Synthesis of a homologous series of galactofuranose-containing mycobacterial arabinogalactan fragments

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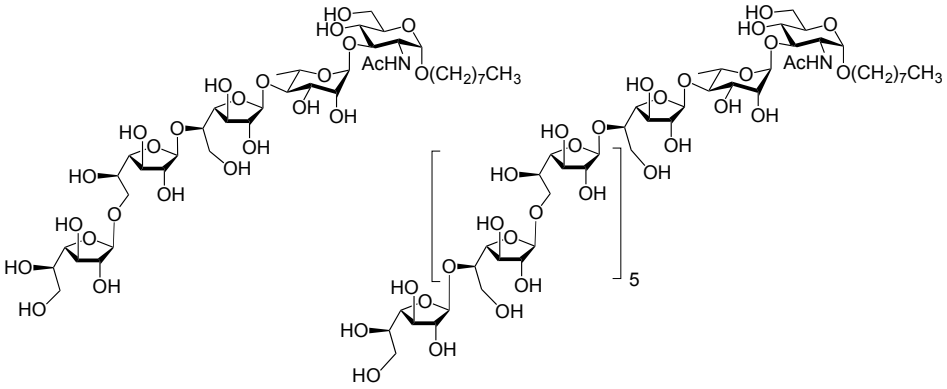
Graphical Abstract



Abstract

Mycobacteria, including the human pathogen *Mycobacterium tuberculosis* the causative agent of tuberculosis, produce a complex cell wall structure made of carbohydrates and lipids. The major structural element of the mycobacterial cell wall is a glycoconjugate called the mycolic acid–arabinogalactan–peptidoglycan (mAGP) complex. Inhibition of mAGP biosynthesis is a proven strategy for developing anti-mycobacterial drugs and thus understanding the pathways and enzymes involved in the assembly of this molecule is of interest. In this paper we describe the chemical synthesis of a panel nine oligosaccharides fragments (**4**–**12**) of the galactan domain of the mAGP complex designed as biosynthetic probes. These structures, ranging in size from a hexasaccharide to a tetradecasaccharide, are potential substrates for two biosynthetic enzymes, GlfT2 and AftA, and represent the largest mycobacterial galactan fragments synthesized to date. The route developed was iterative and provided multi-milligram quantities of the target molecules **4**–**12** in good overall yield.

Keywords

mycobacteria, galactan, oligosaccharides, synthesis, cell wall

Introduction

An integral component of the mycobacterial cell wall is a large glycoconjugate, the mycolic acid–arabinogalactan–peptidoglycan (mAGP) complex.[1,2] This structure, in which an arabinogalatan polysaccharide is covalently-linked to peptidoglycan and capped with long chain branched lipids (mycolic acids), presents a particularly impenetrable barrier to the environment, in turn making it difficult to treat infections caused by mycobacteria.[2] Among these are the human diseases tuberculosis and Hansen's disease (leprosy). Production of a complete mAGP complex is essential for mycobacterial viability[3] and there has consequently been significant interest in identifying inhibitors of mAGP biosynthesis as novel drugs.[4-6] Such a strategy has been demonstrated to be feasible. Two clinically used anti-tuberculosis drugs, isoniazid and ethambutol, act by inhibiting the biosynthesis of this complex glycoconjugate.[7]

At the heart of the mAGP is the arabinogalactan (AG), which is composed of a D-galactofuranose (Gal*f*)-containing galactan and a D-arabinofuranose (Ara*f*)-containing arabinan (Figure 1A).[1,2] The galactan domain, containing alternating β-(1→5)- and (1→6)-linked Gal*f* residues, is attached to a rhamnose–N-acetyl-glucosamine disaccharide, which serves as the linker between the AG and the peptidoglycan. Three arabinan chains are attached to the galactan through O-5 of a Gal*f* residue. Previous structural work has indicated that the arabinan domains are linked to the eighth, tenth and twelfth Gal*f* residues from the rhamnose.[1,2]

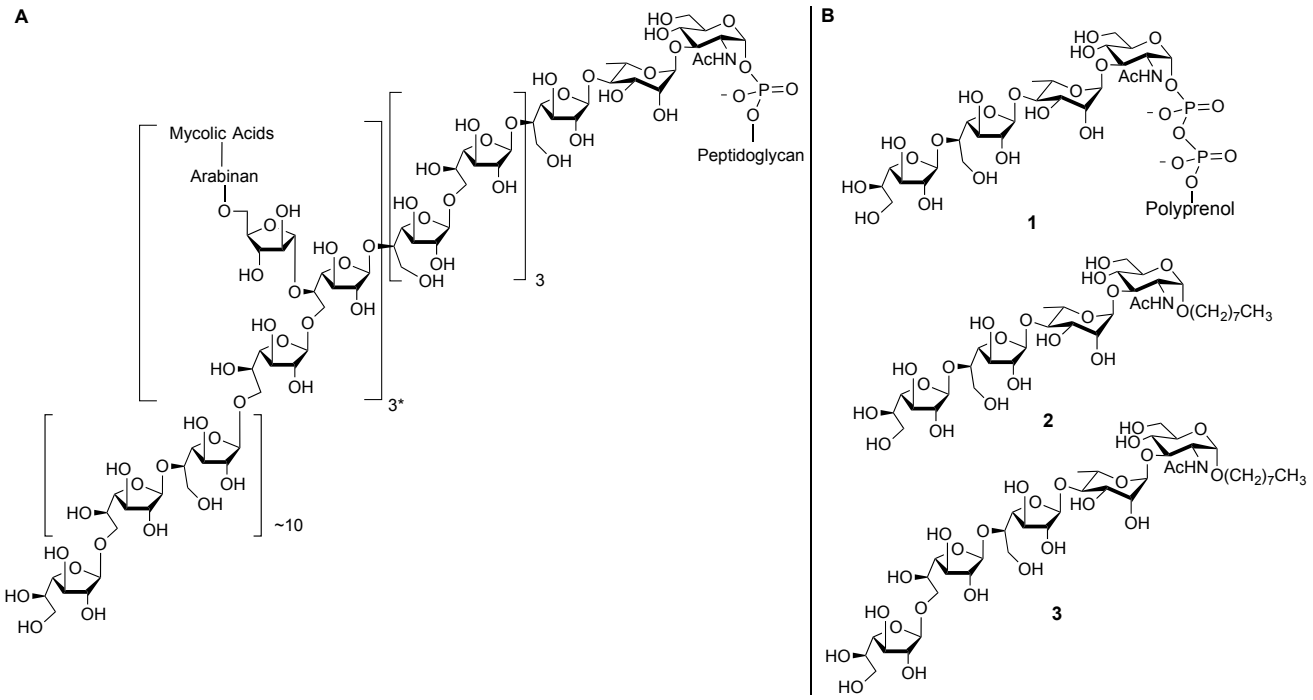


Figure 1. **A**) Structure of the mycobacterial mAGP complex, highlighting the galactan domain and the linkage to the arabinan. B) Minimal in vivo GlfT2 acceptor substrate (**1**) and two synthetic analogs (**2** and **3**) that have been demonstrated to be acceptor substrates for the enzyme.

The biosynthetic pathway by which the mAGP is assembled has received increasing attention and many of the enzymes involved in the process have been identified, although most remain poorly characterized with regard to substrate specificity and mechanism of catalysis.[1,2,8] Significant work has focused on the enzyme that assembles the bulk of the galactan, the bifunctional polymerizing galactofuranosyltransferase, GlfT2.[9] The minimal natural substrate for GlfT2 is a tetrasaccharide consisting of two Gal*f* residues and the linker disaccharide bound to a decaprenol pyrophosphate moiety (**1**, Figure 1B).[9,10] Previous studies established that, in vitro, the enzyme does not require the phospholipid domain and the simplified octyl tetrasaccharide **2** is efficiently turned over, as the next higher homologue, pentasaccharide **3** (Figure 1B).[10]

As part of investigations to better characterize the substrate specificity of GlfT2, we desired to prepare a homologous series of oligosaccharides containing 4–12 Gal*f* residues (**4**–**12**, Figure 2) extending previous investigations involving the preparation of **2** and **3**.[11] Access to

these compounds would provide probes enabling investigations of the enzyme to gain insights into how GlfT2 processes its acceptor substrate as the chain length increases. Such insights would complement previous work with **2** and **3**.[10] We expected that **4**–**12** could also serve another purpose: as probes for the arabinofuranosyltransferase that adds the first Ara*f* residues to the galactan. This 'priming' enzyme, AftA, has been identified, but demonstrating the function of its enzymatic activity has to date focused on the use of materials purified from bacterial cultures,[12] or on trisaccharides.[13] Oligosaccharides **4**–**12**, which range in size from a hexasaccharide containing four Gal*f* residues to a tetradecasaccharide containing 12 Gal*f* residues, would facilitate a detailed characterization of AftA, in particular the fidelity of the enzyme with regard to the addition of Ara*f* moieties to the eighth, tenth and twelfth Gal*f* residues.

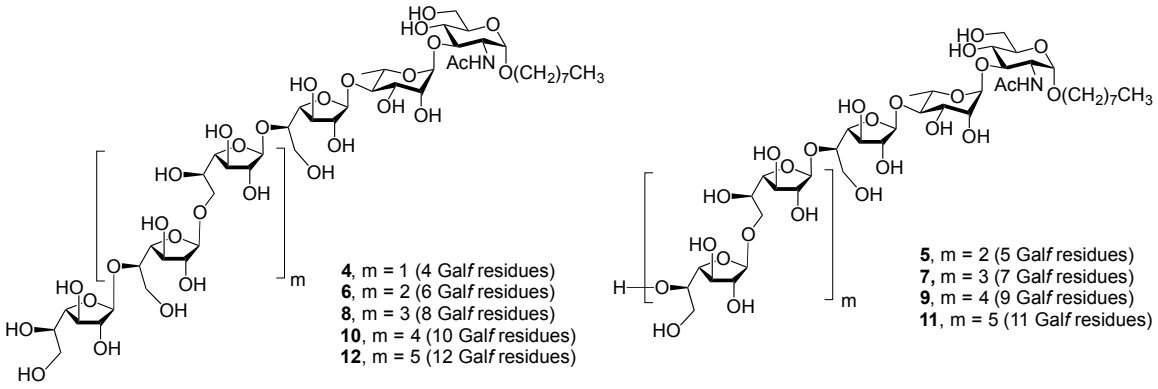
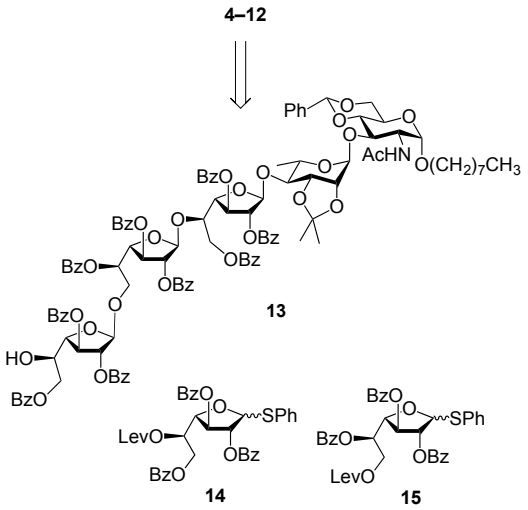


Figure 2. Synthetic targets **4**–**12**, designed to be acceptor substrates of mycobacterial GlfT2 and AftA.

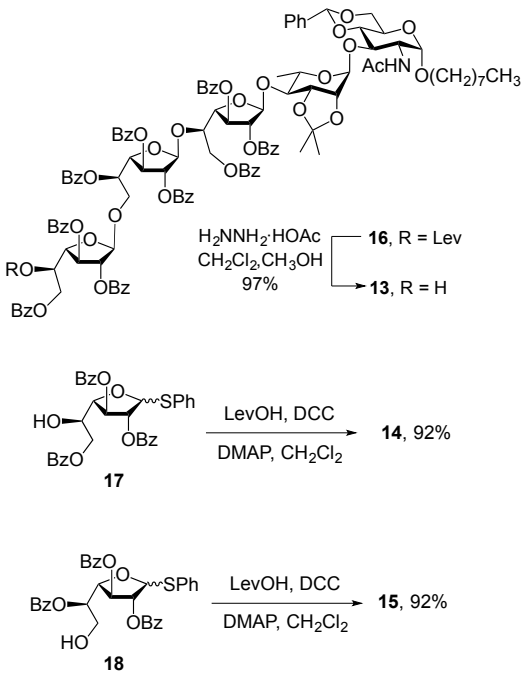
In this manuscript, we describe the synthesis of **4**–**12** through an iterative process. This work extends earlier work focused on the preparation of mycobacterial galactan-related oligosacchrides[14-22] and **4**–**12** represent the largest fragments of this important biomolecule chemically synthesized to date. Furthermore, the systematic approach by which these oligosaccharides were assembled allowed us to probe changes in the chemistry that occurred as the size of the molecule increased, providing information of potential use in the synthesis of even more complex mycobacterial AG fragments.

Results and Discussion

In designing an approach to oligosaccharides **4**–**12**, we envisioned that they could come from three building blocks (Scheme 1): pentasaccharide alcohol **13** and thioglycosides **14** and **15**. The latter two compounds are isomeric, orthogonally-protected, Gal*f* derivatives that would enable the facile assembly of the oligomers with alternating β-Gal*f*-(1 →5)-β-Gal*f* and β-Gal*f*-(1 →6)-β-Gal*f* linkages. Alcohol **13** was prepared, in 97% yield, from the previously reported pentasaccharide **16**,[23] by treatment with hydrazine acetate,[24] which selectively cleaved the levulinate ester while leaving the benzoate esters intact. Thioglycosides **14** and **15** were prepared from the known[25] alcohols **17** and **18**, respectively (Scheme 2). Reaction of **17** with levulinic acid and dicylcohexylcarbodiimide (DCC) in dichloromethane gave an 92% yield of **14**. Similar treatment of **18** led to the formation of **15**, also in 92% yield.



Scheme 1. Retrosynthetic analysis of oligosaccharides **1**–**9**.

