Chemical synthesis of fragments of galactosaminogalactan and pel polysaccharides

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Chapter 2

Synthesis of α-galactose, α-galactosamine and α-*N*-acetyl galactosamine galactosaminogalactan homo-oligomers from *Aspergillus fumigatus*

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Introduction

Aspergillus fumigatus is an opportunistic pathogenic fungus that causes invasive infections in immunocompromised patients, with a mortality rate of 60-80%.[1-4] Galactosaminogalactan (GAG), a prominent cell wall component of *A. fumigatus*, has been identified as an important factor during invasion and infection of the host.[5-10] It hides the immunostimulatory β-glucans from the host immune system and functions as an immunomodulatory polysaccharide by inhibiting the generation of proinflammatory cytokines.[7] The GAG polysaccharide is composed of galactose (Gal), galactosamine (GalN) and *N*-acetylgalactosamine (GalNAc) residues that are interconnected through 1,4-*cis*-glycosidic linkages and are distributed in a seemingly random order[9-11] (Figure 1A). To

unravel the mode of action of enzymes involved in GAG-biosynthesis, well-defined GAG-fragments are indispensable tools.[12-13] Pure GAG-oligosaccharide fragments can also be employed to study their interaction with components of the host immune system and map interactions with antibodies at the molecular level. This can inspire the development of anti-fungal vaccines and diagnostics. The random distribution of the Gal, GalN- and GalNAc monosaccharides in the GAG chains impedes the isolation of pure and well-defined specimens from natural sources and therefore the synthesis of a set of structurally well-defined GAG homopolymers was undertaken (See Figure 1B). Recently, Nifantiev and co-workers[14] reported on the assembly of a small set of GAG homo-oligomers up to the hexamer level, containing either GalN or GalNAc residues. Because enzymes involved in GAG biosynthesis may require longer oligosaccharides, structures up to the dodecasaccharide level were assembled here.

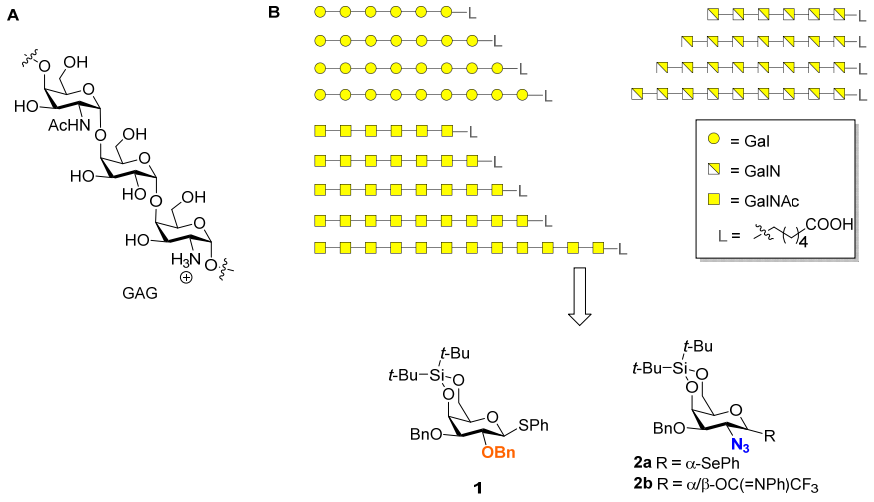


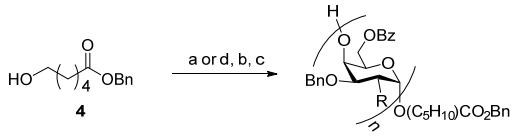
Figure 1. A) Structure of GAG. B) The designed GAG homo-oligomers and building blocks utilized in the here-presented studies to prepare the GAG homopolymers.

To be able to generate various GAG structures, Kiso's di-*tert*-butylsilylidene (DTBS) galactosylation methodology should be especially suited, as this approach gives unusual high α-stereoselectivity even when a C2 group is present, that is capable of neighboring group participation.[15-20] Therefore donors **1** and **2** were designed to assemble a library of GAG homo-oligomers, as depicted in Figure 1B. A hexanoic acid spacer was incorporated at the reducing end of the fragments for future conjugation purposes. The $GalN_3$ donor **2** will serve as precursor for GalN and GalNAc residues in the homo-oligomers.

Results and discussion

The building blocks **1**, **2a**, **b** and **4**, needed for the assembly the projected Gal- and $GalN_3$ homo-oligomers, were prepared using published procedures.[21-23] Application of Kiso's galactosylation methodology is bound to a stepwise elongation procedure that consists of the following three reactions; 1) glycosylation; 2) DTBS-removal and 3) regioselective benzoylation of the primary alcohol group. For the latter transformation benzoyl-hydroxybenzotriazole (BzOBt), a mild acylating agent proved to be suited.[24] Table 1 summarizes the result of each reaction *en route* to the fully protected Gal- and $GalN_3$ homo-oligomers.

Table 1. Synthesis of homo-oligomers of Gal and $GalN_3$.



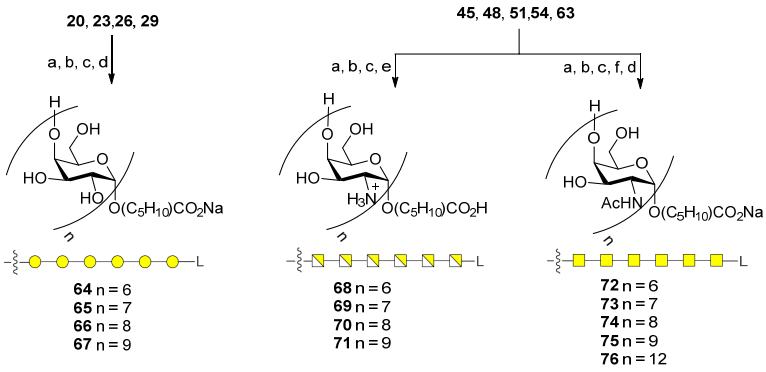
n	R	Glycosylation[a]	Desilylation[b]	Benzoylation[c]
1	OBn	**5** (86%)	**6** (92%)	**7** (94%)
2	OBn	**8** (91%)	**9** (96%)	**10** (95%)
3	OBn	**11** (84%)	**12** (94%)	**13** (95%)
4	OBn	**14** (80%)	**15** (93%)	**16** (92%)
5	OBn	**17** (80%)	**18** (92%)	**19** (90%)
6	OBn	**20** (72%)	**21** (93%)	**22** (95%)
7	OBn	**23** (76%)	**24** (95%)	**25** (94%)
8	OBn	**26** (81%)	**27** (93%)	**28** (95%)
9	OBn	**29** (65%)	-	-
1	N_3	**30** (83%) (64%)[d]	**31** (94%)	**32** (93%)
2	N_3	**33** (91%) (67%)[d]	**34** (95%)	**35** (92%)
3	N_3	**36** (84%) (60%)[d]	**37** (92%)	**38** (94%)
4	N_3	**39** (82%)	**40** (91%)	**41** (92%)
5	N_3	**42** (90%)	**43** (93%)	**44** (90%)
6	N_3	**45** (89%)	**46** (92%)	**47** (90%)
7	N_3	**48** (88%)	**49** (94%)	**50** (92%)
8	N_3	**51** (87%)	**52** (91%)	**53** (94%)
9	N_3	**54** (89%)	**55** (94%)	**56** (90%)
10	N_3	**57** (65%)	**58** (96%)	**59** (94%)
11	N_3	**60** (73%)	**61** (84%)	**62** (93%)
12	N_3	**63** (79%)	-	-

[a] **1**, NIS, TfOH, 4Å MS, DCM, 0 °C; or **2b**, TfOH, 4Å MS, DCM, 0 °C. [b] HF/pyridine, THF, rt. [c] BzOBt, Et_3N, DCM, rt. [d] **2a**, NIS, TfOH, 4Å MS, DCM, 0 °C.

As can be seen from the Table, all glycosylations using the Gal-donor **1** proceeded efficiently providing the oligomers (n = 1-9, R = OBn) with excellent stereoselectivity. Removal of the silylidene ketals and subsequent regioselective protection of the liberated C6-hydroxyl groups also proceeded uneventfully and the efficiency of all reaction steps did not diminish with growing chain length. For the assembly of the GalN/GalNAc homo-oligomers the use of selenophenyl donor **2a** was explored first. The relatively moderate yield of the glycosylation for the mono-, di- and trimer ($R = N_3$, 64% for **30**, 67% for **33** and 60% for **36**), was an incentive to switch to the use of *N*-phenyltrifluoroacetimidate donor **2b**. As can be seen in Table 1, this donor performed well and all glycosylation reactions proceeded effectively up to the dodecasaccharide level. Similar to the chemistry developed for the Gal-oligomers, the protecting group manipulations posed no problems in the $GalN_3$ series and the desilylation and regioselective benzoylation reactions proceeded in excellent yields (84%-96% and 90%-94%, respectively) also with the longer oligomers.

With all protected fragments in hand deprotection conditions were developed to complete the assembly of the GAG homo-oligomers (Scheme 1). First the set of Gal-oligomers was brought to the end stage by removing the silylidene ketal, followed by saponification of the benzoates and benzyl ester, hydrogenolysis of all benzyl ethers and an ion exchange procedure to furnish the sodium salts of the target compounds. Following this sequence of events, hexasaccharide **64** and heptasaccharide **65** were obtained in 69% and 75% yield, respectively. The octasaccharide **66** and nonasaccharide **67** on the other hand were obtained in significantly lower yields (25% and 29% respectively), because their solubility in water - quite surprisingly- turned out to be relatively poor.

Next $GalN_3$ oligomers **45**, **48**, **51**, **54** and **63** were transformed into the set of GalN- and GalNAc-target compounds **68**-**71** and **72**-**76**. Similar to the Gal-series, removal of the silylidene groups from these substrates was followed by saponification and reduction of the benzyl esters and azide moieties. An anion ion exchange reaction (to change the acetate counterions for chlorides) delivered the GalN-oligomers **68**-**71**, all in good yield. No solubility issues were encountered in this series. The free amines generated could also be chemoselectively acetylated to provide the GalNAc-oligosaccharides **72**-**76**. Also, these oligomers proved to be well soluble in water and were obtained as their sodium salts in 39%-62% yield (over 5 steps).



Scheme 1. Deprotection of synthesized oligosaccharides. a) HF/pyridine (70%), THF, 0 ºC to rt; b) 1M NaOH, THF, MeOH; c) $Pd(OH)_2/C$, THF/H_2O/*t*-BuOH, H_2; d) Dowex-Na^+, **64**: 69%; **65**: 75%; **66**: 25%; **67**: 29%; **72**: 44%; **73**: 47%; **74**: 46%; **75**: 62%; **76**: 39%. e) Amberlite Cl^- form, **68**: 67%; **69**: 56%; **70**: 66%; **71**: 55%. f) Ac_2O, $NaHCO_3$, H_2O/THF, g) 2M NaOH, THF, MeOH.

To investigate the conformation and spatial presentation of the synthetic GAGs, the conformational and dynamic properties of these molecules were studied by a combination of NMR and computational methods.[25-31] These have revealed that the glycosidic linkages of these GAGs show a conformational equilibrium between two major conformers. Interestingly, the dynamic equilibrium provides an overall extended shape that does not substantially change between the two Ψ+ and Ψ- geometries. All molecules display elongated, almost straight, geometries, in which the only inter-residue contacts occur between directly linked residues (Figure 2). In both canonical structures, the hydroxymethyl groups and those at C2 (OH/NHAc/NH_2) are presented towards the bulk solvent with an almost perpendicular orientation to the oligosaccharide main chain axis, properly oriented to interact with binding partners, such as biomachinery enzymes or antibodies. DFT calculations indicated a series of inter-residue hydrogen bonds stabilizing both conformations, amongst which a *non-conventional* C-H···O HB between H5 of residue (i+1) and the O3 of residue (i), which was revealed by a significant downfield chemical shift for the non-reducing-end H5 protons in the NMR spectra. This is the first time that this type of *non-conventional* C-H···O HB is reported for linear oligosaccharide structures.

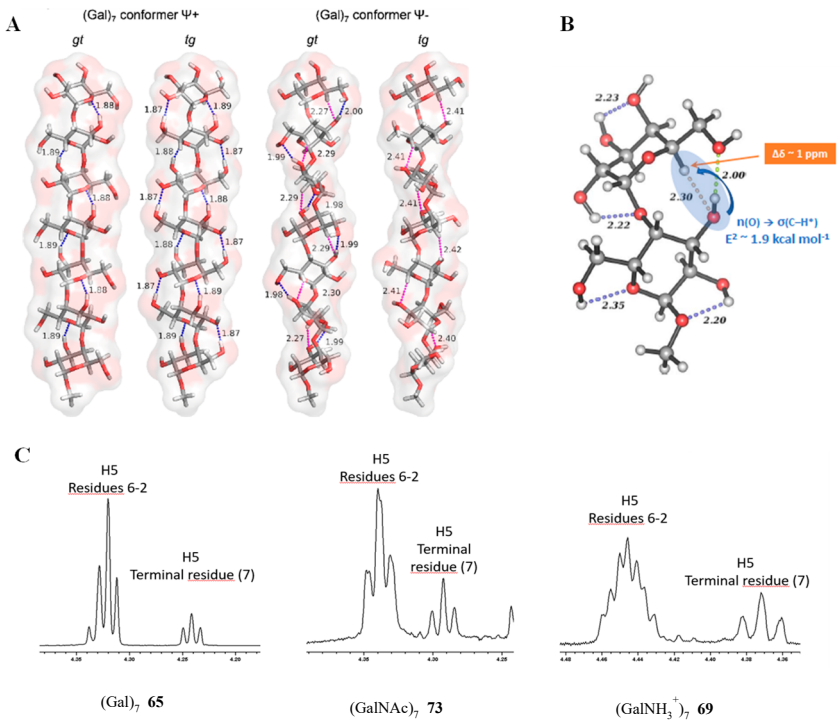


Figure 2. A) Quantum mechanically (QM)-optimized structures for the Gal heptamer in the typically dominant *gt* and *tg* hydroxymethyl group conformations. van der Waals surfaces are shown with 80% transparency. B) View of the **Ψ**-conformer for the disaccharide unit with the theoretical HBs. The non-conventional C5-H5(i+1)···O3(i). HB is highlighted, along with the energy value (ca. 2 kcal/mol) estimated from the NBO calculations and the expected deshielding for H5 (Δδ ca. 1 ppm). C) The shape of the ^{1}H NMR signals observed for H5 protons (except for the reducing end) for the heptamers of Gal, GalNAc and $GalNH_3^+$. There is a slight difference in the chemical shift of those of the $GalNH_3^+$moieties while those of the Gal and GalNAc analogues are identical.

Conclusion

Synthetic methodology enabling the assembly of GAG homo-oligomers has been developed. Key features of the synthetic strategy include the use of di-*tert*-butylsilylidene directed α-galactosylation methodology and regioselective benzoylation reactions using Bz-OBt. With the use of silylidene protected Gal or $GalNH_2$ donors, the required *cis*-Gal/$GalNH_2$ linkages were installed in a highly stereoselective manner. Structural analysis of the Gal, GalN and GalNAc oligomers by a combination of NMR and MD approaches revealed that the oligomers adopt an elongated, almost straight structure, stabilized by inter-residue H-bonds, one of which is a non-conventional C-H⋯O hydrogen bond between H5 of the residue (i+1) and O3 of the residue (i). The structures position the C2 substituents almost perpendicular to the oligosaccharide main chain axis, pointing outward to the environment and available for interactions with antibodies or other binding partners. The generated oligosaccharides and established structures can find application in future binding studies to establish GAG-epitopes, that may be used in anti-fungal conjugate vaccine modalities.

Experimental section

General procedure for glycosylation with thiodonor 1 (procedure A)

DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$. 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 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 donor 2b (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).

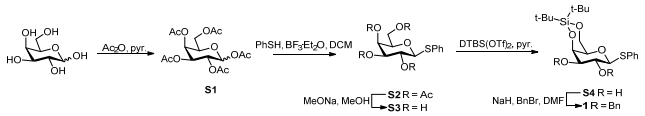
General procedure for saponification and hydrogenation of the oligosaccharides (general procedure E)

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 Amberlite (Cl form) and water, after which the compounds were lyophilized.

Experimental Procedures and Characterization Data of Products

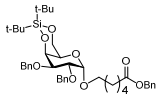
2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-1-thio-β-D-galactopyranoside 1



Galactose (100 g) was suspended in pyridine (448 ml), which was cooled in ice-bath. Then Ac_2O (526 ml) was added to the reaction solution, which was allowed to warm to room temperature and stirred for overnight. MeOH was added to quench the reaction and the solution was concentrated to form the crude product **S1**. The crude **S1** (50 g) was dissolved in DCM (100 ml) and cooled in ice-bath. Then PhSH and $BF_3{\cdot}Et_2O$ were added to the solution and the reaction solution was allowed to warm to room temperature and stirred for overnight. Then the solution was washed with water, sat. $NaHCO_3$ solution and sat. NaCl solution subsequently. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was purified by silica gel column chromatography (pentane:Et_2O = 3:1- 2:1) to give **S2** in 88% yield. **S2** (50 g) was suspended in MeOH (150 ml) and cooled in ice-bath. MeONa was added to the solution and the reaction solution was allowed to warm to room temperature and stirred for overnight. The solution was neutralized with Dowex ion-exchange resin, filtered and concentrated. The crude product **S3** was used directly to the next step. **S3** (5.26 g, 19.3 mmol) was dissolved in pyridine (100 ml) and cooled to -30 °C. $DTBS(OTf)_2$ (6.3 ml, 19.3 mmol) was added to the reaction solution, which was allowed to warm to room temperature and stirred for 2h. MeOH (3 ml) was added to the solution and concentrated *in vacuo*. The crude was washed with 1M HCl, sat. $NaHCO_3$ solution and sat. NaCl solution subsequently. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was purified by silica gel column chromatography (pentane:EtOAc = 5:1- 3:1) to give **S4** in 87% yield. S4 (4.5g, 11 mmol) was dissolved in DMF (60 ml) and cooled in ice-bath. Then BnBr (5.3 ml, 44 mmol) and NaH (1.06g, 26.4 mmol) were added subsequently to the reaction mixture, which was allowed to stir in ice-bath for 3h. MeOH was added to quench the reaction, and the solution was diluted in Et_2O and washed with water and sat. NaCl solution subsequently. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was purified by silica gel column chromatography (pentane:Et_2O = 10:1-8:1) to give compound **1** in 82% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.50 (ddd, J = 9.8, 7.7, 2.1 Hz, 4H), 7.45 – 7.28 (m, 9H), 4.98 (d, J = 2.0 Hz, 2H), 4.90 – 4.70 (m, 3H), 4.56 (d, J = 2.9 Hz, 1H), 4.33 – 4.19 (m, 2H), 3.93 (td, J = 9.5, 2.3 Hz, 1H), 3.55 (dt, J = 9.0, 2.5 Hz, 1H), 3.34 (d, J = 2.0 Hz, 1H), 1.27 – 1.12 (m, 18H). ^{13}C NMR

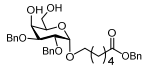
(101 MHz, $CDCl_3$) δ 138.44, 138.42, 134.92, 132.14, 128.85, 128.56, 128.54, 128.41, 127.92, 127.84, 127.37, 88.76, 82.90, 77.31, 76.05, 74.82, 71.11, 70.06, 67.48, 27.80, 27.76, 23.54, 20.84.

6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranoside (5)



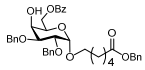
The reaction was carried out according to the general procedure A. The donor **1**[21] (3.5 g, 5.9 mmol) and the acceptor **4**[22] (1.44 g, 6.5 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 65 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 3Å. The solution was cooled to 0 ºC, after which NIS (2.65 g, 11.8 mmol) and TfOH (105 µl, 1.18 mmol) were added. The reaction was stirred at 0 ºC 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:Et_2O = 10:1- 5:1). Compound **5** (3.57 g, 86% yield, pentane:EtOAc = 10:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ -13.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1096, 1264, 1455, 1473, 1734, 2859, 2932. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.46 – 7.41 (m, 2H, *aromatic* H), 7.38 – 7.22 (m, 13H, *aromatic* H), 5.10 (s, 2H, *PhC*H_{2C}*OO*), 4.86 (d, *J* = 11.9 Hz, 1H, *PhC*H_2), 4.73 (s, 2H, *PhC*H_2), 4.70 (d, *J* = 3.7 Hz, 1H, H-1), 4.65 (d, *J* = 12.0 Hz, 1H, *PhC*H_2), 4.51 (d, *J* = 2.8 Hz, 1H, H-4), 4.20 (dd, *J* = 12.5, 2.1 Hz, 1H, H-6), 4.08 (dd, *J* = 12.4, 1.7 Hz, 1H, H-6), 3.97 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2), 3.82 (dd, *J* = 10.0, 3.0 Hz, 1H, H-3), 3.62 – 3.54 (m, 2H, H-5, H-7), 3.47 – 3.36 (m, 1H, H-7), 2.33 (t, *J* = 7.5 Hz, 2H, H-11), 1.70 – 1.55 (m, 4H, H-8, H-10), 1.44 – 1.29 (m, 2H, H-9), 1.06 (s, 9H, *C*H_3), 1.00 (s, 9H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4 (C=O), 139.1, 138.7, 136.1, 128.6, 128.3, 128.2, 127.6, 127.5 (*aromatic* C/C*H*), 98.0 (C-1), 77.7 (C-3), 74.4 (C-2), 73.6 (CH_2*Ph*), 71.2 (C-4), 71.1 (CH_2*Ph*), 67.9 (C-7), 67.3 (C-6), 67.2 (C-5), 66.1 (*C*=*O*CH_2*Ph*), 34.2 (C-11), 29.1 (C-8), 27.7 (CH_3), 27.4 (CH_3), 25.7 (C-9), 24.7 (C-10), 23.5 (C-*Si*), 20.7 (C-*Si*). ^{13C}-HMBC ($CDCl_3$, 100 MHz): 98.0 ($J_{C1,H1}$ = 168 Hz). HR-MS: Calculated for $C_{41}H_{56}O_8Si$ $[M+Na]^+$: 727.3642, found: 727.3637.

6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-α-D-galactopyranoside (6)



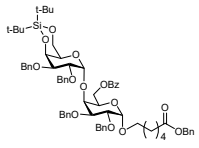
The reaction was carried out according to the general procedure C using compound **3** (3.26 g, 4.62 mmol) and HF/pyridine (70%, 960 µl). The product was purified by column chromatography (pentane:EtOAc = 1:1). Compound **6** (2.4 g, 92% yield, pentane:EtOAc = 1:2, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +97.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 967, 1027, 1045, 1076, 1093, 1149, 1212, 1453, 1731, 2869, 2925, 3463. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.40 – 7.24 (m, 15H, *aromatic* H), 5.11 (s, 2H, *PhC*H_{2C}=*O*), 4.85 – 4.76 (m, 3H, *C*H_2*Ph*, H-1), 4.69 (d, *J* = 11.4 Hz, 1H, *C*H_2*Ph*), 4.64 (d, *J* = 12.1 Hz, 1H, *C*H_2*Ph*), 4.08 (d, *J* = 2.9 Hz, 1H, H-4), 3.95 – 3.73 (m, 5H, H-2, 3, 5, 6), 3.68 – 3.59 (m, 1H, H-7), 3.47 – 3.37 (m, 1H, H-7), 2.41 (bs, 2H, *O*H), 2.36 (t, *J* = 7.5 Hz, 3H, H-11), 1.73 – 1.56 (m, 4H, H-8, H-10), 1.45 – 1.33 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7 (C=O), 138.6, 138.3, 136.2, 128.8, 128.7, 128.6, 128.4, 128.1, 128.0 (*aromatic* C/C*H*), 97.5 (C-1), 77.6, 76.0, 73.5 (CH_2*Ph*), 73.1 (CH_2*Ph*), 69.2, 68.1 (C-7), 66.4 (*C*=*O*CH_2*Ph*), 63.2 (C-6), 34.4 (C-11), 29.2 (C-8), 25.9 (C-9), 24.8 (C-10). HR-MS: Calculated for $C_{33}H_{40}O_8$ $[M+Na]^+$: 587.2621, found: 587.2615.

6-(Benzyl hexanoyl) 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (7)



The reaction was carried out according to the general procedure D using compound **6** (1.87 g, 3.33 mmol), PhCOOBt (3.18 g, 13.3 mmol) and Et_3N (2 ml, 14.7 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **7** (2.1 g, 94% yield, pentane:EtOAc = 3:1, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +37.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1027, 1040, 1095, 1153, 1270, 1452, 1720, 2868, 2927, 3463. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.05 – 7.98 (m, 2H), 7.58 – 7.51 (m, 1H), 7.47 – 7.26 (m, 17H, *aromatic* H), 5.09 (s, 2H, *Ph*CH_{2C}=*O*), 4.86 – 4.77 (m, 3H, *C*H_2*Ph*, H-1), 4.70 (d, *J* = 11.5 Hz, 1H, *C*H_2*Ph*), 4.64 (d, *J* = 12.1 Hz, 1H, *C*H_2*Ph*), 4.56 (dd, *J* = 11.5, 4.8 Hz, 1H, H-6), 4.48 (dd, *J* = 11.5, 7.6 Hz, 1H, H-6), 4.14 – 4.05 (m, 2H, H-4, H-5), 3.91 (dd, *J* = 9.8, 3.2 Hz, 1H, H-2), 3.84 (dd, *J* = 9.8, 3.6 Hz, 1H, H-3), 3.64 – 3.56 (m, 1H, H-7), 3.44 – 3.36 (m, 1H, H-7), 2.51 (bs, 1H, *O*H), 2.28 (t, *J* = 7.5 Hz, 2H, H-11), 1.65 – 1.56 (m, 4H, H-8, H-10), 1.35 – 1.23 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3 (C=O), 166.3 (C*OPh*), 138.4, 138.1, 136.1, 133.1, 129.9, 129.6, 128.6, 128.5, 128.4, 128.2, 127.9, 127.8 (*aromatic* C/*CH*), 97.2 (C-1), 77.6 (C-2), 75.8 (C-3), 73.3 (C*H*$_2$*Ph*), 73.0 (C*H*$_2$*Ph*), 68.0 (C-7), 67.9 (C-4), 67.7 (C-5), 66.1 (*C*=*OCH*$_2$*Ph*), 64.2 (C-6), 34.1 (C-11), 29.0 (C-8), 25.7 (C-9), 24.6 (C-10). HR-MS: Calculated for $C_{40}H_{44}O_9$ [M+Na]$^+$: 691.2883, found: 691.2878.

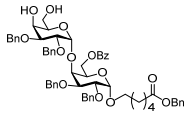
6-(Benzyl hexanoyl) pentyl 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (8)



The reaction was carried out according to the general procedure A. The donor **1** (2.00 g, 3.37 mmol) and the acceptor **7** (1.50 g, 2.24 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 NIS (1.51 g, 6.72 mmol) and TfOH (60 µl, 0.67 mmol) were added. The reaction was stirred at 0 ºC 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 = 7:1). Compound **8** (2.40 g, 91% yield, pentane:EtOAc = 3:1, R*f* = 0.65-0.75) was obtained as colorless syrup. $[\alpha]_D^{25}$ +57.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 444, 651, 737, 797, 826, 977, 1009, 1027, 1046, 1092, 1131, 1274, 1453, 1724, 2858, 2932. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.03 – 7.95 (m, 2H, *aromatic* H), 7.60 – 7.52 (m, 1H, *aromatic* H), 7.50 – 7.11 (m, 27H, *aromatic* H), 5.08 (s, 2H, *Ph*CH_2C=*O*), 4.93 – 4.86 (m, 2H, *C*H_2*Ph*, H-1^A), 4.84 (d, *J* = 3.6 Hz, 1H, H-1^B), 4.78 – 4.61 (m, 8H, *C*H_2*Ph*, H-6^A), 4.55 (dd, *J* = 11.1, 6.2 Hz, 1H, H-6^A), 4.45 (d, *J* = 2.4 Hz, 1H, H-4^B), 4.07 (d, *J* = 2.6 Hz, 1H, H-4^A), 4.05 – 3.98 (m, 2H, H-2^B, H-5^A), 3.96 (q, *J* = 1.6 Hz, 1H, H-5^B), 3.91 – 3.81 (m, 3H, H-3A, H-3^B, H-2^A), 3.73 – 3.69 (m, 2H, H-6^B), 3.64 – 3.56 (m, 1H, H-7), 3.46 – 3.38 (m, 1H, H-7), 2.28 (t, *J* = 7.6 Hz, 2H, H-11), 1.64 – 1.53 (m, 4H, H-10, H-8), 1.34 – 1.22 (m, 2H, H-9), 1.01 (s, 9H, *C*H_3), 0.94 (s, 9H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6 (C=O), 166.2 (C*OPh*), 139.3, 138.7, 138.5, 136.3, 133.3, 130.1, 129.8, 129.1, 128.8, 128.5, 128.4, 128.2, 127.9, 127.8, 127.6, 127.5 (*aromatic* C/*CH*), 100.4 (C-1^B), 97.2 (C-1^A), 78.2 (C-2^A), 77.3 (C-3^A), 75.8 (C-3^B), 75.5 (C-4^A), 74.4 (C*H*$_2$*Ph*), 73.6 (C-5^A),

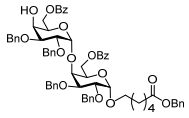
73.1 (C*H*$_2$*Ph*), 73.0 (C*H*$_2$*Ph*), 70.9 (C-4^B), 70.5 (C*H*$_2$*Ph*), 68.8 (C-2^B), 68.1 (C-7), 67.8 (C-5^B), 67.2 (C-6^B), 66.3 (*C*=O*C*H$_2$*Ph*), 63.1 (C-6^A), 34.3 (C-11), 29.2 (C-8), 27.9 (C*H*$_3$), 27.5 (C*H*$_3$), 25.9 (C-9), 24.8 (C-10), 23.6 (C-*Si*), 20.9 (C-*Si*). HR-MS: Calculated for $C_{68}H_{82}O_{14}Si$ [M+Na]$^+$: 1173.5372, found: 1173.5366.

