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# Blockwise Approach to Fragments of the O-Specific Polysaccharide of *Shigella flexneri* Serotype 2a: Convergent Synthesis of a Decasaccharide Representative of a Dimer of the Branched Repeating Unit[1]

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The **D′A′B′(E′)C′DAB(E)C** decasaccharide representative of a dimer of a frame-shifted pentasaccharide repeating unit of the O-specific polysaccharide of *Shigella flexneri* 2a was synthesized as its methyl glycoside by condensing a pentasaccharide donor (**D′A′B′(E′)C′**) and a pentasaccharide acceptor (**DAB(E)C**-OMe). Several convergent routes to these two building blocks, involving either the **AB** linkage or the **BC** linkage as the disconnection site, were evaluated in comparison to the linear strategy. The latter was preferred. It is based on the use of the trichloroacetimidate chemistry. The target branched oligosaccharide was designed to probe the recognition at the molecular level of the natural polysaccharide by protective monoclonal antibodies.

## Introduction

Shigellosis or bacillary dysentery is a worldwide disease, occurring in humans only, caused by organisms of the genus *Shigella*. Responsible for an estimated 200 million cases annually, *Shigella* is increasingly resistant to antimicrobial drugs.[2] Shigellosis is a priority target for vaccine development as defined by the World Health Organization since this disease is a major cause of mortality in developing countries, especially among children under 5 years of age and in the immunocompromised population.[3] Although no vaccine is yet available against shigellosis, several programs targeting the eradication of this bacterial infection are under development,[2] with emphasis on vaccination strategies involving either live attenuated strains of *Shigella*[4] or acellular vaccines based on lipopolysaccharide (LPS) antigens and derivatives thereof.[5] Of particular interest in the later approach is the design of glycoconjugate vaccines based on the use of detoxified LPS. Indeed, there is evidence that natural and experimental infections with *Shigella* confer type-specific immunity,[6] which points to the O-specific polysaccharide (O-SP) moiety of the LPS as the target antigen of the host's protective immune response to infection. Besides, data show that significant levels of preexisting antibodies specific for the O-SP correlate with a diminished attack rate of shigellosis.[7] Furthermore, it was recently demonstrated in field trials that protein conjugates of detoxified LPS provided protection to human volunteers against infections caused by *S. sonnei*.[8] As was particularly emphasized in the case of *S. dysenteriae* type 1, conjugates incorporating oligosaccharide fragments of the native bacterial polysaccharides may be even more immunogenic than their counterparts made of the detoxified LPS.[9]

Of most concern among the different species of *Shigella* is *S. flexneri* serotype 2a, the prevalent infective agent responsible for the endemic form of the disease.[10] Indeed, major efforts from different laboratories, including the development of conventional polysaccharide−protein conjugates,[11] aim at the development of a vaccine against the disease associated with this particular serotype. In parallel, we are developing a program aimed at the design of chemically defined glycoconjugate vaccines

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(1) Part 10 of the series Synthesis of ligands related to the O-specific polysaccharides of *Shigella flexneri* serotype 2a and *Shigella flexneri* serotype 5a. For part 9, see ref 19.

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based on the use of synthetic fragments of the O-SP of *S. flexneri* 2a. To achieve this goal, we adopted a rational approach, involving a preliminary study of the interaction between the bacterial O-SP and homologous protective monoclonal antibodies. The O-SP of *S. flexneri* 2a is a

**D** **A** **B**

3)-β-D-GlcNAc*p*(1→2)-α-L-Rha*p*-(1→2)-α-L-Rha*p*-(1→3)-

**E** **C**

[α-D-Glc*p*-(1→4)]-α-L-Rha*p*-(1→

**I**

heteropolysaccharide defined by its biological repeating unit, the **AB(E)CD** sequence,[12,13] corresponding to a frame-shifted pentasaccharide **I**. It features a linear tetrasaccharide backbone, which is common to all *S. flexneri* O-antigens and comprises a *N*-acetyl glucosamine and three rhamnose residues, together with an α-D-glucopyranose residue branched at position 4 of one of the rhamnoses. Besides the known methyl glycoside of the **EC** disaccharide,[14,15] a set of di- to pentasaccharides[16−18] and more recently an octasaccharide[19] representative of fragments of *S. flexneri* 2a O-SP have been synthesized. The use of these compounds as molecular probes for mapping at the molecular level the binding characteristics of a set of protective antibodies against *S. flexneri* 2a infection indicated that access to larger oligosaccharides would help the characterization of the carbohydrate antigenic determinants. For this purpose, methodologies allowing a straightforward access to *S. flexneri* 2a oligosaccharides of larger size are under study in this laboratory. We now report the synthesis of the first decasaccharide in the series, namely the **D′A′B′(E′)-C′DAB(E)C** fragment, which was prepared as its methyl glycoside (**1**).

## Results and Discussion

Considering its dimeric nature, a convergent synthetic strategy to the target **1** was considered. Indeed, retrosynthetic analysis, supported by previous work in the field,[19−22] indicated that disconnections at the **C**−**D** linkage, thus based on two **DAB(E)C** branched pentasaccharides **I**, would be the most advantageous (Scheme 1). Such a strategy would involve a pentasaccharide acceptor easily derived from the known methyl glycoside **2**[17] or from the corresponding *N*-acetylated analogue **3** and a pentasaccharide donor bearing a 2-*O*-acyl protecting group at the reducing residue (**C**) in order to direct glycosylation toward the desired stereochemistry. Depending on the nature of the 2-*N*-acyl group in residue **D**, the latter could derive from the allyl glycosides **4** or **5**.

Besides, bearing in mind that the major drawbacks of the linear synthesis of pentasaccharide **2** reported so far[17] dealt with the selective deblocking of key hydroxyl groups to allow further chain elongation, we describe herein various attempts at a convergent synthesis of the fully protected **DAB(E)C** pentasaccharide as its methyl (**2**, **3**) or allyl (**4**, **5**) glycosides. Precedents concerning a related serotype of *S. flexneri* have indicated that disconnection at the **D**−**A** linkage should be avoided.[21,22] To our knowledge, disconnection at the **B**−**C** linkage was never attempted in the series. However, disconnection at the **A**−**B** linkage, based on the use of a combination of a bromide disaccharide donor and $Hg(CN)_2/HgBr_2$ as the promoter, was reported once.[20] In the latter case concerning the synthesis of the linear **DABC** tetrasaccharide, the condensation of two disaccharide building blocks was found more effective than the stepwise strategy. Both routes were considered in the following study. The nature of the repeating unit **I** indicated that any blockwise synthesis involving such linkages would rely on donors lacking any participating group at position 2 of the reducing residue, thus the relevance of this strategy may be questioned. Nevertheless, although *β*-glycoside formation was observed occasionally,[23−25] the good α-stereoselectivity reported on several occasions in the literature for glycosylation reactions based on mannobiosyl donors[26] and derivatives such as perosamine analogues[27,28] or rhamnopyranosyl donors that were either glycosylated at C-2[20,29] or blocked at this position with a nonparticipating group[30,31] encouraged the evaluation of the above-mentioned block strategies. To follow up the work developed thus far in the *S. flexneri* 2a series, emphasis was placed on the use of the trichloroacetimidate (TCA) chemistry.[32]

**Strategy Based on the Disconnection at the A−B Linkage (Scheme 1, route a).** Such a strategy involves the coupling of suitable **DA** donors to an appropriate **B-(E)C** acceptor. Taking into account the glycosylation chemistry, two sets of disaccharide building blocks (**6**, **7**, **8**), easily obtained from known monosaccharide precursors which were readily available by standard protecting group/activation strategies, were selected (Scheme 1).

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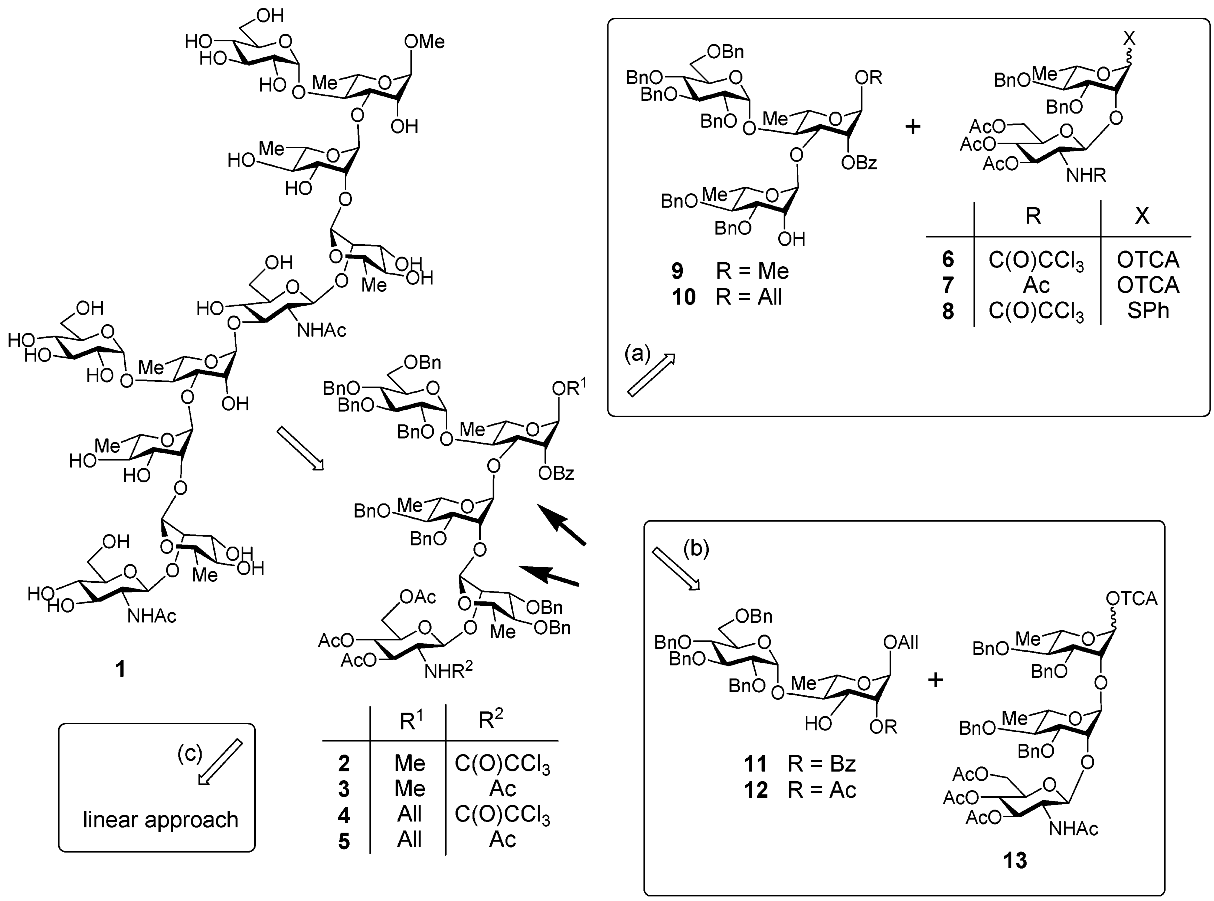
**SCHEME 1**[a]




[a] Retrosynthetic analysis of the target decasaccharide **1**.

Thus, condensation of the allyl rhamnopyranoside **14**,[33] as precursor to residue **A**, with the glucosaminyl trichloroacetimidate **16**,[34] as precursor to residue **D**, was performed in the presence of a catalytic amount of TMSOTf to give the fully protected disaccharide **17** in 99% yield (Scheme 2). Selective deallylation of **17** proceeded in two steps involving (i) iridium(I)-catalyzed isomerization of the allyl glycoside into the corresponding 1-*O*-propenyl glycoside[35] and (ii) hydrolysis of the latter.[36] The resulting hemiacetal **18** (81%) was converted into the trichloroacetimidate **6** (78%) by treatment with trichloroacetonitrile in the presence of a catalytic amount of DBU. Knowing from previous experience that conversion of the trichloroacetamide moiety at position 2 of residue **D** ($2_D$-*N*-trichloroacetyl moiety) into the required $2_D$-*N*-acetyl group could be somewhat low-yielding, we took advantage of the blockwise approach to perform the above-mentioned transformation at an early stage in the synthesis. Thus, the disaccharide intermediate **17** was converted to the corresponding **19** (90%) upon overnight treatment with a saturated ammonia methanolic solution and subsequent peracetylation. Conversion of **19** into the hemiacetal **20** (69%), and next into the required trichloroacetimidate donor **7** (86%), followed the procedure described above for the preparation of **6** from **17**. Where glycosylation is concerned, the bifunctional role of thioglycosides as protected acceptors and masked donors is highly appreciated.[37] Thus, the thiophenyl disaccharide **8** was considered as a possible alternative to the use of the more reactive trichloroacetimidates **6** and **7**. It was synthesized in 97% yield by condensing the known thiophenyl rhamnopyranoside **15**[38] and **16** in the presence of a catalytic amount of TMSOTf (Scheme 2). To fulfill the requirements of the synthesis of **1**, two different trisaccharide building blocks were used, namely either the known methyl glycoside **9**[17] or the corresponding allyl glycoside **10**, obtained from the known $2_B$-*O*-acetylated trisaccharide **42** (see below and Scheme 5).[18] Condensation of the trisaccharide acceptor **9** and the trichloroacetimidate donor **6** was attempted under various conditions of solvent, temperature, and promoter. The α-linked condensation product, i.e. the known pentasaccharide **2**,[17] was at best isolated in 41% yield providing that the glycosylation reaction was run in acetonitrile in the presence of a catalytic amount of TMSOTf, following the

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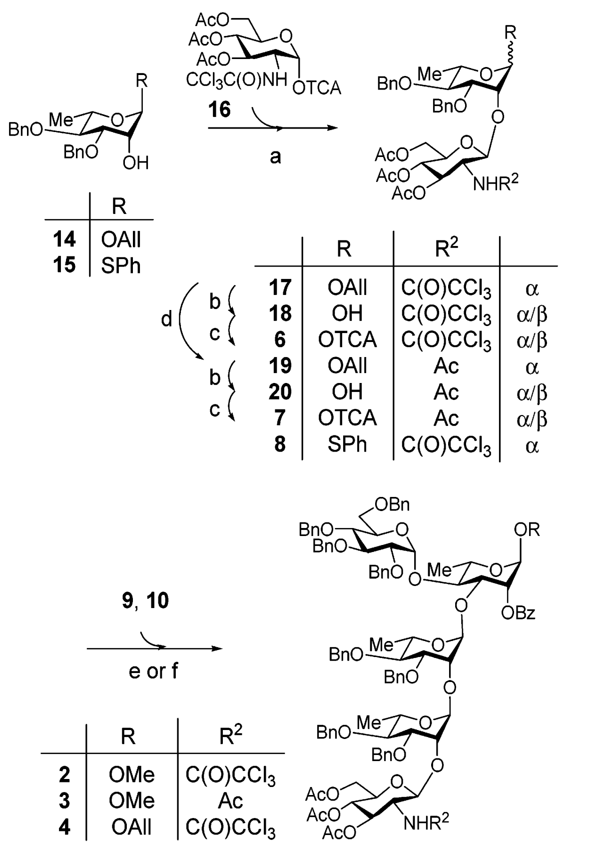
**SCHEME 2**[a]




[a] Reagents and conditions: (a) cat. TMSOTf, anhydrous DCM, 0.5 h, 0 °C, 97% (**8**), 99% (**17**); (b) (i) cat. [Ir(COD){$PCH_3(C_6H_5)_2$}$_2$]$^+PF_6^-$, THF, rt, 20 h, (ii) HgO, $HgCl_2$, acetone/water, rt, 2 h, 81% (**18**), 69% (**20**); (c) $CCl_3CN$, DBU, DCM, 0 °C, 1 h, 78% (**6**), 86% (**7**); (d) (i) $NH_3$, MeOH, 20 h, 0 °C, (ii) $Ac_2O$, MeOH, (iii) $Ac_2O$, Py, 90%; (e) cat. TMSOTf, $CH_3CN$, 0 °C, 41% (**2**); (f) cat. TfOH, NIS, $Et_2O$, 1,2-DCE, 0 °C, 10% (**4**).

inverted procedure protocol,[39,40] to minimize degradation of the donor. Although the α-selectivity of the glycosylation reaction was good, yields of pentasaccharide remained low, and as anticipated, use of the alternate trichloroacetimidate donor **7** to give **3** did not result in any improvement (not described). Rearrangement of the activated donor into the corresponding inert trichloroacetamide was observed previously in glycosylation reactions based on trichloroacetimidate donors lacking a participating group at position 2 of the reducing residue.[23] Although the expected side product was not isolated in any of the attempted glycosylation with **6** or **7**, it was anticipated that the use of an alternate glycosylation chemistry would prevent such side reaction, and possibly favor the condensation. However, reaction of thiophenyl donor **8** and acceptor **10** in the presence of *N*-iodosuccinimide and catalytic triflic acid did not prove any better as it resulted in mixtures of products from which the target **4** was isolated in very low yield, 10% at best. This strategy was thus not considered any further.

**Strategy Based on the Disconnection at the B−C Linkage (Scheme 1, route b).** It was hypothesized that the good α-selectivity, but poor yields, of the condensation of the various **DA** donors with the **B(E)C** acceptors **9** and **10** might result from the poor nucleophilicity of the axial hydroxyl at position $2_B$. Thus, we next turned to the $3_C$-OH as a possible elongation site in the design of a block synthesis of pentasaccharide **5**. Considering such a disconnection approach suggests the use of a **DAB** trisaccharide donor for coupling to an **EC** disaccharide acceptor. As the target pentasaccharide should serve as an appropriate donor in the construction of **1**, we reasoned that an acyl participating group had to be present at its position $2_C$. Thus, two $2_C$-*O*-acylated **EC** building blocks, **11** or **12**, were considered. To avoid any unnecessary deprotection step at the pentasaccharide level, the trisaccharide **13**, bearing an acetamido functionality at position $2_D$, was selected as the donor. Indeed, as it involves the less readily available **EC** structure in fewer synthetic steps and does not rely on selective deprotection at the $2_A$ position, this path was found particularly attractive. Again, it relies on the use of appropriately functionalized known monosaccharide intermediates (Scheme 3).

The known key di-rhamnoside core structure **22**[41] was formed by glycosylation of the allyl rhamnoside **14** with the trichloroacetimidate donor **21**[42] in the presence of a catalytic amount of TMSOTf. It should be pointed out that using diethyl ether as the solvent, the isolated yield of **22** was 92%, which compares favorably with yields obtained previously, 60% and 76.2%,[41] when running the reaction in dichloromethane (DCM) under promotion by TMSOTf or $BF_3{\cdot}OEt_2$, respectively. Sodium methoxide promoted de-*O*-acetylation afforded the $2_A$-*O*-unprotected acceptor **23**[21] in 93% yield.

