Universiteit
Leiden
The Netherlands

Chemical synthesis of fragments of galactosaminogalactan and pel polysaccharides

Zhang, Y.

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Chapter 3

Synthesis of GAG hetero-oligomers featuring α-galactose, α-galactosamine and α-*N*-acetyl galactosamines linkages

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Introduction

Galactosaminogalactan (GAG), a heteropolysaccharide that is bound to and secreted by the hyphae of *Aspergillus fumigatus,* has been identified as an important factor during infection and invasion of this pathogen into the host. It is not only required for biofilm formation and adherence of the fungus to host cells, but GAG also hides the immunostimulatory β-glucans from the host immune system and inhibits the generation of proinflammatory T-helper 1 and T-helper 17 cytokines.[1-6] Given the multiple roles that GAG plays in pathogenesis, the biosynthetic pathway of GAG is a promising target for the development of novel antifungal therapies. Sheppard's group proposed a biosynthesis route through gene disruption and structural and biochemical studies.[1, 7] At the start of the biosynthesis the cytosolic enzyme glucose-4 epimerase (Uge3) transforms UDP-*N*-GlcNAc

and UDP-Glc into UDP-*N*-GalNAc and UDP-Gal. It is postulated that the glycosyl transferase Gtb3 uses these substrates for linking of the saccharides and subsequent export of the polymer to the extracellular space. Three other enzymes with carbohydrate modifying capacity were discovered of which the hydrolases Sph3 and Ega3 seem to be involved in the export of the mature GAG polymer. Lastly, the enzyme Agd3 deacetylates GalNAc residues in the secreted GAG polymer, a process that is required for adhesion to the surface of hyphae and biofilm formation.

To deepen the insight of the biosynthesis of GAG at the molecular level and characterize the enzymes involved therein, well-defined fragments of GAG polymers are indispensable tools. Chapter 2 described the successful synthesis of homo-oligomers of Gal, GalN and GalNAc up to a dodecasaccharide by application of Kiso's di-*tert*-butylsilyene (DTBS)-directed α-selective galactosylation methodology.[8-15] The Gal, GalN and GalNAc constituents are interconnected through 1,4-*cis* glycosidic linkages but their distribution in the GAG polymer is unknown. It is likely that this structural variation is important for the interaction with both fungal biosynthesis enzymes and the host immune system. On this basis attention was focused on the construction of four sets of α-1,4 linked hetero-oligomers composed of: (i) GalN and GalNAc, (ii) Gal, GalN and GalNAc, (iii) Gal and GalN, (iv) Gal and GalNAc (Figure 1). To enable the assembly of these hetero-oligosaccharides, the same methodology as outlined in Chapter 2 will be used, requiring the availability of glycosyl donors **1**, **2** and **3** as well as the hexanoic acid spacer. The Gal donor **1** and $GalN_3$ donor **2** will serve as precursors for Gal and GalN, respectively. The trichloroacetamide donor **3**, the neighboring-group participation capacity of which is lost by the presence of the 4,6-O-DTBS group, will be used for the introduction of α-GalNAc moieties.

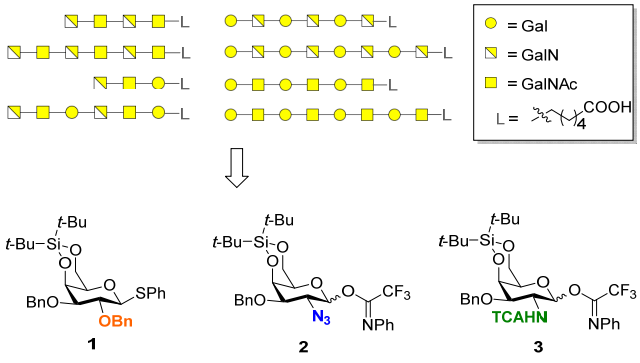


Figure 1. The designed GAG hetero-oligomers and building blocks utilized to prepare the GAG fragment library.

Results and discussion

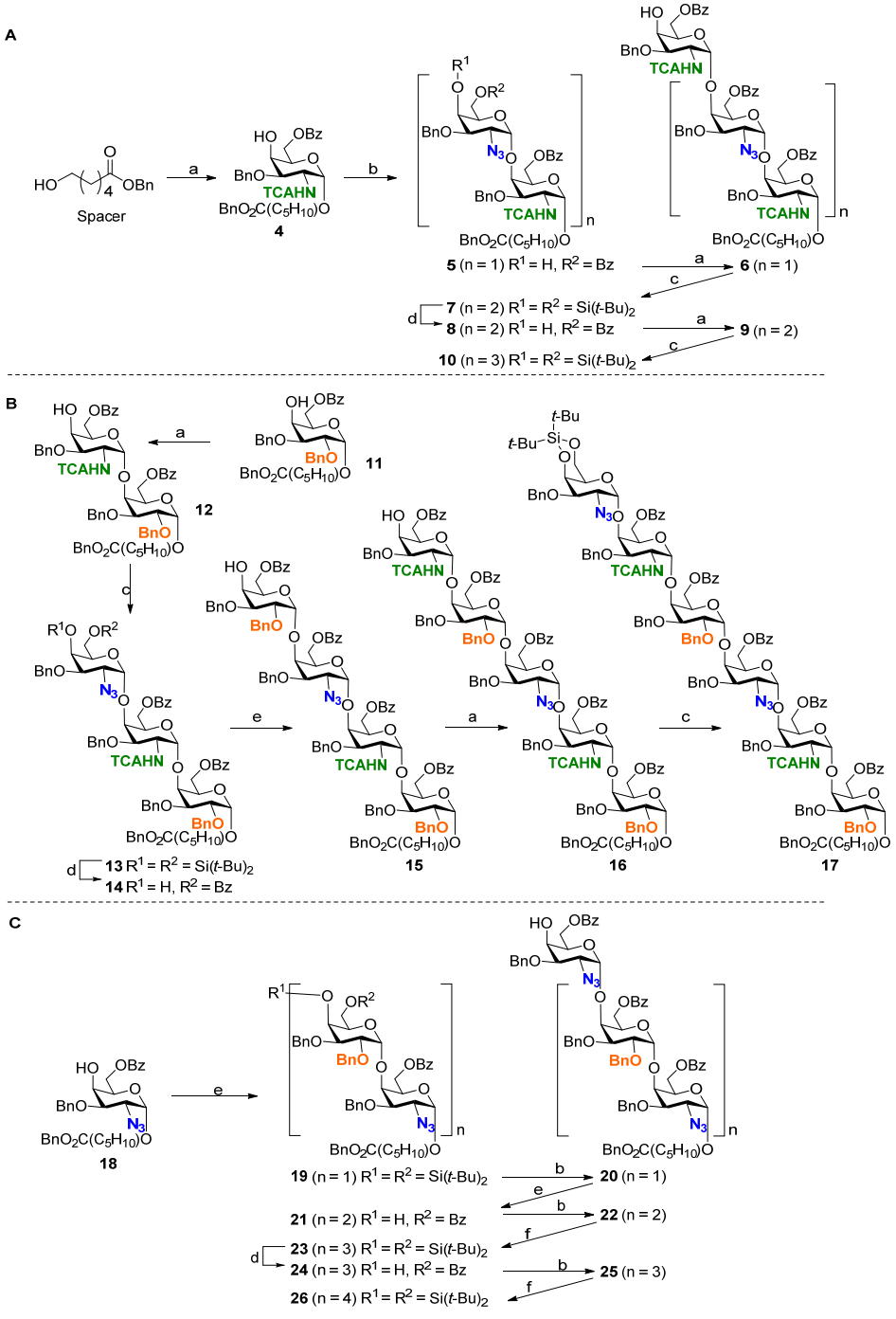
The projected GAG oligomers were constructed by the same elongation cycle as described in Chapter 2, comprising the following three reactions: 1) DTBS-directed glycosylation; 2) DTBS-removal with HF/pyridine and 3) selective benzoylation of the primary alcohol group with benzoyl-hydroxybenzotriazole (BzOBt) as a mild acylating agent[16].

The assembly of hetero-oligomers containing alternating $GalN_3$ and GalNTCA is depicted in Scheme 1A. The synthesis of the fully protected oligomers **7** and **10** started with the triflic acid mediated condensation of the GalNTCA-donor **3** with the spacer benzyl 6-hydroxyhexanoate. Even though donor **3** is equipped with a C-2-trichloroacetamide group, intrinsically capable of neighboring group participation, the α-linked product was selectively formed (94% yield, α/β = 8:1) when the reaction was performed at 0 °C. Lowering the temperature to -20 °C increased the selectivity to 14:1 (α/β). The α-linked product was then transformed into the C4-OH acceptor **4**, using the desilylation-benzoylation sequence as described above. Next, the $GalN_3$-GalNTCA dimer **5** was obtained by coupling of **4** with $GalN_3$ donor **2**, followed by protective group manipulation in which DTBS is replaced by the benzoyl at the C6-OH (80% yield over three steps). Repetition of the elongation cycle, using alternatively GalNTCA donor **3** and $GalN_3$ donor **2** in the coupling step afforded after two cycles tetrasaccharide **7** and after another two cycles hexasaccharide **10**.

The assembly of hetero-oligomers containing alternating Gal, GalNTCA and $GalN_3$ is depicted in Scheme 1B. Fully protected hexasaccharide **17** was synthesized using donors **1**, **2** and **3** in combination with the above-described elongation cycle. Thus, spacer containing acceptor Gal acceptor **11** (See Chapter 2) in combination with GalNTCA donor **3** delivered Gal-GalNTCA dimer **12**. Elongation of this dimer with $GalN_3$ **2** delivered the trisaccharide **14**, featuring the three structural C2 modifications. Similar elongation of **14**, using consecutively donors **1**, **3** and **2** in the coupling step furnished the fully protected hexasaccharide **17**.

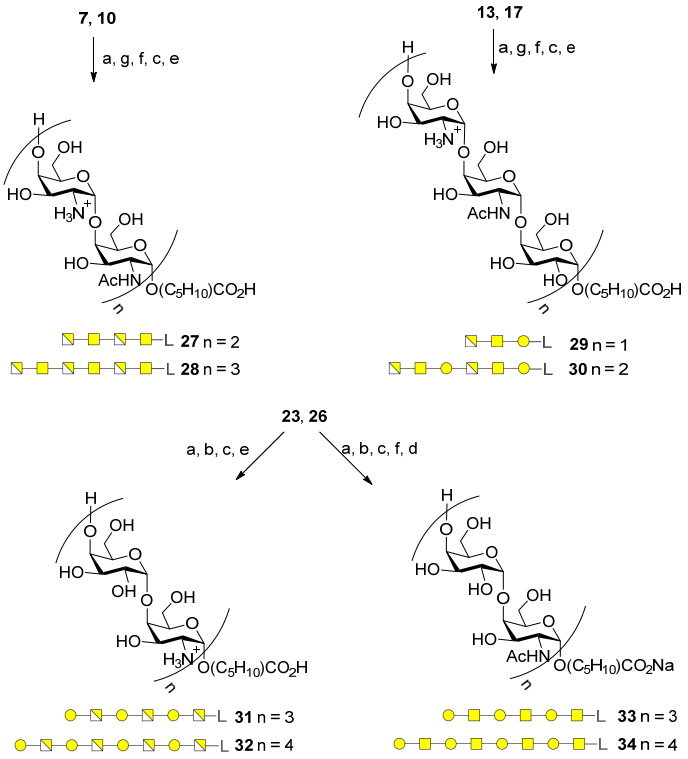
The remaining two sets of oligomers featuring Gal and GalN or Gal and GalNAc are accessible from the same protected oligomers, the synthesis route of which is shown in Scheme 1C. Known $GalN_3$ acceptor **18** (Chapter 2) was coupled with Gal donor **1**, affording the Gal-$GalN_3$ dimer **19** in 77% yield. After the same two step protecting group manipulation sequence, dimer **20** was elongated seven times, using the same cycle with consecutively $GalN_3$ donor **2**, and Gal donor **1** in the coupling step. All elongations, including the cycles to the protected hexamer **23** and octamer **26,** containing 3 and 4 Gal-$GalN_3$ repeating units

proceeded uneventfully, showing the chemistry developed to be applicable to any type of GAG-target.



Scheme 1. Synthesis of heteropolymers of Gal, $GalN_3$ and GalNTCA. a) i) **3**, TfOH, 4Å MS, DCM, 0 °C; ii) HF/pyridine (70%), THF, rt; iii) BzOBt, Et_3N, DCM, rt, yields (over 3 steps) for **4**: 70% or 69% (-20 °C); for **6**: 76%; for **9**: 78%; for **12**: 78%; for **16**: 63%. b) i) **2**, TfOH, 4Å MS, DCM, 0 °C; ii) HF/pyridine (70%), THF, rt; iii) BzOBt, Et_3N, DCM, rt, yields (over 3 steps) for **5**: 80%; for **20**: 83%; for **22**: 80%; for 2**5**: 79%. c) **2**, TfOH, 4Å MS, DCM, 0 °C, for **7**: 91%; for **10**: 86%; for **13**: 86%; for **17**: 73%. d) i) HF/pyridine (70%), THF, rt; ii) BzOBt, Et_3N, DCM, rt, yields (over 2 steps) for **8**: 86%; for **14**: 88%; for **24**: 91%. e) i) **1**, NIS, TfOH, 4Å MS, DCM, 0 °C, 87%; ii) HF/pyridine (70%), THF, rt, 97%; iii) BzOBt, Et_3N, DCM, rt, yields (over 3 steps) for **15**: 92%; for **19**: 77%; for **21**: 75%. f) **1**, NIS, TfOH, 4Å MS, DCM, 0 °C, for **23**: 82%; for **26**: 80%.

With all protected GAG hetero-oligomers available attention was directed to the removal of all protecting groups in each type of GAG oligomer (Scheme 2). The GalN-GalNAc tetra- and hexasaccharide **27** and **28**, were obtained from the fully protected $GalN_3$-GalNTCA tetramer **7** and hexamer **10** in 34% and 44% yield, respectively by the following sequence of events; 1) removal of the silylidene ketal, 2) saponification of the benzoates, benzyl ester and trichloroacetamides, 3) acetylation of the exposed amines, 4) hydrogenolysis of the benzyl ethers and reduction of the azides, 5) ion exchange to give the ammonium function chloride counterions. Next, the GalN-GalNAc-Gal-trisaccharide **29** and hexasaccharide **30** were generated in 68% and 65% yield, respectively from the fully protected progenitors **13** and **17** using the same deprotection procedure. Finally, the fully protected Gal-$GalN_3$ hexamer **23** and octamer **26** were subjected to the following four steps: 1) removal of the silylidene ketal; 2) saponification of the benzoates and benzyl ester; 3) hydrogenolysis the benzyl ethers and reduction of the azides; and 4) ion exchange, delivering **31** and **32** in 62% and 55% yield respectively. The corresponding Gal-GalNAc oligomers were also generated from Gal-$GalN_3$ hexamer **23** and octamer **26**, by acetylation of the released amines after the third reaction to afford **33** and **34** in 54% and 59%, respectively, after an ion exchange.



Scheme 2. Deprotection of synthesized oligosaccharides. a) HF/pyridine (70%), THF, 0 °C to rt; b) 1M NaOH, THF, MeOH; c) $Pd(OH)_2/C$, THF/H_2O/*t*-BuOH, H_2; d) Dowex-Na^+, **33**: 54%; **34**: 59%. e) Amberlite Cl form, **27**: 34%; **28**: 44%; **29**: 68%; **30**: 65%; **31**: 62%; **32**: 55%. f) Ac_2O, $NaHCO_3$, H_2O/THF, g) 2M NaOH, THF, MeOH.

In the groups of Sheppard and Howell, the GAG oligomers, described above and in the previous Chapter, have been used to investigate the glycosidases and deacetylase involved in the GAG-biosynthetic pathway. The α-1,4-GalNAc hexamers and heptamers were treated with the Sph3 hydrolase to determine the minimum substrate length that can be cleaved by $Sph3_h$ and the degradation products were analyzed by MALDI-TOF MS fingerprinting.[17] As shown in Figure 2B and 2C, GalNAc heptasaccharides but not hexamers were rapidly hydrolyzed by the enzyme $Sph3_h$, indicating that the minimum substrate size of the hydrolase Sph3 is seven. Hydrolysis of GalNAc heptamer by $Sph3_h$ resulted in the accumulation of pentasaccharides (Figure 2C), suggesting that it functions as an endo-α-1,4-*N*-acetylgalactosaminidase. In contrast, Ega 3 was shown to be only capable of cleaving GalN linkages and a 24-h treatment of α-1,4-$(GalN)_9$ with Ega3 resulted in the disappearance of this nonamer and emergence of trisaccharide products suggesting that Ega3 also acts as

endoglycosidase (Figure 2D).[18] Figure 2E shows the substrate specificity of the deacetylase Agd3 using the synthesized GAG oligosaccharides.[3] No statistically significant difference was found between the binding of $(GalNAc)_6$ and $(GalNAc)_7$, suggesting that the binding site spans six or fewer residues. Agd3 binding of $(Gal)_6$ was negligible, suggesting that Agd3 is specific for regions of the GAG polymer that are GalNAc/GalN rich. Interestingly, there was slight, but significant, higher affinity for a mixed GalN-GalNAc oligosaccharide (Ka 400 ± 90M^{-1}). This finding suggests that partial deacetylation of the polymer could lead to higher affinity, and hence accelerated deacetylation after the initial deacetylation events have occurred.

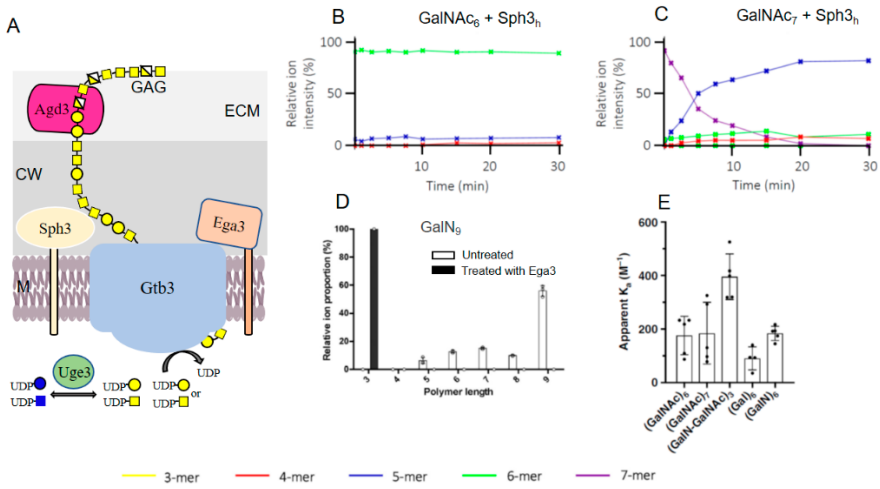


Figure 2. A) Biosynthetic pathway of GAG polysaccharide. B) $Sph3_h$ degradation kinetic of α-1,4-GalNAc 6-mers. C) $Sph3_h$ degradation kinetics of α-1,4-GalNAc 7-mers. D) MS analyses of α-1,4-GalNAc 9-mers before (*white bars*) and after treatment with 10_M Ega3 for 24 h (*black bars*). E) Apparent K_a (M^{-1}) for Agd3 for α-1,4-linked carbohydrate ligands determined by a direct ESI-MS assay.

Conclusion

In conclusion, the palette of GAG homo-oligomers was significantly expanded by the assembly of GAG hetero-oligomers incorporating all possible natural structural variations. The developed strategy, based on the use of silylidene protected Gal or GalN donors proved to be effective for the introduction of all required *cis*- Gal/GalN linkages in a highly stereoselective manner. These synthetic GAG fragments have allowed to map substrate specificities of the enzymes Sph3, Ega3 and Agd3 involved in the biosynthetic pathway of GAG. Sph3 and Ega3 were found to be endoglycosidases, with the former cleaving *N*-acetylgalactosamine linkages and the latter only capable of hydrolysing galactosamine linkages. The deacetylase Agd3 is specific for GAG polymers and has higher affinity for partially deacetylated polymers. The chemistry described here may be used to generate fluorogenic substrates that can be used in the discovery of inhibitors of these enzymes and in the conception of endo-galactosaminidase probes and inhibitors to further explore and exploit the GAG-biomachinery in the development of anti-fungal agents.

Experimental section

General procedure for glycosylation with thiodonor 1 (procedure A)

The donor (1.5 – 3.0 eq) and the 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 3Å. The solution was cooled to 0 ºC, after which NIS (2.0 – 6.0 eq) and TfOH (0.1 – 0.3 eq) were added. The reaction was stirred at 0 ºC until TLC-analysis showed complete conversion of the acceptor. The reaction was quenched with saturated $Na_2S_2O_3$, 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 glycosylation with imidate donors (2, 3) (procedure B)

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 C)

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).

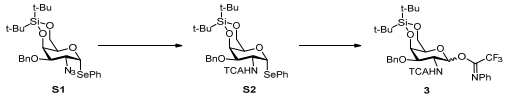
General procedure for selective benzoylation of primary alcohol (general procedure D)

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).

General procedure for saponification and hydrogenation of the oligosaccharides (general procedure E)

1 M NaOH solution was added to the mixture of the starting material in THF/MeOH (2 ml/0.9 ml) at 0 ºC. The solution was warmed to room temperature slowly and stirred overnight. The reaction was cooled to 0 ºC and neutralized by Amberlite IR120 (H+) resin. After filtration, the filtrate was concentrated *in vacuo*. The residue was dissolved in THF/H_2O/*tert*-BuOH (2 ml/2 ml/0.8 ml) before a catalytic amount of $Pd(OH)_2/C$ was added. The reaction mixture was stirred for 3 days under a H_2 atmosphere, filtered and concentrated *in vacuo*. A white powder was obtained, which was purified by gel filtration (HW-40, 0.15M NH_4OAc in H_2O). The products were transformed into the sodium salts over a short Dowex Na^+ column or chloride salts in the mixture of Ambelite (Cl form) and water, after which the compounds were lyophilized.

Experimental Procedures and Characterization Data of Products



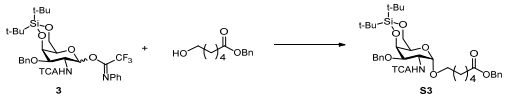
Phenyl 3-*O*-benzyl-2-deoxy-1-seleno-4,6-di-*tert*-butylsilylidene-2-trichloroacetamido-α-D-galactopyranoside (S2)

1,3-Dithiolpropane (5.1 ml, 51 mmol) and trimethylamine (5.9 ml, 42.5 mmol) were added to the solution of compound **S1** in pyridine/water (32 ml/8ml). 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 30 ml pyridine, after which TCACl (1.4 ml, 12.8 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 = 40:1 – 15:1). Compound **S2** (5.42 g, 92% yield, pentane: EtOAc = 10:1, R*f* = 0.40-0.50) was obtained as white solid. $[\alpha]_D^{25}$ +148.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 653, 740, 798, 824, 1070, 1082, 1163, 1475, 1508, 1717, 2859, 2933, 3417. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.55 – 7.49 (m, 2H), 7.41 – 7.22 (m, 8H), 6.90 (d, *J* = 7.0 Hz, 1H, *N*H), 6.14 (d, *J* = 4.7 Hz, 1H, H-1), 4.83 – 4.73 (m, 2H, *CHH*, H-2), 4.70 (d, *J* = 2.8, 1H, H-4), 4.58 (d, *J* = 11.8 Hz, 1H, *CHH*), 4.33 (dd, *J* = 12.6, 2.2 Hz, 1H, H-6), 4.17 (dd, *J* = 12.7, 1.6 Hz, 1H, H-6), 4.06 (q, *J* = 1.6 Hz, 1H, H-5), 3.51 (dd, *J* = 11.0, 2.7 Hz, 1H, H-3), 1.08 (s, 9H, *CH*$_3$), 1.07 (s, 9H, *CH*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.75 (*CONH*), 137.45, 134.49, 134.44, 134.39, 129.45, 128.81, 128.59, 128.24, 128.21, 127.90, 92.53 (*CCl*$_3$), 89.20 (C-1), 76.55 (C-3), 70.94 (C-5), 69.72 (*CH*$_2$), 69.07 (C-4), 67.28 (C-6), 51.03 (C-2), 27.75 (*CH*$_3$), 27.41 (*CH*$_3$), 23.54, 20.92 (C-*Si*). HR-MS: Calculated for $C_{29}H_{38}Cl_3NO_5SiSe$ $[M+H]^+$: 694.0828, found: 694.0819.

