Chemical synthesis of fragments of galactosaminogalactan and pel polysaccharides

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Chapter 5

Assembly of a library of Pel oligosaccharides featuring α-glucosamine and α-galactosamine linkages

Introduction

Pseudomonas aeruginosa is an opportunistic Gram-negative pathogen that can cause both acute and chronic infections in immunocompromised patients.[1-6] *P. aeruginosa* can become resistant to antibiotics due to its ability to form biofilm which complicates the treatment of its infections. As part of the biofilm formation three exopolysaccharides are synthesized, alginate, Pel and Psl.[4] Alginate is a negatively charged polymer of mannuronic and guluronic acid,[7] while Psl is a neutral polysaccharide composed of a pentasaccharide repeat containing glucose, rhamnose and mannose.[8] Pel is a positively charged polymer, and although its structure has not been fully characterized it is thought to be composed of α-1,4-linked *N*-acetylgalactosamine (GalNAc) and *N*-acetyl-glucosamine (GlcNAc), both of which also can be de-acetylated to give galactosamine (GalN) and glucosamine (GlcN) residues,

respectively (Figure 1A). The GalN(Ac) : GlcN(Ac) ratio has been reported to be ± 6:1. Pel plays an important role in maintaining cell-cell interactions in biofilms and affords protection to the bacterium by enhancing resistance to aminoglycoside antibiotics.[9] Well-defined fragments of the Pel polymer can serve as powerful research tools in various interconnected fields of research. They may serve as synthetic antigens in the generation of potential Pseudomonas vaccines and they can be used in elucidating biosynthesis pathways and charactering the enzymes involved therein. This may open up avenues to interfere with the biosynthesis and eventually generate anti-bacterial compounds. Because of the seemingly random distribution of monosaccharides in Pel, it is impossible to isolate well defined fragments from natural sources and therefore organic synthesis is the method of choice to provide these.

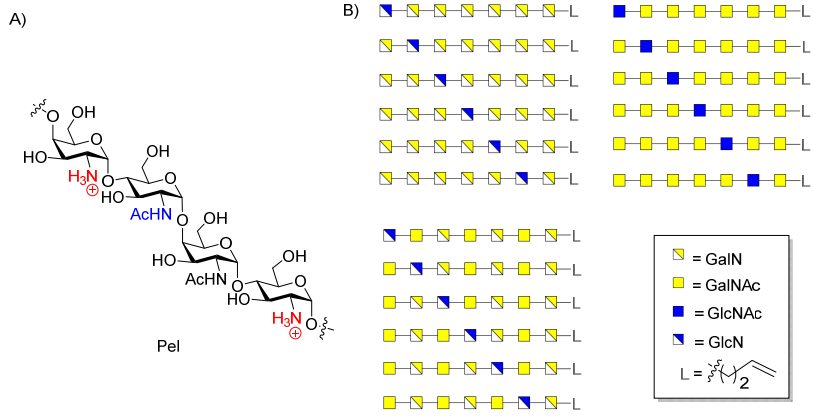


Figure 1. A) Structure of Pel. B) Structures of designed Pel oligomers.

The key to the assembly of Pel fragments is the stereoselective introduction of α-GalN, α-GalNAc, α-GlcN and α-GlcNAc linkages. The Chapters 2, 3 and 4 described the successful application of the 4,6-*O*-DTBS directed α-galactosylation methodology, developed by Kiso's group[10-15], for the synthesis of galactosaminogalactan (GAG) homo- and hetero-oligosaccharides, occurring in the cell wall of *Aspergillus fumigatus*. Application of 4,6-*O*-DTBS protected $GalN_3$ and GalNHTCA donors resulted in glycosylations with high α-stereoselectivity to give a row of GAG fragments, composed of GalN and GalNAc. The high α-stereoselectivity proved to be insensitive with respect to the nature of a C-2-*N*-acyl group, capable of neighboring group participation. On the basis of these results, DTBS-protected GalN donors were chosen as building blocks for the construction of α-GalN and α-GalNAc linkages in Pel.

The formation of similar α-GlcN linkages is more challenging and substantial effort has been expended to develop a procedure for the stereoselective introduction of α-GlcN linkages.[16-26] Recently, Wang *et al.* have reported an effective synthetic strategy to assemble Pel fragments containing 1,4-linked GalNAc and GlcNAc residues.[14] A [2+2+2] strategy was developed for the synthesis of a hexasaccharide in which the α-GlcN linkages were constructed *via* *N*-methyl-*N*-phenylformamide (MPF)-modulated glycosylation methodology. Furthermore, a set of glycosylation reactions between a series of 4,6-tethered glucosazide donors and a panel of acceptors were systematically evaluated by van der Vorm *et al*.[16] They reported that with the increasing reactivity of donors and decreasing nucleophilicity of acceptors, the α-selectivity of the glycosylations increased. Reaction of the most reactive DTBS-protected $GlcN_3$ donor with the acceptor trifluoroethanol (TFE) gave the α-linked product exclusively. As the nucleophilicity of the C-4-OH in GalN moieties is relatively low, the DTBS-$GlcN_3$ donors represent promising building blocks for the construction of α-GlcN-(1→4)-GalN linkages.

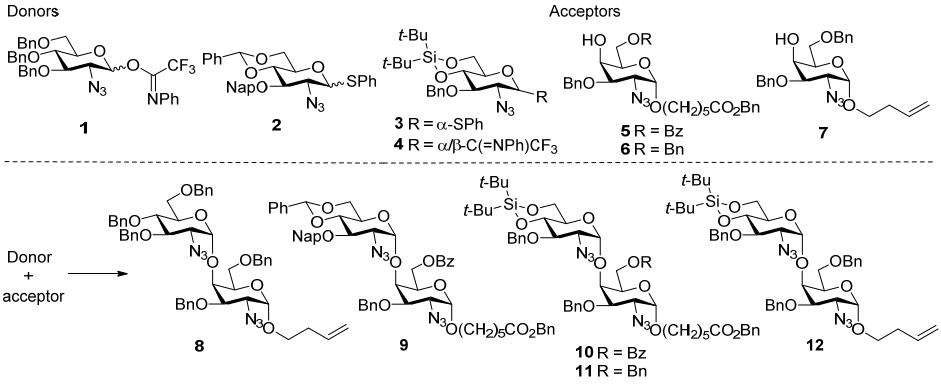
This chapter describes the synthesis of a library of Pel fragments with DTBS-directed glycosylation methodology. A library of hetero-oligomers containing α-GalN/α-GalNAc and α-GlcN/α-GlcNAc residues at predetermined positions, was designed (Figure 1B). A set of heptamers, each of which contains one GlcN/GlcNAc and six GalN/GalNAc residues, was selected because of the ±6:1 GalNAc:GlcNAc ratio that is present in naturally occurring Pel polysaccharides, while some of the residues have been deacetylated.[1] Also a spacer was incorporated at the reducing end of the heptamers for future conjugation purposes.

Results and discussion

As the DTBS-directed α-galactosylation methodology is well established, attention was first paid to the formation of α-$GlcN_3$-(1→4)-$GalN_3$ linkages. A set of glycosylation reactions was investigated using $GlcN_3$ donors **1**-**4** and $GalN_3$ acceptors **5**-**7** (Table 1). First, the additive *N*-methyl-*N*-phenylformamide (MPF) controlled α-glycosylation methodology was attempted to introduce the α-GlcN linkage. With this methodology, glycosylation of benzylated $GlcN_3$ donor **1** with benzylated $GalN_3$ acceptor **7** led to the disaccharide **8** with 7:1 α/β-selectivity, but the yield was only 47% (Table 1, entry 1). Using the same conditions, coupling of 4,6-DTBS-tethered $GlcN_3$ donor **4** with $GalN_3$ **7** afforded the dimer in only 5% yield (entry 2), owing to the low reactivity of C4-OH in $GalN_3$ acceptor. Next, a pre-activation strategy, using thioglucosides **2** and **3** as donors was explored. Benzylidene-protected donor **2** reacted with acceptor **5**, at -78 ^{o}C to -40 ^{o}C to afford disaccharide **9** in 38% yield and with a 3.5/1 α/β ratio (entry 3). When the more reactive DTBS-protected donor **3**

was treated with **5**, a slightly better α-selectivity was obtained (α/β = 5/1, entry 4). Surprisingly, condensation of donor **3** with 6-O-Bn substituted acceptor **6** led to **11** in excellent yield and α-selectivity (entry 5). By contrast, changing the linker of the acceptor to 3-buten-ol, which is more convenient for future conjugation, gave no glycosylation product (entry 6). Condensation of $GlcN_3$ donor **3** and acceptor **7**, promoted by NIS and TfOH at -40 °C, also failed to afford the product (entry 7). To further improve the reaction, the imidate donor **4** was coupled with acceptor **5**, under influence of TBSOTf, giving dimer **10** with moderate α-selectivity (α/β = 3.7/1, entry 8). Gratifyingly, performing the glycosylation of donor **4** and acceptor **7**, at -10 °C with TfOH as promotor, furnished the desired disaccharide **12** in 77% yield and with excellent α-selectivity (>20:1, entry 9). Based on these model reactions, the DTBS-tethered $GlcN_3$ donor **4** was chosen for the construction of α-$GlcN_3$-(1→4)-$GalN_3$ linkages, and the benzyl group was preferred for the protection of C6-OH in GalN acceptors. Of note, the implementation of this strategy would match exceptionally well with the strategy developed for the introduction of the α-GalN linkages in the target compounds.

Table 1. Glycosylation between $GlcN_3$ donors and $GalN_3$ acceptors.



Ent.	Don.	Acc.	Reagents and conditions	Temp.	Pro.	α/β	Yield
1	**1**	**7**	TfOH, MPF, DCM	-78 to 0 °C	**8**	7/1	47%
2	**4**			-78 to 0 °C	**12**	>10/1	5%
3	**2**	**5**	Tf_2O, Ph_2SO, TTBP, DCM	-78 to -40 °C	**9**	3.5/1	38%
4	**3**	**5**		-40 °C	**10**	5/1	65%
5		**6**		-40 °C	**11**	13/1	81%

6		**7**		-40 °C	**12**	-	-
7	**3**	**7**	NIS, TfOH, DCM	-40 °C to 0 °C	**12**	-	-
8	**4**	**5**	TBSOTf, DCM	-78 to -40 °C	**10**	3.7/1	62%
9		**7**	TfOH, DCM	-10 °C	**12**	>20/1	77%

With conditions in hand to construct the required α-GalN and α-GlcN linkages, attention was directed to the assembly of a library of Pel heptamers, consisting of (3x6) members, that can be made available by the synthesis of six protected heptameric precursors and subjecting these to different deprotection procedures. The projected eighteen heptamers contain one GlcN or GlcNAc, differently positioned in the heptameric chain, while the remaining residues are all GalN, all GalNAc or alternating GalN and GalNAc (Figure 1B). The retrosynthesis of Pel heptamers **A-C** with either GlcN or GlcNAc at second position from the reducing end of the heptamer chain is depicted in Figure 2. This retrosynthesis also applies to the remaining members of the projected library that can be accessed using the same strategy. The deprotected heptamers **A**-**C** are derived from protected heptamer **D** through different procedures for the removal of the protecting groups. In path a, the sequence of deprotection steps include DTBS removal, reduction of azido groups, and removal of Bn and TFA groups via Birch reduction to afford compound **A**, containing GalN and GlcN residues. Birch reduction is chosen to avoid reduction of C-C double bond in the linker.[27] Acetylation of free amine groups in **A** can furnish heptamer **B**. In path b, the C2-N-TFA groups are first removed, followed by desilylation and acetylation of the released amino groups, after which reduction the amino and Bn groups should give the heptamer **C**. The common protected heptamer **D** can be constructed with $GlcN_3$ donor **4**, $GalN_3$ donor **13** and GalNHTFA donor **14**, which would serve as precursors for GlcN, GlcNAc, GalN and GalNAc separately.

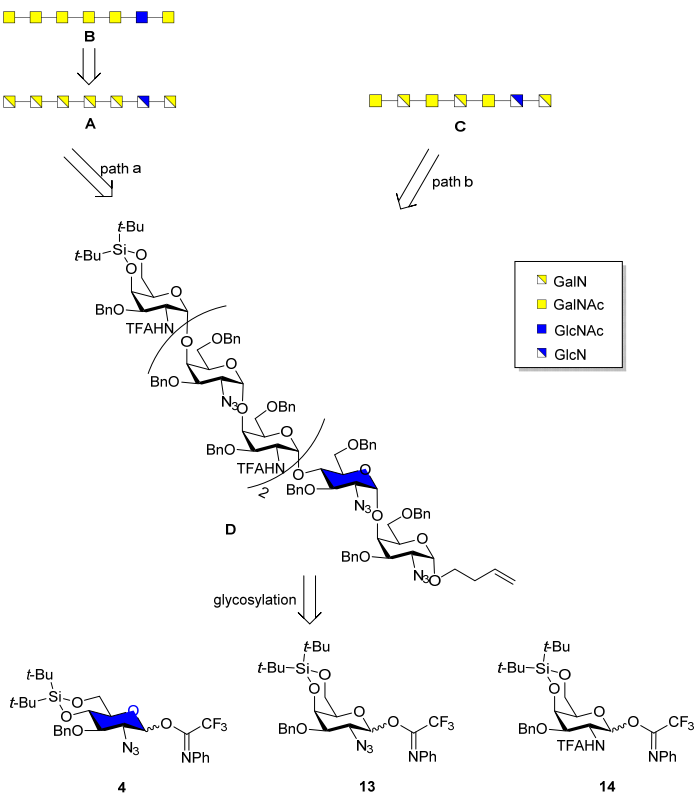


Figure 2. Retrosynthetic analysis of Pel heptasaccharides

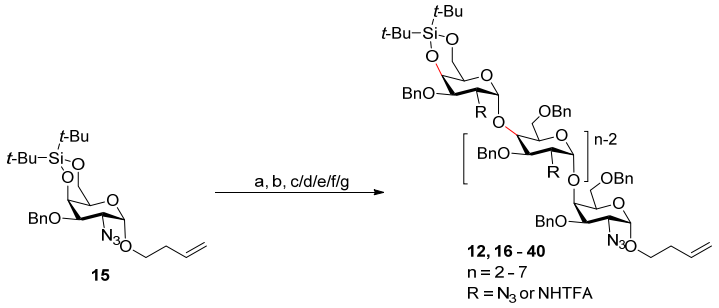
Table 2 summarizes the syntheses of the six fully protected Pel heptasaccharides (**20**, **26**, **31**, **35**, **38**, **40**) with one $GlcN_3$ residue at different positions. The elongation cycle consisted of the following three-steps: 1) glycosylation using the donor of choice, 2) DTBS-removal with HF/pyridine and 3) selective benzylation of the primary alcohol group. The Bn group can be regioselectively introduced under the aegis of Taylor's borinic acid catalyst.[28-30]

As can be seen from the table, the heptasaccharide **20** (or E in Figure 2) with $GlcN_3$ moiety at the second position from the reducing end of the heptamer chain was first synthesized. The acceptor **7** was obtained from **15** through desilylation and regioselective C6-OH benzylation. Condensation of $GlcN_3$ donor **4** and acceptor **7** led to the disaccharide **12** using TfOH promoted condensation at -10 °C, then the DTBS group was cleaved and the liberated 6-OH was benzylated selectively to form the desired 4-OH acceptor, which was reacted with GalNHTFA donor **14** giving the trisaccharide **16** with 73% yield for over three steps. However, the relatively moderate yield of the glycosylation for the tetra- and pentamer (56%

for **17** and 51 % for **18**) was an incentive to optimize the glycosylation reaction conditions. It was found that implementation of a "reverse addition sequence" strategy, in which the acceptor and activator are mixed, after which the donor is slowly added, greatly improved the reaction yields (71% for **17** and 72% for **18**). Elongation of the pentamer with another copy of the $GalN_3$ donor **13** and subsequently the GalNHTFA building block **14**, delivered heptasaccharide **20** in excellent yields.

In an analogous way, the assembly of target heptasaccharides **26**, **31**, **35**, **38** and **40** with $GlcN_3$ moiety at the positions 3-7 was accomplished with building blocks **4**, **13** and **14**. Repetition of the elongation cycle, comprising the same three steps as described above led to all target heptasaccharides. The glycosylation reactions proceeded efficiently providing the intermediate and target oligosaccharides (n = 2-7) with excellent stereoselectivity and good yields (50-79% yields for three steps). The mixed sequence structures were generated uneventfully, showing the chemistry developed to be applicable to any type of Pel-target.

Table 2. Synthesis of Pel oligomers



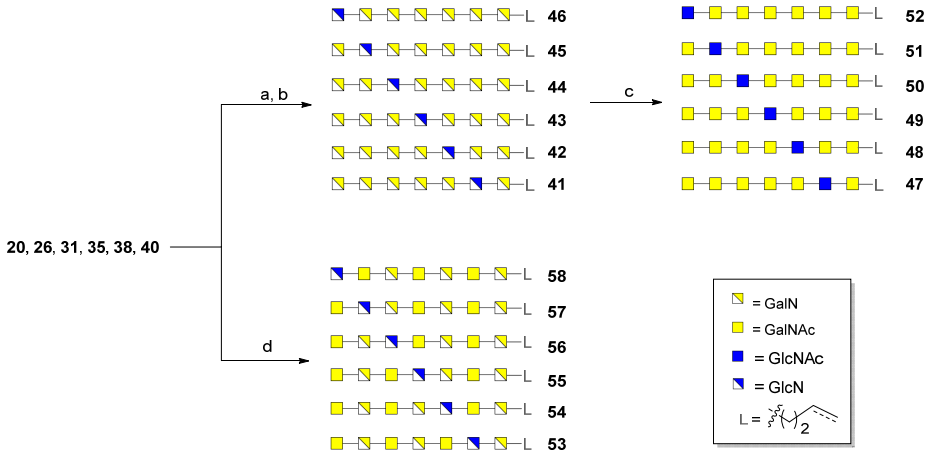
n	$(GluR)_m$ $GalN_3$	Yield[h]
2	$GlcN_3$ $GalN_3$	**12** (71%)[c]
3	GalNHTFA $GlcN_3$ $GalN_3$	**16** (73%)[e]
4	$GalN_3$ GalNHTFA $GlcN_3$ $GalN_3$	**17** (56%)[d] (71%)[f]
5	GalNHTFA $GalN_3$ GalNHTFA $GlcN_3$ $GalN_3$	**18** (51%)[e] (72%)[g]
6	$GalN_3$ GalNHTFA $GalN_3$ GalNHTFA $GlcN_3$ $GalN_3$	**19** (69%)[f]
7	GalNHTFA $GalN_3$ GalNHTFA $GalN_3$ GalNHTFA $GlcN_3$ $GalN_3$	**20** (67%)[g]
2	GalNHTFA $GalN_3$	**21** (79%)[e]
3	$GlcN_3$ GalNHTFA $GalN_3$	**22** (74%)[c]
4	$GalN_3$ $GlcN_3$ GalNHTFA $GalN_3$	**23** (68%)[f]
5	GalNHTFA $GalN_3$ $GlcN_3$ GalNHTFA $GalN_3$	**24** (78%)[g]
6	$GalN_3$ GalNHTFA $GalN_3$ $GlcN_3$ GalNHTFA $GalN_3$	**25** (68%)[f]
7	GalNHTFA $GalN_3$ GalNHTFA $GalN_3$ $GlcN_3$ GalNHTFA $GalN_3$	**26** (76%)[g]

3	$GalN_3$ GalNHTFA $GalN_3$	**27** (79%)[f]
4	$GlcN_3$ $GalN_3$ GalNHTFA $GalN_3$	**28** (73%)[c]
5	GalNHTFA $GlcN_3$ $GalN_3$ GalNHTFA $GalN_3$	**29** (70%)[g]
6	$GalN_3$ GalNHTFA $GlcN_3$ $GalN_3$ GalNHTFA $GalN_3$	**30** (73%)[f]
7	GalNHTFA $GalN_3$ GalNHTFA $GlcN_3$ $GalN_3$ GalNHTFA $GalN_3$	**31** (74%)[g]
4	GalNHTFA $GalN_3$ GalNHTFA $GalN_3$	**32** (66%)[g]
5	$GlcN_3$ GalNHTFA $GalN_3$ GalNHTFA $GalN_3$	**33** (74%)[c]
6	$GalN_3$ $GlcN_3$ GalNHTFA $GalN_3$ GalNHTFA $GalN_3$	**34** (56%)[f]
7	GalNHTFA $GalN_3$ $GlcN_3$ GalNHTFA $GalN_3$ GalNHTFA $GalN_3$	**35** (52%)[g]
5	$GalN_3$ GalNHTFA $GalN_3$ GalNHTFA $GalN_3$	**36** (74%)[f]
6	$GlcN_3$ $GalN_3$ GalNHTFA $GalN_3$ GalNHTFA $GalN_3$	**37** (77%)[c]
7	GalNHTFA $GlcN_3$ $GalN_3$ GalNHTFA $GalN_3$ GalNHTFA $GalN_3$	**38** (50%)[g]
6	GalNHTFA $GalN_3$ GalNHTFA $GalN_3$ GalNHTFA $GalN_3$	**39** (67%)[g]
7	$GlcN_3$ GalNHTFA $GalN_3$ GalNHTFA $GalN_3$ GalNHTFA $GalN_3$	**40** (60%)[c]

a) HF/pyridine, THF, 0 °C to rt. b) $Ph_2BO(CH_2)_2NH_2$, KI, K_2CO_3, BnBr, MeCN, 60 °C. c) **4**, TfOH, 4Å MS, DCM, -10 °C. d) **13**, TfOH, 4Å MS, DCM, 0 °C. e) **14**, TfOH, 4Å MS, DCM, 0 °C. f) TfOH, 4Å MS, DCM, then **13** added in 1h, 0 °C for 3, 4 and 5-mers, -20 °C for 6 and 7-mers. g) TfOH, 4Å MS, DCM, then **14** added in 1h, 0 °C for 4 and 5-mers, -20 °C for 6 and 7-mers. h) yields for over three steps.

With all six protected heptasacharides in hand deprotection conditions were developed to complete the assembly of all projected Pel oligomers (Scheme 1). First, the set of 7-mers containing solely α-GalN and α-GlcN moieties was generated. Removal of the DTBS-group in heptamers **20**, **26**, **31**, **35**, **38** and **40** was performed with HF/pyridine and the azido-groups could be reduced with $HS(CH_2)_3SH$, after which the Bn groups together with the TFA groups were cleaved using sodium in ammonia and THF, affording the 7-mers **41**-**46** in 48%-85% yields. In the Birch reduction, allyl carbinol was used as a scavenger to prevent reduction of the C-C double bond. A portion of the 7-mers **41**-**46** was chemoselectively acetylated to provide the second set of heptamers **47**-**52**, composed of α-GalNAc and α-GlcNAc moieties. Furthermore the heptamers **20**, **26**, **31**, **35**, **38** and **40** were transformed into the third set of GalN-, GalNAc and GlcN- containing heptamers **53**-**58**. Similar to the first series, silylidene groups were first removed. However, the TFA groups could not be cleaved even with strong basic conditions and high temperature (4M NaOH, 80 °C). Also attempts to remove the TFA groups with the assistance of microwave failed (see experimental section table S1). A solution for this problem was found by first removing the benzyl ethers and concomittant reduction of the azido groups, followed by temporily protection of the generated free amino groups with Boc groups. At this stage the TFA groups could be removed with $NH_3{\cdot}H_2O$ at

60 °C, after which acetylation of generated amines and subsequent removal of Boc groups with 30% TFA provided the heptamers **53**-**58** in 18%-31% yields.



Scheme 1. Deprotection of synthetic Pel heptasaccharides. a) i) HF/pyridine, THF, rt; ii) $HS(CH_2)_3SH$, Et_3N, pyridine/H_2O, rt. b) Na, NH_3 (liq.), THF, t-BuOH, 3-buten-1-ol, -78 °C, yields for **41**: 69% (12/1 with:without C=C); **42**: 48% (23/1); **43**: 84% (19/1); **44**: 53% (50/1); **45**: 59% (25/1); **46**: 85% (43/1). c) Ac_2O, H_2O, $NaHCO_3$, rt, yields for **47**: 90%; **48**: 91% (11/1); **49**: 91% (32/1); **50**: 90% (32/1); **51**: 89% (21/1); **52**: 88% (12/1). d) i) HF/pyridine, THF, rt; ii) $Pd(OH)_2/C$, H_2, AcOH, THF/t-BuOH/H_2O, rt; iii) Boc_2O, $NaHCO_3$, H_2O, rt; iv) $NH_3 \cdot H_2O$, 60 °C; v) Ac_2O, $NaHCO_3$, H_2O, rt; vi) 30% TFA in H_2O, L = $(CH_2)_3CH_3$, yields for **53**: 31%; **54**: 25%; **55**: 24%; **56**: 18%; **57**: 30%; **58**: 18%.

In addition to the three sets of heptamers obtained above, another set composed of GalN, GalNAc and GlcNAc residues can be produced by desilylation, reduction of the azides to the amines, chemoselective acetylation of these groups to provide the acetamides, and Birch reduction to remove the banzyl and TFA-groups. Using this strategy, **35** and **38** were brought to the end stage to furnish compounds **59** and **60** containing α-GalN, α-GalNAc and α-GlcNAc moieties (Scheme I).

Scheme I: Synthesis of heptamers **59** and **60**. Reagents and conditions: i) HF/pyridine, THF, rt; ii) $HS(CH_2)_3SH$, Et_3N, pyridine/H_2O, rt; iii) Ac_2O, $NaHCO_3$, H_2O/THF, rt; iv) Na, NH_3 (liq.), THF, t-BuOH, 3-buten-1-ol, -78 °C, yields for **59**: 62%; **60**: 77%.

Conclusion

In conclusion, synthetic methodology enabling the assembly of Pel fragments has been developed. Key features of the synthetic strategy include the use of DTBS-directed α-glycosylation methodology and a regioselective benzylation procedure. The DTBS-directed glycosylation was not only successfully applied for the construction of α-$GalN_3$ and α-GalNTFA linkages, as already described in previous Chapters, it also proved applicable for the synthesis of α-$GlcN_3$ linkages. With the increasing length of the oligosaccharides, the glycosylation yields decreased significantly, owing to the reduced nucleophilicity of the acceptors. Application of a reverse-addition-sequence strategy adequately improved the yields of the glycosylations providing the longer oligosaccharides in good yield. Six protected heptamers with different composition were subjected to different deprotection protocols, providing three sets of heptamers; α-GlcN-α-GalN; α-GlcNAc-α-GalNAc and α-GlcN-α-GalNAc-α-GalN. Unexpectedly, it proved impossible to effectively remove the *N*-TFA groups in the heptamers carrying benzyl protecting groups. Fortunately, a protocol in which the benzyl and azide groups were first reduced, after which the liberated amines were temporarily masked with the use of Boc protection, allowed for removal of the TFA groups, using aqueous ammonia hydroxide. The synthetic Pel heptamers will be valuable for the studies of their biosynthesis and the development of vaccines against *P. aeruginosa*.

Experimental section

General procedure for glycosylation with imidate donors 4, 13 and 14 (procedure A)

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

General procedure for glycosylation with imidate donors 13 and 14 (Reverse-addition sequence, procedure B)

The acceptor (1.0 eq) was co-evaporated with toluene (three times), and 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 solution of donor (1.5 -4.0 eq) in dry DCM was added slowly into the reaction mixture within 1 hour. 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).

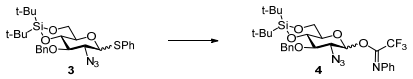
General procedure for the deprotection of di-*tert*-butyl silylidene group (general procedure C)

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 benzylation of primary alcohol (general procedure D)

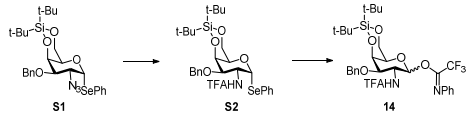
K_2CO_3 (1.1 eq), KI (1.5 eq) and $Ph_2BO(CH_2)_2NH_2$ (0.1-0.2 eq) were added to the solution of starting material in MeCN (0.05 M). Then BnBr was added in the solution. The reaction was allowed to stirred at 60 ºC until TLC-analysis showed complete conversion of the starting material. Then reaction was quenched with H2O after completed checking by TLC, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (See experimental description below for eluent system).

Experimental Procedures and Characterization Data of Products



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

NIS (525 mg, 2.33 mmol) was added to the solution of compound **3**[16](820 mg, 1.55 mmol) in Acetone/H_2O (16 ml/1.6 ml) 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 S1 was purified by silica gel column chromatography (pentane:EtOAc = 8:1). Cs_2CO_3 (440 mg, 1.35 mmol) was added to the solution of the residue in 15 ml acetone. The mixture was stirred at 0 ºC for 15 minutes. Then $CF_3C(=NPh)Cl$ (420 mg, 2.03 mmol) was added to the solution. which was slowly warmed to room temperature and stirred overnight. The reaction was quenched with Et_3N and concentrated *in vacuo*. The product **4** was purified by silica gel column chromatography (pentane:Et_2O = 30:1 – 10:1). Compound **4** (828 mg, α:β = 2:1, 88% yield) was obtained as yellow syrup. α-Isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 – 7.39 (m, 2H), 7.38 – 7.24 (m, 6H), 7.13 – 7.04 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 2H, *aromatic* H), 6.25 (s, 1H, H-1), 5.09 (d, *J* = 10.6 Hz, 1H, *Ph*C*H*HO), 4.84 (d, *J* = 10.6 Hz, 1H, *Ph*C*H*HO), 4.15 (dd, *J* = 9.2, 3.9 Hz, 1H, H-6), 4.07 – 3.82 (m, 4H, H-3, 4, 5, 6), 3.61 – 3.47 (m, 1H, H-2), 1.09 (s, 9H, *C*H_3), 1.04 (s, 9H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.22, 137.92, 129.36, 128.89, 128.55, 128.47, 128.44, 128.09, 126.36, 124.66, 119.44 (*aromatic* C/C*H*), 116.03 (*a*d, *J* = 286 Hz, C*F*$_3$), 93.58 (C-1), 79.42 (C-3), 78.36 (C-4), 75.70 (CH_2*Ph*), 68.96 (C-5), 66.38 (C-6), 61.79 (C-2), 27.46, 26.99 (2 CH_3), 22.74, 20.03 (2 C-*Si*). β-Isomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 (d, *J* = 6.9 Hz, 2H, *aromatic* H), 7.38 – 7.24 (m, 5H, *aromatic* H), 7.11 – 7.05 (m, 1H, *aromatic* H), 6.83 (d, *J* = 7.7 Hz, 2H, *aromatic* H), 5.60 (bs, 1H, H-1), 5.01 (d, *J* = 11.0 Hz, 1H, *Ph*C*H*HO), 4.83 (d, *J* = 11.0 Hz, 1H, *Ph*C*H*HO), 4.24 – 4.09 (m, 1H, H-6), 4.03 – 3.85 (m, 2H, H-4, 6), 3.67 – 3.20 (m, 3H, H-2, 3, 5), 1.08 (s, 9H, *C*H_3), 1.00 (s, 9H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.16, 137.91, 128.86, 128.50, 128.40, 128.07, 124.61, 119.28 (*aromatic* C/C*H*), 116.03 (*a*d, *J* = 286 Hz, C*F*$_3$), 95.54 (C-1), 82.08 (C-3), 77.63 (C-4), 75.37 (CH_2*Ph*), 71.15 (C-5), 66.04 (C-6), 64.47 (C-2), 27.45 (CH_3), 27.05 (CH_3), 22.73, 20.01 (2 C-*Si*). HR-MS: Calculated for $C_{29}H_{37}N_4O_5F_3Si$ $[M+Na]^+$: 629.2383, found: 629.2378.