As shown previously in the construction of the **DA** intermediate **17**, the *N*-trichloroacetyl trichloroacetimidate **16** appears to be a highly suitable precursor to residue **D** when involved in the formation of the *β*-GlcNAc linkage at the poorly reactive $2_A$ position. Indeed, reaction of **16** with the acceptor **23** in 1,2-dichloroethane (1,2-DCE) in the presence of TMSOTf went smoothly and gave the trisaccharide **25** in 96% yield. However, conversion of the *N*-trichloroacetyl group to the *N*-acetyl derivative **27** was rather less successful as the desired trisaccharide was obtained in only 42% yield when treated under conditions that had previously been used in the case of a related oligosaccharide (sodium methoxide, $Et_3N$, followed by re-*N*,*O*-acetylation).[17] This result led us to reconsider the protection pattern of the glucosamine donor. The *N*-tetrachlorophthalimide group has been proposed as an alternative to overcome problems associated with the widely spread phthalimido procedure when introducing a 2-acetamido-2-deoxy-*β*-D-glucopyranosidic linkage.[43] Thus, the *N*-tetrachlorophthalimide trichloroacetimidate donor **24** was selected as an alternative. It was prepared as described from commercially available D-glucosamine,[44] apart from the final imidate formation step, where we found the use of potassium carbonate as

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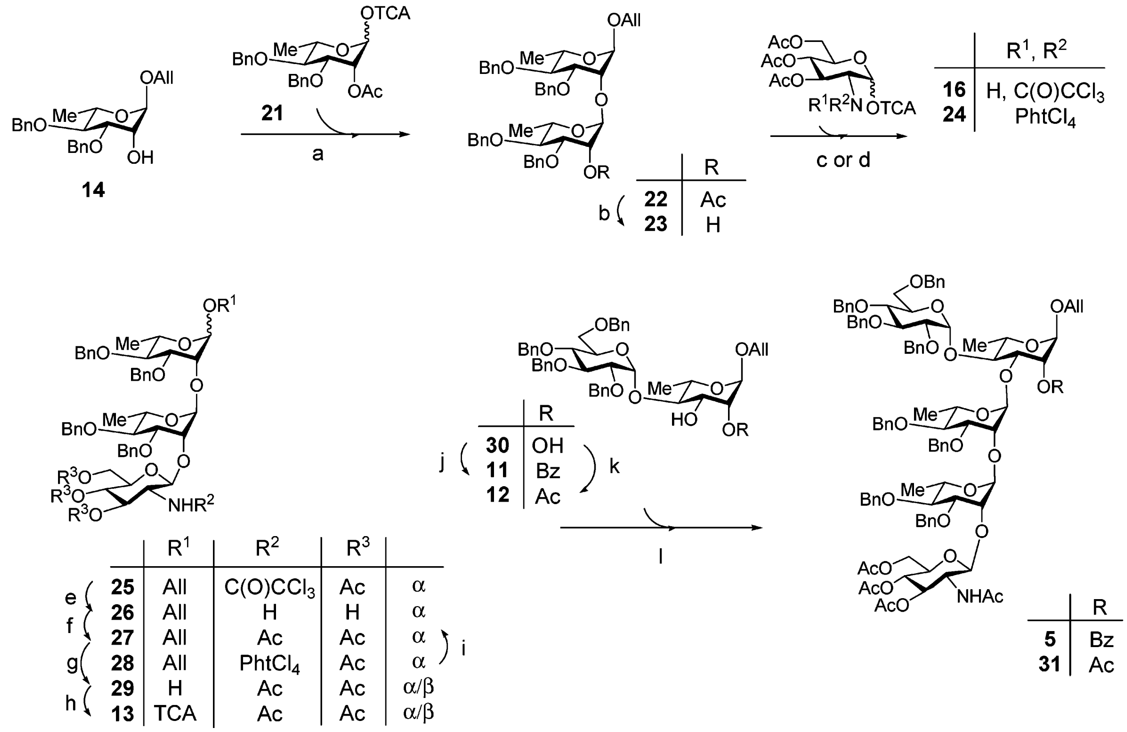
**SCHEME 3**[a]



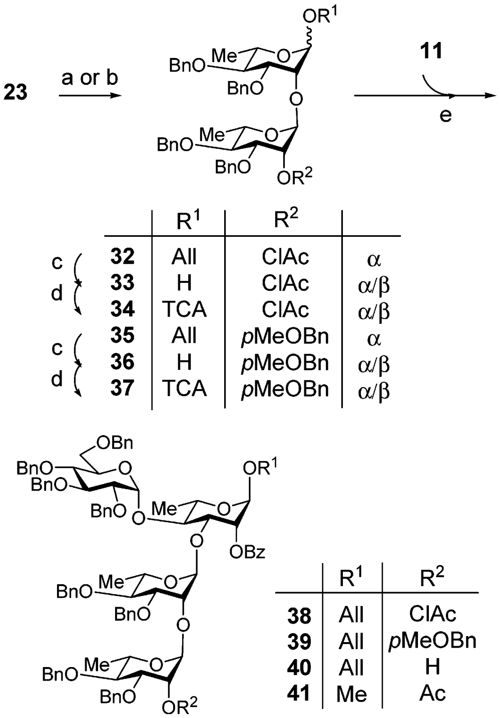
[a] Reagents and conditions: (a) cat. TMSOTf, anhydrous $Et_2O$, 3 h, −55 to −20 °C, 92%; (b) MeONa, MeOH, 3 h, rt, 93%; (c) cat. TMSOTf, 4 Å molecular sieves, 1,2-DCE, 3 h, −20 to 0 °C, 96%; (d) cat. TMSOTf, anhydrous $Et_2O$, 4 h, 0 °C to rt, 65%; (e) (i) MeONa, MeOH, $Et_3N$, rt, 18 h, (ii) $Ac_2O$, 0.5 h, 0 °C to rt, 45%; (f) Py, $Ac_2O$, 18 h, 0 °C to rt, 94%; (g) (i) cat. $[Ir(COD)\{PCH_3(C_6H_5)_2\}_2]^+PF_6^-$, THF, rt, 20 h, (ii) HgO, $HgCl_2$, acetone/water, rt, 2 h, 83%; (h) $CCl_3CN$, DBU, DCM, 0 °C, 40 min, 94%; (i) (i) ethylenediamine, THF, EtOH, 55 °C, 4 h, (ii) $Ac_2O$, rt, 1.5 h, (iii) Py, $Ac_2O$, 0 °C, overnight, 68%; (j) (i) $PhC(OMe)_3$, CSA, DCM, (ii) 50% aq TFA, DCM, 87%; (k) (i) $MeC(OMe)_3$, CSA, DCM, (ii) 50% aq TFA, DCM, 90%; (l) $BF_3{\cdot}Et_2O$, anhydrous $Et_2O$, 4 Å molecular sieves, 0 °C to rt, 18 h, 44%.

base to be more satisfactory than DBU. Glycosylation of **23** with **24** in the presence of TMSOTf resulted in the trisaccharide **28** in 65% yield. The tetrachlorophthaloyl group was then removed by the action of ethylenediamine, and subsequent re-*N*,*O*-acetylation gave the trisaccharide **27** in 68% yield. The latter was next converted into the donor **13** in two steps, analogous to those described for the preparation of **6** from **17**. Indeed, de-*O*-allylation of **27** cleanly gave the hemiacetal **29** (83%), which was then activated into the required trichloroacetimidate (94%). It is worth mentioning that although they involve a different **D** precursor, both strategies give access to the intermediate **27** in closely related yields, 40 and 42%, respectively.

Initial attempts to form the pentasaccharide **5** from **13** and the previously described acceptor **11**[18] in the presence of TMSOTf as promoter were rather unsuccessful, resulting in at best 17% of the desired product, accompanied by decomposition of the donor into the hemiacetal **29** (75%). By using $BF_3{\cdot}OEt_2$ as the promoter in place of TMSOTf, reaction of **11** with **13** at rt provided **5** in 44% yield, with the acceptor **11** and hemiacetal **29** also recovered in 54% and 29% yield, respectively. We considered that the poor reactivity of the acceptor was responsible for these results, since the $^{13}C$ NMR spectrum of **5**, showing several broaden signals (notably C-$1_B$, as well as most certainly C-$3_C$ and C-$4_C$), suggests restricted conformational flexibility around position $3_C$. For that matter, the $2_C$-*O*-acetylated disaccharide **12** was considered as an alternate acceptor. Analogously to the preparation of **11**, it was obtained from the known diol **30** through regioselective opening of the intermediate ortho ester. However, coupling of the potentially less hindered acceptor **12** and the trisaccharide donor **13** resulted, at best, in the isolation of the condensation product **31** in 42% yield (not described).

The modest yield of **5** and **31** obtained by this route made the alternative reaction path (Scheme 4) worth investigating, despite the more numerous synthetic steps required. Indeed, it was found rather appealing when evaluated independently in a closely related series (unpublished results). By this route, a tetrasaccharide acceptor can be formed from two disaccharide building blocks (**EC** and **AB**), and coupled with an appropriate monosaccharide donor as precursor to **D**. Considering that selective deprotection of the $2_A$ hydroxyl group would occur in the course of the synthesis, glycosylation attempts were limited to the 2-*O*-benzoylated acceptor **11**. The disaccharide donor necessary for this path could be derived from the building block **23**, already in hand. The choice of temporary protecting group at position $2_A$ was determined by our experience of the stepwise synthesis of the corresponding methyl pentasaccharide,[17] where we noted that an acetate group at this position may not be fully orthogonal to the benzoate located at position $2_C$. The chosen group had also to support removal of the anomeric allyl group and the subsequent conversion to the trichloroacetimidate. At first, a chloroacetate group was anticipated to fulfill these requirements. Thus, the disaccharide **23** was treated with chloroacetic anhydride and pyridine to give the derivative **32** (57%). Anomeric deprotection to give the hemiacetal **33** (84%) and subse-

**SCHEME 4**[a]




| | R1 | R2 | |
|---|---|---|---|
| 32 | All | ClAc | α |
| 33 | H | ClAc | α/β |
| 34 | TCA | ClAc | α/β |
| 35 | All | *p*MeOBn | α |
| 36 | H | *p*MeOBn | α/β |
| 37 | TCA | *p*MeOBn | α/β |

| | R1 | R2 |
|---|---|---|
| 38 | All | ClAc |
| 39 | All | *p*MeOBn |
| 40 | All | H |
| 41 | Me | Ac |

[a] Reagents and conditions: (a) $ClAc_2O$, Py, 0 °C to rt, overnight, 57%; (b) *p*MeOBnCl, NaH, DMF, rt, overnight, 97%; (c) (i) cat. $[Ir(COD)\{PCH_3(C_6H_5)_2\}_2]^+PF_6^-$, THF, rt, 20 h, (ii) HgO, $HgCl_2$, acetone/water, rt, 2 h, 84% (**33**), 73% (**36**); (d) $CCl_3CN$, DBU, DCM, 0 °C, 1 h, 83% (**34**), 82% (**37**); (e) cat. TMSOTf, anhydrous $Et_2O$, −60 °C to rt, overnight, 22% (**38**), 44% (**39**).

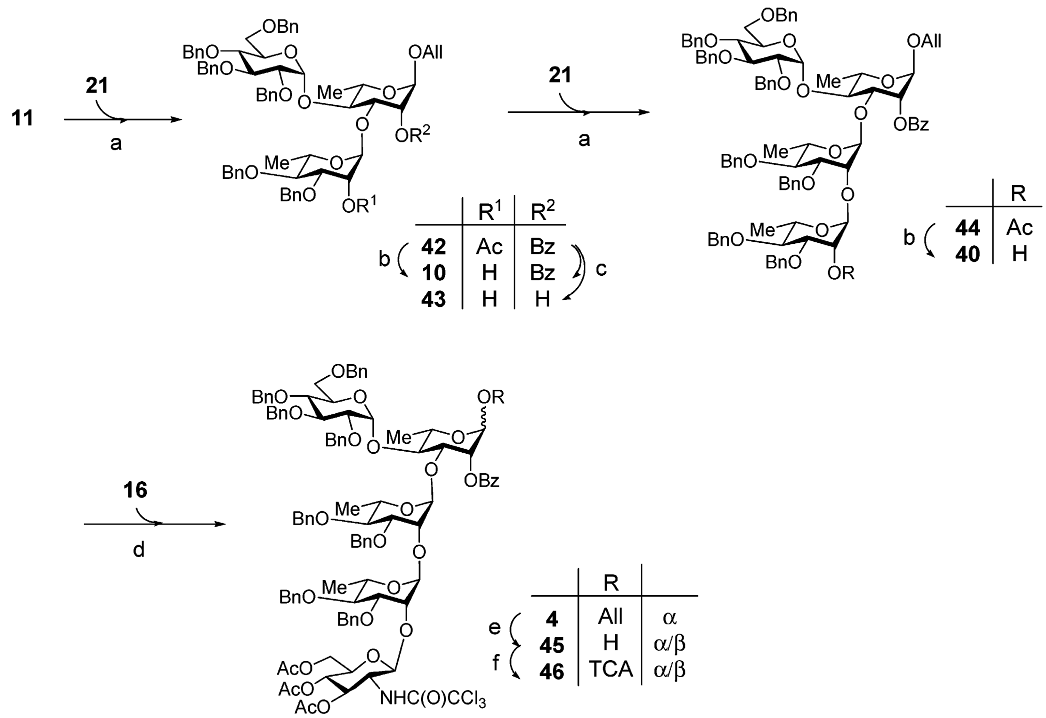
quent trichloroacetimidate activation of the latter into the donor **34** (83%) were performed in the same way as before. Coupling of **11** with **34**, carried out in the presence of TMSOTf at −40 °C, yielded a complex mixture of products. When the temperature was lowered to −60 °C, the condensation product **38** could be isolated in 22% yield. Alternative donor protection was attempted. Treatment of **23** with *p*-methoxybenzyl chloride and sodium hydride gave the fully protected derivative **35** (97%), which was cleanly converted into the trichloroacetimidate donor **37** (82%) in two steps involving the hemiacetal intermediate **36** (73%). Glycosylation of **11** with **37** in the presence of TMSOTf at −40 °C gave the desired tetrasaccharide **39** in 44% yield. When the temperature was lowered to −60 °C, the yield of **39** fell to 34% and a second major product **40** (21%) was observed in the mixture. Indeed, examination of the NMR spectra of this product revealed that the *p*MeOBn group had been lost. The α-stereoselectivity of the glycosylation was ascertained from the observation that **40** was the acceptor required for the next step. Consequently, the estimated yield of condensation was brought to 55%. Nevertheless, the overall outcome of this blockwise strategy did not match our expectations, and this route was abandoned.

**Linear Strategy to the Fully Protected Pentasaccharide 4 (Scheme 5).** As preliminary studies have demonstrated, rapid access to suitable building blocks allowing the synthesis of higher order oligosaccharides representative of fragments of the O−SP of *S. flexneri* 2a remains a challenge. Major conclusions drawn from our studies favor the design of a linear synthesis of the target **4**. Indeed, when put together with our previous work, such as the synthesis of tetrasaccharide **41** (95%)[17] or that of trisaccharide **42** (97%),[18] all the above-described attempted couplings outlined the loss of efficiency of glycosylation reactions involving rhamnopyranosyl donors glycosylated at position 2 in comparison to those involving the corresponding acetylated donor. Thus, matching the linear strategy of the methyl pentasaccharide **2** described previously,[17] a synthesis of **4**, based on donors bearing a participating group at O-2, was designed. Three key building blocks were selected. These were the readily accessible **EC** disaccharide acceptor **11** benzoylated at C-2 as required for the final condensation step leading to the fully protected decasaccharide intermediate; the rhamnopyranosyl trichloroacetimidate **21**, which serves as a precursor to residues **A** and **B**, and bears both a temporary and participating group at position 2; and the trichloroacetamide glucosaminyl donor **16** as a precursor to residue **D**. As stated above, coupling of **11** and **21** gave **42** in high yield. As observed in the methyl glycoside series,[17] de-*O*-acetylation with MeONa or methanolic HCl was poorly selective. Although guanidine/guanidinium nitrate was proposed as a mild and selective *O*-deacetylation reagent compatible with the presence of benzoyl protecting groups,[45] none of the conditions tested prevented partial debenzoylation leading to diol **43**, as easily confirmed from NMR analysis (not described). The required alcohol **10** was readily obtained in an acceptable yield of 84% by a 4-day acid-catalyzed methanolysis, using $HBF_4$ in diethyl ether/methanol,[17,46] of the fully protected intermediate **42**. Repeating this two-step process with **10** as the acceptor and **21** as the donor resulted first in the intermediate **44** (90%) and next in the tetrasaccharide acceptor **40** (84%). Glycosylation of the latter with **16** gave the fully protected pentasaccharide **4** in high yield (98%), thus confirming that the combination of the trichloroacetamide participating group and the trichloroacetimidate activation mode in **16** results in a potent donor to be used as a precursor to residue **D** in the *S. flexneri* series, where low-reactive glycosyl acceptors are concerned. Following the above-described procedure, selective anomeric deprotection of **4** furnished the hemiacetal **45**, which was smoothly converted to the trichloroacetimidate donor **46** (66% from **4**). From these data, the linear synthesis of **4,** truly benefiting from the use of **21** as a common precursor to residues **A** and **B**, appears as a reasonable alternative to the block syntheses which were evaluated in parallel.