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

NIS (1.76 g, 7.83 mmol) was added to the solution of compound **S2** (3.87 g, 5.59 mmol) in Acetone/H_2O (30 ml/3 ml) at 0 ºC. The reaction was slowly warmed to room temperature stirred for about 2 hours. Then the mixture was

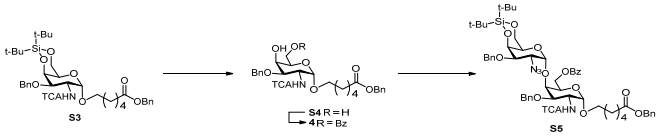
diluted with DCM and washed with saturated $Na_2S_2O_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (pentane:EtOAc = 3:1) to get S2. $Cs_{2C}O_3$ was added to the solution of hemiacetal S2 in 30 ml acetone. The mixture was stirred at 0 °C for 15 minutes. Then CF_{3C}(=NPh)Cl (1.38 g, 6.68 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 = 10:1-5:1). Compound **3** (3.20 g, 79% yield, pentane: Et_2O = 5:1, R*f* = 0.25-0.35) was obtained as white solid. ^{1}H-NMR ($CDCl_3$, 500 MHz, 333 K) δ 7.90 (s, 1H), 7.56 – 7.49 (m, 1H), 7.39 – 7.18 (m, 10H), 7.11 – 7.04 (m, 1H), 6.80 – 6.74 (m, 2H), 6.56 (d, *J* = 7.4 Hz, 1H), 6.51 (bs, 1H, H-1α), 6.14 (bs, H-1β), 4.78 (d, *J* = 11.8 Hz, 1H), 4.75 – 4.65 (m, 2H), 4.59 (d, *J* = 11.9 Hz, 1H), 4.32 – 4.16 (m, 2H), 3.79 (dd, *J* = 11.0, 2.6 Hz, 1H), 3.72 (s, 1H), 1.14 – 1.03 (m, 20H). ^{13}C NMR (125 MHz, $CDCl_3$, 333K) δ 161.96, 143.06, 137.38, 135.18, 129.22, 128.66, 128.56, 128.54, 128.43, 128.01, 127.97, 127.90, 127.81, 127.71, 126.23, 124.51, 124.26, 120.56, 119.33, 119.28, 117.34, 94.70 (C-1α), 93.65 (C-1β), 92.35, 75.61, 74.38, 72.38, 70.79, 70.20, 69.84, 69.07, 68.97, 66.80, 66.77, 53.82, 49.53, 27.54, 27.52, 27.31, 27.16, 23.28, 20.70. HR-MS: Calculated for $C_{31}H_{38}Cl_{3F3}N_2O_6Si$ $[M+Na]^+$: 747.1415, found: 747.1409.



6-(Benzyl hexanoyl) 3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-2-trichloroacetamido-α-D-galactopyranoside (S3)

The reaction was carried out according to the general procedure B. The donor **3** (2.0 g, 2.76 mmol) and linker alcohol (613 mg, 2.76 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 27 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to -20 °C, after which TfOH (25 µl, 0.28 mmol) was added. The reaction was stirred at -20 °C 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 **S3** (2.09 g, 88% yield, pentane: EtOAc = 3:1, R*f* = 0.65-0.75) was obtained as yellow syrup. α isomer: $[\alpha]_D^{25}$ +87.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 651, 678, 697, 736, 763, 796, 823, 863, 920, 974, 1003, 1029, 1047, 1066, 1080, 1100, 1172, 1474, 1511, 1724, 2858, 2929, 3429. ^{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 (CH_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 $C_{36}H_{50}Cl_3NO_8Si$ $[M+NH_4]^+$: 775.2715, found: 775.2707. β isomer: $[\alpha]_D^{25}$ +87.2 (c=1, $CHCl_3$). 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 ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.25 (m, 10H, aromatic H), 6.95 (d, *J* = 7.1 Hz, 1H, *N*H), 5.10 (s, 2H, *C*H$_2$*Ph*), 4.94 (d, *J* = 8.3 Hz, 1H, H-1), 4.68 (d, *J* = 11.5 Hz, 1H, *C*H$_2$*Ph*), 4.58 (d, *J* = 11.5 Hz, 1H, *C*H$_2$*Ph*), 4.51 (d, *J* = 2.9 Hz, 1H, H-4), 4.27 – 4.14 (m, 3H, H-3, 6), 3.90 – 3.69 (m, 2H, H-2, 7), 3.48 (dt, *J* = 9.7, 6.4 Hz, 1H, H-7), 3.37 (s, 1H, H-5), 2.33 (t, *J* = 7.6 Hz, 2H, H-11), 1.70 – 1.50 (m, 4H, H-10, 8), 1.43 – 1.30 (m, 2H, H-9), 1.10 – 1.04 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.66 (C-12), 161.98 (C*ONH*), 137.87, 136.18, 128.68, 128.66, 128.61, 128.31, 128.23, 128.11, 127.79 (aromatic C/C*H*), 98.91 (C-1), 92.73 (C*Cl*$_3$), 75.70 (C-3), 71.36 (C-5), 71.02 (C*H*$_2$*Ph*), 69.45 (C-7), 69.42 (C-4), 67.47 (C-6), 66.24 (C*H*$_2$*Ph*), 55.18 (C-2), 34.29 (C-11), 29.33 (C-8), 27.71 (C*H*$_3$), 27.67 (C*H*$_3$), 25.68 (C-9), 24.74 (C-10), 23.56 (C-*Si*), 20.93 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 98.91 ($J_{C1,H1}$ = 162 Hz). HR-MS: Calculated for $C_{36}H_{50}Cl_3NO_8Si$ $[M+NH_4]^+$: 775.2715, found: 775.2705.



6-(Benzyl hexanoyl) 3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranoside (S4)

The reaction was carried out according to the general procedure C using compound **S3** (1.12 g, 1.47 mmol) and HF/pyridine (70%, 612 µl, 23.6 mmol). The product was purified by column chromatography (pentane:EtOAc = 1:1). Compound **S4** (982 mg, 92% yield, pentane:EtOAc = 1:2, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +68.9 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 820, 1029, 1052, 1098, 1152, 1713, 2872, 2933, 3421. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.44 – 7.19 (m, 10H, aromatic H), 6.84 (d, *J* = 9.2 Hz, 1H, *N*H), 5.10 (s, 2H, *C*H$_2$*Ph*), 4.91 (d, *J* = 3.7 Hz, 1H, H-1), 4.68 (d, *J* = 11.9 Hz, 1H, *C*H$_2$*Ph*), 4.53 (d, *J* = 12.3 Hz, 1H, *C*H$_2$*Ph*), 4.46 (ddd, *J* = 10.6, 9.2, 3.7 Hz, 1H, H-2), 4.19 (d, *J* = 3.0 Hz, 1H, H-4), 3.97 – 3.75 (m, 3H, H-5, 6), 3.75 – 3.61 (m, 2H, H-3, 7), 3.39 (dt, *J* = 10.0, 6.4 Hz, 1H, H-7), 3.10 (bs, 1H, *O*H), 2.34 (t, *J* = 7.4 Hz, 2H, H-11), 1.74 – 1.47 (m, 4H, H-10, 8), 1.41 – 1.28 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.45 (C-12), 161.77 (C*ONH*), 137.28, 135.92, 128.56, 128.24, 128.16, 127.99, 127.71 (aromatic C/C*H*), 96.96 (C-1), 92.65 (C*Cl*$_3$), 76.00 (C-3), 71.10 (C*H*$_2$*Ph*), 69.93 (C-5), 67.88 (C-7), 66.20 (C*H*$_2$*Ph*), 66.19 (C-4), 62.42 (C-6), 50.50 (C-2), 34.05 (C-11), 28.88 (C-8), 25.70 (C-9), 24.53 (C-10). HR-MS: Calculated for $C_{28}H_{34C}l_3NO_8$ $[M+H]^+$: 618.1428, found: 618.1423.

6-(Benzyl hexanoyl) 6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranoside (4)

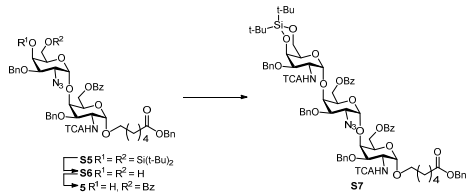
The reaction was carried out according to the general procedure D using compound **S4** (950 mg, 1.54 mmol), PhCOOBt (1.84 g, 7.70 mmol) and Et_3N (1.2 ml, 8.50 mmol). The product was purified by column chromatography

(pentane:EtOAc = 4:1). Compound **4** (1.01 g, 91% yield, pentane:EtOAc = 3:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +57.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 780, 821, 839, 1027, 1050, 1065, 1100, 1126, 1153, 1241, 1278, 1294, 1316, 1341, 1452, 1523, 1706, 2869, 2938, 3327, 3499. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.06 – 8.00 (m, 2H, *C*H, Bz), 7.59 – 7.22 (m, 13H), 6.82 (d, *J* = 9.2 Hz, 1H, *N*H), 5.08 (s, 2H, *C*H_2*Ph*), 4.92 (d, *J* = 3.7 Hz, 1H, H-1), 4.69 (d, *J* = 11.9 Hz, 1H, *C*H_2*Ph*), 4.63 (dd, *J* = 11.5, 4.7 Hz, 1H, H-6), 4.60 – 4.53 (m, 2H, *C*H_2*Ph*, H-6), 4.50 (ddd, *J* = 10.5, 9.2, 3.8 Hz, 1H, H-2), 4.17 (d, *J* = 2.6 Hz, 1H, H-4), 4.09 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H, H-5), 3.72 (dd, *J* = 10.6, 3.0 Hz, 1H, H-3), 3.65 (dt, *J* = 10.0, 6.5 Hz, 1H, H-7), 3.40 (dt, *J* = 10.0, 6.6 Hz, 1H, H-7), 2.28 (t, *J* = 7.4 Hz, 2H, H-11), 1.65 – 1.49 (m, 4H, H-10, 8), 1.33 – 1.23 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.27 (C-12), 166.32 (C=O, Bz), 161.69 (C*ONH*), 137.20, 135.94, 133.18, 130.05, 129.81, 129.61, 128.58, 128.53, 128.41, 128.37, 128.33, 128.21, 128.12, 128.04, 127.73, 127.70 (aromatic C/C*H*), 96.87 (C-1), 92.65 (C*Cl*$_3$), 76.03 (C-3), 71.41 (CH_2*Ph*), 68.22 (C-5), 67.93 (C-7), 66.12 (CH_2*Ph*), 65.68 (C-4), 64.14 (C-6), 50.43 (C-2), 33.99 (C-11), 28.82 (C-8), 25.64 (C-9), 24.45 (C-10). ^{13C}-HMBC ($CDCl_3$, 100 MHz): 96.87 ($J_{C1,H1}$ = 171 Hz). HR-MS: Calculated for $C_{35}H_{38}Cl_3NO_9$ $[M+H]^+$: 722.1690, found: 722.1685.

6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranoside (S5)

The reaction was carried out according to the general procedure B. The donor **2** (2.35 g, 3.88 mmol) and the acceptor **4** (1.12 g, 1.55 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 16 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TfOH (14 µl, 0.16 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 = 6:1). Compound **S5** (1.69 g, 92% yield, pentane: EtOAc = 5:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +107.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 738, 796, 823, 980, 1009, 1027, 1046, 1063, 1105, 1168, 1271, 1454, 1508, 1721, 2112, 2859, 2933, 3424. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.09 – 8.01 (m, 2H, *C*H, Bz), 7.61 – 7.22 (m, 1H), 7.50 – 7.42 (m, 4H), 7.40 – 7.22 (m, 14H, aromatic H), 6.83 (d, *J* = 9.5 Hz, 1H, *N*H), 5.10 - 5.06 (m, 3H, *C*H_2*Ph*, H-1^B), 4.98 (d, *J* = 3.7 Hz, 1H, H-1^A), 4.82 – 4.48 (m, 8H, *C*H_2*Ph*, H-2^A, 6^A, 4^B), 4.27 (d, *J* = 2.6 Hz, 1H, H-4^A), 4.16 (q, *J* = 1.6 Hz, 1H, H-5^B), 4.11 (t, *J* = 6.8 Hz, 1H, H-5^A), 4.04 (dd, *J* = 10.6, 2.7 Hz, 1H, H-3^B), 3.94 (dd, *J* = 10.6, 3.5 Hz, 1H, H-2^B), 3.73 – 3.63 (m, 4H, H-3^A, 6^B, 7), 3.44 (dt, *J* = 10.0, 6.5 Hz, 1H, H-7), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.65 – 1.50 (m, 4H, H-10, 8), 1.36 – 1.22 (m, 2H, H-9), 1.06 – 0.96 (m, 18H, *C*H_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.24 (C-12), 166.08 (C=O, Bz), 161.81 (C*ONH*), 137.90, 137.15, 136.01, 133.43, 129.71, 129.64, 128.61, 128.59, 128.55, 128.50, 128.29, 128.21, 128.09, 127.81, 127.79, 126.99 (aromatic C/C*H*), 99.44 (C-1^B), 97.01 (C-1^A), 92.70 (C*Cl*$_3$), 76.24 (C-3^A), 76.05 (C-3^B), 72.46 (C-4^A), 71.77 (CH_2*Ph*), 70.68 (CH_2*Ph*), 69.60 (C-4^B), 69.08 (C-5^A), 68.06 (C-7), 67.96 (C-5^B), 66.91 (C-6^B), 66.19 (CH_2*Ph*), 62.76 (C-6^A), 58.84 (C-2^B), 50.89 (C-2^A), 34.05 (C-11), 28.94 (C-8), 27.65 (3xCH_3), 27.38 (3xCH_3), 25.72 (C-9), 24.52 (C-10),

23.33 (C-*Si*), 20.74 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 99.44 ($J_{C1,H1}$ = 170Hz), 97.01 ($J_{C1,H1}$ = 173Hz). HR-MS: Calculated for $C_{56}H_{69}Cl_3N_4O_{13}Si$ $[M+H]^+$: 1139.3774, found: 1139.3769.



6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranoside (S6)

The reaction was carried out according to the general procedure C using compound **S5** (1.65 g, 1.45 mmol) and HF/pyridine (70%, 0.6 ml, 23.2 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:1 - 1:1). Compound **S6** (1.35 g, 93% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +77.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 555, 698, 713, 736, 820, 1027, 1046, 1154, 1272, 1315, 1453, 1511, 1717, 2110, 2872, 2929, 3421, 3500. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 8.00 (m, 2H, *C*H, Bz), 7.62 – 7.53 (m, 1H), 7.52 – 7.22 (m, 18H, aromatic H), 6.88 (d, *J* = 9.4 Hz, 1H, *N*H), 5.07 (s, 2H, *CH*$_2$*Ph*), 5.04 (d, *J* = 3.6 Hz, 1H, H-1^B), 4.97 (d, *J* = 3.7 Hz, 1H, H-1^A), 4.80 – 4.63 (m, 5H, *CH*$_2$*Ph*, H-6^A), 4.59 – 4.49 (m, 2H, *CHHPh*, H-2^A), 4.27 – 4.15 (m, 3H, H-4^B, 5^B, 4^A), 4.10 (t, *J* = 6.8 Hz, 1H, H-5^A), 4.03 (dd, *J* = 10.5, 3.0 Hz, 1H, H-3^B), 3.90 (dd, *J* = 10.4, 3.5 Hz, 1H, H-2^B), 3.75 – 3.63 (m, 2H, H-3^A, 7), 3.54 – 3.37 (m, 3H, H-6^B, 7), 2.97 (bs, 1H, *O*H), 2.50 (bs, 1H, *O*H), 2.29 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.49 (m, 4H, H-10, 8), 1.35 – 1.22 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.23 (C-12), 166.04 (C=O, Bz), 162.01 (C*ONH*), 137.21, 137.13, 135.92, 133.37, 129.62, 129.55, 128.60, 128.55, 128.23, 128.14, 128.06, 127.96, 127.33 (aromatic C/C*H*), 99.64 (C-1^B), 96.91 (C-1^A), 92.53 (C*Cl*$_3$), 76.76 (C-3^B), 76.06 (C-3^A), 73.87 (C-4^A), 71.89 (C*H*$_2$*Ph*), 71.81 (C*H*$_2$*Ph*), 69.87 (C-5^B), 69.07 (C-5^A), 68.03 (C-7), 67.39 (C-4^B), 66.14 (C*H*$_2$*Ph*), 62.69 (C-6^A), 62.54 (C-6^B), 59.79 (C-2^B), 50.91 (C-2^A), 33.98 (C-11), 28.85 (C-8), 25.64 (C-9), 24.44 (C-10). HR-MS: Calculated for $C_{48}H_{53}Cl_3N_4O_{13}$ $[M+H]^+$: 999.2753, found: 999.2748.

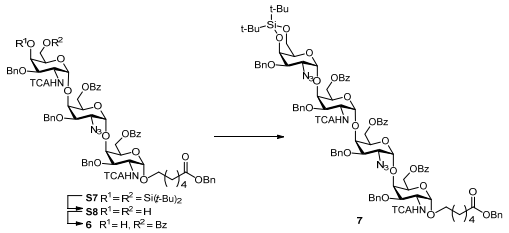
6-(Benzyl hexanoyl) 2-azido-6-O-benzoyl-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranoside (5)

The reaction was carried out according to the general procedure D using compound **S6** (1.31 g, 1.31 mmol), PhCOOBt (1.41 g, 5.90 mmol) and Et_3N (913 µl, 6.55 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **5** (1.36 g, 94% yield, pentane:EtOAc = 3:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +88.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 689, 698, 711, 736, 820, 1027, 1049, 1109, 1156, 1271, 1315, 1452, 1511, 1717, 2111, 2871, 2929, 3486, 3506. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.09 – 8.01 (m, 2H, *C*H, Bz), 7.98 – 7.89 (m, 2H, *C*H, Bz), 7.63 – 6.98 (m, 21H, aromatic H), 6.80 (d, *J* = 9.2 Hz, 1H, *N*H), 5.09 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.08 (s, 2H, *CH*$_2$*Ph*), 5.01 (d, *J* = 3.7 Hz, 1H, H-1^A), 4.87 – 4.70 (m, 4H, 3x*CHHPh*, H-6^A), 4.69 – 4.49 (m, 4H, *CHHPh*, H-2^A, 6^A, 4^B), 4.43 (dd, *J* = 10.6, 8.7 Hz, 1H, H-6^B), 4.26 (d, *J* = 2.6 Hz, 1H, H-4^A), 4.19 – 4.07

(m, 3H, H-5^{A}, 3^{B}, 5^{B}), 3.95 – 3.83 (m, 2H, H-2^{B}, 6^{B}), 3.77 – 3.64 (m, 2H, H-3^{A}, 7), 3.44 (dt, *J* = 9.9, 6.5 Hz, 1H, H-7), 2.51 (bs, 1H, *O*H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.48 (m, 4H, H-10, 8), 1.37 – 1.20 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.32 (C-12), 166.07 (C=O, Bz), 165.97 (C=O, Bz), 161.85 (C*ONH*), 137.25, 136.99, 135.99, 133.48, 133.01, 129.90, 129.84, 129.70, 129.56, 128.67, 128.63, 128.61, 128.49, 128.45, 128.31, 128.29, 128.21, 128.18, 127.79, 127.03 (aromatic C/C*H*), 99.34 (C-1^{B}), 96.96 (C-1^{A}), 92.68 (CCl_3), 76.52 (C-3^{B}), 75.77 (C-3^{A}), 72.97 (C-4^{A}), 72.28 (CH_2Ph), 71.89 (CH_2Ph), 68.90 (C-5^{A}), 68.13 (C-7), 68.11 (C-4^{B}), 66.21 (CH_2Ph), 65.48 (C-5^{B}), 62.53 (C-6^{A}), 62.02 (C-6^{B}), 59.58 (C-2^{B}), 51.02 (C-2^{A}), 34.06 (C-11), 28.93 (C-8), 25.71 (C-9), 24.52 (C-10). HR-MS: Calculated for $C_{55}H_{57}Cl_3N_4O_{14}$ $[M+Na]^+$: 1125.2835, found: 1125.2829.

6-(Benzyl hexanoyl) 3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-6-O-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloro-acetamido-α-D-galactopyranoside (S7)

The reaction was carried out according to the general procedure B. The donor **3** (1.55 g, 2.14 mmol) and the acceptor **5** (1.31 g, 1.19 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 12 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (11 µl, 0.12 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 = 5:1). Compound **S7** (1.83 g, 93% yield, pentane: EtOAc = 3:1, R*f* = 0.50-0.60) was obtained as yellow syrup. $[\alpha]_D^{25}$ +129.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 651, 685, 697, 711, 734, 797, 820, 859, 1003, 1027, 1046, 1158, 1266, 1315, 1452, 1508, 1720, 2111, 2859, 2933, 3423. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.09 – 8.00 (m, 2H, *C*H, Bz), 7.98 – 7.91 (m, 2H, *C*H, Bz), 7.68 – 7.03 (m, 26H, aromatic H), 6.84 (d, *J* = 9.1 Hz, 1H, *N*H), 6.71 (d, *J* = 9.1 Hz, 1H, *N*H), 5.19 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.05 (d, *J* = 3.6 Hz, 1H, H-1^{B}), 4.97 (d, *J* = 3.7 Hz, 1H, H-1^{A}), 4.81 – 4.47 (m, 11H, 3x*C*H$_2$*Ph*, H-2^{A}, 6^{A}, 5^{B}, 2^{C}), 4.41 (d, *J* = 2.6 Hz, 1H, H-4^{B}), 4.39 – 4.31 (m, 2H, H-4^{C}, 6^{B}), 4.22 (d, *J* = 2.6 Hz, 1H, H-4^{A}), 4.14 – 4.05 (m, 2H, H-3^{B}, 5^{A}), 4.03 – 3.89 (m, 2H, H-5^{C}, 6^{B}), 3.77 – 3.61 (m, 5H, H-2^{B}, 3^{A}, 3^{C}, 6^{C}, 7), 3.48 – 3.30 (m, 2H, H-6^{C}, 7), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.68 – 1.48 (m, 4H, H-10, 8), 1.37 – 1.20 (m, 2H, H-9), 1.05 – 0.92 (m, 18H, 6x*C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.25 (C-12), 165.94 (C=O, Bz), 164.99 (C=O, Bz), 161.76, 161.47 (2 C*ONH*), 137.83, 137.09, 136.95, 135.97, 133.63, 133.21, 129.85, 129.61, 129.51, 129.39, 128.72, 128.59, 128.57, 128.53, 128.41, 128.28, 128.19, 128.00, 127.87, 127.85, 127.52, 126.97 (aromatic), 98.83 (C-1^{B}), 97.09 (C-1^{C}), 96.95 (C-1^{A}), 92.69 (CCl_3), 92.56 (CCl_3), 76.14 (C-3^{B}), 74.98 (C-3^{A}), 74.67 (C-3^{C}), 72.95 (C-4^{A}), 72.47, 72.22, 69.79 (3 CH_2Ph), 69.59 (C-4^{B}), 69.32 (C-4^{C}), 68.82 (C-5^{B}), 68.67 (C-5^{A}), 68.12 (C-7), 67.99 (C-5^{C}), 66.80 (C-6^{C}), 66.18 (CH_2Ph), 62.47 (C-6^{A}), 60.58 (C-2^{B}), 60.23 (C-6^{B}), 51.00 (C-2^{A}), 49.78 (C-2^{C}), 34.03 (C-11), 28.89 (C-8), 27.60 (CH_3), 27.25 (CH_3), 25.67 (C-9), 24.49 (C-10), 23.31 (C-*Si*), 20.65 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 98.83 ($J_{C1,H1}$ = 171 Hz), 97.09 ($J_{C1,H1}$ = 174 Hz), 96.95 ($J_{C1,H1}$ = 172 Hz). HR-MS: Calculated for $C_{78}H_{89}Cl_6N_5O_{19}Si$ $[M+H]^+$: 1638.4130, found: 1638.4125.



