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Synthesis of Two Tetra- and Four Pentasaccharide Fragments of *Shigella flexneri* Serotypes 3a and X O-Antigens from a Common Tetrasaccharide Intermediate

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Relying on trichloroacetimidate chemistry, six tetra- and pentasaccharide fragments of the {2)-[α-D-Glc*p*-(1→3)]-α-L-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-[Ac→2]-α-L-Rha*p*-(1→3)-β-D-Glc*p*NAc-(1→}$_n$ (**(E)AB$_{Ac}$CD**)$_n$ polymer were synthesized as their propyl glycosides by use of a common fully protected **(E)AB$_{Ac}$C** intermediate (**9**). Tetrasaccharide **9** derived from the condensation of an **EA** donor and a **B$_{Ac}$C** acceptor. Partial and full deprotection gave free tetrasaccharides **(E)AB$_{Ac}$C** and **(E)ABC**, respectively. Alternatively, **9** was converted into a trichloroacetimidate donor, which provided linear pentasaccharides **(E)AB$_{Ac}$CD** and **(E)ABCD**, following a reaction with a **D** acceptor and subsequent partial or total deprotection, respectively. Additionally, the selective removal of the 2$_A$-levulinoyl protecting group in **9** allowed for chain elongation at this position. The glycosylation of the resulting acceptor with a **D** donor, and subsequent partial or total deprotection, gave branched pentasaccharides **D(E)AB$_{Ac}$C** and **D(E)ABC**. All targets are parts of the O-antigen of *Shigella flexneri* 3a, a prevalent serotype. Non-*O*-acetylated oligosaccharides are shared by the *S. flexneri* serotype X O-antigen.

Introduction

Enteric infections, which are responsible for some 1.7–2.5 million deaths per year, rank third among all causes of disease burden worldwide.[1] Most of these deaths occur in resource-poor countries, particularly in children younger than five years old. In this population, enteric infections are the second most common cause of death (18%) after pneumonia (19%).[2] A major drawback to the efficient prevention of diarrhoeal diseases through vaccination is the large number of pathogens involved. Among those is *Shigella*, a Gram-negative enterobacterium causing shigellosis or bacillary dysentery, which is an invasive infection of the human colon often associated with blood and mucus in the stool. Humans are the only reservoir for this highly contagious infection, which is also increasingly associated with antibiotic resistance.[3,4] In the absence of a vaccine, shigellosis remains a major health concern.[5] *Shigella flexneri*, one of the four *Shigella* species, is the one most frequently isolated worldwide. It is endemic to developing countries and prevails in children below five years old.[5,6] Based on the carbohydrate repeating unit of its O-antigen (O-Ag), which is the specific polysaccharide part of the bacterial lipopolysaccharide (LPS), *S. flexneri* is divided into 15 serotypes.[7] Several serotypes are isolated from individual patients, emphasizing the need for a multivalent vaccine providing broad serotype coverage. Although strain prevalence highly depends on geographic areas, serotype 2a and, among others, serotype 3a are predominant.[5,6] Investigations in the field indicated that clinical infection protects against subsequent exposure to a homologous serotype.[8,9] This is a good indication that in addition to playing a key role in bacterial virulence and resistance to innate immunity,[10] *S. flexneri* O-Ags are also crucial targets of the host protective adaptive immunity. All *S. flexneri* serotypes but one share a linear tetrasaccharide backbone, made of 3 α-linked L-rhamnosyl residues (**A**, **B**, **C**) and a 2-acetamido-2-deoxy-β-D-glucopyranosyl residue (**D**). Tetrasaccharide **ABCD** (**I**) is the basic repeating unit of serotype Y (Figure 1). Additional serotype specificity is associated with the presence of branched α-D-glucopyranosyl (**E**) and O-acetyl (O-Ac) decorations (Figure 1).[7] It is noteworthy that LPS glucosylation affects the *S. flexneri* 5a O-Ag conformation, resulting in a shortened length.[11] A strong impact on bacterial virulence was hypothesized.[10] However, the influence of *O*-acetylation remains unknown.

In order to gain a better understanding of the key role played by *S. flexneri* O-Ag decorations in bacterial virulence and resistance to innate immunity by investigating conformational behaviour, we initiated our study on *S. flexneri* 5a[11,12] and *S. flexneri* 2a.[13,14] More recently, we investigated additional serotype-specific glucosylation and *O*-acetylation patterns.[15] In a continuation of that study, we focused herein on *S. flexneri* 3a. The successful use of well-

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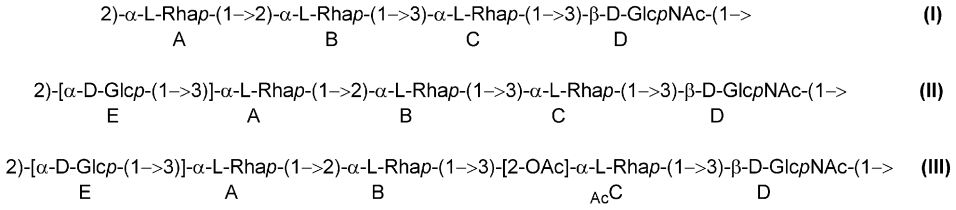


Figure 1. Repeating units of the O-Ags of *S. flexneri* serotypes Y (**I**), X (**II**) and 3a (**III**).

defined synthetic fragments of the native polymer to probe O-Ag structure and antibody recognition was demonstrated by others for serotype Y[16] and by us for serotype 5a[11] and 2a.[14] In this context, we report below on the synthesis of fragments of *S. flexneri* serotype X and 3a O-Ags, whose repeating units are the branched pentasaccharides **(E)ABCD** (**II**) and **(E)AB$_{Ac}$CD** (**III**),[17] respectively (Figure 1). We note that the *S. flexneri* X O-Ag is the non-*O*-acetylated form of the *S. flexneri* 3a O-Ag.

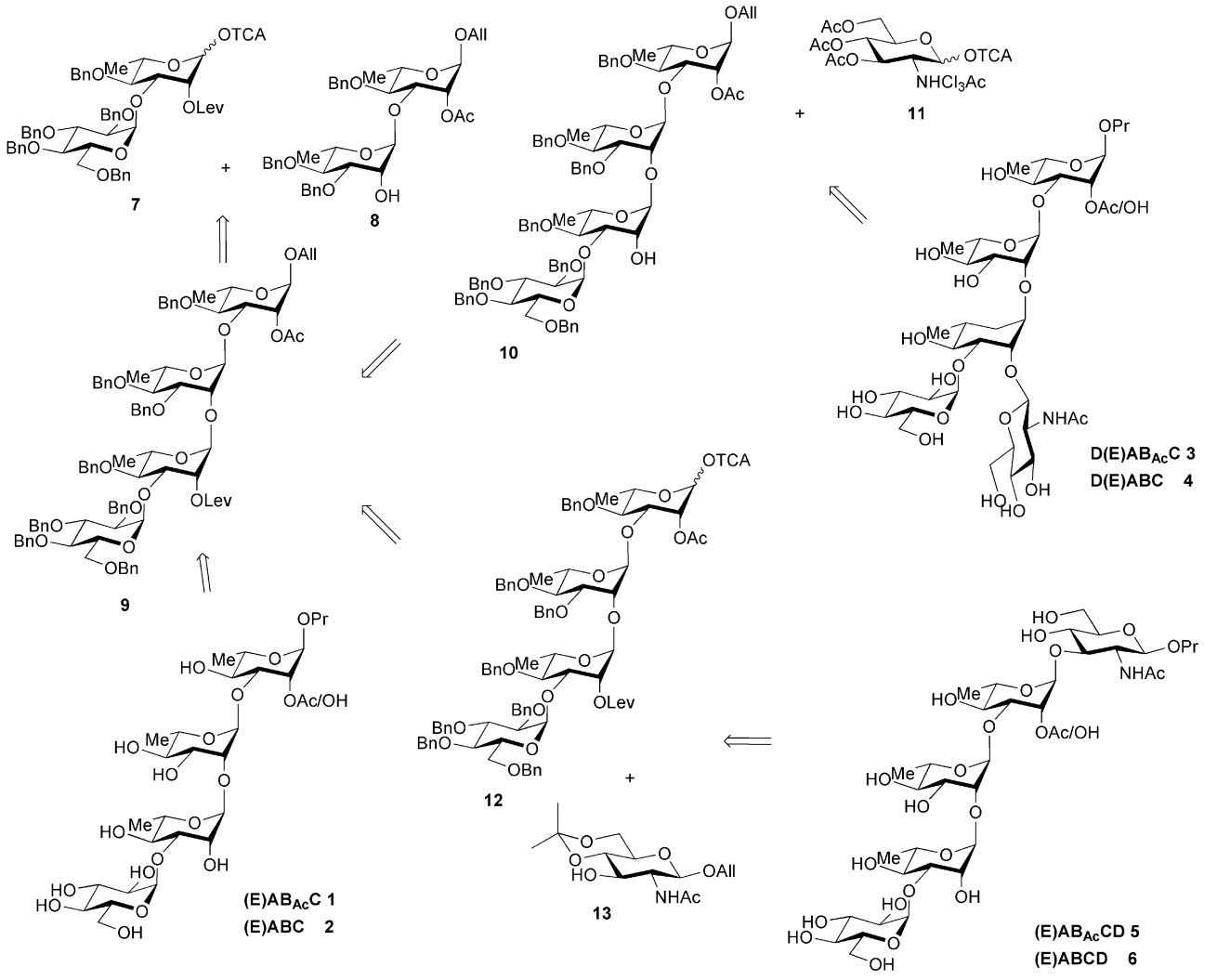
Results and Discussion

Following our recent contribution[15] on the synthesis of fragments **EA**, **D(E)A**, **CD(E)A**, **$_{Ac}$CD(E)A**, **BCD(E)A** and **B$_{Ac}$CD(E)A**, we report herein on the chemical synthesis of tetrasaccharides **(E)AB$_{Ac}$C** (**1**) and **(E)ABC** (**2**), as well as on that of pentasaccharides **D(E)AB$_{Ac}$C** (**3**), **D(E)ABC** (**4**), **(E)AB$_{Ac}$CD** (**5**), and **(E)ABCD** (**6**). Contrary to previous work on *S. flexneri* Y,[18] 2a,[19] and 5a[20] where methyl glycosides were the targets, all fragments bearing either L-rhamnoside **C** or 2-acetamido-2-deoxy-D-glucopyranoside **D** at their reducing end were synthesized as their propyl glycosides according to the following reasoning. All the glycosylation steps relied on highly efficient trichloroacetimidate (TCA) chemistry,[21] thus requiring temporary masking at the anomeric position of the various building blocks. Allyl glycosides match this requirement and are often efficiently used as intermediates in complex oligosaccharide synthesis.[22] Interestingly, in addition to being orthogonal to a number of protecting groups, allyl ethers are easily reduced to propyl ethers upon hydrogenation with Pd/C as catalyst.[15] We took advantage of this property to block the reducing end of the oligosaccharide targets in a form mimicking the anomeric group found in the O-Ag.

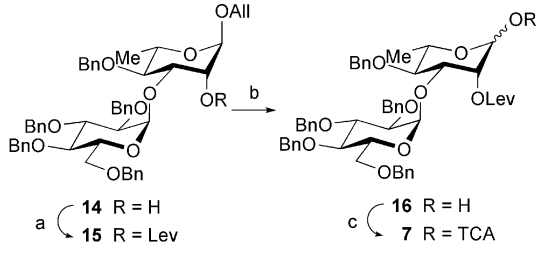
The combined retrosynthetic analysis of **1**–**6** led to two major conclusions, which served as a basis for the whole strategy (Scheme 1): (i) fully protected tetrasaccharide **(E)AB$_{Ac}$C** (**9**), bearing a levulinoyl group at position 2$_A$ and an allyl aglycon, could serve as a common intermediate to all desired targets and (ii) the levulinoyl group, being orthogonal to an acetyl group, could serve as a suitable protecting group, ensuring anchimeric assistance when using donors activated at position 1$_A$ or 1$_B$. Based on these assumptions, tetrasaccharide **9** would result from the condensation of an **EA** donor (**7**) and a **BC** acceptor (**8**), both of which are readily available from commercial monosaccharides. Partial and full deprotection of **9** should provide easy access to tetrasaccharides **1** and **2**, respectively. Alternatively, the selective removal of the levulinate at position 2$_A$ of tetrasaccharide **9** would result in acceptor **10**, whose condensation with the known glucosamine donor **11**[23,24] would give a precursor to both pentasaccharides **3** and **4**. Furthermore, the selective cleavage of the allyl aglycon and subsequent trichloroacetimidate activation would turn **9** into donor **12**. The latter should react with known acceptor **13**[24,25] to give a pentasaccharide serving as a key intermediate for both mono-acetate **5** and fully deprotected **6**.

Synthesis of the EA Disaccharide Donor 7

The **E**–**A** linkage is the only 1,2-*cis* glycosidic linkage in the targeted sequences, and for that reason, it was built at an early stage in the synthesis. The known disaccharide **14**,[26] prepared as described,[15] served as an exquisite precursor to **7** (Scheme 2). However, levulinoylation at position 2$_A$ of **14** could not be completed and resulted in an inseparable 3:2 mixture of levulinate **15** and starting **14** when attempted by the treatment of **14** with levulinic acid, DCC, and DMAP in CH_2Cl_2, according to a known protocol.[27] Analogously to previous observations,[12,26] the failure to go to completion was tentatively explained by the 2,3,4,5-tetra-*O*-benzyl-α-D-glucopyranosyl residue at O-3$_A$ causing steric hindrance at OH-2$_A$ in **14**. Benzoylation at OH-2$_A$ succeeded when performed at 70 °C.[26] However, the conversion of **14** to **15** with levulinic acid reached 80% at best when heating the reaction mixture or changing the solvent. Therefore, other reagents were envisioned. Instead of levulinoyl chloride, which is known to form labile pseudo esters,[28] we investigated the use of levulinic anhydride.[29,30] Under conventional conditions, the reaction was sluggish. However, increasing the amount of levulinic anhydride and DMAP up to 10 and 5 equiv., respectively, while performing the esterification at 50 °C allowed for complete conversion. The fully protected disaccharide **15** was isolated in an excellent 95% yield. Allyl glycoside **15** was then converted to hemiacetal **16** (92%) following a two-step selective deallylation procedure involving: (i) the isomerisation of the allyl ether into the corresponding prop-1-enyl ether with a cationic iridium complex[31] and (ii) subsequent iodine-mediated hydrolysis.[32] Finally, the **EA** disaccharide donor **7** was obtained as an anomeric mixture in 97% yield by reacting hemiacetal **16** with trichloroacetonitrile with a catalytic amount of DBU.



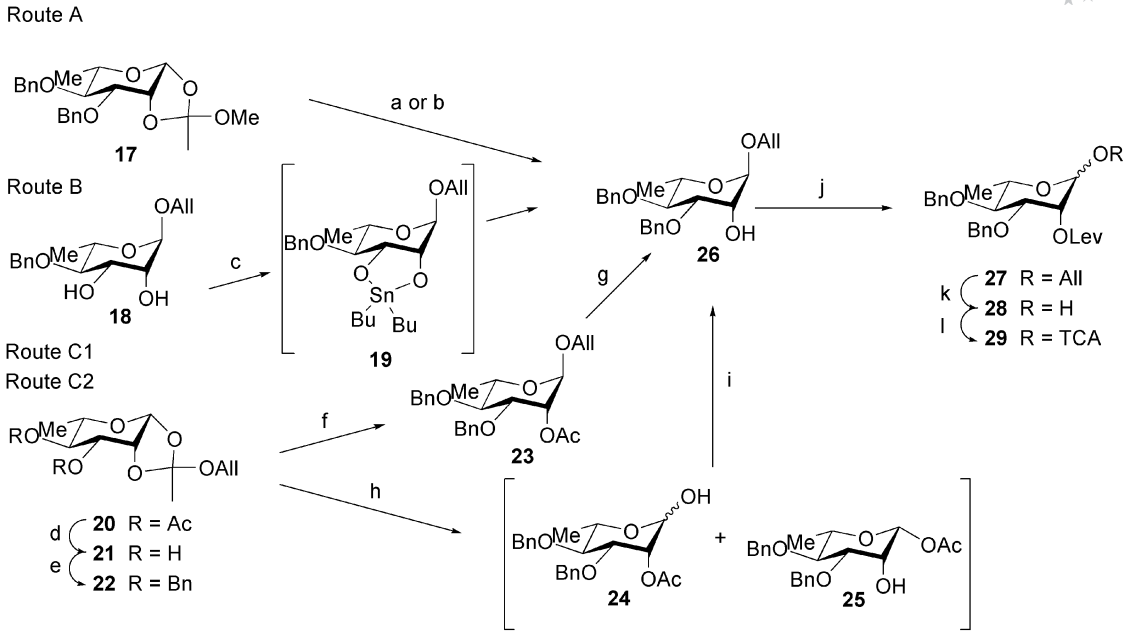
Scheme 1. Retrosynthetic analysis of propyl glycosides **1**–**6**.



Scheme 2. Synthesis of the **EA** disaccharide donor **7**: (a) Levulinic anhydride, DMAP, pyridine, 50 °C, 95%; (b) i; catalytic $[Ir(COD)\{PCH_3(C_6H_5)_2\}_2]^+PF_6^-$, THF, room temp.; ii. I_2, THF/H_2O, room temp., 92%; (c) CCl_3CN, DBU, DCE, –5 °C, 97%.

Synthesis of the BC Disaccharide Acceptor 8

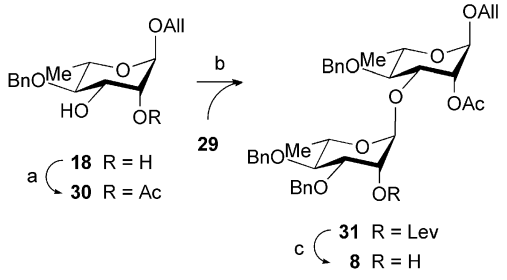
Disaccharide **8** could be most conveniently prepared by the condensation of known acceptor[33] **30** and the as yet undisclosed trichloroacetimidate **29**. The latter was obtained from alcohol **26**, which often derives from the high-yielding $BF_3{\cdot}OEt_2$-[34] or TMSOTf-mediated[35] allyl glycosidation of methyl orthoester **17** and subsequent transesterification. Alternatively, taking advantage of the easy accessibility of large amounts of crystalline diol **18**,[15] a key precursor to donor **7**, alcohol **26** was prepared in 88% yield by the regioselective benzylation at position 3 of **18** upon treatment of stannylene intermediate **19** with benzyl bromide and caesium fluoride.[36] Additionally, our investigation on allyl orthoester **22**, obtained in 5 steps and 76% yield from L-rhamnose through diacetate **20** and diol **21**,[37] opened new routes to alcohol **26**. On one hand, the TMSOTf-mediated intramolecular rearrangement of **22** gave acetate **23** (88%), which was turned into **26** upon treatment with methanolic MeONa (92%), in a strategy similar to one involving the corresponding methyl orthoester **17**. On the other hand, heating the 3:2 mixture of mono-*O*-acetylated regioisomers **24** ($\delta_{C\text{-}1}$ = 92.4 ppm, $^1J_{C,H}$ = 170.9 Hz and $\delta_{H\text{-}1}$ = 5.15 ppm, $\delta_{H\text{-}2}$ = 5.41 ppm), and **25** ($\delta_{C\text{-}1}$ = 93.32 ppm, $^1J_{C,H}$ = 158.7 Hz and $\delta_{H\text{-}1}$ = 5.67 ppm, $\delta_{H\text{-}2}$ = 4.16 ppm), resulting from the 10% aqueous HCl-mediated hydrolysis of orthoester **22**, in allylic alcohol containing acetyl chloride gave **26** in 85% yield from the dibenzyl orthoester. This alternative conversion of **22** into **26** is



Scheme 3. Synthesis of the **B** monosaccharide donor **29**: (a) see ref.[34] (b) see ref.[35] (c) i. Bu_2SnO, 4-Å MS, toluene; ii. CsF, BnBr, DMF, 88%; (d) K_2CO_3, MeOH; (e) NaH, BnBr, DMF, 76%; (f) TMSOTf, 4-Å MS, CH_2Cl_2, 88%; (g) NaOMe, MeOH, 92%; (h) 10% aqueous HCl, EtOAc; (i) AllOH, AcCl, 85%; (j) Levulinic acid, DCC, DMAP, room temp., 89%; (k) i. catalytic $[Ir(COD)\{PCH_3(C_6H_5)_2\}_2]^+PF_6^-$, THF, room temp.; ii. I_2, THF/H_2O, room temp., 96%; (l) CCl_3CN, DBU, DCE, –5 °C, 92%.

comparable to more conventional ones.[34,35] According to this route, alcohol **26** was isolated in 72% from L-rhamnose after 6 steps with only one chromatographic purification. Despite a larger number of steps, we found this route to be superior to that involving diol **18** (68% from L-rhamnose) since the overall yield was comparable, but tin was avoided (Scheme 3).

