Chemical synthesis of fragments of galactosaminogalactan and pel polysaccharides

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Chapter 4

Synthesis of an azido-GAG heptasaccharide featuring α-GalN_3 and α-GalNAc linkages

Introduction

Aspergillus fumigatus is a saprophytic mold that causes invasive and chronic infections in immunocompromised patients with high mortality rates.[1-5] Galactosaminogalactan (GAG), an extracellular polysaccharide produced by *A. fumigatus*, is a key virulence factor and plays an essential role in biofilm formation. This exopolysaccharide, which is composed of 1,4-linked α-Gal, α-GalN and α-GalNAc residues that are distributed in a seemingly random manner, is a potential lead compound in the development of anti-inflammatory therapies. Chapter 2 and 3 described the synthesis of a library of GAG oligomers, comprising both homo- and hetero-oligomers. Some of the synthetic GAG oligomers have been applied to

probe enzymes involved in the GAG biosynthetic pathway, resulting in better structural and mechanistic understanding of the hydrolases Sph3 and Ega3 as well as the involvement of the deacetylase Agd3.[6-8] Sph3 is a retaining endoglycoside hydrolase, which belongs to glycoside hydrolase family 135 (GH 135)[9]. Retaining glycoside hydrolases can also perform transglycosylation reactions and have been used in the laboratory to produce polysaccharides as an substitution of glycosyltransferases (GT).[10-14] They generally operate through a "Koshland" double displacement mechanism (Figure 1).[15] First a covalent glycosyl enzyme intermediate is formed by attack of the active site nucleophilic carboxylate promoted by the protonation of the leaving group by an acid residue on the opposite side of the substrate. In the second displacement, the intermediate is hydrolyzed or attacked by a nucleophilic acceptor, such as an alcohol, with the assistance of the deprotonated carboxylate, giving the hydrolyzed or glycosylated product.

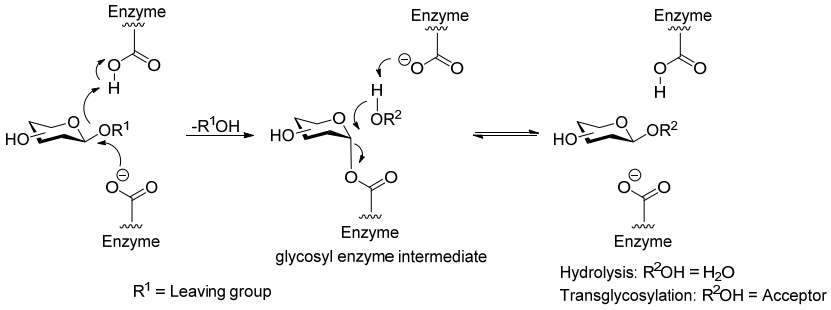

Figure 1. Hydrolysis and transglycosylation reactions of the retaining GH enzymes

Metabolic glycan labeling has recently been introduced as a powerful method that enables the visualization of glycans as they function in their native setting.[16-17] It has been applied for imaging cell-surface glycans in living organisms, such as plants, zebrafish and mice.[16, 18-29] This labeling approach comprises two steps, in which the first step is to metabolically incorporate an unnatural and modified monosaccharide into the organism's glycome. The modified monomer contains a reactive group, which functions as a "chemical reporter". Subsequently, the chemical reporter can be labeled and visualized with an imaging probe *via* a bioorthogonal reaction.

Though a handful of reactions possess the quality of bioorthogonality, the azide group is often chosen as chemical reporter. This functional group is small enough not to interfere with normal uptake and often has relatively little influence on the recognition by (biosynthetic) enzymes. What's more, azides are capable of undergoing chemoselective reactions, such as the copper-catalyzed 1,3-cycloaddition, the Staudinger ligation with phosphines and Cu-free

click chemistry with strained alkynes. To probe potential transglycosylase activity of Sph3, this Chapter describes the conception of an azido-GAG oligosaccharide, that can be used to introduce azido groups in the GAG exopolysaccharide, which can then be visualized with a fluorogenic click reagent. On the basis of the finding that the minimal GAG length of the substrates for the hydrolase Sph3 are seven monomers in length the azide-containing heptasaccharide **1** was designed (Figure 2). Because of the similar size of the azide, in comparison to the native acetamide, it is expected that this modification in the oligosaccharide probe is well tolerated by the hydrolase.

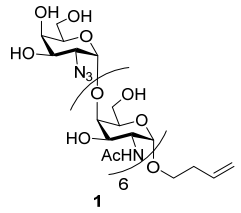

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Figure 2. Structure of azido-GAG **1**.

Results and discussion

The retrosynthesis, depicted in Figure 3 shows that the target heptasaccharide **1** can be obtained from the protected heptamer **2** by a final three-steps deprotection sequence, including the desilylation of DTBS group and saponification of benzoyl esters and trifluoroacetamides, followed by *N*-acetylation. The trichloroacetyl (TCA) group, used in the synthesis of GAG hetero-oligomers as described in Chapter 3, is replaced in the current synthetic route by the more base-labile TFA-group. Kiso's di-*tert*-butylsilyene (DTBS)-directed α-selective galactosylation methodology, which has been successfully used for the synthesis of GAG homo- and heteropolymers, described in Chapter 2 and 3, is applied again to ensure the stereoselective construction of the α-galactosamine linkages.[30-35] These considerations, together with the moderate glycosylating properties of the selenophenyl $GalN_3$ donor (See Chapter 2) led to the design of the imidate donors **3** and **4** to assemble the heptamer **2**. The elongation procedure toward the heptamer consists of repetition of the following three-steps: 1) glycosylation; 2) DTBS-removal and 3) selective benzoylation of the primary alcohol group with benzoyl-hydroxybenzotriazole (BzOBt) as a mild, regioselective acylating agent.[36] The $GalN_3$ donor **3** will serve as precursor of $GalN_3$ and the GalNHTFA donor **4** will serve as precursor of the GalNAc residues.

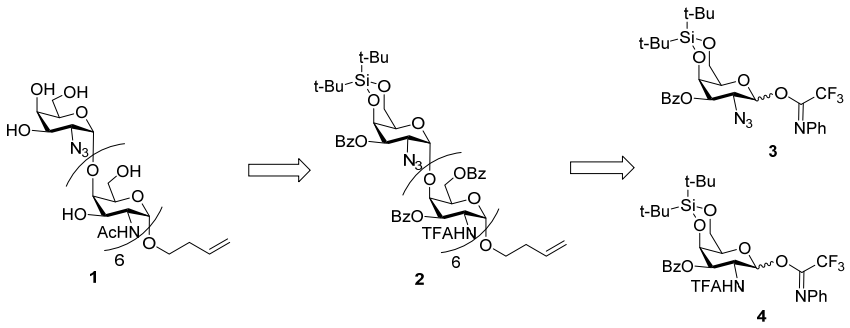
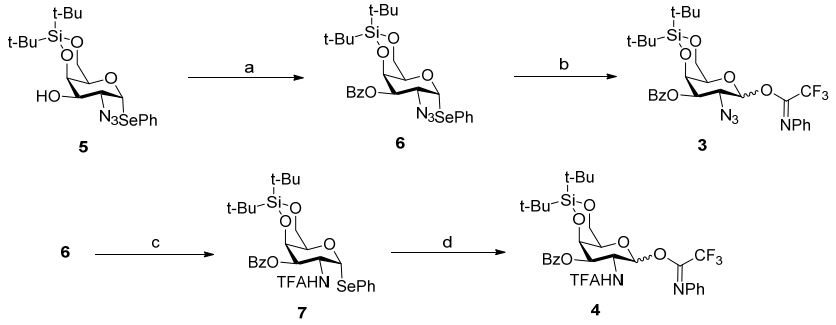


Figure 3. Retrosynthetic analysis towards target azido-GAG **1**

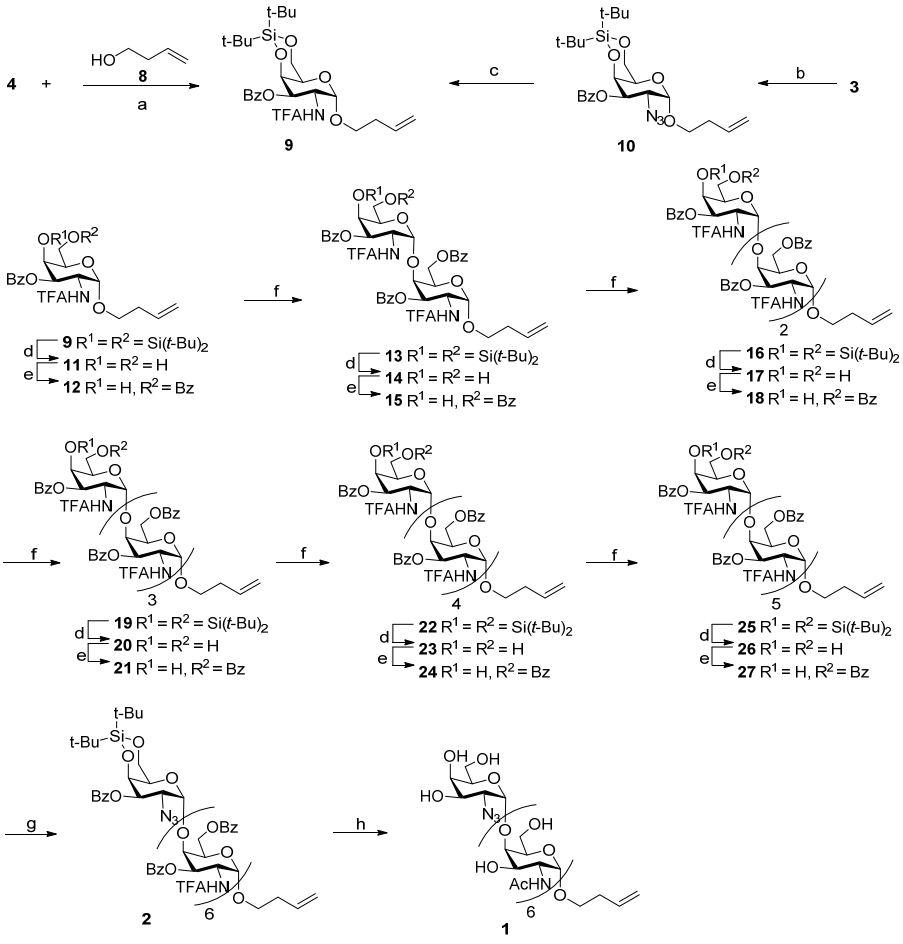
The preparation of the $GalN_3$ and GalNHTFA donors is described in Scheme 1. First $GalN_3$ donor **3** was obtained from known $GalN_3$ **5** through benzoylation, hydrolysis of the selenophenyl acetal and reaction of the anomeric hydroxyl with *N*-phenyltrifluoroacetamidoyl chloride, affording donor **3** in 72% yield over these three steps. To generate the GalNHTFA donor **4**, the azido group in compound **6** was first reduced with $HS(CH_2)_3SH$, followed by trifluoroacetylation of the formed amino group to give the selenophenyl glycoside **7** in 86% yield, which was transformed to trifluoroacetimidate donor **4** in 79% yield through the same procedure as described for the conversion of **6** into **3.**



Scheme 1. Preparation of donors **3** and **4**. a) BzCl, pyridine, DMAP, DCM, 0 °C to rt, 95%. b) i) NIS, Acetone/H_2O (10/1), 0 °C; ii) $CF_3C(=NPh)Cl$, Cs_2CO_3, acetone, 76%. c) i) $HS(CH_2)_3SH$, Et_3N, pyridine/H_2O; ii) TFA_2O, pyridine, 86%. d) i) NIS, Acetone/H_2O (10/1), 91%; ii) $CF_3C(=NPh)Cl$, K_2CO_3, acetone, 87%.

