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Immunogens related to the synthetic tetrasaccharide side chain of the *Bacillus anthracis* exosporium

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Abstract—The known methyl 2-*O*-acetyl-3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**3**) was converted to the corresponding 5-methoxycarbonylpentyl glycoside **4** which was deacetylated. The product **5** was used as the initial glycosyl acceptor to construct two trirhamnoside glycosyl acceptors having HO-3^{III} flanked by either benzoyl or benzyl groups, compounds **10** and **29**, respectively [fully protected, except HO-3^{III}, α-L-Rha-(1 → 3)-α-L-Rha-(1 → 2)-α-L-Rha-1-*O*-$(CH_2)_5COOCH_3$]. When these were glycosylated with ethyl 4-azido-3-*O*-benzyl-4,6-dideoxy-2-*O*-bromoacetyl-1-thio-β-D-glucopyranoside (**18**), only the benzylated glycosyl acceptor **29** gave good yield of the desired tetrasaccharide **30**. The α- and β-linked products, together with the corresponding orthoester **23**, were formed in almost equal amount when glycosylation of **10** was performed with the glycosyl donor carrying the 2-*O*-bromoacetyl protecting group. Deprotection at *O*-2 of **30**, followed by further functionalization of the molecule and global deprotection, gave the 5-methoxycarbonylpentyl glycoside of the title tetrasaccharide, β-Ant-(1 → 3)-α-L-Rha-(1 → 3)-α-L-Rha-(1 → 2)-α-L-Rha (**35**). Except for differences due to presence of the anomeric 5-methoxycarbonylpentyl group, the fully assigned NMR spectra of glycoside **35** were found to be virtually identical to those reported for the parent tetrasaccharide isolated from *Bacillus anthracis* exosporium, thus proving the correct structure assigned to the naturally occurring substance. All theoretically possible structural fragments of **35**, as well as analog of **35** lacking the 2-*O*-methyl group at the terminal 4,6-dideoxyglucosyl residue, compound **40**, were also synthesized. Tetrasaccharide **35**, its β-linked and non-methylated analogs **2** and **40**, respectively, as well as the trirhamnoside fragment of **35**, glycoside **12**, were further functionalized and conjugated to BSA using squaric acid chemistry, to give neoglycoconjugates with a predetermined carbohydrate–protein ratio of ∼3 and ∼6.
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1. Introduction

Anthrax is predominantly a disease of animals but humans can become infected by contact through a cut in skin (cutaneous anthrax), by contaminated food or soil, or by inhaling the spores (inhalational anthrax). Until recently, the disease had not caused serious health problems in the civilized world, but new concerns regarding anthrax have recently emerged in context with bioterrorism. Therefore, development of a potent vaccine for anthrax has become a pressing issue worldwide. Approaches to developing a synthetic vaccine for anthrax[1–3] have been focused mainly on the use of immunogenic conjugates from capsular polypeptide (polyglutamic acid) of *Bacillus anthracis*, which is the etiologic agent of anthrax. The bacterium is housed in a spore, which may come to life in the right conditions. Spores of *B. anthracis* are enclosed in a layer of exosporium whose components are the first to interact with the host. An approach to control anthrax by targeting spores with neutralizing antibodies has thus far not been fully developed. This is partially due to our poor understanding of the structure of components of anthrax spores. Daubenspeck and coworkers[4] have recently determined the structure of the tetrasaccharide side chain of the collagen-like region of the major glycoprotein of the *B. anthracis* exosporium (BclA). The tetrasaccharide (**1**, Fig. 1) is unique in that it contains the newly discovered sugar anthrose[4] [4,6-dideoxy-4-(3-hydroxy-3-methylbutyramido)-2-*O*-methyl-D-glucopyranose] as the upstream[5] terminal moiety.

Studies aimed at better understanding of the role of BclA in the *B. anthracis* exosporium, preparation of diagnostic probes, and, perhaps, vaccine for anthrax call for further investigations involving the tetrasaccharide whose isolation from the exosporium in larger quantities is difficult. More importantly, if prepared in this way,

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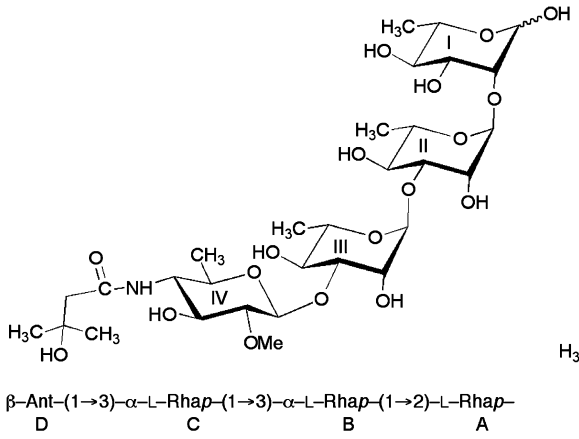

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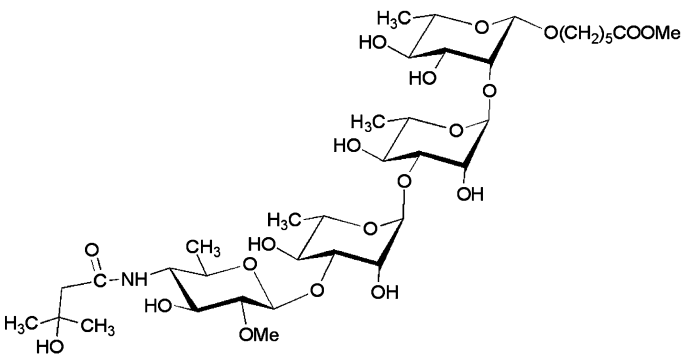

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Figure 1. Structure of the tetrasaccharide side chain of the major glycoprotein of the *Bacillus anihracis* exosporium (**1**) and its methyl 6-hydroxyhexanoyl β-glycoside (**2**).

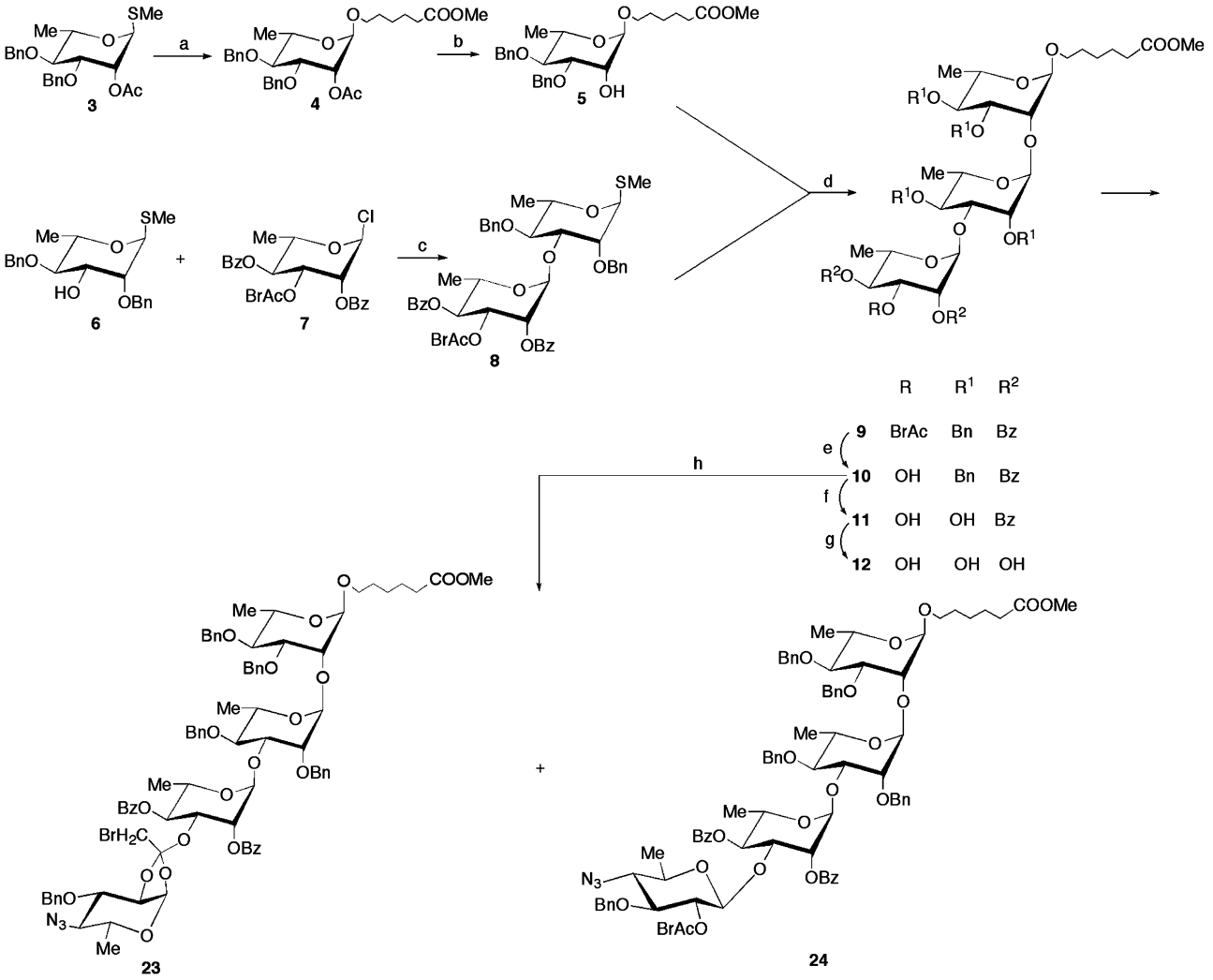
the tetrasaccharide would be obtained as a mixture of anomers. Results of binding or inhibition studies with material that does not completely imitate the structure of the tetrasaccharide, including the anomeric configuration at the site of attachment to the exosporium, would likely be inconclusive. Studies of such nature require the tetrasaccharide in a form where the anomeric configuration is locked, as, for example, in a glycoside. Syntheses of α-benzyl and α-pentenyl glycosides of **1** have been reported.[6,7] The α-pentenyl glycoside of **1** was used in work toward generating monoclonal IgG antibodies specific to *B. anthracis* endospores.[8] More recently, Mehta et al.[9] described an independent approach to the tetrasaccharide–BSA and tetrasaccharide–KLH conjugates.

In order to obtain optimal immune response from neoglycoconjugates prepared from **1**, the anomeric configuration of the terminal, downstream[5] L-rhamnosyl residue in the conjugates must be the same as in BclA. With that information unknown,[4] our initial work toward immunogens for anti-*B. anthracis* exosporium antibodies involves synthesis of neoglycoconjugates from each of the α- and β-forms of **1** and evaluation of immunogenicity thereof. We have recently reported[10] the synthesis of spacer-equipped β glycoside of **1** (compound **2**), and its structural fragments. Here we report full details of the synthesis[11] of the α glycoside of **1** (compound **35**), and its conversion to BSA-conjugates. Similar conjugates were prepared from β glycoside **2**, the non-methylated analog of **35** (glycoside **40**), and trirhamnoside fragment of **35** (compound **12**). Syntheses of other spacer-equipped structural fragments of **35** are also described. Compounds **2**, **35**, and some fragments thereof, were instrumental in developing photogenerated glycan arrays that are useful to identify immunogenic sugar moieties of *B. anthracis* exosporium.[12]

2. Results and discussion

The purpose of this work was to prepare spacer-equipped α-glycoside of the title tetrasaccharide and its structural fragments (Fig. 1, A, AB, ABC, BC, BCD, CD, and D) suitable for conjugation to carrier proteins. To facilitate preparation of the large number of substances, we employed intermediates that were previously found useful in preparation of rhamnooligosaccharides, for example, Refs. 13–21. The initial glycosyl acceptor for the synthesis of **35**, monosaccharide **5**, was readily obtained (Scheme 1) by NIS/AgOTf-mediated reaction of the known thioglycoside **3**[16] with methyl 6-hydroxyhexanoate,[22] to give **4** (along with a small amount of the β-anomer **87**) followed by deacetylation (Zemplén) of the linker equipped rhamnoside **4** (Scheme 1). To extend the oligosaccharide chain by two L-rhamnosyl residues, alcohol **5** was coupled with the disaccharide glycosyl donor **8**, obtained by condensation of methyl 2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside[23] (**6**) with 2,4-di-*O*-benzoyl-3-*O*-bromoacetyl-α-L-rhamnopyranosyl chloride (**7**), which was available in this laboratory from previous work.[18] Subsequent debromoacetylation of the trisaccharide **9** thus formed gave trisaccharide glycosyl acceptor **10**, and complete deprotection of **9** gave, through benzoate **11**, glycoside **12**, the trirhamnoside fragment of **35**.

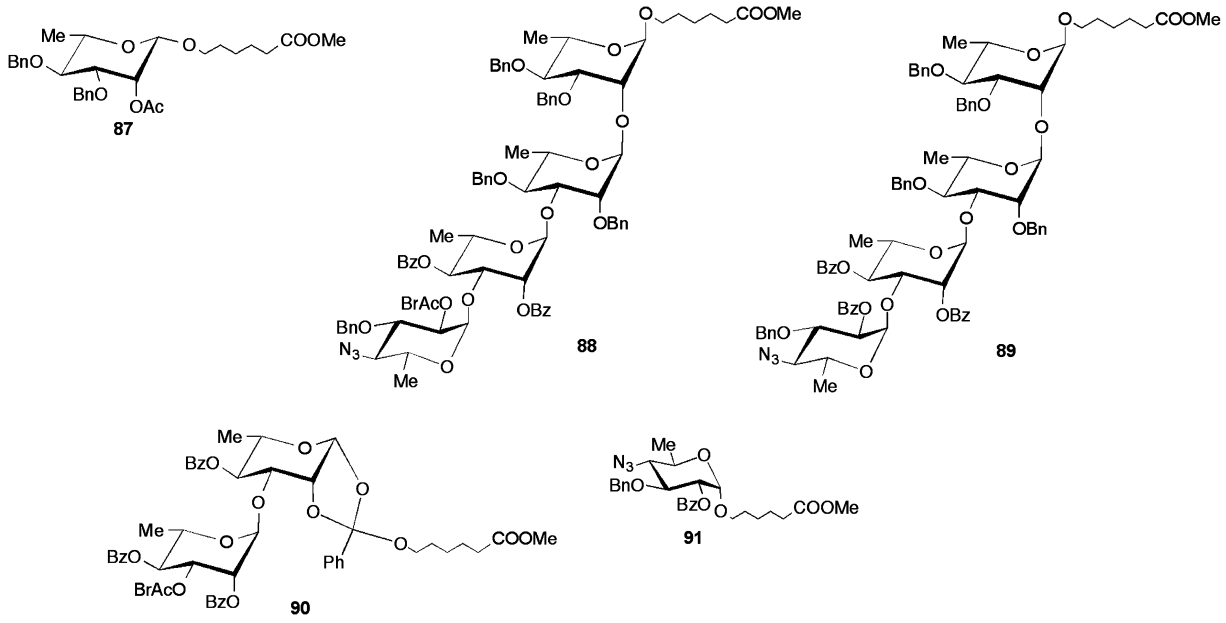
Synthesis of the target tetrasaccharide required stereoselective construction of the β-anthrosyl linkage. Synthesis of such linkage with high stereoselectivity could be problematic using a glycosyl donor derived from anthrose, due to the presence of the nonparticipating methyl group at *O*-2. Therefore, instead of using a glycosyl donor derived from anthrose, or the known ethyl 4-azido-3-*O*-benzyl-4,6-dideoxy-2-*O*-methyl-1-thio-β-D-glucopyranoside,[24] we have prepared the latent anthrosyl donor **18** (Scheme 2) from the known[24] glucosides **13** or **19**, or from thioglycoside **21**. We presumed that the bromoacetyl protecting group at *O*-2 in **18** would be particularly advantageous because it can be selectively removed in the presence of other acyl groups. Thus, compound **18** could be used as a versatile glycosyl donor in related syntheses involving presence or absence of acyl groups in intermediates. Once attached, the terminal β-D-glucopyranosyl moiety would be transformed into β-anthrosyl residue as described previously.[24]



Scheme 1. Synthesis of trirhamnoside **12** and tetrasaccharide **24**. Reagents: (a) methyl 6-hydroxyhexanoate, NIS, AgOTf; (b) NaOMe, MeOH; (c) AgOTf, DBMP; (d) NIS, AgOTf; (e) thiourea; (f) H_2Pd/C; (g) NaOMe, MeOH; (h) **18**, NIS, AgOTf.

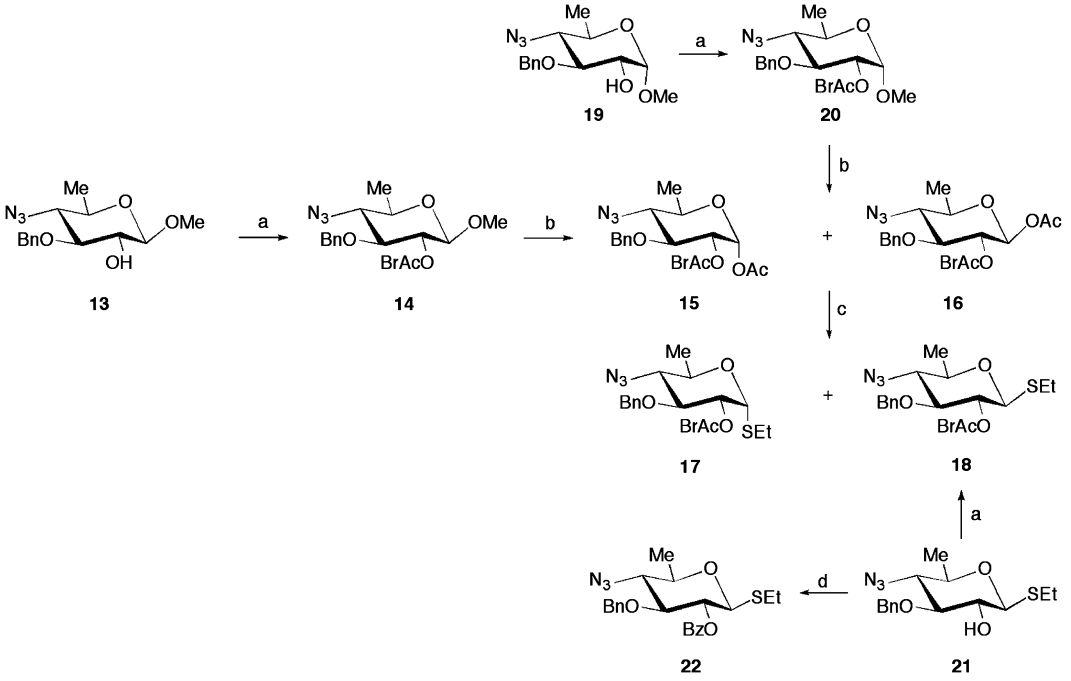
The silver triflate/NIS-mediated glycosylation of **10** with **18** (Scheme 1) was performed under base-deficient conditions.[25] Chromatography of the crude product afforded orthoester **23**, the desired β-linked tetrasaccharide **24** and the α-anomer **88**, together with unidentified byproducts. A considerable amount of unchanged glycosyl acceptor was recovered. The problem of orthoester formation was solved when the more reactive trisaccharide **29** was used as the glycosyl acceptor for **18** (Scheme 3). To obtain **29**, L-rhamnose was converted, through methyl 1-thiopyranoside,[16] to methyl 3-*O*-acetyl-2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside[17,23] (**25**). The latter was treated with chlorine,[26] and condensation of glycosyl chloride **26** thus formed with di-*O*-benzyl derivative[23] **6** gave disaccharide glycosyl donor **27**. Reaction of donor **27** with **5** gave the linker-equipped trisaccharide **28**. When the latter was deacetylated, and the formed glycosyl acceptor **29** was treated with **18**, the desired tetrasaccharide **30** was obtained in 84% yield. After subsequent debromoacetylation of **30**, further conversion to the title tetrasaccharide **35** comprised a series of conventional transformations established during the synthesis of anthrose and its methyl glycosides.[24] ^1H and ^{13}C NMR spectra of glycoside **35**, fully assigned by 2D experiments, were found to be virtually identical to those reported for the parent tetrasaccharide isolated from *B. anthracis* exosporium (Tables 1 and 2), thus proving the correct structure assigned to the naturally occurring substance. The differences in chemical shifts found for some nuclei (Tables 1 and 2) were due to presence of the anomeric 5-methoxycarbonylpentyl group.

Orthoester formation from alcohol **10** was less pronounced when the same acceptor was glycosylated with the benzoylated donor **22** (Scheme 4), prepared from **21** as shown in Scheme 2. The latter reaction afforded the fully protected product **36** in 67% yield with some α product **89** (see Section 3). The latter was then converted to the non-methylated analog of **35**, tetrasaccharide **40**, by the same sequence of reactions as described for the conversion **32** → **35** (Scheme 4). The following conclusions could be made from observations during glycosylations leading to tetrasaccharides described above: The prerequisite to obtaining a good yield of the desired β product was the correct combination of coupling synthons. Desired tetrasaccharides, that is, **30** or **36**, could

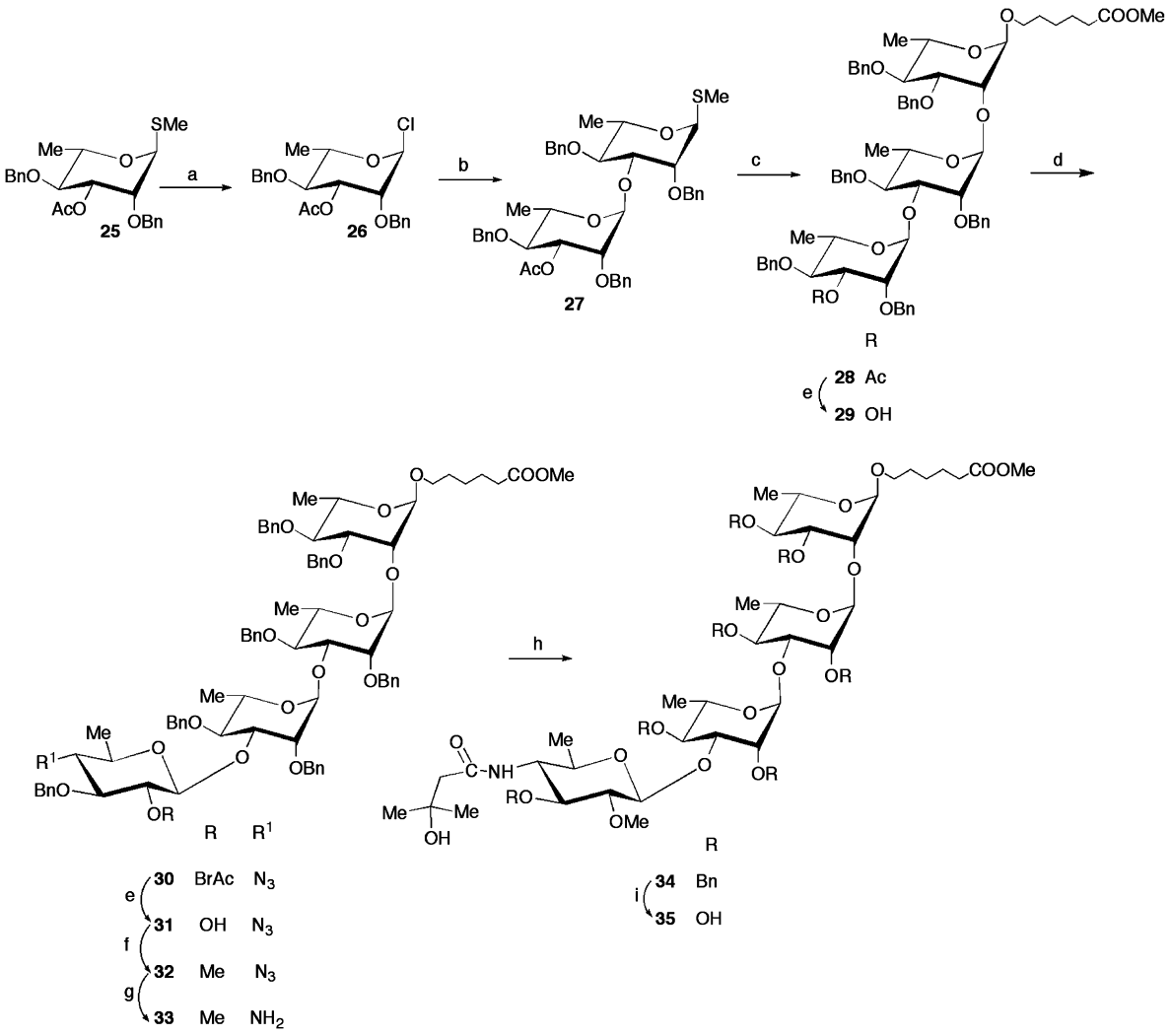


be obtained in good to excellent yields from reactions involving either 2-*O*-bromoacetylated or 2-*O*-benzoylated glycosyl donor when the hydroxyl group to be glycosylated was flanked by benzyloxy groups. An acceptable yield of glycosylation could also be obtained from 2-*O*-benzoylated glycosyl donor when the hydroxyl group to be glycosylated was flanked with benzoyl groups. On the other hand, α- and β-linked products, together with the corresponding orthoester **23**, were formed in almost equal amount when glycosylation of **10**, whose hydroxyl group was flanked with benzoyl groups, was performed with the glycosyl donor **18** carrying the 2-*O*-bromoacetyl protecting group. We have previously reported the tendency of 2-*O*-chloroacetylated glycosyl donors to form stable orthoesters.[27]

Binding and inhibition studies with antibodies specific for anthrax exosporium require a large repertoire of substances related to tetrasaccharide **1**. Synthesis of the trirhamnoside fragment (ABC) of **35** (compound **12**) has already been mentioned (Scheme 1), and syntheses of structural fragments of the β-glycoside **2** have been reported.[10] Syntheses of the remaining, theoretically possible partial structures of **35** (for alphabetical



Scheme 2. Synthesis of glycosyl donors **18** and **22**. Reagents: (a) $BrCH_2COBr$, TMU; (b) Ac_2O, H_2SO_4; (c) EtSH, $BF_3{\cdot}Et_2O$; (d) PhCOCl.



Scheme 3. Synthesis of the tetrasaccharide side chain of the major glycoprotein of *Bacillus anthracis* exosporium (**35**). Reagents: (a) Cl_2; (b) 6, AgOTf, DBMP; (c) 5, NIS, AgOTf; (d) **18**, NIS, AgOTf; (e) NaOMe, MeOH; (1) MeI, Ag_2O; (g) H_2S; (h) 3-hydroxy-3-methylbutyric acid, HATU; (i) H_2, Pd/C.

Table 1. Comparison of ^1H chemical shifts[a] for tetrasaccharide **35** with data reported for **1** in Ref. 4

Ring	H-1	H-2	H-3	H-4	H-5	H-6
I	4.566 [1.5]	3.634	3.530	3.155	3.373	1.134
	4.870	3.601	3.615	3.144	3.592	1.114
II	4.842 [1.4]	3.775	3.572	3.325	3.487	1.101
	4.848	3.783	3.592	3.339	3.504	1.103
III	4.857 [1.4]	3.872	3.745	3.402	3.636	1.132
	4.876	3.880	3.760	3.404	3.655	1.142
IV	4.577 [7.9]	2.845	3.281	3.402	3.275	1.074
	4.582	2.850	3.301	3.401	3.278	1.082
	NH	CH_2	CH_3	OCH_3		
Other[b,c]	7.706	2.204	1.155, 1.143	3.519		
	7.754	2.211	1.160, 1.148	3.526		

[a] Spectra taken at 600 MHz for a solution in DMSO-d_6 at 25 °C. Selected, structurally significant coupling constants [Hz] are in brackets. Data for **1** (the second row for each ring) were taken from Ref. 4.

[b] δ_{OH} (disappear on deuteration): 4.995 (d, J 6.0 Hz, OH-2^{IV}), 4.945 (d, J 6.8 Hz, OH-4^{II}), 4.885 (d, J 5.3 Hz, OH-4^{I}), 4.875 (d, J 5.8 Hz, OH-3^{I}), 4.831 (s, OH-3′), 4.779 (d, J 4.9 Hz, OH-2^{II}), 4.718 (d, J 5.3 Hz, OH-4^{III}), 4.534 (d, J 4.6 Hz, OH-2^{III}). Not reported in Ref. 4.