6-(Benzyl hexanoyl) 3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-6-O-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacet-amido-α-D-galactopyranoside (S8)

The reaction was carried out according to the general procedure C using compound **S7** (1.78 g, 1.09 mmol) and HF/pyridine (70%, 450 µl, 17.4 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S8** (1.55 g, 95% yield, pentane:EtOAc = 1:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +128.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 685, 700, 713, 738, 820, 1007, 1027, 1046, 1109, 1158, 1269, 1315, 1452, 1511, 1720, 2111, 2875, 2929, 3420, 3500. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.09 – 8.01 (m, 2H, *C*H, Bz), 7.97 – 7.88 (m, 2H, *C*H, Bz), 7.68 – 6.97 (m, 26H, aromatic), 6.84 (d, *J* = 9.4 Hz, 1H, *N*H), 6.77 (d, *J* = 9.2 Hz, 1H, *N*H), 5.07 (d, *J* = 5.6 Hz, 4H, *CH*$_2$*Ph*, H-1^B, 1^C), 4.97 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.87 (d, *J* = 11.6 Hz, 1H, *CHHPh*), 4.83 – 4.44 (m, 10H), 4.34 (d, *J* = 2.5 Hz, 1H, H-4^B), 4.23 (d, *J* = 2.5 Hz, 1H, H-4^A), 4.17 – 4.02 (m, 6H), 3.79 – 3.62 (m, 4H), 3.43 (dt, *J* = 9.9, 6.4 Hz, 2H), 3.34 (dd, *J* = 11.8, 4.1 Hz, 1H, H-6^C), 2.94 (bs, 1H, *O*H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.49 (m, 4H, H-10, 8), 1.38 – 1.23 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.31 (C-12), 165.99, 165.15 (2 C=O, Bz), 161.81, 161.53 (2 C*ONH*), 137.23, 137.07, 136.90, 135.97, 133.64, 133.28, 129.94, 129.63, 129.53, 129.34, 128.73, 128.68, 128.67, 128.61, 128.56, 128.44, 128.30, 128.21, 128.11, 128.07, 128.02, 127.98, 127.27 (aromatic), 98.97 (C-1^B), 97.66 (C-1^C), 97.03 (C-1^A), 92.60 (2xC*Cl*$_3$), 76.10 (C-3^B), 75.54 (C-3^A), 75.24 (C-3^C), 73.21 (C-4^A), 72.55, 72.43, 71.00 (3 C*H*$_2$*Ph*), 70.57 (C-4^B), 69.54, 68.89 (C-5^A), 68.17 (C-7), 66.58, 66.22 (C*H*$_2$*Ph*), 62.56 (C-6^A), 62.42 (C-6^C), 60.54 (C-2^B), 60.52 (C-6^B), 51.03 (C-2^A), 50.33 (C-2^C), 34.05 (C-11), 28.92 (C-8), 25.70 (C-9), 24.51 (C-10). HR-MS: Calculated for $C_{70}H_{73}Cl_6N_5O_{19}$ $[M+H]^+$: 1498.3109, found: 1498.3104.

6-(Benzyl hexanoyl) 6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-6-O-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacet-amido-α-D-galactopyranoside (6)

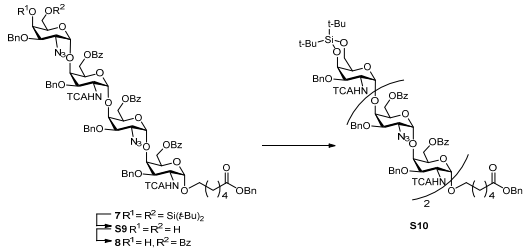
The reaction was carried out according to the general procedure D using compound **S8** (1.52 g, 1.01 mmol), PhCOOBt (1.10 g, 4.56 mmol) and Et_3N (710 µl, 5.07 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:1). Compound **6** (1.40 g, 86% yield, pentane:EtOAc = 2:1, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +114.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 689, 700, 711, 737, 820, 1027, 1047, 1109, 1159, 1269, 1315, 1452, 1508, 1717, 2111, 2879, 2931, 3420, 3504. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.13 – 8.07 (m, 2H, *C*H, Bz), 8.00 – 7.92 (m, 4H, *C*H, Bz), 7.72 – 7.47 (m, 7H), 7.45 – 7.22 (m, 19H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.13 – 7.07 (m,

1H), 7.07 – 6.99 (m, 1H), 6.92 (d, *J* = 9.3 Hz, 1H, *N*H), 6.83 (d, *J* = 9.2 Hz, 1H, *N*H), 5.19 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 5.12 (s, 3H, *C*H$_2$*Ph*, H-1^{B}), 5.02 (d, *J* = 3.6 Hz, 1H, H-1^{A}), 4.91 (d, *J* = 11.6 Hz, 1H), 4.87 – 4.79 (m, 2H), 4.79 – 4.46 (m, 10H), 4.39 – 4.27 (m, 2H), 4.26 – 3.99 (m, 6H), 3.87 – 3.68 (m, 4H), 3.48 (dt, *J* = 10.0, 6.5 Hz, 1H, H-7), 2.73 (bs, 1H, *O*H), 2.35 (t, *J* = 7.4 Hz, 2H, H-11), 1.73 – 1.54 (m, 4H, H-10, 8), 1.42 – 1.28 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.28 (C-12), 165.97, 165.91, 165.07 (3 C=O, Bz), 161.76, 161.51 (C*ONH*), 137.08, 136.85, 136.81, 135.94, 133.61, 133.23, 133.14, 129.84, 129.79, 129.61, 129.60, 129.47, 129.26, 128.70, 128.68, 128.63, 128.57, 128.51, 128.48, 128.44, 128.35, 128.26, 128.17, 128.15, 128.03, 127.90, 127.86, 127.21, 127.17 (aromatic), 98.88 (C-1^{B}), 97.00 (C-1^{A}, 1^{C}), 92.59 (C*Cl$_3$*), 75.87 (C-3^{B}), 75.46 (C-3^{A}), 75.26 (C-3^{C}), 73.04 (C-4^{B}), 72.75, 72.35, 71.37 (3 C*H$_2$Ph*), 70.04 (C-4^{C}), 68.86, 68.73, 68.19, 68.12 (C-7), 66.18 (C*H$_2$Ph*), 65.03, 62.76 (C-6^{A}), 62.56 (C-6^{C}), 60.45 (C-2^{B}), 60.40 (C-6^{B}), 50.98 (C-2^{A}), 50.40 (C-2^{C}), 34.01 (C-11), 28.88 (C-8), 25.66 (C-9), 24.47 (C-10). HR-MS: Calculated for $C_{77}H_{77}Cl_6N_5O_{20}$ $[M+H]^+$: 1602.3371, found: 1602.3366.

6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-6-O-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranoside (7)

The reaction was carried out according to the general procedure B. The donor **2** (1.03 g, 1.70 mmol) and the acceptor **6** (1.37 g, 0.85 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 9 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TfOH (8 µl, 0.09 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 = 3:1). Compound **7** (1.57 g, 91% yield, pentane: EtOAc = 5:2, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +131.9 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 555, 651, 685, 698, 710, 736, 796, 820, 977, 1005, 1027, 1046, 1063, 1166, 1266, 1315, 1452, 1508, 1720, 2111, 2859, 2933, 3420. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.09 – 8.01 (m, 2H, *C*H, Bz), 7.97 – 7.86 (m, 4H, *C*H, Bz), 7.67 – 7.17 (m, 34H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.05 – 6.95 (m, 2H), 6.89 (d, *J* = 9.6 Hz, 1H, *N*H), 6.76 (d, *J* = 9.3 Hz, 1H, *N*H), 5.14 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 5.08 (s, 2H, *C*H$_2$*Ph*), 5.04 (d, *J* = 3.6 Hz, 1H, H-1^{B}), 4.97 (d, *J* = 3.7 Hz, 1H, H-1^{A}), 4.92 – 4.84 (m, 2H, H-1^{D}), 4.84 – 4.34 (m, 18H), 4.26 (dd, *J* = 19.4, 4.0 Hz, 2H), 4.19 – 4.05 (m, 5H), 4.05 – 3.91 (m, 2H), 3.86 – 3.65 (m, 7H), 3.60 (dd, *J* = 10.7, 3.6 Hz, 1H, H-2^{B}), 3.44 (dt, *J* = 10.1, 6.5 Hz, 1H, H-7), 2.31 (t, *J* = 7.4 Hz, 2H, H-11), 1.67 – 1.49 (m, 4H, H-10, 8), 1.38 – 1.23 (m, 2H, H-9), 1.00 – 0.93 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.29 (C-12), 165.98, 165.42, 165.18 (3 C=O, Bz), 161.77, 161.64 (C*ONH*), 137.95, 137.06, 136.89, 136.79, 135.99, 133.67, 133.37, 133.26, 129.92, 129.72, 129.64, 129.62, 129.53, 129.31, 128.76, 128.63, 128.57, 128.45, 128.42, 128.33, 128.23, 128.03, 127.98, 127.93, 127.69, 127.60, 127.26, 127.19 (aromatic), 99.51 (C-1^{D}), 98.92 (C-1^{B}), 97.08 (C-1^{A}, 1^{C}), 92.66, 92.62 (2 C*Cl$_3$*), 76.28 (C-3^{D}), 75.61 (C-3^{A}, 3^{B}), 75.57 (C-3^{C}), 74.97 (C-4^{B}), 73.07, 72.67 (2 C*H$_2$Ph*),

72.49 (C-4^{D}), 72.22, 71.43 (2 CH_2Ph), 70.60, 70.15, 69.58, 68.89, 68.74, 68.19 (C-7), 67.97 (C-5^{d}), 67.05 (C-6^{D}), 66.24 (CH_2Ph), 62.53 (C-6), 61.72 (C-6), 60.45 (C-2^{B}), 58.88 (C-2^{D}), 51.02 (C-2^{A}), 50.79 (C-2^{C}), 34.07 (C-11), 28.95 (C-8), 27.67 (CH_3), 27.35 (CH_3), 25.73 (C-9), 24.53 (C-10), 23.31 (C-*Si*), 20.71 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 99.51 ($J_{C1,H1}$ = 170 Hz), 98.92 ($J_{C1,H1}$ = 171 Hz), 97.08 ($J_{C1,H1}$ = 174 Hz). HR-MS: Calculated for $C_{98}H_{108}Cl_6N_8O_{24}Si$ $[M+NH_4]^+$: 2036.5721, found: 2036.5763.



6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-6-O-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranoside (S9)

The reaction was carried out according to the general procedure C using compound **7** (1.54 g, 0.76 mmol) and HF/pyridine (70%, 320 µl, 12.2 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S9** (1.33 g, 93% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +111.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 687, 700, 711, 737, 820, 1005, 1027, 1046, 1109, 1156, 1269, 1315, 1452, 1509, 1720, 2111, 2926, 3418, 3526. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.10 – 8.02 (m, 2H, *C*H, Bz), 7.98 – 7.90 (m, 2H, *C*H, Bz), 7.90 – 7.82 (m, 2H, *C*H, Bz), 7.66 – 7.55 (m, 3H), 7.53 – 7.40 (m, 6H), 7.39 – 7.21 (m, 19H), 7.20 – 7.07 (m, 4H), 7.03 – 6.89 (m, 3H), 6.81 (d, *J* = 9.3 Hz, 1H, *N*H), 5.09 (d, *J* = 3.5 Hz, 1H, H-1^{C}), 5.07 (s, 2H, *C*H$_2Ph$), 5.04 (d, *J* = 3.7 Hz, 1H, H-1^{B}), 4.97 (d, *J* = 3.7 Hz, 1H, H-1^{A}), 4.90 – 4.34 (m, 17H), 4.28 – 3.96 (m, 9H), 3.92 (dd, *J* = 10.4, 3.0 Hz, 1H, H-3^{D}), 3.81 – 3.65 (m, 4H), 3.65 – 3.50 (m, 3H), 3.44 (dt, *J* = 10.0, 6.5 Hz, 1H, H-7), 2.62 (bs, 1H, *O*H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 2.03 (bs, 1H, *O*H), 1.69 – 1.49 (m, 4H, H-10, 8), 1.38 – 1.21 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.24 (C-12), 165.91, 165.31, 165.11 (3 C=O, Bz), 161.95, 161.75 (C*ONH*), 137.13, 137.04, 136.80, 136.66, 135.91, 133.62, 133.32, 133.15, 129.85, 129.67, 129.57, 129.50, 129.45, 129.24, 128.69, 128.62, 128.55, 128.52, 128.48, 128.46, 128.42, 128.25, 128.14, 128.06, 128.04, 127.99, 127.88, 127.82, 127.04, 126.99 (aromatic), 100.00 (C-1^{D}), 98.90 (C-1^{B}), 97.22 (C-1^{C}), 97.03 (C-1^{A}), 92.58, 92.42 (2 CCl_3), 77.00 (C-3^{D}), 75.77 (C-3^{A}), 75.72 (C-3^{B}), 74.57 (C-3^{C}), 74.05, 73.24, 72.63, 72.49, 71.86, 71.44 (4 CH_2Ph), 70.20, 70.02, 69.47, 68.85, 68.65, 68.13 (C-7), 67.21 (C-5^{D}), 66.16 (CH_2Ph), 62.47 (C-6^{A}, 6^{D}), 61.54 (C-6^{C}), 60.49 (C-2^{B}), 60.36 (C-6^{B}), 59.90 (C-2^{d}), 50.95 (C-2^{A}), 50.77 (C-2^{C}), 33.98 (C-11), 28.86 (C-8), 25.64 (C-9), 24.44 (C-10). HR-MS: Calculated for $C_{90}H_{92C}l_6N_8O_{24}$ $[M+H]^+$: 1879.4434, found: 1879.4428.

6-(Benzyl hexanoyl) 2-azido-6-O-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-6-O-benzoyl-3-*O*-benzyl-2-

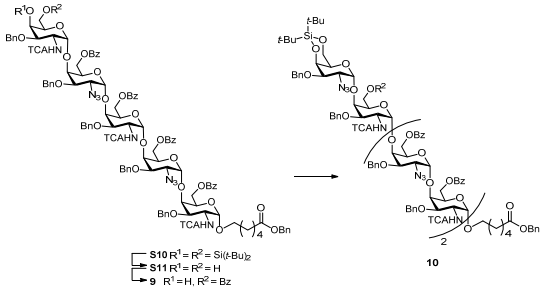
deoxy-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranoside (8)

The reaction was carried out according to the general procedure D using compound **S9** (1.15 g, 0.61 mmol), PhCOOBt (660 mg, 2.75 mmol) and Et_3N (430 µl, 3.05 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:2). Compound **8** (1.12 g, 92% yield, pentane:EtOAc = 2:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +107.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 687, 711, 737, 820, 1005, 1027, 1047, 1110, 1158, 1268, 1315, 1452, 1508, 1720, 2111, 2874, 2929, 3423, 3509. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.16 – 7.89 (m, 8H, *C*H, Bz), 7.70 – 7.12 (m, 38H), 7.07 – 6.98 (m, 2H), 6.91 (d, *J* = 9.4 Hz, 1H, *N*H), 6.85 (d, *J* = 9.3 Hz, 1H, *N*H), 5.20 (d, *J* = 3.5 Hz, 1H, H-1^C), 5.12 (s, 2H, *C*H_2*Ph*), 5.09 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.03 (d, *J* = 3.7 Hz, 1H, H-1^A), 4.97 – 4.55 (m, 16H, H-1^D), 4.54 – 4.41 (m, 4H), 4.30 (d, *J* = 2.6 Hz, 1H, H-4A), 4.25 – 4.06 (m, 8H), 4.03 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.90 – 3.78 (m, 3H), 3.74 (dt, *J* = 10.0, 6.4 Hz, 1H), 3.66 (dd, *J* = 10.7, 3.5 Hz, 1H), 3.49 (dt, *J* = 10.0, 6.4 Hz, 1H, H-7), 2.63 (bs, 1H, *O*H), 2.35 (t, *J* = 7.4 Hz, 2H, H-11), 1.71 – 1.54 (m, 4H, H-10, 8), 1.42 – 1.26 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.20 (C-12), 165.97, 165.89, 165.23, 165.08 (C=O, Bz), 161.70, 161.53 (*CONH*), 137.19, 136.88, 136.82, 136.70, 135.90, 133.56, 133.24, 133.20, 133.16, 132.90, 129.96, 129.92, 129.84, 129.79, 129.57, 129.54, 129.50, 129.44, 129.26, 128.65, 128.52, 128.51, 128.48, 128.46, 128.35, 128.32, 128.24, 128.21, 128.11, 128.04, 127.98, 127.85, 127.80, 127.70, 127.06 (aromatic), 99.39 (C-1^D), 98.85 (C-1^B), 97.21 (C-1^C), 96.99 (C-1^A), 92.57, 92.51 (2 C*Cl$_3$*), 76.59 (C-3^D), 75.68 (C-3^B), 75.60 (C-3^A), 74.24 (C-3^C), 73.07, 72.92, 72.61, 72.39, 72.08, 71.51 (4 C*H$_2$Ph*), 70.24, 69.34 (C-5^C), 68.83 (C-5^A), 68.69 (C-5^B), 68.08 (C-7), 66.12 (C*H$_2$Ph*), 65.38 (C-5^D), 62.48 (C-6^A), 61.91 (C-6^D), 61.50 (C-6^C), 60.45 (C-2^B), 60.41 (C-6^B), 59.60 (C-2^D), 50.94 (C-2^A), 50.75 (C-2^C), 33.95 (C-11), 28.83 (C-8), 25.61 (C-9), 24.41 (C-10). HR-MS: Calculated for $C_{97}H_{96}Cl_6N_8O_{25}$ $[M+H]^+$: 1983.4696, found: 1983.4690.

Pentasaccharide S10

The reaction was carried out according to the general procedure B. The donor **3** (630 mg, 0.87 mmol) and the acceptor **8** (1.08 g, 0.54 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 5.5 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TfOH (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 = 4:1). Compound **S10** (1.19 g, 87% yield, pentane: EtOAc = 5:2, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +138.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 651,685, 698, 710, 736, 819, 1003, 1027, 1046, 1096, 1108,1159, 1266, 1315, 1452, 1508, 1720, 2111, 2860, 2933, 3421. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.09 – 8.03 (m, 2H, *C*H, Bz), 8.00 – 7.94 (m, 2H, *C*H, Bz), 7.94 – 7.86 (m, 4H, *C*H, Bz), 7.71 – 7.60 (m, 2H), 7.59 – 7.47 (m, 6H), 7.46 – 7.38 (m, 4H), 7.37 – 7.09 (m, 30H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.76 - 6.74 (m, 3H, 3x*N*H), 5.16 (d, *J* = 3.6 Hz, 1H, H-1^E), 5.07 (s, 3H, H-1C, *C*H_2*Ph*), 5.01 (d, *J* = 3.6 Hz, 1H, H-1^B), 4.97 (d, *J* =

3.7 Hz, 1H, H-1^{A}), 4.90 – 4.47 (m, 19H, H-1^{D}), 4.46 – 4.31 (m, 6H), 4.23 (d, *J* = 2.6 Hz, 1H, H-4^{A}), 4.15 – 3.85 (m, 9H), 3.82 – 3.53 (m, 6H), 3.52 – 3.39 (m, 2H), 3.32 (dd, *J* = 12.9, 2.0 Hz, 1H, H-6^{E}), 2.31 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.51 (m, 4H, H-10, 8), 1.36 – 1.23 (m, 2H, H-9), 1.00 – 0.91 (m, 18H, *C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.26 (C-12), 165.96, 165.19, 165.08, 165.06 (4 C=O, Bz), 161.78, 161.53, 161.45 (3 C*ONH*), 137.76, 137.11, 136.92, 136.86, 136.77, 135.97, 133.67, 133.49, 133.29, 133.17, 129.90, 129.62, 129.55, 129.53, 129.32, 128.75, 128.71, 128.69, 128.61, 128.54, 128.52, 128.49, 128.41, 128.30, 128.20, 128.13, 128.05, 127.95, 127.83, 127.81, 127.76, 127.18, 126.98, 126.88, 98.92 (C-1^{D}), 98.89 (C-1^{B}), 97.30 (C-1^{C}), 97.09 (C-1^{E}), 97.07 (C-1^{A}), 92.62 (2x C*Cl$_3$*), 92.47 (C*Cl$_3$*), 76.24 (C-3^{D}), 75.97 (C-3^{B}), 75.62 (C-3^{A}), 74.44 (C-3^{E}), 73.51, 73.19, 72.84, 72.64, 72.47, 72.36, 71.98, 70.15, 69.75, 69.58, 69.31, 69.24, 68.90, 68.73, 68.63, 68.18 (C-7), 67.98 (C-5E), 66.78 (C-6^{E}), 66.21 (C*H$_2$Ph*), 62.50 (C-6), 61.49 (C-6), 60.61 (C-2^{B}), 60.58 (C-2^{D}), 60.39 (C-6), 60.05 (C-6), 50.99 (C-2^{A}), 50.71 (C-2^{C}), 49.74 (C-2^{E}), 34.04 (C-11), 28.92 (C-8), 27.61 (C*H$_3$*), 27.28 (C*H$_3$*), 25.70 (C-9), 24.51 (C-10), 23.31 (C-*Si*), 20.66 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 98.92 ($J_{C1,H1}$ = 172 Hz), 98.89 ($J_{C1,H1}$ = 171 Hz), 97.30 ($J_{C1,H1}$ = 174 Hz), 97.09 ($J_{C1,H1}$ = 174 Hz), 97.07 ($J_{C1,H1}$ = 173 Hz). MALDI-MS: Calculated for $C_{120}H_{128}Cl_9N_9O_{30}Si$ $[M+Na]^+$: 2540.5631, found: 2540.5485.



Pentasaccharide S11

The reaction was carried out according to the general procedure C using compound **S10** (1.16 g, 0.46 mmol) and HF/pyridine (70%, 190 µl, 7.34 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S11** (1.04 g, 94% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +126.0 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 711, 738, 820, 1005, 1027, 1046, 1110, 1158, 1268, 1315, 1508, 1720, 2111, 2872, 2929, 3419, 3509. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.09 – 8.01 (m, 2H, *C*H, Bz), 8.00 – 7.85 (m, 6H, *C*H, Bz), 7.72 – 7.07 (m, 42H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.84 – 6.71 (m, 3H, 3x*N*H), 5.08 (d, *J* = 3.3 Hz, 1H, H-1^{E}), 5.07 (s, 2H, *CH$_2$Ph*), 5.04 - 5.31 (m, 2H, H-1^{B}, 1^{C}), 4.97 (d, *J* = 3.7 Hz, 1H, H-1^{A}), 4.86 (d, *J* = 11.7 Hz, 1H), 4.82 – 4.34 (m, 20H, H-1^{D}), 4.31 (d, *J* = 2.6 Hz, 1H, H-4^{B}), 4.23 (d, *J* = 2.6 Hz, 1H, H-4^{A}), 4.20 – 3.92 (m, 11H), 3.83 – 3.65 (m, 3H), 3.64 – 3.55 (m, 2H), 3.50 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.47 – 3.35 (m, 2H), 3.28 (dt, *J* = 12.0, 3.5 Hz, 1H), 2.90 (bs, 1H, *O*H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.67 – 1.50 (m, 4H, H-10, 8), 1.37 – 1.23 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.27 (C-12), 165.95, 165.20, 165.16, 165.08 (4 C=O, Bz), 161.78, 161.54, 161.45 (C*ONH*), 137.19, 136.96, 136.84, 136.81, 136.73, 135.94, 133.64, 133.45, 133.29, 133.20, 129.95, 129.87, 129.61, 129.59, 129.54, 129.49, 129.41, 129.28, 128.71, 128.64, 128.58, 128.55, 128.51, 128.49, 128.40, 128.27,

128.17, 128.07, 128.05, 127.92, 127.78, 127.19, 127.14, 126.83, 99.01 (C-1^D), 98.91 (C-1^B), 97.60 (C-1^C), 97.36 (C-1^E), 97.04 (C-1^A), 92.59, 92.49, 92.45 (3 C*Cl*$_3$), 76.16 (C-3^D), 75.96 (C-3), 75.62 (C-3^A), 74.85, 74.06 (C-3^E), 73.24, 73.08, 72.64, 72.46, 72.36, 72.12, 70.83, 70.46, 70.25, 69.44, 69.29, 68.88, 68.79, 68.70, 68.16 (C-7), 66.51, 66.18 (C*H*$_2$*Ph*), 62.51 (C-6A), 62.36 (C-6^E), 61.46 (C-6), 60.57 (C-2^B), 60.54 (C-2^D), 60.37 (C-6), 60.29 (C-6), 50.98 (C-2^A), 50.71 (C-2^C), 50.21 (C-2^E), 34.01 (C-11), 28.89 (C-8), 25.67 (C-9), 24.47 (C-10). HR-MS: Calculated for $C_{112}H_{112}Cl_9N_9O_{30}$ $[M+NH_4]^+$: 2395.50556, found: 2395.50778.

