Differently Glycosidated 2-Amino-2-deoxy-D-glucopyranosiduronic Acids as Building Blocks in Peptide Synthesis[1])

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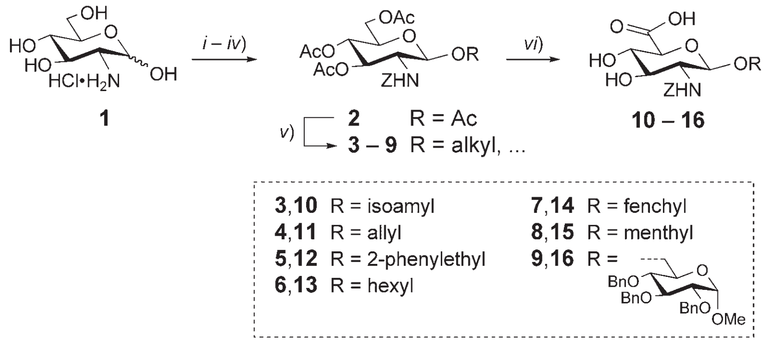
Seven differently glycosidated sugar amino acids (SSAs) derived from glucosamine have been prepared. Following standard solution-phase peptide-coupling procedures, the glycosidated 2-amino-2-deoxy-D-glucopyranosiduronic acids were condensed with natural amino acids to furnish useful heterodi- and -trimeric building blocks to be used in peptide synthesis. Combinations of these building blocks yielded hetero-oligomeric peptides with two sugar amino acid units in different distances to each other. These were prepared to evaluate the influence of glycosidic side chains on the peptide backbone. Conformations of selected examples were examined by means of ROESY spectroscopy in combination with molecular dynamics (MD) simulations and circular-dichroism (CD) studies.

Introduction. – Artificial building blocks for the synthesis of artificial peptides have gained widespread interest. Sugar amino acids (SAAs) constitute a very interesting class amongst artificial building blocks, offering attractive features like mimicking of carbohydrate structures, modification of polarity, introduction of stereochemically defined H-bond donors, and introduction of conformationally rigid elements [1–13]. The majority of studies published so far have focused on the conformational influence of pyranoid and furanoid rings bearing carboxyl and amine groups at different positions. The diversifying possibilities of different functionalization at the anomeric C-atom have not been explored so far, although similar approaches to broaden the synthetic range have been suggested [14][15]. Beside the glycosyl nucleic acids developed in the groups of *Goodnow* and *Tam* [16–18], little use has been made of the possibility to achieve a spectrum of diverse building blocks simply by varying the glycosyl moiety of the sugar amino acids. This paper reports an optimized synthetic route of known reactions to prepare a variety of differently glycosidated alkyl 2-amino-2-deoxy-D-glucopyranosiduronic acids (see *Table* below), and demonstrates their use in the synthesis of artificial peptides.

Results and Discussion. – The synthetic approach to alkyl 2-{[(benzyloxy)carbonyl]amino}-2-deoxy-β-D-glucopyranosiduronic acids is summarized in the *Scheme* below. Starting from glucosamine hydrochloride (**1**), 1,3,4,6-tetra-*O*-acetyl-2-{[(benzyloxy)carbonyl]amino}-2-deoxy-β-D-glucopyranose (**2**) was prepared in anomerically pure form using the anchimeric influence of the temporary anisylidene protecting group. Compound **2** is a starting material for the synthesis of glycosyl halides, glycosyl

1) Part of this work was presented at the 11th European Carbohydrate Symposium, Lisbon, Portugal, September 2–7, 2001 (PA082).

Scheme 1. *Synthetic Route to the Differently Glycosidated Alkyl 2-{[(benzyloxy)carbonyl]amino}-2-deoxy-*D-*glucopyranosiduronic Acids* **10**–**16**



i) Anisaldehyde (1 equiv.), NaOH (1.1. equiv.). *ii*) Ac_2O, pyridine, r.t., 2–4 h. *iii*) acetone, HCl (1.1. equiv), reflux. *iv*) ZCl (1.5 equiv.), $NaHCO_3$ (2.5 equiv.), $CHCl_3/H_2O$ 1:2, r.t., 3–24 h. *v*) R–OH, TMSTf, mol. sieves, anh. CH_2Cl_2, 4°, 15–46 min. *vi*) 1. Na (s), MeOH, 0.5–3 h; 2. *Dowex WX4-100* (H^+), evaporation; 3. TEMPO (cat.), NaClO, $NaClO_2$, MeCN/*Borax* (pH 9.0) 1:1.