6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (9)



The reaction was carried out according to the general procedure C using compound **8** (2.39 g, 2.08 mmol) and HF/pyridine (70%, 860 µl, 33.3 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1 - 1:1). Compound **9** (2.0 g, 96% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +58.1 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 737, 1027, 1046, 1093, 1155, 1274, 1453, 1720, 2868, 2924, 3492. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.05 – 7.97 (m, 2H, *aromatic* H), 7.62 – 7.54 (m, 1H, *aromatic* H), 7.51 – 7.16 (m, 27H, *aromatic* H), 5.10 (s, 2H, *Ph*CH_2C=*O*), 4.98 (d, *J* = 2.3 Hz, 1H, H-1^B), 4.88 (s, 1H, H-1^A), 4.85 – 4.63 (m, 9H, *C*H$_2$*Ph*, H-6^A), 4.58 (dd, *J* = 11.2, 6.1 Hz, 1H, *C*H$_2$*Ph*, H-6^A), 4.13 – 3.99 (m, 4H, H-4, H-5), 3.91 – 3.85 (m, 4H, H-3, H-2), 3.65 – 3.56 (m, 2H, H-6^B, H-7), 3.55 – 3.40 (m, 2H, H-6^B, H-7), 2.61 (bs, 2H, *O*H), 2.30 (t, *J* = 7.6 Hz, 2H, H-11), 1.67 – 1.55 (m, 4H, H-10, H-8), 1.33 – 1.24 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5 (C=O), 166.1 (C*OPh*), 138.6, 138.4, 138.1, 136.1, 133.3, 129.9 (*aromatic* C), 129.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8 (*aromatic* C*H*), 100.6 (C-1^B), 97.3 (C-1^A), 78.2 (C-2^A), 77.8 (C-5^B), 77.4 (C-2^B), 75.4 (C-3^A, C-3^B), 74.2 (C*H*$_2$*Ph*), 73.4 (C*H*$_2$*Ph*), 73.0 (C*H*$_2$*Ph*), 72.4 (C*H*$_2$*Ph*), 69.8 (C-4^B), 69.2 (C-4^A), 68.7 (C-5^A), 68.1 (C-7), 66.2 (*C*=O*C*H$_2$*Ph*), 63.1 (C-6), 34.2 (C-11), 29.1 (C-8), 25.8 (C-9), 24.7 (C-10). HR-MS: Calculated for $C_{60}H_{66}O_{14}$ [M+Na]$^+$: 1033.4350, found: 1033.4345.

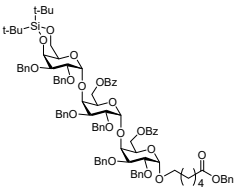
6-(Benzyl hexanoyl) 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (10)



The reaction was carried out according to the general procedure D using compound **9** (2.01 g, 1.99 mmol), PhCOOBt (2.14 g, 8.96 mmol) and Et_3N (1.4 ml, 9.95 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:1 - 3:1). Compound **10** (2.1 g, 94% yield, pentane:EtOAc = 3:1, R*f* = 0.40-0.50) was obtained as yellow syrup. $[\alpha]_D^{25}$ +42.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 738, 1047, 1098, 1275, 1452, 1720, 2869, 2916, 2496. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.02 – 7.91 (m, 4H, *aromatic* H), 7.62 – 7.09 (m, 31H, *aromatic* H), 5.08 (s, 2H, *Ph*CH_2C=*O*), 5.01 (s, 1H, H-1^B), 4.87 – 4.60 (m, 10H, H-1^A, *C*H$_2$*Ph*, H-6^A), 4.57 – 4.44 (m, 3H, H-6^A, H-4^A, H-5^B), 4.16 – 4.03 (m, 3H, H-3^A, H-4^B, H-6^B), 4.01 (t, *J* = 6.7 Hz, 1H, H-5^A), 3.95 – 3.83 (m, 4H, H-2^A, 2^B, 3^B, 6^B), 3.62 – 3.53 (m, 1H, H-7), 3.45 – 3.37 (m, 1H, H-7), 2.27 (t, *J* = 7.6 Hz, 2H, H-11), 1.64 – 1.52 (m, 4H, H-10, H-8), 1.30 – 1.21 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6 (C=O), 166.2 (C*OPh*), 138.8, 138.2, 136.3, 133.7, 133.4, 133.2, 130.3, 130.0, 129.9, 128.8, 128.6, 128.5, 128.4, 127.9, 127.7 (*aromatic* C*H*/C), 100.3 (C-1^B), 97.5 (C-1^A), 78.3 (C-2^B), 77.3 (C-3^B), 77.1 (C-3^A), 75.7 (C-5^B), 75.6 (C-2^A), 74.5 (C*H*$_2$*Ph*), 73.3 (C*H*$_2$*Ph*), 73.2 (C*H*$_2$*Ph*), 72.7 (C*H*$_2$*Ph*), 68.8 (C-5^A), 68.2 (C-7), 68.1 (C-4^A), 67.1

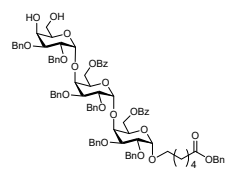
(C-4^{B}), 66.3 (*C*=O*C*H_2*Ph*), 63.1 (C-6^{A}), 62.7 (C-6^{B}), 34.3 (C-11), 29.2 (C-8), 25.9 (C-9), 24.8 (C-10). HR-MS: Calculated for $C_{67}H_{70}O_{15}$ $[M+Na]^+$: 1137.4612, found: 1137.4607.

6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (11)



The reaction was carried out according to the general procedure A. The donor **1** (1.82 g, 3.07 mmol) and the acceptor **10** (1.90 g, 1.71 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 17 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 3Å. The solution was cooled to 0 ºC, after which NIS (1.38 g, 6.14 mmol) and TfOH (54 µl, 0.61 mmol) were added. The reaction was stirred at 0 ºC 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 = 5:1). Compound **11** (2.28 g, 84% yield, pentane:EtOAc = 5:2, R*f* = 0.40-0.50) was obtained as colorless syrup. $[\alpha]_D^{25}$ +47.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 444, 475, 650, 734, 795, 824, 914, 937, 977, 1005, 1025, 1044, 1063, 1090, 1270, 1452, 1724, 2859, 2932. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.02 – 7.96 (m, 2H, *aromatic* H, Bz), 7.95 – 7.90 (m, 2H, *aromatic* H, Bz), 7.61 – 7.03 (m, 44H, *aromatic* H), 5.09 (d, *J* = 3.3 Hz, 1H, H-1C), 5.07 (s, 2H, *Ph*CH_2C=*O*), 4.97 – 4.89 (m, 2H, CH_2*Ph*, H-1^{B}), 4.86 – 4.50 (m, 16H, H-1^{A}, CH_2*Ph*, H-6^{B}, 6^{A}), 4.49 – 4.42 (m, 2H, H-4^{B}, H-4^{C}), 4.15 (d, *J* = 2.6 Hz, 1H, H-4^{A}), 4.04 – 3.92 (m, 5H, H-2^{B}, 2^{C}, 5^{A}, 5^{B}, 5^{C}), 3.90 – 3.77 (m, 4H, H-2^{A}, 3^{A}, 3^{B}, 3^{C}), 3.75 – 3.64 (m, 2H, H-6^{C}), 3.61 – 3.51 (m, 1H, H-7), 3.46 – 3.37 (m, 1H, H-7), 2.27 (t, *J* = 7.6 Hz, 2H, H-11), 1.58 (p, *J* = 7.5 Hz, 4H, H-10, H-8), 1.31 – 1.21 (m, 2H, H-9), 1.02 (s, 9H, CH_3), 0.91 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4 (C=O), 165.9 (C*OPh*), 165.4 (C*OPh*), 139.1, 138.4, 136.1, 133.2, 129.6, 128.9, 128.5, 128.4, 127.9, 127.5, 127.1 (*aromatic* C/C*H*), 99.94 (C-1^{C}), 99.89 (C-1^{B}), 97.3 (C-1^{A}), 78.1, 77.6 (C-2^{A}), 77.2, 76.4, 75.4, 75.0, 74.5 (C-4^{A}), 74.0 (CH_2*Ph*), 73.5 (CH_2*Ph*), 73.0 (CH_2*Ph*), 72.9 (CH_2*Ph*), 72.6 (CH_2*Ph*), 70.6 (C-4^{B}), 70.1 (CH_2*Ph*), 69.0 (C-4^{C}), 68.6, 67.9 (C-7), 67.4 (C-5^{C}), 67.1 (C-6^{C}), 66.0 (*C*=O*C*H_2*Ph*), 62.8 (C-6^{A}), 61.3 (C-6^{B}), 34.1 (C-11), 29.0 (C-8), 27.7 (CH_3), 27.2 (CH_3), 25.6 (C-9), 24.6 (C-10), 23.4 (C-*Si*), 20.6 (C-*Si*). HR-MS: Calculated for $C_{95}H_{108}O_{20}Si$ $[M+H]^+$: 1597.7281, found: 1597.7276.

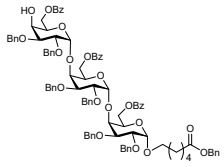
6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (12)



The reaction was carried out according to the general procedure C using compound **11** (2.03 g, 1.27 mmol) and HF/pyridine (70%, 530 µl, 33.3 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **12** (1.74 g, 94% yield, pentane:EtOAc = 2:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +42.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 736, 1005, 1027, 1046, 1092, 1272, 1315, 1452, 1720, 2870, 2923, 3454. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.04 – 7.99 (m, 2H, m, 2H, *aromatic* H, Bz), 7.97 – 7.91

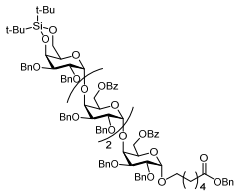
(m, 2H, m, 2H, *aromatic* H, Bz), 7.61 – 7.05 (m, *aromatic* H), 5.09 – 5.05 (m, 3H, *Ph*CH_2C=*O*, H-1^C), 5.04 (d, *J* = 3.3 Hz, 1H, H-1^B), 4.95 – 4.53 (m, 16H, H-1A, *Ph*CH_2, 6^A, 6^B), 4.51 – 4.39 (m, 2H, H-4^B, 6^B), 4.17 – 4.03 (m, 4H, H-3^B, 4^A, 4^C, 5^C), 4.01 (t, *J* = 6.7 Hz, 1H, H-5^A), 3.98 – 3.77 (m, 6H, H-2, H-3^A, H-3^C, H-5^B), 3.65 – 3.36 (m, 4H, H-6C, H-7), 2.80 (bs, 1H, *O*H), 2.47 (bs, 1H, *O*H), 2.27 (t, *J* = 7.5 Hz, 2H, H-11), 1.65 – 1.51 (m, 4H, H-10, H-8), 1.33 – 1.21 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3 (C-12), 165.9 (C*OPh*), 165.4 (C*OPh*), 138.7, 138.5, 138.2, 137.8, 136.0, 133.1, 129.8, 129.6, 128.5, 128.4, 128.2, 127.9, 127.3 (aromatic C/C*H*), 100.2 (C-1^C), 99.8 (H-1^B), 97.2 (H-1^A), 78.0 (C-2^B), 77.6 (C-5^B), 76.9 (C-5^C), 76.6 (C-3), 76.3 (C-3^B), 75.6 (C-2^A), 74.7 (C-3), 74.5 (C-2^C), 74.0 (CH_2*Ph*), 73.3 (CH_2*Ph*), 72.93 (CH_2*Ph*), 72.91 (CH_2*Ph*), 72.9 (CH_2*Ph*), 72.0 (CH_2*Ph*), 69.09 (C-4), 69.06 (C-4), 69.01 (C-4), 68.5 (C-5^A), 67.9 (C-7), 66.0 (*C*=*O*CH_2*Ph*), 62.85 (C-6^A), 62.80 (C-6^C), 61.3 (C-6^B), 34.1 (C-11), 28.9 (C-8), 25.6 (C-9), 24.6 (C-10). HR-MS: Calculated for $C_{87}H_{92}O_{20}$ $[M+NH_4]^+$: 1474.6526, found: 1474.6520.

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



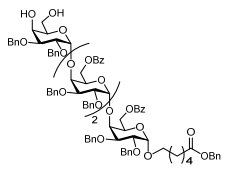
The reaction was carried out according to the general procedure D using compound **12** (1.45 g, 1.0 mmol), PhCOOBt (1.07 g, 4.49 mmol) and Et_3N (700 µl, 5.0 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:2). Compound **13** (1.48 g, 95% yield, pentane:EtOAc = 2:1, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +31.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 464, 734, 964, 1003, 1026, 1046, 1070, 1091, 1156, 1271, 1315, 1452, 1497, 1720, 2869, 2925, 3497. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.05 – 7.88 (m, 6H, *aromatic* H, Bz), 7.66 – 7.01 (m, 44H, *aromatic* H), 5.12 – 5.04 (m, 3H, *C*H_2*Ph*, H-1^C), 5.01 (d, *J* = 3.2 Hz, 1H, H-1^B), 4.93 – 4.38 (m, 20H, *C*H_2*Ph*, H-1^A, H-4, H-6^A, 6^B), 4.12 (s, 2H), 4.05 – 3.76 (m, 9H), 3.62 – 3.51 (m, 1H, H-7), 3.47 – 3.35 (m, 1H, H-7), 2.53 (bs, 1H, *O*H), 2.27 (t, *J* = 7.6 Hz, 2H, H-11), 1.64 – 1.50 (m, 4H, H-10, 8), 1.33 – 1.22 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4 (C-12), 166.0 (C*OPh*), 165.9 (C*OPh*), 165.4 (C*OPh*), 138.81, 138.59, 138.32, 138.30, 138.14, 137.89, 136.07, 133.22, 133.18, 133.02, 130.01, 129.97, 129.87, 129.85, 129.65, 129.60, 128.55, 128.52, 128.50, 128.48, 128.34, 128.31, 128.25, 128.18, 128.17, 127.93, 127.87, 127.75, 127.72, 127.62, 127.53, 127.46, 127.41, 127.35 (*aromatic* C/C*H*), 100.1 (C-1^B), 100.0 (C-1^C), 97.3 (C-1^A), 78.2, 77.7, 76.4, 76.3, 75.7, 75.1, 74.4, 74.2 (CH_2*Ph*), 73.6 (CH_2*Ph*), 73.1 (CH_2*Ph*), 73.0 (CH_2*Ph*), 72.9 (CH_2*Ph*), 72.3 (CH_2*Ph*), 69.0, 68.6, 68.0 (C-7), 67.7, 66.6, 66.1 (CH_2*Ph*), 62.9 (C-6^A), 62.3 (C-6^C), 61.3 (C-6^B), 34.1 (C-11), 29.0 (C-8), 25.7 (C-9), 24.6 (C-10). HR-MS: Calculated for $C_{94}H_{96}O_{21}$ $[M+H]^+$: 1561.6522, found: 1561.6517.

6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-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 A. The donor **1** (1.65 g, 2.79 mmol) and the acceptor **13** (1.45 g, 0.93 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 28 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 3Å. The solution was cooled to 0 ºC, after which NIS (1.26 g, 5.58 mmol) and TfOH (50 µl, 0.56 mmol) were added. The reaction was stirred at 0 ºC 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:DCM = 20:3:1). Compound **14** (2.28 g, 84% yield, pentane:EtOAc = 5:2, R*f* = 0.40-0.50) was obtained as colorless syrup. $[\alpha]_D^{25}$ +36.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 444, 469, 474, 650, 732, 797, 824, 977, 1003, 1026, 1045, 1090, 1269, 1452, 1725, 2859, 2932. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.06 – 7.87 (m, 6H, *aromatic* H, Bz), 7.67 – 6.99 (m, 54H, *aromatic* H), 5.11 (d, *J* = 3.5 Hz, 1H, H-1^D), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.02 (d, *J* = 2.2 Hz, 1H, H-1^C), 4.94 (d, *J* = 3.6 Hz, 1H, H-1^B), 4.93 – 4.33 (m, 26H), 4.17 (d, *J* = 2.6 Hz, 1H), 4.14 – 3.88 (m, 8H), 3.86 – 3.71 (m, 4H), 3.71 – 3.53 (m, 3H, H-6^D, H-7), 3.47 – 3.35 (m, 1H, H-7), 2.27 (t, *J* = 7.5 Hz, 2H, H-11), 1.64 – 1.51 (m, 4H, H-10, H-8), 1.33 – 1.22 (m, 2H, H-9), 1.01 (s, 9H, *C*H$_3$), 0.89 (s, 9H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4 (C-12), 166.0 (C*OPh*), 165.4 (2 C*OPh*), 139.05, 138.74, 138.67, 138.47, 138.35, 138.33, 138.03, 138.00, 136.00, 133.11, 133.00, 129.85, 129.81, 129.78, 129.56, 129.53, 128.95, 128.91, 128.56, 128.50, 128.46, 128.42, 128.39, 128.37, 128.19, 128.15, 128.09, 128.08, 127.85, 127.81, 127.57, 127.54, 127.51, 127.46, 127.39, 127.28, 127.25, 127.23, 126.86 (aromatic C/C*H*), 100.1 (H-1^C), 100.0 (H-1^B), 99.9 (H-1^D), 97.3 (H-1^A), 78.2, 77.9, 76.9, 76.7, 76.4, 75.9, 74.7, 74.5, 74.1 (C*H$_2$Ph*), 73.5 (C*H$_2$Ph*), 73.4 (C*H$_2$Ph*), 73.2 (C*H$_2$Ph*), 72.9 (C*H$_2$Ph*), 72.4 (C*H$_2$Ph*), 70.6, 70.1 (C*H$_2$Ph*), 68.94, 68.85, 68.6, 67.9 (C-7), 67.4, 67.1 (C-6), 66.1 (C*H$_2$Ph*), 62.9 (C-6), 61.3 (C-6), 61.2 (C-6), 34.1 (C-11), 29.0 (C-8), 27.7 (C*H$_3$*), 27.2 (C*H$_3$*), 25.7 (C-9), 24.6 (C-10), 23.4 (C-*Si*), 20.6 (C-*Si*). HR-MS: Calculated for $C_{122}H_{134}O_{26}$ $[M+NH_4]^+$: 2060.9276, found: 2060.9271.

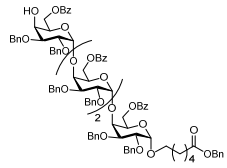
6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (15)



The reaction was carried out according to the general procedure C using compound **14** (1.30 g, 0.64 mmol) and HF/pyridine (70%, 266 µl, 10.2 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2-1:1). Compound **15** (1.13 g, 93% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +38.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 734, 1003, 1026, 1045, 1092, 1271, 1315, 1452, 1497, 1720, 2870, 2925, 3473. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.18 – 8.02 (m, 6H, *aromatic* H, Bz), 7.74 – 7.14 (m, 55H, *aromatic* H), 5.20 (d, *J* = 3.2 Hz, 1H, H-1^D), 5.19 – 5.13 (m, 4H, *C*H$_2$*Ph*, H-1^C, H-1^B), 5.07 – 4.67 (m, 21H), 4.67 – 4.51 (m, 4H), 4.30 – 4.10 (m, 6H), 4.09 – 4.01 (m, 3H), 4.01 – 3.93 (m, 4H), 3.86 (dd, *J* = 10.0, 3.1 Hz, 1H, H-3), 3.77 – 3.65 (m, 1H, H-7), 3.63 – 3.47 (m, 3H, H-6, H-7), 2.99 (s, 1H, *O*H), 2.61 (s, 1H, *O*H), 2.38 (t, *J* = 7.5

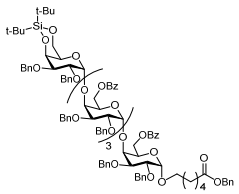
Hz, 2H, H-11), 1.76 – 1.62 (m, 4H, H-10, H-8), 1.46 – 1.36 (m, 2H, H-9). ^{13C} NMR (100 MHz, $CDCl_3$) δ 173.3 (C-12), 165.9 (C*OPh*), 165.4 (C*OPh*), 165.3 (C*OPh*), 138.7, 138.6, 138.5, 138.3, 138.1, 138.0, 137.8, 136.0, 133.2, 133.1, 129.9, 129.8, 129.7, 129.6, 129.5, 128.6, 128.54, 128.53, 128.52, 128.43, 128.42, 128.34, 128.32, 128.24, 128.22, 128.21, 128.14, 128.13, 128.11, 127.84, 127.82, 127.81, 127.64, 127.63, 127.62, 127.60, 127.5, 127.44, 127.42, 127.41, 127.33, 127.31, 127.2 (aromatic C/*CH*), 100.2 (C-1^C), 99.9 (C-1^B), 99.8 (C-1^D), 97.2 (C-1^A), 78.0, 77.8, 76.8, 76.6, 76.4, 76.3, 75.8, 74.8, 74.7, 74.0 (CH_2*Ph*), 73.9, 73.5, 73.2, 73.0, 72.84, 72.83, 72.7, 71.9(6xCH_2*Ph*), 69.1, 69.0, 68.6, 67.9 (C-7), 66.0 (CH_2*Ph*), 62.9, 62.8, 61.3, 61.1 (4xC-6), 34.0 (C-11), 28.9 (C-8), 25.6 (C-9), 24.5 (C-10). HR-MS: Calculated for $C_{114}H_{118}O_{26}$ $[M+H]^+$: 1903.7990, found: 1903.7984.

6-(Benzyl hexanoyl) 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galacto-pyranoside (16)



The reaction was carried out according to the general procedure D using compound **15** (1.12 g, 0.59 mmol), PhCOOBt (633 mg, 2.65 mmol) and Et_3N (410 µl, 2.94 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **16** (1.09 g, 92% yield, pentane:EtOAc = 3:2, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +29.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 736, 1005, 1026, 1046, 1070, 1092, 1156, 1271, 1315, 1452, 1720, 2869, 2926, 3500. ^{1}H-NMR ($CDCl_3$, 400 MHz) 8.05 – 7.87 (m, 8H, *aromatic* H, Bz), 7.66 – 6.97 (m, 57H, *aromatic* H), 5.07 (s, 2H, CH_2*Ph*), 5.06 (d, *J* = 3.5 Hz, 1H, H-1^D), 5.04 – 5.00 (m, 2H, H-1^C, H-1^B), 4.89 – 4.33 (m, 26), 4.20 – 3.74 (m, 14H), 3.60 – 3.51 (m, 1H, H-7), 3.44 – 3.34 (m, 1H, H-7), 2.26 (t, *J* = 7.6 Hz, 2H, H-11), 1.63 – 1.50 (m, 4H, H-10, H-8), 1.30 – 1.21 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4 (C-12), 166.0 (C=*O*, Bz), 165.9 (C=*O*, Bz), 165.5 (C=*O*, Bz), 165.3 (C=*O*, Bz), 138.8, 138.7, 138.6, 138.34, 138.32, 138.2, 138.1, 137.8, 136.1, 133.3, 133.2, 133.0, 130.1, 130.0, 129.9, 129.8, 129.7, 129.64, 129.63, 128.62, 128.61, 128.60, 128.54, 128.52, 128.43, 128.41, 128.33, 128.31, 128.30, 128.23, 128.22, 128.21, 128.19, 127.93, 127.91, 127.73, 127.71, 127.70, 127.6, 127.53, 127.51, 127.4, 127.32, 127.30 (*aromatic* C/*CH*), 100.2 (C-1^C), 100.0 (C-1^B, C-1^D), 97.3 (C-1^A), 78.2, 78.1, 76.9, 76.7, 76.5, 76.4, 76.0, 75.9, 75.0, 74.3 (CH_2*Ph*), 73.8, 73.7, 73.4, 73.1, 72.9, 72.7, 72.2 (6xCH_2*Ph*), 69.1, 68.9, 68.6, 67.9 (C-7), 67.6, 66.4, 66.1 (CH_2*Ph*), 62.9, 62.1, 61.3, 61.1 (4xC-6), 34.1 (C-11), 29.0 (C-8), 25.7 (C-9), 24.6 (C-10). HR-MS: Calculated for $C_{94}H_{96}O_{21}$ $[M+NH_4]^+$: 2024.8517, found: 2024.8512.

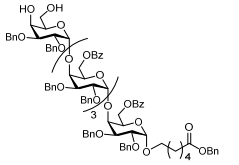
6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (17)



The reaction was carried out according to the general procedure A. The donor **1** (1.26 g, 2.13 mmol) and the acceptor **16** (1.07 g, 0.53 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 5.3 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 3Å. The solution was cooled to 0 ºC, after which NIS (719 mg, 3.20 mmol) and TfOH (5 µl, 0.05 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 = 4:1). Compound **17** (1.06 g, 84% yield, pentane:EtOAc = 5:2, R*f* = 0.45-0.55) was obtained as colorless syrup. $[\alpha]_D^{25}$ +38.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 737, 1005, 1027, 1047, 1095, 1271, 1315, 1362, 1452, 1725, 2859, 2931. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.05 – 7.96 (m, 6H, C*H*, Bz), 7.95 – 7.90 (m, 2H, C*H*, Bz), 7.63 – 6.98 (m, 72H, *aromatic* H), 5.12 (d, *J* = 3.4 Hz, 1H, H-1^E), 5.06 (d, *J* = 4.3 Hz, 4H, *C*H$_2$*Ph*, H-1^D, H-1^C), 4.93 (d, *J* = 3.5 Hz, 1H, H-1^B), 4.91 – 4.70 (m, 17H), 4.68 – 4.33 (m, 16H), 4.21 – 4.10 (m, 3H), 4.06 (s, 1H, H-5), 4.03 – 3.81 (m, 10H), 3.80 – 3.71 (m, 2H, H-3), 3.69 – 3.54 (m, 3H, H-6^E, H-7), 3.46 – 3.36 (m, 1H, H-7), 2.27 (t, *J* = 7.5 Hz, 2H, H-11), 1.58 (p, *J* = 7.7 Hz, 4H, H-10, 8), 1.31 – 1.25 (m, 2H, H-9), 1.01 (s, 9H, *C*H$_3$), 0.89 (s, 9H, *C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3 (C-12), 166.0 (C=*O*, Bz), 165.5 (C=*O*, Bz), 165.3 (C=*O*, Bz), 139.1, 138.8, 138.7, 138.64, 138.61, 138.4, 138.33, 138.32, 138.13, 138.12, 136.10, 133.24, 133.23, 133.1, 133.01, 130.00, 129.92, 129.91, 129.63, 129.62, 129.61, 129.0, 128.7, 128.6, 128.52, 128.51, 128.44, 128.42, 128.3, 128.22, 128.20, 128.13, 128.11, 128.0, 127.9, 127.63, 127.62, 127.60, 127.53, 127.51, 127.42, 127.41, 127.34, 127.32, 126.9 (aromatic C/C*H*), 100.1 (C-1^D), 100.0 (C-1^C, C-1^B), 99.9 (C-1^E), 97.3 (C-1^A), 78.1, 77.9, 77.4, 77.2, 76.9, 76.6, 76.5, 76.2, 75.8, 75.3, 74.4, 74.34, 74.31, 74.0, 73.8, 73.44, 73.41, 73.1, 72.9 (6 C*H*$_2$*Ph*), 72.83, 72.81, 72.6, 72.3 (3 C*H*$_2$*Ph*), 70.6, 70.1 (C*H*$_2$*Ph*), 69.1, 68.94 68.91, 68.7, 67.9(C-7), 67.4, 67.0 (C-6^E), 66.0 (C*H*$_2$*Ph*), 63.0 (C-6^A), 61.4 (C-6^D), 61.1 (C-6^C, 6^B), 34.1 (C-11), 29.0 (C-8), 27.7 (3xC*H*$_3$), 27.2 (3xC*H*$_3$), 25.7 (C-9), 24.6 (C-10), 23.4 (C-*Si*), 20.6 (C-*Si*). MALDI-MS: Calculated for $C_{149}H_{160}O_{32}Si$ $[M+Na]^+$: 2512.0560, found: 2512.0364.

