DOI: 10.1002/ejoc.200600078

Synthesis of Pentasaccharide Fragments Related to the *O*-Specific Polysaccharide of *Shigella flexneri* Serotype 1a[‡]

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Keywords: Carbohydrates / Glycosylation / Oligosaccharides / Spacers

The synthesis of the pentasaccharide 5-aminopentyl glycosides α-L-Rha*p*-(1→3)-[α-D-Glc*p*-(1→4)]-β-D-Glc*p*NAc-(1→2)-α-L-Rha*p*-(1→2)-α-L-Rha*p*-1-*O*-$(CH_2)_5NH_2$ (**29**) and α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→3)-[α-D-Glc*p*-(1→4)]-β-D-Glc*p*NAc-(1→2)-α-L-Rha*p*-1-*O*-$(CH_2)_5NH_2$ (**28**), related to the *O*-specific polysaccharide of *Shigella flexneri* serotype 1a by coupling of the suitably protected trisaccharides α-D-Glc*p*-(1→4)-β-D-Glc*p*(1→2)-α-L-Rha*p*-1-*O*-$(CH_2)_5NH_2$ (**23**) and α-L-Rha*p*-(1→3)-[α-D-Glc*p*-(1→4)]-β-D-Glc*p*-1-SPh (**26**) with the corresponding rhamnosyl glycosides α-L-Rha*p*-(1→3)-α-L-Rha*p*-1-SEt (**17**) and α-L-Rha*p*-(1→3)-α-L-Rha*p*-1-*O*-$(CH_2)_5NH_2$ (**13**), is described. Building blocks **23** and **26** were prepared by intramolecular glycosylation of an unsymmetrically tethered cellobiosamine derivative.

Introduction

Recently, the World Health Organization estimated that more than one million deaths per year occur due to infections with *Shigella* spp. The victims are mostly young children of the developing world but often also humans in industrialized countries.[1–9] *Shigella flexneri*,[10–13] a gram-negative enteropathogenic bacterium, is responsible for the endemic form of shigellosis, a highly infectious dysenteric syndrome in humans that causes diarrheal fever, violent cramps, and discharge of mucous membranes and bloody stools.[14–19] Shigellosis is characterized by a high morbidity and mortality. It is transmitted by person-to-person contact or indirectly through contaminated food or water. Currently, however, there are no licensed vaccines against this pathogen available yet. Existing antimicrobial treatments are becoming increasingly ineffective due to the growing antibiotic resistance[5,20] among *Shigella* spp. Therefore, the development of novel treatments and the accelerated search for vaccines for prevention of shigellosis is strongly advized in order to provide protection against the most common serotypes of *Shigella* spp.[21,22] In case of non-encapsulated gram-negative bacteria, such as *Shigella*, the *O*-specific polysaccharides (*O*-SP) of their lipopolysaccharides are essential virulent factors and serve as a protective antigen for the host's immunity. Thus, serum antibodies to the *O*-SP may well provide protection against infections through vaccination although the *O*-specific polysaccharide moieties are often not immunogenic enough. However, it has been demonstrated for several enterobacteria that corresponding protein conjugates were sufficiently immunogenic in humans.[23–25] For immunological studies of such neoglycoconjugates toward their application as vaccines it is desirable to have variations of the polysaccharide repeating unit available. Several syntheses of di- to pentasaccharide structures, as well as an octa- and a decasaccharide fragment related to the *O*-SP of *Shigella flexneri* serotypes 2a,[26–32] 5a,[33–39] and others[40–43] were published already. We were especially interesting in the *O*-SP of *Shigella flexneri* 1a (Figure 1),[13,44–46] the *O*-specific polysaccharide of which is characterized by a branched pentasaccharide repeating unit containing α-linked L-rhamnose, β-linked *N*-acetyl-D-glucosamine and α-D-glucose.

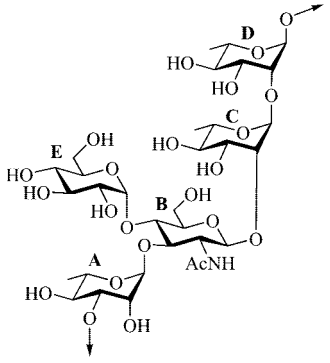

Figure 1. Repeating unit of the *O*-specific polysaccharide of *Shigella flexneri* serotype 1a antigen.

Here, we describe the syntheses of the pentasaccharide sequences **A(E)BCD** and **DA(E)BC** – as their 5-aminopentyl glycosides – of *Shigella flexneri* 1a *O*-specific polysaccharide using our recently developed method of intramolecular glycosylation through prearranged glycosides.[47–55]

[‡] Prearranged Glycosides, XV. Part XIV: Ref.[53]

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In particular, we apply the intramolecular glycosylation strategy by unsymmetrically tethered glycosides[53,56] (i.e. carboxybenzyl moieties) to a highly flexible synthesis of *Shigella flexneri* 1a *O*-specific pentasaccharide aminopentyl glycosides.

Results and Discussion

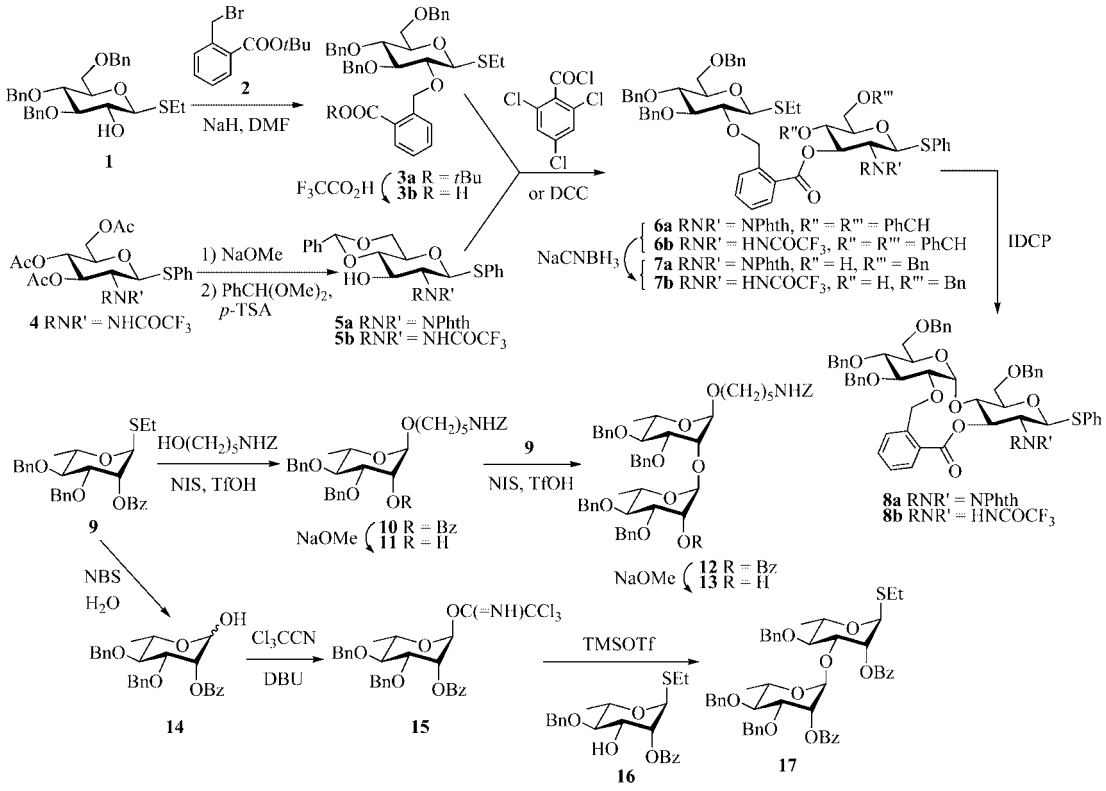
For the synthesis of the pentasaccharide fragments related to the *O*-SP of *Shigella flexneri* 1a a convergent blockwise approach was chosen. For both sequences **A(E)BCD** and **DA(E)BC** three disaccharide building blocks were needed: an α-D-Glc*p*-(1→4)-D-Glc*p*NAc disaccharide for fragment **EB** suitable for being used as donor and acceptor, an α-L-Rha*p*-(1→2)-L-Rha*p* disaccharide acceptor for fragment **CD** and an α-L-Rha*p*-(1→3)-L-Rha*p* disaccharide donor for fragment **DA**. The required building block **EB** contains an α-D-glucosyl residue which was planned to be established by intramolecular glycosylation of an appropriately prearranged glycoside. For that purpose, the ethyl 1-thio-glucoside **1**[57] was alkylated with *tert*-butyl 2-(bromomethyl)benzoate[53] (**2**) by means of NaH in DMF to afford the crystalline glucoside **3a** (89%), and the *tert*-butyl ester was hydrolyzed by treatment of the glucoside **3a** with trifluoroacetic acid (TFA) in dichloromethane to give the glucoside **3b** in 90% yield. The *o*-methylbenzoyl tether was chosen for linking the glucoside **3b** with the known glucosamine **5a**[58] because similarly tethered prearranged glycosides have previously been shown to produce high α-stereoselectivities during intramolecular glycosylations.[53] The amino group in the glucosamine acceptor was protected as phthalimide in order to avoid low yields and the formation of stable oxazolines during the following glycosylation steps. *N*-Phthalimido groups can be easily converted into the *N*-acetyl groups later on.[59–62] Furthermore, the combination of a phenylthio group in the glucosamine moiety and an ethylthio group in the glucose moiety allows for a selective activation of the ethylthio group without affecting the phenylthio group. Thus, the hydroxy group at the 3-position of glucosamine **5a** was first condensed with the glucoside **3b** in the presence of DCC/DMAP to yield the prearranged bis(glycoside) **6a** in 73% yield. Next, the benzylidene acetal of the glucosamine moiety was reductively opened with $NaCNBH_3$[63,64] to afford the bis(glycoside) **7a** in 63% yield. Intramolecular glycosylation of the latter with iodonium dicollidine perchlorate[65–67] (IDCP) as promoter in dichloromethane proceeded smoothly and gave the desired α-D-Glc*p*-(1→4)-D-Glc*p*NPhth-linked disaccharide **8a** stereoselectively in 69% yield. The anomeric configuration of the newly formed *O*-glycosidic linkage was unambiguously assigned by measuring a vicinal $^3J_{1,2}$ coupling constant of 3.4 Hz at the anomeric center of the glucose moiety which is typical for the α-D-glucosidic linkages. In addition, the related $^1J_{C\text{-}1,1\text{-}H}$ heteronuclear coupling constant of 169.8 Hz also proved the α-linkage.[92–94]

The α-L-Rha*p*-(1→2)-L-Rha*p* disaccharide acceptor related to fragment **CD** was synthesized from known ethyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside[68] (**9**). First, coupling of the latter with 5-[(benzyloxycarbonyl)amino]pentanol by means of *N*-iodosuccinimide (NIS) in the presence of a catalytic amount of trifluoromethanesulfonic acid (TfOH) in dichloromethane afforded the rhamnoside **10** in 80% yield, which was then debenzoylated with sodium methoxide in methanol to provide the rhamnosyl acceptor **11** in a virtually quantitative yield. Next, the rhamnosides **9** and **11** were coupled with NIS/TfOH to afford the disaccharide **12** in 70% yield. Finally, Zemplén deacylation[69] gave the desired α-L-Rha*p*-(1→2)-L-Rha*p* disaccharide **13** in 95% yield (Scheme 1).

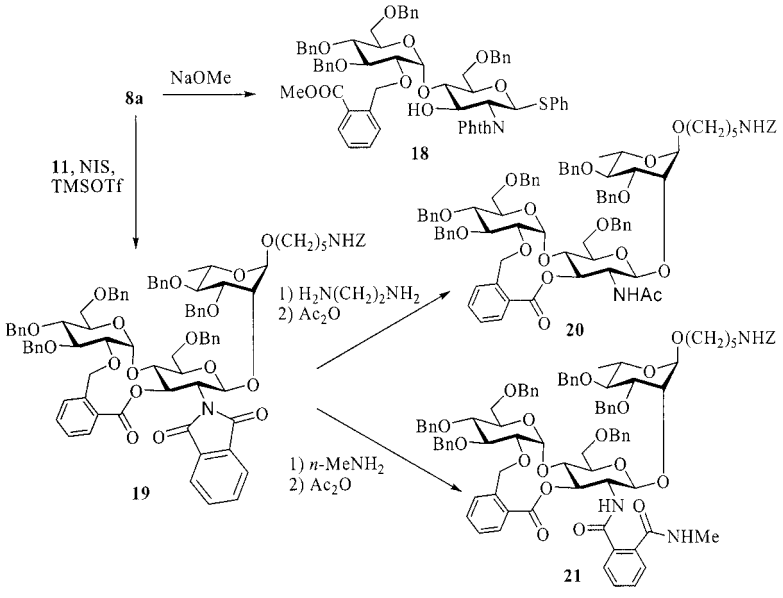
For the preparation of the α-L-Rha*p*-(1→3)-L-Rha*p* disaccharide donor related to fragment **DA**, the rhamnoside **9** was first converted with NBS/water into monosaccharide **14** in 91% yield, obtained as an anomeric mixture. Next, the rhamnose derivative **14** was converted into the corresponding trichloroacetimidate **15** (79%) by treatment with Cl_3CCN and DBU. Trimethylsilyl trifluoromethanesulfonate (TMSOTf) catalyzed glycosylation of ethyl 2-*O*-benzoyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside[70] (**16**) with the imidate **15** afforded the disaccharide **17** in 76% yield.

