Total synthesis of alginate and zwitterionic SP1 oligosaccharides

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Total Synthesis of Zwitterionic SP1 Oligosaccharides

7.1 Introduction

Zwitterionic polysaccharides (ZPSs) are found on the surface of *Bacteroides fragilis* and *Streptococcus pneumoniae* and they exhibit unique immunomodulatory properties.[1] ZPSs are the only known carbohydrate antigens to induce an immune response by a T cell-dependent pathway.[2] They are taken up by antigen presenting cells, processed and loaded in major histocompatibility complex class II (MHC-II) molecules and presented to T-cells.[2] To understand the mechanism of their immunomodulatory activity, get a detailed picture how these unique polysaccharides bind MHC-II molecules and their T-cell receptors, and eventually develop a synthetic vaccine, well-defined oligosaccharides of ZPSs are needed. The synthesis of ZPSs oligosaccharides represents a major challenge because of the presence of rare monosaccharide constituents, such as the trideoxy-diaminogalactose residues, the 1,2-*cis*-glycosidic bonds, and the presence of both positive

and negative charges in the molecules.[3] This Chapter describes the assembly of oligosaccharides of the capsular polysaccharide of *Streptococcus pneumoniae* type 1 (Sp1), composed of 1,2-*cis*-linked 2,4,6-trideoxy-2-*N*-acetamido-4-amino-α-D-galactopyranose (TDDAG) and galacuronic acid residues (See Figure 7.1), up to the dodecamer level, the longest zwitterionic polysaccharide fragment synthesized to date.

7.2 Results and discussion

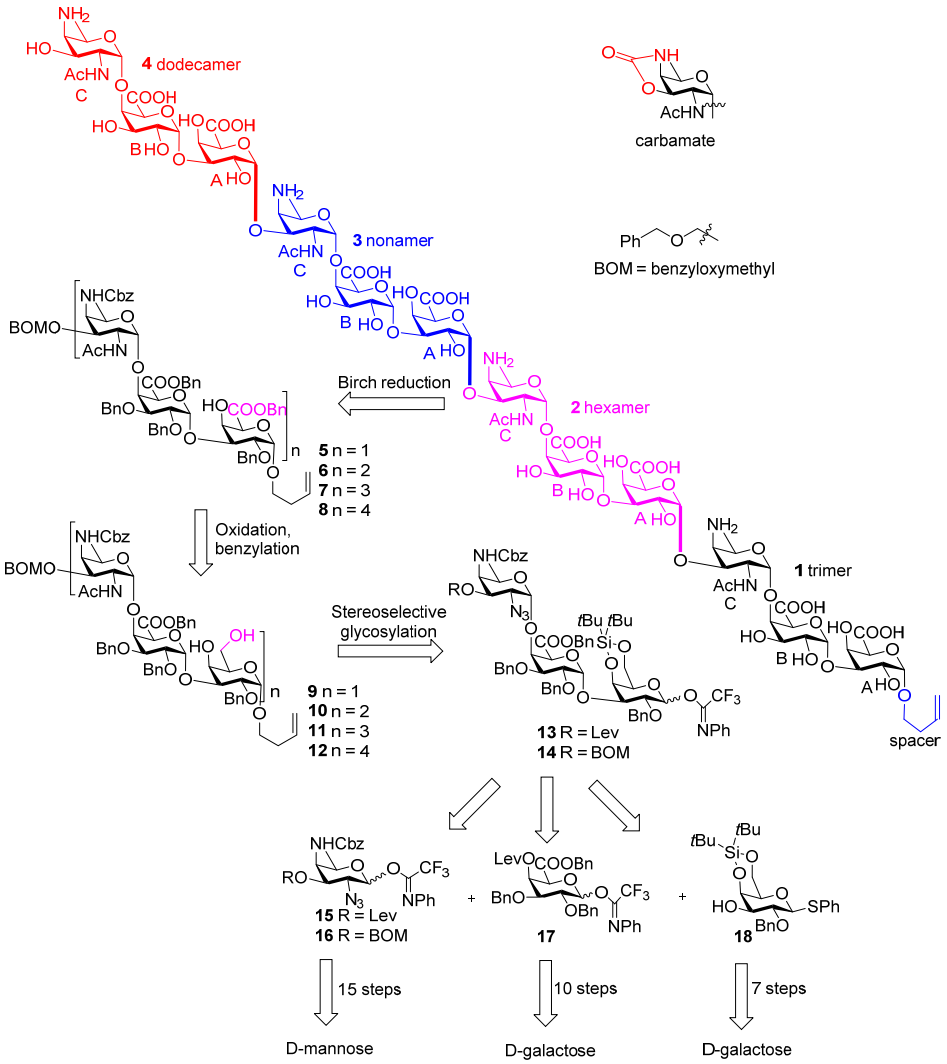
7.2.1 Synthetic approach

Chapter 2 reviewed the synthetic work, reported to date, directed at the assembly of the zwitterionic polysaccharides PS A1 and Sp1.[3] The described Sp1 syntheses clearly illustrate the challenges associated with the assembly of these molecules: the generation of sufficient amounts of the rare 2,4,6-trideoxy-2-*N*-acetamido-4-amino-α-D-galactopyranose (TDDAG) residues, effecting high yielding and stereoselective *cis*-glycosylations and effectively installing the uronic acid residues. The longest ZPS assembled to date was reported by Bundle and co-workers who assembled an Sp1-hexasaccharide (*i.e.* two repeating units). They described that extensive optimizations were required for the construction of the glycosidic linkages.[4] Christina *et al.* assembled all three possible repeating units of the Sp1 polysaccharide using galacturonic acid lactone building blocks. Although these synthons are very effective for the stereoselective installation of 1,2-*cis*-linkages, construction of the crucial linkage between the two galacturonic acid residues failed and a 5:4 α/β-mixture was obtained.[5] Seeberger *et al*. and co-workers described the assembly of a spacer-equipped Sp1-trisaccharide but also did not succeed in the stereoselective construction of the α-galacturonic acid residues.[6]

All these syntheses clearly indicate the stereoselective construction of the glycosidic linkages as a major bottle neck.

One of the most powerful means to introduce 1,2-*cis*-galactosyl linkages in a stereoselective manner reported to date, builds on the use of 4,6-silylidene protected galactose configured building blocks. The bulky silyl protecting group effectively shields the top face of the galactose ring thereby guiding the incoming nucleophile to the α-face. The stereodirecting effect of the 4,6-silylidene is in fact so strong that it overrides the generally very powerful neighboring group participation from an acyl protecting group at the C2-hydroxyl or amine functionality.[7] It was therefore decided to employ the silylidene strategy to construct the Sp1 oligosaccharides as retrosynthetically depicted in figure 7.1 using trisaccharide **13**/**14** as the key building block. The simultaneous oxidation of multiple alcohols can be extremely difficult[4,8] and it was therefore planned to already install one of the uronic acid residues in the trisaccharide building block, before the assembly of longer oligomers. From previous syntheses it has also become apparent that the removal of a protecting group at the TDDAG C-3-OH under basic conditions leads to formation of the C-3, N-4 carbamate,[5,6] both levulinoyl (Lev) ester- and benzyloxymethyl (BOM) ether protected building blocks (**13** and **14**, respectively) are investigated. For future functionalization, a 3-butenol moiety, was installed, as the double bond in this spacer can be functionalized in a mild and chemoselective manner using a thiol-ene reaction.[9] The key trisaccharides donors **13** and **14** were synthesized from monosaccharide **15**-**18** which were produced from D-mannose and D-galactose in 7-15 steps.

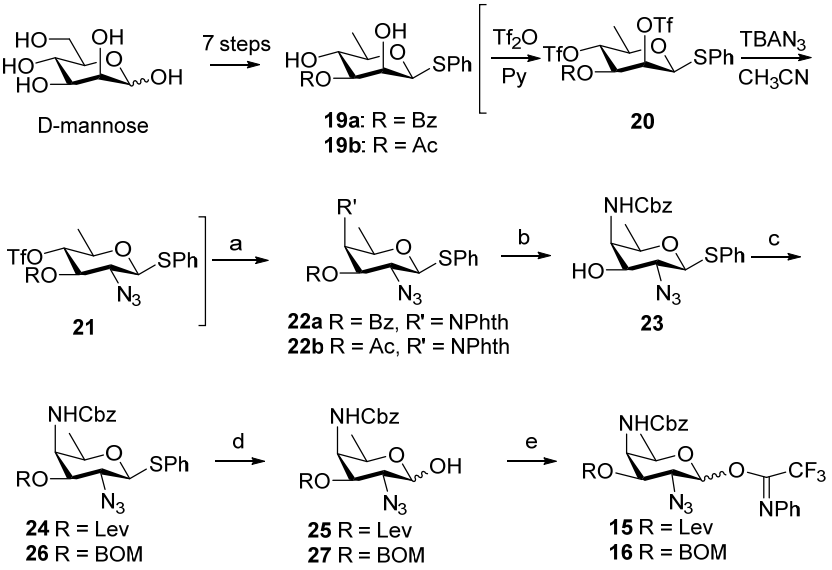
Figure 7.1 Retrosynthesis analysis of zwitterionic **SP1** oligosaccharides (**1**, **2**, **3** and **4**).



7.2.2 Synthesis of zwitterionic SP1 oligosaccharides (**1**, **2**, **3** and **4**).

The synthesis of the TDDAG donors **15** and **16** is depicted in Scheme 7.1. Following Kulkarni's protocol,[10] the syntheses started from D-mannose, to give, after 7 steps, phenyl 3-*O*-benzoyl-6-deoxy-1-thio-β-D-mannose **19a**. Triflation of both alcohols in **19a**, regioselective substitution of the C-2-*O*-triflate using tetrabutyl ammonium azide ($TBAN_3$), and consecutive replacement of the C-4-*O*-triflate for an *N*-phthalimide functionality provided the TDDAG building block **22a** in 48% yield. Unfortunately, the removal of the benzoate ester and phthaloyl groups and installation of the carboxylbenyl (Cbz) carbamate at the liberated C-4-amine proceeded in very low yield. To increase the overall efficiency the benzoate in **19b** was replaced for an acetyl ester. Although **19b** was obtained in a moderate yield (30% over three steps), the subsequent steps proceeded in a reliable manner to produce **23** in 69% yield. The free alcohol in **23** was protected with a Lev-ester or BOM-ether to yield **24** and **26**, respectively. Hydrolysis of the thioacetal (to give **25** and **27**) and installation of the *N*-phenyltrifluoroacetimidate group then gave donors **15** and **16**, respectively.

Scheme 7.1 Synthesis of 2,4,6-trideoxy-raregalactose donors **15** and **16**.

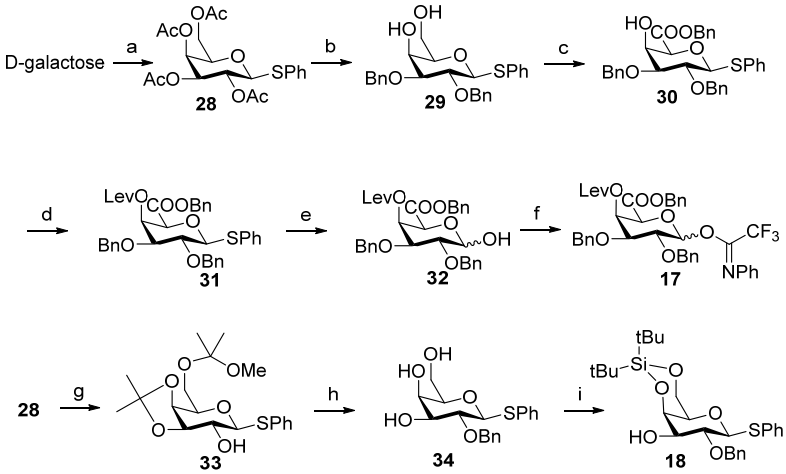


Reagents and conditions: (a) PhthNK, DMF, **22a**: 48% (over three steps); **22b**: 30% (over three steps). (b) i. ethylenediamine, butanol, reflux; ii. CbzCl, $NaHCO_3$, THF/H_2O, from **22b**: 69% (over two steps). (c) For **24**: LevOH, EDCI, DIPEA, DMAP, DCM, 91%; for **26**: BOMCl, DIPEA, TBAI, DCM, 79%. (d) NIS, TFA, DCM, **25**: 100%; **27**: 97%. (e) *N*-phenyltrifluoroacetimidoyl chloride, K_2CO_3, acetone, **15**: 79%, **16**: 88%.

The synthesis of the galacturonic acid donor **17** and galactose building block **18** is depicted in Scheme 7.2. Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside **28**, synthesized from D-galactose, was transformed into diol **29** in four steps (86% yield). Regio- and chemoselective oxidation of the C-6-OH was accomplished by a TEMPO/BAIB-mediated oxidation to provide, after benzylation of the resulting acid, galacturonic acid **30**. Donor **17** was accessed by levulinoylation (to give **31**), hydrolysis of the thioacetal (to give **32**), and installation of the *N*-phenyltrifluoroacetimidate group. To acquire silylidene galactoside **18**, **28** was first transformed into mono-alcohol **33**.[11] Benzylation of the free alcohol and acid mediated liberation of the other alcohols then provided **34** in 56% yield

(over four steps). Installation of the di-*tert*-butylsilylidene group proceeded uneventfully to give the last monosaccharide synthon **18**.

Scheme 7.2 Synthesis of galacturonic acid donor **17** and silylidene galactose **18**.

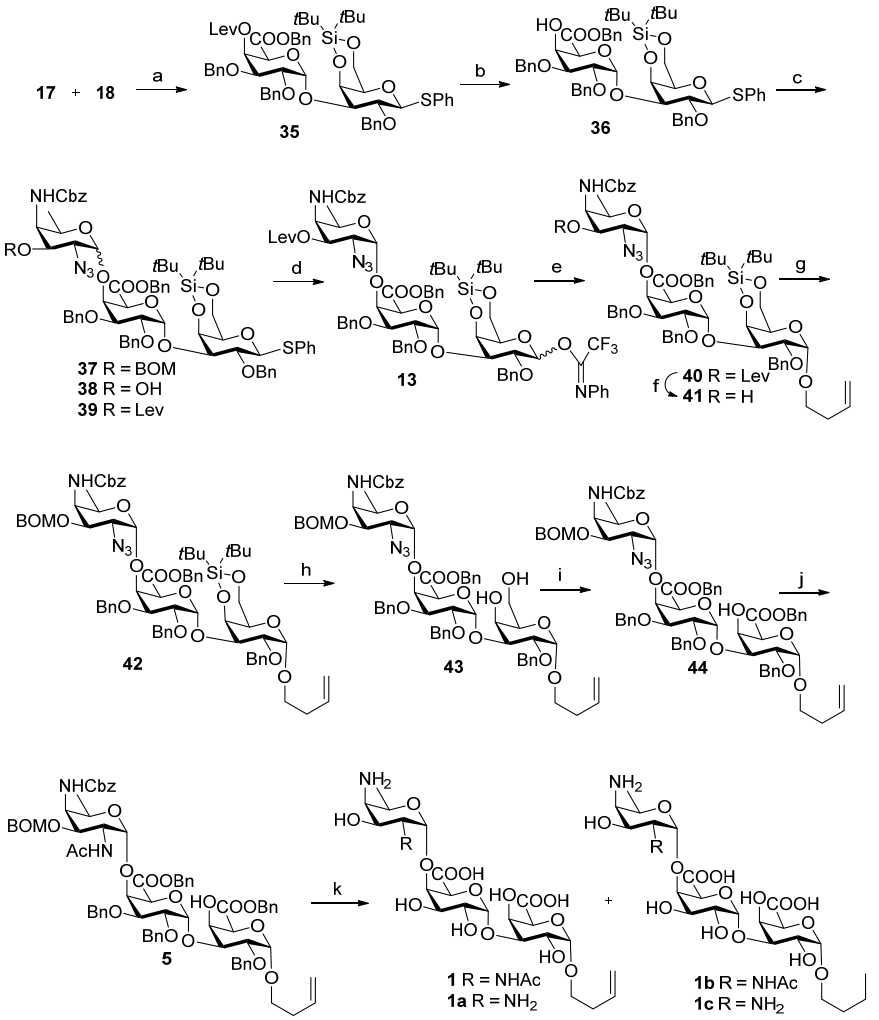


Reagents and conditions: (a) i. Ac_2O, catalytic amount H_2SO_4, 0 °C to rt; ii. Thiophenol, $BF_3 \bullet OEt_2$, DCM, 70% (over two steps). (b) i. NaOMe, MeOH, rt, overnight; ii. Benzaldehyde dimethyl acetal, camphorsulfonic acid, CH_3CN, rt, 24 h; iii. NaH, BnBr, DMF, overnight; iv. MeOH, $TsOH \bullet H_2O$, overnight, 86% (over four steps). (c) i. TEMPO, BAIB, DCM/*t*BuOH/H_2O, 4 °C, overnight; ii. BnBr, $CsCO_3$, DMF, 67% (over two steps). (d) LevOH, EDCI, DIPEA, DMAP, DCM, 97%. (e) NIS, TFA, DCM, 81%. (f) *N*-phenyltrifluoroacetimidoyl chloride, K_2CO_3, acetone, 93%. (g) i. NaOMe, MeOH, rt, overnight; ii. Dimethoxypropane, CSA, rt, 48 h. (h) i. NaH, BnBr, DMF, overnight; ii. 80% AcOH, 70 °C, 3 h, 56% (over two steps). (i) Di-*tert*-butylsilyl bis(trifluoromethanesulfonate), pyridine, 89%.

With all required monosaccharide building blocks in hand, Sp1 trisaccharide **1** was assembled to probe all of the chemical transformations required for the generation of the larger target oligosaccharides (Scheme 7.3). First, galacturonic acid **17** and silylidene galactose **18** were combined to assemble disaccharide **35**. After several optimization attemps with different catalysts, molecular sieves and work-up procedures, disaccharide **35** was produced in good yield and selectivity (77%, α:β = 13:1) by use of TfOH as catalyst,

5Å molecular sieves at low temperature and finally quenching with sat aq. $NaHCO_3$ (If the reaction was quenched with Et_3N or pyridine, some byproducts were formed for unclear reasons). From **35**, disaccharide acceptor **36** was accessed by delevulinoylation of the C-4-OH to set the stage for the assembly of the trisaccharide. Unfortunately, the glycosylation of disaccharide acceptor **36** with the TDDAG donor **16** provided the desired trimer (**37**) in low yield (25%) and with poor selectivity (α:β = 2.9:1). The trimer of which the BOM had been removed (**38**) was isolated as a major side product. Gratifyingly, when levulinoyl TDDAG donor **15** was coupled with disaccharide acceptor **36**, trisaccharide **39** was obtained in good yield and selectivity (85%, α:β = 13:1). From **39**, the key trisaccharide donor **13** was obtained by hydrolysis of the thioacetal and installation of *N*-phenyltrifluoroacetimidate group.

Scheme 7.3 Synthesis of trisaccharide **1**.



Reagents and conditions: (a) TfOH, DCM, -78 °C, 6 h, 77%, α:β = 13:1. (b) N_2H_4•H_2O, pyridine, AcOH, 0 °C to rt, 20 min, 89%. (C) donor **16**, TBSOTf, DCM, 0 °C, overnight, **37**: 25%, α:β = 2.9:1 and **38**: 29%, α only, total yield 54%; or donor **15**, TBSOTf, DCM, 0 °C, 4 h, **39**: 85%, α:β = 13:1. (d) i. NIS, TFA, DCM, 96%; ii. *N*-phenyltrifluoroacetimidoyl chloride, K_2CO_3, acetone, 89%. (e) Allylcarbinol, TBSOTf, DCM, 0 °C, 3 h, 82%, α only. (f) N_2H_4•H_2O, pyridine, AcOH, 0 °C to rt, 20 min, 98%. (g) BOMCl, DIPEA, TBAI, DCM, 89%. (h) HF/Py, pyridine, THF, 0 °C to rt, 20 min, 94%. (i) i. TEMPO, BAIB, DCM/*t*BuOH/H_2O, 4 °C, overnight; ii. $CsCO_3$, BnBr, DMF, 0 °C to rt, overnight, 84%. (j) AcSH, pyridine, rt, 20 h, 66%. (k) Birch reduction, see Table 7.1.

The glycosylation of the key trisaccharide donor **13** with allylcarbinol to install the spacer formed **40** in excellent yield and selectivity (82%, α only), indicating the apt glycosylating properties of the trisaccharide donor. The fully protected trimer was then transformed into diol **43** by exchange of the C-3"-*O*-Lev ester **40** for a BOM ether and removal of the silylidene ketal. Regioselective TEMPO/BAIB oxidation of C-6 proceeded uneventfully to provide the carboxylic acid, which was benzylated to give trimer **44**. Global deprotection of this trimer was accomplished as follows. First, the azide was transformed into the corresponding acetamido unit using thio acetic acid to give **5**.[12] Next the benzyl esters were saponified to provide the dicarboxylate for the final birch-type reduction,[6,13] by which the remainig benzyl, Cbz and BOM protecting groups should be removed. The successful removal of all these masking groups however proved challenging and the first attempt (See Table 7.1, Entry 1), using sodium in ammonia and THF, delivered a mixture of products **1a**, in which the *N*-acetyl had been removed and **1c** of which the butene double bond had been reduced. The addition of *tert*-butanol to the reaction mixture successfully prevented the deacetylation (Table 7.1, Entry 2) and delivered the desired trimer **1** and its butanol counterpart **1b** in a 7:1 ratio, in 75% combined yield. To prevent reduction of the C-C double bond, allylcarbinol was used as a scavenger. This improved the reaction further to give the desired trisaccharide **1** and only a minor amount of the saturated side product **1b** in excellent yield (95%, Entry 3). The addition of more allylcarbinol did not improve the reaction (Entry 4), nor did the use of lithium instead of sodium (Entry 5).

Table 7. 1 The conditions for Birch reduction of trisaccharide.

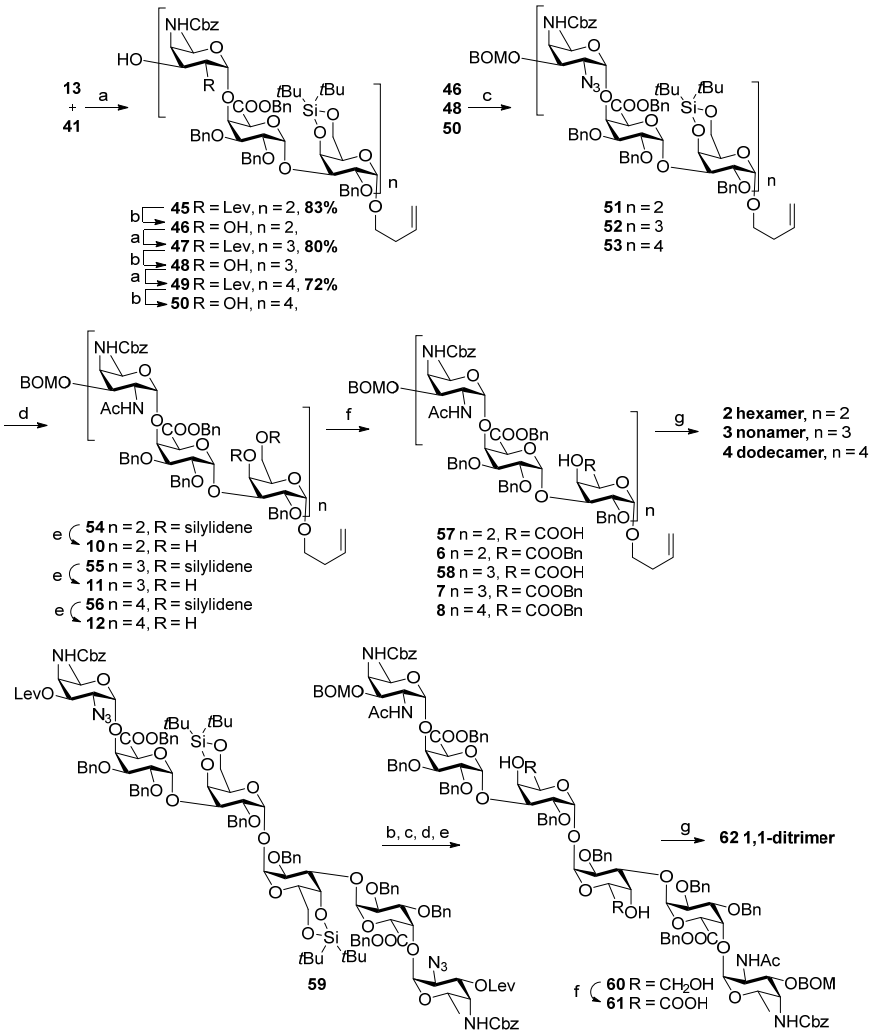
Entry	SM	*t*BuOH	Na/Li	Additive	Time	Ratio[a]	Ratio[b]	Product (Yield)
1	**5**	No	Na	No	25min	6:1	0:1	**1a**,**1c** (55%)
2	**5**	0.8 ml	Na	No	10min	7:1	1:0	**1**,**1b** (74%)
3	**5**	0.8 ml	Na	(50 ul)	25min	14:1	1:0	**1**,**1b** (95%)
4	**5**	0.8 ml	Na	(500 ul)	25min	10:1	1:2	**1**,**1a**,**1b**,**1c** (83%)
5	**5**	0.8 ml	Li	(50 ul)	25min	5.7:1	5:1	**1**,**1a**,**1b**,**1c** (85%)

a. The ratio of (**1**+**1a**, with C=C):(**1b**+**1c**, without C=C); b. (**1**+**1b**, with Ac):(**1a**+**1c**, without Ac).

With the succesfull synthesis of trisaccharide **1** and the chemistry established to accomplish all the required transformations, the assembly of the larger oligomers **2**-**4** was undertaken as depicted in Scheme 7.4. First, trisaccharide acceptor **41** was condensed with trimer donor **13** to give the required hexasaccharide **45** with excellent yield and stereoselectivity (83%, α only). The hexamer **45** was delevulinoylated (to give **46**) and coupled with **13**, to provide the nonasaccharide **47** in equally good yield and stereoselectivity (80%, α only). Finally, the nonamer **47** was elongated in a subsequent delevulinoylation-glycosylation sequence to deliver the desired dodecasaccharide **49** in 72% yield. Also, in this glycosylation the desired α-product was formed as the sole anomer, showing the effectiveness of the silylidene donor and glycosylation strategy devised. The only side product that was formed during the latter glycosylations was the 1,1-coupled hexasaccharide **59**. This byproduct was used to optimize reaction conditions for the steps to come, as described below and the fully deprotected 1,1'-linked hexasaccharide will serve as a control substance in future biological evaluation studies. Hexamer **45**, nonamer **47** and dodecamer **49**, were next transformed into the oxidation precursors **10**, **11** and **12** by removal of the levulinoyl ester, installation of the BOM ether (to give **51**, **52** and **53**, respectively), and the conversion of the azides to their corresponding acetamido units. For

the larger oligosaccharides, the AcSH-mediated method did not proceed well and therefore a Staudinger reaction was used to reduce the azides and liberate the amines.[14] Acetylation then gave **54**, **55** and **56**, respectively, which were desilylated to provide **10**, **11** and **12**. Following the same reaction sequence, 1,1'-linked hexasaccharide **60** was obtained from **59.**

Scheme 7.4 Synthesis of hexasaccharide **10**, nonasaccharide **11**, **57** and dodecasaccharide **13**.



Reagents and condations: (a) TBSOTf, DCM, 0 °C, **45**: 83%, α only; **47**: 80%, α only; **49**: 72%, α only. (b) $N_2H_4 \bullet H_2O$, pyridine, AcOH, 0 °C to rt, 20 min, **46**: 97%; **48**: 89%; **50**: 91%. (c) BOMCl, DIPEA, TBAI, DCM, **51**: 81%; **52**: 89%; **53**: 84%. (d) i. PPh_3, pyridine, H_2O, THF, reflux, 7 h, ; ii. Ac_2O, pyridine, rt, overnight, **54**: 93%; **55**: 88%; **56**: 99%. (e) HF/Py, pyridine, THF, 0 °C to rt, 20 min, **10**: 91%; **11**: 88%; **12**: 91%; **60**: 93%. (f) oxidation see table 6. (g) i. 1 M NaOH, THF, MeOH, 0 °C to rt, 2 d; ii. Birch reduction, **62**: 31%; **2**: 39%; **3**: 55%; **4**: 47% (yield for two steps).

Although the TEMPO/BAIB oxidation was effective in the synthesis of trisaccharide **1**, it failed in the assembly of the larger oligosaccharides (Table 7.2, Entry 1), underscoring the difficulty in affecting multiple simultaneous oxidation reactions. Chapter 6 described a new two-step one-pot TEMPO/BAIB-Pinnick oxidation protocol for the selective oxidation of primary alcohols to the corresponding carboxylic acids. It was shown that this protocol not only works well on glucose-, galactose-, gulose- and mannose-based monosaccharide building blocks, but also on more complex oligosaccharides, where the 'classic' TEMPO/BAIB conditions failed. Thus, 1,1'-linked hexasaccharide **60** was used as a model substrate to explore this oxidation strategy. Following the two-step oxidation sequence,[8c] the required di-carboxylic acid **61** was obtained in 85% yield (Table 7.2, Entry 2). Using this method, the hexamer **10** was successfully transformed into carboxylic acid **57** in 63% yield. Benzylation of the two carboxylates in **57** then provided fully protected hexasaccharide **6** in 67% yield (Entry 3). Unfortunately, the oxidation of the three alcohols in nonamer **11** could not be accomplished using the TEMPO/BAIB-Pinnick reaction sequence, and a complex product mixture was obtained (Entry 4).

