 (100 %, $[M + NH_4]^+$).

Anal. Calcd for $C_{66}H_{78}O_{20}$: C, 66.54; H, 6.60. Found: C, 66.49; H, 6.68.

***O*- α-D-Glucopyranosyl- (1→4) -*O*--β-D-glucopyranosyl- (1→4) -α-D-glucopyranosyl 4-Deoxy-α-D-glucopyranoside (9).** A soln of **8** (510 mg, 0.43 mmol) in ethanol/water 1:2 (15 mL) was hydrogenated in the presence of 10 % palladium on charcoal (200 mg) at 1.1 bar for 5 d. 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 methanol/water 1:1 as eluent to obtain pure **9** (250 mg, 90 %) as a colourless solid: $[\alpha]_D$ +152.5 ° (*c* 0.2, water); MS (ionspray) *m/z* 673.2 (55 %, $[M + Na]^+$); ^1H NMR (D_2O, 400 MHz) δ 5.42 (d, 1H, $J_{1''',2'''}$ = 3.8 Hz, H-1'''), 5.22, 5.20 (2 d, 2H, $J_{1,2}$ = 3.6 Hz, $J_{1',2'}$ = 3.9 Hz, H-1, H-1'), 4.54 (dd, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 2.03 (ddd, 1H, H-4_{eq}), 1.49 (ddd ~ q, 1H, H-4_{ax}).

Anal. Calcd for $C_{24}H_{42}O_{20}$: C, 44.31; H, 6.51. Found: C, 44.18; H, 6.59.

Allyl *O*-(2,3-Di-*O*-acetyl-6-*O*-benzoyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (11) and Allyl *O*-(2,3-Di-*O*-acetyl-4,6-di-*O*-benzoyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (12). To a soln of diol **10** (1.04 g, 1.76 mmol) in acetonitrile (5 mL) and triethylamine (0.49 mL) was added benzoyl cyanide (253 mg, 1.93 mmol). The reaction mixture was stirred at 0 °C for 30 min, poured on ice/ water, and extracted with ethyl acetate. The organic phases were washed with cold water, dried over sodium sulfate, and concentrated. The crude reaction product was purified by MPLC using hexane/ ethyl acetate 1:1 as eluents to afford pure **12** (147 mg, 10 %) followed by **11** (1.03 g, 84 %) as a colourless foam.

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Data for **11**: $[\alpha]_D$ +24.5 ° (*c* 0.2, dioxane); MS (FAB) *m/z* 735 (50 %, $[M + K]^+$), 719 (30 %, $[M + Na]^+$), 697 (10 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.07 (m_c ~ d, 2H, aromat), 7.61 (m_c ~ t, 1H, aromat), 7.48 (m_c ~ t, 2H, aromat), 5.85 (dddd, 1H, allyl), 5.28, 5.21 (2 dddd ~ dq, 2H, allyl), 4.32, 4.10 (2 dddd ~ ddt, 2H, allyl), 3.18 (d, 1H, $J_{4',4'\text{-OH}}$ = 5.4 Hz, 4'-OH), 2.16, 2.08, 2.05, 2.03, 1.99 (5 s, 15H, OAc); for further ^1H NMR data see Tables 1 and 2.

Anal. Calcd for $C_{32}H_{40}O_{17}$: C, 55.17; H, 5.79. Found: C, 55.02; H, 5.85.

Data for **12**: $[\alpha]_D$ +57.0 ° (*c* 0.2, dioxane); MS (FAB) *m/z* 839 (60 %, $[M + K]^+$), 823 (50 %, $[M + Na]^+$), 801 (10 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.03 (m_c ~ d, 2H, aromat), 7.96 (m_c ~ d, 2H, aromat), 7.59 - 7.54 (m ≈ 2 m_c ~ t, 2H, aromat), 7.41 (m_c ~ t, 4H, aromat), 5.85 (dddd, 1H, allyl), 5.28, 5.21 (2 dddd ~ dq, 2H, allyl), 4.32, 4.10 (2 dddd ~ ddt, 2H, allyl), 2.15, 2.07, 2.04, 2.02, 1.91 (5 s, 15H, OAc); for further ^1H NMR data see Tables 1 and 2.

Anal. Calcd for $C_{39}H_{44}O_{18}$: C, 58.50; H, 5.54. Found: C, 58.41; H, 5.61.