Alcohol **26** was treated with levulinic acid in the presence of DCC and DMAP to give ester **27** (89%), which was converted to hemiacetal **28** (96%) upon anomeric deallylation. The latter was then activated as the trichloroacetimidate **29** (92%). The TMSOTf-mediated condensation of donor **29** and acceptor **30**,[38] resulting from the regioselective acetylation of diol **18**, was attempted in both CH_2Cl_2 and toluene. In toluene, the fully protected disaccharide **31** was isolated in higher yield, reaching 89% when the reaction was performed on 7 g of **18**. The removal of the 2_B-levulinoyl ester of **31** by reaction with hydrazine in pyridine/AcOH gave the required disaccharide acceptor **8** (81%, Scheme 4).



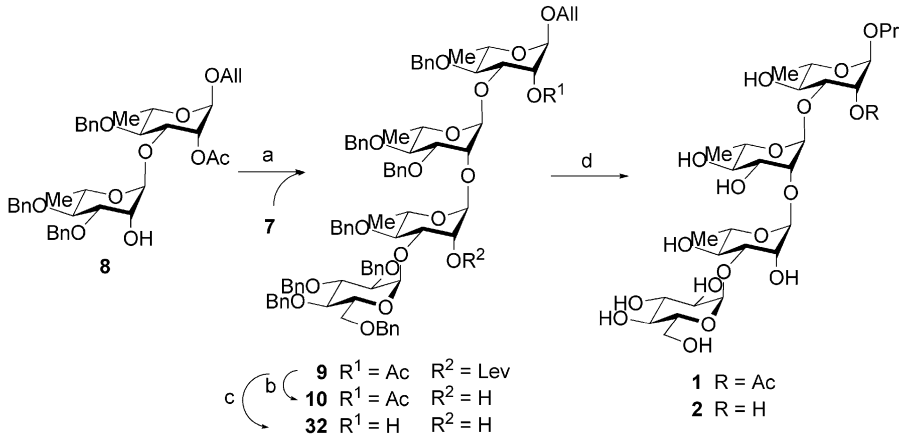
Scheme 4. Synthesis of the **BC** disaccharide acceptor **8**: (a) i. $MeC(OMe)_3$, PTSA, CH_3CN; ii. 80% aqueous AcOH, quant.; (b) catalytic TMSOTf, 4-Å MS, –78 °C, toluene, 89%; (c) hydrazine hydrate, pyridine/AcOH (3:2, v/v), room temp., 81%.

Synthesis of the (E)AB$_{Ac}$C and (E)ABC Tetrasaccharides 1 and 2

Performing the condensation of donor **7** and acceptor **8** in CH_2Cl_2 containing a catalytic amount of TMSOTf gave the fully protected tetrasaccharide **9** in 69% yield. In toluene, the yield of **9** reached 75% and was even brought up to 92% when the condensation was performed on 4 g of **8** instead of 200 mg (Scheme 5). The NMR analysis of **9**, showing $^1J_{C,H}$ = 176.6 Hz, indicated an α-AB linkage and confirmed that the levulinic ester had played its role as a participating group. The selective removal of the levulinoyl group gave alcohol **10** (89%), which was submitted to hydrogenolysis and concomitant Pd/C-mediated allyl reduction under neutral conditions to give the mono-*O*-acetylated tetrasaccharide **1** (76%). Alternatively, refluxing **9** in methanolic MeONa gave diol **32** (95%), which was then converted into the target tetrasaccharide **2** (81%).

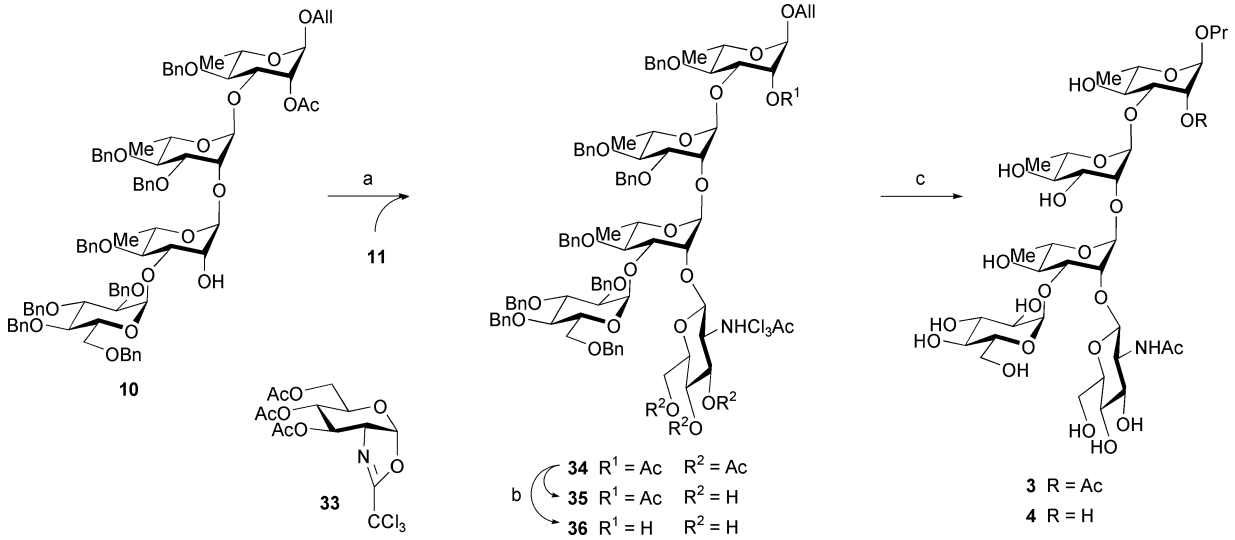
Synthesis of the D(E)AB$_{Ac}$C and D(E)ABC Pentasaccharides 3 and 4

Alcohol **10** served as an ideal intermediate in the synthesis of pentasaccharides **3** and **4** (Scheme 6). As for the preparation of pentasaccharide **BCD(E)A**,[15] we reasoned that a controlled transesterification would allow for the selective



Scheme 5. Synthesis of tetrasaccharides **1** and **2**: (a) catalytic TMSOTf, 4-Å MS, –78 °C, toluene, 92%; (b) hydrazine hydrate, pyridine/AcOH (3:2, v/v), room temp., 89%; (c) NaOMe, MeOH, reflux, 95%; (d) Pd/C, H_2, EtOH, 76% **1**, 81% **2**.

removal of vicinal acetates in the presence of an isolated 2_C-acetate. Therefore, the triacetate donor **11**, having an *N*-trichloroacetyl (Cl_3Ac) protecting pattern, was selected as a precursor to residue **D**. When tetrasaccharide **10** and donor **11** were reacted in CH_2Cl_2 containing TMSOTf under conditions successfully used for the condensation of disaccharide **14** and **11**,[15,24] the condensation product **34** was isolated in only 20% yield, together with unreacted oxazoline **33** (40%, $\delta_{H\text{-}1}$ = 6.35 ppm, $J_{1,2}$ = 7.5 Hz).[23] This result was tentatively explained by the increased steric hindrance at the 2_A-hydroxy group on going from **14** to **10**. Based on this hypothesis, attempts to improve the outcome of the glycosylation relied on investigating the impact of four parameters, including the solvent, temperature, and the amounts of donor **11** and TMSOTf (Table 1). Comparison of Entries 1 and 6 with 2 and 7 of Table 1, respectively, shows that for this specific condensation, toluene is a better solvent than CH_2Cl_2, although the improvement in yield was minor. However, increasing the amount of TMSOTf from 0.3 to 0.5 equiv. had an additional benefit as seen from Entries 2 and 3 of Table 1. In addition to the observed significant effect of the reaction temperature (Table 1, Entries 3–5), increasing the amount of donor **11** from 1.3 to 2 equiv. had the most visible impact (Table 1, Entries 4, 7, and 8). Taking into account all of these observations, pentasaccharide **34** was isolated in a satisfactory 82% yield (Table 1, Entry 8). Conversion of **34** to triol **35** was the next step. Contrary to previous observations on a related system,[15] methanolic K_2CO_3 was poorly selective. The regioselectivity was barely improved with Et_3N/MeOH/H_2O or methanolic MeONa (data not shown). Under the best identified conditions, triol **35** and tetraol **36** were isolated following column chromatography in 56 and 30% yield, respectively. The high-pressure Pd/C-mediated hydrogenation[15] of **35** and **36**, allowing concomitant benzyl hydrogenolysis, allyl reduction, and trichloroacetamide reductive hydrodechlorination, gave the pentasaccharide targets **3** (74%, 2 d) and **4** (74%, 1 d), respectively. The transformation of tri-



Scheme 6. Synthesis of pentasaccharides **3** and **4**: (a) TMSOTf (0.5 equiv.), 4-Å MS, –40 °C, toluene, 82%; (b) NaOMe, MeOH, room temp., 25 min, 86%; (c) Pd/C, H_2, 45 bar, EtOH, 74% **3**, 74% **4**.

chloroacetamide **35** into the 2_C-acetate target **3** was much faster than the analogous conversion performed to obtain $_{Ac}$**CD(E)A** (76%, 10 d) and **B**$_{Ac}$**CD(E)A** (70%, 10 d).[15] Interestingly, monitoring the conversion by mass and NMR spectroscopy in the latter cases showed that the chloroacetamide to acetamide conversion was the rate-limiting step. Steric hindrance at NH-2_D was hypothesized.[15] The data presented here for obtaining pentasaccharide **D(E)ABC** (**3**), with monosaccharide **D** acting as an end-chain residue support this hypothesis.

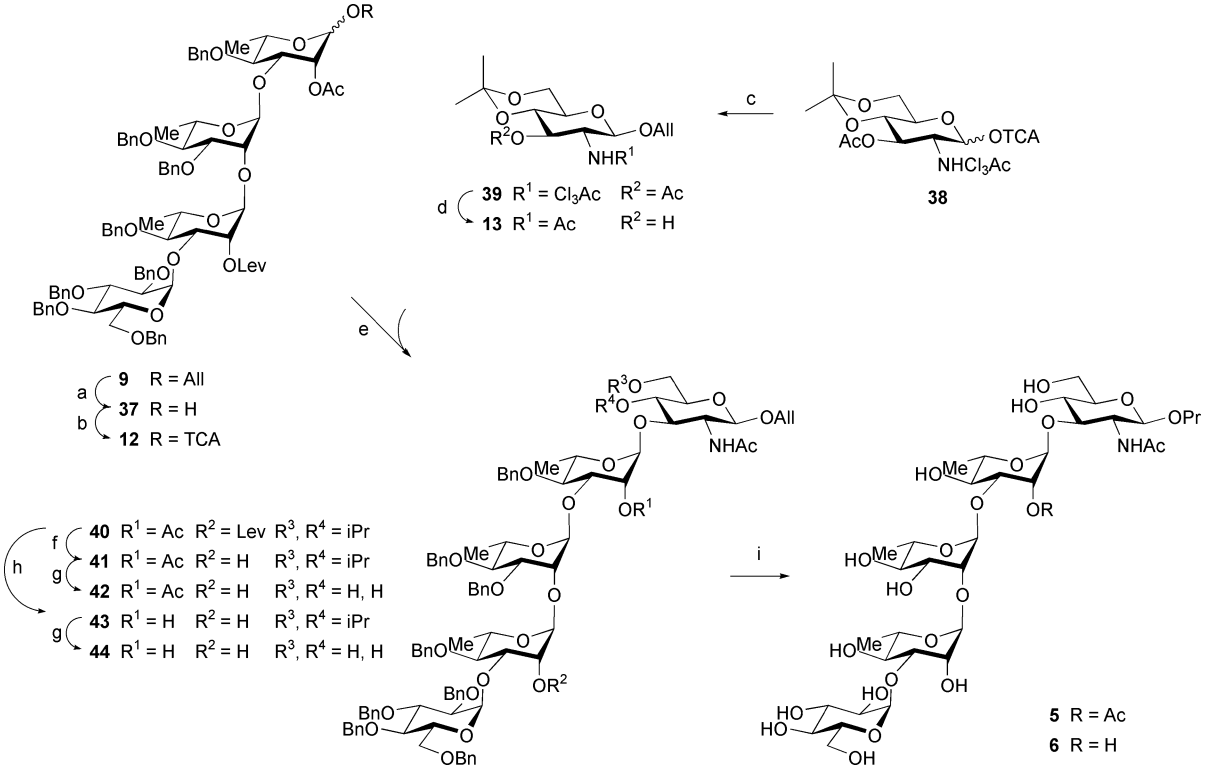
Table 1. Coupling of monosaccharide donor **11** and tetrasaccharide acceptor **10** under various conditions.

Entry	TMSOTf [equiv.]	Temp. [°C]	Donor **11** [equiv.]	Solvent	Yield [%]
1	0.3	–78	1.3	CH_2Cl_2	20
2	0.3	–78	1.3	toluene	30
3	0.5	–78	1.3	toluene	50
4	0.5	–40	1.3	toluene	65
5	0.5	–20	1.3	toluene	60
6	0.5	–40	1.6	CH_2Cl_2	67
7	0.5	–40	1.6	toluene	72
8	0.5	–40	2.0	toluene	82

Synthesis of the (E)AB$_{Ac}$CD and (E)ABCD Pentasaccharides 5 and 6

Donor **12**, easily obtained from the fully protected tetrasaccharide **9** in two steps, served as an exquisite intermediate in the synthesis of pentasaccharides **5** and **6** (Scheme 7). The anomeric deallylation of **9** gave hemiacetal **37** (90%), which was converted into trichloroacetimidate **12** (88%) following a reaction with trichloroacetonitrile. Donor **12** was subsequently reacted with acceptor **13**.[24,25] As an alternative to its known synthesis,[25] the latter was obtained in two steps from the known 4,6-*O*-isopropylidene acetal donor[15,24] **38**. Trichloroacetimidate **38** was treated with allyl alcohol and a catalytic amount of TMSOTf in CH_2Cl_2 to give allyl glycoside **39** (82%). The saponification of **39** and subsequent *N*-acetylation of the resulting amino alcohol gave **13** (71%). The attempted condensation of **12** and **13** was performed under conditions that took advantage of the knowledge gained in the synthesis of *S. flexneri* 3a oligosaccharides as well as of the expertise derived from studying a related system in the *S. flexneri* 2a series.[22] Thus, tetrasaccharide **12** was treated with acceptor **13** (2.5 equiv.) and TfOH (0.9 equiv.) in toluene at 70 °C to give the condensation product **40** in a satisfactory 78% yield. The use of a large excess of acceptor **13** was found necessary to overcome its low reactivity, which leads to the hydrolysis of unreacted **12**.

The selective removal of the levulinoyl ester in **40** gave alcohol **41** (85%), which was converted to triol **42** by the acidic hydrolysis of the 4,6-*O*-isopropylidene acetal (92%). The Pd/C-mediated benzyl hydrogenolysis and concomitant allyl reduction of **42** gave the target acetate **5** in 77% yield. Alternatively, the transesterification of **40** in refluxing methanolic MeONa gave diol **43** (94%), which was subsequently converted into the corresponding tetraol **44** (66%) upon



Scheme 7. Synthesis of pentasaccharides **5** and **6**: (a) i. catalytic [Ir(COD){$PCH_3(C_6H_5)_2$}$_2$]$^+PF_6^-$, THF, room temp.; ii. I_2, THF/H_2O, room temp., 90%; (b) CCl_3CN, DBU, DCE, –5 °C, 88%; (c) AllOH, catalytic TMSOTf, CH_2Cl_2, –78 °C, 82%; (d) 1 M aqueous NaOH, MeOH, 71%; (e) TfOH (0.9 equiv.), 4-Å MS, 70 °C, toluene, 78%; (f) hydrazine hydrate, pyridine/AcOH, room temp., 85%; (g) 50% aqueous TFA, CH_2Cl_2, 0 °C, 92% **42**, 70% **44**; (h) NaOMe, MeOH, reflux, 94%; (i) Pd/C, H_2, EtOH, 77% **5**, 70% **6**.

acidic hydrolysis of the 4,6-*O*-isopropylidene protecting group. The final debenzylation and allyl reduction of **44** gave the free pentasaccharide **6** (70%).

Conclusions

The synthesis of the two linear tetrasaccharides **1**, **2** and of the four branched pentasaccharides **3**–**6**, representative of fragments of *S. flexneri* 3a and X O-Ags, was described. The overall strategy relied on the use of a common tetrasaccharide **EABC** intermediate **9**, obtained in 28 synthetic steps. Indeed, fully protected **9**, having an allyl aglycon, a 2_C-acetate, and a 2_A-levulinoyl ester, served as a convenient precursor, providing easy access to all targets. Thus, starting from **9**, both oligosaccharides **1** and **2** were synthesized in 2 steps. Pentasaccharides **3** and **4** were obtained in 7 steps, whereas pentasaccharides **5** and **6** were prepared in 13 steps from the shared intermediate **9**. All targets were synthesized as their propyl glycosides. The overall strategy took advantage of the recently disclosed neutral conditions[15] allowing for concomitant benzyl hydrogenolysis, allyl reduction, and reductive trichloroacetamide conversion to acetamide.

Experimental Section

General: TLC was performed with precoated slides of Silica Gel 60 F_{254} (Merck). Detection was effected when applicable, with UV light, and/or by charring in orcinol (35 mM) in 4 N aqueous sulfuric acid and ethanol (95:5). Preparative chromatography was performed by elution from columns of Silica Gel 60 (particle size 0.040–0.063 mm). NMR spectra were recorded at 30 °C for solutions in $CDCl_3$ or D_2O (400 MHz for ^1H, 100 MHz for ^{13}C). Residual $CHCl_3$ (δ = 7.28 ppm for ^1H and 77.0 ppm for ^{13}C) and HOD (δ = 4.79 ppm) were used as internal references for solutions in $CDCl_3$ and D_2O, respectively. Proton signal assignments were made by first-order analysis of the spectra, as well as analysis of 2D ^1H-^1H correlation maps (COSY). Of the two magnetically non-equivalent geminal protons at C-6, the one resonating at lower field is denoted H-6a, and the one at higher field is denoted H-6b. The ^{13}C NMR assignments were supported by 2D ^{13}C-^1H correlation maps (HMBC and HSQC). Interchangeable assignments are marked with an asterisk in the listing of signal assignments. Sugar residues are serially lettered according to the lettering of the repeating unit of the *S. flexneri* 3a O-Ag and identified by a subscript in the listing of signal assignments. Electrospray ionisation/time-of-flight (ESI-TOF) mass spectra were recorded in the positive-ion mode with 1:1 acetonitrile (CH_3CN)/H_2O containing 0.1% formic acid as the ESI-TOF spectrometer solution. Anhydrous dichloromethane (CH_2Cl_2) and 1,2-dichloroethane (DCE), delivered on molecular sieves, were used as such. 4-Å MS were activated before use by heating at 250 °C under vacuum. Additional solvents commonly cited in the text are abbreviated as Chex (cyclohexane), THF (tetrahydrofuran), and Tol (toluene).