**Synthesis of the Target Decasaccharide 1 (Scheme 6).** Having a pentasaccharide donor in hand, focus was next placed on the synthesis of an appropriate pentasaccharide acceptor. In our recent description of the convergent synthesis of the **B′(E′)C′DAB(E)C** octasaccharide,[19] the pentasaccharide **48**, bearing a $4_D,6_D$-*O*-isopropylidene protecting group, was found a most convenient acceptor, which encouraged its selection in the present work. Briefly, **48** was prepared in two steps from the known **2**. Thus, mild transesterification of **2** under Zemplén conditions allowed the selective removal of the acetyl groups to give triol **47**, which was converted to the required

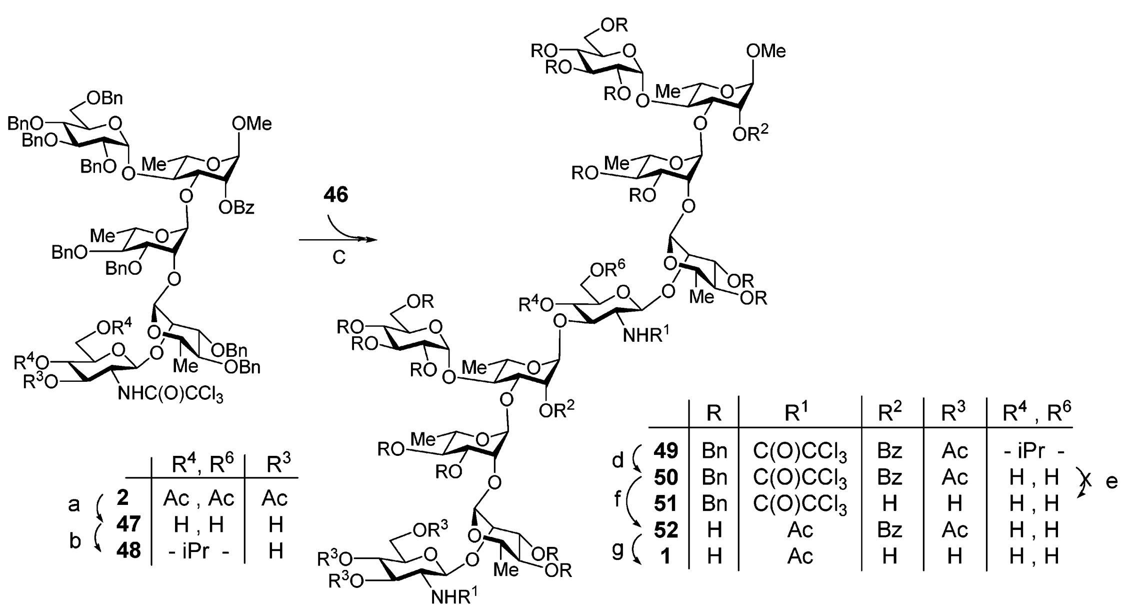
(45) Ellervik, U.; Magnusson, G. *Tetrahedron Lett.* **1997**, *38*, 1627−1628.
(46) Pozsgay, V.; Coxon, B. *Carbohydr. Res.* **1994**, *257*, 189−215.

**SCHEME 5**[a]




[a] Reagents and conditions: (a) cat. TMSOTf, anhydrous $Et_2O$, −50 °C to rt, overnight, 97% (**42**), 90% (**44**); (b) $HBF_4/Et_2O$, MeOH, rt, 4 days, 84% (**10**), 84% (**40**); (c) guanidine, DCM, rt; (d) cat. TMSOTf, anhydrous DCM, 4 Å molecular sieves, 0 °C to rt, 3 h, 98%; (e) (i) cat. $[Ir(COD)\{PCH_3(C_6H_5)_2\}_2]^+PF_6^-$, THF, rt, 20 h, (ii) HgO, $HgCl_2$, acetone/water, rt, 2 h; (f) $CCl_3CN$, DBU, DCM, 0 °C, 1 h, 66% (2 steps).

**SCHEME 6**[a]




[a] Reagents and conditions: (a) MeONa, MeOH, rt, 0.5 h; (b) 2-methoxypropene, CSA, DMF, 72% (2 steps); (c) cat. TfOH, anhydrous 1,2-DCE, 4 Å molecular sieves, −35 °C to −10 °C, 2.5 h; (d) TFA, water/DCM, 0 °C, 3 h, 72% (2 steps); (e) MeONa, MeOH, DCM, 55 °C; (f) (i) $H_2$, Pd/C, EtOH, EtOAc, 1 M HCl, rt, 72 h, (ii) $H_2$, Pd/C, MeOH, $Et_3N$, rt, 24 h; (g) MeONa, MeOH, DCM, 55 °C, overnight, 37% (3 steps).

acceptor **48** (72% from **2**) upon subsequent treatment with 2-methoxypropene. Relying on previous optimization of the glycosylation step,[19] the condensation of **48** and **46** was performed in the presence of a catalytic amount of triflic acid. However, probably due to the closely related nature of the donor and acceptor, the reaction resulted in an inseparable mixture of the fully protected **49** and the hemiacetal **45** resulting from partial hydrolysis of the donor. Most conveniently, acidic hydrolysis of the mixture, allowing the selective removal of the isopropylidene group in **49**, gave the intermediate diol **50** in a satisfactory yield of 72% for the two steps. According to the deprotection strategy used for the preparation of the closely related octasaccharide,[19] diol **50** was engaged in a controlled de-*O*-acylation process upon treatment with hot methanolic sodium methoxide. However, partial cleavage of the trichloroacetyl moiety, leading to an inseparable mixture, was observed, which prevented further use of this strategy. Indeed, it was assumed that besides being isolated and therefore resistant to Zemplén transacetylation conditions,[31,47] the $2_C$-*O*-benzoyl groups were most probably highly hindered, which contributed to their slow deprotection. Alternatively, **50** was submitted to an efficient two-step in-house process involving, first, hydrogenolysis under acidic conditions which allowed the removal of the benzyl groups and, second, basic hydrochlorination that resulted in the conversion of the *N*-trichloroacetyl groups into the required *N*-acetyl ones, thus affording **52**. Subsequent transesterification gave the final target **1** in 37% yield from **50**.

## Conclusion

The decasaccharide **1**, corresponding to two consecutive repeating units of the O-Ag of *S. flexneri* 2a, was synthesized successfully based on the condensation of two key pentasaccharide intermediates, the donor **46** and acceptor **48**. Several routes to these two building blocks were investigated, involving either blockwise strategies or a linear one. The latter was the preferred one based on yields of condensation and the number of steps.

## Experimental Procedure

**General Methods.** Optical rotations were measured for $CHCl_3$ solutions at 25 °C, expect where indicated otherwise. TLC were performed on precoated slides of Silica Gel 60 $F_{254}$ (Merck). Detection was effected when applicable, with UV light, and/or by charring in 5% sulfuric acid in ethanol. Preparative chromatography was performed by elution from columns of Silica Gel 60 (particle size 0.040−0.063 mm). NMR spectra were recorded at 25 °C for solutions in $CDCl_3$ or $D_2O$ (400 MHz for $^1$H, 100 MHz for $^{13}$C) except where otherwise indicated. TMS (0.00 ppm for both $^1$H and $^{13}$C) was used as an external reference for solutions in $CDCl_3$. Proton-signal assignments were made by first-order analysis of the spectra, as well as analysis of 2D $^1$H−$^1$H correlation maps (COSY) and selective TOCSY experiments. Of the two magnetically nonequivalent geminal protons at C-6, the one resonating at lower field is denoted H-6a and the one at higher field is denoted H-6b. The $^{13}$C NMR assignments were supported by 2D $^{13}$C−$^1$H correlation maps (HETCOR). Interchangeable assignments are marked with an asterisk in the listing of signal assignments. Sugar residues in oligosaccharides are serially lettered according to the lettering of pentasaccharide **I** and identified by a subscript in the listing of signal assignments. Fast atom bombardment mass spectra (FAB-MS) were recorded in the positive-ion mode with dithioerythridol/dithio-L-threitol (4:1, MB) as the matrix, in the presence of NaI, and Xenon as the gas. Anhydrous dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE), and $Et_2O$, sold on molecular sieves, were used as such. 4 Å powder molecular sieves was kept at 100 °C and activated before use by heating at 250 °C under vacuum.

**Phenyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (8).** A mixture of alcohol **15**[38] (0.12 g, 0.27 mmol) and imidate **16**[34] (0.245 g, 0.41 mmol) in anhydrous DCM (10 mL) was stirred for 15 min under dry Ar. After the solution was cooled at 0 °C, $Me_3SiOTf$ (28 $\mu$L) was added dropwise and the mixture was stirred for 0.5 h. Triethylamine (60 $\mu$L) was added and the mixture was concentrated. The residue was eluted from a column of silica gel with 4:1 cyclohexane−EtOAc to give **8** (227 mg, 97%) as a colorless foam: $[\alpha]_D$ −63 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 7.40−7.10 (m, 15H, Ph), 6.73 (d, 1H, $J_{2,NH}$ = 8.5 Hz, $NH_D$), 5.47 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-$1_A$), 5.07 (pt, 1H, $J_{2,3}$ = $J_{3,4}$ = 10.0 Hz, H-$3_D$), 4.99 (pt, 1H, $J_{4,5}$ = 10.0 Hz, H-$4_D$), 4.80−4.55 (m, 4H, C$H_2$Ph), 4.52 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-$1_D$), 4.13−3.95 (m, 2H, $J_{5,6}$ = 5.3 Hz, $J_{6a,6b}$ = 12.2 Hz, H-$6a_D$, $6b_D$), 4.10 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.1 Hz, H-$5_A$), 4.00 (dd, 1H, $J_{2,3}$ = 3.0 Hz, H-$2_A$), 3.99 (m, 1H, H-$2_D$), 3.77 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-$3_A$), 3.50 (m, 1H, H-$5_D$), 3.39 (dd, 1H, H-$4_A$), 1.95, 1.93, 1.90 (3s, 9H, OAc), 1.23 (d, 3H, H-$6_A$); $^{13}$C NMR ($CDCl_3$) $\delta$ 171.1, 170.9, 169.6, 162.1 (C═O), 138.5−127.2 (Ph), 102.1 (C-$1_D$), 92.7 ($CCl_3$), 87.4 (C-$1_A$), 81.3 (C-$4_A$), 80.5 (C-$3_A$), 79.1 (C-$2_A$), 76.4, 74.1 (2C, $CH_2$-Ph), 72.4 (C-$5_D$), 72.4 (C-$3_D$), 69.8 (C-$5_A$), 68.7 (C-$4_D$), 62.3 (C-$6_D$), 56.2 (C-$2_D$), 21.0, 20.9, 20.8 (3C, OAc), 18.1 (C-$6_A$). FAB-MS for $C_{40}H_{44}Cl_3NO_{12}S$ (M, 867), *m/z* 890 [M + Na]$^+$. Anal. Calcd for $C_{40}H_{44}Cl_3NO_{12}S$: C, 55.27; H, 5.10; N, 1.61. Found: C, 55.16; H, 5.18; N, 1.68.

**Allyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (17).** A mixture of alcohol **14**[33] (1.86 g, 4.86 mmol) and imidate **16** (3.85 g, 6.47 mmol) in anhydrous $CH_3CN$ (80 mL) was stirred for 15 min under dry Ar. After the solution was cooled at 0 °C, $Me_3SiOTf$ (46 $\mu$L) was added dropwise and the mixture was stirred for 0.5 h. Triethylamine (150 $\mu$L) was added, and the mixture was concentrated. The residue was eluted from a column of silica gel with 7:3 cyclohexane−EtOAc to give **17** (4.0 g, 99%) as a white solid: $[\alpha]_D$ −3 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 7.32−7.18 (m, 10H, Ph), 6.70 (d, 1H, $J_{2,NH}$ = 8.4 Hz, $NH_D$), 5.82−5.78 (m, 1H, All), 5.20−5.05 (m, 2H, All), 5.00 (m, 2H, H-$3_D$, $4_D$), 4.75−4.45 (m, 4H, C$H_2$Ph), 4.76 (d, 1H, $J_{1,2}$ = 1.1 Hz, H-$1_A$), 4.60 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-$1_D$), 4.15−4.05 (m, 2H, $J_{5,6}$ = 4.8 Hz, $J_{6a,6b}$ = 12.2 Hz, H-$6a_D$, $6b_D$), 3.98 (m, 1H, H-$2_D$), 3.90 (m, 2H, All), 3.86 (dd, 1H, $J_{2,3}$ = 3.2 Hz, H-$2_A$), 3.81 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-$3_A$), 3.62 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.1 Hz, H-$5_A$), 3.50 (m, 1H, H-$5_D$), 3.32 (pt, 1H, H-$4_A$), 2.02, 1.97, 1.93 (3 s, 9H, OAc), 1.24 (d, 3H, H-$6_A$); $^{13}$C NMR ($CDCl_3$) $\delta$ 171.0, 170.9, 169.6, 162.1 (C═O), 138.5−117.1 (Ph, All), 101.8 (C-$1_D$), 98.5 (C-$1_A$), 92.6 ($CCl_3$), 81.4 (C-$4_A$), 80.4 (C-$3_A$), 77.1 (C-$2_A$), 75.9, 74.1 (2C, $CH_2$Ph), 72.7 (C-$3_D$), 72.5 (C-$5_D$), 68.6 (C-$4_D$), 68.3 (C-$5_A$), 68.1 (All), 62.3 (C-$6_D$), 56.1 (C-$2_D$), 21.1, 20.9, 20.9 (3C, OAc), 18.2 (C-$6_A$). FAB-MS for $C_{37}H_{44}Cl_3NO_{13}$ (M, 815), *m/z* 838 [M + Na]$^+$. Anal. Calcd for $C_{37}H_{44}Cl_3NO_{13}$: C, 54.39; H, 5.43; N, 1.71. Found: C, 54.29; H, 5.45; N: 1.72.

**(3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranose (18).** 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)-iridium hexafluorophosphate (120 mg, 140 $\mu$mol) was dissolved in THF (10 mL), and the resulting red solution was degassed in an argon stream. Hydrogen was then bubbled through the solution, causing the color to change to yellow. The solution was then degassed again in an argon stream. A solution of **17** (1.46 g, 1.75 mmol) in THF (20 mL) was degassed and added. The mixture was stirred at rt overnight, then concentrated. The residue was taken up in acetone (27 mL) and water (3 mL). Mercuric bromide (949 mg, 2.63 mmol) and mercuric oxide (761 mg, 3.5 mmol) were added, and the mixture, protected from light, was stirred for 2 h at rt, then concentrated. The residue was taken up in DCM and washed three times with satd aqueous KI, then with brine. The organic phase was dried and concentrated. The residue was purified by column chromatography (cyclohexane−EtOAc, 4:1) to give **18** (1.13 g, 81%) as a white foam: $[\alpha]_D$ +4 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 7.35−7.05 (m, 10H, Ph), 6.74 (d, 1H, $J_{2,NH}$ = 8.5 Hz, $NH_D$), 5.10 (d, 1H, $J_{1,2}$ = 1.1 Hz, H-$1_A$), 5.02 (m, 2H, H-$3_D$, $4_D$), 4.80−4.50 (m, 4H, C$H_2$Ph), 4.61 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-$1_D$), 4.15−4.08 (m, 2H, $J_{5,6}$ = 4.5 Hz, $J_{6a,6b}$ = 12.3 Hz,

(47) Szurmai, Z.; Lipták, A.; Snatzke, G. *Carbohydr. Res.* **1990**, *200*, 201−208.

H-6a$_D$, 6b$_D$), 4.00 (m, 1H, H-2$_D$), 3.90 (dd, 1H, $J_{2,3}$ = 3.3 Hz, H-2$_A$), 3.86 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3$_A$), 3.85 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5$_A$), 3.50 (m, 1H, H-5$_D$), 3.30 (pt, 1H, H-4$_A$), 2.85 (d, 1H, $J_{1,OH}$ = 3.5 Hz, OH), 2.02, 1.97, 1.94 (3s, 9H, OAc), 1.23 (d, 3H, H-6$_A$); $^{13}$C NMR ($CDCl_3$) $\delta$ 171.1, 170.0, 169.6, 162.1 (C═O), 138.5−127.1 (Ph), 101.7 (C-1$_D$), 94.1 (C-1$_A$), 92.6 ($CCl_3$), 81.4 (C-4$_A$), 79.9 (C-2$_A$), 77.3 (C-3$_A$), 75.9, 74.1 (2C, $CH_2$Ph), 72.7 (C-3$_D$), 72.5 (C-5$_D$), 68.6 (C-4$_D$), 68.4 (C-5$_A$), 62.2 (C-6$_D$), 56.1 (C-2$_D$), 21.1, 21.0, 20.9 (3C, OAc), 18.3 (C-6$_A$). FAB-MS for $C_{34}H_{40}Cl_3NO_{13}$ (M, 775), *m/z* 789 [M + Na]$^+$. Anal. Calcd for $C_{34}H_{40}Cl_3NO_{13}$: C, 52.55; H, 5.19; N, 1.80. Found: C, 52.48; H, 5.37; N, 1.67.

**(3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl Trichloroacetimidate (6).** The hemiacetal **18** (539 mg, 0.68 mmol) was dissolved in DCM (50 mL), placed under argon, and cooled to 0 °C. Trichloroacetonitrile (0.6 mL, 6.8 mmol) then DBU (10 $\mu$L, 70 $\mu$mol) were added. The mixture was stirred at 0 °C for 30 min. The mixture was concentrated and toluene was coevaporated from the residue. The residue was eluted from a column of silica gel with 7:3 cyclohexane−EtOAc containing 0.2% of $Et_3N$ to give **6** (498 mg, 78%) as a colorless foam: $[\alpha]_D$ −18 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 8.48 (s, 1H, NH), 7.40−7.15 (m, 10H, Ph), 6.75 (d, 1H, $J_{2,NH}$ = 8.5 Hz, NH$_D$), 6.18 (d, 1H, $J_{1,2}$ = 1.1 Hz, H-1$_A$), 5.15 (pt, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3$_D$), 5.07 (pt, 1H, $J_{4,5}$ = 9.5 Hz, H-4$_D$), 4.82−4.50 (m, 4H, C$H_2$Ph), 4.62 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1$_D$), 4.20−4.03 (m, 2H, $J_{5,6}$ = 4.5 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a$_D$, 6b$_D$), 3.98 (m, 1H, H-2$_D$), 3.85 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5$_A$), 3.84 (dd, 1H, $J_{2,3}$ = 3.3 Hz, H-2$_A$), 3.83 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3$_A$), 3.55 (m, 1H, H-5$_D$), 3.45 (pt, 1H, H-4$_A$), 1.98, 1.96, 1.93 (3s, 9H, OAc), 1.23 (d, 3H, H-6$_A$); $^{13}$C NMR ($CDCl_3$) $\delta$ 171.1, 170.0, 169.6, 162.1 (C═O), 138.4−127.2 (Ph), 101.7 (C-1$_D$), 97.2 (C-1$_A$), 92.6 ($CCl_3$), 80.5 (C-4$_A$), 79.1 (C-3$_A$), 76.2 (C-2$_A$), 76.2, 74.1 (2C, $CH_2$Ph), 74.4 (C-3$_D$), 74.1 (C-5$_D$), 71.3 (C-5$_A$), 68.6 (C-4$_D$), 62.3 (C-6$_D$), 56.3 (C-2$_D$), 21.1, 21.0, 20.9 (3C, OAc), 18.2 (C-6$_A$). Anal. Calcd for $C_{36}H_{40}Cl_6N_2O_{13}$: C, 46.93; H, 4.38; N, 3.04. Found: C, 46.93; H, 4.52; N, 2.85.

