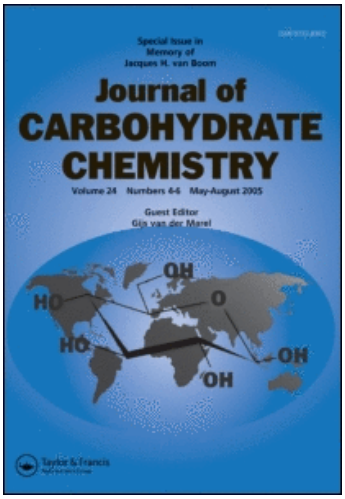

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Mulard, Laurence A. and Ughetto-Monfrin, Joël(2000) 'First Synthesis of A Branched Pentasaccharide Representative of The Repeating Unit of The *Shigella Flexneri* Serotype 5A *O*-Antigen', Journal of Carbohydrate Chemistry, 19: 2, 193 — 220

To link to this Article: DOI: 10.1080/07328300008544074

URL: http://dx.doi.org/10.1080/07328300008544074

J. CARBOHYDRATE CHEMISTRY, 19(2), 193–220 (2000)

FIRST SYNTHESIS OF A BRANCHED PENTASACCHARIDE REPRESENTATIVE OF THE REPEATING UNIT OF THE *Shigella flexneri* SEROTYPE 5a *O*-ANTIGEN[1]

Laurence A. Mulard* and Joël Ughetto-Monfrin

Unité de Chimie Organique, BGM, Institut Pasteur, 28 rue du Dr. Roux, 75724 Paris Cedex 15, France. E-mail: lmulard@pasteur.fr

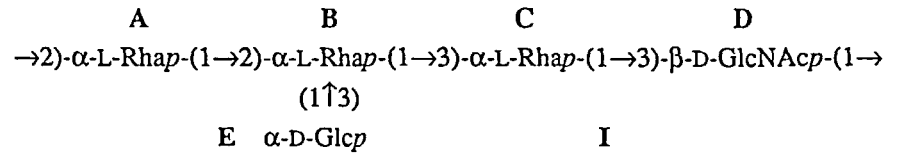
Received August 9, 1999 - Final Form December 7, 1999

ABSTRACT

Based on the use of a 2-deoxy-2-trichloroacetamido-D-glucopyranosyl donor, a stepwise synthesis of methyl α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl- (1→2)-α-L- rhamnopyranosyl-(1→2)- [α-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranoside (**CDA(E)B-OMe, 3**) is described. This branched pentasaccharide constitutes a methyl glycoside representative of the repeating unit of the *O*-antigen of *Shigella flexneri* serotype 5a. Two routes to **3** were undertaken. Route 1 involved the coupling of a rhamnopyranosyl trichloroacetimidate (**7**) to a **DA(E)B** acceptor bearing an *N*-trichloroacetyl functionality at position 2 of residue **D**. Transformation of the trichloroacetamide moiety into an acetamide group was performed either by radical dechlorination or by catalytic hydrogenation. In route 2, the latter conversion was performed at the tetrasaccharide stage by Zemplén deacylation and subsequent acetylation of the free amino group. Coupling of the resulting **DA(E)B** to **7** gave the fully protected 2-acetamido pentasaccharide intermediate. The reactivity of the two tetrasaccharide acceptors differed, the acetamido one requiring harsher coupling conditions. Besides, when performed at the tetrasaccharide stage, conversion of the trichloroacetamide group into the desired acetamide group was rather delicate. For these reasons, route 1 was preferred. In any case, distortion of several signals in the ^{13}C NMR spectra of many synthetic intermediates showed that steric hindrance had a major impact on the outcome of the glycosylation steps.

INTRODUCTION

Since the development of the first carbohydrate-based vaccine against *Haemophilus influenza* type b (Hib) suitable for use in infants,[2] the glycoconjugate approach to human vaccines against encapsulated bacteria has gained wide use.[3,4] Furthermore, increasing evidence supports the hypothesis that humoral antibodies against the *O*-specific polysaccharide (*O*-SP) component of surface lipopolysaccharides (LPSs) may confer protective immunity in humans.[5] Indeed, the potential for vaccine development of various *O*-SP:protein conjugates has been demonstrated for several human enteropathogenic bacteria.[6] Nevertheless, despite parallel studies in this direction, our understanding of the important features necessary for optimal immunogenicity of glycoconjugate vaccine constructs still needs improvement.[7] Recently, it has been demonstrated that the presence of a secretory IgA antibody, IgA C5, specific for an epitope located on the *O*-antigen of the model bacterium *Shigella flexneri* serotype 5a, is sufficient to confer protection if present locally prior to infection.[8] These results suggest that the characterisation of the saccharidic motif recognised by IgA C5 could provide the basis for developing a synthetic vaccine against this pathogen. In fact, a possible substitute approach to the use of *O*-SP:protein conjugates as human vaccines could be the development of multivalent constructs involving immunogenic mimics of the antigenic polysaccharides. Approaches based on carbohydrate as well as non-carbohydrate mimics of the *O*-antigen are under study in our laboratory, on the model *Shigella flexneri* serotype 5a.[9] In particular, to help our understanding of the optimal features necessary for the optimization of such constructs, we are investigating the molecular specificity of the complementarity between the *O*-SP and homologous protective antibodies, among which is the IgA C5. Our approach relies, for the most part, on the availability in rather large quantities of synthetic saccharidic haptens representative of the *O*-SP of *S. flexneri* serotype 5a. Thus, in spite of the large amount of synthetic work on fragments of the *O*-SP of various bacteria of the *Shigella flexneri* family reported before by D. R. Bundle's group[10,11] and N. K. Kochetkov's group,[12,13] the synthesis of the required oligosaccharides was undertaken.



The repeating unit of the *O*-SP of *S. flexneri* serotype 5a is the branched pentasaccharide[14,15] **I**, composed of α-linked L-rhamnose, β-linked 2-acetamido-2-deoxy-D-glucose and α-D-glucose branches.

α-L-Rha*p*-(1→2)-[α-D-Glc*p*(1→3)]-α-L-Rha*p*-OMe
1 **A(E)B-OMe**

β-D-GlcNAc*p*-(1→2)-α-L-Rha*p*-(1→2)-[α-D-Glc*p*(1→3)]-α-L-Rha*p*-OMe
2 **DA(E)B-OMe**

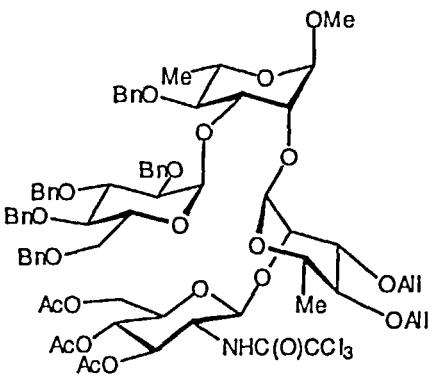
α-L-Rha*p*-(1→3)-β-D-GlcNAc*p*-(1→2)-α-L-Rha*p*-(1→2)-[α-D-Glc*p*(1→3)]-α-L-Rha*p*-OMe
3 **CDA(E)B-OMe**

In the first paper in this series,[16] we reinvestigated the preparation of the already known methyl glycosides **1**[17,18] and **2**[13,19] of the branched tri- and tetrasaccharide fragments **A(E)B** and **DA(E)B**, respectively. The synthesis of methyl glycoside derivatives was preferred to allow binding and structural studies in solution. As part of this project, we report here on the synthesis of the methyl glycoside of the branched pentasaccharide **CDA(E)B (3)**. To our knowledge, this is the first reported synthesis of any pentasaccharide representative of the repeating unit of *S. flexneri* serotype 5a *O*-SP. Also included is a simplified approach to compound **2**.

RESULTS AND DISCUSSION

The approach used in this study was based on the knowledge gained from the synthesis of the trisaccharide **1** and tetrasaccharide **2**.[16] Basically, previous results had shown that one of the major problems encountered during the preparation of compounds **1** and **2** was the apparent lack of reactivity of the *HO*-2 of rhamnoses **A** and **B** during the glycosylation steps. Furthermore, kinetics and NMR analysis suggested that steric hindrance had a major impact on the outcome of attempted glycosylations at these positions. For these reasons, we had anticipated that the stepwise introduction of each residue at the non reducing end of the molecule would be a more reasonable approach to the target **3** than the building block strategy. Thus, the synthesis reported here involves the construction of appropriately chosen heterofunctional monosaccharide intermediates, which were then combined according to a linear strategy.

Actually, a key intermediate to the synthesis of pentasaccharide **3** is the fully protected tetrasaccharide **4**, previously described as a precursor to tetrasaccharide **2**.[16] The intermediate **4** was designed in order to minimise steric hindrance at all glycosylation sites. Briefly, relevant features that should be kept in mind were (i) the introduction of the allyl moiety, as a relatively non-bulky protecting group at positions 3 and 4 of rhamnose **A**, (ii) the choice of the trichloroacetamide functionality as a participating group at position 2 of residue **D**.[20] As its glucosaminyl residue is the only one to comprise ester protecting groups, the crucial intermediate **4** is highly suitable for further chain elongation. In fact,



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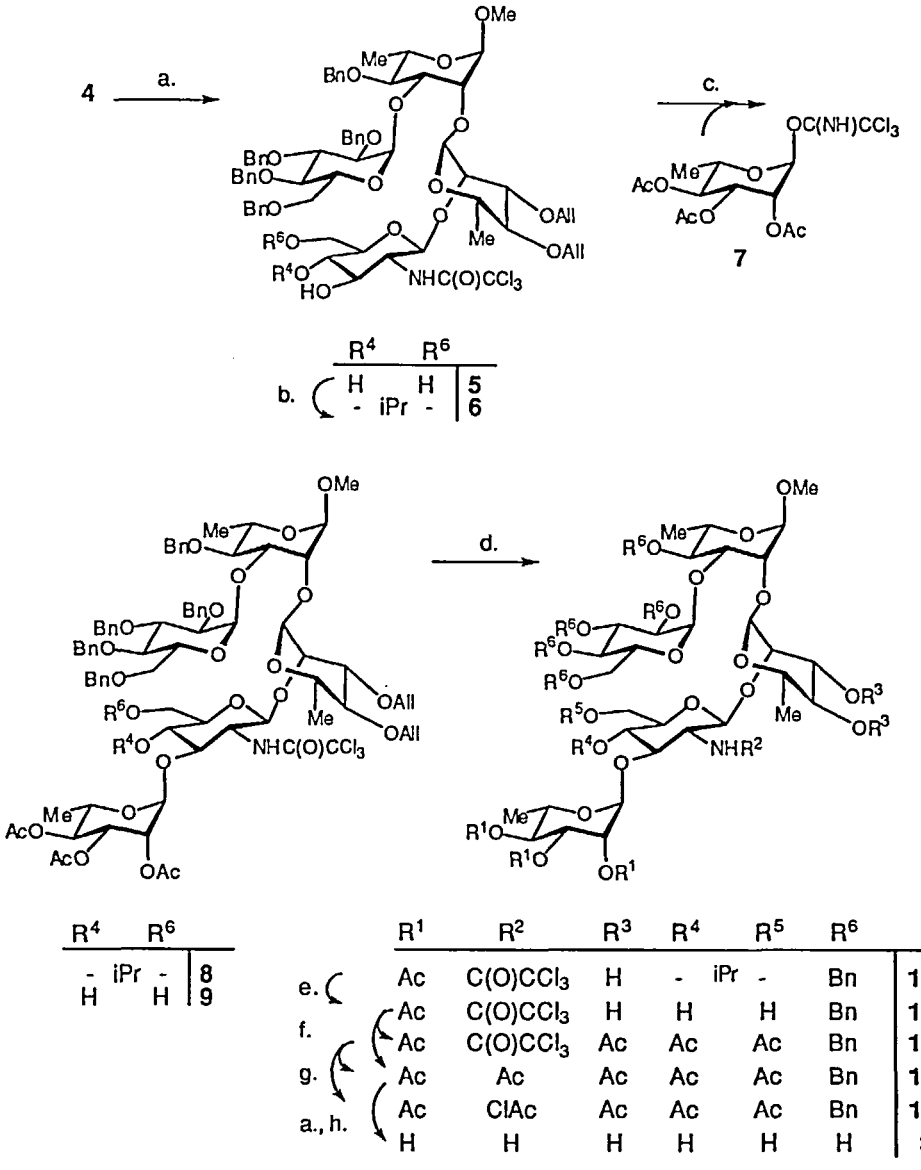
starting from **4**, two routes to the target pentasaccharide **3** were developed. In route 1, rhamnose **C** was introduced at the nonreducing end of a tetrasaccharide precursor still comprising a 2-*N*-trichloroacetyl functionality, whereas in route 2, transformation of the trichloroacetamide protecting group into the corresponding acetamide moiety was performed at the tetrasaccharide stage.

In route 1 (Scheme 1), the first stage of the synthesis was the selective removal, under Zemplén conditions, of the acetyl groups in tetrasaccharide **4** to give the triol **5** in 95% yield. Control of the kinetics of the reaction was necessary in order to avoid the formation of side-products, resulting from partial deblocking of the trichloroacetamide moiety. Next, the triol **5** was selectively isopropylidenated at positions 4 and 6 of the glucosaminyl residue by reaction with 2,2-dimethoxypropane under acid catalysis to give **6** (87%). Coupling of the resulting glycosyl acceptor **6** and the trichloroacetimidate donor[21] **7** was performed in the presence of a catalytic amount of trimethylsilyl trifluoromethanesulfonate (TMSOTf) using diethyl ether as the solvent. Under careful control, the condensation proceeded smoothly to give the fully protected pentasaccharide **8** in a yield of 84%. Still, partial loss of the isopropylidene acetal could hardly be avoided and the diol **9** was also isolated in 10% yield. In fact, when the condensation was run overnight, the only isolated material was the diol **9** (83%). That no glycosylation product at position 6 of the glucosaminyl residue was isolated ascertained that condensation at position 3 of the nonreducing end residue occurred first. The α-interglycosidic linkage for residue **C** in compound **8** was indicated by the $^{1}J_{C\text{-}1,H\text{-}1}$ heteronuclear coupling constant for the rhamnopyranosyl unit of 173 Hz. Next, the key intermediate **8** was submitted to stepwise deprotection. Direct conversion of the *N*-trichloroacetyl group into the corresponding *N*-acetyl group can be performed either by radical dechlorination mediated by tributyl stannane[22] or by catalytic hydrogenation. None of these pathways is compatible with the presence of allyl groups,[16] which for that reason were removed first. Isomerisation of the allyl groups to the corresponding prop-1-enyl groups, achieved using

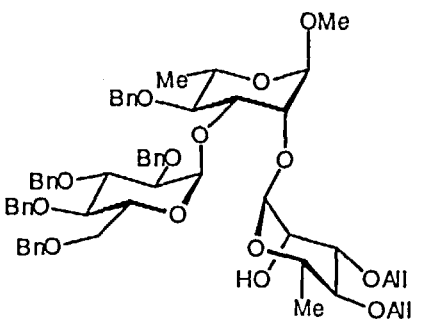


(a) MeONa, MeOH; (b) $Me_2C(OMe)_2$, H^+; (c) TMSOTf, Et_2O; (d) i. Ir(I), THF; ii. HgO, $HgBr_2$, Acetone/ H_2O; (e) CF_3CO_2H 50% aq; (f) Ac_2O, Pyr; (g) Bu_3SnH, AIBN, $PhCH_3$; (h) H_2, Pd/C.

