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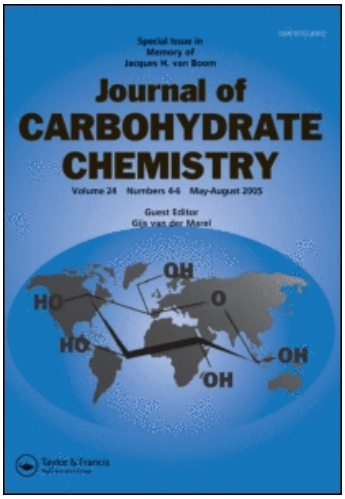

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J. CARBOHYDRATE CHEMISTRY, 19(7), 939-958 (2000)

VINYL GLYCOSIDES IN OLIGOSACCHARIDE SYNTHESIS (PART 6): 3-BUTEN-2-YL 2-AZIDO-2-DEOXY GLYCOSIDES AND 3-BUTEN-2-YL 2-PHTHALIMIDO-2-DEOXY GLYCOSIDES AS NOVEL GLYCOSYL DONORS

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ABSTRACT

An extension of the latent-active glycosylation strategy is reported whereby 3-buten-2-yl 2-deoxy-2-azidoglycosides and 3-buten-2-yl 2-deoxy-2-phthalimidoglycosides are used as building blocks for the preparation of amino sugar containing oligosaccharides. The allyl moieties of the latent substrates **5**, **16** and **19** can be conveniently isomerised by treatment with a catalytic amount of $(Ph_3P)_3RhCl/BuLi$ to give the active vinyl glycosides **6**, **17** and **20** in high yield. These glycosyl donors were successfully used in glycosylations with acceptors **7**, **9** and **11**. In the case of glycosyl donor **6**, the disaccharides **8**, **10** and **12** could be obtained as anomeric mixtures or with high α-or β-selectivities depending on the reaction conditions selected. Glycosylations with glycosyl donors **17** and **20** in each case gave solely the β-linked products only in high yields.

INTRODUCTION

The latent-active glycosylation strategy developed in our laboratory is based on the isomerization of an anomeric substituted allyl moiety to a vinyl glycoside, which can be

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employed in Lewis acid catalyzed glycosylations.[1] In this strategy, the allyl group functions initially as an anomeric-protecting group (latent), which, when required, can be isomerized to an active vinyl group, which offers an efficient anomeric-leaving group. The use of this anomeric functionality in combination with a set of orthogonal protecting groups allows one common building block to be easily converted into a range of glycosyl donors and acceptors. Furthermore, a disaccharide obtained by coupling of an active vinyl glycoside with a latent allyl glycoside can be elongated at either the reducing or non-reducing end, by either isomerization and glycosidation or, selective deprotection and glycosylation. These features make the latent-active glycosylation strategy very attractive for the assembly of complex oligosaccharides. Moreover, the convergent nature of this approach has been utilized for the synthesis of relatively large saccharide libraries from a small number of common building blocks.[2]

We report here an extension of the latent-active glycosylation strategy whereby 3-buten-2-yl 2-deoxy-2-azidoglycosides and 3-buten-2-yl 2-deoxy-2-phthalimidoglycosides are demonstrated to be efficient building blocks for the preparation of oligosaccharides which contain amino sugars.

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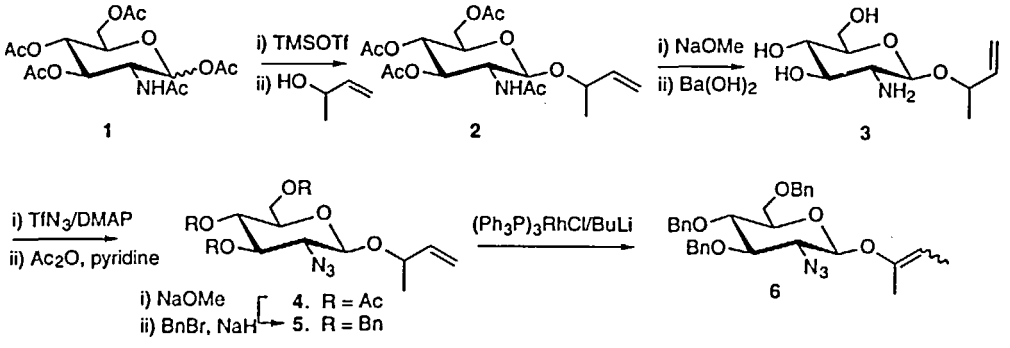
Amino sugars are widely distributed in living organisms and occur as constituents of glycoproteins, glycolipids, bacterial lipopolysaccharides, proteoglycans and nodulation factors associated with leguminous plants. The chemical synthesis of complex oligosaccharides containing amino sugars requires amino protecting or masking groups, which are compatible with common protecting group manipulations and glycosylations and can be removed or exchanged readily under mild conditions.[3,4] Use of 2-amino-2-deoxy-phthalimido-protected glycosyl donors has been the method of choice for the preparation of 1,2-*trans*-glycosides of 2-amino-2-deoxyglycosides. The *N*-phthalimido group can be readily introduced by reaction with phthalic anhydride[3] and cleaved with hydrazine,[5] butylamine,[6] hydroxylamine,[7] $NaBH_4$[8] or alkyldiamines immobilized on polysyrene beads.[9] Recently, the tetrachlorophthalimido, dithiosuccinoyl, NTroc, *N*-pentenoyl and *N,N*-diacetyl groups have been proposed as alternatives to the *N*-phthalimido group.[4] These protecting groups can be removed under milder reaction conditions. 2-Azido-2-deoxy-glycosyl donors are another group of substrates commonly used for the preparation of 2-amino-2-deoxyglycosides.[10] The azido group is stable to many reaction conditions and therefore can be introduced at an early stage of the synthesis. It is a non-participating functionality and by careful choice of solvent and reaction conditions both 1,2-*cis*- and 1,2-*trans*-glycosides can be synthesized. Conversion of an azido group to an amine is readily achieved by reduction by a wide range of reagents.

RESULTS AND DISCUSSION

Compound **6** was selected as a model glycosyl donor to study glycosylations with 2-buten-2-yl 2-azido-2-deoxyglycosides (Scheme 1). A key step in the preparation of **6** is the introduction of an azido group at C-2. Several methods are available for the preparation of azido sugars.[4] The method selected was a metal catalyzed azido-transfer reaction, which offers a mild and stereospecific approach for the conversion of amino into azido sugars.[11,12] The synthesis started with the coupling of the readily available *N*-acetylglucosamine penta-acetate with buten-2-ol in the presence if TMSOTf to give the allyl glycoside **2** in a yield of 68%.[13] This reaction proceeds through an intermediate 1,2-oxazoline, which is glycosylated *in situ* to give exclusively the β-glycoside. The *O*-acetyl groups of **2** were cleaved by treatment with NaOMe in methanol and the *N*-acetyl functionality with aqueous $Ba(OH)_2$[14] to give compound **3**, which was used directly in the next reaction without purification. The amino functionality of **3** was converted into an azido moiety by treatment with triflic azide and dimethylaminopyridine (DMAP) in methanol. The speed and reliability of this transformation could be improved by the addition of divalent Cu-ions. The crude product was immediately acetylated with acetic anhydride in pyridine to assist purification and afford compound **4** in a yield of 73% and an overall yield of 39% (based on **1**). Compound **4** was then deacetylated under Zemplén conditions. The hydroxyls of the resulting product were then benzylated with benzyl bromide and NaH in acetonitrile to give compound **5** in a yield of 93%. Finally, isomerization of the allyl moiety of the latent glycoside **5** with Wilkinson's catalyst, which was treated with BuLi,[15] gave the active vinyl glycoside **6** in an excellent yield of 90%.



Scheme 1

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It has been reported that the isomerization of an anomeric allyl group with an adjacent azido group can result in the formation of a 1,3-dipolar cyclo-addition adduct.[16] Fortunately, the cyclo-addition product was not observed in the isomerization of **5**. This observation was thought to be due to the β-configuration of the anomeric allyl moiety precluding the required orientation for cyclo-addition.

The glycosyl donor **6** was used to glycosylate glycosyl acceptors **7**, **9** and **11** (Scheme 2, Table 1). The primary alcohol of compound **7** is highly reactive whereas the reactivity of the hydroxyl in **9** is somewhat reduced because of the neighboring electron withdrawing benzoyl functionalities. The C-4 hydroxyl of compound **11** is the least reactive hydroxyl group when functioning as a glucosyl acceptor. Glycosylation conditions were investigated for the formation of anomeric mixtures as well as for achieving high α- or β-selectivities. The need for glycosylations with high anomeric selectivity is obvious; however, the desire to prepare mixtures of anomers needs some discussion. As part of our combinatorial chemistry projects, we have shown that it may be more efficient to prepare oligosaccharides as mixtures of anomers. Mixtures can be screened for biological activity and only saccharides that give a positive result have to be prepared as single anomers.