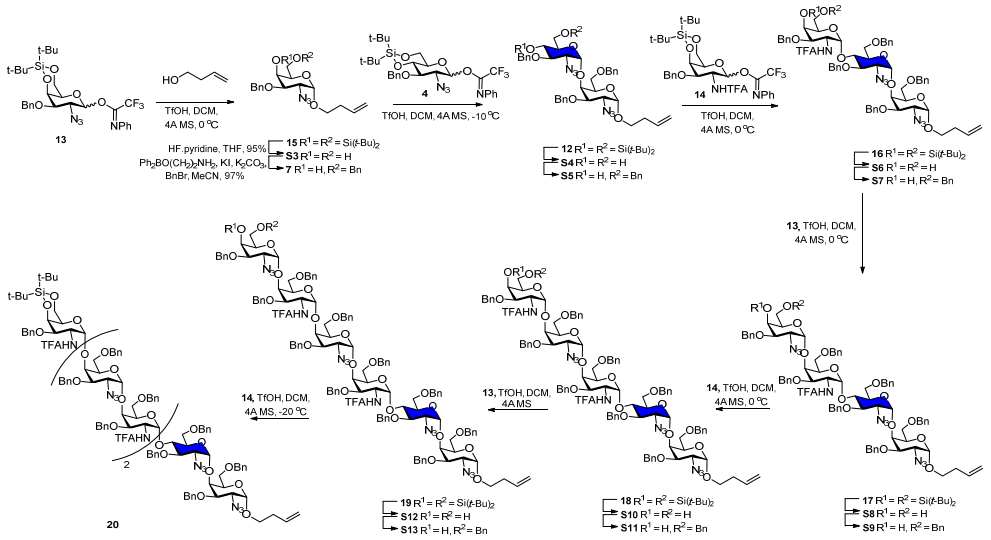
Phenyl 3-*O*-benzyl-2-deoxy-1-seleno-4,6-di-*tert*-butylsilylidene-2-trifluoroacetamido-α-D-galactopyranoside (S2)

1,3-Dithiolpropane (10.1 ml, 100 mmol) and trimethylamine (11.6 ml, 83.5 mmol) were added to the solution of compound **S1** (9.6 g, 16.7 mmol) in pyridine/water (80 ml/20 ml). The mixture was protected from light and stirred at room temperature overnight. The fluent was evaporated and co-evaporated with toluene. The residue was

dissolved in 50 ml pyridine, after which TFA_2O (3.5 ml, 25 mmol) was added at 0 ºC. The reaction was slowly warmed to room temperature and stirred overnight. The reaction was quenched with Methanol and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 50:1 – 10:1). Compound **S2** (9.58 g, 89% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +205.4 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H), 7.44 – 7.21 (m, 8H, *aromatic* H), 6.59 (d, *J* = 7.0 Hz, 1H, NH), 6.12 (d, *J* = 4.8 Hz, 1H, H-1), 4.83 – 4.73 (m, 2H, H-2, *PhC*H*H*O), 4.71 (d, *J* = 2.7 Hz, 1H, H-5), 4.50 (d, *J* = 11.7 Hz, 1H, *PhC*H*H*O), 4.33 (dd, *J* = 12.7, 2.3 Hz, 1H, H-6), 4.17 (dd, *J* = 12.7, 1.7 Hz, 1H, H-6), 4.05 (d, *J* = 2.3 Hz, 1H, H-4), 3.51 (dd, *J* = 11.0, 2.7 Hz, 1H, H-3), 1.07 (d, *J* = 4.2 Hz, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.26 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 149.79, 137.33, 136.16, 134.43, 134.38, 134.33, 129.46, 128.85, 128.59, 128.37, 128.32, 128.24, 127.95, 127.89, 123.86 (*aromatic* C/C*H*), 115.68 (*a*d, *J* = 286 Hz, C*F$_3$*), 88.66 (C-1), 76.06 (C-3), 70.90 (C-4), 69.65 (C*H$_2$Ph*), 68.82 (C-5), 67.23 (C-6), 49.95 (C-2), 27.72, 27.37 (2 C*H$_3$*), 23.50, 20.87 (2 C-*Si*). HR-MS: Calculated for $C_{29}H_{38}NO_5F_3SiSe$ $[M+Na]^+$: 668.1534, found: 668.1529.

3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-2-trifluoroacetamido-1-*O*-(*N*-phenyl-trifluoroacetimidoyl)-α/β-D-galactopyranoside (14)

NIS (944 mg, 4.19 mmol) was added to the solution of compound **S2** (1.65 g, 2.8 mmol) in Acetone/H_2O (15 ml/3 ml) 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 was purified by silica gel column chromatography (pentane:EtOAc = 4:1). Cs_2CO_3 (2.77 g, 8.5 mmol) was added to the solution of the hemiacetal (4.3 g, 8.5 mmol) in 45 ml acetone. The mixture was stirred at 0 ºC for 15 minutes. Then $CF_3C(=NPh)Cl$ (2.29 g, 11.06 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 **14** was purified by silica gel column chromatography (pentane:Et_2O = 50:1 – 10:1). Compound **14** (5.15 g, α:β = 7:1, 90% yield) was obtained as syrup. α-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.22 (m, 7H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 2H, *aromatic* H), 6.57 (bs, H-1), 6.11 (d, *J* = 7.3 Hz, 1H, *N*H), 4.80 (d, *J* = 11.8 Hz, 1H, *PhC*H*H*O), 4.72 (s, 2H, H-2, 5), 4.52 (d, *J* = 11.8 Hz, 1H, *PhC*H*H*O), 4.33 – 4.12 (m, 2H, H-6), 3.82 – 3.66 (m, 2H, H-3, 4), 1.14 – 0.97 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.53 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 143.09, 137.25, 128.90, 128.44, 128.01, 119.33 (*aromatic* C/C*H*), 115.72(*a*d, *J* = 286 Hz, C*F$_3$*), 96.81 (C-1), 73.91 (C-3), 70.16 (C-4), 69.96 (C*H$_2$Ph*), 68.77 (C-5), 66.87 (C-6), 48.40 (C-2), 27.72, 27.30 (2 C*H$_3$*), 23.51, 20.85 (2 C-*Si*). β-Isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.27 (m, 7H), 7.20 – 7.08 (m, 1H), 6.84 (d, *J* = 7.7 Hz, 2H, *aromatic* H), 6.56 (d, *J* = 7.2 Hz, 1H, NH), 6.19 (bs, 1H, H-1), 4.73 (d, *J* = 11.6 Hz, 1H, *PhC*H*H*O), 4.64 – 4.47 (m, 2H, *PhC*H*H*O, H-5), 4.42 – 3.90 (m, 5H, H-2, 3, 4, 6), 1.20 – 1.03 (m, 18H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.68 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 143.28, 137.42, 128.85, 128.78, 128.33, 128.05, 124.57, 119.38 (*aromatic* C/C*H*), 115.60 (*a*d, *J* = 286 Hz, C*F$_3$*), 93.70 (C-1), 75.46 (C-3), 72.36 (C-4), 70.61 (C*H$_2$Ph*), 68.61 (C-5), 66.90 (C-6), 52.93 (C-2), 27.74, 27.44 (2 C*H$_3$*), 23.54, 20.91 (2 C-*Si*). HR-MS: Calculated for $C_{31}H_{38}N_2O_6F_6Si$ $[M+Na]^+$: 699.2301, found: 699.2296.



3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranoside (15)

The reaction was carried out according to the general procedure A. The donor **13** (1.8 g, 2.97 mmol) was co-evaporated with toluene (three times). The the linker alcohol (511 ul, 5.94 mmol) was added, the mixture was dissolved in dry 30 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (26 µl, 0.23 mmol) was added. The reaction was stirred at 0 ºC for 2 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 50:1). Compound **15** (1.30 g, 89% yield) was obtained as colorless syrup. $[\alpha]_D^{25}$ +146.7 (c=2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.22 (m, 5H, *aromatic* H), 5.86 – 5.71 (m, 1H, H-9), 5.13 – 5.00 (m, 2H, H-10), 4.93 (d, *J* = 3.5 Hz, 1H, H-1), 4.74 (d, *J* = 11.5 Hz, 1H, *PhCHH*O), 4.65 (d, *J* = 11.5 Hz, 1H, *PhCHH*O), 4.57 (dd, *J* = 2.9, 1.0 Hz, 1H, H-4), 4.24 (dd, *J* = 12.6, 2.1 Hz, 1H, H-6), 4.13 (dd, *J* = 12.5, 1.7 Hz, 1H, H-6), 3.87 (dd, *J* = 10.6, 2.8 Hz, 1H, H-3), 3.77 (dd, *J* = 10.6, 3.5 Hz, 1H, H-2), 3.73 – 3.62 (m, 2H, H-7, 5), 3.59 – 3.48 (m, 1H, H-7), 2.41 – 2.30 (m, 2H, H-8), 1.07 (s, 9H, *CH*$_3$), 1.04 (s, 9H, *CH*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.85 (*aromatic* C), 134.66 (C-9), 128.49, 127.91, 127.83 (*aromatic CH*), 116.89 (C-10), 98.40 (C-1), 75.36 (C-3), 70.40 (C*H*$_2$*Ph*), 69.82 (C-4), 67.67 (C-7), 67.46 (C-5), 67.17 (C-6), 58.23 (C-2), 33.90 (C-8), 27.66, 27.34 (2 C*H*$_3$), 23.42, 20.73 (2 C-*Si*). HR-MS: Calculated for $C_{25}H_{39}N_3O_5Si$ $[M+Na]^+$: 512.2557, found: 512.2551.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S3)

The reaction was carried out according to the general procedure C using compound **15** (1.27 g, 2.59 mmol) and HF/pyridine (70%, 1.1 ml, 41.5 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S3** (860 mg, 95% yield) was obtained as white solid. $[\alpha]_D^{25}$ +135.4 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.26 (m, 5H, *aromatic* H), 5.80 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, H-9), 5.18 – 5.01 (m,

2H, H-10), 4.93 (d, *J* = 3.5 Hz, 1H, H-1), 4.77 – 4.61 (m, 2H, 2x*PhCHH*O), 4.10 (d, *J* = 3.1 Hz, 1H, H-4), 3.94 – 3.83 (m, 2H, H-3, 6), 3.83 – 3.68 (m, 3H, H-5, 6, 7), 3.65 (dd, *J* = 10.4, 3.6 Hz, 1H, H-2), 3.52 (dt, *J* = 9.7, 6.6 Hz, 1H, H-7), 2.97 (bs, 1H, OH), 2.71 (bs, 1H, OH), 2.37 (qt, *J* = 6.8, 1.4 Hz, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.12 (*aromatic* C), 134.62 (C-9), 128.73, 128.34, 128.11 (*aromatic* C*H*), 117.03 (C-10), 98.07 (C-1), 75.81 (C-3), 72.02 (CH_2*Ph*), 69.50 (C-5), 67.68 (C-7), 67.50 (C-4), 62.80 (C-6), 58.97 (C-2), 33.87 (C-8). HR-MS: Calculated for $C_{17}H_{23}N_3O_5$ $[M+Na]^+$: 372.1535, found: 372.1530.

3-Butenyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (7)

The reaction was carried out according to the general procedure D using compound **S3** (900 mg, 2.58 mmol), K_2CO_3 (392 mg, 2.84 mmol), KI (428 mg, 2.58 mmol) and $Ph_2BO(CH_2)_2NH_2$ (58 mg, 0.26 mmol). The product was purified by column chromatography (pentane:EtOAc = 7:1). Compound **7** (1.07 g, 94% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +75 (c=2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 10H, *aromatic* H), 5.80 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H, H-9), 5.14 – 5.01 (m, 2H, H-10), 4.91 (d, *J* = 3.6 Hz, 1H, H-1), 4.66 (s, 2H, *PhCHH*O), 4.58 (d, *J* = 11.9 Hz, 1H, *PhCHH*O), 4.56 (d, 1H, *PhCHH*O), 4.10 (dd, *J* = 3.2, 1.3 Hz, 1H, H-4), 3.93 (td, *J* = 5.8, 1.3 Hz, 1H, H-5), 3.87 (dd, *J* = 10.4, 3.1 Hz, 1H, H-3), 3.79 – 3.64 (m, 4H, H-2, 6, 7), 3.52 (dt, *J* = 9.7, 6.5 Hz, 1H, H-7), 2.73 (bs, 1H, OH), 2.37 (qt, *J* = 6.8, 1.4 Hz, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.87, 137.24 (*aromatic* C), 134.67 (C-9), 128.97, 128.61, 128.42, 128.15, 128.01, 127.75, 127.66 (*aromatic* C*H*), 116.87 (C-10), 98.00 (C-1), 75.97 (C-3), 73.60, 71.77 (2 CH_2*Ph*), 69.43 (C-6), 68.80 (C-5), 67.58 (C-7), 66.55 (C-4), 58.97 (C-2), 33.84 (C-8). HR-MS: Calculated for $C_{24}H_{29}N_3O_5$ $[M+Na]^+$: 462.2005, found: 462.1999.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (12)

The reaction was carried out according to the general procedure A. The donor **4** (808 mg, 1.33 mmol) and acceptor **7** (293 mg, 0.67 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 6 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to -10 ºC, after which TfOH (12 µl, 0.13 mmol) was added. The reaction was stirred at -10 ºC for 2 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:Et_2O = 10:1). Compound **12** (422 mg, 74% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +121.5 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.33 (m, 15H, *aromatic* H), 5.87 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H, H-9), 5.23 – 5.10 (m, 3H, H-10), 5.04 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.92 (d, *J* = 5.4 Hz, 1H, *PhCHH*O), 4.91 – 4.87 (m, 2H, H-1^B), 4.76 – 4.63 (m, 2H, *PhCHH*O), 4.58 (d, *J* = 11.8 Hz, 1H, *PhCHH*O), 4.43 (td, *J* = 9.7, 4.7 Hz, 1H), 4.27 (d, *J* = 2.7 Hz, 1H, H-4^A), 4.12 – 4.03 (m, 1H), 4.03 – 3.88 (m, 5H), 3.86 – 3.71 (m, 3H), 3.67 – 3.56 (m, 2H), 3.37 – 3.27 (m, 1H, H-2^B), 2.43 (qt, *J* = 6.8, 1.4 Hz, 2H, H-8), 1.15 (s, 9H, *C*H_3), 1.08 (s, 9H, *C*H_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.13, 137.38, 137.26 (*aromatic* C), 134.60 (C-9), 128.50, 128.38, 128.35, 128.32, 128.21, 128.10, 127.88, 127.82, 127.63 (*aromatic* C*H*), 116.88 (C-10), 98.64 (C-1^B), 97.85 (C-1^A), 79.26, 79.17,

75.46, 75.37, 73.59, 73.51, 71.97, 69.02, 67.56, 66.76, 66.74, 66.64, 62.92 (C-2^B), 60.01 (C-2^A), 33.83 (C-8), 27.35, 27.04 (2 C*H*$_3$), 22.55, 19.98 (2 C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 98.64 ($J_{C1,H1}$ = 172 Hz), 97.85 ($J_{C1,H1}$ = 171 Hz). HR-MS: Calculated for $C_{45}H_{60}N_6O_9Si$ $[M+Na]^+$: 879.4089, found: 879.4083.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S4)

The reaction was carried out according to the general procedure C using compound **12** (422 mg, 0.49 mmol) and HF/pyridine (70%, 205 µl, 7.88 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:1). Compound **S4** (342 mg, 97% yield) was obtained as white solid. $[\alpha]_D^{25}$ +146.8 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.20 (m, 15H, *aromatic* H), 5.78 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H, H-9), 5.11 – 5.00 (m, 2H, H-10), 4.93 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.89 – 4.77 (m, 3H, H-1^B, *PhC*H*H*O), 4.72 (d, *J* = 12.0 Hz, 1H, *PhC*H*H*O), 4.61 – 4.46 (m, 3H), 4.21 (d, *J* = 2.7 Hz, 1H, H-4^A), 3.99 – 3.76 (m, 5H), 3.73 – 3.46 (m, 5H), 3.35 (dd, *J* = 12.2, 2.7 Hz, 1H), 3.19 (td, *J* = 11.1, 10.3, 3.5 Hz, 2H), 2.41 – 2.26 (m, 2H, H-8). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.04, 137.34, 137.26 (*aromatic* C), 134.56 (C-9), 128.42, 128.36, 127.99, 127.97, 127.90, 127.77, 127.73, 127.20 (*aromatic* C*H*), 116.80 (C-10), 98.58 (C-1^B), 98.01 (C-1^A), 79.59, 75.17, 75.00, 73.42, 73.00, 71.57, 71.32, 70.88, 69.01, 67.56, 66.88, 63.35, 61.24, 59.31, 33.77 (C-8). HR-MS: Calculated for $C_{37}H_{44}N_6O_9$ $[M+Na]^+$: 739.3067, found: 739.3062.

3-Butenyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S5)

The reaction was carried out according to the general procedure D using compound **S4** (337 mg, 0.47 mmol), K_2CO_3 (71 mg, 0.52 mmol), KI (78 mg, 0.47 mmol) and $Ph_2BO(CH_2)_2NH_2$ (11 mg, 0.047 mmol). The product was purified by column chromatography (pentane:EtOAc = 10:1). Compound **S5** (363 g, 96% yield) was obtained as colorless syrup. $[\alpha]_D^{25}$ +135.8 (c=2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.28 (m, 20H, *aromatic* H), 5.93 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H, H-9), 5.27 – 5.15 (m, 2H, H-10), 5.10 (d, *J* = 3.6 Hz, 1H, H-1^A), 5.06 (d, *J* = 3.7 Hz, 1H, H-1^B), 5.05 – 4.95 (m, 2H, *PhC*H*H*O), 4.90 (d, *J* = 12.0 Hz, 1H, *PhC*H*H*O), 4.74 – 4.62 (m, 3H), 4.44 – 4.35 (m, 2H), 4.33 – 4.20 (m, 2H), 4.17 – 4.05 (m, 2H), 4.04 – 3.79 (m, 5H), 3.75 – 3.61 (m, 3H), 3.40 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.35 (dd, *J* = 10.3, 3.2 Hz, 1H), 3.24 (dd, *J* = 10.4, 4.4 Hz, 1H, H-6^B), 2.84 (bs, 1H, OH), 2.54 – 2.45 (m, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.13, 137.64, 137.49, 137.39 (*aromatic* C), 134.59 (C-9), 128.88, 128.44, 128.39, 128.35, 128.33, 128.26, 128.02, 127.98, 127.95, 127.75, 127.62, 127.56, 127.14, 127.07 (*aromatic* C*H*), 116.82 (C-10), 98.74 (C-1^B), 98.07 (C-1^A), 79.59 (C-3^B), 75.53 (C-3^A), 74.99, 73.46, 73.25 (3 C*H*$_2$*Ph*), 73.20 (C-4^A), 72.45 (C-4^B), 71.66 (C*H*$_2$*Ph*), 69.96 (C-5^B), 69.09 (C-$6^{B)}$, 69.07 (C-5^A), 67.60 (C-7), 66.85 (C-6^A), 63.27 (C-2^B), 59.42 (C-2^A), 33.81 (C-8). HR-MS: Calculated for $C_{44}H_{50}N_6O_9$ $[M+Na]^+$: 829.3537, found: 829.3532.

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

The reaction was carried out according to the general procedure A. The donor **14** (559 mg, 0.83 mmol) and acceptor **S5** (370 mg, 0.46 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 4.5 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (7.5 µl, 0.083 mmol) was added. The reaction was stirred at 0 ºC for 2 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 8:1). Compound **16** (506 mg, 85% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +117.9 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 23H, *aromatic* H), 7.18 – 7.12 (m, 2H, *aromatic* H), 6.98 (d, *J* = 9.5 Hz, 1H, NH), 5.89 – 5.72 (m, 1H, H-9), 5.45 (d, *J* = 3.5 Hz, 1H, H-1^C), 5.14 – 5.02 (m, 2H, H-10), 5.01 – 4.97 (m, 2H, H-1^A, 1^B), 4.82 – 4.42 (m, 10H), 4.28 (dd, *J* = 18.5, 3.6 Hz, 3H), 4.04 – 3.79 (m, 8H), 3.71 (dt, *J* = 9.8, 6.8 Hz, 1H, H-7), 3.62 (dd, *J* = 10.9, 3.5 Hz, 1H, H-2^A), 3.60 – 3.51 (m, 3H), 3.47 (dd, *J* = 10.9, 2.6 Hz, 1H), 3.31 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2^B), 3.20 (dd, *J* = 11.5, 2.3 Hz, 1H, H-6), 3.08 (dd, *J* = 11.4, 1.8 Hz, 1H, H-6), 2.37 (qt, *J* = 6.7, 1.4 Hz, 2H, H-8), 1.03 (s, 9H, *C*H$_3$), 1.02 (s, 9H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.38 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 138.07, 137.59, 137.45, 137.38, 136.35 (*aromatic* C), 134.66 (C-9), 128.67, 128.65, 128.53, 128.51, 128.47, 128.33, 128.24, 128.17, 127.94, 127.91, 127.80, 127.77, 127.45, 127.25 (*aromatic* C*H*), 117.04 (C-10), 115.89 (*a*d, *J* = 287 Hz, C*F$_3$*), 98.53 (C-1^B), 98.22 (C-1^A), 97.45 (C-1^C), 79.79, 75.58, 75.11, 74.69, 73.70, 73.53 (3 C*H$_2$Ph*), 73.21, 72.94, 72.03, 70.86, 69.74, 69.58, 69.13, 68.59, 67.94 (C-6), 67.86 (C-7), 67.12 (C-6), 66.89 (C-6), 64.39 (C-2^B), 59.72 (C-2^A), 48.67 (C-2^C), 33.96 (C-8), 27.67, 27.36 (2 C*H$_3$*), 23.41, 20.81 (2 C-*Si*). HR-MS: Calculated for $C_{67}H_{82}N_7O_{14}F_3Si$ $[M+Na]^+$: 1316.5539, found: 1316.5533.

3-Butenyl 3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S6)

The reaction was carried out according to the general procedure C using compound **16** (417 g, 0.33 mmol) and HF/pyridine (70%, 134 µl, 5.15 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S6** (341 mg, 92% yield) was obtained as yellow solid. $[\alpha]_D^{25}$ +132.2 (c=1, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.16 (m, 25H, *aromatic* H), 7.08 (d, *J* = 9.9 Hz, 1H, NH), 5.79 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, H-9), 5.25 (d, *J* = 3.6 Hz, 1H, H-1^C), 5.14 – 5.02 (m, 2H, H-10), 5.01 – 4.95 (m, 2H, H-1^A, 1^B), 4.75 (dd, *J* = 14.9, 11.5 Hz, 2H), 4.62 – 4.46 (m, 6H), 4.40 – 4.23 (m, 4H), 4.06 (d, *J* = 2.9 Hz, 1H), 4.03 – 3.93 (m, 2H), 3.93 – 3.80 (m, 4H), 3.76 – 3.50 (m, 7H), 3.44 (dd, *J* = 10.7, 2.9 Hz, 1H), 3.32 – 3.21 (m, 2H), 3.10 (dd, *J* = 11.6, 2.1 Hz, 1H), 2.94 (s, 1H, OH), 2.43 – 2.30 (m, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.38 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 137.55, 137.34, 137.09, 136.49 (*aromatic* C), 134.63 (C-9), 128.60, 128.52, 128.43, 128.23, 128.17, 128.12, 128.09, 127.98, 127.89, 127.88, 127.83, 127.43, 127.24 (*aromatic* C*H*), 116.98 (C-10), 115.89 (*a*d, *J* = 286 Hz, C*F$_3$*), 98.45 (C-1^B), 98.21 (C-1^A), 97.76 (C-1^C), 79.64, 75.81, 75.39, 74.50, 74.38, 73.62, 73.47, 73.04, 71.98, 70.96, 70.92, 70.60, 69.07, 67.79 (C-7), 67.48 (C-6), 66.90 (C-6), 66.22, 64.23 (C-2), 62.52 (C-6), 59.56 (C-2), 49.25 (C-2^C), 33.90 (C-8). HR-MS: Calculated for $C_{59}H_{66}N_7O_{14}F_3$ $[M+Na]^+$: 1176.4518, found: 1176.4512.

3-Butenyl 3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S7)

The reaction was carried out according to the general procedure D using compound **S6** (286 mg, 0.25 mmol), K_2CO_3 (38 mg, 0.27 mmol), KI (41 mg, 0.25 mmol) and $Ph_2BO(CH_2)_2NH_2$ (5.6 mg, 0.025 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S7** (279 mg, 90% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +118 (c=0.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.13 (m, 30H, *aromatic* H), 7.09 (d, *J* = 9.9 Hz, 1H, NH), 5.78 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, H-9), 5.25 (d, *J* = 3.6 Hz, 1H, H-1^C), 5.13 – 5.00 (m, 2H, H-10), 5.00 – 4.96 (m, 2H, H-1^A, 1^B), 4.81 – 4.66 (m, 2H), 4.63 – 4.21 (m, 13H), 4.17 – 3.79 (m, 9H), 3.75 – 3.42 (m, 8H), 3.40 – 3.23 (m, 2H), 3.14 (dd, *J* = 11.3, 2.1 Hz, 1H), 2.62 (s, *O*H), 2.35 (qt, *J* = 6.7, 1.4 Hz, 2H, H-8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.34 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 137.90, 137.74, 137.35, 137.32, 137.23, 136.51 (*aromatic* C), 134.63 (C-9), 128.58, 128.54, 128.48, 128.43, 128.36, 128.34, 128.22, 128.14, 128.07, 128.03, 127.94, 127.90, 127.86, 127.82, 127.81, 127.76, 127.72, 127.69, 127.39, 127.33 (*aromatic* C*H*), 116.96 (*a*d, *J* = 286 Hz, C*F$_3$*), 98.49 (C-1^B), 98.18 (C-1^A), 97.91 (C-$^{1C)}$, 79.59, 76.01, 75.13, 74.70, 74.53, 73.70, 73.60, 73.17, 73.03, 71.84, 70.90, 70.87, 69.63, 69.06, 68.81, 67.75, 67.69, 66.93, 65.22, 64.27 (C-2), 59.55 (C-2), 49.40 (C-2^C), 33.89 (C-8). HR-MS: Calculated for $C_{66}H_{72}N_7O_{14}F_3$ $[M+Na]^+$: 1266.4987, found: 1266.4982.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (17)

The reaction was carried out according to the general procedure A. The donor **13** (535 mg, 0.88 mmol) and acceptor **S7** (366 mg, 0.29 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 3 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 ºC, after which TfOH (8 µl, 0.088 mmol) was added. The reaction was stirred at 0 ºC for 2 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 6:1). Compound **17** (343 mg, 70% yield) was obtained as yellow solid. $[\alpha]_D^{25}$ +159.3 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.12 (m, 35H, *aromatic* H), 7.05 (d, *J* = 10.0 Hz, 1H, NH), 5.79 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H, H-9), 5.36 (d, *J* = 3.6 Hz, 1H, H-1C), 5.13 – 5.02 (m, 2H, H-10), 5.01 – 4.97 (m, 2H, 2xH-1), 4.94 (d, *J* = 3.6 Hz, 1H, H-1), 4.81 – 4.52 (m, 10H), 4.50 (d, *J* = 2.9 Hz, 1H), 4.45 – 4.36 (m, 2H), 4.35 – 4.21 (m, 5H), 4.10 – 3.79 (m, 11H), 3.77 – 3.45 (m, 8H), 3.38 (dd, *J* = 8.3, 5.0 Hz, 1H), 3.34 – 3.25 (m, 2H), 3.14 (dd, *J* = 11.5, 1.9 Hz, 1H), 2.41 – 2.32 (m, 2H, H-8), 1.02 (s, 9H, *C*H$_3$), 0.96 (s, 9H, *C*H$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.52 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 137.94, 137.39, 137.35, 137.29, 137.23, 136.42 (*aromatic* C), 134.66 (C-9), 128.65, 128.63, 128.60, 128.55, 128.49, 128.46, 128.30, 128.22, 128.17, 128.14, 127.99, 127.79, 127.76, 127.68, 127.64, 127.33, 126.21, 124.43, 123.56 (*aromatic* C*H*), 117.04 (C-10), 115.94 (*a*d, *J* = 286 Hz, C*F$_3$*), 98.85 (C-1), 98.58 (C-1), 98.28 (C-1), 97.75 (C-1C), 79.78, 76.20, 75.66, 75.39, 74.55, 73.91, 73.69, 73.30, 73.06, 72.00, 71.03, 70.91, 70.64, 70.61, 70.31, 69.61, 69.11, 67.85, 67.57, 67.08, 66.94, 66.63, 64.32, 59.58, 58.51, 49.73

(4 C-2), 33.96 (C-8), 27.64, 27.47 (2 CH_3), 23.31, 20.77 (2 C-*Si*). ^{13}C-HMBC ($CDCl_3$, 100 MHz): 98.85 ($J_{C1,H1}$ = 174 Hz), 98.58 ($J_{C1,H1}$ = 171 Hz), 97.75 ($J_{C1,H1}$ = 171 Hz). HR-MS: Calculated for $C_{87}H_{103}N_{10}O_{18}F_3Si$ $[M+Na]^+$: 1683.7071, found: 1683.7065.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S8)

The reaction was carried out according to the general procedure C using compound **17** (112 mg, 0.067 mmol) and HF/pyridine (70%, 28 µl, 1.1 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S8** (89 mg, 87% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +133.7 (c=0.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.27 (m, 35H, *aromatic* H), 7.23 (d, *J* = 9.9 Hz, 1H, NH), 5.89 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H, H-9), 5.44 (d, *J* = 3.6 Hz, 1H, H-1^C), 5.23 – 5.12 (m, 2H, H-10), 5.12 – 5.08 (m, 2H, 2xH-1), 5.06 (d, *J* = 3.6 Hz, 1H, H-1), 4.88 (d, *J* = 11.1 Hz, 1H), 4.81 (dd, *J* = 12.1, 4.0 Hz, 2H), 4.76 (s, 2H), 4.75 – 4.69 (m, 1H), 4.68 – 4.59 (m, 4H), 4.53 – 4.44 (m, 3H), 4.43 – 4.37 (m, 2H), 4.37 – 4.30 (m, 2H), 4.30 – 4.24 (m, 1H), 4.24 – 4.18 (m, 1H), 4.15 – 3.92 (m, 9H), 3.85 – 3.75 (m, 2H), 3.71 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.69 – 3.57 (m, 3H), 3.54 – 3.43 (m, 2H), 3.44 – 3.33 (m, 3H), 3.24 (dd, *J* = 11.4, 2.0 Hz, 1H), 3.03 (s, 1H, OH), 2.46 (q, *J* = 6.8 Hz, 2H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.50 (*a*d, *J* = 37 Hz, *C*F_3*C*O), 137.79, 137.34, 137.27, 137.20, 137.11, 136.38 (*aromatic* C), 134.54 (C-9), 128.51, 128.46, 128.44, 128.41, 128.31, 128.20, 128.07, 128.05, 127.99, 127.84, 127.73, 127.71, 127.62, 127.57, 127.19, 126.44 (*aromatic* C*H*), 116.86 (C-10), 115.77 (*a*d, *J* = 286 Hz, CF_3), 99.15 (C-1), 98.43 (C-1), 98.14 (C-1), 97.61 (C-1^C), 79.58, 76.19, 75.93, 75.21, 74.23, 73.91, 73.51, 73.46, 73.15, 72.97, 72.03, 71.84, 71.64, 71.02, 70.73, 70.33, 69.16, 68.96, 67.69, 67.66, 67.33 (C-7), 66.81, 66.63 (2 C-6), 64.13 (C-2), 62.37 (C-6), 59.42, 59.36 (2 C-2), 49.73 (C-2^C), 33.81 (C-8). HR-MS: Calculated for $C_{79}H_{87}N_{10}O_{18}F_3$ $[M+Na]^+$: 1543.6050, found: 1543.6044.

