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Synthetic studies toward the anthrax tetrasaccharide: alternative synthesis of this antigen

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ABSTRACT

The synthesis of the anthrax tetrasaccharide, amenable for conjugation, has been envisaged by both [2+2] and [1+3] approaches from D-fucose and L-rhamnose. The successful route reported herein relies on a [1+3] strategy in which the 1,2-*trans*-glycosidic linkages have been secured using a participating group at the 2-position of the donors using conventional thio as well as trichloroacetimidate glycosylation chemistry. The exchange of the ester to benzyl protective groups on the rhamnosyl moiety was key to achieve the final assembly and functionalization of the tetrasaccharide.

1. Introduction

Anthrax is a worldwide disease of sheep, cattle, horses, and other mammals caused by the spore-forming soil bacterium, *Bacillus anthracis*. The ease of production and dissemination of the spores as well as the high lethality that results from their inhalation have designed *B. anthracis* as a potential bioterrorism weapon.[1] This threat has stressed the development of alternative vaccines to the less than optimal currently licensed ones.[2–4] Along this line specific oligosaccharides found at the outermost layer of the spores could be used as antigens to prepare glycoconjugate vaccines, known to be efficient and safe in humans,[5] to inactivate the bacterium at an early stage of the infection. Therefore much attention has been paid to a linear tetrasaccharide **1**, abundantly expressed on the *B. anthracis* exosporium glycoprotein BclA (*Bacillus* collagen-like protein of *anthracis*), which comprises a rare sugar called anthrose [4,6-dideoxy-4-(3-hydroxy-3-methylbutanamido)-2-methyl-D-glucopyranose] (Chart 1).[6]

Several laboratories have succeeded in preparing tetrasaccharide **1**[7–13] and further established that it could be used both as a diagnostic probe and as an antigen in vaccine formulations.[7a,14–16]

We also embarked some years ago on the preparation of fragments and analogues of **1**[17,18] and wish to report herein our own investigations toward and the synthesis of an anthrax tetrasaccharide analogue **2**, equipped with a spacer arm for further conjugation (Scheme 1). All reported syntheses of tetrasaccharide analogues of **1** make use of L-rhamnose and either D-fucose or D-galactose as precursors, with the exception of O'Doherty's fascinating but perhaps less efficient de novo approach,[11] and have been indifferently carried out by adopting either a [2+2][7,12,13] or a [1+3][8–11,13] strategy. Similarly, and independently of the actual strategy retained, we have envisioned that unit **A** of compound **2** could arise from anthrosyl donor **3**[17] while units **B**, **C**, and **D** could be obtained from a common precursor such as rhamnopyranosides **4**[18] or **5**. Pursuing step-economy syntheses, the groups of Kováč, Crich, and Wang[8–10,12,13]

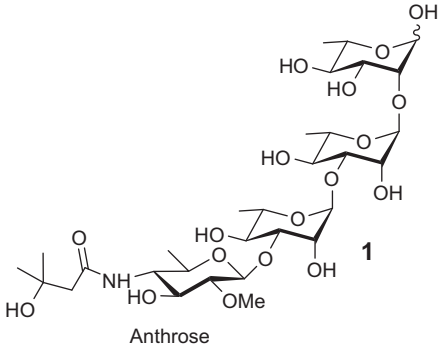

Chart 1. Structure of the *B. anthracis* anthrose-terminated tetrasaccharide antigen **1**.

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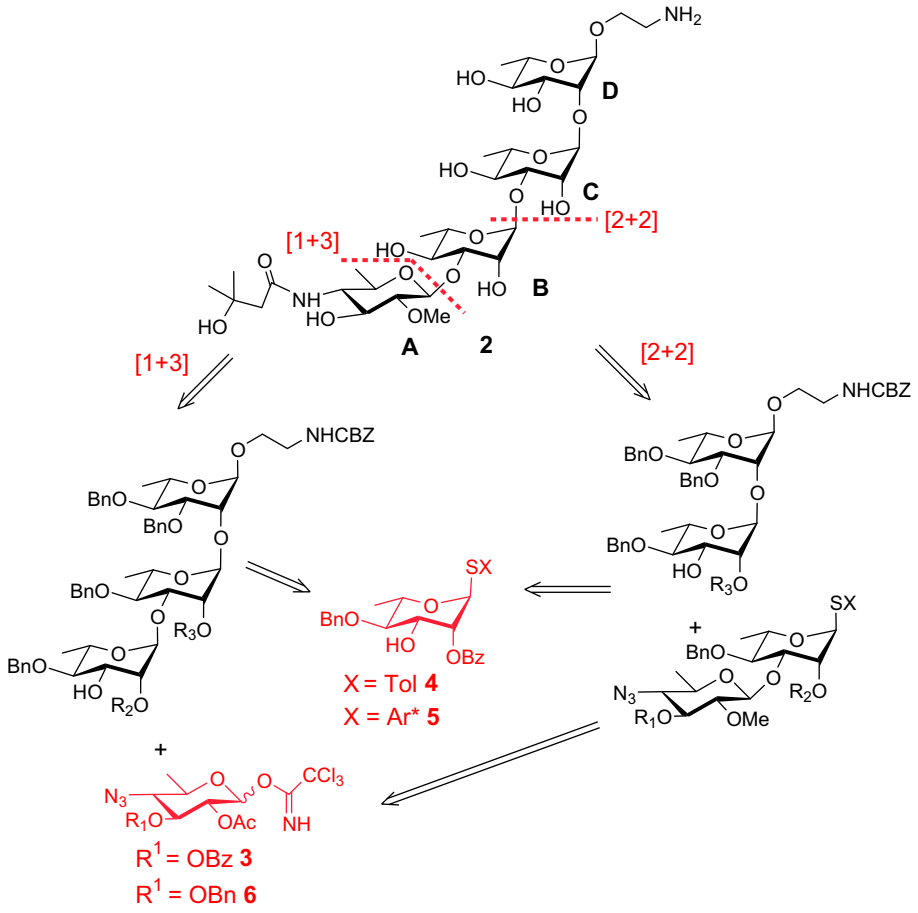


Scheme 1. Retrosynthesis of anthrax tetrasaccharide analogue **2** (*Ar = 5-*tert*-butyl-2-methylphenyl).

elected to secure the α-linkage in the rhamnosylation reactions without anchimeric assistance. However, in the absence of neighboring group participation, the stereoselectivity seems to strongly depend on the choice of the glycosylation conditions and has been fully controlled only by the Kováč's group.[8,9,12] Anomeric mixtures have not been reported by Seeberger, who uses rhamnose building blocks ester-protected at the 2-position,[7] consolidating our initial choice. Finally, construction of the β-linkage of the terminal anthrose unit would analogously rely on the participation of an ester group since attempts to glycosylate an anthrose precursor already methylated at the C-2 position has led to a 7:2 or a 4:1 β/α anomeric mixture depending on the conditions.[10,19]

2. Results and discussion

2.1. Preliminary data

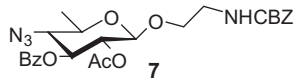
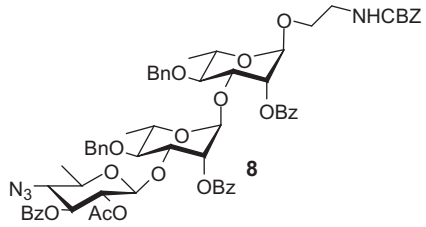
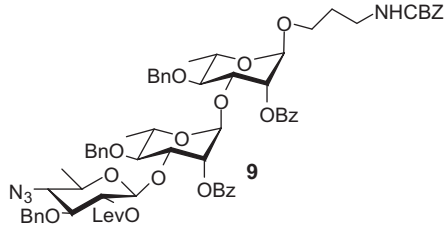
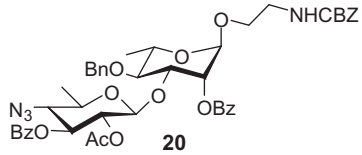
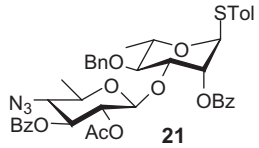
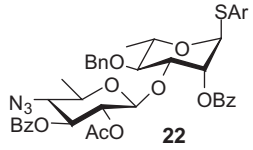
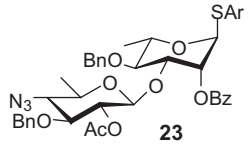
We have recently reported the preparation of a trisaccharide analogue from intermediate **3** according to a **A** + **BC** (equivalent to the present 1+3) strategy.[18] However, this synthesis suffered from several drawbacks. Firstly, key intermediate **3** was obtained from D-galactose following a rather lengthy route, in 13 steps and 11% overall yield. Secondly, contrasting with our previous observations made with a simple anthrose-related monosaccharide **7** (Table 1, entry 1),[17] methylation of the **A** residue of intermediate **8**, after deacetylation, led to an intractable mixture under Kuhn's conditions,[20] apparently due to instability of at least one among the three benzoyl groups and, probably, that at the C-3 position of the **A** unit: Indeed, no such troubles were noticed by Boons and coworkers upon methylation under the same conditions of a closely related trisaccharide, bearing a benzyl rather than a benzoyl protecting group at this position (Table 1, entry 3).[19] Methylation of **8** was actually achieved with diazomethane but in low yield (Table 1, entry 2). To circumvent these limitations, we first decided to design a more efficient synthesis of derivative **3,** to prepare the corresponding benzylated compound **6** and to study the methylation of anthrose-related disaccharides, for which no data were available, to further determine whether a [2+2] strategy would be more efficient than a [1+3] one for synthesizing **2**. We recently fulfilled our first aim, by synthesizing donors **3** and **6** in only nine steps from D-(+)-fucose in 22% and 13% yields, respectively: The syntheses relied on a key pyranose intermediate featuring a 3,4-cyclic sulfate function which served successively as a protecting and a leaving group.[21] The preparation of the **B** and the **CD** unit precursors has been undertaken to achieve our second objective.

2.2. Synthesis of the B precursors and of a CD acceptor

The key 5-*tert*-butyl-2-methylphenyl 4-*O*-benzyl-2-*O*-benzoyl-1-thio-α-L-rhamnopyranoside **5** was prepared analogously to known compound **4**[18] from the non-smelling 5-*tert*-butyl-2-methylthiophenol to compare their respective reactivity (Scheme 2).

Peracetylated aryl 1-thio-L-rhamnopyranoside **10** was obtained as an α/β (9:1) mixture in two steps according to a known procedure in a 91% yield.[22] Zemplèn deprotection of compound **10** afforded triol **11** which was next transformed into acceptor **5**, following a one pot three step sequence developed by Field and co-workers,[23] comprising the formation of a 2,3-orthoester, the benzylation

Table 1
Selective deacetylation and methylation of synthetic anthrax tetrasaccharide fragments

Entry	Compound	Deprotection	Methylation	Ref.
1	 **7**	AcCl, MeOH, 0 °C→rt, 24 h, 70%	MeI, Ag_2O CH_2Cl_2 8 days, 91%	17
2	 **8**	6 days, 50%	CH_2N_2, $BF_3{\cdot}Et_2O$ CH_2Cl_2, 0 °C→rt, 3 h, 35–40%	18
3	 **9**	$NH_2NH_2{\cdot}HOAc$ MeOH/CH_2Cl_2, rt, 93%	MeI, Ag_2O, Me_2S CH_2Cl_2, 12 h, 51%	19
4	 **20**	6 days, **24** (48%), **20** (14%)	6 days, **25** (20%), **26** (20%), **27** (26%),	This work
5	 **21**	8 days, **28** (75%)	8 days, **29** (73%), **28** (12%)	This work
6	 **22**	6 days, **30** (63%), **22** (19%)	Decomposition	This work
7	 **23**	4 days, **23** (17%), **31** (29%), **5** (24%)	Not attempted	This work

of the 4-OH and the regioselective opening of the orthoester to selectively install a benzoyl group at the C-2 position. The orthoester proved to be rather resistant to acid hydrolysis, perhaps due to the steric hindrance of the thioaryl substituent, and compound **5** was finally obtained in a markedly lower yield than its analogue **4** (46% vs 75% yield from triol **11**).

Acceptor **14** was prepared from intermediate **5** either by direct condensation of *N*-CBZ-ethanolamine in the presence of *N*-iodosuccinimide (NIS) and silver(I) trifluoromethanesulfonate (50% yield) or following chloroacetylation to give **12**, glycosylation with *N*-CBZ-ethanolamine, and selective chloroacetyl deprotection (59% overall yield from **5**). Acceptor **14** was designed to further prepare a disaccharide analogous to mono- and tri-saccharide **7** and **8** (see Table 1, entries 1 and 2) for the methylation study (Scheme 2).

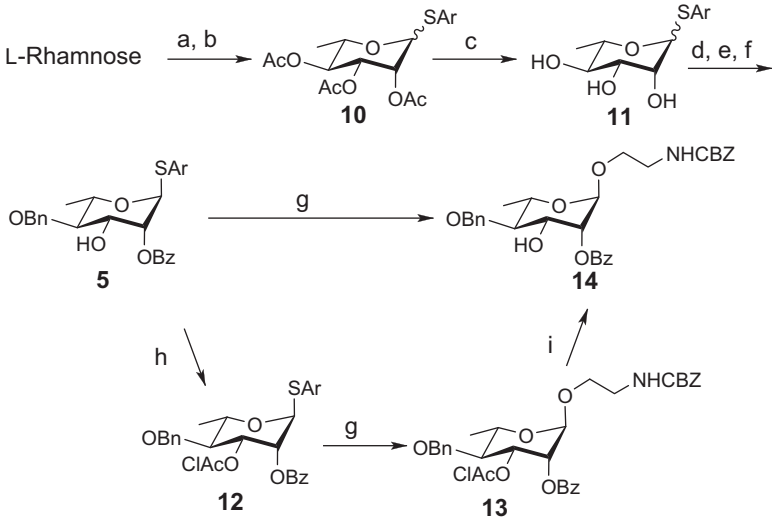
Attempts to benzylate **5** to prepare a **D** acceptor, using benzyl trichloroacetimidate in the presence of catalytic trifluoromethanesulfonic acid, failed. Therefore, compound **5** was treated with sodium methoxide to give diol **15** which was further selectively monobenzylated at the 3-OH according to Matta's protocol (Scheme 3).[24]

Alcohol **16** was benzoylated, glycosylated with *N*-CBZ-aminoethanol in the presence of *N*-iodosucinimide and silver(I) trifluoromethanesulfonate and deprotected to provide acceptor **17** (precursor of the **D** unit) in 71% overall yield.

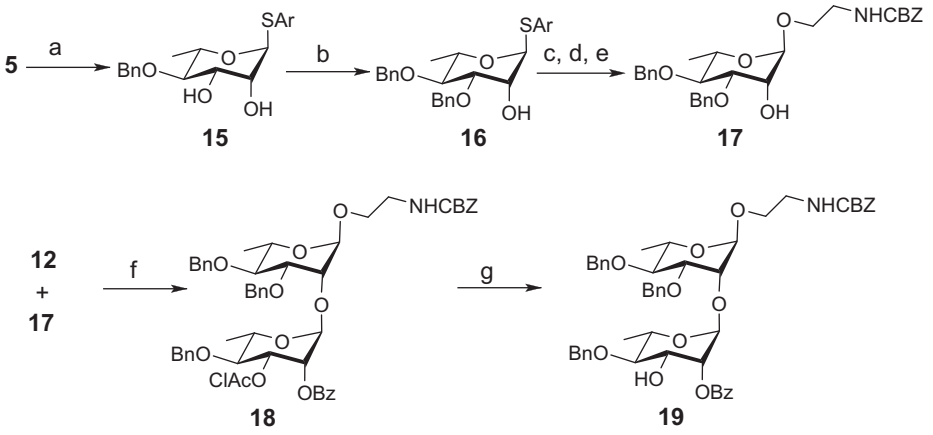
Then NIS/silver(I) trifluoromethanesulfonate-promoted glycosylation of intermediate **12**, now considered as a donor, with acceptor **17** gave disaccharide **18** in 79% yield. The latter was selectively deprotected upon thiourea treatment to provide alcohol **19** in 62% yield.

2.3. Synthesis of the AB disaccharides and deacetylation/methylation study

Having prepared some donors and acceptors, we next envisaged the synthesis of a set of disaccharides to test the [2+2] approach.



Scheme 2. Reagents and conditions: (a) Ac_2O, pyridine, 24 h; (b) 2-methyl-5-*tert*-butylthiophenol, CH_2Cl_2, $BF_3{\cdot}Et_2O$, −40→0 °C, 12 h, 91% (2 steps); (c) MeONa 0.2 M, MeOH, 1 h; (d) triethylorthobenzoate, camphorsulfonic acid, DMF, 3 h; (e) NaH, BnBr, DMF, 2 h, 0 °C→rt; (f) aqueous HCl 2 M 46% (α) (4 steps); (g) *N*-CBZ-ethanolamine, NIS, AgOTf, MS 4 Å, CH_2Cl_2, 30 min, 50% (**5**→**14**), 80% (**12**→**14**); (h) $(ClAc)_2O$, DMAP, Et_3N, CH_2Cl_2, 0 °C→rt, 2 h, 95%; (i) thiourea, $NaHCO_3$, Bu_4NI, CH_2Cl_2, 55 °C, 24 h, 78%.



Scheme 3. Reagents and conditions: (a) MeONa 0.2 M, MeOH, 1 h, quantitative; (b) (i) Bu_2SnO, MeOH, 6 h, reflux; (ii) BnBr, DMF, 90 °C, 71%; (c) BzCl, pyridine, 0 °C→rt, 12 h, quantitative; (d) *N*-CBZ-ethanolamine, NIS, AgOTf, MS 4 Å, CH_2Cl_2, 30 min, quantitative; (e) MeONa 0.2 M, MeOH, 12 h, quantitative; (f) NIS, AgOTf, MS 4 Å, CH_2Cl_2, 30 min, 79%; (g) thiourea, $NaHCO_3$, Bu_4NI, THF, 55 °C, 12 h, 62%.

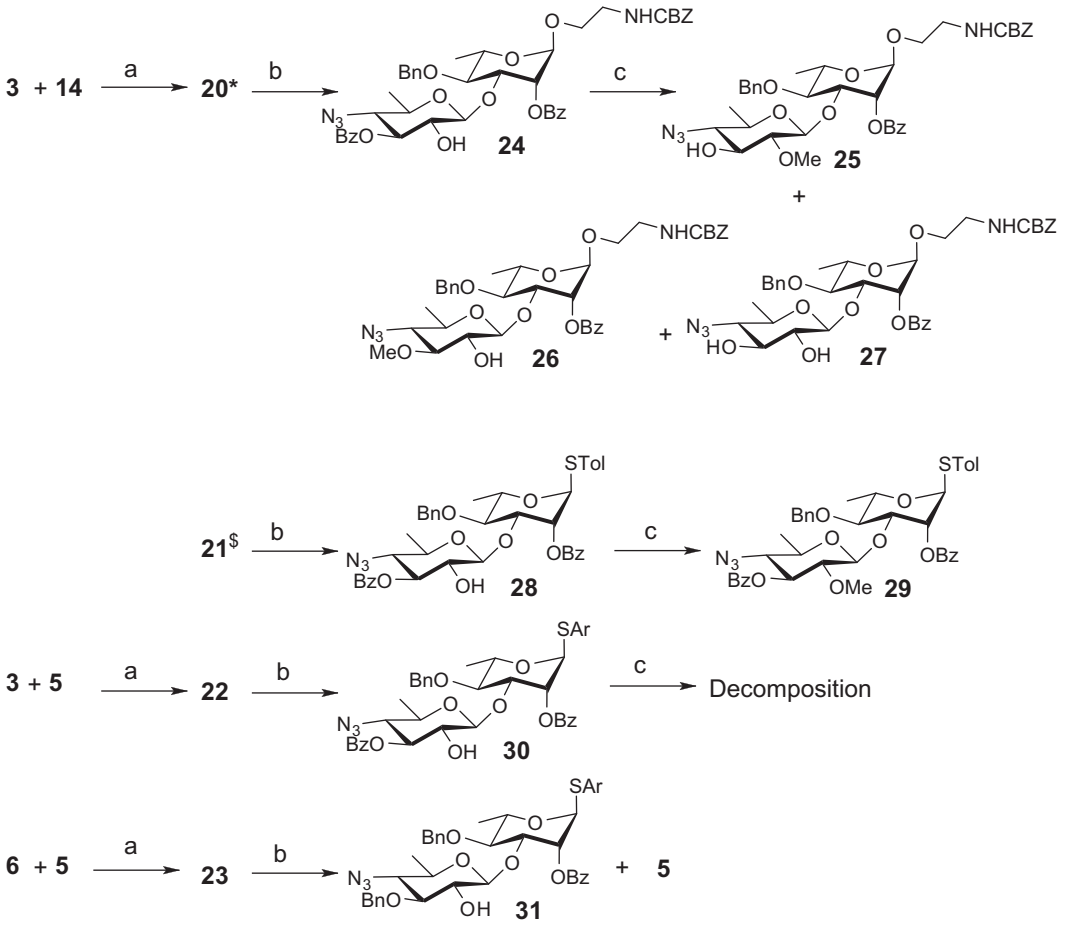
Condensation of donor **3** with acceptors **14** and **5** was performed in the presence of TMSOTf to afford disaccharides **20** and **22** in 48% and 68% yields, respectively (Scheme 4 and Table 1).