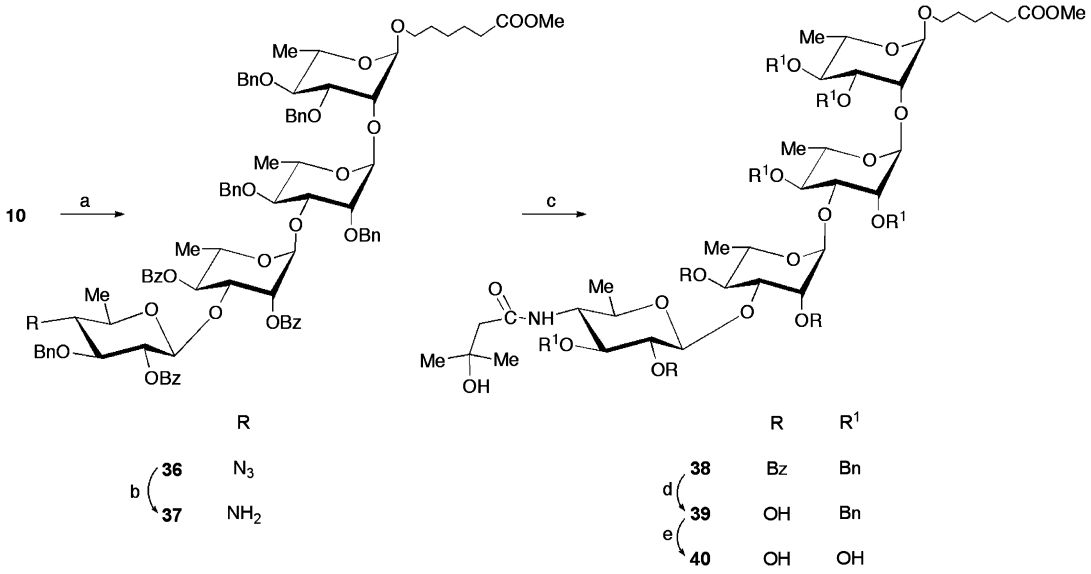
[c] δ_{Spacer}: 3.57 ($COOCH_3$), 3.52 (H-1″a), 3.33 (H-1″b), 2.29 (t, J 7.4 Hz, H-5″a,b), 1.56–1.45 (m, H-2″a,b,4″a,b), 1.36–1.26 (m, H-3″a,b).

notation of sequences, see Fig. 1), saccharides A (**42**), AB (**45**), BC (**48**), BCD (**70**), CD (**62**), and D (**54**), are shown in Schemes 5 and 6. Methyl 6-hydroxyhexanoyl-α-L-rhamnopyranoside (**42**), which imitates the reducing end in **1**, was obtained (Scheme 5) by reaction of 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide[28]

Table 2. Comparison of ^{13}C chemical shifts[a] for tetrasaccharide **35** with data for **1** reported in Ref. 4

Ring	C-1	C-2	C-3	C-4	C-5	C-6
A	103.50; $J_{C,H}$ 160.7	84.36	72.77	56.42	70.34	18.18
	103.4; $J_{C,H}$ 161	84.3	72.7	56.4	70.3	18.1
B	101.71; $J_{C,H}$ 171.3	69.67	79.48	71.65	68.31	17.73
	101.6; $J_{C,H}$ 171	69.6	79.4	71.6	68.2	17.6
C	101.76; $J_{C,H}$ 170.6	69.97	76.28	71.37	69.04	17.81
	101.6; $J_{C,H}$ 170	69.9	76.2	71.4	68.8	17.9
D	98.62; $J_{C,H}$ 167.6	76.66	70.56	72.22	68.58	18.02
	92.8; $J_{C,H}$ 166	77.7	70.1	72.6	67.7	17.9
Other[b]	CO	CH_2	CH_3	C'_{quat}	OCH_3	
	171.45	48.67	29.58, 29.48	68.71	60.16	
	171.4	48.6	29.5, 29.4	not reported	59.9	

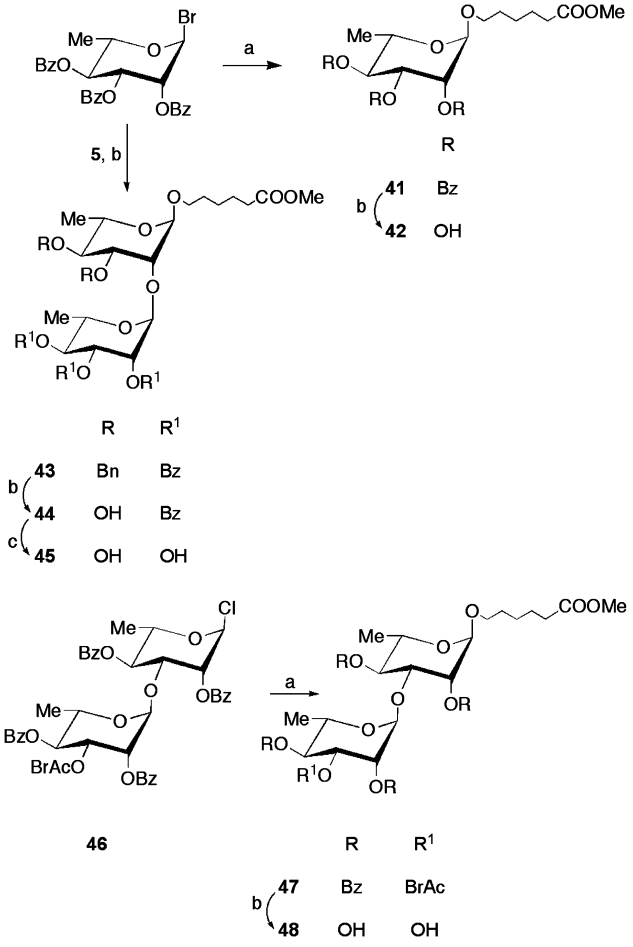
[a] Spectra taken at 150 MHz for a solution in DMSO-d_6 at 25 °C. Data for **1** (the second row for each ring) were taken from Ref. 4.
[b] δ_{Spacer}: 173.36 (CO), 66.32 (C-1″), 51.25 ($COOCH_3$), 33.26 (C-5″), 28.66 (C-2″), 25.21 (C-3″), 24.25 (C-4″).



Scheme 4. Synthesis of tetrasaccharide **40**, the non-methylated analog of the tetrasaccharide side chain of the major glycoprotein of *Bacillus anthracis* exosporium. Reagents: (a) **22**, AgOTf, NIS; (b) H_2S; (c) 3-hydroxy-3-methylbutyric acid, HATU; (d) NaOMe, MeOH; (e) H_2, Pd/C.

with methyl 6-hydroxyhexanoate (→**41**) followed by debenzoylation. To obtain the same-spacer-equipped, (1 → 2)-linked dirhamnoside **45**, alcohol **5** was treated with the same glycosyl donor, and the formed disaccharide **43** was subjected to a two-step deprotection (Scheme 5). The analogous (1 → 3)-linked disaccharide **48** was obtained by condensation of methyl 6-hydroxyhexanoate and the disaccharide glycosyl chloride **46**, which was available from previous work,[18] followed by deprotection (Scheme 5). The yield of glycosylation was high (78%), but a large amount of the corresponding orthoester (**90**, 34%) was isolated by chromatography along with the desired product **47** (44%). The three, anthrose-containing partial structures of the title tetrasaccharide **35** were synthesized as follows (Scheme 6). Reaction of methyl 6-hydroxyhexanoate with the 2-*O*-benzoylated glycosyl donor **22** gave the fully protected glycoside **49** in excellent yield of 87%, together with a small amount of the α-anomer **91**. After debenzoylation (→**50**) and methylation, the fully protected azido compound **51** was subjected to the series of transformations described for tetrasaccharide **32**, to give methyl 6-hydroxyhexanoyl β-anthroside (**54**). To obtain compound **62** that mimics the anthrose-containing terminal disaccharide of **1**, thioglycoside donor **25**[16,23] was treated with methyl 6-hydroxyhexanoate (Scheme 6) and the product **55** was deacetylated. Alcohol **56** thus formed was condensed with latent anthrose precursor **18** to give fully protected disaccharide **57**, which was transformed to the desired structural fragment of **1** (compound **62**) as described above for conversions **30** → **35**.

Our original plan to prepare the terminal spacer-equipped fragment of **1**, trisaccharide **70**, was based on the use of disaccharide **47** which, after debromoacetylation, was expected to give a suitable glycosyl acceptor for donor **22** (cf. glycosylation of that donor with acceptor **10**, which gave a good yield of the expected β-linked product). However, since glycosylation leading to **47** (Scheme 5) was low-yielding, a more efficient route was sought. This was found in a stepwise approach, starting with condensation of glycosyl donor **25** with alcohol **56**. After deacetylation of the formed disaccharide **63**, the resulting alcohol **64** was treated with anth-



Scheme 5. Synthesis of partial structures of tetrasaccharide **35**; saccharides A (**42**), AB (**45**), and BC (**48**). Reagents: (a) methyl 6-hydroxy-hexanoate, AgOTf, DBMP; (b) AgOTf, DBMP.

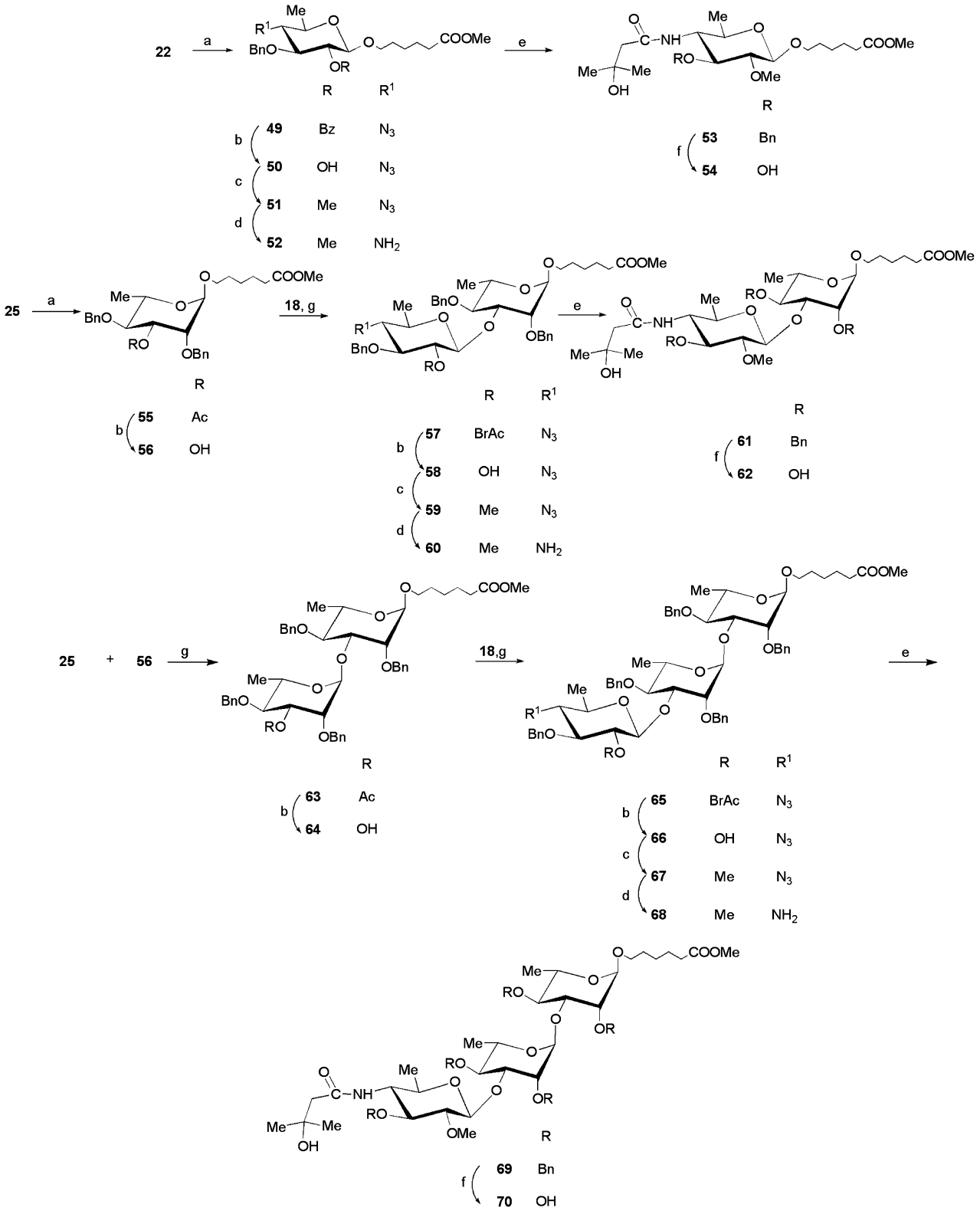
rose precursor **18**. The β product **65** (82%) was then converted to the desired trisaccharide **70** through the same series of transformations (Scheme 6) as for **57** → **62**. NMR and MS data fully confirmed structures of substances described above.

For future immunological studies, glycoconjugates were prepared from the title tetrasaccharide **35** (**35** → **73**, **35** → **74**) and the corresponding trisaccharide lacking the anthrose residue **12** (**12** → **77**, **12** → **78**), by chemical linking to BSA through squaric acid chemistry. To be able to evaluate the importance of anomeric configuration of the tetrasaccharide and the methyl group in the anthrose residue, we also made similar neoglycoconjugates from the corresponding β-glycoside **2**[10] (**2** → **81**, **2** → **82**) and the analog of **35** lacking the 2-*O*-methyl group in the anthrose residue, tetrasaccharide **40** (**40** → **85**, **40** → **86**). Two conjugates from each oligosaccharide were prepared. They were targeted to show carbohydrate–protein ratio of 3 and 6. To minimize waste of the precious oligosaccharides, conjugations described here were performed at a considerably lower initial hapten/carrier ratio (20:1) than in our earlier work.[29–31] The expected slower reaction rate due to conducting the conjugation under these conditions[32] was fully compensated for by running conjugations at a higher concentration only in the case of hapten **84** (Table 3). We have no other explanation for the much slower rate of conjugation with haptens **2**, **12**, and **35**, other than, as we pointed out previously,[29] that we may not be aware of some parameters that affect conjugation. Because the reaction rate is not quite predictable, having a method that allows monitoring of conjugation of synthetic carbohydrates to proteins in virtually real time is invaluable. The utility of the SELDI-TOF method for this purpose by this technique[29,33] is evident from the but small differences between the targeted carbohydrate–protein ratios and those observed in the products (Table 3). The conjugates were made according to a new protocol. Compared to our previously developed procedure, it involved more efficient purification of products of transformation of the ester function in the 5-methoxycarbonylpentyl spacer molecule to the corresponding amines and squaric acid derivatives. Also, purification of the final glycoconjugates was done with the aid of ultrafiltration devices (see Section 3) having vertical, rather than horizontal, orientation of the membrane. As a result of this configuration, the centrifugal force pulls material away from the membrane to the bottom of the device. This, in turn, reduces axial pressure on the filtration membrane and minimizes losses due to adherence of the glycoprotein to it, resulting consistently in high yields of the final product. Table 3 shows the content of carbohydrates in the glycoconjugates prepared from haptens **72**, **76**, **80**, and **84**, as well as reaction times required to reach these carbohydrate–protein ratios.

3. Experimental

3.1. General methods

Unless stated otherwise, optical rotations were measured at ambient temperature for solutions in $CHCl_3$, with a Perkin-Elmer automatic polarimeter, Model 341. All reactions were monitored by thin-layer chromatography (TLC) on Silica gel 60 coated glass slides. Column chromatography was performed by gradient elution from columns of silica gel with the High Performance Rapid Flash Chromatography System (RT Scientific) or with the CombiFlash Companion Chromatograph (Isco, Inc.). Solvent mixtures less polar than those used for TLC were used at the onset of separation. FAB Mass spectra were obtained with Jeol SX 102 spectrometer. Liquid Chromatography–Electron Spray-Ionization Mass Spectrometry (ESI-MS) was performed with a Hewlett-Packard 1100 MSD spectrometer. Nuclear Magnetic Resonance (NMR) spectra were measured with a Varian Gemini or Varian Mercury at 300 MHz (^{1}H) and 75 MHz (^{13}C), or with Bruker Avance 600 spectrometers. *J* values are given in Hertz. For measurements in D_2O, chemical shifts for ^{1}H and ^{13}C are reported relative to Me_2CO ($\delta_{^1H}$ 2.218; $\delta_{^{13}C}$ 33.0); for measurements in $CDCl_3$, chemical shifts for ^{1}H and ^{13}C are reported relative to Me_4Si ($\delta_{^1H}$ 0; $\delta_{^{13}C}$ 0) and $CDCl_3$, $\delta_{^{13}C}$ 77.0, respectively. Assignments of NMR signals were made by homonuclear and heteronuclear two-dimensional correlation spectroscopy, run



Scheme 6. Synthesis of partial structures of tetrasaccharide **35**; saccharides D (**54**), CD (**62**), and BCD (**70**). Reagents and conditions: (a) methyl 6-hydroxyhexanoate, AgOTf, NIS; (b) NaOMe, MeOH; (c) MeI, Ag_2O, Me_2S; (d) H_2S; (e) 3-hydroxy-3-methylbutyric acid, HATU; (f) H_2, Pd/C; (g) AgOTf, NIS.

with the software supplied with the spectrometers. When reporting assignment of NMR signals, nuclei associated with the *N*-amido side chain are denoted with a prime, and those with the other aglycone (the linker) are denoted with a double prime even in cases when the prime nuclei are absent. Sugar residues in oligosaccharides are serially numbered, beginning with the one bearing the aglycone, and are identified by a Roman numeral super-

Table 3. Reaction times, yields, and carbohydrate–protein ratios in prepared neoglycoconjugates

Hapten	Reaction time [h]	Conjugate	(Targeted) and final hapten/BSA ratio [M:M]	Yield mg (%)
72	48	**73**	(3) 3.1	14.7 (94)
72	240	**74**	(6) 6.0	14.0 (86)
76	24	**77**	(3) 2.9	14.0 (92)
76	216	**78**	(6) 5.5	14.0 (88)
80	24	**81**	(3) 2.6	15.0 (96)
80	192	**82**	(6) 5.9	14.0 (86)
84	4	**85**	(3) 3.5	13.0 (83)
84	12	**86**	(6) 5.7	15.0 (93)

script in listings of signal assignments. NMR spectra of amines **71**, **75**, **79**, and **83** as well as those of squaric acid derivatives **72**, **76**, **80**, and **84** were very similar to those of the corresponding esters. Spectra of amines showed that, due to hindered rotation around the CN bond in amides,[34] each of these substances was a mixture of two isomers, whose ratio varied with the structure. The presence of isomers manifested itself by splitting of signals not only of some nuclei in the linker but also some ring protons and, mainly, carbons of some sugar moieties. Due to the double bond nature of the vinylogous amide group, the NMR spectra of squaric acid esters **72**, **76**, **80**, and **84** showed further splitting of some signals.[35] When reporting NMR data of these substances only resonances originating from the major isomer are listed. Assignments denoted with an asterisk may be reversed. Attempts have been made to obtain correct analytical data for all new compounds. However, some compounds tenaciously retained traces of solvents, despite exhaustive drying, and analytical figures for carbon could not be obtained within ±0.4%. Structures of these compounds follow unequivocally from the mode of synthesis, NMR data, and *m*/*z* values found in their mass spectra, and their purity was verified by TLC and NMR spectroscopy. Carbohydrate–protein conjugates were rid of low-molecular mass materials by filtration through either Amicon Ultra-15 Centrifugal Filter (Millipore Corporation) or similar Vivaspin 15 R (Sartorius Group) devices. Palladium-on-charcoal catalyst (5%, ESCAT 103) was a product of Engelhard Industries. HATU {*N*-[(dimethylamino)-1*H*-1,2,3-triazolo-[4,5-*b*]-pyridin-1-ylmethylene]-*N*-methylmethanaminium hexafluorophosphate *N*-oxide} was purchased from Applied Biosystems. 3-Hydroxy-3-methylbutyric acid was purchased from Alfa Aesar Chemical Company. A stock solution of chlorine[26] in CCl_4 contained 1.06 mmol Cl_2/mL (determined by weighing). Solutions in organic solvents were dried with anhydrous Na_2SO_4 and concentrated at 40 °C/2 kPa.

3.2. General method for glycosylation with glycosyl halides

2,6-Di-*t*-butyl-4-methylpyridine (DBMP) followed by silver triflate (AgOTf, 1.2 mmol) was added to a mixture of glycosyl acceptor (1 mmol), glycosyl halide (1.3 mmol), and 4 Å molecular sieves (0.5 g/mmol) in CH_2Cl_2 (10 mL/mmol), which had been stirred for 15 min. The mixture was stirred until TLC showed that the reaction was complete (0.5–3 h) and filtered through a Celite pad, and the filtrate was partitioned between a mixture of aq $NaHCO_3$ and $Na_2S_2O_3$. After concentration of the organic phase, the material in the residue was chromatographed. The ratio between the glycosyl donor and the glycosyl acceptor was such that the less labor-intensive material was kept at ~1.3 equiv excess, to assure complete consumption of the more labor-intensive reactant. The amount of DBMP and AgOTf was 0.9 and 1.2 equiv, respectively, of that of the glycosyl halide, to assure complete consumption of the halide. In spite of these base deficient conditions, which favor isomerization of the intermediate orthoester, the latter was present among the final products of some reactions.

3.3. General method for glycosylation with thioglycosides

Except when stated otherwise, NIS (1.4 mmol/mmol of thioglycoside) followed by AgOTf (0.4 mmol/mmol of thioglycoside) was added to a mixture of thioglycoside, glycosyl acceptor, and 4 Å molecular sieves (0.5 g/mmol), which had been stirred at room temperature for 15 min. For ratio between the glycosyl donor and the glycosyl acceptor, see above. The mixture turned red and, after ~15 min, TLC showed that all glycosyl donor was consumed. The mixture was filtered through a Celite pad into mixed aq solutions of $NaHCO_3$ and $Na_2S_2O_3$. After partitioning of solutes, the colorless organic phase was concentrated, and the residue was chromatographed.

3.4. General procedure for the conversion of azides to amines

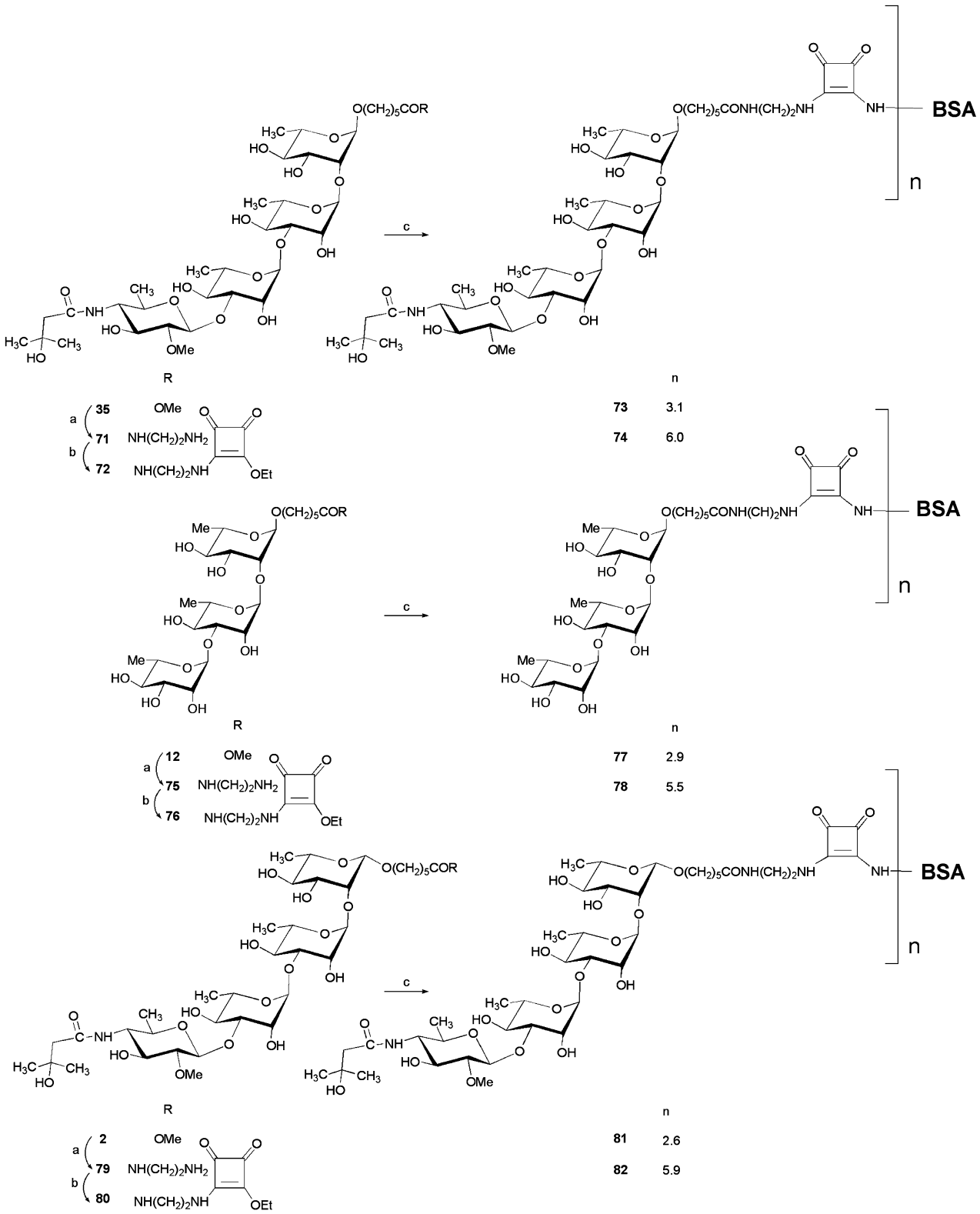
Water (~1 mL) was added dropwise and with stirring to a solution of an azide (1 mmol) in pyridine (4 mL). If slight turbidity developed a few drops of pyridine were added. A slow stream of H_2S gas was passed for 1 h through the resulting clear solution, which was then kept overnight at 40 °C in a loosely closed flask. After concentration with co-evaporation of water, chromatography gave the corresponding amine.

3.5. General procedure for amidation with HATU

HATU (1 mmol) followed by *N*,*N*-diisopropylethylamine (1 mmol) was added to a solution of amine (1 mmol) and carboxylic acid (1.2 mmol) in CH_2Cl_2, and the mixture was stirred at room temperature for 2 h. TLC then showed that virtually all amine was consumed and that one faster moving product was formed. The mixture was concentrated, and the residue was chromatographed to give pure amide.

3.6. General procedure for deacetylation and debenzoylation

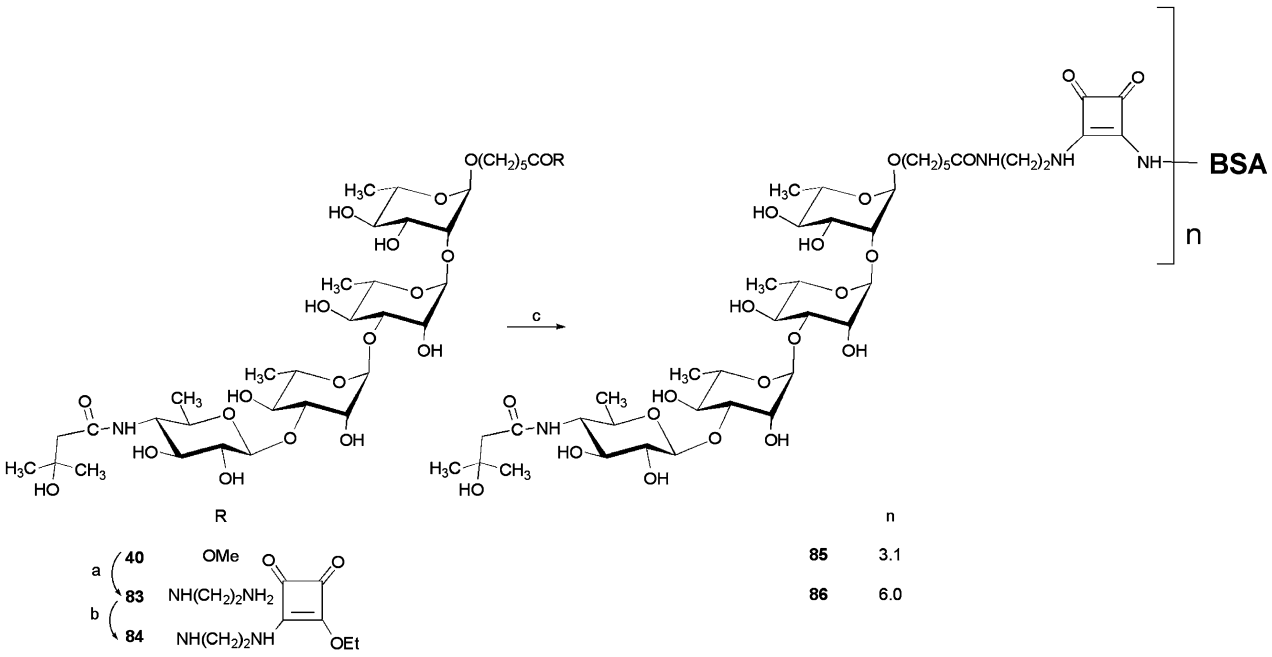
Methanolic (~1 M) NaOMe was added to a solution of the starting material (1 mmol) in MeOH (5 mL) until the solution was strongly alkaline to litmus, and the solution was kept at room temperature until the reaction was complete (1–24 h TLC). After neutralization with a cation-exchange resin (H^+-form), filtration, and concentration of the filtrate, the residue was eluted from a small column of silica gel.



