Pergamon

Bioorganic & Medicinal Chemistry, Vol. 5, No. 1, pp 1–19, 1997

PII: S0968-0896(96)00209-X
0968-0896/97 $17.00+0.00

Glycosyl Azides as Building Blocks in Convergent Syntheses of Oligomeric Lactosamine and Lewis^x Saccharides

Wolfgang Bröder and Horst Kunz*
Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz, Becher-Weg 18-20, D-55128 Mainz, Germany

Abstract—Oligosaccharides containing type 2 lactosamine repeating units, e.g. neo-lacto-octaose and trimeric Lewis^x derivatives, are constructed using neo-lactosamine azide building blocks. The azido group provides a favorable protection of the anomeric position which is stable to versatile protecting group manipulations and glycosylation reactions. On the other hand, glycosyl azides can be converted into glycosyl fluorides via a 1,3-dipolar cycloaddition with di-*tert*-butyl-acetylenedicarboxylate and subsequent treatment of the resulting *N*-glycosyl triazoles with hydrogen fluoride–pyridine complex. Activation of the lactosamine fluorides with Lewis acids affords the possibility to extend the oligosaccharide chain with disaccharide units. Suitable protecting group combinations within the galactose and the glucosamine portion of the lactosamine unit enable selective deprotection reactions and, subsequently, chain extension or branching, e.g. to yield Lewis^x structures. Copyright © 1997 Elsevier Science Ltd

Introduction

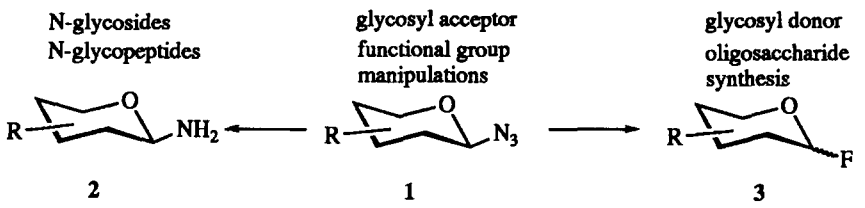
Biological recognition processes which involve oligosaccharide structures of glycoproteins and glycolipids are based on weak-force interactions.[1] The binding and its specificity are often dramatically enhanced with multiple ligands, as was demonstrated in particular for the binding to lectins.[2] In many cases, the saccharide portions of natural glycoconjugates contain repeating units. For example, the band 3 glycoprotein of erythrocytes is characterized by asparagine-linked oligosaccharides of polylactosamine structure.[3] These polylactosamines are subject to a characteristic change during the developments from fetal to adult erythrocytes. The fetal form (i antigen) consists of linear polylactosamine, whereas typical lactosamine branchings are present in the adult form (I antigen).[4] Oligomeric Lewis^x antigens, which are oligomeric type 2 lactosamines fucosylated in the 3-position of the glycosamine units, were found to be tumor-associated antigens in adenocarcinoma tissues.[5] For the investigation of such immunodifferentiations and recognition phenomena model oligosaccharides of oligolactosamine or Lewis antigen structure are of interest. Syntheses of oligomeric Lewis^x antigen saccharides and glycopeptides have been achieved using thioglycoside building blocks.[7,8]

Norberg et al.[7] synthesized a lactosamine ethylthioglycoside as the key intermediate. This building block was obtained from an *N*-phthaloyl-protected glycosamine ethylthioglycoside glycosylacceptor via glycosylation with a suitably protected galactosyl bromide.[9] The ethylthioglycoside group was shown to be stable during the formation of the disaccharide, and it can be activated with dimethyl (methylthio)sulfonium trifluoromethanesulfonate.[10] Repeated glycosylations led to oligomeric lactosamine glycosides if disaccharide thioglycosides were employed which are selectively deprotectable in the 3-position of the galactose unit.

In the synthesis of oligomeric Lewis^x saccharides by Nicolaou et al.[8] glucosamine phenylthioglycosides served as the glycosyl acceptors. Regio- and stereoselective β-galactosylation and α-fucosylations were carried out with glycosyl fluorides. The monomeric Lewis^x trisaccharide phenylthioglycoside containing selectively removable protecting groups in the 3- and 4-position of the galactose residue was converted into the corresponding Lewis^x trisaccharide fluoride via treatment with the NBS/hydrogen fluoride–pyridine complex. Repeated glycosylation, deprotection, and regioselective glycosylation gave the dimeric and trimeric Lewis^x antigen derivatives.[11] The strategy developed by R. R. Schmidt et al.[12] begins with a 2-azido glucose acceptor which carries a *tert*-butyl dimethylsilyl (TBS) protecting group at the anomeric position. Regio- and stereoselective α-fucosylation and β-galactosylation were conducted with the corresponding trichloroacetimidates.[13] Cleavage of the Lewis^x silylglycoside using tetrabutylammonium fluoride (TBAF) and subsequent transformation into the trichloroacetimidate furnished a reactive trisaccharide glycosyl donor. Its repeated use resulted in the successful synthesis of oligomeric Lewis^x saccharides and glycolipids.[8]

We report here the construction of oligomeric lactosamine and Lewis^x saccharides, during which the azido function serves as the anomeric protecting group. Recently, glycosyl azides **1** were shown to be stable towards numerous protecting group manipulations[14,15] and can be readily converted into glycosamines **2** (Scheme 1). The efficiency of the glycosyl azide–glycosylamine conversion was demonstrated in the syntheses

Key words: glycosyl azides, glycosyl fluorides, oligosaccharide synthesis, trimeric Lewis^x, oligomeric lactosamines.



Scheme 1.

of *N*-glycopeptides with a variety of oligosaccharide side chains including 6-*O* fucosyl chitobiose,[14,16] Lewis^a,[17] Lewis^x,[18] and sialyl Lewis^x.[19,20]

Conversion of glycosyl azides into glycosyl-fluorides: synthesis of neolactopentaose of the H2-type

Recently, we found a method[21] to convert the glycosyl azides, which have been shown to be useful glycosyl-acceptors in a number of glycosylation reactions, into glycosyl fluorides **3**, which are valuable glycosyl donors.

The principle of the glycosyl azide–glycosyl fluoride conversion is illustrated for the lactosamine azide **4**.[21] 1,3-Dipolar cycloaddition with di-*tert*-butyl acetylene dicarboxylate (TBAC) yielded the *N*-lactosaminyl triazole **5**.[22] Treatment of **5** with the hydrogen fluoride–pyridine complex gave the desired lactosamine fluoride **6**.[21] Activation of **6** using boron trifluoride etherate[23,24] in the presence of benzyl lactoside **7**[25] furnished the neolactotetraose **8**.

It should be mentioned in this context that a number of other concepts of intermediate anomeric protection which allow later activation have been described during the past years. These include the use of thioglycosides in combination with glycosyl fluorides as glycosyl donors as was already outlined for the syntheses of Lewis^x saccharides.[7,8] This combination was recently improved by variation of the activation of the glycosyl fluorides.[26] In addition, thioglycosides with electron-withdrawing S-substituents[27] or reactivity-reducing *O*-acyl protecting groups[28] were investigated as glycosyl acceptors. Rather stable glycosyl acceptors are pentenyl glycosides which later can be activated by electrophilic attack at the carbon–carbon double bond.[29] Another strategy takes advantage of allyl-type glycosides which after isomerization to the propenyl-type glycosides also can be activated by electrophiles.[30]

After removal of the 2′-*O*-acetyl group, α-fucosylation of **9** to give the H2-type pentasaccharide **11** was achieved using the *O*-benzylated thiofucoside **10**,[31] which was reacted with bromine to give the fucosylbromide, and the latter activated under in situ anomerization conditions (Scheme 2).[32]

It is noteworthy that the deacetylation of **8** proceeded very slowly and required a reaction time of 5 days. The yield of **9**, however, was quantitative, and the *N*-phthaloyl group was not affected. The formation of the tetrasaccharide **8** was completed within 3 h, whereas the fucosylation of **9** again required a long reaction time of 10 days illustrating the low reactivity of the 2-OH group of the terminal galactose unit.

Lactosamine building block functionalizable in three positions

The convergent synthesis of oligomeric lactosamines which should be susceptible to subsequent introduction of the α-fucoside branchings demands a lactosamine building block which can be selectively functionalized in three positions: (a) activation at the anomeric center, (b) selective deprotection at the 3-O of the galactose unit as a prerequisite for repeated lactosamine chain extensions, and (c) selective removal of the protecting group at the 3-O of the glucosamine residue making the fucosylation possible. Since the glycosyl azide/glycosyl fluoride conversion was to be employed as the anomeric protection/activation principle, glycosyl acceptors with mainly ether-type protecting groups were considered favorable. The lactosamine azide building block **12** fulfils these requirements.

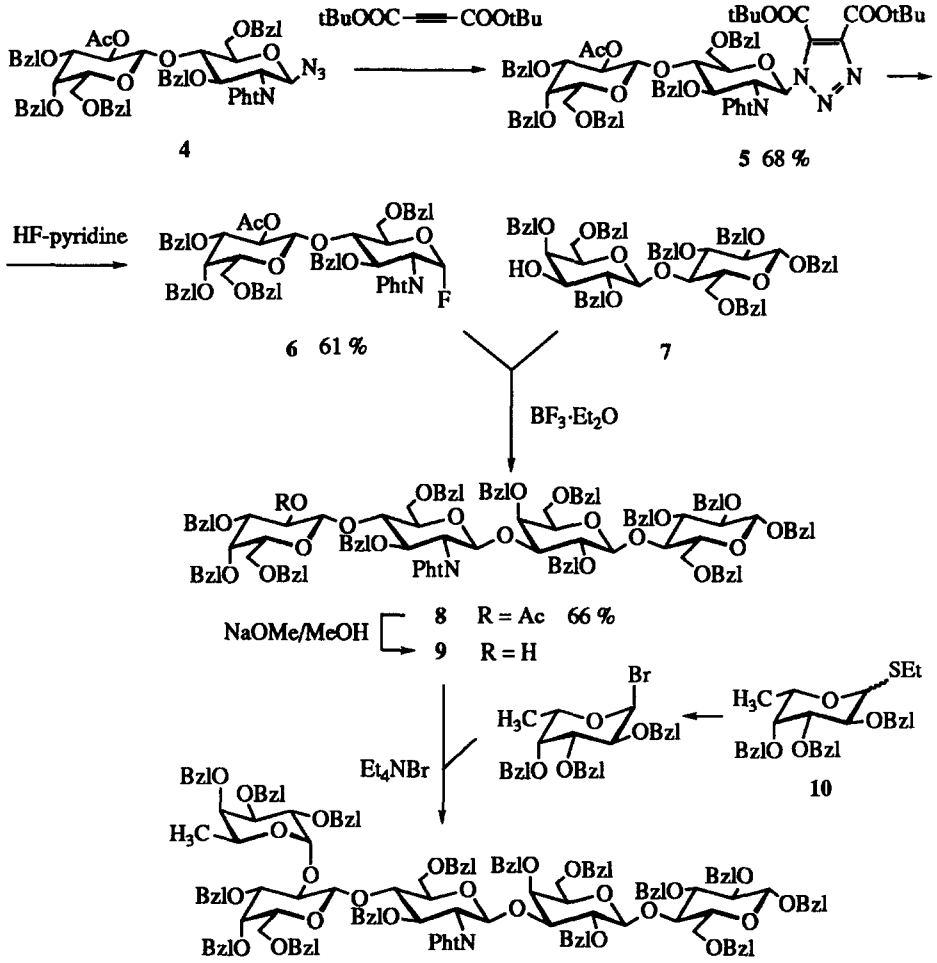
Taking advantage of the stability of the glycosyl azides, the synthesis of **12** was carried out starting from the lactosamine azide **13**. Deacetylation of **13** with sodium methoxide/methanol, subsequent 3,4-stannylation of the crude product with dibutyltinoxide and regioselective alkylation with *p*-methoxybenzyl chloride yielded the *p*-methoxybenzyl (Mpm)-protected lactosamine azide **14**. The attempt to *O*-benzylate this product surprisingly gave unsatisfactory results: treatment of **14** with sodium hydride/benzylbromide in dimethylformamide at room temperature resulted in only incomplete benzylation. Raising the temperature to 50 °C led to decomposition and formation of numerous polar products. Application of barium oxide or silver oxide/potassium iodide as bases gave unsatisfactory results (yield of 5% of the desired product), in contrast to the successful 3-*O*-alkylations of the *N*-phthaloyl-glucosaminyl azide[21] and the benzyl lactoside precursor of **2**.[21] Since the Mpm group may exhibit steric hindrance, in particular on the 2-OH group of the galactose unit of **14**, other potential 3-OH hydroxy protecting groups were investigated on galactosyl azide as a simple monosaccharide model compound. The allyloxycarbonyl (Aloc) group can be selectively introduced at the 3-OH position via the stannylene procedure, but was unstable in **16** even under mild benzylation conditions. Selective 3-*O*-alkylation was possible with methoxyethoxymethyl chloride. However, the obtained product **17** tightly adhered tin compounds which cause side reactions during the subsequent benzylation. The ethoxymethyl (Em) group,[35] which does not contain a

second coordinating oxygen, proved to be a useful protecting group for this purpose. Its regioselective introduction with ethoxymethyl chloride gave the 3-O-Em-protected product **18** which could be benzylated to afford **19** with high efficiency (Scheme 3).

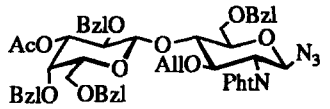
The adaptation of this ethoxymethylation and benzylation sequence to the lactosamine **13** as the substrate resulted in disappointingly low yields of both the regioselective ethoxymethylation (24%) and the benzylation (26%) products. Obviously, the greater number of coordinating nucleophilic groups within the disaccharide and the high reactivity of the ethoxymethyl chloride are responsible for side reactions. Furthermore, free hydroxyl groups of the disaccharide can be involved in a nucleophilic attack on the *N*-phthaloyl group during the benzylation reactions.

As a consequence, we carried out a partial *O*-benzylation prior to the ethoxymethylation on the lactosamine azide **13**. To this end, deacetylation of **13** was followed by 3′,4′-isopropylidenation to yield **21**. The outcome of this reaction depends upon the solvent and the concentration of the substrate. Reaction with low concentration (1 mmol/100 mL) in pure acetone gave optimal results. Alternative selective silylation of 6′-OH with *tert*-butyldiphenylsilyl chloride/imidazole[36] to give **22** followed by isopropylidenation (**23**) and cleavage of the silylether with TBAF resulted in a lower overall yield of **21**. Benzylation of **21** was conducted with benzylbromide and silver oxide/tetrabutylammonium iodide furnished **24** in a yield of 79%. Benzylation of **21** was also achieved after deprotonation with sodium hydride (56%). The isopropylidene acetal was cleaved by treatment of **24** with 60% acetic acid at 65 °C (Scheme 4).

The partially *O*-benzylated lactosamine azide **25** was subjected to stannylation with dibutyltinoxide and subsequent regioselective ethoxymethylation to form **26**. After benzylation of the 4′-OH group (**27**), the ethoxymethyl (Em) group was selectively removed using thiophenol/boron-trifluoride etherate[37] to give **28** as a potential acceptor in polylactosamine syntheses. The desired key building block **12** was obtained by acetylation of **28** and constitutes the precursor of the required lactosamine glycosyl donor.



Scheme 2.



12

Considering the reactions described in this section, one should note that the anomeric azido group remained stable during the numerous transformations performed under different reaction conditions.

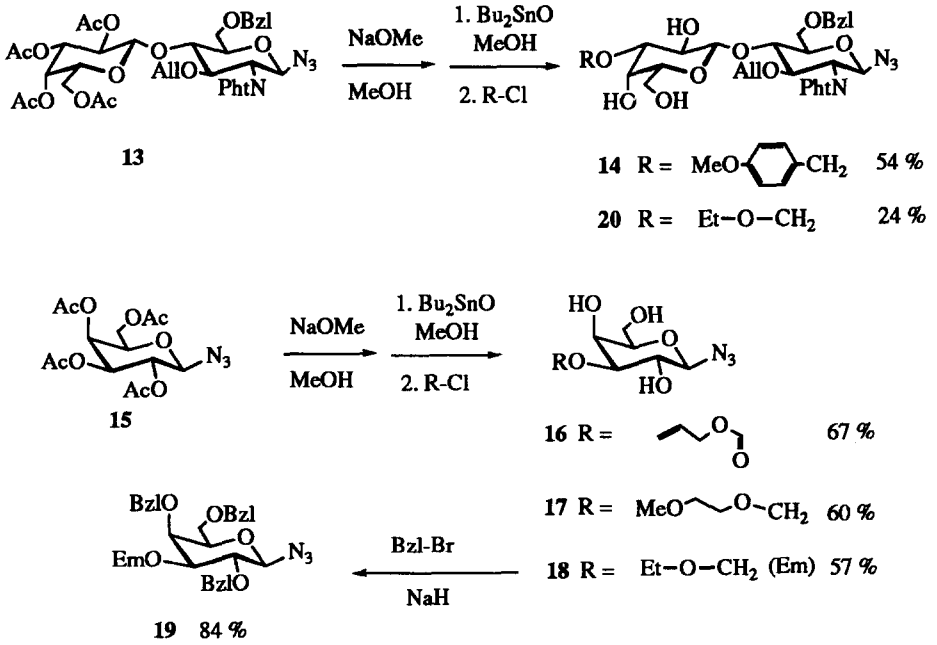
Synthesis of neolactooctaose and trimeric Lewis^x saccharides

According to the synthetic strategy pursued in this work, the major effort in protecting group manipulations was concentrated on the formation of the disaccharide building block **12**. As an advantage of the strategy, the construction of the oligomeric lactosamines and Lewis antigen saccharides should be achieved within a few steps.