Allyl *O*-[2,3-Di-*O*-acetyl-6-*O*-benzoyl-4-*O*-(imidazol-1-ylthiocarbonyl)-α-D-glucopyranosyl]-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (13). A soln of disaccharide **11** (7.0 g, 10.05 mmol) in tetrahydrofuran (30 mL) and 1,2-dichloroethane (30 mL) was refluxed under argon in the presence of 1,1'-thiocarbonyldiimidazole (2.69 g, 15.07 mmol) for 3h. The reaction mixture was concentrated and purified by MPLC using hexane/ ethyl acetate 1:1 as eluents to afford pure **13** (8.03 g, 98 %) as a colourless foam: $[\alpha]_D$ +82.0 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 807 (100 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.28 (~s, 1H, imidazolyl), 7.99 (m_c ~ d, 2H, benzoyl), 7.60 - 7.55 (m, 2H, benzoyl and imidazolyl), 7.43 (m_c ~ t, 2H, benzoyl), 7.02 (~s, 1H, imidazolyl), 5.85 (dddd, 1H, allyl), 5.28, 5.21 (2 dddd ~ dq, 2H, allyl), 4.38 - 4.32 (m, 2H, H-5', H-6b'), 4.33, 4.11 (2 dddd ~ ddt, 2H, allyl), 2.14, 2.07, 2.04, 2.02, 1.94 (5 s, 15H, OAc); for further ^1H NMR data see Tables 1 and 2.

Anal. Calcd for $C_{36}H_{42}N_2O_{17}S$: C, 53.59; H, 5.25; N, 3.47; S, 3.97. Found: C, 53.54; H, 5.30; N, 3.38; S, 3.96.

Allyl *O*-(2,3-Di-*O*-acetyl-6-*O*-benzoyl-4-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (14). To a refluxing soln of tributyltin hydride (5.26 mL, 19.7 mmol) and AIBN (150 mg) in toluene (15 mL) was added dropwise a soln of thiocarbonylimidazole derivative **13** (4.0 g, 4.93 mmol) in toluene (10 mL) during 15 min. After another 15 min at reflux the reaction mixture was concentrated and purified by chromatography on silica gel using hexane/ ethyl acetate 2:1 as eluents to afford pure **14** (3.12 g,

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92 %) as a colourless foam: $[\alpha]_D$ +35.0 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 703 (25 %, $[M + Na]^+$), 698 (100 %, $[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.05 (m_c ~ d, 2H, aromat), 7.59 (m_c ~ t, 1H, aromat), 7.47 (m_c ~ t, 2H, aromat), 5.84 (dddd, 1H, allyl), 5.27, 5.20 (2 dddd ~ dq, 2H, allyl), 4.31, 4.09 (2 dddd ~ ddt, 2H, allyl), 2.11, 2.07 (2 s, 6H, OAc), 2.03 (s, 6H, OAc), 2.01 (s, 3H, OAc); for further ^1H NMR data see Tables 1 and 2.

Anal. Calcd for $C_{32}H_{40}O_{16}$: C, 56.47; H, 5.92. Found: C, 56.25; H, 5.97.

***O*- (2,3-Di-*O*-acetyl-6-*O*-benzoyl-4-deoxy-α-D-glucopyranosyl) - (1→4)-1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranose (15), *O*-(2,3-Di-*O*-acetyl-6-*O*-benzoyl-4-deoxy-α-D-glucopyranosyl)-(1→4)-1,2,3,6-tetra-*O*-acetyl-α-D-glucopyranose (16), and Oxopropyl *O*-(2,3-Di-*O*-acetyl-6-*O*-benzoyl-4-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (17).** To a soln of allyl glycoside **14** (550 mg, 0.81 mmol) in 90 % aqueous acetic acid (50 mL) was added palladium chloride (573 mg, 3.23 mmol) and sodium acetate (573 mg). The reaction mixture was sonicated for 3 h. 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 (15 mL) in pyridine (20 mL) for 18 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 was separated by MPLC using ethyl acetate/ hexane 1:1 as eluent to afford pure **15** (101 mg, 18 %), a mixture of anomers **15**/ **16** (175 mg, 32 %) and pure **16** (80 mg, 14 %) followed by **17** (115 mg, 20 %).