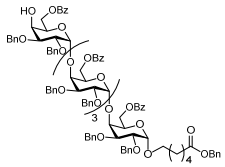
6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (18)

The reaction was carried out according to the general procedure C using compound **17** (1.04 g, 0.42 mmol) and HF/pyridine (70%, 170 µl, 6.67 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2-1:1). Compound **18** (916 mg, 92% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +40.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 734, 1000, 1026, 1045, 1090, 1269, 1315, 1360, 1452, 1720, 2925, 3030, 3486. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.04 – 7.91 (m, 8H, C*H*, Bz), 7.64 – 6.97 (m, 67H, aromatic H), 5.11 – 5.03 (m, 5H, *C*H$_2$*Ph*, H-1^E, 1^D, 1^C), 5.01 (d, *J* = 3.4 Hz, 1H, H-1^B), 4.95 – 4.54 (m, 25H), 4.52 – 4.28 (m, 6H), 4.19 – 4.10 (m, 3H), 4.09 – 4.03 (m, 2H), 4.02 – 3.96 (m, 2H, H-5^A, 5^E), 3.94 – 3.86 (m, 5H), 3.86 – 3.77 (m, 4H), 3.73 (dd, *J* =



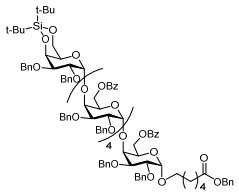
10.0, 3.1 Hz, 1H, H-3^{B}), 3.62 – 3.52 (m, 1H, H-7), 3.47 – 3.33 (m, 3H, H-7, H-6^{E}), 2.26 (t, *J* = 7.5 Hz, 2H, H-11), 1.62 – 1.52 (m, 4H, H-10, 8), 1.35 – 1.21 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4 (C-12), 166.0 (C=O, Bz), 165.5 (C=O, Bz), 165.4 (C=O, Bz), 165.3 (C=O, Bz), 138.8, 138.7, 138.62, 138.59, 138.33, 138.32, 138.30, 138.1, 138.0, 137.9, 136.1, 133.23, 133.21, 129.92, 129.91, 129.90, 129.7, 129.62, 129.60, 129.1, 128.9, 128.73, 128.71, 128.6, 128.53, 128.52, 128.50, 128.42, 128.40, 128.33, 128.31, 128.24, 128.23, 128.22, 128.21, 128.19, 128.0, 127.94, 127.92, 127.8, 127.72, 127.71, 127.64, 127.62, 127.51, 127.50, 127.43, 127.41, 127.3, 126.6, 126.3 (aromatic C/*CH*), 100.2 (C-1^{D}, 1^{B}), 100.1 (C-1^{C}), 99.9 (C-1^{E}), 97.3 (C-1^{A}), 78.1, 77.9, 77.2, 76.63, 76.61, 76.2, 76.1, 75.9, 75.4, 74.7, 74.5, 74.1, 73.8, 73.5, 73.3, 73.1, 72.9, 72.8, 72.7, 72.1 (9 C*H*$_2$*Ph*), 69.23, 69.21, 69.1, 68.7, 67.9 (C-7), 66.1 (C*H*$_2$*Ph*), 63.1, 62.9, 61.5, 61.3, 61.1 (5 C-6), 34.1 (C-11), 29.0 (C-8), 25.7 (C-9), 24.6 (C-10). HR-MS: Calculated for $C_{141}H_{144}O_{32}$ $[M+NH_4]^+$: 2366.9984, found: 2366.9979.

6-(Benzyl hexanoyl) 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galacto-pyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (19)



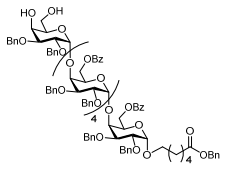
The reaction was carried out according to the general procedure D using compound **18** (897 mg, 0.38 mmol), PhCOOBt (411 mg, 1.72 mmol) and Et_3N (266 µl, 1.91 mmol). The product was purified by column chromatography (pentane:EtOAc:DCM = 7:2:1). Compound **19** (1.09 g, 92% yield, pentane:EtOAc = 3:2, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +22.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 414, 417, 452, 468, 734, 1000, 1026, 1046, 1070, 1092, 1156, 1269, 1315, 1452, 1720, 2870, 2923, 3509. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.04 – 7.91 (m, 10H, C*H*, Bz), 7.63 – 6.97 (m, 70H, aromatic H), 5.11 – 5.03 (m, 6H, *C*H$_2$*Ph*, H-1^{E}, 1^{D}, 1^{C}, 1^{B}), 4.95 – 4.38 (m, 34H), 4.34-4.31 (m, 1H, H-6), 4.21 – 4.05 (m, 5H), 4.04 – 3.83 (m, 11H), 3.80 (dd, *J* = 10.0, 3.1 Hz, 1H, H-3^{B}), 3.58 (dt, *J* = 10.0, 7.0 Hz, 1H, H-7), 3.41 (dt, *J* = 10.0, 6.6 Hz, 1H, H-7), 2.27 (t, *J* = 7.5 Hz, 2H, H-11), 1.58 (p, *J* = 7.7 Hz, 4H, H-10, 8), 1.32 – 1.24 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3 (C-12), 166.0, 165.8, 165.5, 165.4, 165.3 (5 C=O, Bz), 138.74, 138.72, 138.64, 138.61, 138.33, 138.31, 138.23, 138.21, 138.1, 137.8, 136.1, 133.1, 132.9, 130.0, 129.93, 129.92, 129.90, 129.63, 129.61, 129.52, 129.51, 128.64, 128.61, 128.53, 128.51, 128.43, 128.42, 128.33, 128.31, 128.24, 128.22, 128.11, 128.10, 127.83, 127.81, 127.7, 127.61, 127.60, 127.5, 127.4, 127.32, 127.31, 127.2 (*aromatic* C/C*H*), 100.2 (C-1), 100.1 (C-1), 99.9 (2xC-1), 97.3 (C-1^{A}), 78.14, 78.11, 77.2, 76.8, 76.6, 76.5, 76.3, 76.1, 75.9, 75.3, 75.0, 74.5, 74.2, 73.7, 73.5, 73.4, 73.1, 72.84, 72.82, 72.7, 72.6, 72.2 (10 *CH*$_2$*Ph*), 69.1, 69.0, 68.9, 68.7, 67.9 (C-7), 67.6, 66.5, 66.0 (*CH*$_2$*Ph*), 63.0, 62.1, 61.5, 61.2, 61.1 (5 C-6), 34.1 (C-11), 28.9 (C-8), 25.6 (C-9), 24.6 (C-10). MALDI-MS: Calculated for $C_{148}H_{148}O_{33}$ $[M+Na]^+$: 2475.9801, found: 2475.9603.

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



The reaction was carried out according to the general procedure A. The donor **1** (995 mg, 1.68 mmol) and the acceptor **19** (916 mg, 0.37 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 3.7 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 3Å. The solution was cooled to 0 ºC, after which NIS (545 mg, 2.42 mmol) and TfOH (4 µl, 0.04 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:DCM = 40:9:2). Compound **20** (790 mg, 72% yield, pentane:EtOAc = 5:2, R*f* = 0.45-0.55) was obtained as colorless syrup. $[\alpha]_D^{25}$ +35.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 445, 474, 651, 734, 797, 824, 1003, 1026, 1046, 1062, 1092, 1269, 1315, 1452, 1721, 2860, 2931. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.04 – 7.88 (m, 8H, *C*H, Bz), 7.93 – 7.88 (m, 2H, *C*H, Bz), 7.64 – 6.92 (m, 80H, aromatic H), 5.11 – 4.99 (m, 6H, *C*H$_2$*Ph*, H-1^F, 1^E, 1^D, 1^C), 4.95 – 4.33 (m, 41H), 4.24 (s, 1H, H-5), 4.17 – 4.08 (m, 4H), 4.05 (s, 1H), 4.01 – 3.78 (m, 12H), 3.76 – 3.68 (m, 2H, H-3^F, 3^B), 3.67 – 3.50 (m, 3H, H-6^F, 7), 3.45 – 3.35 (m, 1H, H-7), 2.27 (t, *J* = 7.5 Hz, 2H, H-11), 1.64 – 1.51 (m, 4H, H-10, 8), 1.31 – 1.20 (m, 2H, H-9), 1.00 (s, 9H, 3x*C*H$_3$), 0.87 (s, 9H, 3x*C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4 (C-12), 166.0, 165.5, 165.4, 165.3, 165.3 (5 C=O, Bz), 139.2, 138.8, 138.74, 138.71, 138.6, 138.4, 138.3, 138.2, 138.13, 138.11, 136.10, 133.2, 133.1, 130.03, 130.01, 129.9, 129.7, 129.64, 129.62, 129.61, 129.0, 128.7, 128.63, 128.62, 128.60, 128.54, 128.52, 128.51, 128.4, 128.35, 128.32, 128.26, 128.23, 128.21, 127.9, 127.7, 127.68, 127.63, 127.61, 127.53, 127.51, 127.45, 127.42, 127.3, 127.2, 126.9 (*aromatic* C), 100.2 (C-1), 100.0 (3xC-1), 99.9 (C-1^F), 97.3 (C-1^A), 78.1, 77.9, 77.4, 77.3, 77.2, 76.9, 76.7, 76.5, 76.3, 76.1, 75.9, 75.3, 74.9, 74.3, 74.2, 74.0, 73.8, 73.7, 73.5, 73.4, 73.2, 72.9 (7 C*H$_2$Ph*), 72.84, 72.81, 72.6, 72.4 (3 C*H$_2$Ph*), 70.6, 70.1 (C*H$_2$Ph*), 69.2, 69.0, 68.9, 68.7, 68.0 (C-7), 67.4, 67.1 (C-6^F), 66.1 (C*H$_2$Ph*), 63.0, 61.5, 61.3, 61.14, 61.05 (5 C-6), 34.2 (C-11), 29.0 (C-8), 27.7 (3xC*H$_3$*), 27.2 (3xC*H$_3$*), 25.7 (C-9), 24.7 (C-10), 23.4 (C-*Si*), 20.6 (C-*Si*). MALDI-MS: Calculated for $C_{176}H_{186}O_{38}Si$ $[M+Na]^+$: 2958.2289, found: 2958.2033.

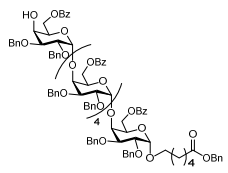
6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl -(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galacto-pyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside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



The reaction was carried out according to the general procedure C using compound **20** (768 mg, 0.26 mmol) and HF/pyridine (70%, 110 µl, 4.19 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **21** (664 mg, 91% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +36.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 464, 734, 1000, 1026, 1045, 1090, 1156, 1269, 1315, 1452, 1720, 2869, 2925, 3461. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.04 – 7.95 (m, 8H, *C*H, Bz), 7.95 – 7.90 (m, 2H, *C*H, Bz), 7.62 – 6.94 (m, 80H, *aromatic* H), 5.10 – 5.03 (m, 6H, *C*H$_2$*Ph*, H-1^F, 1^E, 1^D, 1^C), 5.00 (d, *J* = 3.5 Hz,

1H, H-1^{B}), 4.92 – 4.54 (m, 32H), 4.51 – 4.35 (m, 6H), 4.32 – 4.23 (m, 2H), 4.19 – 4.09 (m, 4H), 4.08 – 3.75 (m, 15H), 3.71 (dd, *J* = 10.0, 3.1 Hz, 1H, H-3^{B}), 3.57 (dt, *J* = 10.0, 7.0 Hz, 1H, H-7), 3.47 – 3.33 (m, 3H, H-7, 6^{F}), 2.26 (t, *J* = 7.5 Hz, 2H, H-11), 1.57 (p, *J* = 7.4 Hz, 4H, H-10, 8), 1.30 – 1.25 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3 (C-12), 166.0, 165.5 , 165.4, 165.34, 165.31 (5 C=O, Bz), 138.7, 138.63, 138.61, 138.3, 138.24, 138.21, 138.1, 138.0, 137.8, 136.1, 133.2, 133.14, 133.11, 129.95, 129.93, 129.91, 129.63, 129.61, 129.60, 129.5, 128.7, 128.6, 128.54, 128.52, 128.51, 128.50, 128.4, 128.34, 128.32, 128.24, 128.22, 128.21, 128.11, 128.10, 127.9, 127.8, 127.7, 127.64, 127.62, 127.52, 127.51, 127.50, 127.4, 127.34, 127.32, 127.31, 127.2, 127.1 (*aromatic* C/C*H*), 100.2 (2xC-1), 100.1 (C-1^{B}), 99.9 (C-1), 99.8 (C-1^{F}), 97.3 (C-1^{A}), 78.0, 77.8, 77.4, 77.2, 76.63, 76.61, 76.2, 76.1, 75.9, 75.3, 74.9, 74.7, 74.4, 74.04 (CH_2*Ph*), 74.01, 73.8, 73.7, 73.5, 73.2, 73.1, 72.8, 72.7, 72.64, 72.62, 72.0 (10 CH_2*Ph*), 69.2, 69.1, 69.0, 68.7, 67.9 (C-7), 66.0 (CH_2*Ph*), 63.0, 62.8, 61.5, 61.3, 61.2, 61.1 (6 C-6), 34.1 (C-11), 29.0 (C-8), 25.7 (C-9), 24.6 (C-10). MALDI-MS: Calculated for $C_{168}H_{170}O_{38}$ $[M+Na]^+$: 2818.1268, found: 2818.1032.

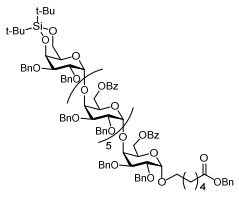
6-(Benzyl hexanoyl) 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galacto-pyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (22)



The reaction was carried out according to the general procedure D using compound **21** (614 mg, 0.22 mmol), PhCOOBt (289 mg, 1.21 mmol) and Et_3N (183 µl, 1.31 mmol). The product was purified by column chromatography (pentane:EtOAc:DCM = 7:2:1). Compound **22**(620 mg, 95% yield, pentane:EtOAc = 3:2, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +37.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 419, 1005, 1027, 1047, 1070, 1096, 1272, 1315, 1723, 2872, 2923, 3480. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.02 – 7.91 (m, 12H, *C*H, Bz), 7.63 – 6.94 (m, 83H, *aromatic* H), 5.11 – 5.03 (m, 6H, *C*H_2*Ph*, H-1^{F}, 1^{E}, 1^{D}, 1^{C}), 5.02 (d, *J* = 3.5 Hz, 1H, H-1^{B}), 4.92 – 4.22 (m, 42H), 4.18 – 4.03 (m, 6H), 3.99 (t, *J* = 6.8 Hz, 1H, H-5^{A}), 3.96 – 3.79 (m, 12H), 3.77 (dd, *J* = 10.0, 3.1 Hz, 1H, H-3), 3.57 (dt, *J* = 9.9, 7.0 Hz, 1H, H-7), 3.41 (dt, *J* = 9.9, 6.6 Hz, 1H, H-3), 2.58 (bs, 1H, *O*H), 2.26 (t, *J* = 7.6 Hz, 2H, H-11), 1.61 – 1.52 (m, 4H, H-10, 8), 1.29 – 1.24 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4 (C-12), 166.0, 165.9, 165.5, 165.4, 165.4, 165.3 (6 C=O, Bz), 138.8, 138.7, 138.6, 138.4, 138.33, 138.31, 138.25, 138.21, 138.1, 137.9, 136.1, 133.2, 133.2, 133.0, 130.1, 130.04, 130.01, 129.9, 129.7, 129.5, 129.4, 129.3, 128.7, 128.64, 128.62, 128.61, 128.56, 128.53, 128.42, 128.41, 128.33, 128.31, 128.24, 128.22, 128.21, 128.0, 127.9, 127.8, 127.74, 127.72, 127.63, 127.61, 127.5, 127.42, 127.40, 127.36, 127.33, 127.31, 127.22, 127.21 (aromatic C/C*H*), 100.2 (C-1), 100.1 (C-1), 99.9 (3xC-1), 97.3 (C-1^{A}), 78.2, 77.3, 77.2, 76.7, 76.6, 76.2, 76.1, 76.0, 75.9, 75.8, 75.4, 75.0, 74.9, 74.5, 74.2, 73.8 (2 CH_2*Ph*), 73.73, 73.71, 73.6, 73.4, 73.2, 72.9, 72.7, 72.64, 72.61, 72.2 (9 CH_2*Ph*), 69.2, 69.0, 68.9, 68.7, 68.0 (C-7), 67.6, 66.5, 66.1 (CH_2*Ph*), 63.1, 62.1, 61.5, 61.3, 61.2, 61.1 (6 C-6), 34.2 (C-11), 29.0 (C-8), 25.7 (C-9), 24.6 (C-10). MALDI-MS: Calculated for $C_{175}H_{174}O_{39}$ $[M+Na]^+$: 2922.1530, found: 2922.1282.

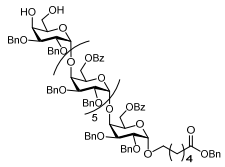
6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-

_O_-benzoyl-2,3-di-_O_-benzyl-α-D-galactopyranosyl-(1→4)-6-_O_-benzoyl-2,3-di-_O_-benzyl-α-D-galactopyranosyl-(1→4)-6-_O_-benzoyl-2,3-di-_O_-benzyl-α-D-galactopyranosyl-(1→4)-6-_O_-benzoyl-2,3-di-_O_-benzyl-α-D-galactopyranoside (23)



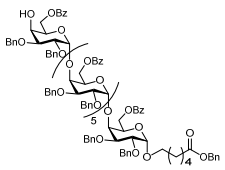
The reaction was carried out according to the general procedure A. The donor **1** (610 mg, 1.04 mmol) and the acceptor **22** (604 mg, 0.21 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 3.7 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 3Å. The solution was cooled to 0 ºC, after which NIS (304 mg, 1.35 mmol) and TfOH (2 µl, 0.02 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:DCM = 40:9:2). Compound **23** (531 mg, 76% yield, pentane:EtOAc = 2:1, R*f* = 0.55-0.55) was obtained as colorless syrup. $[\alpha]_D^{25}$ +34.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 736, 1005, 1027, 1046, 1063, 1093, 1271, 1452, 1723, 2859, 2929. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.05 – 7.84 (m, 12H, *C*H, Bz), 7.69 – 6.88 (m, 93H, *aromatic* H), 5.12 – 5.01 (m, 6H, *C*H_2*Ph*, H-1^G, 1^F, 1^E, 1^D), 4.99 (d, *J* = 3.3 Hz, 1H, H-1^C), 4.92 – 4.08 (m, 57H), 4.05 – 3.75 (m, 16H), 3.70 (dd, *J* = 10.2, 2.7 Hz, 2H, H-3), 3.66 – 3.50 (m, 3H, H-7, 6^G), 3.40 (dt, *J* = 9.9, 6.6 Hz, 1H, H-7), 2.26 (t, *J* = 7.5 Hz, 2H, H-11), 1.56 (q, *J* = 7.4 Hz, 4H, H-10, 8), 1.32 – 1.21 (m, 2H, H-9), 0.99 (s, 9H, 3x*C*H_3), 0.86 (s, 9H, 3x*C*H_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3 (C-12), 166.0, 165.5, 165.4 (3 C=O, Bz), 165.3 (2xC=O, Bz), 165.2 (C=O, Bz), 139.1, 138.7, 138.7, 138.6, 138.6, 138.6, 138.4, 138.3, 138.3, 138.2, 138.2, 138.1, 138.1, 136.1, 133.1, 133.0, 130.0, 129.9, 129.9, 129.6, 129.6, 129.6, 128.9, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 127.8, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 127.3, 127.2, 127.1, 127.1, 126.9 (aromatic C/*CH*), 100.1 (C-1), 100.0 (3xC-1), 99.8 (C-1), 97.3 (C-1^A), 78.1, 77.8, 77.4, 77.2, 76.6, 76.5, 76.2, 76.1, 75.9, 75.3, 74.8, 74.3, 74.1, 73.9, 73.7, 73.6, 73.44, 73.41, 73.1, 72.9 (7 CH_2*Ph*), 72.8, 72.7, 72.63, 72.61, 72.4 (4 CH_2*Ph*), 70.6, 70.1 (CH_2*Ph*), 69.1, 68.9, 68.7, 67.9 (C-7), 67.4, 67.0 (C-6^G), 66.0 (CH_2*Ph*), 63.0, 61.5, 61.3, 61.2, 61.1, 61.1 (6 C-6), 34.1 (C-11), 29.0 (C-8), 27.7 (3xCH_3), 27.2 (3xCH_3), 25.7 (C-9), 24.6 (C-10), 23.3 (C-*Si*), 20.6 (C-*Si*). MALDI-MS: Calculated for $C_{203}H_{212}O_{44}Si$ $[M+Na]^+$: 3404.4018, found: 3404.3707.

6-(Benzyl hexanoyl) 2,3-di-_O_-benzyl-α-D-galactopyranosyl-(1→4)-6-_O_-benzoyl-2,3-di-_O_-benzyl-α-D-galactopyranosyl-(1→4)-6-_O_-benzoyl-2,3-di-_O_-benzyl-α-D-galactopyranosyl-(1→4)-6-_O_-benzoyl-2,3-di-_O_-benzyl-α-D-galactopyranosyl-(1→4)-6-_O_-benzoyl-2,3-di-_O_-benzyl-α-D-galactopyranosyl-(1→4)-6-_O_-benzoyl-2,3-di-_O_-benzyl-α-D-galactopyranoside (24)



The reaction was carried out according to the general procedure C using compound **23** (508 mg, 0.15 mmol) and HF/pyridine (70%, 62 µl, 2.40 mmol). The product was purified by column chromatography (pentane:EtOAc:DCM = 12:5:1). Compound **24** (463 mg, 95% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +32.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 734, 803, 1003, 1026, 1046, 1093, 1269, 1315, 1360, 1723, 2869, 2925, 3416. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.05 – 7.88 (m, 12H, *C*H, Bz), 7.61 – 6.91 (m, 93H), 5.13 – 5.00 (m, 7H, *CH*$_2$*Ph*, H-1^G, 1^F, 1^E, 1^D, 1^C), 4.99 (d, *J* = 3.5 Hz, 1H, H-1^B), 4.90 – 4.52 (m, 33^H), 4.50 – 3.73 (m, 30H), 3.69 (dd, *J* = 10.0, 3.1 Hz, 1H, H-3^B), 3.57 (dt, *J* = 10.0, 7.0 Hz, 1H, H-7), 3.47 – 3.28 (m, 3H, H-7, 6^G), 2.72 (bs, 1H, *O*H), 2.32 (bs, 1H, *O*H), 2.27 (t, *J* = 7.5 Hz, 2H, H-11), 1.66 – 1.51 (m, 4H, H-10, 8), 1.31 – 1.25 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1 (C-12), 165.8, 165.3, 165.2, 165.17, 165.12 (6 C=O, Bz), 138.6, 138.5, 138.4, 138.3, 138.2, 138.1, 138.0, 137.9, 137.8, 137.7, 135.9, 133.0, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 128.6, 128.5, 128.43, 128.41, 128.35, 128.31, 128.2, 128.1, 128.04, 128.02, 128.01, 127.7, 127.5, 127.4, 127.3, 127.23, 127.21, 127.1, 127.0, 126.9 (aromatic C/C*H*), 100.0 (C-1), 99.9 (C-1), 99.8 (C-1), 99.7 (C-1), 97.2 (C-1^A), 77.9, 77.7, 77.4, 77.1, 76.8, 76.5, 76.4, 76.0, 75.7, 75.1, 74.6, 74.2, 73.9 (C*H*$_2$*Ph*), 73.8, 73.6, 73.5, 73.4, 73.1, 72.9, 72.7, 72.6, 72.5, 72.5, 71.9 (10 C*H*$_2$*Ph*), 69.0, 68.9, 68.5, 67.8 (C-7), 65.8 (C*H*$_2$*Ph*), 62.9, 62.7, 61.3, 61.2, 61.1, 61.0 (7 C-6), 33.9 (C-11), 28.8 (C-8), 25.5 (C-9), 24.4 (C-10). MALDI-MS: Calculated for $C_{195}H_{196}O_{44}$ $[M+Na]^+$: 3264.2997, found: 3264.2726.

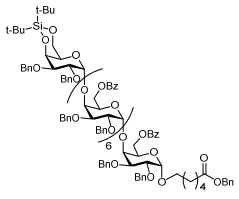
6-(Benzyl hexanoyl) 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galacto-pyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (25)



The reaction was carried out according to the general procedure D using compound **24** (393 mg, 0.12 mmol), PhCOOBt (174 mg, 0.73 mmol) and Et_3N (110 µl, 0.79 mmol). The product was purified by column chromatography (pentane:EtOAc:DCM = 12:4:1). Compound **25** (402 mg, 94% yield, pentane:EtOAc = 3:2, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +24.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 734, 1003, 1026, 1046, 1070, 1093, 1157, 1269, 1315, 1452, 1721, 2872, 2925. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.11 – 7.94 (m, 14H, *C*H, Bz), 7.68 – 6.99 (m, 96H, *aromatic* H), 5.14 (s, 2H, *CH*$_2$*Ph*), 5.13 – 5.06 (m, 5H, H-1^G, 1^F, 1^E, 1^D, 1^C), 5.05 (d, *J* = 3.4 Hz, 1H, H-1^B), 4.97 – 4.36 (m, 46H), 4.35 – 4.08 (m, 10H), 4.04 (t, *J* = 6.8 Hz, 1H, H-5^A), 4.00 – 3.76 (m, 15H), 3.63 (dt, *J* = 10.2, 7.1 Hz, 1H, H-7), 3.47 (dt, *J* = 10.1, 6.7 Hz, 1H, H-7), 2.58 (bs, 1H, H-*O*H), 2.33 (t, *J* = 7.5 Hz, 2H, H-11), 1.73 – 1.54 (m, 4H, H-10, 8), 1.38 – 1.29 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4 (C-12), 166.0, 165.8, 165.5, 165.4, 165.34, 165.32, 165.2 (7 C=O, Bz), 138.8, 138.64, 138.62, 138.5, 138.3, 138.23, 138.21, 138.1, 137.9, 136.1, 133.2, 133.2, 133.1, 130.04, 130.01, 129.94, 129.92, 129.8, 129.7, 129.64, 129.61, 129.5, 128.7, 128.64, 128.62, 128.6,1 128.53, 128.51, 128.4, 128.34, 128.32, 128.31, 128.24, 128.22, 128.21,

128.20, 128.1, 127.9, 127.8, 127.74, 127.72, 127.64, 127.62, 127.61, 127.5, 127.4, 127.34, 127.32, 127.31, 127.23, 127.21, 127.15, 127.13 (aromatic C/C*H*), 100.2, 100.03, 99.98, 99.95 (4 C-1), 99.94 (2xC-1), 97.3 (C-1^{A}), 78.2, 77.3, 77.0, 76.6, 76.5, 76.1, 75.9, 75.8, 75.3, 75.0, 74.8, 74.7, 74.3, 74.2, 73.8, 73.74, 73.72, 73.6, 73.4, 73.1, 72.9, 72.8, 72.73, 72.71, 72.63, 72.61, 72.2 (14 CH_2Ph), 69.1, 69.0, 68.7, 67.9 (C-7), 67.6, 66.4, 66.1 (CH_2Ph), 63.0, 62.0, 61.5, 61.3, 61.2, 61.1, 61.0 (7 C-6), 34.1 (C-11), 29.0 (C-8), 25.7 (C-9), 24.6 (C-10). MALDI-MS: Calculated for $C_{202}H_{200}O_{45}$ [M+Na]$^{+}$: 3368.3259, found: 3368.2962.

