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Efficient Synthesis of Six Tri- to Hexasaccharide Fragments of *Shigella flexneri* Serotypes 3a and/or X O-Antigen, Including a Study on Acceptors Containing *N*-Trichloroacetylglucosamine versus *N*-Acetylglucosamine

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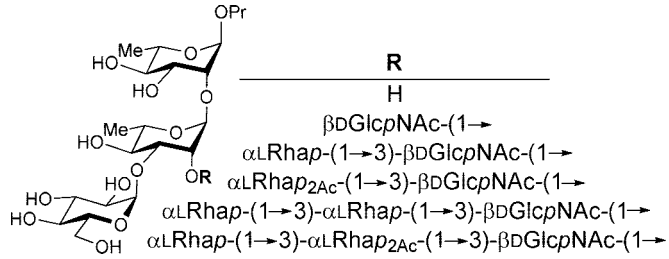

Six tri- to hexasaccharide fragments of the {2)-[α-D-Glc*p*-(1→3)]-α-L-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-[Ac→2]-α-L-Rha*p*-(1→3)-*β*-D-Glc*p*NAc-(1→}$_n$ polymer ([**(E)AB$_{Ac}$CD**]$_n$) were synthesized as their propyl glycosides. All targets share the **(E)AB** sequence. Following a thorough investigation on the use of *N*-trichloroacetylglucosamine- versus *N*-acetylglucosamine-containing tri- and tetrasaccharide acceptors, the successful strategy was based on an efficient combination of the trichloroacetimidate chemistry, a trichloroacetyl used as permanent *N*-protection, and an allyl aglycon as temporary and/or permanent anomeric protection of selected building blocks. Use of an **EAB** intermediate orthogonally protected at 2$_A$ provided both the trisaccharide target and acceptor **12**, the condensation of which with a chain terminator **D** followed by full deprotection, gave tetrasaccharide **D(E)AB**. Alternatively, stepwise glycosylation of **12** with a **D** donor compatible with a selective deblocking at position 3$_D$ and a 2-*O*-acetyl **C** donor following exposure of OH-3$_D$ led to a pentasaccharide, which was partially and fully deprotected into free $_{Ac}$**CD(E)AB** and **CD(E)AB**, respectively. Furthermore, chain elongation of the common **D(E)AB** acceptor with a 2$_B$-*O*-levulinoyl rhamnobiose donor **BC** and subsequent partial or total deprotection of the resulting hexasaccharide provided **B$_{Ac}$CD(E)AB** and **BCD(E)AB**, respectively. All of the synthesized oligosaccharides are parts of the O-antigen of *Shigella flexneri* 3a, a prevalent serotype. Moreover, the non-*O*-acetylated fragments are also parts of the *S. flexneri* serotype X O-antigen.

Introduction

Shigellosis, also termed bacillary dysentery, is an invasive infection of the human colon often associated with blood and mucus in the stools.[1] It is one among the many forms of enteric infections, which altogether rank third among all causes of disease burden worldwide.[2] Shigellosis is a disease of the most impoverished areas and a major health concern particularly in the pediatric population between 1 and 5 years. Humans are the only reservoir of this highly contagious infection associated with increased antibiotic resistance.[1,3,4] The World Health Organization (WHO) has set it as one of its priorities for the

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(1) Niyogi, S. K. *J. Microbiol.* **2005**, *43*, 133–143.

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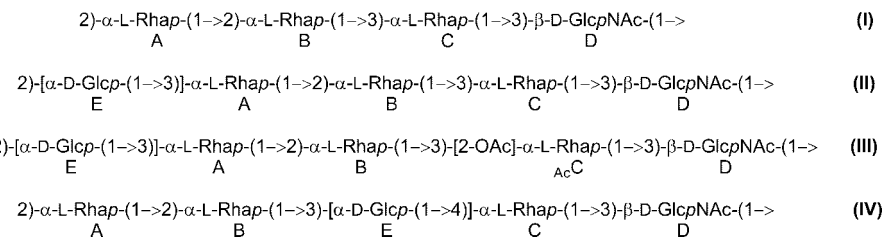


FIGURE 1. Repeating units of the O-Ags of *S. flexneri* serotypes Y (**I**), X (**II**), 3a (**III**), and 2a (**IV**).

development of a vaccine, and a number of candidates have undergone clinical trials. However, as an additional complexity,[4] the large number of pathogens involved seriously hampers the development of an efficacious vaccine against shigellosis, and there is yet no broadly distributed vaccine against this disease.[5] *Shigella flexneri*, one of the four *Shigella* species, is the most frequently isolated causative bacteria worldwide. It is endemic in developing countries and prevails in children less than 5 years old.[5,6] *S. flexneri* is divided into 15 serotypes, differentiated on the basis of the carbohydrate repeating unit of the O-antigen (O-Ag), which is the specific polysaccharide part of the bacterial lipopolysaccharide (LPS),[7] a key player in bacterial virulence and resistance to innate immunity.[8] As a number of different *S. flexneri* serotypes, including serotype 3a, are isolated from patients, there is an inherent need for a multivalent vaccine in order to provide a broad protection.[5,6] Investigations in the field have shown that an initial infection protects against subsequent exposure to homologous serotype.[9,10] This suggests that *S. flexneri* O-Ags are crucial targets used by the host protective adaptive immunity. Interestingly, all *S. flexneri* but serotype 6 share a linear tetrasaccharide backbone, made of three α-linked L-rhamnosyl residues (**A**, **B**, **C**) and a 2-acetamido-2-deoxy-β-D-glucopyranosyl residue (**D**). This tetrasaccharide **ABCD** (**I**) is the basic repeating unit (RU) of serotype Y (Figure 1). Additional serotype-specificity is associated with the presence of branched α-D-glucopyranosyl (**E**) and *O*-acetyl decorations.[7] Noteworthy, the LPS glucosylation affects *S. flexneri* 5a O-Ag conformation, resulting in a shortened length.[8,11,12] Impact on bacterial virulence was hypothesized.[8] To our knowledge, the influence of the *O*-acetylation remains yet unknown. Considering the close resemblance of the O-Ag RUs of the various serotypes, *S. flexneri* was selected as an attractive model to investigate the key role played by bacterial O-Ag decorations in virulence, resistance to innate immunity and immunodominant epitope composition. Having initiated our study on *S. flexneri* 5a[11,13] and *S. flexneri* 2a,[12,14] we focused more recently on additional serotype-specific glucosylation and *O*-acetylation patterns.[15,16] Along this line, we report here the synthesis of fragments of *S. flexneri* serotype X and 3a O-Ags, the repeating units of which are the branched pentasaccharides **(E)ABCD** (**II**) and **(E)AB$_{Ac}$CD** (**III**),[7] respectively (Figure 1). These well-defined synthetic fragments of the native polymer will serve to probe O-Ag structure and antibody recognition as previously reported for serotypes Y,[17] 5a,[11] and 2a.[12] Interestingly, the *S. flexneri* X O-Ag is the non-*O*-acetylated form of the *S. flexneri* 3a O-Ag.

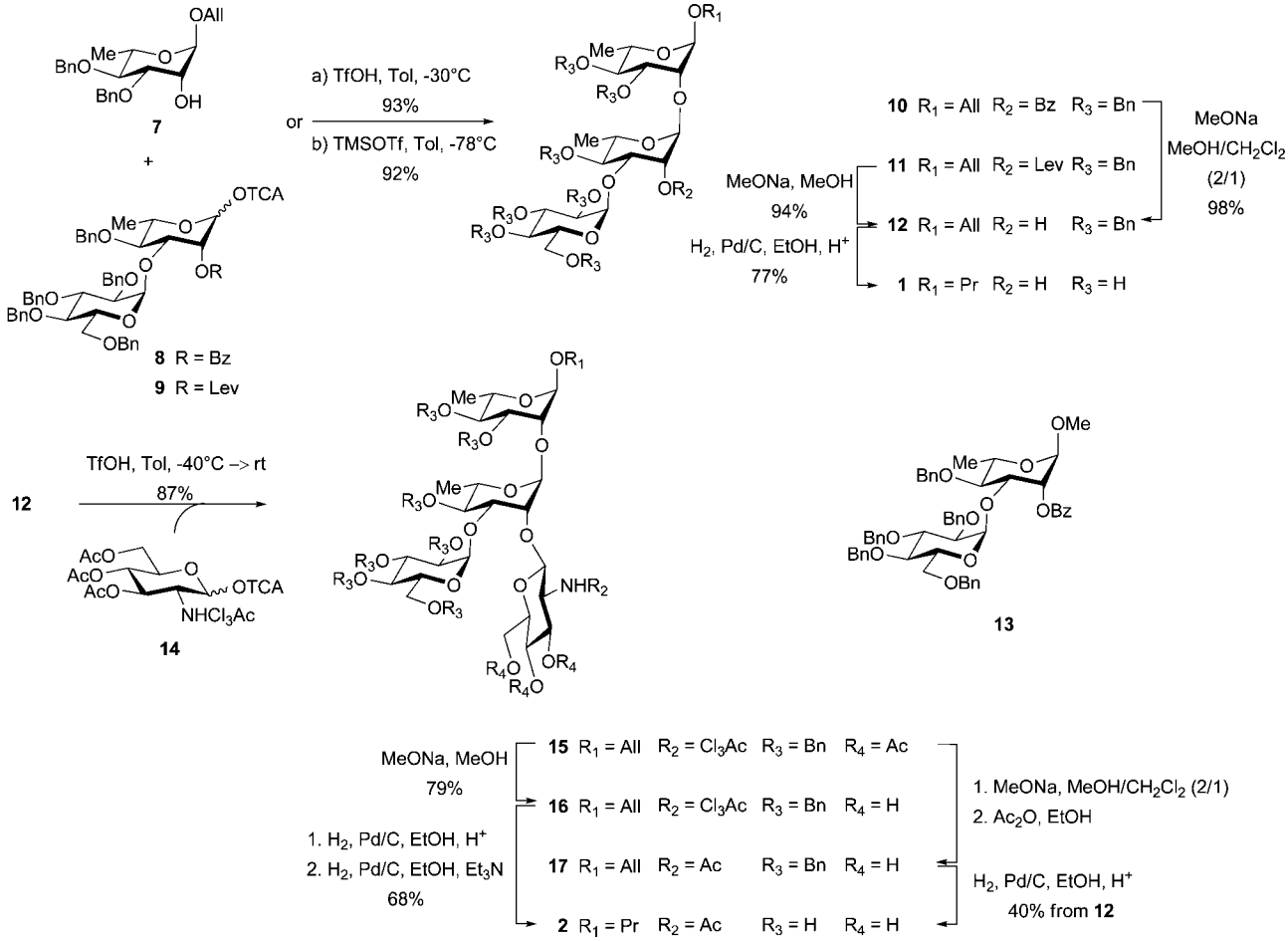
Results and Discussion

The syntheses of all glucosylated di- to pentasaccharide fragments of *S. flexneri* 3a and *S. flexneri* X O-Ags having residue **A**, **C**, or **D**, at their reducing end have been described previously.[15,16] We report here the synthesis of the tri-, tetra-, and pentasaccharides **EAB** (**1**), **D(E)AB** (**2**), **$_{Ac}$CD(E)AB** (**3**), and **CD(E)AB** (**4**). These compounds complete the panel of frame-shifted glucosylated di- to pentasaccharide fragments of *S. flexneri* 3a O-Ag needed for a detailed investigation of the recognition specificity of *S. flexneri* 3a LPS by protective monoclonal antibodies. In addition, as we are aware of a possible migration of the acetyl group from position 2 of rhamnose **C** to the *cis*-vicinal hydroxyl in pentasaccharide **3**, we also prepared the 2$_C$-*O*-acetylated and non-*O*-acetylated hexasaccharides **B$_{Ac}$CD(E)AB** (**5**), and **BCD(E)ABC** (**6**), respectively. Moreover, we propose an optimized protocol for the conversion of a trichloroacetamide moiety vicinal to an ester into the corresponding acetamido alcohol product. Taking advantage of this procedure, two routes to **5** and **6** were studied. The first one involves a 2$_D$-acetamido **D(E)AB** acceptor, and the second one uses a 2$_D$-trichloroacetamido **D(E)AB** acceptor. A comparative study was first made on the more readily available 2$_D$-acetamido **D(E)A** and 2$_D$-trichloroacetamido **D(E)A** acceptors, respectively.

As for other compounds we synthesized in the *S. flexneri* 3a and X series,[15,16] the target products **1**−**6** were obtained as propyl glycosides. Relying on our previous experience in the synthesis of *S. flexneri* 2a and *S. flexneri* 5a oligosaccharides,[18,19] all glycosylation steps used the efficient trichloroacetimidate

(2) Girard, M. P.; Steele, D.; Chaignat, C. L.; Kieny, M. P. *Vaccine* **2006**, *24*, 2732–2750.
(3) von Seidlein, L.; Kim, D. R.; Ali, M.; Lee, H.; Wang, X.; Thiem, V. D.; Canh do, G.; Chaicumpa, W.; Agtini, M. D.; Hossain, A.; Bhutta, Z. A.; Mason, C.; Sethabutr, O.; Talukder, K.; Nair, G. B.; Deen, J. L.; Kotloff, K.; Clemens, J. *PLoS Med.* **2006**, *3*, e353.
(4) Phalipon, A.; Mulard, L. A.; Sansonetti, P. J. *Microbes Infect.* **2008**, *10*, 1057–1062.
(5) Levine, M. M.; Kotloff, K. L.; Barry, E. M.; Pasetti, M. F.; Sztein, M. B. *Nat. Rev. Microbiol.* **2007**, *5*, 540–553.
(6) Kotloff, K. L.; Winickoff, J. P.; Ivanoff, B.; Clemens, J. D.; Swerdlow, D. L.; Sansonetti, P. J.; Adak, G. K.; Levine, M. M. *Bull. W. H. O.* **1999**, *77*, 651–666.
(7) Lindberg, A. A.; Karnell, A.; Weintraub, A. *Rev. Infect. Dis.* **1991**, *13*, S279–S284.
(8) West, N. P.; Sansonetti, P.; Mounier, J.; Exley, R. M.; Parsot, C.; Guadagnini, S.; Prevost, M. C.; Prochnicka-Chalufour, A.; Delepierre, M.; Tanguy, M.; Tang, C. M. *Science* **2005**, *307*, 1313–1317.
(9) Ferreccio, C.; Prado, V.; Ojeda, A.; Cayyazo, M.; Abrego, P.; Guers, L.; Levine, M. M. *Am. J. Epidemiol.* **1991**, *134*, 614–627.
(10) Formal, S. B.; Oaks, E. V.; Olsen, R. E.; Wingfield-Eggleston, M.; Snoy, P. J.; Cogan, J. P. *J. Infect. Dis.* **1991**, *164*, 533–537.
(11) Clément, M. J.; Imberty, A.; Phalipon, A.; Perez, S.; Simenel, C.; Mulard, L. A.; Delepierre, M. *J. Biol. Chem.* **2003**, *278*, 47928–47936.
(12) Vulliez-Le Normand, B.; Saul, F. A.; Phalipon, A.; Bélot, F.; Guerreiro, C.; Mulard, L. A.; Bentley, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 9976–9981.
(13) Mulard, L. A.; Ughetto-Monfrin, J. *J. Carbohydr. Chem.* **1999**, *18*, 721–753.
(14) Costachel, C.; Sansonetti, P. J.; Mulard, L. A. *J. Carbohydr. Chem.* **2000**, *19*, 1131–1150.
(15) Boutet, J.; Guerreiro, C.; Mulard, L. A. *Tetrahedron* **2008**, *64*, 10558–10572.
(16) Boutet, J.; Mulard, L. A. *Eur. J. Org. Chem.* **2008**, 5526–5542.
(17) Vyas, N. K.; Vyas, M. N.; Chervenak, M. C.; Johnson, M. A.; Pinto, B. M.; Bundle, D. R.; Quiocho, F. A. *Biochemistry* **2002**, *41*, 13575–13586.
(18) Mulard, L. A.; Ughetto-Monfrin, J. *J. Carbohydr. Chem.* **2000**, *19*, 193–220.

SCHEME 1. Synthesis of Propyl Glycosides 1 and 2



(TCA) chemistry.[20] The allyl group, often used in complex oligosaccharide synthesis,[21,22] was selected for temporary protection at the anomeric position of the various building blocks. Interestingly, in addition to being orthogonal to a number of protecting groups, an allyl ether is easily reduced to a propyl ether upon Pd/C catalyzed hydrogenation. We took advantage of this property to block the reducing end of the target oligosaccharides in a form mimicking the anomery found in the O-Ag.

Synthesis of Trisaccharide EAB (1) and Tetrasaccharide D(E)AB(2). We first undertook the preparation of trisaccharide **1** and tetrasaccharide **2**, which did not require chain elongation at the **D** residue and did not comprise the 2-*O*-acetyl **C** residue. As depicted in Scheme 1, the allyl rhamnoside **7**,[16,23] featuring permanent benzyl groups at O-3 and O-4, was glycosylated with the known disaccharide trichloroacetimidate **8**,[24] bearing a benzoyl participating group on position 2_A. The condensation was run in toluene in the presence of catalytic TfOH to give the 2_A-*O*-benzoyl trisaccharide **10** in 93% yield. On the basis of previous observations, made when working on the corresponding **EA** methyl glycoside **13**, which suggested the partial masking at OH-2_A by the vicinal 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl residue,[13] a steric hindrance surrounding OH-2_A was anticipated. Accordingly, debenzoylation of trisaccharide **10** into alcohol **12** (98%) was achieved using a large excess of sodium methoxide in a 1:2 refluxing mixture of dichloromethane and methanol. Moreover, the recently reported levulinate analogue **9**[16] was investigated as an alternative glycosyl donor. To our satisfaction, condensation of trichloroacetimidate **9** with acceptor **7** led to the fully protected 2_A-*O*-levulinoyl trisaccharide **11** in 92% yield when the reaction was run in toluene. This solvent was preferred to dichloromethane, in which the reaction led to a lower isolated yield of levulinate **11** (82%). The NMR analysis of **11** showed a $^1J_{C1A,H1A}$ of 173.4 Hz, which indicated an α-AB linkage[25] and ascertained that the levulinic ester had played its role of participating group. Interestingly, treatment of the fully protected **11** in refluxing methanolic sodium methoxide gave alcohol **12** in a satisfactory 94% yield, confirming the potential of donor **9** as an alternative to donor **8**. As shown previously, this is of special interest when orthogonality to acetate is required.[16] Pd/C mediated hydrogenolysis and concomitant allyl reduction of alcohol **12** next provided the linear trisaccharide **1** (77%).

(19) Bélot, F.; Wright, K.; Costachel, C.; Phalipon, A.; Mulard, L. A. *J. Org. Chem.* **2004**, *69*, 1060–1074.
(20) Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–123.
(21) Auzanneau, F. I.; Forooghian, F.; Pinto, B. M. *Carbohydr. Res.* **1996**, *291*, 21–41.
(22) Bélot, F.; Guerreiro, C.; Baleux, F.; Mulard, L. A. *Chem. Eur. J.* **2005**, *11*, 1625–1635.
(23) Westerduin, P.; de Haan, P. E.; Dees, M. J.; van Boom, J. H. *Carbohydr. Res.* **1988**, *180*, 195–205.
(24) Mulard, L. A.; Clément, M. J.; Segat-Dioury, F.; Delepierre, M. *Tetrahedron* **2002**, *58*, 2593–2604.
(25) Bock, K.; Pedersen, C. M. *Acta Chem. Scand., Ser. B* **1975**, *29*, 258–264.

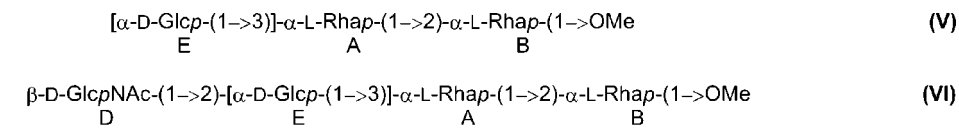


FIGURE 2. Known methyl glycoside analogues of targets **1** (**V**) and **2** (**VI**).

Interestingly, alcohol **12** could serve as an ideal acceptor in the synthesis of the branched tetrasaccharide **2** (Scheme 1). Thus, acceptor **12** was reacted with the readily available glucosamine donor **14**[26,27] in toluene in the presence of a catalytic amount of TfOH, to give the tri-*O*-acetyl tetrasaccharide **15** (87%). Transesterification of the acetates gave triol **16** (79%), which was next converted to target **2** (68%), following a Pd/C mediated two-step hydrogenation process allowing hydrogenolysis of the benzyl ethers, reduction of the allyl into a propyl, and reduction of the trichloroacetamide into the corresponding acetamide. Alternatively, target **2** was obtained in 40% overall yield from alcohol **12** via acetamidotriol **17**, issued from concomitant *N*,*O*-transesterification and selective *N*-acetylation of the fully protected tetrasaccharide **15**. Considering the scale on which the latter transformation was evaluated, both routes appeared comparable. Noteworthy, the methyl glycoside analogues of targets **1** and **2**, compounds **V** and **VI** (Figure 2), respectively, have been reported before.[28] Interestingly, the strategy disclosed here differs quite a lot from the one used previously, in terms of both the glycosylation chemistry and the protecting group pattern used for precursors to residues **A**, **B**, and **D**. However, the use of an **EA** donor, as reported here, is probably the main difference between the two disclosed strategies. It was found advantageous in order to avoid the difficult separation between the αE- and βE-**EAB** trisaccharide isomers obtained when following the formerly reported linear route, which used an **AB** acceptor and an **E** donor.[28]

Synthesis of Pentasaccharides $_{Ac}$CD(E)AB (3) and CD(E)-AB(4) and Hexasaccharides B$_{Ac}$CD(E)AB (5) and BCD(E)-AB (6). The retrosynthetic analysis of **3**−**6** showed that all target oligosaccharides could derive from a common fully protected **D(E)AB** precursor **19**. Intermediate **19** is blocked at positions 4_D and 6_D via an isopropylidene acetal, which we found appropriate on several occasions in the *S. flexneri* series[18,19] following reports by others[29] and our own observations[13] on the potential interference of the more common benzylidene acetal due to anisotropic shielding of H-6_C (Scheme 2). The use of tetrasaccharide **19** opened the way to two potential acceptors differentiated at position 2_D, namely, a 2_D-*N*-trichloroacetyl intermediate **20**, bearing a masked acetamido function at position 2_D, and the 2_D-*N*-acetyl analogue **21**, corresponding to the introduction of the 2_D-acetamido moiety at an early stage in the synthesis. Indeed, available data suggest that acceptors containing *N*-acetylglucosamine are less reactive than their masked acetamido counterparts and occasionally prone to side reactions[30−32] but can be used successfully in complex oligosaccharide synthesis.[22] On one hand, chain elongation with the known trichloroacetimidate rhamnosyl donor[33] **22** having the 2_C-*O*-acetyl in place would lead to the pentasaccharides **3** and **4**. On the other hand, chain elongation with the newly disclosed rhamnobiosyl trichloroacetimidate **23** would provide both 2_C-*O*-acetyl hexasaccharide **5** and free hexasaccharide **6**. Indeed, as for rhamnose **22**, position 2_C of rhamnobiose **23** is acetylated, whereas position 2_B is blocked as a levulinate, selected for its orthogonality to an acetate. Noteworthy, both acetyl and levulinoyl protecting groups in donors **22** and **23** served as a participating group when required at the glycosylation stage.

The synthesis of pentasaccharides **3** and **4** was inspired from that of trisaccharide **1** and tetrasaccharide **2**. Thus, trisaccharide **12** was used as an intermediate. Since chain elongation was at position 3_D, we favored the recently reported, orthogonally protected glucosamine trichloroacetimidate[27] **18** instead of the corresponding triacetate **14** to serve as donor. However, the fully protected tetrasaccharide **19** was isolated in rather low yields, when the condensation of acceptor **12** and donor **18** was run at −40 °C in either dichloromethane or toluene (Table 1, entries 1 and 2, respectively), although these conditions had been found satisfactory for a similar condensation yielding the **D(E)ABC** analogue.[16] A closer investigation of the reaction showed that unreacted acceptor remained, whereas the donor was totally consumed. Other conditions, focusing on temperature, amounts of catalyst, and amounts of donor were therefore studied (Table 1, entry 4; entries 3 and 4; and entries 5 and 6, respectively). Since we had previously noticed the degradation of donor **18** at temperatures above −20 °C,[16] this temperature was set as a limit. Indeed, our new data confirmed that the ideal reaction temperature for compound **18** is closer to −40 °C. Increasing the amount of catalyst did not improve the outcome of the condensation; however, increasing the amount of donor **18** up to 1.7 equiv allowed total consumption of the trisaccharide acceptor **12**, resulting in a 95% isolated yield of tetrasaccharide **19** (Table 1, entry 6). Relying on our findings made during the synthesis of the tetrasaccharide **2**, the trichloroacetamide **19** was converted to the acetamido alcohol **21** (77%) via concomitant *N*,*O*-transesterification using an excess of sodium methoxide in a 1:8 dichloromethane/methanol mixture and subsequent *N*-acetylation of the resulting aminoalcohol **24**. Indeed, early conversion of the 2_D-*N*-trichloroacetyl moiety into an acetamide was favored to prevent, if possible, any unwanted *O*-acetyl migration at the final Pd/C catalyzed deprotection stage providing target **3**. The TfOH-mediated glycosylation of acceptor **21** with trichloroacetimidate **22** was run in toluene to give the condensation product **25** in 71% yield. Interestingly, the various side products observed previously upon glycosylation of the 2_D-trichloroacetamide **D(E)A** acceptor[15] **27** with the same donor **22**[15] were not isolated. Acidic hydrolysis of the 4,6-*O*-isopropylidene acetal gave the intermediate diol **26**. Conventional Pd/C catalyzed hydrogenation of the latter gave the mono-*O*-acetylated pentasaccharide **3** (67%), which was isolated following RP-HPLC purification in a form of regioisomers whereby the 2_C- and 3_C-*O*-acetyl isomers coexisted in a complex

(26) Blatter, G.; Beau, J. M.; Jacquinet, J. C. *Carbohydr. Res.* **1994**, *260*, 189–202.
(27) Boutet, J.; Kim, T. H.; Guerreiro, C.; Mulard, L. A. *Tetrahedron Lett.* **2008**, *49*, 5339–5342.
(28) Bakinovskii, L. V.; Gomtsyan, A. R.; Bairamova, N. E.; Kochetkov, N. K. *Bioorg. Khim.* **1985**, *11*, 254–263.
(29) Bundle, D. R.; Josephson, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2736–2739.
(30) Crich, D.; Dudkin, V. *J. Am. Chem. Soc.* **2001**, *123*, 6819–6825.
(31) Lucas, R.; Hamza, A.; Lubineau, A.; Bonnaffe, D. *Eur. J. Org. Chem.* **2004**, 2107–2117.
(32) Liao, L.; Auzanneau, F. I. *J. Org. Chem.* **2005**, *70*, 6265–6273.
(33) Castro-Palomino, J. C.; Hernandez Rensoli, M.; Verez Bencomo, V. *J. Carbohydr. Chem.* **1996**, *15*, 137–146.