It has previously been shown that efficiency of TEMPO mediated oxidations can be significantly improved under basic conditions.[15] Presumably, this accelerates the formation of the hydrate from the intermediately formed aldehyde. To test whether basic conditions could improve the challenging oxidations reactions, required here, model hexasaccharide **60** was subjected to TEMPO/BAIB treatment in the presence of $NaHCO_3$. Under these conditions the dicarboxylic acid **61** was obtained in 73% yield (Entry 5). Satisfyingly, also hexamer **10** and nonasaccharide **11** could be transformed into the desired di- and tricarboxylic acids, respectively. After benzylation of the tricarboxylic acid,

nonasaccharide **7** was obtained in 51% yield (over two steps, Entry 7). Application of this protocol to the most complex substrate, oligosaccharide dodecamer **12**, delivered, after benzylation using benzylbromide and K_2CO_3, dodecamer **8** in only 19% yield over the two steps (Entry 8). To further improve on the protocol, milder and more efficient benzylation conditions, using phenyldiazomethane,[8b,16] were used. Using these conditions, dodecasaccharide **8** was obtained in 49% over the two steps (Entry 9). To complete the syntheses of hexamer **2**, nonamer **3**, dodecamer **4** and 1,1-linked hexasaccharide **61** the oligosaccharides were deprotected by saponification of the benzyl esters and final Birch reaction to provide the target oligomers in 39% (for **2**), 55% (for **3**), 47% (for **4**) and 31% (for **61**) yield, respectively.

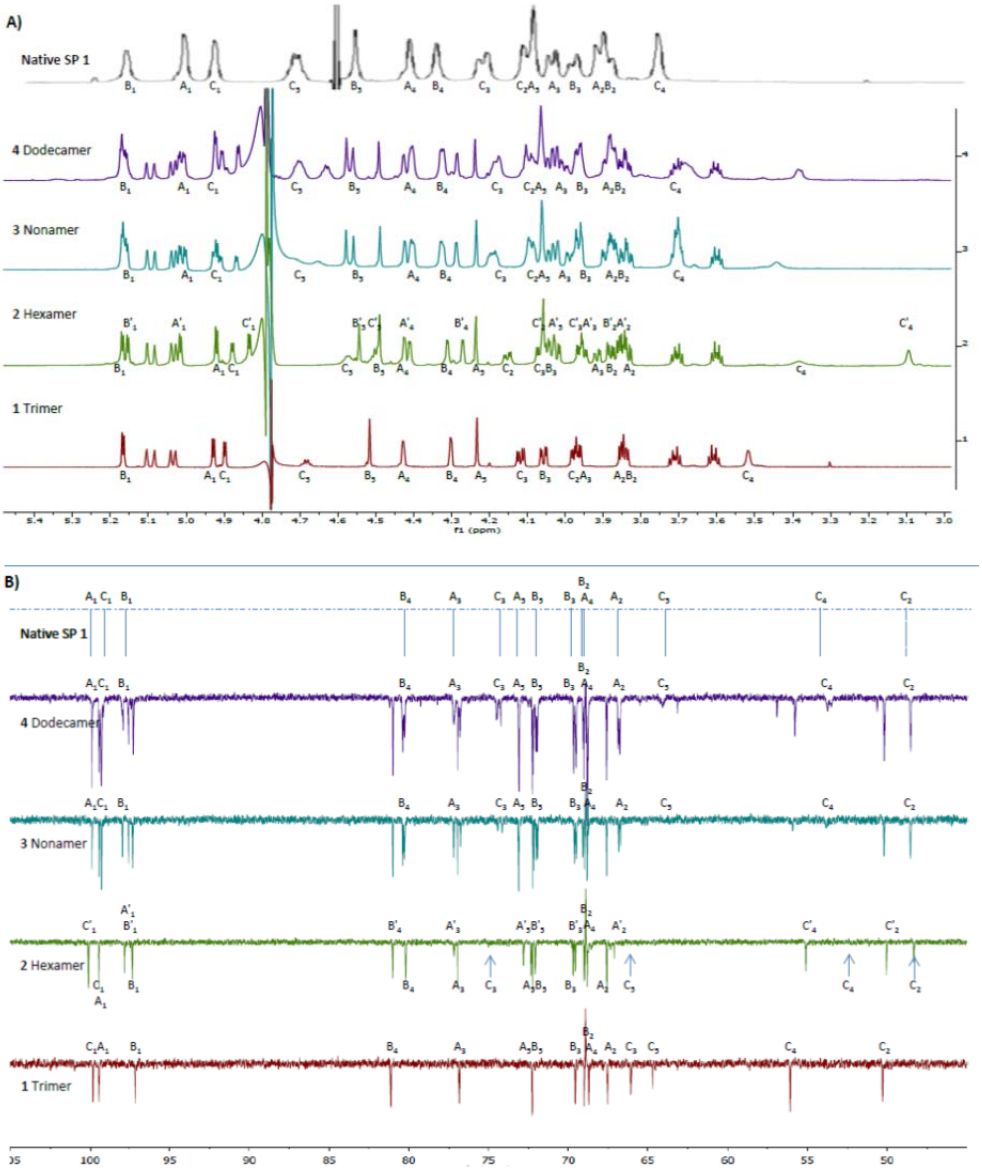
Table 7.2 The oxidation benzylation of hexasaccharide, nonasaccharide and dodecasaccharide.

entry	SM	reagents	solvent	Temp	Time	Product/yield for oxidation	Product/yield of benzylation
1	**10**	TEMPO/BAIB (0.2 eq /2,5 eq)	DCM/*t*BuOH/H_2O	4 °C	12h	failed	
2	**60**	TEMPO/BAIB-Pinnick oxidation	THF/DCM	rt	2d	**61**/85%	
3	**10**	TEMPO/BAIB-Pinnick oxidation	THF/DCM	rt	2,5d	**57**/63%	**6**/67%
4	**11**	TEMPO/BAIB-Pinnick oxidation	THF/DCM	rt	2d	failed	
5	**60**	TEMPO/BAIB (0.4 eq /2.5 eq), $NaHCO_3$	EA/*t*BuOH/H_2O	4 °C	4d	**61**/73%	
6	**10**	TEMPO/BAIB (0.8 eq /4.0 eq), $NaHCO_3$	EA/*t*BuOH/H_2O	4 °C	3d	**57**/67%	**6**/67%
7	**11**	TEMPO/BAIB (0.8 eq /5.0 eq), $NaHCO_3$	EA/*t*BuOH/H_2O	4 °C	4d	**58**/89%	**7**/57%
8	**12**	TEMPO/BAIB (0.6 eq /5.0 eq), $NaHCO_3$	EA/*t*BuOH/H_2O	4 °C	5d		**8**/19%
9	**12**	TEMPO/BAIB (0.6 eq /5.0 eq), $NaHCO_3$	EA/*t*BuOH/H_2O	4 °C	5d		**8**/49%

7.2.3 Structural analysis of ZPS-Sp1 oligosaccharides

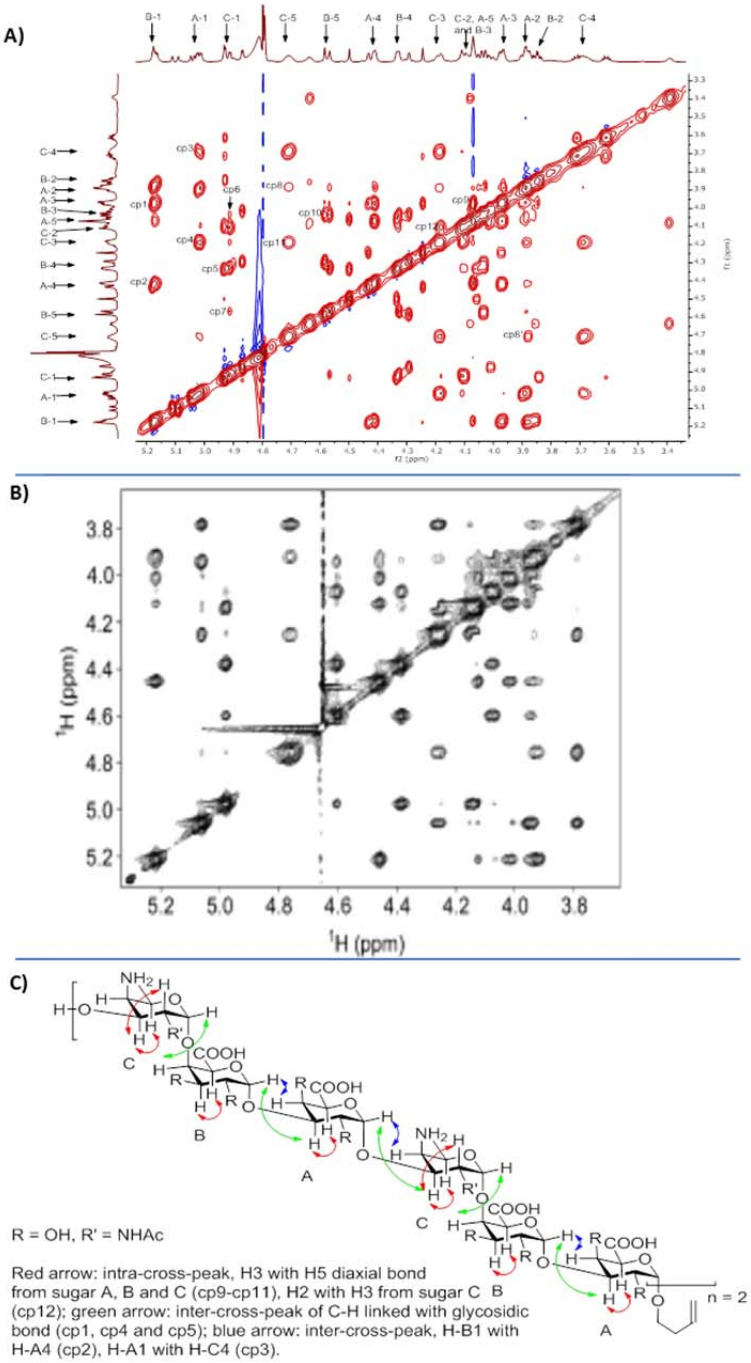
It has been proposed that the secondary structure of ZPSs is of crucial importance to their activity. Both the PS A1 and Sp1 polysaccharides can take up helical shapes and it has been suggested that these structures position the negative and positive charges, present in the polysaccharide fragments, properly in space to effectively interact with MHC-II molecules.[16] To compare the structures of the here synthesized oligosaccharides to the polysaccharide, obtained from natural sources, Figure 7.2A and 7.2B provide the ^{1}H and ^{13}C spectra of the generated compounds as well as the ^{1}H NMR spectrum of the native Sp1.[17b] As the ^{13}C NMR spectrum of the Sp1 polysaccharide is not available, the ^{13}C NMR resonances that have been reported in a previous study, obtained from HMQC experiments,[17b] are used for comparison. When the ^{1}H NMR spectra of trimer **1**, hexamer **2**, nonamer **3**, dodecamer **4** and native Sp1 are compared (Figure 7.2.A), it becomes clear that the ^{1}H resonances of the internal sugar residues of the nonamer **3** and dodecamer **4** correspond well with the resonances of the native Sp1 polysaccharide. The resonances of the terminal residues and the trisaccharide **1** differ siginificantly. In the spectra of hexamer **2** and nonamer **3**, the resonances corresponding to H-4 and H-5 of the 2,4,6-trideoxy-2-*N*-acetamido-4-amino-α-D-galactopyranose appear as broad signals. This may either indicate that the residues are relatively flexible and can adopt several low energy conformations, or the presence of different *N*-acetyl rotamers. When the ^{13}C NMR spectra of trimer **1**, hexamer **2**, nonamer **3**, dodecamer **4** and native Sp1 are compared (Figure 7.2B), a similar picture emerges: the resonances of nonamer **3** and dodecamer **4** are well in agreement with those reported for the native Sp1, except for the peaks from terminal residues. The signals for the C4 and C5 carbons of the TDDAG residues show significant broadening.

Figure 7.2. A) ^{1}H NMR spectra of Sp1 oligosaccharides (**1, 2, 3** and **4**) and native Sp1 polysaccharide [17b] **B)** ^{13}C NMR spectra of oligosaccharides (**1, 2, 3** and **4**) and the ^{13}C NMR-resonances of the native Sp1 polysaccharide [17b,17c]



Because 2-D NOESY spectra can provide information on the 3D-structure of molecules, NOESY spectra of trimer **1**, hexamer **2**, nonamer **3**, dodecamer **4** were recorded and compared to the NOESY spectrum of the native Sp1 polysaccharide. In Figure 7.3A and 7.3B the NOESY spectrum of dodecasaccharide **4** and the native Sp1 are depicted, respectively. Figure 7.3C shows the structure of the dodecasaccharide with selected NOESY interactions. Characteristic intraresidue (within the same monosaccharide) and interresidue (between adjacent residues) NOESY cross-peaks are apparent. For example a strong intraresidual cross-peak is observed for the axial C-3 and C-5 protons of the galacturonic acid (sugar A and B, see Figure 7.3A, cross-peaks cp9 and cp10). Within the TDDAG residue (sugar C) strong cross-peaks were not only observed for the protons at C-3 and C-5 (Figure 7.3A, cp11), but also the protons at the C-2 and C-3 (Figure 7.3A, cp12). The following strong interresidue cross-peaks were observed: H_{C1} with H_{B4}, (cp1), H_{B1} with H_{A3} (cp 4), H_{A1} with H_{C3} (cp5), H_{B1} with H_{A4} (cp2), H_{A1} with H_{C4} (cp3). The NOESY spectrum of dodecamer **4** also nicely matches the simulated NOESY spectrum of the Sp1 polysaccharide, that was used to establish the secondary helical structure of the polysaccharide. Altogether these preliminary structural studies indicate that the longer structures (the nona- and dodecasaccahride **3** and **4**) resemble the native polysaccharide. Further studies have to establish whether the nona- and dodecasaccharides can indeed take up a helical structure to properly mimic the native polysaccharide.

Figure 7.3 NOE spectrum of dodecamer **4** (with selected NOESY interactions) and native SP1[17b]



7.3 Conclusion

This Chapter has described the first synthesis of long zwitterionic oligosaccharides corresponding to the *Streptococcus pneumonia* type 1 polysaccharide. The successful syntheses were built on the use of trisaccharide building blocks, featuring a silylidene protected galactose donor-part to ensure complete stereoselectivity in the construction of the *cis*-linkages between the repeating units. The uronic acid moiety of the middle galacturonic acid residue was installed in the trisaccharide building blocks, to avoid the necessity of many simultaneous oxidation events at the end of the assembly. Indeed, the simultaneous oxidation of three or four primary alcohols at the nona- and dodecasaccharide stage, respectively, already proved to be extremely challenging. A new TEMPO/BAIB oxidation protocol in basic milieu was set up to enable the generation of the oligo-acids. A mild and chemoselective benzylation reaction, entailing the use of phenyldiazomethane, allowed for the effective generation of four benzyl esters in the dodecasaccharide. It is envisaged that the here-developed oxidation-benzylation protocol can be applied in the assembly of many complex uronic acid containing oligosaccharides. Initial structural analyses indicate that the longer oligosaccharides may start to resemble the native polysaccharide. The availability of the large ZPS structures opens up the way to study the interaction with MHC-II molecules at the molecular level. This will finally show how a MHC molecule presents a sugar to the outside world to set T-cell signaling in motion.

7.4 Experimental section

General experimental procedures

All reagents were of commercial grade and used as received. All moisture sensitive reactions were performed under an argon atmosphere. DCM used in the glycosylation was distilled over P_2O_5 and stored on activated 5Å molecular sieves before being used. Reactions were monitored by TLC analysis with detection by UV (254 nm) and where applicable by spraying with 20% sulfuric acid in EtOH or with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (25 g/L) and $(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$ (10 g/L) in 10% sulfuric acid (aq.) followed by charring at ~150 °C. Flash column chromatography was performed on silica gel (40-63µm). ^1H and ^{13}C spectra were recorded on a Bruker AV 400, AV 500, AV 600 or AV 850 in $CDCl_3$, D_2O, CD_3CN, MeOD. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard (^1H NMR in $CDCl_3$) or the residual signal of the deuterated solvent. Coupling constants (*J*) are given in Hz. All ^{13}C spectra are proton decoupled. NMR peak assignments were made using COSY and HSQC experiments. Where applicable NOESY, HMBC and HMBCipvGATED experiments were used to further elucidate the structure. The anomeric product ratios were analysed through integration of proton NMR signals.

General procedure for hydrolysis of thioglycosidic bond

NIS (5.0 mmol) and TFA (462 ul, 6.0 mmol) were added to a solution of thioglycoside (5.0 mmol) in CH_2Cl_2 (40 ml) at 0 °C. After analysis by TLC showed complete consumption of the starting material, the reaction was quenched with Et_3N. Saturated $Na_2S_2O_3$ (aq) was added to the reaction mixture, which was then stirred for 30 min. The aqueous layer was extracted twice with CH_2Cl_2 and concentrated *in vacuo*. Purification by column chromatography yielded hydrolysized product as a colourless oil in good yield.

General procedure for the synthesis of *N*-phenyl-trifluoroacetimidate donors

The starting hemiacetal (8 mmol) was dissolved in acetone (75 ml) and the solution was cooled to 0 °C. *N*-phenyl-trifluoroacetimidoyl chloride (12 mmol) and cesium carbonate (8 mmol) were added and the resulting suspension was stirred overnight at room temperature. Then Et_3N was added to the reaction mixture, after which it was filtered and the filtrate was concentrated *in vacuo*. Purification by column chromatography (silica gel, pentane/EtOAc/Et_3N, 20/1/trace, v/v/trace) yielded *N*-phenyl-trifluoroacetimidate donor in good yield.

General procedure for delevulinoylation

The starting material was dissolved in a mixture of acetic acid and pyridine (1/4, v/v), the mixture was cooled to 0°C and hydrazine monohydrate (5.0 eq) was added to the solution. The reaction was allowed to stir for 20 min at room temperature. Then the mixture was diluted with EtOAc, washed with 1 N aq. HCl, sat. aq. $NaHCO_3$ and sat. aq. NaCl. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography yielded the product.

General procedure for introduction of the BOM group

The alcohol (0.046 mmol) was dissolved in dry DCM (1 ml), DIPEA (300 ul, 1.72 mmol), BOMCl (267 ul, 1.03 mmol) and TBAI (6.7 mg) was added to the reaction mixture at 0 °C subsequentely. The reaction mixture was allowed to stir at room temperature for 1-3 d and monitored by TLC analysis. The reaction mixture was diluted with EtOAc and washed with 1 M HCl, sat. aq. $NaHCO_3$ and brine and then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (pentane/DCM/acetone, 10:1:1→3:1:1). product was obtained in good yield.

General procedure for deprotection of the di-*tert*-butyl silylidene ketal

A solution of HF/Pyridine solution (0.5 mmol, 5.0 eq) was added to a solution of starting material in a mixture of THF and pyridine (1/1 v/v, 2 ml) at 0 °C. The reaction was allowed to stir overnight at room temperature. Sat. aq. $NaHCO_3$ was added to neutralize the mixture, which was then diluted with EtOAc and washed with sat. aq. NaCl. The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatograpy yielded the deprotected product.

General procedure of glycosylation reactions toward long oligosaccharides (hexasaccharide, nonasaccharide and dodecasaccharide)

Trisaccharide Imidate donor **13** (2.0 - 3.0 eq) and acceptor **41**, **46** or **48** (1.0 eq) were co-evaporated with toluene (three times). The residue was dissolved in dry DCM (0.05 M acceptor in DCM). The solution was cooled to 0 °C and followed by adding TBSOTf (0.1-0.2 eq) and the reaction was allowed to stir for 3-6 h at 0 °C. The reaction was quenched with Et_3N (0.4 eq), diluted with DCM, washed with sat. aq. NaCl and the organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography yielded the products in 72-83% yield.

General oxidation procedure A: TEMPO/BAIB oxidation and benzyl ester formation

The starting material was dissolved in DCM/*tert*-BuOH/H_2O (4/4/1,v/v/v). The mixture was cooled to 0°C and TEMPO (0.2 eq) and BAIB (2.5 eq) were added. After stirring the mixture overnight at 4 °C, $Na_2S_2O_3$ was added and the heterogeneous mixture was stirred for 30 minutes, diluted with EtOAc and washed with sat. aq. NaCl. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was dissolved in DMF, followed by the addition of Cs_2CO_3 (1.0 eq) and BnBr (> 2.0 eq) at 0 °C. The mixture was allowed to stir overnight at room temperature and was then diluted with EtOAc and washed with sat. aq. NaCl. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatograpy (silica gel, pentane/EtOAc, v/v) yielded the benzyl ester product.

General oxidation procedure B: TEMPO/BAIB-Pinnick oxidation

To a stirred solution of the carbohydrate (0.02 mmol, 1.0 eq.) in THF/CH_2Cl_2 (2:1 v/v, 0.6 mL) was added, at 0 °C, TEMPO (2.5 mg, 0.016 mmol, 0.8 eq/per one primary alcohol) and $PhI(OAc)_2$ (13 mg, 0.04 mmol, 2.0 eq/per one

primary alcohol) and the reaction mixture was allowed to warm to room temperature. After 2 d, *tert*-butanol (0.5 mL) and *iso*-amylene (0.05 mL) were added and the reaction mixture was cooled to 0 °C. A solution of $NaClO_2$ (3.6 mg, 0.04 mmol, 2.0 eq/per one primary alcohol.) and NaH_2PO_4 (4.8 mg, 0.04 mmol, 2.0 eq/per one primary alcohol.) in water (0.1 mL) was slowly added and the reaction mixture was allowed to stir for 1 hour at 0 °C to room temperature. The reaction was quenched by addition of sat. aq. $Na_2S_2O_3$, and the mixture diluted with EtOAc, and NaH_2PO_4 (sat. aq., 0.5 mL) and brine (1 mL) were subsequently added. The layers were separated, and the aqueous phase was extracted with EtOAc. The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (generally, CH_2Cl_2/MeOH/AcOH, 200:1:0 → 200:10:1) furnished the corresponding uronic acid or used for next step benzylation without purification.

General oxidation procedure C: TEMPO/BAIB with $NaHCO_3$ oxidation

To a stirred solution of the carbohydrate (0.02 mmol, 1.0 eq.) in EtOAc/*t*BuOH/H_2O (1:1:1, v/ v/v, 0.6 mL), TEMPO (2.5 mg, 0.016 mmol, 0.8 eq/per one primary alcohol) and $NaHCO_3$ (8.4 mg, 0.1 mmol, 5 eq/per one primary alcohol) was added at 0 °C, after 10 min, $PhI(OAc)_2$ (26 mg, 0.08 mmol, 4.0 eq/per one primary alcohol) was added and the reaction mixture was allowed to stir 2-5 d at 4 °C. The reaction was quenched by addition of sat. aq. $Na_2S_2O_3$, and the mixture diluted with EtOAc, and NaH_2PO_4 (sat. aq., 0.5 mL) and brine (1 mL) were subsequently added. The layers were separated, and the aqueous phase was extracted with EtOAc. The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Column chromatography (generally, CH_2Cl_2/MeOH/AcOH, 200:1:0 → 200:10:1) furnished the corresponding uronic acid or used for next step benzylation without purification.

General procedure for transferred azide into acetylamino reactions for long oligosaccharides (hexasaccharide, nonasaccharide and dodecasaccharide)

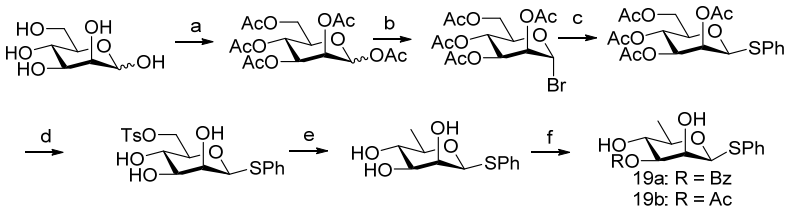
The oligosaccharide containing azide **51**, **52**, **53** or **1,1-di-trimer-di-azide** (1.0 eq) was dissolved in THF (0.005 M in THF). Pyridine (15 eq/one azide), H_2O (15 eq/one azide) and Ph_3P (4 eq/one azide, partially, three times and 1 h in between) were added to reaction mixture and the reaction was allowed to stir for 7 h at 70 °C. The reaction mixture was concentrated *in vacuo*. The residue was dissolved in pyridine (1 ml), Ac_2O (0.5 ml) was added at 0 °C and stirred for overnight. The reaction mixture was diluted with EtOAc and washed with sat. aq., $NaHCO_3$ and brine then dried over Na_2SO_4, filtered and concentrated *in vacuo*. Column chromatography (generally, CH_2Cl_2/MeOH, 200:1 → 60:1) and then run size exclusion (HW-20) to obtain pure product in good yield (88-99%).

General procedure for fully deprotection (saponification and Birch reduction)

The compound **5**, **6**, **7**, **8** or **1,1-ditrimer-di-COOH** (7-20 mg) was dissolved in THF (2 ml) and MeOH (0.75 ml), 1 M NaOH (0.8 ml) was added to reaction mixture at 0 °C. The mixture was allowed to stir 48 h at room temperature, and then neutralized by H_2SO_4 (1 M). Diluted with EtOAc and the water layer was extracted with EtOAc (2x20 ml). The combined organic layers was washed with brine then dried over Na_2SO_4 and concentrated in vacuo. The

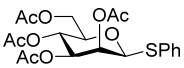
residue was co-evaporated with toluene (three times) for the next step. Ammonia (10 ml) was condensed at -70 °C, the residue was dissolved in THF (2 ml) and tert-butanol (0.8 ml) and slowly added to reaction flask containing ammonia. Additive (Allylcarbinol or CH_2=$CHCH_2CH_2O$-PEG_4-OCH_2CH_2CH=CH_2, 50 ul) was added to the reaction mixture. Small pieces sodium added to the reaction mixture one by one to keep deep blue for 15 min. Then ammonia acetate (100 mg) was added to reaction mixture. The solution was allowed to come to room temperature and stirred until all of ammonia was evaporated. Then the solution was concentrated in vacuo and purification 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. The products were transformed into the sodium salts by passing an aqueous solution of the compounds over a short Dowex Na^+ column, after which the compounds were lyophilized and obtained **1**, **2**, **3**, **4** or **1,1-di-trimer**.

Scheme 6. Synthesis of 19a and 19b



Reagents and condations: (a) Ac_2O, catalytic amount H_2SO_4, 0 °C to rt. (b) HBr/AcOH, AcOH. (C) PhSH, NaH, three steps yield: 79%. (d) i. NaOMe, MeOH; ii. TsCl, pyridine. (e) $LiAlH_4$, THF, three steps yield: 53%. (f) BzCl or AcCl, dichloro-dimethyl selenium, DIPEA, DCM, 19a yield:81%, 19b yield: 90%.

