JOC Article

First Synthesis of Pentasaccharide Glycoform I of the Outer Core Region of the *Pseudomonas aeruginosa* Lipopolysaccharide

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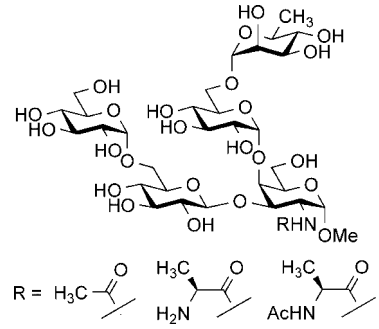

The synthesis of a pentasaccharide representing the glycoform **I**, which is one of two naturally occurring glycoforms of the outer core of *Pseudomonas aeruginosa* lipopolysaccharide, and its analogues, differing in the *N*-substituent in the galactosamine unit, is reported. The main features of the synthetic scheme included the assembly of the pentasaccharide backbone by successive introduction of monosaccharide units, the use of glucosyl donors with specific location of acyl protecting groups capable of the remote anchimeric participation for highly stereoselective α-glucosylation, and efficient reduction of the azido group allowing high-yielding transformation of the intermediary azido pentasaccharide into final products.

Introduction

Cystic fibrosis (CF) is a congenital disease wherein there is a high susceptibility to *Pseudomonas aeruginosa* infection in the lungs.[1] By late adolescence, over 80% of CF patients will be infected with this organism.[2] It was previously shown that the outer core region of the lipopolysaccharide of *P. aeruginosa* influences a critical step in the elimination of this bacterium from a normal host by binding to the CF transmembrane conductance regulator (CFTR), the protein that is missing or is dysfunctional in CF. This interaction is thought to induce effective innate immune responses in normal hosts, which, when missing in CF, allows the microbe to persist in the airway and initiate colonization that will eventually lead to chronic infection.[1]

In order to ascertain which of the two naturally occurring glycoforms[3] **I** and **II** (Figure 1) of the LPS outer core interact with the CFTR receptor on respiratory epithelial cells, we performed a systematic synthesis of the oligosaccharides representing these two glycoforms. Here we describe the synthesis of the *N*-(L-alanyl)pentasaccharide **36** corresponding to glycoform **I**, as well as its *N*-acetyl- **32** and *N*-(*N*-acetyl-L-alanyl)- **37** analogues. The latter compounds were prepared to elucidate the role of the L-alanine residue and its amino group in the host recognition of the presence of *P. aeruginosa* bacterial cells.

Results and Discussion

Three important points were taken into consideration while planning the synthesis of the target pentasaccharides. First, they

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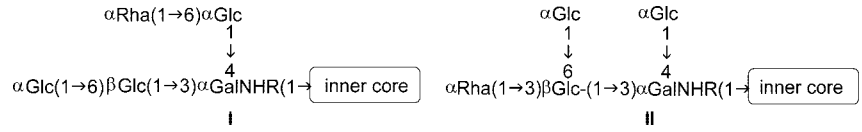
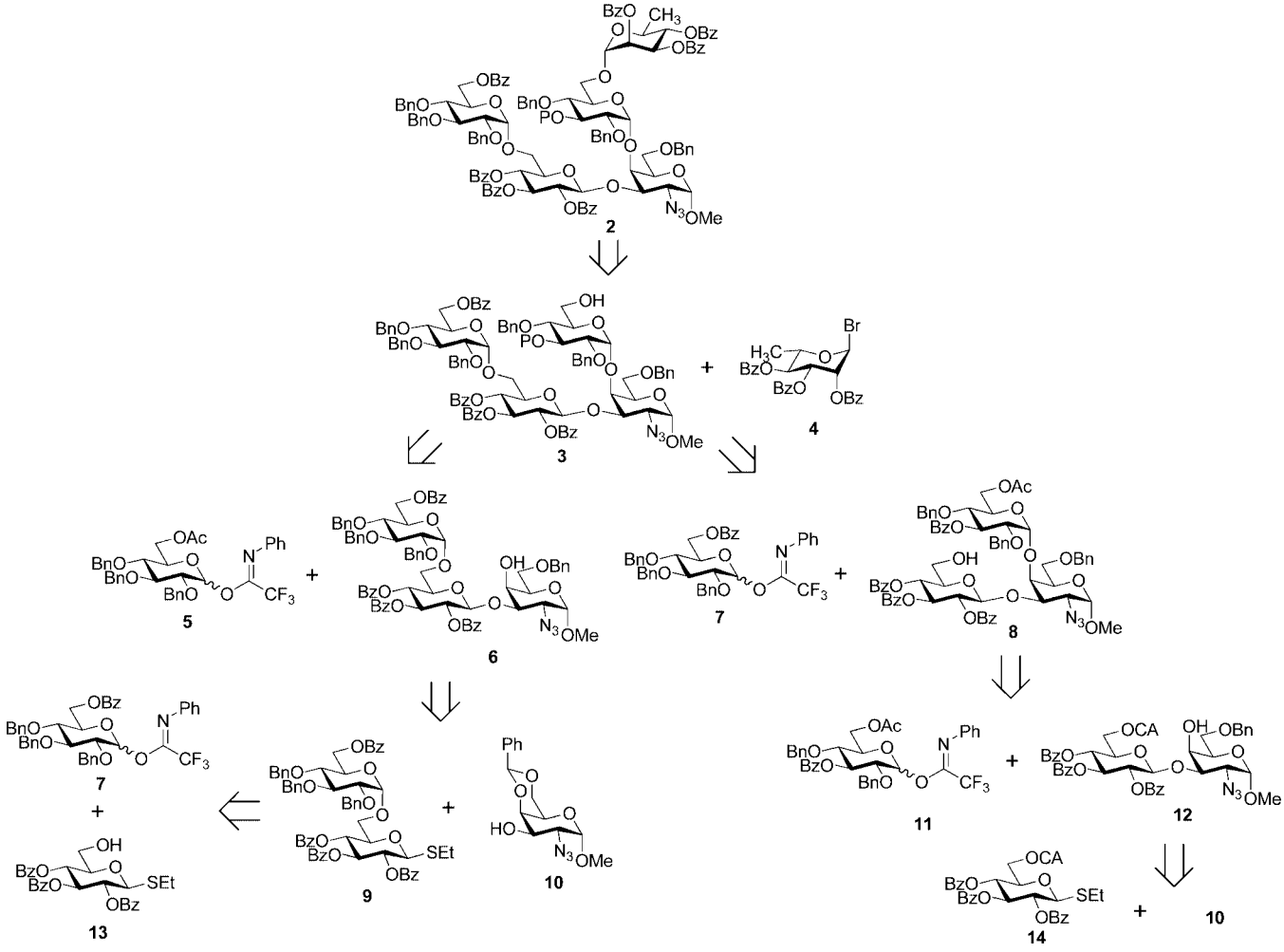


FIGURE 1. Glycoforms of the outer core region of *P. aeruginosa* lipopolysaccharide.

SCHEME 1. Retrosynthetic Scheme toward Protected Pentasaccharide Precursor



contain three 1,2-*cis*-glycoside bonds, which are still not easily synthesized.[4,5] These bonds are α-D-Gal*p*N-OMe, α-D-Glc*p*-(1→6)-*β*-D-Glc*p*, and α-D-Glc*p*-(1→4)-α-D-Gal*p*N. The first α-glycoside bond could be introduced at the stage of the synthesis of the corresponding monosaccharide blocks, and therefore, the effectiveness of this stage was not deemed to be critical. On the contrary, the effectiveness of α-stereoselective construction of the two other fragments (Scheme 1) may have a decisive influence on the feasibility of the whole synthetic scheme. As we showed recently,[6,7] glucosyl *N*-phenyltrifluoroacetimidates with acyl groups at O-3 and/or O-6, which are capable of remote anchimeric participation, provide the necessary material for efficient and highly stereoselective α-glucosylation.

The second difficulty is the presence of a 3,4-branch in the galactosamine fragment. Specific properties of the hydroxyl groups at C-3 and C-4 of galactosamine, as well as the interdependence of the reactivity of these two groups, are well documented.[8−10] It has been demonstrated that the 4-OH in the GalNAc residue can be glycosylated successfully only if the adjacent hydroxyl groups carry electron-donating protecting groups. The hydroxyl group at the position 3 of GalNAc can be glycosylated without special conditions,[8,9] although an example of unsuccessful glycosylation of a 4,6-benzylidene derivative of *N*-trichloroacetylgalactosamine has been reported.[11] However, when a glycosyl substituent is present at position 4 of GalNAc, glycosylation of 3-OH becomes impossible due to steric hindrance.[8,9] Thus, the most realistic way to 3,4-bis-glycosylated GalNAc would include initial 3-*O*-glycosylation followed by 4-*O*-glycosylation. As we have shown during the synthesis of trisaccharides **1a**−**c**,[6] the same is true for 2-azido-

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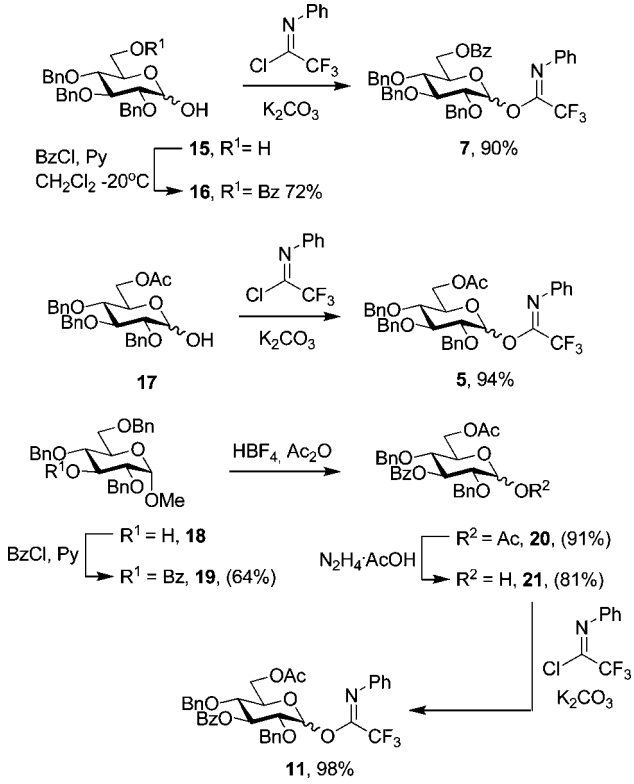
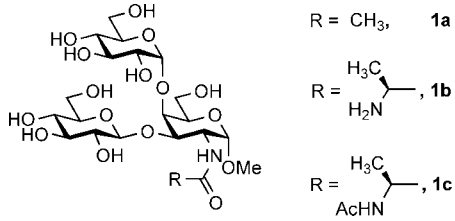
SCHEME 2. Preparation of α-Stereoselective Glucosyl Donors



2-deoxygalactose: the successful preparation of the target structure was possible if β-(1→3)-glucosylation of a galactosamine acceptor preceded α-(1→4)-glucosylation. In contrast, an alternative sequence of glycosylations, which involves β-glucosylation of an α-(1→4)-linked Glc-GalN_3 unit, did not lead at all to the target trisaccharide backbone.



The target pentasaccharides contain different acyl substituents on the nitrogen of the galactosamine unit, and it would be most convenient to synthesize them from a single amino precursor. Thus, the third point of the synthetic strategy was based on the proper choice of a masked form of the amino group. Azide seemed to be the best choice because it is stable under a variety of conditions of glycosylation and protecting group manipulations. It can be reduced into an amino group at one of the final steps of the synthesis. Simultaneous reduction of the azido group and debenzylation by catalytic hydrogenolysis[12] would provide the simplest way to such an amino precursor. However, hydrogenolysis sometimes may give low yields, especially in the case of complex oligosaccharides, because of catalyst poisoning by amines arising from azides and perhaps other obscure processes (see, for example, ref 13). That is why an alternative synthetic pathway is sometimes necessary for the azido group reduction. The choice of the proper reducing agent is usually complicated by the lack of a universal method.[14]

Taking the aforementioned considerations into account, two retrosynthetic schemes for the synthesis of the pentasaccharide could be proposed (Scheme 1). The first retrosynthetic step in both schemes is the cleavage of the pentasaccharide backbone on the α-L-Rha*p*-(1→6)-α-D-Glc*p* linkage to give tetrasaccharide acceptor **3** and rhamnosyl donor **4**. Then, according to the first scheme (left), the tetrasaccharide **3** is divided onto glycosyl donor **5** and linear trisaccharide acceptor **6**, which could be obtained in turn by glycosylation of monosaccharide acceptor **10** with disaccharide thioglycoside **9**. In the second scheme (right), tetrasaccharide **3** is divided onto glucosyl donor **7** and branched trisaccharide acceptor **8**. The latter could be assembled from monosaccharide precursors **10**, **11**, and **14** via intermediate disaccharide **12**.