SCHEME 2. Retrosynthetic Analysis of Propyl Glycosides 3−6

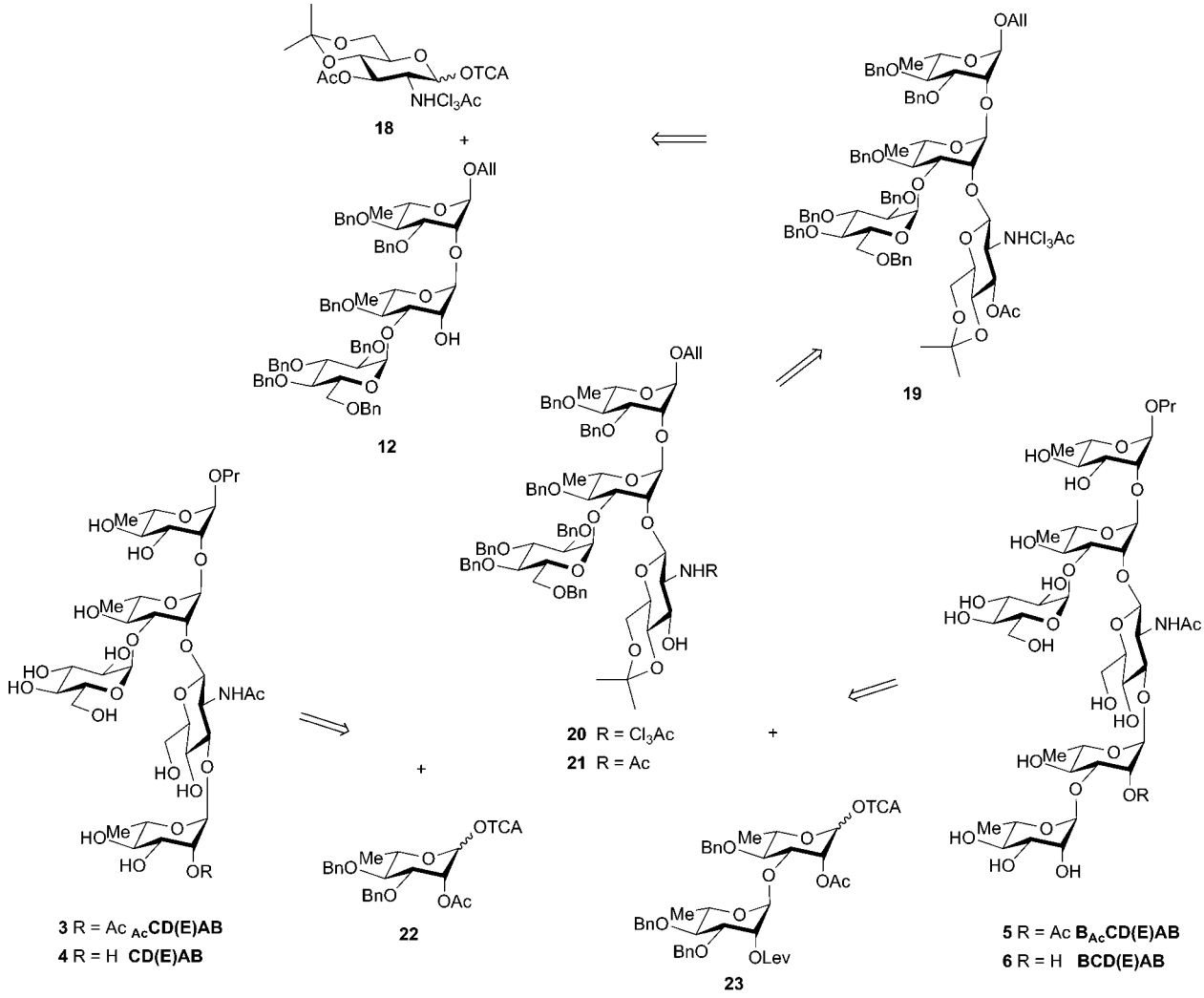


TABLE 1. Study on the Condensation of Acceptor 12 and Donor 18

entry	TMSOTf (equiv)	temp (°C)	donor **18** (equiv)	solvent	yield (%)
1	0.3	−40	1.4	CH_2Cl_2	35
2	0.3	−40	1.4	toluene	56
3	0.4	−40	1.5	toluene	77
4	0.4	−20	1.5	toluene	70
5	0.3	−40	1.5	toluene	75
6	0.3	−40	1.7	toluene	95

equilibrium, based on NMR data (δ(H-2_C) = 4.88 ppm, bs) and (δ(H-3_C) = 4.93 ppm, dd), respectively. RP-HPLC analysis also suggested the presence of a third regioisomer. This result confirmed our previous observations on the **$_{Ac}$CD(E)A** fragment,[15] although exceptions do exist.[34] Subsequent *O*-deacetylation of the propyl glycoside **3**, followed by RP-HPLC purification, gave the free pentasaccharide **4** (63%).

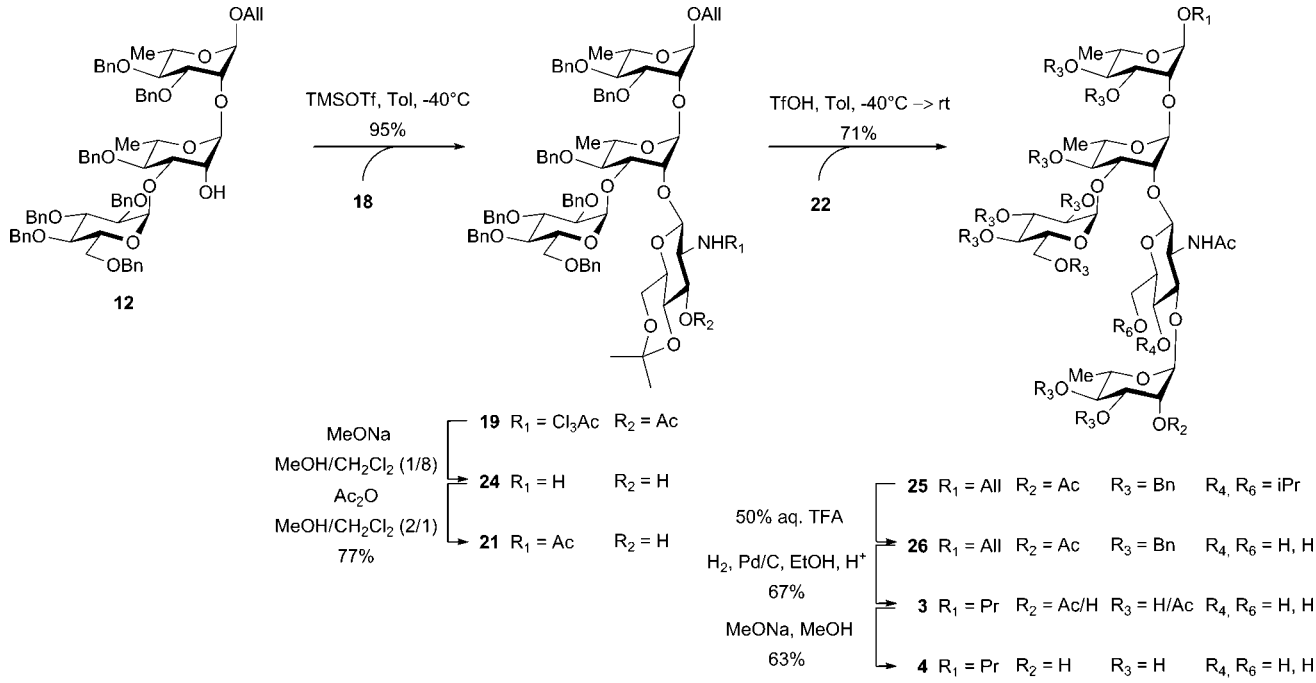
The synthesis of hexasaccharides **5** and **6** was envisioned in the context of a more ambitious goal, that is, the development of a synthetic strategy that would open the way to a variety of larger fragments of *S. flexneri* 3a O-Ag. For that reason, different routes to a suitable **D(E)AB** acceptor were investigated. We first focused on the construction of a fully protected **D(E)AB** intermediate. As an alternative to the pathway described using the **D** donor **18** and the **EAB** trisaccharide acceptor **12** (Scheme 3), the condensation of a **D(E)A** trichloroacetimidate donor having a levulinoyl protecting group at position 3_D **30** and the rhamnoside acceptor **7** was investigated as a potential inroad to a more convergent strategy (Scheme 4). Indeed the 3_D-*O*-levulinoyl protecting pattern was selected in anticipation to any requirement for orthogonality to the 2_C-acetate. Trichloroacetimidate **30** was obtained in three steps from alcohol **27**.[15] Thus, treatment of trisaccharide **27** with levulinic acid in the presence of DCC and DMAP gave the fully protected **28** (90%). Next, allyl glycoside **28** was converted to hemiacetal **29** (80%) following a two-step selective deallylation procedure involving (i) isomerization of the allyl ether into the corresponding prop-1-enyl ether using a cationic iridium complex[35] and (ii) subsequent iodine-mediated hydrolysis.[36] Finally, the **D(E)A** trisaccharide donor **30** was obtained as an anomeric mixture in 85% yield by reacting hemiacetal **29** with trichloroacetonitrile in the presence of catalytic DBU. Running the condensation of the latter with the allyl rhamnoside **7** in toluene containing a catalytic amount of TMSOTf gave mostly unreacted **7** and hemiacetal **29**. When toluene was changed for dichloromethane,

(34) Das, S. K.; Roy, N. *Carbohydr. Res.* **1995**, *271*, 177–183.

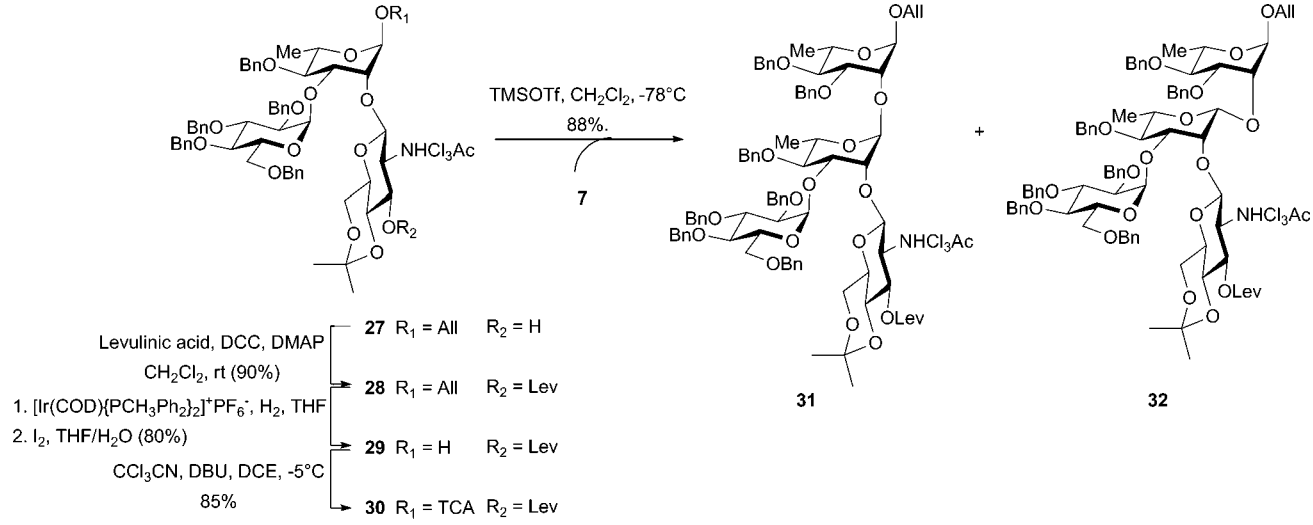
(35) Oltvoort, J. J.; van Boeckel, C. A. A.; der Koning, J. H.; van Boom, J. H. *Synthesis* **1981**, 305–308.

(36) Nashed, M. A.; Anderson, L. *Chem. Commun.* **1982**, 1274–1276.

SCHEME 3. Synthesis of Propyl Glycosides 3 and 4



SCHEME 4. Study on the Synthesis of D(E)AB According to a D(E)A + B Protocol



the acceptor **7** was totally consumed. Two major compounds **31** and **32**, both corresponding to condensation products, as seen by mass spectrometry analysis, were isolated in a 1:1 ratio (88%). Careful NMR analysis confirmed that **31**, the faster eluting product, was the expected tetrasaccharide having an α-AB linkage ($^1J_{C1A,H1A}$ = 171.3 Hz). Interestingly, compound **32** was the stereoisomer having a *β*-AB linkage ($^1J_{C1A,H1A}$ = 155.1 Hz). Although formation of the latter was anticipated in the absence of a participating group at position 2_A of trichloroacetimidate **30**, its isolation in such a high yield prevented any further investigation of this strategy. The **D** + **EAB** route was therefore adopted.

N-Acetyl-*β*-D-glucosamine is present in numerous oligosaccharides of natural origin. However, the acetamido moiety can hardly be used for anchimeric assistance in complex oligosaccharide synthesis. For that reason, a number of N-protecting groups serving as participating groups, or on the contrary preventing anchimeric assistance, were developed.[37] Whether these protecting groups should be regarded as permanent or temporary acetamido masking patterns is often defined on a case by case basis. For example, in the synthesis of a number of oligosaccharides representative of *S. flexneri* 2a O-Ag, with pentasaccharide **IV** (Figure 1), a regioisomer of **II**, as a repeating unit, chain elongation at OH-3_D was performed using acceptors containing *N*-acetylglucosamine residues.[22] However, others encountered difficulties when attempting to glycosylate poorly reactive hydroxyl groups as part of *N*-acetylglucosamine-containing acceptors.[21,31] Aiming at reducing the number of deprotection steps that could potentially interfere with the 2_C-acetate at the late stage of the synthesis, the next step was thus to investigate the best protecting group pattern of the amino group of glucosamine **D** when involved in building blocks

(37) Bongat, A. F.; Demchenko, A. V. *Carbohydr. Res.* **2007**, *342*, 374–406.

SCHEME 5. Conversion of the 2_D-Trichloroacetamide 33 into the 2_D-Acetamide 36

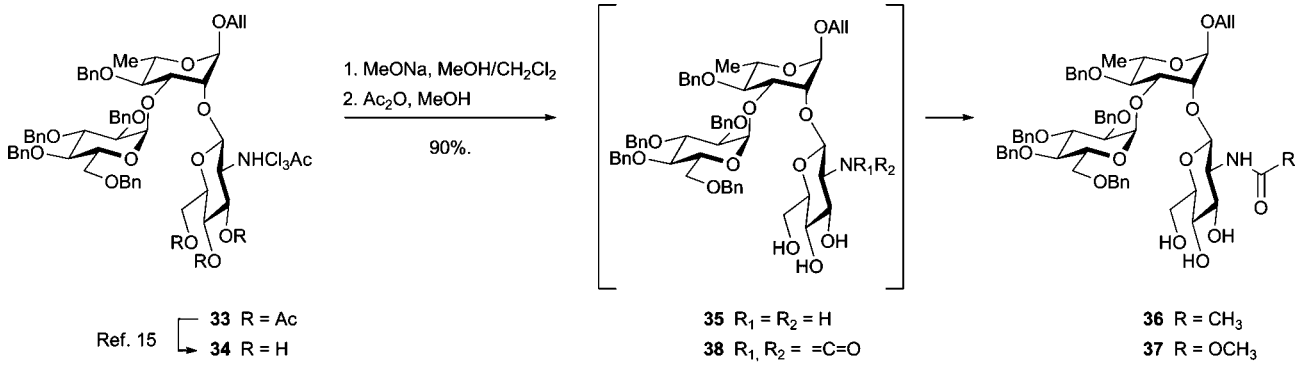
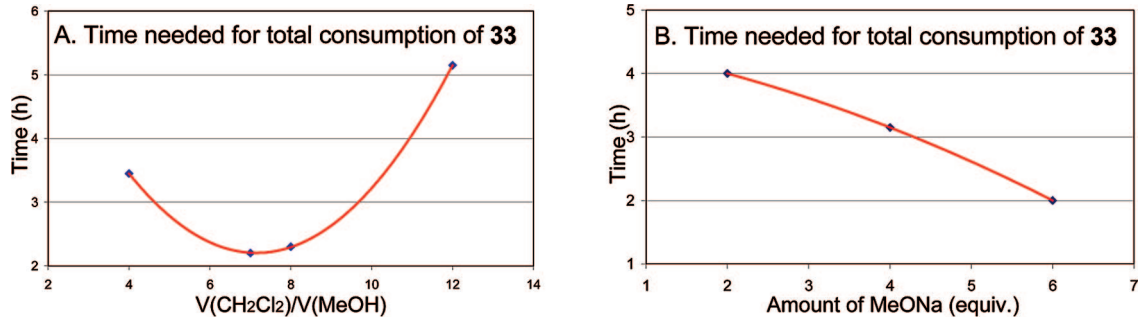


CHART 1. Study on the Conversion of 33 into 36[a]



[a] (A) The initial concentration of **33** in MeOH was 0.4 M (5 equiv of MeONa). (B) The CH_2Cl_2/MeOH ratio (v/v) was constant at 8.

required for chain elongation at position 3_D, such as **D(E)AB**. To broaden the analysis, the study was initiated on the more readily available **D(E)A**.

Finding appropriate conditions to ensure efficient conversion of the *N*-trichloroacetyl moiety into the corresponding acetamide was our first goal. Most commonly used methodologies include basic trichloroacetyl removal and subsequent *N*-acetylation of the resulting amine,[24,38,39] direct reduction under neutral conditions such as Bu_3SnH-mediated radical hydrodechlorination,[22,26] or often at the final stage of the synthesis, nonspecific palladium-mediated reductive hydrodechlorination.[19,39] Avoiding the tin methodology, we focused on finding chemoselective conditions applicable to nonpolar compounds by taking advantage of former observations. Indeed, we have reported the high-yielding transesterification of the triacetate **33**[15] into triol **34**[15] by use of a methanolic solution of sodium methoxide under controlled conditions. However, we also reported *O*-deacetylation and a concomitant vicinal *N*-trichloroacetyl conversion into the corresponding amine in the presence of additional Et_3N[14] or dichloromethane.[15,24] We now report on a detailed investigation of the latter conditions resulting in the efficient conversion of triacetate **33** into acetamidotriol **36**[15] (Scheme 5).

When running the deprotection step in a mixture of dichloromethane and methanol, two closely migrating compounds were isolated following subsequent *N*-acetylation of the aminotriol intermediate **35**. On the basis of NMR and mass spectrometry data, the more polar one was the expected acetamido triol **36** (HRMS (ESI^+) for $C_{58}H_{69}NO_{15}$ ($[M + H]^+$, 1020.4745) found *m/z* 1020.4739, δ_{CO} = 173.3 ppm, δ_{Me} = 23.6 ppm),[15] whereas the first migrating compound was identified as the methyl carbamate **37** (HRMS (ESI^+) for $C_{58}H_{69}NO_{16}$ ($[M + Na]^+$, 1058.4514) found *m/z* 1058.4514, δ_{CO} = 159.4 ppm, δ_{oMe} = 52.9 ppm), the formation of which is tentatively explained via the addition of methanol onto isocyanate **38**.[40] Varying the reaction conditions in terms of dichloromethane/methanol ratio and amount of sodium methoxide highlighted the impact of these two parameters on the consumption of the starting triacetate **33** (Chart 1). Under the best conditions (6 equiv of sodium methoxide in a 8:1 (v/v) mixture of dichloromethane/MeOH), the transformation was completed within 2 h, providing acetamido **36** and carbamate **37** in 90% and 5% yield post *N*-acetylation, respectively. Satisfactorily, treatment of the 3_D-acetate **39**[15] under the same conditions gave the known 2_D-acetamido acceptor **40**[15] in 90% yield.[15]

This new route to acceptor **40** involving the isopropylidene donor **18** was compared to the one reported earlier using the triacetate donor **14**.[15] The corresponding overall yields of acetamide **40** from allyl glycoside **41**, 81% via isopropylidene **39** and 70% via triacetate **33**, respectively, were clearly in favor of the methodology just disclosed when working below the millimolar scale (Scheme 6). When working on 2.1 g of acceptor **41**[24] (2.6 mmol), the yield of trisaccharide **40** via route 1 was 86% and involved one purification step only.

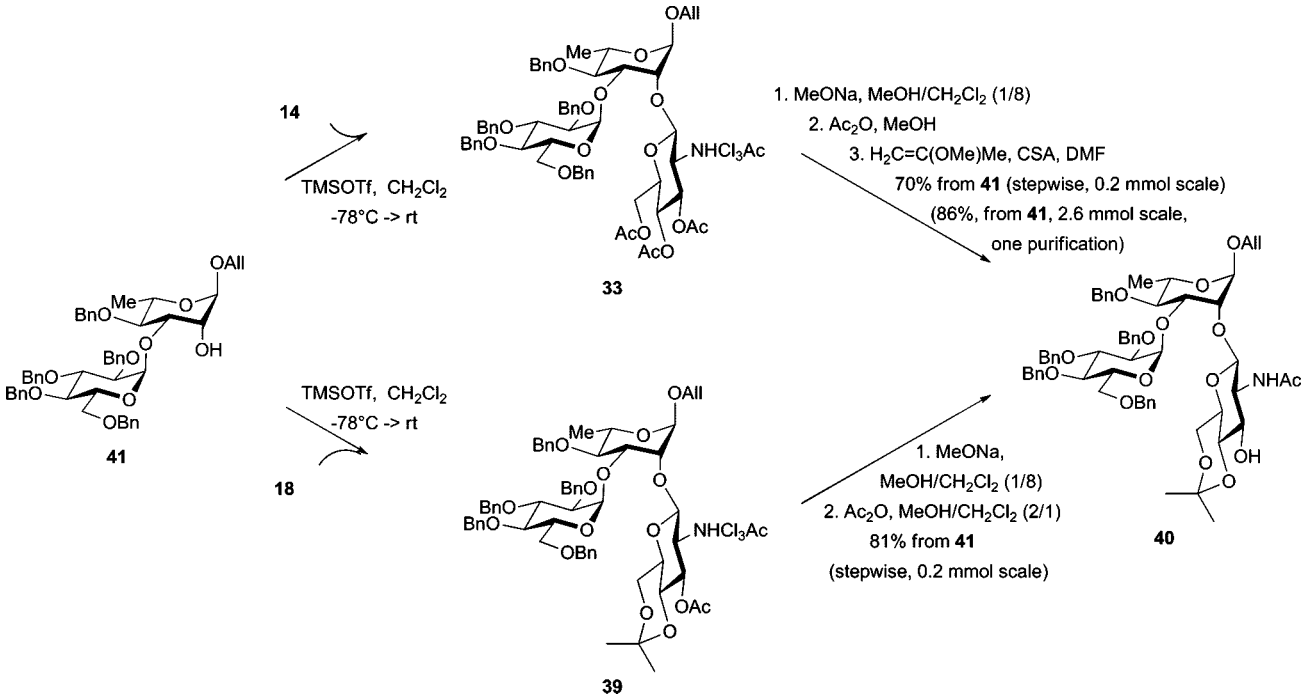
The new conditions were successfully applied to the synthesis of the tetrasaccharide acceptor **D(E)AB**, resulting in an improved yield of acetamide **21** from intermediate **19**, 83% versus 77%. Alternatively, selective removal of the 3_D-acetate in tetrasaccharide **19** by use of potassium carbonate in methanol gave acceptor **20** in 92% yield (Scheme 7).

(38) Sherman, A. A.; Yudina, O. N.; Mironov, Y. V.; Sukhova, E. V.; Shashkov, A. S.; Menshov, V. M.; Nifantiev, N. E. *Carbohydr. Res.* **2001**, *336*, 13–46.

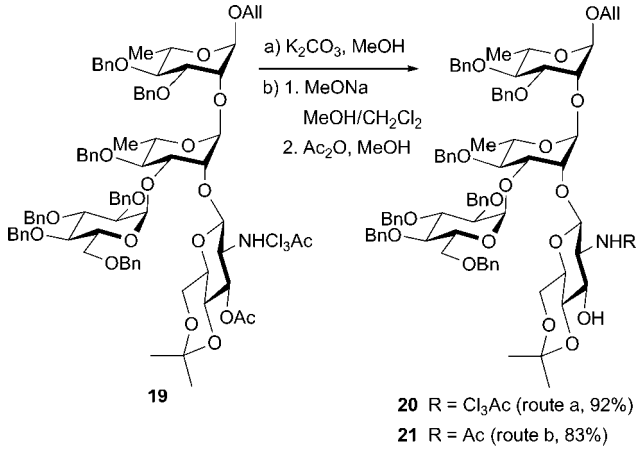
(39) Donohoe, T. J.; Logan, J. G.; Laffan, D. D. *Org. Lett.* **2003**, *5*, 4995–4998.

(40) Nishikawa, T.; Urabe, D.; Tomita, M.; Tsujimoto, T.; Iwabuchi, T.; Isobe, M. *Org. Lett.* **2006**, *8*, 3263–3265.

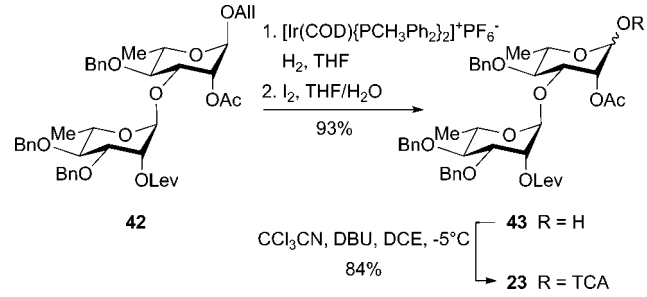
SCHEME 6. Access to Acceptor 40 by Condensation of 41 with Donor 14 (Route 1) and Donor 18 (Route 2)



SCHEME 7. Conversion of Fully Protected 19 into Acceptor 20 or 21



SCHEME 8. Synthesis of Donor 23



Having all four different acceptors **20**, **21**, **27**, and **40** in hands, the next step was to synthesize the rhamnobiose donor **23**. This was easily achieved from the known allyl glycoside **42**.[16] Indeed, selective cleavage of the allyl aglycon gave hemiacetal **43** (93%), which was converted into trichloroacetimidate **23** (84%), when treated with trichloroacetonitrile in the presence of a catalytic amount of DBU (Scheme 8).