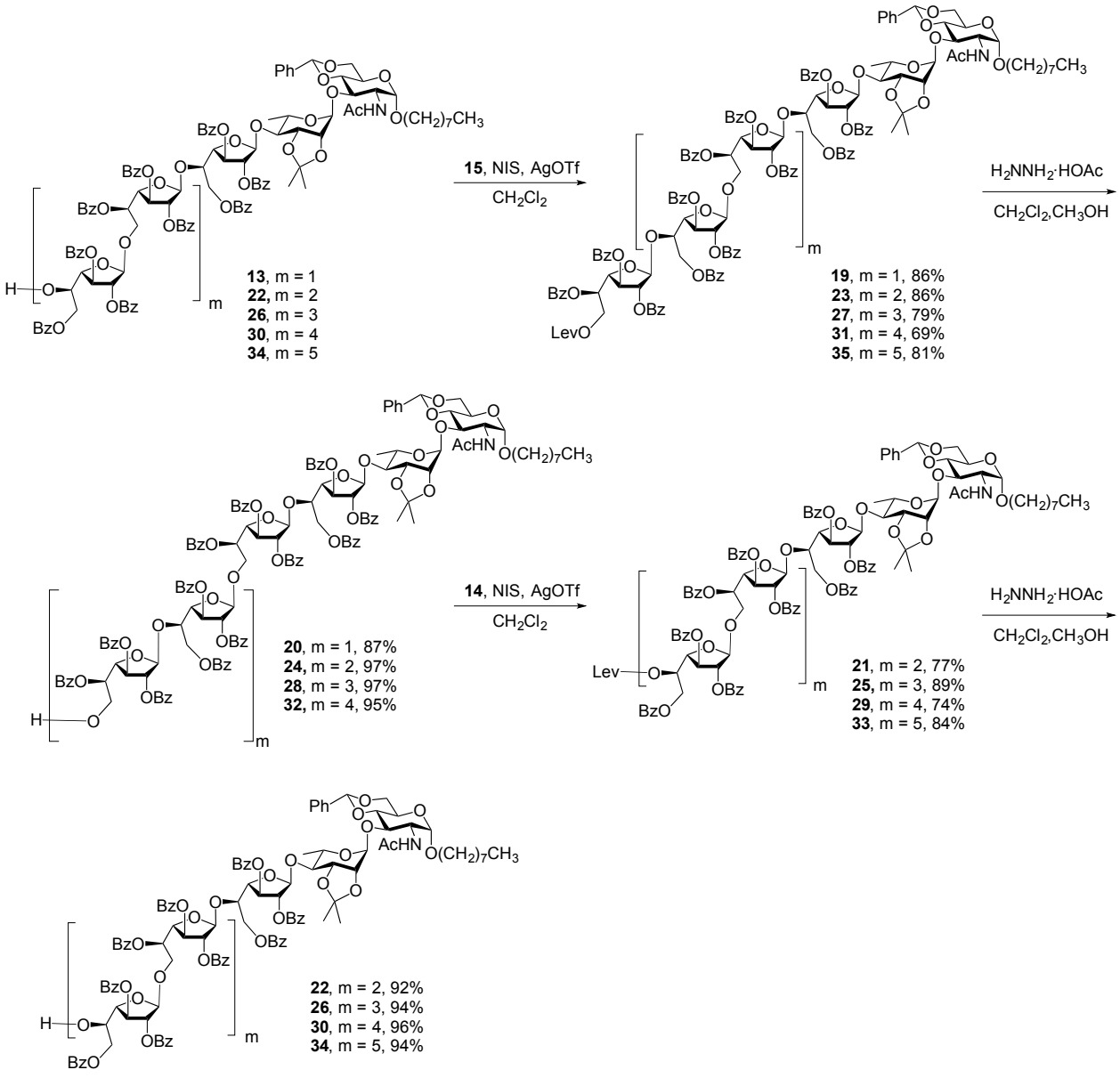


Scheme 2. Synthesis of **13–15**.

With compounds **13**–**15** in hand, their assembly into a homologous series of oligosaccharides was achieved using the process outlined in Scheme 3. General features of the iterative approach were: 1) glycosylations using thioglycoside activation with *N*-iodosuccinimide, silver triflate and trimethysilyl triflate[26] (e.g., **13**→**19**) and then 2) hydrazine acetate-mediated selective deprotection of the levulinate ester[24] in the resulting product to give an alcohol ready for another round of glycosylation (e.g., **19**→**20**).

In all cases the yields of the glycosylations were good to excellent (69–89%). These yields could typically be achieved by using a 1.2–1.5 equivalents of the donor (e.g., **14**/**15**) relative to the acceptor. However, it was discovered that in some of the glycosylations leading to the larger products (e.g., the synthesis of **31**) it was necessary to add additional amounts of donor and promotors in order for the acceptor to be consumed and for maximal product yields to be obtained. The stereochemistry of the resulting glycsidic linkage could be unequivocally

ascertained using NMR spectroscopy. In the ^{13}C NMR spectrum of the products, the chemical shift of the newly-introduced anomeric carbon was found between 105 and 110 ppm and in the ^{1}H spectrum the nascent anomeric hydrogen appeared as a singlet. Both of these data are consistent with the 1,2-*trans* (e.g., β-Gal*f*) stereochemistry.[27]

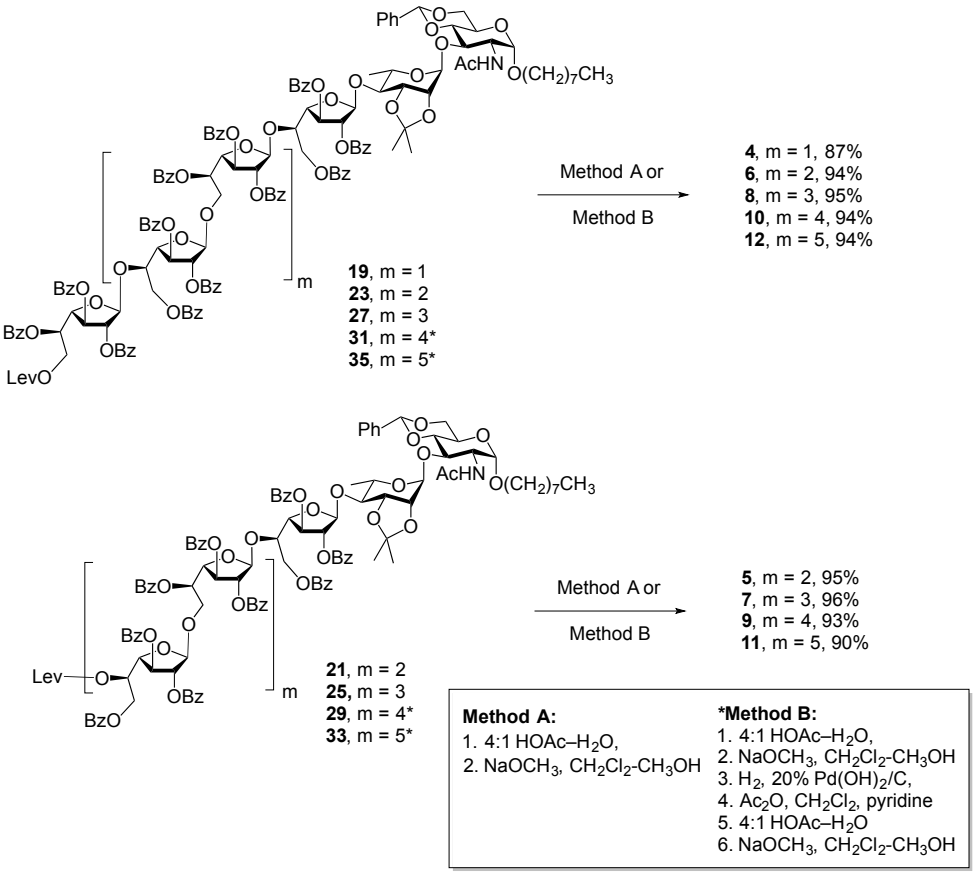


Scheme 3. Synthesis of protected oligosaccharide precursors to **4**–**12**.

Conversion of the protected oligosaccharides into **4**–**12** required the cleavage of the benzylidene acetal, isopropylidene ketal, benzoate and levulinate protecting groups. For the synthesis of the hexasaccharide to decasaccharide (**4**–**8**), this was achieved in two steps (Scheme 4, Method A). The acetal and ketal were first cleaved by acid hydrolysis (HOAc–H_2O) at elevated temperature and then the resulting product, without purification, was treated with sodium methoxide in a mixture of dichloromethane and methanol. The reactions were done in this order given concerns about the acid lability of the Gal*f* linkages in the fully deprotected oligosaccharides. That is, it was anticipated that the removal of the electron-withdrawing acyl groups first would provide compounds susceptible to cleavage during the acetal/ketal hydrolysis. In all cases, the compounds were achieved in excellent (>85%) yield. It should be noted that as ester cleavage proceeded, partially/fully deacylated products precipitated from solution, presumably given their increased polarity compared to the starting material. Therefore, as the reaction proceeded it was necessary to add additional methanol to solubilize all reaction components in turn facilitating the completion of the deacylation.

With the precursors leading to **9**–**12** (oligosaccharides **29**, **31**, **33** and **35**) a more complicated deprotection procedure was required. It was discovered that after application of Method A to these compounds that a small amount of compound containing the benzylidene acetal remained. Unfortunately, this acetal-containing byproduct was impossible to separate from the desired compound, either immediately following the hydrolysis, or after deacylation. Attempts to convert the small amount of the benzylidene acetal containing product to the fully deprotected compound using hydrogenation were unsuccessful. Therefore, the compound was acetylated and then subjected again to the acidic hydrolysis and deacylation. This resulted in complete deprotection of the material to the desired product. These problems highlight some of the challenges that arise when attempting to remove protecting groups from large molecules, and

mirror similar issues (unpublished) we have encountered in the preparation of other compounds of comparable, or larger, size.



Scheme 4. Synthesis of **4**–**12** via deprotection of the corresponding oligosaccharide precursors.

In summary, we describe here the chemical synthesis of a panel of nine oligosaccharides related to mycobacterial galactan. The compounds are a homologous series of fragments, which range in size from a hexasaccharide to a tetradecasaccharide. Access to these compounds was achieved using an iterative strategy involving the use of thioglycoside donors and subsequent removal of a levulinate ester in the glycosylation products to provide an alcohol that could be used in another round of chain extension. The glycosylation reactions proceeded in good to excellent yield, although with some of the larger compounds additional donor and promoter had to be added. Final removal of all protecting groups could be done efficiently in two steps for the

decasaccharide and smaller compounds. However, for the undecasaccharide to tetradecasaccharide, complete cleavage of the benzylidene acetal was problematic and required a more complicated deprotection strategy. This finding suggests that in future syntheses of larger galactan fragments, it may be advantageous to avoid the use of benzylidene acetal protecting groups, or develop a strategy in which they are removed/replaced at an earlier stage. Use of **4**–**12** in investigations as substrates for Glft2 and AftA will be reported in the future.

Experimental

General Methods. Reactions were carried out in oven–dried glassware. All reagents used were purchased from commercial sources and were used without further purification unless noted. Reaction solvents were purified by successive passage through columns of alumina and copper under nitrogen. Unless stated otherwise, all reactions were carried out at room temperature under a positive pressure of argon and were monitored by TLC on Silica Gel 60 F_{254} (0.25 mm, E. Merck). Spots were detected under UV light or by charring with acidified *p*-anisaldehyde solution in EtOH. Unless otherwise indicated, all column chromatography was performed on Silica Gel (40–60 μM). The ratio between silica gel and crude product ranged from 100 to 50:1 (w/w). Optical rotations were measured at 22 ± 2 °C at the sodium D-line (589 nm) and are in units of deg•mL(dm•g)$^{-1}$ ^{1}H NMR spectra were recorded at 500 MHz or 600 MHz, and chemical shifts are referenced to either TMS (0.0, $CDCl_3$) or HOD (4.78, D_2O). ^{1}H data are reported as though they are first order. ^{13}C NMR (APT) spectra were recorded at 125 MHz and ^{13}C chemical shifts are referenced to internal $CDCl_3$ (77.23, $CDCl_3$) or external acetone (31.07, D_2O). Organic solutions were concentrated under vacuum at < 40 °C. Electrospray mass spectra (time-of-flight analyzer) were recorded on samples suspended in mixtures of THF with CH_3OH and added NaCl.

Deprotection of oligosaccharides: Method A (for compounds 19, 21, 23, 25 and 27).

The oligosaccharide (**19, 21, 23, 25** or **27**) was dissolved in 4:1 HOAc–H_2O (6–12 mL depending on the amount) and heated at 70–75 °C for 4–6 h. Upon completion of the reaction, the solvent was evaporated and the residue was dissolved in CH_2Cl_2–CH_3OH (7:3, 5–6 mL) followed by the drop wise addition of $NaOCH_3$ in CH_3OH (0.1 M, enough to maintain p*H* of the solution ~8 as determined by spotting a drop of the reaction solution on wet pH paper). The reaction mixture was stirred at for 16–24 h. Additional CH_3OH (up to 10–15 mL, depending on the solubility as the reaction progressed) was added at intervals. When the reaction was complete as determined by TLC the solution was neutralized by the addition of Amberlyst-15 (H+) cation exchange resin. The solution was filtered and the filtrate concentrated to give a syrupy residue, which was then dissolved in a minimum amount of H_2O water and was purified by C-18 column chromatography, using a H_2O-CH_3OH gradient (100% H_2O to 40:60 H_2O–CH_3OH). The fractions containing the product were combined, concentrated, re-dissolved in deionized water and lyophilized to obtain the deprotected oligosaccharide as a foam.

Deprotection of oligosaccharides: Method B (for compounds 29, 31, 33 and 35).

For the larger compounds (**29, 31, 33 and 35**) complete deprotection was not achieved for when only method A was followed. Incomplete hydrolysis of both the benzylidene and isopropylidene acetals was observed. A modified approach was therefore developed. The oligosaccharide was dissolved in 4:1 HOAc–H_2O (6–12 mL depending on the amount) and heated at 70–75 °C for 4–6 h. Upon completion of the reaction, the solvent was completely evaporated and the residue was dissolved in ethyl acetate (10–15 mL). Then, 20% $Pd(OH)_2$/C (30–40 weight%) and HOAc (4–5 drops) were added and the mixture was stirred under an atmosphere of hydrogen for 4–5 h. The

catalyst was filtered and the filtrate was concentrated to a residue that was dried overnight under vacuum. To increase the solubility of this material in subsequent transformations, this residue was then dissolved in a solution of CH_2Cl_2 and pyridine (1:1, 20 mL) and acetic anhydride (1 mL) was added. After stirring for 2 h at 40 °C, the mixture was cooled to room temperature, diluted with CH_2Cl_2 (10 mL) and chilled H_2O was added (5 mL). The organic layer was separated, washed with water (5 mL), 10% aq. copper sulfate (until TLC under uv indicated the absence of pyridine) and water (5–10 mL). The organic layer was dried (Na_2SO_4) and concentrated to a syrupy residue that was purified on a short silica gel column using ethyl acetate containing 2% of methanol. The fractions containing the product were combined and evaporated to give a syrup/foam that was subjected to method A again to obtain the final compounds.

Octyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→4)-α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (4)

Prepared from **19** (0.2 g, 0.077 mmol) as described in the general procedure (Method A) to afford **4** (0.076 g, 87%) as a foam. ^{1}H NMR (600 MHz, D_2O, δ_H): 5.27 (s, 1 H, H-1), 5.24–5.22 (m, 2 H, H-1 x 2), 5.02 (s, 1 H, H-1), 4.85 (s, 1 H, H-1), 4.82 (d, 1 H, J = 3.6 Hz, H-1), 4.16–3.92 (m, 18 H), 3.91–3.60 (m, 17 H), 3.58–3.47 (m, 2 H, octyl OCH_2), 2.05 (s, 3 H, NHCOCH_3), 1.64–1.55 (m, 2 H, octyl CH_2), 1.38–1.23 (m, 13 H, octyl CH_2, CH_3-6′), 0.85 (t, 3 H, J = 7.0 Hz, octyl CH_3); ^{13}C NMR (125 MHz, D_2O, δ_C): 175.1 (C=O), 109.4 (C-1), 108.8 (C-1), 108.1 (C-1), 108.0 (C-1), 102.1 (C-1), 97.8 (C-1), 83.9 (C-4), 83.6 (C-2), 82.8 (C-2), 82.7, 82.5 (C-4), 82.2 (C-2), 81.9(5) (C-2), 80.6 (C-2), 79.2 (C-4), 77.6 (C-3), 77.5, 76.8 (C-3), 76.5 (C-3), 73.0 (C-4), 72.0 (C-3), 71.6 (C-5), 71.5 (C-5), 70.5 (C-5), 70.3 (C-6), 69.3 (C-5), 69.1 (octyl O*C*H$_2$), 68.3 (C-5), 63.8 (C-6), 62.2 (C-6), 61.9(8) (C-6), 61.5 (C-6), 54.2 (C-2), 32.1 (octyl *C*H$_2$),

29.5 (octyl *C*H_2), 29.4 (octyl *C*H_2), 26.3 (octyl *C*H_2), 23.0 (octyl *C*H_2), 22.9 (NHCO*C*H_3), 17.9 (C-6'), 14.4 (octyl *C*H_3). ESI-MS *m*/*z* calcd for $[M + Na]^+$ $C_{46}H_{81}NO_{30}Na$: 1150.4736. Found: 1150.4735.

Octyl β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→4)-α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (5)

Prepared from compound **21** (0.15 g, 0.049 mmol) as described in the general procedure (Method A) to afford **5** (0.064 g, 95%) as a foam. ^{1}H NMR (600 MHz, D_2O, δ_H): 5.27 (s, 1 H, H-1), 5.23 (s, 2 H, H-1 x 2), 5.05 (s, 1 H, H-1), 5.03 (s, 1 H, H-1), 4.85 (s, 1 H, H-1), 4.82 (d, 1 H, *J* = 3.6 Hz, H-1), 4.18–3.90 (m, 22 H), 3.90–3.60 (m, 20 H), 3.58–3.47 (m, 2 H, octyl OC*H*$_2$), 2.06 (s, 3 H, NHCOC*H*$_3$), 1.64–1.55 (m, 2 H, octyl C*H*$_2$), 1.38–1.23 (m, 13 H, octyl C*H*$_2$, C*H*$_3$-6′), 0.85 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, D_2O, δ_C): 175.1 (C=O), 109.4 (C-1), 108.8 (C-1 x 2), 108.1 (C-1), 107.9(6) (C-1), 102.2 (C-1), 97.8 (C-1), 83.9 (C-4), 82.9 (C-2), 82.7 (C-2), 82.5, 82.2 (C-4), 81.9(9) (C-2), 81.92 (C-2), 80.6 (C-2), 79.2 (C-4), 77.7 (C-3), 77.6(6) (C-3), 77.6(0) (C-3), 77.4, 76.7 (C-3), 76.5 (C-3), 73.0 (C-4), 72.0 (C-3), 71.8 (C-5), 71.6 (C-5), 70.5 (C-5), 70.2 (C-6), 70.1(5), 69.3 (C-5), 69.1 (octyl O*C*H_2), 68.3 (C-5), 63.7 (C-6), 62.2 (C-6), 61.9(5) (C-6), 61.5 (C-6), 61.4, 54.2 (C-2), 32.1 (octyl *C*H_2), 29.5 (octyl *C*H_2), 29.4 (octyl *C*H_2), 26.3 (octyl *C*H_2), 23.0 (octyl *C*H_2), 22.9 (NHCO*C*H_3), 17.9 (C-6'), 14.4 (octyl *C*H_3). ESI-MS *m*/*z* calcd for $[M + Na]^+$ $C_{52}H_{91}NO_{35}Na$: 1312.5264. Found: 1312.5259.

Octyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→4)-α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (6)

Prepared from compound **23** (0.1 g, 0.028 mmol) as described in the general procedure (Method A) to afford **6** (0.039 g, 94%) as a foam. ^{1}H NMR (600 MHz, D_2O, δ_H): 5.27 (s, 1 H, H-1), 5.24–5.20 (m, 3 H, H-1 x 3), 5.03 (br. s, 2 H, H-1 × 2), 5.03 (s, 1 H, H-1), 4.85 (s, 1 H, H-1), 4.82 (d, 1 H, *J* = 3.6 Hz, H-1), 4.18–3.92 (m, 26 H), 3.91–3.60 (m, 23 H), 3.59–3.48 (m, 2 H, octyl OC*H*$_2$), 2.07 (s, 3 H, NHCOC*H*$_3$), 1.67–1.54 (m, 2 H, octyl C*H*$_2$), 1.42–1.23 (m, 13 H, octyl C*H*$_2$, C*H*$_3$-6′), 0.85 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, D_2O, δ_C): 175.1 (C=O), 109.4 (C-1), 108.8 (C-1 x 2), 108.7(7) (C-1), 108.1 (C-1), 108.0(5) (C-1), 107.9(5) (C-1), 102.2 (C-1), 97.8 (C-1), 83.9 (C-4), 83.6, 82.9 (C-2), 82.8, 82.7 (C-2), 82.5, 82.2 (C-4), 82.1(9), 82.0, 81.9(8) (C-2), 80.6 (C-2), 79.2 (C-4), 77.7 (C-3), 77.6(6) (C-3), 77.6(4) (C-3), 77.62, 77.5(9), 77.5, 77.4, 76.8, 76.7 (C-3), 76.5 (C-3), 73.0 (C-4), 72.7, 72.0 (C-3), 71.9 (C-5), 71.6 (C-5), 71.5, 70.5 (C-5), 70.4(6), 70.3, 70.2 (C-6), 69.3 (C-5), 69.1 (octyl O*C*H$_2$), 68.3 (C-5), 63.8 (C-6), 62.2 (C-6), 62.0, 61.9(6) (C-6), 61.5 (C-6), 61.4, 54.3 (C-2), 32.1 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 23.0 (octyl *C*H$_2$), 22.9 (NHCO*C*H$_3$), 17.9 (C-6’), 14.4 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + Na]^+$ $C_{58}H_{101}NO_{40}Na$: 1474.5792. Found: 1474.5787.

Octyl β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→4)-α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (7)

Prepared from compound **25** (0.125 g, 0.031 mmol) as described in the general procedure (Method A) to afford **7** (0.048 g, 96%) as a foam. ^{1}H NMR (600 MHz, D_2O, δ_H): 5.27 (s, 1 H, H-1), 5.24–5.20 (br. s, 3 H, H-1 x 3), 5.05 (s, 1 H, H-1), 5.03 (br. s, 2 H, H-1 x 2), 4.85 (s, 1 H, H-1), 4.82 (d, 1 H, *J* = 3.6 Hz, H-1), 4.19–3.92 (m, 29 H), 3.91–3.60 (m, 25 H), 3.59–3.48 (m, 2 H, octyl OC*H*$_2$), 2.07 (s, 3 H, NHCOC*H*$_3$), 1.67–1.54 (m, 2 H, octyl C*H*$_2$), 1.42–1.23 (m, 13 H, octyl C*H*$_2$, C*H*$_3$-6′), 0.85 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, D_2O, δ_C): 175.1 (C=O), 109.4 (C-1), 108.8 (C-1 x 2), 108.1 (C-1), 108.0, (C-1), 107.9(5) (C-1), 102.1 (C-1), 97.8 (C-1), 84.0, 83.92 (C-4), 83.9(0) (C-4), 82.9 (C-2), 82.87, 82.7 (C-2), 82.6, 82.2 (C-4), 82.0, 81.9(9) (C-2), 81.92 (C-2), 80.6 (C-2), 79.2 (C-4), 77.7 (C-3), 77.6(8) (C-3), 77.6(7) (C-3), 77.6(4) (C-3), 77.6(1) (C-3), 77.4, 76.7 (C-3), 76.6(5), 76.5 (C-3), 73.0 (C-4), 72.7, 72.0 (C-3), 71.9, 71.8 (C-5), 71.6 (C-5), 70.5 (C-5), 70.4(9), 70.3, 70.2 (C-6), 69.3 (C-5), 69.1 (octyl O*C*H$_2$), 68.3 (C-5), 63.7 (C-6), 62.2 (C-6), 62.0, 61.5 (C-6), 61.4, 54.2 (C-2), 32.1 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 23.0 (octyl *C*H$_2$), 22.9 (NHCO*C*H$_3$), 17.9 (C-6’), 14.4 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + Na]^+$ $C_{64}H_{111}NO_{45}Na$: 1636.632. Found: 1636.6302.

Octyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→4)-α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (8)

Prepared from compound **27** (0.11 g, 0.025 mmol) as described in the general procedure (Method A) to afford **8** (0.042 g, 95%) as a foam. ^{1}H NMR (600 MHz, D_2O, δ_H): 5.25 (s, 1 H, H-1), 5.23–5.20 (m, 4 H, H-1 x 4), 5.0 (br. s, 3 H, H-1 x 3), 4.84 (s, 1 H, H-1), 4.81 (d, 1 H, J = 3.6 Hz, H-1), 4.16–3.92 (m, 34 H), 3.91–3.60 (m, 28 H), 3.59–3.48 (m, 2 H, octyl OCH_2), 2.04 (s, 3 H, NHCOCH_3), 1.67–1.54 (m, 2 H, octyl CH_2), 1.42–1.23 (m, 13 H, octyl CH_2, CH_3-6′), 0.85 (t, 3 H, J = 7.0 Hz, octyl CH_3); ^{13}C NMR (125 MHz, D_2O, δ_C): 175.1 (C=O), 109.4 (C-1), 108.8 (C-1 x 2), 108.7(7) (C-1), 108.1 (C-1), 108.0(5) (C-1), 107.9(6) (C-1), 102.2 (C-1), 97.8 (C-1), 84.0, 83.6 (C-4), 82.9 (C-2), 82.8, 82.7 (C-2), 82.5, 82.2 (C-4), 82.1(8), 82.0, 81.9(8) (C-2), 80.6 (C-2), 79.2 (C-4), 77.7 (C-3), 77.6(4) (C-3), 77.6(1) (C-3), 77.5(9), 77.4, 76.7(7) (C-3), 77.4(3) (C-3), 76.8, 76.7, 76.5 (C-3), 73.0 (C-4), 72.0 (C-3), 71.6 (C-5), 71.5 (C-5), 70.5 (C-5), 70.3 (C-6), 69.3 (C-5), 69.1 (octyl O*C*H$_2$), 68.3 (C-5), 63.8 (C-6), 62.2 (C-6), 62.0, 61.9(7) (C-6), 61.5 (C-6), 61.4, 54.2 (C-2), 32.1 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 23.0 (octyl *C*H$_2$), 22.9 (NHCO*C*H$_3$), 17.9 (C-6’), 14.4 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + Na]^+$ $C_{70}H_{121}NO_{50}Na$: 1798.6849. Found: 1798.6856.

Octyl β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→4)-α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (9)

Prepared from compound **29** (0.125 g, 0.026 mmol) as described in the general procedure (Method B) to afford **9** (0.046 g, 93%) as a foam. ^{1}H NMR (600 MHz, D_2O, δ_H): 5.25 (s, 1 H, H-1), 5.23–5.20 (br. s, 4 H, H-1 x 4), 5.04–4.99 (m, 4 H, H-1 x 4), 4.84 (s, 1 H, H-1), 4.81 (d, 1 H, *J* = 3.6 Hz, H-1), 4.16–3.92 (m, 39 H5), 3.91–3.60 (m, 31 H), 3.59–3.48 (m, 2 H, octyl OC*H*$_2$), 2.04 (s, 3 H, NHCOC*H*$_3$), 1.67–1.54 (m, 2 H, octyl C*H*$_2$), 1.42–1.23 (m, 13 H, octyl C*H*$_2$, C*H*$_3$-6′), 0.85 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, D_2O, δ_C): 175.1 (C=O), 109.4 (C-1), 108.8 (C-1 x 2), 108.1 (C-1), 107.9(5) (C-1), 102.2 (C-1), 97.8 (C-1), 83.9 (C-4), 82.9 (C-2), 82.7 (C-2), 82.5, 82.2 (C-4), 81.9(9) (C-2), 81.92 (C-2), 80.6 (C-2), 79.2 (C-4), 77.7 (C-3), 77.6(5) (C-3), 77.6(0) (C-3), 77.4, 76.7 (C-3), 76.5 (C-3), 73.0 (C-4), 72.0 (C-3), 71.8 (C-5), 71.6 (C-5), 70.5 (C-5), 70.2 (C-6), 70.1(5), 69.3 (C-5), 69.1 (octyl O*C*H$_2$), 68.3 (C-5), 63.7 (C-6), 62.2 (C-6), 61.9(5) (C-6), 61.5 (C-6), 61.4, 54.2 (C-2), 32.1 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 23.0 (octyl *C*H$_2$), 22.9 (NHCO*C*H$_3$), 17.9 (C-6’), 14.4 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + Na]^+$ $C_{76}H_{131}NO_{55}Na$: 1960.7377. Found: 1960.7364.

Octyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→4)-α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (10)

Prepared from compound **31** (0.05 g, 0.01 mmol) as described in the general procedure (Method B) to afford **10** (0.018 g, 94%) as a foam. ^{1}H NMR (600 MHz, D_2O, δ_H): 5.25 (s, 1 H, H-1), 5.23–5.20 (m, 5 H, H-1 x 5), 5.03–4.99 (br. s, 4 H, H-1 x 4), 4.84 (s, 1 H, H-1), 4.81 (d, 1 H, *J* = 3.6 Hz, H-1), 4.16–3.92 (m, 42 H), 3.91–3.60 (m, 34 H), 3.59–3.48 (m, 2 H, octyl OC*H*$_2$), 2.04 (s, 3 H, NHCOC*H*$_3$), 1.67–1.54 (m, 2 H, octyl C*H*$_2$), 1.42–1.23 (m, 13 H, octyl C*H*$_2$, C*H*$_3$-6′), 0.85 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, D_2O, δ_C): 175.1 (C=O), 109.4 (C-1), 108.8 (C-1 × 2), 108.7(7) (C-1), 108.1 (C-1), 108.0(9) (C-1), 108.0(5) (C-1), 107.9(5) (C-1), 102.1 (C-1), 97.8 (C-1), 84.0, 83.6 (C-4), 82.9 (C-2), 82.8, 82.7 (C-2), 82.6, 82.2 (C-4), 82.1(8), 82.1, 82.0, 81.9(8) (C-2), 80.6 (C-2), 79.2 (C-4), 77.7 (C-3), 77.6(8) (C-3), 77.6(0) (C-3), 77.5(9), 77.5, 77.4, 76.8, 76.7 (C-3), 76.5 (C-3), 73.0 (C-4), 72.7, 72.0 (C-3), 71.9 (C-5), 71.6 (C-5), 71.5, 70.5 (C-5), 70.4(5), 70.3, 70.2 (C-6), 69.3 (C-5), 69.1 (octyl O*C*H$_2$), 68.3 (C-5), 63.8 (C-6), 63.5, 62.2 (C-6), 62.1, 62.0, 61.9(7) (C-6), 61.5 (C-6), 61.4, 54.2 (C-2), 32.1 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 23.0 (octyl *C*H$_2$), 22.9 (NHCO*C*H$_3$), 17.9 (C-6’), 14.4 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + Na]^+$ $C_{82}H_{141}NO_{60}Na$: 2122.7905. Found: 2122.786.

Octyl β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→4)-α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (11)

Prepared from compound **33** (0.11 g, 0.019 mmol) as described in the general procedure (Method B) to afford **11** (0.038 g, 90%) as a foam. ^{1}H NMR (600 MHz, D_2O, δ_H): 5.25 (s, 1 H, H-1), 5.23–5.20 (m, 5 H, H-1 × 5), 5.04–4.99 (m, 5 H, H-1 × 5), 4.84 (s, 1 H, H-1), 4.81 (d, 1 H, *J* = 3.6 Hz, H-1), 4.16–3.92 (m, 46 H), 3.91–3.60 (m, 37 H), 3.59–3.48 (m, 2 H, octyl OC*H*$_2$), 2.04 (s, 3 H, NHCOC*H*$_3$), 1.67–1.54 (m, 2 H, octyl C*H*$_2$), 1.42–1.23 (m, 13 H, octyl C*H*$_2$, C*H*$_3$-6′), 0.85 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, D_2O, δ_C): 175.1 (C=O), 109.4 (C-1), 108.8 (C-1 × 2), 108.1 (C-1), 107.9(5) (C-1), 102.2 (C-1), 97.8 (C-1), 83.9 (C-4), 82.9 (C-2), 82.7 (C-2), 82.5, 82.2 (C-4), 81.9(9) (C-2), 81.92 (C-2), 80.6 (C-2), 79.2 (C-4), 77.7 (C-3), 77.6(5) (C-3), 77.6(0) (C-3), 77.4, 76.7 (C-3), 76.5 (C-3), 73.0 (C-4), 72.0 (C-3), 71.8 (C-5), 71.6 (C-5), 70.5 (C-5), 70.2 (C-6), 70.1(5), 69.3 (C-5), 69.1 (octyl O*C*H$_2$), 68.3 (C-5), 63.7 (C-6), 62.2 (C-6), 61.9(5) (C-6), 61.5 (C-6), 61.4, 54.2 (C-2), 32.1 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 23.0 (octyl *C*H$_2$), 22.9 (NHCO*C*H$_3$), 17.9 (C-6'), 14.4 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + 2Na]^{+2}$ $C_{88}H_{151}NO_{65}Na_2$: 1153.9163. Found: 1153.917.

Octyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→4)-α-L-rhamnopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (12)

Prepared from compound **35** (0.097 g, 0.015 mmol) as described in the general procedure (Method B) to afford **12** (0.035 g, 94%) as a foam. ^{1}H NMR (600 MHz, D_2O, δ_H): 5.25 (s, 1 H, H-1), 5.23–5.20 (m, 6 H, H-1 × 6), 5.01 (br. s, 5 H, H-1 × 5), 4.84 (s, 1 H, H-1), 4.81 (d, 1 H, *J* = 3.6 Hz, H-1), 4.16–3.92 (m, 50 H), 3.91–3.60 (m, 40 H), 3.59–3.48 (m, 2 H, octyl OC*H*$_2$), 2.04 (s, 3 H, NHCOC*H*$_3$), 1.67–1.54 (m, 2 H, octyl C*H*$_2$), 1.42–1.23 (m, 13 H, octyl C*H*$_2$, C*H*$_3$-6′), 0.85 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$); ^{13}C NMR (125 MHz, D_2O, δ_C): 175.1 (C=O), 109.4 (C-1), 108.8 (C-1 x 2), 108.1 (C-1), 107.9(5) (C-1), 102.2 (C-1), 97.8 (C-1), 83.9 (C-4), 82.9 (C-2), 82.7 (C-2), 82.5, 82.2 (C-4), 81.9(9) (C-2), 81.92 (C-2), 80.6 (C-2), 79.2 (C-4), 77.7 (C-3), 77.6(5) (C-3), 77.6(0) (C-3), 77.4, 76.7 (C-3), 76.5 (C-3), 73.0 (C-4), 72.0 (C-3), 71.8 (C-5), 71.6 (C-5), 70.5 (C-5), 70.2 (C-6), 70.1(5), 69.3 (C-5), 69.1 (octyl O*C*H$_2$), 68.3 (C-5), 63.7 (C-6), 62.2 (C-6), 61.9(5) (C-6), 61.5 (C-6), 61.4, 54.2 (C-2), 32.1 (octyl *C*H$_2$), 29.5 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 26.3 (octyl *C*H$_2$), 23.0 (octyl *C*H$_2$), 22.9 (NHCO*C*H$_3$), 17.9 (C-6’), 14.4 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + 2Na]^{+2}$ $C_{94}H_{161}NO_{70}Na_2$: 1234.9427. Found: 1234.9429.

Octyl 2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (13)

To a solution of **16** (1.94 g, 0.9 mmol) in CH_2Cl_2–CH_3OH (9:1 v/v, 60 mL) was added hydrazine acetate (0.2 g, 2.2 mmol) and the mixture was stirred for 100 min. The solution was poured into chilled H_2O (30 mL) and the CH_2Cl_2 layer was separated, washed with H_2O (30 mL), separated again, dried with anhydrous Na_2SO_4 and concentrated to a syrup that was purified by column chromatography (2:1 hexane–EtOAc) to give **13** (1.8 g, 97%) as a foam. R_f 0.44 (1:1, hexane–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.91 (m, 15 H, Ar), 7.88–7.76 (m, 5 H, Ar), 7.60–7.04 (m, 30 H, Ar), 5.90 (ddd, 1 H, *J* = 3.9, 7.7, 11.6 Hz), 5.81–5.74 (m, 4 H), 5.63 (s, 1 H), 5.59 (dd, 1 H, *J* = 1.5, 4.9 Hz), 5.56–5.52 (m, 3 H), 5.37 (s, 1 H), 5.19 (s, 1 H), 5.11 (s, 1 H), 4.82 (dd, 1 H, *J* = 3.9, 4.7 Hz), 4.74–4.64 (m, 4 H), 4.57–4.50 (m, 1 H), 4.50–4.30 (m, 5 H), 4.30–4.24 (m, 2 H), 4.12–4.04 (m, 2 H), 4.04–3.90 (m, 3 H), 3.90–3.80 (m, 1 H), 3.79–3.66 (m, 2 H), 3.60 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.57 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.40 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.02 (s, 3 H, NHCOCH_3), 1.64–1.58 (m, 3 H), 1.52 (s, 3 H, C(CH_3)$_2$) 1.40–1.20 (m, 13 H, octyl CH_2, C(CH_3)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.8 (C=O), 166.4 (C=O), 166.1 (C=O), 165.8 (C=O), 165.7 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 164.9 (C=O), 137.1 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 132.9 (Ar), 132.8(8) (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.1(Ar), 129.0 (Ar), 128.8 (Ar), 128.4 (Ar), 128.3(7) (Ar), 128.2(9) (Ar), 128.1(7) (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*(CH$_3$)$_2$), 106.8 (C-1), 105.8 (C-1), 103.9 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.0 (C-1), 83.6, 82.8, 82.5, 82.0, 81.8, 81.4, 80.1, 77.9, 77.8, 77.7(7), 77.6, 76.3, 76.2, 74.8, 73.4, 71.7, 69.4, 68.9, 68.3, 67.8, 66.2, 64.9, 64.4, 63.1, 53.6, 31.8 (octyl *C*H$_2$), 29.3

(octyl *C*H$_2$), 29.2(5) (octyl *C*H$_2$), 27.9 (C(*C*H$_3$)$_2$), 26.4 (C(*C*H$_3$)$_2$), 26.2, 23.4 (NHCOC*H*$_3$), 22.6, 17.2 (C-6'), 14.1 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $(M+Na)^+$ $C_{113}H_{115}NO_{34}Na$: 2052.7192. Found: 2052.7201.

Phenyl 2,3,6-tri-O-benzoyl-5-O-levulinoyl-1-thio-α/β-D-galactofuranoside (14)

To a solution of compound **17** (1:6 α/β mixture, 3.7 g, 6.3 mmol) in CH_2Cl_2 (80 mL) under argon was added DMAP (0.38 g, 3.1 mmol). The solution was cooled to 0 °C and then levulinic acid (0.95 mL, 9.2 mmol) was added followed by DCC (2.0 g, 9.6 mmol). The reaction mixture was stirred for 90 min and then filtered through Celite. The filtrate was washed successively with satd aqueous $NaHCO_3$ solution and brine. The organic layer was then separated, dried (Na_2SO_4), filtered and concentrated to a syrup that was purified by column chromatography (3:1 hexane–EtOAc) to obtain the **14** (3.97 g, 92%) as an α/β (1:6) mixture; R_f 0.26 (7:3, hexane–EtOAc); Data for major isomer: ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.12–8.06 (m, 4 H, Ar), 8.02–7.98 (m, 2 H, Ar), 7.63–7.51 (m, 5 H, Ar), 7.51–7.35 (m, 6 H, Ar), 7.35–7.25 (m, 3 H, Ar), 5.83–5.78 (m, 2 H, H-1, H-5), 5.70 (dd, 1 H, *J* = 1.9, 1.9 Hz, H-2), 5.64 (dd, 1 H, *J* = 1.9, 5.1 Hz, H-3), 4.82 (dd, 1 H, *J* = 4.8, 4.8 Hz, H-4), 4.68 (dd, 1 H, *J* = 4.3, 11.9 Hz, H-6), 4.57 (dd, 1 H, *J* = 6.4, 11.9 Hz, H-6'), 2.72–2.53 (m, 4 H, lev C*H*$_2$C*H*$_2$), 2.08 (s, 3 H, lev C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 205.9 (C=O), 171.9 (C=O), 166.0 (C=O), 165.4 (C=O), 165.3 (C=O), 133.7 (Ar), 133.3 (Ar), 133.1 (Ar), 133.0 (Ar), 132.4 (Ar), 130.1 (Ar), 129.9(6) (Ar), 129.8 (Ar), 129.6 (Ar), 129.1 (Ar), 128.9(6) (Ar), 128.9(2) (Ar), 128.5(6) (Ar), 128.5(5) (Ar), 128.4 (Ar), 128.3 (Ar), 127.9 (Ar), 91.2 (C-1), 82.1 (C-2), 81.2 (C-4), 77.4 (C-3), 69.9 (C-5), 63.2 (C-6), 37.9 (lev *C*H$_2$), 29.7 (lev *C*H$_3$), 28.0 (lev *C*H$_2$). ESI-MS *m*/*z* calcd for $[M + Na]^+$ $C_{38}H_{34}O_{10}SNa$: 705.1765. Found: 705.1751.

Phenyl 2,3,5-tri-O-benzoyl-6-O-levulinoyl-1-thio-α/β-D-galactofuranoside (15)

Prepared from **18** (1:5 α/β mixture, 4.68 g, 8.0 mmol), DMAP (0.48 g, 4.0 mmol), levulinic acid (1.2 mL, 11.7 mmol) and DCC (2.5 g, 12.1 mmol) in CH_2Cl_2 (100 mL) as described for the synthesis of **14** to afford **15** (5.0 g, 92%) as an α/β (1:5) mixture; R_f 0.23 (7:3, hexane–EtOAc); Data for major isomer: ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.12–8.04 (m, 4 H, Ar), 7.91–7.89 (m, 2 H, Ar), 7.62–7.40 (m, 7 H, Ar), 7.40–7.24 (m, 7 H, Ar), 5.94 (app dt, 1 H, *J* = 4.4, 6.7 Hz, H-5), 5.83 (d, 1 H, *J* = 1.8 Hz, H-1), 5.65 (app t, 1 H, *J* = 1.6 Hz, H-2), 5.63 (ddd, 1 H, *J* = 0.6, 1.5, 4.9 Hz, H-3), 4.86 (ddd, 1 H, *J* = 0.6, 3.9, 4.9 Hz, H-4), 4.57 (dd, 1 H, *J* = 4.4, 11.8 Hz, H-6), 4.47 (dd, 1 H, *J* = 8.5, 11.8 Hz, H-6'), 2.61–2.40 (m, 4 H, lev C*H*$_2$C*H*$_2$), 2.09 (s, 3 H, lev C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2 (C=O), 172.2 (C=O), 165.7 (C=O), 165.5 (C=O), 165.3 (C=O), 133.7 (Ar), 133.5 (Ar), 133.3 (Ar), 133.2 (Ar), 132.4 (Ar), 132.1 (Ar), 130.1 (Ar), 130.0 (Ar), 129.9(9) (Ar), 129.9(1) (Ar), 129.8(5) (Ar), 129.4 (Ar), 129.1 (Ar), 129.0(5) (Ar), 128.8(9) (Ar), 128.8 (Ar), 128.5 (Ar), 128.4(9) (Ar), 128.4(3) (Ar), 128.3 (Ar), 127.9 (Ar), 91.3 (C-1), 82.4 (C-2), 81.4 (C-4), 77.8 (C-3), 70.2 (C-5), 62.9(5) (C-6), 37.8 (lev *C*H$_2$), 29.7 (lev *C*H$_3$), 27.8 (lev *C*H$_2$). ESI-MS *m*/*z* calcd for $[M + Na]^+$ $C_{38}H_{34}O_{10}SNa$: 705.1765. Found: 705.1749.