The known benzylidene derivative of 2-azido-2-deoxygalactose **10**[6] and β-thioglucoside **13**[15] were used as starting materials in the synthesis of the pentasaccharide. A set of α-glucosyl donors, namely *N*-phenyltrifluoroacetimidates **7**, **5**, and **11** (Scheme 2) with different protecting group patterns, was prepared as follows: Selective benzoylation of the primary hydroxyl group in diol **15**[16] afforded 6-monobenzoate **16**, and treatment with *N*-phenyltrifluoroacetimidoyl chloride (PTAIC) in the presence of potassium carbonate gave glucosyl donor **7**. Similarly, imidate **5** was obtained from the known[16] 6-*O*-acetylated hemiacetal **17**, while 3,6-diacylated imidate **11** was

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(13) Amin, M. N.; Ishiwata, A.; Ito, Y. *Tetrehedron* **2007**, *63*, 8181–8198.
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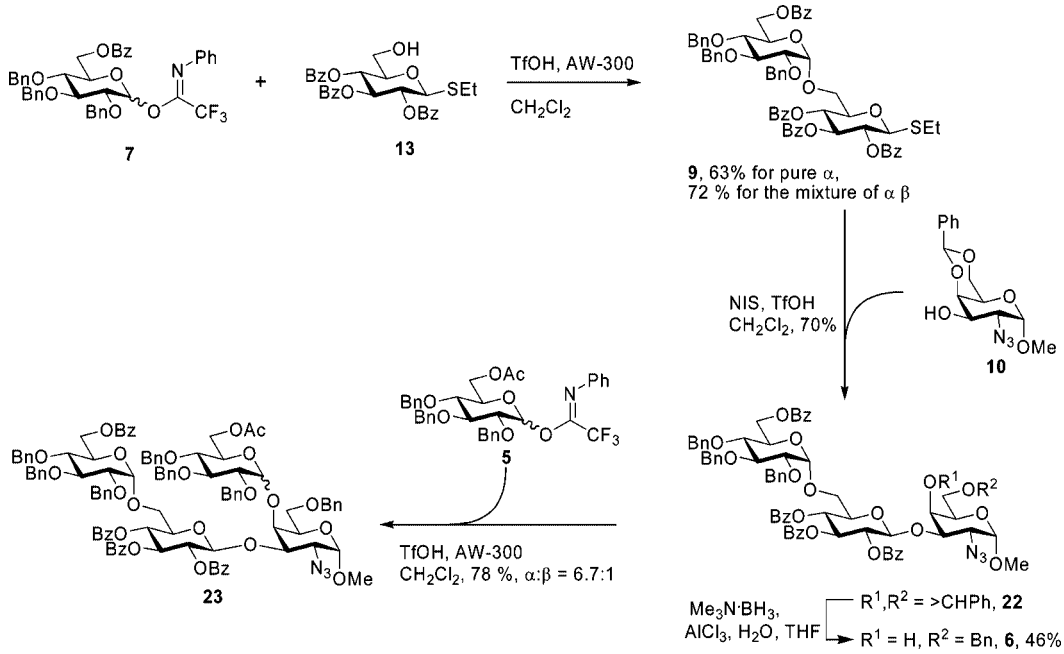
SCHEME 3. First Approach to the Pentasaccharide



prepared from the known[17] tribenzylated methyl glucoside **18**. Benzoylation of **18** and subsequent acetolysis of benzoate **19** produced diacetate **20**. Tetrafluoroboric acid etherate was found to be the promoter of choice that allowed for preparation of **20** with an excellent yield of 91% without affecting benzyl groups at O-2 and O-4. Anomeric deacetylation of **20** followed by treatment of the formed hemiacetal **21** with PTAIC gave target imidate **11**. All the glucosyl donors contain acyl group(s) at O-6 or at O-3 and O-6, which is able to control anomeric stereoselectivity owing to remote anchimeric participation.[6,7] On the other hand, both imidates **5** and **11** bear a selectively removable acetyl group at O-6, thus enabling further glycosylation at this site. With the above monosaccharide precursors in hand, we started the assembly of the pentasaccharide **28**.

Our first approach to the assembly of the pentasaccharide is shown in the Scheme 3. Thioglycoside acceptor **13** was subjected to AgOTf-promoted glycosylation with imidate **7** to prepare α-glucosyl-(1→6)-glucose block. However, unlike the published data related to AgOTf-promoted glycosylation with similar trichloracetimidates[18] and our own previous results,[6] AgOTf from a freshly opened package did not promote this glycosylation. We thus assumed that the actual promoter in the cited works was possibly traces of triflic acid, which is produced from AgOTf upon hydrolysis. The replacement of AgOTf with catalytic amount of triflic acid brought the reaction of **13** with **7** to completion within a few hours and provided disaccharide thioglycoside **9** as a mixture of α,*β*-anomers in a ratio of 8.4:1. The α-anomer was isolated by preparative HPLC in 63% yield. The configuration of the (1→6)-glycoside bond was confirmed by the characteristic coupling constant value $J_{1',2'}$ of 3.5 Hz for the nonreducing Glc unit in the ^{1}H NMR spectrum of **9**.

NIS-TfOH-promoted coupling of acceptor **10** with disaccharide thioglycoside **9** yielded trisaccharide **22** in 70% yield. The *β*-configuration of the newly formed (1→3)-glycosidic bond was deduced from the $J_{1',2'}$ value of 7.9 Hz in the ^{1}H NMR spectrum of **22**. Conversion of the benzylidene acetal **22** into 6-*O*-benzyl ether **6** under the described conditions[19] proceeded slowly so that a substantial amount of starting compound **22** was observed in the reaction mixture even with a prolonged reaction time, which was 10 times longer than that usually needed for the transformation of related disaccharide *β*-D-Glc*p*-(1→3)-α-D-Gal*p*N_3-OMe substrates. As product **6** and starting material **22** were difficult to separate, isolation of **6** required a tedious chromatographic separation accompanied by the loss of the material. As a result, trisaccharide acceptor **6** was obtained in only 46% yield. The modest yield at this step prompted us to abandon this approach, despite the fact that trial glycosylation of **6** with imidate **5** in the presence of catalytic amount of TfOH gave tetrasaccharide **23** in reasonable yield (78% for α,*β*-mixture) and with good α-stereoselectivity (α/*β* ratio 6.7:1).

We next explored a synthetic approach, which was based on the successive introduction of monosaccharide units into the growing oligosaccharide backbone (Scheme 4). The glucosyl donor **14** was obtained from derivative **13** by conventional chloroacetylation. Chloroacetyl groups can be selectively removed when necessary in the presence of other acyl protecting groups and thus provide the site for further α-glucosylation. NIS-TfOH-promoted coupling of donor **14** and acceptor **10** gave *β*-(1→3)-linked disaccharide **24**. Contrary to the findings with the trisaccharide derivatives **22**, regioselective reductive opening of the benzylidene ring of disaccharide **24** was accomplished without complications and efficiently produced disaccharide acceptor **12**. Its α-glucosylation with imidate **11** in the presence of catalytic amounts of TfOH and MS AW-300 gave branched α-trisaccharide **25** along with minor amounts of the corresponding *β*-anomer (α/*β*-ratio ~11:1). Pure compound **25** was isolated in 75% yield by preparative HPLC. The α-configuration of the (1→4)-glucoside bond was confirmed by the corresponding coupling constant value $J_{1,2}$ (<4.4 Hz, the exact value could not be determined due to signal overlap) in the ^{1}H NMR spectrum of **25**. The chloroacetyl group was removed from **25**

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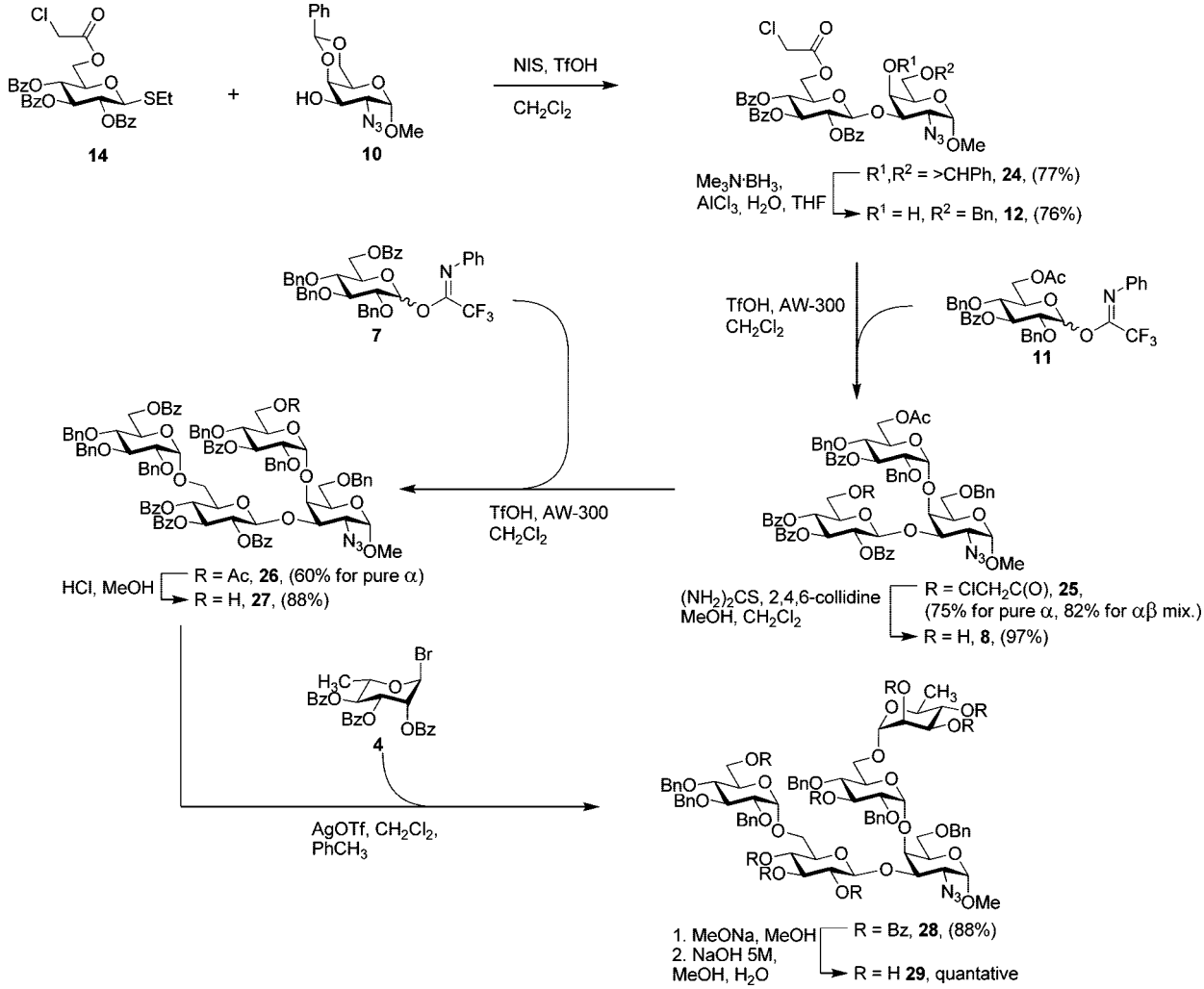
SCHEME 4. Second Approach to the Pentasaccharide



nearly quantitatively on treatment with thiourea in the presence of 2,4,6-collidine to give trisaccharide acceptor **8**. The position of the free OH group was deduced from the upfield shift of signals for H-6 of the β-glucose residue (δ 4.51, 4.37 → 3.84, 3.72) in the ^{1}H NMR spectrum of **8** as compared to those of starting **25**.

6-*O*-Benzoylated imidate **7** was applied to introduce the second α-glucose residue. Its TfOH-promoted coupling with acceptor **8** yielded target tetrasaccharide **26** isolated by preparative HPLC in 60% yield. The α-configuration of (1→6)-glucoside bond was deduced from the corresponding coupling constant value $J_{1,2}$ (3.5 Hz) in the ^{1}H NMR spectrum of **26**. Removal of the sole acetyl group by mild acidic methanolysis[20] produced tetrasaccharide acceptor **27** in high yield. Its final AgOTf-promoted glycosylation with rhamnosyl bromide **4** produced the target protected pentasaccharide **28** in 88% yield.

Benzoyl protecting groups in **28** were removed by treatment with methanolic MeONa and then with aqueous 5 M NaOH, as MeONa did not provide complete debenzoylation. Attempts at reducing the azido group in the resultant compound **29** by $Pd(OH)_2$/C-catalyzed hydrogenation either with periodic addition of ethyl trifluoracetate to bind free amine formed or without it (Scheme 5) always led to complex mixtures of products. Only hydrogenation in a mixture of MeOH−AcOH−HCO_2H for 7 days afforded an isolatable product, which was shown to be bismethylated amine **30**. Reductive alkylation of free amines with traces of formaldehyde present in methanol on prolonged hydrogenolysis has been described.[21]

Reduction with H_2S was next tried for the transformation of the azido group in **29** into an amine. Optimization of the reaction conditions with respect to the solvent and including a basic additive has shown that application of an aq THF−Et_3N−pyridine mixture instead of conventional aq pyridine[22] provided for a smooth transformation of **29** into **31** within 2.5 h. A combination of aq acetonitrile−Et_3N−diisopropylamine was found to be even more effective. TLC showed that H_2S under these conditions completely reduced the azido group in **29** within a few minutes. However, the reduction with H_2S was accompanied by the formation of sulfur-containing contaminants, presumably polysulfides, amounts of which were proportional to the reaction time. Although the latter reaction conditions allowed for a significant decrease in the quantity of sulfur-containing contaminants, the resultant amine **31** and its *N*-acyl derivatives can retain some of these byproducts even after silica gel column chromatog-

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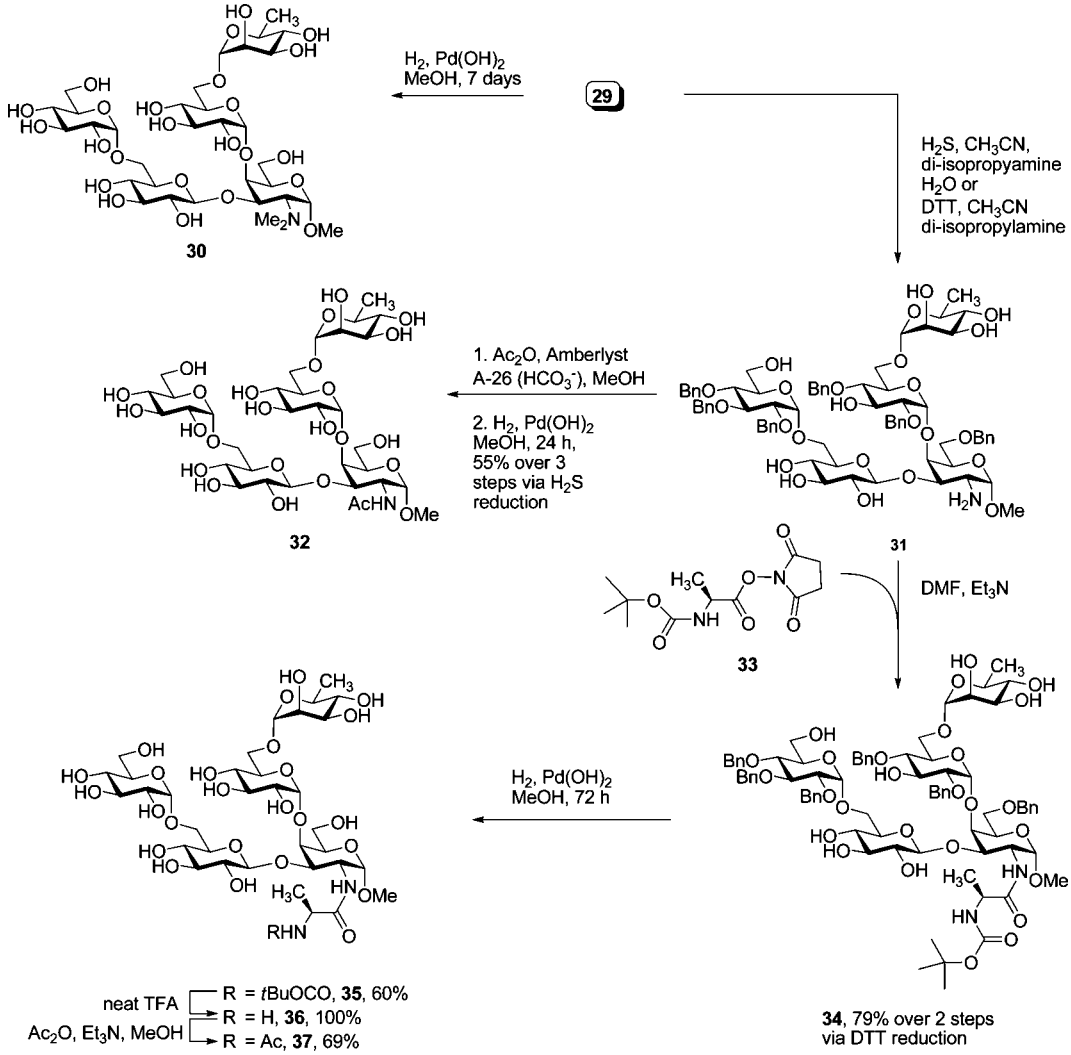
SCHEME 5. Azido Group Reduction and Final Deprotection



raphy or treatment with a strongly basic anion-exchanger Amberlyst A-26 (OH^-) judging from the poor reproducibility of further catalytic hydrogenolysis of the benzyl groups.

