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ARTICLE

Convergent synthesis of isomeric heterosaccharides related to the fragments of galactomannan from *Aspergillus fumigatus*

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D.A. Argunov, V.B. Krylov, N.E. Nifantiev*

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Aspergillus fumigatus is a very common fungus with severe pathogenic potential for immunosuppressed hospital patients. *A. fumigatus* galactomannan, being the part of its cell-wall, is considered as a promising candidate for vaccine and diagnostic test-systems. In this article we report the convergent synthesis of pentasaccharide fragments of the galactomannan containing β-(1→5)-linked galactofuranoside chain attached to O-3 or O-6 of spacer-armed mannopyranoside residue. The synthesis of selectively protected galactofuranoside precursors has been performed using recently developed pyranoside-*into*-furanoside (PIF) rearrangement. For the assembling of the target galactomannan structures the [1+2+2]-scheme was applied. This strategy was shown to be highly efficient and can easily be extended to the synthesis of longer fragments of the galactomannan.

Introduction

Aspergillus fumigatus is the most prevalent airborne fungal pathogen, causing severe and usually fatal invasive aspergillosis (IA) in immunocompromised patients.[1] At risk are patients with cancer and undergoing intensive immunosuppressive therapy after receiving organ transplants. An important factor for the successful treatment of IA is its early diagnosis.

Galactomannan, built up from α-(1→2) and α-(1→6)-linked poly-D-mannose backbone with short (4-5 units) β-(1→5)-linked galactofuranoside branches at O-3 or O-6 of some of the mannose units, is an essential cell-wall component of *A. fumigatus*.[2] The detection of this antigen in biological fluids is currently widely used for the diagnosis of aspergillosis.[1] The structurally specified oligosaccharides related to galactomannan fragments are strongly demanded for immunological studies and particularly for the development of more sensitive and selective diagnostic test systems for the detection of this dangerous pathogen.

Laboratory of Glycoconjugate Chemistry, N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prospect 47, 119991 Moscow, Russian Federation. Fax: (+) 7-499-135-87-84. E-mail: nen@ioc.ac.ru

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Previously, the syntheses of different oligosaccharide fragments of galactomannan corresponding to the homo-galactofuranosyl[3-5] or heterosaccharide[6] chains were described. However, a more representative series of oligosaccharides built up from both galactofuranosyl and mannopyranoside units is demanded as antigens for immunological investigation. Herein, we describe the first synthesis of two galactomannan related heterosaccharides **1** and **2** containing β-(1→5)-linked tetragalactofuranoside blocks attached to either O-6 or O-3 of the spacer-armed mannopyranoside residue (Fig. 1).

Results and discussion

The assembling of target galactomannanosides **1** and **2** was performed applying a [1+2+2]-scheme. The key synthetic blocks were spaced-armed mannosides **3** and **4** containing free OH-groups at C-6 and C-3, respectively, and disaccharide donors **5** and **6** (Scheme 1). Difuranoside **5** contained a temporary chloroacetyl group at O-5 of the "non-reducing" unit for further deprotection to the free OH-group followed by chain elongation, while donor **6** was used only at the final glycosylation step when further chain elongation was not required.

The methods for preparation of selectively *O*-substituted furanoside derivatives are poorly developed as compared to synthesis of corresponding pyranoside analogues. Nowadays, the most widely used protocols for furanoside synthesis are based on the Fischer reaction or high-temperature acylation of

unprotected sugars.[7] However, the resulting products are often difficult to use for further regioselective introduction of protective groups of required types.

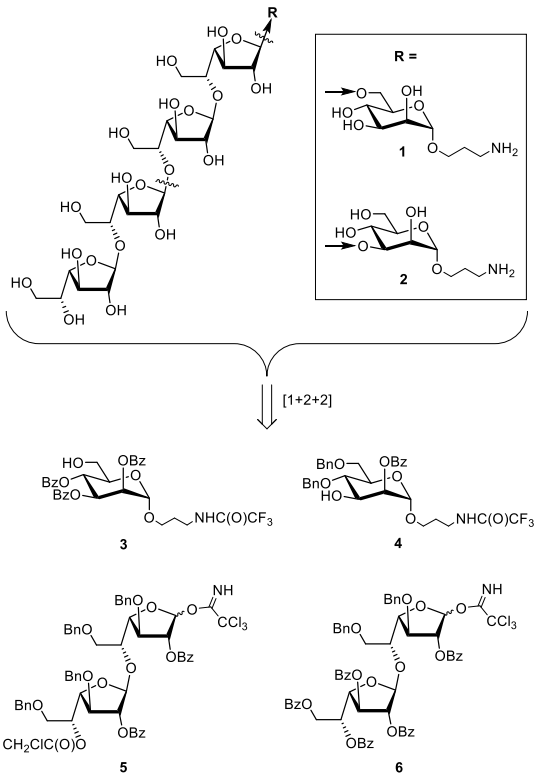
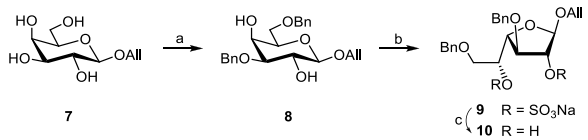


Fig. 1 Target galactomannan related pentasaccharides **1** and **2** and their key synthetic precursors **3**-**6**, as revealed by retrosynthetic analysis.

Recently, we have discovered a new reaction of pyranoside-*into*-furanoside (PIF) rearrangement permitting the transformation of selectively *O*-substituted pyranosides into corresponding furanosides.[8,9] The herein reported first syntheses of heterosaccharides related to the galactomannan from *A. fumigatus* were performed with the use of PIF rearrangement as a key step.

According to the substrate requirements for PIF-rearrangement, the starting pyranosides should have β-configuration of the anomeric center and free OH-groups at C-2 and C-4 of pyranose ring.[8] In order to obtain an appropriately substituted furanoside for the simplification of the final orthogonal protective groups placement, galactopyranoside **8** was chosen as a substrate for the PIF-rearrangement (Scheme 1). This compound was prepared by regioselective benzylation of allyl galactoside **7**[10] *via* the organotin intermediate.[11] Isomerization of pyranoside **8** into furanoside **10** was performed in DMF with Py·SO_3 complex and chlorosulfonic acid followed by solvolytic O-desulfation of isolated crude per-*O*-sulfated derivative **9** in dioxane in presence of Amberlite IR-120(H^+). NMR-monitoring of the reaction mixture (see the supplementary information) permitted to optimize the amount of the sulfating reagents, to decrease the heating temperature and to shorten the reaction time.

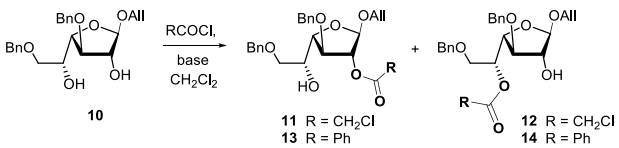
The synthesis of target galactomannan pentasaccharides **1** and **2** required further regioselective protection of O-5 in diol **10**. The results of the studied acylation reactions of diol **10** are summarized in Table 1. The chloroacetylation of **10** in presence of Py in DCM at low temperatures smoothly gave 5-*O*-acylated product **12** (entry 1), while only traces of 2-*O*-acylated and 2,5-di-*O*-acylated derivatives were detected. This was contrary to the result of the previously observed preferential 2-*O*-acylation of 2,5-diol on the basis of 1,6-anhydrogalactofuranose derivative.[12]



Scheme 1 Synthesis of dibenzylated galactofuranoside **10** by PIF rearrangement of pyranoside **8**. (a) $(Bu_3Sn)_2O$, toluene, Δ, 6 h, then BnBr, TBAI, 100 °C, 70%; (b) Py·SO_3, HSO_3Cl, DMF, 40 °C, 1 h, then excess of $NaHCO_3$ aq.; (c) IR-120(H^+), dioxane, Δ, 59% over two steps.

The presence of 5-*O*-acyl group in **12** was confirmed by the downfield shift of H-5 (3.89→5.34 ppm) in the ^{1}H NMR spectrum. Surprisingly, the analogous acylation, but in the presence of Et_3N instead of Py, resulted in the predominant formation of 2-*O*-substituted derivative **11** (entry 2), which was confirmed by the downfield location of H-2 signal (4.16→5.20 ppm). In the same way, benzoylation of furanoside **10** by BzCl in presence of Et_3N also gave 2-*O*-benzoylated derivative **13** predominantly (entry 3). The difference in regioselectivity of the acylation reaction in the precence of Et_3N or Py can be explaned by the influence of steric and polar factors. It is known that the base involved both in the activation of an acid chloride and polarization of an O–H bond.[13] Thus, the difference in basicity and spatial hindrance of the intermolecular interaction can dramatically change the regioselectivity.

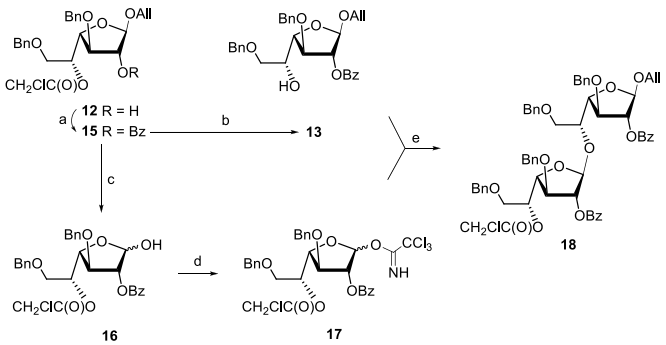
Table 1. Regioselective acylation of diol **10**.



Entry	Acylation conditions	2-*O*-Acylated product, yield	5-*O*-Acylated product, yield
1	$ClCH_2C(O)Cl$ (1.3 eq.), Py (1.5 eq.), -78→0 °C, 1 h	**11**, <5% (TLC)	**12**, 69%
2	$ClCH_2C(O)Cl$ (1.3 eq.), Et_3N (1.5 eq.), -78→0 °C, 1 h	**11**, 56%[a]	**12**, 17%[a]
3	PhC(O)Cl (2.0 eq.), Et_3N (2.5 eq.), -20→+8 °C, 16 h	**13**, 58%[a]	**14**, 16%[a]

[a] Ratio of isomers was calculated from ^{1}H-NMR spectra.

Chloroacetylation of diol **10** in Py (entry 1) due to its better regioselectivity was employed in the further synthesis towards pentasaccharides **1** and **2** (Scheme 2). Obtained 5-*O*-substituted furanoside **12** was then benzoylated to give orthogonally protected precursor **15** (Scheme 2). A portion of compound **15** was dechloroacylated by treatment with $NH_2C(S)NH_2$[14] to give monohydroxy compound **13**, which was further used as a glycosyl acceptor in the synthesis of β-(1→5)-linked disaccharide **18** (Scheme 2). On the other hand, *O*-deallylation[15-17] and subsequent trichloroacetimidation of monosaccharide **15** afforded glycosyl donor **17**. Its coupling with acceptor **13** in presence of TMSOTf gave exclusively β-linked disaccharide **18**. The configuration of the newly formed glycoside bond was confirmed by the singlet shaped H-1' signal in the ^{1}H NMR spectrum and characteristic downfield location of the C-1' signal (106.2 ppm) in the ^{13}C NMR spectrum.



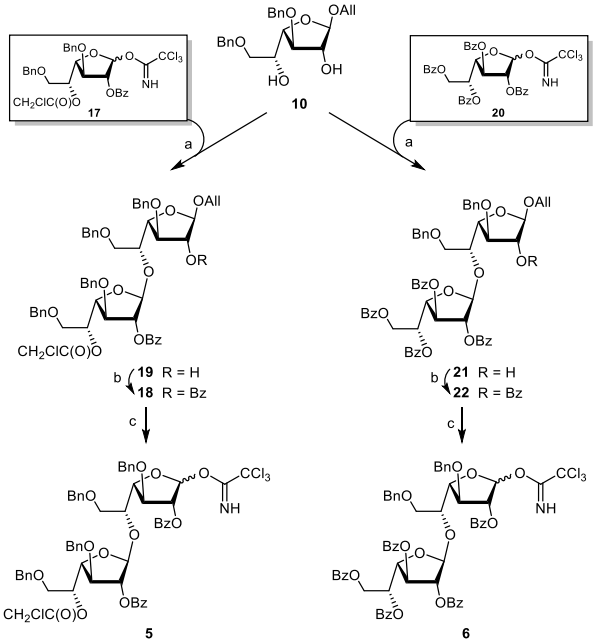
Scheme 2 Synthesis of disaccharide **18**. (a) BzCl, Py, CH_2Cl_2, 90%; (b) $H_2NC(S)NH_2$, 2,4,6-collidine, MeOH (dry), Δ, 85%.; (c) $PdCl_2$, MeOH (dry), 67%; (d) CCl_3CN, DBU, CH_2Cl_2, –50 → 0 °C, 88%; (e) TMSOTf, MS 4Å, CH_2Cl_2, –78 → –20 °C, 68%.

The excellent regioselectivity of 5-*O*-chloroacylation of diol **10** challenged us to examine the regioselectivity of its glycosylation (Scheme 3). Fortunately, coupling of diol **10** both with donors **17** and **20** resulted in predominant formation of desired β-(1→5)-linked products **19** and **21**, which were separated by chromatography from trace amounts of the (1→2)-linked isomers.

Benzoylation of derivatives **19** and **21** with BzCl in Py gave corresponding disaccharides **18** and **22**. Thus, the strategy based on the regioselective 5-*O*-glycosylation of diol **10** (Scheme 3) also represents a highly efficient and short way to the required β-(1→5)-linked disaccharides. Anomeric *O*-deallylation and subsequent trichloroacetimidation of disaccharides **18** and **22** gave desired disaccharide donors **5** and **6**.

Spacer-armed mannosides **3** and **4** were synthesized from described precursors **23**[18] and **24**[19] by mannosylation of 3-trifluoroacetamidopropanol and subsequent manipulation with blocking groups (Scheme 4). Further coupling of acceptors **3** and **4** with disaccharide donor **5** gave corresponding trisaccharides **25** and **28** in yields of 85% and 60%. The lower yield in the latter case could be explained by lower reactivity of acceptor **4** which required application of slightly higher reaction temperature.

O-Dechloroacetylation and subsequent glycosylation of trisaccharide acceptors **26** and **29** by trichloroacetimidates **5** and **6**, respectively, gave pentasaccharides **27** and **30**. Full deprotection of these compounds yielded target spacer armed pentasaccharides **1** and **2**. Their structures were unambiguously confirmed by NMR and mass-spectrometry.



Scheme 3 Synthesis of disaccharide donors **5** and **6**. (a) TMSOTf, MS300 AW, CH_2Cl_2, –78 → –20 °C, 65% for **19**, 62% for **21**; (b) BzCl, Py, CH_2Cl_2, 87% for **18**, 84% for **22**; (c) *i*: $PdCl_2$, MeOH; *ii*: CCl_3CN, DBU, CH_2Cl_2, –50 → 0 °C, 55% on 2 steps for **5**, 59% on 2 steps for **6**.