In order to construct the **DA(E)BC** pentasaccharide repeating unit of *Shigella flexneri* serotype 1a, the disaccharide donor **8a** was first coupled to the 2-position of the rhamnoside **11** using NIS and a catalytic amount of TMSOTf as promoter. Thus, the trisaccharide **19** was obtained in 57% yield. The NMR spectra showed a heteronuclear $^1J_{C\text{-}1,1\text{-}H}$ coupling constant of 163.8 Hz for the anomeric center at the glucosamine moiety which proved the β-linkage. Originally, it was planned to open the *o*-benzylbenzoate tether in the disaccharides **8a** and **19** by transesterification with methanol in order to deprotect the 3-position of the glucosamine moieties for further elongation of the saccharide chains with the rhamnosyl donor **9** and **17**, respectively. However, treatment of the disaccharide **8a** under Zemplén conditions (NaOMe in methanol) resulted in extensive decomposition and afforded the acceptor **18** in poor 45% yield. The selective ring opening of the *o*-benzylbenzoate tether in **19** proved to be even more difficult. Under Zemlpén conditions or by treatment with hydrazine hydrate[59] complete decomposition occurred. Saponification of the ester group in **19** with sodium borohydride[61] or hydrolysis under acidic conditions failed completely. Treatment with $MeNH_2$ only opened the phthalimide ring and gave the trisaccharide **21** in 54% yield. Ethylenediamine[60] removed the phthalimide group completely but did not cleave the ester group at all. Solely the trisaccharide **20** could be isolated in poor 45% yield after reacetylation with acetic anhydride (Scheme 2).

In order to circumvent these persisting problems, other amino protecting groups were needed. However, commonly used *N*-protecting groups like *N*-dichlorophthaloyl,[71] *N*-tetrachlorophthaloyl,[72–74] *N*-chloroacetyl,[75] *N*-trichloroacetyl,[76,77] *N*-trichloroethoxycarbonyl,[78,79] or *N*,*N*-diacetyl[80] were not applicable here due to their high sensibility under conditions required for saponification of the tether. The use of 2-azido-2-deoxy glucose derivatives as starting



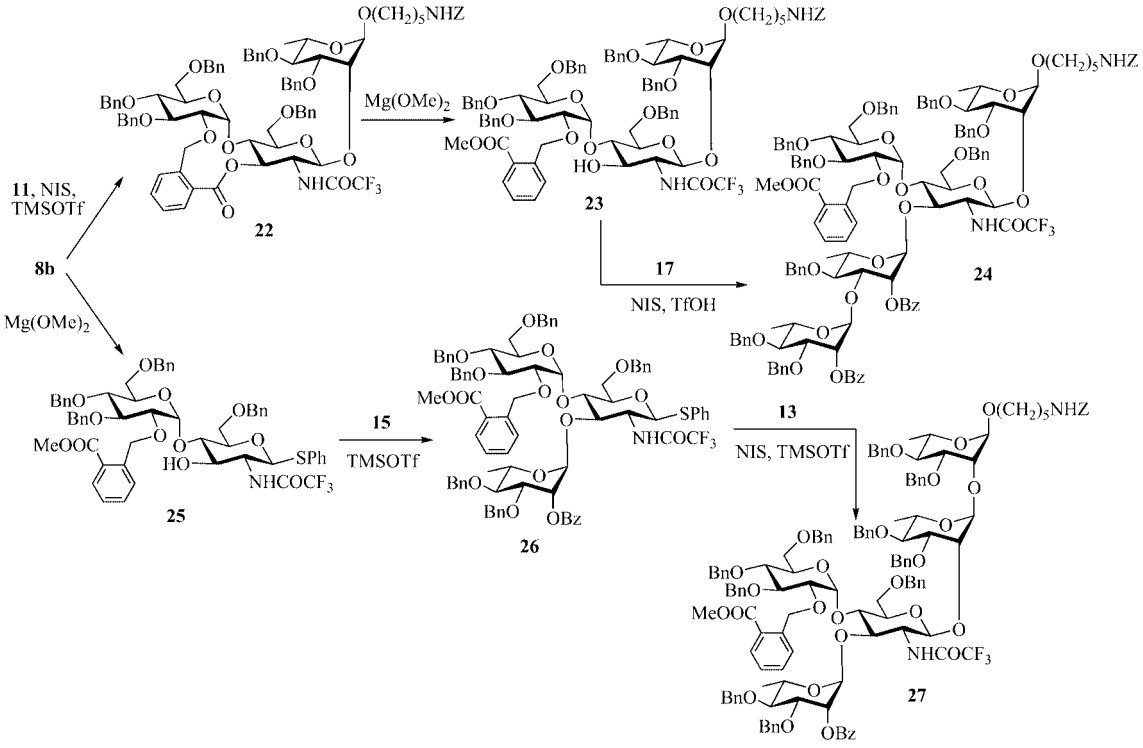
Scheme 1.



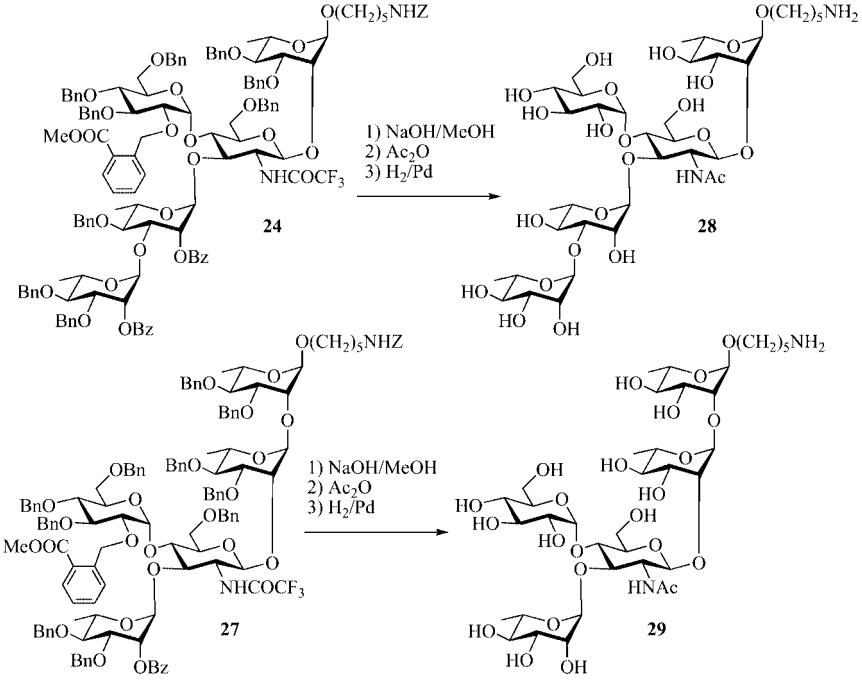
Scheme 2.

materials appeared impractical as well, because this avenue would require employment of triflyl azide which is, however, inconvenient on a large scale.[81] The *N*-acetyl-*N*-benzyl group is also not recommendable for protecting amino groups in glucosamine-containing oligosaccharides, because rotamers at the amide bond complicate assignment of NMR signals considerably.[82–85] Solely the trifluoroacetyl group appeared to be suitable here because trifluoroacetamides are stable during deprotection of other acyl groups,[89–91] but are still easily removed and ensure high β-selectivities and good yields during glycosylation reactions.[86] Thus, the *N*-trifluoroacetyl-protected glucosamine **4**[86] was first converted into the glucoside **5b** in 85% yield by sequential deprotection with NaOMe in methanol, fol-

lowed by reaction with benzaldehyde dimethylacetal and a catalytic amount of *p*-toluenesulfonic acid. Esterification of the glucosamine **5b** with the glucoside **3b** and DDC turned out to be sluggish though. Better results were obtained by first converting **3b** into the mixed anhydride with trichlorobenzoyl chloride and Et_3N in CH_2Cl_2, followed by DMAP-catalyzed alcoholysis of the latter with the glucoside **5b** in THF.[87] This way, the prearranged bis(glycoside) **6b** was obtained in 70% overall yield. Next, the benzylidene acetal group of the glucosamine moiety was regioselective opened with $NaCNBH_3$ to give the prearranged bis(glucoside) **7b** in 63% yield. Intramolecular glycosylation of the latter by promotion with IDCP in CH_2Cl_2 afforded the disaccharide **8b** in 72% yield. Once again the heteronuclear $^1J_{C\text{-}1,1\text{-}H}$



Scheme 3.



Scheme 4.

coupling constant of 169.9 Hz in the NMR spectra of the glucose moiety of **8b** showed unambiguously an α-linkage at the anomeric center.

Coupling of unsymmetrically tethered disaccharide block **8b** with the rhamnoside **11** by activation of the donor with NIS/TMSOTf afforded the β-linked trisaccharide **22** in 65% yield with $^1J_{C\text{-}1,1\text{-}H}$ = 161.0 Hz for the anomeric center of the glucosylamino moiety. Treatment of the latter with magnesium methoxide[90,91] proceeded smoothly and gave the desired trisccharide **23** in 77% yield. Finally, rhamnosylation to the 3-position of **23** with 1-thiorhamnoside **17** and NIS/TfOH in dichloromethane afforded the pentasaccharide **24** in 62% yield. Similarly, the tethered disaccharide block **8b** was transferred into the acceptor building block **25** by transesterification with magnesium methoxide in 76% yield followed by glycosylation with rhamnosyl imidate **15** under TMSOTf catalysis to give the α-linked trisaccharide donor **26** in 71% yield. Subsequent condensation of the latter with rhamnosyl acceptor **13** under NIS/TMSOTf activation furnished the pentasaccharide **27** in 55% yield; the newly formed β-linkage of the glucosylamino group was once again proven by measuring a $^1J_{C\text{-}1,1\text{-}H}$ coupling constant of 160.8 Hz at the anomeric center (Scheme 3).

Sequential deblocking of pentasaccharides **24** and **27** was achieved by first converting the *N*-trifluoroacetyl group into an *N*-acetyl group by saponification with aqueous NaOH in methanol, followed by *N*-acetylation with Ac_2O of the intermediate amine. Benzoyl groups were also removed during this step and final hydrogenolysis of the intermediates furnished the deblocked 5-aminopentyl glycoside pentasaccharides **28** and **29** in 81% and 79% yield, respectively (Scheme 4).

Conclusion

In conclusion, we have successfully demonstrated the efficient construction of the α-glucosyl-containing blocks **8a**, **8b** by using our intramolecular glycosylation method via unsymmetrical tethers. Furthermore, the usefulness of this approach as a new flexible strategy for the synthesis of complex oligosaccharides is impressively demonstrated.

Experimental Section

General: Thin-layer chromatography (TLC) was performed on precoated plastics sheets, Polygram SIL G/UV$_{254}$, 40× 80 mm (Macherey–Nagel). Spots were detected by UV light and by charring with 5% sulfuric acid in ethanol. Column chromatography (CC) was performed by elution from columns of silica gel (Macherey–Nagel, 0.032–0.063 mm). Solutions in organic solvents were dried with anhydrous sodium sulfate, and concentrated at 40 °C, <200 Pa. NMR spectra were recorded with Bruker Advance 400 Ultra Shield (400 MHz) and Bruker AMX 400 (400 MHz) instruments and calibrated with TMS as internal standard. Proton signal assignments were made by first-order analysis of the spectra by H,H COSY techniques. Of two magnetically nonequivalent geminal protons, the one resonating at lower field was designated as H_a and the one resonating at higher field was designated as H_b. Carbon signal assignments were made by C,H correlation. Optical rotations were measured at 20 °C with a Perkin–Elmer polarimeter, model 341. Melting points were determined with a Büchi apparatus, model 510. FAB mass spectra were recorded with a TSQ 70 Finnigan spectrometer. Elemental analyses were performed with a HEKAtech CHNS-Euro 3000 instrument.

Ethyl 3,4,6-Tri-*O*-benzyl-2-*O*-(2-*tert*-butyloxycarbonylbenzyl)-1-thio-α-D-glucopyranoside (3a): NaH (0.21 g, 8.90 mmol) and *tert*-butyl 2-(bromomethyl)benzoate (**2**)[53] (1.81 g, 6.68 mmol) were added with stirring at 0 °C to a solution of **1**[57] (2.20 g, 4.45 mmol) in DMF (75 mL), and the mixture was stirred at room temp. for 40 min. MeOH was added in order to destroy excess NaH and the mixture was poured onto ice. After extraction with CH_2Cl_2, the organic phases were washed with brine and water. After concentration and chromatography (petroleum ether/acetone, 10:1) of the residue, crystallization afforded **3a** (2.71 g, 89%), m.p. 80–81 °C (EtOH). $[\alpha]_D^{20}$ = –13.1 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.33 (d, *J* = –14.4 Hz, 1 H, $PhCH_2$), 5.21 (d, *J* = –14.3 Hz, 1 H, $PhCH_2$), 4.82 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.77 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.61 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.59 (s, 1 H, $PhCH_2$), 4.56 (s, *J* = –10.9 Hz, 1 H, $PhCH_2$), 4.54 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.49 (d, $J_{1,2}$ = 9.6 Hz, 1 H, 1-H), 3.76 (dd, $J_{6a,6b}$ = –10.9 Hz, 1 H, 6a-H), 3.72 (t, $J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 3.68 (dd, 1 H, 6b-H), 3.61 (t, $J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.53 (dd, $J_{2,3}$ = 8.6 Hz, 1 H, 2-H), 3.52–3.48 (m, $J_{5,6a}$ = 1.9 Hz, $J_{5,6b}$ = 4.6 Hz, 1 H, 5-H), 2.79–2.69 (m, 2 H, SCH_2CH_3), 1.56 [s, 9 H, $(CH_3)_3C$], 1.29 (t, *J* = 7.5 Hz, 3 H, SCH_2CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.2 (CO), 86.6 (C-3), 85.0 (C-1), 82.0 (C-2), 81.3 [$C(CH_3)_3$], 79.2 (C-5), 78.0 (C-4), 75.7 ($PhCH_2$), 75.0 ($PhCH_2$), 73.4 ($PhCH_2$), 72.8 ($PhCH_2$), 69.2 (C-6), 28.2 [$C(CH_3)_3$], 24.9 (SCH_2CH_3), 15.1 (SCH_2CH_3). $C_{41}H_{48}O_7S$ (684.89): calcd. C 71.90, H 7.06; found C 71.94, H 7.08.