**Allyl (2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (19).** A mixture of the protected disaccharide **17** (3.0 g, 3.61 mmol) in MeOH (50 mL) was cooled to 0 °C and treated with $NH_3$ gas overnight. The solution was concentrated and the residue (2.02 g) was dissolved again in MeOH (50 mL) and treated with $Ac_2O$ (3.98 mL, 36.1 mol). The solution was stirred for 2 h and then concentrated. The residue was eluted from a column of silica gel with 95:5 DCM−EtOAC to give the intermediate triol that was dissolved in pyridine (5 mL), cooled to 0 °C, and treated with $Ac_2O$ (2.4 mL). The mixture was stirred overnight and concentrated. The residue was eluted from a column of silica gel with 3:2 cyclohexane−EtOAC to give **19** (2.3 g, 90%) as a colorless foam: $[\alpha]_D$ −12 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 7.32−7.18 (m, 10H, Ph), 5.80−5.70 (m, 1H, All), 5.40 (d, 1H, $J_{2,NH}$ = 8.1 Hz, NH), 5.20−5.10 (m, 2H, All), 4.96 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4$_D$), 4.90 (pt, 1H, $J_{2,3}$ = 9.5 Hz, H-3$_D$), 4.80 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-1$_A$), 4.76−4.52 (m, 4H, C$H_2$Ph), 4.46 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1$_D$), 4.10−4.02 (m, 2H, $J_{5,6}$ = 4.7 Hz, $J_{6a,6b}$ = 11.2 Hz, H-6a$_D$, 6b$_D$), 3.92 (m, 1H, H-2$_D$), 3.87 (m, 2H, All), 3.86 (dd, 1H, $J_{2,3}$ = 3.5 Hz, H-2$_A$), 3.82 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3$_A$), 3.62 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5$_A$), 3.52 (m, 1H, H-5$_D$), 3.30 (pt, 1H, H-4$_A$), 1.98, 1.94, 1.92 (3 s, 9H, OAc), 1.26 (d, 3H, H-6$_A$); $^{13}$C NMR ($CDCl_3$) $\delta$ 171.1, 171.0, 170.3, 169.6 (C═O), 138−117 (Ph, All), 103.4 (C-1$_D$), 98.5 (C-1$_A$), 81.3 (C-4$_A$), 80.4 (C-3$_A$), 78.5 (C-2$_A$), 75.9, 73.9 (2C, $CH_2$Ph), 73.6 (C-3$_D$), 72.4 (C-5$_D$), 68.7 (C-4$_D$), 68.2 (C-5$_A$), 68.1 (All), 62.5 (C-6$_D$), 54.5 (C-2$_D$), 23.4 (NHAc), 21.2, 21.1, 21.0 (3C, OAc), 18.1 (C-6$_A$). FAB-MS for $C_{37}H_{47}NO_{13}$ (M, 713.3), *m/z* 736.2 [M + Na]$^+$. Anal. Calcd for $C_{37}H_{47}NO_{13}$: C, 62.26; H, 6.64; N, 1.96. Found: C, 62.12; H, 6.79; N, 1.87.

**(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α/*β*-L-rhamnopyranose (20).** 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)iridium-hexafluorophosphate (10 mg, 12 $\mu$mol) was dissolved in THF (10 mL), and the resulting red solution was processed as described for the preparation of **18**. A solution of **19** (830 mg, 1.16 mmol) in THF (40 mL) was degassed and added. The mixture was stirred at rt overnight, then concentrated. The residue was taken up in acetone (90 mL), and water (10 mL) was added. Mercuric chloride (475 mg, 1.75 mmol) and mercuric oxide (504 mg, 2.32 mmol) were added. The mixture, protected from light, was stirred for 2 h at rt, then concentrated. The residue was taken up in DCM and washed three times with satd aqueous KI, then with brine. The organic phase was dried and concentrated. The residue was purified by column chromatography (cyclohexane−EtOAc, 3:7) to give **20** (541 mg, 69%) as a white foam: $[\alpha]_D$ +16 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 7.35−7.05 (m, 10H, Ph), 5.50 (d, 1H, $J_{2,NH}$ = 8.2 Hz, NH$_D$), 5.22 (d, 1H, $J_{1,2}$ = 1.1 Hz, H-1$_A$), 5.06 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4$_D$), 5.00 (pt, 1H, $J_{2,3}$ = 9.5 Hz, H-3$_D$), 4.85−4.60 (m, 4H, C$H_2$Ph), 4.56 (d, 1H, $J_{1,2}$ = 7.0 Hz, H-1$_D$), 4.22−4.13 (m, 2H, $J_{5,6}$ = 4.5 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a$_D$, 6b$_D$), 4.03 (m, 1H, H-2$_D$), 4.00 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5$_A$), 3.96 (dd, 1H, $J_{2,3}$ = 3.3 Hz, H-2$_A$), 3.90 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3$_A$), 3.60 (m, 1H, H-5$_D$), 3.48 (d, 1H, $J_{1,OH}$ = 3.5 Hz, OH), 3.40 (pt, 1H, H-4$_A$), 2.08, 2.03, 2.01 (3s, 9H, OAc), 1.65 (s, 3H, NHAc), 1.30 (d, 3H, H-6$_A$); $^{13}$C NMR ($CDCl_3$) $\delta$ 171.2, 171.0, 170.4, 169.6 (C═O), 138.2−128.0 (Ph), 103.3 (C-1$_D$), 94.1 (C-1$_A$), 81.4 (C-4$_A$), 79.9 (C-2$_A$), 78.7 (C-3$_A$), 75.8, 73.9 (2C, $CH_2$-Ph), 73.6 (C-3$_D$), 72.4 (C-5$_D$), 68.7 (C-4$_D$), 68.2 (C-5$_A$), 62.4 (C-6$_D$), 54.5 (C-2$_D$), 23.3 (NHAc), 21.1, 21.0, 21.0 (3C, OAc), 18.3 (C-6$_A$). FAB-MS for $C_{34}H_{43}NO_{13}$ (M, 673.2), *m/z* 696.3 [M + Na]$^+$. Anal. Calcd for $C_{34}H_{43}NO_{13}$: C, 60.61; H, 6.43; N, 2.08. Found: C, 60.46; H, 6.61; N, 1.95.

**(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-αα-L-rhamnopyranosyl Trichloroacetimidate (7).** The hemiacetal **20** (541 mg, 0.80 mmol) was dissolved in DCM (20 mL), placed under argon, and cooled to 0 °C. Trichloroacetonitrile (0.81 mL, 8 mmol), then DBU (10 $\mu$L, 80 $\mu$mol) were added. The mixture was stirred at 0 °C for 1 h. The mixture was concentrated and toluene was coevaporated from the residue. The residue was eluted from a column of silica gel with 1:1 cyclohexane−EtOAc containing 0.2% of $Et_3N$ to give **7** (560 mg, 86%) as a colorless foam: $[\alpha]_D$ +2 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 8.56 (s, 1H, NH), 7.50−7.20 (m, 10H, Ph), 6.29 (d, 1H, $J_{1,2}$ = 1.3 Hz, H-1$_A$), 5.50 (d, 1H, $J_{2,NH}$ = 8.3 Hz, NH$_D$), 5.17 (pt, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3$_D$), 5.09 (dd, 1H, $J_{4,5}$ = 9.5 Hz, H-4$_D$), 4.85−4.60 (m, 4H, C$H_2$Ph), 4.68 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1$_D$), 4.22−4.10 (m, 2H, $J_{5,6}$ = 5.0 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a$_D$, 6b$_D$), 4.00 (m, 1H, H-2$_D$), 3.99 (dd, 1H, $J_{2,3}$ = 3.5 Hz, H-2$_A$), 3.90 (dq, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 6.2 Hz, H-5$_A$), 3.89 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3$_A$), 3.62 (m, 1H, H-5$_D$), 3.50 (dd, 1H, H-4$_A$), 2.02, 2.00, 1.98 (3s, 9H, OAc), 1.65 (s, 3H, NHAc), 1.32 (d, 3H, H-6$_A$); $^{13}$C NMR ($CDCl_3$) $\delta$ 171.2, 171.0, 170.4, 169.6 (C═O), 160.5 (C═NH), 138.2−128.0 (Ph), 103.3 (C-1$_D$), 97.3 (C-1$_A$), 91.4 ($CCl_3$), 80.3 (C-4$_A$), 79.9 (C-3$_A$), 77.5 (C-2$_A$), 76.0, 73.8 (2C, $CH_2$Ph), 73.1 (C-3$_D$), 72.2 (C-5$_D$), 71.1 (C-5$_A$), 68.8 (C-4$_D$), 62.5 (C-6$_D$), 54.8 (C-2$_D$), 23.3 (NHAc), 21.4, 21.1, 21.0 (3C, OAc), 18.4 (C-6$_A$). Anal. Calcd for $C_{36}H_{43}Cl_3N_2O_{13}$: C, 52.85; H, 5.30; N, 3.42. Found: C, 52.85; H, 5.22; N, 3.47.

**Allyl (2-*O*-Acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (22).** The acceptor **14** (1.78 g, 4.65 mmol) and the trichloroacetimidate donor **21**[42] (2.96 g, 5.58 mmol) were dissolved in anhydrous $Et_2O$ (100 mL). The mixture was placed under argon and cooled to −55 °C. TMSOTf (335 $\mu$L, 1.86 mmol) was added dropwise. The mixture was stirred at −55 to −20 °C over 3 h. Triethylamine (0.75 mL) was added, and the mixture was allowed to warm to rt. The mixture was concentrated. The residue was purified by column chromatography (cyclohexane−EtOAc, 7:3) to give **22** as a colorless syrup (3.21 g, 92%): $[\alpha]_D$ −16 (*c*, 0.55, $CHCl_3$) {lit.[41] $[\alpha]_D$ −19.3° (*c*, 1.2, $CHCl_3$)}; $^1$H NMR ($CDCl_3$) $\delta$ 7.42−7.30 (m, 20H, Ph), 5.92−5.82 (m, 1H, All), 5.62 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.2 Hz, H-2$_A$), 5.32−5.20 (m, 2H, All), 5.07 (d, 1H, H-1$_A$), 4.82 (d, 1H, $J_{1,2}$ = 1.0 Hz, H-1$_B$), 4.95−4.60 (m, 8H, C$H_2$Ph), 4.20−4.15 (m, 1H, All), 4.09 (d, 1H, $J_{2,3}$ = 3.0 Hz, H-2$_B$), 4.05 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3$_A$), 4.05−3.95 (m, 1H, All), 3.96 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3$_B$), 3.89 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.3 Hz, H-5$_A$), 3.76 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-5$_B$), 3.52 (m, 1H, H-4$_B$), 3.50 (m, 1H, H-4$_A$), 2.18 (s, 3H, OAc), 1.39 (d, 3H, H-6$_A$), 1.36 (d, 3H, H-6$_B$); $^{13}$C NMR (CDCl$_3$) $\delta$ 170.8 (C═O), 138.4−117.1 (Ph, All), 99.5 (C-1$_A$), 98.4 (C-1$_B$), 80.5 (2C, C-4$_A$, 4$_B$), 80.0 (C-3$_B$), 78.1 (C-3$_A$), 75.8, 75.7 (2C, $C$H$_2$Ph), 74.9 (C-2$_B$), 72.5, 72.2 (2C, $C$H$_2$Ph), 69.3 (C-2$_A$), 68.6 (C-5$_A$), 68.4 (C-5$_B$), 68.0 (All), 21.5 (OAc), 18.4, 18.2 (2C, C-6$_A$, 6$_B$). CI-MS for $C_{45}H_{52}O_{10}$ (M, 752) $m/z$ 770 [M + NH$_4$]$^+$. Anal. Calcd for $C_{45}H_{52}O_{10}$: C, 71.79; H, 6.96. Found: C, 70.95; H, 7.01.

**Allyl (3,4-Di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (23).** A 1 M solution of sodium methoxide in methanol (1.1 mL) was added to a solution of **22** (3.10 g, 4.13 mmol) in methanol. The mixture was stirred at rt for 3 h. The mixture was neutralized with Amberlite IR-120 (H$^+$) resin, filtered, and concentrated to give **23** (2.72 g, 93%) as a colorless syrup that crystallized on standing: mp 98−99 °C (lit.[21] mp 100 °C (hexane)); [α]$_D$ −30 ($c$ 0.5, CHCl$_3$) {lit.[21] [α]$_D$ −32.5 ($c$, 0.4, CHCl$_3$)}; $^1$H NMR (CDCl$_3$) $\delta$ 7.42−7.30 (m, 20H, Ph), 5.90−5.80 (m, 1H, All), 5.32−5.20 (m, 2H, All), 5.13 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1$_A$), 4.82 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1$_B$), 4.95−4.60 (m, 8H, C$H_2$Ph), 4.20−4.12 (m, 1H, All), 4.19 (m, 1H, $J_{2,3}$ = 3.2 Hz, $J_{2,OH}$ = 1.8 Hz, H-2$_A$), 4.09 (d, 1H, $J_{2,3}$ = 3.2 Hz, H-2$_B$), 4.00−3.95 (m, 1H, All), 3.95 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3$_A$), 3.93 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3$_B$), 3.87 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz, H-5$_A$), 3.74 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz, H-5$_B$), 3.53 (pt, 1H, H-4$_A$), 3.46 (pt, 1H, H-4$_B$), 2.52 (d, 1H, OH), 1.35 (m, 6H, H-6$_A$, 6$_B$); $^{13}$C NMR (CDCl$_3$) $\delta$ 138.4−117.1 (Ph, All), 101.2 (C-1$_A$), 98.4 (C-1$_B$), 80.8, 80.4 (2C, C-4$_A$, 4$_B$), 80.3 (C-3$_B$), 80.0 (C-3$_A$), 75.8, 75.7 (2C, $C$H$_2$Ph), 75.0 (C-2$_B$), 72.7, 72.6 (2C, $C$H$_2$Ph), 69.1 (C-2$_A$), 68.4 (C-5$_B$), 68.3 (C-5$_A$), 68.1 (All), 18.4, 18.3 (2C, C-6$_A$, 6$_B$). CI-MS for $C_{43}H_{50}O_9$ (M, 710) $m/z$ 728 [M + NH$_4$]$^+$.

**3,4,6-Tri-*O*-acetyl-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranosyl Trichloroacetimidate (24).**[44] Trichloroacetonitrile (2.5 mL) and anhydrous potassium carbonate were added to a suspension of 3,4,6-tri-*O*-acetyl-2-deoxy-2-tetrachlorophthalimido-α/*β*-D-glucopyranose (7.88 g, 13.75 mmol) in 1,2-DCE (120 mL). The mixture was stirred at rt overnight. TLC (cyclohexane−EtOAc, 3:2) showed that no starting material remained. The mixture was filtered through a pad of Celite, and the filtrate was concentrated to give the target **24** as a slightly brownish solid (9.08 g, 92%).

**Allyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (25).** 1,2-DCE (35 mL) was added to the trichloroacetimidate donor **16** (2.49 g, 4.20 mmol), the acceptor **23** (2.48 g, 3.50 mmol), and 4 Å powdered molecular sieves (4 g). The mixture was stirred for 1.5 h at rt under argon. The mixture was cooled to −20 °C and TMSOTf (230 $\mu$L, 1.26 mmol) was added. The temperature was allowed to rise to 0 °C over 1 h, and the mixture was stirred for an additional 2 h at this temperature. Triethylamine (0.5 mL) was added and the mixture was allowed to warm to rt. The mixture was diluted with DCM and filtered. The filtrate was concentrated. The residue was purified by column chromatography with 3:1 cyclohexane−EtOAc to give **25** (3.83 g, 96%) as a colorless amorphous solid: [α]$_D$ −6 ($c$ 0.5, CHCl$_3$); $^1$H NMR (CDCl$_3$) $\delta$ 7.52−7.28 (m, 20H, Ph), 6.83 (d, 1H, $J_{2,NH}$ = 8.4 Hz, NH), 5.85 (m, 1H, All), 5.26−5.09 (m, 4H, H-3$_D$, 4$_D$, All), 4.98 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1$_A$), 4.98−4.58 (m, 10H, H-1$_B$, 1$_D$, C$H_2$Ph), 4.08 (m, 4H, H-2$_A$, 2$_D$, 6a$_D$, All), 3.91 (m, 5H, H-2$_B$, 3$_A$, 3$_B$, 6b$_D$, All), 3.79 (m, 2H, H-5$_A$, 5$_B$), 3.45 (m, 3H, H-4$_A$, 4$_B$, 5$_D$), 2.04, 2.02, 1.97 (3s, 9H, OAc), 1.30 (m, 6H, H-6$_A$, 6$_B$); $^{13}$C NMR (CDCl$_3$) $\delta$ 170.6, 170.3, 169.1, 161.6 (C═O), 138.4−117.1 (Ph, All), 101.3 (C-1$_D$), 100.9 (C-1$_A$), 97.6 (C-1$_B$), 92.0 (CCl$_3$), 80.9, 80.4 (2C, C-4$_A$, 4$_B$), 79.1, 79.0 (2C, C-3$_A$, 3$_B$), 77.3 (C-2$_A$), 76.5 (C-2$_B$), 75.4, 75.2, 73.6 (3C, $C$H$_2$Ph), 72.2 (C-3$_D$), 71.9 (C-5$_D$), 71.6 ($C$H$_2$Ph), 68.2 (C-5$_B$*), 67.8 (C-4$_D$), 67.5 (C-5$_A$*), 67.5 (CH$_2$O), 61.3 (C-6$_D$), 55.7 (C-2$_D$), 20.5, 20.4 (3C, OAc), 17.9, 17.7 (2C, C-6$_A$, 6$_B$). FAB-MS for $C_{57}H_{66}Cl_3NO_{17}$ (M, 1141.3) $m/z$ 1164.3 [M + Na]$^+$. Anal. Calcd for $C_{57}H_{66}Cl_3NO_{17}$: C, 59.87; H, 5.82; N, 1.22. Found: C, 59.87; H, 5.92; N, 1.16.

**Allyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-tetrachlorophthalimido-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (28).** Anhydrous Et$_2$O (30 mL) and DCM (15 mL) were added to the trichloroacetimidate donor **24** (3.34 g, 4.66 mmol) and the acceptor **23** (2.20 g, 3.10 mmol). The mixture was cooled to 0 °C and TMSOTf (85 $\mu$L, 0.466 mmol) was added dropwise. The mixture was stirred at 0 °C for 1 h, then at rt for 3 h. Triethylamine (1 mL) was added and the mixture was stirred for 10 min, then concentrated. The mixture was taken up in Et$_2$O and the resulting precipitate was filtered off. The filtrate was concentrated. The residue was purified by column chromatography with 7:3 cyclohexane−EtOAc to give **28** (2.57 g, 65%) as a colorless amorphous solid: [α]$_D$ +22 ($c$ 1.0, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.42−7.16 (m, 20H, Ph), 5.91 (dd, 1H, H-3$_D$), 5.81 (m, 1H, All), 5.24−5.10 (m, 4H, H-1$_D$, 4$_D$, All), 4.93 (s, 1H, H-1$_A$), 4.81−4.53 (m, 5H, H-1$_B$, CH$_2$Ph), 4.45−4.23 (m, 5H, H-2$_D$, CH$_2$Ph), 4.05 (m, 2H, H-6a$_D$, All), 3.91−3.58 (m, 8H, H-2$_A$, 2$_B$, 3$_A$, 3$_B$, 5$_A$, 5$_B$, 6b$_D$, All), 3.38 (m, 1H, H-5$_D$), 3.21−3.13 (m, 2H, H-4$_A$, 4$_B$), 2.05, 2.02, 2.00 (3s, 9H, OAc), 1.24 (m, 6H, H-6$_A$, 6$_B$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.5, 170.4, 169.3 (C═O), 138.4−117.1 (Ph, All), 101.1 (C-1$_A$), 99.9 (C-1$_D$), 97.7 (C-1$_B$), 80.6 (2C, C-4$_A$, 4$_B$), 79.7, 78.9 (2C, C-3$_A$, 3$_B$), 78.2 (C-2$_A$), 76.3 (C-2$_B$), 75.2, 75.1, 72.6, 71.3 (4C, CH$_2$Ph), 71.2 (C-5$_D$), 70.1 (C-3$_D$), 68.4 (C-5$_B$*), 68.4 (C-4$_D$), 67.6 (C-5$_A$*), 67.6 (All), 61.3 (C-6$_D$), 55.4 (C-2$_D$), 20.6, 20.5 (3C, OAc), 18.0, 17.6 (2C, C-6$_A$, 6$_B$). FAB-MS for $C_{63}H_{65}Cl_4NO_{18}$ (M, 1263.3) $m/z$ 1288.4, 1286.4 [M + Na]$^+$. Anal. Calcd for $C_{63}H_{65}Cl_4NO_{18}$: C, 59.77; H, 5.17; N, 1.11. Found: C, 60.19; H, 5.53; N, 1.18.

**Allyl (2-Acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (26).** The trisaccharide **25** (1.71 g, 1.50 mmol) was dissolved in MeOH (20 mL). A 1 M solution of sodium methoxide in methanol (9 mL) and triethylamine (5 mL) were added, and the mixture was stirred at rt for 18 h. The mixture was cooled to 0 °C and acetic anhydride was added dropwise until the pH reached 6. A further portion of acetic anhydride (0.4 mL) was added, and the mixture was stirred at rt for 30 min. The mixture was concentrated, and toluene was coevaporated from the residue. The residue was purified by column chromatography with 95:5 DCM−MeOH to give **26** (623 mg, 45%) as a colorless amorphous solid: [α]$_D$ −16 ($c$ 0.5, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.48−7.24 (m, 20H, Ph), 6.79 (d, 1H, NH), 5.73 (m, 1H, All), 5.12 (m, 3H, H-1$_A$, All), 4.86−4.52 (m, 9H, H-1$_B$, CH$_2$Ph), 4.34 (d, 1H, H-1$_D$), 4.08−3.79 (m, 6H, H-2$_A$, 2$_B$, 3$_A$, 3$_B$, All), 3.74−3.53 (m, 3H, H-5$_A$, 5$_B$, 6a$_D$), 3.45−3.24 (m, 6H, H-2$_D$, 3$_D$, 4$_A$, 4$_B$, 4$_D$, 6b$_D$), 3.20 (m, 1H, H-5$_D$), 1.46 (s, 3H, NHAc), 1.24 (m, 6H, H-6$_A$, 6$_B$); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 173.6 (C═O), 137.4−117.3 (Ph, All), 103.2 (C-1$_D$), 100.3 (C-1$_A$), 97.9 (C-1$_B$), 81.3, 80.4 (2C, C-4$_A$, 4$_B$), 79.9 (2C, C-3$_A$, 3$_B$), 79.9 (C-2$_B$*), 78.9 (C-3$_D$), 75.7 (C-5$_D$), 75.6, 75.3, 74.5 (3C, CH$_2$Ph), 73.6 (C-2$_A$*), 72.5 (CH$_2$Ph), 71.9 (C-4$_D$), 68.2, 68.0 (2C, C-5$_A$, 5$_B$), 67.7 (CH$_2$O), 62.5 (C-6$_D$), 58.8 (C-2$_D$), 22.3 (NHAc), 18.0, 17.8 (2C, C-6$_A$, 6$_B$). FAB-MS for $C_{51}H_{63}NO_{14}$ (M, 913.4) $m/z$ 936.6 [M + Na]$^+$. Anal. Calcd for $C_{51}H_{63}NO_{14}\cdot H_2O$: C, 65.72; H, 7.03; N, 1.50. Found: C, 65.34; H, 7.03; N, 1.55.

**Allyl (2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (27).** (a) Pyridine (5 mL) was added to **26** (502 mg, 0.55 mmol) and the mixture was cooled to 0 °C. Acetic anhydride (3 mL) was added. The mixture was stirred at rt for 18 h. The mixture was concentrated and toluene was coevaporated from the residue. The residue was taken up in DCM and washed successively with 5% aq HCl and saturated aq $NaHCO_3$. The organic phase was dried and concentrated to give **27** (538 mg, 94%) as a colorless foam.

(b) THF (3 mL) and ethanol (3.3 mL) were added to **28** (384 mg, 0.30 mmol). Ethylenediamine (90 $\mu$L, 1.36 mmol) was added and the mixture was heated at 55 °C for 4 h. The mixture was allowed to cool to rt. Acetic anhydride (1.0 mL) was added, and the mixture was stirred at rt for 1.5 h. The mixture was concentrated. The residue was taken up in pyridine (5 mL) and the mixture was cooled to 0 °C. Acetic anhydride (2.5 mL) was added. The mixture was stirred at rt for 18 h. The mixture was concentrated and toluene was coevaporated from the residue. The residue was taken up in DCM, which caused the formation of a white precipitate. The mixture was filtered through a plug of silica gel, eluting with 7:3 cyclohexane−acetone. The filtrate was concentrated to give **27** (215 mg, 68%) as a colorless foam: $[\alpha]_D$ −7 (*c* 0.5, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.48−7.24 (m, 20H, Ph), 5.84 (m, 1H, All), 5.53 (d, 1H, NH), 5.19 (m, 2H, All), 5.03 (dd, 1H, H-$4_D$), 4.98 (m, 2H, H-$1_A$, $3_D$), 4.95−4.54 (m, 10H, H-$1_B$, $1_D$, $CH_2$Ph), 4.07 (m, 4H, H-$2_A$, $2_D$, $6a_D$, All), 3.88 (m, 5H, H-$2_B$, $3_A$, $3_B$, $6b_D$, All), 3.79, 3.68 (2m, 2H, H-$5_A$, $5_B$), 3.42 (m, 3H, H-$4_A$, $4_B$, $5_D$), 2.02, 2.01, 1.97, 1.64 (4s, 12H, OAc, NHAc), 1.30 (m, 6H, H-$6_A$, $6_B$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 170.7, 170.4, 169.9, 169.1 (C=O), 138.5−117.1 (Ph, All), 102.9 (C-$1_D$), 101.2 (C-$1_A$), 97.7 (C-$1_B$), 81.0, 80.5 (2C, C-$4_A$, $4_B$), 79.5, 79.1 (2C, C-$3_A$, $3_B$), 78.2 (C-$2_A$), 76.1 (C-$2_B$), 75.5, 75.2, 73.6 ($CH_2$Ph), 73.3 (C-$3_D$), 71.9 (C-$5_D$), 71.7 ($CH_2$Ph), 68.3 (C-$5_A$*), 68.0 (C-$4_D$), 67.6 (C-$5_B$*), 67.6 ($CH_2$O), 61.6 (C-$6_D$), 54.1 (C-$2_D$), 22.9 (NHAc), 20.7, 20.6 (3C, OAc), 18.0, 17.7 (2C, C-$6_A$, $6_B$). FAB-MS for $C_{57}H_{69}NO_{17}$ (M, 1039.5) *m/z* 1062.4 [M + Na]$^+$. Anal. Calcd for $C_{57}H_{69}NO_{17}$: C, 65.82; H, 6.69; N, 1.35. Found: C, 65.29; H, 6.82; N, 1.29.

**(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α/*β*-L-rhamnopyranose (29).** 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)iridium hexafluorophosphate (30 mg, 35 $\mu$mol) was dissolved in THF (5 mL), and the resulting red solution was processed as described for the preparation of **18**. A solution of **27** (805 mg, 0.775 mmol) in THF (10 mL) was degassed and added. The mixture was stirred at rt overnight, then concentrated. The residue was taken up in acetone (15 mL) and water (1.5 mL). Mercuric chloride (315 mg, 1.16 mmol) and mercuric oxide (335 mg, 1.55 mmol) were added. The mixture, protected from light, was stirred for 1 h at rt, then concentrated. The residue was taken up in DCM and washed three times with satd aqueous KI, then with brine. The organic phase was dried and concentrated. The residue was purified by column chromatography with 2:3 EtOAc−cyclohexane to give **29** (645 mg, 83%) as a white foam. The $^1$H NMR spectra showed the α:$\beta$ ratio to be 3.3:1; $[\alpha]_D$ +3 (*c* 0.5, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) α-anomer, $\delta$ 7.47−7.30 (m, 20H, Ph), 5.53 (d, 1H, NH), 5.17 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-$1_B$), 5.08 (m, 1H, H-$4_D$), 5.03 (d, 1H, $J_{1,2}$ = 1.5 Hz, H-$1_A$), 4.99 (m, 1H, H-$3_D$), 4.92−4.62 (m, 8H, $CH_2$Ph), 4.60 (d, 1H, $J_{1,2}$ = 8.4 Hz, H-$1_D$), 4.18−4.01 (m, 3H, H-$2_A$, $2_D$, $6a_D$), 3.97−3.90 (m, 5H, H-$2_B$, $3_A$, $3_B$, $5_A$*, $6b_D$), 3.83 (m, 1H, H-$5_B$*), 3.45−3.37 (m, 3H, H-$4_A$, $4_B$, $5_D$), 2.04, 2.03, 1.99, 1.68 (4s, 12H, OAc, NHAc), 1.32 (m, 6H, H-$6_A$, $6_B$); $^{13}$C NMR (75 MHz, $CDCl_3$) α-anomer, $\delta$ 170.7, 170.4, 169.9, 169.1 (C=O), 138.5−129.3 (Ph), 103.3 (C-$1_D$), 101.6 (C-$1_A$), 93.9 (C-$1_B$), 81.5, 80.8 (2C, C-$4_A$, $4_B$), 79.9, 78.9 (2C, C-$3_A$, $3_B$), 78.6 (C-$2_A$), 76.8 (C-$2_B$), 76.0, 75.5, 74.0 (3C, $CH_2$Ph), 73.7 (C-$3_D$), 72.4 (C-$5_D$), 72.2 ($CH_2$Ph), 68.7 (C-$5_A$*), 68.5 (C-$4_D$), 68.2 (C-$5_B$*), 62.0 (C-$6_D$), 54.6 (C-$2_D$), 23.4 (NHAc), 21.1, 21.0 (3C, OAc), 18.5, 18.1 (2C, C-$6_A$, $6_B$). FAB-MS for $C_{54}H_{65}NO_{17}$ (M, 999.4) *m/z* 1022.5 [M + Na]$^+$. Anal. Calcd for $C_{54}H_{65}NO_{17}$: C, 64.85; H, 6.55; N, 1.40. Found: C, 64.55; H, 7.16; N, 1.15.

**(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α/*β*-L-rhamnopyranosyl Trichloroacetimidate (13).** The hemiacetal **29** (595 mg, 0.59 mmol) was dissolved in DCM (10 mL), placed under argon, and cooled to 0 °C. Trichloroacetonitrile (0.6 mL, 6 mmol), then DBU (10 $\mu$L, 59 $\mu$mol) were added. The mixture was stirred at 0 °C for 20 min, then at rt for 20 min. The mixture was concentrated and toluene was coevaporated from the residue. The residue was purified by flash chromatography with 1:1 cyclohexane−EtOAc containing 0.2% of $Et_3N$ to give **13** (634 mg, 94%) as a colorless foam. The $^1$H NMR spectra showed the α:$\beta$ ratio to be 10:1: $[\alpha]_D$ −20 (*c* 1, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) α-anomer, $\delta$ 8.47 (s, 1H, C=NH), 7.38−7.20 (m, 20H, Ph), 6.10 (d, 1H, $J_{1,2}$ = 1.3 Hz, H-$1_B$), 5.40 (d, 1H, NH), 5.01 (m, 1H, H-$4_D$), 4.95 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-$1_A$), 4.89 (m, 1H, H-$3_D$), 4.85−4.55 (m, 9H, H-$1_D$, $CH_2$Ph), 4.07 (dd, 1H, H-$6a_D$), 4.03 (m, 1H, H-$2_A$), 3.97 (m, 1H, H-$2_D$), 3.91 (dd, 1H, H-$6b_D$), 3.85−3.71 (m, 5H, H-$2_B$, $3_A$, $3_B$, $5_A$, $5_B$), 3.45−3.31 (m, 3H, H-$4_A$, $4_B$, $5_D$), 1.99, 1.96, 1.91, 1.58 (4s, 12H, OAc, NHAc), 1.26 (m, 6H, H-$6_A$, $6_B$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.1, 170.9, 170.3, 169.6 (C=O), 160.6 (C=NH), 138.6−128.1 (Ph), 103.3 (C-$1_D$), 101.6 (C-$1_A$), 96.9 (C-$1_B$), 91.3 ($CCl_3$), 81.4, 80.2 (2C, C-$4_A$, $4_B$), 79.9, 78.5 (2C, C-$3_A$, $3_B$), 78.3 (C-$2_A$), 75.9 (2C, $CH_2$Ph), 75.0 (C-$2_B$), 73.7 ($CH_2$Ph), 73.7 (C-$3_D$), 72.4 ($CH_2$Ph), 72.4 (C-$5_D$), 71.0, 69.0 (2C, C-$5_A$, $5_B$), 68.5 (C-$4_D$), 62.1 (C-$6_D$), 54.6 (C-$2_D$), 23.4 (NHAc), 21.1, 21.0 (3C, OAc), 18.5, 18.0 (2C, C-$6_A$, $6_B$). Anal. Calcd for $C_{56}H_{65}Cl_3N_2O_{17}$: C, 58.77; H, 5.72; N, 2.45. Found: C, 58.78; H, 5.83; N, 2.45.

**Allyl (2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-benzoyl-α-L-rhamnopyranoside (5).** Anhydrous $Et_2O$ (5 mL) was added to the donor **13** (500 mg, 0.44 mmol), the acceptor **11**[18] (242 mg, 0.29 mmol), and powdered 4 Å molecular sieves. The mixture was placed under argon and cooled to 0 °C. Boron trifluoride etherate (415 $\mu$L, 3.27 mmol) was added. The mixture was stirred at 0 °C for 1 h, then at rt for 18 h. The mixture was diluted with DCM and triethylamine (1 mL) was added. The mixture was filtered through a pad of Celite and the filtrate was concentrated. The residue was purified by column chromatography with 3:2 cyclohexane−EtOAc to give, in order, the acceptor **11** (132 mg, 54%), **5** (231 mg, 44%), and the hemiacetal **29** (129 mg, 29%). The desired pentasaccharide **5** was obtained as a colorless foam: $[\alpha]_D$ +10 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 8.02−7.09 (m, 45H, Ph), 5.92 (m, 1H, All), 5.65 (d, 1H, NH), 5.37 (m,1H, H-$2_C$), 5.19 (m, 2H, All), 5.13 (br s, 1H, H-$1_A$), 4.96−4.35 (m, 15H, H-$1_B$, $1_C$, $1_D$, $1_E$, $2_B$, $3_D$, $4_D$, $CH_2$Ph), 4.17 (m, 2H, H-$2_A$, All), 4.04−3.87 (m, 8H, H-$2_D$, $3_A$, $3_C$, $3_E$, $5_A$, $5_E$, $6a_D$, All), 3.81−3.63 (m, 7H, H-$3_B$, $4_C$, $4_E$, $5_C$, $6a_E$, $6b_E$, $6b_D$), 3.59 (m, 1H, H-$5_B$), 3.43 (m, 3H, H-$2_E$, $4_A$, $5_D$), 3.28 (pt, 1H, H-$4_B$), 2.01, 1.99, 1.71, 1.66 (4s, 12H, OAc, NHAc), 1.34 (m, 6H, H-$6_A$, $6_C$), 1.00 (d, 3H, H-$6_B$); $^{13}$C NMR ($CDCl_3$) $\delta$ 170.5, 170.0, 169.3, 165.8, 163.5 (C=O), 138.7−117.6 (Ph, All), 102.7 (C-$1_D$), 100.8 (2C, C-$1_A$, $1_B$), 98.1 (C-$1_E$), 95.9 (C-$1_C$), 81.8 (C-$3_E$), 81.2 (2C, C-$2_E$, $4_A$), 80.0 (C-$4_B$), 79.7 (2C, C-$3_A$, $3_C$), 78.2 (C-$3_B$), 77.7 (C-$2_A$), 77.3 (2C, C-$4_C$, $4_E$), 75.6, 75.4, 74.9 ($CH_2$Ph), 74.3 (C-$2_B$), 73.8 ($CH_2$Ph), 73.7 (C-$3_D$), 72.8 ($CH_2$Ph), 72.3 (C-$2_C$), 72.1 (C-$5_D$), 71.5 (C-$5_E$), 70.2 ($CH_2$Ph), 68.5 (C-$5_B$), 68.4 (C-$5_A$, $CH_2$O), 68.2 (C-$4_D$), 67.9 (C-$6_E$), 67.4 (C-$5_C$), 61.8 (C-$6_D$), 54.3 (C-$2_D$), 23.1 (NHAc), 20.7, 20.6, 20.4 (3C, OAc), 18.6 (C-$6_A$), 18.0 (C-$6_C$), 17.8 (C-$6_B$). FAB-MS for $C_{104}H_{117}NO_{27}$ (M, 1812.1) *m/z* 1836.2, 1835.2 [M + Na]$^+$. Anal. Calcd for $C_{104}H_{117}NO_{27}$: C, 68.90; H, 6.50; N, 0.77. Found: C, 68.64; H, 6.66; N, 1.05.