3-Butenyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S9)

The reaction was carried out according to the general procedure D using compound **S8** (129 mg, 0.085 mmol), K_2CO_3 (13 mg, 0.09 mmol), KI (14 mg, 0.085 mmol) and $Ph_2BO(CH_2)_2NH_2$ (1.9 mg, 0.0085 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S9** (129 mg, 94% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +136.4 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.23 (m, 40H, *aromatic* H), 7.17 (d, *J* = 9.9 Hz, 1H, NH), 5.92 (ddt, *J* = 17.0, 10.3, 6.8 Hz, 1H, H-9), 5.50 (d, *J* = 3.6 Hz, 1H, H-1^C), 5.25 – 5.16 (m, 2H, H-10), 5.15 – 5.10 (m, 3H, 3xH-1), 4.90 (d, *J* = 11.6 Hz, 2H, *PhC*H*H*O), 4.87 – 4.81 (m, 2H, *PhC*H*H*O, H-2^C), 4.81 – 4.74 (m, 2H), 4.72 – 4.61 (m, 5H), 4.57 – 4.47 (m, 3H), 4.46 – 4.39 (m, 4H), 4.37 (d, *J* = 2.9 Hz, 1H), 4.35 – 4.25 (m, 2H), 4.22 – 3.93 (m, 12H), 3.83 (dt, *J* = 9.8, 6.9 Hz, 1H, H-7), 3.76 (dd, *J* = 10.9, 3.5 Hz, 1H, H-2), 3.72 – 3.60 (m, 3H), 3.59 – 3.51 (m, 1H), 3.50 – 3.36 (m, 4H), 3.32 (dd, *J* = 10.0, 3.9 Hz, 1H), 3.29 – 3.22 (m, 1H), 2.48 (q, *J* = 6.9 Hz, 2H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.25 (*a*d, *J* = 37 Hz, *C*F_3*C*O), 137.73, 137.53, 137.45,

137.38, 137.31, 137.22, 137.19, 136.32 (*aromatic* C), 134.50 (C-9), 128.46, 128.42, 128.38, 128.34, 128.32, 128.26, 128.18, 128.16, 128.03, 128.00, 127.98, 127.95, 127.89, 127.76, 127.71, 127.58, 127.56, 127.53, 127.51, 127.45, 127.28, 127.08, 126.71, 126.39 (*aromatic* C*H*), 116.85 (C-10), 115.72 (*a*d, *J* = 286 Hz, C*F*$_3$), 99.35 (C-1), 98.37 (C-1), 98.08 (C-1), 97.48 (C-1^C), 79.52, 76.15, 76.04, 75.20, 74.20 (C*H*$_2$*Ph*), 73.70, 73.45 (C*H*$_2$*Ph*), 73.41 (C*H*$_2$*Ph*), 73.20 (C*H*$_2$*Ph*), 73.10 (C*H*$_2$*Ph*), 72.89, 71.99, 71.75 (C*H*$_2$*Ph*), 71.16 (C*H*$_2$*Ph*), 70.99 (C*H*$_2$*Ph*), 70.69, 70.24, 69.76 (C-6), 68.92, 68.21, 67.63 (C-7), 66.84, 66.76 (C-6), 66.57 (C-6), 64.79 (C-6), 64.07 (C-2), 59.40 (C-2), 59.20 (C-2), 49.60 (C-2^C), 33.77 (C-8). HR-MS: Calculated for $C_{86}H_{93}N_{10}O_{18}F_3$ $[M+Na]^+$: 1633.6519, found: 1633.6514.

Pentasaccharide 18

The reaction was carried out according to the general procedure B using donor **14** (586 mg, 0.87 mmol) and acceptor **S9** (558 mg, 0.35 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **S8** (642 mg, 88% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +134.2 (c=0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 41H, *aromatic* H), 7.17 – 7.15 (m, 2H, *aromatic* H), 7.05 – 7.01 (m, 2H, *aromatic* H), 6.99 (d, *J* = 10.0 Hz, 1H, NH), 6.23 (d, *J* = 9.5 Hz, 1H, NH), 5.79 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H, H-9), 5.34 (d, *J* = 3.6 Hz, 1H, H-1), 5.12 – 5.02 (m, 2H, H-10), 4.99 (d, *J* = 3.6 Hz, 3H, 3xH-1), 4.82 (d, *J* = 3.8 Hz, 1H, H-1), 4.80 – 4.68 (m, 5H), 4.65 – 4.33 (m, 13H), 4.32 – 4.17 (m, 5H), 4.05 – 3.80 (m, 11H), 3.76 – 3.53 (m, 7H), 3.50 (dd, *J* = 11.1, 2.5 Hz, 1H), 3.44 (dd, *J* = 12.7, 2.1 Hz, 1H), 3.40 (dd, *J* = 8.3, 4.9 Hz, 1H), 3.37 – 3.28 (m, 2H), 3.26 (dd, *J* = 11.5, 2.1 Hz, 1H), 3.12 (dd, *J* = 11.5, 1.9 Hz, 1H), 2.96 (t, *J* = 9.5 Hz, 1H), 2.86 (dd, *J* = 8.9, 5.4 Hz, 1H), 2.41 – 2.32 (m, 2H, H-8), 1.06 (s, 9H, *C*H$_3$), 0.97 (s, 9H, *C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.41 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 156.57 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 138.03, 137.94, 137.61, 137.56, 137.41, 137.36, 137.28, 136.92, 136.44 (*aromatic* C), 134.67 (C-9), 128.65, 128.62, 128.60, 128.54, 128.49, 128.44, 128.34, 128.22, 128.20, 128.16, 128.14, 128.12, 127.97, 127.93, 127.80, 127.77, 127.74, 127.72, 127.64, 127.34, 126.83, 126.41 (*aromatic* C*H*), 117.04 (C-10), 115.92 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 99.03 (C-1), 98.56 (C-1), 98.29 (C-1), 97.62 (C-1), 96.74 (C-1), 79.79, 76.46, 75.98, 75.42, 74.90, 74.55, 73.78, 73.69, 73.48, 73.31, 73.11, 73.09, 72.02, 71.95, 71.63, 71.46, 70.90, 70.17, 69.55, 69.51, 69.39, 69.13, 68.79, 67.87 (C-7), 67.79, 67.02, 66.95, 66.76, 65.76, 64.40, 60.27, 59.60, 49.67, 48.25 (5 C-2), 33.96, 27.64 (2 C*H*$_3$), 27.46, 23.35 (2 C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 99.03 ($J_{C1,H1}$ = 171 Hz), 98.56 ($J_{C1,H1}$ = 173 Hz), 98.29 ($J_{C1,H1}$ = 170 Hz), 97.62 ($J_{C1,H1}$ = 176 Hz), 96.74 ($J_{C1,H1}$ = 174 Hz). HR-MS: Calculated for $C_{109}H_{125}N_{11}O_{23}F_6Si$ $[M+Na]^+$: 2120.8521, found: 2120.8517.

Pentasaccharide S10

The reaction was carried out according to the general procedure C using compound **18** (641 mg, 0.31 mmol) and HF/pyridine (70%, 130 µl, 5.0 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S10** (547 mg, 91% yield) was obtained as white solid. $[\alpha]_D^{25}$ +164.8 (c=0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.21 (m, 43H, *aromatic* H), 7.14 (dd, *J* = 8.1, 1.6 Hz, 3H), 6.53 (d, *J* = 9.5 Hz, 1H, NH), 5.87 (ddt, *J* = 17.0, 10.3, 6.8 Hz, 1H, H-9), 5.45 (d, *J* = 3.6 Hz, 1H, H-1), 5.21 – 5.10 (m, 2H, H-10), 5.09 – 5.05 (m, 2H, 2xH-1), 5.02 (d, *J* = 3.6 Hz, 1H, H-1), 4.92 (d, *J* = 3.7 Hz, 1H, H-1), 4.88 – 4.76 (m, 3H), 4.76 – 4.58 (m, 8H), 4.52 –

4.41 (m, 5H), 4.41 – 4.34 (m, 4H), 4.31 (d, *J* = 2.4 Hz, 1H), 4.26 (d, *J* = 12.4 Hz, 1H), 4.18 (d, *J* = 1.9 Hz, 1H), 4.12 – 3.89 (m, 12H), 3.82 (d, *J* = 11.8 Hz, 1H), 3.81 – 3.75 (m, 1H), 3.69 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.67 – 3.33 (m, 11H), 3.26 – 3.18 (m, 1H), 3.11 – 2.95 (m, 3H), 2.44 (q, *J* = 6.8 Hz, 2H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.34 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 156.65 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 137.88, 137.56, 137.39, 137.34, 137.26, 137.14, 136.98, 136.38 (*aromatic* C), 134.60 (C-9), 128.58, 128.55, 128.51, 128.46, 128.36, 128.34, 128.14, 128.11, 128.06, 128.03, 128.01, 127.96, 127.89, 127.86, 127.84, 127.82, 127.78, 127.67, 127.56, 127.28, 127.11, 126.48 (*aromatic* C*H*), 116.97 (C-10), 115.88 (*a*d, *J* = 286 Hz, C*F$_3$*), 98.97, 98.52, 98.20, 97.57, 96.90 (5 C-1), 79.75, 76.18, 75.85, 75.25, 75.22, 74.43, 73.63, 73.59, 73.34, 73.23, 73.09, 73.03, 72.02, 71.89, 71.77, 71.37, 70.81, 70.64, 70.52, 70.08, 69.32, 69.04, 68.70, 67.76 (C-7), 67.72, 66.86, 66.67 (3 C-6), 66.30, 65.81 (C-6), 64.29 (C-2), 62.37 (C-6), 60.17, 59.48, 49.58, 48.77 (4 C-2), 33.88 (C-8). HR-MS: Calculated for $C_{101}H_{109}N_{11}O_{23}F_6$ $[M+Na]^+$: 1980.7500, found: 1980.7494.

Pentasaccharide S11

The reaction was carried out according to the general procedure D using compound **S10** (546 mg, 0.28 mmol), K_2CO_3 (42.6 mg), KI (46.5 mg) and $Ph_2BO(CH_2)_2NH_2$ (6.3 mg). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S11** (531 mg, 92% yield) was obtained as white foam. $[\alpha]_D^{25}$ +127 (c=0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.22 (m, 48H, *aromatic* H), 7.19 – 7.14 (m, 2H, *aromatic* H), 7.10 (d, *J* = 9.9 Hz, 1H, NH), 6.52 (d, *J* = 9.6 Hz, 1H, NH), 5.89 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H, H-9), 5.44 (d, *J* = 3.6 Hz, 1H, H-1), 5.22 – 5.12 (m, 2H, H-10), 5.08 (t, *J* = 3.1 Hz, 2H, 2xH-1), 5.04 (d, *J* = 3.7 Hz, 1H, H-1), 4.92 (d, *J* = 3.8 Hz, 1H), 4.90 (d, *J* = 4.5 Hz, 1H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.83 – 4.73 (m, 3H), 4.73 – 4.55 (m, 7H), 4.53 – 4.24 (m, 15H), 4.13 – 3.90 (m, 11H), 3.86 (d, *J* = 11.7 Hz, 1H), 3.80 (dt, *J* = 9.8, 6.9 Hz, 1H), 3.71 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.68 – 3.62 (m, 3H), 3.61 – 3.54 (m, 2H), 3.52 – 3.43 (m, 2H), 3.39 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.35 (dd, *J* = 11.5, 2.1 Hz, 1H), 3.30 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.22 (dd, *J* = 11.4, 1.9 Hz, 1H), 3.12 (t, *J* = 9.5 Hz, 1H), 3.07 – 3.00 (m, 2H), 2.46 (qt, *J* = 6.8, 1.4 Hz, 2H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.28 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 156.60 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 137.85, 137.68, 137.53, 137.41, 137.38, 137.33, 137.28, 137.04, 136.37 (*aromatic* C), 134.60 (C-9), 128.58, 128.52, 128.50, 128.48, 128.46, 128.42, 128.36, 128.33, 128.15, 128.12, 128.06, 128.04, 127.89, 127.87, 127.78, 127.76, 127.74, 127.69, 127.67, 127.61, 127.57, 127.23, 126.50 (*aromatic* C*H*), 116.97 (C-10), 115.89 (*a*d, *J* = 286 Hz, C*F$_3$*), 99.02, 98.48, 98.20, 97.55, 97.08 (5 C-1), 79.70, 76.16, 75.77, 75.44, 75.34, 74.43, 73.67, 73.60, 73.46, 73.35, 73.22, 73.00, 72.96, 71.90, 71.87, 71.79, 71.33, 70.79, 70.57, 70.45, 70.08, 69.09 (C-6), 69.03, 68.79, 68.60, 67.77 (C-7), 67.74, 66.86, 66.66, 65.76 (4 C-6), 65.63, 64.27, 60.00, 59.51, 49.59, 48.86 (5 C-2), 33.88 (C-8). HR-MS: Calculated for $C_{108}H_{115}N_{11}O_{23}F_6$ $[M+Na]^+$: 2070.7969, found: 2070.7964.

Hexasaccharide 19

The reaction was carried out according to the general procedure B using donor **13** (164 mg, 0.27 mmol) and acceptor **S11** (185 mg, 0.09 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **19** (546 mg, 82% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +155.0 (c=0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 4H, *aromatic* H), 7.47 – 7.25 (m, 50H, *aromatic* H), 7.18 – 7.14 (m, 2H, *aromatic*

H), 7.12 (d, *J* = 9.9 Hz, 1H, NH), 6.40 (d, *J* = 9.8 Hz, 1H, NH), 5.90 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H, H-9), 5.45 (d, *J* = 3.6 Hz, 1H, H-1), 5.24 – 5.13 (m, 2H, H-10), 5.10 (d, *J* = 3.6 Hz, 2H, 2xH-1), 5.04 (dd, *J* = 7.9, 4.6 Hz, 3H, 2xH-1), 4.91 (d, *J* = 3.8 Hz, 1H, H-1), 4.90 – 4.60 (m, 14H), 4.57 – 4.22 (m, 15H), 4.15 – 3.92 (m, 14H), 3.88 – 3.57 (m, 12H), 3.55 – 3.48 (m, 1H), 3.46 – 3.39 (m, 2H), 3.39 – 3.33 (m, 1H), 3.26 – 3.20 (m, 1H), 3.16 (dd, *J* = 8.3, 5.1 Hz, 1H), 3.08 (t, *J* = 9.4 Hz, 1H), 3.00 (dd, *J* = 9.0, 5.4 Hz, 1H), 2.50 – 2.43 (m, 2H, H-8), 1.13 (s, 9H, *C*H_3), 1.09 (s, 9H, *C*H_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.33 (*a*d, *J* = 37 Hz, *C*F_3*C*O), 156.56 (*a*d, *J* = 37 Hz, *C*F_3*C*O), 137.92, 137.85, 137.61, 137.58, 137.43, 137.33, 137.30, 137.17, 136.92, 136.34 (*aromatic* C), 134.60 (C-9), 128.65, 128.60, 128.54, 128.51, 128.46, 128.44, 128.37, 128.24, 128.17, 128.16, 128.08, 128.06, 128.02, 127.98, 127.96, 127.88, 127.75, 127.69, 127.59, 127.56, 127.23, 126.85, 126.70, 126.46 (*aromatic* C*H*), 117.00 (C-10), 115.88 (*a*d, *J* = 286 Hz, C*F*$_3$), 99.13, 98.50, 98.43, 98.22, 97.64, 97.04 (6 C-1), 79.67, 76.30, 76.23, 75.90, 75.35, 75.24, 74.49, 73.85, 73.62, 73.36, 73.23, 73.09, 73.00, 72.03, 71.92, 71.63, 71.35, 70.83, 70.63, 70.60, 70.30, 70.21, 70.11, 69.64, 69.55, 69.04, 68.77, 67.79 (C-7), 67.71 (C-6), 67.42, 67.14, 66.85, 66.70, 66.38, 65.56 (5 C-6), 64.29, 59.97, 59.53, 58.46, 49.64, 49.11 (6 C-2), 33.90 (C-8), 27.60, 27.43 (2 C*H*$_3$), 23.27, 20.73 (2 C-*Si*). ^{13}C-HMBC ($CDCl_3$, 125 MHz): 99.13 ($J_{C1,H1}$ = 171 Hz), 98.50 ($J_{C1,H1}$ = 173 Hz), 98.43 ($J_{C1,H1}$ = 172 Hz), 98.22 ($J_{C1,H1}$ = 171 Hz), 97.64 ($J_{C1,H1}$ = 174 Hz), 97.04 ($J_{C1,H1}$ = 175 Hz).

Hexasaccharide S12

The reaction was carried out according to the general procedure C using compound **19** (215 mg, 0.087 mmol) and HF/pyridine (70%, 36 µl, 1.39 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S12** (177 mg, 87% yield) was obtained as white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.12 (m, 53H, *aromatic* H), 7.08 – 7.02 (m, 3H), 6.42 (d, *J* = 9.7 Hz, 1H, NH), 5.79 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H, H-9), 5.33 (d, *J* = 3.6 Hz, 1H, H-1), 5.13 – 5.02 (m, 2H, H-10), 4.98 (t, *J* = 2.8 Hz, 2H, 2xH-1), 4.92 (dd, *J* = 5.7, 3.7 Hz, 2H, 2xH-1), 4.89 (d, *J* = 12.3 Hz, 1H), 4.81 (d, *J* = 3.8 Hz, 1H, H-1), 4.79 – 4.73 (m, 2H), 4.74 – 4.64 (m, 4H), 4.63 – 4.48 (m, 6H), 4.45 – 4.13 (m, 16H), 4.03 – 3.81 (m, 14H), 3.80 – 3.64 (m, 4H), 3.61 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.58 – 3.36 (m, 7H), 3.34 – 3.22 (m, 3H), 3.16 – 3.05 (m, 2H), 2.99 (t, *J* = 9.5 Hz, 1H), 2.90 (dd, *J* = 9.2, 5.4 Hz, 1H), 2.78 (bs, 1H, OH), 2.36 (q, *J* = 6.8 Hz, 2H, H-8), 2.28 (bs, 1H, OH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.34 (*a*d, *J* = 37 Hz, *C*F_3*C*O), 156.82 (*a*d, *J* = 37 Hz, *C*F_3*C*O), 137.85, 137.58, 137.52, 137.47, 137.45, 137.42, 137.33, 137.28, 137.16, 137.03, 136.36 (*aromatic* C), 134.61 (C-9), 128.64, 128.60, 128.53, 128.52, 128.50, 128.47, 128.40, 128.38, 128.34, 128.29, 128.17, 128.13, 128.09, 128.03, 127.97, 127.95, 127.90, 127.87, 127.86, 127.77, 127.76, 127.69, 127.63, 127.59, 127.25, 127.13, 126.86, 126.50 (*aromatic* C*H*), 116.99 (C-10), 115.87 (*a*d, *J* = 286 Hz, C*F*$_3$), 99.13, 98.94, 98.50, 98.21, 97.64, 97.05 (6 C-1), 79.69, 76.62, 76.27, 76.12, 75.33, 75.22, 74.47, 73.82, 73.62, 73.36, 73.23, 73.15, 73.03, 72.08, 71.93, 71.89, 71.83, 71.71, 71.37, 70.56, 70.10, 69.71, 69.18, 69.04, 68.74, 67.79 (C-7), 67.72 (C-6), 67.47, 66.86, 66.71, 66.52, 65.64 (4 C-6), 64.28 (C-2), 62.61 (C-6), 59.98, 59.51, 59.48, 49.63, 49.32 (5 C-2), 33.90 (C-8).

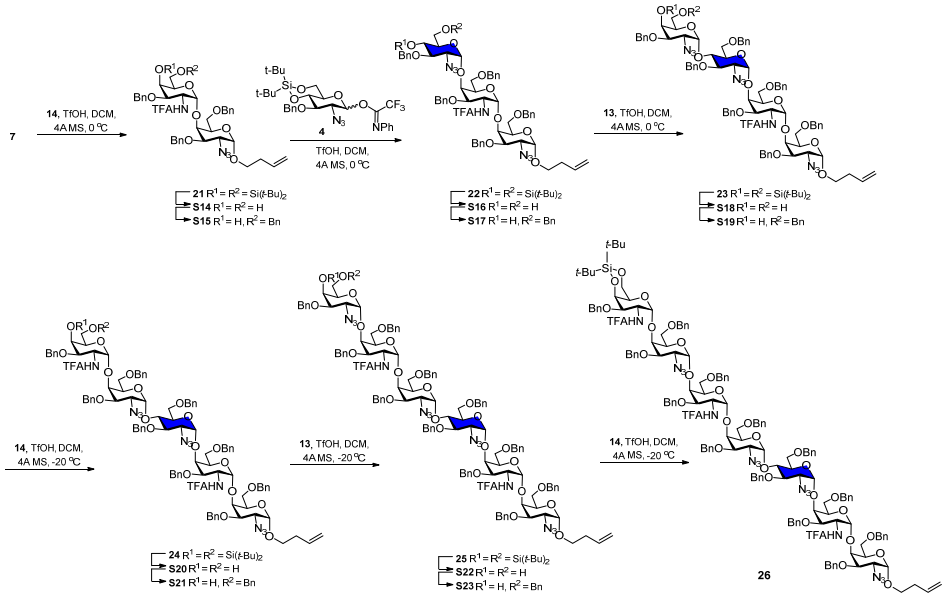
Hexasaccharide S13

The reaction was carried out according to the general procedure D using compound **S12** (173 mg, 0.074 mmol), K_2CO_3 (11 mg, 0.081 mmol), KI (12 mg, 0.074 mmol) and $Ph_2BO(CH_2)_2NH_2$ (1.7 mg, 0.0074 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S13** (170 mg, 95% yield) was obtained as white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 4H, *aromatic* H), 7.36 – 7.14 (m, 54H, *aromatic* H), 7.08 – 7.04 (m, 2H, *aromatic* H), 7.02 (d, *J* = 9.9 Hz, 1H, NH), 6.35 (d, *J* = 9.7 Hz, 1H, NH), 5.79 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H, H-9), 5.33 (d, *J* = 3.6 Hz, 1H, H-1), 5.12 – 5.02 (m, 2H, H-10), 5.01 – 4.96 (m, 2H), 4.94 (t, *J* = 3.8 Hz, 2H, 2xH-1), 4.89 (d, *J* = 12.3 Hz, 1H, *PhC*H*H*O), 4.80 (d, *J* = 3.8 Hz, 1H, H-1), 4.78 – 4.50 (m, 12H), 4.46 – 4.21 (m, 15H), 4.18 – 4.13 (m, 2H), 4.02 – 3.74 (m, 17H), 3.70 (dt, *J* = 9.8, 6.9 Hz, 1H), 3.62 – 3.37 (m, 7H), 3.33 – 3.21 (m, 4H), 3.15 – 3.04 (m, 3H), 2.99 (t, *J* = 9.4 Hz, 1H), 2.91 (dd, *J* = 9.1, 5.4 Hz, 1H), 2.36 (q, *J* = 6.8 Hz, 2H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.32 (*a*d, *J* = 37 Hz, *CF*$_3$*C*O), 156.61 (*a*d, *J* = 37 Hz, *CF*$_3$*C*O), 137.84, 137.68, 137.60, 137.58, 137.55, 137.47, 137.44, 137.39, 137.32, 137.28, 137.02, 136.35 (*aromatic* C), 134.60 (C-9), 128.58, 128.52, 128.50, 128.48, 128.46, 128.39, 128.36, 128.33, 128.32, 128.31, 128.16, 128.12, 128.07, 128.01, 127.96, 127.94, 127.89, 127.86, 127.75, 127.72, 127.67, 127.65, 127.58, 127.23, 127.16, 126.80, 126.52 (*aromatic* C*H*), 116.98 (C-10), 115.88 (*a*d, *J* = 286 Hz, C*F*$_3$), 99.10, 99.00, 98.48, 98.20, 97.60, 97.11 (6 C-1), 79.67, 76.58, 76.19, 76.16, 75.33, 75.12, 74.45, 73.79, 73.60, 73.38, 73.35, 73.22, 73.13, 73.01, 72.98, 72.00, 71.91, 71.69, 71.59, 71.44, 71.32, 70.81, 70.78, 70.49, 70.09, 69.86, 69.65, 69.03, 68.79, 68.21, 67.78, 67.72, 66.97, 66.85, 66.71, 66.50, 65.65, 64.26, 59.97, 59.51, 59.33, 49.62, 49.23 (6 C-2), 33.89 (C-8).

Heptasaccharide 20

The reaction was carried out according to the general procedure B using donor **14** (142 mg, 0.21 mmol) and acceptor **S13** (170 mg, 0.07 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **20** (165 mg, 81% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +176 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.18 (m, 61H, *aromatic* H), 7.16 – 7.12 (m, 2H, *aromatic* H), 7.11 – 7.06 (m, 2H, *aromatic* H), 7.05 (d, *J* = 9.7 Hz, 1H, NH), 6.34 (t, *J* = 12.4, 9.6 Hz, 2H, 2xNH), 5.92 – 5.78 (m, 1H, H-9), 5.38 (d, *J* = 3.6 Hz, 1H, H-1), 5.18 – 5.08 (m, 2H, H-10), 5.06 (d, *J* = 3.6 Hz, 1H, H-1), 5.05 – 5.02 (m, 2H, 2xH-1), 4.99 (d, *J* = 3.7 Hz, 1H, H-1), 4.95 (d, *J* = 12.3 Hz, 1H, *PhC*H*H*O), 4.87 (d, *J* = 3.7 Hz, 1H, H-1), 4.85 (d, *J* = 3.7 Hz, 1H, H-1), 4.83 – 4.24 (m, 32H), 4.22 (d, *J* = 12.4 Hz, 1H), 4.09 – 3.42 (m, 31H), 3.40 – 3.27 (m, 4H), 3.21 – 2.92 (m, 6H), 2.42 (qt, *J* = 6.7, 1.4 Hz, 2H, H-8), 1.11 (s, 9H, *C*H$_3$), 1.03 (s, 9H, *C*H$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.40 (*a*d, *J* = 37 Hz, *CF*$_3$*C*O), 156.65 (*a*d, *J* = 37 Hz, *CF*$_3$*C*O), 137.97, 137.92, 137.70, 137.68, 137.64, 137.56, 137.46, 137.41, 137.36, 137.29, 137.09, 136.96, 136.43 (*aromatic* C), 134.68 (C-9), 128.67, 128.60, 128.58, 128.55, 128.52, 128.48, 128.44, 128.43, 128.39, 128.36, 128.24, 128.22, 128.16, 128.12, 128.10, 128.02, 127.97, 127.94, 127.92, 127.90, 127.85, 127.83, 127.80, 127.76, 127.66, 127.32, 127.01, 126.83, 126.59 (*aromatic* C*H*), 117.06 (C-10), 115.96 (*a*d, *J* = 286 Hz, 3xC*F*$_3$), 99.19, 98.59, 98.47, 98.29, 97.71, 97.23, 96.77 (7 C-1), 79.77, 76.29, 76.22, 75.43, 75.40, 74.87, 74.57, 73.90, 73.70, 73.43, 73.30, 73.13, 73.11, 73.10, 73.01, 72.07, 72.00, 71.86, 71.77, 71.42, 71.13, 71.05, 70.90, 70.67, 70.17, 69.64, 69.59, 69.42, 69.35, 69.12, 68.86, 68.66, 67.88, 67.80, 67.77, 67.02, 66.94, 66.80, 66.59, 65.85, 65.81, 64.38, 60.23, 60.08, 59.60, 49.70, 49.21, 48.28 (7 C-2), 33.98(C-8), 27.66, 27.47 (2 C*H*$_3$), 23.37, 20.77 (2 C-*Si*).

^{13}C-HMBC ($CDCl_3$, 125 MHz): 99.19 ($J_{C1,H1}$ = 172 Hz), 98.59 ($J_{C1,H1}$ = 172 Hz), 98.47 ($J_{C1,H1}$ = 177 Hz), 98.29 ($J_{C1,H1}$ = 172 Hz), 97.71 ($J_{C1,H1}$ = 175 Hz), 97.23 ($J_{C1,H1}$ = 175 Hz), 96.77 ($J_{C1,H1}$ = 177 Hz).



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

The reaction was carried out according to the general procedure A. The donor **14** (2.98 g, 4.4 mmol) and acceptor **7** (1.29 g, 2.94 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 29 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to 0 °C, after which TfOH (39 µl, 0.44 mmol) was added. The reaction was stirred at 0 °C for 2 h. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 15:1). Compound **21** (2.34 g, 86% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +165.7 (c=0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 15H, *aromatic* H), 6.32 (d, *J* = 9.4 Hz, 1H, NH), 5.77 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, H-9), 5.14 – 5.00 (m, 3H, H-10, 1^B), 4.84 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.75 (d, *J* = 12.0 Hz, 1H, *PhCHH*O), 4.69 (d, *J* = 11.9 Hz, 1H, *PhCHH*O), 4.66 – 4.61 (m, 1H, H-2^B), 4.60 (d, *J* = 11.8 Hz, 1H, *PhCHH*O), 4.49 (d, *J* = 2.4 Hz, 1H, H-4^B), 4.47 (d, *J* = 11.8 Hz, 2H, *PhCHH*O), 4.39 (d, *J* = 11.4 Hz, 1H, *PhCHH*O), 4.36 (d, *J* = 2.7 Hz, 1H, H-4^A), 4.04 (d, *J* = 2.4 Hz, 1H, , H-5^B), 3.91 (dd, *J* = 9.2, 5.8 Hz, 1H, H-5^A), 3.81 (dd, *J* = 10.7, 2.8 Hz, 1H, , H-3^A), 3.76 (dd, *J* = 12.8, 1.6 Hz, 1H, , H-6^B), 3.72 – 3.65 (m, 1H, H-7), 3.65 – 3.56 (m, 2H, H-3^B, 6^B), 3.55 – 3.48 (m, 1H, H-7), 3.45 – 3.30 (m, 3H, , H-2^A, 6^A), 2.34 (qt, *J* = 6.7, 1.3 Hz, 2H, H-8), 1.09 (s, 9H, *CH*$_3$), 1.00 (s, 9H, *CH*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.94 (*ad*, *J* = 37 Hz, *CF*$_3$*CO*), 137.88, 137.12, 136.90 (*aromatic* C), 134.59 (C-9), 128.75, 128.71, 128.68, 128.62, 128.52, 128.43, 128.35, 128.07, 128.01, 127.96, 127.72, 127.67,

127.19, 127.13 (*aromatic* C*H*), 117.08 (C-10), 115.96 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.03 (C-1^A), 97.27 (C-1^B), 75.79 (C-3^A), 74.34 (C-3^B), 73.79 (C*H*$_2$*Ph*), 71.82 (C*H*$_2$*Ph*), 70.33 (C-4^A), 69.65 (C*H*$_2$*Ph*), 69.30 (C-4^B), 68.87 (C-5^A), 68.03 (C-5^B), 67.88 (C-7), 67.05 (C-6^B), 66.63 (C-6^A), 59.81 (C-2^A), 48.45 (C-2^B), 33.93 (C-8), 27.69, 27.47 (2 C*H*$_3$), 23.41, 20.80 (2 C-*Si*). HR-MS: Calculated for $C_{47}H_{61}N_4O_{10}F_3Si$ $[M+Na]^+$: 949.4007, found: 949.4001.

3-Butenyl 3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S14)

The reaction was carried out according to the general procedure C using compound **21** (3.6 g, 3.88 mmol) and HF/pyridine (70%, 1.6 ml, 62.1 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S14** (2.78 g, 91% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +128.2 (c=0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 15H), 6.56 (d, *J* = 9.4 Hz, 1H), 5.77 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.11 – 5.01 (m, 2H), 4.98 (d, *J* = 3.6 Hz, 1H), 4.85 (d, *J* = 3.6 Hz, 1H), 4.79 (d, *J* = 11.8 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.55 – 4.46 (m, 1H), 4.45 – 4.37 (m, 3H), 4.31 (d, *J* = 2.7 Hz, 1H), 4.15 (dd, *J* = 2.9, 1.4 Hz, 1H), 4.12 – 4.06 (m, 1H), 3.89 (dd, *J* = 8.8, 5.9 Hz, 1H), 3.83 (dd, *J* = 10.8, 2.7 Hz, 1H), 3.71 – 3.28 (m, 8H), 3.13 (s, 1H), 2.34 (qt, *J* = 6.8, 1.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.08 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 137.21, 137.13, 136.94 (*aromatic* C), 134.53 (C-9), 128.65, 128.63, 128.59, 128.23, 128.15, 128.10, 128.08, 127.94, 127.38 (*aromatic* C*H*), 116.99 (C-10), 115.87 (*a*d, *J* = 286 Hz, C*F*$_3$), 97.99, 97.40, 75.48, 74.70, 73.58, 71.89, 71.18, 70.75, 69.50, 68.93, 67.80, 66.63, 66.60, 62.55, 59.64, 48.93, 33.82. HR-MS: Calculated for $C_{39}H_{45}N_4O_{10}F_3$ $[M+Na]^+$: 809.2986, found: 809.2980.