The lactosamine azide **12** was subjected to 1,3-dipolar cycloaddition with TBAC to yield the N^1-lactosaminyl triazole **29**, which was converted into the lactosaminyl fluoride **30** using a hydrogen fluoride–pyridine complex. On activation with BF_3 etherate, the fluoride **30** and the selectively deblocked benzyl lactoside **7** formed the neolactotetroside **31** in high yield. Removal of the *O*-acetyl group from the terminal galactose of **31** gave the new acceptor **32**, which was glycosylated again using the lactosaminyl fluoride **30**. The neolactohexaoside **33** obtained in high yield was de-*O*-acetylated, and a further glycosylation of **34** was carried out using the lactosaminyl fluoride **35**,[21] formed by conversion of the lactosamine azide **13**, to furnish the neolactooctaoside **36** in high yield (Scheme 5).

The selective cleavage of the three 3-*O*-allyl ether groups of the oligomeric lactoside was accomplished only by application of the reactive catalyst 1,5-cyclooctadiene-bis(methyldiphenyl)phosphine)iridium-hexafluorophosphate[38] and subsequent solvomercuration of the intermediate tri-*O*-propenyl ether to give **37**. The simultaneous threefold α-fucosylation of **37** was carried out under in situ anomerization conditions with a large excess of the *O*-benzylated fucosyl-bromide freshly prepared from the thiofucoside **10** and gave the desired trimeric Lewis^x undecasaccharide **38**. Purification of **38** was carried out by flash-chromatography in petroleum ether/ethyl acetate in the presence of 0.1% of triethylamine in order to avoid attack on the acid labile α-fucoside bonds. The structure of **38** was confirmed by FAB mass and NMR spectra including COSY, TOCSY and NOESY experiments.[39]

The de-*O*-acetylation, the removal of the phthaloyl groups and hydrogenolytic cleavage of the *O*-benzyl protecting groups have been described by others.[7,8,12] It should, however, be pointed out that in our preliminary experiments incomplete hydrogenolyses of the benzyl ethers were observed. By-products which contain one or two benzyl groups could not be separated. At higher pressure and elevated temperature, side reactions occurred which are caused by the deprotectable anomeric group. As a consequence, it is recommended to avoid the benzyl glycoside as the protection of the anomeric position in syntheses of these higher oligosaccharides.



Scheme 3.

The convergent strategy, however, to construct oligomers, in particular oligomeric lactosamines, from disaccharide building blocks, via the glycosyl azide/glycosyl fluoride conversion is very efficient and was also demonstrated in the synthesis of a neolactohexosamine azide from the lactosamine azide **28** as the glycosyl acceptor and the lactosamine azide **12** after its conversion into the glycosyl fluoride **30**. The dimeric lactosamine azide **39** was isolated in good yield. After deacetylation, **40** was coupled once more with the glycosyl fluoride **30** to afford the hexasaccharide azide **41** of the lactosamine series in good yield (Scheme 6).

From these efficient convergent syntheses of oligomeric lactosamines from disaccharide building blocks it is concluded that the azido function constitutes a useful protection of the anomeric carbon during protecting group manipulations and glycosylation reactions. At the same time, the glycosyl azides can readily be converted into glycosyl donors,[21,20] e.g. glycosyl fluorides, and are valuable precursors of glycosylamines.

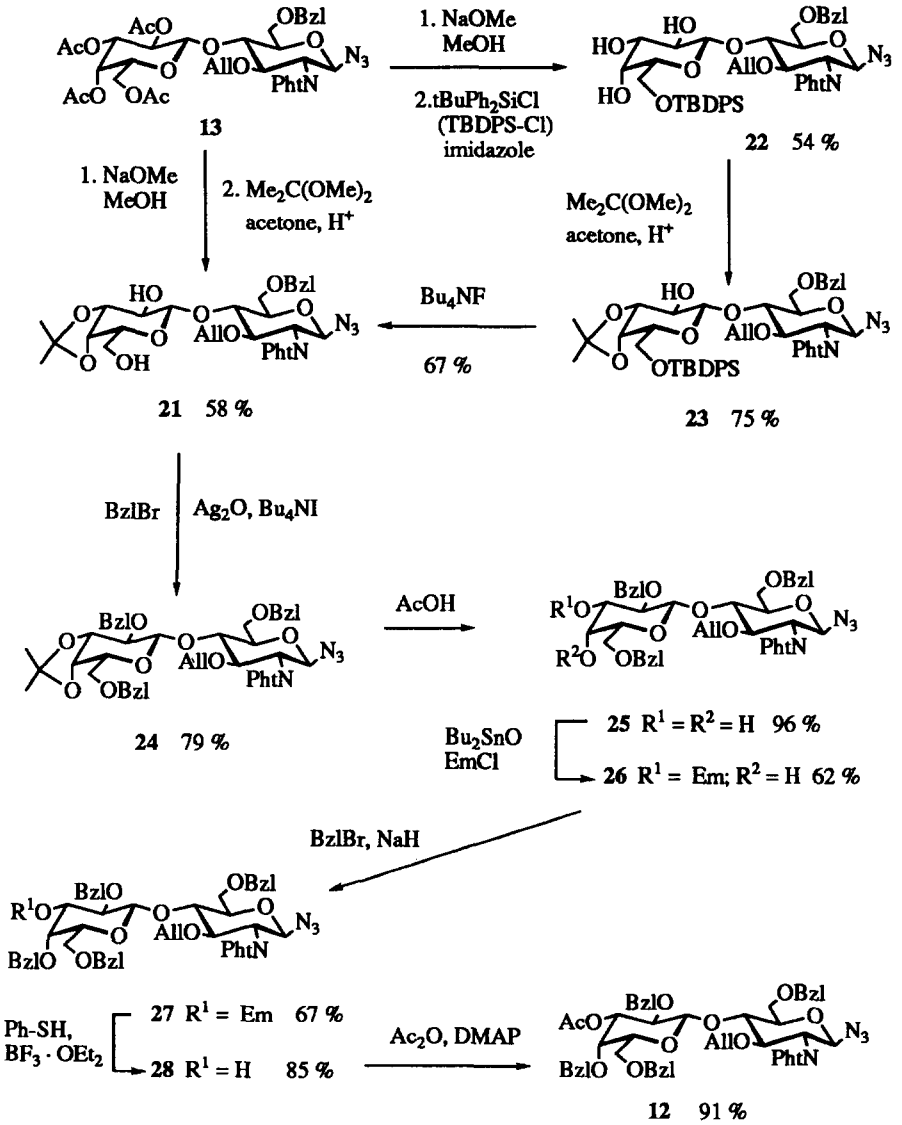
Experimental

General methods

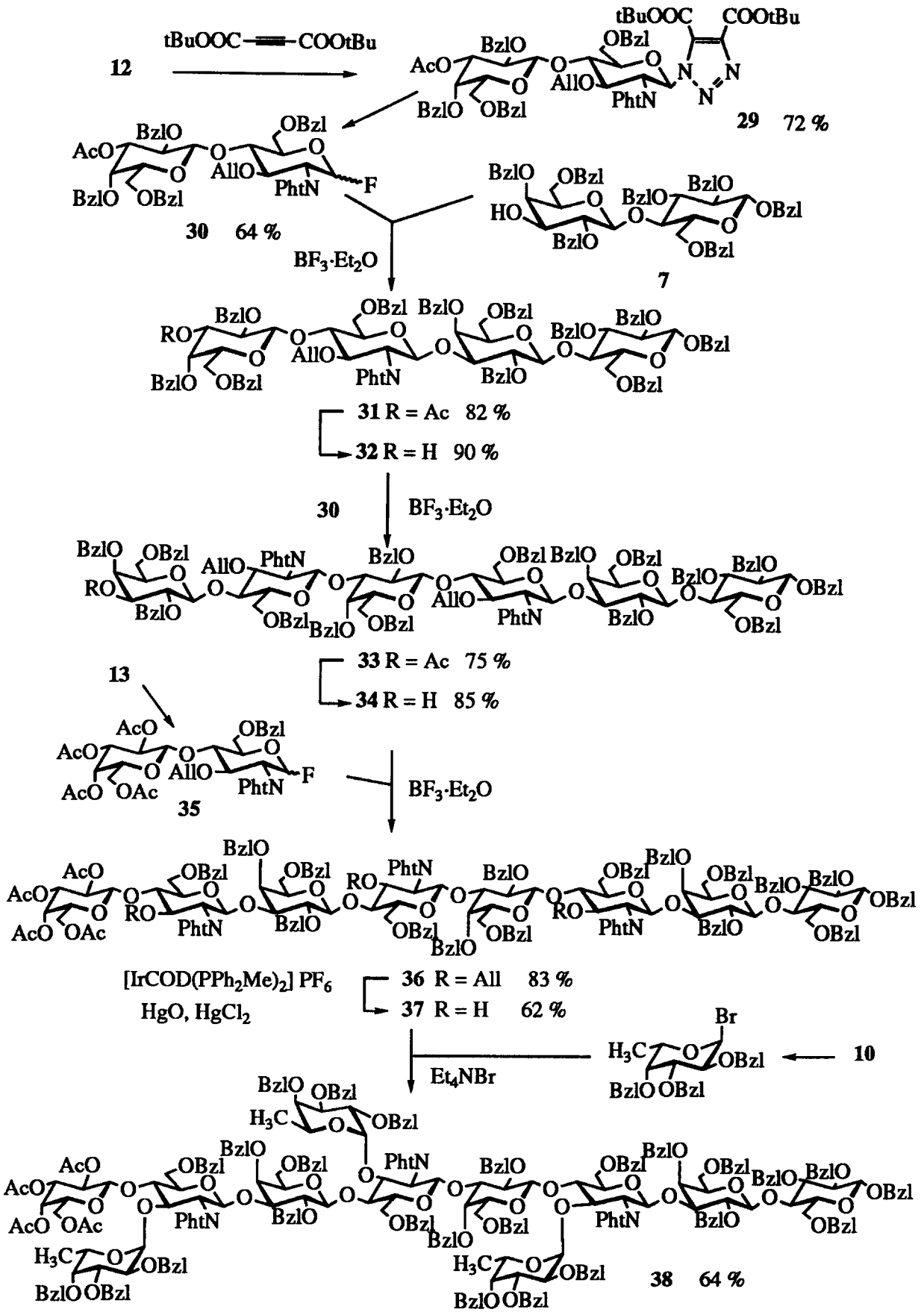
Melting points were determined with a Büchi apparatus (Dr Totolli) and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. IR spectra were recorded with a Perkin–Elmer FTIR spectrometer and resolution of 2 cm^{-1}. ^1H NMR spectra (200 and 400 MHz) and ^{13}C NMR spectra (50.3 and 100.6 MHz) were recorded with a Bruker WT 200 and a Bruker AM 400 spectrometer, respectively.

600 MHz ^1H NMR spectra were recorded on a Bruker AMX 600 spectrometer at the Universität Frankfurt by Professor Ch. Griesinger and Dr R. Wechselberger. The values of δ are expressed relative to the signal of Me_4Si in $CDCl_3$ unless otherwise noted.

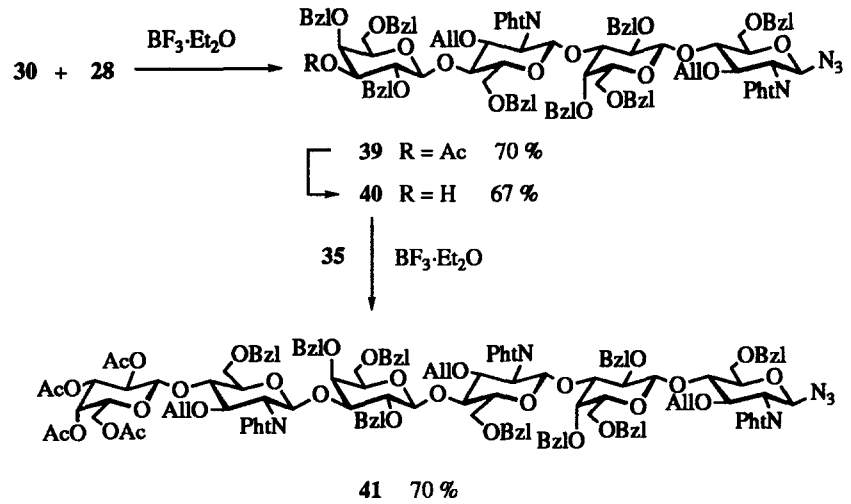
NMR signals of larger oligosaccharides are quoted by indication of the monosaccharide units starting from



Scheme 4.

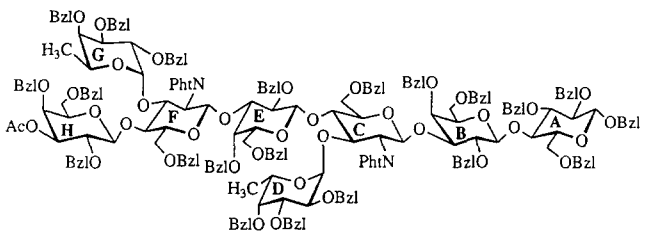

12
29 72 %
30 64 %
BF3·Et2O
7
31 R = Ac 82 %
32 R = H 90 %
30
BF3·Et2O
33 R = Ac 75 %
34 R = H 85 %
13
35
BF3·Et2O
[IrCOD(PPh2Me)2] PF6
HgO, HgCl2
36 R = All 83 %
37 R = H 62 %
Et4NBr
10
38 64 %

Scheme 5.



Scheme 6.

the reducing end, as is shown for the following example:



TLC and HPTLC monitoring were carried out on Silica gel-60 F_{254} (Merck) or on RP-18 glass plates (Merck) with detection by UV fluorescence ($\lambda = 254$ nm) or spraying with a 1:1 mixture of 1 M H_2SO_4 and a 0.3% solution of resorcinol monomethyl ether in methanol. Flash chromatography was performed on columns of silica gel-60 (Merck, 0.04–0.06 mm). Solvents were freshly dried and distilled.

Benzyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-(*O*)-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (8). A mixture of benzyl-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside,[25] **7** (114 mg, 117 mmol), and 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-D-glucopyranosyl-fluoride,[21] **6** (120 mg, 124 μmol), was dried in high vacuum and dissolved in dichloromethane (10 mL) under addition of molecular sieves 4 Å. After stirring for 1 h at 0 °C, a solution of borontrifluoride etherate (0.07 mL, 0.55 mmol) in 5 mL of dry dichloromethane was added dropwise. After 1 h at 0 °C, the mixture was stirred for 2 h at room temperature, filtered through Celite, which was washed with small portions of dichloromethane. The organic layers were washed with satd $NaHCO_3$ solution and dried with $MgSO_4$. After addition of silica gel, the solvent was evaporated in vacuo and the product was purified by flash chromatography (petroleum ether:ethyl acetate 4:1, silica gel 16 g) to give **8**. Yield: 140 mg (66 %), amorphous; $[\alpha]_D^{22}$ +60.1° (*c* 1, $CHCl_3$); $R_f = 0.52$ (HPTLC: light petroleum:ethyl acetate 1:1). Anal. calcd for $C_{118}H_{119}NO_{23}$ (1919.2): C, 73.85; H, 6.25; N, 0.73. Found C, 73.72; H, 6.37; N, 0.57%. See Table 1.

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 169.2 (Ac—C=O), 139.4, 139.0, 138.8, 138.7, 138.6, 138.5, 138.3, 138.0, 137.9, 137.6 (Bzl-C_{ipso}), 133.3 (Pht-C-4/5), 131.2 (Pht-C-1/2), 128.3–126.5 (Bzl-C_{arom}), 123.0 (Pht-C-3/6), 102.4, 100.8, 99.7 (C-1A, C-1B, C-1C, C-1D), 82.9, 82.0, 81.6, 80.4, 78.8, 77.8, 76.8, 75.9, 74.8, 73.3, 73.1, 72.7, 72.0 (C-2A, C-2B, C-2D, C-3A, C-3B, C-3C, C-3D, C-4A, C-4B, C-4C, C-4D, C-5A, C-5B, C-5C, C-5D), 75.3, 75.0, 74.9, 74.6, 74.4, 74.0, 73.6, 73.4, 73.3, 72.9, 71.7, 70.7 (pH-CH_2), 68.33, 68.25, 68.05, 67.69 (C-6A, C-6B, C-6C, C-6D), 56.4 (C-2C), 21.0 (Ac-CH_3).

Benzyl (2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (11). To a solution of **8** (118 mg, 61.9 μmol) in dry tetrahydrofuran (2 mL) and dry methanol (6 mL) were added 3 mL of a 0.1 M solution of sodium methanolate in methanol. The mixture was stirred for 5 days at room

Table 1. Assignment of 400 MHz ^1H NMR signals of **8** ($CDCl_3$, δ in ppm, *J* in Hz)

Type	Position	1-H ($J_{1,2}$)	2-H ($J_{2,3}$)	3-H ($J_{3,4}$)	4-H ($J_{4,5}$)	5-H ($J_{5,6a}$)	6a-H ($J_{6a,6b}$)	6b-H
Glc	A	4.30	3.36	3.34	3.84	2.94	3.48	3.31
Gal	B	4.22	3.44 (10.0)	3.53 (2.9)	3.98	n.d.	n.d.	n.d.
GlcNPht	C	5.36 (8.3)	4.24	4.37	4.02 (10.0)	3.58 (3.2)	3.77 (10.9)	3.75
Gal	D	4.50 (7.9)	5.35 (9.9)	3.36 (2.7)	3.92	n.d.	n.d.	n.d.

n.d.: not determined.

temperature and then neutralized by addition of ion exchange resin IR-120 (H^+ form). The ion exchange resin was filtered off and washed with tetrahydrofuran. After evaporation of the solvent from the combined organic layers in vacuo and drying in high vacuum, the deacetylated product **9** was isolated as a colourless oil and immediately subjected to the fucosylation reaction.

