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Synthesis of mucin *O*-glycan core structures as their *p*-nitro- and *p*-aminophenyl glycosides

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Dedicated to Professor András Lipták on the occasion of his 75th birthday

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ABSTRACT

For the investigation of glycosidases, and for the construction of glycan arrays the *p*-nitrophenyl- and *p*-aminophenyl glycosides of mucin *O*-glycan core structures 1–7 and the 2,6-ST-antigen have been chemically synthesized using D-galactose as a precursor for GalNAc residues. GlcNAc residues have partly been introduced using a 4,6-di-*O*-benzoyl-2,3-*N*,*O*-oxazolidinone-protected donor, which allowed deprotection of the formed di- and tri-saccharides in one step using sodium methoxide.

1. Introduction

In contrast to N-glycosylated proteins there are still difficulties to selectively cleave whole *O*-glycan chains from glycoproteins. Chemical methods often lead to so called 'peeling;, where the glycan is further truncated starting at its reducing end. Therefore enzymes are intensively sought to release whole *O*-glycans selectively. To find feasible enzymes we were envisaging fluorogenic substrates of the core 1–core 7 structures and the 2,6-ST-antigen. Our goal was furthermore to use the same core structures as linkable derivatives for interaction studies via glycan arrays. For these purposes, the fluorogenic *p*-nitrophenyl (*p*NP) glycoside derivatives seemed to be ideal, as they can be converted in one single step into their *p*-aminophenyl (*p*AP) analogues containing an easily linkable amino group (Fig. 1). The *p*NP structures of core 1–7[1–4] and the *p*AP structures of core 1 and 2[5,6] are known, where the *p*NP analogues of core 1–4 and 6 are commercially available. Although chemical synthesis has been reported for the *p*NP glycosides of core 1, 4, 5, 6 and 7[1,2] to the best of our knowledge previous synthesis utilized quite expensive galactosamine as the precursor for the GalNAc residues. We now report on the synthesis of the *p*NP glycosides of all target core structures starting from D-galactose via azidonitration and their subsequent transformation into the corresponding *p*AP glycosides.

2. Results and discussions

To synthesize the envisaged core structures we chose a linear approach, where first the α-*p*NP glycoside of 2-azido-2-deoxy-D-galactose was built up as acceptor that afterwards was glycosylated at the 3 and/or 6 position(s). Azides have been widely used as precursors for GalNAc residues for the synthesis of mucin *O*-glycan core structures linked to serine or threonine.[7–9] In case of *p*NP glycosides, the azide and nitro function are not orthogonal under most reductive conditions but the azide function can be selectively converted into the acetamido moiety in one step using thioacetic acid without any reduction of the nitro group.

Two different acceptors, **19** and **21** (Scheme 1), allowing regioselective glycosylations either at the 3- and/or 6-position were designed to eventually obtain all desired target structures. These acceptors were synthesized starting from trichloroacetimidate donor **17**[10] obtained from D-galactose in six steps. As previously reported[11] imidate **17** was coupled with *p*-nitrophenol to afford the α-glycoside **18** exclusively in 70% yield. Zemplén deprotection followed by selective 4,6-*O*-*p*-methoxybenzylidene protection gave the '3-OH' acceptor **19** in 73% yield. Because *p*NP glycosides are known to be quite acid labile,[12] the *p*-methoxybenzylidene acetal was chosen instead of other more acid stable acetals. Subsequent benzoylation of **19** at the 3-OH position and removal of the *p*-methoxybenzylidene acetal yielded the '6-OH' acceptor **21** in 80% yield over two steps.

For the efficient synthesis of the β-linked GlcNAc containing structures (core 2, 3, 4 and 6) we focused on a donor that could give the desired structures by an easy deprotection method. For the introduction of β-GlcNAc residues donors with a participating

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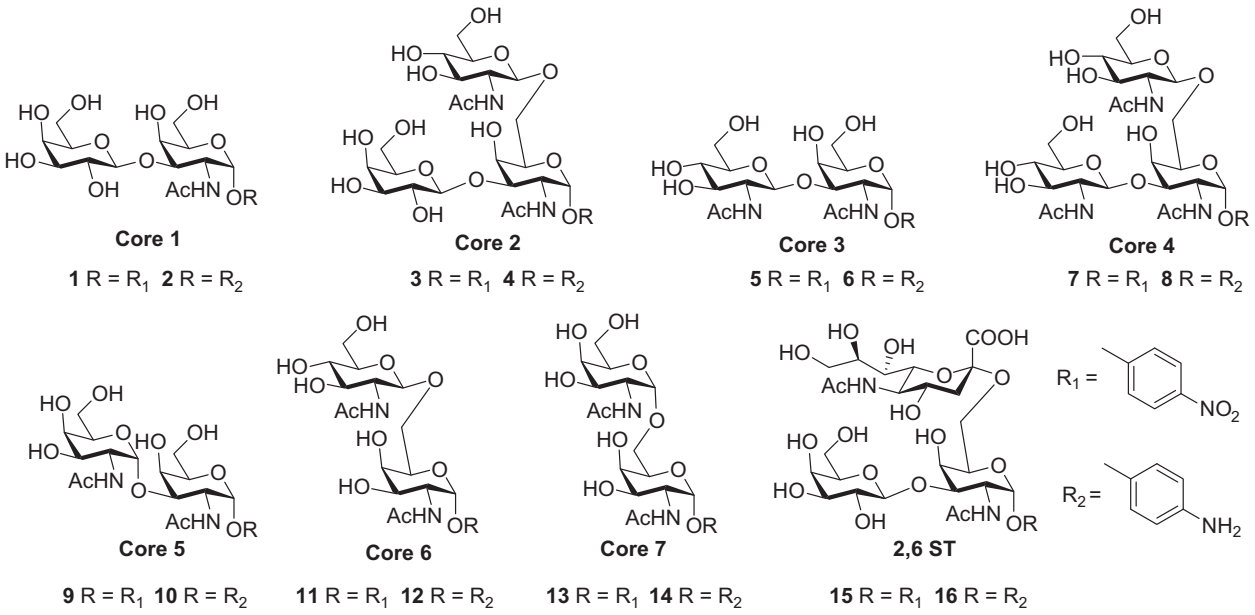
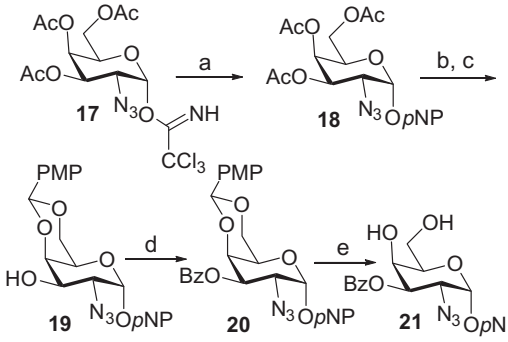


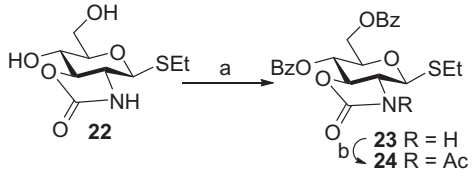
Figure 1. Structures of all the synthesized target compounds: the mucin core structures 1–7 and the 2,6-ST-antigen.



Scheme 1. Synthesis of glycosyl acceptors **19** and **21**. Reagents and conditions: (a) *p*-nitrophenol, TMSOTf, CH_2Cl_2, −20 °C, 70%; (b) NaOMe, MeOH, rt; (c) 1-(dimethoxymethyl)-4-methoxybenzene, *p*-TsOH, CH_3CN, DMF, rt, 73%; (d) BzCl, pyridine, 0 °C, 94%; (e) 80% AcOH, rt and 50 °C, 85%.

2-amino protecting groups, like Phth or Troc, are commonly used, which have to be converted into the *N*-acetyl moiety in multiple steps later in the synthetic route. In contrast, the 2,3-*N*,*O*-oxazolidinone protected GlcNAc structures can be deprotected together with acyl protecting groups by using mild sodium methoxide treatment affording directly the desired deprotected N-acetylated target structures in only one step.[13] Nevertheless the use of sodium methoxide can also lead to the formation of undesired methyl carbamates.[14] For the synthesis of GlcNAc containing core structures, we decided to use a new oxazolidinone donor, which was 4,6-di-*O*-benzoyl protected in contrast to the known 4,6-di-*O*-acetyl protected one,[15] partly to avoid purification problems due to very similar polarities between used acceptors and the acetylated donor. The syntheses started from the known 2,3-*N*,*O*-oxazolidinone **22**,[15] which was benzoylated to afford **23** in 86% yield. Following acetylation of the oxazolidinone nitrogen gave donor **24** in 89% yield (Scheme 2).

For the synthesis of the disaccharide *p*NP derivatives (**27–30**), the glycosylation of acceptor **19** with the respective donors was carried out using different promoters and donors (Table 1). The *p*-methoxybenzylidene acetal of the afforded disaccharides was subsequently removed using 80% acetic acid.

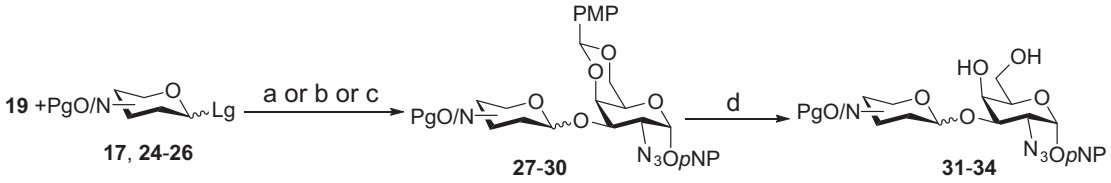


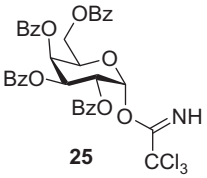
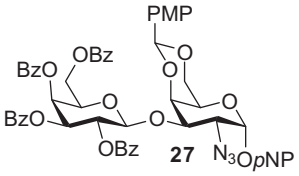
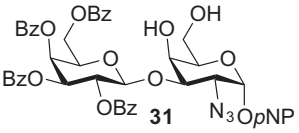
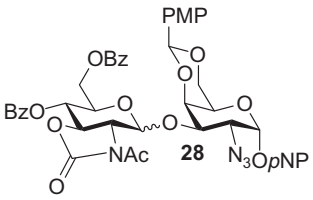
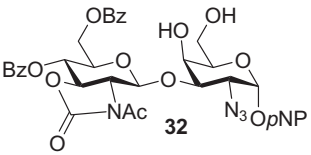
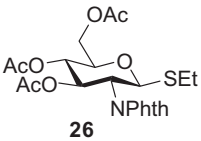
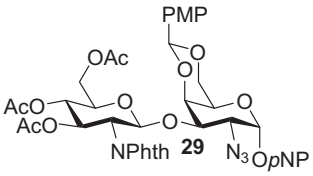
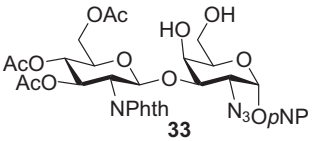
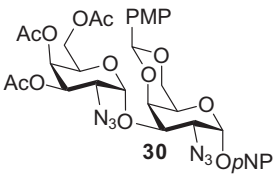
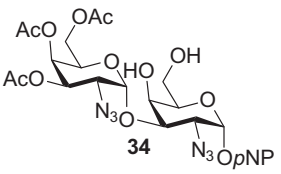
Scheme 2. Synthesis of 2,3-*N*,*O*-oxazolidinone donor **24**. Reagents and conditions: (a) BzCl, pyridine, 0 °C, 86%; (b) AcCl, DIPEA, CH_2Cl_2, 0 °C, 89%.

The synthesis of core 1 intermediate **27** was achieved with the per-benzoylated α-trichloroacetimidate **25**[16] and TMSOTf as the promoter in a high yield of 80%. It should be mentioned that under the same conditions use of a per-acetylated α-trichloroacetimidate afforded only the orthoester instead of the β-glycoside. The glycosylation of **19** with our new donor **24** was carried out with DMTST as promoter and DTBMP as buffer instead of the NIS–AgOTf system to prevent in situ anomerization.[15] Nevertheless, and surprisingly, **28** was obtained as an α/β (1:7) mixture and only in a moderate yield of 40%. In contrast, the use of the phthalimido protected donor **26**[17] and NIS–TMSOTf as activator afforded the core 3 intermediate **29** in 87% yield. The TMSOTf promoted glycosylation of **19** with trichloroacetimidate donor **17** afforded disaccharide **30**, where, due to separation problems, the *p*-methoxybenzylidene acetal was directly removed to afford **34** in 58% yield over two steps.

Glycosylation reactions to obtain the 6-O-substituted di- and tri-saccharides are shown in Table 2. The new donor **24** was successfully applied in DMTST-promoted glycosylations to obtain disaccharide **38** and trisaccharide **36** in 64% and 72% yield, respectively, as β-anomers exclusively. These obtained yields using the new donor **24** are very similar to the reported yield in coupling reactions with the corresponding 4,6-di-O-acetylated oxazolidinone donor.[15] Because the molecule already contained a NPhth group, acceptor **33** was glycosylated with the GlcNPhth donor **26** and TMSOTf–NIS as activator system, which surprisingly gave core 4 intermediate **37** in only 51% yield. Core 7 intermediate **39** was obtained using trichloroacetimidate **17**, acceptor **21** and TMSOTf as promoter in 88% yield as a separable α/β (5:1) mixture. Attempts to increase the ratio of the α-anomer using a protocol[18] with addi-

Table 1
Synthesis of disaccharides **27**–**34**



Entry	Donor	Condition	Product	Yield (%)	Product	Yield (%)
1	 **25**	a	 **27**	80	 **31**	72
2	**24**	b	 **28**	40	 **32**	71
3	 **26**	c	 **29**	87	 **33**	77
4	**17**	a	 **30**		 **34**	58[a]

Reagents and conditions: (a) TMSOTf, CH_2Cl_2, 4 Å MS, −20 °C; (b) DMTST, DTBMP, CH_2Cl_2, 4 Å MS, 0 °C; (c) NIS, TMSOTf, CH_2Cl_2, 4 Å MS, −30 °C; (d) 80% AcOH, rt.
[a] Yield was determined over two steps due to separation problems of **30**.

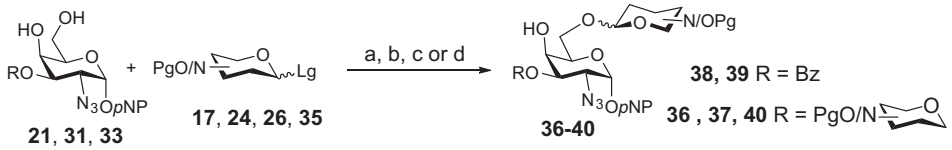
tion of thiophene at 0 °C resulted in an improved α/β ratio of 17:1 but led to a decrease in yield to 60%. The coupling of acceptor **31** with the *N*-acetylneuraminic acid donor **35**[19] using AgOTf–IBr[20] gave the trisaccharide **40** as a separable α/β (5:1) mixture in a yield of 73%.

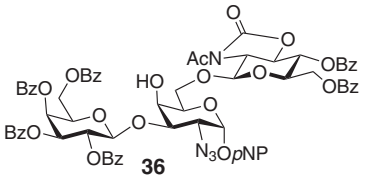
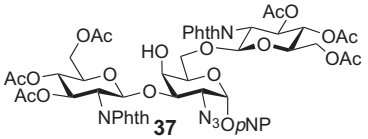
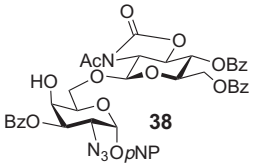
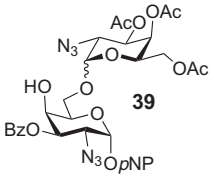
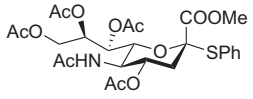
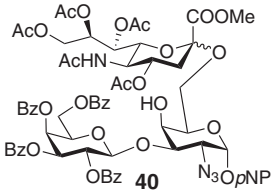
To obtain the target compounds, the corresponding acetamido groups of the di- and trisaccharides had to be introduced and the structures globally deprotected (Scheme 3). Therefore, the phthalimido-protected derivatives **33** and **37** were deactetylated using Zemplén conditions, their *N*-phthalimido groups were removed using hydrazine hydrate and the obtained intermediates were completely acetylated to yield the corresponding acetamido derivatives **43** and **44**. Subsequently, the azido function(s) of all compounds were converted into the acetamido moiety(ies) using thioacetic acid in pyridine. After workup and purification the acetamides were directly used for complete deprotection without further characterization. Deprotection was carried out using sodium methoxide in methanol. In some cases, water was added to aid solubility. Alternatively, a mixture of methanol–dichloromethane (1:1) was used as solvent where additional methanol and sodium methoxide were added.