3-Butenyl 3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S15)

The reaction was carried out according to the general procedure D using compound **S14** (1.83 g, 2.33 mmol), K_2CO_3 (354 mg, 2.56 mmol), KI (387 mg, 2.33 mmol) and $Ph_2BO(CH_2)_2NH_2$ (53 mg, 0.233 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:1). Compound **S15** (1.96 g, 96% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +129.9 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.18 (m, 20H), 6.44 (d, *J* = 9.4 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.11 – 5.00 (m, 2H), 4.97 (d, *J* = 3.6 Hz, 1H), 4.83 (d, *J* = 3.6 Hz, 1H), 4.79 (d, *J* = 12.3 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.62 – 4.50 (m, 2H), 4.45 – 4.38 (m, 3H), 4.37 – 4.23 (m, 4H), 4.22 – 4.17 (m, 1H), 3.87 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.78 (dd, *J* = 10.8, 2.7 Hz, 1H), 3.69 – 3.58 (m, 2H), 3.58 – 3.45 (m, 2H), 3.43 – 3.29 (m, 4H), 2.93 (s, 1H), 2.32 (qt, *J* = 6.8, 1.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.99 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 137.67, 137.37, 137.31, 137.01 (*aromatic* C), 134.57 (C-9), 129.04, 128.63, 128.56, 128.47, 128.40, 128.25, 128.12, 127.99, 127.94, 127.89, 127.86, 127.79, 127.48 (*aromatic* C*H*), 117.00 (C-10), 115.83 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.06, 97.47, 75.33, 74.88, 73.60, 73.59, 71.74, 71.14, 70.64, 69.23, 68.96, 67.79, 66.68, 65.72, 59.60, 49.02, 33.86. HR-MS: Calculated for $C_{46}H_{51}N_4O_{10}F_3$ $[M+Na]^+$: 899.3455, found: 899.3450.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (22)

The reaction was carried out according to the general procedure A. The donor **4** (934 mg, 1.54 mmol) and acceptor **S15** (450 mg, 0.51 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 5 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to -10 °C, after which TfOH (14 µl, 0.15 mmol) was added. The reaction was stirred at -10 °C for overnight. 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 = 12:1). Compound **22** (583 mg, 85% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +114.3 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.18 (m, 25H), 6.03 (d, *J* = 9.2 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.10 (d, *J* = 10.4 Hz, 1H), 5.08 – 5.00 (m, 3H), 4.89 – 4.76 (m, 4H), 4.73 (d, *J* = 3.6 Hz, 1H), 4.60 – 4.41 (m, 4H), 4.40 – 4.28 (m, 3H), 4.25 (d, *J* = 2.6 Hz, 1H), 4.22 (d, *J* = 2.4 Hz, 1H), 4.10 (d, *J* = 11.6 Hz, 1H), 4.00 – 3.73 (m, 8H), 3.68 – 3.57 (m, 2H), 3.48 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.33 (dd, *J* = 9.1, 5.8 Hz, 1H), 3.29 – 3.10 (m, 4H), 2.31 (qt, *J* = 6.8, 1.4 Hz, 2H), 1.05 (s, 9H), 1.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.62 (*a*d, *J* = 37 Hz, *CF₃CO*), 138.32, 137.51, 137.33, 137.19 (*aromatic* C), 134.62 (C-9), 128.84, 128.67, 128.63, 128.55, 128.52, 128.48, 128.34, 128.29, 128.15, 128.14, 127.98, 127.89, 127.11 (*aromatic* C*H*), 117.02 (C-10), 115.84 (*a*d, *J* = 286 Hz, C*F₃*), 98.20, 98.08, 97.55, 79.40, 79.32, 75.79, 75.76, 73.53, 73.32, 72.59, 71.71, 71.33, 71.14, 70.68, 69.74, 68.99, 67.80, 67.12, 66.79, 66.65, 66.29, 62.90, 59.60, 49.40, 33.92, 27.45, 27.06, 22.74, 20.07. HR-MS: Calculated for $C_{67}H_{82}N_7O_{14}F_3Si$ $[M+Na]^+$: 1316.5539, found: 1316.5533.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S16)

The reaction was carried out according to the general procedure C using compound **22** (655 mg, 0.51 mmol) and HF/pyridine (70%, 210 µl, 8.1 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S16** (497 mg, 84% yield) was obtained as white foam. $[\alpha]_D^{25}$ +139.7 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.16 (m, 25H), 6.40 (d, *J* = 9.5 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.11 – 4.96 (m, 3H), 4.93 – 4.79 (m, 4H), 4.78 (d, *J* = 3.7 Hz, 1H), 4.71 (d, *J* = 12.3 Hz, 1H), 4.55 – 4.37 (m, 4H), 4.33 – 4.24 (m, 3H), 4.21 (d, *J* = 2.3 Hz, 1H), 4.09 (s, 3H), 3.94 (dd, *J* = 10.3, 8.8 Hz, 1H), 3.89 – 3.74 (m, 3H), 3.73 – 3.44 (m, 5H), 3.43 – 3.17 (m, 7H), 2.32 (qt, *J* = 6.8, 1.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.09 (*a*d, *J* = 37 Hz, *CF₃CO*), 138.30, 137.43, 137.39, 137.24, 136.82 (*aromatic* C), 134.55 (C-9), 128.67, 128.63, 128.62, 128.52, 128.44, 128.38, 128.31, 128.27, 128.19, 128.03, 127.96, 127.89, 127.85, 127.63, 127.15 (*aromatic* C*H*), 117.02 (C-10), 115.83 (*a*d, *J* = 286 Hz, C*F₃*), 98.73, 98.06, 97.25, 80.00, 75.56, 75.22, 74.15, 73.65, 73.28, 72.24, 71.90, 71.59, 71.47, 70.90, 70.61, 69.91, 68.81, 67.83, 66.55, 66.33, 63.53, 62.20, 59.54, 49.49, 33.86. HR-MS: Calculated for $C_{59}H_{66}N_7O_{14}F_3$ $[M+Na]^+$: 1176.4518, found: 1176.4512.

3-Butenyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoro-acetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S17)

The reaction was carried out according to the general procedure D using compound **S16** (482 mg, 0.42 mmol), K_2CO_3 (64 mg, 0.46 mmol), KI (70 mg, 0.42 mmol) and $Ph_2BO(CH_2)_2NH_2$ (9.4 mg, 0.042 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **S17** (506 mg, 97% yield) was obtained as colorless syrup. $[\alpha]_D^{25}$ +139.8 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.12 (m, 30H), 6.36 (d, *J* = 9.5 Hz, 1H), 5.74 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.10 – 4.97 (m, 3H), 4.95 (d, *J* = 3.6 Hz, 1H), 4.91 (d, *J* = 3.6 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.84 – 4.73 (m, 2H), 4.67 (d, *J* = 12.4 Hz, 1H), 4.55 (td, *J* = 10.3, 3.6 Hz, 1H), 4.51 – 4.36 (m, 3H), 4.35 – 4.16 (m, 7H), 4.13 – 4.00 (m, 2H), 3.93 (t, *J* = 9.5 Hz, 1H), 3.90 – 3.71 (m, 4H), 3.68 – 3.14 (m, 10H), 2.76 (d, *J* = 4.2 Hz, 1H), 2.30 (q, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.03 (*a*d, *J* = 37 Hz, *CF*$_3$*C*O), 138.22, 137.79, 137.33, 137.29, 136.74 (*aromatic* C), 134.41 (C-9), 128.80, 128.49, 128.45, 128.37, 128.34, 128.26, 128.18, 128.16, 128.11, 128.08, 127.99, 127.83, 127.68, 127.64, 127.58, 127.54, 127.48, 127.22, 126.91 (*aromatic* C*H*), 116.83 (C-10), 115.84 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.67, 97.94, 97.21, 79.77, 75.48, 74.97, 74.24, 73.45, 73.19, 73.07, 72.35, 71.78, 71.43, 70.77, 70.45, 70.36, 69.69, 69.06, 68.70, 67.62, 66.42, 66.23, 63.28, 59.37, 58.71, 58.10, 54.60, 49.25, 33.70. HR-MS: Calculated for $C_{66}H_{72}N_7O_{14}F_3$ $[M+Na]^+$: 1266.4987, found: 1266.4982.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (23)

The reaction was carried out according to the general procedure B using donor **13** (722 mg, 1.19 mmol) and acceptor **S17** (494 mg, 0.40 mmol). The product was purified by column chromatography (pentane:EtOAc = 8:1). Compound **23** (547 mg, 83% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +126.6 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.17 (m, 35H), 6.39 (d, *J* = 9.6 Hz, 1H), 5.75 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.52 (d, *J* = 3.6 Hz, 1H), 5.10 – 4.99 (m, 3H), 4.99 – 4.90 (m, 3H), 4.84 (d, *J* = 12.4 Hz, 1H), 4.81 (d, *J* = 3.6 Hz, 1H), 4.78 – 4.72 (m, 2H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.63 – 4.56 (m, 1H), 4.53 (d, *J* = 12.4 Hz, 1H), 4.49 – 4.40 (m, 3H), 4.37 – 4.19 (m, 7H), 4.14 (d, *J* = 11.4 Hz, 1H), 4.12 – 4.03 (m, 2H), 4.00 (dd, *J* = 9.7, 8.5 Hz, 1H), 3.96 – 3.76 (m, 7H), 3.68 – 3.55 (m, 3H), 3.53 – 3.44 (m, 2H), 3.43 – 3.32 (m, 4H), 3.23 (dd, *J* = 8.4, 5.2 Hz, 1H), 3.12 (dd, *J* = 11.3, 1.9 Hz, 1H), 2.32 (qt, *J* = 6.7, 1.3 Hz, 2H), 1.02 (s, 9H), 0.97 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.64 (*a*d, *J* = 37 Hz, *CF*$_3$*C*O), 138.22, 137.87, 137.65, 137.62, 137.46, 137.01 (*aromatic* C), 134.56 (C-9), 128.66, 128.51, 128.48, 128.36, 128.27, 128.20, 128.17, 128.05, 128.01, 127.93, 127.89, 127.78, 127.71, 127.56, 127.49, 127.37, 127.14 (*aromatic* C*H*), 117.02 (C-10), 116.02 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.98, 98.14, 97.94, 97.58, 80.94, 75.87, 75.64, 74.97, 74.69, 74.31, 73.64, 73.29, 73.16, 72.93, 71.70, 71.16, 70.98, 70.66, 69.99, 69.89, 68.92, 68.86, 67.89, 67.86, 67.04, 66.71, 66.58, 64.81, 59.61, 58.65, 49.49, 33.88, 27.67, 27.36, 23.39, 20.77. HR-MS: Calculated for $C_{87}H_{103}N_{10}O_{18}F_3Si$ $[M+Na]^+$: 1683.7071, found: 1683.7065.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S18)

The reaction was carried out according to the general procedure C using compound **23** (530 mg, 0.32 mmol) and HF/pyridine (70%, 133 µl, 5.1 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S18** (436 mg, 89% yield) was obtained as white foam. $[\alpha]_D^{25}$ +120.5 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.12 (m, 35H), 6.46 (d, *J* = 9.6 Hz, 1H), 5.76 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.36 (d, *J* = 3.6 Hz, 1H), 5.12 – 4.99 (m, 3H), 4.94 – 4.87 (m, 3H), 4.84 (d, *J* = 12.4 Hz, 1H), 4.81 (d, *J* = 3.6 Hz, 1H), 4.72 (d, *J* = 12.3 Hz, 1H), 4.68 (s, 2H), 4.57 – 4.39 (m, 4H), 4.37 – 4.19 (m, 7H), 4.18 – 4.01 (m, 5H), 3.97 (dd, *J* = 10.5, 3.0 Hz, 1H), 3.94 – 3.76 (m, 4H), 3.71 (dd, *J* = 10.5, 3.6 Hz, 1H), 3.65 (td, *J* = 6.9, 3.1 Hz, 4H), 3.57 (dd, *J* = 11.0, 2.2 Hz, 1H), 3.50 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.43 – 3.29 (m, 4H), 3.23 (dd, *J* = 8.3, 5.2 Hz, 1H), 3.13 (d, *J* = 11.4 Hz, 1H), 2.67 (d, *J* = 7.1 Hz, 2H), 2.32 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.97 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 138.19, 137.97, 137.58, 137.48, 137.40, 137.30, 136.86 (*aromatic* C), 134.53 (C-9), 128.66, 128.65, 128.49, 128.46, 128.33, 128.29, 128.26, 128.17, 128.01, 127.89, 127.84, 127.75, 127.70, 127.55, 127.35, 127.10 (*aromatic* C*H*), 117.03 (C-10), 115.98 (*a*d, *J* = 286 Hz, C*F*$_3$), 99.00, 98.10, 97.99, 97.34, 80.15, 76.36, 75.94, 75.60, 75.05, 74.66, 73.63, 73.27, 73.20, 73.00, 71.81, 71.65, 71.08, 70.96, 70.71, 70.32, 69.92, 68.76, 68.47, 67.86, 67.02, 66.65, 66.31, 64.54, 62.51, 59.61, 59.56, 49.47, 33.85. HR-MS: Calculated for $C_{79}H_{87}N_{10}O_{18}F_3$ $[M+Na]^+$: 1543.6050, found: 1543.6044.

3-Butenyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S19)

The reaction was carried out according to the general procedure D using compound **S18** (421 mg, 0.28 mmol), K_2CO_3 (42 mg, 0.30 mmol), KI (46 mg, 0.28 mmol) and $Ph_2BO(CH_2)_2NH_2$ (6.2 mg, 0.028 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S19** (436 mg, 98% yield) was obtained as white foam. $[\alpha]_D^{25}$ +136.2 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.26 (m, 40H), 6.46 (d, *J* = 9.5 Hz, 1H), 5.87 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.69 (d, *J* = 3.7 Hz, 1H), 5.22 – 5.12 (m, 3H), 5.12 – 5.04 (m, 3H), 4.96 (d, *J* = 12.4 Hz, 1H), 4.91 (d, *J* = 3.6 Hz, 1H), 4.82 (d, *J* = 12.0 Hz, 3H), 4.70 (ddd, *J* = 13.2, 9.7, 3.6 Hz, 1H), 4.64 (d, *J* = 12.4 Hz, 1H), 4.59 – 4.51 (m, 2H), 4.51 – 4.33 (m, 9H), 4.30 – 4.22 (m, 3H), 4.21 – 4.13 (m, 3H), 4.07 – 3.96 (m, 3H), 3.91 (dd, *J* = 10.8, 2.6 Hz, 1H), 3.86 (dd, *J* = 10.6, 3.6 Hz, 1H), 3.79 – 3.41 (m, 11H), 3.39 – 3.31 (m, 2H), 2.88 (s, 1H), 2.49 – 2.38 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.52 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 138.47, 137.92, 137.79, 137.65, 137.56, 137.40, 136.89 (*aromatic* C), 134.51 (C-9), 128.97, 128.60, 128.58, 128.53, 128.43, 128.41, 128.32, 128.25, 128.21, 128.17, 128.14, 128.12, 127.95, 127.91, 127.83, 127.82, 127.71, 127.67, 127.49, 127.34, 127.30, 127.07 (*aromatic* C*H*), 116.95 (C-10), 116.02 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.89, 98.05, 98.03, 97.42, 80.62, 76.17, 75.57, 74.61, 74.57, 74.44, 73.57, 73.56, 73.23, 72.95, 72.70, 71.69, 71.58, 70.94, 70.82, 70.48, 69.90, 69.42, 68.86, 68.83, 67.77, 66.70, 66.67, 66.43, 64.86, 59.53, 59.21, 58.60, 58.19, 54.74, 49.39, 33.81. HR-MS: Calculated for $C_{86}H_{93}N_{10}O_{18}F_3$ $[M+Na]^+$: 1633.6519, found: 1633.6514.

Pentasaccharide 24

The reaction was carried out according to the general procedure B using donor **14** (542 mg, 0.80 mmol) and acceptor **S19** (430 mg, 0.27 mmol). The product was purified by column chromatography (pentane:EtOAc = 7:1). Compound **24** (501 mg, 89% yield) was obtained as yellow foam. $[\alpha]_D^{25}$ +150.6 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.21 (m, 45H), 6.42 (d, *J* = 9.6 Hz, 2H), 5.86 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.59 (d, *J* = 3.7 Hz, 1H), 5.22 – 5.02 (m, 7H), 4.94 (d, *J* = 12.4 Hz, 1H), 4.90 (d, *J* = 3.6 Hz, 1H), 4.86 – 4.71 (m, 5H), 4.70 – 4.33 (m, 14H), 4.32 – 4.15 (m, 6H), 4.15 – 4.04 (m, 3H), 4.04 – 3.93 (m, 2H), 3.90 (dd, *J* = 10.7, 2.5 Hz, 1H), 3.81 (d, *J* = 12.6 Hz, 1H), 3.78 – 3.66 (m, 3H), 3.65 – 3.56 (m, 4H), 3.54 (dd, *J* = 10.1, 3.3 Hz, 1H), 3.51 – 3.40 (m, 3H), 3.40 – 3.33 (m, 2H), 3.32 – 3.23 (m, 2H), 2.48 – 2.37 (m, 2H), 1.20 (s, 10H), 1.10 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.71 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.38, 138.17, 137.85, 137.52, 137.45, 137.39, 136.96, 136.78 (*aromatic* C), 134.51 (C-9), 128.61, 128.55, 128.53, 128.50, 128.47, 128.44, 128.27, 128.25, 128.15, 128.07, 127.99, 127.85, 127.78, 127.76, 127.68, 127.66, 127.48, 127.42, 127.20, 127.08, 126.63 (*aromatic* C*H*), 116.97 (C-10), 115.89 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.82, 98.06, 97.47, 97.39, 96.90, 79.98, 76.10, 75.59, 74.63, 74.29, 73.90, 73.49, 73.27, 73.03, 72.51, 71.77, 71.62, 70.97, 70.62, 70.60, 69.87, 69.54, 69.34, 69.22, 68.81, 68.73, 67.78, 67.75, 66.99, 66.65, 66.44, 66.17, 64.72, 60.20, 59.56, 49.37, 48.29, 33.83, 27.59, 27.41, 23.30, 20.72. HR-MS: Calculated for $C_{109}H_{125}N_{11}O_{23}F_6Si$ $[M+Na]^+$: 2120.8521, found: 2120.8516.

Pentasaccharide S20

The reaction was carried out according to the general procedure C using compound **24** (490 mg, 0.23 mmol) and HF/pyridine (70%, 97 µl, 3.7 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S20** (395 mg, 86% yield) was obtained as white foam. $[\alpha]_D^{25}$ +117.6 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.09 (m, 43H), 6.44 (d, *J* = 9.5 Hz, 1H), 6.40 (d, *J* = 9.6 Hz, 1H), 5.74 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.48 (d, *J* = 3.7 Hz, 1H), 5.09 – 4.90 (m, 7H), 4.87 – 4.74 (m, 3H), 4.72 – 4.48 (m, 5H), 4.46 – 4.20 (m, 12H), 4.19 – 4.01 (m, 8H), 3.99 – 3.91 (m, 2H), 3.90 – 3.82 (m, 2H), 3.78 (dd, *J* = 10.7, 2.6 Hz, 1H), 3.66 – 3.52 (m, 3H), 3.52 – 3.39 (m, 5H), 3.39 – 3.27 (m, 4H), 3.27 – 3.19 (m, 2H), 3.19 – 3.09 (m, 2H), 2.90 (s, 1H), 2.36 – 2.25 (m, 2H), 2.02 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.78 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.34, 138.16, 137.60, 137.55, 137.42, 137.40, 137.05, 136.98, 136.84 (*aromatic* C), 134.53 (C-9), 128.59, 128.58, 128.54, 128.49, 128.47, 128.42, 128.22, 128.17, 128.14, 128.12, 128.05, 127.96, 127.88, 127.85, 127.75, 127.67, 127.46, 127.42, 127.25, 127.10, 126.99 (*aromatic* C*H*), 116.95 (C-10), 115.93 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.80, 98.05, 97.53, 97.43, 97.13, 80.03, 75.92, 75.58, 74.84, 74.58, 74.24, 73.82, 73.48, 73.45, 73.25, 73.05, 72.58, 71.97, 71.65, 71.07, 70.84, 70.60, 70.58, 69.86, 69.29, 69.24, 68.84, 68.71, 67.79, 66.67, 66.24, 64.71, 62.45, 60.11, 59.56, 49.41, 48.83, 33.81. HR-MS: Calculated for $C_{101}H_{109}N_{11}O_{23}F_6$ $[M+Na]^+$: 1980.7500, found: 1980.7494.

Pentasaccharide S21

The reaction was carried out according to the general procedure D using compound **S20** (389 mg, 0.2 mmol), K_2CO_3 (30 mg, 0.22 mmol), KI (33 mg, 0.2 mmol) and $Ph_2BO(CH_2)_2NH_2$ (4.5 mg, 0.02 mmol). The product was

purified by column chromatography (pentane:EtOAc = 4:1). Compound **S21** (369 mg, 90% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +143.7 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.06 (m, 48H), 6.44 (dd, *J* = 14.6, 9.5 Hz, 2H), 5.73 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.47 (d, *J* = 3.7 Hz, 1H), 5.08 – 4.90 (m, 7H), 4.86 – 4.76 (m, 3H), 4.57 (ddd, *J* = 53.0, 25.7, 12.7 Hz, 6H), 4.42 – 4.00 (m, 21H), 3.98 – 3.82 (m, 4H), 3.78 (dd, *J* = 10.6, 2.5 Hz, 1H), 3.60 (dq, *J* = 13.3, 6.6 Hz, 3H), 3.55 – 3.29 (m, 9H), 3.29 – 3.09 (m, 5H), 2.95 (s, 1H), 2.29 (q, *J* = 6.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.55 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.29, 138.07, 137.72, 137.66, 137.48, 137.34, 137.33, 137.24, 136.90 (*aromatic* C), 134.44 (C-9), 128.86, 128.49, 128.45, 128.40, 128.37, 128.36, 128.33, 128.31, 128.29, 128.21, 128.11, 128.05, 128.02, 127.99, 127.87, 127.85, 127.73, 127.66, 127.62, 127.57, 127.55, 127.49, 127.41, 127.36, 127.30, 127.15, 127.09, 126.99 (*aromatic* C*H*), 116.84 (C-10), 115.83 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.70, 97.98, 97.48, 97.33, 97.22, 79.87, 75.75, 75.52, 74.83, 74.49, 74.18, 73.72, 73.37, 73.24, 73.14, 72.93, 72.47, 71.75, 71.54, 70.98, 70.86, 70.52, 70.49, 70.47, 69.77, 69.25, 69.07, 68.78, 68.70, 68.61, 67.68, 66.60, 66.41, 66.19, 65.56, 64.58, 59.95, 59.47, 58.61, 58.12, 54.68, 49.34, 48.89, 33.72. HR-MS: Calculated for $C_{108}H_{115}N_{11}O_{23}F_6$ $[M+Na]^+$: 2070.7969, found: 2070.7964.

Hexasaccharide 25

The reaction was carried out according to the general procedure B using donor **13** (346 mg, 0.57 mmol) and acceptor **S21** (390 mg, 0.19 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **25** (415 mg, 88% yield) was obtained as white foam. $[\alpha]_D^{25}$ +130.6 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.09 (m, 57H), 7.03 – 6.96 (m, 1H), 6.31 (d, *J* = 9.5 Hz, 1H), 6.25 (d, *J* = 9.7 Hz, 1H), 5.73 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.41 (d, *J* = 3.7 Hz, 1H), 5.08 – 4.89 (m, 9H), 4.85 – 4.72 (m, 3H), 4.70 – 4.43 (m, 8H), 4.37 – 4.18 (m, 14H), 4.17 – 3.93 (m, 10H), 3.92 – 3.82 (m, 3H), 3.81 – 3.52 (m, 8H), 3.50 – 3.19 (m, 9H), 3.18 – 3.06 (m, 3H), 2.29 (q, *J* = 6.6 Hz, 2H), 1.03 (s, 10H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.60 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.34, 138.10, 137.89, 137.82, 137.51, 137.39, 137.35, 137.14, 137.06, 136.87, 136.71 (*aromatic* C), 134.45 (C-9), 128.55, 128.50, 128.48, 128.42, 128.40, 128.37, 128.29, 128.16, 128.14, 128.08, 128.01, 127.91, 127.79, 127.69, 127.66, 127.62, 127.48, 127.36, 127.34, 127.12, 127.00, 126.49 (*aromatic* C*H*), 116.92 (C-10), 115.84 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.85, 98.34, 98.03, 97.77, 97.34, 97.29, 80.22, 76.19, 75.76, 75.55, 74.73, 74.42, 74.37, 74.01, 73.44, 73.42, 73.18, 72.91, 72.70, 71.64, 71.56, 70.91, 70.75, 70.68, 70.56, 70.52, 70.14, 69.83, 69.61, 69.56, 69.21, 68.75, 68.65, 67.73, 67.36, 67.07, 66.63, 66.34, 65.97, 64.78, 59.87, 59.50, 58.44, 49.33, 49.10, 33.78, 27.55, 27.39, 23.20, 20.67.

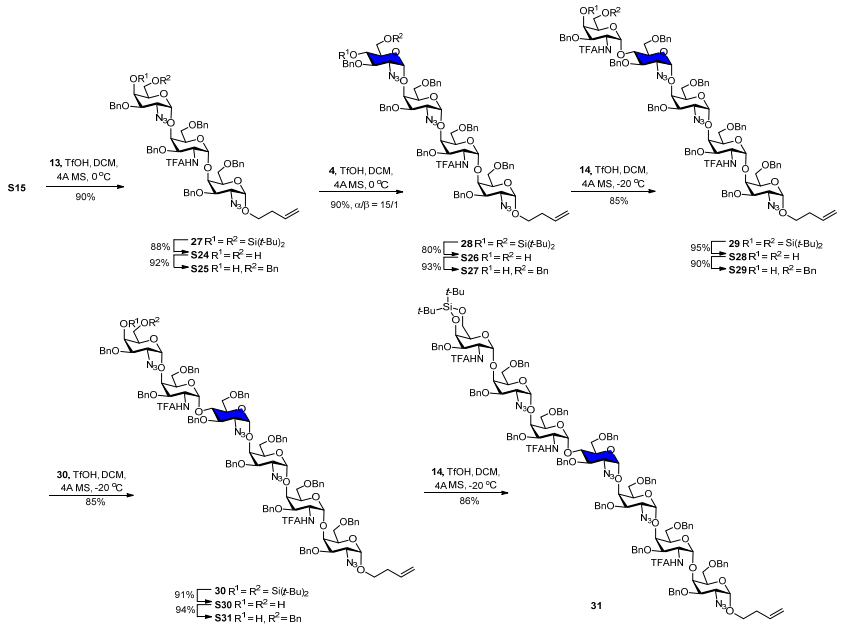
Hexasaccharide S22

The reaction was carried out according to the general procedure C using compound **25** (409 mg, 0.17 mmol) and HF/pyridine (70%, 69 µl, 2.65 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S22** (347 mg, 90% yield) was obtained as white foam. $[\alpha]_D^{25}$ +147 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.09 (m, 55H), 7.02 (td, *J* = 6.3, 2.9 Hz, 1H), 6.39 (t, *J* = 11.1 Hz, 2H), 5.81 – 5.68 (m, 1H), 5.42 (d, *J* = 3.7 Hz, 1H), 5.09 – 4.76 (m, 11H), 4.73 – 4.61 (m, 4H), 4.61 – 4.48 (m, 3H), 4.44 (td, *J* = 10.4, 3.6 Hz, 1H),

4.40 – 4.24 (m, 9H), 4.23 – 4.08 (m, 10H), 4.08 – 4.01 (m, 2H), 4.01 – 3.91 (m, 5H), 3.90 – 3.82 (m, 2H), 3.81 – 3.73 (m, 2H), 3.68 – 3.53 (m, 4H), 3.51 – 3.27 (m, 9H), 3.27 – 3.19 (m, 2H), 3.18 – 3.05 (m, 3H), 2.84 (s, 1H), 2.35 – 2.24 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.77 (*a*d, *J* = 37 Hz, *CF₃CO*), 138.36, 138.13, 137.75, 137.56, 137.46, 137.45, 137.38, 137.22, 136.95, 136.87 (*aromatic* C), 134.49 (C-9), 128.59, 128.56, 128.53, 128.49, 128.46, 128.44, 128.41, 128.39, 128.34, 128.20, 128.18, 128.14, 128.08, 128.04, 127.92, 127.88, 127.81, 127.67, 127.65, 127.58, 127.39, 127.35, 127.30, 127.16, 127.07, 126.71 (*aromatic* C*H*), 116.92 (C-10), 115.87 (*a*d, *J* = 286 Hz, C*F₃*), 98.84, 98.75, 98.05, 97.80, 97.41, 97.31, 80.24, 76.38, 76.02, 75.55, 74.70, 74.37, 74.34, 74.01, 73.45, 73.38, 73.21, 73.13, 72.97, 72.72, 71.76, 71.73, 71.63, 71.59, 71.04, 70.81, 70.69, 70.59, 69.84, 69.73, 69.20, 69.08, 68.83, 68.64, 67.76, 67.45, 66.67, 66.54, 66.45, 66.09, 64.79, 62.60, 59.91, 59.53, 59.41, 49.40, 49.32, 33.79.

Heptasaccharide 26

The reaction was carried out according to the general procedure B using donor **14** (381 mg, 0.56 mmol) and acceptor **S23** (340 mg, 0.14 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **26** (358 mg, 88% yield) was obtained as yellow foam. $[\alpha]_D^{25}$ +157.6 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.02 (m, 69H), 6.42 – 6.34 (m, 2H), 6.31 (d, *J* = 9.4 Hz, 1H), 5.73 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.43 (d, *J* = 3.6 Hz, 1H), 5.08 – 4.87 (m, 9H), 4.86 – 4.76 (m, 3H), 4.72 (dd, *J* = 12.0, 7.2 Hz, 2H), 4.68 – 4.42 (m, 10H), 4.41 – 4.19 (m, 15H), 4.12 (d, *J* = 11.1 Hz, 4H), 4.09 – 3.82 (m, 12H), 3.81 – 3.72 (m, 2H), 3.71 – 3.53 (m, 5H), 3.50 – 2.96 (m, 16H), 2.35 – 2.26 (m, 2H), 1.07 (s, 9H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.69 (*a*d, *J* = 37 Hz, 3x*CF₃CO*), 138.32, 138.13, 137.87, 137.80, 137.62, 137.52, 137.41, 137.37, 137.29, 137.21, 136.90, 136.84 (*aromatic* C), 134.47 (C-9), 128.56, 128.52, 128.49, 128.46, 128.44, 128.41, 128.39, 128.31, 128.28, 128.17, 128.16, 128.11, 128.09, 128.05, 127.97, 127.93, 127.81, 127.79, 127.74, 127.72, 127.67, 127.64, 127.39, 127.36, 127.16, 127.09, 127.02, 126.73, 126.57 (*aromatic* C*H*), 116.94 (C-10), 115.83 (*a*d, *J* = 286 Hz, C*F₃*), 98.83, 98.31, 98.05, 97.75, 97.49, 97.40, 96.73, 80.24, 76.20, 76.05, 75.57, 74.70, 74.51, 74.31, 73.97, 73.44, 73.39, 73.20, 73.05, 72.94, 72.90, 72.68, 71.85, 71.61, 71.19, 71.06, 70.99, 70.95, 70.64, 70.58, 69.83, 69.57, 69.49, 69.36, 69.27, 68.79, 68.56, 67.76, 67.72, 66.91, 66.63, 66.49, 66.36, 66.14, 65.74, 64.78, 60.15, 59.92, 59.51, 49.37, 49.20, 48.21, 33.80, 27.56, 27.38, 23.25, 20.67.