To a solution of ethyl tri-*O*-benzyl-1-thio-L-fucopyranoside **10**[31] (300 mg, 0.61 mmol) in dry dichloromethane (10 mL) dried bromine (0.04 mL) at 5 °C was added. After 30 min at this temperature, cyclohexene was added until the solution became colourless. The solvent was evaporated in vacuo, the remaining oily fucosyl bromide was dried in high vacuum and dissolved in dry dimethylformamide (2 mL). The obtained solution was added dropwise to a solution of **9** (vide supra) and dry tetraethylammonium bromide (130 mg, 0.61 mmol) in dimethylformamide (4 mL), which prior to this addition was stirred with molecular sieves 4 Å for 1 h at room temperature under argon atmosphere. The mixture was stirred for 10 days, diluted with ethanol (0.5 mL) and filtered through Celite. The Celite was washed with dichloromethane (50 mL), and the combined organic solutions were extracted with 50 mL of satd $NaHCO_3$ solution. After addition of triethylamine (0.02 mL) the solvent was evaporated in vacuo and then in high vacuum (bath temperature below 35 °C). The oily remainder was dissolved in a small amount of dichloromethane. Silica gel and a drop of triethylamine were added and the solvents evaporated in vacuo. Flash chromatography on silica gel (16 g) in petroleum ether:ethyl acetate (4:1 + 0.1% of triethylamine) gave pure **11**. Yield: 97 mg (68%), amorphous (lyophilized from benzene solution); $[\alpha]_D^{22}$ −31.8° (*c* 1, $CHCl_3$); $R_f = 0.72$ (HPTLC: petroleum ether:ethyl acetate 1:1); Anal. calcd for $C_{143}H_{145}NO_{27}$ (2309.7): C, 74.36; H, 6.33; N, 0.61. Found: C, 74.64; H, 6.30; N, 0.72. See Table 2.

Table 2. Assignment of 400 MHz ^{1}H NMR signals of **11** ($CDCl_3$, δ in ppm, *J* in Hz)

Type	Position	1-H ($J_{1,2}$)	2-H ($J_{2,3}$)	3-H ($J_{3,4}$)	4-H	5-H ($J_{5,6}$)	6a-H	6b-H
Glc	A	4.32	3.38	3.37	3.86	2.95	3.51	3.31
Gal	B	4.28	3.48 (9.9)	3.59 (2.8)	4.04	n.d.	n.d.	n.d.
GlcNPht	C	5.37 (7.8)	4.30	n.d.	4.10	3.53	n.d.	n.d.
Gal	D	4.56	4.25 (9.7)	3.64 (2.7)	3.95 (3.95)	n.d.	n.d.	n.d.
Fuc	E	5.73 (3.8)	4.07 (10.2)	3.91 (2.6)	3.81	4.43 (6.5)	1.39	—

n.d.: not determined.

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 139.35, 139.05, 138.84, 138.74, 138.70, 138.64, 138.55, 138.49, 138.44, 138.26, 138.10,. 138.03, 137.57 (Bzl-C_{ipso}), 133.4 (Pht-C-4/5), 131.3 (Pht-C-1/2), 128.4–126.2 (Bzl-C_{arom}), 123.0 (Pht-C-3/6), 102.4, 102.3, 100.7, 100.1 (C-1A, C-1B, C-1C, C-1D), 97.6 (C-1E), 83.9, 83.0, 82.3, 81.6, 79.3, 78.8, 78.1, 76.7, 76.6, 76.5, 75.9, 75.6, 74.8, 73.5, 73.2, 73.1, 72.2 (C-2A, C-2B, C-2D, C-2E, C-3A, C-3B, C-3C, C3-D, C-3E, C-4A, C-4B, C-4C, C-4D, C-4E, C-5A, C-5B, C-5C, C-5D, C-5E), 68.7, 68.4, 68.3, 67.7 (C-6A, C-6B, C-6C, C-6D), 56.3 (C-2C), 16.8 (C-6E).

(3-*O*-*p*-Methoxybenzyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (14). To a solution of (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide,[21] **13** (2.34 g, 3 mmol), in dry dichloromethane (50 mL) and methanol (50 mL) was added 3 mL of a 0.1 M methanolic sodium methanolate solution. The mixture was stirred for 4 h at room temperature, neutralized by the addition of ion exchange resin IR-120 (H^+ form), stirred once more for 1 h, filtered and ion exchange resin was washed twice with 100 mL portions of dichloromethane. The combined filtrates were evaporated in vacuo and the remaining residue was dried in high vacuum. To this product were added di-*n*-butyltin-oxide (821 mg, 3.3 mmol) and dry methanol (100 mL). The mixture was refluxed for 3 h under dry argon atmosphere. The solvent was evaporated in vacuo and the oily residue dried in high vacuum to give an amorphous solid. This product was dissolved in dry 1,4-dioxane (150 mL). After addition of *p*-methoxybenzyl chloride (2.1 mL, 15 mmol) and tetrabutylammonium iodide (1.1 g, 3 mmol), the mixture was stirred at 80 °C under dry argon atmosphere for 3.5 h. Methanol (2 mL) was added and the solvents were evaporated in vacuo. Purification was carried out by flash chromatography (chloroform:methanol 50:1) on 140 g of silica gel. Yield: 1.38 g (54%), amorphous; $[\alpha]_D^{22}$ +9.4° (*c* 1, methanol); $R_f = 0.11$ (chloroform:methanol 50:1), $R_f = 0.73$ (ethyl acetate:acetone 1:2). 400 MHz ^{1}H NMR (DMSO-d_6): δ (ppm) 7.95–7.88 (m, 4H, Pht-H), 7.35–7.26 (m, 7H, Ph-H), 6.89–6.87 (m, 2H, Ph-H), 5.89–5.40 (m, $J_{1,2} = 9.6$ Hz, 2H, 1A-H, H_2C=C$\underline{H}$—CH_2), 5.24 (d, $J_{vic} = 5.1$ Hz, OH), 4.84 (dd, $J_{vic(trans)} = 17.2$ Hz, 1H, $\underline{H}_2C$=CH—CH_2), 4.68 (dd, $J_{vic(cis)} = 10.3$ Hz, 1H, $\underline{H}_2C$=CH—CH_2), 4.62 (d, $J_{gem} = 11.8$ Hz, 1H, Ph—CH_2), 4.58 (d, $J_{gem} = 12.1$ Hz, 1H, PhCH_2), 4.52–4.44 (m, 4H, 2 × OH, 2 × Ph—CH_2), 4.32 (dd, $J_{gem} = 13.1$ Hz, $J_{vic} = 5.0$ Hz, 1H, H_2C=CH—C$\underline{H}_2$), 4.25 (d, $J_{1,2} = 7.7$ Hz, 1H, 1B-H), 4.11 (dd, $J_{2,3} = 10.6$ Hz, $J_{3,4} = 7.9$ Hz, 1H, 3A-H), 3.99 (dd, $J_{5,6a} = 3.3$ Hz, $J_{6a,6b} = 11.4$ Hz, 1H, 6Aa-H), 3.87–3.73 (m, 6H, 2A-H, 4A-H, 4B-H, 5A-H, H_2C=CH—C$\underline{H}_2$), 3.72 (s, 3H, CH_3—O—Ph), 3.54 (ddd, $J_{5,6a} = 7.8$ Hz, $J_{5,6b} = 10.0$ Hz, 1H, 6Ba-H), 3.47 (ddd, $J_{OH,2} = 5.1$ Hz, $J_{2,3} = 9.7$ Hz, 1H, 2B-H), 3.39 (ddd, $J_{5,6b} = 6.3$ Hz, 1H, 6Bb-H), 3.18 (dd, 1H, 5B-H), 3.13 (dd, $J_{3,4} = 3.1$ Hz, 1H, 3B-H).

100.6 MHz ^{13}C NMR (DMSO-d_6): δ (ppm) 158.5 (Mpm-C-4), 138.3 (Bzl-C_{ipso}), 135.1, 135.0 (Pht-C-4/5, H_2C=C$\underline{H}$—CH_2), 130.8, 130.6 (Pht-C-1/2, Mpm-C_{ipso}), 129.0–127.3 (C_{arom}), 123.5 (Pht-C-3/6), 115.7 ($H_2\underline{C}$=CH—CH_2), 113.3 (Mpm-C_{arom}), 103.6 (C-1B), 85.0 (C-1A), 80.8, 77.2, 76.8, 76.7, 74.8, 69.9, 64.0 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 72.5, 72.1 (H_2C=CH—$\underline{C}H_2$, pH—CH_2), 69.7, 67.8, 59.8 (C-6A, C-6B, Mpm-CH_2), 55.0 (2A-H, CH_3—O—Ph).

3-*O*-Protected galactopyranosyl azides. General procedure. A solution of tetra-*O*-acetyl-β-D-galactopyranosyl azide[40,41] **15** (1.87 g, 5 mmol) in 100 mL of methanol and 5 mL of 0.1 M sodium methanolate in methanol was stirred at room temperature for 1 h. After neutralization with ion exchange resin IR-120 (H^+ form), filtration, washing of the ion exchange resin with methanol, and evaporation of the solvent from the combined filtrates, the remaining residue was dried in high vacuum. Di-*n*-butyltinoxide (1.4 g, 5.6 mmol) and methanol (150 mL) were added and the mixture was stirred under reflux for 3 h. After evaporation of the solvent in vacuo, the residue was dried in high vacuum.

For the introduction of the allyloxycarbonyl group, the residue was dissolved in dry tetrahydrofuran (100 mL). At 2 °C, allyl chloroformate (0.58 mL, 5.5 mmol) was added and the mixture was stirred at 0 °C for 1 h. After addition of methanol (5 mL), the solvent was evaporated in vacuo and the remaining **16** was purified by flash chromatography (ethyl acetate:acetone 10:1) on 70 g of silica gel.

For the introduction of the alkyl groups, the residue was dissolved in dry 1,4-dioxane (100 mL). After addition of the methoxyethoxymethyl chloride (0.85 mL, 7.5 mmol) or the ethoxymethyl chloride (0.51 mL, 7.5 mmol), the mixture was stirred at 40 °C for 2 h. Methanol (2 mL) and silica gel was added, and the solvent was evaporated in vacuo. Purification was carried out by flash chromatography (Mem derivative **17**: ethyl acetate:petroleum ether 1:1; Em derivative **18** ethyl acetate:petroleum ether 2:1) on 40 g of silica gel.

3-*O*-Allyloxycarbonyl-β-D-galactopyranosyl azide (16). Yield: 963 mg (67%), amorphous; $[\alpha]_D^{22}$ +29.9° (*c* 1, methanol); R_f = 0.71 (ethyl acetate:acetone 2:1). IR (KBr) ν (cm^{-1}): 2119 (N_3), 1723 (carbonate); 200 MHz ^{1}H NMR (DMSO-d_6): δ (ppm) 6.02–5.85 (m, 1H, H_2C=C<u>H</u>—CH_2), 5.80 (d, $J_{OH,2}$ = 6.0 Hz, 1H, 2-OH), 5.36 (dd, $J_{vic(trans)}$ = 17.3 Hz, 1H, <u>H</u>$_2$C=CH—CH_2), 5.26 (dd, $J_{vic(cis)}$ = 10.5 Hz, 1H, <u>H</u>$_2$C=CH—CH_2), 5.16 (d, $J_{OH,4}$ = 6.1 Hz, 1H, 4-OH), 4.63–4.57 (m, 3H, 1-H, H_2C=CH—C<u>H</u>$_2$), 4.48 (dd, $J_{2,3}$ = 9.9 Hz, $J_{3,4}$ = 3.1 Hz, 1H, 3-H), 3.93 (dd, 1H, 4-H), 3.64–3.47 (m, 4H, 2-H, 5-H, 6a-H, 6b-H).

50.3 MHz ^{13}C NMR (DMSO-d_6): δ (ppm) 154.0 (Aloc-C=O), 132.1 (H_2C=C<u>H</u>—CH_2), 118.3 (H_2C<u>=</u>CH—CH_2), 90.3 (C-1), 79.7, 76.8, 67.5, 65.1 (C-2, C-3, C-4, C-5), 67.8 (H_2C=CH—C<u>H</u>$_2$), 59.8 (C-6).

3-*O*-(2-Methoxyethoxymethyl)-β-D-galactopyranosyl azide (17). Yield: 877 mg (60%), colorless oil; $[\alpha]_D^{22}$ −19.0° (*c* 1, methanol); R_f = 0.27 (ethyl acetate:acetone 2:1).

400 MHz ^{1}H NMR (DMSO-d_6): δ (ppm) = 5.48 (d, $J_{OH,2}$ = 5.5 Hz, 1H, 2-OH), 4.73–4.70 (m, 3H, 6-OH, H_3C—O—CH_2CH_2—O—C<u>H</u>$_2$), 4.66 (d, $J_{OH,4}$ = 5.1 Hz, 1H, 4-OH), 4.44 (d, $J_{1,2}$ = 8.3 Hz, 1H, 1-H), 3.84 (d, $J_{3,4}$ = 3.4 Hz, 1H, 4-H), 3.71–3.60 (m, 2H, H_3C—O—CH_2C<u>H</u>$_2$—O—CH_2), 3.54–3.43 (m, 6H, 2-H, 5-H, 6a-H, 6b-H, H_3C—O—C<u>H</u>$_2$$CH_2$—O—$CH_2$), 3.41 (dd, $J_{2,3}$ = 9.6 Hz, 1H, 3-H), 3.23 (s, 3H, <u>H</u>$_3$C—O—CH_2CH_2—O—CH_2).

3-*O*-Ethoxymethyl-β-D-galactopyranosyl azide (18). Yield: 750 mg (57%), colorless oil; $[\alpha]_D^{22}$ −13.2° (*c* 1, methanol); R_f = 0.47 (ethyl acetate:acetone 2:1).

400 MHz ^{1}H NMR (DMSO-d_6): δ (ppm) 5.49 (d, $J_{OH,2}$ = 5.6 Hz, 1H, 2-OH), 4.73–4.68 (m, 3H, 2 × H_3C—CH_2—O—C<u>H</u>$_2$, 6-OH), 4.67 (d, $J_{OH,4}$ = 5.2 Hz, 1H, 4-OH), 4.45 (d, $J_{1,2}$ = 8.4 Hz, 1H, 1-H), 3.81 (dd, $J_{3,4}$ = 3.0 Hz, 1H, 4-H), 3.62–3.55 (m, 2H, H_3C—C<u>H</u>$_2$—O—CH_2), 3.53–3.43 (m, 4H, 2H, 5-H, 6a-H, 6b-H), 3.40 (dd, $J_{2,3}$ = 9.6 Hz, 1H, 3-H), 1.10 (t, J_{vic} = 7.1 Hz, 3H, H_3C—CH_2—O—CH_2).

100.6 MHz ^{13}C NMR (DMSO-d_6): δ (ppm) 93.4 (H_3C—CH_2—O—C<u>H</u>$_2$), 90.1 (C-1), 78.5, 77.3, 69.1, 65.9 (C-2, C-3, C-4, C-5), 62.3, 60.2 (C-6, H_3C—C<u>H</u>$_2$—O—CH_2), 14.9 (H_3C—CH_2—O—CH_2).

2,4,6-Tri-*O*-benzyl-3-*O*-ethoxymethyl-β-D-galactopyranosyl azide (19). To a stirred solution of **18** (527 mg, 2 mmol) and benzyl bromide (1.9 mL, 16 mmol) in dry dimethylformamide (30 mL) were added at 0 °C 480 mg (16 mmol) of sodium hydride (80% in paraffin). After 3 h, methanol (5 mL) was added dropwise and the solvent was evaporated in high vacuum. The oily remainder was dissolved in 10 mL of dichloromethane, silica gel was added and the solvent was evaporated in vacuo. Purification was achieved by flash chromatography (petroleum ether:ethyl acetate 10:1) on silica gel (40 g). Yield: 898 mg (84%), colourless oil: $[\alpha]_D^{22}$ −18.8° (*c* 1, $CHCl_3$); R_f = 0.50 (petroleum ether:ethyl acetate 4:1). Anal. calcd for $C_{30}H_{35}N_3O_6$ (533.6): C, 67.53; H, 6.61; N, 7.87. Found: C, 67.21; H, 6.54; N, 7.83%.