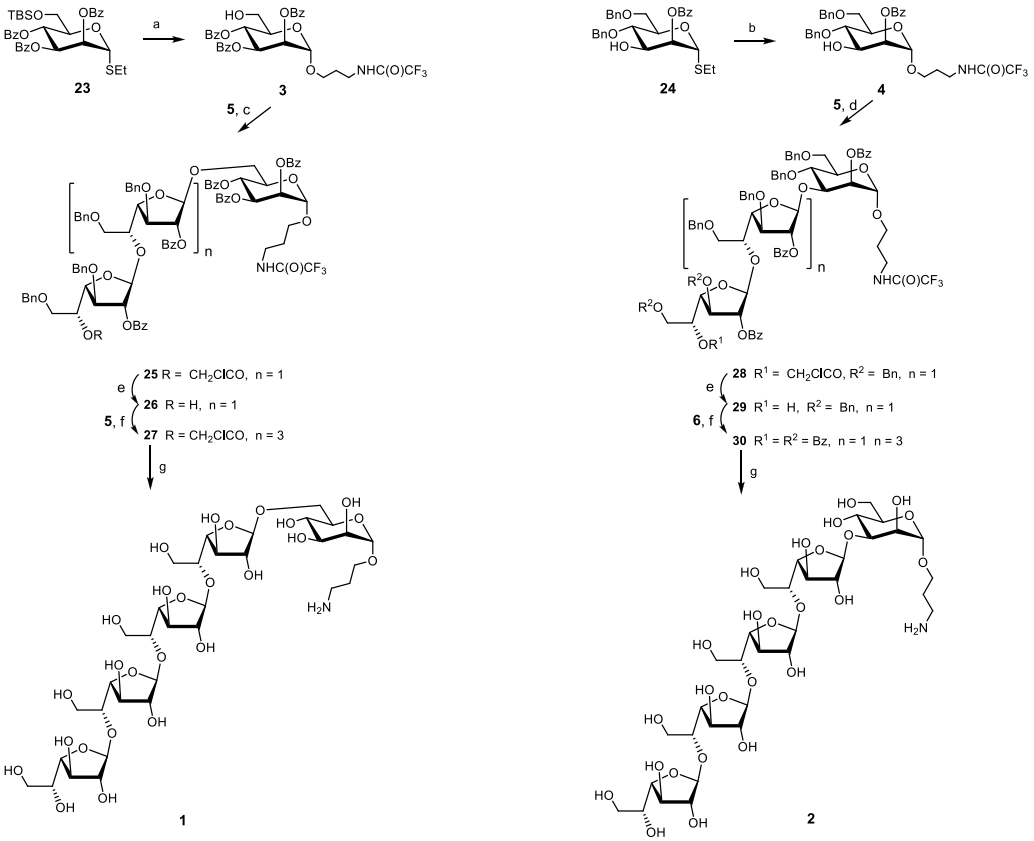
Conclusions

The first synthesis of isomeric heteropentasaccharides **1** and **2** structurally related to fragments of the galactomannan from *Aspergillus fumigatus* has been performed. The new strategy based on the PIF-rearrangement of the appropriately O-substituted galactopyranoside precursor into the corresponding furanoside block has been proved efficient and competitive to the known approaches for synthesis of oligo-β-(1→5)-galactofuranoside chains. The developed synthetic scheme is applicable for the synthesis of oligosaccharides representing larger galactomannan fragments. The synthesis of glycoconjugates of obtained pentasacharides **1** and **2** and their glycobiological evaluation will be published elsewhere.

Experimental

General methods

Commercial chemicals were used without purification unless noted. All solvents were distilled and dried if necessary according to standard procedures or purchased dry (DMF,



Scheme 4. Synthesis of monosaccharide acceptors **3** and **4**, their coupling with tetrasaccharide donor **5** and obtaining of target pentasaccharides **1** and **2**. (a) *i*: $HO(CH_2)_3NHTFA$, NIS, TfOH, Ms 4Å, CH_2Cl_2, –40 → –15°; *ii*: TFA 90% aq., 62% on 2 steps; (b) *i*: $CH_2ClC(O)Cl$, Py, CH_2Cl_2; *ii*: $HO(CH_2)_3NHTFA$, NIS, TfOH, Ms300 AW, CH_2Cl_2, –40 → –15°; *iii*: $H_2NC(S)NH_2$, 2,4,6-collidine, MeOH (dry), Δ, 55% on 3 steps; (c) TMSOTf, Ms 4Å, CH_2Cl_2, –78 → –20 °C, 85%; (d) TMSOTf, MS300 AW, CH_2Cl_2, –78 → –10 °C, 60%; (e) $H_2N(S)NH_2$, 2,4,6-collidine, MeOH (dry), Δ, 86% for **26**, 80% for **29**; (f) TMSOTf, MS300 AW, CH_2Cl_2, –78 → –20 °C, 71% for **27**, 80% for **30**; (g) *i*: H_2, Pd/C (10% Pd), EtOAc-MeOH 1:1; *ii*: MeONa, MeOH, then H_2O, 83% for **1**, 70% for **2**.

Acrus). All reactions involving air- or moisture-sensitive reagents were carried out using dry solvents under Ar-atmosphere. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F_{254} (Merck). TLC plates were inspected in UV light (λ = 254 nm) and developed by treatment with a mixture of 15% H_3PO_4 and orcinol (1.8 g/l) in EtOH/H_2O (95:5, v/v) followed by heating. Column chromatography was performed with Silica Gel 60 (40-63 μm, E. Merck). Solvents for column and thin layer chromatography (TLC) are listed in volume to volume ratios. Gel-filtration was performed on a TSK-40 HW(S) column (400 × 17 mm) by elution with 0.1 M AcOH in water at a flow rate of 0.5 mL/min.

NMR spectra were recorded on Bruker AMX400 (400 MHz), Bruker DRX-500 (500 MHz), or Bruker AV600 (600 MHz) spectrometers equipped with 5-mm pulsed-field-gradient (PFG) probes at temperatures denoted in the spectra in supplementary. Microtubes (Shigemi, Inc.) were used for sensitivity enhancement of small concentration probes of compounds **1**, **2**, and **30**. The resonance assignment in ^1H and ^{13}C NMR spectra was performed using various 2D-experiments (e.g., COSY, NOESY, HSQC, HMBC, TOCSY, HSQC-TOCSY, and ROESY). Chemical shifts are reported in ppm referenced to the solvent residual peaks as standard (δ 7.27 for chloroform or δ 3.31 methanol for ^1H NMR and δ 77.0 and δ 49.0 for ^{13}C NMR). The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad, dd = doublet of doublets and dt = doublet of triplets. Monosaccharide residues in oligosaccharides are numbered by the Roman numerals starting from the reducing end. For carbohydrate numbering nomenclature in pyranoside and furanoside systems see below.

Optical rotations were measured using a JASCO DIP-360 polarimeter at ambient temperature (22-25 °C) in ethyl acetate.

High-resolution mass spectra (HR MS) were recorded on a Bruker micrOTOF II instrument using electrospray ionization (ESI).[20] The measurements were performed in a positive ion mode (interface capillary voltage –4500 V) or in a negative ion mode (3200 V); mass range from *m/z* 50 to *m/z* 3000 Da; external or internal calibration was made with Electrospray

Calibrant Solution (Fluka). A syringe injection was used for solutions in a mixture of acetonitrile and water (50:50 v/v, flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

Synthesis

General procedure for chloroacetyl group removal (GP I). To a stirred solution of starting sugar (1 mmol) and thiourea (10 mmol) in anhydrous MeOH (30 mL) 2,4,6-collidine (0.125 mmol) was added and the mixture was refluxed until TLC showed reaction completion. Then the mixture was filtered, the residue was washed with MeOH, and the filtrate was concentrated *in vacuo*.

General procedure for allyl group cleavage(GP II). To a stirred solution of starting sugar (1 mmol) in anhydrous MeOH (17 mL) $PdCl_2$ (0.4 mmol) was added and the mixture was virgiosly stirred until TLC showed reaction completion. Then the mixture was filtered through *celite* layer, the residue washed with MeOH, 1-2 drops of Et_3N and 10 mL of toluene were added, and the filtrate was concentrated *in vacuo*.

General procedure for the preparation of trichloroacetimidates (GP III). To a stirred solution of starting hemiacetal (1 mmol) in CH_2Cl_2 (7-8 mL) trichloroacetonitrile (8 mmol) and a catalytic amount of DBU (approx. 50 μL) were added at –50 °C. The reaction mixtute was allowed to warm to 0 °C in 30 min and subjected to flashchromatography on passivated by Et_3N silica gel.

Allyl 3,6-di-O-benzyl-β-D-galactopyranoside (8). To a stirred suspension of allyl β-D-galactopyranoside **7**[10] (1.1 g, 5 mmol) in toluene (50 mL) $(Bu_3Sn)_2O$ (3.8 mL, 7.5 mmol) was added and mixture was refluxed for 6 h accompanied by azeotropic removal of water. Then BnBr (1.8 mL, 10 mmol) and TBAI (5.5 g, 15 mmol) were added and the mixture was stirred at 100 °C overnight. The solvents were removed *in vacuo*, the residue was diluted with CH_2Cl_2 and washed by sat. aq. $NaHCO_3$. Organic layer was concentrated and column chromatography (toluene—EtOAc 4:1) gave disered product **8** (1.4 g, 70%) as a yellowish oil. $[\alpha]_D$=−4° (c = 1, EtOAc). ^{1}H NMR (400 MHz, CD_3OD): δ 7.46-7.23 (m, 10H, PhH), 6.02-5.91 (m, 1H, OCH_2CHCH_2), 5.31 (m, 1H, OCH_2CHCH_2), 5.15 (m, 1H, OCH_2CHCH_2), 4.80-4.72 (m, 3H, $PhCH_2$), 4.66 (d, $^2J_{ab}$=11.8 Hz, 1H, $PhCH_2$), 4.37-4.30 (m, 1H, OCH_2CHCH_2), 4.28 (d, J_{12}=7.8 Hz, 1H, H-1), 4.17-4.10 (m, 1H, OCH_2CHCH_2), 4.10 (dd, J_{43}=3.3 Hz, J_{45}≈0.9 Hz, 1H, H-4), 3.74 (dd, $^2J_{6a6b}$=10.2, J_{56a}=5.8, 1H, H-6a), 3.71 (dd, J_{21}=7.8 Hz, J_{23}=9.7 Hz, 1H, H-2), 3.70 (dd, $^2J_{6a6b}$=10.2, J_{56b}=6.4, 1H, H-6b), 3.61 (dt, J_{54}≈0.9 Hz, J_{56a}≈J_{56b}≈6.0 Hz, 1H, H-5), 3.37 (dd, J_{32}=9.7 Hz, J_{34}=3.3 Hz, 1H, H-3). ^{13}C NMR (100 MHz, CD_3OD): δ 139.9, 139.6 (quat. Ph), 139.8 (OCH_2CHCH_2), 129.4-128.6 (Ph), 117.4 (OCH_2CHCH_2), 103.9 (C-1), 82.40 (C-3), 74.9 (C-5), 74.3 ($PhCH_2$), 72.6 ($PhCH_2$), 71.7 (C-6), 71.1 (C-2), 70.7 (C-4), 67.4 (OCH_2CHCH_2). HRMS(ESI): Calcd *m/z* for $[M+Na]^+$ $C_{23}H_{28}O_6$ 423.1778, found 423.1770. Calcd *m/z* for $[M+K]^+$ $C_{23}H_{28}O_6$ 439.1517, found 439.1516.

Disodium salt of allyl 3,6-di-O-benzyl-2,4-di-O-sulfo-β-D-galactofuranoside (9). To a stirred solution of **8** (1.0 g, 2.5 mmol) and $Py{\cdot}SO_3$ (3.2 mg, 20.0 mmol) in DMF (16 mL) $ClSO_3H$ was added dropwise (550 μL, 8 mmol) and the mixture was kept at 40 °C for 1 h. Then the reaction was quenched by addition of $NaHCO_3$ (5.6 g, 67 mmol) solution in water (160 mL) and concentrated *in vacuo*. MeOH (100 mL) was added, the suspension was filtered through the cotton, the residue was washed twice with MeOH (2x50mL), and the filtrate was evaporated and carefully dried. Resulted crude product **9** was analyzed and used in the next step without purification. ^{1}H NMR (400 MHz, CD_3OD): δ 7.42-7.20 (m, 10H, PhH), 6.02-5.88 (m, 1H, OCH_2CHCH_2), 5.29-5.25 (m, 1H, OCH_2CHCH_2), 5.26 (s, 1H, H-1), 5.12-5.09 (m, 1H, OCH_2CHCH_2), 4.84 (d, J_{23}=2.0 Hz, 1H, H-2), 4.82-4.54 (m, 5H, $2PhCH_2$, H-5), 4.46 (dd, J_{32}=2.0 Hz, J_{34}=6.7 Hz, 1H, H-3), 4.43 (dd, J_{43}=6.7 Hz, J_{45}=3.0 Hz, 1H, H-4), 4.19-4.14 (m, 1H, OCH_2CHCH_2), 4.04-3.98 (m, 1H, OCH_2CHCH_2), 3.88-3.76 (m, 2H, H-6a, H-6b). ^{13}C NMR (100 MHz, CD_3OD): δ 139.6, 139.5 (quat. Ph), 135.6 (OCH_2CHCH_2), 129.3-128.5 (Ph), 117.2 (OCH_2CHCH_2), 106.8 (C-1), 87.2 (C-2), 85.1 (C-3), 81.3 (C-4), 75.7 (C-5), 74.3 ($PhCH_2$), 73.5 ($PhCH_2$), 69.6 (C-6), 68.8 (OCH_2CHCH_2). HRMS(ESI): Calcd *m/z* for $[M-2Na]^{2-}$ $C_{23}H_{26}O_{12}S_2Na_2$ 279.0438, found 279.0436. Calcd *m/z* for $[M-Na]^-$ $C_{23}H_{26}O_{12}S_2Na_2$ 581.0769, found 581.0777. Calcd *m/z* for $[M-2Na+H]^-$ $C_{23}H_{26}O_{12}S_2Na_2$ 559.0949, found 559.0928.

