Tetrahedron: *Asymmetry* 20 (2009) 808–820

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Synthesis of three regioisomers of the pentasaccharide part of the Skp1 glycoprotein of *Dictyostelium discoideum*

Zoltán B. Szabó [a], Mihály Herczeg [a], Anikó Fekete [a], Gyula Batta [b], Anikó Borbás [a], András Lipták [a,b,*], Sándor Antus [a,c]

[a] *Research Group for Carbohydrates of the Hungarian Academy of Sciences, University of Debrecen, PO Box 94, H-4010, Hungary*
[b] *Department of Biochemistry, University of Debrecen, PO Box 55, H-4010, Hungary*
[c] *Department of Organic Chemistry, University of Debrecen, PO Box 20, H-4010, Hungary*

ARTICLE INFO

Article history:
Received 2 February 2009
Accepted 12 February 2009
Available online 1 April 2009

This paper is dedicated to Professor George Fleet, on the occasion of his 65th birthday

ABSTRACT

Three regioisomers of the linear pentasaccharide part of the Skp1 glycoprotein, found in *Dictyostelium discoideum*, were prepared in the form of (2-trimethylsilyl)ethyl glycosides by means of 2+3 block syntheses using the disaccharide donor at the non-reducing end, and three different trisaccharide acceptors at the reducing end. Fucosylation of (2-trimethylsilyl)ethyl 3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-*N*Phth-β-D-glucopyranoside with different fucosyl donors carrying an *O*-(2-naphthyl)methyl ether as a temporary-protecting group at positions C2, C3 or C4 gave rise to the protected core trisaccharides. After selective removal of the (2-naphthyl)methyl group, the resulting acceptors were glycosylated with the α(1→6) linked digalactosyl donor to yield the respective three regioisomeric pentasaccharides. Transformation of the phthalimido moiety into an *N*-acetyl group, followed by catalytic hydrogenation of the reducible-protecting groups furnished the free target pentasaccharides, which should be able to assist during the elucidation of the exact structure of the natural pentasaccharide.

1. Introduction

Skp1 protein, a part of an enzyme complex SCF, named as an acronym of the participating proteins,[1] is expressed ubiquitously in eukaryotes to facilitate the selection of other proteins for specific posttranslational modifications. Skp1, found in the soil-living amoeba *Dictyostelium discoideum,* is located in the cytoplasm and involved in the ubiquitination of certain cell cycle and nutritional regulatory processes. It was found that the 143th amino acid (hydroxyproline, HyPro) of Skp1 is glycosylated with a galactose- and a fucose-containing oligosaccharide, which is unusual for a cytoplasmic protein. This glycan side-chain on a cytoplasmic/nuclear protein suggested a novel glycosylation pathway in the cytoplasm; supposedly the oligosaccharide was formed via complex glycosylation. The analysis of the saccharide chain revealed that it is a linear pentasaccharide; West et al. proposed the following structure:[1] Galpα(1→6)Galpα(1→?)Fucα(1→2)Galpβ(1→3)GlcpNAc(1→?)HyPro (Fig. 1). The trisaccharide part (core) at the reducing end [Fucα(1→2)Galpβ(1→3)GlcpNAc(1→] has been known as the blood group type H antigen, but the Galpα(1→6)Galpα(1→ cap structure has not been found elsewhere. The exact linkage of the Galpα(1→6)Galpα(1→?) (**E** + **D**)[†] disaccharide at the [Fucα(1→2)Galpβ(1→3)GlcNAc] (**C** + **B** + **A**) core-trisaccharide could not be determined by the authors.[1–4] It is also supposed that the glycosylation of the core is carried out in the cytoplasm and not in the nucleus of the cell. To investigate the biology of the glycosylation process of the core region, the structure of the pentasaccharide must be determined as the first step.

2. Results and discussion

We proposed that the required structural elucidation could be solved in a synthetic manner, thus we planned to prepare the three possible regioisomeric pentasaccharides in the form of glycosides (compounds **1**, **2** and **3**, Scheme 1). Meanwhile, West et al. reported[5] the determination of the linkage between the digalactosyl cap structure and the core trisaccharide. In their experiments, model compounds acting as substrates were used and enzymatic synthesis showed that a galactose unit is placed on the 1-*O*Bn-α-L-Fucp moiety. Co-chromatography with model compounds proved that galactose was attached to the 3-position of L-fucose. We thought that a more precise way to determine the exact linkage

* Corresponding author. Tel.: +36 52512900/22256; fax: +36 52512900/22342.
E-mail address: liptaka@puma.unideb.hu (A. Lipták).

† The monossacharide constituents of the isomeric pentasaccharides are denoted with capital letters starting with '**A**' from the reducing end.

0957-4166/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2009.02.040

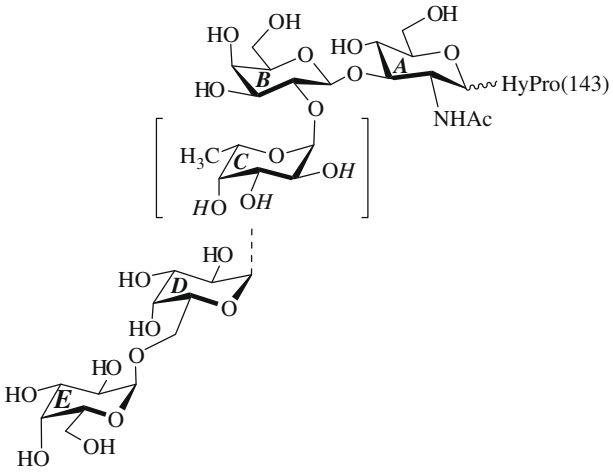


Figure 1. Structure of the pentasaccharide part of the Skp1 glycoprotein.

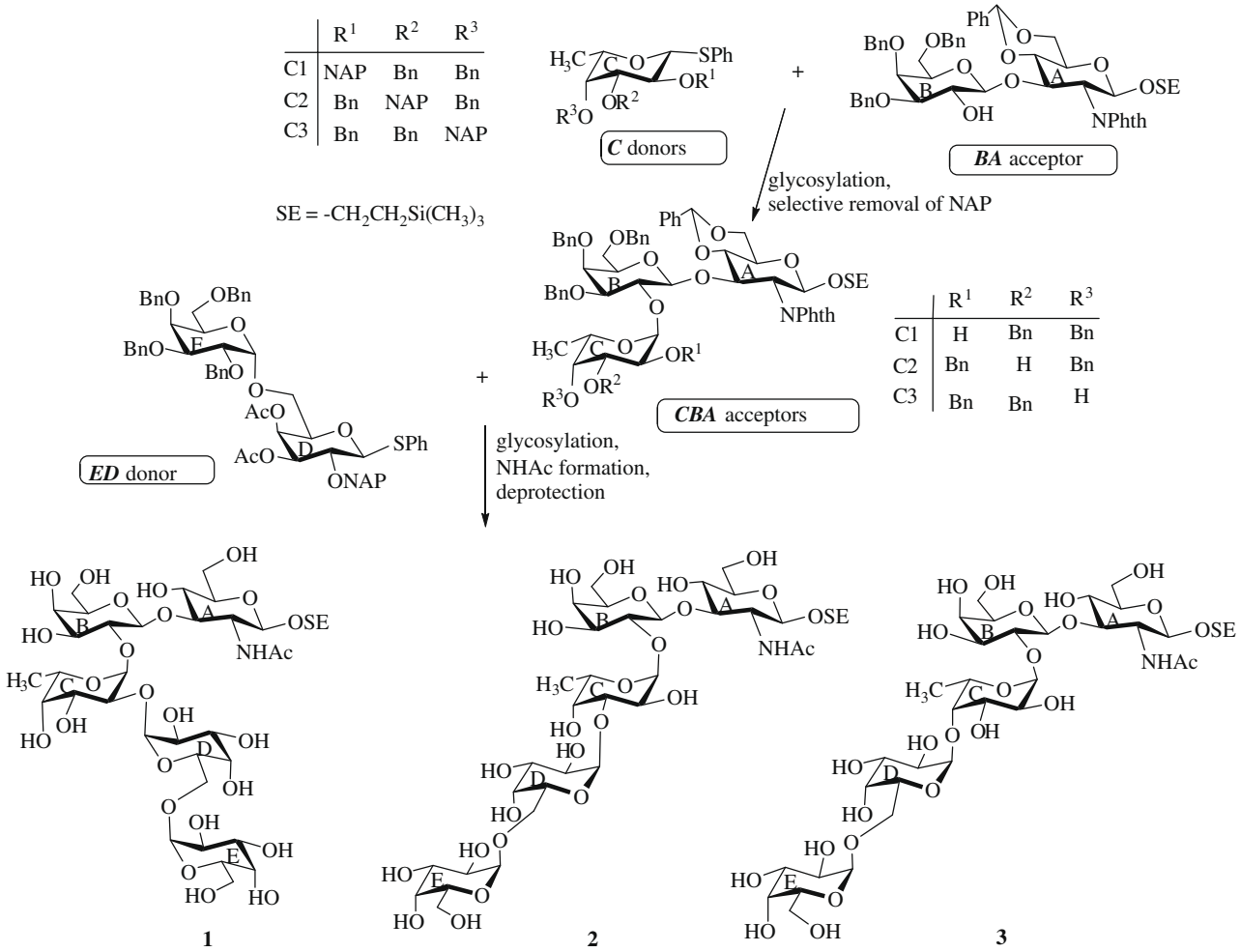
of galactose on fucose is the synthesis of the possible isomeric pentasaccharides, thus we continued our experiments on the construction of the isomeric structures.

The preparation of the pentasaccharides was based on (2-trimethylsilyl)ethyl (SE) glycosides and we planned to perform with a 2+3 block synthesis (Scheme 1), that is, attaching the digalactosyl residue (**E** + **D**) to the appropriate reducing-end trisaccharide acceptor (**C1**+**B**+**A, C2**+**B**+**A** or **C3**+**B**+**A)** bearing one free OH-group at a fixed position. The **B** + **A** and the **E** + **D** building blocks were designed to be built up from monosaccharide fragments with the appropriate-protecting groups, which allow the formation of the interglycosidic bonds with the correct stereochemistry, and subsequent transformations. The protected **B** + **A** and **E** + **D** disaccharide fragments should be converted into an acceptor and a donor, respectively. We have published[6] the preparation of the fucose building blocks (**C1**, **C2** and **C3**), carrying one temporary-protecting group at the suitable position and the other two hydroxyls blocked with permanent-protecting groups. Although examples of the synthesis of the Galpα(1→6)Galp[7,8] and the Fucpα(1→2)Galpβ(1→3)GlcNAc[9–12] oligosaccharide moieties have already been reported, the protecting groups employed in these works were not suitable for our purposes.

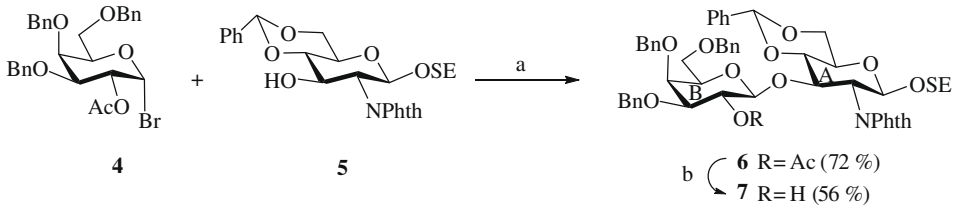
Herein, the total synthesis of the regioisomeric pentasaccharides from monosaccharide building blocks is discussed in detail.

2.1. Synthesis of the *B+A* disaccharide moiety

The fully protected bromosugar **4**[13] with a 2-*O*-acetyl-participating group was reacted with the *N*-phthalimidoglucosamine acceptor **5**[14] in the presence of AgOTf to give **6**, a compound with a β(1→3) interglycosidic linkage (Scheme 2). Cleavage of the 2-*O*-acetyl group of **6** with the Zemplén method did not result in the formation of acceptor **7** directly, since under the conditions of



Scheme 1. Synthetic pathway for the target pentasaccharides **1**–**3**.

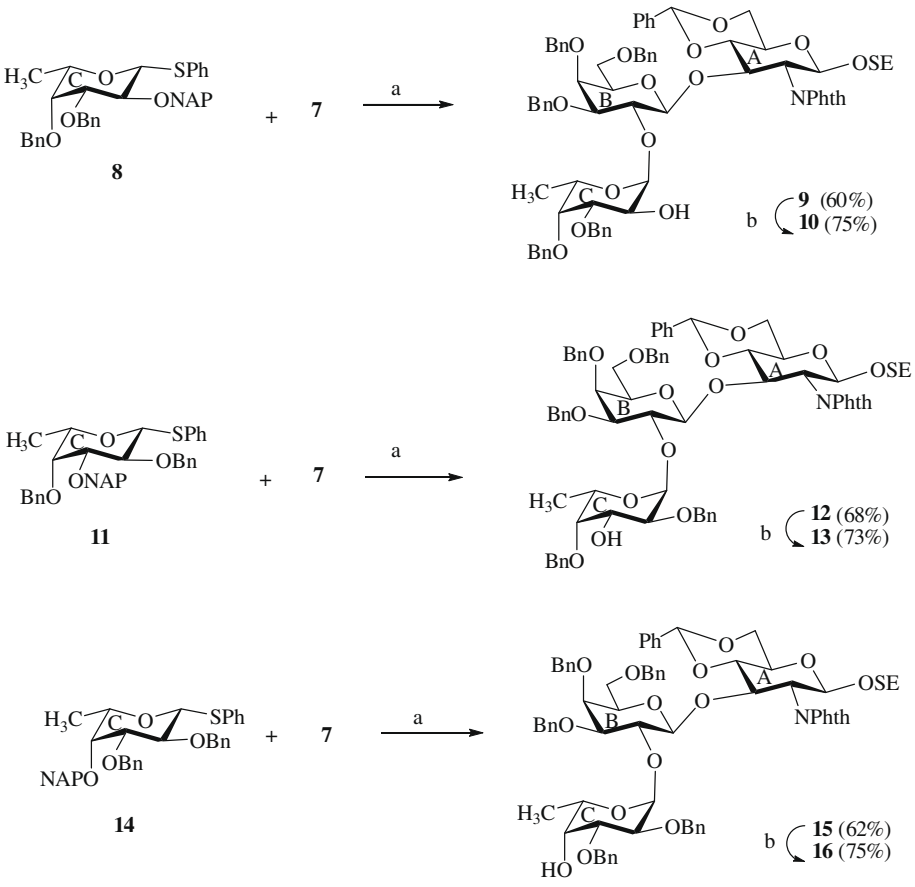


Scheme 2. Reagents and conditions: (a) AgOTf, *sym*-collidine, DCM, toluene, −74 °C→+25 °C, overnight; (b) (i) NaOMe, MeOH–DCM, rt, 72 h; (ii) TFAA, pyridine, 30 min; (iii) cat. NaOMe, MeOH–DCM, rt, 2.5 h.