Data for **15**: $[\alpha]_D$ +51.5 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 705 (25 %, $[M + Na]^+$), 700 (100 %, $[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.05 (m_c ~ d, 2H, aromat), 7.59 (m_c ~ t, 1H, aromat), 7.47 (m_c ~ t, 2H, aromat), 2.11, 2.10, 2.07, 2.03, 2.02, 2.01 (6s, 18H, OAc), 1.73 (ddd ~ q, 1H, $J_{4'eq,4'ax} \approx 12.7$ Hz, H-$4'_{ax}$); for further ^1H NMR data see Tables 1 and 2.

Anal. Calcd for $C_{31}H_{38}O_{17}$: C, 54.55; H, 5.61. Found: C, 54.53; H, 5.70.

Data for **16**: $[\alpha]_D$ +110.0 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 705 (25 %, $[M + Na]^+$), 700 (100 %, $[M + NH_4]^+$), 623 (80 %, $[M + H - AcOH]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.05 (m_c ~ d, 2H, aromat), 7.59 (m_c ~ t, 1H, aromat), 7.47 (m_c ~ t, 2H, aromat), 2.21, 2.11, 2.10, 2.034, 2.026, 1.99 (6s, 18H, OAc), 1.76 (ddd ~ q, 1H, $\Sigma J = 36.2$ Hz, H-$4'_{ax}$); for further ^1H NMR data see Tables 1 and 2.

Anal. Calcd for $C_{31}H_{38}O_{17}$: C, 54.55; H, 5.61. Found: C, 54.39; H, 5.67.

Data for **17**: $[\alpha]_D$ +35.0 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 719 (30 %, [M +

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Na]$^+$), 714 (100 %, [M + NH_4]$^+$), 697 (15 %, [M + H]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (m_c ~ d, 2H, aromat), 7.59 (m_c ~ t, 1H, aromat), 7.47 (m_c ~ t, 2H, aromat), 4.21, 4.13 (2 d, 2H, CH_2), 2.15, 2.10, 2.07, 2.06, 2.03, 2.02 (6s, 18H, OAc), 1.73 (ΣJ = 36.3 Hz); for further ^{1}H NMR data see Tables 1 and 2.

Anal. Calcd for $C_{32}H_{40}O_{17}$: C, 55.17; H, 5.79. Found: C, 55.13; H, 5.82.

***O*- (2,3-Di-*O*-acetyl-6-*O*-benzoyl-4-deoxy-α-D-glucopyranosyl)- (1→4)-2,3,6-tri-*O*-acetyl-D-glucopyranose (18).** A soln of allyl glycoside **14** (3.0 g, 4.41 mmol) in 90 % aqueous acetic acid (50 mL) was evacuated several times followed by flushing with argon. Then palladium chloride (3.13 g, 17.63 mmol) and sodium acetate (3.13 g) were added, and the reaction mixture was sonicated for 3 h. The mixture was worked up as described above for **15**. The crude product was purified by MPLC using ethyl acetate/ hexane 1:1 as eluent to afford pure crystalline **18** (2.77 g, 98 %): mp 185.4 - 186.3 °C; MS (ionspray) *m/z* 679 (20 %, [M + K]$^+$), 663 (50 %, [M + Na]$^+$), 658 (100 %, [M + NH_4]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (m_c ~ d, 2H, aromat), 7.59 (m_c ~ t, 1H, aromat), 7.47 (m_c ~ t, 2H, aromat), 5.45 (d, 0.7H, $J_{1',2'}$ = 3.9 Hz, H-1'(α)), 5.41 (d, 0.3H, $J_{1',2'}$ = 3.9 Hz, H-1'(β)), 5.37 (dd ~ t, 0.7H, $J_{1,2}$ = 3.6 Hz, H-1(α)), 3.72 (ddd, 0.3H, $J_{4,5}$ = 9.5 Hz, H-5(β)), 3.40 (d, 0.3H, $J_{1,1\text{-OH}}$ = 7.5 Hz, OH-1(β)), 3.04 (d, 0.7H, $J_{1,1\text{-OH}}$ = 3.2 Hz, OH-1(α)), 2.30 - 2.23 (2 ddd, 1H, H-4'$_{eq}$), 2.12 - 2.02 (5s, 15H, OAc), 1.80 - 1.70 (2 ddd ~ q, 1H, H-4'$_{ax}$).

Anal. Calcd for $C_{29}H_{36}O_{16}$: C, 54.37; H, 5.66. Found: C, 54.30; H, 5.68.