Allyl (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-4-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranoside (15): DMAP (13.9 g, 114 mmol, 5 equiv.) was added to a solution of alcohol **14**[26] (18.6 g, 22.8 mmol) in pyridine (150 mL). The mixture was stirred at 50 °C, and levulinic anhydride[30] (48.8 g, 228 mmol, 10 equiv.) in pyridine (150 mL) was added dropwise to the solution. After 3 h, TLC (Chex/EtOAc, 7:3) showed the complete disappearance of the starting material and the presence of one more polar product. The reaction mixture was concentrated under reduced pressure. Chromatography of the residue (Chex/EtOAc, 90:10 → 75:25) gave disaccharide **15** (19.7 g, 95%) as a colourless syrup. Compound **15** had R_f = 0.3 (Chex/EtOAc, 7:3). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.10 (m, 25 H, CH_{Ph}), 5.87 (m, 1 H, CH=), 5.39 (m, 1 H, H-2_A), 5.28 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.19 (d, $J_{1,2}$ = 5.6 Hz, 1 H, H-1_E), 5.28 (m, J_{cis} = 10.3 Hz, 1 H, =CH_2), 5.02 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.96–4.85 (m, 3 H, H_{Bn}), 4.78 (d, $J_{1,2}$ = 1.8 Hz, 1 H, H-1_A), 4.78–4.59 (m, 4 H, H_{Bn}), 4.50 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.36 (d, J = 12.0 Hz, 1 H, H_{Bn}), 4.26 (dd, $J_{2,3}$ = 3.2, $J_{3,4}$ = 9.6 Hz, 1 H, H-3_A), 4.18–4.04 (m, 3 H, H_{All}, H-3_E, H-5_E), 3.97 (m, 1 H, H_{All}), 3.80 (m, 1 H, H-5_A), 3.77 (pt, $J_{4,5}$ = 9.2 Hz, 1 H, H-4_E), 3.64–3.52 (m, 4 H, H-2_E, H-$6a_E$, H-4_A, H-$6b_E$), 2.55 (m, 4 H, 2 × CH_{2Lev}), 2.09 (s, 3 H, CH_{3Lev}), 1.40 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.5 (C_{Lev}), 172.5 (C_{Lev}), 139.2–138.1 (C_{Ph}), 134.0 (CH=), 129.0–127.8 (CH_{Ph}), 117.8 (=CH_2), 97.0 ($^1J_{C,H}$ = 170.2 Hz, C-1_E), 93.3 ($^1J_{C,H}$ = 167.5 Hz, C-1_A), 82.5 (C-3_E), 80.3 (C-4_A), 80.0 (C-2_E), 78.3 (C-4_E), 76.5, 75.9, 75.3, 73.7, 72.8 (5 C, C_{Bn}), 72.8 (C-3_A), 70.6 (C-5_E), 68.7 (C-6_E), 68.6 (C-2_A), 68.5 (C_{All}), 68.4 (C-5_A), 38.2 (CH_{2Lev}), 30.0 (CH_{3Lev}), 28.4 (CH_{2Lev}), 18.3 (C-6_A) ppm. HRMS (ESI$^+$): calcd. for $C_{55}H_{62}O_{12}$ $[M + Na]^+$ 937.4139; found 937.4109, calcd. for $[M + NH_4]^+$ 932.4585; found 932.4542.

(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-4-*O*-benzyl-2-*O*-levulinoyl-α/β-L-rhamnopyranose (16): 1,5-Cyclooctadiene-bis-(methyldiphenylphosphane)iridium hexafluorophosphate (250 mg) was dissolved in THF (100 mL), and the resulting red solution was degassed under an argon stream. Hydrogen was bubbled through the solution, causing the colour to change to yellow. The solution was then degassed again under an argon stream. A solution of **15** (8.5 g, 9.3 mmol) in THF (15 mL) was added. The mixture was stirred overnight at room temp. TLC (Chex/EtOAc, 7:3) showed the complete disappearance of the starting material and the presence of a single less polar product. The mixture was treated with a solution of iodine (4.7 g, 18.6 mmol) in THF/H_2O (50 mL, 4:1 v/v) for 1 h at room temp. TLC (Chex/EtOAc, 7:3 and CH_2Cl_2/MeOH, 98:2) showed the complete disappearance of the intermediate and the presence of a single more polar product. Excess iodine was destroyed by the addition of a solution of freshly prepared sodium bisulfite (5% aqueous, 40 mL). CH_2Cl_2 (300 mL) was added, and the organic phase was washed with brine (3 × 50 mL), H_2O (3 × 50 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (CH_2Cl_2/MeOH, 99:1 → 9:1) gave disaccharide **16** (α/β: 7:3, 7.5 g, 92%) as a yellow syrup. Hemiacetal **16** had R_f = 0.2 (CH_2Cl_2/MeOH, 98:2); α anomer: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.14 (m, 25 H, CH_{Ph}), 5.43 (m, 1 H, H-2_A), 5.25 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1_E), 5.15 (d, $J_{1,2}$ = 1.7 Hz, 1 H, H-1_A), 5.07–4.87 (m, 3 H, H_{Bn}), 4.80 (d, J = 12.2 Hz, 1 H, H_{Bn}), 4.74–4.59 (m, 3 H, H_{Bn}), 4.52 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.46–4.36 (d, 2 H, H_{Bn}), 4.34 (m, 1 H, H-3_A), 4.20–4.10 (m, 2 H, H-3_E, H-5_E), 4.05 (m, 1 H, H-5_A), 3.78–3.73 (m, 2 H, OH, H-4_E), 3.70–3.55 (m, 4 H, H-2_E, H-$6a_E$, H-4_A, H-$6b_E$), 2.55 (m, 4 H, 2 × CH_{2Lev}), 2.11 (s, 3 H, CH_{3Lev}), 1.41 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ = 206.9 (C_{Lev}), 172.6 (C_{Lev}), 139.2–138.9 (C_{Ph}), 129.0–127.8 (CH_{Ph}), 93.0 ($^1J_{C,H}$ = 169.0 Hz, C-1_E), 92.4 ($^1J_{C,H}$ = 170.7 Hz, C-1_A), 82.5 (C-3_E), 80.3 (C-4_A), 79.9 (C-2_E), 78.3 (C-4_E), 76.5, 75.9, 75.4, 73.6, 73.2 (5 C, C_{Bn}), 72.3 (C-3_A), 70.5 (C-5_E), 69.0 (C-2_A), 68.7 (C-6_E), 68.3 (C-5_A), 38.3 (CH_{2Lev}), 30.1 (CH_{3Lev}), 28.6 (CH_{2Lev}), 18.5 (C-6_A) ppm. β anomer: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.14 (m, 25 H, CH_{Ph}), 5.62 (d, $J_{2,3}$ = 2.7 Hz, 1 H, H-2_A), 5.38 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1_E), 5.07–4.87 (m, 3 H, H_{Bn}), 4.80 (d, J = 12.2 Hz, 1 H, H_{Bn}),

4.79 (s, 1 H, H-1_A), 4.74–4.59 (m, 3 H, H_{Bn}), 4.53 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.46–4.36 (d, 2 H, H_{Bn}), 4.20–4.10 (m, 2 H, H-3_E, H-5_E), 4.00 (m, 1 H, H-3_A), 3.75 (m, 1 H, H-4_E), 3.70–3.55 (m, 3 H, H-2_E, H-$6a_E$, H-$6b_E$), 3.53 (pt, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 3.44 (m, 1 H, H-5_A), 2.55 (m, 4 H, 2 × CH_{2Lev}), 2.14 (s, 3 H, CH_{3Lev}), 1.47 (d, $J_{5,6}$ = 6.0 Hz, 3 H, H-6_A) ppm. ^{13}C NMR ($CDCl_3$): δ = 208.6 (C_{Lev}), 173.1 (C_{Lev}), 139.2–138.9 (C_{Ph}), 129.0–127.8 (CH_{Ph}), 93.6 ($^1J_{C,H}$ = 160.9 Hz, C-1_A), 92.6 ($^1J_{C,H}$ = 169.1 Hz, C-1_E), 82.4 (C-3_E), 79.6 (C-4_A), 80.0 (C-2_E), 78.4 (C-4_E), 76.6, 76.0, 75.5 (3 C, C_{Bn}), 74.2 (C-3_A), 73.6, 73.4 (2 C, C_{Bn}), 72.3 (C-5_A), 70.5 (C-5_E), 69.0 (C-2_A), 68.8 (C-6_E), 39.1 (CH_{2Lev}), 30.0 (CH_{3Lev}), 28.5 (CH_{2Lev}), 18.5 (C-6_A) ppm. HRMS (ESI^+): calcd. for $C_{52}H_{58}O_{12}$ $[M + Na]^+$ 897.3826; found 897.3777, calcd. for $[M + NH_4]^+$ 892.4272; found 892.4234.

(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-4-*O*-benzyl-2-*O*-levulinoyl-α/β-L-rhamnopyranose Trichloracetimidate (7): Hemiacetal **16** (7.1 g, 8.1 mmol) was dissolved in DCE (30 mL), placed under argon, and cooled to –5 °C. Trichloroacetonitrile (4.0 mL, 40.5 mmol, 5 equiv.) and DBU (340 μL, 2.3 mmol, 0.28 equiv.) were added. The mixture was stirred at –5 °C for 10 min. TLC (Chex/EtOAc + Et_3N, 7:3) showed the complete disappearance of **16** and the presence of a single less polar product. The mixture was directly chromatographed (Chex/EtOAc + 5% Et_3N, 7:3 → 1:1) to give **7** (8.0 g, 97%) as a yellow syrup. Trichloroacetimidate **7** (α anomer) had R_f = 0.35 (Chex/EtOAc, 7:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (s, 1 H, NH), 7.42–7.14 (m, 25 H, CH_{Ph}), 6.24 (d, $J_{1,2}$ = 2.0 Hz, 1 H, H-1_A), 5.61 (m, 1 H, H-2_A), 5.27 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1_E), 5.05–4.99 (m, 2 H, H_{Bn}), 4.92–4.88 (m, 2 H, H_{Bn}), 4.80 (d, J = 12.0 Hz, 1 H, H_{Bn}), 4.74–4.53 (m, 4 H, H_{Bn}), 4.42 (d, J = 12.2 Hz, 1 H, H_{Bn}), 4.34 (dd, $J_{2,3}$ = 3.1, $J_{3,4}$ = 9.7 Hz, 1 H, H-3_A), 4.16–4.06 (m, 2 H, H-3_E, H-5_E), 4.02 (m, 1 H, H-5_A), 3.79 (pt, $J_{3,4}$ = 9.3 Hz, 1 H, H-4_E), 3.71–3.62 (m, 3 H, H-4_A, H-$6a_E$, H-2_E), 3.52 (m, 1 H, H-$6b_E$), 2.59 (m, 4 H, 2 × CH_{2Lev}), 2.11 (s, 3 H, CH_{3Lev}), 1.45 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.3 (C_{Lev}), 172.5 (C_{Lev}), 160.5 (C=NH), 139.1–137.9 (C_{Ph}), 129.2–127.8 (CH_{Ph}), 95.4 ($^1J_{C,H}$ = 178.9 Hz, C-1_A), 93.4 ($^1J_{C,H}$ = 168.3 Hz, C-1_E), 91.3 (CCl_3), 82.4 (C-3_E), 79.8 (C-2_E), 79.5 (C-4_A), 78.2 (C-4_E), 76.8, 75.9, 75.4, 73.8, 73.2 (5 C, C_{Bn}), 72.5 (C-3_A), 71.4 (C-5_A), 70.8 (C-5_E), 68.4 (C-6_E), 66.9 (C-2_A), 38.2 (CH_{2Lev}), 30.0 (CH_{3Lev}), 28.4 (CH_{2Lev}), 18.4 (C-6_A) ppm.

3,4-Di-*O*-benzyl-1,2-(allyloxyethylidene)-β-L-rhamnopyranose (22): Acetic anhydride (100 mL) was added dropwise to a solution of L-rhamnose (36.4 g, 200 mmol) in anhydrous pyridine (100 mL). The resulting mixture was stirred at room temp. under argon. After 1 d, TLC (CH_2Cl_2/MeOH, 8:2) showed the complete disappearance of the starting material. The mixture was concentrated under reduced pressure, and volatiles were eliminated by repeated coevaporation with toluene to provide the tetra-acetate (66.3 g) as a colourless syrup. The product had R_f = 0.3 (Chex/EtOAc, 6:4); α anomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (d, $J_{1,2}$ = 1.9 Hz, 1 H, H-1), 5.27 (dd, $J_{3,4}$ = 10.1, $J_{2,3}$ = 3.5 Hz, 1 H, H-3), 5.22 (m, 1 H, H-2), 5.09 (pt, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 3.91 (dq, 1 H, H-5), 2.14, 2.13, 2.05, 1.98 (4 s, 12 H, H_{Ac}), 1.20 (d, $J_{5,6}$ = 6.3 Hz, 3 H, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ = 170.5, 170.2, 170.0, 168.6 (4 C, C_{Ac}), 91.0 ($^1J_{C,H}$ = 177.0 Hz, C-1), 71.8 (C-5_β), 70.8 (C-4), 69.1 (C-3), 69.1 (C-5), 69.0 (C-2), 21.4, 21.2, 21.0, 20.8 (8 C, C_{Ac}), 17.8 (C-6_α), 17.7 (C-6) ppm. β Anomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.84 (d, $J_{1,2}$ = 1.2 Hz, 1 H, H-1), 5.45 (m, 1 H, H-2), 5.05 (m, 2 H, H-3, H-4), 3.65 (dq, 1 H, H-5), 2.20, 2.12, 2.07, 1.95 (4 s, 12 H, H_{Ac}), 1.26 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ = 170.3, 170.1, 169.9, 168.7 (4 C, C_{Ac}), 91.0 ($^1J_{C,H}$ = 162.6 Hz, C-1), 71.8 (C-5), 71.1, 70.6 (2 C, C-3*, C-4*), 68.9 (C-2), 21.3, 21.1, 20.9, 20.7 (8 C, C_{Ac}), 17.8 (C-6_α), 17.7 (C-6) ppm. HBr (33% solution in AcOH, 23 mL) was added dropwise to a solution of the crude peracetate in CH_2Cl_2 (100 mL), which was stirred at room temp. After 5 h, TLC (Chex/EtOAc, 6:4) showed the complete disappearance of the starting material. Volatiles were evaporated under reduced pressure and eliminated by repeated coevaporation with toluene to provide the bromide (70.6 g) as a light yellow syrup; R_f = 0.35 (Chex/EtOAc, 6:4); α anomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.26 (d, $J_{1,2}$ = 0.8 Hz, 1 H, H-1), 5.66 (dd, $J_{3,4}$ = 10.2, $J_{2,3}$ = 3.4 Hz, 1 H, H-3), 5.44 (m, 1 H, H-2), 5.14 (pt, $J_{4,5}$ = 10.0 Hz, 1 H, H-4), 4.10 (dq, 1 H, H-5), 2.14, 2.06, 1.99 (3 s, 9 H, H_{Ac}), 1.25 (d, $J_{5,6}$ = 6.3 Hz, 3 H, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 170.0, 169.9 (3 C, C_{Ac}), 84.1 ($^1J_{C,H}$ = 184.3 Hz, C-1), 72.8 (C-2), 71.5 (C-5), 70.7 (C-4), 68.3 (C-3), 21.1, 21.0, 20.9 (3 C, C_{Ac}), 17.3 (C-6) ppm. 2,6-Lutidine (28 mL) was added to a stirred suspension of the crude bromide (70.6 g) and allyl alcohol (200 mL) in anhydrous CH_2Cl_2 (200 mL) containing 4-Å MS (10 g). The mixture was stirred at room temp. for 12 h, at which time TLC (Chex/EtOAc, 7:3) indicated the complete disappearance of the stating material. The mixture was diluted with CH_2Cl_2 (100 mL), washed with cold citric acid (3 × 20 mL), cold saturated $NaHCO_3$ (2 × 20 mL), and H_2O (50 mL), dried on Na_2SO_4, filtered, and concentrated under reduced pressure to provide crude **20** (66.0 g) as a light yellow syrup. Diacetate **20**[37] had R_f = 0.35 (Chex/EtOAc, 7:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85 (m, 1 H, CH=), 5.39 (d, 1 H, $J_{1,2}$ = 2.4 Hz, H-1), 5.22 (m, 1 H, J_{trans} = 17.2 Hz, =CH_2), 5.09 (m, 1 H, J_{cis} = 11.8 Hz, =CH_2), 5.06 (dd, $J_{2,3}$ = 3.9 Hz, $J_{3,4}$ = 9.7 Hz, 1 H, H-3), 5.01 (pt, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 4.56 (dd, $J_{1,2}$ = 2.4 Hz, $J_{2,3}$ = 3.9 Hz, 1 H, H-2), 4.00 (m, 2 H, H_{All}), 3.49 (dq, 1 H, H-5), 2.07, 2.02 (2 s, 6 H, H_{Ac}), 1.72 (s, 3 H, CH_{3ortho}), 1.20 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 170.3 (2 C, C_{Ac}), 134.5 (CH=), 124.5 (C_{ortho}), 116.9 (=CH_2), 97.4 ($^1J_{C,H}$ = 175.0 Hz, C-1), 77.0 (C-2), 71.1 (C-3), 70.7 (C-4), 69.5 (C-5), 64.0 (C_{All}), 24.5 (CH_{3ortho}), 21.2, 21.0 (2 C, C_{Ac}), 17.8 (C-6) ppm. Anhydrous K_2CO_3 (1.1 g, 8.0 mmol) was added to a stirred solution of crude **20** (66.0 g) in dry MeOH (250 mL). The mixture was stirred at room temp. for 6 h, at which time TLC (CH_2Cl_2/MeOH, 9:1) indicated the total conversion of **20** into a single product. Volatiles were removed under reduced pressure to give diol **21** (49.2 g) as a pale foam. Diol **21**[37] had R_f = 0.5 (CH_2Cl_2/MeOH, 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85 (m, 1 H, CH=), 5.39 (d, $J_{1,2}$ = 2.0 Hz, 1 H, H-1), 5.26 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.15 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 4.48 (m, 1 H, H-2), 4.07 (m, 2 H, H_{All}), 3.70 (dd, $J_{3,4}$ = 9.2, $J_{2,3}$ = 4.0 Hz, 1 H, H-3), 3.42 (pt, $J_{4,5}$ = 9.2 Hz, 1 H, H-4), 3.30 (dq, 1 H, H-5), 1.71 (s, 3 H, CH_{3ortho}), 1.31 (d, $J_{5,6}$ = 6.0 Hz, 3 H, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4 (CH=), 124.0 (C_{ortho}), 116.8 (=CH_2), 97.7 ($^1J_{C,H}$ = 175.1 Hz, C-1), 79.6 (C-2), 72.9 (C-3), 72.7 (C-4), 71.1 (C-5), 64.0 (C_{All}), 25.5 (CH_{3ortho}), 17.8 (C-6) ppm. Sodium hydride (60% suspension in oil, 24.0 g, 600 mmol) was added portionwise to a solution of crude **21** (49.2 g) in dry DMF (300 mL), while the temperature was maintained below 5 °C. Stirring was continued for 1 h at room temp., and benzyl bromide (57.3 mL, 480.0 mmol, 2.4 equiv.) was then added dropwise to the reaction mixture, which was kept under strong stirring below 10 °C. The solution was then stirred at room temp. for 4 h, when TLC (Chex/EtOAc, 8:2) indicated the presence of a single less polar product. The mixture was cooled to 0 °C, and MeOH (30 mL) was added dropwise. After 2 h, EtOAc (400 mL) was added, and the organic phase was washed with H_2O (3 × 50 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (Chex/EtOAc, 9:1 → 7:3) gave **22** (64.8 g, 76% from L-rhamnose) as a colourless syrup. Compound **22** had R_f = 0.5 (Chex/EtOAc, 7:3). ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 7.47–7.35 (m, 10 H, CH_{Ph}), 5.96 (m, 1 H, CH=), 5.33 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.31 (d, $J_{1,2}$ = 1.7 Hz, 1 H, H-1), 5.22 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 4.99 (d, J = 10.8 Hz, 1 H, H_{Bn}), 4.80 (m, 2 H, H_{Bn}), 4.71 (d, J = 10.8 Hz, 1 H, H_{Bn}), 4.41 (dd, $J_{1,2}$ = 1.7, $J_{2,3}$ = 4.1 Hz, 1 H, H-2), 4.08 (m, 2 H, H_{All}), 3.73 (dd, $J_{3,4}$ = 9.1, $J_{2,3}$ = 4.1 Hz, 1 H, H-3), 3.52 (pt, $J_{4,5}$ = 9.1 Hz, 1 H, H-4), 3.37 (dq, 1 H, H-5), 1.80 (s, 3 H, CH_{3ortho}), 1.34 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7–138.3 (C_{Ph}), 135.0 (CH=), 129.0–128.3 (CH_{Ph}), 124.1 (C_{ortho}), 116.9 (=CH_2), 97.8 ($^1J_{C,H}$ = 173.6 Hz, C-1), 79.9 (C-4), 79.6 (C-3), 77.5 (C-2), 76.6, 72.6 (2 C, C_{Bn}), 70.7 (C-5), 64.0 (C_{All}), 25.4 (CH_{3ortho}), 18.4 (C-6) ppm. HRMS (ESI$^+$): calcd. for $C_{25}H_{30}O_6$ [M + Na]$^+$ 449.1940; found 449.1940.