**Allyl (3,4-Di-*O*-benzyl-2-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (32).** To a solution of **23** (3.8 g, 5.35 mmol) in pyridine (40 mL) was added chloroactic anhydride (1.83 g, 10.7 mmol) at 0 °C. The mixture was stirred overnight at 0 °C. MeOH (10 mL) was added and the mixture was concentrated. The residue was eluted from a column of silica gel with 95:5 cyclohexane−acetone to give **32** (2.4 g, 57%) as a colorless syrup: $[\alpha]_D$ −15 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 7.30−7.15 (m, 20H, Ph), 5.81−5.71 (m, 1H, All), 5.49 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.2

Hz, H-$2_A$), 5.20−5.08 (m, 2H, All), 4.90 (d, 1H, H-$1_A$), 4.84−4.50 (m, 8H, $PhCH_2$), 4.65 (d, 1H, $J_{1,2}$ < 1.0 Hz, H-$1_B$), 4.04−3.85 (m, 2H, All), 4.02 (m, 2H, $CH_2Cl$), 3.93 (dd, 1H, $J_{2,3}$ = 3.0 Hz, H-$2_B$), 3.88 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-$3_A$), 3.81 (pt, 1H, $J_{3,4}$ = 9.5 Hz, H-$3_B$), 3.73 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-$5_A$), 3.62 (dq, 1H, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.1 Hz, H-$5_B$), 3.34 (dd, 1H, H-$4_B$), 3.30 (dd, 1H, H-$4_A$), 1.22 (d, 3H, H-$6_A$), 1.21 (d, 3H, H-$6_B$); $^{13}$C NMR ($CDCl_3$) δ 166.9 (C=O), 138.5−117.2 (Ph, All), 99.2 (C-$1_A$), 98.2 (C-$1_B$), 80.4 (C-$4_A$), 80.3 (C-$3_B$), 80.2 (C-$4_B$), 77.9 (C-$3_A$), 75.8, 75.7, 72.6, 72.4 (4C, Ph*C*$H_2$), 74.9 (C-$2_B$), 71.2 (C-$2_A$), 68.6 (C-$5_A$), 68.4 (C-$5_B$), 68.0 (All), 41.3 ($CH_2Cl$), 18.3 (2C, C-$6_A$, $6_B$). FAB-MS for $C_{45}H_{51}ClO_{10}$ (M, 786.3), *m/z* 809.3 [M + Na]$^+$. Anal. Calcd for $C_{45}H_{51}ClO_{10}$: C, 68.65; H, 6.53. Found: C, 68.51; H, 6.67.

**(3,4-Di-*O*-benzyl-2-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α/*β*-L-rhamnopyranose (33).** 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)iridium hexafluorophosphate (40 mg, 46 μmol) was dissolved in THF (7 mL), and the resulting red solution was processed as described for the preparation of **18**. A solution of **32** (2.39 g, 3.04 mmol) in THF (18 mL) was degassed and added. The mixture was stirred at rt overnight. The mixture was concentrated. The residue was taken up in acetone (30 mL) and water (5 mL). Mercuric chloride (1.24 g, 4.56 mmol) and mercuric oxide (1.3 g, 6.08 mmol) were added. The mixture, protected from light, was stirred for 2 h at rt, then concentrated. The residue was taken up in DCM and washed three times with satd aqueous KI, then with brine. The organic phase was dried and concentrated. The residue was purified by column chromatography (cyclohexane−EtOAc, 4:1) to give **33** (1.91 g, 84%) as a white foam: $[\alpha]_D$ −2 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) δ 7.40−7.10 (m, 20H, Ph), 5.49 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.2 Hz, H-$2_A$), 4.99 (d, 1H, $J_{1,2}$ < 1.0 Hz, H-$1_B$), 4.90 (d, 1H, H-$1_A$), 4.85−4.45 (m, 8H, $PhCH_2$), 4.01 (m, 2H, $CH_2Cl$), 3.93 (dd, 1H, $J_{2,3}$ = 3.0 Hz, H-$2_B$), 3.90 (dd, 1H, $J_{3,4}$ = 9.3 Hz, H-$3_A$), 3.84 (dd, 1H, $J_{3,4}$ = 9.0 Hz, H-$3_B$), 3.81 (dq, 1H, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.2 Hz, H-$5_B$), 3.72 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.2 Hz, H-$5_A$), 3.33 (pt, 1H, H-$4_B$), 3.30 (dd, 1H, H-$4_A$), 2.81 (d, 1H, $J_{2,OH}$ = 3.4 Hz, OH), 1.22 (d, 3H, H-$6_A$), 1.20 (d, 3H, H-$6_B$); $^{13}$C NMR ($CDCl_3$) δ 167.0 (C=O), 138.5−127.2 (Ph), 99.1 (C-$1_A$), 93.9 (C-$1_B$), 80.3 (C-$4_B$), 80.2 (C-$4_A$), 79.7 (C-$3_B$), 77.8 (C-$3_A$), 75.8, 75.7, 72.6, 72.4 (4C, Ph*C*$H_2$), 75.0 (C-$2_B$), 71.1 (C-$2_A$), 68.6 (C-$5_A$), 68.4 (C-$5_B$), 41.3 ($CH_2Cl$), 18.1 (2C, C-$6_A$, $6_B$). FAB-MS for $C_{42}H_{47}ClO_{10}$ (M, 746.3), *m/z* 769.3 [M + Na]$^+$. Anal. Calcd for $C_{42}H_{47}ClO_{10}$: C, 67.51; H, 6.34. Found: C, 67.46; H, 6.39.

**(3,4-Di-*O*-benzyl-2-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl Trichloroacetimidate (34).** The hemiacetal **33** (1.80 g, 2.41 mmol) was dissolved in DCM (25 mL), placed under argon, and cooled to 0 °C. Trichloroacetonitrile (2.4 mL, 24 mmol), then DBU (35 μL, 0.24 mmol) were added. The mixture was stirred at 0 °C for 40 min. The mixture was concentrated and toluene was coevaporated from the residue. The residue was eluted from a column of silica gel with 4:1 cyclohexane−EtOAc containing 0.2% of $Et_3N$ to give **34** (1.78 g, 83%) as a colorless foam: $[\alpha]_D$ −12 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) δ 8.60 (s, 1H, NH), 7.50−7.30 (m, 20H, Ph), 6.21 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-$1_B$), 5.63 (dd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.2 Hz, H-$2_A$), 5.07 (d, 1H, H-$1_A$), 5.00−4.65 (m, 8H, $PhCH_2$), 4.19 (m, 2H, $CH_2Cl$), 4.09 (dd, 1H, $J_{2,3}$ = 3.2 Hz, H-$2_B$), 4.04 (dd, 1H, $J_{3,4}$ = 9.0 Hz, H-$3_B$), 3.95 (m, 3H, H-$3_A$, $5_A$, $5_B$), 3.58 (dd, 1H, H-$4_A$), 3.48 (dd, 1H, H-$4_B$), 1.39 (m, 6H, H-$6_A$, $6_B$); $^{13}$C NMR ($CDCl_3$) δ 167.1 (C=O), 160.7 (C=N), 138.3−127.0 (Ph), 99.4 (C-$1_A$), 97.5 (C-$1_B$), 91.4 ($CCl_3$), 80.1 (C-$4_B$), 80.0 (C-$4_A$), 79.2 (C-$3_A$), 77.9 (C-$3_B$), 75.9, 75.8, 73.0, 72.6 (4C, Ph*C*$H_2$), 73.7 (C-$2_B$), 71.4 (C-$2_A$), 71.2, 68.9 (2C, C-$5_A$, $5_B$), 41.3 ($CH_2Cl$), 18.4, 18.2 (2C, C-$6_A$, $6_B$). Anal. Calcd for $C_{44}H_{47}Cl_4NO_{10}$: C, 59.27; H, 5.31; N, 1.57. Found: C, 59.09; H, 5.49; N, 1.53.

**Allyl (3,4-Di-*O*-benzyl-2-*O*-*p*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (35).** The alcohol **23** (3.8 g, 5.35 mmol) was dissolved in DMF (25 mL). The mixture was cooled to 0 °C and NaH (320 mg, 8.02 mmol) was added in 3 parts, one part each 10 min. Then *p*MeOBnCl (1.8 mL, 13.34 mmol) was added and the mixture was stirred overnight at rt. MeOH (5 mL) was added and the solution was stirred for 10 min. The solution was concentrated and the residue was eluted from a column of silica gel with 95:5 cyclohexane−acetone to give **35** (4.34 g, 97%) as a colorless syrup: $[\alpha]_D$ −8 (*c* 1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.20−6.80 (m, 24H, Ph), 5.90−5.80 (m, 1H, All), 5.30−5.15 (m, 2H, All), 5.12 (d, 1H, $J_{1,2}$ < 1.0 Hz, H-$1_A$), 4.73 (d, 1H, $J_{1,2}$ < 1.0 Hz, H-$1_B$), 4.70−4.40 (m, 10H, $PhCH_2$), 4.20−4.08 (m, 1H, All), 4.10 (dd, 1H, $J_{2,3}$ = 3.0 Hz, H-$2_B$), 3.95−3.88 (m, 3H, H-$3_A$, $3_B$, All), 3.80−3.78 (m, 2H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.1 Hz, H-$2_A$, $5_A$), 3.72 (s, 3H, $OCH_3$), 3.70 (m, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.1 Hz, H-$5_B$), 3.61 (dd, 1H, H-$4_A$), 3.32 (dd, 1H, H-$4_B$), 1.18 (d, 3H, H-$6_A$), 1.10 (d, 3H, H-$6_B$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 133.9−113.8 (Ph, All), 99.0 (C-$1_A$), 97.8 (C-$1_B$), 80.4 (C-$4_A$), 80.2 (C-$4_B$), 80.0 (C-$3_B$), 79.0 (C-$3_A$), 75.2, 72.3, 71.8, 71.5, 71.3, 67.5 (5C, Ph*C*$H_2$, All), 74.1 (C-$2_A$), 73.8 (C-$2_B$), 68.3 (C-$5_A$), 67.8 (C-$5_B$), 55.0 ($OCH_3$), 17.8, 17.9 (2C, C-$6_A$, $6_B$). FAB-MS for $C_{51}H_{58}O_{10}$ (M, 830.4) *m/z* 853.5 [M + Na]$^+$. Anal. Calcd for $C_{51}H_{58}O_{10}$: C, 73.71; H, 7.03. Found: C, 73.57; H, 7.21.

**(3,4-Di-*O*-benzyl-2-*O*-*p*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranose (36).** 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)iridiumhexafluorophosphate (50 mg, 60 μmol) was dissolved in THF (6 mL), and the resulting red solution was processed as described for the preparation of **18**. A solution of **35** (4.23 g, 5.09 mmol) in THF (24 mL) was degassed and added. The mixture was stirred at rt overnight, then concentrated. The residue was taken up in acetone (45 mL), and water (5 mL) was added. Mercuric chloride (2.07 g, 7.63 mmol) and mercuric oxide (2.2 g, 10.2 mmol) were added. The mixture, protected from light, was stirred for 2 h at rt, then concentrated. The residue was taken up in DCM and washed three times with satd aqueous KI, then with brine. The organic phase was dried and concentrated. The residue was purified by column chromatography (cyclohexane−EtOAc, 4:1) to give **36** (2.97 g, 73%) as a white foam: $[\alpha]_D$ +8 (*c* 1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.40−7.25 (m, 20H, Ph), 7.18−6.73 (m, 4H, Ph), 5.12 (d, 1H, $J_{1,2}$ < 1.0 Hz, H-$1_A$), 5.05 (d, 1H, $J_{1,2}$ < 1.0 Hz, H-$1_B$), 4.80−4.40 (m, 10H, $PhCH_2$), 4.08 (dd, 1H, $J_{2,3}$ = 3.0 Hz, H-$2_B$), 3.90−3.80 (m, 2H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.1 Hz, H-$3_B$, $5_B$), 3.80−3.78 (m, 2H, $J_{2,3}$ = 3.1 Hz, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.1 Hz, H-$2_A$, $5_A$), 3.73 (m, 1H, $J_{3,4}$ = 9.4 Hz, H-$3_A$), 3.72 (s, 3H, $OCH_3$), 3.60 (pt, 1H, H-$4_A$), 3.33 (pt, 1H, H-$4_B$), 1.34 (d, 3H, H-$6_A$), 1.24 (d, 3H, H-$6_B$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 113.2−129.8 (Ph), 99.1 (C-$1_A$), 93.8 (C-$1_B$), 80.7 (C-$4_A$), 80.3 (C-$4_B$), 79.7 (C-$3_B$), 79.2 (C-$3_A$), 75.5, 75.4, 72.6, 72.5, 72.4 (5C, Ph*C*$H_2$), 74.2 (C-$2_A$), 74.1 (C-$2_B$), 68.5 (C-$5_A$), 68.1 (C-$5_B$), 55.3 ($OCH_3$), 18.1 (2C, C-$6_A$, $6_B$). FAB-MS for $C_{48}H_{54}O_{10}$ (M, 790.4) *m/z* 813.4 [M + Na]$^+$. Anal. Calcd for $C_{48}H_{54}O_{10}$: C, 72.89; H, 6.88. Found: C, 72.86; H, 6.98.

**(3,4-Di-*O*-benzyl-2-*O*-*p*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α/*β*-L-rhamnopyranosyl Trichloroacetimidate (37).** The hemiacetal **36** (2.1 g, 2.66 mmol) was dissolved in DCM (20 mL), placed under argon, and cooled to 0 °C. Trichloroacetonitrile (2.7 mL, 26 mmol), then DBU (40 μL, 0.26 mmol) were added. The mixture was stirred at 0 °C for 30 min. The mixture was concentrated and toluene was coevaporated from the residue. The residue was eluted from a column of silica gel with 8:2 cyclohexane−EtOAc containing 0.2% of $Et_3N$ to give **37** (2.03 g, 82%) as a colorless foam: $[\alpha]_D$ −10 (*c* 1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 1H, NH), 7.25−7.05 (m, 20H, Ph), 7.05−6.62 (m, 4H, Ph), 6.08 (d, 1H, $J_{1,2}$ < 1.0 Hz, H-$1_B$), 5.10 (d, 1H, $J_{1,2}$ < 1.0 Hz, H-$1_A$), 4.80−4.40 (m, 10H, $PhCH_2$), 4.10 (dd, 1H, $J_{2,3}$ = 3.0 Hz, H-$2_B$), 3.90−3.80 (m, 4H, H-$3_B$, $2_A$, $3_A$, $5_A$), 3.80−3.72 (m, 1H, H-$5_B$), 3.72 (s, 3H, $OCH_3$), 3.63 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-$4_A$), 3.42 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-$4_B$), 1.30 (d, 3H, H-$6_B$), 1.25 (d, 3H, H-$6_A$); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 161.1 (C=NH), 129.5−113.4 (Ph), 99.6 (C-$1_A$), 97.0 (C-$1_B$), 80.6

(C-4$_A$), 79.6 (C-4$_B$), 79.3 (2C, C-3$_A$, 3$_B$), 75.7, 75.5, 72.8, 72.3, 72.0 (5C, Ph$CH_2$), 74.4 (C-2$_A$), 72.6 (C-2$_B$), 71.1 (C-5$_A$), 68.9 (C-5$_B$), 55.3 ($OCH_3$), 18.1 (2C, C-6$_A$, 6$_B$). Anal. Calcd for $C_{50}H_{54}Cl_3NO_{10}$: C, 64.21; H, 5.82; N, 1.50. Found: C, 64.67; H, 6.01; N, 1.28.

**Allyl (3,4-Di-*O*-benzyl-2-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-benzoyl-α-L-rhamnopyranoside (38).** A mixture of alcohol **11** (212 mg, 0.255 mmol) and imidate **34** (270 mg, 0.33 mmol) in anhydrous $Et_2O$ (4 mL) was stirred for 15 min under dry argon. After the solution was cooled at −60 °C, TMSOTf (30 μL, 0.166 mmol) was added dropwise and the mixture was stirred overnight and allowed to reach rt. Triethylamine (120 μL) was added and the mixture was concentrated. The residue was eluted from a column of silica gel with 7:1 cyclohexane−EtOAc to give **38** (86 mg, 22%) as a foam: $[\alpha]_D$ +5 (*c* 1.0, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.00−6.95 (m, 45H, Ph), 6.00−5.80 (m, 1H, All), 5.56 (dd, 1H, H-2$_A$), 5.40 (dd, 1H, $J_{1,2}$ < 1.0 Hz, $J_{2,3}$ = 3.0 Hz, H-2$_C$), 5.37−5.20 (m, 2H, All), 5.08 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1$_E$), 5.04 (d, 1H, $J_{1,2}$ < 1.0 Hz, H-1$_A$), 5.00 (d, 1H, $J_{1,2}$ < 1.0 Hz, H-1$_B$), 4.99 (d, 1H, H-1$_C$), 4.90−4.30 (m, 16H, $CH_2$Ph), 4.35 (dd, 1H, $J_{2,3}$ = 3.0 Hz, H-2$_B$), 4.14 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3$_C$), 4.03 (pt, 1H, $J_{2,3}$ = $J_{3,4}$ = 10.0 Hz, H-3$_E$), 4.20−3.90 (m, 2H, All), 4.00−3.75 (m, 4H, $CH_2$Cl, H-6a$_E$, 6b$_E$), 3.96 (dd, 1H, H-3$_A$), 3.95 (m, 1H, H-5$_A$), 3.95 (m, 1H, H-5$_E$), 3.83 (dd, 1H, H-4$_C$), 3.80 (m, 1H, H-5$_C$), 3.72 (dd, 1H, H-4$_E$), 3.64 (dd, 1H, H-3$_B$), 3.60 (m, 1H, H-5$_B$), 3.52 (dd, 1H, H-2$_E$), 3.39 (dd, 1H, H-4$_A$), 3.30 (dd, 1H, H-4$_B$), 1.35 (d, 1H, H-6$_A$), 1.30 (d, 1H, H-6$_C$), 1.00 (d, 1H, H-6$_B$); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 166.1, 165.7 (C=O), 133.4−117.0 (Ph), 100.9 (C-1$_B$), 98.9 (C-1$_A$), 97.8 (C-1$_E$), 96.0 (C-1$_C$), 81.8 (C-3$_E$), 80.9 (C-2$_E$), 79.9 (C-4$_A$), 79.6 (C-4$_B$), 79.6 (C-3$_C$), 78.9 (C-3$_B$), 78.0 (C-4$_C$), 77.5 (C-4$_E$), 77.3 (C-3$_A$), 75.6, 75.3, 75.0, 74.7, 73.9, 73.5, 72.8, 70.9 (9C, $CH_2$Ph, All), 74.9 (C-2$_B$), 72.5 (C-2$_C$), 71.2 (C-5$_E$), 70.9 (C-2$_A$), 68.8 (C-5$_B$), 68.5 (C-6$_E$), 68.3 (C-5$_A$), 67.5 (C-5$_C$), 40.9 ($CH_2$Cl), 18.8 (C-6$_A$), 18.2 (C-6$_C$), 17.8 (C-6$_B$). FAB-MS for $C_{92}H_{99}ClO_{20}$ (M, 1558.6) *m/z* 1581.7 [M + Na]$^+$. Anal. Calcd for $C_{92}H_{99}ClO_{20}$: C, 70.82; H, 6.40. Found: C, 70.67; H, 6.58.