3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (27)

The reaction was carried out according to the general procedure B using donor **13** (1.07 g, 1.77 mmol) and acceptor **S15** (620 mg, 0.71 mmol). The product was purified by column chromatography (pentane:EtOAc = 10:1). Compound **27** (828 mg, 90% yield) was obtained as white foam. $[\alpha]_D^{25}$ +176.3 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.14 (m, 26H), 6.31 (d, *J* = 9.7 Hz, 1H), 5.76 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.12 – 4.99 (m, 2H), 4.95 (dd, *J* = 5.6, 3.6 Hz, 2H), 4.87 (d, *J* = 12.3 Hz, 1H), 4.81 – 4.62 (m, 4H), 4.59 – 4.23 (m, 9H), 4.20 – 4.06 (m, 2H), 4.02 – 3.92 (m, 2H), 3.87 (dd, *J* = 9.0, 5.9 Hz, 1H), 3.85 – 3.60 (m, 6H), 3.57 (dd, *J* = 11.1, 2.4 Hz, 1H), 3.55 – 3.45 (m, 1H), 3.43 – 3.26 (m, 3H), 3.16 (dd, *J* = 8.4, 5.2 Hz, 1H), 2.33 (qt, *J* = 6.8, 1.4 Hz, 2H), 1.03 (s, 9H), 1.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.96 (*a*d, *J* = 37 Hz, *C*F_3*CO*), 137.99, 137.49, 137.24, 137.20, 136.89 (*aromatic* C), 134.58 (C-9), 128.70, 128.69, 128.65, 128.54, 128.36, 128.29, 128.20, 128.13, 127.90, 127.87, 127.83, 127.28, 127.06 (*aromatic* C*H*), 117.06 (C-10), 115.95 (*a*d, *J* = 286 Hz, CF_3), 98.55, 98.14, 97.51, 76.02, 75.80, 74.48, 73.76, 73.41, 71.68, 70.94, 70.69, 70.64, 70.37, 69.88, 69.67, 68.89, 67.89, 67.55, 67.23, 66.50, 66.44, 59.55, 58.60, 49.27, 33.91, 27.68, 27.50, 23.36, 20.80. HR-MS: Calculated for $C_{67}H_{82}N_7O_{14}F_3Si$ $[M+Na]^+$: 1316.5539, found: 1316.5533.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoro-acetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S24)

The reaction was carried out according to the general procedure C using compound **27** (910 mg, 0.70 mmol) and HF/pyridine (70%, 292 µl, 11.2 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S24** (710 mg, 88% yield) was obtained as white foam. $[\alpha]_D^{25}$ +155.4 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.20 (m, 25H), 6.54 (d, *J* = 10.3, 3.9 Hz, 1H), 5.82 (ddt, *J* = 17.0, 10.4, 6.7 Hz, 1H), 5.18 – 5.06 (m, 2H), 5.04 (d, *J* = 3.6 Hz, 1H), 5.01 (d, *J* = 3.6 Hz, 1H), 4.93 – 4.73 (m, 5H), 4.62 – 4.54 (m, 2H), 4.49 (s, 2H), 4.42 – 4.27 (m, 5H), 4.27 – 4.22 (m, 1H), 4.20 – 4.12 (m, 2H), 4.06 (dd, *J* = 10.5, 3.0 Hz, 1H), 3.97 – 3.81 (m, 3H), 3.76 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.73 – 3.64 (m, 2H), 3.63 – 3.49 (m, 3H), 3.48 – 3.34 (m, 3H), 3.28 (dd, *J* = 8.6, 5.3 Hz, 1H), 2.95 (d, *J* = 8.1 Hz, 1H), 2.44 (s, 1H), 2.38 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.11 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 137.38, 137.37, 137.35, 137.20, 136.91 (*aromatic* C), 134.52 (C-9), 128.65, 128.61, 128.41, 128.27, 128.22, 128.17, 128.14, 128.09, 128.00, 127.95, 127.87, 127.44, 127.14 (*aromatic* C*H*), 116.98 (C-10), 115.81 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.86, 98.07, 97.42, 76.53, 75.51, 74.37, 73.62, 73.26, 71.84, 71.69, 71.65, 71.10, 70.81, 69.94, 69.16, 68.82, 67.81, 67.56, 66.53, 66.49, 62.71, 59.51, 59.47, 49.40, 33.83. HR-MS: Calculated for $C_{59}H_{66}N_7O_{14}F_3$ $[M+Na]^+$: 1176.4518, found: 1176.4512.

3-Butenyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S25)

The reaction was carried out according to the general procedure D using compound **S24** (983 mg, 0.85 mmol), K_2CO_3 (129 mg, 0.94 mmol), KI (141 mg, 0.85 mmol) and $Ph_2BO(CH_2)_2NH_2$ (19 mg, 0.085 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S25** (973 mg, 92% yield) was obtained as white foam. $[\alpha]_D^{25}$ +141.7 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.14 (m, 32H), 6.32 (d, *J* = 9.5 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.10 – 5.00 (m, 2H), 4.98 (d, *J* = 3.7 Hz, 1H), 4.95 (d, *J* = 3.7 Hz, 1H), 4.82 (d, *J* = 12.4 Hz, 1H), 4.79 – 4.66 (m, 4H), 4.52 (t, *J* = 12.7 Hz, 2H), 4.42 (s, 2H), 4.37 (q, *J* = 5.3, 3.9 Hz, 1H), 4.34 – 4.17 (m, 7H), 4.07 (d, *J* = 1.5 Hz, 2H), 4.00 (dd, *J* = 10.5, 2.9 Hz, 1H), 3.90 – 3.80 (m, 2H), 3.77 (dd, *J* = 10.6, 3.1 Hz, 2H), 3.67 – 3.55 (m, 2H), 3.53 – 3.43 (m, 2H), 3.40 – 3.25 (m, 4H), 3.19 (dd, *J* = 8.5, 5.2 Hz, 1H), 3.09 (s, 1H), 2.31 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.86 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 137.61, 137.55, 137.47, 137.39, 137.37, 136.93 (*aromatic* C), 134.53 (C-9), 128.98, 128.61, 128.55, 128.52, 128.44, 128.42, 128.35, 128.31, 128.22, 128.14, 128.03, 128.01, 127.94, 127.85, 127.78, 127.72, 127.53, 127.24, 127.08 (*aromatic* C*H*), 116.98 (C-10), 115.92 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.94, 98.04, 97.42, 76.56, 75.62, 74.20, 73.61, 73.46, 73.25, 71.62, 71.50, 71.41, 71.00, 70.74, 69.89, 69.77, 68.84, 68.32, 67.78, 66.88, 66.50, 59.52, 59.36, 49.33, 33.84. HR-MS: Calculated for $C_{66}H_{72}N_7O_{14}F_3$ $[M+Na]^+$: 1266.4987, found: 1266.4982.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (28)

The reaction was carried out according to the general procedure A. The donor **4** (585 mg, 0.96 mmol) and acceptor **S25** (400 mg, 0.32 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 4 ml

DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to -10 ºC, after which TfOH (9 µl, 0.01 mmol) was added. The reaction was stirred at -10 ºC for overnight. 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). Compound **28** (487 mg, 90% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +134.9 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.16 (m, 39H), 6.28 (d, *J* = 9.6 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.13 – 4.98 (m, 3H), 4.96 (d, *J* = 3.8 Hz, 1H), 4.94 (d, *J* = 3.7 Hz, 1H), 4.88 – 4.70 (m, 6H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.55 – 4.19 (m, 12H), 4.17 – 4.02 (m, 3H), 3.94 (dd, *J* = 11.7, 3.3 Hz, 3H), 3.88 – 3.74 (m, 6H), 3.72 – 3.56 (m, 5H), 3.48 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.42 – 3.25 (m, 3H), 3.22 – 3.13 (m, 2H), 3.08 (dd, *J* = 8.7, 5.2 Hz, 1H), 2.36 – 2.26 (m, 2H), 1.03 (s, 9H), 0.98 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.79 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 138.23, 137.72, 137.60, 137.44, 137.32, 136.98 (*aromatic* C), 134.57 (C-9), 128.70, 128.64, 128.56, 128.50, 128.46, 128.44, 128.38, 128.34, 128.30, 128.27, 128.25, 128.19, 128.15, 128.10, 127.98, 127.90, 127.87, 127.79, 127.76, 127.66, 127.62, 127.24, 127.15, 127.11 (*aromatic* C*H*), 117.02 (C-10), 115.86 (*a*d, *J* = 286 Hz, C*F$_3$*), 98.64, 98.47, 98.11, 97.53, 79.33, 79.24, 76.28, 75.60, 75.51, 74.59, 73.66, 73.28, 73.06, 72.99, 72.24, 71.64, 71.16, 71.10, 70.74, 69.91, 69.07, 68.91, 67.82, 66.77, 66.71, 66.59, 66.38, 66.07, 62.99, 60.27, 59.54, 49.33, 33.89, 27.45, 27.19, 22.64, 20.04. HR-MS: Calculated for $C_{87}H_{103}N_{10}O_{18}F_3Si$ $[M+Na]^+$: 1683.7071, found: 1683.7065.

3-Butenyl 2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S26)

The reaction was carried out according to the general procedure C using compound **28** (638 mg, 0.38 mmol) and HF/pyridine (70%, 160 µl, 6.14 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:1). Compound **S26** (469 mg, 80% yield) was obtained as white foam. $[\alpha]_D^{25}$ +187.5 (c=1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.14 (m, 37H), 6.52 (d, *J* = 9.6 Hz, 1H), 5.74 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.10 – 4.98 (m, 3H), 4.95 (d, *J* = 3.7 Hz, 1H), 4.90 (d, *J* = 3.7 Hz, 1H), 4.87 (s, 2H), 4.82 (d, *J* = 4.3 Hz, 1H), 4.81 – 4.76 (m, 2H), 4.72 (d, *J* = 12.7 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.56 (td, *J* = 10.4, 3.6 Hz, 1H), 4.49 (d, *J* = 12.4 Hz, 1H), 4.46 – 4.37 (m, 3H), 4.34 – 4.23 (m, 5H), 4.14 – 3.97 (m, 5H), 3.95 – 3.71 (m, 6H), 3.69 – 3.57 (m, 4H), 3.48 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.41 – 3.26 (m, 3H), 3.20 (dq, *J* = 8.4, 5.0, 4.6 Hz, 2H), 3.15 – 3.02 (m, 4H), 2.31 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.94 (*a*d, *J* = 37 Hz, *CF$_3$CO*), 138.21, 137.63, 137.59, 137.39, 137.34, 136.93 (*aromatic* C), 134.53 (C-9), 128.61, 128.54, 128.49, 128.45, 128.37, 128.35, 128.21, 128.14, 128.02, 128.00, 127.92, 127.87, 127.86, 127.78, 127.69, 127.22, 127.12, 126.90 (*aromatic* C*H*), 117.00 (C-10), 115.95 (*a*d, *J* = 286 Hz, C*F$_3$*), 98.79, 98.28, 98.08, 97.61, 79.64, 76.04, 75.55, 75.06, 74.52, 73.61, 73.27, 72.97, 72.15, 71.71, 71.68, 71.63, 71.21, 71.18, 70.81, 70.75, 69.82, 68.98, 68.92, 67.81, 66.54, 66.44, 66.23, 63.34, 61.97, 59.99, 59.48, 49.36, 33.84. HR-MS: Calculated for $C_{79}H_{87}N_{10}O_{18}F_3$ $[M+Na]^+$: 1543.6050, found: 1543.6044.

3-Butenyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S27)

The reaction was carried out according to the general procedure D using compound **S26** (452 mg, 0.30 mmol), K_2CO_3 (45 mg, 0.33 mmol), KI (49 mg, 0.30 mmol) and $Ph_2BO(CH_2)_2NH_2$ (6.7 mg, 0.03 mmol). The product was purified by column chromatography (pentane:EtOAc = 5:1). Compound **S27** (445 mg, 93% yield) was obtained as white foam. $[\alpha]_D^{25}$ +147.6 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.11 (m, 43H), 6.36 (d, *J* = 9.6 Hz, 1H), 5.80 – 5.69 (m, 1H), 5.09 – 4.99 (m, 3H), 4.96 (d, *J* = 3.7 Hz, 2H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.88 – 4.83 (m, 2H), 4.80 (d, *J* = 12.4 Hz, 1H), 4.76 (d, *J* = 3.6 Hz, 1H), 4.72 (d, *J* = 12.7 Hz, 1H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.56 (ddd, *J* = 13.3, 9.8, 3.7 Hz, 1H), 4.48 (d, *J* = 12.4 Hz, 1H), 4.45 – 4.36 (m, 3H), 4.36 – 4.23 (m, 5H), 4.18 (d, *J* = 12.0 Hz, 1H), 4.13 – 4.03 (m, 6H), 4.01 (dd, *J* = 11.0, 2.6 Hz, 1H), 3.88 – 3.70 (m, 6H), 3.67 (dd, *J* = 11.0, 3.6 Hz, 1H), 3.65 – 3.56 (m, 2H), 3.47 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.39 – 3.25 (m, 3H), 3.25 – 3.18 (m, 2H), 3.15 (dd, *J* = 8.7, 5.2 Hz, 1H), 3.09 (dd, *J* = 10.3, 3.3 Hz, 1H), 3.00 (dd, *J* = 10.3, 4.8 Hz, 1H), 2.68 (d, *J* = 2.8 Hz, 1H), 2.38 – 2.25 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.82 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 138.27, 137.74, 137.73, 137.72, 137.54, 137.37, 137.33, 136.91 (*aromatic* C), 134.51 (C-9), 128.57, 128.53, 128.47, 128.43, 128.37, 128.35, 128.32, 128.17, 128.12, 128.07, 128.02, 127.97, 127.82, 127.78, 127.76, 127.70, 127.65, 127.43, 127.27, 127.10, 126.88 (*aromatic* C*H*), 116.95 (C-10), 115.89 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.78, 98.59, 98.04, 97.49, 79.66, 76.27, 75.54, 75.04, 74.40, 73.59, 73.28, 73.26, 72.95, 72.93, 72.75, 71.79, 71.59, 71.10, 71.05, 70.68, 69.81, 69.67, 69.38, 69.08, 68.87, 67.76, 66.53, 66.44, 66.27, 63.32, 59.96, 59.49, 49.32. HR-MS: Calculated for $C_{86}H_{93}N_{10}O_{18}F_3$ $[M+Na]^+$: 1633.6519, found: 1633.6514.

Pentasaccharide 29

The reaction was carried out according to the general procedure B using donor **14** (550 mg, 0.81 mmol) and acceptor **S27** (437 mg, 0.27 mmol). The product was purified by column chromatography (pentane:EtOAc = 7:1). Compound **29** (488 mg, 85% yield) was obtained as yellow foam. $[\alpha]_D^{25}$ +157.8 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.16 (m, 47H), 7.15 – 7.09 (m, 2H), 6.89 (d, *J* = 9.5 Hz, 1H), 6.31 (d, *J* = 9.6 Hz, 1H), 5.75 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.48 (d, *J* = 3.5 Hz, 1H), 5.11 – 4.99 (m, 4H), 4.96 (d, *J* = 3.6 Hz, 1H), 4.86 – 4.63 (m, 8H), 4.61 – 4.37 (m, 10H), 4.37 – 4.17 (m, 7H), 4.16 – 4.01 (m, 5H), 4.00 – 3.58 (m, 13H), 3.54 – 3.41 (m, 3H), 3.40 – 3.14 (m, 6H), 3.07 – 3.01 (m, 1H), 2.97 (d, *J* = 10.7 Hz, 1H), 2.31 (qt, *J* = 6.7, 1.4 Hz, 2H), 1.03 (d, *J* = 4.7 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.08 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.07, 137.63, 137.55, 137.45, 137.38, 136.92, 136.42 (*aromatic* C), 134.51 (C-9), 128.61, 128.59, 128.49, 128.44, 128.42, 128.38, 128.33, 128.22, 128.19, 128.13, 128.08, 127.93, 127.89, 127.86, 127.84, 127.83, 127.74, 127.72, 127.33, 127.10, 126.83 (*aromatic* C*H*), 116.98 (C-10), 115.96 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.75, 98.07, 98.01, 97.48, 97.04, 76.12, 75.57, 75.26, 74.39, 74.20, 73.62, 73.49, 73.27, 73.00, 72.40, 71.90, 71.88, 71.64, 71.20, 71.06, 70.75, 70.61, 69.79, 69.68, 69.57, 68.98, 68.81, 68.44, 67.80, 67.05, 66.55, 66.52, 66.23, 63.95, 60.35, 59.52, 49.30, 48.57, 33.84, 27.62, 27.32. HR-MS: Calculated for $C_{109}H_{125}N_{11}O_{23}F_6Si$ $[M+Na]^+$: 2120.8521, found: 2120.8516.

Pentasaccharide S28

The reaction was carried out according to the general procedure C using compound **29** (478 mg, 0.23 mmol) and HF/pyridine (70%, 95 µl, 3.64 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S28** (423 mg, 95% yield) was obtained as white foam. $[\alpha]_D^{25}$ +135.4 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.14 (m, 46H), 7.08 (d, *J* = 9.8 Hz, 1H), 6.40 (d, *J* = 9.6 Hz, 1H), 5.74 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.26 (d, *J* = 3.6 Hz, 1H), 5.11 – 4.98 (m, 4H), 4.95 (d, *J* = 3.6 Hz, 1H), 4.85 – 4.74 (m, 4H), 4.69 (d, *J* = 12.6 Hz, 1H), 4.63 (d, *J* = 11.8 Hz, 1H), 4.59 – 4.43 (m, 6H), 4.39 (d, *J* = 12.5 Hz, 3H), 4.35 – 4.22 (m, 7H), 4.15 – 4.01 (m, 6H), 3.97 (d, *J* = 9.0 Hz, 1H), 3.92 – 3.82 (m, 3H), 3.78 (dq, *J* = 9.4, 2.7 Hz, 2H), 3.73 – 3.58 (m, 7H), 3.48 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.42 (dd, *J* = 10.6, 2.8 Hz, 1H), 3.39 – 3.26 (m, 3H), 3.25 – 3.14 (m, 3H), 3.11 (d, *J* = 10.4 Hz, 1H), 3.00 (d, *J* = 11.0 Hz, 1H), 2.35 – 2.24 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.08 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 137.60, 137.54, 137.46, 137.43, 137.36, 137.14, 136.88, 136.55 (*aromatic* C), 134.49 (C-9), 128.55, 128.54, 128.37, 128.33, 128.17, 128.14, 128.09, 128.03, 127.99, 127.92, 127.86, 127.82, 127.79, 127.59, 127.34, 127.25, 127.05, 126.92 (*aromatic* C*H*), 116.91 (C-10), 115.89 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.73, 98.03, 97.96, 97.49, 97.46, 79.52, 75.91, 75.56, 74.39, 74.05, 73.87, 73.58, 73.38, 73.21, 72.94, 72.05, 71.90, 71.61, 71.12, 71.08, 70.87, 70.74, 70.71, 70.57, 69.72, 68.93, 68.82, 67.76, 67.32, 66.55, 66.52, 66.26, 66.10, 63.81, 62.38, 60.18, 59.48, 49.28, 49.20, 33.79. HR-MS: Calculated for $C_{101}H_{109}N_{11}O_{23}F_6$ $[M+Na]^+$: 1980.7500, found: 1980.7494.

Pentasaccharide S29

The reaction was carried out according to the general procedure D using compound **S28** (416 mg, 0.21 mmol), K_2CO_3 (32 mg, 0.23 mmol), KI (35 mg, 0.21 mmol) and $Ph_2BO(CH_2)_2NH_2$ (4.8 mg, 0.021 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S29** (391 mg, 90% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +169 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.05 (m, 54H), 6.42 (d, *J* = 9.5 Hz, 1H), 5.74 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.28 (d, *J* = 3.6 Hz, 1H), 5.10 – 4.99 (m, 4H), 4.95 (d, *J* = 3.6 Hz, 1H), 4.85 – 4.72 (m, 4H), 4.67 (d, *J* = 12.6 Hz, 1H), 4.63 – 4.19 (m, 20H), 4.16 – 3.96 (m, 7H), 3.94 – 3.83 (m, 4H), 3.82 – 3.74 (m, 2H), 3.73 – 3.57 (m, 5H), 3.56 – 3.41 (m, 3H), 3.33 (ddt, *J* = 26.5, 10.2, 4.8 Hz, 3H), 3.24 – 3.11 (m, 4H), 3.04 (d, *J* = 10.8 Hz, 1H), 2.76 (s, 1H), 2.29 (q, *J* = 6.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.93 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 137.88, 137.74, 137.49, 137.37, 137.31, 137.29, 137.23, 136.83, 136.53 (*aromatic* C), 134.43 (C-9), 128.46, 128.43, 128.41, 128.30, 128.29, 128.24, 128.19, 128.13, 128.06, 128.02, 127.90, 127.86, 127.78, 127.71, 127.68, 127.65, 127.59, 127.53, 127.49, 127.24, 127.22, 126.96 (*aromatic* C*H*), 116.82 (C-10), 115.77 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.62, 97.97, 97.94, 97.46, 97.38, 79.38, 75.98, 75.71, 75.51, 74.25, 73.88, 73.53, 73.49, 73.14, 73.04, 72.84, 72.01, 71.74, 71.52, 70.99, 70.69, 70.65, 70.60, 69.67, 69.49, 68.85, 68.76, 68.69, 67.67, 67.55, 66.46, 66.22, 65.10, 63.71, 60.08, 59.41, 49.25, 49.21, 33.71. HR-MS: Calculated for $C_{108}H_{115}N_{11}O_{23}F_6$ $[M+Na]^+$: 2070.7969, found: 2070.7964.

Hexasaccharide 30

The reaction was carried out according to the general procedure B using donor **13** (344 mg, 0.57 mmol) and acceptor **S29** (388 mg, 0.19 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **30** (401 mg, 85% yield) was obtained as white foam. $[\alpha]_D^{25}$ +150 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.40 – 7.12 (m, 55H), 7.01 (d, *J* = 9.8 Hz, 1H), 6.28 (d, *J* = 9.6 Hz, 1H), 5.80 – 5.68 (m, 1H), 5.38 (d, *J* = 3.5 Hz, 1H), 5.11 – 4.99 (m, 4H), 4.96 (dd, *J* = 5.9, 3.6 Hz, 2H), 4.84 – 4.21 (m, 29H), 4.15 – 3.95 (m, 9H), 3.94 – 3.44 (m, 16H), 3.40 – 3.09 (m, 8H), 3.03 (d, *J* = 11.0 Hz, 1H), 2.30 (q, *J* = 6.7 Hz, 2H), 1.03 (s, 9H), 0.96 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.05 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 137.90, 137.84, 137.50, 137.41, 137.37, 137.31, 137.29, 137.23, 137.14, 136.81, 136.39 (*aromatic* C), 134.44 (C-9), 128.53, 128.51, 128.47, 128.44, 128.37, 128.34, 128.31, 128.29, 128.18, 128.15, 128.09, 128.05, 127.98, 127.89, 127.86, 127.81, 127.78, 127.76, 127.67, 127.62, 127.57, 127.51, 127.26, 126.99, 126.84, 126.04 (*aromatic* C*H*), 116.92 (C-10), 115.81 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.74, 98.68, 98.01, 97.40, 97.37, 79.54, 76.28, 75.88, 75.53, 74.31, 73.98, 73.56, 73.30, 73.20, 73.17, 72.91, 71.96, 71.82, 71.55, 71.01, 70.95, 70.91, 70.64, 70.53, 70.50, 70.10, 69.70, 69.55, 68.90, 68.73, 67.72, 67.51, 67.46, 66.96, 66.48, 66.41, 66.21, 63.78, 60.12, 59.44, 58.42, 49.60, 49.20, 33.77, 27.52, 27.37, 23.17.

Hexasaccharide S30

The reaction was carried out according to the general procedure C using compound **30** (394 mg, 0.16 mmol) and HF/pyridine (70%, 66 µl, 2.56 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S30** (340 mg, 91% yield) was obtained as white foam. $[\alpha]_D^{25}$ +149.2 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.12 (m, 63H), 7.08 (d, *J* = 9.8 Hz, 1H), 6.42 (d, *J* = 9.6 Hz, 1H), 5.74 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.34 (d, *J* = 3.5 Hz, 1H), 5.11 – 4.91 (m, 7H), 4.85 – 4.74 (m, 4H), 4.72 – 4.52 (m, 9H), 4.52 – 3.57 (m, 41H), 3.52 – 3.43 (m, 2H), 3.43 – 3.07 (m, 11H), 3.01 (d, *J* = 10.9 Hz, 1H), 2.90 (s, 1H), 2.30 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.11 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 137.88, 137.54, 137.44, 137.42, 137.39, 137.33, 137.15, 136.86, 136.49 (*aromatic* C), 134.46 (C-9), 128.52, 128.47, 128.44, 128.33, 128.29, 128.19, 128.14, 128.11, 128.06, 128.04, 127.92, 127.83, 127.77, 127.73, 127.72, 127.60, 127.58, 127.20, 127.02, 126.88, 126.40 (*aromatic* C*H*), 116.88 (C-10), 115.84 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 99.15, 98.69, 98.02, 97.41, 79.47, 76.15, 75.84, 75.51, 74.35, 73.82, 73.54, 73.47, 73.18, 73.16, 72.89, 72.10, 72.04, 71.85, 71.66, 71.58, 71.09, 71.05, 71.01, 70.65, 70.27, 69.68, 69.17, 68.89, 68.77, 67.72, 67.49, 67.43, 66.65, 66.53, 66.48, 63.76, 62.43, 60.13, 59.44, 59.40, 49.76, 49.24, 33.76.

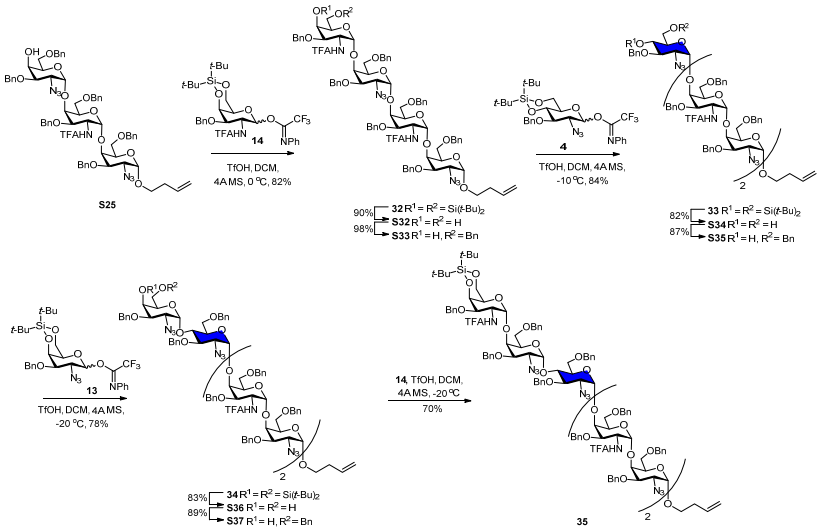
Hexasaccharide S31

The reaction was carried out according to the general procedure D using compound **S30** (333 mg, 0.14 mmol), K_2CO_3 (22 mg, 0.16 mmol), KI (24 mg, 0.14 mmol) and $Ph_2BO(CH_2)_2NH_2$ (6.4 mg, 0.029 mmol). The product was purified by column chromatography (pentane:EtOAc = 7:2). Compound **S31** (325 mg, 94% yield) was obtained as white foam. $[\alpha]_D^{25}$ +146.2 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.09 (m, 62H), 6.99 (d, *J* = 9.7 Hz, 1H), 6.32 (d, *J* = 9.5 Hz, 1H), 5.80 – 5.67 (m, 1H), 5.37 (d, *J* = 3.5 Hz, 1H), 5.09 – 5.00 (m, 4H), 4.99 (d, *J* = 3.7 Hz, 1H), 4.95 (d, *J* = 3.6 Hz, 1H), 4.83 – 4.73 (m, 5H), 4.72 – 4.52 (m, 7H), 4.51 – 4.43 (m, 2H), 4.43 – 4.17 (m, 15H), 4.16 – 3.57 (m, 21H), 3.50 – 3.42 (m, 2H), 3.42 – 3.07 (m, 11H), 3.01 (d, *J* = 11.0 Hz, 1H), 2.29 (q, *J* = 6.7

Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.99 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 137.82, 137.61, 137.51, 137.46, 137.40, 137.37, 137.35, 137.28, 137.25, 136.77, 136.42 (*aromatic* C), 134.41 (C-9), 128.48, 128.44, 128.40, 128.34, 128.29, 128.28, 128.26, 128.23, 128.19, 128.17, 128.14, 128.10, 128.04, 128.00, 127.98, 127.91, 127.81, 127.75, 127.73, 127.70, 127.56, 127.50, 127.45, 127.19, 126.94, 126.77, 126.37 (*aromatic* C*H*), 116.86 (C-10), 115.83 (*a*d, *J* = 286 Hz, C*F*$_3$), 99.39, 98.63, 97.97, 97.34, 97.27, 79.45, 76.26, 76.16, 75.83, 75.49, 74.27, 73.82, 73.50, 73.42, 73.21, 73.14, 73.11, 72.85, 72.02, 71.94, 71.75, 71.50, 71.19, 71.07, 70.96, 70.89, 70.59, 70.17, 69.78, 69.65, 68.84, 68.69, 68.24, 67.67, 67.42, 66.86, 66.56, 66.44, 66.37, 66.17, 63.71, 60.06, 59.39, 59.25, 58.09, 49.60, 49.17, 33.72.

Heptasaccharide 31

The reaction was carried out according to the general procedure B using donor **14** (381 mg, 0.56 mmol) and acceptor **S31** (330 mg, 0.14 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **31** (341 mg, 86% yield) was obtained as yellow foam. $[\alpha]_D^{25}$ +149.8 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.09 (m, 67H), 7.08 – 7.02 (m, 2H), 7.00 (d, *J* = 9.7 Hz, 1H), 6.37 (d, *J* = 9.5 Hz, 1H), 6.27 (d, *J* = 9.4 Hz, 1H), 5.74 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.36 (d, *J* = 3.5 Hz, 1H), 5.10 – 4.98 (m, 5H), 4.97 – 4.93 (m, 1H), 4.86 – 4.66 (m, 9H), 4.66 – 4.52 (m, 6H), 4.52 – 4.19 (m, 20H), 4.14 – 3.83 (m, 15H), 3.81 – 3.55 (m, 9H), 3.53 – 3.26 (m, 8H), 3.26 – 3.08 (m, 4H), 3.06 – 2.93 (m, 2H), 2.92 – 2.85 (m, 1H), 2.30 (q, *J* = 6.8 Hz, 2H), 1.07 (s, 9H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.80 (*a*d, *J* = 37 Hz, *CF*$_3$*CO*), 137.89, 137.51, 137.50, 137.42, 137.39, 137.33, 137.31, 137.15, 136.84, 136.80, 136.39 (*aromatic* C), 134.45 (C-9), 128.60, 128.53, 128.50, 128.47, 128.42, 128.37, 128.34, 128.32, 128.28, 128.23, 128.18, 128.14, 128.08, 128.06, 128.01, 127.98, 127.86, 127.83, 127.81, 127.79, 127.76, 127.70, 127.67, 127.63, 127.61, 127.57, 127.53, 127.24, 127.00, 126.84, 126.72, 126.21 (*aromatic* C*H*), 116.91 (C-10), 115.83 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.89, 98.68, 98.03, 97.97, 97.43, 97.28, 96.59, 79.56, 76.55, 75.91, 75.84, 75.55, 74.74, 74.35, 74.02, 73.55, 73.34, 73.19, 73.17, 72.98, 72.91, 71.95, 71.83, 71.58, 71.46, 71.38, 71.05, 70.99, 70.68, 70.61, 69.95, 69.69, 69.42, 69.34, 69.23, 68.89, 68.75, 68.65, 67.74, 67.67, 67.53, 66.89, 66.58, 66.42, 66.20, 65.64, 63.86, 60.16, 60.12, 59.44, 53.44, 49.54, 49.23, 48.13, 33.77, 27.52, 27.35, 23.21, 20.64.



3-Butenyl 3-*O*-benzyl-2-deoxy-4,6-di-*tert*-butylsilylidene-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoro-acetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (32)

The reaction was carried out according to the general procedure B using donor **14** (2.44 g, 3.61 mmol) and acceptor **S25** (1.5 g, 1.2 mmol). The product was purified by column chromatography (pentane:EtOAc = 8:1). Compound **32** (1.70 g, 82% yield) was obtained as yellow foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.10 (m, 37H), 6.28 (dd, *J* = 9.7, 3.6 Hz, 2H), 5.75 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.09 – 5.00 (m, 3H), 4.95 (d, *J* = 3.6 Hz, 1H), 4.87 – 4.83 (m, 1H), 4.82 (s, 1H), 4.79 (d, *J* = 3.6 Hz, 1H), 4.75 (d, *J* = 3.5 Hz, 1H), 4.73 (d, *J* = 3.3 Hz, 1H), 4.67 – 4.62 (m, 2H), 4.62 – 4.56 (m, 1H), 4.55 – 4.44 (m, 4H), 4.44 – 4.34 (m, 4H), 4.31 (dd, *J* = 9.9, 5.3 Hz, 1H), 4.27 (d, *J* = 2.9 Hz, 2H), 4.25 – 4.22 (m, 1H), 4.11 (d, *J* = 11.6 Hz, 1H), 4.06 (d, *J* = 11.6 Hz, 1H), 4.02 (d, *J* = 11.5 Hz, 1H), 3.98 – 3.89 (m, 3H), 3.85 (dd, *J* = 9.0, 5.8 Hz, 1H), 3.83 – 3.76 (m, 2H), 3.70 – 3.57 (m, 4H), 3.53 – 3.43 (m, 2H), 3.40 – 3.28 (m, 4H), 3.21 (dd, *J* = 8.6, 5.2 Hz, 1H), 3.12 – 3.01 (m, 2H), 2.32 (qt, *J* = 6.7, 1.3 Hz, 2H), 1.07 (s, 9H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.81 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 137.98, 137.61, 137.45, 137.40, 137.29, 136.97, 136.94 (*aromatic* C), 134.57 (C-9), 128.69, 128.66, 128.65, 128.57, 128.52, 128.50, 128.45, 128.37, 128.25, 128.19, 128.17, 128.10, 127.97, 127.90, 127.83, 127.81, 127.75, 127.37, 127.11, 126.80 (*aromatic* C*H*), 117.02 (C-10), 115.87 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.47, 98.12, 97.54, 96.85, 76.25, 75.76, 74.77, 74.53, 73.67, 73.18, 73.12, 71.79, 71.77, 71.21, 71.14, 70.97, 69.68, 69.65, 69.56, 69.36, 68.88, 68.73, 67.87, 67.83, 67.00, 66.58, 65.86, 60.29, 59.60, 49.31, 48.30, 33.89, 27.64, 27.45, 23.34, 20.75. HR-MS: Calculated for $C_{89}H_{104}N_8O_{19}F_6Si$ $[M+Na]^+$: 1753.6989, found: 1753.6983.