Ethyl 3,4,6-Tri-*O*-benzyl-2-*O*-(2-carboxybenzyl)-1-thio-α-D-glucopyranoside (3b): A solution of **3a** (3.64 g, 5.32 mmol) and TFA (5.4 mL, 53.20 mmol) in CH_2Cl_2 (60 mL) was stirred at room temp. After 2 h, the mixture was diluted twice with toluene and the solvents were evaporated. Crystallization of the crude product afforded **3b** (3.02 g, 90%), m.p. 123–124 °C (petroleum ether/acetone). $[\alpha]_D^{20}$ = –15.7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (s, 2 H, $PhCH_2$), 4.83 (d, *J* = –11.5 Hz, 1 H, $PhCH_2$), 4.82 (d, *J* = –10.6 Hz, $PhCH_2$), 4.61 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.57 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.55 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.50 (s, 1 H, $PhCH_2$), 4.47 (d, $J_{1,2}$ = 9.6 Hz, 1 H, 1-H), 3.78–3.70 (m, 2 H, 6a-H, 6b-H), 3.71 (t, $J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 3.64 (t, $J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.52–3.48 (m, $J_{5,6a}$ = 1.7 Hz, 1 H, 5-H), 3.57 (t, $J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 2.80 –2.66 (m, 2 H, SCH_2CH_3), 1.28 (t, *J* = 7.5 Hz, 3 H, SCH_2CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 171.7 (COOH), 86.7 (C-3), 84.8 (C-1), 81.6 (C-2), 79.2 (C-5), 78.0 (C-4), 75.7 ($PhCH_2$), 75.0 ($PhCH_2$), 73.4 ($PhCH_2$), 72.7 ($PhCH_2$), 69.2 (C-6), 24.7 (SCH_2CH_3), 15.1 (SCH_2CH_3). $C_{37}H_{40}O_7S$ (628.78): calcd. C 70.68, H 6.41, S 5.10; found C 70.67, H 6.43, S 4.81.

Phenyl 4,6-*O*-Benzylidene-2-deoxy-1-thio-2-trifluoroacetamido-β-D-glucopyranoside (5b): A solution of **4**[86] (24.72 g, 50.10 mmol) and NaOMe in methanol (500 mL) was stirred at room temp. for 2 h, neutralized (ion exchange resin, H^+ form), filtered and concentrated. Benzaldehyde dimethylacetal (18 mL, 120.24 mmol) and *p*-toluenesulfonic acid (0.95 g, 5.00 mmol) were added to the crude compound in acetonitrile (500 mL), and the forming solution was stirred at room temp. for 18 h. The mixture was neutralized with

Et_3N and poured into water. The precipitate was collected by filtration and recrystallization from acetone/ethanol afforded **5b** (19.45 g, 85%), m.p. 264 °C (dec.). $[a]_D^{20}$ = –17.6 (*c* = 1.0, acetone). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.77 (d, *J* = 7.8 Hz, 1 H, NH), 5.65 (s, 1 H, $PhCH_2$), 5.14 (d, $J_{1,2}$ = 10.1 Hz, 1 H, 1-H), 5.09 (d, *J* = 4.5 Hz, 1 H, OH), 4.29 (dd, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = –10.2 Hz, 1 H, 6a-H), 4.07–4.00 (m, $J_{3,4}$ = 9.2 Hz, 2 H, 2-H, 3-H), 3.81 (t, $J_{5,6b}$ = 10.1 Hz, 1 H, 6b-H), 3.64 (t, $J_{4,5}$ = 9.1 Hz, 1 H, 4-H), 3.56 (ddd, 1 H, 5-H). ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 157.8 (NH*C*OCF$_3$, $J_{C,F}$ = 36.2 Hz), 117.2 (NHCO*C*F$_3$, $J_{C,F}$ = 287.6 Hz), 102.2 (PhCH), 87.5 (C-1), 82.1 (C-4), 72.9 (C-3), 71.4 (C-5), 68.9 (C-6), 56.7 (C-2). $C_{21}H_{20}NO_5SF_3$ (455.45): calcd. C 55.38, H 4.43, N 3.08, S 7.04; found C 55.37, H 4.59, N 2.99, S 6.91.

Ethyl 3,4,6-Tri-*O*-benzyl-2-*O*-[(4,6-*O*-benzylidene-2-deoxy-1-phenylthio-2-phthalimido-β-D-glucopyranos-3-yloxy)-2-carbonylbenzyl]-1-thio-β-D-glucopyranoside (6a): DCC (0.46 g, 2.23 mmol) and a catalytic amount of DMAP were added at room temp. to a solution of **3b** (1.17 g, 1.86 mmol) and **5a**[58] (0.91 g, 1.86 mmol) in CH_2Cl_2 (60 mL). After stirring for 24 h, the mixture was diluted with CH_2Cl_2 and filtered through a layer of Celite®. The filtrate was subsequently washed with aqueous HCl and saturated aqueous $NaHCO_3$ solution, dried and concentrated. Chromatography (toluene/acetone, 55:1) of the residue afforded **6a** (1.48 g, 73%) as colorless foam. $[a]_D^{20}$ = +27.6 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.12 (t, $J_{3,4}$ = 9.5 Hz, 1 H, 3$_B$-H), 5.90 (d, $J_{1,2}$ = 10.6 Hz, 1 H, 1$_B$-H), 5.52 (s, 1 H, $PhCH_2$), 5.03 (d, *J* = –14.8 Hz, 1 H, $PhCH_2$), 4.80 (d, *J* = –10.9 Hz, 1 H, $PhCH_2$), 4.77 (d, *J* = –14.8 Hz, 1 H, $PhCH_2$), 4.63 (s, 1 H, $PhCH_2$), 4.61 (d, *J* = –12.0 Hz, 1 H, $PhCH_2$), 4.57 (s, 1 H, $PhCH_2$), 4.55 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.54 (d, *J* = –12.5 Hz, 1 H, $PhCH_2$), 4.51 (dd, $J_{2,3}$ = 9.9 Hz, 1 H, 2$_B$-H), 4.44 (m, 1 H, 6a$_B$-H), 4.30 (d, $J_{1,2}$ = 9.7 Hz, 1 H, 1$_E$-H), 3.86–3.78 (m, 3 H, 4$_B$-H, 5$_B$-H, 6b$_B$-H), 3.74 (dd, $J_{5,6b}$ = 4.6 Hz, 1 H, 6a$_E$-H), 3.67 (dd, $J_{6a,6b}$ = –10.9 Hz, 1 H, 6b$_E$-H), 3.56 (t, $J_{3,4}$ = 8.7 Hz, 1 H, 3$_E$-H), 3.49 (t, $J_{4,5}$ = 9.0 Hz, 1 H, 4$_E$-H), 3.43–3.39 (m, $J_{5,6a}$ = 1.9 Hz, 1 H, 5$_E$-H), 3.17 (dd, $J_{2,3}$ = 8.4 Hz, 1 H, 2$_E$-H), 2.65–2.49 (m, 2 H, SC*H*$_2$CH$_3$), 1.18 (t, *J* = 7.4 Hz, 3 H, SCH$_2$C*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.9 (NCO), 167.1 (NCO), 165.8 (CO), 101.4 (PhCH), 86.4 (C-3$_E$), 84.8 (C-1$_E$), 84.1 (C-1$_B$), 81.7 (C-2$_E$), 79.1, 79.0 (1 C, 1 C, C-5$_B$, C-5$_E$), 77.8 (C-4$_E$), 75.5 ($PhCH_2$), 74.9 ($PhCH_2$), 73.4 ($PhCH_2$), 72.1 ($PhCH_2$), 71.0 (C-3$_B$), 70.6 (C-4$_B$), 69.1 (C-6$_E$), 68.5 (C-6$_B$), 54.3 (C-2$_B$), 24.7 (S*C*H$_2$CH$_3$), 15.1 (SCH$_2$*C*H$_3$). $C_{64}H_{61}NO_{12}S_2$ (1100.31): calcd. C 69.86, H 5.59, N 1.27, S 5.83; found C 69.79, H 5.66, N 1.33, S 5.96.

Ethyl 3,4,6-Tri-*O*-benzyl-2-*O*-[(4,6-*O*-benzylidene-2-deoxy-1-phenylthio-2-trifluoroacetamido-β-D-glucopyranos-3-yloxy)-2-carbonylbenzyl]-1-thio-β-D-glucopyranoside (6b): A solution of **3b** (2.31 g, 3.67 mmol) and triethylamine (0.51 mL, 3.67 mmol) in CH_2Cl_2 (15 mL) was added dropwise at 0 °C to a solution of 2,4,6-trichlorobenzoyl chloride (1.07 g, 4.40 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temp. for 16 h, then diluted with CH_2Cl_2, washed with water, dried and concentrated. To the crude anhydride in THF (20 mL) was added dropwise a solution of **5b** (1.66 g, 3.67 mmol) and DMAP (0.45 g, 3.67 mmol) in THF (20 mL). After stirring at room temp. for 1 h, the mixture was diluted with CH_2Cl_2, washed with water, dried and concentrated. Chromatography (toluene/ethyl acetate, 15:1) of the residue afforded **6b** (2.74 g, 70%). $[a]_D^{20}$ = –27.6 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.56 (t, $J_{3,4}$ = 9.7 Hz, 1 H, 3$_B$-H), 5.49 (s, 1 H, $PhCH_2$), 5.20 (d, *J* = –14.4 Hz, 1 H, $PhCH_2$), 5.12 (d, *J* = –14.4 Hz, 1 H, $PhCH_2$), 4.85 (d, $J_{1,2}$ = 10.6 Hz, 1 H, 1$_B$-H), 4.82 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.78 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.74 (d, *J* = –10.9 Hz, 1 H, $PhCH_2$), 4.73–4.52 (m, 3 H, $PhCH_2$), 4.38 (d, $J_{1,2}$ = 9.9 Hz, 1 H, 1$_E$-H), 4.28–4.20 (m, $J_{2,3}$ = 9.9 Hz, 1 H, 2$_B$-H), 4.08 (dd, $J_{5,6a}$ = 4.5 Hz, $J_{6a,6b}$ = –10.2 Hz, 1 H, 6a$_B$-H), 3.75–3.64 (m, $J_{5,6a}$ = 3.4 Hz, 5 H, 3$_E$-H, 4$_B$-H, 6b$_B$-H, 6a$_E$-H, 6b$_E$-H), 3.56–3.49 (m, $J_{4,5}$ = 9.7 Hz, 2 H, 4$_E$-H, 5$_B$-H), 3.46–3.43 (m, 1 H, 5$_E$-H), 3.34 (t, $J_{2,3}$ = 9.4 Hz, 1 H, 2$_E$-H), 2.61–2.46 (m, 2 H, SC*H*$_2$CH$_3$), 1.16 (t, *J* = 7.3 Hz, 3 H, SCH$_2$C*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.8 (PhCO), 157.1 (NH*C*OCF$_3$, $J_{C,F}$ = 37.7 Hz), 115.6 (NHCO*C*F$_3$, $J_{C,F}$ = 288.3 Hz), 101.0 (PhCH), 87.3 (C-1$_B$), 86.6 (C-3$_E$), 84.9 (C-1$_E$), 81.9 (C-2$_E$), 79.0 (C-5$_E$), 77.9 (2 C, C-4$_E$, C-5$_B$), 75.7 ($PhCH_2$), 75.0 ($PhCH_2$), 73.4 ($PhCH_2$), 73.3 (C-3$_B$), 72.3 ($PhCH_2$), 70.8 (C-4$_B$), 69.1 (C-6$_E$), 68.1 (C-6$_B$), 53.8 (C-2$_B$), 24.7 (S*C*H$_2$CH$_3$), 15.1 (SCH$_2$*C*H$_3$). $C_{58}H_{58}F_3NO_{11}S_2$ (1066.22): calcd. C 65.34, H 5.48, N 1.31, S 6.01; found C 65.51, H 5.47, N 1.35, S 5.80.

Ethyl 3,4,6-Tri-*O*-benzyl-2-*O*-[(6-*O*-benzyl-2-deoxy-1-phenylthio-2-phthalimido-β-D-glucopyranos-3-yloxy)-2-carbonylbenzyl]-1-thio-β-D-glucopyranoside (7a): A solution of HCl in THF was added portionwise at room temp. to a suspension of **6a** (2.68 g, 2.44 mmol), $NaCNBH_3$ (1.38 g, 21.96 mmol) and molecular sieves (3 Å) in THF (90 mL) until the evolution of gas had ceased. The mixture was then diluted with CH_2Cl_2 and filtered through a layer of Celite®. The filtrate was washed with saturated aqueous $NaHCO_3$ solution, dried and concentrated. Chromatography (toluene/acetone, 25:1) afforded **7a** (1.70 g, 63%) as a colorless foam. $[a]_D^{20}$ = +20.7 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.87 (dd, $J_{3,4}$ = 9.0 Hz, 1 H, 3$_B$-H), 5.79 (d, $J_{1,2}$ = 10.5 Hz, 1 H, 1$_B$-H), 5.11 (d, *J* = –13.7 Hz, 1 H, $PhCH_2$), 5.02 (d, *J* = –13.7 Hz, 1 H, $PhCH_2$), 4.74 (d, *J* = –11.0 Hz, 1 H, $PhCH_2$), 4.68–4.54 (m, 4 H, $PhCH_2$), 4.58 (d, *J* = –10.7 Hz, 1 H, $PhCH_2$), 4.51 (d, *J* = –11.0 Hz, 1 H, $PhCH_2$), 4.49 (d, *J* = –10.5 Hz, 1 H, $PhCH_2$), 4.41 (t, $J_{2,3}$ = 10.4 Hz, 1 H, 2$_B$-H), 4.34 (d, $J_{1,2}$ = 9.5 Hz, 1 H, 1$_E$-H), 3.88–3.76 (m, 3 H, 5$_B$-H, 6a$_B$-H, 6b$_B$-H), 3.65–3.58 (m, $J_{6a,6b}$ = –10.9 Hz, 2 H, 4$_B$-H, 6b$_E$-H), 3.54–3.48 (m, 2 H, 3$_E$-H, 4$_E$-H), 3.44–3.40 (m, $J_{5,6a}$ = 1.8 Hz, 2 H, 2$_E$-H, 5$_E$-H), 2.73–2.59 (m, 2 H, SC*H*$_2$CH$_3$), 1.24 (t, *J* = 7.4 Hz, 3 H, SCH$_2$C*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 167.8 (NCO), 167.3 (NCO), 167.0 (CO), 86.3 (C-3$_E$), 84.8 (C-1$_E$), 83.1 (C-1$_B$), 82.3 (C-2$_E$), 79.1, 79.0 (1 C, 1 C, C-5$_B$, C-5$_E$), 77.7 (C-4$_E$), 75.8 ($PhCH_2$), 75.2 (C-3$_B$), 74.8 ($PhCH_2$), 73.5 ($PhCH_2$), 73.4 ($PhCH_2$), 73.0 ($PhCH_2$), 70.0 (C-4$_B$), 69.7 (C-6$_B$), 69.0 (C-6$_E$), 53.5 (C-2$_B$), 24.6 (S*C*H$_2$CH$_3$), 15.0 (SCH$_2$*C*H$_3$). $C_{64}H_{63}NO_{12}S_2$ (1102.33): calcd. C 69.74, H 5.76, N 1.27; found C 69.93, H 5.84, N 1.33.