400 MHz ^{1}H NMR ($CDCl_3$): δ (ppm) 7.36–7.25 (m, 15H, Ph-H), 4.89 (d, J_{gem} = 11.6 Hz, 1H, Ph—C<u>H</u>$_2$), 4.84 (d, J_{gem} = 10.8 Hz, 1H, Ph—C<u>H</u>$_2$), 4.78, 4.74 (d, J_{gem} = 6.9 Hz, 1H, H_3C—CH_2—O—C<u>H</u>$_2$), 4.72 (d, J_{gem} = 10.8 Hz, 1H, Ph—C<u>H</u>$_2$), 4.60 (d, $J_{1,2}$ = 6.9 Hz, 1H, 1-H), 4.49, 4.42 (J_{gem} = 11.9 Hz, 1H, Ph—C<u>H</u>$_2$), 3.89 (dd, $J_{3,4}$ = 2.3 Hz, $J_{4,5}$ = 1.5 Hz, 1H, 4-H), [3.74–3.66 (m, 3H), 3.63–3.54 (m, 4H) (2-H, 3-H, 5-H, 6a-H, 6b-H, H_3C—C<u>H</u>$_2$—O—CH_2)], 1.15 (t, J_{vic} = 7.1 Hz, 3H, <u>H</u>$_3$C—CH_2—O—CH_2).

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 138.3, 137.9, 137.7 (Bzl—C_{ipso}), 128.3–127.5 (Bzl—C_{arom}), 94.7 (H_3C—CH_2—O—C<u>H</u>$_2$), 90.5 (C-1), 78.8, 78.5, 75.5, 74.4 (C-2, C-3, C-4, C-5), 75.2, 74.5, 73.4 (Ph—CH_2), 68.3, 63.6 (C-6, H_3C—C<u>H</u>$_2$—O—CH_2), 14.9 (H_3C—CH_2—O—CH_2).

(3-*O*-Ethoxymethyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (20). The synthesis of **20** was performed in analogy to that of **14** starting from 2.34 g (3 mmol) of the lactosamine azide **13**. Ethoxymethyl chloride (0.33 mL, 3.6 mmol) was added to the amorphous

residue obtained after treatment with di-*n*-butyltin-oxide dissolved in 1,4-dioxane (150 mL). After 2 h at 40 °C and addition of 2 mL of methanol, the solvent was evaporated in vacuo. Purification was achieved by flash chromatography (petroleum ether:ethyl acetate 1:1) on silica gel (40 g). Yield: 473 mg (24%), amorphous; $[\alpha]_D^{22}$ 0° (*c* 0.5, methanol); $R_f = 0.63$ (ethyl acetate:acetone 2:1).

400 MHz ^{1}H NMR (DMSO-d_6): δ (ppm) 7.95–7.88 (m, 4H, Pht-H), 7.36 (m_c, 4H, Ph—H), 7.34–7.28 (m, 1H, Ph—H), 5.47 (d, $J_{1,2} = 9.5$ Hz, 1H, 1A-H), 5.48–5.39 (m, 1H, H_2C=CH—CH_2), 5.24 (d, $J_{vic} = 5.1$ Hz, 1H, OH), 4.84 (dd, $J_{vic(trans)} = 17.3$ Hz, 1H, $\underline{H}_2C$=CH—CH_2), 4.73, 4.70 (d, $J_{gem} = 7.0$ Hz, 1H, H_3C—CH_2—O—$C\underline{H}_2$), 4.69 (dd, $J_{vic(cis)} = 11.4$ Hz, 1H, $\underline{H}_2C$=CH—CH_2), 4.59 (d, $J_{gem} = 12.0$ Hz, 1H, Ph—CH_2), 4.54–4.50 (m, 2H, Ph—CH_2, 6B-OH), 4.47 (d, $J_{vic} = 5.0$ Hz, 1H, OH), 4.32 (dd, $J_{gem} = 13.1$ Hz, $J_{vic} = 5.0$ Hz, 1H, H_2C=CH—$C\underline{H}_2$), 4.27 (d, $J_{1,2} = 7.6$ Hz, 1H, 1B-H), 4.11 (dd, $J_{2,3} = 10.6$ Hz, $J_{3,4} = 7.9$ Hz, 1H, 3A-H), 3.98 (dd, $J_{5,6a} = 3.1$ Hz, $J_{6a,6b} = 11.0$ Hz, 1H, 6Aa-H), 3.89–3.79 (m, 4H, 2A-H, 4A-H, 5A-H, 6Ab-H), 3.76 (dd, $J_{vic} = 6.5$ Hz, 1H, H_2C=CH—$C\underline{H}_2$), 3.63–3.36 (m, 6H, 2B-H, 4B-H, 6Ba-H, 6Bb-H, H_3C—$C\underline{H}_2$—O—CH_2), 3.29 (dd, $J_{2,3} = 10.3$ Hz, $J_{3,4} = 3.9$ Hz, 1H, 3B-H), 3.22 (dd, $J_{5,6a} = 6.5$ Hz, $J_{5,6b} = 7.7$ Hz, 1H, 5B-H), 1.10 (t, $J_{vic} = 7.1$ Hz, 3H, $\underline{H}_3C$—CH_2—O—CH_2).

100.6 MHz ^{13}C NMR (DMSO-d_6): δ (ppm) 138.4 (Bzl—C_{ipso}), 135.2, 135.1 (Pht-C-4/5, H_2C=$\underline{C}$H—CH_2), 130.6 (Pht—C-1/2), 128.2, 127.5, 127.4 (Bzl—C_{arom}), 123.5 (Pht—C-3/6), 115.8 ($H_2\underline{C}$=CH—CH_2), 103.6 (C-1B), 93.4 (H_3C—CH_2—O—$\underline{C}H_2$), 85.0 (C-1A), 78.7, 77.3, 76.8, 76,7, 74.8, 69.7, 65.3, (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 72.5, 72.2 (H_2C=CH—$\underline{C}H_2$, Ph—CH_2), 67.8, 62.2, 59.7 (C-6A, C-6B, H_3C—$\underline{C}H_2$—O—CH_2), 54.7 (C-2A), 14.9 ($H_3\underline{C}$—CH_2—O—CH_2).

3,4-*O*-Isopropylidene-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (21). To a solution of **13** (8 g, 10.1 mmol) in dry dichloromethane (100 mL) and dry methanol (100 mL) was added 0.1 M sodium methanolate in methanol (10.1 mL) and the mixture was stirred at room temperature for 3 h. After neutralization with ion exchange resin IR-120 (H^+ form), filtration, washing of the resin with methanol and evaporation of the solvent from the combined organic solutions in vacuo, the remaining residue was dried in high vacuum. The product was dissolved in acetone (1 L) and, after addition of *p*-toluenesulfonic acid monohydrate (333 mg, 1.75 mmol), heated under reflux for 2 h. Triethylamine (3 mL, 22 mmol) was added and the solvent evaporated at room temperature in vacuo. Purification was carried out by flash chromatography on 140 g of silica gel in pretroleum ether:ethyl acetate 2:1; yield 3.9 g (58%); amorphous $[\alpha]_D^{22}$ +38.4° (*c* 1, $CHCl_3$); $R_f = 0.26$ (petroleum ether:ethyl acetate 1:1). Anal. calcd for $C_{33}H_{38}N_4O_{11}$ (666.7): C, 59.45; H, 5.75; N, 8.40. Found: C, 59.68; H, 5.97; N, 8.02. IR (NaCl) ν (cm^{-1}): 2118 (N_3), 1778, 1718 (phthalimide).

400 MHz ^{1}H NMR (DMSO-d_6): δ (ppm) 7.95–7.88 (m, 4H, Pht-H), 7.37–7.27 (m, 5H, Ph-H), 5.50–5.40 (m, 3H, 1A-H, 2B-OH, H_2C=$C\underline{H}$—CH_2), 4.85 (ddd, $J_{vic(trans)} = 17.3$ Hz, 1H, $\underline{H}_2C$=CH—CH_2), 4.70–4.67 (m, 2H, 6B-OH, $\underline{H}_2C$=CH—CH_2), 4.60, 4.51 (d, $J_{gem} = 11.9$ Hz, 1H, Ph—CH_2), 4.28 (dd, $J_{gem} = 13.0$ Hz, $J_{vic} = 5.0$ Hz, 1H, H_2C=CH—$C\underline{H}_2$), 4.22 (d, $J_{1,2} = 8.1$ Hz, 1H, 1B-H), 4.12 (dd, $J_{2,3} = 10.5$ Hz, $J_{3,4} = 8.3$ Hz, 1H, 3A-H), 4.10 (dd, $J_{3,4} = 5.2$ Hz, $J_{4,5} = 2.0$ Hz, 1H, 4B-H), 3.92 (dd, $J_{5,6a} = 3.8$ Hz, $J_{6a,6b} = 11.3$ Hz, 1H, 6Aa-H), 3.89–3.74 (m, 6H, 2A-H, 3B-H, 4A-H, 5A-H, 6Ab-H, H_2C=CH—$C\underline{H}_2$), 3.60 (ddd, $J_{5,6a} = J_{5,6a} = 6.4$ Hz, 1H, 5B-H), 3.56–3.47 (m, 2H, 6Ba-H, 6Bb-H), 3.19 (ddd, $J_{2,3} = 7.4$ Hz, 1H, 2B-H), 1.36, 1.23 (s, 3H, isopropylidene-CH_3).

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 137.6 (Bzl—C_{ipso}), 134.4, 134.2 (Pht—C-4/5, H_2C=$\underline{C}$H—CH_2), 131.5 (Pht—C-1/2), 128.4, 128.0, 127.8 (C_{arom}), 123.5 (Pht—C-3/6), 116.8 ($H_2\underline{C}$=CH—CH_2), 110.2 [isopropylidene-$C(CH_3)_2$], 102.1 (C-1B), 85.8 (C-1A), 79.4, 77.7, 77.4, 77.0, 74.1, 73.9 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 73.5 (H_2C=CH—$\underline{C}H_2$, Ph—CH_2), 67.8, 62.1 (C-6A, C-6B), 55.4 (C-2A), 28.0, 26.2 (isopropylidene-CH_3).

(6-*O*-*tert*-Butyldiphenylsilyl)-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl azide (22). Deacetylation of **13** (1.1 g, 1.5 mmol) was carried out as described for the synthesis of **20**. The obtained product was dissolved in dry dimethylformamide (15 mL). Imidazole (204 mg, 3 mmol) and *tert*-butyl-diphenylsilylchloride (1.5 mL, 6 mmol) were added and the mixture stirred at room temperature for 3 h. After addition of ethyl acetate (100 mL), the solution was washed with satd NaCl solution (100 mL) and satd $NaHCO_3$ solution (50 mL). The collected aqueous layers were re-extracted twice with ethyl acetate (50 mL). The combined organic solutions were dried with $MgSO_4$. After evaporation of the solvent in vacuo, the product was purified by flash chromatography on silica gel (40 g) in petroleum ether: ethyl acetate 1:1; yield: 706 mg (54%), amorphous; $[\alpha]_D^{22}$ +9.1° (*c* 1, $CHCl_3$); $R_f = 0.69$ (ethyl acetate:acetone 2:1). Anal. calcd for $C_{46}H_{52}N_4O_{11}Si$ (865.0): C, 63.87; H, 6.06; N, 6.48. Found: C, 63.87; H, 6.09; N, 6.44%.

400 MHz ^{1}H NMR (DMSO-d_6): δ (ppm) 7.93–7.87, 7.63–7.58 (2m, 2H, Pht-H), 7.44–7.26 (m, 15H, Ph—H), 5.44 (d, $J_{1,2} = 9.5$ Hz, 1H, 1A-H), 5.37–5.26 (m, 1H, H_2C=$C\underline{H}$—CH_2), 5.16 (d, $J_{vic} = 4.6$ Hz, 1H, OH), 4.88 (d, $J_{vic} = 4.3$ Hz, 1H, OH), 4.72 (dd, $J_{vic(trans)} = 17.3$ Hz, 1H, $\underline{H}_2C$=CH—CH_2), 4.59 (d, $J_{gem} = 11.9$ Hz, 1H, Ph—CH_2), 4.52 (m_c, 2H, Ph—CH_2, $\underline{H}_2C$=CH—CH_2), 4.48 (d, $J_{vic} = 4.4$ Hz, 1H, OH), 4.26 (d, $J_{1,2} = 7.4$ Hz, 1H, 1B-H), 4.23 (dd, $J_{gem} = 12.8$ Hz, $J_{vic} = 4.9$ Hz, 1H, H_2C=CH—$C\underline{H}_2$), 4.12 (dd, $J_{2,3} = 10.6$ Hz, $J_{3,4} = 8.6$ Hz, 1H, 3A-H), 4.00 (dd, $J_{5,6a} = 3.6$ Hz, $J_{6a,6b} = 11.1$ Hz, 1H, 6Ba-H), 3.88–3.81

(m, 2H, 2A-H, 4A-H), 3.79–3.72 (m, 4H, 5B-H, 6Aa-H, 6Bb-H, H_2C=CH—CH_2), 3.69 (m_c, 1H, 4B-H), 3.59 (dd, $J_{5,6b}$ = 6.3 Hz, $J_{6a,6b}$ = 9.7 Hz, 1H, 6Ab-H), 3.38 (dd, $J_{4,5}$ = 6.3 HZ, 1H, 5A-H), 3.32 (m_c, 1H, 2B-H), 3.25 (m_c, 1H, 3B-H), 0.97 [s, 9H, TBDPS-C(CH_3)$_3$].

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 137.2 (Bzl—C_{ipso}), 135.3 (TBDPS—Ph—C-4), 134.1, 134.0 (Pht—C-4/5, H_2C=CH—CH_2), 132.7, 132.4, 131.3 (TBDPS—Ph—C_{ipso}, Pht—C-1/2), 129.6–127.6 (C_{arom}), 123.5 (Pht—C-3/6), 116.2 (H_2C=CH—CH_2), 103.2 (C-1B), 85.7 (C-1A), 77.9, 77.0, 74.2, 73.8, 72.8, 68.3 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 73.7, 73.5 (H_2C=CH—CH_2, Ph—CH_2), 68.0, 62.6 (C-6A, C-6B), 55.5 (C-2A), 27.0 [TBDPS—C(CH_3)$_3$], 19.3 [TBDPS-C(CH_3)$_3$].

(6-*O*-*tert*-Butyldiphenylsilyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (23). To a solution of **22** (568 mg, 0.66 mmol) in acetone (30 mL) and 2,2-dimethyloxypropane (30 mL) was added *p*-toluenesulfonic acid monohydrate (0.1 g, 0.53 mmol). The mixture was stirred for 4 h at room temperature. Triethylamine (0.07 mL, 0.95 mmol) was added and the solvent evaporated in vacuo. The crude **23** was purified by flash chromatography on silica gel (16 g) in petroleum ether:ethyl acetate 3:1; yield: 449 mg (75%), amorphous; $[\alpha]_D^{22}$ +20.3° (*c* 1, $CHCl_3$); R_f = 0.70 (petroleum ether:ethyl acetate 1:1). Anal. calcd for $C_{49}H_{56}N_4O_{11}Si$ (905.6): C, 65.03; H, 6.24; N, 6.19. Found: C, 64.91; H, 6.32; N, 6.01%.

400 MHz ^{1}H NMR (DMSO-d_6): δ (ppm) 7.93–7.87, 7.64–7.59 (2m, 2H, Pht—H), 7.45–7.25 (m, 15H, Ph—H), 5.52 (d, J_{vic} = 5.0 Hz, 1H, 2B-OH), 5.44 (d, $J_{1,2}$ = 9.5 Hz, 1H, 1A-H), 5.37–5.28 (m, 1H, H_2C=CH—CH_2), 4.73 (dd, $J_{vic(trans)}$ = 17.2 Hz, 1H, H_2C=CH—CH_2), 4.61 (d, J_{gem} = 12.0 Hz, 1H, Ph—CH_2), 4.53 (dd, $J_{vic(cis)}$ = 10.3 Hz, 1H, H_2C=CH—CH_2), 4.51 (d, 1H, Ph—CH_2), 4.26 (d, $J_{1,2}$ = 8.1 Hz, 1H, 1B-H), 4.20–4.15 (m, 2H, 6Ba-H, H_2C=CH—CH_2), 4.13 (dd, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 9.0 Hz, 1H, 3A-H), 3.95–3.65 (m, 10H, 2A-H, 3B-H, 4A-H, 4B-H, 5A-H, 5B-H, 6Aa-H, 6Ab-H, 6Bb-H, H_2C=CH—CH_2), 3.21 (m_c, 1H, 2B-H), 1.36, 1.24 (s, 3H, isopropylidene-CH_3), 0.98 [s, 9H, TBDPS—C(CH_3)$_3$].

100.6 MHz ^{13}C NMR (DMSO-d_6): δ (ppm) 138.3 (Bzl—C_{ipso}), 135.0 (TBDPS—Ph—C-4), 134.8 (Pht—C-4/5, H_2C=CH—CH_2), 132.8, 130.6 (TBDPS—Ph—C_{ipso}, Pht—C-1/2), 129.8–127.3 (C_{arom}), 123.6 (Pht—C-3/6), 115.5 (H_2C=CH—CH_2), 108.5 [isopropylidene-C(CH_3)$_2$], 102.4 (C-1B), 85.1 (C-1A), 79.3, 76.7, 76.6, 76.5, 72.8, 72.5, (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 72.3, 72.2 (H_2C=CH—CH_2, Ph—CH_2), 67.6, 62.5 (C-6A, C-6B), 54.6 (C-2A), 28.0, 26.2 (isopropylidene-CH_3), 26.2 [TBDPS—C(CH_3)$_3$], 18.7 [TBDPS—C(CH_3)$_3$].

Formation of 21 from 23. To a solution of **23** (387 mg, 0.43 mmol) in dry tetrahydrofuran (15 mL) was added tetrabutylammonium fluoride (0.6 mL of a 1 M solution in tetrahydrofuran). The mixture was stirred at room temperature for 1 day. Silica gel was added and the solvent was evaporated in vacuo. Flash chromatography was carried out on 16 g of silica gel in petroleum ether:ethyl acetate to give **21** (191 mg, 67%). Its data are identical with the material described above.