Application of dithiothreitol (DTT) in CH_2Cl_2 for reduction of the sugar azides is known.[23] We have found that the reducing system DTT−diisopropylamine in acetonitrile, being less active than H_2S, is free from the above disadvantage because oxidized DTT can be easily separated by conventional column chromatography.

Reduction of the azide group in **29** with DTT under the described optimal conditions followed by acylation of amine **31** formed with *N*-Boc-L-alanine active ester **33** afforded *N*-alanyl derivative **34** with an overall yield of 79%. The characteristic doublet at δ 1.35 and singlet at δ 1.46 in the ^{1}H NMR spectrum revealed the presence of the *N*-Boc-L-alanyl moiety in **34**. Catalytic hydrogenolysis of **34** gave debenzylated pentasaccharide **35**. Subsequent removal of the *N*-Boc protecting group with neat TFA provided target pentasaccharide **36** in a quantitative yield corresponding to glycoform **I**. The structure of **36** was confirmed by ^{1}H and ^{13}C NMR and MS data. Conventional *N*-acetylation of the free amino group in **36** produced the second target *N*-(*N*-acetyl-L-alanyl) product **37**. *N*-Acetylated pentasaccharide **32** was obtained via H_2S reduction of the azido group followed by *N*-acetylation and hydrogenolysis of benzyl groups with 55% overall yield from azide **29**.

Conclusions

In summary, the synthesis of the pentasaccharide **36** corresponding to the glycoform I of the outer core region of the *Pseudomonas aeruginosa* lipopolysaccharide, as well as its two closely related analogues **32** and **37**, was achieved. The synthetic scheme, which was based on consecutive addition of monosaccharide units, proved to be the most convenient. Anomeric stereocontrol of remote acyl groups in glucosyl donors ensured highly stereoselective α-glucosylation at the key steps of the synthesis. New conditions for efficient reduction of sugar azides, viz. DTT−diisopropylamine in acetonitrile, were the second key feature of the synthesis. The biological evaluation of synthetic pentasaccharides **32**, **36**, and **37** in relation to development of cystic fibrosis is in progress.

Experimental Section

For general experimental methods, see the Supporting Information.

Methyl 2,3,4-Tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[6-*O*-acetyl-3-*O*-benzoyl-2,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (8). A solution of trisaccharide **25** (728 mg, 0.54 mmol), thiourea (190 mg, 2.5 mmol), and 2,4,6-collidine (65 μL, 0.49 mmol) in a mixture of CH_2Cl_2 (23 mL) and MeOH (10 mL) was kept for 48 h at room temperature and then taken to dryness. Flash chromatography of the residue

(3:1 toluene−EtOAc) provided **8** (662 mg, 97%): R_f 0.26 (3:1 toluene−EtOAc); $[\alpha]^{21}_D$ +52.7 (*c* 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.05−7.10 (m, 35H, Ar), 5.94 (t, $J_{3^{II},4^{II}}$ = 9.8 Hz, 1H, H-3^{II}), 5.89 (t, $J_{3^{III},4^{III}}$ = 9.7 Hz, 1H, H-3^{III}), 5.62 (dd, $J_{2^{II},3^{II}}$ = 9.9 Hz, $J_{2^{II},1^{II}}$ = 8.0 Hz, 1H, H-2^{II}), 5.58 (t, $J_{4^{II},5^{II}}$ = 9.7 Hz, 1H, H-4^{II}), 5.42 (d, $J_{1^{III},2^{III}}$ = 3.2 Hz, 1H, H-1^{III}), 5.08 (d, $J_{1^{II},2^{II}}$ = 8.0 Hz, 1H, H-1^{II}), 4.79 (d, $J_{1^{I},2^{I}}$ = 3.5 Hz, 1H, H-1^{I}), 4.59−4.49 (m, 5H, PhCH_2, PhCH_2', H-6A^{III}), 4.42 (d, $J_{A'',B''}$ = 11.9 Hz, 1H, PhCH_2''A), 4.41 (dd, $J_{6B^{III},6A^{III}}$ = 12.0 Hz, $J_{6B^{III},5^{III}}$ = 3.3 Hz, 1H, H-6B^{III}), 4.34 (br d, 1H, H-4^{I}), 4.32 (d, $J_{B'',A''}$ = 11.9 Hz, 1H, PhCH_2''B), 4.30 (m, 1H, H-5^{III}), 4.02 (dd, $J_{3^{I},4^{I}}$ = 2.5 Hz, $J_{3^{I},2^{I}}$ = 10.9 Hz, 1H, H-3^{I}), 3.94 (m, 1H, H-5^{I}), 3.87 (m, 1H, H-6A^{I}), 3.84 (m, 1H, H-6A^{II}), 3.77 (m, 1H, H-5^{II}), 3.76−3.60 (m, 5H, H-4^{III}, H-6B^{II}, H-2^{III}, H-6B^{I}, H-2^{I}), 3.39 (s, 3H, CH_3O), 2.10 (s, 3H, CH_3CO); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C) 170.8 (CH_3*C*O), 166.2, 165.6, 165.4, 164.6 (Ph*C*O), 138.2, 137.7, (*ipso*-Ph (Bn)), 133.6, 133.1, 132.9, ((*ipso*-Ph (Bz)), 130.1, 129.9, 129.7, 129.2, 128.9, 128.4, 128.3, 128.2, 128.1, 127.7, 127.5, 127.4 (Ar), 103.3 (C-1^{II}), 98.9 (C-1^{I}), 98.2 (C-1^{III}), 78.6 (C-3^{I}), 78.4 (C-4^{I}), 78.1 (C-2^{III}), 76.0 (C-4^{III}), 74.6 (C-5^{II}), 74.2 (C-3^{III}, Ph*C*H$_2'$), 73.2 (Ph*C*H$_2''$), 72.7 (C-3^{II}), 72.6 (Ph*C*H$_2$), 71.3 (C-2^{II}), 69.9 (C-5^{I}), 69.21 (C-4^{II}), 69.16 (C-5^{III}), 68.9 (C-6^{I}), 62.9 (C-6^{III}), 60.8 (C-6^{II}), 59.5 (C-2^{I}), 55.3 (*C*H$_3$O), 20.9 (*C*H$_3$CO). Anal. Calcd for $C_{70}H_{69}N_3O_{20}$: C, 66.08; H, 5.47; N, 3.30. Found: C, 66.35; H, 5.52; N, 3.37.

O*-(6-*O*-Acetyl-3-*O*-benzoyl-2,4-di-*O*-benzyl-D-glucopyranosyl) *N*-Phenyltrifluoroacetimidate (11).** A solution of PTAIC (468 mg, 2.26 mmol) in acetone (10 mL) was added to a solution of **21** (954 mg, 1.88 mmol) in acetone (25 mL) followed by K_2CO_3 (400 mg, 2.9 mmol). The reaction mixture was vigorously stirred for 7 h at rt and filtered through a pad of Celite. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography (40:1 toluene−EtOAc) to yield **11** (1.253 g, 1.85 mmol, 98%) as a colorless foam: R_f 0.25 (35:1 toluene−EtOAc). Data for **11α**: ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−6.70 (m, 20 H, Ar), 6.54 (br s, 1H, H-1), 5.89 (t, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 4.70−4.47 (m, 4H, PhCH_2), 4.39 (d, $J_{6A,6B}$ = 12.2 Hz, 1H, H-6A), 4.29 (dd, $J_{6B,6A}$ = 12.2 Hz, $J_{6B,5}$ = 3.9 Hz, 1H, H-6B), 4.13 (m, 1H, H-5), 3.80−3.71 (m, 2H, H-2, H-4), 2.09 (s, 3H, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$, δ_H): 170.4 (CH_3*C*O), 165.3 (Ph*C*O), 143.4 (*ipso*-Ph (NPh)), 137.1, 136.8 (*ipso*-Ph (Bn)), 133.2 (*ipso*-Ph (Bz)), 129.8, 128.7, 128.4, 128.2, 128.1, 127.9, 127.8 (Ar), 124.3, 119.3 (Ph (NPh)), 92.5 (C-1), 75.9 (C-2), 75.1 (C-4), 74.6 (Ph*C*H$_2$), 73.7 (C-3), 72.7 (Ph*C*H$_2$), 71.2 (C-5), 62.4 (C-6), 20.8 (*C*H$_3$CO). Data for **11*β: ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.05−6.71 (m, 20 H, Ar), 5.79 (br s, 1H, H-1), 5.58 (br t, 1H, H-3), 4.80 (d, $J_{A,B}$ = 11.6 Hz, 1H PhCH_2A), 4.65 (d, $J_{B,A}$ = 11.6 Hz, 1H PhCH_2B), 4.56 (d, $J_{A,B}$ = 11.0 Hz, 1H PhCH_2'A), 4.49 (d, $J_{B,A}$ = 11.0 Hz, 1H PhCH_2'B), 4.37 (d, $J_{6A,6B}$ = 11.9 Hz, 1H, H-6A), 4.25 (dd, $J_{6B,6A}$ = 11.9 Hz, $J_{6B,5}$ = 3.2 Hz, 1H, H-6B), 3.84−3.73 (m, 2H, H-4,H-2), 2.08 (s, 3H, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.4 (CH_3*C*O), 165.3 (Ph*C*O), 143.2 (*ipso*-Ph (NPh)), 137.0, 136.8 (*ipso*-Ph (Bn)), 133.3 (*ipso*-Ph (Bz)), 129.8, 128.7, 128.4, 128.3, 128.2, 128.1, 127.9 (Ar), 124.5, 119.2 (Ph (NPh)), 96.9 (C-1), 77.5 (C-2), 76.0 (C-3), 75.1 (C-4), 74.4, 74.0 (Ph*C*H$_2$), 73.3 (C-5), 62.4 (C-6), 20.7 (*C*H$_3$CO). Data for **11**: Anal. Calcd for $C_{37}H_{34}F_3NO_8$: C, 65.58; H, 5.06; N, 2.07. Found: C, 65.81; H, 5.07; N, 2.04.

Methyl 2,3,4-Tri-*O*-benzoyl-6-*O*-chloracetyl-*β*-D-glucopyranosyl-(1→3)-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (12). To a chilled (4 °C) solution of **24** (1.74 g, 2.03 mmol) in dry THF (86 mL) were added $Me_3N\cdot BH_3$ (0.61 g, 8.42 mmol) and $AlCl_3$ (1.64 g, 12.34 mmol) followed by water (75 μL, 4.13 mmol), and the resulting mixture was vigorously stirred for 20 h at rt. The reaction was quenched by adding HCl 1 M (140 mL) and water (130 mL). The mixture was extracted with EtOAc (250 mL), the aqueous layer was additionally extracted with EtOAc (3 × 50 mL), and the combined organic extracts were successively washed with water and saturated aq $NaHCO_3$, dried (Na_2SO_4), and concentrated. The resulting solid was purified by flash chromatography (1:0.4:0.2, light petroleum−EtOAc−Et_2O) to provide **12** (1.33 g, 1.55 mmol, 76%) as a colorless foam: R_f 0.2 (8:1 toluene−EtOAc); $[\alpha]^{23}_D$ +44.5 (*c* 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 7.97−7.20 (m, 20H, Ar), 5.90 (t, $J_{3^{II},4^{II}}$ = 9.7 Hz, 1H, H-3^{II}), 5.57 (dd, $J_{2^{II},3^{II}}$ = 9.7 Hz, $J_{2^{II},1^{II}}$ = 8.0 Hz, 1H, H-2^{II}), 5.53 (t, $J_{4^{II},5^{II}}$ = 9.7 Hz, 1H, H-4^{II}), 5.08 (d, $J_{1^{II},2^{II}}$ = 7.9 Hz, 1H, H-1^{II}), 4.78 (d, $J_{1^{I},2^{I}}$ = 3.5 Hz, 1H, H-1^{I}), 4.61 (d, $J_{A,B}$ = 12.0, 1H, PhCH_2A), 4.56 (d, $J_{B,A}$= 12.0 Hz, 1H, PhCH_2B), 4.38 (d, $J_{6^{II},5^{II}}$ = 4.2 Hz, 2H, H-6^{II}), 4.20 (br d, 1H, H-4^{I}), 4.07 (m, 1H, H-5^{II}), 4.05 (dd, $J_{3^{I},4^{I}}$ = 3.0 Hz, 1H, H-3^{I}), 4.01 (s, 2H, ClCH_2CO), 3.96 (m, $J_{5^{I},6^{I}}$ = 5.6 Hz, 1H, H-5^{I}), 3.78 (dd, $J_{6A^{I},6B^{I}}$ = 10.0 Hz, $J_{6A^{I},5^{I}}$ = 5.5 Hz, 1H, H-6A^{I}), 3.72−3.66 (m, 2H, H-6B^{I}, H-2^{I}), 3.38 (s, 3H, CH_3O); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 167.0 (ClCH_2*C*O), 165.6, 165.2 (Ph*C*O), 137.9 (*ipso*-Ph (Ph)), 133.7, 133.3, 133.2 (*ipso*-Ph (Bz)), 129.8, 129.7, 129.0, 128.5, 128.4, 128.3, 127.8, 127.7 (Ar), 101.8 (C-1^{II}), 98.8 (C-1^{I}), 78.5 (C-3^{I}), 73.6 (Ph*C*H$_2$), 72.4 (C-3^{II}), 72.2 (C-5^{II}), 71.5 (C-2^{II}), 69.2 (C-6^{I}), 69.1 (C-4^{II}), 68.62 (C-5^{I}), 68.57 (C-4^{I}), 63.7 (C-6^{II}), 58.9 (C-2^{I}), 55.3 (*C*H$_3$O), 40.5 (Cl*C*H$_2$CO). Anal. Calcd for $C_{43}H_{42}ClN_3O_{14}$: C, 60.04; H, 4.92; N, 4.88. Found: C, 60.11; H, 5.24; N, 4.83.