Allyl 3,6-di-O-benzyl-β-D-galactofuranoside (10). Crude product **9** was desulfated by refluxing in dioxane (100 mL) in the presence of IR-120H$^+$ (1.5 g) for 40 min. Then inorganic salts were filtered off, washed with EtOAc, and the filtrate was neutralized by Et_3N to pH 8-9. Solvents were evaporated *in vacuo* and column chromatography (toluene—EtOAc 2:1) gave product **10** (0.59 g, 59% over two steps) as a colorless oil. $[\alpha]_D$=62° (c = 1, EtOAc). ^{1}H NMR (600 MHz, CD_3OD): δ 7.36-7.23 (m, 10H, PhH), 5.96-5.89 (m, 1H, OCH_2CHCH_2), 5.28 (m, 1H, OCH_2CHCH_2), 5.14 (m, 1H, OCH_2CHCH_2), 4.94 (s, 1H, H-1), 4.69 (d, $^2J_{ab}$=11.8 Hz, 1H, $PhCH_2$), 4.53 (d, $^2J_{ab}$=12.0 Hz, 1H, $PhCH_2$), 4.52 (d, $^2J_{ab}$=11.8 Hz, 1H, $PhCH_2$), 4.50 (d, $^2J_{ab}$=12.0 Hz, 1H, $PhCH_2$), 4.21-4.15 (m, 2H, OCH_2CHCH_2, H-2), 4.09 (dd, J_{32}=3.8 Hz, J_{34}=6.1 Hz, 1H, H-3), 4.01-3.91 (m, 1H, OCH_2CHCH_2), 3.94 (dd, J_{43}=6.1 Hz, J_{45}=2.6 Hz, 1H, H-4), 3.84 (m, 1H, H-5), 3.56 (dd, $^2J_{6a6b}$=9.9, J_{56a}=5.5, 1H, H-6a), 3.52 (dd, $^2J_{6a6b}$=9.9, J_{56b}=6.7, 1H, H-6b). ^{13}C NMR (150 MHz, CD_3OD): δ 139.6, 139.4 (quat. Ph), 135.8 (OCH_2CHCH_2), 129.3-128.6 (Ph), 117.1 (OCH_2CHCH_2), 109.1 (C-1), 86.8 (C-3), 83.6 (C-4), 81.4 (C-2), 74.3 ($PhCH_2$), 73.1 ($PhCH_2$), 72.6 (C-6), 71.1 (C-5), 69.0 (OCH_2CHCH_2). HRMS(ESI): Calcd *m/z* for $[M+Na]^+$ $C_{23}H_{28}O_6$ 423.1778, found 423.1770.

Allyl 3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranoside (12). To a stirred solution of **10** (700 mg, 1.75 mmol) in CH_2Cl_2 (10 mL) at –78 °C pyridine (0.31 mL, 3.85 mmol) and chloroacetyl chloride (155 μL, 0.19 mmol) were slowly added. The reaction mixtute was allowed to warm to 0 °C over 1 h and diluted with CH_2Cl_2, washed by 1 M HCl, sat. aq. $NaHCO_3$ and concentrated *in vacuo*. Column chromatography (toluene—EtOAc 7:1) gave **12** (575 mg, 69%) as a colorless oil. R_f=0.37 (toluene-ethyl acetate 5:1). $[\alpha]_D$=58° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38-7.28

(m, 10H, PhH), 5.94-5.86 (m, 1H, OCH_2CHCH_2), 5.33 (m, 1H, H-5), 5.29 (m, 1H, OCH_2CHCH_2), 5.18 (m, 1H, OCH_2CHCH_2), 4.98 (s, 1H, H-1), 4.66 (d, $^2J_{ab}$=12.0 Hz, 1H, $PhCH_2$), 4.56 (d, $^2J_{ab}$=12.0 Hz, 1H, $PhCH_2$), 4.53 (d, $^2J_{ab}$=12.1 Hz, 1H, $PhCH_2$), 4.50 (d, $^2J_{ab}$=12.1 Hz, 1H, $PhCH_2$), 4.25 (dd, J_{43}=5.8 Hz, J_{45}=4.0 Hz, 1H, H-4), 4.21-4.17 (m, 2H, H-2, OCH_2CHCH_2), 4.02-3.96 (m, 3H, $C(O)CH_2Cl$, OCH_2CHCH_2), 3.77 (dd, J_{32}=2.2 Hz, J_{34}=5.8 Hz, 1H, H-3), 3.73 (dd, $^2J_{6a6b}$=10.7, J_{56a}=6.5, 1H, H-6a), 3.62 (dd, $^2J_{6a6b}$=10.7, J_{56b}=4.7, 1H, H-6b), 2.15 (br. s, 1H, OH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8 ($C(O)CH_2Cl$), 137.5 (Ph), 134.0 (OCH_2CHCH_2), 128.5-127.7 (Ph), 117.4 (OCH_2CHCH_2), 107.4 (C-1), 85.0 (C-3), 80.3 (C-4), 80.2 (C-2), 73.3 ($PhCH_2$), 72.9 (C-5), 72.4 ($PhCH_2$), 68.3 (C-6), 68.2 (OCH_2CHCH_2), 40.8 ($C(O)CH_2Cl$). HRMS(ESI): Calcd *m/z* for $[M+Na]^+$ $C_{25}H_{29}ClO_7$ 499.1494, found 499.1486. Calcd *m/z* for $[M+K]^+$ $C_{25}H_{29}ClO_7$ 515.1233, found 515.1226.

Allyl 3,6-di-O-benzyl-2-O-chloroacetyl-β-D-galactofuranoside (11). To a stirred solution of **10** (20 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) at –78 °C Et_3N (20 μL, 0.15 mmol) and chloroacetyl chloride (5 μL, 0.06 mmol) were slowly added. The reaction mixtute was allowed to warm 0 °C for 1 h and diluted with CH_2Cl_2, washed by 1 M HCl, sat. aq. $NaHCO_3$ and concentrated *in vacuo*. Column chromatography (toluene—EtOAc 7:1) gave a mixture of **11** (13 mg, 56%) and **12** (4 mg, 17%) as a colorless oil (ratio **12**/**11** calculated from H-1 signals in NMR). Data for **11**: R_f=0.41 (toluene-ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 10H, Ph*H*), 5.96 – 5.84 (m, 1H, $OCH_2CH=CH_2$), 5.31 (dd, *J* = 17.3 Hz, *J* = 1.6 Hz, 1H, $OCH_2CH=CH_aH_b$), 5.21 (dd, *J* = 10.4, *J* = 1.3 Hz, 1H, $OCH_2CH=CH_aH_b$), 5.20 (d, $J_{2,3}$ = 1.4 Hz, 1H, H-2), 5.10 (s, 1H, H-1), 4.75 (d, *J* = 12.0 Hz, 1H, $PhCH_aH_b$), 4.60 – 4.54 (m, 3H, 3xPh*H*H), 4.24 – 4.18 (m, 1H, $OCH_aH_bCH=CH_2$), 4.17 (dd, $J_{4,5}$ = 5.9 Hz, $J_{4,3}$ = 3.3 Hz, 1H, H-4), 4.07 – 4.00 (m, 4H, H-3, CH_2Cl, $OCH_aH_bCH=CH_2$), 3.93 – 3.86 (m, 1H, H-5), 3.57 (dd, $J_{6a,6b}$ = 9.7 Hz, $J_{6a,5}$ = 7.1 Hz, 1H, H-6_a), 3.52 (dd, $J_{6a,6b}$ = 9.7 Hz, $J_{6b,5}$ = 5.0 Hz, 1H, H-6_b), 2.28 (d, J_{HOH} = 6.3 Hz, 1H, *OH*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.33 (C=O), 137.86 (quat. Ph), 137.44 (quat. Ph), 133.64 ($OCH_2CH=CH_2$), 128.45, 128.03, 127.95, 127.80, 127.72 (Ph), 117.70 ($OCH_2CH=CH_2$), 104.69 (C-1), 83.10 (C-3), 82.97 (C-2), 82.49 (C-4), 73.48 ($PhCH_2$), 72.57 ($PhCH_2$), 71.52 (C-6), 69.63 (C-5), 67.95 ($OCH_2CH=CH_2$), 40.59 (CH_2Cl). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{25}H_{29}ClO_7$ 494.1940, found 494.1935. Calcd *m/z* for $[M+Na]^+$ $C_{25}H_{29}ClO_7$ 499.1494, found 499.1496. Calcd *m/z* for $[M+K]^+$ $C_{25}H_{29}ClO_7$ 515.1233, found 515.1234.

Allyl 2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside (13) from diol 10. To a stirred solution of **10** (20 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) at –20 °C Et_3N (40 μL, 0.3 mmol) and BzCl (9 μL, 0.075 mmol) were added. The reaction mixtute was allowed to warm 8 °C over 2 h and kept at this temperature overnight. Then it was diluted by CH_2Cl_2, washed with sat. aq. $NaHCO_3$, and concentrated *in vacuo*. Column chromatography (toluene—EtOAc 12:1) gave **13** (14.5 mg, 58%) and **14** (4 mg, 16%) as a colorless oil (ratio **13**/**14** calculated from H-6 signals in NMR). All data for **13** were in agreement with the same compound obtained from **15**.

Allyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranoside (15). To a solution of **12** (575 mg, 1.21 mmol) and pyridine (0.47 mL, 6.0 mmol) in CH_2Cl_2 (5 mL) BzCl (0.42 mL, 3.6 mmol) was added dropwise under r.t. After completion of the reaction by TLC (approx. 4 h) the mixture was diluted with CH_2Cl_2, washed by 1 M HCl, sat. aq. $NaHCO_3$, and concentrated *in vacuo*. Column chromatography (toluene—EtOAc 15:1) gave **15** (630 mg, 90%) as a colorless oil. R_f=0.62 (toluene-ethyl acetate 10:1). $[\alpha]_D$=-21° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J*=8.2 Hz, 2H, *o*-C(O)Ph), 7.61 (t, *J*=7.5 Hz, 1H, *p*-C(O)Ph), 7.47 (dd, *J*=8.2 Hz, *J*=7.5 Hz, 2H, *m*-C(O)Ph), 7.34-7.26 (m, 10H, PhH), 5.96-5.89 (m, 1H, OCH_2CHCH_2), 5.39 (d, J_{12}=1.6 Hz, 1H, H-2), 5.37 (m, 1H, H-5), 5.33 (m, 1H, OCH_2CHCH_2), 5.22-5.19 (m, 2H, H-1, OCH_2CHCH_2), 4.82 (d, $^2J_{ab}$=11.9 Hz, 1H, $PhCH_2$), 4.57 (d, $^2J_{ab}$=11.9 Hz, 1H, $PhCH_2$), 4.52 (d, $^2J_{ab}$=12.1 Hz, 1H, $PhCH_2$), 4.47 (d, $^2J_{ab}$=12.1 Hz, 1H, $PhCH_2$), 4.37 (dd, J_{43}=6.0 Hz, J_{45}=4.5 Hz, 1H, H-4), 4.23 (m, 1H, OCH_2CHCH_2), 4.06 (m, 1H, OCH_2CHCH_2), 3.97 (d, $^2J_{ab}$=14.7 Hz, 1H, $C(O)CH_2Cl$), 3.94 (br. d, J_{34}=6.0 Hz, 1H, H-3), 3.92 (d, $^2J_{ab}$=14.7 Hz, 1H, $C(O)CH_2Cl$), 3.66 (dd, $^2J_{6a6b}$=10.4, J_{56a}=6.5, 1H, H-6a), 3.64 (dd, $^2J_{6a6b}$=10.4, J_{56b}=4.9, 1H, H-6b). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7 ($C(O)CH_2Cl$), 165.3 ($PhCO$), 134.0 (OCH_2CHCH_2), 133.8-127.6 (Ph), 117.6 (OCH_2CHCH_2), 105.0 (C-1), 83.0 (C-3), 81.8 (C-4), 80.7 (C-2), 73.2 ($PhCH_2$), 72.7 (C-5), 72.5 ($PhCH_2$), 68.4 (C-6), 68.0 (OCH_2CHCH_2), 40.7 ($C(O)CH_2Cl$). HRMS(ESI): Calcd *m/z* for $[M+Na]^+$ $C_{32}H_{33}ClO_8$ 603.1756, found 603.1752. Calcd *m/z* for $[M+K]^+$ $C_{32}H_{33}ClO_8$ 619.1496, found 619.1494.

Allyl 3,6-di-O-benzyl-2-O-benzoyl-β-D-galactofuranoside (13). Furanoside **15** (170 mg, 0.29 mmol) was treated as described in **GP I** by thiourea (220 mg, 2.9 mmol) and collidine (48 μL, 0.36 mmol) in 10 mL of MeOH. Column chromatography (toluene—EtOAc 8:1) gave **13** (125 mg, 85%) as a colorless oil. R_f=0.40 (toluene-ethyl acetate 8:1). $[\alpha]_D$=-46° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, *J*=8.2 Hz, 2H, *o*-C(O)Ph), 7.59 (t, *J*=7.5 Hz, 1H, *p*-C(O)Ph), 7.45 (dd, *J*=8.2 Hz, *J*=7.5 Hz, 2H, *m*-C(O)Ph), 7.35-7.26 (m, 10H, PhH), 5.97-5.90 (m, 1H, OCH_2CHCH_2), 5.42 (d, J_{12}=1.5 Hz, 1H, H-2), 5.34 (m, 1H, OCH_2CHCH_2), 5.22 (**s**, 1H, H-1), 5.21 (m, 1H, H-1, OCH_2CHCH_2), 4.83 (d, $^2J_{ab}$=12.0 Hz, 1H, $PhCH_2$), 4.61 (d, $^2J_{ab}$=12.0 Hz, 1H, $PhCH_2$), 4.57 (d, $^2J_{ab}$=12.0 Hz, 1H, $PhCH_2$), 4.53 (d, $^2J_{ab}$=12.0 Hz, 1H, $PhCH_2$), 4.27-4.23 (m, 2H, OCH_2CHCH_2, H-4), 4.17 (br. d, J_{34}=5.8 Hz, 1H, H-3), 4.08 (m, 1H, OCH_2CHCH_2), 3.94 (m, 1H, H-5), 3.58 (dd, $^2J_{6a6b}$=9.8, J_{56a}=7.1, 1H, H-6a), 3.54 (dd, $^2J_{6a6b}$=9.8, J_{56b}=4.9, 1H, H-6b), 2.44 (br. d, J_{HOH}=6.1 Hz, 1H, OH). ^{13}C NMR (150 MHz): δ 165.4 ($PhCO$), 137.9, 137.5 (quat. Ph), 133.8 (OCH_2CHCH_2), 133.6, 133.3, 129.7-127.6 (Ph), 117.5 (OCH_2CHCH_2), 105.2 (C-1), 83.5 (C-3), 82.6 (C-4), 81.8 (C-2), 73.4 ($PhCH_2$), 72.4 ($PhCH_2$), 71.5 (C-6), 70.0 (C-5), 67.9 (OCH_2CHCH_2). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{30}H_{32}O_7$ 522.2486, found 522.2480. Calcd *m/z* for $[M+Na]^+$ $C_{30}H_{32}O_7$ 527.2040, found 527.2034. Calcd *m/z* for $[M+K]^+$ $C_{30}H_{32}O_7$ 543.1780, found 543.1776.