3-Butenyl 3-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S32)

The reaction was carried out according to the general procedure C using compound **32** (2.33 g, 1.35 mmol) and HF/pyridine (70%, 560 µl, 21.5 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S32** (1.9 g, 90% yield) was obtained as white foam. $[\alpha]_D^{25}$ +179.4 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.10 (m, 37H), 6.52 (d, *J* = 9.5 Hz, 1H), 6.33 (d, *J* = 9.7 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.09 – 5.00 (m, 2H), 4.99 (d, *J* = 3.7 Hz, 1H), 4.93 (d, *J* = 3.6 Hz, 1H), 4.87 (d, *J* = 3.7 Hz, 1H), 4.84 – 4.75 (m, 3H), 4.65 (dd, *J* = 11.8, 3.1 Hz, 2H), 4.51 (dp, *J* = 13.4, 3.6, 3.1 Hz, 3H), 4.47 – 4.35 (m, 5H), 4.33 (d, *J* = 2.6 Hz, 1H), 4.30 (dd, *J* = 9.9, 5.4 Hz, 1H), 4.26 (d, *J* = 2.6 Hz, 1H), 4.23 – 4.17 (m, 2H), 4.14 – 3.98 (m, 6H), 3.96 (dd, *J* = 10.9, 2.6 Hz, 1H), 3.85 (dd, *J* = 9.0, 5.8 Hz, 1H), 3.82 – 3.75 (m, 2H), 3.67 – 3.53 (m, 3H), 3.53 – 3.43 (m, 2H), 3.40 – 3.32 (m, 3H), 3.32 – 3.23 (m, 2H), 3.20 (dd, *J* = 8.6, 5.2 Hz, 1H), 3.09 (d, *J* = 7.5 Hz, 2H), 2.90 (s, 1H), 2.32 (qt, *J* = 6.7, 1.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.88 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 137.63, 137.42, 137.29, 137.15, 137.03, 136.95 (*aromatic* C), 134.56 (C-9), 128.66, 128.64, 128.46, 128.42, 128.24, 128.22, 128.16, 128.11, 128.02, 127.99, 127.96, 127.92, 127.87, 127.63, 127.18, 127.08 (*aromatic* C*H*), 117.00 (C-10), 115.87 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.49, 98.07, 97.51, 97.12, 76.14, 75.74, 75.20, 74.06, 73.65, 73.12, 73.05, 72.02, 71.74, 71.26, 71.14, 70.89, 70.84, 70.76, 69.63, 69.42, 68.86, 68.70, 67.84, 66.60, 66.55, 66.40, 65.86, 62.44, 60.21, 59.57, 49.26, 48.89, 33.86. HR-MS: Calculated for $C_{81}H_{88}N_8O_{19}F_6$ $[M+Na]^+$: 1613.5968, found: 1613.5962.

3-Butenyl 3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside (S33)

The reaction was carried out according to the general procedure D using compound **S32** (1.84 g, 1.16 mmol), K_2CO_3 (240 mg, 1.73 mmol), KI (249 mg, 1.5 mmol) and $Ph_2BO(CH_2)_2NH_2$ (53 mg, 0.23 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S33** (1.90 g, 98% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +77.4 (c=3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.11 (m, 46H), 6.42 (d, *J* = 9.5 Hz, 1H), 6.24 (d, *J* = 9.7 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.09 – 5.00 (m, 2H), 4.99 (d, *J* = 3.8 Hz, 1H), 4.91 (d, *J* = 3.6 Hz, 1H), 4.87 – 4.78 (m, 3H), 4.76 (d, *J* = 3.6 Hz, 1H), 4.71 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.56 – 4.32 (m, 10H), 4.31 – 4.16 (m, 9H), 4.10 (d, *J* = 11.6 Hz, 1H), 4.07 – 4.01 (m, 3H), 3.94 (dd, *J* = 10.9, 2.6 Hz, 1H), 3.84 (dd, *J* = 9.0, 5.8 Hz, 1H), 3.80 – 3.73 (m, 2H), 3.66 – 3.53 (m, 4H), 3.48 (dq, *J* = 9.5, 6.4 Hz, 2H), 3.39 – 3.31 (m, 2H), 3.31 – 3.17 (m, 4H), 3.15 – 3.05 (m, 2H), 2.91 (s, 1H), 2.32 (qt, *J* = 6.7, 1.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.85 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 137.76, 137.62, 137.55, 137.44, 137.31, 137.12, 136.96 (*aromatic* C), 134.59 (C-9), 128.68, 128.66, 128.60, 128.54, 128.51, 128.49, 128.44, 128.43, 128.28, 128.22, 128.07, 128.04, 127.96, 127.90, 127.87, 127.83, 127.79, 127.73, 127.71, 127.28, 127.11 (*aromatic* C*H*), 117.03 (C-10), 115.92 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.57, 98.09, 97.50, 97.30, 76.12, 75.77, 75.44, 74.03, 73.68, 73.57, 73.11, 72.03, 71.74, 71.13, 71.07, 70.88, 70.86, 70.59, 69.68, 69.23, 68.87, 68.81, 68.70, 67.87, 66.61, 66.57, 65.85, 65.78, 60.09, 59.60, 49.26, 48.99, 33.89. HR-MS: Calculated for $C_{88}H_{94}N_8O_{19}F_6$ $[M+Na]^+$: 1703.6437, found: 1703.6432.

Pentasaccharide 33

The reaction was carried out according to the general procedure A. The donor **4** (713 mg, 0.36 mmol) and acceptor **S33** (495 mg, 0.089 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 5 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to -10 ºC, after which TfOH (10 µl, 0.036 mmol) was added. The reaction was stirred at -10 ºC for overnight. 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). Compound **33** (676 mg, 84% yield) was obtained as white foam. $[\alpha]_D^{25}$ +119.6 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.11 (m, 48H), 7.07 (h, *J* = 4.2 Hz, 1H), 6.13 (d, *J* = 9.6 Hz, 1H), 6.08 (d, *J* = 9.4 Hz, 1H), 5.74 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.12 – 4.99 (m, 4H), 4.97 – 4.89 (m, 2H), 4.87 – 4.77 (m, 4H), 4.76 (d, *J* = 3.7 Hz, 1H), 4.74 (d, *J* = 3.7 Hz, 1H), 4.62 – 4.31 (m, 11H), 4.30 – 4.09 (m, 8H), 4.06 – 3.70 (m, 13H), 3.65 – 3.57 (m, 2H), 3.53 (dd, *J* = 11.1, 2.4 Hz, 1H), 3.51 – 3.44 (m, 1H), 3.34 (dd, *J* = 9.3, 5.8 Hz, 1H), 3.29 – 3.17 (m, 4H), 3.16 – 3.01 (m, 4H), 2.31 (qt, *J* = 6.7, 1.3 Hz, 2H), 1.04 (s, 9H), 1.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.61 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.33, 137.71, 137.69, 137.41, 137.38, 137.25, 136.94 (*aromatic* C), 134.56 (C-9), 128.67, 128.64, 128.59, 128.54, 128.50, 128.46, 128.44, 128.41, 128.34, 128.28, 128.26, 128.24, 128.23, 128.18, 128.12, 128.10, 128.05, 127.94, 127.91, 127.89, 127.84, 127.81, 127.64, 127.12, 126.81 (*aromatic* C*H*), 117.01 (C-10), 115.93 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.57, 98.11, 98.06, 97.40, 79.41, 79.29, 76.46, 75.73, 75.73, 75.71, 73.65, 73.55, 73.21, 73.17, 73.05, 73.01, 71.93, 71.69, 71.30, 70.95, 70.79, 70.66, 69.62, 69.53, 68.88, 68.84, 67.82, 67.09, 66.78, 66.73, 66.54, 66.26, 65.75, 62.90, 60.02, 59.58, 49.31, 49.22, 33.87, 27.43, 27.05, 22.69, 20.02. HR-MS: Calculated for $C_{109}H_{125}N_{11}O_{23}F_6Si$ $[M+Na]^+$: 2120.8521, found: 2120.8516.

Pentasaccharide S34

The reaction was carried out according to the general procedure C using compound **33** (740 mg, 0.35 mmol) and HF/pyridine (70%, 146 µl, 5.64 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S34** (568 mg, 82% yield) was obtained as white foam. $[\alpha]_D^{25}$ +144.6 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.10 (m, 46H), 7.06 (dd, *J* = 8.1, 6.4 Hz, 1H), 6.40 (d, *J* = 9.5 Hz, 1H), 6.36 (d, *J* = 9.5 Hz, 1H), 5.74 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.10 – 4.97 (m, 3H), 4.97 – 4.76 (m, 8H), 4.67 (d, *J* = 12.4 Hz, 1H), 4.61 – 4.46 (m, 4H), 4.45 – 4.32 (m, 5H), 4.32 – 3.89 (m, 16H), 3.88 – 3.73 (m, 4H), 3.72 – 3.44 (m, 6H), 3.40 – 2.97 (m, 11H), 2.41 (s, 1H), 2.30 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.80 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.30, 137.57, 137.53, 137.47, 137.36, 137.31, 137.24, 136.87, 136.84 (*aromatic* C), 134.49 (C-9), 128.56, 128.52, 128.49, 128.45, 128.42, 128.36, 128.34, 128.31, 128.29, 128.28, 128.17, 128.13, 128.11, 127.94, 127.89, 127.87, 127.83, 127.81, 127.76, 127.73, 127.61, 127.42, 127.32, 127.01, 126.82 (*aromatic* C*H*), 116.93 (C-10), 115.79 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.68, 98.51, 98.03, 97.50, 96.88, 79.97, 76.28, 75.67, 75.12, 74.66, 74.21, 73.57, 73.15, 73.07, 72.98, 72.17, 71.88, 71.73, 71.68, 71.43, 71.17, 71.12, 70.84, 70.50, 70.41, 69.67, 69.54, 68.81, 68.63, 67.78, 66.56, 66.45, 65.44, 63.47, 62.03, 59.95, 59.51, 49.38, 49.22, 33.79. HR-MS: Calculated for $C_{101}H_{109}N_{11}O_{23}F_6$ $[M+Na]^+$: 1980.7500, found: 1980.7494.

Pentasaccharide S35

The reaction was carried out according to the general procedure D using compound **S34** (552 mg, 0.28 mmol), K_2CO_3 (58 mg, 0.42 mmol), KI (60 mg, 0.36 mmol) and $Ph_2BO(CH_2)_2NH_2$ (12.7 mg, 0.056 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S35** (501 mg, 87% yield) was obtained as white foam. $[\alpha]_D^{25}$ +144 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 6.99 (m, 64H), 6.45 – 6.25 (m, 2H), 5.80 – 5.65 (m, 1H), 5.12 – 4.63 (m, 14H), 4.60 – 3.70 (m, 38H), 3.66 – 2.98 (m, 19H), 2.78 (d, *J* = 4.7 Hz, 1H), 2.51 (d, *J* = 5.8 Hz, 1H), 2.28 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.53 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.70, 138.24, 137.84, 137.44, 137.42, 137.38, 137.24, 137.13, 136.81, 136.71 (*aromatic* C), 134.37 (C-9), 128.75, 128.43, 128.38, 128.28, 128.25, 128.22, 128.18, 128.15, 128.12, 128.10, 128.05, 128.00, 127.97, 127.94, 127.79, 127.76, 127.68, 127.65, 127.57, 127.48, 127.44, 127.40, 127.01, 126.97, 126.89, 126.81, 126.69 (*aromatic* C*H*), 116.79 (C-10), 115.74 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.67, 98.38, 97.92, 97.26, 96.96, 79.83, 76.11, 75.58, 74.92, 74.86, 73.92, 73.43, 73.11, 72.97, 72.92, 72.83, 72.35, 71.88, 71.58, 71.48, 70.91, 70.80, 70.61, 70.47, 70.37, 69.52, 69.42, 69.04, 68.65, 68.56, 67.61, 66.44, 66.27, 65.41, 63.30, 59.78, 59.37, 58.71, 58.07, 54.59, 49.19, 49.06, 33.66. HR-MS: Calculated for $C_{108}H_{115}N_{11}O_{23}F_6$ $[M+Na]^+$: 2070.7969, found: 2070.7964.

Hexasaccharide 34

The reaction was carried out according to the general procedure B using donor **13** (568 mg, 0.94 mmol) and acceptor **S35** (480 mg, 0.23 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **34** (450 mg, 78% yield) was obtained as white foam. $[\alpha]_D^{25}$ +140.9 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.06 (m, 59H), 6.41 (d, *J* = 9.5 Hz, 1H), 6.21 (d, *J* = 9.6 Hz, 1H), 5.74 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.51 (d, *J* = 3.6 Hz, 1H), 5.09 – 4.98 (m, 4H), 4.97 – 4.88 (m, 4H), 4.84 (d, *J* = 3.7 Hz, 1H), 4.82 – 4.72 (m, 4H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.63 – 4.53 (m, 2H), 4.53 – 4.35 (m, 8H), 4.29 (td, *J* = 14.0, 13.3, 8.9 Hz, 5H), 4.23 – 4.13 (m, 5H), 4.13 – 3.73 (m, 18H), 3.66 – 3.53 (m, 4H), 3.47 (q, *J* = 6.3 Hz, 2H), 3.42 – 3.05 (m, 10H), 2.30 (q, *J* = 6.7 Hz, 2H), 1.03 (s, 10H), 0.97 (d, *J* = 1.5 Hz, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.55 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.18, 138.16, 137.82, 137.65, 137.58, 137.52, 137.33, 137.20, 137.02, 136.82 (*aromatic* C), 134.46 (C-9), 128.55, 128.52, 128.45, 128.41, 128.39, 128.38, 128.33, 128.30, 128.25, 128.18, 128.13, 128.11, 127.99, 127.96, 127.92, 127.89, 127.86, 127.81, 127.78, 127.68, 127.66, 127.59, 127.51, 127.43, 127.39, 127.04, 126.97, 126.77 (*aromatic* C*H*), 116.93 (C-10), 115.90 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.93, 98.48, 98.01, 97.90, 97.34, 97.25, 80.90, 76.30, 75.83, 75.67, 75.53, 74.67, 74.47, 73.88, 73.57, 73.10, 73.04, 73.00, 72.95, 71.78, 71.61, 70.99, 70.90, 70.87, 70.72, 70.64, 70.61, 70.58, 69.84, 69.71, 69.57, 68.78, 68.73, 68.67, 67.79, 67.74, 66.96, 66.66, 66.51, 66.41, 65.63, 64.78, 59.91, 59.50, 49.36, 49.15, 33.79, 27.58, 27.28, 23.28, 20.67.

Hexasaccharide S36

The reaction was carried out according to the general procedure C using compound **34** (440 mg, 0.18 mmol) and HF/pyridine (70%, 74 µl, 2.85 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S36** (346 mg, 83% yield) was obtained as white foam. $[\alpha]_D^{25}$ +118.6 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.01 (m, 59H), 6.44 (d, *J* = 9.5 Hz, 1H), 6.31 (d, *J* = 9.6 Hz, 1H), 5.74 (ddt, *J* = 17.0, 10.3, 6.7 Hz,

1H), 5.32 (d, *J* = 3.6 Hz, 1H), 5.10 – 4.98 (m, 3H), 4.96 – 4.85 (m, 5H), 4.83 (d, *J* = 3.7 Hz, 1H), 4.80 (d, *J* = 12.3 Hz, 1H), 4.77 (d, *J* = 3.6 Hz, 1H), 4.73 (d, *J* = 12.3 Hz, 1H), 4.66 (s, 2H), 4.61 – 4.47 (m, 4H), 4.47 – 4.34 (m, 5H), 4.34 – 4.00 (m, 18H), 4.01 – 3.75 (m, 10H), 3.74 – 3.42 (m, 9H), 3.42 – 3.02 (m, 11H), 2.88 – 2.64 (m, 2H), 2.30 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.73 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.15, 137.94, 137.61, 137.49, 137.45, 137.31, 137.23, 137.22, 136.90, 136.80 (*aromatic* C), 134.46 (C-9), 128.52, 128.49, 128.38, 128.36, 128.33, 128.32, 128.27, 128.16, 128.14, 128.08, 128.02, 128.01, 127.91, 127.86, 127.78, 127.76, 127.58, 127.55, 127.44, 127.40, 127.01, 126.94, 126.72 (*aromatic* C*H*), 116.89 (C-10), 115.81 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.94, 98.47, 97.98, 97.36, 96.90, 80.07, 76.25, 76.19, 75.64, 75.59, 74.68, 74.15, 73.54, 73.08, 73.00, 72.96, 71.69, 71.61, 71.12, 71.02, 70.96, 70.79, 70.63, 70.40, 70.26, 69.63, 69.51, 68.72, 68.53, 68.40, 67.72, 66.80, 66.62, 66.46, 66.39, 65.37, 64.49, 62.27, 59.89, 59.60, 59.46, 49.35, 49.15, 33.75.

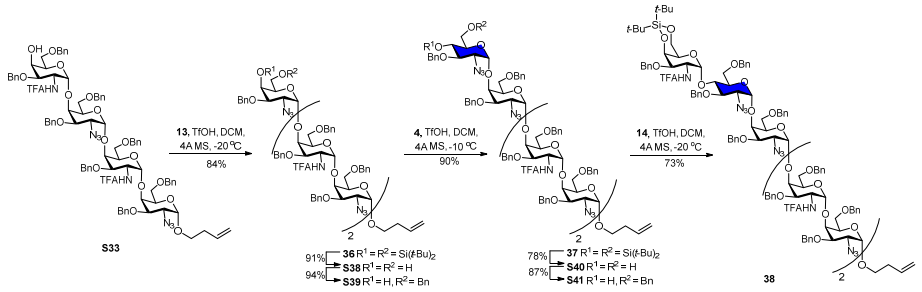
Hexasaccharide S37

The reaction was carried out according to the general procedure D using compound **S36** (340 mg, 0.15 mmol), K_2CO_3 (30 mg, 0.22 mmol), KI (32 mg, 0.19 mmol) and $Ph_2BO(CH_2)_2NH_2$ (6.6 mg, 0.029 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S37** (309 g, 88% yield) was obtained as white foam. $[\alpha]_D^{25}$ +128 (c=0.2, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 – 7.03 (m, 65H), 6.37 (d, *J* = 9.5 Hz, 1H), 6.26 (d, *J* = 9.6 Hz, 1H), 5.74 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.55 (d, *J* = 3.7 Hz, 1H), 5.10 – 4.89 (m, 8H), 4.83 (d, *J* = 3.7 Hz, 1H), 4.80 (d, *J* = 12.3 Hz, 1H), 4.77 – 4.68 (m, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.03 (m, 65H), 6.37 (d, *J* = 9.5 Hz, 1H), 6.26 (d, *J* = 9.6 Hz, 1H), 5.74 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.55 (d, *J* = 3.7 Hz, 1H), 5.10 – 4.89 (m, 8H), 4.83 (d, *J* = 3.7 Hz, 1H), 4.80 (d, *J* = 12.3 Hz, 1H), 4.77 – 4.68 (m, 4H), 4.62 – 4.45 (m, 5H), 4.43 – 4.00 (m, 26H), 4.00 – 3.70 (m, 9H), 3.66 – 3.03 (m, 18H), 2.78 (s, 1H), 2.30 (q, *J* = 6.8 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 156.52 (*a*d, *J* = 37 Hz, 2x*CF*$_3$C*O*), 138.48, 137.90, 137.78, 137.65, 137.62, 137.56, 137.51, 137.32, 137.20, 136.93, 136.81 (*aromatic* C), 134.46 (C-9), 128.53, 128.49, 128.47, 128.37, 128.36, 128.29, 128.27, 128.20, 128.15, 128.09, 128.02, 127.93, 127.88, 127.85, 127.81, 127.79, 127.76, 127.65, 127.60, 127.56, 127.50, 127.28, 127.22, 127.18, 126.95, 126.75 (*aromatic* C*H*), 116.90 (C-10), 115.85 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.89, 98.45, 97.99, 97.35, 97.15, 80.62, 76.27, 76.14, 75.66, 75.22, 74.63, 74.42, 73.89, 73.55, 73.50, 73.09, 73.01, 72.97, 72.85, 72.76, 71.72, 71.63, 71.60, 70.98, 70.91, 70.78, 70.70, 70.46, 69.66, 69.54, 69.37, 68.80, 68.74, 68.65, 67.72, 66.69, 66.64, 66.50, 66.40, 65.53, 64.87, 59.89, 59.48, 59.19, 58.14, 49.31, 49.15, 33.76.

Heptasaccharide 35

The reaction was carried out according to the general procedure B using donor **14** (338 mg, 0.50 mmol) and acceptor **S37** (302 mg, 0.13 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **35** (276 mg, 76% yield) was obtained as yellow syrup. $[\alpha]_D^{25}$ +110.5 (c=0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 4H), 7.40 – 7.07 (m, 64H), 6.36 (d, *J* = 9.6 Hz, 1H), 6.30 (d, *J* = 9.3 Hz, 1H), 6.19 (d, *J* = 9.6 Hz, 1H), 5.83 – 5.67 (m, 1H), 5.44 (d, *J* = 3.6 Hz, 1H), 5.09 – 4.89 (m, 9H), 4.84 – 4.78 (m, 2H), 4.75 (d, *J* = 3.6 Hz, 1H), 4.73 – 4.67 (m, 3H), 4.66 – 4.55 (m, 3H), 4.54 – 4.43 (m, 6H), 4.42 – 3.91 (m, 30H), 3.89 – 3.72

(m, 4H), 3.73 – 3.31 (m, 11H), 3.30 – 3.04 (m, 10H), 2.31 (qt, *J* = 6.7, 1.4 Hz, 2H), 1.07 (s, 9H), 0.97 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.73 (*a*d, *J* = 37 Hz, 3x*CF$_3$CO*), 138.50, 138.24, 137.92, 137.71, 137.68, 137.64, 137.59, 137.53, 137.44, 137.29, 137.13, 136.97, 136.89 (*aromatic* C), 134.59 (C-9), 128.68, 128.64, 128.61, 128.58, 128.56, 128.52, 128.51, 128.46, 128.44, 128.34, 128.31, 128.28, 128.25, 128.23, 128.21, 128.06, 128.03, 127.94, 127.92, 127.88, 127.82, 127.75, 127.72, 127.70, 127.56, 127.47, 127.24, 127.21, 127.14, 126.87, 126.72 (*aromatic* C*H*), 117.04 (C-10), 116.00 (*a*d, *J* = 286 Hz, 3xC*F$_3$*), 98.90, 98.59, 98.10, 97.68, 97.47, 97.29, 97.02, 80.37, 76.46, 76.18, 75.76, 75.43, 74.37, 74.22, 73.91, 73.70, 73.55, 73.24, 73.11, 73.06, 73.02, 72.72, 71.92, 71.89, 71.75, 71.15, 71.04, 70.84, 70.77, 70.75, 70.70, 70.03, 69.74, 69.68, 69.65, 69.43, 69.27, 68.87, 68.76, 68.70, 67.88, 67.83, 67.06, 66.76, 66.64, 66.58, 66.23, 65.68, 64.94, 60.23, 60.04, 59.62, 49.44, 49.26, 48.35, 33.91, 27.66, 27.47, 23.38, 20.79.



Pentasaccharide 36

The reaction was carried out according to the general procedure B using donor **13** (1.33 g, 2.19 mmol) and acceptor **S33** (1.23 g, 0.73 mmol). The product was purified by column chromatography (pentane:EtOAc = 8:1). Compound **36** (1.29 g, 84% yield) was obtained as white foam. $[\alpha]_D^{25}$ +144 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.08 (m, 50H), 6.32 (d, *J* = 9.8 Hz, 1H), 6.22 (d, *J* = 9.7 Hz, 1H), 5.75 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.09 – 5.00 (m, 2H), 4.98 (d, *J* = 3.7 Hz, 1H), 4.97 – 4.91 (m, 3H), 4.85 – 4.81 (m, 1H), 4.80 – 4.71 (m, 3H), 4.71 – 4.55 (m, 3H), 4.54 – 4.45 (m, 5H), 4.42 – 4.32 (m, 5H), 4.32 – 4.18 (m, 6H), 4.16 – 4.02 (m, 4H), 4.00 (s, 1H), 3.98 (s, 1H), 3.96 (dd, *J* = 10.7, 2.6 Hz, 2H), 3.88 – 3.59 (m, 9H), 3.55 (ddd, *J* = 10.7, 7.9, 2.4 Hz, 2H), 3.49 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.35 (dd, *J* = 9.2, 5.8 Hz, 1H), 3.31 – 3.19 (m, 4H), 3.13 – 3.03 (m, 3H), 2.31 (qt, *J* = 6.7, 1.4 Hz, 2H), 1.02 (s, 9H), 0.98 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.81 (*a*d, *J* = 37 Hz, 2x*CF$_3$CO*), 138.02, 137.70, 137.66, 137.42, 137.33, 137.31, 137.26, 137.00, 136.95 (*aromatic* C), 134.58 (C-9), 128.71, 128.69, 128.67, 128.62, 128.55, 128.51, 128.43, 128.35, 128.28, 128.21, 128.16, 128.13, 128.12, 128.02, 127.96, 127.91, 127.80, 127.72, 127.66, 127.64, 127.13, 126.96, 126.77 (*aromatic* C*H*), 117.03 (C-10), 115.95 (*a*d, *J* = 286 Hz, 2xC*F$_3$*), 98.65, 98.49, 98.10, 97.48, 97.28, 76.51, 76.07, 75.73, 75.16, 74.20, 73.69, 73.32, 73.23, 73.09, 71.85, 71.74, 71.21, 71.06, 70.88, 70.71, 70.69, 70.64, 70.34, 69.69, 69.66, 68.86, 68.79, 67.87, 67.50, 67.22, 66.66, 66.56, 66.45, 65.70, 60.01, 59.61, 58.60, 49.27, 49.25, 33.89, 27.66, 27.49, 23.33, 20.79. HR-MS: Calculated for $C_{109}H_{125}N_{11}O_{23}F_6Si$ $[M+Na]^+$: 2120.8521, found: 2120.8516.

Pentasaccharide S38

The reaction was carried out according to the general procedure C using compound **36** (1.20 g, 0.57 mmol) and HF/pyridine (70%, 238 µl, 9.14 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S38** (1.02 g, 91% yield) was obtained as white foam. $[\alpha]_D^{25}$ +158.2 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.09 (m, 48H), 6.47 (d, *J* = 9.7 Hz, 1H), 6.36 (d, *J* = 9.6 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.09 – 4.96 (m, 3H), 4.96 – 4.89 (m, 3H), 4.85 (d, *J* = 3.7 Hz, 1H), 4.80 (d, *J* = 12.4 Hz, 1H), 4.77 (d, *J* = 3.6 Hz, 1H), 4.75 – 4.65 (m, 3H), 4.58 (d, *J* = 12.2 Hz, 1H), 4.54 – 4.43 (m, 4H), 4.41 – 4.34 (m, 4H), 4.34 – 4.23 (m, 4H), 4.23 – 4.04 (m, 8H), 4.03 – 3.94 (m, 5H), 3.87 – 3.75 (m, 4H), 3.67 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.65 – 3.54 (m, 3H), 3.47 (dq, *J* = 8.4, 5.9, 5.3 Hz, 2H), 3.43 – 3.24 (m, 5H), 3.21 (dd, *J* = 8.7, 5.2 Hz, 1H), 3.15 – 3.02 (m, 3H), 2.84 (s, 1H), 2.37 – 2.29 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.86 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 137.58, 137.54, 137.45, 137.38, 137.35, 137.29, 137.19, 137.00, 136.87 (*aromatic* C), 134.50 (C-9), 128.61, 128.57, 128.54, 128.49, 128.39, 128.38, 128.34, 128.31, 128.28, 128.18, 128.12, 128.05, 127.96, 127.94, 127.90, 127.86, 127.83, 127.81, 127.64, 127.52, 127.17, 127.03, 126.85 (*aromatic* C*H*), 116.95 (C-10), 115.85 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.85, 98.56, 98.04, 97.45, 97.17, 76.58, 76.29, 75.65, 74.97, 74.13, 73.60, 73.16, 73.06, 72.98, 71.84, 71.79, 71.68, 71.18, 71.06, 70.81, 70.79, 70.75, 69.74, 69.55, 69.12, 68.81, 68.67, 67.78, 67.50, 66.58, 66.54, 66.48, 65.66, 62.63, 59.95, 59.51, 59.48, 49.36, 49.21, 33.81. HR-MS: Calculated for $C_{101}H_{109}N_{11}O_{23}F_6$ $[M+Na]^+$: 1980.7500, found: 1980.7494.

Pentasaccharide S39

The reaction was carried out according to the general procedure D using compound **S38** (1.06 g, 0.54 mmol), K_2CO_3 (112 mg, 0.81 mmol), KI (117 mg, 0.7 mmol) and $Ph_2BO(CH_2)_2NH_2$ (24 mg, 0.11 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S39** (1.05 g, 94% yield) was obtained as white foam. $[\alpha]_D^{25}$ +162.6 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.07 (m, 57H), 6.34 (d, *J* = 9.7 Hz, 1H), 6.23 (d, *J* = 9.6 Hz, 1H), 5.74 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.09 – 4.98 (m, 3H), 4.96 (d, *J* = 3.7 Hz, 1H), 4.94 – 4.90 (m, 2H), 4.83 (d, *J* = 3.7 Hz, 1H), 4.80 (d, *J* = 12.3 Hz, 1H), 4.77 – 4.65 (m, 4H), 4.57 (d, *J* = 12.3 Hz, 1H), 4.54 – 4.45 (m, 4H), 4.42 – 4.33 (m, 5H), 4.32 – 4.23 (m, 7H), 4.22 – 4.11 (m, 4H), 4.10 – 4.02 (m, 3H), 4.01 – 3.94 (m, 4H), 3.87 – 3.74 (m, 5H), 3.66 – 3.54 (m, 3H), 3.51 – 3.41 (m, 2H), 3.39 – 3.18 (m, 6H), 3.14 – 3.05 (m, 4H), 2.30 (qt, *J* = 6.8, 1.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.69 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 137.62, 137.59, 137.57, 137.56, 137.47, 137.44, 137.33, 137.22, 137.00, 136.84 (*aromatic* C), 134.49 (C-9), 128.56, 128.52, 128.46, 128.41, 128.38, 128.33, 128.29, 128.18, 128.11, 127.98, 127.95, 127.93, 127.86, 127.81, 127.70, 127.62, 127.61, 127.21, 127.01, 126.78 (*aromatic* C*H*), 116.94 (C-10), 115.75 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.94, 98.53, 98.00, 97.37, 97.20, 77.36, 76.61, 76.33, 75.65, 74.89, 73.97, 73.58, 73.36, 73.13, 73.06, 72.98, 71.81, 71.63, 71.55, 71.44, 71.08, 70.95, 70.77, 70.75, 70.66, 69.78, 69.69, 69.57, 68.77, 68.70, 68.24, 67.76, 66.89, 66.58, 66.50, 66.45, 65.65, 59.92, 59.51, 59.36, 49.27, 49.17, 33.80. HR-MS: Calculated for $C_{108}H_{115}N_{11}O_{23}F_6$ $[M+Na]^+$: 2070.7969, found: 2070.7964.