Table 1
Selected ^{1}H and ^{13}C NMR data of compounds **6** and **7**

Compound	Monosaccharide unit	^{1}H NMR—δ (ppm) ^{3}J (Hz), ^{13}C NMR—δ (ppm) $^{1}J_{C1,H1}$ (Hz)					
		1	**2**	**3**	**4**	**5**	**6a,b**
6	GlcNPhth (**A**)	5.12 (d, $J_{1,2}$ = 10.0) 98.17 (J = 163.6)	4.36–4.26 (m)[a] 55.61	4.67 (dd, J_A = 10.2, J_B = 8.8) 75.28	3.84–3.77 (m)[a] 81.17[b]	3.30–3.22 (m)[a] 80.37	a: 3.30–3.22 (m)[a] b: 3.61–3.55 (m)[a] 68.03
	Galp (**B**)	4.44 (d, $J_{1',2'}$ = 8.0) 100.63 (J = 160.7)	5.13 (t, J = 8.5) 71.64	3.30–3.22 (m)[a] 70.81	3.84–3.77 (m)[a] 72.05[b]	3.61–3.55 (m)[a] 66.35	a: 4.36–4.26 (m)[a] b: 3.84–3.77 (m)[a] 68.68
7	GlcNPhth (**A**)	5.34 (d, $J_{1,2}$ = 8.5) 98.34 (J = 164.5)	4.29–4.24 (m)[a] 55.99	4.81 (t, J = 9.5) 72.07	3.83 (t, J = 10.3) 73.46	3.27–3.18 (m)[a] 81.50[b]	a: 2.87 (t, J = 9.0) b: 2.37 (m) 66.58
	Galp (**B**)	4.29–4.24 (m)[a] 102.70 (J = 162.5)	3.97–3.88 (m)[a] 68.90	3.27–3.18 (m) [a] 73.04[b]	3.79–3.74 (m)[a] 81.00	3.69 (m) 65.77	a: 4.40 (m) b: 3.79–3.74 (m)[a] 68.78

[a] Overlap.
[b] Interchangeable assignments.



Scheme 3. Reagents and conditions: (a) NIS/TMSOTf, CH_2Cl_2, −50 °C, 30 min; (b) DDQ, CH_2Cl_2–H_2O 9:1, rt, 25 min.

the deacetylation opening of the phthalimido group also occurred. Reclosure of the phthalimido ring and removal of the formed 2′-*O*-trifluoroacetyl group required two additional steps, following the procedure described by Oscarson et al. [11] to afford compound **7** in 56% overall yield. Our efforts to avoid the cumbersome preparation of the **B** + **A** disaccharide acceptor by using the more readily removable chloroacetyl group at the 2-position of the Gal moiety were unsuccessful. Glycosylation of **5** with different chloroacetylated donors did not give the desired compounds. These results will be published elsewhere soon.

Surprisingly, the NMR spectra of compounds **6** and **7** differed to a great extent, supposedly due to an intramolecular hydrogen bond formed between the 2′-OH and the phthaloyl-*C*=*O* after cleavage of the 2′-*O*-acyl group. The interaction fixed **7** in a definite conformation proved by the shift of the signals of both carbohydrate moieties and the splitting of the phthaloyl-*C*=O (^{13}C NMR) in compound **7** as compared to **6**. The NMR-data of compounds **6** and **7** are presented in Table 1.

2.2. Preparation of the *Cx+B+A* trisaccharides

The protected core trisaccharide was synthesized by coupling the appropriate fucoside donor **8**, **11** or **14**[6] and disaccharide acceptor **7** in the presence of NIS/TMSOTf promoter to yield **9**, **12** or **15**, respectively. The fucosylation reactions were carried out under the same conditions and the desired compounds with an α-fucosidic linkage were obtained in each case (Scheme 3). The next step was the selective cleavage of the 2-*O*-naphthylmethyl ether from the trisaccharides to unblock the OH group at suitable positions. Deprotection of the NAP-ether in the presence of benzyl ethers and the other protecting groups could be achieved with DDQ, and compounds **10**, **13** and **16** were obtained in good yields. The appropriate positions of the free OH-groups on the trisaccharides were confirmed by NMR and the data are presented in Table 2. The α- and β-shifts of the carbon atoms and the protons attached to the L-fucose skeleton of the derivatives were characterized. In the case of compounds **10** and **13**, hydrogen bonding between the free hydroxyl and the phthaloyl-*C*=*O* could again be observed, as confirmed by the $^{3}J_{H,OH}$ coupling constants of the OH′s.

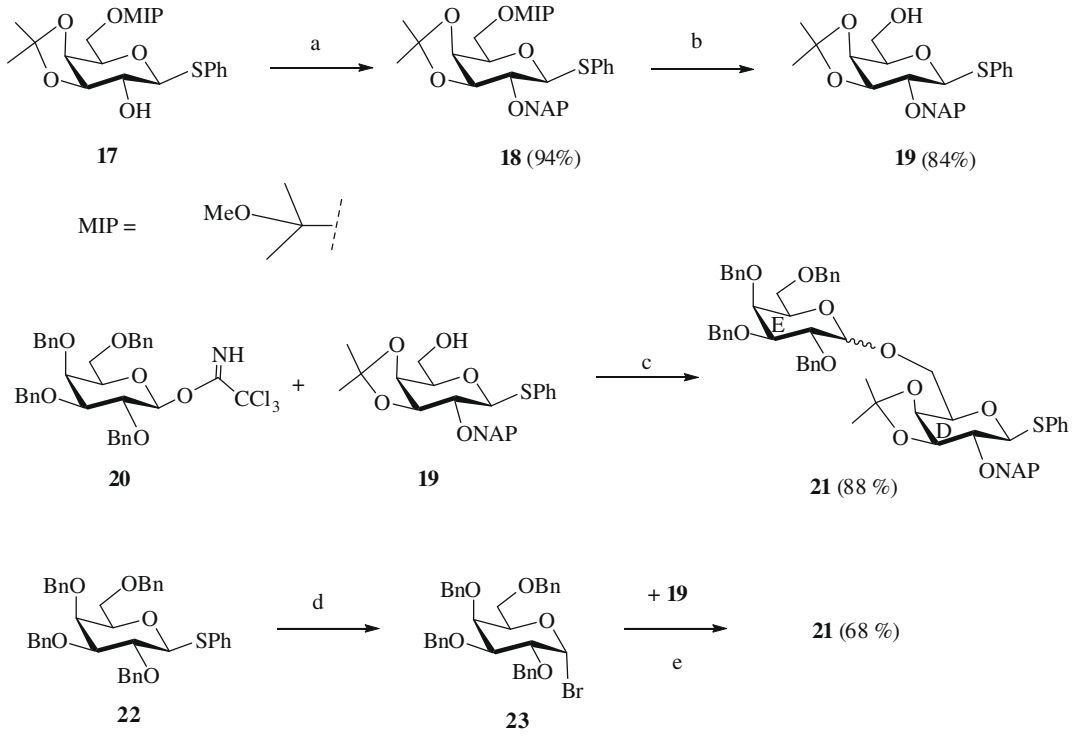
2.3. Synthesis of the *E+D* disaccharide building block

Development of the desired α(1→6) linkage between the **E** and **D** units was planned by the coupling of a tetra-*O*-benzyl-galactopyranosyl donor and an acceptor with a single OH group at the

Table 2
Selected ^{1}H and ^{13}C NMR data of compounds **9**, **10**, **12**, **13**, **15** and **16**

Compound	Monosaccharide unit	^{1}H NMR—δ (ppm) ^{3}J (Hz), ^{13}C NMR—δ (ppm) $^{1}J_{C1,H1}$ (Hz)						
		1	**2**	**3**	**4**	**5**	**6**	Misc. signal
9$_{(2\text{-ONAP})}$	D-GlcNPhth (**A**)	5.13 (d, $J_{1,2}$ = 8.5) 98.38 (J = 164.0)	4.42–4.27 (m)[a] 56.43	5.04 (t, J = 9.5) 72.53	3.83–3.72 (m)[a] 78.21	3.69–3.55 (m)[a] 66.48[a]	a: 4.42–4.27 (m)[a,b] b: 3.83–3.72 (m)[a,b] 68.52[a]	PhC*H*: 5.55 (s) 100.64 (J = 162.5)
	D-Galp (**B**)	4.50–4.46 (m)[a] 100.38 (J = 159.0)	4.12 (dd, $J_{1,2}$ = 7.6; $J_{2,3}$ = 9.5) 75.46[a]	3.50 (dd, $J_{2,3}$ = 9.6; $J_{3,4}$ = 2.8) 83.15	3.91–3.83 (m)[a] 72.16	3.38 (m) 72.78	a,b: 3.69–3.55 (m)[a] 68.52[a]	
	L-Fucp (**C**)	5.39 (d, $J_{1,2}$ = 3.5) 97.37 (J = 170.5)	3.69–3.55 (m)[a] 75.46[a]	3.83–3.72 (m)[a] 79.01	4.42–4.27 (m)[a] 80.31	4.42–4.27 (m)[a] 66.48[a]	1.26 (d, $J_{5,6}$ = 6.4) 16.49	
10$_{(2\text{-OH})}$	D-GlcNPhth (**A**)	5.29 (d, $J_{1,2}$ = 8.6) 98.12 (J = 166.0)	4.36–4.28 (m)[a] 56.01	4.81–4.73 (m)[a] 74.00	3.91–3.75 (m)[a] 80.76	3.63–3.56 (m)[a] 66.26	a: 4.36–4.28 (m)[a,b] b: 3.91–3.75 (m)[a,b] 68.69	PhC*H*: 5.49 (s) 100.94 (J = 160.0)
	D-Galp (**B**)	4.46–4.40 (m)[a] 100.72 (J = 161.0)	3.91–3.75 (m)[a] 77.34	3.42–3.31 (m)[a] 82.45	3.91–3.75 (m)[a] 71.69	3.27 (m) 72.64	a: 3.63–3.56 (m)[a,b] b: 3.50–3.43 (m)[a,b] 68.53	
	L-Fucp (**C**)	4.81–4.73 (m)[a] 99.91 (J = 170.0)	3.42–3.31 (m)[a] 69.46	3.42–3.31 (m)[a] 80.30	3.54 (br s) 77.75	3.99 (m) 67.37	1.21 (d, $J_{5,6}$ = 6.4) 16.63	O*H*: 2.44 (d, $J_{OH,H}$ = 8.6)
12$_{(3\text{-ONAP})}$	D-GlcNPhth (**A**)	5.15 (d, $J_{1,2}$ = 8.5) 98.43 (J = 163.0)	4.36–4.23 (m)[a] 56.43	4.99 (t, J = 9.5) 72.84	3.84–3.71 (m)[a] 78.45	3.62–3.52 (m)[a] 66.54[a]	a: 4.36–4.23 (m)[a,ba,b] b: 3.84–3.71 (m)[a,b] 68.63	PhC*H*: 5.55 (s) 100.74 (J = 163.0)
	D-Galp (**B**)	4.49–4.36 (m)[a] 100.54 (J = 161.0)	4.06 (t, J = 8.4) 75.81	3.48–3.41 (m)[a] 83.11	3.84–3.71 (m)[a] 72.48	3.34 (m) 72.88	a: 3.64 (t, J = 8.3)[b] b: 3.62–3.52 (m)[a,b] 68.68	
	L-Fucp (**C**)	5.31 (d, $J_{1,2}$ = 3.2) 97.45 (J = 172.0)	3.62–3.52 (m)[a] 75.90	3.84–3.71 (m)[a] 79.07	4.49–4.36 (m)[a] 80.41	4.36–4.23 (m)[a] 66.54[a]	1.25 (d, 6.4) 16.56	
13$_{(3\text{-OH})}$	D-GlcNPhth (**A**)	5.13 (d, $J_{1,2}$ = 8.5) 98.53 (J = 164.0)	4.37–4.27 (m)[a] 56.25	4.97 (t, J = 9.5) 72.86	3.77–3.71 (m)[a] 80.11	3.67–3.51 (m)[a] 66.60	a: 4.37–4.27 (m)[a,b] b: 3.79 (t, J = 10.2)[b] 68.60	PhC*H*: 5.53 (s) 100.75 (J = 161.0)
	D-Galp (**B**)	4.46–4.39 (m)[a] 100.39 (J = 160.0)	4.02 (dd, $J_{1,2}$ = 7.5; $J_{2,3}$ = 9.3) 75.61	3.41–3.36 (m)[a] 83.17	3.91–3.84 (m)[a] 72.14	3.41–3.36 (m)[a] 72.80	a,b: 3.67–3.51 (m)[a] 68.50	
	L-Fucp (**C**)	5.29 (d, $J_{1,2}$ = 3.3) 96.77 (J = 171.0)	3.24 (dd, $J_{1,2}$ = 3.3, $J_{2,3}$ = 10.2) 76.28	3.77–3.71 (m)[a] 69.73	3.67–3.51 (m)[a] 80.15	4.19 (m) 66.43	1.25 (d, $J_{5,6}$ = 6.5) 16.46	O*H*: 1.92 (d, $J_{OH,H}$ = 4.6)
15$_{(4\text{-ONAP})}$	D-GlcNPhth (**A**)	5.14 (d, $J_{1,2}$ = 8.5) 98.41 (J = 164.0)	4.36–4.25 (m)[a] 56.44	5.01 (t)[a] 72.77	3.81–3.73 (m)[a] 78.36	3.61–3.53 (m)[a] 66.52	a: 4.36–4.25 (m)[a,b] b: 3.81–3.73 (m)[a,b] 68.60	PhC*H*: 5.54 (s) 100.73 (J = 161.0)
	D-Galp (**B**)	4.47 (d, $J \cong$ 7.6)[a] 100.45 (J = 161.0)	4.07 (dd)[a] 75.66	3.47–3.41 (m)[a] 83.13	3.89–3.82 (m)[a] 72.46	3.35 (t, J = 6.5) 72.87	a: 3.65 (t, J = 8.4)[b] b: 3.61–3.53 (m)[a,b] 68.67	
	L-Fucp (**C**)	5.33 (d, $J_{1,2}$ = 3.5) 97.50 (J = 172.0)	3.61–3.53 (m)[a] 75.84	3.81–3.73 (m)[a] 79.25	3.81–3.73 (m)[a] 80.38	4.36–4.25 (m)[a] 66.56	1.27 (d, $J_{5,6}$ = 6.5) 16.62	
16$_{(4\text{-OH})}$	D-GlcNPhth (**A**)	5.17 (d, $J_{1,2}$ = 8.5) 98.40 (J = 164.0)	4.41–4.25 (m)[a] 56.44	5.01 (t, J = 9.5) 72.57	3.82–3.72 (m)[a] 77.80	3.60 (m) 66.49	a: 4.41–4.25 (m)[a,b] b: 3.82–3.72 (m)[a,b] 68.57	PhC*H*: 5.54 (s) 100.69 (J = 161.0)
	D-Galp (**B**)	4.43 (d, $J_{1,2}$ = 7.5) 100.37 (J = 161.0)	4.08 (dd, $J_{1,2}$ = 7.5, $J_{2,3}$ = 9.5) 75.85	3.42 (dd, $J_{2,3}$ = 9.5, $J_{3,4}$ = 2.6) 82.93	3.83 (m)[a] 72.35	3.39–3.33 (m)[a] 72.89	a: 3.66 (m)[a,b] b: 3.55 (m)[b] 68.52	
	L-Fucp (**C**)	5.31 (d, $J_{1,2}$ = 3.6) 97.28 (J = 171.0)	3.39–3.33 (m)[a] 75.03	3.70 (dd, $J_{2,3}$ = 10.1, $J_{3,4}$ = 3.1)[a] 80.21	3.94 (br s) 69.82	4.41–4.25 (m)[a] 65.36	1.31 (d, $J_{5,6}$ = 6.6) 16.02	O*H*: 2.07 (s)