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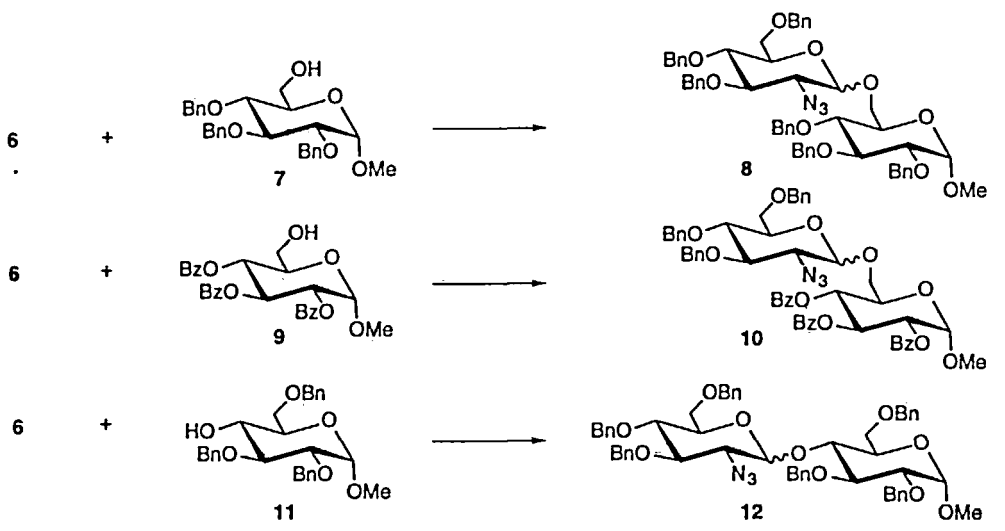
It is well established that glycosylations in acetonitrile at low temperature proceed with high β-selectivity; the reactions proceed through the formation of an intermediate α-nitrillium ion.[17] Recently, we showed that a mixture of dioxane/toluene is superior to diethyl ether/CH_2Cl_2 as a glycosylation solvent for obtaining high α-selectivities.[18] Furthermore, we observed that glycosylations of vinyl glycosides in CH_2Cl_2 at room temperature consistently give mixtures of anomers. As shown in Table 1, TMSOTf promoted glycosylations in acetonitrile at –30 °C, gave the disaccharides **8**, **10** and **12** in good yields with very high β-selectivities. Glycosylations in dichloromethane at room temperature in the presence of TMSOTf gave the disaccharides as mixtures of anomers, whereas acceptable α-selectivities were obtained when the same reactions were performed in dioxane/toluene in the presence of NIS/TMSOTf. Slightly reduced anomeric ratios were obtained when the latter glycosylations were promoted with TMSOTf only. As expected, the best yield was obtained with the most reactive glycosyl acceptor **6**, however, even satisfactory results were obtained in the case of the highly unreactive glycosyl acceptor **11**. The results presented demonstrate that 2-buten-2-yl 2-azido-2-deoxyglycosides are attractive glycosyl donors for the preparation of well-defined complex oligosaccharides as well as for the assembly of saccharide libraries.

Having successfully glycosylated 2-buten-2-yl 2-deoxy-2-azidoglycosides, we turned our attention to the use of 2-buten-2-yl 2-deoxy-2-phthalimidoglycosides **17** and **20** as glycosyl donors.

The synthesis of these derivatives started with the glycosylation of known[19] bromide **13** with 3-butene-2-ol in the presence of $Hg(CN)_2$ and $HgBr_2$ to give **14** in a yield of 76%.



Scheme 2

Table 1: Reactions of glycosyl donor **6** with acceptors **7**, **9** and **11**

Acceptor	Promoter	Solvent	Temperature	Product	Anomeric ratio (α/β)	Yield (%)
7	TMSOTf	MeCN	-30 °C	8	>5/95	83
7	TMSOTf	CH_2Cl_2	RT	8	1/1	75
7	NIS/TMSOTf	Dioxane/Tol	RT	8	4/1	85
9	TMSOTf	MeCN	-30 °C	10	>5/95	63
9	TMSOTf	CH_2Cl_2	RT	10	1/1	67
9	NIS/TMSOTf	Dioxane/Tol	RT	10	4/1	55
11	TMSOTf	MeCN	-30 °C	12	>5/95	68
11	TMSOTf	CH_2Cl_2	RT	12	1/1	66
11	NIS/TMSOTf	Dioxane/Tol	RT	12	4/1	54

The *O*-acetyl groups of **14** were cleaved under Zemplén conditions and the 4,6-diol of the resulting product was protected as a benzylidene acetal by reaction with benzaldehyde dimethyl acetal in the presence of a catalytic amount of camphorsulfonic acid (CSA) in DMF to give **15** in a good overall yield (92%). Next, benzylation of **15** with benzyl bromide and sodium hydride in THF provided **16** and finally, the isomerisation of the allyl moiety of **16** under standard conditions gave the glycosyl donor **17** in an excellent yield of 91%.

Compound **20** was prepared by regioselective reductive opening of the benzylidene acetal[20] of **16** with $NaCNBH_3$/HCl (**18**) followed by *p*-methoxybenzylation with *p*-methoxybenzyl chloride and sodium hydride in THF (**19**) and finally isomerisation of the allyl moiety of **19** with Wilkinson's catalyst treated with BuLi.

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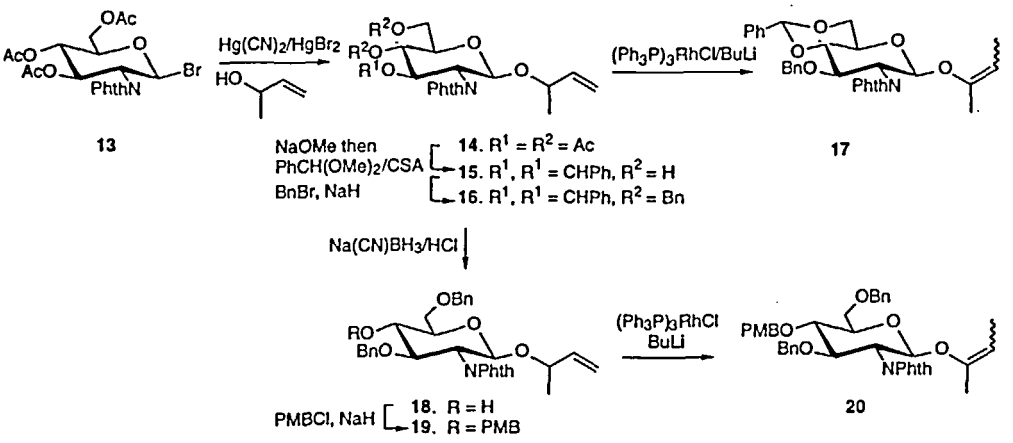

Scheme 3

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In order to investigate the versatility of the new class of glycosyl donor, a series of glycosylations were performed with glycosyl donor **17** and **20** and acceptors **7**, **9**, **11**, and **18**. The coupling reactions were performed in CH_2Cl_2 at room temperature in the presence of a catalytic amount of TMSOTf. As shown in Scheme 4, only the β-linked product was isolated in a good yield in each case. The successful preparation of chitobiose derivative **24** is of particular interest because it constitutes an important building block for the preparation of the oligosaccharide portion of *N*-linked glycopeptides and proteins. Two-dimensional homo- and heteronuclear NMR spectroscopy and FABMS established the identities of the new compounds. The β-selectivities of the disaccharides were confirmed by measuring the coupling constant $J_{1,2}$, which, in each case, was 8Hz.

The results presented here demonstrate that 3-buten-2-yl 2-deoxy-2-phthalimidoglycosides can easily be converted into the active 2-buten-2-yl glycosides by reaction with $(PPh_3)_3RhH$, which is prepared *in situ* by treatment of Wilkinson's catalyst with BuLi. The active glycosides proved to be efficient glycosyl donors in TMSOTf-promoted glycosylations to give β-glycosides in high yields.

EXPERIMENTAL

General Methods and Materials. All solvents were distilled from the appropriate drying agent. dichloromethane, toluene, benzene were distilled from P_2O_5 and stored over molecular sieves 4Å; DMF and CH_3CN were distilled from CaH_2 and stored

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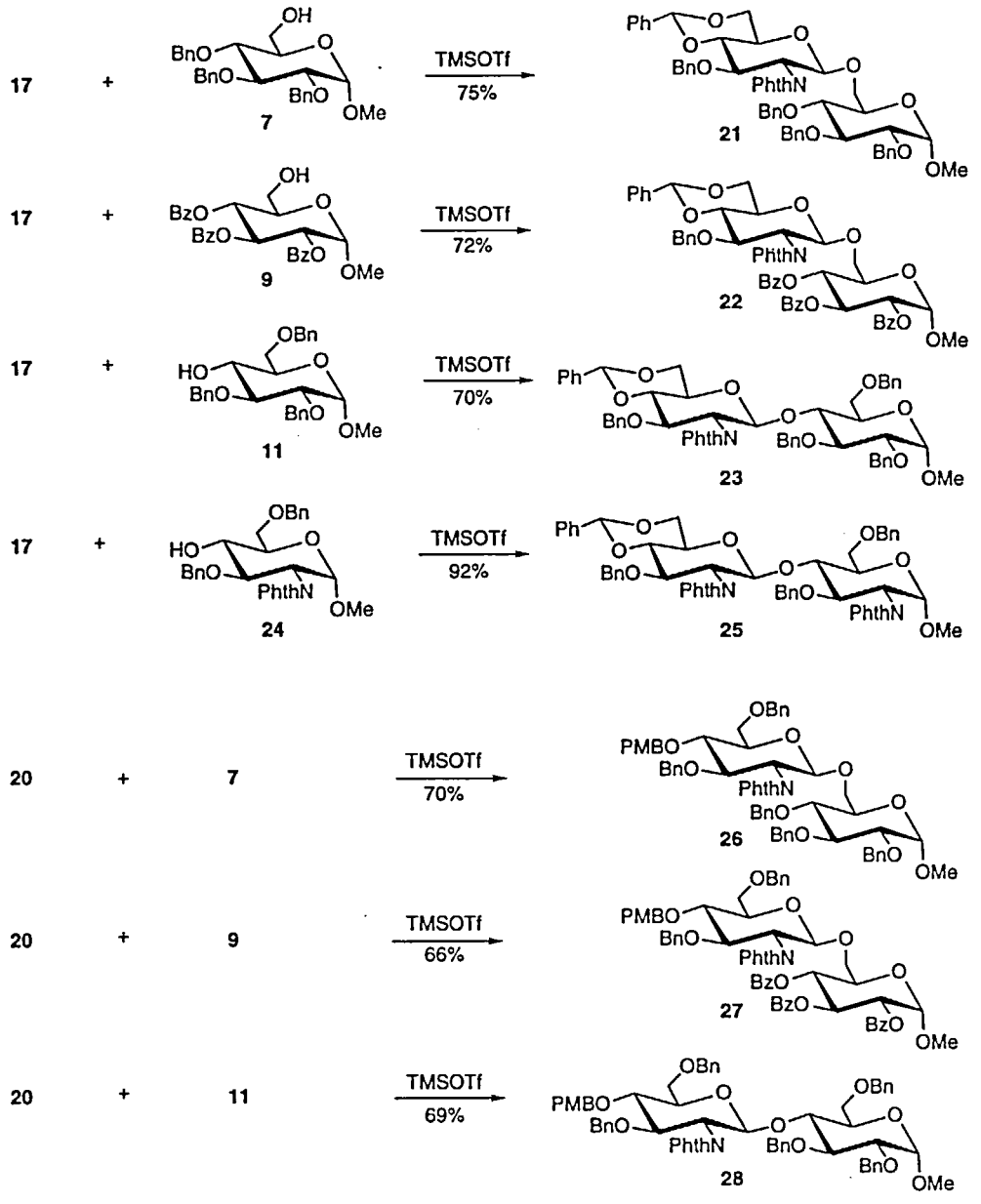