The same conditions were applied to the glycosylation of donor **6** with **5** to give disaccharide **23** in 85% yield.

Selective deacetylation of disaccharide **20** was performed by acid-catalyzed methanolysis[25] to give alcohol **24** in a modest 48% yield together with recovered compound **20** (14%) after 6 days. Methylation of intermediate **24** according to Kuhn's procedure gave rise to a 1:1 mixture of the two monomethylated alcohols **25** and **26** (40%) together with diol **27** (26%), underlining the instability of the benzoyl group vicinal to the hydroxy group that we suspected from our earlier results (see Section 2.1).[18] The loss of a benzoyl group has been confirmed by mass spectrometry (*m*/*z* signals at 743 and 729 corresponding to their sodium adducts) and by NMR spectrometry (in particular, disappearance of five aromatic proton signals and of one peak in the carbonyl region). Sites of debenzoylation and methylation of each product have been deduced from the chemical shifts of the H-2, H-3, C-2, and C-3 atoms (Table 2).

In particular, the chemical shifts of H-2B and C-2B remain unaffected while H-3A resonances of products **27**, **25,** and **26** appear about 1.7 ppm upfield compared to that of parent compound **24**, suggesting the presence and the absence of an ester group at C-2B and C-3A, respectively. In parallel, the strong deshielding of the C-2A (respectively C-3A) signal of compound **25** (respectively compound **26**) compared with those of compounds **24** and **27** indicates a possible methylation at this position.

The same reaction sequence was then investigated with disaccharides **21**,[26] **22** and, notably, **23** for which the labile benzoyl at the C-3A position was replaced by a benzyl protecting group, thereby being more likely to survive the methylation reaction in light of the above mentioned observations and the previously reported data (compare entries 1–3 in Table 1). While methanolysis of compounds **21** and **22** gave rise to alcohols **28** and **30** in good yields (75% and 63%, respectively), that of compound **23** proved impracticable and was accompanied with competitive hydrolysis as witnessed by the substantial isolation of acceptor **5** (24%). This observation suggests that the presence of an electron-withdrawing group like a benzoyl on residue **A** is crucial to stabilize the



Scheme 4. Reagents and conditions: (a) TMSOTf (0.4 or 0.5 equiv), −40 °C, CH_2Cl_2, 30 min; (b) AcCl, MeOH, 0 °C→rt; (c) MeI, Ag_2O, CH_2Cl_2. *See structures, reaction times and yields in Table 1; $known compound, see Ref. 26.

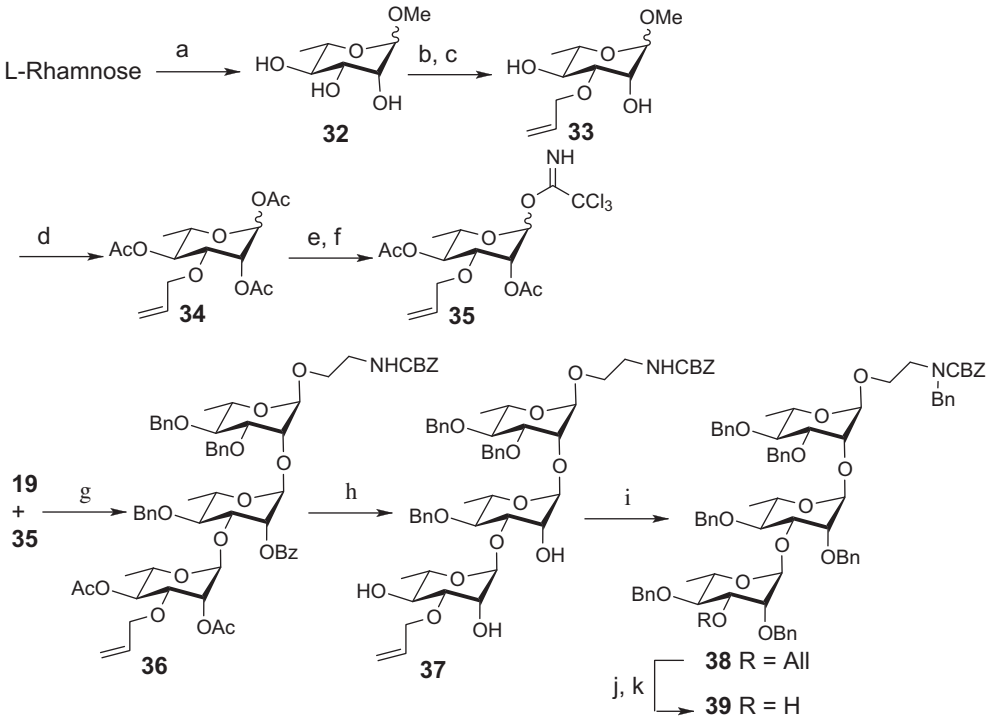
Table 2
Selected ^1H and ^{13}C NMR chemical shifts (ppm) and coupling constants (Hz) of derivatives **24**–**27**

Compound	δ H-2A J_{HH}	δ H-3A J_{HH}	δ H-2B J_{HH}	δ C-2A	δ C-3A	δ C-2B
24	3.63–3.47 m	5.19 t, 9.5	5.42 dd, 1.7, 3.5	73.3	76.4	72.4
27	3.30 dd, 7.8, 9.2	3.48 t, 9.2	5.37 dd, 1.8, 3.5	74.6	75.5	72.5
25	2.95–2.83 m	3.41–3.29 m	5.37–5.34 m	83.7	74.8	73.1, 72.4
26	3.41–3.29 m	3.02 t, 9.5	5.37–5.34 m	75.3	84.7	

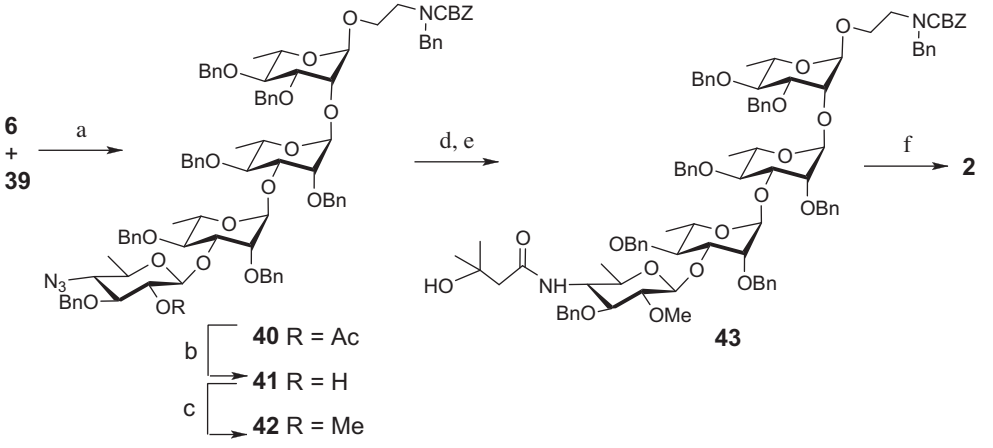
inter-glycoside bond.[27] In view of this latter result, the methylation was only attempted on intermediates **28** and **30**. While compound **28** afforded donor **29** (73%), alcohol **30** decomposed upon methyl iodide/silver(I) oxide treatment. Immediate purple coloration of the reaction mixture was observed upon addition of the reagents, suggesting an activation of sulfur which could reflect a higher reactivity of the 5-*tert*-butyl-2-methyl-1-thiophenyl group compared to toluol despite the higher steric hindrance. Final the preparation of anthrax tetrasaccharide could, in principle, have been achieved from thio-disaccharide **29**. However, this donor did not react with acceptors like disaccharide **19** in the presence of thiophilic promoters either at 0 °C or rt. In the latter condition, TLC and mass spectrometry monitoring of the reaction only revealed the presence of the intact acceptor and that of hydrolyzed donor **29**. We hypothesized that the deactivating benzoyl protecting groups as well as the poor toluol leaving-group properties of compound **29** were partly responsible for the absence of reactivity. Exchange of the toluol to the more reactive trichloroacemididate group was, however, not attempted so as to not lengthen the synthesis. From this preliminary study, we concluded that the synthesis of **2** could not be efficiently achieved according to a [2+2] strategy and that we should privilege the use of ether protecting groups to favor both the final functionalization of the anthrose residue and the glycosylation steps. Similar reasoning was adopted by Kováč[12] and, more recently, by Wang.[13] The preparation of the tetrasaccharide was thus revisited from donor **6** following a [1+3] strategy.

2.4. Synthesis of the ABCD tetrasaccharide adopting a [1+3] strategy

Having donor **6** and acceptor **19**, respectively precursors of the **A** and **CD** units, in hands, we focused on the preparation of a novel donor, precursor of the **B** unit. To this aim, methyl α-L-rhamnopyranoside **32**, obtained as a α/β (9:1) mixture (70%) according to Gin's procedure,[28] was further selectively allylated at the 3-OH to give diol **33**[29] (Scheme 5). Acetolysis of **33** afforded intermediate **34** which was further activated as the trichloroacetimidate donor **35** (38% for the three steps). Schmidt's glycosylation[30] of donor



Scheme 5. Reagents and conditions: (a) AcCl, MeOH, −20 °C→rt, 18 h, 70%; (b) Bu_2SnO, MeOH, reflux, 6 h; (c) AllBr, DMF, 48 h, 70 °C, 40% (2 steps); (d) $Ac_2O/AcOH/H_2SO_4$, 1.5 h, 67%; (e) $BnNH_2$, THF, 12 h, 71%; (f) Cl_3CCN, DBU, CH_2Cl_2, 0 °C→rt, 2 h, 80%; (g) TMSOTf, MS 4 Å, CH_2Cl_2, 0 °C, 30 min, 99%; (h) MeONa, MeOH, 1 h, rt, 70%; (i) BnBr, NaH, DMF, 0 °C→rt, 2 h, 87%; (j) $(Ph_3P)_3RhCl$, DABCO, EtOH/toluene/H_2O, reflux, 16 h; (k) $HgCl_2$, HgO, acetone/H_2O, 4 h, rt, 88% (2 steps).



Scheme 6. Reagents and conditions: (a) TMSOTf, MS 4 Å CH_2Cl_2, −40 °C, 30 min, 56%; (b) MeONa, MeOH, 12 h, 85%; (c) MeI, NaH, DMF, 0 °C→rt, 12 h, 96%; (d) $NaBH_4$, $NiCl_2{\cdot}6H_2O$, EtOH/CH_2Cl_2, 1 h; (e) β-hydroxyisovaleric acid, HATU, DIPEA, DMF, 18 h, 40% (2 steps); (f) H_2, 10 bars, Pd/C, MeOH/AcOH, 50 °C, 30 min, 88%.

35 with acceptor **19** afforded trisaccharide **36** in 99% yield. The exchange of ester to ether protecting groups was then performed upon treatment of **36** with sodium methoxide leading to intermediate **37** followed by perbenzylation to provide compound **38** (48% for the two steps). Allyl protecting group was finally removed by double bond isomerisation followed by hydrolysis[31] to afford the trirhamnosyl acceptor **39**.

Glycosylation of **6** with **39** in the presence of TMSOTf afforded the tetrasaccharide **40** in 56% yield (Scheme 6). 2-*O*-Deacetylation gave alcohol **41** which was further methylated to give **42**. Reduction of azide in **42** was carried out with sodium borohydride in the presence of nickel chloride[32] to provide an intermediate amine which was not isolated but further acylated to introduce the characteristic anthrose amide side-chain (40% for the two steps). Final catalytic hydrogenolysis of the benzyl and carbamate groups in **43** gave the anthrax tetrasaccharide derivative **2** (88%).

3. Conclusion

In conclusion, we have reported the synthesis of the *B. anthracis* tetrasaccharide antigen ready for conjugation in 37 steps from D-fucose and L-rhamnose. The synthesis of the trirhamnan relies on the use of a common thio-rhamnopyranoside precursor while that of the anthrosyl was achieved from donor **6**, efficiently prepared from a cyclic sulfate fucopyranose intermediate.[21] The presence of an acetate protecting group at the 2-position of donor **6**, which

is mandatory to its preparation, has precluded a [2+2] approach making the [1+3] approach the strategy of choice.

4. Experimental methods

4.1. General methods

All reactions were monitored by TLC on Kieselgel 60 F254 (E. Merck). Detection was achieved by charring with vanillin. Silica gel (E. Merck, 240–400 mesh) was used for chromatography. Optical rotations were measured with a JASCO DIP-370 digital polarimeter, using a sodium lamp (λ = 589 nm) at 20 °C. All NMR experiments were performed at 300.13 MHz using Bruker DMX300 spectrometer equipped with a Z-gradient unit for pulsed-field gradient spectroscopy. Assignments were performed by stepwise identification using COSY, and HSQC experiments using standard pulse programs from the Bruker library. Chemical shifts are given relative to external TMS with calibration involving the residual solvent signals.

Low-resolution ESI mass spectra were obtained on a hybrid quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass). High-resolution mass spectra were recorded in positive mode on a ZabSpec TOF (Micromass, UK) tandem hydrid mass spectrometer with EBETOF geometry. The compounds were individually dissolved in MeOH at a concentration of 10 μg mL^{-1} and then infused into the electrospray ion source at a flow rate of 10 μL min^{-1} at 60 °C. The mass spectrometer was operated at 4 kV while scanning the magnet at a typical range of 4000–100 Da. The mass spectra were collected as continuum profile data. Accurate mass measurement was achieved using polyethylene glycol as internal reference with a resolving power set to a minimum of 10,000 (10% valley).

4.2. Synthesis of anthrax tetrasaccharide

4.2.1. 2-Methyl-5-*tert*-butylphenyl 2,3,4-tri-*O*-acetyl-1-thio-L-rhamnopyranoside (10)

To a solution of L-rhamnose (10.0 g, 61 mmol) in pyridine (70 mL) was added acetic anhydride (70 mL, 635 mmol). The reaction mixture was stirred at rt for 24 h and was then quenched by MeOH (70 mL). The reaction mixture was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and was washed with saturated aqueous $KHSO_4$, saturated aqueous $NaHCO_3$ and water. The organic layer was then dried over Na_2SO_4, filtered, and concentrated in vacuo to give **1** as a 8:2 mixture of α/β anomers. This material was used in the next step without purification. To a solution of 1,2,3,4-tetra-*O*-acetyl-L-rhamnopyranose[33] (19.9 g, 60.0 mmol) in CH_2Cl_2 (300 mL) was added 2-methyl-5-*tert*-butylthiophenol (18.4 mL, 100.0 mmol). The mixture was cooled to −40 °C and $BF_3{\cdot}Et_2O$ (12.7 mL, 100.0 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 12 h and was then washed with saturated aqueous $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using cyclohexane/EtOAc (95:5→8:2) as eluent to give **10** as a 9:1 mixture of α/β anomers as a colorless oil (24.7 g, 91%). R_f 0.45 (cyclohexane/EtOAc 8:2); ^1H NMR (300 MHz, $CDCl_3$) δ (α anomer) 7.61–7.06 (m, 3H, $SC_6H_3C(CH_3)_3CH_3$), 5.59–5.57 (m, 1H, H-2), 5.44–5.40 (m, 2H, H-1, H-3), 5.22 (t, 1H, $J_{4,5} = J_{5,6}$ = 9.6 Hz, H-4), 4.46 (dq, 1H, $J_{5,6}$ = 6.1 Hz, $J_{4,5}$ = 9.6 Hz, H-5), 2.44 (s, 3H, $C_6H_3C(CH_3)_3CH_3$), 2.14 (s, 3H, $OCOCH_3$), 2.09 (s, 3H, $OCOCH_3$), 2.02 (s, 3H, OCH_3CO), 1.31 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6), 1.29 (s, 9H, $C_6H_3C(CH_3)_3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ (α anomer) 169.5 (3 × $OCOCH_3$), 149.5, 136.6, 130.0, 129.8, 126.8, 125.1, 122.8 ($SC_6H_3C(CH_3)_3CH_3$), 85.1 (C-1), 71.5 (C-2), 70.9 (C-4), 69.3 (C-3), 67.7 (C-5), 34.2 ($SC_6H_3C(CH_3)_3CH_3$), 31.1 ($SC_6H_3C(CH_3)_3CH_3$), 20.5, 20.3, 20.2, 20.0 (3 × $OCOCH_3$, $SC_6H_3C(CH_3)_3CH_3$), 17.2 (C-6); HR-ESI-MS *m/z* calcd for $C_{23}H_{32}O_7S$ 475.1766 $[M+Na]^+$, found 475.1762.

4.2.2. 2-Methyl-5-*tert*-butylphenyl 1-thio-L-rhamnopyranoside (11)

Compound **10** (24.7 g, 54.6 mmol) was treated with NaOMe (0.2 M solution in MeOH) (546 mL, 109.2 mmol) for 1 h at rt. The reaction mixture was then neutralized by resin Amberlite 120 H^+. The resin was filtered off and the filtrate was concentrated in vacuo to give **11** which was used in the next step without any further purification. R_f 0.20 (cyclohexane/EtOAc 8:2); HR-ESI-MS *m/z* calcd for $C_{17}H_{26}O_4S$ 349.1450 $[M+Na]^+$, found 349.1460.