[a] Overlap.
[b] Interchangeable assignments.

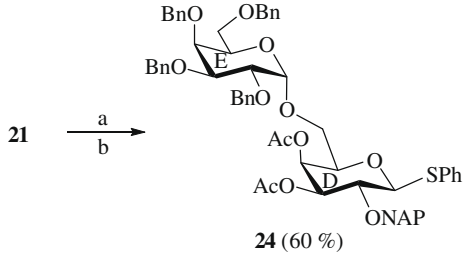


Scheme 4. Reagents and conditions: (a) NAPBr, NaH, DMF, 0 °C→rt, 3 h; (b) $CH_3COOH_{(aq)}$, CH_2Cl_2, 55 °C, 2.5 h; (c) TMSOTf, Et_2O, −30 °C, 45 min; (d) Br_2, CH_2Cl_2, 0 °C, 10 min; (e) Bu_4NBr, DCM–DMF, 0 °C, 24 h.

6-position. The **D** unit also needs a non-participating group at the 2-position for the synthesis of the planned pentasaccharides, and to fulfill this requirement the 2-naphthylmethyl-protecting group was selected.

Compound **17**[15] was the starting material for the synthesis of the partially protected **D** unit; first the 2-OH group was reacted with (2-bromomethyl)naphthalene to furnish **18**. Selective cleavage of the mixed (methoxydimethyl)methyl (MIP) acetal from the primary position in a mild acidic medium resulted in the formation of acceptor **19** from **17** in good overall yield (Scheme 4). Galactosylation of **19** was attempted with **20**,[16] but the NMR spectra of the chromatographically homogeneous material showed that a mixture of both disaccharide stereoisomers was produced. Hoping to obtain a pure α-linked product, glycosylation of **19** was repeated with bromosugar **23**, derived from **22**.[17] The reaction under in situ anomerization conditions, introduced by Lemieux for *cis*-glycoside synthesis, gave, again a mixture of the anomers.

The desired α-anomer could be isolated in pure form only after protecting group manipulation; the 3,4-*O*-isopropylidene group of **21** was hydrolyzed and the crude product was directly acetylated to furnish a separable mixture of the anomers. In a subsequent chromatographic step, donor **24** (**E** + **D**) was obtained in an acceptable yield (Scheme 5). The NMR data for compound **24** are presented in Table 3.



Scheme 5. Reagents and conditions: (a) (i) $HCl_{(aq)}$, THF, 50 °C, 5 h; (ii) Ac_2O, pyridine, 0 °C→rt, overnight; (iii) chromatographic separation (*n*-hexane–ethyl acetate 65:35).

2.4. Synthesis of the pentasaccharides and removal of their protecting groups

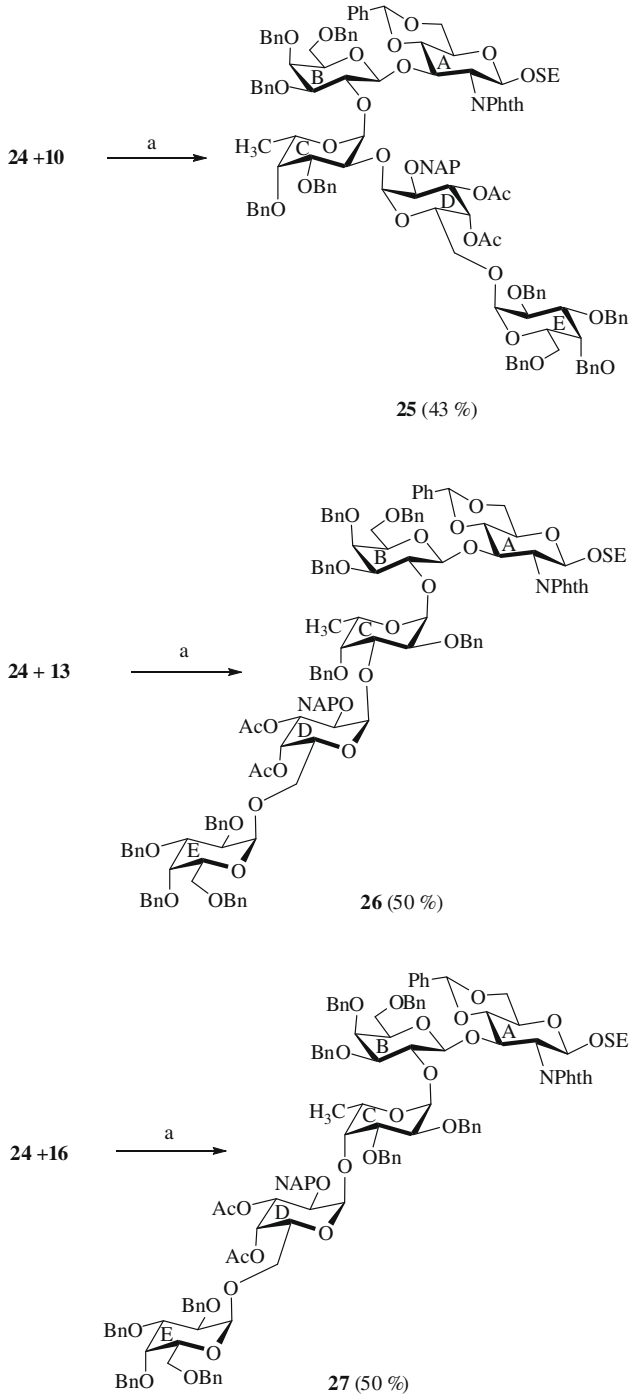
The **E** + **D** donor **24** and the appropriate trisaccharide acceptors **10**, **13** and **16** were reacted and the planned three isomeric pentasaccharides **25**, **26** and **27** were obtained in acceptable yields. The reactions were promoted by NIS/AgOTf and products with α-interglycosidic linkages were isolated in each case (Scheme 6).

For deblocking, first the transformation of the phthalimido moiety into an *N*-acetyl and then removal of the reducible groups by catalytic hydrogenation were planned. Treatment of

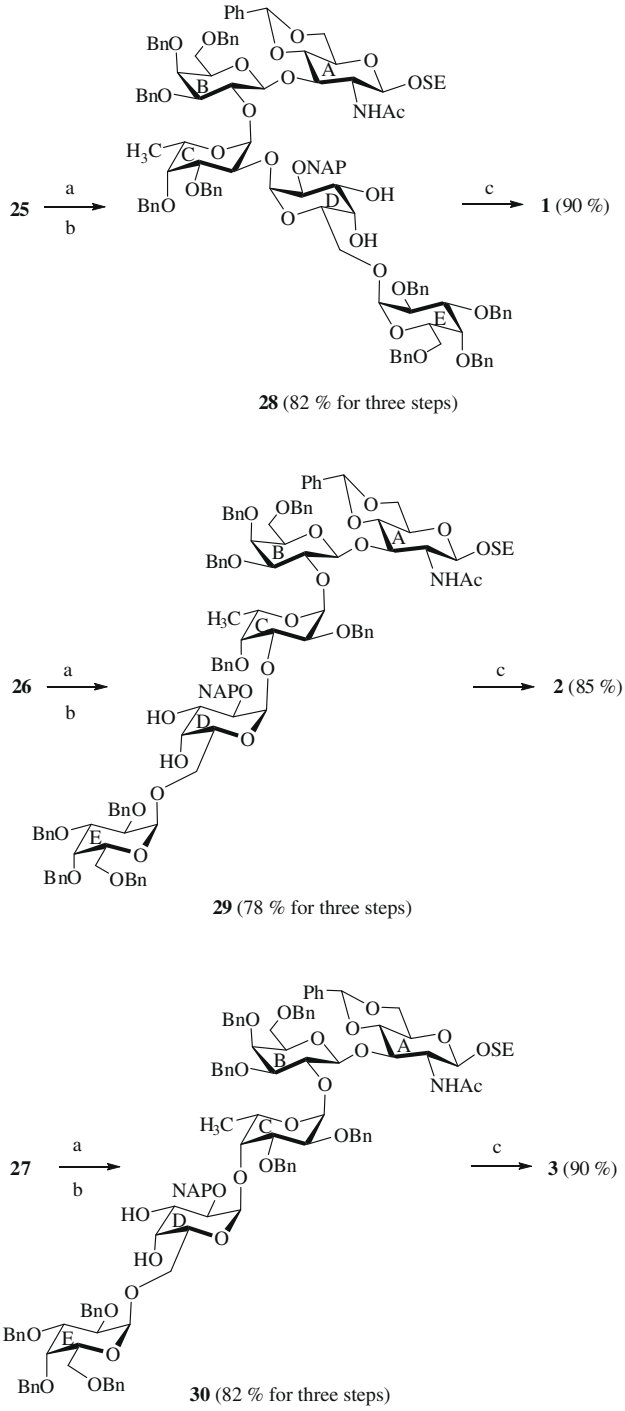
Table 3
Selected ^1H and ^{13}C NMR data of compound **24**

Compound	Monosaccharide unit	^1H NMR—δ (ppm) ^3J (Hz), ^{13}C NMR—δ (ppm) $^1J_{C1,H1}$ (Hz)					
		1	**2**	**3**	**4**	**5**	**6a,b**
24	Galp (**D**)	4.82–4.67 (m)[a] 87.48 (J = 156.0)	3.81–3.72 (m)[a] 76.48	5.09 (dd, $J_{2,3}$ = 9.6, $J_{3,4}$ = 3.1) 74.16	5.43 (d, J = 2.7) 68.47	4.03–3.96 (m)[a] 75.39[b]	a:, b: 3.57–3.45 (m)[a] 69.03
	Galp (**E**)	4.82–4.67 (m)[a] 98.32 (J = 168.0)	4.03–3.96 (m)[a] 69.42	3.84 (dd, $J_{2,3}$ = 10.1, $J_{3,4}$ = 2.5) 78.84	3.89 (br s) 75.32	4.03–3.96 (m)[a] 75.08[b]	a: 3.57–3.45 (m)[a] b: 3.81–3.72 (m)[a] 67.12

[a] Overlap.
[b] Interchangeable assignments.



Scheme 6. Reagents and conditions: (a) NIS/AgOTf, DCM, −8 °C, 3 h.



Scheme 7. Reagents and conditions: (a) $NH_2NH_2{\cdot}H_2O$, EtOH, reflux, **28**: 24 h, **29**, **30**: 5 h; (b) (i) Ac_2O, pyridine, 0 °C→rt, overnight; (ii) NaOMe, MeOH–CH_2Cl_2, rt, 5 h; (c) Pd(C), H_2, EtOH–THF 2:1, rt, overnight.

the fully blocked pentasaccharides with hydrazine hydrate cleaved the phthaloyl groups, and the resulting mixture was acetylated in pyridine to introduce the *N*-acetyl residue. The 3,4-di-*O*-acetyl groups, present at the **D** unit, were removed by the Zemplén method and compounds **28**, **29** and **30** were isolated (Scheme 7).

The residual benzyl, 2-naphthylmethyl- and benzylidene groups were reduced under hydrogen pressure in the presence of Pd/C catalyst, to give the target free pentasaccharides **1**, **2** and **3**. The NMR data for the anomeric centres of compounds **25**, **26**, **27** and **1**, **2**, **3** are presented in Tables 4 and 5.