Allyl 2-*O*-Acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (23): TMSOTf (4.5 mL, 25.2 mmol, 0.2 equiv.) was added to a solution of **22** (53.8 g, 126 mmol) in CH_2Cl_2 (300 mL) containing 4-Å MS (55 g), and the mixture was stirred at 0 °C. The reaction mixture was stirred for 3 h while the temperature was slowly raised to room temp. TLC (Chex/EtOAc, 7:3) showed the complete disappearance of the starting material and the presence of a major less polar product. Et_3N (5 mL) was added, and the mixture was filtered. The filtrate was concentrated to dryness. Chromatography of the residue (Chex/EtOAc, 9:1 → 7:3) gave **23** (47.5 g, 88%) as a colourless syrup. Analytical data were identical to those published.[35]

Allyl 3,4-Di-*O*-benzyl-α-L-rhamnopyranoside (26): Route B (Scheme 3). Diol **18**[15,39] (1.9 g, 6.6 mmol), dibutyltin oxide (1.8 g, 7.2 mmol, 1.1 equiv.), and 3-Å MS in toluene (50 mL) were heated at reflux for 8 h. The reaction mixture was cooled to room temp. and transferred to a flask containing caesium fluoride (1.5 mL, 13.1 mmol, 2 equiv.). Volatiles were removed, and DMF (50 mL) was added to the residue, followed by benzyl bromide (1.6 mL, 13.1 mmol, 2 equiv.). The reaction mixture was then stirred at room temp. overnight. TLC (Chex/EtOAc, 7:3) showed the complete disappearance of the starting material and the presence of a single less polar product. The mixture was filtered. CH_2Cl_2 (200 mL) was added, and the organic phase was washed with brine (3 × 50 mL) and H_2O (3 × 50 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (Chex/EtOAc, 8:2 → 1:1) gave **26** (2.2 g, 88%) as a colourless syrup. Analytical data were identical to those published.[35,40]

Route C2 (Scheme 3): Crude orthoester **22** (85.2 g), derived from L-rhamnose (36.4 g, 200 mmol), was dissolved in EtOAc (300 mL), and the organic phase was washed with HCl (10% aqueous, 3 × 50 mL), brine (3 × 50 mL), and H_2O (3 × 50 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. The crude material was added at 0 °C to allyl alcohol (300 mL) containing acetyl chloride (35.5 mL, 500 mmol, 2.5 equiv.). The reaction mixture was stirred at 70 °C for 2.5 h and then at 40 °C overnight. The mixture was neutralized with solid $NaHCO_3$, filtered through a Celite pad, and the filtrate was concentrated. Repeated co-evaporation with toluene gave a brownish syrup, which was purified by column chromatography (Chex/EtOAc, 8:2 → 1:1) to give **26** (55.0 g, 72% from L-rhamnose) as a colourless syrup.

Allyl 3,4-Di-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranoside (27): DCC (1.8 g, 8.5 mmol, 1.5 equiv.) and levulinic acid (1.1 mL, 10.2 mmol, 1.8 equiv.), dissolved in CH_2Cl_2 (120 mL), were added to a solution of alcohol **26** (2.2 g, 5.7 mmol) and DMAP (3.6 g, 29.3 mmol, 2 equiv.) in CH_2Cl_2 (100 mL). The mixture was stirred overnight at room temp. TLC (CH_2Cl_2/EtOAc, 9:1) showed the complete disappearance of the starting material and the presence of one less polar product. Dicyclohexylurea was filtered away, and the reaction mixture was diluted with CH_2Cl_2 and then washed with H_2O, saturated $NaHCO_3$ (3 × 20 mL), brine (3 × 20 mL) and H_2O (3 × 20 mL). The organic layer was dried on Na_2SO_4, filtered, and concentrated under reduced pressure. Chromatography of the residue (Chex/EtOAc, 85:15 → 8:2) gave **27** (2.4 g, 89%) as a colourless syrup. Compound **27** had R_f = 0.4 (Chex/EtOAc, 7:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.30 (m, 10 H, CH_{Ph}), 5.91 (m, 1 H, CH=), 5.43 (m, 1 H, H-2), 5.28 (m, J_{trans} = 15.8 Hz, 1 H, =CH_2), 5.22 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 4.95 (d, J = 10.8 Hz, 1 H, H_{Bn}), 4.81 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1), 4.72 (d, J = 11.2 Hz, 1 H, H_{Bn}), 4.65 (d, J = 10.8 Hz, 1 H, H_{Bn}), 4.55 (d, J = 11.2 Hz, 1 H, H_{Bn}), 4.16 (m, 1 H, H_{All}), 3.99 (m, 2 H, H_{All}, H-3), 3.81 (m, 1 H, H-5), 3.46 (pt, $J_{4,5}$ = 9.4 Hz, 1 H, H-4), 2.74 (m, 4 H, 2 × CH_{2Lev}), 2.19 (s, 3 H, CH_{3Lev}), 1.37 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.6 (C_{Lev}), 172.5 (C_{Lev}), 138.9–138.5 (C_{Ph}), 133.9 (CH=), 128.9–128.1 (CH_{Ph}), 118.0 (=CH_2), 97.1 ($^1J_{C,H}$ = 169.8 Hz, C-1), 80.5 (C-4), 78.5 (C-3), 75.8, 72.0 (2 C, C_{Bn}), 69.5 (C-2), 68.4 (C_{All}), 68.1 (C-5), 38.4 (CH_{2Lev}), 30.2 (CH_{3Lev}), 28.6 (CH_{2Lev}), 18.4 (C-6) ppm. HRMS (ESI$^+$): calcd. for $C_{28}H_{34}O_7$ [M + Na]$^+$ 505.2202; found 505.2201.

3,4-Di-*O*-benzyl-2-*O*-levulinoyl-α/β-L-rhamnopyranose (28): 1,5-Cyclooctadiene-bis(methyldiphenylphosphane)iridium hexafluorophosphate (120 mg) was dissolved in THF (30 mL), and the resulting red solution was degassed under an argon stream. Hydrogen was bubbled through the solution, causing the colour to change to yellow. The solution was then degassed again under an argon stream. A solution of **27** (2.7 g, 5.7 mmol) in THF (8 mL) was added. The mixture was stirred overnight at room temp. TLC (Chex/EtOAc, 7:3) showed the complete disappearance of the starting material and the presence of a single less polar product. The mixture was treated with iodine (2.9 g, 11.3 mmol) in THF/H_2O (30 mL, 4:1 v/v) for 1 h at room temp. TLC (Chex/EtOAc, 7:3 and CH_2Cl_2/MeOH, 98:2) showed the complete disappearance of the intermediate and the presence of a single more polar product. Excess iodine was destroyed by the addition of a solution of freshly prepared sodium bisulfite (5% aqueous, 20 mL). CH_2Cl_2 (100 mL) was added, and the organic phase was washed with brine (3 × 30 mL) and H_2O (3 × 30 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (CH_2Cl_2/MeOH, 99:1 → 9:1) gave compound **28** (α/β: 75:25, 2.4 g, 96%) as a yellow syrup. Hemiacetal **28** had R_f = 0.25 (CH_2Cl_2/MeOH, 98:2); α anomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 10 H, CH_{Ph}), 5.40 (m, 1 H, H-2), 5.13 (m, 1 H, H-1), 4.95 (d, J = 10.9 Hz, 1 H, H_{Bn}), 4.75–4.51 (m, 2 H, H_{Bn}), 4.20 (d, J = 10.7 Hz, 1 H, H_{Bn}), 4.03–3.98 (m, 2 H, H-3, H-5), 3.43 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4), 2.73 (m, 4 H, 2 × CH_{2Lev}), 2.18 (s, 3 H, CH_{3Lev}), 1.33 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ = 206.8 (C_{Lev}), 172.5 (C_{Lev}), 138.9–138.0 (C_{Ph}), 128.8–128.0 (CH_{Ph}), 92.7 ($^1J_{C,H}$ = 170.3 Hz, C-1), 80.5 (C-4), 77.9 (C-3), 75.7, 72.0 (2 C, C_{Bn}), 70.0 (C-2), 68.1 (C-5), 38.5 (CH_{2Lev}), 30.1 (CH_{3Lev}), 28.6 (CH_{2Lev}), 18.4 (C-6) ppm; β anomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 10 H, CH_{Ph}), 5.56 (m, 1 H, H-2), 4.95 (d, J = 10.9 Hz, 1 H, H_{Bn}), 4.77 (d, 1 H, H-1), 4.75–4.51 (m, 2 H, H_{Bn}), 4.20 (d, J = 10.7 Hz, 1 H, H_{Bn}), 3.66 (dd, $J_{2,3}$ = 3.3, $J_{3,4}$ = 8.9 Hz, 1 H, H-3), 3.38 (m, 1 H, H-5), 3.21 (m, 1 H, H-4), 2.73 (m, 4 H, 2 × CH_{2Lev}), 2.20 (s, 3 H, CH_{3Lev}), 1.38 (d, $J_{5,6}$ = 5.9 Hz, 3 H, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.2 (C_{Lev}), 173.0 (C_{Lev}), 138.9–138.0 (C_{Ph}), 128.8–128.0 (CH_{Ph}), 93.5 ($^1J_{C,H}$ = 158.8 Hz, C-1β), 80.4 (C-3), 79.9 (C-4) 75.8, 71.9 (2 C, C_{Bn}), 72.1 (C-5), 70.5 (C-2), 39.0 (CH_{2Lev}), 30.2 (CH_{3Lev}), 28.8 (CH_{2Lev}), 18.4 (C-6) ppm. HRMS (ESI$^+$): calcd. for $C_{25}H_{30}O_7$ [M + Na]$^+$ 465.1889; found 465.1876.

3,4-Di-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranose Trichloroacetimidate (29): Hemiacetal **28** (2.1 g, 4.8 mmol) was dissolved in

DCE (15 mL), placed under argon, and cooled to –5 °C. Trichloroacetonitrile (2.4 mL, 24.2 mmol, 5 equiv.) and DBU (202 μL, 1.3 mmol, 0.28 equiv.) were added. The mixture was stirred at –5 °C for 10 min. TLC (Chex/EtOAc + Et_3N, 7:3) showed the complete disappearance of **28** and the presence of a single less polar product. The mixture was directly chromatographed (Chex/EtOAc + 5% Et_3N, 7:3 → 1:1) to give **29** (2.6 g, 92%) as a yellow syrup. Trichloroacetimidate **29** (α anomer) had R_f = 0.4 (Chex/EtOAc, 7:3). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.68 (s, 1 H, NH), 7.37–7.28 (m, 10 H, CH_{Ph}), 6.20 (d, $J_{1,2}$ = 1.9 Hz, 1 H, H-1), 5.50 (m, 1 H, H-2), 4.97 (d, J = 10.8 Hz, 1 H, H_{Bn}), 4.74 (d, J = 11.3 Hz, 1 H, H_{Bn}), 4.67 (d, J = 10.8 Hz, 1 H, H_{Bn}), 4.58 (d, J = 11.3 Hz, 1 H, H_{Bn}), 4.03–3.94 (m, 2 H, H-3, H-5), 3.53 (pt, $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 2.78 (m, 4 H, 2×CH_{2Lev}), 2.19 (s, 3 H, CH_{3Lev}), 1.37 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.4 (C_{Lev}), 172.2 (C_{Lev}), 160.7 (C=NH), 138.5–138.0 (C_{Ph}), 128.8–128.2 (CH_{Ph}), 95.5 ($^1J_{C,H}$ = 178.6 Hz, C-1), 91.3 (CCl_3), 79.7 (C-4), 77.6 (C-3), 76.0, 72.3 (2 C, C_{Bn}), 71.1 (C-5), 68.2 (C-2), 38.4 (CH_{2Lev}), 30.2 (CH_{3Lev}), 28.5 (CH_{2Lev}), 18.4 (C-6) ppm.

Allyl (3,4-Di-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside (31): TMSOTf (1.1 mL, 6.0 mmol, 0.3 equiv.) was added to a solution of trichloroacetimidate **29** (14.2 g, 24.2 mmol, 1.2 equiv.) and acceptor **30** (6.8 g), obtained from **18** (6.0 g, 20.4 mmol),[38] in toluene (250 mL) containing 4-Å MS (17 g), and the mixture was stirred at –78 °C. The reaction mixture was stirred for 1 h, while the temperature was slowly raised to room temp. TLC (Tol/EtOAc, 8:2) showed the complete disappearance of the acceptor and the presence of a major less polar product. Et_3N (2 mL) was added, and the mixture was filtered and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 95:5 → 85:15) gave **31** (13.3 g, 89%) as a colourless syrup. Disaccharide **31** had R_f = 0.5 (Chex/EtOAc, 6:4). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.27 (m, 15 H, CH_{Ph}), 5.89 (m, 1 H, CH=), 5.46 (m, 1 H, H-2_B), 5.29 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.21 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.17 (m, 1 H, H-2_C), 5.05 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_B), 4.91 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.87 (d, J = 10.9 Hz, 1 H, H_{Bn}), 4.80 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_C), 4.67–4.60 (d, 3 H, H_{Bn}), 4.45 (d, J = 11.3 Hz, 1 H, H_{Bn}), 4.20–4.13 (m, 2 H, H-3_C, H_{All}), 3.98 (m, 1 H, H_{All}), 3.90 (dd, $J_{2,3}$ = 3.3, $J_{3,4}$ = 9.3 Hz, 1 H, H-3_B), 3.83–3.74 (m, 2 H, H-5_B, H-5_C), 3.47 (pt, $J_{3,4}$ = 9.5 Hz, 1 H, H-4_C), 3.43 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4_B), 2.71 (m, 4 H, 2×CH_{2Lev}), 2.18 (s, 3 H, CH_{3Lev}), 2.14 (s, 3 H, H_{Ac}), 1.31 (m, 6 H, H-6_C, H-6_B) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.4 (C_{Lev}), 172.2 (C_{Lev}), 170.6 (C_{Ac}), 138.9–138.4 (C_{Ph}), 133.9 (CH=), 128.9–128.0 (CH_{Ph}), 117.8 (=CH_2), 100.0 ($^1J_{C,H}$ = 169.5 Hz, C-1_B), 96.6 ($^1J_{C,H}$ = 170.0 Hz, C-1_C), 80.7 (C-4_C), 80.2 (C-4_B), 78.1 (C-3_C), 78.0 (C-3_B), 75.9, 75.6 (2 C, C_{Bn}), 72.7 (C-2_C), 71.9 (C_{Bn}), 69.7 (C-2_B), 69.0 (C-5_B), 68.6 (C_{All}), 68.2 (C-5_C), 38.4 (CH_{2Lev}), 30.2 (CH_{3Lev}), 28.6 (CH_{2Lev}), 21.4 (C_{Ac}), 18.3 (2 C, C-6_B, C-6_C) ppm. HRMS (ESI$^+$): calcd. for $C_{43}H_{52}O_{12}$ [M + Na]$^+$ 783.3356; found 783.3364, calcd. for [M + K]$^+$ 778.3802; found 778.3829.

Allyl (3,4-Di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside (8): A solution of hydrazine hydrate (55 μL, 1.1 mmol, 5 equiv.) in pyridine/AcOH (3:2, v/v, 5 mL) was added to a solution of fully protected **31** (172 mg, 23 μmol) in pyridine (1 mL). After 30 min at room temp., TLC (Tol/EtOAc, 8:2) showed the complete disappearance of **31** and the presence of a major more polar product. H_2O (10 mL) and CH_2Cl_2 (50 mL) were added to the mixture, and the organic phase was washed with brine (3×10 mL) and H_2O (3×10 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 90:10 → 75:25) gave disaccharide **8** (121 mg, 81%) as a colourless syrup. Alcohol **8** had R_f = 0.3 (Tol/EtOAc, 8:2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 15 H, CH_{Ph}), 5.89 (m, 1 H, CH=), 5.29 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.21 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.17 (m, 1 H, H-2_C), 5.10 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_B), 4.88 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.80 (d, $J_{1,2}$ = 1.6 Hz, 1 H, H-1_C), 4.87 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.69–4.60 (d, 4 H, H_{Bn}), 4.18–4.13 (m, 2 H, H-3_C, H_{All}), 4.01–3.96 (m, 2 H, H-2_B, H_{All}), 3.83–3.74 (m, 3 H, H-3_B, H-5_B, H-5_C), 3.48 (pt, $J_{3,4}$ = 9.1 Hz, 1 H, H-4_B), 3.46 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4_C), 2.14 (s, 3 H, H_{Ac}), 1.31 (m, 6 H, H-6_B, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7 (C_{Ac}), 138.8–138.3 (C_{Ph}), 133.9 (CH=), 129.4–128.1 (CH_{Ph}), 117.9 (=CH_2), 101.8 ($^1J_{C,H}$ = 171.0 Hz, C-1_B), 96.6 ($^1J_{C,H}$ = 169.2 Hz, C-1_C), 80.7 (C-4_C), 80.2 (C-4_B), 80.1 (C-3_B), 78.5 (C-3_C), 75.9, 75.6 (2 C, C_{Bn}), 72.9 (C-2_C), 72.4 (C_{Bn}), 69.4 (C-2_B), 68.7 (C-5_B), 68.6 (C_{All}), 68.1 (C-5_C), 21.5 (C_{Ac}), 18.3, 18.2 (2 C, C-6_B, C-6_C) ppm. HRMS (ESI$^+$): calcd. for $C_{38}H_{46}O_{10}$ [M + Na]$^+$ 685.2989; found 685.2993, calcd. for [M + NH_4]$^+$ 680.3434; found 680.3472, calcd. for [M + K]$^+$ 701.2728; found 701.2731.

Allyl (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside (9): TMSOTf (340 μL, 1.9 mmol, 0.3 equiv.) was added to a solution of acceptor **8** (4.2 g, 6.3 mmol) and trichloroacetimidate **7** (8.0 g, 7.8 mmol, 1.2 equiv.) in toluene (100 mL) containing 4-Å MS (5.3 g), and the mixture was stirred at –78 °C. The reaction mixture was stirred for 1 h while the temperature was slowly raised to room temp. TLC (Tol/EtOAc, 8:2) showed the complete disappearance of the acceptor and the presence of a major less polar product. Et_3N (1 mL) was added, and the mixture was filtered and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 95:5 → 85:15) gave **9** (8.8 g, 92%) as a colourless syrup. Tetrasaccharide **9** had R_f = 0.45 (Chex/EtOAc, 7:3). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.15 (m, 40 H, CH_{Ph}), 5.89 (m, 1 H, CH=), 5.58 (m, 1 H, H-2_A), 5.31 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.28 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1_E), 5.21 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.19 (m, 1 H, H-2_C), 5.04 (d, J = 11.0 Hz, 1 H, H_{Bn}), 5.01 (d, $J_{1,2}$ = 1.4 Hz, 1 H, H-1_B), 5.00 (d, $J_{1,2}$ = 1.6 Hz, 1 H, H-1_A), 4.98–4.87 (m, 4 H, H_{Bn}), 4.84 (d, $J_{1,2}$ = 1.6 Hz, 1 H, H-1_C), 4.82–4.61 (m, 8 H, H_{Bn}), 4.57 (d, J = 11.1 Hz, 1 H, H_{Bn}), 4.52 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.36 (d, J = 12.0 Hz, 1 H, H_{Bn}), 4.28 (dd, $J_{2,3}$ = 3.1, $J_{3,4}$ = 9.6 Hz, 1 H, H-3_A), 4.19 (m, 1 H, H_{All}), 4.17–4.07 (m, 3 H, H-3_E, H-3_C, H-5_E), 4.04 (m, 1 H, H_{All}), 3.99 (m, 1 H, H-2_B), 3.90 (m, 1 H, H-5_A), 3.88–3.81 (m, 2 H, H-3_B, H-4_E), 3.79–3.74 (m, 1 H, H-5_C), 3.73 (m, 1 H, H-5_B), 3.69–3.65 (m, 2 H, H-2_E, H-$6a_E$), 3.60–3.56 (m, 2 H, H-$6b_E$, H-4_A), 3.54 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4_B), 3.45 (pt, $J_{3,4}$ = 9.5 Hz, 1 H, H-4_C), 2.57 (m, 4 H, 2×CH_{2Lev}), 2.17 (s, 3 H, H_{Ac}), 2.11 (s, 3 H, CH_{3Lev}), 1.35 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A), 1.30 (m, 6 H, H-6_C, H-6_B) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.6 (C_{Lev}), 172.1 (C_{Lev}), 170.8 (C_{Ac}), 138.6–138.4 (C_{Ph}), 134.0 (CH=), 129.0–127.9 (CH_{Ph}), 117.9 (=CH_2), 101.7 ($^1J_{C,H}$ = 169.9 Hz, C-1_B), 99.5 ($^1J_{C,H}$ = 176.6 Hz, C-1_A), 96.5 ($^1J_{C,H}$ = 170.6 Hz, C-1_C), 93.3 ($^1J_{C,H}$ = 168.8 Hz, C-1_E), 82.6 (C-3_E), 80.7 (C-4_B), 80.3 (C-4_C), 80.2 (C-4_A), 79.8 (C-2_E), 79.7 (C-3_B), 79.4 (C-3_C), 78.2 (C-4_E), 76.5, 76.0, 75.9 (3 C, C_{Bn}), 75.8 (C-2_B), 75.7, 75.4, 73.8, 73.2 (4 C, C_{Bn}), 72.9 (C-2_C), 72.6 (C-3_A), 72.5 (C_{Bn}), 70.6 (C-5_E), 69.4 (C-5_B), 69.0 (C-5_A), 68.7 (C_{All}), 68.6 (C-6_E), 68.4 (C-2_A), 68.1 (C-5_C), 38.3 (CH_{2Lev}), 30.1 (CH_{3Lev}), 28.5 (CH_{2Lev}), 21.5 (C_{Ac}), 18.4, 18.3, 18.2 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI$^+$): calcd. for $C_{90}H_{102}O_{21}$ [M + Na]$^+$ 1541.6812; found 1541.6769, calcd. for [M + NH_4]$^+$ 1536.7257; found 1536.7207.