Ethyl 3,4,6-Tri-*O*-benzyl-2-*O*-[(6-*O*-benzyl-2-deoxy-1-phenylthio-2-trifluoroacetamido-β-D-glucopyranos-3-yloxy)-2-carbonylbenzyl]-1-thio-β-D-glucopyranoside (7b): A solution of HCl in Et_2O was added portionwise at room temp. to a suspension of **6b** (2.15 g, 2.02 mmol), $NaCNBH_3$ (1.14 g, 18.18 mmol) and molecular sieves (3 Å) in THF (40 mL) until the evolution of gas had ceased. The mixture was diluted with CH_2Cl_2 and filtered through a layer of Celite®. The filtrate was washed with an aqueous $NaHCO_3$ solution, dried and concentrated. Chromatography (toluene/ethyl acetate, 10:1) gave **7b** (1.36 g, 63%) as a colorless foam. $[a]_D^{20}$ = –22.2 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85 (d, *J* = 9.6 Hz, 1 H, N*H*CO), 5.27 (d, *J* = –12.6 Hz, 1 H, $PhCH_2$), 5.25 (t, $J_{3,4}$ = 9.7 Hz, 1 H, 3$_B$-H), 5.11 (d, *J* = –13.3 Hz, 1 H, $PhCH_2$), 4.80 (d, $J_{1,2}$ = 10.4 Hz, 1 H, 1$_B$-H), 4.73 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.63 (d, *J* = –11.6 Hz, 1 H, $PhCH_2$), 4.58–4.49 (m, 8 H, $PhCH_2$), 4.39 (d, $J_{1,2}$ = 9.6 Hz, 1 H, 1$_E$-H), 3.83 (dd, $J_{5,6a}$ = 2.5 Hz, $J_{6a,6b}$ = –10.6 Hz, 1 H, 6a$_B$-H), 3.74 (dd, $J_{5,6b}$ = 5.3 Hz, 1 H, 6b$_B$-H), 3.71–3.63 (m, 3 H, 5$_B$-H, 6a$_E$-H, 6b$_E$-H), 3.61–3.51 (m, 3 H, 3$_E$-H, 4$_B$-H, 4$_E$-H), 3.49–3.42 (m, 2 H, 2$_E$-H, 5$_E$-H), 2.73–2.61 (m, 2 H, SC*H*$_2$CH$_3$), 1.25 (t, *J* = 7.5 Hz, 3 H, SCH$_2$C*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.3 (PhCO), 158.4 (NH*C*OCF$_3$, $J_{C,F}$

= 38.1 Hz), 116.8 (NHCOCF_3, $J_{C,F}$ = 287.6 Hz), 86.6 (C-3_E), 86.5 (C-1_B), 85.2 (C-1_E), 82.9 (C-2_E), 79.6 (C-5_B), 79.5 (C-5_E), 78.3 (C-4_E), 77.7 (C-3_B), 76.2 ($PhCH_2$), 75.3 ($PhCH_2$), 74.0 ($PhCH_2$), 73.9 ($PhCH_2$), 73.8 ($PhCH_2$), 72.3 ($PhCH_2$), 70.0 (C-6_B), 69.4 (2 C, C-4_B, C-6_E), 53.4 (C-2_B), 25.2 (S$CH_2$$CH_3$), 15.4 (S$CH_2$$CH_3$). $C_{58}H_{60}F_3NO_{11}S_2$ (1068.23): calcd. C 65.21, H 5.66, N 1.31, S 6.00; found C 65.43, H 5.68, N 1.41, S 5.83.

Phenyl 2′,3-*O*-(2-Methylenebenzoyl)-(3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (8a): IDCP[88] (0.52 g, 1.44 mmol) was added at room temp. under argon to a mixture of **7a** (0.79 g, 0.72 mmol) and molecular sieves (4 Å) in CH_2Cl_2 (40 mL). The mixture was stirred for 3 h, diluted with CH_2Cl_2 and filtered. The filtrate was washed with aqueous sodium thiosulfate solution, water, dried and concentrated. Chromatography (toluene/ethyl acetate, 15:1) afforded **8a** (0.52 g, 69%) as a colorless foam. $[\alpha]_D^{20}$ = +53.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (dd, $J_{3,4}$ = 9.1 Hz, 1 H, 3_B-H), 5.88 (d, $J_{1,2}$ = 10.4 Hz, 1 H, 1_B-H), 5.21 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1_E-H), 5.01 (d, *J* = –10.4 Hz, 1 H, $PhCH_2$), 4.82 (d, *J* = –11.0 Hz, 1 H, $PhCH_2$), 4.66 (d, *J* = –12.9 Hz, 1 H, $PhCH_2$), 4.61 (d, *J* = –12.0 Hz, 1 H, $PhCH_2$), 4.57 (s, 2 H, $PhCH_2$), 4.52 (s, 1 H, $PhCH_2$), 4.47 (d, *J* = –12.4 Hz, 1 H, $PhCH_2$), 4.45 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.39 (d, *J* = –10.5 Hz, 1 H, $PhCH_2$), 4.30 (t, $J_{2,3}$ = 10.4 Hz, 1 H, 2_B-H), 3.96 (t, $J_{4,5}$ = 9.1 Hz, 1 H, 4_B-H), 3.86–3.69 (m, $J_{5,6a}$ = 4.1 Hz, 4 H, 3_E-H, 5_B-H, $6a_E$-H, $6b_E$-H), 3.61 (dd, $J_{5,6b}$ = 1.8 Hz, 1 H, $6a_B$-H), 3.53 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4_E-H), 3.52 (dd, $J_{6a,6b}$ = –10.5 Hz, 1 H, $6b_B$-H), 3.42 (dd, $J_{2,3}$ = 9.7 Hz, 1 H, 2_E-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.6 (CO), 168.1 (CO), 167.2 (CO), 100.0 (C-1_E, $J_{C,H}$ = 169.8 Hz), 82.5 (C-1_B), 81.1 (C-3_E), 80.7 (C-2_E), 79.9 (C-4_B), 78.9 (C-5_E), 76.9 (C-4_E), 75.7 ($PhCH_2$), 74.8 (1 C, 2 C, C-3_B, $PhCH_2$), 73.5 ($PhCH_2$), 73.1 ($PhCH_2$), 71.5 (C-5_B), 70.9 ($PhCH_2$), 68.8 (C-6_E), 68.6 (C-6_B), 53.9 (C-2_B). $C_{62}H_{57}NO_{12}S$ (1040.20): calcd. C 71.59, H 5.52, N 1.35, S 3.08; found C 71.60, H 5.61, N 1.40, S 3.15.

Phenyl 2′,3-*O*-(2-Methylenebenzoyl)-(3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-1-thio-2-trifluoroacetamido-β-D-glucopyranoside (8b): IDCP (0.77 g, 2.14 mmol) was added at 0 °C under argon to a mixture of **7b** (1.14 g, 1.07 mmol) and molecular sieves (4 Å) in CH_2Cl_2 (40 mL). The mixture was stirred for 40 min, diluted with CH_2Cl_2 and filtered. The filtrate was washed with aqueous thiosulfate solution, water, dried and concentrated. Chromatography (toluene/ethyl acetate, 20:1) afforded **8b** (0.78 g, 72%) as a colorless foam. $[\alpha]_D^{20}$ = +17.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.55 (t, $J_{3,4}$ = 9.9 Hz, 1 H, 3_B-H), 5.18 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1_E-H), 5.04 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.88 (d, $J_{1,2}$ = 10.1 Hz, 1 H, 1_B-H), 4.83 (d, *J* = –10.9 Hz, 1 H, $PhCH_2$), 4.77–4.69 (m, 2 H, $PhCH_2$), 4.54 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.51 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.44 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.42 (s, 1 H, $PhCH_2$), 4.36 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.31 (d, *J* = –11.9 Hz, 1 H, $PhCH_2$), 4.11–4.03 (m, $J_{2,3}$ = 10.0 Hz, 1 H, 2_B-H), 3.91 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4_B-H), 3.82 (t, $J_{5,6a}$ = 9.9 Hz, $J_{6a,6b}$ = –10.0 Hz, $6a_B$-H), 3.78–3.71 (m, 4 H, 3_E-H, 5_B-H, 5_E-H, $6b_E$-H), 3.60–3.54 (m, 2 H, 4_E-H, $6a_E$-H), 3.48–3.43 (m, 2 H, 2_E-H, $6b_B$-H), ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 171.4 (PhCO), 157.3 (NH$CO$$CF_3$, $J_{C,F}$ = 37.3 Hz), 116.2 (NHCOCF_3, $J_{C,F}$ = 287.6 Hz), 100.7 (C-1_E, $J_{C,H}$ = 169.9 Hz), 85.1 (C-1_B), 81.7 (C-3_E), 81.0 (C-2_E), 79.4 (C-4_B), 79.3 (C-5_E), 77.3 (2 C, C-3_B, C-4_E), 76.2 ($PhCH_2$), 75.5 ($PhCH_2$), 73.9 ($PhCH_2$), 73.4 ($PhCH_2$), 71.9 (C-5_B), 71.6 ($PhCH_2$), 69.0 (C-6_E), 68.8 (C-6_B), 53.2 (C-2_B). $C_{56}H_{54}F_3NO_{11}S$ (1006.10): calcd. C 66.85, H 5.41, N 1.39, S 3.19; found C 67.11, H 5.44, N 1.40, S 3.30.

5-[(Benzyloxycarbonyl)amino]pentyl 2-*O*-Benzoyl-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (10): A mixture of **9**[68] (1.12 g, 2.27 mmol), 5-[(Benzyloxycarbonyl)amino]pentanol (0.54 g, 2.27 mmol) and molecular sieves (4 Å) in CH_2Cl_2 (50 mL) was cooled under argon to –10 °C and stirred for 10 min. NIS (0.51 g, 2.27 mmol) and TfOH (20 μL, 0.23 mmol) were successively added, the mixture was stirred for 10 min, neutralized by addition of triethylamine, diluted with CH_2Cl_2 and filtered through a layer of Celite®. The filtrate was washed with aqueous $Na_2S_2O_3$ solution, water, dried and concentrated. Chromatography (petroleum ether/ethyl acetate, 4:1) of the residue afforded **10** (1.21 g, 80%) as an oil. $-[\alpha]_D^{20}$ = +11.7 (*c* = 1.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.57 (dd, $J_{2,3}$ = 3.3 Hz, 1 H, 2-H), 5.09 (br. s, 1 H, $PhCH_2OCO$), 4.91 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.83 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 4.79 (br. s, 1 H, NH), 4.77 (d, *J* = –11.3 Hz, 1 H, $PhCH_2$), 4.64 (d, *J* = –10.9 Hz, 1 H, $PhCH_2$), 4.56 (d, *J* = –11.3 Hz, 1 H, $PhCH_2$), 4.03 (dd, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 3.82–3.75 (m, $J_{5,6}$ = 6.2 Hz, 1 H, 5-H), 3.70–3.62 (m, 1 H, OCH_2), 3.53 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.44–3.36 (m, 1 H, OCH_2), 3.23–3.16 (m, 2 H, NHCH_2), 1.63–1.47 (m, 4 H, CH_2), 1.41–1.35 (m, 2 H, CH_2), 1.36 (d, 3 H, 6-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 165.8 (PhCO), 156.4 (OCONH), 97.6 (C-1, $J_{C-1,1-H}$ = 169.3 Hz), 80.1 (C-4), 78.2 (C-3), 75.4 ($PhCH_2$), 71.5 ($PhCH_2$), 69.5 (C-2), 67.6 (2 C, $PhCH_2$, C-5), 66.6 (Ph$C$$H_2OCO$), 40.9 ($CH_2NH$), 29.7 ($CH_2$), 29.0 ($CH_2$), 23.4 ($CH_2$), 18.1 (C-6). $C_{40}H_{45}NO_8$ (667.8): calcd. C 71.94, H 6.79, N 2.10; found C 71.75, H 6.81, N 1.93.

5-[(Benzyloxycarbonyl)amino]pentyl 3,4-Di-*O*-benzyl-α-L-rhamnopyranoside (11): A solution of **10** (202 mg, 0.30 mmol) and a catalytic amount of NaOMe (1 M in methanol) in MeOH (5 mL) were stirred at room temp. for 24 h, neutralized with ion exchange resin (Dowex 50 W X 8, H^+), filtered and concentrated. Chromatography (petroleum ether/acetone, 3:1) of the residue afforded **11** (167 mg, 98%) as a colorless foam. $[\alpha]_D^{20}$ = –24.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.09 (br. s, 2 H, $PhCH_2OCO$), 4.88 (d, *J* = –10.9 Hz, 1 H, $PhCH_2$), 4.77 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 4.68 (br. s, 3 H, $PhCH_2$, NH), 4.63 (d, *J* = –10.9 Hz, 1 H, $PhCH_2$), 4.01 (dd, $J_{2,3}$ = 3.5 Hz, 1 H, 2-H), 3.83 (dd, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 3.75–3.68 (m, $J_{5,6}$ = 6.3 Hz, 1 H, 5-H), 3.67–3.59 (m, 1 H, OCH_2), 3.45 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.40–3.33 (m, 1 H, OCH_2), 3.21–3.15 (m, 2 H, CH_2NH), 1.60–1.43 (m, 1 H, CH_2), 1.39–1.34 (m, 2 H, CH_2), 1.30 (d, 3 H, 6-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 156.3 (OCONH), 98.9 (C-1, $J_{C-1,1-H}$ = 167.9 Hz), 80.1 (C-3), 79.9 (C-4), 75.4 ($PhCH_2$), 71.9 ($PhCH_2$), 68.5 (C-2), 67.3 (OCH_2), 67.2 (C-5), 66.5 (Ph$C$$H_2OCO$), 40.9 ($CH_2NH$), 29.7 ($CH_2$), 29.0 ($CH_2$), 23.3 ($CH_2$), 17.8 (C-6). $C_{33}H_{41}NO_7$ (563.68): calcd. C 70.32, H 7.33, N 2.49; found C 69.99, H 7.31, N 2.51.