Scheme 7. Synthesis of neoglycoconjugates **73**, **74**, **77**, **78**, **81**, **82**, **85**, and **86**. Reagents and conditions: (a) ethylenediamine; (b) diethyl squarate, pH 7; (c) BSA, pH 9.

3.7. General procedure for debenzylation

A mixture of benzylated compound (500 mg) and palladium-on-charcoal catalyst (150–200 mg) in methanol (~25 mL) was stirred at room temperature under hydrogen until the reaction was complete (~8–24 h). After filtration through a Celite pad and concentration of the filtrate, the material in the residue was passed through a small silica gel column, to remove residual carbon. A solution of the pure, deprotected compound in water



Scheme 7. (*continued*)

(HPLC grade) was filtered through sterile syringe filter (0.22 μm) and freeze-dried.

3.8. General procedure for methylation

Me_2S (2 drops) was added to a mixture of alcohol (0.1 g), MeI (0.5 mL) and Ag_2O (0.2 g) in 1,2-dimethoxyethane (2 mL), and the mixture was stirred in the dark at room temperature until the conversion was complete. After filtration through a Celite pad, the filtrate was concentrated, and chromatography gave the desired product.

3.9. General procedure for functionalization of the spacer

(A) Conversion of esters to amides using 1,2-diaminoethane: A solution of an ester (0.1 mmol) in freshly distilled 1,2-diaminoethane (3 mL) was kept at 50 °C until all starting material was consumed (24–48 h), while progress of the reaction was monitored by TLC. After concentration and purification by reverse-phase chromatography, the pure (TLC, NMR) product was freeze-dried, to give white, amorphous material.

(B) Conversion of amides to squaric acid monoethyl esters: A solution of amine (0.02 mmol) and diethyl squarate (2.5 equiv, 0.05 mmol) in borate buffer (1 mL, pH 7.00) was stirred until the reaction was complete (3–24 h, TLC). After concentration, the crude product was adsorbed on silica gel and chromatographed. A solution of the pure compound in water (HPLC grade) was filtered through 0.22 μm Millex sterile syringe filter and freeze-dried, to give white amorphous solid.

3.10. General procedure for conjugation of squaric acid derivatives to BSA

The conjugates, showing carbohydrate–protein ratio ~3 and ~6, were prepared from BSA and oligosaccharides **2**, **12**, **35**, and **40** (after conversion to squaric acid monoester derivatives **72**, **76**, **80**, and **84** see text below, Table 3, and Scheme 7), applying a slightly modified one-pot protocol.[30] The initial hapten/BSA ratio of 20:1 was chosen, to maintain reasonable reaction rate. To a solution of BSA (30 mg, 0.45 μmol, obtained by sonication) in borate buffer, pH 9 (180 μL) was added squaric acid monoester (9 μmol), to form a 50 mM solution with respect to the squaric acid derivative. The mixture was stirred at room temperature and the progress of conjugation was monitored[33] by SELDI-TOF-MS. When the desired carbohydrate ratio ~3 was reached, as determined by SELDI-TOF-MS, 90 μL of the reaction mixture was withdrawn and added with stirring into borate buffer, pH 7 (5 mL), to terminate the reaction. The rest of the mixture was allowed to react until the next desired carbohydrate protein ratio was reached and then processed as described below. The mixture that was diluted with pH 7 buffer was transferred into a centrifugal filter device and processed to remove salts. A minimum of eight washes with aq 10 mM $(NH_4)_2CO_3$ were applied, to ensure complete removal of the buffer. Freeze-drying afforded conjugates (**73**, **74**, **77**, **78**, **81**, **82**, **85**, and **86**) as white solids. Reaction times and results are summarized in Table 3.

3.11. 5-(Methoxycarbonyl)pentyl 2-*O*-acetyl-3,4-di-*O*-benzyl-α-(4) and β-L-rhamnopyranoside (87)

Starting with methyl 2-*O*-acetyl-3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**3**)[16] (470 mg, 1.12 mmol) and methyl 6-hydroxyhexanoate[22] (197 mg, 1.35 mmol), glycosylation according to the general protocol gave, after chromatography, first the α-anomer **4** (420 mg, 81%); $[\alpha]_D$ −6° (*c* 1.0). ^1H NMR (600 MHz, $CDCl_3$): δ 5.35 (dd, 1H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.4 Hz, H-2), 4.91–4.61 (2d, 2H, *J* 10.7 Hz, CH_2Ph), 4.70–4.53 (2d, 2H, *J* 11.2 Hz, CH_2Ph), 4.69 (br s, 1H, H-1), 3.92 (dd, 1H, $J_{3,4}$ 9.4

Hz, H-3), 3.75–3.71 (m, 1H, H-5), 3.66 (s, 3H, OCH_3); 3.65–3.61 (m, 1H, H-1a″), 3.43 (t, 1H, H-4), 3.39–3.35 (m, 1H, H-1b″), 2.32 (t, *J* 7.5 Hz, 2H, H-5″), 2.15 (s, 3H, CH_3CO), 1.66–1.61 (m, 4H, H-4″), 1.58–1.52 (m, 2H, H-2″), 1.38–1.34 (m, 2H, H-3″), 1.33 (d, 1H, $J_{5,6}$ 6.3 Hz, H-6); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.14, 170.46 (CO), 97.60 (C-1, $J_{C\text{-}1,H\text{-}1}$ 170.2 Hz), 80.04 (C-4), 78.05 (C-3), 75.45 (CH_2Ph), 71.71 (CH_2Ph), 69.03 (C-2), 67.60 (C-5), 67.49 (C-1″), 51.48 (OCH_3), 33.91 (C-5″), 29.05 (C-2″), 25.69 (C-3″), 24.67 (C-4″), 21.12 (CH_3CO), 17.94 (C-6). CIMS: *m*/*z* 537.2467 $[M+Na]^+$. Anal. Calcd for $C_{29}H_{38}O_8$: C, 67.68; H, 7.44. Found: C, 67.96; H, 7.43.

Second eluted was 5-(methoxycarbonyl)pentyl 2-*O*-acetyl-3,4-di-*O*-benzyl-β-L-rhamnopyranoside (**87**, 60 mg, 12%); $[\alpha]_D$ +47° (*c* 0.6). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.61 (dd, 1H, $J_{1,2}$, $J_{2,3}$ 3.4 Hz, H-2), 4.91–4.60 (d, 2H, *J* 10.7 Hz, CH_2Ph), 4.76–4.49 (2d, 2H, *J* 11.2 Hz, CH_2Ph), 4.46 (d, 1H, H-1), 3.87–3.84 (m, 1H, H-1a′), 3.66 (s, 3H, $COOCH_3$), 3.61 (dd, 1H, $J_{3,4}$ 9.0 Hz, H-3), 3.48–3.45 (m, 1H, H-1b′), 3.42 (t, 1H, H-4), 3.39–3.35 (m, 1H, H-5), 2.31 (t, 2H, *J* 7.4 Hz, H-5″), 2.20 (s, 3H, CH_3CO), 1.66–1.57 (m, 4H, H-4″,2″), 1.38–1.34 (m, partially overlapped, H-3″), 1.37 (d, 1H, $J_{5,6}$ 6.0 Hz, H-6); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.67, 170.62 (CO), 98.65 (C-1, $J_{C\text{-}1,H\text{-}1}$ 152.9 Hz), 80.08 (C-3), 79.64 (C-4), 75.38 (CH_2Ph), 71.63 (C-5), 71.33 (CH_2Ph), 69.50 (C-2), 68.16 (C-1′), 51.42 ($COOCH_3$), 33.88 (C-5″), 29.04 (C-2″), 25.44 (C-3″), 24.59 (C-4″), 21.08 (CH_3CO), 17.87 (C-6). CIMS: *m*/*z* 537.2480 $[M+Na]^+$. Anal. Calcd for $C_{29}H_{38}O_8$: C, 67.68; H, 7.44. Found: C, 67.51; H, 7.42.

3.12. 5-(Methoxycarbonyl)pentyl 3,4-di-*O*-benzyl-L-rhamnopyranoside (5)

This compound was obtained in virtually theoretical yield by deacetylation of methyl 2-*O*-acetyl-3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside,[16] $[\alpha]_D$ −38.6° (*c* 0.9). ^{1}H NMR ($CDCl_3$): δ 4.88, 4.70, 4.64 (2d, s, 4H, *J* 11.1 Hz, 2 CH_2Ph), 4.70 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1), 4.03–4.01 (m, 1H, H-2), 3.84 (dd, 1H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.0 Hz, H-3), 3.76–3.60 (m, 5H, H-5,1″, incl., s, 3.66, OCH_3), 3.45 (t, 1H, *J* 9.0 Hz, H-4), 3.40, 3.36 (2t, 1H, *J* 6.4 Hz, H-1″b), 2.52 (d, 1H, $J_{2,OH}$ 2.0 Hz, OH), 2.31 (t, 2H, *J* 7.4 Hz, H-5″), 1.69–1.52 (m, 4H, H-2″a,b,4″a,b), 1.41–1.30 (m, 5H, H-3″, incl., d, 1.31, $J_{5,6}$ 6.3 Hz, H-6); ^{13}C NMR ($CDCl_3$): δ 98.83 (C-1), 80.06 (C-3), 79.90 (C-4), 75.34, 71.90 (2 CH_2Ph), 68.51 (C-2), 67.21 (C-1″), 67.13 (C-5), 51.39 (OCH_3), 33.85 (C-5″), 29.01 (C-2″), 25.64 (C-3″), 24.61 (C-4″), 17.79 (C-6); ESI-MS: *m*/*z* 473.2539 $([M+H]^+)$. Anal. Calcd for $C_{27}H_{36}O_7$: C, 68.62; H, 7.68. Found: C, 68.86; H, 7.76.

3.13. Methyl 2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (6)

This compound was prepared as described for the amorphous substance,[23] and for which incomplete NMR data were reported. The compound solidified on standing, mp 51–52 °C (from *i*-Pr_2O–hexane), $[\alpha]_D$ −87° (*c* 0.5, $CHCl_3$); lit. $[\alpha]_D$ −82° (*c* 0.7). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.23 (br s, 1H, H-1), 4.91–4.51 (4d, 4H, *J* 11.3 Hz, 2 CH_2Ph), 4.05–3.96 (m, partially overlapped, 1H, H-5), 3.91 (ddd, partially overlapped, 1H, $J_{2,3}$ 3.7 Hz, $J_{3,OH} = J_{3,4}$ 9.3 Hz, H-3), 3.83 (dd, 1H, $J_{1,2}$ 0.9, $J_{2,3}$ 3.3 Hz, H-2), 3.35 (t, 1H, *J* 9.3 Hz, H-4), 2.35 (d, 1H, OH), 2.10 (s, 3H, SMe), 1.34 (d, 1H, $J_{5,6}$ 6.0 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): δ 82.42 (C-4), 82.28 (C-1), 79.84 (C-2), 74.96, 72.28 (2CH_2Ph), 72.02 (C-3), 67.54 (C-5), 17.96 (C-6), 13.56 (SCH_3). CIMS: *m*/*z* 397.1467 ($[M+Na]^+$). Anal. Calcd for $C_{21}H_{26}O_4S$: C, 67.35; H, 7.00. Found: C, 67.40; H, 7.05.

3.14. Methyl 2,4-di-*O*-benzoyl-3-*O*-bromoacetyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (8)

Reaction of alcohol **6** (93 mg, 0.24 mmol) and chloride **7**,[18] as described in the general procedure, gave **8** (170 mg, 80%) as a white solid, after freeze drying its solution in benzene, $[\alpha]_D$ −0.5 (*c* 0.5). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.71 (dd, 1H, $J_{2,3}$ 3.3, $J_{3,4}$ 10.0 Hz, H-3^{II}), 5.68 (dd, 1H, $J_{1,2}$ 1.7 Hz, H-2^{II}), 5.46 (t, *J* 9.9 Hz, H-4^{II}), 5.29 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1^{I}), 5.27 (d, 1H, H-1^{II}), 4.91, 4.88, 4.70, 4.60 (4d, 4H, 2 CH_2Ph), 4.10 (dd, partially overlapped, $J_{2,3}$ 3.3, $J_{3,4}$ 9.5 Hz, H-3^{I}), 4.09–4.01 (2 m, partially overlapped, H-5^{II}, 5^{I} in that order), 3.92 (dd, 1H, H-2^{I}), 3.73 (t, 1H, H-4^{I}), 3.67, 3.62 (2d, 2H, *J* 12.4 Hz, CH_2Br), 2.13 (s, 3H, SCH_3), 1.36 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.23 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{II}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 166.50, 165.52, 165.34 (3 CO), 99.44 ($J_{C\text{-}1,H\text{-}1}$ 173.5 Hz, H-1^{II}), 82.28 ($J_{C\text{-}1,H\text{-}1}$ 163.7 Hz, H-1^{I}), 80.61 (H-4^{I}), 79.37 (br, C-3^{I}), 79.27 (C-2^{I}), 75.52, 71.48 (2 CH_2Ph), 71.26 (C-4^{II}), 71.12 (C-3^{II}), 70.19 (C-2^{II}), 68.54 (C-5^{I}), 67.14 (C-5^{II}), 25.13 (CH_2Br), 17.96 (C-6^{I}), 17.59 (C-6^{II}), 13.77 (SCH_3); ESI-MS: *m*/*z* 871.1764 ($[M+Na]^+$). Anal. Calcd for $C_{43}H_{45}BrO_{11}S$: C, 60.78; H, 5.34. Found: C, 60.90; H, 5.35.

3.15. 5-Methoxycarbonylpentyl 2,4-di-*O*-benzoyl-3-*O*-bromoacetyl-α-L-rhamnopyranosyl-(1 → 3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (9)

Reaction of alcohol **5** (1.2 g, 2.6 mmol) and disaccharide thioglycoside **8**, as described above, gave the fully protected trisaccharide **9** (2.9 g, 90%), $[\alpha]_D$ +17° (*c* 0.5). ^{1}H NMR ($CDCl_3$): δ 5.69 (dd, 1H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.4 Hz, H-2^{III}), 5.66 (dd, 1H, $J_{3,4}$ 10.1 Hz, H-3^{III}), 5.45 (t, 1H, *J* 9.8 Hz, H-4^{III}), 5.29 (bd, 1H, H-1^{III}), 5.18 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.91–4.36 (m, 9H, 4 CH_2Ph, incl., br s, partially overlapped, H-1^{I}), 4.19 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.3 Hz, H-3^{II}), 4.06–4.01 (m, 2H, H-5^{III}, incl., 4.04, dd, H-2^{I}), 3.85 (dd, partially overlapped, H-2^{II}), 3.85 (dd, partially overlapped, H-3^{I}), 3.83–3.78 (m, partially overlapped, 5^{II}), 3.68 (t, 1H, *J* 9.4 Hz, H-4^{II}), 3.65 (s, 3H, OCH_3), 3.64–3.58 (m, 2H, H-5^{I},1″a), 3.52, 3.50 (2d, 2H, *J* 10.2 Hz, CH_2Br), 3.38–3.33 (m, 2H, H-1″b, incl., t, 3.37, *J* 9.5 Hz, H-4^{I}), 2.31 (t, 2H, *J* 7.6 Hz, H-5″), 1.66–1.61 (m, 2H, H-4″), 1.58–1.53 (m, 2H, H-2″), 1.38–1.32 (m, 5H, H-3″, incl., d, $J_{5,6}$ 6.2 Hz, H-6″), 1.22 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.15 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{III}); ^{13}C NMR ($CDCl_3$): δ 174.02, 168.11, 165.59, 165.35 (4 CO), 99.20 (br, $J_{C\text{-}1,H\text{-}1}$

173 Hz, C-1^{III}), 98.79 ($J_{C\text{-}1,H\text{-}1}$ 169 Hz, C-1^{I}), 98.46 (br, $J_{C\text{-}1,H\text{-}1}$ 169 Hz, C-1^{II}), 80.54 (C-4^{II}), 80.33 (C-4^{I}), 80.13 (C-3^{I}), 78.20 (br, C-3^{II}), 77.72 (C-2^{II}), 75.50, 75.32, 72.48, 71.61 (4 *C*H$_2$Ph), 74.80 (C-2^{I}), 71.31 (C-4^{III}), 70.87 (C-3^{III}) 70.33 (C-2^{III}), 68.66 (C-5^{II}), 67.79 (C-5^{I}), 67.16 (C-1″), 67.04 (C-5^{III}), 51.45 (COO*C*H$_3$), 33.93 (C-5″), 29.11 (C-2″), 25.73 (C-3″), 25. 17 (CH$_2$Br) 24.70 (C-4″), 18.11 (C-6^{II}), 17.89 (C-6^{I}), 17.47 (C-6^{III}); ESI-MS: *m*/*z* 1295.4218 ([M+Na]$^+$). Anal. Calcd for $C_{69}H_{77}BrO_{18}$: C, 65.04; H, 6.09. Found: C, 65.23; H, 6.16.

3.16. 5-Methoxycarbonylpentyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl-(1 → 3)-(2,4-di-*O*-benzyl-α- L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (10)

A solution of thiourea (626 mg, 8.24 mmol) in MeOH (30 mL) was added to a solution of the foregoing trisaccharide **9** (3.5 g, 2.75 mmol) in CH_2Cl_2 (50 mL), and the mixture was stirred at room temperature for 4 h. After concentration, the residue was partitioned between CH_2Cl_2 and aq $NaHCO_3$. The organic phase was concentrated and chromatography gave **10** (3.1 g, 96%), $[\alpha]_D$ +11° (*c* 0.5). ^{1}H NMR ($CDCl_3$): δ 5.54 (dd, 1H, $J_{1,2}$ 1.5, $J_{2,3}$ 3.3 Hz, H-2^{III}), 5.31 (br s, 1H, H-1^{III}), 5.22 (t, 1H, *J* 9.8 Hz, H-4^{III}), 5.17 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.94–4.35 (m, 9H, incl., d, 4.68, $J_{1,2}$ 1.6 Hz, 4 *C*H$_2$Ph, H-1^{I}), 4.31 (ddd, 1H, $J_{3,4}$ 10.0, $J_{3,OH}$ 7.8 Hz, H-3^{III}), 4.19 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.1 Hz, H-3^{II}), 4.08–4.04 (m, 2H, H-2^{I},5^{III}), 3.86–3.79 (m, 3H, H-2^{II},3^{I},5^{II}), 3.67–3.59 (m, 6H, H-4^{II},5^{I},1″a, incl., 3.65, s, OCH$_3$), 3.39 (t, 1H, *J* 9.5 Hz, H-4^{I}), 3.35, 3.34 (2t, 1H, *J* 6.8 Hz, H-1″b), 2.46 (d, 1H, OH), 2.31 (t, 2H, *J* 7.4 Hz, H-5″a,b), 1.66–1.61 (m, 2H, H-4″a,b), 1.58–1.53 (m, 2H, H-2″a,b), 1.39–1.35 (m, partially overlapped, H-3″), 1.32 (d, partially overlapped, $J_{5,6}$ 6.1 Hz, H-6^{II}), 1.23 (d, 3H, $J_{5,6}$ 6.5 Hz, H-6^{I}), 1.17 (d, 3H, H-6^{III}); ^{13}C NMR ($CDCl_3$): δ 98.95 (br, C-1^{III}), 98.89 (C-1^{I}), 98.75 (C-1^{II}), 80.69 (C-4^{II}), 80.50 (C-4^{I}), 80.17 (C-3^{I}), 78.10 (C-2^{II}), 77.88 (br, C-3^{II}), 75.49 (C-4^{III}), 75.34 (2C, 2 *C*H$_2$Ph), 74.95 (C-2^{I}), 73.29 (C-2^{III}), 72.50, 71.79 (2 *C*H$_2$Ph), 69.10 (C-3^{III}), 68.59 (C-5^{II}), 67.87 (C-5^{I}), 67.19 (C-1″), 66.58 (C-5^{III}), 51.42 (OCH$_3$), 33.94 (C-5″), 29.12 (C-2″), 25.74 (C-3″), 24.71 (C-4″), 18.17 (C-6^{II}), 17.91 (C-6^{I}), 17.53 (C-6^{III}); ESI-MS: *m*/*z* 1174.4980 ([M+Na]$^+$). Anal. Calcd for $C_{67}H_{76}O_{17}$: C, 69.77; H, 6.64. Found: C, 69.80; H, 6.95.

3.17. 5-Methoxycarbonylpentyl α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-L-rhamnopyranoside (12)

Hydrogenolysis of compound **10** (300 mg) in MeOH (10 mL) followed by deacylation with 1 M NaOMe in MeOH gave amorphous **12** as a white solid (135 mg, 88%, over 2 steps), $[\alpha]_D$ −71° (*c* 0.5, H_2O). ^{1}H NMR (D_2O, 600 MHz): 5.04 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{III}), 4.93 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.89 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.15 (dd, 1H, $J_{2,3}$ 3.2 Hz, H-2^{II}), 4.06 (dd, 1H, $J_{2,3}$ 3.4 Hz, H-2^{III}), 3.92 (dd, 1H, $J_{2,3}$ 3.4 Hz, H-2^{I}), 3.86–3.76 (m, 5H, H-3$^{I\text{-}III}$, 5^{II,III}), 3.72–3.66 (m, 5H, H-5^{I},1″a, incl., 3.69, s, COOCH$_3$), 3.56–3.52 (m, 2H, H-4^{II},1″b), 3.48 (t, partially overlapped, *J* 9.7 Hz, H-4^{I}), 3.46 (t, partially overlapped, *J* 9.6 Hz, H-4^{III}), 2.41 (t, 2H, *J* 7.3 Hz, H-5″a,b), 1.66–1.58 (m, H-2″a,b,4″a,b), 1.44–1.34 (m, 2H, H-3″a,b), 1.30 (d, 6H, $J_{5,6}$ 6.3 Hz, H-6^{I,III}), 1.28 (d, $J_{5,6}$ 6.3 Hz, H-6^{II}); ^{13}C NMR (D_2O, 150 MHz): δ 105.18 (C-1^{III}), 104.87 (C-1^{II}), 101.04 (C-1^{I}), 81.47 (C-2^{I}), 80.81 (C-3^{II}), 74.94 (C-4^{I}), 74.71 (C-4^{III}), 74.04 (C-4^{II}), 72.88 (C-2^{III}), 72.83 (2C, C-3^{I,II}), 72.61 (C-2^{II}), 72.10 (C-5^{II}), 71.90 (C-5^{III}), 71.55 (C-5^{I}), 70.58 (C-1″), 54.86 (COO*C*H$_3$), 36.35 (C-5″), 30.84 (C-2″), 27.67 (C-3″), 26.76 (C-4″), 19.43 (C-6^{II}), 19.38 (2 C, C-6^{I,III}); ESI-MS: 607.2579 $C_{25}H_{44}O_{15}Na$ requires 607.2578.

3.18. Methyl 4-azido-3-*O*-benzyl-2-*O*-bromoacetyl-4,6-dideoxy-β-D-glucopyranoside (14)

A solution of methyl 4-azido-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranoside[24] (**13**, 4 g, 13.6 mmol) and tetramethylurea (18 mL, 150 mmol) in CH_2Cl_2 (70 mL) was treated with bromoacetyl bromide (12 mL, 136 mmol), and the mixture was stirred at room temperature overnight. The mixture was poured into stirred aq $NaHCO_3$ solution and, after 3 h the product was extracted into CH_2Cl_2. After concentration, chromatography gave **14** (5.6 g, 86%), mp 73–74 °C (from EtOH), $[\alpha]_D$ +75° (*c* 0.7). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.96 (dd, 1H, $J_{1,2}$ 8.0, $J_{2,3}$ 9.5 Hz, H-2), 4.83, 4.69 (2d, 2H, *J* 11.3 Hz, C*H*$_2$Ph), 4.26 (d, 1H, H-1), 3.68, 3.64 (2d, 2H, *J* 12.3 Hz, CH$_2$Br), 3.56 (t, *J* 9.2 Hz, H-3), 3.46 (s, 3H, OCH$_3$), 3.33–3.20 (m, 2H, H-4,5), 1.39 (d, 3H, $J_{5,6}$ 5.8 Hz, H-6); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 101.36 (C-1), 81.13 (C-3), 75.06 (*C*H$_2$Ph), 74.81 (C-2), 70.82 (C-5), 67.80 (C-4), 56.80 (OCH$_3$), 25.35 (CH$_2$Br), 18.28 (C-6). FAB MS: *m*/*z* 382.4 ([M+H−MeOH]$^+$). Anal. Calcd for $C_{16}H_{20}BrN_3O_5$: C, 46.39; H, 4.87; N, 10.14. Found: C, 46.25; H, 4.82; N, 10.09.

3.19. Methyl 4-azido-3-*O*-benzyl-2-*O*-bromoacetyl-4,6-dideoxy-α-D-glucopyranoside (20)

Methyl 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-glucopyranoside[24] (**19**, 2.08 g, 7.1 mmol) was converted to the title compound in the manner described above for the β anomer, to give amorphous **20** (2.6 g, 89.5%), $[\alpha]_D$ +204° (*c* 0.5). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 4.86 (d, partially overlapped, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.84 (dd, partially overlapped, $J_{2,3}$ 9.7 Hz, H-2), 4.84 (d, partially overlapped, *J* 11.2 Hz, C*H*Ph), 4.77 (d, 1H, C*H*Ph), 3.87 (t, 1H, *J* 9.7 Hz, H-3), 3.74, 3.68 (2d, 2H, *J* 12.2, CH$_2$Br), 3.62–3.57 (m, 1H, H-5), 3.35 (s, 3H, OCH$_3$), 3.17 (dd, 1H, $J_{4,5}$ 10.1 Hz, H-4), 1.32 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 96.41 (C-1), 78.05 (C-3), 75.38 (*C*H$_2$Ph), 75.21 (C-2), 67.92 (C-4), 65.85 (C-5), 55.24 (OCH$_3$), 25.28 (CH$_2$Br), 18.17 (C-6); ESI-MS: *m*/*z* 436.0484 ([M+Na]$^+$). Anal. Calcd for $C_{16}H_{20}BrN_3O_5$: C, 46.39; H, 4.87; N, 10.14. Found: C, 46.45; H, 4.81; N, 10.05.

3.20. 1-*O*-acetyl-4-azido-3-*O*-benzyl-2-*O*-bromoacetyl-4,6-dideoxy-α- (15) and β-D-glucopyranose (16)

(a) From methyl 4-azido-3-*O*-benzyl-2-*O*-bromoacetyl-4,6-dideoxy-α-D-glucopyranoside (**20**): Compound **20** (1.4 g) was treated, at room temperature, with a mixture

of 25:10:0.25 Ac_2O/AcOH/H_2SO_4 (28 mL). After 30 min, TLC (4:1 hexane/EtOAc) showed that all starting material was consumed and that two products were formed, the faster moving of the two largely predominating. Solid NaOAc trihydrate was added, to neutralize sulfuric acid, and the reaction mixture was poured into a stirred aq $NaHCO_3$ solution, to destroy excess Ac_2O. After 3 h the mixture was partitioned between water and CH_2Cl_2, the organic phase was dried and concentrated, to give a mixture of anomers (1.3 g, 87%), α:β = ~4.4 (NMR). The material was used for the next step without further purification. For characterization, a portion was chromatographed to give first the α-anomer **15**, mp 97–98 °C (from EtOH), $[\alpha]_D$ +162°, (*c* 0.5), ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.24 (d, $J_{1,2}$ 3.7 Hz, H-1), 5.01 (dd, $J_{2,3}$ 9.9 Hz, H-2), 4.86, 4.79 (2d, *J* 11.2 Hz, CH_2Ph), 3.87 (t, *J* 9.9 Hz, H-3), 3.74–3.63 (m, H-5), 3.67, 3.65 (2 d, *J* 12.8 Hz, CH_2Br), 3.25 (t, *J* 9.9 Hz, H-4), 2.15 (s, $COCH_3$), 1.33 (d, $J_{5,6}$ 6.2 Hz, H-6); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 89.04 ($J_{C\text{-}1,H\text{-}1}$ 177.3 Hz, C-1), 77.77 (C-3), 75.46 (CH_2Ph), 73.59 (C-2), 68.88 (C-5), 67.33 (C-4), 24.90 (CH_2Br), 20.91 (CO*C*H_3), 18.33 (C-6); ESI-MS: *m*/*z* 448.03 ([M+Li]$^+$). Anal. Calcd for $C_{17}H_{20}BrN_3O_6$: C, 46.17; H, 4.56; N, 9.50. Found: C, 46.14; H, 4.38; N, 9.45.