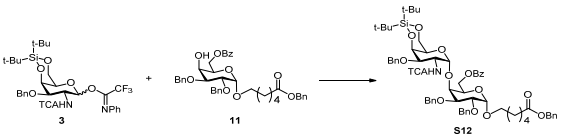
Pentasaccharide 9

The reaction was carried out according to the general procedure D using compound **S11** (1.0 g, 0.42 mmol), PhCOOBt (451 mg, 1.89 mmol) and Et_3N (300 µl, 2.1 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:2). Compound **9** (994 mg, 95% yield, pentane:EtOAc = 2:1, R*f* = 0.25-0.30) was obtained as yellow syrup. $[\alpha]_D^{25}$ +131.0 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 711, 738, 820, 1005, 1027, 1047, 1110, 1159, 1269, 1315, 1508, 1720, 2110, 2872, 2929, 3421. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.05 (d, *J* = 7.7 Hz, 2H, *C*H, Bz), 7.99 – 7.81 (m, 8H, *C*H, Bz), 7.71 – 7.04 (m, 43H), 7.03 – 6.86 (m, 3H), 6.85 – 6.73 (m, 3H, 3x*N*H), 5.11 (d, *J* = 3.6 Hz, 1H, H-1^E), 5.09 (d, *J* = 3.4 Hz, 1H, H-1^C), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.03 (d, *J* = 3.6 Hz, 1H, H-1^B), 4.97 (d, *J* = 3.7 Hz, 1H, H-1^A), 4.90 – 4.33 (m, 23H, H-1^D), 4.34 - 4.23 (m, 3H), 4.16 – 3.89 (m, 10H), 3.84 – 3.65 (m, 4H), 3.63 – 3.52 (m, 2H), 3.44 (dt, *J* = 10.1, 6.5 Hz, 1H, H-7), 2.60 (bs, 1H, *O*H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.49 (m, 4H, H-10, 8), 1.36 – 1.21 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.26 (C-12), 165.95, 165.88, 165.18, 165.11, 165.08 (5 C=O, Bz), 161.78, 161.51, 161.46 (3 C*ONH*), 136.99, 136.85, 136.80, 136.74, 135.94, 133.63, 133.46, 133.28, 133.16, 133.08, 129.86, 129.79, 129.59, 129.53, 129.48, 129.35, 129.28, 128.71, 128.66, 128.63, 128.57, 128.51, 128.49, 128.42, 128.39, 128.35, 128.33, 128.26, 128.16, 128.13, 128.06, 127.91, 127.78, 127.73, 127.15, 127.13, 126.86, 98.96 (C-1^D), 98.90 (C-1^B), 97.36 (C-1^C), 97.03 (C-1^E), 96.99 (C-1^A), 92.59, 92.50, 92.49 (3 CCl_3), 75.94, 75.90, 75.62, 74.99, 73.96, 73.22, 72.95, 72.62, 72.59, 72.44, 72.09, 71.26, 70.22, 69.93, 69.29, 68.88, 68.68, 68.15 (C-7), 68.09, 66.17 (C*H*$_2$*Ph*), 64.97 (C-5^E), 62.69 (C-6), 62.52 (C-6), 61.49 (C-6), 60.55 (C-2^B), 60.51 (C-2^D), 60.38 (C-6), 60.20 (C-6), 50.98 (C-2^A), 50.69 (C-2^C), 50.33 (C-2^E), 34.00 (C-11), 28.88 (C-8), 25.66 (C-9), 24.46 (C-10). MALDI-MS: Calculated for $C_{119}H_{116}Cl_9N_9O_{31}$ $[M+Na]^+$: 2504.4872, found: 2504.4680.

Hexasaccharide 10

The reaction was carried out according to the general procedure B. The donor **2** (469 mg, 0.77 mmol) and the acceptor **9** (961 mg, 0.39 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 TfOH (4 µl, 0.04 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 = 7:2). Compound **10** (970 mg, 87% yield, pentane: EtOAc = 2:1, R*f* = 0.55-0.65)

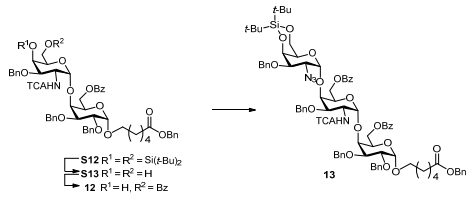
was obtained as yellow syrup. $[\alpha]_D^{25}$ +137.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 685, 710, 737, 820, 1005, 1027, 1046, 1063, 1109, 1159, 1266, 1315, 1452, 1507, 1720, 2111, 2860, 2932, 3419. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.08 – 8.02 (m, 2H, *C*H, Bz), 7.99 – 7.94 (m, 2H, *C*H, Bz), 7.94 – 7.84 (m, 6H, *C*H, Bz), 7.67 – 7.07 (m, 49H), 7.03 – 6.97 (m, 1H), 6.94 – 6.87 (m, 2H), 6.82 – 6.72 (m, 3H, 3x*N*H), 5.11 (d, *J* = 3.5 Hz, 1H, H-1^E), 5.07 (s, 3H, *CH*$_2$*Ph*, H-1^C), 5.02 (d, *J* = 3.6 Hz, 1H, H-1^B), 4.96 (d, *J* = 3.7 Hz, 1H, H-1^A), 4.89 – 4.83 (m, 2H, *CHHPh*, H-1^D), 4.82 – 3.90 (m, 41H), 3.85 – 3.56 (m, 8H), 3.49 – 3.36 (m, 2H), 2.31 (t, *J* = 7.4 Hz, 2H, H-11), 1.67 – 1.51 (m, 4H, H-10, 8), 1.38 – 1.23 (m, 2H, H-9), 0.96 (d, *J* = 15.7 Hz, 18H, *C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.28 (C-12), 165.98, 165.38, 165.24, 165.19, 165.13 (C=O, Bz), 161.82, 161.59, 161.52 (C*ONH*), 138.00, 136.98, 136.90, 136.86, 136.79, 136.02, 133.68, 133.50, 133.34, 133.30, 133.19, 129.96, 129.93, 129.76, 129.67, 129.65, 129.60, 129.58, 129.44, 129.35, 128.77, 128.71, 128.69, 128.64, 128.59, 128.55, 128.47, 128.44, 128.41, 128.33, 128.23, 128.11, 128.08, 128.02, 128.00, 127.95, 127.84, 127.79, 127.74, 127.67, 127.23, 127.21, 126.92, 99.51 (C-1^D), 99.01 (C-1^F), 98.98 (C-1^B), 97.42 (C-1^C), 97.11 (C-1A, 1^E), 92.66 (C*Cl*$_3$), 92.56 (2x C*Cl*$_3$), 76.33, 76.01, 75.67, 74.51, 74.17, 73.29, 73.00, 72.70, 72.54, 72.50, 72.22, 71.25, 70.61, 70.27, 70.04, 69.60, 69.43, 69.36, 68.95, 68.78, 68.69, 68.23 (C-7), 67.98, 67.09 (C-6^F), 66.24 (C*H*$_2$*Ph*), 62.55 (2xC-6), 61.71 (C-6), 61.53 (C-6), 60.63 (C-2B), 60.50 (C-2^D), 60.42 (C-6), 60.30 (C-6), 58.92 (C-2^F), 51.04 (C-2^A), 50.74 (C-2C, 2^E), 34.07 (C-11), 28.96 (C-8), 27.68 (C*H*$_3$), 27.36 (C*H*$_3$), 25.74 (C-9), 24.54 (C-10), 23.32 (C-*Si*), 20.72 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 99.51 ($J_{C1,H1}$ = 171 Hz), 99.01 ($J_{C1,H1}$ = 174 Hz), 98.98 ($J_{C1,H1}$ = 171 Hz), 97.42 ($J_{C1,H1}$ = 174 Hz), 97.11 ($J_{C1,H1}$ = 173 Hz). MALDI-MS: Calculated for $C_{140}H_{147}Cl_9N_{12}O_{35}Si$ $[M+Na]^+$: 2921.6959, found: 2921.6714.



6-(Benzyl hexanoyl) 3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (S12)

The reaction was carried out according to the general procedure B. The donor **3** (205 mg, 0.28 mmol) and the acceptor **11** (96 mg, 0.14 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 1.5 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TfOH (2 µl, 0.01 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 **S12** (150 mg, 88% yield, pentane: EtOAc = 3:1, R*f* = 0.50-0.60) was obtained as yellow syrup. $[\alpha]_D^{25}$ +99.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 651, 698, 713, 738, 796, 824, 1005, 1027, 1047, 1098, 1271, 1508, 1724, 2859, 2933, 3418. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.04 – 7.97 (m, 2H, *C*H, Bz), 7.59 – 7.51 (m, 1H), 7.46 – 7.23 (m, 22H, aromatic H), 6.94 (d, *J* = 9.1 Hz, 1H, *N*H), 5.22 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.08 (s, 2H, *C*H$_2$*Ph*), 4.82 (d, *J* = 11.4 Hz, 1H, *CHHPh*), 4.79 – 4.66 (m, 4H, *C*H$_2$*Ph*, H-1A, 2^B), 4.65 – 4.51 (m, 4H,

*C*H$_2$*Ph*, H-6^A), 4.41 (d, *J* = 2.8 Hz, 1H, H-4^B), 4.26 (d, *J* = 3.0 Hz, 1H, H-4^A), 4.21 (dd, *J* = 11.1, 6.9 Hz, 1H, H-6^A), 4.11 - 4.04 (m, 2H, H-5^A, 5^B), 3.86 (dd, *J* = 10.1, 3.0 Hz, 1H, H-3^A), 3.80 – 3.71 (m, 2H, H-2^A, 6^B), 3.66 (dd, *J* = 10.8, 2.5 Hz, 1H, H-3^B), 3.59 (dt, *J* = 9.9, 6.9 Hz, 1H, H-7), 3.48 (dd, *J* = 12.8, 2.1 Hz, 1H, H-6^B), 3.40 (dt, *J* = 9.8, 6.6 Hz, 1H, H-7), 2.28 (t, *J* = 7.5 Hz, 2H, H-11), 1.64 – 1.52 (m, 4H, H-10, 8), 1.34 – 1.22 (m, 2H, H-9), 1.07 (s, 9H, *C*H$_3$), 1.01 (s, 9H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.35 (C-12), 165.71 (C=O, Bz), 161.69 (C*ONH*), 138.22, 138.04, 136.07, 133.38, 129.72, 129.43, 128.55, 128.52, 128.47, 128.45, 128.42, 128.19, 128.15, 128.01, 127.94, 127.91, 127.77, 127.73, 127.70, 127.44, 97.00 (C-1^B), 96.96 (C-1^A), 92.65 (C*Cl$_3$*), 76.81 (C-3^A), 76.58 (C-2^A), 75.16 (C-3^B), 73.61 (C*H$_2$Ph*), 73.07 (C*H$_2$Ph*), 72.07 (C-4^A), 69.60 (C*H$_2$Ph*), 69.43 (C-4^B), 68.08 (C-7), 67.95 (C-5^A), 67.85 (C-5^B), 66.84 (C-6^B), 66.07 (C*H$_2$Ph*), 62.07 (C-6^A), 49.94 (C-2^B), 34.10 (C-11), 29.02 (C-8), 27.64 (C*H$_3$*), 27.37 (C*H$_3$*), 25.67 (C-9), 24.60 (C-10), 23.35 (C-*Si*), 20.72 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 97.00 ($J_{C1,H1}$ = 170 Hz), 96.96 ($J_{C1,H1}$ = 169 Hz). HR-MS: Calculated for $C_{63}H_{76}Cl_3NO_{14}Si$ $[M+H]^+$: 1204.4179, found: 1204.4173.



6-(Benzyl hexanoyl) 3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (S13)

The reaction was carried out according to the general procedure C using compound **S12** (2.70 g, 2.24 mmol) and HF/pyridine (70%, 0.93 ml, 35.84 mmol). The product was purified by column chromatography (pentane:EtOAc = 1:1). Compound **S13** (2.17 g, 95% yield, pentane:EtOAc = 1:1, R*f* = 0.20-0.30) was obtained as yellow syrup. $[\alpha]_D^{25}$ +83.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 580, 598, 697, 713, 734, 819, 1026, 1040, 1095, 1156, 1271, 1452, 1511, 1720, 2872, 2933, 3411. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.06 – 7.96 (m, 2H, *C*H, Bz), 7.60 – 7.51 (m, 1H), 7.49 – 7.27 (m, 22H, aromatic H), 6.98 (d, *J* = 9.2 Hz, 1H, *N*H), 5.16 (d, *J* = 3.7 Hz, 1H, H-1^B), 5.10 (s, 2H, *C*H$_2$*Ph*), 4.87 – 4.77 (m, 3H, H-1^A, *C*H$_2$*Ph*), 4.76 – 4.65 (m, 3H, *C*H$_2$*Ph*), 4.62 – 4.43 (m, 3H, H-2^B, 6^A, *C*H$_2$*Ph*), 4.30 (dd, *J* = 11.1, 6.2 Hz, 1H, H-6^A), 4.25 (d, *J* = 2.9 Hz, 1H, H-4^A), 4.23 – 4.18 (m, 1H, H-5^B), 4.17 – 4.13 (m, 1H, H-4^B), 4.13 – 4.07 (m, 1H, H-5^A), 3.90 (dd, *J* = 10.1, 2.8 Hz, 1H, H-3^A), 3.78 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2^A), 3.69 – 3.47 (m, 4H, H-3^B, 6^B, 7), 3.42 (dt, *J* = 9.8, 6.6 Hz, 1H, H-7), 3.17 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.54 (m, 4H, H-10, 8), 1.35 – 1.24 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.39 (C-12), 165.80 (C=O, Bz), 161.81 (C*ONH*), 138.30, 138.26, 137.19, 136.06, 133.39, 129.69, 129.41, 128.62, 128.56, 128.53, 128.48, 128.45, 128.20, 128.15, 128.07, 127.91, 127.88, 127.77, 127.66, 97.44 (C-1^B), 96.98 (C-1^A), 92.52 (C*Cl$_3$*), 76.90 (C-3^A), 76.18 (C-2^A), 75.78 (C-3^B), 73.54 (C*H$_2$Ph*), 73.34 (C-4^A), 72.90, 70.98 (2 C*H$_2$Ph*), 69.55 (C-5^B), 68.34 (C-5^A), 68.08 (C-7), 66.73 (C-

4^B), 66.09 (CH_2Ph), 62.61 (C-6^B), 62.58 (C-6^A), 50.65 (C-2^B), 34.11 (C-11), 29.00 (C-8), 25.66 (C-9), 24.60 (C-10). HR-MS: Calculated for $C_{55}H_{60}Cl_3NO_{14}$ $[M+H]^+$: 1064.3158, found: 1064.3152.

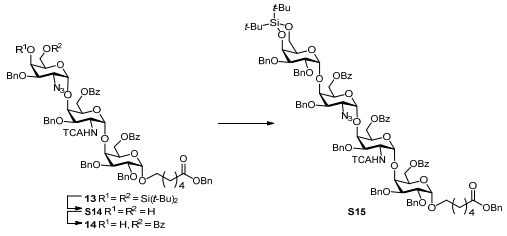
6-(Benzyl hexanoyl) 6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (12)

The reaction was carried out according to the general procedure D using compound **S13** (2.26 g, 2.21 mmol), PhCOOBt (2.38 g, 11.05 mmol) and Et_3N (1.54 ml, 8.47 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:1). Compound **12** (2.31 g, 93% yield, pentane:EtOAc = 2:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +78.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 711, 736, 820, 1027, 1049, 1070, 1096, 1159, 1271, 1315, 1452, 1511, 1720, 2869, 2929, 3416, 3500. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.01 – 7.96 (m, 2H, *C*H, Bz), 7.93 – 7.87 (m, 2H, *C*H, Bz), 7.57 – 7.47 (m, 2H), 7.42 – 7.22 (m, 23H), 7.21 – 7.15 (m, 2H), 7.13 – 7.07 (m, 1H), 6.94 (d, *J* = 9.2 Hz, 1H, *N*H), 5.17 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.08 (s, 2H, CH_2Ph), 4.82 (d, *J* = 11.7 Hz, 1H, C*H*HPh), 4.79 – 4.74 (m, 2H, H-1A, C*H*HPh), 4.73 – 4.46 (m, 7H, C*H*HPh, H-2^B, 5^B, 6^A), 4.37 (dd, *J* = 11.0, 6.9 Hz, 1H, H-6^B), 4.30 (d, *J* = 3.0 Hz, 1H, H-4^A), 4.24 - 4.20 (m, 2H, H-6^A, 6^B), 4.09 (t, *J* = 7.2 Hz, 1H, H-5^A), 4.05 (dd, *J* = 2.9, 1.4 Hz, 1H, H-4^B), 3.89 (dd, *J* = 10.1, 3.0 Hz, 1H, H-3^A), 3.78 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2^A), 3.71 (dd, *J* = 10.6, 2.8 Hz, 1H, H-3^B), 3.60 (dt, *J* = 9.9, 6.9 Hz, 1H, H-7), 3.40 (dt, *J* = 9.8, 6.6 Hz, 1H, H-7), 2.72 (bs, 1H, *O*H), 2.29 (t, *J* = 7.5 Hz, 2H, H-11), 1.68 – 1.51 (m, 4H, H-10, 8), 1.35 – 1.21 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.41 (C-12), 165.98, 165.77 (2 C=O, Bz), 161.76 (C*ONH*), 138.30, 138.12, 137.23, 136.08, 133.41, 133.09, 129.91, 129.71, 129.63, 129.34, 128.68, 128.58, 128.52, 128.46, 128.37, 128.32, 128.23, 128.19, 128.15, 127.93, 127.90, 127.86, 127.68, 127.41 (aromatic), 97.05 (C-1^A), 96.88 (C=1^B), 92.59 (CCl_3), 76.66 (C-3^A), 76.21 (C-2^A), 75.88 (C-3^B), 73.57, 72.89 (2 CH_2Ph), 72.39 (C-4^A), 71.40 (CH_2Ph), 68.18 (C-5^B), 68.15 (C-7), 68.10 (C-5^A), 66.12 (CH_2Ph), 65.26 (C-4^B), 62.98 (C-6^B), 62.25 (C-6^A), 50.62 (C-2^B), 34.14 (C-11), 29.03 (C-8), 25.67 (C-9), 24.63 (C-10). HR-MS: Calculated for $C_{62}H_{64}Cl_3NO_{15}$ $[M+H]^+$: 1168.3420, found: 1168.3414.

6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (13)

The reaction was carried out according to the general procedure B. The donor **2** (1.94 g, 3.20 mmol) and the acceptor **12** (2.40 g, 2.13 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 12 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TfOH (19 µl, 0.21 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 = 6:1). Compound **13** (2.92 g, 86% yield, pentane: EtOAc = 3:1, R*f* = 0.50-0.60) was obtained as yellow syrup. $[\alpha]_D^{25}$ +96.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 442, 474, 650, 697, 711, 734, 796, 823, 977, 1009, 1027, 1043, 1065, 1098, 1166, 1268, 1315, 1452, 1508, 1724, 2112, 2859, 2932, 3413. ^{1}H-NMR ($CDCl_3$,

400 MHz) δ 8.03 – 7.96 (m, 2H, *C*H, Bz), 7.94 – 7.87 (m, 2H, *C*H, Bz), 7.62 – 7.50 (m, 2H), 7.49 – 7.14 (m, 30H), 7.13 – 7.05 (m, 1H), 7.02 (d, *J* = 9.5 Hz, 1H, *N*H), 5.24 (d, *J* = 3.6 Hz, 1H, H-1^{B}), 5.08 (s, 2H, *C*H$_2$*Ph*), 5.04 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 4.88 (d, *J* = 11.9 Hz, 1H, *CHHPh*), 4.79 (d, *J* = 3.6 Hz, 1H, H-1^{A}), 4.77 – 4.70 (m, 4H, *C*H$_2$*Ph*), 4.70 – 4.43 (m, 8H, *C*H$_2$*Ph*, H-2^{B}, 5^{B}, 6^{A}, 6^{B}), 4.40 (dd, *J* = 10.2, 7.8 Hz, 1H, H-6^{B}), 4.31 (d, *J* = 3.0 Hz, 1H, H-4^{A}), 4.27 – 4.16 (m, 3H, H-4^{B}, 5^{C}, 6^{A}), 4.09 (t, *J* = 7.1 Hz, 1H, H-5^{A}), 4.03 (dd, *J* = 10.6, 2.7 Hz, 1H, H-3^{C}), 3.92 – 3.84 (m, 2H, H-2^{A}, 2^{C}), 3.76 (dd, *J* = 10.0, 3.6 Hz, 1H, H-3^{A}), 3.74 – 3.66 (m, 3H, H-3^{B}, 6^{C}), 3.61 (dt, *J* = 9.9, 6.9 Hz, 1H, H-7), 3.40 (dt, *J* = 9.9, 6.6 Hz, 1H, H-7), 2.29 (t, *J* = 7.5 Hz, 2H, H-11), 1.68 – 1.53 (m, 4H, H-10, 8), 1.35 - 1.32 (m, 2H, H-9), 0.99 (s, 9H, *C*H$_3$), 0.99 (s, 9H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.38 (C-12), 165.77, 165.47 (2 C=O, Bz), 161.87 (C*ONH*), 138.25, 138.22, 137.92, 137.19, 136.09, 133.48, 133.26, 129.75, 129.70, 129.60, 129.33, 128.59, 128.57, 128.54, 128.52, 128.47, 128.44, 128.35, 128.24, 128.19, 128.09, 127.96, 127.91, 127.88, 127.83, 127.76, 127.68, 127.37, 127.00 (aromatic), 99.37 (C-1^{C}), 97.00 (C-1^{A}), 96.79 (C-1^{B}), 92.62 (C*Cl$_3$*), 76.29 (C-3^{A}), 76.17 (C-3^{C}), 76.07 (C-2^{A}, 3^{B}), 73.47 (C*H$_2$*), 72.76 (C*H$_2$*), 72.40 (C-4^{A}), 72.02 (C-4^{B}), 71.62, 70.68 (C*H$_2$*), 69.64 (C-4^{C}), 69.26 (C-5^{B}), 68.15 (C-7), 68.06 (C-5^{A}), 67.94 (C-5^{C}), 66.97 (C-6^{C}), 66.13 (C*H$_2$*), 62.26 (C-6^{A}), 61.74 (C-6^{B}), 58.80 (C-2^{C}), 51.05 (C-2^{B}), 34.14 (C-11), 29.03 (C-8), 27.67 (C*H$_3$*), 27.40 (C*H$_3$*), 27.35 (C-8), 25.70 (C-9), 24.64 (C-10), 23.32 (C-*Si*), 20.71 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 99.37 ($J_{C1,H1}$ = 171 Hz), 97.00 ($J_{C1,H1}$ = 168 Hz), 96.79 ($J_{C1,H1}$ = 172 Hz). HR-MS: Calculated for $C_{83}H_{95}Cl_3N_4O_{19}Si$ $[M+H]^+$: 1585.5504, found: 1585.5498.



6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (S14)

The reaction was carried out according to the general procedure C using compound **13** (2.87 g, 1.81 mmol) and HF/pyridine (70%, 750 µl, 28.93 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1-3:2). Compound **S14** (2.54 g, 97% yield, pentane:EtOAc = 1:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +85.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 711, 737, 820, 1027, 1046, 1156, 1271, 1315, 1452, 1511, 1720, 2111, 2870, 2927, 3421, 3500. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.04 – 7.96 (m, 2H, *C*H, Bz), 7.94 – 7.87 (m, 2H, *C*H, Bz), 7.62 – 6.99 (m, 33H), 5.20 (d, *J* = 3.6 Hz, 1H, H-1^{B}), 5.07 (s, 2H, *C*H$_2$), 4.94 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 4.90 – 4.44 (m, 13H, H-1^{A}), 4.38 – 4.17 (m, 5H), 4.15 – 4.06 (m, 2H), 4.00 (dd, *J* = 10.4, 2.9 Hz, 1H, H-3^{C}), 3.90 (dd, *J* = 10.0, 3.0 Hz, 1H, H-3^{A}), 3.85 – 3.70 (m, 3H), 3.62 (dt, *J* = 9.8, 6.9 Hz, 1H, H-7), 3.51 (d, *J* = 4.7 Hz, 2H), 3.41 (dt,

J = 9.9, 6.6 Hz, 1H, H-7), 2.94 (bs, 1H, *O*H), 2.57 (bs, 1H, *O*H), 2.28 (t, *J* = 7.5 Hz, 2H, H-11), 1.68 – 1.52 (m, 4H, H-10, 8), 1.38 – 1.21 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.29 (C-12), 165.68, 165.42 (2 C=O, Bz), 162.09 (C*ONH*), 138.15, 138.02, 137.22, 137.13, 135.98, 133.40, 133.15, 129.63, 129.48, 129.25, 128.53, 128.49, 128.46, 128.43, 128.37, 128.33, 128.26, 128.14, 128.08, 128.03, 127.97, 127.95, 127.84, 127.74, 127.62, 127.42, 127.27 (aromatic), 99.79 (C-1^{C}), 96.93 (C-1^{A}), 96.81 (C-1^{B}), 92.41 (C*Cl*$_3$), 76.79 (C-3^{C}), 76.34 (C-2^{A}), 76.31 (C-3^{A}), 75.72 (C-3^{B}), 73.77 (C-4^{B}), 73.51 (C*H*$_2$), 72.78 (C*H*$_2$), 72.51 (C-4^{A}), 71.81 (C*H*$_2$), 71.62 (C*H*$_2$), 69.90 (C-5^{C}), 69.27 (C-5^{B}), 68.08 (C-7), 68.03 (C-5^{A}), 67.33 (C-4^{C}), 66.02 (C*H*$_2$), 62.48 (C-6^{C}), 62.25 (C-6^{A}), 61.64 (C-6^{B}), 59.80 (C-2^{C}), 51.04 (C-2^{B}), 34.03 (C-11), 28.93 (C-8), 25.59 (C-9), 24.53 (C-10). HR-MS: Calculated for $C_{75}H_{79}Cl_3N_4O_{19}$ $[M+H]^+$: 1445.4482, found: 1445.4477.