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-mannopyranoside, D-mannose (54 g, 0.3 mol) was added to Ac_2O (170.4 ml, 1.8 mol), then H_2SO_4 (two drops, do not add too much because the reaction is going too fast) was added to the reaction mixture at 0 °C. The reaction mixture was allowed to stir for 2 h at 0 °C and the reaction mixture was clear solution. The reaction mixture was allowed to stir at room temperature and monitored by TLC analysis. Then do next step without any work up: HBr/AcOH (33%, w/w, 150 ml) was slowly added to the previous reaction mixture at 0 °C, and then stir at room temperature for 3 h. The reaction mixture was poured into ice-water. The crude bromide was extracted using EtOAc (3 x 400 ml) and the combined organic fractions were washed with sat. aq. $NaHCO_3$, dried over Na_2SO_4 and concentrated in vacuo. A solution of glycosidic bromide and PhSH (30.8 ml, 0.3 mol) in DMF (600 ml) was cooled to 0 °C and NaH (60% dispersion in mineral oil, 12 g, 0.3 mol) was added. The mixture was stirred until full consumption of the bromide and subsequently quenched by the addition of aq. HCl (1 M). The product was extracted with EtOAc and the combined organic layers was washed with brine then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (96 g, three steps yield: 73%). The analytical data were in full accord with



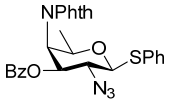
reported previously.[10]

Phenyl 6-deoxy-1-thio-β-D-mannopyranoside: Phenyl 2,3,4,6-tetra-acetyl-1-thio-β-D-mannopyranoside (69.5 g, 157.8 mmol) was dissolved in MeOH (600 ml), NaOMe in MeOH solution (1 ml) was added to reaction mixture at 0 °C and then the reaction was allowed to stir at room temperature for 4 h. After adding AcOH (2 ml) and toluene (100 ml), the reaction mixture was concentrated in vacuo. The residue was dissolved in pyridine (350 ml), and TsCl (39.1 g, 205.4 mmol) in pyridine (250 ml) was slowly added to reaction mixture at 0 °C. Then the reaction was allowed to stir for overnight at room temperature. The reaction was quenched with MeOH (3 ml), and then concentrated in vacuo. The residue was dissolved in EtOAc (400 ml), washed with H_2O (100 ml) and brine, the water layer was extracted again with EtOAc (200 ml). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was dissolved in dry THF (800 ml) and cooled down to 0 °C. $LiAlH_4$ in THF (2.3 M solution 206 ml, should be very careful for this step) was slowly added to reaction mixture at 0 °C (2-4 h) and then stirred at room temperature for 1 h, then reflux for 6 h. The reaction was quenched by slowly adding EtOAc at 0 °C. And then more EtOAc and 3 M HCl solution was added. The water layer was extracted again with EtOAc (2x500 ml). The combined organic layers were washed with brine then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (DCM/acetone, 50:1→20:1→2:1, 96 g, three steps yield: 53%). The analytical data were in full accord with reported previously.[10]

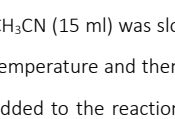
Phenyl 3-*O*-Bz-6-deoxy-1-thio-β-D-mannopyranoside (19a): Phenyl 6-deoxy-1-thio-β-D-mannopyranoside (3.5 g, 13.65 mmol) was dissolved in dry THF (70 ml), DIPEA (4.73 ml) and Me_2SnCl_2 (148 mg) was added to the reaction mixture at 0 °C and stirred for 20 min. Then BzCl (1.75 ml) was added to the reaction mixture. The reaction was allowed to stir for 1 h at room temperature. The reaction mixture was diluted with EtOAc and washed with H_2O, sat. aq. $NaHCO_3$ and brine and then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (DCM/acetone, 10:1→4:1, product 4 g, yield: 81%). The analytical data were in full accord with reported previously. [10]

Phenyl 3-*O*-Ac-6-deoxy-1-thio-β-D-mannopyranoside (19b): Phenyl 6-deoxy-1-thio-β-D-mannopyranoside (3.95 g, 15.41 mmol) was dissolved in dry THF (70 ml), DIPEA (5.5 ml) and Me_2SnCl_2 (175 mg) was added to the reaction mixture at 0 °C and stirred for 20 min. Then AcCl (1.75 ml) was added to the reaction mixture. The reaction was allowed to stir for 2 h at room temperature. The reaction mixture was diluted with EtOAc and washed with H_2O, sat. aq. $NaHCO_3$ and brine and then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (DCM/acetone, 10:1→4:1, product 4.12 g, yield: 90%). The analytical data were in full accord with reported previously.[10]

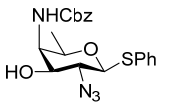
Phenyl 2-N_3-3-*O*-Bz-4-*N*-Phth-6-deoxy-1-thio-β-D-galactopyranoside (22a): The compound **19a** (2.2 g, 6.11 mmol) was dissolved in DCM (60 ml) with pyridine (5 ml), Tf_2O (5 ml) was added to the reaction mixture at -10 °C, and slowly warm up to 10 °C in 2 h. The reaction mixture was diluted with DCM and washed with water and sat. aq. $NaHCO_3$ and then dried over Na_2SO_4 and concentrated in vacuo. The residue was dissolved in dry CH_3CN (105 ml), $TBAN_3$ (1.65 g, 5.81 mmol) solution in CH_3CN (15 ml) was slowly added to the reaction mixture at -30 °C. The reaction was allowed to stir for 2 d at same temperature and then concentrated in vacuo. The residue was dissolved in DMF (60 ml), and then PhthK (2 g) was added to the reaction mixture and stirred for overnight at room temperature. The reaction mixture was diluted with EtOAc and washed with water and brine and then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (Pentane/EtOAc, 8:1, product 1.51 g, yield: 48%). The analytical data were in full accord with reported previously.[10]



Phenyl 2-N_3-3-*O*-Ac-4-*N*-Phth-6-deoxy-1-thio-β-D-galactopyranoside (22b): The compound **19b** (1.43 g, 4.8 mmol) was dissolved in DCM (42 ml) with pyridine (5.16 ml), Tf_2O (5.04 ml) was added to the reaction mixture at -10 °C, and slowly warm up to 10 °C in 2 h. The reaction mixture was diluted with DCM and washed with water and sat. aq. $NaHCO_3$ and then dried over Na_2SO_4 and concentrated in vacuo. The residue was dissolved in dry CH_3CN (20 ml), $TBAN_3$ (1.56 g, 5.48 mmol) solution in CH_3CN (4 ml) was slowly added to the reaction mixture at -20 °C. The reaction was allowed to stir for overnight at same temperature and then concentrated in vacuo. The residue was dissolved in DMF (24 ml), and then PhthK (1.8 g) was added to the reaction mixture and stirred for overnight at room temperature. The reaction mixture was diluted with EtOAc and washed with water and brine and then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (Pentane/EtOAc, 8:1, product 896 mg, yield: 41%). The analytical data were in full accord with reported previously. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.85 (m, 2H), 7.79 (dd, *J* = 5.6, 3.0 Hz, 2H), 7.68 – 7.51 (m, 2H), 7.41 – 7.28 (m, 3H), 5.19 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H, H-3), 4.87 (dd, *J* = 6.8, 2.8 Hz, 1H, H-4), 4.73 – 4.57 (m, 2H, H-1, H-2), 3.95 (qd, *J* = 6.4, 2.8 Hz, 1H, H-5), 1.94 (s, 3H), 1.17 (d, *J* = 6.4 Hz, 3H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169. 5, 133.4, 132.3, 129.0, 127.9, 123.7, 88.57 (C-1), 73.2 (C-5), 72.4 (C-3), 61.5 (C-2), 51.5 (C-4), 2056, 16.9. IR (neat): 691, 719, 746, 870, 893, 984, 1025, 1048, 1087, 1103, 1159, 1232, 1350, 1355, 1374, 1387, 1440, 1456, 1481, 1507, 1576, 1653, 1684, 1695, 1715, 1730, 2113, 3735. HR-MS: [M+Na$^+$] Calculated for $C_{22}H_{20}N_4O_5S$: 475.1047; found: 475.1056.

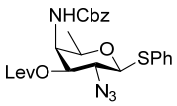


Phenyl 2-N_3-4-*N*-Cbz-6-deoxy-1-thio-β-D-galactopyranoside (23): The compound **22b** (1.22 g, 2.7 mmol) was dissolved in butanol (20 ml) with ethylenediamine (5 ml), the reaction mixture was refluxed for 24 h. The reaction mixture concentrated in vacuo. The residue was dissolved in THF (10 ml) and water (5 ml), $NaHCO_3$ (1.8 g, 21.6 mmol) was added to the reaction mixture at 0 °C. Then CbzCl (1.54 ml, 10.8 mmol) was added into the reaction mixture. The reaction was allowed to stir for 4 h at

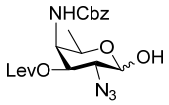


same temperature and then diluted with EtOAc and washed brine and then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (Pentane/EtOAc, 3:1, product 662 mg, two steps yield: 59%). *Rf* = 0.31 (pentane/EtOAc, 2:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.48 – 7.25 (m, 8H), 5.20 – 5.03 (m, 2H, CH_2-Cbz), 4.96 (d, *J* = 9.1 Hz, 1H, N-H), 4.39 (d, *J* = 10.2 Hz, 1H, H-1), 3.97 (m, 1H, H-4), 3.80 – 3.58 (m, 2H, H-3, H-5), 3.39 (d, *J* = 4.2 Hz, 1H, -OH), 3.20 (t, *J* = 9.9 Hz, 1H, H-2), 1.25 (d, *J* = 6.5 Hz, 3H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 136.0, 133.6, 131.6, 129.2, 128.7, 128.5, 128.2, 86.7 (C-1), 74.8 (C-3), 73.9 (C-5), 67.7 (Bn), 63.1 (C-2), 55.1 (C-4), 17.2 (C-6). $[\alpha]^{20}_D$ = -20° (c = 1.0, $CHCl_3$). IR (neat): 625, 668, 698, 748, 1000, 1043, 1218, 1328, 1458, 1507, 1521, 1695, 1717, 2113. HR-MS: [M+Na^+] Calculated for $C_{20}H_{22}N_4O_4S$: 437.1254; found: 437.1265.

Phenyl 2-N_3-3-levulinoyl-4-*N*-Cbz-6-deoxy-1-thio-β-D-galactopyranoside (24): The compound **23** (863 mg, 2.081 mmol) was dissolved in DCM (4.6 ml) with LevOH (363 mg, 3.2 mmol) and DMAP (351 mg, 3.2 mmol), then EDCI (799 mg, 4.16 mmol) and DIPEA (545 ul) were added to the reaction mixture at 0 °C. The reaction mixture was stirred for overnight at room temperature. The reaction mixture was diluted with EtOAc and washed with 1M HCl, sat. aq. $NaHCO_3$ and brine and then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (Pentane/DCM/EtOAc, 4:1:1, product 1.021 g, yield: 96%). *Rf* = 0.52 (toluene/EtOAc, 7:3). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.42 – 7.30 (m, 8H), 5.14 – 5.01 (dd, *J* = 18.4 Hz, *J* = 6.0 Hz, 2H, CH_2-Cbz), 4.97 (d, *J* = 9.7 Hz, 1H, N-H), 4.78 (dd, *J* = 10.2, 3.8 Hz, 1H, H-3), 4.45 (d, *J* = 10.2 Hz, 1H, H-1), 4.12 (m, 1H, H-4), 3.72 (qd, *J* = 6.3, 1.4 Hz, 1H, H-5), 3.49 – 3.23 (m, 1H, H-2), 2.74 (m, 1H), 2.69 – 2.49 (m, 2H), 2.48 – 2.32 (m, 1H), 2.12 (s, 3H), 1.22 (d, *J* = 6.4 Hz, 3H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3, 171.8, 156.4, 136.3, 133.3, 131.3, 129.1, 128.6, 128.5, 128.1, 127.8, 86.5 (C-1), 74.9 (C-3), 73.5 (C-5), 66.9 (Bn), 59.7 (C-2), 51.9 (C-4), 37.8, 27.8, 16.8 (C-6). $[\alpha]^{20}_D$ = -24° (c = 0.25, $CHCl_3$). IR (neat): 742, 1045, 1066, 1151, 1205, 1216, 1228, 1507, 1700, 1704, 1710, 2114. HR-MS: [M+Na^+] Calculated for 535.1622; found: 535.1627.

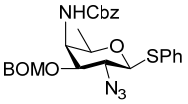


2-N_3-3-*O*-levulinoyl-4-*N*-Cbz-6-deoxy-1-*O*-α/β-D-galactopyranoside (25): The title compound was obtained as decribed in the general procedure for hydrolysis of thioglycosidic bond from compound 24. 1.18 g, quantitative yield. *Rf* = 0.2 (pentane/EtOAc, 3:2). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.28 (m, 5H), 5.89 (d, *J* = 10.3 Hz, 0.17H, -NH), 5.55 (d, *J* = 9.9 Hz, 0.83H, -NH), 5.28 (d, *J* = 3.7 Hz, 0.83H, αH-1), 5.25 (d, *J* = 3.8 Hz, 0.17H), 5.19 (d, *J* = 9.6 Hz), 5.18 – 5.02 (m), 4.71 (dd, *J* = 10.8, 4.0 Hz), 4.67 (dd, *J* = 10.9, 4.0 Hz), 4.59 (d, *J* = 8.0 Hz), 4.48 (tt, *J* = 7.6, 3.7 Hz), 4.21 (ddd, *J* = 9.7, 3.9, 1.7 Hz), 4.11 (ddd, *J* = 9.9, 4.1, 1.5 Hz), 4.08 – 4.01 (m), 3.80 – 3.66 (m), 3.60 (dd, *J* = 10.9, 7.9 Hz), 3.55 – 3.42 (m), 3.38 (d, *J* = 9.7 Hz), 2.87 – 2.32 (m, 4H), 2.16 (d, *J* = 1.1 Hz, 3H), 1.22 (d, *J* = 6.4 Hz), 1.16 (d, *J* = 6.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 172.2, 157.0, 136.5, 128.7, 128.4, 128.0, 96.5 (C-1β), 92.1 (C-1α), 73.3 (C-3β), 70.6 (C-3α), 69.6 (C-5β), 67.5, 67.2, 64.5 (C-5α), 62.3 (C-2β), 58.4 (C-2α), 52.9 (C-4α), 52.1 (C-4β), 38.0, 29.9, 29.7, 28.0, 16.7 (C-6). $[\alpha]^{20}_D$ = 153°



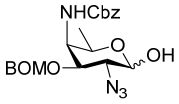
(c = 0.1, $CHCl_3$). IR (neat): 697, 741, 1030, 1083, 1154, 1232, 1264, 1327, 1363, 1524, 1695, 1713, 2110. HR-MS: [M+Na^+] Calculated for $C_{19}H_{24}N_4O_7$: 443.1537; found: 443.1545.

Phenyl 2-N_3-3-*O*-Lev-4-*N*-Cbz-6-deoxy-1-thio-β-D-galactopyranoside (26): The title compound was obtained as



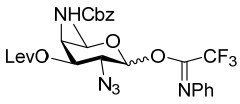
decribed in the general procedure for BOM protection from compound **23**. 42 mg, yield: 79%. *Rf* = 0.69 (pentane/EtOAc, 3:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.50 (m, 2H), 7.35 (m, 13H), 5.10 (q, *J* = 12.4 Hz, 2H), 4.99 (d, *J* = 7.5 Hz, 1H), 4.87 – 4.67 (m, 3H), 4.61 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 10.2 Hz, 1H, H-1), 4.09 (ddd, *J* = 10.2, 4.1, 1.3 Hz, 1H, H-4), 3.80 (dd, *J* = 10.0, 4.0 Hz, 1H, H-3), 3.63 (qd, *J* = 6.3, 1.3 Hz, 1H, H-5), 3.23 (t, *J* = 10.1 Hz, 1H, H-2), 1.24 (d, *J* = 6.3 Hz, 3H, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 137.4, 136.4, 133.8, 131.3, 129.3, 128.8, 128.6, 128.6, 128.4, 128.3, 128.0, 127.9, 92.1 (BOM), 86.5 (C-1), 76.4 (C-3), 74.2 (C-5), 69.9, 67.1, 61.6 (C-2), 51.7 (C-4), 17.2 (C-6). $[\alpha]^{20}_D$ = 3° (c = 0.84, $CHCl_3$). IR (neat): 694, 739, 976, 1036, 1224, 1457, 1507, 1653, 1715, 2111. HR-MS: [M+Na^+] Calculated for $C_{28}H_{29}N_4O_5S$: 556.1750; found: 556.2771.

2-N_3-3-*O*-BOM-4-*N*-Cbz-6-deoxy-1-α/β-D-galactopyranoside (27): The title compound was obtained as described in



the general procedure for hydrolysis of thioglycosidic bond from compound **26**. 80 mg, yield: 97%. *Rf* = 0.28 (pentane/DCM/EtOAc, 2:1:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.25 (m, 10H), 5.82 (d, *J* = 10.3 Hz), 5.53 (d, *J* = 10.2 Hz), 5.28 – 4.87 (m), 4.89 – 4.54 (m), 4.46 (dd, *J* = 15.5, 6.9 Hz), 4.36 – 4.22 (m), 4.20 – 4.10 (m), 4.06 (m), 3.71 (dd, *J* = 10.5, 4.2 Hz), 3.64 – 3.43 (m, 1H), 3.43 – 3.29 (m, 1H), 1.19 (d, *J* = 6.3 Hz), 1.14 (d, *J* = 6.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 137.5, 136.4, 128.6, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 96.4 (C-1β), 92.12, 91.9 (C-1α), 74.5 (C-3β), 71.5 (C-3α), 70.1 (C-5β), 69.9, 69.8, 67.1, 65.0 (C-5α), 64.1 (C-2β), 60.0 (C-2α), 52.6 (C-4α), 51.8 (C-4β), 16.8 (C-6). $[\alpha]^{20}_D$ = 9° (c = 0.23, $CHCl_3$). IR (neat): 698, 748, 1039, 1222, 1457, 1507, 1560, 1700, 1715, 2110. HR-MS: [M+Na^+] Calculated for $C_{22}H_{26}N_4O_6$: 465.1745; found: 465.1738.

2-N_3-3-*O*- levulinoyl -4-*N*-Cbz-6-deoxy-1-*O* -(*N*-phenyl-trifluoroacetimidoyl)-α/β-D-galactopyranoside (15): The title



compound was obtained as decribed in the general procedure for yield *N*-phenyl-trifluoroacetimidate donor from compound **25**. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.28 (m, 7H), 7.22 – 7.05 (m, 1H), 6.92 – 6.74 (m, 2H), 5.43 (d, *J* = 75.1 Hz, 1H, H-1), 5.17 (d, *J* = 12.2 Hz, 1H), 5.13 – 5.00 (m, 2H), 4.76 (s, 1H, H-3), 4.40 – 4.25 (m, 0H), 4.15 (dt, *J* = 7.1, 3.6 Hz, 1H, H-4), 3.74 (m, 2H, H-2, H-5), 2.89 – 2.72 (m, 1H), 2.72 – 2.52 (m, 2H), 2.52 – 2.33 (m, 1H), 2.17 (s, 3H), 1.31 – 1.12 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 172.0, 156.6, 143.0, 136.3, 128.9, 128.7, 128.5, 128.2, 124.8, 119.3, 95.8 (C-1), 73.3 (C-3), 70.8 (C-5), 67.3, 60.19 (C-2), 51.9 (C-4), 37.9, 29.9, 27.9, 16.5 (C-6). HR-MS: [M+Na^+] Calculated for C27H28$F_3N_5O_7$: 614.1833; found: 614.1841.

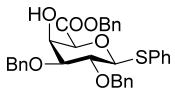
2-N_3-3-*O*-BOM-4-*N*-Cbz-6-deoxy-1-*O* -(*N*-phenyl-trifluoroacetimidoyl)-α/β-D-galactopyranoside (16): The title compound was obtained as decribed in the general procedure for yield *N*-phenyl-trifluoroacetimidate donor from compound **27**. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.47 (m, 0.6H), 7.47 – 7.21 (m, 13H), 7.16 – 7.05 (m, 1H), 6.91 – 6.75 (m, 2H), 6.36 (s, 0.13H), 5.39 (d, *J* = 66.2 Hz, 1H), 5.05 (d, *J* = 61.5 Hz, 5H), 4.87 – 4.69 (m, 2H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.51 – 4.37 (m, 0.35H), 4.35 – 4.16 (m, 0.65H), 4.16 – 4.02 (m, 1H), 3.79 (bs, 1H), 3.60 (bs, 2H), 1.32 – 1.18 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 143.2, 137.4, 136.3, 129.4, 128.9, 128.7, 128.6, 128.3, 128.1, 128.0, 126.4, 124.7, 120.7, 119.30, 95.9 (C-1), 92.2, 74.6 (C-3), 71.5, 71.2 (C-5), 69.9, 68.2, 67.3, 62.1 (C-2), 58.9, 52.1 (C-4), 46.2, 16.6 (C-6). HR-MS: [M-OC(CF_3)=NPh+H_2O+Na^+] Calculated for $C_{22}H_{26}N_4O_6$: 465.1745; found: 465.1752.

Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (28), D-galactose (90 g, 0.5 mol) was added to Ac_2O (284 ml, 3 mol), then H_2SO_4 (three drops, can not add too much in case the reaction is going too fast) was added to the reaction mixture at 0 °C. The reaction mixture was allowed to stir for 2 h at 0 °C and the reaction mixture was clear solution. The reaction mixture was allowed to stir at room temperature and monitored by TLC analysis. The reaction mixture was poured into ice-water. The product was extracted using EtOAc (3 x 400 ml) and the combined organic fractions were washed with sat. aq. $NaHCO_3$, dried over Na_2SO_4 and concentrated in vacuo. A solution of penta-*O*-acetyl-D-galactopyranoside and PhSH 90.6 ml, 0.9 mol) in DCM (600 ml) was cooled to 0 °C and $Et_2O•BF_3$ (48%, w/w, 103.1 ml) was added. The mixture was stirred for 2 days at room temperature. The reaction was quenched by the addition of Et_3N and diluted with DCM, washed with 1 M NaOH and brine then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (154.6 g, two steps yield: 70%). The analytical data were in full accord with reported previously.[19]

Phenyl 2,3-di-*O*-benzyl-1-thio-β-D-galactopyranoside (29), Phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (33.3 g, 75.75 mmol) was added to MeOH (500 ml), then NaOMe in MeOH (5 ml) was added to the reaction mixture at 0 °C. The reaction mixture was allowed to stir for overnight at room temperature and monitored by TLC analysis. The reaction mixture was neutralized by Amberlite H^+ resin. After filtration. The reaction solution was concentrated in vacuo. The residue was dissolved in CH_3CN (434 ml), benzaldehyde dimeth acetal (17.13 ml) and camphorsulfonic acid (5.25 g) were added to the reaction mixture at 0 °C. The reaction mixture was allowed to stir for overnight at room temperature and monitored by TLC analysis. The reaction was quenched by the addition of Et_3N and diluted with EtOAc, washed with sat. aq. $NaHCO_3$ and brine then dried over Na_2SO_4 and concentrated in vacuo. The residue was dissolved in DMF (250 ml), NaH (60% in mineral oil, 9 g) was slowly added to the reaction mixture at 0 °C. After 20 min, BnBr (27 ml) was added to the reaction mixture. The reaction mixture was allowed to stir for overnight at room temperature. The reaction was quenched by the addition of water and diluted with EtOAc, washed with

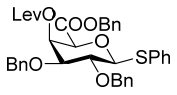
brine then dried over Na_2SO_4 and concentrated in vacuo. The residue was dissolved in MeOH (900 ml), DCM (400 ml), TsOH•H_2O was added to the reaction mixture until PH = 2. The reaction mixture was allowed to stir for overnight at room temperature and monitored by TLC analysis. The reaction was quenched by the addition of Et_3N and diluted with EtOAc, washed with brine then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (pentane/EtOAc, 6:1→1:1, product 29.5 g, four steps yield: 86%). The analytical data were in full accord with reported previously.[20]

Benzyl phenyl-2,3-di-*O*-benzyl-1-thio-β-D-galactopyranosyl uronate (30): Compound **29** (6.17 g, 13.63 mmol) was



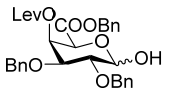
dissolved in DCM/*tert*-BuOH/H_2O (90 ml, 4/4/1,v/v/v). The mixture was cooled to 0°C and treated with TEMPO (426 mg, 2.73 mmol) and BAIB (11 g, 34.08 mmol). After stirring for overnight at 4 0°C, $Na_2S_2O_3$ was added, the mixture was diluted with EtOAc, washed with sat. aq. NaCl and the organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was dissolved in DMF (50 ml), followed by addition of Cs_2CO_3(4.44 g, 13.63 mmol) and BnBr (2.41 ml, 20.45 mmol) at 0°C. The mixture was allowed to stir overnight at room temperature, and then diluted with EtOAc, washed with sat. aq. NaCl. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (silica gel, pentane/DCM/EtOAc, 8/1/1, v/v/v) yielded 30 as white solid (5.09 g, two steps yield 67%). TLC: R_f = 0.5 (pentane/EtOAc, 2/1, v/v).[21]

Benzyl phenyl-2,3-di-*O*-benzyl-4-*O*- levulinoyl -1-thio-β-D-galactopyranosyl uronate (31): The compound **30** (9.5 g,



17.07 mmol) was dissolved in DCM (80 ml) with LevOH (3.96 g, 34.14 mmol) and DMAP (4.16 g, 34.14 mmol), then EDCI (6.56 g, 34.14 mmol) and DIPEA (5.95 ml, 34.14 mmol) were added to the reaction mixture at 0 °C. The reaction mixture was stirred for overnight at room temperature. The reaction mixture was diluted with EtOAc and washed with 1M HCl, sat. aq. $NaHCO_3$ and brine and then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (Pentane/DCM/EtOAc, 6:1:1, product 10.35 g, yield: 93%). *Rf* = 0.7 (toluene/EtOAc, 3:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.61 (m, 2H), 7.45 – 7.23 (m, 18H), 5.82 (dd, *J* = 3.1, 1.3 Hz, 1H, H-4), 5.19 (s, 2H), 4.82 – 4.65 (m, 3H), 4.60 (d, *J* = 9.3 Hz, 1H, H-1), 4.45 (d, *J* = 11.1 Hz, 1H), 4.14 (d, *J* = 1.3 Hz, 1H, H-5), 3.71 – 3.49 (m, 2H, H-3, H-2), 2.69 – 2.41 (m, 4H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 171.5, 166.3, 138.1, 137.4, 135.1, 133.3, 132.7, 129.0, 128.8, 128.6, 128.6, 128.4, 128.4, 128.2, 128.2, 128.0, 127.9, 87.3 (C-1), 80.5 (C-3), 76.0 (C-2), 75.7, 75.5 (C-5), 71.9, 67.8 (C-4), 67.6, 37.9, 29.8, 27.9. $[\alpha]^{20}_D$ = +12° (c = 1.0, $CHCl_3$). IR (neat): 697, 738, 1028, 1104, 1121, 1154, 1202, 1266, 1747. HR-MS: [M+Na^+] Calculated for $C_{38}H_{38}SO_8$: 677.2180; found: 677.2187.

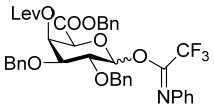
Benzyl 2,3-di-*O*-benzyl-4-*O*-levulinoyl-1-α/β-D-galactopyranosyl uronate (32): The title compound was obtained as



decribed in the general procedure for hydrolysis of thioglycosidic bond. 8.91 g, yield: 91%. *Rf* = 0.2 (pentane/DCM/EtOAc, 2:1:1, v/v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.18

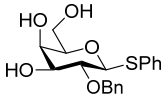
(m, 15H), 5.87 (dd, *J* = 3.5, 1.7 Hz, 1H, H-4α), 5.78 (dd, *J* = 3.2, 1.4 Hz, 0.2H), 5.37 (d, *J* = 3.5 Hz, 1H, H-1α), 5.27 – 5.10 (m, 2H), 4.89 (d, *J* = 11.0 Hz, 0.2H), 4.85 – 4.59 (m, 4H, H-5α), 4.50 (t, *J* = 11.3 Hz, 1H), 4.12 (d, *J* = 1.4 Hz, 0.2H), 4.00 (dd, *J* = 9.9, 3.5 Hz, 1H, H-3α), 3.76 (dd, *J* = 9.8, 3.6 Hz, 1H, H-2α), 3.63 – 3.42 (m, 0.2H), 2.69 – 2.36 (m, 4H), 2.16 (s, 0H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.2, 171.6, 167.8, 137.9, 135.1, 129.2, 129.2, 128.7, 128.5, 128.4, 128.4, 128.2, 128.2, 128.1, 128.0, 127.8, 97.4 (C-1β), 92.2 (C-1α), 79.3, 78.7, 75.4 (C-3α), 75.3 (C-2α), 74.9, 73.8, 72.4, 72.1, 68.9 (C-5α), 68.7 (C-4α), 67.9, 67.8, 67.7, 38.1, 29.8, 28.0. $[\alpha]^{20}_D$ = 40° (c = 1.0, $CHCl_3$). IR (neat): 697, 737, 906, 1028, 1100, 1151, 1206, 1361, 1455, 1715, 1739. HR-MS: [M+Na$^+$] Calculated for $C_{32}H_{34}O_9$: 585.2095; found: 585.2104.

Benzyl 2,3-di-*O*-benzyl-4-*O*-levulinoyl-1-*O*-(*N*-phenyl-trifluoroacetimidoyl)-α/β-D-galactopyranosyl uronate (17): The



title compound was obtained as decribed in the general procedure for yield *N*-phenyl-trifluoroacetimidate donor from compound **32**. 1.53 g, yield: 93%. *Rf* = 0.88 (pentane/DCM/EtOAc, 2:1:1, v/v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.15 (m, 17H), 7.14 – 6.98 (m, 1H), 6.78 (d, *J* = 7.7 Hz, 2H), 5.80 (bs, 1H, H-4), 5.34 – 5.13 (m, 2H), 4.95 – 4.64 (m, 3H, H-5), 4.50 (d, *J* = 11.3 Hz, 1H), 3.80 (bs, 1H, H-3), 3.65 (bs, 1H, H-2), 2.74 – 2.40 (m, 4H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.1, 171.5, 165.8, 137.7, 137.4, 135.0, 129.3, 129.3, 128.8, 128.7, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.9, 127.7, 124.4, 119.4, 96.5 (C-1), 78.8 (C-2), 76.9 (C-3), 75.9, 75.1, 74.1, 73.8, 73.1 (C-5), 72.3, 71.2, 68.4, 67.9, 67.5 (C-4), 38.0, 29.9, 29.4, 28.0. HR-MS: [M+Na$^+$] Calculated for $C_{40}H_{38}F_3NO_9$: 756.2391; found: 756.2405.

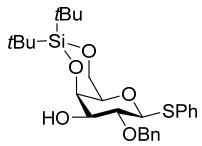
Phenyl 2-*O*-benzyl-1-thio-β-D-galactopyranoside (34): Compound **28** (27.9 g, 63.34 mmol) was added to MeOH



(450 ml), then NaOMe in MeOH (4.5 ml) was added to the reaction mixture at 0 °C. The reaction mixture was allowed to stir for overnight at room temperature and monitored by TLC analysis. The reaction mixture was neutralized by Amberlite H$^+$ resin. After filtration. The reaction solution was concentrated in vacuo. The residue was added in dimethoxypropane (290 ml), and camphorsulfonic acid (724 mg) were added to the reaction mixture at 0 °C. The reaction mixture was allowed to stir for 48 h at room temperature and monitored by TLC analysis. The reaction was quenched by the addition of Et_3N and diluted with EtOAc, washed with sat. aq. $NaHCO_3$ and brine then dried over Na_2SO_4 and concentrated in vacuo. The residue was dissolved in DMF (200 ml), NaH (60% in mineral oil, 3.8 g, 95 mmol) was slowly added to the reaction mixture at 0 °C. After 20 min, BnBr (11.3 ml) was added to the reaction mixture. The reaction mixture was allowed to stir for overnight at room temperature. The reaction was quenched by the addition of water and diluted with EtOAc, washed with brine then dried over Na_2SO_4 and concentrated in vacuo. The residue was dissolved in AcOH/H_2O (80% /20%, v/v). The reaction mixture was allowed to stir for 3 h at 70 °C and monitored by TLC analysis. The reaction mixture concentrated in vacuo. The product was purified by column chromatography (DCM/acetone, 4:1, product 12.9 g, four steps yield: 56%). The analytical data were in full accord with reported

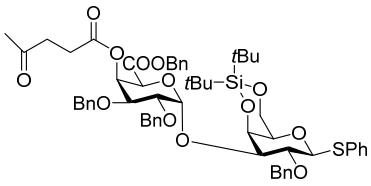
previously.