Eluted next was the β-anomer **16**, mp 61–62 °C (from EtOH) $[\alpha]_D$ +83° (*c* 1.6). ^{1}H NMR ($CDCl_3$): δ 5.58 (d, $J_{1,2}$ 8.4 Hz, H-1), 5.07 (dd, $J_{2,3}$ 9.4 Hz, H-2), 4.87, 4.66 (2d, *J* 11.5 Hz, CH_2Ph), 3.60 (t, *J* 9.6 Hz, H-3), 3.54, 3.51 (2d, CH_2Br), 3.45–3.40 (m, H-5), 3.26 (t, *J* 9.7 Hz, H-4), 2.17 (s, $COCH_3$), 1.38 (d, $J_{5,6}$ 6.1 Hz, H-6); ^{13}C NMR ($CDCl_3$, 15 MHz): δ 91.41 ($J_{C\text{-}1,H\text{-}1}$ 164.4 Hz. C-1), 81.06 (C-3), 75.31 (*C*H_2Ph),), 73.44 (C-2), 71.83 (C-5), 67.50 (C-4), 24.82 (CH_2Br), 20.85 ($COCH_3$), 18.20 (C-6); FAB: *m*/*z* 448.0696 ([M+Li]$^+$). Anal. Calcd for $C_{17}H_{20}BrN_3O_6$: C, 46.17; H, 4.56; N, 9.50. Found: C, 46.34; H, 4.60; N, 9.47.

(b) From methyl 4-azido-3-*O*-benzyl-2-*O*-bromoacetyl-4,6-dideoxy-β-D-glucopyranoside (**14**): Compound **14** (4.68 g) was treated as described above. After 2 h when the reaction was complete, the mixture was processed as described above to give an anomeric mixture of **15** and **16** (4.68 g, 94%).

3.21. Ethyl 4-azido-3-*O*-benzyl-2-*O*-bromoacetyl-4,6-dideoxy-1-thio-α- (17) and β-D-glucopyranoside (18)

(a) From ethyl 4-azido-3-*O*-benzyl-4,6-dideoxy-1-thio-β-D-glucopyranoside (**21**). Methyl 4-azido-3-*O*-benzyl-4,6-dideoxy-1-thio-β-D-glucopyranoside (**21**)[24] (313 mg, 1 mmol) in CH_2Cl_2 (5 mL) was treated with tetramethylurea (0.239 mL, 2.0 mmol) and bromoacetyl bromide (0.13 mL, 1.5 mmol) in dichloromethane (5 mL) as described for the preparation of **14**, to give the β-compound **18** (0.260 g, 67%), mp 82–83 °C (from ethanol), $[\alpha]_D$ +60° (*c* 0.5). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.01 (dd, 1H, $J_{1,2}$ 10.0 Hz, $J_{2,3}$ 9.0 Hz, H-2), 4.83, 4.71 (2d, 2H, *J* 11.2 Hz, CH_2Ph), 4.34 (d, 1H, H-1), 3.69, 3.65 (2d, 2H, *J* 12.5 Hz, CH_2Br), 3.57 (t, *J* 9.1 Hz, H-3), 3.31–3.27 (m, 1H, H-5), 3.23 (bdd, 1H, H-4), 2.72–2.61 (m, 2H, CH_2CH$_3$), 1.38 (d, 3H, $J_{5,6}$ 6.0 Hz, H-6), 1.24 (t, 3H, CH$_2$CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 82.82 (C-1), 82.28 (C-3), 75.17 (*C*H_2Ph), 75.09 (C-5), 73.31 (C-2), 67.68 (C-4), 25.40 (CH_2Br), 23.80 (*C*H_2CH$_3$), 18.55 (C-6), 14.67 (CH$_2$*C*H_3); ESI-MS: *m*/*z* 466.0412 ([M+Na]$^+$) Anal. Calcd for $C_{17}H_{22}BrN_3O_4S$: C, 45.95; H, 4.99; N, 9.46. Found: C, 46.05; H, 4.91; N, 9.50.

(b) From a mixture of acetates **15** and **16**. BF_3.Et_2O (2.5 mL, 20 mmol) was added dropwise at 0 °C to a solution of the starting acetates (6.1 g, 13.8 mmol) and EtSH (3 mL, 40 mmol) in CH_2Cl_2 (70 mL). After 3 h at room temperature, when TLC showed that the reaction was complete, the mixture was poured into aq $NaHCO_3$, and the product was extracted with CH_2Cl_2. After concentration of the extracts, chromatography gave first the ethyl 1-thio-α-glycoside (**17**, 1.6 g, 23%), mp 31–32 °C (from hexane at 0 °C), $[\alpha]_D$ +266° (*c* 0.9). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.57 (d, 1H, $J_{1,2}$ 5.7 Hz, H-1), 4.97 (dd, 1H, $J_{2,3}$ 9.9 Hz, H-2), 4.83, 4.78 (2d, 2H, *J* 11.0 Hz, *C*H_2Ph), 4.04–4.94 (m, 1H, H-5), 3.75 (t, 1H, partially overlapped, H-3), 3,73, 3.69 (2d, 2H, partially overlapped, *J* 12.6 Hz, CH_2Br), 3.18 (t, 1H, H-4), 2.59–2.46 (m, 2H, CH_2CH$_3$), 1.32 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6), 1.24 (7, 3H, *J* 7.4 Hz, CH$_2$CH_3); ^{13}C NMR ($CDCl_3$): δ 81.27 ($J_{C\text{-}1,H\text{-}1}$ 168 Hz, C-1), 78.60 (C-3), 75.41 (*C*H_2Ph), 75.21 (C-2), 67.89 (C-4), 66.39 (C-5), 25.24 (CH_2Br), 24.35 (*C*H_2CH$_3$), 18.11 (C-6), 14.77 (*C*H_3CH$_2$); ESI-MS: *m*/*z* 444.0593 ([M+H]$^+$). Anal. Calcd for $C_{17}H_{22}BrN_3O_4S$: C, 45.95; H, 4.99; N, 9.46. Found: C, 46.25; H, 4.86; N, 9.42.

Eluted later was ethyl 1-thio-β-glycoside **18** (4.1 g, 62%), which was identical with the above described substance.

3.22. Ethyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-1-thio-β-D-glucopyranoside (22)

Benzoyl chloride (0.6 mL, 5.3 mmol) was added at 0 °C to a solution of methyl 4-azido-3-*O*-benzyl-4,6-dideoxy-1-thio-β-D-glucopyranoside[24] (**21**, 427 mg, 1.32 mmol) in pyridine (10 mL) and the mixture was kept at room temperature overnight. Conventional processing and chromatography gave **22** (842 mg, 97%), mp 64–66 °C (from MeOH), $[\alpha]_D$ +124° (*c* 0.9). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.30 (dd, 1H, $J_{1,2}$ 10.1, $J_{2,3}$ 9.0 Hz, H-2), 4.75, 4.65 (2d, 2H, CH_2Ph), 4.50 (d, 1H, H-1), 3.71 (t, 1H, *J* 9.9 Hz, H-3), 3.40–3.26 (m, 2H, H-4,5), 2.78–2.61 (m, 2H, CH_2CH$_3$), 1.41 (d, 1H, $J_{5,6}$ 5.7 Hz, H-6), 1.22 (t, *J* 7.5 Hz, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 83.29 (C-1), 82.50 (C-3), 75.22 (C-5), 75.08 (*C*H_2Ph), 72.50 (C-2), 67.72 (C-4), 23.83 (*C*H_2CH$_3$), 18.67 (C-6), 14.73 (CH$_2$*C*H_3). ESI-MS 434.1713 ([M+Li]$^+$). Anal. Calcd for $C_{22}H_{25}N_3O_4S$: C, 61.81; H, 5.89; N, 9.83. Found: C, 61.99; H, 5.86; N, 9.76.

3.23. 5-Methoxycarbonylpentyl 4-azido-3-*O*-benzyl-2-*O*-bromoacetyl-4,6-dideoxy-β-D-glucopyranosyl-(1 → 2)-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzyl-α- L-rhamnopyranoside (24)

A mixture of acceptor **10** (288 mg, 0.25 mmol), donor **18** (111 mg, 0.25 mmol), and 4 Å molecular sieves was

allowed to react as described in the general method for glycosylation of thioglycosides and chromatography gave first orthoester **23** (60 mg, 16.2% and 26%, based on the initial amount of the acceptor and that consumed, respectively). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.93 (d, 1H, $J_{1,2}$ 5.7 Hz, H-1^{IV}), 5.68 (dd, 1H, $J_{2,3}$ 2.0, $J_{3,4}$ 3.3 Hz, H-2^{III}), 5.42 (t, 1H, J 9.9 Hz, H-4^{III}), 5.26 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{III}), 5.19 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 4.96–4.43 (m, 12H, 5 CH_2Ph, incl., ~4.69, d, overlapped, H-1^{I}, 4.50, dd, 1H, $J_{3,4}$ 9.7 Hz, H-3^{III}), 4.26 (dd, 1H, $J_{2,3}$ 4.2 Hz, H-2^{IV}), 4.21 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.4 Hz, H-3^{II}), 4.12–4.07 (m, partially overlapped, H-5^{III}), 4.06 (dd, partially overlapped, H-2^{I}), 3.91 (d, 1H, $J_{2,3}$ 3.3 Hz, H-2^{II}), 3.86–3.78 (m, 3H, H-3^{I},5^{IV},3^{IV}, in that order), 3.69 (t, partially overlapped, J 9.4 Hz, H-4^{II}), 3.67 (m, partially overlapped, H-1″a,CHaBr, incl., s, 3.64, OCH_3), 3.41 (t, 1H, J 9.4 Hz, H-4^{I}), 3.36, 3.34 (2 t, 1H, H-1″b), 3.25 (d, 1H, J 11.7 Hz, CHbBr), 3.02 (dd, 1H, $J_{3,4}$ 8.2, $J_{4,5}$ 10.1 Hz, H-4^{IV}), 2.31 (t, 2H, J 7.4 Hz, H-5″), 1.66–1.61 (m, 2H, H-4″a,b), 1.59–1.54 (m, 2H, H-2″a,b), 1.40–1.33 (m, partially overlapped, H-3″a,b), 1.34, 1.23, 1.21, 1.18 (4d, 3H each, $J_{5,6} \sim 6.1$ Hz, H-6^{II,I,III} in that order); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 173.94, 165.56, 165.20 (3 CO), 118.27 (quart C, orthoester), 99.54 (C-1^{III}), 98.77 (C-1^{IV}), 98.72 (C-1^{I}), 98.22 (C-1^{II}), 80.27 (C-4^{I}), 80.09 (C-3^{I}), 80.07 (C-4^{II}), 79.80 (C-3^{IV}), 79.13 (C-3^{II}), 78.51 (C-2^{II}), 76.90 (C-2^{IV}), 75.49, 75.28, 72.46, 71.71 (4 CH$_2$Ph), 75.02 (C-2^{I}), 72.03 (C-4^{III}), 71.77 (C-2^{III}), 70.17 (C-3^{III}), 68.43 (C-5^{II}), 67.73 (C-5^{I}), 67.34 (C-5^{IV}), 67.25 (C-5^{III}), 67.08 (C-1″), 64.38 (C-4^{IV}), 51.53 (COOCH$_3$), 33.96 (C-5″), 31.56 (CH$_2$Br), 29.16 (C-2″), 25.83 (C-3″), 24.50 (C-4″), 18.09 (C-6^{II}), 17.98 (C-6^{IV}), 17.82 (C-6^{I}), 17.62 (C-6^{III}). ESI-MS: m/z 1556.5332 ([M+Na]$^+$) $C_{82}H_{92}BrN_3O_{21}Na$ requires 1556.5304.

Eluted next was the α-linked tetrasaccharide **88** (75 mg, 20.2% and 32%, based on the initial amount of the acceptor and that consumed, respectively). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.60 (dd, 1H, $J_{1,2}$ 1.9, $J_{2,3}$ 3.0 Hz, H-2^{III}), 5.50 (t, 1H, J 9.8 Hz, H-4^{III}), 5.25 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1^{III}), 5.14 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 5.04 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1^{IV}), 4.87–4.38 (m, 11H, 5 CH_2Ph, incl., 1.66, d, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.72 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-2^{IV}), 4.34 (dd, $J_{2,3}$ 3.1, $J_{3,4}$ 9.7 Hz, H-3^{III}), 4.17 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.4 Hz, H-3^{II}), 4.06 (m, 1H, H-5), 4.02 (dd, 1H, $J_{1,2}$ 1.8, $J_{2,3}$ 2.8 Hz, H-2^{I}), 3.85 (dd, partially overlapped, $J_{2,3}$ 3.1 Hz, H-2^{II}), 3.84 (dd, partially overlapped, $J_{2,3}$ 3.0, $J_{3,4}$ 9.5 Hz, H-3^{I}), 3.80 (m, H-5^{II}), 3.66–3.58 (m, 6H, H-4^{II},5^{I}, 1″a, incl., 3.65, s OCH_3), 3.52 (t, 1H, J 9.6 Hz, H-3^{IV}), 3.41 (m, 1H, H-5^{IV}), 3.38–3.32 (m, 3H, H-4^{I},1″b, incl., 3.35, d, CHaBr), 3.17 (d, 1H, ^2J 12.9 Hz, CHbBr), 2.92 (dd, 1H, $J_{3,4}$ 9.5, $J_{4,5}$ 10.2 Hz, H-4^{IV}), 2.31 (t, 2H, J 7.6 Hz, H-5″a,b), 1.66–1.61 (m, 2H, H-4″a,b), 1.58–1.53 (m, 2H, H-2″a,b), 1.37–1.32 (m, partially overlapped, H-3″a,b), 1.32 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{II}), 1.22 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.20 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{III}), 0.88 (d, 3H, $J_{5,6}$ 5.9 Hz, H-6^{IV}); ^{13}C NMR ($CDCl_3$): 99.38 (br, $J_{C\text{-}1,H\text{-}1}$ 174 Hz, C-1^{III}), 98.79 ($J_{C\text{-}1,H\text{-}1}$ 169 Hz, C-1^{I}), 98.57 (br, $J_{C\text{-}1,H\text{-}1}$ 169 Hz, C-1^{II}), δ 93.81 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz, C-1^{IV}), 80.49 (C-4^{II}), 80.44 (C-4^{I}), 80.08 (C-3^{I}), 78.25 (br, C-3^{II}), 77.93 (C-2^{II}), 77.31 (C-3^{IV}),75.41, 75.36, 75.19 (3 CH$_2$Ph), 74.93 (C-2^{I}), 74.21 (C-2^{IV}), 72.70 (C-3^{III}), 72.45 (CH$_2$Ph), 72.41 (C-4^{III}), 71.83 (CH$_2$Ph), 69.02 (C-2^{III}), 68.58 (C-5^{II}), 67.80 (C-5^{I}), 67.53 (C-4^{IV}), 67.19 (C-1″), 67.14 (C-5^{III}), 66.70 (C-5^{IV}), 51.52 (COOCH$_3$), 34.00 (C-5″), 29.17 (C-2″), 25.76 (C-3″), 25.43 (CH$_2$Br), 24.77 (C-4″), 18.13 (C-6^{II}), 17.90 (C-6^{I}), 17.88 (C-6^{IV}), 17.57 (C-6^{III}). ESI-MS: m/z 1556.5303 ([M+Na]$^+$) $C_{82}H_{92}BrN_3O_{21}Na$ requires 1556.5304.

Eluted next was the desired β-linked tetrasaccharide **24** (46 mg, 12.4% and 20%, based on the initial amount of the acceptor and that consumed, respectively) ^{1}H NMR ($CDCl_3$, 600 MHz): 5.53 (dd, 1H, $J_{1,2}$ 1.9, $J_{2,3}$ 3.4 Hz, H-2^{III}), 5.44 (t, 1H, J 9.4 Hz, H-4^{III}), 5.31 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1^{III}), 5.17 (d, 1H, $J_{1,2}$ 2.0 Hz, H-1^{II}), 5.00–4.28 (m, 10H, 5 CH_2Ph), 4.81 (dd, 1H, $J_{1,2}$ 7.9, $J_{2,3}$ 9.5 Hz, H-2^{IV}), 4.66 (d, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.38 (d, partially overlapped, H-1^{IV}), 4.36 (dd, partially overlapped, $J_{2,3}$ 3.5, $J_{3,4}$ 9.9 Hz, H-3^{III}), 4.18 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.0 Hz, H-3^{II}), 4.11–4.06 (m, 1H, H-5^{III}), 4.03 (dd, 1H, $J_{1,2}$ 2.0, $J_{2,3}$ 3.0 Hz, H-2^{I}), 3.89 (dd, 1H, $J_{2,3}$ 3.0 Hz, H-2^{II}), 3.84 (dd, partially overlapped, $J_{2,3}$ 3.0, $J_{3,4}$ 9.2 Hz, H-3^{I}), 3.84–3.80 (m, partially overlapped, H-5^{II}), 3.66–3.58 (m, 6H, H-5^{I}, 1″a, incl., 3.65, s OCH_3, 3.60, t, J 9.5 Hz, H-4^{II}), 3.40 (t, 1H, J 9.5 Hz, H-4^{I}), 3.36–3.32 (m, 2H, H-1″b, incl., 3.50, d, J 12.5 Hz, CHaBr), 3.23 (d, 1H, J 12.5 Hz, CHbBr), 3.17 (t, 1H, J 9.3 Hz, H-3^{IV}), 3.03–3.00 (m, 2H, H-5^{IV},4^{IV}), 2.31 (t, 2H, J 7.5 Hz, H-5″a,b), 1.66–1.61 (m, 2H, H-4″a,b), 1.58–1.53 (m, 2H, H-2″a,b), 1.37–1.32 (m, partially overlapped, H-3″a,b), 1.32 (d, partially overlapped, $J_{5,6}$ 6.1 Hz, H-6^{II}), 1.23 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6^{I}), 1.16 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{III}), 1.09 (d, 3H, $J_{5,6}$ 5.9 Hz, H-6^{IV}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 100.48 (C-1^{IV}), 99.07 (br, C-1^{III}), 98.79 (C-1^{I}), 98.31 (br, C-1^{II}), 80.57 (C-3^{IV}), 80.40 (C-4^{I}), 80.16 (C-4^{II}), 80.09 (C-3^{I}), 79.33 (C-3^{II}), 78.20 (C-2^{II}), 75.38 (2 C, 2 CH$_2$Ph), 75.05 (C-2^{I}), 74.65 (CH$_2$Ph), 74.53 (C-3^{III}), 74.34 (C-2^{IV}), 73.52 (C-4^{III}), 72.53 (CH$_2$Ph), 72.47 (C-2^{III}), 71.57 (CH$_2$Ph), 70.78 (C-4^{IV}), 68.39 (C-5^{II}), 67.82 (C-5^{I}), 67.14 (2 C, C-5^{IV},1″), 66.59 (C-5^{III}), 51.47 (OCH_3), 33.96 (C-5″), 31.56 (CH$_2$Br), 29.11 (C-2″), 25.72 (C-3″), 24.71 (C-4″), 18.16 (C-6^{II}), 17.99 (C-6^{IV}), 17.85 (C-6^{I}), 17.52 (C-6^{III}); ESI-MS: m/z 1556.5385 ([M+Na]$^+$).

Eluted last was the unchanged glycosyl acceptor **10** (109 mg, 38%).

3.24. Methyl 3-*O*-acetyl-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (27)

Methyl 1-thio-α-L-rhamnopyranoside[16] was converted to 3-*O*-acetyl-2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**25**) as described.[23] A solution of **25** (1.77 g, 4.7 mmol) in CCl_4 (6 mL) was treated with a stock solution[26] of Cl_2 in CCl_4 (6 mL, ~6 mmol). The resulting yellow solution was concentrated after 3 min, when NMR spectra of products of preliminary experiments showed that the conversion was complete and that

3-*O*-acetyl-2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranosyl chloride (**26**) was stereospecifically formed. After concentration and co-evaporation with dry toluene, the material in the residue was used for the next step without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.98 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1), 5.42 (dd, 1H, $J_{2,3}$ 3.5, $J_{3,4}$ 9.8 Hz, H-3), 4.73, 4.65 (2 d, partially overlapped, ^2J 11.1 Hz, CH_2Ph), 4.67, 4.56 (2 d, partially overlapped, ^2J 12.1 Hz, CH_2Ph), 4.10–4.00 (m, 2H, H-2,5), 3.68 (t, 1H, *J* 9.6 Hz, H-4), 1.96 (d, 3H, $COCH_3$), 1.36 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6); ^{13}C NMR ($CDCl_3$,75 MHz): δ 90.55 ($J_{C\text{-}1,H\text{-}1}$ 182.8 Hz, C-1), 78.89 (C-2), 78.35 (C-4), 75.06, 73.30 (2 *C*H_2Ph), 72.16 (C-3), 70.73 (C-5), 20.88 (CO*C*H_3), 17.61 (C-6).

A solution of the foregoing glycosyl chloride and **6** (1.2 g, 2.9 mmol) were allowed to react as described above in the general procedure to give **27** (1.25 g, 52%), mp 84–85 ° (from MeOH), $[\alpha]_D$ −42° (*c* 0.5). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.27 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.4 Hz, H-3^{II}), 5.18, (d, 1H, $J_{1,2}$ 1.4 Hz, H-1^{I}), 5.11, (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.81–4.17 (8d, 8H, 4 CH_2Ph), 4.05 (dd, partially overlapped, $J_{2,3}$ 3.1, $J_{3,4}$ 9.6 Hz, H-3^{I}), 4.04–3.99 (m, partially overlapped, H-5^{I}), 3.85–3.84 (m, 2H, H-2^{I,II}), 3.80–3.76 (m, 1H, H-5^{II}), 3.66 (t, 1H, *J* 9.4 Hz, H-4^{I}), 3.60 (t, 1H, *J* 9.4 Hz, H-4^{II}), 2.11 (s, 3H, SCH_3), 1.93 (s, 3H, $COCH_3$), 1.30 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.24 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{II}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 99.53 (C-1^{II}), 83.09 (C-1^{I}), 80.74 (C-4^{I}), 79.23 (C-2^{I}), 78.97 (C-4^{II}), 78.55 (C-3^{I}), 76.64 (C-2^{II}), 74.74, 74.66 (2 *C*H_2Ph), 73.45 (C-3^{I}), 68.62 (C-5^{I}), 68.28 (C-5^{II}), 21.05 ($COOCH_3$), 17.99 (C-6^{II}), 17.85 (C-6^{I}), 13.82 (SCH_3); ESI-MS: *m*/*z* 765.3066 ([M+Na]$^+$). Anal. Calcd for $C_{43}H_{50}O_9S$: C, 69.52; H, 6.78. Found: C, 69.30; H, 6.74.

3.25. 5-Methoxycarbonylpentyl 3-*O*-acetyl-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 (28)

Reaction of alcohol **5** (390 mg, 0.82 mmol) and glycosyl donor **27** (798 mg, 1.07 mmol), as described in the general procedure, gave amorphous trisaccharide **28** (880 mg,94%), $[\alpha]_D$ −5° (*c* 0.9). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.29 (dd, 1H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.6 Hz, H-3^{III}), 5.16 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{III}), 5.11 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.87–4.35 (m, 12H, 11 C*H*Ph, incl., d, 4.69, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.17 (m, 2H, C*H*Ph, H-3^{II}), 4.02 (dd, 1H, $J_{1,2}$ 1.9, $J_{2,3}$ 3.0 Hz, H-2^{I}), 3.85 (dd, 1H, $J_{1,2}$ 1.9, $J_{2,3}$ 3.3 Hz, H-2^{II}), 3.83 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.4 Hz, H-3^{I}),3.81–3.75 (m, 3H, H-2^{II},5^{II},5^{III}), 3.66 (s, 3H, $COOCH_3$), 3.65–3.58 (m, 4H, H-4^{II},4^{III},5^{I},H-1″a), 3.39 (t, *J* 9.4 Hz, H-4^{I}), 3.48 (t, 1H, *J* 9.4 Hz, H-4^{I}), 3.36, 3.35 (2t, 1H, *J* 6.4 Hz, H-1″b), 2.31 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.94 (s, 3H, $COCH_3$), 1.66–1.61 (m, 2H, H-4″a,b), 1.58–1.53 (m, 2H, H-2″a,b), 1.38–1.32 (m, H-3″a,b), 1.29 (d, $J_{5,6}$ 6.2 Hz, H-6^{II}), 1.27 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.21 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{III}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 99.25 (C-1^{III}), 98.98 (C-1^{II}), 98.87 (C-1^{I}), 80.70 (C-4^{III}), 80.44 (C-4^{I}), 80.01 (C-3^{I}), 78.95 (C-4^{II}), 77.63 (C-2^{II}), 77.21 (C-3^{II}), 76.73 (C-2^{III}), 75.41, 74.67, 74.64 (3 *C*H_2Ph), 74.49 (C-2^{I}), 73.53 (C-3^{III}), 72.62, 72.33, 72.18 (3 *C*H_2Ph), 68.75 (C-5^{II}), 68.12 (C-5^{III}), 67.84 (C-5^{I}), 67.15 (C-1″), 51.46 (COO*C*H_3), 33.92 (C-5″), 29.11 (C-2″), 25.72 (C-3″), 24.69 (C-4″), 21.04 (CO*C*H_3), 17.93 (C-6^{II}), 17.92 (C-6^{I}), 17.89 (C-6^{III}); ESI-MS: *m*/*z* 1189.5475 ([M+Na]$^+$). Anal. Calcd for $C_{69}H_{82}O_{16}$: C, 70.99; H, 7.08. Found: C, 70.85; H, 7.13.

3.26. 5-Methoxycarbonylpentyl 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 (29)

Deacetylation of **28** (880 mg) gave amorphous **29** (716 mg, 85%), $[\alpha]_D$ −7° (*c* 0.6). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.21 (br s, 1H, H-1^{III}), 5.11 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.89–4.08 (m, 13H, 6 CH_2Ph, incl., 4.70, d, partially overlapped, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.19 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.6 Hz, H-3^{II}), 4.03 (dd, 1H, $J_{2,3}$ 2.8 Hz, H-2^{I}), 3.96 (ddd, 1H, H-3^{III}), 3.84 (dd, partially overlapped, H-3^{I}), 3.82 (m, partially overlapped, H-5^{II}), 3.79 (dd, 1H, H-2^{II}), 3.73–3.59 (m, 2H, H-2^{III},5^{III}), 3.66 (m, partially overlapped, H-5^{I}), 3.64 (s, partially overlapped, $COOCH_3$), 3.65–3.59 (m, partially overlapped, H-4^{II},1″a), 3.40 (t, 1H, *J* 9.6 Hz, H-4^{I}), 3.37, 3.35 (2t, 1H, *J* 6.5 Hz, H-1″b), 3.29 (t, 1H, *J* 9.3 Hz, H-4^{III}), 2.31 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.82 (s, 1H, OH), 1.66–1.61 (m, 2H, H-4″), 1.59–1.54 (m, 2H, H-2″), 1.38–1.32 (m, 2H, H-3″), 1.31 (d, 2H, $J_{5,6}$ 6.3 Hz, H-6^{II}), 1.28 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.23 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{III}); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 98.93 (C-1^{II}), 98.82 (C-1^{I}), 98.34 (C-1^{III}), 82.01 (C-4^{III}), 80.89 (C-4^{II}), 80.40 (C-4^{I}), 79.93 (C-3^{I}), 78.98 (C-2^{III}), 77.65 (C-2^{II}), 76.57 (C-3^{II}), 75.35, 74.74, 74.51, 72.35, 72.27, 72.11 (6*C*H_2Ph), 74.46 (C-2^{I}), 71.54 (C-3^{II}), 68.68 (C-5^{II}), 67.79 (C-5^{I}), 67.49 (C-5^{III}), 67.08 (C-1″), 51.38 (COO*C*H_3), 33.87 (C-5″), 29.03 (C-2″), 25.67 (C-3″), 24.64 (C-4″), 17.94 (C-6^{II}), 17.87 (C-6^{I}), 17.82 (C-6^{III}). ESI-MS: *m*/*z* 1147.5365 ([M+Na]$^+$). Anal. Calcd for $C_{67}H_{80}O_{15}$: C, 71.51; H, 7.17. Found: C, 71.69; H, 6.99.