With $GalN_3$ and GalNHTFA donors in hand, elongation of the N_3-GAG chain was performed, as outlined in Scheme 2. Owing to the neighboring group participation effect and high nucleophilicity of the homoallylic alcohol, coupling of GalNHTFA donor **4** with the acceptor **8** at -40 °C afforded the α/β-glycosylation mixture **9** in 91% yield with the ratio

3.2/1. To avoid the formation of β-product, 3-buten-1-ol **8** was treated with $GalN_3$ donor **3**, affording compound **10** in 85% yield and with complete α-selectivity. The azido group in **10** could be reduced with Staudinger reaction, after which the generated amino group was protected with TFA group to give compound **9** in 83% yield. Removal of the silylidene ketal in the α-linked product was performed in HF/pyridine solution and then the liberated C6-hydroxyl group was benzoylated selectively with BzOBt to afford the C4-OH acceptor **12**. Condensation of the formed monomer **12** with GalNHTFA donor **4** provided the dimer **13** in 86% yield with exclusive α-selectivity, overcoming the neighboring group participation effect of C2-NHTFA group. The DTBS-protected dimer was transformed to the C4-OH acceptor **15** by desilylation and selective benzoylation reactions in 72% yield. Elongation of this dimer with another copy of the GalNHTFA donor **4** delivered trisaccharide **16** in good yield. Repetition of the three-step elongation procedure for another three times led to the hexasaccharide **25**. All glycosylation reactions resulted in excellent α-selectivity, and the desilylation and regioselective benzoylation reactions proceeded in excellent yields (84%-96% and 80%-97%, respectively). However, it needs to be noted that the glycosylation yields for the pentamer **22** and hexamer **25** decreased to 68% (for the pentamer) and 18% (for the hexamer), as the reactivity of the acceptors diminishes with growing chain length. The yield of hexamer **25** could be increased to 54% by increasing the concentration of the condensation from 0.05 M to 0.2 M. In the last coupling protected heptamer **2** was isolated in 84% yield by treatment of the hexamer acceptor **27** with $GalN_3$ donor **3**. Finally, the protecting groups in heptamer **2** were removed through desilylation, saponification and chemo-selective acetylation reactions, furnishing the target compound **1** in 60% yield.



Scheme 2. Synthesis of azido-GAG **1**. a) TfOH, DCM, 3Å MS, -40 °C, 91% (α/β = 3.2/1). b) **8**, TfOH, DCM, 3Å MS, 0 °C, 86%; c) i) PPh_3, H_2O, pyridine, THF ii) TFA_2O, pyridine, 83%. d) HF/pyridine, THF, yields for **11**: 89%; for **14**: 90%; for **17**: 90%; for **20**: 88%; for **23**: 96%; for **26**: 84%. e) BzOBt, Et_3N, DCM, yields for **12**: 97%; for **15**: 80%; for **18**: 96%; for **21**: 94%; for **24**: 84%; for **27**: 91%. f) **4**, TfOH, DCM, 3Å MS, 0 °C, yields for **13**: 86%; for **16**: 75%; for **19**: 84%; for **22**: 68%; for **25**: 18% (0.05M), 54% (0.2 M). g) **3**, TfOH, DCM, 3Å MS, 0 °C, 84%. h) i) HF/pyridine, THF; ii) 1M NaOH, THF/MeOH; iii) Ac_2O, $NaHCO_3$, H_2O, 60%.

Conclusion

In conclusion, an azido-GAG heptamer with a C2-N_3 group at the non-reducing end was successfully assembled based on the previously developed synthesis approach. The glycosylation results show that in DTBS-protected $GalN_3$ and GalNHTFA donors the ability of neighboring group participation can be overruled to afford excellent α-stereoselectivity. Although the use of the benzoyl group to mask the C3-OH in the glycosyl building blocks facilitated the deprotection of the target heptamer in the final stage of the synthesis, the reactivities of corresponding donors and acceptors are reduced at the same time. Since the reactivity of acceptors decreases with growing chain length, lower yields were obtained for the glycosylation reactions toward the penta- and hexamer. Increasing the concentration of the reaction significantly improved the yields of the couplings. The developed synthetic methodology will be applicable for the assembly of other azido-GAGs. The synthesized azido-GAG will be used to probe transglycosylation activity of the Sph3 *N*-acetyl galactosaminidase in the biosynthetis of GAG-polysaccharides at the cellular level.

Experimental section

General procedure for glycosylation with imidate donors 3 and 4 (procedure A)

The donor (1.5 – 3.0 eq) and acceptor (1.0 eq) were co-evaporated with toluene (three times). The residue was dissolved in dry DCM (0.1 M acceptor in DCM) under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (0.1 – 0.3 eq) was added. The reaction was stirred at 0 ºC until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The products were purified by silica gel column chromatography (See experimental description below for eluent system).

General procedure for the deprotection of di-*tert*-butyl silylidene group (general procedure B)

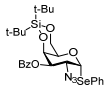
HF/pyridine (16 eq) solution was added to a solution of starting material in THF at 0 ºC. The reaction was warmed to room temperature and stirred until TLC-analysis indicated full consumption of the starting material (± 1h). Then the mixture was diluted with DCM and washed with saturated $NaHCO_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (See experimental description below for eluent system).

General procedure for selective benzoylation of primary alcohol (general procedure C)

PhCOOBt (4.5 eq) and Et_3N (5.0 eq) were added to the solution of starting material in DCM (0.05 M). The reaction was allowed to stirred overnight at room temperature. Then the mixture was diluted with DCM and washed with saturated $NaHCO_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (See experimental description below for eluent system).

Experimental Procedures and Characterization Data of Products

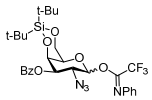
Phenyl 2-azido-3-*O*-benzoyl-2-deoxy-1-seleno-4,6-di-*tert*-butylsilylidene-α-D-galactopyranoside (6)



To the solution of **5**[1] (1.0 g, 2.06 mmol) in 10 mL DCM and 1.7 mL pyridine (20.6 mmol) was added BzCl (360 ul, 3.1 mmol, 1.5 mmol) and DMAP (25 mg, 0.21 mmol), which was allowed to stir at rt for overnight. The reaction mixture was washed with water, sat. $NaHCO_3$ solution and brine subsequently, and dried with $MgSO_4$. The product was purified by silica gel column chromatography (pentane:Et_2OAc = 50:1 – 20:1). Compound **6** (1.1 g, 95% yield) was obtained as colorless syrup. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.13 – 8.06 (m, 2H, *C*H, Bz), 7.64 – 7.56 (m, 3H, *aromatic*), 7.51 – 7.44 (m, 2H, *aromatic*), 7.33 – 7.25 (m, 3H, *aromatic*), 6.05 (d, *J* = 5.2 Hz, 1H, H-1), 5.15 (dd, *J* = 10.6, 3.0 Hz, 1H, H-3), 4.90 (dd, *J* = 3.1, 1.0 Hz, 1H, H-4), 4.58 (dd, *J* = 10.6, 5.2 Hz, 1H, H-2), 4.33 – 4.23 (m, 2H, H-5, 6), 4.03 (dd, *J* = 12.6, 1.5 Hz, 1H, H-6), 1.05 (s, 9H, *C*H_3), 0.94 (s, 9H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.92 (C=O, Bz), 134.70, 133.54, 129.84, 129.57, 129.30, 128.63, 128.31, 128.08 (*aromatic* C/*CH*), 85.39 (C-1), 74.60 (C-3), 69.87 (C-4), 69.79 (C-5), 66.90 (C-6),

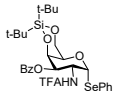
59.00 (C-2), 27.58 (CH_3), 27.34 (CH_3), 23.28 (C-*Si*), 20.80 (C-*Si*). HR-MS: Calculated for $C_{27}H_{35}N_3O_5SeSi$ [M+H]$^+$: 612.1409, found: 612.1403.

2-Azido-3-*O*-benzoyl-2-deoxy-4,6-di-*tert*-butylsilylidene-1-*O*-(*N*-phenyl-trifluoroacetimidoyl)-α/β-D-galactopyranoside (3)



NIS (1.65 g, 8.65 mmol) was added to the solution of compound **6** (3.3 g, 5.76 mmol) in Acetone/H_2O (40 ml/4 ml) at 0 ºC. The reaction was slowly warmed to room temperature stirred for about 2 hours. Then the mixture was diluted with DCM and washed with saturated $Na_2S_2O_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (pentane:EtOAc = 4:1) to get the hemiacetyl. K_2CO_3 (919 mg, 6.65 mmol) was added to the solution of hemiacetal in 25 ml acetone. The mixture was stirred at 0 ºC for 15 minutes. Then $CF_3C(=NPh)Cl$ (1.49 g, 7.20 mmol) was added to the solution, which was slowly warmed to room temperature and stirred overnight. The reaction was quenched with Et_3N and concentrated *in vacuo*. The product **3** was purified by silica gel column chromatography (pentane:Et_2O = 10:1). Compound **3** (1.10 g, 76% yield) was obtained as white solid. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07 – 7.97 (m, 2H, *C*H, Bz), 7.63 – 7.52 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.18 – 7.09 (m, 1H), 6.98 (d, *J* = 8.5 Hz, 1H, *N*H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.58 (bs, 1H, H-1), 5.47 – 5.32 (m, 1H, H-3), 5.15 – 4.97 (m, 1H, H-2), 4.82 (d, *J* = 4.1 Hz, 1H, H-4), 4.39 – 4.16 (m, 2H, H-6), 3.94 (bs, 1H, H-5), 1.10 (s, 9H, *C*H_3), 1.02 (s, 9H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.39 (C=O, Bz), 157.72 (*a*d, *J* = 37 Hz, *CF_3CO*), 142.96, 133.99, 129.95, 128.99, 128.86, 128.75, 124.90, 119.90, 115.61 (*a*d, *J* = 286 Hz, C*F_3*), 94.68 (C-1), 70.71 (C-3), 70.13 (C-4), 69.92 (C-5), 66.62 (C-6), 48.14 (C-2), 27.61 (CH_3), 27.25 (CH_3), 23.41 (C-*Si*), 20.87 (C-*Si*). HR-MS: Calculated for $C_{29}H_{35}N_4O_6F_3Si$ [M+Na]$^+$: 643.2176, found: 643.2170.

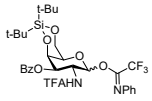
Phenyl 3-*O*-benzoyl-2-deoxy-1-seleno-4,6-di-*tert*-butylsilylidene-2-trifluoroacetamido-α-D-galactopyranoside (7)



1,3-Dithiolpropane (3.0 ml, 29.6 mmol) and trimethylamine (3.4 ml, 24.7 mmol) were added to the solution of compound **6** (2.83 g, 4.94 mmol)in pyridine/water (20 ml/5 ml). The mixture was protected from light and stirred at room temperature overnight. The fluent was evaporated and co-evaporated with toluene. The residue was dissolved in 25 ml pyridine, after which TFA_2O (1.0 ml, 7.41 mmol) was added at 0 ºC. The reaction was slowly warmed to room temperature and stirred overnight. The reaction was quenched with Methanol and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 30:1 – 20:1). Compound **7** (2.90 g, 89% yield) was obtained as white solid. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.25 – 8.11 (m, 2H, *C*H, Bz), 7.66 – 7.63 (m, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.31 – 7.23 (m, 1H), 7.21 – 7.14 (m, 1H), 6.93 (d, *J* = 7.7 Hz, 2H), 6.71 (bs, 1H, H-1), 5.49 (dd, *J* = 10.7, 2.8 Hz, 1H, H-3), 5.08 – 4.93 (m, 1H, H-4), 4.51 – 4.23 (m, 3H, H-2, 6), 4.02 (s, 1H, H-5), 1.13 (s, 9H, *C*H_3), 1.03 (s, 9H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.10 (C=O, Bz), 143.25, 135.35, 133.66, 129.85, 129.41, 129.32, 128.88, 128.72, 128.65, 126.34, 124.60, 120.75, 119.39, 94.41 (C-1), 72.06 (C-3), 69.90 (C-4),

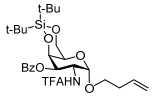
69.65 (C-5), 66.60 (C-6), 57.11 (C-2), 27.51 (CH_3), 27.23 (CH_3), 23.24 (C-*Si*), 20.77 (C-*Si*). HR-MS: Calculated for $C_{29}H_{36}NO_6SeSi$ $[M+H]^+$: 682.1327, found: 682.1322.