Scheme 1

[1,5-cyclooctadiene-bis(methyldiphenylphosphine)-iridium]hexafluorophosphate complex as the promoter,[23] and subsequent hydrolysis with mercury(II) bromide:mercury(II) oxide[24] gave the diol **10** in an overall yield of 79%. Attempted deallylation of **8** with palladium dichloride[25,26] did not prove any better (not described). Next, trifluoroacetic acid hydrolysis of the isopropylidene acetal gave the tetraol **11** (64% from **8**).

Starting from **11**, two ways to the target pentasaccharide **3** were considered. In the first approach, compound **11** was fully acetylated. Surprisingly, when run at rt, the reaction led to two compounds of close mobility (TLC, cyclohexane : ethyl acetate, 3:2). Mass spectrometric analysis showed that the slower moving product was lacking one acetyl group and that the faster moving one was the required heptaacetate **12**. Unless heated, acetylation did not go to completion. But when acetylation of **11** was performed at 70 °C, the fully protected **12** was isolated in a yield of 97%. This behaviour was related to the distorted signals observed repeatedly in the ^{13}C NMR spectra of several of the synthetic intermediates. As a general rule, the most apparent distortions occurred for carbons C-1_E, C-2_B, C-3_B, and C-4_B as well as to a lesser extent, for carbon C-1_A, of the fully and partially protected tetra- and pentasaccharides. This phenomenon was noted previously[16] as a consequence of the introduction of the glucosaminyl residue at the reducing end of the trisaccharide[16] **15**. A tentative explanation of this apparent perturbation of the overall conformation of these intermediates is steric hindrance, most probably generated at the branching point. That heating renders possible the completion of the acetylation of **11** is in total agreement with the fact that steric constraint, and the apparent inaccessibility of selected hydroxyl groups, should diminish upon heating. Next, radical dechlorination of the trichloroacetamide **12**, using tributyltin hydride in the presence of a catalytic amount of 2,2'-azobis(2-methylpropionitrile) (AIBN), resulted in the required *N*-acetylated pentasaccharide **13** (67%). As observed previously,[16] this step was somewhat unpredictable. As the reaction did not go to completion, the monochloroacetamide **14** was isolated as well (23%). Lastly, compound **13** was fully deprotected by (i) transesterification (MeONa-MeOH), and (ii) hydrogenolysis using Pd/C as a catalyst into the free pentasaccharide **3** (69%).



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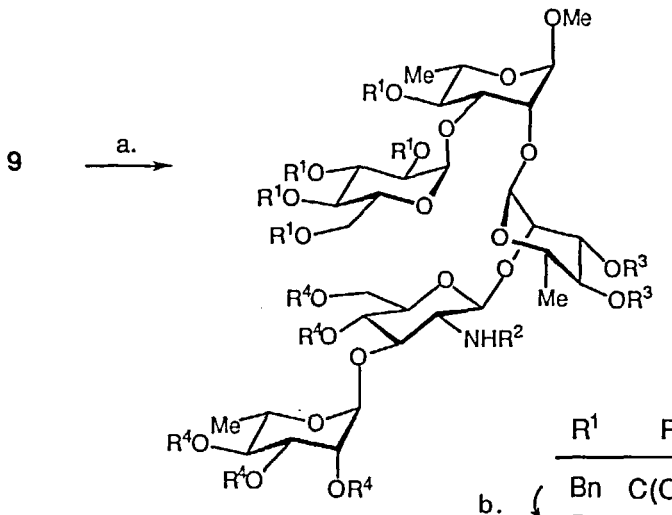
The second approach (Scheme 2), also applicable to the tetraol **11**, is illustrated in the following, starting from the side-product **9** isolated during the glycosylation step. Thus,



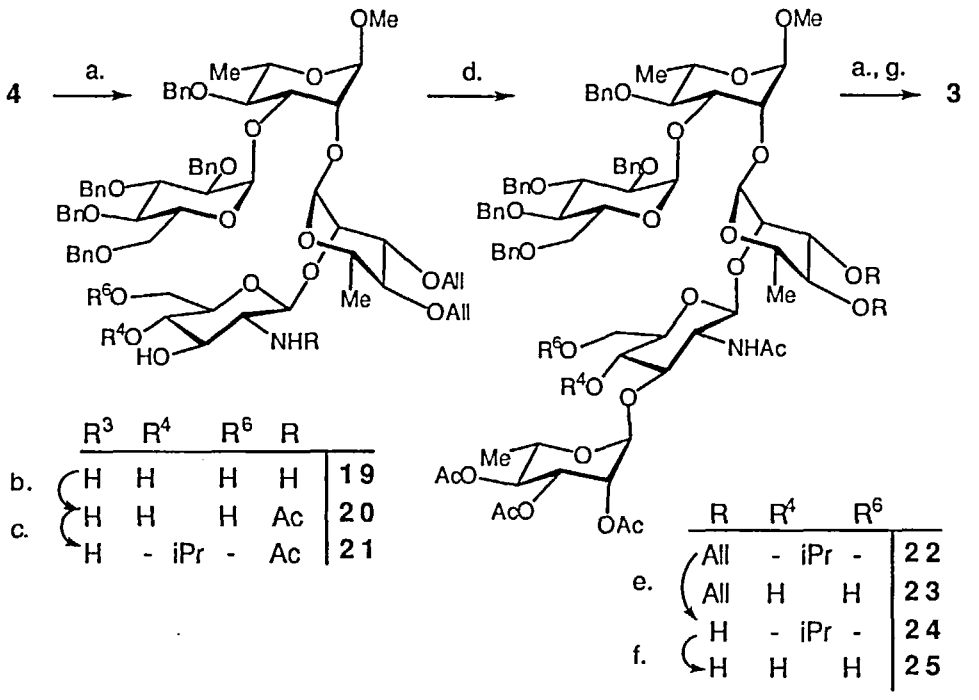
	R1	R2	R3	R4	
b.	Bn	$C(O)CCl_3$	All	Ac	16
c.	Bn	$C(O)CCl_3$	H	Ac	17
d.	Bn	$C(O)CCl_3$	H	H	18
	H	Ac	H	H	3

(a) Ac_2O, Pyr; (b) $PdCl_2$, NaOAc, H_2O; (c) MeONa, MeOH; (d) H_2, Pd/C.

Scheme 2

diol **9** was first acetylated as described above to give the pentaacetate **16** (94%). Deallylation of the latter using palladium dichloride[25,26] gave the diol **17** (59%), which was submitted to Zemplén transesterification to yield the heptaol **18** (81%). Lastly, compound **18** underwent a two step catalytic hydrogenation using Pd/C as the catalyst. Debenzylation was performed as usual in a 4:1 methanol:acetic acid mixture. Under such conditions, previous results had shown that the trichloroacetimidate moiety had turned into the corresponding monochloroacetamide functionality (not described). In order to complete the dechlorination step, a slightly basic medium was required. Thus, the latter reduction was run in the presence of triethylamine and the target pentasaccharide **3** was isolated in a 45% yield after purification by reverse phase chromatography.

In route 2 (Scheme 3), the *N*-acetylated tetrasaccharide **21** was used as the acceptor. Thus, treatment of the key intermediate **4** in a 1N methanolic sodium methoxide solution led to the complete removal of both the acetyl and trichloroacetyl protecting groups, to give the aminotriol **19** (58%). On the contrary, treatment of the pentasaccharide



(a) MeONa, MeOH; (b) Ac_2O, MeOH; (c) $Me_2C(OMe)_2$, H^+ ; (d) **7**, $BF_3.OEt_2$, Et_2O; (e) i. Ir(I), THF ; ii. HgO, $HgBr_2$, acetone/H_2O; (f) CF_3CO_2H 50% aq; (g) H_2, Pd/C.

Scheme 3

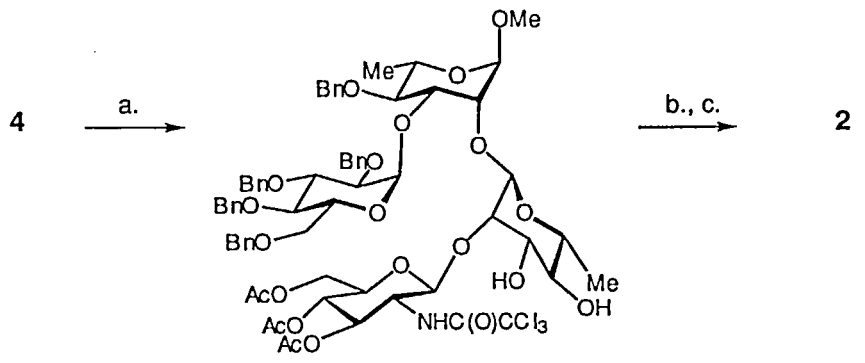
17 under the same conditions led to the isolation of the corresponding trichloroacetamide **18**. This observation assured that the deblocking of the trichloroacetyl moiety resulted from an intramolecular process and not from the direct action of sodium methoxide. When the crude aminotriol **19** was selectively *N*-acetylated upon treatment with acetic anhydride in methanol, the triol **20** was isolated in an overall yield of 88%. Next, treatment of the intermediate **20** with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid (TsOH) afforded the key *N*-acetylated acceptor **21** (95%). The latter was tentatively glycosylated with the trichloroacetimidate donor **7** under promotion with TMSOTf in diethyl ether. Even though such conditions were adopted in the case of the preparation of the trichloroacetamide **15**, they proved not to be appropriate when **21** was used as the acceptor (not described). Under such conditions, several products were formed and the *N*-acetylated tetrasaccharide **21** was partially recovered, indicating that the conversion rate, which could not be improved, was 54%, at the most. In contrast, when performed in the presence of a large excess of boron trifluoride etherate complex, the condensation of **21**

and **7** proceeded smoothly to give the *N*-acetylated pentasaccharide **22** (88%) together with a slight amount of the diol **23** (8%). The former was then deprotected sequentially. As before, deallylation of the fully protected **22** was accomplished first, following a two-step process using the cationic iridium complex,[23] as described for the preparation of the corresponding **8**, to give the diol **24** (79%). Next, trifluoroacetic acid hydrolysis of the diol **24** allowed the selective removal of the isopropylidene acetal to give the tetraol **25** (91%). As described above, Zemplén transesterification and subsequent hydrogenolysis of **25** gave the target pentasaccharide **3**.

Overall, the condensation of the acetamido **21** to donor **7** required harsher conditions than those used for the coupling of the trichloroacetamido **6** to **7**. Besides, when performed at the tetrasaccharide stage, conversion of the trichloroacetamide group into the desired acetamide one was rather delicate. For these reasons, route 1 was found preferable for the preparation of pentasaccharide **3**. As already mentionned, significant signal distortion was observed in the ^{13}C NMR spectra of several of the tetra- and pentasaccharide intermediates, whether fully or partially protected. Nevertheless, it should be emphasized that addition of residue **C** at the nonreducing end of either one of the tetrasaccharide precursors **6** and **21** did not enhance the distortions previously observed in the ^{13}C NMR spectra at the tetrasaccharide stage. Most probably, residue **C** does not interfere directly with the constrained region present in the **DA(E)B** structures.

In a previous paper,[16] we described the conversion of the crucial intermediate **4** to the tetrasaccharide[13,19] **2** in 5 steps (overall yield 55%), involving the dibutyl stannane mediated radical reduction of the trichloroacetamide moiety. Observations made during the synthesis of the pentasaccharide **3** were adapted successfully to the above conversion. Thus, the key precursor **4** was transformed into the target tetrasaccharide **2** in 3 steps (Scheme 4). Conventional deallylation of **4** was performed as described previously[16] leading to the known diol[16] **26** (71%). Next, the latter was submitted to Zemplén transesterification, *N*-acetylation and subsequent hydrogenolysis to afford the target **2** in a yield of 78%.

The reaction products were characterised by fully assigned ^{1}H and ^{13}C NMR spectra. Assignment of the ^{1}H NMR spectra was made possible by analysis of the experimental subspectra generated when running selective TOCSY experiments[27] to identify sets of signals attributed to individual rings, followed by unambiguous identification of one of the signals for each residue in one particular compound. Next, the assignment of the ^{13}C NMR spectra, the assignment of the $^{13}C\{^{1}H\}$ NMR signals followed directly from the analysis of the ^{13}C-^{1}H chemical shift correlated spectrum. The anomeric configurations of the newly formed glycosidic linkages were established by measurement of anomeric $^{1}J_{C,H}$ coupling constants.[28,29]



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(a) i. Ir(I), THF; ii. HgO, $HgBr_2$, acetone/H_2O; (b) MeONa, MeOH; (c) H_2, Pd/C.