(2,6-Di-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl-(14)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (24). To a stirred mixture of **21** (207 mg, 0.31 mmol), freshly prepared and carefully dried silver oxide (868 mg, 3.75 mmol), and dried tetrabutylammonium iodide (687 mg, 1.86 mmol), was added at 0 °C a solution of benzyl bromide (0.44 mL, 3.72 mmol) in dry dimethylformamide (7 mL). After stirring at 0 °C for 16 h, the mixture was poured into diethyl ether (100 mL) and filtered through Celite. The filtrate was washed with sodium thiosulfate solution (30%, 100 mL), dried with $MgSO_4$, evaporated to dryness in vacuo, and then dried in high vacuum. Purification was carried out by flash chromatography on 14 g of silica gel in petroleum ether:ethyl acetate 4:1; yield: 207 mg (79%); colorless oil; $[\alpha]_D^{22}$ +13.9° (*c* 1, $CHCl_3$; R_f = 0.85 (petroleum ether:ethyl acetate 1:1). Anal. calcd for $C_{47}H_{50}N_4O_{11}$ (846.9): C, 66.65; H, 5.95; N, 6.62. Found: C, 66.75; H, 6.03; N, 6.55%. IR (NaCl) ν (cm^{-1}): 2116 (N_3), 1778, 1717 (phthalimide).

400 MHz ^{1}H NMR ($CDCl_3$): δ (ppm) 7.85 (m_c, 2H, Pht—H), 7.75–7.71 (m, 2H, Pht—H), 7.36–7.25 (m, 15H, Ph—H), 5.50–5.41 (m, 1H, H_2C=CH—CH_2), 5.36 (d, $J_{1,2}$ = 9.4 Hz, 1H, 1A-H), 4.91 (dd, $J_{vic(trans)}$ = 17.2 Hz, 1H, H_2C=CH—CH_2), 478 (d, J_{gem} = 11.7 Hz, 1H, Ph—CH_2), 4.71–4.66 (m, 2H, Ph—CH_2, H_2C=CH—CH_2), 4.62 (d, J_{gem} = 11.7 Hz, 1H, Ph—CH_2), 4.56 (d, J_{gem} = 12.2 Hz, 1H, Ph—CH_2), 4.49 (d, J_{gem} = 12.0 Hz, 1H, Ph—CH_2), 4.40 (d, J_{gem} = 12.2 Hz, 1H, Ph—CH_2), 4.36 (d, $J_{1,2}$ = 8.1 Hz, 1H, 1B-H), 4.31 (dd, J_{gem} = 12.9 Hz, J_{vic} = 5.3 Hz, 1H, H_2C=CH—CH_2), 4.22 (dd, $J_{2,3}$ = 10.6 Hz, $J_{3,4}$ = 8.6 Hz, 1H, 3A-H), 4.11 (dd, 1H, 2A-H), 4.08 (dd, $J_{3,4}$ = 7.0 Hz, $J_{4,5}$ = 1.4 Hz, 1H, 4B-H), 3.90–3.84 (m, 2H, 6Aa-H, H_2C=CH—CH_2), 3.75–3.65 (m, 4H, 5A-H, 6Ab-H, 6Ba-H, 6Bb-H), 3.63 (m_c, 1H, 5B-H), 3.27 (dd, 1H, 2B-H), 1.35, 1.31 (s, 3H, isopropylidene-CH_3).

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 138.5, 138.4, 138.1 (Bzl—C_{ipso}), 135.0, 134.2 (Pht—C-4/5, H_2C=CH—CH_2), 131.7 (Pht—C-1/2), 128.6–127.0 (Bzl—C_{arom}), 116.5 (H_2C=CH—CH_2), 109.8 [isopropylidene-C(CH_3)$_2$], 102.3 (C-1B), 85.8 (C-1A), 80.5, 79.4, 77.6, 77.5, 77.1, 73.8, 72.2 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 73.5 73.4, 73.3 (H_2C=CH—CH_2, Ph × CH_2), 69.3 67.6 (C-6A, C-6B), 55.3 (C-2A), 27.8, 26.3 (isopropylidene-CH_3).

(2,6-Di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (25). A solution of **24** (161 mg, 0.19

mmol) in 60% aq acetic acid (20 mL) was vigorously stirred at 65 °C for 2 h. After evaporation of the solvent in vacuo, toluene (3 × 50 mL) was distilled from the residue in vacuo. The remaining oil was dissolved in dichloromethane (100 mL), washed with satd $NaHCO_3$ solution and dried with $MgSO_4$. After evaporation of the solvent in vacuo and drying in high vacuum, pure **25** was obtained. Yield: 148 mg (96%); amorphous; $[\alpha]_D^{22}$ +7.0° (*c* 1, $CHCl_3$); R_f = 0.56 (petroleum ether:ethyl acetate 1:1). Anal. calcd for $C_{44}H_{46}N_4O_{11}$ (806.9): C, 65.50; H, 5.75; N, 6.94. Found: C, 65.44; H, 5.82; N, 6.86%. IR (NaCl) ν (cm^{-1}): 2116 (N_3), 1776, 1715 (phthalimide).

400 MHz ^{1}H NMR (DMSO-d_6): δ (ppm) 7.96–7.89 (m, 4H, Pht—H), 7.41–7.23 (m, 15H, Ph—H), 5.49–5.41 (m, 1H, H_2C=C<u>H</u>—CH_2), 4.98 (d, $J_{OH,3}$ = 6.4 Hz, 1H, 3B-OH), 4.84 (dd, $J_{vic(trans)}$ = 17.2 Hz, 1H, <u>H</u>$_2$C=CH—CH_2), 4.73 (s, 2H, Ph—CH_2), 4.70 (d, $J_{OH,4}$ = 4.6 Hz, 4B-OH), 4.67 (dd, $J_{vic(cis)}$ = 10.4 Hz, 1H, <u>H</u>$_2$C=CH—CH_2), 4.56, 4.46 (d, J_{gem} = 12.0 Hz, 1H, Ph—CH_2), 4.43 (d, J_{gem} = 11.6 Hz, 1H, Ph—CH_2), 4.39–4.33 (m, $J_{1,2}$ = 7.5 Hz, 3H, 1B-H, Ph—CH_2, H_2C=CH—C<u>H</u>$_2$), 4.14 (dd, $J_{2,3}$ = 10.6 Hz, $J_{3,4}$ = 8.0 Hz, 1H, 3A-H), 3.85 (dd, 1H, 2A-H), 3.83–3.79 (m, 4H, 4A-H, 5A-H, 6Aa-H, H_2C=CH—C<u>H</u>$_2$), 3.70 (d, $J_{6a,6b}$ = 10.3 Hz, 1H, 6Ab-H), 3.62–3.59 (m, 2H, 4B-H, 6Ba-H), 3.52–3.49 (m, 2H, 5B-H, 6Bb-H), 3.42 (ddd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.3 Hz, 1H, 3B-H), 3.33 (dd, 1H, 2B-H).

100.6 MHz ^{13}C NMR (DMSO-d_6): δ (ppm) 139.0, 138.7, 138.1 (Bzl—C_{ipso}), 135.1, 135.0 (Pht-C-4/5, H_2C=C<u>H</u>—CH_2), 130.6, (Pht—C-1/2), 128.1–127.1 (Bzl-C_{arom}), 123.5 (Pht—C-3/6), 115.7 (H_2C=CH—CH_2), 102.5 (C-1B), 85.0 (C-1A), 79.8, 76.8, 76.6, 73.7, 72.9, 68.7 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 74.1, 72.5, 72.3, 72.0 (H_2C=CH—C<u>H</u>$_2$, Ph—CH_2), 69.4, 67.5 (C-6A, C-6B), 55.7 (C-2A).

(2,6-Di-*O*-benzyl-3-*O*-ethoxymethyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (26). A solution of **25** (137 mg, 0.17 mmol) and di-*n*-butyltinoxide (47 mg, 0.19 mmol) in dry methanol (10 mL) was heated under reflux for 3 h. The solvent was evaporated in vacuo. The residue was dried in high vacuum and dissolved in 1,4-dioxane (10 mL). To this solution was added ethoxymethyl chloride (0.25 mL of a 1 M solution in dry 1,4-dioxane). The mixture was stirred at 50 °C for 21 h. After addition of methanol (0.2 mL), the solvent was evaporated in vacuo and the crude **26** purified by flash chromatography on 16 g of silica gel in petroleum ether:ethyl acetate 4:1; yield: 91 mg (62%), amorphous; $[\alpha]_D^{22}$ −12.1° (*c* 1, $CHCl_3$); R_f = 0.71 (petroleum ether: ethyl acetate 1:1). Anal. calcd for $C_{47}H_{52}N_4O_{12}$ (865.0): C, 65.27; H, 6.06; N, 6.48. Found: C, 64.97; H, 6.12; N, 6.09%.

400 MHz ^{1}H NMR (DMSO-d_6): δ (ppm) 7.96–7.89 (m, 4H, Pht-H), 7.38–7.24 (m, 15H, Ph-H), 5.49–5.40 (m, $J_{1,2}$ = 9.5 Hz, 2H, 1A-H, H_2C=C<u>H</u>—CH_2), 4.84 (ddd, $J_{vic(trans)}$ = 17.2 Hz, 1H, <u>H</u>$_2$C=CH—CH_2), 4.76 (d, $J_{OH,4}$ = 5.3 Hz, 4B-OH), 4.75–4.65 (m, 4H, Ph—CH_2, <u>H</u>$_2$C=CH—CH_2, 2 × H_3C—CH_2—O—C<u>H</u>$_2$), 4.62 (d, J_{gem} = 11.4 Hz, 1H, Ph—CH_2), 4.55 (d, J_{gem} = 12.1 Hz, 1H, Ph—CH_2), 4.46 (d, J_{gem} = 12.0 Hz, 1H, Ph—CH_2), 4.40–4.34 (m, $J_{1,2}$ = 7.5 Hz, 3H, 1B-H, Ph—CH_2, H_2C=CH—C<u>H</u>$_2$), 4.15 (dd, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 8.3 Hz, 1H, 3A-H), 3.88–3.78 (m, 6H, 2A-H, 4A-H, 4B-H, 5A-H, 6Aa-H, H_2C=CH—C<u>H</u>$_2$), 3.69 (d, $J_{6a,6b}$ = 10.6 Hz, 1H, 6Ab-H), 3.65–3.42 (m, 7H, 2B-H, 3B-H, 5B-H, 6Ba-H, 6Bb-H, H_3C—C<u>H</u>$_2$—O—CH_2), 1.06 (t, J_{vic} = 7.1 Hz, 3H <u>H</u>$_3$C—CH_2—O—CH_2).

100.6 MHz ^{13}C NMR (DMSO-d_6): δ (ppm) 138.6, 138.0 (Bzl—C_{ipso}), 135.1, 135.0 (Pht—C-4/5), H_2C=C<u>H</u>—CH_2), 130.6 (Pht—C-1/2), 128.1–127.2 (Bzl—C_{arom}), 123.5 (Pht—C/3/6), 115.7 (H_2C=CH—CH_2), 102.4 (C-1B), 93.1 (H_3C—CH_2—O—C<u>H</u>$_2$), 85.0 (C-1A), 78.5, 77.8, 76.9, 76.5, 76.4, 73.4, 66.1 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 74.3, 72.5, 72.3, 72.1 (H_2C=CH—C<u>H</u>$_2$, Ph—CH_2), 69.2, 67.5 (C-6A, C-6B), 62.3 (H_3C—C<u>H</u>$_2$—O—CH_2), 54.6 (C-2A), 14.8 (H_3C—CH_2—O—CH_2).

(2,4,6-Tri-*O*-benzyl-3-*O*-ethoxymethyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (27). To a suspension of sodium hydride (32 mg, 1.07 mmol) in dry dimethylformamide (10 mL) was added benzyl bromide (0.13 mL, 1.1 mmol) and, subsequently, a solution of **26** (234 mg, 0.27 mmol) in dimethylformamide (3 mL). After 2 h at room temperature, methanol (0.2 mL) was added and the solvent removed in high vacuum. The remainder was purified by flash chromatography on 20 g of silica gel in petroleum ether:ethyl acetate 6:1; yield: 173 mg (67%); colourless oil; $[\alpha]_D^{22}$ −15.4° (*c* 1, $CHCl_3$); R_f = 0.65; Anal. calcd for $C_{54}H_{58}N_4O_{12}$ (955.1): C, 67.91; H, 6.12; N, 5.87. Found: C, 68.05; H, 5.98; N, 5.89%. IR (NaCl) ν (cm^{-1}): 2113 (N_3), 1752, 1730 (phthalimide).

400 NMR ^{1}H NMR ($CDCl_3$): δ (ppm) 7.85 (s_{breit}, 2H, Pht—H), 7.75–7.71 (m, 2H, Pht-H), 7.38–7.19 (m, 20H, Ph—H), 5.51–5.41 (m, 1H, H_2C=C<u>H</u>—CH_2), 5.34 (d, $J_{1,2}$ = 9.3 Hz, 1H, 1A-H), 4.90 (ddd, $J_{vic(trans)}$ = 17.3 Hz, 1H, *H*$_2$C=CH—CH_2), 4.89 (d, J_{gem}) = 11.7 Hz, 1H, Ph—CH_2), 4.85–4.62 (m, 5H, 2 × Ph—CH_2, <u>H</u>$_2$C=CH—CH_2, 2 × H_3C—CH_2—O—C<u>H</u>$_2$), 4.57 (d, J_{gem} = 10.6 Hz, 1H, Ph—CH_2), 4.54 (d, J_{gem} = 13.0 Hz, 1H, Ph—CH_2), 4.48 (d, J_{gem} = 11.8 Hz, 1H, Ph—CH_2), 4.42–4.35 (m, 4H, 1B-H, 2 × Ph—CH_2, H_2C=CH—C<u>H</u>$_2$), 4.20 (dd, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 8.5 Hz, 1H, 3A-H), 4.10 (dd, 1H, 2A-H), 3.99 (dd, $J_{4,5}$ = 9.8 Hz, 1H, 4A-H), 3.87 (ddd, J_{gem} = 12.9 Hz, J_{vic} = 6.2 Hz, 1H, H_2C=CH—C<u>H</u>$_2$), 3.83–3.80 (m, 2H, 4B-H, 6Aa-H), 3.77–3.53 (m, 9H, 2B-H, 3B-H, 5A-H, 5B-H, 6Ab-H, 6Ba-H, 6Bb-H, H_3C—C<u>H</u>$_2$—O—CH_2), 1.18 (t, J_{vic} = 7.1 Hz, 3H, <u>H</u>$_3$C—CH_2—O—CH_2).

100 MHz ^{13}C NMR ($CDCl_3$); δ (ppm) 139.0, 138.6, 138.1, 138.0 (Bzl—C_{ipso}), 135.1, 134.1 (Pht—C-4/5, H_2C=C<u>H</u>—CH_2), 131.6 (Pht—C-1/2), 128.3–127.2 (Bzl—C_{arom}), 116.1, (H_2C=CH—CH_2), 102.8 (C-1B), 94.9 (H_3C—CH_2—O—C<u>H</u>$_2$), 85.8 (C-1A), 79.8, 78.8,

77.6, 77.1, 76.9, 75.0, 73.1 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 75.2, 74.3, 73.6, 73.5, 73.2 (H_2C=CH—$\underline{C}H_2$, Ph—CH_2), 68.4, 67.6 (C-6A, C-6B), 63.5 (H_3C—$\underline{C}H_2$—O—CH_2), 55.3 (C-2A), 15.1 ($H_3\underline{C}$—CH_2—O—CH_2).

2,4,6-Tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (28). To a solution of **27** (704 mg, 0.74 mmol) in dry dichloromethane (50 mL) was added thiophenol (0.15 mL, 1.46 mmol) and under dry argon atmosphere at 0 °C a solution of borontrifluoride etherate (0.46 mL, 3.7 mmol) in 10 mL of dichloromethane. After 3 h at 0 °C, the solution was washed with satd $NaHCO_3$ solution, dried with $MgSO_4$, and the solvent was evaporated in vacuo. The product was purified by flash chromatography in petroleum ether: ethyl acetate 3:1 on 16 g of silica gel; yield: 564 mg (85%), colorless oil; $[\alpha]_D^{22}$ −5.9° (*c* 1, $CHCl_3$); R_f = 0.42 (petroleum ether:ethyl acetate 2:1). Anal. calcd for $C_{51}H_{52}N_4O_{11}$ (897.0): C, 68.29; H, 5.84; N, 6.25. Found: C, 68.28; H, 5.75; N, 6.22%. IR (NaCl) ν (cm^{-1}): 2116 (N_3), 1777, 1716 (phthalimide).