3. Conclusion

The planned isomeric pentasaccharides **1**, **2** and **3** were successfully prepared in deblocked forms. Over the course of the synthetic experiments known glycosylation methods and the 2-naphthylmethyl ether as a temporary-protecting group were used. Glycosylation reactions by using fucosyl donors bearing one *O*-(2-naphthyl)methyl ether group at the 2-, 3- or 4-position and benzyl groups at the other positions led to the formation of the

Table 4
The ^{1}H and ^{13}C NMR data for the anomeric centres of compounds **25**, **26** and **27**

Compound	Monosaccharide unit/PG	^{1}H NMR δ (ppm) $^3J_{1,2}$ (Hz)	^{13}C NMR δ (ppm) $^1J_{C1,H1}$ (Hz)
25	D-GlcNPhth (**A**)	5.11–5.05 (m)[a]	98.58 (J = 163.0)
	D-Galp (**B**)	4.51–4.43 (m)[a]	99.98 (J = 161.0)
	L-Fucp (**C**)	5.49 (br s)	98.51 (J = 174.5)
	D-Galp (**D**)	5.72 (br s)	96.90 (J = 173.5)
	D-Galp (**E**)	4.72–4.68 (m)[a]	97.36 (J = 169.5)
	Benzylidene acetal	5.57 (s)	100.50 (J = 161.0)
26	D-GlcNPhth (**A**)	5.33–5.29 (m)[a]	98.14 (J = 164.0)
	D-Galp (**B**)	4.46–4.40 (m)[a]	101.11 (J = 160.0)
	L-Fucp (**C**)	5.49–5.43 (m)[a]	97.91 (J = 173.0)
	D-Galp (**D**)	5.04–4.95 (m)[a]	96.62 (J = 168.0)
	D-Galp (**E**)	4.82–4.75 (m)[a]	98.75 (J = 168.0)
	Benzylidene acetal	5.49–5.43 (m)[a]	100.88 (J = 162.0)
27	D-GlcNPhth (**A**)	5.15 (d, J = 8.5)	98.43 (J = 164.0)
	D-Galp (**B**)	4.51–4.39 (m)[a]	100.32 (J = 160.0)
	L-Fucp (**C**)	5.23 (d, J = 3.2)	97.45 (J = 171.5)
	D-Galp (**D**)	5.82 (d, J = 3.8)	96.64 (J = 169.5)
	D-Galp (**E**)	4.85–4.75 (m)[a]	99.31 (J = 168.0)
	Benzylidene acetal	5.55 (s)	100.69 (J = 160.5)

[a] Overlap.

Table 5
The ^{1}H and ^{13}C NMR data for the anomeric centres of compounds **1**, **2** and **3**

Compound	Monosaccharide unit/PG	^{1}H NMR δ (ppm) $^3J_{1,2}$ (Hz)	^{13}C NMR δ (ppm) $^1J_{C1,H1}$ (Hz)
1	D-GlcNAc (**A**)	4.47 (d, J = 7.5)	100.23 (J = 165.0)
	D-Galp (**B**)	4.28 (d, $J\cong$ 8.5)[Ψ]	101.35 (J = 160.5)
	L-Fucp (**C**)	4.79 (d, J = 3.2)	98.65 (J = 169.5)
	D-Galp (**D**)	5.13 (d, $J\cong$ 2.2)[Ψ]	99.50 ($J\cong$ 174.5)[*]
	D-Galp (**E**)	5.13 (d, $J\cong$ 2.2)[Ψ]	99.71 ($J\cong$ 174.5)[*]
2	D-GlcNAc (**A**)	4.52 (d, J = 7.6)	100.22 (J = 164.0)
	D-Galp (**B**)	4.29 (d, J = 8.5)	101.32 (J = 160.0)
	L-Fucp (**C**)	4.83 (d, J = 3.6)	98.99 (J = 169.5)
	D-Galp (**D**)	5.06 (d, J = 4.0)	99.63 (J = 172.5)
	D-Galp (**E**)	5.08 (d, J = 3.8)	101.42 (J = 171.0)
3	D-GlcNAc (**A**)	4.48 (d, J = 7.6)	100.43 (J = 164.5)
	D-Galp (**B**)	4.29 (d, J = 8.5)	101.26 (J = 160.5)
	L-Fucp (**C**)	4.80 (d, J = 2.7)	98.94 (J = 171.0)
	D-Galp (**D**)	5.06[Ψ]	99.72 (J = 173.0)
	D-Galp (**E**)	5.06[Ψ]	102.03 (J = 170.0)

[Ψ] Overlap.
[*] Interchangeable assignments

three trisaccharides which could be used, after selective removal of the 2-naphthylmethyl-protecting group—as acceptors in the 2+3 block syntheses of the target regioisomeric pentasaccharides. The *O*NAP-protecting group was also present at the C-2 position of two donor compounds and behaved as a non-participating group, as was expected. The synthesized molecules are suitable for the structure elucidation of the natural pentasaccharide.

4. Experimental

4.1. General methods

Optical rotations were measured at room temperature with a Perkin–Elmer 241 automatic polarimeter. TLC was performed on Kieselgel 60 F_{254} (Merck) with detection by immersing into 5% ethanolic sulfuric acid solution followed by heating. Column chromatography was performed on Silica Gel 60 (Merck 0.063–0.200 mm). Organic solutions were dried over $MgSO_4$, and concentrated in vacuum. The ^{1}H (200.13, 360.13 and 500.13 MHz) and ^{13}C NMR (50.3, 90.54 and 125.76 MHz) spectra were recorded with Bruker AC-200, Bruker DRX-360 and Bruker DRX-500 spectrometers in $CDCl_3$ solutions. The use of a different solvent is indicated therein. Chemical shifts are referenced to Me_4Si (0.00 ppm for ^{1}H) or to the residual solvent signals (77.00 ppm for ^{13}C). The F2-coupled ^{1}H–^{13}C-HSQC experiments were performed on Bruker DRX-500 spectrometer at 298 K. Selected NMR-data of compounds **1–3**, **6**, **7**, **9**, **10**, **12**, **13**, **15**, **16**, **24** and **25–27** are presented in Tables 1–5, included in Section 2. Additional NMR signals of these compounds are given below separately at each experiment.

MALDI-TOF MS analyses of the compounds were carried out in the positive reflectron mode using a BIFLEX III mass spectrometer (Bruker, Germany) equipped with delayed-ion extraction. The matrix solution was a saturated 2,4,6-trihydroxy-acetophenone (THAP) solution in MeCN. ESI-TOF MS analyses of the compounds were carried out in the positive reflectron mode using a MicrO-TOF-Q mass spectrometer (Bruker, Germany). Elemental analyses were performed at the analytical laboratories of the University of Debrecen.

4.2. General method A for the coupling reaction using NIS-TMSOTf activation

To a solution of the disaccharide acceptor **7** (2.7 g, 2.9 mmol, 1.0 equiv) and the appropriate fucoside donor (7.25 mmol, 2.5 equiv) in dry DCM (80 mL), 4 Å molecular sieves (7.5 g) were added and stirred for 3 h at room temperature. Then the solution was cooled to −55 °C and a solution of NIS (9.3 mmol, 3.2 equiv) and TMSOTf (1.8 mL, 0.63 equiv) in a mixture of dry THF (9 mL) and dry DCM (5 mL) was added. The reaction mixture was kept at −55 °C until TLC showed the disappearance of the acceptor (0.5–3 h), after which it was quenched by the addition of pyridine (0.5 mL) and allowed to warm up to room temperature. The mixture was filtered, the filtrate was diluted with CH_2Cl_2, washed with 5% $Na_2S_2O_3$ and with satd $NaHCO_3$ solutions and with water. The organic layer was dried and evaporated. The residue was then purified by column chromatography.

4.3. General method B for oxidative removal of *O*-(2-naphthyl)methyl group

The starting material (1.6 mmol, 1.0 equiv) was dissolved in a mixture of DCM and H_2O (9:1, 140 mL) and freshly crystallized DDQ (2.6 mmol, 1.6 equiv) was added. The reactions reached completion within 25 min. Next the mixture was diluted with CH_2Cl_2, and washed three times with satd $NaHCO_3$ solution. The organic layer was dried and evaporated. The residue was then purified by column chromatography.

4.4. General method C for coupling reaction using NIS-AgOTf promoter

To a solution of the trisaccharide acceptors **10**, **13** or **16** (1.7 mmol, 1.0 equiv) and the disaccharide donor **24** (2.7 mmol, 1.6 equiv) in dry DCM (50 mL), 4 Å molecular sieves (5 g) were added and stirred for 3 h at room temperature, after which the solution was cooled to −8 °C. A solution of NIS (3.51 mmol, 2.1 equiv) in dry THF (2.2 mL) and a solution of AgOTf (0.41 mmol, 0.24 equiv) in dry toluene (2.2 mL) were mixed and added into the cooled reaction mixture. The reaction mixture was kept at −8 °C until TLC showed completion of the reaction (0.5–3 h). Then it was neutralized by the addition of pyridine (0.5 mL) and allowed to warm up to room temperature. The mixture was diluted with CH_2Cl_2 and filtered through a pad of Celite. The filtrate was washed

with 5% $Na_2S_2O_3$ and satd $NaHCO_3$ solutions and with water. The organic layer was dried and evaporated. The residue was then purified by column chromatography.

4.5. General method D for conversion of *N*-phthaloyl-group into *N*-acetyl group

Dephthaloylation step: To a solution of the starting material (0.14 mmol) in abs EtOH (7 mL) hydrazine-hydrate was added (1 mL) and the mixture was refluxed overnight. The presence of the free amine was detected with TLC by immersing into 1% ethanolic ninhydrine solution followed by heating. The solvent was evaporated in vacuo and co-evaporated with toluene. *Acetylation step*: the residue obtained was dissolved in pyridine (5 mL) and acetic anhydride (5 mL) was added at 0 °C. After 10 h the mixture was evaporated in vacuo and co-evaporated with toluene. The residue was diluted with CH_2Cl_2, washed with 10% aq citric acid solution, with water and satd $NaHCO_3$ solution, then with water again. The organic layer was dried and evaporated.

O-Deacetylation step: For the removal of the *O*-acetyl groups present in the molecule the crude material was dissolved in a 1:2 mixture of DCM–MeOH (6 mL) and was treated with catalytic amount of NaOMe (~20 mg). After complete conversion the mixture was neutralized with Amberlite IR-120 H^+ ion exchange resin, filtered and evaporated. The residue was purified by column chromatography.

4.6. General method E for catalytic hydrogenation

To a solution of the starting material (0.07 mmol) in a mixture of 96% EtOH (2 mL) and THF (1 mL) in an autoclave 10% Pd/C (0.100 g) was added. The autoclave was degassed by applying vacuum and filled with 26 bar pressure of hydrogen. After overnight of vigorous stirring TLC showed complete conversion. The catalyst was removed by filtration through Celite and was washed twice with aq MeOH. The filtrate was evaporated and the crude product was purified by column chromatography.

4.7. (2-Trimethylsilyl)ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 6

To a solution of donor **4**[13] (18.022 g) and acceptor **5**[14] (12.036 g) in dry dichloromethane (250 mL) 4 Å powdered molecular sieves (18.5 g) and *sym*-collidine (4.4 mL) were added and the mixture was stirred for 30 min in the dark. Then it was cooled into −74 °C and AgOTf (10.900 g) in dry toluene (120 mL) was added. After overnight stirring, the mixture was diluted with dichloromethane, filtered through a pad of Celite, evaporated in vacuo, and the residue was purified by column chromatography (*n*-hexane–EtOAc = 67:33) to yield **6** as a white foam (16.930 g, 72%), R_f = 0.47, $[\alpha]_D = -6.1$ (*c* 0.16, $CHCl_3$). ^{1}H NMR (500 MHz) δ (ppm) 7.85 (br s, 2H, arom.), 7.75–7.71 (m, 2H, arom.), 7.48–7.44 (m, 2H, arom.), 7.34–7.11 (m, 18H, arom.), 5.51 (s, 1H, $^1J_{C,H}$ = 162.5 Hz, $H_{acetalic}$), 4.80 (d, 1H, J_{gem} = 11.7 Hz, PhCH*H*), 4.51–4.45 (m, 2H, 2 × PhC*H*H), 4.19 (q, 2H, PhCH_2), 3.89 (ddd, 1H, OCH*H*CH_2Si), 3.46 (ddd, 1H, OC*H*HCH_2Si), 2.14 (s, 3H, COCH_3), 0.81–0.73 (m, 1H, CH*H*Si), 0.73–0.66 (m, 1H, C*H*HSi), −0.15 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR δ (ppm) 168.74 (*C*=O), 138.41, 137.86, 137.70, 137.38 (*C*q, arom.), 128.87, 128.28, 128.12, 128.06, 127.99, 127.94, 127.85, 127.69, 127.36, 127.27, 126.97, 126.05 ($C_{arom.}$), 101.10 ($C_{acetalic}$), 74.27, 73.34, 71.46 (PhCH_2), 67.10 (OCH_2CH_2Si), 20.24 (CH_3CO), 17.74 (OCH_2CH_2Si), −1.64 (Si(CH_3)$_3$). ESI-TOF: *m/z* calcd for $C_{55}H_{61}NO_{13}Si$ (972.16) $[M+Na]^+$: 994.383. Measured: 994.383.

4.8. (2-Trimethylsilyl)ethyl 3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 7

To a solution of **6** (16.930 g, 17 mmol) in a mixture of DCM–MeOH = 1:2 (350 ml) 1 M methanolic NaOMe solution was added (32 ml) and it was stirred overnight. Then another portion of methanolic NaOMe (25 ml) was added. The reaction was monitored by TLC (DCM–acetone = 97:3), the disappearance of the starting material required 5 days. The mixture was neutralized with Amberlite IR-120 H^+ ion exchange resin, filtered and evaporated. The residue was dissolved in dry pyridine (300 ml), cooled in an ice bath and trifluoroacetic anhydride was added dropwise. After 45 min TLC showed the formation of a product of high mobility. (DCM–acetone = 97:3, R_f = 0.81). The mixture was diluted with dichloromethane, washed with water (400 mL), with 10% aq $CuSO_4$ (400 mL), with 1 M HCl solution (2 × 300 mL), water (300 mL) then washed until neutral pH with satd $NaHCO_3$ solution and water. The solution was dried and evaporated, and the 2-*O*-trifluoroacetylated intermediate was analyzed by ESI-TOF: *m/z* calcd for $C_{55}H_{58}F_3NO_{13}Si$ (1026.13) $[M+H]^+$: 1026.370. Measured: 1026.372).