The methyl ester of the *N*-acetylneuraminic acid residue of the 2,6-ST-antigen derivative was converted into the free acid **15** by saponification. All deprotected *p*NP structures were purified by reversed phase column chromatography to obtain the pure target compounds in yields between 37% and 74% over two steps. The deprotection of oxazolidinone-containing structures to give compounds **3** and **11** resulted in the formation of the corresponding deacetylated carbamates as side products in small amounts. This is illustrated for compound **41** in Scheme 4, where both products were isolated and characterized. The ratio acetamide to carbamate of 3.4:1 (calculated on basis of isolated yields after HPLC) emphasizes the possibility to preferably obtain the desired acetamide containing structures just using sodium methoxide, which is in agreement with our previous studies.[13] In contrast, Kerns and Wei reported the formation of the deacetylated carbamate (85%) by treatment with sodium methoxide in methanol from a β-linked GlcNAc oxazolidinone benzyl glycoside with different protecting groups at position 4 and 6.[14] Thus, these results show that, in addition to the known effect of the anomeric configuration,[21] the ratio of acetamide to carbamate upon one-step deprotection of oxazolidinones depends highly on the type of the aglycon and/or the protecting group pattern.

First attempts to reduce the *p*NP derivatives into their corresponding *p*AP derivatives were carried out with hydrogen and palladium on activated carbon in methanol similar to the procedure reported for the *p*AP structures of core 1 and 2.[5] In our case, using methanol as the solvent caused problems due to the formation of side products and due to poor solubility. The products had to be purified by reversed phase column chromatography and could, ex-

Table 2
Synthesis of compounds **36**–**40**



Entry	Acceptor	Donor	Conditions	Product	Yield (%)
1	**31**	**24**	b	 **36**	64
2	**33**	**26**	c	 **37**	51
3	**21**	**24**	b	 **38**	72
4	**21**	**17**	a	 **39**	88
5	**31**	 **35**	d	 **40**	73

Reagents and conditions: (a) TMSOTf, CH_2Cl_2, 4 Å MS, −20 °C; (b) DMTST, DTBMP, CH_2Cl_2, 4 Å MS, 0 °C; (c) NIS, TMSOTf, CH_2Cl_2, 4 Å MS, −30 °C; (d) IBr, AgOTf, CH_2Cl_2,, 3 Å MS, −78 °C.

cept for core 1 (92%), only be afforded in poor yields between 33% and 69%. These problems were solved by changing the reaction solvent to water to obtain all *p*AP derivatives without the need of further purification in very high to quantitative yields.

3. Conclusions

We have successfully synthesized the *p*NP- and *p*AP glycosides of mucin *O*-glycan core 1–7 and 2,6-ST-antigen starting from D-galactose by a linear approach. For the synthesis of GlcNAc containing structures we introduced a new 4,6-di-*O*-benzoyl-2,3-*N*,*O*-oxazolidinone-protected donor, which could be converted into the acetamide by mild sodium methoxide deprotection allowing one-step deprotection to target structures.

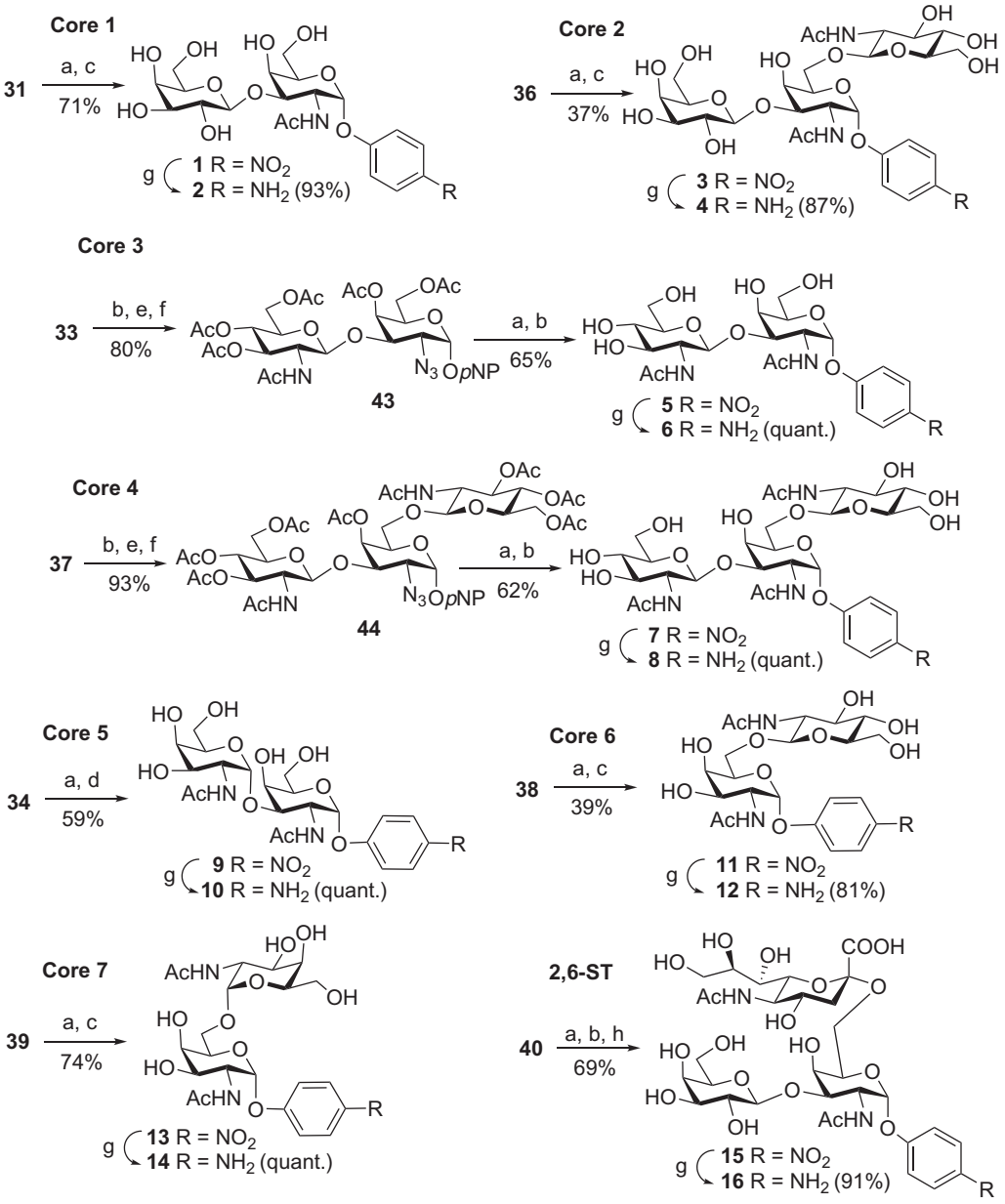
4. Experimental

4.1. General methods

The ^1H and ^{13}C NMR spectra (δ in ppm, relative to Me_4Si in $CDCl_3$, relative to solvent peak in CD_3CN or relative to acetone in D_2O) were recorded with Varian instruments (500/125 MHz or 600/150 MHz) at 25 °C. Assignments were aided by ^1H–^1H and ^1H–^{13}C correlation experiments. HRMS spectra were recorded on a micromass LCT instrument from Waters. Optical rotations were measured on a Perkin Elmer polarimeter with a Na lamp (589 nm) at 20 °C and are not corrected. TLC was carried out on precoated 60 F254 silica gel alumina plates (Merck) using UV-light, H_2SO_4 (10% in ethanol), ninhydrin solution (ninhydrin–CH_3COOH–ethanol [0.3:3:100 w/v/v] and/or AMC-solution (ammonium sulphate cerium (IV) sulphate, 10% H_2SO_4 [5:0.1:100 w/w/v]). Column chromatography was performed on silica gel (Apollo scientific, pore size 60 Å, particle size 40–63 μm), C18 silica gel (SDS, pore size 60 Å, particle size 40–63 μm) and on HPLC with a Gilson system on a C18 RP-phase column (VP 250/21 Nucleosil 100-5 C18, Machery Nagel).

4.2. *p*-Nitrophenyl 2-azido-2-deoxy-4,6-*O*-*p*-methoxybenzylidene-α-D-galactopyranoside (19)

NaOMe (1 M in MeOH) was added drop-wise to a solution of *p*-nitrophenyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopy-

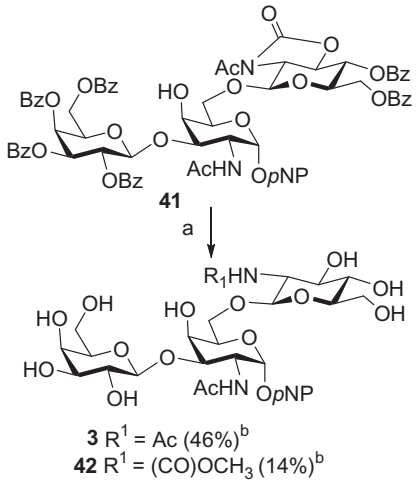


Scheme 3. Deprotection to the target *p*NP-glycosides and subsequent transformation to target *p*AP derivatives. Reagents and conditions: (a) thioacetic acid, pyridine; (b) NaOMe, MeOH; (c) NaOMe, MeOH→MeOH, H_2O; (d) NaOMe, MeOH, CH_2Cl_2; (e) hydrazine hydrate, EtOH, 70 °C; (f) acetic anhydride, pyridine; (g) H_2, Pd–C, H_2O; (h) NaOH, H_2O.

ranoside (**18**)[11] (5.73 g, 12.7 mmol) in dry MeOH (130 mL) until pH 10 was reached. The reaction mixture was stirred for 30 min and then neutralized with Dowex H^+ ion exchange resin. The solution was filtered, concentrated and the residue was dried in vacuo to afford a white solid which was directly used for the next reaction. The material was dissolved in CH_3CN (80 mL) and DMF (32 mL), *p*-methoxybenzylidene dimethylacetal (3.17 mL, 18.6 mmol) and *p*-TsOH (0.284 g, 1.49 mmol) were added and the reaction mixture was stirred for 1 h. Et_3N (0.208 μL, 1.49 mmol) was added, the mixture was diluted with $CHCl_3$ (400 mL), washed with water (150 mL), satd aq $NaHCO_3$ (2 × 150 mL) and water (150 mL), dried over $MgSO_4$ and concentrated. The crude product was purified by FC on silica gel (toluene–EtOAc 5:1) to afford **19** (4.01 g, 73%) as a white solid: R_f 0.55 (toluene–EtOAc 2:1); $[\alpha]_D^{20}$ +68 (*c* 1.7, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.25–8.21 (m, 2H, $OC_6H_4NO_2$), 7.45–7.41 (m, 2H, $C_6H_4OCH_3$), 7.24–7.20 (m, 2H, $OC_6H_4NO_2$), 6.95–6.91 (m, 2H, $C_6H_4OCH_3$), 5.78 (d, $J_{1,2}$ 3.3 Hz, 1H, H-1), 5.57 (s, 1H, $CHC_6H_4OCH_3$), 4.43–4.36 (m, 2H, H-3, H-4), 4.25 (dd, $J_{6a,6b}$ 12.9 Hz, $J_{5,6a}$ 1.3 Hz, 1H, H-6a), 4.06 (dd, $J_{6a,6b}$ 12.9 Hz, $J_{5,6b}$ 1.6 Hz, 1H, H-6b), 3.85–3.80 (m, 4H, $C_6H_4OCH_3$, H-2), 3.80–3.78 (m, 1H, H-5), 2.55 (d, *J* 10.7 Hz, 1H, OH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1 ($OC_6H_4NO_2$), 160.5 ($C_6H_4OCH_3$), 143.1 ($OC_6H_4NO_2$), 129.5 ($C_6H_4OCH_3$), 127.5 (2C, $C_6H_4OCH_3$), 126.0 (2C, $OC_6H_4NO_2$), 116.4 (2C, $OC_6H_4NO_2$), 113.8 (2C, $C_6H_4OCH_3$), 101.4 ($CHC_6H_4OCH_3$), 97.5 (C-1), 75.0 (C-4), 68.9 (C-6), 67.6 (C-3), 64.1 (C-5), 60.2 (C-2), 55.4 ($C_6H_4OCH_3$). ES-HRMS calcd for $C_{20}H_{20}N_4O_8$ $[H]^+$ 445.1359, found 445.1342.

4.3. *p*-Nitrophenyl 2-azido-3-*O*-benzoyl-2-deoxy-4,6-*O*-*p*-methoxybenzylidene-α-D-galactopyranoside (20)

Benzoyl chloride (0.219 mL, 1.89 mmol) was added to an ice-cooled solution of compound **19** (0.700 g, 1.58 mmol) in dry pyridine (8 mL) and the solution was stirred for 1 h. The mixture was



Scheme 4. Deprotection of 2,3-*N*,*O*-oxazolidinone derivative **41**. Reagents and conditions: (a) NaOMe, MeOH, CH_2Cl_2. [b]Isolated yields after separation by HPLC.

diluted with CH_2Cl_2 (100 mL) and washed with satd aq $CuSO_4$ (2 × 100 mL), water (100 mL) and satd aq $NaHCO_3$ (100 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. FC on silica gel (toluene–EtOAc 5:1) afforded **20** (0.810 g, 94%) as a white solid: R_f 0.60 (toluene–EtOAc 2:1); $[\alpha]_D^{20}$ +267 (*c* 0.48, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27–8.22 (m, 2H, $OC_6H_4NO_2$), 8.14–8.11 (m, 2H, C_6H_5), 7.64–7.59 (m, 1H, C_6H_5), 7.51–7.46 (m, 2H, C_6H_5), 7.43–7.39 (m, 2H, $C_6H_4OCH_3$), 7.27–7.23 (m, 2H, $OC_6H_4NO_2$), 6.91–6.87 (m, 2H, $C_6H_4OCH_3$), 5.90 (d, $J_{1,2}$ 3.3 Hz, 1H, H-1), 5.77 (dd, $J_{2,3}$ 11.1 Hz, $J_{3,4}$ 3.3 Hz, 1H, H-3), 5.54 (s, 1H, $CHC_6H_4OCH_3$), 4.70–4.67 (m, 1H, H-4), 4.36 (dd, $J_{2,3}$ 11.1 Hz, $J_{1,2}$ 3.3 Hz, 1H, H-2), 4.26 (dd, $J_{6a,6b}$ 12.8 Hz, $J_{5,6a}$ 1.4 Hz, 1H, H-6a), 4.07 (dd, $J_{6a,6b}$ 12.8 Hz, $J_{5,6b}$ 1.4 Hz, 1H, H-6b), 3.91–3.88 (m, 1H, H-5), 3.81 (s, 3H, $C_6H_4OCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0 (COC_6H_5), 160.9 ($OC_6H_4NO_2$), 160.2 ($C_6H_4OCH_3$), 143.1 ($OC_6H_4NO_2$), 133.7 (C_6H_5), 130.0 (2C, C_6H_5), 129.7 ($C_6H_4OCH_3$), 129.1 (C_6H_5), 128.6 (2C, C_6H_5), 127.3 (2C, $C_6H_4OCH_3$), 126.0 (2C, $OC_6H_4NO_2$), 116.5 (2C, $OC_6H_4NO_2$), 113.6 (2C, $C_6H_4OCH_3$), 100.7 ($CHC_6H_4OCH_3$), 97.4 (C-1), 73.2 (C-4), 69.8 (C-3), 68.8 (C-6), 64.0 (C-5), 57.3 (C-2), 55.3 ($C_6H_4OCH_3$). ES-HRMS calcd for $C_{27}H_{24}N_4O_9$ [Na]$^+$ 571.1441, found 571.1449.