Scheme 4

over molecular sieves 4Å; diethyl ether, THF and 1,4-dioxane were distilled from $LiAlH_4$. Chemicals were purchased from Aldrich and Fluka and used without further purification. Flash chromatography was performed on silica gel (Merck, mesh 70-230). Size exclusion column chromatography was performed on Sephadex LH-20 (Pharmacia Biotech AB, Uppsala, Sweden) and TLC analysis was carried out on silica gel plates (Merck 1.05554 Kieselgel 60 F254). Compounds were visualized by UV light (254 nm) or by dipping with concentrated H_2SO_4-methanol, 1/10, v/v. All 1D ^1H NMR and 2D correlated spectroscopy (^1H-^1H COSY, ^1H-^{13}C correlation) were recorded on a Bruker DRX500 spectrometer. Chemical shifts (δ) are given in ppm relative to the internal standard signal of tetramethylsilane. *J*-values are given in Hz. Fast-atom bombardment mass spectra were recorded using a VG ZabSpec spectrometer with *m*-nitrobenzyl alcohol as the matrix. Optical rotations were measured on a Perkin-Elmer 241 polarimeter, and $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}.

***(R/S)* (3-Buten-2-yl) 3,4,6-tri-*O*-acetyl-2-*N*-acetyl-2-deoxy-β-D-glucopyranoside (2).** TMSOTf (2.1 mL, 11.6 mmol) was added dropwise to a solution of 1,3,4,6-tetra-*O*-acetyl-2-acetamido-2-deoxy-α-D-glucopyranose (3.33 g, 8.9 mmol) in dichloroethane (60 mL). The mixture was heated at 60 °C for 18 h. The reaction mixture was allowed to cool to ambient temperature and 4 Å activated powdered molecular sieves (3.4 g) were added. After stirring for 1.5 h, (*R/S*)-3-buten-2-ol (6 mL, 69 mmol) was added and the resulting reaction mixture was stirred for 30 h. The reaction was quenched by addition of triethylamine, filtered and the residue was washed with 10 % MeOH/CH_2Cl_2. The combined filtrates were concentrated *in vacuo*, redissolved in ethyl acetate (75 mL) and washed successively with $NaHCO_3$ (2 x 10 mL), NaCl (1 x 10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (MeOH/CH_2Cl_2, 5/95, v/v) to give 2 (2.77g, 77 %) as a white solid. δ_H(300 MHz; $CDCl_3$) 6.10 (1H, d, *J* 8.8, N*H*Ac), 5.87 (0.5 H, ddd, J_{trans} 16.9, J_{cis} 10.6, *J* 6.6, C*H*=CH_2), 5.61 (0.5 H, ddd, J_{trans} 17.3, J_{cis} 10.3, *J* 7.7, C*H*=CH_2), 5.38 (1H, dd, $J_{3,4} = J_{2,3}$ 10.3, H-3), 5.28-5.12 (1H, m, H-4), 5.08-4.82 (2H, m, CH=CH_2), 4.64 (1H, d, $J_{1,2}$ 8.5, H-1), 4.29-4.03 (3H, m, CH_3CH, H-6, H-6b), 3.92-3.82 (1H, m, H-2), 3.72-3.60 (1H, m, H-5), 2.07, 2.01, 1.98, 1.92 (12H, 4 x s, CH_3CO), 1.26, 1.23 (3H, 2 x d, *J* 6.5, CH_3CH); δ_C(75 MHz; $CDCl_3$) 170.6, 170.3, 170.1, 169.3 (4 x CH_3CO), 139.7, 138.8 (*C*H=CH_2), 116.9, 115.0 (CH=*C*H_2), 98.9, 98.1 (C-1), 77.2, 75.6 (CH_3-*C*H), 72.5, 72.2, 71.4, 68.9 68.8 and 68.4 (C-3, C-4, C-5), 62.2 (C-6), 55.2, 54.5 (C-2), 23.1, 21.4 and 20.6 (4 × *C*H_3CO), 20.1 (*C*H_3CH); *m/z* (FAB) 424 $[M+Na]^+$

Anal. Calcd for $C_{18}H_{27}NO_9$: C 56.1, H 7.01, N 3.64. Found: C 55.97, H 6.95, N 3.56.

***(R/S)* (3-Buten-2-yl) 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (4).** *R/S* (3-buten-2-yl) 3,4,6-tri-*O*-acetyl-2-*N*-acetyl-2-deoxy-β-D-

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glucopyranoside (2) (13.3g, 33.1 mmol) was dissolved in MeOH (50 mL) and adjusted to pH 10 with NaOMe. After stirring for 1 h, the reaction mixture was neutralized with DOWEX-H^+, filtered and the filtrate concentrated *in vacuo*. The residue was dissolved in H_2O (100 mL) and $Ba(OH)_2.8H_2O$ (15.6 g, 49.6 mmol) was added in four portions. The solution was stirred at 90 °C for 18 h. After cooling to ambient temperature, the mixture was filtered and the filtrate was neutralised by passing CO_2 through the mixture until no further precipitation occurred. The precipitate of $Ba(CO_3)_2$ was filtered off and the filtrate was concentrated *in vacuo* and the residue was coevaporated from toluene (2x 50 mL) to yield (*R/S*)-(3-buten-2-yl) 2-amino-2-deoxy-β-D-glucopyranoside (7.11 g, 92%) as a slightly yellow sticky foam. The yellow foam was then dissolved in MeOH (250 mL) and DMAP (4.1 g, 33 mmol) and $CuSO_4$ hydrate (33 mg, 0.2 mmol) was added, followed by the dropwise addition of TfN_3 (1M) (5 x 60 mL) over a period of 36 h. TLC analysis (EtOAc/MeO[illegible]$_2$O, 7/2/1, v/v/v) showed that the starting material (R_f 0.28) had been converted into a higher running product (R_f 0.72). The reaction mixture was reduced *in vacuo* to a volume of *ca.* 20 mL and the residue was dissolved in pyridine (30 mL) and acetic anhydride (10 mL). After stirring for 2 h the reaction mixture was quenched with H_2O (5 mL), stirred for 1 h and then concentrated *in vacuo* and the residue coevaporated with toluene (5 x 15 mL). Flash column chromatography (eluent: acetone/CH_2Cl_2, 1/49, v/v) afforded 4 as a white solid (9.3 g, 80%). δ_H(300 MHz; $CDCl_3$) 5.88 (0.5 H, ddd, J_{trans} 16.9, J_{cis} 10.6, *J* 6.6, C*H*=CH_2), 5.62 (0.5 H, ddd, J_{trans} 17.3, J_{cis} 10.3, *J* 7.7, C*H*=CH_2), 5.22-5.13 (2H, m, CH=CH_2), 4.96-4.88 (2H, m, H-3, H-4), 4.42 (1H, d, $J_{1,2}$ 8.5, H-1), 4.32-4.14 (2H, m, CH_3CH, H-6a), 4.03 (1H, dd, $J_{6a,6b}$ 10.3, $J_{6b,5}$ H-6b), 3.61-3.53 (1H, m, H-5), 3.45 (1H, dd, $J_{2,3}$ 9.6, H-2), 2.10-1.99 (9H, 3 x s, CH_3CO), 1.37-1.31 (3H, m, CH_3CH); δ_C(75 MHz; $CDCl_3$) 170.6, 170.0, 169.1 (3 x CH_3*C*O), 139.6, 138.3 (*C*H=CH_2), 118.4, 115.3 (CH=*C*H_2), 100.4, 98.6 (C-1), 78.0, 75.6 (CH_3-*C*H), 72.4, 71.0, 68.5 (C-3, C-4, C-5), 63.5, 63.0 (C-2), 62.0 (C-6), 21.5, 21.1, 20.9 (3 x *C*H_3CO), 20.1 (*C*H_3CH); IR ν 2108 cm^{-1} (N_3); *m/z* (FAB) 408 $[M+Na]^+$

Anal. Calcd for $C_{16}H_{23}N_3O_8$: C 49.87, H 6.02, N 10.90. Found: C 50.10, H 5.80, N 10.79).

***(R/S)* (3-Buten-2-yl) 3,4,6-tri-*O*-benzyl-2-azido-2-deoxy-β-D-gluco pyranoside (5).** The pH of a stirred solution of 4 (0.80 g, 2.1 mmol) in MeOH (15 mL) was adjusted to pH 10 with NaOMe. The reaction mixture was stirred for 18 h and then neutralized with DOWEX-H^+, filtered and the filtrate concentrated *in vacuo*. The residue was dissolved in DMF (12 mL) and cooled (0 °C). NaH (0.29 g, 12.1 mmol) and BnBr (1.11 mL, 9.3 mmol) were added, the reaction mixture was stirred for 10 min and then allowed to warm to room temperature. After stirring for 2 h, the reaction mixture was quenched with MeOH (30 mL) and then stirred for a further 0.5 h. The solution was diluted

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with Et_2O (100 mL) and washed with H_2O (4 x 30 mL), aq NH_4Cl (2 x 20 mL) and aq $NaHCO_3$ (3 x 20 mL). The organic layer was dried ($MgSO_4$), filtered and the filtrate concentrated *in vacuo*. Flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether (60-80 °C), 1/5, v/v) afforded **5** as a colorless viscous oil (0.92 g, 83%). δ_H(300 MHz; $CDCl_3$) 7.45-7.17 (15H, m, Ar-H), 5.98 (0.5 H, ddd, J_{trans} 16.9, J_{cis} 10.6, J 6.6, C*H*=CH_2), 5.62 (0.5 H, ddd, J_{trans} 17.3, J_{cis} 10.3, J 7.7, C*H*=CH_2), 5.30-5.07 (2H, m, CH=CH_2), 4.93-4.76 (3H, m, 1.5 AB q, OCH_2Ph), 4.66-4.52 (2H, m, AB q, OCH_2Ph), 4.60-4.88 (1H, d, $J_{1,2}$ 8.5, H-1), 4.40-4.30 (2H, m, CH_3C*H*, 0.5AB q, OCH_2Ph), 3.76-3.68 (2H, m, H-6a, H-6b), 3.62 (1H, dd, $J_{2,3}$ 8.9, H-2), 3.50-3.37 (3H, m, H-3, H-4, H-5) and 1.36, 0.89 (3H, 2 x d, J 6.6, CH_3CH); δ_C(75 MHz; $CDCl_3$) 140.1, 138.9 (*C*H=CH_2), 138.1 (Cq, Ar-C), 128.5-127.8 (Ar-C), 117.6, 115.2 (CH=*C*H_2), 100.7, 99.0 (C-1), 83.4, 77.9 (CH_3-*C*H), 77.5, 75.7, 75.0 (C-3, C-4, C-5), 75.6, 75.1, 73.5 (3 x OCH_2Ph), 68.8 (C-6), 66.5 (C-2), 21.8, 20.4 (*C*H_3CH); *m/z* (FAB) 552 $[M+Na]^+$

Anal. Calcd for $C_{31}H_{35}N_3O_5$: C 70.30, H 6.66, N 7.94. Found: C 70.21, H 6.58, N 7.99.