We next focused on the condensation of donor **23** with the 3_D-acetamido acceptor **21** and the subsequent transformation of the condensation product. Taking into account the fact that TfOH-mediated glycosylation of acceptor **21** with trichloroacetimidate **22** in toluene succeeded in providing **25** (Scheme 3), while conventional TMSOTf-mediated glycosylation of acceptor **40** with the same donor was somewhat unsuccessful,[15] we chose to first investigate the use of both catalysts in the condensation of trisaccharide **40** and donor **23**. Running the reaction in the presence of 0.3 equiv of TMSOTf, at −20 °C, in toluene or dichloromethane, resulted at best in 25% yield of the pentasaccharide **44**, thus confirming our previous observations. Degradation of the donor was observed, whereas unreacted **40** was recovered. Turning to TfOH, this time used in larger amounts (0.9 equiv) was more satisfactory (Scheme 9, route a). Indeed, running the reaction in toluene at 0 °C resulted in 74% of isolated pentasaccharide **44**. Since the yield of **44** was not higher when running the condensation between acceptor **40** and donor **23** at 70 °C,[22] the TMSOTf-mediated condensation of the same donor **23** with the tetrasaccharide acceptor **21** was run at 0 °C, providing hexasaccharide **45** in 65% yield (Scheme 9, route b). However, careful NMR analysis of the condensation products **44** and **45** suggested, in both cases, the presence of small amounts of a coeluting contaminant (5−10%). Attempts to remove this unidentified side product after cleavage of either the levuniloyl ester or the isopropylidene acetal failed (not described). We thus turned to the use of the corresponding 2_D-trichloroacetamide acceptors **27** and **20**.

When applying the reaction conditions found successful for the condensation of acceptor **27** and the chain-terminator **BC** donor **46**[15] to the glycosylation of **27** and donor **23**, we could confirm the stability of the isopropylidene acetal at −78 °C. However, the yield of the condensation product **48** (63%) was lower than expected. Indeed, although the reaction was run for a longer period (1 h instead of 15 min), some starting acceptor remained (16%), whereas the donor was degraded (Table 2, entry 1). Interestingly, when the condensation was run on a 2 g

SCHEME 9. Condensation of Acceptors 40 (D(E)A) (Route a) and 21 (D(E)AB) (Route b) with the BC Donor 23

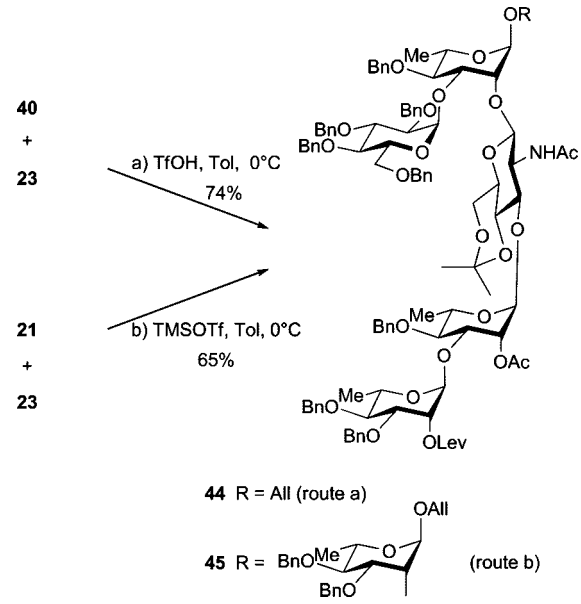


TABLE 2. Study on the Condensation of Acceptor 27 and Donor 23

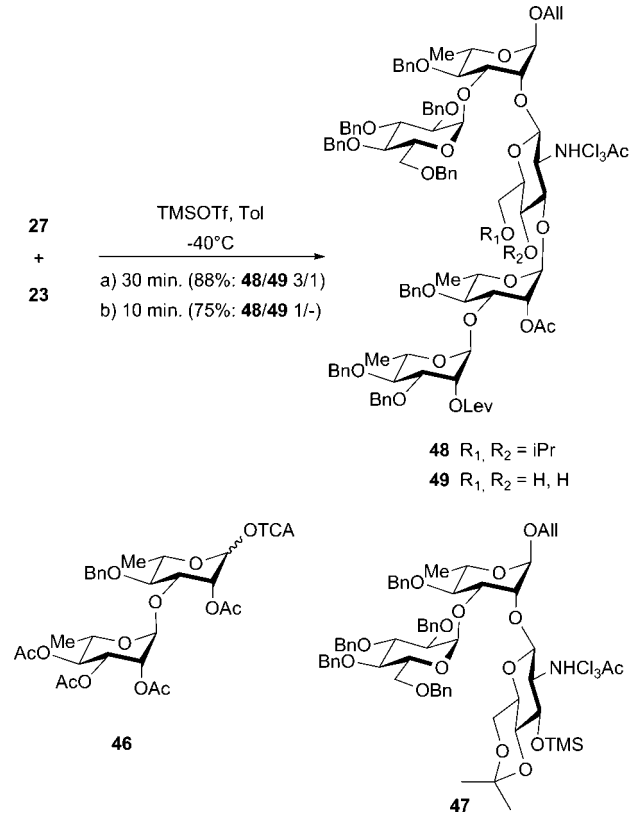
entry	temp (°C)	solvent	time	acceptor **27** (%)	**48** (%)	**49** (%)
1	−78	toluene	1 h	16	63	no[a]
2	−78	CH_2Cl_2	1 h	30	42	no
3	−40	toluene	30 min	no	66	22
4	−20	toluene	30 min	no	66	13
5	−40	toluene	10 min	no	75	no

[a] no = not observed.

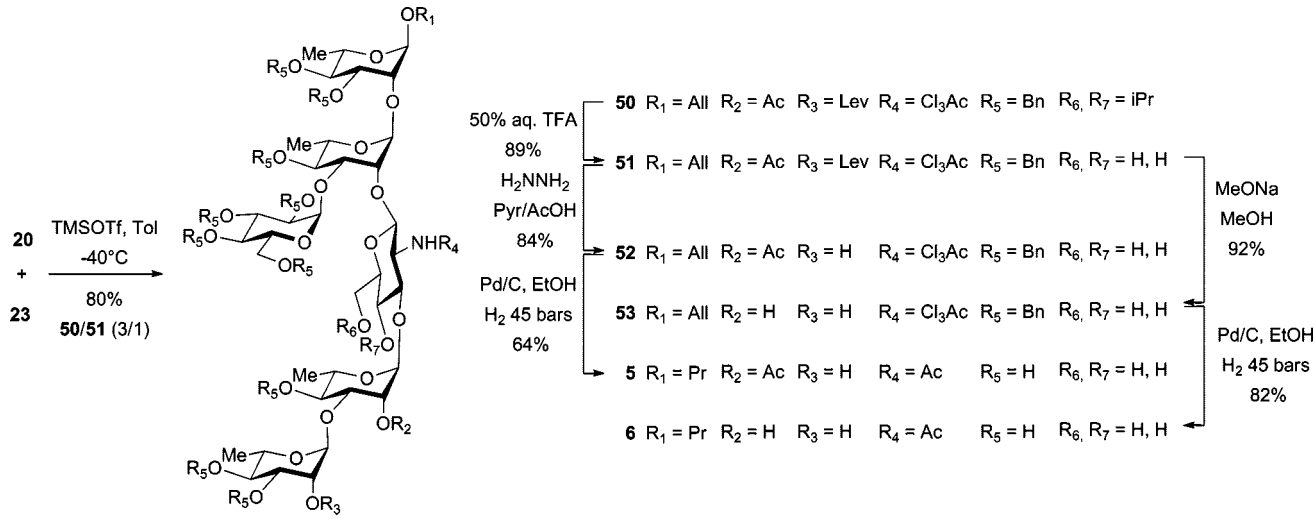
scale of acceptor **27**, the silylated analogue **47** was isolated (11%) in addition to pentasaccharide **48** (52%). Adding more donor or increasing the amount of TMSOTf had no impact. Changing toluene for dichloromethane worsened the outcome of the glycosylation (Table 2, entry 2), since 30% of unreacted acceptor was recovered in addition to **48** (42%). The temperature of the reaction was investigated next in order to overcome this unexpected outcome. Increasing the reaction temperature to −40 °C was highly satisfactory, since neither the remaining acceptor **27** nor the silylated **47** were apparent. In these conditions (Table 2, entry 3), the overall condensation yield was 88% (Scheme 10, route a). However, the poor stability at this temperature of the $4_D,6_D$-*O*-isopropylidene resulted in the isolation of two products, the expected **48** ($^1J_{C1C,H1C}$ = 167.6 Hz, 66%) together with the corresponding diol **49** (22%, not described), resulting from isopropylidene loss post condensation, as ascertained by mass spectrometry analysis (HRMS (ESI^+) for $C_{98}H_{112}Cl_3NO_{26}$ ($[M + Na]^+$ 1846.643) *m/z* 1846.6403) and reacetalation. Additional increase of the temperature had no positive effect (Table 2, entry 4). Running the condensation in toluene, at −40 °C, for a shorter period of time (10 min), finally provided pentasaccharide **48** in 75% yield (Table 2, entry 5). Under these conditions, the diol **49** was not isolated (Scheme 10, route b).

Having demonstrated the crucial importance of temperature on the outcome of the condensation between the trisaccharide acceptor **27** and the disaccharide donor **23**, we turned to the preparation of hexasaccharide **50** (Scheme 11). Taking advantage of the study made for obtaining pentasaccharide **48**, the condensation of the trichloroacetimidate **23** and the tetrasaccharide acceptor **20** was run in toluene, at −40 °C, for 10 min in the presence of a catalytic amount of TMSOTf. Under those conditions, the yield of the condensation was 80%, matching our expectations. However, two products were isolated, the fully protected **50** (59%) and a more polar product (21%). Mass spectrometry and NMR analysis of the latter indicated the formation of diol **51**, corresponding to the $4_D,6_D$-*O*-isopropylidene loss. Treatment of **51** with 2-methoxypropene and CSA in DMF confirmed this assumption, since the fully protected **50** was isolated in 93% yield. Since diol **51** was a suitable intermediate in the synthesis targets **5** and **6**, preventing acetal loss was not attempted. To our satisfaction, running the condensation on larger amounts of acceptor **20** (1.1 mmol instead of 0.2 mmol) under the same conditions but for longer time (45 min) to ensure total consumption of the acceptor, provided **50** and **51** in a 3:1 ratio and 80% total yield. Subsequent partial and total deprotection of the condensation product **50** provided hexasaccharides **5** and **6**, respectively. Indeed, TFA-mediated hydrolysis of the $4_D,6_D$-*O*-isopropylidene of **50** gave diol **51** (89%). The following selective removal of the levuniloyl protecting group in hexasaccharide **51**, using aqueous hydrazine in pyridine/acetic acid, gave triol **52** (84%). Alternatively, reacting **51** with sodium methoxide in refluxing methanol gave tetraol **53** (92%). Conversion of the allyl glycosides **52** and **53** into the propyl glycosides **5** and **6**, respectively, took advantage of the neutral conditions used previously for the synthesis of related *S. flexneri* 3a oligosaccharides.[15,16] In practice, treatment of ethanolic solutions of triol **52** and tetraol **53** under a hydrogen atmosphere (50 bar), in the presence of Pd/C catalyst for 10 days each, allowed concomitant benzyl removal, allyl reduction into propyl, and trichloroacetamide conversion into the required acetamide. The hexasaccharide targets **5** and **6** were finally isolated in 64% and 82% yield,

SCHEME 10. Condensation of Acceptor 27 and Donor 23



SCHEME 11. Synthesis of Hexasaccharides 5 and 6 from Acceptor 20 (D(E)AB) and Donor 23 (BC)



respectively. Overall, the efficiency of the **20** + **23** glycosylation step along with this one-step conversion fully supported the selection of trichloroacetamide **20** as the acceptor in the synthesis of hexasaccharides **5** and **6**.

Conclusion

We have described the synthesis of a linear trisaccharide (**1**) and five branched tetra-, penta-, or hexasaccharides (**2**−**6**) representative of fragments of *S. flexneri* 3a and/or X O-Ags. All the oligosaccharide targets share the **EAB** sequence, whereby residue **B** is blocked at the anomeric position with a propyl aglycon. They were synthesized from a common **EAB** allyl glycoside **12**, obtained in 18 synthetic steps. A one-step deprotection and concomitant allyl to propyl conversion of alcohol **12** gave the trisaccharide target **1**. Alternatively, glycosylation of acceptor **12** with **D** donors **14** (4 steps) and **18** (5 steps) gave tetrasaccharides **15** and **19**, respectively. On one hand, conventional deprotection of the triacetate **15** gave the tetrasaccharide target **2** (3 steps from intermediate **12**). On the other hand, the 4_D,6_D-*O*-isopropylidene tetrasaccharide **19** served as key intermediate to either the *N*-trichloroacetyl acceptor **20** or the *N*-acetyl analogue **21**. Noteworthy, the one-step basic conversion of the fully protected **19** into acceptor **21** (83%) relied on in-house conditions, the optimization of which is also disclosed here. Acceptors containing *N*-acetylglucosamine have some limitations, potentially preventing their use in complex oligosaccharide synthesis. In the course of this work, two of such acceptors, trisaccharide **40** and tetrasaccharide **21**, were compared to their *N*-trichloroacetyl counterparts **27** and **20**, respectively. Independently of the acceptor used, our work pointed out (i) the lower stability of the 4_D,6_D-*O*-isopropylidene acetal when located on the trichloroacetamide derivatives **27** and **20** than when located on the acetamido analogues **40** and **21**, (ii) the crucial impact of temperature on the glycosylation outcome, and (iii) the key input of the condensation duration in controlling the compromise between glycosylation yield and isopropylidene loss. Optimizing both parameters resulted in good yields of glycosylation in all cases. Nevertheless, the presence of tiny amounts of unidentified contaminants associated with the use of the acetamido acceptors **40** and **21** encouraged the use of the *N*-trichloroacetyl derivatives **27** and **20**, despite their higher propensity to acetal loss. Finally, chain elongation of acceptor **20** with donor **23** provided the fully protected hexasaccharide **50**. Conversion of the latter into targets **5** and **6** took advantage of the feasible concomitant removal and/or transformation of the protecting groups, including benzyl hydrogenolysis, allyl reduction, and reductive trichloroacetamide conversion to acetamide. Therefore, partial deprotection of the allyl glycoside **50** gave monoacetate **5** (3 steps), whereas full deprotection provided hexasaccharide **6** (3 steps). Data reported herein provide the chemical tools for further synthesis of larger fragments of *S. flexneri* serotypes 3a and/or X O-Ags.

Experimental Section

Allyl (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (10). TfOH (16 μL, 186 μmol, 0.2 equiv) was added to a solution of acceptor **7**[16,23] (463 mg, 1.2 mmol, 1.3 equiv) and trichloroacetimidate **8**[24] (953 mg, 0.93 mmol) in toluene (10 mL) containing 4Å MS (500 mg), stirred at −30 °C. The reaction mixture was stirred for 1 h while slowly coming back to rt. TLC (CH_2Cl_2/EtOAc, 98:2) showed the complete disappearance of the acceptor and the presence of a major less polar product. Et_3N (300 μL) was added. The mixture was filtered and concentrated to dryness. Chromatography of the residue (Chex/EtOAc, 100:0 → 80:20) gave the allyl glycoside **10** (1.08 g, 93%) as a colorless syrup. Trisaccharide **10** had R_f = 0.5 (Chex/EtOAc, 8:2), ^{1}H NMR ($CDCl_3$) δ 8.09−8.07 (m, 2H, CH_{Bz}), 7.59 (m, 1H, CH_{Bz}), 7.47−7.08 (m, 37H, CH_{Ph}), 5.89 (m, 1H, CH=), 5.84 (dd, 1H, $J_{1,2}$ = 2.1 Hz, H-2_A), 5.37 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1_E), 5.28 (m, 1H, J_{trans} = 17.3 Hz, =CH_2), 5.20 ($m_{overlapped}$, 1H, =CH_2), 5.19 ($m_{overlapped}$, 1H, H-1_A), 5.00 (d, 1H, J = 10.2 Hz, H_{Bn}), 4.96 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.86 (d, 1H, J = 10.9 Hz, H_{Bn}), 4.84 (d, 1H, J = 10.9 Hz, H_{Bn}), 4.78 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1_B), 4.75 (d, 1H, J = 10.9 Hz, H_{Bn}), 4.72 (s, 2H, H_{Bn}), 4.67−4.63 (m, 3H, H_{Bn}), 4.60 (d, 1H, J = 12.1 Hz, H_{Bn}), 4.47−4.44 (m, 2H, H_{Bn}), 4.39 (dd, 1H, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 9.8 Hz, H-3_A), 4.36 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.15 (m, 1H, H_{All}), 4.08−4.03 (m, 3H, H-3_E, H-5_E, H-2_B), 3.97−3.90 (m, 3H, H_{All}, H-5_A, H-3_B), 3.79 (dd, 1H, $J_{4,5}$ = 9.4 Hz, $J_{3,4}$ = 9.7 Hz, H-4_E), 3.76−3.69 (m, 3H, H-5_B, H-$6a_E$, H-4_A), 3.62 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2_E), 3.59 (m, 1H, $J_{5,6}$ = 1.7 Hz, H-$6b_E$), 3.56 (pt, 1H, $J_{4,5}$ = $J_{3,4}$ = 9.4 Hz, H-4_B), 1.43 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), 1.35 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_B); ^{13}C NMR ($CDCl_3$) δ 166.0 (C_{Bz}), 139.1−138.0 (C_{Ph}), 134.2 (CH=), 133.5, 130.4 (3C, CH_{Bz}), 129.2−127.7 (CH_{Ph}, CH_{Bz}), 117.6 (=CH_2), 99.6 (C-1_A, $^1J_{CH}$ = 172.0 Hz), 98.2 (C-1_B, $^1J_{CH}$ = 169.5 Hz), 93.1 (C-1_E, $^1J_{CH}$ = 169.2 Hz), 82.4 (C-3_E), 80.9 (C-4_B), 80.3 (C-4_A), 80.1 (C-3_B), 79.3

(C-2_E), 77.8 (C-4_E), 76.7, 76.0, 75.9, 75.3, (4C, C_{Bn}), 75.1 (C-2_B), 73.8 (C_{Bn}), 72.9 (C-3_A), 72.6, 72.5 (2C, C_{Bn}), 70.6 (C-5_E), 68.8 (2C, C-2_A, C-5_B*), 68.6 (C-6_E), 68.4 (C-5_A*), 68.0 (C_{All}), 18.5, 18.4 (2C, C-6_A, C-6_B); HRMS (ESI$^+$) for $C_{75}H_{82}O_{15}$ ([M + Na]$^+$, 1269.5552) found *m/z* 1269.5563.

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-rhamnopyranoside (11). TMSOTf (210 μL, 1.2 mmol, 0.3 equiv) was added to a solution of acceptor **7** (1.5 g, 3.9 mmol) and trichloroacetimidate **9**[16] (5.1 g, 5.1 mmol, 1.3 equiv) in toluene (100 mL) containing 4Å MS (3.4 g), stirred at −78 °C. The reaction mixture was stirred for 15 min while slowly coming back to rt. TLC (Tol/EtOAc, 85:15) showed the complete disappearance of the acceptor and the presence of a major less polar product. Et_3N (1 mL) was added. The mixture was filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 95:5 → 85:15) gave **11** (4.5 g, 92%) as a colorless syrup. Trisaccharide **11** had R_f = 0.5 (Chex/EtOAc, 85:15); ^{1}H NMR ($CDCl_3$) δ 7.45−7.12 (m, 35H, CH_{Ph}), 5.87 (m, 1H, CH=), 5.61 (dd, 1H, $J_{1,2}$ = 2.1 Hz, H-2_A), 5.32 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1_E), 5.31 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.23 (m, 1H, J_{cis} = 10.3 Hz, =CH_2), 5.06 (d_{po}, 1H, J = 10.5 Hz, H_{Bn}), 5.05 (d_{po}, 1H, H-1_A), 5.00−4.89 (m, 5H, H_{Bn}), 4.82 (d_{po}, 1H, J = 12.2 Hz, H_{Bn}), 4.81 (bs_o, 1H, H-1_B), 4.74−4.64 (m, 5H, H_{Bn}), 4.53 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.38 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.26 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, H-3_A), 4.20−4.09 (m, 3H, H_{All}, H-3_E, H-5_E), 4.03 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 2.9 Hz, H-2_B), 3.97 (m, 1H, H_{All}), 3.96−3.90 (m, 2H, H-5_A, H-3_B), 3.83 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4_E), 3.75 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5_B), 3.69 (dd_{po}, 1H, $J_{5,6a}$ = 2.7 Hz, $J_{6a,6b}$ = 10.9 Hz, H-$6a_E$), 3.68 (dd_{po}, 1H, $J_{2,3}$ = 9.6 Hz, H-2_E), 3.61 (pt_{po}, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4_A), 3.60 (dd_{po}, 1H, H-$6b_E$), 3.53 (pt, 1H, $J_{3,4}$ = 9.4 Hz, H-4_B), 2.55 (m, 4H, H_{Lev}), 2.11 (s, 3H, CH_{3Lev}), 1.42 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), 1.37 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_B); ^{13}C NMR ($CDCl_3$) δ 206.2 (C_{Lev}), 171.8 (C_{Lev}), 138.7−137.7 (C_{Ph}), 133.9 (CH=), 129.1−127.6 (CH_{Ph}), 117.2 (=CH_2), 99.2 (C-1_A, $^1J_{CH}$ = 173.4 Hz), 97.9 (C-1_B, $^1J_{CH}$ = 170.8 Hz), 92.9 (C-1_E, $^1J_{CH}$ = 168.9 Hz), 82.1 (C-3_E), 80.5 (C-4_B), 79.9 (C-4_A), 79.6 (C-3_B), 79.5 (C-2_E), 77.8 (C-4_E), 76.2, 75.6, 75.5 (3C, C_{Bn}), 75.1 (C-2_B), 75.0, 73.4, 72.8 (3C, C_{Bn}), 72.3 (C-3_A), 72.2 (C_{Bn}), 70.3 (C-5_E), 68.4 (C-5_A), 68.3 (C-6_E), 68.1 (C-5_B), 68.0 (C-2_A), 67.7 (C_{All}), 38.0 (CH_{2Lev}), 29.7 (CH_{3Lev}), 28.2 (CH_{2Lev}), 18.1, 18.0 (2C, C-6_A, C-6_B); HRMS (ESI$^+$) for $C_{75}H_{84}O_{16}$ ([M + Na]$^+$, 1263.5657) found *m/z* 1263.5437, ([M + NH_4]$^+$, 1258.6104) found *m/z* 1258.5887.

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-rhamnopyranoside (12). Route a. Methanolic MeONa (0.5 M, 10 mL, 5 mmol, 6.6 equiv) was added to a solution of benzoylated **10** (935 mg, 750 μmol) in a 1:1 MeOH/CH_2Cl_2 (v/v) mixture (12 mL), and the mixture was refluxed for 3 h. TLC (Chex/EtOAc, 7:3) showed the complete disappearance of **10** 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. Volatiles were evaporated. The resulting syrup was chromatographied (Chex/EtOAc, 100:0 → 7:3) to give **12** (845 mg, 98%) as a colorless oil.

Route b. Methanolic MeONa (0.5 M, 12.2 mL, 6.1 mmol, 1.7 equiv) was added to a solution of fully protected **11** (4.5 g, 3.6 mmol) in MeOH (200 mL), and the mixture was refluxed for 1 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 addition of Dowex X8-200 ion-exchange resin (H^+) and filtered. Volatiles were evaporated. The resulting syrup was chromatographied (Tol/EtOAc, 98:2 → 9:1) to give **12** (3.9 g, 94%). Trisaccharide **12** had R_f = 0.6 (Chex/EtOAc, 7:3); ^{1}H NMR ($CDCl_3$) δ 7.47−7.19 (m, 35H, CH_{Ph}), 5.93 (m, 1H, CH=), 5.32 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.25 (m, 1H, J_{cis} = 10.3 Hz, =CH_2), 5.22 (bs, 1H, H-1_A), 5.05−4.99 (m, 3H, H_{Bn}), 4.97 (d_{po}, 1H, $J_{1,2}$ = 3.5 Hz, H-1_E), 4.91−4.88 (m, 2H, H_{Bn}), 4.84 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1_B), 4.83−4.67 (m, 6H, H_{Bn}), 4.60 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.54 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.36 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.19 (m, 1H, H_{All}), 4.14−4.09 (m, 4H, H-2_A, H-2_B, H-3_A, H-3_E), 4.04−3.99 (m, 2H, H_{All}, H-5_E), 3.98 (dd, 1H, $J_{2,3}$ = 2.9 Hz, $J_{3,4}$ = 9.5 Hz, H-3_B), 3.92 (dq, 1H, H-5_A), 3.82 (dd, 1H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.8 Hz, H-4_E), 3.75 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5_B), 3.66 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.6 Hz, H-2_E), 3.75 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, H-4_A), 3.55−3.49 (m, 2H, H-$6a_E$, H-4_B), 3.45 (dd, 1H, $J_{5,6a}$ = 1.8 Hz, $J_{6a,6b}$ = 10.8 Hz, H-$6b_E$), 1.43 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6_A), 1.39 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_B); ^{13}C NMR ($CDCl_3$) δ 138.7−137.6 (C_{Ph}), 133.9 (CH=), 129.1−127.0 (CH_{Ph}), 117.2 (=CH_2), 101.0 (C-1_A, $^1J_{CH}$ = 170.3 Hz), 98.1 (C-1_B, $^1J_{CH}$ = 170.3 Hz), 94.0 (C-1_E, $^1J_{CH}$ = 166.7 Hz), 82.4 (C-3_E), 80.6 (C-4_B), 80.0 (C-3_B), 79.3 (C-4_A), 79.0 (C-2_E), 77.8 (C-4_E), 76.5 (C-3_A), 75.6, 75.6, 75.5 (3C, C_{Bn}), 75.0 (C-2_B), 74.9, 74.4, 73.4, 72.5 (4C, C_{Bn}), 70.7 (C-5_E), 68.1 (C-5_B), 68.0 (C-6_E), 67.7 (C-5_A), 67.7 (C_{All}), 67.4 (C-2_A), 18.0, 17.9 (2C, C-6_A, C-6_B); HRMS (ESI$^+$) for $C_{70}H_{78}O_{14}$ ([M + Na]$^+$, 1165.5289) found *m/z* 1165.5283, ([M + NH_4]$^+$, 1160.5735) found *m/z* 1160.5674.