4.4. *p*-Nitrophenyl 2-azido-3-*O*-benzoyl-2-deoxy-α-D-galactopyranoside (21)

Acetic acid (aq 80%, 30 mL) was added to a solution of compound **20** (0.790 g, 1.44 mmol) in CH_2Cl_2 (5 mL) and the mixture was stirred at room temperature for 2 d and then heated to 50 °C and stirred for additional 2 h until no starting material was left (as monitored by TLC). The mixture was diluted with $CHCl_3$ (100 mL) and carefully washed with satd aq $NaHCO_3$ (2 × 150 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude product was purified by FC on silica gel (toluene–EtOAc 1:1) to obtain **21** (0.528 g, 85%) as a white solid: R_f 0.44 (toluene–EtOAc 1:1); $[\alpha]_D^{20}$ +280 (*c* 0.78, CH_3CN). ^{1}H NMR (500 MHz, CD_3CN) δ 8.26–8.20 (m, 2H, $OC_6H_4NO_2$), 8.17–8.12 (m, 2H, C_6H_5), 7.71–7.65 (m, 1H, C_6H_5), 7.59–7.53 (m, 2H, C_6H_5), 7.34–7.28 (m, 2H, $OC_6H_4NO_2$), 5.93 (d, $J_{1,2}$ 3.5 Hz, 1H, H-1), 5.60 (dd, $J_{2,3}$ 11.0 Hz, $J_{3,4}$ 3.0 Hz, 1H, H-3), 4.33–4.29 (m, 1H, H-4), 4.24 (dd, $J_{2,3}$ 11.0 Hz, $J_{1,2}$ 3.5 Hz, 1H, H-2), 4.01–3.96 (m, 1H, H-5), 3.72 (d, *J* 4.5 Hz, 1H, OH-4), 3.67–3.60 (m, 2H, H-6a,b), 2.89–2.83 (m, 1H, OH-6). ^{13}C NMR (125 MHz, CD_3CN) δ 166.5 (COC_6H_5), 162.3 and 144.0 ($OC_6H_4NO_2$), 134.6 and 130.8 (C_6H_5), 130.7 (2C, C_6H_5), 129.7 (2C, C_6H_5), 126.7 (2C, $OC_6H_4NO_2$), 118.0 (2C, $OC_6H_4NO_2$), 97.9 (C-1), 73.3 (C-5), 72.8 (C-3), 67.6 (C-4), 62.0 (C-6), 58.7 (C-2). ES-HRMS calcd for $C_{19}H_{18}N_4O_8$ [Na]$^+$ 453.1022, found 453.1020.

4.5. Ethyl 4,6-di-*O*-benzoyl-2,3-*N*,*O*-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (23)

Benzoyl chloride (1.21 mL, 10.4 mmol) was added to an ice-cooled solution of ethyl 2,3-*N*,*O*-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (**22**)[17] (1.18 g, 4.73 mmol) in dry pyridine (15 mL) and the solution was stirred for 1 h. The mixture was poured into ice water (100 mL) and extracted with CH_2Cl_2 (2 × 100 mL). The organic layer was washed with satd aq $CuSO_4$ (2 × 100 mL), water (50 mL) and satd aq $NaHCO_3$ (50 mL), dried over $MgSO_4$, filtered, and concentrated. FC on silica gel (toluene–EtOAc 3:1) afforded **23** (1.86 g, 86%) as a white foam: R_f 0.36 (toluene–EtOAc 3:1); $[\alpha]_D^{20}$ −14 (*c* 0.46, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05–7.95 (m, 4H, C_6H_5), 7.61–7.50 (m, 2H, C_6H_5), 7.46–7.35 (m, 4H, C_6H_5), 5.67 (dd, *J* 10.0 Hz, 9.2 Hz, 1H, H-4), 5.43–5.39 (m, 1H, NH), 4.73 (d, $J_{1,2}$ 9.6 Hz, 1H, H-1), 4.63 (dd, $J_{6a,6b}$ 12.2 Hz, $J_{5,6a}$ 2.9 Hz, 1H, H-6a), 4.46 (dd, $J_{6a,6b}$ 12.2 Hz, $J_{5,6b}$ 5.5 Hz, 1H, H-6b), 4.43–4.38 (m, 1H, H-3), 4.11–4.04 (m, 1H, H-5), 3.74–3.66 (m, 1H, H-2), 2.80–2.67 (m, 2H, SCH_2CH_3), 1.30 (t, J_{CH2CH3} = 7.4 Hz, 3H, SCH_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3 and 165.1 (COC_6H_5), 158.2 (*C*ONH), 133.9 and 133.4 (C_6H_5), 130.2 (2C, C_6H_5), 129.9 (2C, C_6H_5), 129.8 and 128.9 (C_6H_5), 128.7 (2C, C_6H_5), 128.6 (2C, C_6H_5), 83.4 (C-1), 82.2 (C-3), 77.7 (C-5), 68.9 (C-4), 63.4 (C-6), 59.5 (C-2), 25.2 (SCH_2CH_3), 15.6 (SCH_2CH_3). ES-HRMS calcd for $C_{23}H_{23}NO_7S$ [Na$^+$] 480.1093, found 480.1091.

4.6. Ethyl 2-acetamido-4,6-di-*O*-benzoyl-2,3-*N*,*O*-carbonyl-2-deoxy-1-thio-β-D-glucopyranoside (24)

DIPEA (3.55 mL, 20.3 mmol) and acetyl chloride (1.44 mL, 20.3 mmol) were added to an ice-cooled solution of compound **23** (1.89 g, 4.06 mmol) in dry CH_2Cl_2 (34 mL) and the reaction mixture was stirred for 1.5 h. The solution was diluted with CH_2Cl_2 (150 mL) and the organic layer was washed with satd aq $NaHCO_3$ (50 mL) and 1 M HCl (50 mL), dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by FC on silica gel (toluene–EtOAc 5:1) to afford **24** (1.81 g, mmol, 89%) as a white foam: R_f 0.55 (toluene–EtOAc 3:1); $[\alpha]_D^{20}$ −16 (*c* 1.22, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–8.00 (m, 2H, C_6H_5), 7.99–7.96 (m, 2H, C_6H_5), 7.61–7.56 (m, 1H, C_6H_5), 7.56–7.51 (m, 1H, C_6H_5), 7.47–7.41 (m, 2H, C_6H_5), 7.41–7.36 (m, 2H, C_6H_5), 5.64 (dd, *J* 10.1, 9.0 Hz, 1H, H-4), 4.88 (d, $J_{1,2}$ 8.6 Hz, 1H, H-1), 4.65 (dd, $J_{6a,6b}$ 12.2 Hz, $J_{5,6a}$ 3.0 Hz, 1H, H-6a), 4.52–4.42 (m, 2H, H-6b, H-3), 4.19 (dd, $J_{2,3}$ 11.4 Hz, $J_{1,2}$ 8.6 Hz, 1H, H-2), 4.16–4.11 (m, 1H, H-5), 2.72–2.61 (m, 2H, SCH_2CH_3), 2.54 (s, 3H, $COCH_3$), 1.25 (t, J_{CH2CH3} 7.5 Hz, 3H, CH_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6 ($COCH_3$), 166.0 and 164.8 (COC_6H_5), 153.3 ($CONCOCH_3$), 133.9 and 133.3 (C_6H_5), 130.0 (2C, C_6H_5), 129.7 (2C, C_6H_5), 129.5 (C_6H_5), 128.6 (2C, C_6H_5), 128.5 (C_6H_5), 128.4 (2C, C_6H_5), 85.1 (C-1), 79.6 (C-3), 77.4 (C-5), 68.9 (C-4), 63.2 (C-6), 60.3 (C-2), 25.4 (SCH_2CH_3), 24.7 ($COCH_3$), 14.2 (SCH_2CH_3). ES-HRMS calcd for $C_{25}H_{25}NO_8S$ [H]$^+$ 500.1379, found 500.1382.

4.7. *p*-Nitrophenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-azido-2-deoxy-4,6-*O*-*p*-methoxybenzylidene-α-D-galactopyranoside (27)

A mixture of acceptor **19** (0.600 g, 1.35 mmol), trichloroacetimidate **25**[16] (1.401 g, 1.890 mmol), and 4 Å MS in dry CH_2Cl_2 (26 mL) was stirred for 20 min under a N_2 atmosphere and then cooled to −20 °C. TMSOTf (12 μL, 68 μmol) was added and the reaction mixture was stirred at −20 °C for 2 h. Upon complete glycosylation (as

monitored by TLC) the mixture was diluted with CH_2Cl_2 (50 mL) and filtered through a pad of Celite. The filtrate was washed with 1 M HCl (50 mL), satd aq $NaHCO_3$ (50 mL), and water (50 mL), dried over $MgSO_4$, filtered and concentrated. FC on silica gel (toluene–EtOAc 20:1) afforded **27** (1.101 g, 80%) as a white solid: R_f 0.35 (toluene–EtOAc 7:1); $[\alpha]_D^{20}$ +156 (*c* 1.63, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20–8.16 (m, 2H, $OC_6H_4NO_2$), 8.11–8.06 (m, 2H, C_6H_5), 8.04–8.00 (m, 2H, C_6H_5), 8.00–7.96 (m, 2H, C_6H_5), 7.82–7.77 (m, 2H, C_6H_5), 7.64–7.58 (m, 1H, C_6H_5), 7.54–7.50 (m, 1H, C_6H_5), 7.50–7.40 (m, 6H, C_6H_5, $C_6H_4OCH_3$), 7.40–7.36 (m, 2H, C_6H_5), 7.36–7.32 (m, 2H, C_6H_5), 7.27–7.22 (m, 2H, C_6H_5), 7.16–7.10 (m, 2H, $OC_6H_4NO_2$), 6.90–6.84 (m, 2H, $C_6H_4OCH_3$), 6.04–6.01 (m, 1H, H-4^{II}), 5.95 (dd, $J_{2,3}$ 10.3 Hz, $J_{1,2}$ 7.9 Hz, 1H, H-2^{II}), 5.73 (d, $J_{1,2}$ 3.3 Hz, 1H, H-1^{I}), 5.64 (dd, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.4 Hz, 1H, H-3^{II}), 5.48 (s, 1H, C*H*$C_6H_4OCH_3$), 5.25 (d, $J_{1,2}$ 7.9 Hz, 1H, H-1^{II}), 4.81 (dd, $J_{6a,6b}$ 12.8 Hz, $J_{5,6a}$ 8.7 Hz, 1H, H-6a^{II}), 4.56–4.52 (m, 1H, H-4^{I}), 4.48–4.42 (m, 2H, H-5^{II}, H-6b^{II}), 4.34 (dd, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 3.3 Hz, 1H, H-3^{I}), 4.12–4.03 (m, 2H, H-6a^{I}, H-2^{I}), 3.81 (s, 3H, $C_6H_4OCH_3$), 3.74–3.68 (m, 1H, H-6b^{I}), 3.53–3.48 (m, 1H, H-5^{I}). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 165.8, 165.8 and 165.4 (*C*OC_6H_5), 161.2 ($OC_6H_4NO_2$), 160.3 ($C_6H_4OCH_3$), 143.2 ($OC_6H_4NO_2$), 133.9, 133.7, 133.6 and 133.4 (C_6H_5), 130.3 (2C, C_6H_5), 130.2 ($C_6H_4OCH_3$), 130.0 (2C, C_6H_5), 129.9 (2C, C_6H_5), 129.9 (2C, C_6H_5), 129.6, 129.6 and 129.2 (C_6H_5), 128.9 (2C, C_6H_5), 128.9 (C_6H_5), 128.8 (2C, C_6H_5), 128.5 (2C, C_6H_5), 128.5 (2C, C_6H_5), 127.6 (2C, $C_6H_4OCH_3$), 126.1 (2C, $OC_6H_4NO_2$), 116.6 (2C, $OC_6H_4NO_2$), 113.8 (2C, $C_6H_4OCH_3$), 103.1 (C-1^{II}), 100.9 (*C*H$C_6H_4OCH_3$), 97.8 (C-1^{I}), 76.1 (C-3^{I}), 75.6 (C-4^{I}), 72.1 (C-3^{II}), 72.0 (C-5^{II}), 69.8 (C-2^{II}), 68.8 (C-6^{I}), 68.4 (C-4^{II}), 64.6 (C-5^{I}), 62.8 (C-6^{II}), 58.4 (C-2^{I}), 55.5 ($C_6H_4OCH_3$). ES-HRMS calcd for $C_{54}H_{46}N_4O_{17}$ $[H]^+$ 1021.2780, found 1021.2729.

4.8. *p*-Nitrophenyl 2-acetamido-4,6-di-*O*-benzoyl-2,3-*N*,*O*-carbonyl-2-deoxy-α/β-D-glucopyranosyl-(1→3)-2-azido-2-deoxy-4,6-O-p-methoxybenzylidene-α-D-galactopyranoside (28)

A mixture of acceptor **19** (0.150 g, 0.338 mmol), donor **24** (0.337 g, 0.675 mmol), and DTBMP (0.277 g, 1.350 mmol) in dry CH_2Cl_2 (6 mL) containing 4 Å MS was stirred under a N_2 atmosphere at room temperature for 20 min. The mixture was cooled to 0 °C, DMTST (0.262 g, 1.013 mmol) was added and the reaction mixture was stirred for 3 h while allowed to warm up to room temperature. Thereafter the reaction was quenched by the addition of Et_3N (150 μL), diluted with CH_2Cl_2 (50 mL) and the mixture was filtered through Celite. The filtrate was washed with 1 M HCl (2 × 50 mL), satd aq $NaHCO_3$ (50 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified by FC on silica gel (toluene–EtOAc 5:1) to afford the α/β (1:7) mixture **28** (0.118 g, 40% or 62% when considering the recovered acceptor **19** (0.054 g)) as a white solid. A sample of the pure β anomer was obtained by repeated FC on silica gel: R_f 0.55 (toluene–EtOAc 5:2); $[\alpha]_D^{20}$ +100 (*c* 0.29, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCL_3$) δ 8.25–8.19 (m, 2H, $OC_6H_4NO_2$), 8.06–8.02 (m, 2H, C_6H_5), 7.99–7.95 (m, 2H, C_6H_5), 7.64–7.59 (m, 1H, C_6H_5), 7.53–7.44 (m, 3H, C_6H_5), 7.41–7.33 (m, 4H, $C_6H_4OCH_3$, C_6H_5), 7.22–7.17 (m, 2H, $OC_6H_4NO_2$), 6.81 (m, 2H, $C_6H_4OCH_3$), 5.79 (d, $J_{1,2}$ 3.4 Hz, 1H, H-1^{I}, 5.61 (dd, *J* 9.7 Hz, 5.0 Hz, 1H, H-4^{II}), 5.50 (d, $J_{1,2}$ 6.9 Hz, 1H, H-1^{II}), 5.45 (s, 1H, C*H*$C_6H_4OCH_3$), 4.69 (dd, $J_{6a,6b}$ 12.1 Hz, $J_{5,6a}$ 5.5 Hz, 1H; H-6a^{II}), 4.62 (dd, $J_{6a,6b}$ 12.1 Hz, $J_{5,6b}$ 5.6 Hz, 1H, H-6b^{II}), 4.48 (dd, *J* 12.5, 9.7 Hz, 1H, H-3^{II}), 4.44–4.40 (m, 2H, H-4^{I}, H-3^{I}), 4.34–4.29 (m, 1H, H-5^{II}), 4.29–4.21 (m, 2H, H-2^{II}, H-2^{I}), 4.11 (dd, $J_{6a,6b}$ 12.6 Hz, $J_{5,6a}$ 1.3 Hz, 1H, H-6a^{I}), 3.84 (dd, $J_{6a,6b}$ 12.7 Hz, $J_{5,6b}$ 1.1 Hz, 1H, H-6b^{I}), 3.71 (s, 3H, $C_6H_4OCH_3$), 3.56–3.54 (m, 1H, H-5^{I}), 2.55 (s, 3H, $COCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5 (*C*OCH_3), 165.8 and 165.0 (*C*OC_6H_5), 161.0 ($OC_6H_4NO_2$), 160.2 ($C_6H_4OCH_3$), 153.1 (*C*ONCOCH_3), 143.0 ($OC_6H_4NO_2$), 133.9 and 133.3 (C_6H_5), 129.9 (2C, C_6H_5), 129.7 ($C_6H_4OCH_3$), 129.6 (2C, C_6H_5), 129.5 and 128.6 (C_6H_5), 128.6 (2C, C_6H_5), 128.5 (2C, C_6H_5), 127.5 (2C, $C_6H_4OCH_3$), 125.9 (2C, $OC_6H_4NO_2$), 116.5 (2C, $OC_6H_4NO_2$), 113.6 (2C, $C_6H_4OCH_3$), 101.5 (C-1^{II}), 101.0 (*C*H$C_6H_4OCH_3$), 97.3 (C-1^{I}), 77.2 (C-5^{II}), 75.7 (C-3^{II}), 75.2 (C-3^{I}), 74.8 (C-4^{I}), 70.2 (C-4^{II}), 68.7 (C-6^{I}), 64.2 (C-5^{I}), 64.0 (C-6^{II}), 60.4 (C-2^{II}), 58.3 (C-2^{I}), 55.2 ($C_6H_4OCH_3$), 24.5 (*C*O*C*H$_3$). ES-HRMS calcd for $C_{43}H_{39}N_5O_{16}$ $[H]^+$ 882.2470, found 882.2503.