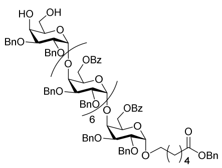
6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galacto-pyranoside (26)



The reaction was carried out according to the general procedure A. The donor **1** (337 mg, 0.57 mmol) and the acceptor **25** (381 mg, 0.11 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 3Å. The solution was cooled to 0 ºC, after which NIS (167 mg, 0.74 mmol) and TfOH (1 µl, 0.01 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:DCM = 16:4:1). Compound **26** (352 mg, 81% yield, pentane:EtOAc = 2:1, R*f* = 0.55-0.55) was obtained as colorless syrup. $[\alpha]_D^{25}$ +31.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 736, 1005, 1027, 1046, 1062, 1095, 1271, 1315, 1362, 1724, 2859, 2931. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.04 – 7.93 (m, 12H, *C*H, Bz), 7.93 – 7.87 (m, 2H, *C*H, Bz), 7.61 – 6.89 (m, 106H*, aromatic* H), 5.11 – 5.00 (m, 7H, *C*H$_2$*Ph*, H-1^{h}, 1^{G}, 1^{F}, 1^{E}, 1^{D}), 4.97 (d, *J* = 3.4 Hz, 1H, H-1^{C}), 4.92 – 3.67 (m, 80H), 3.66 – 3.52 (m, 3H, H-7, 6h), 3.43 – 3.39 (m, H-7), 2.27 (t, *J* = 7.5 Hz, 2H, H-11), 1.64 – 1.51 (m, 4H, H-10, 8), 1.32 – 1.20 (m, 2H, H-9), 0.99 (s, 9H, *C*H$_3$), 0.87 (s, 9H, *C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3 (C-12), 165.9, 165.4, 165.3, 165.27, 165.26, 165.2, 165.1 (7 C=O, Bz), 139.1, 138.7, 138.6, 138.58, 138.55, 138.51, 138.4, 138.3, 138.26, 138.22, 138.17, 138.12, 138.07, 138.01, 136.0, 133.1, 133.0, 132.99, 129.93, 129.88, 129.85, 129.61, 129.57, 129.55, 129.52, 128.9, 128.6, 128.55, 128.52, 128.50, 128.47, 128.44, 128.41, 128.38, 128.28, 128.20, 128.17, 128.13, 128.11, 128.08, 128.06, 127.8, 127.6, 127.53, 127.51, 127.48, 127.43, 127.41, 127.31, 127.28, 127.24, 127.21, 127.19, 127.11, 127.0, 126.9 (aromatic C/C*H*), 100.07 (C-1), 99.9 (C-1), 99.9 (C-1), 97.3 (C-1^{A}), 78.0, 77.7, 77.28, 77.21, 76.8, 76.6, 76.5, 76.2, 76.1, 75.8, 75.7, 75.6, 75.22, 74.7, 74.6, 74.3, 74.2, 74.0, 73.9, 73.72, 73.7, 73.64, 73.60, 73.4, 73.1, 72.8 (8 CH_2Ph), 72.7, 72.6, 72.55, 72.53, 72.3 (4 CH_2Ph), 70.5, 70.0 (CH_2Ph), 69.1, 68.98, 68.93, 68.88, 68.84, 68.83, 68.6, 67.9 (C-7), 67.4, 67.0 (C-6h), 66.01 (CH_2Ph), 62.9, 61.4, 61.2, 61.14, 61.12, 61.06, 60.9 (7 C-6), 34.1 (C-11), 28.9 (C-8), 27.6 (3xCH_3), 27.2 (3xCH_3), 25.6 (C-9),

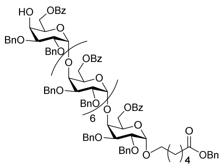
24.6 (C-10), 23.3 (C-*Si*), 20.6 (C-*Si*). MALDI-MS: Calculated for $C_{230}H_{238}O_{50}Si$ $[M+Na]^+$: 3850.5748, found: 3850.5363.

6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl -2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (27)



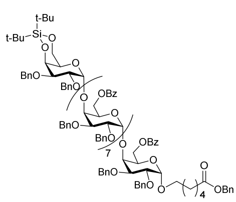
The reaction was carried out according to the general procedure C using compound **26** (330 mg, 86 μmol) and HF/pyridine (70%, 25 μl, 1.38 mmol). The product was purified by column chromatography (pentane:EtOAc:DCM = 6:4:1). Compound **27** (296 mg, 93% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +34.1 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 738, 1003, 1027, 1047, 1095, 1271, 1452, 1723, 2873, 2925, 3506. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.06 – 7.87 (m, 14H, *C*H, Bz), 7.63 – 6.90 (m, 106H, *aromatic* H), 5.07 (s, 2H, CH_2Ph), 5.06 – 4.99 (m, 6H, H-1), 4.98 (d, *J* = 3.5 Hz, 1H, H-1^B), 4.92 – 3.71 (m, 80H), 3.68 (dd, *J* = 10.0, 3.1 Hz, 1H, H-3^B), 3.56 (dt, *J* = 10.2, 7.1 Hz, 1H, H-7), 3.45 – 3.27 (m, 3H, H-7, 6^H), 2.71 (bs, 1H, *O*H), 2.26 (t, *J* = 7.6 Hz, 2H, H-11), 1.64 – 1.47 (m, 4H, H-10, 8), 1.31 – 1.21 (m, 4H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4 (C-12), 166.0, 165.5, 165.4, 165.43, 165.35, 165.32, 165.30 (7 C=O, Bz), 138.8, 138.7, 138.66, 138.64, 138.61, 138.4, 138.34, 138.32, 138.31, 138.23, 138.22, 138.1, 138.0, 137.9, 136.1, 133.24, 133.21, 130.0, 129.94, 129.92, 129.7, 129.6, 129.5, 129.4, 128.7, 128.64, 128.62, 128.61, 128.53, 128.51, 128.42, 128.41, 128.33, 128.31, 128.23, 128.21, 128.20, 128.19, 128.14, 128.0, 127.9, 127.8, 127.73, 127.71, 127.70, 127.64, 127.62, 127.61, 127.5, 127.42, 127.41, 127.33, 127.32, 127.31, 127.30, 127.2, 127.09, 127.06 (aromatic C/C*H*), 100.2 (C-1), 100.1 (C-1), 100.0 (C-1), 99.8 (C-1), 97.3 (C-1^A), 78.0, 77.9, 77.3, 77.0, 76.7, 76.6, 76.1, 76.0, 75.9, 75.7, 75.3, 74.8, 74.7, 74.6, 74.3, 74.0 (C*H₂Ph*), 73.9, 73.8, 73.74, 73.72, 73.71, 73.5, 73.23, 73.21, 72.9, 72.7, 72.68, 72.63, 72.1 (12 CH_2*Ph*), 69.4, 69.2, 69.0, 68.7, 68.0 (C-7), 66.1 (CH_2*Ph*), 63.1, 62.9, 61.5, 61.3, 61.21, 61.19, 61.17, 61.08 (8 C-6), 34.2 (C-11), 29.0 (C-8), 25.7 (C-9), 24.7 (C-10). MALDI-MS: Calculated for $C_{222}H_{222}O_{50}$ $[M+Na]^+$: 3710.4727, found: 3710.4379.

6-(Benzyl hexanoyl) 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galacto-pyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galacto-pyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyrano-syl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (28)



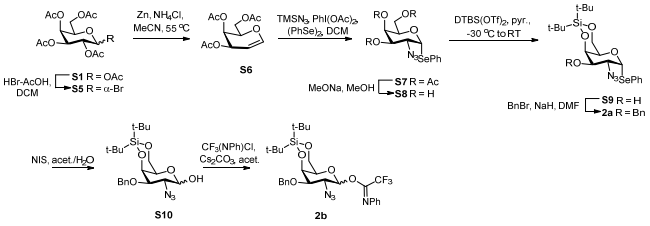
The reaction was carried out according to the general procedure D using compound **27** (179 mg, 49 μmol), PhCOOBt (70 mg, 0.29 mmol) and Et_3N (44 μl, 0.32 mmol). The product was purified by column chromatography (pentane:EtOAc:DCM = 12:4:1). Compound **28** (175 mg, 95% yield, pentane:EtOAc = 3:2, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +26.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1027, 1047, 1096, 1272, 1452, 1724, 2870, 2926, 3489. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.03 – 7.84 (m, 16H, *C*H, Bz), 7.65 – 6.87 (m, 109H, *aromatic* H), 5.07 (s, 2H, *C*H_2*Ph*), 5.04 – 4.92 (m, 6H), 4.90 – 3.66 (m, 80H), 3.59 – 3.49 (m, 1H, H-7), 3.45 – 3.33 (m, 1H, H-7), 2.46 (s, 1H, *O*H), 2.26 (t, *J* = 7.6 Hz, 2H, H-11), 1.62 – 1.47 (m, 4H, H-10, 8), 1.32 – 1.24 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.42 (C-12), 166.05, 165.87, 165.53, 165.45, 165.37, 165.33, 165.28 (C=O, Bz), 138.81, 138.67, 138.63, 138.59, 138.38, 138.28, 138.23, 138.20, 137.90, 136.15, 133.20, 133.01, 130.08, 129.97, 129.94, 129.71, 129.67, 129.64, 129.61, 129.57, 128.70, 128.64, 128.59, 128.53, 128.50, 128.46, 128.37, 128.33, 128.28, 128.24, 128.21, 128.17, 127.91, 127.87, 127.73, 127.69, 127.64, 127.60, 127.50, 127.42, 127.38, 127.35, 127.28, 127.24, 127.20, 127.11 (aromatic C/C*H*), 100.20 (C-1), 100.03 (C-1), 100.00 (C-1), 97.37 (C-1), 78.19, 77.31, 76.98, 76.68, 76.60, 76.15, 75.93, 75.81, 75.34, 75.01, 74.73, 74.36, 74.25, 73.81, 73.74, 73.70, 73.57, 73.44, 73.19, 72.90, 72.73, 72.63, 72.24, 69.20, 69.00, 68.75, 67.98 (C-7), 67.62, 66.49, 66.11 (C*H_2Ph*), 63.09, 62.07, 61.54, 61.35, 61.23, 61.08 (C-6), 34.19 (C-11), 29.03 (C-8), 25.73 (C-9), 24.69 (C-10). MALDI-MS: Calculated for $C_{229}H_{226}O_{51}$ $[M+Na]^+$: 3814.4989, found: 3814.4630.

6-(Benzyl hexanoyl) 2,3-di-*O*-benzyl-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl -(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranosyl-(1→4)-6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (29)



The reaction was carried out according to the general procedure A. The donor **1** (117 mg, 0.20 mmol) and the acceptor **28** (150 mg, 40 μmol) were co-evaporated with toluene (three times). The residue was dissolved in 1 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 3Å. The solution was cooled to 0 ºC, after which NIS (58 mg, 0.26 mmol) and TfOH (1 μl, 4 μmol) 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:DCM = 16:4:1). Compound **29** (110 mg, 65% yield, pentane:EtOAc = 2:1, R*f* = 0.55-0.55) was obtained as colorless syrup. $[\alpha]_D^{25}$ +35.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 731, 1027, 1045, 1062, 1315, 1725, 2932, 3062. ^{1}H-NMR ($CDCl_3$, 500 MHz) 8.07 – 7.91 (m, 16H, *C*H, Bz), 7.64 – 6.92 (m, 119H, *aromatic* H), 5.12 (s, 2H, *C*H_2*Ph*), 5.10 – 5.02 (m, 6H, H-1), 5.00 (d, *J* = 3.3 Hz, 1H, H-1^C), 4.95 – 4.05 (m, 72H), 4.04 – 3.55 (m, 25H), 3.47

– 3.40 (m, 1H, H-7), 2.31 (t, *J* = 7.6 Hz, 2H, H-11), 1.67 – 1.55 (m, 4H, H-10, 8), 1.33 – 1.27 (m, 2H, H-9), 1.03 (s, 9H, CH_3), 0.90 (s, 9H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4 (C-12), 166.1, 165.55, 165.47, 165.37, 165.34, 165.30 (6 CH_2*Ph*), 139.2, 138.8, 138.7, 138.6, 138.5, 138.4, 138.4, 138.3, 138.2, 138.1, 136.2, 133.1, 130.1, 130.0, 129.7, 129.6, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0 (aromatic C/C*H*), 100.0 (C-1), 99.9 (C-1), 97.4 (C-1^A), 78.2, 77.9, 77.4, 77.3, 77.0, 76.7, 76.6, 76.3, 76.2, 76.0, 75.8, 75.4, 74.83, 74.81, 74.74, 74.72, 74.42, 74.40, 74.2, 74.0, 73.83, 73.81, 73.7, 73.4, 73.2, 72.93 (7 CH_2*Ph*), 72.91, 72.8, 72.7, 72.6, 72.4 (4 CH_2*Ph*), 70.6, 70.1 (CH_2*Ph*), 69.2, 69.0, 68.8, 68.0 (C-7), 67.5, 67.1 (C-6i), 66.1 (CH_2*Ph*), 63.1, 61.6, 61.4, 61.33, 61.31, 61.24, 61.21, 61.1 (8 C-6), 34.2 (C-11), 29.1 (C-8), 27.7 (3xCH_3), 27.3 (3xCH_3), 25.8 (C-9), 24.7 (C-10), 23.4 (C-*Si*), 20.7 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 97.4 ($J_{C1A,H1A}$ = 167 Hz), 100.0 ($J_{C1,H1}$ = 167 Hz, 170 Hz, 169 Hz, 171 Hz). MALDI-MS: Calculated for $C_{257}H_{264}O_{56}Si$ $[M+Na]^+$: 4296.7477, found: 4296.7031.



Phenyl 3,4,6-tri-*O*--acetyl-2-azido-2-deoxy-1-seleno-α-D-galactopyranoside (S7)

Compound **S1** (75.6 g, 193.8 mmol) was dissolved in DCM (500 ml) and cooled in ice-bath, then HBr-AcOH (67 ml, 387.6 mmol) was added slowly to the solution, which was allowed to warm to room temperature and stirred for 4h. The solution was poured into ice-water and washed with water, sat. $NaHCO_3$ solution, sat. NaCl solution subsequently. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was dissolved in MeCN (500 ml), then zinc (95g, 1.45 mol) and NH_4Cl (77.75 g, 1.45 mol) were added to the solution. The reaction mixture was warmed to 55 ºC and allowed to stir for overnight. The solid was filtered and the filtrate was concentrated *in vacuo*. The product **S6** was purified by silica gel column chromatography (pentane:EtOAc = 4:1) to give the target in 75% yield. S6 (33.2 g, 122 mmol) was dissolved in DCM (600 ml) and cooled to -30 ºC, then $(PhSe)_2$ (38g, 122 mmol), $PhI(OAc)_2$ (39.3 g, 122 mmol) and $TMSN_3$ (34.4 ml, 244 mmol) were added to the solution. The reaction mixture was allowed to warm to 0 ºC slowly and stirred at 0 ºC for overnight. The solution was washed with sat. $NaHCO_3$ solution, sat. NaCl solution subsequently. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude was recrystallized with pentane and Et_2O to afford **S7** in 71% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.35 – 7.25 (m, 4H), 6.00 (d, *J* = 5.4 Hz, 1H), 5.47 (dd, *J* = 3.3, 1.3 Hz, 1H), 5.11 (dd, *J* = 10.9, 3.2 Hz, 1H), 4.67 (ddd, *J* = 7.1, 5.7, 1.3 Hz, 1H), 4.26 (dd, *J* = 10.8, 5.4 Hz, 1H), 4.12 – 3.98 (m, 2H), 2.15 (s, 3H), 2.06 (s, 3H), 1.97 (s, 3H).

Phenyl 2-azido-2-deoxy-1-seleno-4,6-*tert*-butylsilylidene-α-D-galactopyranoside (2a)[23]

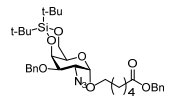
S7 (22 g, 47 mmol) was suspended in MeOH (150 ml) and cooled in ice-bath, then MeONa (508 mg, 9.4 mmol) was added to the mixture, which allowed to warm to room temperature and stirred for overnight. The solution was neutralized with Dowex ion-exchange resin, filtered and concentrated in vacuo. The crude was dissolved in pyridene (150 ml) and cooled to -30 ºC. $DTBS(OTf)_2$ (16 ml, 49.5 mmol) was added to the reaction solution, which was allowed to warm to room temperature and stirred for 2h. MeOH (5 ml) was added to the solution and concentrated *in vacuo*. The crude was washed with 1M HCl, sat. $NaHCO_3$ solution and sat. NaCl solution subsequently. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was purified by silica gel column chromatography (pentane:EtOAc = 20:1) to give **S9** in 88% yield. **S9** (7.6 g, 15.7 mmol) was dissolved in DMF (120 ml) and cooled in ice-bath. Then BnBr (2.1 ml, 17.2 mmol) and NaH (815 mg, 20.4 mmol) were added subsequently to the reaction mixture, which was allowed to stir in ice-bath for 3h. MeOH was added to quench the reaction, and the solution was diluted in Et_2O and washed with water and sat. NaCl solution subsequently. The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was purified by silica gel column chromatography (pentane:Et_2O = 40:1) to give compound **2a** in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.46 – 7.24 (m, 10H), 5.94 (d, *J* = 5.2 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.59 (dd, *J* = 3.1, 1.1 Hz, 1H), 4.35 – 4.28 (m, 1H), 4.24 (dd, *J* = 12.5, 2.2 Hz, 1H), 4.04 (d, *J* = 2.3 Hz, 1H), 4.00 (dd, *J* = 12.5, 1.7 Hz, 1H), 3.64 (dd, *J* = 10.2, 3.0 Hz, 1H), 1.05 (d, *J* = 13.2 Hz, 18H).

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

NIS (9.15 g, 40.68 mmol) was added to the solution of compound **2a**[23] (18 g, 31.3 mmol) in Acetone/H_2O (210 ml/72ml) at 0 ºC. The reaction was slowly 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 $Na_2S_2O_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product **S10** was purified by silica gel column chromatography (pentane:EtOAc = 4:1). Cs_2CO_3 was added to the solution of compound **S10** (10.59g, 24.33 mmol) in 140 ml acetone. The mixture was stirred at 0 ºC for 15 minutes. Then CF_{3C}(=NPh)Cl (6.06 g, 29.2 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 **2b** was purified by silica gel column chromatography (pentane:Et_2O = 30:1 – 10:1). Compound **2b** (13.3 g, α/β = 2:1, 90% yield, pentane: Et_2O = 10:1, R*f* = 0.45-0.55) was obtained as white solid. α isomer: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.50 – 7.24 (m, 7H, aromatic H), 7.15 – 7.05 (m, 1H, aromatic H), 6.84 (d, *J* = 7.7 Hz, 2H, aromatic H), 6.47 (bs, 1H, H-1), 4.78 (d, *J* = 11.4 Hz, 1H, *C*H_2*Ph*), 4.69 (d, *J* = 11.4 Hz, 1H, *C*H_2*Ph*), 4.63 (s, 1H, H-4), 4.22 (q, *J* = 12.8 Hz, 2H. H-6), 4.10 (t, *J* = 6.3 Hz, 1H, H-2), 3.89 (d, *J* = 9.5 Hz, 1H, H-3), 3.76 (s, 1H, H-5), 1.09-1.02 (m, 18H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.29, 137.45, 128.74, 128.56, 128.01, 127.91, 124.40, 119.35 (aromatic C/C*H*), 94.73 (C-1), 76.04 (C-3), 70.71 (C*H*$_2$*Ph*), 69.89 (C-5), 69.16 (C-4), 66.76 (C-6), 57.71 (C-2), 27.59 (C*H*$_3$), 27.23 (C*H*$_3$), 23.38 (C-*Si*), 20.73 (C-*Si*). *β* isomer: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.48 – 7.25 (m, 7H, aromatic H), 7.14 – 7.04 (m, 1H, aromatic H), 6.85 (d, *J* = 7.7 Hz, 2H, aromatic H), 5.50 (bs, 1H, H-1), 4.77 (d, *J* = 11.9 Hz, 1H, *C*H_2*Ph*), 4.66 (d, *J* = 11.9 Hz,

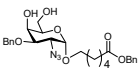
1H, *C*H$_2$*Ph*), 4.43 (s, 1H, H-5), 4.19 (s, 2H, H-6), 4.02 (s, 1H, H-4), 3.30 (s, 2H, H-2, 3), 1.15 – 1.00 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.45, 137.54, 128.83, 128.71, 128.17, 127.97, 124.48, 119.42 (aromatic C/*CH*), 95.82 (C-1), 79.55 (C-3), 72.18 (C-2), 70.99 (C*H$_2$Ph*), 68.57 (C-5), 66.84 (C-6), 60.79 (C-4), 27.72 (C*H$_3$*), 27.42 (C*H$_3$*), 23.55 (C-*Si*), 20.89 (C-*Si*). HR-MS: Calculated for $C_{29}H_{37}F_3N_4O_5Si$ [M+Na]$^+$: 629.2383, found: 629.2376.

6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranoside (30)



The reaction was carried out according to the general procedure B. The donor **2b** (1.5 g, 2.47 mmol) and acceptor **4** (1.1 g, 4.95 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 25 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (22 µl, 0.25 mmol) was added. The reaction was stirred at 0 ºC for 1 h. Then the reaction was quenched with Et$_3$N, diluted with DCM, washed with saturated NaHCO$_3$ and brine. The organic phase was dried with anhydrous MgSO$_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:Et$_2$O = 20:1 - 6:1). Compound **30** (1.31 g, 83% yield, pentane: Et$_2$O = 10:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +68.6 (c=1, CHCl$_3$). IR (neat, cm^{-1}) ν 442, 651, 797, 826, 962, 980, 1006, 1043, 1067, 1080, 1100, 1141, 1171, 1455, 1474, 1736, 2109, 2859, 2933. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 7.47 – 7.27 (m, 10H, aromatic H), 5.13 (s, 2H, *C*H$_2$*Ph*), 4.93 (d, *J* = 3.5 Hz, 1H, H-1), 4.77 (d, *J* = 11.5 Hz, 1H, *C*H$_2$*Ph*), 4.67 (d, *J* = 11.5 Hz, 1H, *C*H$_2$*Ph*), 4.61 (dd, *J* = 2.9, 1.1 Hz, 1H, H-4), 4.27 (dd, *J* = 12.5, 2.1 Hz, 1H, H-6), 4.16 (dd, *J* = 12.5, 1.7 Hz, 1H, H-6), 3.89 (dd, *J* = 10.6, 2.9 Hz, 1H, H-3), 3.79 (dd, *J* = 10.6, 3.5 Hz, 1H, H-2), 3.71 – 3.61 (m, 2H, H-5, 7), 3.47 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.38 (t, *J* = 7.5 Hz, 2H, H-11), 1.77 – 1.57 (m, 4H, H-10, 8), 1.47 – 1.34 (m, 2H, H-9), 1.14 – 1.01 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 173.46 (C-12), 137.94, 136.12, 128.63, 128.58, 128.28, 128.25, 127.99, 127.92 (aromatic C/*CH*), 98.43 (C-1), 75.50 (C-3), 70.48 (C*H$_2$Ph*), 69.87 (C-4), 68.17 (C-6), 67.47 (C-5), 67.28 (C-7), 66.20 (C*H$_2$Ph*), 58.33 (C-2), 34.21 (C-11), 29.12 (C-8), 27.74 (3xCH$_3$), 27.41 (3xCH$_3$), 25.72 (C-9), 24.70 (C-10), 23.51 (C-*Si*), 20.80 (C-*Si*). HR-MS: Calculated for $C_{34}H_{49}N_3O_7Si$ [M+Na]$^+$: 662.3237, found: 662.3232.

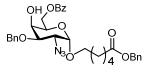
6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (31)



The reaction was carried out according to the general procedure C using compound **30** (1.14 g, 1.78 mmol) and HF/pyridine (70%, 740 µl, 28.5 mmol). The product was purified by column chromatography (pentane:EtOAc = 1:1). Compound **31** (831 mg, 94% yield, pentane:EtOAc = 1:2, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +73.8 (c=1, CHCl$_3$). IR (neat, cm^{-1}) ν 966, 736, 966, 1027, 1143, 1213, 1232, 1731, 2106, 2858, 2925, 3460. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 7.43 – 7.27 (m, 10H, aromatic H), 5.11 (s, 2H, *C*H$_2$*Ph*), 4.88 (d, *J* = 1.2 Hz, 1H, H-1), 4.78 (d, *J* = 11.7 Hz, 1H, *C*H$_2$*Ph*), 4.61 (d, *J* = 11.7 Hz, 1H, *C*H$_2$*Ph*), 4.07 (s, 1H, H-5), 3.92 (dd, *J* = 11.6, 6.6 Hz, 1H, H-6), 3.86 – 3.77 (m, 3H, H-2, 3, 6), 3.75 – 3.68 (m, 1H, H-4), 3.68 – 3.62 (m, 1H, H-7), 3.39 (dt, *J* = 9.7, 6.3 Hz, 1H, H-7), 3.05 (bs, 1H, *O*H), 2.36 (t, *J* = 7.4 Hz, 2H, H-11), 1.72 – 1.60 (m, 2H, H-10), 1.60 – 1.50 (m, 2H, H-8), 1.41 – 1.29 (m, 2H, H-9). ^{13}C NMR (100 MHz, CDCl$_3$) δ 173.55 (C-12), 137.44, 136.04, 128.64, 128.60, 128.32, 128.25, 128.02, 127.64 (aromatic C/*CH*), 98.56 (C-1), 72.96

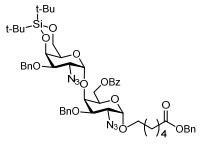
(C-3), 70.68 (C-4), 70.21 (CH_2Ph), 67.72 (C-7), 67.31 (C-5), 66.27 (CH_2Ph), 62.72 (C-6), 60.72 (C-2), 34.18 (C-11), 28.99 (C-8), 25.73 (C-9), 24.63 (C-10). HR-MS: Calculated for $C_{26}H_{33}N_3O_7$ $[M+H]^+$: 500.2397, found: 500.2391.

6-(Benzyl hexanoyl) 2-azido-6-O-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (32)



The reaction was carried out according to the general procedure D using compound **31** (831 mg, 1.66 mmol), PhCOOBt (1.79 g, 7.49 mmol) and Et_3N (1.2 ml, 8.3 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **32** (931 mg, 93% yield, pentane:EtOAc = 3:1, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +42.9 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 989, 1027, 1042, 1096, 1115, 1151, 1269, 1315, 1452, 1717, 2106, 2870, 2933, 3484. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.15 – 8.08 (m, 2H, *aromatic* H), 7.64 – 7.55 (m, 1H, *aromatic* H), 7.53 – 7.27 (m, 11H, *aromatic* H), 7.25 – 7.18 (m, 1H, *aromatic* H), 5.15 (s, 2H, CH_2Ph), 4.98 (d, *J* = 3.6 Hz, 1H, H-1), 4.76 (s, 2H, CH_2Ph), 4.71 – 4.58 (m, 2H, H-6), 4.23 – 4.14 (m, 2H, H-4, 5), 4.01 (dd, *J* = 10.5, 3.0 Hz, 1H, H-3), 3.79 (dd, *J* = 10.4, 3.6 Hz, 1H, H-2), 3.72 (dt, *J* = 9.8, 6.7 Hz, 1H, H-7), 3.49 (dt, *J* = 9.8, 6.5 Hz, 1H, H-7), 3.13 (bs, 1H, *O*H), 2.36 (t, *J* = 7.5 Hz, 2H, H-11), 1.74 – 1.59 (m, 4H, H-10, 8), 1.46 – 1.32 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.15 (C-12), 166.09 (C=O, Bz), 137.09, 135.87, 133.08, 132.98, 129.85, 129.66, 129.42, 128.83, 128.41, 128.41, 128.33, 128.23, 128.17, 128.03, 127.97, 127.94, 127.89, 127.78, 125.11 (aromatic C/C*H*), 97.69 (C-1), 75.82 (C-3), 71.69 (CH_2Ph), 67.95 (C-5), 67.83 (C-7), 66.15 (C-4), 65.86 (CH_2Ph), 63.99 (C-6), 58.76 (C-2), 33.86 (C-11), 28.76 (C-8), 25.42 (C-9), 24.33 (C-10). HR-MS: Calculated for $C_{33}H_{37}N_3O_8$ $[M+H]^+$: 604.2659, found: 604.2653.

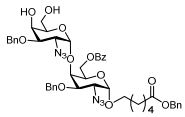
6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (33)



The reaction was carried out according to the general procedure B. The donor **2b** (3.24 g, 5.34 mmol) and the acceptor **32** (2.15 g, 3.56 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 50 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (60 µl, 0.67 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 = 10:1 – 6:1). Compound **33** (3.29 g, 91% yield, pentane: EtOAc = 6:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +111.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 738, 796, 826, 1010, 1027, 1045, 1139, 1270, 1454, 1472, 1727, 2109, 2859, 2933. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 8.00 (m, 2H, aromatic H), 7.60 – 7.53 (m, 1H, aromatic H), 7.48 – 7.40 (m, 4H, aromatic H), 7.39 – 7.24 (m, 13H, aromatic H), 5.11 (d, *J* = 2.9 Hz, 1H, H-1^B), 5.07 (s, 2H, CH_2Ph), 5.00 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.80 – 4.62 (m, 5H, CH_2Ph, H-6^A), 4.56 (dd, *J* = 11.1, 6.3 Hz, 1H, H-6^A), 4.51 – 4.47 (m, 1H, H-5^B), 4.30 (d, *J* = 2.8 Hz, 1H, H-4^A), 4.16 – 4.08 (m, 1H, H-3^B), 4.07 – 4.03 (m, 1H, H-5^A), 3.96 – 3.85 (m, 3H, H-3^A, 2^B, 4^B), 3.76 (dd, *J* = 12.9, 1.5 Hz, 1H, H-6^B), 3.72 – 3.58 (m, 3H, H-2^A, 6^B, 7), 3.46 (dt,

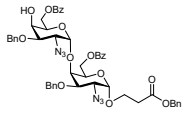
J = 9.8, 6.4 Hz, 1H, H-7), 2.31 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.54 (m, 4H, H-10, 8), 1.39 – 1.26 (m, 2H, H-9), 1.06 – 0.95 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 173.36 (C-12), 165.98 (C=O, Bz), 137.73, 137.14, 136.08, 133.40, 129.70, 129.60, 128.59, 128.57, 128.56, 128.53, 128.21, 128.17, 127.98, 127.96, 127.92, 127.20 (aromatic C/C*H*), 98.96 (C-1^B), 97.93 (C-1^A), 75.72 (C-3^A), 75.30 (C-4^B), 72.40 (C-4^A), 72.16 (C*H$_2$Ph*), 70.37 (C*H$_2$Ph*), 69.50 (C-5^B), 68.63 (C-3^B), 68.16 (C-7), 67.76 (C-5^A), 66.92 (C-6^B), 66.11 (C*H$_2$Ph*), 62.65 (C-6^A), 59.70 (C-2^A), 58.60 (C-2^B), 34.11 (C-11), 28.99 (C-8), 27.62 (C*H$_3$*), 27.34 (C*H$_3$*), 25.66 (C-9), 24.57 (C-10), 23.35 (C-*Si*), 20.73 (C-*Si*). HR-MS: Calculated for $C_{54}H_{68}N_6O_{12}Si$ [M+H]$^+$: 1021.4743, found: 1021.4737.