Propyl α-D-Glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (1). Alcohol **12** (260 mg, 209 μmol) was dissolved in EtOH (10 mL) containing 1 M aq HCl (155 μL) and treated with 10% Pd/C catalyst (250 mg), and the suspension was stirred at rt for 1 night, under a hydrogen atmosphere. TLC (*i*PrOH/H_2O/NH_3, 7:1:2) showed the conversion of **12** into a major polar product. The suspension was filtered on Acrodisc LC 25 mm, and the filtrate was concentrated. HPLC purification of the residue (0.01 M aq TFA/CH_3CN, 100:0 → 60:40 over 20 min, 5 mL/min, 215 nm, C-18 Kromasil column), followed by freeze-drying, gave target **1** (83 mg, 77%) as a white powder. Trisaccharide **1** had R_f = 0.5 (*i*PrOH/H_2O/NH_3, 4:1:2); ^{1}H NMR (D_2O) δ 5.09 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1_E), 4.98 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1_A), 4.88 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-1_B), 4.25 (dd, 1H, $J_{2,3}$ = 2.7 Hz, H-2_A), 3.94 (ddd, 1H, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.1 Hz, $J_{4,5}$ = 10.1 Hz, H-5_E), 3.90 (dd, 1H, $J_{2,3}$ = 3.3 Hz, H-2_B), 3.94 (dd_{po}, 1H, $J_{3,4}$ = 9.6 Hz, H-3_A), 3.83 (dd, 1H, $J_{3,4}$ = 9.6 Hz, H-3_B), 3.79−3.72 (m, 4H, H-3_E, H-$6a_E$, H-$6b_E$, H-5_A), 3.69 (dq, 1H, $J_{4,5}$ = 9.6 Hz, H-5_B), 3.63 (dt, 1H, J = 7.0 Hz, J = 9.8 Hz, H_{Pr}), 3.56 (dd_{po}, 1H, $J_{2,3}$ = 9.9 Hz, H-2_E), 3.54 (pt_{po}, $J_{4,5}$ = 9.5 Hz, H-4_A), 3.52 (dt, 1H, J = 6.3 Hz, H_{Pr}), 3.44 (pt, 2H, H-4_E, H-4_B), 1.64−1.57 (m, 2H, CH_2), 1.27 (d, 6H, $J_{5,6}$ = 6.2 Hz, H-6_A, H-6_B), 0.90 (t, 3H, J = 7.4 Hz, CH_3); ^{13}C NMR (D_2O) δ 102.4 (C-1_A, $^1J_{CH}$ = 169.9 Hz), 99.0 (C-1_B, $^1J_{CH}$ = 170.5 Hz), 95.7 (C-1_E, $^1J_{CH}$ = 168.8 Hz), 79.5 (C-2_B), 75.6 (C-3_A), 73.3 (C-3_E), 72.6 (C-4_E*), 72.1 (C-2_E), 71.8 (C-5_E), 70.7 (C-3_B), 70.5 (C-4_A), 70.2(C_{Pr}), 69.9 (C-4_B*), 69.7 (C-5_A), 69.1 (C-5_B), 67.1 (C-2_A), 60.8 (C-6_E), 22.3 (CH_2), 17.2, 17.0 (2C, C-6_A, C-6_B), 10.3 (CH_3). HRMS (ESI$^+$) for $C_{21}H_{38}NO_{14}$ ([M + Na]$^+$, 537.2159) found *m/z* 537.2147.

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-rhamnopyranoside (15). TfOH (4 μL, 45 μmol, 0.3 equiv) was added to a solution of acceptor **12** (163 mg, 143 μmol) and trichloroacetimidate **14**[26,27] (110 mg, 185 μmol, 1.3 equiv) in toluene (5 mL) containing 4Å MS (300 mg), stirred at −40 °C. The reaction mixture was stirred for 1.5 h at this temperature, then for 1 h at rt. More donor **14** (20 mg, 34 μmol, 0.23 equiv) was added, and the reaction mixture was stirred at rt overnight. TLC (Chex/EtOAc, 7:3) showed the complete disappearance of **12** and the presence of a major more polar product. Et_3N was added. The mixture was filtered and concentrated to dryness. Chromatography of the residue (Chex/EtOAc, 100:0 → 70:30) gave the allyl glycoside **15** (196 mg, 87%). Tetrasaccharide **15** had R_f = 0.3 (Chex/EtOAc, 7:3). ^{1}H NMR ($CDCl_3$) δ 7.42−7.05 (m, 36H, NH, CH_{Ph}), 5.87 (m, 1H, CH=), 5.25 ($m_{overlapped}$, 1H, =CH_2), 5.22 ($d_{overlapped}$, 1H, H-1_E), 5.18 (m, 1H, J_{cis} = 10.4 Hz, =CH_2), 5.08 (bs, 1H, H-1_A), 5.02 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4_D), 4.93 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.87 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1_D), 4.82 (dd, $J_{2,3}$= 10.4 Hz, H-3_D), 4.76 ($bs_{overlapped}$, 1H, H-1_B), 4.79−4.54 (m, 11H, H_{Bn}), 4.46 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.30 (d, 1H, J = 12.0

Hz, H_{Bn}), 4.21 (ddd, 1H, 1H, $J_{2,NH}$ = 8.7 Hz, H-2_D), 4.16−4.07 (m, 5H, H-2_A, H-3_A, H-3_E, H_{All}, H-5_E), 3.95−3.87 (m, 5H, H_{All}, H-2_B, H-2_E, H-$6a_D$, H-3_B), 3.85−3.79 (m, 3H, H-4_E, H-5_A*, H-$6b_D$), 3.71 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5_B*), 3.47 (pt, 2H, $J_{3,4} = J_{4,5}$ = 9.3 Hz, H-4_A, H-4_B), 3.44−3.39 (m, 2H, H-$6a_E$, H-$6b_E$), 2.93 (ddd, 1H, $J_{5,6a}$ = 2.7 Hz, $J_{5,6b}$ = 3.4 Hz, H-5_D), 2.03, 2.00, 1.95 (3s, 9H, H_{Ac}), 1.37 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6_A*), 1.33 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_B*); ^{13}C NMR ($CDCl_3$) δ 171.0, 170.8, 169.5 (3C, C_{Ac}), 162.4 (C_{NTCA}), 138.9−137.9 (C_{Ph}), 134.2 (CH=), 128.7−127.7 (CH_{Ph}), 117.5 (=CH_2), 101.4 (C-1_A, $^1J_{CH}$ = 175.8 Hz), 101.0 (C-1_D, $^1J_{CH}$ = 161.1 Hz), 98.2 (C-1_B, $^1J_{CH}$ = 171.0 Hz), 95.0 (C-1_E, $^1J_{CH}$ = 166.9 Hz), 93.1 (CCl_3), 83.8 (C-3_E), 81.0, 80.2 (2C, C-4_B, C-4_A), 79.3, 79.9 (2C, C-2_E, C-3_B), 78.9 (C-4_E), 76.5 (C_{Bn}), 76.0 (C-2_B), 75.7, 75.6, 75.3 (3C, C_{Bn}), 75.0 (C-3_A), 74.5 (C-2_A), 74.2, 73.8 (2C, C_{Bn}), 73.6 (C-3_D), 72.2 (C-5_D), 72.1 (C_{Bn}), 70.3 (C-5_E), 68.9, 68.2 (2C, C-5_A, C-5_B), 68.1 (2C, C-4_D, C-6_E), 68.0 (C_{All}), 61.8 (C-6_D), 56.1 (C-2_D), 21.0, 20.9 (3C, C_{Ac}), 18.4, 18.2 (2C, C-6_B, C-6_A); HRMS (ESI$^+$) for $C_{84}H_{94}Cl_3NO_{22}$ ([M + Na]$^+$, 1598.5234) found *m/z* 1598.5170.

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-rhamnopyranoside (16). Methanolic MeONa (0.5 M, 1.4 mL, 0.75 mmol, 6 equiv) was added to a solution of triacetate **15** (185 mg, 117 μmol) in MeOH (5 mL), and the mixture was stirred at rt for 3 h. TLC (CH_2Cl_2/MeOH, 95:5) showed the presence of a new more polar product. The mixture was neutralized by addition of Dowex X8-200 ion-exchange resin (H^+) and filtered. Volatiles were evaporated. The resulting syrup was chromatographied (Chex/EtOAc, 100:0 → 70:30) to give triol **16** (135 mg, 79%) as a white foam. Tetrasaccharide **16** had R_f = 0.58 (CH_2Cl_2/MeOH, 9:1). ^{1}H NMR ($CDCl_3$) δ 7.52 (d, 1H, $J_{2,NH}$ = 6.0 Hz, NH), 7.43−7.05 (m, 35H, CH_{Ph}), 5.87 (m, 1H, CH=), 5.37 (bs, 1H, H-1_A), 5.26 (m, 1H, J_{trans} = 17.3 Hz, =CH_2), 5.19 (m, 1H, J_{cis} = 10.4 Hz, =CH_2), 5.15 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1_E), 5.10 (d, 1H, J = 11.1 Hz, H_{Bn}), 5.05 (d, 1H, J = 11.1 Hz, H_{Bn}), 5.00 (d, 1H, J = 12.2 Hz, H_{Bn}), 4.92 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.90 (d, 1H, J = 12.3 Hz, H_{Bn}), 4.79 (d, 1H, J = 10.9 Hz, H_{Bn}), 4.73−4.59 (m, 5H, H_{Bn}), 4.76 ($bs_{overlapped}$, 1H, H-1_B), 4.54 ($d_{overlapped}$, 1H, $J_{1,2}$ = 8.3 Hz, H-1_D), 4.53 ($d_{overlapped}$, 1H, J = 10.2 Hz, H_{Bn}), 4.49 (d, 1H, J = 10.9 Hz, H_{Bn}), 4.35 (d, 1H, J = 11.9 Hz, H_{Bn}), 4.17 (dd, 1H, $J_{1,2}$ = 1.9 Hz, H-2_B), 4.15−4.07 (m, 5H, H_{All}, H-3_E, H-2_A, H-3_A, H-5_E), 3.93 (m_{po}, 1H, H_{All}), 3.91 (dd_{po}, 1H, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.5 Hz, H-3_B), 3.83 (dd_{po}, 1H, $J_{3,4}$ = 2.9 Hz, $J_{4,5}$ = 9.5 Hz, H-4_E), 3.81 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2_E), 3.76−3.67 (m, 3H, H-2_D, H-5_A, H-5_B), 3.59 (dd, 1H, $J_{6a,6}$ = 12.2 Hz, $J_{5,6a}$ = 2.9 Hz, H-$6a_D$), 3.51−3.44 (m, 4H, H-4_A, H-4_B, H-$6a_E$, H-$6b_E$), 3.11 (dd, 1H, H-4_D), 3.05 (m, 1H, $J_{4,5}$ = 9.8 Hz, H-5_D), 2.88 (dd, 1H, $J_{5,6}$ = 7.7 Hz, H-$6b_D$), 2.37 (dd, 1H, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 8.3 Hz, H-3_D), 1.44 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A*), 1.36 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_B*); ^{13}C NMR ($CDCl_3$) δ 164.9 (C_{NTCA}), 139.0−137.6 (C_{Ph}), 137.6 (CH=), 129.5−128.1 (CH_{Ph}), 111.5 (=CH_2), 101.2 (C-1_D), 100.4 (C-1_A), 98.5 (C-1_B), 94.6 (C-1_E), 92.9 (CCl_3), 83.6 (C-3_E), 80.9 (C-3_B), 80.8 (C-4_B), 80.1 (C-4_A), 79.5 (C-2_E), 79.0 (C-4_E), 76.7 (C_{Bn}), 76.7 (C-3_D), 76.0 (C-5_D), 75.6, 75.4, 75.3 (4C, C_{Bn}), 74.5 (C-2_A), 74.3 (C-3_A), 73.9, 73.3 (2C, C_{Bn}), 73.0 (C-4_D), 71.7 (C-2_B), 70.4 (C-5_E), 69.0, 68.7 (C-5_A, C-5_B), 68.1 (C-6_E), 68.0 (C_{All}), 62.8 (C-6_D), 58.3 (C-2_D), 18.3, 18.2 (2C, C-6_B, C-6_A). HRMS (ESI$^+$) for $C_{78}H_{88}Cl_3NO_{19}$ ([M + Na]$^+$, 1472.4913) found *m/z* 1472.4921.

Propyl (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-[α-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (2). Route a. Triol **16** (108 mg, 75 μmol) was dissolved in EtOH (10 mL) containing 1 M aq HCl (110 μL) and treated with 10% Pd/C catalyst (108 mg), and the suspension was stirred at rt for 1 night, under a hydrogen atmosphere. TLC (*i*PrOH/H_2O/NH_3, 7:1:2) showed the conversion of **12** into a more polar product. The suspension was filtered on a pad of Celite, and the filtrate was concentrated under vacuum. The residue was dissolved in EtOH (10 mL) containing Et_3N (100 μL) and treated with 10% Pd/C catalyst (100 mg), and the suspension was stirred at rt for 1 night, under a hydrogen atmosphere. TLC (*i*PrOH/H_2O/NH_3, 7:1:2) showed reaction completion. The suspension was filtered on a pad of Celite, and the filtrate was concentrated under vacuum. RP-HPLC purification of the residue (0.01 M aq TFA/CH_3CN, 100:0 → 60:40 over 20 min, 5 mL min^{-1}, 215 nm, C-18 Kromasil column), followed by freeze-drying, gave target **2** (36 mg, 68%) as a white powder.

Route b. A 2% TfOH solution in toluene (100 μL, 23 μmol, 0.35 equiv) was added to a solution of acceptor **12** (82 mg, 66 μmol) and trichloroacetimidate **14** (82 mg, 135 μmol, 2.0 equiv) in toluene (2 mL) containing 4Å MS (200 mg), stirred at −30 °C. The reaction mixture was stirred for 1 h at this temperature and then for 1 h at rt. More donor **14** (10 mg, 17 μmol, 0.25 equiv) was added, and the reaction mixture was stirred for 3 h while slowly coming back to rt. Et_3N was added. The mixture was filtered and concentrated to dryness. Chromatography of the residue (Chex/EtOAc, 100:0 → 70:30) gave contaminated **15** (90 mg). The whole material was solubilized in CH_2Cl_2 (1 mL) and 0.5 M methanolic sodium methoxide was added (500 μL). The reaction mixture was stirred for 3 h at rt. TLC (CH_2Cl_2/MeOH, 9:1) showed the presence of a more polar product that reacted with ninhydrin. The mixture was neutralized by addition of Dowex X8-200 ion-exchange resin (H^+) and filtered. Volatiles were evaporated. The residue was taken in ethanol (2 mL), and acetic anhydride (1 mL) was added. After 2 h at rt, volatiles were evaporated and coevaporated with toluene. The crude material was chromatographied (CH_2Cl_2/MeOH, 95:5) to give the acetamidotriol **17** (54 mg, 56% from **12**). The latter was dissolved in EtOH (5 mL) containing 1 M aq HCl (110 μL) and treated with 10% Pd/C catalyst (50 mg), and the suspension was stirred at rt for 1 night, under a hydrogen atmosphere. TLC (*i*PrOH/H_2O/NH_3, 7:1:2) showed the conversion of **17** into a more polar product. The suspension was filtered on a pad of Celite, and the filtrate was concentrated under vacuum. The residue was purified as above to give target **2** as a white powder (19 mg, 40% from **12**). Tetrasaccharide **2** had R_f = 0.32 (*i*PrOH/H_2O/NH_3, 4:1:2); HPLC (215 nm): t_R = 14.2 min (Kromasil 5 μm C18 100Å 4.6 × 250 mm analytical column, using a 0−35% linear gradient over 20 min of CH_3CN in 0.01 M aq TFA at 1 mL min^{-1} flow rate); ^{1}H NMR (D_2O) δ 5.15 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1_E), 5.07 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1_A), 4.86 (d, 1H, $J_{1,2}$ = 1.3 Hz, H-1_B), 4.79 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1_D), 4.40 (dd, 1H, $J_{2,3}$ = 2.3 Hz, H-2_A), 4.02 (ddd, 1H, $J_{4,5}$ = 10.1 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.4 Hz, H-5_E), 3.92−3.85 (m, 3H, H-2_B, H-$6a_D$, H-3_A), 3.84−3.66 (m, 9H, H-3_B, H-$6a_E$, H-3_E, H-$6b_E$, H-$6b_D$, H-5_A, H-2_D, H-5_B, H-2_E), 3.61 (dt, 1H, J = 6.9 Hz, J = 9.8 Hz, H_{Pr}), 3.50−3.39 (m, 6H, H-4_E, H_{Pr}, H-3_D, H-4_B, H-5_D, H-4_D), 3.34 (pt, 1H, $J_{3,4} = J_{4,5}$ = 9.7 Hz, H-4_A), 2.07 (s, 3H, H_{NAc}), 1.61−1.54 (m, 2H, CH_2), 1.26 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6_A*), 1.12 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6_B*), 0.80 (t, 3H, J = 7.4 Hz, CH_3). ^{13}C NMR (D_2O) δ 174.9 (C_{NAc}), 102.3 (C-1_D, $^1J_{CH}$ = 157.0 Hz), 101.7 (C-1_B, $^1J_{CH}$ = 173.2 Hz), 98.6 (C-1_A, $^1J_{CH}$ = 170.6 Hz), 95.0 (C-1_E, $^1J_{CH}$ = 167.0 Hz), 79.5 (C-2_B), 76.4, 74.6 (2C, C-4_D, C-4_B), 74.4 (C-2_A), 74.1 (C-3_A), 73.5 (C-3_E), 72.6 (C-3_D), 71.8 (C-5_E), 71.7 (C-2_E), 71.2 (C-4_A), 70.4 (C-3_B), 70.2 (C-5_D), 70.0 (C_{Pr}), 69.9 (2C, C-4_E, C-5_A), 69.1 (C-5_B), 61.0 (C-6_D), 60.8 (C-6_E), 56.0 (C-2_D), 23.0 (C_{NAc}), 22.3 (CH_2), 17.2, 17.0 (2C, C-6_A, C-6_B), 10.2 (CH_3). HRMS (ESI$^+$) for $C_{29}H_{51}NO_{19}$ ([M + H]$^+$, 718.3134) found *m/z* 718.3198 ([M + Na]$^+$, 740.2953) found *m/z* 740.3021.

Allyl (3-*O*-Acetyl-2-deoxy-4,6-*O*-isopropylidene-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-rhamnopyranoside (19). TMSOTf (69 μL, 380 μmol, 0.3 equiv) was added to a solution of acceptor **12** (1.5 g, 1.3 mmol) and trichloroacetimidate **18**[27] (1.2 g, 2.2 mmol 1.7 equiv) in toluene (30 mL) containing 4Å MS (1.1 g), stirred at −40 °C. The reaction mixture was stirred for 1 h while slowly coming back to rt. TLC (Tol/EtOAc, 85:15) showed the complete disappearance of **12** 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 → 1:1) gave **19** (1.9 g, 95%) as a white foam. Tetrasaccharide **19** had R_f = 0.45 (Tol/EtOAc, 85:15); ^{1}H NMR ($CDCl_3$) δ 7.54−7.09 (m, 36H, NH, CH_{Ph}), 5.91 (m, 1H, CH=), 5.30 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.23 (m, 1H, J_{cis} = 10.5 Hz, =CH_2), 5.23−5.19 (m, 3H, H-1$_E$, H_{Bn}), 5.15 (bs, 1H, H-1$_A$), 5.11 (d, 1H, J = 10.9 Hz, H_{Bn}), 5.08 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.96 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.88−4.84 (m, 2H, $J_{1,2}$ = 8.5 Hz, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz, H-1$_D$, H-3$_D$), 4.83 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.81 (bs, 1H, H-1$_B$), 4.79 (d, 1H, J = 10.3 Hz, H_{Bn}), 4.74 (d, 1H, J = 11.8 Hz, H_{Bn}), 4.69 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.68 (d, 1H, J = 11.8 Hz, H_{Bn}), 4.52 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.36 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.25−4.12 (m, 6H, H-2$_D$, H-3$_E$, H-2$_A$, H-3$_A$, H_{All}, H-5$_E$), 4.03 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 2.8 Hz, H-2$_B$), 4.01−3.92 (m, 3H, H_{All}, H-2$_E$, H-3$_B$), 3.88−3.80 (m, 2H, H-4$_E$, H-5$_A$), 3.75 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5$_B$), 3.68 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4$_D$), 3.57−3.46 (m, 5H, H-6a$_D$, H-4$_A$, H-4$_B$, H-6a$_E$, H-6b$_E$), 3.43 (pt, 1H, $J_{5,6a}$ = $J_{6a,6b}$ = 10.4 Hz, H-6b$_D$), 2.83 (ddd, 1H, $J_{5,6b}$ = 5.3 Hz, H-5$_D$), 2.11 (s, 3H, H_{Ac}), 1.49 (s, 3H, H_{iPr}), 1.44 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_A$), 1.41 (s, 3H, H_{iPr}), 1.36 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_B$); ^{13}C NMR ($CDCl_3$) δ 170.8 (C_{Ac}), 162.2 (C_{NTCA}), 138.6−137.6 (C_{Ph}), 133.9 (CH=), 129.1−127.4 (CH_{Ph}), 117.2 (=CH_2), 101.4 (C-1$_D$, $^1J_{CH}$ = 164.1 Hz), 101.0 (C-1$_A$, $^1J_{CH}$ = 172.5 Hz), 99.7 (C_{iPr}), 97.9 (C-1$_B$, $^1J_{CH}$ = 167.9 Hz), 94.6 (C-1$_E$, $^1J_{CH}$ = 167.1 Hz), 92.8 (CCl_3), 83.5 (C-3$_E$), 80.5 (C-4$_B$), 79.8 (C-4$_A$), 79.6 (C-3$_B$), 78.6 (C-4$_E$), 78.2 (C-2$_E$), 76.2, 75.3, 75.2, 75.0 (4C, C_{Bn}), 74.9 (C-2$_B$), 74.4 (C-3$_A$), 74.0 (C_{Bn}), 73.9 (C-2$_A$), 73.5 (C_{Bn}), 72.6 (C-3$_D$), 72.2 (C_{Bn}), 71.3 (C-4$_D$), 70.0 (C-5$_E$), 68.7 (C-5$_A$), 68.0 (C-5$_B$), 67.9 (C-6$_E$), 67.7 (C_{All}), 67.4 (C-5$_D$), 61.8 (C-6$_D$), 56.6 (C-2$_D$), 29.0 (C_{iPr}), 20.9 (C_{Ac}), 19.1 (C_{iPr}), 18.0 (C-6$_B$), 17.9 (C-6$_A$); HRMS (ESI$^+$) for $C_{83}H_{94}Cl_3NO_{20}$ ([M + Na]$^+$, 1552.5332) found *m*/*z* 1552.5430, ([M + NH_4]$^+$, 1547.5779) found *m*/*z* 1547.5880

Allyl (2-Acetamido-2-deoxy-4,6-*O*-isopropylidene-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-rhamnopyranoside (21). Methanolic MeONa (0.5 M, 5.7 mL, 2.8 mmol, 6.9 equiv) was added to a solution of fully protected tetrasaccharide **19** (630 mg, 412 μmol) in CH_2Cl_2 (45 mL), and the mixture was stirred for 6.5 h. TLC (CH_2Cl_2/MeOH, 98:2 and Tol/EtOAc, 85:15) showed the complete disappearance of the monoacetate and the presence of a single more polar product which reacted with ninhydrin, thus corresponding to intermediate **24** (MS (ESI$^+$) of $C_{79}H_{93}NO_{18}$ ([M + H]$^+$, 1344.6) found *m*/*z* 1344.7). MeOH (91 mL) and acetic anhydride (400 μL) were added. After 2 h at rt, TLC (Tol/EtOAc, 85:15) showed the complete disappearance of **24**. Evaporation of the filtrate gave a syrup which was purified by chromatography (Tol/EtOAc, 6:4 → 4:6) to give compound **21** (470 mg, 83%) as a white foam. Tetrasaccharide **21** had R_f = 0.35 (Tol/EtOAc, 6:4); ^{1}H NMR ($CDCl_3$) δ 7.43−7.07 (m, 36H, NH, CH_{Ph}), 5.89 (m, 1H, CH=), 5.27 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.20 (m, 1H, J_{cis} = 11.7 Hz, =CH_2), 5.18 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1$_E$), 5.12 ($bs_{overlapped}$, 1H, H-1$_A$), 5.11 (d_{po}, 1H, H_{Bn}), 5.01 (d, 1H, J = 11.8 Hz, H_{Bn}), 4.95 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.91 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.89 (d, 1H, J = 11.7 Hz, H_{Bn}), 4.82 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.80 (d, 1H, J = 9.9 Hz, H_{Bn}), 4.77 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1$_B$), 4.71 (d, 1H, J = 11.9 Hz, H_{Bn}), 4.66−4.63 (m, 3H, H_{Bn}), 4.60 (d, 1H, J = 10.1 Hz, H_{Bn}), 4.55 (d, 1H, J = 10.9 Hz, H_{Bn}), 4.40−4.35 (m, 2H, H_{Bn}, H-1$_D$), 4.19−4.11 (m, 4H, H-3$_A$, H-5$_E$, H_{All}, H-3$_E$), 4.06 (dd, 1H, $J_{1,2}$ = 2.1 Hz, $J_{2,3}$ = 2.4 Hz, H-2$_A$), 4.02 (dd, 1H, $J_{2,3}$ = 2.9 Hz, H-2$_B$), 3.95−3.79 (m, 6H, H_{All}, H-4$_E$, H-3$_B$, H-2$_E$, H-2$_D$, H-5$_A$), 3.73 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5$_B$), 3.59−3.46 (m, 7H, H-6a$_D$, H-6b$_D$, H-6a$_E$, H-6b$_E$, H-4$_D$, H-4$_A$, H-4$_B$), 2.83 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = 5.7 Hz, $J_{5,6b}$ = 9.8 Hz, H-5$_D$), 2.78 (pt, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3$_D$), 2.40 (s, 3H, H_{NAc}), 1.50 (s, 3H, H_{iPr}), 1.48 (s, 3H, H_{iPr}), 1.40 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_A$), 1.35 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_B$); ^{13}C NMR ($CDCl_3$) δ 172.9 (C_{NAc}), 138.5−137.1 (C_{Ph}), 133.8 (CH=), 129.2−127.4 (CH_{Ph}), 117.2 (=CH_2), 102.4 (C-1$_D$, $^1J_{CH}$ = 162.8 Hz), 101.0 (C-1$_A$, $^1J_{CH}$ = 177.5 Hz), 99.6 (C_{iPr}), 97.8 (C-1$_B$, $^1J_{CH}$ = 169.0 Hz), 94.1 (C-1$_E$, $^1J_{CH}$ = 167.0 Hz), 83.3 (C-3$_E$), 80.5 (C-4$_B$), 80.0 (C-4$_A$), 79.4 (C-2$_E$), 79.2 (C-3$_B$), 78.7 (C-4$_E$), 76.3 (C_{Bn}), 75.9 (C-2$_A$), 75.7 (C_{Bn}), 75.5 (C-2$_B$), 75.4 75.3, 75.0 (3C, C_{Bn}), 74.2 (C-3$_A$), 74.1 (C-4$_D$), 74.0 (C-3$_D$), 73.5, 72.0 (2C, C_{Bn}), 70.1 (C-5$_E$), 68.8 (C-5$_A$), 67.9 (2C, C-5$_B$, C-6$_E$), 67.7 (C_{All}), 66.9 (C-5$_D$), 61.7 (C-6$_D$), 58.5 (C-2$_D$), 29.1 (C_{iPr}), 23.2 (C_{NAc}), 19.0 (C_{iPr}), 18.1 (C-6$_B$), 17.7 (C-6$_A$); HRMS (ESI$^+$) of $C_{81}H_{95}NO_{19}$ ([M + H]$^+$, 1386.6577) found *m*/*z* 1386.6625, ([M + Na]$^+$, 1408.6396) found *m*/*z* 1408.6478.