***E/Z* (2-Buten-2-yl) 3,4,6-tri-*O*-benzyl-2-azido-2-deoxy-β-D-gluco pyranoside (6).** A solution of Wilkinson's catalyst (241 mg, 0.26 mmol) and *n*-BuLi (116 μL, 0.29 mmol) in THF (3 mL) was transferred, with the strict exclusion of air, to a refluxing solution of **5** (0.92 g, 1.7 mmol) in THF (5 mL) under an inert atmosphere of argon. The reaction mixture was heated under reflux for 2 h, cooled and concentrated *in vacuo* to a brown sticky residue. Flash column chromatography on silica gel (eluent: acetone/CH_2Cl_2, 1/49, v/v) afforded **6** as a pale yellow solid (830 mg, 90%). δ_H(300 MHz; $CDCl_3$) 7.41-7.12 (15H, m, Ar-H, 3 x Bn), 4.93-4.49 (7H, m, 3 x OCH_2Ph, CH_3C*H*), 4.62 (1H, d, $J_{1,2}$ 8.1, H-1), 3.77-3.39 (6H, m, H-2, H-3, H-4, H-5, H-6a, H-6b), 1.92, 1.87 (3H, 2 × s, CH_3C), 1.70-1.57 (3H, m, CHCH_3); δ_C(75 MHz; $CDCl_3$) 152.1, 150.9 (*C*=CH), 138.0 (Cq, Ar-C), 128.5-127.7 (Ar-C), 106.3 (*C*HCH_3), 99.2, 98.4 (C-1), 77.7, 66.8, 66.0 (C-3, C-4, C-5), 75.6, 75.1, 73.5 (3 x OCH_2Ph), 68.7 (C-6), 56.8 (C-2), 16.1 (C*C*H_3), 11.9, 10.3 (CH*C*H_3); *m/z* (FAB) 552 $[M+Na]^+$

Anal. Calcd for $C_{31}H_{35}N_3O_5$: C 70.30, H 6.66 N 7.94. Found: C 70.18, H 6.60, N 8.00.

***(R/S)* (3-Buten-2-yl) 3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (14).** (*R/S*) 3-Buten-2-ol (5 mL, 57.96 mmol) and powdered activated molecular sieves (4Å, 4 g) were added to a solution of **13** (4.5 g, 9.05 mmol) in acetonitrile (60 mL). The mixture was stirred under an atmosphere of argon for 2 h. $Hg(CN)_2$ (3.4 g, 13.5 mmol) and $HgBr_2$ (5.5 g, 15.4 mmol) were added and the reaction mixture was stirred for 2 h. The solids were filtered and the filtrate was concentrated under

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reduced pressure to give an oil. The oil was dissolved in CH_2Cl_2 (50 mL) and washed with aqueous $NaHCO_3$ (15%, 3 × 50 mL) and brine (2 × 50 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure to give crude product which was purified by flash silica gel column chromatography (eluent: ethyl acetate/petroleum ether (60-80 °C), 1/1, v/v) to give compound **14** (3.35 g, 76%) as a white solid. δ_H(300 MHz; $CDCl_3$) 7.83-7.73 (4H, m, Ar-H, Phth), 5.89-5.73 (2H, m, H-3, C*H*=CH_2), 5.45 (1H, d, $J_{1,2}$ 8.5, H-1), 5.42-5.31 (1H, m, C*H*-CH_3), 5.18-4.98 (3H, m, CH=CH_2, H-4), 4.38-4.22 (2H, m, H-2, H-6a), 4.19-4.10 (1H, m, H-6b), 3.87-3.76 (1H, m, H-5), 2.10, 2.04, 1.85 (9H, 3 x s, 3 x CH_3CO) and 1.18, 1.04 (3H, 2 x d, CH-CH_3); δ_C(75 MHz; $CDCl_3$) 173.6, 173.2 (2 x C=O, Phth), 170.7, 170.2, 169.5 (4 x CH_3*C*O), 139.5, 138.3 (*C*H=CH_2), 134.3, 131.3, 123.6 (Ar-C, Phth), 117.4, 115.3 (CH_2=CH), 96.7, 95.5 (C-1), 77.3, 75.9 (*C*H-CH_3), 71.7, 70.8, 69.1 (C-3, C-4, C-5), 62.2, 56.6 (C-6), 54.8 (C-2), 21.4 (CH-*C*H_3) and 20.8, 20.7, 20.1 (3 x *C*H_3CO); *m/z* (FAB) 512.1 $[M+Na]^+$

***(R/S)* (3-Buten-2-yl) 4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (15)** A stirred solution of **14** (3.35 g, 6.85 mmol) in CH_3OH (100 mL) was adjusted to pH 10 using $NaOCH_3$, and left to stir for 1 h. The reaction was neutralized with Dowex 50X8 H^+, filtered and the filtrate was concentrated *in vacuo*. The product (*R/S*) (3-buten-2-yl)-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside was dried *in vacuo* for 18 h and dissolved in acetonitrile (30 mL). Benzylidene dimethyl acetal (2.3 mL, 15.5 mmol) was added and the solution was acidified with camphorsulfonic acid to pH 3. After stirring the resulting mixture for 15 h, the solution was neutralized with triethylamine and the solvents were evaporated. The residue was dissolved in CH_2Cl_2 and washed with aqueous $NaHCO_3$ (15%, 3 x 20 mL), brine (2 x 20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (eluent: toluene/ethyl acetate, 9/1, v/v) to give **15** as a white foam (2.8 g, 92%). δ_H(300 MHz; $CDCl_3$) 7.90-7.68 (4H, m, Ar-H, Phth), 7.5-7.32 (5H, m, Ar-H, Ph-CH), 5.89-5.73 (1H, m, C*H*=CH_2), 5.56 (1H, s, Ph-C*H*), 5.38 (1H, d, $J_{1,2}$ 8.5, H-1), 5.20-4.90 (2H, m, CH=CH_2), 5.70-4.55 (1H, m, C*H*-CH_3), 4.44-4.32 (1H, m, H-3), 4.30-4.11 (2H, m, H-2, H-4), 3.90-3.80 (1H, m, H-6a), 3.65-3.55 (2H, m, H-6b, H-5), 2.47 (1H, dd, *J* 6.9, *J* 3.3, C3-OH) and 1.18, 1.03 (3H, 2 x d, *J* 6.2, CH-CH_3); δ_C(75 MHz; $CDCl_3$) 139.4, 138.5 (*C*H=CH_2), 137.0 (Cq, Ar-C, Ph-CH), 131.6 (Cq, Phth), 134.1, 129.4-123.4 (Ar-C, Phth, benzylidene), 117.2, 115.2 (CH_2=CH), 101.9 (Ph-*C*H), 97.2, 96.6 (C-1), 82.2 (*C*H-CH_3), 76.2, 68.5, 66.1, 56.8 (C-3, C-4, C-5, C-2), 68.7 (C-6), 21.6 and 20.1 (CH-*C*H_3); *m/z* (FAB) 474 $[M+Na]^+$.

***(R/S)* (3-Buten-2-yl) 3-*O*-benzyl-4,6-*O*-bezylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (16).** NaH (60% dispersion in mineral oil, 0.17 g, 4.13 mmol) and Bu_4NI (0.06 g, 0.17 mmol) were added to a stirred solution of **15** (1.5

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g, 3.3 mmol) in freshly distilled THF (30 mL). Benzyl bromide (0.98 mL, 8.25 mmol) was added dropwise into the above solution. After refluxing the reaction mixture for 3 h, TLC showed completion of the reaction. The solids were filtered off over a bed of Celite and washed with THF. The filtrate was concentrated *in vacuo* and the residue redissolved in CH_2Cl_2 (50 mL) and the resulting solution was washed with aqueous NH_4Cl (15%, 2 x 20 mL), dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum ether (60-80 °C), 1/4, v/v) to give **16** as a white foam (1.54 g, 86%). δ_H(300 MHz; $CDCl_3$) 7.80-6.80 (14H, m, Ar-H, Bn, Ph-CH, Phth,), 5.85-5.70 (1H, m, C*H*=CH_2), 5.60 (1H, s, Ph-C*H*), 5.30 (1H, d, $J_{1,2}$ 8.8, H-1), 5.15-4.85 (2H, m, CH=CH_2), 4.82, 4.80, 4.77, 4.75; 4.53, 4.51, 4.48, 4.46 (2H, AB q, J_{AB} 12.1, OCH_2Ph), 4.45-4.32 (2H, m, C*H*-CH_3, H-4), 426-4.06 (2H, m, H-3, H-2), 3.90-3.75 (2H, m, H-6a, H-6b), 3.67-3.54 (1H, m, H-5) and 1.15, 0.98 (3H, 2 x d, *J* 6.6, CH-CH_3); δ_C(75 MHz; $CDCl_3$) 139.9, 138.5 (*C*H=CH_2), 133.8 (Ar-C, Phth), 131.6 (Cq, Ar-C),129.0, 128.3, 128.0, 127.3, 126.0, 123.3 (Ar-C), 117.1, 115.0 (*C*H_2=CH), 101.3 (Ph-*C*H), 97.2, 96.6 (C-1), 83.1 (*C*H-CH_3), 75.9, 74.4, 74.35 (C-3, C-4), 74.1 (O*C*H_2Ph), 68.8 (C-6), 65.9, 56.5, 56.0 (C-5, C-2) and 21.5, 20.0 (CH-*C*H_3); *m/z* (FAB) 564.2 $[M+Na]^+$

Anal. Calcd for $C_{32}H_{31}NO_7$: C 70.97, H 5.77, N 2.59. Found: C 71.14, H 5.88, N 2.58.