Ethyl 2,3,4-Tri-*O*-benzoyl-6-*O*-chloracetyl-1-thio-*β*-D-glucopyranoside (14). To a solution of **13** (1.95 g, 3.64 mmol) in dry CH_2Cl_2 (60 mL) were added chloroacetyl chloride (0.726 mL, 9.1 mmol) and pyridine (1.2 mL) at −5 °C, and the reaction mixture was stirred for 20 min and then quenched with water (50 mL). The product was extracted with CH_2Cl_2 (3 × 50 mL), and combined organic solutions were successively washed with HCl 1 M and water and concentrated. The residue was purified by column chromatography (4:1 petroleum ether−EtOAc) to provide **14** (95%, 2.10 g, 3.43 mmol): R_f 0.22 (4:1 petroleum ether−EtOAc); $[\alpha]^{25}_D$ +5.8 (*c* 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H) 8.00−7.25 (m, 15H, Ar), 5.92 (t, $J_{3,4}$ = $J_{3,2}$ = 9.5 Hz, 1H, H-3), 5.63−5.52 (m, 2H, H-2, H-4), 4.85 (d, $J_{1,2}$ = 10.0 Hz, 1H, H-1), 4.46−4.41 (m, 2H, H-6), 4.12−4.05 (m, 3H, ClCH_2CO, H-5), 2.80 (m, 2H, SCH_2CH$_3$), 1.30 (t, 3H, SCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C) 167.0 (ClCH_2*C*O), 165.7, 165.3, 165.1 (Ph*C*O), 133.6, 133.3 (*ipso*-Ph (Bz)), 129.8, 129.7, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3 (Ph), 84.0 (C-1), 76.0, 74.0, 70.5, 69.2 (C-3, C-5, C-2, C-4), 64.1 (C-6), 40.6 (Cl*C*H$_2$CO), 24.3 (S*C*H$_2$CH$_3$), 14.9 (SCH$_2$*C*H$_3$). Anal. Calcd for $C_{31}H_{29}ClO_9S$: C, 60,73; H, 4.77; Cl, 5.78; S, 5.23. Found: C, 60.66; H, 4.80; Cl, 5.50; S, 4.97.

6-*O*-Benzoyl-2,3,4-tri-*O*-benzyl-D-glucopyranose (16). Benzoyl chloride (23 μL, 0.20 mmol) was added to a solution of diol **15** (82 mg, 0.18 mmol) in pyridine (2 mL) and CH_2Cl_2 (2 mL) at −20 °C. The mixture was stirred for 10 min and then poured into ice-cold aq saturated $NaHCO_3$ solution, and the product **16** was extracted three times with EtOAc. Combined organic extracts were successively washed with 1 M HCl, water, and aq saturated $NaHCO_3$ and concentrated. The residue was purified by silica gel column chromatography (7.5:1 toluene−EtOAc) to give hemiacetal **16** (73 mg, 0.13 mmol, 72%) as a 2.5:1 α,*β*-mixture: R_f 0.17 (8:1 toluene−EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.09−7.11 (m, 28.1H, Ar), 5.26 (br s, 1H, H-1$^{\alpha}$), 5.04−4.84 (m, 4.5H, PhC$H_2^{\alpha,\beta}$), 4.82−4.59 (m, 5.5H, PhC$H_2^{\alpha,\beta}$, H-1$^{\beta}$, H-6A$^{\beta}$, H-6A$^{\alpha}$), 4.54−4.46 (m, 1.4H, H-6B$^{\alpha}$, H-6A$^{\beta}$), 4.25 (m, 1H, H-5$^{\alpha}$), 4.09 (t, $J_{3^{\alpha},4^{\alpha}}$ = $J_{3^{\alpha},2^{\alpha}}$ = 9.0 Hz, 1H, H-3$^{\alpha}$), 3.75−3.61 (m, 3.2H, H-3$^{\beta}$, H-4$^{\beta}$, H-4$^{\alpha}$, H-5$^{\beta}$, H-2$^{\alpha}$), 3.53−3.43 (m, 1.4H, H-2$^{\beta}$, OH); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 116.3 (PHCO), 138.5, 138.3, 137.8 (ipso-Ph (Bz)), 133.1 (ipso-Ph (Bn)), 129.9, 129.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8 (Ph), 97.6 (C-1$^{\beta}$), 91.1 (C-1$^{\alpha}$), 84.6 (C-3$^{\beta}$), 83.2 (C-2$^{\beta}$), 81.8 (C-3$^{\alpha}$), 80.3 (C-2$^{\alpha}$), 77.54 (C-4$^{\alpha}$), 77.47 (C-4$^{\beta}$). 75.9, 75.8, 75.2, 74.6 (Ph$CH_2^{\alpha,\beta}$), 73.2 (C-5$^{\beta}$), 69.0 (C-5$^{\alpha}$), 63.4 (C-6$^{\alpha,\beta}$). Anal. Calcd for $C_{34}H_{34}O_7$: C, 73.63; H, 6.18. Found: C, 73.91; H, 6.41.

1,6-Di-*O*-acetyl-3-*O*-benzoyl-2,4-di-*O*-benzyl-D-glucopyranose (20). Benzoyl chloride (2.2 mL, 19.0 mmol) was added dropwise to a chilled (4 °C) solution of **18** (4.29 g, 9.22 mmol) in pyridine (40 mL). The mixture was stirred for 10 h at rt and then poured into a

(23) Meijohannes, E.; Meldal, M.; Jensen, T.; Werdelin, O.; Galli-Stampino, L.; Mouritsen, S.; Bock, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 871–884.

mixture of crushed ice and saturated aq $NaHCO_3$. The product **19** was extracted with EtOAc (4 × 100 mL). Combined organic extracts were concentrated, and pyridine was coevaporated several times with toluene. Pure **19** (3.35 g, 64%) was isolated by column chromatography (3:1 light petroleum−EtOAc): R_f 0.19 (4:1 light petroleum−EtOAc).

To a solution of **19** (3.35 g, 5.90 mmol) in acetic anhydride (22 mL) was slowly added tetrafluoroboric acid etherate (4 mL of 54 wt % solution in diethyl ether, 25 mmol) at 4 °C. The reaction mixture was kept for 2.5 h at rt and poured into a mixture of crushed ice and saturated aq $NaHCO_3$. The mixture was extracted four times with EtOAc, and the combined extracts were washed with water, dried (Na_2SO_4), and concentrated. Purification of the residue by column chromatography (10:1 toluene−acetone) afforded **20** (2.94 g, 5.36 mmol, 91%) as a 2.5:1 α,β-mixture: R_f 0.22 (3:1 light petroleum−EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.10−7.10 (m, 21H Ar), 6.40 (d, $J_{1^\alpha,2^\alpha}$ = 3.5 Hz, 1H, H-1$^\alpha$), 5.82 (t, $J_{3^\alpha,4^\alpha}$ = 9.6 Hz, 1H, H-3$^\alpha$), 5.73 (d, $J_{1^\beta,2^\beta}$ = 8.0 Hz, 0.4H, H-1$^\beta$), 5.62 (t, $J_{3^\beta,4^\beta}$ = 9.1 Hz, 0.4H, H-3$^\beta$), 4.70−4.42 (m, 3H CH_2Ph), 4.33 (m, 0.4H, H-6A$^\beta$), 4.30 (d, $J_{6^\alpha,5^\alpha}$ = 3.0 Hz, 1H, H-6$^\alpha$), 4.27 (m, 0.4H, H-6B$^\beta$), 4.07 (m, 1H, H-5$^\alpha$), 3.80 (m, 0.4H, H-5$^\beta$), 3.77−3.68 (m, 2.4H, H-4$^\beta$, H-4$^\alpha$, H-2$^\alpha$), 3.66 (t, $J_{2^\beta,3^\beta}$ = 9.0 Hz, 0.4H, H-2$^\beta$), 2.28−2.05 (m, 4.2H, CH_3C(O)); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.5, 169.3, 168.7, 165.5 (C═O), 137.1, 136.9, (*ipso*-Ph (Bn)), 133.3 (*ipso*-Ph (Bz)), 129.8−127.8 (Ar), 93.9 (C-1$^\beta$), 89.1 (C-1$^\alpha$), 77.9 (C-2$^\beta$), 76.3 (C-3$^\beta$), 75.4 (C-4$^\beta$), 75.4,75.1 (C-2$^\alpha$,C-4$^\alpha$), 74.7, 74.4, 74.2 (Ph*C*H$_2$), 73.5 (C-5$^\beta$), 72.3 (Ph*C*H$_2$), 70.9 (C-5$^\alpha$), 62.54 (C-6$^\beta$), 62.45 (C-6$^\alpha$), 21.0, 20.8 (*C*H$_3$CO). Anal. Calcd for $C_{31}H_{32}O_9$: C, 67.87; H, 5.88. Found: C, 68.04; H, 5.92.

6-*O*-Acetyl-3-*O*-benzoyl-2,4-di-*O*-benzyl-D-glucopyranose (21). Hydrazine acetate (761 mg, 8.27 mmol) was added to a solution of **20** (2.94 g, 5.36 mmol) in DMF (30 mL). The solution was stirred for 1 h, and then the reaction was quenched by adding saturated aq $NaHCO_3$ solution. The mixture was extracted four times with EtOAc, and the combined extracts were washed with water, dried (Na_2SO_4), and concentrated. Chromatographic purification on silica gel (7:1 toluene−acetone) gave **21** (2.04 g, 4.03 mmol, 81%) as a 1.5:1 α,β-mixture: R_f 0.32 (5:1 toluene−acetone); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) for (1.5:1) 8.08−7.05 (m, 37.5H, Ar), 5.82 (t, $J_{3^\alpha,4^\alpha}$ = 9.4 Hz, 1.5H, H-3$^\alpha$), 5.55 (t, $J_{3^\beta,4^\beta}$ = 9.1 Hz, 1H, H-3$^\beta$), 5.31 (d, $J_{1^\alpha,2^\alpha}$ = 3.3 Hz, 1.5H, H-1$^\alpha$), 4.86 (d, $J_{1^\beta,2^\beta}$ = 7.6 Hz, 1H, H-1$^\beta$), 4.82−4.42 (m, 5H, CH_2Ph), 4.38 (d, $J_{6A^\beta,6B^\beta}$ = 11.7 Hz, 1H, H-6A$^\beta$), 4.32 (dd, $J_{6A^\alpha,6B^\alpha}$ = 12.0 Hz, $J_{6A^\alpha,5^\alpha}$ = 1.8 Hz, 1.5H, H-6A$^\alpha$), 4.27−4.18 (m, 4H, H-6B$^\alpha$, H-5$^\alpha$, H-6B$^\beta$), 3.68−3.61 (m, 5H, H-4$^\beta$, H-5$^\beta$, H-4$^\alpha$, H-2$^\alpha$), 3.43 (dd, $J_{2^\beta,3^\beta}$ = 9.4 Hz, $J_{2^\beta,1^\beta}$ = 7.8 Hz, 1H, H-2$^\beta$), 2.05 (s, 7.5H, CH_3C(O)); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.7 (CH$_3$*C*O), 165.6 (Ph*C*O), 137.7, 137.1, 137.0 (*ipso*-Ph (Bn)), 133.1 (*ipso*-Ph (Bz)), 130.0, 129.7, 128.4, 128.3, 128.1, 127.9, 127.5 (Ar), 97.4 (C-1$^\beta$), 90.7 (C-1$^\alpha$), 79.6 (C-2$^\beta$), 77.2 (C-2$^\alpha$), 76.3 (C-3$^\beta$), 75.9 (C-4$^\beta$), 75.8 (C-4$^\alpha$), 74.5, 74.3 (Ph*C*H$_2$), 74.1 (C-3$^\alpha$), 73.8 (Ph*C*H$_2$), 72.8 (C-5$^\beta$), 72.4 (Ph*C*H$_2$), 68.5 (C-5$^\alpha$), 63.0 (C-6$^\alpha$, C-6$^\beta$) 20.8 (*C*H$_3$CO). Anal. Calcd for $C_{29}H_{30}O_8$: C, 68.76; H, 5.97. Found: C, 68.85; H, 5.97.

Methyl 2,3,4-Tri-*O*-benzoyl-6-*O*-chloracetyl-β-D-glucopyranosyl-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside (24). A solution of compounds **14** (2.14 g, 3.49 mmol) and **10** (0.89 g, 2.89 mmol) in CH_2Cl_2 (45 mL) was added through a cannula into a flask containing 4 Å molecular sieves (4.90 g) under argon; the resulting mixture was stirred for 1 h at rt and cooled to −20 °C. Then NIS (0.86 mg, 3.51 mmol) was added followed by TfOH (100 μL, 1.13 mmol), and the mixture was stirred for 1.5 h at −20 °C. The reaction was quenched by adding pyridine (1 mL), the mixture was filtered through a pad of Celite, and the filtrate was poured into saturated $NaHCO_3$. The mixture was extracted three times with $CHCl_3$, and the combined organic solutions were successively washed with 1 M aq $Na_2S_2O_3$, saturated aq $NaHCO_3$, and concentrated. Column chromatography (8:1 toluene−EtOAc) of the residue gave disaccharide **24** (1.86 g, 75%) as a colorless foam: R_f 0.15 (8:1 toluene−EtOAc); $[\alpha]^{31}_D$ +76.1 (*c* 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H) δ 7.99−7.15 (m, 20 H, Ar), 5.89 (t, $J_{3^{II},4^{II}}$ = 9.6 Hz, 1H, H-3^{II}), 5.62 (t, $J_{2^{II},3^{II}}$ = 8.0 Hz, 1H, H-2^{II}), 5.61 (s, 1H, CHPh), 5.58 (t, $J_{4^{II},5^{II}}$ = 9.7 Hz, 1H, H-4^{II}), 5.17 (d, $J_{1^{II},2^{II}}$ = 7.9 Hz, 1H, H-1^{II}), 4.88 (d, $J_{1^I,2^I}$ = 3.3 Hz, 1H, H-1^I), 4.53 (dd, $J_{6A^{II},6B^{II}}$ = 12.2 Hz, $J_{6A^{II},5^{II}}$ = 2.4 Hz, 1H, H-6A^{II}), 4.44 (d, $J_{4^I,3^I}$ = 3.0 Hz, 1H, H-4^I), 4.39 (dd, $J_{6B^{II},6A^{II}}$ = 12.2 Hz, $J_{6B^{II},5^{II}}$ = 5.1 Hz, 1H, H-6B^{II}), 4.25 (d, 1H, H-6A^I), 4.16 (dd, $J_{3^I,4^I}$ = 3.2 Hz, $J_{3^I,2^I}$ = 10.7 Hz, 1H, H-3^I), 4.11 (d, 1H, H-6B^I), 4.05 (s, 2H, ClCH$_2$CO), 4.04 (m, 1H, H-5^{II}), 3.84 (dd, $J_{2^I,3^I}$ = 10.8 Hz, $J_{2^I,1^I}$ = 3.4 Hz, 1H, H-2^I) 3.68 (s, 1H, H-5^I), 3.43 (s, 3H, CH_3O); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C) 166.9 (ClCH$_2$*C*O), 165.7, 165.2, 165.0 (Ph*C*O), 137.7 (*ipso*-Ph (CHPh)), 133.6, 133.2, 133.1 (*ipso*-Ph (Bz)), 129.8, 129.7, 129.2, 129.0, 128.8, 128.7, 128.5, 128.2, 128.1, 126.1, 125.3 (Ph (Bz)), 102.1 (C-1^{II}), 100.5 (*C*HPh), 99.5 (C-1^I), 75.7 (C-4^I, C-3^I), 72.9 (C-3^{II}), 72.2 (C-5^{II}), 71.7 (C-2^{II}), 69.1 (C-6^I), 69.0 (C-4^{II}), 63.5 (C-6^{II}), 63.0 (C-5^I), 59.0 (C-2^I), 55.5 (*C*H$_3$O), 40.6 (Cl*C*H$_2$CO). Anal. Calcd for $C_{43}H_{40}ClN_3O_{14}$: C, 60.18; H, 4.70; Cl, 4.13; N, 4.90. Found: C, 60.34; H, 4.89; Cl, 4.11; N, 4.95.