3.27. 5-Methoxycarbonylpentyl 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 (31)

Alcohol **29** (580 mg, 0.5 mmol) was treated with thioglycoside **18** (271 mg, 0.612 mmol) as described above and chromatography gave 5-methoxycarbonylpentyl 4-azido-3-*O*-benzyl-2-*O*-bromoacetyl-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 (**30**, 630 mg, 84%), $[\alpha]_D$ +2.3° (*c* 0.8). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.10 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 5.09 (br s, 1H, H-1^{III}), 5.05 (dd, 1H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 9.6 Hz, H-2^{IV}), 4.86–4.55 (m, 16H, 7 CH_2Ph, incl, ∼4.70, d, partially overlapped, $J_{1,2}$ ∼ 8 Hz, H-1^{IV}, 4.66, partially overlapped, H-1^{I}), 4.12 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.4 Hz, H-3^{II}), 4.09 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.7 Hz, H-3^{III}), 4.01 (dd, 1H, $J_{1,2}$ 2.0, $J_{2,3}$ 2.9 Hz, H-2^{I}), ∼3.84 (dd, 1H, H-2^{II}), 3.83 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.4 Hz, H-3^{I}), 3.82 (dd, 1H, H-2^{III}), 3.80–3.76 (m, 2H, H-5^{II,III}), 3.65 (s, 3H, $COOCH_3$), 3.64–3.50 (m,

5H, H-2^{II}, 4^{II,III},5^{I},1″a), 3.40 (t, 2H, *J* 9.3 Hz, H-4^{I},3^{IV}), 3.38 (m, H-1″b), 3.35, 3.32 (2d, ^{2}J 12.6 Hz, CH_2Br), 3.14 (dd, 1H, $J_{3,4}$ 9.3, $J_{4,5}$ 9.8 Hz, H-4^{IV}), 3.83 (m, 1H, H-5^{IV}), 2.31 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.66–1.61 (m, 2H, H-4″a,b), 1.58–1.53 (m, 2H, H-2″a,b), 1.39–1.32 (m, 2H, H-3″a,b), 1.27 (d, 6H, $J_{5,6}$ 6.2 Hz, H-6^{I,II}), 1.21 (d, $J_{5,6}$ 6.3 Hz, H-6^{III}), 1.13 (d, $J_{5,6}$ 5.9 Hz, H-6^{IV}). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 100.62 (C-1^{IV}), 102.23 (br, C-1^{III}), 98.87 (C-1^{I}), 98.75 (br, C-1^{II}), 81.06 (C-3^{IV}), 80.52 (C-4^{III}), 80.51 (C-4^{I}), 80.45 (C-4^{II}), 80.06 (C-3^{I}), 78.87 (C-3^{III}), 78.58 (C-2^{II}), 78.00 (2 C, C-2^{III},3^{II}), 75.45 (*C*H_2Ph), 75.10 (C-2^{IV}), 75.04, 74.83 (2 *C*H_2Ph), 74.66 (C-2^{I}), 74.54, 73.32, 72.40, 71.96 (4 *C*H_2Ph), 70.61 (C-5^{IV}), 68.52 (C-5^{II}), 68.37 (C-5^{III}), 67.84 (C-5^{I}), 67.72 (C-4^{IV}), 67.14 (C-1″), 51.48 (COO*C*H_3), 33.93 (C-5″), 29.11 (C-2″), 25.73 (C-3″), 25.20 (CH_2Br), 24.70 (C-4″), 18.21 (C-6^{IV}), 18.01, 17.90 (C-6^{I,II}), 17.85 (C-6^{III}). ESI-MS: *m*/*z* 1550.5834 ([M−H+HCOOH]$^+$) $C_{82}H_{96}BrN_3O_{19}$–H+HCOOH requires 1550.5798.

Deacylation of the foregoing fully protected tetrasaccharide **30** (0.63 g) gave alcohol **31** (0.53g, 93%), $[\alpha]_D$ +10.5° (*c* 0.5). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.11 (d, 1H, $J_{1,2}$ 2.0 Hz, H-1^{II}), 5.08 (br s, 1H, H-1^{III}), 4.91–4.37 (m, 16H, 7 C*H*$_2$Ph, incl., ∼4.67 d, partially overlapped, $J_{1,2}$ ∼ 1.7 Hz, H-1^{I}), 4.39, d, partially overlapped, $J_{1,2}$ 7.7 Hz, H-1^{IV}, 4.11 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.3 Hz, H-3^{II}), 4.04 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.6 Hz, H-3^{III}), 4.02 (dd, 1H, $J_{2,3}$ 2.9 Hz, H-2^{I}), 3.86 (dd, 1H, H-2^{III}), 3.84 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.4 Hz, H-3^{I}), 3.80 (dd, 1H, H-2^{II}), 3.78–3.74 (m, 2H, H-5^{II,III}), 3.67–3.59 (m, 6H, H-4^{III},5^{I},1″a, incl., 3.65, s, $COOCH_3$), 3.53–3.50 (m, 2H, H-2^{IV},4^{II}), 3.40 (t, 1H, *J* 9.2 Hz, H-4^{I}), 3.36–3.31 (m, 2H, H-3^{IV},1″b), 3.09–3.06 (m, 2H, H-4^{IV},5^{IV}), 2.69 (br s, 1H, OH), 2.31 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.66–1.61 (m, 2H, H-4″a,b), 1.58–1.53 (m, 2H, H-2″a,b), 1.40–1.32 (m, 2H, H-3″a,b), 1.28 (d, partially overlapped, $J_{5,6}$ H-6^{I}), 1.25 (d, partially overlapped, $J_{5,6}$ 6.1 Hz, H-6^{III}), 1.24 (d, partially overlapped, $J_{5,6}$ 6.1 Hz, H-6^{II}), 1.17 (d, $J_{5,6}$ 5.8 Hz, H-6^{IV}). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 103.70 (C-1^{IV}), 99.97 (br, C-1^{III}), 98.86 (C-1^{I}), 98.70 (br, C-1^{II}), 82.05 (C-3^{IV}), 80.64 (C-4^{III}), 80.56 (C-4^{I}), (C-3^{I}), 80.53 (C-4^{II}), 80.05 (C-3^{I}), 79.92 (C-3^{III}), 78.25 (C-2^{III}), 77.85 (C-2^{II}), 77.49 (C-3^{II}), 75.71 (C-2^{IV}), 75.47, 75.23, 74.81 (2 C) (4 *C*H_2Ph), 74.60 (C-2^{I}), 73.17, 72.42, 72.00 (3 *C*H_2Ph), 70.67 (C-5^{IV}), 68.52 (C-5^{II}), 68.44 (C-5^{III}), 67.85 (C-5^{I}), 67.15 (C-1″), 67.03 (C-4^{IV}), 51.48 (COO*C*H_3), 33.93 (C-5″), 29.11 (C-2″), 25.73 (C-3″), 24.70 (C-4″), 18.50 (C-6^{IV}), 18.01 (2 C, C-6^{II,III}), 17.93 (C-6^{I}). ESI-MS: *m*/*z* 1430.6578 ([M−H+HCOOH]$^+$). Anal. Calcd for $C_{85}H_{90}N_3O_{18}$: C, 69.29; H, 6.91; N, 3.03. Found: C, 69.51; H, 7.16; N, 2.92.

3.28. 5-Methoxycarbonylpentyl 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-rha-mnopyranoside (32)

Methylation of alcohol **31** (600 mg, 0.43 mmol), as described above for similar conversions, gave amorphous **32** (579 mg, 96%), $[\alpha]_D$ +2° (*c* 1). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.11 (br s, 1H, H-1^{III}), 5.08 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 4.97–4.43 (m, 16H, 7C*H*$_2$Ph, incl, ∼4.66, d, partially overlapped, $J_{1,2}$ ∼ 1.8 Hz, H-1^{I}, 4.61, d, partially overlapped, $J_{1,2}$ 8.0 Hz, H-1^{IV}), 4.13 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.4 Hz, H-3^{II}), 4.10 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.7 Hz, H-3^{III}), 4.00 (dd, 1H, $J_{2,3}$ 2.8 Hz, H-2^{I}), 3.88 (dd, 1H, $J_{1,2}$ 1.7 Hz, H-2^{III}), 3.82 (dd, partially overlapped, H-3^{I}), 3.81–3.75 (m, 3H, H-2^{II},5^{II,III}), 3.65–3.58 (m, 9H, H-4^{III},5^{I},1″a, incl., 3.65, s, $COOCH_3$, OCH_3-2), 3.56 (bt, 1H, H-4^{II}), 3.40 (t, 1H, *J* 9.5 Hz, H-4^{I}), 3.36–3.31 (m, H-3^{IV}, 1″b), 3.12 (dd, 1H, $J_{2,3}$ 9.1 Hz, H-2^{IV}), 3.10–3.04 (m, 2H, H-4^{IV},5^{IV}), 2.31 (t, 2H, *J* 7.4 Hz, H-5″a,b), 1.66–1.61 (m, 2H, H-4″a,b), 1.57–1.53 (m, 2H, H-2″a,b), 1.37–1.32 (m, 2H, H-3″a,b), 1.27 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{III}), 1.26 (d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.25 (d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6^{II}), 1.10 (d, $J_{5,6}$ 5.8 Hz, H-6^{IV}). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 103.51 ($J_{C\text{-}1,H\text{-}1}$ 159 Hz, C-1^{IV}), 100.23 (br, $J_{C\text{-}1,H\text{-}1}$ 167 Hz, C-1^{III}), 98.96 (br, $J_{1,2}$ 168 Hz, C-1^{II}), 98.90 ($J_{C\text{-}1,H\text{-}1}$ 170 Hz, C-1^{I}), 84.76 (C-2^{IV}), 82.66 (C-3^{IV}), 80.90 (C-4^{III}), 80.56 (C-4^{I}), 80.53 (C-4^{II}), 80.06 (C-3^{I}), 79.27 (C-2^{III}), 78.50 (C-3^{III}), 78.01 (C-2^{II}), 77.69 (C-3^{II}), 75.46, 75.40, 74.73, (3 *C*H_2Ph), 74.72 (C-2^{I}), 74.57, 73.30, 72.36, 72.09 (4 *C*H_2Ph), 70.18 (C-5^{IV}), 68.59 (C-5^{II}), 68.35 (C-5^{III}), 67.87 (C-5^{I}), 67.57 (C-4^{IV}), 67.16 (C-1″), 60.72 (OCH_3), 51.46 (COO*C*H_3), 33.94 (C-5″), 29.14 (C-2″), 25.74 (C-3″), 24.71 (C-4″), 18.00 (C-6^{IV}), 17.99, 17.94, 17.92 (C-6^{I,II,III}). ESI-MS: *m*/*z* 1422.6631 ([M+Na]$^+$). Anal. Calcd for $C_{81}H_{97}N_3O_{18}$: C, 69.46; H, 6.98; N, 3.00. Found: C, 69.73; H, 7.09; N, 3.00.

3.29. 5-Methoxycarbonylpentyl 3-*O*-benzyl-4,6-dideoxy-4-(3-hydroxy-3-methylbutyramido)-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 (34)

Azide **32** (560 mg) was treated with hydrogen sulfide as described in the general procedure for azide to amine conversions, to give 5-methoxycarbonylpentyl 4-amino-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 (**33**, 490 mg, 88%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.12 (br s, 1H, H-1^{III}), 5.08 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 5.01–4.45 (m, 16H, 7 C*H*$_2$Ph, incl, 4.70, d, partially overlapped, $J_{1,2}$ ∼ 7.7 Hz, H-1^{IV}, ∼4.66, d, overlapped, H-1^{I}), 4.17 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.6 Hz, H-3^{III}), 4.13 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.6 Hz, H-3^{II}), 3.99 (dd, 1H, $J_{2,3}$ 2.8 Hz, H-2^{I}), 3.92 (dd, 1H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.0 Hz, H-2^{III}), 3.82 (dd, partially overlapped, H-3^{I}), 3.82–3.75 (m, 3H, H-2^{II},5^{II,III}), 3.65–3.58 (m, 9H, H-4^{III},5^{I},1″a, incl., 3.65, s, $COOCH_3$, OCH_3-2), 3.56 (bt, 1H, H-4^{II}), 3.40 (t, 1H, *J* 9.5 Hz, H-4^{I}), 3.46, 3.33 (2t, *J* 6.4 Hz, H-1″b), 3.16–3.12 (m, 2H, H-3^{IV},2^{IV}), 3.05 (m, 1H, H-5^{IV}), 2.48 (m, 1H, H-4^{IV}), 2.31 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.66–1.61 (m, 2H, H-4″a,b), 1.57–1.52 (m, 2H, H-2″a,b), 1.37–1.32 (m, 2H, H-3″a,b), 1.27 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{III}), 1.26 (d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.24 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{II}), 1.06 (d, $J_{5,6}$ 6.1 Hz, H-6^{IV}). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 103.81 (C-1^{IV}), 100.37 (br,

C-1^{III}), 99.03 (br, C-1^{II}), 98.90 (C-1^{I}), 85.36 (C-3^{IV}), 84.11 (C-2^{IV}), 81.00 (C-4^{III}), 80.55 (2 C, C-4^{I},4^{II}), 80.05 (C-3^{I}), 79.37 (C-2^{III}), 78.11 (C-3^{III}), 77.97 (C-2^{II}), 77.53 (C-3^{II}), 75.45, 75.01 (2 C), (3 *C*H_2Ph), 74.73 (C-2^{I}), 74.52, 73.31, 72.35, 72.11 (4 *C*H_2Ph), 72.53 (C-5^{IV}), 68.63 (C-5^{II}), 68.37 (C-5^{III}), 67.86 (C-5^{I}), 67.14 (C-1″), 60.43 (OCH_3), 58.14 (C-4^{IV}), 51.46 ($COOCH_3$), 33.94 (C-5″), 29.12 (C-2″), 25.74 (C-3″), 24.71 (C-4″), 18.03 (C-6^{IV}), 17.96, 17.92 (2 C) (C-$6^{I,II,III}$). ESI-MS: *m*/*z* 1396.6710 ($[M+Na]^+$) $C_{81}H_{99}NO_{18}Na$ requires 1396.6760.

A stirred solution of the foregoing amine (430 mg, 0.31 mmol) and 3-hydroxy-3-methylbutyric acid (55 mg, 0.65 mmol) in CH_2Cl_2 (15 mL) was treated with *N*-ethyldiisopropylamine (60 μL, 0.46 mmol) and HATU (176 mg, 0.65 mmol). After 1 h the mixture was concentrated, and chromatography of the residue gave amorphous **34** (445 mg, 97%), $[\alpha]_D$ −26° (*c* 0.8). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.32 (d, 1H, $J_{4,NH}$ 9.3 Hz, NH), 5.09 (br s, 1H, H-1^{III}), 5.08 (d, 1H, $J_{1,2}$ 2 Hz, H-1^{II}), 5.01–4.43 (m, 16H, 7 CH_2Ph, incl., ~4.66, d, overlapped, H-1^{I}, ~4,62, d, partially overlapped, H-1^{IV}), 4.12 (dd, partially overlapped, $J_{2,3}$ 3.0, $J_{3,4}$ 9.1 Hz, H-3^{II}), 4.11 (dd, partially overlapped, $J_{2,3}$ 3.0, $J_{3,4}$ ~ 9.6 Hz, H-3^{III}), 4.00 (dd, 1H, $J_{1,2}$ 2.0, $J_{2,3}$ 2.8 Hz, H-2^{I}), 3.91 (dd, 1H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.0 Hz, H-2^{III}), 3.83–3.75 (m, 4H, H-3^{I},2^{II},5^{III},5^{II}), 3.68–3.58 (m, 10H, H-4^{IV},4^{III},5^{I},1″a, incl., 3.65, s, $COOCH_3$, and 3.64, s, OCH_3-2), 3.56–3.50 (m, 1H, H-4^{II}), 3.40 (t, 1H, *J* 9.6 Hz, H-4^{I}), 3.35, 3.33 (2t, partially overlapped, H-1″b), 3.30 (t, partially overlapped, *J* 9.7 Hz, H-3^{IV}), 3.19–3.15 (m, 2H, H-2^{IV},5^{IV}), 2.31 (t, 2H, *J* 7.5 Hz, H-5″a,b), 2.19, 2.08 (2d, *J* 14.9 Hz, H-2′a,b), 1.66–1.61 (m, 4H, H-4″a,b, 2″a,b), 1.38–1.30 (m, 2H, H-3″a,b), 1.28 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{III}), 1.27 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.22, 1.18 (2 s, 6H, 2 CH_3'), 1.03 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6^{IV}). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 103.69 (C-1^{IV}), 100.34 (C-1^{III}), 98.94 (C-1^{II}), 98.86 (C-1^{I}), 84.91 (C-2^{IV}), 80.83 (C-4^{III}), 80.51 (C-4^{I}), 80.47 (C-4^{II}), 80.02 (C-3^{I}), 79.97 (C-3^{IV}), 79.15 (C-2^{III}), 78.71 (C-3^{III}), 77.91 (br, 2 C, C-2^{II},3^{II}), 74.66 (C-2^{I}), 75.45, 74.69, 74.51, 73.70, 73.37, 72.31, 72.04 (7 *C*H_2Ph), 70.85 (C-5^{IV}), 69.39 (C-3′), 68.56 (C-5^{II}), 68.31 (C-5^{III}), 67.83 (C-5^{I}), 67.12 (C-1″), 60.55 (OCH_3-2), 55.52 (C-4^{IV}), 51.47 ($COOCH_3$), 47.70 (C-2′), 33.93 (C-5″), 29.30, 29.28 (2 CH_3'), 29.10 (C-2″), 25.72 (C-3″), 24.69 (C-4″), 18.08 (C-6^{IV}), 17.99 (C-6^{II}), 17.92, 17.90 (C-$6^{I,III}$). ESI-MS: *m*/*z* 1496.7297 ($[M+Na]^+$). Anal. Calcd for $C_{86}H_{107}NO_{20}$: C, 70.04; H, 7.31; N, 0.95. Found: C, 70.00; H, 7.43; N, 1.03.

3.30. 5-Methoxycarbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutyramido)-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranoside (35)

Compound **34** (450 mg) was treated with hydrogen in the presence of palladium-on charcoal catalyst (150 mg), as described above for similar conversion, to give, after freeze-drying, the title tetrasaccharide as a white solid, (0.211 g, 83%); $[\alpha]_D$ −52.6° (*c* 0.5, H_2O); $[\alpha]_D$ −67° (*c* 0.6, MeOH). ^{1}H NMR (D_2O, 600 MHz): δ 5.04 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1^{III}), 4.94 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 4.88 (d, 1H, $J_{1,2}$ 1.4 Hz, H-1^{I}), 4.74 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^{IV}), 4.28 (dd, 1H, $J_{2,3}$ 3.2 Hz, H-2^{III}), 4.15 (dd, 1H, $J_{2,3}$ 3.1 Hz, H-2^{II}), 3.99 (dd, 1H, $J_{3,4}$ 9.6 Hz, H-3^{III}), 3.92 (dd, 1H, $J_{2,3}$ 3.3 Hz, H-2^{I}), 3.86 (m, partially overlapped, H-5^{III}), 3.84 (dd, partially overlapped, H-$3^{I,II}$), 3.79 (m, 1H, H-5^{II}), 3.72–3.66 (m, 2H, H-5^{I},1″a), 3.69 (s, partially overlapped, $COOCH_3$), 3.63 (t, partially overlapped, H-4^{IV}), 3.63 (s, partially overlapped, $COOCH_3$), 3.62 (t, partially overlapped, H-4^{III}), 3.58–3.51 (m, H-5^{IV},1″b, incl., 3.54, t, H-4^{II}, 3.53, t, H-3^{IV}), 3.48 (t, 1H, H-4^{I}), 3.13 (dd, 1H, $J_{2,3}$ 9.1 Hz, H-2^{IV}), 2.47, 2.44 (2d, 2H, *J* 13.8 Hz, H-2′a,b), 2.41 (t, 2H, *J* 7.4 Hz, H-5″), 1.66–1.58 (m, 4H, H-2″a,b,4″a,b), 1.43–1.34 (m, 2H, H-3″a,b), 1.32 (d, partially overlapped, H-6^{III}), 1.31, 1.30 (2 s, partially overlapped, 2 CH_3'), 1.29 (d, partially overlapped, H-6^{I}), 1.28 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{II}), 1.22 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6^{IV}); ^{13}C NMR (D_2O, 150 MHz): δ 106.38 (C-1^{IV}), 104.83 (C-1^{II*}), 104.82 (C-1^{III*}), 101.00 (C-1^{I}), 85.99 (C-2^{IV}), 82.32 (C-3^{III}), 81.43 (C-2^{I}), 80.69 (C-3^{II}), 75.56 (C-3^{IV}), 74.89 (C-4^{I}), 74.01 (C-4^{II}), 73.84 (C-4^{III}), 73.49 (C-5^{IV}), 72.93 (C-3′), 72.78 (C-3^{I}), 72.55 (C-2^{II}), 72.53 (C-2^{III}), 72.06 (C-5^{II}), 72.03 (C-5^{III}), 71.51 (C-5^{I}), 70.53 (C-1″), 62.77 (OCH_3-2), 59.29 (C-4^{IV}), 54.81 ($COOCH_3$), 51.64 (C-2′), 36.30 (C-5″), 31.00, 30.82 (2 CH_3'), 30.80 (C-2″), 27.63 (C-3″), 26.72 (C-4″), 19.77 (C-6^{IV}), 19.40 (C-6^{II}), 19.35 (C-6^{I}), 19.34 (C-6^{III}); ESI-MS: *m*/*z* 866.4018 ($[M+Na]^+$) $C_{37}H_{65}NO_{20}Na$ requires 866.3998.

3.31. 5-Methoxycarbonylpentyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranosyl-(1 → 2)-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (36)

Glycosyl acceptor **10** (576 mg, 0.49 mol) and glycosyl donor **22** were treated as described in the general procedure, and chromatography gave first the desired β-linked substance **36** (480 mg, 66.3%), $[\alpha]_D$ +39° (*c* 0.9). ^{1}H NMR ($CDCl_3$, 600 MHz): 5.58 (dd, 1H, $J_{1,2}$ 1.9, $J_{2,3}$ 3.3 Hz, H-2^{III}), 5.39 (t, 1H, *J* 9.7 Hz, H-4^{III}), 5.31 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{III}), 5.14 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 5.08 (dd, 1H, $J_{1,2}$ 7.8, $J_{2,3}$ 9.3 Hz, H-2^{IV}), 5.05–4.29 (5 d, partially overlapped, 5 CH_2Ph), 4.66 (d, partially overlapped, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.56 (d, partially overlapped, H-1^{IV}), 4.37 (dd, 1H, $J_{2,3}$ 3.4, $J_{3,4}$ 9.5 Hz, H-3^{III}), 4.18 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.3 Hz, H-3^{II}), 4.03–3.98 (m, 2H, H-2^{I},5^{III}), 3.85 (dd, 1H, $J_{2,3}$ 3.1 Hz, H-2^{II}), 3.83–3.79 (m, 2H, H-3^{I}, 5^{II}), 3.64 (t, partially overlapped, *J* 9.4 Hz, H-4^{II}), 3.65 (s, partially overlapped, $COOCH_3$), 3.64–3.55 (m, 3H, H-5^{I}, 1″a), 3.42 (t, 1H, *J* 9.2 Hz, H-3^{IV}), 3.37 (t, 1H, *J* 9.5 Hz, H-4^{I}) 3.34, 3.32 (2t, 1H, *J* 6.5 Hz, H-1″b), 3.13–3.06 (m, 2H, H-5^{IV},4^{IV}), 2.31 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.65–1.60 (m, 2H, H-4″a,b), 1.55–1.52 (m, 2H, H-2″a,b), 1.37–1.31 (m, partially overlapped, H-3″a,b), 1.31 (d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6^{II}), 1.22 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.09 (d, 3H, $J_{5,6}$ 5.7 Hz, H-6^{IV}), 1.06 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{III}); ^{13}C NMR ($CDCl_3$): δ 100.76 (C-1^{IV}), 99.01 (br, C-1^{III}), 98.77 (C-1^{I}), 98.38 (C-1^{II}), 80.89 (C-3^{IV}), 80.39 (C-4^{I}), 80.21 (C-4^{II}), 80.12 (C-3^{I}), 78.97 (C-3^{II}), 78.11 (C-2^{II}), 75.38, 75.32 (2 *C*H_2Ph), 75.04

(C-2^{I}), 75.00 (C-3^{III}) 74.45 (*C*H_2Ph), 73.54 (C-2^{IV}), 72.98 (C-4^{III}), 72.47 (*C*H_2Ph), 72.25 (C-2^{III}), 71.59 (*C*H_2Ph), 70.67 (C-5^{IV}), 68.41 (C-5^{II}), 67.82 (C-5^{I}), 67.06 (C-1″), 67.03 (C-4^{IV}), 66.79 (C-5^{III}), 51.43 (COO*C*H_3), 33.91 (C-5″), 28.09 (C-2″), 25.71 (C-3″), 24.68 (C-4″), 18.12 (C-6^{II}), 17.99 (C-6^{I}), 17.83 (C-6^{IV}), 17.51 (C-6^{III}); ESI-MS: *m*/*z* 1540.6309 ($[M+Na]^+$). Anal. Calcd for $C_{87}H_{95}N_3O_{21}$: C, 68.80; H, 6.31; N, 2.77. Found: C, 68.76; H, 6.47; N, 2.74.

Eluted next was a small amount of material whose NMR data ($CDCl_3$, 600 MHz) showed that it was the α-anomer, 5-methoxycarbonylpentyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranosyl-(1 → 2)-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**89**): ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.55 (dd, 1H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.0 Hz, H-2^{III}), 5.45 (t, 1H, *J* 9.8 Hz, H-4^{III}), 5.28 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1^{IV}), 5.15 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1^{III}), 5.04 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{II}), 4.89 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-2^{IV}), 4.76–4.33 (5 d, partially overlapped, 5 CH_2Ph), 4.57 (d, partially overlapped, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.32 (dd, $J_{2,3}$ 3.2, $J_{3,4}$ 9.9 Hz, H-3^{III}), 4.07 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.3 Hz, H-3^{II}), 4.03–3.96 (m, 1H, H-5^{III}), 3.92 (dd, 1H, $J_{2,3}$ 3.0 Hz, H-2^{I}), 3.76–3.74 (m, 2H, H- 2^{II},3^{I}), 3.71–3.66 (m, H, H-5^{II}), 3.61 (t, *J* 9.7 Hz, H-3^{IV}), 3.57 (s, 3H, COOCH_3), 3.54–3.49 (m, 3H, H-5^{I},4^{II},1″a), 3.45–3.40 (m, 1H, H-5^{IV}), 3.27 (t, partially overlapped, *J* 9.5 Hz, H-4^{I}), 3.23 (m, partially overlapped, H-1″b), 2.92 (dd, 1H, $J_{4,5}$ 10.1 Hz, H-4^{IV}), 2.23 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.58–1.52 (m, 2H, H-4″a,b), 1.49–1.46 (m, 2H, H-2″a,b), 1.30–1.24 (m, partially overlapped, H-3″a,b), 1.21 (d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6^{II}), 1.22 (d, 6H, $J_{5,6}$ 6.2 Hz, H-$6^{I,III}$), 0.90 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{IV}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 99.27 (br, C-1^{III}), 98.77 (C-1^{I}), 98.68 (C-1^{II}), 93.72 (C-1^{IV}), 80.39 (C-4^{I}), 80.35 (C-4^{II}), 80.05 (C-3^{I}), 78.30 (C-3^{II}), 77.96 (C-2^{II}), 77.62 (C-3^{IV}), 75.47, 75.34, 75.24 (3 *C*H_2Ph), 74.96 (C-2^{I}), 73.52 (C-2^{IV}), 72.64 (C-4^{III}), 72.39 (*C*H_2Ph), 72.17 (C-3^{III}), 71.89 (*C*H_2Ph), 68.73 (C-2^{III}), 68.57 (C-5^{II}), 67.78 (C-5^{I}), 67.33 (C-4^{IV}), 67.15 (C-1″), 67.08 (C-5^{III}), 66.51 (C-5^{IV}), 51.46 (COO*C*H_3), 33.94 (C-5″), 29.11 (C-2″), 25.74 (C-3″), 24.71 (C-4″), 18.08 (C-6^{II}), 17.99 (C-6^{IV}), 17.88, 17.60 (C-$6^{I,III}$); ESI-MS: *m*/*z* 1535.6843 ($[M+NH_4]^+$) $C_{87}H_{96}N_4O_{21}$ requires 1535.6802.