The crude product was dissolved in a 1:2 mixture of DCM–MeOH (350 mL) and treated with 1 M methanolic NaOMe (6 × 1 mL), the reaction was monitored by TLC (DCM–acetone = 98:2, R_f = 0.39). After complete conversion of the trifluoroacetylated intermediate the mixture was neutralized with Amberlite IR-120 H^+ ion exchange resin, filtered and evaporated. The syrupy residue was purified by column chromatography (DCM–EtOAc = 95:5) to yield **7** as a white foam (9.070 g, 56%), $[\alpha]_D^{25} = -48.5$ (*c* 0.24, $CHCl_3$). ^{1}H NMR (500 MHz) δ (ppm) 7.75 (br s, 1H, arom.), 7.57–7.45 (m, 5H, arom.), 7.40–7.16 (m, 17H, arom.), 7.11–7.06 (m, 2H, arom.), 5.60 (s, 1H, $^1J_{C,H}$ = 164.0 Hz, $H_{acetalic}$), 4.93 (d, 1H, J_{gem} = 11.9 Hz, PhCH*H*), 4.52 (q, 2H, PhCH_2), 4.44 (d, J_{gem} = 11.9 Hz, 1H, PhC*H*H), 4.02 (q, 2H, PhCH_2), 3.97–3.88 (m, 2H, OCH*H*CH_2Si, H-2′), 3.49 (ddd, 1H, OC*H*HCH_2Si), 3.27–3.18 (m, 3H, O*H*, H-5, H-3″), 0.86–0.77 (m, 1H, CH*H*Si), 0.76–0.69 (m, 1H, C*H*HSi), –0.14 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR δ (ppm) 168.18, 167.49 (*C*=O), 139.24, 138.60, 137.77, 136.23, 132.06 (*C*q, arom.), 133.50, 129.34, 128.27, 128.08, 128.01, 127.57, 127.37, 127.24, 127.06, 126.25, 123.15 ($C_{arom.}$), 102.11 ($C_{acetalic}$), 74.47, 72.87, 72.50 (PhCH_2), 67.32 (OCH_2CH_2Si), 17.77 (CH_2Si), −1.60 (Si(CH_3)$_3$). ESI-TOF: *m/z* calcd for $C_{53}H_{59}NO_{12}Si$ (930.1) $[M+Na]^+$: 952.370. Measured: 952.373.

4.9. (2-Trimethylsilyl)ethyl 3,4-di-*O*-benzyl-2-*O*-(2-naphthyl)methyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 9

Compound **8** (4.063 g, 7.194 mmol) was reacted with **7** (2.669 g, 2.869 mmol) according to general method **A** at −55 °C. T.l.c: DCM–acetone 99:1, R_f = 0.54. Purification of the crude product by column chromatography (*n*-hexane–ethylacetate 7:3) afforded **9** as a foam (2.406 g, 60%); $[\alpha]_D = -37.7$ (*c* 0.13, $CHCl_3$); ^{1}H NMR (500 MHz) δ (ppm) 7.71 (d, 1H, arom.), 7.65 (br s, 1H, arom.) 7.52–7.44 (m, 6H, arom.), 7.41–7.14 (m, 33H, arom.), 7.02 (dd, 1H, arom.), 4.87–4.75 (m, 4H, ArCH_2), 4.62 (s, 2H, ArCH_2), 4.55 (d, 2H, J_{gem} = 11.1 Hz, ArC*H*H), 4.50–4.46 (m, 2H, ArC*H*H, H-1'), 4.42–4.27 (m, 6H, H-4″, H-5″, H-6a, H-2, ArC*H*H), 3.90–3.84 (m, 2H, H-4″, OCH*H*CH_2Si), 3.44 (ddd, 1H, OC*H*HCH_2Si), 0.76–0.63 (m, 2H, CH_2Si), −0.15 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR δ (ppm) 139.15, 138.89, 138.59, 138.33, 137.74, 137.38, 135.68, 132.98, 132.60, 131.47 (*C*q, arom.), 128.51, 128.32, 128.24, 128.17, 128.01, 127.99, 127.90, 127.83, 127.76, 127.69, 127.44, 127.39, 127.31, 127.20, 127.18, 127.10, 127.04, 126.14, 126.07, 125.68, 125.50, 125.32, 123.47 ($C_{arom.}$),

75.00, 74.31, 73.53, 72.60, 71.80, 71.22 (ArCH$_2$), 67.26 (OCH$_2$CH$_2$Si), 17.87 (CH$_2$Si), –1.67 (Si(CH$_3$)$_3$). ESI-TOF: *m/z* calcd for $C_{84}H_{89}NO_{16}Si$ (1395.595) [M+Na]$^+$: 1418.585. Found 1418.642. Calcd for [M+2Na]$^{2+}$: 720.787. Found: 720.786.

4.10. (2-Trimethylsilyl)ethyl 3,4-di-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 10

Trisaccharide **9** (2.250 g, 1.61 mmol) was treated with DDQ according to general method **B**. Purification of the crude product by column chromatography (DCM–acetone 99:1, R_f = 0.60) afforded **10** as a foam (1.518 g, 75%); $[\alpha]_D = -47.4$ (*c* 0.15); ^{1}H NMR (500 MHz) δ (ppm) 7.62 (br s, 2H, arom.), 7.45 (d, 2H, arom.), 7.37–7.18 (m, 30H, arom.), 4.81–4.73 (m, 4H, 3-H, H1–1″, PhC*HH*), 4.58–4.41 (m, 7H, H-1′, 3 × PhC*H*$_2$), 4.36–4.23 (m, 4H, 2-H, H-6a, PhC*HH*), 3.91–3.75 (m, 5H, H-2′, H-4′, H-4, H-6b, OCH*H*CH$_2$Si), 3.50–3.43 (m, 2H, H-6′b, OC*H*HCH$_2$Si), 0.75, 0.68 (m, 2H, C*HH*Si), –0.16 (Si(C*H*$_3$)$_3$). ^{13}C NMR δ (ppm) 139.02, 138.74, 138.35, 137.63, 137.42, 137.23 (*C*q, arom.), 133.66, 128.71, 128.38, 128.34, 128.31, 128.14, 128.08, 128.04, 128.00, 127.96, 127.89, 127.73, 127.63, 127.45, 127.34, 127.23, 127.19, 127.12, 126.05 ($C_{arom.}$), 74.92, 74.30, 73.45, 72.31, 71.75 (PhCH$_2$), 67.13 (OCH$_2$CH$_2$Si), 17.77 (CH$_2$Si), –1.65 (Si(CH$_3$)$_3$). Anal. Calcd for $C_{73}H_{81}NO_{16}Si$ (1256.51): C, 69.78; H, 6.50. Found: C, 69.95; H, 6.47. MALDI-TOF: *m/z* calcd for [M+Na]$^+$: 1278.522. Found 1278.620.

4.11. (2-Trimethylsilyl)ethyl 2,4-di-*O*-benzyl-3-*O*-(2-naphthyl) methyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 12

Compound **11** (3.795 g, 6.719 mmol) was reacted with **7** (2.500 g, 2.687 mmol) according to general method **A** at –58 °C. Purification of the crude product by column chromatography (*n*-hexane–ethyl acetate 7:3, R_f = 0.60) afforded **12** as a foam (2.570 g, 68%); $[\alpha]_D = -33.8$ (*c* 0.21, $CHCl_3$); ^{1}H NMR (500 MHz) δ (ppm) 7.82–7.73 (m, 3H, arom.), 7.64–7.58 (d, 3H, arom.), 7.49, (d, 2H, arom.), 7.46–7.00 (m, 33H, arom.), 4.93–4.87 (m, 2H, ArC*HH*), 4.83 (d, 1H, J_{gem} = 12.3 Hz, ArC*H*H), 4.79 (d, 1H, J_{gem} = 11.6 Hz, ArC*H*H), 4.63–4.54 (m, 3H, ArCH*H*), 4.49–4.36 (m, 4H, H-1′, H-4″, ArC*HH*), 4.36–4.23 (m, 5H, H-2, H-5″, H-6a, ArC*HH*), 3.87 (ddd, 1H, OCH*H*CH$_2$Si), 3.48–3.41 (m, 2H, H-3′, OC*H*HCH$_2$Si), 0.77–0.63 (m, 2H, CH$_2$Si), –0.15 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR δ (ppm) 139.10, 138.69, 138.45, 138.39, 137.87, 137.48, 136.79, 133.28, 132.71, 131.55 (*C*q, arom.), 133.96, 128.56, 128.34, 128.29, 128.14, 128.10, 128.04, 127.98, 127.89, 127.83, 127.68, 127.53, 127.41, 127.22, 127.04, 126.99, 126.36, 126.12, 125.89, 125.57, 125.50, 125.30. 123.47 ($C_{arom.}$), 75.08, 74.33, 73.55, 72.50, 72.07, 71.60 (ArCH$_2$), 67.25 (OCH$_2$CH$_2$Si), 17.92 (CH$_2$Si), –1.63 (Si(CH$_3$)$_3$). Anal. Calcd for $C_{84}H_{89}NO_{16}Si$ (1396.69): C, 72.24; H, 6.42. Found: C, 72.50; H, 6.39. MALDI-TOF: *m/z* calcd for [M+Na]$^+$: 1418.584. Found 1418.590.

4.12. (2-Trimethylsilyl)ethyl 2,4-di-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 13

Trisaccharide **12** (2.550 g, 1.825 mmol) was treated with DDQ according to general method **B**. Purification of the crude product by column chromatography (DCM–acetone 99:1) afforded **13** as a foam (1.562 g, 77%); R_f = 0.39 (*n*-hexane–ethyl acetate 7:3); $[\alpha]_D = -61.0$ (*c* 0.12, $CHCl_3$). ^{1}H NMR (500 MHz) δ (ppm) 7.77 (br s, 2H, arom.), 7.56 (br s, 2H, arom.), 7.49 (d, 2H, arom.), 7.36–7.13 (m, 26H, arom.), 6.95 (d, 2H, arom.), 4.78 (d, 1H, J_{gem} = 11.6 Hz, PhC*H*H), 4.71 (d, 1H, J_{gem} = 11.4 Hz, PhC*H*H), 4.63–4.58 (m, 2H, PhC*HH*), 4.48 (d, 1H, J_{gem} = 11.6 Hz, PhC*H*H), 4.45–4.39 (m, 3H, H-1′, PhC*HH*), 4.39–4.26 (m, 4H, H-6a, H-2, PhC*HH*), 3.96 (d, 1H, J_{gem} = 12.2 Hz, PhC*H*H), 3.88 (ddd, 1H, OC*H*HCH$_2$Si), 3.44 (ddd, 1H, OCH*H*CH$_2$Si), 0.79–0.64 (m, 2H, CH$_2$Si), –0.14 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR δ (ppm) 138.85, 138.64, 138.23, 138.08, 137.85, 137.45, 131.53 (*C*q, arom.), 134.00, 128.55, 128.21, 128.13, 128.03, 127.92, 127.74, 127.66, 127.51, 127.44, 127.29, 127.21, 127.06, 126.25, 126.12, 123.48 ($C_{arom.}$), 75.55, 74.30, 73.50, 71.21, 71.16 (PhCH$_2$), 67.22 (OCH$_2$CH$_2$Si), 17.86 (CH$_2$Si), –1.64 (Si(C*H*$_3$)$_3$). Anal. Calcd for $C_{73}H_{81}NO_{16}Si$ (1256.51): C, 69.78; H, 6.50. Found: C, 69.55; H, 6.52. MALDI-TOF: *m/z* calcd for [M+Na]$^+$: 1278.522. Found 1278.314.

4.13. (2-Trimethylsilyl)ethyl 2,3-di-*O*-benzyl-4-*O*-(2-naphthyl) methyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 15

Compound **14** (3.795 g, 6.720 mmol) was reacted with **7** (2.500 g, 2.687 mmol) according to general method **A** at –58 °C. Purification of the crude product by column chromatography (*n*-hexane–ethyl acetate 7:3, R_f = 0.60) afforded **15** as a foam (2.328 g, 62%); $[\alpha]_D = -40.5$ (*c* 0.22, $CHCl_3$). ^{1}H NMR (500 MHz) δ (ppm) 7.83–7.74 (m, 4H, arom.), 7.64 (br s, 2H, arom.), 7.52–7.41 (m, 7H, arom.), 7.37–7.11 (m, 24H, arom.), 7.06 (t, 2H, arom.), 7.00 (d, 2H, arom.), 5.03–4.97 (m, 2H, 3-H, ArCH*H*), 4.80–4.69 (m, 4H, ArC*H*$_2$), 4.58 (q, 2H, ArC*H*$_2$), 4.49–4.45 (m, 2H, H-1′, ArCH*H*), 4.42–4.37 (m, 2H, ArC*HH*), 4.36–4.25 (m, 5H, H-6a, H-5″, H-2, ArC*HH*), 3.86 (ddd, 1H, OCH*H*CH$_2$Si), 3.47–3.41 (m, 2H, H-3′, OC*H*HCH$_2$Si), 0.75–0.62 (m, 2H, C*HH*Si), –0.16 (s, 9H, Si(CH$_3$)$_3$). ^{13}C NMR δ (ppm) 139.23, 138.67, 138.38, 137.85, 137.46, 136.59, 133.17, 132.89, 131.55 (*C*q, arom.), 133.97, 128.54, 128.32, 128.20, 128.12, 128.01, 127.96, 127.93, 127.86, 127.74, 127.67, 127.58, 127.50, 127.20, 127.15, 127.09, 127.01, 126.97, 126.69, 126.56, 126.31, 126.11, 125.79, 125.59, 123.43 ($C_{arom.}$), 74.97, 74.31, 73.54, 72.66, 72.16, 71.52 (ArCH$_2$), 67.21 (OCH$_2$CH$_2$Si), 17.89 (CH$_2$Si), –1.66 (SiCH$_3$)$_3$). Anal. Calcd for $C_{84}H_{89}NO_{16}Si$ (1396.69): C, 72.24; H, 6.42. Found: C, 72.08; H, 6.44. MALDI-TOF: *m/z* calcd for (M+Na)$^+$: 1418.584. Found 1418.654.