Phenyl 2-*O*-benzyl-4,6-di-*tert*-butyl-silylidene-1-thio-β-D-galactopyranoside (18): Compound **34** (12.9 g, 35.59 mmol)

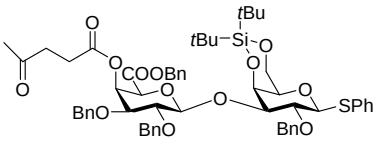


was added to pyridine (200 ml), then di-*tert*-butylsilyl bis(trifluoromethanesulfonate (12.17 ml, 37.37 mmol) was added to the reaction mixture at -30 °C. The reaction mixture was allowed to slowly warm up to room temperature and stir for 4 h. The reaction was quenched by the addition of MeOH and concentrated in vacuo. The residue was diluted with EtOAc, washed with brine then dried over Na_2SO_4 and concentrated in vacuo. The product was purified by column chromatography (pentane/EtOAc, 8:1, product 15.95 g, yield: 89%). *Rf* = 0.46 (pentane/EtOAc, 6:1, v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.11 (m, 10H), 4.93 (bs, 2H), 4.63 (d, *J* = 9.5 Hz, 1H, H-1), 4.37 (m, 1H, H-4), 4.20 (t, *J* = 1.7 Hz, 2H, H-6), 3.74 – 3.45 (m, 2H, H-3, H-2), 3.42 – 3.24 (m, 1H, H-5), 2.72 (s, 1H, -OH), 1.16 – 1.09 (m, 9H), 1.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 134.5, 132.3, 128.8, 128.5, 127.9, 127.5, 88.1 (C-1), 79.1 (C-2), 75.7, 75.5 (C-3), 74.8 (C-5), 73.1 (C-4), 67.1 (C-6), 27.7, 20.8. $[\alpha]^{20}_D$ = -17° (c = 1.0, $CHCl_3$). IR (neat): 611, 631, 649, 675, 690, 735, 737, 780, 809, 824, 885, 917, 961, 1048, 1077, 1161, 1471, 2857, 2932. HR-MS: [M+Na$^+$] Calculated for $C_{27}H_{38}SSiO_5$: 525.2101; found: 525.2103.

Phenyl 2-*O*-benzyl-3-*O*-(benzyl 2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-galactopyranosyl urinate)-4,6-di-*tert*-butyl-silylidene-1-thio-β-D-galactopyranoside (35): Donor **17** (5.34 g, 7.28 mmol) and acceptor **18** (2.44 g, 4.85 mmol)

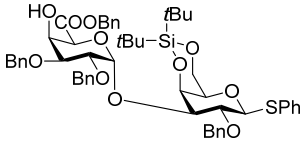


were co-evaporated with toluene (three times). The residue was dissolved in dry DCM (48 ml) and stirred for 30 min with activated 5A molecular sieves at room temperature. The solution was cooled to -70 °C, followed by the addition of TfOH (75 ul, 0.49 mmol) and the reaction was allowed to stir for 6 h at -70 °C. The reaction was quenched with sat. aq. $NaHCO_3$ and diluted with DCM, filtrated and washed with sat. aq. NaCl. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatograpy yielded the product 3.9 g, yield: 77%. *Rf* = 0.27 (toluene/EtOAc, 6:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.46 (m, 2H), 7.40 – 7.19 (m, 20H), 7.14 (dd, *J* = 5.2, 1.9 Hz, 3H), 5.57 (dd, *J* = 3.4, 1.7 Hz, 1H, H-4'), 5.46 (d, *J* = 3.3 Hz, 1H, H-1'), 5.16 (d, *J* = 11.9 Hz, 1H), 5.02 (dd, *J* = 11.3, 7.5 Hz, 2H), 4.79 (d, *J* = 11.7 Hz, 1H), 4.69 (m, 5H, H-4, H-5', H-1), 4.60 (d, *J* = 11.2 Hz, 1H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.18 (qd, *J* = 12.4, 1.8 Hz, 2H, H-6), 3.98 – 3.78 (m, 3H, H-3', H-3, H-2'), 3.67 (dd, *J* = 9.4, 2.9 Hz, 1H, H-2), 3.30 (d, *J* = 2.0 Hz, 1H, H-5), 2.62 – 2.35 (m, 4H), 2.06 (s, 3H), 1.09 (s, 9H), 1.02 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 171.3, 167.4, 138.2, 138.0, 135.0, 134.7, 129.1, 128.9, 128.5, 128.5, 128.3, 128.2, 127.9, 127.8, 127.6, 127.6, 127.5, 127.4, 93.1 (C-1'), 88.7 (C-1), 77.9 (C-3), 76.5 (C-2'), 75.8, 75.4 (C-3'), 74.6 (C-5), 73.9 (C-2'), 72.3, 72.0, 69.0 (C-5'), 68.6 (C-4'), 68.3 (C-4), 67.6, 67.3 (C-6), 37.9, 29.7, 27.9, 27.7, 23.3, 20.7. $[\alpha]^{20}_D$ = +81° (c = 1.0, $CHCl_3$). IR (neat): 651, 697, 737, 786, 809, 826, 918, 969, 1044, 1080, 1118, 1151, 1211, 1363, 1454, 1718, 1749, 2856, 2934. HR-MS: [M+Na$^+$] Calculated for $C_{59}H_{70}SSiO_{13}$: 1069.4199; found: 1069.4232.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.48 (m, 2H), 7.47 – 7.02 (m, 30H), 5.71 (dd, *J* = 3.7, 1.4 Hz, 1H), 5.23 – 5.02 (m, 3H), 4.98 (d, *J* = 7.9 Hz, 1H), 4.91 – 4.81 (m, 2H), 4.78 – 4.51 (m, 6H), 4.27 – 4.13 (m, 2H), 4.07 – 3.80 (m, 3H), 3.58 (dd, *J* = 9.7, 7.8 Hz, 1H), 3.42 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.37 (s, 1H), 2.70 – 2.42 (m, 4H), 2.12 (s, 3H), 1.15 (s, 8H), 1.10 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3, 171.6, 166.6, 138.6, 138.1, 135.0, 132.0, 129.1, 129.0, 128.7, 128.7, 128.7, 128.6, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.5, 102.6, 89.0, 78.8, 78.1, 75.3, 75.1, 73.2, 72.5, 72.1, 68.1, 67.7, 67.3, 38.1, 30.0, 28.1, 27.8, 23.5, 20.9.

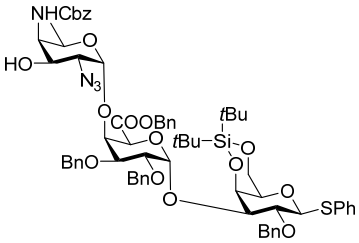
Phenyl 2-*O*-benzyl-3-*O*-(benzyl 2,3-di-*O*-benzyl-α-D-galactopyranosyl urinate)-4,6-di-*tert*-butyl-silylidene-1-thio-β-D-galactopyranoside (36): The title compound was obtained by general procedure for delevulinoylation from compound **35**. 0.97 g, yield: 89%. *Rf* = 0.28 (toluene/EtOAc, 5:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.40 – 7.21 (m, 20H), 7.21 – 7.09 (m, 3H), 5.50 (d, *J* = 3.3 Hz, 1H, H-1'), 5.22 (d, *J* = 12.3 Hz, 1H), 5.09 (d, *J* = 12.4 Hz, 1H), 5.01 (d, *J* = 10.6 Hz, 1H), 4.84 (d, *J* = 11.7 Hz, 1H), 4.77 – 4.51 (m, 8H, H-4, H-1, H-5'), 4.26 – 4.13 (m, 2H, H-6), 4.10 (m, 1H, H-4'), 3.98 (dd, *J* = 9.7, 3.3 Hz, 1H, H-2'), 3.92 – 3.81 (m, 2H, H-3', H-2), 3.69 (dd, *J* = 9.3, 2.9 Hz, 1H, H-3), 3.30 (bs, 1H, H-5), 1.08 (d, *J* = 1.1 Hz, 9H), 1.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 138.3, 138.2, 137.9, 135.5, 134.8, 132.1, 128.9, 128.6, 128.5, 128.4, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.7, 127.7, 127.5, 92.6 (C-1'), 88.8 (C-1), 77.8 (C-3), 76.8 (C-2), 76.6 (C-3'), 75.9, 74.6 (C-5), 74.4 (C-3), 72.9, 72.1, 69.9 (C-5'), 68.5 (C-4), 68.4 (C-4'), 67.4 (C-6), 67.1, 27.8, 27.7, 23.4, 20.8. $[\alpha]^{20}_D$ = +79° (c = 1.0, $CHCl_3$). IR (neat): 650, 695, 734, 789, 809, 825, 949, 967, 1027, 1078, 1154, 1210, 1363, 1761, 2112, 2856. HR-MS: [M+Na$^+$] Calculated for $C_{54}H_{64}SSiO_{11}$: 971.3831; found: 971.3859.



Phenyl (2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-azide-3-*O*-BOM-4-*N*-Cbz-6-deoxy-1-α-D-galactopyranoside}-α-D-galactopyranosyl urinate]-4,6-di-*tert*-butyl-silylidene-1-thio-β-D-galactopyranoside) (37): Donor **16** (85 mg, 0.139 mmol) and acceptor 36 (88.3 g, 0.093 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry DCM (0.93 ml). The solution was cooled to 0 °C, followed by the addition of TBSOTf (2.1 ul, 9.3 umol) and the reaction was allowed to stir for overnight at 0 °C. The reaction was quenched with Et_3N and diluted with DCM, washed with sat. aq. NaCl. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatograpy yielded the product (α/β = 2.9:1) 32 mg, yield: 25%. And also found the BOM protecting group was removed byproduct 38 34 mg, yield: 29%.

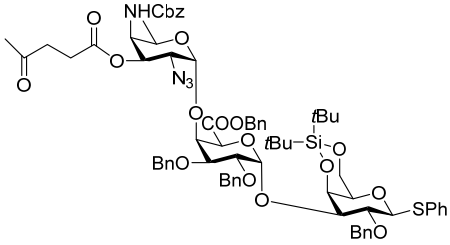
Data for 37α product: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.47 (m, 2H), 7.45 – 7.08 (m, 33H), 5.52 (d, *J* = 3.5 Hz, 1H, H-1'), 5.29 (d, *J* = 7.8 Hz, 1H), 5.25 (s, 1H), 5.14 – 5.05 (m, 2H), 5.04 – 4.86 (m, 4H), 4.82 (d, *J* = 9.9 Hz, 1H), 4.78 – 4.54 (m, 10H, H-4, H-1, H-1''), 4.49 (s, 1H, H-5'), 4.27 – 4.10 (m, 4H, H-5'', H-4', H-6), 4.09 – 3.92 (m, 3H, H-3'', H-4'', H-2'), 3.83 (m, 2H, H-2, H-3'), 3.69 (dd, *J* = 9.4, 2.8 Hz, 1H, H-3), 3.27 (d, *J* = 1.9 Hz, 1H, H-5), 2.96 (dd, *J* = 10.8, 4.0 Hz, 1H, H-2''), 1.07 (s, 9H), 1.01 (s, 9H), 0.79 (d, *J* = 6.3 Hz, 3H, H-6''). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 156.9, 138.4, 138.1, 138.0, 137.8, 136.4, 134.9, 134.8, 132.1, 128.9, 128.9, 128.8, 128.7, 128.5, 128.5, 128.3, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 98.8 (C-1''), 92.5, 92.1 (C-1'), 88.8 (C-1), 77.6 (C-3), 76.7 (C-4'), 76.2 (C-3'), 75.8 (C-2), 75.8, 74.6 (C-5), 74.5 (C-2'), 73.2, 71.9, 71.5 (C-3''), 70.1 (C-5'), 68.2 (C-4), 67.4 (C-6), 67.1, 65.5 (C-5''), 59.6 (C-2''), 52.8 (C-4''), 29.9, 29.5, 27.8, 27.7, 23.7, 20.8, 16.4 (C-6''). $[\alpha]^{20}_{D}$ = +135° (c = 0.4, $CHCl_3$). IR (neat): 697, 740, 827, 969, 1039, 1092, 1167, 1212, 1237, 1456, 1726, 2109, 2858, 2925. HR-MS:

Phenyl (2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-azide-4-*N*-Cbz-6-deoxy-1-α-D-galactopyranoside}- α-D-galactopyranosyl urinate]-4,6-di-*tert*-butyl-silylidene-1-thio-β-D-galactopyranoside) (38):



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.43 – 7.10 (m, 28H), 5.53 (d, *J* = 3.5 Hz, 1H, H-1'), 5.24 (d, *J* = 12.1 Hz, 1H), 5.11 (s, 2H), 5.05 – 4.85 (m, 4H), 4.71 (d, *J* = 2.8 Hz, 1H, H-4), 4.68 – 4.55 (m, 6H, H-1, H-1''), 4.55 – 4.47 (m, 1H, H-5'), 4.32 – 4.24 (m, 1H, H-5''), 4.24 – 4.11 (m, 3H, H-4', H-6), 4.00 (m, 2H, H-3'', H-2'), 3.84 (m, 3H, H-4'', H-3', H-2), 3.69 (dd, *J* = 9.4, 2.8 Hz, 1H, H-3), 3.27 (d, *J* = 2.1 Hz, 1H, H-5), 2.94 (dd, *J* = 10.7, 3.8 Hz, 1H, H-2''), 1.08 (s, 9H), 1.02 (s, 9H), 0.79 (d, *J* = 6.4 Hz, 3H, H-6''). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 158.4, 138.3, 138.1, 138.1, 136.0, 135.0, 134.8, 132.1, 128.9, 128.8, 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.3, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.5, 99.1 (C-1''), 92.1 (C-1'), 88.8 (C-1), 77.6 (C-1), 76.7 (C-4'), 76.3 and 76.0 (C-3', C-2), 75.8, 74.6 (C-5), 74.4 (C-2'), 73.2, 71.8, 70.1 (C-5'), 68.8 (C-3'', C-4), 68.3 (C-4'), 67.7, 67.48, 67.4 (C-6), 65.1 (C-5''), 60.8 (C-2''), 56.0 (C-4''), 29.8, 27.8, 27.7, 23.4, 20.8, 16.4 (C-6''). $[\alpha]^{20}_{D}$ = +107° (c = 1.0, $CHCl_3$). IR (neat): 655, 697, 735, 827, 968, 1028, 1091, 1167, 1213, 1458, 1507, 1706, 2110, 2358, 2856. HR-MS: [M+Na^+] Calculated for $C_{68}H_{80}N_4O_{16}SSi$: 1275.5002; found: 1275.5022.

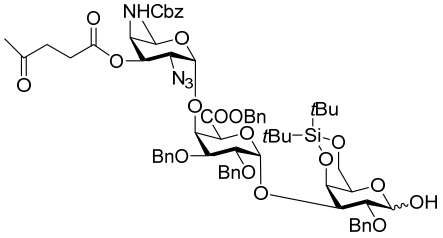
Phenyl (2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-azide-3-*O*-levulinoyl-4-*N*-Cbz-6-deoxy-1-α-D-galactopyranoside}-α-D-galactopyranosyl urinate]-4,6-di-*tert*-butyl-silylidene-1-thio-β-D-galactopyranoside) (39):



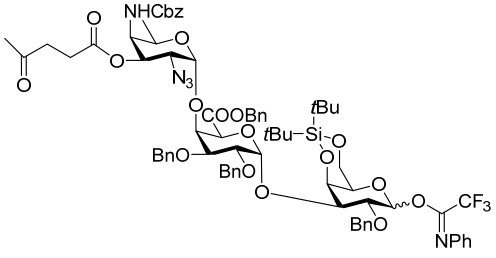
Donor **15** (890 mg, 1.5 mmol) and acceptor **36** (950 mg, 1.0 mmol) were co-evaporated with toluene (three times). The residue was dissolved in dry DCM (0.93 ml) and stirred for 30 min with activated 5Å molecular sieves at room temperature. The solution was cooled to 0 °C, followed by the addition of TBSOTf (23 ul, 0.1 mmol) and the reaction

was allowed to stir for 4 h at 0 °C. The reaction was quenched with Et_3N (30 ul) and diluted with DCM, washed with sat. aq. NaCl. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatograpy yielded the product (α/β = 13:1) 1.152 g, yield: 85%. *Rf* = 0.14 (pentane/DCM/EtOAc, 6:1:1, v/v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.44 – 7.08 (m, 28H), 5.53 (d, *J* = 3.5 Hz, 1H, H-1'), 5.25 (d, *J* = 12.2 Hz, 1H), 5.18 – 4.78 (m, 7H, H-3''), 4.75 – 4.57 (m, 7H, H-4, H-1, H-1''), 4.48 (s, 1H, H-5'), 4.39 – 4.26 (m, 1H, H-5''), 4.24 – 4.10 (m, 3H, H-4', H-6), 4.05 (m, 2H, H-4'', H-2'), 3.90 – 3.79 (m, 2H, H_2, H-3'), 3.67 (dd, *J* = 9.4, 2.8 Hz, 1H, H-3), 3.25 (s, 1H, H-5), 3.17 (dd, *J* = 11.2, 3.9 Hz, 1H, H-2''), 2.88 – 2.34 (m, 4H), 2.17 (s, 3H), 1.07 (s, 9H), 1.01 (s, 9H), 0.74 (d, *J* = 6.3 Hz, 3H, H-6''). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 172.0, 167.9, 156.6, 138.3, 138.1, 138.0, 136.4, 134.9, 134.8, 132.1, 128.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.4, 128.4, 128.4, 128.4, 128.3, 128.1, 128.1, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.2, 98.9 (C-1''), 92.1 (C-1'), 88.8 (C-1), 77.7 (C-3), 76.8 (C-4'), 76.2, 75.8 (C-2, C-3'), 75.7, 74.7, 74.6 (C-2', C-5), 73.3, 72.0, 70.3 (C-3''), 70.0 (C-5'), 68.3 (C-4), 67.4 (C-6), 67.1, 64.9 (C-5''), 57.8 (C-2''), 52.7 (C-4''), 38.1, 29.9, 28.1, 27.8, 27.7, 23.3, 20.7, 16.1 (C-6''). $[\alpha]^{20}_D$ = +72° (c = 1.0, $CHCl_3$). IR (neat): 651, 697, 737, 827, 969, 1029, 1092, 1149, 1262, 1363, 1714, 2111, 2858, 2931. HR-MS: [M+Na^+] Calculated for $C_{73}H_{86}N_4O_{17}SSi$: 1373.5370; found: 1373.5414.

2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-azide-3-*O*-levulinoyl-4-*N*-Cbz-6-deoxy-1-α-D-galactopyranoside}- α-D-galactopyranosyl urinate]-4,6-di-*tert*-butyl-silylidene-1-α/β-D-galactopyranoside: The title compound was obtained as decribed in the general procedure for hydrolysis of thioglycosidic bond from compound **39**. 1.642 g, yield: 90%. *Rf* = 0.07 (pentane/DCM/EtOAc, 2:1:1, v/v/v). ^{13}C NMR (101 MHz, CDCl3) δ 206.7, 172.0, 168.3, 156.8, 138.2, 137.7, 136.5, 135.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.1, 128.1, 127.9, 127.8, 127.7, 127.7, 99.0, 97.8, 92.4, 92.3, 92.0, 78.0, 77.5, 75.8, 75.5, 75.1, 74.8, 74.6, 73.5, 73.3, 73.1, 72.8, 72.1, 72.0, 71.5, 70.5, 70.4, 70.3, 70.0, 69.4, 68.4, 67.5, 67.3, 67.3, 67.2, 65.0, 58.0, 57.9, 52.8, 38.1, 30.4, 29.7, 28.1, 27.8, 27.5, 27.3, 23.3, 22.8, 20.8, 20.7, 16.2. $[\alpha]^{20}_D$ = +68° (c = 0.25, $CHCl_3$). IR (neat): 651, 697, 744, 827, 975, 1037, 1096, 1260, 1363, 1717, 2111, 2855, 2924. HR-MS: [M+Na^+] Calculated for $C_{67}H_{82}N_4O_{18}Si$: 1281.5286; found: 1281.5328.

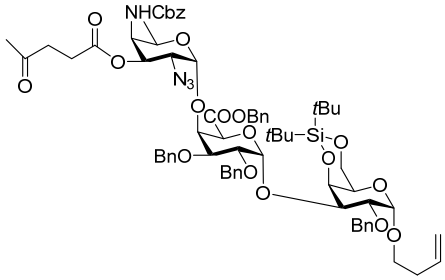


2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-azide-3-*O*-levulinoyl-4-*N*-Cbz-6-deoxy-1-α-D-galactopyranoside}- α-D-galactopyranosyl urinate]-4,6-di-*tert*-butyl-silylidene-1-*O*-(*N*-phenyl-trifluoroacetimidoyl)- α/β-D-galactopyranoside (13): The title compound was obtained as decribed in the general procedure to yield *N*-phenyl-trifluoroacetimidate donor. 1.024 g, yield: 89%. *Rf* = 0.24 (pentane/DCM/EtOAc, 5:1:1, v/v/v). ^{1}H



NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.03 (m, 27H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 2H), 6.47 (bs, 1H, H-1), 5.49 (bs, 1H, H-1'), 5.39 – 4.94 (m, 5H, H-3''), 4.85 (dd, *J* = 13.5, 7.3 Hz, 2H), 4.78 – 4.47 (m, 7H, H-1'', H-5'), 4.47 – 4.25 (m, 2H, H-5'', H-4'), 4.23 – 3.93 (m, 5H, H-6, H-4'', H-3, H-2'), 3.92 – 3.76 (m, 1H, H-3'), 3.18 (m, 1H, H-2''), 2.88 – 2.34 (m, 4H), 2.18 (d, *J* = 1.6 Hz, 3H), 1.06 – 0.93 (m, 12H), 0.88 (s, 6H), 0.82 – 0.74 (m, 3H, H-6''). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 172.0, 168.1, 168.0, 156.7, 143.7, 138.3, 138.2, 138.2, 138.1, 137.8, 136.5, 135.0, 129.3, 128.9, 128.8, 128.8, 128.7, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.3, 124.3, 119.5, 98.9, 98.8 (C-1''), 92.6, 92.4 (C-1'), 76.6 (C-4'), 76.1, 75.8, 75.7, 75.4 (C-3'), 74.9, 74.7 (C-2'), 73.5, 73.3, 73.2, 72.3, 72.2 (C-3), 72.1, 71.9, 70.3, 70.1, 70.0, 69.97 (C-3'', C-5'), 69.0, 68.2, 67.6, 67.5, 67.1, 66.8, 65.0 (C-5''), 57.8 (C-2''), 52.8 (C-4''), 38.1, 29.9, 28.8, 28.1, 27.8, 27.7, 27.3, 27.2, 23.3, 23.3, 20.8, 20.7, 16.2, 16.1 (C-6''). $[\alpha]^{20}_{D}$ = +118° (c = 1.0, $CHCl_3$). IR (neat): 651, 698, 735, 827, 857, 979, 1002, 1058, 1098, 1146, 1213, 1456, 1721, 2110, 2856, 2925. HR-MS: [M+Na^+] Calculated for $C_{75}H_{86}N_5O_{18}F_3Si$: 1452.5581; found: 1452.5610.

3-butenyl (2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-azide-3-*O*-levulinoyl-4-*N*-Cbz-6-deoxy- 1-α-D-galactopyranoside}-α-D-galactopyranosyl urinate]-4,6-di-*tert*-butyl-silylidene-1-*O*-α-D-galactopyranoside) (40): Donor



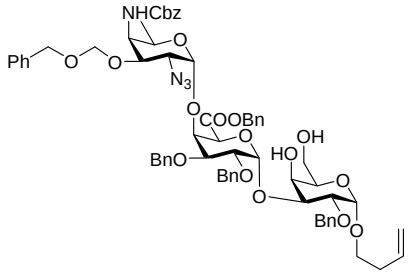
13 (1.024 g, 0.716 mmol) was co-evaporated with toluene (three times) and acceptor allylcarbinol (187 ul, 2.16 mmol) was added. The residue was dissolved in dry DCM (7.2 ml) and stirred for 30 min with activated 4A molecular sieves at room temperature. The solution was cooled to 0 °C, followed by the addition of TBSOTf (17 ul, 0.07 mmol) and the reaction was allowed to stir for 3 h at 0 °C. The reaction was quenched with Et_3N (30 ul) and diluted with DCM, washed with sat. aq. NaCl. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. Purification by column chromatograpy yielded the product (α only) 771 mg, yield: 82%. *Rf* = 0.4 (toluene/EtOAc, 4:1, v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.09 (m, 25H), 5.74 (m, 1H), 5.57 (d, *J* = 3.5 Hz, 1H, H-1'), 5.29 (d, *J* = 12.2 Hz, 1H), 5.21 – 4.95 (m, 6H, H-3''), 4.90 (dd, *J* = 10.4, 4.8 Hz, 2H), 4.78 – 4.47 (m, 9H, H-1'', H-4, H-1', H-5', H-5''), 4.35 (d, *J* = 2.9 Hz, 1H, H-4'), 4.23 – 3.86 (m, 7H, H-6, H-4'', H-2', H-3, H-3', H-2), 3.58 (m, 2H, H-5), 3.47 (dt, *J* = 9.9, 6.8 Hz, 1H), 3.22 (dd, *J* = 11.2, 3.9 Hz, 1H, H-2''), 2.90 – 2.37 (m, 4H), 2.36 – 2.24 (m, 2H), 2.17 (s, 3H), 0.99 (s, 9H), 0.83 (d, *J* = 3.0 Hz, 12H, H-6''). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 172.0, 168.1, 156.6, 138.4, 138.3, 138.2, 136.4, 135.0, 134.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.1, 127.9, 127.8, 127.8, 127.8, 127.6, 116.8, 98.9 (C-1''), 97.9 (C-1), 91.8 (C-1), 77.0 (C-4'), 75.1 (C-3'), 75.0 (C-2'), 73.5, 73.1, 72.7 (C-3), 72.4 (C-2), 71.7, 70.5 (C-3''), 70.3 (C-5'), 69.4 (C-4), 67.5, 67.4, 67.1, 67.1 (C-5), 64.9 (C-5''), 57.9 (C-2''), 52.8 (C-4''), 38.1, 33.9, 29.9, 29.8, 28.1, 27.8, 27.2, 23.3, 20.6, 16.2 (C-6''). IR (neat): 615, 698, 975, 1040, 1101, 1150, 1242, 1338, 1506, 1521, 1717, 1732, 2112, 2916, 2930. HR-MS: [M+Na^+] Calculated for $C_{71}H_{88}N_4O_{18}Si$: 1335.5755; found: 1335.5792.

3-butenyl (2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-azide-4-*N*-Cbz-6-deoxy-1-α-D-galactopyranoside}- α-D-galactopyranosyl urinate]-4,6-di-*tert*-butyl-silylidene-1-*O*-α-D-galactopyranoside) (41): The title compound was obtained by general procedure for delevulinoylation from compound **40**. 670 mg, yield: 98%. *Rf* = 0.26 (toluene/EtOAc, 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.10 (m, 25H), 5.74 (m, 1H), 5.57 (d, *J* = 3.2 Hz, 1H, H-1'), 5.29 (d, *J* = 12.1 Hz, 1H), 5.15 – 4.96 (m, 6H), 4.89 (d, *J* = 11.7 Hz, 1H), 4.76 – 4.65 (m, 4H, H-4), 4.67 – 4.54 (m, 4H, H-5'), 4.48 (d, *J* = 12.1 Hz, 1H), 4.43 – 4.28 (m, 2H, H-5'', H-4'), 4.24 – 3.82 (m, 8H, H-2', H-3', H-4''), 3.68 – 3.37 (m, 3H, H-5), 3.00 (dd, *J* = 10.7, 3.8 Hz, 1H, H-2''), 2.29 (qt, *J* = 6.8, 1.4 Hz, 2H), 1.00 (s, 9H), 0.87 (d, *J* = 11.0 Hz, 12H, H-6''). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 158.3, 138.4, 138.3, 138.2, 136.0, 135.1, 134.9, 128.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 127.9, 127.8, 127.8, 127.7, 127.5, 126.7, 125.1, 116.8, 99.1 (C-1''), 97.8 (C-1), 91.9 (C-1'), 76.7 (C-4'), 75.3, 74.71 (C-2', C-3'), 73.4, 72.9, 72.7, 72.5 (C-2, C-3), 71.5, 70.4 (C-5'), 69.5 (C-4), 68.8 (C-3''), 67.6, 67.5, 67.4, 67.1, 67.1 (C-5), 65.1 (C-5''), 60.8 (C-2''), 56.04 (C-4''), 33.9, 27.8, 27.2, 23.3, 20.6, 16.4 (C-6''). $[\alpha]^{20}_{D}$ = +122° (c = 1.0, $CHCl_3$). IR (neat): 650, 698, 737, 799, 976, 999, 1028, 1082, 1101, 1261, 1456, 1516, 1716, 2110, 2858, 2932. HR-MS: [M+Na$^+$] Calculated for $C_{66}H_{82}N_4O_{16}Si$: 1237.5387; found: 1237.5396.

3-butenyl (2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-azide-3-*O*-BOM-4-*N*-Cbz-6-deoxy- 1-α-D-galactopyranoside}-α-D-galactopyranosyl urinate]-4,6-di-*tert*-butyl-silylidene-1-*O*-α-D-galactopyranoside) (42): The title compound was obtained by general procedure for BOM protection from compound **41**. 112 mg, yield: 84%. *Rf* = 0.25 (pentane/EtOAc, 5:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.07 (m, 30H), 5.74 m, 1H), 5.57 (d, *J* = 3.4 Hz, 1H, H-1'), 5.31 (d, *J* = 12.1 Hz, 1H), 5.17 – 4.95 (m, 6H), 4.87 (dd, *J* = 10.7, 8.8 Hz, 2H), 4.81 – 4.44 (m, 12H, H-1'', H-4, H-5'), 4.41 – 4.27 (m, 2H, H-4', H-5''), 4.25 – 3.83 (m, 8H, H-6, H-3'', H-4'', H-2', H-2, H-3', H-3), 3.68 – 3.38 (m, 3H, H-5), 3.02 (dd, *J* = 10.9, 3.9 Hz, 1H, H-2''), 2.30 (qt, *J* = 6.9, 1.4 Hz, 2H), 0.99 (s, 9H), 0.86 (d, *J* = 15.3 Hz, 12H, H-6''). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.08, 156.91, 138.42, 138.33, 138.23, 137.79, 136.45, 135.05, 134.97, 128.91, 128.73, 128.66, 128.63, 128.51, 128.46, 128.45, 128.41, 128.29, 128.24, 128.08, 127.91, 127.85, 127.82, 127.77, 127.54, 116.78, 98.82 (C-1''), 97.89 (C-1), 92.51, 91.84 (C-1'), 76.71 (C-4'), 75.20 (C-2'), 74.86 (C-3'), 73.45, 73.05, 72.66, 72.46 (C-2, C-3), 71.65 (C-3''), 71.60, 70.38 (C-5'), 70.07, 69.42 (C-4), 67.53, 67.44, 67.19, 67.11 (C-5), 67.08 (C-6), 65.49 (C-5''), 59.72 (C-2''), 52.88 (C-4''), 33.93, 27.84, 27.27, 23.31, 20.66, 16.47 (C-6''). $[\alpha]^{20}_{D}$ = +119° (c =

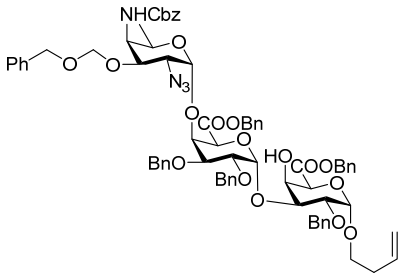
1.0, $CHCl_3$). IR (neat): 650, 696, 734, 826, 908, 997, 1036, 1457, 1507, 1653, 1700, 1717, 2109, 2857, 2931. HR-MS: [M+Na^+] Calculated for $C_{74}H_{90}N_4O_{17}Si$: 1357.5962; found: 1357.5975.