Scheme 4

EXPERIMENTAL

General Methods. Optical rotations were measured for $CHCl_3$ solutions at 25 °C, except where indicated otherwise, with a Perkin-Elmer automatic polarimeter, Model 241 MC. TLC on precoated slides of Silica Gel 60 F_{254} (Merck) was performed with solvent mixtures of appropriately adjusted polarity consisting of *A*, dichloromethane-methanol; *B*, cyclohexane-ethyl acetate, *C*, cyclohexane-acetone, *D*, toluene-acetone, *E*, toluene-EtOAc, *F*, water-acetonitrile. Detection was effected when applicable, with UV light, and/or by charring with orcinol (35 mM) in aqueous 4N H_2SO_4. Preparative chromatography was performed by elution from columns of Silica Gel 60 (particle size 0.040-0.063 mm). The NMR spectra were recorded at 25 °C for solutions in $CDCl_3$, unless stated otherwise, on a Bruker AC 300P spectrometer (300 MHz for ^1H, 75 MHz for ^{13}C). External references: for solutions in $CDCl_3$, TMS (0.00 ppm for both ^1H and ^{13}C); for solutions in D_2O, dioxane (67.4 ppm for ^{13}C) and 3-(trimethylsilyl)propionic acid sodium salt (0.00 ppm for ^1H). Proton-signal assignments were made by first-order analysis of the spectra, as well as analysis of two-dimensional ^1H-^1H correlation maps (COSY) and selective TOCSY experiments. Of the two magnetically non-equivalent geminal protons at C-6, the one resonating at lower field is denoted H-6a and the one at higher field is denoted H-6b. The ^{13}C NMR assignments were supported by two-dimensional ^{13}C-^1H correlation maps (HETCOR). Interchangeable assignments are marked with an asterisk in listing of signal assignments. Sugar residues in oligosaccharides are serially lettered according to the lettering of the repeating unit of the *O*-SP and identified by a subscript in listing of signal assignments. Low resolution mass spectra were obtained by either chemical ionisation (CIMS) using NH_3 as the ionising gas or by electrospray mass spectrometry (ESMS). Et_2O

and THF were distilled over sodium/benzophenone. CH_3CN, suitable for DNA synthesis, was kept on Trap-Pack molecular sieves bags, and used as such. Solutions in organic solvents were dried by passing through phase separator filters.

Methyl (2-Deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1→ 2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (5). 1N Sodium methoxide was added dropwise to a solution of the fully protected tetrasaccharide[16] **4** (978 mg, 0.67 mmol) in a mixture of methanol and dichloromethane (9:1, 50 mL) until pH 9 was reached. The mixture was stirred at rt for 5 h and neutralised with resin IR (H^+). The crude material was column chromatographed (solvent *C*, 7:3) to give the triol **5** (850 mg, 95%) as a white foam, $[\alpha]_D$ -12° (*c* 1.0); ^1H NMR: δ 7.57 (d, 1H, $J_{NH,2}$ = 3.4 Hz, NH); 7.43-7.00 (m, 25H, Ph), 5.91 (m, 2H, C*H*=CH_2), 5.76 (bs, 1H, H-1_A), 5.29 (m, 2H, CH=CH_2), 5.20 (m, 3H, CH_2=CH, H-1_E), 5.06-4.90 (m, 4H, OCH_2), 4.73 (d, 1H, J = 10.8 Hz, OCH_2), 4.70 (d, 1H, J = 12.7 Hz, OCH_2), 4.58 (d, 1H, $J_{1,2}$ = 8.4 Hz, H-1_D), 4.57 (d, 1H, J = 11.9 Hz, OCH_2), 4.56 (bs, 1H, H-1_B), 4.40 (d, 1H, J = 10.9 Hz, OCH_2), 4.34 (d, 1H, J = 12.0 Hz, OCH_2), 4.31-4.08 (m, 7H, 4 OCH_2, H-2_B, 3_B, 3_E), 4.02 (m, 2H, H-2_A, 5_E), 3.87 (ddd, 1H, H-$6a_D$), 3.57-3.38 (m, 4H, H-5_A, 4_B, 2_D, 5_D), 3.28 (s, 3H, OCH_3), 3.26 (t, 1 H, $J_{4,5}$ = 9.5 Hz, H-4_D), 3.25 (t, 1 H, $J_{4,5}$ = 9.5 Hz, H-4_A), 2.58 (d, 1 H, $J_{OH,4}$ = 2.2 Hz, HO-4_D), 1.36 (d, 3H, $J_{5,6}$ = 5.9 Hz, H-6_B), and 1.35 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6_A); ^{13}C NMR: δ 164.7 (NC(=O)CH_3), 139.1-127.3 (CH=CH_2, Ph), 118.0, 116.6 (2 C, CH=*C*H_2), 102.3 (C-1_D*), 100.3 (C-1_B*), 97.6 (C-1_A), 92.3 (C-1_E), 92.0 (CCl_3), 81.7 (C-3_E), 81.0 (C-4_A), 79.5 (C-4_B), 78.9 (C-2_A), 78.7 (C-3_A), 78.5 (C-2_E*), 77.6 (C-4_E*), 76.4 (C-3_D), 76.2 (OCH_2), 75.5 (C-5_D), 75.0, 74.8 (2 C, OCH_2), 74.5 (C-3_B), 74.3, 73.2, 72.9 (4 C, OCH_2), 72.1 (C-4_D), 69.6 (C-5_E), 68.6 (C-5_B), 68.3 (C-5_A), 68.2 (C-6_E), 66.3 (C-2_B), 62.0 (C-6_D), 59.4 (C-2_D), 54.6 (OCH_3), 18.0 (C-6_A), and 17.9 (C-6_B); CIMS of $C_{68}H_{82}Cl_3NO_{19}$ (M, 1323.7) *m/z* 1341 $[M+NH_4]^+$.

Anal. Calcd for $C_{68}H_{82}Cl_3NO_{19}$: C, 61.70; H, 6.24; N, 1.06%. Found: C, 61.76; H, 6.24; N, 0.97%.

Methyl .(2-Deoxy-3,4-*O*-isopropylidene-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→ 3)]-4-*O*-benzyl-α-L-rhamnopyranoside (6). To a solution of the crude triol **5** (obtained from **4**, 2.25 g, 1.55 mmol) in anhydrous DMF (15 mL) were added 2,2-dimethoxypropane (30 mL) and TsOH (60 mg). The mixture was stirred under vacuum for 15 min. Et_3N was added, and the mixture was concentrated to dryness. Chromatography of the residue gave the alcohol **6** (1.98 g, 94%) as a white foam, $[\alpha]_D$ -9° (*c* 1.0); ^1H NMR: δ 7.40-7.08 (m, 26H, Ph, NH), 5.92 (m, 2H,

C*H*=CH_2), 5.39 (bs, 1H, H-1_A), 5.28 (m, 2H, CH=C*H*$_2$), 5.19 (m, 2H, C*H*$_2$=CH), 5.07 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1_E), 4.96-4.78 (m, 5H, 4 OCH_2, H-1_D), 4.69 (d, 1H, $J_{1,2}$ = 1.5 Hz, H-1_B), 4.67 (d, 1H, OCH_2), 4.56 (d, 1H, J = 10.3 Hz, OCH_2), 4.55 (d, 1H, J = 12.0 Hz, OCH_2), 4.43 (d, 1H, J = 11.0 Hz, OCH_2), 4.29 (d, 1H, J = 12.0 Hz, OCH_2), 4.28 (d, 1H, OCH_2), 4.21 (d, 1H, OCH_2), 4.13 (bs, 1H, H-2_A), 4.12 (m, 1H, H-3_B), 4.10 (m, 2H, H-2_B, OCH_2), 4.03 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-3_E), 4.00 (m, 1 H, H-5_E), 3.80-3.71 (m, 3H, H-3_D, 3_A, $6a_D$), 3.68-3.51 (m, 7H, H-5_A, 5_B, 2_E, $6b_D$, H-$6a_E$, 4_B, 2_D), 3.45 (bd, 1H, $J_{6a,6b}$ = 10.7 Hz, H-$6b_E$), 3.32 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-4_D), 3.29 (m, 4H, OCH_3, H-4_A), 3.12 (ddd, 1H, $J_{5,6a}$ = 5.3, $J_{4,5}$ = 10.0, $J_{5,6b}$ = 5.0 Hz, H-5_D), 1.36 (s, 3H, CCH_3), 1.33 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6_B), 1.27 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), and 1.21 (s, 3H, CCH_3); ^{13}C NMR: δ 163.6 (C(=O)), 138.6-127.5 (*C*H=CH_2, Ph), 117.7, 116.6 (2C, CH=*C*H_2), 101.0 (C-1_D), 99.9 (*C*Me_2), 99.7 (C-1_B), 99.2 (C-1_A), 94.3 (C-1_E), 92.2 (CCl_3), 82.2 (C-3_E), 81.0 (C-4_A), 79.7 (C-4_B), 79.2 (C-3_A), 78.9 (C-2_E), 77.7 (C-5_A*), 75.9 (C-2_A), 75.5 (OCH_2), 75.4 (C-3_B), 74.9, 74.1 (2C, OCH_2), 74.0 (C-4_D), 73.3 (OCH_2), 72.8 (C-3_D), 72.6, 72.5 (2C, OCH_2), 72.2 (C-2_B), 70.3 (C-5_E), 68.3 (2C, C-5_B, 6_E), 67.4 (C-5_D), 61.8 (C-6_D), 60.0 (C-2_D), 54.8 (OCH_3), 28.9 (CCH_3), 18.8 (CCH_3), 18.1 (C-6_B), and 17.8 (C-6_A); ESMS for $C_{71}H_{86}Cl_3NO_{19}$ (M, 1363.8) *m/z* 1364.7 $[M+H]^+$.

Anal. Calcd for $C_{71}H_{86}Cl_3NO_{19}$: C, 62.53; H, 6.36; N, 1.03%. Found: C, 62.65; H, 6.42; N, 0.96%.

Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-(2-deoxy-3,4-*O*-isopropylidene-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (8) and Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-(2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→ 2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1 → 2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→ 3)]-4-*O*-benzyl-α-L-rhamnopyranoside (9). A solution of disaccharide **6** (2.1 g, 1.54 mmol) and donor[21] **7** (828 mg, 1.98 mmol) in anhydrous Et_2O (40 mL) was stirred at -78 °C for 30 min. TMSOTf (30 μL, 155 μmol) was added, and the mixture was stirred for 15 h while slowly warming up to rt. As no starting material could be detected (solvent *B*, 1:1), Et_3N (200 μL, 275 μmol) was added and the solvent was evaporated. Chromatography of the crude mixture (solvent *B*, 1:1) gave the fully protected pentasaccharide **8** (2.05 g, 81%) as the first eluting product, and the diol **9** (320 mg, 13%) as the slower eluting product.

Compound **8**, isolated as a colourless foam, had $[\alpha]_D$ -15° (*c* 1.0); ^{1}H NMR: δ 7.43-7.10 (m, 25H, Ph), 6.82 (d, 1H, $J_{NH,2}$ = 7.4 Hz, NH), 5.91 (m, 2H, C*H*=CH_2), 5.40 (bs, 1H, H-1_A), 5.36 (m, overlapped, 1H, H-2_C), 5.26 (m, 2H, CH=C*H*$_2$), 5.21

(m, 2H, H-1_D, 3_C), 5.13 (m, 2H, CH_2=CH), 5.10 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1_E), 5.01 (dd, 1H, $J_{3,4}$ = 10.0, $J_{4,5}$ = 9.6 Hz, H-4_C), 4.96 (d, 2H, J = 10.5 Hz, OCH_2), 4.89 (d, 1H, J = 12.7 Hz, OCH_2), 4.88 (d, 2H, J = 13.5 Hz, OCH_2), 4.83 (d, 1H, J = 10.8 Hz, OCH_2), 4.75 (d, 1H, $J_{1,2}$ = 1.3 Hz, H-1_C), 4.69 (d, 1H, J = 11.3 Hz, OCH_2), 4.68 (bs, 1H, H-1_B), 4.56 (d, 1H, J = 10.3 Hz, OCH_2), 4.55 (d, 1H, J = 12.1 Hz, OCH_2), 4.43 (d, 1H, J = 11.1 Hz, OCH_2), 4.29 (d, 2H, J = 12.0 Hz, OCH_2), 4.20 (bs, 1H, H-2_A), 4.12-3.99 (m, 8H, H-3_D, 3_B, 2_B, 5_C, 3_E, 3 OCH_2), 3.77 (dd, 1H, $J_{5,6}$ = 5.2, $J_{6a,6b}$ = 10.8 Hz, H-$6a_D$), 3.72-3.43 (m, 7H, H-3_A, 5_A, 5_B, $6b_D$, $6a_E$, 4_B, $6b_E$), 3.29 (dd, overlapped, 1H, H-4_D), 3.28 (s, 3H, OCH_3), 3.24 (dd, overlapped, 1H, H-4_A), 3.20 (m, overlapped, 1H, H-5_D), 3.12 (m, 1H, $J_{2,3}$ = 8.3 Hz, H-2_D), 2.09, 2.06, 1.98 (3s, 9H, 3 C(=O)CH_3), 1.43 (s, 3H, CCH_3), 1.31 (d, partially overlapped, 3H, H-6_B), 1.27 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6_A), 1.14 (s, 3H, CCH_3) and 1.13 (d, partially overlapped, 3H, H-6_C); ^{13}C NMR: δ 170.0, 169.7 (3C, OC=O), 161.4 (NC=O), 138.6-127.5 (CH=CH_2, Ph), 116.9, 116.6 (2C, CH=CH_2), 99.8 (C-1_B, $J_{C,H}$ = 169 Hz), 99.4 (2C, CMe_2, C-1_A, $J_{C,H}$ = 175 Hz), 98.9 (C-1_D, $J_{C,H}$ = 163 Hz), 98.2 (C-1_C, $J_{C,H}$ = 173 Hz), 94.2 (C-1_E, $J_{C,H}$ = 170 Hz), 92.4 (CCl_3), 82.1 (C-3_E), 80.4 (C-4_A), 79.8 (C-4_B), 79.5 (C-2_E), 79.3 (C-3_A*), 77.8 (C-4_E*), 75.6 (2C, OCH_2), 75.4 (C-3_B), 75.2 (C-3_D), 74.9, 74.3 (2C, OCH_2), 74.0 (C-2_A), 73.3, 72.8 (2C, OCH_2), 72.7 (C-4_D), 71.9 (C-2_B), 71.6 (OCH_2), 70.9 (C-4_C), 70.3 (C-5_E), 69.5 (C-2_C), 69.2 (C-2_C), 68.6 (C-5_A*), 68.2 (2C, C-6_E, 5_B*), 67.0 (C-5_D), 66.4 (C-5_C), 62.0 (C-6_D), 59.8 (C-2_D), 54.7 (OCH_3), 29.0 (CCH_3), 20.9, 20.8 (3C, C(=O)CH_3), 19.0 (CCH_3), 18.1 (C-6_B), 18.0 (C-6_A), and 17.3 (C-6_C); ESMS for $C_{83}H_{102}Cl_3NO_{26}$ (M, 1633.6) *m/z* 1634.6 $[M+H]^+$.