2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-D-galactofuranose (16). Allylgalactoside **15** (545 mg, 0.94 mmol) in 16 mL of MeOH

was treated according to **GP II** by $PdCl_2$ (67 mg, 0.38 mmol) for 2.5 h. Column chromatography (hexane—EtOAc 5:2) gave **16** (340 mg, 67%) as white solid (β/α=2:1 based on H-1 integral in NMR). R_f=0.38 (toluene-ethyl acetate 10:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14-8.07, 7.65-7.19 (m, 22.5H, PhH), 5.69 (d, J_{12}=4.3 Hz, 0.5H, H-1$^{\alpha}$), 5.53 (d, $J_{1\text{-}1OH}$=6.0 Hz, 1H, H-1β), 5.43 (m, 0.5H, H-5$^{\alpha}$), 5.39 (br. s, 1H, H-2$^{\beta}$), 5.34 (m, 1H, H-5$^{\beta}$), 5.30 (dd, J_{21}=4.3 Hz, J_{23}=5.7, 1H, H-2$^{\beta}$), 4.84 (d, J_{ab}=11.8 Hz, 1H, PhCH_2^{β}), 4.76 (d, J_{ab}=11.7 Hz, 0.5H, PhCH_2^{α}), 4.66 (d, J_{ab}=11.7 Hz, 0.5H, PhCH_2^{α}), 4.62 (d, J_{ab}=11.8 Hz, 1H, PhCH_2^{β}), 4.57 (dd, J_{43}=4.1 Hz, J_{45}=6.3 Hz, 1H, H-4$^{\beta}$), 4.55 (d, J_{ab}=12.0 Hz, 0.5H, PhCH_2^{α}), 4.51 (d, J_{ab}=12.0 Hz, 0.5H, PhCH_2^{α}), 4.47 (d, J_{ab}=12.1 Hz, 1H, PhCH_2^{β}), 4.42 (d, J_{ab}=12.1 Hz, 1H, PhCH_2^{β}), 4.41 (t, J_{32}=J_{34}=5.7 Hz, 0.5H, H-3$^{\alpha}$), 4.21 (dd, J_{43}=5.7 Hz, J_{45}=6.3 Hz, 0.5H, H-4$^{\alpha}$), 4.12 (d, J_{ab}=15.0 Hz, 0.5H, C(O)CH_2Cl$^{\alpha}$), 4.09 (br. d, J_{34}=4.1 Hz, 1H, H-3$^{\beta}$), 4.09 (d, J_{ab}=15.0 Hz, 0.5H, C(O)CH_2Cl$^{\alpha}$), 4.02 (d, J_{ab}=14.9 Hz, 1H, C(O)CH_2Cl$^{\beta}$), 3.99 (d, J_{ab}=14.9 Hz, 1H, C(O)CH_2Cl$^{\beta}$), 3.69 (dd, $^2J_{6a6b}$=10.9, J_{56a}=6.0, 0.5H, H-6a$^{\alpha}$), 3.65(dd, $^2J_{6a6b}$=10.9, J_{56a}=4.5, 0.5H, H-6b$^{\alpha}$), 3.60 (m, 2H, H-6a, H-6b). ^{13}C NMR (150 MHz, $CDCl_3$): 166.8 (*C*(O)CH_2Cl), 165.4 (Ph*C*O), 137.4-136.8, 133.7-127.6 (Ph), 101.1 (C-1$^{\beta}$), 95.8 (C-1$^{\alpha}$), 82.1 (C-3$^{\beta}$, C-4$^{\beta}$), 80.7 (C-2$^{\beta}$), 80.3 (C-3$^{\alpha}$), 78.9 (C-4$^{\alpha}$), 78.7 (C-2$^{\alpha}$), 74.5 (C-5$^{\alpha}$), 73.3 (Ph*C*H$_2^{\alpha}$), 73.2 (Ph*C*H$_2^{\beta}$, C-5$^{\beta}$), 72.5 (PhCH_2^{β}), 72.3 (Ph*C*H$_2^{\alpha}$), 68.4 (C-6$^{\beta}$), 68.2 (C-6$^{\alpha}$), 40.9(C(O)CH_2Cl$^{\alpha}$), 40.7 (C(O)*C*H_2Cl$^{\beta}$). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{29}H_{29}ClO_8$ 558.1889, found 558.1886. Calcd *m/z* for $[M+Na]^+$ $C_{29}H_{29}ClO_8$ 563.1443, found 563.1434. Calcd *m/z* for $[M+K]^+$ $C_{29}H_{29}ClO_8$ 579.1153, found 579.1171.

2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranoside trichloroacetimidate (17). Starting hemiacetal **16** (340 mg, 0.63 mmol) in CH_2Cl_2 (5 mL) was treated by CCl_3CN (0.35 mL, 3.5 mmol) and DBU (60 μL, cat) according to **GP III**. Column chromatography (toluene—EtOAc 20:1 + 1 vol.% of Et_3N) gave product **17** (380 mg, 88%) as a colorless oil. R_f=0.69 (toluene-ethyl acetate 10:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.63 (s, 1H, =NH), 8.07-7.16 (m, 15H, PhH), 6.50 (s, 1H, H-1), 5.64 (d, J_{23}≈1.0 Hz, 1H, H-2), 5.39 (m, 1H, H-5), 4.88 (d, J_{ab}=11.8 Hz, 1H, PhCH_2), 4.63-4.60 (m, 2H, PhCH_2, H-4), 4.50 (d, J_{ab}=12.1 Hz, 1H, PhCH_2), 4.46 (d, J_{ab}=12.1 Hz, 1H, PhCH_2), 4.10 (br. d, J_{34}=5.3 Hz, 1H, H-3), 3.95 (d, J_{ab}=14.8 Hz, 1H, C(O)CH_2Cl), 3.90 (d, J_{ab}=14.8 Hz, 1H, C(O)CH_2Cl), 3.68 (dd, $^2J_{6a6b}$=9.5, J_{56a}=5.3, 1H, H-6a), 3.65 (dd, $^2J_{6a6b}$=9.5, J_{56b}=4.3, 1H, H-6b). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8 (*C*(O)CH_2Cl), 166.5 (Ph*C*O), 160.7 (*C*(NH)CCl_3), 137.1, 133.8-127.5 (Ph), 103.6 (C-1), 83.6 (C-4), 82.4 (C-3), 80.33 (C-2), 73.2 (PhCH_2), 72.4 (PhCH_2, C-5), 68.1 (C-6), 40.7 (C(O)*C*H_2Cl). HRMS(ESI): Calcd *m/z* for $[M+Na]^+$ $C_{31}H_{29}Cl_4NO_8$ 706.0539, found 706.0539. Calcd *m/z* for $[M+K]^+$ $C_{31}H_{29}Cl_4NO_8$ 722.0279, found 722.0273.

Allyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside (18). Carefully dried mixture of **13** (125 mg, 0.25 mmol) and **17** (219 mg, 0.32 mmol) was dissolved in CH_2Cl_2 (8 mL), powder MS 4Å (130 mg) was added, and the mixture was stirred for 20 min. Then temperature was decreased to –78 °C and TMSOTf (17 μL, 0.096 mmol) was added. The reaction mixture was kept at –40…–30 °C for 1 h and then at –20 °C was stopped by 1 drop of Et_3N. Column chromatography (toluene—EtOAc 20:1) gave **18** (175 mg, 68%) as a colorless oil. R_f=0.59 (toluene-ethyl acetate 10:1). $[\alpha]_D$=-44° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07-8.03, 7.65-7.08 (m, 30H, PhH), 5.97-5.90 (m, 1H, OCH_2CHCH_2), 5.59 (s, 1H, H-1^{II}), 5.53 (d, J_{23}=1.5 Hz, 1H, H-2^{II}), 5.44 (d, J_{23}=1.5 Hz, 1H, H-2^{I}), 5.33 (m, 1H, OCH_2CHCH_2), 5.30 (ddd, J_{45}=4.9 Hz, J_{56a}=7.3 Hz, J_{56b}=4.2 Hz, 1H, H-5^{II}), 5.20 (m, 1H, OCH_2CHCH_2), 5.19 (s, 1H, H-1^{I}), 4.80 (d, J_{ab}=11.7 Hz, 1H, 3-*O*-PhCH_2^{I}), 4.76 (d, J_{ab}=12.0 Hz, 1H, 3-*O*-PhCH_2^{II}), 4.60 (d, J_{ab}=11.7 Hz, 1H, 3-*O*-PhCH_2^{I}), 4.54 (d, J_{ab}=12.0 Hz, 1H, 3-*O*-PhCH_2^{II}), 4.53 (d, J_{ab}=11.9 Hz, 2H, 6-*O*-PhCH_2^{I}), 4.50 (d, J_{ab}=11.9 Hz, 2H, 6-*O*-PhCH_2^{I}), 4.43 (dd, J_{43}=5.8 Hz, J_{45}=4.9 Hz, 1H, H-4^{II}), 4.38 (d, J_{ab}=12.1 Hz, 1H, 6-*O*-PhCH_2^{II}), 4.34 (dd, J_{43}=6.1 Hz, J_{45}=4.2 Hz, 1H, H-4^{I}), 4.30 (d, J_{ab}=12.1 Hz, 1H, 6-*O*-PhCH_2^{II}), 4.27 (br. d, J_{34}=6.1 Hz, 1H, H-3^{I}), 4.25-4.21 (m, 2H, H-5^{I}, OCH_2CHCH_2), 4.06 (m, 1H, OCH_2CHCH_2), 3.91 (br. d, J_{34}=5.8 Hz, 1H, H-3^{II}), 3.88 (d, J_{ab}=14.2 Hz, 1H, C(O)CH_2Cl), 3.83 (d, J_{ab}=14.2 Hz, 1H, C(O)CH_2Cl), 3.78 (dd, $^2J_{6a6b}$=10.2, J_{56a}=7.4, 1H, H-6a^{I}), 3.74 (dd, $^2J_{6a6b}$=10.2, J_{56b}=4.1, 1H, H-6b^{I}), 3.52 (dd, $^2J_{6a6b}$=10.9, J_{56a}=7.3, 1H, H-6a^{II}), 3.47 (dd, $^2J_{6a6b}$=10.9, J_{56b}=4.2, 1H, H-6b^{II}). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7 (*C*(O)CH_2Cl), 165.4 (Ph*C*O), 165.2 (Ph*C*O), 138.0, 137.8, 137.6, 137.3 (quat. Ph), 135.0 (OCH_2CHCH_2), 134.5-127.4 (Ph), 117.4 (OCH_2CHCH_2), 106.2 (C-1^{II}), 105.0 (C-1^{I}), 83.8 (C-3^{I}), 83.0 (C-3^{II}), 82.1 (C-2^{I}), 82.0 (C-4^{I}), 81.6 (C-2^{II}), 82.1 (C-4^{II}), 74.6 (C-5^{I}), 73.4 (6-*O*-Ph*C*H$_2^{I}$), 72.9 (6-*O*-Ph*C*H$_2^{II}$), 72.8 (C-5 ^{II}), 72.5 (3-*O*-Ph*C*H$_2^{I}$), 72.3 (3-*O*-Ph*C*H$_2^{II}$), 80.0 (C-6^{I}), 68.6 (C-6^{II}), 67.8 (OCH_2CHCH_2), 40.6 (C(O)*C*H_2Cl). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{59}H_{59}ClO_{14}$ 1044.3932, found 1044.3923. Calcd *m/z* for $[M+Na]^+$ $C_{59}H_{59}ClO_{14}$ 1049.3486, found 1049.3487. Calcd *m/z* for $[M+K]^+$ $C_{59}H_{59}ClO_{14}$ 1065.3225, found 1065.3220.

Allyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-3,6-di-O-benzyl-β-D-galactofuranoside (19). Carefully dried mixture of **10** (25 mg, 0.062 mmol) and **17** (44 mg, 0.065 mmol) was dissolved in CH_2Cl_2 (2 mL), powder MS300 AW (30 mg) was added, and the mixture was stirred for 20 min. Then temperature was decreased to –78 °C and TMSOTf (1 μL, cat.) was added. After 1 h at –15 °C the reaction was stopped by 1 drop of MeOH and Et_3N. Column chromatography (toluene—EtOAc 10:1) gave **19** (35 mg, 65%) as a colorless oil. R_f=0.67 (toluene-ethyl acetate 5:1). $[\alpha]_D$=-48° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J*=8.2 Hz, 2H, *o*-C(O)Ph), 7.64 (t, *J*=7.5 Hz, 1H, *p*-C(O)Ph), 7.49 (dd, *J*=8.2 Hz, *J*=7.5 Hz, 2H, *m*-C(O)Ph), 7.37-7.18 (m, 20H, PhH), 5.97-5.90 (m, 1H, OCH_2CHCH_2), 5.64 (s, 1H, H-1^{II}), 5.42 (br. s, 1H, H-2^{II}), 5.32 (m, 1H, OCH_2CHCH_2), 5.25 (m, 1H, H-5^{II}), 5.20 (m, 1H, OCH_2CHCH_2), 5.02 (s, 1H, H-1^{I}), 4.82 (d, J_{ab}=12.1 Hz, 1H, 3-*O*-PhCH_2^{II}), 4.69 (d, J_{ab}=12.0 Hz, 1H, 3-*O*-PhCH_2^{I}), 4.63 (d, J_{ab}=12.1 Hz, 1H, 3-*O*-PhCH_2^{II}), 4.56 (d, J_{ab}=12.2 Hz, 1H, 6-*O*-PhCH_2^{I}), 4.54 (d, J_{ab}=12.0 Hz, 1H, 3-*O*-PhCH_2^{II}), 4.53 (d, J_{ab}=12.2 Hz, 1H, 6-*O*-PhCH_2^{I}), 4.42 (d, J_{ab}=12.1 Hz, 1H, 6-*O*-PhCH_2^{II}), 4.41 (dd, J_{43}=4.0 Hz, J_{45}=5.6 Hz, 1H, H-4^{II}), 4.35 (d, J_{ab}=12.1 Hz, 1H, 6-*O*-PhCH_2^{II}), 4.26 (dd, J_{43}=3.9 Hz, J_{45}=2.1 Hz, 1H, H-4^{I}), 4.21 (m, 1H, OCH_2CHCH_2), 4.15 (d, J_{HOH}=10.4 Hz, 1H, H-2^{I}), 4.09 (m, 1H, H-5^{I}), 4.03 (m, 1H, OCH_2CHCH_2), 3.98 (d, J_{34}=3.9. Hz, 1H, H-3^{I}), 3.97 (d, J_{34}=4.0 Hz, 1H, H-3^{II}), 3.90 (d,

J_{ab}=14.9 Hz, 1H, C(O)CH_2Cl), 3.85 (dd, $^2J_{6a6b}$=10.0, J_{56a}=7.4, 1H, H-6a^I), 3.84 (d, J_{ab}=14.9 Hz, 1H, C(O)CH_2Cl), 3.73 (dd, $^2J_{6a6b}$=10.2, J_{56b}=4.3, 1H, H-6b^I), 3.51-3.44 (m, 2H, H-6a^{II}, H-6b^{II}), 2.99 (d, J_{HOH}=10.4 Hz, 1H, OH).^{13}C NMR (150 MHz): 166.7 (*C*(O)CH$_2$Cl), 165.2 (Ph*C*O), 138.0, 137.8, 137.5, 136.9 (quat. Ph), 134.3 (OCH$_2$*C*HCH$_2$), 133.6, 129.8-127.5 (Ph), 117.2 (OCH$_2$CH*C*H$_2$), 107.8 (C-1^I), 105.9 (C-1^{II}), 86.4 (C-3^I), 83.4 (C-4^I), 82.6 (C-4^{II}), 82.2 (C-3^{II}), 80.7 (C-2^{II}), 78.3 (C-2^I), 75.1 (C-5^I), 73.5 (6-*O*-PhCH_2^I), 73.0 (C-5 ^{II}, 6-*O*-PhCH_2^{II}), 72.3 (3-*O*-PhCH_2^{II}), 72.1 (3-*O*-PhCH_2^I), 71.0 (C-6^I), 68.3 (C-6^{II}), 68.0 (O*C*H$_2$CHCH$_2$), 40.7 (C(O)*C*H$_2$Cl). HRMS(ESI): Calcd *m/z* for [M+NH$_4$]$^+$ $C_{52}H_{55}ClO_{13}$ 940.3669, found 940.3669. Calcd *m/z* for [M+Na]$^+$ $C_{52}H_{55}ClO_{13}$ 945.3223, found 945.3229. Calcd *m/z* for [M+K]$^+$ $C_{52}H_{55}ClO_{13}$ 961.2963, found 961.2972.

Allyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside (18) (alternative method via benzoylation of 19). To a solution of disaccharide **19** (35 mg, 0.038 mmol) and pyridine (30 μL, 0.38 mmol) in CH_2Cl_2 (2 mL) BzCl (26 μL, 0.22 mmol) was added. After completion of the reaction (overnight) the mixture was diluted with CH_2Cl_2, washed by sat. aq. $NaHCO_3$, and concentrated *in vacuo* with toluene. Column chromatography (toluene—EtOAc 15:1) gave **18** (34 mg, 87%) as a colorless oil.

2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside trichloroacetimidate (5). Allyl galactoside **18** (310 mg, 0.30 mmol) was deallylated according to **GP II** in MeOH (6 mL) by $PdCl_2$ (22 mg, 0.12 mmol). Resulting crude product was treated according to **GP III** in CH_2Cl_2 (2 mL) by CCl_3CN (150 μL, 1.50 mmol) and DBU (50 μL). Column chromatography (toluene—EtOAc 20:1 + 1 vol.% of Et_3N) gave **5** (190 mg, 55%) as a colorless syrup. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.62 (s, 1H, =NH), 8.07-8.01, 7.65-7.18 (m, 30H, PhH), 6.59 (s, 1H, H-1^I), 5.66 (br. s, 1H, H-2^I), 5.51 (s, 1H, H-1^I), 5.47 (d, J_{23}=1.4 Hz, 1H, H-2^I), 5.28 (m, 1H, H-5^{II}), 4.85 (d, J_{ab}=11.5 Hz, 1H, 3-*O*-PhCH_2^I), 4.72 (d, J_{ab}=11.9 Hz, 1H, 3-*O*-PhCH_2^{II}), 4.62 (d, J_{ab}=11.5 Hz, 1H, 3-*O*-PhCH_2^I), 4.34 (t, J_{43}=J_{45}=4.9 Hz, 1H, H-4^I), 4.50 (d, J_{ab}=11.9 Hz, 1H, 3-*O*-PhCH_2^{II}), 4.48 (m, 2H, 6-*O*-PhCH_2^I), 4.40-4.35 (m, 3H, H-4^{II}, H-3^I, 6-*O*-PhCH_2^{II}), 4.27-4.23 (m, 2H, 6-*O*-PhCH_2^{II}, H-5^I), 3.89 (br. d, J_{34}=6.5 Hz, 1H, H-3^{II}), 3.88 (d, J_{ab}=14.7 Hz, 1H, C(O)CH_2Cl), 3.84 (d, J_{ab}=14.7 Hz, 1H, C(O)CH_2Cl), 3.78 (dd, $^2J_{6a6b}$=10.2, J_{56a}=3.8, 1H, H-6a^I), 3.72 (dd, $^2J_{6a6b}$=10.2, J_{56b}=7.5, 1H, H-6b^I), 3.51 (dd, $^2J_{6a6b}$=11.0, J_{56a}=7.7, 1H, H-6a^{II}), 3.44 (dd, $^2J_{6a6b}$=11.0, J_{56b}=3.9, 1H, H-6b^{II}). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.2 (*C*(O)CH$_2$Cl, 2Ph*C*O), 160.8 (*C*(NH)CCl$_3$), 137.7-137.2 (quat. Ph), 133.6-127.4 (Ph), 106.5 (C-1^{II}), 103.7 (C-1^I), 85.2 (C-4^I), 82.9 (C-3^{II}), 82.8 (C-4^{II}), 81.6 (C-2^{II}), 81.0 (C-3^I), 80.6 (C-2^I), 75.0 (C-5^I), 73.4 (6-*O*-PhCH_2^I), 72.9 (6-*O*-PhCH_2^{II}), 72.6 (C-5^{II}), 72.4 (3-*O*-PhCH_2^I, 3-*O*-PhCH_2^{II}), 70.3 (C-6^I), 68.8 (C-6^{II}), 40.6 (C(O)*C*H$_2$Cl). HRMS(ESI): Calcd *m/z* for Calcd *m/z* for [M+Na]$^+$ $C_{85}H_{55}Cl_4NO_{14}$ 1152.2269, found 1152.2241.

Allyl 2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl-(1→5)-3,6-di-O-benzyl-β-D-galactofuranoside (21). Carefully dried mixture of **10** (37 mg, 0.092 mmol) and **20**[21] (74 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (4 mL), powder MS300 AW (30 mg) was added, and the mixture was stirred for 20 min. Then temperature was decreased to –78 °C and TMSOTf (1 μL, cat.) was added. After 1 h at –15 °C the reaction was stopped by 1 drop of MeOH and Et_3N. Column chromatography (toluene—EtOAc 8:1) gave **21** (56 mg, 62%) as a colorless oil. R_f=0.57 (toluene-ethyl acetate 5:1). $[\alpha]_D$=-24° (c = 1, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-7.85, 7.58-7.16 (m, 30H, PhH), 5.97 (m, 1H, H-5^{II}), 5.93-5.83 (m, 1H, OCH$_2$C*H*CH$_2$), 5.70 (s, 1H, H-1^{II}), 5.63 (d, J_{34}=5.0 Hz, 1H, H-3^{II}), 5.53 (br. s, 1H, H-2^{II}), 5.27 (m, 1H, OCH$_2$CHC*H*$_2$), 5.16 (m, 1H, OCH$_2$CHC*H*$_2$), 5.01 (s, 1H, H-1^I), 4.80 (dd, J_{43}=5.0 Hz, J_{45}=3.7 Hz, 1H, H-4^{II}), 4.68 (m, 2H, H-6a^{II}, H-6b^{II}), 4.63 (d, J_{ab}=12.2 Hz, 1H, PhCH_2), 4.56 (d, J_{ab}=11.9 Hz, 1H, PhCH_2), 4.49 (d, J_{ab}=11.9 Hz, 1H, PhCH_2), 4.46 (d, J_{ab}=12.2 Hz, 1H, PhCH_2), 4.26 (dd, J_{43}=4.1 Hz, J_{45}=3.0 Hz, 1H, H-4^I), 4.20-4.14 (m, 2H, OCH_2CHCH$_2$, H-2^I), 4.09 (m, 1H, H-5^I), 4.00-3.93 (m, 2H, H-3^I, OCH_2CHCH$_2$), 3.84 (dd, $^2J_{6a6b}$=10.0, J_{56a}=7.0, 1H, H-6a^I), 3.71 (dd, $^2J_{6a6b}$=10.0, J_{56b}=4.3, 1H, H-6b^I), 2.78 (d, J_{HOH}=10.1 Hz, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 165.7, 165.3 (Ph*C*O), 137.9, 137.8, (quat. Ph), 134.2 (OCH$_2$*C*HCH$_2$), 133.5, 133.3, 133.2, 133.1 (quat. Ph), 130.1-127.6 (Ph), 117.1 (OCH$_2$CH*C*H$_2$), 107.6 (C-1^I), 105.0 (C-1^{II}), 85.8 (C-3^I), 83.1 (C-4^I), 82.3 (C-2^{II}), 82.0 (C-4^{II}), 78.7 (C-2^I), 77.7 (C-3^{II}), 75.8 (C-5^I), 73.5 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 70.8 (C-6^I), 70.5 (C-5^{II}), 68.0 (O*C*H$_2$CHCH$_2$), 63.6 (C-6^{II}). HRMS(ESI): Calcd *m/z* for [M+NH$_4$]$^+$ $C_{57}H_{54}O_{15}$ 996.3801, found 996.3793. Calcd *m/z* for [M+Na]$^+$ $C_{57}H_{54}O_{15}$ 1001.3355, found 1001.3348. Calcd *m/z* for [M+K]$^+$ $C_{57}H_{54}O_{15}$ 1017.3094, found 1017.3104.

Allyl 2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside (22). To a solution of **21** (56 mg, 0.057 mmol) and pyridine (50 μL, 0.6 mmol) in CH_2Cl_2 (2 mL) BzCl (50 μL, 0.6 mmol) was added and the reaction was left overnight. Then the mixture was diluted with CH_2Cl_2, washed by sat. aq. $NaHCO_3$, and concentrated *in vacuo* with toluene. Column chromatography (toluene—EtOAc 15:1) gave **22** (52 mg, 84%) as a colorless oil. R_f=0.66 (toluene-ethyl acetate 10:1). $[\alpha]_D$=-18° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17-7.92, 7.55-7.17 (m, 35H, PhH), 6.01 (m, 1H, H-5^{II}), 5.88-5.80 (m, 1H, OCH$_2$C*H*CH$_2$), 5.69 (s, 1H, H-1^{II}), 5.65 (d, J_{34}=5.1 Hz, 1H, H-3^{II}), 5.62 (br. s, 1H, H-2^{II}), 5.42 (br. s, 1H, H-2^I), 5.25 (m, 1H, OCH$_2$CHC*H*$_2$), 5.19 (s, 1H, H-1^I), 5.14 (m, 1H, OCH$_2$CHC*H*$_2$), 4.82-4.78 (m, 2H, H-4^{II}, Ph*C*H$_2$), 4.69 (m, 2H, H-6a^{II}, H-6b^{II}), 4.56 (d, J_{ab}=11.9 Hz, 1H, PhCH_2), 4.51 (d, J_{ab}=12.0 Hz, 1H, PhCH_2), 4.46 (d, J_{ab}=12.0 Hz, 1H, PhCH_2), 4.30 (t, J_{43}= J_{45}=5.7 Hz, 1H, H-4^I), 4.24 (m, 1H, H-5^I), 4.18-4.13 (m, 2H, OCH_2CHCH$_2$, H-3^I), 3.98 (m, 1H, OCH_2CHCH$_2$), 3.73 (m, 1H, H-6a^I), 3.67 (m, 1H, H-6b^I). ^{13}C NMR (125 MHz): δ 166.0, 165.6, 165.5, 165.4, 165.2 (Ph*C*O), 137.9, 137.4, (quat. Ph), 134.5 (OCH$_2$*C*HCH$_2$), 133.8, 133.3, 133.2, 133.1, 132.9 (quat. Ph), 130.5-127.5 (Ph), 117.4 (OCH$_2$CH*C*H$_2$), 105.6 (C-1^{II}), 104.8 (C-1^I), 83.7 (C-3^I), 82.1, 82.0 (C-2^I, C-2^{II}), 81.9 (C-4^I), 81.5 (C-4^{II}), 82.0 (C-4^{II}), 77.5 (C-3^{II}), 75.4 (C-5^I), 73.4 (Ph*C*H$_2$), 72.4 (Ph*C*H$_2$), 70.8 (C-6^I), 70.4 (C-5^{II}), 67.7 (O*C*H$_2$CHCH$_2$), 63.8 (C-6^{II}). HRMS(ESI): Calcd *m/z* for [M+NH$_4$]$^+$ $C_{64}H_{58}O_{16}$ 1100.4063, found 1100.4054. Calcd *m/z* for [M+Na]$^+$

$C_{64}H_{58}O_{16}$ 1105.3617, found 1105.3612. Calcd *m/z* for $[M+K]^+$ $C_{64}H_{58}O_{16}$ 1121.3356, found 1121.3366.

2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside trichloroacetimidate (6). Allylgalactoside **22** (47 mg, 0.043 mmol) was treated by $PdCl_2$ (4 mg, 0.022 mmol) according to **GP II** in 1 mL of MeOH. Resulted crude product was treated according to **GP III** in CH_2Cl_2 (2 mL) by CCl_3CN (22 μL, 0.22 mmol) and DBU (20 μL). Column chromatography (toluene—EtOAc 20:1 + 1 vol.% of Et_3N) gave **6** (30 mg, 59%) as a yellowish syrup. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.55 (s, 1H, =NH), 8.04-7.88, 7.54-7.15 (m, 30H, PhH), 6.49 (s, 1H, H-1^I), 6.00 (m, 1H, H-5^{II}), 5.65 (br. s, 1H, H-2^I), 5.62 (s, 1H, H-1^{II}), 5.60 (d, J_{34}=5.1 Hz, 1H, H-3^{II}), 5.57 (br. s, 1H, H-2^{II}), 5.42 (br. s, 1H, H-2^I), 4.84 (d, J_{ab}=11.7 Hz, 1H, PhCH_2), 4.80 (dd, J_{43}=5.1 Hz, J_{45}=3.6 Hz, 1H, H-4^{II}), 4.67 (m, 2H, H-6a^{II}, H-6b^{II}), 4.56 (d, J_{ab}=11.7 Hz, 1H, PhCH_2), 4.52 (t, J_{43}=J_{45}=5.7 Hz, 1H, H-4^I), 4.49 (d, J_{ab}=12.0 Hz, 1H, PhCH_2^{II}), 4.45 (d, J_{ab}=12.0 Hz, 1H, PhCH_2), 4.31 (d, J_{34}=5.5 Hz, 1H, H-3^I), 4.24 (m, 1H, H-5^I), 3.71 (m, 2H, H-6a^I, H-6b^I). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 165.7, 165.6, 165.2, 165.2 (Ph*C*O), 160.7 (*C*(NH)CCl_3), 137.8, 137.3, (quat. Ph), 133.6, 133.4, 133.2, 133.0, 132.9 (quat. Ph), 129.9-127.5 (Ph), 105.8 (C-1^{II}), 103.4 (C-1^I), 84.9 (C-4^I), 83.0 (C-3^I), 81.8 (C-2^{II}), 81.6 (C-4^{II}), 80.8 (C-2^I), 77.4 (C-3^{II}), 75.8 (C-5^I), 73.4 (Ph*C*H_2), 72.3 (Ph*C*H_2), 70.5 (C-5^{II}), 70.3 (C-6^I), 64.0 (C-6^{II}). HRMS(ESI): Calcd *m/z* for $[M+Na]^+$ 1208.2400, found 1208.2390. Calcd *m/z* for $[M+K]^+$ 1224.2140, found 1224.2130.