2-Trifluoroacetamido-3-*O*-benzoyl-2-deoxy-4,6-di-*tert*-butylsilylidene-1-*O*-(*N*-phenyl-trifluoroacetimidoyl)-α/β-D-galactopyran-oside (4)



NIS (410 mg, 1.82 mmol) was added to the solution of compound **7** (800 g, 1.21 mmol) in Acetone/H_2O (10 ml/1 ml) at 0 ºC. The reaction was slowly warmed to room temperature stirred for about 2 hours. Then the mixture was diluted with DCM and washed with saturated $Na_2S_2O_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (pentane:EtOAc = 4:1) to get the hemiacetal. K_2CO_3 (183 mg, 1.32 mmol) was added to the solution of hemiacetal in 11 ml acetone. The mixture was stirred at 0 ºC for 15 minutes. Then $CF_3C(=NPh)Cl$ (343 mg, 1.65 mmol) was added to the solution, which was slowly warmed to room temperature and stirred overnight. The reaction was quenched with Et_3N and concentrated *in vacuo*. The product **4** was purified by silica gel column chromatography (pentane:Et_2O = 50:1-20:1). Compound **4** (580 mg, α:β > 10:1, 81% yield) was obtained as syrup. α-Isomer: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07 – 7.97 (m, 2H, *C*H, Bz), 7.63 – 7.52 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.18 – 7.09 (m, 1H), 6.98 (d, *J* = 8.5 Hz, 1H, *N*H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.58 (bs, 1H, H-1), 5.47 – 5.32 (m, 1H, H-3), 5.15 – 4.97 (m, 1H, H-2), 4.82 (d, *J* = 4.1 Hz, 1H, H-4), 4.39 – 4.16 (m, 2H, H-6), 3.94 (bs, 1H, H-5), 1.10 (s, 9H, CH_3), 1.02 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.39 (C=O, Bz), 157.72 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 142.96, 133.99, 129.95, 128.99, 128.86, 128.75, 124.90, 119.90, 115.61 (*a*d, *J* = 286 Hz, C*F*$_3$), 94.68 (C-1), 70.71 (C-3), 70.13 (C-4), 69.92 (C-5), 66.62 (C-6), 48.14 (C-2), 27.61 (CH_3), 27.25 (CH_3), 23.41 (C-*Si*), 20.87 (C-*Si*). HR-MS: Calculated for $C_{31}H_{36}N_2O_7F_6Si$ $[M+Na]^+$: 713.2094, found: 713.2088.

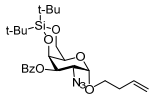
3-Butenyl 3-*O*-benzoyl-2-deoxy-4,6-di-*tert*-butylsilylidene-2-trifluoroacetamido-α-D-galactopyranoside (9)



The reaction was carried out according to the general procedure A. The donor **4** (200 mg, 0.29 mmol) and acceptor **8** (51 µL, 0.59 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 5 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to -40 ºC, after which TfOH (3 µl, 0.03 mmol) was added. The reaction was stirred at -40 ºC for 2 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 6:1). Compound **9** (151 mg, 91% yield, a/b = 3.2/1) was obtained as yellow solid. **α isomer**: $[\alpha]_D^{25}$ +131.2 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.09 – 8.01 (m, 2H, *C*H, Bz), 7.61 – 7.53 (m, 1H), 7.50 – 7.40 (m, 2H), 6.64 (d, *J* = 9.6 Hz, 1H, *N*H), 5.86 – 5.72 (m, 1H, H-9), 5.23 (dd, *J* = 10.9, 2.9 Hz, 1H, H-3), 5.17 – 5.06 (m, 2H, H-10), 5.02 (d, *J* = 3.7 Hz, 1H, H-1), 4.97 – 4.88 (m, 1H, H-2), 4.81 – 4.76 (m, 1H, H-4), 4.32 (dd, *J* = 12.6, 2.1 Hz, 1H, H-6), 4.22 (dd, *J* = 12.6, 1.7 Hz, 1H, H-6), 3.89 – 3.76 (m, 2H, H-5, 7), 3.57 (dt, *J* = 10.0, 6.5 Hz, 1H, H-7), 2.36 (qd, *J* = 6.1, 3.0 Hz, 2H, H-8), 1.11 (s, 9H, CH_3), 0.99 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.87 (C=O, Bz), 157.20 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 134.65 (C-9),

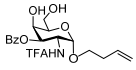
133.55, 129.93, 129.31, 128.59, 117.42 (C-10), 115.61 (*a*d, *J* = 286 Hz, C*F*$_3$), 97.18 (C-1), 71.90 (C-3), 70.40 (C-4), 67.64 (C-5), 67.32 (C-7), 67.03 (C-6), 47.99 (C-2), 33.72 (C-8), 27.59 (C*H*$_3$), 27.33 (C*H*$_3$), 23.38 (C-*Si*), 20.81 (C-*Si*). HR-MS: HR-MS: Calculated for $C_{27}H_{28}O_7NF_3Si$ $[M+NH_4]^+$: 591.2713, found: 591.2711. **β isomer**: $[\alpha]_D^{25}$ +46.3 (c=2, $CHCl_3$). IR (neat, cm^{-1}) ν 650, 697, 734, 796, 826, 863, 920, 1003, 1046, 1066, 1100, 1124, 1172, 1212, 1473, 1522, 1701, 1731, 2859, 2933, 3427. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.06 – 7.96 (m, 2H, *C*H, Bz), 7.64 – 7.55 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 1H, *N*H), 5.78 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H, H-9), 5.39 – 5.30 (m, 1H, H-3), 5.14 – 4.99 (m, 2H, H-10), 4.75 (d, *J* = 8.3 Hz, 1H, H-1), 4.72 (d, *J* = 3.0 Hz, 1H, H-4), 4.42 (dt, *J* = 11.1, 8.5 Hz, 1H, H-2), 4.35 – 4.24 (m, 2H, H-6), 3.95 (dt, *J* = 9.7, 6.5 Hz, 1H, H-7), 3.63 – 3.51 (m, 2H, H-5, 7), 2.33 (qt, *J* = 6.7, 1.4 Hz, 2H, H-8), 1.11 (s, 9H, *C*H$_3$), 0.98 (s, 9H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.66 (C=O, Bz), 157.55 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*),, 134.87 (C-9), 133.66, 129.91, 129.39, 128.67, 116.73 (C-10), 115.72 (*a*d, *J* = 286 Hz, C*F*$_3$), 100.09 (C-1), 72.79 (C-3), 71.39 (C-5), 70.13 (C-4), 68.77 (C-7), 67.15 (C-6), 51.70 (C-2), 34.03 (C-8), 27.60 (C*H*$_3$), 27.53 (C*H*$_3$), 23.41 (C-*Si*), 20.90 (C-*Si*). HR-MS: Calculated for $C_{27}H_{28}O_7NF_3Si$ $[M+NH_4]^+$: 591.2713, found: 591.2710.

3-Butenyl 2-azido-2-deoxy-3-*O*-benzoyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranoside (10)



The reaction was carried out according to the general procedure A. The donor **3** (1.2 g, 1.93 mmol) and acceptor **8** (333 µL, 3.87 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 17 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (17 µl, 0.19 mmol) was added. The reaction was stirred at 0 ºC for 2 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:Et_2O = 20:1). Compound **10** (834 mg, 86% yield) was obtained as white foam. $[\alpha]_D^{25}$ +101.6 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.21 (m, 10H, aromatic H), 6.79 (d, *J* = 8.7 Hz, 1H, *N*H), 5.10 (s, 2H, *C*H$_2$*Ph*), 5.00 (d, *J* = 3.6 Hz, 1H, H-1), 4.74 (d, *J* = 12.2 Hz, 1H, *C*H$_2$*Ph*), 4.64 – 4.54 (m, 3H, *C*H$_2$*Ph*, H-2, 4), 4.26 (dd, *J* = 12.5, 2.1 Hz, 1H, H-6), 4.16 (dd, *J* = 12.5, 1.7 Hz, 1H, H-6), 3.72 – 3.58 (m, 3H, H-3, 5, 7), 3.40 (dt, *J* = 10.0, 6.5 Hz, 1H, H-7), 2.33 (t, *J* = 7.4 Hz, 2H, H-11), 1.70 – 1.49 (m, 4H, H-10, 8), 1.41 – 1.28 (m, 2H, H-9), 1.16 – 1.00 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.23 (C-12), 161.64 (C*ONH*), 137.96, 128.55, 128.46, 128.23, 128.15, 127.75, 127.64 (aromatic C/C*H*), 97.03 (C-1), 92.74 (C*Cl*$_3$), 75.30 (C-3), 69.82 (C*H*$_2$*Ph*), 69.53 (C-4), 67.96 (C-7), 67.65 (C-5), 67.22 (C-6), 66.13 (C*H*$_2$*Ph*), 49.93 (C-2), 34.02 (C-11), 28.93 (C-8), 27.66 (C*H*$_3$), 27.37 (C*H*$_3$), 25.69 (C-9), 24.55 (C-10), 23.43 (C-*Si*), 20.74 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 97.03 ($J_{C1,H1}$ = 171 Hz). HR-MS: HR-MS: Calculated for $C_{25}H_{37}N_3O_6Si$ $[M+Na]^+$: 526.2349, found: 526.2344.

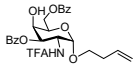
3-Butenyl 3-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (11)



The reaction was carried out according to the general procedure B using compound **9** (1.15 g, 2.0 mmol) and HF/pyridine (70%, 830 µl, 32.1 mmol). The product was purified by column

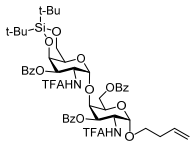
chromatography (pentane:EtOAc = 3:2). Compound **11** (771 mg, 89% yield) was obtained as white foam. $[\alpha]_D^{25}$ +127.4 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.04 – 7.89 (m, 2H, *C*H, Bz), 7.52 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 6.75 (d, *J* = 9.6 Hz, 1H, *N*H), 5.77 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, H-9), 5.27 (dd, *J* = 11.0, 2.8 Hz, 1H, H-3), 5.18 – 5.04 (m, 2H, H-10), 4.98 (d, *J* = 3.7 Hz, 1H, H-1), 4.87 (td, *J* = 10.3, 3.7 Hz, 1H, H-2), 4.37 (s, 1H, H-4), 4.02 – 3.75 (m, 4H, H-5, 6, 7), 3.51 (dt, *J* = 9.9, 6.5 Hz, 1H, H-7), 3.18 (s, 1H, *O*H), 2.47 – 2.27 (m, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.73 (C=O, Bz), 157.46 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 134.64 (C-9), 133.73, 129.93, 128.85, 128.60, 117.45 (C-10), 115.60 (*a*d, *J* = 286 Hz, C*F*$_3$), 97.02 (C-1), 72.30 (C-3), 69.84 (C-5), 68.28 (C-4), 67.26 (C-7), 62.76 (C-6), 48.29 (C-2), 33.64 (C-8). HR-MS: Calculated for $C_{19}H_{22}O_7NF_3$ $[M+Na]^+$: 456.1246, found: 456.1241.