4.14. (2-Trimethylsilyl)ethyl 2,3-di-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 16

Trisaccharide **15** (2.000 g, 1.431 mmol) was treated with DDQ according to general method **B**. Purification of the crude product by column chromatography (DCM–acetone 98:2) afforded **16** as a foam (1.350 g, 75%); R_f = 0.39 (*n*-hexane–ethyl acetate 7:3); $[\alpha]_D = -34.2$ (*c* 0.16). ^{1}H NMR (500 MHz) δ (ppm) 7.78–7.62 (m, 4H, arom.), 7.50 (d, 2H, arom.), 7.34–7.06 (m, 26H, arom.), 6.98 (d, 2H, arom.), 4.79 (d, 1H, $J_{gem.}$ = 11.7 Hz, PhCH*H*), 4.67 (s, 2H, PhC*H*$_2$), 4.54 (q, 2H, PhC*H*$_2$), 4.48 (d, 1H, J_{gem} = 11.7 Hz, PhC*H*H), 4.45–4.25 (m, 8H, H-1′, H-2, H-6a, H-5″, PhC*HH*), 3.89 (ddd, 1H, OC*H*HCH$_2$Si), 3.46 (ddd, 1H, OCH*H*CH$_2$Si), 0.79–0.64 (m, 2H, CH$_2$Si), –0.14 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR δ (ppm) 138.62, 138.46, 138.30, 138.23, 137.80, 137.43, 131.62 (*C*q, arom.), 134.04, 128.51, 128.28, 128.09, 128.00, 127.91, 127.85, 127.75, 127.64, 127.46, 127.29, 127.18, 127.01, 126.26, 126.07, 123.37 ($C_{arom.}$), 74.28, 73.50, 71.99, 71.83, 71.36 (PhCH$_2$), 67.21 (OCH$_2$CH$_2$Si), 17.84 (CH$_2$Si), –1.66 (Si(C*H*$_3$)$_3$). Anal. Calcd for $C_{73}H_{81}NO_{16}Si$ (1256.51): C, 69.78; H, 6.50. Found: C, 69.50; H, 6.46. MALDI-TOF: *m/z* calcd for [M+Na]$^+$: 1278.522. Found 1278.368.

4.15. Phenyl 3,4-*O*-isopropylidene-6-*O*-(methoxydimethyl) methyl-2-*O*-(2-naphthyl)methyl-1-thio-β-D-galactopyranoside 18

Compound **17**[15] (3.340 g, 8.7 mmol) was dissolved in dry DMF (15 mL) and cooled to 0 °C. NaH (13.0 mmol, 1.5 equiv, 60%,

previously treated with hexane) was added carefully to the mixture and stirred for half an hour. Then 2-bromomethylnaphthalene (1.923 g, 10.44 mmol, 1.2 equiv) was added. The reaction reached completion within 3 h. The excess of NaH was decomposed by the addition of MeOH and the solvent was evaporated in vacuo. The residue was dissolved in DCM, extracted three times with water, then the organic layer was dried and evaporated. Column chromatographic purification (DCM–acetone 99:1 +1% Et_3N) afforded **18** as a colourless oil (4.298 g, 94%); R_f = 0.46 (DCM–acetone 98:2 +1% Et_3N); $[\alpha]_D$ = +2.7 (*c* 1.01, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$ + TEA) δ (ppm) 7.84–7.53 (m, 7H, arom.), 7.47–7.21 (m, 5H, arom.), 4.89 (q, 2H, J_{gem} = 11.3 Hz, ArC*H*$_2$), 4.67 (d, 1H, $J_{1,2}$ = 9.5 Hz, H-1), 4.28 (t, 1H, *J* = 5.8 Hz), 4.20 (dd, 1H), 3.86 (m, 1H), 3.66 (m, 3H), 3.17 (s, 3H, OC*H*$_3$), 1.36, 1.34, 1.33 (3s, 12H, 4 × C*H*$_3$). ^{13}C NMR δ (ppm) 135.26, 134.10, 133.17, 133.03, 131.52, 128.60, 127.96, 127.83, 127.56, 127.03, 126.26, 125.87, 125.75 ($C_{arom.}$), 109.97 ($C_{acetalic}$), 100.00 (MIP-$C_{acetalic}$), 86.04 (*C*-1), 79.73, 78.06, 75.73, 73.83 (skeleton *C*s), 73.31 (ArCH$_2$), 60.21 (*C*-6), 48.45 (OCH$_3$), 27.66, 26.17 (IP *C*H$_3$), 24.28 (MIP *C*H$_3$); Anal. Calcd for $C_{30}H_{36}O_6S$ (524.16): C, 54.72; H, 6.34; S, 6.96. Found: C, 54.51; H, 6.37; S 6.92.

4.16. Phenyl 3,4-*O*-isopropylidene-2-*O*-(2-naphthyl)methyl-1-thio-β-D-galactopyranoside 19

To a solution of **18** (4.200 g, 0.001 mol) in DCM (71 mL) acetic acid (96%, 5.7 mL) and water (0.08 mL) were added and the mixture was kept at 55 °C under reflux conditions. After completion of the reaction (2.5 h) the mixture was diluted with DCM, washed with satd $NaHCO_3$ solution, dried and evaporated. Column chromatographic purification (DCM–acetone 9:1) afforded **19** as a colourless oil (3.231 g, 84%); R_f = 0.29 (DCM–acetone 97:3 +1% Et_3N); $[\alpha]_D$ = +12.8 (*c* 1.03, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$ + 1% TEA) δ (ppm) 7.84–7.22 (m, 12H, arom.), 4.89 (q, 2H, J_{gem} = 11.3 Hz, ArC*H*$_2$), 4.65 (d, 1H, $J_{1,2}$ = 9.5 Hz, H-1), 4.27 (t, 1H, *J* = 5,8 Hz), 4.12 (dd, 1H, J_A = 5.4 Hz, J_B = 1.4 Hz, H-4), 3.84 (m, 3H, H-5, H-6a,b), 3.55 (dd, 1H, J_A = 9.5 Hz, J_B = 6.2 Hz), 2.31 (s, 1H, O*H*), 1.34, 1.32 (2s, C*H*$_3$). ^{13}C NMR δ (ppm) 135.16, 133.37, 133.15, 133.00, 131.83, 128.80, 127.97, 127.85, 127.59, 127.42, 127.01, 126.23, 125.94, 125.82 ($C_{arom.}$), 110.21 ($C_{acetalic}$), 85.80 (*C*-1), 79.66, 78.06, 76.70, 73.79 (skeleton *C*s), 73.33 (ArCH$_2$), 62.40 (*C*-6), 27.59, 26.20 (Ip *C*H$_3$). Anal. Calcd for $C_{26}H_{28}O_5S$ (452.57): C, 52.51; H, 5.44; S, 8.25. Found: C, 52.28; H, 5.41; S, 8.29.

4.17. Phenyl 2,3,4,6-tetra-*O*-benzyl-α,β-D-galactopyranosyl-(1→6)-3,4-*O*-isopropylidene-2-*O*-(2-naphthyl)methyl-1-thio-β-D-galactopyranoside 21

*Glycosylation with the imidate donor **20***: To a solution of **19** (1.596 g, 3.64 mmol) and freshly prepared **20**[16] (3.323 g, 4.91 mmol, 1.35 equiv) in dry DCM (30 mL) 4 Å molecular sieves (4.0 g) were added and the mixture was stirred for 2 h under Argon. Then it was cooled to −30 °C and TMSOTf (117 μl, 0.18 equiv) in dry DCM (6 mL) was added. After completion of the reaction (1.5 h) it was quenched by the addition of Et_3N (0.2 mL), the mixture was diluted with DCM, filtered and evaporated. Column chromatographic purification afforded **21** as a colourless oil (3.077 g, 88%); R_f = 0.60 (*n*-hexane–ethyl acetate 65:35).

*Glycosylation with the bromosugar donor **23***: To a stirred solution of **22**[17] (3.200 g, 5.06 mmol, 1.0 equiv) in DCM (50 mL) at 0 °C Br_2 (245 μl, 4.80 mmol, 0.95 equiv) was added. After complete conversion of **22** 4 Å powdered molecular sieves (5 g) were added into the mixture and stirred for another half an hour at 0 °C. Then compound **19** (1.585 g, 3.52 mmol, 0.7 equiv) and Bu_4NBr (2.453 g, 7.58 mmol, 1.5 equiv) in dry DMF (40 mL) were added and the mixture was allowed to warm up to room temperture slowly. The reaction took place within 24 h. The mixture was diluted with CH_2Cl_2 and filtered through a pad of Celite, the filtrate was washed with 5% $Na_2S_2O_3$ and with satd $NaHCO_3$ solutions then with water. The organic layer was dried and evaporated. The residue was then purified by column chromatography to give **21** as a colourless oil (2.347 g, 68%); R_f = 0.60 (*n*-hexane–ethyl acetate 65:35); $[\alpha]_D$ = +26.7 (*c* 1.05, $CHCl_3$); ^{1}H NMR (360 MHz) δ (ppm) 7.84–7.11 (m, 32H, arom.), 4.91–3.43 (m, 24H, skeleton *H*s, 5 × Ph-C*H*$_2$), 1.32, 1.30 (2s, 6H, Ip-C*H*$_3$). ^{13}C NMR δ (ppm) 138.79, 138.61, 138.05, 135.15, 133.88, 133.12, 133.00, 131.48, 130.60, 128.69, 128.28, 128.13, 127.98, 127.84, 127.69, 127.60, 127.78 ($C_{arom.}$), 110.07 ($C_{acetalic}$), 97.76 (*C*-1′), 85.80 (*C*-1), 79.67, 79.08, 77.85, 76.47, 75.02, 73.48, 73.20, 68.92 (skeleton *C*s), 74.79, 73.47, 73.20, 73.12, 72.95 (ArCH$_2$), 68.68 (*C*-6), 67.31 (*C*-6′), 27.72, 26.37 (Ip *C*H$_3$). Anal. Calcd for $C_{60}H_{62}O_{10}S$ (975.19): C, 73.90; H, 6.41; S, 3.29. Found: C, 74.18; H, 6.38; S, 3.31. MALDI-TOF: *m/z* calcd for $[M+Na]^+$: 997.396. Found: 997.343.

4.18. Phenyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-*O*-(2-naphthyl)methyl-1-thio-β-D-galactopyranoside 24

Compound **21** (2.248 g, 2.22 mmol) was dissolved in THF (15 mL) and a mixture of concd HCl–H_2O (1:3, 0.68 mL) was added. The mixture was kept at 45 °C for 5 h. Then the mixture was diluted with DCM, washed with satd $NaHCO_3$ solution and with water, the organic layer was dried and evaporated. The residue was then purified by column chromatography (DCM–MeOH 97:3) to give the diol intermediate as a colourless oil (1.795 g, 91%); R_f = 0.26 (*n*-hexane–ethyl acetate 65:35); ^{1}H NMR (360 MHz) δ (ppm) 7.81–7.03 (m, 32H, arom.), 5.05–3.28 (m, 24H, skeleton *H*s, 5 × Ph-C*H*$_2$), 2.61 (s, 2H, 2 × O*H*). ^{13}C NMR δ (ppm) 138.52, 138.41, 138.06, 137.88, 135.56, 134.06, 133.18, 132.98, 131.63, 131.21, 128.84, 128.31, 128.12, 128.01, 127.90, 127.75, 127.69, 127.60, 127.51, 127.28, 126.95, 126.16, 125.98, 125.84 ($C_{arom.}$), 98.52 (*C*-1′), 87.66 (*C*-1), 78.79, 78.32, 76.37, 76.18 75.06, 74.71, 73.53, 69.44 (skeleton *C*s), 75.38, 73.30, 72.82, (ArCH$_2$), 68.77 (*C*-6′), 67.78 (*C*-6). Anal. Calcd for $C_{57}H_{58}O_{10}S$ (935.13): C, 73.21; H, 6.25; S, 3.43. Found: C, 73.25; H, 6.23; S, 3.41. MALDI-TOF: *m/z* calcd for $[M+Na]^+$: 957.364. Found: 956.257.

To a solution of the diol intermediate (1.700 g, 1.78 mmol) in pyridine (15 mL) acetic anhydride was added (8 mL) and the mixture was stirred overnight. Then the mixture was evaporated in vacuo and co-evaporated with toluene. The residue was diluted with CH_2Cl_2 washed with satd $NaHCO_3$ solution, the organic layer was dried and evaporated. The residue was then purified by column chromatography to give **24** as colourless oil (1.112 g, 60%); R_f = 0.48 (*n*-hexane–ethyl acetate 65:35); $[\alpha]_D$ = +28.2 (*c* 0.99, $CHCl_3$). ^{1}H NMR (500 MHz) δ (ppm) 7.82–7.76 (m, 3H, arom.), 7.70 (s, 1H, arom.), 7.58 (d, 2H, arom.), 7.48–7.42 (m, 3H, arom.), 7.40–7.19 (m, 23H, arom.), 4.50 (d, 1H, J_{gem} = 11.3 Hz, ArCH*H*), 4.92 (d, 1H, J_{gem} = 11.4 Hz, ArC*H*H), 4.80 (d, 1H, J_{gem} = 11.6 Hz, PhCH*H*), 4.78–4.71 (m, 4H, H-1, H-1′, ArC*H*$_2$), 4.70 (d, 1H, J_{gem} = 11.6 Hz, ArCH*H*), 4.64 (d, 1H, J_{gem} = 11.8 Hz, ArC*H*H), 4.55 (d, 1H, J_{gem} = 11.4 Hz, ArCH*H*), 4.43 (q, 2H, ArC*H*$_2$), 2.00, 1.87 (2s, 6H, COC*H*$_3$). ^{13}C NMR δ (ppm) 170.08, 169.73 (*C*=O), 138.84, 138.59, 138.39, 138.09, 135.29, 133.55, 133.15, 132.95 (*C*q, arom.), 131.69, 128.86, 128.30, 128.25, 128.13, 128.07, 128.00, 127.81, 127.73, 127.67, 127.60, 127.48, 127.42, 127.38, 127.30, 126.50, 126.06, 125.91, 125.83 ($C_{arom.}$), 75.37, 74.69, 73.47, 73.22, 73.17 (ArCH$_2$), 20.64, 20.60 (COCH$_3$). Anal. Calcd for $C_{61}H_{62}O_{12}S$ (1019.20): C, 71.88; H, 6.13; S, 3.15. Found: C, 71.92; H, 6.10; S, 3.13. MALDI-TOF: *m/z* calcd for $[M+Na]^+$: 1041.385. Found 1041.671.