6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (34)



The reaction was carried out according to the general procedure C using compound **33** (3.29 g, 3.22 mmol) and HF/pyridine (70%, 1.2 ml, 51.5 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1 - 1:1). Compound **34** (2.62 g, 92% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +85.4 (c=1, CHCl$_3$). IR (neat, cm^{-1}) ν 1271, 1725, 2107, 2858, 2935, 3460. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 8.06 – 7.98 (m, 2H, *C*H, Bz), 7.61 – 7.52 (m, 1H, aromatic H), 7.48 – 7.24 (m, 17H, aromatic H), 5.06 (s, 2H, *C*H$_2$*Ph*), 5.04 (d, *J* = 3.5 Hz, 1H, H-1^B), 4.98 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.80 (d, *J* = 11.7 Hz, 1H, *C*H$_2$*Ph*), 4.73 – 4.57 (m, 5H, *C*H$_2$*Ph*, H-6^A), 4.22 (d, *J* = 2.7 Hz, 1H, H-4^A), 4.15 – 4.05 (m, 3H, H-5^A, 4^B, 5^B), 3.97 – 3.88 (m, 2H, H-3^A, 3^B), 3.84 (dd, *J* = 10.5, 3.4 Hz, 1H, H-2^B), 3.72 – 3.60 (m, 2H, H-2^A, 7), 3.55 – 3.38 (m, 3H, H-6^B, 7), 3.07 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.51 (m, 4H, H-10, 8), 1.37 – 1.27 (m, 2H, H-9). ^{13}C NMR (100 MHz, CDCl$_3$) δ 173.20 (C-12), 165.83 (C=O, Bz), 137.04, 136.86, 135.84, 133.19, 129.46, 129.37, 128.45, 128.44, 128.36, 128.04, 128.00, 127.95, 127.94, 127.84, 127.37 (aromatic C/C*H*), 99.08 (H-1^B), 97.75 (H-1^A), 76.01 (H-3^B), 75.45 (H-3^A), 73.76 (H-4^A), 72.15 (C*H$_2$Ph*), 71.55 (C*H$_2$Ph*), 69.41 (H-5^B), 68.51 (H-5^A), 67.97 (H-7), 67.23 (H-4^B), 65.91 (C*H$_2$Ph*), 62.52 (H-6^A), 62.46 (H-6^B), 59.56 (C-2), 59.55 (C-2), 33.89 (H-11), 28.75 (C-8), 25.42 (C-9), 24.34 (C-10). HR-MS: Calculated for $C_{46}H_{52}N_6O_{12}$ [M+H]$^+$: 881.3721, found: 881.3716.

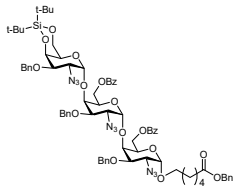
6-(Benzyl hexanoyl) 2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (35)



The reaction was carried out according to the general procedure D using compound **34** (2.61 g, 2.97 mmol), PhCOOBt (2.84 g, 11.87 mmol) and Et$_3$N (1.9 ml, 13.37 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:1 - 4:1). Compound **35** (2.88 g, 92% yield, pentane:EtOAc = 3:1, R*f* = 0.40-0.50) was obtained as yellow syrup. $[\alpha]_D^{25}$ +85.6 (c=1, CHCl$_3$). IR (neat, cm^{-1}) ν 1002, 1027, 1047, 1113, 1156, 1272, 1316, 1452, 1720, 2108, 2870, 2928, 3496. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 8.08 – 8.00 (m, 2H, *C*H, Bz), 7.94 – 7.85 (m, 2H, *C*H, Bz), 7.60 – 7.48 (m, 2H, aromatic H), 7.46 – 7.24 (m, 16H, aromatic H), 7.22 – 7.15 (m, 2H, aromatic H), 7.11 – 7.04 (m, 1H, aromatic H), 5.09 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.00 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.81 (d, *J* = 11.9 Hz, 1H, *C*H$_2$*Ph*), 4.76 – 4.63 (m,

4H, *CH*$_2$*Ph*, H-6^A), 4.60 (dd, *J* = 11.2, 6.5 Hz, 1H, H-6^A), 4.53 – 4.41 (m, 2H, H-5^B, 6^B), 4.27 (d, *J* = 2.8 Hz, 1H, H-4^A), 4.13 (t, *J* = 6.7 Hz, 1H, H-5^A), 4.10 – 3.99 (m, 4H, H-5^A, 3^B, 4^B, 6^B), 3.93 (dd, *J* = 10.8, 2.8 Hz, 1H, H-3^A), 3.87 (dd, *J* = 10.4, 3.5 Hz, 1H, H-2^B), 3.74 – 3.62 (m, 2H, H-2^A, 7), 3.45 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.72 (bs, 1H, *OH*), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.52 (m, 4H, H-10, 8), 1.37 – 1.25 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.31 (C-12), 165.91 (C=O, Bz), 137.13, 136.99, 136.00, 133.33, 133.01, 129.70, 129.65, 129.59, 129.51, 128.58, 128.50, 128.42, 128.24, 128.16, 128.14, 128.10, 127.99, 127.83, 127.32 (aromatic C/*CH*), 98.93 (C-1B), 97.97 (C-1^A), 76.06 (C-3^B), 75.30 (C-3^A), 73.45 (C-4^A), 72.28 (*CH*$_2$*Ph*), 71.96 (*CH*$_2$*Ph*), 68.56 (C-5^A), 68.12 (C-7), 68.07 (C-5^B), 66.04 (*CH*$_2$*Ph*), 65.41 (C-4^B), 62.55 (C-6^A), 62.33 (C-6^B), 59.52 (C-2^A), 59.48 (C-2^B), 34.03 (C-11), 28.90 (C-8), 25.56 (C-9), 24.48 (C-10). HR-MS: Calculated for $C_{53}H_{56}N_6O_{13}$ $[M+H]^+$: 985.3984, found: 985.3978.

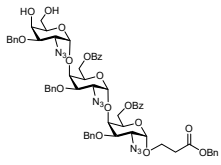
6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (36)



The reaction was carried out according to the general procedure B. The donor **2b** (3.54 g, 5.85 mmol) and the acceptor **35** (2.88 g, 2.92 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 29 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (26 µl, 0.29 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 = 8:1 – 5:1). Compound **36** (3.42 g, 84% yield, pentane: EtOAc = 4:1, R*f* = 0.40-0.50) was obtained as yellow syrup. $[\alpha]_D^{25}$ +142.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 651, 737, 796, 826, 979, 1006, 1027, 1045, 1063, 1098, 1268, 1315, 1454, 1724, 2108, 2859, 2932. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.06 – 8.00 (m, 2H, *CH*, Bz), 7.95 – 7.88 (m, 2H, *CH*, Bz), 7.62 – 7.53 (m, 2H, aromatic H), 7.50 – 7.26 (m, 22H, aromatic H), 7.22 – 7.17 (m, 1H, aromatic H), 7.13 – 7.05 (m, 1H, aromatic H), 5.17 (d, *J* = 3.5 Hz, 1H, H-1^C), 5.08 (s, 2H, *CH*$_2$*Ph*), 5.05 (d, *J* = 3.5 Hz, 1H, H-1^B), 4.96 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.88 – 4.61 (m, 7H, *CH*$_2$*Ph*, H-6^A), 4.59 – 4.45 (m, 3H, H-6^A, 6^B, 4^B), 4.43 – 4.37 (m, 2H, H-3^C, 4^B), 4.28 (dd, *J* = 9.6, 2.7 Hz, 2H, H-4^A, 4^C), 4.10 (t, 1H, H-5^A), 4.03 – 3.96 (m, 2H, H-5^B, 5^C), 3.94 – 3.84 (m, 2H, H-3^A, 3^B), 3.83 – 3.77 (m, 2H, H-2^B, 2^C), 3.72 (dd, *J* = 12.8, 1.6 Hz, 1H, H-6^C), 3.68 – 3.61 (m, 2H, H-2^A, 7), 3.58 (dd, *J* = 12.7, 2.1 Hz, 1H, H-6^C), 3.44 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.66 – 1.52 (m, 4H, H-10, 8), 1.36 – 1.25 (m, 2H, H-9), 1.00 – 0.91 (m, 18H, *CH*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.40 (C-12), 166.01 (C=O, Bz), 165.40 (C=O, Bz), 137.78, 137.12, 137.04, 136.10, 133.47, 133.28, 129.71, 129.70, 129.59, 129.58, 128.61, 128.57, 128.55, 128.50, 128.26, 128.22, 127.98, 127.93, 127.51, 127.21 (aromatic C/*CH*), 98.92 (C-1^B), 98.77 (C-1^C), 98.00 (C-1^A), 75.58 (C-3^C), 75.34 (C-3^B), 74.97 (C-3^A), 73.35 (C-4^A), 72.39 (*CH*$_2$*Ph*), 72.09 (*CH*$_2$*Ph*), 71.68 (C-4^C), 70.36 (*CH*$_2$*Ph*), 69.56 (C-4^B), 68.82 (C-5^C), 68.62 (C-5^A), 68.21 (C-7), 67.75 (C-5^B), 66.90 (C-6^C), 66.16 (*CH*$_2$*Ph*), 62.63 (C-6^A), 61.28 (C-6^B), 60.38 (C-2^C), 59.73 (C-2^A), 58.64 (C-2^B), 34.15 (C-11), 29.00 (C-8), 27.63 (CH_3), 27.30 (CH_3),

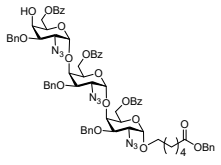
25.68 (C-9), 24.60 (C-10), 23.36 (C-*Si*), 20.71 (C-*Si*). HR-MS: Calculated for $C_{74}H_{87}N_9O_{17}Si$ $[M+H]^+$: 1402.6067, found: 1402.6062.

6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (37)



The reaction was carried out according to the general procedure C using compound **36** (3.42 g, 2.44 mmol) and HF/pyridine (70%, 1.0 ml, 39 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1 - 3:2). Compound **37** (2.90 g, 92% yield, pentane:EtOAc = 1:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +117.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 737, 1009, 1027, 1045, 1110, 1055, 1110, 1155, 1269, 1315, 1452, 1720, 2106, 2873, 2928, 3470. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.07 – 8.00 (m, 2H, *C*H, Bz), 7.92 – 7.86 (m, 2H, *C*H, Bz), 7.62 – 7.55 (m, 2H), 7.48 – 7.27 (m, 21H), 7.18 (t, *J* = 7.7 Hz, 2H), 7.05 – 6.98 (m, 1H, aromatic H), 5.15 (d, *J* = 3.5 Hz, 1H, H-1^B), 5.07 (s, 2H, *C*H$_2$*Ph*), 4.98 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.93 (d, *J* = 3.6 Hz, 1H, H-1^C), 4.84 (dd, *J* = 18.0, 11.7 Hz, 2H, *C*H$_2$*Ph*), 4.76 – 4.62 (m, 5H, *C*H$_2$*Ph*, H-6^A), 4.61 – 4.50 (m, 2H, H-6^A, 6^B), 4.47 (dd, *J* = 9.6, 5.2 Hz, 1H, H-5^B), 4.28 (d, *J* = 2.8 Hz, 1H, H-4^A), 4.18 (d, *J* = 2.5 Hz, 1H, H-4^B), 4.16 – 4.08 (m, 3H, H-5^A, 6^B, 4^C), 4.06 – 3.99 (m, 2H, H-3^B, 5^C), 3.92 (dd, *J* = 10.8, 2.7 Hz, 1H, H-3^A), 3.87 (dd, *J* = 10.4, 3.0 Hz, 1H, H-3^C), 3.79 (dd, *J* = 10.9, 3.5 Hz, 1H, H-2^B), 3.75 (dd, *J* = 10.4, 3.5 Hz, 1H, H-2^C), 3.70 – 3.62 (m, 2H, H-2^A, 7), 3.50 – 3.38 (m, 3H, H-6^C, 7), 2.83 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 2.14 (bs, 1H, *O*H), 1.65 – 1.53 (m, 4H, H-10, 8), 1.36 – 1.27 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.39 (C-12), 165.98 (C=O, Bz), 165.40 (C=O, Bz), 137.09, 137.05, 137.01, 136.05, 133.45, 133.24, 129.68, 129.65, 129.56, 129.54, 128.66, 128.59, 128.57, 128.52, 128.47, 128.25, 128.22, 128.19, 128.17, 128.02, 127.92, 127.60, 127.27 (aromatic C/C*H*), 99.46 (C-1^C), 98.80 (C-1^B), 97.98 (C-1^A), 76.32 (C-3^C), 75.52 (C-3^B), 75.26 (C-3^A), 73.61 (C-4^B), 73.30 (C-4^A), 72.49, 72.35, 71.85 (3 C*H*$_2$*Ph*), 69.61 (C-5^C), 68.89 (C-5^B), 68.60 (C-5^A), 68.20 (C-7), 67.51 (C-4C), 66.12 (C*H*$_2$*Ph*), 62.65 (C-6^C), 62.58 (C-6^A), 61.30 (C-6^B), 60.17 (C-2^B), 59.75 (C-2^A), 59.63 (C-2^C), 34.11 (C-11), 28.97 (C-8), 25.64 (C-9), 24.56 (C-10). HR-MS: Calculated for $C_{66}H_{71}N_9O_{17}$ $[M+H]^+$: 1262.5046, found: 1262.5041.

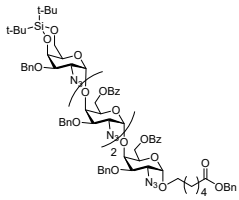
6-(Benzyl hexanoyl) 2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (38)



The reaction was carried out according to the general procedure D using compound **37** (2.92 g, 2.31 mmol), PhCOOBt (2.49 g, 10.4 mmol) and Et_3N (1.6 ml, 11.6 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **38** (3.24 g, 94% yield, pentane:EtOAc = 3:1, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +113.0 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 737, 1005, 1027, 1046, 1098, 1112, 1156, 1268, 1315, 1452, 1717, 2106, 2872, 2929, 2490. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07 – 8.00 (m, 2H, *C*H, Bz), 7.94

– 7.85 (m, 4H, *C*H, Bz), 7.61 – 6.98 (m, 29H, aromatic H), 5.16 (d, *J* = 3.5 Hz, 1H, H-1), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.02 – 4.94 (m, 2H, H-1^A, 1^C), 4.91 – 4.78 (m, 2H, *C*H$_2$*Ph*), 4.78 – 4.63 (m, 5H, *C*H$_2$*Ph*, H-6^A), 4.58 (dd, *J* = 11.1, 6.5 Hz, 1H, H-6^A), 4.54 – 4.45 (m, 2H, H-5^B, 6^B), 4.44 – 4.36 (m, 2H, H-5^A, 6^C), 4.29 (d, *J* = 2.7 Hz, 1H, H-4^A), 4.24-4.19 (m, 2H, H-4^B, 6^B), 4.12 (t, *J* = 6.7 Hz, 1H, H-5^C), 4.06 – 3.89 (m, 5H, H-3^A, 3^C, 3^B, 3^C, 6^C), 3.85 (dd, *J* = 10.8, 3.5 Hz, 1H, H-2^B), 3.77 (dd, *J* = 10.4, 3.5 Hz, 1H, H-2^C), 3.71 – 3.60 (m, 2H, H-2^A, 7), 3.45 (dt, *J* = 9.7, 6.4 Hz, 1H, H-7), 2.57 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.51 (m, 4H, H-10, 8), 1.37 – 1.25 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.35 (C-12), 165.95 (2xC=O), 165.32 (C=O), 137.15, 136.98, 136.86, 136.03, 133.43, 133.22, 133.07, 129.75, 129.68, 129.65, 129.60, 129.51, 128.61, 128.56, 128.54, 128.49, 128.44, 128.37, 128.30, 128.19, 128.14, 128.00, 127.93, 127.89, 127.45, 127.25 (aromatic C/C*H*), 99.03 (C-1^C), 98.78 (C-1^B), 97.94 (C-1^A), 76.18 (C-3^C), 75.22 (C-3^B), 75.17 (C-3^A), 73.18 (C-4^B), 73.08 (C-4^A), 72.40, 72.34, 72.04 (3 C*H*$_2$*Ph*), 68.83 (C-5^B), 68.59 (C-5^C), 68.16 (C-7), 68.08 (C-5^A), 66.09 (C*H*$_2$*Ph*), 65.45 (C-4^C), 62.58 (C-6^A), 62.32 (C-6^C), 61.21 (C-6^B), 60.16 (C-2^B), 59.71 (C-2^A), 59.57 (C-2^C), 34.08 (C-11), 28.94 (C-8), 25.61 (C-9), 24.52 (C-10). HR-MS: Calculated for $C_{73}H_{75}N_9O_{18}$ $[M+H]^+$: 1366.5308, found: 1366.5303.

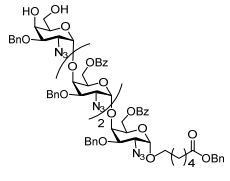
6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (39)



The reaction was carried out according to the general procedure B. The donor **2b** (2.66 g, 4.39 mmol) and the acceptor **38** (3.0 g, 2.2 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 4Å. The solution was cooled to 0 ºC, after which TfOH (19 µl, 0.22 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 **39** (3.68 g, 92% yield, pentane: EtOAc = 4:1, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +188.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 444, 475, 651, 736, 826, 1005, 1027, 1045, 1063, 1098, 1266, 1315, 1452, 1721, 2108, 2859, 2932. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07 – 8.00 (m, 2H, *C*H, Bz), 7.95 – 7.87 (m, 4H, *C*H, Bz), 7.64 – 7.03 (m, 34H, aromatic H), 5.16 – 5.11 (m, 1H, H-1), 5.07 (d, *J* = 6.8 Hz, 3H, *C*H$_2$*Ph*, H-1), 5.02 – 4.94 (m, 2H, 2xH-1), 4.89 (d, *J* = 11.9 Hz, 1H, *C*H$_2$*Ph*), 4.85 – 4.14 (m, 20H), 4.10 (t, *J* = 7.2 Hz, 1H), 4.04 – 3.61 (m, 12H), 3.57 (d, *J* = 12.7 Hz, 1H), 3.50 – 3.41 (m, 1H, H-7), 2.31 (t, *J* = 7.4 Hz, 2H, H-11), 1.59 (h, *J* = 7.3 Hz, 4H, H-10, 8), 1.31 (p, *J* = 8.9, 8.2 Hz, 2H, H-9), 1.00 – 0.91 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.36 (C-12), 165.97, 165.42, 165.36 (3 C=O, Bz), 137.76, 137.04, 136.92, 136.07, 133.44, 133.31, 133.23, 129.68, 129.66, 129.62, 129.55, 128.59, 128.55, 128.52, 128.48, 128.23, 128.18, 128.00, 127.93, 127.85, 127.55, 127.24, 127.21 (aromatic C/C*H*), 98.89 (C-1), 98.85 (C-1), 98.76 (C-1), 97.96 (C-1^A), 75.61, 75.46, 75.31, 74.92, 73.20, 72.88, 72.47, 72.34, 72.06 (3 C*H*$_2$*Ph*), 71.85, 70.33 (C*H*$_2$*Ph*), 69.50, 68.82, 68.62, 68.20 (C-7), 67.70, 66.86 (C-6^D), 66.12 (C*H*$_2$*Ph*), 62.61 (C-6^A), 61.30 (C-6^B, 6^C),

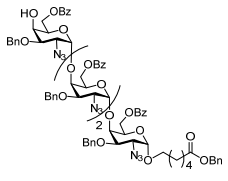
60.41, 60.31, 59.78, 58.67 (4 C-2), 34.12 (C-11), 28.98 (C-8), 27.60 (3xC*H*$_3$), 27.28 (3xC*H*$_3$), 25.65 (C-9), 24.57 (C-10), 23.32 (C-*Si*), 20.67 (C-*Si*). HR-MS: Calculated for $C_{94}H_{106}N_{12}O_{22}Si$ $[M+NH_4]^+$: 1800.7658, found: 1800.7652.

6-(Benzyl hexanoyl) 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (40)



The reaction was carried out according to the general procedure C using compound **39** (3.68 g, 2.06 mmol) and HF/pyridine (70%, 860 µl, 33.0 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2-1:1). Compound **40** (3.27 g, 91% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +126.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 737, 1005, 1027, 1046, 1112, 1155, 1269, 1316, 1452, 1721, 2108, 2872, 2929, 3463. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.06 – 8.00 (m, 2H, *C*H, Bz), 7.94 – 7.86 (m, 4H, *C*H, Bz), 7.64 – 6.98 (m, 34H, aromatic H), 5.14 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.03 (d, *J* = 3.6 Hz, 1H, H-1^C), 4.97 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.90 – 4.85 (m, 2H, *C*H$_2$*Ph*, H-1^D), 4.82 (dd, *J* = 11.8, 7.1 Hz, 2H), 4.76 (d, *J* = 11.8 Hz, 1H), 4.74 – 4.60 (m, 5H), 4.60 – 4.44 (m, 4H), 4.41 (dd, *J* = 9.6, 5.4 Hz, 1H), 4.28 (d, *J* = 2.8 Hz, 1H, H-4^A), 4.25 (d, *J* = 2.6 Hz, 1H, H-4^B), 4.18 – 4.09 (m, 3H), 4.08 – 3.89 (m, 6H), 3.85 – 3.78 (m, 2H), 3.75 – 3.63 (m, 4H, 3xH-2, H-7), 3.49 – 3.37 (m, 3H, H-6^D, 7), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.65 – 1.53 (m, 4H, H-10, 8), 1.36 – 1.27 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.35 (C-12), 165.96, 165.37, 165.34 (3 C=O, Bz), 137.08, 137.03, 137.01, 136.83, 136.05, 133.42, 133.29, 133.19, 129.67, 129.65, 129.61, 129.53, 129.51, 128.62, 128.60, 128.56, 128.55, 128.51, 128.48, 128.44, 128.19, 128.14, 127.98, 127.94, 127.88, 127.64, 127.29, 127.20 (aromatic C/C*H*), 99.47 (C-1^D), 98.86 (C-1^C), 98.76 (C-1^B), 97.95 (C-1^A), 76.35, 75.49, 75.34, 75.16, 73.78, 73.25, 72.75, 72.49, 72.41, 72.33, 71.80 (4 C*H*$_2$*Ph*), 69.59, 68.90, 68.80, 68.60, 68.19 (C-7), 67.49 (C-4^D), 66.09 (C*H*$_2$*Ph*), 62.63 (C-6C, 6D), 62.58 (C-6A), 61.28 (C-6B), 60.35, 60.19, 59.76, 59.65 (4 C-2), 34.09 (C-11), 28.95 (C-8), 25.62 (C-9), 24.54 (C-10). HR-MS: Calculated for $C_{86}H_{90}N_{12}O_{22}$ $[M+H]^+$: 1643.6371, found: 1643.6365.

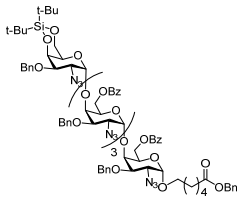
6-(Benzyl hexanoyl) 2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-6-*O*-benzoyl-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (41)



The reaction was carried out according to the general procedure D using compound **40** (3.24 g, 1.97 mmol), PhCOOBt (2.12 g, 8.88 mmol) and Et_3N (1.4 ml, 9.85 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1 – 3:1). Compound **41** (3.37 g, 92% yield, pentane:EtOAc = 2:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +115.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 737, 1005, 1027, 1046, 1063, 1098, 1110, 1156, 1268, 1315, 1452, 1720, 2106, 2872, 2929, 3477. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07 – 8.00 (m, 2H, *C*H, Bz), 7.95 – 7.84 (m, 6H, *C*H, 3xBz), 7.62 – 6.96 (m, 37H, aromatic H), 5.15 (d, *J* = 3.6 Hz, 1H,

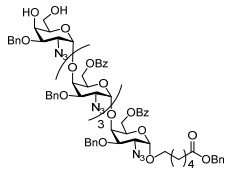
H-1^{B}), 5.06 (s, 2H, *C*H$_2$*Ph*), 5.04 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 4.98 (d, *J* = 3.6 Hz, 1H, H-1^{A}), 4.92 (d, *J* = 3.6 Hz, 1H, H-1^{D}), 4.90 – 4.54 (m, 10H), 4.53 – 4.33 (m, 6H), 4.28-4.25 (m, 2H, H-4^{A}, 4^{B}), 4.20 – 4.05 (m, 4H), 4.04 – 3.87 (m, 6H), 3.84 – 3.73 (m, 3H, 3xH-2), 3.71 – 3.62 (m, 2H, H-2, 7), 3.45 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.55 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.68 – 1.52 (m, 4H, H-10, 8), 1.37 – 1.27 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.32 (C-12), 165.93, 165.88, 165.34, 165.25 (4 C=O, Bz), 137.12, 136.98, 136.85, 136.80, 136.01, 133.40, 133.28, 133.18, 133.02, 129.74, 129.65, 129.63, 129.56, 129.53, 129.48, 129.46, 128.55, 128.54, 128.52, 128.49, 128.46, 128.44, 128.42, 128.33, 128.26, 128.17, 128.12, 127.96, 127.90, 127.89, 127.85, 127.47, 127.23, 127.15 (aromatic C/*CH*), 99.11 (C-1^{D}), 98.86 (C-1^{C}), 98.72 (C-1^{B}), 97.91 (C-1^{A}), 76.26, 75.30, 75.16, 75.08, 73.34, 73.19, 72.62, 72.42 (C*H$_2$Ph*), 72.31 (C*H$_2$Ph*), 71.99 (C*H$_2$Ph*), 68.82, 68.75, 68.56, 68.14 (C-7), 68.02, 66.06 (C*H$_2$Ph*), 65.35 (C-4^{D}), 62.56, 62.18, 61.24, 61.18 (4 C-6), 60.32, 60.16, 59.71, 59.58 (4 C-2), 34.05 (C-11), 28.92 (C-8), 25.59 (C-9), 24.50 (C-10). HR-MS: Calculated for $C_{93}H_{94}N_{12}O_{23}$ $[M+H]^+$: 1747.6633, found: 1747.6628.

Pentasaccharide 42



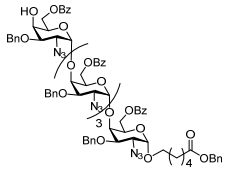
The reaction was carried out according to the general procedure B. The donor **2b** (2.90 g, 4.78 mmol) and the acceptor **41** (3.34 g, 1.91 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 19 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TfOH (17 µl, 0.19 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 **42** (3.72 g, 90% yield, pentane: EtOAc = 4:1, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +151.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1003, 1027, 1045, 1063, 1096, 1156, 1266, 1315, 1452, 1721, 2108, 2859, 2933. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 8.00 (m, 2H, *C*H, Bz), 7.95 – 7.86 (m, 6H, *C*H, Bz), 7.64 – 6.97 (m, 42H, aromatic H), 5.13 (d, *J* = 3.5 Hz, 1H, H-1^{B}), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.04 – 4.95 (m, 4H, 4xH-1), 4.91 – 4.54 (m, 13H), 4.51 – 4.33 (m, 8H), 4.31 – 3.84 (m, 14H), 3.82 – 3.74 (m, 3H), 3.74 – 3.60 (m, 5H), 3.54 (dd, *J* = 12.8, 2.1 Hz, 1H, H-6^{D}), 3.46 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.31 (t, *J* = 7.4 Hz, 2H, H-11), 1.67 – 1.53 (m, 4H, H-10, 8), 1.37 – 1.28 (m, 2H, H-9), 1.00 – 0.89 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.36 (C-12), 165.98 (C=O, Bz), 165.36 (C=O, Bz), 165.30 (C=O, Bz), 137.75, 137.03, 137.01, 136.92, 136.87, 136.07, 133.45, 133.30, 133.20, 129.68, 129.65, 129.62, 129.57, 129.54, 129.52, 128.60, 128.58, 128.52, 128.49, 128.46, 128.44, 128.22, 128.18, 127.95, 127.92, 127.87, 127.84, 127.57, 127.23, 127.18 (aromatic C/*CH*), 98.92 (C-1), 98.85 (2xC-1), 98.78 (C-1), 97.97 (C-1^{A}), 75.60, 75.49, 75.31, 75.23, 74.87, 73.27, 73.09, 72.62, 72.47, 72.39, 72.32, 72.00 (4 C*H$_2$Ph*), 71.78, 70.32 (C*H$_2$Ph*), 69.48, 68.82, 68.78, 68.61, 68.20 (C-7), 67.67, 66.83 (C-6^{E}), 66.12 (C*H$_2$Ph*), 62.57 (C-6^{A}), 61.27 (C-6), 61.17 (C-6), 60.43, 60.38, 60.30, 59.76, 58.68 (5 C-2), 34.11 (C-11), 28.98 (C-8), 27.59 (C*H$_3$*), 27.26 (C*H$_3$*), 25.65 (C-9), 24.56 (C-10), 23.30 (C-*Si*), 20.66 (C-*Si*). HR-MS: Calculated for $C_{114}H_{125}N_{15}O_{27}Si$ $[M+NH_4]^+$: 2181.89823, found: 2181.89769.