Octyl 2,3,5-tri-O-benzoyl-6-O-levulinoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (19)

To a solution of alcohol **13** (1.8 g, 0.9 mmol), and thioglycoside **15** (0.73 g, 1.1 mmol), in CH_2Cl_2 (60 mL) under argon atmosphere was added powdered 4 Å molecular sieves (0.63 g). The solution was stirred for 30 min before cooling it to 0 °C. *N*-iodosuccinimide (0.67 g, 3.0 mmol), silver triflate (0.07 g, 0.3 mmol) and TMSOTf (10 μL) were added and the solution was continued to stir at 0 °C until the reaction was complete. The reaction was then quenched by adding triethylamine dropwise until the pH of the solution was slightly basic (~8). The reaction mixture was then quickly filtered into a solution of satd aq sodium thiosulfate (80 mL) and extracted with CH_2Cl_2. The organic layer was then washed with water (2 × 40 mL), separated, dried (Na_2SO_4) and concentrated under vacuum to give a syrupy residue that was purified through column chromatography (1:1, hexane–EtOAc) to afford **19** (2.0 g, 86%) as a foam; R_f 0.24 (1:1, hexane–EtOAc), $[\alpha]_D$ −10.8 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.75 (m, 24 H, Ar), 7.52–7.05 (m, 41 H, Ar), 5.89 (ddd, 1 H, *J* = 3.9, 7.7, 11.6 Hz), 5.84–5.68 (m, 7 H), 5.67–5.62 (m, 4 H), 5.56–5.50 (m, 4 H), 5.37 (s, 1 H), 5.18 (s, 1 H), 5.10 (s, 1 H), 4.86-4.82 (m, 2 H), 4.75–4.58 (m, 6 H), 4.52 (dd, 1 H, *J* = 3.9, 11.9 Hz), 4.45–4.34 (m, 3 H), 4.31–4.25 (m, 2 H), 4.12–4.06 (m, 2 H), 4.02–3.82 (m, 3 H), 3.78–3.68 (m, 2 H), 3.62 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.55 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.61–2.40 (m, 4 H, lev CH_2CH_2), 2.02 (s, 3 H, lev CH_3), 2.01 (s, 3 H, NHCOCH_3), 1.64–1.58 (m, 3 H), 1.53 (s, 3 H, C(CH_3)$_2$), 1.40–1.20 (m, 13 H, octyl CH_2, C(CH_3)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2 (C=O), 172.1 (C=O), 169.9 (C=O), 166.1 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7(5) (C=O), 165.7(0) (C=O), 165.6 (C=O),

165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 165.1 (C=O), 165.0 (C=O), 137.1 (Ar), 133.4 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 132.8 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 129.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.7 (Ar), 128.5 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 ($C(CH_3)_2$), 106.7 (C-1), 105.8 (C-1), 105.5 (C-1), 104.0 (C-1), 101.7 (PhCH), 98.2 (C-1), 98.1 (C-1), 82.9, 82.8, 82.7, 82.0, 81.8, 81.7, 80.1, 77.9, 77.7, 77.6, 77.0, 76.4, 76.2, 74.9, 73.0, 72.9, 71.9, 70.3, 68.9, 68.3, 67.6, 65.3, 65.0, 64.4, 53.6, 37.8 (lev CH_2), 31.8 (octyl CH_2), 29.6 (lev CH_3), 29.3 (octyl CH_2), 29.2 (octyl CH_2), 28.0 (lev CH_2), 27.8 ($C(CH_3)_2$), 26.4 ($C(CH_3)_2$), 26.2, 23.5 ($NHCOCH_3$), 22.7, 17.2 (C-6'), 14.1 (octyl CH_3). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{145}H_{143}NO_{44}Na_2$: 1323.9383. Found: 1323.9369.

Octyl 2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (20)

Prepared from **19** (1.79 g, 0.69 mmol) and hydrazine acetate (0.2 g, 2.1 mmol) in CH_2Cl_2–CH_3OH (9:1 v/v, 40 mL) as described for the synthesis of compound **13** to afford **20** (1.5 g, 87%) as a foam. R_f 0.44 (1:1, hexane–EtOAc), $[\alpha]_D$ −11.4 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.75 (m, 24 H, Ar), 7.52–7.05 (m, 41 H, Ar), 5.89 (ddd, 1 H, *J* = 3.9, 7.7, 11.6 Hz), 5.84–5.68 (m, 7 H), 5.67–5.62 (m, 4 H), 5.56–5.50 (m, 4 H), 5.35 (s, 1 H), 5.2 (s, 1 H), 5.10 (s, 1 H), 4.96 (dd, 1 H, *J* = 2.6, 5.9 Hz), 4.84 (dd, 1 H, *J* = 4.3, 4.3 Hz), 4.74–4.60 (m, 7 H), 4.44–4.38 (m, 2 H), 4.31–4.24 (m, 2 H), 4.12–4.06 (m, 2 H), 4.02–3.82 (m, 5 H), 3.78–3.66 (m, 2 H), 3.61 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.55 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.40 (dd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.02 (s, 3 H, $NHCOCH_3$), 1.64–1.58 (m, 3 H), 1.53 (s, 3 H, $C(CH_3)_2$), 1.40–1.20 (m, 13 H, octyl CH_2, $C(CH_3)_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6'); ^{13}C NMR

(125 MHz, $CDCl_3$, δ_C) 169.8 (C=O), 166.4 (C=O), 166.1 (C=O), 166.0 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 137.1 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 130.0 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.0 (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (Ar), 128.6 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 ($C(CH_3)_2$), 106.6 (C-1), 106.1 (C-1), 105.8 (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 82.8, 82.6, 82.5, 82.4, 82.0, 81.8, 81.7, 81.3, 80.1, 77.8, 77.7, 77.5, 76.4, 76.2, 75.0, 73.8, 73.0, 72.8, 72.0, 68.9, 68.3, 67.6, 65.3, 65.0, 64.4, 63.2, 61.1, 53.6, 31.8 (octyl CH_2), 29.4 (octyl CH_2), 29.3 (octyl CH_2), 29.2 (octyl CH_2), 27.9, ($C(CH_3)_2$), 26.4 ($C(CH_3)_2$), 26.2, 23.4 ($NHCOCH_3$), 22.6, 17.2 (C-6'), 14.1 (octyl CH_3). ESI-MS *m*/*z* calcd for $[M + Na]^+$ $C_{140}H_{137}NO_{42}Na$: 2526.8507. Found: 2526.8516.

Octyl 2,3,6-tri-O-benzoyl-5-O-levulinoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (21).

Prepared from alcohol **20** (1.47 g, 0.59 mmol), thioglycoside **14** (0.6 g, 0.9 mmol), powdered 4 Å molecular sieves (0.57 g), *N*-iodosuccinimide (0.7 g, 3.1 mmol), silver triflate (0.04 g, 0.16 mmol) and TMSOTf (10 μL) in CH_2Cl_2 (50 mL) as described for the synthesis of **19** to afford **21** (1.4 g, 77%) as a foam. R_f 0.25 (1:1, hexane–EtOAc, $[\alpha]_D$ –3.4 (*c* 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.75 (m, 30 H, Ar), 7.52–7.05 (m, 50 H, Ar), 5.93–5.86 (m, 2 H), 5.84–5.67 (m, 7 H), 5.67–5.62 (m, 4 H), 5.59–5.52 (m, 3 H), 5.40 (dd, 1 H, *J* = 0.8, 5.0 Hz), 5.36 (d, 1 H, *J* = 1.8 Hz), 5.31 (d, 1 H, *J* = 1.4 Hz), 5.18 (s, 1 H), 5.16 (s, 1 H), 5.10 (s, 1 H), 4.84 (dd, 1 H, *J* = 4.4, 4.4 Hz), 4.80 (d, 1 H, *J* = 4.4 Hz), 4.75–4.48 (m, 10 H), 4.44–4.38 (m, 2 H),

4.30–4.24 (m, 2 H), 4.10–4.04 (m, 3 H), 4.02–3.82 (m, 4 H), 3.78–3.66 (m, 2 H), 3.61 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.54 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.62–2.40 (m, 4 H, lev CH_2CH_2), 2.02 (s, 3 H, lev CH_3), 2.00 (s, 3 H, NHCOCH_3), 1.64–1.58 (m, 3 H), 1.53 (s, 3 H, C(CH_3)$_2$), 1.40–1.20 (m, 13 H, octyl CH_2, C(CH_3)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 205.9 (C=O), 171.9 (C=O), 169.8 (C=O), 166.1 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7(4) (C=O), 165.7(0) (C=O), 165.5 (C=O), 165.4(5) (C=O), 165.2 (C=O), 165.1 (C=O), 164.9(0) (C=O), 137.1 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 132.8 (Ar), 129.9 (Ar), 129.8 (Ar), 129.6 (Ar), 129.0(4), 128.9(5) (Ar), 128.9(0), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*(CH$_3$)$_2$), 106.7 (C-1), 105.8 (C-1), 105. 7(7) (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 82.8, 82.7, 82.6, 82.5, 82.0, 81.8, 81.6, 81.5, 80.1, 77.8, 77.7(5), 77.6, 76.3, 76.2, 74.9, 73.1, 73.0, 71.9, 70.2, 68.9, 68.3, 67.8, 67.6, 65.4, 65.0, 64.4, 63.5, 63.2, 53.6, 37.8 (lev *C*H$_2$), 31.8 (octyl *C*H$_2$), 29.6 (lev *C*H$_3$), 29.3 (octyl *C*H$_2$), 29.2 (octyl *C*H$_2$), 28.0 (lev *C*H$_2$), 27.9 (C(CH_3)$_2$), 26.4 (C(CH_3)$_2$), 26.2, 23.5 (NHCO*C*H$_3$), 22.6, 17.2 (C-6'), 14.1 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{172}H_{165}NO_{52}Na_2$: 1561.0041. Found: 1561.0043.

Octyl 2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-Oopylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (22)

Prepared from compound **21** (1.27 g, 0.41 mmol) and hydrazine acetate (0.2 g, 2.1 mmol) in CH_2Cl_2–CH_3OH (4:1 v/v, 40 mL) as described for the synthesis of **13** to afford **22** (1.13 g, 92%) as a foam. R_f 0.30 (1:1, hexane–EtOAc), $[\alpha]_D$ −3.9 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.75 (m, 30 H, Ar), 7.52–7.05 (m, 50 H, Ar), 5.93–5.86 (m, 2 H), 5.82–5.73 (m, 6 H), 5.72–5.61 (m, 4 H), 5.58–5.50 (m, 4 H), 5.36 (d, 1 H, *J* = 0.4, 1.6 Hz), 5.35 (d, 1 H, *J* = 1.5 Hz), 5.18 (s, 1 H), 5.17 (s, 1 H), 5.10 (s, 1 H), 4.84 (dd, 1 H, *J* = 4.4, 4.4 Hz), 4.78 (dd, 1 H, *J* = 4.4, 4.4 Hz), 4.75–4.62 (m, 7 H), 4.60–4.48 (m, 2 H), 4.47–4.24 (m, 7 H), 4.10–3.82 (m, 8 H), 3.98–3.68 (m, 2 H), 3.61 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.54 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.02 (s, 3 H, NHCOCH_3), 1.64–1.58 (m, 3 H), 1.53 (s, 3 H, C(CH_3)$_2$), 1.40–1.20 (m, 13 H, octyl CH_2, C(CH_3)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.8 (C=O), 166.4 (C=O), 166.0 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7(4) (C=O), 165.7(0) (C=O), 165.5 (C=O), 165.4(5) (C=O), 165.2 (C=O), 165.12 (C=O), 165.1 (C=O), 164.9(0) (C=O), 137.1 (Ar), 133.4 (Ar), 133.32 (Ar), 133.3(0) (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 132.8(9) (Ar), 132.82 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.0(3) (Ar), 129.0 (Ar), 128.9(5) (Ar), 128.8 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*(CH$_3$)$_2$), 106.9 (C-1), 106.7 (C-1), 105.8 (C-1), 105. 7(7) (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 83.6, 82.8, 82.7, 82.4, 82.0, 81.8, 81.4, 80.1, 77.8, 77.7 , 77.6, 76.8, 76.3, 76.2, 74.9, 73.3, 73.0, 71.9, 69.4, 68.9, 68.3, 67.9, 67.6, 66.2, 65.4, 65.0, 64.4, 63.2, 53.6, 31.8 (octyl *C*H$_2$), 29.3(4) (octyl *C*H$_2$), 29.3 (octyl

*C*H$_2$), 27.9 (C(*C*H$_3$)$_2$), 26.4 (C(*C*H$_3$)$_2$), 26.2, 23.5 (NHCO*C*H$_3$), 22.6, 17.2 (C-6'), 14.1 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{167}H_{159}NO_{50}Na_2$: 1511.9857. Found: 1511.9856.