4.9. *p*-Nitrophenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-2-azido-2-deoxy-4,6-*O*-*p*-methoxybenzylidene-α-D-galactopyranoside (29)

A solution of **19** (0.300 g, 0.675 mmol), ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**26**)[17] (0.453 g, 0.945 mmol) and NIS (0.334 g, 1.485 mmol) in CH_2Cl_2 (12 mL) containing 4 Å MS was stirred under N_2 at room temperature for 20 min. The mixture was cooled to −30 °C, TMSOTf (12 μL, 0.068 mmol) was added and the mixture was stirred for 1 h. The mixture was diluted with CH_2Cl_2 (100 mL), filtered through Celite and the filtrate was washed with satd aq $Na_2S_2O_3$ (50 mL), satd aq $NaHCO_3$ (50 mL) and water (50 mL), dried over $MgSO_4$ and concentrated. The crude product was purified by FC on silica gel (toluene–EtOAc 4:1) to afford **29** (0.509 g, 87%) as a white foam: R_f 0.39 (toluene–EtOAc 2:1); $[\alpha]_D^{20}$ +135 (*c* 0.57, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21–8.16 (m, 2H, $OC_6H_4NO_2$), 7.87–7.81 (m, 2H, Phth), 7.73–7.68 (m, 2H, Phth), 7.45–7.40 (m, 2H, $C_6H_4OCH_3$), 7.18–7.14 (m, 2H, $OC_6H_4NO_2$), 6.93–6.88 (m, 2H, $C_6H_4OCH_3$), 5.85–5.77 (m, 2H, H-3^{II}, H-1^{II}), 5.68 (d, $J_{1,2}$ 3.4 Hz, 1H, H-1^{I}), 5.55 (s, 1H, C*H*$C_6H_4OCH_3$), 5.26–5.20 (m, 1H, H-4^{II}), 4.54–4.51 (m, 1H, H-4^{I}, 4.50–4.42 (m, 2H, H-2^{II}, H-6a^{II}), 4.25–4.15 (m, 3H, H-3^{I}, H-6b^{II}, H-6a^{I}), 4.05–4.00 (m, 1H, H-6b^{I}), 3.98–3.92 (m, 2H, H-2^{I}, H-5^{II}), 3.82 (s, 3H, $C_6H_4OCH_3$), 3.70–3.67 (m, 1H, H-5^{I}), 2.06, 2.05 and 1.87 (3s, 9H, $COCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 170.1 and 169.4 (*C*OCH_3), 167.8 (2C, Phth), 161.0 ($OC_6H_4NO_2$), 160.1 ($C_6H_4OCH_3$), 143.0 ($OC_6H_4NO_2$), 134.3 (2C, Phth), 131.5 (2C, Phth), 130.0 ($C_6H_4OCH_3$), 127.4 (2C. $C_6H_4OCH_3$), 125.9 (2C, $OC_6H_4NO_2$), 123.6 (2C, Phth), 116.4 (2C, $OC_6H_4NO_2$), 113.6 (2C, $C_6H_4OCH_3$), 100.6 (*C*H$C_6H_4OCH_3$), 99.5 (C1^{II}), 97.3 (C-1^{I}), 76.4 (C-3^{I}), 75.0 (C-4^{I}), 72.1 (C-5^{II}), 70.7 (C-3^{II}), 68.8 (2C, C-4^{II}, C-6^{I}), 64.3 (C-5^{I}), 61.7 (C-6^{II}), 58.2 (C-2^{I}), 55.3 ($C_6H_4OCH_3$), 54.7 (C-2^{II}), 20.8, 20.7 and 20.4 ($COCH_3$). Due to very broad peaks carbonyl carbons of the phthalimido group were determined by HMBC. ES-HRMS calcd for $C_{40}H_{39}N_5O_{17}$ $[Na]^+$ 884.2239 found 884.2211.

4.10. *p*-Nitrophenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-azido-2-deoxy-α-D-galactopyranoside (31)

Acetic acid (aq 80%, 20 mL) was added to a solution of compound **27** (0.924 g, 0.903 mmol) in CH_2Cl_2 (4 mL) and the reaction mixture was stirred at room temperature overnight. The mixture was diluted with CH_2Cl_2 (100 mL) and carefully washed with satd aq $NaHCO_3$ (2 × 150 mL), dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by FC on silica gel (toluene–EtOAc 3:1→2:1) to afford **31** (0.592 g, 72%) as a white solid: R_f 0.31 (toluene–EtOAc 2:1); $[\alpha]_D^{20}$ +167 (*c* 0.15, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20–8.16 (m, 2H, $OC_6H_4NO_2$), 8.13–8.09 (m, 2H, C_6H_5), 8.03–7.97 (m, 4H, C_6H_5), 7.81–7.77 (m, 2H, C_6H_5), 7.68–7.63 (m, 1H, C_6H_5), 7.58–7.48 (m, 4H, C_6H_5), 7.47–7.34 (m, 5H, C_6H_5), 7.28–7.23 (m, 2H, C_6H_5), 7.14–7.10 (m, 2H, $OC_6H_4NO_2$), 6.02 (m, 1H, H-4^{II}), 5.93 (dd, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, 1H, H-2^{II}), 5.69–5.63 (m, 2H, H-3^{II}, H-1^{I}), 5.16 (d, $J_{1,2}$ 8.0 Hz, 1H, H-1^{II}), 4.70 (dd, $J_{6a,6b}$ 11.7 Hz, $J_{5,6a}$ 7.4 Hz, 1H, H-6a^{II}), 4.53 (dd, $J_{6a,6b}$ 11.7 Hz, $J_{5,6b}$ 4.7 Hz, 1H, H-6b^{II}), 4.46–4.42 (m, 1H, H-5^{II}), 4.35–4.32 (m, 1H, H-4^{I}), 4.25 (dd, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.1 Hz, 1H, H-3^{I}), 3.85 (dd, $J_{2,3}$ 10.5 Hz, $J_{1,2}$ 3.4 Hz, 1H, H-2^{I}), 3.77–3.73 (m, 1H, H-5^{I}), 3.72–3.66

(m, 1H, H-6a^{I}), 3.62–3.55 (m, 1H, H-6b^{I}), 3.00 (m, 1H, OH-4), 2.17 (dd, *J* 8.5, 3.8 Hz, 1H, OH-6). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 165.6, 165.5 and 165.4 (COC_6H_5), 160.9 and 143.1 ($OC_6H_4NO_2$), 133.9, 133.6, 133.5 and 133.4 (C_6H_5), 130.1 (2C, C_6H_5), 129.8 (2C, C_6H_5), 129.8 (2C, C_6H_5), 129.7 (2C, C_6H_5), 129.2, 129.1 and 128.8 (C_6H_5), 128.8 (2C, C_6H_5), 128.6 (2C, C_6H_5), 128.5 (C_6H_5), 128.4 (4C, C_6H_5), 125.9 (2C, $OC_6H_4NO_2$), 116.6 (2C, $OC_6H_4NO_2$), 102.5 (C-1^{I}), 97.3 (C-1^{II}), 78.1 (C-3^{I}) , 72.4 (C-5^{II}), 71.4 (C-3^{II}), 70.6 (C-5^{I}), 69.4 (2C, C-2^{II}, C-4^{I}), 68.2 (C-4^{II}), 62.4 (C-6^{II}), 62.4 (C-6^{I}), 58.1 (C-2^{I}). ES-HRMS calcd for $C_{46}H_{40}N_4O_{16}$ $[Na]^+$ 927.2337, found 927.2377.

4.11. *p*-Nitrophenyl 2-acetamido-4,6-di-*O*-benzoyl-2,3-*N*,*O*-carbonyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-azido-2-deoxy-α-D-galactopyranoside (32)

Acetic acid (aq 80%, 10 mL) was added to a solution of compound **28** (0.090 g, 0.102 mmol) in CH_2Cl_2 (2 mL) and the reaction mixture was stirred at room temperature for 12 h. Workup as described for **31** [Section 4.10] and purification by FC on silica gel (toluene–EtOAc 1:1) afforded **32** (0.055 g, 71%) as a white solid: R_f 0.20 (toluene–EtOAc 1:1); $[\alpha]_D^{20}$ +102 (*c* 0.49, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22–8.17 (m, 2H, $OC_6H_4NO_2$), 8.08–8.03 (m, 4H, C_6H_5), 7.66–7.61 (m, 1H, C_6H_5), 7.58–7.53 (m, 1H, C_6H_5), 7.51–7.46 (m, 2H, C_6H_5), 7.45–7.40 (m, 2H, C_6H_5), 7.15–7.10 (m, 2H, $OC_6H_4NO_2$), 5.68 (d, $J_{1,2}$ 3.5 Hz, 1H, H-1^{I}), 5.56–5.49 (m, 2H, H-4^{II}, H-1^{II}), 4.84 (dd, $J_{6a,6b}$ 12.3 Hz, $J_{5,6a}$ 3.1 Hz, 1H, H-6a^{II}), 4.68 (dd, $J_{6a,6b}$ 12.3 Hz, $J_{5,6b}$ 7.6 Hz, 1H, H-6b^{II}), 4.51 (dd, $J_{2,3}$ 12.3 Hz, $J_{3,4}$ 10.0 Hz, 1H, H-3^{II}), 4.46–4.37 (m, 2H, H-3^{I}, H-5^{II}), 4.22–4.20 (m, 1H, H-4^{I}), 4.17 (dd, $J_{2,3}$ 12.3 Hz, $J_{1,2}$ 7.2 Hz, 1H, H-2^{II}), 3.89 (dd, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 3.5 Hz, 1H, H-2^{I}), 3.81–3.75 (m, 1H, H-6a^{I}), 3.72–3.65 (m, 2H, H-6b^{I}, H-5^{I}), 3.56–3.52 (m, 1H, OH-4^{I}), 2.55 (s, 3H, COC*H*$_3$), 2.34–2.27 (m, 1H, OH-6^{I}). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3 ($COCH_3$), 166.0 and 165.2 (COC_6H_5), 160.9 ($OC_6H_4NO_2$), 152.9 ($CONCOCH_3$), 143.1 ($OC_6H_4NO_2$), 134.1 and 133.7 (C_6H_5), 130.0 (2C, C_6H_5), 129.7 (2C, C_6H_5), 129.1 (C_6H_5), 128.7 (2C, C_6H_5), 128.6 (2C, C_6H_5), 128.3 (C_6H_5), 125.9 (2C, $OC_6H_4NO_2$), 116.7 (2C, $OC_6H_4NO_2$), 100.4 (C-1^{II}), 97.3 (C-1^{I}), 76.9 (C-5^{II}), 75.6 (C-3^{II}), 75.3 (C-3^{I}), 70.6 (C-5^{I}), 69.6 (C-4^{II}), 69.1 (C-4^{I}), 63.8 (C-6^{II}), 62.5 (C-6^{I}), 60.6 (C-2^{II}), 57.9 (C-2^{I}), 24.6 ($COCH_3$). ES-HRMS calcd for $C_{35}H_{33}N_5O_{15}$ $[Na]^+$ 786.1871, found 786.1862.

4.12. *p*-Nitrophenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-2-azido-2-deoxy-α-D-galactopyranoside (33)

Acetic acid (aq 80%, 10 mL) was added to a solution of compound **29** (0.500 g, 0.580 mmol) in CH_2Cl_2 (2 mL) and the reaction mixture was stirred at room temperature for 2 d. Workup as described for **31** [Section 4.10] and FC on silica gel (toluene–EtOAc 1:1→0:1) afforded **33** (0.331 g, 77%) as a white solid: R_f 0.77 (EtOAc); $[\alpha]_D^{20}$ +213 (*c* 0.63, $CHCl_3$). ^{1}H NMR (500 MHz, CD_3CN) δ 8.20–8.14 (m, 2H, $OC_6H_4NO_2$), 7.89–7.83 (m, 2H, Phth), 7.83–7.78 (m, 2H, Phth), 7.20–7.15 (m, 2H, $OC_6H_4NO_2$), 5.78 (dd, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 9.2 Hz, 1H, H-3^{II}), 5.72–5.67 (m, 2H, H-1^{I}, H-1^{II}), 5.09 (dd, $J_{4,5}$ 10.0 Hz, $J_{3,4}$ 9.3 Hz, 1H, H-4^{II}), 4.34 (dd, $J_{2,3}$ 10.8 Hz, $J_{1,2}$ 8.5 Hz, 1H, H-2^{II}), 4.31–4.24 (m, 2H, H-4^{I}, H-6a^{II}), 4.22–4.14 (m, 2H, H-6b^{II}, H-3^{I}), 4.03 (ddd, *J* 10.1, 5.8, 2.6 Hz, 1H, H-5^{II}), 3.77 (m, 1H, H-5^{I}), 3.71 (dd, $J_{2,3}$ 10.7 Hz, $J_{1,2}$ 3.5 Hz, 1H, H-2^{I}), 3.63–3.57 (m, 2H, H-6a,b^{I}), 3.19 (dd, *J* 3.5, 0.9 Hz, 1H, OH-4^{I}), 2.84–2.79 (m, 1H, OH-6^{I}), 2.05, 2.02 and 1.81 (3s, 9H, COC*H*$_3$). ^{13}C NMR (125 MHz, CD_3CN) δ 171.6, 171.1 and 170.7 ($COCH_3$), 168.9 (2C, Phth), 162.2 and 143.9 ($OC_6H_4NO_2$), 135.7 (2C, Phth), 132.5 (2C, Phth), 126.7 (2C, $OC_6H_4NO_2$), 124.3 (2C, Phth), 117.9 (2C, $OC_6H_4NO_2$), 99.9 (C-1^{II}), 97.8 (C-1^{I}), 79.5 (C-3^{I}), 73.0 (C-5^{II}), 72.9 (C-5^{I}), 71.3 (C-3^{II}), 70.0 (C-4^{II}), 68.9 (C-4^{I}), 63.0 (C-6^{II}), 62.1 (C-6^{I}), 59.3 (C-2^{I}), 55.5 (C-2^{II}), 21.0, 20.9 and 20.8 ($COCH_3$). (Due to very broad peaks carbonyl carbons of the phthalimido group were determined by HMBC). ES-HRMS calcd for $C_{32}H_{33}N_5O_{16}$ $[Na]^+$ 766.1820, found 766.1843.