Anal. Calcd for $C_{83}H_{102}Cl_3NO_{26}$: C, 60.93; H, 6.28; N, 0.86%. Found: C, 60.82; H, 6.34; N, 0.81%.

Compound **9**, isolated as a white foam, had $[\alpha]_D$ +2° (*c* 1.0); ^{1}H NMR: δ 7.49-7.00 (m, 25H, Ph), 6.90 (d, 1H, $J_{NH,2}$ = 7.1 Hz, NH), 5.92 (m, 2H, CH=CH_2), 5.72 (bs, 1H, H-1_A), 5.29-5.14 (m, 5H, H-1_E, 2_C, 3_C, 2 CH=CH_2), 5.08 (dd, 2H, $J_{3,4}$ = 10.0, $J_{4,5}$ = 9.6 Hz, H-4_C, OCH_2), 5.03-4.96 (m, 4H, 2 OCH_2, CH=CH_2), 4.94 (d, 1H, J = 11.5 Hz, OCH_2), 4.80 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1_C), 4.73 (d, 1H, J = 10.5 Hz, OCH_2), 4.69 (d, 1H, J = 12.5 Hz, OCH_2), 4.57 (m, 3H, 2 OCH_2, H-1_B), 4.41 (d, 1H, J = 10.9 Hz, OCH_2), 4.37-4.27 (m, 2H, OCH_2), 4.22 (bd, 1H, H-2_B), 4.19 (bd, 1H, H-3_B), 4.15-4.01 (m, 8H, H-3_E, 3_D, 5_E, 2_A, 5_C, 3 OCH_2), 3.86 (dd, 1H, H-$6a_D$), 3.75-3.46 (m, 9H, H-3_A, 5_A, 5_B, $6b_D$, 4_B, $6a_E$, 4_E, 2_E, $6b_E$), 3.37 (m, 1H, H-5_D), 3.28 (s, 3H, OCH_3), 3.26 (dd, 1H, J = 9.5 Hz, H-4_A), 3.10 (bdd, 1H, J = 8.5, J = 9.1 Hz, H-4_D), 2.99 (ddd, 1H, J = 9.6, J = 8.1 Hz, H-2_D), 2.11, 2.08, 1.97 (3s, 9H, 3 C(=O)CH_3), 1.36 (d, partially overlapped, 3H, $J_{5,6}$ = 5.7 Hz, H-6_B), 1.27 (d, partially overlapped, 3H, $J_{5,6}$ = 6.0 Hz, H-6_A), and 1.24 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C); ^{13}C NMR: δ 169.8, 169.6

(3C, O(C=O)), 161.7 (N(C=O)), 139.4-127.2 (*C*H=CH_2, Ph), 116.9, 116.8 (2C, CH=*C*H_2), 100.4 (2C, C-1_B, 1_D), 99.5 (C-1_C), 97.9 (C-1_A), 92.4 (CCl_3), 92.1 (C-1_E), 83.8 (C-3_D), 81.6 (C-3_E), 80.2 (C-4_A), 79.6 (bs, C-4_B), 78.9 (C-2_E), 78.6 (C-3_A*), 78.2 (C-4_E*), 77.2 (C-5_E), 76.1 (bs, OCH_2), 75.0 (C-5_D), 74.9, 74.8 (2C, OCH_2), 74.5 (C-3_B), 74.3, 73.3, 73.2, 71.8 (4C, OCH_2), 70.4 (2C, C-4_D, 4_C), 69.6 (C-2_A), 69.4 (C-2_C), 68.6 (3C, C-3_C, 5_A, 5_B), 68.6 (C-6_E), 67.8 (C-5_C), 66.1 (bs, C-2_B), 61.9 (C-6_D), 57.3 (C-2_D), 54.6 (OCH_3), 29.0, 20.7 (3C, C(=O)CH_3), 18.2 (C-6_A), 18.0 (C-6_B), and 17.5 (C-6_C); ESMS for $C_{83}H_{102}Cl_3NO_{26}$ (M, 1593.5) *m/z* 1594.6 $[M+H]^+$.

Anal. Calcd for $C_{80}H_{98}Cl_3NO_{26}$: C, 60.21; H, 6.19; N, 0.88%. Found: C, 60.22; H, 6.27; N, 0.81%.

Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-(2-deoxy-3,4-*O*-isopropylidene-2-trichloroacetamido-β-D-glucopyranosyl)-(1→ 2)-α-L-rhamnopyranosyl-(1→ 2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1 →3)]-4-*O*-benzyl-α-L-rhamnopyranoside (10). The fully protected **8** (450 mg, 0.28 mmol) was dissolved in anhydrous THF (10 mL). The solution was degassed and placed under Ar. 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)iridium hexafluorophosphate (37 mg, 136 μmol) was added, and the solution was degassed again. The catalyst was activated by passing over a stream of hydrogen until the solution had turned yellow (3-4 min). The reaction mixture was degassed and stirred under an Ar atmosphere for 15 h, then concentrated to dryness. The residue was dissolved in acetone (37 mL), then water (3.9 mL), mercuric oxide (228 mg, 1.06 mmol), and mercuric bromide (242 mg, 0.89 mmol) were added successively. The mixture, protected from light, was stirred at rt for 4 h and acetone was evaporated. The resulting suspension was taken up in CH_2Cl_2, washed twice with 50% aq KI, water and satd NaCl, dried and concentrated. Column chromatography (solvent *B*, 2:3) of the crude material gave the diol **10** as a colourless foam (337 mg, 78%), $[\alpha]_D$ -11° (*c* 1.0); ^{1}H NMR: δ 7.45-7.05 (m, 25H, Ph), 7.01 (d, 1H, $J_{NH,2}$ = 6.6 Hz, NH), 5.28 (dd, 1H, $J_{1,2}$ = 1.8, $J_{2,3}$ = 3.4 Hz, H-2_C), 5.27 (bs, 1H, H-1_A), 5.20 (dd, 1H, $J_{3,4}$ = 10.1 Hz, H-3_C), 5.10 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1_E), 5.02 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4_C), 4.94 (d, 1H, J = 10.8 Hz, OCH_2), 4.86 (bs, 1H, H-1_C), 4.82 (m, 5H, H-1_D, 4 OCH_2), 4.75 (bs, 1H, H-1_B), 4.73 (d, 1H, J = 12.3 Hz, OCH_2), 4.56 (d, 2H, J = 11.8 Hz, 2 OCH_2), 4.45 (d, 1H, J = 11.0 Hz, OCH_2), 4.31 (d, 1H, J = 12.0 Hz, OCH_2), 4.12 (m, 2H, H-3_B, 5_C), 4.06-4.00 (m, 3H, H-3_E, 5_E, 2_B), 3.99 (bd, 1H, H-2_A), 3.94 (dd, 1H, $J_{2,3}$ = 8.8, $J_{3,4}$ = 8.8 Hz, H-3_D), 3.91 (m, 1H, H-3_A), 3.78-3.68 (m, 3H, H-$6a_D$, 5_A, 4_E), 3.66-3.58 (m, 3H, H-5_B, 2_E, $6b_D$), 3.54-3.42 (m, 6H, H-$6a_E$, 4_D, 4_B, $6b_E$, 2_D, 4_A), 3.29 (s, 3H, OCH_3), 3.15 (m, 1H, H-5_D), 2.51 (bs, 1H, OH-4_D), 2.31 (bd, 1H, $J_{OH,3}$ = 5.2 Hz, OH-3_D), 2.10, 2.05, 1.98 (3s, 9H, 3 C(=O)CH_3), 1.33 (s, overlapped, 3H, CCH_3), 1.32 (d, 3H, H-6_B), 1.29 (s, 3H, CCH_3), 1.28 (d, 3H,

$J_{5,6}$ = 6.0 Hz, H-6_A), and 1.16 (d, partially overlapped, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C); ^{13}C NMR: δ 170.1, 169.9, 169.7 (3C, O(C=O)), 161.8 (N(C=O)), 138.5-127.4 (Ph), 100.5 (C-1_C), 99.9 (C-1_A), 99.5 (2C, CMe_2, C-1_B), 97.9 (C-1_D), 93.7 (C-1_E), 92.2 (CCl_3), 82.1 (C-3_E), 79.8 (C-4_B), 79.2 (C-2_E), 78.1 (C-2_A), 77.8 (C-4_E), 75.9 (C-3_D), 75.8, 75.5, 74.9 (3C, OCH_2), 74.6 (C-3_B), 73.5 (C-2_B), 73.3 (OCH_2), 73.2 (C-4_A), 72.5 (OCH_2), 72.4 (C-4_D), 71.4 (C-3_A), 70.8 (C-4_C), 70.3 (C-5_E), 69.4 (C-2_C), 69.3 (C-3_C), 68.7 (C-5_A), 68.2 (C-6_E), 68.0 (C-5_B), 67.0 (C-5_D), 66.5 (C-5_C), 62.1 (C-6_D), 58.9 (C-2_D), 54.8 (OCH_3), 28.9 (CCH_3), 20.7 (3C, C(=O)CH_3), 19.0 (CCH_3), 18.0 (C-6_B), 17.5 (C-6_A), and 17.2 (C-6_C); ESMS for $C_{77}H_{94}Cl_3NO_{26}$ (M, 1553.5) *m/z* 1554.6 $[M+H]^+$.

Anal. Calcd for $C_{77}H_{94}Cl_3NO_{26}\cdot H_2O$: C, 58.76; H, 6.15; N, 0.89%. Found C, 58.59; H, 6.00; N, 0.81%.

Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-(2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-α-L-rhamnopyranosyl-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (11). 50% Aq CF_3CO_2H (5 mL) was added to a solution of the crude diol **10**, resulting from the deallylation of the fully protected pentasaccharide **8** (670 mg, 0.406 mmol), in CH_2Cl_2 (20 mL). The mixture was kept under vigorous stirring at 0 °C for 3 h. At this time, TLC (solvent *B*, 4:6) showed that the reaction was finished. Extraction and evaporation of the solvent, followed by column chromatography (solvent *A*, 96:4) of the crude residue gave the tetraol **11** as a colourless foam (393 mg, 64%), $[\alpha]_D$ +42° (*c* 1.2); ^{1}H NMR: δ 7.52-7.00 (m, 26H, Ph, NH), 5.77 (bs, 1H, H-1_A), 5.33 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1_E), 5.23 (bs, partially overlapped, 1H, H-2_C), 5.20 (dd, partially overlapped, 1H, $J_{2,3}$ = 3.2 Hz, H-3_C), 5.10 (t, 1H, $J_{3,4}$ = 9.5 Hz, H-4_C), 5.10-5.01 (m, 4H, H-1_D, 3 OCH_2), 4.94 (d, 1H, J = 12.0 Hz, OCH_2), 4.80 (d, 1H, $J_{1,2}$ = 1.1 Hz, H-1_C), 4.74 (d, 1H, J = 10.3 Hz, OCH_2), 4.70 (d, 1H, J = 12.0 Hz, OCH_2), 4.58 (m, 3H, H-1_B, 2 OCH_2), 4.42 (d, 1H, J = 10.8 Hz, OCH_2), 4.35 (d, 1H, J = 12.0 Hz, OCH_2), 4.23 (bs, overlapped, 1H, H-2_B), 4.21 (dd, partially overlapped, 1H, H-3_B), 4.16 (t, partially overlapped, 1H, H-3_E), 4.05 (m, 2H, H-5_C, 5_E), 4.02 (bs, 1H, H-2_A), 3.85 (m, 3H, H-5_A, 3_D, $6a_D$), 3.72-3.63 (m, 5H, H-2_E, 4_E, $6a_E$, $6a_D$, 5_B), 3.59-3.53 (m, 2H, H-$6b_E$, 4_B), 3.48 (dq, partially overlapped, 1H, H-5_A), 3.41 (t, 1H, $J_{4,5}$ = 9.4, $J_{3,4}$ = 9.4 Hz, H-4_A), 3.37 (m, 1H, H-5_D), 3.28 (s, 3H, OCH_3), 3.11 (bt, 1H, H-4_D), 3.09 (m, 1H, H-2_D), 2.11, 2.09, 1.98 (3s, 9H, 3 C(=O)CH_3), 1.36 (d, 3H, $J_{5,6}$ = 5.9 Hz, H-6_B), 1.35 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6_A), and 1.22 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6_C); ^{13}C NMR: δ 169.9, 169.8 (3C, O(C=O)), 162.3 (N(C=O)), 139.3-127.3 (Ph), 100.7 (C-1_D), 100.3 (C-1_B), 99.2 (C-1_C), 98.0 (C-1_A), 92.0 (bs, C-1_E), 84.2 (C-3_D), 81.5 (C-3_E), 79.6 (bs, C-4_B), 79.2 (2C, C-4_E*, 2_A), 78.6 (C-2_E*), 76.1 (OCH_2), 75.5 (C-5_D), 74.9 (2C,

OCH_2), 74.4 (bs, C-3_B), 73.5 (OCH_2), 73.4 (C-4_A), 73.3 (OCH_2), 70.9 (C-5_A), 70.3 (2C, C-4_C, 4_D), 69.6 (C-5_E), 69.4 (C-2_C), 68.8 (C-5_A), 68.7 (C-5_B), 68.6 (C-3_C), 68.2 (C-6_E), 67.9 (C-5_C), 66.3 (C-2_B), 61.6 (C-6_D), 57.2 (C-2_D), 54.7 (OCH_3), 20.8, 20.7 (3C, C(=O)CH_3), 17.9 (2C, C-6_B, 6_A), and 17.4 (C-6_C); ESMS for $C_{74}H_{90}Cl_3NO_{26}$ (M, 1513.5) *m/z* 1514.5 $[M+H]^+$.

Anal. Calcd for $C_{74}H_{90}Cl_3NO_{26}$: C, 58.63; H, 5.98; N, 0.92%. Found: C, 58.45; H, 6.00; N, 0.90%.

Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-[(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (12). (a) Acetic anhydride (1.0 mL, 10.6 mmol) was added to a solution of the tetraol **11** (400 mg, 0.26 mmol) in pyridine (5.0 mL), and the mixture was stirred at rt for 48 h. TLC (solvent *B*, 3:2) showed that no starting material remained, and that two products of close mobility were present in the reaction mixture. MeOH was added, and the mixture was stirred at rt for 2 h. Evaporation of the solvent, followed by conventional extraction and column chromatography of the residue (solvent *B*, 70:30), gave the heptaacetate **12** (345 mg, 79 %) as the first eluting product. MS analysis showed that the slower moving product, isolated as a colourless foam (84 mg, 19 %), was lacking one acetyl group; ESMS for $C_{80}H_{96}Cl_3NO_{29}$ (M, 1639.5) *m/z* 1640.7 $[M+H]^+$.