Pentasaccharide 43



The reaction was carried out according to the general procedure C using compound **42** (3.4 g, 1.57 mmol) and HF/pyridine (70%, 460 µl, 25.1 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2-1:1). Compound **43** (3.16 g, 93% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +141.0 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 736, 1004, 1027, 1045, 1063, 1098, 1110, 1156, 1268, 1315, 1452, 1720, 2108, 2875, 2926, 3504. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.03 (d, *J* = 7.7 Hz, 2H, *C*H, Bz), 7.95 – 7.84 (m, 6H, *C*H, Bz), 7.66 – 6.98 (m, 42H, aromatic H), 5.14 (s, 1H, H-1^B), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.03 (d, *J* = 3.5 Hz, 1H, H-1^C), 4.98-4.96 (m, 2H, H-1), 4.90 – 4.32 (m, 19H), 4.28 - 4.24 (m, 2H, H-4^A, 4^B), 4.21 – 3.87 (m, 12H), 3.84 – 3.76 (m, 2H), 3.75 – 3.61 (m, 5H), 3.50 – 3.32 (m, 3H, H-6^D, 7), 2.78 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 2.10 (bs, 1H, *O*H), 1.65 – 1.52 (m, 4H, H-10, 8), 1.37 – 1.29 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.33 (C-12), 165.95, 165.36, 165.30, 165.28 (C=O, Bz), 137.03, 137.01, 136.83, 136.04, 133.41, 133.28, 133.15, 129.64, 129.59, 129.54, 129.51, 129.49, 128.58, 128.56, 128.54, 128.48, 128.46, 128.42, 128.18, 128.17, 128.13, 128.10, 127.96, 127.90, 127.87, 127.60, 127.29, 127.21, 127.18 (aromatic H), 99.42 (C-1^E), 98.92 (C-1^D), 98.84 (C-1^C), 98.75 (C-1^B), 97.95 (C-1^A), 76.36, 75.47, 75.29, 75.24, 75.12, 73.69, 73.28, 72.94, 72.70, 72.46, 72.40, 72.38, 72.25, 71.79 (5 C*H*$_2$*Ph*), 69.54, 68.84, 68.79, 68.59, 68.18 (C-7), 67.49, 66.08 (C*H*$_2$*Ph*), 62.62 (C-6), 62.56 (C-6), 61.24 (C-6), 61.16 (C-6), 60.36, 60.34, 60.20, 59.74, 59.64 (5 C-2), 34.08 (C-11), 28.93 (C-8), 25.61 (C-9), 24.52 (C-10). HR-MS: Calculated for $C_{106}H_{109}N_{15}O_{27}$ $[M+NH_4]^+$: 2041.79611, found: 2041.79556.

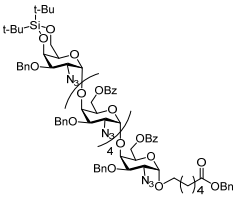
Pentasaccharide 44



The reaction was carried out according to the general procedure D using compound **43** (3.12 g, 1.54 mmol), PhCOOBt (1.66 g, 6.93 mmol) and Et_3N (1.1 ml, 7.7 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:2). Compound **44** (1.09 g, 92% yield, pentane:EtOAc = 2:1, R*f* = 0.25-0.30) was obtained as yellow syrup. $[\alpha]_D^{25}$ +128.1 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 736, 1003, 1027, 1046, 1063, 1096, 1110, 1156, 1176, 1266, 1315, 1452, 1720, 2106, 2873, 2929, 3504. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, *J* = 7.7 Hz, 2H, *C*H, Bz), 7.95 (dd, *J* = 16.7, 7.7 Hz, 8H, *C*H, Bz), 7.69 – 7.04 (m, 45H, aromatic H), 5.20 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.13 (s, 2H, *C*H$_2$*Ph*), 5.09 (d, *J* = 3.6 Hz, 1H, H-1C), 5.05 – 5.00 (m, 2H, H-1D, 1A), 4.99 – 4.60 (m, 14H), 4.57 – 4.37 (m, 8H), 4.34-4.31 (m, 2H, H-4^A, 4^B), 4.26 – 3.91 (m, 14H), 3.89 – 3.67 (m, 6H), 3.51 (dt, *J* = 9.9, 6.4 Hz, 1H, H-7), 2.54 (bs, 1H, *O*H), 2.36 (t, *J* = 7.5 Hz, 2H, H-11), 1.65 (h, *J* = 7.9 Hz, 4H, H-10, 8), 1.43 – 1.32 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.34 (C-12), 165.96, 165.90, 165.38, 165.33, 165.24 (C=O, Bz), 137.16, 137.03, 136.86, 136.84, 136.06, 133.42, 133.28, 133.18, 133.03, 129.79, 129.67, 129.66, 129.58, 129.57, 129.56, 129.54, 129.52, 128.59, 128.57, 128.55, 128.50, 128.48, 128.43, 128.39, 128.28, 128.20, 128.17, 128.15, 127.99, 127.91, 127.89, 127.52, 127.31, 127.23 (aromatic C/C*H*), 99.12 (C-1^E), 98.94 (C-1^D), 98.85 (C-1^C), 98.77 (C-1^B), 97.97 (C-1^A), 76.32, 75.30, 75.26, 75.18, 75.08, 73.34, 73.29, 72.86, 72.72, 72.47, 72.40, 72.35, 72.30, 72.05 (5 C*H*$_2$*Ph*), 68.83, 68.61, 68.19 (C-7), 68.03, 66.10 (C*H*$_2$*Ph*), 65.41, 62.58 (C-6), 62.19 (C-6), 61.27 (C-6), 61.13

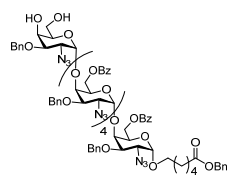
(C-6), 60.38 (C-2), 60.24 (C-2), 59.76 (C-2), 59.64 (C-2), 34.10 (C-11), 28.95 (C-8), 25.63 (C-9), 24.54 (C-10). HR-MS: Calculated for $C_{113}H_{113}N_{15}O_{28}$ $[M+NH_4]^+$: 2145.82232, found: 2145.82117.

Hexasaccharide 45



The reaction was carried out according to the general procedure B. The donor **2b** (2.20 g, 3.62 mmol) and the acceptor **44** (3.08 g, 1.45 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 TfOH (13 µl, 0.14 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 **45** (3.30 g, 89% yield, pentane: EtOAc = 2:1, R*f* = 0.55-0.65) was obtained as yellow syrup. $[\alpha]_D^{25}$ +134.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 651, 736, 797, 824, 1003, 1027, 1045, 1063, 1098, 1109, 1156, 1266, 1315, 1452, 1721, 2108, 2859, 2932. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.07 – 8.00 (m, 2H, *C*H, Bz), 7.95 – 7.86 (m, 8H, *C*H, Bz), 7.62 – 6.99 (m, 50H, aromatic H), 5.14 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.07 (s, 2H, *C*H_2*Ph*), 5.02 (d, *J* = 3.6 Hz, 1H, H-1^C), 5.00 – 4.93 (m, 4H, H-1^A, 1^D, 1^E, 1^F), 4.90 – 4.55 (m, 14H), 4.51 – 4.32 (m, 9H), 4.29 – 4.22 (m, 3H), 4.20 – 3.97 (m, 9H), 3.96 – 3.84 (m, 5H), 3.82 – 3.75 (m, 3H), 3.73 – 3.62 (m, 6H), 3.55 (dd, *J* = 12.9, 2.1 Hz, 1H, H-6^F), 3.46 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.66 – 1.52 (m, 4H, H-10, 8), 1.37 – 1.27 (m, 2H, H-9), 1.00 – 0.89 (m, 18H, *C*H_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.29 (C-12), 165.93, 165.36, 165.30, 165.26 (C=O, Bz), 137.75, 137.03, 137.00, 136.86, 136.08, 133.41, 133.28, 133.23, 133.15, 129.65, 129.61, 129.59, 129.57, 129.55, 129.53, 128.56, 128.55, 128.50, 128.48, 128.45, 128.43, 128.41, 128.19, 128.14, 127.91, 127.88, 127.85, 127.80, 127.58, 127.27, 127.25, 127.23, 127.19 (aromatic C/C*H*), 98.86 (2xC-1), 98.84 (C-1), 98.76 (C-1), 97.98 (C-1^A), 75.58, 75.45, 75.31, 75.21, 75.18, 74.80, 73.28, 73.01, 72.81, 72.74, 72.49, 72.39, 72.36, 72.25, 72.00 (5 CH_2*Ph*), 71.81, 70.29 (CH_2*Ph*), 69.49, 68.83, 68.77, 68.62, 68.19 (C-7), 67.67, 66.82 (C-6^F), 66.08 (CH_2*Ph*), 62.57 (C-6), 61.28 (C-6), 61.18 (C-6), 60.45, 60.40, 60.38, 60.33, 59.77, 58.69 (6 C-2), 34.09 (C-11), 28.95 (C-8), 27.57 (CH_3), 27.25 (CH_3), 25.63 (C-9), 24.54 (C-10), 23.27 (C-*Si*), 20.64 (C-*Si*). MALDI-MS: Calculated for $C_{134}H_{144}N_{18}O_{32}Si$ $[M+Na]^+$: 2567.9861, found: 2567.9677.

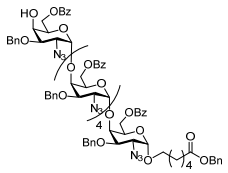
Hexasaccharide 46



The reaction was carried out according to the general procedure C using compound **45** (2.97 g, 1.17 mmol) and HF/pyridine (70%, 490 µl, 18.7 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **46** (2.90 g, 92% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +132.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 736, 1003, 1027, 1045, 1063, 1096, 1110, 1156, 1267, 1315, 1452, 1720, 2106, 2873, 2926, 3473. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.03 (d, *J* = 7.7 Hz, 2H, *C*H, Bz),

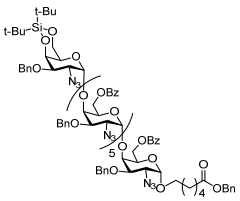
7.95 – 7.83 (m, 8H, *C*H, Bz), 7.64 – 6.95 (m, 50H, aromatic H), 5.13 (d, *J* = 3.5 Hz, 1H, H-1^{B}), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.01 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 4.99 – 4.91 (m, 3H, H-1^{A}, 1^{D}, 1^{E}), 4.90 – 4.54 (m, 15H, H-1^{F}), 4.53 – 4.31 (m, 8H), 4.30 – 4.21 (m, 2H), 4.21 – 3.84 (m, 15H), 3.84 – 3.76 (m, 2H), 3.74 – 3.61 (m, 6H), 3.45 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 3.42 – 3.34 (m, 2H, H-6^{F}), 2.71 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.66 – 1.53 (m, 4H, H-10, 8), 1.35 – 1.27 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.34 (C-12), 165.95, 165.37, 165.32, 165.27 (C=O, Bz), 137.04, 137.02, 136.85, 136.78, 136.06, 133.42, 133.29, 133.26, 133.15, 129.65, 129.59, 129.56, 129.54, 129.51, 128.60, 128.57, 128.55, 128.50, 128.48, 128.45, 128.42, 128.19, 128.15, 128.10, 127.98, 127.91, 127.89, 127.88, 127.61, 127.30, 127.23, 127.22 (aromatic C/*CH*), 99.43 (C-1^{F}), 98.91 (C-1^{E}, 1^{D}), 98.86 (C-1^{C}), 98.77 (C-1^{B}), 97.96 (C-1^{A}), 76.37, 75.52, 75.31, 75.24, 75.22, 75.10, 73.71, 73.29, 72.90, 72.78, 72.48, 72.40, 72.33, 72.28, 71.82 (5 C*H*$_2$*Ph*), 69.54, 68.82, 68.61, 68.19 (C-7), 67.53, 66.10 (C*H*$_2$*Ph*), 62.65 (C-6), 62.57 (C-6), 61.25 (C-6), 61.14 (C-6), 60.38, 60.23, 59.76, 59.65 (C-2), 34.09 (C-11), 28.95 (C-8), 25.63 (C-9), 24.54 (C-10). HR-MS: Calculated for $C_{126}H_{128}N_{18}O_{32}$ $[M+NH_4]^+$: 2422.92858, found: 2422.92803.

Hexasaccharide 47



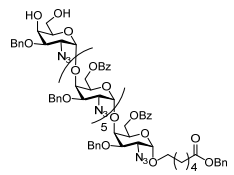
The reaction was carried out according to the general procedure D using compound **46** (2.90 g, 1.20 mmol), PhCOOBt (1.59 g, 6.6 mmol) and Et_3N (1.0 ml, 7.20 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **47** (2.77 mg, 90% yield, pentane:EtOAc = 3:2, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +130.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) 1027, 1047, 1065, 1112, 1271, 1723, 2109, 2879, 2929, 3509. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.03 (d, *J* = 7.8 Hz, 2H, *C*H, Bz), 7.96 – 7.82 (m, 10H, *C*H, Bz), 7.61 – 6.95 (m, 53H), 5.14 (d, *J* = 3.7 Hz, 1H, H-1^{B}), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.02 (d, *J* = 3.7 Hz, 1H, H-1^{C}), 4.99 – 4.92 (m, 3H, H-1^{A}, 1^{D}, 1^{E}), 4.92 – 4.53 (m, 15H, H-1^{F}), 4.52 – 4.30 (m, 10H), 4.29 – 4.21 (m, 2H, H-4^{A}, 4^{B}), 4.18 – 3.83 (m, 16H), 3.82 – 3.61 (m, 7H), 3.45 (dt, *J* = 10.6, 6.5 Hz, 1H, H-7), 2.44 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.60 (dt, *J* = 16.0, 7.9 Hz, 4H, H-10, 8), 1.37 – 1.28 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.34 (C-12), 165.97, 165.91, 165.38, 165.34, 165.29, 165.24 (6 C=O, Bz), 137.16, 137.03, 136.87, 136.85, 136.80, 136.07, 133.43, 133.30, 133.27, 133.18, 133.03, 129.80, 129.68, 129.66, 129.59, 129.56, 129.52, 128.59, 128.56, 128.51, 128.49, 128.46, 128.43, 128.39, 128.29, 128.21, 128.18, 128.16, 128.00, 127.93, 127.90, 127.88, 127.53, 127.31, 127.25, 127.23 (aromatic C/*CH*), 99.12 (C-1^{F}), 98.92 (C-1^{E}, 1^{D}), 98.87 (C-1^{C}), 98.78 (C-1^{B}), 97.98 (C-1^{A}), 76.33, 75.33, 75.25, 75.22, 75.06, 73.36, 73.30, 72.91, 72.80, 72.78, 72.50, 72.40, 72.32, 72.29, 72.07 (5 C*H*$_2$*Ph*), 68.83, 68.62, 68.21 (C-7), 68.02, 66.11 (C*H*$_2$*Ph*), 65.42 (C-4^{F}), 62.59, 62.18, 61.27, 61.17, 61.11 (C-6), 60.42, 60.39, 60.26, 59.77, 59.65 (C-2), 34.11 (C-11), 28.97 (C-8), 25.64 (C-9), 24.56 (C-10). MALDI-MS: Calculated for $C_{133}H_{132}N_{18}O_{33}$ $[M+Na]^+$: 2531.9102, found: 2531.8920.

Heptasaccharide 48



The reaction was carried out according to the general procedure B. The donor **2b** (1.66 g, 2.73 mmol) and the acceptor **47** (2.74 g, 1.09 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 = 4:1). Compound **48** (2.83 g, 88% yield, pentane: EtOAc = 2:1, R*f* = 0.55-0.65) was obtained as yellow syrup. $[\alpha]_D^{25}$ +152.4 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 651, 736, 824, 1003, 1027, 1045, 1063, 1098, 1109, 1156, 1266, 1315, 1452, 1721, 2108, 2860, 2932. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.06 – 8.00 (m, 2H, *C*H, Bz), 7.95 – 7.85 (m, 10H, *C*H, Bz), 7.62 – 6.97 (m, 58H, aromatic H), 5.14 (s, 1H, H-1B), 5.07 (s, 2H, *C*H_2*Ph*), 5.02 (d, *J* = 3.3 Hz, 1H, H-1^C), 4.99 – 4.91 (m, 5H, 5xH-1), 4.90 – 4.62 (m, 14H), 4.62 – 4.55 (m, 2H), 4.51 – 3.82 (m, 31H), 3.79 (d, *J* = 2.8 Hz, 3H), 3.72 – 3.61 (m, 7H), 3.58-3.53 (m, 1H, H-6^G), 3.50 – 3.41 (m, 1H, H-7), 2.31 (t, *J* = 7.4 Hz, 2H, H-11), 1.67 – 1.53 (m, 4H, H-10, 8), 1.37 – 1.27 (m, 2H, H-9), 1.00 – 0.89 (m, 18H, *C*H_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.31 (C-12), 165.96, 165.38, 165.33, 165.30, 165.28 (C=O, Bz), 137.77, 137.04, 137.01, 136.87, 136.83, 136.09, 133.43, 133.30, 133.23, 133.16, 129.67, 129.62, 129.58, 129.56, 129.54, 128.58, 128.56, 128.52, 128.50, 128.45, 128.42, 128.20, 128.16, 127.94, 127.90, 127.86, 127.81, 127.59, 127.27, 127.24, 127.21 (aromatic C/*CH*), 98.92 (C-1), 98.86 (4xC-1), 98.78 (C-1), 97.99 (C-1^A), 75.59, 75.48, 75.33, 75.23, 75.20, 75.17, 74.84, 73.31, 73.02, 72.93, 72.76, 72.51, 72.42, 72.38, 72.32, 72.26, 72.01 (6 CH_2*Ph*), 71.83, 70.30 (CH_2*Ph*), 69.50, 68.81, 68.63, 68.21 (C-7), 67.68, 66.83 (C-6^G), 66.10 (CH_2*Ph*), 62.59, 61.28, 61.17 (C-6), 60.46, 60.43, 60.40, 60.35, 59.79, 58.70 (C-2), 34.11 (C-11), 28.97 (C-8), 27.58 (CH_3), 27.26 (CH_3), 25.65 (C-9), 24.56 (C-10), 23.29 (C-*Si*), 20.65 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 98.92 ($J_{C1,H1}$ = 172 Hz), 98.86 ($J_{C1,H1}$ = 172 Hz), 98.78 ($J_{C1,H1}$ = 173 Hz), 97.99 ($J_{C1,H1}$ = 172 Hz). MALDI-MS: Calculated for $C_{154}H_{163}N_{21}O_{37}Si$ $[M+Na]^+$: 2949.1186, found: 2949.0945.

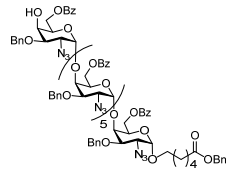
Heptasaccharide 49



The reaction was carried out according to the general procedure C using compound **48** (2.40 g, 0.82 mmol) and HF/pyridine (70%, 340 µl, 13.1 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2-1:1). Compound **49** (2.20 g, 94% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +137.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1003, 1027, 1046, 1063, 1098, 1112, 1156, 1268, 1315, 1452, 1720, 2108, 2872, 2926, 3484. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.05 – 8.00 (m, 2H, *C*H, Bz), 7.94 – 7.83 (m, 10H, *C*H, Bz), 7.62 – 6.95 (m, 58H, aromatic H), 5.13 (d, *J* = 3.6 Hz, 1H, H-1B), 5.07 (s, 2H, *C*H_2*Ph*), 5.01 (d, *J* = 3.6 Hz, 1H, H-1^C), 4.97 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.96 – 4.90 (m, 3H, 3xH-1), 4.90 – 4.55 (m, 17H, H-1), 4.52 – 4.30 (m, 10H), 4.26 (dd, *J* = 15.3, 2.7 Hz, 2H), 4.19 – 3.84 (m, 18H), 3.84 – 3.75 (m, 2H), 3.74 – 3.60 (m, 7H), 3.49 -3.42 (m, 1H, H-7), 3.40 – 3.32 (m, 2H, H-6^G), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.67 – 1.53 (m, 4H, H-10,

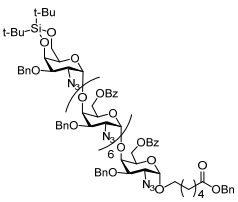
8), 1.36 – 1.25 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.35 (C-12), 165.96, 165.37, 165.32, 165.28, 165.25 (C=O, Bz), 137.04, 137.01, 136.85, 136.80, 136.78, 136.05, 133.43, 133.30, 133.26, 133.15, 129.66, 129.64, 129.59, 129.55, 129.53, 129.50, 128.60, 128.57, 128.56, 128.51, 128.49, 128.47, 128.44, 128.42, 128.20, 128.19, 128.15, 128.10, 127.98, 127.91, 127.89, 127.87, 127.83, 127.60, 127.28, 127.23, 127.21, 127.19 (aromatic C/C*H*), 99.43 (C-1^G), 98.93 (C-1^F), 98.90 (3xC-1), 98.78 (C-1B), 97.96 (C-1^A), 76.39, 75.53, 75.32, 75.23, 75.13, 73.70, 73.29, 72.96, 72.91, 72.83, 72.76, 72.48, 72.40, 72.38, 72.33, 72.27, 71.83 (6 CH_2*Ph*), 69.52, 68.81, 68.60, 68.20 (C-7), 67.54 (C-4^G), 66.10 (CH_2*Ph*), 62.66, 62.56, 61.24, 61.22, 61.12 (C-6), 60.39, 60.36, 60.23, 59.76, 59.65 (C-2), 34.10 (C-11), 28.96 (C-8), 25.63 (C-9), 24.55 (C-10). MALDI-MS: Calculated for $C_{146}H_{147}N_{21}O_{37}$ $[M+Na]^+$: 2809.0164, found: 2808.9943.

Heptasaccharide 50



The reaction was carried out according to the general procedure D using compound **49** (2.04 g, 0.73 mmol), PhCOOBt (963 mg, 4.03 mmol) and Et_3N (610 µl, 4.38 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **50** (2.10 g, 92% yield, pentane:EtOAc = 3:2, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +108.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1005, 1027, 1047, 1063, 1112, 1269, 1315, 1721, 2109, 2873, 2926, 3473. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.07 – 8.00 (m, 2H, *C*H, Bz), 7.96 – 7.82 (m, 12H, *C*H, Bz), 7.64 – 6.95 (m, 61H), 5.14 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.01 (d, *J* = 3.6 Hz, 1H, H-1^C), 4.98 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.96 – 4.55 (m, 20H, 4xH-1), 4.54 – 4.23 (m, 14H), 4.20 – 3.61 (m, 27H), 3.45 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.50 (bs, 1H, *O*H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.69 – 1.50 (m, 4H, H-10, 8), 1.39 – 1.23 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.34 (C-12), 165.94, 165.87, 165.35, 165.30, 165.25, 165.19 (C=O, Bz), 137.12, 136.99, 136.83, 136.81, 136.78, 136.75, 136.02, 133.42, 133.29, 133.25, 133.16, 133.02, 130.01, 129.74, 129.64, 129.62, 129.55, 129.51, 129.49, 129.46, 128.56, 128.54, 128.49, 128.47, 128.45, 128.42, 128.40, 128.36, 128.26, 128.19, 128.14, 127.97, 127.89, 127.86, 127.83, 127.81, 127.46, 127.23, 127.18, 127.16 (aromatic C/C*H*), 99.09 (C-1), 98.88 (C-1), 98.76 (C-1), 97.93 (C-1^A), 76.32, 75.29, 75.21, 75.06, 73.31, 73.25, 72.92, 72.79, 72.75, 72.72, 72.44, 72.37, 72.34, 72.26, 72.01 (5 CH_2*Ph*), 68.76, 68.57, 68.16 (C-7), 67.97, 66.08 (CH_2*Ph*), 65.32 (C-4^g), 62.54, 62.11, 61.20, 61.07 (C-6), 60.37, 60.33, 60.20, 59.72, 59.60 (C-2), 34.07 (C-11), 28.93 (C-8), 25.61 (C-9), 24.52 (C-10). MALDI-MS: Calculated for $C_{153}H_{151}N_{21}O_{38}$ $[M+Na]^+$: 2913.0427, found: 2913.0199.

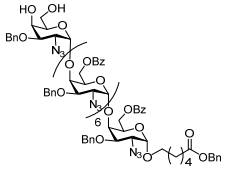
Octasaccharide 51



The reaction was carried out according to the general procedure B. The donor **2b** (1.08 g, 1.77 mmol) and the acceptor **50** (2.05 g, 0.71 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 7 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (6 µl, 0.07 mmol) was added. The reaction was stirred at 0 ºC for

1 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 3:1). Compound **51** (2.07 g, 87% yield, pentane: EtOAc = 2:1, R*f* = 0.55-0.65) was obtained as yellow syrup. $[\alpha]_D^{25}$ +140.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 442, 469, 651, 1003, 1026, 1045, 1063, 1096, 1109, 1156, 1266, 1315, 1452, 1720, 2109, 2862, 2932. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.08 – 8.00 (m, 2H, *C*H, Bz), 7.96 – 7.83 (m, 12H, *C*H, Bz), 7.61 – 6.95 (m, 66H, aromatic H), 5.14 (d, *J* = 3.5 Hz, 1H, H-1^B), 5.07 (s, 2H, *C*H$_2$*Ph*), 5.01 (d, *J* = 3.6 Hz, 1H, H-1^C), 4.98 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.96 – 4.53 (m, 24H, 5xH-1), 4.53 – 3.76 (m, 40H), 3.74 – 3.60 (m, 8H), 3.59 – 3.40 (m, 2H, H-6^H, 7), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.68 – 1.52 (m, 4H, H-10, 8), 1.39 – 1.23 (m, 2H, H-9), 1.02 – 0.85 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.30 (C-12), 165.93, 165.33, 165.28, 165.24, 165.21 (C=O, Bz), 137.72, 136.99, 136.97, 136.82, 136.78, 136.03, 133.42, 133.29, 133.22, 133.14, 129.64, 129.62, 129.59, 129.52, 129.50, 129.47, 128.56, 128.54, 128.49, 128.47, 128.42, 128.40, 128.19, 128.14, 127.87, 127.81, 127.79, 127.52, 127.18, 127.13 (aromatic C/C*H*), 98.84 (C-1), 98.79 (C-1), 97.94 (C-1^A), 75.58, 75.46, 75.29, 75.19, 74.81, 73.25, 72.98, 72.91, 72.82, 72.71, 72.46, 72.36, 72.27, 72.20, 71.95 (5 C*H*$_2$*Ph*), 71.74, 70.27 (C*H*$_2$*Ph*), 69.44, 68.74, 68.56, 68.17 (C-7), 67.62, 66.78 (C-6^H), 66.07 (C*H*$_2$*Ph*), 62.52, 61.20, 61.09 (C-6), 60.34, 59.73, 58.65 (C-2), 34.07 (C-11), 28.94 (C-8), 27.55 (C*H*$_3$), 27.23 (C*H*$_3$), 25.61 (C-9), 24.52 (C-10), 23.26 (C-*Si*), 20.61 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 98.84 ($J_{C1,H1}$ = 171 Hz), 98.79 ($J_{C1,H1}$ = 173 Hz), 97.94 ($J_{C1,H1}$ = 171 Hz). MALDI-MS: Calculated for $C_{174}H_{182}N_{24}O_{42}Si$ $[M+Na]^+$: 3330.2510, found: 3330.2209.