***O*- (2,3-Di-*O*-acetyl-6-*O*-benzoyl-4-deoxy-α-D-glucopyranosyl)- (1→4) -*O*-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-trichloroacetimidate (19).** To a soln of **18** (150 mg, 0.23 mmol) in dichloromethane (2 mL) and trichloroacetonitrile (0.2 mL) was added sodium hydride (40 mg, 80 % in oil) at 0 °C. After 24 h at rt the reaction mixture was filtered over Speedex and concentrated. Purification by MPLC using toluene/ ethyl acetate as eluents gave pure **19** (130 mg, 71 %). MS (ionspray) *m/z* 806 (30 %, [M + Na]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.66 (s, 1H, NH), 8.05 (m_c ~ d, 2H, aromat), 7.59 (m_c ~ t, 1H, aromat), 7.49 (m_c ~ t, 2H, aromat), 6.48 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.62 (dd ~ t, 1H, $J_{3,4}$ = 9.0 Hz, H-3), 5.44 (d, 1H, $J_{1',2'}$ = 3.9 Hz, H-1'), 3.81 (ddd ~ dt, 1H, $J_{3',4'eq}$ = 5.0 Hz, $J_{3',4'ax}$ = 10.4 Hz, H-3'), 5.00 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 4.86 (dd, 1H, $J_{2',3'}$ = 10.4 Hz, H-2), 4.52 (dd, 1H, $J_{5,6a}$ = 1.8 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.36 (d, 2H, $J_{5',6'}$ = 4.0 Hz, H-6'), 4.24 (dd, 1H, $J_{5,6b}$ = 4.0 Hz, H-6b), 4.22 - 4.15 (m, 2H, H-5, H-5'), 4.08 (dd ~ t, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 2.27 (ddd, 1H, H-4'$_{eq}$), 2.10, 2.09, 2.04, 2.03, 1.99 (5 s, 15H, OAc), 1.74 (ddd ~ q, 1H, H-4'$_{ax}$).

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***O*- (2,3-Di-*O*-acetyl-6-*O*-benzoyl-4-deoxy-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-4,6-*O*-benzylidene-α-D-glucopyranoside (21).** A soln of imidate **19** (170 mg, 0.22 mmol) and glycosyl acceptor **20** (190 mg, 0.22 mmol) in abs dichloromethane (2 mL) was stirred at rt in the presence of 4 Å molecular sieves for 1 h. A soln of trimethylsilyl triflate (25 µL) in dichloromethane (1 mL) was added at -30 °C, and the mixture was stirred at -25 °C for 3 h. Then the reaction mixture was poured into ice/ aqueous sodium bicarbonate soln and extracted with ethyl acetate. The organic phases were washed with ice/ water, dried over sodium sulfate, and concentrated. The residue was purified by MPLC using ethyl acetate/ hexane 2:3 as eluent to afford pure tetrasaccharide **21** (230 mg, 71 %) as a colourless syrup; $[\alpha]_D$ +80.5 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 1520.5 (50 %, $[M + NH_4]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.04 (m_c ~ d, 2H, benzoyl), 7.59 (m_c ~ t, 1H, benzoyl), 7.50 - 7.20 (m, 32H, aromat), 5.53 (s, 1H, CHPh), 5.32 (d, 1H, $J_{1''',2'''}$ = 3.9 Hz, H-1'''), 5.26 (ddd ~ dt, 1H, $J_{3''',4'''eq}$ = 5.0 Hz, $J_{3''',4'''ax}$ = 11.0 Hz, H-3'''), 5.13, 5.12 (2 d ~ t, 1H, H-1, H-1'), 5.03 (dd ~ t, 1H, $J_{3'',4''}$ ≈ 8 Hz, H-3''), 5.02, 4.72 (2 d, 2H, CH_2Ph), 5.00, 4.89 (2 d, 2H, J_{gem} = 11.0 Hz, CH_2Ph), 4.83 (dd, 1H, $J_{2''',3'''}$ = 10.5 Hz, H-2'''), 4.74, 4.39 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.73 (dd ~ t, 1H, H 2''), 4.72, 4.68 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.66, 4.61 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.51 (d, 1H, $J_{1'',2''}$ = 8.0 Hz, H-1''), 4.32 (dd, 1H, $J_{5''',6a'''}$ = 4.0 Hz, $J_{6a''',6b'''}$ ≈ 12 Hz, H-6a'''), 4.29 (dd, 1H, $J_{5''',6b'''}$ ≈ 3.5 Hz, H-6b'''), 4.25 (ddd, 1H, $J_{5,6a}$ = 5.0 Hz, H-5), 4.20 (dd, 1H, $J_{5'',6a''}$ = 1.9 Hz, H-6a''), 4.14 (dd ~ t, 1H), 4.12 - 3.98 (m, 4H), 3.93 - 3.84 (m, 3H), 3.66 - 3.50 (m, 6H), 3.46 (dd, 1H, $J_{5',6b'}$ ≈ 1 Hz, $J_{6a',6b'}$ ≈ 10.5 Hz, H-6b'), 3.15 (ddd, 1H, $J_{4'',5''}$ = 9.5 Hz, $J_{5'',6a''}$ = 2.5 Hz, $J_{5'',6b''}$ = 43.8 Hz, H-5''), 2.22 (ddd, 1H, $H\text{-}4'''_{eq}$), 2.11, 2.03, 1.97, 1.89, 1.71 (5 s, 15H, OAc), 1.74 (ddd ~ q, 1H, $H\text{-}4'''_{ax}$).