3-butenyl (2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-azide-3-*O*-BOM-4-*N*-Cbz-6-deoxy- 1-α-D-galactopyranoside}-α-D-galactopyranosyl urinate]-1-*O*-α-D-galactopyranoside) (43): The title compound was



obtained by general procedure for deprotecting of the di-*tert*-butyl silylidene ketal from compound **42**. 140 mg, yield: 94%. *Rf* = 0.34 (pentane/EtOAc, 1:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.11 (m, 30H), 5.78 (m, 1H), 5.22 (d, *J* = 12.1 Hz, 1H), 5.15 – 4.95 (m, 6H, H-1'), 4.90 (d, *J* = 9.9 Hz, 1H, N-H), 4.85 (d, *J* = 3.6 Hz, 1H, H-1), 4.82 – 4.59 (m, 7H, H-1''), 4.47 (d, *J* = 14.5 Hz, 3H, H-5'), 4.36 (d, *J* = 2.8 Hz, 1H, H-4'), 4.34 – 4.26 (m, 1H, H-5''), 4.18 – 4.00 (m, 3H, H-3'', H-4'', H-5), 3.90 (m, 3H, H-2', H-4, H-6), 3.83 – 3.70 (m, 4H, H-3', H-2, H-3, H-6), 3.65 (m, 1H), 3.45 (m, 1H), 2.98 (dd, *J* = 10.8, 4.0 Hz, 1H, H-2''), 2.42 – 2.28 (m, 2H), 0.87 (d, *J* = 6.3 Hz, 3H, H-6''). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 156.8, 138.2, 137.9, 137.7, 137.1, 136.3, 134.9, 134.8, 128.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.8, 127.4, 116.8, 98.4 (C-1''), 96.9 (C-1), 94.1 (C-1'), 92.4, 76.2 (C-3'), 75.9 (C-4'), 75.0 (C-2'), 74.8, 74.4 (C-2), 74.2 (C-3), 72.8, 72.4, 71.2 (C-3''), 70.5 (C-5'), 70.1, 68.9 (C-5), 67.5, 67.4, 67.4 (C-4), 67.0, 65.5 (C-5''), 63.4 (C-6), 59.3 (C-2''), 52.7 (C-4''), 33.8, 16.4 (C-6''). $[\alpha]^{20}_D$ = 123° (c = 0.32, $CHCl_3$). IR (neat): 698, 735, 986, 1028, 1035, 1096, 1238, 1263, 1338, 1454, 1497, 1717, 2108, 2926. HR-MS: [M+Na^+] Calculated for $C_{66}H_{74}N_4O_{17}$: 1217.4941; found: 1217.4946.

Benzyl (3-butenyl 2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-azide-3-*O*-BOM-4-*N*-Cbz-6-deoxy- 1-α-D-galactopyranoside}-α-D-galactopyranosyl urinate]-1-*O*-α- D -galactopyranosyl uronate) (44): Compound **43** (135 mg,



0.113 mmol) was dissolved in DCM/*tert*-BuOH/H_2O (2.25 ml, 4/4/1,v/v/v). The mixture was cooled to 0 °C and treated with TEMPO (3.5 mg, 0.023 mmol) and BAIB (91 g, 0.282 mmol). After stirring for overnight at 4 0 °C, $Na_2S_2O_3$ was added, the mixture was diluted with EtOAc, washed with sat. aq. NaCl and the organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was dissolved in DMF (1 ml), followed by addition of Cs_2CO_3 (37 mg, 0.113 mmol) and BnBr (27 ul, 0.226 mmol) at 0 °C. The mixture was allowed to stir overnight at room temperature, and then diluted with EtOAc, washed with sat. aq. NaCl. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (silica gel, pentane /EtOAc, 4:1→2:1, v/v) yielded 44 (124 mg, two steps yield 84%). TLC:

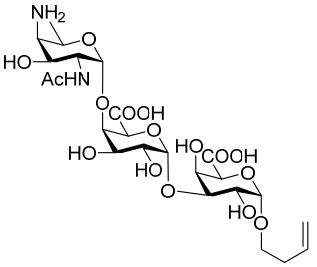
R_f = 0.82 (pentane/EtOAc, 3/2, v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.25 (m, 25H), 7.22 – 7.09 (m, 10H), 5.75 (m, 1H), 5.37 – 5.25 (m, 2H), 5.22 (d, *J* = 12.1 Hz, 1H), 5.14 – 4.95 (m, 6H), 4.95 – 4.83 (m, 3H, H-1, H-1'), 4.80 – 4.56 (m, 8H, H-1''), 4.52 – 4.38 (m, 4H, H-5, H-5'), 4.36 – 4.24 (m, 3H, H-4', H-4, H-5''), 4.10 (m, 3H, H-3, H-3'', H-4''), 3.91 – 3.71 (m, 3H, H-2', H-2, H-3'), 3.67 (m, 1H), 3.49 (m, 1H), 2.98 (dd, *J* = 10.6, 4.0 Hz, 1H, H-2''), 2.38 – 2.24 (m, 2H), 0.88 (d, *J* = 6.3 Hz, 3H, H-6''). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 167.9, 156.8, 138.0, 137.9, 137.7, 136.9, 136.3, 135.4, 134.8, 134.7, 128.9, 128.8, 128.7, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 127.9, 127.9, 127.7, 127.4, 117.0, 98.4 (C-1''), 97.2 (C-1), 94.3 (C-1'), 92.4, 76.0 (C-3'), 76.0 (C-4'), 74.3, 73.9 and 73.9 (C-3, C-2, C-2'), 72.8, 72.7, 71.3 (C-3''), 70.5 and 69.5 (C-5, C-5') 70.0, 68.0, 67.4, 67.0, 67.0, 66.8 (C-4), 65.5 (C-5''), 59.3 (C-2''), 52.7 (C-4''), 33.8, 16.4. $[\alpha]^{20}_D$ = +123° (c = 1.0, $CHCl_3$). IR (neat): 698, 737, 1039, 1099, 1236, 1456, 1506, 1521, 1717, 2108, 2326, 2934. HR-MS: [M+Na^+] Calculated for $C_{73}H_{78}N_4O_{18}$: 1321.5203; found: 1321.5215.

Benzyl (3-butenyl 2-*O*-benzyl-3-*O*-[benzyl 2,3-di-*O*-benzyl-4-*O*-{2-acetylamino-3-*O*-BOM-4-*N*-Cbz-6-deoxy- 1-α-D-galactopyranoside}-α-D-galactopyranosyl urinate]-1-*O*-α- D -galactopyranosyl uronate) (5): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.25 (m, 25H), 7.21 (bs, 5H), 7.12 (bs, 5H), 5.75 (m, 1H), 5.61 (d, *J* = 9.5 Hz, 1H, N-H), 5.40 – 5.23 (m, 2H), 5.19 – 4.96 (m, 7H), 4.95 – 4.83 (m, 4H, H-1, H-1'), 4.75 (dd, *J* = 12.3, 3.4 Hz, 2H), 4.71 – 4.57 (m, 5H), 4.50 (d, *J* = 3.9 Hz, 1H, H-1''), 4.46 – 4.35 (m, 5H, H-5, H-5'), 4.28 (m, 2H, H-4, H-5''), 4.20 – 4.02 (m, 4H, H-4', H-4'', H-3, H-2''), 3.86 – 3.61 (m, 5H, H-2, H-2', H-3', H-3''), 3.52 (m, 1H), 2.41 – 2.29 (m, 2H), 0.90 (d, *J* = 6.3 Hz, 3H, H-6''). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 168.5, 168.1, 157.1, 137.9, 137.8, 137.8, 136.8, 135.5, 134.8, 134.2, 129.1, 129.0, 129.0, 128.9, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.7, 117.1, 99.8 (C-1''), 97.1 (C-1), 94.5 (C-1'), 92.5, 77.1 (C-4'), 75.9 (C-3'), 74.4, 74.3 (C-3), 74.1 (C-2), 73.3 (C-2'), 73.0, 73.0, 72.3 (C-3''), 70.9 (C-5'), 69.6 (C-5), 68.1, 67.6, 67.3, 67.1, 66.9 (C-4), 66.2 (C-5''), 52.8 (C-4''), 48.5 (C-2''), 33.9, 23.7, 16.6 (C-6''). $[\alpha]^{20}_D$ = +85° (c = 0.5, $CHCl_3$). IR (neat): 697, 733, 1028, 1038, 1097, 1244, 1457, 1507, 1558, 1653, 1700, 2931, 3735. HR-MS: [M+Na^+] Calculated for $C_{75}H_{82}N_2O_{19}$: 1337.5404; found: 1337.5421.

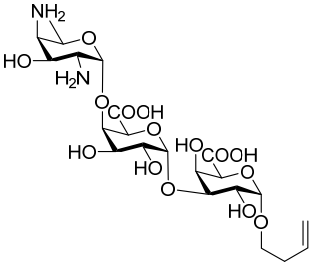
CH_2=CH$CH_2CH_2O(CH_2CH_2O)_4CH_2CH_2CH$=$CH_2$: 3-butenol (11.7 ml, 136 mmol) was added to DMF (100 ml), then NaH (60% in oil, 8.2 g, 204.24 mmol) was slowly added to the reaction mixture at 0 °C. After 15 min, $MsO(CH_2CH_2O)_4Ms$ (9.7 g, 27.71 mmol) was added to the reaction mixture then the reaction was stirred at room temperature for two days. The reaction was quenched with H_2O and then diluted with $HCCl_3$, washed with sat. aq. NaCl. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (silica gel, pentane /EtOAc, 20:1→4:1, v/v) yielded CH_2=CH$CH_2CH_2O(CH_2CH_2O)_4CH_2CH_2CH$=$CH_2$ (6.3 g, 68%). TLC: R_f = 0.6 (DCM/MeOH, 20/1, v/v). ^{1}H NMR (400 MHz, Chloroform-d) δ 5.82 (m, 2H), 5.17 – 4.96 (m, 4H), 3.71 – 3.56 (m,

16H), 3.52 (t, J = 6.9 Hz, 2H), 2.35 (qt, J = 6.9, 1.4 Hz, 4H); ^{13}C NMR (101 MHz, CDCl3) δ 135.23, 116.42, 70.73, 70.70, 70.68, 70.65, 70.22, 34.20.

ZPS-SP 1 Trisaccharide 1: The compound **5** (10.2 mg) was dissolved in THF (2 ml) and MeOH (0.75 ml), 1 M NaOH (0.8 ml) was added to reaction mixture at 0 °C. The mixture was allowed to stir 48 h at room temperature, and



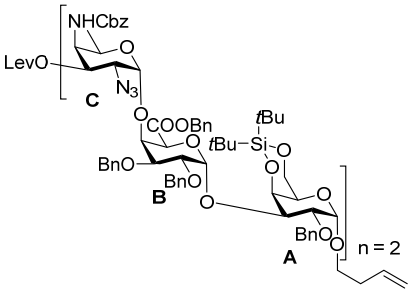
then neutralized by H_2SO_4 (1 M). Diluted with EtOAc and the water layer was extracted with EtOAc (2x20 ml). The combined organic layers were washed with brine then dried over Na_2SO_4 and concentrated in vacuo. The residue was co-evaporated with toluene (three times) for the next step. Ammonia (10 ml) was condensed at -70 °C, the residue was dissolved in THF (2 ml) and tert-butanol (0.8 ml) and slowly added to reaction flask containing ammonia. Allylcarbinol (50 ul) was added to the reaction mixture. Small pieces sodium added to the reaction mixture one by one to keep deep blue for 15 min. Then ammonia acetate (100 mg) was added to reaction mixture. The solution was allowed to come to room temperature and stirred until all of ammonia was evaporated. Then the solution was concentrated in vacuo and purification 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. The products were transformed into the sodium salts by passing an aqueous solution of the compounds over a short Dowex Na^+ column, after which the compounds were lyophilized and obtained 4.5 mg, 95% (1/1b, 14:1). ^{1}H NMR (500 MHz, Deuterium Oxide) δ 5.94 – 5.79 (m, 1H, -OCH_2CH_2CH=CH_2), 5.20 (d, *J* = 3.9 Hz, 1H, H_{B1}), 5.17 – 5.03 (m, 2H, -OCH_2CH_2CH=CH_2), 4.96 (d, *J* = 4.0 Hz, 1H, H_{A1}), 4.93 (d, *J* = 3.8 Hz, 1H, H_{C1}), 4.71 (q, *J* = 6.6 Hz, 1H, H_{C5}), 4.54 (s, 1H, H_{B5}), 4.46 (d, *J* = 3.4 Hz, 1H, H_{A4}), 4.33 (d, *J* = 3.0 Hz, 1H, H_{B4}), 4.26 (d, *J* = 1.3 Hz, 1H, H_{A5}), 4.11 (m, 2H, H_{C3}, H_{B3}), 4.04 – 3.96 (m, 2H, H_{C2}, H_{A3}), 3.93 – 3.84 (m, 2H, H_{A2}, H_{B2}), 3.74 (dt, *J* = 10.0, 6.7 Hz, 1H, -OCH_2CH_2CH=CH_2), 3.69 – 3.58 (m, 1H, -OCH_2CH_2CH=CH_2), 3.53 (d, *J* = 4.4 Hz, 1H, H_{C4}), 2.36 (q, *J* = 6.9 Hz, 2H, -OCH_2CH_2CH=CH_2), 2.08 (d, *J* = 1.1 Hz, 3H, CH_3CONH-), 1.23 (d, *J* = 6.7 Hz, 3H, H_{C6}). ^{13}C NMR (126 MHz, D_2O) δ 175.6, 175.1, 174.7, 136.0, 116.6, 98.9 (C_{C1}), 98.5 (C_{B1}), 96.2 (C_{A1}), 80.2 (C_{B4}), 75.9 (C_{A3}), 71.3 and 71.3 (C_{A5} and C_{B5}), 68.6 (C_{B3}), 68.1 (C_{B2}), 68.0 (-OCH_2CH_2CH=CH_2), 67.8 (C_{A4}), 66.6 (C_{A2}), 65.1 (C_{C3}), 63.8 (C_{C5}), 55.2 (C_{C4}), 49.3 (C_{C2}), 33.4 (-OCH_2CH_2CH=CH_2), 22.4 (CH_3CO), 15.5 (C_{C6}). $[\alpha]^{20}_D$ = +59° (c = 0.2, H_2O). HR-MS: [M+H$^+$] Calculated for $C_{24}H_{38}N_2O_{16}$: 611.2294; found: 611.2302.



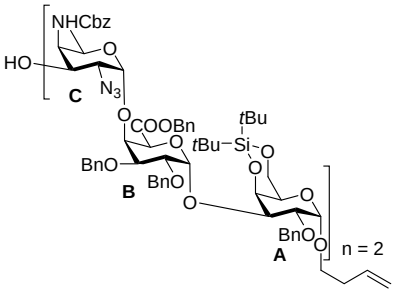
ZPS-SP 1 Trisaccharide 1b: ^{1}H NMR (400 MHz, Deuterium Oxide) δ 5.84 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H), 5.19 (d, *J* = 3.9 Hz, 1H), 5.15 (d, *J* = 4.0 Hz, 1H), 5.13 – 5.00 (m, 2H), 4.95 (d, *J* = 3.9 Hz, 1H), 4.75 (d, *J* = 12.1 Hz, 5H), 4.58 (d, *J* = 1.0 Hz, 1H), 4.44 (dd, *J* = 3.2, 1.4 Hz, 1H), 4.37 (dd, *J* = 11.5, 4.1 Hz, 2H), 4.28 (d, *J* = 1.4 Hz, 1H), 4.10 (dd, *J* = 10.6, 3.1 Hz, 1H), 3.96 (dd, *J* = 10.3, 3.1 Hz, 1H), 3.87 (dt, *J* = 10.3, 3.7 Hz, 2H), 3.72 (dt, *J* = 10.1, 6.7 Hz, 1H), 3.66 –

3.56 (m, 2H), 3.32 (dd, *J* = 11.3, 3.9 Hz, 1H), 2.33 (q, *J* = 6.5 Hz, 2H), 1.23 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, D_2O) δ 175.4, 135.9, 116.6, 98.5, 96.1, 95.8, 79.4, 75.6, 71.2, 70.8, 68.3, 67.9, 67.8, 67.6, 66.4, 63.4, 63.1, 55.0, 50.2, 33.3, 15.3.

Hexasaccharide 45: The title compound was obtained as decribed in the general procedure of glycosylation reactions for synthesis long oligosaccharides from trisaccharide donor **13** and trisaccharide acceptor **41**. 590 mg, yield: 83%. *Rf* = 0.30 (toluene/EtOAc, 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.09 (m, 50H), 5.74 (m, 1H), 5.59 (d, *J* = 3.5 Hz, 1H, $H_{B1\ or\ B'1}$), 5.54 (s, 1H, $H_{B1\ or\ B'1}$), 5.32 – 4.95 (m, 12H, $H_{A'1}$, $H_{C'3}$), 4.89 (dd, *J* = 10.7, 6.4 Hz, 4H), 4.79 (d, *J* = 2.8 Hz, 1H, H_{A4}), 4.76 – 4.38 (m, 17H, H_{C1}, $H_{C'1}$, H_{A1}, H_{B5}, H_{C5}), 4.32 – 3.83 (m, 18H, H_{B4}, $H_{B'4}$, H_{C4}, $H_{C'4}$, H_{A2}, $H_{A'2}$, H_{B2}, $H_{B'2}$, H_{C3}), 3.72 (s, 1H, H_{A5}), 3.63 – 3.52 (m, 2H, $H_{A'5}$), 3.47 (dt, *J* = 10.0, 6.8 Hz, 1H), 3.21 (dd, *J* = 11.2, 3.9 Hz, 1H, $H_{C'2}$), 3.09 (dd, *J* = 10.9, 4.0 Hz, 1H, H_{C2}), 2.88 – 2.34 (m, 4H), 2.36 – 2.24 (m, 2H), 2.16 (s, 3H), 1.02 (d, *J* = 8.6 Hz, 18H), 0.83 (m, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 171.9, 168.0, 167.8, 156.9, 156.6, 138.3, 138.3, 138.2, 138.2, 136.4, 136.2, 135.1, 134.9, 134.9, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 116.7, 98.6 and 98.4 (C_{C1} and $C_{C'1}$), 97.8 (C_{A1}), 93.1 ($C_{A'1}$), 91.6 and 91.5 (C_{B1} and $C_{B'1}$), 76.9 (C_{B4} and $C_{B'4}$), 75.4, 75.2, 74.9 and 74.6 (C_{B3} and $C_{B'3}$, C_{B2} and $C_{B'2}$), 73.4, 73.2, 73.1, 72.8, 72.6 and 72.3 (C_{A2} and C_{A3}), 71.6, 71.5, 70.6 and 70.4 (C_{B5}, $C_{C'3}$ and $C_{A'2}$), 69.3 (C_{A4}, $C_{A'4}$, and C_{C3}), 67.4, 67.4, 67.4, 67.2, 67.1, 67.0 (C_{A5}, $C_{A'5}$), 67.0, 67.0, 65.7 and 64.9 (C_{C5}, $C_{C'5}$), 59.8 and 57.9 (C_{C2}, $C_{C'2}$), 52.7 and 50.5 (C_{C4}, $C_{C'4}$), 38.0, 33.9, 27.9, 27.8, 27.2, 23.3, 23.3, 20.6, 20.6, 16.3 and 16.1 (C_{C6}, $C_{C'6}$). $[\alpha]^{20}_D$ = +135° (c = 1.0, $CHCl_3$). IR (neat): 651, 697, 736, 799, 827, 975, 997, 1028, 1036, 1080, 1090, 1146, 1237, 1260, 1456, 1507, 1715, 2108, 2856, 2929. HR-MS: [M+H$^+$] Calculated for $C_{133}H_{162}N_8O_{33}Si_2$: 2456.0856; found: 2456.0830.

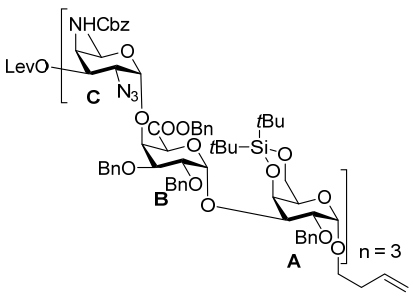


Hexasaccharide 46: The title compound was obtained by general procedure for delevulinoylation from compound **45**. 283 mg, yield: 97%. *Rf* = 0.24 (toluene/EtOAc, 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.15 (m, 50H), 5.83 – 5.66 (m, 1H), 5.59 (d, *J* = 3.4 Hz, 1H, $H_{B1\ or\ B'1}$), 5.54 (s, 1H, $H_{B1\ or\ B'1}$), 5.31 – 4.97 (m, 9H, $H_{A'1}$), 4.96 – 4.85 (m, 3H), 4.82 – 4.44 (m, 17H, H_{A4}, $H_{A'4}$, H_{C1}, $H_{C'1}$, H_{A1}, $H_{A'1}$, H_{B5}, $H_{B'5}$), 4.40 – 3.82 (m, 18H, , H_{A3}, $H_{A'3}$, H_{C5}, $H_{C'5}$, H_{B4}, $H_{B'4}$, H_{C4}, $H_{C'4}$, H_{A2}, $H_{A'2}$, H_{B2}, $H_{B'2}$, H_{C3}, $H_{C'3}$, H_{A6}, $H_{A'6}$), 3.73 (s, 1H, $H_{A5\ or\ A'5}$), 3.63 – 3.54 (m, 2H, $H_{A5\ or\ A'5}$), 3.47 (dt, *J* = 10.0, 6.7 Hz, 1H), 3.11 (m, 2H, $H_{C'2}$), 3.00 (dd, *J* = 10.6, 3.8 Hz, 1H, H_{C2}), 2.36 – 2.24 (m, 2H), 1.04 (s, 9H), 1.02 (s, 9H), 0.90 – 0.81 (m, 24H, H_{C6}, $H_{C'6}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 167.9, 158.2, 156.8, 138.3, 138.3, 138.2,

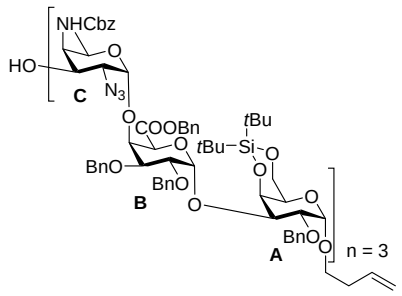


138.2, 138.1, 136.2, 135.9, 135.1, 134.8, 134.8, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.4, 116.7, 98.6 and 98.4 (C_{C1} and $C_{C'1}$), 97.8 and 93.0 (C_{A1} and $C_{A'1}$), 91.6 and 91.5 (C_{B1} and $C_{B'1}$), 76.5 (C_{B4} and $C_{B'4}$), 75.6, 74.9 and 74.5 (C_{B3} and $C_{B'3}$, C_{B2} and $C_{B'2}$), 73.3, 73.0; 72.6 and 72.2, 70.7, ($C_{A'2}$ and C_{A3}, C_{A2} and C_{A3}), 71.4, 71.4; 70.4 and 70.3 (C_{B5} and $C_{B'5}$), 69.3, 69.3 and 68.8 ($C_{A'4}$, C_{A4} and C_{C3}, $C_{C'3}$), 67.5, 67.4, 67.4, 67.3, 67.3, 67.1; 67.0 (C_{A5} and $C_{A'5}$), 66.9 (C_{A6} and $C_{A'6}$), 65.6 and 65.1 (C_{C5} and $C_{C'5}$), 60.8 and 59.8 (C_{C2} and $C_{C'2}$), 55.9 and 50.5 (C_{C4} and $C_{C'4}$), 33.8, 27.9, 27.8, 27.7, 27.2, 23.3, 23.2, 20.6, 20.6, 16.3 and 16.2 (C_{C6} and $C_{C'6}$). $[\alpha]^{20}_{D}$ = +133° (c = 1.0, $CHCl_3$). IR (neat): 650, 696, 735, 798, 826, 912, 975, 996, 1028, 1067, 1093, 1240, 1346, 1458, 1498, 1723, 2109, 2875, 2929. HR-MS [M+H$^+$] Calculated for $C_{128}H_{156}N_8O_{31}Si_2$: 2358.0488; found: 2358.0405.

Nonasaccharide 47: The title compound was obtained as decribed in the general procedure of glycosylation reactions for synthesis long oligosaccharides from trisaccharide donor **13** and hexasaccharide acceptor **46**. 358 mg, yield: 80%. *Rf* = 0.28 (toluene/EtOAc, 4:1). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 – 7.04 (m, 75H), 5.74 (m, 1H), 5.64 – 5.48 (m, 3H, 3xH_{B1}), 5.30 – 4.95 (m, 15H, 2xH_{A1}, $H_{C''3}$), 4.93 – 4.81 (m, 6H), 4.81 – 4.36 (m, 24H, 3xH_{A4}, 1xH_{A1}, 3xH_{C1}, 3xH_{B5}, 3xH_{C5}), 4.32 – 3.78 (m, 25H, 3xH_{A6}, 3xH_{C4}, 3xH_{B4}, 3xH_{B2}, 3xH_{B3}, 3xH_{C5}, 3xH_{A2}, 3xH_{A3}), 3.71 (d, *J* = 9.0 Hz, 2H, 2xH_{A5}), 3.66 – 3.54 (m, 2H, H_{A5}), 3.47 (dt, *J* = 10.0, 6.7 Hz, 1H), 3.19 (dd, *J* = 11.2, 3.9 Hz, 1xH_{C2}), 3.09 (dt, *J* = 10.3, 5.0 Hz, 2H, 2xH_{C2}), 2.78 (m, 1H), 2.68 (m, 1H), 2.56 (m, 1H), 2.43 (m, 1H), 2.29 (q, *J* = 7.0 Hz, 2H), 2.15 (d, *J* = 11.7 Hz, 3H), 1.05 (s, 9H), 1.03 (s, 9H), 1.02 (s, 9H), 0.88 (d, *J* = 7.3 Hz, 3H, 1xH_{C6}), 0.86 (s, 9H), 0.83 (d, *J* = 5.3 Hz, 21H, 1xH_{C6}), 0.76 (d, *J* = 6.4 Hz, 3H, 1xH_{C6}). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.4, 171.9, 168.0, 167.9, 167.7, 156.9, 156.6, 138.3, 138.3, 138.3, 138.3, 138.2, 138.2, 136.4, 136.2, 135.2, 135.0, 134.9, 134.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.4, 116.7; 98.5, 98.4 and 98.0 (3xC_{C1}); 97.8 (1xC_{A1}), 93.1 (2xC_{A1}); 91.7, 91.6 and 91.5 (3xC_{B1}); 76.9, 76.8 and 76.8 (3xC_{B4}); 75.5, 75.4, 75.2, 75.0, 75.0 and 74.6 (3xC_{B2}, 3xC_{B3}); 73.4, 73.3, 73.2, 73.1, 72.8; 72.8, 72.6 and 72.4 (1xC_{A2}, 3xC_{A3}); 71.6, 71.5; 70.9, 70.7, 70.6, 70.4 and 70.4 (3xC_{B5}, 2xC_{A2}, 1xC_{C3}); 69.5, 69.4, 69.4 and 69.3 (3xC_{A4}, 2xC_{C3}); 67.5, 67.4, 67.2, 67.2, 67.1, 67.0, 66.9; 67.1, 65.7 and 64.8 (3xC_{C5}); 60.0, 59.9 and 57.9 (3xC_{C2}); 52.7 and 50.6 (3xC_{C4}), 38.0, 33.9, 28.0, 27.9, 27.8, 27.3, 27.2, 27.2, 23.3, 23.30, 23.3, 20.6, 20.6, 16.3 (1xC_{C6}), 16.2 (1xC_{C6}), 16.1 (1xC_{C6}). $[\alpha]^{20}_{D}$ = +120° (c = 0.6, $CHCl_3$). IR (neat): 697, 735, 826, 976, 998, 1036, 1232, 1457, 1507, 1653, 1700, 1717, 2108, 2859, 2923. HR-MS: [M+2H$^+$] Calculated for $C_{195}H_{236}N_{12}O_{48}Si_3$: 1799.7924; found: 1799.7880.