Octyl 2,3,5-tri-O-benzoyl-6-O-levulinoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)- 2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (23)

Prepared from alcohol **22** (1.13 g, 0.38 mmol), thioglycoside **15** (0.39 g, 0.57 mmol), powdered 4 Å molecular sieves (0.37 g), *N*-iodosuccinimide (0.58 g, 2.6 mmol), silver triflate (0.04 g, 0.15 mmol) and TMSOTf (10 μL) in CH_2Cl_2 (30 mL) as described for the synthesis of **19** to afford **23** (1.15 g, 86%) as a foam. R_f 0.13 (1:1, hexane–EtOAc), $[\alpha]_D$ −9.4 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.75 (m, 35 H, Ar), 7.53–7.05 (m, 60 H, Ar), 5.94–5.86 (m, 2 H), 5.84–5.70 (m, 9 H), 5.68–5.62 (m, 4 H), 5.60–5.50 (m, 4 H), 5.37 (d, 1 H, *J* = 1.5 Hz), 5.35 (d, 1 H, *J* = 1.4 Hz), 5.18 (s, 1 H), 5.17 (s, 1 H), 5.10 (s, 1 H), 4.88–4.82 (m, 2 H), 4.80 (dd, 1 H, *J* = 4.4 Hz), 4.76–4.63 (m, 9 H), 4.62–4.54 (m, 2 H), 4.52 (dd, 1 H, *J* = 4.0, 11.9 Hz), 4.46–4.38 (m, 2 H), 4.36 (dd, 1 H, *J* = 7.8, 11.9 Hz), 4.32–4.26 (m, 2 H), 4.12–4.04 (m, 3 H), 4.03–3.82 (m, 5 H), 3.78–3.67 (m, 2 H), 3.61 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.55 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.62–2.40 (m, 4 H, lev C*H*$_2$C*H*$_2$), 2.02 (s, 3 H, lev C*H*$_3$), 2.0 (s, 3 H, NHCOC*H*$_3$), 1.64–1.58 (m, 3 H), 1.52 (s, 3 H, C(C*H*$_3$)$_2$), 1.40–1.20 (m, 13 H, octyl C*H*$_2$, C(C*H*$_3$)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$), 0.83 (d, 3 H, *J* = 6.0 Hz, C*H*$_3$-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2 (C=O), 172.1 (C=O), 169.8 (C=O), 166.1 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7(4) (C=O), 165.7(0) (C=O), 165.5 (C=O), 165.4(5) (C=O), 165.2 (C=O), 165.1 (C=O), 165.0 (C=O), 137.1 (Ar), 133.3 (Ar), 133.2(8) (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar),

132.8 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 129.0, 128.9 (Ar), 128.7(0), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*(CH_3)$_2$), 106.7 (C-1), 105.9 (C-1), 105.8 (C-1), 105.5 (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 82.8, 82.6, 82.5, 82.0, 81.8, 80.1, 77.8, 77.7, 77.6(5), 77.62, 76.5, 76.3, 76.2, 74.9, 73.2, 72.9, 72.0, 71.9, 70.4, 68.9, 68.3, 67.7, 67.6, 65.4, 65.2, 65.0, 64.4, 53.6, 37.8 (lev *C*H_2), 31.8 (octyl *C*H_2), 29.6 (lev *C*H_3), 29.4 (octyl *C*H_2), 29.3 (octyl *C*H_2), 29.2 (octyl *C*H_2), 28.0 (lev *C*H_2), 27.8 (C(*C*H_3)$_2$), 26.4 (C(*C*H_3)$_2$), 26.2, 23.5 (NHCO*C*H_3), 22.7, 17.2 (C-6'), 14.1 (octyl *C*H_3). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{199}H_{187}NO_{60}Na_2$: 1798.0698. Found: 1798.0709.

Octyl 2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (24)

Prepared from compound **23** (1.0 g, 0.29 mmol) and hydrazine acetate (0.2 g, 2.1 mmol) in CH_2Cl_2–CH_3OH (4:1 v/v, 30 mL) as described for the synthesis of **13** to afford **24** (0.98 g, 97%) as a foam. R_f 0.25 (1:1, hexane–EtOAc, $[\alpha]_D$ −10.1 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.04–7.70 (m, 35 H, Ar), 7.52–7.03 (m, 60 H, Ar), 5.93–5.87 (m, 2 H), 5.83–5.68 (m, 8 H), 5.67–5.62 (m, 4 H), 5.59–5.48 (m, 4 H), 5.37 (d, 1 H, *J* = 1.4 Hz), 5.34 (d, 1 H, *J* = 1.1 Hz), 5.19 (s, 1 H), 5.17 (s, 1 H), 5.10 (s, 1 H), 4.95 (dd, 1 H, *J* = 2.5, 5.7 Hz), 4.85 (dd, 1 H, *J* = 4.3, 4.3 Hz), 4.79 (dd, 1 H, *J* = 4.3, 4.3 Hz), 4.75–4.54 (m, 12 H), 4.45–4.38 (m, 2 H), 4.31–4.24 (m, 2 H), 4.12–4.04 (m, 3 H), 4.02–3.82 (m, 7 H), 3.78–3.67 (m, 2 H), 3.61 (dd, 1 H, *J* = 9.6 Hz), 3.55 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 3.33 (dd, 1 H, *J* = 6.0, 6.0 Hz), 2.03 (s, 3 H, NHCOC*H*$_3$),1.64–1.58 (m, 3 H), 1.53 (s, 3 H, C(C*H*$_3$)$_2$), 1.40–1.20 (m, 13 H,

octyl C*H*$_2$, C(C*H*$_3$)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$), 0.83 (d, 3 H, *J* = 6.0 Hz, C*H*$_3$-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.8 (C=O), 166.4 (C=O), 166.1 (C=O), 166.0 (C=O), 165.9 (C=O), 165.7 (C=O), 165.6(7) (C=O), 165.5(0) (C=O), 165.4 (C=O), 165.1(4) (C=O), 165.1 (C=O), 164.9(0) (C=O), 137.1 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0(5) (Ar), 132.9(5) (Ar), 132.8 (Ar), 129.9(7) (Ar), 129.9 (Ar), 129.8 (Ar), 129.7(5) (Ar), 129.6 (Ar), 129.0 (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (Ar), 128.6 (Ar), 128.4 (Ar), 128.3(7) (Ar), 128.3 (Ar), 128.2(5) (Ar), 128.1 (Ar), 128.0 (Ar), 109.4 (*C*(CH$_3$)$_2$), 106.7 (C-1), 106.6 (C-1), 106.1 (C-1), 105.9 (C-1), 105.8 (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 82.8, 82.6, 82.5, 82.3, 82.0, 81.8, 81.3, 80.1, 77.8, 77.6 , 77.5, 76.6, 76.5, 76.3, 76.2, 74.9, 73.9, 73.2, 72.9(5), 72.7, 72.1, 71.9, 68.9, 68.3, 67.6, 65.4, 65.3, 65.0, 64.4, 63.2, 61.0 53.6, 31.8 (octyl *C*H$_2$), 29.3(4) (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 27.9(5) (C(*C*H$_3$)$_2$), 26.4 (C(*C*H$_3$)$_2$), 26.2, 23.5 (NHCO*C*H$_3$), 22.7, 17.2 (C-6'), 14.1 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{194}H_{181}NO_{58}Na_2$: 1749.0514. Found: 1749.0493.

Octyl 2,3,6-tri-O-benzoyl-5-O-levulinoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)- 2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (25)

Prepared from alcohol **24** (0.98 g, 0.28 mmol), thioglycoside **14** (0.29 g, 0.4 mmol), powdered 4 Å molecular sieves (0.3 g), *N*-iodosuccinimide (0.29 g, 1.29 mmol), silver triflate (0.03 g, 0.12 mmol) and TMSOTf (10 μL) in CH_2Cl_2 (25 mL) as described for the synthesis of **19** to afford **25** (1.01 g, 89%) as a foam. R_f 0.29 (45:55, hexane–EtOAc, two developments), $[\alpha]_D$ –4.9 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.70 (m, 42 H, Ar), 7.60–7.04 (m, 68 H, Ar), 5.93–5.86 (m, 2 H), 5.84–5.67 (m, 10 H), 5.67–5.60 (m, 5 H), 5.60–5.52 (m, 3 H), 5.40 (dd, 1 H, *J* = 5.1 Hz), 5.36 (d, 1 H, *J* = 1.4 Hz), 5.35 (d, 1 H, *J* = 1.4 Hz), 5.31 (d, 1 H, *J* = 1.2 Hz), 5.19–5.14 (m, 3 H), 5.10 (s, 1 H), 4.84 (dd, 1 H, *J* = 4.3, 4.3 Hz), 4.78 (dd, 1 H, *J* = 3.8, 8.0 Hz), 4.75–4.48 (m, 15 H), 4.44–4.38 (m, 2 H), 4.30–4.24 (m, 2 H), 4.10–3.82 (m, 10 H), 3.78–3.66 (m, 2 H), 3.61 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.54 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.62–2.40 (m, 4 H, lev CH_2CH_2), 2.03 (s, 3 H, lev CH_3), 1.99 (s, 3 H, NHCOCH_3), 1.64–1.58 (m, 3 H), 1.53 (s, 3 H, C(CH_3)$_2$), 1.40–1.20 (m, 13 H, octyl CH_2, C(CH_3)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 205.9 (C=O), 171.9 (C=O), 169.8 (C=O), 166.1 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7 (C=O), 165.6(0) (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 165.1 (C=O), 165.0 (C=O), 164.9 (C=O), 137.1 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 132.9 (Ar), 132.8 (Ar), 129.9 (Ar), 129.8 (Ar), 129.6 (Ar), 129.0 (Ar), 128.9(4) (Ar), 128.8(5), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*(CH$_3$)$_2$), 106.7 (C-1),

105.9 (C-1), 105. 8 (C-1), 104.0 (C-1), 101.7 (PhCH), 98.2 (C-1), 98.1 (C-1), 82.8, 82.6, 82.5, 82.0, 81.8, 81.6, 81.5, 80.1, 77.8, 77.7(5), 77.6, 76.6, 76.5, 76.3, 76.2, 74.9, 73.2, 72.9, 72.0, 71.9, 70.2, 68.9, 68.3, 67.8, 67.7, 67.6, 65.4, 65.0, 63.5, 63.2, 53.6, 37.8 (lev CH_2), 31.8 (octyl CH_2), 29.6 (lev CH_3), 29.3 (octyl CH_2), 29.2 (octyl CH_2), 28.0 (lev CH_2), 27.9(8) ($C(CH_3)_2$), 26.4 ($C(CH_3)_2$), 26.2, 23.5 ($NHCOCH_3$), 22.6, 17.2 (C-6'), 14.1 (octyl CH_3). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{226}H_{209}NO_{68}Na_2$: 2035.1355. Found: 2035.1355.

Octyl 2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)- 2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (26)

Prepared from compound **25** (0.68 g, 0.17 mmol) and hydrazine acetate (0.065 g, 0.7 mmol) in CH_2Cl_2–CH_3OH (5:1 v/v, 50 mL) as described for the synthesis of **13** to afford **26** (0.61 g, 94%) as a foam. R_f 0.27 (45:55, hexane–EtOAc), $[\alpha]_D$ –4.3 (*c* 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.70 (m, 42 H, Ar), 7.58–7.05 (m, 68 H, Ar), 5.90–5.84 (m, 2 H), 5.82–5.66 (m, 9 H), 5.65–5.58 (m, 4 H), 5.58–5.48 (m, 6 H), 5.36–5.32 (m, 4 H), 5.18–5.14 (m, 3 H), 5.08 (s, 1 H), 4.84 (dd, 1 H, *J* = 4.4, 4.4 Hz), 4.78–4.60 (m, 11 H), 4.58–4.47 (m, 3 H), 4.45–4.24 (m, 6 H), 4.10–3.80 (m, 9 H), 3.77–3.66 (m, 2 H), 3.60 (dd, 1 H, *J* = 9.5, 9.5 Hz), 3.54 (dd, 1 H, *J* = 7.5, 9.9 Hz), 3.40 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.69 (d, 1 H, *J* = 7.5 8.5 Hz, OH), 2.02 (s, 3 H, $NHCOCH_3$), 1.64–1.58 (m, 3 H), 1.51 (s, 3 H, $C(CH_3)_2$), 1.40–1.20 (m, 13 H, octyl CH_2, $C(CH_3)_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.8 (C=O), 166.4 (C=O), 166.1 (C=O), 166.0 (C=O), 165.9 (C=O), 165.8

(C=O), 165.7 (C=O), 165.6(0) (C=O), 165.4(3) (C=O), 165.4 (C=O), 165.2 (C=O), 165.1 (C=O), 165.0 (C=O), 164.9 (C=O), 137.1 (Ar), 133.4 (Ar), 133.32 (Ar), 133.3(0) (Ar), 133.1 (Ar), 132.8(7) (Ar), 132.7(8) (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.0 (Ar), 128.9(5) (Ar), 128.8 (Ar), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 126.1 (Ar), 109.4 ($C(CH_3)_2$), 106.9 (C-1), 106.7 (C-1), 105.8 (C-1), 105. 7(5) (C-1), 104.0 (C-1), 101.7 (PhCH), 98.2 (C-1), 98.1 (C-1), 83.6, 82.7, 82.6, 82.5, 82.4, 82.0, 81.8, 81.4, 80.0, 77.8, 77.7, 77.6, 76.2, 74.9, 73.4, 73.2, 72.9, 72.0, 71.9, 69.4, 68.9, 68.3, 67.9, 67.7, 67.6, 66.2, 65.4, 65.3, 64.9, 64.4, 63.1, 53.6, 31.8 (octyl CH_2), 29.3(3) (octyl CH_2), 29.2(5) (octyl CH_2), 27.9 ($C(CH_3)_2$), 26.4 ($C(CH_3)_2$), 26.2, 23.4 ($NHCOCH_3$), 22.6, 17.2 (C-6'), 14.1 (octyl CH_3).

Octyl 2,3,5-tri-O-benzoyl-6-O-levulinoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (27)

Prepared from alcohol **26** (0.61 g, 0.15 mmol), thioglycoside **15** (0.16 g, 0.2 mmol), powdered 4 Å molecular sieves (0.17 g), *N*-iodosuccinimide (0.18 g, 0.8 mmol), silver triflate (0.02 g, 0.07 mmol) and TMSOTf (10 μL) in CH_2Cl_2 (15 mL) as described for the synthesis of **19** to afford **27** (0.55 g, 79%) as a foam. R_f 0.21 (45:55, hexane–EtOAc), $[\alpha]_D$ −10.2 (*c* 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.72 (m, 47 H, Ar), 7.53–7.05 (m, 78 H, Ar), 5.91–5.82 (m, 3 H), 5.82–5.66 (m, 12 H), 5.65–5.58 (m, 5 H), 5.58–5.47 (m, 5 H), 5.35–5.31 (m, 3 H), 5.16–5.12 (m, 3 H), 5.08 (s, 1 H), 4.84–4.80 (m, 2 H), 4.80–4.74 (m, 2 H), 4.74–4.58 (m, 14 H), 4.58–4.46 (m, 4 H), 4.43–4.24 (m, 4 H), 4.10–3.80 (m, 8 H), 3.78–3.66 (m, 2 H), 3.60 (dd, 1 H, *J*

= 9.6, 9.6 Hz), 3.53 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.40 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.61–2.40 (m, 4 H, lev C*H*$_2$C*H*$_2$), 2.02 (s, 3 H, lev C*H*$_3$), 2.0 (s, 3 H, NHCOC*H*$_3$), 1.64–1.58 (m, 3 H), 1.52 (s, 3 H, C(C*H*$_3$)$_2$), 1.40–1.20 (m, 13 H, octyl C*H*$_2$, C(C*H*$_3$)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$), 0.83 (d, 3 H, *J* = 6.0 Hz, C*H*$_3$-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2 (C=O), 172.0 (C=O), 169.8 (C=O), 166.1 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7 (C=O), 165.6 (C=O), 165.4(4) (C=O), 165.3(8) (C=O), 165.2 (C=O), 165.1 (C=O), 165.0 (C=O), 137.1 (Ar), 133.3 (Ar), 133.2(5) (Ar), 133.1(5) (Ar), 133.1 (Ar), 132.9 (Ar), 132.8 (Ar), 129.9 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 129.0, 128.9 (Ar), 128.7(0), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0(5) (Ar), 127.9(8) (Ar), 126.1 (Ar), 109.4 (*C*(CH$_3$)$_2$), 106.7 (C-1), 105.9 (C-1), 105. 8 (C-1), 105.5 (C-1), 103.9(5) (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 82.8, 82.7, 82.6, 82.5, 82.0, 81.8, 80.0, 77.8, 77.7, 77.6, 76.3, 76.2, 74.9, 73.1(9), 73.1(4), 73.0, 72.0, 71.9, 70.4, 68.9, 68.3, 67.6(4), 67.6, 65.4, 65.2, 65.0, 64.4, 53.6, 37.8 (lev *C*H$_2$), 31.8 (octyl *C*H$_2$), 29.6 (lev *C*H$_3$), 29.32, 29.2(5) (octyl *C*H$_2$), 27.9 (C(*C*H$_3$)$_2$), 27.8 (lev *C*H$_2$), 26.4 (C(*C*H$_3$)$_2$), 26.2, 23.4 (NHCO*C*H$_3$), 22.6, 17.2 (C-6'), 14.1 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{253}H_{231}NO_{76}Na_2$: 2272.2013. Found: 2272.2010.