Hexasaccharide 37

The reaction was carried out according to the general procedure A. The donor **4** (178 mg, 0.29 mmol) and acceptor **S39** (150 mg, 0.073 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 2 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to -10 ºC, after which TfOH (2.6 µl, 0.03 mmol) was added. The reaction was stirred at -10 ºC for overnight. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 6:1). Compound **37** (162 mg, 90% yield) was obtained as white foam. $[\alpha]_D^{25}$ +135.6 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.08 (m, 64H), 6.31 (d, *J* = 9.7 Hz, 1H), 6.17 (d, *J* = 9.7 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.12 – 5.00 (m, 3H), 4.98 (d, *J* = 3.7 Hz, 1H), 4.95 – 4.89 (m, 3H), 4.86 – 4.73 (m, 7H), 4.58 (dd, *J* = 14.7, 12.1 Hz, 2H), 4.53 – 4.44 (m, 4H), 4.41 – 4.18 (m, 15H), 4.18 – 3.87 (m, 13H), 3.86 – 3.73 (m, 8H), 3.70 – 3.52 (m, 7H), 3.49 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.34 (dd, *J* = 9.2, 5.8 Hz, 1H), 3.31 – 3.18 (m, 4H), 3.16 – 3.00 (m, 5H), 2.31 (qt, *J* = 6.8, 1.4 Hz, 2H), 1.02 (s, 10H), 0.97 (s, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.77 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.29, 137.84, 137.74, 137.68, 137.58, 137.43, 137.35, 137.32, 137.12, 136.97 (*aromatic* C), 134.59 (C-9), 128.68, 128.62, 128.57, 128.52, 128.48, 128.46, 128.45, 128.37, 128.32, 128.29, 128.25, 128.22, 128.14, 128.05, 127.97, 127.95, 127.92, 127.85, 127.83, 127.79, 127.73, 127.67, 127.50, 127.15, 126.98, 126.91, 119.42, 119.33 (*aromatic* C*H*), 117.05 (C-10), 116.00 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.68, 98.66, 98.48, 98.11, 97.47, 97.42, 79.36, 79.27, 76.41, 76.36, 75.73, 75.53, 75.36, 73.98, 73.71, 73.22, 73.19, 73.11, 72.97, 72.30, 71.93, 71.74, 71.31, 71.14, 71.03, 70.87, 70.84, 69.77, 69.69, 69.06, 68.89, 68.85, 67.88, 66.79, 66.72, 66.60, 66.43, 66.13, 65.82, 63.04, 60.34, 60.00, 59.63, 49.34, 49.28, 33.92, 27.48, 27.22, 22.67, 20.07.

Hexasaccharide S40

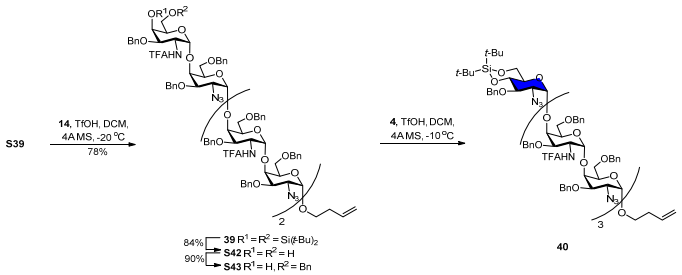
The reaction was carried out according to the general procedure C using compound **37** (555 mg, 0.23 mmol) and HF/pyridine (70%, 94 µl, 3.6 mmol). The product was purified by column chromatography (pentane:EtOAc = 2:1). Compound **S40** (463 mg, 88% yield) was obtained as white foam. $[\alpha]_D^{25}$ +148.5 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.11 (m, 59H), 6.45 (d, *J* = 9.0 Hz, 2H), 5.73 (ddd, *J* = 16.9, 10.6, 5.1 Hz, 1H), 5.12 – 4.62 (m, 16H), 4.62 – 3.69 (m, 40H), 3.60 (dq, *J* = 30.8, 12.9, 11.5 Hz, 6H), 3.44 (q, *J* = 7.2 Hz, 1H), 3.38 – 2.91 (m, 13H), 2.28 (q, *J* = 6.9 Hz, 2H), 1.91 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.57 (*a*d, *J* = 37 Hz, 2x*CF*$_3$*CO*), 138.14, 137.55, 137.50, 137.44, 137.27, 137.22, 137.19, 136.85, 136.73 (*aromatic* C), 134.37 (C-9), 128.63, 128.44, 128.39, 128.32, 128.27, 128.24, 128.21, 128.15, 128.06, 127.99, 127.97, 127.88, 127.82, 127.79, 127.75, 127.69, 127.65, 127.62, 127.52, 127.46, 127.28, 126.88, 126.84, 126.70 (*aromatic* C*H*), 116.84 (C-10), 115.78 (*a*d, *J* = 286 Hz, 2xC*F*$_3$), 98.58, 98.41, 98.15, 97.93, 97.39, 97.12, 79.37, 76.11, 75.77, 75.53, 74.71, 74.02, 73.43, 73.01, 72.92, 72.83, 72.79, 71.98, 71.57, 71.38, 70.99, 70.64, 70.46, 69.48, 69.39, 68.73, 68.72, 67.64, 66.51, 66.28, 65.58, 63.15, 61.33, 59.78, 59.37, 49.12, 49.10, 33.66.

Hexasaccharide S41

The reaction was carried out according to the general procedure D using compound **S40** (450 mg, 0.19 mmol), K_2CO_3 (40 mg, 0.29 mmol), KI (42 mg, 0.25 mmol) and $Ph_2BO(CH_2)_2NH_2$ (8.7 mg, 0.039 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S41** (402 mg, 97% yield) was obtained as white foam. $[\alpha]_D^{25}$ +148.6 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.13 (m, 62H), 6.40 (d, *J* = 9.4 Hz, 1H), 6.32 (d, *J* = 9.4 Hz, 1H), 5.73 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.10 – 4.70 (m, 15H), 4.63 – 3.93 (m, 35H), 3.89 – 3.70 (m, 7H), 3.69 – 3.41 (m, 7H), 3.38 – 2.95 (m, 13H), 2.76 (s, 1H), 2.28 (q, *J* = 6.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.55 (*a*d, *J* = 37 Hz, *CF*$_3$*C**O***), 138.20, 137.67, 137.65, 137.58, 137.48, 137.43, 137.27, 137.24, 137.14, 136.86, 136.71 (*aromatic* C), 134.37 (C-9), 128.79, 128.45, 128.40, 128.34, 128.30, 128.28, 128.26, 128.22, 128.20, 128.15, 128.08, 128.02, 127.91, 127.87, 127.83, 127.81, 127.78, 127.74, 127.70, 127.68, 127.64, 127.59, 127.54, 127.50, 127.46, 127.28, 127.07, 126.89, 126.85, 126.78, 126.72 (*aromatic* C*H*), 116.83 (C-10), 115.79 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.62, 98.44, 97.93, 97.28, 97.15, 79.46, 76.13, 75.58, 74.90, 74.83, 73.88, 73.46, 73.12, 73.04, 72.94, 72.85, 72.75, 72.61, 71.63, 71.51, 70.95, 70.82, 70.62, 70.55, 69.60, 69.51, 69.44, 69.23, 68.91, 68.67, 68.61, 67.64, 66.49, 66.29, 66.17, 65.57, 63.18, 59.84, 59.78, 59.39, 58.56, 58.04, 54.55, 49.15, 49.08, 33.68.

Heptasaccharide 38

The reaction was carried out according to the general procedure B using donor **14** (442 mg, 0.65 mmol) and acceptor **S41** (395 mg, 0.16 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **38** (380 mg, 80% yield) was obtained as white foam. $[\alpha]_D^{25}$ +120 (c=0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.39 – 7.11 (m, 69H), 6.89 (d, *J* = 9.5 Hz, 1H), 6.36 (d, *J* = 9.7 Hz, 1H), 6.22 (d, *J* = 9.6 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.45 (d, *J* = 3.5 Hz, 1H), 5.10 – 4.97 (m, 5H), 4.95 – 4.89 (m, 2H), 4.84 (d, *J* = 3.7 Hz, 1H), 4.83 – 4.62 (m, 8H), 4.61 – 4.33 (m, 15H), 4.33 – 4.13 (m, 11H), 4.11 – 3.87 (m, 14H), 3.87 – 3.74 (m, 5H), 3.72 – 3.41 (m, 9H), 3.35 (dd, *J* = 9.2, 5.8 Hz, 1H), 3.31 – 3.18 (m, 5H), 3.15 – 3.06 (m, 4H), 3.05 – 2.99 (m, 1H), 2.95 (d, *J* = 10.5 Hz, 1H), 2.31 (qt, *J* = 6.7, 1.3 Hz, 2H), 1.02 (d, *J* = 6.0 Hz, 17H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.99 (*a*d, *J* = 37 Hz, 3x*CF*$_3$*C**O***), 138.12, 137.68, 137.66, 137.62, 137.59, 137.52, 137.39, 137.29, 137.08, 136.92, 136.46 (*aromatic* C), 134.55 (C-9), 128.64, 128.60, 128.56, 128.53, 128.48, 128.44, 128.42, 128.38, 128.36, 128.26, 128.22, 128.19, 128.07, 128.01, 128.00, 127.91, 127.89, 127.86, 127.78, 127.75, 127.74, 127.69, 127.62, 127.37, 127.11, 127.04, 126.87 (*aromatic* C*H*), 117.03 (C-10), 115.97 (*a*d, *J* = 286 Hz, 3xC*F*$_3$), 98.80, 98.63, 98.08, 98.01, 97.45, 97.38, 97.13, 79.80, 76.38, 76.22, 75.70, 75.31, 75.19, 74.27, 74.06, 73.67, 73.52, 73.21, 73.14, 73.06, 72.99, 72.52, 71.95, 71.92, 71.71, 71.35, 71.19, 71.02, 70.87, 70.84, 70.62, 69.74, 69.65, 69.61, 68.98, 68.84, 68.77, 68.48, 67.85, 67.80, 67.10, 66.68, 66.62, 66.54, 66.30, 65.79, 63.99, 60.43, 59.99, 59.59, 49.31, 49.24, 48.61, 33.88, 27.66, 27.36, 23.39, 20.80.



Hexasaccharide 39

The reaction was carried out according to the general procedure B using donor **14** (597 mg, 0.94 mmol) and acceptor **S39** (480 mg, 0.23 mmol). The product was purified by column chromatography (pentane:EtOAc = 6:1). Compound **39** (462 mg, 78% yield) was obtained as white foam. $[\alpha]_D^{25}$ +149.7 (c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.10 (m, 56H), 6.34 (d, *J* = 9.5 Hz, 1H), 6.26 (dd, *J* = 15.4, 9.4 Hz, 2H), 5.81 – 5.67 (m, 1H), 5.08 – 4.98 (m, 4H), 4.96 – 4.89 (m, 2H), 4.89 – 4.55 (m, 11H), 4.54 – 4.42 (m, 7H), 4.42 – 4.33 (m, 6H), 4.33 – 4.09 (m, 9H), 4.06 – 3.91 (m, 9H), 3.88 – 3.74 (m, 5H), 3.71 – 3.53 (m, 5H), 3.46 (dt, *J* = 14.0, 8.6 Hz, 2H), 3.38 – 3.17 (m, 6H), 3.16 – 2.96 (m, 5H), 2.30 (q, *J* = 6.8 Hz, 2H), 1.07 (s, 11H), 0.98 (s, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.59 (*a*d, *J* = 37 Hz, 3x*CF*$_3$*CO*), 137.84, 137.59, 137.57, 137.52, 137.36, 137.31, 137.18, 137.17, 136.95, 136.84, 136.80 (*aromatic* C), 134.44 (C-9), 128.60, 128.53, 128.48, 128.43, 128.39, 128.35, 128.33, 128.30, 128.24, 128.15, 128.13, 128.08, 128.04, 128.01, 127.90, 127.88, 127.81, 127.79, 127.77, 127.71, 127.70, 127.62, 127.56, 126.98, 126.94, 126.71 (*aromatic* C*H*), 116.90 (C-10), 115.81 (*a*d, *J* = 286 Hz, 3xC*F*$_3$), 98.49, 98.31, 98.01, 97.33, 97.22, 96.65, 76.35, 76.14, 75.66, 75.07, 74.65, 73.97, 73.55, 73.02, 72.94, 72.91, 71.83, 71.60, 71.05, 70.93, 70.88, 70.72, 69.52, 69.44, 69.38, 69.22, 68.72, 68.66, 68.56, 67.73, 67.69, 66.87, 66.57, 66.48, 66.38, 65.73, 65.66, 60.20, 59.94, 59.49, 49.15, 48.19, 33.77, 27.52, 27.35, 23.21, 20.63.

Hexasaccharide S42

The reaction was carried out according to the general procedure C using compound **39** (445 mg, 0.18 mmol) and HF/pyridine (70%, 73 µl, 2.8 mmol). The product was purified by column chromatography (pentane:EtOAc = 3:2). Compound **S42** (353 mg, 84% yield) was obtained as white foam. $[\alpha]_D^{25}$ +141.8 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.11 (m, 64H), 6.46 (d, *J* = 9.5 Hz, 1H), 6.33 (d, *J* = 9.6 Hz, 1H), 6.30 (d, *J* = 9.6 Hz, 1H), 5.83 – 5.67 (m, 1H), 5.09 – 5.00 (m, 2H), 4.99 (d, *J* = 3.6 Hz, 1H), 4.97 (d, *J* = 3.7 Hz, 1H), 4.95 – 4.89 (m, 2H), 4.86 (d, *J* = 3.7 Hz, 1H), 4.84 (d, *J* = 3.7 Hz, 1H), 4.80 (d, *J* = 12.3 Hz, 1H), 4.77 (d, *J* = 3.6 Hz, 1H), 4.73 (d, *J* = 11.8 Hz, 1H), 4.65 – 4.46 (m, 9H), 4.45 – 4.33 (m, 8H), 4.32 – 4.12 (m, 10H), 4.07 – 3.90 (m, 12H), 3.87 – 3.70 (m, 5H), 3.65 – 3.42 (m, 7H), 3.39 – 3.20 (m, 8H), 3.14 – 3.02 (m, 5H), 2.90 (s, 1H), 2.31 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.73 (*a*d, *J* = 37 Hz, 3x*CF*$_3$*CO*), 137.67, 137.63, 137.57, 137.37, 137.31, 137.28, 137.10, 137.01, 136.89 (*aromatic* C), 134.52 (C-9), 128.58, 128.53, 128.51, 128.39, 128.37, 128.34, 128.18, 128.13, 128.11, 128.03, 127.95, 127.88, 127.84, 127.81, 127.60, 127.53, 127.29, 127.12, 127.05, 126.75 (*aromatic* C*H*), 116.95 (C-10),

115.86 (*a*d, *J* = 286 Hz, 3x*CF*$_3$), 98.53, 98.40, 98.04, 97.43, 97.24, 96.93, 76.42, 76.09, 75.68, 75.14, 74.71, 74.08, 73.60, 73.08, 73.06, 72.97, 72.91, 71.92, 71.90, 71.68, 71.20, 71.11, 71.06, 70.93, 70.78, 70.71, 70.67, 69.53, 69.42, 69.29, 68.80, 68.70, 68.59, 67.78, 66.64, 66.58, 66.51, 66.39, 65.86, 65.73, 62.44, 60.18, 60.00, 59.53, 49.22, 49.18, 48.82, 33.82.

Hexasaccharide S43

The reaction was carried out according to the general procedure D using compound **S42** (347 mg, 0.15 mmol), K_2CO_3 (30 mg, 0.22 mmol), KI (31 mg, 0.19 mmol) and $Ph_2BO(CH_2)_2NH_2$ (6.5 g, 0.03 mmol). The product was purified by column chromatography (pentane:EtOAc = 4:1). Compound **S43** (330 mg, 92% yield) was obtained as white foam. $[\alpha]_D^{25}$ +145.6 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.08 (m, 66H), 6.43 (d, *J* = 9.5 Hz, 1H), 6.31 (t, *J* = 8.8 Hz, 2H), 5.74 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.08 – 4.87 (m, 6H), 4.86 – 4.78 (m, 4H), 4.76 (d, *J* = 3.6 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.60 – 4.43 (m, 8H), 4.42 – 4.12 (m, 20H), 4.07 – 3.90 (m, 9H), 3.89 – 3.71 (m, 4H), 3.68 – 3.43 (m, 7H), 3.40 – 3.18 (m, 7H), 3.15 – 3.02 (m, 5H), 2.96 (s, 1H), 2.30 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.62 (*a*d, *J* = 37 Hz, 3x*CF*$_3$*CO*), 137.68, 137.59, 137.51, 137.40, 137.32, 137.25, 137.22, 137.05, 136.93, 136.83 (*aromatic* C), 134.46 (C-9), 128.89, 128.52, 128.46, 128.44, 128.38, 128.34, 128.32, 128.31, 128.27, 128.14, 128.07, 128.05, 127.96, 127.91, 127.89, 127.86, 127.78, 127.76, 127.72, 127.62, 127.58, 127.54, 127.50, 127.31, 127.20, 126.96, 126.70 (*aromatic* C*H*), 116.89 (C-10), 115.87 (*a*d, *J* = 286 Hz, C*F*$_3$), 98.49, 98.41, 97.99, 97.39, 97.16, 97.09, 76.35, 75.97, 75.65, 75.25, 74.55, 74.05, 73.54, 73.41, 73.02, 72.93, 72.91, 72.87, 71.85, 71.79, 71.13, 71.04, 71.01, 70.81, 70.75, 70.69, 70.59, 70.38, 69.52, 69.38, 69.08, 68.76, 68.65, 68.62, 67.73, 66.58, 66.50, 66.43, 65.75, 65.65, 65.58, 59.95, 59.48, 58.14, 49.17, 49.11, 48.88, 33.76.

Heptasaccharide 40

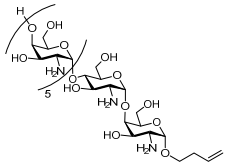
The reaction was carried out according to the general procedure A. The donor **4** (312 mg, 0.51 mmol) and acceptor **S43** (320 mg, 0.13 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry 3 ml DCM under nitrogen and stirred over fresh flame-dried molecular sieves 4Å. The solution was cooled to -10 °C, after which TfOH (7.7 µl, 0.05 mmol) was added. The reaction was stirred at -10 °C for overnight. Then the reaction was quenched with Et_3N, diluted with DCM, washed with saturated $NaHCO_3$ and brine. The organic phase was dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by silica gel column chromatography (pentane:EtOAc = 6:1). Compound **40** (320 mg, 85% yield) was obtained as white foam. $[\alpha]_D^{25}$ +131.6 (c=0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.03 (m, 81H), 6.19 (d, *J* = 9.6 Hz, 2H), 6.07 (d, *J* = 9.4 Hz, 1H), 5.82 – 5.67 (m, 1H), 5.12 – 4.99 (m, 5H), 4.96 (d, *J* = 3.6 Hz, 1H), 4.94 – 4.88 (m, 4H), 4.85 – 4.73 (m, 8H), 4.61 – 4.11 (m, 32H), 4.10 – 3.97 (m, 6H), 3.96 – 3.71 (m, 17H), 3.66 – 3.44 (m, 6H), 3.35 (dd, *J* = 9.2, 5.8 Hz, 1H), 3.30 – 3.19 (m, 6H), 3.17 – 3.00 (m, 8H), 2.31 (qt, *J* = 6.8, 1.4 Hz, 2H), 1.04 (s, 9H), 1.01 (s, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.69 (*a*d, *J* = 37 Hz, 3x*CF*$_3$*CO*), 138.33, 137.81, 137.71, 137.68, 137.61, 137.40, 137.32, 137.29, 137.28, 137.22, 137.04, 136.93 (*aromatic* C), 134.56 (C-9), 128.65, 128.58, 128.53, 128.44, 128.38, 128.32, 128.26, 128.24, 128.18, 128.10, 128.08, 128.02, 128.00, 127.92, 127.90, 127.87, 127.84, 127.79, 127.75,

127.72, 127.69, 127.67, 127.63, 127.11, 126.84, 126.82 (*aromatic* C*H*), 117.03 (C-10), 115.96 (*a*d, *J* = 286 Hz, 3xCF_3), 98.60, 98.54, 98.11, 98.08, 97.45, 97.34, 97.24, 79.40, 79.29, 76.50, 76.45, 75.74, 74.28, 74.04, 73.67, 73.23, 73.20, 73.13, 73.06, 72.98, 72.93, 71.93, 71.73, 71.28, 71.16, 71.04, 71.02, 70.83, 70.78, 70.76, 70.67, 69.64, 69.49, 69.44, 68.84, 68.77, 67.85, 67.10, 66.81, 66.55, 66.27, 65.76, 62.89, 60.04, 59.59, 49.30, 49.24, 49.19, 33.88, 27.44, 27.06, 22.70.

General procedure for desilylation and Birch reduction of the oligosaccharides towards 41 - 46 (general procedure E)

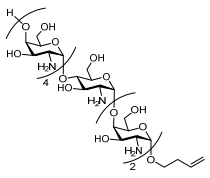
HF/pyridine (16 eq) solution was added to a solution of starting material in THF at 0 ºC. The reaction was warmed to room temperature and stirred until TLC-analysis indicated full consumption of the starting material (± 1h). Then the mixture was diluted with DCM and washed with saturated $NaHCO_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography. Ammonia (10 ml) was condensed at -78 oC, the residue was dissolved in THF (2 ml) and tert-butanol (0.8 ml) and slowly added to the flask containing ammonia. Allyl carbinol (200 ul) was added to the reaction mixture. Small pieces of sodium was added to the reaction mixture one by one to keep deep blue for 15 min. Then ammonia acetate (100 mg) was added. The solution was allowed to warm to room temperature and stirred until all of the ammonia was evaporated. The solution was concentrated *in vacuo* and purified by gel filtration (HW-40, 0.15M NH_4OAc in H_2O). The product containing fractions were pooled and lyophilized (4x) to yield the final products as a white solid.

Heptasaccharide (41)



(69% yield, 12/1 with:without C=C). The reaction was carried out according to the general procedure E. ^{1}H NMR (500 MHz, Deuterium Oxide) δ 5.88 (ddt, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.67 (d, *J* = 4.0 Hz, 1H), 5.33 – 5.23 (m, 4H), 5.19 – 5.12 (m, 3H), 5.11 – 5.07 (m, 1H), 4.48 (q, *J* = 5.4 Hz, 3H), 4.41 (t, *J* = 6.4 Hz, 1H), 4.31 – 4.20 (m, 5H), 4.19 – 4.00 (m, 11H), 3.86 – 3.71 (m, 16H), 3.66 – 3.53 (m, 6H), 3.49 (dd, *J* = 10.9, 3.8 Hz, 1H), 3.19 (dd, *J* = 10.8, 3.6 Hz, 1H), 2.42 – 2.35 (m, 2H). ^{13}C NMR (125 MHz, D_2O) δ 135.71, 116.71, 97.36, 97.19, 96.91, 96.79, 96.53, 95.49, 76.54, 76.28, 76.23, 76.15, 75.34, 71.53, 71.44, 70.98, 70.90, 70.72, 67.90, 67.65, 66.76, 66.68, 66.52, 60.56, 60.47, 60.26, 60.10, 54.77, 50.98, 50.91, 33.10.

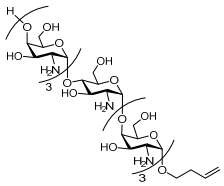
Heptasaccharide (42)



(48% yield, 25/1 with:without C=C). The reaction was carried out according to the general procedure E. ^{1}H NMR (500 MHz, Deuterium Oxide) δ 5.88 (ddt, *J* = 17.1, 10.4, 6.6 Hz, 1H), 5.70 (d, *J* = 3.9 Hz, 1H), 5.32 (d, *J* = 3.8 Hz, 1H), 5.29 (dd, *J* = 5.7, 3.9 Hz, 2H), 5.26 (d, *J* = 3.8 Hz, 1H), 5.22 (d, *J* = 3.8 Hz, 1H), 5.19 (d, *J* = 3.8 Hz, 1H), 5.18 – 5.13 (m, 1H), 5.09 (ddt, *J* = 10.4, 2.3, 1.3 Hz, 1H), 4.53 – 4.46 (m, 3H), 4.42 (t, *J* = 6.4 Hz, 1H), 4.33 – 4.00 (m, 19H), 3.87 – 3.69 (m, 18H), 3.67 – 3.59 (m, 5H), 3.59 – 3.50 (m, 3H), 3.26 (dd, *J* = 11.0,

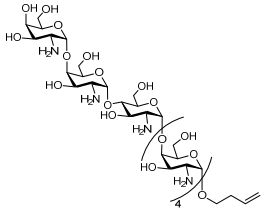
3.5 Hz, 1H), 2.39 (q, *J* = 6.6 Hz, 2H). ^{13}C NMR (125 MHz, D_2O) δ 135.70, 116.72, 97.13, 96.81, 96.65, 96.48, 96.31, 95.33, 76.50, 76.30, 76.19, 76.13, 75.17, 71.44, 71.22, 70.97, 70.72, 70.66, 67.87, 67.67, 66.59, 66.40, 60.58, 60.54, 60.47, 60.26, 60.13, 60.01, 54.67, 51.00, 50.91, 50.85, 33.11. HR-MS: Calculated for $C_{46}H_{85}N_7O_{29}$ $[M+2H]^{2+}$: 600.7774, found: 600.7769.

Heptasaccharide (43)



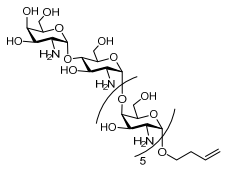
(84% yield, 19/1). The reaction was carried out according to the general procedure E. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.88 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.71 (d, *J* = 3.9 Hz, 1H), 5.31 (q, *J* = 4.2, 3.5 Hz, 3H), 5.28 (d, *J* = 3.8 Hz, 1H), 5.24 (d, *J* = 3.7 Hz, 1H), 5.19 (d, *J* = 3.8 Hz, 1H), 5.15 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.09 (ddt, *J* = 10.3, 2.4, 1.3 Hz, 1H), 4.49 (t, *J* = 5.7 Hz, 3H), 4.42 (t, *J* = 6.4 Hz, 1H), 4.33 – 4.00 (m, 18H), 3.90 – 3.70 (m, 18H), 3.69 – 3.58 (m, 7H), 3.53 (dd, *J* = 11.0, 3.8 Hz, 1H), 3.32 (dd, *J* = 10.6, 3.6 Hz, 1H), 2.38 (q, *J* = 6.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.23, 119.25, 99.41, 98.91, 98.75, 98.71, 97.82, 78.92, 78.80, 78.70, 78.61, 77.47, 73.94, 73.49, 73.36, 73.13, 73.11, 73.05, 70.39, 70.20, 69.01, 68.85, 68.76, 68.62, 68.56, 63.11, 63.05, 63.01, 62.76, 62.60, 57.09, 53.52, 53.40, 53.37, 53.32, 35.64. HR-MS: Calculated for $C_{46}H_{85}N_7O_{29}$ $[M+2H]^{2+}$: 600.7774, found: 600.7769.

Heptasaccharide (44)



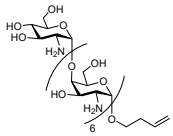
(53% yield, 50/1). The reaction was carried out according to the general procedure E. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.85 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.64 (d, *J* = 4.0 Hz, 1H), 5.23 (d, *J* = 3.9 Hz, 1H), 5.22 (d, *J* = 3.9 Hz, 1H), 5.20 (d, *J* = 3.9 Hz, 1H), 5.18 (d, *J* = 3.9 Hz, 1H), 5.15 (d, *J* = 3.8 Hz, 1H), 5.14 – 5.11 (m, 1H), 5.10 (d, *J* = 3.7 Hz, 1H), 5.06 (d, *J* = 10.3 Hz, 1H), 4.44 (p, *J* = 6.5, 6.1 Hz, 3H), 4.37 (t, *J* = 6.4 Hz, 1H), 4.25 (dt, *J* = 10.1, 3.2 Hz, 1H), 4.19 (dd, *J* = 9.3, 2.9 Hz, 3H), 4.15 (t, *J* = 3.6 Hz, 2H), 4.11 – 4.06 (m, 5H), 4.05 (t, *J* = 5.7 Hz, 1H), 4.03 – 3.97 (m, 5H), 3.82 – 3.72 (m, 15H), 3.70 – 3.67 (m, 2H), 3.62 – 3.52 (m, 4H), 3.51 – 3.45 (m, 3H), 3.41 (dd, *J* = 10.9, 3.8 Hz, 1H), 3.09 (dd, *J* = 10.6, 3.7 Hz, 1H), 2.36 (q, *J* = 7.2 Hz, 2H). ^{13}C NMR (214 MHz, D_2O) δ 135.63, 116.60, 97.66, 97.35, 97.12, 96.79, 95.47, 76.44, 76.41, 76.34, 76.25, 76.22, 75.43, 71.97, 71.48, 71.32, 71.04, 70.85, 70.84, 70.78, 70.74, 67.85, 67.51, 67.22, 66.98, 66.66, 66.62, 60.54, 60.52, 60.49, 60.06, 60.01, 59.96, 54.82, 50.94, 50.92, 50.89, 50.88, 50.76, 33.02. HR-MS: Calculated for $C_{46}H_{85}N_7O_{29}$ $[M+H]^+$: 1200.5470, found: 1200.5464. HR-MS: Calculated for $C_{46}H_{85}N_7O_{29}$ $[M+2H]^{2+}$: 600.7774, found: 600.7769.

Heptasaccharide (45)



(59% yield, 25/1). The reaction was carried out according to the general procedure E. ^{1}H NMR (500 MHz, Deuterium Oxide) δ 5.91 (ddt, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.44 (d, *J* = 4.0 Hz, 1H), 5.17 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.12 – 5.08 (m, 1H), 5.06 – 4.93 (m, 6H), 4.41 – 4.33 (m, 4H), 4.21 – 3.95 (m, 11H), 3.87 – 3.72 (m, 23H), 3.67 – 3.58 (m, 2H), 3.18 – 3.09 (m, 6H), 2.85 – 2.79 (m, 1H), 2.42 – 2.35 (m, 2H). ^{13}C NMR (214 MHz, D_2O) δ 135.78, 116.48, 100.11, 100.09, 99.97, 99.65, 98.56, 77.46, 77.45, 77.40, 77.34, 76.84, 76.57, 73.88, 72.00, 71.94, 71.92, 71.80, 71.79, 71.61, 71.09, 70.10, 69.83, 69.76, 69.65, 68.41, 68.39, 67.45, 61.20, 61.18, 60.67, 60.32, 60.23, 60.18, 60.14, 55.19, 51.41, 51.39, 51.32, 51.05, 50.75, 33.09. HR-MS: Calculated for $C_{46}H_{85}N_7O_{29}$ $[M+2H]^{2+}$: 600.7774, found: 600.7769.

Heptasaccharide (46)

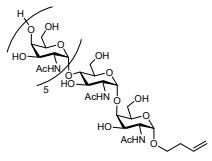


(85% yield, 43/1). The reaction was carried out according to the general procedure E. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.90 – 5.82 (m, 1H), 5.28 – 5.23 (m, 4H), 5.23 – 5.14 (m, 3H), 5.14 – 5.11 (m, 1H), 5.06 (d, *J* = 10.3 Hz, 1H), 4.45 (q, *J* = 5.7, 4.9 Hz, 5H), 4.24 – 4.08 (m, 13H), 4.01 (t, *J* = 5.8 Hz, 1H), 3.84 – 3.72 (m, 15H), 3.59 (dt, *J* = 9.9, 6.3 Hz, 1H), 3.58 – 3.52 (m, 6H), 3.51 – 3.45 (m, 1H), 3.20 (dd, *J* = 10.7, 3.6 Hz, 1H), 2.36 (q, *J* = 7.2 Hz, 2H). ^{13}C NMR (214 MHz, D_2O) δ 135.63, 116.61, 96.85, 96.74, 95.37, 76.36, 76.30, 76.28, 76.21, 72.36, 70.78, 70.70, 70.65, 70.30, 69.15, 67.52, 66.71, 66.58, 66.50, 60.53, 60.09, 60.07, 60.06, 60.02, 59.95, 54.34, 50.84, 50.74, 33.02. HR-MS: Calculated for $C_{46}H_{85}N_7O_{29}$ $[M+2H]^{2+}$: 600.7774, found: 600.7769.

General procedure for acetylation of the oligosaccharides towards 47 - 52 (general procedure F)

To a solution of starting material in H_2O (1 ml) was added Ac_2O at 0 °C. Then $NaHCO_3$ was added to the solution until the pH is 8~9. The reaction was warmed to room temperature and stirred for 3h. Then the mixture was neutralized with AcOH and then concentrated *in vacuo*, which was purified by gel filtration (HW-40, 0.15M NH_4OAc in H_2O). The product containing fractions were pooled and lyophilized (4x) to yield the final products as a white solid.