4.2.3. 2-Methyl-5-*tert*-butylphenyl 2-*O*-benzoyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (5)

To a suspension of triol **11** (3.0 g, 9.2 mmol) in dry MeCN (100 mL), camphor-10-sulfonic acid (880 mg, 3.7 mmol) and triethylorthobenzoate (8.2 mL, 38.6 mmol), were added. The mixture was stirred at rt for 12 h and Et_3N (1.5 mL) was added to neutralize the solution. The mixture was then evaporated to dryness and the residue was diluted with DMF (100 mL). NaH (60% dispersion in mineral oil, 542 mg, 18.4 mmol) was added at 0 °C followed by dropwise addition of BnBr (1.8 mL, 16.6 mmol). The reaction mixture was stirred at rt for 2 h and the excess of sodium hydride was neutralized by dropwise addition of MeOH (20 mL) at 0 °C. The mixture was then evaporated to dryness and the residue was dissolved with EtOAc. The organic phase was washed with water and then with 2 M aqueous HCl (×3). The opening of the orthoester was checked by TLC. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using cyclohexane/EtOAc (98:2→9:1) as eluent to give **5** (2.2 g, 46%) and its β-anomer 2-methyl-5-*tert*-butylphenyl 2-*O*-benzoyl-4-*O*-benzyl-1-thio-β-L-rhamnopyranoside (340 mg, 7%) as colorless oils. (α anomer) R_f 0.42 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −93 ($CHCl_3$, *c* 0.7); ^1H NMR (300 MHz, $CDCl_3$) δ 8.24–7.27 (m, 13H, $SC_6H_3C(CH_3)_3CH_3$, $OCH_2C_6H_5$, $OCOC_6H_5$), 5.82 (dd, 1H, $J_{1,2}$ = 1.3 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.66 (br s, 1H, H-1), 5.11 (d, 1H, $J_{A,B}$ = 11.2 Hz, A part of an AB system, $OCHHC_6H_5$), 4.93 (d, 1H, $J_{A,B}$ = 11.2 Hz, B part of an AB system, $OCHHC_6H_5$), 4.55–4.43 (m, 2H, H-3, H-5), 3.78 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.2 Hz, H-4), 2.59 (s, 3H, $SC_6H_3C(CH_3)_3CH_3$), 1.59 (d, 3H, $J_{5,6}$ = 5.9 Hz, H-6), 1.46 (s, 9H, $SC_6H_3C(CH_3)_3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4 ($OCOC_6H_5$), 149.8, 138.4, 137.0, 133.5, 133.0, 132.9, 130.2, 130.1, 130.0, 129.7, 128.7, 128.6, 128.5, 128.3, 128.1, 127.6, 125.2, 124.0, ($SC_6H_3C(CH_3)_3CH_3$, $OCOC_6H_5$, $OCH_2C_6H_5$) 85.8 (C-1), 81.8 (C-2), 75.6 (C-4), 75.3 ($OCH_2C_6H_5$), 71.3 (C-3), 69.0 (C-5), 34.6 ($SC_6H_3C(CH_3)_3CH_3$) 31.5 ($SC_6H_3C(CH_3)_3CH_3$), 20.5 ($SC_6H_3C(CH_3)_3CH_3$), 18.3 (C-6); HR-ESI-MS *m/z* calcd for $C_{31}H_{36}O_5S$ 543.2175 $[M+Na]^+$, found 543.2160.

4.2.4. 2-Methyl-5-*tert*-butylphenyl 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-chloroacetyl-1-thio- α-L-rhamnopyranoside (12)

To a solution of alcohol **5** (1 g, 1.9 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added chloroacetic anhydride (975 mg, 5.7 mmol), DMAP (71 mg, 0.6 mmol), and Et_3N (800 μL, 8.5 mmol). The reaction mixture was warmed to rt and stirred for 2 h. The mixture was then diluted with CH_2Cl_2 and washed with saturated aqueous $KHSO_4$, saturated aqueous $NaHCO_3$, and water. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using cyclohexane/EtOAc (95:5) as eluent to provide **12** (1.1 g, 95%) as a white solid. R_f 0.65 (cyclohexane/EtOAc 8:2); $[\alpha]_D^{20}$ −33 ($CHCl_3$, *c* 0.7); ^1H NMR (300 MHz, $CDCl_3$) δ 8.18–8.14 (m, 3H, $SC_6H_3C(CH_3)_3CH_3$), 7.56–

7.27 (m, 10H, $OCH_2C_6H_5$, $OCOC_6H_5$), 5.91 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.63 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3) 5.54 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1), 4.86 (d, 1H, $J_{A,B}$ = 11.4 Hz, A part of an AB system, $OCHHC_6H_5$), 4.81 (d, 1H, $J_{A,B}$ = 11.4 Hz, B part of an AB system, $OCHHC_6H_5$), 4.61–4.52 (m, 1H, H-5), 4.02 (d, 1H, $J_{A,B}$ = 14.9 Hz, A part of an AB system, $OCOCHHCl$), 3.94 (d, 1H, $J_{A,B}$ = 14.9 Hz, B part of an AB system, $OCOCHHCl$), 3.86 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4), 2.48 (s, 3H, $SC_6H_3C(CH_3)_3CH_3$), 1.53 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6), 1.40 (s, 9H, $SC_6H_3CH_3C(CH_3)_3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5 and 165.7 ($OCOC_6H_5$ and $OCOCH_2Cl$), 149.8, 137.9, 137.3, 133.6, 132.0, 130.2, 130.0, 129.6, 128.7, 128.6, 128.5, 128.1, 128.0, 125.5 ($SC_6H_3C(CH_3)_3CH_3$, $OCOC_6H_5$, $OCH_2C_6H_5$) 85.4 (C-1), 78.8 (C-4), 75.4 ($OCH_2C_6H_5$), 74.4 (C-3), 72.2 (C-2), 69.3 (C-5), 40.7 ($OCOCH_2Cl$), 34.5 ($SC_6H_3C(CH_3)_3CH_3$) 31.4 ($SC_6H_3C(CH_3)_3CH_3$), 20.4 ($SC_6H_3C(CH_3)_3CH_3$), 18.1 (C-6); HR-ESI-MS *m/z* calcd for $C_{33}H_{37}ClO_6S$ 619.1897 $[M+Na]^+$, found 619.1902.

4.2.5. 2-[(*N*-Benzyloxycarbonyl)amino]ethyl 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-L-rhamnopyranoside (13)

To a mixture of **12** (1.1 g, 1.8 mmol), 2-(*N*-benzyloxycarbonyl)-aminoethanol (448 mg, 2.3 mmol) and 4 Å molecular sieves (1.0 g) in dry CH_2Cl_2 (20 mL) was added NIS (562 mg, 2.5 mmol) followed by AgOTf (180 mg, 0.7 mmol). The reaction mixture was stirred at rt under inert atmosphere for 30 min and was filtered. The filtrate was washed by a mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was then purified by flash chromatography using cyclohexane/EtOAc (9:1) as eluent to give **13** (880 mg, 80%) as a white solid. R_f 0.27 (cyclohexane/EtOAc 8:2); ^1H NMR (300 MHz, $CDCl_3$) δ 8.12–7.30 (m, 15H, $OCH_2C_6H_5$, $OCOC_6H_5$, $NHCOOCH_2C_6H_5$), 5.58 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.48 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 5.40 (br s, 1H, NH), 5.19 (s, 2H, $NHCOOCH_2C_6H_5$), 4.90 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.77 (d, 1H, $J_{A,B}$ = 11.4 Hz, A part of an AB system, $OCHHC_6H_5$), 4.73 (d, 1H, $J_{A,B}$ = 11.4 Hz, B part of an AB system, $OCHHC_6H_5$), 4.00–3.87 (m, 1H, H-5), 3.87–3.77 (m, 1H, A part of an AB system, $OCHHCH_2NH$), 3.93 (d, 1H, $J_{A,B}$ = 14.9 Hz, A part of an AB system, $OCOCHHCl$), 3.86 (d, 1H, $J_{A,B}$ = 14.9 Hz, B part of an AB system, $OCOCHHCl$), 3.70 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.7 Hz, H-4), 3.65–3.52 (m, 1H, B part of an AB system, $OCHHCH_2NH$), 3.52–3.35 (m, 2H, OCH_2CH_2NH), 1.44 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 165.7 ($OCOC_6H_5$, $OCOCH_2Cl$), 156.5 ($NHCOOCH_2C_6H_5$), 137.8, 136.3, 133.6, 129.9, 129.4, 128.6, 128.5, 128.1, 128.0, 127.9 (COC_6H_5, $OCH_2C_6H_5$, $NHCOOCH_2C_6H_5$), 97.7 (C-1), 78.5 (C-4), 75.3 ($OCH_2C_6H_5$), 74.0 (C-3), 70.3 (C-2), 68.0 (C-5), 67.2 (OCH_2CH_2NH), 66.8 ($NHCOOCH_2C_6H_5$), 40.7 (OCH_2CH_2NH and $OCOCH_2Cl$), 18.1 (C-6); ESI-MS *m/z* 633.8 $[M+Na]^+$.

4.2.6. 2-[(*N*-Benzyloxycarbonyl)amino]ethyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (14)

From **13**: To a solution of **67** (880 mg, 1.4 mmol) in THF (70 mL) were added thiourea (212 mg, 2.8 mmol), $NaHCO_3$ (235 mg, 2.8 mmol) and a catalytic amount of Bu_4NI (25 mg, 67 μmol). The reaction mixture was stirred at 55 °C for 24 h and was then cooled to rt. The mixture was diluted with CH_2Cl_2 and washed with water. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to give alcohol **14** (477 mg, 78%) as a white solid.

From **5**: To a mixture of **5** (1.0 g, 1.9 mmol), 2-(*N*-benzyloxycarbonyl)-aminoethanol (370 mg, 1.9 mmol) and 4 Å molecular sieves (1.0 g) in dry CH_2Cl_2 (20 mL) was added NIS (600 mg, 2.5 mmol) followed by AgOTf (196 mg, 0.6 mmol). The reaction mixture was stirred at rt for 30 min and was then filtered. The filtrate was washed by a mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was then purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to give known alcohol **14**[18] (508 mg, 50%).

4.2.7. 2-Methyl-5-*tert*-butylphenyl 4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (15)

Compound **5** (2.2 g, 4.2 mmol) was treated with NaOMe (0.2 M solution in MeOH) (42 mL, 8.4 mmol) for 1 h at rt. The reaction mixture was then neutralized by resin Amberlite $120H^+$. The resin was filtered off and the filtrate was concentrated in vacuo. The crude was then purified by flash chromatography using cyclohexane/EtOAc (7:3) as eluent to give **15** (1.7 g, quantitative). R_f 0.17 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −63 ($CHCl_3$, *c* 0.6); ^1H NMR (300 MHz, $CDCl_3$) δ 7.65–7.16 (m, 8H, $SC_6H_3C(CH_3)_3CH_3$, $OCH_2C_6H_5$); 5.47 (d, 1H, $J_{1,2}$ = 1.5 Hz, H-1), 4.84 (d, 1H, $J_{A,B}$ = 11.4 Hz, A part of an AB system, $OCHHC_6H_5$), 4.80 (d, 1H, $J_{A,B}$ = 11.4 Hz, B part of an AB system, $OCHHC_6H_5$), 4.32 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 4.26 (br s, 1H, H-2), 4.06 (m, 1H, H-3), 3.50 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.4 Hz, H-4), 3.09 (br s, 1H, OH-2), 2.85 (br s, 1H, OH-3) 2.43 (s, 3H, $SC_6H_3C(CH_3)_3CH_3$), 1.42 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6), 1.36 (s, 9H, $SC_6H_3C(CH_3)_3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 138.2, 136.6, 132.9, 130.0, 129.4, 128.7, 128.1, 128.0, 124.7 ($SC_6H_3C(CH_3)_3CH_3$, $OCH_2C_6H_5$) 87.1 (C-1), 81.2 (C-4), 75.1 ($OCH_2C_6H_5$), 73.0 (C-2), 72.1 (C-3), 68.7 (C-5), 34.5 ($SC_6H_3C(CH_3)_3CH_3$) 31.4 ($SC_6H_3C(CH_3)_3CH_3$), 20.2 ($SC_6H_3C(CH_3)_3CH_3$), 18.0 (C-6); ESI-MS *m/z* calcd for $C_{24}H_{32}O_4S$ 439.1919 $[M+Na]^+$, found 439.1926.

4.2.8. 2-Methyl-5-*tert*-butylphenyl 3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (16)

A mixture of diol **15** (1.0 g, 2.4 mmol) and dibutyltin oxide (657 mg, 2.6 mmol) in dry MeOH (20 mL) was heated to reflux under inert atmosphere for 6 h and was then evaporated to dryness. The residue was dried under vacuum for 2 h and was dissolved in dry DMF (20 mL). BnBr (344 μL, 2.9 mmol) was added dropwise and the reaction mixture was stirred at 90 °C for 48 h. The mixture was then concentrated in vacuo and the residue was purified by flash chromatography using cyclohexane/EtOAc (98:2) to afford **16** (863 mg, 71%) and 2-methyl-5-*tert*-butylphenyl 2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (316 mg, 26%) as colorless oils. **16**: R_f 0.64 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −149 ($CHCl_3$, *c* 1.0); ^1H NMR (300 MHz, $CDCl_3$) δ 7.73–7.22 (m, 13H, $SC_6H_3C(CH_3)_3CH_3$, 2 × $OCH_2C_6H_5$), 5.61 (d, 1H, $J_{1,2}$ = 1.3 Hz, H-1), 5.03 (d, 1H, $J_{A,B}$ = 11.0 Hz, A part of an AB system, $OCHHC_6H_5$), 4.84 (br s, 2H, $OCH_2C_6H_5$), 4.78 (d, 1H, $J_{A,B}$ = 11.0 Hz, B part of an AB system, $OCHHC_6H_5$), 4.42–4.35 (m, 2H, H-2, H-5), 4.04 (dd, 1H, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.50 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.4 Hz, H-4), 3.03 (br s, 1H, OH-2), 2.50 (s, 3H, $SC_6H_3C(CH_3)_3CH_3$), 1.45 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6), 1.42 (s, 9H, $SC_6H_3CH_3C(CH_3)_3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 138.4, 137.8, 136.3, 133.0, 130.1, 129.4, 128.8, 128.6, 128.2, 128.1, 127.9, 127.5, 127.3, 127.3, 124.7, 124.0 ($SC_6H_3C(CH_3)_3CH_3$, 2 × $OCH_2C_6H_5$), 86.6 (C-1), 80.4 (C-3), 80.3 (C-4), 75.6 ($OCH_2C_6H_5$), 72.3 ($OCH_2C_6H_5$), 70.5 (C-2), 68.9 (C-5), 34.6 ($SC_6H_3C(CH_3)_3CH_3$), 31.4 ($SC_6H_3C(CH_3)_3CH_3$), 20.3 ($SC_6H_3C(CH_3)_3CH_3$), 18.0 (C-6); HR-ESI-MS *m/z* calcd for $C_{31}H_{38}O_4S$ 529.2389 $[M+Na]^+$, found 529.2381.

4.2.9. 2-[(*N*-Benzyloxycarbonyl)amino]ethyl 3,4-di-*O*-benzyl-α-L-rhamnopyranoside (17)

To a solution of **16** (863 mg, 1.7 mmol) in pyridine (20 mL) at 0 °C was added BzCl (391 μL, 3.4 mmol) dropwise. The reaction mixture was stirred at rt for 12 h and was then quenched by the addition of MeOH. The mixture was diluted with CH_2Cl_2 was washed aq HCl 1 M, with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude was purified by flash chromatography using cyclohexane/EtOAc (95:5) as eluent to give 2-methyl-5-*tert*-butylphenyl 2-*O*-benzoyl-3,4-di-*O*-

benzyl-1-thio-α-L-rhamnopyranoside (1.0 g, quantitative) as a white solid. R_f 0.68 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −59 ($CHCl_3$, *c* 0.6); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25–7.28 (m, 18H, $SC_6H_3C(CH_3)_3CH_3$, 2 × $OCH_2C_6H_5$, $OCOC_6H_5$), 6.00 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.58 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1), 5.04 (d, 1H, $J_{A,B}$ = 11.0 Hz, A part of an AB system, $OCHHC_6H_5$), 4.91 (d, 1H, $J_{A,B}$ = 11.4 Hz, A part of an AB system, $OCHHC_6H_5$), 4.77 (d, 1H, $J_{A,B}$ = 11.0 Hz, B part of an AB system, $OCHHC_6H_5$), 4.71 (d, 1H, $J_{A,B}$ = 11.4 Hz, B part of an AB system, $OCHHC_6H_5$), 4.55 (dq, 1H, $J_{4,5}$ = 9.2 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 4.20 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 3.76 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, H-4), 2.51 (s, 3H, $SC_6H_3C(CH_3)_3CH_3$), 1.49 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6), 1.35 (s, 9H, $SC_6H_3C(CH_3)_3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8 ($OCOC_6H_5$), 149.9, 138.5, 138.0, 137.1, 133.4, 132.9, 132.9,132.7, 130.5, 130.2, 130.1, 128.6, 128.5, 128.3, 128.2, 127.7, 125.3 ($SC_6H_3C(CH_3)_3CH_3$, $OCH_2C_6H_5$, $OCOC_6H_5$), 86.0 (C-1), 80.3 (C-4), 78.8 (C-3), 75.5 ($OCH_2C_6H_5$), 71.8 ($OCH_2C_6H_5$) 71.5 (C-2), 69.3 (C-5), 34.6 ($SC_6H_3C(CH_3)_3CH_3$), 31.5 ($SC_6H_3C(CH_3)_3CH_3$), 20.5 ($SC_6H_3C(CH_3)_3CH_3$), 18.3 (C-6); HR-ESI-MS *m/z* calcd for $C_{38}H_{42}O_5S$ 633.2632 $[M+Na]^+$, found 633.2645.

To a mixture of 2-methyl-5-*tert*-butylphenyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (1.0 g, 1.7 mmol), 2-(*N*-benzyloxycarbonyl)-aminoethanol (332 mg, 1.7 mmol) and 4 Å molecular sieves (1.0 g) in dry CH_2Cl_2 (20 mL) was added NIS (495 mg, 2.2 mmol) followed by AgOTf (128 mg, 0.5 mmol). The reaction mixture was stirred at rt for 30 min and was then filtered. The filtrate was washed by a mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was then purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to give 2-[(*N*-benzyloxycarbonyl)amino]ethyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (1.1 g, quantitative). R_f 0.31 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ +14 ($CHCl_3$, *c* 1.1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19–7.30 (m, 20H, $NHCOOCH_2C_6H_5$, 2 × $OCH_2C_6H_5$, $OCOC_6H_5$), 5.67 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 5.26 (br s, 1H, N*H*), 5.20 (s, 2H, $NHCOOCH_2C_6H_5$), 5.00 (d, 1H, $J_{A,B}$ = 11.0 Hz, A part of an AB system, $OCHHC_6H_5$), 4.95 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1), 4.86 (d, 1H, $J_{A,B}$ = 11.2 Hz, A part of an AB system, $OCHHC_6H_5$), 4.73 (d, 1H, $J_{A,B}$ = 11.0 Hz, B part of an AB system, $OCHHC_6H_5$), 4.65 (d, 1H, $J_{A,B}$ = 11.2 Hz, B part of an AB system, $OCHHC_6H_5$), 4.11 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.2 Hz, H-3), 3.91–3.83 (m, 2H, H-5, A part of an AB system, $OCHHCH_2NH$), 3.65 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, H-4), 3.62–3.57 (m, 1H, B part of an AB system, $OCHHCH_2NH$), 3.55–3.37 (m, 2H, OCH_2CH_2NH), 1.45 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9 ($OCOC_6H_5$), 156.4 ($NHCOOCH_2C_6H_5$), 138.4, 138.1, 136.6, 133.3, 130.0, 128.6, 128.5, 128.4, 128.2, 128.1, 127.8, 127.7 (2 × $OCH_2C_6H_5$, $OCOC_6H_5$, $NHCOOCH_2C_6H_5$), 98.0 (C-1), 80.0 (C-4), 78.1 (C-3), 75.5 ($OCH_2C_6H_5$), 71.7 ($OCH_2C_6H_5$), 69.4 (C-2), 68.1 (C-5), 67.1 and 66.9 ($NHCOOCH_2C_6H_5$, OCH_2CH_2NH), 40.9 (OCH_2CH_2NH), 18.2 (C-6); HR-ESI-MS *m/z* calcd for $C_{37}H_{39}NO_8$ 648.2573 $[M+Na]^+$, found 648.2582.