Allyl (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamno-

pyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside (10): A solution of hydrazine hydrate (88 μL, 1.8 mmol, 5 equiv.) in pyridine/AcOH (3:2, v/v, 5 mL) was added to a solution of fully protected **9** (552 mg, 1.8 mmol) in pyridine (1 mL). After 30 min at room temp., TLC (Tol/EtOAc, 8:2) showed the complete disappearance of the starting material and the presence of a major less polar product. H_2O (10 mL) and CH_2Cl_2 (50 mL) were added to the mixture, and the organic phase was washed with brine (3 × 10 mL) and H_2O (3 × 10 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 9:1 → 8:2) gave disaccharide **10** (456 mg, 89%) as a colourless syrup. Alcohol **10** had R_f = 0.7 (Tol/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.23 (m, 40 H, CH_{Ph}), 5.89 (m, 1 H, CH=), 5.35 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.25 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.22 (m, 1 H, H-2_C), 5.19 (s, 1 H, H-1_A), 5.06 (d, $J_{1,2}$ = 1.4 Hz, 1 H, H-1_B), 5.03–4.96 (m, 3 H, H_{Bn}), 4.97 (d, $J_{1,2}$ = 3.7 Hz, 1 H, H-1_E), 4.91–4.89 (m, 3 H, H_{Bn}), 4.81 (d, $J_{1,2}$ = 1.3 Hz, 1 H, H-1_C), 4.81 (d, J = 10.7 Hz, 1 H, H_{Bn}), 4.75–4.68 (m, 3 H, H_{Bn}), 4.66–4.53 (m, 5 H, H_{Bn}), 4.36 (d, J = 11.9 Hz, 1 H, H_{Bn}), 4.19 (m, 1 H, H_{All}), 4.17–4.08 (m, 5 H, H-3_C, H-2_A, H-2_B, H-3_E, H-3_A), 4.03 (m, 1 H, H_{All}), 4.01 (m, 1 H, H-5_E), 3.93 (m, 1 H, H-5_A), 3.89 (dd, $J_{2,3}$ = 2.8, $J_{3,4}$ = 9.4 Hz, 1 H, H-3_B), 3.85 (m, 1 H, H-5_C), 3.79 (pt, $J_{3,4}$ = 9.7 Hz, 1 H, H-4_E), 3.74 (m, 1 H, H-5_B), 3.66 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.6 Hz, 1 H, H-2_E), 3.57 (pt, $J_{3,4}$ = 9.3 Hz, 1 H, H-4_A), 3.54–3.43 (m, 4 H, H-$6a_E$, H-4_B, H-4_C, H-$6b_E$), 2.19 (s, 3 H, H_{Ac}), 1.37 (d, $J_{5,6}$ = 6.3 Hz, 3 H, H-6_A), 1.35 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_B), 1.33 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8 (C_{Ac}), 138.8–138.6 (C_{Ph}), 134.0 (CH=), 129.1–128.1 (CH_{Ph}), 117.9 (=CH_2), 101.9 ($^1J_{C,H}$ = 168.4 Hz, C-1_B), 101.3 ($^1J_{C,H}$ = 173.1 Hz, C-1_A), 96.6 ($^1J_{C,H}$ = 170.4 Hz, C-1_C), 94.3 ($^1J_{C,H}$ = 167.2 Hz, C-1_E), 82.8 (C-3_E), 80.8 (C-4_B), 80.4 (C-4_C), 80.0 (C-3_B), 79.6 (C-4_A), 79.4 (2 C, C-2_E, C-3_C), 78.2 (C-4_E), 76.8 (C-3_A), 76.0, 75.9, 75.7 (4 C, C_{Bn}), 75.6 (C-2_B), 75.3, 74.8, 73.8 (3 C, C_{Bn}), 73.0 (C-2_C), 72.7 (C_{Bn}), 71.1 (C-5_E), 69.4 (C-5_B), 68.7 (C_{All}), 68.7 (C-6_E), 68.3 (C-5_A), 68.2 (C-5_C), 67.8 (C-2_A), 21.6 (C_{Ac}), 18.4, 18.3, 18.2 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI$^+$): calcd. for $C_{85}H_{96}O_{19}$ [M + Na]$^+$ 1443.6444; found 1443.6505, calcd. for [M + NH_4]$^+$ 1438.6890; found 1438.6960.

Propyl α-D-Glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-2-*O*-acetyl-α-L-rhamnopyranoside (1): Mono-hydroxy compound **10** (400 mg, 281 μmol) was dissolved in EtOH (30 mL) and treated with Pd/C (10%, 300 mg), and the suspension was stirred at room temp. overnight under a hydrogen atmosphere. TLC (*i*PrOH/H_2O/NH_3, 4:1:0.5 and Tol/EtOAc, 8:2) showed that starting material had been transformed into a major polar product. The suspension was filtered through an Acrodisc LC (25 mm), and the filtrate was concentrated. Reverse phase chromatography (H_2O/CH_3CN, 100:0 → 70:30) of the residue, followed by freeze-drying, gave the target tetrasaccharide **1** (150 mg, 76%) as a white foam. Tetrasaccharide **1** had R_f = 0.8 (*i*PrOH/H_2O/NH_3, 4:1:0.5). ^{1}H NMR (400 MHz, D_2O): δ = 5.09 (d, $J_{1,2}$ = 1.0 Hz, 1 H, H-1_B), 5.07 (m, 1 H, H-2_C), 5.00 (d, $J_{1,2}$ = 3.8 Hz, 1 H, H-1_E), 4.88 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_A), 4.72 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_C), 4.17 (dd, $J_{2,3}$ = 2.5 Hz, 1 H, H-2_A), 3.91–3.83 (m, 3 H, H-2_B, H-3_C, H-5_E), 3.75–3.61 (m, 7 H, H-3_A, H-5_C, H-$6a_E$, H-$6b_E$, H-3_E, H-5_A, H-3_B), 3.60–3.54 (m, 2 H, H_{Pr}, H-5_B), 3.49 (pt, $J_{3,4}$ = 9.7 Hz, 1 H, H-4_C), 3.48–3.37 (m, 3 H, H-2_E, H-4_A, H_{Pr}), 3.42 (pt, $J_{3,4}$ = 10.0 Hz, 1 H, H-4_B), 3.42 (pt, $J_{3,4}$ = 9.2 Hz, 1 H, H-4_E), 2.07 (s, 3 H, H_{Ac}), 1.60 (sext, 2 H, CH_2), 1.27 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_C), 1.18–1.16 (m, 6 H, H-6_A, H-6_B), 0.88 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 173.4 (C_{Ac}), 102.4 ($^1J_{C,H}$ = 175.5 Hz, C-1_A), 101.2 ($^1J_{C,H}$ = 173.2 Hz, C-1_B), 97.2 ($^1J_{C,H}$ = 172.3 Hz, C-1_C), 95.8 ($^1J_{C,H}$ = 167.3 Hz, C-1_E), 78.8 (C-2_B), 76.2 (C-3_C), 75.7 (C-3_A), 73.3 (C-3_E), 72.5 (C-4_C), 72.4 (C-4_E), 72.3 (C-2_C), 72.1 (C-5_E), 71.8 (C-2_E), 70.7 (C-4_A), 70.3 (C_{Pr}), 70.2 (C-5_A), 69.8 (2 C, C-4_B, C-5_B), 69.7 (C-3_B), 69.0 (C-5_C), 67.1 (C-2_A), 60.7 (C-6_E), 22.4 (CH_2), 20.7 (C_{Ac}), 17.2, 17.1, 16.9 (3 C, C-6_A, C-6_B, C-6_C), 10.3 (CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{29}H_{50}O_{19}$ [M + Na]$^+$ 725.2844; found 725.2827.

Allyl (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-4-*O*-benzyl-α-L-rhamnopyranoside (32): MeONa (0.5 M in MeOH, 770 μL, 390 μmol, 1.1 equiv.) was added to a solution of fully protected **9** (500 mg, 350 μmol) in MeOH (10 mL), and the mixture was refluxed for 3 h. TLC (Chex/EtOAc, 7:3) showed the complete disappearance of the starting material and the presence of a single more polar product. The mixture was neutralized by the addition of Dowex X8-200 ion-exchange resin (H^+), and filtered. The evaporation of the filtrate gave a syrup, which was chromatographed (Chex/EtOAc, 75:25 → 7:3) to give **32** (461 mg, 95%) as a white foam. Tetrasaccharide **32** had R_f = 0.3 (Chex/EtOAc, 7:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.20 (m, 40 H, CH_{Ph}), 5.93 (m, 1 H, CH=), 5.33 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.23 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.18 (s, 1 H, H-1_A), 5.10 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_B), 5.03–4.98 (m, 3 H, H_{Bn}), 4.95 (d, $J_{1,2}$ = 3.3 Hz, 1 H, H-1_E), 4.92–4.87 (m, 3 H, H_{Bn}), 4.84 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_C), 4.79 (d, J = 11.4 Hz, 1 H, H_{Bn}), 4.75–4.69 (m, 5 H, H_{Bn}), 4.60–4.56 (m, 2 H, H_{Bn}), 4.52 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.33 (d, J = 12.0 Hz, 1 H, H_{Bn}), 4.19 (m, 1 H, H_{All}), 4.13–4.07 (m, 5 H, H-2_A, H-3_E, H-2_B, H-3_A, H-2_C), 4.03 (m, 1 H, H_{All}), 4.01–3.98 (m, 2 H, H-3_C, H-5_E), 3.93–3.87 (m, 3 H, H-3_B, H-5_B, H-5_A), 3.81–3.76 (m, 2 H, H-4_E, H-5_C), 3.65 (dd, $J_{1,2}$ = 3.5, $J_{2,3}$ = 9.7 Hz, 1 H, H-2_E), 3.56 (pt, $J_{3,4}$ = 9.5 Hz, 1 H, H-4_A), 3.54–3.43 (m, 4 H, H-4_B, H-$6a_E$, H-4_C, H-$6b_E$), 2.19 (s, 1 H, OH), 1.37 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A), 1.34 (d, $J_{5,6}$ = 6.3 Hz, 3 H, H-6_B, H-6_A), 1.30 (d, $J_{5,6}$ = 6.3 Hz, 3 H, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6–138.2 (C_{Ph}), 134.0 (CH=), 129.0–128.1 (CH_{Ph}), 117.7 (=CH_2), 101.5 ($^1J_{C,H}$ = 170.1 Hz, C-1_B), 10143 ($^1J_{C,H}$ = 170.1 Hz, C-1_A), 98.8 ($^1J_{C,H}$ = 167.2 Hz, C-1_C), 94.3 ($^1J_{C,H}$ = 169.2 Hz, C-1_E), 82.8 (C-3_E), 81.5 (C-3_C), 80.7 (C-4_B), 80.2 (C-4_C), 80.0 (C-3_B), 79.6 (C-4_A), 79.3 (C-2_E), 78.2 (C-4_E), 76.8 (C-3_A), 76.0, 75.9, 75.8 (4 C, C_{Bn}), 75.9 (C-2_B), 75.3, 74.8, 73.8, 72.7 (4 C, C_{Bn}), 71.3 (C-2_C), 71.1 (C-5_E), 69.6 (C-5_B), 68.4 (C_{All}), 68.3 (C-6_E), 68.3 (C-5_A), 68.0 (C-5_C), 67.7 (C-2_A), 18.4, 18.3, 18.2 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI$^+$): calcd. for $C_{83}H_{94}O_{18}$ [M + Na]$^+$ 1401.6338; found 1401.6403, calcd. for [M + NH_4]$^+$ 1396.6783; found 1396.6854.

Propyl α-D-Glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranoside (2): Diol **32** (360 mg, 261 μmol) was dissolved in EtOH (30 mL), treated with Pd/C (10%, 300 mg), and the suspension was stirred at room temp. overnight under a hydrogen atmosphere. TLC (*i*PrOH/H_2O/NH_3, 4:1:0.5 and Chex/EtOAc, 7:3) showed that the starting material had been transformed into a major more polar product. The suspension was filtered through an Acrodisc LC (25 mm), and the filtrate was concentrated. Reverse-phase chromatography (H_2O/CH_3CN, 100:0 → 70:30) of the residue, followed by freeze-drying, gave the target tetrasaccharide **2** (140 mg, 81%) as a white foam. Tetrasaccharide **2** had R_f = 0.5 (*i*PrOH/H_2O/NH_3, 4:1:0.5). ^{1}H NMR (400 MHz, D_2O): δ = 5.10 (br. s, 1 H, H-1_B), 4.99 (d, $J_{1,2}$ = 3.8 Hz, 1 H, H-1_E), 4.89 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_A), 4.65 (d, $J_{1,2}$ = 1.4 Hz, 1 H, H-1_C), 4.17 (dd, $J_{2,3}$ = 2.4 Hz, 1 H, H-2_A), 3.95 (m, 1 H, H-2_B) 3.88–3.81 (m, 3 H, H-2_C, H-5_E, H-3_B), 3.73 (dd, $J_{2,3}$ = 3.0, $J_{3,4}$ = 9.7 Hz, 1 H, H-3_A), 3.71–3.59 (m, 7 H, H-3_C, H-$6a_E$, H-$6b_E$, H-5_B, H-3_E, H-5_C, H-5_A), 3.53 (m, 1 H, H_{Pr}), 3.48–3.37 (m, 5 H, H-2_E, H-4_A, H-4_C, H_{Pr}, H-4_B), 3.34 (pt, $J_{3,4}$ = 9.3 Hz, 1 H, H-4_E), 1.50

(sext, 2 H, CH_2), 1.18–1.16 (m, 9 H, H-6_A, H-6_B, H-6_C), 0.81 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 102.3 ($^1J_{C,H}$ = 167.2 Hz, C-1_A), 101.0 ($^1J_{C,H}$ = 173.1 Hz, C-1_B), 99.8 ($^1J_{C,H}$ = 169.4 Hz, C-1_C), 95.7 ($^1J_{C,H}$ = 169.5 Hz, C-1_E), 78.8 (C-2_B), 77.7 (C-3_C), 75.5 (C-3_A), 73.2 (C-3_E), 72.4 (C-4_B), 72.2 (C-4_C), 72.0 (C-5_E), 71.7 (C-4_A), 70.6 (C-2_E), 70.3 (C-2_C), 70.2 (C-3_B), 69.9 (C_{Pr}), 69.7 (C-5_B), 69.6 (C-4_E), 69.5 (C-5_C), 68.9 (C-5_A), 67.0 (C-2_A), 60.6 (C-6_E), 22.3 (CH_2), 17.1, 17.0, 16.8 (3 C, C-6_A, C-6_B, C-6_C), 10.2 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{27}H_{48}O_{18}$ [M + Na]$^+$ 683.2739; found 683.2729.

Allyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside (34): TMSOTf (28 μL, 160 μmol, 0.5 equiv.) was added to a solution of acceptor **10** (442 mg, 310 μmol) and trichloroacetimidate **11** (370 mg, 620 μmol, 2 equiv.) in toluene (8 mL) containing 4-Å MS (253 mg), and the mixture was stirred at –40 °C. The reaction mixture was stirred for 1 h while the temperature was slowly raised to room temp. TLC (Tol/EtOAc, 8:2) showed the complete disappearance of the acceptor and the presence of a major less polar product. Et_3N (0.1 mL) was added, and the mixture was filtered and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 9:1 → 7:3) gave **34** (469 mg, 82%) as a white foam. Pentasaccharide **34** had R_f = 0.45 (Tol/EtOAc, 8:2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.09 (m, 41 H, CH_{Ph}, NH), 5.89 (m, 1 H, CH=), 5.31 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.26 (d, $J_{1,2}$ = 3.5 Hz, 1 H, H-1_E), 5.22 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.18 (m, 2 H, H_{Bn}), 5.16 (m, 1 H, H-2_C), 5.19 (d, $J_{1,2}$ = 1.1 Hz, 1 H, H-1_A), 5.06 (m, 1 H, H-4_D), 5.05 (m, 2 H, H_{Bn}), 5.00 (d, $J_{1,2}$ = 1.0 Hz, 1 H, H-1_B), 4.96 (m, 1 H, H_{Bn}), 4.94 (m, 1 H, H-1_D), 4.88 (pt, $J_{3,4}$ = 10.4 Hz, 1 H, H-3_D), 4.81 (d, $J_{1,2}$ = 1.6 Hz, 1 H, H-1_C), 4.77–4.85 (m, 4 H, H_{Bn}), 4.62–4.56 (m, 4 H, H_{Bn}), 4.52–4.47 (m, 2 H, H_{Bn}), 4.32 (d, J = 11.9 Hz, 1 H, H_{Bn}), 4.26 (m, 1 H, H-2_D), 4.20 (m, 1 H, H-2_A), 4.18–4.14 (m, 3 H, H_{All}, H-3_A, H-3_E), 4.12–4.08 (m, 2 H, H-5_E, H-3_C), 4.01 (m, 1 H, H_{All}), 3.98 (m, 1 H, H-6a$_D$), 3.96–3.92 (m, 2 H, H-2_B, H-2_E), 3.87–3.82 (m, 4 H, H-6b$_D$, H-4_E, H-5A, H-3_B), 3.79 (m, 1 H, H-5_C), 3.74 (m, 1 H, H-5_B), 3.50 (pt, $J_{3,4}$ = 9.3 Hz, 1 H, H-4_B), 3.48 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4_A), 3.54–3.40 (m, 3 H, H-6a$_E$, H-6b$_E$, H-4_C), 2.97 (m, 1 H, H-5_D), 2.15, 2.08, 2.03, 1.90 (4 s, 12 H, H_{Ac}), 1.34 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A), 1.32 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_B) 1.27 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 170.9, 170.8, 169.6 (4 C, C_{Ac}), 162.6 (C_{NTCA}), 139.0–138.0 (C_{Ph}), 134.0 (CH=), 129.0–127.8 (CH_{Ph}), 117.9 (=CH_2), 101.7 ($^1J_{C,H}$ = 173.2 Hz, C-1_B), 101.3 ($^1J_{C,H}$ = 171.0 Hz, C-1_A), 101.2 ($^1J_{C,H}$ = 161.0 Hz, C-1_D), 96.5 ($^1J_{C,H}$ = 168.8 Hz, C-1_C), 95.1 ($^1J_{C,H}$ = 164.5 Hz, C-1_E), 93.1 (CCl_3), 82.8 (C-3_E), 80.8 (C-4_B), 80.3 (C-4_C), 80.1 (C-4_A), 79.3 (C-3_C), 79.2 (C-2_E), 79.1 (C-4_E), 78.9 (C-3_B), 76.4 (C_{Bn}), 76.0 (C-2_B), 75.9, 75.7, 75.5, 75.3 (4 C, C_{Bn}), 75.1 (C-3_A), 74.4 (C-2_A), 74.3, 73.8 (2 C, C_{Bn}), 73.6 (C-3_D), 72.9 (C-2_C), 72.3 (C_{Bn}), 72.2 (C-5_D), 70.4 (C-5_E), 69.2 (C-5_B), 69.1 (C-5_A), 68.6 (C_{All}), 68.2 (2 C, C-4_D, C-6_E), 68.1 (C-5_C), 61.9 (C-6_D), 56.2 (C-2_D), 21.5, 21.0, 20.9, 20.8 (4 C, C_{Ac}), 18.3, 18.2, 18.1 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI^+): calcd. for $C_{99}H_{112}Cl_3NO_{27}$ [M + Na]$^+$ 1874.6385; found 1874.6638, calcd. for [M + NH_4]$^+$ 1869.6831; found 1869.6978.