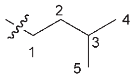
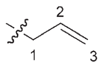
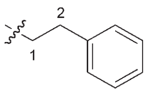
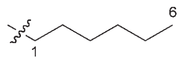
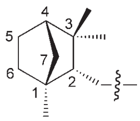
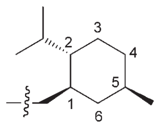
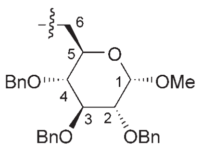
trichloroacetimidates, or other glycosyl donors, and can be used directly as a glycosyl donor in *Lewis* acid catalyzed glycosidation reactions.

With trimethylsilyl 1,1,1-trifluoromethanesulfonate (TMSTf) as a catalyst [19], various primary and secondary alcohols were introduced as aglycones in good-to-excellent yields. The alcohols used comprise primary alcohols with branched or unbranched side chains, unsaturated alcohols, and sterically hindered secondary alcohols like fenchol or menthol (compounds **3**–**9**; *Scheme* and *Table*).

After *O*-deacetylation following standard procedures, IBX/$NaClO_2$ oxidation, as well as the usual TEMPO oxidation according to *Flitsch* and *Davis* [20], furnished the desired uronic acids **10**–**16** (*Table*). However, these procedures were encumbered by tedious workup and moderate yields; furthermore, aromatic groups and unsaturated bonds were not left intact when using the two-phase variant of the TEMPO oxidation. Therefore, the deacetylated glycosides were oxidized according to a homogenous variant of the TEMPO oxidation described by *Zhao* [21], which afforded the differently glycosidated 2-{[(benzyloxy)carbonyl]amino}-2-deoxy-D-glucopyranosiduronic acids in good to excellent yields.

The (benzyloxy)carbonyl-protected (Z-protected) compounds **10**–**16** can be used as building blocks for peptide synthesis in solution. In solid-phase peptide synthesis, Z-protection is unfavorable, owing to the lack of on-bead hydrogenolytic-cleavage methods. This problem might be overcome by simply altering the amino protection in a final step; yet another problem is the close distance of unprotected OH and NH_2 groups, giving rise to *O*- and *N*-acylation. This problem is worse in solid-phase peptide synthesis due to the strong activation conditions usually employed, and due to the lack of monitoring possibilities. Instead of introducing additional protection/deprotection steps, we decided to react the SAAs in solution to higher building blocks. Flanking the amino uronic acids **I** C- and/or N-terminally with standard amino acids yields the di- and trimeric building blocks **II**–**IV** (*Fig. 1*), which enlarges the distance between the desired coupling sites and the unprotected OH groups.

Table. *Total Yields of the Glycosides* **3**–**9** *and the Corresponding Alkyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxyglucopyranosiduronic Acids* **10**–**16**

Glycosyl residue (R)	Acetylated glycoside (yield [%])	Uronic acid (yield [%])
	**3** (94)	**10** (71–95)
	**4** (90)	**11** (94)
	**5** (43)	**12** (60)
	**6** (60)	**13** (92–99)
	**7** (91)	**14** (53)
	**8** (59)	β-**15** (95) α-**15** (68)
	**9** (17)	**16** (40)

The obvious advantage of this approach is that every single step can be controlled, and that the products can be readily purified and characterized. With the N-terminally (**II**) and C-terminally (**III**, **IV**) deprotected compounds, standard peptide coupling between amino acids is possible.

In a first step, the glycosidated compounds **10**–**16** were coupled with amino acid methyl ester hydrochlorides (Gly, Ala or Val) *via* EDC/HOBt activation to afford the resulting heterodimeric compounds **17**–**25** (*Fig. 2*). The latter can, after appropriate deprotection, be used as building blocks **II** and **III** in peptide synthesis. Following hydrogenolytic cleavage of the Z-group and coupling with Boc-protected amino acids