Octyl 2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (28)

Prepared from compound **27** (0.54 g, 0.12 mmol) and hydrazine acetate (0.03 g, 0.3 mmol) in CH_2Cl_2–CH_3OH (5:1 v/v, 30 mL) as described for the synthesis of **13** to afford **28** (0.51 g, 97%) as a foam. R_f 0.31 (45:55, hexane–EtOAc), $[\alpha]_D$ −11.7 (*c* 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.04–7.70 (m, 47 H, Ar), 7.52–7.03 (m, 78 H, Ar), 5.92–5.86 (m, 3 H), 5.81 (dd, 1 H, *J* = 0.5, 5.3 Hz), 5.84–5.69 (m, 8 H), 5.68–5.61 (m, 5 H), 5.59–5.48 (m, 6 H), 5.36 (d, 1 H, *J* = 1.6 Hz), 5.34 (d, 1 H, *J* = 1.2 Hz), 5.33 (d, 1 H, *J* = 1.8 Hz), 5.19–5.15 (m, 3 H), 5.10 (s, 1 H), 4.95 (dd, 1 H, *J* = 2.4, 5.7 Hz), 4.85 (dd, 1 H, *J* = 4.3, 4.3 Hz), 4.80–4.75 (m, 2 H), 4.75–4.59 (m, 14 H), 4.58–4.54 (m, 2 H), 4.44–4.38 (m, 2 H), 4.31–4.26 (m, 2 H), 4.10–4.03 (m, 4 H), 4.02–3.83 (m, 8 H), 3.78–3.68 (m, 2 H), 3.62 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.55 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 3.33 (dd, 1 H, *J* = 6.0, 6.0 Hz), 2.03 (s, 3 H, NHCOC*H*$_3$),1.64–1.58 (m, 3 H), 1.53 (s, 3 H, C(C*H*$_3$)$_2$), 1.40–1.20 (m, 13 H, octyl C*H*$_2$, C(C*H*$_3$)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$), 0.83 (d, 3 H, *J* = 6.0 Hz, C*H*$_3$-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.8 (C=O), 166.4 (C=O), 166.1 (C=O), 166.0 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7 (C=O), 165.6(5) (C=O), 165.5(0) (C=O), 165.4 (C=O), 165.1(3) (C=O), 165.1 (C=O), 137.1 (Ar), 133.4 (Ar), 133.32 (Ar), 133.3(0) (Ar), 133.1 (Ar), 133.0(8) (Ar), 133.0(4) (Ar), 132.9 (Ar), 132.8 (Ar), 132.82 (Ar), 130.0 (Ar), 129.9(5) (Ar), 129.8(7) (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.0 (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (Ar), 128.6 (Ar), 128.4 (Ar), 128.3(6) (Ar), 128.2(8) (Ar), 128.2(4) (Ar), 128.1 (Ar), 128.0 (Ar), 126.1 (Ar), 109.4 (*C*(CH$_3$)$_2$),

106.7(3) (C-1), 106.7(1) (C-1), 106.6 (C-1), 106.1 (C-1), 105.9 (C-1), 105.8 (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 82.8, 82.6, 82.4, 82.3, 82.0, 81.8, 81.3, 80.0, 77.8, 77.7 , 77.6, 77.5, 76.3, 76.2, 74.9, 73.9, 73.3, 73.2, 73.0, 72.7, 72.1, 72.0, 71.9, 68.9, 68.3, 67.6(6), 67.6(0), 67.5(6), 65.4, 65.2, 65.0, 64.4, 63.2, 61.0 53.6, 31.8 (octyl *C*H_2), 29.3(3) (octyl *C*H_2), 29.2(5) (octyl *C*H_2), 27.9 (C(*C*H_3)$_2$), 26.4 (C(*C*H_3)$_2$), 26.2, 23.4 (NHCO*C*H_3), 22.6, 17.2 (C-6'), 14.1 (octyl *C*H_3). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{248}H_{225}NO_{74}Na_2$: 2223.1829. Found: 2223.1829.

Octyl 2,3,6-tri-O-benzoyl-5-O-levulinoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (29)

Prepared from alcohol **28** (0.4 g, 0.09 mmol), thioglycoside **14** (0.1 g, 0.14 mmol), powdered 4 Å molecular sieves (0.11 g), *N*-iodosuccinimide (0.1 g, 0.5 mmol), silver triflate (0.01 g, 0.04 mmol) and TMSOTf (10 μL) in CH_2Cl_2 (12 mL) as described for the synthesis of **19** to afford **29** (0.34 g, 74%) as a foam. R_f 0.16 (45:55, hexane–EtOAc), $[\alpha]_D$ −6.9 (*c* 0.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$, δ_H) 8.00–7.72 (m, 52 H, Ar), 7.60–7.03 (m, 88 H, Ar), 5.93–5.86 (m, 4 H), 5.81 (d, 1 H, *J* =5.4 Hz), 5.80–5.67 (m, 10 H), 5.67–5.60 (m, 5 H), 5.60–5.52 (m, 5 H), 5.40 (d, 1 H, *J* = 4.8 Hz), 5.36 (d, 1 H, *J* = 1.8 Hz), 5.34 (d, 1 H, *J* = 1.2 Hz), 5.31 (d, 1 H, *J* = 1.8 Hz), 5.19–5.14 (m, 4 H), 5.10 (s, 1 H), 4.84 (dd, 1 H, *J* = 4.8, 4.8 Hz), 4.80–4.76 (m, 3 H), 4.75–4.50 (m, 21 H), 4.44–4.38 (m, 2 H), 4.30–4.25 (m, 2 H), 4.10–3.82 (m, 10 H), 3.78–3.67 (m, 2

H), 3.62 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.54 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.62–2.40 (m, 4 H, lev C*H*$_2$C*H*$_2$), 2.03 (s, 3 H, lev C*H*$_3$), 1.99 (s, 3 H, NHCOC*H*$_3$), 1.64–1.58 (m, 3 H), 1.53 (s, 3 H, C(C*H*$_3$)$_2$), 1.40–1.20 (m, 13 H, octyl C*H*$_2$, C(C*H*$_3$)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$), 0.83 (d, 3 H, *J* = 6.0 Hz, C*H*$_3$-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 205.9 (C=O), 171.9 (C=O), 169.9 (C=O), 166.1 (C=O), 165.9 (C=O), 165.8(5) (C=O), 165.8 (C=O), 165.7 (C=O), 165.5(0) (C=O), 165.4 (C=O), 165.2 (C=O), 165.1 (C=O), 165.0(7) (C=O), 164.9 (C=O), 137.1 (Ar), 133.4 (Ar), 133.3(6) (Ar), 133.2(7) (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.8 (Ar), 129.9 (Ar), 129.8 (Ar), 129.6 (Ar), 129.1 (Ar), 129.0 (Ar), 128.9(6) (Ar), 128.8(9), 128.4 (Ar), 128.3 (Ar), 128.2(6) (Ar), 128.1(4) (Ar), 128.1(0) (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*(CH$_3$)$_2$), 106.8 (C-1), 106.7 (C-1), 105.9 (C-1), 105.8 (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 82.8, 82.7, 82.6, 82.5, 82.0, 81.8, 81.7, 81.6, 80.1, 77.9, 77.8, 77.6, 76.3, 76.2, 74.9, 73.2, 72.9(5), 72.0, 71.9, 70.2, 68.9, 68.3, 67.8, 67.7, 67.6, 65.4, 65.0, 64.4, 63.5, 63.2, 53.6, 37.9 (lev *C*H$_2$), 36.7, 31.8 (octyl *C*H$_2$), 29.6 (lev *C*H$_3$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 28.0 (lev *C*H$_2$), 27.9(5) (C(*C*H$_3$)$_2$), 26.4 (C(*C*H$_3$)$_2$), 26.2, 23.5 (NHCO*C*H$_3$), 22.7, 17.2 (C-6'), 14.1 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{280}H_{253}NO_{84}Na_2$: 2509.2670. Found: 2509.2723.

Octyl 2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (30)

Prepared from **29** (0.46 g, 0.09 mmol) and hydrazine acetate (0.025 g, 0.27 mmol) in CH_2Cl_2–CH_3OH (9:1 v/v, 10 mL) as described for the synthesis of **13** to afford **30** (0.43 g, 96%) as a foam. R_f 0.33 (45:55, hexane–EtOAc), $[\alpha]_D$ –4.2 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.70 (m, 52 H, Ar), 7.59–7.03 (m, 88 H, Ar), 5.92–5.84 (m, 2 H), 5.81 (d, 1 H, *J* =5.4 Hz), 5.78–5.59 (m, 15 H), 5.59–5.49 (m, 6 H), 5.36–5.31 (m, 4 H), 5.18–5.13 (m, 3 H), 5.09 (s, 1 H), 4.84 (dd, 1 H, *J* = 4.2, 4.2 Hz), 4.80–4.58 (m, 18 H), 4.58–4.46 (m, 4 H), 4.46–4.24 (m, 6 H), 4.10–3.80 (m, 12 H), 3.78–3.66 (m, 2 H), 3.61 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.54 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.40 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.02 (s, 3 H, NHCOCH_3), 1.64–1.58 (m, 3 H), 1.51 (s, 3 H, C(CH_3)$_2$), 1.40–1.20 (m, 13 H, octyl CH_2, C(CH_3)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.8 (C=O), 166.4 (C=O), 166.1 (C=O), 166.0 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7 (C=O), 165.6 (C=O), 165.4(4) (C=O), 165.4 (C=O), 165.2 (C=O), 165.1 (C=O), 165.0 (C=O), 164.9 (C=O), 137.0 (Ar), 133.4 (Ar), 133.32 (Ar), 133.3(0) (Ar), 133.1 (Ar), 133.0(5) (Ar), 132.9 (Ar), 132.7(8) (Ar), 129.9 (Ar), 129.7 (Ar), 129.6 (Ar), 129.0 (Ar), 128.9(4) (Ar), 128.8(7) (Ar), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*(CH$_3$)$_2$), 106.9 (C-1), 106.7 (C-1), 105.9 (C-1), 105. 8 (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 83.6, 82.8, 82.7, 82.5, 82.4, 82.0, 81.8, 81.4, 80.1, 77.8, 77.7, 77.6, 76.3, 76.2, 74.9, 73.4, 73.2, 72.9, 72.0, 71.9, 69.4, 68.9,

68.3, 67.9, 67.7, 67.6, 66.2, 65.4, 65.3, 64.9(9), 64.4, 63.2, 53.6, 31.8 (octyl *C*H_2), 29.3(4) (octyl *C*H_2), 29.3 (octyl *C*H_2), 27.9 (C(*C*H_3)$_2$), 26.4 (C(*C*H_3)$_2$), 26.2, 23.5 (NHCO*C*H_3), 22.6, 17.2 (C-6'), 14.1 (octyl *C*H_3). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{275}H_{247}NO_{82}Na_2$: 2460.7503. Found: 2460.7534.

Octyl 2,3,5-tri-O-benzoyl-6-O-levulinoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (31)

Prepared from alcohol **30** (0.4 g, 0.08 mmol), thioglycoside **15** (0.13 g, 0.19 mmol), powdered 4 Å molecular sieves (0.18 g), *N*-iodosuccinimide (0.4, 1.8 mmol, added in five portions), and TMSOTf (30 μL added in five portions) in CH_2Cl_2 (15 mL) as described for the synthesis of **19** to afford **31** (0.3 g, 69%) as a foam. R_f 0.15 (45:55, hexane–EtOAc), $[\alpha]_D$ −7.9 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.01–7.72 (m, 58 H, Ar), 7.53–7.05 (m, 97 H, Ar), 5.91–5.84 (m, 4 H), 5.84–5.60 (m, 20 H), 5.60–5.50 (m, 6 H), 5.38–5.33 (m, 4 H), 5.18–5.14 (m, 4 H), 5.10 (s, 1 H), 4.87–4.75 (m, 4 H), 4.75–4.48 (m, 21 H), 4.46–4.32 (m, 3 H), 4.32–4.25 (m, 2 H), 4.12–3.82 (m, 11 H), 3.79–3.68 (m, 2 H), 3.62 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.55 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.42 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.61–2.40 (m, 4 H, lev C*H*$_2$C*H*$_2$), 2.03 (s, 3 H, lev C*H*$_3$), 2.0 (s, 3 H, NHCOC*H*$_3$), 1.64–1.58 (m, 3 H), 1.54 (s, 3 H, C(C*H*$_3$)$_2$), 1.40–1.20 (m, 13 H, octyl C*H*$_2$, C(C*H*$_3$)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl C*H*$_3$), 0.83 (d, 3 H, *J* = 6.0 Hz, C*H*$_3$-6');

^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2 (C=O), 172.1 (C=O), 169.8 (C=O), 166.1 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7 (C=O), 165.6 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 165.1 (C=O), 165.0(5) (C=O), 137.1 (Ar), 133.3 (Ar), 133.2(6) (Ar), 133.1(8) (Ar), 133.1 (Ar), 133.0 (Ar), 132.8 (Ar), 129.9 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5(5) (Ar), 129.0, 128.9 (Ar), 128.7(0), 128.4 (Ar), 128.3 (Ar), 128.2(5) (Ar), 128.1 (Ar), 128.0(6) (Ar), 126.2 (Ar), 109.4 ($C(CH_3)_2$), 106.7 (C-1), 105.9 (C-1), 105.8 (C-1), 105.5 (C-1), 103.9(7) (C-1), 101.7 (PhCH), 98.2 (C-1), 98.1 (C-1), 82.8, 82.7, 82.5, 82.0, 81.8, 80.1, 77.8, 77.7, 77.6, 76.3, 76.2, 74.9, 73.2, 73.0, 72.0, 71.9, 70.4, 68.9, 68.3, 67.6(6), 67.6, 65.4, 65.3, 65.0, 64.4, 53.6, 37.8 (lev CH_2), 31.8 (octyl CH_2), 29.6 (lev CH_3), 29.32, 29.2(7) (octyl CH_2), 27.9(5) ($C(CH_3)_2$), 27.8 (lev CH_2), 26.4 ($C(CH_3)_2$), 26.2, 23.5 ($NHCOCH_3$), 22.6, 17.2 (C-6'), 14.1 (octyl CH_3). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{307}H_{275}NO_{92}Na_2$: 2746.3328. Found: 2746.3334.