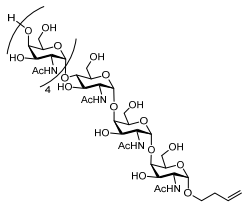
Heptasaccharide (47)



(90% yield). The reaction was carried out according to the general procedure F. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.85 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.42 (d, *J* = 3.9 Hz, 1H), 5.13 – 5.04 (m, 2H), 5.02 – 4.98 (m, 2H), 4.97 – 4.92 (m, 3H), 4.86 (d, *J* = 3.7 Hz, 1H), 4.40 – 4.35 (m, 3H), 4.33 (t, *J* = 6.6 Hz, 1H), 4.29 – 4.23 (m, 4H), 4.22 – 4.16 (m, 3H), 4.14 – 3.96 (m, 16H), 3.94 – 3.88 (m, 1H), 3.83 (dd, *J* = 12.4, 3.2 Hz, 1H), 3.77 – 3.72 (m, 2H), 3.71 – 3.53 (m, 15H), 2.38 – 2.29 (m, 2H), 2.07 – 1.97 (m, 21H). ^{13}C NMR (214 MHz, D_2O) δ 174.64, 174.52, 174.49, 174.48, 174.42, 174.34, 135.78, 116.39, 98.23, 98.15, 98.12, 98.07, 98.01, 97.98, 96.67, 77.18, 76.66, 76.33, 76.16, 76.07, 75.29, 72.24, 71.52, 71.22, 71.17, 71.13, 70.59, 70.53, 68.09, 67.10, 67.07, 66.94,

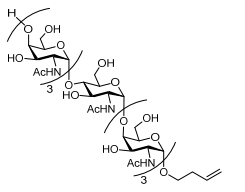
66.80, 66.60, 66.53, 66.40, 60.36, 60.21, 59.90, 59.47, 59.35, 54.33, 50.19, 50.03, 49.91, 32.96, 21.93, 21.82, 21.78, 21.77. HR-MS: Calculated for $C_{60}H_{99}N_7O_{36}$ $[M+2H]^{2+}$: 747.8144, found: 747.8138.

Heptasaccharide (48)



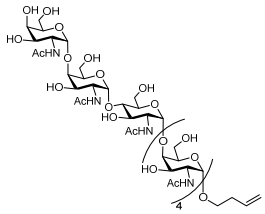
(91% yield, 7/1). The reaction was carried out according to the general procedure F. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.85 (ddt, *J* = 17.1, 10.4, 6.7 Hz, 1H), 5.43 (d, *J* = 3.9 Hz, 1H), 5.13 – 5.04 (m, 2H), 5.00 (d, *J* = 3.8 Hz, 1H), 4.97 – 4.95 (m, 2H), 4.94 (d, *J* = 3.8 Hz, 1H), 4.93 (d, *J* = 3.8 Hz, 1H), 4.92 (d, *J* = 3.7 Hz, 1H), 4.40 – 4.36 (m, 3H), 4.33 (t, *J* = 6.5 Hz, 1H), 4.29 – 4.23 (m, 4H), 4.21 – 4.16 (m, 3H), 4.15 – 3.96 (m, 16H), 3.92 (dd, *J* = 10.8, 3.7 Hz, 1H), 3.84 (dd, *J* = 12.5, 3.2 Hz, 1H), 3.77 – 3.72 (m, 2H), 3.71 – 3.57 (m, 14H), 3.54 (dt, *J* = 10.4, 6.2 Hz, 1H), 2.39 – 2.27 (m, 2H), 2.05 – 1.98 (m, 21H). ^{13}C NMR (214 MHz, D_2O) δ 174.63, 174.56, 174.48, 174.42, 174.35, 135.78, 116.38, 98.24, 98.17, 98.10, 98.08, 97.98, 96.61, 76.68, 76.53, 76.36, 76.08, 75.27, 72.23, 71.47, 71.29, 71.22, 71.16, 70.60, 70.54, 68.11, 68.09, 67.10, 67.04, 66.96, 66.82, 66.61, 66.40, 60.35, 60.21, 59.92, 59.47, 59.38, 59.34, 54.28, 50.21, 50.08, 50.03, 49.94, 32.95, 21.93, 21.82, 21.77. HR-MS: Calculated for $C_{60}H_{99}N_7O_{36}$ $[M+2H]^{2+}$: 747.8144, found: 747.8138.

Heptasaccharide (49)



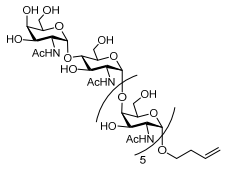
(91% yield, 32/1). The reaction was carried out according to the general procedure F. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.85 (ddt, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.43 (d, *J* = 3.9 Hz, 1H), 5.13 – 5.08 (m, 1H), 5.07 – 5.04 (m, 1H), 5.00 (d, *J* = 3.8 Hz, 1H), 4.97 – 4.90 (m, 5H), 4.40 – 4.36 (m, 3H), 4.34 – 4.31 (m, 1H), 4.30 – 4.22 (m, 4H), 4.22 – 4.15 (m, 3H), 4.14 – 4.10 (m, 3H), 4.09 – 3.96 (m, 12H), 3.92 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.84 (dd, *J* = 12.4, 3.2 Hz, 1H), 3.78 – 3.71 (m, 2H), 3.71 – 3.56 (m, 14H), 3.54 (dt, *J* = 10.4, 6.2 Hz, 1H), 2.37 – 2.28 (m, 2H), 2.05 – 1.99 (m, 21H). ^{13}C NMR (214 MHz, D_2O) δ 174.63, 174.56, 174.48, 174.46, 174.43, 174.41, 174.36, 135.79, 116.38, 98.19, 98.17, 98.12, 98.08, 98.03, 97.97, 96.61, 76.77, 76.68, 76.24, 76.02, 75.27, 72.23, 71.49, 71.28, 71.23, 71.16, 71.12, 70.59, 70.58, 68.11, 68.09, 67.11, 67.04, 66.98, 66.82, 66.53, 66.48, 66.38, 60.36, 60.35, 60.23, 59.93, 59.50, 59.32, 54.29, 50.23, 50.20, 50.03, 49.95, 32.95, 21.82, 21.81, 21.78. HR-MS: Calculated for $C_{60}H_{99}N_7O_{36}$ $[M+2H]^{2+}$: 747.8144, found: 747.8139.

Heptasaccharide (50)



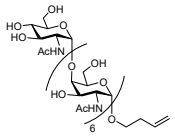
(90% yield, 32/1). The reaction was carried out according to the general procedure F. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.85 (ddt, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.43 (d, *J* = 4.0 Hz, 1H), 5.13 – 5.08 (m, 1H), 5.08 – 5.04 (m, 1H), 5.01 (d, *J* = 3.8 Hz, 1H), 5.00 (d, *J* = 3.8 Hz, 1H), 4.95 – 4.90 (m, 4H), 4.40 – 4.36 (m, 3H), 4.33 (t, *J* = 6.6 Hz, 1H), 4.30 – 4.22 (m, 4H), 4.22 – 4.14 (m, 3H), 4.14 – 4.10 (m, 3H), 4.09 – 3.95 (m, 13H), 3.92 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.84 (dd, *J* = 12.6, 3.2 Hz, 1H), 3.77 – 3.56 (m, 17H), 3.54 (dt, *J* = 10.4, 6.1 Hz, 1H), 2.36 – 2.29 (m, 2H), 2.06 – 2.02 (m, 15H), 2.02 – 2.00 (m, 6H). ^{13}C NMR (214 MHz, D_2O) δ 174.64, 174.55, 174.47, 174.46, 174.44, 174.42, 174.35, 135.79, 116.38, 98.28, 98.15, 98.08, 98.02, 97.98, 96.61, 76.87, 76.75, 76.74, 76.65, 76.09, 75.25, 72.33, 71.49, 71.29, 71.15, 71.10, 70.60, 70.58, 70.55, 68.09, 68.07, 67.03, 66.97, 66.90, 66.51, 66.40, 60.39, 60.37, 60.34, 59.91, 59.34, 59.30, 54.29, 50.20, 50.16, 50.07, 50.04, 49.97, 32.95, 21.94, 21.93, 21.84, 21.83, 21.82, 21.81, 21.79, 21.78, 21.77. HR-MS: Calculated for $C_{60}H_{99}N_7O_{36}$ $[M+2H]^{2+}$: 747.8144, found: 747.8138.

Heptasaccharide (51)



(89% yield, 13/1). The reaction was carried out according to the general procedure F. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.76 (ddt, *J* = 17.1, 10.4, 6.7 Hz, 1H), 5.27 (d, *J* = 4.0 Hz, 1H), 5.04 – 4.99 (m, 1H), 4.98 – 4.95 (m, 1H), 4.93 – 4.89 (m, 3H), 4.86 – 4.82 (m, 3H), 4.31 – 4.26 (m, 4H), 4.22 – 4.13 (m, 4H), 4.13 – 4.05 (m, 3H), 4.05 – 3.96 (m, 8H), 3.93 – 3.87 (m, 6H), 3.84 – 3.80 (m, 1H), 3.79 – 3.76 (m, 2H), 3.67 – 3.47 (m, 16H), 3.45 (dt, *J* = 10.4, 6.2 Hz, 1H), 2.29 – 2.19 (m, 2H), 1.97 – 1.93 (m, 15H), 1.91 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (214 MHz, D_2O) δ 174.56, 174.51, 174.49, 174.46, 174.44, 174.35, 135.79, 116.38, 98.16, 98.12, 98.09, 98.07, 98.00, 96.61, 76.74, 76.61, 76.17, 76.08, 75.54, 71.54, 71.49, 71.15, 70.61, 68.34, 68.33, 67.48, 67.03, 66.97, 66.52, 66.39, 61.05, 60.37, 59.93, 59.33, 54.28, 50.20, 50.16, 50.04, 49.84, 32.95, 21.96, 21.83, 21.78, 21.77. HR-MS: Calculated for $C_{60}H_{99}N_7O_{36}$ $[M+2H]^{2+}$: 747.8144, found: 747.8138.

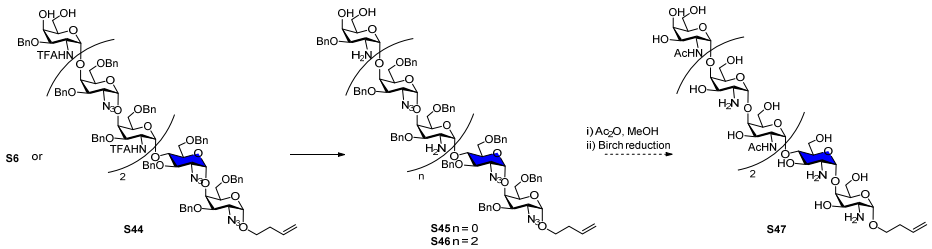
Heptasaccharide (52)



(88% yield, 12/1). The reaction was carried out according to the general procedure F. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.85 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.13 – 5.08 (m, 1H), 5.07 – 5.04 (m, 1H), 5.01 – 4.98 (m, 4H), 4.95 – 4.92 (m, 3H), 4.40 – 4.35 (m, 5H), 4.28 – 4.22 (m, 5H), 4.18 (dd, *J* = 11.2, 3.7 Hz, 1H), 4.14 – 4.04 (m, 10H), 4.01 – 3.95 (m, 3H), 3.89 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.83 – 3.77 (m, 2H), 3.76 – 3.71 (m, 1H), 3.70 – 3.49 (m, 15H), 2.37 – 2.28 (m, 2H), 2.05 – 2.02 (m, 17H), 1.99 (s, 7H). ^{13}C NMR (214 MHz, D_2O) δ 174.55, 174.48, 174.45, 174.41, 174.23, 135.79, 116.39, 98.23, 98.11, 98.08, 96.61, 76.76, 76.74, 76.63, 76.61, 76.15, 76.08, 71.87, 71.49, 71.15, 71.13, 70.38, 69.47, 67.03, 66.97, 66.52, 66.40, 60.37, 59.75, 59.34, 53.96, 50.20, 50.17, 50.11, 50.03, 32.95, 21.84, 21.83, 21.78, 21.77, 21.73, 21.72. HR-MS: Calculated for $C_{60}H_{99}N_7O_{36}$ $[M+2H]^{2+}$: 747.8144, found: 747.8138.

Removal of TFA group was first attempted on trisaccharide **S6** in 1 M NaOH solution at 40 ºC, giving S45 in 92% yield (Table S1, entry 1). However, the TFA groups in heptamer **S44** could not be cleaved even with strong basic conditions and high temperature (4M KOH, 80 ºC, entry 2). Also attempts to remove the TFA groups with the assistance of microwave failed (entry 3). Considering the possible solubility problem of the intermediates, ammonia in methanol and 1,4-dioxane was applied, but only afforded a mixture of incompletely deprotected products (entries 4 and 5). Another attempt by the combination of KOH and H_2O_2 in 37 ºC led to a mixture (entry 6). When the reaction was proceed at 100 ºC with ammonium salt and ethylenediamine as reagents, which could be used for the deacylation of unactivated amides to generate amines[31], still failed to give the target **S46** (entry 7).

Table S1. Attempts of N-TFA removal of heptasaccharide **S44**



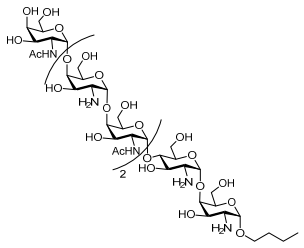
Entry	RN-TFA	Reagents and conditions	Yield
1	**S6**	1M NaOH, THF, MeOH, 40 ºC, 24h	92% (**S45**)
2	**S44**	4M KOH, THF, MeOH, 80 ºC, 5d	mixture
3	**S44**	4M KOH, THF, MeOH, 60 ºC, microwave, 6h	mixture
4	**S44**	NH_3 in MeOH, 65 ºC, 7d	mixture
5	**S44**	$NH_3.H_2O$, 1,4-dioxane, 60 ºC, 4d	mixture
6	**S44**	KOH, H_2O_2, H_2O, THF, 37 ºC, 2d	mixture
7	**S44**	$H_2N(CH_2)_2NH_2$, NH_4Br, 100 ºC, 24h	mixture

General procedure for heptasaccharides 53 - 58 (general procedure G)

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 residue was purified by silica gel column chromatography. 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*. Then Boc_2O and Et_3N were added to the solution of the residue in methanol at 0 ºC. The reaction was slowly warmed to room temperature and stirred for overnight. The reaction was concentrated *in vacuo* and co-evaporated with toluene for 3 times. The residue was dissolved in $NH_3{\cdot}H_2O$ (2 ml), which was warmed to 60 ºC and stirred for overnight. The

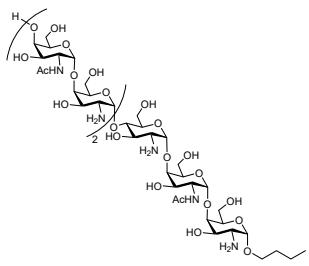
solution was concentrated *in vacuo* and then dissolved in H_2O. Ac_2O was added at 0 ºC and $NaHCO_3$ was added to the solution until the pH is 8~9. The reaction was warmed to room temperature and stirred for 3h. Then the mixture was neutralized with AcOH and then concentrated *in vacuo*. The residue was dissolved in 30% TFA in H_2O, and allowed to stirred at rt for overnight. The solution was concentrated *in vacuo*, which was purified by gel filtration (HW-40, 0.15M NH_4OAc in H_2O). The product containing fractions were pooled and lyophilized (4x) to yield the final products as a white solid.

Heptasaccharide (53)



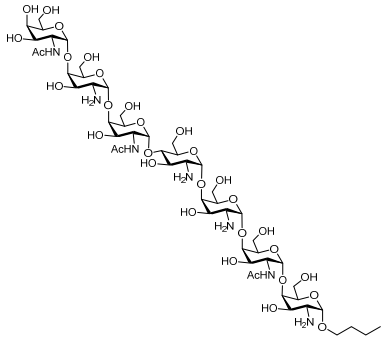
(31% yield). The reaction was carried out according to the general procedure G. ^{1}H NMR (500 MHz, Deuterium Oxide) δ 5.44 (d, *J* = 3.9 Hz, 1H), 5.28 (d, *J* = 3.9 Hz, 1H), 5.20 (d, *J* = 3.8 Hz, 1H), 5.13 (d, *J* = 3.8 Hz, 1H), 5.05 (d, *J* = 3.6 Hz, 1H), 5.00 (d, *J* = 3.8 Hz, 1H), 4.96 (d, *J* = 3.9 Hz, 1H), 4.42 (q, *J* = 4.4, 2.8 Hz, 3H), 4.36 (t, *J* = 6.4 Hz, 1H), 4.31 – 4.22 (m, 4H), 4.21 – 3.91 (m, 17H), 3.84 – 3.58 (m, 18H), 3.58 – 3.43 (m, 5H), 3.01 (d, *J* = 10.6 Hz, 1H), 2.09 – 1.98 (m, 9H), 1.64 – 1.53 (m, 2H), 1.41 – 1.28 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (214 MHz, D_2O) δ 175.70, 175.48, 175.39, 99.27, 99.08, 98.38, 96.38, 96.29, 77.50, 77.13, 76.71, 75.78, 72.70, 72.58, 72.39, 71.84, 71.21, 70.09, 69.30, 69.04, 68.07, 67.75, 67.64, 67.51, 61.59, 61.49, 61.43, 61.14, 61.07, 60.61, 60.39, 56.02, 52.07, 51.99, 51.79, 51.02, 50.98, 50.81, 31.62, 22.93, 22.79, 22.74, 19.66, 13.95. HR-MS: Calculated for $C_{52}H_{93}N_7O_{32}$ $[M+2H]^{2+}$: 664.8011, found: 664.8005.

Heptasaccharide (54)



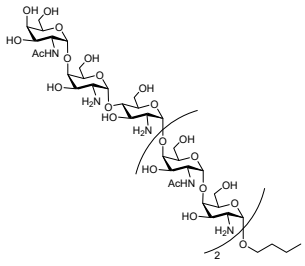
(25% yield). The reaction was carried out according to the general procedure G. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.46 (d, *J* = 4.0 Hz, 1H), 5.03 (d, *J* = 3.7 Hz, 1H), 4.95 – 4.92 (m, 4H), 4.90 (d, *J* = 3.8 Hz, 1H), 4.40 – 4.33 (m, 4H), 4.30 (t, *J* = 6.4 Hz, 1H), 4.26 – 4.20 (m, 3H), 4.17 – 4.11 (m, 4H), 4.10 (d, *J* = 2.8 Hz, 1H), 4.04 – 4.00 (m, 5H), 3.99 – 3.95 (m, 5H), 3.93 – 3.90 (m, 2H), 3.89 – 3.86 (m, 2H), 3.82 – 3.62 (m, 25H), 3.48 (dt, *J* = 9.8, 6.4 Hz, 1H), 2.04 – 2.01 (m, 9H), 1.58 – 1.52 (m, 2H), 1.37 – 1.32 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (214 MHz, D_2O) δ 175.45, 175.41, 100.99, 100.94, 100.59, 99.30, 99.22, 99.15, 78.43, 77.93, 77.82, 76.95, 74.73, 73.37, 72.84, 72.64, 72.24, 72.17, 72.04, 71.92, 70.62, 70.42, 69.24, 69.14, 68.09, 67.76, 67.73, 61.56, 61.45, 61.36, 60.98, 60.83, 56.17, 52.33, 52.00, 51.91, 51.32, 51.17, 51.06, 31.66, 22.79, 22.74, 19.72, 13.99. HR-MS: Calculated for $C_{52}H_{93}N_7O_{32}$ $[M+2H]^{2+}$: 664.8011, found: 664.8005.

Heptasaccharide (55)



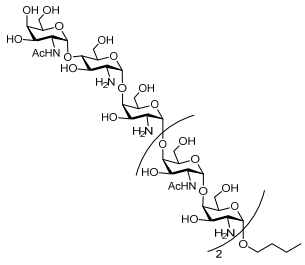
(24% yield). The reaction was carried out according to the general procedure G. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.43 (d, *J* = 3.9 Hz, 1H), 5.21 – 5.14 (m, 2H), 5.09 (d, *J* = 3.8 Hz, 1H), 5.06 – 5.02 (m, 1H), 4.95 (d, *J* = 4.0 Hz, 1H), 4.93 (d, *J* = 3.9 Hz, 1H), 4.40 (dt, *J* = 11.4, 5.6 Hz, 3H), 4.33 (t, *J* = 6.4 Hz, 1H), 4.28 – 4.20 (m, 4H), 4.20 – 4.11 (m, 5H), 4.10 – 3.95 (m, 13H), 3.95 – 3.87 (m, 3H), 3.84 – 3.59 (m, 21H), 3.50 (dt, *J* = 9.7, 6.4 Hz, 1H), 3.47 – 3.32 (m, 3H), 2.95 (s, 1H), 2.05 – 1.99 (m, 11H), 1.60 – 1.52 (m, 2H), 1.37 – 1.29 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (214 MHz, D_2O) δ 174.64, 174.45, 174.39, 98.26, 98.13, 97.35, 76.72, 76.63, 76.34, 74.96, 71.74, 71.59, 71.06, 70.88, 70.81, 70.63, 68.23, 68.07, 67.08, 66.88, 66.55, 60.57, 60.47, 60.23, 60.16, 59.91, 59.82, 59.69, 51.16, 51.08, 50.89, 50.04, 49.89, 30.62, 18.67, 12.96. HR-MS: Calculated for $C_{52}H_{93}N_7O_{32}$ $[M+2H]^{2+}$: 664.8011, found: 664.8005.

Heptasaccharide (56)



(18% yield). The reaction was carried out according to the general procedure G. ^{1}H NMR (500 MHz, Deuterium Oxide) δ 5.53 (d, *J* = 4.0 Hz, 1H), 5.08 (d, *J* = 3.9 Hz, 1H), 5.03 – 4.93 (m, 5H), 4.45 – 4.37 (m, 3H), 4.34 (t, *J* = 6.4 Hz, 1H), 4.32 – 4.24 (m, 2H), 4.22 – 4.14 (m, 4H), 4.11 – 3.65 (m, 34H), 3.53 (dt, *J* = 9.8, 6.3 Hz, 1H), 3.26 (dd, *J* = 11.1, 3.9 Hz, 1H), 3.21 – 3.14 (m, 2H), 2.85 (dd, *J* = 10.5, 3.6 Hz, 1H), 2.11 – 2.02 (m, 9H), 1.64 – 1.56 (m, 2H), 1.43 – 1.34 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (214 MHz, D_2O) δ 174.44, 174.41, 100.08, 99.72, 98.54, 98.24, 98.23, 98.12, 77.56, 77.09, 76.92, 76.55, 75.95, 73.77, 72.46, 71.75, 71.67, 71.31, 71.23, 71.07, 70.87, 70.86, 69.89, 69.44, 69.38, 68.39, 68.23, 68.13, 68.11, 67.00, 66.89, 66.73, 60.53, 60.52, 60.00, 59.84, 59.68, 55.18, 51.27, 51.07, 50.93, 50.33, 50.17, 50.09, 30.67, 21.80, 21.75, 19.95, 18.73, 13.00. HR-MS: Calculated for $C_{52}H_{93}N_7O_{32}$ $[M+2H]^{2+}$: 664.8011, found: 664.8005.

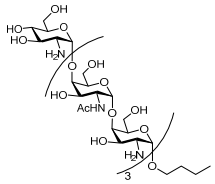
Heptasaccharide (57)



(30% yield). The reaction was carried out according to the general procedure G. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.26 (d, *J* = 3.9 Hz, 1H), 5.20 – 5.14 (m, 2H), 5.06 (s, 1H), 5.03 (d, *J* = 3.8 Hz, 1H), 4.89 (d, *J* = 3.9 Hz, 1H), 4.84 (d, *J* = 3.9 Hz, 1H), 4.36 – 4.29 (m, 4H), 4.26 – 4.21 (m, 1H), 4.19 – 4.14 (m, 2H), 4.13 – 4.08 (m, 5H), 4.05 (dd, *J* = 11.2, 3.9 Hz, 2H), 4.01 – 3.95 (m, 6H), 3.94 (t, *J* = 6.3 Hz, 1H), 3.92 – 3.88 (m, 2H), 3.87 (d, *J* = 3.2 Hz, 1H), 3.79 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.74 (dd, *J* = 12.3, 4.0 Hz, 1H), 3.70 – 3.59 (m, 13H), 3.59 – 3.52 (m, 4H), 3.50 (dd, *J* = 10.9, 6.3 Hz, 1H), 3.47 – 3.38 (m, 4H), 1.96 – 1.89 (m, 9H), 1.51 – 1.43 (m, 2H), 1.28 – 1.22 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (214 MHz, D_2O) δ 174.47, 98.10, 96.60, 95.30,

76.73, 76.51, 76.16, 75.97, 75.70, 75.13, 71.60, 71.56, 70.66, 70.54, 70.32, 70.26, 68.23, 67.21, 66.56, 66.46, 61.09, 60.16, 60.04, 59.90, 59.37, 54.83, 50.99, 50.87, 50.00, 49.95, 49.88, 30.61, 23.13, 23.12, 21.91, 21.74, 18.66, 12.95. HR-MS: Calculated for $C_{52}H_{93}N_7O_{32}$ $[M+2H]^{2+}$: 664.8011, found: 664.8005.

Heptasaccharide (58)

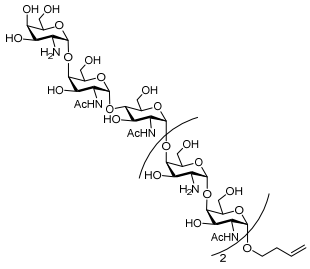


(18% yield). The reaction was carried out according to the general procedure G. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.29 – 5.22 (m, 2H), 5.20 (d, *J* = 4.0 Hz, 1H), 5.12 (d, *J* = 3.8 Hz, 1H), 4.99 (d, *J* = 4.1 Hz, 2H), 4.94 (d, *J* = 3.9 Hz, 1H), 4.44 – 4.38 (m, 5H), 4.29 – 4.23 (m, 3H), 4.23 – 4.17 (m, 3H), 4.15 – 4.03 (m, 10H), 4.02 – 3.96 (m, 3H), 3.86 (t, *J* = 9.9 Hz, 1H), 3.81 – 3.56 (m, 19H), 3.54 – 3.46 (m, 5H), 3.20 (d, *J* = 10.3 Hz, 1H), 2.05 – 1.99 (m, 11H), 1.60 – 1.52 (m, 2H), 1.36 – 1.29 (m, 2H), 0.86 (t, *J* = 7.5, 3.2 Hz, 3H). ^{13}C NMR (214 MHz, D_2O) δ 174.49, 174.48, 174.43, 98.11, 95.39, 95.13, 77.01, 76.60, 76.55, 76.20, 75.77, 72.39, 71.58, 71.02, 70.36, 69.04, 68.24, 66.85, 66.58, 66.48, 61.04, 60.44, 60.19, 60.08, 59.65, 59.41, 54.41, 51.01, 50.89, 50.02, 49.95, 30.62, 21.75, 18.67, 12.96. HR-MS: Calculated for $C_{52}H_{93}N_7O_{32}$ $[M+2H]^{2+}$: 664.8011, found: 664.8002.

General procedure for desilylation, reduction, acetylation and Birch reduction of the oligosaccharides towards 59 and 60 (general procedure H)

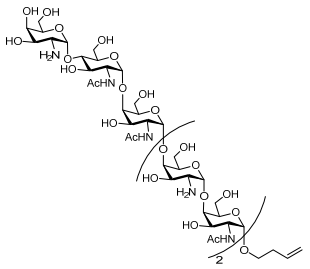
HF/pyridine (16 eq) solution was added to a solution of starting material in THF at 0 ºC. The reaction was warmed to room temperature and stirred until TLC-analysis indicated full consumption of the starting material (± 1h). Then the mixture was diluted with DCM and washed with saturated $NaHCO_3$ and brine, dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography. 1,3-Dithiolpropane and trimethylamine were added to the solution of the residue in pyridine/water. The mixture was protected from light and stirred at room temperature for overnight. The fluent was evaporated and co-evaporated with toluene. The residue was dissolved in THF/H_2O (2 ml, 2/1), after which Ac_2O and $NaHCO_3$ were added (pH~8). The reaction was allowed to stir at rt for 2 days. The reaction was concentrated *in vacuo* and the residue was purified by silica gel column chromatography. Ammonia (10 ml) was condensed at -78 ºC, the residue was dissolved in THF (2 ml) and tert-butanol (0.8 ml) and slowly added to the flask containing ammonia. Allyl carbinol (200 ul) was added to the reaction mixture. Small pieces of sodium was added to the reaction mixture one by one to keep deep blue for 15 min. Then ammonia acetate (100 mg) was added. The solution was allowed to warm to room temperature and stirred until all of the ammonia was evaporated. The solution was concentrated *in vacuo* and purified by gel filtration (HW-40, 0.15M NH_4OAc in H_2O). The product containing fractions were pooled and lyophilized (4x) to yield the final products as a white solid.

Heptasaccharide 59



(77% yield, 9/1). The reaction was carried out according to the general procedure H. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.82 (ddt, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.37 (d, *J* = 3.9 Hz, 1H), 5.10 – 5.06 (m, 1H), 5.05 – 5.01 (m, 2H), 4.99 – 4.97 (m, 2H), 4.94 (d, *J* = 3.9 Hz, 1H), 4.89 (d, *J* = 3.8 Hz, 1H), 4.85 (d, *J* = 3.7 Hz, 1H), 4.37 – 4.31 (m, 4H), 4.28 – 4.25 (m, 1H), 4.24 – 4.17 (m, 4H), 4.14 (dd, *J* = 11.3, 3.8 Hz, 1H), 4.12 – 4.08 (m, 3H), 4.07 – 3.86 (m, 20H), 3.85 – 3.67 (m, 18H), 3.66 – 3.56 (m, 10H), 3.51 (dt, *J* = 10.2, 6.2 Hz, 1H), 3.15 – 3.07 (m, 4H), 2.34 – 2.26 (m, 2H), 2.01 – 1.95 (m, 12H). ^{13}C NMR (214 MHz, D_2O) δ 174.70, 174.62, 174.54, 174.41, 135.87, 116.45, 99.71, 98.21, 97.95, 97.85, 96.72, 77.45, 77.22, 77.04, 76.57, 76.29, 75.69, 72.05, 71.80, 71.66, 71.35, 71.21, 71.06, 70.46, 69.14, 68.23, 67.33, 67.28, 67.14, 66.88, 60.71, 60.66, 60.17, 59.97, 59.75, 59.63, 54.26, 51.36, 51.26, 51.01, 50.35, 50.20, 50.15, 33.00, 21.99, 21.91, 21.84. HR-MS: Calculated for $C_{54}H_{93}N_7O_{33}$ $[M+2H]^{2+}$: 684.7986, found: 684.7980.

Heptasaccharide 60



(69% yield, 23/1). The reaction was carried out according to the general procedure H. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.82 (ddt, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.36 (d, *J* = 4.1 Hz, 1H), 5.09 – 5.05 (m, 1H), 5.04 – 5.01 (m, 1H), 4.99 (d, *J* = 3.8 Hz, 1H), 4.97 – 4.92 (m, 3H), 4.90 – 4.87 (m, 2H), 4.36 – 4.30 (m, 4H), 4.24 – 4.19 (m, 3H), 4.17 – 4.12 (m, 2H), 4.09 (d, *J* = 2.8 Hz, 1H), 4.06 – 3.91 (m, 12H), 3.91 – 3.87 (m, 3H), 3.86 – 3.83 (m, 2H), 3.81 – 3.77 (m, 2H), 3.75 – 3.56 (m, 18H), 3.51 (dt, *J* = 10.3, 6.1 Hz, 1H), 3.11 – 3.04 (m, 3H), 2.34 – 2.25 (m, 2H), 2.02 – 1.95 (m, 12H). ^{13}C NMR (214 MHz, D_2O) δ 174.61, 174.54, 174.51, 174.33, 135.88, 116.46, 100.13, 100.06, 98.24, 98.22, 98.08, 96.71, 77.32, 77.11, 76.95, 76.93, 76.67, 71.85, 71.84, 71.59, 71.43, 71.33, 70.86, 70.62, 69.52, 69.44, 68.48, 68.46, 67.37, 67.13, 66.93, 66.64, 61.22, 60.66, 59.97, 59.80, 59.73, 53.78, 51.40, 51.38, 50.88, 50.38, 50.23, 50.15, 33.00, 21.84, 21.81, 21.80. Calculated for $C_{54}H_{93}N_7O_{33}$ $[M+2H]^{2+}$: 684.7986, found: 684.7980.

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