***(E/Z)* (2-Buten-2-yl) 3-*O*-benzyl-4,6-*O*-bezylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (17).** *n*-Butyllithium (2.5M in hexane, 60 μL, 0.15 mmol) was added to a stirred solution of Wilkinson's catalyst (70 mg, 0.074 mmol) in THF (1.5 mL) that was thoroughly degassed and placed under argon. The resulting red solution was stirred at 20 °C for 5 minutes and then transferred *via* syringe into a refluxing solution of **16** (212 mg, 0.39 mmol) and PPh_3 (39 mg, 0.15 mmol) in THF (2 mL) under argon. After 2 h, TLC analysis (acetone/CH_2Cl_2, 1/49, v/v) showed completion of the reaction. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and concentrated to an orange / red residue. Purification of the residue by silica gel flash column chromatography (eluent: acetone/CH_2Cl_2, 1/49, v/v) gave **17** as light yellow foam (192 mg, 91%). δ_H(300 MHz; $CDCl_3$) 7.80-6.80 (14H, m, Ar-H, Phth, Bn, Ph-CH), 5.63 (1H, s, Ph-C*H*), 5.58-5.51 (C*H*-CH_3), 4.82, 4.77, 4.55, 4.49 (2H, AB q, *J* 12.1, OCH_2Ph), 4.48-4.32 (3H, m, H-1, H-3, H-4), 4.16-4.08 (1H, m, H-2), 3.92-3.80 (2H, m, H-6a, H-6b), 3.78-3.54 (1H, m, H-5), 1.72, 1.57 (3H, 2 x s, O-C(CH_3)) 1.46, 1.30 (3H, 2 x d, *J* 7.0, CHCH_3); δ_C(75 MHz; $CDCl_3$) 150.9, 148.5 (Cq, O-*C*(CH_3)), 137.9, 137.3 (C=O, Phth), 133.9, 128.1-123.4 (Ar-C), 131.6 (Cq, Ar-C), 106.2, 99.4 (*C*H-CH_3), 101.4 (Ph-*C*H), 95.9, 95.6 (C-1), 83.0 (C-3), 74.1 (C-5), 74.2 (O*C*H_2Ph), 68.6 (C-6), 66.1 (C-4), 55.8 (C-2), 21.0, 18.3 (O-C(*C*H_3)) and 15.2, 14.9 (CH-*C*H_3); *m/z* (FAB) 564.2 $[M+Na]^+$. (Found: $[M+Na]^+$ 564.1974. $C_{32}H_{31}NO_7Na$ requires *m/z*, 564.1998)

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(R/S) **(3-Buten-2-yl) 3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (18).** A solution of HCl in ether (1M, 20 mL) was added to a mixture of **16** (1.06 g, 1.96 mmol), sodium cyanoborohydride (1.23 g, 19.5 mmol) and powdered 3 Å molecular sieves (1.5 g) in THF (20 mL). TLC analysis (ethyl acetate/petroleum (60-80 °C), 1/2, v/v) was performed 5 min after the evolution of gas had ceased and showed completion of reaction. The mixture was diluted with CH_2Cl_2 (40 mL) and filtered through Celite. The filtrate was washed with water (2 x 30 mL) and aqueous $NaHCO_3$ (2 x 30 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated under reduced pressure. The product was purified using silica gel column chromatography (eluent: ethyl acetate/petroleum ether (60-80 °C), 1/2, v/v) to give **18** (0.91 g, 86%) as a waxy white solid. δ_H(300 MHz; $CDCl_3$) 7.90-7.30, 7.13-6.82 (14H, m, Ar-H, 2 x Bn, Phth), 5.87-5.29 (1H, m, C*H*=CH_2), 5.28-5.66 (1H, 2 x d, $J_{1,2}$ 8.1, H-1), 5.28-4.87 (2H, m, CH=CH_2), 4.82-4.49 (4H, m, 2 x OCH_2Ph), 4.30-4.05 (3H, m, C*H*- CH_3, H-4, H-3), 3.89-3.73 (3H, m, H-2, H-6a, H-6b), 3.70-3.56 (1H, m, H-5), 3.07-2.98 (1H, dd, *J* 2.5, 4-OH) and 1.13, 0.98 (3H, 2 x d, *J* 6.6, CH-CH_3); δ_C (75 MHz; $CDCl_3$) 139.8, 138.7 (*C*H=CH_2), 138.2, 137.6 (2 x Cq, 2 x Bn), 133.8, 123.1 (Ar-C, Phth), 131.6, 128.7 (Cq, Phth), 128.5-127.4 (Ar-C, 2 x Bn), 116.8, 114.8 (CH_2=CH), 96.7, 95.9 (C-1), 78.5, 76.3, 75.6, 74.7, 74.6 (C-3, *C*H-CH_3, C-4), 74.2, 73.7 (2 x OCH_2Ph), 73.4, 73.2 (C-2), 70.9 (C-6), 56.7, 55.4 (C-5) and 21.6, 20.0 (CH-*C*H_3); *m/z* (FAB) 566.2 $[M+Na]^+$. (Found: $[M+Na]^+$, 566.217857. $C_{32}H_{33}O_7Na$ requires *m/z*, 566.215473.)

(E/Z) **(2-Buten-2-yl) 3,6-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (20).** *n*-Butyl lithium (2.5M in hexane, 50 μL, 0.12 mmol) was added to a stirred solution of Wilkinson's catalyst (57 mg, 0.06 mmol) in THF (1.5 mL) under argon. The resulting red solution was stirred at 20 °C for 5 min and then transferred *via* syringe into a refluxing solution of **19** (200 mg, 0.31 mmol) and triphenylphosphine (31 mg, 0.12 mmol) in THF (2 mL) under argon. After 1 h, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and concentrated *in vacuo* to give an orange-red residue. Purification of the residue by flash silica gel column chromatography (eluent: acetone/CH_2Cl_2, 1/49, v/v) gave **20** as light yellow syrup (174 mg, 87%). δ_H(400 MHz; $CDCl_3$) 7.80-6.70 (18H, m, Ar-H, Phth, 2 x Bn, PMB), 5.47 (1H, dd, $J_{1,2}$ 8.1, H-1), 4.89-4.75 (1H, m, *C*H-CH_3), 4.72-4.42 (6H, m, 2 x OCH_2Ph, OCH_2PhOCH_3), 4.41-4.26 (2H, m, H-3, H-2), 3.78 (3H, s, OCH_3), 3.77-3.63 (4H, m, H-6a, H-6b, H-4, H-5), 1.77, 1.56 (3H, 2 x s, O-C(CH_3)) and 1.47, 1.28 (3H, 2 x d, *J* 6.98, CH-CH_3); δ_C(75 MHz; $CDCl_3$) 162.85, 159.40 (2C, C=O), 151.11, 148.90 (Cq, O-*C*(CH_3)), 138.3-113.48 (Ar-C, 2 x Bn, PMB, Phth), 105.9, 99.2 (*C*H-CH_3), 95.6, 95.2 (C-1), 79.4, 79.35, 79.3, 79.1 (C-3, C-4), 75.2, 75.1 (C-2), 74.8, 74.8 (OCH_2Ph), 74.7, 74.7 (OCH_2Ph), 73.5, 73.5 (OCH_2Ph), 68. 8, 68.6 (C-6), 56.5, 55.9 (C-5), 55.8, 55.3 (ArOCH_3), 18.5, 15.3

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(O-C(CH_3)), 11.9, 10.0 (CH-CH_3); *m/z* (FAB) 686 $[M+Na]^+$ (Found: $[M+Na]^+$, 686.27442. $C_{40}H_{41}NO_8Na$ requires *m/z*, 686.2730).

General procedure for the glycosidation of compound 6

Method A: Activation with TMSOTf. Compound **6** (108 mg, 0.2 mmol) and glycosyl acceptor **7**, **9** or **11** (0.18 mmol) were coevaporated with toluene (10 mL) and dried *in vacuo* for 1 h. The reagents were then dissolved in the appropriate solvent (2 mL) and stirred over activated 4 Å molecular sieves (200 mg) for 1.5 h. After cooling the reaction mixture to the appropriate temperature, TMSOTf (4.6 μL, 24 μmol) was added. Upon completion, the reaction mixture was neutralized (TEA), diluted with CH_2Cl_2 (25 mL), filtered through a pad of Celite and the filtrate was washed with aqueous $NaHCO_3$ (2 × 10 mL) and brine (2 × 10 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate concentrated *in vacuo*. The crude product was purified by silica gel column chromatography.