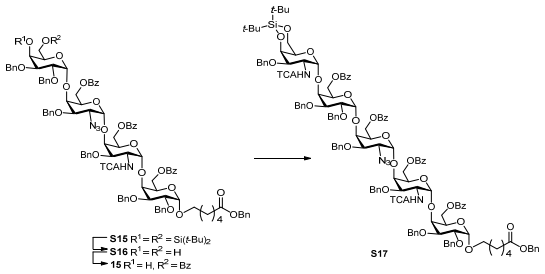
6-(Benzyl hexanoyl) 2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (14)

The reaction was carried out according to the general procedure D using compound **S14** (2.30 g, 1.59 mmol), PhCOOBt (1.71 g, 7.15 mmol) and Et_3N (1.1 ml, 7.95 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:1). Compound **14** (2.35 g, 95% yield, pentane:EtOAc = 2:1, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +81.1 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 711, 736, 820, 1027, 1047, 1070, 1096, 1109, 1157, 1269, 1315, 1452, 1508, 1720, 2111, 2929, 3422, 3500. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.06 – 7.88 (m, 6H, *C*H, Bz), 7.61 – 7.49 (m, 3H), 7.47 – 7.12 (m, 31H), 7.10 – 6.96 (m, 3H), 5.26 (d, *J* = 3.6 Hz, 1H, H-1B), 5.07 (s, 2H, *C*H$_2$), 5.02 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 4.92 - 4.83 (m, 2H), 4.80 (d, *J* = 3.6 Hz, 1H, H-1^{A}), 4.79 – 4.56 (m, 8H), 4.54 – 4.38 (m, 5H), 4.34 – 4.22 (m, 2H), 4.19 (d, *J* = 2.3 Hz, 1H), 4.16 – 4.05 (m, 3H), 3.96 – 3.82 (m, 3H), 3.81 – 3.73 (m, 2H), 3.61 (dt, *J* = 9.8, 6.9 Hz, 1H, H-7), 3.40 (dt, *J* = 9.8, 6.5 Hz, 1H, H-7), 2.60 (bs, 1H, *O*H), 2.28 (t, *J* = 7.5 Hz, 2H, H-11), 1.66 – 1.52 (m, 4H, H-10, 8), 1.36 – 1.22 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.31 (C-12), 165.90, 165.70, 165.34 (3 C=O, Bz), 161.81 (C*ONH*), 138.21, 138.11, 137.21, 136.99, 136.01, 133.38, 133.24, 132.91, 129.91, 129.78, 129.66, 129.58, 129.52, 129.30, 128.54, 128.51, 128.48, 128.47, 128.44, 128.37, 128.28, 128.24, 128.15, 128.10, 128.07, 128.04, 127.83, 127.76, 127.74, 127.62, 127.30, 127.04 (aromatic), 99.29 (C-1^{C}), 96.95 (C-1^{A}), 96.90 (C-1^{B}), 92.52 (C*Cl*$_3$), 76.47 (C-3^{C}), 76.32 (C-2^{A}), 76.29 (C-3^{A}), 75.47 (C-3^{B}), 73.49, 72.77, 72.72 (C-4^{B}), 72.69 (C-4^{A}), 72.14, 71.72, 69.12 (C-5^{B}), 68.09 (C-5^{A}, 5^{C}, 7), 66.04, 65.41 (C-4^{C}), 62.28 (C-6^{C}), 61.92 (C-6^{A}), 61.53 (C-6^{B}), 59.55 (C-2^{C}), 51.08 (C-2^{B}), 34.05 (C-11), 28.95 (C-8), 25.61 (C-9), 24.55 (C-10). HR-MS: Calculated for $C_{82}H_{83C}l_3N_4O_{20}$ $[M+H]^+$: 1549.4744, found: 1549.4739.

6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (S15)

The reaction was carried out according to the general procedure A. The donor **1** (2.65 g, 4.47 mmol) and the acceptor **14** (2.12 g, 1.37 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 15 ml

dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which NIS (1.68 g, 7.45 mmol) and TfOH (13 µl, 0.149 mmol) were added. The reaction was stirred at 0 ºC for 2 h. Then the reaction was quenched with saturated $Na_2S_2O_3$, 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 **S15** (2.42 g, 87% yield, pentane:EtOAc = 4:1, R*f* = 0.50-0.55) was obtained as colorless syrup. $[\alpha]_D^{25}$ +105.1 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 444, 474, 650, 697, 710, 734, 734, 797, 822, 976, 1005, 1027, 1047, 1095, 1269, 1315, 1452, 1497, 1721, 2110, 2859, 2932, 3421. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.02 – 7.89 (m, 6H), 7.65 – 6.99 (m, 46H), 6.89 (d, *J* = 9.2 Hz, 1H), 5.23 (d, *J* = 3.5 Hz, 1H, H-1^B), 5.07 (s, 2H), 5.05 (d, *J* = 3.5 Hz, 1H, H-1^C), 4.95 – 4.82 (m, 4H, H-1^D), 4.77 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.82 – 4.04 (m, 25H), 4.02 – 3.70 (m, 7H), 3.67 – 3.55 (m, 3H), 3.39 (dt, *J* = 9.8, 6.5 Hz, 1H, H-7), 2.28 (t, *J* = 7.5 Hz, 2H, H-11), 1.66 – 1.51 (m, 4H, H-10, 8), 1.35 – 1.22 (m, 2H, H-9), 0.96 (s, 9H), 0.84 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.33 (C-12), 165.73, 165.40, 165.38 (3 C=O, Bz), 161.74 (C*ONH*), 139.00, 138.30, 138.16, 138.11, 137.36, 137.16, 136.07, 133.39, 133.30, 132.99, 129.95, 129.80, 129.71, 129.65, 129.62, 129.34, 128.86, 128.56, 128.48, 128.44, 128.40, 128.37, 128.31, 128.25, 128.21, 128.16, 127.88, 127.81, 127.77, 127.65, 127.60, 127.46, 127.37, 127.30, 127.22, 100.10 (C-1^D), 99.33 (C-1^C), 97.00 (C-1^A), 96.84 (C-1^B), 92.51 (C*Cl*$_3$), 77.86 (C-3^D), 76.58 (C-2^A), 76.44 (C-3^A), 76.13 (C-3^C), 74.91 (C-3^B), 73.93, 73.56, 72.97, 72.72 (C-2^D), 72.68 (C-4^C), 72.50 (C-4^A, 4^B), 72.24, 71.62, 70.54 (C-4^D), 70.09, 69.36 (C-5^C), 69.12 (C-5^B), 68.10 (C-7), 68.06 (C-5^A), 67.59 (C-5^D), 66.95 (C-6^D), 66.08, 62.23 (C-6^C), 61.61 (C-6^A), 60.86 (C-6^B), 60.27 (C-2^C), 51.12 (C-2^B), 34.11 (C-11), 29.01 (C-8), 27.66, 27.19, 25.67 (C-9), 24.61 (C-10), 23.31, 20.57 (2 C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 100.10 ($J_{C1,H1}$ = 169 Hz), 99.33 ($J_{C1,H1}$ = 172 Hz), 97.00 ($J_{C1,H1}$ = 168 Hz), 96.84 ($J_{C1,H1}$ = 173 Hz). HR-MS: Calculated for $C_{110}H_{121C}l_3N_4O_{25}Si$ $[M+NH_4]^+$: 2048.7498, found: 2048.7493.



6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (S16)

The reaction was carried out according to the general procedure C using compound **S15** (2.37 g, 1.17 mmol) and HF/pyridine (70%, 485 µl, 18.6 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S16** (2.14 g, 97% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$

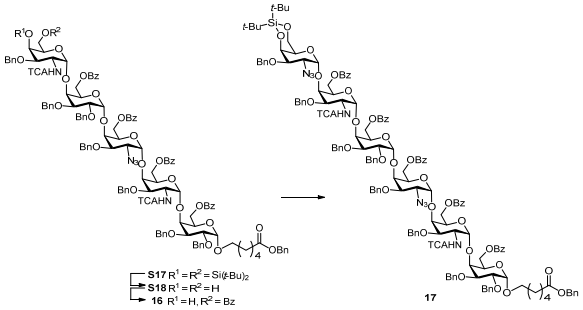
+105.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 711, 736, 820, 1005, 1047, 1096, 1296, 1315, 1360, 1452, 1497, 1720, 2111, 2870, 2926, 3421, 3500. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.04 – 7.89 (m, 6H), 7.65 – 6.98 (m, 45H), 6.93 (d, *J* = 9.3 Hz, 1H, *N*H), 5.24 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.07 (s, 2H), 5.05 (d, *J* = 3.6 Hz, 1H, H-1^C), 4.93 (d, *J* = 3.5 Hz, 1H, H-1^D), 4.91 – 4.83 (m, 3H), 4.78 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.77 – 4.02 (m, 25H), 3.96 – 3.69 (m, 6H), 3.60 (dt, *J* = 9.9, 6.9 Hz, 1H, H-7), 3.45 – 3.31 (m, 2H), 2.78 (bs, 1H), 2.28 (t, *J* = 7.5 Hz, 2H, H-11), 1.68 – 1.49 (m, 4H, H-10, 8), 1.36 – 1.21 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.33 (C-12), 165.71, 165.37, 165.36 (3 C=O, Bz), 161.72 (C*ONH*), 138.23, 138.11, 137.91, 137.25, 137.05, 136.02, 133.38, 133.26, 133.03, 129.80, 129.68, 129.59, 129.29, 128.52, 128.49, 128.45, 128.40, 128.37, 128.32, 128.27, 128.20, 128.17, 128.12, 127.91, 127.84, 127.76, 127.73, 127.62, 127.55, 127.26, 127.19, 100.27 (C-1^D), 99.26 (C-1^C), 96.95 (C-1^A), 96.85 (C-1^B), 92.48 (C*Cl$_3$*), 77.80 (C-3^D), 76.49 (C-2^A), 76.41 (C-3^A), 76.10 (C-3^C), 75.07 (C-3^B), 74.59 (C-2^D), 74.39 (C-4^C), 73.83, 73.53, 72.87, 72.62, 72.49 (C-4^B), 72.40 (C-4^A), 72.08, 71.61, 69.38 (C-5^C, 5^D), 69.11 (C-4^D), 69.03 (C-5^B), 68.08 (C-7), 68.02 (C-5^A), 66.06 (C*H$_2$*), 62.76, 62.21, 61.61, 60.93 (4 C-6), 60.12 (C-2^C), 51.06 (C-2^B), 34.07 (C-11), 28.96 (C-8), 25.62 (C-9), 24.56 (C-10). HR-MS: Calculated for $C_{102}H_{105Cl}l_3N_4O_{25}$ $[M+NH_4]^+$: 1908.6477, found: 1908.6472.

6-(Benzyl hexanoyl) 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranosyl-(1→4)-6-O-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (15)

The reaction was carried out according to the general procedure D using compound **S16** (2.10 g, 1.11 mmol), PhCOOBt (1.33 g, 5.55 mmol) and Et_3N (850 µl, 6.11 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:2). Compound **15** (1.98 g, 92% yield, pentane:EtOAc = 2:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +96.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 697, 710, 735, 820, 1003, 1026, 1047, 1070, 1095, 1156, 1269, 1315, 1361, 1452, 1497, 1508, 1720, 2111, 2870, 2927, 3422. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.05 – 7.89 (m, 8H), 7.63 – 6.99 (m, 48H), 6.94 (d, *J* = 9.3 Hz, 1H), 5.24 (d, *J* = 3.5 Hz, 1H, H-1^B), 5.07 (s, 3H, *C*H$_2$, H-1^C), 4.97 (d, *J* = 3.5 Hz, 1H, H-1^D), 4.92 - 4.83 (m, 3H), 4.79 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.78 – 4.13 (m, 24H), 4.09 (t, *J* = 7.1 Hz, 1H), 4.05 – 3.71 (m, 8H), 3.60 (dt, *J* = 9.8, 6.9 Hz, 1H, H-7), 3.40 (dt, *J* = 9.9, 6.6 Hz, 1H, H-7), 2.28 (t, *J* = 7.5 Hz, 2H, H-11), 1.66 – 1.51 (m, 4H, H-10, 8), 1.32 – 1.20 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.34 (C-12), 165.92, 165.73, 165.38, 165.36 (4 C=O, Bz), 161.72 (C*ONH*), 138.24, 138.12, 138.03, 137.95, 137.11, 137.06, 136.03, 133.39, 133.28, 133.05, 132.91, 129.99, 129.93, 129.82, 129.78, 129.69, 129.60, 129.31, 128.53, 128.49, 128.47, 128.43, 128.41, 128.36, 128.33, 128.29, 128.24, 128.18, 128.13, 127.86, 127.81, 127.76, 127.65, 127.63, 127.59, 127.56, 127.28, 127.17, 99.77 (C-1^D), 99.28 (C-1^C), 96.96 (C-1^A), 96.89 (C-1^B), 92.52 (C*Cl$_3$*), 77.81 (C-3^D), 76.48 (C-2^A), 76.43 (C-3^A), 75.96 (C-3^C), 75.11 (C-3^B), 74.93 (C-2^D), 73.93, 73.88 (C-4^C), 73.53, 72.88, 72.69, 72.52 (C-4^A), 72.36 (C-4^B), 72.27, 71.64, 69.35 (C-5^C), 69.13 (C-5^B), 68.09 (C-7), 68.05 (C-5^A), 67.83 (C-5^D), 66.60 (C-4^D), 66.07 (C*H$_2$*), 62.31, 62.24, 61.63, 60.95 (4 C-6), 60.19 (C-2^C), 51.08 (C-2^B), 34.08 (C-11), 28.98 (C-8), 25.64 (C-9), 24.57 (C-10). HR-MS: Calculated for $C_{109}H_{109}Cl_3N_4O_{26}$ $[M+NH_4]^+$: 2012.6739, found: 2012.6734.

Pentasaccharide S17

The reaction was carried out according to the general procedure B. The donor **3** (968 mg, 1.34 mmol) and the acceptor **15** (1.78 g, 0.89 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 9 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (8 µl, 0.09 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 **S17** (1.60 g, 71% yield, pentane: EtOAc = 5:2, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +107.1 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 711, 736, 820, 1003, 1027, 1047, 1096, 1269, 1452, 1508, 1724, 2111, 2860, 2932, 3416. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.04 – 7.88 (m, 8H), 7.68 – 7.08 (m, 51H), 7.06 – 6.91 (m, 3H), 6.81 (d, *J* = 9.2 Hz, 1H), 5.22 (d, *J* = 3.5 Hz, 1H, H-1^B), 5.11 (d, *J* = 3.6 Hz, 1H, H-1^E), 5.07 (s, 2H), 5.01 (d, *J* = 3.5 Hz, 1H, H-1^D), 4.79 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.92 – 3.66 (m, 44H), 3.61 (dt, *J* = 9.8, 6.9 Hz, 1H, H-7), 3.52 (dd, *J* = 10.7, 2.5 Hz, 1H), 3.49 – 3.34 (m, 2H), 2.29 (t, *J* = 7.5 Hz, 2H, H-11), 1.66 – 1.52 (m, 4H, H-10, 8), 1.35 – 1.26 (m, 2H, H-9), 1.02 – 0.92 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.36 (C-12), 165.77, 165.39, 165.38, 165.15 (4 C=O, Bz), 161.73, 161.52 (2 C*ONH*), 138.26, 138.15, 138.05, 137.87, 137.13, 137.03, 136.06, 133.45, 133.29, 133.20, 133.16, 129.87, 129.77, 129.75, 129.73, 129.66, 129.62, 129.50, 129.33, 128.57, 128.54, 128.52, 128.48, 128.46, 128.43, 128.41, 128.39, 128.32, 128.30, 128.22, 128.17, 128.03, 127.88, 127.83, 127.80, 127.71, 127.69, 127.66, 127.55, 127.31, 127.26, 126.94, 99.22 (C-1^D), 99.08 (C-1^C), 96.98 (C-1^A, 1^B), 96.85 (C-1^E), 92.65, 92.58 (2 C*Cl$_3$*), 76.42, 75.64 (C-3^D), 75.53 (C-3^B), 75.43 (C-3^E), 74.02 (C-3^C), 73.66, 73.54, 72.98, 72.92, 72.84, 72.55 (C-4^A), 72.31 (C-4^C), 71.74, 71.36 (C-4^D), 69.67, 69.45, 69.25, 69.23 (C-5^D), 68.42 (C-5^C), 68.13 (C-7), 68.09 (C-5^A), 67.72 (C-5^E), 66.88 (C-6^E), 66.11 (C*H$_2$*), 62.28, 61.64, 61.26, 60.98 (4 C-6), 60.27 (C-2^C), 51.07 (C-2^B), 49.84 (C-2^E), 34.12 (C-11), 29.02 (C-8), 27.62, 27.29, 25.68 (C-9), 24.61 (C-10), 23.34, 20.66. ^{13}C-HMBC ($CDCl_3$, 100 MHz): 99.22 ($J_{C1,H1}$ = 171 Hz), 99.08 ($J_{C1,H1}$ = 169 Hz), 96.98 ($J_{C1,H1}$ = 170 Hz), 96.85 ($J_{C1,H1}$ = 173 Hz). MALDI-MS: Calculated for $C_{132}H_{141}Cl_6N_5O_{31}Si$ $[M+Na]^+$: 2552.7409, found: 2552.7212.



Pentasaccharide S18

The reaction was carried out according to the general procedure C using compound **S17** (1.57 g, 0.62 mmol) and HF/pyridine (70%, 260 µl, 9.9 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2).

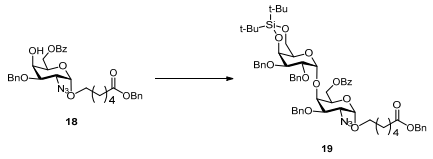
Compound **S18** (1.39 g, 94% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +105.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 698, 711, 736, 820, 1003, 1027, 1046, 1096, 1157, 1269, 1315, 1452, 1508, 1720, 2111, 2872, 2928, 3413. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.04 – 7.87 (m, 8H), 7.67 – 7.50 (m, 4H), 7.49 – 7.07 (m, 48H), 7.07 – 6.94 (m, 3H), 6.80 (d, *J* = 9.4 Hz, 1H, *N*H), 5.22 (d, *J* = 3.4 Hz, 1H, H-1^B), 5.07 (s, 2H), 5.02 (d, *J* = 3.6 Hz, 1H, H-1^D), 4.98 (d, *J* = 3.6 Hz, 1H, H-1^E), 4.90 – 4.21 (m, 28H), 4.21 – 3.87 (m, 12H), 3.82 (dd, *J* = 10.7, 3.5 Hz, 1H), 3.76 (dd, *J* = 10.1, 3.7 Hz, 2H), 3.69 (dd, *J* = 10.2, 3.4 Hz, 1H), 3.61 (dt, *J* = 9.9, 6.9 Hz, 1H, H-7), 3.51 – 3.36 (m, 4H), 2.96 (bs, 1H), 2.28 (t, *J* = 7.5 Hz, 2H, H-11), 1.65 – 1.53 (m, 4H), 1.34 – 1.27 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.37 (C-12), 165.76, 165.40, 165.38, 165.21 (4 C=O, Bz), 161.77, 161.59 (2 C*ONH*), 138.24, 138.12, 138.02, 137.96, 137.11, 137.00, 136.04, 133.44, 133.30, 133.22, 133.18, 129.85, 129.75, 129.70, 129.63, 129.61, 129.38, 129.31, 128.55, 128.53, 128.50, 128.46, 128.45, 128.41, 128.31, 128.28, 128.20, 128.15, 128.00, 127.86, 127.83, 127.78, 127.74, 127.69, 127.65, 127.62, 127.57, 127.30, 126.87, 99.22 (C-1^D), 99.00 (C-1^C), 97.51 (C-1^E), 96.97 (C-1^A, 1^B), 92.56, 92.48 (2 C*Cl$_3$*), 76.75, 76.41 (C-3^C), 76.38 (C-3^D, 3^E), 75.92 (C-3^B), 75.58, 75.14 (C-4^B), 73.89, 73.89, 73.54, 73.33, 72.97, 72.80, 72.70 (C-4^D), 72.62 (C-4^A), 72.40 (C-4^C), 71.77, 71.11, 69.28 (C-5^D), 69.21 (C-5^B), 68.67 (C-5^C), 68.12 (C-7), 68.09 (C-5^A), 66.79 (C-5^E), 66.09 (C*H$_2$*), 62.56, 62.29, 61.60, 61.28, 61.17 (5 C-6), 60.33 (C-2^C), 51.05 (C-2^B), 50.44 (C-2^E), 34.10 (C-11), 28.99 (C-8), 25.65 (C-9), 24.59 (C-10). HR-MS: Calculated for $C_{124}H_{125}Cl_6N_5O_{31}$ $[M+NH_4]^+$: 2407.68334, found: 2407.68279.

Pentasaccharide 16

The reaction was carried out according to the general procedure D using compound **S18** (1.38 g, 0.58 mmol), PhCOOBt (689 mg, 2.88 mmol) and Et_3N (440 µl, 3.17 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:2). Compound **16** (1.35 g, 94% yield, pentane:EtOAc = 2:1, R*f* = 0.25-0.30) was obtained as yellow syrup. $[\alpha]_D^{25}$ +105.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 700, 711, 737, 819, 1003, 1027, 1047, 1096, 1159, 1269, 1315, 1452, 1508, 1720, 2111, 2872, 2929, 3413. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.05 – 7.86 (m, 10H), 7.69 – 6.92 (m, 57H), 6.79 (d, *J* = 9.4 Hz, 1H), 5.23 (d, *J* = 3.5 Hz, 1H, H-1^B), 5.07 (s, 2H), 5.05 - 5.01 (m, 2H, H-1^D, 1^E), 4.85 (d, *J* = 3.5 Hz, 1H, H-1^C), 4.90 – 4.42 (m, 23H), 4.40 – 4.06 (m, 12H), 4.02 – 3.85 (m, 5H), 3.84 – 3.69 (m, 4H), 3.66 – 3.57 (m, 1H), 3.54 (dd, *J* = 10.6, 2.8 Hz, 1H), 3.44 – 3.36 (m, 1H), 2.60 (bs, 1H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.66 – 1.52 (m, 4H), 1.36 – 1.22 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.37 (C-12), 165.90, 165.76, 165.39, 165.17 (C=O, Bz), 161.76, 161.54 (C*ONH*), 138.25, 138.14, 137.98, 137.83, 137.16, 137.08, 137.01, 136.06, 133.45, 133.31, 133.20, 133.10, 129.90, 129.85, 129.76, 129.74, 129.72, 129.64, 129.62, 129.57, 129.36, 129.32, 128.58, 128.56, 128.55, 128.51, 128.48, 128.44, 128.43, 128.40, 128.35, 128.32, 128.29, 128.21, 128.20, 128.16, 128.06, 127.88, 127.81, 127.79, 127.75, 127.71, 127.67, 127.64, 127.34, 127.30, 126.90, 99.23 (C-1^D), 99.13 (C-1^C), 96.97 (C-1^A, 1^B), 96.93 (C-1^E), 92.57, 92.53 (C*Cl$_3$*), 76.67, 76.44, 76.42, 76.10, 75.82, 75.57, 75.03, 73.92, 73.56, 73.36, 73.00, 72.95, 72.81, 72.59, 72.37, 71.90, 71.52, 69.27, 69.22, 68.51, 68.13, 68.09, 67.99, 66.10, 65.26, 62.87, 62.29, 61.64, 61.26, 61.05 (5 C-6), 60.35 (C-2C), 51.06 (C-2B), 50.47 (C-2^E), 34.11 (C-11), 29.01 (C-8), 25.67 (C-9), 24.61 (C-10). MALDI-MS: Calculated for $C_{131}H_{129}Cl_6N_5O_{32}$ $[M+Na]^+$: 2516.6650, found: 2516.6458.