4.13. *p*-Nitrophenyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl-(1→3)-2-azido-2-deoxy-α-D-galactopyranoside (34)

To a solution of compound **19** (0.050 g, 0.113 mmol) and trichloroacetimidate **17** (0.075 g, 0.158 mmol) in dry CH_2Cl_2 (2 mL) was added 4 Å MS and the mixture was stirred under a N_2 atmosphere at room temperature for 20 min. The mixture was cooled to −20 °C, TMSOTf (2.0 μL, 0.011 mmol) was added and the reaction mixture was stirred for 1 h. Upon complete glycosylation (monitored by TLC) Et_3N (100 μL) was added, the mixture was diluted with CH_2Cl_2 (50 mL), filtered and the filtrate was washed with satd aq $NaHCO_3$ (25 mL), 1 M HCl (25 mL) and satd aq $NaHCO_3$ (25 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude product was directly used for the next step. The material was dissolved in aq acetic acid (80%, 10 mL) and the solution was stirred at room temperature overnight. Workup as described for **31** [Section 4.10] and purification by FC on silica gel (toluene–EtOAc 1:1) afforded **34** (0.042 g, 58%) as a white solid: R_f 0.32 (toluene–EtOAc 1:2); $[\alpha]_D^{20}$ +236 (*c* 0.8, CH_3CN). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25–8.20 (m, 2H, $OC_6H_4NO_2$), 7.24–7.18 (m, 2H, $OC_6H_4NO_2$), 5.79 (d, $J_{1,2}$ 3.5 Hz, 1H, H-1^{I}), 5.52 (dd, $J_{3,4}$ 3.0 Hz, $J_{4,5}$ 1.0 Hz, 1H, H-4^{II}), 5.40 (dd, $J_{2,3}$ 10.9 Hz, $J_{3,4}$ 3.2 Hz, 1H, H-3^{II}), 5.18 (d, $J_{1,2}$ 3.7 Hz, 1H, H-1^{II}), 4.54 (m, 1H, H-5^{II}), 4.32 (dd, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.1 Hz, 1H, H-3^{I}), 4.28–4.25 (m, 1H, H-4^{I}), 4.21 (dd, $J_{6a,6b}$ 11.3 Hz, $J_{5,6a}$ 6.8 Hz, 1H, H-6a^{II}), 4.16–4.11 (m, 1H, H-6b^{II}), 4.08 (dd, $J_{2,3}$ 10.8 Hz, $J_{1,2}$ 3.7 Hz, 1H, H-2^{II}), 3.97–3.89 (m, 2H, H-6a^{I}, H-5^{I}), 3.89–3.83 (m, 1H, H-6b^{I}), 3.78 (dd, $J_{2,3}$ 10.5 Hz, $J_{1,2}$ 3.4 Hz, 1H, H-2^{I}), 3.49–3.44 (m, 1H, OH-4^{I}), 2.36–2.30 (m, 1H, OH-6^{I}), 2.19, 2.08 and 2.06 (3s, 9H, COC*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 169.9 and 169.6 ($COCH_3$), 160.9 and 143.2 ($OC_6H_4NO_2$), 126.0 (2C, $OC_6H_4NO_2$), 116.7 (2C, $OC_6H_4NO_2$), 97.5 (C-1^{I}), 95.1 (C-1^{II}), 74.1 (C-3^{I}), 70.7 (C-5^{I}), 69.8 (C-3^{II}), 68.0 (C-5^{II}), 67.3 (C-4^{II}), 66.5 (C-4^{I}), 62.4 (C-6^{I}), 61.5 (C-6^{II}), 58.5 (C-2^{II}), 57.4 (C-2^{I}), 20.7 ($COCH_3$), 20.6 (2C, $COCH_3$). ES-HRMS calcd for $C_{24}H_{29}N_7O_{14}$ $[Na]^+$ 662.1670, found 662.1652.

4.14. *p*-Nitrophenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-benzoyl-2,3-*N*,*O*-carbonyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-azido-2-deoxy-α-D-galactopyranoside (36)

A mixture of acceptor **31** (0.200 g, 0.221 mmol), donor **24** (0.166 g, 0.332 mmol), and DTBMP (0.123 g, 0.597 mmol) in dry CH_2Cl_2 (4.5 mL) containing 4 Å MS was stirred under N_2 for 20 min. The mixture was then cooled to 0 °C, DMTST (0.126 mg, 0.486 mmol) was added and the reaction mixture was stirred for 1 h and during this time allowed to warm up to room temperature. The reaction was quenched by the addition of Et_3N (200 μL) and the mixture was diluted with CH_2Cl_2 (100 mL) and filtered through a pad of Celite. The filtrate was washed with 1 M HCl (50 mL), satd aq $NaHCO_3$ (50 mL), dried over $MgSO_4$ and filtered. The solvent was evaporated and the crude product was purified by FC on silica gel (toluene–EtOAc 6:1) to afford **36** (0.190 g, 64%) as a white solid: R_f 0.42 (toluene–EtOAc 4:1); $[\alpha]_D^{20}$ +120 (*c* 0.71, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16–8.10 (m, 4H, $OC_6H_4NO_2$, C_6H_5), 8.05–7.95 (m, 8H, C_6H_5), 7.81–7.77 (m, 2H, C_6H_5), 7.66–7.58 (m, 2H, C_6H_5), 7.57–7.35 (m, 14H, C_6H_5), 7.27–7.23 (m, 2H, C_6H_5), 7.17–7.13 (m, 2H, $OC_6H_4NO_2$), 6.04–6.02 (m, 1H, H-4^{II}), 5.93 (dd, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, 1H, H-2^{II}), 5.66 (dd, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.4 Hz, 1H, H-3^{II}), 5.53 (d, $J_{1,2}$ 3.5 Hz, 1H, H-1^{I}), 5.37 (dd, $J_{3,4}$ 9.7 Hz, $J_{4,5}$ 3.5 Hz, 1H, H-4^{III}),

5.10–5.06 (m, 2H, H-1^{II}, H-1^{III}), 4.71–4.55 (m, 3H, H-6a^{II}, H-6a,b^{III}), 4.44 (dd, $J_{2,3}$ 12.7 Hz, $J_{3,4}$ 9.7 Hz, 1H, H-3^{III}), 4.41–4.34 (m, 4H, H-4^{I}, H-6b^{II}, H-5^{II}, H-5^{III}), 4.17 (dd, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 2.8 Hz, 1H, H-3^{I}), 4.00–3.94 (m, 2H, H-6a^{I}, H-5^{I}), 3.82–3.75 (m, 2H, H-2^{I}, H-2^{III}), 3.72 (m, 1H, H-6b^{I}), 2.99 (d, J 1.8 Hz, 1H, OH-4^{I}), 2.49 (s, 3H, COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7 (*C*OCH$_3$), 166.0, 165.9, 165.6, 165.6, 165.3 and 165.3 (*C*OC$_6H_5$), 161.4 (OC$_6H_4NO_2$), 152.9 (*C*ONCOCH$_3$), 143.1 (OC$_6H_4NO_2$), 133.9, 133.7, 133.5 and 133.4 (C$_6H_5$), 133.3 (2C, C$_6H_5$), 130.1 (2C, C$_6H_5$), 129.9 (2C, C$_6H_5$), 129.9 (2C, C$_6H_5$), 129.8 (2C, C$_6H_5$), 129.8 (2C, C$_6H_5$), 129.7 (2C, C$_6H_5$), 129.5, 129.2, 129.2 and 128.9 (C$_6H_5$), 128.7 (2C, C$_6H_5$), 128.7 (2C, C$_6H_5$), 128.6 and 128.6 (C$_6H_5$), 128.6 (2C, C$_6H_5$), 128.6 (2C, C$_6H_5$), 128.3 (2C, C$_6H_5$), 128.3 (2C, C$_6H_5$), 125.7 (2C, OC$_6H_4NO_2$), 117.0 (2C, OC$_6H_4NO_2$), 102.3 (C-1^{III}), 100.0 (C-1^{II}), 97.8 (C-1^{I}), 78.4 (C-3^{I}), 77.9 (C-5^{III}), 74.6 (C-3^{III}), 72.0 (C-5^{II}), 71.6 (C-3^{II}), 70.9 (C-4^{III}), 69.4 (C-2^{II}), 69.3 (C-5^{I}), 68.1 (C-4^{II}), 67.6 (C-4^{I}), 66.8 (C-6^{I}), 65.1 (C-6^{III}), 62.1 (C-6^{II}), 60.6 (C-2^{III}), 57.9 (C-2^{I}), 24.6 (COCH_3). ES-HRMS calcd for $C_{69}H_{59}N_5O_{24}$ [Na]$^+$ 1364.3448, found 1364.3481.

4.15. *p*-Nitrophenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-azido-2-deoxy-α-D-galactopyranoside (37)

To a solution of **33** (0.100 g, 0.134 mmol), donor **26**[17] (0.097 g, 0.202 mmol) and NIS (0.067 g, 0.296 mmol) in dry CH_2Cl_2 (2.4 mL) was added 4 Å MS and the mixture was stirred under a N_2 atmosphere at room temperature for 20 min. The mixture was cooled to −30 °C, TMSOTf (2.4 μL, 0.013 mmol) was added and the reaction mixture was stirred for 1 h. Thereafter the mixture was diluted with CH_2Cl_2 (50 mL), filtered through Celite and the filtrate was washed with satd aq $Na_2S_2O_3$ (50 mL), satd aq $NaHCO_3$ (50 mL) and water (50 mL), dried over $MgSO_4$ and concentrated. The crude product was purified by FC on silica gel (toluene–EtOAc 2:1) to afford **37** (0.080 g, 51%) as a white solid: R_f 0.39 (toluene–EtOAc 1:1); $[\alpha]_D^{20}$ +125 (*c* 0.75, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13–8.09 (m, 2H, OC$_6H_4NO_2$), 7.91–7.83 (m, 4H, Phth), 7.81–7.77 (m, 2H, Phth), 7.75–7.71 (m, 2H, Phth), 6.99–6.96 (m, 2H, OC$_6H_4NO_2$), 5.77 (dd, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 9.1 Hz, 1H, H-3^{II}), 5.70 (dd, J 10.6, 9.1 Hz, 1H, H-3^{III}), 5.59 (d, $J_{1,2}$ 8.5 Hz, 1H, H-1^{II}), 5.36 (d, $J_{1,2}$ 8.5 Hz, 1H, H-1^{III}), 5.30 (d, $J_{1,2}$ 3.5 Hz, 1H, H-1^{I}), 5.16–5.06 (m, 2H, H-4^{II}, H-4^{III}), 4.40 (dd, $J_{2,3}$ 10.7 Hz, $J_{1,2}$ 8.5 Hz, 1H, H-2^{II}), 4.28–4.19 (m, 4H, H-6a^{III}, H-6a,b^{II}, H-2^{III}), 4.15 (dd, $J_{6a,6b}$ 12.2 Hz, $J_{5,6b}$ 2.3 Hz, 1H, H-6b^{III}), 4.12–4.09 (m, 1H, H-4^{I}), 4.05–3.99 (m, 2H, H-6a^{I}, H-3^{I}), 3.92–3.87 (m, 1H, H-5^{I}), 3.83–3.75 (m, 2H, H-5^{III}, H-5^{II}), 3.70 (dd, $J_{6a,6b}$ 10.5 Hz, $J_{5,6b}$ 7.0 Hz, 1H, H-6b^{I}), 3.61 (dd, $J_{2,3}$ 10.5 Hz, $J_{1,2}$ 3.5 Hz, 1H, H-2^{I}), 2.81 (dd, J 3.2 Hz, J 1.2 Hz, 1H, OH-4), 2.13, 2.11, 2.07, 2.02, 1.87 and 1.84 (6s, 18H, COCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.6, 170.1, 170.1, 169.4 and 169.3 (*C*OCH$_3$), 168.0 (2C, Phth), 167.8 (2C, Phth), 161.2 and 143.2 (OC$_6H_4NO_2$), 134.7 (2C, Phth), 134.4 (2C, Phth), 131.4 (2C, Phth), 131.3 (2C, Phth), 125.8 (2C, OC$_6H_4NO_2$), 123.7 (4C, Phth), 117.0 (2C, OC$_6H_4NO_2$), 98.7 (C-1^{II}), 98.2 (C-1^{III}), 97.5 (C-1^{I}), 78.2 (C-3^{I}), 72.3 (C-5^{II}), 72.1 (C-5^{III}), 70.7 (C-3^{III}), 70.4 (C-3^{II}), 69.7 (C-5^{I}), 68.9 (C-4^{III}), 68.7 (C-4^{II}), 68.3 (C-6^{I}), 67.3 (C-4^{I}), 62.0 (C-6^{III}), 61.8 (C-6^{II}), 57.8 (C-2^{I}), 54.6 (C-2^{III}), 54.4 (C-2^{II}), 20.8, 20.7, 20.6, 20.6, 20.4 and 20.4 (COCH_3). Due to very broad peaks carbonyl carbons of the phthalimido group were determined by HMBC. ES-HRMS calcd for $C_{52}H_{52}N_6O_{25}$ [Na]$^+$ 1183.2880, found 1183.2888.

4.16. *p*-Nitrophenyl 2-acetamido-4,6-di-*O*-benzoyl-2,3-*N*,*O*-carbonyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-azido-3-*O*-benzoyl-2-deoxy-α-D-galactopyranoside (38)

A solution of compound **21** (0.105 g, 0.210 mmol), donor **24** (0.136 g, 0.315 mmol) and DTBMP (0.129 g, 0.631 mmol) in 10 mL CH_2Cl_2 containing 4 Å MS was stirred under a N_2 atmosphere at room temperature for 20 min. The mixture was cooled to 0 °C, DMTST (0.136 g, 0.525 mmol) was added and the reaction mixture was stirred for 1 h and during the time allowed to warm up to room temperature. When no starting was left the reaction was quenched by the addition of Et_3N (200 μL) and diluted with CH_2Cl_2 (50 mL), filtered through Celite and the filtrate was washed with satd aq $NaHCO_3$ (25 mL), 1 M HCl (25 mL) and satd aq $NaHCO_3$ (25 mL), dried over $MgSO_4$ and filtered. The solvent was evaporated and the crude product was purified by FC on silica gel (toluene–EtOAc 5:1) to afford **38** (0.131 g, 72%) as a white solid: R_f 0.54 (toluene–EtOAc 2:1); $[\alpha]_D^{20}$ +105 (*c* 0.75, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21–8.13 (m, 4H, OC$_6H_4NO_2$, C$_6H_5$), 8.08–8.03 (m, 2H, C$_6H_5$), 7.95–7.91 (m, 2H, C$_6H_5$), 7.65–7.59 (m, 2H, C$_6H_5$), 7.57–7.45 (m, 5H, C$_6H_5$), 7.39–7.34 (m, 2H, C$_6H_5$), 7.23–7.18 (m, 2H, OC$_6H_4NO_2$), 5.67 (d, $J_{1,2}$ 3.5 Hz, 1H, H-1^{I}), 5.62 (dd, $J_{2,3}$ 11.0 Hz, $J_{3,4}$ 2.8 Hz, 1H, H-3^{I}), 5.58 (dd, J 9.7, 3.7 Hz, 1H, H-4^{II}), 5.17 (d, $J_{1,2}$ 6.5 Hz, 1H, H-1^{II}), 4.77–4.67 (m, 2H, H-6a,b^{II}), 4.55–4.48 (m, 2H, H-3^{II}, H-4^{I}), 4.43–4.38 (m, 1H, H-5^{II}), 4.22 (dd, $J_{6a,6b}$ 9.8 Hz, $J_{5,6a}$ 5.9 Hz, 1H, H-6a^{I}), 4.14–4.09 (m, 2H, H-5^{I}, H-2^{II}), 4.06 (dd, $J_{2,3}$ 11.0 Hz, $J_{1,2}$ 3.5 Hz, 1H, H-2^{I}), 3.75 (d, J 2.6 Hz, 1H, OH-4^{I}), 3.71 (dd, J 9.8, 3.4 Hz, 1H, H-6b^{I}), 2.51 (s, 3H, COCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5 (*C*OCH$_3$), 166.8, 166.0 and 165.4 (*C*OC$_6H_5$), 161.3 (OC$_6H_4NO_2$), 152.9 (*C*ONCOCH$_3$), 143.2 (OC$_6H_4$-NO$_2$), 134.2, 133.8 and 133.7 (C$_6H_5$), 130.3 (2C, C$_6H_5$), 130.2 (2C, C$_6H_5$), 129.9 (2C, C$_6H_5$), 129.6 and 129.4 (C$_6H_5$), 128.8 (2C, C$_6H_5$), 128.8 (2C, C$_6H_5$), 128.8 (3C, C$_6H_5$), 126.1 (2C, OC$_6H_4NO_2$), 116.8 (2C, OC$_6H_4NO_2$), 100.3 (C-1^{II}), 97.4 (C-1^{I}), 78.4 (C-5^{II}), 74.9 (C-3^{II}), 71.3 (C-3^{I}), 70.8 (C-4^{II}), 69.5 (C-5^{I}), 68.2 (C-4^{I}), 67.7 (C-6^{I}), 65.6 (C-6^{II}), 60.7 (C-2^{II}), 57.4 (C-2^{I}), 24.6 (COCH_3). ES-HRMS calcd for $C_{42}H_{37}N_5O_{16}$ [Na]$^+$ 890.2133, found 890.2158.