**Allyl (3,4-Di-*O*-benzyl-2-*O*-*p*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-benzoyl-α-L-rhamnopyranoside (39).** A mixture of alcohol **11** (125 mg, 0.15 mmol) and 4 Å molecular sieves in anhydrous $Et_2O$ (3 mL) was stirred for 45 min under dry argon. After the mixture was cooled at −40 °C, $Me_3SiOTf$ (20 μL, 0.112 mmol) was added dropwise. A solution of the donor **37** (210 mg, 0.225 mmol) in anhydrous $Et_2O$ (2 mL) was added dropwise to the solution of the acceptor over 1 h. The mixture was stirred for 3 h at −40 °C. Triethylamine (100 μL) was added and the mixture was filtered and concentrated. The residue was eluted from a column of silica gel with 85:15 cyclohexane−EtOAc to give **39** (107 mg, 44%) as a foam: $[\alpha]_D$ +12 (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 8.10−7.10 (m, 45H, Ph), 7.00−6.50 (m, 4H, $CH_2$PhOMe), 5.90−5.70 (m, 1H, All), 5.32 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.1 Hz, H-2$_C$), 5.25−5.10 (m, 2H, All), 5.05 (d, 1H, H-1$_B$), 4.98 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1$_E$), 4.85 (m, 2H, H-1$_A$, 1$_C$), 4.80−4.20 (m, 18H, C$H_2$Ph), 4.20−3.90 (m, 2H, All), 4.20−3.00 (m, 20H, H-2$_A$, 2$_B$, 2$_E$, 3$_A$, 3$_B$, 3$_C$, 3$_E$, 4$_A$, 4$_B$, 4$_C$, 4$_E$, 5$_A$, 5$_B$, 5$_C$, 5$_E$, 6a$_E$, 6b$_E$, $OCH_3$), 1.30−0.82 (3 d, 9H, H-6$_A$, 6$_B$, 6$_C$); $^{13}C$ NMR ($CDCl_3$) δ 166.3 (C=O), 138.5−118.2 (Ph, All), 99.5, 99.3 (2C, C-1$_A$, 1$_B$), 98.4 (C-1$_E$), 96.4 (C-1$_C$), 82.3, 81.4, 81.1, 80.5, 80.3, 79.5, 78.2, 77.6 (8C, C-2$_E$, 3$_A$, 3$_B$, 3$_C$, 3$_E$, 4$_A$, 4$_B$, 4$_C$), 76.0, 75.5, 75.3, 74.9, 74.3, 73.3, 72.3, 71.8, 71.6 (9C, $CH_2$Ph), 74.1, 73.8 (2C, C-2$_A$, 2$_B$), 72.5 (C-2$_C$), 72.0 (C-4$_E$), 69.2, 69.0, 68.9 (3C, C-5$_A$, 5$_B$, 5$_C$), 68.8, 68.6 (All, C-6$_E$), 67.8 (C-5$_E$), 55.5 ($OCH_3$), 19.0, 18.8, 18.4 (3C, C-6$_A$, 6$_B$, 6$_C$). FAB-MS for $C_{98}H_{106}O_{20}$ (M, 1603.8) *m/z* 1626.6 [M + Na]$^+$.

**Allyl (3,4-Di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-benzoyl-α-L-rhamnopyranoside (10).** A mixture of the trisaccharide **42**[18] (8.0 g, 6.5 mmol) in MeOH (128 mL) was treated with 5.7 mL of $HBF_4/Et_2O$ at rt. The solution was stirred for 4 days. $Et_3N$ was added until neutralization and concentrated. The residue was diluted with DCM, then washed with satd aq $NaHCO_3$ and water. The organic layer was dried on $MgSO_4$, filtered, and concentrated. The residue was eluted from a column of silica gel with 15:1 toluene−EtOAc to give **10** (6.31 g, 84%) as a foam: $[\alpha]_D$ +14 (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 8.10−7.05 (m, 35H, Ph), 5.82 (m, 1H, All), 5.25 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.1 Hz, H-2$_C$), 5.19 (m, 2H, All), 5.00 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1$_E$), 4.87 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1$_B$), 4.81 (d, 1H, H-1$_C$), 4.90−4.35 (m, 12H, C$H_2$Ph), 4.20−4.00 (m, 2H, All), 4.10 (dd, 1H, $J_{3,4}$ = 8.5 Hz, H-3$_C$), 4.09 (dd, 1H, $J_{2,3}$ = 3.2 Hz, H-2$_B$), 3.95 (m, 1H, $J_{4,5}$ = 9.5 Hz, H-5$_E$), 3.92 (pt, 1H, $J_{2,3}$ = 9.5 = $J_{3,4}$ = 9.5 Hz, H-3$_E$), 3.78 (dq, 1H, $J_{5,6}$ = 6.0 Hz, H-5$_C$), 3.70 (m, 1H, H-4$_C$), 3.62−3.58 (m, 2H, H-6a$_E$, 6b$_E$), 3.59 (m, 1H, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.2 Hz, H-5$_B$), 3.54 (dd, 1H, H-4$_E$), 3.48 (dd, 1H, $J_{3,4}$ = 8.5 Hz, H-3$_B$), 3.45 (dd, 1H, H-2$_E$), 3.31 (dd, 1H, H-4$_B$), 2.68 (d, 1H, $J_{2,OH}$ = 2.3 Hz, OH), 1.29 (d, 3H, H-6$_C$), 1.09 (d, 3H, H-6$_B$); $^{13}C$ NMR ($CDCl_3$) δ 166.2 (C=O), 137.5−118.2 (Ph, All), 103.1 (C-1$_B$), 98.5 (C-1$_E$), 96.6 (C-1$_C$), 82.1 (C-3$_E$), 81.4 (C-2$_E$), 80.4 (C-4$_B$), 79.7 (C-3$_B$), 79.4 (C-4$_C$), 78.9 (C-3$_C$), 78.1 (C-4$_E$), 76.0, 75.5, 74.5, 74.2, 73.6, 72.1 (6C, $CH_2$Ph), 73.7 (C-2$_C$), 71.6 (C-2$_B$), 68.9 (C-6$_E$), 68.8 (C-5$_B$), 68.7 (All, C-5$_E$), 68.1 (C-5$_C$), 19.1 (C-6$_C$), 18.2 (C-6$_B$). FAB-MS of $C_{70}H_{76}O_{15}$ (M, 1156.5), *m/z* 1179.5 [M + Na]$^+$. Anal. Calcd for $C_{70}H_{76}O_{15}$: C, 72.64; H, 6.62. Found: C, 72.49; H, 6.80.

**Allyl (2-*O*-Acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-benzoyl-α-L-rhamnopyranoside (44).** A mixture of alcohol **10** (5.2 g, 4.49 mmol), imidate **21** (3.58 g, 6.74 mmol), and 4 Å molecular sieves in anhydrous $Et_2O$ (117 mL) was stirred for 1 h under dry argon. After the solution was cooled at −30 °C, $Me_3SiOTf$ (580 μL, 3.2 mmol) was added dropwise and the mixture was stirred and allowed to reach rt overnight. Triethylamine (1.2 mL) was added and the mixture was filtered and concentrated. The residue was eluted from a column of silica gel with 9:1 cyclohexane−EtOAc to give **44** (6.16 g, 90%) as a white foam: $[\alpha]_D$ +13 (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$) δ 8.10−7.00 (m, 45H, Ph), 5.82 (m, 1H, All), 5.45 (dd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 2.5 Hz, H-2$_A$), 5.29 (dd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 2.5 Hz, H-2$_C$), 5.19 (m, 2H, All), 4.97 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1$_E$), 4.95 (d, 1H, H-1$_A$), 4.91 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1$_B$), 4.84 (d, 1H, H-1$_C$), 4.90−4.35 (m, 16H, C$H_2$Ph), 4.29 (dd, 1H, $J_{2,3}$ = 2.6 Hz, H-2$_B$), 4.10−4.00 (m, 2H, All), 4.02 (dd, 1H, $J_{3,4}$ = 8.5 Hz, H-3$_C$), 3.90 (m, 2H, $J_{2,3}$ = $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-3$_E$, 5$_E$), 3.85 (m, 2H, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 9.5 Hz, H-3$_A$, 5$_A$), 3.72 (m, 2H, $J_{5,6}$ = 6.0 Hz, H-4$_C$, 5$_C$), 3.66−3.62 (m, 2H, H-6a$_E$, 6b$_E$), 3.61 (dd, 1H, H-4$_E$), 3.54 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3$_B$), 3.45 (dd, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.1 Hz, H-5$_B$), 3.39 (dd, 1H, H-2$_E$), 3.34 (dd, 1H, H-4$_A$), 3.21 (dd, 1H, H-4$_B$), 1.89 (s, 3H, OAc), 1.26 (2d, 6H, H-6$_A$, 6$_C$), 0.89 (d, 3H, H-6$_B$); $^{13}C$ NMR ($CDCl_3$) δ 170.2, 166.1 (C=O), 138.4−118.1 (Ph, All), 101.3 (C-1$_B$), 99.8 (C-1$_A$), 98.2 (C-1$_E$), 96.4 (C-1$_C$), 82.2 (C-3$_E$), 81.4 (C-2$_E$), 80.6 (C-4$_A$), 80.5 (C-3$_C$), 80.1 (C-4$_B$), 79.3 (C-3$_B$), 78.5 (C-4$_C$), 78.1 (C-3$_A$), 78.0 (C-4$_E$), 76.0, 75.9, 75.7, 75.2, 74.3, 73.3, 72.1, 71.1 (8C, $CH_2$Ph), 75.2 (C-2$_B$), 72.9 (C-2$_C$), 71.7 (C-5$_E$), 69.5 (C-2$_A$), 69.2 (2C, C-5$_A$, 5$_B$), 68.9 (All), 68.9 (C-6$_E$), 67.9 (C-5$_C$), 21.4 (OAc), 19.1 (C-6$_A$), 18.7 (C-6$_C$), 18.1 (C-6$_B$). FAB-MS of $C_{90}H_{100}O_{20}$ (M, 1524.7), *m/z* 1547.8 [M + Na]$^+$. Anal. Calcd for $C_{92}H_{100}O_{20}$: C, 72.42; H, 6.61. Found: C, 72.31; H, 6.75.

**Allyl (3,4-Di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-benzoyl-α-L-rhamnopyranoside (40).** A mixture of **44** (6.0 g, 3.93 mmol) in MeOH (200 mL) was treated with 10 mL of $HBF_4/Et_2O$ at rt. The solution was stirred for 5 days. $Et_3N$ was added until neutralization and the solution was concentrated. The residue was diluted with DCM and washed with satd aq $NaHCO_3$ and water. The organic layer was dried on $MgSO_4$, filtered, and concentrated. The residue was eluted from a column of silica gel with 6:1 cyclohexane−EtOAc to give **40** (5.0 g, 84%) as a colorless foam: $[\alpha]_D$ +12 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 8.00−7.00 (m, 45H, Ph), 5.83 (m, 1H, All), 5.29 (dd, 1H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 2.9 Hz, H-2$_C$), 5.19 (m, 2H, All), 4.99 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1$_A$), 4.97 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1$_E$), 4.94 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1$_B$), 4.83 (d, 1H, H-1$_C$), 4.90−4.35 (m, 16H, C*H*$_2$Ph), 4.30 (dd, 1H, $J_{2,3}$ = 2.7 Hz, H-2$_B$), 4.10−4.00 (m, 2H, All), 4.02 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 8.5 Hz, H-3$_C$), 3.98 (m, 1H, H-2$_A$), 3.95−3.91 (m, 3H, H-5$_E$, 6a$_E$, 6a$_E$), 3.90 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 9.4 Hz, H-3$_E$), 3.82−3.73 (m, 4H, H-3$_A$, 5$_A$, 4$_C$, 5$_C$), 3.66 (dd, 1H, $J_{4,5}$ = 9.6 Hz, H-4$_E$), 3.53 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3$_B$), 3.48 (m, 1H, $J_{4,5}$ = 9.5 Hz, H-5$_B$), 3.44−3.40 (m, 2H, H-4$_A$, 2$_E$), 3.17 (pt, 1H, H-4$_B$), 2.18 (d, 1H, $J_{2,OH}$ = 2.0 Hz, OH), 1.26 (d, 3H, $J_{5,6}$ = 5.5 Hz, H-6$_C$), 1.25 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_A$), 0.90 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6$_B$); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.2 (C═O), 138.3−118.0 (Ph, All), 101.5 (C-1$_B$), 101.4 (C-1$_A$), 98.2 (C-1$_E$), 96.4 (C-1$_C$), 82.2 (C-3$_E$), 81.4 (C-2$_E$), 80.6 (C-4$_A$), 80.3 (C-4$_B$), 79.9 (2C, C-3$_C$, 3$_A$), 79.2 (C-3$_B$), 78.3 (C-4$_C$), 78.0 (C-4$_E$), 75.9, 75.6, 75.5, 74.8, 74.2, 73.5, 72.4, 71.0 (8C, *C*H$_2$Ph), 75.3 (C-2$_B$), 72.9 (C-2$_C$), 71.6 (C-2$_A$), 69.2, 69.1, 68.3, 67.9 (4C, C-5$_A$, 5$_B$, 5$_C$, 5$_E$), 68.9, 68.7 (3C, C-6$_D$, 6$_E$, All), 19.1 (C-6$_C$), 18.6 (C-6$_A$), 18.1 (C-6$_B$). FAB-MS of $C_{90}H_{98}O_{19}$ (M, 1482.7), *m/z* 1505.8 [M + Na]$^+$. Anal. Calcd for $C_{90}H_{98}O_{19}\cdot 2H_2O$: C, 71.12; H, 6.77. Found: C, 71.21; H, 6.78.

**Allyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-benzoyl-α-L-rhamnopyranoside (4).** (a) A mixture of the donor **8** (200 mg, 230 $\mu$mol) and the acceptor **10** (188 mg, 144 $\mu$mol), 4 Å molecular sieves, and dry $Et_2O$:1,2-DCE (1:1, 5 mL) was stirred for 1.5 h then cooled to 0 °C. NIS (104 mg, 0.46 mmol) and triflic acid (4 mL, 0.05 mmol) were successively added. The stirred mixture was allowed to reach rt in 1 h. $Et_3N$ (25 mL) was added and the mixture filtered. After evaporation, the residue was eluted from a column of silica gel with 4:1 to 2:1 cyclohexane−EtOAc to give **4** (28 mg, 10%).

(b) A mixture of alcohol **40** (5.0 g, 3.37 mmol), imidate **16** (3.0 g, 5.04 mmol), and 4 Å molecular sieves in anhydrous DCM (120 mL) was stirred for 1 h under dry argon. After the solution was cooled at 0 °C, TMSOTf (240 $\mu$L, 1.32 mmol) was added dropwise and the mixture was stirred for 2.5 h while coming back to rt. $Et_3N$ (800 $\mu$L) was added, and the mixture was filtered and concentrated. The residue was eluted from a column of silica gel with 4:1 to 2:1 cyclohexane−EtOAc to give **4** (6.27 g, 98%) as a colorless foam: $[\alpha]_D$ +1.5 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 8.00−7.00 (m, 45H, Ph), 6.68 (d, 1H, $J_{2,NH}$ = 8.5 Hz, NH$_D$), 5.82 (m, 1H, All), 5.29 (dd, 1H, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 2.3 Hz, H-2$_C$), 5.19 (m, 2H, All), 5.00 (d, 1H, $J_{1,2}$ = 1.0 Hz, H-1$_A$), 4.96 (dd, 1H, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 10.5 Hz, H-3$_D$), 4.88 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1$_E$), 4.85 (d, 1H, H-1$_C$), 4.82 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1$_B$), 4.81 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4$_D$), 4.72 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1$_D$), 4.90−4.35 (m, 16H, C*H*$_2$Ph), 4.38 (m, 1H, H-2$_B$), 4.10−4.00 (m, 2H, All), 4.05 (dd, 1H, $J_{2,3}$ = 2.7 Hz, H-2$_A$), 3.95 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 8.5 Hz, H-3$_C$), 3.90 (m, 2H, H-5$_E$, 4$_E$), 3.86−3.82 (m, 2H, H-6a$_D$, 6b$_D$), 3.84−3.70 (m, 6H, H-3$_E$, 6a$_E$, 6b$_E$, 3$_A$, 5$_A$, 2$_D$), 3.68 (m, 1H, H-5$_C$), 3.61 (dd, 1H, $J_{4,5}$ = 9.0 Hz, H-4$_C$), 3.56 (dd, 1H, $J_{3,4}$ = 9.5 Hz, H-3$_B$), 3.47 (m, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.1 Hz, H-5$_B$), 3.35−3.33 (m, 3H, H-4$_A$, 5$_D$, 2$_E$), 3.17 (dd, 1H, H-4$_B$), 2.02, 2.00, 1.98 (3s, 9H, OAc), 1.24 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6$_A$), 1.23 (d, 3H, $J_{5,6}$ = 5.9 Hz, H-6$_C$), 0.90 (d, 3H, H-6$_B$); $^{13}$C NMR ($CDCl_3$) $\delta$ 170.9, 170.7, 169.6, 166.1, 162.1 (C═O), 138.3−118.1 (Ph, All), 101.5 (C-1$_D$), 101.4 (C-1$_B$), 101.1 (C-1$_A$), 98.5 (C-1$_E$), 96.4 (C-1$_C$), 92.6 (*C*Cl$_3$), 82.1 (C-3$_E$), 81.7 (C-3$_C$), 81.6 (C-2$_E$), 80.4 (C-4$_B$), 80.1 (C-3$_A$), 79.1 (br s, C-4$_C$), 78.5 (C-3$_B$), 77.9 (C-4$_A$), 77.6 (C-4$_E$), 76.4 (C-2$_A$), 76.1, 75.8, 75.4, 74.7, 74.3, 74.2, 73.2, 70.4 (8C, *C*H$_2$Ph), 74.9 (C-2$_B$), 72.9 (C-3$_D$), 72.7 (C-2$_C$), 72.5 (C-5$_D$), 71.9 (C-5$_E$), 68.4 (C-6$_E$), 68.8 (All), 68.9, 68.7, 68.5, 67.7 (4C, C-4$_D$, 5$_A$, 5$_B$, 5$_C$), 62.1 (C-6$_D$), 56.2 (C-2$_D$), 20.9, 20.7 (3C, OAc), 19.0 (C-6$_A$), 18.5 (C-6$_C$), 18.2 (C-6$_B$). FAB-MS of $C_{104}H_{114}Cl_3NO_{27}$ (M, 1916.4), *m/z* 1938.9 [M + Na]$^+$. Anal. Calcd for $C_{104}H_{114}Cl_3NO_{27}$: C, 65.18; H, 6.00; N, 0.73. Found: C, 64.95; H, 6.17; N, 0.76.