Hexasaccharide 17

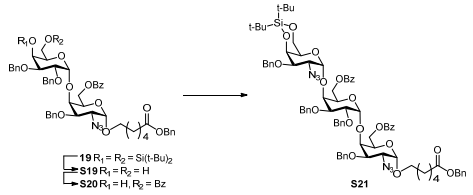
The reaction was carried out according to the general procedure B. The donor **2** (655 mg, 1.08 mmol) and the acceptor **16** (1.31 g, 0.54 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 6 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 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 = 7:2). Compound **17** (1.19 g, 73% yield, pentane: EtOAc = 3:1, R*f* = 0.40-0.50) was obtained as yellow syrup. $[\alpha]_D^{25}$ +116.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 651, 698, 710, 736, 797, 820, 1003, 1027, 1046, 1096, 1267, 1315, 1452, 1508, 1720, 2111, 2860, 2932, 3420. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.02 – 7.90 (m, 10H), 7.62 – 7.50 (m, 5H), 7.49 – 6.90 (m, 57H), 6.84 (d, *J* = 9.6 Hz, 1H), 5.23 (d, *J* = 3.5 Hz, 1H, H-1^B), 5.07 (s, 3H, *C*H$_2$, H-1^E), 5.03 (d, *J* = 3.5 Hz, 1H, H-1^D), 5.00 (d, *J* = 3.6 Hz, 1H, H-1^F), 4.89 – 4.44 (m, 27H), 4.43 – 4.06 (m, 14H), 4.03 – 3.57 (m, 13H), 3.53 (dd, *J* = 10.8, 2.3 Hz, 1H), 3.45 – 3.36 (m, 1H, H-7), 2.29 (t, *J* = 7.5 Hz, 2H, H-11), 1.66 – 1.54 (m, 4H, H-10, 8), 1.35 – 1.27 (m, 2H, H-9), 1.00 – 0.92 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.33 (C-12), 165.76, 165.40, 165.24 (C=O, Bz), 161.76, 161.67 (2 C*ONH*), 138.28, 138.16, 138.00, 137.93, 137.16, 137.11, 137.03, 136.09, 133.44, 133.31, 133.28, 133.25, 133.18, 129.87, 129.77, 129.73, 129.68, 129.63, 129.56, 129.40, 129.36, 128.57, 128.54, 128.52, 128.49, 128.46, 128.44, 128.40, 128.33, 128.26, 128.22, 128.16, 128.14, 128.05, 127.88, 127.82, 127.79, 127.75, 127.72, 127.68, 127.66, 127.44, 127.33, 126.94, 126.86, 99.32 (C-1^F), 99.24 (C-1^D), 99.00 (C-1^C), 97.01 (C-1^A, 1^B, 1^E), 92.60, 92.53 (2 C*Cl$_3$*), 76.45, 76.24, 76.12, 76.04, 75.94, 75.61, 75.21, 73.78, 73.58, 73.21, 73.00, 72.94, 72.82, 72.59, 72.43, 72.18, 72.14, 71.82, 71.71, 70.63, 69.61, 69.29, 69.15, 68.15, 68.12, 67.89, 66.93 (C-6F), 66.10 (C*H$_2$*), 62.30, 61.66, 61.63, 61.30, 61.16 (5 C-6), 60.43 (C-2^C), 58.86 (C-2^F), 51.08 (C-2^B), 50.92 (C-2^E), 34.12 (C-11), 29.03 (C-8), 27.64, 27.34, 25.69 (C-9), 24.62 (C-10), 23.27, 20.69. ^{13}C-HMBC ($CDCl_3$, 100 MHz): 99.32 ($J_{C1,H1}$ = 172 Hz), 99.24 ($J_{C1,H1}$ = 171 Hz), 99.00 ($J_{C1,H1}$ = 169 Hz), 97.01 ($J_{C1,H1}$ = 173 Hz, 167 Hz). MALDI-MS: Calculated for $C_{152}H_{160}Cl_6N_8O_{36}Si$ [M+Na]$^+$: 2933.8733, found: 2933.8520.



6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (19)

The reaction was carried out according to the general procedure A. The donor **1** (2.43 g, 4.11 mmol) and the acceptor **18** (1.65 g, 2.74 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 22 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 3Å. The solution was cooled to 0 °C, after which NIS (1.23 g, 5.48 mmol) and TfOH (24 µl, 0.27 mmol) were added. The reaction was stirred at 0 °C for

1 h. Then the reaction was quenched with saturated $Na_2S_2O_3$, 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 = 8:1). Compound **19** (2.52 g, 85% yield) was obtained as colorless syrup. $[\alpha]_D^{25}$ +112.6 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.06 – 7.97 (m, 2H, *aromatic* H), 7.56– 7.09 (m, 23H, *aromatic* H), 5.04 (s, 2H, *PhC*H_2O), 4.97 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.94 – 4.87 (m, 2H, H-1^B, *PhC*H*H*O), 4.86 – 4.70 (m, 4H, 3x*PhC*H*H*O, H-6^A), 4.69 – 4.53 (m, 3H, 2x*PhC*H*H*O, H-6^A), 4.49 (d, *J* = 2.8 Hz, 1H, H-4^B), 4.17 (d, *J* = 2.9 Hz, 1H, H-4^A), 4.13 – 4.00 (m, 3H, H-2^B, 5^A, 5^B), 3.99 – 3.86 (m, 2H, H-3^A, 3^B), 3.78 – 3.60 (m, 4H, H-6^B, 2^A, 7), 3.50 – 3.37 (m, 1H, H-7), 2.27 (t, *J* = 7.4 Hz, 2H, H-12), 1.56 (p, *J* = 8.0 Hz, 4H, H-8, 10), 1.40 – 1.23 (m, 2H, H-9), 1.00 (s, 9H, *C*H_3), 0.97 (s, 9H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.97 (C=O), 165.73 (C*OPh*), 138.80, 138.11, 137.17, 135.97, 133.04, 129.68, 129.46, 128.75, 128.34, 128.32, 128.30, 128.18, 128.13, 127.95, 127.94, 127.62, 127.46, 127.37, 127.26, 127.09 (*aromatic* C/*CH*), 100.36 (C-1^B), 97.86 (C-1^A), 77.77 (C-3^B), 75.51 (C-3^A), 74.00 (CH_2*Ph*), 73.57 (C-4^A), 72.96 (C-2^B), 71.73 (CH_2*Ph*), 70.42 (C-4^B), 70.01 (CH_2*Ph*), 68.69 (C-5^A), 67.86 (C-7), 67.60 (C-5^B), 66.81 (C-6^B), 65.79 (*C*=*O*CH_2*Ph*), 62.55 (C-6^A), 59.37 (C-2^A), 33.85 (C-11), 28.79 (C-8), 27.50 (CH_3), 27.15 (CH_3), 25.46 (C-9), 24.34 (C-10), 23.14 (C-*Si*), 20.49 (C-*Si*). HR-MS: Calculated for $C_{61}H_{75}O_{13}N_3Si$ $[M+Na]^+$: 1108.4967, found: 1108.4960.



6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S19)

The reaction was carried out according to the general procedure C using compound **19** (2.50 g, 2.3 mmol) and HF/pyridine (70%, 960 µl, 36.8 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S19** (2.08 g, 96% yield) was obtained as syrup. $[\alpha]_D^{25}$ +94.5 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.05 – 7.96 (m, 2H, *aromatic* H), 7.62 – 7.13 (m, 23H, *aromatic* H), 5.07 (s, 2H, *C*H_2*Ph*), 4.99 (d, *J* = 2.9 Hz, 1H, H-1^B), 4.96 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.88 – 4.58 (m, 8H, 3X*C*H_2*Ph*, H-6^A), 4.16 – 4.03 (m, 4H), 3.99 – 3.88 (m, 3H), 3.71 – 3.59 (m, 2H, H-2^A, 7), 3.57 – 3.39 (m, 3H, H-6^B, 7), 2.89 (bs, 1H, *O*H), 2.48 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-12), 1.66 – 1.50 (m, 4H, H-8, 10), 1.39 – 1.24 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.36 (C=O), 165.98 (C*OPh*), 138.02, 137.89, 137.24, 136.05, 133.30, 129.72, 129.62, 128.57, 128.54, 128.40, 128.33, 128.17, 128.14, 128.09, 127.96, 127.79, 127.73 (*aromatic* C), 100.63 (C-1B), 98.00 (C-1A), 77.89 (C-3B), 75.80 (C-3A), 75.46 (C-4A), 75.22 (C-2A), 74.25 (CH_2*Ph*), 72.35 (CH_2*Ph*), 72.28 (CH_2*Ph*), 69.69 (C-5B), 69.17 (C-4B), 68.83 (C-5A), 68.13 (C-7), 66.07 (CH_2*Ph*), 62.92 (C-6B), 62.71 (C-6A), 59.50 (C-2B), 34.09 (C-11), 28.96 (C-8), 25.62 (C-9), 24.53 (C-10). HR-MS: Calculated for $C_{53}H_{59}O_{13}N_3$ $[M+Na]^+$: 968.3946, found: 968.3940.

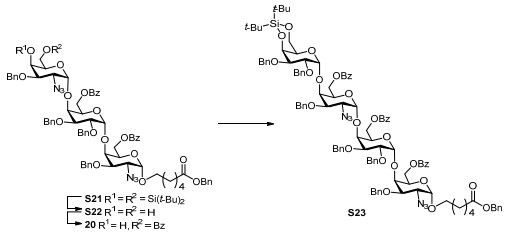
6-(Benzyl hexanoyl) 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S20)

The reaction was carried out according to the general procedure D using compound **S19** (2.06 g, 2.18 mmol), PhCOOBt (2.35 g, 9.81 mmol) and Et_3N (1.52 ml, 10.9 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S20** (2.43 g, 94% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +92.1 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.04 – 7.97 (m, 2H, *aromatic* H), 7.96 – 7.89 (m, 2H, *aromatic* H), 7.61 – 7.49 (m, 2H, *aromatic* H), 7.48 – 7.15 (m, 23H, *aromatic* H), 7.13 – 7.05 (m, 1H, *aromatic* H), 5.07 (s, 2H, *CH*$_2$*Ph*), 5.03 (d, *J* = 3.4 Hz, 1H, H-1^B), 4.96 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.86 (d, *J* = 11.8 Hz, 1H, *CHHPh*), 4.82 – 4.76 (m, 2H, 2x*CHHPh*), 4.76 – 4.57 (m, 5H, 3x*CHHPh*, H-6^A), 4.53 – 4.43 (m, 2H, H-5^B, 6^B), 4.14 (d, *J* = 2.7 Hz, 1H, H-4^A), 4.11 – 4.00 (m, 4H, H-4^B, 5^A, 3^B, 6^B), 3.97 (dd, *J* = 9.9, 3.3 Hz, 1H, H-2^B), 3.89 (dd, *J* = 10.8, 2.7 Hz, 1H, H-3^A), 3.72 (dd, *J* = 10.8, 3.5 Hz, 1H, H-2^A), 3.64 (dt, *J* = 9.7, 6.7 Hz, 1H, H-7), 3.43 (dt, *J* = 9.8, 6.5 Hz, 1H, H-7), 2.69 (s, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.51 (m, 4H, H-8, 10), 1.37 – 1.22 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.38 (C=O), 166.06 (C*OPh*), 165.99 (C*OPh*), 138.07, 138.02, 137.25, 136.08, 133.31, 132.96, 130.07, 129.92, 129.76, 129.62, 128.56, 128.55, 128.53, 128.44, 128.43, 128.40, 128.36, 128.26, 128.20, 128.17, 127.93, 127.83, 127.81, 127.52 (*aromatic CH*/C), 100.27 (C-1^B), 98.05 (C-1^A), 77.92 (C-3^B), 75.47 (C-3^A, 2^B), 75.03 (C-4^A), 74.38, 72.44, 72.27 (3 C*H*$_2$*Ph*), 68.86 (C-5^A), 68.14 (C-7), 68.12 (C-5^B), 66.84 (C-4^B), 66.10 (C*H*$_2$*Ph*), 62.82 (C-6^A), 62.56 (C-6^B), 59.61 (C-2^A), 34.12 (C-11), 28.99 (C-8), 25.64 (C-9), 24.56 (C-10). HR-MS: Calculated for $C_{60}H_{63}O_{14}N_3$ $[M+Na]^+$: 1072.4208, found: 1072.4202.

6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S21)

The reaction was carried out according to the general procedure B. The donor **2** (1.99 g, 3.29 mmol) and the acceptor **S20** (2.30 g, 2.19 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 22 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 3Å. The solution was cooled to 0 ºC, after which TfOH (19 µl, 0.22 mmol) were 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 = 6:1). Compound **S21** (2.77 g, 86% yield) was obtained as white foam. $[\alpha]_D^{25}$ +109 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.05 – 7.99 (m, 2H, *aromatic* H), 7.98 – 7.92 (m, 2H, *aromatic* H), 7.62 – 7.50 (m, 2H, *aromatic* H), 7.49 – 7.15 (m, 28H, *aromatic* H), 7.15 – 7.08 (m, 1H, *aromatic* H), 5.12 (d, *J* = 2.2 Hz, 1H, H-1^B), 5.07 (d, *J* = 2.7 Hz, 1H, H-1^C), 5.06 (s, 2H, *CH*$_2$*Ph*), 4.95 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.87 – 4.55 (m, 10H, 8x*CHHPh*, H-6^A), 4.52 – 4.32 (m, 4H, H-4^C, 5^B, 6^B), 4.26 (d, *J* = 1.7 Hz, 1H, H-4^B), 4.16 (d, *J* = 2.8 Hz, 1H, H-4^A), 4.11 – 4.04 (m, 1H, H-5^A), 4.04 – 3.97 (m, 3H, H-3^B, 2^B, 5^C), 3.89 (dd, *J* = 10.8, 2.7 Hz, 1H, H-3^A), 3.85 – 3.54 (m, 6H, H-2^C, 3^C, 6^C, 2^A, 7), 3.48 – 3.38 (m, 1H, H-7), 2.29 (t, *J* = 7.4 Hz, 2H, H-11), 1.65 – 1.51 (m,

4H, H-8, 10), 1.37 – 1.24 (m, 2H, H-9), 1.02 (s, 9H, C*H*$_3$), 0.97 (s, 9H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.16 (C=O), 165.87 (C*OPh*), 165.31 (C*OPh*), 138.06, 137.89, 137.82, 137.22, 135.99, 133.21, 132.98, 129.66, 129.62, 129.58, 129.51, 128.45, 128.44, 128.41, 128.39, 128.36, 128.30, 128.07, 128.04, 127.76, 127.74, 127.72, 127.54, 127.48, 127.24 (*aromatic* C/*CH*), 99.66 (C-1B), 98.39 (C-1C), 97.92 (C-1A), 76.79 (C-3B), 75.67 (C-3C), 75.37 (C-2B), 75.00 (C-3A), 74.77 (C-4A), 73.88 (C*H*$_2$*Ph*), 73.21 (C-4B), 72.83, 72.11, 70.12 (3 C*H*$_2$*Ph*), 69.50 (C-4C), 68.82 (C-5A), 68.76 (C-5B), 67.97 (C-7), 67.37 (C-5C), 66.82 (C-6C), 65.93 (C*H*$_2$*Ph*), 62.83 (C-6A), 61.34 (C-6B), 59.57 (C-2A), 58.71 (C-2C), 33.97 (C-11), 28.85 (C-8), 27.53 (C*H*$_3$), 27.20 (C*H*$_3$), 25.53 (C-9), 24.43 (C-10), 23.24, 20.58 (2 C-*Si*). HR-MS: Calculated for $C_{81}H_{94}O_{18}N_6Si$ $[M+Na]^+$: 1489.6292, found: 1489.6286.



6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S22)

The reaction was carried out according to the general procedure C using compound **S21** (2.75 g, 1.87 mmol) and HF/pyridine (70%, 780 µl, 30 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S22** (2.46 g, 99% yield) was obtained as syrup. $[\alpha]_D^{25}$ +91.6 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 7.99 (m, 2H, *C*H, Bz), 7.96 – 7.88 (m, 2H, *C*H, Bz), 7.63 – 7.51 (m, 2H), 7.50 – 7.15 (m, 28H), 7.12 – 7.04 (m, 1H), 5.09 (d, *J* = 3.4 Hz, 1H, H-1^B), 5.06 (s, 2H, *PhC*H$_2$), 4.97 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.91 (d, *J* = 3.0 Hz, 1H, H-1^C), 4.85 – 4.78 (m, 5H, 5x*PhCH*H), 4.74 – 4.59 (m, 5H, 3x*PhCH*H, H-6^A), 4.55 (t, *J* = 9.9 Hz, 1H, H-6^B), 4.47 – 4.40 (m, 1H, H-5^B), 4.17 (d, *J* = 2.7 Hz, 1H, H-4^A), 4.14 – 3.98 (m, 6H, H-3^C, 4^A, 4^C, 5^A, 5^C, 6^B), 3.98 – 3.87 (m, 2H, H-2^B, 3^A), 3.79 – 3.61 (m, 4H, H-2^A, 2^C, 3^B, 7), 3.53 – 3.41 (m, 3H, H-6^C, 7), 2.93 (bs, 1H, *O*H), 2.35 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.52 (m, 4H, H-8, 10), 1.39 – 1.25 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.26 (C-12), 165.90, 165.31 (2 C=O, Bz), 137.95, 137.11, 137.05, 135.93, 133.24, 132.97, 129.59, 129.51, 128.50, 128.46, 128.42, 128.38, 128.34, 128.29, 128.26, 128.06, 128.02, 127.80, 127.78, 127.73, 127.69, 127.66, 127.22 (aromatic), 99.74 (C-1^B), 99.14 (C-1^C), 97.90 (C-1^A), 76.90 (C-3^B), 76.63 (C-3^C), 75.65 (C-4^B), 75.17 (C-3^A), 74.83 (C-2^B), 74.64 (C-4^A), 73.57, 72.96, 72.17, 71.69 (4 C*H*$_2$), 69.34 (C-5), 68.89 (C-5), 68.74 (C-5), 68.01 (C-7), 67.38 (C-4^C), 65.96 (C*H*$_2$), 62.64 (C-6), 62.58 (C-6), 61.30 (C-6^B), 59.78 (C-2^C), 59.58 (C-2^A), 33.98 (C-11), 28.85 (C-8), 25.51 (C-9), 24.42 (C-10). HR-MS: Calculated for $C_{73}H_{78}O_{18}N_6$ $[M+Na]^+$: 1349.5270, found: 1349.5265.

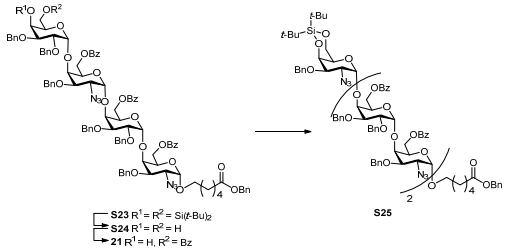
6-(Benzyl hexanoyl) 2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (20)

The reaction was carried out according to the general procedure D using compound **S22** (2.43 g, 1.83 mmol), PhCOOBt (1.97 g, 8.24 mmol) and Et_3N (1.3 ml, 9.15 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **20** (2.56 g, 98% yield) was obtained as white solid. $[\alpha]_D^{25}$ +81 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 8.01 (m, 2H, *C*H, Bz), 7.97 – 7.89 (m, 4H, *C*H, Bz), 7.64 – 7.04 (m, 34H, aromatic), 5.10 (d, *J* = 3.2 Hz, 1H, H-1^B), 5.05 (s, 2H, *PhC*H$_2$), 4.99 (d, *J* = 3.0 Hz, 1H, H-1^C), 4.97 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.91 – 4.77 (m, 5H, 5x*PhCH*H), 4.76 – 4.60 (m, 5H, 3x*PhCH*H, H-6^A), 4.59 – 4.39 (m, 4H, H-5, 6), 4.26 – 4.17 (m, 2H, H-4^A, 4^B), 4.17 – 3.97 (m, 6H), 3.91 (dd, *J* = 10.7, 2.7 Hz, 1H, H-3^A), 3.85 – 3.74 (m, 2H, H-2^C, 3^C), 3.73 – 3.58 (m, 2H, H-2^A, 7), 3.44 (dt, *J* = 9.6, 6.3 Hz, 1H, H-7), 2.73 (bs, 1H, *O*H), 2.29 (t, *J* = 7.4 Hz, 2H, H-11), 1.68 – 1.50 (m, 4H, H-8, 10), 1.41 – 1.23 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.12 (C-12), 165.78, 165.73, 165.16 (3 C=O, Bz), 137.95, 137.82, 137.08, 137.03, 135.84, 133.13, 132.89, 129.63, 129.50, 129.46, 129.41, 129.36, 128.36, 128.31, 128.24, 128.20, 128.18, 128.16, 128.14, 127.95, 127.91, 127.70, 127.58, 127.43, 127.30, 127.14 (aromatic), 99.79 (C-1^B), 98.66 (C-1^C), 97.80 (C-1^A), 76.71 (C-3^B), 76.35 (C-3^C), 75.02 (C-3^A), 74.81, 74.71, 74.50 (C-4^A), 73.59, 72.74, 72.01, 71.73 (4 C*H*$_2$), 68.73 (C-5), 68.65 (C-5), 67.88 (C-7), 67.76 (C-5^C), 65.83 (C*H*$_2$), 65.35 (C-4^C), 62.56 (C-6^A), 62.27 (C-6^C), 61.17 (C-6^B), 59.60 (C-2^C), 59.48 (C-2^A), 33.85 (C-11), 28.74 (C-8), 25.40 (C-9), 24.30 (C-10). HR-MS: Calculated for $C_{80}H_{82}O_{19}N_6$ $[M+Na]^+$: 1453.5532, found: 1453.5527.

6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S23)

The reaction was carried out according to the general procedure A. The donor **1** (2.09 g, 3.53 mmol) and the acceptor **20** (2.53 g, 1.77 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 18 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which NIS (2.07 g, 9.2 mmol) and TfOH (16 µl, 0.18 mmol) were added. The reaction was stirred at 0 ºC for 2 h. Then the reaction was quenched with saturated $Na_2S_2O_3$, 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 **S23** (2.85 g, 84% yield) was obtained as white solid. $[\alpha]_D^{25}$ +110 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07 – 7.99 (m, 2H, *C*H, Bz), 7.96 – 7.89 (m, 4H, *C*H, Bz), 7.62 – 7.53 (m, 3H. aromatic), 7.48 – 7.38 (m, 10H, aromatic), 7.37 – 7.03 (m, 31H, aromatic), 5.06 (d, *J* = 4.8 Hz, 3H, *PhC*H$_2$, H-1), 5.03 – 4.94 (m, 4H, 3xH-1, *PhCH*H,), 4.92 – 4.45 (m, 18H), 4.37 (dd, *J* = 9.5, 5.5 Hz, 1H), 4.20 (d, *J* = 2.5 Hz, 1H, H-4^B), 4.15 (d, *J* = 2.8 Hz, 1H, H-4^A), 4.11 (d, *J* = 2.5 Hz, 1H, H-4^C), 4.09 – 3.85 (m, 8H), 3.84 – 3.71 (m, 2H), 3.70 – 3.56 (m, 4H), 3.45 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.52 (m, 4H, H-8, 10), 1.38 – 1.24 (m, 2H, H-9), 0.97 (s, 9H, *C*H$_3$), 0.90 (s, 9H, *C*H$_3$). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 173.32 (C-12), 165.98, 165.38, 165.34 (3 C=O, Bz), 138.90, 138.37, 138.27, 138.12, 137.37, 137.21, 136.05, 133.31, 133.19, 133.11, 129.80, 129.72, 129.69, 129.67, 129.62, 129.60, 128.85, 128.55, 128.53, 128.51, 128.43, 128.41, 128.37, 128.33, 128.29, 128.25, 128.17, 128.13, 127.76, 127.69, 127.65, 127.62, 127.58, 127.55, 127.52, 127.39, 127.29, 126.83 (*aromatic*), 100.04 (C-1^B, 1^C), 98.95 (C-1^D), 98.01 (C-1^A), 77.81, 77.36, 76.36, 76.15, 75.46, 75.28, 75.06, 74.60 (C-4^A), 74.03, 73.76, 72.83 (3 CH_2), 72.70, 72.54, 72.19, 71.90 (2 CH_2), 70.50, 70.07 (CH_2), 68.90, 68.84, 68.08 (C-7), 67.59, 66.92 (C-6^D), 66.06 (CH_2), 62.72 (C-6^A), 61.33 (C-6), 61.09 (C-6), 60.62 (C-2^C), 59.66 (C-2^A), 34.08 (C-11), 28.96 (C-8), 27.64, 27.20, 25.63 (C-9), 24.53 (C-10), 23.29, 20.60 (2 C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 100.04 ($J_{C1,H1}$ = 169 Hz, 170 Hz), 98.95 ($J_{C1,H1}$ = 172 Hz), 98.01 ($J_{C1,H1}$ = 171 Hz). HR-MS: Calculated for $C_{108}H_{120}O_{24}N_6Si$ $[M+Na]^+$: 1935.8021, found: 1935.8016.