5-[(Benzyloxycarbonyl)amino]pentyl (2-*O*-Benzoyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (12): A mixture of **9**[68] (180 mg, 0.365 mmol), **11** (206 mg, 0.365 mmol) and molecular sieves (4 Å) in CH_2Cl_2 (10 mL) was cooled under argon to –10 °C and stirred for 10 min. NIS (82 mg, 0.365 mmol) and TfOH (ca. 4 μL, 37 μmol) were successively added, the mixture was stirred for 15 min, neutralized by addition of triethylamine, diluted with CH_2Cl_2 and filtered through a layer of Celite®. The filtrate was washed with aqueous $Na_2S_2O_3$ solution, water, dried and concentrated. The crude compound was purified by chromatography (petroleum ether/ethyl acetate, 4:1) to yield pure **12** as colorless foam (253 mg, 70%). $[\alpha]_D^{20}$ = +12.8 (*c* = 1.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.76 (dd, $J_{2,3}$ = 3.1 Hz, 1 H, 2_C-H), 5.13 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1_C-H), 5.08 (br. s, 2 H, $PhCH_2OCO$), 4.90 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.82 (d, *J* = –11.3 Hz, 1 H, $PhCH_2$), 4.78 (br. s, 1 H, NH), 4.70 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1_D-H), 4.67 (s, 3 H, $PhCH_2$), 4.64 (d, *J* = –10.9 Hz, $PhCH_2$), 4.61 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.58 (d, *J* = –11.3 Hz, 1 H,

$PhCH_2$), 4.08 (dd, $J_{3,4}$ = 9.3 Hz, 1 H, 3_C-H), 3.98 (br. t, $J_{2,3}$ = 2.9 Hz, 1 H, 2_D-H), 3.92–3.89 (m, $J_{5,6}$ = 6.2 Hz, 1 H, 5_C-H), 3.85 (dd, $J_{3,4}$ = 9.2 Hz, 1 H, 3_D-H), 3.68–3.58 (m, $J_{5,6}$ = 6.2 Hz, 2 H, 5_D-H, OCH_2), 3.53 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4_C-H), 3.44 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4_D-H), 3.36–3.29 (m, 1 H, OCH_2), 3.20–3.14 (m, 2 H, C*H*$_2$NH), 1.57–1.42 (m, 4 H, CH_2), 1.36 (d, 3 H, 6_C-H), 1.34–1.30 (m, 2 H, OCH_2), 1.29 (d, 3 H, 6_D-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 165.4 (PhCO), 156.3 (OCONH), 99.2 (C-1_C, $J_{C,H}$ = 170.0 Hz), 98.7 (C-1_D, $J_{C,H}$ = 168.8 Hz), 80.0 (2 C, C-4_C, C-4_D), 79.8 (C-3_D), 77.7 (C-3_C), 75.3 (2 C, $PhCH_2$), 74.7 (C-2_D), 72.1 ($PhCH_2$), 71.5 ($PhCH_2$), 69.4 (C-2_C), 68.2 (C-5_C), 67.8 (C-5_D), 67.2 (OCH_2), 66.5 (Ph*C*H$_2$OCO), 40.9 (CH_2NH), 29.7 (CH_2), 29.0 (CH_2), 23.3 (CH_2), 18.2 (C-6_C), 18.0 (C-6_D). $C_{60}H_{67}NO_{12}$ (994.17): calcd. C 72.49, H 6.79, N 1.41; found C 72.55, H 6.81, N 1.35.

5-[(Benzyloxycarbonyl)amino]pentyl (3,4-Di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (13): A solution of **12** (1.08 g, 1.09 mmol) and a catalytic amount of NaOMe (1 M in methanol) in MeOH (30 mL) was stirred at room temp. for 48 h, neutralized with ion exchange resin (Dowex 50 W X 8, H^+), filtered and concentrated. Chromatography (petroleum ether/acetone, 4:1) of the residue afforded **13** (0.92 g, 95%) as a colorless foam. $[\alpha]_D^{20}$ = –27.3 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.09 (br. d, 2 H, $PhCH_2OCO$), 5.08 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1_C-H), 4.88 (d, *J* = –10.9 Hz, 1 H, $PhCH_2$), 4.86 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.75 (br. s, 1 H, NH), 4.71 (s, 2 H, $PhCH_2$), 4.68 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1_D-H), 4.66 (s, 2 H, $PhCH_2$), 4.63 (d, *J* = –11.7 Hz, 1 H, $PhCH_2$), 4.59 (d, *J* = –11.5 Hz, 1 H, $PhCH_2$), 4.13 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2_C-H), 3.98 (br. t, $J_{2,3}$ = 3.3 Hz, 1 H, 2_D-H), 3.88 (dd, $J_{3,4}$ = 9.4 Hz, 1 H, 3_D-H), 3.85–3.77 (m, $J_{5,6}$ = 6.2 Hz, 1 H, 5_C-H), 3.83 (dd, $J_{3,4}$ = 9.3 Hz, 1 H, 3_C-H), 3.68–3.63 (m, $J_{5,6}$ = 6.2 Hz, 1 H, 5_D-H), 3.61–3.54 (m, 1 H, OCH_2), 3.47 (t, $J_{4,5}$ = 9.3 Hz, 1 H, 4_C-H), 3.38 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4_D-H), 3.36–3.28 (m, 1 H, OCH_2), 3.21–3.14 (m, 2 H, C*H*$_2$NH), 1.59–1.31 (m, 6 H, CH_2), 1.30 (d, 3 H, 6_C-H), 1.28 (d, 3 H, 6_D-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 156.3 (OCONH), 100.7 (C-1_C), 98.8 (C-1_D), 80.4 (C-4_D), 80.0 (C-4_C), 79.8 (C-3_D), 79.5 (C-3_C), 75.3 (2 C, $PhCH_2$), 74.7 (C-2_D), 72.2 ($PhCH_2$), 72.1 ($PhCH_2$), 68.7 (C-2_C), 67.8 (2 C, C-5_C, C-5_D), 67.2 (OCH_2), 66.6 (Ph*C*H$_2$OCO), 40.9 (CH_2NH), 29.8 (CH_2), 29.1 (CH_2), 23.4 (CH_2), 18.0 (C-6_C), 17.9 (C-6_D). $C_{53}H_{63}NO_{11}$ (890.07): calcd. C 71.52, H 7.13, N 1.57; found C 71.21, H 7.11, N 1.50.

2-*O*-Benzoyl-3,4-di-*O*-benzyl-α/β-L-rhamnopyranose (14): A mixture of **9**[68] (0.74 g, 1.50 mmol) in acetone/water (23 mL, 9:1 v/v) was treated with NBS (1.07 g, 6.00 mmol). After stirring at room temp. for 20 min, the solution was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ solution, water and dried. The reaction solution was filtered, and the solvent was removed in vaco. The crude product was purified by chromatography (petroleum ether/acetone, 5:1) to yield pure **14** as a colorless foam (0.61 g, 91%) as an anomeric mixture (α/β, 4:1). $[\alpha]_D^{20}$ = +51.9 (*c* = 2.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$; α-anomer): δ = 5.61 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 5.26 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 4.11 (dd, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 4.07–4.02 (m, $J_{5,6}$ = 6.2 Hz, 1 H, 5-H), 1.35 (d, 3 H, 6-H). ^{13}C NMR (100.6 MHz, $CDCl_3$; α-anomer): δ = 165.8 (PhCO), 92.5 (C-1), 80.0 (C-4), 77.6 (C-3), 75.3 ($PhCH_2$), 71.5 ($PhCH_2$), 69.7 (C-2), 67.9 (C-5), 18.2 (C-6). $C_{27}H_{28}O_6$ (448.52): calcd. C 72.30, H 6.29; found C 72.38, H 6.42.

2-*O*-Benzoyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl Trichloroacetimidate (15): DBU (23 μL, 0.15 mmol) was added to a stirred solution of **14** (0.67 g, 1.49 mmol) and trichloroacetonitrile (0.43 g, 2.98 mmol) in CH_2Cl_2 (15 mL) at 0 °C. After 2 h at 0 °C, the mixture was concentrated in vaco and the residue was chromatographed (petroleum ether/acetone, 4:1 + 0.5% Et_3N) to yield **15** (0.70 g, 79%) as colorless foam. $[\alpha]_D^{20}$ = –3.8 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (s, 1 H, CNH), 6.31 (d, $J_{1,2}$ = 1.9 Hz, 1 H, 1-H), 5.72 (br. t, $J_{2,3}$ = 3.2 Hz, 1 H, 2-H), 4.93 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.80 (d, *J* = –11.4 Hz, 1 H, $PhCH_2$), 4.66 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.61 (d, *J* = –11.4 Hz, 1 H, $PhCH_2$), 4.11 (dd, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 4.03–3.98 (m, $J_{5,6}$ = 6.2 Hz, 1 H, 5-H), 3.64 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 1.39 (d, 3 H, 6-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 165.5 (PhCO), 160.1 (CNH), 95.2 (C-1), 90.7 (CCl_3), 79.3 (C-4), 77.3 (C-3), 75.6 ($PhCH_2$), 71.8 ($PhCH_2$), 70.5 (C-2), 68.0 (C-5), 75.6 ($PhCH_2$), 18.1 (C-6). $C_{29}H_{28}Cl_3NO_6$ (592.91): calcd. C 58.75, H 4.76, N 2.36; found C 58.77, H 4.77, N 2.13.

Ethyl (2-*O*-Benzoyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2-*O*-benzoyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (17): A mixture of **15** (0.29 g, 0.49 mmol) and **16**[70] (0.17 g, 0.41 mmol) in CH_2Cl_2 (15 mL) was cooled under argon to –10 °C and stirred for 10 min. TMSOTf (8 μL, 45 μmol) was successively added, the mixture was stirred for 15 min, neutralized by addition of triethylamine, diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ solution, water and concentrated. Chromatography (petroleum ether/ethyl acetate, 10:1) of the residue afforded **17** (0.26 g, 76%) as colorless foam. $[\alpha]_D^{20}$ = –0.7 (*c* = 1.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.60 (dd, $J_{2,3}$ = 3.1 Hz, 1 H, 2_D-H), 5.49 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2_A-H), 5.33 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1_A-H), 5.17 (d, $J_{1,2}$ = 1.7 Hz, 1 H, 1_D-H), 4.87 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.79 (d, *J* = –11.3 Hz, 1 H, $PhCH_2$), 4.66 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.58 (d, *J* = –11.3 Hz, 1 H, $PhCH_2$), 4.55 (d, *J* = –10.1 Hz, 1 H, $PhCH_2$), 4.36 (d, *J* = –11.4 Hz, 1 H, $PhCH_2$), 4.23 (dd, $J_{3,4}$ = 9.4 Hz, 1 H, 3_A-H), 4.16–4.08 (m, $J_{5,6}$ = 6.1 Hz, 1 H, 5_A-H), 3.90 (dd, $J_{3,4}$ = 9.3 Hz, 1 H, 3_D-H), 3.85–3.78 (m, $J_{5,6}$ = 6.2 Hz, 1 H, 5_D-H), 3.64 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4_A-H), 3.47 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4_D-H), 2.70–2.56 (m, 2 H, S*C*H$_2$CH$_3$), 1.34 (d, 3 H, 6_A-H), 1.28 (t, *J* = 7.4 Hz, 3 H, SCH$_2$C*H*$_3$), 1.18 (d, 3 H, 6_D-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 165.8 (PhCO), 165.6 (PhCO), 99.5 (C-1_D, $J_{C,H}$ = 171.9 Hz), 82.0 (C-1_A), 80.6 (C-4_A), 79.7 (C-4_D), 78.0 (C-3_A), 77.7 (C-3_D), 75.6 ($PhCH_2$), 74.7 (C-2_A), 74.6 ($PhCH_2$), 71.5 ($PhCH_2$), 69.7 (C-2_D), 68.6, 68.8 (1 C, 1 C, C-5_A, C-5_D), 25.8 (S*C*H$_2$CH$_3$), 17.9, 18.0 (1 C, 1 C, C-6_A, C-6_D), 15.1 (SCH$_2$*C*H$_3$). $C_{49}H_{52}O_{10}S$ (833.01): calcd. C 70.65, H 6.29; found C 70.59, H 6.39.

Phenyl *O*-[3,4,6-Tri-*O*-benzyl-2-*O*-(2-methoxycarbonylbenzyl)-α-D-glucopyranosyl]-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (18): Sodium methoxide (1 M in MeOH, 200 μL) was added to a solution of **8a** (60 mg, 58 μmol) in a mixture of CH_2Cl_2 (1 mL) and MeOH (3 mL) and stirred at 40 °C temp. for 48 h. After neutralization with ion-exchange resin (Dowex 50 W X 8, H^+) and filtration, the solvent was evaporated and the crude product was purified by chromatography (toluene/ethyl acetate, 10:1) to afford **18** (28 mg, 45%) as a foam. $[\alpha]_D^{20}$ = +46.7 (*c* = 1.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (d, $J_{1,2}$ = 10.0 Hz, 1 H, 1_B-H), 5.23 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1_E-H), 5.08 (d, *J* = –10.4 Hz, 1 H, $PhCH_2$), 4.85 (d, *J* = –10.3 Hz, 1 H, $PhCH_2$), 4.83 (d, *J* = –10.9 Hz, 1 H, $PhCH_2$), 4.67 (d, *J* = –11.2 Hz, 1 H, $PhCH_2$), 4.63 (d, *J* = –10.9 Hz, 1 H, $PhCH_2$), 4.55 (d, *J* = –11.9 Hz, 1 H, $PhCH_2$), 4.54 (d, *J* = –12.8 Hz, 1 H, $PhCH_2$), 4.50 (d, *J* = –10.3 Hz, 1 H, $PhCH_2$), 4.46 (d, *J* = –10.5 Hz, 1 H, $PhCH_2$), 4.42 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.28 (dd, $J_{3,4}$ = 9.2 Hz, 1 H, 3_B-H), 4.10 (t, $J_{2,3}$ = 10.0 Hz, 1 H, 2_B-H), 3.91 (t, $J_{4,5}$ = 9.1 Hz, 1 H, 4_B-H), 3.90–3.82 (m, $J_{5,6a}$ = 4.4 Hz, $J_{6a,6b}$ = –10.6 Hz, 6 H, 3_E-H, 5_B-H, $6a_B$-H, OCH_3), 3.80–3.61 (m, 3 H, 5_E-H, $6a_E$-H, $6b_E$-H), 3.63 (dd, $J_{5,6b}$ = 1.9 Hz, 1 H, $6b_B$-H), 3.55 (t, $J_{4,5}$ = 9.4 Hz, 1 H,

4_E-H), 3.46 (dd, $J_{2,3}$ = 9.7 Hz, 1 H, 2_E-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.0, 167.9, 167.7 (3 C, CO), 100.0 (C-1_E), 82.8 (C-1_B), 81.2 (C-4_B), 81.0 (C-2_E), 80.5 (C-3_E), 79.0 (C-5_E), 77.0 (C-4_E), 75.6 ($PhCH_2$), 75.0 ($PhCH_2$), 74.2 (C-3_B), 73.4 ($PhCH_2$), 73.1 ($PhCH_2$), 71.0 (2 C, C-5_B, $PhCH_2$), 68.9 (C-6_E), 68.5 (C-6_B), 55.4 (C-$_B$), 51.2 (OCH_3). $C_{63}H_{61}NO_{13}S$ (1072.24): calcd. C 70.57, H 5.73, N 1.31, S 2.99; found C 70.61, H 5.75, N 1.33, S 2.89.