**(2,3,4-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-benzoyl-α-L-rhamnopyranosyl Trichloroacetimidate (46).** Compound **4** (3.5 g, 1.8 mmol) was dissolved in anhydrous THF (35 mL). The solution was degassed and placed under argon. 1,5-Cyclooctadiene-bis(methyldiphenylphosphine)iridium hexafluorophosphate (81 mg) was added, and the solution was degassed again. The catalyst was activated by passing over a stream of hydrogen until the solution turned yellow. The reaction mixture was degassed again and stirred under an argon atmosphere, then concentrated to dryness. The residue was dissolved in acetone (15 mL), then water (3 mL), mercuric chloride (490 mg), and mercuric oxide (420 mg) were added successively. The mixture, protected from light, was stirred at rt for 2 h and acetone was evaporated. The resulting suspension was taken up in DCM, washed twice with 50% aq KI, water and brine, dried, and concentrated. The residue was eluted from a column of silica gel with 2:1 petroleum ether−EtOAc to give the corresponding hemiacetal **45**. Trichloroacetonitrile (6.5 mL) and DBU (97 $\mu$L) were added to a solution of the residue in anhydrous DCM (33 mL) at 0 °C. After 1 h, the mixture was concentrated. The residue was eluted from a column of silica gel with 5:2 cyclohexane−EtOAc and 0.2% of $Et_3N$ to give **46** (2.48 g, 66%) as a colorless foam: $[\alpha]_D$ +4 (*c* 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 8.71 (s, 1H, NH), 8.00−7.00 (m, 45H, Ph), 6.80 (d, 1H, $J_{2,NH}$ = 8.6 Hz, NH$_D$), 6.37 (d, 1H, $J_{1,2}$ = 2.7 Hz, H-1$_C$), 5.59 (dd, 1H, $J_{2,3}$ = 2.9 Hz, H-2$_C$), 5.10 (br s, 1H, H-1$_A$), 5.05 (pt, 1H, $J_{2,3}$ = 9.8 Hz, H-3$_D$), 5.02−4.96 (m, 4H, H-1$_E$, 1$_B$, 4$_D$, CH$_2$Ph), 5.00−4.42 (m, 17H, 15 C*H*$_2$Ph, H-1$_D$, 3$_C$), 4.14 (br s, 1H, H-2$_A$), 4.05−3.68 (m, 14H, H-3$_E$, 4$_E$, 5$_E$, 6a$_E$, 6b$_E$, 4$_C$, 5$_C$, 2$_B$, 3$_B$, 3$_A$, 5$_A$, 2$_D$, 6a$_D$, 6b$_D$), 3.61 (dq, 1H, $J_{5,6}$ = 6.2 Hz, $J_{4,5}$ = 9.3 Hz, H-5$_B$), 3.51−3.41 (m, 3H, H-2$_E$, 4$_A$, 5$_D$), 3.30 (pt, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4$_B$), 2.03, 2.02, 1.80 (3s, 9H, OAc), 1.39, 1.32 (2d, 6H, H-6$_A$, 6$_C$), 1.00 (br d, 3H, H-6$_B$); $^{13}$C NMR ($CDCl_3$) $\delta$ 169.7, 169.5, 168.3, 164.5, 160.9 (C═O, C═N), 137.5−126.2 (Ph), 101.6 (C-1$_D$), 101.3 (2C, C-1$_A$, 1$_B$), 98.7 (C-1$_E$), 94.8 (C-1$_C$), 91.3 ($CCl_3$), 82.1, 81.5, 80.4, 80.1, 78.4, 77.9, 77.6, 76.5 (10C, C-2$_A$, 2$_E$, 3$_A$, 3$_B$, 3$_C$, 3$_E$, 4$_A$, 4$_B$, 4$_C$, 4$_E$), 76.0, 75.9, 75.5, 74.9, 74.3, 73.3 (8C, CH$_2$Ph), 72.9, 72.6, 71.9, 70.9, 70.6, 69.1, 68.8, 68.5 (9C, C-2$_B$, 2$_C$, 3$_D$, 4$_D$, 5$_A$, 5$_B$, 5$_C$, 5$_D$, 5$_E$), 68.3 (C-6$_E$), 62.1 (C-6$_D$), 56.2 (C-2$_D$), 21.0, 20.9, 20.8 (3C, OAc), 19.1, 18.3, 18.1 (3C, C-6$_A$, 6$_B$, 6$_C$). Anal. Calcd for $C_{103}H_{110}Cl_6N_2O_{27}$: C, 61.22; H, 5.49; N, 1.39. Found: C, 61.24; H, 5.50; N, 1.21.

**Methyl (2-Deoxy-4,6-*O*-isopropylidene-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-benzoyl-α-L-rhamnopyranosiden (48).** The pentasaccharide **2** (578 mg, 0.321 mmol) was dissolved in MeOH (10 mL). MeONa was added until pH 10. The mixture was stirred for 25 min then treated by IR 120 (H$^+$) until neutral pH. The solution was filtered and concentrated. The residue was eluted from a column of silica gel with 9:1 DCM−MeOH to give the expected triol **47** (505 mg, 89%). To a mixture of **47** (505 mg, 0.286 mmol) in dry DMF (2 mL) was added 2-methoxypropene (60 $\mu$L, 2.5 equiv) and CSA (14 mg, cat.). The mixture was stirred 1 h and $Et_3N$ (200 $\mu$L) was added. After evaporation, the residue was eluted from a column of silica gel with 5:2 cyclohexane−EtOAc containing 0.3% of $Et_3N$ to give **48** (420 mg, 81%) as a colorless foam: $^1$H NMR ($CDCl_3$) $\delta$ 8.00−7.00 (m, 45H, Ph), 7.17 (d, 1H, NH$_D$), 5.39 (dd, 1H, $J_{1,2}$ = 1.2 Hz, $J_{2,3}$ = 3.0 Hz, H-2$_C$), 5.13 (d, 1H, $J_{1,2}$ = 1.1 Hz, H-1$_A$), 5.01 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1$_E$), 4.99 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1$_B$), 4.80 (d, 1H, H-1$_C$), 4.70 (d, 1H, H-1$_D$), 4.90−4.35 (m, 16H, C*H*$_2$Ph), 4.40 (m, 1H, H-2$_B$), 4.10 (dd, 1H, H-2$_A$), 4.05 (dd, 1H, H-3$_C$), 4.00−3.00 (m, 20H, H-4$_C$, 5$_C$, 3$_B$, 4$_B$, 5$_B$, 3$_A$, 4$_A$, 5$_A$, 2$_D$, 3$_D$, 4$_D$, 5$_D$, 6a$_D$, 6b$_D$, 2$_E$, 3$_E$, 4$_E$, 5$_E$, 6a$_E$,

$6b_E$), 3.40 (s, 3H, $OCH_3$), 1.40−1.00 (m, 15H, $C(CH_3)_2$, H-$6_A$, $6_B$, $6_C$); $^{13}$C NMR ($CDCl_3$) partial, $\delta$ 166.2, 164.4 (C=O), 137.5−126.5 (Ph), 101.8 (C-$1_D$), 101.4 (C-$1_B$), 101.2 (C-$1_A$), 100.2 ($C(CH_3)_2$), 98.4 (C-$1_E$), 98.2 (C-$1_C$), 92.4 ($CCl_3$), 68.5 (C-$6_E$), 61.8 (C-$6_D$), 60.1 (C-$2_D$), 55.5 ($OCH_3$), 29.3, 19.4 ($C(CH_3)_2$), 19.1, 18.6, 18.2 (C-$6_A$, $6_B$, $6_C$). FAB-MS of $C_{99}H_{110}Cl_3N_1O_{24}$ (M, 1804.1), $m/z$ 1827.0 $[M + Na]^+$. Anal. Calcd for $C_{99}H_{110}Cl_3N_1O_{24}$: C, 65.90; H, 6.15; N, 0.78. Found: C, 65.89; H, 6.29; N, 0.68.

**Methyl (3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(2-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→3)-(2-deoxy-2-trichloroacetamido-*β*-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-benzoyl-α-L-rhamnopyranoside (50).** A mixture of **46** (154 mg, 76 $\mu$mol) and **48** (92 mg, 51 $\mu$mol), 4 Å molecular sieves, and dry 1,2-DCE (3 mL) was stirred for 1 h, then cooled to −35 °C. Triflic acid (6 $\mu$L) was added. The stirred mixture was allowed to reach 10 °C in 2.5 h. $Et_3N$ (25 $\mu$L) was added and the mixture was filtered. After evaporation, the residue was eluted from a column of silica gel with 2:1 cyclohexane−EtOAc containing 0.5% of $Et_3N$ to give **49** (186 mg) as a contaminated material. To a solution of the isolated contaminated **49** (186 mg) in DCM (3 mL) was added dropwise, at 0 °C, a solution of TFA (0.5 mL) and water (0.5 mL). The mixture was stirred for 3 h, then concentrated by coevaporation with water then toluene. The residue was eluted from a column of silica gel with 2:1 to 1:1 petroleum ether−EtOAc to give **50** (134 mg, 72%, 2 steps) as a white solid: $[\alpha]_D$ +6 ($c$ 1.0, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ 8.05−7.10 (m, 90H, Ph), 6.86−6.82 (2d, 2H, $J_{2,NH}$ = 8.0 Hz, $J_{2,NH}$ = 8.5 Hz, $NH_D$, $NH_{D'}$), 5.35−5.19 (m, 2H, H-$2_C$, $2_{C'}$), 5.20, 5.08 (2s, 2H, H-$1_A$, $1_{A'}$), 5.05 (dd, 1H, H-$3_{D'}$), 4.99−4.80 (m, 9H, H-$1_B$, $1_{B'}$, $1_C$, $1_{C'}$, $1_D$, $1_{D'}$, $1_E$, $1_{E'}$, $4_{D'}$), 4.80−4.30 (m, 32H, $OCH_2Ph$), 4.10−3.15 (m, 44H, H-$2_A$, $2_{A'}$, $2_B$, $2_{B'}$, $2_D$, $2_{D'}$, $2_E$, $2_{E'}$, $3_A$, $3_{A'}$, $3_B$, $3_{B'}$, $3_C$, $3_{C'}$, $3_D$, $3_E$, $3_{E'}$, $4_A$, $4_{A'}$, $4_B$, $4_{B'}$, $4_C$, $4_{C'}$, $4_D$, $4_E$, $4_{E'}$, $5_A$, $5_{A'}$, $5_B$, $5_{B'}$, $5_C$, $5_{C'}$, $5_D$, $5_{D'}$, $5_E$, $5_{E'}$, $6a_D$, $6b_D$, $6a_{D'}$, $6b_{D'}$, $6a_E$, $6b_E$, $6a_{E'}$, $6b_{E'}$), 3.42 (3H, s, OMe), 2.08, 2.04, 2.02 (9H, 3s, OAc), 1.40−0.96 (18H, m, H-$6_A$, $6_{A'}$, $6_B$, $6_{B'}$, $6_C$, $6_{C'}$); $^{13}$C NMR ($CDCl_3$) $\delta\delta$ 171.5, 170.9, 170.8, 169.6, 166.2, 162.4, 162.1 (C=O), 139.5−127.2 (Ph), 101.9, 101.6, 101.5, 101.3, 99.2, 98.8, 98.2 (10C, C-$1_A$, $1_{A'}$, $1_B$, $1_{B'}$, $1_C$, $1_{C'}$, $1_D$, $1_{D'}$, $1_E$, $1_{E'}$), 92.7, 92.6 (2C, $CCl_3$), 82.1, 81.8, 81.7, 80.5, 80.3, 80.1, 79.3, 77.9, 77.8, 73.0, 72.6, 72.5, 72.0, 69.4, 69.0, 68.9, 67.4 (39C, C-$2_A$, $2_{A'}$, $2_B$, $2_{B'}$, $2_C$, $2_{C'}$, $2_E$, $2_{E'}$, $3_A$, $3_{A'}$, $3_B$, $3_{B'}$, $3_C$, $3_{C'}$, $3_D$, $3_{D'}$, $3_E$, $3_{E'}$, $4_A$, $4_{A'}$, $4_B$, $4_{B'}$, $4_C$, $4_{C'}$, $4_D$, $4_{D'}$, $4_E$, $4_{E'}$, $5_A$, $5_{A'}$, $5_B$, $5_{B'}$, $5_C$, $5_{C'}$, $5_D$, $5_{D'}$, $5_E$, $5_{E'}$, $6_{D'}$), 76.0, 75.9, 74.8, 74.3, 73.6, 73.2, 68.6 ($CH_2Ph$), 62.3, 62.2, 60.7 (3C, C-$6_D$, $6_E$, $6_{E'}$), 55.5, 56.2 (3C, C-$2_D$, $2_{D'}$, $OCH_3$), 21.0, 20.9, 20.8 (OAc), 19.0, 18.7, 18.6, 18.2, 17.9 (6C, C-$6_A$, $6_{A'}$, $6_B$, $6_{B'}$, $6_C$, $6_{C'}$). FAB-MS for $C_{197}H_{214}Cl_6N_2O_{50}$ (M, 3622.5), $m/z$ 3645.3 $[M + Na]^+$. Anal. Calcd for $C_{197}H_{214}Cl_6N_2O_{50}$: C, 65.32; H, 5.95; N, 0.77. Found: C, 65.20; H, 6.03; N, 0.78.

**Methyl (2-Acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-(α-L-rhamnopyranosyl)-(1→2)-(α-L-rhamnopyranosyl)-(1→3)-[α-D-glucopyranosyl-(1→4)]-(α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→2)-(α-L-rhamnopyranosyl)-(1→2)-(α-L-rhamnopyr-anosyl)-(1→3)-[α-D-glucopyranosyl-(1→4)]-α-L-rhamno-pyranoside (1).** A solution of **50** (183 mg, 50 $\mu$mol) in EtOH (3 mL), EtOAc (0.3 mL), and 1 M HCl (100 $\mu$L) was hydrogenated in the presence of Pd/C (250 mg) for 72 h at rt. The mixture was filtered and concentrated. A solution of the residue in MeOH (4 mL) and $Et_3N$ (200 $\mu$L) was hydrogenated in the presence of Pd/C (200 mg) for 24 h at rt. The mixture was filtered and concentrated. A solution of the residue (50 mg, 25 $\mu$mol) in MeOH (3 mL) and DCM (0.5 mL) was treated by MeONa until pH 10. The mixture was stirred overnight at 55 °C. After the solution was cooled at rt, IR 120 ($H^+$) was added until neutral pH, and the solution was filtered and concentrated, then was eluted from a column of C-18 with water/$CH_3CN$ and freeze-dried to afford amorphous **1** (30 mg, 37%): $[\alpha]_D$ −1 ($c$ 1.0, $H_2O$); $^1$H NMR ($D_2O$) $\delta$ 5.13 (2d, 2H, $J_{1,2}$ = 3.5 Hz, H-$1_E$, $1_{E'}$), 5.05, 4.95, 4.75 (m, 5H, H-$1_A$, $1_B$, $1_{A'}$, $1_{B'}$, $1_{C'}$), 4.64−4.62 (2d, 2H, $J_{1,2}$ = 7.0 Hz, $J_{1,2}$ = 8.0 Hz, H-$1_D$, $1_{D'}$), 4.58 (d, 1H, $J_{1,2}$ = 2.2 Hz, H-$1_C$), 4.10−3.20 (m, 51H, H-$2_A$, $2_{A'}$, $2_B$, $2_{B'}$, $2_C$, $2_{C'}$, $2_D$, $2_{D'}$, $2_E$, $2_{E'}$, $3_A$, $3_{A'}$, $3_B$, $3_{B'}$, $3_C$, $3_{C'}$, $3_D$, $3_{D'}$, $3_E$, $3_{E'}$, $4_A$, $4_{A'}$, $4_B$, $4_{B'}$, $4_C$, $4_{C'}$, $4_D$, $4_{D'}$, $4_E$, $4_{E'}$, $5_A$, $5_{A'}$, $5_B$, $5_{B'}$, $5_C$, $5_{C'}$, $5_D$, $5_{D'}$, $5_E$, $5_{E'}$, $6a_D$, $6b_D$, $6a_{D'}$, $6b_{D'}$, $6a_E$, $6b_E$, $6a_{E'}$, $6b_{E'}$, $OCH_3$), 1.99, 1.97 (2s, 6H, 2 NHAc), 1.33−1.15 (6d, 18H, $J_{5,6}$ = 6.3 Hz, H-$6_A$, $6_B$, $6_C$, $6_{A'}$, $6_{B'}$, $6_{C'}$); $^{13}$C NMR ($D_2O$) $\delta\delta$ 175.2, 174.7 (C=O), 103.1 (2C, C-$1_{D'}$, $1_D$), 102.6, 101.7, 101.3, 100.8 (6C, C-$1_A$, $1_B$, $1_C$, $1_{A'}$, $1_{B'}$, $1_{C'}$), 98.0 (2C, C-$1_E$, $1_{E'}$), 81.6, 79.7, 79.6, 79.1, 76.2, 76.1, 73.9, 73.0, 72.7, 72.6, 72.5, 72.2, 72.1, 71.6, 70.1, 70.0, 69.7, 69.0, 68.5 (38C, C-$2_A$, $2_{A'}$, $2_B$, $2_{B'}$, $2_C$, $2_{C'}$, $2_E$, $2_{E'}$, $3_A$, $3_{A'}$, $3_B$, $3_{B'}$, $3_C$, $3_{C'}$, $3_D$, $3_{D'}$, $3_E$, $3_{E'}$, $4_A$, $4_{A'}$, $4_B$, $4_{B'}$, $4_C$, $4_{C'}$, $4_D$, $4_{D'}$, $4_E$, $4_{E'}$, $5_A$, $5_{A'}$, $5_B$, $5_{B'}$, $5_C$, $5_{C'}$, $5_D$, $5_{D'}$, $5_E$, $5_{E'}$), 60.9 (4C, C-$6_E$, $6_{E'}$, $6_D$, $6_{D'}$), 56.2, 56.0, 55.3 (3C, C-$2_D$, $2_{D'}$, $OCH_3$), 22.7, 22.6 (2C, NHAc), 18.3, 18.1, 17.2, 17.1, 17.0, 16.9 (6C, C-$6_A$, $6_B$, $6_C$, $6_{A'}$, $6_{B'}$, $6_{C'}$). HR-MS calcd for $[C_{65}H_{110}N_2O_{45} + Na]^+$ 1661.6278, found 1661.6277.

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**Supporting Information Available:** $^1$H, $^{13}$C, and DEPT 1D NMR spectra and $^1$H−$^1$H and $^1$H−$^{13}$C 2D NMR correlation spectra of compounds **1**, **4**−**8**, **10**, **17**−**20**, **22**−**23**, **25**, **32**−**34**, **39**, **44**, **46**, **48**, and **50**. This material is available free of charge via the Internet at http://pubs.acs.org.

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