Allyl (2-*O*-Acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-2-deoxy-4,6-*O*-isopropylidene-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-rhamnopyranoside (25). TfOH (2 μL, 23 μmol, 0.3 equiv) was added to a solution of acceptor **21** (128 mg, 94 μmol) and trichloroacetimidate **22**[33] (97 mg, 188 μmol, 2 equiv) in toluene (1.5 mL) containing 4Å MS (200 mg), stirred at −40 °C. The reaction mixture was stirred for 1 h at this temperature, then for 2 h at rt. TLC (CH_2Cl_2/MeOH, 97.5:2.5) showed the presence of a major less polar product together with traces of **21**. Et_3N (200 μL) was added. The mixture was filtered, and concentrated to dryness. Chromatography of the residue (Chex/EtOAc, 100:0 → 50:50) gave the allyl glycoside **25** (116 mg, 71%) as a white solid. Pentasaccharide **25** had R_f = 0.58 (CH_2Cl_2/MeOH, 98.5:2.5); ^{1}H NMR ($CDCl_3$) δ 7.44−7.06 (m, 45H, CH_{Ph}), 6.40 (d, 1H, $J_{1,2}$ = 8.9 Hz, NH), 5.85 (m, 1H, CH=), 5.24 (d, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.17 (m, 2H, H-1$_E$, =CH_2), 5.13 (dd, 1H, $J_{1,2}$ = 2.2 Hz, $J_{2,3}$ = 3.0 Hz, H-2$_C$), 5.07−5.04 (m, 2H, H_{Bn}, H-1$_A$), 5.01−4.97 (m, 5H, H_{Bn}), 4.81 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.76 (d, 1H, J = 10.1 Hz, H_{Bn}), 4.72 (bs, 1H, H-1$_B$), 4.69−4.55 (m, 9H, H-1$_C$, H_{Bn}), 4.48 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.33 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.27 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1$_D$), 4.19−4.08 (m, 5H, H-3$_E$, H-5$_E$, H-2$_D$, H-3$_A$, H_{All}), 3.98−3.87 (m, 8H, H-2$_A$, H-3$_C$, H-5$_C$, H-2$_B$, H_{All}, H-3$_B$, H-2$_E$, H-4$_E$), 3.75 (dq, 1H, $J_{4,5}$ = 9.3 Hz, $J_{5,6}$ = 6.6 Hz, H-5$_A$), 3.69 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.1 Hz, H-5$_B$), 3.52−3.41 (m, 8H, H-6a$_D$, H-6b$_D$, H-6a$_E$, H-6b$_E$, H-4$_A$, H-4$_B$, H-4$_D$, H-4$_C$), 2.74 (dt, 1H, $J_{5,6a}$ = 5.3 Hz, $J_{4,5}$ = $J_{5,6b}$ = 9.8 Hz, H-5$_D$), 2.62 (pt, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz, H-3$_D$), 2.28 (s, 3H, H_{Ac}), 2.08 (s, 3H, H_{NAc}), 1.39 (s, 6H, H_{iPr}), 1.33−1.30 (m, 6H, H-6$_A$, H-6$_B$), 1.24 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6$_C$). ^{13}C NMR ($CDCl_3$) δ 170.9 (C_{Ac}), 170.5 (C_{NAc}), 139.2−18.7 (C_{Ph}), 134.2 (CH=), 129.7−127.8 (CH_{Ph}), 117.6 (=CH_2), 103.8 (C-1$_D$), 101.5 (C-1$_A$, $^1J_{CH}$ = 172.8 Hz), 99.6 (C_{iPr}), 98.8 (C-1$_B$, $^1J_{CH}$ = 172.9 Hz),), 98.2 (C-1$_C$), 94.4 (C-1$_E$), 83.7 (C-3$_E$), 80.8−78.9 (7C, C-3$_D$, C-4$_B$, C-2$_E$, C-4$_C$, C-4$_A$, C-3$_B$, C-4$_E$), 78.1 (C-3$_C$), 76.6 (C_{Bn}), 76.4 (C-2$_A$), 75.6 (C-2$_B$), 76.0−75.4 (5C, C_{Bn}), 74.6 (C-3$_A$), 73.9 (C_{Bn}), 72.4 (C-4$_D$), 72.3, 71.8 (2C, C_{Bn}), 70.3 (2C, C-2$_C$, C-5$_E$), 69.2 (C-5$_A$), 68.2 (C-5$_B$), 68.0 (2C, C-6$_E$, C_{All}), 67.8 (C-5$_C$), 67.5 (C-5$_D$), 62.3 (C-6$_D$), 55.7 (C-2$_D$), 29.5 (C_{iPr}), 24.4 (C_{NAc}), 21.5 (C_{Ac}), 19.5 (C_{iPr}), 18.4, 18.3, 18.0 (3C, C-6$_A$, C-6$_B$, C-6$_C$); HRMS (ESI$^+$) for $C_{103}H_{119}NO_{24}$ ([M + H]$^+$, 1754.8201) found *m*/*z* 1755.8307.

Propyl (2-*O*-Acetyl-α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-[α-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (3). TFA (2 mL 50% aq) was added, at 0 °C, to a solution of pentasaccharide **25** (105 mg, 84 μmol) in CH_2Cl_2 (2 mL) at 0 °C, and the biphasic mixture was stirred vigorously at this temperature for 1 h. TLC (CH_2Cl_2/MeOH, 95:5) showed the complete disappearance of **25** and the presence of a major more polar product. Repeated coevaporation with toluene provided crude diol **26** (103 mg). Checking the ^{1}H NMR spectrum ensured the complete disappearance of the isopropylidene signals. The crude material was directly engaged in the next step. Crude diol **26** (102 mg, 60 μmol) was dissolved in EtOH (4 mL), treated with 10% Pd/C catalyst (100 mg), and the suspension was stirred at rt for 6 h, under a hydrogen atmosphere. TLC (*i*PrOH/H_2O/NH_3, 7:1:2) showed that the starting material had been transformed into a major polar product. The suspension was filtered on a pad of Celite, and the filtrate was concentrated. HPLC purification (t_R = 14.6 min, C-18 Kromasil column, 0.01 M aq TFA/CH_3CN, 100:0 → 70:30 over 20 min, 5.5 mL min^{-1}, 215 nm) of the residue, followed by freeze-drying, gave the target pentasaccharide **3** (36 mg, 67%) as a white

foam. Pentasaccharide **3** was isolated as a mixture of regioisomers resulting from the migration of the acetyl group. Pentasaccharide **3** had R_f = 0.5 (*i*PrOH/H_2O/NH_3, 7:1:2); HPLC (215 nm): t_R = 14.7 min (52.3%), 15.4 min (29.4%), 15.9 min (16.9%) (Kromasil 5 μm C-18 100Å 4.6 × 250 mm analytical column, using a 0−35% linear gradient over 20 min of CH_3CN in 0.01 M aq TFA at 1 mL min^{-1} flow rate); ^{1}H NMR (D_2O, selected signals) δ 5.18 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1_E), 5.08 (bs, 1H, H-1_A), 4.93 (dd, 0.3H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 10.0 Hz, H-3_C), 4.90−4.87 (m, 3H, H-1_C, H-2_C, H-1_B), 4.84−4.79 (m, 1H, $J_{1,2}$ = 8.7 Hz, H-1_D), 4.42 (bs, 1H, H-2_A), 4.15−4.00 (m, 2H, H-5_C, H-5_E), 3.94−3.90 (m, 4H, H-3_C, H-3_A, H-2_B, H-6a_D), 3.87−3.58 (m, 11H, H-2_D, H-3_E, H-3_B, H-6a_E, H-6b_E, H-5_A, H-6b_D, H-5_B, H-2_E, H-4_C, H_{Pr}), 3.53−3.38 (m, 7H, H-4_D, H-4_E, H_{Pr}, H-4_C, H-4_B, H-3_D, H-5_D), 3.34 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4_A), 2.14, 2.13 (s, 3H, H_{NAc}), 2.10, 2.07 (s, 3H, H_{Ac}), 1.64−1.55 (m, 2H, CH_2), 1.27 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_B$), 1.25−1.20 (m, 5H, H-6$_A$, H-6$_C$), 1.10 (d, 1H, $J_{5,6}$ = 6.2 Hz, H-6$_C$), 0.89 (t, 3H, J = 7.9 Hz, CH_3). ^{13}C NMR (D_2O, selected signals) δ 173.3 (C_{NAc}), 101.5 (C-1_D, $^1J_{CH}$ = 164.0 Hz), 101.2 (C-1_A, $^1J_{CH}$ = 172.8 Hz), 98.5, 98.2 (2C, C-1_B, $^1J_{CH}$ = 172.9 Hz, C-1_C, $^1J_{CH}$ = 169.8 Hz), 94.3 (C-1_E), 82.3 (C-3_D), 79.1 (C-2_B), 76.1 (C-5_D), 74.3 (C-2_A), 73.6−73.0 (2C, C-3_A, C-3_E), 72.2 (2C, C-2_C, C-4_B), 71.5, 71.4 (2C, C-2_E, C-5_E), 70.8 (C-4_A), 69.3 (C-3_B), 69.8 (C_{Pr}), 69.6, 69.5 (3C, C-4_C, C-4_E, C-5_A), 68.9−68.3 (4C, C-3_C, C-5_B, C-5_C, C-4_D), 60.7 (C-6_D), 60.4 (C-6_E), 55.5 (C-2_D), 22.8, 22.5 (C_{NAc}), 21.9 (CH_2), 20.4, 20.9 (C_{Ac}), 16.8, 16.6, 16.5, 16.4 (3C, C-6_A, C-6_B, C-6_C), 9.8 (CH_3); HRMS (ESI$^+$) for $C_{37}H_{63}NO_{24}$ ([M + Na]$^+$, 928.3638) found *m/z* 928.3660.

Propyl α-L-Rhamnopyranosyl-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-[α-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (4). A mixture of regioisomers **3** (10 mg, 60 μmol) was dissolved in water (1 mL) and methanolic sodium methoxide (0.5 M, 100 μL) was added. The reaction mixture was stirred for 3 h at rt. Following RP-HPLC control (C18 Kromasil column, 4.6 × 150, CH_3CN/0.01 M aq TFA 0 → 30% over 20 min, 215 nm), the reaction mixture was purified by preparative RP-HPLC (C18 Kromasil column, 10 × 250) using the same elution system. Freeze-drying gave the target pentasaccharide **4** (6 mg, 63%) as a white foam. Pentasaccharide **4** had HPLC (215 nm): t_R = 14.6 min (Kromasil 5 μm C-18 100Å 4.6 × 250 mm analytical column, using a 0−40% linear gradient over 20 min of CH_3CN in 0.01 M aq TFA at 1 mL min^{-1} flow rate); ^{1}H NMR (D_2O) δ 5.18 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1_E), 5.08 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1_A), 4.88 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-1_B), 4.85 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1_C), 4.82 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1_D), 4.25 (dd, 1H, $J_{2,3}$ = 2.2 Hz, H-2_A), 4.03 (ddd, 1H, $J_{4,5}$ = 10.1 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.4 Hz, H-5_E), 3.96 (dq, 1H, $J_{4,5}$ = 9.7 Hz, H-5_C), 3.94−3.90 (m, 2H, H-3_A, H-2_B), 3.89 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6a}$ = 1.8 Hz, H-6a_D), 3.85−3.76 (m, 5H, H-3_B, H-2_D, H-3_E, H-6a_E, H-2_C), 3.75−3.69 (m, 6H, H-6b_E, H-5_A, H-6b_D, H-3_C, H-2_E, H-5_B), 3.62 (dt, 1H, J = 7.0 Hz, J = 9.8 Hz, H_{Pr}), 3.51−3.41 (m, 6H, H_{Pr}, H-4_D, H-4_E, H-3_D, H-4_B, H-5_D), 3.40 (pt, 1H, $J_{3,4}$ = 9.7 Hz, H-4_C), 3.35 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4_A), 2.10 (s, 3H, H_{NAc}), 1.62−1.54 (m, 2H, CH_2), 1.27 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_B$), 1.24 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6$_A$), 1.21 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6$_C$), 0.89 (t, 3H, J = 7.4 Hz, CH_3). ^{13}C NMR (D_2O) δ 174.2 (C_{NAc}), 101.4 (C-1_D), 101.3 (C-1_C), 101.2 (C-1_A), 98.2 (C-1_B, $^1J_{CH}$ = 171.8 Hz), 94.4 (C-1_E, $^1J_{CH}$ = 171.8 Hz), 81.4 (C-3_D), 79.1 (C-2_B), 76.1 (C-5_D), 74.3 (C-2_A), 73.5 (C-3_A), 73.2 (C-3_E), 72.2 (C-4_B), 71.9 (C-4_C), 71.5, 71.4 (2C, C-2_E, C-5_E), 70.8 (C-2_C), 70.7 (C-4_A), 70.2 (C-3_C), 70.0 (C-3_B), 69.8 (C_{Pr}), 69.5 (2C, C-5_A, C-4_E), 69.0 (C-5_C), 68.7 (C-5_B), 68.4 (C-4_D), 60.7 (C-6_D), 60.4 (C-6_E), 55.6 (C-2_D), 22.5 (C_{NAc}), 21.9 (CH_2), 16.8 (C-6_A), 16.6 (C-6_B), 16.5 (C-6_C), 9.8 (CH_3); HRMS (ESI$^+$) for $C_{35}H_{61}NO_{23}$ ([M + H]$^+$, 864.3713) found *m/z* 864.3704, ([M + Na]$^+$, 886.3532) found *m/z* 886.3489.

Allyl (2-Deoxy-4,6-*O*-isopropylidene-3-*O*-levulinoyl-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (28). DCC (532 mg, 2.6 mmol, 1.5 equiv) and levulinic acid (317 μL, 3.0 mmol, 1.8 equiv) dissolved in CH_2Cl_2 (15 mL) was added to a solution of alcohol **27**[15] (2.0 g, 1.7 mmol) and DMAP (420 mg, 3.4 mmol, 2 equiv) in CH_2Cl_2 (15 mL). The mixture was stirred for 1 h at rt. TLC (Tol/EtOAc, 7:3) showed the complete disappearance of the starting material and the presence of one less polar product. DCU was filtered and the reaction mixture was diluted with CH_2Cl_2, then washed with water, saturated aq $NaHCO_3$ (3 × 20 mL), brine (3 × 20 mL), and water (3 × 20 mL). The organic layer was dried on Na_2SO_4, filtered, and concentrated under reduced pressure. Chromatography of the residue (Tol/EtOAc, 85:15 → 80:20) gave levulinate **28** (1.9 g, 90%) as a colorless syrup. Compound **28** had R_f = 0.5 (Tol/EtOAc, 7:3); ^{1}H NMR ($CDCl_3$) δ 7.47−7.05 (m, 26H, NH, CH_{Ph}), 5.94 (m, 1H, CH=), 5.29 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.21 (m, 1H, J_{cis} = 10.4 Hz, =CH_2), 5.15−5.09 (m, 3H, H-1_E, H_{Bn}), 5.07 (s, 2H, H_{Bn}), 4.80−4.69 (m, 5H, H-1_A, H_{Bn}, H-3_D, H_{Bn}, H-1_D), 4.59−4.54 (m, 2H, H_{Bn}), 4.90 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.32 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.18−4.07 (m, 5H, H_{All}, H-2_D, H-3_E, H-3_A), 4.08 (ddd, 1H, $J_{4,5}$ = 10.2 Hz, H-5_E), 3.99 (dd$_{po}$, 1H, $J_{1,2}$ = 2.3 Hz, H-2_A), 3.94 (m$_{po}$, 1H, H_{All}), 3.90 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.7 Hz, H-2_E), 3.85 (dd, 1H, $J_{5,6a}$ = 5.4 Hz, $J_{6a,6b}$ = 10.7 Hz, H-6a_D), 3.79 (dd, 1H, $J_{3,4}$ = 9.0 Hz, H-4_E), 3.74−3.69 (m, 2H, H-6b_D, H-5_A), 3.67 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4_D), 3.45 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4_A), 3.45−3.39 (m, 2H, H-6a_E, H-6b_E), 2.76−2.63 (m, 5H, H-5_D, 4H_{Lev}), 2.20 (s, 3H, CH_{3Lev}), 1.47 (s, 3H, H_{iPr}), 1.42 (s, 3H, H_{iPr}), 1.39 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6$_A$); ^{13}C NMR ($CDCl_3$) δ 206.4 (C_{Lev}), 172.6 (C_{Lev}), 162.5 (C_{NTCA}), 139.0−138.5 (C_{Ph}), 134.2 (CH=), 129.6−127.7 (CH_{Ph}), 117.6 (=CH_2), 101.8 (C-1_D, $^1J_{CH}$ = 163.0 Hz), 100.1 (C_{iPr}), 98.7 (C-1_A, $^1J_{CH}$ = 171.6 Hz), 95.1 (C-1_E, $^1J_{CH}$ = 165.2 Hz), 93.2 (CCl_3), 83.8 (C-3_E), 80.2 (C-4_A), 79.3 (C-2_E), 79.1 (C-4_E), 76.4, 75.5, 75.3 (3C, C_{Bn}), 75.0 (C-3_A), 74.7 (C_{Bn}), 74.6 (C-2_A), 73.8 (C_{Bn}), 73.3 (C-3_D), 71.6 (C-4_D), 70.3 (C-5_E), 68.7 (C-5_A), 68.3, 68.2 (2C, C_{All}, C-6_E), 67.5 (C-5_D), 62.4 (C-6_D), 56.9 (C-2_D), 38.4 (CH_{2Lev}), 30.2 (CH_{3Lev}), 29.4 (C_{iPr}), 28.5 (CH_{2Lev}), 19.3 (C_{iPr}), 18.3 (C-6_A); HRMS (ESI$^+$) for $C_{66}H_{76}Cl_3NO_{17}$ ([M + Na]$^+$, 1282.4076) found *m/z* 1282.4189, ([M + NH_4]$^+$, 1277.4523) found *m/z* 1277.4634.

(2-Deoxy-4,6-*O*-isopropylidene-3-*O*-levulinoyl-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α/β-L-rhamnopyranose (29). 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)-iridium hexafluorophosphate (30 mg) was dissolved in THF (11 mL) and the resulting red solution was degassed under an argon stream. Hydrogen was bubbled through the solution, causing the color to change to yellow. The solution was then degassed again under an argon stream. A solution of allyl glycoside **28** (1.8 g, 1.5 mmol) in THF (15 mL) was added. The mixture was stirred overnight at rt. TLC (Tol/EtOAc, 8:2) showed the complete disappearance of **28** and the presence of a single less polar product. The mixture was treated with a solution of iodine (740 mg, 2.9 mmol) in THF/water (10 mL, 4:1 v/v) for 1 h at rt. TLC (Tol/EtOAc, 8:2 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 adding a solution of freshly prepared 5% aq sodium bisulphite (4 mL). CH_2Cl_2 (50 mL) was added, and the organic phase was washed with brine (3 × 30 mL), water (3 × 30 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (CH_2Cl_2/MeOH, 99:1 → 90:10) gave **29** (1.4 g, 80%) as a yellow syrup. Hemiacetal **29** had R_f = 0.3 (CH_2Cl_2/MeOH, 98:2); ^{1}H NMR ($CDCl_3$) δ 7.45−7.05 (m, 26H, NH, CH_{Ph}), 5.16 (dd, 1H, $J_{1,2}$ = 2.2 Hz, H-1_A), 5.15−5.07 (m, 5H, H-1_E, H_{Bn}), 4.78−4.68 (m, 4H, H-3_D, H_{Bn}, H-1_D, H_{Bn}), 4.58−4.44 (m, 3H, H_{Bn}), 4.30 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.21 (dd, 1H, $J_{2,3}$ = 2.9 Hz, $J_{3,4}$ = 9.6 Hz, H-3_A), 4.16−4.07 (m, 3H, H-2_D, H-3_E, H-5_E), 4.01 (dd, 1H, H-2_A), 3.95 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5_A), 3.90 (dd, 1H, $J_{1,2}$ = 2.3 Hz, $J_{2,3}$ = 9.6 Hz, H-2_E), 3.85 (dd, 1H, $J_{5,6a}$ = 5.1 Hz, $J_{6a,6b}$ = 10.4 Hz, H-6a_D), 3.76 (dd, 1H, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.9 Hz, H-4_E), 3.70 (dd, 1H, $J_{5,6b}$ = 1.6 Hz, H-6b_D), 3.66 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4_D), 3.45 (pt, 1H, H-4_A), 3.39 (m, 2H, H-6a_E,

H-6b$_E$), 3.30 (d, 1H, $J_{1,OH}$ = 3.4 Hz, OH-1$_A$), 2.77−2.61 (m, 5H, H-5$_D$, 4H$_{Lev}$), 2.19 (s, 3H, CH$_{3Lev}$), 1.47 (s, 3H, H$_{iPr}$), 1.42 (s, 3H, H$_{iPr}$), 1.38 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_A$); ^{13}C NMR ($CDCl_3$) δ 206.2 (C$_{Lev}$), 172.2 (C$_{Lev}$), 162.1 (C$_{NTCA}$), 138.6−137.6 (C$_{Ph}$), 129.3−127.2 (CH$_{Ph}$), 101.4 (C-1$_D$, $^1J_{CH}$ = 167.7 Hz), 99.7 (C$_{iPr}$), 94.6 (C-1$_E$, $^1J_{CH}$ = 167.2 Hz), 93.9 (C-1$_A$, $^1J_{CH}$ = 171.7 Hz), 92.8 (CCl_3), 83.4 (C-3$_E$), 79.7 (C-4$_A$), 78.8 (C-2$_E$), 78.7 (C-4$_E$), 76.2, 75.9, 75.1 (3C, C$_{Bn}$), 74.5 (C-2$_A$), 74.4 (C$_{Bn}$), 74.1 (C-3$_A$), 73.3 (C$_{Bn}$), 72.8 (C-3$_D$), 71.2 (C-4$_D$), 69.9 (C-5$_E$), 68.3 (C-5$_A$), 67.8 (C-6$_E$), 67.1 (C-5$_D$), 62.0 (C-6$_D$), 56.4 (C-2$_D$), 38.0 (CH$_{2Lev}$), 29.8 (CH$_{3Lev}$), 28.9 (C$_{iPr}$), 28.0 (CH$_{2Lev}$), 18.9 (C$_{iPr}$), 17.9 (C-6$_A$); HRMS (ESI$^+$) for $C_{63}H_{72}Cl_3NO_{17}$ ([M + Na]$^+$, 1242.3763) found *m*/*z* 1242.3856, ([M + NH$_4$]$^+$, 1237.4209) found *m*/*z* 1237.4213.

(2-Deoxy-4,6-*O*-isopropylidene-3-*O*-levulinoyl-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranose Trichloroacetimidate (30). Hemiacetal **29** (1.3 g, 1.1 mmol) was dissolved in DCE (10 mL), placed under argon, and cooled to −5 °C. Trichloroacetonitrile (525 μL, 5.2 mmol, 5 equiv) and DBU (44 μL, 308 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 **29** and the presence of a less polar product. The mixture was directly chromatographied (Chex/EtOAc + 5‰ Et_3N, 7:3 → 1:1) to give **30** (1.2 g, 85%) as a yellow syrup. Trichloroacetimidate **30** (α anomer) had R_f = 0.45 (Chex/EtOAc, 6:4); ^{1}H NMR ($CDCl_3$) δ 8.65 (s, 1H, NH), 7.45−7.06 (m, 26H, NH, CH$_{Ph}$), 6.22 (s, 1H, H-1$_A$), 5.11−5.01 (m, 5H, H-1$_E$, 4H$_{Bn}$), 4.82−4.75 (m, 3H, H-3$_D$, H$_{Bn}$) 4.73 (d, 1H, $J_{1,2}$ = 8.4 Hz, H-1$_D$), 4.57−4.49 (m, 3H, H$_{Bn}$), 4.33 (d, 1H, J = 12.1 Hz, H$_{Bn}$), 4.22−4.07 (m, 5H, H-2$_D$, H-3$_A$, H-2$_A$, H-3$_E$, H-5$_E$), 3.92 (dq, 1H, $J_{4,5}$ = 9.5 Hz, H-5$_A$), 3.90−3.85 (m, 2H, H-2$_E$, H-6a$_D$), 3.82−3.74 (m, 2H, H-4$_E$, H-6b$_D$), 3.71 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4$_D$), 3.56 (pt, 1H, $J_{3,4}$ = 9.6 Hz, H-4$_A$), 3.47 (dd, 1H, $J_{5,6a}$ = 2.5 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6a$_E$), 3.37 (bd, 1H, H-6b$_E$), 2.85 (ddd, 1H, $J_{5,6a}$ = 5.2 Hz, H-5$_D$), 2.77−2.58 (m, 4H, 2CH$_{2Lev}$), 2.20 (s, 3H, CH$_{3Lev}$), 1.49 (s, 3H, H$_{iPr}$), 1.43 (s, 3H, H$_{iPr}$), 1.42 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6$_A$); ^{13}C NMR ($CDCl_3$) δ 206.0 (C$_{Lev}$), 172.3 (C$_{Lev}$), 162.1 (C$_{NTCA}$), 160.2 (*C*=NH), 138.5−137.4 (C$_{Ph}$), 129.2−127.4 (CH$_{Ph}$), 101.3 (C-1$_D$, $^1J_{CH}$ = 159.2 Hz), 99.8 (C$_{iPr}$), 96.9 (C-1$_A$, $^1J_{CH}$ = 182.6 Hz), 95.0 (C-1$_E$, $^1J_{CH}$ = 165.6 Hz), 92.7 (CCl_3), 91.1 (CCl_3), 83.3 (C-3$_E$), 79.2 (C-4$_A$), 78.7 (C-2$_E$), 78.6 (C-4$_E$), 76.3, 75.3, 75.0, 74.4 (4C, C$_{Bn}$), 74.3 (C-3$_A$), 73.3 (C$_{Bn}$), 72.7 (C-3$_D$), 72.2 (C-2$_A$), 71.2 (C-4$_D$), 71.1 (C-5$_A$), 70.1 (C-5$_E$), 67.9 (C-6$_E$), 67.3 (C-5$_D$), 61.9 (C-6$_D$), 56.5 (C-2$_D$), 38.0 (CH$_{2Lev}$), 29.8 (CH$_{3Lev}$), 29.0 (C$_{iPr}$), 28.1 (CH$_{2Lev}$), 18.9 (C$_{iPr}$), 17.9 (C-6$_A$).