Method B: *Activation with NIS/TMSOTf.* Compound **6** (108 mg, 0.2 mmol) and glycosyl acceptor **7**, **9** or **11** (0.18 mmol) are coevaporated with toluene (10 mL) and dried *in vacuo* for 1 h. The reagents were dissolved in toluene-1,4-dioxane (2 mL, 1/3, v/v) and stirred over activated 4 Å molecular sieves (200 mg) for 1.5 h. NIS (74 mg, 0.32 mmol) and TMSOTf (4.2 μL, 22 μmol) were added. Upon completion, the reaction mixture was neutralized (TEA), diluted with CH_2Cl_2 (25 mL), filtered through a pad of Celite and the filtrate concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (25 mL) and washed with aqueous $NaHCO_3$ (2 x 10 mL) and brine (2 x 10 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate concentrated *in vacuo*. The crude product was purified by silica gel column chromatography.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-benzyl-2-azido-2-deoxy-β-D-glucopyranosyl)-α-D-glucopyranoside (8β). $[\alpha]_D^{21}$ +0.9 (*c* 1.3 in $CHCl_3$). δ_H(500 MHz; $CDCl_3$) 7.40-7.15 (30H, m, Ar-H), 4.99-4.76, 4.68-4.50 (12H, m, 6 x OCH_2Ph), 4.63 (1H, d, $J_{1,2}$ 3.5, H-1), 4.17 (1H, d, $J_{1',2'}$ 7.7, H-1'), 4.13 (1H, dd, $J_{5',6'a}$ 1.8, $J_{6'a,6'b}$ 10.80, H-6'a), 4.01 (1H, dd, $J_{2,3}$ 9.2, $J_{3,4}$ 9.4, H-3), 3.82 (1H, ddd, $J_{5,6a}$ 2.0, $J_{5,6b}$ 4.4, $J_{4,5}$ 9.9, H-5), 3.72-3.64 (3H, m, H-6a, H-6b, H-6'b), 3.60-3.53 (3H, m, H-4, H-3', H-2), 3.47-3.34 (3H, m, H-4', H-2', H-5'), 3.38 (3H, s, OCH_3); δ_C(125 MHz; $CDCl_3$) 137.9 (Cq, Ar-C), 128.5-127.7 (30C, Ar-C in 6 x Bn), 102.1 (C-1'), 98.2 (C-1), 83.3, 82.1, 79.3, 77.8, 74.5, 70.2 (C-2, C-3, C-4, C-5, C-3', C-4', C-5'), 75.8, 75.1 (6 x OCH_2Ph), 73.5, 68.7 (C-6, C-6'), 66.4 (C-2'), 55.3 (OCH_3); *m/z* (FAB) 944 $[M+Na]^+$ (Found: $[M+Na]^+$, 944.4134. $C_{55}H_{59}N_3O_{10}Na$ requires *m/z*, 944.4098).

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-benzyl-2-azido-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranoside (8α). $[\alpha]_D^{21}$ +37.4 (*c* 1.2 in $CHCl_3$). δ_H(500 Mz; $CDCl_3$) 7.38-7.11 (30H, m, Ar-H), 5.00 (1H, d, $J_{1',2'}$ 4.0, H-1'), 4.99-4.40

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(12H, m, 6 x OCH_2Ph), 4.60 (1H, d, $J_{1,2}$ 4.5, H-1), 3.99 (1H, dd, $J_{2,3}$ 9.0, $J_{3,4}$ 10.0, H-3), 3.91 (1H, dd, $J_{2',3'}$ 8.0, $J_{3',4'}$ 7.5, H-3'), 3.84-3.72 (2H, m, H-6a, H-5), 3.70-3.65 (2H, m, H-4, H-6b), 3.66-3.57 (2H, m, H-6'a, H-6'b), 3.57-3.50 (3H, m, H-5', H-4', H-2), 3.38, 3.36 (3H, 2 _ s, OCH_3), 3.32 (1H, dd, H-2'); δ_C(125 MHz; $CDCl_3$) 138.2 (Cq, Ar-C), 128.5-127.7 (30C, Ar-C in 6 x Bn), 98.3, 98.0 (C-1', C-1), 82.1, 80.1, 79.9, 78.2, 77.8, 70.7, 70.0 (C-2, C-3, C-4, C-5, C-3', C-4', C-5'), 75.9, 75.3, 75.0, 73.6 (6 x OCH_2Ph), 68.7, 68.1 (C-6, C-6'), 63.5 (C-2'), 55.3 (OCH_3); *m/z* (FAB) 944 $[M+Na]^+$.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(3,4,6-tri-*O*-benzyl-2-azido-2-deoxy-β-D-glucopyranosyl)-α-D-glucopyranoside (10β). $[\alpha]_D^{21}$ +13.2 (*c* 1.6 in $CHCl_3$). δ_H(500 MHz; $CDCl_3$) 8.02-7.83, 7.55-7.12 (30H, m, Ar-H), 6.15 (1H, dd, $J_{2,3}$ 9.7, $J_{3,4}$ 9.5, H-3), 5.52 (1H, dd, $J_{4,5}$ 10.1, H-4), 5.31-5.19 (2H, m, H-1, H-2), 4.90, 4.45 (2H, AB, OCH_2Ph), 4.78 (2H, AB, OCH_2Ph), 4.55, 4.53 (2H, AB, OCH_2Ph), 4.35 (1H, d, $J_{1',2'}$ 7.7, H-1'), 4.36-4.30 (1H, m, H-5), 4.09 (1H, dd, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 11.4, H-6a), 3.77 (1H, dd, $J_{5,6b}$ 6.8, H-6b), 3.66 (2H, m, H-6a', H-6'b), 3.63-3.58 (1H, m, H-5'), 3.50 (3H, s, OCH_3), 3.44-3.37 (3H, m, H-2', H-3', H-4'); δ_C(125 MHz; $CDCl_3$) 165.8 (CH_3CO), 138.0 (Cq, Ar-C), 133.4-127.8 (Ar-C, 3 x Bn, 3 x Bz), 102.5 (C-1), 96.8 (C-1'), 83.1, 77.6, 72.1, 70.4, 69.7, 68.9 (C-2, C-3, C-4, C-5, C-3', C-4', C-5'), 75.6, 73.5 (3 x OCH_2Ph), 68.4 (C-6, C-6'), 66.5 (C-2'), 55.6 (OCH_3); *m/z* (FAB) 986 $[M+Na]^+$ (Found: $[M+Na]^+$, 986.3458. $C_{55}H_{53}N_3O_{13}Na$ requires *m/z*, 986.3476).

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(3,4,6-tri-*O*-benzyl-2-azido-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranoside (10α). $[\alpha]_D^{21}$ +61.6 (*c* 1.6 in $CHCl_3$). δ_H(400 MHz; $CDCl_3$) 8.00-7.14 (30H, m, Ar-H), 6.21-6.12 (1H, dd, $J_{2,3}$ 9.9, $J_{3,4}$ 9.7, H-3), 5.63-5.58, 5.56-5.51 (1H, 2 x dd, $J_{4,5}$ 9.9, H-4), 5.28-5.21 (3H, m, H-1, H-2, 0.5 AB, OCH_2Ph), 4.97-4.95 (1H, d, $J_{1,2}$ 3.5, H-1'), 4.89-4.32 (5H, 2 0.5 AB , OCH_2Ph), 4.30-4.25 (1H, m, H-5), 4.03 (1H, dd, $J_{2',3'}$ 9.0, $J_{3',4'}$ 8.8, H-3'), 3.89 (1H, dd, $J_{5,6a}$ 5.9, $J_{6a,6b}$ 11.2, H-6a), 3.82-3.77 (1H, m, H-5'), 3.71-3.59 (3H, m, H-4', H-6b, H-6'a), 3.51-3.41 (1H, m, H-6'b), 3.46 (3H, s, OCH_3), 3.34 (1H, dd, $J_{2',3'}$ 10.3, H-2'); δ_C(75 MHz; $CDCl_3$) 165.9, 165.2 (CH_3CO), 138.1, 137.8 (Cq, Ar-C), 133.4-127.7 (Ar-C, 3 x Bn, 3 x Bz), 102.5 (C-1'), 96.9 (C-1), 79.8, 78.2, 72.1, 70.8, 70.5, 69.4, 68.3 (C-2, C-3, C-4, C-5, C-3', C-4', C-5'), 75.3, 74.9 (3 x OCH_2Ph), 68.0, 67.1 (C-6, C-6'), 63.3 (C-2'), 55.6 (OCH_3); *m/z* (FAB) 986 $[M+Na]^+$.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-benzyl-2-azido-2-deoxy-β-D-glucopyranosyl)-α-D-glucopyranoside (12β). $[\alpha]_D^{21}$ +2.5 (*c* 2.1 in $CHCl_3$). δ_H(400 MHz; $CDCl_3$) 7.37-7.13 (30H, m, Ar-H), 5.03-4.35 (12H, m, 6 x OCH_2Ph), 4.59 (1H, d, $J_{1,2}$ 3.5, H-1), 4.25 (1H, d, $J_{1',2'}$ 8.0, H-1'), 3.96-3.86 (3H, m, H-3, H-4, H-6a), 3.77 (1H, m, H-5), 3.71-3.65 (2H, m, H-3', H-6b), 3.61-3.55 (2H, m, H-4', H-6'a), 3.50-3.46 (2H, m, H-6'b, H-2), 3.37 (3H, s, OCH_3); δ_C(100 MHz; $CDCl_3$) 139.5, 138.3,

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138.0 (Cq, Ar-C), 128.3-127.0 (Ar-C, 6 x Bn), 100.9 (C-1'), 98.3 (C-1), 83.3, 80.3, 79.0, 77.8, 76.7, 69.6 (C-2, C-3, C-4, C-5, C-3', C-4', C-5'), 75.4, 75.3, 75.0, 74.7, 73.4, 73.3 (6 x OCH_2Ph), 68.5, 68.1 (C-6, C-6'), 66.8 (C-2'), 55.3 (OCH_3); *m/z* (FAB) 944 $[M+Na]^+$ (Found: $[M+Na]^+$, 944.4092. $C_{55}H_{59}N_3O_{10}Na$ requires *m/z*, 944.4098).