Allyl (2-Deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside (35) and Allyl (2-Deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-4-*O*-benzyl-α-L-rhamnopyranoside (36): MeONa (0.5 M in MeOH, 431 μL, 200 μmol, 2 equiv.) was added to a solution of fully protected **34** (200 mg, 100 μmol) in MeOH (12 mL), and the mixture was stirred for 25 min at room temp. TLC (CH_2Cl_2/MeOH, 95:5 and Chex/EtOAc, 6:4) showed the complete disappearance of the starting material and the presence of two more polar products. The mixture was neutralized by the addition of Dowex X8-200 ion-exchange resin (H^+), filtered, and the solvents were evaporated to dryness. Chromatography of the residue (Tol/EtOAc, 7:3 → 1:1) gave, by order of elution, first triol **35** (103 mg, 56%) and then tetraol **36** (55 mg, 30%), both as white foams. Triol **35** had R_f = 0.3 (CH_2Cl_2/MeOH, 95:5). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, $J_{2,NH}$ = 6.1 Hz, 1 H, NH), 7.39–7.08 (m, 40 H, CH_{Ph}), 5.94 (m, 1 H, CH=), 5.38 (br. s, 1 H, H-1_A), 5.33 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.23 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.19–5.15 (m, 4 H, H-2_C, H-1_E, 2H_{Bn}), 5.12–5.01 (m, 2 H, H_{Bn}), 4.96 (d, J = 10.7 Hz, 1 H, H_{Bn}), 4.91 (br. s, 1 H, H-1_B), 4.82 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_C), 4.80–4.64 (m, 5 H, H_{Bn}), 4.55 (m, 1 H, H-1_D), 4.54–4.49 (m, 5 H, H_{Bn}), 4.32 (d, J = 11.9 Hz, 1 H, H_{Bn}), 4.20 (m, 1 H, H-2_B), 4.17 (m, 1 H, H_{All}), 4.15 (m, 1 H, H-2_A), 4.13–4.08 (m, 4 H, H-3_E, H-3_A, H-3_C, H-5_E), 4.11 (m, 1 H, H_{All}), 3.89–3.82 (m, 3 H, H-4_E, H-3_B, H-2_E), 3.79–3.69 (m, 4 H, H-2_D, H-5_C, H-5_A, H-5_B), 3.63 (m, 1 H, H-6a$_D$), 3.52–3.36 (m, 5 H, H-4_B, H-4_A, H-6a$_E$, H-6b$_E$, H-4_C), 3.12 (pt, $J_{3,4}$ = 9.3 Hz, 1 H, H-4_D), 3.05 (m, 1 H, H-5_D), 2.92 (m, 1 H, H-6b$_D$), 2.37 (m, 1 H, H-3_D), 2.14 (s, 3 H, H_{Ac}), 1.34–1.27 (m, 6 H, H-6_A, H-6_B), 1.28 (d, $J_{5,6}$ = 6.1 Hz, 3 H, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8 (C_{Ac}), 164.9 (C_{NTCA}), 138.7–138.1 (C_{Ph}), 134.0 (CH=), 129.5–127.7 (CH_{Ph}), 118.2 (=CH_2), 102.0 ($^1J_{C,H}$ = 170.5 Hz, C-1_B), 101.3 ($^1J_{C,H}$ = 161.0 Hz, C-1_D), 100.4 ($^1J_{C,H}$ = 171.2 Hz, C-1_A), 96.5 ($^1J_{C,H}$ = 171.2 Hz, C-1_C), 94.6 ($^1J_{C,H}$ = 169.8 Hz, C-1_E), 92.9 (CCl_3), 83.4 (C-3_E), 80.6 (C-4_B), 80.5 (C-4_E), 80.1 (C-4_C), 80.0 (C-3_C), 79.9 (C-3_B), 79.4 (C-4_A), 79.0 (C-2_E), 76.6 (C_{Bn}), 76.5 (C-3_D), 76.1 (C-5_D), 75.9, 75.6, 75.4, 75.3 (5 C, C_{Bn}), 74.4 (C-3_A), 74.1 (C-2_A), 73.9, 73.2 (2 C, C_{Bn}), 72.9 (C-4_D), 72.8 (C-2_C), 72.1 (C-2_B), 70.4 (C-5_B), 69.7 (C-5_E), 69.2 (C-5_A), 68.8 (C_{All}), 68.0 (C-6_E), 67.9 (C-5_C), 62.9 (C-6_D), 58.8 (C-2_D), 21.5 (C_{Ac}), 18.3, 18.2, 18.1 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI^+): calcd. for $C_{93}H_{106}Cl_3NO_{24}$ [M + Na]$^+$ 1748.6068; found 1748.6366, calcd. for [M + NH_4]$^+$ 1743.6514; found 1743.6545.

Tetraol **36** had R_f = 0.2 (CH_2Cl_2/MeOH, 95:5). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, $J_{2,NH}$ = 6.6 Hz, 1 H, NH), 7.40–7.11 (m, 40 H, CH_{Ph}), 5.92 (m, 1 H, CH=), 5.38 (br. s, 1 H, H-1_A), 5.31 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.23 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.19 (d, $J_{1,2}$ = 3.5 Hz, 1 H, H-1_E), 5.14–4.98 (m, 4 H, H_{Bn}), 4.96 (br. s, 1 H, H-1_B), 4.93 (d, J = 12.3 Hz, 1 H, H_{Bn}), 4.81 (d, $J_{1,2}$ = 1.3 Hz, 1 H, H-1_C), 4.80 (d, J = 10.7 Hz, 1 H, H_{Bn}), 4.74–4.66 (m, 6 H, H_{Bn}), 4.55 (m, $J_{1,2}$ = 4.4 Hz, 1 H, H-1_D), 4.55–4.69 (m, 3 H, H_{Bn}), 4.37 (d, J = 11.9 Hz, 1 H, H_{Bn}), 4.20 (m, 1 H, H_{All}), 4.18–4.10 (m, 5 H, H-2_B, H-2_A, H-3_A, H-3_E, H-5_E), 4.07 (m, 1 H, H-2_C), 4.11 (m, 1 H, H_{All}), 3.97 (m, 1 H, H-3_C), 3.92 (m, 1 H, H-3_B), 3.89–3.83 (m, 3 H, H-4_E, H-2_E, H-2_D), 3.88 (m, 1 H, H-5_B), 3.76 (m, 1 H, H-5_C), 3.72 (m, 1 H, H-5_A), 3.67 (m, 1 H, H-6a$_D$), 3.56 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4_B), 3.53–3.39 (m, 4 H, H-6a$_E$, H-6b$_E$, H-4_A, H-4_C), 3.18 (pt, $J_{3,4}$ = 8.9 Hz, 1 H, H-4_D), 3.13 (m, 1 H, H-5_D), 3.08 (m, 1 H, H-6b$_D$), 2.48 (m, 1 H, H-3_D), 1.46 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_B), 1.32 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A), 1.28 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ = 164.7 (C_{NTCA}), 138.7–138.2 (C_{Ph}), 134.2 (CH=), 129.6–127.7 (CH_{Ph}), 117.9 (=CH_2), 101.7 ($^1J_{C,H}$ = 170.5 Hz, C-1_B), 101.4 ($^1J_{C,H}$ = 158.1 Hz, C-1_D), 100.6 ($^1J_{C,H}$ = 173.4 Hz, C-1_A), 98.8 ($^1J_{C,H}$ = 169.8 Hz, C-1_C), 94.7 ($^1J_{C,H}$ = 168.3 Hz, C-1_E), 93.0 (CCl_3), 83.7 (C-3_E), 81.9 (C-3_C), 80.7 (C-4_B), 80.3 (C-3_B), 80.1 (C-4_A), 80.0 (C-

4_C), 79.4 (C-4_E), 79.1 (C-2_E), 76.6 (C_{Bn}), 76.5 (C-3_D), 76.2 (C-5_D), 75.8, 75.7, 75.4, 75.3 (5 C, C_{Bn}), 74.4 (C-3_A), 74.3 (C-2_A), 73.9, 73.4 (2 C, C_{Bn}), 72.8 (C-4_D), 72.7 (C-2_B), 71.3 (C-2_C), 70.4 (C-5_E), 69.7 (C-5_B), 69.3 (C-5_A), 68.4 (C-6_E), 68.2 (C_{All}), 67.9 (C-5_C), 63.0 (C-6_D), 58.8 (C-2_D), 18.4, 18.3, 18.2 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI^+): calcd. for $C_{91}H_{104}Cl_3NO_{23}$ $[M + Na]^+$ 1706.5962; found 1706.6206, calcd. for $[M + NH_4]^+$ 1701.6409; found 1701.6571.

Propyl (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-[α-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-2-*O*-acetyl-α-L-rhamnopyranoside (3): Triol **35** (310 mg, 180 μmol) was dissolved in EtOH (20 mL), treated with Pd/C (10%, 300 mg), and the suspension was stirred at room temp. for 2 d under a hydrogen atmosphere (45 bar). TLC (*i*PrOH/H_2O/NH_3, 4:1:0.5 and CH_2Cl_2/MeOH, 95:5) showed that the starting material had been transformed into a more polar product. The suspension was filtered through an Acrodisc LC (25 mm), and the filtrate was concentrated. Reverse phase chromatography (H_2O/CH_3CN, 100:0 → 70:30) of the residue, followed by freeze-drying, gave the target pentasaccharide **3** (119 mg, 74%) as a white foam. Pentasaccharide **3** had R_f = 0.2 (*i*PrOH/H_2O/NH_3, 4:1:0.5). ^1H NMR (400 MHz, D_2O): δ = 5.09 (br. s, 1 H, H-1_B), 5.08 (m, 1 H, H-2_C), 5.07 (d, $J_{1,2}$ = 3.5 Hz, 1 H, H-1_E), 4.99 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_A), 4.73 (br. s, 1 H, H-1_C), 4.72 (d, $J_{1,2}$ = 8.5 Hz, 1 H, H-1_D), 4.33 (m, 1 H, H-2_A), 3.95 (m, 1 H, H-5_E), 3.93 (m, 1 H, H-2_B), 3.88 (dd, $J_{2,3}$ = 3.4, $J_{3,4}$ = 9.6 Hz, 1 H, H-3_C), 3.83–3.79 (m, 2 H, H-3_A, H-6a$_D$), 3.76–3.68 (m, 4 H, H-3_E, H-5_C, H-6a$_E$, H-6b$_E$), 3.66–3.52 (m, 7 H, H-6b$_D$, H-2_D, H-3_B, H-5_A, H-2_E, H_{Pr}, H-5_B), 3.49 (pt, $J_{3,4}$ = 9.7 Hz, 1 H, H-4_C), 3.42 (m, 1 H, H_{Pr}), 3.38 (m, 1 H, H-4_E), 3.37–3.29 (m, 4 H, H-4_B, H-5_D, H-4_D, H-3_D), 3.26 (pt, $J_{3,4}$ = 9.7 Hz, 1 H, H-4_A), 2.08 (s, 3 H, H_{Ac}), 2.00 (s, 3 H, H_{NAc}), 1.53 (sext, 2 H, CH_2), 1.22 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_C), 1.17 (m, $J_{5,6}$ = 6.4 Hz, 3 H, H-6_B), 1.15 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A), 0.83 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 174.8 (C_{NAc}), 173.3 (C_{Ac}), 102.2 ($^1J_{C,H}$ = 163.9 Hz, C-1_D), 101.7 ($^1J_{C,H}$ = 173.4 Hz, C-1_A), 101.0 ($^1J_{C,H}$ = 172.7 Hz, C-1_B), 97.1 ($^1J_{C,H}$ = 172.0 Hz, C-1_C), 94.9 ($^1J_{C,H}$ = 170.5 Hz, C-1_E), 78.7 (C-2_B), 76.3 (C-4_D), 76.0 (C-3_C), 74.5 (C-3_D), 74.4 (C-2_A), 74.1 (C-3_A), 73.4 (C-3_E), 72.5 (C-4_C), 72.3 (C-2_C), 72.2 (C-4_B), 71.7 (C-5_E), 71.6 (C-2_E), 71.1 (C-4_A), 70.2 (C_{Pr}), 70.1 (C-5_D), 69.8 (C-3_B), 69.7 (3 C, C-4_E, C-5_A, C-5_B), 68.9 (C-5_C), 61.0 (C-6_D), 60.6 (C-6_E), 56.0 (C-2_D), 23.0 (C_{NAc}), 22.3 (CH_2), 20.7 (C_{Ac}), 17.2, 17.0, 16.8 (3 C, C-6_A, C-6_B, C-6_C), 10.2 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{37}H_{63}NO_{24}$ $[M + Na]^+$ 928.3638; found 928.3652, calcd. for $[M + H]^+$ 906.3818; found 906.3831.

Propyl (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-[α-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranoside (4): Tetraol **36** (240 mg, 143 μmol) was dissolved in EtOH (15 mL), treated with Pd/C (10%, 250 mg), and the suspension was stirred at room temp. for 1 d under a hydrogen atmosphere (45 bar). TLC (*i*PrOH/H_2O/NH_3, 4:1:0.5 and CH_2Cl_2/MeOH, 95:5) showed that the starting material had been transformed into a more polar product. The suspension was filtered through an Acrodisc LC (25 mm), and the filtrate was concentrated. Reverse phase chromatography (H_2O/CH_3CN, 100:0 → 70:30) of the residue, followed by freeze-drying, gave the target **4** (91 mg, 74%) as a white foam. Pentasaccharide **4** had R_f = 0.15 (*i*PrOH/H_2O/NH_3, 4:1:0.5). ^1H NMR (400 MHz, D_2O): δ = 5.17 (br. s, 1 H, H-1_B), 5.14 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H-1_E), 5.06 (d, $J_{1,2}$ = 1.2 Hz, 1 H, H-1_A), 4.78 (d, $J_{1,2}$ = 8.5 Hz, 1 H, H-1_D), 4.73 (br. s, 1 H, H-1_C), 4.39 (m, 1 H, H-2_A), 4.03 (m, 1 H, H-2_B), 4.00 (m, 1 H, H-5_E), 3.95 (m, 1 H, H-2_C), 3.90 (m, 1 H, H-3_B), 3.89–3.85 (m, 2 H, H-3_A, H-6a$_D$), 3.82–3.72 (m, 5 H, H-3_E, H-6a$_E$, H-6b$_E$, H-5_B, H-3_C), 3.73–3.65 (m, 5 H, H-2_D, H-6b$_D$, H-5_A, H-2_E, H-5_C), 3.61 (m, 1 H, H_{Pr}), 3.51 (pt, $J_{3,4}$ = 9.6 Hz, 1 H, H-4_C), 3.47 (m, 1 H, H_{Pr}), 3.45 (m, 1 H, H-4_E), 3.43 (m, 1 H, H-4_B), 3.41–3.3 (m, 3 H, H-5_D, H-4_D, H-3_D), 3.32 (pt, $J_{3,4}$ = 9.7 Hz, 1 H, H-4_A), 2.06 (s, 3 H, H_{NAc}), 1.57 (sext, 2 H, CH_2), 1.25 (m, 6 H, H-6_B, H-6_C), 1.22 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A), 0.88 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 174.8 (C_{NAc}), 102.3 ($^1J_{C,H}$ = 163.2 Hz, C-1_D), 101.7 ($^1J_{C,H}$ = 170.5 Hz, C-1_A), 101.0 ($^1J_{C,H}$ = 172.7 Hz, C-1_B), 99.9 ($^1J_{C,H}$ = 169.8 Hz, C-1_C), 95.0 ($^1J_{C,H}$ = 170.5 Hz, C-1_E), 78.9 (C-2_B), 77.8 (C-3_C), 76.3 (C-4_D), 74.6 (C-3_D), 74.5 (C-2_A), 74.2 (C-3_A), 73.5 (C-3_E), 72.6 (C-4_B), 72.5 (C-4_C), 71.8 (C-5_E), 71.7 (C-2_E), 71.2 (C-4_A), 70.4 (C-2_C), 70.2 (2 C, C-5_D, C-3_B), 70.0 (C_{Pr}), 69.9 (2 C, C-5_A, C-4_E), 69.5 (C-5_B), 69.0 (C-5_C), 61.1 (C-6_D), 60.7 (C-6_E), 56.0 (C-2_D), 23.0 (C_{NAc}), 22.4 (CH_2), 17.2, 17.1, 16.9 (3 C, C-6_A, C-6_B, C-6_C), 10.3 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{35}H_{61}NO_{23}$ $[M + Na]^+$ 886.3532; found 886.3522, calcd. for $[M + H]^+$ 864.3713; found 864.3726.

(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α/β-L-rhamnopyranose (37): 1,5-Cyclooctadiene-bis(methyldiphenylphosphane)-iridium hexafluorophosphate (25 mg) was dissolved in THF (30 mL), and the resulting red solution was degassed under an argon stream. Hydrogen was bubbled through the solution, causing the colour to change to yellow. The solution was then degassed again under an argon stream. A solution of allyl glycoside **9** (1.9 g, 1.2 mmol) in THF (15 mL) was added. The mixture was stirred overnight at room temp. TLC (Tol/EtOAc, 9:1) showed the complete disappearance of the starting material and the presence of a single less polar product. The mixture was treated with iodine (340 mg, 2.5 mmol) in THF/H_2O (10 mL, 4:1 v/v) for 1 h at room temp. TLC (Tol/EtOAc, 9:1 and CH_2Cl_2/MeOH, 99:1) showed the complete disappearance of the intermediate and the presence of a single more polar product. Excess iodine was destroyed by the addition of a solution of freshly prepared sodium bisulfite (5% aqueous, 5 mL). CH_2Cl_2 (50 mL) was added, and the organic phase was washed with brine (3 × 20 mL) and H_2O (3 × 20 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (CH_2Cl_2/MeOH, 100:0 → 99:1) gave tetrasaccharide **37** (1.7 g, 90%) as a yellow syrup. Hemiacetal **37** had R_f = 0.25 (CH_2Cl_2/MeOH, 99:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.15 (m, 40 H, CH_{Ph}), 5.56 (m, 1 H, H-2_A), 5.26 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1_E), 5.19 (m, 2 H, H-2_C, H-1_C), 5.04 (d, J = 10.9 Hz, 1 H, H_{Bn}), 5.01 (d, $J_{1,2}$ = 1.2 Hz, 1 H, H-1_B), 4.97 (d, $J_{1,2}$ = 1.4 Hz, 1 H, H-1_A), 4.96–4.81 (m, 14 H, H_{Bn}), 4.35 (d, J = 12.0 Hz, 1 H, H_{Bn}), 4.28 (dd, $J_{2,3}$ = 3.0, $J_{3,4}$ = 9.6 Hz, 1 H, H-3_A), 4.17–3.97 (m, 5 H, H-3_C, H-3_E, H-5_E, H-5_C, H-2_B), 3.88 (m, 1 H, H-5_A), 3.86–3.78 (m, 2 H, H-3_B, H-4_E), 3.71 (m, 1 H, H-5_B), 3.67–3.63 (m, 2 H, H-2_E, H-6a$_E$), 3.56 (pt, $J_{3,4}$ = 9.3 Hz, 1 H, H-4_A), 3.55 (m, 1 H, H-6b$_E$), 3.51 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4_B), 3.43 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4_C), 3.13 (m, 1 H, OH), 2.53 (m, 4 H, 2 × CH_{2Lev}), 2.16 (s, 3 H, H_{Ac}), 2.10 (s, 3 H, CH_{3Lev}), 1.34 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A), 1.29 (d, $J_{5,6}$ = 6.1 Hz, 3 H, H-6_B), 1.27 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.7 (C_{Lev}), 172.1 (C_{Lev}), 170.9 (C_{Ac}), 139.1–138.8 (C_{Ph}), 129.1–127.9 (CH_{Ph}), 101.6 ($^1J_{C,H}$ = 171.8 Hz, C-1_B), 99.5 ($^1J_{C,H}$ = 169.9 Hz, C-1_A), 93.2 ($^1J_{C,H}$ = 169.6 Hz, C-1_E), 92.0 ($^1J_{C,H}$ = 170.2 Hz, C-1_C), 82.5 (C-3_E), 80.6 (C-4_B), 80.2 (C-4_A), 80.1 (C-4_C), 79.7 (C-2_E), 79.6 (C-3_B), 78.8 (C-3_C), 78.1 (C-4_E), 76.6, 76.0 (2 C, C_{Bn}), 75.8 (C-2_B), 75.8, 75.7, 75.4, 74.0 (4 C, C_{Bn}), 73.2 (C-2_C), 73.1 (C_{Bn}), 72.6 (C-3_A), 72.4 (C_{Bn}), 70.5 (C-5_E), 69.3 (C-5_B), 69.0 (C-5_A), 68.6 (C-6_E), 68.4 (C-2_A), 68.1 (C-5_C), 38.3 (CH_{2Lev}), 30.1 (CH_{3Lev}), 28.5 (CH_{2Lev}), 21.5 (C_{Ac}), 18.4, 18.3, 18.2 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI^+): calcd.

for $C_{87}H_{98}O_{21}$ [M + Na]$^+$ 1501.6498; found 1501.6665, calcd. for [M + NH_4]$^+$ 1496.6945; found 1496.7114.