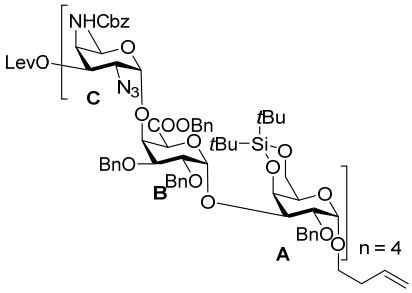


Nonasaccharide 48: The title compound was obtained by the general procedure for delevulinoylation from



compound **47**. 317 mg, yield: 89%. *Rf* = 0.4 (toluene/EtOAc, 3:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.13 (m, 75H), 5.84 – 5.68 (m, 1H), 5.65 – 5.49 (m, 3H, 3xH_{B1}), 5.29 – 4.96 (m, 15H, 2xH_{A1}), 4.89 (m, 5H), 4.81 – 4.43 (m, 25H, 3xH_{A4}, 1xH_{A1}, 3xH_{B5}, 3xH_{C1}), 4.41 – 3.79 (m, 23H, 3xH_{C5}, 3xH_{A6}, 3xH_{C4}, 3xH_{B4}, 3xH_{B2}, 3xH_{B3}, 3xH_{C5}, 3xH_{A2}, 3xH_{A3}), 3.72 (d, *J* = 3.0 Hz, 2H, 2xH_{A5}), 3.64 – 3.54 (m, 2H, 1xH_{A5}), 3.47 (m, 1H), 3.12 (m, 2H, 2xH_{C2}), 2.99 (dd, *J* = 10.6, 3.8 Hz, 1H, 1xH_{C2}), 2.30 (m, 2H), 1.05 (s, 9H), 1.04 (s, 9H), 1.02 (s, 9H), 0.91 – 0.78 (m, 36H, 3xH_{C6}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 167.9, 167.6, 158.2, 156.8, 138.3, 138.3, 138.3, 138.2, 138.1, 136.2, 135.9, 135.1, 134.9, 134.8, 134.8, 128.8, 128.7, 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 116.7; 98.5, 98.3, 98.0 and 97.8 (1xC_{A1}, 3xC_{C1}), 93.0 (2xC_{A1}); 91.6, 91.5 and 91.3 (3xC_{B1}); 76.8 and 76.4 (3xC_{B4}); 75.7, 75.3, 74.9 and 74.5 (3xC_{B2}, 3xC_{B3}), 73.3, 73.3, 73.0, 72.7; 71.4, 71.4, 71.3; 72.5, 72.2, 70.8, 70.5, 70.4, 70.3, 70.3, 69.5, 69.5, 69.4, 69.3 and 68.8 (3xC_{B5}, 3xC_{A2}, 3xC_{A3}, 3xC_{A4}, 3xC_{C3}); 67.5, 67.4, 67.3, 67.2, 67.2, 67.1, 67.0, 66.9, 66.9 (3xC_{A5}, 3xC_{A6}); 65.6 and 65.0 (3xC_{C5}); 60.9, 60.0 and 59.9 (3xC_{C2}); 55.9 and 50.5 (3xC_{C4}), 33.8, 27.9, 27.9, 27.8, 27.3, 27.16, 27.1, 23.3, 23.3, 23.2, 20. 6, 20.5, 16.3 (1xC_{C6}), 16.2 (1xC_{C6}), 16.2 (1xC_{C6}). $[\alpha]^{20}_{D}$ = +141° (c = 1.0, $CHCl_3$). IR (neat): 696, 736, 799, 976, 993, 1028, 1097, 1419, 1457, 1507, 1560, 1653, 1700, 1717, 2106, 2857, 2924. HR-MS [M+2H^{+}] Calculated for $C_{190}H_{230}N_{12}O_{46}Si_3$: 1750.7740; found: 1750.7676.

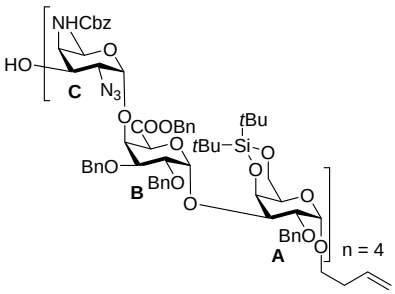
Dodecasaccharide 49: The title compound was obtained by the general procedure of glycosylation reactions for



synthesis long oligosaccharides from trisaccharide donor 13 and nonasaccharide acceptor **48**. 101 mg, yield: 72%. *Rf* = 0.5 (toluene/EtOAc, 3:1). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.10 (m, 100H), 5.74 (m, 1H), 5.60 – 5.50 (m, 4H, 4xH_{B1}), 5.31 – 4.97 (m, 19H, 3xH_{A1}, $H_{C'''3}$), 4.95 – 4.81 (m, 8H), 4.80 – 4.37 (m, 29H, 4xH_{A4}, 1xH_{A1}, 4xH_{C1}, 4xH_{B5}, 1xH_{C5}), 4.32 – 3.78 (m, 29H, 4xH_{A6}, 4xH_{C4}, 4xH_{B4}, 4xH_{B2}, 4xH_{B3}, 3xH_{C5}, 4xH_{A2}, 4xH_{A3}), 3.75 – 3.65 (m, 3H, 3xH_{A5}), 3.63 – 3.53 (m, 2H, 1xH_{A5}), 3.47 (m, 1H), 3.19 (dd, *J* = 11.2, 3.9 Hz, 1H, 1xH_{C2}), 3.14 – 3.02 (m, 3H, 3xH_{C2}), 2.78 (m, 1H), 2.68 (m, 1H), 2.62 – 2.51 (m, 1H), 2.43 (m, 1H), 2.29 (m, 2H), 2.16 (s, 3H), 1.10 – 0.97 (m, 36H), 0.93 – 0.73 (m, 48H, 4xH_{C6}). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.5, 172.0, 168.0, 167.8, 156.9, 156.9, 156.6, 139.4, 138.4, 138.4, 138.3, 138.3, 138.3, 138.2, 138.2, 136.5, 136.3, 136.2, 135.9, 135.2, 135.0, 134.9, 134.9, 134.8, 129.1, 128.9, 128.9, 128.8, 128.8, 128.8, 128.8, 128.7, 128.7, 128.7, 128.7, 128.6, 1286, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3,

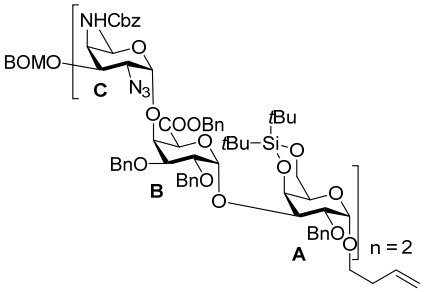
128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.3, 125.4, 124.9, 116.8, 114.2; 98.5, 98.4, 98.0 and 97.9 (1xC_{A1}, 4xC_{C1}); 93.1 and 93.1 (3xC_{A1}); 91.7, 91.6, 91.5 and 91.5 (1xC_{A1}, 3xC_{C1}); 77.0, 76.9, 76.8 and 76.7 (4xC_{B4}); 75.5, 75.4, 75.4, 75.2, 75.0, 74.9 and 74.6 (4xC_{B2}, 4xC_{B3}); 73.5, 73.4, 73.4, 73.3, 73.2, 72.9, 72.8, 71.7, 71.5, 71.5 (Bn); 72.9, 72.6, 72.3, 70.8, 70.6, 70.5, 70.5, 70.4, 70.4, 69.7, 69.6, 69.5, 69.4 and 69.4 (4xC_{B5}, 4xC_{A2}, 4xC_{A3}, 4xC_{A4}, 4xC_{C3}); 67.5, 67.5, 67.4, 67.4, 67.3, 67.2, 67.1, 67.0, 67.0 (4xC_{A6}, Bn); 67.4, 67.3 and 67.1 (4xC_{A5}); 65.7, 65.7, 65.6 and 64.9 (4xC_{C5}); 60.1, 60.0 and 60.0 (4xC_{C2}); 58.0, 52.7 and 50.6 (4xC_{C4}); 38.1, 33.9, 32.0, 30.4, 29.8, 28.0, 28.0, 27.9, 27.9, 27.3, 27.2, 27.2, 23.4, 23.4, 23.4, 23.3, 22.8, 20.7, 20.6; 16.3 and 16.3 (4xC_{C6}). $[\alpha]^{20}_{D}$ = +141° (c = 1.0, $CHCl_3$). IR (neat): 668, 698, 799, 827, 1036, 1096, 1457, 1507, 1560, 1653, 1700, 1734, 2108, 2918. HR-MS: [M+2H$^+$] Calculated for $C_{257}H_{310}N_{16}O_{63}Si_4$: 2371.0384; found: 2371.0382.

Dodecasaccharide 50: The title compound was obtained by the general procedure for delevulinoylation from compound **49**. 358 mg, yield: 91%. *Rf* = 0.4 (toluene/EtOAc, 3:1). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 – 7.09 (m, 100H), 5.74 (m, 1H), 5.61 – 5.48 (m, 4H, 4xH_{B1}), 5.32 – 4.96 (m, 18H, 3xH_{A1}), 4.95 – 4.81 (m, 7H), 4.79 – 4.42 (m, 28H, 4xH_{A4}, 1xH_{A1}, 4xH_{C1}, 4xH_{B5}), 4.40 – 3.78 (m, 29H, 4xH_{A6}, 4xH_{C4}, 4xH_{B4}, 4xH_{B2}, 4xH_{B3}, 4xH_{C5}, 4xH_{A2}, 4xH_{A3}), 3.70 (d, *J* = 7.5 Hz, 3H, 3xH_{A5}), 3.64 – 3.53 (m, 2H, 1xH_{A5}), 3.47 (m, 1H), 3.16 – 3.04 (m, 3H, 3xH_{C2}), 2.96 (dd, *J* = 10.6, 3.8 Hz, 1H, 1xH_{C2}), 2.34 – 2.23 (m, 2H), 1.03 (m, 36H), 0.93 – 0.71 (m, 48H, 4xH_{C6}).

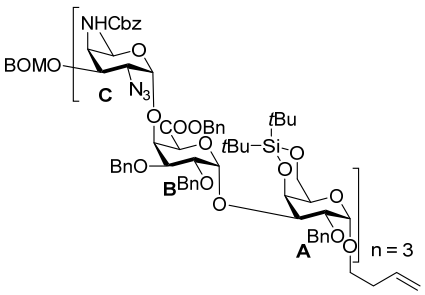


^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 167.8, 158.3, 156.9, 138.5, 138.4, 138.4, 138.4, 138.3, 138.3, 138.2, 136.3, 136.0, 135.2, 135.0, 135.0, 135.0, 134.9, 128.9, 128.8, 128.8, 128.8, 128.8, 128.7, 128.7, 128.7, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.5, 116.8; 98.6, 98.5, 98.0, 98.0 and 97.9 (1xC_{A1}, 4xC_{C1}); 93.1 and 93.1 (3xC_{A1}); 91.8, 91.7, 91.6 and 91.6 (4xC_{B1}); 77.0, 76.9, 76.8 and 76.5 (4xC_{B4}); 75.9, 75.6, 75.5, 75.1, 75.0, 75.0 and 74.6 (4xC_{B2}, 4xC_{B3}); 73.5, 73.4, 73.2, 73.2, 72.8, 72.8, 71.6, 71.5 (Bn); 72.9, 72.7, 72.4, 71.1, 70.8, 70.8, 70.5, 70.5, 70.4, 69.7, 69.6, 69.6, 69.5, 69.4, 69.4 and 69.1 (4xC_{B5}, 4xC_{A2}, 4xC_{A3}, 4xC_{A4}, 4xC_{C3}); 67.6, 67.6, 67.5, 67.4, 67.4, 67.3, 67.3, 67.2; 67.0, 67.0 (4xC_{A6} and Bn); 67.4 and 67.1 (4xC_{A5}); 65.7, 65.7 and 65.1 (4xC_{C5}); 61.1, 60.1 and 60.0 (4xC_{C2}); 60.0 and 50.6 (4xC_{C4}); 33.9, 28.0, 28.0, 28.0, 27.9, 27.3, 27.3, 23.4, 23.4, 23.4, 20.7, 20.7, 20.7, 16.4 and 16.3 (4xC_{C6}). $[\alpha]^{20}_{D}$ = +120° (c = 1.0, $CHCl_3$). IR (neat): 698, 738, 827, 976, 1028, 1099, 1457, 1507, 1560, 1653, 1684, 1700, 2918, 3675.

Hexasaccharide 51: The title compound was obtained by the general procedure for BOM protection from compound **46**. 101 mg, yield: 81%. *Rf* = 0.43 (toluene/EtOAc, 5:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.07 (m, 55H), 5.74 (m, 1H), 5.59 (d, *J* = 3.5 Hz, 1H, $H_{B1\ or\ B'1}$), 5.53 (bs, 1H, $H_{B1\ or\ B'1}$), 5.29 – 4.44 (m, 35H, $2xH_{C1}$, 2x H_{A1}, $2xH_{B5}$, $2xH_{A4}$), 4.36 – 3.82 (m, 21H, $2xH_{B4}$, $2xH_{C5}$, $2xH_{C4}$, $2xH_{C3}$, $2xH_{A2}$, $2xH_{A3}$, $2xH_{B2}$, $2xH_{B3}$, $2xH_{A6}$), 3.72 (s, 1H, $1xH_{A5}$), 3.63 – 3.54 (m, 2H, $1xH_{A5}$), 3.47 (m, 1H), 3.12 (dd, *J* = 10.9, 4.0 Hz, 1H, $1xH_{C2}$), 3.02 (dd, *J* = 10.8, 4.0 Hz, 1H, $1xH_{C2}$), 2.29 (q, *J* = 6.9 Hz, 2H), 1.03 (s, 9H), 1.01 (s, 9H), 0.91 – 0.78 (m, 24H, $2xH_{C6}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 167.9, 156.9, 156.9, 138.4, 138.3, 138.3, 138.2, 137.8, 136.4, 136.3, 135.2, 134.9, 128.9, 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.0, 128.0, 128.0, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 116.8; 98.5, 98.4 and 97.9 ($1xC_{A1}$ and $2xC_{C1}$); 93.1 ($1xC_{A1}$); 92.5; 91.8 and 91.7 ($2xC_{B1}$); 77.0 and 76.5 ($2xC_{B4}$); 75.6, 75.1, 75.0 and 74.6 ($2xC_{B2}$ and $2xC_{B3}$); 73.4, 73.2, 73.1 and 72.8 (Bn); 72.8, 72.7, 72.4 and 71.8 ($2xC_{A2}$ and $2xC_{A3}$); 71.6 and 70.0 (Bn); 71.6, 70.8, 70.4, 70.4, 70.0, 69.5, 69.4 and 69.3 ($2xC_{A4}$, $2xC_{B5}$ and $2xC_{C3}$); 67.5, 67.4, 67.4, 67.3, 67.2, 67.1, 67.0 and 67.0 (Bn, $2xC_{A5}$ and $2xC_{A6}$); 65.7 and 65.4 ($2xC_{C5}$); 59.9 and 59.8 ($2xC_{C2}$), 52.9 and 50.6 ($2xC_{C4}$); 41.0, 33.9, 28.0, 27.9, 27.3, 24.0, 23.3, 20.6, 20.6, 16.4 and 16.3 ($2xC_{C6}$). $[\alpha]^{20}_{D}$ = +125° (c = 1.0, $CHCl_3$). IR (neat): 651, 697, 733, 799, 825, 862, 907, 913, 917, 976, 996, 1027, 1035, 1093, 1263, 1387, 1457, 1507, 1653, 1700, 2108, 2853, 2932. HR-MS [M+H$^+$] Calculated for $C_{133}H_{162}N_8O_{33}Si_2$: 2478.1063; found: 2478.0825.

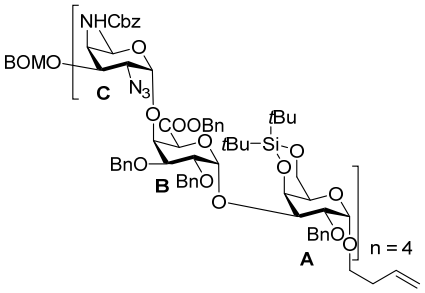


Nonasaccharide 52: The title compound was obtained by the general procedure for BOM protection from compound **48**. 147 mg, yield: 89%. *Rf* = 0.4 (toluene/EtOAc, 4:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.08 (m, 80H), 5.74 (m, 1H), 5.62 – 5.49 (m, 3H, $3xH_{B1}$), 5.29 – 4.93 (m, 13H, $2xH_{A1}$), 4.92 – 4.41 (m, 31H, $3xH_{C1}$, $1xH_{A1}$, $3xH_{B5}$, $3xH_{A4}$), 4.36 – 3.80 (m, 31H, $3xH_{B4}$, $3xH_{C5}$, $3xH_{C4}$, $3xH_{C3}$, $3xH_{A2}$, $3xH_{A3}$, $3xH_{B2}$, $3xH_{B3}$, $3xH_{A6}$), 3.70 (d, *J* = 2.3 Hz, 2H, $2xH_{A5}$), 3.64 – 3.53 (m, 2H, $1xH_{A5}$), 3.47 (m, 1H), 3.11 (dt, *J* = 10.9, 3.9 Hz, 2H, $2xH_{C2}$), 3.01 (dd, *J* = 10.8, 3.9 Hz, 1H, $1xH_{C2}$), 2.29 (q, *J* = 6.9 Hz, 2H), 1.04 (s, 9H), 1.02 (s, 9H), 1.01 (s, 9H), 0.90 – 0.77 (m, 36H, $3xH_{C6}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 167.9, 167.8, 156.9, 156.9, 138.4, 138.4, 138.4, 138.3, 138.2, 137.8, 136.5, 136.3, 136.3, 135.2, 135.0, 134.9, 134.9, 129.0, 128.9, 128.8, 128.8, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 116.8; 98.5, 98.3, 98.1 and 97.9 ($1xC_{A1}$ and $3xC_{C1}$); 93.1 ($2xC_{A1}$), 92.5 (BOM), 91.7, 91.5 and 91.4 ($3xC_{B1}$); 77.0 and 76.5 ($3xC_{B4}$); 75.6, 75.4, 75.2, 75.0, 74.9 and 74.6 ($3xC_{B2}$ and $3xC_{B3}$), 73.5, 73.4, 73.3, 73.2, 72.9 (Bn); 72.8,



72.6, 72.3, 71.9 (3xC_{A2} and 3xC_{A3}); 71.5, 71.5, 70.0 (Bn); 70.7, 70.5, 70.4, 69.6, 69.4, 69.4 (3xC_{A4}, 3xC_{B5} and 3xC_{C3}); 67.5, 67.5, 67.3, 67.2, 67.1, 67.1, 67.0, 67.0 (Bn, 3xC_{A5} and 3xC_{A6}); 65.7 and 65.4 (3xC_{C5}); 60.1, 60.0 and 59.8 (2xC_{C2}); 53.9, 52.9 and 50.6 (3xC_{C4}); 33.9, 28.0, 28.0, 27.9, 27.3, 27.2, 23.4, 23.4, 20.7, 20.6; 16.4, 16.3 and 16.3 (3xC_{C6}). $[\alpha]^{20}_{D}$ = +135° (c = 0.84, $CHCl_3$). IR (neat): 698, 741, 799, 827, 1037, 1101, 1457, 1507, 1560, 1653, 1700, 1717, 1734, 2108, 2875, 2924, 3675.

Dodecasaccharide 53: The title compound was obtained by the general procedure for BOM protection from compound **50**. 43 mg, yield: 84%. *Rf* = 0.31 (toluene/EtOAc, 4:1). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 – 7.09 (m, 105H), 5.73 (m, 1H), 5.61 – 5.49 (m, 4H, 4xH_{B1}), 5.32 – 4.93 (m, 19H, 3xH_{A1}), 4.92 – 4.38 (m, 41H, 4xH_{C1}, 1xH_{A1}, 4xH_{B5}, 4xH_{A4}), 4.36 – 3.76 (m, 40H, 4xH_{B4}, 4xH_{C5}, 4xH_{C4}, 4xH_{C3}, 4xH_{A2}, 4xH_{A3}, 4xH_{B2}, 4xH_{B3}, 4xH_{A6}), 3.69 (d, *J* = 6.1 Hz, 3H, 3xH_{A5}), 3.60 – 3.54 (m, 2H, 1xH_{A5}), 3.46 (m, 1H), 3.10 (ddq, *J* = 12.8, 9.4, 4.0 Hz, 3H, 3xH_{C2}), 3.00 (dd, *J* = 10.8, 3.9 Hz, 1H, 1xH_{C2}), 2.28 (q, *J* = 7.0 Hz, 2H), 1.10 – 0.95 (m, 36H), 0.93 – 0.75 (m, 48H, 4xH_{C6}). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 167.8, 167.8, 157.0, 156.9, 156.9, 138.4, 138.4, 138.4, 138.3, 138.3, 138.2, 137.8, 136.5, 136.3, 136.3, 135.2, 135.0, 134.9, 134.9, 134.8, 129.0, 128.9, 128.9, 128.8, 128.8, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.51, 127.5, 116.84; 98.5, 98.33, 98.0, 97.9 and 97.9 (1xC_{A1} and 4xC_{C1}); 93.1 (3xC_{A1}); 92.5 (BOM), 91.7, 91.6, 91.5 and 91.5 (4xC_{B1}); 77.1, 76.8 and 76.5 (4xC_{B4}); 75.6, 75.4, 75.4, 75.1, 75.0, 74.9 and 74.6 (4xC_{B2} and 4xC_{B3}); 73.5, 73.5, 73.3, 73.2, 72.9, 72.9 (Bn); 72.6, 72.3, 71.8 (4xC_{A2} and 4xC_{A3}); 71.6, 71.5, 70.0 (Bn); 70.8, 70.6, 70.5, 70.5, 70.4, 69.7, 69.7, 69.4, 69.4, 69.4 (4xC_{A4}, 4xC_{B5} and 4xC_{C3}); 67.5, 67.5, 67.4, 67.3, 67.2, 67.1, 67.1, 67.0, 67.0 (Bn, 4xC_{A5} and 4xC_{A6}); 65.7, 65.7, 65.7, 65.4 (4xC_{C5}); 60.1, 60.1, 60.0 and 59.8 (4xC_{C5}); 52.9 and 50.6 (4xC_{C5}); 33.9, 28.1, 28.0, 28.0, 27.99, 27.9, 27.3, 27.3, 27.2, 23.4, 23.4, 23.4, 23.4, 20.7, 20.6; 16.3 (4xC_{C6}). $[\alpha]^{20}_{D}$ = +128° (c = 1.0, $CHCl_3$). IR (neat): 651, 696, 734, 799, 826, 976, 996, 1028, 1034, 1095, 1260, 1457, 1507, 1653, 1700, 1717, 2108, 2857, 2930, 3675. HR-MS [M+2H$^+$] Calculated for $C_{260}H_{312}N_{16}O_{62}Si_4$: 2382.0488; found: 2382.0444.

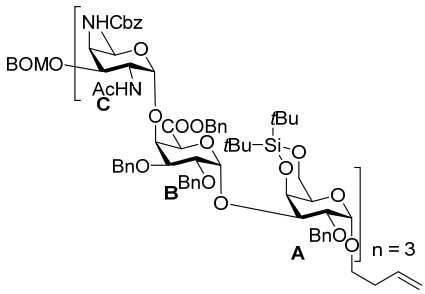


Hexasaccharide 54: The title compound was obtained by the general procedure for transferred azide into acetylamino reactions for long oligosaccharides from compound **51**. 113 mg, yield: 93%. *Rf* = 0.75 (DCM/MeOH, 20:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.04 (m, 55H), 5.83 – 5.67 (m, 2H), 5.57 (d, *J* = 3.3 Hz, 1H, 1xH_{B1}), 5.46 (d, *J* = 3.2 Hz, 1H, 1xH_{B1}), 5.21 (d, *J* = 11.6 Hz, 1H), 5.17 – 4.83 (m, 14H, 1xH_{A1}), 4.75 – 4.37 (m, 23H, 2xH_{C1}, 1xH_{A1}, 2xH_{B5}, 2xH_{A4}), 4.25 (m, 1H, 1xH_{C5}), 4.22 – 3.82 (m, 20H, 2xH_{B4}, 1xH_{C5}, 2xH_{C4}, 2xH_{A2}, 2xH_{A3}, 2xH_{B2}, 2xH_{B3}, 2xH_{A6}), 3.77 (dd, *J* = 11.3, 4.2 Hz, 1H, 1xH_{C3}), 3.65 – 3.56 (m, 3H, 1xH_{C3}, 1xH_{A5}), 3.54 – 3.43 (m, 2H, 1xH_{A5}), 2.35 – 2.25 (m, 2H), 2.11 (s, 3H), 2.01 (s, 3H), 1.04 (s, 9H), 1.03 (s, 9H), 0.89 (s, 9H), 0.89 – 0.87 (m, 3H, 1xH_{C6}), 0.85 (s, 9H), 0.76 (d, *J* = 6.2 Hz, 3H, 1xH_{C6}). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 170.4, 168.9, 168.6, 157.1, 138.5, 138.3, 138.2, 138.1, 138.1, 137.9, 136.7, 136.6, 135.0, 134.8, 134.1, 129.3, 129.1, 129.1, 129.0, 129.0, 128.8, 128.7, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 116.8; 100.1 and 99.9 (2xC_{C1}); 97.7 and 92.8 (2xC_{A1}); 92.6 (BOM), 92.9 and 91.3 (2xC_{B1}); 77.6 (2xC_{B4}); 73.3, 73.2, 73.1, 72.0, 71.5, 69.6 (Bn); 75.9, 75.1, 74.4, 74.0, 72.8, 72.6, 72.3, 71.4, 70.6, 69.7, 69.2 (3xC_{B2}, 3xC_{B3}, 2xC_{A4}, 2xC_{B5} and 2xC_{C3}, 2xC_{A2} and 2xC_{A3}); 67.7, 67.6, 67.3, 67.2, 67.2, 67.0, 66.6 (Bn, 2xC_{A5} and 2xC_{A6}); 66.5, 66.0 (2xC_{C5}); 53.0 and 51.4 (2xC_{C4}); 48.7 and 48.5 (2xC_{C2}); 34.0, 28.0, 27.8, 27.4, 27.3, 27.3, 23.8, 23.4, 23.4, 20.7; 16.5 and 16.4 (2xC_{C6}). $[\alpha]^{20}_{D}$ = +113° (c = 1.0, $CHCl_3$). IR (neat): 695, 741, 829, 1038, 1103, 1419, 1457, 1507, 1558, 1653, 1700, 1718, 1734, 2930, 3675.

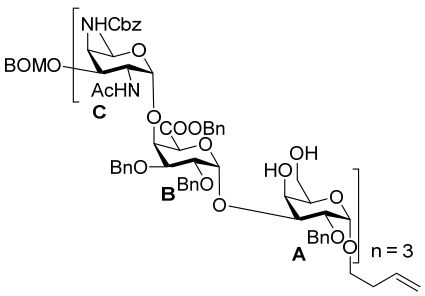
Hexasaccharide 10: The title compound was obtained by the general procedure for deprotecting of the di-*tert*-butyl silylidene ketal from compound **54**. 87 mg, yield: 91%. *Rf* = 0.3 (DCM/MeOH, 20:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.09 (m, 52H), 7.04 – 6.92 (m, 3H), 5.98 (d, *J* = 9.1 Hz, 1H, N-H), 5.85 – 5.72 (m, 1H), 5.69 (d, *J* = 9.5 Hz, 1H, N-H), 5.28 (d, *J* = 3.7 Hz, 1H, 1xH_{B1}), 5.20 – 4.39 (m, 31H, 1xH_{B1}, 2xH_{A1}, 1xH_{B5}, 2xH_{C1}), 4.33 – 3.56 (m, 23H, 1xH_{B5}, 2xH_{B4}, 2xH_{C5}, 2xH_{C4}, 2xH_{C2}, 2xH_{A2}, 2xH_{A3}, 2xH_{B2}, 2xH_{B3}, 2xH_{A6}, 2xH_{A4}, 2xH_{A5}), 3.47 (m, 1H), 2.35 (q, *J* = 6.8 Hz, 2H), 2.10 (s, 3H), 2.06 (s, 3H), 0.84 (dd, *J* = 6.3, 3.5 Hz, 6H, 2xH_{C6}). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 170.8, 168.1, 168.0, 157.1, 157.0, 138.5, 138.2, 138.0, 137.8, 137.8, 137.3, 137.0, 136.5, 136.5, 134.9, 134.4, 134.3, 129.1, 129.0, 129.0, 128.9, 128.9, 128.9, 128.8, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.5, 116.9, 116.9; 99.9 and 99.2 (2xC_{C1}); 96.9 (1xC_{A1}), 94.4 and 94.3 (1xC_{A1}, 1xC_{B1}), 92.6 (1xC_{B1}); 77.1 and 76.4 (2xC_{B4}, 2xC_{B3}); 74.8, 74.6, 74.3, 74.2, 72.4 (2xC_{B2}, 2xC_{A2}, 2xC_{A3}); 74.7, 73.0, 72.6, 72.1 (Bn); 70.8 (Bn), 70.7, 69.9,

69.6 (2xC_{B5}, 2xC_{C3}); 68.6 (Bn), 67.7, 67.6, 67.0, 66.6 (Bn); 67.4, 66.8, 66.7, 66.6 (2xC_{A4}, 2xC_{A5}), 66.1 (2xC_{C5}); 63.5, 63.3 (2xC_{A6}); 53.9, 52.9 (2xC_{C4}); 51.2, 48.5 (2xC_{C2}); 33.9, 29.4, 23.8, 23.7; 16.6, 16.5 (2xC_{C6}). $[\alpha]^{20}_{D}$ = +160° (c = 1.0, $CHCl_3$). IR (neat): 698, 735, 1028, 1040, 1094, 1457, 1507, 1558, 1653, 1717, 2930, 3675. HR-MS [M+H^+] Calculated for $C_{124}H_{140}N_4O_{34}$: 2229.9422; found: 2229.9382.