Allyl (2-Deoxy-4,6-*O*-isopropylidene-3-*O*-levulinoyl-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-rhamnopyranoside (31) and Allyl (2-Deoxy-4,6-*O*-isopropylidene-3-*O*-levulinoyl-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-*β*-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (32). TMSOTf (10 μL, 56 μmol, 0.3 equiv) was added to a solution of acceptor **7**[23] (71 mg, 185 μmol) and trichloroacetimidate **30** (380 mg, 280 μmol 1.5 equiv) in CH_2Cl_2 (5 mL) containing 4Å MS (160 mg), stirred at −78 °C. The reaction mixture was stirred for 15 min while slowly coming back to rt. TLC (Tol/EtOAc, 7:3) showed the complete disappearance of the acceptor and the presence of two new compounds. Et_3N (1 mL) was added and the mixture was filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 9:1 → 1:1) gave, by order of elution, first **31** (130 mg, 44%), and then the β anomer **32** (130 mg, 44%), both as colorless syrups. Tetrasaccharide **31** had R_f = 0.65 (Tol/EtOAc, 7:3); ^{1}H NMR ($CDCl_3$) δ 7.49−7.07 (m, 36H, NH, CH$_{Ph}$), 5.89 (m, 1H, CH=), 5.27 (m, 1H, J_{trans} = 17.2 Hz, =CH$_2$), 5.21 (m, 1H, J_{cis} = 10.3 Hz, =CH$_2$), 5.16 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1$_E$), 5.12 (bs, 3H, H-1$_A$, 2H$_{Bn}$), 5.09 (d, 1H, J = 11.5 Hz, H$_{Bn}$), 5.07 (d, 1H, J = 11.4 Hz, H$_{Bn}$), 4.93 (d, 1H, J = 10.8 Hz, H$_{Bn}$), 4.83−4.76 (m, 5H, H-3$_D$, H$_{Bn}$, H-1$_D$, H-1$_B$, H$_{Bn}$), 4.71 (d, 1H, J = 11.8 Hz, H$_{Bn}$), 4.67 (d, 1H, J = 10.8 Hz, H$_{Bn}$), 4.66 (d, 1H, J = 11.8 Hz, H$_{Bn}$), 4.60−4.54 (m, 3H, H$_{Bn}$), 4.33 (d, 1H, J = 12.0 Hz, H$_{Bn}$), 4.20−4.09 (m, 6H, H-3$_E$, H-2$_D$, H-2$_A$, H-3$_A$, H$_{All}$, H-5$_E$), 4.00 (dd, 1H, $J_{1,2}$ = 2.1 Hz, $J_{2,3}$ = 2.9 Hz, H-2$_B$), 3.98 (m, 1H, H$_{All}$), 3.93−3.89 (m, 2H, H-3$_B$, H-2$_E$), 3.85−3.77 (m, 2H, H-4$_E$, H-5$_B$), 3.73 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5$_A$), 3.64 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4$_D$), 3.54−3.42 (m, 5H, H-6a$_D$, H-4$_A$, H-4$_B$, H-6a$_E$, H-6b$_E$), 3.39 (pt, 1H, $J_{5,6b}$ = $J_{6a,6b}$ = 10.4 Hz, H-6b$_D$), 2.80−2.72 (m, 3H, H-5$_D$, 2H$_{Lev}$), 2.68−2.62 (m, 2H, H$_{Lev}$), 2.20 (s, 3H, CH$_{3Lev}$), 1.44 (s, 3H, H$_{iPr}$), 1.40 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6$_B$), 1.39 (s, 3H, H$_{iPr}$), 1.32 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_A$); ^{13}C NMR ($CDCl_3$) δ 206.2 (C$_{Lev}$), 172.3 (C$_{Lev}$), 162.2 (C$_{NTCA}$), 138.6−137.5 (C$_{Ph}$), 133.8 (CH=), 129.2−127.3 (CH$_{Ph}$), 117.2 (=CH$_2$), 101.3 (C-1$_D$, $^1J_{CH}$ = 162.0 Hz), 100.9 (C-1$_A$, $^1J_{CH}$ = 171.3 Hz), 99.7 (C$_{iPr}$), 97.9 (C-1$_B$, $^1J_{CH}$ = 170.2 Hz), 94.6 (C-1$_E$, $^1J_{CH}$ = 165.1 Hz), 92.8 (CCl_3), 83.4 (C-3$_E$), 80.4 (C-4$_B$), 79.8 (C-4$_A$), 79.5 (C-2$_E$), 78.6 (C-4$_E$), 78.4 (C-3$_B$), 76.1, 75.3, 75.2, 74.9 (4C, C$_{Bn}$), 74.8 (C-2$_B$), 74.4 (C-3$_A$), 74.1 (C$_{Bn}$), 73.8 (C-2$_A$), 73.5 (C$_{Bn}$), 72.9 (C-3$_D$), 72.1 (C$_{Bn}$), 71.3 (C-4$_D$), 69.9 (C-5$_E$), 68.6 (C-5$_B$), 68.0 (C-5$_A$), 67.9 (C-6$_E$), 67.7 (C$_{All}$), 67.2 (C-5$_D$), 61.7 (C-6$_D$), 56.6 (C-2$_D$), 38.0 (CH$_{2Lev}$), 29.7 (CH$_{3Lev}$), 29.0 (C$_{iPr}$), 28.1 (CH$_{2Lev}$), 19.0 (C$_{iPr}$), 18.0 (C-6$_A$), 17.9 (C-6$_B$); HRMS (ESI$^+$) for $C_{86}H_{98}Cl_3NO_{21}$ ([M + Na]$^+$, 1608.5594) found *m*/*z* 1608.5730, ([M + NH$_4$]$^+$, 1603.6041) found *m*/*z* 1603.6112.

Tetrasaccharide **32** had R_f = 0.6 (Tol/EtOAc, 7:3); ^{1}H NMR ($CDCl_3$) δ 7.67 (d, 1H, $J_{NH,2}$ = 8.9 Hz, NH), 7.53−7.05 (m, 35H, CH$_{Ph}$), 5.89 (m, 1H, CH=), 5.31 (m, 1H, J_{trans} = 17.2 Hz, =CH$_2$), 5.22 (m, 1H, J_{cis} = 10.3 Hz, =CH$_2$), 5.20 (s, 2H, H$_{Bn}$), 5.11 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1$_E$), 5.07 (d, 1H, J = 11.0 Hz, H$_{Bn}$), 5.03 (d, 1H, J = 12.2 Hz, H$_{Bn}$), 4.95−4.86 (m, 5H, H-1$_D$, H-3$_D$, 2H$_{Bn}$, H-1$_B$), 4.84−4.79 (m, 2H, H$_{Bn}$), 4.59−4.48 (m, 5H, 3H$_{Bn}$, H-1$_A$, 2H$_{Bn}$), 4.34 (d, 1H, J = 12.2 Hz, H$_{Bn}$), 4.24−4.11 (m, 6H, H-2$_D$, H$_{All}$, H-2$_B$, H-2$_A$, H-3$_E$, H-5$_E$), 4.00 (m, 1H, H$_{All}$), 3.98−3.93 (m, 2H, H-3$_B$, H-2$_E$), 3.88 (dd, 1H, $J_{5,6a}$ = 5.2 Hz, $J_{6a,6b}$ = 10.6 Hz, H-6a$_D$), 3.80 (dd, 1H, $J_{2,3}$ = 2.5 Hz, $J_{3,4}$ = 9.5 Hz, H-3$_A$), 3.78−3.67 (m, 3H, H-5$_B$, H-4$_E$, H-6b$_D$), 3.60−3.40 (m, 5H, H-4$_D$, H-4$_A$, H-4$_B$, H-6a$_E$, H-6b$_E$), 3.28 (dq, 1H, $J_{4,5}$ = 9.2 Hz, $J_{5,6}$ = 6.2 Hz, H-5$_A$), 2.83 (ddd, 1H, $J_{5,6b}$ = 9.8 Hz, H-5$_D$), 2.78−2.75 (m, 2H, H$_{Lev}$), 2.68−2.64 (m, 2H, H$_{Lev}$), 2.18 (s, 3H, CH$_{3Lev}$), 1.37 (s, 3H, H$_{iPr}$), 1.39−1.37 (m, 9H, H$_{iPr}$, H-6$_A$, H-6$_B$), 1.32 (s, 3H, H$_{iPr}$); ^{13}C NMR ($CDCl_3$) δ 206.1 (C$_{Lev}$), 172.2 (C$_{Lev}$), 162.0 (C$_{NTCA}$), 139.1−137.5 (C$_{Ph}$), 134.0 (CH=), 129.1−127.3 (CH$_{Ph}$), 117.2 (=CH$_2$), 100.7 (C-1$_D$, $^1J_{CH}$ = 163.8 Hz), 99.7 (C$_{iPr}$), 97.5 (C-1$_A$, $^1J_{CH}$ = 155.1 Hz), 96.9 (C-1$_B$, $^1J_{CH}$ = 167.2 Hz), 94.1 (C-1$_E$, $^1J_{CH}$ = 167.7 Hz), 92.8 (CCl_3), 83.7 (C-3$_E$), 81.0 (C-4$_B$), 79.7 (C-4$_A$), 78.7 (C-4$_E$), 77.8 (C-2$_E$), 77.4 (C-3$_B$), 76.4 (C-3$_A$), 76.2, 75.3, 75.1, 74.6, 73.6 (5C, C$_{Bn}$), 73.3 (3C, C-2$_A$, C-2$_B$, C-3$_D$), 73.5 (C$_{Bn}$), 72.4 (C-5$_A$), 71.3 (C-4$_D$), 71.0 (C$_{Bn}$), 69.9 (C-5$_E$), 68.0 (2C, C-5$_B$, C-6$_E$), 67.8 (C$_{All}$), 67.0 (C-5$_D$), 62.4 (C-6$_D$), 56.7 (C-2$_D$), 38.0 (CH$_{2Lev}$), 29.8 (CH$_{3Lev}$), 29.0 (C$_{iPr}$), 28.1 (CH$_{2Lev}$), 19.9 (C$_{iPr}$), 18.4 (C-6$_A$), 18.0 (C-6$_B$); HRMS (ESI$^+$) for $C_{86}H_{98}Cl_3NO_{21}$ ([M + Na]$^+$, 1608.5594) found *m*/*z* 1608.5914, ([M + NH$_4$]$^+$, 1603.6041) found *m*/*z* 1603.6248.

Allyl (2-Acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (36) and Allyl (2-Deoxy-2-methylcarbamate-α-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (37). Methanolic MeONa (0.5 M, 4.8 mL, 2.4 mmol, 6 equiv) was added to a solution of triacetate **33**[27] (0.5 g, 0.4 mmol) in CH_2Cl_2 (38 mL), and the mixture was stirred for 9 h. TLC (CH_2Cl_2/MeOH, 92:8) showed the complete disappearance of **33** and the presence of a more polar product. MeOH (77 mL) and acetic anhydride (300 μL) were added. After 2 h, TLC (CH_2Cl_2/MeOH, 92:8) showed the complete disappearance of the aminotriol intermediate **35**. Evaporation of the filtrate gave a syrup which was purified by chromatography (CH_2Cl_2/MeOH, 98:2 → 95:5) to give, by order of elution, first carbamate **37** (20 mg, 5%), and then acetamide **36**[15] (371 mg, 90%) as white foams. Carbamate **37** had R_f = 0.45 (CH_2Cl_2/MeOH, 92:

8); ^{1}H NMR ($CDCl_3$) δ 7.42−7.08 (m, 25H, CH_{Ph}), 6.52 (d, 1H, $J_{NH,2}$ = 7.0 Hz, NH), 5.90 (m, 1H, CH=), 5.29 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.20 (m, 1H, J_{cis} = 10.4 Hz, =CH_2), 5.11−4.96 (m, 4H, 2H_{Bn}, H-1$_E$, H_{Bn}), 4.92 (bs, 1H, H-1$_A$), 4.83 (d, 1H, J = 10.9 Hz, H_{Bn}), 4.81 (d, 1H, J = 11.8 Hz, H_{Bn}), 4.73 (d, 1H, J = 10.4 Hz, H_{Bn}), 4.63−4.55 (m, 2H, H_{Bn}), 4.45−4.42 (m, 2H, H-1$_D$, H_{Bn}), 4.29 (dd, 1H, $J_{2,3}$ = 9.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3$_E$), 4.27 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.15 (m, 1H, H_{All}), 4.12−4.09 (m, 2H, H-3$_A$, H-5$_E$), 3.98 (m, 1H, H_{All}), 3.87 (bs, 1H, H-2$_A$), 3.84−3.70 (m, 8H, H-4$_E$, OMe, H-6a$_D$, H-6b$_D$, H-2$_E$, H-5$_A$), 3.63 (m, 1H, $J_{1,2}$ = 8.1 Hz, H-2$_D$), 3.51 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4$_A$), 3.49 (d, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4$_D$), 3.33 (bs, 2H, H-6a$_E$, H-6b$_E$), 2.90 (m, 1H, H-5$_D$), 2.61 (pt, 1H, $J_{2,3}$ = 9.8 Hz, H-3$_D$), 1.40 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_A$); ^{13}C NMR ($CDCl_3$) δ 159.4 (C_{NOMe}), 139.7−137.8 (C_{Ph}), 134.2 (CH=), 129.4−127.9 (CH_{Ph}), 117.9 (=CH_2), 103.2 (C-1$_D$, $^1J_{CH}$ = 161.6 Hz), 98.6 (C-1$_A$, $^1J_{CH}$ = 171.5 Hz), 95.8 (C-1$_E$, $^1J_{CH}$ = 170.5 Hz), 83.1 (C-3$_E$), 80.1 (C-2$_E$), 79.9 (C-4$_A$), 78.7 (C-4$_E$), 78.1 (C-2$_A$), 77.1 (C-3$_D$), 76.1 (C_{Bn}), 76.0 (C-3$_A$), 75.7, 75.6, 75.4 (3C, C_{Bn}), 75.2 (C-5$_D$), 73.8 (C_{Bn}), 71.5 (C-4$_D$), 70.6 (C-5$_E$), 69.0 (C-5$_A$), 68.3 (C_{All}), 68.1 (C-6$_E$), 62.7 (C-6$_D$), 58.4 (C-2$_D$), 52.9 (OMe), 18.1 (C-6$_A$); HRMS (ESI$^+$) for $C_{58}H_{69}NO_{16}$ ([M + Na]$^+$, 1058.4514) found *m*/*z* 1058.4514, ([M + NH_4]$^+$, 1053.4960) found *m*/*z* 1053.4946.

Allyl (2-Acetamido-2-deoxy-4,6-*O*-isopropylidene-*β*-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (40).[15] Route a. Methanolic MeONa (0.5 M, 3.7 mL, 1.9 mmol, 6 equiv) was added to a solution of fully protected trisaccharide **39**[15,27] (375 mg, 310 μmol) in CH_2Cl_2 (30 mL), and the mixture was stirred for 9 h. TLC (Chex/EtOAc, 1:1) showed the complete disappearance of **39**, and the presence of a single more polar product which reacted with ninhydrin. MeOH (60 mL) and acetic anhydride (300 μL) were added. After 2 h, TLC (Chex/EtOAc, 1:1) showed the complete disappearance of the aminotriol intermediate. Evaporation of the filtrate gave a syrup which was purified by chromatography (Chex/EtOAc, 1:1) to give compound **40** (258 mg, 90%) as a white foam.

Route b. Alternatively, starting from acceptor **41**[24] (2.1 g, 2.6 mmol) and donor **14** (1.8 g, 3.1 mmol, 1.2 equiv), the condensation, transesterification, and acetalation steps were run without any intermediate purification. Column chromatography (Chex/EtOAc, 9:1 → 1:1) of the residue gave the expected **40** (2.4 g, 87%) over three steps.

Route c. Alternatively, starting from acceptor **41** (250 mg, 310 μmol) and donor **18**[27] (220 mg, 400 μmol, 1.3 equiv), the condensation and transesterification steps were run without any intermediate purification. Column chromatography (Chex/EtOAc, 1:1) of the residue gave the expected **40** (258 mg, 80%) over two steps. Data for alcohol **40** were as described.[15]

Allyl (2-Deoxy-4,6-*O*-isopropylidene-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-rhamnopyranoside (20). Anhydrous K_2CO_3 (175 mg, 1.3 mmol, 1 equiv) was added to a stirred solution of **19** (1.9 g, 1.3 mmol) in dry MeOH (20 mL). The mixture was stirred at rt for 1 night, at which time TLC (Tol/EtOAc, 7:3) indicated total conversion of **19** into a single product. Volatiles were removed under reduced pressure to give crude alcohol **20** (1.7 g, 92%) as a white foam. Tetrasaccharide **20** had R_f = 0.45 (Tol/EtOAc, 7:3); ^{1}H NMR ($CDCl_3$) δ 7.43−7.08 (m, 36H, NH, CH_{Ph}), 5.88 (m, 1H, =CH), 5.29 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.23−5.20 (m, 2H, H-1$_E$, =CH_2), 5.13 (d, 1H, J = 11.0 Hz, H_{Bn}), 5.12 (bs, 1H, H-1$_A$), 5.08 (d, 1H, J = 11.9 Hz, H_{Bn}), 5.06 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.95 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.90 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.82 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.79−4.77 (m, 2H, H_{Bn}, H-1$_B$), 4.72 (d, 1H, J = 11.8 Hz, H_{Bn}), 4.70−4.61 (m, 4H, 2H_{Bn}, H-1$_D$, H_{Bn}), 4.56 (d, 1H, J = 10.2 Hz, H_{Bn}), 4.53 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.37 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.19−4.13 (m, 5H, H-3$_A$, H-2$_A$, H-3$_E$, H_{All}, H-5$_E$), 4.02 (dd, 1H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 2.8 Hz, H-2$_B$), 4.01−3.92 (m, 5H, H_{All}, H-3$_B$, H-2$_D$, H-4$_E$, H-2$_E$), 3.80 (dq, 1H, $J_{4,5}$ = 9.2 Hz, H-5$_A$), 3.73 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5$_B$), 3.56 (dd, 1H, $J_{5,6}$ = 5.3 Hz, $J_{6a,6b}$ = 10.8 Hz, H-6a$_D$), 3.52−3.47 (m, 4H, H-6a$_E$, H-6b$_E$, H-4$_A$, H-4$_B$), 3.41 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, H-4$_D$), 3.38 (pt, 1H, $J_{5,6b}$ = $J_{6a,6b}$ = 10.0 Hz, H-6b$_D$), 2.85 (m, 1H, OH), 2.82 (ddd, 1H, $J_{5,6a}$ = 5.4 Hz, H-5$_D$), 2.45 (ddd, 1H, $J_{2,3}$ = 9.6 Hz, $J_{3,OH}$ = 2.1 Hz, H-3$_D$), 1.47 (s, 3H, H_{iPr}), 1.46 (s, 3H, H_{iPr}), 1.41 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_A$), 1.35 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_B$); ^{13}C NMR ($CDCl_3$) δ 163.7 (C_{NTCA}), 138.6−137.5 (C_{Ph}), 133.8 (CH=), 129.3−127.4 (CH_{Ph}), 117.2 (=CH_2), 101.0 (C-1$_D$, $^1J_{CH}$ = 159.1 Hz), 101.0 (C-1$_A$, $^1J_{CH}$ = 170.3 Hz), 99.7 (C_{iPr}), 97.9 (C-1$_B$, $^1J_{CH}$ = 168.6 Hz), 94.1 (C-1$_E$, $^1J_{CH}$ = 166.2 Hz), 92.7 (CCl_3), 83.3 (C-3$_E$), 80.5 (C-4$_B$), 79.8 (C-4$_A$), 79.7 (C-2$_E$), 79.5 (C-3$_B$), 78.7 (C-4$_E$), 76.3, 75.4, 75.3, 74.9 (5C, C_{Bn}), 74.7 (C-2$_B$), 74.1 (C-3$_A$), 74.0 (C-4$_D$), 73.5 (C_{Bn}), 73.3 (C-2$_A$), 73.0 (C-3$_D$), 72.1 (C_{Bn}), 70.0 (C-5$_E$), 68.7 (C-5$_A$), 68.0 (C-5$_B$), 67.9 (C-6$_E$), 67.7 (C_{All}), 67.1 (C-5$_D$), 61.4 (C-6$_D$), 58.8 (C-2$_D$), 29.1 (C_{iPr}), 19.0 (C_{iPr}), 18.0 (C-6$_B$), 17.8 (C-6$_A$); HRMS (ESI$^+$) for $C_{81}H_{92}Cl_3NO_{19}$ ([M + Na]$^+$, 1510.5227) found *m*/*z* 1510.5243, ([M + NH_4]$^+$, 1505.5673) found *m*/*z* 1505.5669.

(3,4-Di-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α/*β*-L-rhamnopyranose (43). 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)-iridium hexafluorophosphate (175 mg) was dissolved in THF (90 mL) and the resulting red solution was degassed under an argon stream. Hydrogen was bubbled through the solution, causing the color to change to yellow. The solution was then degassed again under an argon stream. A solution of **42**[16] (8.0 g, 10.6 mmol) in THF (15 mL) was added. The mixture was stirred overnight at rt. TLC (Tol/EtOAc, 8:2) showed the complete disappearance of **42** and the presence of a less polar product. The mixture was treated with a solution of iodine (5.4 g, 21.2 mmol) in THF/water (30 mL, 4:1 v/v), and stirred for 1 h at rt. TLC (Tol/EtOAc, 8:2 and CH_2Cl_2/MeOH, 98:2) showed the conversion of the intermediate into a more polar product. Excess iodine was destroyed by adding a solution of freshly prepared 5% aq sodium bisulphite (25 mL). CH_2Cl_2 (200 mL) was added, and the organic phase was washed with brine (3 × 50 mL), water (3 × 50 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (CH_2Cl_2/MeOH, 99:1 → 90:10) gave **43** (7.1 g, 93%) as a yellow syrup. Hemiacetal **43** had R_f = 0.45 (CH_2Cl_2/MeOH, 98:2); ^{1}H NMR ($CDCl_3$) δ 7.39−7.28 (m, 15H, CH_{Ph}), 5.44 (dd, 1H, $J_{1,2}$ = 1.9 Hz, H-2$_B$), 5.16 (dd, 1H, $J_{1,2}$ = 1.8 Hz, H-2$_C$), 5.12 (dd, 1H, $J_{1,OH}$ = 3.9 Hz, H-1$_C$), 5.05 (d, 1H, H-1$_B$), 4.92 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.83 (d, 1H, J = 10.9 Hz, H_{Bn}), 4.66 (d, 1H, J = 11.1 Hz, H_{Bn}), 4.63−4.60 (m, 2H, H_{Bn}), 4.45 (d, 1H, J = 11.3 Hz, H_{Bn}), 4.20 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.5 Hz, H-3$_C$), 3.98 (dq, 1H, $J_{4,5}$ = 9.5 Hz, H-5$_C$), 3.89 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.3 Hz, H-3$_B$), 3.83 (dq, 1H, $J_{4,5}$ = 9.3 Hz, H-5$_B$), 3.77 (d, 1H, OH-1$_C$), 3.47 (pt, 1H, H-4$_C$), 3.43 (pt, 1H, H-4$_B$), 2.70 (m, 4H, 4H_{Lev}), 2.18 (s, 3H, CH_{3Lev}), 2.14 (s, 3H, H_{Ac}), 1.29 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6$_B$), 1.30 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_C$); ^{13}C NMR ($CDCl_3$) δ 206.8 (C_{Lev}), 172.6 (C_{Lev}), 171.6 (C_{Ac}), 138.8−138.4 (C_{Ph}), 128.9−128.1 (CH_{Ph}), 99.9 (C-1$_B$, $^1J_{CH}$ = 173.3 Hz), 92.0 (C-1$_C$, $^1J_{CH}$ = 170.0 Hz), 80.7 (C-4$_C$), 80.2 (C-4$_B$), 78.0 (C-3$_B$), 77.7 (C-3$_C$), 75.8, 75.6 (2C, C_{Bn}), 73.2 (C-2$_C$), 72.0 (C_{Bn}), 69.7 (C-2$_B$), 69.0 (C-5$_B$), 68.0 (C-5$_C$), 38.4 (CH_{2Lev}), 30.2 (CH_{3Lev}), 28.5 (CH_{2Lev}), 21.5 (C_{Ac}), 18.5, 18.4 (2C, C-6$_B$, C-6$_C$); HRMS (ESI$^+$) for $C_{40}H_{48}O_{12}$ ([M + Na]$^+$, 743.3043) found *m*/*z* 743.3173, ([M + NH_4]$^+$, 738.3489) found *m*/*z* 738.3627.