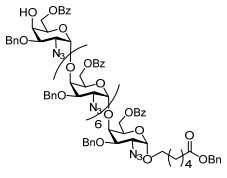
Octasaccharide 52



The reaction was carried out according to the general procedure C using compound **51** (2.0 g, 0.60 mmol) and HF/pyridine (70%, 250 µl, 9.68 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2-1:1). Compound **52** (1.80 g, 91% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +127.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1003, 1027, 1046, 1063, 1112, 1269, 1723, 2109, 2872, 2926, 3457. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.14 – 8.08 (m, 2H, *C*H, Bz), 8.03 – 7.90 (m, 12H, *C*H, Bz), 7.68 – 7.02 (m, 66H, aromatic H), 5.22 (d, *J* = 3.5 Hz, 1H, H-1^B), 5.14 (s, 2H, *C*H$_2$*Ph*), 5.10 (d, *J* = 3.7 Hz, 1H, H-1^C), 5.07 – 4.99 (m, 5H, H-1^A, 1^D, 1^E, 1^F, 1^G), 4.98 – 3.68 (m, 65H, H-1H), 3.58 – 3.41 (m, 3H, H-6^H, 7), 2.90 (bs, 1H, *O*H), 2.37 (t, *J* = 7.4 Hz, 2H, H-11), 1.73 – 1.59 (m, 4H, H-10, 8), 1.47 – 1.32 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.10 (C-12), 165.87, 165.30, 165.25, 165.20, 165.18 (C=O, Bz), 136.97, 136.95, 136.78, 136.73, 136.70, 135.98, 133.34, 133.21, 133.17, 133.07, 129.57, 129.55, 129.50, 129.46, 129.43, 128.49, 128.46, 128.43, 128.41, 128.38, 128.36, 128.34, 128.10, 128.05, 128.01, 127.87, 127.84, 127.80, 127.77, 127.56, 127.23, 127.17, 127.15 (aromatic C/C*H*), 99.35 (C-1), 98.89 (C-1), 98.80 (C-1), 98.69 (C-1), 97.89 (C-1^A), 76.25, 75.36, 75.25, 75.14, 75.08, 75.02, 73.62, 73.22, 72.87, 72.79, 72.75, 72.69, 72.40, 72.32, 72.30, 72.24, 72.18, 72.15, 72.09, 72.01, 71.64 (6 C*H*$_2$*Ph*), 69.50, 68.77, 68.73, 68.54, 67.96 (C-7), 67.24 (C-4^H), 65.85 (C*H*$_2$*Ph*), 62.40, 62.37, 61.05, 60.94,

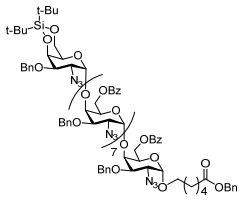
60.91 (C-6), 60.18, 60.00, 59.54, 59.43 (C-2), 33.86 (C-11), 28.72 (C-8), 25.40 (C-9), 24.31 (C-10). MALDI-MS: Calculated for $C_{166}H_{166}N_{24}O_{42}$ $[M+Na]^+$: 3190.1489, found: 3190.1224.

Octasaccharide 53



The reaction was carried out according to the general procedure D using compound **52** (1.49 g, 0.46 mmol), PhCOOBt (601 mg, 2.50 mmol) and Et_3N (380 µl, 2.74 mmol). The product was purified by column chromatography (pentane:EtOAc:DCM = 10:3:2). Compound **53** (1.62 g, 94% yield, pentane:EtOAc:DCM = 5:2:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +118.6 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1003, 1027, 1046, 1063, 1096, 1110, 1156, 1176, 1266, 1315, 1452, 1720, 2106, 2875, 2928. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.06 – 8.00 (m, 2H, *C*H, Bz), 7.95 – 7.82 (m, 14H, *C*H, Bz), 7.60 – 6.94 (m, 69H, aromatic H), 5.15 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.06 (s, 2H, *C*H$_2$*Ph*), 5.03 (d, *J* = 3.6 Hz, 1H, H-1^C), 4.98 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.97 – 4.92 (m, 4H, 4xH-1), 4.91 – 4.55 (m, 19H, H-1H), 4.53 – 4.31 (m, 14H), 4.30 – 4.24 (m, 2H, H-4^A, 4^B), 4.21 – 3.84 (m, 22H), 3.80 (dd, *J* = 10.7, 3.4 Hz, 1H), 3.76 – 3.62 (m, 8H), 3.45 (dt, *J* = 9.9, 6.4 Hz, 1H, H-7), 2.51 (bs, 1H, *O*H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.52 (m, 4H, H-10, 8), 1.38 – 1.25 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.26 (C-12), 165.90, 165.84, 165.32, 165.27, 165.23, 165.18 (C=O, Bz), 137.12, 136.98, 136.81, 136.78, 136.76, 136.74, 136.02, 133.37, 133.23, 133.19, 133.11, 132.97, 129.74, 129.60, 129.58, 129.52, 129.50, 129.47, 128.51, 128.49, 128.46, 128.44, 128.42, 128.39, 128.37, 128.31, 128.22, 128.13, 128.09, 127.93, 127.87, 127.83, 127.81, 127.79, 127.48, 127.27, 127.21, 127.19, 127.17 (aromatic C/C*H*), 99.04 (C-1), 98.83 (C-1), 98.72 (C-1), 97.92 (C-1^A), 76.24, 75.28, 75.17, 75.11, 75.00, 73.26, 72.90, 72.84, 72.78, 72.73, 72.43, 72.36, 72.34, 72.27, 72.23, 71.96 (6 C*H*$_2$*Ph*), 68.77, 68.58, 68.14 (C-7), 68.00, 66.03 (C*H*$_2$*Ph*), 65.37 (C-4^H), 62.55, 62.18, 61.23, 61.10 (C-6), 60.38, 60.34, 60.20, 59.72, 59.60 (C-2), 34.04 (C-11), 28.90 (C-8), 25.58 (C-9), 24.49 (C-10). MALDI-MS: Calculated for $C_{173}H_{170}N_{24}O_{43}$ $[M+Na]^+$: 3294.1751, found: 3294.1474.

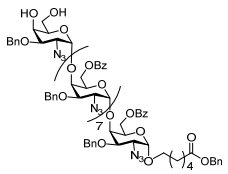
Nonasaccharide 54



The reaction was carried out according to the general procedure B. The donor **2b** (1.08 g, 1.77 mmol) and the acceptor **53** (732 mg, 1.21 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:DCM = 6:1:1). Compound **54** (1.58 g, 89% yield, pentane:EtOAc:DCM = 21:5:5, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +137.3 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 824, 1003, 1027, 1046, 1063, 1098, 1109, 1156, 1266, 1315, 1452, 1721, 2108, 2862, 2932. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.07 – 8.00 (m, 2H), 7.95 – 7.85 (m, 15H), 7.61 – 7.51 (m, 9H), 7.49 – 7.09

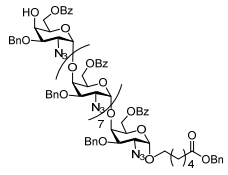
(m, 66H), 7.08 – 6.95 (m, 8H), 5.15 (d, *J* = 3.5 Hz, 1H, H-1^{B}), 5.06 (s, 2H), 5.03 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 5.00 – 4.90 (m, 7H, 7xH-1), 4.90 – 3.75 (m, 68H), 3.73 – 3.61 (m, 10H), 3.55 (d, *J* = 12.4 Hz, 1H), 3.46 (dt, *J* = 9.9, 6.4 Hz, 1H, H-7), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.53 (m, 4H, H-10, 8), 1.38 – 1.27 (m, 2H, H-9), 0.99 – 0.90 (m, 18H, *C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.23 (C-12), 165.89, 165.31, 165.27, 165.22 (C=O, Bz), 137.70, 136.99, 136.95, 136.81, 136.77, 136.03, 133.37, 133.24, 133.20, 133.17, 133.10, 129.60, 129.57, 129.52, 129.48, 128.52, 128.50, 128.47, 128.45, 128.43, 128.39, 128.14, 128.09, 127.88, 127.84, 127.80, 127.76, 127.54, 127.21, 127.18, 127.15 (aromatic C/C*H*), 98.80 (C-1), 98.73 (C-1), 97.94 (C-1^{A}), 75.52, 75.41, 75.29, 75.13, 74.76, 73.25, 72.97, 72.90, 72.82, 72.73, 72.69, 72.45, 72.37, 72.34, 72.26, 72.20, 71.95, 71.77, 70.24, 69.44, 68.75, 68.57, 68.15 (C-7), 67.62, 66.77 (C-6^{I}), 66.02 (C*H*$_2$*Ph*), 62.53, 61.23, 61.11 (C-6), 60.38, 60.35, 60.29, 59.73, 58.65 (C-2), 34.04 (C-11), 28.91 (C-8), 27.53 (C*H*$_3$), 27.21 (C*H*$_3$), 25.59 (C-9), 24.49 (C-10), 23.22 (C-*Si*), 20.59 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 98.80 ($J_{C1,H1}$ = 173 Hz), 98.73 ($J_{C1,H1}$ = 172 Hz), 97.94 ($J_{C1,H1}$ = 172 Hz). MALDI-MS: Calculated for $C_{194}H_{201}N_{27}O_{47}Si$ $[M+Na]^+$: 3711.3835, found: 3711.3517.

Nonasaccharide 55



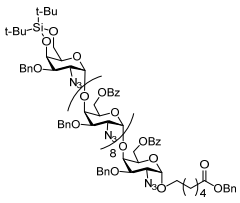
The reaction was carried out according to the general procedure C using compound **54** (1.16 g, 0.31 mmol) and HF/pyridine (70%, 49 µl, 1.89 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2-1:1). Compound **55** (1.04 g, 94% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{25}$ +122.1 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1003, 1027, 1046, 1063, 1098, 1112, 1156, 1268, 1315, 1452, 1721, 2108, 2875, 2928, 3524. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.06 – 8.00 (m, 2H), 7.94 – 7.83 (m, 14H), 7.62 – 7.52 (m, 8H), 7.49 – 7.39 (m, 17H), 7.39 – 7.07 (m, 45H), 7.07 – 6.94 (m, 7H), 5.14 (d, *J* = 3.5 Hz, 1H, H-1^{B}), 5.06 (s, 2H), 5.01 (d, *J* = 3.5 Hz, 1H, H-1^{C}), 4.97 (d, *J* = 3.5 Hz, 1H, H-1^{A}), 4.96 – 4.54 (m, 27H, 6xH-1), 4.51 – 3.61 (m, 53H), 3.45 (dt, *J* = 9.6, 6.4 Hz, 1H, H-7), 3.38 (t, *J* = 5.8 Hz, 2H, H-6^{I}), 2.76 (bs, 1H, *O*H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 2.10 (bs, 1H, *O*H), 1.65 – 1.53 (m, 4H, H-10, 8), 1.38 – 1.27 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.35 (C-12), 165.98, 165.40, 165.35, 165.29 (C=O, Bz), 137.05, 136.88, 136.82, 133.44, 133.26, 133.16, 129.67, 129.64, 129.60, 129.57, 129.53, 128.61, 128.58, 128.50, 128.46, 128.21, 128.19, 128.16, 128.12, 127.99, 127.90, 127.85, 127.65, 127.63, 127.34, 127.32, 127.25, 99.44 (C-1), 98.90 (C-1), 98.79 (C-1), 97.99 (C-1^{A}), 76.38, 75.52, 75.34, 75.22, 73.74, 73.32, 72.91, 72.80, 72.51, 72.41, 72.34, 72.29, 71.83, 69.58, 68.82, 68.63, 68.22 (C-7), 67.53, 66.11 (C*H*$_2$*Ph*), 62.65, 62.59, 61.15 (C-6), 60.42, 60.26, 59.79, 59.68 (C-2), 34.11 (C-11), 28.97 (C-8), 25.65 (C-9), 24.56 (C-10). MALDI-MS: Calculated for $C_{186}H_{185}N_{27}O_{47}$ $[M+Na]^+$: 3571.2814, found: 3571.2493.

Nonasaccharide 56



The reaction was carried out according to the general procedure D using compound **55** (802 mg, 0.23 mmol), PhCOOBt (270 mg, 1.13 mmol) and Et_3N (173 µl, 1.24 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1-3:2). Compound **56** (743 mg, 90% yield, pentane:EtOAc = 3:2, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +128.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 474, 804, 820, 1002, 1026, 1045, 1063, 1096, 1109, 1156, 1176, 1266, 1315, 1452, 1720, 2108, 2873, 2926. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.96 – 7.81 (m, 16H), 7.64 – 6.91 (m, 80H), 5.14 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.07 (s, 2H), 5.01 (d, *J* = 3.6 Hz, 1H, H-1^C), 4.98 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.96 – 3.60 (m, 81H, 6xH-1), 3.45 (dt, *J* = 9.9, 6.5 Hz, 1H, H-7), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.67 – 1.52 (m, 4H, H-10, 8), 1.38 – 1.23 (m, 2H, H-9). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.32 (C-12), 165.94, 165.88, 165.35, 165.30, 165.25, 165.20 (C=O, Bz), 137.13, 137.00, 136.83, 136.81, 136.78, 136.76, 136.03, 133.42, 133.29, 133.24, 133.15, 133.01, 129.75, 129.64, 129.61, 129.55, 129.52, 129.48, 128.56, 128.54, 128.47, 128.42, 128.26, 128.18, 128.14, 127.97, 127.90, 127.86, 127.82, 127.48, 127.26, 127.19, 99.09 (C-1), 98.87 (C-1), 98.76 (C-1), 97.95 (C-1^A), 76.31, 75.30, 75.20, 75.05, 73.32, 73.28, 72.93, 72.86, 72.76, 72.46, 72.38, 72.28, 72.02, 68.76, 68.58, 68.17 (C-7), 67.98, 66.08, 65.36 (C-4^I), 62.55, 62.14, 61.22, 61.08 (C-6), 60.37, 60.22, 59.74, 59.62 (C-2), 34.08 (C-11), 28.94 (C-8), 25.61 (C-9), 24.52 (C-10). MALDI-MS: Calculated for $C_{193}H_{189}N_{27}O_{48}$ $[M+Na]^+$: 3675.3076, found: 3675.2795.

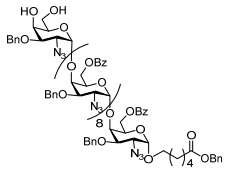
Decasaccharide 57



The reaction was carried out according to the general procedure B. The donor **2b** (327 mg, 0.54 mmol) and the acceptor **56** (690 mg, 0.19 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 3 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (2 µl, 0.02 mmol) was added. The reaction was stirred at 0 ºC for 1 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 3:1). Compound **57** (499 mg, 65% yield, pentane: EtOAc = 2:1, R*f* = 0.55-0.65) was obtained as yellow syrup. $[\alpha]_D^{25}$ +135.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 737, 824, 1003, 1027, 1046, 1063, 1096, 1109, 1156, 1266, 1315, 1452, 1721, 2108, 2859, 2929. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.07 – 8.01 (m, 2H), 7.96 – 7.84 (m, 16H), 7.62 – 7.51 (m, 9H), 7.49 – 7.08 (m, 68H), 7.07 – 6.94 (m, 8H), 5.15 (d, *J* = 3.6 Hz, 1H, H-1^B), 5.07 (s, 2H), 5.02 (d, *J* = 3.6 Hz, 1H, H-1^C), 4.98 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.96 – 3.76 (m, 78H, 7xH-1), 3.73 – 3.60 (m, 10H), 3.54 (d, *J* = 12.4 Hz, 1H), 3.46 (dt, *J* = 9.8, 6.3 Hz, 1H, H-7), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.68 – 1.52 (m, 4H, H-10, 8), 1.38 – 1.27 (m, 2H, H-9), 0.95 (d, *J* = 13.3 Hz, 18H, *C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.11 (C-12), 165.75, 165.17, 165.12, 165.08, 165.06, 165.04 (C=O, Bz), 137.54, 136.83, 136.79, 136.65, 136.61, 135.87, 133.23, 133.10, 133.06, 133.03, 132.96, 129.46, 129.42, 129.37, 129.35, 129.31, 128.38, 128.36, 128.32, 128.30, 128.28, 128.24, 128.22, 128.00, 127.95, 127.73, 127.70, 127.64, 127.62, 127.36, 127.03, 126.98, 98.66 (C-1), 97.78 (C-1^A), 75.39, 75.27, 75.13, 75.00, 74.62,

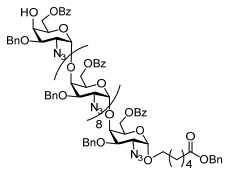
73.10, 72.81, 72.75, 72.67, 72.55, 72.29, 72.20, 72.12, 72.09, 72.04, 71.79, 71.60, 70.10, 69.28, 68.58, 68.41, 68.00 (C-7), 67.45, 66.61 (C-6^{J}), 65.89 (CH_2*Ph*), 62.37, 61.07, 60.94 (C-6), 60.21, 59.57, 58.49 (C-2), 33.89 (C-11), 28.76 (C-8), 27.38 (CH_3), 27.05 (CH_3), 25.44 (C-9), 24.34 (C-10), 23.08 (C-*Si*), 20.44 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 98.66 ($J_{C1,H1}$ = 173 Hz), 97.78 ($J_{C1,H1}$ = 174 Hz). MALDI-MS: Calculated for $C_{214}H_{220}N_{30}O_{52}Si$ $[M+Na]^+$: 4092.5160, found: 4092.4824.

Decasaccharide 58



The reaction was carried out according to the general procedure C using compound **57** (472 mg, 0.12 mmol) and HF/pyridine (70%, 48 µl, 1.85 mmol). The product was purified by column chromatography (DCM:EtOAc = 15:1-10:1). Compound **58** (450 g, 96% yield, pentane:EtOAc = 1:1, R*f* = 0.55-0.65) was obtained as yellow syrup. $[\alpha]_D^{25}$ +122.2 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1005, 1027, 1046, 1065, 1098, 1112, 1269, 1315, 1724, 2109, 2873, 2928, 3502. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.15 – 7.81 (m, 18H), 7.69 – 6.90 (m, 83H), 5.14 (d, *J* = 3.6 Hz, 1H, H-1B), 5.06 (s, 2H), 5.02 (d, *J* = 3.6 Hz, 1H, H-1C), 4.98 (d, *J* = 3.5 Hz, 1H, H-1A), 4.96 – 3.59 (m, 84H, 7xH-1), 3.51 – 3.33 (m, 3H, H-6^{j}, 7), 2.77 (bs, 1H, *O*H), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 2.10 (bs, 1H, *O*H), 1.68 – 1.49 (m, 4H, H-10, 8), 1.38 – 1.21 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.27 (C-12), 165.90, 165.32, 165.27, 165.21 (C=O, Bz), 136.99, 136.81, 136.75, 136.73, 136.02, 133.38, 133.25, 133.20, 133.10, 129.60, 129.58, 129.54, 129.50, 129.46, 128.53, 128.50, 128.47, 128.44, 128.41, 128.39, 128.14, 128.09, 128.05, 127.92, 127.87, 127.84, 127.79, 127.58, 127.25, 127.18, 99.38 (C-1), 98.83 (C-1), 98.73 (C-1), 97.92 (C-1^{A}), 76.30, 75.42, 75.28, 75.17, 75.14, 73.65, 73.25, 72.90, 72.83, 72.73, 72.44, 72.36, 72.34, 72.27, 72.20, 71.71, 69.51, 68.74, 68.56, 68.14 (C-7), 67.44, 66.04 (CH_2*Ph*), 62.58, 62.53, 61.22, 61.08 (C-6), 60.36, 60.18, 59.72, 59.61 (C-2), 34.04 (C-11), 28.90 (C-8), 25.58 (C-9), 24.49 (C-10). MALDI-MS: Calculated for $C_{206}H_{204}N_{30}O_{52}$ $[M+Na]^+$: 3952.4139, found: 3952.3777.

Decasaccharide 59



The reaction was carried out according to the general procedure D using compound **58** (430 mg, 0.11 mmol), PhCOOBt (118 mg, 0.49 mmol) and Et_3N (76 µl, 0.55 mmol). The product was purified by column chromatography (DCM:EtOAc = 10:1). Compound **59** (420 mg, 94% yield, pentane:EtOAc:DCM = 5:2:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{25}$ +135.5 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 737, 1003, 1027, 1046, 1063, 1098, 1112, 1156, 1268, 1315, 1452, 1720, 2108, 2872, 2928. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.09 – 8.00 (m, 2H), 7.97 – 7.82 (m, 18H), 7.60 – 6.94 (m, 87H), 5.14 (d, *J* = 3.6 Hz, 1H, H-1^{B}), 5.06 (s, 2H), 5.02 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 4.98 (d, *J* = 3.5 Hz, 1H, H-1^{A}), 4.96 – 4.55 (m, 29H, 7xH-1), 4.54 – 3.59 (m, 59H), 3.45 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.48 (bs, 1H, *O*H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.53 (m, 4H, H-10, 8), 1.36 – 1.27 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.29 (C-12), 165.91, 165.85, 165.32, 165.27, 165.21, 165.17 (C=O, Bz), 137.11, 136.98, 136.81, 136.79, 136.76, 136.74, 136.01, 133.40, 133.26, 133.22, 133.13, 132.99, 129.73,

129.62, 129.59, 129.53, 129.50, 129.46, 128.54, 128.52, 128.47, 128.45, 128.43, 128.39, 128.24, 128.16, 128.11, 127.94, 127.88, 127.84, 127.80, 127.46, 127.23, 127.16, 99.06 (C-1), 98.85 (C-1), 98.74 (C-1), 97.93 (C-1^{A}), 76.28, 75.28, 75.19, 75.15, 75.03, 73.25, 72.91, 72.83, 72.78, 72.73, 72.44, 72.36, 72.26, 71.99, 68.74, 68.56, 68.15 (C-7), 67.97, 66.05 (CH_2*Ph*), 65.34 (C-4^{J}), 62.53, 62.13, 61.21, 61.06 (C-6), 60.36, 60.20, 59.72, 59.59 (C-2), 34.05 (C-11), 28.92 (C-8), 25.59 (C-9), 24.50 (C-10). MALDI-MS: Calculated for $C_{213}H_{208}N_{30}O_{53}$ $[M+Na]^+$: 4056.4401, found: 4056.4084.

Undecasaccharide 60

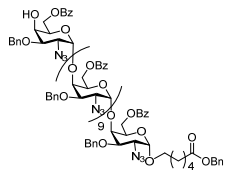
The reaction was carried out according to the general procedure B. The donor **2b** (180 mg, 0.30 mmol) and the acceptor **59** (400 mg, 0.10 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 1 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (1 µl, 0.01 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 (DCM:EtOAc = 20:1). Compound **60** (315 mg, 73% yield, pentane:EtOAc:DCM = 21:5:5, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{25}$ +134.8 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1005, 1046, 1065, 1112, 1269, 1315, 1452, 1724, 2109, 2860, 2931. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.96 – 7.77 (m, 18H), 7.66 – 6.89 (m, 100H), 5.12 (d, *J* = 3.7 Hz, 1H, H-1B), 5.07 (s, 2H), 4.99 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 4.97 (d, *J* = 3.7 Hz, 1H, H-1^{A}), 4.95 – 4.51 (m, 35H, 8xH-1), 4.53 – 3.72 (m, 58H), 3.72 – 3.57 (m, 12H), 3.56 – 3.41 (m, 2H), 2.30 (t, *J* = 5.6 Hz, 2H, H-11), 1.71 – 1.52 (m, 4H, H-10, 8), 1.39 – 1.24 (m, 2H, H-9), 1.01 – 0.85 (m, 18H, *C*H_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.02 (C-12), 165.73, 165.19, 165.15, 165.10 (C=O, Bz), 137.60, 136.90, 136.83, 136.70, 136.65, 135.95, 133.19, 133.06, 133.02, 132.95, 129.46, 129.42, 128.36, 128.34, 128.30, 128.26, 128.24, 128.00, 127.97, 127.92, 127.74, 127.69, 127.60, 127.48, 127.18, 127.09, 98.66 (C-1), 97.83 (C-1^{A}), 75.35, 75.22, 74.96, 74.61, 73.17, 72.73, 72.62, 72.35, 72.25, 72.16, 72.10, 71.85, 71.74, 70.10, 69.37, 68.67, 68.50, 68.02 (C-7), 67.53, 66.66 (C-6^{k}), 65.85 (CH_2*Ph*), 62.45, 61.19, 61.06 (C-6), 60.30, 59.65, 58.57 (C-2), 33.89 (C-11), 28.76 (C-8), 27.42 (CH_3), 27.10 (CH_3), 25.45 (C-9), 24.35 (C-10), 23.07 (C-*Si*), 20.46 (C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 98.66 ($J_{C1,H1}$ = 172 Hz, 171Hz), 97.83 ($J_{C1,H1}$ = 173 Hz). MALDI-MS: Calculated for $C_{234}H_{239}N_{33}O_{57}Si$ $[M+Na]^+$: 4473.6485, found: 4473.6102.

Undecasaccharide 61

The reaction was carried out according to the general procedure C using compound **60** (300 mg, 69 µmol) and HF/pyridine (70%, 29 µl, 1.1 mmol). The product was purified by column chromatography (DCM:MeOH = 150:1). Compound **61** (244 mg, 84% yield, pentane:EtOAc = 1:1, R*f* = 0.25-0.35) was obtained as yellow syrup. $[\alpha]_D^{20}$ +138.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1047, 1112, 1271, 1316, 1452, 1724, 2109,

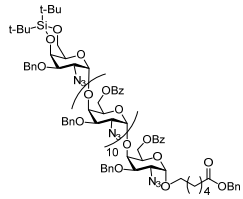
2873, 2929. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.08 – 8.00 (m, 2H), 7.95 – 7.84 (m, *J* = 7.5 Hz, 18H), 7.64 – 7.51 (m, 10H), 7.49 – 7.08 (m, 75H), 7.07 – 6.92 (m, 9H), 5.14 (d, *J* = 3.5 Hz, 1H, H-1^{B}), 5.06 (s, 2H), 5.03 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 5.00 – 3.83 (m, 83H, 9xH-1), 3.79 (dd, *J* = 10.2, 3.0 Hz, 2H), 3.75 – 3.60 (m, 11H), 3.52 – 3.34 (m, 3H), 2.77 (s, 1H), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 2.08 (bs, *O*H), 1.67 – 1.53 (m, 4H, H-10, 8), 1.40 – 1.21 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.25 (C-12), 165.89, 165.32, 165.27, 165.21 (C=O, Bz), 136.99, 136.98, 136.80, 136.74, 136.72, 136.01, 133.36, 133.23, 133.19, 129.59, 129.56, 129.53, 129.49, 129.46, 128.51, 128.49, 128.45, 128.43, 128.40, 128.37, 128.13, 128.08, 128.04, 127.90, 127.86, 127.83, 127.78, 127.58, 127.26, 127.18, 127.17, 99.37 (C-1), 98.82 (C-1), 98.71 (C-1), 97.92 (C-1^{A}), 77.36, 76.28, 75.41, 75.28, 75.14, 73.65, 73.25, 72.83, 72.72, 72.43, 72.35, 72.33, 72.26, 72.19, 71.69, 69.52, 68.75, 68.56, 68.14 (C-7), 67.43 (C-4^{K}), 66.02 (C*H*$_2$*Ph*), 62.58, 62.53, 61.22, 61.09 (C-6), 60.36, 60.18, 59.72, 59.61 (C-2), 34.03 (C-11), 28.89 (C-8), 25.57 (C-9), 24.48 (C-10). MALDI-MS: Calculated for $C_{226}H_{223}N_{33}O_{57}$ $[M+Na]^+$: 4333.5463, found: 4333.5101.

Undecasaccharide 62



The reaction was carried out according to the general procedure D using compound **61** (238 mg, 56.5 µmol), PhCOOBt (61 mg, 0.25 mmol) and Et_3N (39 µl, 0.28 mmol). The product was purified by column chromatography (DCM:Acetone = 200:1-50:1). Compound **62** (227 mg, 93% yield, DCM:Acetone = 50:1, R*f* = 0.30-0.40) was obtained as yellow syrup. $[\alpha]_D^{20}$ +152.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1047, 1098, 1112, 1271, 1315, 1452, 1724, 2111, 2872, 2928, 3510. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.97 – 7.83 (m, 20H), 7.63 – 6.92 (m, 96H), 5.15 (d, *J* = 3.6 Hz, 1H, H-1^{B}), 5.06 (s, 2H), 5.03 (d, *J* = 3.6 Hz, 1H, H-1^{C}), 4.99 – 4.54 (m, 33H, 9xH-1), 4.53 – 3.57 (m, 66H), 3.51 – 3.39 (m, 1H, H-7), 2.30 (t, *J* = 7.4 Hz, 2H, H-11), 1.66 – 1.52 (m, 4H, H-10, 8), 1.38 – 1.28 (m, 2H, H-9). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.26 (C-12), 165.90, 165.85, 165.33, 165.28, 165.22, 165.18 (C=O, Bz), 137.12, 136.99, 136.81, 136.79, 136.76, 136.74, 136.02, 133.37, 133.24, 133.20, 133.11, 132.97, 129.74, 129.61, 129.58, 129.50, 129.47, 128.52, 128.50, 128.47, 128.44, 128.41, 128.38, 128.23, 128.14, 128.09, 127.93, 127.88, 127.84, 127.80, 127.49, 127.26, 127.20, 99.05 (C-1), 98.83 (C-1), 98.72 (C-1), 97.93 (C-1), 76.24, 75.29, 75.15, 75.00, 73.27, 72.91, 72.84, 72.75, 72.44, 72.37, 72.35, 72.27, 72.24, 71.97, 68.76, 68.73, 68.58, 68.15 (C-7), 68.00, 66.03 (C*H*$_2$*Ph*), 65.37 (C-4^{K}), 62.54, 62.18, 61.23, 61.08 (C-6), 60.37, 60.21, 59.73, 59.61 (C-2), 34.04 (C-11), 28.90 (C-8), 25.58 (C-9), 24.49 (C-10). MALDI-MS: Calculated for $C_{233}H_{227}N_{33}O_{58}$ $[M+Na]^+$: 4437.5725, found: 4437.5306.