Nonasaccharide 55: The title compound was obtained by general procedure for transferred azide into acetylamino reactions for long oligosaccharides from compound **52**. 40 mg, yield: 88%. *Rf* = 0.25 (DCM/MeOH, 30:1). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.00 (m, 55H), 5.80 (d, *J* = 9.5 Hz, 1H, N-H), 5.78 – 5.70 (m, 1H), 5.65 (d, *J* = 9.5 Hz, 1H, N-H), 5.56 (d, *J* = 3.4 Hz, 1H, 1xH_{B1}), 5.52 (d, *J* = 2.7 Hz, 1H, 1xH_{B1}), 5.45 (d, *J* = 3.3 Hz, 1H, 1xH_{B1}), 5.29 – 4.78 (m, 21H, 2xH_{A1}), 4.76 – 4.32 (m, 32H, 3xH_{C1}, 1xH_{A1}, 3xH_{B5}, 3xH_{A4}), 4.28 – 3.36 (m, 43H, 3xH_{B4}, 3xH_{C5}, 3xH_{C4}, 3xH_{C2}, 3xH_{A2}, 3xH_{A3}, 3xH_{B2}, 3xH_{B3}, 3xH_{A6}, 3xH_{A5}), 2.30 (q, *J* = 6.8 Hz, 2H), 2.11 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.03 (d, *J* = 4.1 Hz, 27H), 0.89 (s, 9H), 0.86 (s, 9H), 0.83 (s, 9H), 0.75 (dd, *J* = 6.2, 3.3 Hz, 6H, 3xH_{C6}). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 170.6, 170.3, 169.2, 168.7, 157.1, 157.0, 138.5, 138.3, 138.2, 138.1, 138.0, 137.9, 136.8, 136.6, 136.5, 135.0, 134.7, 134.5, 134.0, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.4, 116.9; 100.5, 100.1, 100.0 (3xC_{C1}); 97.7, 94.7, 94.2 (3xC_{A1}); 92.7 (BOM); 92.6, 91.3, 91.2 (3xC_{B1}); 78.2, 77.7 (3xC_{B4}); 75.8, 75.7, 74.4, 74.1, 73.9; (3xC_{B2}, 3xC_{B3}, 3xC_{A2}, 3xC_{A3}) 73.3, 73.2, 72.8, 73.1, 72.7 (Bn); 72.6, 72.2, 71.9, 71.6, 71.5, 71.4, 70.8, 70.6, 69.6, 69.5, 69.1, 69.0 (Bn, 3xC_{A4}, 3xC_{B5} and 3xC_{C3}); 68.0, 67.8, 67.5, 67.3, 67.2, 67.1, 67.0, 66.6, 66.5, 66.4, 66.0 (Bn, 3xC_{C5}, 3xC_{A5} and 3xC_{A6}); 53.0, 51.6, 51.2 (3xC_{C4}); 48.7, 48.4 (3xC_{C2}); 34.0, 28.0, 27.8, 27.3, 27.3, 27.3, 23.8, 23.6, 23.5, 23.4, 20.7; 16.5, 16.4, 16.4 (3xC_{C6}). $[\alpha]^{20}_{D}$ = +118° (c = 0.8, $CHCl_3$). IR (neat): 650, 698, 734, 798, 825, 977, 999, 1038, 1098, 1244, 1362, 1456, 1497, 1668, 1717, 1757, 2857, 2928. HR-MS [M+2H^+] Calculated for $C_{204}H_{250}N_6O_{50}Si_3$: 1834.8329; found: 1834.8264.

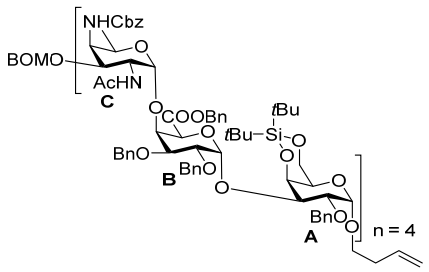


Nonasaccharide 11: The title compound was obtained by the general procedure for deprotecting of the di-*tert*-butyl silylidene ketal from compound **55**. 31 mg, yield: 88%. *Rf* = 0.47 (DCM/MeOH, 15:1). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 6.93 (m, 80H), 6.22 (d, *J* = 9.3 Hz, 1H, N-H), 6.05 (d, *J* = 9.4 Hz, 1H, N-H), 5.78 (m, 1H), 5.70 (d, *J* = 9.6 Hz, 1H, N-H), 5.29 (dd, *J* = 12.3, 3.9 Hz, 2H, 2xH_{B1}), 5.17 – 4.35 (m, 42H, 1xH_{B1}, 3xH_{A1}, 1xH_{B5}, 3xH_{C1}), 4.34 – 3.43 (m, 39H, 2xH_{B5}, 3xH_{B4}, 3xH_{C5}, 3xH_{C4}, 3xH_{C2}, 3xH_{A2}, 3xH_{A3}, 3xH_{B2}, 3xH_{B3}, 3xH_{A6}, 3xH_{A4},

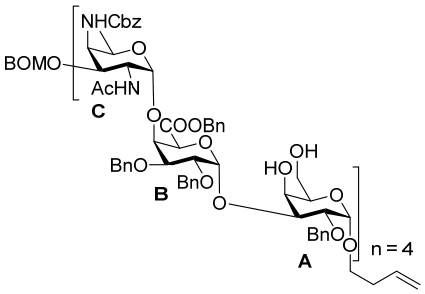


3xH_{A5}), 2.40 – 2.32 (m, 2H), 2.15 – 2.02 (m, 9H, 3xCH_3CONH-), 0.83 (dd, *J* = 11.2, 6.3 Hz, 6H, 2xH_{C6}), 0.74 (d, *J* = 6.2 Hz, 3H, 1xH_{C6}). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 170.9, 168.2, 168.0, 157.1, 157.0, 138.6, 138.5, 138.1, 138.0, 137.9, 137.8, 137.7, 137.2, 137.1, 136.9, 136.5, 136.4, 134.9, 134.3, 134.3, 134.1, 129.2, 129.1, 129.1, 129.0, 128.9, 128.9, 128.9, 128.9, 128.8, 128.8, 128.7, 128.6, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.4, 127.4, 127.3, 117.0; 100.0, 99.3, 99.2 (3xC_{C1}); 96.8, 95.1, 94.4, 94.2, 92.8 (3xC_{A1}, 3xC_{B1}); 92.5 (BOM), 76.6, 76.3, 76.2, 76.2, 75.6, 75.0, 74.8, 74.7, 74.7, 74.4, 74.1, 74.0, 74.0 (Bn, 3xC_{B4}, 3xC_{B3}, 3xC_{B2}, 3xC_{A2}, 3xC_{A3}); 73.0, 73.0, 72.8, 72.6, 71.9, 71.8 (Bn); 72.3, 70.8, 70.7, 70.2, 69.9 (3xC_{B5}, 3xC_{C3}); 69.6, 68.5, 67.7, 67.6, 67.4, 67.2, 67.0, 66.7, 66.6, 66.5, 66.5, 66.1 (Bn, 3xC_{A4}, 3xC_{A5}, 3xC_{C5}); 63.4, 63.0 (3xC_{A6}); 52.8, 51.1, 51.0 (3xC_{C4}); 48.5 (3xC_{C2}); 33.9, 23.8, 23.6, 23.6; 16.5, 16.5, 16.4 (3xC_{C6}). IR (neat): 613, 698, 737, 1030, 1098, 1456, 1506, 1558, 1717, 1749, 2313, 2849, 2916.

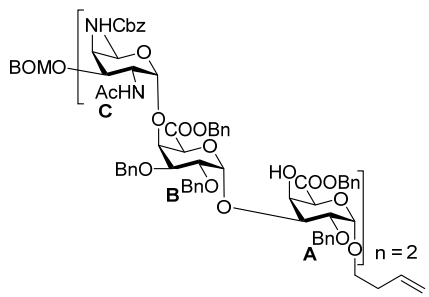
Dodecaasaccharide 56: The title compound was obtained by the general procedure for transferred azide into acetylamino reactions for long oligosaccharides from compound **53**. 199 mg, yield: 99%. *Rf* = 0.71 (DCM/MeOH, 20:1). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 – 6.99 (m, 105H), 5.80 (d, *J* = 9.5 Hz, 1H, N-H), 5.78 – 5.71 (m, 1H), 5.69 (m, 2H, N-H), 5.56 (d, *J* = 3.4 Hz, 1H, 1xH_{B1}), 5.51 (s, 2H, 2xH_{B1}), 5.44 (d, *J* = 3.3 Hz, 1H, 1xH_{B1}), 5.40 – 5.31 (m, 3H, N-H), 5.20 – 4.80 (m, 26H, 3xH_{A1}), 4.74 – 4.32 (m, 43H, 4xH_{C1}, 1xH_{A1}, 4xH_{B5}, 4xH_{A4}), 4.28 – 3.42 (m, 56H, 4xH_{B4}, 4xH_{C5}, 4xH_{C4}, 4xH_{C2}, 4xH_{A2}, 4xH_{A3}, 4xH_{B2}, 4xH_{B3}, 4xH_{A6}, 4xH_{A5}), 2.30 (q, *J* = 6.9 Hz, 2H), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.06 – 1.00 (m, 36H), 0.90 (s, 9H), 0.86 (s, 12H, 1xH_{C6}), 0.84 (s, 9H), 0.82 (s, 9H), 0.75 (d, *J* = 6.2 Hz, 9H, 3xH_{C6}). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 170.6, 170.4, 169.3, 169.0, 168.7, 157.1, 157.1, 138.4, 138.4, 138.3, 138.3, 138.2, 138.1, 138.1, 138.1, 138.0, 137.9, 136.9, 136.8, 136.7, 136.6, 135.0, 134.7, 134.5, 134.5, 134.0, 129.3, 129.2, 129.2, 129.1, 129.0, 129.0, 128.9, 128.9, 128.8, 128.7, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 116.8; 100.5, 100.1, 99.9 (4xC_{C1}); 97.7, 95.0, 94.6 (4xC_{A1}); 92.7 (BOM), 92.9, 91.4, 91.3, 91.2 (4xC_{B1}); 78.2, 77.7 (4xC_{B4}); 75.9, 75.8, 75.1, 74.4, 74.1, 74.1, 73.9, 73.4, 73.3, 73.2, 73.2, 73.1, 72.9, 72.9, 72.9, 72.8, 72.6, 72.2, 72.0, 71.6, 71.5, 71.5, 71.4, 70.8, 70.6, 69.7, 69.6, 69.1, 69.1 (Bn, 4xC_{B2}, 4xC_{B3}, 4xC_{A2}, 4xC_{A3}, 4xC_{A4}, 4xC_{B5} and 4xC_{C3}); 68.0, 67.8, 67.7, 67.6, 67.5, 67.5, 67.3, 67.2, 67.2, 67.0, 66.6, 66.5, 66.5, 66.4, 66.1, 65.9 (Bn, 4xC_{C5}, 4xC_{A5} and 4xC_{A6}); 53.0, 51.6, 51.5, 51.2 (4xC_{C4}); 48.7, 48.5 (4xC_{C2}); 34.0, 28.0, 27.8, 27.3, 27.3, 27.3, 23.8, 23.5, 23.5, 23.4, 23.4, 20.8, 20.7; 16.5, 16.4, 16.3 (4xC_{C6}). $[\alpha]^{20}_D$ = +105° (c = 1.0, $CHCl_3$). IR (neat): 645, 649, 695, 733, 798, 825, 862, 907, 919, 922, 976, 998, 1028, 1037, 1094, 1457, 1507, 1653, 1684, 1700, 1717, 2930, 3675. HR-MS: [M+2H$^+$] Calculated for $C_{268}H_{328}N_8O_{66}Si_4$: 2414.0889; found: 2414.0906.



Dodecaasaccharide 12: The title compound was obtained by the general procedure for deprotecting of the di-*tert*-butyl silylidene ketal from compound **56**. 161 mg, yield: 91%. *Rf* = 0.24 (DCM/MeOH, 30:1). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 – 6.95 (m, 105H), 6.21 (d, *J* = 9.3 Hz, 1H, N-H), 6.16 (d, *J* = 9.3 Hz, 1H, N-H), 6.09 (d, *J* = 9.4 Hz, 1H, N-H), 5.79 (m, 1H), 5.71 (d, *J* = 9.6 Hz, 1H, N-H), 5.29 (bs, 3H, 3xH_{B1}), 5.22 – 4.36 (m, 47H, 1xH_{B1}, 4xH_{A1}, 1xH_{B5}, 4xH_{C1}), 4.35 – 3.41 (m, 42H, 3xH_{B5}, 4xH_{B4}, 4xH_{C5}, 4xH_{C4}, 4xH_{C2}, 4xH_{A2}, 4xH_{A3}, 4xH_{B2}, 4xH_{B3}, 4xH_{A6}, 4xH_{A4}, 4xH_{A5}), 2.49 (bs, 8H, 8x-OH), 2.35 (q, *J* = 6.9 Hz, 2H), 2.13 – 2.02 (m, 12H, 4xCH_3CONH-), 0.93 – 0.66 (m, 12H, 4xH_{C6}). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 171.3, 171.0, 170.9, 168.2, 168.1, 168.0, 157.1, 157.1, 138.7, 138.6, 138.5, 138.2, 138.2, 138.0, 138.0, 137.9, 137.9, 137.7, 137.3, 137.1, 137.1, 137.0, 136.6, 136.3, 134.9, 134.4, 134.3, 134.2, 134.2, 129.2, 129.2, 129.2, 129.1, 129.1, 129.0, 129.0, 129.0, 128.9, 128.9, 128.9, 128.8, 128.8, 128.8, 128.7, 128.66, 128.6, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.5, 127.5, 127.5, 127.4, 127.4, 127.3, 117.0; 99.9, 99.4, 99.2 (4xC_{C1}); 96.9, 95.1, 94.5 (4xC_{A1}); 94.3, 92.8, 92.7, 92.6, 92.4 (BOM, 4xC_{B1}); 76.6, 76.5, 76.4, 75.8, 75.7, 75.0, 74.8, 74.7, 74.7, 74.6, 74.6, 74.5, 74.1, 74.1, 74.0, 72.4 (Bn, 4xC_{B4}, 4xC_{B3}, 4xC_{B2}, 4xC_{A2}, 4xC_{A3}); 73.0, 73.0, 72.9, 72.8, 72.7, 71.9, 71.8, 71.6 (Bn), 70.8, 70.7, 70.6, 70.4, 70.0, 69.6, 68.6, 67.8, 67.8, 67.6, 67.6, 67.5, 67.2, 67.1, 67.0, 66.7, 66.6, 66.5, 66.1 (Bn, 4xC_{B5}, 4xC_{C3}, 4xC_{A4}, 4xC_{A5}, 4xC_{C5}); 63.4, 63.4, 63.0 (4xC_{A6}); 52.9, 51.1, 51.0 (4xC_{C4}); 48.50 (4xC_{C2}); 33.9, 23.6, 23.6; 16.6, 16.5, 16.4, 16.4 (4xC_{C6}). $[\alpha]^{20}_{D}$ = +126° (c = 1.0, $CHCl_3$). IR (neat): 697, 733, 749, 800, 825, 977, 995, 1028, 1079, 1093, 1241, 1457, 1507, 1653, 1684, 1700, 1717, 2930, 3675. HR-MS [M+2H^{+}] Calculated for $C_{236}H_{264}N_8O_{66}$: 2133.8847; found: 2133.8735.

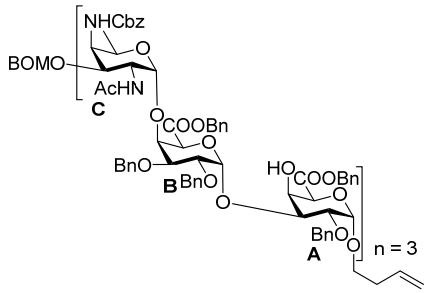


Hexasaccharide 6: The title compound was obtained by the general oxidation procedure B or C, then do benzylation by use of BnBr and Cs_2CO_3. 15 mg, yield: 67%/63%. *Rf* = 0.27 (DCM/MeOH, 20:1). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.51 – 7.08 (m, 65H), 6.64 (d, *J* = 10.0 Hz, 1H, N-H), 6.52 (d, *J* = 10.1 Hz, 1H, N-H), 6.26 (d, *J* = 8.7 Hz, 1H, N-H), 6.19 (d, *J* = 9.3 Hz, 1H, N-H), 5.96 – 5.77 (m, 1H), 5.39 – 4.92 (m, 19H, 2xH_{A1}, 2xH_{B1}), 4.89 – 4.40 (m, 21H, 2xH_{C1}, 2xH_{A4}, 2xH_{A5}, 2xH_{B5}), 4.39 – 3.64 (m, 18H, 2xH_{C5}, 2xH_{C3}, 2xH_{C4}, 2xH_{C2}, 2xH_{A3}, 2xH_{A2}, 2xH_{B4}, 2xH_{B3}, 2xH_{B2}), 3.61 – 3.46 (m, 1H), 2.42 – 2.29 (m, 2H), 1.96 (s, 3H), 1.91 (s, 3H), 0.87 – 0.75 (m, 6H, 2xH_{C6}). ^{13}C NMR (126 MHz, Acetone) δ 170.7, 170.5, 169.1, 168.9, 168.7, 158.2, 158.1, 139.9, 139.8, 139.8, 139.7, 139.6, 138.8, 138.7, 138.5, 137.3, 137.2, 136.3, 136.1, 129.8, 129.8, 129.6, 129.6, 129.5, 129.5, 129.4, 129.4, 129.3, 129.2, 129.2, 129.2, 129.1, 129.1, 128.9,

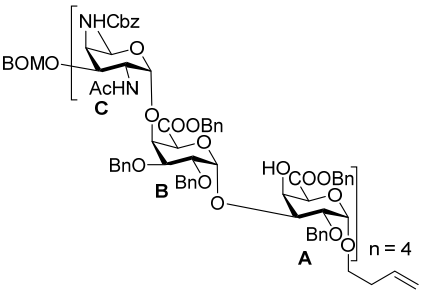


128.9, 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 116.9; 100.4, 100.1 (2xC_{C1}); 98.0, 96.0, 95.6, 94.9 (2xC_{A1}, 2xC_{B1}); 93.9 (BOM), 77.7, 77.5, 77.2, 77.1, 76.0, 75.9, 75.5, 75.2, 75.0, 74.8 (2xC_{B4}, 2xC_{B3}, 2xC_{B2}, 2xC_{A3}, 2xC_{A2}); 74.5, 74.4 (Bn), 73.5, 73.4 (2xC_{C3}); 73.3, 73.2, 73.0, 72.9 (Bn); 71.7, 71.5, 71.2, 70.7 (2xC_{A5}, 2xC_{B5}); 69.9, 68.8 (Bn); 68.3, 68.2 (2xC_{A4}); 67.8, 67.8 (Bn); 67.1, 66.9, 66.8, 66.6, 66.5 (Bn, 2xC_{C5}); 54.3, 52.6 (2xC_{C4}); 49.5, 49.2 (2xC_{C2}); 34.8, 23.8, 23.7; 17.1, 17.1 (2xC_{C6}). $[\alpha]^{20}_{D}$ = +87° (c = 0.33, $CHCl_3$). IR (neat): 603, 650, 700, 723, 739, 752, 789, 800, 825, 974, 1001, 1047, 1076, 1099, 1112, 1175, 1263, 1371, 1472, 1714, 2857, 2931. HR-MS: [M+H^+] Calculated for $C_{138}H_{148}N_4O_{36}$: 2437.9946; found: 2437.9851.

Nonasaccharide 7: The title compound was obtained by the general oxidation procedure B or C, then do benzylation by use of BnBr and Cs_2CO_3 or phenyldiazomethane. 8 mg, yield: 89%/57%. *Rf* = 0.28 (DCM/MeOH, 20:1). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 – 6.89 (m, 80H), 5.83 – 5.70 (m, 3H, 3xN-H, -OCH_2CH_2CH=CH_2), 5.64 (d, *J* = 9.5 Hz, 1H), 5.43 – 4.80 (m, 24H, 3xH_{A1}, 3xH_{B1}), 4.76 – 4.19 (m, 30H, 3xH_{C1}, 3xH_{A4}, 3xH_{A5}, 3xH_{B5}), 4.19 – 3.42 (m, 25H, 3xH_{C5}, 3xH_{C3}, 3xH_{C4}, 3xH_{C2}, 2xH_{A3}, 2xH_{A2}, 2xH_{B4}, 2xH_{B3}, 2xH_{B2}), 2.39 – 2.29 (m, 2H), 2.07 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 0.93 – 0.71 (m, 9H, 3xH_{C6}). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 170.9, 170.8, 168.5, 168.1, 168.0, 157.1, 157.0, 138.5, 138.5, 138.0, 138.0, 137.9, 137.9, 137.9, 137.0, 136.8, 136.7, 136.5, 135.6, 135.5, 135.4, 134.8, 134.4, 134.3, 134.3, 129.2, 129.2, 129.1, 129.0, 129.0, 129.0, 128.9, 128.9, 128.8, 128.8, 128.8, 128.8, 128.6, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 127.4, 117.1; 99.8, 99.6, 99.5 (3xC_{C1}); 97.2, 95.4, 95.2, 94.7, 94.5, 94.4 (3xC_{A1}, 3xC_{B1}); 92.5 (BOM), 77.2, 77.1, 77.0 (3xC_{B4}); 76.3, 75.9, 75.6, 74.6, 74.5, 74.4, 74.3, 74.2, 74.2, 74.0 (Bn, 3xC_{B3}, 3xC_{B2}, 3xC_{A3}, 3xC_{A2}); 73.2, 73.2, 73.0, 72.8, 72.3 (Bn, 3xC_{C3}); 71.0, 70.9, 70.8, 70.4, 70.3, 69.6 (3xC_{B5}, 3xC_{A5}); 69.6, 68.2, 67.7, 67.7, 67.6, 67.3, 67.2, 67.2, 67.1 (Bn); 67.0, 66.9 (3xC_{A4}); 66.5 (Bn), 66.3, 66.2 (3xC_{C5}); 52.9, 51.7 (3xC_{C4}); 48.5, 48.4 (3xC_{C2}); 33.9, 23.8, 23.6; 16.6, 16.6, 16.5 (3xC_{C6}). $[\alpha]^{20}_{D}$ = +102° (c = 1.0, $CHCl_3$). IR (neat): 699, 803, 1030, 1095, 1363, 1419, 1457, 1507, 1560, 1653, 1684, 1700, 1717, 1734, 2930, 3675. HR-MS: [M+2H^+] Calculated for $C_{201}H_{214}N_6O_{53}$: 1780.7190; found: 1780.6991.

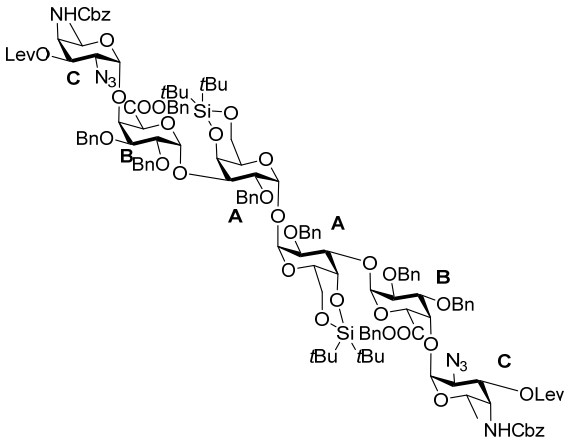


Dodecasaccharide 8: The title compound was obtained by the general oxidation procedure B or C, then do benzylation by use of phenyldiazomethane. 18 mg, yield: 49%.



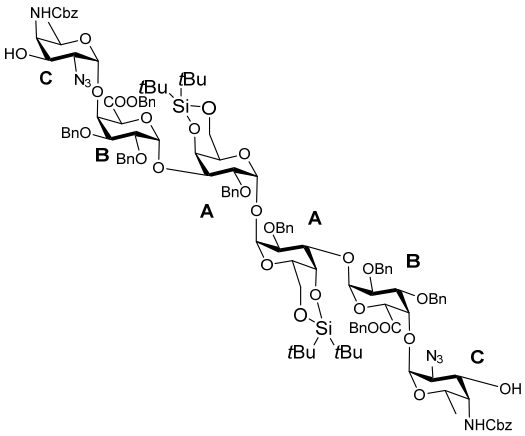
Rf = 0.7 (toluene/acetone, 2:1). ^{1}H NMR (600 MHz, Acetonitrile-d_3) δ 7.50 – 6.98 (m, 125H), 6.08 (m, 4H, 4xN-H), 5.98 – 5.69 (m, 5H, 4xN-H, -OCH_2CH_2CH=CH_2), 5.37 – 4.89 (m, 27H, 4xH_{A1}, 4xH_{B1}), 4.85 – 4.40 (m, 27H, 4xH_{C1}, 4xH_{A5}), 4.40 – 3.45 (m, 87H, 4xH_{A4}, 4xH_{B5}, 3xH_{C5}, 3xH_{C3}, 3xH_{C4}, 3xH_{C2}, 2xH_{A3}, 2xH_{A2}, 2xH_{B4}, 2xH_{B3}, 2xH_{B2}), 3.32 (bs, 1H, -OH), 3.28 (d, *J* = 5.1 Hz, 1H, -OH), 2.38 – 2.27 (m, 2H), 1.97 (m, 6H, 2xCH_3CONH-), 1.91 (s, 3H, 1xCH_3CONH-), 1.89 (s, 3H, 3xCH_3CONH-), 0.81 – 0.52 (m, 12H, 4xH_{C6}). ^{13}C NMR (151 MHz, CD_3CN) δ 170.8, 170.6, 170.6, 169.2, 169.2, 169.1, 169.0, 168.8, 168.7, 158.1, 158.0, 139.6, 139.6, 139.5, 139.5, 139.4, 138.7, 138.4, 138.4, 138.3, 138.1, 137.0, 137.0, 137.0, 136.9, 136.5, 136.4, 136.0, 135.9, 135.9, 129.9, 129.9, 129.8, 129.7, 129.7, 129.7, 129.7, 129.7, 129.6, 129.6, 129.6, 129.6, 129.5, 129.5, 129.5, 129.5, 129.4, 129.4, 129.4, 129.4, 129.3, 129.3, 129.3, 129.2, 129.2, 129.2, 129.2, 129.1, 129.1, 129.1, 129.1, 129.0, 128.9, 128.9, 128.9, 128.8, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 117.0, 116.9; 99.9, 99.7, 99.3, 99.1 (4xC_{C1}); 97.7, 95.9, 95.7, 95.5, 93.9, 93.7 (4xC_{A1} and 4xC_{B1}); 93.8 (BOM), 79.5, 77.3, 77.1, 76.9, 76.7, 76.5, 75.8, 75.6, 75.3, 75.2, 75.1, 74.9, 74.7, 74.3, 74.3, 73.3, 73.2, 73.2, 73.1, 73.0, 73.0, 72.4, 72.2 (Bn, 4xC_{B4}, 4xC_{B3}, 4xC_{B2}, 4xC_{A3}, 4xC_{A2}, 4xC_{C3}); 71.6, 71.6, 71.3, 71.2, 70.9, 70.8, 70.4 (4xC_{B5}, 4xC_{A5}); 70.0, 68.6 (Bn), 68.2, 68.1, 68.1 (4xC_{A4}); 68.1, 68.0, 68.0, 67.9, 67.9, 67.2, 67.2, 67.1, 66.9, 66.8, 66.7, 66.7 (Bn); 66.5, 66.4 (4xC_{C5}); 55.0, 53.9, 51.9, 51.8 (4xC_{C4}); 49.2, 48.9 (4xC_{C2}); 34.5, 23.8, 23.8, 23.6; 16.9, 16.7, 16.7 (4xC_{C6}). $[\alpha]^{20}_{D}$ = +101° (c = 0.5, $CHCl_3$). IR (neat): 698, 737, 799, 1028, 1092, 1260, 1339, 1458, 1507, 1521, 1653, 1700, 1734, 2930, 3675. HR-MS: [M+2H$^+$] Calculated for $C_{264}H_{280}N_8O_{70}$: 2341.9371; found: 2341.9355.

59 1,1-di-trimer-di-Lev: The byproduct from glycosylation. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.08 (m, 50H), 5.56 (d, *J* = 3.4 Hz, 2H, H_{B1}), 5.23 (d, *J* = 12.3 Hz, 2H), 5.18 – 5.07 (m, 4H, H_{C3}), 5.07 – 4.98 (m, 6H, H_{A1}), 4.84 (dd, *J* = 24.0, 10.5 Hz, 4H), 4.72 – 4.59 (m, 10H, H_{C1}, H_{B5}), 4.58 – 4.51 (m, 4H, H_{A4}), 4.42 – 4.31 (m, 6H, H_{B4}, H_{C5}), 4.07 (m, 2H, H_{C4}), 4.01 – 3.88 (m, 8H, H_{A2}, H_{A3}, H_{B2}, H_{B3}), 3.82 (q, *J* = 14.2, 13.0 Hz, 6H, H_{A5}, H_{A6}), 3.11 (dd, *J* = 11.3, 4.0 Hz, 2H, H_{C2}), 2.83 – 2.73 (m, 2H), 2.68 (m, 2H), 2.63 – 2.52 (m, 2H), 2.43 (m, 2H), 2.17 (d, *J* = 1.8 Hz, 6H), 0.93 (s, 18H), 0.87 (s, 18H), 0.76 (d, *J* = 6.3 Hz, 6H, H_{C6}). ^{13}C

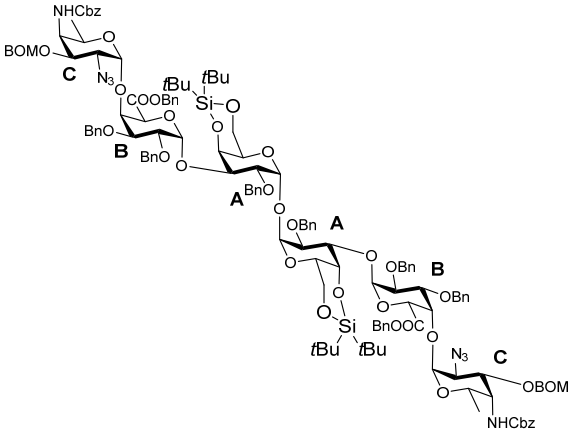


NMR (151 MHz, $CDCl_3$) δ 172.0, 168.2, 156.7, 138.4, 138.2, 138.1, 136.5, 135.2, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 98.8 (C_{C1}), 94.3 (C_{A1}), 93.6 (C_{B1}), 77.1 (C_{B4}), 75.6 (C_{B3}), 75.3 (C_{B2}), 74.2 (C_{A3}), 73.6 (C_{A2}), 73.3, 73.2, 72.4 (Bn), 70.6 (C_{A4}), 70.4 (C_{B5}), 70.2 (C_{C3}), 67.5 (Bn), 67.4 (C_{A5}), 67.1 and 67.1 (Bn, and C_{A6}), 64.9 (C_{C5}), 57.7 (C_{C2}), 52.8 (C_{C4}), 38.1, 27.7, 27.4, 23.3, 20.7, 16.2 (C_{C6}). IR (neat): 650, 698, 737, 798, 827, 977, 999, 1038, 1099, 1148, 1456, 1521, 1717, 2112, 2859, 2934. HR-MS: [M+H^+] Calculated for $C_{134}H_{162}N_8O_{35}Si_2$: 2500.0754; found: 2500.0710.