3.32. 5-Methoxycarbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutyramido)-β-D-glucopyranosyl-(1 → 2)-(α-L-rhamnopyranosyl)-(1 → 3)-(α-L-rhamnopyranosyl)-(1 → 2)-α-L-rhamnopyranoside (40)

Azide **36** (290 mg) was converted to the corresponding amine, 5-methoxycarbonylpentyl 4-amino-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranosyl-(1 → 2)-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**37**, 109 mg, 55%) as described in the general procedure; some unchanged starting azide was recovered. The intended conversion was confirmed by the ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of the product, which was very similar to that of the starting azide and showed the characteristic upfield shift of the signal for H-4^{IV}(δ 2.56 vs 3.07 in **36**). The same could be concluded from the ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) showing upfield shift of the signal for C-4^{IV} (δ 57.38 vs 67.03), ESI-MS: *m*/*z* 1492.6567 ($[M+1]^+$) $C_{87}H_{98}NO_{21}$ requires 1492.6631.

The foregoing amine (109 mg, 0.073 mmol) was processed according to the general procedure for amidation to give, after chromatography, 5-methoxycarbonylpentyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-4-(3-hydroxy-3-methylbutyramido)-β-D-glucopyranosyl-(1 → 2)-(2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 3)-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**38**, 90 mg, 78%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.83 (d, 1H, $J_{4,NH}$ 8.3 Hz, NH), 5.62 (dd, 1H, $J_{1,2}$ 2.0, $J_{3,4}$ 3.3 Hz, H-2^{III}), 5.42 (t, 1H, *J* 9.5 Hz, H-4^{III}), 5.33 (d, 1H $J_{1,2}$ 1.9 Hz, H-1^{III}), 5.16–5.13 (m, 2H, H-1^{II},2^{IV}), 5.07–4.30 (5 d, partially overlapped, 5 CH_2Ph), 4.67 (d, partially overlapped, $J_{1,2}$ 7.7 Hz, H-1^{IV}), 4.66 (d, partially overlapped, $J_{1,2}$ ~ 2.0 Hz, H-1^{I}), 4.39 (dd, partially overlapped, $J_{2,3}$ 3.5, $J_{3,4}$ 9.6 Hz, H-3^{III}), 4.18 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.2 Hz, H-3^{II}), 4.00 (m, 2H, H-2^{I},5^{III}), 3.87 (t, partially overlapped, *J* 9.9 Hz, H-3^{IV}), 3.86 (dd, partially overlapped, H-2^{II}), 3.83–3.80 (m, 2H, H-3^{I},5^{II}), 3.65 (t, partially overlapped, H-4^{II}), 3.64 (s, partially overlapped, $COOCH_3$), 3.63–3.57 (m, 3H, H-5^{I}, 5^{IV},1″a), 3.38-3.32 (m, 3H, H-4^{I},4^{II},1′b), 2.30 (t, 2H, *J* 7.3 Hz, H-5″a,b), 2.11 (dd, 2H, *J* 15.1 Hz, H-2′), 1.66–1.60 (m, 2H, H-4″a,b), 1.57–1.52 (m, 2H, H-2″a,b), 1.37–1.32 (m, partially overlapped, 2H, H-3″a,b), 1.31 (d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6^{II}), 1.22 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.16, 1.14 (2 CH_3'), 1.06 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{III}), 0.99 (d, $J_{5,6}$ 6.4 Hz, H-6^{IV}). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 100.99 (C-1^{IV}), 99.09 (br, C-1^{III}), 98.76 (C-1^{I}), 98.44 (br, C-1^{II}), 80.39 (C-4^{I}), 80.29 (C-4^{II}), 80.10 (C-3^{I}), 78.91 (C-3^{II}), 78.12 (C-2^{II}), 77.97 (C-3^{IV}), 75.42, 75.33 (2 *C*H_2Ph), 75.22 (C-3^{III}), 75.03 (C-2^{I}), 73.43 (C-2^{IV}), 72.95 (C-4^{III}), 72.45 (*C*H_2Ph), 72.31 (C-2^{III}), 71.86, 71.61 (2 *C*H_2Ph), 70.05 (C-5^{IV}), 69.43 (C-3′), 68.42 (C-5^{II}), 67.82 (C-5^{I}), 67.10 (C-1″), 66.82 (C-5^{III}), 56.38 (C-4^{IV}), 51.44 (COO*C*H_3), 47.70 (C-2′), 33.92 (C-5″), 29.30, 29.26 (2 CH_3'), 29.09 (C-2″), 25.71 (C-3″), 24.69 (C-4″), 18.11 (C-6^{IV}), 17.83 (C-6^{I}), 17.63 (C-6^{III}), 17.50 (C-6^{IV}). ESI-MS: *m*/*z* 1614.6956 ($[M+Na]^+$) $C_{92}H_{105}NO_{23}Na$ requires 1614.6975.

The foregoing tetrasaccharide **38** (90 mg) was debenzoylated, to give alcohol **39** (50 mg, 92%), ESI-MS: *m*/*z* 1302.6256 ($[M+Na]^+$) $C_{71}H_{93}NO_{20}Na$ requires 1302.6341.

Debenzylation of **39**, as described above for similar conversions, gave, after freeze-drying, the title tetrasaccharide **40** as a white solid (23 mg, 72%), $[\alpha]_D$ −63° (*c* 0.5, H_2O). ^{1}H NMR (D_2O, 600 MHz): δ 5.04 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{III}), 4.93 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.88 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.70 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1^{IV}), 4.28 (dd, 1H, $J_{2,3}$ 3.3 Hz, H-2^{III}), 4.15 (dd, 1H, $J_{2,3}$ 3.2 Hz, H-2^{II}), 4.01 (dd, 1H, $J_{3,4}$ 9.6 Hz, H-3^{III}), 3.91 (dd, 1H, $J_{2,3}$ 3.3 Hz, H-2^{I}), 3.88 (m, H-5^{III}), 3.84 (dd, 2H, $J_{3,4}$ 9.7 Hz, superimposed, H-$3^{I,II}$), 3.79 (m,

1H, H-5^{II}), 3.72–3.66 (m, 5H, H-5^{I},1″a, incl., s, 3.69, COOCH$_3$), 3.64 (t, partially overlapped, H-4^{IV}), 3.63 (t, partially overlapped, H-4^{III}), 3.60 (m, partially overlapped, H-5^{IV}), 3.54 (m, partially overlapped, H-1″b), 3.54 (t, partially overlapped, H-4^{II}), 3.52 (t, partially overlapped, H-3^{IV}), 3.48 (t, 1H, H-4^{I}), 3.41 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-2^{IV}), 2.48, 2.45 (2 d, 2H, J 13.8 Hz, H-2′a,b), 2.41 (t, 2H, J 7.4 Hz, H-5″), 1.66–1.56 (m, 4H, H-2″a,b, 4″a,b), 1.44–1.33 (m, 2H, H-3″), 1.31 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{III}), 1.31, 1.30 (2 s, partially overlapped, 2 CH′$_3$), 1.29 (d, partially overlapped, H-6^{I}), 1.28 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{II}), 1.23 (d, 3H, $J_{5,6}$ 6.0 Hz, H-6^{IV}); ^{13}C NMR (D$_2$O, 150 MHz): δ 106.27 ($J_{C\text{-}1,H\text{-}1}$ 162 Hz, C-1^{IV}), 104.86, 104.85 (C-1^{II}, C-1^{III}), 101.04 (C-1^{I}), 82.36 (C-3^{III}), 81.46 (C-2^{I}), 80.75 (C-3^{II}), 76.82 (C-2^{IV}), 76.15 (C-3^{IV}), 74.95 (C-4^{I}), 74.05 (C-4^{II}), 73.99 (C-4^{III}), 73.75 (C-5^{IV}), 72.97 (C-3′), 72.84 (C-3^{I}), 72.59 (C-2^{II}), 72.56 (C-2^{III}), 72.10 (C-5^{II}), 71.77 (C-5^{III}), 71.56 (C-5^{I}), 70.59 (C-1″), 59.33 (C-4^{IV}), 54.86 (COO*C*H$_3$), 51.66 (C-2′), 36.35 (C-5″), 31.05, 30.88 (2 CH′$_3$), 30.83 (C-2″), 27.67 (C-3″), 26.75 (C-4″), 19.86 (C-6^{IV}), 19.44 (C-6^{II}), 19.42 (C-6^{I}), 19.38 (C-6^{III}); ESI-MS: *m*/*z* 852.3842 ([M+Na]$^+$) $C_{36}H_{63}NO_{20}$ requires 852.3841.

3.33. 5-Methoxycarbonylpentyl 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranoside (41)

Methyl 6-hydroxyhexanoate[22] (0.64 g, 4.4 mmol) and 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide[28] (2 g, 3.6 mmol) were condensed as described above for similar conversions, to give the amorphous glycoside **41** (1.88 g, 84%), $[\alpha]_D$ +121° (*c* 0.9). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 5.83 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 10.1 Hz, H-3), 5.67 (t, partially overlapped, J 9.8 Hz, H-4), 5.65 (dd, partially overlapped, $J_{1,2}$ 1.8, $J_{2,3}$ 3.6 Hz, H-2), 4.99 (d, 1H, H-1), 4.23–4.13 (m, 1H, H-5), 3.81, 3.79 (2 t, 1H, J 6.5 Hz, H-1′a), 3.69 (s, 3H, COOCH$_3$), 3.56, 3.52 (2 t, 1H, H-1′b), 2.38 (t, 2H, J 7.5 Hz, H-5″), 1.77–1.66 (m, 4H, H-4″a,b,2″a,b), 1.53–1.43 (m, 2H, H-3″a,b), 1.36 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 97.54 (C-1), 71.89 (C-4), 70.95 (C-3), 70.05 (C-2), 68.11 (C-1″), 66.63 (C-5), 51.48 (COO*C*H$_3$), 33.94 (C-5″), 29.09 (C-2″), 25.70 (C-3″), 24.69 (C-4), 17.67 (C-6). ESI-MS: *m*/*z* 627.2211 ([M+Na]$^+$). Anal. Calcd for $C_{34}H_{36}O_{10}$: C, 67.54; H, 6.00. Found: C, 67.80; H, 5.94.

3.34. 5-Methoxycarbonylpentyl α-L-rhamnopyranoside (42)

Conventional debenzoylation of **41** gave the title rhamnoside **42** in virtually theoretical yield, mp 62–63 °C (from EtOAc), $[\alpha]_D$ −58.6° (*c* 1.1). ^{1}H NMR (CD$_3$OD, 600 MHz): δ 4.65 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1), 3.78 (dd, 1H, $J_{2,3}$ 3.4 Hz, H-2), 3.68, 3.65 (2 t, partially overlapped, J 6.5 Hz, H-1′a), 3.66 (s, partially overlapped, COOCH$_3$), 3.63 (dd, 1H, $J_{3,4}$ 9.5 Hz, H-3), 3.59–3.54 (m, 1H, H-5), 1.41, 1.38 (2, t, 1H, H-1′b), 3.36 (t, 1H, J 9.5 Hz, H-4), 2.34 (t, 2H, J 7.6 Hz, H-5″a,b), 1.66–1.57 (m, 4H, H-4″a,b,2″a,b), 1.44–1.37 (m, 2H, H-3″a,b), 1.26 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6); ^{13}C NMR (CD$_3$OD, 150 MHz): δ 101.58 (C-1), 73.93 (C-4), 72.41 (C-3), 72.28 (C-2), 69.71 (C-5), 68.23 (C-1″), 51.99 (COO*C*H$_3$), 34.67 (C-5″), 30.26 (C-2″), 26.88 (C-3″), 25.76 (C-4″), 18.02 (C-6). ESI-MS: *m*/*z* 315.1 ([M+Na]$^+$). Anal. Calcd for $C_{13}H_{24}O_7$: C, 53.41; H, 8.28. Found: C, 53.43; H, 8.31.

3.35. 5-Methoxycarbonylpentyl (2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (43)

Compound **5** (380 mg, 0.8 mmol) was treated with 2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl bromide,[28] as described for preparation of **41**. After processing and chromatography, disaccharide **43** (500 mg, 67%) had $[\alpha]_D$ +9.8° (*c* 0.4). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 5.91–5.86 (m, 2H, H-2^{II},3^{II}), 5.68–5.61 (m, 1H, H-4^{II}), 5.22 (d, 1H, H-1^{II}), 4.97–4.67 (m, 5H, 2 C*H*$_2$Ph, incl., 4.81, d, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.34–4.25 (m, 1H, H-5^{II}), 4.03 (bt, 1H, H-2^{I}), 3.90 (dd, 1H, $J_{2,3}$ 3.8, $J_{3,4}$ 8.8 Hz, H-3^{I}), 3.78–3.60 (m, 6H, H-4^{I},5,1′a, incl., 3.66, s, COOCH$_3$), 3.42, 3.86 (2 t, 1H, J 6.5 Hz, H-1′a), 2.32 (t, 2H, J 7.5 Hz, H-5″a,b), 1.71–1.55 (m, 4H, H-4″a,b,2″a,b), 1.44–1.34 (m, partially overlapped, H-3″a,b), 1.39 (d, partially overlapped, $J_{5,6}$ 5.9 Hz, H-6^{I}), 1.35 (d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6^{II}); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 99.35 (C-1^{II}), 98.76 (C-1^{I}), 80.08 (C-4^{I}), 79.69 (C-3^{I}), 76.15 (C-2^{I}), 75.48, 72.42 (2 *C*H$_2$Ph), 71.80 (C-4^{II}), 70.52 (C-3^{II}), 69.88 (C-2^{II}), 68.08 (C-5^{I}), 67.23 (C-1″), 66.99 (C-5^{II}), 51.39 (COO*C*H$_3$), 33.85 (C-5″), 29.05 (C-2″), 25.66 (C-3″), 24.63 (C-4″), 17.88 (C-6^{I}), 17.61 (C-6^{II}). ESI-MS: *m*/*z* 953.3739 ([M+Na]$^+$). Anal. Calcd for $C_{54}H_{58}O_{14}$: C, 69.66; H, 6.28; N,. Found: C, 69.56; H, 6.34.

3.36. 5-Methoxycarbonylpentyl (2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1 → 2)-α-L-rhamnopyranoside (44)

Hydrogenolysis of the fully protected disaccharide **43** (450 mg) gave amorphous **44** (340 mg, 94%), $[\alpha]_D$ +73° (*c* 0.6). ^{1}H NMR (CDCl$_3$): δ 5.86 (dd, 1H, $J_{1,2}$ 1.9, $J_{2,3}$ 3.3 Hz, H-2^{II}), 5.77 (dd, 1H, $J_{3,4}$ 10.0 Hz, H-3^{II}), 5.69 (t, 1H, H-4^{II}), 5.24 (d, 1H, H-1^{II}), 4.94 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.43–4.34 (m, 1H, H-5^{II}), 4.99 (dd, 1H, $J_{2,3}$ 3.3 Hz, H-2^{I}), 3.92 (bdd, 1H, $J_{3,4}$ 9.4 Hz, H-3^{I}), 3.74–3.64 (m, 6H, H-4^{I},5^{I},1″a, incl., 3.67, s, COOCH$_3$), 3.43, 3.40 (2 t, 1H, J 6.3 Hz, H-1″b), 2.33 (t, 2H, J 7.5 Hz, H-5″a,b), 1.71–1.56 (m, 4H, H-4″a,b,2″a,b), 1.45–1.34 (m, 8H, H-3″a,b, incl., 1.40, d, $J_{5,6}$ 5.7 Hz, 6^{I}, incl., 1.35, d, $J_{5,6}$ 1.35 Hz, 6^{II}). ^{13}C NMR (CDCl$_3$): δ 99.88 (C-1^{II}), 98.50 (C-1^{I}), 80.83 (C-2^{I}), 73.23 (C-4^{I}), 71.43 (C-4^{II}), 71.34 (C-3^{I}), 70.41, 70.38 (C-2^{II},3^{II}), 68.27 (C-5^{I}), 67.29 (C-1″), 67.05 (C-5^{II}), 51.38 (COO*C*H$_3$), 33.81 (C-5″), 29.00 (C-2″), 25.62 (C-3″), 24.56 (C-4″), 17.72, 17.55 (C-6^{I,II}). ESI-MS: *m*/*z* 773.2749 ([M+Na]$^+$). Anal. Calcd for $C_{40}H_{46}O_{14}$: C, 63.99; H, 6.18. Found: C, 63.85; H, 6.23.

3.37. 5-Methoxycarbonylpentyl α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranoside (45)

Debenzoylation (Zemplén) of **44** (280 mg), as described above, gave the amorphous disaccharide glycoside **45** (157 mg, 97%), $[\alpha]_D$ −31° (*c* 0.5). ^{1}H NMR (D$_2$O,

600 MHz): δ 4.94 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 4.87 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.06 (dd, 1H, $J_{2,3}$ 3.3 Hz, H-2^{II}), 3.89 (dd, 1H, $J_{2,3}$ 3.5 Hz, H-2^{I}), 3.82 (dd, 1H, $J_{3,4}$ 9.7 Hz, H-3^{I}), 3.78 (dd, 1H, $J_{3,4}$ 9.8 Hz, H-3^{II}), ~3.74 (m, partially overlapped, H-5^{II}), ~3.70 (m, partially overlapped, H-1″a), 3.69 (s, partially overlapped, $COOCH_3$), ~3.68 (m, partially overlapped, H-5^{I}), 3.53, 3.52 (2 t, 1H, H-1″a), 3.46, 3.44 (2 t, 2H, $J \sim 9.6$ Hz, H-4^{I,II} in that order), 2.40 (t, 1 H, J 7.4 Hz, H-5″a,b), 1.65–1.56 (m, 4H, H-4″a,b,2″a,b), 1.43–1.34 (m, 2H, H-3″a,b), 1.28 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.26 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{II}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 105.06 ($J_{C\text{-}1,H\text{-}1}$ 170.4 Hz, C-1^{II}), 101.08 ($J_{C\text{-}1,H\text{-}1}$ 171.0 Hz, C-1^{I}), 81.50 (C-2^{I}), 74.88 (C-4^{I}), 74.70 (C-4^{II}), 72.82 (C-3^{I}), 72.79 (C-3^{II}), 72.77 (C-2^{II}), 71.84 (C-5^{II}), 71.46 (C-5^{I}), 70.52 (C-1″), 54.84 ($COOCH_3$), 36.33 (C-5″), 30.85 (C-2″), 27.68 (C-3″), 26.76 (C-4″), 19.40 (C-6^{II}), 19.37 (C-6^{I}). ESI-MS: m/z 461.2007 ([M+Na]$^+$) $C_{19}H_{34}NO_{11}Na$ requires 461.1999.

3.38. 5-Methoxycarbonylpentyl 2,4-di-*O*-benzoyl-3-*O*-bromoacetyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (47)

Glycosyl chloride[18] **46** (500 mg, 0.58 mmol) was treated with methyl 6-hydroxyhexanoate[22] (130 mg, mmol), as described for the preparation of **41**. After processing, chromatography gave first the desired glycoside **47** (248 mg, 44%), $[\alpha]_D$ +99° (c 0.7). ^{1}H NMR ($CDCl_3$, 300 MHz): 5.56 (t, 1H, J 9.7 Hz, H-4^{I}), 5.48 (dd, 1H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.4 Hz, H-2^{I}), 5.41 (dd, 1H, $J_{2,3}$ 2.7, $J_{3,4}$ 10.0 Hz, H-3^{II}), 5.34 (t, partially overlapped, H-4^{II}), 5.16–5.15 (m, 2H, H-1^{II},2^{II}), 4.98 (d, 1H, H-1^{I}), 4.45 (dd, 1H, $J_{3,4}$ 9.9 Hz, H-3^{I}), 4.10–4.01 (m, 2H, H-5^{I,II}), 3.76, 3.73 (2 t, 1H, J 6.5 Hz, H-1′a), 3.66 (s, 3H, $COOCH_3$), 3.54–3.42 (m, partially overlapped, H-1″b), 3.45, 3.50 (2 d, partially overlapped, J 12.2 Hz, CH_2Br), 2.36 (t, J 7.5 Hz, H-5″a,b), 1.75–1.63 (m, 4H, H-4″a,b, 2″a,b, in that order), 1.49–1.39 (m, 2H, H-3″), 1.34 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.14 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{II}); ^{13}C NMR ($CDCl_3$, 75 Hz): δ 99.13 ($J_{C\text{-}1,H\text{-}1}$ 172 Hz, C-1^{II}), 97.25 ($J_{C\text{-}1,H\text{-}1}$ 172 Hz, C-1^{I}), 76.27 (C-3^{I}), 73.17 (C-4^{I}), 72.33 (C-2^{I}), 71.21 (C-3^{II}), 70.41 (C-4^{II}), 71.17 (C-2^{II}), 60.00 (C-1″), 67.39 (C-5^{II}), 66.69 (C-5^{I}), 51.41 ($COOCH_3$), 33.88 (C-5″), 29.05 (C-4″), 25.69 (C-3″), 24.88 (CH_2Br), 24.65 (C-2″), 17.70 (C-6^{I}), 17.28 (C-6^{II}); ESI-MS: m/z 997.1 ([M+Na]$^+$). Anal. Calcd for $C_{49}H_{51}BrO_{16}$: C, 60.31; H, 5.27. Found: C, 60.24; H, 5.28.

Eluted next was the orthoester **90** (190 mg, 34%, total yield of glycosylation, 78%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.64 (dd, 1H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.1 Hz, H-3^{II}), 5.58 (d, 1H, $J_{1,2}$ 2.7 Hz, H-1^{I}), 5.49 (t, J 10.0 Hz, H-4^{II}), 5.36 (t, 1H, J 9.4 Hz, H-4^{I}), 5.28 (dd, 1H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.4 Hz, H-2^{II}), 5.19 (d, 1H, H-1^{II}), 4.87 (dd, 1H, $J_{2,3}$ 4.2 Hz, H-2^{I}), 4.48–4.44 (m 1H, H-5^{II}), 4.19 (dd, 1H, $J_{3,4}$ 9.7 Hz, H-3^{I}), 3.68–3.64 (m, 1H, H-5^{I}), 3.60 (s, 3H, $COOCH_3$), 3.55, 3.52 (2 d, 2H, J 12.2 Hz, CH_2Br), 3.48–3.39 (m, 2H, H-1″a,b), 2.16 (t, 2H, J 7.1 Hz, H-5″a,b), 1.59–1.49 (m, 4H, H-2″a,b, 4″a,b), 1.34 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{II}), 1.32–1.26 (m, 2H, H-3″), 1.20 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{I}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 122.64 (C_{quart}, orthobenzoate), 99.53 (C-1^{II}), 97.35 (C-1^{I}), 78.47 (C-3^{I}), 78.01 (C-2^{I}), 71.84 (C-4^{I}), 71.30 (C-4^{II}), 70.49 (C-3^{II}), 70.26 (C-2^{II}), 69.94 (C-5^{I}), 67.42 (C-5^{II}), 63.60 (C-1″), 51.34 ($COOCH_3$), 33.71 (C-5″), 29.10 (C-2″), 25.53 (C-3″), 24.90 (CH_2Br), 24.48 (C-4″), 17.76 (C-6^{I}), 17.30 (C-6^{II}); TOF-MS: m/z 997.1 ([M+Na]$^+$) $C_{49}H_{51}BrO_{16}Na$ requires 997.2.

3.39. 5-Methoxycarbonylpentyl α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranoside (48)

Deacylation of **47** (248 mg) gave, after removal of methyl benzoate by chromatography and freeze-drying, disaccharide **48** (57 mg, 52%), $[\alpha]_D$ −62° (c 0.5). ^{1}H NMR (D_2O, 600 MHz): δ 5.02 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1^{II}), 4.74 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.05 (dd, 1H, $J_{2,3}$ 3.4 Hz, H-2^{II}), 3.99 (dd, 1H, $J_{2,3}$ 3.4 Hz, H-2^{I}), 3.83 (dd, partially overlapped, $J_{3,4}$ 9.8 Hz, H-3^{II}), ~3.80 (m, partially overlapped, H-5^{II}), 3.78 (dd, partially overlapped, $J_{3,4}$ 9.8 Hz, H-3^{I}), 3.74–3.68 (m, 5H, H-5^{I}, 1″a, incl., 3.68, s, $COOCH_3$), 3.54–3.50 (m, 2H, H-4^{I},1″b), 3.45 (t, 1H, J 9.7 Hz, H-4^{II}), 2.40 (t, 2H, J 7.4 Hz, H-5″), 1.66–1.58 (m, 4H, H-2″a,b,4″a,b), 1.42–1.35 (m, 2H, H-3″a,b), 1.28 (dd, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.27 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{II}); ^{13}C NMR (H_2O, 150 MHz): δ 105.10 ($J_{C\text{-}1,H\text{-}1}$ 170. 7 Hz, C-1^{II}), 102.42 ($J_{C\text{-}1,H\text{-}1}$ 170. 7 Hz, C-1^{I}), 80.89 (C-3^{I}), 74.78 (C-4^{II}), 74.18 (C-4^{I}), 72.91 (C-2^{II}), 72.87 (C-3^{II}), 72.71 (C-2^{I}), 71.81 (C-5^{II}), 71.50 (C-5^{I}), 70.46 (C-1″), 54.87 ($COOCH_3$), 36.39 (C-5″), 30.90 (C-2″), 27.73 (C-3″), 26.79 (C-4″), 19.37, 19.36 (C-6^{I,II}); ESI-MS: m/z 461.1972 ([M+Na]$^+$) $C_{19}H_{34}O_{11}Na$ requires 461.1999.

3.40. 5-Methoxycarbonylpentyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranoside (49)

Thioglycoside **22** (400 mg, 0.85 mmol) was treated with methyl 6-hydroxynexanoate (190 mg, 1.1 mmol) as described for the preparation of **4**. After work-up, chromatography gave first 5-methoxycarbonylpentyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-D-glucopyranoside (**91**, 21 mg, 3.5%), $[\alpha]_D$ +254° (c 0.5); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.08–5.05 (m, 2H, H-1,2), 4.83, 4.80 (2 d, 2H, J 10.7 Hz, CH_2Ph), 4.06–4.02 (m, 1H, H-3), 3.69–3.64 (m, 5H, H-5,1″a, incl., 3.64, s, COOMe), 3.37, 3.35 (2 t, 1H, J 6.4 Hz, H-1″b), 3.23 (t, 1H, J 9.8 Hz, H-4), 2.16 (t, 2 H, J 7.6 Hz, H-5″a,b), 1.58–1.52 (m, 4H, H-2″a,b, 4″a,b), 1.33 (d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6), 1.34–1.29 (m, partially overlapped, H-3″a,b); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 95.95 ($J_{C\text{-}1,H\text{-}1}$ 170 Hz, C-1), 78.27 (C-3), 75.41 (CH_2Ph), 74.31 (C-2), 68.04 (2 C, C-4,1″), 66.06 (C-5), 51.43 ($COOCH_3$), 33.82 (C-5″), 28.99 (C-2″), 25.65 (C-3″), 24.57 (C-4″), 18.35 (C-6). ESI-MS: m/z 518.2479 ([M+Li]$^+$). Anal. Calcd for $C_{27}H_{33}N_3O_7$: C, 63.39; H, 6.50; N, 8.21. Found: C, 53.56; H, 6.56; N, 8.23.

Eluted next was the β-anomer **49** (499 mg, 84%), $[\alpha]_D$ +110° (c 0.9). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.24 (dd, 1H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.4 Hz, H-2), 4.74, 4.65 (2 d, 2H, CH_2Ph), 4.45 (d, 1H, H-1), 3.85, 3.83 (2 t, 1H, J 6.1 Hz, H-1″a), 3.69 (t, 1H, J 9.1 Hz, H-3), 3.61 (s,

3H, $COOCH_3$), 3.43–3.39 (m, 1H, H-1″b), 3.35 (m, partially overlapped, H-5), 3.29 (t, partially overlapped, H-4), 2.07–1.95 (m, 2H, H-5″a,b), 1.54–1.39 (m, 7H, H-2″a,b, 4″, incl., d, 1.40, $J_{5,6}$ 5.8 Hz, H-6), 1.24–1.11 (m, 2H, H-3″). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 100.88 (C-1), 81.03 (C-3), 74.82 (CH_2Ph), 73.86 (C-2), 70.77 (C-5), 69.48 (C-1″), 67.59 (C-4), 51.33 ($COOCH_3$), 33.63 (C-5″), 28.98 (C-2″), 25.26 (C-3″), 24.35 (C-4″), 18.38 (C-6). ESI-MS: 518.2463 ($[M+Li]^+$). Anal. Calcd for $C_{27}H_{33}N_3O_7$: C, 63.39; H, 6.50; N, 8.21. Found: C, 63.53; H, 6.66; N, 8.01.