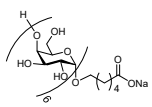
Dodecasaccharide 63



The reaction was carried out according to the general procedure B. The donor **2b** (94 mg, 0.16 mmol) and the acceptor **62** (223 mg, 0.05 mmol) were co-evaporated with toluene (three times). The residue was dissolved in 1 ml dry DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (0.5 µl, 5.2 µmol) was added. The reaction was stirred at 0

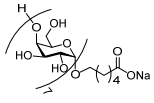
ºC for 1 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (DCM:EtOAc = 20:1). Compound **63** (194 mg, 79% yield, pentane:EtOAc:DCM = 21:5:5, R*f* = 0.35-0.45) was obtained as yellow syrup. $[\alpha]_D^{20}$ +140.7 (c=1, $CHCl_3$). IR (neat, cm^{-1}) ν 1003, 1027, 1046, 1065, 1112, 1269, 1452, 1724, 2109, 2869, 3932. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 8.05 – 7.99 (m, 2H), 7.94 – 7.81 (m, 20H), 7.62 – 7.51 (m, 11H), 7.50 – 6.91 (m, 94H), 5.12 (d, *J* = 3.6 Hz, 1H, H-1B), 5.07 (s, 2H), 4.99 (d, *J* = 3.6 Hz, 1H, H-1C), 4.96 (d, *J* = 3.6 Hz, 1H, H-1A), 4.94 – 4.52 (m, 36H, 9xH-1), 4.51 – 3.72 (m, 60H), 3.70 – 3.57 (m, 12H), 3.56 – 3.49 (m, 1H, H-6^I), 3.45 (dt, *J* = 9.8, 6.4 Hz, 1H, H-7), 2.30 (t, *J* = 7.5 Hz, 2H, H-11), 1.68 – 1.54 (m, 4H, H-10 ,8), 1.38 – 1.26 (m, 2H, H-9), 0.98 – 0.87 (m, 18H, *C*H_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.30 (C-12), 165.93, 165.35, 165.29, 165.25, 165.23 (C=O, Bz), 137.72, 137.00, 136.97, 136.83, 136.78, 136.04, 133.42, 133.29, 133.24, 133.21, 133.14, 129.64, 129.60, 129.52, 129.48, 128.56, 128.54, 128.49, 128.46, 128.42, 128.40, 128.19, 128.14, 127.91, 127.88, 127.81, 127.79, 127.53, 127.19, 127.15, 98.87 (C-1), 98.80 (C-1), 97.95 (C-1A), 77.36, 75.57, 75.46, 75.30, 75.19, 74.81, 73.27, 72.99, 72.93, 72.85, 72.75, 72.70, 72.47, 72.38, 72.29, 72.21, 71.97, 71.77, 70.28, 69.45, 68.75, 68.58, 68.18 (C-7), 67.63 (C-4^I), 66.79 (C-6^I), 66.08 (C*H*$_2$*Ph*), 62.54, 61.22, 61.09 (C-6), 60.38, 59.74, 58.66 (C-2), 34.08 (C-11), 28.94 (C-8), 27.56 (C*H*$_3$), 27.23 (C*H*$_3$), 25.62 (C-9), 24.53 (C-10), 23.26 (C-*Si*), 20.62 (C-*Si*). MALDI-MS: Calculated for $C_{254}H_{258}N_{36}O_{62}Si$ $[M+Na]^+$: 4854.7809, found: 4854.7480.

Hexasaccharide 64



(4.0 mg, 69% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.02 – 4.93 (m, 6H, 6xH-1), 4.41 – 4.33 (m, 4H, H-5), 4.29 (t, *J* = 6.5 Hz, 1H, H-5^B), 4.11 (d, *J* = 2.9 Hz, 4H, H-4), 4.05 (d, *J* = 3.2 Hz, 1H, H-4^B), 4.01 – 3.74 (m, 24H), 3.72 – 3.66 (m, 3H, H-6^F, H-7), 3.52 (dt, *J* = 9.8, 6.1 Hz, 1H, H-7), 2.16 (t, *J* = 7.4 Hz, 2H, H-11), 1.72 – 1.50 (m, 4H, H-8, H-10), 1.43 – 1.28 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 183.95 (C-12), 100.45 (C-1), 100.35 (C-1), 100.28 (C-1), 98.25 (C-1^A), 78.81 (C-4^A), 78.52 (C-4^B), 78.43 (C-4), 71.17 (C-5), 71.03 (C-5), 70.94 (C-5), 69.12, 69.03, 68.90, 68.86, 68.80, 68.73, 68.54, 68.38, 68.29 (C-7), 60.50 (C-6), 60.35 (C-6), 59.87 (C-6), 59.70 (C-6), 37.47 (C-11), 28.35 (C-8), 25.57 (C-10), 25.32 (C-9). HR-MS: Calculated for $C_{42}H_{72}O_{33}$ $[M+H]^+$: 1105.4034, found: 1105.4029.

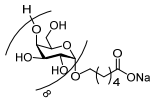
Heptasaccharide 65



(6.0 mg, 75% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.07 – 4.96 (m, 7H, H-1), 4.41 (m, 5H, H-5), 4.32 (t, *J* = 6.5 Hz, 1H, H-5^B), 4.14 (d, *J* = 2.9 Hz, 5H, H-4), 4.09 (d, *J* = 3.1 Hz, 1H, H-4^B), 4.06 – 3.77 (m, 29H), 3.75-3.66 (m, 3H, H-6^G, H-7), 3.56 (dt, *J* = 9.9, 6.2 Hz, 1H, H-7), 2.19 (t, *J* = 7.4 Hz, 11H), 1.71 - 1.52 (m, 4H, H-8, H-10), 1.43 – 1.33 (m, *J* = 6.3 Hz, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 184.06 (C-12), 100.58 (C-1), 100.48 (C-1), 100.41 (C-1), 98.38 (C-1^A), 78.94 (C-4), 78.66 (C-4), 78.58 (C-4), 71.29 (C-5), 71.19 (C-5), 71.13

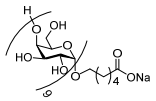
(C-5), 71.09 (C-5), 69.25, 69.17, 69.04, 69.00, 68.94, 68.87, 68.67, 68.52, 68.43 (C-7), 60.65 (C-6), 60.48 (C-6), 60.03 (C-6), 59.86 (C-6), 37.60 (C-11), 28.48 (C-8), 25.69 (C-10), 25.45 (C-9). HR-MS: Calculated for $C_{48}H_{82}O_{38}$ $[M+H]^+$: 1267.4562, found: 1267.4557.

Octasaccharide 66



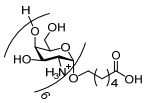
(2.5 mg, 25% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.07 – 4.95 (m, 8H, H-1), 4.40 (q, *J* = 5.9 Hz, 6H, H-5), 4.32 (t, *J* = 6.5 Hz, 1H, H-5^B), 4.18 – 4.11 (m, 6H, H-4), 4.08 (d, *J* = 3.2 Hz, 1H, H-4^B) 4.05 – 3.77 (m, 31H), 3.75 - 3.68 (m, 3H, H-6^H, H-7), 3.55 (dt, *J* = 9.9, 6.2 Hz, 1H, H-7), 2.18 (t, *J* = 7.4 Hz, 2H, H-11), 1.71 - 1.52 (m, 4H, H-8, H-10), 1.41-1.33 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 184.05 (C-12), 100.55 (C-1), 100.45 (C-1), 98.35 (C-1^A), 78.91, 78.62, 78.54, 71.27, 71.14, 71.05, 69.21, 69.13, 69.00, 68.84, 68.64, 68.48, 68.39 (C-7), 60.60 (C-6), 60.45 (C-6), 59.98 (C-6), 59.81 (C-6), 37.57 (C-11), 28.45 (C-8), 25.66 (C-10), 25.42 (C-9). HR-MS: Calculated for $C_{54}H_{92}O_{43}$ $[M+H]^+$: 1429.5091, found: 1429.5085.

Nonasaccharide 67



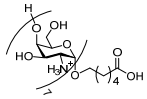
(3.5 mg, 29% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.04 (d, *J* = 4.0 Hz, 9H, H-1), 4.40 (t, *J* = 6.2 Hz, 7H, H-5), 4.32 (t, *J* = 6.5 Hz, 2H, H-5^B), 4.16 – 3.77 (m, 45H), 3.75 – 3.69 (m, 3H, H-6^C, H-7), 3.58 – 3.52 (m, 1H, H-7), 2.18 (t, *J* = 7.4 Hz, 2H, H-11), 1.68 - 1.53 (m, 4H, H-8, H-10), 1.44 - 1.32 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 183.45 (C-12), 100.46 (C-1), 98.37 (C-1), 78.94, 78.57, 71.17, 69.24, 69.04, 68.86, 68.66, 68.51, 68.42, 60.64, 60.47, 60.02, 59.85, 37.59, 28.47, 25.68, 25.44, 23.32. HR-MS: Calculated for $C_{60}H_{102}O_{48}$ $[M+H]^+$: 1591.5619, found: 1591.5613.

Hexasaccharide 68



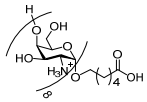
(7.3 mg, 67% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.48-5.31 (m, 5H, H-1), 5.23 (d, *J* = 3.8 Hz, 1H, H-1^A), 4.58 – 4.44 (m, 5H, H-5), 4.35 – 4.11 (m, 13H), 4.10 - 4.02 (m, 3H), 3.95 – 3.54 (m, 24H), 2.41 (t, *J* = 7.3 Hz, 2H, H-11), 1.73 – 1.59 (m, 4H, H-8, H-10), 1.48 - 1.35 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 179.41 (C-12), 96.04 (C-1), 95.95 (C-1), 95.89 (C-1), 95.28 (C-1^A), 76.46 (C-4), 76.31 (C-4), 71.44 (C-5^F), 70.55 (C-5), 70.52 (C-5), 70.44 (C-5), 68.47 (C-7), 67.90, 66.36, 65.99, 65.84, 60.74 (C-6), 60.57 (C-6), 60.34 (C-6), 60.28 (C-6), 51.05 (C-2), 50.91 (C-2), 50.83 (C-2), 33.93 (C-11), 28.28 (C-8), 24.94 (C-10), 24.10 (C-9). HR-MS: Calculated for $C_{42}H_{78}N_6O_{27}$ $[M+2H]^{2+}$: 550.25357, found: 550.25302.

Heptasaccharide 69



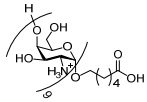
(7.6 mg, 56% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.45 - 5.29 (m, 6H, H-1), 5.21 (d, *J* = 3.8 Hz, 1H, H-1^{A}), 4.56 – 4.41 (m, 6H, H-5), 4.36 – 4.16 (m, 12H), 4.16 – 3.99 (m, 5H), 3.89 – 3.70 (m, 21H), 3.65 (dd, *J* = 11.1, 3.8 Hz, 1H), 3.62 - 3.52 (m, 3H, H-2, H-7), 2.39 (t, *J* = 7.3 Hz, 2H, H-11), 1.72 – 1.58 (m, 4H, H-8, H-10), 1.46 – 1.37 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 179.48 (C-12), 96.03 (C-1), 95.93 (C-1), 95.87 (C-1), 95.26 (C-1^{A}), 76.44 (C-4), 76.29 (C-4), 76.27 (C-4), 71.43 (C-5^{G}), 70.55 (C-5), 70.50 (C-5), 70.45 (C-5), 68.46 (C-7), 67.87, 66.35, 66.31, 65.98, 65.83, 60.71 (C-6), 60.55 (C-6), 60.32 (C-6), 60.25 (C-6), 51.04 (C-2), 50.90 (C-2), 50.81 (C-2), 33.96 (C-11), 28.26 (C-8), 24.93 (C-10), 24.10 (C-9). HR-MS: Calculated for $C_{48}H_{89}N_7O_{31}$ $[M+2H]^{2+}$: 630.78798, found: 630.78743.

Octasaccharide 70



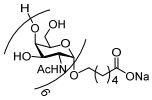
(7.1 mg, 66% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.30 (dd, *J* = 24.1, 3.8 Hz, 7H, H-1), 5.14 (d, *J* = 3.9 Hz, 1H, H-1^{A}), 4.50 - 4.43 (m, 5H), 4.39 (t, *J* = 6.4 Hz, 2H), 4.27 – 4.10 (m, 16H), 4.06 (dd, *J* = 11.0, 3.1 Hz, 2H), 3.98 (dd, *J* = 12.3, 4.2 Hz, 4H), 3.83 – 3.45 (m, 32H), 2.32 (t, *J* = 7.3 Hz, 2H, H-11), 1.65 – 1.51 (m, 4H, H-10, 8), 1.39 – 1.29 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 179.14 (C-12), 95.98 (C-1), 95.90 (C-1), 95.84 (C-1), 95.24 (C-1), 76.41, 76.26, 71.39, 70.49, 70.42, 68.42, 67.85, 66.31, 65.94, 65.79, 65.73, 60.71, 60.52, 60.29, 60.24, 60.20, 51.00, 50.86, 50.78, 33.70 (C-11), 28.24 (C-8), 24.88 (C-10), 23.98 (C-9). HR-MS: Calculated for $C_{54}H_{100}N_8O_{35}$ $[M+3H]^{3+}$: 474.55086, found: 474.55031.

Nonasaccharide 71



(9.0 mg, 55% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.45 – 5.31 (m, 8H, H-1), 5.22 (d, *J* = 3.8 Hz, 1H, H-1), 4.58 – 4.44 (m, 8H), 4.38 – 3.99 (m, 23H), 3.90 – 3.70 (m, 28H), 3.66 (dd, *J* = 11.0, 3.8 Hz, 2H), 3.58 (dt, *J* = 9.7, 3.0 Hz, 3H), 2.40 (t, *J* = 7.3 Hz, 2H, H-11), 1.72 – 1.58 (m, 4H, H-10, 8), 1.47 – 1.37 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 179.65 (C-12), 96.03 (C-1), 95.94 (C-1), 95.27 (C-1), 76.46, 76.29, 71.44, 70.52, 70.46, 68.47, 67.89, 66.36, 65.99, 65.84, 60.73, 60.56, 60.33, 60.27, 51.05, 50.91, 50.83, 34.01 (C-11), 28.27 (C-8), 24.94 (C-10), 24.13 (C-9). HR-MS: Calculated for $C_{60}H_{111}N_9O_{39}$ $[M+3H]^{3+}$: 528.24046, found: 528.23991.

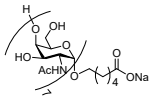
Hexasaccharide 72



(5.0 mg, 44% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.09 – 4.92 (m, 6H, H-1), 4.44 - 4.36 (m, 5H, H-5), 4.35 - 4.36 (m, 4H), 4.26 – 4.20 (m, 2H), 4.19 – 3.99 (m, 13H), 3.76 - 3.62 (m, 13H), 3.53 - 3.45 (m, 1H, H-7), 2.20 (t, *J* = 7.4 Hz, 2H, H-11), 2.13 – 2.02 (m, 18H, *C*H$_3$), 1.64 - 1.52 (m, 4H, H-8, H-10), 1.44 – 1.32 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 183.99 (C-12), 174.75 (C=O, Ac), 174.66 (C=O, Ac), 174.60 (C=O, Ac), 98.42 (C-1), 98.28 (C-1), 96.96 (C-1^{A}), 76.95 (C-4), 76.59 (C-4), 76.39 (C-4), 71.68 (C-5), 71.47 (C-5), 71.38 (C-5), 70.83

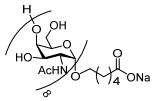
(C-5), 68.38, 68.32 (C-7), 67.30, 67.19, 66.82, 66.74, 66.64, 60.63 (C-6), 60.55 (C-6), 59.73 (C-6), 59.60 (C-6), 50.42 (C-2), 50.30 (C-2), 37.62 (C-2), 28.38 (C-11), 25.66 (C-8), 25.46 (C-10), 22.01 (C-9), 21.97 (CH_3). HR-MS: Calculated for $C_{54}H_{90}N_6O_{33}$ $[M+H]^+$: 1351.5627, found: 1351.5622.

Heptasaccharide 73



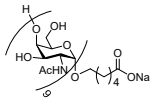
(6.6 mg, 47% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.08 – 4.90 (m, 7H, H-1), 4.46 – 4.33 (m, 6H), 4.33 – 4.25 (m, 5H), 4.24 – 4.18 (m, 3H), 4.18 – 4.08 (m, 9H), 4.07 – 3.96 (m, 7H), 3.80 – 3.57 (m, 17H), 3.52 – 3.45 (m, 1H), 2.18 (t, *J* = 7.4 Hz, 2H), 2.11 – 2.00 (m, 20H), 1.66 – 1.52 (m, 4H), 1.42 – 1.30 (m, 2H). ^{13}C NMR (125 MHz, D_2O) δ 183.97 (C-12), 174.74, 174.65, 174.58 (C=O, Ac), 98.40 (C-1), 98.27 (C-1), 96.95 (C-1), 76.95, 76.57, 76.38, 76.32, 71.65, 71.44, 71.34, 70.79, 68.32, 68.30, 67.27, 67.17, 66.79, 66.71, 66.61, 60.58, 60.53, 59.70, 59.57, 50.39, 50.27, 50.21, 37.60, 28.37, 25.64, 25.45, 22.00, 21.95. HR-MS: Calculated for $C_{62}H_{103}N_7O_{38}$ $[M+H]^+$: 1554.6421, found: 1554.6415.

Octasaccharide 74



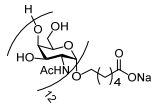
(6.8 mg, 46% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) δ 5.05 – 4.90 (m, 8H, H-1), 4.43 – 4.31 (m, 7H), 4.31 – 4.23 (m, 6H), 4.22 – 4.16 (m, 3H), 4.16 – 4.06 (m, 11H), 4.04 – 3.95 (m, 6H), 3.75 – 3.53 (m, 16H), 3.50 – 3.43 (m, 1H), 2.16 (t, *J* = 7.4 Hz, 2H), 2.08 – 1.98 (m, 24H), 1.64 – 1.50 (m, 4H), 1.39 – 1.29 (m, 2H). ^{13}C NMR (125 MHz, D_2O) δ 183.97 (C-12), 174.70, 174.60, 174.58, 174.53 (C=O, Ac), 98.35 (C-1), 98.24 (C-1), 98.21 (C-1), 96.90 (C-1), 76.89, 76.49, 76.30, 76.23, 71.59, 71.35, 71.26, 70.72, 68.25, 68.23, 67.22, 67.11, 66.73, 66.65, 66.55, 60.49, 59.61, 59.48, 50.31, 50.21, 50.15, 37.56, 28.33, 25.61, 25.41, 21.94, 21.90. HR-MS: Calculated for $C_{70}H_{116}N_8O_{43}$ $[M+H]^+$: 1757.7214, found: 1757.7209.

Nonasaccharide 75



(10 mg, 62% yield). The reaction was carried out according to the general procedure C and E. ^{1}H NMR (500 MHz, D_2O) 5.09 – 4.91 (m, 9H, H-1), 4.47 – 3.93 (m, 39H), 3.78 – 3.57 (m, 21H), 3.54 – 3.45 (m, 1H), 2.18 (t, *J* = 7.4 Hz, 2H), 2.12 – 2.00 (m, 26H), 1.67 – 1.51 (m, 4H), 1.43 – 1.31 (m, 2H). ^{13}C NMR (125 MHz, D_2O) δ 183.97 (C-12), 174.73, 174.64, 174.62, 174.57 (C=O, Ac), 98.40 (C-1), 98.28 (C-1), 96.94 (C-1), 76.94, 76.56, 76.37, 76.31, 71.64, 71.42, 71.33, 70.77, 68.31, 68.29, 67.26, 67.16, 66.78, 66.70, 66.61, 60.56, 60.52, 59.69, 59.55, 50.36, 50.26, 50.20, 37.59, 28.36, 25.64, 25.44, 21.99, 21.95. HR-MS: Calculated for $C_{78}H_{129}N_9O_{48}$ $[M+2H]^{2+}$: 980.90433, found: 980.90377.

Dodecasaccharide 76



(7.2 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 – 4.87 (m, 12H, H-1), 4.43 – 3.92 (m, 49H), 3.74 – 3.54 (m, 25H), 3.50 – 3.42 (m, 1H), 2.15 (t, *J* = 7.4 Hz, 2H, H-11), 2.10 – 1.95 (m, 36H, CH_3), 1.60 – 1.49 (m, 4H, H-10, 8), 1.38 – 1.30 (m, 2H, H-9). ^{13}C NMR (125 MHz, D_2O) δ 183.86 (C-12), 174.60, 174.51, 174.44 (C=O, Ac), 128.71, 128.20, 128.03, 98.26, 98.14, 96.81, 76.80, 76.40, 76.21, 71.50, 71.17, 70.63, 68.16, 68.14, 67.13, 67.02, 66.56, 60.40, 59.52, 59.38, 50.21, 50.12, 50.06, 37.46, 28.24, 25.51, 25.31, 21.85, 21.81. HR-MS: Calculated for $C_{102}H_{168}N_{12}O_{63}$ $[M+2H]^{2+}$: 1285.52338, found: 1285.52283.

References:

[1] N. Singh, D. L. Paterson, *Clin. Microbiol. Rev.* **2005**, *18*, 44-69.

[2] C. D. Lauruschkat, H. Einsele, J. Loeffler, *J. Fungi. (Basel)* **2018**, *4*.

[3] G. D. Brown, D. W. Denning, N. A. Gow, S. M. Levitz, M. G. Netea, T. C. White, *Sci. Transl. Med.* **2012**, *4*, 165rv113.

[4] J. Morgan, K. A. Wannemuehler, K. A. Marr, S. Hadley, D. P. Kontoyiannis, T. J. Walsh, S. K. Fridkin, P. G. Pappas, D. W. Warnock, *Med. Mycol.* **2005**, *43*, 49-58.

[5] C. A. Zacharias, D. C. Sheppard, *Curr. Opin. Microbiol.* **2019**, *52*, 20-26.

[6] C. Speth, G. Rambach, C. Lass-Florl, P. L. Howell, D. C. Sheppard, *Virulence* **2019**, *10*, 976-983.

[7] N. C. Bamford, B. D. Snarr, F. N. Gravelat, D. J. Little, M. J. Lee, C. A. Zacharias, J. C. Chabot, A. M. Geller, S. D. Baptista, P. Baker, H. Robinson, P. L. Howell, D. C. Sheppard, *J. Biol. Chem.* **2015**, *290*, 27438-27450.

[8] M. S. Gresnigt, S. Bozza, K. L. Becker, L. A. Joosten, S. Abdollahi-Roodsaz, W. B. van der Berg, C. A. Dinarello, M. G. Netea, T. Fontaine, A. De Luca, S. Moretti, L. Romani, J. P. Latge, F. L. van de Veerdonk, *PLoS. Pathog.* **2014**, *10*, e1003936.

[9] F. N. Gravelat, A. Beauvais, H. Liu, M. J. Lee, B. D. Snarr, D. Chen, W. Xu, I. Kravtsov, C. M. Hoareau, G. Vanier, M. Urb, P. Campoli, Q. Al Abdallah, M. Lehoux, J. C. Chabot, M. C. Ouimet, S. D. Baptista, J. H. Fritz, W. C. Nierman, J. P. Latge, A. P. Mitchell, S. G. Filler, T. Fontaine, D. C. Sheppard, *PLoS. Pathog.* **2013**, *9*, e1003575.

[10] T. Fontaine, A. Delangle, C. Simenel, B. Coddeville, S. J. van Vliet, Y. van Kooyk, S. Bozza, S. Moretti, F. Schwarz, C. Trichot, M. Aebi, M. Delepierre, C. Elbim, L. Romani, J.-P. Latgé, *PLoS. Pathog.* **2011**, *7*, e1002372.

[11] M. J. Lee, F. N. Gravelat, R. P. Cerone, S. D. Baptista, P. V. Campoli, S. I. Choe, I. Kravtsov, E. Vinogradov, C. Creuzenet, H. Liu, A. M. Berghuis, J. P. Latge, S. G. Filler, T. Fontaine, D. C. Sheppard, *J. Biol. Chem.* **2014**, *289*, 1243-1256.

[12] F. Le Mauff, N. C. Bamford, N. Alnabelseya, Y. Zhang, P. Baker, H. Robinson, J. D. C. Codee, P. L. Howell, D. C. Sheppard, *J. Biol. Chem.* **2019**, *294*, 10760-10772.

[13] N. C. Bamford, F. Le Mauff, A. S. Subramanian, P. Yip, C. Millan, Y. Zhang, C. Zacharias, A. Forman, M. Nitz, J. D. C. Codee, I. Uson, D. C. Sheppard, P. L. Howell, *J. Biol. Chem.* **2019**, *294*, 13833-13849.

[14] E. D. Kazakova, D. V. Yashunsky, V. B. Krylov, J. P. Bouchara, M. Cornet, I. Valsecchi, T. Fontaine, J. P. Latge, N. E. Nifantiev, *J. Am. Chem. Soc.* **2020**, *142*, 1175-1179.

[15] N. Yagami, A. Imamura, *Rev. Agric. Sci.* **2018**, *6*, 1-20.

[16] A. Imamura, N. Matsuzawa, S. Sakai, T. Udagawa, S. Nakashima, H. Ando, H. Ishida, M. Kiso, *J. Org. Chem.* **2016**, *81*, 9086-9104.

[17] M. Kiso, A. Imamura, H. Ando, H. Ishida, *Heterocycles* **2008**, *76*.

[18] A. Imamura, A. Kimura, H. Ando, H. Ishida, M. Kiso, *Chemistry* **2006**, *12*, 8862-8870.

[19] A. Imamura, H. Ando, H. Ishida, M. Kiso, *Org. Lett.* **2005**, *7*, 4415-4418.

[20] A. Imamura, H. Ando, S. Korogi, G. Tanabe, O. Muraoka, H. Ishida, M. Kiso, *Tetrahedron Lett.* **2003**, *44*, 6725-6728.

[21] N. Hada, J. Oka, A. Nishiyama, T. Takeda, *Tetrahedron Lett.* **2006**, *47*, 6647-6650.

[22] G. Hum, K. Wooler, J. Lee, S. D. Taylor, *Can. J. Chem.* **2000**, *78*, 642-655.

[23] B. Hagen, J. H. M. van Dijk, Q. Zhang, H. S. Overkleeft, G. A. van der Marel, J. D. C. Codee, *Org. Lett.* **2017**, *19*, 2514-2517.

[24] S. Kim, H. Chang, W. J. Kim, *J. Org. Chem.* **1985**, *50*, 1751-1752.

[25] A. Arda, J. Jimenez-Barbero, *Chem. Commun. (Camb)* **2018**, *54*, 4761-4769.

[26] T. Aeschbacher, M. Zierke, M. Smiesko, M. Collot, J. M. Mallet, B. Ernst, F. H. Allain, M. Schubert, *Chem. Eur. J.* **2017**, *23*, 11598-11610.

[27] M. Zierke, M. Smiesko, S. Rabbani, T. Aeschbacher, B. Cutting, F. H. Allain, M. Schubert, B. Ernst, *J. Am. Chem. Soc.* **2013**, *135*, 13464-13472.

[28] E. R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garcia, A. J. Cohen, W. Yang, *J. Am. Chem. Soc.* **2010**, *132*, 6498-6506.

[29] K. Bock, J. Ø. Duus, *J. Carbohydr. Chem.* **2006**, *13*, 513-543.

[30] D. A. Case, T. E. Cheatham, 3rd, T. Darden, H. Gohlke, R. Luo, K. M. Merz, Jr., A. Onufriev, C. Simmerling, B. Wang, R. J. Woods, *J. Comput. Chem.* **2005**, *26*, 1668-1688.

[31] R. Stenutz, I. Carmichael, G. Widmalm, A. S. Serianni, *J. Org. Chem.* **2002**, *67*, 949-958.