4.17. *p*-Nitrophenyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl-(1→6)-2-azido-3-benzoyl-2-deoxy-α-D-galactopyranoside (39)

A solution of compound **21** (100 mg, 0.232 mmol) and trichloroacetimidate **17** (155 mg, 0.325 mmol) in dry CH_2Cl_2 (10 mL) containing 4 Å MS was stirred under a N_2 atmosphere at room temperature for 20 min and then cooled to −20 °C. TMSOTf (4.2 μL, 0.023 mmol) was added and the reaction mixture was stirred for 1 h until no starting material was left (monitored by TLC). The mixture was diluted with CH_2Cl_2, filtered through Celite and the filtrate was washed with 1 M HCl (50 mL) and satd aq $NaHCO_3$ (50 mL), dried over $MgSO_4$ and concentrated. The crude product was purified by FC on silica gel (toluene–EtOAc 5:1) to afford the α/β (5:1) mixture **39** (0.152 g, 88%) as a white solid. The pure α anomer could be obtained by additional FC on silica gel (toluene–CH_3CN 4:1→3:1). R_f 0.43 (toluene–CH_3CN 3:1); $[\alpha]_D^{20}$ +242 (*c* 0.74, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29–8.24 (m, 2H, OC$_6H_4$-NO$_2$), 8.14–8.10 (m, 2H, C$_6H_5$), 7.65–7.61 (m, 1H, C$_6H_5$), 7.53–7.47 (m, 2H, C$_6H_5$), 7.26–7.22 (m, 2H, OC$_6H_4NO_2$), 5.84 (d, $J_{1,2}$ 3.4 Hz, 1H, H-1^{I}), 5.73 (dd, J 11.0, 3.0 Hz, 1H, H-3^{I}), 5.43–5.40 (m, 1H, H-4^{II}), 5.12 (dd, $J_{2,3}$ 11.1 Hz, $J_{3,4}$ 3.2 Hz, 1H, H-3^{II}), 4.99 (d, $J_{1,2}$ 3.5 Hz, 1H, H-1^{II}), 4.47–4.44 (m, 1H, H-4^{I}), 4.27–4.12 (m, 4H, H-5^{I}, H-5^{II}, H-2^{I}, H-6a^{I}), 4.05–3.95 (m, 2H, H-6b^{I}, H-6a^{II}), 3.72 (dd, $J_{6a,6b}$ 10.7 Hz, $J_{5,6b}$ 4.5 Hz, 1H, H-6b^{II}), 3.68 (dd, $J_{2,3}$ 11.1 Hz, $J_{1,2}$ 3.5 Hz, 1H, H-2^{II}), 2.67 (d, J 3.2 Hz, 1H, OH-4), 2.13, 2.04, and 2.03 (3s, 9H, COCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 170.1 and 169.8 (*C*OCH$_3$), 165.7 (*C*OC$_6H_5$), 160.9 and 143.6 (OC$_6H_4NO_2$), 134.1 (C$_6H_5$), 130.2 (2C, C$_6H_5$), 129.2 (C$_6H_5$), 128.9 (2C, C$_6H_5$), 126.2 (2C, OC$_6H_4NO_2$), 116.8 (2C, OC$_6H_4NO_2$), 98.0 (C-1^{II}), 97.2 (C-1^{I}), 71.3 (C-3^{I}), 70.2 (C-5^{I}), 68.6 (C-3^{II}), 67.7 (C-4^{I}), 67.6 (C-4^{II}), 67.1 (C-5^{II}), 67.1 (C-6^{II}), 61.9 (C-6^{I}), 57.6 (C-2^{II}), 57.5 (C-2^{I}), 20.9, 20.8 and 20.7 (COCH_3). ES-HRMS calcd for $C_{31}H_{33}N_7O_{15}$ [Na]$^+$ 766.1932, found 766.1945.

4.18. *p*-Nitrophenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galacto-pyranosyl-(1→3)-methyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-di-deoxy-α-D-glycero-D-galacto-2-nonulopyranosid)onate-(1→6)-2-azido-2-deoxy-α-D-galactopyranoside (40)

AgOTf (0.090 g, 0.351 mmol) in dry CH_3CN (5.25 mL) was added to a solution of compound **31** (0.106 g, 0.117 mmol) and donor **35**[19] (0.103 g, 0.176 mmol) in dry CH_2Cl_2 (3.5 mL) containing MS-3 Å. The mixture was stirred under a N_2 atmosphere at room temperature for 20 min and then cooled to −72 °C. Thereafter a solution of IBr (0.234 mL, 1 M in CH_2Cl_2) was added and the reaction mixture was stirred for 2 h. Upon complete glycosylation (monitored by TLC) DIPEA (300 μL) was added, the mixture was diluted with CH_2Cl_2 (50 mL) and filtered through silica gel. The filtrate was washed with 1 M HCl (25 mL) and satd aq $NaHCO_3$ (50 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified by FC on silica gel using Biotage to afford **40** (α: 0.097 g, β: 0.021 g 73% in total) as a white solid where only the α anomer was completely characterized: R_f 0.46 (EtOAc); $[\alpha]_D^{20}$ +118 (*c* 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25–8.20 (m, 2H, $OC_6H_4NO_2$), 8.12–8.09 (m, 2H, C_6H_5), 8.01–7.97 (m, 4H, C_6H_5), 7.80–7.77 (m, 2H, C_6H_5), 7.67–7.62 (m, 1H, C_6H_5), 7.54–7.48 (m, 4H, C_6H_5), 7.46–7.34 (m, 5H, C_6H_5), 7.27–7.20 (m, 4H, C_6H_5, $OC_6H_4NO_2$), 6.06–6.01 (m, 1H, H-4^{II}), 5.91 (dd, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 8.0 Hz, 1H, H-2^{II}), 5.67 (dd, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.5 Hz, 1H, H-3^{II}), 5.60 (d, $J_{1,2}$ 3.4 Hz, 1H, H-1^{I}), 5.42–5.36 (m, 1H, H-8^{III}), 5.34–5.28 (m, 1H, H-7^{III}), 5.21 (d, $J_{1,2}$ 8.0 Hz, 1H, H-1^{II}), 5.15–5.10 (m, 1H, N*H*COCH$_3$), 4.85 (ddd, *J* 12.0, 9.9, 4.7 Hz, 1H, H-4^{III}), 4.73–4.66 (m, 1H, H-6a^{II}), 4.48–4.39 (m, 2H, H-6b^{II}, H-5^{II}), 4.35–4.27 (m, 2H, H-9a^{III}, H-4^{I}), 4.23 (dd, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.0 Hz, 1H, H-3^{I}), 4.12–4.04 (m, 2H, H-5^{III}, H-6^{III}), 4.01 (dd, $J_{9a,9b}$ 12.4 Hz, $J_{8,9b}$ 6.3 Hz, 1H, H-9b^{III}), 3.91 (dd, $J_{6a,6b}$ 10.1 Hz, $J_{5,6a}$ 6.9 Hz, 1H, H-6a^{I}), 3.84 (m, 2H, H-5^{I}, H-2^{I}), 3.74 (s, 3H, COOC*H*$_3$), 3.61 (dd, $J_{6a,6b}$ 10.1 Hz, $J_{5,6b}$ 5.1 Hz, 1H, H-6b^{I}), 2.82 (d, *J* 1.9 Hz, 1H, OH-4^{I}), 2.50 (dd, $J_{3eq,3ax}$ 12.8 Hz, $J_{3eq,4}$ 4.7 Hz, 1H, H-3eq^{III}), 2.12 and 2.11 (2s, 6H, COC*H*$_3$), 2.03–1.99 (m, 6H, 2 × COC*H*$_3$), 1.87 (s, 3H, NH COC*H*$_3$), 1.83–1.76 (m, 1H, H-3ax^{III}). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 170.8, 170.2, 170.2 and 170.0 (*C*OCH$_3$), 168.0 (*C*OOCH$_3$), 165.9, 165.6, 165.5 and 165.4 (*C*OC$_6$H$_5$), 161.2 and 143.2 ($OC_6H_4NO_2$), 133.7, 133.5, 133.4 and 133.3 (C_6H_5), 130.0 (2C, C_6H_5), 129.8 (2C, C_6H_5), 129.8 (2C, C_6H_5), 129.7 (2C, C_6H_5), 129.2, 129.2 and 129.0 (C_6H_5), 128.7 (2C, C_6H_5), 128.6 (C_6H_5), 128.6 (2C, C_6H_5), 128.3 (4C, C_6H_5), 125.7 (2C, $OC_6H_4NO_2$), 117.2 (2C, $OC_6H_4NO_2$), 102.6 (C-1^{II}), 98.5 (C-2^{III}), 97.5 (C-1^{I}), 77.6 (C-3^{I}), 72.9 (C-6^{III}), 71.8 (C-5^{II}), 71.5 (C-3^{II}), 70.0 (C-5^{I}), 69.6 (C-2^{II}), 69.0 (C-8^{III}), 68.9 (C-4^{III}), 68.3 (C-4^{I}), 68.0 (C-4^{II}), 67.7 (C-7^{III}), 63.3 (C-6^{I}), 62.6 (C-9^{III}), 61.8 (C-6^{II}), 58.4 (C-2^{I}, 52.9 (COOCH$_3$), 49.5 (C-5^{III}), 37.6 (C-3^{III}), 23.2, 21.1, 20.9, 20.8 and 20.8 (COC*H*$_3$). ES-HRMS calcd for $C_{66}H_{67}N_5O_{28}$ $[Na]^+$ 1400.3870, found 1400.3877.

4.19. *p*-Nitrophenyl β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (1)

Thioacetic acid (1.5 mL) was added to a solution of **31** (0.183 g, 0.202 mmol) in pyridine (3 mL) and the reaction mixture was stirred at room temperature overnight. The mixture was then concentrated and co-evaporated with toluene (3 × 30 mL) and the crude product was purified by FC on silica gel (toluene–EtOAc 1:1→0:1) to afford a white solid which was directly used in the next step. The material was dissolved in MeOH (5 mL), NaOMe (200 μL, 0.5 M in MeOH) was added and the reaction mixture was stirred for 30 min. H_2O (2 mL) was added and the solution was stirred for 1 h. The solution was neutralized with Dowex H+ ion exchange resins, filtered, and concentrated. The crude product was purified by FC on RP C18 silica gel (H_2O–MeOH 1:0→1:1). After concentration and freeze drying **1** (0.072 g, 71%) was obtained as a white solid: R_f 0.73 (EtOAc–MeOH–H_2O 4:2:1). ^{1}H and ^{13}C NMR were in agreement with the data reported.[22] ES-HRMS calcd for $C_{20}H_{28}N_2O_{13}$ $[Na]^+$ 527.1489, found 527.1465.

4.20. *p*-Aminophenyl β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (2)

A mixture of compound **1** (9.1 mg, 18 μmol) and Pd–C (~3 mg) in water (5 mL) was stirred under a H_2 atmosphere for 1 h. The mixture was afterwards filtered through PTFE frits (5, 10 and 20 μm), the frits were washed with water and the combined filtrates freeze dried to afford **2** (8.0 mg, 93%) as a white solid: $[\alpha]_D^{20}$ +149 (*c* 0.53, H_2O). ^{1}H NMR (500 MHz, D_2O) δ 7.02–6.96 (m, 2H, $OC_6H_4NH_2$), 6.84–6.79 (m, 2H, $OC_6H_4NH_2$), 5.44 (d, $J_{1,2}$ 3.7 Hz, 1H, H-1^{I}), 4.53 (d, $J_{1,2}$ 7.7 Hz, 1H, H-1^{II}), 4.48 (dd, $J_{2,3}$ 11.1 Hz, $J_{1,2}$ 3.7 Hz, 1H, H-2^{I}), 4.33–4.30 (m, 1H, H-4^{I}), 4.23 (dd, $J_{2,3}$ 11.1 Hz, $J_{3,4}$ 2.9 Hz, 1H, H-3^{I}), 4.20–4.15 (m, 1H, H-5^{I}), 3.94–3.91 (m, 1H, H-4^{II}), 3.81–3.66 (m, 5H, H-6a,b^{II}, H-6a,b^{I}, H-5^{II}), 3.64 (dd, $J_{2,3}$ 9.9 Hz, $J_{3,4}$ 3.3 Hz, 1H, H-3^{II}), 3.57–3.53 (m, 1H, H-2^{II}), 2.04 (s, 3H, COC*H*$_3$). ^{13}C NMR (125 MHz, D_2O) δ 175.3 (*C*OCH$_3$), 150.2 and 142.3 ($OC_6H_4NH_2$), 119.4 (2C, $OC_6H_4NH_2$), 118.2 (2C, $OC_6H_4NH_2$), 105.4 (C-1^{II}), 98.1 (C-1^{I}), 77.7 (C-3^{I}), 75.7 (C-5^{II}), 73.2 (C-3^{II}), 72.8 (C-5^{I}), 71.3 (C-2^{II}), 69.4 (C-4^{I}), 69.3 (C-4^{II}), 61.7 (2C, C-6^{II}, C-6^{I}), 49.2 (C-2^{I}), 22.7 (COCH$_3$). ES-HRMS calcd for $C_{20}H_{29}N_2O_{11}^-$ 473.1771, found 473.1758.

4.21. *p*-Nitrophenyl β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside (3)

The azide **36** (0.130 g, 0.097 mmol) was treated as described for **1** [Section 4.19] and the crude product was purified by FC on silica gel (toluene–EtOAc 1:1→0:1) to afford the corresponding acetamide as a white solid. The material was dissolved in MeOH (4 mL) and CH_2Cl_2 (4 mL), NaOMe (16 μL, 0.5 M in MeOH) was added and the reaction mixture was stirred for 10 min and monitored by TLC (EtOAc). Additional NaOMe (200 μL, 0.5 M) was added until a precipitate appeared. MeOH (8 mL) and NaOMe (200 μL, 0.5 M) were added and the mixture was stirred for additional 20 min. The mixture was neutralized with Dowex H+ ion exchange resins, water (2 mL) was added and the mixture was filtered and concentrated. The crude product was purified by RP C18 HPLC. After evaporation and freeze drying the desired structure **3** (0.026 g, 37%) and the carbamate **42** (0.0075 g, 11%) were obtained as white solids: **3**) R_f 0.47 (EtOAc–MeOH–H_2O 4:2:1). ^{1}H and ^{13}C NMR for compound **3** were in agreement with the data reported.[3] ES-HRMS calcd for $C_{28}H_{41}N_3O_{18}$ $[H]^+$ 706.2307, found 706.2288.

4.22. *p*-Aminophenyl β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside (4)

Compound **3** (5.3 mg, 7.5 μmol) was treated as described for **2** [Section 4.20] to afford **4** (4.4 mg, 81%) as a white solid: $[\alpha]_D^{20}$ +92 (*c* 0.29, H_2O). ^{1}H NMR (500 MHz, D_2O) δ 7.00–6.96 (m, 2H, $OC_6H_4NH_2$), 6.86–6.82 (m, 2H, $OC_6H_4NH_2$), 5.43 (d, $J_{1,2}$ 3.7 Hz, 1H, H-1^{I}), 4.53–4.49 (m, 2H, H-1^{II}, H-1^{III}), 4.47 (dd, $J_{2,3}$ 11.1 Hz, $J_{1,2}$ 3.7 Hz, 1H, H-2^{I}), 4.30–4.26 (m, 2H, H-5^{I}, H-4^{I}), 4.22 (dd, $J_{2,3}$ 11.1 Hz, $J_{3,4}$ 3.0 Hz, 1H, H-3^{I}), 4.02 (dd, $J_{6a,6b}$ 11.3 Hz, $J_{5,6a}$ 3.7 Hz, 1H, H-6a^{I}), 3.94–3.91 (m, 1H, H-4^{II}), 3.89 (dd, $J_{6a,6b}$ 12.3 Hz, $J_{5,6a}$ 1.9 Hz, 1H, H-6a^{III}), 3.81–3.73 (m, 3H, H-6b^{I}, H-6a,b^{II}), 3.71–3.61 (m, 4H, H-6b^{III}, H-5^{II}, H-3^{II}, H-2^{III}), 3.54 (dd, *J* 9.9, 7.8 Hz, 1H, H-2^{II}), 3.47–3.35 (m, 3H, H-3^{III}, H-5^{III}, H-4^{III}), 2.03 and 1.88 (2s, 6H, COC*H*$_3$). ^{13}C NMR (125 MHz, D_2O) δ 175.3 and 175.0 (*C*OCH$_3$), 150.3 and 142.3 ($OC_6H_4NH_2$), 119.2 (2C, $OC_6H_4NH_2$), 118.3 (2C, $OC_6H_4NH_2$), 105.4 (C-1^{II}), 101.6 (C-1^{III}), 98.0 (C-1^{I}), 77.3 (C-3^{I}), 76.5 (C-5^{III}), 75.7 (C-5^{II}), 74.7 (C-3^{III}), 73.2 (C-3^{II}), 71.3 (C-2^{II}),

71.2 (C-4^{I}), 70.6 (C-4^{III}), 69.6 (2C(C-6^{I}, C-5^{I})), 69.3 (C-4^{II}), 61.7 (C-6^{II}), 61.4 (C-6^{III}), 56.0 (C-2^{III}), 49.1 (C-2^{I}), 22.7 and 22.6 (COCH$_3$). ES-HRMS calcd for $C_{28}H_{42}N_3O_{16}^-$ 676.2565, found 676.2581.