4.19. (2-Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-*O*-(2-naphthyl)methyl-α-D-galactopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 25

Compound **24** (0.521 g, 0.511 mmol) was reacted with **10** (0.428 g, 0.340 mmol) according to general method **C** at −5 °C. Purification of the crude product by column chromatography ((1) DCM–acetone 98:2; (2) *n*-hexane–ethyl acetate 65:35) afforded **25** as a foam (0.319 g, 43%); R_f = 0.65 (DCM–acetone 97:3); $[\alpha]_D$ = +64.8 (*c* 0.13); ^{1}H NMR (500 MHz) δ (ppm) 7.79 (m, 1H, arom.), 7.64 (m, 3H, arom.), 7.58 (d, 2H, *J* = 7.5 Hz, arom.), 7.46 (m, 2H, arom.), 7.36 (m, 11H, arom.), 7.31–6.97 (m, 41H, arom.), 6.79 (t, 1H, *J* = 7.4 Hz, arom.), 5.72 (br s, 1H), 5.58 (s, 1H, $H_{acetalic}$), 5.49 (br s, 1H), 5.23–5.17 (m, 2H), 5.11–5.06 (m, 2H), 4.94 (d, 1H, J_{gem} = 13.8 Hz, CH*H*), 4.86 (d, 1H, J_{gem} = 11.3 Hz, CH*H*), 4.81–4.68 (m, 7H), 4.65 (br s, 1H), 4.60–4.39 (m, 9H), 4.38–4.18 (m, 9H), 4.11 (t, 1H, *J* = 6.3 Hz) 4.03 (dd, 1H, J_A = 10.5 Hz, J_B = 2.1 Hz), 4.00 (br s, 1H), 3.98–3.89 (m, 3H), 3.86 (m, 1H), 3.82–3.76 (m, 2H), 3.74–3.70 (m, 2H), 3.69–3.63 (m, 4H), 3.62–3.56 (m, 2H), 3.51 (m, 1H), 3.46–3.41 (m, 2H), 3.27 (t, 1H, *J* = 8.7 Hz), 1.94 (s, 3H, COCH_3), 1.76 (s, 3H, COCH_3), 1.19 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, H-6″), 0.68 (m, 2H, CH_2Si), −0.16 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR δ (ppm) 169.98, 169.85 (*C*=O), 139.39, 139.17, 139.11, 139.07, 138.63, 138.48, 138.12, 137.97, 137.44, 135.57, 133.02, 132.71, 131.48 (*C*q), 133.97, 128.45–127.38, 127.13, 127.05, 126.97, 126.47, 126.03, 126.00, 125.94, 125.72, 125.52, 125.15, 123.37 ($C_{arom.}$), 100.50 ($C_{acetalic}$), 99.98, 98.58, 98.51, 97.36, 96.90 (anomer *C*s), 82.57, 80.13, 79.14, 77.76, 75.93, 75.72, 73.23, 73.00, 70.96, 69.58, 69.43, 69.00, 67.67, 66.65, 66.14 (skeleton *C*s), 75.33, 74.60, 73.98, 73.37, 73.03, 72.84, 72.60, 70.98, 70.81, 69.61, 68.82, 68.53, 67.31, 65.78 (OCH_2), 56.70 (*C*-2), 20.77, 20.46 (COCH_3), 17.95 (*C*H_2Si), 16.65 (C-6″), −1.66 (Si(*C*H_3)$_3$). Anal. Calcd for $C_{128}H_{137}NO_{28}Si$ (2165.53): C, 70.99; H, 6.38. Found: C, 71.15; H, 6.35. MALDI-TOF: *m/z* calcd for [M+Na]$^+$: 2186.899. Found: 2186.637.

4.20. (2-Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-*O*-(2-naphthyl)methyl-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 26

Compound **24** (0.520 g, 0.510 mmol) was reacted with **13** (0.428 g, 0.340 mmol) according to general method **C** at −8 °C. Purification of the crude product by column chromatography (DCM–acetone 98.5:1.5) afforded **26** as a foam (0.369 g, 50%); R_f = 0.70 (DCM–acetone 98:2); $[\alpha]_D$ = −23.6 (*c* 0.12, $CHCl_3$); ^{1}H NMR^{1}H NMR (500 MHz) δ (ppm) 7.81 (m, 1H, arom.), 7.72–7.59 (m, 3H, arom.), 7.52–7.38 (m, 12H, arom.), 7.34–7.11 (m, 42H, arom.), 7.10–7.05 (m, 3H, arom.), 7.03–6.97 (m, 3H, arom.), 5.50–5.43 (m, 3H), 5.35–5.29 (m, 2H), 5.04–4.91 (m, 3H), 4.85–4.76 (m, 5H), 4.70–4.61 (m, 4H), 4.57–4.49 (m, 4H), 4.45–4.41 (m, 2H), 4.35–4.21 (m, 9H), 4.17 (d, 1H, *J* = 6.5 Hz), 4.09–4.02 (m, 2H), 4.01–3.90 (m, 5H), 3.86–3.78 (m, 2H), 3.77–3.67 (m, 4H), 3.63 (t, 1H, *J* = 10.3 Hz), 3.59–3.41 (m, 8H), 3.33 (dd, 1H, J_A = 9.5 Hz, J_B = 2.3 Hz), 3.26 (m, 1H), 1.94 (s, 3H, COCH_3), 1.87 (s, 3H, COCH_3), 1.36 (d, 3H, $J_{5'',6''}$ = 6.3 Hz, H-6″), 0.73 (m, 1H, CH*H*Si), 0.64 (m, 1H, C*H*HSi), −0.18 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR δ (ppm) 169.94, 169.52 (*C*=O), 139.41, 138.70, 138.69, 138.63, 138.56, 138.32, 138.25, 138.06, 137.74, 137.53, 135.74, 133.07, 132.69 (*C*q), 132.18, 129.79, 129.24, 128.64, 128.29–127.90, 127.69–127.29, 126.97, 126.93, 126.60, 126.05, 125.93, 125.66, 125.43, 125.03 ($C_{arom.}$), 100.88 ($C_{acetalic}$), 101.11, 98.75, 98.14, 97.91, 96.62 (anomer *C*s), 82.29, 81.16, 80.71, 79.10, 76.31, 76.13, 75.49, 74.95, 74.47, 73.02, 72.56, 69.68, 68.92, 68.78, 67.36, 66.42 (skeleton *C*s), 75.69, 74.68, 74.38, 73.43, 73.10, 72.73, 72.64, 70.91, 70.87, 69.06, 68.71, 68.62, 67.16, 66.99 (OCH_2), 55.89 (*C*-2), 20.74, 20.52 (COCH_3), 17.83 (*C*H_2Si), 17.00 (*C*-6″), −1.68 (Si(*C*H_3)$_3$). Anal. Calcd for $C_{128}H_{137}NO_{28}Si$ (2165.53): C, 70.75; H, 6.42. Found: C, 70.69; H, 6.44. MALDI-TOF: *m/z* calcd for [M+Na]$^+$: 2186.899. Found: 2187.079.

4.21. (2-Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-3,4-di-*O*-acetyl-2-*O*-(2-naphthyl)methyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside 27

Compound **24** (0.521 g, 0.511 mmol) was reacted with **16** (0.428 g, 0.340 mmol) according to general method **C** at −8 °C. Purification of the crude product by column chromatography ((1) DCM–acetone 98.5:1.5; (2) *n*-hexane–ethyl acetate 65:35) afforded **27** as a foam (0.370 g, 50%); R_f = 0.78 (DCM–acetone 97:3); $[\alpha]_D$ = −4.3 (*c* 0.14); ^{1}H NMR (500 MHz) δ (ppm) 7.70 (m, 1H, arom.), 7.58–7.48 (m, 5H, arom.), 7.41–6.95 (m, 51H, arom.), 6.79 (d, 2H, *J* = 7.2 Hz), 5.82 (d, 1H, *J* = 3.82 Hz), 5.59 (d, 1H, *J* = 2.6 Hz), 5.55 (s, 1H, $H_{acetalic}$), 5.47 (dd, 1H, J_A = 10.7 Hz, J_B = 3.1 Hz), 5.23 (d, 1H, *J* = 3.1 Hz), 5.15 (d, 1H, *J* = 8.5 Hz), 5.01 (t, 1H, *J* = 9.5 Hz), 4.91 (d, 1H, *J* = 11.4 Hz), 4.85–4.76 (m, 4H), 4.74–4.65 (m, 4H), 4.64–4.52 (m, 4H), 4.51–4.39 (m, 7H), 4.37–4.25 (m, 5H), 4.15 (s, 1H), 4.11–3.97 (m, 6H), 3.94 (dd, 1H, J_A = 10.1 Hz, J_B = 2.5 Hz), 3.86 (m, 1H), 3.83–3.74 (m, 5H), 3.73–3.52 (m, 9H), 3.44 (m, 1H), 3.41–3.35 (m, 2H), 2.02 (s, 3H, COCH_3), 1.92 (s, 3H, COCH_3), 1.36 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, H-6″), 0.77–0.63 (m, 2H, CH_2Si), −0.16 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR δ (ppm) 169.98, 169.70 (*C*=O), 138.86, 138.68, 138.61, 138.58, 138.51, 138.19, 137.88, 137.49, 135.86, 132.93, 132.61 (*C*q), 128.48–127.90, 127.71–127.39, 127.25, 127.13, 126.91, 126.82, 126.71, 126.19, 126.11, 125.78, 125.55, 125.45, 125.33 ($C_{arom.}$), 100.69 ($C_{acetalic}$), 100.32, 99.31, 98.43, 97.45, 96.64 (anomer *C*s), 83.04, 80.12, 79.40, 78.74, 76.67, 76.46, 75.81, 75.14, 74.98, 72.92, 72.87, 72.50, 72.40, 69.80, 69.16, 66.83, 66.61, 66.52 (skeleton *C*s), 74.75, 74.22, 73.59, 73.50, 73.32, 73.13, 73.09, 72.18, 71.43, 71.14, 68.68, 68.48, 67.49, 67.25 (OCH_2), 56.48 (*C*-2), 20.82, 20.61 (COCH_3), 17.88 (*C*H_2Si), 17.54 (*C*-6″), −1.67 (Si(*C*H_3)$_3$). Anal. Calcd for $C_{128}H_{137}NO_{28}Si$ (2165.53): C, 70.99; H, 6.38. Found: C, 71.20; H, 6.34. MALDI-TOF: *m/z* calcd for [M+Na]$^+$: 2186.899. Found 2186.666.

4.22. (2-Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-2-*O*-(2-naphthyl)methyl-α-D-galactopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside 28

Compound **25** (0.280 g, 0.129 mmol) was converted to the title compound in three steps according to general method **D**. *Dephthaloylation step*: TLC (DCM–MeOH 99:1), $R_{f,free\ amine}$ = 0.32. *Acetylation step*: white crystals (0.236 g, 88%); R_f = 0.53 (*n*-hexane–ethyl acetate 55:45); mp 166–168 °C (ethyl acetate–*n*-hexane); $[\alpha]_D$ = +36.0 (*c* 0.38, $CHCl_3$); $C_{122}H_{137}NO_{27}Si$ (2077.47). *O-Deacetylation step*: crude product was purified by column chromatography (DCM–acetone 91:9), R_f = 0.34 to give **28** as a foam (0.211 g, 82% over three steps); $[\alpha]_D$ = + 6.8 (*c* 0.13, $CHCl_3$); ^{1}H NMR (200 MHz) δ (ppm) 7.70–7.05 (m, 62H, arom.), 6.59 (d, 1H, *J* = 7.2 Hz), 5.58 (s, 1H), 5.42 (s, 2H), 5.12–3.30 (m, 59H), 2.05 (s, 2H), 1.89 (s, 3H), 1.32–1.16 (m, 5H), 0.96–0.80 (m, 2H CH_2Si), −0.07 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR δ (ppm) 170.41 (*C*OCH$_3$), 138.71, 138.65, 138.50, 138.39, 138.18, 138.14, 137.72, 137.43, 135.56, 132.94, 132.65 (*C*q), 128.53–127.11, 126.58, 126.37, 125.98, 125.61, 125.48 ($C_{arom.}$) 101.81, 100.73, 98.44, 98.24 ($C_{acetalic}$, anomer *C*s), 82.19, 80.05, 79.27, 78.84, 76.84, 76.23, 75.68, 74.73, 72.83, 70.75, 69.72, 69.27, 68.64, 67.12, 66.14 (skeleton *C*s), 74.67, 74.53, 74.27,

73.28, 73.18, 72.93, 72.57, 72.33, 71.98, 71.47, 68.47, 68.33, 67.88, 66.91 (OCH_2), 57.23 (*C*-2), 23.15 ($COCH_3$), 18.04 (CH_2Si), 16.75 (*C*-6‴), –1.66 ($Si(CH_3)_3$). Anal. Calcd for $C_{118}H_{133}NO_{25}Si$ (1993.40): C, 71.10; H, 6.73. Found: C, 71.36; H, 6.70. MALDI-TOF: *m/z* calcd for $[M+Na]^+$: 2014.883. Found 2014.719.