(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α/β-L-rhamnopyranose Trichloroacetimidate (12): Hemiacetal **37** (1.5 g, 1.0 mmol) was dissolved in DCE (10 mL), placed under argon, and cooled to –5 °C. Trichloroacetonitrile (520 μL, 5.2 mmol, 5 equiv.) and DBU (42 μL, 280 μmol, 0.28 equiv.) were added. The mixture was stirred at –5 °C for 10 min. TLC (Chex/EtOAc + Et_3N, 7:3) showed the complete disappearance of **37** and the presence of a single less polar product. The mixture was directly chromatographed (Chex/EtOAc + 5% Et_3N, 8:2 → 7:3) to give donor **12** (1.5 g, 88%) as a yellow syrup. Trichloroacetimidate **12** (α anomer) had R_f = 0.35 (Chex/EtOAc, 7:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (s, 1 H, NH), 7.37–7.14 (m, 40 H, CH_{Ph}), 6.24 (d, $J_{1,2}$ = 1.9 Hz, 1 H, H-1_C), 5.56 (dd, $J_{1,2}$ = 2.7, $J_{1,2}$ = 4.9 Hz, 1 H, H-2_A), 5.32 (dd, $J_{1,2}$ = 2.2, $J_{1,2}$ = 3.1 Hz, 1 H, H-2_C), 5.26 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1_E), 5.04 (d, J = 10.9 Hz, 1 H, H_{Bn}), 5.03 (d, $J_{1,2}$ = 1.3 Hz, 1 H, H-1_B), 4.99 (d, $J_{1,2}$ = 1.6 Hz, 1 H, H-1_A), 4.97–4.79 (m, 6 H, H_{Bn}), 4.73–4.49 (m, 8 H, H_{Bn}), 4.35 (d, J = 12.0 Hz, 1 H, H_{Bn}), 4.25 (dd, $J_{2,3}$ = 3.1, $J_{3,4}$ = 9.6 Hz, 1 H, H-3_A), 4.19 (dd, $J_{2,3}$ = 3.3, $J_{3,4}$ = 9.5 Hz, 1 H, H-3_C), 4.14 (pt, $J_{3,4}$ = 9.3 Hz, 1 H, H-3_E), 4.08 (m, 1 H, H-5_E), 3.98–3.88 (m, 3 H, H-2_B, H-5_C, H-5_A), 3.86–3.81 (m, 2 H, H-3_B, H-4_E), 3.73 (m, 1 H, H-5_B), 3.67–3.64 (m, 2 H, H-2_E, H-$6a_E$), 3.58 (m, 1 H, H-$6b_E$), 3.57 (pt, $J_{3,4}$ = 9.6 Hz, 1 H, H-4_A), 3.54 (pt, $J_{3,4}$ = 9.5 Hz, 1 H, H-4_C), 3.52 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4_B), 2.55 (m, 4 H, 2×CH_{2Lev}), 2.19 (s, 3 H, H_{Ac}), 2.10 (s, 3 H, CH_{3Lev}), 1.34 (d, $J_{5,6}$ = 6.3 Hz, 3 H, H-6_A), 1.31 (d, $J_{5,6}$ = 6.1 Hz, 3 H, H-6_B), 1.28 (d, $J_{5,6}$ = 6.0 Hz, 3 H, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.7 (C_{Lev}), 172.2 (C_{Lev}), 170.3 (C_{Ac}), 160.5 (C=NH), 139.1–138.8 (C_{Ph}), 129.1–127.9 (CH_{Ph}), 101.5 ($^1J_{C,H}$ = 178.7 Hz, C-1_B), 99.8 ($^1J_{C,H}$ = 174.2 Hz, C-1_A), 94.6 ($^1J_{C,H}$ = 178.5 Hz, C-1_C), 93.3 ($^1J_{C,H}$ = 170.0 Hz, C-1_E), 93.3 (CCl_3), 82.5 (C-3_E), 80.6 (C-4_C), 80.1 (C-4_A), 79.8 (C-4_B), 79.6 (C-2_E), 79.4 (C-3_B), 78.2 (C-3_C), 78.1 (C-4_E), 76.7 (C_{Bn}), 76.4 (C-2_B), 76.0, 75.9, 75.8, 75.4, 73.8, 73.2 (6 C, C_{Bn}), 72.6 (C-3_A), 72.6 (C_{Bn}), 71.3 (C-2_C), 71.0 (C-5_C), 70.6 (C-5_E), 69.5 (C-5_B), 68.9 (C-5_A), 68.5 (C-6_E), 68.4 (C-2_A), 38.3 (CH_{2Lev}), 30.1 (CH_{3Lev}), 28.5 (CH_{2Lev}), 21.4 (C_{Ac}), 18.4, 18.3, 18.2 (3 C, C-6_A, C-6_B, C-6_C) ppm.

Allyl 3-*O*-Acetyl-2-deoxy-4,6-*O*-isopropylidene-2-trichloroacetamido-β-D-glucopyranoside (39): TMSOTf (360 μL, 2.0 mmol, 0.2 equiv.) was added to a solution of **38**[24] (5.5 g, 10.1 mmol) and allyl alcohol (1.4 mL, 20.1 mmol, 2 equiv.) in CH_2Cl_2 (70 mL) containing 4-Å MS (3.9 g), and the mixture was stirred at –78 °C. The reaction mixture was stirred for 30 min. TLC (Tol/EtOAc, 8:2) showed the complete disappearance of the starting material and the presence of a major less polar product. Et_3N (1 mL) was added. The mixture was filtered, and the filtrate was concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 9:1 → 75:25) gave **39** (3.7 g, 82%) as a white foam. Allyl glycoside **39** had R_f = 0.45 (Tol/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, $J_{NH,2}$ = 9.6 Hz, 1 H, NH_{NTCA}), 5.81 (m, 1 H, CH=), 5.38 (pt, $J_{2,3}$ = 9.3 Hz, 1 H, H-3), 5.25 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.15 (m, J_{cis} = 9.2 Hz, 1 H, =CH_2), 4.62 (d, $J_{1,2}$ = 8.3 Hz, 1 H, H-1), 4.29 (m, 1 H, H_{All}), 4.18 (m, 1 H, H-2), 4.10 (m, 1 H, H_{All}), 3.99 (dd, $J_{5,6a}$ = 5.5, $J_{6a,6b}$ = 10.8 Hz, 1 H, H-6A), 4.17 (m, 1 H, H-6B), 3.81 (pt, $J_{3,4}$ = 9.5 Hz, 1 H, H-4), 3.75 (ddd, $J_{4,5}$ = 9.9 Hz, 1 H, H-5), 2.08 (s, 3 H, H_{Ac}), 1.51 (s, 3 H, Hi_{Pr}), 1.38 (s, 3 H, Hi_{Pr}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.0 (C_{Ac}), 162.7 (C_{NTCA}), 133.7 (CH=), 118.0 (=CH_2), 100.9 ($^1J_{C,H}$ = 158.1 Hz, C-1), 100.1 (Ci_{Pr}), 93.1 (CCl_3), 72.5 (C-3), 72.1 (C-4), 70.6 (C_{All}), 67.4 (C-5), 62.2 (C-6), 56.1 (C-2), 29.1 (Ci_{Pr}), 21.1 (C_{Ac}), 19.3 (Ci_{Pr}) ppm. HRMS (ESI$^+$): calcd. for $C_{16}H_{22}NO_7Cl_3$ [M + Na]$^+$ 468.0359; found 468.0359.

Allyl 2-Acetamido-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (13):[25] NaOH (1 M, 6.7 mL, 6.7 mmol, 3 equiv.) was added to **39** (1.0 g, 2.2 mmol) in methanol (40 mL), and the suspension was stirred at room temp. After 1 d, TLC (CH_2Cl_2/MeOH, 9:1) showed the presence of a single more polar product. Acetic anhydride (1 mL) was added dropwise to the suspension, and after 3 h, the volatiles were evaporated. Chromatography of the residue (CH_2Cl_2/MeOH, 98:2 → 9:1) gave **13** (476 mg, 71%) as a white foam. Acceptor **13** had R_f = 0.5 (CH_2Cl_2/MeOH, 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.90 (m, 1 H, CH=), 5.74 (d, $J_{NH,2}$ = 4.6 Hz, 1 H, NH_{NAc}), 5.32 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.26 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 4.68 (d, $J_{1,2}$ = 8.3 Hz, 1 H, H-1), 4.37 (m, 1 H, H_{All}), 4.10 (m, 1 H, H_{All}), 4.00–3.93 (m, 2 H, H-3, H-6A), 3.82 (m, 1 H, H-6B), 3.61 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4), 3.49 (m, 1 H, H-2), 3.31 (ddd, $J_{5,6b}$ = 5.4, $J_{4,5}$ = 10.0 Hz, 1 H, H-5), 2.07 (s, 3 H, H_{NAc}), 1.55 (s, 3 H, Hi_{Pr}), 1.47 (s, 3 H, Hi_{Pr}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7 (C_{NAc}), 134.2 (CH=), 117.8 (=CH_2), 100.9 ($^1J_{C,H}$ = 162.1 Hz, C-1), 100.1 (Ci_{Pr}), 74.6 (C-4), 71.8 (C-3), 70.5 (C_{All}), 67.5 (C-5), 62.4 (C-6), 57.9 (C-2), 29.4 (Ci_{Pr}), 23.7 (C_{NAc}), 19.5 (Ci_{Pr}) ppm. HRMS (ESI$^+$): calcd. for $C_{14}H_{23}NO_6$ [M + Na]$^+$ 324.123; found 321.1412, calcd. for [M + H]$^+$ 302.1604; found 302.1599.

Allyl (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-acetamido-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (40): TfOH (45 μL, 515 μmol, 0.9 equiv.) was added to a solution of acceptor **13** (432 mg, 1.4 mmol, 2.5 equiv.) and trichloroacetimidate **12** (926 mg, 571 μmol) in toluene (25 mL) containing 4-Å MS (253 mg), and the mixture was stirred at 0 °C. The reaction mixture was stirred for 1 h at 75 °C. TLC (Tol/EtOAc, 7:3) showed the presence of a major new product. Et_3N (0.2 mL) was added, and the mixture was filtered. The filtrate was concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 7:3 → 6:4) gave **40** (780 mg, 78%) as a white foam. Pentasaccharide **40** had R_f = 0.45 (Tol/EtOAc, 6:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.10 (m, 40 H, CH_{Ph}), 5.89 (m, 2 H, NH, CH=), 5.56 (dd, $J_{1,2}$ = 2.2 Hz, 1 H, H-2_A), 5.30 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.25 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1_E), 5.21 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.15 (d, $J_{1,2}$ = 8.3 Hz, 1 H, H-1_D), 5.07 (dd, $J_{1,2}$ = 1.6, $J_{1,2}$ = 3.2 Hz, 1 H, H-2_C), 5.02 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.98 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_A), 4.96 (d, $J_{1,2}$ = 1.3 Hz, 1 H, H-1_B), 4.97–4.86 (m, 4 H, H_{Bn}), 4.80 (br. s, 1 H, H-1_C), 4.78 (d, J = 11.9 Hz, 1 H, H_{Bn}), 4.73 (d, J = 11.5 Hz, 1 H, H_{Bn}), 4.67 (d, J = 13.4 Hz, 1 H, H_{Bn}), 4.62 (d, J = 12.3 Hz, 1 H, H_{Bn}), 4.61–4.53 (m, 6 H, H_{Bn}), 4.50 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.39 (pt, $J_{3,4}$ = 9.2 Hz, 1 H, H-3_D), 4.31 (m, 1 H, H_{All}), 4.26 (dd, $J_{2,3}$ = 3.0, $J_{3,4}$ = 9.6 Hz, 1 H, H-3_A), 4.15–4.06 (m, 3 H, H-3_E, H_{All}, H-5_E), 4.04–3.94 (m, 4 H, H-5_C, H-3_C, H-2_B, H-$6a_D$), 3.88 (dq, $J_{4,5}$ = 9.5 Hz, 1 H, H-5_A), 3.84–3.77 (m, 3 H, H-3_B, H-4_E, H-$6b_D$), 3.71–3.62 (m, 3 H, H-5_B, H-$6a_E$, H-2_E), 3.60–3.52 (m, 3 H, H-$6b_E$, H-4_A, H-4_D), 3.50 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-4_B), 3.40 (m, 1 H, H-5_D), 3.38 (pt, $J_{3,4}$ = 9.6 Hz, 1 H, H-4_C), 3.49 (m, $J_{2,NH}$ = 8.0 Hz, 1 H, H-2_D), 2.53 (m, 4 H, 2×CH_{2Lev}), 2.11 (s, 3 H, H_{NAc}), 2.09 (s, 3 H, CH_{3Lev}), 2.04 (s, 3 H, H_{Ac}), 1.50 (s, 3 H, Hi_{Pr}), 1.42 (s, 3 H, Hi_{Pr}), 1.35 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A), 1.26 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_B), 1.20 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ = 206.1 (C_{Lev}), 171.7 (C_{Lev}), 171.3 (C_{Ac}), 170.5 (C_{NAc}), 138.8–137.6 (C_{Ph}), 133.8 (CH=), 129.1–127.4 (CH_{Ph}), 117.5 (=CH_2), 101.2 ($^1J_{C,H}$ = 169.4 Hz, C-1_B), 99.4 (Ci_{Pr}), 99.0 ($^1J_{C,H}$ = 173.7 Hz, C-1_A), 98.9 ($^1J_{C,H}$ = 162.7 Hz, C-1_D), 97.6 ($^1J_{C,H}$ = 171.0 Hz, C-1_C), 92.8 ($^1J_{C,H}$

= 167.6 Hz, C-1_E), 82.1 (C-3_E), 80.2 (C-4_B), 79.8 (C-4_A), 79.6 (C-4_C), 79.5 (C-2_E), 79.4 (2 C, C-3_B, C-3_C), 77.8 (C-4_E), 76.3 (C_{Bn}), 76.1 (C-3_D), 75.6, 75.5, 75.3 (3 C, C_{Bn}), 75.2 (C-2_B), 75.1, 75.0, 73.4 (3 C, C_{Bn}), 73.1 (C-4_D), 72.8 (C-2_C), 72.8 (C_{Bn}), 72.2 (C-3_A), 72.0 (C_{Bn}), 70.5 (C_{All}), 70.3 (C-5_E), 69.0 (C-5_B), 68.6 (C-5_A), 68.3 (C-6_E), 68.0 (C-2_A), 67.6 (C-5_C), 67.0 (C-5_D), 62.3 (C-6_D), 59.6 (C-2_D), 37.9 (CH_{2Lev}), 29.7 (CH_{3Lev}), 29.1 (Ci_{Pr}), 28.1 (CH_{2Lev}), 23.5 (C_{Ac}), 21.2 (C_{NAc}), 19.3 (Ci_{Pr}), 18.0, 17.9, 17.8 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI$^+$): calcd. for $C_{101}H_{119}NO_{26}$ [M + Na]$^+$ 1784.7917; found 1784.7917, calcd. for [M + H]$^+$ 1762.8098; found 1762.8038, calcd. for [M + NH_4]$^+$ 1779.8364; found 1779.8289.

Allyl (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-acetamido-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (41): Hydrazine hydrate (200 μL, 4.0 mmol, 10 equiv.) in pyridine/AcOH (3:2, v/v, 20 mL) was added to a fully protected **40** (720 mg, 4.0 mmol) in pyridine (3 mL). After 30 min at 0 °C, TLC (Tol/EtOAc, 6:4) showed the complete disappearance of the starting material and the presence of a major less polar product. H_2O (20 mL) and CH_2Cl_2 (100 mL) were added to the mixture, and the organic phase was washed with brine (3 × 30 mL) and H_2O (3 × 30 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 9:1 → 75:25) gave alcohol **41** (580 mg, 85%) as a white foam. Pentasaccharide **41** had R_f = 0.45 (Tol/EtOAc, 6:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.18 (m, 40 H, CH_{Ph}), 5.96 (d, $J_{NH,2}$ = 6.8 Hz, 1 H, NH), 5.91 (m, 1 H, CH=), 5.32 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.24 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.20 (br. s, 1 H, H-1_A), 5.16 (d, $J_{1,2}$ = 8.4 Hz, 1 H, H-1_D), 5.12 (dd, $J_{1,2}$ = 1.6, $J_{1,2}$ = 3.2 Hz, 1 H, H-2_C), 5.03 (d, $J_{1,2}$ = 1.3 Hz, 1 H, H-1_B), 5.02–4.95 (d, J = 11.0 Hz, 3 H, H_{Bn}), 4.95 (d, $J_{1,2}$ = 3.9 Hz, 1 H, H-1_E), 4.91–4.86 (m, 3 H, H_{Bn}), 4.86 (br. s, 1 H, H-1_C), 4.84–4.81 (m, 2 H, H_{Bn}), 4.72–4.70 (m, 3 H, H_{Bn}), 4.63–4.58 (m, 4 H, H_{Bn}), 4.53 (d, J = 11.0 Hz, 1 H, H_{Bn}), 4.41 (pt, $J_{3,4}$ = 9.3 Hz, 1 H, H-3_D), 4.34 (m, 1 H, H_{All}), 4.15–3.96 (m, 9 H, H_{All}, H-2_B, H-3_E, H-2_A, H-3_A, H-5_C, H-3_C, H-5_E, H-6a$_D$), 3.91 (dq, $J_{4,5}$ = 9.6 Hz, 1 H, H-5_A), 3.88 (dd, $J_{2,3}$ = 2.7, $J_{3,4}$ = 9.4 Hz, 1 H, H-3_B), 3.83 (m, 1 H, H-6b$_D$), 3.80 (pt, $J_{3,4}$ = 10.1 Hz, 1 H, H-4_E), 3.72 (dq, $J_{4,5}$ = 9.4 Hz, 1 H, H-5_B), 3.66 (dd, $J_{2,3}$ = 3.6, $J_{3,4}$ = 9.6 Hz, 1 H, H-2_E), 3.62–3.56 (m, 2 H, H-4_D, H-4_A), 3.54–3.40 (m, 5 H, H-6a$_E$, H-4_B, H-6b$_E$, H-4_C, H-5_D) 3.16 (m, $J_{2,NH}$ = 8.0 Hz, 1 H, H-2_D), 2.16 (s, 3 H, H_{Ac}), 2.09 (s, 3 H, H_{NAc}), 1.54 (s, 3 H, Hi_{Pr}), 1.46 (s, 3 H, Hi_{Pr}), 1.38 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_A), 1.33 (d, $J_{5,6}$ = 6.5 Hz, 3 H, H-6_B), 1.26 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3 (C_{NAc}), 170.5 (C_{Ac}), 138.7–137.6 (C_{Ph}), 133.9 (CH=), 129.1–127.7 (CH_{Ph}), 117.6 (=CH_2), 101.6 ($^1J_{C,H}$ = 171.0 Hz, C-1_B), 100.8 ($^1J_{C,H}$ = 175.0 Hz, C-1_A), 99.4 (Ci_{Pr}), 99.0 ($^1J_{C,H}$ = 160.7 Hz, C-1_D), 97.6 ($^1J_{C,H}$ = 170.8 Hz, C-1_C), 94.0 ($^1J_{C,H}$ = 166.2 Hz, C-1_E), 82.4 (C-3_E), 80.4 (C-4_B), 79.7 (2 C, C-4_C, C-3_B), 79.5 (C-3_C), 79.3 (C-4_A), 79.0 (C-2_E), 77.8 (C-4_E), 76.5 (C-3_A), 76.2 (C-3_D), 75.7, 75.6, 75.4, 75.3, 75.0 (5 C, C_{Bn}), 74.9 (C-2_B), 74.5, 73.5 (2 C, C_{Bn}), 73.1 (C-4_D), 72.9 (C-2_C), 72.3 (C_{Bn}), 70.8 (C-5_E), 70.5 (C_{All}), 69.0 (C-5_B), 68.0 (C-6_E), 67.9 (C-5_A), 67.6 (C-5_C), 67.4 (C-2_A), 67.1 (C-5_D), 62.3 (C-6_D), 59.7 (C-2_D), 29.2 (Ci_{Pr}), 23.6 (C_{NAc}), 21.2 (C_{Ac}), 19.3 (Ci_{Pr}), 18.0, 17.9, 17.8 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI$^+$): calcd. for $C_{96}H_{113}NO_{24}$ [M + Na]$^+$ 1686.7550; found 1686.7488, calcd. for [M + H]$^+$ 1664.7731; found 1664.7709, calcd. for [M + NH_4]$^+$ 1681.7997; found 1681.7993.