The faster eluting product, isolated as a colourless foam, had $[\alpha]_D$ +12° (*c* 1.0); ^1H NMR: δ 7.44-7.05 (m, 25H, Ph), 6.82 (d, 1H, $J_{NH,2}$ = 6.3 Hz, NH), 5.52 (bs, 1H, H-1_A), 5.32 (dd, 1H, $J_{2,3}$ = 3.2, $J_{3,4}$ = 10.4 Hz, H-3_A), 5.26 (d, 1H, $J_{1,2}$ = 2.8 Hz, H-1_E), 5.15 (dd, 1H, H-2_C), 5.17 (dd, 1H, $J_{2,3}$ = 3.3 Hz, H-3_C), 5.00 (t, 3H, H-4_C, 4_A, OCH_2), 4.96-4.87 (m, 4H, H-1_D, 3 OCH_2), 4.79 (d, 1H, J = 11.1 Hz, OCH_2), 4.77 (bt, 1H, J = 9.0 Hz, H-4_D), 4.72 (bs, 2H, H-1_B, 1_C), 4.65 (d, 1H, J = 11.9 Hz, OCH_2), 4.57 (d, 1H, J = 12.0 Hz, OCH_2), 4.55 (d, 1H, J = 10.3 Hz, OCH_2), 4.45 (d, 1H, J = 10.9 Hz, OCH_2), 4.43 (t, 1H, J = 9.7 Hz, H-3_D), 4.32 (d, 1H, J = 11.0 Hz, OCH_2), 4.22-4.03 (m, 7H, H-$6a_D$, 3_B, 2_B, 2_A, 5_E, 3_E, $6b_D$), 3.87 (dq, 1H, $J_{4,5}$ = 9.8 Hz, H-5_A), 3.79-3.64 (m, 4H, H-5_C, 4_E, 2_E, 5_B), 3.59-3.48 (m, 3H, H-4_B, $6a_E$, $6b_E$), 3.31 (s, 3H, OCH_3), 3.25 (bd, 1H, H-5_D), 2.55 (m, 1H, H-2_D), 2.10, 2.08, 2.06, 2.05, 2.01, 1.97, 1.96 (7s, 21H, C(=O)CH_3), 1.40 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6_B), 1.23 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), and 1.12 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C); ^{13}C NMR: δ 170.6, 170.3, 169.9, 169.7 (OC(=O)), 162.1 (NC(=O)), 138.9-127.3 (Ph), 99.8 (C-1_C), 99.6 (C-1_B), 98.9 (C-1_A), 97.7 (C-1_D), 93.8 (C-1_E), 91.9 (CCl_3), 81.8 (C-3_E), 80.6 (C-2_E), 77.9 (C-3_D), 77.8 (C-4_E), 77.2 (C-4_B), 75.4 (OCH_2), 75.1 (bs, C-3_B), 74.9 (2C, OCH_2), 74.5 (2C, C-2_B, 2_A), 73.2 (2C, OCH_2), 72.0 (C-5_D), 71.6 (C-4_A*), 70.7 (2C, C-4_C*, 4_D), 70.1 (2C, C-

3_A, 5_A), 69.8 (C-3_C), 68.7 (C-2_C), 68.5 (C-5_B), 68.3 (C-6_E), 67.6 (C-5_C), 66.8 (C-5_A), 62.4 (C-6_D), 58.7 (C-2_D), 54.7 (OCH_3), 21.1, 21.0, 20.8, 20.6 (7C, C(=O)CH_3), 18.0 (C-6_B), 17.6 (C-6_A), and 17.0 (C-6_C); ESMS for $C_{82}H_{101}NO_{30}$ (M, 1681.5) *m/z* 1682.6 $[M+H]^+$.

Anal. Calcd for $C_{82}H_{98}Cl_3NO_{30}$: C, 58.49; H, 5.87; N, 0.83%. Found C, 58.54; H, 5.89; N, 0.81%.

(b) Acetic anhydride (1.15 mL, 12.3 mmol) was added to a solution of the tetraol **11** (574 mg, 0.35 mmol) in pyridine (5.0 mL), and the mixture was stirred overnight at 70 °C. TLC (solvent *B*, 3:2) showed that no starting material remained, and that one product was present in the reaction mixture. The latter was processed as described in (a) to give the heptaacetate **12** (588 mg, 97%).

Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→ 2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1→2)-[(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (13). A mixture of the trichloroacetamide **12** (280 mg, 166 μmol), and tributyltin hydride (300 μL, 1.1 mmol) in dry toluene (12 mL) and dry *N,N*-dimethylacetamide (4 mL) was stirred for 20 min under a flow of dry Ar. α,α'-Azobisisobutyronitrile (3 mg, 18 μmol) was added, and the mixture was stirred under Ar at rt, then heated at 90 °C for 1.5 h, cooled and concentrated. The oily residue was then triturated with petroleum ether (3 times 10 mL) to give a white solid which was eluted from a column of silica gel (solvent *D*, 85:15) to give the monochloroacetamide **14** (62 mg, 23 %) as the first eluting product, and the acetamide **13** as the slower eluting product. The latter was column chromatographed again (solvent *C*, 75:25, then solvent *B*, 72:28) to give the acetamide **13** (176 mg, 67 %) as a colourless foam free of any tin contaminants, $[\alpha]_D$ +5° (*c* 1.0); ^{1}H NMR: δ 7.40-7.05 (m, 25H, Ph), 6.11 (d, 1H, $J_{NH,2}$ = 6.5 Hz, NH), 5.32 (dd, partially overlapped, 1H, $J_{3,4}$ = 10.1 Hz, H-3_A), 5.31 (bs, 1H, H-1_A), 5.19 (bs, 1H, H-2_C), 5.15 (m, 2H, H-3_C, 1_E), 5.11 (dd, 1H, $J_{3,4}$ = 10.0 Hz, H-4_A), 5.05 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1_D), 5.03 (dd, 1H, $J_{3,4}$ = 9.8 Hz, H-4_C), 4.94-4.80 (m, 7H, H-4_D, 1_B, OCH_2), 4.67 (m, 3H, H-1_C, 3_D, OCH_2), 4.62 (d, 1H, J = 11.1 Hz, OCH_2), 4.55 (d, 1H, J = 12.0 Hz, OCH_2), 4.43 (d, 1H, J = 11.0 Hz, OCH_2), 4.31 (d, 1H, J = 12.0 Hz, OCH_2), 4.18-4.07 (m, 5H, H-3_B, 2_A, 2_B, $6a_D$, 3_E), 4.04-3.96 (m, 3H, H-6_D, 5_A, 5_E), 3.84 (dq, 1H, $J_{4,5}$ = 9.6 Hz, H-5_C), 4.71-3.58 (m, 5H, H-5_B, 4_E, 2_E, 4_B, $6a_E$), 3.51 (bd, 1H, H-$6b_E$), 3.30 (s, 3H, OCH_3), 3.23 (bd, 1H, H-5_D), 2.68 (m, 1H, H-2_D), 2.11, 2.09, 2.06, 2.05, 2.04, 1.99, 1.87 (7s, 24H, C(=O)CH_3), 1.34 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6_B), 1.23 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), and 1.13 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C); ^{13}C NMR: δ 172.1, 170.6, 170.4, 170.3, 170.0 169.9, 169.6 (8C, C(=O)), 138.7-127.4 (Ph), 100.5 (C-1_C), 99.5 (2C, C-1_B, 1_A), 98.6 (C-1_D), 94.1 (bs, C-1_E), 81.9 (C-3_E),

79.8 (bs, C-4_B), 79.7 (C-3_D), 79.2 (C-2_E), 77.7 (C-4_E), 75.4 (2C, OCH_2), 75.2 (C-2_A), 74.8 (OCH_2), 74.5 (bs, C-3_B), 73.6 (bs, C-2_B), 73.2, 72.4 (2C, OCH_2), 71.5 (C-5_D*), 71.4 (C-4_A*), 70.9 (C-3_A), 70.4 (C-4_C), 70.2 (C-5_E), 70.1 (C-4_D), 69.5 (C-2_C*), 69.3 (C-3_C*), 68.3 (2C, C-5_B, 6_E), 67.8 (C-5_C), 66.9 (C-5_A), 61.8 (C-6_D), 59.0 (C-2_D), 54.8 (OCH_3), 23.4, 21.1, 20.9, 20.8, 20.7, 20.6 (8C, C(=O)CH_3), 18.1 (C-6_B), 17.4 (C-6_C*), and 17.3 (C-6_A*); ESMS for $C_{82}H_{101}NO_{30}$ (M, 1579.6) *m/z* 1580.7 $[M+H]^+$.

Anal. Calcd for $C_{82}H_{101}NO_{30}$: C, 62.31; H, 6.44; N, 0.89%. Found: C, 62.22; H, 6.51; N, 0.79%.

Compound **14** had ESMS for $C_{80}H_{100}ClNO_{30}$ (M, 1613.6) *m/z* 1614.8 $[M+H]^+$.

Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1→ 2)-[(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (16). Acetic anhydride (1.0 mL, 10.6 mmol) was added to a solution of the diol **9** (262 mg, 0.17 mmol) in pyridine (3.0 mL) and the mixture was stirred overnight at 70 °C. MeOH was added and the mixture was stirred at rt for 2 h. Evaporation of the solvent was followed by conventional extraction. The residue was eluted from a column of silica gel (solvent *E*, 75:25) to give the pentaacetate **16** (268 mg, 94 %) as a colourless foam, $[\alpha]_D$ +4° (*c* 1.0); ^1H NMR: δ 7.43-7.05 (m, 25H, Ph), 6.84 (d, 1H, $J_{NH,2}$ = 6.8 Hz, NH), 5.91 (m, 2H, C*H*=CH_2), 5.51 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1_D), 5.34 (bs, 1H, H-1_A), 5.25 (m, 2H, CH=CH_2), 5.18 (m, 2H, H-2_C, 3_C), 5.16 (d, partially overlapped, 1H, H-1_E), 5.15 (m, 2H, CH=CH_2), 4.99 (dd, 1H, $J_{3,4}$ = 9.8, $J_{4,5}$ = 9.8 Hz, H-4_C), 4.91 (m, 2H, OCH_2), 4.82 (m, 4H, H-4_D, 3 OCH_2), 4.74 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1_C), 4.68 (bs, 1H, H-1_B), 4.67 (d, 1H, J = 12.4 Hz, OCH_2), 4.58 (d, 1H, J = 11.2 Hz, OCH_2), 4.54 (d, 1H, J = 12.1 Hz, OCH_2), 4.43 (d, 1H, J = 10.9 Hz, OCH_2), 4.39 (dd, 1H, J = 8.7 Hz, H-3_D), 4.31 (m, 3H, H-2_A, 2 OCH_2), 4.17-3.99 (m, 6H, H-$6a_D$, 3_B, 2_B, 3_E, $6b_D$, 5_E), 3.79 (dq, 1H, $J_{4,5}$ = 9.8 Hz, H-5_C), 3.75 (dd, 1H, $J_{2,3}$ = 2.7, $J_{3,4}$ = 9.6 Hz, H-3_A), 3.68 (dd, 1H, J = 9.0 Hz, H-4_E), 3.67-3.38 (m, 7H, H-5_A, 5_B, 2_E, 4_B, $6a_E$, $6b_E$, 5_D), 3.29 (s, 3H, OCH_3), 3.27 (dd, 1H, $J_{3,4}$ = 9.4, $J_{4,5}$ = 9.6 Hz, H-4_A), 2.81 (m, 1H, H-2_D), 2.10, 2.07, 2.05, 1.96 (4s, 15H, C(=O)CH_3), 1.35 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6_B), 1.29 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), and 1.14 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C); ^{13}C NMR: δ 170.5, 170.0, 169.9, 169.8, 169.7 (5C, C(=O)), 161.7 (NC(=O)), 138.8-127.4 (Ph, *C*H=CH_2), 116.6, 116.5, (CH=*C*H_2), 99.9 (C-1_B), 99.5 (C-1_C), 99.1 (C-1_A), 97.2 (C-1_D), 93.8 (C-1_E), 82.1 (C-3_E), 80.2 (C-4_A), 79.8 (C-4_B), 79.6 (C-3_A), 79.5 (C-2_E), 78.2 (C-3_D), 77.8 (C-4_E), 75.8, 75.5, (2C, OCH_2), 75.0 (C-3_B*), 74.9, 74.4, 73.2, 72.9 (4C, OCH_2), 72.7 (C-2_A), 71.9 (C-5_D), 71.3 (OCH_2), 71.2 (C-2_B*), 70.7 (C-4_C), 70.6 (C-4_D), 70.1 (C-5_E), 69.9 (C-3_C), 68.8 (C-5_B), 68.7 (C-2_C), 68.2 (C-6_E), 68.1 (C-5_A), 67.6 (C-5_C), 62.5 (C-6_D), 62.4 (C-6_D),

59.0 (C-2_D), 54.7 (OCH_3), 21.2, 20.9, 20.8, 20.7 (5C, C(=O)CH_3), 18.1 (C-6_B), 18.0 (C-6_A), and 17.2 (C-6_C); ESMS for $C_{84}H_{102}Cl_3NO_{28}$ (M, 1679.7) *m/z* 1680.7 ($[M+H]^+$).

Anal. Calcd for $C_{84}H_{102}Cl_3NO_{28}$: C, 60.05; H, 6.12; N, 0.83%. Found: C, 60.18; H, 6.11; N, 0.78%.

Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→2)-α-L-rhamnopyranosyl-(1→2)-[(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (17). The fully protected **16** (225 mg, 0.13 mmol) dissolved in acetic acid (12 mL) was stirred for 48 h, in the dark, at rt, with palladium dichloride (104 mg, 587 μmol), sodium acetate (166 mg, 1.22 mmol) and water (2 drops). The solvents were removed by coevaporation with toluene and cyclohexane, and the residue, taken up in ethyl acetate, was extracted conventionally. Column chromatography of the crude material (solvent *A*, 98:2) gave the diol **17** as a colourless foam (123 mg, 59%); $[\alpha]_D$ +10° (*c* 1.0); 1H NMR: δ 7.42-7.06 (m, 26H, Ph, NH), 5.34 (bs, 1H, H-1_A), 5.22 (dd, 1H, $J_{1,2}$ = 1.9 Hz, H-2_C), 5.17 (dd, 1H, $J_{1,2}$ = 3.3, $J_{1,2}$ = 10.0 Hz, H-3_C), 5.02 (dd, 1H, $J_{1,2}$ = 9.8 Hz, H-4_C), 4.93 (d, overlapped, H-1_D), 4.92 (d, 1H, OCH_2), 4.91 (dd, partially overlapped, 1H, J = 9.8 Hz, H-4_D), 4.89 (d, 1H, OCH_2), 4.83 (d, 1H, J = 10.8 Hz, OCH_2), 4.82 (d, 1H, J = 10.6 Hz, OCH_2), 4.81 (bs, 1H, H-1_C), 4.79 (d, 1H, J = 12.6 Hz, OCH_2), 4.77 (bs, 1H, H-1_B), 4.74 (d, 1H, J = 12.5 Hz, OCH_2), 4.58 (d, 1H, J = 10.3 Hz, OCH_2), 4.55 (d, 1H, J = 12.0 Hz, OCH_2), 4.45 (d, 1H, J = 11.1 Hz, OCH_2), 4.30 (d, 1H, J = 12.0 Hz, OCH_2), 4.15-3.99 (m, 8H, H-$6a_D$, $6b_D$, 5_E, 3_B, 3_E, 2_B, 2_A, 3_D), 3.91-3.60 (m, 6H, H-3_A, 5_C, 5_A, 4_E, 5_B, 2_E), 3.55-3.42 (m, 5H, H-4_B, $6a_E$, $6b_E$, 4_A, 5_D), 3.35 (bd, 1H, $J_{4,5}$ = 8.5 Hz, H-2_D), 3.30 (s, 3H, OCH_3), 2.54 (d, 1H, $J_{OH,4}$ = 3.3 Hz, OH-4_A), 2.30 (d, 1H, $J_{OH,3}$ = 7.1 Hz, OH-3_A), 2.13, 2.06, 2.02, 1.97 (4s, 15H, C(=O)CH_3), 1.35 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_B), 1.31 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), and 1.16 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C); ^{13}C NMR: δ 170.4, 170.1, 170.0, 169.9, 169.4 (5C, OC(=O)), 162.0 (NC(=O)), 138.7-127.4 (Ph), 99.5 (2C, C-1_B, C-1_A), 99.4 (C-1_D), 99.1 (C-1_C), 93.8 (bs, C-1_E), 82.0 (C-3_E), 79.9 (bs, C-4_B), 79.2 (C-2_E), 78.2 (C-2_A), 78.1 (C-3_D), 77.8 (C-4_E), 75.8, 75.4, 74.9 (3C, OCH_2), 74.7 (C-3_B), 73.3 (2C, C-2_B, OCH_2), 73.2 (C-4_A), 72.5 (OCH_2), 72.0 (C-5_D), 71.3 (C-3_A), 70.6 (C-4_C), 70.1 (C-5_E), 69.8 (2C, C-2_C, 4_D), 68.9 (C-3_C), 68.8 (C-5_A), 68.2 (C-6_E), 68.1 (C-5_B), 67.7 (C-5_C), 62.5 (C-6_D), 56.9 (C-2_D), 54.8 (OCH_3), 21.0, 20.8, 20.7, 20.6 (5C, C(=O)CH_3), 18.1 (C-6_B), 17.5 (C-6_A), and 17.1 (C-6_C); ESMS $C_{78}H_{94}Cl_3NO_{28}$ for (M, 1597.5) *m/z* 1598.5 ($[M+H]^+$).

Anal. Calcd for $C_{78}H_{94}Cl_3NO_{28}$: C, 58.56; H, 5.92; N, 0.88%. Found: C, 58.36; H, 6.08; N, 0.68%.

Methyl α-L-Rhamnopyranosyl-(1→2)-(2-deoxy-2-trichloroacetamido-β-D-glucopyranosyl)-(1→ 2)-α-L-rhamnopyranosyl-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (18). 1N Sodium methoxide (500 µL, 0.5 mmol) was added dropwise to a solution of the pentaacetate **17** (60 mg, 37 µmol) in methanol:dichloromethane (1:1, 4 mL). The mixture was stirred overnight at rt. At this time, TLC (solvent *A*, 9:1) showed the presence of one more polar compound only. No product was detected when using ninhydrin. The reaction mixture was brought to neutral pH by addition of resin IR 120 (H^+), filtered and concentrated. The crude material was column chromatographed (solvent *A*, 92:8) to give the heptaol **21** (42 mg, 81%) as a colourless foam, $[\alpha]_D$ –1° (*c* 1.0, MeOH); ^1H NMR (DMSO-d_6): δ 8.91 (d, 1H, $J_{NH,2}$ = 8.4 Hz, NH), 7.52-6.98 (m, 25H, Ph), 5.22 (bs, 1H, H-1_E), 5.31 (bs, 1H, H-1_A), 4.84 (m, 5H, H-1_D, 4 OCH_2), 4.74 (bs, 1H, H-1_B), 4.66 (d, 1H, J = 10.5 Hz, OCH_2), 4.64 (bs, 1H, H-1_C), 4.61 (d, partially overlapped, 2H, OCH_2), 4.50 (d, 1H, J = 11.9 Hz, OCH_2), 4.18 (bs, 1H, H-2_B), 4.03-3.90 (m, 4H, H-2_A, 3_B, 5_E, 3_E), 3.79 (dq, 1H, $J_{4,5}$ = 9.2, $J_{5,6}$ = 6.1 Hz, H-5_C), 3.70-3.31 (m, 6H, H-3_A, 3_D, 5_A, 2_C, $6a_E$, $6b_E$, 5_B, $6a_E$, $6b_E$, 5_B, 4_B, 4_E, 3_C, 2_E), 3.24 (dd, partially overlapped, 1H, J = 9.5 Hz, H-4_A), 3.21 (s, 3H, OCH_3), 3.12 (dd, 1H, $J_{3,4}$ = 9.6, $J_{4,5}$ = 9.6 Hz, H-4_C), 3.07 (m, 1H, H-5_D), 2.97 (m, 1H, H-4_D), 1.26 (d, 3H, $J_{5,6}$ = 5.1 Hz, H-6_B), 1.13 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6_A) and 1.05 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6_C); ^{13}C NMR (DMSO-d_6): δ 128.4-127.4 (Ph), 101.2 (C-1_D), 99.5 (C-1_A), 99.2 (C-1_B), 90.4 (C-1_E), 81.0 (C-3_E), 80.5 (C-3_D), 79.0 (C-4_B), 77.7 (C-2_E), 77.2 (C-4_E), 76.5 (C-5_D), 76.4 (C-2_A), 75.2, 74.4, 74.1 (3C, OCH_2), 72.6 (C-3_B), 71.8 (C-4_A), 71.7 (OCH_2), 71.6 (2C, C-2_B, 4_C), 70.4 (2C, OCH_2, 2_C), 70.3 (2C, C-3_A, 3_C), 69.3 (C-4_D), 69.0 (C-5_E), 68.9 (C-5_A), 68.4 (C-6_E), 68.3 (C-5_C), 67.5 (C-5_B), 60.9 (C-6_D), 57.0 (C-2_D), 54.5 (OCH_3), 18.0 (C-6_B), 17.8 (C-6_A) and 17.7 (C-6_C); ESMS for $C_{68}H_{84}Cl_3NO_{23}$ (M, 1387.4) *m/z* 1388.4 $[M+H]^+$.

Anal. Calcd for $C_{74}H_{93}NO_{26}$: C, 58.77; H, 6.09; N, 1.01%. Found: C, 58.63; H, 6.27; N, 0.86%.

Methyl (2-Amino-2-deoxy-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1→ 2)-[(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (19). 1N Sodium methoxide (6 mL, 6 mmol) was added dropwise to a solution of the fully protected tetrasaccharide[16] **4** (1.19 g, 0.82 mmol) in methanol (30 mL). The mixture was stirred overnight at rt. At this time, TLC (solvent *A*, 95:5) showed the presence of a major compound which reacted with ninhydrin. The reaction mixture was brought to pH 9 by addition of resin IR 120 (H^+), filtered and concentrated. The crude material was column chromatographed (solvent *A*, 94:6) to give the aminotriol **19** (560 mg, 58%) as a colourless foam, $[\alpha]_D$ –2° (*c* 1.0); ^1H

NMR: δ 7.71-6.99 (m, 25H, Ph), 5.92 (m, 2H, C*H*=CH$_2$), 5.80 (bs, 1H, H-1$_A$), 5.30 (bs, overlapped, 1H, H-1$_E$), 5.26 (m, 2H, CH=C*H*$_2$), 5.15 (m, 2H, CH=C*H*$_2$), 5.01 (d, 1H, J = 11.2 Hz, OCH$_2$), 4.98 (d, 2H, J = 11.9 Hz, OCH$_2$), 4.85 (d, 1H, J = 11.2 Hz, OCH$_2$), 4.70 (t, 2H, OCH$_2$), 5.58 (bs, overlapped, 1H, H-1$_B$), 4.57 (m, 2H, OCH$_2$), 4.38 (d, 1H, J = 10.6 Hz, OCH$_2$), 4.34 (d, 2H, J = 12.0 Hz, OCH$_2$), 4.31 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1$_D$), 4.28 (bs, 1H, H-2$_B$), 4.19-4.02 (m, 7H, H-3$_B$, 3$_E$, 5$_E$, 2$_A$, 3 OCH$_2$), 3.83 (bd, 1H, $J_{6a,6b}$ = 10.1 Hz, H-6a$_D$), 3.70 (dd, 1H, $J_{2,3}$ = 3.3, $J_{3,4}$ = 9.5 Hz, H-3$_A$), 3.68-3.48 (m, 6H, H-6b$_D$, 5$_B$, 2$_E$, 4$_E$, 4$_B$, 5$_A$), 3.35-3.21 (m, 7H, 5$_D$, 4$_A$, 3$_D$, 4$_D$, OCH$_3$), 2.84 (m, 5H, OH, NH$_2$), 2.53 (dd, 1H, $J_{2,3}$ = 8.7 Hz, H-2$_D$), and 1.36 (d, 6H, $J_{5,6}$ = 6.0 Hz, H-6$_B$, 6$_A$); ^{13}C NMR: δ 139.2-127.2 (Ph, *C*H=CH$_2$), 117.1, 116.4 (2C, CH=*C*H$_2$), 106.3 (C-1$_D$), 100.4 (C-1$_B$), 97.8 (C-1$_A$), 91.7 (C-1$_E$), 81.6 (C-3$_E$), 80.0 (C-4$_A$), 79.4 (C-4$_B$), 78.5 (2C, C-2$_A$, 3$_A$), 78.4 (C-4$_E$*), 77.3 (C-2$_E$*), 76.9 (C-3$_D$*), 76.2 (OCH$_2$), 75.8 (C-5$_D$), 74.9, 74.8 (2C, OCH$_2$), 74.3 (C-3$_B$), 74.2, 73.2, 72.6, 71.3 (4C, OCH$_2$), 70.8 (C-4$_D$), 69.5 (C-5$_E$), 68.5 (C-5$_B$), 68.3 (C-5$_A$), 68.2 (C-6$_E$), 66.2 (C-2$_B$), 62.0 (C-6$_D$), 57.3 (C-2$_D$), 54.6 (OCH$_3$), 18.2 (C-6$_B$*), and 18.1 (C-6$_A$*); ESMS for C$_{66}$H$_{83}$NO$_{18}$ (M, 1177.6) *m/z* 1178.6 [M+H]$^+$.

Anal. Calcd for C$_{66}$H$_{83}$NO$_{18}$: C, 67.27; H, 7.10; N, 1.19%. Found: C, 67.31; H, 7.14; N, 1.10%.

Methyl (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1→ 2)-[(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (20). Compound[16] **4** (200 mg, 0.13 mmol) in methanol (10 mL) was treated with 1N sodium methoxide (1.5 mL, 1.5 mmol) as described for the preparation of **19**. The crude reaction mixture was disolved in methanol (20 mL) and acetic anhydride (2 mL) was added at 0 °C. The mixture was stirred at rt for 2 h. Et$_3$N (5 drops) was added, and the volatiles were eliminated by repeated coevaporation with cyclohexane and methanol. The residue was chromatographed on a column of silica gel (solvent *A*, 96:4) to give the triol **20** (140 mg, 88%) as a colourless foam, [α]$_D$ -17° (*c* 1.0); ^{1}H NMR: δ 7.41-7.00 (m, 25H, Ph), 6.58 (bs, 1H, NH), 5.97 (m, 2H, C*H*=CH$_2$), 5.80 (bs, 1H, H-1$_A$), 5.36-5.19 (m, 4H, CH=C*H*$_2$), 5.16 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1$_E$), 5.03 (d, 1H, J = 11.1 Hz, OCH$_2$), 4.97 (d, 1H, J = 9.7 Hz, OCH$_2$), 4.93 (d, 1H, J = 11.5 Hz, OCH$_2$), 4.90 (d, 1H, J = 10.9 Hz, OCH$_2$), 4.73 (d, 1H, J = 10.6 Hz, OCH$_2$), 4.70 (d, 1H, J = 12.5 Hz, OCH$_2$), 4.57 (d, 2H, J = 11.6 Hz, OCH$_2$), 4.56 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1$_B$), 4.45 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1$_D$), 4.42 (d, 1H, J = 10.9 Hz, OCH$_2$), 4.35-4.21 (m, 4H, OCH$_2$), 4.23 (bs, 1H, H-2$_B$), 4.16 (dd, 2H, $J_{2,3}$ = 2.3 Hz, H-3$_B$, OCH$_2$), 4.08 (dd, 1H, J = 9.3 Hz, H-3$_E$), 4.01 (bd, 1H, H-5), 3.86 (d, 1H, $J_{6a,6b}$ = 9.9 Hz, H-6a$_D$), 3.79 (dd, 1H, $J_{2,3}$ = 3.4, $J_{3,4}$ = 9.4 Hz, H-3$_A$), 3.66-3.39 (m, 11H, H-5$_B$, 4$_E$, 6a$_E$, 2$_E$, 4$_B$, 5$_D$, 6b$_E$, 6b$_D$, 5$_A$, 3$_D$, 2$_D$), 3.30 (dd, 1H, $J_{4,5}$ =

9.4 Hz, H-4_A), 3.28 (s, 3H, OCH_3), 3.23 (dd, 1H, $J_{3,4}$ = 9.2, $J_{4,5}$ = 9.2 Hz, H-4_D), 2.04 (s, 3H, (C=O)CH_3), 1.37 (d, partially overlapped, 3H, H-6_A), and 1.35 (d, partially overlapped, 3H, H-6_B); ^{13}C NMR: δ 173.7 (C=O), 139.1-117.2 (Ph, *C*H=CH_2), 119.0, 117.2 (2C, CH=*C*H_2), 103.8 (C-1_D), 100.3 (C-1_B), 97.5 (C-1_A), 92.3 (bs, C-1_E), 81.8 (C-3_E), 80.9 (C-4_A), 80.2 (C-2_A), 79.6 (C-3_A), 79.3 (bs, C-4_B), 78.5 (C-4_E), 77.2 (C-2_E), 77.1 (C-5_A), 76.2 (OCH_2), 75.6 (C-3_D), 74.9, 74.8 (2C, OCH_2), 74.5 (bs, C-3_B), 74.3, 73.3, 73.2, 73.0 (4C, OCH_2), 72.6 (C-4_D), 69.6 (C-5_E), 68.6 (C-5_B), 68.3 (2C, C-5_D, C-6_E), 66.3 (C-2_B), 62.5 (C-6_D), 59.1 (C-2_D), 54.6 (OCH_3), 23.1 (C(=O)CH_3), and 17.9 (2C, C-6_B, 6_A); ESMS for $C_{68}H_{85}NO_{19}$ (M, 1219.6) *m/z* 1220.6 $[M+H]^+$.