3.41. 5-Methoxycarbonylpentyl 4-azido-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranoside (50)

Debenzoylation of the foregoing benzoate **49** (520 mg) gave alcohol **50** (380 mg, 92%), $[\alpha]_D$ +47° (*c* 1). ^{1}H NMR (CDCl, 600 MHz): δ 4.79, 4.83 (2 d, 2H, ^2J 11.0 Hz, 2 CH_2Ph), 4.18 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 3.90, 3.88 (2 t, 1H, *J* 6.3 Hz, H-1′a), 3.66 (s, 3H, $COOCH_3$), 3.53 (ddd, 1H, $J_{2,3}$ 9.1, $J_{2,OH}$ 2.6 Hz, H-2), 3.48, 3.50 (2 t, 1H, H-1″b), 3.22 (m, 1H, H-5), 3.14 (dd, 1H, $J_{3,4}$ 9.6 Hz, H-4), 2.79 (d, *J* 2.6 Hz, 1H, OH), 2.32 (t, 2H, *J* 7.4 Hz, H-5″a,b), 1.70–1.58 (m, 4H, H-2″a,b, 4″a,b), 1.45–1.36 (m, 2H, H-3″a,b), 3.34 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 102.45 (C-1), 82.40 (C-3), 74.90 (C-2), 74.88 (CH_2Ph), 70.60 (C-5), 69.59 (C-1″), 67.18 (C-4), 51.47 ($COOCH_3$), 33.71 (C-5″), 28.88 (C-2″), 25.33 (C-3″), 24.32 (C-4″), 18.38 (C-6). ESI-MS 430.1926 ($[M+Na]^+$) Anal. Calcd for $C_{20}H_{29}NO_6$: C, 58.95; H, 7.17; N, 10.31. Found: C, 51.18; H, 7.34; N, 10.27.

3.42. 5-Methoxycarbonylpentyl 4-azido-3-*O*-benzyl-4,6-dideoxy-2-*O*-methyl-β-D-glucopyranoside (51)

Methylation of **50** (400 mg, 1 mmol), as described above, gave the title methyl ether (390 mg, 97.5%), $[\alpha]_D$ +38° (*c* 1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.89, 4.79 (2 d, 2H, CH_2Ph), 4.21 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 3.89, 3.87 (2 t, 1H, *J* 6.4 Hz, H-1″a), 3.66 (s, 3H, $COOCH_3$), 3.59 (s, 3H, OCH_3-2), 3.49–3.48 (2 t, 1H, H-1″b), 3.38 (t. 1H, *J* 9.2 Hz, H-3), 3.18 (m, H-5), 3.12–3.08 (m, 2H, H-2,4), 2.32 (t, 2H, *J* 7.4 Hz, H-5″a,b), 1.70–1.59 (m, 4H, H-2″,a,b, 4″), 1.47–1.36 (m, 2H, H-3″), 1.32 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6). ^{13}C NMR (150 MHz, $CDCl_3$): δ 103.25 (C-1), 84.22 (C-2), 82.72 (C-3), 75.40 (CH_2Ph), 70.31 (C-5), 69.74 (C-1″), 67.42 (C-4), 60.55 (OCH_3), 51.46 ($COOCH_3$), 33.94 (C-5″), 29.30 (C-2″), 25.59 (C-3″), 24.65 (C-4″), 18.41 (C-6). ESI-MS: *m*/*z* 428.2354 ($[M+Li]^+$). Anal. Calcd for $C_{21}H_{31}N_3O_6$: C, 59.84; H, 7.41; N, 9.97. Found: C, 60.08; H, 7.59; N, 9.99.

3.43. 5-Methoxycarbonylpentyl 4,6-dideoxy-3-*O*-benzyl-4-(3-hydroxy-3-methylbutyramido)-2-*O*-methyl-β-D-glucopyranoside (53)

The foregoing azide (400 mg) was treated with H_2S as described above for similar conversion, to give 5-methoxycarbonylpentyl 4-amino-3-*O*-benzyl-4,6-dideoxy-2-*O*-methyl-β-D-glucopyranoside (**52**, 340 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.97, 4.66 (2 d, *J* 11.5 Hz, 2H, CH_2Ph), 4.26 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 3.92, 3.90 (2 t, 1H, *J* 6.5 Hz, H-1″a), 3.66 (s, 3H, $COOCH_3$), 3.60 (s, 3H, OCH_3-2), 3.54–3.48 (2 t, 1H, H-1″b), 3.20–3.16 (m, 2H, H-3,5), 3.12 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-2), 2.53 (t, 1H, *J* 9.3 Hz, H-4), 2.32 (t, 2H, *J* 7.4 Hz, H-5″a,b), 1.71–1.61 (m, 4H, H-2″a,b, 4″a,b), 1.48–1.41 (m, 2H, H-3″), 1.40–1.32 (br s, 2H, NH_2), 1.26 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6). ^{13}C NMR (150 MHz, $CDCl_3$): δ 103.55 (C-1), 84.72 (C-2), 84.05 (C-3), 74.96 (CH_2Ph), 72.57 (C-5), 69.57 (C-1″), 60.26 (OCH_3), 57.84 (C-4), 51.41 ($COOCH_3$), 33.93 (C-5″), 29.33 (C-2″), 25.61 (C-3″), 24.65 (C-4″), 17.95 (C-6). ESI-MS 418.2219 ($[M+Na]^+$) $C_{21}H_{33}O_6Na$ requires 418.2206.

Condensation of the foregoing amine (340 mg, 0.86 mmol) with 3-hydroxy-3-methylbutyric acid (152 mg, 1.3 mmol), as described above for similar conversions, gave amide **53** (324 mg, 76%), mp 80–81 °C (from *i*-Pr_2O containing a few drops of EtOH), $[\alpha]_D$ −50° (*c* 0.7). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.68 (d, 1H, $J_{NH,4}$ 8.8 Hz, NH), 4.85, 4.62 (2 d, 2H, *J* 11.8 Hz, CH_2Ph), 4.25 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1), 4. (2 s, 1H, OH), 3.91, 3.89 (2 t, 1H, *J* 6.4 Hz, H-1a″), 3.66 (s, 3H, $COOCH_3$), 3.60 (ddd, partially overlapped, H-4), 3.59 (s, partially overlapped, OCH_3-2), 3.50, 3.49 (2 t, partially overlapped, H-1b″), ~3.46 (t, partially overlapped, H-3), ~3.44 (m, partially overlapped, H-5), 3.15 (dd, $J_{2,3}$ 8.8 Hz, H-2), 2.32 (t, 2H, *J* 7.4 Hz, H-5″a,b), 2.22, 2.13 (2 d, 2H, *J* 15.0 Hz, H-2′a,b), 1.70–1.62 (m, 4H, H-2″a,b, 4″a,b), 1.48–1.37 (m, 2H, H-3″a,b), 1.23, 1.20 (2 s, 6H, 2 CH_3'), 1.22 (d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6); ^{13}C NMR (150 MHz, $CDCl_3$): δ 103.27 (C-1), 84.44 (C-2), 79.98 (C-3), 73.81 (CH_2Ph), 70.64 (C-5), 69.60 (C-3′), 69.41 (C-1″), 60.38 (OCH_3-2), 56.02 (C-4), 51.45 ($COOCH_3$), 47.74 (C-2′), 33.95 (C-5″), 29.31 (3 C, 2 CH_3', 2″), 25.60 (C-3″), 24.65 (C-4″), 18.06 (C-6). ESI-MS 518.2760 ($[M+Na]^+$) Anal. Calcd for $C_{26}H_{41}NO_8$: C, 63.01; H, 8.34; N, 2.83. Found: C, 62.96; H, 8.40; N, 2.87.

3.44. 5-Methoxycarbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutyramido)-2-*O*-methyl-β-D-glucopyranoside (54)

Compound **53** (315 mg) was deprotected as described in the general procedure for debenzylation, to give amide **54** (250 mg, 76%), $[\alpha]_D$ −15° (*c* 0.6, H_2O). ^{1}H NMR (600 MHz, D_2O): δ 4.43 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 3.91, 3.89 (2 t, 1H, *J* 6.3 Hz, H-1a″), 3.68 (s, 3H, $COOCH_3$), 3.65, 3.64 (2 t, partially overlapped, H-1″b), 3.61 (t, partially overlapped, H-4), 3.59 (s, partially overlapped, OCH_3-2), ~3.54 (m, partially overlapped, H-5), 3.52 (t, partially overlapped, H-3), 3.03 (dd, $J_{2,3}$ 9.1 Hz, H-2), 2.47, 2.44 (2 d, 2H, *J* 13.6 Hz, H-2′a,b), 2.40 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.66–1.61 (m, 4H, H-2″a,b, 4″a,b), 1.44–1.35 (m, 2H, H-3″a,b), 1.30, 1.29 (2 s, 6H, 2 CH_3'), 1.21 (d, $J_{5,6}$ 6.1 Hz, H-6); ^{13}C NMR (150 MHz, D_2O): δ 104.85 (C-1), 86.16 (C-2), 75.84 (C-3), 73.56 (C-5), 73.06 (C-1″), 72.92 (C-3′), 63.06 (OCH_3-2), 59.33 (C-4), 54.82 ($COOCH_3$), 51.64 (C-2′), 36.35 (C-5″), 31.19 (C-2″), 31.04, 30.87 (2 CH_3''), 27.53 (C-3″), 26.76 (C-4″), 19.72 (C-6). ESI-MS: *m*/*z* 428.2264 ($[M+Na]^+$) $C_{19}H_{35}NO_8Na$ requires 428.2260.

3.45. 5-Methoxycarbonylpentyl 3-*O*-acetyl-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (55)

Reaction of thioglycoside **25** (2 g, 4.8 mmol) with methyl 6-hydroxyhexanoate[22] (1.05 g, 7.2 mmol), as described in the general procedure, gave amorphous **55** (2.3 g, 96%), $[\alpha]_D$ −6.5° (*c* 1.3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.18 (dd, 1H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.5 Hz, H-3), 4.70 (d, partially overlapped, $J_{1,2}$ 1.8 Hz, H-1), 4.72–4.55 (4 d, partially overlapped, 2 CH_2Ph), 3.83 (dd, 1H, H-2), 3.80–3.69 (m, 1H, H-5), 3.66–3.58 (m, 5H, H-4,1′a, incl., 3.65, s, OCH_3), 3.70, 3.34 (2 t, 1H, H-1′b), 2.30 (t, 2H, *J* 7.6 Hz, H-5″a,b), 1.96 (s, 3H, $COOCH_3$), 1.68–1.51 (m, 4H, H-4″a,b,2″a,b), 1.40–1.32 (m, partially overlapped, H-3), 1.32 (d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 97.66 (C-1), 79.19 (C-4), 76.31 (C-2), 74.93, 73.06 (2 *C*H_2Ph), 73.76 (C-3), 73.06 (C -4), 67.61 (C-5), 67.34 (C-1″), 51.40 (COO*C*H_3), 33.88 (C-5″), 29.00 (C-2″), 25.63 (C-3″), 24.63 (C-4″), 21.03 ($COCH_3$), 17.96 (C-6). ESI-MS: *m*/*z* 537.2 ($[M+Na]^+$). Anal. Calcd for $C_{29}H_{38}O_8$: C, 67.68; H, 7.44. Found: C, 67.84; H, 7.42.

3.46. 5-Methoxycarbonylpentyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside (56)

Conventional deacetylation of the foregoing acetate **55** (2 g) gave glycosyl acceptor **56** (1.6 g, 89%); $[\alpha]_D$ −14.7° (*c* 0.8). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.88, 4.74, 4.64, 4.59 (4 d, 4H, *J* 11.8 Hz, 2 CH_2Ph), 4.77 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 3.94, 3.92 (2 t, 1H, *J* 9.6 Hz, H-3), 3.70 (dd, 1H, $J_{2,3}$ 3.7 Hz, H-2), 3.68–3.59 (m, 5H, H-5, 1″a, incl., 3.65, s, $COOCH_3$), 3.40–3.28 (m, 2H, H-4,1″b), 2.30 (t, 2H, *J* 7.4 Hz, H-5″), 1.67–1.49 (m, 4H, H-4″a,b, 2″,a,b), 1.39–1.29 (m, 5H, H-3″, incl., 1.32, d, $J_{5,6}$ 6.3 Hz, H-6); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 96.79 (C-1), 82.27 (C-4), 78.72 (C-2), 75.03, 72.96 (2 *C*H_2Ph), 71.63 (C-3), 67.16 (C-1″), 67.05 (C-5), 51.40 (COO*C*H_3), 33.85 (C-5″), 29.02 (C-2″), 25.65 (C-3″), 24.60 (C-4″), 17.96 (C-6). ESI-MS: *m*/*z* 495.2338 ($[M+Na]^+$). Anal. Calcd for $C_{27}H_{36}O_7$: C, 67.54; H, 6.00. Found: C, 67.80; H, 5.94.

3.47. 5-Methoxycarbonylpentyl 4-azido-3-*O*-benzyl-2-*O*-bromoacetyl-4,6-dideoxy-β-D-glucopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (57)

Compound **18** (825 mg, 1.85 mmol) was treated with alcohol **56** (800 mg, 1.69 mmol) according to the general procedure, to afford **57** (950 mg, 68%), $[\alpha]_D$ +0.3° (*c* 0.8). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.10 (dd, 1H, $J_{1,2}$ 8.1 Hz, $J_{2,3}$ 9.6 Hz, H-2^{II}), 4.82–4.56 (m, 6 d, partially overlapped, *J* ∼ 11 Hz, 6 CH_2Ph), 4.76 (d, partially overlapped, *J* 8.1 Hz, H-1^{II}), 4.62 (d, partially overlapped, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.02 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.5 Hz, H-3^{I}), 3.76 (dd, 1H, H-2^{I}), 3.66 (s, partially overlapped, $COOCH_3$), 3.66–3.56 (m, partially overlapped, H-5^{I},1″a), 3.56 (t, partially overlapped, H-4^{I}), 3.49 (t, 1H, *J* 9.3 Hz, H-3^{II}), 3.38, 3.35 (2 d, 2H, *J* 12.6 Hz, CH_2Br), 3.32 (m, partially overlapped, H-1″b), 3.27 (m, partially overlapped, H-5^{II}), 3.22 (t, partially overlapped, H-4^{II}), 2.30 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.64–1.59 (m, 2H, H-4″a,b), 1.55–1.50 (m, 2H, H-2″), 1.35–1.30 (m, partially overlapped, H-3″a,b), 1.33 (d, partially overlapped, $J_{5,6}$ 5.9 Hz, H-6^{II}), 1.27 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6^{I}); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 100.68 ($J_{C\text{-}1,H\text{-}1}$ 162 Hz, C-1^{II}), 98.36 ($J_{C\text{-}1,H\text{-}1}$ 168 Hz, C-1^{I}), 81.13 (C-3^{II}), 80.46 (C-4^{I}), 79.22 (C-3^{I}), 78.04 (C-2^{I}), 75.16 (C-2^{II}), 75.06, 74.82, 73.37 (3 *C*H_2Ph), 70.66 (C-5^{II}), 67.87 (C-5^{I}), 67.85 (C-4^{II}), 67.13 (C-1″), 33.90 (C-5″), 29.01 (C-2″), 25.66 (C-3″), 25.24 (CH_2Br), 24.64 (C-4″), 18.32 (C-6^{II}), 17.81 (C-6^{I}). ESI-MS: *m*/*z* 876.2692 ($[M+Na]^+$). Anal. Calcd for $C_{42}H_{52}N_3O_{11}$: C, 59.02; H, 6.13; N, 4.92. Found: C, 59.20; H, 6.15; N, 4.89.

3.48. 5-Methoxycarbonylpentyl 4-azido-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (58)

Debromoacetylation (Zemplén) of **57** (900 mg) gave alcohol **58** (693 mg, 88%), $[\alpha]_D$ +2° (*c* 0.8). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 4.92–4.63 (m, 6 d, partially overlapped, *J* ∼ 11.5 Hz, 6 CH_2Ph), 4.59 (d, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.45 (d, partially overlapped, $J_{1,2}$ 7.8 Hz, H-1^{I}), 3.99 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.1 Hz, H-3^{I}), 3.78 (dd, 1H, H-2^{I}), 3.69–3.61 (m, 5H, H-4^{I},5^{I},1″a, incl., 3.65 s, $COOCH_3$), 3.59–3.55 (m, 2H, H-2^{II},1″), 3.40 (t, 1H, *J* 9.2 Hz, H-3^{II}), 3.30, 3.28 (2 t, 1H, *J* 6.4 Hz, H-1″b), 3.27–3.23 (m, partially overlapped, H-5^{II}), 3.14 (dd, $J_{4,5}$ 9.8 Hz, 1H, H-4^{II}), 2.74 (d, 1H, $J_{2,OH}$ 2.2 Hz, OH), 2.29 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.63–1.58 (m, 2H, H-4″a,b), 1.53–1.48 (m, 2H, H-2″), 1.35 (d, 3H, $J_{5,6}$ 6.0 Hz, H-6^{I}), 1.33 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6^{II}),1.33–1.28 (m, partially overlapped, H-3″a,b); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 103.83 (C-1^{II}), 98.36 (C-1^{I}), 82.17 (C-3^{II}), 80.68 (C-4^{I}), 80.53 (br, C-3^{I}), 77.57 (C-2^{I}), 75.69 (C-2^{II}), 75.47, 74.81, 73.29 (3 *C*H_2Ph), 70.74 (C-5^{II}), 67.92 (C-5^{I}), 67.15 (C-1″), 67.10 (C-4^{II}), 51.46 (COO*C*H_3), 33.87 (C-5″), 28.97 (C-2″), 25.63 (C-3″), 24.62 (C-4″), 18.59 (C-6^{II}), 18.04 (C-6^{I}). ESI-MS: *m*/*z* 778.3537 ($[M+HCOO]^-$). Anal. Calcd for $C_{40}H_{51}N_3O_{10}$: C, 65.47; H, 7.00; N, 5.73. Found: C, 65.55; H,7.02; N, 5.70.

3.49. 5-Methoxycarbonylpentyl 4-azido-3-*O*-benzyl-4,6-dideoxy-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (59)

When treated as described in the general procedure for methylation, compound **58** (693 mg, 0.94 mmol) gave methyl ether **59** (600 mg, 86%), $[\alpha]_D$ −1.3° (*c* 0.6). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 4.97–4.58 (m, 8H, 3 CH_2Ph, incl., 4.63, d, $J_{1,2}$ 1.8 Hz, H-1^{I}; 4.62 d, $J_{1,2}$ 7.8 Hz, H-1^{II}), 4.04 (d, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.3 Hz, H-3^{I}), 3.79 (d, 1H, H-2^{I}), 3.69–3.64 (m, partially overlapped, H-5^{I}), 3.66 (s, partially overlapped, OCH_3-2), 3.64 (s, partially overlapped, $COOCH_3$), 3.61 (t, partially overlapped, *J* 9.5 Hz, H-4^{I}), 3.59, 3.58 (2, t, partially overlapped, *J* 6.7 Hz, H-1″a), 3.39 (t, 1H, *J* 9.2 Hz, H-3^{II}), 3.32, 3.30 (2, t, 1H, H-1″b), 3.19–3.14 (m, 2H, H-2^{II},5^{II}), 3.10 (bt, 1H, H-4^{II}), 2.28 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.63–1.58 (m, 2H, H-4″a,b), 1.53–1.49 (m, 2H, H-2″a,b), 1.34 (d, $J_{5,6}$ 6.1 Hz, partially overlapped, H-6^{I}), 1.35–1.30 (m, partially overlapped, H-3″a,b), 1.27 (d, 3H, $J_{5,6}$ 6.0 Hz, H-6^{II}); ^{13}C NMR ($CDCl_3$): δ 103.59 (C-1^{II}), 98.47 (C-1^{I}), 84.79 (C-2^{II}), 82.76 (C-3^{II}), 80.87

(C-4^{I}), 78.86 (C-3^{I}), 78.68 (C-2^{I}), 75.41, 74.84, 73.41 (3 *C*H$_2$Ph), 70.20 (C-5^{II}), 67.81 (C-5^{I}), 67.69 (C-4^{II}), 67.08 (C-1″), 60.72 (OCH$_3$-2), 51.43 (COO*C*H$_3$), 33.90 (C-5″), 29.02 (C-2″), 25.66 (C-3″), 24.64 (C-4″), 18.46 (C-6^{II}), 17.92 (C-6^{I}); ESI-MS 770.3636 ([M+Na]$^+$). Anal. Calcd for $C_{41}H_{53}N_3O_{10}$: C, 65.08; H, 7.14; N, 5.62. Found: C, 65.86; H, 7.22; 5.58N.

3.50. 5-Methoxycarbonylpentyl 4,6-dideoxy-3-*O*-benzyl-4-(3-hydroxy-3-methylbutyramido)-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (61)

Azide **59** was converted to 5-methoxycarbonylpentyl 4-amino-3-*O*-benzyl-4,6-dideoxy-2-*O*-methyl-β-D-glucopyranosyl-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (**60**) (500 mg, 93%) by treatment with H_2S as described above. ^{1}H NMR ($CDCl_3$, 600MHz): δ 5.01–4.58 (6 d, partially overlapped, 3 C*H*$_2$Ph), 4.68 (d, partially overlapped, $J_{1,2}$ 7.5 Hz, H-1^{II}), 4.63 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.08 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.4 Hz, H-3^{I}), 3.83 (dd, 1H, H-2^{I}), 3.68 (m, partially overlapped, H-5^{I}), 3.67 (s, partially overlapped, OCH$_3$-2), 3.65 (s, COOCH$_3$), 3.62 (t, partially overlapped, J 9.4 Hz, H-4^{I}), 3.60, 3.58 (2 t, partially overlapped, J 6.2 Hz, H-1″a), 3.32, 3.30 (2 t, 1H, H-1″b), ~3.2 (t, partially overlapped, H-3^{II}), ~3.19 (t, partially overlapped, H-2^{II}), 3.16 (m, partially overlapped, H-5^{II}), 2.53 (m, 1H, H-4^{II}), 2.28 (t, 2H, J 7.3 Hz, H-5″a,b), 1.63–1.58 (m, 2H, H-4″a,b), 1.54–1.50 (m, 2H, H-2″a,b), 1.47–1.29 (m, NH$_2$, H-3″a,b, incl., d, 1.35, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.22 (d, $J_{5,6}$ 6.2 Hz, H-6^{II}). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 103.86 (C-1^{II}), 98.58 (C-1^{I}), 85.37 (C-2^{II}), 84.24 (C-3^{II}), 80.96 (C-4^{I}), 78.74 (C-2^{I}), 78.51 (C-3^{I}), 75.02, 74.79, 73.41 (3 *C*H$_2$Ph), 72.51 (C-5^{I}), 67.82 (C-5^{I}), 76.05 (C-1″), 60.23 (OCH$_3$-2), 58.22 (C-4^{II}), 51.42 (COO*C*H$_3$), 33.91 (C-5″), 29.03 (C-2″), 25.65 (C-3″), 24.64 (C-4″), 18.06 (C-6^{II}), 17.93 (C-6^{I}). ESI-MS: *m*/*z* 722.3863 $C_{41}H_{56}NO_{10}$+H requires 722.3904.

The foregoing amine (500 mg, 0.69 mmol) was treated with 3-hydroxy-3-methylbutyric acid (120 mg, 1 mmol), HATU (395 mg, 1 mmol), and *N*-diisopropylethylamine (0.13 mL, 1 mmol), as described in the general procedure, to give amide **61** (495 mg, 90%), $[\alpha]_D$ −60° (*c* 1). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.49 (d, 1H, $J_{4,NH}$ 9.1 Hz, NH), 5.00–4.59 (m, 8H, 3 C*H*$_2$Ph, incl., 4.63, d, $J_{1,2}$ 7.8 Hz, H-1^{II}, 4.62, d, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.04 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.3 Hz, H-3^{I}), 3.82 (dd, 1H, $J_{2,3}$ 3.3 Hz, H-2^{I}), 3.72 (q, 1H, J 10.0 Hz, H-4^{II}), ~3.68 (m, partially overlapped, H-5^{II}), 3.66 (s, partially overlapped, OCH$_3$-2), 3.64 (s, partially overlapped, COOCH$_3$), 3.62 (t, partially overlapped, J 9.3 Hz, H-4^{I}), 3.59, 3.57 (2 t, partially overlapped, J 6.6 Hz, H-1″a), 3.39 (dd, 1H, $J_{2,3}$ 8.9 Hz, H-3^{II}), 3.33 (m, partially overlapped, H-5^{II}), 3.31, 3.29 (2 t, partially overlapped, H-1″b), 3.22 (dd, 1H, H-2^{II}), 2.27 (t, 2H, J 7.5 Hz, H-5″a,b), 2.23, 2.13 (2 d, 2H, J 15 Hz, CH$_2$Br), 1.62–1.57 (m, 2H, H-4″a,b), 1.53–1.48 (m, 2H, H-2″), 1.34 (d, partially overlapped, J 6.2 Hz, H-6^{I}), 1.34–1.25 (m, partially overlapped, H-3″), 1.24, 1.21 (2 s, 6H, 2 CH$_3'$), 1.18 (d, 3H, J 6.2 Hz, H-6^{I}). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 103.77 ($J_{C\text{-}1,H\text{-}1}$ 159.0 Hz, C-1^{II}), 98.60 (J 167.0 Hz, C-1^{I}), 84.98 (C-2^{II}), 80.82 (C-4^{I}), 80.21 (C-3^{II}), 79.09 (C-3^{I}), 78.59 (C-2^{I}), 74.82, 73.77, 73.49 (3 *C*H$_2$Ph), 70.87 (C-5^{II}), 69.42 (C-3′), 67.81 (C-5^{I}), 67.05 (C-1″), 60.57 (OCH$_3$-2), 55.72 (C-4^{II}), 51.44 (COO*C*H$_3$), 47.77 (C-2′), 33.92 (C-5″), 29.32 (2 C, 2 CH$_3'$), 29.02 (C-2″), 25.66 (C-3″), 24.64 (C-4″), 18.12 (C-6^{II}), 17.93 (C-6^{I}). ESI-MS: 844.4289 ([M+Na]$^+$) Anal. Calcd for $C_{46}H_{63}NO_{12}$: C, 67.21; H, 7.73; N, 1.70. Found: C, 67.36; H, 7.66; N, 1.61.

3.51. 5-Methoxycarbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutyramido)-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-α-L-rhamnopyranoside (62)

Hydrogenolysis of **61** (500 mg), as described above for similar conversions, gave the deprotected disaccharide **62** (335 mg, 85%), $[\alpha]_D$ −38° (*c* 0.6). ^{1}H NMR (600 MHz, D_2O): δ 4.76 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.68 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^{II}), 4.11 (dd, 1H, $J_{2,3}$ 3.3 Hz, H-2^{I}), 3.82 (dd, 1H, $J_{3,4}$ 9.6 Hz, H-3^{I}), 3.69 (m, partially overlapped, H-5^{I}), 3.68 (s, partially overlapped, COOCH$_3$), 3.63 (t, partially overlapped, J 10.0 Hz, C-4^{II}), 3.62 (s, partially overlapped, OCH$_3$-2), 3.58 (t, 1H, J 9.6 Hz, H-4^{I}), 3.54 (m, partially overlapped, H-5^{II}), 3.53 (t, partially overlapped, H-3^{II}), 3.13 (dd, 1H, $J_{2,3}$ 9.2 Hz, H-2^{II}), 2.46, 2.43 (2 d, 2H, J 13.6 Hz, H-2′a,b), 2.40 (t, 2H, J 7.3 Hz, H-5″a,b), 1.67–1.57 (m, 4H, H-2″a,b,4″a,b), 1.43–1.34 (H-3″a,b), 1.30, 1.29 (2 s, 6H, 2 CH$_3'$), 1.29 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6^{I}), 1.21 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{II}); ^{13}C NMR (150 MHz, D_2O): δ 106.55 (C-1^{II}), 102.18 (C-1^{I}), 85.96 (C-2^{III}), 82.74 (C-3^{I}), 75.52 (C-3^{II}), 73.79 (C-4^{I}), 73.47 (C-5^{II}), 72.89 (C-3′), 72.77 (C-2^{I}), 71.52 (C-5^{I}), 70.36 (C-1″), 62.74 (OCH$_3$-2), 59.29 (C-4^{II}), 54.80 (COO*C*H$_3$), 51.60 (C-2′), 36.32 (C-5″), 31.03 (CH$_3'$), 30.89 (CH$_3'$,2″), 27.72 (C-3″), 26.77 (C-4″), 19.87 (C-6^{II}), 19.38 (C-6^{I}); ESI-MS 574.2856 ([M+Na]$^+$) $C_{25}H_{45}NO_{12}Na$ requires 574.2839.