3-Butenyl 3-*O*-benzoyl-6-O-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (12)



The reaction was carried out according to the general procedure C using compound **11** (66 mg, 0.15 mmol), PhCOOBt (164 mg, 0.68 mmol) and Et_3N (105 µl, 0.75 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **12** (79 mg, 97% yield) was obtained as white power. $[\alpha]_D^{25}$ +58.3 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.04 – 7.96 (m, 4H, *C*H, Bz), 7.61 – 7.50 (m, 2H), 7.47 – 7.35 (m, 4H), 6.68 (d, *J* = 9.6 Hz, 1H, NH), 5.76 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, H-9), 5.36 (dd, *J* = 11.0, 2.9 Hz, 1H, H-3), 5.16 – 5.04 (m, 2H, H-10), 5.02 (d, *J* = 3.7 Hz, 1H, H-1), 4.91 (ddd, *J* = 11.0, 9.7, 3.7 Hz, 1H, H-2), 4.63 (dd, *J* = 11.6, 5.5 Hz, 1H, H-6), 4.54 (dd, *J* = 11.5, 7.0 Hz, 1H, H-6), 4.35 (dd, *J* = 3.0, 1.1 Hz, 1H, H-4), 4.30 (ddd, *J* = 6.8, 5.5, 1.2 Hz, 1H, H-5), 3.84 (dt, *J* = 10.0, 6.3 Hz, 1H, H-7), 3.58 (dt, *J* = 10.0, 6.5 Hz, 1H, H-7), 3.04 (bs, 1H, OH), 2.38 (qt, *J* = 6.9, 1.3 Hz, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.59, 166.58 (2 C=O, Bz), 157.40 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 134.52 (C-9), 133.80, 133.43, 130.01, 129.79, 129.63, 128.82, 128.67, 128.57, 117.50 (C-10), 115.60 (*a*d, *J* = 286 Hz, C*F*$_3$), 96.99 (C-1), 72.05 (C-3), 68.65 (C-5), 67.41 (C-7), 67.20 (C-4), 63.62 (C-6), 48.28 (C-2), 33.72 (C-8). HR-MS: Calculated for $C_{26}H_{26}O_8NF_3$ $[M+Na]^+$: 560.1508, found: 560.1503.

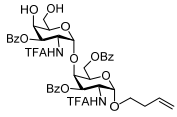
3-Butenyl 3-*O*-benzoyl-2-deoxy-4,6-di-*tert*-butylsilylidene-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (13)



The reaction was carried out according to the general procedure A. The donor **4** (385 mg, 0.56 mmol) and the acceptor **12** (200 mg, 0.37 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 4 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TBSOTf (17 µl, 0.07 mmol) was added. The reaction was stirred at 0 °C for 1 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:Et_2O = 10:1). Compound **13** (59 g, 86% yield) was obtained as white foam. $[\alpha]_D^{25}$ +121.4 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07 – 7.96 (m, 6H, *C*H, Bz), 7.64 – 7.55 (m, 3H), 7.51 – 7.42 (m, 6H), 7.05 (d, *J* = 9.2 Hz, 1H, *N*H), 6.56 (d, *J* = 9.7 Hz, 1H, *N*H), 5.82 – 5.70 (m, 1H, H-9), 5.43 (dd, *J* = 11.2, 2.7 Hz, 1H,

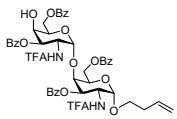
H-3^{B}), 5.34 (dd, *J* = 11.3, 2.6 Hz, 1H, H-3^{A}), 5.27 (d, *J* = 3.7 Hz, 1H, H-1^{B}), 5.14 – 4.97 (m, 4H, H-10, 1A, 2^{B}), 4.96 – 4.86 (m, 1H, H-2^{A}), 4.69 (d, *J* = 2.7 Hz, 1H, H-4^{B}), 4.63 (dd, *J* = 11.1, 7.2 Hz, 1H, H-6^{A}), 4.49 (d, *J* = 2.6 Hz, 1H, H-4^{A}), 4.38 (t, *J* = 6.9 Hz, 1H, H-5^{A}), 4.27 (dd, *J* = 11.1, 6.7 Hz, 1H, H-6^{A}), 4.08 (s, 1H, H-5^{B}), 3.87 (dt, *J* = 10.0, 6.2 Hz, 1H, H-7), 3.61 (dt, *J* = 10.0, 6.5 Hz, 1H, H-7), 3.45 – 3.30 (m, 2H, H-6^{B}), 2.39 (q, *J* = 6.2 Hz, 2H, H-8), 1.03 (s, 9H, *C*H$_3$), 0.91 (s, 9H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.12, 166.24, 165.85 (3 C=O, Bz), 157.53 (*a*d, *J* = 37 Hz, 2x*CF$_3$CO*), 134.44 (C-9), 134.19, 133.72, 133.67, 133.65, 130.00, 129.86, 129.20, 129.17, 129.04, 128.69, 128.67, 128.59, 117.73 (C-10), 115.70 (*a*d, *J* = 286 Hz, 2x*CF$_3$*), 98.12 (C-1B), 96.90 (C-1A), 73.29 (C-4A), 71.39 (C-3A), 71.17 (C-3B), 70.49 (C-4B), 68.74 (C-5A), 68.25 (C-5B), 67.49 (C-7), 66.31 (C-6B), 61.73 (C-6A), 48.64 (C-2B), 48.20 (C-2A), 33.68 (C-8), 27.53 (*CH$_3$*), 27.26 (*CH$_3$*), 23.31 (C-*Si*), 20.75 (C-*Si*). HR-MS: Calculated for $C_{49}H_{56}O_{14}N_2F_6Si$ $[M+Na]^+$: 1061.3303, found: 1061.3297.

3-Butenyl 3-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (14)



The reaction was carried out according to the general procedure B using compound **13** (417 mg, 0.40 mmol) and HF/pyridine (70%, 0.17 ml, 6.4 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **14** (360 mg, 90% yield) was obtained as white foam. $[\alpha]_D^{25}$ +89.4 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.04 – 7.91 (m, 6H, *C*H, Bz), 7.63 – 7.45 (m, 3H), 7.45 – 7.37 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 9.0 Hz, 1H, *N*H), 6.74 (d, *J* = 9.6 Hz, 1H, *N*H), 5.71 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, H-9), 5.47 (dd, *J* = 11.3, 2.7 Hz, 1H, H-3^{B}), 5.32 (dd, *J* = 11.3, 2.6 Hz, 1H, H-3^{A}), 5.21 (d, *J* = 3.7 Hz, 1H, H-1^{B}), 5.12 – 5.00 (m, 3H, H-10, 1^{A}), 4.96 (ddd, *J* = 11.2, 9.1, 3.6 Hz, 1H, H-2^{B}), 4.88 (ddd, *J* = 11.2, 9.7, 3.8 Hz, 1H, H-2^{A}), 4.59 – 4.49 (m, 1H, H-6^{A}), 4.46 (d, *J* = 2.6 Hz, 1H, H-4^{A}), 4.40 – 4.35 (m, 2H, H-4^{B}, 6^{A}), 4.13 – 4.08 (m, 1H, H-5^{B}), 4.04 – 3.99 (m, 1H, H-5^{A}), 3.81 (dt, *J* = 10.0, 6.3 Hz, 1H, H-7), 3.56 (dt, *J* = 10.0, 6.5 Hz, 1H, H-7), 3.22 (q, *J* = 13.0, 8.8 Hz, 2H, H-6^{B}), 2.70 (s, 1H, OH), 2.39 – 2.28 (m, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.94, 166.38, 165.91 (3 C=O, Bz), 157.53 (*a*d, *J* = 37 Hz, 2x*CF$_3$CO*), 134.31 (C-9), 134.04, 133.65, 133.50, 129.95, 129.88, 129.85, 129.70, 129.13, 128.85, 128.82, 128.63, 128.55, 128.48, 117.45 (C-10), 115.60 (*a*d, *J* = 286 Hz, 2x*CF$_3$*), 98.19 (C-1^{B}), 96.65 (C-1^{A}), 73.86 (C-4^{A}), 71.46 (C-3^{A}), 71.35 (C-3^{B}), 70.08 (C-5^{B}), 68.95 (C-4^{B}), 68.49 (C-5^{A}), 67.32 (C-7), 62.41 (C-6^{B}), 62.25 (C-6^{A}), 48.90 (C-2^{B}), 48.33 (C-2^{A}), 33.50 (C-8). HR-MS: Calculated for $C_{41}H_{40}O_{14}N_2F_6$ $[M+Na]^+$: 921.2281, found: 921.2276.

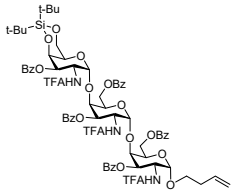
3-Butenyl 3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (15)



The reaction was carried out according to the general procedure C using compound **14** (0.53 g, 0.59 mmol), PhCOOBt (634 mg, 2.65 mmol) and Et_3N (493 µl, 3.54 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **15** (472 mg, 80% yield) was obtained as white foam. $[\alpha]_D^{25}$ +100.4 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07 – 7.97 (m, 4H, *C*H, Bz), 7.89 – 7.80 (m, 2H, *C*H, Bz), 7.77 – 7.69 (m, 2H, *C*H, Bz), 7.58 – 7.47 (m, 3H), 7.43

– 7.32 (m, 6H), 7.23 – 7.11 (m, 4H, *aromatic*, *N*H), 6.67 (d, *J* = 9.6 Hz, 1H, *N*H), 5.73 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H, H-9), 5.61 (dd, *J* = 11.2, 2.7 Hz, 1H, H-3^{B}), 5.35 (dd, *J* = 10.8, 2.8 Hz, 1H, H-3^{A}), 5.28 (d, *J* = 3.7 Hz, 1H, H-1^{B}), 5.13 – 4.90 (m, 5H, H-2^{A}, 2^{B}, 1^{A}, 10), 4.68 – 4.53 (m, 2H, 4^{A}, 6^{A}), 4.43 (dt, *J* = 16.8, 6.7 Hz, 2H, H-5^{B}, 5^{A}), 4.34 – 4.24 (m, 2H, H-4^{B}, 6^{A}), 4.13 (dd, *J* = 11.0, 8.3 Hz, 1H, H-6^{B}), 3.83 (dt, *J* = 10.1, 6.2 Hz, 1H, H-7), 3.68 – 3.51 (m, 2H, H-7, 6^{B}), 3.30 (bs, 1H, OH), 2.42 – 2.29 (m, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.62, 166.28, 165.91, 165.79 (4 C=O, Bz), 157.46 (*a*d, *J* = 37 Hz, 2x*CF$_3$CO*), 134.33 (C-9), 133.84, 133.70, 133.56, 133.22, 129.93, 129.72, 129.70, 129.65, 129.32, 129.07, 128.79, 128.77, 128.64, 128.59, 128.55, 128.49, 128.29, 128.23, 117.55 (C-10), 115.61 (*a*d, *J* = 286 Hz, 2x*CF$_3$*), 97.47 (C-1^{B}), 96.69 (C-1^{A}), 72.17 (C-4^{A}), 71.38 (C-3^{A}), 71.00 (C-3^{B}), 68.71 (C-5^{B}), 68.53 (C-5^{A}), 67.36 (C-7), 66.29 (C-4^{B}), 61.78 (C-6^{B}), 61.69 (C-6^{A}), 48.64 (C-2^{B}), 48.21 (C-2^{A}), 33.53 (C-8). HR-MS: Calculated for $C_{48}H_{44}O_{15}N_2F_6$ $[M+Na]^+$: 1025.2544, found: 1025.2538.