1,1-di-trimer-di-OH: The title compound was obtained by the general procedure for delevulinoylation. ^{1}H NMR



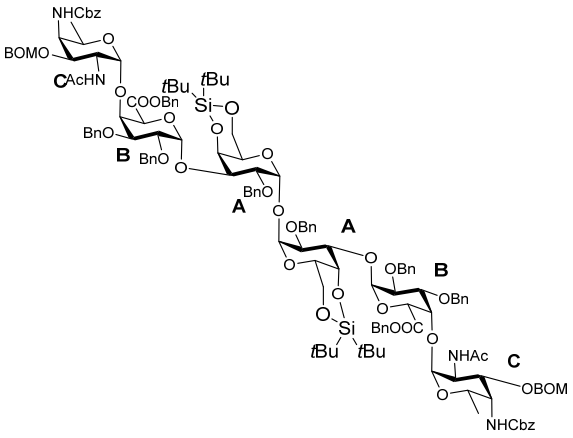
(400 MHz, Chloroform-*d*) δ 7.45 – 7.01 (m, 50H), 5.58 (s, 2H, H_{B1}), 5.21 (d, *J* = 12.2 Hz, 2H), 5.14 – 5.04 (m, 8H, H_{A1}), 5.01 (d, *J* = 7.8 Hz, 2H), 4.92 (d, *J* = 8.8 Hz, 2H, N-H), 4.83 (d, *J* = 11.9 Hz, 2H), 4.76 – 4.47 (m, 16H, H_{B5}, H_{A4}, H_{C1}), 4.45 – 4.34 (m, 4H, H_{B4}), 4.30 (d, *J* = 7.2 Hz, 2H, H_{C5}), 4.13 – 3.72 (m, 18H, H_{C3}, H_{A2}, H_{A3}, H_{B2}, H_{B3}, H_{C4}, H_{A5}, H_{A6}), 2.87 (dd, *J* = 10.7, 3.8 Hz, 2H, H_{C2}), 0.94 (s, 18H), 0.90 (s, 18H), 0.80 (d, *J* = 6.4 Hz, 6H, H_{C6}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 158.4, 138.4, 138.3, 138.1, 136.0, 135.1, 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.1, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 98.9 (C_{C1}), 94.3 (C_{A1}), 93.8 (C_{B1}), 76.7 (C_{B4}), 75.9 (C_{B3}), 75.0 (C_{B21}), 74.4 (C_{A3}), 73.7 (C_{A2}), 73.2, 73.1, 72.2 (Bn), 70.8 (C_{A4}), 70.47 (C_{B5}), 68.6 (C_{C3}), 67.7, 67.5 (Bn), 67.5 (C_{A5}), 67.1 (C_{A6}), 65.1 (C_{C5}), 60.7 (C_{C2}), 56.0 (C_{C4}), 27.7, 27.4, 27.3, 23.3, 20.8, 16.4 (C_{C6}). $[\alpha]^{20}_D$ = 134° (c = 0.68, $CHCl_3$). IR (neat): 668, 698, 976, 1029, 1099, 1340, 1419, 1457, 1653, 1700, 1717, 1739, 2930, 3675. HR-MS: [M+H^+] Calculated for $C_{124}H_{150}N_8O_{31}Si_2$: 2304.0018; found: 2303.9976.



1,1-di-trimer-di-BOM: The title compound was obtained by the general procedure for BOM protection from compound **1,1-di-trimer-di-OH**. 94 mg, yield: 64%. *Rf* = 0.8 (toluene/EtOAc, 3:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.07 (m, 50H), 5.58 (d, *J* = 3.0 Hz, 2H, H_{B1}), 5.25 (d, *J* = 12.2 Hz, 2H), 5.12 – 4.94 (m, 8H, H_{A1}), 4.88 – 4.51 (m, 24H, H_{B5}, H_{A4}, H_{C1}), 4.46 – 4.33 (m, 4H, H_{B4}), 4.23 (d, *J* = 6.6 Hz, 2H, H_{C5}), 4.08 (dd, *J* = 10.9, 4.0

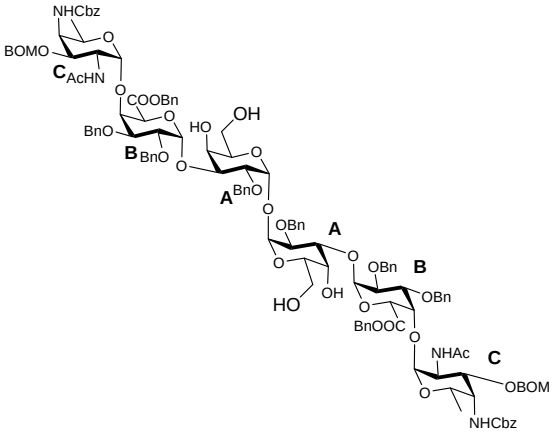
Hz, 2H, H_{C3}), 4.04 – 3.75 (m, 16H, H_{A2}, H_{A3}, H_{B2}, H_{B3}, H_{C4}, H_{A5}, H_{A6}), 2.88 (dd, *J* = 10.9, 3.9 Hz, 2H), 0.93 (s, 18H), 0.88 (s, 18H), 0.80 (d, *J* = 6.3 Hz, 6H, H_{C6}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 156.9, 138.3, 138.2, 138.0, 137.8, 136.4, 135.1, 128.7, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 128.3, 128.1, 128.1, 128.1, 127.9, 127.8, 127.7, 127.7, 127.6, 98.7 (C_{C1}), 94.3 (C_{A1}), 93.6 (C_{B1}), 92.4 (BOM), 76.7 (C_{B4}), 75.5 (C_{B3}), 75.1 (C_{B2}), 74.1 (C_{A3}), 73.6 (C_{A2}), 73.2, 73.1, 72.2 (Bn); 71.1, 70.6 and 70.4 (C_{A4}, C_{B5}, C_{C3}), 70.0 and 67.5 (Bn), 67.4 (C_{A5}), 67.1 (Bn), 65.4 (C_{C5}), 59.3 (C_{C2}), 52.7 (C_{C4}), 27.7, 27.3, 23.3, 20.7, 16.4 (C_{C6}). $[\alpha]^{20}_{D}$ = 168° (c = 0.78, $CHCl_3$). IR (neat): 698, 738, 800, 826, 1040, 1097, 1363, 1458, 1507, 1653, 1700, 1717, 1734, 2109, 2875, 2924, 3675.

1,1-di-trimer-di-acetylamide: The title compound was obtained by the general procedure for transferring an azide into acetylamino reactions for long oligosaccharides from compound **1,1-di-trimer-di-BOM**. 42 mg, yield: 88%. *Rf* = 0.73 (DCM/MeOH, 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.01 (m, 60H), 5.73 (bs, 2H, N-H), 5.48 (d, *J* = 1.9 Hz, 2H, H_{B1}), 5.18 – 4.97 (m, 8H, H_{A1}, N-H), 4.85 (m, 8H), 4.75 – 4.41 (m, 16H, H_{B5}, H_{A4}, H_{C1}), 4.25 – 3.59 (m, 22H, H_{B4}, H_{C5}, H_{C3}, H_{A2}, H_{A3}, H_{B2}, H_{B3}, H_{C4}, H_{A5}, H_{A6}), 1.98 (s, 6H), 0.95 (s, 18H), 0.91 (s, 18H), 0.84 (d, *J* = 6.2 Hz, 6H, H_{C6}). ^{13}C NMR

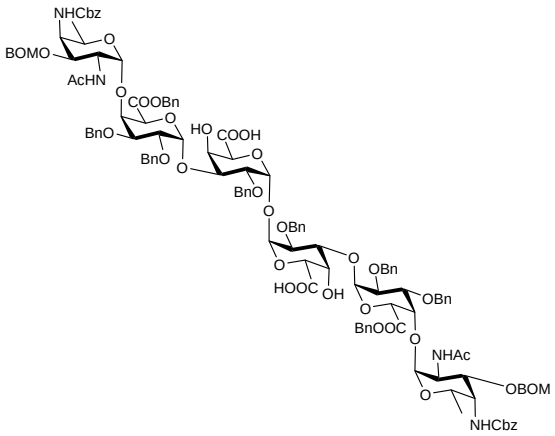


(101 MHz, $CDCl_3$) δ 170.7, 157.1, 138.3, 137.9, 137.9, 137.8, 136.5, 134.1, 129.0, 128.9, 128.9, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.3, 99.5 (C_{C1}), 95.6 (C_{B1}), 94.6 (C_{A1}), 92.6 (BOM), 77.4 (C_{B4}), 75.9, 75.5, 74.4 and 73.7 (C_{B3}, C_{B2}, C_{A3}, C_{A2}); 73.4 (Bn); 72.6 (C_{C3}), 72.5 (Bn), 71.1 and 70.7 (C_{A4}, C_{B5}), 69.5 (Bn), 67.5, 67.0, 66.9 (Bn, C_{A6}), 65.9 (C_{C5}), 52.8, 48.6, 27.6, 27.4, 23.6, 23.4, 20.7, 16.5 (C_{C6}). $[\alpha]^{20}_{D}$ = +139° (c = 0.72, $CHCl_3$). IR (neat): 698, 736, 1045, 1104, 1419, 1457, 1507, 1560, 1653, 1700, 1717, 1734, 2875, 2924, 3675. HR-MS [M+H$^+$] Calculated for $C_{144}H_{174}N_4O_{35}Si_2$: 2576.1570; found: 2576.1548.

60 1,1-di-trimer-tetra-OH: The title compound was obtained by general procedure for deprotecting of the di-*tert*-butyl silylidene ketal from compound **1,1-di-trimer-di-acetylamide**. 29 mg, yield: 77%. *Rf* = 0.45 (DCM/MeOH, 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.03 (m, 60H), 5.66 (d, *J* = 9.5 Hz, 2H, H_{B1}), 5.27 (d, *J* = 3.8 Hz, 2H), 5.18 – 4.83 (m, 12H, H_{A1}), 4.81 – 4.60 (m, 10H), 4.55 (d, *J* = 11.9 Hz, 2H), 4.46 (d, *J* = 3.9 Hz, 2H, H_{C1}), 4.44 – 4.34 (m, 4H, H_{B5}), 4.30 (d, *J* = 6.6 Hz, 2H, H_{C5}), 4.20 (d, *J* = 2.7 Hz, 2H, H_{B4}), 4.17 – 3.65 (m, 16H, H_{A2}, H_{A3}, H_{B2}, H_{B3}, H_{C2}, H_{C3}, H_{C4}), 3.43 (qd, *J* = 12.1, 4.6 Hz, 4H, H_{A6}), 2.11 (s, 6H), 0.87 (d, *J* = 6.3 Hz, 6H, H_{C6}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 168.0, 157.1, 138.0, 137.8, 137.7, 136.7, 136.4, 134.1, 129.1, 129.0, 129.0, 128.9, 128.9, 128.8, 128.8, 128.7, 128.6, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 128.0, 127.8, 127.5, 127.1, 127.0, 99.5 (C_{C1}), 95.7 (C_{A1}), 94.7 (C_{B1}), 92.6 (BOM), 76.6 (C_{B4}), 76.4 and 76.3 (C_{B3}, C_{A3}), 75.2 (Bn), 74.9 and 74.0 (C_{B2}, C_{A2}), 72.9 (Bn), 72.4 (C_{C3}), 72.0 (Bn), 70.7 (C_{B5}), 69.7 (Bn), 68.5 and 68.1 (C_{A4}, C_{A5}), 67.6 and 67.1 (Bn), 66.1 (C_{C5}), 63.2(C_{A6}), 52.7 (C_{C4}), 48.5 (C_{C2}), 23.8, 16.6 (C_{C6}). IR (neat): 698, 736, 987, 1028, 1045, 1092, 1115, 1457, 1507, 1560, 1653, 1700, 1717, 1734, 2875, 2924, 3675. HR-MS [M+H$^+$] Calculated for $C_{128}H_{142}N_4O_{35}$: 2295.9527; found: 2295.9502.



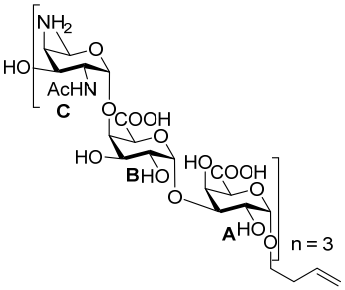
61 1,1-di-trimer-di-COOH: The title compound was obtained by the general oxidation procedure B or C. 12 mg, yield: 85%. *Rf* = 0.4(DCM/MeOH/AcOH, 20:2:0.05). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 6.82 (m, 60H), 5.70 (d, *J* = 9.3 Hz, 2H), 5.25 (s, 2H), 5.18 – 4.86 (m, 10H), 4.83 – 4.52 (m, 14H), 4.51 – 4.22 (m, 8H), 4.20 – 3.95 (m, 6H), 3.92 – 3.55 (m, 6H), 2.04 (s, 6H), 0.89 (d, *J* = 5.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 167.7, 157.1, 137.8, 137.67, 137.2, 136.4, 136.4, 134.2, 129.1, 129.0, 129.0, 128.8, 128.6, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.5, 99.4, 95.3, 92.6, 76.4, 76.0, 75.4, 74.8, 73.8, 73.5, 73.1, 72.8, 72.3, 70.7, 69.6, 67.6, 67.1, 66.8, 66.1, 52.7, 48.5, 29.8, 23.7, 16.6. $[\alpha]^{20}_{D}$ = +118° (c = 0.48, $CHCl_3$). HR-MS: [M+H$^+$] Calculated for $C_{128}H_{138}N_4O_{37}$: 2323.9113; found: 2323.9050.



62 1,1-di-trimer: The title compound was obtained by the general procedure for fully deprotection (saponification and Birch reduction) from compound **1,1-di-trimer-di-COOH**. ^{1}H NMR (500 MHz, Deuterium Oxide) δ 5.23 (dd, *J* = 7.7, 4.0 Hz, 4H, H_{A1}, H_{B1}), 4.93 (d, *J* = 3.8 Hz, 2H, H_{C1}), 4.74 – 4.67 (m, 2H, H_{C5}), 4.55 (s, 2H, H_{B5}), 4.46 (d, *J* = 3.2 Hz, 2H, H_{A4}), 4.34 (m, 4H, H_{A5}, H_{B4}), 4.25 – 4.06 (m, 6H, H_{A3}, H_{B3}, H_{C3}), 4.01 (dd, *J* = 11.3, 3.7 Hz, 2H, H_{C2}), 3.90 (ddd, *J* = 23.7, 10.5, 3.9 Hz, 4H, H_{A2}, H_{B2}), 3.54 (d, *J* = 4.4 Hz, 2H, H_{C4}), 2.14 – 2.00 (m, 6H, CH_3CONH-), 1.23 (d, *J* = 6.7 Hz, 6H, H_{C6}). ^{13}C NMR (126 MHz, D_2O) δ 175.3, 175.1, 174.7, 99.0 (C_{C1}), 97.9 (C_{B1}), 93.5 (C_{A1}), 80.4 (C_{B4}), 77.3 (C_{A3}), 71.6 and 71.4 (C_{A5}, C_{B5}), 68.6 (C_{A4}), 68.5 (C_{B3}), 68.0 (C_{B2}), 66.5 (C_{A2}), 65.1 (C_{C3}), 63.8 (C_{C5}), 55.2 (C_{C4}), 49.3 (C_{C2}), 22.4 (C_{AcNH}), 15.5 (C_{C6}). $[\alpha]^{20}_{D}$ = 20° (c = 0.1, $CHCl_3$). HR-MS: [M+H$^+$] Calculated for $C_{40}H_{62}N_4O_{31}$: 1095.3471; found: 1095.3478.

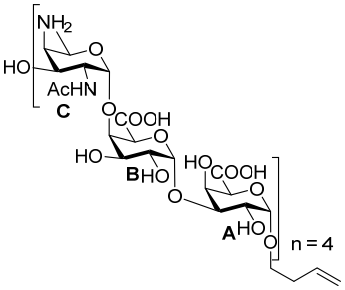
Hexasaccharide 2: The title compound was obtained by the general procedure for fully deprotection (saponification and Birch reduction) from compound **6**. ^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.83 (m, 1H, -OCH_2CH_2CH=CH_2), 5.17 (d, *J* = 3.9 Hz, 1H, H_{B1}), 5.15 (d, *J* = 3.9 Hz, 1H, $H_{B'1}$), 5.09 (dd, *J* = 17.3, 2.0 Hz, 1H, -OCH_2CH_2CH=CH_2), 5.05 – 5.02 (m, 1H, -OCH_2CH_2CH=CH_2), 5.01 (d, *J* = 4.1 Hz, 1H, $H_{A'1}$), 4.92 (d, *J* = 4.0 Hz, 1H, H_{A1}), 4.88 (d, *J* = 4.2 Hz, 1H, H_{C1}), 4.74 (d, *J* = 3.8 Hz, 1H, $H_{C'1}$), 4.58 (bs, 1H, H_{C5}), 4.54 (s, 1H, H_{B5}), 4.53 – 4.47 (m, 2H, $H_{C'5}$, H_{B5}), 4.45 – 4.38 (m, 2H, H_{A4}, $H_{A'4}$), 4.34 – 4.29 (m, 1H, H_{B4}), 4.28 – 4.25 (m, 1H, $H_{B'4}$), 4.24 (s, 1H, H_{A5}), 4.15 (dd, *J* = 11.2, 4.0 Hz, 1H, H_{C2}), 4.09 – 4.00 (m, 5H, $H_{C'2}$, H_{C3}, $H_{A'5}$, H_{B3}, $H_{B'3}$), 3.99 – 3.81 (m, 7H, $H_{C'3}$, H_{A3}, $H_{A'3}$, H_{B2}, $H_{B'2}$, H_{A2}, $H_{A'2}$), 3.70 (m, 1H, -OCH_2CH_2CH=CH_2), 3.60 (m, 1H, -OCH_2CH_2CH=CH_2), 3.39 (bs, 1H, H_{C4}), 3.10 (s, 1H, $H_{C'4}$), 2.32 (q, *J* = 6.8 Hz, 2H, -OCH_2CH_2CH=CH_2), 2.04 (s, 3H, CH_3CONH-), 2.00 (s, 3H, CH_3CONH-), 1.16 (dd, *J* = 14.8, 6.4 Hz, 6H, 2xH_{C6}). ^{13}C NMR (214 MHz, D_2O) δ 176.6, 176.0, 175.9, 175.7, 175.5, 175.5, 136.9 (-OCH_2CH_2CH=CH_2), 117.5 (-OCH_2CH_2CH=CH_2), 100.1 ($C_{C'1}$), 99.5 (C_{C1}), 99.4 (C_{A1}), 96.9 ($C_{A'1}$), 97.8 ($C_{B'1}$), 97.34 (C_{B1}), 81.0 ($C_{B'4}$), 80.2 (C_{B4}), 77.2 ($C_{A'3}$), 77.0 (C_{A3}), 75.0 (C_{C3}), 72.8 ($C_{A'5}$), 72.3 ($C_{B'5}$), 72.3 ($C_{B'5}$), 72.1 (C_{B5}), 69.7 and 69.6 (C_{B3}, $C_{B'3}$), 68.9 (-OCH_2CH_2CH=CH_2), 69.0, 69.0, 68.8, 68.8 (C_{A4}, $C_{A'4}$, C_{B2}, $C_{B'2}$), 68.5 ($C_{C'3}$), 67.6 (C_{A2}), 67.3 ($C_{C'5}$), 67.1 ($C_{A'2}$), 55.1 ($C_{C'4}$), 52.3 (C_{C4}), 50.0 ($C_{C'2}$), 48.3 (C_{C2}), 34.3 (-OCH_2CH_2CH=CH_2), 23.3 and 23.3 (CH_3CONH-), 16.7 and 16.7 ($C_{C'6}$, C_{C6}). $[\alpha]^{20}_{D}$ = +178° (c = 0.1, H_2O). HR-MS: [M+H$^+$] Calculated for $C_{44}H_{68}N_4O_{31}$: 1149.3940; found: 1149.3940.

Nonasaccharide 3: The title compound was obtained by general procedure for fully deprotection (saponification and Birch reduction) from compound **7**.



^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.85 (m, 1H, -OCH$_2$CH$_2$C*H*=CH$_2$), 5.21 – 5.16 (m, 3H, 3xH$_{B1}$), 5.11 (dq, *J* = 17.3, 1.7 Hz, 1H, -OCH$_2$CH$_2$CH=C*H*$_2$), 5.06 – 5.04 (m, 1H, -OCH$_2$CH$_2$CH=C*H*$_2$), 5.03 (d, *J* = 4.2 Hz, 1H, 1xH$_{A'1}$), 5.02 (d, *J* = 4.4 Hz, 1H, 1xH$_{A''1}$), 4.94 (m, 3H, 1xH$_{A1}$, 1xH$_{C1}$, 1xH$_{C'1}$), 4.88 (d, *J* = 4.0 Hz, 1H, 1xH$_{C''1}$), 4.74 (m, 2H, 1xH$_{C5}$, 1xH$_{C'5}$), 4.67 (bs, 1xH$_{C''5}$), 4.59 (s, 1H, 1xH$_{B''5}$), 4.58 (s, 1H, 1xH$_{B'5}$), 4.51 (s, 1H, 1xH$_{B5}$), 4.44 (bs, 1H, 1xH$_{A4}$), 4.42 (m, 2H, 1xH$_{A'4}$, 1xH$_{A''4}$), 4.36 – 4.33 (m, 2H, 1xH$_{B4}$, 1xH$_{B'4}$), 4.32 – 4.29 (m, 1H, 1xH$_{B''4}$), 4.25 (d, *J* = 1.4 Hz, 1H, 1xH$_{A5}$), 4.21 (m, 2H, 1xH$_{C3}$, 1xH$_{C'3}$), 4.14 – 4.02 (m, 8H, H$_{C2}$, H$_{C'2}$, H$_{C''3}$, H$_{A'5}$, H$_{A''5}$, H$_{B3}$, H$_{B'3}$, H$_{B''3}$), 4.03 – 3.96 (m, 4H, H$_{C''2}$, 3xH$_{A3}$), 3.94 – 3.82 (m, 6H, 3xH$_{A2}$, 3xH$_{B2}$), 3.77 – 3.70 (m, 2H, H$_{C4}$, H$_{C'4}$, -OC*H*$_2$CH$_2$CH=CH$_2$), 3.62 (m, 1H, -OC*H*$_2$CH$_2$CH=CH$_2$), 3.46 (bs, 1H, H$_{C''4}$), 2.34 (q, *J* = 7.6, 7.0 Hz, 2H), 2.06 (s, 3H, CH$_3$CONH-), 2.01 (s, 3H, CH$_3$CONH-), 2.00 (s, 3H, CH$_3$CONH-), 1.21 (m, 9H, 3xH$_{C6}$). ^{13}C NMR (214 MHz, D$_2$O) δ 176.6, 176.0, 175.9, 175.6, 175.6, 175.5, 175.5, 175.4, 136.9 (-OCH$_2$CH$_2$*C*H=CH$_2$), 117.5 (-OCH$_2$CH$_2$CH=*C*H$_2$); 99.9, 99.4 and 99.3 (3xC$_{C1}$, 3xC$_{A1}$); 98.0, 97.6, 97.3 (3xC$_{B1}$); 81.0, 80.4, 80.3 (3xC$_{B4}$); 77.2, 77.0, 76.8 (3xC$_{A3}$); 74.4, 74.1 (C$_{C3}$, C$_{C'3}$); 73.1 (C$_{A'5}$, C$_{A''5}$), 72.3 (C$_{A5}$); 72.2, 72.0 and 71.9 (3xC$_{B5}$); 69.6, 69.5, 69.5 (3xC$_{B3}$); 69.1, 69.0, 68.8, 68.8, 68.8 (3xC$_{A4}$, 3xC$_{B2}$); 68.9 (-O*C*H$_2$CH$_2$CH=CH$_2$); 67.6, 66.8 and 66.7 (3xC$_{A2}$); 65.2 (C$_{C''5}$) and 64.0 (C$_{C5}$, C$_{C'5}$, according to HSQC), 55.9 (C$_{C''4}$) and 53.8 (C$_{C4}$, C$_{C'4}$); 50.2 (C$_{C''2}$), 48.5 (C$_{C2}$, C$_{C'2}$); 34.3 (-OCH$_2$*C*H$_2$CH=CH$_2$), 23.2 (*C*H$_3$CONH-), 16.4 (3xC$_{C6}$). [α]$^{20}_{D}$ = +162° (c = 0.05, H$_2$O). HR-MS: [M+2H$^+$] Calculated for C$_{25}$H$_{31}$N$_3$O$_7$: 844.2830; found: 844.2855.

Dodecasaccharide 4: The title compound was obtained by the general procedure for fully deprotection (saponification and Birch reduction) from compound **8**.



^{1}H NMR (850 MHz, Deuterium Oxide) δ 5.83 (m, 1H, -OCH$_2$CH$_2$C*H*=CH$_2$), 5.19 – 5.13 (m, 4H, 4xH$_{B1}$), 5.09 (dd, *J* = 17.3, 1.8 Hz, 1H, -OCH$_2$CH$_2$CH=C*H*$_2$), 5.02 (m, 4H, -OCH$_2$CH$_2$CH=C*H*$_2$, H$_{A'1}$, H$_{A''1}$, H$_{A'''1}$), 4.94 – 4.88 (m, 4H, H$_{C1}$, H$_{A1}$, H$_{C'1}$, H$_{C''1}$), 4.86 (d, *J* = 3.9 Hz, 1H, H$_{C'''1}$), 4.70 (m, 3H, H$_{C5}$, H$_{C'5}$, H$_{C''5}$), 4.63 (m, 1H, H$_{C'''5}$), 4.58 (s, 1H, 1xH$_{B5}$), 4.56 (d, *J* = 2.7 Hz, 2H, 2xH$_{B5}$), 4.49 (s, 1H, 1xH$_{B5}$), 4.45 – 4.37 (m, 4H, 4xH$_{A4}$), 4.32 (m, 3H, 3xH$_{B4}$), 4.29 (bs, 1H, H$_{B4}$), 4.24 (d, *J* = 1.3 Hz, 1H, H$_{A5}$), 4.22 – 4.14 (m, 3H, 3xH$_{C3}$), 4.13 – 3.93 (m, 16H, 4xH$_{C2}$, H$_{C'''3}$, H$_{A'5}$, H$_{A''5}$, H$_{A'''5}$, 4xH$_{B3}$, 4xH$_{A3}$), 3.92 – 3.81 (m, 8H, 4xH$_{A2}$, 4xH$_{B2}$), 3.74 – 3.64 (m, 4H, 3xH$_{C4}$, -OC*H*$_2$CH$_2$CH=CH$_2$), 3.60 (m, 1H -OC*H*$_2$CH$_2$CH=CH$_2$), 3.38 (d, *J* = 5.9 Hz, 1H, H$_{C'''4}$), 2.33 (q, *J* = 6.7 Hz, 2H), 2.05 (s, 3H, 1xCH$_3$CONH-), 2.02 – 1.92 (m, 9H, 3xCH$_3$CONH-), 1.19 (m, 12H, 4xH$_{C6}$). ^{13}C NMR (214 MHz, D$_2$O) δ 176.5, 176.0, 175.9, 175.8, 175.6, 175.6, 175.5, 175.5, 175.4, 136.9 (-OCH$_2$CH$_2$*C*H=CH$_2$), 117.5 (-OCH$_2$CH$_2$CH=*C*H$_2$); 99.9, 99.4, 99.3 and 99.2 (4xC$_{C1}$, 4xC$_{A1}$); 98.0, 97.6, 97.4, 97.3 (4xC$_{B1}$); 81.0, 80.4, 80.3 (4xC$_{B4}$); 77.2, 77.2, 76.9, 76.8 (4xC$_{A3}$); 74.5, 74.2 (3xC$_{C3}$); 73.1 (C$_{A5}$); 72.3, 72.2, 72.0, 72.0 (4xC$_{B5}$); 69.7, 69.6, 69.5 (4xC$_{B3}$); 68.9 (-O*C*H$_2$CH$_2$CH=CH$_2$), 69.1,

69.0, 68.9, 68.8 (4xC_{A4}, 4xC_{B2}); 67.6, 66.9, 66.8 (4xC_{A2}); 65.5 ($C_{C'''5}$, according to HSQC), 64.0(C_{C5}, $C_{C'5}$, $C_{C'5}$), 55.8, 53.7, 53.5 (4xC_{C4}); 50.2, 48.5 (4xC_{C2}); 34.3 (-$OCH_2CH_2CH{=}CH_2$), 23.3 (CH_3CONH-), 23.2 (CH_3CONH-); 16.5, 16.5, 16.4 (4xC_{C6}). $[\alpha]^{20}_{D}$ = +192° (c = 0.05, H_2O). HR-MS: [M+H^+] Calculated for $C_{84}H_{128}N_8O_{61}$: 2225.7233; found: 2225.6348.

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