(3,4-Di-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α/*β*-L-rhamnopyranose Trichloroacetimidate (23). Hemiacetal **43** (8.7 g, 12.1 mmol) was dissolved in DCE (50 mL), placed under argon, and cooled to −5 °C. Trichloroacetonitrile (6.1 mL, 60.7 mmol, 5 equiv) and DBU (508 μL, 3.3 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 **43** and the presence of a single less polar product. The mixture was directly chromatographied (Chex/EtOAc + 5‰ Et_3N, 7:3 → 1:1) to give **23** (8.7 g, 84%) as a yellow syrup. Trichloroacetimidate **23** (α anomer) had R_f = 0.4 (Chex/EtOAc,

7:3); ^{1}H NMR ($CDCl_3$) δ 8.72 (s, 1H, NH), 7.42−7.29 (m, 15H, CH_{Ph}), 6.22 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1_C), 5.48 (dd, 1H, $J_{1,2}$ = 1.8 Hz, H-2_B), 5.31 (dd, 1H, H-2_C), 5.10 (d, 1H, H-1_B), 4.92 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.85 (d, 1H, J = 10.8 Hz, H_{Bn}), 4.68−4.62 (m, 3H, H_{Bn}), 4.51 (d, 1H, J = 11.3 Hz, H_{Bn}), 4.26 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.5 Hz, H-3_C), 3.96 (dq, 1H, $J_{4,5}$ = 9.5 Hz, H-5_C), 3.89 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.3 Hz, H-3_B), 3.82 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5_B), 3.58 (pt, 1H, H-4_C), 3.44 (pt, 1H, H-4_B), 2.72 (m, 4H, $4H_{Lev}$), 2.18 (s, 3H, CH_{3Lev}), 2.17 (s, 3H, H_{Ac}), 1.36 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C), 1.29 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_B); ^{13}C NMR ($CDCl_3$) δ 206.5 (C_{Lev}), 172.3 (C_{Lev}), 170.3 (C_{Ac}), 160.5 (*C*=NH), 138.8−138.0 (C_{Ph}), 129.2−127.9 (CH_{Ph}), 99.9 (C-1_B, $^1J_{CH}$ = 168.1 Hz), 94.5 (C-1_C, $^1J_{CH}$ = 178.7 Hz), 91.2 (CCl_3), 80.2 (C-4_C), 80.1 (C-4_B), 77.9 (C-3_B), 76.5 (C-3_C), 76.1, 75.7, 72.0 (3C, C_{Bn}), 71.2 (C-2_C), 71.1 (C-5_C), 69.6 (C-2_B), 69.1 (C-5_B), 38.4 (CH_{2Lev}), 30.2 (CH_{3Lev}), 28.5 (CH_{2Lev}), 21.3 (C_{Ac}), 18.4, 18.3 (2C, C-6_B, C-6_C).

Allyl (3,4-Di-*O*-benzyl-2-*O*-levulinoyl-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-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (44). TfOH (23 μL, 263 μmol, 0.9 equiv) was added to a solution of trisaccharide acceptor **40** (310 mg, 290 μmol) and trichloroacetimidate **23** (379 mg, 440 μmol, 1.5 equiv) in toluene (10 mL) containing 4Å MS (1.7 g), stirred at 0 °C. After 15 min, TLC (Chex/EtOAc, 1:1) showed the presence of a single more polar product. Et_3N (0.2 mL) was added. The mixture was filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 8:2 → 6:4) gave **44** (383 mg, 74%) as a white foam slightly contaminated. Pentasaccharide **44** had R_f = 0.35 (Chex/EtOAc, 1:1); ^{1}H NMR ($CDCl_3$) δ 7.45−7.07 (m, 40H, CH_{Ph}), 6.47 (d, 1H, $J_{NH,2}$ = 9.0 Hz, NH), 5.90 (m, 1H, CH=), 5.46 (dd, 1H, $J_{2,3}$ = 3.0 Hz, H-2_B), 5.29 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.20 (m, 1H, J_{cis} = 10.4 Hz, =CH_2), 5.15 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1_E), 5.09−4.98 (m, 5H, H-1_B, H_{Bn}), 4.94 (dd, 1H, $J_{1,2}$ = 2.1 Hz, $J_{2,3}$ = 2.7 Hz, H-2_C), 4.93−4.88 (m, 3H, H_{Bn}), 4.84 (bs, 1H, H-1_A), 4.79−4.77 (bs, 2H, H-1_C, H_{Bn}), 4.67−4.60 (m, 5H, H_{Bn}), 4.52 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.42 (d, 1H, J = 11.4 Hz, H_{Bn}), 4.35 (d, 1H, J = 11.9 Hz, H_{Bn}), 4.28 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1_D), 4.21−4.13 (m, 6H, H-3_E, H-2_D, H-5_E, H-3_C, H_{All}, H-3_A), 4.00 (dq, 1H, $J_{4,5}$ = 9.6 Hz, H-5_C), 3.97−3.83 (m, 6H, H_{All}, H-3_B, H-2_E, H-2_A, H-4_E, H-$6a_D$), 3.79 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5_B), 3.73 (bd, 1H, $J_{5,6b}$ = 10.3 Hz, H-$6b_D$), 3.70 (dq, 1H, $J_{4,5}$ = 9.5 Hz, H-5_A), 3.52 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, H-4_D), 3.58−3.40 (m, 5H, H-4_A, H-$6a_E$, H-$6b_E$, H-4_C, H-4_B), 2.7−2.68 (m, 6H, H-5_D, $4H_{Lev}$, H-3_D), 2.35 (s, 3H, H_{NAc}), 2.19 (s, 3H, CH_{3Lev}), 2.06 (s, 3H, H_{Ac}), 1.48 (s, 3H, H_{iPr}), 1.45 (s, 3H, H_{iPr}), 1.38 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), 1.34 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_B), 1.27 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C); ^{13}C NMR ($CDCl_3$) δ 206.1 (C_{Lev}), 171.8 (C_{Lev}), 170.5 (C_{Ac}), 170.1 (C_{NAc}), 138.7−137.5 (C_{Ph}), 134.0 (CH=), 129.4−127.8 (CH_{Ph}), 117.1 (=CH_2), 103.7 (C-1_D, $^1J_{CH}$ = 159.9 Hz), 99.5 (C-1_B, $^1J_{CH}$ = 169.7 Hz), 99.3 (C_{iPr}), 98.4 (C-1_A, $^1J_{CH}$ = 174.4 Hz), 97.5 (C-1_C, $^1J_{CH}$ = 170.6 Hz), 94.4 (C-1_E, $^1J_{CH}$ = 170.1 Hz), 83.5 (C-3_E), 80.7 (C-3_D), 80.4 (C-2_E), 80.1, 80.0 (2C, C-4_B, C-4_C), 79.8 (C-4_A), 78.5 (C-4_E), 78.2 (C-3_C), 77.9 (C-3_B), 76.7 (C-2_A), 76.1, 75.9, 75.5, 75.4, 75.1, 75.0 (6C, C_{Bn}), 74.8 (C-3_A), 73.4 (C_{Bn}), 73.3 (C-2_C), 72.4 (C-4_D), 71.3 (C_{Bn}), 70.0 (C-5_E), 69.3 (C-2_B), 68.6 (C-5_A), 68.5 (C-5_B), 67.9 (C-6_E), 67.8 (C_{All}), 67.4 (C-5_D), 67.3 (C-5_C), 62.2 (C-6_D), 55.0 (C-2_D), 38.1 (CH_{2Lev}), 29.8 (CH_{3Lev}), 29.2 (C_{iPr}), 28.3 (CH_{2Lev}), 24.1 (C_{NAc}), 21.1 (C_{Ac}), 19.1 (C_{iPr}), 17.9, 17.8, 17.7 (3C, C-6_A, C-6_B, C-6_C); HRMS (ESI^+) for $C_{101}H_{119}NO_{26}$ ([M + H]$^+$, 1762.8098) found *m*/*z* 1762.8198, ([M + Na]$^+$, 1784.7917) found *m*/*z* 1784.7988.

Allyl (3,4-Di-*O*-benzyl-2-*O*-levulinoyl-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-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-rhamnopyranoside (45). TMSOTf (18 μL, 100 μmol, 0.9 equiv) was added to a solution of acceptor **21** (150 mg, 110 μmol) and trichloroacetimidate **23** (140 mg, 160 μmol, 1.5 equiv) in toluene (5 mL) containing 4Å MS (620 mg), stirred at 0 °C. After 45 min, TLC (Tol/EtOAc, 75:25; Chex/EtOAc, 1:1) showed the presence of a single less polar product. Et_3N (0.2 mL) was added and the mixture was filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 75:25 → 1:1) gave **45** (149 mg, 65%) as a white foam slightly contaminated. Hexasaccharide **45** had R_f = 0.55 (Chex/EtOAc, 1:1); ^{1}H NMR ($CDCl_3$) δ 7.47−7.06 (m, 50H, CH_{Ph}), 6.38 (d, 1H, $J_{NH,2}$ = 9.1 Hz, NH), 5.86 (m, 1H, CH=), 5.44 (dd, 1H, $J_{2,3}$ = 3.2 Hz, H-$2_{B'}$), 5.26 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.21−5.17 (m, 2H, =CH_2, H-1_E), 5.07 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1_A), 5.05 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-$1_{B'}$), 5.04−4.87 (m, 9H, $4H_{Bn}$, H-2_C, $2H_{Bn}$), 4.84 (d, 2H, J = 11.2 Hz, H_{Bn}), 4.78 (d, 1H, J = 10.2 Hz, H_{Bn}), 4.75 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1_B), 4.70 (bs, 1H, H-1_C), 4.68−4.57 (m, 9H, H_{Bn}), 4.50 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.41 (d, 1H, J = 11.3 Hz, H_{Bn}), 4.35 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.28 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1_D), 4.21−4.08 (m, 6H, H-3_E, H-5_E, H-2_D, H-3_A, H_{All}, H-3_C), 3.99 (dd, 1H, $J_{2,3}$ = 2.6 Hz, H-2_A), 3.96−3.84 (m, 7H, H-5_C, H-2_B, H_{All}, H-3_B, H-$3_{B'}$, H-2_E, H-4_E), 3.81−3.73 (m, 2H, H-5_A, H-$5_{B'}$), 3.71 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz, H-5_B), 3.54−3.38 (m, 8H, H-$6a_D$, H-$6b_D$, H-$6a_E$, H-$6b_E$, H-4_A, H-4_B, H-4_D, H-4_C, H-$4_{B'}$), 2.75−2.64 (m, 6H, H-5_D, $4H_{Lev}$, H-3_D), 2.31 (s, 3H, H_{NAc}), 2.18 (s, 3H, CH_{3Lev}), 2.05 (s, 3H, H_{Ac}), 1.42 (s, 3H, H_{iPr}), 1.39 (s, 3H, H_{iPr}), 1.35−1.31 (m, 9H, H-6_A, H-6_B, H-$6_{B'}$), 1.24 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C); ^{13}C NMR ($CDCl_3$) δ 206.1 (C_{Lev}), 171.7 (C_{Lev}), 170.4 (C_{Ac}), 170.0 (C_{NAc}), 138.6−137.5 (C_{Ph}), 133.8 (CH=), 129.3−127.7 (CH_{Ph}), 117.1 (=CH_2), 103.6 (C-1_D, $^1J_{CH}$ = 159.0 Hz), 101.1 (C-1_A, $^1J_{CH}$ = 172.8 Hz), 99.5 (C-$1_{B'}$, $^1J_{CH}$ = 167.8 Hz), 99.2 (C_{iPr}), 97.9 (C-1_B, $^1J_{CH}$ = 172.8 Hz), 97.8 (C-1_C, $^1J_{CH}$ = 172.8 Hz), 94.2 (C-1_E, $^1J_{CH}$ = 165.3 Hz), 83.4 (C-3_E), 80.5 (C-3_D), 80.4 (C-4_B), 80.2 (C-2_E), 80.1 (C-$4_{B'}$), 80.0 (C-4_C), 79.8 (C-4_A), 79.2 (C-3_B), 78.5 (C-4_E), 78.2 (C-3_C), 77.9 (C-$3_{B'}$), 76.2 (C-2_A), 76.1, 75.7, 75.4 (3C, C_{Bn}), 75.3 (C-2_B), 75.2, 75.1, 75.0, 74.5 (4C, C_{Bn}), 74.5 (C-3_A), 73.5 (C_{Bn}), 73.2 (C-2_C), 72.1 (C-4_D), 71.9, 71.4 (2C, C_{Bn}), 70.0 (C-5_E), 69.3 (C-$2_{B'}$), 68.9 (C-5_A), 68.5 (C-$5_{B'}$), 67.9 (C-6_E), 67.8 (C-5_B), 67.7 (C_{All}), 67.3 (C-5_C), 67.2 (C-5_D), 62.0 (C-6_D), 55.0 (C-2_D), 38.1 (CH_{2Lev}), 29.8 (CH_{3Lev}), 29.2 (C_{iPr}), 28.2 (CH_{2Lev}), 24.1 (C_{NAc}), 21.0 (C_{Ac}), 19.1 (C_{iPr}), 18.0, 17.9, 17.8, 17.7 (4C, C-6_A, C-6_B, C-$6_{B'}$, C-6_C); HRMS (ESI^+) for $C_{121}H_{141}NO_{30}$ ([M + H]$^+$, 2088.9617) found *m*/*z* 2088.9619, ([M + Na]$^+$, 2110.9436) found *m*/*z* 2110.9497.

Allyl (2-Deoxy-4,6-*O*-isopropylidene-2-trichloroacetamido-3-*O*-trimethylsilyl-*β*-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (47). TMSOTf (61.0 μL, 340 μmol, 0.3 equiv) was added to a solution of acceptor **27** (1.3 g, 1.1 mmol) and trichloroacetimidate **23** (1.5 g, 1.7 mmol, 1.5 equiv) in toluene (30 mL) containing 4Å MS (960 mg), stirred at −78 °C. After 15 min, TLC (Tol/EtOAc, 8:2) showed the absence of **27**. Et_3N (0.2 mL) was added and the mixture was filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 9:1 → 7:3) gave first **47** (233 mg, 11%), and then pentasaccharide **48** (1.1 g, 52%), both as white foams. Trisaccharide **47** had R_f = 0.5 (Tol/EtOAc, 8:2); ^{1}H NMR ($CDCl_3$) δ 7.47−7.08 (m, 26H, NH, CH_{Ph}), 5.89 (m, 1H, CH=), 5.32 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.23 (m, 1H, J_{cis} = 10.6 Hz, =CH_2), 5.12 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1_E), 5.11−5.05 (m, 3H, H_{Bn}), 4.93 (d, 1H, J = 12.8 Hz, H_{Bn}), 4.86 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1_A), 4.83−4.76 (m, 3H, H_{Bn}, H-1_D, H_{Bn}), 4.61−4.56 (m, 2H, H_{Bn}), 4.50 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.32 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.22−4.10 (m, 4H, H-3_E, H_{All}, H-3_A, H-5_E), 4.08−3.97 (m, 3H, H-2_A, H-2_D, H_{All}), 3.90 (dd, 1H, $J_{5,6a}$ = 5.3 Hz, $J_{6a,6b}$ = 10.7 Hz, H-$6a_D$), 3.83−3.72 (m, 4H, H-2_E, H-4_E, H-$6b_D$, H-5_A), 3.58−3.52 (m, 2H, H-4_D, H-4_A), 3.45 (dd, 1H, $J_{5,6a}$ = 1.5 Hz, $J_{6a,6b}$ = 10.8 Hz, H-$6a_E$), 3.40 (dd, 1H, $J_{5,6b}$ = 1.5 Hz, H-$6b_E$), 3.36 (pt, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3_D), 2.96 (ddd, 1H, $J_{5,6b}$ = $J_{4,5}$ = 9.8 Hz, H-5_D), 1.51 (s, 3H, H_{iPr}), 1.45 (s, 3H, H_{iPr}), 1.44 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), 0.13 (s, 9H, H_{Si}); ^{13}C NMR ($CDCl_3$) δ 161.7 (C_{NTCA}), 138.7−137.7 (C_{Ph}), 134.0 (CH=), 129.1−127.3 (CH_{Ph}), 117.1 (=CH_2), 101.5 (C-1_D, $^1J_{CH}$ = 163.6 Hz), 99.4 (C_{iPr}), 98.5 (C-1_A, $^1J_{CH}$ = 174.0 Hz), 95.2 (C-1_E, $^1J_{CH}$ = 167.5 Hz), 93.3 (CCl_3), 83.3 (C-3_E), 79.8 (C-4_A), 78.7, 78.6 (2C, C-2_E, C-4_E), 75.9 (C_{Bn}), 75.4 (C-3_A), 75.3,

74.9 (2C, C_{Bn}), 74.3 (C-3_D), 74.3 (C_{Bn}), 74.2 (C-4_D), 74.1 (C-2_A), 73.4 (C_{Bn}), 70.0 (C-5_E), 68.5 (C-5_A), 67.9 (C-6_E), 67.8 (C_{All}), 67.2 (C-5_D), 62.1 (C-6_D), 58.6 (C-2_D), 29.1 (C_{iPr}), 19.0 (C_{iPr}), 18.0 (C-6_A), 0.7 (C_{Si}); HRMS (ESI$^+$) for $C_{64}H_{78}Cl_3NO_{15}Si$ ([M + Na]$^+$, 1256.4104) found *m/z* 1256.4188, ([M + NH_4]$^+$, 1251.4550) found *m/z* 1251.4548.

Allyl (3,4-Di-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-deoxy-4,6-*O*-isopropylidene-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (48). TMSOTf (49 μL, 270 μmol, 0.3 equiv) was added to a solution of acceptor **27** (1.1 g, 0.9 mmol) and trichloroacetimidate **23** (1.2 g, 1.4 mmol, 1.5 equiv) in toluene (30 mL) containing 4Å MS (1.1 g), stirred at −40 °C. After 15 min, TLC (Tol/EtOAc, 8:2) showed the absence of **27**. Et_3N (0.2 mL) was added. The mixture was filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 9:1 → 7:3) gave **48** (1.4 g, 75%) as a white foam. Pentasaccharide **48** had R_f = 0.35 (Tol/EtOAc, 8:2); ^{1}H NMR ($CDCl_3$) δ 7.51−7.13 (m, 40H, CH_{Ph}), 6.94 (d, 1H, $J_{NH,2}$ = 8.9 Hz, NH), 5.94 (m, 1H, CH=), 5.48 (dd, 1H, H-2_B), 5.33 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.24 (m, 1H, J_{cis} = 10.4 Hz, =CH_2), 5.24 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1_E), 5.16 (m, 2H, H_{Bn}), 5.12 (dd, 1H, $J_{2,3}$ = 2.8 Hz, H-2_C), 5.11 (d, 1H, $J_{1,2}$ = 1.3 Hz, H-1_B), 5.07 (d, 1H, J = 12.2 Hz, H_{Bn}), 4.98−4.94 (m, 2H, H_{Bn}), 4.89 (d, 2H, J = 11.0 Hz, H_{Bn}), 4.84 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1_A), 4.79 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1_C), 4.76 (d, 1H, J = 10.2 Hz, H_{Bn}), 4.71 ((d, 1H, J = 11.2 Hz, H_{Bn}), 4.67−4.54 (d, 6H, H_{Bn}, H-1_D), 4.46 (d, 1H, J = 11.3 Hz, H_{Bn}), 4.36 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.24−4.15 (m, 5H, H-3_E, H-3_C, H_{All}, H-3_A, H-5_E), 4.09−3.96 (m, 5H, H-2_D, H-2_A, H-5_C, H_{All}, H-5_B), 3.95 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.2 Hz, H-3_B), 3.91−3.85 (m, 3H, H-6a_D, H-2_E, H-4_E), 3.78−3.73 (m, 2H, H-5_A, H-6b_D), 3.57 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, H-4_D), 3.52 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4_A), 3.50−3.44 (m, 4H, H-6a_E, H-6b_E, H-4_C, H-4_B), 2.87 (ddd, 1H, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 9.8 Hz, H-5_D), 2.77 (m, 5H, H-3_D, $4H_{Lev}$), 2.21 (s, 3H, CH_{3Lev}), 2.16 (s, 3H, H_{Ac}), 1.52 (s, 3H, H_{iPr}), 1.50 (s, 3H, H_{iPr}), 1.46 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_A$), 1.40 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_B$), 1.31 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_C$); ^{13}C NMR ($CDCl_3$) δ 206.5 (C_{Lev}), 172.1 (C_{Lev}), 169.9 (C_{Ac}), 162.4 (C_{NTCA}), 139.1−138.8 (C_{Ph}), 134.4 (CH=), 129.5−127.8 (CH_{Ph}), 117.5 (=CH_2), 101.7 (C-1_D, $^1J_{CH}$ = 163.9 Hz), 99.9 (C_{iPr}), 99.4 (C-1_B, $^1J_{CH}$ = 174.7 Hz), 98.8 (C-1_A, $^1J_{CH}$ = 171.5 Hz), 98.1 (C-1_C, $^1J_{CH}$ = 167.6 Hz), 94.9 (C-1_E, $^1J_{CH}$ = 165.3 Hz), 93.5 (CCl_3), 83.5 (C-3_E), 80.9 (C-2_E), 80.8 (C-4_B), 80.3 (C-4_C), 80.1 (C-4_A), 79.2 (C-3_D), 79.1 (C-4_E), 78.0 (C-3_B),77.1 (C-3_C), 76.4, 75.8, 75.7, 75.4, 75.3, 75.2 (6C, C_{Bn}), 75.1 (C-3_A), 74.2 (C-2_A), 73.8 (C_{Bn}), 73.1 (C-4_D), 72.8 (C-2_C), 71.9 (C_{Bn}), 70.3 (C-5_E), 69.9 (C-2_B), 69.0 (C-5_B), 68.8 (C-5_A), 68.4 (C-6_E), 68.3 (C-5_C), 68.2 (C_{All}), 67.4 (C-5_D), 62.5 (C-6_D), 57.8 (C-2_D), 38.6 (CH_{2Lev}), 30.3 (CH_{3Lev}), 29.6 (C_{iPr}), 28.7 (CH_{2Lev}), 21.5 (C_{Ac}), 19.4 (C_{iPr}), 18.5 (C-6_C), 18.4 (C-6_A), 18.3 (C-6_B); HRMS (ESI$^+$) for $C_{101}H_{116}Cl_3NO_{26}$ ([M + Na]$^+$, 1886.6749) found *m/z* 1886.6445, ([M + NH_4]$^+$, 1881.7195) found *m/z* 1881.6897.

Allyl (3,4-Di-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-deoxy-4,6-*O*-isopropylidene-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-rhamnopyranoside (50). TMSOTf (61 μL, 340 μmol, 0.3 equiv) was added to a solution of acceptor **20** (1.7 g, 1.1 mmol) and trichloroacetimidate **23** (1.5 g, 1.7 mmol, 1.5 equiv) in toluene (35 mL) containing 4Å MS (975 mg), stirred at −40 °C. After 1 h, TLC (Tol/EtOAc, 8:2) showed the absence of **20**. Et_3N (0.2 mL) was added. The mixture was filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 95:5 → 70:30) gave, by order of elution, first **50** (1.45 g, 59%), and then diol **51** (505 mg, 21%), both as white foams. Hexasaccharide **50** had R_f = 0.45 (Tol/EtOAc, 8:2); ^{1}H NMR ($CDCl_3$) δ 7.47−7.10 (m, 50H, CH_{Ph}), 6.94 (d, 1H, $J_{NH,2}$ = 8.8 Hz, NH), 5.92 (m, 1H, CH=), 5.46 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 3.0 Hz, H-$2_{B'}$), 5.30 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.25−5.22 (m, 2H, H-1_E, =CH_2), 5.15−5.12 (m, 3H, H-1_A, $2H_{Bn}$), 5.11−5.09 (m, 2H, H-$1_{B'}$, H-2_C), 5.06 (d, 1H, J = 12.2 Hz, H_{Bn}), 4.98−4.93 (m, 3H, H_{Bn}), 4.89−4.83 (m, 3H, H_{Bn}), 4.81 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1_B), 4.72−4.58 (m, 10H, H-1_C, H_{Bn}, H-1_D), 4.54 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.45 (d, 1H, J = 11.3 Hz, H_{Bn}), 4.37 (d, 1H, J = 12.0 Hz, H_{Bn}), 4.24−4.14 (m, 5H, H-3_E, H-3_C, H_{All}, H-3_A, H-2_A, H-5_E), 4.07−3.86 (m, 9H, H-2_B, H-2_D, H_{All}, H-5_C, H-$5_{B'}$, H-3_B, H-$3_{B'}$, H-2_E, H-4_E), 3.80 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5_A), 3.74 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-5_B), 3.58 (dd, 1H, $J_{5,6a}$ = 5.2 Hz, H-6a_D), 3.56−3.43 (m, 8H, H-4_A, H-4_B, H-6a_E, H-6b_E, H-4_D, H-$4_{B'}$, H-4_C), 3.35 (m, 1H, $J_{6a,6b}$ = 10.4 Hz, H-6b_D), 2.82 (ddd, 1H, $J_{5,6b}$ = 1.5 Hz, $J_{4,5}$ = 9.7 Hz, H-5_D), 2.75−2.69 (m, 5H, $4H_{Lev}$, H-3_D), 2.21 (s, 3H, CH_{3Lev}), 2.14 (s, 3H, H_{Ac}), 1.44−1.43 (m, 9H, H_{iPr}, H-6$_A$), 1.39 (d_{po}, 3H, H-6$_{B'}$), 1.37 (d_{po}, 3H, H-6$_B$), 1.37 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_C$); ^{13}C NMR ($CDCl_3$) δ 206.3 (C_{Lev}), 171.8 (C_{Lev}), 169.6 (C_{Ac}), 162.0 (C_{NTCA}), 138.7−137.6 (C_{Ph}), 133.9 (CH=), 129.4−127.5 (CH_{Ph}), 117.2 (=CH_2), 101.2 (C-1_D, $^1J_{CH}$ = 163.9 Hz), 100.9 (C-1_A, $^1J_{CH}$ = 172.0 Hz), 99.4 (C_{iPr}), 99.0 (C-$1_{B'}$, $^1J_{CH}$ = 168.3 Hz), 98.0 (C-1_B, $^1J_{CH}$ = 168.7 Hz), 97.6 (C-1_C, $^1J_{CH}$ = 170.4 Hz), 94.3 (C-1_E, $^1J_{CH}$ = 167.5 Hz), 93.1 (CCl_3), 83.1 (C-3_E), 80.4, 80.1, 79.9, 79.7, 79.6, 79.0 (7C, C-3_B, C-$3_{B'}$, C-4_A, C-4_B, C-$4_{B'}$, C-4_C, C-4_E), 78.7 (C-3_D), 77.6 (C-2_E), 76.8 (C-3_C), 76.2, 75.4, 75.3, 75.2, 75.0, 74.9, 74.8 (7C, C_{Bn}), 74.3 (C-2_B), 74.2 (C-3_A), 73.5 (C_{Bn}), 73.4 (C-2_A), 72.6 (C-4_D), 72.1 (C-2_C), 72.0, 71.5 (2C, C_{Bn}), 69.9 (C-5_E), 69.4 (C-$2_{B'}$), 68.7 (C-5_A), 68.5 (C-$5_{B'}$), 68.0 (C-5_B), 67.9 (C-6_E), 67.8 (C-5_C), 67.7 (C_{All}), 67.0 (C-5_D), 61.8 (C-6_D), 57.4 (C-2_D), 38.2 (CH_{2Lev}), 29.9 (CH_{3Lev}), 29.2 (C_{iPr}), 28.2 (CH_{2Lev}), 21.2 (C_{Ac}), 19.1 (C_{iPr}), 18.3, 18.1, 18.0, 17.9 (4C, C-6_A, C-6_B, C-$6_{B'}$, C-6_C); HRMS (ESI$^+$) for $C_{121}H_{138}Cl_3NO_{30}$ ([M + H]$^+$, 2190.8447) found *m/z* 2190.8403, ([M + Na]$^+$, 2212.8267) found *m/z* 2212.8215.