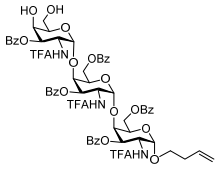
3-Butenyl 3-*O*-benzoyl-2-deoxy-4,6-di-*tert*-butylsilylidene-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (16)



The reaction was carried out according to the general procedure A. The donor **4** (464 mg, 0.67 mmol) and the acceptor **15** (450 mg, 0.45 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 4.5 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TfOH (4 µl, 0.05 mmol) was added. The reaction was stirred at 0 °C for 1 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 10:1). Compound **16** (504 mg, 75% yield) was obtained as yellow foam. $[\alpha]_D^{25}$ +120.3 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.11 – 7.99 (m, 6H, *C*H, Bz), 7.96 – 7.90 (m, 2H, *C*H, Bz), 7.84 – 7.77 (m, 2H, *C*H, Bz), 7.68 – 7.61 (m, 1H), 7.61 – 7.49 (m, 5H), 7.42 (td, *J* = 7.7, 3.4 Hz, 6H), 7.31 – 7.23 (m, 2H), 7.22 – 7.15 (m, 1H), 7.05 (d, *J* = 9.6 Hz, 1H, *N*H), 6.84 (d, *J* = 9.3 Hz, 1H, *N*H), 6.64 (d, *J* = 9.7 Hz, 1H, *N*H), 5.86 – 5.72 (m, 1H, H-9), 5.70 (dd, *J* = 11.5, 2.5 Hz, 1H, H-3^{B}), 5.47 (dd, *J* = 11.1, 2.9 Hz, 1H, H-3^{C}), 5.44 (d, *J* = 3.7 Hz, 1H, H-1^{B}), 5.39 (dd, *J* = 11.2, 2.7 Hz, 1H, H-3^{A}), 5.15 – 5.05 (m, 5H, H-1^{A}, 1^{C}, 2^{B}, 10), 5.00 (td, *J* = 10.3, 3.9 Hz, 1H, H-2^{C}), 4.93 (ddd, *J* = 11.2, 9.3, 3.7 Hz, 1H, H-2^{A}), 4.78 – 4.60 (m, 4H, H-4^{A}, 4^{C}, 5^{B}, 6^{A}), 4.56 (d, *J* = 2.4 Hz, 1H, H-4^{B}), 4.46 (t, *J* = 7.3 Hz, 1H, H-5^{A}), 4.27 (dd, *J* = 11.2, 7.5 Hz, 1H, H-6^{A}), 4.10 (s, 1H, H-5^{C}), 3.97 (dd, *J* = 11.2, 6.6 Hz, 1H, H-6^{B}), 3.88 (dt, *J* = 10.0, 6.2 Hz, 1H, H-7), 3.74 (dd, *J* = 11.1, 8.6 Hz, 1H, H-6^{B}), 3.62 (dt, *J* = 10.1, 6.5 Hz, 1H, H-7), 3.43 (d, *J* = 12.9 Hz, 1H, H-6^{C}), 3.34 (d, *J* = 12.0 Hz, 1H, H-6^{C}), 2.39 (q, *J* = 6.6 Hz, 2H, H-8), 0.93 (s, 9H, *C*H$_3$), 0.90 (s, 9H, *C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.84, 166.12, 166.07, 165.63, 164.68 (5 C=O, Bz), 157.43 (*a*d, *J* = 37 Hz, 3x*CF$_3$CO*), 134.31 (C-9), 134.27, 134.14, 133.98, 133.93, 133.67, 133.61, 133.55, 133.32, 131.12, 130.25, 130.09, 129.91, 129.83, 129.79, 129.67, 129.65, 129.60, 129.03, 128.95, 128.91, 128.83, 128.71, 128.60, 128.52, 128.50, 128.36, 128.04, 117.60 (C-10), 115.54 (*a*d, *J* = 286 Hz, 3x*CF$_3$*), 97.93 (C-1^{C}), 96.90 (C-1^{B}), 96.76 (C-1^{A}), 72.46 (C-4^{B}), 71.50 (C-4^{A}), 70.94 (C-3^{C}), 70.92 (C-3^{A}), 70.47 (C-

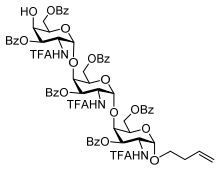
3^{B}), 70.32 (C-4^{C}), 69.03 (C-5^{B}), 68.23 (C-5^{A}), 68.12 (C-5^{C}), 67.49 (C-7), 66.21 (C-6^{C}), 61.25 (C-6^{A}), 60.38 (C-6^{B}), 48.34 (C-2^{C}), 48.29 (C-2^{B}), 48.17 (C-2^{A}), 33.52 (C-8), 27.40 (C*H*$_3$), 26.99 (C*H*$_3$), 23.14 (C-*Si*), 20.52 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 97.93 ($J_{C1,H1}$ = 172 Hz), 96.90 ($J_{C1,H1}$ = 174 Hz), 96.76 ($J_{C1,H1}$ = 172 Hz). HR-MS: Calculated for $C_{71}H_{74}O_{21}N_3F_9Si$ $[M+Na]^+$: 1526.4338, found: 1526.4333.

3-Butenyl 3-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (17)



The reaction was carried out according to the general procedure B using compound **16** (486 mg, 0.32 mmol) and HF/pyridine (70%, 134 µl, 5.17 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **17** (392 mg, 90% yield) was obtained as white foam. $[\alpha]_D^{25}$ +113.8 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 7.93 (m, 6H, *C*H, Bz), 7.92 – 7.84 (m, 2H, *C*H, Bz), 7.79 – 7.70 (m, 2H, *C*H, Bz), 7.66 – 7.30 (m, 12H), 7.26 – 7.04 (m, 4H), 7.00 (d, *J* = 9.4 Hz, 1H, *N*H), 6.76 (d, *J* = 9.5 Hz, 1H, *N*H), 5.74 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H, H-9), 5.65 (d, *J* = 12.0 Hz, 1H, H-3B), 5.51 – 5.37 (m, 2H, H-3A, 3C), 5.35 (d, *J* = 3.6 Hz, 1H, H-1B), 5.16 – 4.92 (m, 6H, H-1A, 1C, 2B, 2C, 10), 4.91 – 4.81 (m, 1H, H-2A), 4.71 – 4.47 (m, 4H, H-4A, 4B, 5B, 6A), 4.42 (t, *J* = 7.1 Hz, 1H, H-5A), 4.33 – 4.16 (m, 2H, H-4C, 6A), 4.09 (d, *J* = 4.6 Hz, 1H, H-5C), 3.92 – 3.72 (m, 3H, H-6B, 7), 3.59 (dt, *J* = 10.3, 6.5 Hz, 1H, H-7), 3.09 (s, 2H, H-6C), 2.76 (bs, 1H, OH), 2.36 (q, *J* = 6.6 Hz, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.76, 166.23, 166.11, 165.84, 164.64 (6 C=O, Bz), 157.47 (*a*d, *J* = 37 Hz, 3x*CF*$_3$*C*O), 134.22 (C-9), 134.03, 133.90, 133.62, 133.25, 129.86, 129.81, 129.67, 129.59, 129.46, 128.80, 128.78, 128.66, 128.58, 128.54, 128.37, 128.28, 127.90, 117.46 (C-10), 115.40 (*a*d, *J* = 286 Hz, 3xC*F*$_3$), 98.20 (C-1C), 96.84 (C-1B), 96.64 (C-1A), 72.79 (C-4B), 71.68 (C-4A), 70.98 (C-3A), 70.86 (C-3C), 70.62 (C-3B), 69.80 (C-5C), 69.13 (C-5B), 68.63 (C-4C), 68.24 (C-5A), 67.39 (C-7), 62.32 (C-6C), 61.69 (C-6A), 60.36 (C-6B), 48.51 (C-2), 48.27 (C-2), 33.43 (C-8). HR-MS: Calculated for $C_{63}H_{58}O_{21}N_3F_9$ $[M+Na]^+$: 1386.3317, found: 1386.3311.

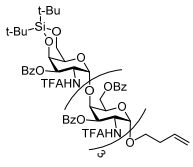
3-Butenyl 3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (18)



The reaction was carried out according to the general procedure C using compound **17** (377 mg, 0.28 mmol), PhCOOBt (297 mg, 1.24 mmol) and Et_3N (192 µl, 1.38 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:1). Compound **18** (390 mg, 96% yield) was obtained as white foam. $[\alpha]_D^{25}$ +115.9 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.10 – 7.94 (m, 4H, *C*H, Bz), 7.92 – 7.66 (m, 8H, *C*H, Bz), 7.66 – 7.06 (m, 19H), 7.03 – 6.87 (m, 2H), 6.70 (d, *J* = 9.5 Hz, 1H, NH), 5.81 – 5.62 (m, 2H, H-9, 3), 5.59 (d, *J* = 11.2 Hz, 1H, H-3), 5.47 – 5.31 (m, 2H, H-1^{C}, 3), 5.24 – 5.13 (m, 1H, H-2), 5.10 – 5.00 (m, 3H, H-1^{B},

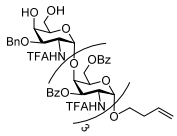
10), 4.95 (td, *J* = 10.4, 3.3 Hz, 1H, H-2), 4.87 (td, *J* = 10.3, 3.6 Hz, 1H, H-2), 4.79 – 4.55 (m, 5H, H-1^{A}, 4^{A}, 4B, 5, 6^{A}), 4.43 (dt, *J* = 33.8, 7.4 Hz, 2H, 2xH-5), 4.28 (s, 1H, H-4^{C}), 4.25 – 4.09 (m, 2H, H-6^{A}, 6^{C}), 3.90 – 3.68 (m, 3H, H-6^{B}, 7), 3.58 – 3.46 (m, 2H, H-6^{C}, 7), 3.39 (bs, 1H, *O*H), 2.31 (t, *J* = 6.5 Hz, 2H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.52, 166.02, 165.92, 165.86, 165.65, 164.50 (6 C=O, Bz), 157.64 (*a*d, *J* = 37 Hz, 3x*CF*$_3$*CO*), 134.20 (C-9), 133.94, 133.61, 133.54, 133.37, 133.24, 129.80, 129.69, 129.62, 129.58, 129.52, 129.41, 129.36, 128.87, 128.78, 128.72, 128.70, 128.54, 128.37, 128.35, 128.31, 128.14, 127.77, 117.45 (C-10), 115.40 (*a*d, *J* = 286 Hz, 3xC*F*$_3$), 97.41 (C-1^{C}), 96.80 (C-1^{B}), 96.45 (C-1^{A}), 71.36 (C-4^{A}), 71.16 (C-4^{B}), 70.82 (C-3), 70.72 (C-3), 70.49 (C-3), 68.80 (C-5), 68.67 (C-5), 68.10 (C-5^{A}), 67.27 (C-7), 65.97 (C-4^{C}), 61.65 (C-6^{C}), 61.26 (C-6^{A}), 60.07 (C-6^{B}), 48.22 (3xC-2), 33.34 (C-8). HR-MS: Calculated for $C_{70}H_{62}O_{22}N_3F_9$ [M+Na]$^{+}$: 1490.3579, found: 1490.3574.

3-Butenyl 3-*O*-benzoyl-2-deoxy-4,6-di-*tert*-butylsilylidene-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (19)



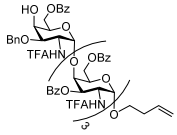
The reaction was carried out according to the general procedure A. The donor **4** (527 mg, 0.76 mmol) and the acceptor **18** (374 mg, 0.26 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 3 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TfOH (5 µl, 0.05 mmol) was added. The reaction was stirred at 0 °C for 1 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 7:1). Compound **19** (422 mg, 84% yield) was obtained as yellow foam. $[\alpha]_D^{25}$ +106.6 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.15 – 7.82 (m, 12H, *C*H, Bz), 7.81 – 7.72 (m, 2H, *C*H, Bz), 7.65 – 7.30 (m, 17H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.04 (m, 3H), 7.03 – 6.90 (m, 2H), 6.77 – 6.65 (m, 2H), 5.87 – 5.62 (m, 3H, H-10, 2xH-3), 5.48 – 5.38 (m, 2H), 5.32 – 5.24 (m, 1H), 5.23 – 4.84 (m, 9H), 4.84 – 4.25 (m, 9H), 4.14 – 3.52 (m, 7H), 3.48 – 3.24 (m, 2H, H-6), 2.38 (q, *J* = 6.5 Hz, 2H, H-8), 0.92 (s, 9H, C*H*$_3$), 0.88 (s, 9H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.62, 166.05, 165.91, 165.58, 164.65, 164.43 (C=O, Bz), 157.35 (*a*d, *J* = 37 Hz, 4x*CF*$_3$*CO*), 134.24 (C-9), 134.04, 133.93, 133.61, 133.44, 131.07, 129.84, 129.71, 129.58, 129.56, 129.45, 128.92, 128.88, 128.83, 128.80, 128.78, 128.62, 128.52, 128.48, 128.39, 128.32, 128.05, 127.80, 117.50 (C-10), 115.40 (*a*d, *J* = 286 Hz, 4xC*F*$_3$), 97.87 (C-1), 96.92 (C-1), 96.70 (C-1), 96.64 (C-1^{A}), 72.49, 72.00, 71.14, 70.86, 70.35, 70.21, 70.12, 69.96, 68.95, 68.59, 68.17, 67.98, 67.39 (C-7), 66.10 (C-6), 61.25 (C-6), 60.53 (C-6), 59.94 (C-1), 48.46 (C-2), 48.16 (C-2), 47.98 (C-2), 33.43 (C-8), 27.27 (C*H*$_3$), 26.91 (C*H*$_3$), 23.04 (C-*Si*), 20.42 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 97.87 ($J_{C1,H1}$ = 173 Hz), 96.92 ($J_{C1,H1}$ = 171 Hz), 96.70 ($J_{C1,H1}$ = 172 Hz), 96.64 ($J_{C1,H1}$ = 171 Hz). HR-MS: Calculated for $C_{93}H_{92}O_{28}N_4F_{12}Si$ [M+Na]$^{+}$: 1991.5373, found: 1991.5368.