Anal. Calcd for $C_{68}H_{85}NO_{19}$: C, 66.92; H, 7.02; N, 1.15%. Found: C, 66.78; H, 7.10; N, 1.09%.

Methyl (2-Acetamido-2-deoxy-3,4-*O*-isopropylidene-β-D-glucopyranosyl)-(1→ 2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1→ 2)-[(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1 → 3)]-4-*O*-benzyl-α-L-rhamnopyranoside (21). Compound[16] **4** (421 mg, 0.29 mmol) in methanol (20 mL) was treated first with 1N sodium methoxide (3 mL, 3.0 mmol), then with acetic anhydride (4 mL) in methanol (40 mL) as described for the preparation of **20**. The crude reaction mixture was disolved in methanol (20 mL) and acetic anhydride (2 mL) was added at 0 °C. The crude reaction mixture was coevaporated repeatedly with anhydrous DMF, then solubilized in DMF (5 mL). 2,2-Dimethoxypropane (10 mL), and TsOH (50 mg) were added and the reaction mixture was stirred under reduced pressure for 20 min. Et_3N (500 μL) was added, and the volatiles were eliminated. The residue was chromatographed on a column of silica gel (solvent *C*, 70:3) to give the alcohol **21** (335 mg, 95%) as a colourless foam, $[\alpha]_D$ –11° (*c* 1.0); ^{1}H NMR: δ 7.41-7.08 (m, 26H, Ph, NH), 5.95 (m, 2H, C*H*=CH_2), 5.40 (bs, 1H, H-1_A), 5.38-5.18 (m, 4H, CH=CH_2), 5.04 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1_E), 4.92-4.79 (m, 5H, OCH_2), 4.71 (d, 1H, H-1_B), 4.67 (d, 1H, J = 12.3 Hz, OCH_2), 4.58 (d, 1H, J = 10.0 Hz, OCH_2), 4.54 (d, 1H, J = 12.0 Hz, OCH_2), 4.43 (d, 1H, J = 10.9 Hz, OCH_2), 4.41 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1_D), 4.34-4.16 (m, 4H, OCH_2), 4.12 (m, 3H, H-2_B, 3_B, OCH_2), 4.05-3.97 (m, 3H, H-2_A, 3_E, 5_E), 3.80 (dd, 1H, $J_{2,3}$ = 3.1, $J_{3,4}$ = 9.4 Hz, H-3_A), 3.75-3.64 (m, 5H, H-$6a_D$, 5_A, 4_B, 4_E, 5_B), 3.61-3.43 (m, 7H, H-2_E, $6b_D$, $6b_E$, 2_D, $6a_E$, 3_D, $6b_E$, 4_D), 3.30 (s, 3H, OCH_3), 3.26 (dd, 1H, $J_{4,5}$ = 9.4 Hz, H-4_A), 3.06 (m, 1H, H-5_D), 2.05 (s, 3H, (C=O)CH_3), 1.39 (s, 3H, CH_3), 1.34 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6_B), 1.31 (d, partially overlapped, 3H, H-6_A), and 1.29 (s, 3H, CH_3); ^{13}C NMR: δ 179.5 (C=O), 138.6-127.5 (Ph, *C*H=CH_2), 119.3, 117.1 (2C, CH=*C*H_2), 103.0 (C-1_D), 99.8 (*C*Me_2), 99.6 (C-1_B), 99.0 (bs, C-1_A), 94.1 (bs, C-1_E), 82.3 (C-3_E), 81.5 (C-4_A), 79.8 (C-3_A), 79.6 (bs, C-4_B), 78.7 (C-2_A), 78.6 (C-2_E), 77.7 (C-4_E), 75.7, 75.5 (2C, OCH_2), 75.1 (bs, C-3_B), 74.9, 74.3 (2C, OCH_2), 74.2 (C-3_D), 74.0 (C-4_D), 73.3, 73.2, 72.6

(3C, OCH_2), 72.1 (C-2_B), 70.3 (C-5_E), 68.2 (C-6_E, 5_B, C-5_A), 67.4 (C-5_D), 61.9 (C-6_D), 60.2 (C-2_D), 54.8 (OCH_3), 29.0 (CH_3), 23.2 (C(=O)CH_3), 18.8 (CH_3), 18.1 (C-6_B), and 17.8 (C-6_A); ESMS for $C_{71}H_{89}NO_{19}$ (M, 1219.6) *m/z* 1260.6 $[M+H]^+$.

Anal. Calcd for $C_{68}H_{85}NO_{19}$: C, 67.66; H, 7.12; N, 1.11%. Found: C, 67.48; H, 7.18; N, 1.07%.

Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-2-deoxy-3,4-*O*-isopropylidene-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1→ 2)-[(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (22). To a solution of the acceptor **21** (347 mg, 0.27 mmol) and donor[21] **7** (168 mg, 0.38 mmol) in anhydrous Et_2O (10 mL), molecular sieves 4Å were added, and the mixture was stirred at -78 °C for 30 min under dry Ar. Boron trifluoride etherate (135 μL, 1.11 mmol) was added sequentially, and the mixture was stirred overnight while coming back to rt. TLC (solvent *C*, 7:3) showed almost complete conversion of the starting materials into a major product. Et_3N (850 μL, 1.17 mmol) was added, and the mixture was filtered on a pad of Celite and then concentrated. The residue was eluted from a column of silica gel (solvent *C*, 75:25) to give the fully protected pentasaccharide **22** (363 mg, 88 %) as the first eluting product and methyl (2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-allyl-α-L-rhamnopyranosyl)-(1→ 2)-[(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (**23**) (35 mg, 8%) as the slower eluting product. Compound **22** had $[\alpha]_D$ -9° (*c* 1.0); ^1H NMR: δ 7.43-7.08 (m, 25H, Ph), 5.94 (m, 2H, CH=CH_2), 5.73 (d, 1H, $J_{NH,2}$ = 7.4 Hz, NH), 5.34 (bs, 1H, H-1_A), 5.32-5.15 (m, 3H, CH=CH_2, 3_C), 5.10 (dd, 1H, $J_{1,2}$ = 1.7, $J_{2,3}$ = 3.3 Hz, H-2_C), 5.07 (d, 1H, $J_{1,2}$ = 2.8 Hz, H-1_E), 5.04 (dd, 1H, $J_{3,4}$ = 10.0, $J_{4,5}$ = 10.0 Hz, H-4_C), 4.95-4.81 (m, 7H, 6 OCH_2, H-1_D), 4.80 (d, 1H, H-1_C), 4.70 (d, 1H, H-1_B), 4.66 (d, 1H, J = 12.5 Hz, OCH_2), 4.57 (d, 1H, J = 10.3 Hz, OCH_2), 4.43 (d, 1H, J = 11.0 Hz, OCH_2), 4.30 (d, 2H, J = 12.0 Hz, OCH_2), 4.11 (m, 5H, H-5_C, 3_B, 3 OCH_2), 4.08 (bs, 2H, H-2_A, 2_B), 4.06-3.94 (m, 2H, H-5_E, 3_D), 3.79-3.43 (m, 10H, H-3_A, $6a_D$, 5_A, 5_B, 2_E, $6b_D$, $6a_E$, 4_E, 4_B, $6b_E$), 3.40-3.35 (m, 2H, H-4_D, 2_D), 3.28 (s, 3H, OCH_3), 3.24 (dd, 1H, $J_{4,5}$ = 9.4 Hz, H-4_A), 3.11 (m, 1H, H-5_D), 2.13, 2.05, 2.01, 1.99 (4s, 12H, (C=O)CH_3), 1.32 (d, partially overlapped, 3H, H-6_B), 1.30 (s, 3H, CH_3), 1.29 (d, partially overlapped, 3H, H-6_A), 1.20 (s, 3H, CH_3), and 1.13 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C); ^{13}C NMR: δ 171.0, 170.3, 170.1 (3C, OC(=O)), 163.4 (NC(=O)), 138.7-127.5 (Ph, *C*H=CH_2), 117.4, 116.8 (2C, CH=*C*H_2), 101.1 (C-1_D), 99.7 (C-1_B), 99.5 (bs, C-1_A), 99.2 (*C*Me_2), 97.6 (C-1_C), 94.0 (bs, C-1_E), 82.2 (C-3_E), 80.7 (C-4_A), 79.6 (bs, C-4_B), 79.3 (C-3_A), 78.9 (C-2_E), 77.7 (C-4_E), 77.4 (C-3_D), 76.2 (C-2_A), 75.5 (2C, OCH_2), 75.0 (bs, C-3_B), 74.9, 74.2, 73.3 (3C, OCH_2), 72.6 (C-4_D), 72.5 (2C, OCH_2, 2_B), 71.9

(OCH_2), 71.3 (C-4_C), 70.5 (C-2_C), 70.2 (C-5_E), 68.9 (C-3_C), 68.5 (C-5_A), 68.2 (C-6_E), 68.1 (C-5_B), 67.1 (C-5_D), 66.1 (C-5_C), 62.2 (C-6_D), 58.0 (C-2_D), 54.8 (OCH_3), 29.0 (CH_3), 23.7, 21.0, 20.9, 20.8 (4C, C(=O)CH_3), 19.1 (CH_3), 18.1 (C-6_B), 18.0 (C-6_A) and 17.8 (C-6_C); ESMS for $C_{83}H_{105}NO_{26}$ (M, 1531.7) *m/z* 1532.7 $[M+H]^+$.

Anal. Calcd for $C_{83}H_{105}NO_{26}\cdot 2H_2O$: C, 63.55; H, 7.00; N, 0.89%. Found: C, 63.70; H, 6.90; N, 0.91%.

Compound **23** had ^{1}H NMR: δ 7.46-7.01 (m, 25H, Ph), 6.01-5.89 (m, 2H, C*H*=CH_2), 5.76 (bs, 1H, H-1_A), 5.75 (d, partially overlapped, 1H, NH), 5.35-5.19 (m, 4H, CH=C*H*$_2$), 5.28 (d, overlapped, 1H, H-1_E), 5.23 (dd, overlapped, 1H, H-3_C), 5.18 (bd, overlapped, 1H, H-2_C), 5.09 (dd, 1H, $J_{3,4}$ = 9.8, $J_{4,5}$ = 9.8 Hz, H-4_C), 5.12-4.89 (m, 4H, 4 OCH_2), 4.90 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1_D), 4.83 (bs, 1H, H-1_C), 4.75 (d, 1H, J = 9.8 Hz, OCH_2), 4.70 (d, 1H, J = 12.0 Hz, OCH_2), 4.58 (m, 3H, H-1_B, 2 OCH_2), 4.40 (d, 1H, J = 11.9 Hz, OCH_2), 4.37-4.32 (m, 2H, OCH_2), 4.21-4.01 (m, 9H, H-2_B, 3_B, 5_C, 3_D, 3_E, 5_E, 2_A, 2 OCH_2), 3.84 (dd, 1H, $J_{6a,6b}$ = 10.1 Hz, H-$6a_D$), 3.73-3.49 (m, 10H, H-3_A, $6a_E$, 5_B, $6b_D$, 2_E, 4_E, 4_B, 5_A, $6b_E$, 5_D), 3.38 (m, 1H, H-5_D), 3.30 (dd, partially overlapped, 1H, $J_{4,5}$ = 9.5 Hz, H-4_A), 3.28 (s, 3H, OCH_3), 3.14 (m, 2H, H-4_D, 2_D), 2.14, 2.06, 2.00 (3s, 12H, (C=O)CH_3), 1.36 (d, 6H, H-6_B, 6_A) and 1.21 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6_C); ^{13}C NMR: δ 171.0, 170.3, 170.1, 169.9 (4C, OC(=O)), 139.3-127.2 (Ph, *C*H=CH_2), 117.0 (2C, CH=*C*H$_2$), 101.7 (C-1_D), 100.4 (C-1_B), 99.3 (C-1_C), 97.8 (C-1_A), 92.0 (bs, C-1_E), 84.4 (C-3_E), 81.6 (C-3_D), 80.1 (C-4_A), 79.5 (bs, C-4_B), 78.7 (C-3_A), 78.5 (C-4_E*), 78.1 (C-2_E*), 78.0 (C-2_A), 76.1 (bs, OCH_2), 75.2 (C-5_D), 74.9, 74.8 (2C, OCH_2), 74.5 (bs, C-3_B), 74.2, 73.2, 73.0, 71.8 (4C, OCH_2), 70.7 (C-4_C), 70.6 (C-4_D), 69.8 (C-2_C), 69.5 (C-5_E), 68.7 (C-3_C), 68.5 (2C, C-5_A, 5_B), 68.3 (C-6_E), 67.5 (C-5_C), 66.0 (bs, C-5_C), 62.0 (C-6_D), 56.9 (C-2_D), 54.6 (OCH_3), 23.4, 20.7, 20.6, 20.5 (4C, C(=O)CH_3), 17.9 (C-6_A*), 17.7 (C-6_B*) and 17.2 (C-6_C); ESMS for $C_{80}H_{101}NO_{26}$ (M, 1491.7) *m/z* 1492.7 $[M+H]^+$.

Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-(1→2)-α-L-rhamnopyranosyl-(1→2)-[(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (24). The fully protected **22** (111 mg, 72 μmol) dissolved in anhydrous THF (6 mL) was treated first with 1,5-cyclooctadiene-bis(methyldiphenylphosphine)iridium hexafluorophosphate (20 mg, 24 μmol), then with mercuric oxide (60 mg, 0.28 mmol) and mercuric bromide (62 mg, 0.23 mmol) in a mixture of acetone and water (10 mL, 4:1), as described for the preparation of **10**. Column chromatography (solvent *A*, 96:4) of the crude material gave the diol **24** as a colourless foam (82 mg, 79%), $[\alpha]_D$ –5° (*c* 1.0); ^{1}H NMR (Pyridine-d_5): δ 9.16 (d, 1H, $J_{NH,2}$ = 7.9 Hz, NH), 7.70-7.21 (m, 25H, Ph), 7.05 (bs, 1H, OH), 6.84 (bs, 1H, OH), 5.93 (bs, 1H,

H-1_A), 5.83 (dd, 1H, $J_{2,3}$ = 3.4, $J_{3,4}$ = 10.0 Hz, H-3_C), 5.78 (bs, 1H, H-2_C), 5.76 (d, partially overlapped, 1H, H-1_D), 5.65 (d, partially overlapped, 1H, H-1_E), 5.61 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4_C), 5.51 (bs, 1H, H-1_C), 5.27 (d, 1H, J = 12.7 Hz, OCH_2), 5.25 (d, 1H, J = 11.1 Hz, OCH_2), 5.14 (bs, 1H, H-1_B), 5.16-4.94 (m, 3H, OCH_2), 4.82 (bs, H-2_A), 4.74 (d, 1H, J = 10.2 Hz, OCH_2), 4.67-4.60 (m, 5H, H-3_A, 2_B, 3_D, 5_C, 3_B), 4.57 (d, 2H, OCH_2), 4.46 (m, 2H, H-3_E, 5_E), 4.41 (d, 2H, J = 11.9 Hz, OCH_2), 4.33 (m, 1H, H-5_A), 4.26 (bdd, 1H, H-4_A), 4.12 (ddd, 1H, $J_{1,2}$ = 8.3, $J_{2,3}$ = 9.5 Hz, H-2_D), 3.94-3.87 (m, 5H, H-2_E, 4_B, 4_E, 5_B, $6b_D$), 3.78 (dd, 1H, H-$6a_E$), 3.70 (bd, 1H, H-$6b_E$), 3.66 (d, 1H, $J_{6a,6b}$ = 11.0 Hz, $6b_D$), 3.60 (dd, 1H, J = 9.5, J = 9.1 Hz, H-4_D), 3.37 (m, 1H, H-5_D), 3.26 (s, 3H, OCH_3), 2.25, 2.09, 1.98, 1.97 (4s, 12H, C(=O)CH_3), 1.62 (d, 3H, $J_{5,6}$ = 5.9 Hz, H-6_A), 1.41 (s, 3H, iPr), 1.40 (d, partially overlapped, 3H, H-6_B), 1.40 (d, partially overlapped, 3H, H-6_C), and 1.23 (s, 3H, iPr); ^{13}C NMR (Pyridine-d_5): δ 171.3, 170.1, 169.9 (4C, C(=O)), 139.5-127.6 (Ph), 102.4 (C-1_D), 100.9 (C-1_A), 100.2 (C-1_B), 99.2 (CMe_2), 98.2 (C-1_C), 93.7 (C-1_E), 82.3 (C-3_E), 80.2 (C-4_B), 79.3 (C-4_E*), 78.8 (C-2_A), 78.4 (C-2_E*), 77.7 (C-3_D), 75.4 (OCH_2), 75.1 (C-3_B), 75.0 (OCH_2), 73.6 (C-4_A), 73.4 (C-2_B), 73.1 (2C, OCH_2), 73.0 (C-4_D), 72.2 (C-3_A), 71.9 (OCH_2), 71.6 (C-4_C), 71.1 (C-2_C), 70.8 (C-5_E), 70.5 (C-5_A), 69.5 (C-3_C), 69.3 (C-6_E), 68.5 (C-5_B), 67.4 (C-5_D), 66.5 (C-5_C), 62.4 (C-6_D), 58.0 (C-2_D), 54.6 (OCH_3), 29.1 (iPr), 23.4, 20.5, 20.4, 20.3 (4C, C(=O)CH_3), 19.0 (iPr), 18.3 (2C, C-6_B, 6_A), and 17.5 (C-6_C); ESMS for $C_{77}H_{97}NO_{26}$ (M, 1451.6) *m/z* 1452.7 $[M+H]^+$.

Anal. Calcd for $C_{77}H_{97}NO_{26}$: C, 63.67; H, 6.73; N, 0.96%. Found: C, 63.49; H, 6.91; N, 0.96%.

Methyl (2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1→2)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-α-L-rhamnopyranosyl-(1→2)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)]-4-*O*-benzyl-α-L-rhamnopyranoside (25). 50% Aq CF_3CO_2H (2 mL) was added to a solution of the crude diol **24** (130 mg, 89 μmol) in CH_2Cl_2 (10 mL). The mixture was kept under vigorous stirring at 0 °C for 4 h. At this time, TLC (solvent *D*, 1:1) showed that the reaction was finished. Extraction and evaporation of the solvent, followed by column chromatography (solvent *D*, 50:50 → 40:60) of the crude residue gave the tetraol **25** as a colourless foam (115 mg, 91%), $[\alpha]_D$ +3° (*c* 1.0); ^{1}H NMR: δ 7.88-6.85 (m, 25H, Ph), 6.35 (d, 1H, $J_{NH,2}$ = 6.8 Hz, NH), 5.77 (bs, 1H, H-1_A), 5.31 (d, 1H, H-1_E), 5.24 (dd, 1H, $J_{2,3}$ = 2.9, $J_{3,4}$ = 10.1 Hz, H-3_C), 5.15 (bs, 1H, H-2_C), 5.14 (d, partially overlapped, 1H, H-1_D), 5.10-4.91 (m, 5H, H-4_C, 4 OCH_2), 4.78 (bs, 1H, H-1_C), 4.75 (d, 1H, J = 10.8 Hz, OCH_2), 4.72 (d, 1H, OCH_2), 4.62 (bs, 1H, H-1_B), 4.60 (d, 2H, OCH_2), 4.42 (d, 1H, J = 10.8 Hz, OCH_2), 4.35 (d, 1H, J = 12.0 Hz, OCH_2), 4.24 (bs, 1H, H-2_B), 4.21-3.97 (m, 6H, H-3_B, 3_E, 5_C, 2_A, 5_E, 3_D), 3.89 (m, 2H, H-3_A, $6a_D$), 3.70-3.40 (m, 11H, H-4_E, 5_B, $6b_D$, 2_E, $6a_E$, 4_B, $6b_E$, $6b_D$, 5_A, 4_A, 5_D), 3.28 (s, 3H, OCH_3), 3.19 (m, 1H, H-4_D), 3.11 (m,

1H, H-2_D), 2.17, 2.07, 2.04, 2.02 (4s, 12H, 4 C(=O)CH_3), 1.38 (t, 6H, H-6_B, 6_A), and 1.20 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6_C); ^{13}C NMR: δ 172.2, 170.3, 170.1, 169.9 (4C, O(C=O)), 139.2-125.3 (Ph), 101.4 (C-1_D), 100.3 (C-1_B), 99.1 (C-1_C), 98.2 (C-1_A), 92.2 (C-1_E), 83.8 (C-3_D), 81.7 (C-3_E), 79.6 (C-4_B), 79.4 (C-2_A), 78.5 (C-4_E), 78.3 (C-2_E), 76.2 (OCH_2), 75.8 (C-4_A), 75.0, 74.9 (2C, OCH_2), 74.4 (C-3_B), 73.3 (OCH_2), 73.2 (C-5_D), 73.1 (OCH_2), 71.0 (C-3_A, 4_D), 70.6 (C-4_C), 69.9 (C-2_C), 69.6 (C-5_E), 68.9 (C-5_A), 68.8 (C-3_C), 68.6 (C-5_B), 68.2 (C-6_E), 67.4 (C-5_C), 66.7 (C-2_B), 62.1 (C-6_D), 57.5 (C-2_D), 54.6 (OCH_3), 23.3, 22.5, 20.7, 20.6 (4C, C(=O)CH_3), 17.8 (2C, C-6_B, 6_A), and 17.2 (C-6_C); ESMS for $C_{74}H_{93}NO_{26}$ (M, 1411.6) *m/z* 1412.7 $[M+H]^+$.

Anal. Calcd for $C_{74}H_{93}NO_{26}$: C, 62.92; H, 6.64; N, 0.99%. Found: C, 62.78; H, 6.84; N, 0.96%.

Methyl α-L-Rhamnopyranosyl-(1→2)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-α-L-rhamnopyranosyl-(1→ 2)-α-D-glucopyranosyl-(1→ 3)-α-L-rhamnopyranoside (3). (a) Compound **25** (137 mg, 86 μmol) in methanol (3 mL) was treated with 1N methanolic sodium methoxide as described for the preparation of **5**. The crude residue was added to a suspension of Pd-C catalyst (300 mg) in a 1:4 mixture of acetic acid and methanol. After stirring for 48 h under a hydrogen atmosphere, the suspension was filtered on a pad of Celite, and the filtrate was concentrated. Acetic acid was eliminated by repeated coevaporation with cyclohexane and methanol. Purification of the crude product was achieved by reverse phase chromatography. The column was eluted with solvent *F* (gradient 100:0 → 96:4) to give, after lyophilization, the target pentasaccharide **3** (50 mg, 69%) as a colourless foam, $[\alpha]_D$ +1° (*c* 1.0, water); ^{1}H NMR (D_2O): δ 5.11 (bs, 1H, H-1_A), 5.06 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1_E), 4.86 (bs, 1H, H-1_C), 4.82 (bs, 1H, H-1_B), 4.78 (d, partially overlapped, 1H, H-1_D), 4.15 (m, 2H, H-2_A, 2_B), 4.97 (dq, partially overlapped, 1H, H-5_C), 4.96-3.84 (m, 4H, H-$6a_D$, 3_B, 3_A, 5_E), 3.91-3.69 (m, 9H, H-2_D, 2_C, $6a_E$, $6b_E$, 3_E, 3_C, 5_A, $6b_D$, 5_B), 3.62-3.56 (m, 3H, H-3_D, 4_B, 2_E), 3.48 (m, 2H, H-5_D, 4_D), 3.45 (dd, 1H, J = 9.8 Hz, H-4_E), 3.42 (dd, 1H, J = 9.8 Hz, H-4_C), 3.40 (s, 3H, OCH_3), 3.32 (dd, 1H, $J_{3,4}$ = 9.6, $J_{4,5}$ = 9.6 Hz, H-4_A), 2.07 (s, 3H, C(=O)CH_3), 1.33 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6_B), 1.25 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6_A) and 1.23 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6_C); ^{13}C NMR (D_2O): δ 175.2 (C=O), 102.5 (C-1_D, $J_{C,H}$ = 157 Hz), 102.1 (C-1_C, $J_{C,H}$ = 169 Hz), 101.8 (C-1_A, $J_{C,H}$ = 172 Hz), 100.3 (C-1_B, $J_{C,H}$ = 172 Hz), 95.1 (C-1_E, $J_{C,H}$ = 169 Hz), 82.0 (C-3_D), 79.2 (C-2_A), 76.8 (C-5_D), 75.5 (C-2_B), 74.1 (C-3_B), 73.8 (C-3_E), 72.6 (C-4_C), 72.4 (C-5_E), 71.8 (C-2_E), 71.5 (C-2_C), 71.1 (C-4_B), 70.9 (C-5_A), 70.6 (C-3_A), 70.2 (C-4_E), 70.0 (C-3_C), 69.7 (C-5_C), 69.3 (2C, C-5_B, 4_D), 61.7 (C-6_D), 61.1 (C-6_E), 56.5 (C-2_D), 55.8 (OCH_3), 22.8 (C(=O)CH_3), 17.3 (2C, C-6_A, 6_C) and 17.0 (C-6_B); FABMS for $C_{33}H_{57}NO_{23}$ (M, 834.6) *m/z* 858.4 $[M+Na]^+$.

Anal. Calcd for $C_{33}H_{57}NO_{23}\cdot 3.5H_2O$: C, 44.11; H, 7.17; N, 1.85%. Found: C, 43.92; H, 6.92; N, 1.85%.

(b) A suspension of 10% Pd-C catalyst (200 mg) in a 1:4 mixture of methanol:acetic acid (10 mL) containing the trichloroacetamide **18** (40 mg, 29 μmol) was stirred at rt for 48 h under a hydrogen atmosphere. The suspension was filtered on a pad of Celite. Volatiles were eliminated by repeated coevaporations of the residue with methanol and cyclohexane. Triethylamine (2 drops) was added to a suspension of 10% Pd-C catalyst (80 mg) in a methanolic solution of the residue (5 mL). The reaction mixture was stirred under a hydrogen atmosphere for 48 h, filtered, and concentrated. The residue was purified by reverse phase chromatography, as described above, to give the target **3** (11 mg, 45%).

Methyl (2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-α-L-rhamnopyranosyl-(1→2)-α-D-glucopyranosyl-(1→3)-α-L-rhamnopyranoside (2). Compound[16] **26** (88 mg, 65 μmol) in methanol (3 mL) was treated with 1N methanolic sodium methoxide as described for the preparation of **5**. The crude residue was added to a suspension of Pd-C catalyst (300 mg) in a 1:4 mixture of acetic acid and methanol. After stirring for 48 h under a hydrogen atmosphere, the suspension was filtered on a pad of Celite and the filtrate was concentrated. Acetic acid was eliminated by repeated coevaporation with cyclohexane and methanol. Next, Pd-C catalyst (60 mg) was added to a methanolic solution of the crude residue (5 mL) containing 5 drops of triethylamine. The mixture was stirred under a hydrogen atmosphere for 48 h, and the suspension was filtered on a pad of Celite. Volatiles were eliminated, and the crude product was purified by reverse phase. The column was eluted with solvent *F* (gradient 100:0 → 96:4) to give, after lyophilization, the target tetrasaccharide **2** (35 mg, 78%) as a colourless foam. Analytical data for compound **2** were identical to those reported before.[16]

ACKNOWLEDGMENTS

We are grateful to Dr. A. Namane (Laboratoire de Chimie Structurale des Macromolécules, Institut Pasteur) for performing the electrospray mass spectra.

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