2-[(*N*-Benzyloxycarbonyl)amino]ethyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (1.1 g, 1.7 mmol) was treated with NaOMe (0.2 M solution in MeOH) (17 mL, 3.4 mmol) overnight at rt. The reaction mixture was then neutralized by resin Amberlite 120 H^+. The resin was filtered off and the filtrate was concentrated in vacuo. The residue was then purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to give **17** (887 mg, quantitative). R_f 0.19 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −23 ($CHCl_3$, *c* 1.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.30 (m, 15H, $NHCOOCH_2C_6H_5$, 2 × $OCH_2C_6H_5$), 5.23 (m, 1H, N*H*), 5.16 (s, 2H, $NHCOOCH_2C_6H_5$), 4.93 (d, 1H, $J_{A,B}$ = 10.8 Hz, A part of an AB system, $OCHHC_6H_5$), 4.84 (d, 1H, $J_{1,2}$ = 1.5 Hz, H-1), 4.74 (br s, 2H, $OCH_2C_6H_5$), 4.69 (d, 1H, $J_{A,B}$ = 10.8 Hz, B part of an AB system, $OCHHC_6H_5$), 4.05 (dd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 3.86 (dd, 1H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.1 Hz, H-3), 3.79–3.70 (m, 2H, H-5, A part of an AB system, $OCHHCH_2NH$), 3.59–3.32 (m, 3H, B part of an AB system, $OCHHCH_2NH$, OCH_2CH_2NH), 3.51 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.1 Hz, H-4), 2.87 (s, 1H, O*H*-2), 1.35 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4 ($NHCOOCH_2C_6H_5$), 138.3, 137.9, 136.6, 128.6, 128.5, 128.2, 128.1, 127.9 (2 × $OCH_2C_6H_5$, $NHCOOCH_2C_6H_5$), 99.4 (C-1), 80.0 (C-4), 79.8 (C-3), 75.5 and 72.1 (2 × $OCH_2C_6H_5$), 68.5 (C-2), 67.7 (C-5), 66.9 and 66.8 ($NHCOOCH_2C_6H_5$ and OCH_2CH_2NH), 40.9 (OCH_2CH_2NH), 18.0 (C-6); HR-ESI-MS *m/z* calcd for $C_{30}H_{35}NO_7$ 544.2306 $[M+Na]^+$, found 544.2292.

4.2.10. 2-[(*N*-Benzyloxycarbonyl)amino]ethyl 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (18)

To a mixture of **17** (100 mg, 0.17 mmol), **12** (113 mg, 0.19 mmol) and 4 Å molecular sieves (100 mg) in dry CH_2Cl_2 (5 mL) was added NIS (51 mg, 0.22 mmol) followed by AgOTf (15 mg, 0.06 mmol). The reaction mixture was stirred at rt for 30 min and was then filtered. The filtrate was washed by a mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was then purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to give **18** (126 mg, 79%). R_f 0.33 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ +6 ($CHCl_3$, *c* 1.1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13–7.11 (m, 25H, $NHCOOCH_2C_6H_5$, 3 × $OCH_2C_6H_5$, $OCOC_6H_5$), 5.79 (dd, 1H, $J_{1C,2C}$ = 1.9 Hz, $J_{2C,3C}$ = 3.3 Hz, H-2C), 5.59 (dd, 1H, $J_{2C,3C}$ = 3.3 Hz, $J_{3C,4C}$ = 9.7 Hz, H-3C), 5.18 (s, 2H, $NHCOOCH_2C_6H_5$), 5.15 (d, 1H, $J_{1C,2C}$ = 1.9 Hz, H-1C), 4.97 (d, 1H, $J_{A,B}$ = 11.0 Hz, A part of an AB system, $OCHHC_6H_5$), 4.82 (d, 1H, $J_{1D,2D}$ = 1.5 Hz, H-1D), 4.81–4.66 (m, 5H, B part of an AB system, $OCHHC_6H_5$, 2 × $OCH_2C_6H_5$), 4.15–4.08 (m, 1H, H-5C), 4.02 (d, 1H, $J_{A,B}$ = 14.9 Hz, A part of an AB system, $OCOCHHCl$), 4.04 (br s, 1H, H-2D), 3.92 (d, 1H, $J_{A,B}$ = 14.9 Hz, B part of an AB system, $OCOCHHCl$), 3.91–3.85 (m, 1H, H-3D), 3.82–3.61 (m, 4H, H-4D, H-5D, H-4C, A part of an AB system, $OCHHCH_2NH$), 3.60–3.34 (m, 3H, B part of an AB system, OCH_2CHHNH, OCH_2CH_2NH), 1.47 (d, 3H, $J_{5C,6C}$ = 6.1 Hz, H-6C), 1.39 (d, 3H, $J_{5D,6D}$ = 6.1 Hz, H-6D); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4 and 165.5 ($OCOCH_2Cl$ and $OCOC_6H_5$), 156.4 ($NHCOOCH_2C_6H_5$), 138.5, 138.2, 137.9, 136.5, 133.5, 128.6, 128.4, 127.9, 127.7, 127.5 (3 × $OCH_2C_6H_5$, $OCOC_6H_5$, $NHCOOCH_2C_6H_5$), 99.2 (C-1C), 99.0 (C-1D), 80.2 (C-4C), 79.7 (C-3D), 78.7 (C-4D), 75.7 (C-2D), 75.6 ($OCH_2C_6H_5$), 75.3 ($OCH_2C_6H_5$), 74.0 (C-3C), 72.6 ($OCH_2C_6H_5$), 70.4 (C-2C), 68.6 (C-5D), 68.3 (C-5C), 66.9 ($NHCOOCH_2C_6H_5$, OCH_2CH_2NH), 40.8 (OCH_2CH_2NH, $COCH_2Cl$), 18.2 (C-6C), 18.0 (C-6D); HR-ESI-MS *m/z* calcd for $C_{52}H_{56}ClNO_{13}$ 960.3338 $[M+Na]^+$, found 960.3347.

4.2.11. 2-[(*N*-Benzyloxycarbonyl)amino]ethyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (19)

To a solution of **18** (126 mg, 0.13 mmol) in THF (5 mL) were added thiourea (20 mg, 0.26 mmol), $NaHCO_3$ (22 mg, 0.26 mmol) and a catalytic amount of tetrabutylammonium iodide (2.4 mg, 6.5 μmol). The solution was stirred for 12 h at 55 °C. The reaction mixture was then cooled to room temperature, diluted with CH_2Cl_2, and washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to give **19** (70 mg, 62%) as a pale yellow foam. R_f 0.20 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −8 ($CHCl_3$, *c* 1.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13–7.19 (m, 25H, $NHCOOCH_2C_6H_5$, 3 × $OCH_2C_6H_5$, $OCOC_6H_5$), 5.58 (dd, 1H, $J_{1C,2C}$ = 1.7 Hz, $J_{2C,3C}$ = 3.5 Hz, H-2C), 5.16 (br s, 3H, H-1C, $NHCOOCH_2C_6H_5$), 5.11 (br s, 1H, N*H*), 4.94 (d, 1H, $J_{A,B}$ = 10.9 Hz, A part of an AB system, $OCHHC_6H_5$), 4.90 (d, 1H, $J_{A,B}$ = 11.0 Hz, A part of an AB system, $OCHHC_6H_5$), 4.80 (d, 1H, $J_{1D,2D}$ = 1.7 Hz, H-1D), 4.78 (d, 1H, $J_{A,B}$ = 11.0 Hz, B part of an AB system,

OCH*H*C$_6$H$_5$), 4.72 (s, 2H, OC*H*$_2$C$_6$H$_5$), 4.67 (d, 1H, $J_{A,B}$ = 10.9 Hz, B part of an AB system, OCH*H*C$_6$H$_5$), 4.36 (m, 1H, H-3C), 4.00–3.91 (m, 1H, H-2D, H-5C), 3.88 (dd, 1H, $J_{2D,3D}$ = 3.1 Hz, $J_{3D,4D}$ = 9.2 Hz, H-3D), 3.79–3.65 (m, 2H, H-5D, A part of an AB system, OC*H*HCH$_2$NH), 3.56–3.31 (m, 3H, B part of an AB system, OCH*H*CH$_2$NH, OCH$_2$C*H*$_2$NH), 3.53 (t, 1H, $J_{3D,4D}$ = $J_{4D,5D}$ = 9.2 Hz, H-4D), 3.52 (t, 1H, $J_{3C,4C}$ = $J_{4C,5C}$ = 9.4 Hz, H-4C), 1.43 (d, 3H, $J_{5C,6C}$ = 6.1 Hz, H-6C), 1.34 (d, 3H, $J_{5D,6D}$ = 6.1 Hz, H-6D); ^{13}C NMR (75 MHz, CDCl$_3$) δ 166.3 (*C*OC$_6$H$_5$), 156.4 (NH*C*OOCH$_2$C$_6$H$_5$), 138.4, 138.3, 133.4, 130.0, 128.6, 128.5, 128.4, 128.0, 127.8 (3 × OCH$_2$*C*$_6$H$_5$, OCO*C*$_6$H$_5$, NHCOOCH$_2$*C*$_6$H$_5$), 99.2 (C-1C), 99.1 (C-1D), 81.7 (C-4C), 80.2 (C-4D), 79.5 (C-3D), 75.5 (OCH$_2$C$_6$H$_5$), 75.3 (O*C*H$_2$C$_6$H$_5$), 75.2 (C-2D), 73.3 (C-2C), 72.4 (O*C*H$_2$C$_6$H$_5$), 70.5 (C-3C), 68.3 and 68.2 (C-5C and C-5D), 66.9 (NHCOO*C*H$_2$C$_6$H$_5$, OCH$_2$CH$_2$NH), 40.9 (OCH$_2$*C*H$_2$NH), 18.3 (C-6C), 18.1 (C-6D); HR-ESI-MS *m/z* calcd for C$_{50}$H$_{55}$NO$_{12}$ 884.3622 [M+Na]$^+$, found 884.3607.

4.2.12. 2-[(*N*-Benzyloxycarbonyl)amino]ethyl 2-*O*-acetyl-4-azido-3-*O*-benzoyl-4,6-dideoxy-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (20)

To a solution of **3** (184 mg, 0.38 mmol), **14** (184 mg, 0.34 mmol) and 4 Å molecular sieves (200 mg) in dry CH$_2$Cl$_2$ (10 mL) under inert atmosphere at −40 °C was added TMSOTf (33 μL, 0.19 mmol). After 30 min stirring at this temperature, the reaction mixture was neutralized by Et$_3$N and filtered. The filtrate was washed with water, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to give disaccharide **20** (157 mg, 48%) as a colorless oil. R_f 0.41 (cyclohexane/EtOAc 7:3); $[\alpha]_D$ −3 (CHCl$_3$, *c* 0.9); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.10–7.29 (m, 20H, 2 × OCOC$_6$*H*$_5$, OCH$_2$C$_6$*H*$_5$, NHCOOCH$_2$C$_6$*H*$_5$), 5.42 (dd, 1H, $J_{1B,2B}$ = 1.8 Hz, $J_{2B,3B}$ = 3.5 Hz, H-2B), 5.35 (t, 1H, $J_{2A,3A}$ = $J_{3A,4A}$ = 9.6 Hz, H-3A), 5.33 (br s, 1H, N*H*), 5.16 (dd, 1H, $J_{1A,2A}$ = 7.8 Hz, $J_{2A,3A}$ = 9.6 Hz, H-2A), 5.15 (s, 2H, NHCOOC*H*$_2$C$_6$H$_5$), 4.90–4.85 (m, 2H, H-1B, A part of an AB system, OC*H*HC$_6$H$_5$), 4.83 (d, 1H, $J_{1A,2A}$ = 7.8 Hz, H-1A), 4.66 (d, 1H, $J_{A,B}$ = 11.2 Hz, B part of an AB system, OCH*H*C$_6$H$_5$), 4.26 (dd, 1H, $J_{2B,3B}$ = 3.5 Hz, $J_{3B,4B}$ = 9.4 Hz, H-3B), 3.85–3.72 (m, 2H, H-5B, A part of an AB system, OC*H*HCH$_2$NH), 3.63 (t, 1H, $J_{3B,4B}$ = $J_{4B,5B}$ = 9.4 Hz, H-4B), 3.60–3.50 (m, 1H, B part of an AB system, OCH*H*CH$_2$NH), 3.49–3.39 (m, 3H, H-5A, OCH$_2$C*H*$_2$NH), 3.27 (t, 1H, $J_{3A,4A}$ = $J_{4A,5A}$ = 9.6 Hz, H-4A), 1.65 (s, 3H, OCOC*H*$_3$), 1.33 (d, 3H, $J_{5B,6B}$ = 6.1 Hz, H-6B), 1.27 (d, 3H, $J_{5A,6A}$ = 5.9 Hz, H-6A); ^{13}C NMR (75 MHz, CDCl$_3$) δ 169.5 (O*C*OCH$_3$), 166.0 (O*C*OC$_6$H$_5$), 165.6 (O*C*OC$_6$H$_5$), 156.4 (NH*C*OOCH$_2$C$_6$H$_5$), 138.0, 136.4, 133.2, 133.1, 129.8, 128.5, 128.4, 128.1, 127.8, 127.7 (NHCOOCH$_2$*C*$_6$H$_5$, 2 × OCO*C*$_6$H$_5$, OCH$_2$*C*$_6$H$_5$), 100.4 (C-1A), 97.2 (C-1B), 79.4 (C-4B), 78.8 (C-3B), 75.0 (O*C*H$_2$C$_6$H$_5$), 74.0 (C-3A), 72.1 (C-2B), 71.9 (C-2A), 70.7 (C-5A), 67.7 (C-5B) 67.0 and 66.8 (NHCOO*C*H$_2$C$_6$H$_5$, OCH$_2$CH$_2$NH), 65.7 (C-4A), 40.8 (OCH$_2$*C*H$_2$NH), 20.2 (OCO*C*H$_3$), 17.9 (C-6A and C-6B); HR-ESI-MS *m/z* calcd for C$_{45}$H$_{48}$N$_4$O$_{13}$ 875.3116 [M+Na]$^+$, found 875.3126.

4.2.13. 2-Methyl-5-*tert*-butylphenyl 2-*O*-acetyl-4-azido-3-*O*-benzoyl-4,6-dideoxy-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (22)

To a solution of **3** (184 mg, 0.38 mmol), **5** (177 mg, 0.34 mmol) and 4 Å molecular sieves (200 mg) in dry CH$_2$Cl$_2$ (10 mL) under inert atmosphere at −40 °C was added TMSOTf (33 μL, 0.19 mmol). After 30 min stirring at this temperature, the reaction mixture was neutralized by Et$_3$N, and filtered. The filtrate was washed with water, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to give disaccharide **22** (216 mg, 68%) as a white solid. R_f 0.62 (cyclohexane/EtOAc 7:3); $[\alpha]_D$ −57 (CHCl$_3$, *c* 1.0); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.12–7.13 (m, 18H, 2 × OCOC$_6$*H*$_5$, OCH$_2$C$_6$*H*$_5$, NHCOOCH$_2$C$_6$*H*$_5$, SC$_6$*H*$_3$C(CH$_3$)$_3$CH$_3$), 5.72 (dd, 1H, $J_{1B,2B}$ = 1.7 Hz, $J_{2B,3B}$ = 3.3 Hz, H-2B), 5.60 (d, 1H, $J_{1B,2B}$ = 1.7 Hz, H-1B), 5.44 (t, 1H, $J_{2A,3A}$ = $J_{3A,4A}$ = 9.7 Hz, H-3A), 5.21 (dd, 1H, $J_{1A,2A}$ = 7.8 Hz, $J_{2A,3A}$ = 9.6 Hz, H-2A), 4.94 (d, 1H, $J_{A,B}$ = 11.6 Hz, A part of an AB system, OC*H*HC$_6$H$_5$), 4.91 (d, 1H, $J_{1A,2A}$ = 7.9 Hz, H-1A), 4.71 (d, 1H, $J_{A,B}$ = 11.6 Hz, B part of an AB system, OCH*H*C$_6$H$_5$), 4.41 (dq, 1H, $J_{4B,5B}$ = 9.4 Hz, $J_{5B,6B}$ = 6.3 Hz, H-5B), 4.34 (dd, 1H, $J_{2B,3B}$ = 3.3 Hz, $J_{3B,4B}$ = 9.4 Hz, H-3B), 3.74 (t, 1H, $J_{3B,4B}$ = $J_{4B,5B}$ = 9.4 Hz, H-4B), 3.52 (dq, 1H, $J_{4A,5A}$ = 9.7 Hz, $J_{5A,6A}$ = 5.9 Hz, H-5A), 3.35 (t, 1H, $J_{3A,4A}$ = $J_{4A,5A}$ = 9.7 Hz, H-4A), 2.50 (s, 3H, SC$_6$H$_3$C(CH$_3$)$_3$ C*H*$_3$), 1.71 (s, 3H, OCOC*H*$_3$), 1.38 (d, 3H, $J_{5B,6B}$ = 6.3 Hz, H-6B), 1.35 (d, 3H, $J_{5A,6A}$ = 5.9 Hz, H-6A), 1.34 (s, 9H, SC$_6$H$_3$CH$_3$C(C*H*$_3$)$_3$CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 169.5 (O*C*OCH$_3$), 165.9 (O*C*OC$_6$H$_5$), 165.7 (O*C*OC$_6$H$_5$), 149.8, 138.1, 137.0, 133.6, 133.2, 132.5, 130.3, 130.2, 129.9, 129.0, 128.6, 128.5, 128.0, 127.9, 125.2 (SC$_6$H$_3$C(CH$_3$)$_3$ CH$_3$, 2 × OCO*C*$_6$H$_5$, OCH$_2$*C*$_6$H$_5$), 100.7 (C-1A), 85.3 (C-1B), 79.8 (C-4B), 79.6 (C-3B), 75.2 (O*C*H$_2$C$_6$H$_5$), 74.5 (C-2B), 74.1 (C-3A), 72.0 (C-2A), 70.9 (C-5A), 69.0 (C-5B), 65.8 (C-4A), 34.5 (SC$_6$H$_3$*C*(CH$_3$)$_3$ CH$_3$), 31.4 (SC$_6$H$_3$C(*C*H$_3$)$_3$CH$_3$), 20.4 (SC$_6$H$_3$C(CH$_3$)$_3$*C*H$_3$, OCO*C*H$_3$), 18.1, 18.0 (C-6A, C-6B); HR-ESI-MS *m/z* calcd for C$_{46}$H$_{51}$N$_3$O$_{10}$S 860.3193 [M+Na]$^+$, found 860.3184.