Methyl 2,3,4-Tri-*O*-benzoyl-6-*O*-chloroacetyl-β-D-glucopyranosyl-(1→3)-[6-*O*-acetyl-3-*O*-benzoyl-2,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (25). A solution of a mixture of donor **11** (634 mg, 0.94 mmol) and acceptor **12** (700 mg, 0.82 mmol) in CH_2Cl_2 (17.5 mL) was transferred via cannula into a flask containing AW-300 molecular sieves (1.8 g) under argon. The mixture was vigorously stirred for 1 h at rt, and then TfOH (17.5 μL, 0.20 mmol) was added. After 1 h, TLC showed complete conversion of donor **11**, while acceptor **12** was still present in the reaction mixture. Therefore, more donor **11** (200 mg, 0.30 mmol) in CH_2Cl_2 (4.5 mL) was added via a syringe. After another 1 h, the procedure was repeated with 0.100 g (0.15 mmol) of **11** dissolved in CH_2Cl_2 (1 mL). When TLC showed full conversion of the acceptor **12**, the reaction was quenched by adding pyridine (16 μL, 0.20 mmol). The resulting mixture was diluted with CH_2Cl_2 and filtered through a pad of Celite, and the filtrate was washed with saturated aq $NaHCO_3$ solution. The organic layer was concentrated, and the residue was purified by flash chromatography (10:1 toluene−EtOAc) to give a mixture of **25** and its β-isomer. Preparative HPLC (2:1 light petroleum−EtOAc) of this mixture on a silica gel column (5 μm, 250 × 25 mm) provided **25** (820 mg, 0.61 mmol, 75%) as a colorless foam: R_f 0.61 (3:1 toluene−EtOAc); $[\alpha]^{21}_D$ +58.8 (*c* 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.05−7.10 (m, 35H, Ar), 5.87 (2t, 2H, H-3^{II}, H-3^{III}), 5.62 (dd, $J_{2^{II},3^{II}}$ = 9.6 Hz, $J_{2^{II},1^{II}}$ = 8.1 Hz, 1H, H-2^{II}), 5.57 (t, $J_{4^{II},5^{II}}$ = 9.7 Hz, 1H, H-4^{II}), 5.27 (d, 1H, H-1^{III}), 5.04 (d, $J_{1^{II},2^{II}}$ = 8.0 Hz, 1H, H-1^{II}), 4.79 (d, $J_{1^I,2^I}$ = 3.5 Hz, 1H, H-1^I), 4.57 (d, $J_{A,B}$= 12.0 Hz, 1H, PhCH_2A), 4.53 (m, 2H, PhCH_2'), 4.51 (m, 2H, H-6A^{II}, H-6A^{III}), 4.49 (d, $J_{B,A}$= 12.0 Hz, 1H, PhCH_2B), 4.43 (dd, $J_{6B^{III},6A^{III}}$ = 12.1 Hz, $J_{6B^{III},5^{III}}$ = 2.8 Hz, 1H, H-6B^{III}), 4.37 (dd, $J_{6B^{II},6A^{II}}$ = 12.1 Hz, $J_{6B^{II},5^{II}}$ = 5.6 Hz, 1H, H-6B^{II}), 4.35 (d, $J_{A'',B''}$ = 12.2 Hz, 1H, PhCH_2''A), 4.26 (d, $J_{B'',A''}$ = 12.2 Hz, 1H, PhCH_2''B), 4.24−4.21 (m, 2H, H-5^{III}, H-4^I), 4.03 (m, 1H, H-5^{II}), 4.02 (d, $J_{A,B}$= 14.9 Hz, 1H, ClCH_2COA), 3.98 (dd, 1H, H-3^I), 3.95 (d, $J_{B,A}$= 14.9 Hz, 1H, ClCH_2COB), 3.93 (m, 1H, H-5^I), 3.83 (dd, $J_{6A^I,6B^I}$ = 10.1 Hz, 1H, H-6A^I), 3.74 (t, $J_{4^{III},5^{III}}$ = 9.6 Hz, 1H, H-4^{III}), 3.67−3.63 (m, 2H, H-2^{III}, H-6B^I), 3.60 (dd, $J_{2^I,3^I}$ = 11.0 Hz, $J_{2^I,1^I}$ = 3.5 Hz, 1H, H-2^I), 3.39 (s, 3H, CH_3O) 2.10 (s, 3H, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 170.0 (ClCH$_2$*C*O), 167.1 (CH$_3$*C*O), 165.8 (Ph*C*O), 137.9 (*ipso*-Ph (Ph)), 133.7, 133.2, 133.1 (*ipso*-Ph (Bz)), 130.4, 129.9, 129.3, 128.7, 128.5, 128.4, 128.3, 128.3, 127.8, 127.7, 127.5 (Ar), 103.2 (C-1^{II}), 98.8 (C-1^I), 98.6 (C-1^{III}), 78.9 (C-4^I), 78.4 (C-3^I), 78.2 (C-2^{III}), 76.0 (C-4^{III}), 74.2 (C-3^{II}), 74.1 (Ph*C*H$_2'$), 73.1 (Ph*C*H$_2''$), 72.8 (Ph*C*H$_2$), 72.7 (C-3^{III}), 72.2 (C-5^{II}), 71.2 (C-2^{II}), 70.2 (C-5^I), 69.2 (C-4^{II}), 69.1 (C-5^{III}), 69.0 (C-6^I), 63.4 (C-6^{II}), 62.9 (C-6^{III}), 59.5 (C-2^I), 55.3 (*C*H$_3$O), 40.6 (Cl*C*H$_2$CO), 21.1 (*C*H$_3$CO). Anal. Calcd for $C_{72}H_{70}ClN_3O_{21}$: C, 64.12; H, 5.23; Cl, 2.63; N, 3.12. Found: C, 64.08; H, 5.28; Cl, 2.79; N, 3.15.

Methyl 6-*O*-Benzoyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[6-*O*-acetyl-3-*O*-benzoyl-2,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (26). A solution of donor **7** (423 mg, 0.58 mmol) and acceptor **8** (590 mg, 0.46 mmol) in dry CH_2Cl_2 (35 mL) was poured via cannula into a flask containing AW-300 molecular sieves (3.6 g), and the mixture was stirred for 1 h before TfOH (8 μL, 0.090 mmol) was added. After 1 h, a new portion of donor **7** (270 mg, 0.37 mmol) in CH_2Cl_2 (5 mL) was added, and the mixture was stirred for 16 h. The reaction was quenched with pyridine (40 μL, 0.49 mmol), the resulting mixture was diluted with CH_2Cl_2 and filtered through a pad of Celite, and the filtrate was washed successively with saturated aq $NaHCO_3$ solution and water and concentrated. Column chromatography of the residue (gradient elution 13:1→9:1 toluene−EtOAc) gave a mixture of tetrasaccharide **26** and its β-anomer. Preparative HPLC (17:1 toluene−acetonitrile) of this mixture afforded individual **26** (498 mg, 0.27 mmol, 59%) as well as its β-anomer (66 mg, 8%). Data for **26**: R_f 0.55 (5:1 toluene−EtOAc); $[\alpha]^{19}_D$ +53.7 (*c* 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, δ_H) 8.03−7.03 (m, 55H, Ar), 5.87 (t, $J_{3^{IV},4^{IV}}$ = 9.9 Hz, 1H, H-3^{IV}), 5.85 (t, $J_{3^{II},4^{II}}$ = 9.9 Hz, 1H, H-3^{II}), 5.53 (dd, $J_{2^{II},3^{II}}$ = 9.6 Hz, $J_{2^{II},1^{II}}$ = 8.2 Hz, 1H, H-2^{II}), 5.46 (t, $J_{4^{II},5^{II}}$ = 9.8 Hz, 1H, H-4^{II}), 5.25 (d, $J_{1^{IV},2^{IV}}$ = 3.2 Hz, 1H, H-1^{IV}), 5.04 (d, $J_{1^{II},2^{II}}$ = 8.0 Hz, 1H, H-1^{II}), 4.89 (d, $J_{A,B}$= 10.6 Hz, 1H, PhC*H*$_2$A), 4.82 (m, 1H, PhC*H*$_2'$A), 4.81 (br d, 1H, H-1^{I}), 4.73 (m, 2H, PhC*H*$_2$B, PhC*H*$_2''$A), 4.67 (d, $J_{1^{III},2^{III}}$ = 3.5 Hz, 1H, H-1^{III}), 4.61−4.53 (m, 4H, PhC*H*$_2'$B, PhC*H*$_2''$B, PhC*H*$_2'''$), 4.49 (m, 1H, H-6A^{IV}), 4.45 (d, $J_{A'''',B''''}$ = 12.5 Hz, 1H, PhC*H*$_2''''$A), 4.40 (d, $J_{B'''',A''''}$= 11.9 Hz, 1H, PhC*H*$_2''''$B), 4.37−4.30 (m, 4H, H-6A^{III}, PhC*H*$_2'''''$A, H-5^{IV}, H-6B^{IV}), 4.28 (br d, 1H, H-4^{I}), 4.25 (dd, 1H, H-6B^{III}), 4.21 (d, 1H, PhC*H*$_2'''''$B), 4.15 (dd, $J_{3^{I},4^{I}}$ = 2.3 Hz, $J_{3^{I},2^{I}}$ = 11.2 Hz, 1H, H-3^{I}), 4.06 (m, 1H, H-5^{I}), 4.03 (m, 1H, H-5^{II}), 3.94−3.88 (m, 3H, H-6A^{I}, H-5^{III}, H-3^{III}), 3.85 (dd, $J_{6A^{II},5^{II}}$ = 4.7 Hz, $J_{6A^{II},6B^{II}}$ = 10.4 Hz, 1H, H-6A^{II}), 3.73−3.66 (m, 3H, H-4^{IV}, H-2^{I}, H-6B^{II}), 3.61 (dd, $J_{2^{IV},3^{IV}}$ = 10.1 Hz, $J_{2^{IV},1^{IV}}$ = 3.2 Hz, 1H, H-2^{IV}), 3.58 (m, 1H, H-6B^{I}), 3.53−3.48 (m, 2H, H-4^{III}, H-2^{III}), 3.32 (s, 3H, C*H*$_3$O), 2.10 (s, 3H, C*H*$_3$CO); ^{13}C NMR (75 MHz, $CDCl_3$, δ_C) 170.5 (CH$_3$*C*O), 165.4, 165.1, 164.7 (Ph*C*O), 138.4, 138.3, 137.7, 137.6, (*ipso*-Ph (Bn)), 133.3, 133.0, 132.9 (*ipso*-Ph (Bz)), 130.2, 129.9, 129.7, 129.6, 129.3, 129.0, 128.9, 128.5, 128.1, 127.9, 127.7, 127.6, 127.2, 125.3 (Ar), 102.6 (C-1^{II}), 98.7 (C-1^{I}), 97.9 (C-1^{IV}), 97.3 (C-1^{III}), 82.0 (C-3^{III}), 80.4 (C-4^{III}), 78.2 (C-2^{IV}), 78.1 (C-4^{I}), 77.2 (C-3^{I}), 77.0 (C-2^{III}), 76.1 (C-4^{IV}), 75.7 (Ph*C*H$_2$), 74.8 (Ph*C*H$_2'$), 74.0 (C-3^{IV}), 73.8 (Ph*C*H$_2'''$), 73.6 (C-5^{I}), 73.3 (Ph*C*H$_2''$, Ph*C*H$_2''''$), 73.1 (C-3^{II}), 72.7 (Ph*C*H$_2''''$), 71.4 (C-2^{II}), 70.8 (C-5^{II}), 70.0 (C-4^{II}), 69.4 (C-6^{II}), 69.1 (C-5^{III}), 68.9 (C-5^{IV}), 67.8 (C-6^{I}), 63.4 (C-6^{III}), 63.0 (C-6^{IV}), 59.7 (C-2^{I}), 55.2 (*C*H$_3$O), 20.9 (*C*H$_3$CO). Anal. Calcd for $C_{104}H_{101}N_3O_{26}$: C, 69.05; H, 5.63; N, 2.32. Found: C, 68.99; H, 5.51; N, 2.27.