3-Butenyl 3-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (20)



The reaction was carried out according to the general procedure C using compound **19** (407 mg, 0.21 mmol) and HF/pyridine (70%, 86 µl, 3.31 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **20** (335 mg, 88% yield) was obtained as white foam. $[\alpha]_D^{25}$ +108 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.02 – 7.86 (m, 10H, *C*H, Bz), 7.84 – 7.78 (m, 2H, *C*H, Bz), 7.76 – 7.67 (m, 2H, *C*H, Bz), 7.65 – 7.21 (m, 19H), 7.19 – 7.04 (m, 4H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 9.3 Hz, 1H, *N*H), 6.71 (d, *J* = 8.6 Hz, 2H), 5.83 – 5.68 (m, 2H, H-3, 9), 5.60 (d, *J* = 11.4 Hz, 1H, H-3), 5.46 – 5.35 (m, 2H, H-1, 3), 5.30 (d, *J* = 11.4 Hz, 1H, H-3), 5.20 – 4.54 (m, 15H), 4.51 – 4.38 (m, 2H), 4.34 – 4.13 (m, 2H), 4.01 (s, 1H), 3.86 (d, *J* = 9.0 Hz, 4H), 3.75 – 3.53 (m, 3H, H-6, 7), 3.13 – 2.94 (m, 2H, H-6^D), 2.81 (bs, 1H, *O*H), 2.63 (bs, 1H, *O*H), 2.37 (q, *J* = 6.6 Hz, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.68, 166.18, 166.15, 165.70, 164.71, 164.66 (C=O, Bz), 157.50 (*a*d, *J* = 37 Hz, 4x*CF*$_3$*C*O), 134.29 (C-9), 134.07, 133.70, 133.50, 129.86, 129.71, 129.65, 129.57, 129.48, 128.86, 128.65, 128.59, 128.56, 128.50, 128.38, 128.01, 127.82, 117.57 (C-10), 115.48 (*a*d, *J* = 286 Hz, 4xC*F*$_3$), 98.09 (C-1), 96.93 (C-1), 96.74 (C-1), 72.69 (C-4), 72.01 (C-4), 71.14 (C-3), 70.82 (C-3), 70.72 (C-4), 70.44 (C-3), 70.20 (C-4), 69.66, 69.15, 68.75, 68.61, 68.19, 67.48 (C-7), 62.46 (C-6^D), 61.36 (C-6^A), 60.53 (C-6), 60.04 (C-6), 48.43 (C-2), 48.23 (C-2), 48.11 (C-2), 33.49 (C-8). HR-MS: Calculated for $C_{85}H_{76}O_{28}N_4F_{12}$ $[M+Na]^+$: 1851.4352, found: 1851.4346.

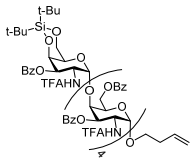
3-Butenyl 3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranoside (21)



The reaction was carried out according to the general procedure C using compound **20** (300 mg, 0.16 mmol), PhCOOBt (176 mg, 0.74 mmol) and Et_3N (114 µl, 0.82 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:1). Compound **21** (297 mg, 94% yield) was obtained as white foam. $[\alpha]_D^{25}$ +120.6 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.04 – 7.96 (m, 4H, *C*H, Bz), 7.95 – 7.90 (m, 2H, *C*H, Bz), 7.89 – 7.81 (m, 4H, *C*H, Bz), 7.81 – 7.70 (m, 6H, *C*H, Bz), 7.65 – 7.22 (m, 19H), 7.21 – 6.95 (m, 9H), 6.75 (d, *J* = 9.3 Hz, 1H, *N*H), 6.66 (d, *J* = 9.5 Hz, 1H, *N*H), 5.82 – 5.65 (m, 2H, H-9, 3), 5.63 (d, *J* = 11.7 Hz, 1H, H-3), 5.47 (d, *J* = 11.4 Hz, 1H, H-3), 5.40 – 5.33 (m, 1H, H-3), 5.30 (d, *J* = 3.7 Hz, 1H, H-1), 5.20 – 5.08 (m, 2H, H-1, 2), 5.09 – 4.97 (m, 4H), 4.96 – 4.84 (m, 2H), 4.75 (s, 2H), 4.65 (d, *J* = 29.1 Hz, 5H), 4.45 – 4.34 (m, 2H), 4.29 – 4.07 (m, 3H), 3.99 – 3.82 (m, 2H, H-6), 3.79 (dt, *J* = 12.3, 6.3 Hz, 1H, H-7), 3.74 – 3.61 (m, 2H, H-6), 3.51 (dt, *J* = 10.4, 6.5 Hz, 1H, H-7), 3.44 – 3.34 (m, 1H, H-6), 2.37 – 2.26 (m, 2H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.38, 166.06, 165.95, 165.86, 165.61, 164.50 (C=O, Bz), 157.72 (*a*d, *J* = 37 Hz, 4x*CF*$_3$*C*O), 134.21 (C-9), 134.01, 133.62, 133.43, 133.23, 133.00, 129.77, 129.70, 129.63, 129.60, 129.51, 129.38, 128.96, 128.85, 128.76, 128.71, 128.54, 128.33, 128.06, 128.03, 127.87, 127.71, 117.51 (C-10), 115.37 (*a*d, *J* = 286 Hz, 4xC*F*$_3$), 97.51 (C-1), 96.77 (C-1), 96.49 (C-1), 71.61, 71.34, 70.93, 70.67, 70.42, 70.04, 68.76, 68.44,

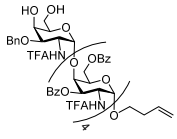
68.14, 67.30 (C-7), 65.82, 61.56 (C-6), 61.27 (C-6), 60.18 (C-6), 59.95 (C-6), 48.41 (C-2), 48.15 (C-2), 48.05 (C-2), 33.37 (C-8). HR-MS: Calculated for $C_{92}H_{80}O_{29}N_4F_{12}$ $[M+Na]^+$: 1955.4614, found: 1955.4609.

Pentasaccharide 22



The reaction was carried out according to the general procedure A. The donor **4** (424 mg, 0.61 mmol) and the acceptor **21** (297 mg, 0.15 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 2 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (3 µl, 0.03 mmol) was added. The reaction was stirred at 0 ºC for 1 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 4:1). Compound **22** (253 mg, 68% yield) was obtained as yellow foam. $[\alpha]_D^{25}$ +143.5 (c=0.2, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.07 – 8.00 (m, 2H, *C*H, Bz), 8.00 – 7.89 (m, 10H, *C*H, Bz), 7.84 – 7.72 (m, 6H, *C*H, Bz), 7.66 – 7.35 (m, 18H), 7.31 – 7.24 (m, 2H), 7.23 – 7.14 (m, 5H), 7.10 – 7.00 (m, 3H), 6.89 (d, *J* = 9.7 Hz, 1H, *N*H), 6.73 (d, *J* = 9.7 Hz, 1H, *N*H), 6.62 (d, *J* = 9.4 Hz, 1H, *N*H), 6.59 (d, *J* = 9.7 Hz, 1H, *N*H), 5.83 – 5.71 (m, 3H), 5.53 (dd, *J* = 11.5, 2.5 Hz, 1H, H-3), 5.44 – 5.41 (m, 1H), 5.40 (d, *J* = 2.8 Hz, 1H, H-1), 5.24 (dd, *J* = 11.2, 2.7 Hz, 1H, H-3), 5.21 – 5.07 (m, 5H), 5.06 (d, *J* = 3.7 Hz, 1H, H-1), 5.00 (qd, *J* = 9.7, 3.7 Hz, 2H, H-2), 4.93 (d, *J* = 3.7 Hz, 1H, H-1), 4.91 – 4.80 (m, 2H, H-2), 4.72 (d, *J* = 2.7 Hz, 1H), 4.70 – 4.54 (m, 7H), 4.49 – 4.42 (m, 2H), 4.27 (dd, *J* = 11.2, 7.6 Hz, 1H, H-6), 3.99 (d, *J* = 2.3 Hz, 1H, H-4), 3.97 – 3.85 (m, 4H), 3.71 (t, *J* = 10.4 Hz, 1H, H-6), 3.67 – 3.52 (m, 3H, H-6, 7), 3.33 (d, *J* = 12.4 Hz, 1H, H-6), 3.24 (d, *J* = 12.2 Hz, 1H, H-6), 2.45 – 2.36 (m, 2H, H-8), 0.88 (s, 9H, *C*H$_3$), 0.85 (s, 9H, *C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.70, 166.19, 166.17, 166.09, 165.91, 165.68, 164.68, 164.57, 164.52 (9 C=O, Bz), 157.55 (*a*d, *J* = 37 Hz, 5x*CF$_3$CO*), 134.31 (C-9), 134.14, 134.11, 134.08, 133.76, 133.65, 133.57, 133.52, 129.92, 129.84, 129.73, 129.69, 129.66, 129.60, 129.58, 129.03, 128.96, 128.93, 128.91, 128.89, 128.84, 128.71, 128.65, 128.63, 128.55, 128.54, 128.50, 128.45, 128.40, 128.00, 127.90, 127.89, 117.73 (C-10), 115.46 (*a*d, *J* = 286 Hz, 5x*CF$_3$*), 97.89 (C-1), 97.02 (C-1), 96.84 (C-1), 96.78 (C-1), 96.69 (C-1), 72.35, 72.02, 71.18, 71.01, 70.93, 70.46, 70.27, 70.21, 69.82, 68.98, 68.68, 68.65, 68.23, 68.05, 67.57 (C-7), 66.18, 61.22, 60.50, 60.15, 60.00 (5 C-6), 48.42, 48.28, 48.25, 47.97, 47.90 (5 C-2), 33.58 (C-8), 27.39 (*CH$_3$*), 27.01 (*CH$_3$*), 23.16 (C-*Si*), 20.52 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 97.89 ($J_{C1,H1}$ = 173 Hz), 97.02 ($J_{C1,H1}$ = 169 Hz), 96.84 ($J_{C1,H1}$ = 172 Hz), 96.78 ($J_{C1,H1}$ = 172 Hz), 96.69 ($J_{C1,H1}$ = 171 Hz). MALDI-MS: Calculated for $C_{115}H_{110}O_{35}N_5F_{15}Si$ $[M+Na]^+$: 2456.6409, found: 2456.6403.