4.2.14. 2-Methyl-5-*tert*-butylphenyl 2-*O*-acetyl-4-azido-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-1-thio-α-D-rhamnopyranoside (23)

TMSOTf (18 μL, 0.1 mmol) was added to a solution of donor **6** (116 mg, 0.25 mmol) and acceptor **5** (104 mg, 0.2 mmol) in CH$_2$Cl$_2$ (4 mL) containing 4 Å molecular sieves at −30 °C under an inert atmosphere. The reaction mixture was stirred at −30 °C over 1 h and then quenched upon addition of excess Et$_3$N. The crude mixture was filtered over a Celite® pad which was further washed with CH$_2$Cl$_2$. The filtrate was next evaporated under reduced pressure and the residue purified by flash chromatography on silica gel using cyclohexane/EtOAc (95:5) as eluent to give disaccharide **23** (170 mg, 85%). R_f 0.54 (cyclohexane/EtOAc 9:1); $[\alpha]_D$ −62 (CHCl$_3$, *c* 1.0); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.16–7.20 (m, 18H, OCOC$_6$*H*$_5$, 2 × OCH$_2$C$_6$*H*$_5$, SC$_6$*H*$_3$C(CH$_3$)$_3$CH$_3$), 5.70 (dd, 1H, $J_{1B,2B}$ = 1.5 Hz, $J_{2B,3B}$ = 3.3 Hz, H-2B), 5.61 (d, 1H, $J_{1B,2B}$ = 1.5 Hz, H-1B), 5.14 (dd, 1H, $J_{1A,2A}$ = 8.1 Hz, $J_{2A,3A}$ = 9.4 Hz, H-2A), 5.00 (d, 1H, $J_{A,B}$ = 11.2 Hz, A part of an AB system, OCH*H*C$_6$H$_5$), 4.87 (d, 1H, $J_{A,B}$ = 11.2 Hz, A part of an AB system, OCH*H*C$_6$H$_5$), 4.75 (d, 1H, $J_{A,B}$ = 11.2 Hz, B part of an AB system, OC*H*HC$_6$H$_5$), 4.73 (d, 1H, $J_{1A,2A}$ = 8.1 Hz, H-1A), 4.69 (d, 1H, $J_{A,B}$ = 11.2 Hz, B part of an AB system, OCH*H*C$_6$H$_5$), 4.49–4.38 (m, 1H, H-5B), 4.30 (dd, 1H, $J_{2B,3B}$ = 3.3 Hz, $J_{3B,4B}$ = 9.5 Hz, H-3B), 3.76 (t, 1H, $J_{3B,4B}$ = $J_{4B,5B}$ = 9.4 Hz, H-4B), 3.56 (t, 1H, $J_{2A,3A}$ = -$J_{3A,4A}$ = 9.4 Hz, H-3A), 3.42–3.28 (m, 1H, H-5A), 3.21 (t, 1H, $J_{3A,4A}$ = -$J_{4A,5A}$ = 9.4 Hz, H-4A), 2.54 (s, 3H, C*H*$_3$), 1.79 (s, 3H, COC*H*$_3$), 1.38 (s, 9H, SC$_6$H$_3$C(C*H*$_3$)$_3$CH$_3$), 1.37 (d, 3H, $J_{5B,6B}$ = 6.3 Hz, H-6B), 1.32 (d, 3H, $J_{5A,6A}$ = 6.1 Hz, H-6A); ^{13}C NMR (75 MHz, CDCl$_3$) δ 169.3 (O*C*OCH$_3$), 166.0 (O*C*OC$_6$H$_5$), 149.8, 138.3, 137.2, 136.9, 133.1, 132.5, 130.4, 130.1, 129.9, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7 (SC$_6$*H*$_3$C(CH$_3$)$_3$CH$_3$, 2 × OCH$_2$*C*$_6$H$_5$, OCO*C*$_6$H$_5$), 101.0 (C-1A), 85.3 (C-1B), 81.5 (C-3A), 79.8 (C-4B), 79.6 (C-3B), 75.1 (O*C*H$_2$C$_6$H$_5$), 74.8 (O*C*H$_2$C$_6$H$_5$), 74.4 (C-2B), 73.1 (C-2A), 70.9 (C-5A), 69.0 (C-5B), 67.5 (C-4A), 34.5 (SC$_6$H$_3$*C*(CH$_3$)$_3$CH$_3$), 31.4 (SC$_6$H$_3$C(*C*H$_3$)$_3$CH$_3$), 20.7 (OCO*C*H$_3$), 20.4 (SC$_6$H$_3$C(CH$_3$)$_3$*C*H$_3$), 18.2 (C-6A), 18.0 (C-6B); HR-ESI-MS *m/z* calcd for C$_{46}$H$_{53}$N$_3$O$_9$S [M+Na]$^+$ 846.3400, found 846.3411.

4.2.15. 2-[(*N*-Benzyloxycarbonyl)amino]ethyl 4-azido-3-*O*-benzoyl-4,6-dideoxy-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (24)

To a solution of ester **20** (157 mg, 0.19 mmol) in CH$_2$Cl$_2$ (5 mL) was added a solution of acetyl chloride (396 μL, 5.5 mmol) in MeOH (8 mL) dropwise. The reaction mixture was stirred at rt for 6 days and was then poured in saturated aqueous NaHCO$_3$.

The layers were separated and the organic phase was washed with water, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to provide recovered **20** (22 mg, 14%) and **24** (72 mg, 48%) and as a colorless oil. R_f 0.26 (cyclohexane/EtOAc 7:3); $[\alpha]_D^{20}$ +8 ($CHCl_3$, *c* 0.3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08–7.29 (m, 20H, 2 × $OCOC_6H_5$, $OCH_2C_6H_5$, $NHCOOCH_2C_6H_5$), 5.42 (dd, 1H, $J_{1B,2B}$ = 1.7 Hz, $J_{2B,3B}$ = 3.5 Hz, H-2B), 5.19 (t, 1H, $J_{2A,3A} = J_{3A,4A}$ = 9.5 Hz, H-3A), 5.12 (br s, 2H, $NHCOOCH_2C_6H_5$), 4.96 (d, 1H, $J_{A,B}$ = 10.6 Hz, A part of an AB system, $OCHHC_6H_5$), 4.84 (d, 1H, $J_{1B,2B}$ = 1.7 Hz, H-1B), 4.69 (d, 1H, $J_{A,B}$ = 11.2 Hz, B part of an AB system, $OCHHC_6H_5$), 4.64 (d, 1H, $J_{1A,2A}$ = 7.7 Hz, H-1A), 4.26 (dd, 1H, $J_{2B,3B}$ = 3.5 Hz, $J_{3B,4B}$ = 9.5 Hz, H-3B), 3.82–3.70 (m, 2H, H-5B, A part of an AB system, $OCHHCH_2NH$), 3.64 (t, 1H, $J_{3B,4B} = J_{4B,5B}$ = 9.5 Hz, H-4B), 3.63–3.47 (m, 2H, H-2A, B part of an AB system, $OCHHCH_2NH$), 3.47–3.35 (m, 3H, H-5A, OCH_2CHNH), 3.24 (t, 1H, $J_{3A,4A} = J_{4A,5A}$ = 9.5 Hz, H-4A), 1.35 (d, 3H, $J_{5B,6B}$ = 6.1 Hz, H-6B), 1.29 (d, 3H, $J_{5A,6A}$ = 6.2 Hz, H-6A); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6 ($OCOC_6H_5$), 165.9 ($OCOC_6H_5$), 156.4 ($NHCOOCH_2C_6H_5$), 137.9, 136.5, 133.6, 130.1, 130.0, 129.9, 129.2, 128.6, 128.5, 128.3, 128.2, 128.1 (NHCO-$OCH_2C_6H_5$, 2 × $OCOC_6H_5$, $OCH_2C_6H_5$), 103.2 (C-1A), 97.4 (C-1B), 80.0 (C-4B), 78.2 (C-3B), 76.4 (C-3A), 75.5 ($OCH_2C_6H_5$), 73.3 (C-2A), 72.4 (C-2B), 70.7 (C-5A), 68.0 (C-5B) 67.1 and 66.9 ($NHCOOCH_2C_6H_5$, OCH_2CH_2NH), 65.8 (C-4A), 40.9 (OCH_2CH_2NH), 18.2 (C-6A), 18.1 (C-6B); HR-ESI-MS *m/z* calcd for $C_{43}H_{46}N_4O_{12}$ 833.3010 $[M+Na]^+$, found 833.3018.

4.2.16. 2-[(*N*-Benzyloxycarbonyl)aminoethyl 4-azido-4,6-dideoxy-2-*O*-methyl-α-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (25) and 2-[(*N*-benzyloxycarbonyl)amino]ethyl 4-azido-4,6-dideoxy-3-*O*-methyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (26), 2-[(*N*-Benzyloxycarbonyl)amino]ethyl 4-azido-4,6-dideoxy-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-β-L-rhamnopyranoside (27)

To a solution of **24** (60 mg, 0.07 mmol) in dry CH_2Cl_2 (1 mL) was added silver (I) oxide (100 mg, 0.42 mmol). The reaction mixture was stirred at rt for 1 h. Iodomethane (43 μL, 0.70 mmol) was then added dropwise and the reaction mixture was stirred at rt for 3 days. Silver (I) oxide was filtered through a Celite® pad and the filtrate was concentrated. The residue was purified by flash chromatography using cyclohexane/EtOAc (7:3) as eluent to give a 1:1 mixture of **25** and **26** (20 mg, 40%) as a colorless oil and **27** (13 mg, 26%) as a colorless oil. **25** (**I**) and **26** (**II**): R_f 0.39 (cyclohexane/EtOAc 7:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15–7.33 (m, 30H, $OCOC_6H_5$ I and II, $OCH_2C_6H_5$ I and II, $NHCOOCH_2C_6H_5$ I and II), 5.37–5.34 (m, 2H, H-2BI, H-2BII), 5.12 (br s, 4H, $NHCOOCH_2C_6H_5$ I and II), 4.91 and 4.93 (2 d, 2H, $J_{A,B}$ = 10.0 Hz and $J_{A,B}$ = 10.3 Hz, 2 × A part of an AB systems, $OCHHC_6H_5$ I and II), 4.86 and 4.84 (2 d, 2H, $J_{1BI,2BI} = J_{1BII,2BII}$ = 1.8 Hz, H-1BI, H-1BII), 4.72 and 4.68 (2 d, 2H, $J_{A,B}$ = 10.0 Hz and $J_{A,B}$ = 10.3 Hz, B part of an AB system, $OCHHC_6H_5$ I and II), 4.51 (d, 1H, $J_{1AI,2AI}$ = 7.8 Hz, H-1AI), 4.35 (d, 1H, $J_{1AII,2AII}$ = 7.8 Hz, H-1AII), 4.18–4.09 (m, 2H, H-3BI, H-3BII), 3.75–3.62 (m, 4H, H-5BI, H-5BII, 2 × A parts of an AB systems, $OCHHCH_2NH$ I and II), 3.59–3.47 (m, 4H, H-4BI, H-4BII, 2 × B parts of an AB systems, $OCHHCH_2NH$ I and II), 3.55 and 3.42 (2s, 2 × 3H, OCH_3), 3.41–3.29 (m, 6H, H-3AI, H-2AII, OCH_2CHNH I and II), 3.20–3.07 (m, 2H, H-5AI, H-5AII), 3.02 (t, 1H, $J_{3AII,4AII} = J_{4AII,5AII}$ = 9.5 Hz, H-3AII), 2.95–2.83 (m, 3H, H-4AI, H-4AII, H-2AI), 2.71 (br s, 1H, O*H*), 2.51 (br s, 1H, O*H*), 1.37 and 1.36 (2 d, 2 × 3H, $J_{5BI,6BI} = J_{5BII,6BII}$ = 6.1 Hz, H-6BI, H-6BII), 1.22 and 1.18 (d, 2 × 3H, $J_{5AI,6AI} = J_{5AII,6AII}$ = 6.1 Hz, H-6AI, H-6AII); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 165.9 ($OCOC_6H_5$ I and II), 156.4 ($NHCOOCH_2C_6H_5$ I and II), 138.0, 133.3, 130.0, 129.9, 128.7, 128.5, 128.3, 128.2 (NHCO-$OCH_2C_6H_5$ I and II, $OCOC_6H_5$ I and II, $OCH_2C_6H_5$ I and II), 103.0 (C-1AII), 102.9 (C-1AI), 97.6 (C-1BI and C-1BII), 84.7 (C-3AII), 83.7 (C-2AI), 81.0, 80.3 (C-4BI, C-4BII), 78.0, 76.1 (C-3BI, C-3BII), 75.7, 75.3 ($NHCOOCH_2C_6H_5$ I and II), 75.3 (C-2AII), 74.8 (C3AI), 73.1, 72.4 (C-2BI, C-2BII), 70.9, 70.7 (C-5AI, C-5AII), 68.1 (C-5BI and C-5BII), 67.4, 67.3 (OCH_2CH_2NH I and II, $OCH_2C_6H_5$ I and II), 67.0, 66.9 (C-4AI, C-4AII), 41.1 (OCH_2CH_2NH I and II), 18.3, 18.2 (C-6AI, C-6AII, C-6BI, C-6BII); ESI-MS *m/z* 743.1 $[M+Na]^+$.

Compound **27**: R_f 0.20 (cyclohexane/EtOAc 7:3); $[\alpha]_D$ +21 ($CHCl_3$, *c* 0.2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98–7.19 (m, 15H, $OCOC_6H_5$, $OCH_2C_6H_5$, $NHCOOCH_2C_6H_5$), 5.37 (dd, 1H, $J_{1B,2B}$ = 1.8 Hz, $J_{2B,3B}$ = 3.5 Hz, H-2B), 5.18 (br s, 1H, N*H*), 5.11 (s, 2H, $NHCOOCH_2C_6H_5$), 4.89 (d, 1H, $J_{A,B}$ = 10.8 Hz, A part of an AB system, $OCHHC_6H_5$), 4.83 (d, 1H, $J_{1B,2B}$ = 1.8 Hz, H-1B), 4.72 (d, 1H, $J_{A,B}$ = 10.8 Hz, B part of an AB system, $OCHHC_6H_5$), 4.41 (d, 1H, $J_{1A,2A}$ = 7.8 Hz, H-1A), 4.20 (dd, 1H, $J_{2B,3B}$ = 3.5 Hz, $J_{3B,4B}$ = 9.4 Hz, H-3B), 3.83–3.74 (m, 2H, H-5B, A part of an AB system, $OCHHCH_2NH$), 3.63 (t, 1H, $J_{3B,4B} = J_{4B,5B}$ = 9.4 Hz, H-4B), 3.57–3.49 (m, 1H, B part of an AB system, $OCHHCH_2NH$), 3.48 (t, 1H, $J_{2A,3A}$ = - $J_{3A,4A}$ = 9.2 Hz, H-3A), 3.43–3.38 (m, 2H, OCH_2CHNH), 3.30 (dd, 1H, $J_{1A,2A}$ = 7.8 Hz, $J_{2A,3A}$ = 9.2 Hz, H-2A) 3.22 (dq, 1H, $J_{4A,5A}$ = 9.2 Hz, $J_{5A,6A}$ = 6.2 Hz, H-5A), 2.95 (t, 1H, $J_{3A,4A} = J_{4A,5A}$ = 9.2 Hz, H-4A), 2.87 (br s, 1H, O*H*), 2.74 (br s, 1H, O*H*), 1.37 (d, 3H, $J_{5B,6B}$ = 6.1 Hz, H-6B), 1.19 (d, 3H, $J_{5A,6A}$ = 6.2 Hz, H-6A); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9 ($OCOC_6H_5$), 156.4 ($NHCOOCH_2C_6H_5$), 137.8, 133.3, 129.9, 128.6, 128.4, 128.2, 128.1 ($NHCOOCH_2C_6H_5$, $OCOC_6H_5$, $OCH_2C_6H_5$), 102.6 (C-1A), 97.4 (C-1B), 80.5 (C-4B), 78.0 (C-3B), 75.8 ($OCH_2C_6H_5$), 75.5 (C-3A), 74.6 (C-2A), 72.5 (C-2B), 71.2 (C-5A), 68.2 (C-5B), 67.4 (C-4A), 67.3 (OCH_2CH_2NH), 67.1 ($NHCOOCH_2C_6H_5$), 41.1 (OCH_2CH_2NH), 18.4 (C-6A and C-6B); HR-ESI-MS *m/z* calcd for $C_{36}H_{42}N_4O_{11}$ 729.2748 $[M+Na]^+$, found 729.2759.

4.2.17. *p*-Methylphenyl 4-azido-3-*O*-benzoyl-4,6-dideoxy-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (28)

To a solution of **21**[26] (220 mg, 0.28 mmol) in CH_2Cl_2 (8 mL) was added a solution of acetyl chloride (600 μL, 8.4 mmol) in MeOH (13 mL) dropwise. The reaction mixture was stirred at rt for 8 days and was then poured in saturated aqueous $NaHCO_3$. The layers were separated and the organic phase was washed with water, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using cyclohexane/EtOAc (9:1) as eluent to provide **28** (156 mg, 75%) as a white powder. R_f 0.50 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −63 ($CHCl_3$, *c* 0.05); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11–7.32 (m, 17H, 2 × $OCOC_6H_5$, $OCH_2C_6H_5$, $SC_6H_2H_2CH_3$), 7.16 (d, 2H, *J* = 8.1 Hz, $SC_6H_2H_2CH_3$), 5.73 (dd, 1H, $J_{1B,2B}$ = 1.6 Hz, $J_{2B,3B}$ = 3.0 Hz, H-2B), 5.54 (d, 1H, $J_{1B,2B}$ = 1.6 Hz, H-1B), 5.26 (t, 1H, $J_{2A,3A} = J_{3A,4A}$ = 9.5 Hz, H-3A), 5.05 (d, 1H, $J_{A,B}$ = 10.6 Hz, A part of an AB system, $OCHHC_6H_5$), 4.76 (d, 1H, $J_{A,B}$ = 10.6 Hz, B part of an AB system, $OCHHC_6H_5$), 4.71 (d, 1H, $J_{1A,2A}$ = 7.7 Hz, H-1A), 4.41–4.31 (m, 2H, H-3B, H-5B), 3.76 (t, 1H, $J_{3B,4B} = J_{4B,5B}$ = 9.4 Hz, H-4B), 3.68–3.64 (m, 1H, H-2A), 3.45 (m, 1H, H-5A), 3.32 (t, 1H, $J_{3A,4A} = J_{4A,5A}$ = 9.5 Hz, H-4A), 2.90 (d, 1H, $J_{2A,OH}$ = 3.4 Hz, OH), 2.36 (s, 3H, $SC_6H_4CH_3$), 1.43 (d, 3H, $J_{5B,6B}$ = 6.2 Hz, H-6B), 1.39 (d, 3H, $J_{5A,6A}$ = 6.0 Hz, H-6A), 1.34 (s, 9H, $SC_6H_3CH_3C(CH_3)_3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5 ($OCOC_6H_5$), 165.6 ($OCOC_6H_5$), 137.9–128.0 ($SC_6H_4CH_3$, 2 × $OCOC_6H_5$, $OCH_2C_6H_5$), 103.2 (C-1A), 85.9 (C-1B), 80.1 (C-4B), 78.4 (C-3B), 76.4 (C-3A), 75.4 ($OCH_2C_6H_5$), 74.4 (C-2B), 73.2 (C-2A), 70.7 (C-5A), 69.0 (C-5B), 65.8 (C-4A), 21.0 ($SC_6H_4CH_3$), 18.2, 17.9 (C-6A, C-6B); HR-ESI-MS *m/z* calcd for $C_{40}H_{41}N_3O_9S$ 762.2461 $[M+Na]^+$, found 762.2444.

4.2.18. *p*-Methylphenyl 4-azido-3-*O*-benzoyl-4,6-dideoxy-2-*O*-methyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (29)

To a solution of **28** (136 mg, 0.18 mmol) in dry CH_2Cl_2 (1.5 mL) was added silver (I) oxide (256 mg, 1.10 mmol). The reaction mixture was stirred at rt for 1 h. Iodomethane (137 μL, 2.21 mmol) was then added dropwise and the reaction mixture was stirred at rt for 8 days. Silver (I) oxide was filtered through a Celite® pad and the filtrate was concentrated. The residue was purified by flash chromatography using cyclohexane/EtOAc (9:1) as eluent to give **29** (104 mg, 73%) as a colorless oil and **28** (16 mg, 12%). R_f 0.65 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −72 ($CHCl_3$, *c* 0.1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02–6.96 (m, 19H, 2 × $OCOC_6H_5$, $OCH_2C_6H_5$, $SC_6H_4CH_3$), 5.52 (dd, 1H, $J_{1B,2B}$ = 1.8 Hz, $J_{2B,3B}$ = 3.6 Hz, H-2B), 5.43 (br s, 1H, H-1B), 4.74 (t, 1H, $J_{2A,3A} = J_{3A,4A}$ = 9.6 Hz, H-3A), 4.74 (d, 1H, $J_{1A,2A}$ = 7.8 Hz, H-1A), 4.71 (d, 1H, $J_{A,B}$ = 10.8 Hz, A part of an AB system, $OCHHC_6H_5$), 4.68 (d, 1H, $J_{A,B}$ = 10.8 Hz, B part of an AB system, $OCHHC_6H_5$), 3.12 (dd, 1H, $J_{2B,3B}$ = 3.6 Hz, $J_{3B,4B}$ = 9.2 Hz, H-3B), 4.14–4.09 (m, 1H, H-5B), 3.48 (t, 1H, $J_{3B,4B} = J_{4B,5B}$ = 9.2 Hz), 3.38–3.33 (m, 1H, H-5A), 3.31 (dd, 1H, $J_{1A,2A}$ = 7.8 Hz, $J_{2A,3A}$ = 9.6 Hz, H-2A) 2.30 (s, 3H, $SC_6H_4CH_3$), 1.36 (d, 3H, $J_{5B,6B}$ = 6.2 Hz, H-6B), 1.29 (d, 3H, $J_{5A,6A}$ = 6.0 Hz, H-6A); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5 ($OCOC_6H_5$), 166.0 ($OCOC_6H_5$), 138.4, 129.9, 129.4, 128.7, 128.1, 128.0, 127.5 ($SC_6H_4CH_3$, 2 × $OCOC_6H_5$, $OCH_2C_6H_5$), 101.6 (C-1A), 86.2 (C-1B), 83.5 (C-2A), 79.9 (C-4B), 78.9 (C-3B), 75.6 ($OCH_2C_6H_5$), 75.4 (C-3A), 74.6 (C-2B), 70.6 (C-5A), 69.0 (C-5B), 66.8 (C-4A), 20.4 ($SC_6H_4CH_3$), 18.1, 17.5 (C-6A, C-6B).