Allyl (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (42): TFA (50% aqueous, 4 mL) was added, at 0 °C, to a solution of pentasaccharide **41** (400 mg, 240 μmol) in CH_2Cl_2 (10 mL), and the biphasic mixture was stirred vigorously at room temp. for 1 h. TLC (Tol/EtOAc, 4:6) showed the complete disappearance of the starting material and the presence of a major more polar product. Repeated coevaporation with toluene and chromatography of the residue (CH_2Cl_2/MeOH, 98:2 → 9:1) provided triol **42** (360 mg, 92%) as a white foam. The triol had R_f = 0.55 (CH_2Cl_2/MeOH, 95:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.13 (m, 40 H, CH_{Ph}), 6.09 (m, 1 H, NH), 5.91 (m, 1 H, CH=), 5.27 (m, 1 H, =CH_2), 5.22 (br. s, 1 H, H-1_A), 5.18 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.16 (m, 2 H, H-1_C, H-2_C), 5.11 (d, $J_{1,2}$ = 8.3 Hz, 1 H, H-1_D), 5.10–4.88 (m, 8 H, H-1B, H-1_E, H_{Bn}), 4.83–4.49 (m, 9 H, H_{Bn}), 4.35–4.29 (m, 2 H, H_{All}, H_{Bn}), 4.14–3.96 (m, 9 H, H-3_E, H_{All}, H-2_A, H-5_C, H-3_A, H-3_C, H-5_E, H-5_A), 3.87–3.73 (m, 4 H, H-3_B, H-6a$_D$, H-6b$_D$, H-4_E), 3.68 (m, 1 H, H-5_B), 3.65 (dd, $J_{2,3}$ = 3.6, $J_{3,4}$ = 9.6 Hz, 1 H, H-2_E), 3.59 (d, $J_{4,5}$ = 9.3 Hz, 1 H, H-4_A), 3.54–3.36 (m, 6 H, H-6a$_E$, H-5_D, H-4_B, H-4_C, H-6b$_E$, H-4_D), 3.16 (m, 1 H, H-2_D), 2.14 (s, 3 H, H_{Ac}), 2.10 (s, 3 H, H_{NAc}), 1.25 (m, 9 H, H-6_A, H-6_B, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5 (2 C, C_{NAc}, C_{Ac}), 138.6–137.5 (C_{Ph}), 133.9 (CH=), 128.6–127.5 (CH_{Ph}), 117.7 (=CH_2), 101.3 (C-1_B), 100.8 ($^1J_{C,H}$ = 168.2 Hz, 2 C, C-1_A, C-1_C), 98.4 ($^1J_{C,H}$ = 169.0 Hz, C-1_D), 94.0 ($^1J_{C,H}$ = 166.3 Hz, C-1_E), 82.4 (C-3_E), 80.2 (C-4_C), 79.4–79.1 (4 C, C-4_B, C-3_B, C-3_C, C-4_A), 79.0 (C-2_E), 77.8 (C-4_E), 76.5 (C-3_A), 75.9, 75.6, 75.4 (3 C, C_{Bn}), 75.1 (C-4_D), 74.9, 74.5, 74.5, 73.5, 73.5 (5 C, C_{Bn}), 72.2 (C-2_C), 70.8 (C-5_E), 70.5 (C_{All}), 70.3 (C-5_D), 69.0 (C-5_B), 68.0 (C-5_A), 67.9 (C-6_E), 67.4 (2 C, C-5_C, C-2_A), 62.3 (C-6_D), 59.7 (C-2_D), 23.2 (C_{NAc}), 21.1 (C_{Ac}), 18.3, 17.9, 17.7 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI$^+$): calcd. for $C_{93}H_{109}NO_{24}$ [M + Na]$^+$ 1646.7238; found 1646.7377, calcd. for [M + H]$^+$ 1624.7418; found 1624.7565, calcd. for [M + NH_4]$^+$ 1641.7683; found 1641.7848.

Propyl α-D-Glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-(2-*o*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (5): Pentasaccharide **42** (230 mg, 142 μmol) was dissolved in EtOH (15 mL), treated with Pd/C (10%, 200 mg), and the suspension was stirred at room temp. for 2 d under a hydrogen atmosphere. TLC (*i*PrOH/H_2O/NH_3, 4:1:0.5 and CH_2Cl_2/MeOH, 95:5) showed that **42** had been transformed into a more polar product. The suspension was filtered through an Acrodisc LC (25 mm), and the filtrate was concentrated. Reverse phase chromatography (H_2O/CH_3CN, 100:0 → 70:30) of the residue, followed by freeze-drying, gave the target pentasaccharide **5** (100 mg, 77%) as a white foam. Pentasaccharide **5** had R_f = 0.35 (*i*PrOH/H_2O/NH_3, 4:1:0.5). ^{1}H NMR (400 MHz, D_2O): δ = 5.03 (br. s, 1 H, H-1_B), 5.00 (d, $J_{1,2}$ = 3.7 Hz, 1 H, H-1_E), 4.90 (m, 2 H, H-1_A, H-2_C), 4.76 (br. s, 1 H, H-1_C), 4.40 (d, $J_{1,2}$ = 8.6 Hz, 1 H, H-1_D), 4.17 (m, 1 H, H-2_A), 3.99 (m, $J_{5,6}$ = 6.3, $J_{4,5}$ = 9.8 Hz, 1 H, H-5_C), 3.92 (dd, $J_{2,3}$ = 5.2 Hz, 1 H, H-2_B), 3.88–3.80 (m, 3 H, H-5E, H-3_C, H-6a$_D$), 3.76–3.61 (m, 9 H, H-3_A, H_{Pr}, H-2_D, H-6a$_E$, H-6b$_E$, H-3_E, H-5_A, H-3_B, H-6b$_D$), 3.51–3.40 (m, 7 H, H-4_C, H-4_A, H-2_E, H-4_D, H_{Pr}, H-3_D, H-5_B), 3.38–3.31 (m, 3 H, H-4_E, H-4_B, H-5_D), 2.07 (s, 3 H, H_{Ac}), 1.94 (s, 3 H, H_{NAc}), 1.49 (sext, J = 7.1 Hz, 2 H, CH_2), 1.19–1.14 (m, 9 H, H-6_A, H-6_B, H-6_C), 0.76 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 174.4 (C_{NAc}), 173.0 (C_{Ac}), 101.9 ($^1J_{C,H}$ = 175.6 Hz, C-1_A), 101.0 ($^1J_{C,H}$ = 172.4 Hz, C-1_B), 100.6 ($^1J_{C,H}$ = 162.7 Hz, C-1_D), 98.5 ($^1J_{C,H}$ = 173.4 Hz, C-1_C), 95.3 ($^1J_{C,H}$ = 170.3 Hz, C-1_E), 82.4 (C-3_D), 78.0 (C-2_B), 76.2 (C-3_C), 76.0 (C-5_D), 75.2 (C-3_A), 72.9 (C-3_E), 72.2 (C_{Pr}), 72.2 (C-2_C), 71.8 (C-4_B), 71.6 (C-5_E), 71.6 (C-4_C), 71.4 (C-4_A), 70.2 (C-4_D), 69.9 (C-3_B), 69.4 (C-2_E), 69.3 (C-4_E), 69.3 (C-5_A), 68.8 (C-5_C), 68.3 (C-5_B), 66.6 (C-2_A), 60.7 (C-6_D), 60.2 (C-6_E), 55.2 (C-2_D), 22.2 (C_{NAc}), 22.1 (CH_2), 20.2 (C_{Ac}), 16.7 (C-

6_A), 16.5 (C-6_B), 16.3 (C-6_C), 9.6 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{37}H_{63}NO_{24}$ [M + Na]$^+$ 928.3638; found 928.3635, calcd. for [M + H]$^+$ 906.3818; found 906.3821, calcd. for [M + K]$^+$ 944.3377; found 944.3279.

Allyl (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-acetamido-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (43): MeONa (0.5 M in MeOH, 830 μL, 414 μmol, 1 equiv.) was added to a solution of compound **40** (729 mg, 414 μmol) in MeOH (20 mL), and the mixture was refluxed for 3 h. TLC (Tol/EtOAc, 1:1) showed the complete disappearance of the starting material and the presence of a single more polar product. The mixture was neutralized by addition of Dowex X8-200 ion-exchange resin (H^+) and filtered. Evaporation of the filtrate gave a syrup, which was chromatographed (Tol/EtOAc, 1:1 → 4:6) to give **43** (631 mg, 94%) as a white foam. Pentasaccharide **43** had R_f = 0.2 (Tol/EtOAc, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.16 (m, 40 H, CH_{Ph}), 5.90 (m, 1 H, CH=), 5.81 (d, $J_{NH,2}$ = 7.9 Hz, 1 H, NH), 5.30 (m, J_{trans} = 17.2 Hz, 1 H, =CH_2), 5.22 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.17 (br. s, 1 H, H-1_B), 5.07 (br. s, 1 H, H-1_A), 5.02–4.97 (m, 2 H, H_{Bn}), 4.94 (d, $J_{1,2}$ = 4.0 Hz, 1 H, H-1_E), 4.90–4.86 (m, 4 H, 2H_{Bn}, H-1_D, H-1_C), 4.80–4.66 (d, 8 H, H_{Bn}), 4.59–4.51 (m, 3 H, H_{Bn}), 4.38–4.32 (m, 2 H, H_{All}, H_{Bn}), 4.21 (pt, $J_{3,4}$ = 9.4 Hz, 1 H, H-3_D), 4.12–4.05 (m, 6 H, H_{All}, H-2_B, H-3_E, H-2_A, H-3_A, H-5_C), 3.99–3.84 (m, 7 H, H-2_C, H-5_E, H-$6a_D$, H-3_B, H-3_C, H-5_A, H-5_B), 3.83 (m, 1 H, H-$6b_D$), 3.78 (pt, $J_{3,4}$ = 9.6 Hz, 1 H, H-4_E), 3.66–3.61 (m, 2 H, H-2_E, H-4_D), 3.57–3.52 (m, 2 H, H-4_A, H-4_B), 3.52–3.49 (m, 2 H, H-2_D, H-$6a_E$), 3.43–3.35 (m, 3 H, H-$6b_E$, H-4_C, H-5_D), 2.02 (s, 3 H, H_{NAc}), 1.53 (s, 3 H, Hi_{Pr}), 1.43 (s, 3 H, Hi_{Pr}), 1.41, 1.28 (m, 6 H, H-6_A, H-6_B), 1.23 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4 (C_{NAc}), 138.6–137.6 (C_{Ph}), 133.8 (CH=), 129.1–127.5 (CH_{Ph}), 117.6 (=CH_2), 101.0 ($^1J_{C,H}$ = 168.4 Hz, C-1_A), 100.9 ($^1J_{C,H}$ = 172.3 Hz, C-1_B), 99.8 ($^1J_{C,H}$ = 170.6 Hz, C-1_C), 99.6 ($^1J_{C,H}$ = 160.5 Hz, C-1_D), 99.5 (Ci_{Pr}), 94.0 ($^1J_{C,H}$ = 167.5 Hz, C-1_E), 82.4 (C-3_E), 80.4 (C-$4_A$$^{\#}$), 80.3 (C-$3_B$§), 79.7 (C-$4_C$), 79.5 (C-$3_C$§), 79.3 (C-$4_B$$^{\#}$), 79.0 (C-$2_E$), 77.8 (C-$4_E$), 76.5 (C-$3_A$), 76.0 (C-$3_D$), 75.6 (3 C, C_{Bn}), 75.4 (C-2_A), 75.0, 74.9, 74.4, 73.5 (4 C, C_{Bn}), 73.0 (C-4_D), 72.5 (C_{Bn}), 71.2 (C-2_C), 70.7 (C-5_E), 70.0 (C_{All}), 69.1 (C-5_A*), 68.0 (C-6_E), 67.9 (C-5_B*), 67.7 (C-5_C), 67.4 (C-2_B), 67.3 (C-5_D), 62.3 (C-6_D), 58.2 (C-2_D), 29.1 (Ci_{Pr}), 23.5 (C_{NAc}), 19.2 (Ci_{Pr}), 18.0, 17.8 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI^+): calcd. for $C_{94}H_{111}NO_{23}$ [M + Na]$^+$ 1644.7445: found 1644.7562, calcd. for [M + H]$^+$ 1622.7626; found 1622.7649.

Allyl (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (44): TFA (50% aqueous, 4 mL) was added at 0 °C to a solution of pentasaccharide **43** (515 mg, 318 μmol) in CH_2Cl_2 (10 mL), and the biphasic mixture was stirred vigorously at room temp. for 1 h. TLC (CH_2Cl_2/MeOH, 95:5) showed the complete disappearance of the starting material and the presence of a major more polar product. Repeated coevaporation with toluene and chromatography of the residue (Tol/EtOAc, 3:7 → 1:9) provided tetraol **44** (330 mg, 66%) as a white foam. The latter had R_f = 0.2 (CH_2Cl_2/MeOH, 95:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.13 (m, 40 H, CH_{Ph}), 5.90 (m, 1 H, CH=), 5.78 (d, $J_{NH,2}$ = 7.2 Hz, 1 H, NH), 5.30 (m, J_{trans} = 17.3 Hz, 1 H, =CH_2), 5.21 (m, J_{cis} = 10.4 Hz, 1 H, =CH_2), 5.17 (br. s, 1 H, H-1_B), 5.01–4.94 (m, 4 H, H-1_D, H-1_A, 2H_{Bn}), 4.92 (d, $J_{1,2}$ = 3.7 Hz, 1 H, H-1_E), 4.89–4.86 (m, 2 H, H_{Bn}), 4.83 (m, $J_{1,2}$ = 2.4 Hz, 1 H, H-1_C), 4.78–4.65 (d, 7 H, H_{Bn}), 4.57–4.49 (m, 3 H, H_{Bn}), 4.37–4.20 (m, 4 H, H_{All}, 2 × H_{Bn}, H-3_D), 4.13 (m, 1 H, H_{All}), 4.09–4.02 (m, 4 H, H-3_E, H-2_B, H-2_A, H-3_A), 4.00–3.91 (m, 5 H, H-2_C, H-5_E, H-5_B, H-3_B, H-$6a_D$), 3.88–3.82 (m, 4 H, H-3_C, H-5_C, H-5_A, H-$6b_D$), 3.77 (pt, $J_{3,4}$ = 9.7 Hz, 1 H, H-4_E), 3.63 (dd, $J_{2,3}$ = 9.6 Hz, 1 H, H-2_E), 3.56–3.49 (m, 3 H, H-4_A, H-$6a_E$, H-4_B), 3.47–3.37 (m, 4 H, H-4_D, H-5_D, H-4_C, H-$6b_E$), 3.15 (m, 1 H, H-2_D), 1.97 (s, 3 H, H_{NAc}), 1.34–1.28 (m, 9 H, H-6_A, H-6_B, H-6_C) ppm. ^{13}C NMR (100 MHz, $CDCl_3$), δ = 170.6 (C_{NAc}), 138.6–137.5 (C_{Ph}), 133.9 (CH=), 128.6–127.5 (CH_{Ph}), 117.5 (=CH_2), 101.5 ($^1J_{C,H}$ = 171.3 Hz, C-1_C), 100.9 ($^1J_{C,H}$ = 168.8 Hz, C-1_A), 100.9 ($^1J_{C,H}$ = 168.8 Hz, C-1_B), 98.7 ($^1J_{C,H}$ = 163.1 Hz, C-1_D), 94.0 ($^1J_{C,H}$ = 165.5 Hz, C-1_E), 84.1 (C-3_D), 82.4 (C-3_E), 80.2 (C-4_B), 79.8 (C-3_B), 79.4 (C-3_C), 79.3 (C-4_A), 79.2 (C-4_C), 79.0 (C-2_E), 77.8 (C-4_E), 76.5 (C-3_A), 75.8, 75.6, 75.5 (3 C, C_{Bn}), 75.1 (C-4_D), 75.0 (C-2_A), 75.0, 74.5, 73.4, 72.6 (5 C, C_{Bn}), 71.1 (C-5_D), 70.8 (2 C, C-2_C, C-5_E), 70.3 (C_{All}), 69.3 (C-5_B), 69.0 (C-5_C), 68.0 (C-6_E), 67.9 (C-5_A), 67.3 (C-2_B), 62.8 (C-6_D), 57.3 (C-2_D), 23.6 (C_{NAc}), 18.0, 17.9, 17.8 (3 C, C-6_A, C-6_B, C-6_C) ppm. HRMS (ESI^+): calcd. for $C_{91}H_{107}NO_{23}$ [M + Na]$^+$ 1604.7131; found 1604.7180, calcd. for [M + H]$^+$ 1582.7312; found 1582.7300.

Propyl α-D-Glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (6): Pentasaccharide **44** (260 mg, 164 μmol) was dissolved in EtOH (15 mL) and treated with Pd/C (10%, 200 mg), and the suspension was stirred at room temp. for 2 d under a hydrogen atmosphere. TLC (*i*PrOH/H_2O/NH_3, 4:1:0.5 and CH_2Cl_2/MeOH, 95:5) showed that **44** had been transformed into a more polar product. The suspension was filtered through an Acrodisc LC (25 mm), and the filtrate was concentrated. Reverse phase chromatography (H_2O/CH_3CN, 100:0 → 70:30) of the residue, followed by freeze-drying, gave the target pentasaccharide **6** (99 mg, 70%) as a white foam. Pentasaccharide **6** had R_f = 0.25 (*i*PrOH/H_2O/NH_3, 4:1:0.5). ^{1}H NMR (400 MHz, D_2O): δ = 5.15 (br. s, 1 H, H-1_B), 5.08 (d, $J_{1,2}$ = 3.8 Hz, 1 H, H-1_E), 4.98 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1_A), 4.79 (d, $J_{1,2}$ = 1.2 Hz, 1 H, H-1_C), 4.50 (d, $J_{1,2}$ = 8.6 Hz, 1 H, H-1_D), 4.17 (dd, $J_{2,3}$ = 2.6 Hz, 1 H, H-2_A), 4.03 (dd, $J_{2,3}$ = 3.0 Hz, 1 H, H-2_B), 3.99 (m, $J_{4,5}$ = 9.8 Hz, 1 H, H-5_C), 3.94 (m, 1 H, H-5_E), 3.92–3.87 (m, 2 H, H-3_B, H-$6a_D$), 3.85–3.68 (m, 11 H, H-3_A, H-2_C, H_{Pr}, H-2_D, H-$6a_E$, H-$6b_E$, H-3_E, H-3_C, H-$6b_D$, H-5_A, H-5_B), 3.58–3.40 (m, 9 H, H-3_D, H-4_A, H-2_E, H_{Pr}, H-4_C, H-4_D, H-4_B, H-4_E, H-5_D), 2.01 (s, 3 H, H_{NAc}), 1.51 (sext, J = 7.2 Hz, 2 H, CH_2), 1.29–1.24 (m, 6 H, H-6_A, H-6_B), 1.20 (d, $J_{5,6}$ = 6.2 Hz, 3 H, H-6_C), 0.83 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 174.1 (C_{NAc}), 102.0 ($^1J_{C,H}$ = 171.5 Hz, C-1_A), 101.3 ($^1J_{C,H}$ = 173.6 Hz, C-1_C), 100.8 ($^1J_{C,H}$ = 177.8 Hz, C-1_B), 100.6 ($^1J_{C,H}$ = 156.2 Hz, C-1_D), 95.4 ($^1J_{C,H}$ = 169.4 Hz, C-1_E), 81.7 (C-3_D), 78.3 (C-2_B), 77.3 (C-3_C), 76.0 (C-5_D), 75.3 (C-3_A), 73.0 (C-3_E), 72.3 (C_{Pr}), 72.2 (C-4_B), 71.7 (2 C, C-4_C, C-5_E), 71.4 (C-4_A), 70.6 (C-2_C), 70.3 (C-2_E), 69.9 (C-3_B), 69.4 (C-4_E), 69.3 (2 C, C-5_A, C-5_B), 68.9 (C-5_C), 68.5 (C-4_D), 66.7 (C-2_A), 60.9 (C-6_D), 60.3 (C-6_E), 55.4 (C-2_D), 22.1 (2 C, C_{NAc}, CH_2), 20.2 (C_{Ac}), 16.8, 16.7 (2 C, C-6_A, C-6_B), 16.4 (C-6_C), 9.6 (CH_3) ppm. HRMS (ESI^+): calcd. for $C_{35}H_{61}NO_{23}$ [M + Na]$^+$ 886.3532; found 886.3501, calcd. for [M + H]$^+$ 864.3713; found 864.3718.

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