Octyl 2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (32)

Prepared from compound **31** (0.27 g, 0.05 mmol) and hydrazine acetate (0.1 g, 1.0 mmol) in CH_2Cl_2–CH_3OH (9:1 v/v, 9 mL) as described for the synthesis of **13** to afford **32** (0.25 g, 95%) as a foam. R_f 0.40 (45:55, hexane–EtOAc), $[\alpha]_D$ −11.1 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.06–7.70 (m, 60 H, Ar), 7.56–7.03 (m, 95 H, Ar), 5.94–5.86 (m, 5 H), 5.84 (d, 1 H, *J*

= 5.4 Hz), 5.82–5.62 (m, 20 H), 5.62–5.48 (m, 6 H), 5.39–5.33 (m, 5 H), 5.22–5.14 (m, 4 H), 5.12 (s, 1 H), 4.96 (dd, 1 H, *J* = 2.0, 5.5 Hz), 4.86 (dd, 1 H, *J* = 4.0, 4.0 Hz), 4.83–4.54 (m, 25 H), 4.46–4.40 (m, 2 H), 4.33–4.26 (m, 2 H), 4.14–3.82 (m, 15 H), 3.82–3.68 (m, 2 H), 3.63 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.56 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.42 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 3.33 (dd, 1 H, *J* = 6.0, 6.0 Hz), 2.03 (s, 3 H, NHCOCH_3), 1.64–1.58 (m, 3 H), 1.53 (s, 3 H, C(CH_3)$_2$), 1.40–1.20 (m, 13 H, octyl CH_2, C(CH_3)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.8 (C=O), 166.4 (C=O), 166.1 (C=O), 166.0 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7(5) (C=O), 165.6(6) (C=O), 165.5 (C=O), 165.4 (C=O), 165.1(3) (C=O), 165.1 (C=O), 137.1 (Ar), 133.4 (Ar), 133.3 (Ar), 133.1(0) (Ar), 133.0 (Ar), 132.8 (Ar), 129.9(7) (Ar), 129.8(9) (Ar), 129.8 (Ar), 129.6 (Ar), 129.0 (Ar), 128.9(5) (Ar), 128.8(8) (Ar), 128.7 (Ar), 128.6 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*(CH$_3$)$_2$), 106.8 (C-1), 106.6 (C-1), 106.1 (C-1), 105.9 (C-1), 105.8 (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 82.8, 82.7, 82.5, 82.4, 82.1, 81.8, 81.3, 80.1, 77.9, 77.8 , 77.6, 77.5, 76.3, 76.2, 74.9, 73.9, 73.3, 73.2, 73.0, 72.8, 72.0, 71.9, 68.9, 68.3, 67.7, 67.6, 65.4, 65.3, 65.0, 64.4, 63.2, 61.1 53.6, 31.8 (octyl *C*H$_2$), 29.7 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 29.2(7), 27.9(6) (C(*C*H$_3$)$_2$), 26.4 (C(*C*H$_3$)$_2$), 26.2, 23.5 (NHCO*C*H$_3$), 22.7, 17.2 (C-6'), 14.1 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + 2(NH_4)]^{2+}$ $C_{302}H_{277}N_3O_{90}$: 2692.359. Found: 2692.354.

Octyl 2,3,6-tri-O-benzoyl-5-O-levulinoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (33)

Prepared from alcohol **32** (0.25 g, 0.05 mmol), thioglycoside **14** (0.05 g, 0.07 mmol), powdered 4 Å molecular sieves (0.05 g), *N*-iodosuccinimide (0.05 g, 0.22 mmol) and silver triflate (0.005 g, 0.02 mmol) in CH_2Cl_2 (6 mL) as described for the synthesis of **19** to afford **33** (0.23 g, 84%) as a foam. R_f 0.28 (45:55, hexane–EtOAc, two developments), $[\alpha]_D$ −5.2 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.00–7.72 (m, 65 H, Ar), 7.60–7.02 (m, 105 H, Ar), 5.93–5.85 (m, 6 H), 5.82 (d, 1 H, *J* = 5.4 Hz), 5.80–5.61 (m, 20 H), 5.60–5.52 (m, 6 H), 5.42 (d, 1 H, *J* = 4.8 Hz), 5.38–5.30 (m, 5 H), 5.20–5.14 (m, 5 H), 5.10 (s, 1 H), 4.83–4.87 (m, 1 H), 4.82–4.48 (m, 31 H), 4.45–4.38 (m, 2 H), 4.32–4.26 (m, 2 H), 4.12–3.82 (m, 14 H), 3.79–3.68 (m, 2 H), 3.62 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.55 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.62–2.40 (m, 4 H, lev CH_2CH_2), 2.03 (s, 3 H, lev CH_3), 1.99 (s, 3 H, $NHCOCH_3$),1.64–1.58 (m, 3 H), 1.53 (s, 3 H, $C(CH_3)_2$), 1.40–1.20 (m, 13 H, octyl CH_2, $C(CH_3)_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6’); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 205.9 (C=O), 171.9 (C=O), 169.8 (C=O), 166.1 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7 (C=O), 165.6 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 165.1 (C=O), 165.0(5) (C=O), 164.9 (C=O), 137.1 (Ar), 133.4 (Ar), 133.3(6) (Ar), 133.2(5) (Ar), 133.1 (Ar),

133.0(7) (Ar), 132.9 (Ar), 132.8 (Ar), 129.9 (Ar), 129.7 (Ar), 129.6 (Ar), 129.0 (Ar), 128.9 (Ar), 128.8(8), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*$(CH_3)_2$), 106.8 (C-1), 106.7 (C-1), 105.9 (C-1), 105.8 (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 82.8, 82.7, 82.6, 82.5, 82.1, 81.8, 81.6, 81.5, 80.1, 77.8, 77.7, 77.6, 76.3, 76.2, 74.9, 73.2, 72.9(5), 72.0, 71.9, 70.2, 68.9, 68.3, 67.8, 67.7, 67.6, 65.4, 65.0, 64.4, 63.5, 63.2, 53.6, 37.9 (lev *C*H_2), 31.8 (octyl *C*H_2), 29.6 (lev *C*H_3), 29.4 (octyl *C*H_2), 29.3 (octyl *C*H_2), 29.2, 28.0 (lev *C*H_2), 27.9 (C(*C*$H_3)_2$), 26.4 (C(*C*$H_3)_2$), 26.2, 23.5 (NHCO*C*H_3), 22.6, 17.2 (C-6’), 14.1 (octyl *C*H_3). ESI-MS *m*/*z* calcd for $[M + 2(NH_4)]^{2+}$ $C_{334}H_{305}N_3O_{100}$: 2978.9448. Found: 2978.9507.

Octyl 2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (34)

Prepared from **33** (0.23 g, 0.04 mmol) and hydrazine acetate (0.1 g, 1.0 mmol) in CH_2Cl_2–CH_3OH (9:1 v/v, 10 mL) as described for the synthesis of **13** to afford **34** (0.21 g, 94%) as a foam. R_f 0.45 (45:55, hexane–EtOAc, two developments), $[\alpha]_D$ –4.1 (*c* 0.3, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$, δ_H) 8.02–7.72 (m, 65 H, Ar), 7.60–7.03 (m, 105 H, Ar), 5.94–5.86 (m, 5 H), 5.83 (dd, 1 H, *J* = Hz), 5.80–5.71 (m, 11 H), 5.69–5.62 (m, 6 H), 5.60–5.52 (m, 7 H), 5.38–5.33 (m, 5 H), 5.21–5.14 (m, 5 H), 5.11 (s, 1 H), 4.86 (dd, 1 H, *J* = 4.2, 4.2 Hz), 4.82–4.62 (m, 20 H),

4.60–4.50 (m, 5 H), 4.48–4.26 (m, 7 H), 4.13–3.83 (m, 14 H), 3.79–3.68 (m, 2 H), 3.62 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.56 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.42 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.02 (s, 3 H, NHCOCH_3), 1.64–1.58 (m, 3 H), 1.51 (s, 3 H, C(CH_3)$_2$), 1.40–1.20 (m, 13 H, octyl CH_2, C(CH_3)$_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6'); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 169.8 (C=O), 166.4 (C=O), 166.1 (C=O), 166.0 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7(5) (C=O), 165.6 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 165.1 (C=O), 165.0 (C=O), 164.9 (C=O), 137.1 (Ar), 133.3 (Ar), 133.1(2) (Ar), 133.0 (Ar), 132.9 (Ar), 132.8 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 129.0 (Ar), 128.9(4) (Ar), 128.8(8) (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*(CH$_3$)$_2$), 106.9 (C-1), 106.7 (C-1), 105.9 (C-1), 105. 8 (C-1), 104.0 (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 83.6, 82.8, 82.7, 82.5, 82.4, 82.1, 81.8, 81.4, 80.1, 77.9, 77.7, 77.6, 76.3, 76.2, 74.9, 73.4, 73.2, 72.9(6), 72.0, 71.9, 69.4, 68.9, 68.3, 67.9, 67.7, 67.6, 66.2, 65.4, 65.0, 64.4, 63.2, 53.6, 31.8 (octyl *C*H$_2$), 29.3(4) (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 27.9 (C(*C*H$_3$)$_2$), 26.4 (C(*C*H$_3$)$_2$), 26.2, 23.5 (NHCO*C*H$_3$), 22.7, 22.6, 17.2 (C-6'), 14.1 (octyl *C*H$_3$). ESI-MS *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{329}H_{291}NO_{98}Na_2$: 2934.3801. Found: 2934.3829.

Octyl 2,3,5-tri-O-benzoyl-6-O-levulinoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-O-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-O-benzoyl-β-D-galactofuranosyl-(1→4)-2,3-isopropylidene-α-L-rhamnopyranosyl-(1→3)-2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (35)

Prepared from alcohol **34** (0.11 g, 0.02 mmol), thioglycoside **15** (0.025 g, 0.04 mmol), powdered 4 Å molecular sieves (0.045 g), *N*-iodosuccinimide (0.039 g, 0.17 mmol) and silver triflate (0.004 mg, 0.01 mmol) in CH_2Cl_2 (4 mL) as described for the synthesis of **19** to afford **35** (0.1 g, 81%) as a foam. R_f 0.2 (45:55, hexane–EtOAc), $[\alpha]_D$ −8.7 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ_H) 8.00–7.70 (m, 70 H, Ar), 7.53–7.02 (m, 114 H, Ar), 5.92–5.84 (m, 5 H), 5.84–5.68 (m, 15 H), 5.68–5.59 (m, 7 H), 5.59–5.48 (m, 7 H), 5.37–5.32 (m, 4 H), 5.18–5.12 (m, 4 H), 5.10 (s, 1 H), 4.86–4.46 (m, 32 H), 4.46–4.31 (m, 3 H), 4.31–4.24 (m, 2 H), 4.12–3.82 (m, 14 H), 3.79–3.67 (m, 2 H), 3.62 (dd, 1 H, *J* = 9.6, 9.6 Hz), 3.55 (dd, 1 H, *J* = 7.2, 10.2 Hz), 3.41 (ddd, 1 H, *J* = 6.6, 9.6, 13.2 Hz), 2.61–2.40 (m, 4 H, lev CH_2CH_2), 2.03 (s, 3 H, lev CH_3), 2.0 (s, 3 H, $NHCOCH_3$), 1.64–1.58 (m, 3 H), 1.54 (s, 3 H, $C(CH_3)_2$), 1.40–1.20 (m, 13 H, octyl CH_2, $C(CH_3)_2$), 0.9 (t, 3 H, *J* = 7.0 Hz, octyl CH_3), 0.83 (d, 3 H, *J* = 6.0 Hz, CH_3-6’); ^{13}C NMR (125 MHz, $CDCl_3$, δ_C) 206.2 (C=O), 172.0 (C=O), 169.8 (C=O), 166.0 (C=O), 165.9 (C=O), 165.8 (C=O), 165.7 (C=O), 165.6 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 165.1 (C=O), 165.0(5) (C=O), 137.1 (Ar), 133.3 (Ar), 133.2 (Ar), 133.1 (Ar), 133.0 (Ar), 132.8 (Ar), 129.9 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 129.0 (Ar), 128.9 (Ar), 128.7 (Ar), 128.4 (Ar), 128.2

(Ar), 128.1 (Ar), 128.0 (Ar), 126.2 (Ar), 109.4 (*C*$(CH_3)_2$), 106.7 (C-1), 105.9 (C-1), 105.8 (C-1), 105.5 (C-1), 103.9(7) (C-1), 101.7 (Ph*C*H), 98.2 (C-1), 98.1 (C-1), 82.8, 82.7, 82.5, 82.0, 81.8, 80.1, 77.8, 77.7, 77.6(5), 76.3, 76.2, 74.9, 73.2, 72.9, 72.0, 71.9, 70.4, 68.9, 68.3, 67.7, 67.6, 65.4, 65.3, 65.0, 64.4, 53.6, 37.8 (lev *C*H_2), 31.8 (octyl *C*H_2), 29.6 (lev *C*H_3), 29.32, 29.2(6) (octyl *C*H_2), 27.9(5) (C(*C*$H_3)_2$), 27.8 (lev *C*H_2), 26.4 (C(*C*$H_3)_2$), 26.2, 23.5 (NHCO*C*H_3), 22.7, 22.6, 17.2 (C-6'), 14.1 (octyl *C*H_3). ESI-MS *m*/*z* calcd for $[M + 3Na]^+$ $C_{361}H_{319}NO_{108}Na_3$: 2154.9737. Found: 2154.9728.

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