HR-ESI-MS *m/z* calcd for $C_{40}H_{41}N_3O_9S$ 776.2618 $[M+Na]^+$, found 776.2627.

4.2.19. 2-Methyl-5-*tert*-butylphenyl 4-azido-3-*O*-benzoyl-4,6-dideoxy-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (30)

To a solution of ester **22** (216 mg, 0.26 mmol) in CH_2Cl_2 (6 mL) was added a solution of acetyl chloride (523 μL, 7.8 mmol) in MeOH (10 mL) dropwise. The reaction mixture was stirred at rt for 6 days and was then poured in saturated aqueous $NaHCO_3$. The layers were separated and the organic phase was washed with water, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to provide recovered **22** (41 mg, 19%) and **30** (130 mg, 63%) as a colorless oil. R_f 0.58 (cyclohexane/EtOAc 7:3); $[\alpha]_D$ −25 ($CHCl_3$, *c* 0.3); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10–7.15 (m, 18H, 2 × $OCOC_6H_5$, $OCH_2C_6H_5$ and $SC_6H_3C(CH_3)_3CH_3$), 5.72 (dd, 1H, $J_{1B,2B}$ = 1.7 Hz, $J_{2B,3B}$ = 3.2 Hz, H-2B), 5.49 (d, 1H, $J_{1B,2B}$ = 1.7 Hz, H-1B), 5.24 (t, 1H, $J_{2A,3A} = J_{3A,4A}$ = 9.6 Hz, H-3A), 5.02 (d, 1H, $J_{A,B}$ = 10.6 Hz, A part of an AB system, $OCHHC_6H_5$), 4.76 (d, 1H, $J_{A,B}$ = 10.6 Hz, B part of an AB system, $OCHHC_6H_5$), 4.71 (d, 1H, $J_{1A,2A}$ = 7.7 Hz, H-1A), 4.41–4.31 (m, 2H, H-3B, H-5B), 3.75 (t, 1H, $J_{3B,4B} = J_{4B,5B}$ = 9.4 Hz, H-4B), 3.64 (dd, 1H, $J_{1A,2A}$ = 7.7 Hz, $J_{2A,3A}$ = 9.6 Hz, H-2A), 3.45 (dq, 1H, $J_{4A,5A}$ = 9.6 Hz, $J_{5A,6A}$ = 6.0 Hz, H-5A), 3.32 (t, 1H, $J_{3A,4A} = J_{4A,5A}$ = 9.6 Hz, H-4A), 2.50 (s, 3H, $SC_6H_3C(CH_3)_3CH_3$), 1.41 (d, 3H, $J_{5B,6B}$ = 6.1 Hz, H-6B), 1.35 (d, 3H, $J_{5A,6A}$ = 6.1 Hz, H-6A), 1.34 (s, 9H, $SC_6H_3CH_3C(CH_3)_3CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8 ($OCOC_6H_5$), 165.8 ($OCOC_6H_5$), 149.8, 138.0, 137.0, 133.7, 133.3, 132.5, 131.0, 130.4, 130.3, 130.2, 130.1, 130.0, 129.3, 129.0, 128.6, 128.5, 128.2, 125.2 ($SC_6H_3C(CH_3)_3CH_3$, 2 × $OCOC_6H_5$, $OCH_2C_6H_5$), 103.4 (C-1A), 85.5 (C-1B), 80.4 (C-4B), 78.8 (C-3B), 76.6 (C-3A), 75.6 ($OCH_2C_6H_5$), 74.9 (C-2B), 73.4 (C-2A), 70.9 (C-5A), 69.2 (C-5B), 66.0 (C-4A), 34.5 ($SC_6H_3C(CH_3)_3CH_3$), 31.4 ($SC_6H_3C(CH_3)_3CH_3$), 20.4 ($SC_6H_3C(CH_3)_3CH_3$), 18.4, 18.2 (C-6A, C-6B); HR-ESI-MS *m/z* calcd for $C_{44}H_{49}N_3O_9S$ 818.3087 $[M+Na]^+$, found 818.3082.

4.2.20. 2-Methyl-5-*tert*-butylphenyl 4-azido-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-1-thio-α-D-rhamnopyranoside (31)

To a solution of **b23** (160 mg, 0.19 mmol) in CH_2Cl_2 (5 mL) was added a solution of acetyl chloride (396 μL, 5.5 mmol) in MeOH (8 mL) dropwise. The reaction mixture was stirred at rt for 4 days and was then poured in saturated aqueous $NaHCO_3$. The layers were separated and the organic phase was washed with water, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using cyclohexane/EtOAc (95:5→9:1) as eluent to provide **23** (27 mg, 17%), **31b** (43 mg, 29%), and **5** (24 mg, 24%). R_f 0.53 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −90 ($CHCl_3$, *c* 1.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16–7.18 (m, 18H, $OCOC_6H_5$, 2 × $OCH_2C_6H_5$, $SC_6H_3C(CH_3)_3CH_3$), 5.71 (dd, 1H, $J_{1B,2B}$ = 1.5 Hz, $J_{2B,3B}$ = 3.3 Hz, H-2B), 5.50 (d, 1H, $J_{1B,2B}$ = 1.5 Hz, H-1B), 5.00 (d, 1H, $J_{A,B}$ = 10.6 Hz, A part of an AB system, $OCHHC_6H_5$), 4.94 (d, 1H, $J_{A,B}$ = 11.2 Hz, A part of an AB system, $OCHHC_6H_5$), 4.87 (d, 1H, $J_{A,B}$ = 11.2 Hz, B part of an AB system, $OCHHC_6H_5$), 4.80 (d, 1H, $J_{A,B}$ = 10.6 Hz, B part of an AB system, $OCHHC_6H_5$), 4.53 (d, 1H, $J_{1A,2A}$ = 7.7 Hz, H-1A), 4.46–4.33 (m, 1H, H-5B), 4.32 (dd, 1H, $J_{2B,3B}$ = 3.3 Hz, $J_{3B,4B}$ = 9.5 Hz, H-3B), 3.95 (s, 1H, OH), 3.77 (t, 1H, $J_{3B,4B} = J_{4B,5B}$ = 9.3 Hz, H-4B), 3.54 (dd, 1H, $J_{1A,2A}$ = 7.7 Hz, $J_{2A,3A}$ = 9.3 Hz, H-2A), 3.43 (t, 1H, $J_{2A,3A} = J_{3A,4A}$ = 9.3 Hz, H-3A), 3.36–3.26 (m, 1H, H-5A), 3.11 (t, 1H, $J_{3A,4A} = J_{4A,5A}$ = 9.3 Hz, H-4A), 2.48 (s, 3H, $SC_6H_3C(CH_3)_3CH_3$), 1.34 (s, 9H, $SC_6H_3CH_3C(CH_3)_3CH_3$), 1.33 (d, 3H, $J_{5B,6B}$ = 6.3 Hz, H-6B), 1.30 (d, 3H, $J_{5A,6A}$ = 6.1 Hz, H-6A); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8 ($OCOC_6H_5$), 149.8, 138.1, 138.0, 137.0, 133.2, 132.4, 130.4, 130.1, 129.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 125.2 ($SC_6H_3C(CH_3)_3CH_3$, 2 × $OCH_2C_6H_5$, $OCOC_6H_5$), 103.1 (C-1A), 85.4 (C-1B), 82.5 (C-3A), 80.6 (C-4B), 78.5 (C-3B), 75.6 ($OCH_2C_6H_5$), 75.1 (C-2A), 75.0 ($OCH_2C_6H_5$), 74.6 (C-2B), 71.0 (C-5A), 69.1 (C-5B), 67.2 (C-4A), 34.5 ($SC_6H_3C(CH_3)_3CH_3$), 31.4 ($SC_6H_3C(CH_3)_3CH_3$), 20.4 ($SC_6H_3C(CH_3)_3CH_3$), 18.3 (C-6A), 18.1 (C-6B); ESI-MS calcd for $C_{44}H_{51}N_3O_8S$ $[M+Na]^+$ 804.3295, found 804.3288.

4.2.21. Methyl L-rhamnopyranoside (32)

To a solution of MeOH (7.0 mL) and acetyl chloride (4.3 mL, 60.8 mmol) at −10 °C was added L-rhamnose (5.0 g, 30.4 mmol). The reaction mixture was then stirred for 12 h at rt before $NaHCO_3$ in excess was added. The solvent was then evaporated in vacuo and the residue was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (9:1) as eluent to afford methyl-D-rhamnopyranoside **32** as a 9:1 mixture of α/β anomers as a white solid (3.8 g, 70%). R_f 0.47 (α) and 0.56 (β) (CH_2Cl_2/MeOH 8:2); ^{1}H NMR (300 MHz, CD_3OD) (α anomer) δ 4.61 (s, 1H, H-1), 3.86–3.83 (m, 1H, H-2), 3.65 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.56 (dq, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.41 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.4 Hz, H-4), 3.37 (s, 1H, OCH_3), 1.30 (d, 1H, $J_{5,6}$ = 9.4 Hz, H-6); ^{13}C NMR (75 MHz, CD_3OD) (α anomer) δ 101.3 (C-1), 72.5 (C-4), 71.1 (C-3), 70.7 (C-2), 68.2 (C-5), 53.9 (OCH_3), 16.8 (C-6); ESI-MS *m/z* 201.9 $[M+Na]^+$.

4.2.22. Methyl 3-*O*-allyl-L-rhamnopyranoside (33)

A mixture of triol **32** (3.8 g, 21.3 mmol) and dibutyltin oxide (5.8 g, 23.4 mmol) in dry MeOH (60 mL) was heated to reflux under inert atmosphere for 6 h and was then evaporated to dryness. The residue was dried under vacuum for 2 h and was dissolved in dry DMF (40 mL). Allyl bromide (2.2 mL, 25.6 mmol) was added dropwise and the reaction mixture was stirred at 90 °C for 48 h. The mixture was then concentrated in vacuo and the residue was purified by flash chromatography using cyclohexane/EtOAc (5:5) to afford **33**[29] (1.9 g, 40%) as a 9:1 α/β mixture as a colorless oil. R_f 0.33 (cyclohexane/EtOAc 5:5); ^{1}H NMR (300 MHz, $CDCl_3$) (α ano-

mer) δ 5.99–5.82 (m, 1H, OCH_2CHCH_2), 5.33–5.26 (m, 1H, A part of an AB system, OCH_2CHCHH), 5.22–5.18 (m, 1H, B part of an AB system, OCH_2CHCHH), 4.68 (br s, 1H, H-1), 4.19–4.13 (m, 1H, A part of an AB system, $OCHHCHCH_2$), 4.07–4.01 (m, 1H, B part of an AB system, $OCHHCHCH_2$), 3.97 (br s, 1H, H-2), 3.62 (dq, 1H, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 5.9 Hz, H-5), 3.51–3.49 (m, 2H, H-3, H-4), 3.33 (s, 3H, OCH_3), 1.28 (d, 3H, $J_{5,6}$ = 5.9 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) (α anomer) δ 134.4 (OCH_2CHCH_2), 117.6 (OCH_2CHCH_2), 100.3 (C-1), 79.1 (C-3), 71.0 (C-4), 70.5 (OCH_2CHCH_2), 67.7 (C-2 and C-5), 54.5 (OCH_3), 17.5 (C-6); ESI-MS *m/z* 240.9 $[M+Na]^+$.

4.2.23. 1,2,4-Tri-*O*-acetyl-3-*O*-allyl-L-rhamnopyranoside (34)

A solution of **33** (1.9 g, 8.7 mmol) in Ac_2O/AcOH/H_2SO_4 (12 mL/2 mL/46 μL) was stirred at rt for 1.5 h. The reaction mixture was then quenched by $NaHCO_3$ in excess. The residue was dissolved in EtOAc and was washed by saturated aqueous $NaHCO_3$ and brine. The organic phase was then dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to give **34** (1.9 g, 67%) as a 10:1 mixture of α/β anomers as a colorless oil. R_f 0.74 (α) and 0.67 (β) (cyclohexane/EtOAc 5:5); ^{1}H NMR (300 MHz, $CDCl_3$) (α anomer) δ 5.81 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 5.68–5.56 (m, 1H, OCH_2CHCH_2), 5.08 (dd, 1H, $J_{1,2}$ = 1.9 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 5.09–5.01 (m, 1H, A part of an AB system, OCH_2CHCHH), 4.98–4.94 (m, 1H, B part of an AB system, OCH_2CHCHH), 4.82 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4), 3.94–3.87 (m, 1H, A part of an AB system, $OCHHCHCH_2$), 3.78–3.72 (m, 1H, B part of an AB system, $OCHHCHCH_2$), 3.67 (dq, 1H, $J_{4,5}$ = 9.8 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.60 (dd, 1H, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.8 Hz, H-3), 1.94 (s, 3H, $OCOCH_3$), 1.93 (s, 3H, $OCOCH_3$), 1.89 (s, 3H, $OCOCH_3$), 1.00 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) (α anomer) δ 169.3 ($OCOCH_3$), 169.3 ($OCOCH_3$), 167.8 ($OCOCH_3$), 134.0 (OCH_2CHCH_2), 116.5 (OCH_2CHCH_2), 100.3 (C-1), 73.8 (C-3), 71.5 (C-4), 70.5 (OCH_2CHCH_2), 68.4 (C-5), 67.3 (C-2), 20.4 (3 × $OCOCH_3$), 17.1 (C-6); HR-ESI-MS *m/z* calcd for $C_{15}H_{22}O_8$ 353.1223 $[M+Na]^+$, found 353.1201.

4.2.24. 2,4-Di-*O*-acetyl-3-*O*-allyl-L-rhamnopyranosyl trichloroacetimidate (35)

To a solution of acetate **34** (1.9 g, 5.7 mmol) in dry THF (30 mL) was added benzylamine (688 μL, 6.3 mmol). The reaction mixture was stirred at rt under inert atmosphere overnight and then quenched with 1 M aqueous HCl. The solvent was evaporated under reduced pressure and the crude residue was purified by flash chromatography using cyclohexane/EtOAc (7:3) as eluent to provide 2,4-di-*O*-acetyl-3-*O*-allyl-L-rhamnopyranoside (1.2 g, 71%) as 9:1 α/β mixture as a white solid. R_f 0.50 (cyclohexane/EtOAc 5:5); ^{1}H NMR (300 MHz, $CDCl_3$) (α anomer) δ 5.74–5.63 (m, 1H, OCH_2CHCH_2), 5.16 (dd, 1H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.11–5.10 (m, 1H, A part of an AB system, OCH_2CHCHH), 5.07–5.06 (m, 1H, B part of an AB system, OCH_2CHCHH), 5.03 (br s, 1H, H-1), 4.86 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.9 Hz, H-4), 4.55 (br s, 1H, OH), 4.04–3.96 (m, 1H, A part of an AB system, $OCHHCHCH_2$), 3.92 (dq, 1H, $J_{4,5}$ = 9.9 Hz, $J_{5,6}$ = 6.4 Hz, H-5), 3.86–3.79 (m, 1H, B part of an AB system, $OCHHCHCH_2$), 3.74 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.9 Hz, H-3), 2.03 (s, 3H, $OCOCH_3$), 1.98 (s, 3H, $OCOCH_3$), 1.07 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) (α anomer) δ 170.6 ($OCOCH_3$), 170.3 ($OCOCH_3$), 134.2 (OCH_2CHCH_2), 117.0 (OCH_2CHCH_2), 92.0 (C-1), 73.9 (C-3), 72.6 (C-4), 70.4 (OCH_2CHCH_2), 69.5 (C-2), 66.1 (C-5), 20.9 and 20.8 (3 × $OCOCH_3$), 17.4 (C-6); ESI-MS *m/z* 310.8 $[M+Na]^+$. To a solution of 2,4-di-*O*-acetyl-3-*O*-allyl-L-rhamnopyranoside (1.2 g, 4.2 mmol) in CH_2Cl_2 (20 mL) were added trichloroacetonitrile (8.4 mL, 84 mmol) and DBU (250, 1.7 mmol) dropwise at 0 °C. The mixture was then stirred at rt for 2 h and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel using 2% Et_3N in cyclohexane/EtOAc (8:2) as eluent to give trichloroacetimide **103** (1.4 mg, 80%) as a white solid as a 20:1 mixture of α/β anomers. R_f 0.76 (cyclohexane/EtOAc 5:5); ^{1}H NMR (300 MHz, $CDCl_3$) δ (α anomer) 8.69 (br s, 1H, NH), 6.14 (d, 1H, $J_{1,2}$ = 2.0 Hz, H-1), 5.76–5.71 (m, 1H, OCH_2CHCH_2), 5.39 (dd, 1H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 5.21–5.15 (m, 1H, A part of an AB system, OCH_2CHCHH), 5.14–5.09 (m, 1H, B part of an AB system, OCH_2CHCHH), 5.03 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.9 Hz, H-4), 4.08–4.01 (m, 1H, A part of an AB system, $OCHHCHCH_2$), 3.96–3.86 (m, 2H, B part of an AB system, $OCHHCHCH_2$, H-5), 3.80 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 9.9 Hz, H-3), 2.11 (s, 3H, $OCOCH_3$), 2.04 (s, 3H, $OCOCH_3$), 1.18 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ (α anomer) 169.9 ($OCOCH_3$), 169.8 ($OCOCH_3$), 159.7 ($OCNHCCl_3$), 134.1 (OCH_2CHCH_2), 117.6 (OCH_2CHCH_2), 95.0 (C-1), 77.4 ($OCNHCCl_3$), 73.9 (C-3), 71.7 (C-4), 70.7 (OCH_2CHCH_2), 69.4 (C-5), 67.2 (C-2), 20.9 (2 × $OCOCH_3$), 17.5 (C-6); ESI-MS *m/z* 453.7 $[M+Na]^+$.