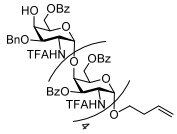
Pentasaccharide 23



The reaction was carried out according to the general procedure B using compound **22** (248 mg, 0.10 mmol) and HF/pyridine (70%, 42 µl, 1.63 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **23** (220 mg, 96% yield) was obtained as white foam. $[\alpha]_D^{25}$ +128.5 (c=0.2, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.05 –

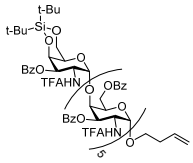
7.98 (m, 2H, *C*H, Bz), 7.97 – 7.88 (m, 10H, *C*H, Bz), 7.80 – 7.70 (m, 6H, *C*H, Bz), 7.63 – 7.52 (m, 5H), 7.51 – 7.32 (m, 13H), 7.23 – 6.95 (m, 10H), 6.81 (d, *J* = 9.6 Hz, 1H, *N*H), 6.68 – 6.55 (m, 3H), 5.85 – 5.63 (m, 3H), 5.47 (dd, *J* = 11.4, 2.4 Hz, 1H), 5.42 – 5.34 (m, 2H), 5.31 – 5.24 (m, 1H), 5.18 – 5.05 (m, 5H), 5.04 – 4.93 (m, 3H), 4.89 (td, *J* = 11.1, 10.5, 6.6 Hz, 1H), 4.84 (d, *J* = 3.6 Hz, 1H), 4.77 (ddd, *J* = 13.0, 9.6, 3.5 Hz, 1H), 4.73 – 4.59 (m, 6H), 4.59 – 4.49 (m, 1H), 4.47 – 4.37 (m, 2H), 4.29 – 4.20 (m, 1H), 4.20 – 4.14 (m, 1H), 3.96 (d, *J* = 4.3 Hz, 1H), 3.94 – 3.81 (m, 3H), 3.78 (q, *J* = 6.4 Hz, 1H), 3.68 (t, *J* = 10.4 Hz, 1H), 3.64 – 3.45 (m, 4H), 3.08 – 2.90 (m, 2H, H-6), 2.57 (bs, 1H, *O*H), 2.38 (q, *J* = 6.8 Hz, 2H, H-8), 2.27 (bs, 1H, *O*H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.62, 166.19, 166.16, 166.10, 165.99, 165.69, 164.63, 164.59, 164.53 (9 C=O, Bz), 157.52 (*a*d, *J* = 37 Hz, 5x*CF*$_3$*CO*), 134.31 (C-9), 134.17, 134.12, 134.08, 133.76, 133.67, 133.64, 133.57, 133.50, 129.91, 129.84, 129.75, 129.72, 129.69, 129.64, 129.58, 129.55, 128.95, 128.93, 128.86, 128.81, 128.65, 128.63, 128.59, 128.55, 128.53, 128.45, 127.91, 127.86, 127.83, 117.71 (C-10), 115.46 (*a*d, *J* = 286 Hz, 5xC*F*$_3$), 98.04 (C-1), 97.04 (C-1), 96.80 (C-1), 72.47, 72.11, 71.20, 71.02, 70.80, 70.75, 70.49, 70.27, 70.02, 69.57, 69.06, 68.89, 68.61, 68.17, 67.55 (C-7), 62.60, 61.22, 60.38, 60.11, 59.94 (5 C-6), 48.38 (C-2), 48.26 (C-2), 48.20 (C-2), 47.85 (C-2), 33.56 (C-8). HR-MS: Calculated for $C_{107}H_{94}O_{35}N_5F_{15}$ $[M+Na]^+$: 2316.5388, found: 2316.5382.

Pentasaccharide 24



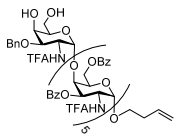
The reaction was carried out according to the general procedure C using compound **23** (220 mg, 0.096 mmol), PhCOOBt (103 mg, 0.43 mmol) and Et_3N (67 µl, 0.48 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:2). Compound **24** (194 mg, 84% yield) was obtained as white power. $[\alpha]_D^{25}$ +131.0 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.02 – 7.90 (m, 8H, *C*H, Bz), 7.90 – 7.85 (m, 2H, *C*H, Bz), 7.82 – 7.69 (m, 10H, *C*H, Bz), 7.65 – 7.41 (m, 15H), 7.39 – 7.32 (m, 4H), 7.25 – 6.98 (m, 14H), 6.79 (d, *J* = 9.6 Hz, 1H, *N*H), 6.68 (d, *J* = 9.5 Hz, 1H, *N*H), 6.59 (d, *J* = 9.6 Hz, 1H, *N*H), 5.78 – 5.67 (m, 3H), 5.50 (dd, *J* = 11.4, 2.5 Hz, 1H), 5.43 (dd, *J* = 11.2, 2.5 Hz, 1H), 5.36 (dd, *J* = 11.0, 2.7 Hz, 1H), 5.30 (d, *J* = 3.7 Hz, 1H), 5.17 – 5.02 (m, 5H), 5.02 – 4.81 (m, 6H), 4.74 – 4.54 (m, 8H), 4.44 – 4.31 (m, 2H), 4.26 – 4.15 (m, 2H), 4.11 (t, *J* = 9.8 Hz, 1H), 3.99 – 3.90 (m, 1H), 3.89 – 3.77 (m, 3H), 3.71 – 3.50 (m, 4H), 3.41 – 3.32 (m, 1H, H-6), 3.04 (bs, 1H, *O*H), 2.56 (bs, 1H, *O*H), 2.35 (q, *J* = 6.5 Hz, 2H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.40, 166.13, 166.03, 165.94, 165.90, 165.67, 164.53, 164.51 (C=O, Bz), 157.54 (*a*d, *J* = 37 Hz, 5x*CF*$_3$*CO*), 134.28 (C-9), 134.22, 134.16, 134.08, 133.73, 133.65, 133.60, 133.51, 133.31, 129.87, 129.70, 129.68, 129.64, 129.57, 129.51, 129.37, 129.04, 128.95, 128.88, 128.76, 128.71, 128.66, 128.63, 128.58, 128.55, 128.45, 128.41, 128.07, 127.84, 127.78, 117.67 (C-10), 115.37 (*a*d, *J* = 286 Hz, 5xC*F*$_3$), 97.53, 96.89, 96.78, 96.70, 96.63 (5 C-1), 71.80, 71.38, 71.06, 70.86, 70.72, 70.62, 70.42, 70.10, 69.93, 68.78, 68.72, 68.56, 68.51, 68.20, 67.42 (C-7), 65.93, 61.53 (C-6), 61.27 (C-6), 60.15 (C-6), 59.99 (C-6), 48.38 (C-2), 48.18 (C-2), 48.04 (C-2), 47.85 (C-2), 33.49 (C-8). HR-MS: Calculated for $C_{114}H_{98}O_{36}N_5F_{15}$ $[M+Na]^+$: 2420.5650, found: 2420.5644.

Hexasaccharide (25)



The reaction was carried out according to the general procedure A. The donor **4** (115 mg, 0.17 mmol) and the acceptor **24** (160 mg, 0.07 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 0.33 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (4 µl, 0.04 mmol) was added. The reaction was stirred at 0 ºC for 1 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 3:1). Compound **25** (52 mg, 54% yield) was obtained as white foam, and **24** (78 mg) was recycled. $[\alpha]_D^{25}$ +90.5 (c=0.4, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.04 – 8.01 (m, 2H), 7.99 – 7.91 (m, 10H), 7.90 – 7.87 (m, 2H), 7.82 – 7.74 (m, 8H), 7.64 – 7.37 (m, 24H), 7.25 – 7.00 (m, 13H), 6.93 (d, *J* = 9.7 Hz, 1H, *N*H), 6.77 (d, *J* = 9.8 Hz, 1H, *N*H), 6.61 (d, *J* = 9.9 Hz, 1H, *N*H), 6.59 – 6.52 (m, 3H), 5.85 – 5.75 (m, 1H), 5.75 – 5.70 (m, 1H), 5.68 (dd, *J* = 11.4, 2.7 Hz, 1H), 5.62 (dd, *J* = 11.4, 2.7 Hz, 1H), 5.49 (dd, *J* = 11.5, 2.5 Hz, 1H), 5.43 – 5.37 (m, 2H), 5.22 (dd, *J* = 11.2, 2.7 Hz, 1H), 5.19 – 4.78 (m, 15H), 4.75 – 4.58 (m, 10H), 4.54 (t, *J* = 7.7 Hz, 1H), 4.48 – 4.40 (m, 2H), 4.26 (dd, *J* = 11.2, 7.6 Hz, 1H), 3.98 (d, *J* = 2.2 Hz, 1H), 3.95 – 3.82 (m, 5H), 3.71 (t, *J* = 10.6 Hz, 1H), 3.67 – 3.49 (m, 4H), 3.30 (d, *J* = 12.8 Hz, 1H, H-6), 3.22 (d, *J* = 12.0 Hz, 1H, H-6), 2.45 – 2.37 (m, 2H, H-8), 0.87 (s, 9H), 0.85 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.72, 166.24, 166.19, 166.12, 165.98, 165.91, 165.69, 164.65, 164.56, 164.53, 164.47 (11 C=O, Bz), 157.56 (*a*d, *J* = 37 Hz, 6x*CF*$_3$*CO*), 134.33 (C-9), 134.21, 134.17, 134.14, 134.11, 133.81, 133.72, 133.66, 133.61, 133.54, 129.95, 129.87, 129.85, 129.77, 129.72, 129.68, 129.65, 129.62, 129.04, 129.02, 128.95, 128.90, 128.84, 128.69, 128.65, 128.60, 128.57, 128.55, 128.52, 128.49, 128.40, 128.35, 127.93, 127.91, 127.87, 127.80, 117.80 (C-10), 115.43 (*a*d, *J* = 286 Hz, 6xC*F*$_3$), 97.91 (C-1), 97.10 (C-1), 96.87 (C-1), 96.74 (C-1), 72.36, 72.18, 71.28, 71.10, 70.93, 70.50, 70.32, 70.27, 70.24, 70.15, 69.86, 69.00, 68.66, 68.23, 68.06, 67.61 (C-7), 66.20, 61.20, 60.45, 60.06, 59.95 (C-6), 48.41, 48.23, 48.11, 48.06, 47.97, 47.85 (6 C-2), 33.63 (C-8), 27.42 (C*H*$_3$), 27.03 (C*H*$_3$), 23.19 (C-*Si*), 20.55 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 97.91 ($J_{C1,H1}$ = 174 Hz), 97.10 ($J_{C1,H1}$ = 172 Hz), 96.87 ($J_{C1,H1}$ = 170 Hz), 96.74 ($J_{C1,H1}$ = 171 Hz). MALDI-MS: Calculated for $C_{137}H_{128}F_{18}N_6O_{42}Si$ $[M+Na]^+$: 2921.7444, found: 2921.6985.

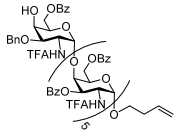
Hexasaccharide 26



The reaction was carried out according to the general procedure A using compound **25** (95 mg, 0.03 mmol) and HF/pyridine (70%, 14 µl, 0.52 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **26** (76 mg, 84% yield) was obtained as yellow syrup. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.03 – 7.98 (m, 2H, *C*H, Bz), 7.96 – 7.85 (m, 12H, *C*H, Bz), 7.78 – 7.71 (m, 8H, *C*H, Bz), 7.60 – 7.32 (m, 22H), 7.20 – 6.99 (m, 13H), 6.87 (d, *J* = 9.7 Hz, 1H, *N*H), 6.74 (d, *J* = 9.7 Hz, 1H, *N*H), 6.66 (d, *J* = 9.7 Hz, 1H, *N*H), 6.61 – 6.54 (m, 2H), 5.87 – 5.64 (m, 3H), 5.57 (dd, *J* = 11.4, 2.7 Hz, 1H), 5.44 (dd, *J* = 11.5, 2.4 Hz, 1H), 5.40 – 5.35 (m, 2H), 5.26 (dd, *J* = 11.2, 2.6 Hz, 1H), 5.17 – 4.85 (m, 12H), 4.82 (d, *J* = 3.8 Hz, 1H), 4.76 (ddd, *J* = 13.1, 9.8, 3.7 Hz, 1H), 4.69 (d, *J* = 2.6 Hz, 1H), 4.68 – 4.54 (m, 7H), 4.48 (d, *J* = 7.7 Hz, 1H), 4.42 (t, *J* = 7.3 Hz, 1H), 4.39 – 4.35 (m, 1H), 4.28 – 4.18 (m, 2H), 3.95 (d,

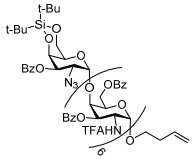
J = 4.4 Hz, 1H), 3.93 – 3.81 (m, 4H), 3.79 – 3.47 (m, 6H), 3.33 (d, *J* = 2.3 Hz, 1H), 3.09 – 2.94 (m, 2H), 2.42 – 2.37 (m, 2H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.57, 166.24, 166.20, 166.12, 166.03, 166.01, 165.73 (C=O, Bz), 157.61 (*a*d, *J* = 37 Hz, 6x*CF*$_3$*CO*), 134.35 (C-9), 134.20, 134.12, 133.81, 133.71, 133.68, 133.62, 133.57, 129.95, 129.90, 129.81, 129.78, 129.73, 129.71, 129.68, 129.65, 129.61, 129.02, 128.95, 128.91, 128.83, 128.70, 128.67, 128.64, 128.60, 128.57, 128.54, 128.49, 127.93, 127.88, 127.82, 124.87, 117.80 (C-10), 115.43 (*a*d, *J* = 286 Hz, 6x*CF*$_3$), 98.05 (C-1), 97.06 (C-1), 96.86 (C-1), 96.75 (C-1), 72.44, 72.10, 71.23, 71.05, 70.96, 70.87, 70.68, 70.52, 70.27, 70.05, 69.99, 69.59, 69.04, 68.93, 68.63, 68.25, 67.61 (C-7), 64.75, 62.69, 61.27, 60.42, 60.13, 59.99 (6 C-6), 48.43, 48.25, 48.19, 48.08, 47.87 (C-2), 33.63 (C-8). MALDI-MS: Calculated for $C_{129}H_{112}F_{18}N_6O_{42}$ $[M+Na]^+$: 2781.6423, found: 2781.5987.