5-[(Benzyloxycarbonyl)amino]pentyl 2′′,3′-*O*-(2-Methylenebenzoyl)-(3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-(6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (19): A mixture of **8a** (54 mg, 96 μmol), **11** (120 mg, 115 μmol) and molecular sieves (4 Å) in CH_2Cl_2 (6 mL) was cooled under argon to –40 °C and stirred for 10 min. NIS (30 mg, 115 μmol) and TMSOTf (ca. 5 μL, 30 μmol) were successively added, the mixture was stirred for 1 h, neutralized by addition of triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was washed with aqueous sodium thiosulfate solution, water, dried and concentrated. The residue was chromatographed (toluene/acetone, 15:1) to yield **19** (81 mg, 57%) as a colorless foam. $[\alpha]_D^{20}$ = +55.1 (*c* = 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.20 (dd, $J_{3,4}$ = 9.0 Hz, 1 H, 3_B-H), 5.54 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1_B-H), 5.23 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1_E-H), 5.08 (br. s, 2 H, $PhCH_2CO$), 5.04 (d, *J* = –10.4 Hz, 1 H, $PhCH_2$), 4.84 (d, *J* = –11.0 Hz, 1 H, $PhCH_2$), 4.77 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1_C-H), 4.70 (br. s, 1 H, NH), 4.64 (d, *J* = –11.3 Hz, 1 H, $PhCH_2$), 4.62 (d, *J* = –12.2 Hz, $PhCH_2$), 4.52 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.44 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.43 (s, 3 H, $PhCH_2$), 4.39 (s, 2 H, $PhCH_2$), 4.38 (br. d, $J_{2,3}$ = 10.7 Hz, 1 H, 2_B-H), 4.24 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.00 (d, *J* = –10.7 Hz, 1 H, $PhCH_2$), 3.94 (d, *J* = –11.0 Hz, 1 H, $PhCH_2$), 3.90–3.73 (m, 6 H, 3_E-H, 4_B-H, 4_E-H, 5_B-H, $6a_E$-H, $6b_E$-H), 3.73 (br. s, 1 H, 2_C-H), 3.66–3.58 (m, 4 H, 3_C-H, 5_E-H, $6a_B$-H, $6b_B$-H), 3.56–3.48 (m, $J_{5,6}$ = 6.1 Hz, 2 H, OCH_2, 5_C-H), 3.44 (dd, $J_{2,3}$ = 9.6 Hz, 1 H, 2_E-H), 3.25–3.20 (m, 1 H, OCH_2), 3.15–3.10 (m, 2 H, CH_2NH), 3.04 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4_C-H), 1.44–1.36 (m, 4 H, CH_2), 1.25–1.22 (m, 2 H, CH_2), 1.15 (d, 3 H, 6_C-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.4 (CO), 168.1 (NCO), 167.7 (NCO), 156.4 (OCONH), 100.1 (C-1_B, $J_{C,H}$ = 163.8 Hz), 99.7 (C-1_E, $J_{C,H}$ = 169.8 Hz), 99.0 (C-1_C, $J_{C,H}$ = 171.1 Hz), 81.2 (C-3_B), 80.7, 80.6 (1 C, 1 C, C-2_E, C-4_B), 80.3 (C-4_C), 78.8 (C-5_E), 78.0 (C-2_C), 76.9 (C-3_C), 75.7 ($PhCH_2$), 74.9 (2 C, $PhCH_2$), 74.4 (C-4_E), 73.5 ($PhCH_2$), 73.4 (C-3_B), 73.1 ($PhCH_2$), 72.2 ($PhCH_2$), 71.5 (C-5_B), 71.0 ($PhCH_2$), 68.9 (C-6_E), 68.6 (C-6_B), 67.9 (C-5_C), 67.1 (OCH_2), 66.6 ($OCOCH_2Ph$), 55.1 (C-2_B), 40.9 (CH_2NH), 29.7 (CH_2), 29.1 (CH_2), 23.3 (CH_2), 17.7 (C-6_C). $C_{89}H_{92}N_2O_{19}$ (1493.72): calcd. C 71.57, H 6.21, N 1.88; found C 71.35, H 6.17, N 1.85.

5-[(Benzyloxycarbonyl)amino]pentyl 2′′,3′-*O*-(2-Methylenebenzoyl)-(3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-(2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (20): Ethylenediamine (5 mL) was added to a solution of compound **19** (133 mg, 92 μmol) in *n*BuOH (15 mL). After stirring at 80 °C for 48 h, the mixture was concentrated and the residue was taken up in pyridine (9 mL) and acetic anhydride (1.4 mL). After 24 h, the solution was poured onto ice and extracted with CH_2Cl_2. The organic layer was washed successively with diluted aqueous HCl solution and saturated aqueous $NaHCO_3$ solution, dried and the solvents were evaporated. The residue was purified by chromatography (toluene/ethanol, 20:1) to give pure **20** (58 mg, 45%) as an oil. $[\alpha]_D^{20}$ = +40.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.50 (br. s, 1 H, N*H*$COCH_3$), 5.25 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1_E-H), 5.23 (t, $J_{3,4}$ = 9.8 Hz, 1 H, 3_B-H), 5.12 (d, *J* = –10.4 Hz, 1 H, $PhCH_2$), 5.08 (br. s, 2 H, $PhCH_2CO$), 4.88 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.78 (br. s, 1 H, 1_C-H), 4.76 (br. s, 1 H, CH_2NH), 4.74 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.65 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.60 (d, *J* = –11.6 Hz, 1 H, $PhCH_2$), 4.58 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1_B-H), 4.57 (d, *J* = –11.2 Hz, 1 H, $PhCH_2$), 4.54 (s, 2 H, $PhCH_2$), 4.47 (s, 2 H, $PhCH_2$), 4.45 (d, *J* = –11.5 Hz, 1 H, $PhCH_2$), 4.43 (d, *J* = –11.5 Hz, 1 H, $PhCH_2$), 4.22 (dd, $J_{2,3}$ = 10.0 Hz, 1 H, 2_B-H), 4.20 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 3.99 (br. s, 1 H, 2_C-H), 3.92 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4_B-H), 3.90 (t, $J_{3,4}$ = 9.6 Hz, 1 H, 3_E-H), 3.82–3.77 (m, 5 H, 3_C-H, 5_B-H, $6a_E$-H, $6b_E$-H, $PhCH_2$), 3.63–3.50 (m, 6 H, 4_E-H, 5_C-H, 5_E-H, $6a_B$-H, $6b_B$-H, OCH_2), 3.50 (dd, $J_{2,3}$ = 9.6 Hz, 1 H, 2_E-H), 3.28 (t, $J_{4,5}$ = 9.6 Hz, 1 H, 4_C-H), 3.22–3.18 (m, 1 H, OCH_2), 3.18–3.10 (m, 2 H, CH_2NH), 1.84 (s, 3 H, NHCOCH_3), 1.50–1.39 (m, 4 H, CH_2), 1.28 (d, $J_{5,6}$ = 6.0 Hz, 3 H, 6_C-H), 1.26–1.21 (m, 2 H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.0 (CO), 165.7 (CO), 156.4 (OCONH), 102.9 (C-1_B, $J_{C,H}$ = 162.9 Hz), 98.9 (C-1_E, $J_{C,H}$ = 169.8 Hz), 97.8 (C-1_C, $J_{C,H}$ = 171.7 Hz), 81.4 (C-3_E), 80.4 (2 C, C-4_C, C-2_E), 79.4 (2 C, C-4_B, C-3_C), 78.8 (C-5_E), 78.0 (C-2_C), 77.6 (C-3_B), 74.8 (C-4_E), 71.4 (C-5_B), 69.3 (C-6_E), 68.3 (C-6_B), 67.7 (C-5_C), 67.3 (OCH_2), 66.6 ($OCOCH_2Ph$), 58.1 (C-2_B), 29.8 (CH_2), 29.1 (CH_2), 23.4 (CH_2), 23.2 (CH_3CONH), 17.8 (C-6_C). $C_{83}H_{92}N_2O_{18}$ (1405.65): calcd. C 70.92, H 6.60, N 1.99; found C 71.23, H 6.55, N 2.05.

5-[(Benzyloxycarbonyl)amino]pentyl 2′′,3′-*O*-(2-Methylenebenzoyl)-(3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-{2-amino-[2-(*N*-methylaminocarbonyl)benzoyl]-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl}-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (21): A solution of **19** (85 mg, 59 μmol) in EtOH (1.7 mL) was treated with $MeNH_2$/EtOH (3.4 mL, 33%), stirred at room temp. for 1 h and at 60 °C for 2 h. After cooling, the mixture was concentrated and the residue was treated with pyridine (5 mL) and acetic anhydride (1.6 mL). After 24 h, the mixture was poured onto ice and extracted with CH_2Cl_2. The organic phase was washed with diluted aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, water, dried and concentrated. Chromatography (toluene/ethanol, 25:1) of the residue afforded **21** (48 mg, 54%) as a colorless foam. $[\alpha]_D^{20}$ = +38.2 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (br. d, *J* = 4.4 Hz, 1 H, CON*H*CH_3), 6.91 (br. d, *J* = 7.1 Hz, 1 H, N*H*CO), 5.32 (t, $J_{3,4}$ = 10.0 Hz, 1 H, 3_B-H), 5.26 (d, $J_{1,2}$ = 3.1 Hz, 1 H, 1_E-H), 5.14 (d, *J* = –10.2 Hz, 1 H, $PhCH_2$), 5.07 (br. s, 2 H, $PhCH_2OCO$), 4.86 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.79 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1_B-H), 4.78 (br. s, 1 H, 1_C-H), 4.31–4.25 (m, 1 H, 2_B-H), 4.74 (br. s, 1 H, CH_2NH), 4.73 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.67 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.62 (d, *J* = –11.9 Hz, 1 H, $PhCH_2$), 4.59 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.55 (s, 3 H, $PhCH_2$), 4.48 (d, *J* = –11.5 Hz, 1 H, $PhCH_2$), 4.47 (d, *J* = –10.2 Hz, 1 H, $PhCH_2$), 4.46 (d, *J* = –11.5 Hz, 1 H, $PhCH_2$), 4.17 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.02 (br. s, 1 H, 2_C-H), 3.94 (t, $J_{4,5}$ = 9.2 Hz, 1 H, 4_B-H), 3.87 (t, $J_{3,4}$ = 9.5 Hz, 1 H, 3_E-H), 3.83–3.79 (m, 4 H, 3_C-H, 5_B-H, $6a_E$-H, $6b_E$-H), 3.72 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 3.65–3.52 (m, $J_{5C,6C}$ = 5.8 Hz, 6 H, 4_E-H, 5_C-H, 5_E-H, $6a_B$-H, $6b_B$-H, OCH_2), 3.49 (dd, $J_{2,3}$ = 9.7 Hz, 1 H, 2_E-H), 3.33–3.31 (m, 1 H, OCH_2), 3.20–3.14 (m, $J_{4,5}$ = 9.7 Hz, 3 H, 4_C-H, CH_2NH), 2.79 (d, *J* = 4.4 Hz, 3 H, CONHCH_3), 1.53–1.45 (m, 4 H, CH_2), 1.30 (d, 1 H, 6_C-H), 1.29–1.26 (m, 2 H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.7 (NHCO), 170.1 (NHCO), 167.5 (CO), 156.5 (OCONH), 102.4 (C-1_B, $J_{C,H}$ = 158.3 Hz), 100.0 (C-1_E, $J_{C,H}$ = 165.9 Hz), 98.8 (C-1_C, $J_{C,H}$ = 170.7 Hz), 80.9, 80.8, 80.7 (1 C, 2 C, 1 C, C-2_E, C-3_E, C-4_B, C-4_C), 79.7 (C-3_C), 77.5 (C-2_C), 76.7 (C-3_B), 75.6 (2 C, C-4_E, $PhCH_2$), 75.3 (C-5_E), 75.1 ($PhCH_2$), 71.5 (C-5_B), 68.7, 68.8 (1 C, 1 C, C-6_B, C-6_E), 67.8 (C-5_C), 67.2 (OCH_2), 66.6 ($OCOCH_2Ph$), 54.9 (C-2_B), 40.9 (CH_2NH), 29.8 (CH_2), 29.1 (CH_2), 26.7 ($NHCOCH_3$), 23.4 (CH_2), 17.8 (C-6_C). $C_{90}H_{97}N_3O_{19}$ (1524.78): calcd. C 70.89, H 6.41, N 2.76; found C 71.15, H 6.38, N 2.83.