400 MHz ^{1}H NMR ($CDCl_3$): δ (ppm) 7.84 (s_{breit}, 2H, Pht—H), 7.74–7.71 (m, 2H, Pht—H), 7.36–7.21 (m, 20H, pH—H), 5.51–5.42 (m, 1H, H_2C=C$\underline{H}$—CH_2), 5.34 (d, $J_{1,2}$ = 9.3 Hz, 1H, 1A-H), 4.91 (ddd, $J_{vic(trans)}$ = 17.2 Hz, 1H, $\underline{H}_2C$=CH—CH_2), 4.78 (d, J_{gem} = 11.4 Hz, 1H, Ph—CH_2), 4.71 (d, J_{gem} = 11.8 Hz, 1H, Ph—CH_2), 4.70 (ddd, $J_{vic(cis)}$ = 10.2 Hz, 1H, H_2C=CH—C$\underline{H}_2$), 4.66 (d, J_{gem} = 11.5 Hz, 1H, Ph—CH_2), 4.58 (d, J_{gem} = 11.8 Hz, 1H, Ph—CH_2), 4.57 (d, J_{gem} = 12.2 Hz, 1H, Ph—CH_2), 4.48 (d, J_{gem} = 11.8 Hz, 1H, Ph—CH_2), 4.43 (d, J_{gem} = 12.0 Hz, 1H, Ph—CH_2), 4.40 (d, J_{gem} = 11.8 Hz, 1H, Ph—CH_2), 4.37–4.33 (m, $J_{1,2}$ = 7.5 Hz, 2H, 1B-H, H_2C=CH—C$\underline{H}_2$), 4.21 (dd, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 8.6 Hz, 1H, 3A-H), 4.10 (dd, 1H, 2A-H), 3.99 (dd, $J_{4,5}$ = 9.6 Hz, 1H, 4A-H), 3.88–3.81 (m, 3H, 4B-H, 6Aa-H, H_2C=CH—C$\underline{H}_2$), 3.71 (d, $J_{6a,6b}$ = 10.3 Hz, 1H, 6Ab-H), 3.65–3.54 (m, 3H, 5A-H, 6Ba-H, 6Bb-H), 3.51 (m, 2H, 3B-H, 5B-H), 3.41 (dd, $J_{2,3}$ = 9.5 Hz, 1H, 2B-H), 2.17 (d, $J_{OH,3}$ = 6.1 Hz, 1H, 3B-OH).

100 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 138.7, 138.3, 138.0, 137.90 (Bzl—C_{ipso}), 135.0, 134.2 (Pht—C-4/5, H_2C=C$\underline{H}$—CH_2), 131.6 (Pht—C-1/2), 128.4–127.5 (Bzl—C_{arom}), 116.2 ($H_2\underline{C}$=CH—CH_2), 102.8 (C-1B), 85.8 (C-1A), 80.6, 77.6, 77.1, 77.0, 75.9, 74.0, 73.3 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C5-B), 75.1, 74.8, 73.6, 73.5, 73.3 (H_2C=CH—$\underline{C}H_2$, Ph—CH_2), 68.3, 67.7 (C-6A, C-6B), 55.3 (C-2A).

(3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (12). *N*,*N*-Dimethylaminopyridine (149 mg, 1.22 mmol) and 0.08 mL (0.81 mmol) acetic anhydride were added to a solution of **28** (365 mg, 0.41 mmol) in dichloromethane (30 mL), and the mixture was stirred for 2 h at room temperature. After addition of methanol (0.1 mL), stirring was continued for one additional hour. The solution was washed with 50 mL of 1 M H_2SO_4 and satd $NaHCO_3$ solution, dried with $MgSO_4$ and the solvent was evaporated in vacuo; yield: 348 mg (91%), amorphous; $[\alpha]_D^{22}$ +7.0° (*c* 1, $CHCl_3$); R_f = 0.56 (petroleum ether:ethyl acetate 2:1). Anal. cald for $C_{53}H_{54}N_4O_{12}$ (939.0): C, 67.79; H, 5.80; N, 5.97. Found: C, 67.49; H, 5.80; N, 6.01%. IR (NaCl) ν (cm^{-1}): 2116 (N_3), 1777, 1716 (phthalimide), 1743 (Ac—C=O).

400 MHz ^{1}H NMR ($CDCl_3$): δ (ppm) 7.86 (s_{breit}, 2H, Pht—H), 7.76–7.72 (m, 2H, Pht—H), 7.40–7.12 (m, 20H, Ph—H), 5.52–5.37 (m, 1H, H_2C=C$\underline{H}$—CH_2), 5.34 (d, $J_{1,2}$ = 9.3 Hz, 1H, 1A-H), 4.91 (dddd, $J_{vic(trans)}$ = 17.2 Hz, 1H, $\underline{H}_2C$=CH—CH_2), 4.79 (dd, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 3.2 Hz, 1H, 3B-H), 4.72 (d, J_{gem} = 11.6 Hz, 1H, Ph—CH_2), 4.69 (ddd, $J_{vic(cis)}$ = 10.4 Hz, 1H, H_2C=CH—C$\underline{H}_2$), 4.61 (d, J_{gem} = 13.0 Hz, 1H, Ph—CH_2), 4.58 (d, J_{gem} = 12.0 Hz, 1H, Ph—CH_2), 4.56 (d, J_{gem} = 12.1 Hz, 1H, Ph—CH_2), 4.47 (d, J_{gem} = 13.0 Hz, 1H, Ph—CH_2), 4.45–4.32 (m, 5H, 1B-H, H_2C=CH—C$\underline{H}_2$, 4 × Ph—CH_2), 4.21 (dd, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 8.6 Hz, 1H, 3A-H), 4.10 (dd, 1H, 2A-H), 4.00 (dd, $J_{4,5}$ = 9.9 Hz, 1H, 4A-H), 3.91 (d, 1H, 4B-H), 3.85 (dd, J_{gem} = 12.9 Hz, J_{vic} = 6.3 Hz, 1H, H_2C=CH—C$\underline{H}_2$), 3.82 (dd, $J_{5,6a}$ = 3.7 Hz, $J_{6a,6b}$ = 11.5 Hz, 1H, 6Aa-H), 3.69 (dd, $J_{5,6b}$ = 1.4 Hz, 1H, 6Ab-H), 3.66 (dd, $J_{1,2}$ = 7.7 Hz, 1H, 2B-H), 3.60–3.49 (m, 4H, 5A-H, 5B-H, 6Ba-H, 6Bb-H), 1.90 (s, 3H, Ac—CH_3).

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 170.2 (Ac—C=O), 138.5, 138.4, 138.0, 137.90 (Bzl—C_{ipso}), 135.0, 134.2 (Pht—C-4/5, H_2C=C$\underline{H}$—CH_2), 131.7 (Pht—C-1/2), 128.4–127.4 (Bzl—C_{arom}), 116.2 ($H_2\underline{C}$=CH—CH_2), 102.8 (C-1B), 85.8 (C-1A), 77.8, 77.6, 77.2, 77.1, 75.3, 74.4, 72.8 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 75.1, 74.7, 73.6, 73.5, 73.2 (H_2C=CH—$\underline{C}H_2$, Ph—CH_2), 67.9, 67.5 (C-6A, C-6B), 55.3 (C-2A), 20.9 (Ac-CH_3).

1′-[*O*-(3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)]-4′,5′-di-*tert*-butyloxycarbonyl-1′,2′,3′-triazole (29). A solution of the azide **12** (447 mg, 0.48 mmol) and 216 mg (0.96 mmol) of di-*tert*-butyl acetylenedicarboxylate in dry toluene (25 mL) was stirred at 90 °C for 3 days. The solvent was evaporated in vacuo and the remaining oil was purified by flash chromatography in petroleum ether:ethyl acetate 4:1 on 16 g of silica gel; yield: 401 mg (72%), amorphous; $[\alpha]_D^{22}$ +12.4° (*c* 1, $CHCl_3$); R_f = 0.40 (petroleum ether:ethyl acetate 2:1); Anal. calcd for $C_{65}H_{72}N_4O_{16}$ (1165.3): C, 67.00; H, 6.23; N, 4.81. Found: C, 67.41; H, 5.97; N, 4.61%.

400 MHz ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.78–7.75, 7.69–7.65 (2m, 2H, Pht-H), 7.35–7.11 (m, 20H, Ph-H), 6.85 (d, $J_{1,2}$ = 10.0 Hz, 1H, 1A-H), 5.47–5.37 (m, 1H, H_2C=C$\underline{H}$—CH_2), 5.26 (dd, $J_{2,3}$ = 10.3 Hz, 1H, 2A-H), 4.92 (ddd, $J_{vic(trans)}$ = 17.2 Hz, 1H, $\underline{H}_2C$=CH—CH_2), 4.79 (dd, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 3.2 Hz, 1H, 3B-H), 4.72 (d, J_{gem} = 11.6 Hz, 1H, Ph—CH_2), 4.69 (ddd, $J_{vic(cis)}$ = 10.3 Hz, 1H, H_2C=CH—CH_2), 4.62 (d, J_{gem} = 11.6 Hz, 1H, Ph—CH_2), 4.57 (d, J_{gem} = 11.8 Hz,

1H, Ph—CH_2), 4.49–4.43 (m, 4H, 1B-H, 3 × Ph—CH_2), 4.40 (d, J_{gem} = 11.8 Hz, 1H, Ph—CH_2), 4.35 (dd, J_{gem} = 12.9 Hz, J_{vic} = 5.2 Hz, 1H, H_2C=CH—CH_2), 4.30 (d, J_{gem} = 12.0 Hz, 1H, Ph—CH_2), 4.26 (dd, $J_{3,4}$ = 8.9 Hz, 1H, 3A-H), 4.13 (dd, $J_{4,5}$ = 9.7 Hz, 1H, 4A-H), 3.91 (d, 1H, 4B-H), 3.88 (dd, J_{vic} = 6.5 Hz, 1H, H_2C=CH—CH_2), 3.78 (dd, $J_{5,6a}$ = 3.7 Hz, $J_{6a,6b}$ = 11.0 Hz, 1H, 6Aa-H), 3.69 (ddd, 1H, 5A-H), 3.67 (dd, $J_{1,2}$ = 7.7 Hz, 1H, 1B-H), 3.61 (d, 1H, 6Ab-H), 3.57–3.48 (m, 3H, 5B-H, 6Ba-H, 6Bb-H), 1.89 (s, 3H, Ac—CH_3), 1.54, 1.53 [s, 9H, triazole-C(CH_3)$_3$].

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 170.3 (Ac—C=O), 159.0, 156.8 (triazole-C=O), 141.1 (triazole-C=C), 138.5, 138.4, 137.9, 137.8 (Bzl—C_{ipso}), 134.8, 134.2 (Pht—C-4/5, H_2C=CH—CH_2), 131.7, 131.6 (Pht—C-1/2, triazole-C=C), 128.4–127.4 (Bzl—C_{arom}), 116.5 (H_2C=CH—CH_2), 102.7 (C-1B), 85.1 [triazole-C(CH_3)$_3$], 82.8 [C-1A, triazole-C(CH_3)$_3$], 78.5, 77.8, 76.8, 75.3, 74.5, 72.8, 75.5, 72.8 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 75.1, 74.7, 73.7, 73.4, 73.2 (H_2C=CH—CH_2, Ph—CH_2), 67.8, 67.5 (C-6A, C-6B), 53.4 (C-2A), 28.1, 27.9 [triazole-C(CH_3)$_3$], 20.8 (Ac—CH_3).

(3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-desoxy-2-phthalimido-D-glucopyranosyl fluoride (30). A solution of the glycosyl triazole **29** (237 mg, 0.20 mmol) in dry dichloromethane (25 mL) under dry argon atmosphere was stirred for 30 min at 0 °C. Hydrogen fluoride–pyridine complex (2 mL) was added and the mixture stirred for 16 h at 0 °C. The mixture was poured into dichloromethane (100 mL), satd $NaHCO_3$ solution (100 mL) and ice (50 g). After careful shaking the organic layer was separated, washed with 100 mL of 1 M H_2SO_4 and twice with 100 mL of $NaHCO_3$ solution. After drying with $MgSO_4$, the solvent was evaporated in vacuo and the product purified by flash chromatography (petroleum ether:ethyl acetate 4:1) on 16 g of silica gel to give **30** as a mixture of anomers (α:β = 10:1, according to ^{1}H NMR). Yield: 120 mg (64%), amorphous; $[\alpha]_D^{22}$ +12.4° (*c* 1, $CHCl_3$); R_f = 0.58 (petroleum ether:ethyl acetate 2:1); Anal. calcd for $C_{53}H_{54}NO_{12}F$ (916.0): C, 69.50; H, 5.94; N, 1.53. Found: C, 69.21; H, 6.07; N, 1.69%.

NMR data of α-anomer: 400 MHz ^{1}H NMR ($CDCl_3$): δ (ppm) 7.87–7.84, 7.75–7.71 (2m, 2H, Pht—H) 7.36–7.21 (m, 20H, Ph—H), 5.66–5.58 (m, 1H, H_2C=CH—CH_2), 5.61 (dd, $J_{F,2}$ = 53.9 Hz, $J_{1,2}$ = 2.4 Hz, 1H, 1A-H), 4.96 (dd, $J_{2,3}$ = 11.3 Hz, $J_{3,4}$ = 8.8 Hz, 1H, 3A-H), 4.93 (ddd, $J_{vic(trans)}$ = 17.3 Hz, 1H, H_2C=CH—CH_2), 4.78 ($J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 3.2 Hz, 1H, 3B-H), 4.75 (dd, $J_{vic(cis)}$ = 10.6 Hz, 1H, H_2C=CH—CH_2), 4.73, 7.63 (d, J_{gem} = 11.6 Hz, 1H, Ph—CH_2), 4.60, 4.57 (d, J_{gem} = 11.9 Hz, 1H, Ph—CH_2), 4.47 (d, J_{gem} = 11.0 Hz, 1H, Ph—CH_2), 4.45 (d, J_{gem} = 11.8 Hz, 1H, Ph—CH_2), 4.42 (d, $J_{1,2}$ = 7.7 Hz, 1H, 1B-H), 4.40 (d, J_{gem} = 11.0 Hz, 1H, Ph—CH_2), 4.38 (d, J_{gem} = 11.8 Hz, 1H, Ph—CH_2), 4.34 (dd, J_{gem} = 11.6 Hz, J_{vic} = 3.0 Hz, 1H, H_2C=CH—CH_2), 4.08 (dd, $J_{4,5}$ = 10.0 Hz, 1H, 4A-H, 4.01–3.96 (m, 2H, 2A-H, H_2C=CH—CH_2), 3.92 (d, 1H, 4B-H), 3.87 dd, $J_{5,6a}$ = 2.7 Hz, $J_{6a,6b}$ = 11.0 Hz, 3.69 (dd, 1H, 2B-H), 3.62–3.53 (m, 4H, 5A-H, 6Ab-H, 6Ba-H, 6Bb-H), 3.49 (dd, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 7.7 Hz, 1H, 5B-H), 1.92 (s, 3H, Ac—CH_3).

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 170.3 (Ac—C=O), 138.5, 138.4, 138.0, 137.7 (Bzl—C_{ipso}), 135.5, 134.2 (Pht—C-4/5, H_2C=CH—CH_2), 131.7 (Pht—C-1/2), 128.5–127.4 (Bzl—C_{arom}), 123.4 (Pht—C-3/6), 115.6 (H_2C=CH—CH_2), 106.6 ($J_{F,C}$ = 228 Hz, C-1A), 102.6 (C-1B), 77.7, 76.8, 75.3, 74.5, 73.4, 72.8 (C-2B, C-3A, C-3B, C-4A, C-4B, C-5A, C-5B), 75.1, 74.7, 73.8, 73.3 (H_2C=CH—CH_2, Ph—CH_2), 67.9, 67.4 (C-6A, C-6B), 55.1 ($J_{F,C}$ = 26.8 Hz, C-2A), 20.9 (Ac—CH_3).

Benzyl-(3-*O*-acetyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (31). A mixture of **7** (362 mg, 0.18 mmol), **30** (409 mg, 0.45 mmol) and molecular sieves 4 Å (0.5 g) was stirred in dry dichloromethane (25 mL) under dry argon atmosphere for 1 h at 0 °C, then a solution of 0.22 mL (1.79 mmol) of borontrifluoride etherate in dichloromethane (5 mL) was added dropwise within 5 min. After 1 h at 0 °C and 2 h at room temperature, the mixture was filtered through Celite. The Celite was washed with several portions of dichloromethane and the combined organic layer were washed with satd $NaHCO_3$ solution and dried with $MgSO_4$. After evaporation of the solvent in vacuo, the product was purified by flash chromatography (petroleum ether:ethyl acetate 2:1) on 20 g of silica gel; yield: 570 mg (82%), amorphous; $[\alpha]_D^{22}$ −5.7° (*c* 0.2, $CHCl_3$); R_f = 0.63 (petroleum ether:ethyl acetate 2:1); Anal. calcd for $C_{114}H_{117}NO_{23}$ (1869.2): C, 73.25; H, 6.13; N, 0.75. Found: C, 72.80; H, 6.35, N, 1.14%. See Table 3.

Table 3. Assignment of the 400 MHz ^{1}H NMR signals of **31** ($CDCl_3$, δ in ppm, *J* in Hz)

Type	Position	1-H ($J_{1,2}$)	2-H ($J_{2,3}$)	3-H ($J_{3,4}$)	4-H	5-H	6a-H	6b-H
Glc	A	4.31	3.36	3.35	3.84	2.95	3.51	3.34
Gal	B	4.25	3.46	3.55	4.00	n.d.	n.d.	n.d.
GlcNPht	C	5.38 (7.7)	4.25	4.30	4.00	3.60	3.82	3.71
Gal	D	4.48 (7.7)	3.68 (10.1)	4.82 (3.2)	3.92	n.d.	n.d.	n.d.

n.d. not determined.