Hexasaccharide 27



The reaction was carried out according to the general procedure B using compound **26** (75 mg, 0.03 mmol), PhCOOBt (29 mg, 0.12 mmol) and Et_3N (19 µl, 0.14 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:2). Compound **27** (71 mg, 91% yield) was obtained as white foam. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.00 – 7.86 (m, 12H), 7.80 – 7.71 (m, 12H), 7.62 – 7.32 (m, 23H), 7.24 – 6.96 (m, 17H), 6.81 (d, *J* = 9.6 Hz, 1H, *N*H), 6.66 (d, *J* = 9.7 Hz, 1H, *N*H), 6.61 (d, *J* = 9.6 Hz, 1H, *N*H), 6.57 – 6.50 (m, 2H), 5.85 – 5.63 (m, 3H), 5.57 (dd, *J* = 11.4, 2.7 Hz, 1H), 5.45 (dd, *J* = 11.4, 2.5 Hz, 1H), 5.42 – 5.28 (m, 3H), 5.18 – 4.77 (m, 15H), 4.72 – 4.49 (m, 11H), 4.40 (t, *J* = 7.2 Hz, 1H), 4.33 (t, *J* = 7.2 Hz, 1H), 4.21 (dd, *J* = 11.2, 7.4 Hz, 1H), 4.15 (d, *J* = 3.3 Hz, 1H), 4.11 – 4.02 (m, 1H), 3.93 – 3.80 (m, 4H), 3.75 (dd, *J* = 11.0, 6.3 Hz, 1H), 3.66 (t, *J* = 10.4 Hz, 1H), 3.62 – 3.48 (m, 4H), 3.46 – 3.36 (m, 1H), 2.71 (s, 1H, *O*H), 2.39 – 2.31 (m, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.39, 166.23, 166.14, 166.11, 166.05, 166.00, 165.91, 165.70 (C=O, Bz), 157.57 (*a*d, *J* = 37 Hz, 6x*CF*$_3$*CO*), 134.32 (C-9), 134.22, 134.14, 133.85, 133.80, 133.70, 133.60, 133.38, 129.94, 129.78, 129.75, 129.73, 129.69, 129.64, 129.61, 129.36, 129.05, 129.00, 128.97, 128.95, 128.78, 128.70, 128.66, 128.60, 128.56, 128.48, 128.46, 128.17, 127.92, 127.87, 127.83, 124.87, 117.79 (C-10), 115.47 (*a*d, *J* = 286 Hz, 6x*CF*$_3$), 97.58 (C-1), 97.05 (C-1), 96.80 (C-1), 72.06, 71.57, 71.21, 71.11, 71.05, 70.75, 70.67, 70.49, 70.30, 70.10, 70.00, 68.87, 68.65, 68.25, 67.57 (C-7), 66.14, 64.75, 61.51, 61.25, 60.22, 60.10, 60.00 (6 C-6), 48.41, 48.24, 48.15, 48.07, 47.89 (C-2), 33.60 (C-8). MALDI-MS: Calculated for $C_{136}H_{116}F_{18}N_6O_{43}$ $[M+Na]^+$: 2885.6685, found: 2885.6282.

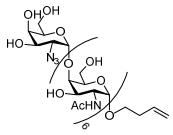
Heptasaccharide 2



The reaction was carried out according to the general procedure C. The donor **3** (46 mg, 0.07 mmol) and the acceptor **27** (70 mg, 0.02 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 0.1 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (1 µl, 7.3 µmol) was added. The reaction was stirred at 0 ºC for 1 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried

with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 5:2). Compound **2** (68 mg, 84% yield) was obtained as white solid. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.09 – 7.87 (m, 16H, *C*H, Bz), 7.84 – 7.71 (m, 10H, *C*H, Bz), 7.68 – 7.37 (m, 25H), 7.25 – 7.14 (m, 11H), 7.12 – 6.95 (m, 7H), 6.71 – 6.53 (m, 2H), 5.86 – 5.69 (m, 3H), 5.63 (dd, *J* = 11.5, 2.7 Hz, 1H), 5.52 (ddd, *J* = 11.5, 7.4, 2.4 Hz, 2H), 5.46 – 5.39 (m, 2H), 5.23 – 4.90 (m, 12H), 4.87 (dd, *J* = 6.8, 3.7 Hz, 2H), 4.81 – 4.50 (m, 12H), 4.49 – 4.42 (m, 2H), 4.32 – 4.24 (m, 2H), 4.11 (t, *J* = 9.9 Hz, 1H), 4.04 (d, *J* = 2.3 Hz, 1H), 3.99 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.96 – 3.51 (m, 13H), 2.42 (q, *J* = 6.5 Hz, 2H, H-8), 0.90 (s, 9H, *C*H$_3$), 0.83 (s, 9H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.47, 166.24, 166.22, 166.14, 166.12, 166.05, 165.76, 165.70, 164.95, 164.66, 164.62, 164.59 (C=O, Bz), 157.68 (*a*d, *J* = 37 Hz, 6x*CF$_3$CO*), 134.36 (C-9), 134.19, 134.13, 133.96, 133.81, 133.68, 133.60, 133.28, 133.22, 130.15, 129.85, 129.77, 129.71, 129.66, 129.63, 129.60, 129.40, 129.03, 128.99, 128.96, 128.89, 128.78, 128.76, 128.70, 128.67, 128.60, 128.57, 128.54, 128.48, 128.45, 128.06, 127.99, 127.93, 127.89, 117.80 (C-10), 115.41 (*a*d, *J* = 286 Hz, 6xC*F$_3$*), 99.85 (C-1^G), 97.35 (C-1), 96.99 (C-1), 96.89 (C-1), 96.77 (C-1), 96.65 (C-1), 75.20, 72.68, 71.93, 71.21, 71.17, 70.89, 70.77, 70.56, 70.17, 69.99, 69.87, 69.37, 68.68, 68.59, 68.32, 68.11, 67.62 (C-7), 66.55 (C-6^G), 61.34, 60.93, 60.23, 60.10 (C-6), 58.62 (C-2^G), 48.53, 48.31, 48.24, 48.17, 47.98 (C-2), 33.65 (C-8), 27.46 (C*H$_3$*), 27.19 (C*H$_3$*), 23.14 (C-*Si*), 20.62 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 99.85 ($J_{C1,H1}$ = 170 Hz), 97.35 ($J_{C1,H1}$ = 174 Hz), 96.99 ($J_{C1,H1}$ = 171 Hz), 96.89 ($J_{C1,H1}$ = 171 Hz), 96.77 ($J_{C1,H1}$ = 174 Hz), 96.65 ($J_{C1,H1}$ = 172 Hz). MALDI-MS: Calculated for $C_{157}H_{145}F_{18}N_9O_{48}Si$ $[M+Na]^+$: 3316.8562, found: 3316.7918.

Heptasaccharide 1



HF/pyridine (16 eq) solution was added to the solution of **2** in THF at 0 ºC. The reaction was warmed to room temperature and stirred until TLC-analysis indicated full consumption of the starting material (± 1h). Then the mixture was diluted with DCM and washed with saturated $NaHCO_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. To the solution of the residue in THF/MeOH (2 ml/0.9 ml), 1 M NaOH solution was added at 0 ºC. The reaction mixture was warmed to room temperature slowly and stirred for overnight. Then the reaction was re-cooled to 0 ºC and neutralized by Amberlite IR120 (H+) resin. After filtration, the filtrate was concentrated *in vacuo* and dissolved in 2 ml water. Then Ac_2O was added at 0 ºC, after which $NaHCO_3$ was added until the pH of the solution was about 9. The mixture was stirred for overnight. After neutralized by Amberlite IR120 (H+) resin and subsequent filtration, the filtrate was concentrated *in vacuo* and purified by gel filtration (HW-40, 0.15M NH_4OAc in H_2O). Compound **1** (5.4 mg, 44% yield) was obtained as white foam. ^{1}H NMR (850 MHz, D_2O) δ 5.91 (ddt, *J* = 17.1, 10.3, 6.6 Hz, 1H, H-9), 5.19 – 5.15 (m, 2H, H-1, 10a), 5.12 (ddt, *J* = 10.3, 2.2, 1.2 Hz, 1H, H-10b), 5.07 – 5.04 (m, 3H, 3xH-1), 5.02 (d, *J* = 3.9 Hz, 1H, H-1), 5.00 (d, *J* = 3.8 Hz, 1H, H-1), 4.98 (d, *J* = 3.7 Hz, 1H, H-1), 4.46 – 4.40 (m, 5H), 4.38 (t, *J* = 6.5 Hz, 1H), 4.34 – 4.28 (m, 5H), 4.23 (dd, *J* = 11.3, 3.7 Hz, 1H), 4.21 – 4.12 (m, 10H), 4.11 (d, *J* = 2.9 Hz, 1H), 4.08 (d, *J* = 3.1 Hz, 1H), 4.06 (d, *J* = 3.0 Hz, 1H), 4.05 – 4.01 (m, 2H), 3.87 (dd, *J* = 11.0, 7.2 Hz, 1H), 3.82 – 3.77 (m, 2H), 3.76 – 3.62 (m, 13H), 3.60 (dt, *J* = 10.2, 6.2 Hz, 1H, H-7), 2.43 – 2.34 (m, 2H, H-8), 2.13 – 2.06 (m, 15H, Ac), 2.04 (s, 3H, Ac). ^{13}C NMR (214 MHz, D_2O) δ 174.63, 174.56, 174.54, 174.49 (C=O, Ac), 135.89 (C-9), 116.45

(C-10), 98.78 (C-1), 98.23 (C-1), 98.20 (C-1), 98.18 (C-1), 98.17 (C-1), 96.70 (C-1), 76.85, 76.33, 76.29, 76.26, 76.21, 71.57, 71.31, 71.26, 71.03, 70.88, 68.67, 67.51, 67.12 (C-7), 67.08, 66.79, 66.62, 66.60, 66.49, 60.52 (C-6), 60.45 (C-6), 60.39, 59.53 (C-6), 59.50 (C-6), 59.47 (C-6), 50.30, 50.27, 50.26, 50.13 (C-2), 33.01 (C-8), 21.92 (CH_3), 21.90 (CH_3), 21.86 (CH_3). HR-MS: Calculated for $C_{58}H_{95}N_9O_{35}$ $[M+H]^+$: 1478.6009, found: 1478.6003.

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