5-[(Benzyloxycarbonyl)amino]pentyl 2′′,3′-*O*-(2-Methylenebenzoyl)-(3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-(6-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (22): A mixture of **11** (135 mg, 0.24 mmol), **8b** (263 mg, 0.26 mmol) and molecular sieves (4 Å) in CH_2Cl_2 (15 mL) was cooled under argon to –30 °C and stirred for 10 min. NIS (59 mg, 0.26 mmol) and TMSOTf (ca. 13 μL, 70 μmol) were successively added, the mixture was stirred for 30 min, neutralized by addition of triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was washed with aqueous $Na_2S_2O_3$ solution, water, dried and concentrated. Chromatography (toluene/acetone, 12:1) of the residue yielded **22** (244 mg, 65%) as a colorless foam. $[\alpha]_D^{20}$ = +13.6 (*c* = 0.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.26 (t, $J_{3,4}$ = 10.2 Hz, 1 H, 3_B-H), 5.22 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1_E-H), 5.10 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 5.08 (br. s, 2 H, $PhCH_2CO$), 4.79 (s, 1 H, 1_C-H), 4.84 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.83 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.77 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.75 (br. s, CH_2NHCO), 4.68 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.63 (d, *J* = –11.4 Hz, 1 H, $PhCH_2$), 4.59 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.57 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.55 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.52 (d, $J_{1,2}$ = 8.8 Hz, 1 H, 1_B-H), 4.51–4.47 (m, 3 H, $PhCH_2$), 4.43 (d, *J* = –11.9 Hz, 1 H, $PhCH_2$), 4.41 (d, *J* = –11.4 Hz, 1 H, $PhCH_2$), 4.13–4.04 (m, 1 H, 2_B-H), 3.90 (br. s, 1 H, 2_C-H), 3.90–3.75 (m, 7 H, 3_C-H, 3_E-H, 4_B-H, 4_E-H, 5_B-H, $6a_E$-H, $6b_E$-H), 3.66–3.56 (m, 5 H, 5_C-H, 5_E-H, $6a_B$-H, $6b_B$-H, OCH_2), 3.47 (dd, $J_{2,3}$ = 9.8 Hz, 1 H, 2_E-H), 3.35–3.31 (m, 1 H, OCH_2), 3.34 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4_C-H), 3.19–3.11 (m, 2 H, CH_2NH), 1.54–1.30 (m, 6 H, CH_2), 1.30 (d, $J_{5,6}$ = 6.1 Hz, 3 H, 6_C-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.2 (PhCO), 157.3 ($NHCOCF_3$), 156.4 (OCONH), 115.8 ($NHCOCF_3$), 102.1 (C-1_B, $J_{C,H}$ = 161.0 Hz), 100.0 (C-1_E), 98.8 (C-1_C), 81.0 (C-3_E), 80.7 (2 C, C-2_E, C-4_B), 80.2 (C-4_C), 79.5 (C-5_E), 77.8 (C-2_C), 76.9 (C-3_C), 75.5 (2 C, $PhCH_2$), 75.4 (2 C, C-4_E, $PhCH_2$), 75.2 (C-3_B), 75.1 ($PhCH_2$), 73.9 ($PhCH_2$), 73.5 ($PhCH_2$), 73.1 ($PhCH_2$), 71.5 (C-5_B), 71.0 (C-6_E), 68.6 (C-6_B), 67.8 (C-5_C), 67.2 (OCH_2), 66.6 ($OCOCH_2Ph$), 54.7 (C-2_B), 40.9 (CH_2NH), 29.8 (CH_2), 29.1 (CH_2), 23.4 (CH_2), 17.8 (C-6_C). $C_{83}H_{89}F_3N_3O_{18}$ (1459.62): calcd. C 68.30, H 6.15, N 1.92; found C 68.53, H 6.17, N 1.91.

5-[(Benzyloxycarbonyl)amino]pentyl [3,4,6-Tri-*O*-benzyl-2-*O*-(2-methoxycarbonylbenzyl)-α-D-glucopyranosyl]-(1→4)-(6-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (23): A solution of **22** (0.25 g, 0.17 mmol) in MeOH (15 mL) and $Mg(OMe)_2$ in MeOH (1 mL) was stirred at room temp. for 3 d. The mixture was diluted with CH_2Cl_2, washed with aqueous HCl solution, water, dried and concentrated. Chromatography (toluene/acetone, 8:1) of the residue afforded **23** (0.19 g, 77%) as a foam. $[\alpha]_D^{20}$ = +10.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.20 (d, $J_{1,2}$ = 3.2 Hz, 1 H, 1_E-H), 5.10 (d, *J* = –11.2 Hz, 1 H, $PhCH_2$), 5.08 (br. s, 2 H, $PhCH_2CO$), 4.85 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.83 (d, $J_{1,2}$ = 8.7 Hz, 1 H, 1_B-H), 4.81 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.80 (s, 1 H, 1_C-H), 4.77 (br. s, 1 H, CH_2NHCO), 4.75 (d, *J* = –10.7 Hz, 1 H, $PhCH_2$), 4.70 (d, *J* = –11.2 Hz, 1 H, $PhCH_2$), 4.64 (d, *J* = –11.3 Hz, 1 H, $PhCH_2$), 4.57 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.55 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.53 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.51–4.44 (m, 3 H, $PhCH_2$), 4.42 (d, *J* = –11.9 Hz, 1 H, $PhCH_2$), 4.39 (d, *J* = –11.4 Hz, 1 H, $PhCH_2$), 3.93–3.83 (m, 7 H, 2_B-H, 2_C-H, 3_C-H, 5_B-H, OCH_3), 3.82–3.71 (m, $J_{3B,4B}$ = 9.9 Hz, 8 H, 3_B-H, 3_E-H, 4_B-H, 4_E-H, $6a_B$-H, $6b_B$-H, $6a_E$-H, $6b_E$-H), 3.63–3.55 (m, 3 H, 5_C-H, 5_E-H, OCH_2), 3.48 (dd, $J_{2,3}$ = 9.6 Hz, 1 H, 2_E-H), 3.38–3.33 (m, $J_{4,5}$ = 9.6 Hz, 2 H, 4_C-H, OCH_2), 3.17–3.10 (m, 2 H, CH_2NH), 1.55–1.30 (m, 6 H, CH_2), 1.27 (d, $J_{5,6}$ = 6.2 Hz, 3 H, 6_C-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 168.9 (CO), 156.9 ($NHCOCF_3$), 156.2 (OCONH), 115.7 ($NHCOCF_3$), 101.8 (C-1_B), 99.9 (C-1_E), 98.6 (C-1_C), 82.2 (C-4_B), 81.0 (C-3_E), 80.8 (C-2_E), 80.0 (C-4_C), 79.6 (C-5_E), 77.6 (C-2_C), 76.7 (C-3_C), 75.6 ($PhCH_2$), 75.5 (C-4_E), 75.4 ($PhCH_2$), 75.2 ($PhCH_2$), 74.6 (2 C, C-3_B, $PhCH_2$), 73.9 ($PhCH_2$), 73.4 ($PhCH_2$), 73.1 ($PhCH_2$), 71.0 (2 C, C-5_B, C-6_E), 68.7 (C-6_B), 67.9 (C-5_C), 67.2 (OCH_2), 66.4 ($OCOCH_2Ph$), 56.8 (C-2_B), 50.8 (OCH_3), 41.0 (CH_2NH), 29.9, 29.3, 23.6 (3 C, CH_2), 18.0 (C-6_C). $C_{84}H_{93}F_3N_2O_{19}$ (1491.67): calcd. C 67.64, H 6.28, N 1.88; found C 67.90, H 6.31, N 1.95.

5-[(Benzyloxycarbonyl)amino]pentyl (2-*O*-Benzoyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-(2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[3,4,6-tri-*O*-benzyl-2-*O*-(2-methoxycarbonylbenzyl)-α-D-glucopyranosyl-(1→4)]-(6-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (24): NIS (33 mg, 147 μmol), followed by trifluoromethanesulfonic acid (ca. 3 μL, 34 μmol), were added under argon to a mixture of **23** (215 mg, 144 μmol), **17** (120 mg, 144 μmol) and molecular sieves (4 Å) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at –10 °C for a period of 30 min and was then diluted with CH_2Cl_2, filtered, washed with sodium thiosulfate solution, saturated aqueous $NaHCO_3$ solution. The organic extracts were finally washed with water, dried and concentrated in vacuo. The crude compound was purified by chromatography (toluene/acetone, 15:1) to yield pure **24** (202 mg, 62%) as an oil. $[\alpha]_D^{20}$ = +35.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.60 (dd, $J_{2,3}$ = 3.1 Hz, 1 H, 2_D-H), 5.53 (dd, $J_{2,3}$ = 3.4 Hz, 1 H, 2_A-H), 5.18 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1_E-H), 5.16 (s, 1 H, 1_D-H), 5.09 (br. s, 2 H, $PhCH_2CO$), 5.06 (d, *J* = –11.2 Hz, 1 H, $PhCH_2$), 4.92 (d, $J_{1,2}$ = 8.7 Hz, 1 H, 1_B-H), 4.88 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.86 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.80 (s, 1 H, 1_C-H), 4.79 (br. s, 1 H, CH_2NHCO), 4.77 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.75 (d, *J* = –11.3 Hz, 1 H, $PhCH_2$), 4.69 (d, *J* = –12.0 Hz, 1 H, $PhCH_2$), 4.67–4.50 (m, 8 H, $PhCH_2$), 4.48 (s, 2 H, $PhCH_2$), 4.46 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.43 (s, 3 H, $PhCH_2$), 4.04–3.94 (m, 5 H, 3_A-H, 3_D-H, 5_B-H, $6a_B$-H, $6b_B$-H), 4.83 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1_A-H), 3.90–3.81 (m, $J_{3B,4B}$ = 9.9 Hz, 6 H, 2_C-H, 3_B-H, 3_C-H, OCH_3), 3.82–3.75 (m, 3 H, 5_A-H, 5_D-H, $6a_E$-H), 3.73–3.53 (m, 8 H, 2_B-H, 3_E-H, 4_A-H, 4_B-H, 5_C-H, 5_E-H, $6b_E$-H, OCH_2), 3.53–3.48 (m, 3 H, 2_E-H, 4_D-H, 4_E-H), 3.40 (t, $J_{4,5}$ = 9.7 Hz, 1 H, 4_C-H), 3.39–3.30 (m, 1 H, OCH_2), 3.17–3.09 (m, 2 H, CH_2NH), 1.55–1.40 (m, 4 H, CH_2), 1.38–1.31 (m, 2 H, CH_2), 1.36 (d, $J_{5,6}$ = 6.2 Hz, 3 H, 6_A-H), 1.34 (d, $J_{5,6}$ = 6.1 Hz, 3 H, 6_D-H), 1.30 (d, $J_{5,6}$ = 6.2 Hz, 3 H, 6_C-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.7, 169.5, 168.9 (3 C, CO), 158.2 ($NHCOCF_3$), 156.5 (OCONH), 115.5 ($NHCOCF_3$), 100.9 (C-1_B), 100.1 (C-1_E), 99.6 (C-1_D), 98.7 (C-1_C), 97.6 (C-1_A, $J_{C,H}$ = 172.8 Hz), 81.2 (2 C, C-3_E, C-4_B), 80.8 (C-2_E), 80.2 (2 C, C-4_A, C-4_C), 79.9 (C-4_D), 79.6 (C-5_E), 78.6 (C-3_B), 78.3 (C-3_A), 77.5 (2 C, C-2_C,C-3_D), 76.6 (C-3_C), 75.7 ($PhCH_2$), 75.5 (C-4_E), 75.4 ($PhCH_2$), 75.2 ($PhCH_2$), 74.9 ($PhCH_2$), 74.6 ($PhCH_2$), 74.3 ($PhCH_2$), 74.0 ($PhCH_2$), 73.7 ($PhCH_2$), 73.1 ($PhCH_2$), 70.8 (C-5_B), 69.8 (C-2_A), 69.6 (C-2_D), 69.3 (C-6_B), 69.0 (C-6_E), 68.8 (C-5_D), 67.7 (3 C, C-5_A, C-5_C, OCH_2), 66.3 ($OCOCH_2Ph$), 57.7 (C-2_B), 52.1 (OCH_3), 40.8 (CH_2NH), 29.5, 29.1, 23.4 (3 C, CH_2), 18.1, 17.8 (1 C, 2 C, C-6_A, C-6_C, C-6_D). $C_{131}H_{139}F_3N_2O_{29}$ (2262.55): calcd. C 69.54, H 6.19, N 1.24; found C 69.73, H 6.25, N 1.30.

Phenyl [3,4,6-Tri-*O*-benzyl-2-*O*-(2-methoxycarbonylbenzyl)-α-D-glucopyranosyl]-(1→4)-6-*O*-benzyl-2-deoxy-1-thio-2-trifluoroacetamido-β-D-glucopyranoside (25): A mixture of **8b** (0.50 g, 0.50 mmol) in MeOH (20 mL) was treated with $Mg(OMe)_2$ in MeOH (2.5 mL) and stirred at 40 °C for 20 h. The solution was neutralized with aqueous HCl solution, extracted with CH_2Cl_2 and the organic phase was washed with water, dried and concentrated. The chromatography (toluene/ethyl acetate, 10:1) of the crude prod-

uct furnished **25** (0.39 g, 76%) as a colorless foam. $[\alpha]_D^{20}$ = +15.3 (*c* = 0.8, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.17 (d, $J_{1,2}$ = 9.9 Hz, 1 H, 1_B-H), 5.16 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1_E-H), 5.11 (d, *J* = 4.5 Hz, 1 H, OH), 5.06 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.90 (d, *J* = –11.2 Hz, 1 H, $PhCH_2$), 4.83 (d, *J* = –11.3 Hz, 1 H, $PhCH_2$), 4.77 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.55 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.50 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.46 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.43 (s, 1 H, $PhCH_2$), 4.37 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.32 (d, *J* = –11.9 Hz, 1 H, $PhCH_2$), 4.07–4.01 (m, 1 H, 3_B-H), 3.90–3.82 (m, 5 H, 2_B-H, 4_B-H, OCH_3), 3.70–3.68 (m, 3 H, 3_E-H, 5_E-H, $6b_E$-H), 3.81–3.75 (m, 3 H, 5_B-H, $6a_E$-H, $6a_B$-H), 3.60–3.55 (m, 1 H, $6b_B$-H), 3.52–3.47 (m, 1 H, 4_E-H), 3.49–3.45 (m, 1 H, 2_E-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.1 (CO), 157.2 ($NHCOCF_3$), 116.0 ($NHCOCF_3$), 100.6 (C-1_E), 84.8 (C-1_B), 81.5 (C-3_E), 81.1 (C-2_E), 80.8 (C-4_B), 79.4 (C-5_E), 77.4 (C-4_E), 76.8 (C-3_B), 76.1 ($PhCH_2$), 75.3 ($PhCH_2$), 73.6 ($PhCH_2$), 72.9 ($PhCH_2$), 71.5 (C-5_B), 71.4 ($PhCH_2$), 68.9 (2 C, C-6_B, C-6_E), 54.3 (C-2_B), 51.2 (OCH_3). $C_{57}H_{58}F_3NO_{12}S$ (1038.15): calcd. C 65.95, H 5.63, N 1.35; found C 65.88, H 5.59, N 2.85.