Methyl 6-*O*-Benzoyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[3-*O*-benzoyl-2,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (27). To a chilled solution of **26** (474 mg, 0.26 mmol) in a mixture of CH_2Cl_2 (15 mL) and MeOH (30 mL) was added a solution of HCl in MeOH prepared by adding AcCl (3.4 mL, 47.9 mmol) to MeOH (15 mL). The reaction mixture was kept at room temperature for 5 h, diluted with toluene, and evaporated, and HCl was removed by coevaporation with toluene. Purification of the residue by flash chromatography (9:1 toluene−EtOAc) yielded **27** (402 mg, 0.23 mmol, 88%): R_f 0.24 (10:1 toluene−EtOAc); $[\alpha]^{20}_D$ +54.7 (*c* 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.04−7.06 (m, 55H, Ar), 5.88 (t, $J_{3^{II},4^{II}}$ = 10.0 Hz, $J_{3^{IV},4^{IV}}$ = 10.0 Hz, 2H, H-3^{II}, H-3^{IV}), 5.69 (t, $J_{2^{II},3^{II}}$ = 8.2 Hz, 1H, H-2^{II}), 5.61 (t, $J_{4^{II},5^{II}}$ = 9.8 Hz, 1H, H-4^{II}), 5.31 (d, $J_{1^{IV},2^{IV}}$ = 3.2 Hz, 1H, H-1^{IV}), 5.05 (d, $J_{1^{II},2^{II}}$ = 7.9 Hz, 1H, H-1^{II}), 4.95 (d, $J_{A,B}$ = 10.7 Hz, 1H, PhC*H*$_2$A), 4.87 (d, $J_{A',B'}$ = 11.2 Hz, 1H, PhC*H*$_2'$A), 4.81 (m, 2H, H-1^{I}, PhC*H*$_2$B), 4.75 (d, $J_{A'',B''}$ = 12.4 Hz, 1H, PhC*H*$_2''$A), 4.66 (d, $J_{1^{III},2^{III}}$ = 3.5 Hz, 1H, H-1^{III}), 4.64−4.56 (m, 4H, PhC*H*$_2''$B, PhC*H*$_2'''$, PhC*H*$_2'$B), 4.47 (d, $J_{A'''',B''''}$ = 12.0 Hz, 1H, PhC*H*$_2''''$A), 4.41 (d, $J_{A'''',B''''}$ =12.0 Hz, $J_{B'''',A''''}$ =12.0 Hz, 2H, PhC*H*$_2''''$B, PhC*H*$_2''''$A), 4.32 (br d, 1H, H-4^{I}), 4.28 (m, 2H, H-6A^{III}, PhC*H*$_2''''$B), 4.22 (m, 1H, H-5^{I}), 4.17 (dd, 1H, H-6B^{III}), 4.14 (dd, $J_{3^{I},4^{I}}$ = 2.2 Hz, 1H, H-3^{I}), 4.09−3.99 (m, 3H, H-5^{IV}, H-5^{II}, H-3^{III}), 3.92 (m, 2H, H-6A^{I}, H-6A^{IV}), 3.88−3.81 (m, 2H, H-5^{III}, H-6A^{II}), 3.77 (m, 1H, H-6B^{IV}), 3.73−3.61 (m, 4H, H-2^{I}, H-6B^{II}, H-4^{IV}, H-6B^{I}), 3.54−3.47 (m, 3H, H-2^{IV}, H-2^{III}, H-4^{III}), 3.35 (s, 3H, C*H*$_3$O), 3.12 (br s, 1H, O*H*); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 165.4, 165.1 (Ph*C*O), 138.6, 138.4, 137.8 (*ipso*-Ph (Bn)), 133.4, 133.2, 133.0, 132.8 (*ipso*-Ph (Bz)), 102.8 (C-1^{II}), 98.7 (C-1^{I}), 98.1 (C-1^{IV}), 97.5 (C-1^{III}), 81.8 (C-3^{III}), 80.2 (C-4^{III}), 78.3 (C-2^{IV}), 78.2 (C-4^{I}), 77.4 (C-2^{III}), 77.3 (C-3^{I}), 76.4 (C-4^{IV}), 75.8 (Ph*C*H$_2$), 74.8 (Ph*C*H$_2'$), 73.9 (C-3^{II} or C-3^{IV}), 73.7 (Ph*C*H$_2'''$), 73.3 (C-5^{II}, Ph*C*H$_2''$, Ph*C*H$_2''''$), 73.1 (C-3^{II} or C-3^{IV}), 72.7 (Ph*C*H$_2''''$), 71.7 (C-5^{I}), 71.6 (C-2^{II}), 70.4 (C-5^{IV}), 69.5 (C-4^{II}), 69.3 (C-6^{II}), 69.2 C-5^{III}), 67.2 (C-6^{I}), 63.3 (C-6^{III}), 61.9 (C-6^{IV}), 59.9 (C-2^{I}), 55.3 (*C*H$_3$O). Anal. Calcd for $C_{102}H_{99}N_3O_{25}$: C, 69.34; H, 5.65; N, 2.38. Found: C, 69.35; H, 5.51; N, 2.33.

Methyl 6-*O*-Benzoyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→6)-3-*O*-benzoyl-2,4-di-O-benzyl-α-D-glucopyranosyl-(1→4)]-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (28). A solution of tetrasaccharide acceptor **27** (356 mg, 0.20 mmol) and rhamnosyl bromide **4** (165 mg, 0.31 mmol) in dry CH_2Cl_2 (16.5 mL) was added via a cannula under argon into a flask containing tetramethylurea (36 μL, 0.30 mmol) and AW-300 molecular sieves (1.9 g). The mixture was stirred for 90 min at room temperature, and then a solution of AgOTf (76 mg, 0.30 mmol) in dry toluene (4 mL) was added. After the mixture was stirred for 2 h, full conversion of acceptor **27** was observed. Pyridine (0.5 mL) was added, and the reaction mixture was diluted with CH_2Cl_2 (70 mL), filtered through a pad of Celite, and successively washed with a mixture of saturated aq $NaHCO_3$ and $Na_2S_2O_3$ 1 M (1:1) and water. After concentration of the organic solution and purification of the residue by flash chromatography (15:1 toluene-EtOAc), pentasaccharide **28** (395 mg, 0.18 mmol, 88%) was obtained: R_f 0.38 (8:1 toluene−EtOAc); $[\alpha]^{21}_D$ +88.0 (*c* 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.14−7.05 (m, 70H, Ar), 6.00−5.90 (m, 3H, H-3^{V}, H-3^{II}, H-3^{IV}), 5.82 (br d, 1H, H-2^{V}), 5.70 (t, 1H, H-4^{V}), 5.57−5.50 (m, 2H, H-2^{II}, H-4^{II}), 5.37 (d, $J_{1^{IV},2^{IV}}$ = 2.7 Hz, 1H, H-1^{IV}), 5.21 (d, $J_{1^{II},2^{II}}$ = 7.9 Hz, 1H, H-1^{II}), 5.93 (d, $J_{1^{I},2^{I}}$ = 3.2 Hz, 1H, H-1^{I}), 4.84 (d, $J_{1^{V},2^{V}}$ = 3.7 Hz, 1H, H-1^{V}), 4.82 (m, 2H, PhC*H*$_2$), 4.73 (d, 1H, H-1^{III}), 4.71−4.47 (m, 8H, PhC*H*$_2$), 4.40−4.35 (m, 3H, H-6A^{III}, H-5^{V}, PhC*H*$_2$), 4.28−4.17 (m, 5H, H-6B^{III}, PhC*H*$_2$, H-4^{I}, H-3^{I}, H-5^{IV}), 4.13−4.02 (m. 3H, H-6A^{IV}, H-5^{I}, H-5^{II}), 3.93−3.87 (m, 3H, H-6A^{I}, H-3^{III}, H-5^{III}), 3.84−3.75 (m, 2H, H-6A^{II}, H-4^{IV}), 3.74−3.68 (m, 3H, H-2^{I}, H-6B^{I}, H-6B^{II}), 3.66 (dd, 1H, H-2^{IV}), 3.52−3.46 (m, 3H, H-4^{III}, H-2^{III}, H-6B^{IV}), 3.36 (s, 3H, C*H*$_3$O), 1.36 (d, 3H, H-6^{V}); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 166.1, 166.0, 165.6, 165.1, 165.0 (Ph*C*O), 138.1, 138.0, 137.7, 137.6 (*ipso*-Ph (Bn)), 133.3, 133.1, 133.0, 132.8 (*ipso*-Ph (Bz)), 101.9 (C-1^{II}), 98.9 (C-1^{I}), 98.4 (C-1^{V}), 98.0 (C-1^{IV}), 97.5 (C-1^{III}), 81.9 (C-3^{III}), 80.2 (C-4^{III}), 78.5 (C-2^{IV}), 78.3 (C-4^{I}), 77.2 (C-2^{III}), 76.2 (C-4^{IV}), 76.0 (C-3^{I}), 75.7, 74.9, 74.4 (Ph*C*H$_2$), 74.3 (C-3^{IV}), 73.4 (C-3^{II}), 73.2 (C-5^{I}, Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.1 (C-4^{V}), 71.9 (C-2^{II}), 70.9 (C-2^{V}), 70.6 (C-5^{II}), 70.4 (C-5^{IV}), 70.2 (C-3^{V}), 70.1 (C-4^{II}), 69.4 (C-6^{II}), 69.3 (C-5^{III}), 68.0 (C-6^{I}), 67.5 (C-6^{IV}), 66.8 (C-5^{V}), 63.4 (C-6^{III}), 59.7 (C-2^{I}), 55.1 (*C*H$_3$O), 17.6 (C-6^{V}). Anal. Calcd for $C_{129}H_{121}N_3O_{32}$: C, 69.62; H, 5.48; N, 1.89. Found: C, 69.42; H, 5.70; N, 1.85.

Methyl 2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→6)-2,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranoside (29). To a solution of pentasaccharide **28** (56 mg, 0.025 mmol) in CH_2Cl_2 (1 mL) and MeOH (1 mL) was added 1 M MeONa in methanol (0.4 mL). After 16 h at rt, TLC (5:1 CH_2Cl_2−MeOH) showed the formation of a single product. The solution was made neutral by Amberlyte IRA-120 (H^+), and then the resin was filtered off and the filtrate was concentrated. NMR spectra of the product showed the presence of one benzoyl group,

presumably at O-3 of the rhamnose residue. A solution of the product in MeOH (3.5 mL) was treated with aq solution of NaOH 5 M (0.5 mL) for 20 h, neutralized with Amberlyte IRA-120 (H^+), filtered, and concentrated. The residue was treated with Amberlyst A-26 (HCO_3^-) in MeOH to remove benzoic acid. The resin was filtered off and the solution was concentrated to provide product **29** (35 mg, 0.025 mmol) quantitatively: R_f 0.41 (10:1 CH_2Cl_2−MeOH); $[\alpha]^{23}_D$ +78.8 (*c* 1, MeOH); ^{1}H NMR (500 MHz, CD_3OD, δ_H) 7.40−7.06 (m, 30H, Ar), 5.03 (d, $J_{1^{IV},2^{IV}}$ = 3.2 Hz, 1H, H-1^{IV}), 4.99 (d, $J_{A,B}$ = 11.1 Hz, 1H, PhCH_2), 4.91 (d, $J_{1^{III},2^{III}}$ = 3.6 Hz, 1H, H-1^{III}), 4.89−4.85 (m, 2H, PhCH_2, H-1^I), 4.83−4.54 (m, 9H, PhCH_2, H-1^V), 4.49 (d, $J_{1^{II},2^{II}}$ = 7.9 Hz, 1H, H-1^{II}), 4.33 (br d, 1H, H-4^I), 4.28 (m, 1H, H-5^{IV}), 4.20 (dd, $J_{3^I,4^I}$ = 2.5 Hz, $J_{3^I,2^I}$ = 11.0 Hz, 1H, H-3^I), 4.17, (d, 1H, PhCH_2), 4.09−4.04 (m, 2H, H-3^{IV}, H-5^I), 4.03 (d, 1H, PhCH_2), 3.93−3.85 (m, 4H, H-6A^{IV}, H-6A^{II}, H-2^V, H-3^{III}), 3.84−3.76 (m, 3H, H-6A^{III}, H-6A^I, H-6B^{II}), 3.76−3.68 (m, 5H, H-6B^{III}, H-5^{III}, H-5^V, H-3^V, H-2^I), 3.62 (dd, $J_{6B^{IV},6A^{IV}}$ = 11.0 Hz, $J_{6B,5}$ = 3.6 Hz, 1H, H-6B^{IV}), 3.58−3.49 (m, 4H, H-6B^I, H-4^{IV}, H-2^{III}, H-4^{III}), 3.41−3.36 (m, 2H, H-3^{II}, H-4^V), 3.32 (m, 1H, H-2^{IV}), 3.31 (s, 3H, CH_3O), 3.23 (t, $J_{4^{II},5^{II}}$ = 9.4 Hz, 1H, H-4^{II}), 3.19 (t, $J_{2^{II},3^{II}}$ = 8.8 Hz, 1H, H-2^{II}), 1.30 (d, 3H, H-6^V); ^{13}C NMR (125 MHz, CD_3OD, δ_C) 140.1, 139.9, 139.6, 139.5 (*ipso*-Ph (Bn)), 133.9, 130.7, 129.6, 129.4, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4 (Ar), 106.4 (C-1^{II}), 102.2 (C-1^V), 100.5 (C-1^I), 98.7 (C-1^{IV}), 98.3 (C-1^{III}), 83.4 (C-3^{III}), 81.6 (C-2^{IV}), 81.3 (C-4^{III}), 79.5 (Ph*C*H$_2$), 79.1 (C-2^{III}), 78.2 (C-3^I), 77.94 (C-4^I), 77.86 (C-4^V), 76.6 (Ph*C*H$_2$), 76.2 (C-4^{IV}), 76.1 (Ph*C*H$_2$), 74.8 (C-2^{II}), 74.7 (C-3^{IV}), 74.3 (Ph*C*H$_2$), 74.1 (C-3^{II}), 74.0 (Ph*C*H$_2$), 72.8 (C-5^{III}), 72.5 (C-4^{II}), 72.3 (C-5^I), 72.2 (C-2^V), 72.1 (C-3^V), 71.3 (C-5^{IV}), 71.0 (C-6^I), 69.9 (C-5^V or C-5^{II}), 69.7 (C-6^{II}), 67.7 (C-6^{IV}), 61.7 (C-6^{III}), 61.1 (C-2^I), 18.5 (C-6^V), 55.5 (*C*H$_3$O); HR ESI MS calcd for $[M + K + H]^{+2}$ ($C_{73}H_{89}N_3O_{24}$ + K + H)/2 715.7776, found 715.7725.