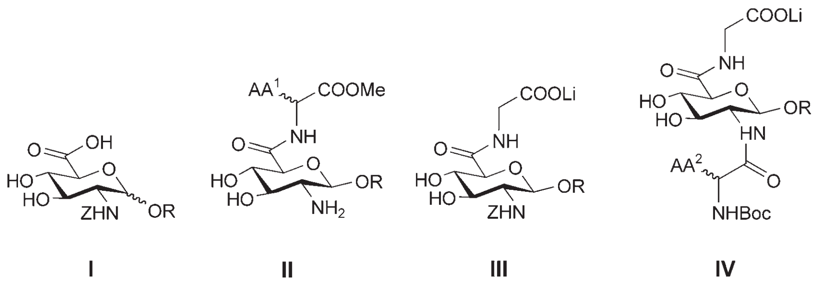
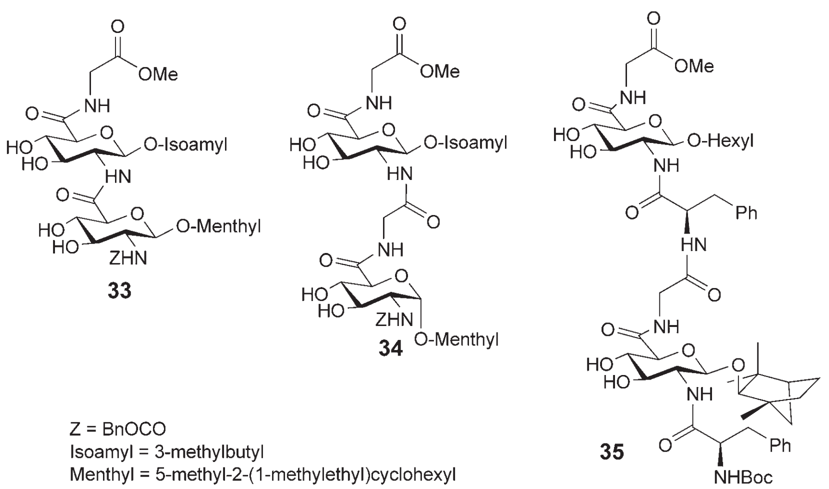


Fig. 1. *Types of building blocks used for solution-phase peptide synthesis.* All compounds are derived from the uronic acids **10**–**16** (type **I**). Saponification or *N*-deprotection (Z group) of **17**–**25** yields the dimeric building blocks **II** and **III**. Coupling of **II** with Boc-protected amino acids, followed by saponification, leads to the trimeric building blocks **IV**.

(EEDQ activation), the Boc- and ester-protected heterotrimeric building blocks **26**–**32** were obtained (*Fig. 2*).

To evaluate the feasibility of the building blocks described, peptide oligomers with two different SAAs moieties were prepared, in which none, one, or two inner amino acid residues are present, respectively. These compounds were synthesized to evaluate the influence of sterically demanding aglycones on the coupling behavior of the building blocks **I**–**IV**, as well as to study the conformation of the resulting oligomers.

For the synthesis of oligomers **33**–**35**, couplings were performed in solution *via* EDC/HOBt or EEDQ activation, with equally good results. The latter method has the advantage of generating no detectable amounts of *O*-acylation products, whereas in EDC/HOBt activation, *O*-acylation and EDC-adduct formation were observed as side reactions to some extent. In one case, quantitative 3-*O*-acylation was observed in EDC/HOBt-mediated fragment condensation of an amino-deprotected type-**II** building block with a trimeric peptide fragment [22] (data not shown). Usually, the slightly



stronger activating EDC/HOBt variant was used for the activation of the uronic acid COOH group, whereas EEDQ was used for the activation of COOH groups to predominantly attack the SAA amino group.

Monomeric menthyl (=5-methyl-2-(1-methylethyl)cyclohexyl) 2-{[(benzyloxy)-carbonyl]amino}-2-deoxy-β-D-glucopyranosiduronic acid (β-**15**) was reacted with amino-deprotected **17** to give β-**33** in 41% yield. Two dimeric building blocks, carboxy-deprotected α-**22** and amino-deprotected **17** were condensed to give tetrameric α-**34** in 17% yield after flash chromatography, the low yield being attributed to very strong adsorption on normal-phase silica gel. Two trimeric building blocks, carboxy-deprotected **29** and amino-deprotected **28**, were coupled to give the oligohexamer **35**, which was isolated, after reverse-phase HPLC, in 42% yield.