***O*- (4-Deoxy-α-D-glucopyranosyl) - (1→4) - *O*- β-D-glucopyranosyl- (1→4)-2,3,6-tri-*O*-benzyl-α-D-gluco-pyranosyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (22).** To a soln of **21** (230 mg, 0.15 mmol) in cyclohexane (1 mL) and methanol (3 mL) was added a soln of sodium methanolate (0.2 mL of 2 g Na/ 100 mL methanol) at rt. The reaction mixture was stirred 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 purified by MPLC using ethyl acetate/ methanol/ water 185:10:5 as eluent to obtain **22** (182 mg) quantitatively as a colourless foam: MS (FAB) *m/z* 1227.4 (40 %, $[M + K]^+$), 1211.4 (90 %, [M +

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Na]$^+$), 1189.4 (20 %, [M + H]$^+$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 - 7.25 (m, 30H, aromat), 5.55 (s, 1H, PhCHO), 5.14 - 5.12 (m, 3H, H-1‴, H-1, H-1'), 4.98, 4.85 (2 d, 2H, J_{gem} = 11.0 Hz, CH_2Ph), 4.95, 4.91 (2 d, 2H, J_{gem} = 11.5 Hz, CH_2Ph), 4.80, 4.63 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.70, 4.67 (2 d, 2H, J_{gem} ≈ 12 Hz, CH_2Ph), 4.59, 4.45 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.41 (d, 1H, $J_{1'',2''}$ = 7.8 Hz, H-1''),4.25 (ddd ~ dt, 1H, $J_{5,6eq}$ = 5.0 Hz, H-5), 1.82 (ddd, 1H, H-4‴$_{eq}$), 1.39 (ddd~ q, 1H, H-4‴$_{ax}$).

***O*-(4-Deoxy-α-D-glucopyranosyl)-(1→4)-*O*-β-D-glucopyranosyl-(1→4)-α-D-glucopyranosyl α-D-Glucopyranoside (23).** A soln of **22** (182 mg, 0.15 mmol) in ethanol/water 3:1 (10 mL) was hydrogenated in the presence of 10 % palladium on charcoal (120 mg) at 1.1 bar for 18 h. The reaction mixture was filtered through a pad of filter aid which was washed with ethanol/ water 1:1. The filtrates were concentrated and filtered over Sephadex LH 20 using water as eluent to obtain pure **23** (92 mg, 96 %) as a colourless solid: $[\alpha]_D$ +164.5 ° (*c* 0.2, water); MS (ionspray) *m/z* 673 (100 %, [M + Na]$^+$); ^{1}H NMR (D_2O, 400 MHz) δ 5.42 (d, 1H, $J_{1''',2'''}$ = 4.0 Hz, H-1‴), 5.20, 5.19 (2d, 2H, H-1, H-1'), 4.53 (dd, 1H, $J_{1'',2''}$ = 7.9 Hz, H-1''), 1.99 (ddd, 1H, H-4‴$_{eq}$), 1.45 (ddd~ q, 1H, H-4‴$_{ax}$).

Anal. Calcd for $C_{24}H_{42}O_{20}$: C, 44.31; H, 6.51. Found: C, 44.27; H, 6.54.

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