4.23. (2-Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-2-*O*-(2-naphthyl)methyl-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside 29

Compound **26** (0.230 g, 0.106 mmol) was converted to the title compound in three steps according to general method **D**. *Dephthaloylation step*: TLC (DCM–MeOH 99:1), $R_{f,free\ amine}$ = 0.50. *Acetylation step*: product was obtained as a foam (0.199 g, 90%); R_f = 0.42 (*n*-hexane–ethyl acetate 6:4); $[\alpha]_D$ = −11.5 (*c* 0.15, $CHCl_3$); MALDI-TOF: *m/z* calcd for $[M+Na]^+$: 2098.904. Found 2097.698. *O-Deacetylation step*: crude product was purified by column chromatography (*n*-hexane–ethyl actetate, 1:1, R_f = 0.34) to give **29** as a foam (0.165 g, 78% over three steps); R_f = 0.68 (DCM–acetone 94:6); $[\alpha]_D$ = +5.8 (*c* 0.12, $CHCl_3$); ^{1}H NMR^{1}H NMR (200 MHz) δ (ppm) 7.85–7.05 (m, 67H, arom.), 6.48 (d, 1H, *J* = 6.8 Hz), 5.58–5.40 (m, 3H), 5.10–3.30 (m, 63H), 2.43 (br s, 1H), 1.82 (s, 3H $COCH_3$), 1.35 (d, 3H, $J_{5'',6''}$ = 6.0 Hz, H-6″), 1.28 (s, 1H), 1.04–0.85 (m, 2H, CH_2Si), 0.00 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR δ (ppm) 170.41 ($COCH_3$), 138.57, 138.49,138.37, 138.04, 137.84, 137.79, 137.49, 135.67, 133.06, 132.77 (*C*q), 128.69, 128.31–127.62, 127.49, 127.46, 127.24, 126.89, 126.08, 126.01, 125.80, 125.58, 125.38 ($C_{arom.}$), 102.31, 100.93, 99.18, 97.67, 97.12 ($C_{acetalic}$, anomer *C*s), 82.46, 80.34, 80.11, 78.84, 78.25, 76.95, 76.83, 76.16, 75.46, 74.62, 74.48, 72.64, 69.76, 68.92, 68.86, 68.59, 67.76, 66.47 (skeleton *C*s), 75.02, 74.67, 74.42, 73.60, 73.44, 73.32, 72.80, 72.58, 71.79, 71.22, 68.71, 68.41, 66.81 (OCH_2), 56.67 (*C*-2), 23.11 ($COCH_3$), 17.92 (CH_2Si), 16.90 (*C*-6″), −1.53 ($Si(CH_3)_3$); Anal. Calcd (%) for $C_{118}H_{133}NO_{25}Si$ (1993.40): C, 71.10; H, 6.73. Found: C, 70.89; H, 6.78. MALDI-TOF: *m/z* calcd for $[M+Na]^+$: 2014.883. Found 2014.717.

4.24. (2-Trimethylsilyl)ethyl 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl-(1→6)-2-*O*-(2-naphthyl)methyl-α-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside 30

Compound **27** (0.330 g, 0.152 mmol) was converted to the title compound according to general method **D**. *Dephthaloylation step*: TLC (DCM–MeOH = 99:1), $R_{f,free\ amine}$ = 0.50. *Acetylation step*: product was obtained as a foam (0.285 g, 90%); R_f = 0.35 (*n*-hexane–ethyl acetate 65:35); $[\alpha]_D$ = −12.8 (*c* 0.16). *O-Deacetylation step*: crude product was purified by column chromatography (DCM–acetone 9:1) to give **30** as a foam (0.249 g, 82% over three steps); R_f = 0.58 (DCM–acetone 91:9); $[\alpha]_D$ = +5.8 (*c* 0.12); ^{1}H NMR (200 MHz) δ (ppm) 7.73–6.82 (m, 62H, arom.), 6.53 (d, 1H, *J* = 7.0 Hz), 5.88 (s, 1H), 5.50 (s, 2H), 5.05–3.30 (m, 58H), 2.65 (s, 1H), 1.84 (s, 3H, $COCH_3$), 1.36–1.24 (m, 4H), 0.98–0.82 (m, 2H, CH_2Si), 0.00 ($Si(CH_3)_3$). ^{13}C NMR δ (ppm) 170.39 ($COCH_3$), 138.46, 138.39, 138.11, 138.05, 138.01, 137.76, 137.67, 137.34, 135.74, 132.95, 132.55 (*C*q), 128.22–127.64, 127.52, 127.50, 127.43, 127.29, 127.17, 127.03, 126.78, 126.00, 125.75, 125.36, 125.11, 124.73 ($C_{arom.}$), 101.97, 100.77, 100.56, 98.56, 97.16, 95.96 ($C_{acetalic}$, anomer *C*s), 82.86, 79.55, 78.64, 76.85, 76.65, 76.11, 75.64, 74.74, 73.71, 72.92, 69.50, 69.12, 68.37, 67.02, 66.12 (skeleton *C*s), 74.56, 74.25, 73.55, 73.28, 73.10, 72.80, 72.57, 72.23, 70.86, 68.67, 68.52, 67.76, 66.85 (OCH_2), 57.54 (*C*-2), 23.17 ($COCH_3$), 18.02 (CH_2Si), 17.76 (*C*-6‴), −1.63 ($Si(CH_3)_3$). Anal. Calcd for $C_{118}H_{133}NO_{25}Si$ (1993.40): C, 71.10; H, 6.73. Found: C, 70.86; H, 6.69. MALDI-TOF: *m/z* calcd for $[M+Na]^+$: 2014.883. Found 2014.716.

4.25. (2-Trimethylsilyl)ethyl α-D-galactopyranosyl-(1→6)-α-D-galactopyranosyl-(1→2)-α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside 1

Compound **28** (0.185 g, 0.092 mmol) was converted to the title compound according to general method **E**. The yield after column chromatography (DCM–MeOH–H_2O 5:5:0.5): White powder (0.080 g, 90%); R_f = 0.46 (DCM–MeOH–H_2O 6:4:0.8); $[\alpha]_D$ = +29.7 (*c* 0.14, MeOH). ^{1}H NMR (500 MHz, D_2O) δ (ppm) 4.32–4.25 (d, 2H), 3.92–3.80 (m, 6H), 3.80–3.54 (m, 17H), 3.54–3.45 (m, 4H), 3.37–3.30 (m, 2H), 1.92 (s, 3H, CH_3CO), 1.09 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, CH_3), 0.81, 0.70 (2 × ddd, 2H, CH_2Si), –0.15 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR δ (ppm) 174.07 (*C*=O), 77.48, 76.83, 75.72, 75.17, 73.89, 72.56, 72.45, 71.34, 69.73, 69.65, 69.55, 69.36, 69.12, 68.81, 68.58, 67.17 (skeleton *C*s), 54.94 (*C*-2), 68.63 (*C*-6‴), 67.51 (OCH_2CH_2Si), 61.51, 61.44, 60.99 (3 × *C*-6), 22.72 (CH_3CO), 17.53 (CH_2Si), 15.57 (*C*-6″), −2.08 ($Si(CH_3)_3$). Anal. Calcd for $C_{37}H_{67}NO_{25}Si$ (954.01): C, 46.58; H, 7.08. Found: C, 46.37; H, 7.12. MALDI-TOF: *m/z* calcd for $[M+Na]^+$: 976.366. Found 976.363.

4.26. (2-Trimethylsilyl)ethyl α-D-galactopyranosyl-(1→6)-α-D-galactopyranosyl-(1→3)-α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside 2

Compound **29** (0.135 g, 0.067 mmol) was converted to the title compound according to general method **E**. The yield after column chromatography (DCM–MeOH–H_2O 4:6:0.8): White powder (0.055 g, 85%); R_f = 0.39 (DCM–MeOH–H_2O 4:6:0.5); $[\alpha]_D$ = +21.1 (*c* 0.18, MeOH). ^{1}H NMR (500 MHz, D_2O) δ (ppm) 4.26–4.20 (m, 2H), 3.94 (br s, 1H), 3.91 (br s, 1H), 3.88–3.72 (m, 10H), 3.72–3.57 (m, 10H), 3.55–3.48 (m, 3H), 3.45 (t, 1H), 3.37–3.30 (m, 2H), 1.90 (s, 3H, $COCH_3$), 1.09 (d, 3H, $J_{5'',6''}$ = 6.5 Hz, CH_3), 0.83 (ddd, 1H, C*H*HSi), 0.76–0.66 (m, 1H, CH*H*Si), −0.14 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR δ (ppm) 173.42 ($COCH_3$), 80.32, 77.39, 77.16, 75.85, 75.35, 73.68, 71.77, 71.29, 70.12, 69.83, 69.58, 69.50, 69.44, 69.09, 68.99, 68.45, 67.13, 66.69 (skeleton *C*s), 68.76 (*C*-6‴), 67.65 (OCH_2CH_2Si), 61.73, 61.50, 61.05 (3 × *C*-6), 55.04 (*C*-2), 22.85 ($COCH_3$), 17.67 (CH_2Si), 15.93 (*C*-6″), −2.08 ($Si(CH_3)_3$). Anal. Calcd for $C_{37}H_{67}NO_{25}Si$ (954.01): C, 46.58; H, 7.08. Found: C, 46.40; H, 7.05. MALDI-TOF: *m/z* calcd for $[M+Na]^+$: 976.366. Found 976.249.

4.27. (2-Trimethylsilyl)ethyl α-D-galactopyranosyl-(1→6)-α-D-galactopyranosyl-(1→4)-α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside 3

Compound **30** (0.220 g, 0.110 mmol) was converted to the title compound according to general method **E**. The yield after column chromatography (DCM–MeOH–H_2O 5:5:0.5): White powder (0.095 g, 90%); R_f = 0.39 (DCM–MeOH–H_2O 5:5:0.5); $[\alpha]_D$ = +22.6 (*c* 0.22, MeOH). ^{1}H NMR (500 MHz, D_2O) δ (ppm) 4.25–4.18 (m, 2H), 3.92 (d, 1H), 3.89–3.56 (m, 22H), 3.56–3.42 (m, 4H), 3.37–3.30 (m, 2H), 1.89 (s, 3H, $COCH_3$), 1.17 (d, 3H, $J_{5'',6''}$ = 6.6 Hz, CH_3), 0.85–0.78 (m, 1H, C*H*HSi), 0.74–0.67 (m, 1H, CH*H*Si), −0.14 (s, 9H, $Si(CH_3)_3$). ^{13}C NMR δ (ppm) 173.84 ($COCH_3$), 83.36, 77.63, 76.85, 75.77, 75.36, 73.72, 71.34, 70.50, 70.34, 69.72, 69.66, 69.55, 69.46, 69.44, 69.05, 69.01, 68.51, 66.63 (skeleton *C*s), 68.53 (*C*-6‴), 67.56 (OCH_2CH_2Si), 61.46, 60.95 (3 × *C*-6), 54.93 (*C*-2), 22.59 ($COCH_3$), 17.49 (CH_2Si), 16.29 (*C*-6″), –2.06 ($Si(CH_3)_3$). Anal. Calcd for $C_{37}H_{67}NO_{25}Si$ (954.01): C, 46.58; H, 7.08. Found: C, 46.75; H, 7.11. MALDI-TOF: *m/z* calcd for $[M+Na]^+$: 976.366. Found 976.424.

Acknowledgement

This work was supported by the Hungarian Research Fund (OTKA NK 48798 to A.L. and K 62802 to A.B.)

References

1. Teng-umnuay, P.; Morris, H. R.; Dell, A.; Panico, M.; Paxton, T.; West, C. M. *J. Biol. Chem.* **1998**, *273*, 18242–18249.
2. West, C. M.; van der Wel, H.; Gaucher, E. A. *Glycobiology* **2002**, *12*, 17R–27R.
3. Sassi, S.; Sweetinburgh, M.; Erogul, J.; Zhang, P.; Teng-umnuay, P.; West, C. M. *Glycobiology* **2001**, *11*, 283–295.
4. van der Wel, H.; Fischer, S. Z.; West, C. M. *J. Biol. Chem.* **2002**, *277*, 46527–46534.
5. Ketcham, C.; Wang, F.; Fisher, S. Z.; Ercan, A.; van der Wel, H.; Locke, R. D.; Sirajud-Doulah, K.; Matta, K. L.; West, C. M. *J. Biol. Chem.* **2004**, *279*, 29050–29059.
6. Szabó, Z. B.; Borbás, A.; Bajza, I.; Lipták, A. *Tetrahedron: Asymmetry* **2005**, *16*, 83–95.
7. Jain, R. K.; Sarkar, A. K.; Matta, K. L. *Carbohydr. Res.* **1991**, *220*, C1–C4.
8. Martín-Lomas, M.; Flores-Mosquera, M.; Chiara, J. L. *Eur. J. Org. Chem.* **2000**, 1547–1562.
9. Matta, K. L.; Rana, S. S.; Piskorz, C. F.; Abbas, S. A. *Carbohydr. Res.* **1984**, *131*, 247–255.
10. Nifant'ev, N. E.; Shashkov, A. S.; Kotchetkov, N. K. *Carbohydr. Res.* **1992**, *226*, 331–336.
11. Chernyak, A.; Oscarson, S.; Turek, D. *Carbohydr. Res.* **2000**, *329*, 309–316.
12. Hiroshi, T.; Nobuatsu, M.; Takashi, T. *Chem. Lett.* **2005**, *34*, 400–401.
13. Hanessian, S.; Liak, T. J.; Dixit, D. M. *Carbohydr. Res.* **1981**, *88*, C14–C19.
14. Jansson, K.; Ahlfors, S.; Frejd, T.; Kihlberg, J.; Magnusson, G. *J. Org. Chem.* **1988**, *53*, 5629–5647.
15. Pozsgay, V. *Tetrahedron: Asymmetry* **2000**, *11*, 151–172.
16. Wegmann, B.; Schmidt, R. R. *J. Carbohydr. Chem.* **1987**, *6*, 357–375.
17. Garegg, P. J.; Hultberg, H.; Lindberg, C. *Carbohydr. Res.* **1980**, *83*, 157–162.