Methyl α-D-Glucopyranosyl-(1→6)-β-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→6)-α-D-glucopyranosyl-(1→4)]-2-deoxy-2-dimethylamino-α-D-galactopyranoside (30). Pd(OH)$_2$/C (20%, 7 mg) was added to a solution of azide **29** (8 mg, 0.0057 mmol) in MeOH (1 mL) containing formic acid (0.5%, v/v) and acetic acid (5%, v/v), and the mixture was stirred in a hydrogen atmosphere. After 3 days, a new portion of the catalyst (4.5 mg) was added, and stirring under hydrogen was continued for 4 days. The catalyst was filtered off through a membrane filter (0.45 μm), and the filtrate was concentrated to give **30** (2.5 mg, 52%): R_f 0.09 (5:5:4:1 BuOH−EtOH−H_2O−NH_3 aq); ^{1}H NMR (500 MHz, D_2O, δ_H) 5.26 (d, $J_{1^I,2^I}$ = 2.9 Hz, 1H, H-1^I), 4.99 (d, $J_{1^{IV},2^{IV}}$ = 3.5 Hz, 1H, H-1^V), 4.97 (d, $J_{1^{III},2^{III}}$ = 3.7 Hz, 1H, H-1^{III}), 4.79 (br s, 1H, H-1^V), 4.72 (d, 1H, H-1^{II}), 4.57 (br dd, 1H, H-3^I), 4.5 (br d, 1H, H-4^I), 4.08 (m, 1H, H-5^{IV}), 4.04−3.98 (m, 2H, H-5^I, H-2^V), 3.92−3.59 (m, 16H, H-6A^{II}, H-6^I, H-6A^{IV}, H-6A^{III}, H-2^I, H-6B^{II}, H-3^V, H-6B^{IV}, H-6B^{III}, H-3^{IV}, H-5^V, H-5^{III}, H-5^{II}, H-3^{III}, H-4^{IV}), 3.57 (dd, $J_{2^{III},3^{III}}$ = 9.9 Hz, $J_{2^{III},1^{III}}$ = 3.7 Hz, 1H, H-2^{III}), 3.53−3.48 (m, 2H, H-2^{IV}, H-3^{II}), 3.47−3.41 (m, 5H, CH_3O, H-4^{III}, H-4^V), 3.31−3.25 (m, 2H, H-4^{II}, H-2^{II}), 2.99 (br s, 6H, (CH_3)$_2$N), 1.30 (d, $J_{6^V,5^V}$ = 6.2 Hz, 3H, H-6^V); ^{13}C NMR (125 MHz, D_2O, δ_C) 105.9 (C-1^{II}), 102.3 (C-1^V), 100.6 (C-1^{IV}), 100.0 (C-1^{III}), 97.1 (C-1^I), 78.3 (C-4^I), 77.0 (C-3^{II}), 76.0 (C-5^{III}), 74.5 (C-5^{II}), 74.3 (C-2^{II}), 73.9 (C-3^{IV}), 73.3 (C-4^{III}, C-3^{III}), 73.0 (C-2^{IV}), 72.4 (C-2^{III}), 71.4 (C-3^V), 71.2 (C-2^V), 70.6 (C-4^V), 70.1 (C-4^{IV}), 70.0 (C-5^V), 69.2 (C-6^{II}), 67.7 (C-6^{IV}), 63.0 (C-2^I), 61.7 (C-6^I, C-6^{III}), 56.0 (*C*H$_3$O), 42.4 ((*C*H$_3$)$_2$N), 18.2 (C-6^V); HR ESI MS calcd for $[M + H]^+$ $C_{33}H_{59}NO_{24}$ + H 854,3505, found 854.3505.

Methyl α-D-Glucopyranosyl-(1→6)-β-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→6)-α-D-glucopyranosyl-(1→4)]-2-acetamido-2-deoxy-α-D-galactopyranoside (32). Azido Group Reduction with Hydrogen Sulfide. Azide **29** (22.9 mg, 0.016 mmol) was dissolved in a mixture of CH_3CN (0.65 mL), triethylamine (0.5 mL), water (0.1 mL), and diisopropylamine (0.2 mL) under Ar, and H_2S was bubbled through the solution until the reaction mixture turned into a slightly yellow gel (∼1 min). More CH_3CN (1 mL) and water (0.3 mL) were added to dissolve the gel. After a few minutes, TLC showed the complete conversion of starting **29**. Amberlyst A-26 (OH^-) was added until the solution became colorless. The resin was filtered, and the solution was concentrated to give amine **31**: ^{1}H NMR (500 MHz, CD_3OD) 7.40−7.05 (m, 30H, Ar), 5.01 (d, $J_{1^{IV},2^{IV}}$ = 3.4 Hz, 1H, H-1^{IV}), 5.00−4.97 (d, 1H, PhCH_2), 4.95 (d, $J_{1^{III},2^{III}}$ = 3.6 Hz, 1H, H-1^{III}), 4.88 (d, 1H, PhCH_2), 4.83−4.74 (m, 3H, PhCH_2), 4.73 (m, 2H, H-1^I, H-1^V), 4.70−4.56 (m, 5H, PhCH_2), 4.39 (d, $J_{1^{II},2^{II}}$ = 7.9 Hz, 1H, H-1^{II}), 4.30 (m, 1H, H-5^{IV}), 4.25 (br d, 1H, H-4^I), 4.14 (d, $J_{A,B}$ = 11.9 Hz, 1H, PhCH_2′), 4.07 (t, $J_{3^{IV},4^{IV}}$ = 9.4 Hz, 1H, H-3^{IV}), 4.01 (m, 3H, H-5^I, PhCH_2), 3.95−3.90 (m, 2H, H-6A^{IV}, H-6A^{II}), 3.88−3.83 (m, 3H, H-3^{III}, H-6A^{III}, H-2^V), 3.82−3.76 (m, 3H, H-6B^{III}, H-3^I, H-6A^I), 3.76−3.70 (m, 4H, H-5^{III}, H-5^V, H-3^V, H-6B^{III}), 3.63 (dd, $J_{6A^{IV},6B^{IV}}$ = 11.1 Hz, $J_{6A^{IV},5^{IV}}$ = 3.4 Hz, 1H, H-6B^{IV}), 3.60−3.55 (m, 2H, H-5^{II}, H-6B^I), 3.54−3.49 (m, 3H, H-2^{III}, H-4^{III}, H-4^{IV}), 3.41−3.35 (m, 2H, H-4^V, H-3^{II}), 3.32 (dd, 1H, H-2^{IV}), 3.31 (s, 3H, OCH_3), 3.23−3.18 (m, 3H, H-2^{II}, H-4^{II}, H-2^I), 1.30 (d, 3H, H-6^V); ^{13}C NMR (125 MHz, CD_3OD) 140.2, 139.9, 139.6 (*ipso*-Ph (Bn)), 129.5, 129.3, 129.2, 129.1, 128.9, 128.8, 128.6, 128.4 (Ar), 107.3 (C-1^{II}), 102.1 (C-1^V), 101.3 (C-1^I), 98.8 (C-1^{IV}), 98.4 (C-1^{III}), 83.4 (C-3^{III}), 82.8 (C-3^I), 81.7 (C-2^{IV}), 81.4 (C-2^{III}), 79.4 (C-4^{IV}), 78.1 (C-3^{II}), 77.8 (C-4^I), 76.6 (Ph*C*H$_2$), 76.4 (C-5^{II}), 76.2, 76.0 (Ph*C*H$_2$), 75.2 (C-2^{II}), 74.6 (C-3^{III}), 74.3, 74.1 (Ph*C*H$_2$), 74.0 (C-4^V), 72.9 (C-5^{III}), 72.5 (C-5^I, C-4^{II}), 72.2 (C-3^V, C-2^V), 71.4 (C-6^I, C-5^{IV}), 70.2 (C-6^{II}), 70.0 (C-5^V), 67.8 (C-6^{IV}), 61.8 (C-6^{III}), 55.6 (O*C*H$_3$), 52.2 (C-2^I), 18.9 (C-6^V).

To a solution of **31** obtained in MeOH (1 mL) were added acetic anhydride (3 μL) and Amberlyst A-26 (HCO_3^-). The mixture was stirred for 20 min and filtered through a membrane filter, and the filtrate was concentrated to provide *N*-acetylated product (18.1 mg, 80%), R_f 0.2 ($CHCl_3$−MeOH, 9:1). It was dissolved in MeOH (1 mL), Pd(OH)$_2$/C (13 mg) was added, the mixture was stirred for 18 h under a hydrogen atmosphere, and then the catalyst was filtered off through a pad of Celite. The filtrate was concentrated, and the residue was purified by size-exclusion chromatography on a TSK HW-40 (S) column (2.5 × 40 cm) in 0.1 M aq AcOH to yield **32** (7.6 mg, 55% over three steps from azide **29**): R_f 0.2 (5:5:4:1 BuOH−EtOH−H_2O−NH_3 aq); $[\alpha]^{23}_D$ +75.2 (*c* 1, H_2O); ^{1}H NMR (300 MHz, D_2O) 4.94 (d, $J_{1^{III},2^{III}}$ = 3.3 Hz, 1H, H-1^{III}), 4.89 (d, $J_{1^{IV},2^{IV}}$ = 3.1 Hz, 1H, H-1^{IV}), 4.80−4.74 (m, 2H, H-1^I, H-1^V), 4.45 (d, $J_{1^{II},2^{II}}$ = 7.7 Hz, 1H, H-1^{II}), 4.39 (dd, $J_{2^I,3^I}$ = 11.2 Hz, $J_{2^I,1^I}$ = 3.4 Hz, 1H, H-2^I), 4.29 (m, $J_{5^{IV},6^{IV}}$ = 10.0 Hz, 1H, H-5^{IV}), 4.16 (br s, 1H, H-4^I), 4.05 (m, 1H, H-3^I), 4.00−3.95 (m, 2H, H-5^I, H-2^V), 3.86−3.51 (m, 16H, H-6^I, H-6A^{II}, H-6A^{IV}, H-3^{IV}, H-6A^{III}, H-3^V, H-6B^{II}, H-6B^{III}, H-6B^{IV}, H-5^V, H-3^{III}, H-5^{III}, H-5^{II}, H-4^{IV}, H-2^{III}), 3.48−3.35 (m, 7H, H-2^{IV}, H-4^{III}, H-3^{II}, H-4^V, CH_3O), 3.25 (t, 1H, H-4^{II}), 3.08 (t, 1H, H-2^{II}), 2.01 (s, 3H, CH_3CO), 1.31 (d, $J_{6^V,5^V}$ = 6.2 Hz, 3H, H-6^V); ^{13}C NMR (125 MHz, D_2O) 176.0 (CH$_3$*C*O), 105.9 (C-1^{II}), 102.5 (C-1^V), 100.5 (C-1^{IV}), 99.7 (C-1^I), 99.4 (C-1^{III}), 77.7 (C-3^I), 77.2 (C-4^I), 77.0 (C-3^{II}), 75.6 (C-5^{II}), 74.7 (C-5^{III}), 74.3 (C-2^{II}), 74.1 (C-3^{IV}), 73.4 (C-4^V), 73.2 (C-5^I, C-2^{IV}, C-3^{III}), 72.6 (C-2^{III}), 72.0 (C-4^{II}), 71.5 (C-5^{IV}, C-3^V), 71.3 (C-2^V), 70.5 (C-4^{III}), 70.4 (C-4^{IV}), 70.1 (C-5^V), 68.5 (C-6^{II}), 67.7 (C-6^{IV}), 61.8 (C-6^I), 61.7 (C-6^{III}), 56.6 (*C*H$_3$O), 50.4 (C-2^I), 23.5 (*C*H$_3$CO), 18.4 (C-6^V); HR ESI MS calcd for $[M + Na]^+$ $C_{33}H_{57}NO_{25}$ + Na 890.3117, found 890.3115.

Methyl α-D-Glucopyranosyl-(1→6)-β-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→6)-α-D-glucopyranosyl-(1→4)]-2-[*N*-(*tert*-butoxycarbonyl)-L-alanylamino]-2-deoxy-α-D-galactopyranoside (35). Azido Group Reduction with DTT. To a solution of azide **29** (33.9 mg, 0.024 mmol) in a mixture of dry MeCN and diisopropylamine (600 μL, 3:1) was added DTT (7.5 mg, 0.049 mmol). After 1 h, the conversion of the starting material was approximately 50%, but then the reaction stopped. More DTT (8.5 mg, 0.055 mmol) was added and the mixture was stirred for next 24 h after which time the full conversion of azide **29** was observed. The reaction mixture was taken to dryness. Amine **31**, identical to that obtained by reduction with H_2S with respect to the R_f value and NMR data, can be purified

by column chromatography (gradient elution 10:1 → 5:1 $CHCl_3$−MeOH). To a solution of the raw reaction mixture in dry DMF (1 mL) were added succinimidyl active ester **33** (10.3 mg, 0.036 mmol) and Et_3N (2 μL, 0.014 mmol), and the solution was stirred for 24 h at rt. Then the mixture was diluted with toluene (2 mL) and taken to dryness. Column chromatography of the residue (gradient elution 15:1 → 10:1 $CHCl_3$−MeOH) provided L-alanyl pentasaccharide **34** (29.0 mg, 0.019 mmol, 79%): R_f 0.20 (11:1 $CHCl_3$−MeOH); $[\alpha]^{16}_D$ +57.6 (*c* 1, MeOH); ^{1}H NMR (500 MHz, CD_3OD) 7.40−7.05 (m, 30H, Ar), 5.00−4.93 (m, 3H, H-1^{III}, H-1^{IV}, PhCH_2), 4.89−4.72 (m, 4H, PhCH_2), 4.72−4.56 (m, 7H, H-1^{I}, H-1^{V}, PhCH_2), 4.47−4.41 (d, 2H, H-1^{II}, H-2^{I}), 4.33 (m, 1H, H-5^{IV}), 4.21 (br s, 1H, H-4^{I}), 4.19−4.12 (m, 2H, H-3^{IV}, PhCH_2), 4.12−3.98 (m, 5H, H-3^{I}, C*H*CH_3 (Ala), H-5^{I}, PhCH_2), 3.96−3.68 (m, 11H, H-6A^{II}, H-6A^{IV}, H-3^{III}, H-6A^{III}, H-2^{V}, H-6A^{I}, H-6B^{II}, H-5^{V}, H-5^{III}, H-3^{V}, H-6B^{III}), 3.64 (m, 1H, H-6B^{IV}), 3.61−3.52 (m, 4H, H-5^{II}, H-4^{IV}, H-6B^{I}, H-2^{III}), 3.49 (m, 1H, H-4^{III}), 3.41−3.33 (m, 3H, H-3^{II}, H-4^{V}, H-2^{IV}), 3.28 (s, 3H, CH_3O), 3.27−3.12 (m, 2H, H-4^{II}, H-2^{II}), 1.40 (s, 9H, (CH_3)$_3$CO), 1.29 (m, 6H, CH_3 (Ala), H-6^{V}); ^{13}C NMR (125 MHz, CD_3OD) 176.0 (C═O (Ala)), 140.1, 140.0, 139.8, 139.7, 139.6 (*ipso*-Ph (Ph)), 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6, 128.4 (Ph), 106.0 (C-1^{II}), 102.3 (C-1^{V}), 99.7 (C-1^{I}), 99.2 (C-1^{IV}), 98.3 (C-1^{III}), 83.4 (C-3^{III}), 81.6 (C-2^{IV}), 81.4 (C-2^{III}), 80.6 ((CH$_3$)$_3$*C*O), 79.4 (C-4^{IV}), 79.2 (C-4^{III}), 78.0 (C-4^{V}), 77.7 (C-4^{I}, C-3^{I}), 76.6 (C-5^{II}, Ph*C*H$_2$), 76.2, 75.9 (Ph*C*H$_2$), 74.7 (C-2^{II}), 74.4 (C-3^{IV}), 74.3 (Ph*C*H$_2$), 74.1 (C-3^{II}), 73.9 (Ph*C*H$_2$), 73.0 (C-5^{III}), 72.3 (C-4^{II}, C-3^{V}), 72.1 (C-2^{V}), 72.0 (C-5^{I}), 71.0 (C-5^{IV}, C-6^{I}), 69.9 (C-5^{V}, C-6^{II}), 67.9 (C-6^{IV}), 61.9 (C-6^{III}), 55.7 (*C*H$_3$O) 51.5 (CH$_3$*C*H (Ala)), 50.8 (C-2^{I}), 28.8 (*C*H$_3$ (Boc)), 18.9 (C-6^{V}), 18.7 (*C*H$_3$CH (Ala)).