3-trifluoroacetamidopropyl 2,3,4-tri-O-benzoyl-α-D-mannopyranoside (3). Carefuly dried suspension of **23** (375 mg, 0.58 mmol) in 3-trifluoroacetamidopropanol (200 mg, 1.16 mmol) was dissolved in CH_2Cl_2 (5 mL), 600 mg of Ms 4Å powder were added, and the mixture was stirred for 20 min. Then at –20 °C NIS (260 mg, 1.16 mmol) was added and after 20 min of stirring at –40 °C TfOH (10 μL, 0.12 mmol) was added. For 1 h the mixture was kept in the temperature range –20…–15 °C, then at –15 °C the reaction mixture was quenched by 3 drops of pyridine. Column chromatography (toluene—EtOAc 15:1) gave product of glycosylation, which was dissolved in 10 mL of TFA (90%, aq.) and stirred for 3 h. Then the mixture was diluted with toluene and concentrated *in vacuo*. Column chromatography (toluene—EtOAc 3:1) gave **3** (235 mg, 62%) as a colorless oil. R_f=0.25 (toluene-ethyl acetate 3:1). $[\alpha]_D$=-121° (c = 1, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.72 (m, 6H, *o*-C(O)Ph), 7.55-7.14 (m, 9H, PhH), 6.95 (br. s, 1H, CH_2NH), 5.84 (dd, J_{34}=10.0 Hz, J_{32}=3.3 Hz, 1H, H-3), 5.76 (t, *J*=10.0 Hz, 1H, H-4), 5.59 (dd, J_{23}=3.3 Hz, J_{21}=1.8 Hz, 1H, H-2), 5.02 (d, J_{12}=1.8 Hz, 1H, H-1), 4.01 (m, 1H, H-5), 3.84 (ddd, $^2J_{ab}$=10.1 Hz, *J*=6.9 Hz, *J*=4.9 Hz, 1H, OC$H_2$$CH_2CH_2N$), 3.76 (dd, $^2J_{ab}$=12.7 Hz, J_{56a}=2.6 Hz, 1H, H-6a), 3.72 (dd, $^2J_{ab}$=12.7 Hz, J_{56b}=4.4 Hz, 1H, H-6b), 3.57 (ddd, $^2J_{ab}$=10.1 Hz, *J*=6.9 Hz, *J*=4.9 Hz, 1H, OC$H_2$$CH_2CH_2N$), 3.52 (m, 1H, OCH_2CH_2CH_2N), 3.49 (m, 1H, OCH_2CH_2CH_2N), 2.70 (br. s, 1H, OH), 1.99-1.87 (m, 2H, OCH_2CH_2CH_2N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 165.6, 165.54 (Ph*C*O), 157.5 (q, $^2J_{CF}$=37.0 Hz, *C*(O)CF_3), 133.7, 133.6, 133.2 (quat. Ph), 130.0-128.3 (Ph), 115.9 (q, $^1J_{CF}$=287.7 Hz, C(O)*C*F_3), 97.9 (C-1), 71.4 (C-5), 70.5 (C-2), 69.7 (C-3), 67.1 (C-4), 66.1 ($OCH_2CH_2CH_2N$), 61.4 (C-6), 37.6 (OCH_2CH_2CH_2N), 28.6 (OCH_2CH_2CH_2N). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{32}H_{34}F_3NO_8$ 663.2160, found 663.2156. Calcd *m/z* for $[M+Na]^+$ $C_{32}H_{34}F_3NO_8$ 668.1714, found 668.1725. Calcd *m/z* for $[M+K]^+$ $C_{32}H_{34}F_3NO_8$ 684.1453, found 684.1452.

3-trifluoroacetamidopropyl 2-O-benzoyl-4,5-di-O-benzyl-α-D-mannopyranoside (4). To a stirred solution of **24** (570 mg, 1.12 mmol) and pyridine (0.31 mL, 3.9 mmol) in CH_2Cl_2 (10 mL) chloroacetyl chloride (160 μL, 2.02 mmol) was slowly added. The reaction mixtute was stirred for 40 min, diluted with CH_2Cl_2, washed by 1 M HCl, sat. aq. $NaHCO_3$, and concentrated *in vacuo*. To a crude product 3-trifluoroacetamidopropanol (380 mg, 2.24 mmol) was added and the mixture was caefuly dried, dissolved in 5 mL of CH_2Cl_2, and stirred with MS300 AW for 20 min. Then the temperature was decreased to –20 °C, NIS (500 mg, 2.24 mmol) was added**,** and after 20 min of stirring at –40 °C TfOH (20 μL, 0.22 mmol) was added. The mixture was kept in the temperature range –20…–15 °C for 1 h, then at –15 °C it was quenched by 3 drops of pyridine. Column chromatography (toluene—EtOAc 10:1) gave product of glycosylation, which was treated according to **GP I** by thiourea (0.83 g, 11 mmol**)** and collidine (185 μL, 1.4 mmol) in MeOH (25 mL). Column chromatography of the residue (toluene—EtOAc 4:1) gave **4** (380 mg, 55%) as a colorless oil. R_f=0.26 (toluene-ethyl acetate 5:1). $[\alpha]_D$=-63° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J*=8.2 Hz, 2H, *o*-C(O)Ph), 7.58 (t, *J*=7.5 Hz, 1H, *p*-C(O)Ph), 7.40 (dd, *J*=8.2 Hz, *J*=7.5 Hz, 2H, *m*-C(O)Ph), 7.39-7.25 (m, 10H, PhH), 6.89 (br. s, 1H, CH_2NH), 5.33 (dd, J_{23}=3.3 Hz, J_{21}=1.8 Hz, 1H, H-2), 4.97 (d, J_{12}=1.8 Hz, 1H, H-1), 4.81 (d, J_{ab}=11.2 Hz, 1H, PhCH_2), 4.71 (d, J_{ab}=12.0 Hz, 1H, PhCH_2), 4.64 (d, J_{ab}=11.2 Hz, 1H, PhCH_2), 4.57 (d, J_{ab}=12.0 Hz, 1H, PhCH_2), 4.21 (m, 1H, H-5), 3.95 (t, *J*=9.5 Hz, 1H, H-4), 3.87-3.78 (m, 4H, H-6a, $OCH_2CH_2CH_2N$, H-6b, H-3), 3.57 (m, 1H, $OCH_2CH_2CH_2N$), 3.51 (m, 1H, $OCH_2CH_2CH_2N$), 3.43 (m, 1H, $OCH_2CH_2CH_2N$), 2.28 (d, J_{HOH}=5.3 Hz, 1H, OH), 1.92-1.86 (m, 2H, $OCH_2CH_2CH_2N$).^{13}C NMR (150 MHz, $CDCl_3$): δ 166.2 (Ph*C*O), 138.1, 138.0 (quat. Ph), 133.4 (*p*-C(O)Ph), 129.8 (*o*-C(O)Ph), 129.5 (quat. Ph), 128.5-127.6 (Ph), 97.7 (C-1), 75.6 (C-4), 74.9 (Ph*C*H_2), 73.5 (Ph*C*H_2), 72.8 (C-2), 71.8 (C-3), 70.5 (C-5), 69.0 (C-6), 66.1 ($OCH_2CH_2CH_2N$), 38.0 ($OCH_2CH_2CH_2N$), 28.3 ($OCH_2CH_2CH_2N$). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{32}H_{34}F_3NO_8$ 635.2575, found 635.2576. Calcd *m/z* for $[M+Na]^+$ $C_{32}H_{34}F_3NO_8$ 640.2129, found 640.2130.

3-trifluoroacetamidopropyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (25). Carefully dried mixture of **3** (72 mg, 0.111 mmol) and **5** (105 mg, 0.093 mmol) was dissolved in CH_2Cl_2 (4 mL), powder MS 4Å (100 mg) was added, and the mixture was stirred for 20 min. Then temperature was decreased to –78 °C and TMSOTf (5 μL, 0.028 mmol) was added. The reaction mixture was kept at –20…–40 °C for 1 h and then at –15 °C was quenched by 1 drop of Et_3N. Column chromatography (toluene—EtOAc 12:1) gave **25** (130 mg, 85%) as a colorless oil. R_f=0.70 (toluene-ethyl acetate 5:1). $[\alpha]_D$=-75° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15-7.83, 7.66-7.10 (m, 45H, PhH), 5.86 (dd, J_{23}=3.4 Hz, J_{34}=10.0 Hz,

1H, H-3^{I}), 5.77 (t, J_{34}=J_{45}=10.0 Hz, 1H, H-4^{I}), 5.67 (dd, J_{12}=1.6 Hz, J_{23}=3.4 Hz, 1H, H-2^{I}), 5.59 (s, 1H, H-1^{III}), 5.51 (d, J_{23}=1.6 Hz, 1H, H-2^{III}), 5.43 (d, J_{23}=1.7 Hz, 1H, H-2^{II}), 5.34 (s, 1H, H-1^{II}), 5.25 (ddd, J_{45}=5.4 Hz, J_{56a}=6.8 Hz, J_{56b}=5.2 Hz, 1H, H-5^{III}), 5.03 (d, J_{12}=1.6 Hz, 1H, H-1^{I}), 4.74 (d, J_{ab}=12.1 Hz, 1H, 3-*O*-PhC*H*$_2^{III}$), 4.68 (d, J_{ab}=11.6 Hz, 1H, 3-*O*-PhC*H*$_2^{II}$), 4.55 (d, J_{ab}=11.6 Hz, 1H, 3-*O*-PhC*H*$_2^{II}$), 4.53 (d, J_{ab}=12.0 Hz, 1H, 3-*O*-PhC*H*$_2^{III}$), 4.45 (m, 2H, 6-*O*-PhC*H*$_2^{II}$), 4.39 (t, J_{43}=J_{45}=5.4 Hz, 1H, H-4^{III}), 4.35-4.28 (m, 4H, H-3^{II}, H-5^{I}, H-4^{II}, 6-*O*-PhC*H*$_2^{III}$), 4.26 (d, J_{ab}=12.1 Hz, 1H, 6-*O*-PhC*H*$_2^{III}$), 4.22 (m, 1H, H-5^{II}), 3.97 (m, 1H, OC*H*$_2$CHCH$_2$), 3.92 (m, 1H, H-3^{III}), 3.90 (m, 2H, H-6a^{I}, H-6b^{I}), 3.84 (d, J_{ab}=14.8 Hz, 1H, C(O)C*H*$_2$Cl), 3.79 (d, J_{ab}=14.8 Hz, 1H, C(O)C*H*$_2$Cl), 3.78 (m, 1H, H-6a^{II}), 3.64 (m, 1H, H-6a^{II}), 3.60-3.48 (m, 3H, OC*H*$_2$CHCH$_2$, 2OCH$_2$CH$_2$C*H*$_2$N), 3.46 (m, 2H, H-6a^{III}, H-6b^{III}), 2.00-1.90 (m, 2H, OCH$_2$C*H*$_2$CH$_2$N). ^{13}C NMR (150 MHz, $CDCl_3$): 166.7 (*C*(O)CH$_2$Cl), 165.7-165.4 (Ph*C*O), 138.0-137.4 (quat. Ph), 133.5-127.4 (Ph), 106.7 (C-1^{II}), 106.3 (C-1^{III}), 97.6 (C-1^{I}), 83.6 (C-3^{II}), 82.9 (C-3^{III}), 82.2 (2C, C-4^{II}, C-2^{II}), 81.6 (C-2^{II}), 81.3 (C-4^{III}), 74.1 (C-5 ^{II}), 73.4 (6-*O*-PhC*H*$_2^{II}$), 72.9 (6-*O*-PhC*H*$_2^{III}$), 72.8 (C-5^{III}), 72.7 (3-*O*-PhC*H*$_2^{II}$), 72.3 (3-*O*-PhC*H*$_2^{III}$), 71.2 (C-5^{I}), 71.1 (C-6^{II}), 70.4 (C-2^{I}), 69.9 (C-3^{I}), 68.4 (C-6^{III}), 67.4 (C-4^{I}), 66.4 (OCH$_2$CH$_2$CH$_2$N), 66.2 (C-6^{I}), 40.6 (C(O)*C*H$_2$Cl), 37.7 (OCH$_2$CH$_2$*C*H$_2$N), 28.5 (OCH$_2$*C*H$_2$CH$_2$N). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{88}H_{83}ClF_3NO_{23}$ 1631.5335, found 1631.5310. Calcd *m/z* for $[M+Na]^+$ $C_{88}H_{83}ClF_3NO_{23}$ 1636.4889, found 1636.4874. Calcd *m/z* for $[M+K]^+$ $C_{88}H_{83}ClF_3NO_{23}$ 1652.4628, found 1652.4607.

3-trifluoroacetamidopropyl 2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (26). Trisaccharide **25** (130 mg, 0.080 mmol) was treated according to **GP I** by thiourea (61 mg, 0.8 mmol) and collidine (14 μL, 0.1 mmol) in MeOH (10 mL). Column chromatography (toluene—EtOAc 7:1) gave **26** (106 mg, 86%) as a colorless oil. R_f=0.41 (toluene-ethyl acetate 5:1). $[\alpha]_D$=-79° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14-7.85, 7.64-7.16 (m, 45H, PhH), 5.89 (dd, J_{23}=3.4 Hz, J_{34}=10.0 Hz, 1H, H-3^{I}), 5.80 (t, J_{34}=J_{45}=10.0 Hz, 1H, H-4^{I}), 5.69 (dd, J_{12}=1.6 Hz, J_{23}=3.4 Hz, 1H, H-2^{I}), 5.64 (s, 1H, H-1^{III}), 5.57 (d, J_{23}=1.6 Hz, 1H, H-2^{III}), 5.46 (d, J_{23}=1.7 Hz, 1H, H-2^{II}), 5.38 (s, 1H, H-1^{II}), (ddd, J_{45}=5.4 Hz, J_{56a}=6.8 Hz, J_{56b}=5.2 Hz, 1H, H-5^{III}), 5.05 (d, J_{12}=1.6 Hz, 1H, H-1^{I}), 4.76 (d, J_{ab}=12.2 Hz, 1H, 3-*O*-PhC*H*$_2^{III}$), 4.70 (d, J_{ab}=11.6 Hz, 1H, 3-*O*-PhC*H*$_2^{II}$), 4.59 (d, J_{ab}=11.6 Hz, 1H, 3-*O*-PhC*H*$_2^{II}$), 4.57 (d, J_{ab}=12.2 Hz, 1H, 3-*O*-PhC*H*$_2^{III}$), 4.48 (m, 2H, 6-*O*-PhC*H*$_2^{II}$), 4.41 (br. d, J_{34}=6.1 Hz, 1H, H-3^{II}), 4.38 (d, J_{ab}=11.9 Hz, 1H, 6-*O*-PhC*H*$_2^{III}$), 4.36-4.32 (m, 3H, 6-*O*-PhC*H*$_2^{III}$, H-5^{I}, H-4^{II}), 4.29-4.26 (m, 2H, H-4^{III}, H-5^{II}), 4.15 (br. d., J_{34}=5.9 Hz, 1H, H-3^{III}), 3.97 (dt, $^2J_{ab}$=10.0 Hz, $^3J_{HCH2}$=6.2 Hz, 1H, OC*H*$_2$CHCH$_2$), 3.94-3.92 (m, 2H, H-6a^{I}, H-6b^{I}), 3.86-3.81 (m, 2H, H-5^{III}, H-6a^{II}), 3.74 (dd, $^2J_{6a6b}$=10.1, J_{56b}=4.1, 1H, H-6b^{II}), 3.60-3.48 (m, 3H, OC*H*$_2$CHCH$_2$, OCH$_2$CH$_2$C*H*$_2$N), 3.44-3.38 (m, 2H, H-6a^{III}, H-6b^{III}), 2.37 (br. s, 1H, 5-OH), 2.01-1.90 (m, 2H, OCH$_2$C*H*$_2$CH$_2$N). ^{13}C NMR (150 MHz, $CDCl_3$): 165.7-165.2 (Ph*C*O), 137.9-137.5 (quat. Ph), 133.5-127.4 (Ph), 106.6 (C-1^{II}), 106.4 (C-1^{III}), 97.5 (C-1^{I}), 83.5 (C-3^{II}), 83.4 (C-3^{III}), 83.2 (C-4^{III}), 82.2 (2C, C-4^{II}, C-2^{II}), 81.8 (C-2^{II}), 73.8 (C-5 ^{II}), 73.4 (6-*O*-PhC*H*$_2^{II}$), 73.2 (6-*O*-PhC*H*$_2^{III}$), 72.7 (3-*O*-PhC*H*$_2^{II}$), 72.2 (3-*O*-PhC*H*$_2^{III}$), 71.4 (C-6^{III}), 71.2 (C-5^{I}), 71.1 (C-6^{II}), 70.4 (C-2^{I}), 70.1 (C-5^{III}), 69.9 (C-3^{I}), 67.3 (C-4^{I}), 66.3 (OCH$_2$CH$_2$CH$_2$N), 66.1 (C-6^{I}), 37.6 (OCH$_2$CH$_2$*C*H$_2$N), 28.4 (OCH$_2$*C*H$_2$CH$_2$N). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{86}H_{82}F_3NO_{22}$ 1555.5619, found 1555.5596. Calcd *m/z* for $[M+Na]^+$ $C_{86}H_{82}F_3NO_{22}$ 1560.5173, found 1560.5162. Calcd *m/z* for $[M+K]^+$ $C_{86}H_{82}F_3NO_{22}$ 1576.4912, found 1576.4896.