4.23. *p*-Nitrophenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranoside (43)

NaOMe (200 μL, 0.5 M in MeOH) was added to a solution of compound **33** (0.130 g, 0.175 mmol) in MeOH (5 mL). The solution was stirred at room temperature for 20 min and then neutralized with Dowex H$^+$ ion exchange resins, filtered and concentrated to afford a white solid, which was directly used in the next step. The residue was dissolved in EtOH (10 mL), hydrazine hydrate (127 μL, 2.63 mmol) was added and the solution was stirred at 70 °C overnight. The mixture was concentrated and co-evaporated with toluene and the crude residue was directly used for the next step. To a solution of the crude material in pyridine (2.5 mL) were added Ac_2O (2.5 ml) and cat. DMAP and the reaction mixture were stirred at room temperature for 2 h. The solution was diluted with EtOAc (50 mL) and subsequently washed with satd aq $CuSO_4$ (2 × 50 mL), water (50 mL) and satd aq $NaHCO_3$ (50 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by FC on silica gel (toluene–EtOAc 1:1) to afford **43** (0.127 g, 80%) as a white solid: R_f 0.56 (EtOAc); $[\alpha]_D^{20}$ +150 (*c* 0.25, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25–8.21 (m, 2H, $OC_6H_4NO_2$), 7.22–7.18 (m, 2H, $OC_6H_4NO_2$), 5.66 (d, $J_{1,2}$ 3.5 Hz, 1H, H-1^{I}), 5.60–5.52 (m, 2H, N*H*COCH$_3$, H-4^{I}), 5.32 (dd, *J* 10.6, 9.4 Hz, 1H, H-3^{II}), 5.15–5.08 (m, 1H, H-4^{II}), 4.99 (d, $J_{1,2}$ 8.2 Hz, 1H, H-1^{II}), 4.32–4.26 (m, 2H, H-6a^{II}, H-3^{I}), 4.20–4.09 (m, 3H, H-5^{I}, H-6b^{II}, H-6a^{I}), 4.03–3.92 (m, 2H, H-6b^{I}, H-2^{I}), 3.89–3.81 (m, 1H, H-2^{II}), 3.73 (ddd, *J* 10.0, 4.1, 2.6 Hz, 1H, H-5^{II}), 2.16 and 2.10 (2s, 6H, COC*H*$_3$), 2.06–2.02 (m, 6H, COC*H*$_3$), 1.96 and 1.91 (2s, 6H, COC*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.7, 170.4, 170.3, 169.5 and 169.3 (*C*OCH$_3$), 160.9 and 143.3 ($OC_6H_4NO_2$), 125.8 (2C, $OC_6H_4NO_2$), 116.9 (2C, $OC_6H_4NO_2$), 101.2 (C-1^{II}), 96.8 (C-1^{I}), 75.0 (C-3^{I}), 72.0 (2C, C-3^{II}, C-5^{II}), 69.0 (2C, C-4^{I}, C-5^{I}) , 68.3 (C-4^{II}), 62.3 (C-6^{I}), 61.4 (C-6^{II}), 59.1 (C-2^{I}), 55.1 (C-2^{II}), 23.4, 20.8, 20.7, 20.7, 20.6 and 20.6 (CO*C*H$_3$). ES-HRMS calcd for $C_{30}H_{37}N_5O_{17}$ [Na]$^+$ 762.2082, found 762.2105.

4.24. *p*-Nitrophenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (5)

The azide **43** (0.164 g, 0.222 mmol) was treated as described for **1** [Section 4.19] and the crude product was purified by FC on silica gel (toluene–EtOAc 1:1→0:1→EtOAc–MeOH 9:1) to afford the corresponding acetamide as a white solid. Deprotection and purification of the obtained material as described for **1** [Section 4.19] afforded compound **5** (0.079 g, 65%) as a white solid: R_f 0.58 (EtOAc–MeOH–H_2O 4:2:1). ^{1}H NMR (500 MHz, D_2O) δ 8.27–8.22 (m, 2H, $OC_6H_4NO_2$), 7.28–7.23 (m, 2H, $OC_6H_4NO_2$), 5.77 (d, $J_{1,2}$ 3.5 Hz, 1H, H-1^{I}), 4.66 (d, $J_{1,2}$ 8.4 Hz, 1H, H-1^{II}), 4.50 (dd, $J_{2,3}$ 11.0 Hz, $J_{1,2}$ 3.5 Hz, 1H, H-2^{I}), 4.30–4.27 (m, 1H, H-4^{I}), 4.23 (dd, $J_{2,3}$ 11.0 Hz, $J_{3,4}$ 2.8 Hz, 1H, H-3^{I}), 4.02–3.97 (m, 1H, H-5^{I}), 3.94–3.88 (m, 1H, H-6a^{II}), 3.80–3.65 (m, 4H, H-6b^{II}, H-2^{II}, H-6a,b^{I}), 3.61–3.55 (m, 1H, H-3^{II}), 3.51–3.43 (m, 2H, H-4^{II}, H-5^{II}, 2.05–2.01 (m, 6H, COC*H*$_3$). ^{13}C NMR (125 MHz, D_2O) δ 175.1 and 174.5 (*C*OCH$_3$), 161.9 and 143.0 ($OC_6H_4NO_2$), 126.7 (2C, $OC_6H_4NO_2$), 117.3 (2C, $OC_6H_4NO_2$), 103.2 (C-1^{II}), 96.4 (C-1^{I}), 76.8 (C-3^{I}), 76.4 (C-5^{II}), 74.1 (C-3^{II}), 72.5 (C-5^{I}), 70.4 (C-4^{II}), 69.2 (C-4^{I}), 61.6 (C-6^{I}), 61.1 (C-6^{II}), 56.3 (C-2^{II}), 48.7 (C-2^{I}), 22.9 and 22.7 (CO*C*H$_3$). ES-HRMS calcd for $C_{22}H_{31}N_3O_{13}$ [Na]$^+$ 568.1755, found 568.1732.

4.25. *p*-Aminophenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (6)

Compound **5** (5.7 mg, 10.5 μmol) was treated as described for **2** [Section 4.20] to afford **6** (5.4 mg, quant) as a white solid: $[\alpha]_D^{20}$ +106 (*c* 0.36, H_2O). ^{1}H NMR (500 MHz, D_2O) δ 6.99–6.95 (m, 2H, $OC_6H_4NH_2$), 6.83–6.79 (m, 2H, $OC_6H_4NH_2$), 5.39 (d, $J_{1,2}$ 3.7 Hz, 1H, H-1^{I}), 4.64 (d, $J_{1,2}$ 8.4 Hz, 1H, H-1^{II}), 4.40 (dd, $J_{2,3}$ 11.1 Hz, $J_{1,2}$ 3.6 Hz, 1H, H-2^{I}), 4.30–4.28 (m, 1H, H-4^{I}), 4.18–4.13 (m, 2H, H-3^{I}, H-5^{I}), 3.91 (dd, $J_{6a,6b}$ 12.3 Hz, $J_{5,6a}$ 1.7 Hz, 1H, H-6a^{II}), 3.79–3.70 (m, 4H, H-6b^{II}, H-2^{II}, H-6a,b^{I}), 3.60–3.55 (m, 1H, H-3^{II}, 3.51–3.42 (m, 2H, H-4^{II}, H-5^{II}), 2.06 and 2.03 (2s, 6H, COC*H*$_3$). ^{13}C NMR (125 MHz, D_2O) δ 175.1 and 174.4 (*C*OCH$_3$), 150.2 and 142.3 ($OC_6H_4NH_2$), 119.4 (2C, $OC_6H_4NH_2$), 118.2 (2C, $OC_6H_4NH_2$), 103.1 (C-1^{II}), 98.0 (C-1^{I}), 77.1 (C-3^{I}), 76.3 (C-5^{II}), 74.1 (C-3^{II}), 71.8 (C-5^{I}), 70.4 (C-4^{II}), 69.3 (C-4^{I}), 61.7 (C-6^{I}), 61.1 (C-6^{II}), 56.3 (C-2^{II}), 49.0 (C-2^{I}), 22.9 and 22.7 (CO*C*H$_3$). ES-HRMS calcd for $C_{22}H_{33}N_3O_{11}$ [Na]$^+$ 538.2013, found 538.2003.

4.26. *p*-Nitrophenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-4-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranoside (44)

To a solution of compound **37** (0.141 g, 0.121 mmol) in CH_2Cl_2 (2 mL) and MeOH (8 mL) was added NaOMe (400 μL, 0.5 M in MeOH). The solution was stirred at room temperature for 20 min and then neutralized with Dowex (H$^+$), filtered and concentrated to afford a white solid, which was directly used for the next step. The material was dissolved in EtOH (12 mL), hydrazine hydrate (117 μL, 2.42 mmol) was added and the solution was stirred at 70 °C overnight. The mixture was concentrated and co-evaporated with toluene and the crude residue was directly used for the next step. To a solution of the crude material in pyridine (2.5 mL) were added Ac_2O (2.5 mL) and cat. DMAP and the reaction mixture were stirred at room temperature for 2 h. The solution was diluted with EtOAc (50 mL) and subsequently washed with satd aq $CuSO_4$ (2 × 50 mL), water (50 mL) and satd aq $NaHCO_3$ (50 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The residue was purified by FC on silica gel (EtOAc) to afford **44** (0.115 g, 93%) as a white solid: R_f 0.47 (EtOAc–MeOH 20:1); $[\alpha]_D^{20}$ +69 (*c* 0.43, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31–8.26 (m, 2H, $OC_6H_4NO_2$), 7.24–7.19 (m, 2H, $OC_6H_4NO_2$), 5.91 (d, *J* 8.3 Hz, 1H, N*H*COCH$_3$^{III}), 5.61–5.56 (m, 2H, H-1^{I}, N*H*COCH$_3$^{II}), 5.52–5.49 (m, 1H, H-4^{I}), 5.38–5.32 (m, 1H, H-3^{III}), 5.31–5.25 (m, 1H, H-3^{II}), 5.19–5.13 (m, 1H, H-4^{II}), 4.97–4.88 (m, 2H, H-1^{II}, H-4^{III}), 4.73 (d, $J_{1,2}$ 8.1 Hz, 1H, H-1^{III}), 4.41 (dd, $J_{6a,6b}$ 12.3 Hz, $J_{5,6a}$ 2.3 Hz, 1H, H-6a ^{II}), 4.28 (dd, *J* 10.6, 3.3 Hz, 1H, H-3^{I}), 4.20–4.15 (m, 2H, H-6a^{III}, H-5^{I}), 4.12–4.06 (m, 2H, H-6b^{II}, H-6b^{III}), 3.94–3.86 (m, 2H, H-2^{II}, H-2^{I}), 3.81 (dd, $J_{6a,6b}$ 10.4 Hz, $J_{5,6a}$ 5.2 Hz, 1H, H-6a^{I}), 3.75–3.70 (m, 1H, H-5^{II}), 3.65 (ddd, *J* 9.9, 4.7, 2.5 Hz, 1H, H-5^{III}), 3.55–3.46 (m, 2H, H-2^{III}, H-6b^{I}), 2.13, 2.12 and 2.05 (3s, 9H, COC*H*$_3$), 2.04 (m, 6H, COC*H*$_3$), 2.01, 2.00, 1.96 and 1.89 (4s, 12H, COC*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 170.9, 170.6, 170.6, 170.4, 170.3, 169.4, 169.4 and 169.3 (*C*OCH$_3$), 161.3 and 143.5 ($OC_6H_4NO_2$), 126.1 (2C, $OC_6H_4NO_2$), 117.4 (2C, $OC_6H_4NO_2$), 101.2 (C-1^{II}), 99.9 (C-1^{III}), 97.5 (C-1^{I}), 74.7 (C-3^{I}), 72.2 (C-3^{II}), 71.9 (C-5^{II}), 71.8 (C-5^{III}), 71.7 (C-3^{III}), 69.9 (C-5^{I}), 69.1 (C-4^{I}), 68.7 (C-4^{III}), 68.2 (C-4^{II}), 66.9 (C-6^{I}), 62.0 (C-6^{III}), 61.2 (C-6^{II}), 59.4 (C-2^{I}), 55.2 (C-2^{III}), 54.8 (C-2^{II}), 23.4, 23.3 and 20.9 (CO*C*H$_3$), 20.7 (2C, CO*C*H$_3$), 20.7, 20.7, 20.6 and 20.6 (CO*C*H$_3$). ES-HRMS calcd for $C_{42}H_{54}N_6O_{24}$ [Na]$^+$ 1049.3087, found 1049.3119.

4.27. *p*-Nitrophenyl-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside (7)

The azide **44** (0.110 g, 0.107 mmol) was treated as described for **1** [Section 4.19] and the crude mixture was purified by FC on silica gel (EtOAc–MeOH 1:0→9:1) to afford the corresponding acetamide as a white solid. Deprotection as described for **1** [Section 4.19] and purification by FC on RP C18 silica gel (H_2O–MeOH 1:0→2:1) afforded **7** (0.042 g, 52%) as a white solid: R_f 0.39 (EtOAc–MeOH–H_2O 4:2:1). ^{1}H NMR was in agreement with the data reported.[1] The published ^{13}C NMR showed differences to the one reported: ^{13}C NMR (125 MHz, D_2O) δ 175.1, 174.8 and 174.5 ($COCH_3$), 162.1 and 143.1 ($OC_6H_4NO_2$), 126.8 (2C, $OC_6H_4NO_2$), 117.4 (2C, $OC_6H_4NO_2$), 103.2 (C-1^{II}), 101.8 (C-1^{III}), 96.7 (C-1^{I}), 76.5 (2C, C-5^{III}, C-3^{I}), 76.4 (C-5^{II}), 74.7 (C-3^{III}), 74.1 (C-3^{II}), 71.3 (C-5^{I}), 70.6 (C-4^{III}), 70.4 (C-4^{II}), 69.8 (C-6^{I}), 69.3 (C-4^{I}), 61.4 (C-6^{III}), 61.2 (C-6^{II}), 56.3 (C-2^{II}), 56.0 (C-2^{III}), 48.7 (C-2^{I}), 22.9, 22.7 and 22.6 ($COCH_3$). ES-HRMS calcd for $C_{30}H_{44}N_4O_{18}$ $[Na]^+$ 771.2548, found 771.2559.

4.28. *p*-Aminophenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside (8)

Compound **7** (7.8 mg, 10.4 μmol) was treated as described for **2** [Section 4.20] to afford **8** (7.5 mg, quant) as a white solid: $[\alpha]_D^{20}$ +59 (*c* 0.33, H_2O). ^{1}H NMR (500 MHz, D_2O) δ 6.99–6.94 (m, 2H, $OC_6H_4NH_2$), 6.86–6.82 (m, 2H, $OC_6H_4NH_2$), 5.38 (d, $J_{1,2}$ 3.7 Hz, 1H, H-1^{I}), 4.63 (d, $J_{1,2}$ 8.4 Hz, 1H, H-1^{II}), 4.50 (d, $J_{1,2}$ 8.5 Hz, 1H, H-1^{III}), 4.39 (dd, $J_{2,3}$ 11.1 Hz, $J_{1,2}$ 3.6 Hz, 1H, H-2^{I}), 4.29–4.24 (m, 2H, H-4^{I}, H-5^{I}), 4.15 (dd, $J_{3,4}$ 11.1 Hz, $J_{3,4}$ 2.8 Hz, 1H, H-3^{I}), 4.02 (dd, $J_{6a,6b}$ 11.3 Hz, $J_{5,6a}$ 3.4 Hz, 1H, H-6a^{I}), 3.93–3.87 (m, 2H, H-6a^{II}, H-6a^{III}), 3.79–3.61 (m, 5H, H-6b^{II}, H-6b^{I}, H-2^{II}, H-6b^{III}, H-2^{III}), 3.59–3.54 (m, 1H, H-3^{II}), 3.50–3.37 (m, 5H, H-4^{II}, H-3^{III}, H-5^{II}, H-5^{III}, H-4^{III}), 2.05, 2.03 and 1.88 (3s, 9H, $COCH_3$). ^{13}C NMR (125 MHz, D_2O) δ 175.1, 175.0 and 174.4 ($COCH_3$), 150.4 and 142.1 ($OC_6H_4NH_2$), 119.2 (2C, $OC_6H_4NH_2$), 118.4 (2C, $OC_6H_4NH_2$), 103.1 (C-1^{II}), 101.6 (C-1^{III}), 97.9 (C-1^{I}), 76.8 (C-3^{I}), 76.6, 76.3 (C-5^{II}, C-5^{III}), 74.7 (C-3^{III}), 74.1 (C-3^{II}), 71.1 (C-5^{I}), 70.6 (C-4^{III}), 70.4 (C-4^{II}), 69.8 (C-6^{I}), 69.6 (C-4^{I}), 61.4 (C-6^{III}), 61.1 (C-6^{II}), 56.3 (C-2^{II}), 56.1 (C-2^{III}), 48.9 (C-2^{I}), 22.9, 22.8 and 22.7 ($COCH_3$). ES-HRMS calcd for $C_{30}H_{45}N_4O_{16}^-$ 717.2831, found 717.2819.