Phenyl (2-*O*-Benzoyl-3,4,-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[3,4,6-tri-*O*-benzyl-2-*O*-(2-methoxycarbonylbenzyl)-α-D-glucopyranosyl-(1→4)]-6-*O*-benzyl-2-deoxy-1-thio-2-trifluoroacetamido-β-D-glucopyranoside (26): A mixture of **25** (0.25 g, 0.24 mmol) and **15** (0.17 g, 0.29 mmol) in CH_2Cl_2 (12 mL) was cooled under argon to –10 °C and stirred for 10 min. TMSOTf (ca. 6 μL, 33 μmol) was successively added. The mixture was stirred for 20 min, neutralized by addition of triethylamine, diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ solution, water, dried and concentrated. Chromatography (toluene/ethyl acetate, 15:1) of the residue gave **26** (0.25 g, 71%) as a colorless foam. $[\alpha]_D^{20}$ = +22.3 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.56 (dd, $J_{2,3}$ = 3.2 Hz, 1 H, 2_A-H), 5.45 (d, $J_{1,2}$ = 9.9 Hz, 1 H, 1_B-H), 5.18 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1_E-H), 5.00 (br. s, $J_{1,2}$ = 1.7 Hz, 1 H, 1_A-H), 4.85 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.82 (d, *J* = –11.6 Hz, 1 H, $PhCH_2$), 4.78 (d, *J* = –11.2 Hz, 1 H, $PhCH_2$), 4.76 (d, *J* = –10.7 Hz, 1 H, $PhCH_2$), 4.70 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.63 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.58 (d, *J* = –10.7 Hz, 1 H, $PhCH_2$), 4.57 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.55 (s, 1 H, $PhCH_2$), 4.51 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.50–4.42 (m, 3 H, $PhCH_2$), 4.40 (d, *J* = –12.0 Hz, 1 H, $PhCH_2$), 3.99–3.88 (m, 6 H, 4_B-H, 5_B-H, $6a_B$-H, OCH_3), 3.80–3.75 (m, 4 H, 3_B-H, 5_A-H, $6a_E$-H, $6b_B$-H), 3.70–3.62 (m, 4 H, 2_B-H, 3_E-H, 5_E-H, $6b_E$-H), 3.55–3.50 (2 H, 2_E-H, 4_E-H), 3.50 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4_A-H), 3.43 (dd, $J_{3,4}$ = 9.4 Hz, 1 H, 3_A-H), 1.23 (d, $J_{5,6}$ = 6.3 Hz, 3 H, 6_A-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 168.7, 166.5 (2 C, CO), 157.8 ($NHCOCF_3$), 115.4 ($NHCOCF_3$), 100.9 (C-1_E), 98.8 (C-1_A, $J_{C,H}$ = 171.7 Hz), 83.9 (C-1_B), 81.6 (C-3_E), 80.8 (2 C, C-2_E, C-3_B), 79.8 (2 C, C-4_A, C-4_B), 79.3 (C-5_E), 77.4 (2 C, C-3_A, C-4_E), 76.1 ($PhCH_2$), 75.7 ($PhCH_2$), 75.5 ($PhCH_2$), 74.6 ($PhCH_2$), 73.9 ($PhCH_2$), 73.3 ($PhCH_2$), 71.3 (C-5_B), 71.6 ($PhCH_2$), 70.0 (C-2_A), 69.5 (C-6_B), 68.9 (C-6_E), 68.5 (C-5_A), 55.2 (C-2_B), 52.6 (OCH_3), 17.8 (C-6_A). $C_{84}H_{84}F_3NO_{17}S$ (1468.65): calcd. C 68.70, H 5.77, N 0.95, S 2.18; found C 68.73, H 5.69, N 1.01, S 2.09.

5-[(Benzyloxycarbonyl)amino]pentyl (2-*O*-Benzoyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[3,4,6-tri-*O*-benzyl-2-*O*-(2-methoxycarbonylbenzyl)-α-D-glucopyranosyl-(1→4)]-(6-*O*-benzyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (27): NIS (24 mg, 107 μmol) and TMSOTf (ca. 9 μL, 51 μmol) were added under argon to a cooled mixture (–20 °C) of **26** (150 mg, 102 μmol), **13** (91 mg, 102 μmol) and molecular sieves (4 Å) in CH_2Cl_2 (7 mL). The suspension was stirred for 35 min, neutralized with triethylamine, diluted with CH_2Cl_2, filtered, washed with aqueous $Na_2S_2O_3$ solution, water, dried and concentrated. The residue was chromatographed (toluene/acetone, 15:1) to afford **27** (126 mg, 55%) as a colorless oil. $[\alpha]_D^{20}$ = +15.6 (*c* = 0.7, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.54 (dd, $J_{2,3}$ = 4.3 Hz, 1 H, 2_A-H), 5.18 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1_E-H), 5.09 (d, *J* = –11.2 Hz, 1 H, $PhCH_2$), 5.08 (br. s, 2 H, $OCOCH_2Ph$), 4.92 (br. s, 2 H, 1_B-H, 1_C-H), 4.88 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1_A-H), 4.87 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.86 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.77 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.75 (d, *J* = –11.1 Hz, 1 H, $PhCH_2$), 4.72 (br. s, 1 H, CH_2NHCO), 4.69 (d, *J* = –12.0 Hz, 1 H, $PhCH_2$), 4.67 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.64 (s, 1 H, 1_D-H), 4.59 (d, *J* = –12.1 Hz, 1 H, $PhCH_2$), 4.56 (s, 2 H, $PhCH_2$), 4.50 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.48 (s, 2 H, $PhCH_2$), 4.46 (d, *J* = –11.3 Hz, 1 H, $PhCH_2$), 4.43 (s, 2 H, $PhCH_2$), 4.39 (d, *J* = –11.9 Hz, 1 H, $PhCH_2$), 4.36 (d, *J* = –11.2 Hz, 1 H, $PhCH_2$), 4.35 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.33 (d, *J* = –11.6 Hz, 1 H, $PhCH_2$), 4.31 (d, *J* = –10.8 Hz, 1 H, $PhCH_2$), 4.29 (s, 2 H, $PhCH_2$), 4.25 (d, *J* = –11.9 Hz, 1 H, $PhCH_2$), 4.16 (d, *J* = –12.2 Hz, 1 H, $PhCH_2$), 4.10 (d, *J* = –10.6 Hz, 1 H, $PhCH_2$), 4.03–3.99 (m, 5 H, 2_C-H, 3_A-H, 5_B-H, $6a_B$-H, $6b_B$-H), 3.91 (dd, $J_{3,4}$ = 9.6 Hz, 1 H, 3_D-H), 3.85 (br. s, $J_{2,3}$ = 2.8 Hz, 1 H, 2_D-H), 3.83–3.66 (m, $J_{3C,4C}$ = 9.4 Hz, $J_{5C,6C}$ = 6.1 Hz, 12 H, 2_B-H, 3_B-H, 3_C-H, 3_E-H, 4_A-H, 4_B-H, 5_A-H, 5_C-H, $6a_E$-H, OCH_3), 3.63–3.56 (m, $J_{5D,6D}$ = 6.1 Hz, 3 H, 5_D-H, 5_E-H, OCH_2), 3.53–3.46 (m, 3 H, 2_E-H, 4_E-H, $6b_E$-H), 3.45 (t, $J_{4,5}$ = 9.4 Hz, 1 H, 4_C-H), 3.41 (t, $J_{4,5}$ = 9.5 Hz, 1 H, 4_D-H), 3.33–3.28 (m, 1 H, OCH_2), 3.18–3.11 (m, 2 H, CH_2NH), 1.56–1.43 (m, 4 H, CH_2), 1.38–1.29 (m, 2 H, CH_2), 1.36 (d, $J_{5,6}$ = 6.2 Hz, 3 H, 6_A-H), 1.35 (d, 3 H, 6_C-H), 1.30 (d, 3 H, 6_D-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 169.9, 168.7 (2 C, CO), 158.0 ($NHCOCF_3$), 156.3 (OCONH), 115.7 ($NHCOCF_3$), 101.6 (C-1_B, $J_{C,H}$ = 160.8 Hz), 99.3 (C-1_C), 98.6 (C-1_D), 97.8 (C-1_A), 81.4 (C-4_B), 80.3 (C-4_C), 80.2 (C-4_A), 80.0 (C-4_D), 78.3 (3 C, C-2_C, C-3_A, C-3_B), 77.7 (C-3_D), 76.7 (C-3_C), 76.5 (C-2_D), 75.7 ($PhCH_2$), 75.5 ($PhCH_2$), 75.0 ($PhCH_2$), 74.7 ($PhCH_2$), 74.5 ($PhCH_2$), 74.0 (2 C, $PhCH_2$), 73.8 ($PhCH_2$), 73.5 ($PhCH_2$), 73.3 ($PhCH_2$), 73.0 ($PhCH_2$), 70.8 (C-5_B), 69.6 (C-2_A), 69.3 (C-6_B), 68.1 (C-5_C), 67.7 (C-5_A), 67.6 (C-5_D), 67.3 (OCH_2), 66.5 ($OCOCH_2Ph$), 56.8 (C-2_B), 52.5 (OCH_3), 41.0 (CH_2NH), 29.7 (CH_2), 29.3 (CH_2), 23.5 (CH_2), 18.2, 18.1, 17.7 (3 C, C-6_A, C-6_C, C-6_D). $C_{131}H_{141}F_3N_2O_{28}$ (2248.56): calcd. C 69.98, H 6.32, N 1.25; found C 69.81, H 6.25, N 1.29.

5-Aminopentyl (α-L-Rhamnopyranosyl)-(1→3)-(α-L-rhamnopyranosyl)-(1→3)-[α-D-glucopyranosyl-(1→4)]-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-α-L-rhamnopyranoside (28): Compound **24** (70 mg, 31 μmol) was dissolved in MeOH (4 mL), aqueous NaOH solution (1 M, 1 mL) was added, the solution was stirred for 16 h, neutralized with ion exchange resin (H^+ form), filtered and concentrated by repeated coevapoartion with toluene. The crude product was dissolved in MeOH (3 mL), cooled to 0 °C and treated with Ac_2O (300 μL) for 2 h. The mixture was then concentrated and coevaporated with methanol. The residue was redissolved in MeOH (4 mL), AcOH (3 drops) and $Pd(OH)_2$ (20% on charcoal, ca. 20 mg) were added and stirred under H_2 at room temp. for 4 d. Filtration of the mixture, concentration and chromatography of the residue with water on Bio Gel P2 and lyophilization of carbohydrate-containing fractions afforded **28** (23 mg, 81%). $[\alpha]_D^{20}$ = –8.6 (*c* = 1.0, H_2O). ^{13}C NMR (100.6 MHz, D_2O): δ = 175.1 (CO), 102.3 (C-1_D), 102.1 (C-1_B), 101.5 (C-1_A), 100.5 (C-1_C), 100.0 (C-1_E), 82.0 (C-3_B), 80.7 (C-4_B), 79.2, 79.1 (2 C, C-2_C, C-3_A), 72.8, 72.7 (1 C, 2 C, C-3_E, C-4_C, C-4_D), 72.3 (C-4_A), 71.9 (C-2_E), 71.2 (2 C, C-5_B, OCH_2), 71.1 (C-2_A), 70.8 (2 C, C-2_D, C-3_D), 70.4, 70.3 (2 C, C-3_C, C-4_E), 70.0 (C-5_A), 69.6, 69.5, 69.4 (3 C, C-5_C, C-5_D, C-5_E), 61.4, 61.1 (2 C, C-6_B, C-6_E), 55.6 (C-2_B), 39.7 (CH_2NH), 28.4, 26.7 (2 C, CH_2), 22.6 ($COCH_3$), 22.4 (CH_2), 17.3, 17.1 (2 C, 1 C, C-6_A,

C-6_C, C-6_D). $C_{37}H_{66}N_2O_{23}$ (906.94): FAB MS: *m/z* = 929.6 [M + Na^+].

5-Aminopentyl (α-L-Rhamnopyranosyl)-(1→3)-[α-D-glucopyranosyl-(1→4)]-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-L-rhamnopyranosyl)-(1→2)-α-L-rhamnopyranoside (29): Deblocking of **27** (95 mg, 42 μmol) as described for compound **28** gave **29** (30 mg, 79%). $[\alpha]_D^{20}$ = +11.8 (*c* = 0.8, H_2O). ^{13}C NMR (100.6 MHz, D_2O): δ = 175.4 (CO), 102.3 (C-1_B), 101.5 (C-1_A), 101.3 (C-1_C), 100.3 (C-1_D), 100.1 (C-1_E), 81.8 (C-3_B), 80.9 (C-4_B), 79.1 79.0 (2 C, C-2_C, C-2_D), 73.1, 73.0 (2 C, C-4_C, C-4_D), 72.7 (C-3_E), 72.4 (C-4_A), 72.0 (C-2_E), 71.2 (OCH_2), 70.9 (2 C, C-5_B, C-5_C), 70.6 (2 C, C-2_A, C-3_C), 70.4, 70.3 (2 C, C-3_D, C-4_E), 70.1 (C-3_A), 69.6, 69.5, 69.4 (3 C, C-5_A, C-5_D, C-5_E), 60.8, 60.5 (2 C, C-6_B, C-6_E), 56.0 (C-2_B), 39.8 (CH_2NH), 22.7 ($COCH_3$), 28.6, 26.5, 22.1 (3 C, CH_2), 17.1, 17.0 (1 C, 2 C, C-6_A, C-6_C, C-6_D). $C_{37}H_{66}N_2O_{23}$ (906.94): FAB MS: *m/z* = 930.3 [M + Na^+].

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. We also thank P. Schuler for measuring the NMR spectra and A. Just for performing the elemental analyses.

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Received: January 31, 2006
Published Online: March 27, 2006