3.52. 5-Methoxycarbonylpentyl 3-*O*-acetyl-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (63)

Condensation of glycosyl acceptor **25** (600 mg, 1.27 mmol) with thioglycoside **56** (624 mg, 1.5 mmol) according to the general procedure gave product **63** (860 mg, 86%), $[\alpha]_D$ −18° (*c* 0.7). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.31 (dd, 1H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.6 Hz, H-3^{II}), 5.15 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.80, 4.76, 4.74, 4.69, 4.47, 4.62, 3.36, 3.18 (8 d, partially overlapped, J ~ 11.7 Hz, 4 C*H*$_2$Ph), 4.73 (d, partially overlapped, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.09 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.5 Hz, H-3^{I}), 3.89–3.85 (m, 2H, H-5^{II}, incl., ~3.87, dd, H-2^{II}), 3.71 (dd, 1H, H-2^{I}), ~3.67 (m, partially overlapped, H-5^{I}), 3.66–3.60 (m, 6H, H-4^{I,II}, H-1″a, incl., 3.65 s, COOCH$_3$), 3.39, 3.33 (2 t, 1H, J 6.4 Hz, H-1″b), 2.31 (t, 2H, J 7.5 Hz, H-5″a,b), 1.94 (s, 3H, COCH$_3$), 1.66–1.61 (m, 2H, H-4″a,b), 1.56–1.52 (m, 2H, H-2″a,b), 1.37–1.31 (m, 2H, H-3″a,b), 1.29 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.26 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{II}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 99.46 ($J_{C\text{-}1,H\text{-}1}$

170.2 Hz, C-1^{II}), 97.57 ($J_{C\text{-}1,H\text{-}1}$ 168 Hz, C-1^{I}), 80.75 (C-4^{II}), 79.01 (C-4^{I}), 78.21 (C-3^{I}), 77.97 (C-2^{I}), 76.77 (C-2^{II}), 74.74, 74.64 (2 CH_2Ph), 73.52 (C3^{II}), 72.69, 72.58 (2 CH_2Ph), 68.23 (C-5^{II}), 68.22 (C-5^{I}), 67.24 (C-1″), 51.43 (COOCH_3), 33.91 (C-5″), 29.06 (C-2″), 25.68 (C-3″), 24.64 (C-4″), 21.02 (COCH_3), 18.01 (C-6^{II}), 17.88 (C-6^{I}); ESI-MS: *m/z* 863.3974 ([M+Na]$^+$). Anal. Calcd for $C_{49}H_{60}O_{12}$: C, 69.98; H, 7.19. Found: C, 70.16; H, 7.29.

3.53. 5-Methoxycarbonylpentyl 2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (64)

Conventional deacetylation (Zemplén) of the foregoing acetate **63** (922 mg) gave alcohol **64** (850 mg, 96%), $[\alpha]_D$ −26° (*c* 0.7). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.19 (d, 1H, $J_{1,2}$ 1.4 Hz, H-1^{II}), 4.90–4.10 (m, 10H, 4 CH_2Ph, incl., 4.72, d, $J_{1,2}$ 1.8 Hz, H-1^{I}, incl., 4.10, dd, $J_{2,3}$ 3.1, $J_{3,4}$ 9.5 Hz, H-3^{I}), 3.99 (dt, 1H, H-3″), 3.81–3.76 (m, 1H, H-5^{I}), 3.71 (dd, 1H, H-2^{II}), ~3.72–3.68 (m, overlapped, H-5^{II}), 3.69 (dd, partially overlapped, H-2^{I}), 3.72–3.59 (m, 6H, H-4^{I},5^{II}, H-1″a, incl., 3.64 s, COOCH_3), 3.35–3.29 (m, 2H, H-4^{II}, 1″b), 2.30, (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.65–1.60 (m, 2H, H-4″a,b), 1.58–1.53 (m, 2H, H-2″a,b), 1.37–1.32 (m, 2H, H-3″a,b), 1.30 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.27 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{II}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 98.65 (C-1^{II}), 97.53 (C-1^{I}), 82.12 (C-4^{II}), 80.95 (C-4^{I}), 79.05 (C-2^{II}), 77.95 (C-2^{I}), 77.74 (C-3^{I}), 74.72, 74.65, 72.62, 72.35 (4 CH_2Ph), 71.52 (C-3^{II}), 68.17 (C-5^{II}), 67.65 (C-5^{I}), 67.22 (C-1″), 51.38 (COOCH_3), 33.85 (C-5″), 29.06 (C-2″), 25.62 (C-3″), 24.59 (C-4″), 17.94 (C-6^{I}), 17.90 (C-6^{II}); ESI-MS: *m/z* 821.3884 ([M+Na]$^+$). Anal. Calcd for $C_{47}H_{58}O_{11}$: C, 70.65; H, 7.32. Found: C, 70.63; H, 7.38.

3.54. 5-Methoxycarbonylpentyl 4-azido-3-*O*-benzyl-2-*O*-bromoacetyl-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-rhamnopyranoside (65)

Reaction of **64** (877 mg, 1.09 mol) and **18** (533 mg, 1.2 mmol) gave trisaccharide **65** (1.05 g, 81%), $[\alpha]_D$ −1° (*c* 0.7). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5. (8 (d, partially overlapped, $J_{1,2}$ ~ 2 Hz, H-1^{II}), 5.06 (dd, partially overlapped, $J_{1,2}$ 8.0, $J_{2,3}$ 9.6 Hz, H-2^{III}), 4.79–4.41 (m, 12H, 5 CH_2Ph, incl., d, 4.74 for H-1^{I} and d, 4.70, H-1^{III}), 4.13 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.7 Hz, H-3^{II}), 4.04 (dd, 1H, $J_{2,3}$ 3.0, $J_{3,4}$ 9.5 Hz, H-3^{I}), 3.87–3.82 (m, 2H, H-2^{II},5^{II} in that order), 3.73 (dd, 1H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.1 Hz, H-2^{I}), 3.69–3.54 (m, 7H, H-5^{I},1″a, 4^{II},4^{I} in that order, incl., s, 3.64, COOCH_3), 3.40 (t, *J* 9.3 Hz, H-3^{III}), 3.34, 3.32 (2 d, partially overlapped, *J* 12.6 Hz, CH_2Br), 1.32 (m, partially overlapped, H-1″a), 3.14 (dd, partially overlapped, $J_{4,5}$ 9.9 Hz, H-4^{III}), 3.11 (m, partially overlapped, H-5^{III}), 2.30 (t, 2H, *J* 7.4 Hz, H-5″a,b), 1.65–1.60 (m, 2H, H-4″a,b), 1.57–1.52 (m, 2H, H-2″), 1.37–1.30 (m, 2H, H-3″a,b), 1.27 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.26 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{II}), 1.14 (d, 3H, $J_{5,6}$ 5.9 Hz, H-6^{III}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 100.56 (C-1^{III}), 100.26 (C-1^{II}), 97.12 (C-1^{I}), 80.96 (C-3^{III}), 80.47, 80.46 (C-4^{I},4^{II}), 78.77 (C-3^{II}), 78.54 (C-3^{I}), 78.48 (C-2^{II}), 78.06 (C-2^{I}), 75.00 (C-2^{III}), 74.96, 74.88, 74.48, 73.16, 72.38 (5 CH_2Ph), 70.54 (C-5^{III}), 68.43 (C-5^{II}), 67.94 (C-5^{I}), 67.63 (C-4^{III}), 67.23 (C-1″), 51.39 (COOCH_3), 33.82 (C-5″), 28.99 (C-2″), 25.60 (C-3″), 25.13 CH_2Br), 24.56 (C-4″), 18.15 (C-6^{III}), 17.86 (2 C, C-$6^{I,II}$); ESI-MS: *m/z* 1202.4205 ([M+Na]$^+$). Anal. Calcd for $C_{62}H_{74}BrN_3O_{15}$: C, 63.04; H, 6.31; N, 3.96. Found: C, 63.28; H, 6.40; N, 4.52.

3.55. 5-Methoxycarbonylpentyl 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-rhamnopyranoside (66)

Deacylation (Zemplén) of **65** (1.02 g) gave **66** (800 mg, 88%), $[\alpha]_D$ +2.5° (*c* 0.7). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.07 (bd, 1H, $J_{1,2}$ ~ 1.3 Hz, H-1^{II}), 4.91–4.44 (m, 11H, 5 CH_2Ph, incl., 4.74, d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.40 (d, 1H, $J_{1,2}$ 8.8 Hz, H-1^{III}), 4.09 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.5 Hz, H-3^{II}), 4.02 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.4 Hz, H-3^{I}), 3.87 (dd, 1H, H-2^{II}), 3.86–3.81 (m, 1H, H-5^{II}), 3.70 (dd, 1H, H-2^{I}), 3.62 (s, partially overlapped, $COOCH_3$), 3.65 (m, partially overlapped, H-5^{I}), 3.64 (t, partially overlapped, H-4^{II}), ~3.53–3.50 (m, 2H, H-4^{I},2^{III}), 3.35–3.30 (m, 2H, H-3^{III},1″a), 3.12–3.05 (m, 3H, H-4^{III},5^{III},1″b), 2.72 (s, 1H, OH), 2.31 (t, 2H, *J* 7.5 Hz, H-5″a,b), 1.66–1.60 (m, 2H, H-4″a,b), 1.56–1.52 (m, 2H, H-2″a,b), 1.36–1.31 (m, 2H, H-3″a,b), 1.31 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{II}), 1.25 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.17 (d, 3H, $J_{5,6}$ 5.7 Hz, H-6^{III}). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 103.68 (C-1^{III}), 100.09 (C-1^{II}), 97.20 (C-1^{I}), 82.07 (C-3^{III}), 80.67 (C-4^{II}), 80.58 (C-4^{I}), 79.79 (C-3^{II}), 78.39 (C-3^{I}), 78.28 (C-2^{II}), 78.10 (C-2^{I}), 75.68 (C-2^{III}), 75.23, 74.83 (2 C), 73.07, 72.53 (5 CH_2Ph), 70.67 (C-5^{III}), 68.57 (C-5^{II}), 68.00 (C-5^{I}), 67.32 (C-1″), 67.04 (C-4^{III}), 51.50 (COOCH_3), 33.92 (C-5″), 29.07 (C-2″), 25.68 (C-3″), 24.65 (C-4″), 18.51 (C-6^{III}), 18.11 (C-6^{II}), 17.92 (C-6^{I}). ESI-MS: *m/z* 1082.4971 ([M+Na]$^+$). Anal. Calcd for $C_{60}H_{73}N_3O_{14}$: C, 67/97; H, 6/94; N, 6.96. Found: C, 68.08; H, 6.91; N, 3.98.

3.56. 5-Methoxycarbonylpentyl 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-rhamnopyranoside (67)

Methylation of **66** (800 mg), as described above for similar conversions, gave **67** (740 mg, 93%). $[\alpha]_D$ −3° (*c* 0.7). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.09 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1^{II}), 4.98–4.45 (m, 12H, 5 CH_2Ph, incl., 4.72, d, $J_{1,2}$ 1.8 Hz, H-1^{I}, incl., 4.61, d, $J_{1,2}$ 7.9 Hz, H-1^{III}), 4.14 (dd, 1H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.6 Hz, H-3^{II}), 4.04 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.5 Hz, H-3^{I}), 3.89 (dd, 1H, H-2^{II}), 3.86 (m, 1H, H-5^{II}), 3.72 (dd, 1H, H-2^{I}), 3.68–3.59 (m, 9H, H-5^{I}, 4^{II}, 1″a, in that order, incl., 3.65, s, $COOCH_3$, 3.64, s, OCH_3-2), 3.55 (t, 1H, *J* 9.5 Hz, H-4^{I}), 3.35–3.30 (m, 2H, H-3^{III},1″b), 3.13 (dd, 1H, $J_{2,3}$ 9.6 Hz, H-2^{III}), 3.06–3.02 (m, 2H, H-3^{III},1″a,b), 3.25 (dd, 1H, H-2^{III}), 3.04–3.02 (H-4^{III},5^{III}), 2.30 (t, 2H, *J* 7.4 Hz, H-5″a,b), 1.65–1.60 (m, 2H, H-4″a,b), 1.56–1.52 (m, 2H, H-2″), 1.38–1.31 (m, partially overlapped, H-3″a,b), 1.31 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{II}), 1.25 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.10 (d, 3H, $J_{5,6}$ 5.8 Hz, H-6^{III}); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 103.54 (C-1^{III}), 100.41

(C-1^{II}), 97.37 (C-1^{I}), 84.75 (C-2^{III}), 82.64 (C-3^{III}), 80.90 (C-4^{II}), 80.58 (C-4^{I}), 79.23 (C-2^{II}), 78.56 (C-3^{I}), 78.48 (C-3^{II}), 78.16 (C-2^{I}), 75.40, 74.92, 74.57, 73.21, 72.55 (5 CH_2Ph), 70.19 (C-5^{III}), 68.46 (C-5^{II}), 68.08 (C-5^{I}), 67.57 (C-4^{III}), 67.29 (C-1″), 60.70 (OCH_3-2), 51.46 ($COOCH_3$), 33.92 (C-5″), 29.07 (C-2″), 25.69 (C-3″), 24.66 (C-4″), 18.40 (C-6^{III}), 18.01 (C-6^{II}), 17.89 (C-6^{I}); ESI-MS: *m/z* 1080.5354 ($[M+Li]^+$). Anal. Calcd for $C_{61}H_{75}N_3O_{14}$: C, 68.20; H, 7.04; N, 3.91. Found: C, 68.44; H, 7.01; N, 3.90.

3.57. 5-Methoxycarbonylpentyl 4,6-dideoxy-3-*O*-benzyl-4-(3-hydroxy-3-methylbutyramido)-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (69)

Treatment of azide **67** (700 mg) with H_2S, as described in the general procedure, gave 5-methoxycarbonylpentyl 4-amino-4,6-dideoxy-3-*O*-benzyl-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1 → 2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**68**, 510 mg, 75%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.11 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{II}), 5.03–4.47 (m, 12H, 5 CH_2Ph, incl, 4.71, d, $J_{1,2}$ 1.9 Hz, H-1^{I}, ~4.71, d, $J_{1,2}$ ~ 7.6 Hz, H-1^{III}), 4.21 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.6 Hz, H-3^{II}), 4.06 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.6 Hz, H-3^{I}), 3.94 (dd, 1H, $J_{2,3}$ 3.2 Hz, H-2^{II}), 3.86 (m, 1H, H-5^{II}), 3.72 (dd, 1H, H-2^{I}), 3.67 (s, partially overlapped, OCH_3-2), ~3.65 (m, partially overlapped, H-5^{I}), 3.65 (s, partially overlapped, $COOCH_3$), 3.66 (t, partially overlapped, H-4^{II}), 3.61, 3.60 (2 t, partially overlapped, *J* 6.5 Hz, H-1″a), 3.57 (t, *J* 9.4 Hz, H-4^{I}), 3.32, 3.30 (2 t, partially overlapped, H-1″b), 3.16 (m, 2H, H-2^{III},3^{III}), 3.07 (m, 1H, H-5^{III}), 2.50–2.49 (m, 1H, H-4^{III}), 2.30 (t, 2H, *J* 7.4 Hz, H-5″a,b), 1.65–1.60 (m, 2H, H-4″a,b), 1.56–1.52 (m, 4H, H-2″a,b), 1.37–1.31 (m, 5H, H-3″a,b, incl., 1.32, d, $J_{5,6}$ 6.2 Hz, H-6^{II}), 1.25 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.07 (d, $J_{5,6}$ 6.2 Hz, H-6^{III}); ^{13}C NMR (150 MHz, $CDCl_3$): δ 103.75 (C-1^{III}), 100.43 (C-1^{II}), 97.36 (C-1^{I}), 85.27 (C-2^{III}), 83.97 (C-3^{III}), 80.91 (C-4^{II}), 80.53 (C-4^{I}), 79.24 (C-2^{II}), 78.33 (C-3^{I}), 78.00, 77.98 (C-2^{I}, 3^{II}), 74.94, 74.83, 74.44, 73.14, 72.47 (5 CH_2Ph), 72.46 (C-5^{III}), 68.39 (C-5^{II}), 68.01 (C-5^{I}), 67.18 (C-1″), 60.35 (OCH_3-2), 58.03 (C-4^{II}), 51.39 ($COOCH_3$), 33.84 (C-5″), 29.00 (C-2″), 25.61 (C-3″), 24.58 (C-4″), 17.98 (C-6^{III}), 17.93 (C-6^{II}), 17.81 (C-6^{I}); ESI-MS 1048.5409 ($[M+H]^+$) $C_{61}H_{78}NO_{14}$+H requires 1048.5422.

Treatment of the foregoing amine (455 mg, 0.43 mmol) with 3-hydroxy-3-methylbutyric acid (76 mg, 0.65 mmol), as described for similar conversions, gave amide **69** (424 mg, 86%), $[\alpha]_D$ −46° (*c* 0.6). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.35 (d, 1H, $J_{4,NH}$ 9.1 Hz, NH), 5.08 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 5.02–4.46 (m,12H, 5 CH_2Ph, incl., 4.71, d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{I}, incl., ~4.62, d, partially overlapped, $J_{1,2}$ ~ 7.7 Hz, H-1^{III}), 4.15 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.6 Hz, H-3^{II}), 4.04 (dd, 1H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.5 Hz, H-3^{I}), 3.92 (dd, partially overlapped, H-2^{II}), 3.91 (s, partially overlapped, OH′), 3.86 (m, 1H, H-5^{II}), 3.71 (dd, 1H, H-2^{I}), ~3.67 (t, partially overlapped, H-4^{III}), 3.65 (s, partially overlapped, $COOCH_3$), ~3.65 (m, partially overlapped, H-5^{I}), 3.64 (s, partially overlapped, OCH_3-2), 3.64 (t, partially overlapped, H-4^{II}), 3.61, 3.60 (2 t, partially overlapped, *J* 6.5 Hz, H-1″a), 3.53 (t, 1H, *J* 9.5 Hz, H-4^{I}), 3.32, 3.30 (2 t, partially overlapped, H-1″b), 3.31 (dd, partially overlapped, H-3^{III}), 3.19–3.18 (m, 2H, 2^{III},5^{III}), 2.30 (t, 2H, *J* 7.6 Hz, H-5″a,b), 2.19, 2.09 (2 d, 2H, *J* 14.9 Hz, H-2′a,b), 1.36–1.31 (m, 5H, H-3″a,b, incl., 1.31, d, $J_{5,6}$ 6.2 Hz, H-6^{II}), 1.24 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6^{I}), 1.21, 1.18 (2 s, 6H, 2 CH_3'), 1.03 (d, $J_{5,6}$ 6.2 Hz, H-6^{III}); ^{13}C NMR ($CDCl_3$): δ 103.74 (C-1^{III}), 100.51 (C-1^{II}), 97.41 (C-1^{I}), 84.93 (C-2^{III}), 80.85 (C-4^{II}), 80.57 (C-4^{I}), 80.04 (C-3^{III}), 79.16 (C-2^{II}), 78.73 (C-3^{II}), 78.49 (C-3^{I}), 78.07 (C-2^{I}), 74.89, 74.52, 73.73, 73.29, 72.51 (5 CH_2Ph), 70.88 (C-5^{III}), 69.39 (C-3′), 68.45 (C-5^{II}), 68.09 (C-5^{I}), 67.27 (C-1″), 60.55 (OCH_3-2), 55.57 (C-4^{III}), 51.45 ($COOCH_3$), 47.73 (C-2′), 33.92 (C-5″), 29.31, 29.29 (2 CH_3'), 29.06 (C-2″), 25.67 (C-3″), 24.65 (C-4″), 18.09 (C-6^{III}), 18.01 (C-6^{II}), 17.89 (C-6^{I}); ESI-MS 1148.5973 ($[M+H]^+$). Anal. Calcd for $C_{66}H_{85}NO_{16}$: C, 69.03; H, 7.46; N, 1.22. Found: C, 69.11; H, 7.43; N, 1.24.

3.58. 5-Methoxycarbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutanamido)-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranoside (70)

Hydrogenolysis of **69** (400 mg), as described above, gave **70** (220 mg, 90%), $[\alpha]_D$ −54° (*c* 0.6, H_2O). ^{1}H NMR (600 MHz, D_2O): δ 5.03 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.75 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.73 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1^{III}), 4.27 (dd, 1H, $J_{2,3}$ 3.3 Hz, H-2^{II}), 4.00 (dd, partially overlapped, H-2^{I}), 3.99 (dd, partially overlapped, H-3^{II}), 3.83 (m, 1H, H-5^{II}), 3.79 (dd, 1H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 9.7 Hz, H-3^{I}) 3.72 (m, partially overlapped, H-5^{I}), ~3.70 (m, partially overlapped, H-1″a), 3.68 (s, partially overlapped, $COOCH_3$), 3.64 (t, partially overlapped, *J* 10.0 Hz, H-4^{III}), 3.60 (t, *J* 9.7 Hz, partially overlapped, H-4^{II}), 3.55 (m, partially overlapped, H-5^{III}), ~3.53 (m partially overlapped, H-1″b), 3.52 (m, partially overlapped, H-3^{III},4^{I}), 3.13 (dd, 1H, $J_{2,3}$ 9.2 Hz, H-2^{III}), 2.47, 2.44 (2 d, 2H, *J* 13.7 Hz, H-2′a,b), 2.41 (t, 2H, *J* 7.3 Hz, H-5″), 1.67–1.57 (m, 4H, H-2″a,b,4″a,b), 1.45–1.33 (m, 2H, H-3″), 1.31, 1.30 (2 s, partially overlapped, 2 CH_3'), 1.29 (d, partially overlapped, $J_{5,6}$ 6.3 Hz, H-6^{II}), 1.30 (d, 3H, $J_{5,6}$ 6.3 Hz, H-6^{I}), 1.22 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C NMR (D_2O, 150 MHz): δ 106.42 (C-1^{III}), 104.80 (C-1^{II}), 102.41 (C-1^{I}), 86.02 (C-2^{III}), 82.39 (C-3^{II}), 80.80 (C-3^{I}), 75.60 (C-3^{III}), 74.17 (C-4^{I}), 73.91 (C-4^{II}), 73.52 (C-5^{III}), 72.97 (C-3′), 72.72 (C-2^{I}), 72.56 (C-2^{II}), 71.98 (C-5^{II}), 71.48 (C-5^{I}), 70.44 (C-1″), 62.81 (OCH_3-2), 59.32 (C-4^{III}), 54.85 ($COOCH_3$), 51.68 (C-2′), 36.36 (C-5″), 31.04, 30.86 (2 OCH_3'), 30.90 (C-2″), 27.72 (C-3″), 26.78 (C-4″), 19.81 (C-6^{III}), 19.36 (2 C, C-$6^{I,II}$), ESI-MS 720.3416 ($[M+18]^+$) $C_{31}H_{55}NO_{16}$Na requires 720.3419.

3.59. (2-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutyramido)-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranoside (71)

Starting with ester **35** (86 mg) and following the general procedure for this conversion gave amine **71** (72 mg, 80%). Characteristic NMR signals were at δ_{1H} 3.32–

3.30 (m, H-6″), 2.85–2.82 (m, H-7″); $\delta_{^{13}C}$ 43.34 (C-6″), 42.83 (C-7″). ESI-MS: *m/z* 872.4615 ($[M+H]^+$) $C_{38}H_{70}N_3O_{19}$ requires 872.4604.

3.60. 1-[2-Aminoethylamido]carbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutanamido)-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranoside]-2-ethoxycyclobutene-3,4-dione (72)

Treatment of amine **71** (20 mg) with squaric acid diethyl ester, as described in the general procedure for preparation of this class of compounds, gave monoester **72** (17 mg, 74%). Characteristic NMR signals were at $\delta_{^1H}$ 4.80–4.69 (m, partially overlapped, CH_2CH$_3$), 1.46–1.42 (m, 3H, CH$_2$CH_3); $\delta_{^{13}C}$ 70.63 (CH_2CH$_3$), 15.02 (CH$_2$CH_3). ESI-MS: *m/z* 996.4748 ($[M+H]^+$) $C_{44}H_{74}N_3O_{22}$ requires 996.4764.

3.61. (2-Aminoethylamido)carbonylpentyl α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-L-rhamnopyranoside (75)

Treatment of ester **12** (44 mg), as described for preparation of **71**, gave **75** (32 mg, 70%). Characteristic NMR signals were at $\delta_{^1H}$ 3.25 (t, *J* 6.3 Hz, H-6″), 2.74 (t, *J* 6.0, H-7″); $\delta_{^{13}C}$ 41.15 (C-6″), 39.66 (C-7″). ESI-MS: *m/z* 613.3184 ($[M+H]^+$) $C_{26}H_{49}N_2O_{14}$ requires 613.3184.

3.62. 1-[2-Aminoethylamido]carbonylpentyl α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-L-rhamnopyranoside]-2-ethoxycyclobutene-3,4-dione (76)

Treatment of amine **75** (20 mg) with squaric acid diethyl ester, as described for preparation of **72**, gave **76** (15 mg, 63%). Characteristic NMR signals were at $\delta_{^1H}$ 4.70–4.63 (m, 2H, CH_2CH$_3$), 1.41, 1.35 (2 t, 3H, CH$_2$CH_3); $\delta_{^{13}C}$ 73.46 (CH_2CH$_3$), 17.78 (CH$_2$CH_3). ESI-MS: *m/z* 735.3177 ($[M-1]^-$) $C_{32}H_{51}N_2O_{17}$ requires 735.3188.

3.63. (2-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutanamido)-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-β-L-rhamnopyranoside (79)

Starting with ester **2** (86 mg) and following the general procedure for this conversion gave amine **79** (40 mg, 44%). Characteristic NMR signals were at $\delta_{^1H}$ 3.31 (t, *J* 6.3 Hz, H-6″), 2.84 (t, *J* 6.3, H-7″); $\delta_{^{13}C}$ 43.40 (C-6″), 42.60 (C-7″). ESI-MS: *m/z* 872.4595 ($[M+H]^+$) $C_{38}H_{70}N_3O_{19}$ requires 872.4604.

3.64. 1-[2-aminoethylamido]carbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutanamido)-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-β-L-rhamnopyranoside]-2-ethoxycyclobutene-3,4-dione (80)

Treatment of amine **79** (20 mg) with squaric acid diethyl ester, as described in the general procedure for preparation of this class of compounds, gave after chromatography ester **80** (16 mg, 70%) Characteristic NMR signals were at $\delta_{^1H}$ 4.75–4.68 (m, partially overlapped, CH_2CH$_3$), 1.45, 1.43 (2 t, 3H, CH$_2$CH_3); $\delta_{^{13}C}$ 73.50 (CH_2CH$_3$), 17.89 (CH$_2$CH_3). ESI-MS: *m/z* 996.4769 ($[M+H]^+$) $C_{44}H_{74}N_3O_{22}$ requires 996.4764.

3.65. (2-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutanamido)-β-D-glucopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranoside (83)

Starting with ester **40** (18.5 mg) and following the general procedure for this conversion gave amine **83** (14.6 mg, 79%). Characteristic NMR signals were at $\delta_{^1H}$ 3.38 (t, H-6″), 2.93 (m, H-7″); $\delta_{^{13}C}$ 41.94 (C-6″), 41.84 (C-7″). ESI-MS: *m/z* 858.4444 ($[M+H]^+$) $C_{37}H_{68}N_3O_{19}$ requires 858.4447.

3.66. 1-[2-Aminoethylamido]carbonylpentyl 4,6-dideoxy-4-(3-hydroxy-3-methylbutanamido)-2-*O*-methyl-β-D-glucopyranosyl-(1 → 3)-(1 → 3)-α-L-rhamnopyranosyl-α-L-rhamnopyranosyl-(1 → 2)-α-L-rhamnopyranoside]-2-ethoxycyclobutene-3,4-dione (84)

Treatment of amine **83** (14.0 mg) with squaric acid diethyl ester, as described in the general procedure for preparation of this class of compounds, gave monoester **84** (14.0 mg, 90%). Characteristic NMR signals were at $\delta_{^1H}$ 4.72–4.64 (m, partially overlapped with H-1^{IV}, CH_2CH$_3$), 1.43–1.38 (m, 3H, CH$_2$CH_3); $\delta_{^{13}C}$ 73.47 (CH_2CH$_3$), 17.87 (CH$_2$CH_3). ESI-MS: *m/z* 1004.4446 ($[M+Na]^+$) $C_{43}H_{71}N_3O_{22}$ requires 1004.4427.

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