4.29. *p*-Nitrophenyl 2-acetamido-2-deoxy-α-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (9)

The azide **34** (0.087 g, 0.136 mmol) was treated as described for **1** [Section 4.19] and the crude product was purified by FC on silica (EtOAc–MeOH 9:1) to afford the corresponding acetamide as a white solid. Deprotection of the obtained material as described for **3** [Section 4.21] and purification of the crude product by FC on RP C18 silica gel (H_2O–MeOH 1:0→1:1) afforded **9** (0.044 g, 59%) as a white solid: R_f 0.69 (EtOAc–MeOH–H_2O 4:2:1). ^{1}H and ^{13}C NMR were in agreement with the data reported.[1] ES-HRMS calcd for $C_{22}H_{31}N_3O_{13}$ $[Na]^+$ 568.1755, found 568.1762.

4.30. *p*-Aminophenyl 2-acetamido-2-deoxy-α-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (10)

Compound **9** (5.0 mg, 9.2 μmol) was treated as described for **2** [Section 4.20] to afford **10** (4.8 mg, quant) as a white solid: $[\alpha]_D^{20}$ +231 (*c* 0.25, H_2O). ^{1}H NMR (500 MHz, D_2O) δ 7.02–6.97 (m, 2H, $OC_6H_4NH_2$), 6.84–6.79 (m, 2H, $OC_6H_4NH_2$), 5.46 (d, $J_{1,2}$ 3.8 Hz, 1H, H-1^{I}), 5.12 (d, $J_{1,2}$ 3.8 Hz, 1H, H-1^{II}, 4.53 (dd, $J_{2,3}$ 11.1 Hz, $J_{1,2}$ 3.8 Hz, 1H, H-2^{I}), 4.26–4.21 (m, 2H, H-4^{I}, H-2^{II}), 4.17 (dd, $J_{2,3}$ 11.1 Hz, $J_{3,4}$ 3.1 Hz, 1H, H-3^{I}), 4.13–4.09 (m, 1H, H-5^{I}), 4.03–4.01 (m, 1H, H-4^{II}), 3.92–3.88 (m, 1H, H-5^{II}), 3.82–3.78 (m, 3H, H-3^{II}, H-6a,b^{II}), 3.75–3.71 (m, 2H, H-6a,b^{I}), 2.08 and 2.05 (2s, 6H, $COCH_3$). ^{13}C NMR (125 MHz, D_2O) δ 175.3 and 175.2 ($COCH_3$), 150.0 and 142.4 ($OC_6H_4NH_2$), 119.6 (2C, $OC_6H_4NH_2$), 118.2 (2C, $OC_6H_4NH_2$), 98.1 (C-1^{I}), 94.1 (C-1^{II}), 72.8 (C-3^{I}), 72.2 (C-5^{I}), 72.0 (C-5^{II}), 69.0 (C-4^{II}), 68.4 (C-3^{II}), 65.1 (C-4^{I}), 61.8 (C-6^{I}), 61.6 (C-6^{II}), 50.1 (C-2^{II}), 48.6 (C-2^{I}), 22.7 (2C, $COCH_3$). ES-HRMS calcd for $C_{22}H_{32}N_3O_2^-$ 514.2037, found 514.2044.

4.31. *p*-Nitrophenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside (11)

The azide **38** (0.099 g, 0.114 mmol) was treated as described **1** [Section 4.19] and the crude product was purified by FC on silica gel (toluene–EtOAc 1:1→0:1) to afford the corresponding acetamide as a white solid. Deprotection of the obtained material and purification as described for **3** [Section 4.21] gave the desired structure **11** (0.024 g, 39%) and the corresponding carbamate (0.0046 g, 7%) as white solids. **11**) R_f 0.62 (EtOAc–MeOH–H_2O 4:2:1). ^{1}H and ^{13}C NMR was in agreement with the data reported.[1] ES-HRMS calcd for $C_{22}H_{31}N_3O_{13}$ $[Na]^+$ 568.1755, found 568.1752.

4.32. *p*-Aminophenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside (12)

Compound **11** (3.9 mg, 7.2 μmol) was treated as described for **2** [Section 4.20] to afford **12** (3.0 mg, 81%) as a white solid: $[\alpha]_D^{20}$ +114 (*c* 0.52, H_2O). ^{1}H NMR (500 MHz, D_2O) δ 6.99–6.95 (m, 2H, $OC_6H_4NH_2$), 6.85–6.81 (m, 2H, $OC_6H_4NH_2$), 5.42 (d, $J_{1,2}$ 3.7 Hz, 1H, H-1^{I}), 4.51 (d, $J_{1,2}$ 8.5 Hz, 1H, H-1^{II}), 4.29 (dd, $J_{2,3}$ 11.0 Hz, $J_{1,2}$ 3.7 Hz, 1H, H-2^{I}), 4.25–4.21 (m, 1H, H-5^{I}), 4.09 (dd, $J_{2,3}$ 11.0 Hz, $J_{3,4}$ 3.2 Hz, 1H, H-3^{I}), 4.05–4.00 (m, 2H, H-4^{I}, H-6a^{I}), 3.90 (dd, $J_{6a,6b}$ 12.3 Hz, $J_{5,6a}$ 1.6 Hz, 1H, H-6a^{II}), 3.77 (dd, $J_{6a,6b}$ 11.3 Hz, $J_{5,6b}$ 7.3 Hz, 1H, H-6b^{I}), 3.71–3.63 (m, 2H, H-6b^{II}, H-2^{II}), 3.49–3.44 (m, 1H, H-3^{II}), 3.44–3.36 (m, 2H, H-5^{II}, H-4^{II}), 2.05 and 1.91 (2s, 6H, $COCH_3$). ^{13}C NMR (125 MHz, D_2O) δ 175.4 and 175.1 ($COCH_3$), 150.4 and 142.4 ($OC_6H_4NH_2$), 119.4 (2C, $OC_6H_4NH_2$), 118.3 (2C, $OC_6H_4NH_2$), 101.6 (C-1^{II}), 98.0 (C-1^{I}), 76.6 (C-5^{II}), 74.7 (C-3^{II}), 71.1 (C-5^{I}), 70.6 (C-4^{II}), 69.4 (C-6^{I}), 69.2 (C-4^{I}), 68.1 (C-3^{I}), 61.4 (C-6^{II}), 56.1 (C-2^{II}), 50.4 (C-2^{I}), 22.7 and 22.6 ($COCH_3$). ES-HRMS calcd for $C_{22}H_{33}N_3O_{11}$ $[Na]^+$ 538.2013, found 538.2037.

4.33. *p*-Nitrophenyl 2-acetamido-2-deoxy-α-D-galactopyranosyl-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside (13)

The azide **39** (0.090 g, 0.121 mmol) was treated and the crude product was purified as described for **1** [Section 4.19] to afford the corresponding acetamide as a white solid. Deprotection and purification of the obtained material as described for **1** [Section 4.19] afforded compound **13** (0.049 g, 74%) as a white solid: R_f 0.56 (EtOAc–MeOH–H_2O 4:2:1). ^{1}H and ^{13}C NMR was in agreement with the data reported.[1] ES-HRMS calcd for $C_{22}H_{31}N_3O_{13}$ $[Na]^+$ 568.1755, found 568.1740.

4.34. *p*-Aminophenyl 2-acetamido-2-deoxy-α-D-galactopyranosyl-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside (14)

Compound **13** (6.3 mg, 12 μmol) was treated as described for **2** [Section 4.20] to afford **14** (6.0 mg, quant) as a white solid: $[\alpha]_D^{20}$ +221 (*c* 0.47, H_2O). ^{1}H NMR (500 MHz, D_2O) δ 7.01–6.96 (m, 2H, $OC_6H_4NH_2$), 6.84–6.79 (m, 2H, $OC_6H_4NH_2$), 5.55 (d, $J_{1,2}$ 3.7 Hz, 1H, H-1^{I}), 4.81 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1^{II}), 4.32 (dd, $J_{2,3}$ 11.0 Hz, $J_{1,2}$ 3.7 Hz, 1H, H-2^{I}), 4.26 (m, 1H, H-5^{I}), 4.14–4.05 (m, 3H, H-3^{I}, H-2^{II}, H-4^{I}), 3.88–3.86 (m, 1H, H-4^{I}), 3.85–3.79 (m, 2H, H-5^{II}, H-6a^{I}), 3.73–3.65 (m, 3H, H-6a,b^{II}, H-6b^{I}), 3.59 (dd, *J* 10.9, 3.0 Hz, 1H, H-3^{II}), 2.05 and 1.94 (2s, 6H, $COCH_3$). ^{13}C NMR (125 MHz, D_2O) δ

175.4 and 175.2 ($COCH_3$), 149.8 and 142.2 ($OC_6H_4NH_2$), 119.0 (2C,$OC_6H_4NH_2$), 118.1 (2C, $OC_6H_4NH_2$), 97.1 (C-1^{II}), 97.0 (C-1^{I}), 71.4 (C-5^{II}), 70.5 (C-5^{I}), 69.5 (C-4^{I}), 69.2 (C-4^{II}), 68.6 (C-3^{II}), 68.4 (C-3^{I}), 67.6 (C-6^{I}), 61.8 (C-6^{II}), 50.4 (2C, C-2^{I}, C-2^{II}), 22.6 and 22.6 ($COCH_3$). ES-HRMS calcd for $C_{22}H_{33}N_3O_{11}$ $[Na]^+$ 538.2013, found 538.2037.

4.35. *p*-Nitrophenyl β-D-galactopyranosyl-(1→3)-(5-acetamido-3,5-di-deoxy-α-D-glycero-D-galacto-2-nonulopyranosidonic) acid-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside (15)

The azide **40** (0.090 g, 0.065 mmol) was treated as described for **1** [Section 4.19] and the crude product was purified by FC on silica (toluene–EtOAc 1:1→0:1→EtOAc–MeOH 9:1) to afford the corresponding acetamide as a white solid. The material was dissolved in MeOH (5 mL) and NaOMe (200 μL, 0.5 M in MeOH) was added and the reaction mixture was stirred for 1 h. The solution was neutralized with Dowex H+ ion exchange resins, filtered and concentrated and then taken in H_2O (4 mL), a pH 12 was adjusted using 1 M NaOH and the reaction mixture was stirred for 1 h. Thereafter the solution was neutralized with 1 M HCl and satd aq $NaHCO_3$ and then concentrated. The crude product was purified by FC on RP C18 silica gel (H_2O). After evaporation and freeze drying **15** (0.036 g, 69%) was obtained as a white solid: R_f 0.81 (EtOAc–MeOH–H_2O 3:3:1 + AcOH); $[\alpha]_D^{20}$ +100 (*c* 0.29, H_2O). ^1H NMR (500 MHz, D_2O) δ 8.31–8.25 (m, 2H, $OC_6H_4NO_2$), 7.31–7.26 (m, 2H, $OC_6H_4NO_2$), 5.77 (d, $J_{1,2}$ 3.6 Hz, 1H, H-1^{I}), 4.58–4.52 (m, 2H, H-2^{I}, H-1^{II}), 4.36–4.34 (m, 1H, H-4^{I}), 4.28 (dd, $J_{2,3}$ 11.1 Hz, $J_{3,4}$ 3.0 Hz, 1H, H-3^{I}), 4.12 (m, 1H, H-5^{I}), 3.94–3.91 (m, 1H, H-4^{II}), 3.86 (dd, $J_{6a,6b}$ 10.6 Hz, $J_{5,6a}$ 7.6 Hz, 1H, H-6a^{I}), 3.82–3.53 (m, 13H), 2.55 (dd, $J_{3eq,3ax}$ 12.4 Hz, $J_{3eq,4}$ 4.7 Hz, 1H, H-3eq^{III}), 2.02, 2.01 (2s, 6H, $COCH_3$), 1.50–1.44 (m, 1H, H-3ax^{III}). ^{13}C NMR (125 MHz, D_2O) δ 175.7 and 175.3 ($COCH_3$), 173.9 (*C*OOH), 162.0 and 143.2 ($OC_6H_4NO_2$), 126.7 (2C, $OC_6H_4NO_2$), 117.7 (2C, $OC_6H_4NO_2$), 105.5 (C-1^{II}), 100.9 (C-2^{III}), 96.8 (C-1^{I}), 77.5 (C-3^{I}), 75.7, 73.2 (2C), 72.3, 71.3, 71.1 (C-5^{I}), 69.3 (C-4^{II}), 69.0 (C-4^{I}), 68.8, 68.7, 63.7 (C-6^{I}), 63.1 (C-6^{II}), 61.7 (C-9^{III}), 52.5, 48.9 (C-2^{I}), 40.9 (C-3^{III}), 22.7 and 22.6 ($COCH_3$). ES-HRMS calcd for $C_{31}H_{45}N_3O_{21}$ $[Na]^+$ 818.2443, found 818.2465.

4.36. *p*-Aminophenyl β-D-galactopyranosyl-(1→3)-(5-acetamido-3,5-di-deoxy-α-D-glycero-D-galacto-2-nonulopyranosidonic) acid-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside (16)

Compound **15** (5.7 mg, 7.2 μmol) was treated as described for **2** [Section 4.20] to afford **16** (5.0 mg, 91%) as a white solid: $[\alpha]_D^{20}$ +80 (*c* 0.33, H_2O). ^1H NMR (500 MHz, D_2O) δ 7.03–6.99 (m, 2H, $OC_6H_4NH_2$), 6.85–6.81 (m, 2H, $OC_6H_4NH_2$), 5.35 (d, $J_{1,2}$ 3.7 Hz, 1H, H-1^{I}), 4.52 (d, $J_{1,2}$ 7.8 Hz, 1H, H-1^{II}), 4.45 (dd, $J_{2,3}$ 11.1 Hz, $J_{1,2}$ 3.7 Hz, 1H, H-2^{I}), 4.36–4.33 (m, 1H, H-4^{I}), 4.30 (dd, *J* 7.8, 4.6 Hz, 1H), 4.20 (dd, $J_{2,3}$ 11.1 Hz, $J_{3,4}$ 3.0 Hz, 1H, H-3^{I}), 3.93–3.86 (m, 2H), 3.82–3.72 (m, 5H), 3.69–3.52 (m, 8H), 2.68 (dd, $J_{3ax,3eq}$ 12.5 Hz, $J_{3eq,4}$ 4.6 Hz, 1H, H-3eq^{III}), 2.05 and 2.02 (2s, 6H, $COCH_3$), 1.60–1.54 (m, 1H, H-3ax^{III}). ^{13}C NMR (125 MHz, D_2O) δ 175.7 and 175.3 ($COCH_3$), 174.1 (*C*OOH), 150.2 and 142.6 ($OC_6H_4NH_2$), 120.2 (2C, $OC_6H_4NH_2$), 118.2 (2C, $OC_6H_4NO_2$), 105.5 (C-1^{II}), 100.9 (C-2^{III}), 98.7 (C-1^{I}), 77.8 (C-3^{I}), 75.7, 73.3, 73.2, 72.3, 71.3, 70.6, 69.3, 69.2 (C-4^{I}), 68.9, 68.8, 64.0, 63.1, 61.7, 52.6, 49.2 (C-2^{I}), 41.0 (C-3^{III}), 22.7 and 22.6 ($COCH_3$). ES-HRMS calcd for $C_{31}H_{47}N_3O_{19}$ $[Na]^+$ 788.2701, found 788.2677.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2011.03.036.

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