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 170.2 (Ac—C=O), 139.39, 139.04, 138.61, 138.59, 138.49, 138.38, 138.34, 138.32, 138.04, 137.88, 137.55, (Bzl—C_{ipso}), 135.2, 133.6 (Pht—C-4/5, H_2C=CH—CH_2), 131.3 (Pht—C-1/2), 128.3–126.3 (Bzl—C_{arom}), 123.0 (Pht—C-3/6), 115.8 (H_2C=CH—CH_2), 102.8 (C-1D), 102.4 (C-1A, C-1B), 99.8 (C-1C), 82.9, 81.6 (C-2A, C-3A), 82.1 (C-3B), 78.8 (C-2B), 77.8, 76.6 (C-4B, C-4C), 77.7 (C-2D), 77.0 (C-3C), 76.0 (C-4A),

75.3 (C-3D), 75.29, 75.01, 74.98, 74.90, 74.63, 73.97, 73.40, 73.22, 72.93, 70.73 (Ph—CH_2, H_2C=CH—CH_2), 75.2 (C-5C), 74.8 (C-5A), 74.5 (C-4D), 73.1, 72.7 (C-5B, C-5D), 68.4, 68.2, 67.8, 67.7 (C-6A, C-6B, C-6C, C-6D), 56.4 (C-2C), 20.8 (Ac—CH_3).

Benzyl-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (32). To a solution of **31** (442 mg, 237 μmol) in dry tetrahydrofuran (7.5 mL) was added methanol (22 mL) and 4.7 mL of 0.1 M sodium methanolate in methanol. After stirring for 24 h at room temperature, ion exchange resin IR-120 (H^+ form) was added and the mixture stirred for 1 h. The resin was filtered off and washed with tetrahydrofuran. The solvent was evaporated in vacuo and **32** was purified by flash chromatography (petroleum ether:ethyl acetate 3:1) on 20 g of silica gel; yield: 389 mg (90%), amorphous; $[\alpha]_D^{22}$ −14.4° (*c* 1, $CHCl_3$); R_f = 0.49 (petroleum ether:ethyl acetate 2:1); Anal. calcd for $C_{112}H_{115}NO_{22}$ (1822.1): C, 73.63; H, 6.34; N, 0.77. Found: C, 74.03; H, 6.34; N, 0.96%.

400 MHz ^{1}H NMR ($CDCl_3$) selected signals: δ (ppm) 5.40 (d, $J_{1,2}$ = 7.8 Hz, 1H, 1C—H), 2.18 (d, $J_{OH,3}$ = 6.1 Hz, 1H, 3D—OH); INDOR-experiment to determine 3D—OH: 3.53 (ddd, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.3 Hz, 3D—H).

100.6 MHz ^{13}C NMR $CDCl_3$): δ (ppm) 139.43, 139.07, 138.71, 138.64, 138.61, 138.38, 138.13, 137.94, 137.59 (Bzl—C_{ipso}), 135.2, 133.6 (Pht—C-4/5, H_2C=CH—CH_2), 131.3, (Pht—C-1/2), 128.5–126.4 (Bzl—C_{arom}), 123.1 (Pht—C-3/6), 115.9 (H_2C=CH—CH_2), 102.9, 102.4, 99.8 (C-1A, C-1B, C-1C, C-1D), 83.0, 82.1, 81.7, 80.6, 78.8, 77.8, 76.0, 75.9, 74.8, 74.0, 73.3, 73.2 (C-2A, C-2B, C-2D, C-3A, C-3B, C-3C, C-3D, C-4A, C-4B, C-4C, C-4D, C-5A, C-5B, C-5C, C-5D), 75.36, 75.09, 75.03, 74.97, 74.01, 73.51, 73.46, 73.28, 72.97, 70.80 (Ph—CH_2, H_2C=CH—CH_2), 68.4, 68.2, 67.8 (C-6A, C-6B, C-6C, C-6D), 56.4 (C-2C).

Benzyl-(3-*O*-acetyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (33). In analogy to the synthesis of the tetrasaccharide **31** the tetrasaccharide acceptor **32** (353 mg, 198 μmol) and the glycosyl fluoride **30** (213 mg, 233 μmol) were reacted with borontrifluoride etherate (0.17 mL, 1.32 mmol). Work up was carried out as described for **31**. Yield: 395 mg (75%), amorphous; $[\alpha]_D^{22}$ −9.6° (*c* 1, $CHCl_3$); R_f = 0.53 (petroleum ether:ethyl acetate 2:1); Anal. calcd for $C_{165}H_{168}N_2O_{34}$ (2723.1): C, 72.78; H, 6.22; N, 1.03. Found: C, 72.75; H, 6.23; N, 1.08%. See Table 4.

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 170.3 (Ac—C=O), 139.53, 139.16, 138.73, 138.68, 138.61, 138.56, 138.49, 138.42, 138.35, 138.14, 138.00, 137.67 (Bzl—C_{ipso}), 135.33, 135.29, 133.70, 133.61 (Pht—C-4/5, H_2C=CH—CH_2), 131.4 (Pht—C-1/2), 128.4–126.4 (Bzl—C_{arom}), 123.1 (Pht—C-3/6), 116.0, 115.7 (H_2C=CH—CH_2), 103.0, 102.7, 102.5, 102.4, 100.0, 99.9 (C-1A, C-1B, C-1C, C-1D, C-1E, C-1F), 83.0, 82.2, 82.1, 81.7, 78.7, 78.0, 77.7, 77.3, 77.1, 77.0, 76.7, 76.6, 76.1, 75.3, 75.0, 74.8, 74.5, 73.2, 73.1, 72.8 (C-2A, C-2B, C-2D, C-2F, C-3A, C-3B, C-3C, C-3D, C-3E, C3-F, C-4A, C4-B, C-4C, C-4D, C-4E, C-4F, C-5A, C-5B, C-5C, C-5D, C-5E, C-5F), 68.9, 68.5, 68.4, 68.0, 67.8 (C-6A, C-6B, C-6C, C-6D, C-6E, C-6F), 56.5 (C-2C, C-2E), 20.9 (Ac—CH_3).

Table 4. Assignment of the 400 MHz ^{1}H NMR signals of **33** ($CDCl_3$, δ in ppm, *J* in Hz)

Type	Position	1-H ($J_{1,2}$)	2-H	3-H	4-H	5-H	6a-H	6b-H
Glc	A	4.32	3.54	3.52	3.80	2.92	3.47	3.28
Gal	B	4.28	3.43	3.58	3.98	n.d.	n.d.	n.d.
GlcNPht	C	5.00 (7.9)	4.25	4.32	4.00	3.62	3.82	3.73
Gal	D	4.18	3.40	3.41	3.89	n.d.	n.d.	n.d.
GlcNPht	E	5.22 (8.0)	4.17	4.41	3.85	3.25	3.55	3.33
Gal	F	4.48	3.69	4.83	3.93	n.d.	n.d.	n.d.

n.d. not determined.

(Notice: sequences B/D and C/E are not proven).

Benzyl-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (34). To a solution of **33** (355 mg, 130 μmol) in dry tetrahydrofuran (4.2 mL) and methanol (12 mL) was added 0.1 M sodium methanolate in methanol (2.6 mL). After stirring for 9 h at room temperature, ion exchange resin IR-120 (H^+ form) was added and stirring was continued for 1 h. After filtration and washing the resin with tetrahydrofuran, the solvent was evaporated in vacuo. Purification was achieved by flash chromatography in petroleum ether:ethyl acetate 3:1 on silica gel (16 g). Yield: 298 mg (85%), amorphous; $[\alpha]_D^{22}$ −9.6° (*c* 1, $CHCl_3$); R_f = 0.35 (petroleum ether:ethyl acetate 2:1). Anal. calcd for: $C_{163}H_{168}N_2O_{33}$ (2723.1): C, 73.02; H, 6.24; N, 1.04. Found: C, 72.34; H, 6.54; N, 1.48%. FABMS *m/z* = 2682.

400 MHz ^{1}H NMR ($CDCl_3$): (ppm) 5.41 (d, $J_{1,2}$ = 7.8 Hz, 1H, 1C/E-H, 5.22 (d, $J_{1,2}$ = 7.9 Hz, 1H, 1C/E-H), 2.18 (d_{broad}, $J_{OH,3} \approx 5.0$ Hz, 1H, 3D-OH).

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 139.48, 139.11, 138.74, 138.68, 138.63, 138.49, 138.38, 138.30, 138.14, 137.98, 137.62 (Bzl—C_{ipso}), 135.28, 135.25, 133.62, 133.51 (Pht—C-4/5, H_2C=CH—CH_2), 131.4 (Pht—C-1/2), 128.5–126.3 (Bzl—C_{arom}), 123.1 (Pht—C-3/6), 115.9, 115.6 (H_2C=CH—CH_2), 102.91, 102.64, 102.62,

102.35, 99.93, 99.80 (C-1A, C-1B, C-1C, C-1D, C-1E, C-1F), 82.0–70.8 (C-2A, C-2B, C-2D, C-2F, C-3A, C-3B, C-3C, C-3D, C-3E, C-3F, C-4A, C-4B, C-4C, C-4D, C-4E, C-4F, C-5A, C-5B, C-5C, C-5D, C-5E, C-5F, Ph—CH_2, H_2C=CH—CH_2), 68.8, 68.5, 68.3, 68.0, 67.8 (C-6A, C-6B, C-6C, C-6D, C-6E, C-6F), 56.4 (C-2C, C-2E).

(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (36). To a solution of hexasaccharide **34** (476 mg, 178 μmol) and (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-desoxy-2-phthalimido-D-glucopyranosyl fluoride,[21] **35** (275 mg, 356 μmol), in dichloromethane (50 mL) was added borontrifluoride etherate (0.4 mL, 3.18 mmol dissolved in 10 mL of dichloromethane). The reaction was conducted as described for **31**. Flash chromatography was carried out with petroleum ether:ethyl acetate 2:1 on 20 g of silica gel; yield: 504 mg (83%), amorphous; $[\alpha]_D^{22}$ −17.3° (*c* 1, $CHCl_3$); R_f = 0.52 (HPTLC: petroleum ether:ethyl acetate 1:1). Anal. calcd for: $C_{140}H_{144}N_6O_{37}$ (2502.7): C, 67.19; H, 5.80; N, 3.36. Found: C, 67.15, H, 5.79; N, 3.36%. IR (KBr) ν (cm^{-1}): 2116 (N_3), 1776 1715 (phthalimide), 1754 (Ac—C=O).

100 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 102.6 (C-1D), 102.3 (C-1B), 100.3 (C-1F), 99.7 (C-1C, C-1E), 85.6 (C-1A), 82.0, 81.9 (C-3B, C-3D), 78.6, 78.4 (C-2B, C-2D), 77.7, 77.2 (C-4B, C-4D), 77.0 (C-5A), 76.9 (C-3A, C-3C), 76.7 (C-3E), 76.4 (C-4A, C-4C, C-4E), 74.6 (C-5C), 74.6, 74.0, 73.7, 73.5, 73.4, 72.9 (Ph—CH_2, H_2C=CH—CH_2), 74.4 (C-4E), 73.1, 72.9 (C-5B, C-5D), 70.9 (C-3F), 70.3 (C-5F), 69.4 (C-2F), 68.8, 68.5, 67.9, 67.0, 60.8 (C-6A, C-6B, C-6C, C-6D, C-6E, C-6F), 66.8 (C-4F), 56.2 (C-2C, C-2E), 55.0 (C-2A).

Benzyl-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (37). [Bis(diphenylmethylphosphin)-1,5-cyclooctadien]iridium(I)-hexafluorophosphate (9 mg, 10.6 mmol) was added to tetrahydrofuran (8 mL) under oxygen-free argon atmosphere. Argon was then exchanged for hydrogen atmosphere and the mixture was stirred for 5 min. After this time, hydrogen was exchanged for argon atmosphere and the octasaccharide **36** (151 mg, 44 μmol) was added to the stirred solution. After 3 days at room temperature, tetrahydrofuran (10 mL), acetone (10 mL), water (1 mL) and a mixture of HgO (56 mg, 0.26 μmol) and $HgCl_2$ (109 mg, 0.4 μmol) were added. The mixture was vigorously stirred for 12 h, filtered through Celite, which was washed several times with small portions of tetrahydrofuran. After evaporation of the solvents from the combined filtrates, the residue was dissolved in dichloromethane (50 mL) and stirred with 10% potassium iodide solution (20 mL) for 30 min, the organic layer was separated, dried with $MgSO_4$ and the solvent was evaporated in vacuo. The remaining **37** was purified by flash chromatography in petroleum ether: ethyl acetate 3:2 on 16 g of silica gel. Yield: 91.2 mg (62%); amorphous after lyophilization from benzene; $[\alpha]_D^{22}$ −11.9° (*c* 1, $CHCl_3$); R_f = 0.61 (HPTLC: petroleum ether:ethyl acetate 1:1). Anal. calcd for: $C_{192}H_{195}N_3O_{48} \cdot 2H_2O$ (3432.8): C, 70.33; H, 6.08; N, 1.22. Found: C, 70.13; H, 6.13; N, 1.44%.

400 MHz ^1H NMR ($CDCl_3$): δ (ppm) 7.68–6.83 (m, 92 H, Ph—H, Pht—H), 5.48 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1C/E/G-H), 5.34 (d, $J_{1,2}$ = 8.1 Hz, 1H, 1C/E/G-H), 5.30–5.28 (m, 2H, 1C/E/G-H, 4H-H), 5.18 (dd, $J_{1H,2H}$ = 8.0 Hz, $J_{2H,3H}$ = 10.5 Hz, 1H, 2H-H), 4.98–4.78 (m, 7H, 3H-H, 6 × Ph—CH_2), 3.09 (m_c, 1H, 5C/E/G-H), 2.90 (m_c, 1H, 5A-H), 2.11, 1.98, 1.96, 1.84 (s, 3H, Ac).

100.6 (MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 133.8, 133.5 (Pht—C-4/5), 128.6–126.0 (Bzl–C_{arom}), 123.3 (Pht—C-3/6), 103.5, 103.4, 102.4, 102.3, 101.6, 99.9, 99.8, 99.4 (C-1A, C-1B, C-1C, C-1D, C-1E, C-1F, C-1G, C-1H), 82.9, 82.4, 82.2, 82.1, 82.0, 81.8, 81.7, 81.6, 78.8, 77.9, 77.8, 77.2, 76.6, 76.2, 76.1, 76.0, 74.7, 73.9, 73.8, 71.2, 70.7, 69.1, 68.7, 66.8 (C-2A, C-2B, C-2D, C-2F, C-2H, C-3A, C-3B, C-3C, C-3D, C-3E, C-3F, C-3G, C-3H, C-4A, C-4B, C-4C, C-4D, C-4E, C-4F, C-4G, C-4H, C-5A, C-5B, C-5C, C-5D, C-5E, C-5F, C-5G, C-5H), 68.9, 68.6, 68.5, 68.3, 67.6, 61.4, (C-6C, C-6D, C-6E, C-6F, C-6G, C-6H), 56.6, 56.5, 56.4 (C-2C, C-2E, C-2G), 20.7, 20.6, 20.5, 20.3 (Ac).

Benzyl-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-[*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-(6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-*O*-[*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-(6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-[*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-(6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (38). A solution of the fucosyl bromide in dimethylformamide (3 mL) was prepared from ethylthio fucoside **10** (364 mg, 0.76 mmol) as described for the preparation of **11** (vide supra). This solution was added dropwise to a solution of the octasaccharide **37** (84 mg, 25.1 μmol) and dry triethylammonium bromide (160 mg, 0.76 mmol) in dimethylformamide (10 mL), which had been previously stirred 1 h at room temperature. After 10 days, dry ethanol (1 mL) was added and the solution filtered through Celite. The Celite was washed with dichloromethane (100 mL). The combined organic solution was washed with satd

Table 5. Assignment of 600 MHz ^{1}H NMR signals of **38** (δ in ppm, *J* in Hz). The assignments were ascertained with the aid of ^{1}H, ^{1}H COSY, TOCSY and NOESY experiments

Type	Position	1-H	2-H	3-H	4-H	5-H	6a-H	6b-H
A	Glc	4.28	3.36	3.32	3.82	2.87	3.44	3.24
B	Gal	4.14	3.36	3.34	3.88	3.29	n.d.	n.d.
C	GlcNPht	5.11	4.41	4.63	4.06	3.16	3.65	3.27
D	Fuc	4.55	3.53	3.74	3.09	4.43	n.d.	—
E	Gal	4.36	3.25	3.41	3.98	3.32	n.d.	n.d.
F	GlcNPht	5.16	4.44	4.71	4.08	3.21	3.72	n.d.
G	Fuc	4.61	3.57	3.76	3.13	4.56	n.d.	—
H	Gal	4.45	3.34	3.58	4.11	3.40	n.d.	n.d.
I	GlcNPht	5.38	4.55	4.87	4.19	3.58	n.d.	n.d.
J	Fuc	4.82	3.79	3.87	3.63	4.65	n.d.	—
K	Gal	4.72	5.04	4.80	5.25	3.54	n.d.	n.d.

n.d.: not determined.

$NaHCO_3$ solution. Triethylamine (0.02 mL) was added and the solvent evaporated in vacuo (bath temperature <35 °C). The remaining oily **38** was purified by flash chromatography in petroleum ether:ethyl acetate 3:2 containing 0.1% of triethylamine on 16 g of silica gel; yield: 75 mg (66%), amorphous after lyophilization from benzene; $[\alpha]_D^{22}$ −47.6° (*c* 1, $CHCl_3$); $R_f = 0.38$ (HPTLC: petroleum ether:ethyl acetate 2:1). Anal. calcd for $C_{273}H_{279}N_3O_{60}$ (4562.1): FABMS *m/z* 4562 (3.3%), 4563 (7.1%), 4564 (14.7%), 4565 (20.9%), 4566 (16.4%), 4567 (3.3%), 4568 (6.2%). See Table 5.