4.2.25. 2-[(*N*-Benzyloxycarbonyl)amino]ethyl 2,4-di-*O*-acetyl-3-*O* -allyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyr anoside (36)

To a solution of donor **35** (45 mg, 0.10 mmol) and acceptor **19** (69 mg, 80 μmol) in dry CH_2Cl_2 (5 mL) containing molecular sieves 4 Å (20 mg) was added TMSOTf (9 μL, 50 μmol) under argon at 0 °C. After 30 min of stirring, the solution was neutralized with Et_3N and the molecular sieves were removed by filtration. The reaction mixture was diluted with CH_2Cl_2, washed with water, dried over Na_2SO_4, and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel using cyclohexane/EtOAc (7:3) as eluent to provide **36** (116 mg, 99%) as a colorless oil. R_f 0.10 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −8 ($CHCl_3$, *c* 1.0); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12–7.16 (m, 25H, $NHCOOCH_2C_6H_5$, 3 × $OCH_2C_6H_5$, $OCOC_6H_5$), 5.77–5.64 (m, 1H, OCH_2CHCH_2), 5.54 (dd, 1H, $J_{1C,2C}$ = 2.0 Hz, $J_{2C,3C}$ = 3.3 Hz, H-2C), 5.33 (dd, 1H, $J_{1B,2B}$ = 1.8 Hz, $J_{2B,3B}$ = 3.3 Hz, H-2B), 5.12–5.11 (m, 4H, H-1B, H-1C, $NHCOOCH_2C_6H_5$), 5.08–4.98 (m, 3H, H-4B, OCH_2CHCH_2), 4.87 (d, 1H, $J_{A,B}$ = 10.7 Hz, A part of an AB system, $OCHHC_6H_5$), 4.82 (d, 1H, $J_{A,B}$ = 10.7 Hz, A part of an AB system, $OCHHC_6H_5$), 4.73 (d, 1H, $J_{1D,2D}$ = 1.6 Hz, H-1D), 4.69 (d, 1H, $J_{A,B}$ = 10.7 Hz, B part of an AB system, $OCHHC_6H_5$), 4.60 (d, 1H, $J_{A,B}$ = 10.7 Hz, B part of an AB system, $OCHHC_6H_5$), 4.67 (s, 2H, $OCH_2C_6H_5$), 4.31 (dd, 1H, $J_{2C,3C}$ = 3.2 Hz, $J_{3C,4C}$ = 9.5 Hz, H-3C), 3.99–3.88 (m, 4H, H-2D, H-5B, H-5C, A part of an AB system, $OCHHCHCH_2$), 3.82 (dd, 1H, $J_{2D,3D}$ = 2.9 Hz, $J_{3D,4D}$ = 9.3 Hz, H-3D), 3.79–3.74 (m, 1H, B part of an AB system, $OCHHCHCH_2$), 3.71–3.63 (m, 3H, H-3B, H-5D, A part of an AB system, $OCHHCH_2NH$), 3.61 (t, 1H, $J_{3C,4C}$ = $J_{4C,5C}$ = 9.5 Hz, H-4C), 3.46 (t, 1H, $J_{3D,4D}$ = $J_{4D,5D}$ = 9.3 Hz, H-4D), 3.51–3.28 (m, 3H, B part of an AB system, $OCHHCH_2NH$, OCH_2CH_2NH), 2.08 (s, 3H, $OCOCH_3$), 2.03 (s, 3H, $OCOCH_3$), 1.35 (d, 3H, $J_{5C,6C}$ = 6.1 Hz, H-6C), 1.29 (d, 3H, $J_{5D,6D}$ = 6.2 Hz, H-6D), 1.09 (d, 3H, $J_{5B,6B}$ = 6.3 Hz, H-6B); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2 (2 × $OCOCH_3$), 165.6 ($OCOC_6H_5$), 156.4 ($NHCOOCH_2C_6H_5$), 138.5, 137.8, 133.4, 129.9, 128.6, 128.5, 128.5, 128.2, 128.2, 128.1, 127.8, 127.6, 123.1 (3 × $OCH_2C_6H_5$, $OCOC_6H_5$, $NHCOOCH_2C_6H_5$), 134.4 (OCH_2CHCH_2), 117.0 (OCH_2CHCH_2), 99.1, 99.0 (C-1B, C-1C, C-1D), 80.9 (C-4C), 80.3 (C-4D), 79.4 (C-3D), 75.6 (C-3C, C-2D, 2 × $OCH_2C_6H_5$), 74.2 (C-3B), 72.7 (C-2C), 72.4 (C-4B), 72.3 ($OCH_2C_6H_5$), 70.6 (OCH_2CHCH_2), 69.0 (C-2B), 68.6 (C-5D), 68.4 (C-5C), 67.6 (C-5B), 66.9 ($NHCOOCH_2C_6H_5$, OCH_2CH_2NH), 41.0 (OCH_2CH_2NH), 21.0 ($OCOCH_3$), 18.3 (C-6C), 18.1 (C-6D), 17.3 (C-6B); HR-ESI-MS *m/z* calcd for $C_{63}H_{73}NO_{18}$ 1154.4725 $[M+Na]^+$, found 1154.4755.

4.2.26. 2-[(*N*-Benzyloxycarbonyl)amino]ethyl 3-*O*-allyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (37)

Compound **36** (116 mg, 0.10 mmol) was treated with NaOMe (0.2 M solution in MeOH) (3 mL, 0.60 mmol) for 1 h at rt. The reaction mixture was then neutralized by resin Amberlite 120 H^+. The

resin was filtered off and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography on silica gel using cyclohexane/EtOAc (7:3) as eluent to provide **37** (66 mg, 70%) as a white solid. R_f 0.36 (cyclohexane/EtOAc 5:5); $[\alpha]_D$ −26 ($CHCl_3$, *c* 0.9); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.27 (m, 20H, NHCO-$OCH_2C_6H_5$, 3 × $OCH_2C_6H_5$), 5.99–5.86 (m, 1H, OCH_2CHCH_2), 5.31–5.24 (m, 1H, A part of an AB system, OCH_2CHCHH), 5.22–5.17 (m, 1H, B part of an AB system, OCH_2CHCHH), 5.18 (br s, 1H, H-1B), 5.11 (br s, 2H, $NHCOOCH_2C_6H_5$), 5.03 (br s, 1H, $NHCOOCH_2C_6H_5$), 5.00 (d, 1H, $J_{1C,2C}$ = 1.5 Hz, H-1C), 4.82 (d, 1H, $J_{A,B}$ = 11.0 Hz, A part of an AB system, $OCHHC_6H_5$), 4.74 (d, 1H, $J_{A,B}$ = 11.0 Hz, A part of an AB system, $OCHHC_6H_5$), 4.70 (d, 1H, $J_{1D,2D}$ = 1.6 Hz, H-1D), 4.63 (d, 1H, $J_{A,B}$ = 11.0 Hz, B part of an AB system, $OCHHC_6H_5$), 4.59 (d, 1H, $J_{A,B}$ = 11.0 Hz, B part of an AB system, $OCHHC_6H_5$), 4.16 (dd, 1H, $J_{1C,2C}$ = 1.5 Hz, $J_{2C,3C}$ = 3.2 Hz, H-2C), 4.12–4.10 (m, 1H, A part of an AB system, $OCHHCHCH_2$), 4.06 (dd, 1H, $J_{2C,3C}$ = 3.2 Hz, $J_{3C,4C}$ = 9.3 Hz, H-3C), 4.05–4.01 (m, 1H, B part of an AB system, $OCHHCHCH_2$), 4.00 (dd, 1H, $J_{1B,2B}$ = 1.6 Hz, $J_{2B,3B}$ = 2.4 Hz, H-2B), 3.96–3.94 (m, 1H, H-2D), 3.88–3.79 (m, 2H, H-5B, H-5C), 3.81 (dd, 1H, $J_{2D,3D}$ = 2.8 Hz, $J_{3D,4D}$ = 9.2 Hz, H-3D), 3.72–3.62 (m, 2H, H-5D, A part of an AB system, $OCHHCH_2NH$), 3.59–3.57 (m, 2H, H-3B, H-4B), 3.47 (t, 1H, $J_{3C,4C}$ = $J_{4C,5C}$ = 9.3 Hz, H-4C), 3.42 (t, 1H, $J_{3D,4D}$ = $J_{4D,5D}$ = 9.3 Hz, H-4D), 3.50–3.29 (m, 3H, B part of an AB system, $OCHHCH_2NH$, OCH_2CH_2NH), 2.27 (m, 3H, 3 × OH), 1.32–1.26 (m, 9H, H-6B, H-6C, H-6D); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.4 ($NHCOOCH_2C_6H_5$), 138.4, 138.2, 136.5, 128.7, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8 (3 × $OCH_2C_6H_5$, $NHCOOCH_2C_6H_5$), 134.3 (OCH_2CHCH_2), 118.1 (OCH_2CHCH_2), 101.2, 101.1 (C-1B, C-1C), 99.2 (C-1D), 80.4, 80.3 (C-4C, C-4D), 79.7 (C-3D), 79.5 (C-3B), 79.3 (C-3C), 75.6, 75.5 (2 × $OCH_2C_6H_5$), 75.2 (C-2D), 72.5 ($OCH_2C_6H_5$), 71.5 (C-4B), 70.9 (C-2C), 70.7 (OCH_2CHCH_2), 68.7, 68.4, 68.3 (C-5B, C-5C, C-5D), 68.2 (C-2B), 67.0, 66.8 ($NHCOOCH_2C_6H_5$, OCH_2CH_2NH), 41.0 (OCH_2CH_2NH), 18.1, 17.8 (C-6B, C-6C, C-6D); HR-ESI-MS *m/z* calcd for $C_{52}H_{65}NO_{15}$ 966.4252 $[M+Na]^+$, found 966.4240.

4.2.27. 2-[(*N,N*′-Benzyl-benzyloxycarbonyl)amino]ethyl 3-*O*-allyl-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (38)

To a solution of **37** (66 mg, 70 μmol) in DMF (1 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 22 mg, 0.56 mmol) followed by dropwise addition of BnBr (40 μL, 0.34 mmol). The reaction mixture was stirred at rt for 2 h and the excess of NaH was neutralized by dropwise addition of MeOH (500 μL) at 0 °C. The mixture was concentrated in vacuo and the residue was purified by flash chromatography using cyclohexane/EtOAc (9:1→7:3) as eluent to give **39** (79 mg, 87%) as a colorless oil (mixture of conformers). R_f 0.60 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ −13 ($CHCl_3$, *c* 1.7); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38–7.17 (m, 40H, $NCOOCH_2C_6H_5$, 6 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 5.93–5.86 (m, 1H, OCH_2CHCH_2), 5.29–5.26 (m, 1H, A part of an AB system, OCH_2CHCHH), 5.19–5.15 (m, 3H, H-1B, $NCOOCH_2C_6H_5$), 5.13–5.11 (m, 1H, B part of an AB system, OCH_2CHCHH), 5.06 (d, 1H, $J_{1C,2C}$ = 1.1 Hz, H-1C), 4.95 (d, 1H, $J_{A,B}$ = 11.0 Hz, A part of an AB system, $OCHHC_6H_5$), 4.86 (d, 1H, $J_{A,B}$ = 10.9 Hz, A part of an AB system, $OCHHC_6H_5$), 4.73 (d, 1H, $J_{A,B}$ = 11.5 Hz, A part of an AB system, $OCHHC_6H_5$), 4.67–4.46 (m, 12H, H-1D, 3 × B part of 3 × AB system, 3 × $OCHHC_6H_5$, $NCH_2C_6H_5$), 4.15 (dd, 1H, $J_{2C,3C}$ = 2.7 Hz, $J_{3C,4C}$ = 9.3 Hz, H-3C), 4.03 (m, 2H, OCH_2CHCH_2), 3.92 (br s, 1H, H-2D), 3.81–3.76 (m, 7H, H-2B, H-3B, H-2C, H-5C, H-3D, H-5B, A part of an AB system, $OCHHCH_2N$), 3.59–3.47 (m, 4H, H-4B, H-5D, H-4C, B part of an AB system, $OCHHCH_2N$), 3.46–3.30 (m, 3H, H-4D, OCH_2CH_2NH), 1.28–1.21 (m, 9H, H-6B, H-6C, H-6D); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6 and 156.3 ($NCOOCH_2C_6H_5$), 139.1, 138.6, 138.3, 128.7, 128.6, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.1 ($NCOOCH_2C_6H_5$, 6 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 135.2 (OCH_2CHCH_2), 116.5 (OCH_2CHCH_2), 99.7 (C-1B), 99.2, 99.1 (C-1C, C-1D), 81.0 (C-4C), 80.5 (C-3D, C-4D), 79.9 (C-4B), 79.8 (C-3B), 78.1 (C-2C), 76.9 (C-3C), 75.7 (C-2B)4, 75.6 ($OCH_2C_6H_5$), 75.3 ($OCH_2C_6H_5$), 74.8 ($OCH_2C_6H_5$), 74.7 (C-2D), 72.7 ($OCH_2C_6H_5$), 72.5 ($OCH_2C_6H_5$), 72.4 ($OCH_2C_6H_5$), 71.1 (OCH_2CHCH_2), 68.8, 68.7 (C-5C, C-5D), 68.3 (C-5B), 67.5 ($NCOOCH_2C_6H_5$), 65.7 (OCH_2CH_2N), 51.8 ($NCH_2C_6H_5$), 47.0 and 45.9 (OCH_2CH_2N), 18.1 (C-6B, C-6C, C-6D); HR-ESI-MS *m/z* calcd for $C_{80}H_{89}NO_{15}$ 1326.6130 $[M+Na]^+$, found 1326.6152.

4.2.28. 2-[(*N,N*′-Benzyl-benzyloxycarbonyl)amino]ethyl 2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (39)

A solution of **38** (79 mg, 60 μmol), $(Ph_3P)_3RhCl$ (4.4 mg, 4.8 μmol), and DABCO (1.3 mg, 12 μmol), in a 7:3:1 mixture of EtOH/toluene/H_2O (4 mL) was stirred at reflux for 16 h. After filtration through a Celite® pad, the reaction mixture was concentrated to dryness and dissolved in a 9:1 mixture of acetone/H_2O (1 mL). $HgCl_2$ (49 mg, 180 μmol) and HgO (1.3 mg, 6 μmol) were then added. After stirring for 4 h at rt, the reaction mixture was concentrated and the residue was dissolved in EtOAc. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography using cyclohexane/EtOAc (8:2) as eluent to give **39** (67 mg, 88%) as a white solid (mixture of conformers). R_f 0.24 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ +2 ($CHCl_3$, *c* 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27–7.15 (m, 40H, $NCOOCH_2C_6H_5$, 6 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 5.15 (br s, 1H, H-1B), 5.11 (br s, 2H, $NCOOCH_2C_6H_5$), 5.02 (br s, 1H, H-1C), 4.80 (d, 1H, $J_{A,B}$ = 11.1 Hz, A part of an AB system, $OCHHC_6H_5$), 4.78 (d, 1H, $J_{A,B}$ = 10.5 Hz, A part of an AB system, $OCHHC_6H_5$), 4.71 (d, 1H, $J_{A,B}$ = 11.7 Hz, A part of an AB system, $OCHHC_6H_5$), 4.64 (d, 1H, $J_{A,B}$ = 11.7 Hz, B part of an AB system, $OCHHC_6H_5$), 4.61 (br s, 1H, H-1D), 4.55 (d, 1H, $J_{A,B}$ = 11.1 Hz, B part of an AB system, $OCHHC_6H_5$), 4.50 (d, 1H, $J_{A,B}$ = 10.5 Hz, B part of an AB system, $OCHHC_6H_5$), 4.56–4.39 (m, 6H, 2 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 4.26 (d, 1H, $J_{A,B}$ = 11.6 Hz, A part of an AB system, $OCHHC_6H_5$), 4.09 (dd, 1H, $J_{2C,3C}$ = 2.4 Hz, $J_{3C,4C}$ = 9.6 Hz, H-3C), 4.05–4.02 (m, 1H, B part of an AB system, $OCHHC_6H_5$), 3.89–3.86 (m, 2H, H-3B, H-2D), 3.72 (br s, 1H, H-2C), 3.64 (br s, 1H, H-2B), 3.75–3.62 (m, 3H, H-5C, H-3D, H-5B), 3.62–3.50 (m, 2H, H-4B, A part of an AB system, $OCHHCH_2N$), 3.50–3.41 (m, 2H, H-5D, H-4C, B part of an AB system, $OCHHCH_2N$), 3.36–3.25 (m, 3H, H-4D, OCH_2CH_2NH), 3.24 (t, 1H, $J_{3B,4B}$ = $J_{4B,5B}$ = 9.4 Hz, H-4B), 1.22 (d, 3H, $J_{5C,6C}$ = 5.9 Hz, H-6C), 1.18–1.16 (m, 9H, H-6B, H-6D); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6 and 156.3 ($NCOOCH_2C_6H_5$), 138.7, 138.3, 137.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.8, 127.0 ($NCOOCH_2C_6H_5$, 6 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 99.3, 99.2 (C-1C, C-1D), 98.6 (C-1B), 82.3 (C-4B), 81.1 (C-4C), 80.6 (C-4D), 79.8 (C-3D), 79.3 (C-2B), 78.0 (C-2C), 76.7 (C-3C), 75.6 ($OCH_2C_6H_5$), 75.0 ($OCH_2C_6H_5$), 74.8 ($OCH_2C_6H_5$), 74.9 (C-2D), 72.7 ($OCH_2C_6H_5$), 72.6 ($OCH_2C_6H_5$), 72.4 ($OCH_2C_6H_5$), 71.8 (C-3B), 69.0 (C-5D), 68.3 (C-5B), 67.9 (C-5C), 67.5 ($NCOOCH_2C_6H_5$), 66.3 (OCH_2CH_2N), 51.8 ($NCH_2C_6H_5$), 47.0 and 46.0 (OCH_2CH_2N), 18.2, 18.1 (C-6B, C-6C, C-6D); HR-ESI-MS *m/z* calcd for $C_{77}H_{85}NO_{15}$ 1286.5817 $[M+Na]^+$, found 1286.5774.

4.2.29. 2-[(*N,N*-Benzyl-benzyloxycarbonyl)amino]ethyl 2-*O*-acetyl-4-azido-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (40)

To a solution of **6** (28 mg, 51.3 μmol), **39** (50 mg, 39.5 mmol) and 4 Å molecular sieves (50 mg) in dry CH_2Cl_2 (2 mL) under inert atmosphere at −40 °C was added TMSOTf (1.2 μL, 25.6 μmol). After 30 min stirring at this temperature, the reaction mixture was neutralized by Et_3N and filtered. The filtrate was washed with water, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue

was purified by flash chromatography using cyclohexane/EtOAc (9:1→7:3) as eluent to give **40** (35 mg, 56%) as a colorless oil (mixture of conformers). R_f 0.45 (cyclohexane/EtOAc 7:3); $[\alpha]_D$ −4 ($CHCl_3$, *c* 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.12 (m, 45H, $NCOOCH_2C_6H_5$, 7 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 5.11 (br s, 2H, $NCOOCH_2C_6H_5$), 5.02–5.01 (m, 2H, H-1B, H-2A), 4.99 (br s, 1H, H-1C), 4.77 (d, 1H, $J_{A,B}$ = 10.8 Hz, A part of an AB system, $OCHHC_6H_5$), 4.70 (d, 2H, $J_{A,B}$ = 11.2 Hz, 2 × A part of an 2 × AB system, 2 × $OCHHC_6H_5$), 4.62–4.38 (m, 13H, H-1A, H-1D, 3 × B part of an 3 × AB system, 3 × $OCHHC_6H_5$), 4.38–4.37 (m, 2H, $NCH_2C_6H_5$), 4.02 (dd, 1H, $J_{2C,3C}$ = 2.4 Hz, $J_{3C,4C}$ = 9.9 Hz, H-3C), 4.01 (dd, 1H, $J_{2B,3B}$ = 2.9 Hz, $J_{3B,4B}$ = 9.9 Hz, H-3B), 3.84 (br s, 1H, H-2D), 3.81 (br s, 1H, H-2B), 3.74 (br s, 1H, H-2C), 3.71–3.67 (m, 4H, H-5B, H-5C, H-3D, A part of an AB system, $OCHHCH_2NH$), 3.51–3.42 (m, 4H, H-4B, H-4C, H-5D, B part of an AB system, $OCHHCH_2N$), 3.35–3.28 (m, 4H, H-3A, H-4D, OCH_2CH_2NH), 3.08 (t, 1H, $J_{3A,4A}$ = $J_{4A,5A}$ = 9.4 Hz, H-4A), 3.04–3.02 (m, 1H, H-5A), 1.71 (s, 3H, $OCOCH_3$), 1.20–1.17 (m, 6H, H-6C, H-6D) 1.14 (d, 3H, $J_{5B,6B}$ = 6.3 Hz, H-6B), 1.06 (d, 3H, $J_{5A,6A}$ = 5.9 Hz, H-6A); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3 ($OCOCH_3$), 156.6 and 156.3 ($NCOOCH_2C_6H_5$), 138.7, 138.5, 138.4, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5 ($NCOOCH_2C_6H_5$, 7 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 101.4 (C-1A), 100.5 (C-1B), 99.1 (C-1C and C-1D), 81.6 (C-3A), 80.6 (C-4B, C-4C and C-4D), 79.9 (C-3D), 79.5 (C-3B), 78.9 (C-2B), 78.2 (C-2C), 78.0 (C-3C), 75.6 ($OCH_2C_6H_5$), 74.8 (2 × $OCH_2C_6H_5$), 74.7 ($OCH_2C_6H_5$), 74.1 (C-2D), 73.6 (C-2A), 72.5 ($OCH_2C_6H_5$), 72.5 ($OCH_2C_6H_5$), 72.3 ($OCH_2C_6H_5$), 70.7 (C-5A), 68.8, 68.6 (C-5B and C-5C), 68.3 (C-5D), 67.8 (C-4A), 67.5 ($NCOOCH_2C_6H_5$), 65.7 (OCH_2CH_2N), 51.8 ($NCH_2C_6H_5$), 47.0 and 46.0 (OCH_2CH_2N), 18.6, 18.5, 18.2, 18.1 (C-6A, C-6B, C-6C and C-6D); HR-ESI-MS *m/z* calcd for $C_{92}H_{102}N_4O_{19}$ 1589.7036 $[M+Na]^+$, found 1589.7084.