6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S24)

The reaction was carried out according to the general procedure C using compound **S23** (1.5 g, 0.78 mmol) and HF/pyridine (70%, 326 µl, 12.5 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S24** (1.29 g, 93% yield) was obtained as white solid. $[\alpha]_D^{25}$ +102 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.06 – 7.99 (m, 2H, *C*H, Bz), 7.98 – 7.90 (m, 4H, *C*H, Bz), 7.61 – 7.52 (m, 3H), 7.50 – 7.37 (m, 10H), 7.36 – 7.03 (m, 31H, *aromatic*), 5.07 (d, *J* = 6.4 Hz, 3H, *Ph*CH_2, H-1^B), 5.04 (d, *J* = 3.3 Hz, 1H, H-1^D), 5.01 (d, *J* = 2.5 Hz, 1H, H-1^C), 4.96 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.94 – 4.75 (m, 6H), 4.74 – 4.35 (m, 13H), 4.21 – 3.84 (m, 12H), 3.84 – 3.74 (m, 2H), 3.71 – 3.58 (m, 2H, H-2^A, 7), 3.51 – 3.30 (m, 3H, H-6, 7), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.69 – 1.50 (m, 4H, H-8, 10), 1.38 – 1.24 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.28 (C-12), 165.94, 165.34, 165.32 (3 C=O, Bz), 138.18, 138.12, 137.89, 137.81, 137.30, 137.15, 135.99, 133.27, 133.21, 133.06, 129.68, 129.64, 129.56, 129.53, 128.51, 128.50, 128.48, 128.43, 128.38, 128.36, 128.27, 128.22, 128.12, 128.08, 127.91, 127.84, 127.70, 127.67, 127.59, 127.54, 127.51, 127.35, 127.21, 100.37 (C-1^B), 99.91 (C-1^D), 98.77 (C-1^C), 97.94 (C-1^A), 77.73 (C-3^D), 76.20, 76.15, 75.29, 75.22, 75.01, 74.66, 74.52, 74.34, 73.99, 73.81, 72.78, 72.21, 72.17, 72.02 (6 CH_2), 69.26, 69.14, 69.02, 68.87, 68.80, 68.04 (C-7), 66.01 (CH_2), 62.78 (C-6), 62.68 (C-6), 61.34 (C-6), 61.22 (C-6), 60.41 (C-2^C), 59.62 (C-2^A), 34.02 (C-11), 28.90 (C-8), 25.57 (C-9), 24.47 (C-10). HR-MS: Calculated for $C_{100}H_{104}O_{24}N_6$ $[M+Na]^+$: 1795.7000, found: 1795.6994.

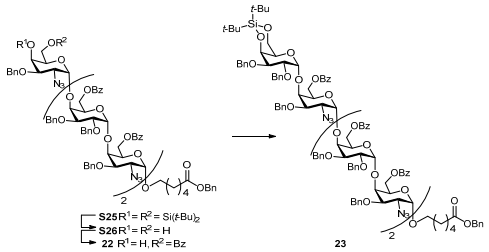
6-(Benzyl hexanoyl) 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (21)

The reaction was carried out according to the general procedure D using compound **S24** (2.33 g, 1.31 mmol), PhCOOBt (1.41 g, 5.9 mmol) and Et_3N (913 µl, 6.55 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:1). Compound **21** (2.36 g, 96% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +86.3 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 7.99 (m, 2H, *C*H, Bz), 7.98 – 7.87 (m, 6H, *C*H, Bz), 7.63 – 7.00 (m, 47H, *aromatic*), 5.11 – 5.06 (m, 2H, H-1^B, 1^D), 5.06 (s, 2H, *PhC*H$_2$), 5.02 (d, *J* = 3.3 Hz, 1H, H-1^C), 4.96 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.93 – 4.35 (m, 21H), 4.20 (d, *J* = 2.4 Hz, 1H, H-4), 4.18 – 4.13 (m, 2H), 4.11 – 3.77 (m, 11H), 3.71 – 3.59 (m, 2H, H-2^A, 7), 3.44 (dt, *J* = 9.7, 6.3 Hz, 1H, H-7), 2.60 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.51 (m, 4H, H-8, 10), 1.39 – 1.24 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.43 (C-12), 166.09, 165.97, 165.48, 165.47 (4 C=O, Bz), 138.38, 138.30, 138.10, 137.34, 137.32, 136.16, 133.42, 133.37, 133.22, 133.01, 130.03, 129.88, 129.83, 129.80, 129.73, 129.67, 128.66, 128.64, 128.56, 128.54, 128.52, 128.48, 128.43, 128.41, 128.33, 128.28, 128.24, 127.95, 127.87, 127.83, 127.77, 127.67, 127.38, 127.31, 100.19 (C-1^B), 100.11 (C-1^D), 99.00 (C-1^C), 98.11 (C-1^A), 78.01, 76.33, 76.20, 75.45, 75.20, 75.11, 74.70, 74.27, 74.03, 72.92, 72.42, 72.34, 72.31 (6 C*H*$_2$), 69.05, 68.97, 68.20 (C-7), 68.03, 66.58, 66.16 (C*H*$_2$), 62.86 (C-6), 62.24 (C-6), 61.52 (C-6), 61.39 (C-6), 60.65 (C-2^C), 59.79 (C-2^A), 34.19 (C-11), 29.07 (C-8), 25.73 (C-9), 24.63 (C-10). HR-MS: Calculated for $C_{107}H_{108}O_{25}N_6$ $[M+Na]^+$: 1899.7262, found: 1899.7256.

Pentasaccharide S25

The reaction was carried out according to the general procedure B. The donor **2** (973 mg, 1.6 mmol) and the acceptor **21** (2.01 g, 1.07 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 11 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TfOH (10 µl, 0.11 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 = 5:1). Compound **S25** (2.10 g, 85% yield) was obtained as syrup. $[\alpha]_D^{25}$ +95.8 (c=2, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07 – 7.99 (m, 2H, *C*H, Bz), 7.99 – 7.87 (m, 6H, *C*H, Bz), 7.64 – 7.02 (m, 52H), 5.13 (d, *J* = 2.9 Hz, 1H, H-1), 5.07 (d, *J* = 3.2 Hz, 1H, H-1), 5.06 (s, 2H, *PhC*H$_2$), 5.00 (d, *J* = 3.0 Hz, 1H, H-1), 4.97 – 4.93 (m, 2H, H-1), 4.93 – 4.33 (m, 24H), 4.23 – 3.52 (m, 21H), 3.44 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.51 (m, 4H, H-8, 10), 1.38 – 1.24 (m, 2H, H-9), 1.00 (s, 9H, *C*H$_3$), 0.94 (s, 9H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.28 (C-12), 165.95, 165.39, 165.35, 165.23 (4 C=O, Bz), 138.19, 138.13, 138.03, 137.94, 137.92, 137.23, 137.19, 136.04, 133.30, 133.08, 132.99, 129.74, 129.71, 129.69, 129.66, 129.61, 129.59, 129.56, 128.57, 128.53, 128.51, 128.44, 128.42, 128.38, 128.31, 128.28, 128.21, 128.15, 128.11, 127.74, 127.72, 127.68, 127.55, 127.52, 127.44, 127.31, 127.25, 127.18, 99.95 (C-1), 99.63 (C-1), 98.77 (C-1), 98.48 (C-1),

97.98 (C-1^{A}), 76.65, 76.33, 75.75, 75.66, 75.46, 75.32, 75.07, 74.74, 74.57, 73.99, 73.65 (2 CH_2), 73.33, 72.82, 72.66, 72.20 (3 CH_2), 70.21 (CH_2), 69.51, 68.92, 68.83, 68.78, 68.07 (C-7), 67.39, 66.88 (C-6^{E}), 66.03 (CH_2), 62.69 (C-6), 61.39 (C-6), 61.16 (C-6), 60.56 (C-2), 59.66 (C-2), 58.86 (C-2), 34.06 (C-11), 28.94 (C-8), 27.58, 27.24, 25.61 (C-9), 24.51 (C-10), 23.30, 20.62 (2 C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 99.95 ($J_{C1,H1}$ = 169 Hz), 99.63 ($J_{C1,H1}$ = 169 Hz), 98.77 ($J_{C1,H1}$ = 171 Hz), 98.48 ($J_{C1,H1}$ = 171 Hz), 97.98 ($J_{C1,H1}$ = 171 Hz). MALDI-MS: Calculated for $C_{128}H_{139}N_9O_{29}Si[M+Na]^+$: 2316.9346, found: 2316.9340.



Pentasaccharide S26

The reaction was carried out according to the general procedure C using compound **S25** (1.52 g, 0.66 mmol) and HF/pyridine (70%, 275 µl, 10.6 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S26** (1.85 g, 96% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +82.6 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 7.91 (m, 6H, *C*H, Bz), 7.87 (d, *J* = 7.7 Hz, 2H, *C*H, Bz), 7.68 – 6.95 (m, 52H), 5.14 – 5.07 (m, 2H, H-1), 5.05 (s, 2H, *PhC*H$_2$), 5.02 (s, 1H, H-1), 4.96 (d, *J* = 3.5 Hz, 1H, H-1^{A}), 4.93 – 4.30 (m, 24H), 4.25 – 3.58 (m, 20H), 3.51 – 3.38 (m, 3H, H-6, 7), 2.93 (bs, 1H, *O*H), 2.36 (bs, 1H, *O*H), 2.29 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.52 (m, 4H, H-8, 10), 1.38 – 1.24 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.15 (C-12), 165.79, 165.23, 165.20, 165.05 (4 C=O, Bz), 137.98, 137.93, 137.84, 137.75, 137.02, 136.97, 135.84, 133.15, 132.95, 132.84, 129.54, 129.50, 129.49, 129.47, 129.41, 129.39, 128.43, 128.36, 128.33, 128.28, 128.24, 128.22, 128.17, 128.13, 128.05, 127.97, 127.92, 127.65, 127.61, 127.57, 127.55, 127.50, 127.37, 127.27, 127.05, 126.77, 99.74 (C-1), 99.58 (C-1), 99.01 (C-1), 98.62 (C-1), 97.81 (C-1^{A}), 76.63, 76.50, 76.17, 75.70, 75.40, 75.19, 74.61, 74.39, 74.13, 73.76, 73.66, 73.20, 72.66, 72.10, 72.04, 71.56, 69.16, 68.74, 68.65, 67.90 (C-7), 67.27, 65.86 (CH_2), 62.52 (C-6), 62.47 (C-6), 61.23 (C-6), 61.14 (C-6), 60.92 (C-6), 60.44 (C-2), 59.70 (C-2), 59.49 (C-2), 33.87 (C-11), 28.75 (C-8), 25.42 (C-9), 24.32 (C-10). HR-MS: Calculated for $C_{120}H_{123}N_9O_{29}[M+NH_4]^+$: 2176.8324, found: 2176.8319.

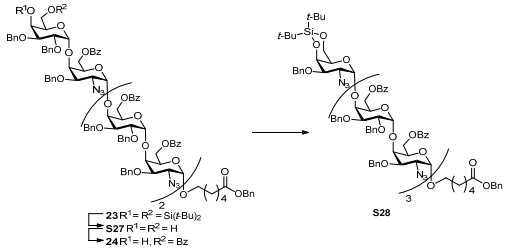
Pentasaccharide 22

The reaction was carried out according to the general procedure D using compound **S26** (1.83 g, 0.85 mmol), PhCOOBt (913 mg, 3.82 mmol) and Et_3N (592 µl, 4.25 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:2). Compound **22** (1.87 g, 98% yield) was obtained as syrup. $[\alpha]_D^{25}$ +79.2 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.11 – 7.83 (m, 10H, *C*H, Bz), 7.70 – 6.98 (m, 55H), 5.09 (d, *J* = 3.3 Hz, 2H, H-1), 5.05 (s, 2H, *PhC*H$_2$), 5.03 (d, *J* = 3.0 Hz, 1H, H-1), 4.97 (d, *J* = 3.5 Hz, 1H, H-1^{A}), 4.96 – 4.34 (m, 26H), 4.26 – 3.58 (m, 20H), 3.44 (dt, *J* = 9.7, 6.3 Hz, 1H, H-7), 2.62 (bs, 1H, *O*H), 2.29 (t, *J* = 7.4 Hz, 2H, H-11), 1.68 – 1.50 (m, 4H, H-

8, 10), 1.39 – 1.24 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.25 (C-12), 165.90, 165.82, 165.34, 165.31, 165.12 (5 C=O, Bz), 138.12, 138.06, 137.79, 137.20, 137.14, 137.10, 135.97, 133.25, 133.05, 133.01, 132.97, 129.76, 129.67, 129.62, 129.61, 129.59, 129.53, 129.51, 129.47, 128.54, 128.47, 128.44, 128.35, 128.33, 128.31, 128.28, 128.24, 128.20, 128.14, 128.08, 128.04, 128.02, 127.78, 127.68, 127.66, 127.62, 127.57, 127.54, 127.50, 127.48, 127.39, 127.17, 126.90, 99.87 (2xC-1), 98.78 (2xC-1), 97.92 (C-1^{A}), 76.63, 76.63, 76.25, 75.76, 75.31, 74.88, 74.72, 74.51, 74.14, 73.87 (CH_2), 73.78, 73.43, 72.77, 72.72, 72.17, 72.15, 71.90 (6 CH_2), 68.86, 68.78, 68.01 (C-7), 67.77, 65.97 (CH_2), 65.39 (C-4), 62.65, 62.25, 61.35, 61.25, 60.98 (5 C-6), 60.57 (C-2), 59.76 (C-2), 59.61 (C-2), 33.99 (C-11), 28.87 (C-8), 25.54 (C-9), 24.43 (C-10). MALDI-MS: Calculated for $C_{127}H_{127}N_9O_{30}$ $[M+Na]^+$: 2280.8587, found: 2280.8581.

Hexasaccharide 23

The reaction was carried out according to the general procedure A. The donor **1** (1.21 g, 2.04 mmol) and the acceptor **22** (1.84 g, 0.82 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 8 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which NIS (597 mg, 2.65 mmol) and TfOH (7 µl, 0.08 mmol) was added. The reaction was stirred at 0 ºC for 1 h. Then the reaction was quenched with $Na_2S_2O_3$, 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 **23** (1.84 g, 82% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +9.1 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.10 – 7.84 (m, 10H, *C*H, Bz), 7.64 – 6.95 (m, 65H), 5.10 (d, *J* = 3.3 Hz, 1H, H-1), 5.07 (d, *J* = 3.4 Hz, 1H, H-1), 5.05 (s, 2H, *PhC*H$_2$), 5.03 (d, *J* = 3.2 Hz, 1H, H-1), 5.00 – 3.52 (m, 59H), 3.51 – 3.40 (m, 1H, H-7), 2.29 (t, *J* = 7.4 Hz, 2H, H-11), 1.69 – 1.52 (m, 4H, H-8, 10), 1.40 – 1.25 (m, 2H, H-9), 0.96 (s, 9H, *C*H$_3$), 0.90 (s, 9H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.15 (C-12), 165.85, 165.30, 165.28, 165.24, 165.06 (5 C=O, Bz), 138.81, 138.19, 138.10, 138.09, 138.06, 138.05, 137.30, 137.14, 137.09, 135.98, 133.22, 133.10, 133.05, 132.98, 129.73, 129.67, 129.63, 129.60, 129.55, 129.51, 129.48, 128.74, 128.51, 128.46, 128.43, 128.35, 128.29, 128.25, 128.22, 128.18, 128.15, 128.06, 128.03, 127.76, 127.68, 127.64, 127.56, 127.48, 127.46, 127.41, 127.38, 127.29, 127.17, 126.81, 126.66, 99.95 (C-1), 99.87 (C-1), 98.82 (C-1), 98.72 (C-1), 97.94 (C-1), 77.69, 76.40, 76.27, 75.83, 75.67, 75.27, 74.67, 74.52, 74.29, 73.90, 73.83, 73.57, 73.34, 72.75, 72.59, 72.55, 72.38, 72.13, 71.81, 70.42, 69.99, 68.89, 68.75, 67.99 (C-7), 67.49, 66.80 (C-6^{F}), 65.92 (CH_2), 62.62 (C-6), 61.30 (C-6), 60.94 (C-6), 60.58 (C-2), 59.61 (C-2), 33.96 (C-11), 28.87 (C-8), 27.55, 27.12, 25.53 (C-9), 24.42 (C-10), 23.19, 20.50. ^{13}C-HMBC ($CDCl_3$, 100 MHz): 99.95 ($J_{C1,H1}$ = 168 Hz, 169 Hz), 99.87 ($J_{C1,H1}$ = 169 Hz), 99.82 ($J_{C1,H1}$ = 172 Hz), 99.72 ($J_{C1,H1}$ = 172 Hz), 97.94 ($J_{C1,H1}$ = 171 Hz). MALDI-MS: Calculated for $C_{155}H_{165}N_9O_{35}Si$ $[M+Na]^+$: 2763.1075, found: 2763.0660.



Hexasaccharide S27

The reaction was carried out according to the general procedure C using compound **23** (1.82 g, 0.66 mmol) and HF/pyridine (70%, 274 µl, 3.96 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S27** (1.62 g, 93% yield) was obtained as white foam. $[\alpha]_D^{25}$ +88.4 (c=10, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 7.84 (m, 10H, *C*H, Bz), 7.63 – 7.51 (m, 5H), 7.50 – 6.95 (m, 60H), 5.10 – 5.07 (m, 2H, 2xH-1), 5.06 (s, 2H, *PhC*H_2), 5.04 – 4.99 (m, 2H, 2xH-1), 4.96 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.94 – 4.27 (m, 31H), 4.25 – 3.58 (m, 24H), 3.44 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 3.40 – 3.28 (m, 2H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.68 – 1.50 (m, 4H, H-8, 10), 1.39 – 1.23 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.25 (C-12), 165.90, 165.34, 165.32, 165.26, 165.13 (5 C=O, Bz), 138.11, 138.08, 137.97, 137.87, 137.79, 137.30, 137.15, 137.09, 135.97, 133.25, 133.18, 133.08, 133.01, 129.68, 129.66, 129.62, 129.59, 129.54, 129.51, 129.49, 128.53, 128.49, 128.46, 128.42, 128.39, 128.36, 128.31, 128.24, 128.21, 128.18, 128.10, 128.05, 127.84, 127.80, 127.68, 127.66, 127.57, 127.55, 127.49, 127.40, 127.23, 127.18, 126.79, 100.32 (C-1), 99.90 (C-1), 99.81 (C-11), 98.73 (C-1), 97.93 (C-1^A), 77.68, 76.34, 76.27, 75.90, 75.79, 75.27, 74.92, 74.71, 74.58, 74.51, 74.20, 73.92, 73.85, 73.58, 73.46, 72.76, 72.59, 72.19, 72.15, 71.98, 69.20, 69.12, 68.91, 68.77, 68.02 (C-7), 65.98 (CH_2*Ph*), 62.73, 62.62, 61.35, 61.25, 61.09, 61.03 (6 C-6), 60.59 (C-2), 60.44 (C-2), 59.61 (C-2^A), 34.00 (C-11), 28.88 (C-8), 25.55 (C-9), 24.45 (C-10). MALDI-MS: Calculated for $C_{147}H_{149}N_9O_{35}$ $[M+Na]^+$: 2623.0054, found: 2622.9908.

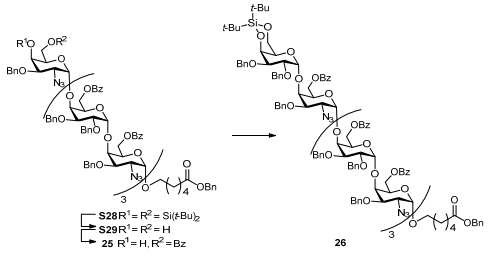
Hexasaccharide 24

The reaction was carried out according to the general procedure D using compound **S27** (1.32 g, 0.51 mmol), PhCOOBt (546 mg, 2.28 mmol) and Et_3N (0.353 ml, 2.54 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:2). Compound **24** (1.34 g, 98% yield) was obtained as white solid. $[\alpha]_D^{25}$ +79.9 (c=2, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.09 – 7.83 (m, 12H), 7.64 – 6.95 (m, 68H), 5.15 – 5.04 (m, 5H, 3xH-1, *PhC*H_2), 5.01 (d, *J* = 3.4 Hz, 1H, H-1), 4.97 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.93 (d, *J* = 3.8 Hz, 1H, H-1), 4.91 – 4.28 (m, 31H), 4.24 – 3.60 (m, 23H), 3.45 (dt, *J* = 9.7, 6.3 Hz, 1H, H-7), 2.59 (bs, 1H, *O*H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.69 – 1.51 (m, 4H, H-8, 10), 1.40 – 1.22 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.24 (C-12), 165.91, 165.75, 165.34, 165.32, 165.23, 165.14 (6 C=O, Bz), 138.12, 138.09, 138.00, 137.92, 137.90, 137.15, 137.13, 137.11, 135.98, 133.25, 133.20, 133.08, 133.01, 132.82, 129.84, 129.70, 129.67, 129.63, 129.60, 129.54, 129.52, 129.47, 128.54, 128.49, 128.46, 128.37, 128.32, 128.25, 128.21, 128.18, 128.14, 128.10, 128.06, 127.76, 127.70, 127.68, 127.66, 127.63, 127.57, 127.52, 127.49, 127.41, 127.19, 127.02, 126.79, 99.99 (C-1), 99.91 (C-1), 99.86 (C-1),

98.81 (C-1), 98.78 (C-1), 97.94 (C-1^{A}), 77.81, 76.27, 76.20, 75.92, 75.81, 75.29, 74.95, 74.87, 74.73, 74.54, 74.05, 73.85, 73.54, 72.77, 72.59, 72.26, 72.15, 68.89, 68.78, 68.03 (C-7), 67.81, 66.36, 65.98 (CH_2*Ph*), 62.64, 61.98, 61.35, 61.25, 61.09, 61.04 (6 C-6), 60.59 (C-2), 60.51 (C-2), 59.62 (C-2^{A}), 34.01 (C-11), 28.89 (C-8), 25.56 (C-9), 24.45 (C-10). MALDI-MS: Calculated for $C_{154}H_{153}N_9O_{36}$ $[M+Na]^+$: 2727.0316, found: 2726.9908.

Heptasaccharide S28

The reaction was carried out according to the general procedure B. The donor **2** (583 mg, 0.96 mmol) and the acceptor **24** (1.30 g, 0.48 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 5 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, 0.05 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 **S28** (1.28 g, 85% yield) was obtained as white solid. $[\alpha]_D^{25}$ +91.2 (c=2, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.10 – 7.86 (m, 12H, *C*H, Bz), 7.64 – 6.92 (m, 73H, aromatic H), 5.25 – 3.52 (m, 73H), 3.50 – 3.39 (m, 1H, H-7), 2.29 (t, *J* = 7.4 Hz, 2H, H-11), 1.67 – 1.51 (m, 4H, H-8, 10), 1.38 – 1.24 (m, 2H, H-9), 1.02 (s, 9H, *C*H_3), 0.95 (s, 9H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.02 (C-12), 165.75, 165.22, 165.18, 165.02 (C=O, Bz), 138.01, 137.99, 137.85, 137.79, 137.75, 137.07, 137.01, 135.91, 133.15, 132.95, 132.83, 129.58, 129.55, 129.50, 129.47, 129.42, 129.38, 128.43, 128.38, 128.33, 128.28, 128.26, 128.20, 128.15, 128.11, 128.07, 128.05, 128.02, 127.96, 127.92, 127.57, 127.52, 127.49, 127.45, 127.40, 127.33, 127.20, 127.08, 126.94, 126.72, 99.79 (C-1), 99.44 (C-1), 98.64 (C-1), 98.33 (C-1), 97.86 (C-1^{A}), 76.38, 76.17, 75.79, 75.57, 75.19, 74.89, 74.62, 74.44, 73.73, 73.51, 73.45, 73.21, 72.69, 72.49, 72.05, 70.04, 69.36, 68.73, 67.89 (C-7), 67.23, 66.71 (C-6^{G}), 65.81 (CH_2*Ph*), 62.56 (C-6), 61.15 (C-6), 61.06 (C-6), 60.99 (C-6), 60.48 (C-2), 60.47 (C-2), 59.53 (C-2), 58.74 (C-2A), 33.85 (C-11), 28.77 (C-8), 27.43 (CH_3), 27.10 (CH_3), 25.44 (C-9), 24.32 (C-10), 23.12 (C-*Si*), 20.45 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 99.79 ($J_{C1,H1}$ = 169 Hz), 99.44 ($J_{C1,H1}$ = 168 Hz), 98.64 ($J_{C1,H1}$ = 170 Hz), 98.33 ($J_{C1,H1}$ = 173 Hz), 97.86 ($J_{C1,H1}$ = 170 Hz). MALDI-MS: Calculated for $C_{175}H_{184}N_{12}O_{40}Si$ $[M+Na]^+$: 3144.2400, found: 3144.1828.