The oligomers **33**–**35** were fully characterized by NMR and MS. The NMR spectra of **35** showed two clearly distinguishable sets of signals, referred here as 'major' and 'minor' form, which varied in chemical shift δ with respect to the linkage region of the fenchyl (=1,3,3-trimethylbicyclo[2.2.1]hept-2-yl) substituent to the carbohydrate moiety and the N-terminal Boc-D-Phe moiety. As both forms showed equivalently large coupling constants for the anomeric H-atoms of the fenchyl glycoside, which is typical for β-anomers, simple anomerization could be ruled out. Judging by ROESY spectroscopy, the most-likely explanation is sterically restricted rotation of the fenchyl ring along the glycosidic linkage. A similar set of signals was already present in the spectra of trimer **29**. Racemization of the adjacent Boc-D-Phe residue during the preparation of **29** was ruled out, as all heterotrimeric components were prepared from one single batch of Boc-D-Phe-OH, so that contamination by Boc-L-Phe-OH or racemization during COOH activation should have been observed at least for compound β-**30**, bearing both a sterically demanding and optically active aglycone. The same holds true for the theoretical *endo*/*exo* epimerization of the norborneol OH group, resulting in a different glycoside; a similar behavior should have been observed in the case of menthol.

For selected compounds, distance information was obtained by ROESY experiments in (D_6)DMSO. Using these information as distance restraints in molecular dynamics (MD) simulations (MM2, *Polak*–*Ribierre* conjugate gradient), structures were derived that suggested a helical conformation. In the case of **34** (*Fig. 3*) and **35** (*Fig. 4*), the pyranose planes were found to be twisted against each other by *ca.* 90°.

An ordered conformation of the SAA peptide chain is in accordance with the circular dichroism (CD) spectra of selected compounds (*Fig. 5*). The CD curves of the subunits **28** and **29** are 'reproduced' by the CD curves of the larger peptide **35** corrected by the number of amide bonds adjacent to stereogenic centers. This suggests that the local environment at the amide bonds is similar in the measured compounds. However, more-detailed structural information could not be derived, as reference spectra for oligo-amides of this type are not known.

Conclusions. – Starting from a simple reaction sequence, a set of differently glycosidated 2-amino-2-deoxy-D-glucopyranosiduronic acids (SAAs), compounds **10**–**16**, were generated. These were coupled with standard amino acids to higher building blocks, which are well-suited for solution-phase peptide synthesis. The possibility to generate differently glycosidated SAAs in good yields using reliable reactions on a