3-trifluoroacetamidopropyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (27). Carefully dried mixture of **26** (77 mg, 0.050 mmol) and **5** (70 mg, 0.062 mmol) was dissolved in CH_2Cl_2 (3 mL), powder MS 4Å (40 mg) was added, and the mixture was stirred for 20 min. Then temperature was decreased to –78 °C and TMSOTf (3.5 μL, 0.019 mmol) was added. The reaction mixture was kept at –30…–40 °C for 1 h and then at –15 °C was stopped by 1 drop of Et_3N. Column chromatography (toluene—EtOAc 8:1) gave **27** (89 mg, 71%) as a colorless oil. R_f=0.67 (toluene-ethyl acetate 5:1). $[\alpha]_D$=-78° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12-7.83, 7.64-7.10 (m, 75H, PhH), 5.86 (dd, J_{23}=3.4 Hz, J_{34}=10.0 Hz, 1H, H-3^{I}), 5.77 (t, J_{34}=J_{45}=10.0 Hz, 1H, H-4^{I}), 5.67 (dd, J_{12}=1.6 Hz, J_{23}=3.3 Hz, 1H, H-2^{I}), 5.60 (s, 1H, H-1^{III}), 5.58(s, 1H, H-1^{IV}), 5.56 (m, 2H, H-1^{V}, H-2^{III}), 5.54 (br. s, 1H, H-2^{IV}), 5.49 (d, J_{23}≈1.3 Hz, 1H, H-2^{V}), 5.40 (d, J_{23}=1.6 Hz, 1H, H-2^{II}), 5.19 (s, 1H, H-1^{II}), (ddd, J_{45}=5.4 Hz, J_{56a}=7.4 Hz, J_{56b}=5.2 Hz, 1H, H-5^{III}), 5.02 (d, J_{12}=1.6 Hz, 1H, H-1^{I}), 4.74-4.43 (m, 10H, PhC*H*$_2$), 4.37 (br. d, J_{34}=6.1 Hz, 1H, H-3^{II}), 4.35-4.20 (m, 13H, H-3^{III}, H-4^{III}, H-5^{I}, H-4^{II}, H-3^{IV}, H-4^{IV}, PhC*H*$_2$, H-4^{V}, H-5^{II}), 4.18 (d, J_{ab}=12.1 Hz, 1H, PhC*H*$_2$), 4.10 (dt, *J*=3.5 Hz, *J*=7.2 Hz, 1H, H-5^{III}), 4.03 (br. d, *J*=7.9 Hz, 1H, H-5^{IV}), 3.95 (dt, *J*=6.3 Hz, $^2J_{ab}$=10.2 Hz, 1H, OC*H*$_2$CHCH$_2$), 3.92-3.88 (m, 2H, H-6a^{I}, H-6b^{I}), 3.85 (br. d., J_{34}=5.8 Hz, 1H, H-3^{V}), 3.79-3.75 (m, 2H, H-6a^{II}, C(O)C*H*$_2$Cl), 3.74-3.67 (m, 4H, C(O)C*H*$_2$Cl, H-6a^{IV}, H-6a^{III}, H-6b^{II}), 3.58-3.48 (m, 5H, H-6b^{III}, OC*H*$_2$CHCH$_2$, OCH$_2$CH$_2$C*H*$_2$N, H-6b^{IV}), 3.39 (dd, $^2J_{6a6b}$=11.0, J_{56a}=7.3, 1H, H-6a^{V}), 3.34 (dd, $^2J_{6a6b}$=11.0, J_{56b}=3.9, 1H, H-6b^{V}), 2.00-1.89 (m, 2H, OCH$_2$C*H*$_2$CH$_2$N). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.6 (*C*(O)CH$_2$Cl), 165.7-165.0 (Ph*C*O), 138.0-137.2 (quat. Ph), 133.5-127.2 (Ph), 106.6 (C-1^{II}), 106.6 (C-1^{V}) 106.5 (C-1^{IV}), 106.2 (C-1^{III}), 97.5 (C-1^{I}), 84.0 (C-3^{IV}), 83.5 (C-3^{II}), 83.5 (C-3^{III}), 82.8 (C-3^{V}), 82.8 (C-4^{III}), 82.6 (C-4^{IV}), 82.2 (2C, C-2^{II}, C-4^{II}), 82.1 (C-2^{III}), 82.1 (C-2^{IV}), 81.4 (C-2^{V}), 81.4 (C-4^{V}), 74.3 (C-5^{IV}), 74.2 (C-5^{III}), 73.7 (C-5^{II}), 73.4 (PhC*H*$_2$), 73.1 (PhC*H*$_2$), 73.1 (PhC*H*$_2$), 72.9 (C-5^{V}, PhC*H*$_2$), 72.8 (PhC*H*$_2$), 72.6 (PhC*H*$_2$), 72.4 (PhC*H*$_2$), 72.1 (PhC*H*$_2$), 72.0 (C-6^{IV}), 71.3 (C-5^{I}), 71.2 (C-6^{III}), 70.7 (C-6^{IV}), 70.4 (C-2^{I}), 69.9 (C-3^{I}), 68.5 (C-6^{V}), 67.3 (C-4^{I}), 66.4 (OC*H*$_2$CH$_2$CH$_2$N), 66.0 (C-6^{I}), 40.5 (C(O)*C*H$_2$Cl), 37.6 (OCH$_2$CH$_2$*C*H$_2$N), 28.5 (OCH$_2$*C*H$_2$CH$_2$N). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{142}H_{135}ClF_3NO_{35}$ 2523.8794, found 2523.8749. Calcd *m/z* for $[M+Na]^+$ $C_{142}H_{135}ClF_3NO_{35}$ 2528.8347, found 2528.8378. Calcd *m/z* for $[M+2NH_4]^{2+}$ $C_{142}H_{135}ClF_3NO_{35}$ 1270.9566, found 1270.9573.

3-aminopropyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→5)-β-D-

galactofuranosyl-(1→6)-α-D-mannopyranoside (1). Compound **27** (35 mg, 0.014 mmol) was dissolved in EtOAc (1 mL), MeOH (1 mL) was added and 10% Pd/C (35 mg) was powdered. The reaction mixture was vigorously stirred in H_2-atmosphere for 3 h and then filtered through the *celite* layer. The filtrate was concentrated *in vacuo*, dissolved in 0.9 mL of 0.1 M MeONa in MeOH, one drop of water was added, and the mixture was kept overnight, then 5 μL of AcOH were added, and the mixture was diluted with water and concentrated *in vacuo*. Gel-chromatography and subsequent lyophilization gave **1** (10 mg, 83%) as a white foam. ^{1}H NMR (600 MHz, D_2O): 5.22 (d, J_{12}=2.0 Hz, 1H, H-1^V), 5.19 (m, 2H, H-1^{III}, H-1^{IV}), 5.03 (d, J_{12}=1.5 Hz, 1H, H-1^{II}), 4.85 (d, J_{12}=1.8 Hz, 1H, H-1^I), 4.17-4.14 (m, 5H, H-4^{III}, H-4^{IV}, H-2^{III}, H-2^{IV}, H-2^V), 4.13-4.08 (m, 5H, H-3^{II}, H-3^{III}, H-3^{IV}, H-2^{II}, H-4^{II}), 4.08-4.06 (m, 2H, H-3^V, H-4^V), 4.02 (m, 1H, H-6a^I), 3.98-3.92 (m, 4H, H-5^{II}, H-5^{III}, H-5^{IV}, H-2^I), 3.87-3.83 (m, 2H, OCH_2, H-5^V), 3.82-3.78 (m, 7H, H-6a^{III}, H-6b^{III}, H-6a^{IV}, H-6b^{IV}, H-6a^{II}, H-6b^{II}, H-3^I), 3.74-3.69 (m, 4H, H-6b^I, H-6a^V, H-5^I, H-4^I), 3.67 (dd, $^2J_{6a6b}$=11.7, J_{56b}=7.3, 1H, H-6b^V), 3.61 (ddd, $^2J_{ab}$=10.2 Hz, J=6.8 Hz, J=5.4 Hz, 1H, OC*H*$_2$CHCH$_2$), 3.17-3.09 (m, 2H, $OCH_2CH_2CH_2N$), 2.02-1.96 (m, 2H, $OCH_2CH_2CH_2N$). ^{13}C NMR (150 MHz, D_2O): δ 108.7 (C-1^{II}), 108.0 (C-1^V) 107.9, 107.9 (C-1^{III}, C-1^{IV}), 100.8 (C-1^I), 83.6 (C-4^V), 82.8 (C-4^{II}), 82.5 (2C, C-4^{III}, C-4^{IV}), 82.3, 82.3, 82.2 (C-2^{III}, C-2^{IV}, C-2^V), 82.0 (C-2^{II}), 77.7 (C-3^{II}), 77.5 (2C, C-3^{III}, C-3^{IV}), 77.3 (C-3^V), 77.0 (C-5^{II}), 76.6, 76.5(C-5^{III}, C-5^{IV}), 72.7 (C-5^I), 71.5 (C-3^I), 71.5 (C-5^V), 70.9 (C-2^I), 67.8 (C-6^I), 67.6 (C-4^I), 66.0 (OCH_2), 63.8 (C-6^V), 62.1 (2C, C-6^{III}, C-6^{IV}), 61.9 (C-6^{II}), 38.5 ($OCH_2CH_2CH_2N$), 27.6 ($OCH_2CH_2CH_2N$). HRMS(ESI): Calcd *m/z* for $[M+H]^+$ $C_{33}H_{59}NO_{26}$ 886.3398, found 886.3396. Calcd *m/z* for $[M+Na]^+$ $C_{33}H_{59}NO_{26}$ 908.3218, found 908.3209.

3-trifluoroacetamidopropyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-α-D-mannopyranoside (28). Carefuly dried mixture of **5** (15 mg, 0.013 mmol) and **4** (14 mg, 0.022 mmol) was dissolved in CH_2Cl_2 (1.5 mL), 30 mg of Ms300 AW powder was added, and the mixture was stirred for 20 min. Then at –78 °C TMSOTf (1 μL, 0.015 mmol) was added and the mixture was kept in the temperature range –20…–10 °C for 1 h, then at –15 °C the reaction mixture was quenched by 1 drop of Et_3N. Column chromatography (toluene—EtOAc 12:1) gave **27** (13 mg, 60%) as a colorless oil. R_f=0.50 (toluene-ethyl acetate 5:1). $[\alpha]_D$=-40° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04-7.96, 7.66-7.10 (m, 45H, PhH), 5.53 (dd, J_{12}=1.8 Hz, J_{23}=3.1 Hz, 1H, H-2^I), 5.49 (s, 1H, H-1^{III}), 5.48 (s, 1H, H-1^{II}), 5.46 (d, J_{23}=1.8 Hz, 1H, H-2^{III}), 5.43 (d, J_{23}=1.3 Hz, 1H, H-2^{II}), 5.22 (m, 1H, H-5^{III}), 4.93 (d, J_{12}=1.8 Hz, 1H, H-1^I), 4.90 (d, J_{ab}=11.2 Hz, 1H, 4-*O*-PhC*H*$_2^I$), 4.74 (d, J_{ab}=11.5 Hz, 1H, PhC*H*$_2$), 4.65 (d, J_{ab}=12.0 Hz, 1H, PhC*H*$_2$), 4.64 (d, J_{ab}=12.0 Hz, 1H, PhC*H*$_2$), 4.53 (d, J_{ab}=12.0 Hz, 1H, PhC*H*$_2$), 4.49-4.42 (m, 3H, PhC*H*$_2$), 4.36 (dd, J_{23}=3.1 Hz, J_{34}=9.5 Hz, 1H, H-3^I), 4.34-4.30 (m, 3H, PhC*H*$_2$), 4.29-4.26 (m, 2H, H-4^{III}, H-4^{II}), 4.22 (d, J_{ab}=12.1 Hz, 1H, PhC*H*$_2$), 4.31 (br. d, J_{34}=5.9 Hz, 1H, H-3^{II}), 4.07 (m, 1H, H-5^{II}), 3.94 (t, J_{34}=J_{45}=9.5 Hz, 1H, H-4^I), 3.82 (d, J_{ab}=14.6 Hz, 1H, C(O)C*H*$_2$Cl), 3.81 (m, 1H, H-3^{III}), 3.78 (d, J_{ab}=14.6 Hz, 1H, C(O)C*H*$_2$Cl), 3.75 (m, 1H, OC*H*$_2$CH$_2$CH$_2$), 3.73 (m, 2H, H-6a^I, H-6b^I), 3.61 (dd, $^2J_{6a6b}$=10.2, J_{56a}=8.0, 1H, H-6a^{II}), 3.52 (m, 1H, OC*H*$_2$CH$_2$CH$_2$), 3.45 (dd, $^2J_{6a6b}$=10.2, J_{56b}=3.6, 1H, H-6b^{II}), 3.44-3.33 (m, 4H, $OCH_2CH_2CH_2N$, H-6a^{III}, H-6b^{III}, $OCH_2CH_2CH_2N$), 1.85 (m, 2H, $OCH_2CH_2CH_2N$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.9 (*C*(O)CH$_2$Cl), 165.7-165.1 (Ph*C*O), 138.3-137.2 (quat. Ph), 133.4-127.3 (Ph), 106.3 (C-1^{III}), 102.7 (C-1^{II}), 98.0 (C-1^I), 84.3 (C-3^{II}), 82.9 (C-3^{III}), 82.8 (C-4^{II}), 81.8 (C-2^{II}), 81.6 (C-2^{III}), 80.9 (C-4^{III}), 75.0 (4-*O*-Ph*C*H$_2^I$), 74.9 (C-5^{II}), 73.5, 73.5 (2Ph*C*H$_2$), 73.3 (Ph*C*H$_2$), 73.1 (C-4^I), 72.8 (Ph*C*H$_2$), 72.6 (C-5^{III}), 72.3 (Ph*C*H$_2$), 72.1 (C-5^I), 71.5 (C-6^{II}), 69.1 (C-6^I), 68.8 (C-6^{III}), 68.1 (C-2^I), 65.6 (O*C*H$_2$CH$_2$CH$_2$N), 40.6 (C(O)*C*H$_2$Cl), 37.5 ($OCH_2CH_2CH_2N$), 28.4 ($OCH_2CH_2CH_2N$). HRMS(ESI): Calcd *m/z* for $[M+Na]^+$ $C_{88}H_{87}ClF_3NO_{21}$ 1608.5303, found 1608.5304. Calcd *m/z* for $[M+K]^+$ $C_{88}H_{87}ClF_3NO_{21}$ 1624.5043, found 1624.5027.