Heptasaccharide S29

The reaction was carried out according to the general procedure C using compound **S28** (1.24 g, 0.40 mmol) and HF/pyridine (70%, 165 µl, 6.35 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S29** (1.13 g, 95% yield) was obtained as white solid. $[\alpha]_D^{25}$ +80.6 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.09 – 7.81 (m, 12H, *C*H, Bz), 7.69 – 6.93 (m, 73H, aromatic H), 5.12 – 5.04 (m, 5H, 3xH-1, *C*H_2*Ph*), 5.01 (d, *J* = 3.5 Hz, 1H, H-1), 4.97 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.93 (d, *J* = 3.1 Hz, 1H, H-1), 4.92 – 4.28 (m, 34H), 4.26 – 4.13 (m, 4H), 4.13 – 3.54 (m, 22H), 3.50 – 3.37 (m, 3H), 2.89 (bs, 1H, *O*H), 2.29 (t, *J* = 7.4 Hz, 2H, H-11), 2.20 (bs, 1H, *O*H), 1.67 – 1.52 (m, 4H, H-8, 10), 1.38 – 1.23 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.24 (C-12), 165.89, 165.32, 165.30, 165.28, 165.14, 165.10 (6 C=O, Bz), 138.09, 138.05, 137.94, 137.90, 137.82, 137.13, 137.07, 137.06, 135.95, 133.24, 133.06, 133.02, 132.92, 129.64, 129.62, 129.60, 129.56, 129.52, 129.48, 128.54, 128.52, 128.46, 128.43, 128.38, 128.34, 128.31, 128.28, 128.23, 128.19, 128.16, 128.13, 128.09, 128.07, 128.03, 128.01, 127.74, 127.67, 127.65, 127.58, 127.55, 127.52, 127.47, 127.39, 127.16, 126.75, 99.87 (C-1), 99.67 (C-1), 99.10 (C-1), 98.72 (C-1), 97.92 (C-1^A), 76.74, 76.53, 76.25, 75.97, 75.49, 75.26, 74.72, 74.65, 74.50, 74.16, 73.83, 73.66, 73.53, 73.26, 72.74, 72.59, 72.23, 72.14, 71.67, 69.23, 68.81, 68.00 (C-7), 67.39, 65.96 (CH_2*Ph*), 62.59 (C-6), 61.33 (C-6), 61.20 (C-6), 61.15 (C-6), 60.97 (C-6), 60.95 (C-6), 60.58 (C-2), 59.80 (C-2), 59.59 (C-2^A), 33.98 (C-11), 28.86 (C-8), 25.53 (C-9), 24.42 (C-10). MALDI-MS: Calculated for $C_{167}H_{168}N_{12}O_{40}$ $[M+Na]^+$: 3004.1378, found: 3004.0885.

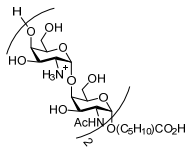
Heptasaccharide 25

The reaction was carried out according to the general procedure D using compound **S29** (1.10 g, 0.37 mmol), PhCOOBt (396 mg, 1.66 mmol) and Et_3N (256 µl, 1.84 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **25** (1.12 g, 98% yield) was obtained as white solid. $[\alpha]_D^{25}$ +71.3 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 7.83 (m, 14H, *C*H, Bz), 7.66 – 6.93 (m, 76H), 5.13 – 5.04 (m, 5H, 3xH-1, *C*H_2*Ph*), 5.02 (d, *J* = 3.5 Hz, 1H, H-1), 4.97 (d, *J* = 3.4 Hz, 1H, H-1^A), 4.94 – 4.29 (m, 38H), 4.24 – 4.14 (m, 4H), 4.11 – 3.60 (m, 23H), 3.45 (dt, *J* = 9.7, 6.3 Hz, 1H, H-7), 2.59 (bs, 1H, OH), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.52 (m, 4H, H-8, 10), 1.39 – 1.24 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.23 (C-12), 165.90, 165.81, 165.33, 165.31, 165.29, 165.14, 165.07 (7 C=O, Bz), 138.11, 138.07, 138.06, 137.93, 137.77, 137.20, 137.15, 137.09, 135.97, 133.25, 133.07, 133.01, 132.95, 129.76, 129.67, 129.65, 129.62, 129.61, 129.57, 129.53, 129.50, 129.47, 128.54, 128.47, 128.46, 128.44, 128.36, 128.31, 128.28, 128.24, 128.20, 128.17, 128.12, 128.10, 128.08, 128.04, 128.01, 127.77, 127.69, 127.66, 127.56, 127.53, 127.50, 127.48, 127.41, 127.18, 126.78, 99.88 (C-1), 98.75 (C-1), 97.93 (C-1^A), 76.64, 76.57, 76.26, 75.94, 75.28, 74.87, 74.73, 74.65, 74.53, 74.06, 73.84, 73.68, 73.55, 73.38, 72.77, 72.71, 72.59, 72.20, 72.15, 71.90, 68.86, 68.77, 68.01 (C-7), 67.74, 65.96 (CH_2*Ph*), 65.39, 62.64, 62.23, 61.35, 61.20, 61.14, 61.05, 60.92 (7 C-6), 60.60 (C-2), 59.76 (C-2), 59.61 (C-2^A), 33.99 (C-11), 28.87 (C-8), 25.54 (C-9), 24.44 (C-10). MALDI-MS: Calculated for $C_{174}H_{172}N_{12}O_{41}$ $[M+Na]^+$: 3108.1641, found: 3108.1095.

Octasaccharide 26

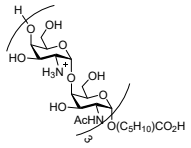
The reaction was carried out according to the general procedure A. The donor **1** (622 mg, 1.05 mmol) and the acceptor **25** (1.08 g, 0.35 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 3.5 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which NIS (307 mg, 1.37 mmol) and TfOH (3 µl, 0.04 mmol) were 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 = 3:1). Compound **26** (1.01 g, 80% yield) was obtained as white solid. $[\alpha]_D^{25}$ +103 (c=1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.07 – 7.84 (m, 14H, *C*H, Bz), 7.61 – 7.50 (m, 7H, aromatic H), 7.48 – 6.94 (m, 79H, aromatic H), 5.17 – 5.07 (m, 2H, H-1), 5.06 (s, 2H, *C*H_2*Ph*), 5.05 – 5.00 (m, 2H, H-1), 4.99 – 3.50 (m, 77H), 3.50 – 3.40 (m, 1H, H-7), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.53 (m, 4H, H-8, 10), 1.39 – 1.24 (m, 2H, H-9), 0.96 (s, 9H, *C*H_3), 0.90 (s, 9H, *C*H_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.18 (C-12), 165.89, 165.34, 165.32, 165.29, 165.26, 165.16, 165.07 (7 C=O, Bz), 138.82, 138.20, 138.12, 138.10, 138.07, 138.05, 137.94, 137.32, 137.16, 137.12, 136.01, 133.23, 133.11, 133.05, 132.98, 129.76, 129.70, 129.66, 129.61, 129.59, 129.56, 129.53, 129.50, 128.75, 128.52, 128.48, 128.45, 128.43, 128.37, 128.33, 128.29, 128.25, 128.17, 128.11, 128.08, 128.06, 128.04, 128.01, 127.83, 127.70, 127.66, 127.59, 127.52, 127.44, 127.42, 127.32, 127.21, 126.84, 126.74, 126.71, 99.95 (C-1), 99.89 (C-1), 99.82 (C-1), 98.82 (C-1), 98.74 (C-1), 97.96 (C-1A), 77.70, 76.40, 76.26, 76.02, 75.92, 75.60, 75.33, 75.24, 74.73, 74.64, 74.56, 74.32, 73.91, 73.86, 73.55, 73.34, 72.79, 72.60, 72.43, 72.17, 71.85, 70.48, 70.05, 68.89, 68.80, 68.03 (C-7), 67.51, 66.81 (C-6H), 65.96 (CH_2*Ph*), 62.67 (C-6), 61.39 (C-6), 61.26 (C-6), 61.21 (C-6), 60.96 (C-6), 60.62 (C-2), 59.64 (C-2), 34.00 (C-11), 28.89 (C-8), 27.57 (CH_3), 27.14 (CH_3), 25.56 (C-9), 24.45 (C-10), 23.21 (C-*Si*), 20.52 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 99.95 ($J_{C1,H1}$ = 171 Hz), 99.89 ($J_{C1,H1}$ = 169 Hz), 99.82 ($J_{C1,H1}$ = 167 Hz), 98.82 ($J_{C1,H1}$ = 172 Hz), 98.74 ($J_{C1,H1}$ = 172 Hz, 171 Hz), 97.96 ($J_{C1,H1}$ = 171 Hz). MALDI-MS: Calculated for $C_{202}H_{210}N_{12}O_{46}Si$ $[M+Na]^+$: 3590.4129, found: 3590.3372.

5-Carboxypentyl 2-amino-2-deoxy-α-D-galactopyranosyl-(1→4)-2-acetamino-2-deoxy-α-D-galactopyranosyl-(1→4)-2-amino-2-deoxy-α-D-galactopyranosyl-(1→4)-2-acetamino-2-deoxy-α-D-galactopyranoside (27)



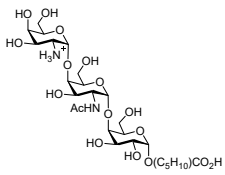
(3.4 mg, 34% yield). The reaction was carried out according to the general procedure C and E. ^{1}H-NMR (H_2O, 500 MHz) δ 5.24 (d, *J* = 3.9 Hz, 1H, H-1), 5.20 (d, *J* = 3.8 Hz, 1H, H-1), 5.02 (d, *J* = 3.8 Hz, 1H, H-1), 4.93 (d, *J* = 3.7 Hz, 1H, H-1), 4.44 (t, *J* = 7.0 Hz, 2H), 4.38 (t, *J* = 6.4 Hz, 1H), 4.30 (dd, *J* = 11.4, 3.8 Hz, 1H), 4.26 – 3.98 (m, 11H), 3.86 – 3.58 (m, 10H), 3.54 – 3.39 (m, 4H), 2.17 (t, *J* = 7.3 Hz, 2H, H-11), 2.06 (s, 3H, *C*H_3), 2.03 (s, 3H, *C*H_3), 1.65 – 1.51 (m, 4H, H-10, 8), 1.41 – 1.30 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 183.70 (C-12), 174.51, 174.41 (C=O, Ac), 98.05 (C-1), 96.77 (C-1), 76.64, 75.80, 71.45, 71.08, 70.62, 70.35, 68.12, 67.84, 66.97, 66.57, 60.56, 60.40, 60.08, 59.31, 50.99, 50.81, 49.98, 49.90, 37.32 (C-11), 28.12 (C-8), 25.35 (C-10), 25.18 (C-9), 21.73 (CH_3), 21.66 (CH_3). HR-MS: Calculated for $C_{34}H_{60}N_4O_{21}$ $[M+2H]^+$: 431.19533, found: 431.19478.

Hexasaccharide 28



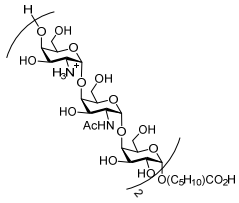
(5.4 mg, 44% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.40 (d, *J* = 3.8 Hz, 1H, H-1), 5.37 (d, *J* = 3.9 Hz, 1H, H-1), 5.35 (d, *J* = 3.8 Hz, 1H, H-1), 5.06 (d, *J* = 3.8 Hz, 2H, H-1C, H-1^{E}), 4.98 (d, *J* = 3.8 Hz, 1H, H-1^{A}), 4.54 – 4.40 (m, 5H, H-5), 4.37 – 3.96 (m, 16H), 3.89 – 3.57 (m, 16H), 3.52 (dt, *J* = 10.1, 6.1 Hz, 1H, H-7), 2.42 (t, *J* = 7.3 Hz, 2H, H-11), 2.13 – 2.03 (m, 9H, Ac), 1.70 – 1.60 (m, 4H, H-8, H-10), 1.47 – 1.38 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 179.15 (C-12), 174.75 (C=O, Ac), 174.67 (C=O, Ac), 98.26 (C-1^{C}, 1^{E}), 97.01 (C-1^{A}), 95.79 (2xC-1), 95.72 (C-1), 76.67 (C-4), 75.72 (C-4), 75.65 (C-4), 71.73 (C-5), 71.65 (C-5), 71.30 (C-5), 70.47 (C-5), 70.29 (C-5), 70.21 (C-12), 68.21 (C-7), 67.97, 67.12, 66.71, 66.31, 65.79, 65.73, 60.92 (C-6), 60.61 (C-6), 60.43 (C-6), 60.38 (C-6), 59.53 (C-6), 59.45 (C-6), 51.11 (C-2), 50.05 (C-2), 33.82 (C-11), 28.18 (C-8), 24.95 (C-10), 24.05 (C-9), 21.96 (C*H*$_3$), 21.93 (C*H*$_3$). HR-MS: Calculated for $C_{48}H_{84}N_6O_{30}$ $[M+2H]^{2+}$: 613.26942, found: 613.26887.

5-Carboxypentyl 2-amino-2-deoxy-α-D-galactopyranosyl-(1→4)-2-acetamino-2-deoxy-α-D-galactopyranosyl -(1→4)-α-D-galactopyranoside (29)



(68% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.31 (d, *J* = 3.9 Hz, 1H, H-1^{C}), 4.95 (d, *J* = 3.9 Hz, 1H, H-1^{A}), 4.93 (d, *J* = 3.8 Hz, 1H, H-1^{B}), 4.43 (t, *J* = 5.6 Hz, 1H, H-5^{B}), 4.41 – 4.36 (m, 1H, H-5^{C}), 4.30 – 4.23 (m, 2H, H-2^{B}, 4^{B}), 4.13 (dd, *J* = 11.1, 3.1 Hz, 1H, H-3^{C}), 4.09 (dd, *J* = 11.5, 2.9 Hz, 1H, H-3^{B}), 4.04 – 3.99 (m, 2H, H-4^{A}, 4^{C}), 3.97 (t, *J* = 6.5 Hz, 1H, H-5^{A}), 3.92 (dd, *J* = 10.6, 3.1 Hz, 1H, H-3^{A}), 3.83 (dd, *J* = 10.5, 3.9 Hz, 1H, H-2^{A}), 3.79 (dd, *J* = 11.7, 5.0 Hz, 1H, H-6^{C}), 3.76 – 3.64 (m, 6H, H-7, 6^{A}, 6^{B}, 6^{C}), 3.56 – 3.49 (m, 2H, H-2^{C}, 7), 2.16 (t, *J* = 7.4 Hz, 2H, H-11), 2.06 (s, 3H, *C*H$_3$), 1.68 – 1.51 (m, 4H, H-10, 8), 1.40 – 1.31 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 183.98 (C-12), 174.61 (C=O, Ac), 98.32 (C-1^{A}, 1^{B}), 96.09 (C-1^{C}), 77.49 (C-4^{A}), 76.94 (C-4^{B}), 71.50 (C-5^{A}), 71.22 (C-5^{C}), 70.07 (C-5^{B}), 68.96 (C-3^{A}), 68.36 (C-7), 68.34 (C-2^{A}), 67.95 (C-4^{C}), 66.69 (C-3^{B}), 66.50 (C-3^{C}), 60.52, 60.34, 60.27 (3 C-6), 51.03 (C-2C), 50.13 (C-2B), 37.51 (C-11), 28.43 (C-8), 25.62 (C-10), 25.41 (C-9), 21.89 (C*H*$_3$). HR-MS: Calculated for $C_{26}H_{46}N_2O_{17}$ $[M+H]^{+}$: 659.2875, found: 659.2869.

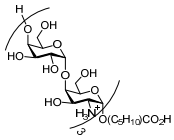
Hexasaccharide 30



(12.9 mg, 65% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.40 (d, *J* = 3.8 Hz, 1H, H-1^{C}), 5.38 (d, *J* = 3.8 Hz, 1H, H-1^{F}), 5.11 (d, *J* = 3.8 Hz, 1H, H-1^{E}), 5.03 (d, *J* = 3.8 Hz, 1H, H-1^{D}), 5.00 (d, *J* = 3.9 Hz, 1H, H-1^{A}), 4.98 (d, *J* = 3.8 Hz, 1H, H-1^{B}), 4.53 – 4.38 (m, 6H), 4.37 – 4.26 (m, 5H), 4.23 – 4.18 (m, 2H), 4.17 – 3.93 (m, 9H), 3.92 – 3.64 (m, 17H), 3.63 – 3.54 (m, 2H), 2.25 (t, *J* = 7.4 Hz, 2H), 2.10 (d, *J* = 3.2 Hz, 6H), 1.73 – 1.56 (m, 4H), 1.47 – 1.33 (m, 2H). ^{13}C NMR (125 MHz, D_2O) δ 183.24 (C-12), 174.65 (C=O, Ac), 100.45 (C-1^{E}), 98.35 (C-1^{A}, 1^{B}, 1^{D}), 95.99 (C-1^{C}), 95.91 (C-1^{F}), 77.52, 77.35, 77.11, 77.03, 71.66, 71.53, 71.38, 71.29, 70.81, 70.09,

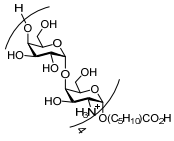
70.02, 69.01, 68.64, 68.57, 68.38, 68.26, 67.97, 66.73, 66.67, 66.35, 65.99, 60.57, 60.46, 60.38, 60.31, 59.80, 59.63 (6 C-6), 51.30, 51.08, 50.17, 50.11 (4 C-2), 36.96 (C-11), 28.44 (C-8), 25.41 (C-10), 25.37 (C-9), 21.95 (C*H*$_3$). HR-MS: Calculated for $C_{46}H_{80}N_4O_{31}$ $[M+2H]^{2+}$: 593.24815, found: 593.24760.

Hexasaccharide 31



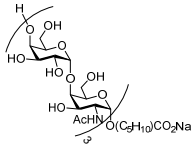
(13.1 mg, 62% yield). The reaction was carried out according to the general procedure C and E. ^{1}H-NMR (H_2O, 500 MHz) 5.27 – 5.22 (m, 2H, H-1^C, 1^E), 5.16 (d, *J* = 3.7 Hz, 1H, H-1^A), 5.07 (d, *J* = 3.9 Hz, 1H, H-1), 5.03 (d, *J* = 3.5 Hz, 1H, H-1), 5.02 (d, *J* = 3.9 Hz, 1H, H-1), 4.48 (t, *J* = 6.2 Hz, 2H, H-5), 4.39 (dt, *J* = 8.0, 5.9 Hz, 2H, H-5), 4.29 (t, 1H, H-5^A), 4.22 (d, *J* = 2.6 Hz, 2H), 4.18 – 4.07 (m, 6H), 4.06 – 3.98 (m, 4H), 3.97 – 3.66 (m, 19H), 3.58 – 3.48 (m, 4H, H-2^A, 2^C, 2^E, 7), 2.18 (t, *J* = 7.2 Hz, 2H, H-11), 1.71 – 1.53 (m, 4H, H-8, 10), 1.38 (q, *J* = 7.5 Hz, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.02 (C-12), 100.62 (C-1B), 100.30 (C-1$^{D/F}$), 100.23 (C-1$^{D/F}$), 96.85 (C-1$^{C/E}$), 96.78 (C-1$^{C/E}$), 95.33 (C-1A), 77.91 (C-3), 77.46 (C-3), 77.16 (C-3), 77.06 (C-3), 71.50 (C-5), 71.36 (C-5), 71.29 (C-5), 70.59 (C-5), 70.49 (C-5), 69.15, 68.96 (C-4A), 68.73, 68.69, 68.48 (C-2), 68.42, 68.33, 66.79 (C-4), 66.70 (C-4), 66.53 (C-4), 60.68 (C-6A), 60.30, 60.22, 60.14, 60.01, 59.71 (5 C-6), 51.39 (C-2), 51.25 (C-2), 51.09 (C-2), 37.45 (C-11), 28.28 (C-8), 25.47 (C-10), 25.32 (C-9). HR-MS: Calculated for $C_{42}H_{75}N_3O_{30}$ $[M+Na]^+$: 1124.4333, found: 1124.4328.

Octasaccharide 32



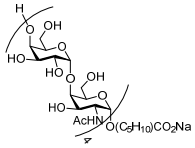
(12.7 mg, 54% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.08 (d, *J* = 4.0 Hz, 1H), 5.04 (d, *J* = 4.1 Hz, 1H), 5.01 (d, *J* = 4.0 Hz, 1H), 4.99 – 4.96 (m, 2H, H-1), 4.93 (d, *J* = 3.7 Hz, 1H, H-1^A), 4.49 – 4.43 (m, 2H, H-5), 4.41 – 4.33 (m, 2H, H-5), 4.31 – 4.23 (m, 3H), 4.19 (dd, *J* = 11.3, 3.7 Hz, 1H, H-2^A), 4.17 – 4.13 (m, 2H), 4.11 – 3.99 (m, 9H), 3.98 – 3.77 (m, 10H), 3.75 – 3.57 (m, 7H), 3.49 (dt, *J* = 10.0, 6.0 Hz, 1H, H-7), 2.21 – 2.14 (m, 2H, H-11), 2.09 – 1.99 (m, 9H, Ac), 1.68 – 1.50 (m, 4H, H-8, 10), 1.36 (p, *J* = 7.1, 6.7 Hz, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 183.96 (C-12), 174.70, 174.61, 174.59 (3 C=O, Ac), 100.72 (C-1), 100.57 (C-1), 100.45 (C-1), 98.40 (C-1), 98.37 (C-1), 96.97 (C-1^A), 78.69 (C-3), 78.30 (C-3), 78.18 (C-3), 77.11, 77.08, 71.56 (C-5), 71.41 (C-5), 71.28 (C-5), 71.11 (C-5), 70.90 (C-5), 69.18, 69.01, 68.76, 68.72, 68.69, 68.65, 68.31 (C-7), 67.25 (C-4), 66.98 (C-4), 66.90 (C-4), 60.61, 60.54, 60.01, 59.82, 59.57, 59.49 (6 C-6), 50.49, 50.44, 50.35 (3 C-2), 37.57 (C-11), 28.36 (C-8), 25.62 (C-10), 25.42 (C-9), 21.96 (C*H*$_3$), 21.91 (C*H*$_3$). HR-MS: Calculated for $C_{54}H_{96}N_4O_{39}$ $[M+2H]^{2+}$: 713.2904, found: 713.2899.

Hexasaccharide 33



(11.5 mg, 55% yield). The reaction was carried out according to the general procedure C and E. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 5.31 (d, *J* = 3.8 Hz, 3H, H-1), 5.18 (d, *J* = 3.7 Hz, 1H, H-1^{A}), 5.09 (d, *J* = 3.9 Hz, 2H, H-1), 5.06 – 5.00 (m, 2H, H-1), 4.51 (t, *J* = 6.3 Hz, 3H, H-5), 4.41 (t, *J* = 5.7 Hz, 3H, H-5), 4.34 – 4.28 (m, 1H, H-5^{A}), 4.27 – 4.13 (m, 10H), 4.10 (d, *J* = 3.2 Hz, 1H), 4.07 – 3.99 (m, 5H), 3.98 – 3.51 (m, 29H), 2.27 (t, *J* = 7.2 Hz, 2H, H-11), 1.75 – 1.53 (m, 4H, H-8, 10), 1.40 (q, *J* = 7.6 Hz, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 182.12 (C-12), 100.64 (C-1), 100.27 (C-1), 100.22 (C-1), 95.93 (C-1), 95.89 (C-1), 95.16 (C-1A), 77.73, 77.45, 76.97, 76.84, 71.50, 71.35, 71.26, 70.34, 70.24, 69.15, 68.94, 68.66, 68.46, 68.40, 68.36, 68.34 (C-7), 66.32 (C-4), 66.04 (C-4), 65.82 (C-4), 60.66, 60.28, 59.95, 59.60 (C-6), 51.33 (C-2), 51.16 (C-2), 51.08 (C-2), 35.98 (C-11), 28.25 (C-8), 25.15 (C-10), 24.89 (C-9). HR-MS: Calculated for $C_{48}H_{81}N_3O_{33}$ $[M+NH_4]^+$: 1245.5096, found: 1245.5091.

Octasaccharide (34)



(13.8 mg, 59% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.08 (d, *J* = 4.0 Hz, 2H, H-1), 5.03 (d, *J* = 4.0 Hz, 1H, H-1), 5.01 (d, *J* = 4.0 Hz, 1H, H-1), 5.00 – 4.95 (m, 3H, H-1), 4.93 (d, *J* = 3.7 Hz, 1H, H-1A), 4.50 – 4.42 (m, 3H, H-5), 4.40 – 4.32 (m, 3H), 4.32 – 4.23 (m, 4H), 4.22 – 4.13 (m, 4H), 4.12 – 3.99 (m, 12H), 3.98 – 3.76 (m, 13H), 3.74 – 3.56 (m, 9H), 3.48 (dt, *J* = 9.9, 6.0 Hz, 1H, H-7), 2.21 – 2.14 (m, 2H, H-11), 2.09 – 1.98 (m, 12H, Ac), 1.66 – 1.52 (m, 4H, H-8, 10), 1.37 (q, *J* = 7.6 Hz, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 183.96 (C-12), 174.70, 174.61, 174.59 (C=O, Ac), 100.72 (C-1), 100.57 (C-1), 100.45 (C-1), 98.40 (C-1), 98.37 (C-1), 96.97 (C-1), 78.69, 78.29, 78.18, 77.11, 77.08, 71.56, 71.41, 71.28, 71.11, 70.90, 69.18, 69.01, 68.72, 68.69, 68.65, 68.31 (C-7), 67.25 (C-4), 66.98 (C-4), 66.89 (C-4), 60.61 (C-6), 60.54 (C-6), 60.02 (C-6), 59.82 (C-6), 59.56 (C-6), 59.49 (C-6), 50.50 (C-2), 50.44 (C-2), 50.35 (C-2), 37.57 (C-11), 28.36 (C-8), 25.62 (C-10), 25.42 (C-9), 21.96 (C*H*$_3$), 21.91 (C*H*$_3$). HR-MS: Calculated for $C_{62}H_{104}N_4O_{43}$ $[M+Na]^+$: 1615.5972, found: 1615.5967.

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