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-benzyl-2-azido-2-deoxy-α-D-glucopyranosyl)-α-D-glucopyranoside (12α). $[\alpha]_D^{21}$ +22.6 (*c* 2.7 in $CHCl_3$). δ_H(500 MHz; $CDCl_3$) 7.38-7.10 (30H, m, Ar-H), 5.72 (1H, d, $J_{1',2'}$ 4.0, H-1'), 5.11-4.25 (12H, m, 6 x OCH_2Ph), 4.61 (1H, d, $J_{1,2}$ 3.5, H-1), 4.06 (1H, dd, $J_{2,3}$=$J_{3,4}$ 9.0, H-3), 3.90 (1H, dd, $J_{4,5}$ 9.5, H-4), 3.87-3.83 (1H, m, H-3'), 3.81-3.76 (1H, m, H-5), 3.72-3.62 (3H, m, H-6a, H-6b, H-4'), 3.57 (1H, dd, H-2), 3.55-3.45 (2H, m, H-6'a, H-5'), 3.38, 3.37 (3H, 2 _ s, OCH_3), 3.34 (1H, m, H-6'b), 3.27 (1H, dd, $J_{2',3'}$ 10.0, H-2'); δ_C(100 MHz; $CDCl_3$) 138.7, 138.1, 138.0, 137.8 (Cq, Ar-C), 128.2-127.3 (Ar-C in 6 x Bn), 98.3, 97.8 (C-1', C-1), 82.1, 80.5, 80.2, 78.1, 73.2, 71.4, 69.5 (C-2, C-3, C-4, C-5, C-3', C-4', C-5'), 75.4, 75.1, 75.0, 73.6, 73.4 (6 x OCH_2Ph), 69.3, 67.8 (C-6, C-6'), 63.3 (C-2'), 55.4 (OCH_3); *m/z* (FAB) 944 $[M+Na]^+$.

General procedure for the glycosidation of 17 and 20. Compounds **17** or **20** (0.09 mmol) and glycosyl acceptor **7**, **9** or **11** and **18** (0.06 mmol) were coevaporated with toluene (10 mL) and dried *in vacuo* for 1 h. The reagents were dissolved in CH_2Cl_2 (2 mL, 1/3, v/v) and stirred over activated 4 Å molecular sieves (100 mg) for 1.5 h after which the reaction was initiated by the addition of TMSOTf (1.9 μL, 10 μmol). Upon completion, the reaction mixture was neutralized (TEA), diluted with CH_2Cl_2 (25 mL), filtered through a pad of celite and the filtrate concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (25 mL) and washed with aqueous $NaHCO_3$ (2 x 10 mL) and brine (2 x 10 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate concentrated *in vacuo*. The crude product was purified by silica gel column chromatography and LH-20 size exclusion column chromatography (eluent; CH_2Cl_2/methanol, 1/1, v/v).

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-deoxy-2-phthalimido-3-benzyl-4,6-*O*-benzylidene)-β-D-glucopyranosyl)-α-D-glucopyranoside (21). $[\alpha]_D^{22}$ +32.16 (*c* 1.1 in $CHCl_3$). δ_H(500 MHz; $CDCl_3$) 7.54-6.81 (29H, m, Ar-H), 5.60 (1H, s, Ph-C*H*), 5.27 (1H, d, $J_{1',2'}$ 8.5, H-1'), 4.85 - 4.61 (2H, AB q, J_{AB} 10.7, OCH_2Ph), 4.78 - 4.47 (2H, AB q, J_{AB} 12.5, OCH_2Ph), 4.72 - 4.55 (2H, AB q, J_{AB} 2.13, OCH_2Ph), 4.43 (1H, dd, $J_{2',3'}$ 10.0, $J_{3',4'}$ 8.9, H-3'), 4.41 (1H, d, $J_{1,2}$ 3.3, H-1), 4.37 (1H, dd, $J_{5,6a}$ 4.9, $J_{6a,6b}$ 10.3, H-6a), 4.31 - 4.00 (2H, AB q, J_{AB} 10.7, OCH_2Ph), 4.30 (1H, dd, $J_{2',3'}$ 10.0, H-2'), 4.10-4.20 (1H, m, H-6'a), 3.90-3.79 (3H, m, H-6b, H-3, H-4'), 3.70-3.60 (3H, m, H-6'b, H-5', H-5), 3.40 (1H, dd, $J_{2,3}$ 9.8, H-2), 3.25 (1H, dd, $J_{3,4}$ 9.6, $J_{4,5}$ 9.20, H-4) and 3.18 (3H, s, OCH_3); δ_C(125 MHz; $CDCl_3$) 138.8, 138.1, 137.9, 137.7, 137.3, 131.8, 131.4 (Cq, Ar-C), 133.6-123.2 (Ar-C), 101.3 (Ph-*C*H), 98.9 (C-1'), 98.0 (C-1), 82.8 (C-

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3), 81.8 (C-4'), 79.9 (C-2), 77.5 (C-4), 75.5 (O*C*H_2Ph), 74.6 (O*C*H_2Ph), 74.4 (C-3'), 74.0 (O*C*H_2Ph), 73.4 (O*C*H_2Ph), 69.2 (C-5), 68.7 (C-6), 68.3 (C-6'), 66.2 (C-5'), 55.6 (C-2') and 54.9 (O*C*H_3); *m/z* (FAB) 956.3 $[M+Na]^+$. (Found: $[M+Na]^+$ 956.3654. $C_{56}H_{49}NO_{15}Na$ requires *m/z*, 956.3622)

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2-deoxy-2-phthalimido-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-α-D-glucopyranoside (22). δ_H(500 MHz; $CDCl_3$) 7.94-6.82 (29H, m, Ar-H), 6.00 (1H, dd, $J_{2,3}$ 9.9, $J_{3,4}$ 9.8, H-3), 5.58 (1H, s, Ph-C*H*), 5.23 (1H, d, $J_{1',2'}$ 8.5, H-1'), 5.26 (1H, dd, $J_{4,5}$ 9.6, H-4), 5.05 (1H, dd, $J_{1,2}$ 3.3, H-2), 4.80 - 4.48 (2H, AB q, J_{AB} 12.2, OC*H*$_2$Ph), 4.78 (1H, d, H-1), 4.43 (1H, dd, $J_{2',3'}$ 10.3, $J_{3',4'}$ 8.5, H-3'), 4.35 (1H, dd, $J_{5',6'a}$ 5.2, $J_{6'a,6'b}$ 10.3, H-6'a), 4.26 (1H, dd, H-2'), 4.10-4.04 (1H, ddd, H-5), 4.00 (1H, dd, $J_{5,6a}$ 2.4, $J_{6a,6b}$ 10.7, H-6a), 3.80 (1H, dd, $J_{5,6'b}$ 6.2, H-6'b), 3.76 (1H, dd, $J_{4',5'}$ 4.0, H-4'), 3.62 (1H, ddd, H-5'), 3.55 (1H, dd, $J_{5,6b}$ 6.6, H-6b), 3.10 (3H, s, OCH_3); δ_C(125 MHz, $CDCl_3$) 165.6, 165.1 (C=O, 3 x Bz, Phth), 137.9, 137.3, 131.9, 129.2-128.8 (Cq, Ar-C), 133.7-132.9, 129.8-123.1 (Ar-C), 101.3 (Ph-*C*H), 99.5 (C-1'), 96.6 (C-1), 82.9 (C-4'), 74.6 (C-3'), 74.1 (O*C*H_2Ph), 71.9 (C-2), 70.4 (C-3), 69.3 (C-4), 68.9 (C-6), 68.7 (C-6'), 68.2 (C-5), 66.1 (C-5'), 55.7 (C-2') and 55.0 (O*C*H_3); *m/z* (FAB) 998.3 $[M+Na]^+$. (Found: $[M+Na]^+$ 998.3008. $C_{56}H_{49}NO_{15}Na$ requires *m/z*, 998.3000)

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-deoxy-2-phthalimido-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-α-D-glucopyranoside (23). $[\alpha]_D^{22}$ +37.76 (*c* 1.1 in $CHCl_3$). δ_H(500 MHz; $CDCl_3$) 7.7-6.8 (29H, m, Ar-H), 5.49 (1H, s, Ph-C*H*), 5.41 (1H, d, $J_{1',2'}$ 8.5, H-1'), 4.94 - 4.88 (2H, AB q, J_{AB} 11.4, OC*H*$_2$Ph), 4.76 - 4.44 (2H, AB q, J_{AB} 12.5, OC*H*$_2$Ph), 4.48 (1H, d, $J_{1,2}$ 3.3, H-1), 4.72 - 4.55 (2H, AB q, J_{AB} 12.1, OC*H*$_2$Ph), 4.35 (1H, dd, $J_{2',3'}$ 10.3, $J_{3',4'}$ 9.2, H-3'), 4.32 - 4.26 (2H, AB q, J_{AB} 12.0, OC*H*$_2$Ph), 4.18 (1H, dd, H-2'), 4.03 (1H, dd, $J_{5',6'a}$ 5.2, $J_{6'a,6'b}$ 10.3, H-6'a), 3.92 (1H, dd, $J_{3,4}$ 9.2, $J_{4,5}$ 9.9, H-4), 3.81 (1H, t, $J_{2,3} = J_{3,4}$ 9.2, H-3), 3.69 (1H, t, $J_{4',5'}$ 9.2, H-4'), 3.54-3.46 (2H, m, H-5, H-6'b), 3.43 (1H, dd, H-2), 3.37-3.28 (3H, m, H-6a, H-6b, H-5') and 3.24 (3H, s, OCH_3); δ_C(125 MHz, $CDCl_3$) 167.9 (2 x C=O), 139.5-131.6 (Cq, Ar-C), 133.8-123.3 (Ar-C), 101.2 (Ph-*C*H), 98.1 (C-1', C-1), 83.0 (C-4'), 80.1 (C-3), 79.4 (C-2), 75.7 (C-4), 74.9 (O*C*H_2Ph), 74.6 (C-3'), 74.0 (O*C*H_2Ph), 73.4 (O*C*H_2Ph), 72.8 (O*C*H_2Ph), 69.5 (C-5), 68.6 (C-6'), 68.2 (C-6), 65.8 (C-5'), 56.6 (C-2'), 55.2 (O*C*H_3); *m/z* (FAB) 956.4 $[M+Na]^+$. (Found: $[M+Na]^+$ 956.3654. $C_{56}H_{55}NO_{12}Na$ requires *m/z*, 956.3622)

Methyl 2-deoxy-2-phthalimido-3,6-di-*O*-benzyl-4-*O*-(2-deoxy-2-phthalimido-4,6-*O*-benzylidene-3-*O*-benzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (25). δ_H(500 MHz) 7.90-6.80 (28H, m, Ar-H, 3 × Bn, Ph-CH, 2 × Phth), 5.75-5.68, 5.30-5.22 (1H, m, C*H*=CH_2), 5.50 (1H, s, Ph-C*H*), 5.38 (1H, d, $J_{1',2'}$ 8.1, H-