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 102.48, 102.40 (C-1A, C-1B), 102.04 (C-1H, C-1E), 99.96, 99.89 (C-1C, C-1F, C-1I), 99.61 (C-1K), 97.26 (C-1J), 97.06 (C-1D, C-1G), 82.93 (C-2A), 82.00, 81.92, 81.86 (C-3B, C-3E, C-3H), 81.60 (C-3A), 79.79 (C-3J), 79.25 (C-3D, C-3G), 78.47 (C-2B, C-2E, C-2H), 78.34 (C-4D, C-4G), 77.02 (C-4J), 76.44, 76.49 (C-4B, C-4E, C-4H), 75.96 (C-4A), 74.99 (C-5C, C-5F, C-4I), 74.89 (C-5I), 74.38 (C-2J), 73.82 (C-2D, C-2G), 73.70 (C-4C, C-4F), 73.02 (C-5B), 72.33 (C-5E, C-5H), 71.69 (C-3I), 71.27 (C-3C, C-3F), 70.96 (C-3K), 70.36 (C-5L), 68.97 (C-2K), 66.64 (C-4K), 66.37 (C-5J), 66.13 (C-5D, C-5G), 57.16, 57.04 (C-2C, C-2F, C-2I).

(3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (39). A dried mixture of disaccharide azide **28** (205 mg, 0.23 mmol) and glycosyl fluoride **30** (421 mg, 0.43 mmol) was dissolved in dry dichloromethane (50 mL). Molecular sieves 4 Å (0.8 g) were added and the mixture stirred at 5 °C under argon atmosphere for 1 h. A solution of borontrifluoride etherate (0.23 mL) in dry dichloromethane (5 mL) was added dropwise within 5 min and the mixture was stirred at 0 °C for 1 h and at room temperature for 2 h and then filtered through Celite, which was washed with several small portions of dichloromethane. The combined organic solutions were extracted with satd $NaHCO_3$ solution and dried with $MgSO_4$. After evaporation of the solvent in vacuo, the remaining **39** was purified by flash chromatography in petroleum ether:ethyl acetate 3:1 on 16 g of silica gel; yield: 287 mg (70%), amorphous; $[\alpha]_D^{22}$ −2.6° (*c* 1, $CHCl_3$); $R_f = 0.32$ (HPTLC: petroleum ether:ethyl acetate 2:1). Anal. calcd for $C_{104}H_{105}N_5O_{23}$ (1793.0): C, 69.64; H, 5.90; N, 3.91. Found; C, 68.97; H, 5.89; N, 3.88%. See Table 6.

Table 6. Assignment of the 400 MHz ^{1}H NMR signals of **39** ($CDCl_3$, δ in ppm, *J* in Hz)

Type	Position	1-H ($J_{1,2}$)	2-H	3-H ($J_{3,4}$)	4-H	5-H	6a-H ($J_{6a,6b}$)	6b-H
GlcNPht	A	5.19 (9.2)	4.00	3.99	3.84	3.18	3.53 (9.9)	3.29
Gal	B	4.21 (8.1)	3.38	3.53	3.97	n.d.	n.d.	n.d.
GlcNPht	C	5.38 (7.9)	4.25	4.31	3.98	3.62	3.81	3.73
Gal	D	4.47	3.68	4.82 (3.2)	3.92	n.d.	n.d.	n.d.

n.d.: not determined.

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 170.3 (Ac—C=O), 139.4, 138.5, 138.4, 138.3, 138.1, 138.0, 137.9 (Bzl—C_{ipso}), 135.2, 135.0, 134.1, 133.6 (H_2C=CH—CH_2, Pht—C-4/5), 131.6, 131.3 (Pht—C-1/2), 128.3–126.5 (Bzl—C_{arom}), 123.1 (Pht—C-3/6), 116.1, 116.0 (H_2C=CH—CH_2), 102.9 (C-1D), 102.5 (C-1B), 99.9 (C-1C), 85.7 (C-1A), 82.2 (C-3B), 78.7 (C-2B), 77.9 (C-4C), 77.7 (C-2D), 77.3 (C-5A), 77.0 (C-3A, C-3C), 76.5 (C-4A, C-4B), 75.3 (C-3D), 75.1, 74.7, 74.6, 74.1, 73.6, 73.5, 73.4, 73.2, 73.0 (Ph—CH_2, H_2C=CH—CH_2), 75.0 (C-5C), 74.5 (C-4D), 73.2, 72.8 (C-5B, C-5D), 68.8, 67.7 (C-6B, C-6D), 68.3 (C-6C), 67.1 (C-6A), 56.4 (C-2C), 55.2 (C-2A), 20.9 (Ac—CH_3).

***O*-(2,4,6-Tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (40).** Deacetylation of the dimeric lactosamine azide **39** (286 mg, 0.16 mmol) in dry tetrahydrofuran (5 mL) was carried out by addition of 3.2 mL of a 0.1 M solution of sodium methanolate at room temperature within 9 h, as described for **8**. Purification was performed by flash chromatography in petroleum ether:ethyl acetate 2:1 on silica gel (16 g); yield: 187 mg (67%), amorphous; $[\alpha]_d^{22}$ −12.6° (*c* 1, $CHCl_3$); $R_f = 0.22$ (HPTLC: petroleum ether:ethyl acetate 2:1). Anal. calcd for $C_{102}H_{103}N_4O_{22}$ (1750.9): C, 69.97; H, 5.93; N, 4.00. Found: C, 69.98; H, 5.96; N, 3.97%. IR (NaCl) ν (cm^{-1}): 2116 (N_3), 1776, 1715 (phthalimide).

400 MHz ^{1}H NMR ($CDCl_3$): δ (ppm) 7.83 (s_{broad}, 2H, Pht—H), 7.74–7.70 (m, 2H, Pht—H), 7.53–7.17 (m, 43H, Ph—H, Pht—H), 6.91 (m_c, 1H, Ph—H), 5.50–5.32 (m, 3H, 2 × H_2C=CH—CH_2, including 5.40, d, $J_{1,2} = 7.7$ Hz, 1C—H), 5.19 (d, $J_{1,2} = 9.2$ Hz, 1H, 1A-H), 5.01 (d, $J_{gem} = 11.7$ Hz, 1H, Ph—CH_2), 4.90 (dd, $J_{vic(trans)} = 17.2$ Hz, 1H, H_2C=CH—CH_2), 4.85 (d, $J_{gem} = 11.3$ Hz, 1H, Ph—CH_2), 4.82 (dd, $J_{vic(trans)} = 17.3$

Hz, 1H, $\underline{H}_2C{=}CH{-}CH_2$), 4.75–4.59 (m, 5H, $3\times Ph{-}CH_2$, $2\times \underline{H}_2C{=}CH{-}CH_2$), 4.53–4.21 (m, 16H, 1B-H, 1D-H, 2C-H, 3C-H, $10\times Ph{-}CH_2$, $2\times H_2C{=}CH{-}C\underline{H}_2$), 4.13–3.98 (m, 5H, 2A-H, 3A-H, 4B-H, 4C-H, $Ph{-}CH_2$), 3.94–3.35 (m, 18H, 2B-H, 3B-H, 3D-H, 4A-H, 4D-H, 5B-H, 5C-H, 5D-H, 6Ab-H, 6Ba-H, 6Bb-H, 6Ca-H, 6Cb-H, 6Da-H, 6Db-H, $Ph{-}CH_2$, $2\times H_2C{=}CH{-}C\underline{H}_2$), 3.30 (d, $J_{6a,6b}=10.3$ Hz, 1H, 6Ab-H), 3.19 (m_c, 1H, 5A-H), 2.20 (s_{broad}, 1H, 3D-OH).

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 139.42, 138.71, 138.40, 138.37, 138.30, 138.14, 138.12, 137.94 ($Bzl{-}C_{ipso}$), 135.2, 135.0, 134.1, 133.6 (Pht—C-4/5, $H_2C{=}\underline{C}H{-}CH_2$), 131.6, 131.3 (Pht—C-1/2), 128.5–126.5 ($Bzl{-}C_{arom}$), 123.1 (Pht—C-3/6), 116.0, 115.9 ($H_2\underline{C}{=}CH{-}CH_2$), 102.9, 102.5, 99.9, 85.7 (C-1A, C-1B, C-1C, C-1D), 82.2, 80.6, 78.7, 77.8, 76.5, 75.9, 75.0, 74.0, 72.2 (C-2B, C-2D, C-3A, C-3B, C-3C, C-3D, C-4A, C-4B, C-4C, C-4D, C-5A, C-5B, C-5C, C-5D), 75.1, 74.8, 74.7, 74.1, 73.6, 73.5, 73.4, 73.0 ($Ph{-}CH_2$, $H_2C{=}CH{-}\underline{C}H_2$), 68.8, 68.4, 68.2, 67.2 (C-6A, C-6B, C-6C, C-6D), 56.4, 55.2 (C-2A, C-2C).

(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (41). In analogy to the synthesis of **39**, the azide **40** (186 mg, 106 μmol) and (2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-D-glucopyranosylfluoride,[21] **35** (164 mg, 212 μmol), were dissolved in dichloromethane (50 mL) and reacted with borontrifluoride etherate (0.25 ml, 2 mmol) in dichloromethane (10 mL). Flash chromatography was carried out with petroleum ether:ethyl acetate (5:1); yield 186 mg (70%), amorphous; $[\alpha]_D^{22}$ −17.3° (*c* 1, $CHCl_3$); $R_f=0.52$ (HPTLC: petroleum ether:ethyl acetate 1:1). Anal. calcd for $C_{140}H_{144}N_6O_{37}$ (2502.7): C, 67.19; H, 5.80; N, 3.36. Found: C, 67.15; H, 5.79; N, 3.36%. IR (KBr) n, (cm^{-1}): 2116 (N_3), 1776, 1715 (phthalimide), 1754 (Ac—C=O).

100.6 MHz ^{13}C NMR ($CDCl_3$): δ (ppm) 102.6 (C-1D), 102.3 (C-1B), 100.3 (C-1F), 99.7 (C-1C, C-1E), 85.6 (C-1A), 82.0, 81.9 (C-3B, C-3D), 78.6, 78.4 (C-2B, C-2D), 77.7, 77.2 (C-4B, C-4D), 77.0 (C-5A), 76.9 (C-3A, C-3C), 76.7 (C-3E), 76.4 (C-4A, C-4C, C-4E), 74.6 (C-5C), 74.6, 74.0, 73.7, 73.5, 73.4, 72.9 ($Ph{-}CH_2$, $H_2C{=}CH{-}\underline{C}H_2$), 74.4 (C-4E), 73.1, 72.9 (C-5B, C-5D), 70.9 (C-3F), 70.3 (C-5F), 69.4 (C-2F), 68.8, 68.5, 67.9, 67.0, 60.8 (C-6A, C-6B, C-6C, C-6D, C-6E, C-6F), 66.8 (C-4F), 56.2 (C-2C, C-2E), 55.0 (C-2A). See Table 7.

Table 7. Assignment of the 400 MHz ^{1}H NMR signals of **41** ($CDCl_3$, δ in ppm, *J* in Hz)

Type	Position	1-H ($J_{1,2}$)	2-H ($J_{2,3}$)	3-H ($J_{3,4}$)	4-H	5-H	6a-H	6b-H
GlcNPht	A	5.16 (7.0)	3.98	3.95	3.80	3.15	3.46	3.25
Gal	B	4.13	3.32	3.37 (2.7)	3.84	n.d.	n.d.	n.d.
GlcNPht	C	5.21 (7.9)	4.15	4.09	3.84	3.27	3.54	3.32
Gal	D	4.27	3.43	3.58 (2.9)	3.98	n.d.	n.d.	n.d.
GlcNPht	E	5.39 (7.9)	4.24	4.27	3.98	3.55	3.74	3.69
Gal	F	4.58 (8.0)	5.07 (10.5)	4.85 (3.5)	5.28	n.d.	n.d.	n.d.

n.d.: not determined.
(Notice: Sequences B/D and C/E are not determined.)

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, by the Bundesminister für Forschung und Technologie and by the Fonds der Chemischen Industrie. We are very grateful to Professor Ch. Griesinger and Dr R. Wechselberger, Universität Frankfurt/Main, Germany, for 600 MHz 2D-NMR experiments.

References

1. Spohr, U.; Hindsgaul, O.; Lemieux, R. U. *Can. J. Chem.* **1985**, *63*, 2644.
2. Lee, Y. C.; Lee, R. T. *Acc. Chem. Res.* **1995**, *28*, 321.
3. Fukuda, M. *Biophys. Acta* **1985**, *780*, 119.
4. Fukuda, M.; Fukuda, M. N.; Hakomori, S. *J. Biol. Chem.* **1979**, *254*, 3700.
5. Hakomori, S.; Nudelman, E.; Levery, S.; Kamagid, R. *J. Biol. Chem.* **1984**, *259*, 4672.
6. Miyazaki, T.; Oikawa, N.; Yadomae, T.; Yamada, H.; Yamada, Y.; Hsu, H.-Y.; Ito, H. *Carbohydr. Res.* **1979**, *69*, 165.
7. Nilsson, M.; Norberg, T. *J. Carbohydr. Chem.* **1989**, *8*, 613.
8. Nicolaou, K. C.; Caulfield, T. J.; Kataoka, H.; Stylianides, N. A. *J. Am. Chem. Soc.* **1990**, *112*, 3693.
9. Nilsson, S.; Lönn, H.; Norberg, T. *J. Carbohydr. Chem.* **1991**, *10*, 1023, and ref therein.
10. Fügedi, P.; Garegg, P. *J. Carbohydr. Res.* **1986**, *149*, C9.
11. Nicolaou, K. C. *Chemtracts-Org. Chem.* **1991**, *4*, 181.
12. Töpfer, A.; Schmidt, R. R. *Tetrahedron Lett.* **1992**, 5161.
13. Schmidt, R. R.; Michel, J. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 731.
14. Kunz, H.; Unverzagt, C. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1697.
15. Unverzagt, C.; Kunz, H. *J. Prakt. Chem.* **1992**, *334*, 570.
16. Unverzagt, C.; Kunz, H. *Bioorg. Med. Chem.* **1994**, *2*, 1189.
17. März, J.; Kunz, H. *Synlett* **1992**, 589.
18. von dem Bruch, K.; Kunz, H. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 101.

19. Sprengard, U.; Kretzschmar, G.; Bartnik, E.; Hüls, C.; Kunz, H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 990.

20. Sprengard, U.; Schudok, M.; Schmidt, W.; Kretzschmar, G.; Kunz, H. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 321.

21. Bröder, W.; Kunz, H. *Carbohydr. Res.* **1993**, *249*, 221.

22. Bröder, W.; Kunz, H. *Synlett* **1990**, 252.

23. Nicolaou, K. C.; Chucholowsky, A.; Dolle, R. E.; Randall, J. L. *J. Chem. Soc. Chem. Commun.* **1984**, 1155.

24. Kunz, H.; Sager, W. *Helv. Chim. Acta* **1985**, *68*, 283; Sager, W. Diplomarbeit, Universität Mainz, 1983.

25. Jung, K. H.; Hoch, M.; Schmidt, R. R. *Liebigs Ann. Chem.* **1989**, 1099.

26. Kanie, O.; Ito, Y.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 12073.

27. Roy, R.; Anderson, F. O.; Letellier, M. *Tetrahedron Lett.* **1992**, *33*, 6053.

28. Sliedregt, L. A. J. M.; Zegelaar-Jaarsveld, K.; van der Marel, G. A.; van Boom, J. A. *Synlett* **1993**, 335.

29. Fraser-Reid, B.; Konradsson, P.; Mootoo, D. R.; Udodong, U. E. *J. Chem. Soc. Chem. Commun.* **1988**, 823.

30. Boons, G.-J.; Isles, S. *Tetrahedron Lett.* **1994**, *35*, 3593.

31. Lönn, H. *Carbohydr. Res.* **1985**, *139*, 105.

32. Lemieux, R. U.; Hendricks, K. B.; Stick, R. V.; James, J. *J. Am. Chem. Soc.* **1975**, *87*, 4056.

33. David, S.; Thieffry, A.; Veyriéres, A. *J. Chem. Soc. Perkin Trans.* I **1981**, 1796.

34. Tsuda, Y.; Haque, M. E.; Yoshimoto, K.; Kitzuchi, T. *Chem. Pharm. Bull.* **1985**, *33*, 2243.

35. Kluge, A. F.; Untsch, K. G.; Fried, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 7827.

36. Dubey, R.; Reynolds, D.; Abbas, A. A.; Matta, K. L. *Carbohydr. Res.* **1988**, *183*, 155.

37. Kieczykowski, G. R.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 1938.

38. Oltvoort, J. J.; van Boeckel, C. A. A.; de König, J. H.; van Boom, J. J. *Synthesis* **1981**, 305.

39. Bröder, W. Dissertation, Universität Mainz, 1992.

40. Bertho, A.; Maier, J. *Liebigs Ann. Chem.* **1932**, *498*, 50; procedure according to ref. 36.

41. Kunz, H.; Pfrengle, W.; Rück, K.; Sager, W. *Synthesis* **1991**, 1039.

(*Received in U.S.A.* 9 *April* 1996; *accepted* 11 *June* 1996)