4.2.30. 2-[(*N,N*-Benzyl-benzyloxycarbonyl)amino]ethyl 4-azido-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (41)

Compound **40** (35 mg, 22.3 μmol) was treated by NaOMe (0.2 M solution in MeOH) (223 μL, 44.6 μmol) for 12 h at rt. The reaction mixture was then neutralized by resin Amberlite IR120 H^+. The resin was filtered off and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography on silica gel using cyclohexane/EtOAc (8:2) as eluent to give **41** (29 mg, 85%) as a colorless oil (mixture of conformers). R_f 0.25 (cyclohexane/EtOAc 8:2); $[\alpha]_D$ +8 ($CHCl_3$, *c* 1.0); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42–7.19 (m, 45H, $NCOOCH_2C_6H_5$, 7 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 5.20 (br s, 2H, $NCOOCH_2C_6H_5$), 5.10 (br s, 2H, H-1B, H-1C), 4.91 (d, 1H, $J_{A,B}$ = 11.0 Hz, A part of an AB system, $OCHHC_6H_5$), 4.88 (d, 1H, $J_{A,B}$ = 10.9 Hz, A part of an AB system, $OCHHC_6H_5$), 4.83 (d, 1H, $J_{A,B}$ = 10.7 Hz, A part of an AB system, $OCHHC_6H_5$), 4.80 (d, 1H, $J_{A,B}$ = 11.0 Hz, B part of an AB system, $OCHHC_6H_5$), 4.68–4.41 (m, 13H, H-1D, 2 × B part of an 2 × AB system, 2 × $OCHHC_6H_5$, 4 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 4.40 (d, 1H, $J_{1A,2A}$ = 7.7 Hz, H-1A), 4.09 (dd, 1H, $J_{2C,3C}$ = 2.8 Hz, $J_{3C,4C}$ = 9.5 Hz, H-3C), 4.08 (dd, 1H, $J_{2B,3B}$ = 1.5 Hz, $J_{3B,4B}$ = 9.4 Hz, H-3B), 3.94 (br s, 1H, H-2D), 3.89 (br s, 1H, H-2B), 3.81 (br s, 1H, H-2C), 3.81–3.71 (m, 4H, H-5B, H-5C, H-3D, A part of an AB system, $OCHHCH_2NH$), 3.64 (t, 1H, $J_{3B,4B}$ = $J_{4B,5B}$ = 9.4 Hz, H-4B), 3.53 (br t, 1H, $J_{1A,2A}$ = 7.8 Hz, $J_{2A,3A}$ = 8.9 Hz, H-2A), 3.58–3.48 (m, 3H, H-4C, H-5D, B part of an AB system, $OCHHCH_2N$), 3.43–3.37 (m, 3H, H-4D, OCH_2CH_2NH), 3.35 (br t, 1H, $J_{2A,3A}$ = $J_{3A,4A}$ = 8.9 Hz, H-3A), 3.08–3.06 (m, 2H, H-4A, H-5A), 1.28–1.25 (m, 9H, H-6B, H-6C, H-6D), 1.06 (d, 3H, $J_{5A,6A}$ = 5.4 Hz, H-6A); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7 and 156.4 ($NCOOCH_2C_6H_5$), 138.8, 138.6, 138.5, 138.3, 137.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9 ($NCOOCH_2C_6H_5$, 7 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 104.0 (C-1A), 100.3 (C-1B), 99.2 (C-1C), 99.1 (C-1D), 82.4 (C-3A), 80.9, 80.8, 80.7 (C-4B, C-4C and C-4D), 80.3 (C-3B), 80.0 (C-3D), 78.6 (C-2B), 78.1 (C-2C), 77.5 (C-3C), 76.0 (C-2A), 75.7 ($OCH_2C_6H_5$), 75.5 ($OCH_2C_6H_5$), 75.1 (2 × $OCH_2C_6H_5$), 74.8 (C-2D), 73.5 ($OCH_2C_6H_5$), 72.6 ($OCH_2C_6H_5$), 72.4 ($OCH_2C_6H_5$), 71.0 (C-5A), 68.9, 68.8 (C-5B and C-5C), 68.4 (C-5D), 67.6 ($NCOOCH_2C_6H_5$), 67.4 (C-4A), 65.9 (OCH_2CH_2N), 51.9 ($NCH_2C_6H_5$), 47.1 and 46.1 (OCH_2CH_2N), 18.8 (C-6A), 18.8, 18.3, 18.2 (C-6B, C-6C and C-6D); HR-ESI-MS *m/z* calcd for $C_{90}H_{100}N_4O_{18}$ 1547.6930 $[M+Na]^+$, found 1547.6984.

4.2.31. 2-[(*N,N*-Benzyl-benzyloxycarbonyl)amino]ethyl 4-azido-3-*O*-benzyl-4,6-dideoxy-2-*O*-methyl-β-D-glucopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (42)

To a solution of **41** (29 mg, 19.0 μmol) in DMF (1 mL) was added NaH (60% dispersion in mineral oil, 1.5 mg, 38.0 μmol) at 0 °C, followed by dropwise addition of MeI (12 μL, 190 μmol). The reaction mixture was stirred at rt overnight and the excess of NaH was neutralized by dropwise addition of MeOH (500 μL) at 0 °C. The mixture was then evaporated to dryness and the residue was purified by flash chromatography on silica gel using cyclohexane/EtOAc (8:2) as eluent to give **42** (29 mg, 96%) as a colorless oil (mixture of conformers). R_f 0.59 (cyclohexane/EtOAc 7:3); $[\alpha]_D$ +2 ($CHCl_3$, *c* 1.1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.19 (m, 45H, $NCOOCH_2C_6H_5$, 7 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 5.16 (br s, 2H, $NCOOCH_2C_6H_5$), 5.11 (br s, 1H, H-1B), 5.06 (br d, 1H, $J_{1C,2C}$ = 1.6 Hz, H-1C), 4.96 (d, 1H, $J_{A,B}$ = 10.5 Hz, A part of an AB system, $OCHHC_6H_5$), 4.90 (d, 1H, $J_{A,B}$ = 10.7 Hz, A part of an AB system, $OCHHC_6H_5$), 4.85 (d, 1H, $J_{A,B}$ = 11.0 Hz, A part of an AB system, $OCHHC_6H_5$), 4.79 (d, 1H, $J_{A,B}$ = 10.7 Hz, B part of an AB system, $OCHHC_6H_5$), 4.69 (d, 1H, $J_{A,B}$ = 11.4 Hz, A part of an AB system, $OCHHC_6H_5$), 4.65–4.44 (m, 13H, H-1A, H-1D, 3 × B part of an 3 × AB system, 3 × $OCHHC_6H_5$, 3 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 4.11 (br dd, 2H, $J_{2B,3B}$ = $J_{2C,3C}$ = 3.0 Hz, $J_{3B,4B}$ = $J_{3C,4C}$ = 9.6 Hz, H-3B, H-3C), 3.84–3.82 (m, 1H, H-2D), 3.82–3.80 (m, 1H, H-2C), 3.81–3.79 (m, 1H, H-2B), 3.79–3.69 (m, 4H, H-5B, H-5C, H-3D, A part of an AB system, $OCHHCH_2NH$), 3.66–3.49 (m, 4H, H-4B, H-4C, H-5D, B part of an AB system, $OCHHCH_2N$), 3.63 (s, 3H, OCH_3), 3.49–3.33 (m, 4H, H-3A, H-4D, OCH_2CH_2NH), 3.11 (dd, 1H, $J_{1A,2A}$ = 7.9 Hz, $J_{2A,3A}$ = 9.0 Hz, H-2A), 3.04–3.02 (m, 2H, H-4A, H-5A), 1.28–1.23 (m, 9H, H-6B, H-6C, H-6D), 1.09 (d, 3H, $J_{5A,6A}$ = 5.7 Hz, H-6A); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9 and 156.5 ($NCOOCH_2C_6H_5$), 138.9, 138.6, 138.3, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5 ($NCOOCH_2C_6H_5$, 7 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 103.7 (C-1A), 100.4 (C-1B), 99.2 (C-1C and C-1D), 85.0 (C-2A), 82.4 (C-3A), 81.1, 80.7, 80.6 (C-4B, C-4C and C-4D), 79.9 (C-3D), 79.5 (C-2B), 78.7 (C-3B), 78.2 (C-2C), 77.4 (C-3C), 75.6 (2 × $OCH_2C_6H_5$), 75.0 (C-2D), 74.8 (2 × $OCH_2C_6H_5$), 73.5 ($OCH_2C_6H_5$), 72.5 ($OCH_2C_6H_5$), 72.3 ($OCH_2C_6H_5$), 70.4 (C-5A), 68.9, 68.6 (C-5B and C-5C), 68.3 (C-5D), 67.8 (C-4A), 67.5 ($NCOOCH_2C_6H_5$), 65.7 (OCH_2CH_2N), 60.9 (OCH_3), 51.8 ($NCH_2C_6H_5$), 47.0 and 45.9 (OCH_2CH_2N), 18.6 (C-6A), 18.1 (C-6B, C-6C and C-6D); HR-ESI-MS *m/z* calcd for $C_{91}H_{102}N_4O_{18}$ 1561.7087 $[M+Na]^+$, found 1561.7028.

4.2.32. 2-[(*N,N*′-Benzyl-benzyloxycarbonyl)amino]ethyl 3-*O*-benzyl-4-(3-hydroxy-3-methyl-butanamido)-4,6-dideoxy-2-*O*-methyl-β-D-glucopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (43)

To a solution of **42** (29 mg, 18.2 μmol) in a mixture of CH_2Cl_2 (250 μL) and EtOH (1 mL) was added sodium borohydride (1.4 mg, 36.4 μmol) and a catalytic amount of $NiCl_2{\cdot}6H_2O$. The reaction mixture was stirred at rt for 1 h and then was concentrated in vacuo. The residue was dissolved in CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4, filtered,

and concentrated in vacuo to provide 2-[(*N*,*N*′-benzyl-benzyloxycarbonyl)amino]ethyl 4-amino-3-*O*-benzyl-4,6-dideoxy-2-*O*-methyl-β-glucopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside which was used in the next step without purification. To a solution of crude amine in dry DMF (1 mL) was added dropwise 3-hydroxy-3-methylbutanoic acid (3 μL, 21.8 μmol), followed by HATU (8.8 mg, 21.8 μmol), and then DIPEA (4 μL, 21.8 μmol). The reaction mixture was stirred under argon at rt for 18 h and was then diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, and water. The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel using cyclohexane/EtOAc (6:4) as eluent to provide **43** (12 mg, 40% over 2 steps) as a colorless oil (mixture of conformers). R_f 0.56 (cyclohexane/EtOAc 5:5); $[\alpha]_D$ −32 ($CHCl_3$, *c* 1.2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42–7.12 (m, 45H, $NCOOCH_2C_6H_5$, 7 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 5.32 (br s, 1H, N*H*), 5.18 (br s, 2H, $NCOOCH_2C_6H_5$), 5.10 (br s, 1H, H-1B), 5.05 (d, 1H, $J_{1C,2C}$ = 1.8 Hz, H-1C), 5.00 (d, 1H, $J_{A,B}$ = 10.6 Hz, A part of an AB system, $OCHC_6H_5$), 4.86 (d, 1H, $J_{A,B}$ = 11.4 Hz, A part of an AB system, $OCHC_6H_5$), 4.68 (d, 1H, $J_{A,B}$ = 11.4 Hz, A part of an AB system, $OCHC_6H_5$), 4.65–4.46 (m, 14H, H-1A, H-1D, 4 × B part of an 4 × AB system, 4 × $OCHCH_6H_5$, 3 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 4.13–4.11 (m, 2H, H-3B, H-3C), 3.92–3.91 (m, 2H, H-2B, H-2D), 3.83–3.79 (m, 2H, H-5B, H-2C), 3.79–3.71 (m, 3H, H-5C, H-3D, A part of an AB system, $OCHCH_2NH$), 3.67–3.62 (m, 3H, H-4A, H-5A, H-4B), 3.64 (s, 3H, OCH_3), 3.58–3.47 (m, 3H, H-4C, H-5D, B part of an AB system, $OCHCH_2N$), 3.47–3.34 (m, 3H, H-4D, OCH_2CH_2NH), 3.33 (br t, *J* = 9.2 Hz, H-3A), 3.18 (dd, 1H, $J_{1A,2A}$ = 7.8 Hz, $J_{2A,3A}$ = 8.7 Hz, H-2A), 2.22–2.18 (m, 1H, A part of an AB system, $NHCOCHC(CH_3)_2OH$), 2.11–2.04 (m, 1H, B part of an AB system, $NHCOCHCH(CH_3)_2OH$), 1.26 (br s, 6H, $NHCOCH_2C(CH_3)_2OH$), 1.35–1.19 (m, 9H, H-6B, H-6C, H-6D), 1.04 (d, 3H, $J_{5A,6A}$ = 6.0 Hz, H-6A); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5 ($NHCOCH_2C(CH_3)_2OH$), 156.9 and 156.4 ($NCOOCH_2C_6H_5$), 139.1, 138.9, 138.6, 138.4, 137.9, 137.8, 128.7, 128.6, 128.4, 128.3, 128.2, 127.8, 127.5 ($NCOOCH_2C_6H_5$, 7 × $OCH_2C_6H_5$, $NCH_2C_6H_5$), 103.9 (C-1A), 100.5 (C-1B), 99.3 (C-1C and C-1D), 85.1 (C-2A), 81.1 (C-4B), 80.7 (C-4C), 80.7 (C-4D), 80.3 (C-3A), 79.9 (C-3D), 79.4 (C-2B), 79.0 (C-3B), 78.1 (C-2C), 77.3 (C-3C), 75.6 ($OCH_2C_6H_5$), 75.0 (C-2D), 74.8 (2 × $OCH_2C_6H_5$), 74.7 ($OCH_2C_6H_5$), 73.9 ($OCH_2C_6H_5$), 72.4 ($OCH_2C_6H_5$), 72.3 ($OCH_2C_6H_5$), 71.1 (C-5A), 69.6 ($NHCOCH_2C(CH_3)_2OH$), 68.9 (C-5C), 68.6 (C-5B), 68.3 (C-5D), 67.5 ($NCOOCH_2C_6H_5$), 65.7 (OCH_2CH_2N), 60.7 (OCH_3), 55.9 (C-4A), 51.9 and 51.8 ($NCH_2C_6H_5$), 47.9 ($NHCOCH_2C(CH_3)_2OH$), 47.0 and 46.0 (OCH_2CH_2N), 18.3, 18.2, 18.1 (C-6A, C-6B, C-6C and C-6D); HR-ESI-MS *m/z* calcd for $C_{96}H_{112}N_2O_{20}$ 1635.7706 $[M+Na]^+$, found 1635.7695.

4.2.33. 2-Aminoethyl 4-(3-hydroxy-3-methyl-butanamido)-4,6-dideoxy-2-*O*-methyl-β-D-glucopyranosyl]-(1→3)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-rhamnopyranoside (2)

Compound **43** (12 mg, 7.8 μmol) in MeOH/AcOH (12 mL/120 μL) was treated with a catalytic amount of a Pd/C under 10 bars of hydrogen at 50 °C for 30 min. The reaction mixture was then concentrated in vacuo. The residue was dissolved in H_2O and was washed with CH_2Cl_2. The organic layer was extracted by water. The aqueous phases were combined and concentrated under vacuum. The crude was then purified by RP-HPLC (0% B during 5 min, 0–100% solvent B over 25 min, 100% B, 5 min [eluent A: 0.05% TFA in H_2O; eluent B: 0.05% TFA in CH_3CN:H_2O 60:40], Grace Prevail C18 column, 3 mL/min, 215 nm) to give tetrasaccharide **2** (6 mg, 88%, with counterion TFA) as a white solid after lyophilization. $[\alpha]_D$ −13 ($CHCl_3$, *c* 1.2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.07 (br s, 1H, H-1B), 4.98 (br s, 1H, H-1C), 4.96 (br s, 1H, H-1D), 4.75 (m, 1H, H-1A (+D_2O)), 4.30 (br s, 1H, H-2B), 4.17 (br s, 1H, H-2C), 4.02–3.98 (m, 3H, H-2D, H-3B, A part of an AB system, $OCHHCH_2NH_3OOCCF_3$), 3.93–3.92 (m, 1H, H-3D), 3.89–3.81 (m, 3H, H-5B, H-3C, H-5C), 3.75–3.67 (m, 2H, H-5D, B part of an AB system, $OCHHCH_2NH_3OOCCF_3$), 3.67–3.62 (m, 2H, H-4A, H-4D), 3.65 (s, 3H, OCH_3), 3.59–3.51 (m, 4H, H-3A, H-4B, H-4C, H-5A), 3.28 (br s, 2H, $OCH_2CH_2NH_3OOCCF_3$), 3.16 (br t, *J* = 8.4 Hz, H-2A), 2.48 (br s, 2H, $NHCOCH_2C(CH_3)_2OH$), 1.36–1.30 (m, 15H, $NHCOCH_2C(CH_3)_2OH$, H-6B, H-6C, H-6D), 1.25 (d, 3H, $J_{5A,6A}$ = 5.7 Hz, H-6A); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1 ($NHCOCH_2C(CH_3)_2OH$), 163.0 (q, $^2J_{C,F}$ = 36 Hz, CF_3COO), 116.3 (q, $^1J_{C,F}$ = 292 Hz, CF_3COO), 103.6 (C-1A), 102.1, 102.0 (C-1B and C-1C), 98.5 (C-1D), 83.3 (C-2A), 79.6 (C-2D), 78.4 (C-3B), 77.9 (C-3C), 72.8 (C-3A), 72.0 (C-4D), 71.3 and 71.1 (C-4B and C-4C), 70.8 (C-5A), 70.2 ($NHCOCH_2C(CH_3)_2OH$), 69.8 (C-2C, C-2B, C-3D), 69.4, 69.3 (C-5B and C-5C), 69.1 (C-5D), 63.5 ($OCH_2CH_2NH_3OOCCF_3$), 60.0 (OCH_3), 56.6 (C-4A), 48.9 ($NHCOCH_2C(CH_3)_2OH$), 39.0 ($OCH_2CH_2NH_3OOCCF_3$), 28.3, 28.1 ($NHCOCH_2C(CH_3)_2OH$), 17.0 (C-6A), 16.7, 16.6 (C-6B, C-6C and C-6D); HR-ESI-MS *m/z* calcd for $C_{32}H_{58}N_2O_{18}$ 759.3763 $[M+H]^+$, found 759.3745.

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