Allyl (3,4-Di-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(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-rhamnopyranoside (51). TFA (50% aq, 8 mL) was added, at 0 °C, to a solution of hexasaccharide **50** (1.9 g, 880 μmol) in CH_2Cl_2 (30 mL), and the biphasic mixture was stirred vigorously at rt for 1 h. TLC (Tol/EtOAc, 7:3) showed the complete disappearance of **50** and the presence of a major more polar product. Repeated coevaporation with toluene, followed by chromatography of the residue (Tol/EtOAc, 8:2 → 6:4) provided diol **51** (1.7 g, 89%) as a white foam. The latter had R_f = 0.4 (Tol/EtOAc, 7:3); ^{1}H NMR ($CDCl_3$) δ 7.62−7.13 (m, 50H, CH_{Ph}), 7.04 (d, 1H, $J_{NH,2}$ = 8.6 Hz, NH), 5.94 (m, 1H, CH=), 5.53 (dd, 1H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H-$2_{B'}$), 5.44 (bs, 1H, H-1_A), 5.34 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.34 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1_E), 5.26 (m, 1H, J_{cis} = 10.4 Hz, =CH_2), 5.21 (d, 1H, J = 11.4 Hz, H_{Bn}), 5.19−5.11 (m, 3H, H_{Bn}, H-$1_{B'}$, H-2_C,), 5.13 (d, 1H, J = 12.7 Hz, H_{Bn}), 5.07−4.88 (m, 7H, H_{Bn}), 4.82−4.78 (m, 3H, $2H_{Bn}$, H-1_B), 4.75−4.58 (m, 9H, H_{Bn}, H-1_C), 4.56 (d, 1H, $J_{1,2}$ = 8.8 Hz, H-1_D), 4.45 (d, 1H, (d, 1H, J = 11.4 Hz, H_{Bn}), 4.43 (d, 1H, J = 11.9 Hz, H_{Bn}), 4.30−4.18 (m, 7H, H-3_C, H-2_A, H-3_A, H-3_E, H-5_E, H-2_B, H_{All}), 4.05−3.70 (m, 7H, H_{All}, H-2_D, H-3_B, H-$3_{B'}$, H-5_C, H-4_E, H-2_E), 3.88 (dq, 1H, $J_{4,5}$ = 9.4 Hz, H-$5_{B'}$), 3.81 (dq, 1H, $J_{4,5}$ = 9.6 Hz, H-5_B), 3.78 (dq, 1H, $J_{4,5}$ = 10.0 Hz, H-5_A), 3.72 (bd, 1H, $J_{6a,6b}$ = 11.3 Hz, H-6a_D), 3.61−3.52 (m, 5H, H-4_B, H-6a_E, H-6b_E, H-4_A, H-4_C), 3.48 (pt, 1H, $J_{3,4}$ = 9.4 Hz, H-$4_{B'}$), 3.12−3.08 (m, 2H, H-4_D, H-5_D), 3.05 (m, 1H, H-6b_D), 2.82−2.73 (m, 4H, H_{Lev}), 2.24 (s, 3H, CH_{3Lev}), 2.23 (s, 3H, H_{Ac}), 2.19 (m, 1H, H-3_D), 1.50 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6$_A$), 1.46 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_B$), 1.38 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6$_{B'}$), 1.37 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6$_C$); ^{13}C NMR ($CDCl_3$) δ 206.1 (C_{Lev}), 171.7 (C_{Lev}), 170.0 (C_{Ac}), 162.2 (C_{NTCA}), 138.8−137.6 (C_{Ph}), 133.9 (CH=), 129.4−127.5 (CH_{Ph}), 117.1 (=CH_2), 101.1 (C-1_D, $^1J_{CH}$ = 165.4 Hz), 100.2 (C-1_A, $^1J_{CH}$ = 175.4 Hz), 99.1 (C-$1_{B'}$, $^1J_{CH}$ = 171.8 Hz), 98.5 (C-1_C, $^1J_{CH}$ = 173.3 Hz), 98.3 (C-1_B, $^1J_{CH}$ = 168.3 Hz), 94.1 (C-1_E, $^1J_{CH}$ = 166.9 Hz), 93.3 (CCl_3), 87.2 (C-3_D), 83.1 (C-3_E), 80.6 (C-3_B), 80.5 (2C, C-2_E, C-4_B), 80.1 (C-$4_{B'}$), 79.7 (C-4_A), 79.5 (C-4_C), 78.8 (C-4_E), 77.7 (C-$3_{B'}$), 77.3 (C-3_C), 76.3 (C_{Bn}), 75.6 (C-5_D), 75.5, 75.4, 75.3, 75.0 (6C, C_{Bn}), 74.1, 74.0 (C-2_B, C-3_A), 73.5, 72.9 (2C, C_{Bn}), 72.1 (C-2_C), 71.4 (C_{Bn}),

71.3 (2C, C-2_A, C-4_D), 70.1 (C-5_E), 69.4 (2C, C-$2_{B'}$, C-5_C), 68.9 (C-5_A), 68.7 (C-$5_{B'}$), 68.4 (C-5_B), 68.0 (C-6_E), 67.6 (C_{All}), 62.8 (C-6_D), 55.5 (C-2_D), 38.2 (CH_{2Lev}), 29.9 (CH_{3Lev}), 28.3 (CH_{2Lev}), 21.1 (C_{Ac}), 18.1, 18.0, 17.8, 17.9 (4C, C-6_A, C-6_B, C-$6_{B'}$, C-6_C); HRMS (ESI^+) for $C_{118}H_{134}Cl_3NO_{30}$ ($[M + Na]^+$, 2172.7954) found *m/z* 2172.8081.

Allyl (3,4-Di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(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-rhamnopyranoside (52). A solution of hydrazine hydrate (158 *μ*L, 3.2 mmol, 10 equiv) in pyridine/acetic acid (3:2, v/v, 5 mL) was added to diol **51** (700 mg, 320 *μ*mol) in pyridine (3 mL). After 25 min at 0 °C, TLC (Tol/EtOAc, 7:3) showed the complete disappearance of the diol and the presence of a major more polar product. Water (10 mL) and CH_2Cl_2 (50 mL) were added, and the organic phase was washed with brine (3 × 20 mL), water (3 × 20 mL), dried on Na_2SO_4, filtered, and concentrated to dryness. Chromatography of the residue (Tol/EtOAc, 9:1 → 7:3) gave triol **52** (560 mg, 84%) as a white foam. Hexasaccharide **52** had R_f = 0.35 (Tol/EtOAc, 7:3); ^{1}H NMR ($CDCl_3$) *δ* 7.48−7.07 (m, 50H, CH_{Ph}), 7.02 (d, 1H, $J_{NH,2}$ = 8.6 Hz, NH), 5.90 (m, 1H, CH=), 5.40 (bs, 1H, H-1_A), 5.30 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1_E), 5.29 (m, 1H, J_{trans} = 17.2 Hz, =CH_2), 5.22 (m, 1H, J_{cis} = 10.4 Hz, =CH_2), 5.17 (d, 1H, J = 11.0 Hz, H_{Bn}), 5.16−5.12 (m, 3H, H-$1_{B'}$, H-2_C, H_{Bn}), 5.10 (d, 1H, J = 13.0 Hz, H_{Bn}), 5.04 (d, 1H, J = 12.8 Hz, H_{Bn}), 5.01 (d, 1H, J = 10.4 Hz, H_{Bn}), 4.93 (d, 1H, J = 10.9 Hz, H_{Bn}), 4.85−4.81 (m, 2H, H_{Bn}), 4.77−4.66 (m, 7H, $3H_{Bn}$, H-1_B, $3H_{Bn}$), 4.62−4.54 (m, 6H, $5H_{Bn}$, H-1_C), 4.51 (d, 1H, $J_{1,2}$ = 8.4 Hz, H-1_D), 4.38 (d, 1H, J = 11.9 Hz, H_{Bn}), 4.23−4.13 (m, 7H, H-2_B, H-3_C, H-3_E, H-3_A, H_{All}, H-5_E, H-2_A), 4.07 (dd, 1H, H-$2_{B'}$), 4.00−3.87 (m, 6H, H_{All}, H-2_D, H-3_B, H-5_C, H-4_E, H-2_E), 3.84−3.81 (m, 1H, H-$3_{B'}$, $J_{2,3}$ = 2.4 Hz, $J_{3,4}$ = 9.1 Hz, H-$5_{B'}$), 3.78−3.69 (m, 2H, H-5_B, H-5_A), 3.65 (bd, 1H, $J_{6a,6b}$ = 11.2 Hz, H-$6a_D$), 3.55−3.49 (m, 5H, H-$6a_E$, H-$6b_E$, H-4_B, H-4_A, H-$4_{B'}$), 3.47 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4_C), 3.06−3.04 (m, 2H, H-4_D, H-5_D), 2.94 (dd, 1H, $J_{5,6b}$ = 5.7 Hz, H-$6b_D$), 2.20 (s, 3H, H_{Ac}), 2.15 (m, 1H, H-3_D), 1.46 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), 1.42 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_B), 1.33−1.30 (m, 6H, H-6_C, H-$6_{B'}$); ^{13}C NMR ($CDCl_3$) *δ* 170.0 (C_{Ac}), 162.3 (C_{NTCA}), 138.7−137.4 (C_{Ph}), 133.8 (CH=), 129.4−127.4 (CH_{Ph}), 117.1 (=CH_2), 101.1 (C-1_D, $^1J_{CH}$ = 161.0 Hz), 100.6 (C-$1_{B'}$, $^1J_{CH}$ = 171.0 Hz), 100.1 (C-1_A, $^1J_{CH}$ = 174.7 Hz), 98.3 (C-1_C, $^1J_{CH}$ = 170.4 Hz), 98.2 (C-1_B, $^1J_{CH}$ = 170.4 Hz), 94.0 (C-1_E, $^1J_{CH}$ = 163.1 Hz), 93.1 (CCl_3), 87.1 (C-3_D), 83.1 (C-3_E), 80.5 (C-3_B), 80.4 (C-4_B), 80.3 (C-2_E), 80.0 (C-4_A), 79.7 (2C, C-$3_{B'}$, C-$4_{B'}$), 79.4 (C-4_C), 78.7 (C-4_E), 77.7 (C-3_C), 76.3 (C_{Bn}), 75.5 (C-5_D), 75.4, 75.4, 75.3, 75.0, 74.9 (6C, C_{Bn}), 74.1 (C-2_A), 73.9 (C-3_A), 73.5, 72.8 (2C, C_{Bn}), 72.0 (C-2_C), 71.7 (C_{Bn}), 71.3 (C-4_D), 71.0 (C-2_B), 70.0 (C-5_E), 69.1 (C-5_C), 68.8 (2C, C-$2_{B'}$, C-5_A), 68.4, 68.3 (2C, C-5_B, C-$5_{B'}$), 67.8 (C-6_E), 67.6 (C_{All}), 62.7 (C-6_D), 55.3 (C-2_D), 21.2 (C_{Ac}), 18.0, 17.8 (4C, C-6_A, C-6_B, C-$6_{B'}$, C-6_C); HRMS (ESI^+) for $C_{113}H_{128}Cl_3NO_{28}$ ($[M + Na]^+$, 2074.7585) found *m/z* 2074.7581, ($[M + NH_4]^+$, 2069.8032) found *m/z* 2069.7925.

Propyl α-L-Rhamnopyranosyl-(1→3)-(2-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-[α-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (5). Hexasaccharide **52** (400 mg, 195 *μ*mol) was dissolved in EtOH (20 mL), treated with 10% Pd/C catalyst (400 mg), and the suspension was stirred at rt for 10 days, under a hydrogen atmosphere (45 bar). TLC (*i*PrOH/H_2O/NH_3, 4:1:0.5 and Tol/EtOAc, 7:3) showed that **52** had been transformed into a more polar product. The suspension was filtered on 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 acetate **5** (131 mg, 64%) as a white foam. Hexasaccharide **5** had R_f = 0.65 (*i*PrOH/H_2O/NH_3, 4:1:0.5); HPLC (215 nm): t_R = 13.3 min (Kromasil 5 *μ*m C-18 100Å 4.6 × 250 mm analytical column, using a 0−40% linear gradient over 20 min of CH_3CN in 0.01 M aq TFA at 1 mL min^{-1} flow rate); ^{1}H NMR (D_2O) *δ* 5.10 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1_E), 5.00 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1_A), 4.91 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 3.1 Hz, H-2_C), 4.89 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-$1_{B'}$), 4.80 (bs, 2H, H-1_B, H-1_C), 4.71 (d, 1H, H-1_D), 4.35 (dd, 1H, $J_{2,3}$ = 2.6 Hz, H-2_A), 4.00 (dq, 1H, $J_{4,5}$ = 9.7 Hz, $J_{5,6}$ = 6.2 Hz, H-5_C), 3.95 (m, 1H, H-5_E), 3.93 (dd, 1H, $J_{2,3}$ = 3.4 Hz, H-$2_{B'}$), 3.89−3.51 (m, 14H, H-3_C, H-2_B, H-3_A, H-$6a_D$, H-2_D, H-3_B, H-3_E, H-$6a_E$, H-$6b_E$, H-5_A, H-$6b_D$, H-2_E, H-5_B, H-$3_{B'}$, H_{Pr}), 3.49 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4_C), 3.46−3.30 (m, 8H, H-4_D, H_{Pr}, H-$5_{B'}$, H-4_E, H-4_B, H-$4_{B'}$, H-5_D, H-3_D), 3.26 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4_A), 2.08 (s, 3H, H_{Ac}), 2.03 (s, 3H, H_{NAc}), 1.54−1.47 (m, 2H, CH_2), 1.22−1.13 (m, 12H, H-6_B, H-6_A, H-$6_{B'}$, H-6_C), 0.82 (t, 3H, J = 7.4 Hz, CH_3); ^{13}C NMR (D_2O) *δ* 174.4 (C_{NAc}), 173.2 (C_{Ac}), 102.7 (C-$1_{B'}$, $^1J_{CH}$ = 170.6 Hz), 101.4 (C-1_D, $^1J_{CH}$ = 166.0 Hz), 101.2 (C-1_A, $^1J_{CH}$ = 173.5 Hz), 98.4 (C-1_C, $^1J_{CH}$ = 167.8 Hz), 98.1 (C-1_B, $^1J_{CH}$ = 171.5 Hz), 94.2 (C-1_E, $^1J_{CH}$ = 172.8 Hz), 82.6 (C-3_D), 79.1(C-2_B), 77.0 (C-3_C), 76.0 (C-5_D), 74.1 (C-2_A), 73.3 (C-3_A), 73.0 (C-3_E), 72.4 (C-2_C), 71.9 (C-4_B), 71.7 (C-$4_{B'}$), 71.3, 71.2, 71.1 (C-5_E, C-2_E, C-4_C), 70.7 (C-4_A), 70.1 (C-$3_{B'}$), 69.9 (2C, C-$2_{B'}$, C-3_B), 69.7 (C_{Pr}), 69.4, 69.3 (3C, C-4_E, C-5_A, C-$5_{B'}$), 68.8 (C-5_C), 68.6 (C-5_B), 68.1 (C-4_D), 60.6 (C-6_D), 60.3 (C-6_E), 55.3 (C-2_D), 22.7 (C_{NAc}), 21.9 (CH_2), 20.2 (C_{Ac}), 16.8, 16.6, 16.5, 16.3 (4C, C-6_A, C-6_B, C-$6_{B'}$, C-6_C), 9.8 (CH_3); HRMS (ESI^+) for $C_{43}H_{73}NO_{28}$ ($[M + H]^+$, 1052.4397) found *m/z* 1052.4360, ($[M + Na]^+$, 1074.4216) found *m/z* 1074.4202.

Allyl (3,4-Di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(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-rhamnopyranoside (53). Methanolic MeONa (0.5 M, 745 *μ*L, 370 *μ*mol, 1 equiv) was added to a solution of diol **51** (800 mg, 370 *μ*mol) in MeOH (20 mL), and the mixture was refluxed for 1 h. TLC (Tol/EtOAc, 6:4) showed the complete disappearance of the diol 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 chromatographied (Tol/EtOAc, 8:2 → 7:3) to give **53** (688 mg, 92%) as a white foam. Hexasaccharide **53** had R_f = 0.45 (Tol/EtOAc, 6:4); ^{1}H NMR ($CDCl_3$) *δ* 7.44−7.05 (m, 50H, CH_{Ph}), 6.86 (d, 1H, $J_{NH,2}$ = 8.6 Hz, NH), 5.89 (m, 1H, CH=), 5.36 (bs, 1H, H-1_A), 5.31−5.25 (m, 2H, =CH_2, H-1_E), 5.21 (m, 1H, J_{cis} = 10.4 Hz, =CH_2), 5.17 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-$1_{B'}$), 5.14 (d, 1H, J = 11.1 Hz, H_{Bn}), 5.08 (m, 1H, J = 11.1 Hz, H_{Bn}), 5.03−4.90 (m, 4H, H_{Bn}), 4.82 (d, 1H, J = 11.0 Hz, H_{Bn}), 4.74−4.52 (m, 13H, H-1_B, H_{Bn}), 4.50 (d, 1H, $J_{1,2}$ = 8.4 Hz, H-1_D), 4.47 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1_C), 4.38 (d, 1H, J = 11.9 Hz, H_{Bn}), 4.19 (dd, 1H, $J_{1,2}$ = 2.1 Hz, $J_{2,3}$ = 2.4 Hz, H-2_B), 4.17−4.12 (m, 5H, H_{All}, H-5_E, H-3_E, H-3_A, H-2_A), 4.06−4.03 (m, 2H, H-3_C, H-$2_{B'}$), 3.99−3.82 (m, 9H, H_{All}, H-2_C, H-2_D, H-3_B, H-5_C, H-$5_{B'}$, H-4_E, H-2_E, H-$3_{B'}$), 3.78−3.70 (m, 2H, H-5_B, H-5_A), 3.65 (bd, 1H, $J_{6a,6b}$ = 11.4 Hz, H-$6a_D$), 3.59−3.45 (m, 6H, H-$4_{B'}$, H-$6a_E$, H-$6b_E$, H-4_B, H-4_A, H-4_C), 3.08−3.03 (m, 2H, H-5_D, H-4_D), 2.94 (m, 1H, H-$6b_D$), 2.23 (dd, 1H, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 7.7 Hz, H-3_D), 1.44 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-$6_{B'}$), 1.43 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6_A), 1.40 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_B), 1.32 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6_C); ^{13}C NMR ($CDCl_3$) *δ* 161.9 (C_{NTCA}), 138.7−137.5 (C_{Ph}), 133.9 (CH=), 129.1−127.3 (CH_{Ph}), 117.1 (=CH_2), 101.0 (C-1_D, $^1J_{CH}$ = 162.7 Hz), 100.8 (C-1_C, $^1J_{CH}$ = 169.2 Hz), 100.1 (C-1_A, $^1J_{CH}$ = 180.3 Hz), 100.0 (C-$1_{B'}$, $^1J_{CH}$ = 180.3 Hz), 98.3 (C-1_B, $^1J_{CH}$ = 170.3 Hz), 94.0 (C-1_E, $^1J_{CH}$ = 168.6 Hz), 93.2 (CCl_3), 86.5 (C-3_D), 83.0 (C-3_E), 80.5 (C-3_B), 80.4 (2C, C-2_E, C-4_B), 79.8, 79.7, 79.6 (4C, C-4_A, C-$3_{B'}$, C-$4_{B'}$, C-4_C), 78.8 (C-4_E), 78.3 (C-3_C), 76.3 (C_{Bn}), 75.5 (C-5_D), 75.4, 75.3, 75.2, 74.9 (6C, C_{Bn}), 74.0 (C-3_A), 73.8 (C-2_A), 73.5, 72.8, 72.0 (3C, C_{Bn}), 71.3 (C-2_B), 71.1 (C-4_D), 70.4 (C-2_C), 70.0 (C-5_E), 68.9 (C-5_C), 68.8 (2C, C-5_A, C-$2_{B'}$), 68.7 (C-$5_{B'}$), 68.3 (C-5_B), 67.9 (C-6_E), 67.6 (C_{All}), 62.7 (C-6_D), 55.8 (C-2_D), 18.1, 18.0, 17.8 (4C, C-6_A, C-6_B, C-$6_{B'}$, C-6_C); HRMS (ESI^+) for $C_{111}H_{126}Cl_3NO_{27}$ ($[M + Na]^+$, 2032.7480) found *m/z* 2032.7448.

Propyl α-L-Rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-(2-acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-[α-D-

glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (6). Hexasaccharide **53** (580 mg, 289 μmol) was dissolved in EtOH (15 mL), treated with 10% Pd/C catalyst (340 mg), and the suspension was stirred at rt for 10 days, under a hydrogen atmosphere (45 bar). TLC (*i*PrOH/H_2O/NH_3, 4:1:0.5 and Tol/EtOAc, 6:4) showed that **53** had been transformed into a more polar product. The suspension was filtered on 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 **6** (240 mg, 82%) as a white foam. Hexasaccharide **6** had $R_f = 0.2$ (*i*PrOH/H_2O/NH_3, 4:1:0.5); HPLC (215 nm): $t_R = 13.4$ min (Kromasil 5 μm C-18 100Å 4.6 × 250 mm analytical column, using a 0−40% linear gradient over 20 min of CH_3CN in 0.01 M aq TFA at 1 mL min^{-1} flow rate); ^1H NMR (D_2O) δ 5.20 (d, 1H, $J_{1,2} = 3.7$ Hz, H-1_E), 5.10 (d, 1H, $J_{1,2} = 1.6$ Hz, H-1_A), 5.01 (d, 1H, $J_{1,2} = 1.2$ Hz, H-$1_{B'}$), 4.90 (bs, 1H, H-1_B), 4.84 (d, 1H, $J_{1,2} = 1.9$ Hz, H-1_C), 4.83 (d, 1H, $J_{1,2} = 9.5$ Hz, H-1_D), 4.44 (dd, 1H, $J_{2,3} = 2.1$ Hz, H-2_A), 4.07−3.99 (m, 3H, H-$2_{B'}$, H-5_E, H-5_C), 3.96−3.93 (m, 2H, H-2_B, H-3_A), 3.92−3.68 (m, 14H, H-$6a_D$, H-2_C, H-2_D, H-3_B, H-3_E, H-$3_{B'}$, H-$6a_E$, H-$6b_E$, H-3_C, H-5_B, H-5_A, H-$6b_D$, H-2_E, H-$5_{B'}$), 3.64 (dt, $J = 9.8$ Hz, $J = 6.9$ Hz, H_{Pr}), 3.55−3.38 (m, 8H, H_{Pr}, H-4_C, H-4_D, H-4_E, H-3_D, H-4_B, H-$4_{B'}$, H-5_D), 3.35 (pt, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4_A), 2.11 (s, 3H, H_{NAc}), 1.65−1.56 (m, 2H, CH_2), 1.31 (d, 3H, $J_{5,6} = 6.3$ Hz, H-6_B), 1.28 (d, 3H, $J_{5,6} = 6.3$ Hz, H-$6_{B'}$), 1.26 (d, 3H, $J_{5,6} = 6.3$ Hz, H-6_A), 1.23 (d, 3H, $J_{5,6} = 6.3$ Hz, H-6_C), 0.91 (t, 3H, $J = 7.4$ Hz, CH_3); ^{13}C NMR (D_2O) δ 174.0 (C_{NAc}), 102.4 (C-$1_{B'}$, $^1J_{CH} = 171.2$ Hz), 101.5 (C-1_D, $^1J_{CH} = 163.6$ Hz), 101.3 (C-1_C, $^1J_{CH} = 169.8$ Hz), 101.2 (C-1_A, $^1J_{CH} = 169.8$ Hz), 98.2 (C-1_B, $^1J_{CH} = 170.5$ Hz), 94.4 (C-1_E, $^1J_{CH} = 171.2$ Hz), 81.7 (C-3_D), 79.1(C-2_B), 78.1 (C-3_C), 76.0 (C-5_D), 74.2 (C-2_A), 73.5 (C-3_A), 73.2 (C-3_E), 72.2 (C-4_B), 72.0 (C-$4_{B'}$), 71.4 (C-5_E), 71.3 (C-2_E) 71.3 (C-4_C), 70.8 (C-4_A), 70.5 (C-2_C), 70.2 (C-$3_{B'}$), 70.2 (C-$2_{B'}$), 70.0 (C-3_B), 69.8 (C_{Pr}), 69.5 (C-4_E), 69.4 (C-5_A), 69.0 (2C, C-5_C, C-5_B), 68.7 (C-$5_{B'}$), 68.3 (C-4_D), 60.7 (C-6_D), 60.4 (C-6_E), 55.5 (C-2_D), 22.6 (C_{NAc}), 21.9 (CH_2), 16.8, 16.7, 16.5 (4C, C-6_A, C-6_B, C-$6_{B'}$, C-6_C), 9.9 (CH_3); HRMS (ESI^+) for $C_{41}H_{71}NO_{27}$ ($[M + H]^+$, 1010.4292) found *m*/*z* 1010.4295, ($[M + Na]^+$, 1032.4111) found *m*/*z* 1032.4116.

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Supporting Information Available: General experimental procedures, ^1H, ^{13}C, and HMBC NMR spectra for compounds **1**−**6**, **10**−**12**, **15**, **16**, **19**−**21**, **23**, **25**, **28**−**32**, **37**, **44**, **45**, **47**, **48**, **50**−**53**. This material is available free of charge via the Internet at http://pubs.acs.org.

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