To a solution of pentasaccharide **34** (29.0 mg, 0.019 mmol) in MeOH (1 mL) was added Pd(OH)$_2$/C (20%, 37 mg), and the reaction mixture was stirred under a slight overpressure of hydrogen for 3 days. Then water (0.2 mL) was added to enhance the solubility of debenzylated products and the stirring was continued for another day. The catalyst was filtered off, the filtrate was concentrated, and the residue was freeze-dried from water to give crude **35** (18.4 mg, 98%). An analytical sample of **35** was obtained by reversed-phase HPLC on a C-18 column (5 μm, 250 × 10 mm, 8:2 H_2O−CH_3CN): R_f 0.44 (5:5:2 $CHCl_3$−MeOH−H_2O), 0.65 (5:5:4:1 BuOH−EtOH−H_2O−NH_3aq); $[\alpha]_D^{13}$ +69.4 (*c* 1, H_2O); ^{1}H NMR (500 MHz, D_2O, δ_H) 4.99 (d, $J_{1^{III},2^{III}}$ = 3.5 Hz, 1H, H-1^{III}), 4.97 (d, $J_{1^{IV},2^{IV}}$ = 2.9 Hz, 1H, H-1^{IV}), 4.85 (d, $J_{1^{I},2^{I}}$ = 3.6 Hz, 1H, H-1^{I}), 4.81 (s, 1H, H-1^{V}), 4.52 (d, $J_{1^{II},2^{II}}$ = 7.9 Hz, 1H, H-1^{II}), 4.45 (dd, $J_{2^{I},3^{I}}$ = 11.2 Hz, 1H, H-2^{I}), 4.32 (m, 1H, H-5^{IV}), 4.23 (br s, 1H, H-4^{I}), 4.18−4.10 (m, 2H, H-3^{I}, C*H*CH_3 (Ala)), 4.06−4.01 (m, 2H, H-5^{I}, H-2^{V}), 3.91−3.56 (m, 16H, H-6^{I}, H-6A^{II}, H-6A^{III}, H-3^{IV}, H-6B^{II}, H-6A^{IV}, H-3^{V}, H-6B^{IV}, H-6B^{III}, H-5^{V}, H-5^{III}, H-3^{III}, H-5^{II}, H-4^{IV}, H-2^{III}), 3.52 (dd, $J_{2^{IV},3^{IV}}$ = 10.0 Hz, 1H, H-2^{IV}), 3.50−3.42 (m, 6H, H-3^{II}, H-4^{III}, H-4^{V}, CH_3O), 3.34 (t, 1H, H-4^{II}), 1.46 (s, 9H, CH_3 (Boc)), 1.35 (d, 3H, $J_{CH,CH3}$ = 7.2 Hz, CH_3CH (Ala)), 1.32 (d, 3H, $J_{6^{V},5^{V}}$ = 6.2 Hz, H-6^{V}); ^{13}C NMR (125 MHz, D_2O, δ_C): 105.5 (C-1^{II}), 102.5 (C-1^{V}), 100.7 (C-1^{IV}), 99.8 (C-1^{I}), 99.6 (C-1^{III}), 77.7 (C-4^{I}), 77.2 (C-3^{II}), 76.9 (C-3^{I}), 76.0 (C-5^{II}), 74.8 (C-5^{III}), 74.5 (C-2^{II}), 74.1 (C-3^{IV}), 73.6 (C-4^{V}), 73.4 (C-3^{III}, C-2^{IV}), 73.2 (C-5^{I}), 72.8 (C-2^{III}), 71.9 (C-4^{II}), 71.7 (C-3^{V}, C-5^{IV}), 71.4 (C-2^{V}), 70.8 (C-4^{III}), 70.6 (C-4^{IV}), 70.2 (C-5^{V}), 68.4 (C-6^{II}), 67.7 (C-6^{IV}), 61.9 (C-6^{I}, C-6^{III}), 56.9 (CH$_3$O), 52.0 (CH$_3$*C*H (Ala)), 50.7 (C-2^{I}), 29.2 (*C*H$_3$ (Boc)), 18.4 (C-6^{V}, *C*H$_3$CH (Ala)); HR ESI MS calcd for [M + K + H]$^{+2}$ ($C_{39}H_{68}N_2O_{27}$ + K + H)/2 518.1862, found 518.1842.

Methyl α-D-Glucopyranosyl-(1→6)-*β*-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→6)-α-D-glucopyranosyl-(1→4)]-2-(L-alanylamino)-2-deoxy-α-D-galactopyranoside (36). Lyophilized **35** (8.9 mg, 0.009 mmol) was dissolved in neat TFA (400 μL), the solution was kept for 5 min at 20 °C, and then taken to dryness (bath temperature <35 °C). The residual TFA was removed by coevaporation with toluene (2 × 1 mL). The residue was lyophilized from water to give **36** (9.0 mg, 100%): R_f 0.09 (5:5:4:1 BuOH−EtOH−H_2O−NH_3aq); $[\alpha]^{23}_D$ +70.3 (*c* 1, H_2O); ^{1}H NMR (500 MHz, D_2O, δ_H) 4.97 (d, 1H, H-1^{III}), 4.96 (d, 1H, H-1^{IV}), 4.83 (d, $J_{1^{I},2^{I}}$ = 3.6 Hz, 1H, H-1^{I}), 4.79 (br s, 1H, H-1^{V}), 4.51 (d, $J_{1^{II},2^{II}}$ = 8.0 Hz, 1H, H-1^{II}), 4.46 (dd, $J_{2^{I},3^{I}}$ = 11.2 Hz, 1H, H-2^{I}), 4.31 (m, 1H, H-5^{IV}), 4.24 (d, $J_{4^{I},3^{I}}$ = 2.7 Hz, 1H, H-4^{I}), 4.17 (dd, $J_{3^{I},4^{I}}$ = 2.8 Hz, $J_{3^{I},2^{I}}$ = 11.2 Hz, 1H, H-3^{I}), 4.04−4.01 (m, 2H, H-5^{I}, H-2^{V}), 3.89−3.55 (m, 17H, H-6^{I}, H-6A^{II}, C*H*CH_3 (Ala), H-6A^{IV}, H-6A^{III}, H-3^{IV}, H-6B^{II}, H-3^{IV}, H-3^{V}, H-6B^{IV}, H-6B^{III}, H-5^{V}, H-5^{III}, H-3^{III}, H-5^{II}, H-4^{IV}, H-2^{III}), 3.52 (dd, $J_{2^{IV},3^{IV}}$ = 10.0 Hz, $J_{2^{IV},1^{IV}}$ = 3.5 Hz, 1H, H-2^{IV}), 3.48−3.42 (m, 3H, H-4^{III}, H-3^{II}, H-4^{V}), 3.41 (s, 3H, CH_3O), 3.30 (t, $J_{4^{II},5^{II}}$ = 9.5 Hz, 1H, H-4^{II}), 3.14 (t, $J_{2^{II},3^{II}}$ = 8.6 Hz, 1H, H-2^{II}), 1.46 (d, $J_{CH3,CH}$ = 7.1 Hz, 3H, CH_3CH (Ala)), 1.31 (d, $J_{6,5}$ = 6.3 Hz, 3H, H-6^{V}); ^{13}C NMR (125 MHz, D_2O, δ_C) 105.7 (C-1^{II}), 102.5 (C-1^{V}), 100.5 (C-1^{IV}), 99.7 (C-1^{I}), 99.6 (C-1^{III}), 77.2 (C-4^{I}, C-3^{II}), 77.1 (C-3^{I}), 75.9 (C-5^{II}), 74.8 (C-5^{III}), 74.5 (C-2^{II}), 74.2 (C-3^{IV}), 73.6 (C-4^{V}), 73.4 (C-2^{IV}), 73.3 (C-3^{III}), 73.2 (C-5^{I}), 72.8 (C-2^{III}), 72.1 (C-4^{II}), 71.8 (C-3^{V}), 71.7 (C-5^{IV}), 71.5 (C-2^{V}), 70.8 (C-4^{III}), 70.6 (C-4^{IV}), 70.3 (C-5^{V}), 68.7 (C-6^{II}), 67.8 (C-6^{IV}), 62.0 (C-6^{I}), 61.9 (C-6^{III}), 56.7 (CH_3O), 51.0 (CH$_3$*C*H (Ala)), 50.9 (C-2^{I}), 18.6 (*C*H$_3$CH (Ala)), 18.5 (C-6^{V}); HR ESI MS calcd for [M + Na] $C_{34}H_{60}N_2O_{25}$ + Na 919.3383, found 919.3417; calcd for [M + H] $C_{34}H_{60}N_2O_{25}$ + H 897.3563, found 897.3593.

Methyl α-D-Glucopyranosyl-(1→6)-*β*-D-glucopyranosyl-(1→3)-[α-L-rhamnopyranosyl-(1→6)-α-D-glucopyranosyl-(1→4)]-2-(*N*-acetyl-L-alanylamino)-2-deoxy-α-D-galactopyranoside (37). To a solution of **36** (9.4 mg, 0.009 mmol) in dry MeOH (400 μL) were added acetic anhydride (1.9 μL, 0.020 mmol) and triethylamine (3.9 μL, 0.028). The solution was kept for 16 h at rt, then more Ac_2O (1.7 μL, 0.015 mmol) was added. After being kept for 2 h, the reaction mixture was diluted with toluene (0.5 mL) and concentrated. The residue was purified by size-exclusion chromatography (Sephadex G-15 column, 348 × 30 mm) in water to give **37** (6.0 mg, 0.006 mmol, 69%): R_f 0.41 (5:5:4:1 BuOH−EtOH−H_2O−NH_3(aq)); $[\alpha]^{23}_D$ +55.6 (*c* 1, H_2O); ^{1}H NMR (500 MHz, D_2O, δ_H) 4.96 (d, $J_{1^{III},2^{III}}$ = 3.7 Hz, 1H, H-1^{III}), 4.94 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1^{IV}), 4.79−4.77 (m, 2H, H-1^{V}, H-1^{IV}), 4.49 (d, $J_{1^{II},2^{II}}$ = 8.0 Hz, 1H, H-1^{II}), 4.43 (dd, $J_{2^{I},3^{I}}$ = 11.2 Hz, $J_{2^{I},1^{I}}$ = 3.6 Hz, 1H, H-2^{I}), 4.33−4.27 (m, 2H, H-5^{IV}, CH_3C*H*(NHAc)CO), 4.20 (d, $J_{4^{I},3^{I}}$ = 2.5 Hz, 1H, H-4^{I}), 4.15 (dd, $J_{3^{I},4^{I}}$ = 2.6 Hz, $J_{3^{I},2^{I}}$ = 11.3 Hz, 1H, H-3^{I}), 4.04−3.99 (m, 2H, H-5^{I}, H-2^{V}), 3.88−3.74 (m, 10H, H-6^{I}, H-6A^{II}, H-6A^{IV}, H-6A^{III}, H-6B^{II}, H-3^{IV}, H-3^{V}, H-6B^{IV}, H-6B^{III}), 3.72 (m, 1H, H-5^{V}), 3.70−3.54 (m, 5H, H-3^{III}, H-5^{III}, H-5^{II}, H-4^{IV}, H-2^{III}), 3.49 (dd, $J_{2^{IV},3^{IV}}$ = 10.0 Hz, $J_{2^{IV},1^{IV}}$ = 3.5 Hz, 1H, H-2^{IV}), 3.48−3.40 (m, 6H, H-3^{II}, H-4^{III}, H-4^{V}, CH_3O), 3.30 (t, $J_{4^{II},5^{II}}$ = $J_{4^{II},3^{II}}$ = 9.4 Hz, 1H, H-3^{II}), 3.11 (t, $J_{2,3}$ = 8.5 Hz, 1H, H-2^{II}), 2.04 (s, 3H, CH_3CO), 1.39 (d, $J_{CH3,CH}$ = 7.2 Hz, 3H, CH_3CH(NHAc)CO), 1.33 (d, $J_{6^{V},5^{V}}$ = 6.2 Hz, 3H, H-6^{V}); ^{13}C NMR (125 MHz, D_2O, δ_C) 175.5, 174.1 (CH$_3$*C*O, CH$_3$CH(NHAc)*C*O), 104.1 (C-1^{II}), 101.1 (C-1^{V}), 99.1 (C-1^{IV}), 98.3 (C-1^{I}), 98.1 (C-1^{III}), 75.8 (C-4^{I}), 75.7 (C-3^{II}), 75.3 (C-3^{I}), 74.4 (C-5^{II}), 73.3 (C-5^{III}), 73.1 (C-2^{II}), 72.9 (C-3^{IV}), 72.1 (C-4^{V}), 71.9 (C-2^{IV}), 71.8 (C-3^{III}, C-5^{I}), 71.3 (C-2^{III}), 70.6 (C-4^{II}), 70.2 (C-5^{IV}, C-3^{V}), 70.0 (C-2^{V}), 69.3 (C-4^{III}), 69.1 (C-4^{IV}), 68.8 (C-5^{V}), 67.1 (C-6^{II}), 66.3 (C-6^{IV}), 60.5 (C-6^{I}), 60.4 (C-6^{III}), 55.5 (*C*H$_3$O), 49.9 (CH$_3$*C*H(NHAc)CO), 49.4 (C-2^{I}), 21.7 (*C*H$_3$CO), 17.0 (*C*H$_3$CH(NHAc)CO), 16.6 (C-6^{V}); HR ESI MS [M + Na] calcd for $C_{36}H_{62}N_2O_{26}$ + Na 961.3489, found: 961.3468.

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Supporting Information Available: Selected ^{1}H, ^{13}C, 2-D NMR spectra and procedures, which were not given in the article, are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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