3-trifluoroacetamidopropyl 2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-α-D-mannopyranoside (29). Trisaccharide **28** (8 mg, 0.005 mmol) was treated according to **GP I** by thiourea (10 mg, 0.14 mmol) and collidine (2.5 μL, 0.017 mmol) in MeOH (1.2 mL). Column chromatography (toluene—EtOAc 7:1) gave **29** (6 mg, 80%) as a colorless oil. R_f=0.47 (toluene-ethyl acetate 5:1). $[\alpha]_D$=-40° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04-7.95, 7.59-7.10 (m, 45H, PhH), 5.54 (dd, J_{12}=1.9 Hz, J_{23}=3.1 Hz, 1H, H-2^I), 5.52 (s, 1H, H-1^{III}), 5.50 (s, 1H, H-1^{II}), 5.48 (d, J_{23}=1.8 Hz, 1H, H-2^{III}), 5.36 (d, J_{23}=1.4 Hz, 1H, H-2^{II}), 4.93 (d, J_{12}=1.9 Hz, 1H, H-1^I), 4.90 (d, J_{ab}=11.2 Hz, 1H, 4-*O*-PhC*H*$_2^I$), 4.74 (d, J_{ab}=11.5 Hz, 1H, PhC*H*$_2$), 4.65 (d, J_{ab}=12.0 Hz, 1H, PhC*H*$_2$), 4.63 (d, J_{ab}=12.0 Hz, 1H, PhC*H*$_2$), 4.53 (d, J_{ab}=12.0 Hz, 1H, PhC*H*$_2$), 4.50-4.44 (m, 3H, PhC*H*$_2$), 4.38 (dd, J_{23}=3.1 Hz, J_{34}=9.5 Hz, 1H, H-3^I), 4.34 (m, 2H, PhC*H*$_2$), 4.32-4.29 (m, 2H, H-4^{II}, PhC*H*$_2$), 4.27 (d, J_{ab}=12.0 Hz, 1H, PhC*H*$_2$), 4.22 (br. d, J_{34}=5.9 Hz, 1H, H-3^{II}), 4.13-4.09 (m, 2H, H-4^{III}, H-5^{II}), 4.04 (dd, J_{32}=1.8 Hz, J_{34}=6.1 Hz, 1H, H-3^{III}), 3.94 (t, J_{34}=J_{45}=9.5 Hz, 1H, H-4^I), 3.83 (m, 1H, H-5^I), 3.79-3.74 (m, 3H, OC*H*$_2$CH$_2$CH$_2$, H-6a^I, H-6b^I), 3.74-3.69 (m, 2H, H-5^{III}, H-6a^{III}), 3.67 (dd, $^2J_{6a6b}$=10.3, J_{56a}=7.9, 1H, H-6a^{II}), 3.52 (m, 1H, OC*H*$_2$CH$_2$CH$_2$), 3.49 (dd, $^2J_{6a6b}$=10.3, J_{56b}=3.6, 1H, H-6b^{II}), 3.44 (m, 1H, $OCH_2CH_2CH_2N$), 3.36 (m, 1H, $OCH_2CH_2CH_2N$), 3.29 (dd, $^2J_{6a6b}$=9.8, J_{56b}=7.8, 1H, H-6a^{III}), 3.26 (dd, $^2J_{6a6b}$=9.8, J_{56b}=4.1, 1H, H-6b^{III}), 2.25 (br. s, 1H, OH), 1.85 (m, 2H, $OCH_2CH_2CH_2N$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.7-165.2 (Ph*C*O), 138.3-137.2 (quat. Ph), 133.3-127.3 (Ph), 106.6 (C-1^{III}), 102.7 (C-1^{II}), 98.0 (C-1^I), 84.3 (C-3^{II}), 83.2 (C-3^{III}), 82.9 (C-4^{II}), 82.8(C-4^{III}), 81.9 (2C, C-2^{II}, C-2^{III}), 75.1 (4-*O*-Ph*C*H$_2^I$), 74.6 (C-5^{II}), 73.5, 73.5 (C-3^I, Ph*C*H$_2$), 73.3 (Ph*C*H$_2$), 73.2 (C-4^I), 72.6 (Ph*C*H$_2$), 72.1 (Ph*C*H$_2$), 72.1 (C-5^I), 71.6, 71.6 (C-6^{II}, C-6^{III}), 70.0 (C-5^I), 69.2 (C-6^I), 68.1 (C-2^I), 65.5 (O*C*H$_2$CH$_2$CH$_2$N), 37.5 ($OCH_2CH_2CH_2N$), 28.3 ($OCH_2CH_2CH_2N$). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{86}H_{86}F_3NO_{20}$ 1527.6034, found 1527.6025. Calcd *m/z* for $[M+Na]^+$ $C_{86}H_{86}F_3NO_{20}$ 1532.5587, found 1532.5586. Calcd *m/z* for $[M+K]^+$ $C_{86}H_{86}F_3NO_{20}$ 1548.5327, found 1548.5319.

3-trifluoroacetamidopropyl 2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-

galactofuranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-α-D-mannopyranoside (30). Carefully dried mixture of **29** (6 mg, 0.004 mmol) and 6 (7 mg, 0.006 mmol) was dissolved in CH_2Cl_2 (0.5 mL), powder Ms300 AW (10 mg) was added, and the mixture was stirred for 20 min. Then temperature was decreased to –78 °C and **a** solution of TMSOTf (0.3 μL, 0.002 mmol) in 0.1 mL CH_2Cl_2 was added. The reaction mixture was kept at –20…–30 °C for 1 h and then at –15 °C was stopped by 1 drop of Et_3N. Column chromatography (toluene—EtOAc 8:1) gave **30** (8 mg, 80%) as a colorless oil. R_f=0.48 (toluene-ethyl acetate 5:1). $[\alpha]_D$=-38° (c = 1, EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03-7.84, 7.56-7.03 (m, 80H, PhH), 6.60 (br. s, 1H, CH_2NH), 5.78 (m, 1H, H-5^V), 5.60 (s, 1H, H-1^{IV}), 5.59 (dd, J_{32}=1.6 Hz, J_{34}=5.1 Hz, 1H, H-3^V), 5.57 (s, 1H, H-1^V), 5.56 (d, J_{23}=1.6 Hz, 1H, H-2^V), 5.55 (m, 1H, H-2^I), 5.54 (s, 1H, H-1^{III}), 5.52 (d, J_{23}=2.3 Hz, 1H, H-2^{III}), 5.50 (d, J_{23}=1.5 Hz, 1H, H-2^{IV}), 5.49 (s, 1H, H-1^{II}), 5.36 (d, J_{23}=1.5 Hz, 1H, H-2^{II}), 4.93 (d, J_{12}=1.9 Hz, 1H, H-1^I), 4.89 (d, J_{ab}=11.2 Hz, 1H, 4-*O*-PhCH_2^I), 4.71 (d, J_{ab}=11.4 Hz, 1H, PhCH_2), 4.66 (d, J_{ab}=11.2 Hz, 1H, PhCH_2), 4.63 (d, J_{ab}=11.9 Hz, 1H, PhCH_2), 4.52 (d, J_{ab}=12.0 Hz, 1H, PhCH_2), 4.51-4.43 (m, 6H, 3PhCH_2, H-6a^V, H-4^V, H-6b^V), 4.38 (dd, J_{32}=3.2 Hz, J_{34}=9.5 Hz, 1H, H-3^I), 4.34-4.31 (m, 3H, 2PhCH_2, H-4^{II}), 4.30 (dd, J_{32}=2.3 Hz, J_{34}=3.4 Hz, 1H, H-3^{III}), 4.24-4.22 (m, 2H, H-3^{II}, PhCH_2), 4.21-4.16 (m, 6H, H-4^{III}, 3PhCH_2, H-3^{IV}, H-4^{IV}), 4.11 (m, 1H, H-5^{II}), 4.02 (m, 1H, H-5^{III}), 3.98 (m, 1H, H-5^{IV}), 3.94 (t, J_{34}=J_{45}=9.5 Hz, 1H, H-4^I), 3.82 (m, 1H, H-5^I), 3.78-3.73 (m, 3H, OCH_2CH$_2$CH$_2$, H-6a^I, H-6b^I), 3.68-3.65 (m, 2H, H-6a^{II}, H-6a^{III}), 3.61 (m, 1H, H-6a^{IV}), 3.52 (m, 1H, OCH_2CH$_2$CH$_2$), 3.50 (dd, $^2J_{6a6b}$=11.0, J_{56b}=4.7, 1H, H-6b^{II}), 3.46-3.33 (m, 4H, OCH$_2$CH$_2$CH_2N, H-6b^{IV}, H-6b^{III}, OCH$_2$CH$_2$CH_2N), 1.85 (m, 2H, OCH$_2$CH_2CH$_2$N). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9-165.1 (Ph*C*O), 138.2-137.7 (quat. Ph), 133.4-127.2 (Ph), 106.4 (C-1^{III}), 106.3, 106.3 (C-1^{III}, C-1^{IV}), 102.9 (C-1^{II}), 98.0 (C-1^I), 84.3 (C-3^{II}), 83.8 (C-3^{III}), 83.5 (C-3^{IV}), 83.0 (C-4^{II}), 82.7 (C-4^{III}), 82.4 (C-4^{IV}), 82.2, 82.1 (C-2^{III}, C-2^{IV}), 81.8 (C-2^{II}), 81.8 (C-4^V), 81.6 (C-2^V), 77.2 (C-3^V), 75.0 (2C, 4-*O*-Ph*C*H$_2^I$, C-5^{IV}), 74.3 (C-5^{II}), 73.6 (C-3^I), 73.5 (C-5^{III}), 73.4 (Ph*C*H$_2$), 73.2 (Ph*C*H$_2$), 73.2 (C-4^I), 73.1 (Ph*C*H$_2$), 72.7 (Ph*C*H$_2$), 72.5 (Ph*C*H$_2$), 72.2 (Ph*C*H$_2$), 72.1 (C-5^I), 72.1 (C-6^{III}), 71.8 (C-6^{IV}), 71.2 (C-6^{II}), 70.4 (C-5^V), 69.2 (C-6^I), 68.2 (C-2^I), 65.5 (O*C*H$_2$CH$_2$CH$_2$N), 63.7 (C-6^{III}), 37.5 (OCH$_2$CH$_2$*C*H$_2$N), 28.3 (OCH$_2$*C*H$_2$CH$_2$N). HRMS(ESI): Calcd *m/z* for $[M+NH_4]^+$ $C_{147}H_{138}F_3NO_{35}$ 2551.9340, found 2551.9316. Calcd *m/z* for $[M+Na]^+$ $C_{147}H_{138}F_3NO_{35}$ 2556.8894, found 2556.8887. Calcd *m/z* for $[M+K]^+$ $C_{147}H_{138}F_3NO_{35}$ 2572.8633, found 2572.8616.

3-aminopropyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside (2). Compound **30** (8 mg, 3.1 μmol) was dissolved in 1 mL of EtOAc-MeOH **(**1:1**)** and 10% Pd/C (11 mg) was added. The Reaction mixture was vigorously stirred in H_2atmosphere for 3 h and then filtred through the *celite* layer. The Filtrate was concentrated *in vacuo*, dissolved in 0.5 mL of 0.1 M MeONa in MeOH, one drop of water was added, and the mixture was kept overnight, then 3 μL of AcOH were added, the mixture was diluted with water and concentrated *in vacuo*. Gel-chromatography and subsequent lyophilization gave **2** (2.0 mg, 72%) as a white foam. ^{1}H NMR (500 MHz, D_2O): δ 5.23 (br. s, 1H, H-1^V), 5.20 (m, 2H, H-1^{III}, H-1^{IV}), 5.13 (br. s, 1H, H-1^{II}), 4.92 (br. s, 1H, H-1^I), 4.20-4.10 (m, 11H, H-4^{II}, H-4^{III}, H-4^{IV}, H-2^{II}, H-2^{III}, H-2^{IV}, H-2^V, H-3^{II}, H-3^{III}, H-3^{IV}, H-3^V), 4.10-4.07 (m, 2H, H-3^V, H-4^V), 4.00-3.91 (m, 4H, H-5^{II}, H-5^{III}, H-5^{IV}, H-6a), 3.91-3.60 (m, 17H), 3.19-3.12 (m, 2H, OCH$_2$CH$_2$CH_2N), 2.06-1.98 (m, 2H, OCH$_2$CH_2CH$_2$N). ^{13}C NMR (125 MHz, D_2O): δ 108.3 (3C, C-1^{III}, C-1^{IV}, C-1^V), 105.7 (C-1^{II}), 100.8 (C-1^I), 83.9 (C-4^V), 83.3 (C-4^{II}), 82.8, 82.7, 82.6, 82.5 (C-4^{III}, C-4^{IV}, C-2^{II}, C-2^{III}, C-2^{IV}, C-2^V), 78.2 (C-3^{II}), 77.7, 77.7, 77.6 (C-3^{III}, C-3^{IV}, C-3^V), 77.2 (C-5^{II}), 76.9, 76.9, 76.8 (C-5^{III}, C-5^{IV}, C-3^I), 74.0 (5-3^I), 71.8 (C-5^V), 67.9 (C-2^I), 66.3 (C-4^I), 66.2 (OCH$_2$), 64.0 (C-6^V), 62.4-62.2 (C-6^I, C-6^{II}, C-6^{III}, C-6^{IV}), 38.7 (OCH$_2$CH$_2$*C*H$_2$N), 27.9 (OCH$_2$*C*H$_2$CH$_2$N). HRMS(ESI): Calcd *m/z* for $[M+H]^+$ $C_{33}H_{59}NO_{26}$ 886.3398, found 886.3402. Calcd *m/z* for $[M+Na]^+$ $C_{33}H_{59}NO_{26}$ 908.3218, found 908.3218.

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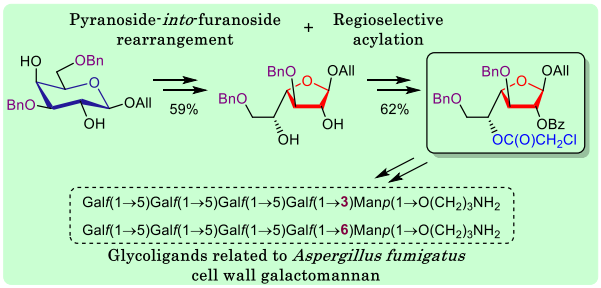
Graphical Abstract



The synthesis of heterosaccharide fragments of fungal galactomannan employing pyranoside-*into*-furanoside rearrangement.