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1'), 5.04, 4.97 (1H, 2xd, $J_{1,2}$ 8.1, H-1), 5.01-4.95, 4.88-4.81 (2H, m, CH_2=CH), 4.81 - 4.76 (2H, AB q, J_{AB} 10.8, OCH_2Ph,), 4.50-4.37 (5H, m, H-3', 2 x OCH_2Ph), 4.25-4.10 (5H, m, H-2', H-6'a, H-2, H-3, H-4), 4.08-3.95 (1H, m, C*H*-CH_3), 3.70 (1H, t, $J_{3',4'}$ 8.9, $J_{4',5'}$ 7.9, H-4'), 3.53 (1H, dd, $J_{5',6'b}$ 8.5, $J_{6'a,6'b}$ 10.5, H-6'b), 3.47-3.25 (4H, m, H-6a, H-5', H-6b, H-5), 1.08, 0.91 (3H, 2 x d, J 6.6, CH_3-CH); δ_C(125 MHz; $CDCl_3$) 167.66, 167.58 (2 x C=O), 139.95, 138.82 (*C*H=CH_2), 138.6, 138.3, 138.0, 137.4, 131.7 (Cq, Ar-C), 133.9, 133.6, 128.9-123.2 (Ar-C), 116.4, 114.5 (CH_2=CH), 101.2 (Ph-*C*H), 97.9, 97.8 (C-1'), 96.7, 95.7 (C-1), 83.2 (C-4'), 76.7 (C-3), 76.6 (C-2), 76.2, 75.2 (*C*H-CH_3), 74.6 (C-3'), 74.4 (C-5), 74.3 (OCH_2Ph), 74.1 (OCH_2Ph), 72.6 (OCH_2Ph), 68.7 (C-6'), 68.1, 68.0 (C-6), 65.8 (C-5'), 56.6 (C-2'), 55. 9, 55.8 (C-4), 21.4, 20.0 (CH-*C*H_3); *m/z* (FAB) 956.4 $[M+Na]^+$. (Found: $[M+Na]^+$ 956.3654. $C_{56}H_{55}NO_{12}Na$ requires *m/z*, 956.3622)

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-deoxy-2-phthalimido-3,6-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-β-D-glucopyranosyl)-α-D-glucopyranoside (26). $[\alpha]_D^{21}$ +41.5 (*c* 1.1 in $CHCl_3$). δ_H(500 MHz; $CDCl_3$) 7.7-6.7 (33H, m, Ar-H), 5.18 (1H, d, $J_{1',2'}$ 8.1, H-1'), 4.83 - 4.62 (2H, AB q, J_{AB} 11.0, OCH_2Ph), 4.80 - 4.41 (2H, AB q, J_{AB} 12.1, OCH_2Ph), 4.75 - 4.55 (2H, AB q, J_{AB} 10.5, OCH_2Ph), 4.69 - 4.53 (2H, AB q, J_{AB} 12.0, OCH_2Ph), 4.65 - 4.57 (2H, AB q, J_{AB} 11.8, OCH_2Ph), 4.34 - 4.07 (2H, AB q, J_{AB} 10.5, OCH_2Ph), 4.34 (1H, dd, $J_{2',3'}$ 10.6, $J_{3',4'}$ 7.2, H-3'), 4.33 (1H, d, $J_{1,2}$ 3.3, H-1), 4.23 (1H, dd, H-2'), 4.08 (1H, dd, $J_{5,6a}$ 4.8, $J_{6a,6b}$ 10.5, H-6a), 3.83-3.67 (4H, m, H-3, H-6'a, H-6'b, H-4'), 3.78 (3H, s, $PhOCH_3$), 3.65 (1H, ddd, H-5'), 3.61 (1H, ddd, H-5), 3.56 (1H, dd, $J_{5,6b}$ 4.7, H-6b), 3.35 (1H, dd, $J_{2,3}$ 9.8, H-2), 3.21 (1H, dd, $J_{3,4}$ 7.8, $J_{4,5}$ 9.2, H-4) and 3.11 (3H, s, OCH_3); δ_C(125 MHz; $CDCl_3$) 159.4 (2 x C=O, Phth), 138.8-130.1 (Cq, Ar-C), 133.5-113.8 (Ar-C), 98.4 (C-1'), 97.8 (C-1), 81.9 (C-3), 79.8 (C-2), 79.5 (C-4'), 79.3 (C-3'), 77.7 (C-4), 75.5 (OCH_2Ph), 74.6 (2 x OCH_2Ph), 73.4 (OCH_2Ph), 73.3 (OCH_2Ph), 69.3 (C-5), 68. 9 (C-6'), 68.2 (C-6), 55.8 (C-2'), 55.3 ($PhOCH_3$) and 54.8 (OCH_3); *m/z* (FAB) 1078.4 $[M+Na]^+$. (Found: $[M+Na]^+$ 1078.4386. $C_{64}H_{59}NO_{13}Na$ requires *m/z*, 1078.4354)

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2-deoxy-2-phthalimido-3,6-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-β-D-glucopyranosyl)-α-D-glucopyranoside (27). δ_H(500 MHz; $CDCl_3$) 7.93-6.78 (33H, m, Ar-H), 5.93 (1H, dd, $J_{2,3}$ 10.2, $J_{3,4}$ 9.8, H-3), 5.23 (1H, dd, $J_{4,5}$ 10.1, H-4), 5.16 (1H, d, $J_{1',2'}$ 8.5, H-1'), 5.03 (1H, dd, $J_{1,2}$ 3.3, H-2), 4.81 - 4.43 (2H, AB q, J_{AB} 12.0, OCH_2Ph), 4.75 - 4.53 (2H, AB q, J_{AB} 10.5, OCH_2Ph), 4.65 (1H, d, H-1), 4.61 - 4.48 (2H, AB q, J_{AB} 12.1, OCH_2Ph), 4.34 (1H, dd, $J_{2',3'}$ 10.08, $J_{3',4'}$ 8.8, H-3'), 4.20 (1H, dd, H-2'), 4.08 (1H, ddd, H-5), 4.02 (1H, dd, $J_{5,6a}$ 2.4, $J_{6a,6b}$ 10.7, H-6a), 3.78 (3H, s, $ArOCH_3$), 3.75-3.70 (3H, m, H-4', H-6'a, H-6'b), 3.60 (1H, ddd, H-5'),.3.52 (1H, dd, $J_{5,6b}$ 7.9, H-6b), 3.00 (3H, s, OCH_3); δ_C(125 MHz,

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$CDCl_3$) 165.6, 165.2, 159.34 (C=O, 3 x Bz, Phth), 138.1, 138.1, 131.9, 130.2, 129.3, 129.1, 128.8 (Cq, 2 x Bn, 3 x Bz, PMB and Phth), 133.6-127.3, 123.0, 113.9, 113.8 (Ar-C), 99.1 (C-1), 96.3 (C-1'), 79.3 (C-3'), 79.3 (C-4'), 75.1 (C-5'), 74.8 (OCH_2Ph), 74.6 (OCH_2Ph), 73.4 (OCH_2Ph), 72.0 (C-2), 70.4 (C-3), 69.5 (C-4), 69.1 (C-6), 68.5 (C-6'), 68.3 (C-5), 55.9 (C-2'), 55.3 ($ArOCH_3$) and 54.8 (OCH_3); *m/z* (FAB) 1120 $[M+Na]^+$. (Found: $[M+Na]^+$ 1120.3755. $C_{64}H_{59}NO_{16}Na$ requires *m/z*, 1120.3732).

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-deoxy-2-phthalimido-3,6-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-β-D-glucopyranosyl)-α-D-glucopyranoside (28). $[\alpha]_D^{21}$ +30.27 (*c* 1.1 in $CHCl_3$). δ_H(500 MHz; $CDCl_3$) 7.80-6.78 (33H, m, Ar-H), 5.40 (1H, d, $J_{1',2'}$ 8.1, H-1'), 5.04 - 4.83 (2H, AB q, J_{AB} 11.4, OCH_2Ph), 4.79 - 4.38 (2H, AB q, J_{AB} 12.1, OCH_2Ph), 4.71 - 4.54 (2H, AB q, J_{AB} 10.3, OCH_2Ph), 4.68 - 4.51 (2H, AB q, J_{AB} 12.0, OCH_2Ph), 4.54 - 4.45 (2H, AB q, J_{AB} 12.1, OCH_2Ph), 4.47 (1H, d, $J_{1,2}$ 3.3, H-1), 4.32 - 4.25 (2H, AB q, J_{AB} 12.0, OCH_2Ph), 4.28 (1H, dd, $J_{2',3'}$ 10. 7, $J_{3',4'}$ 8.5, H-3'), 4.17 (1H, dd, H-2'), 3.92 (1H, t, $J_{3,4} = J_{4,5}$ 9.2, H-4), 3.85 (1H, t, $J_{2,3}$ 8.8, H-3), 3.78 (3H, s, $PhOCH_3$), 3.73 (1H, dd, $J_{4',5'}$ 9.6, H-4'), 3.57-3.50 (2H, m, H-6'a, H-5), 3.47 (1H, dd, $J_{5',6'b}$ 4.0, $J_{6'a,6'b}$ 11.4, H-6'b), 3.41-3.31 (4H, m, H-6a, H-6b, H-2, H-5') and 3.23 (3H, s, OCH_3); δ_C(125 MHz; $CDCl_3$) 159.3 (2 x C=O), 139.6-130.2 (Cq, Ar), 133.6-113.8 (Ar-C), 98.1 (C-1), 97.4 (C-1'), 80.1 (C-3), 79.5 (C-4'), 79.4 (C-2), 79.2 (C-3'), 75.2 (C-4, C-5'), 74.8 (OCH_2Ph), 74.7 (OCH_2Ph), 74.5 (OCH_2Ph), 73.4 (2 x OCH_2Ph), 72.7 (OCH_2Ph), 69.5 (C-5), 68.4 (C-6), 68.2 (C-6'), 56.8 (C-2'), 55.2 ($PhOCH_3$), 55.1 (OCH_3); *m/z* (FAB) 1078.5 $[M+Na]^+$. (Found: $[M+Na]^+$ 1078.4394. $C_{64}H_{59}NO_{13}Na$ requires *m/z*, 1078.4354).

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