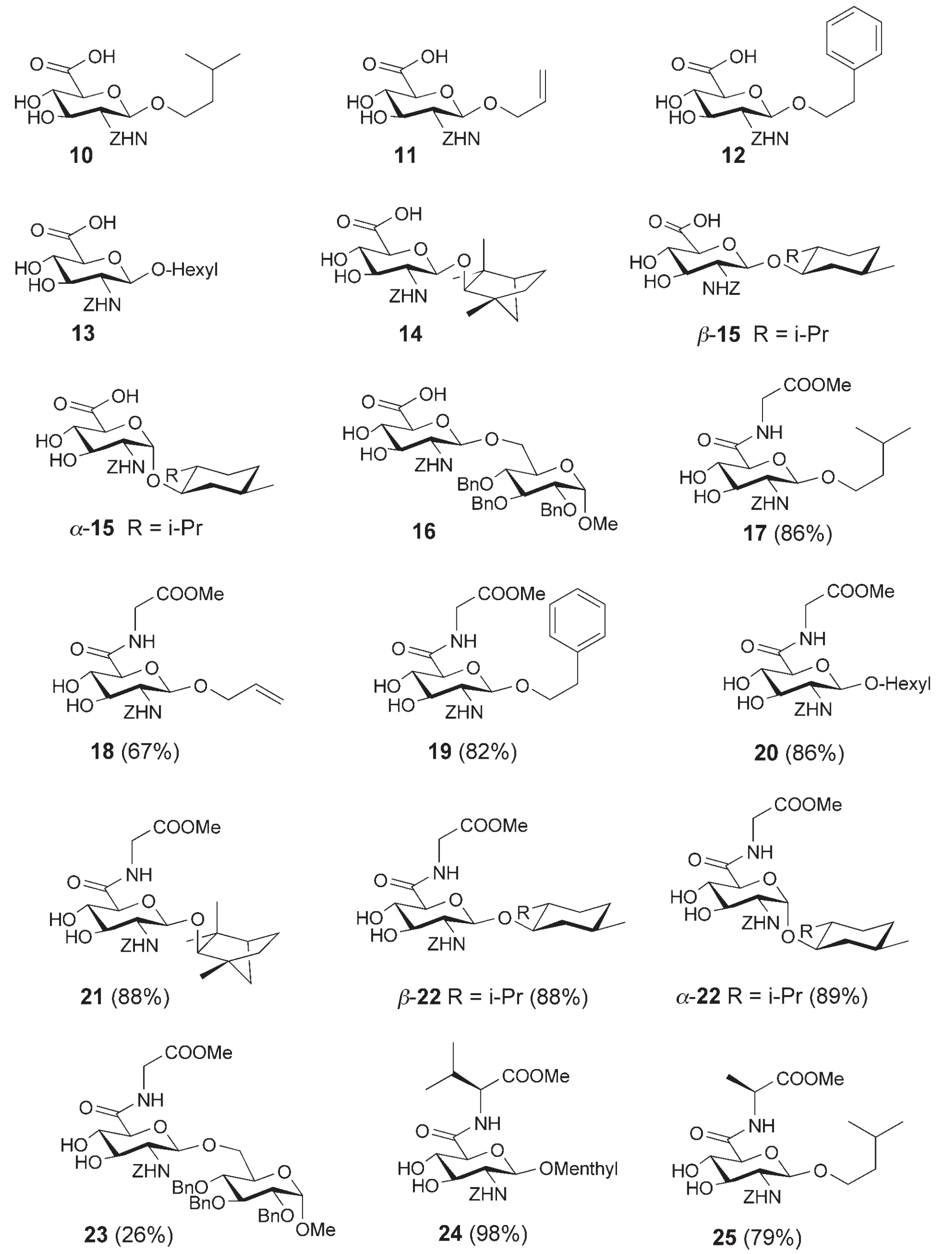
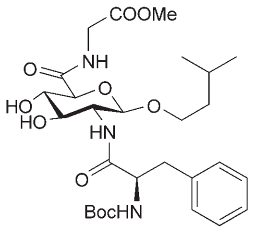
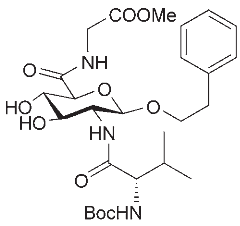


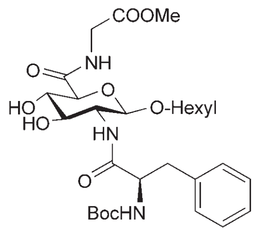
Fig. 2. *Structures and yields of heterodimeric and heterotrimeric building blocks derived from the corresponding sugar amino acids*



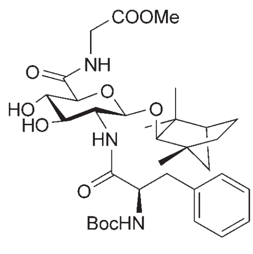
26 (68%)



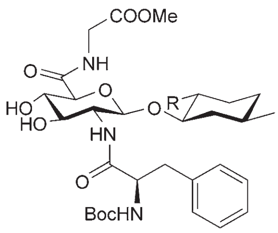
27 (40%)



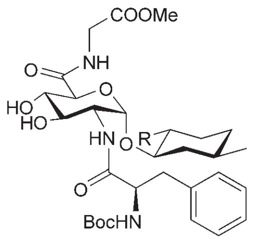
28 (55%)



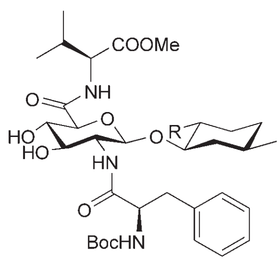
29 (80%)



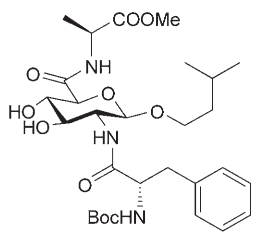
β-**30** R = i-Pr (44%)



α-**30** R = i-Pr (98%)



31 (76%)



32 (64%)

Fig. 2 *(cont.)*

gram scale should be especially interesting for combinatorial purposes, thus broadening the repertoire of carbohydrate-based building blocks.

Experimental Part

1. *General*. Solvents and chemicals were obtained from *Acros*, *J. T. Baker*, *Biosolve*, *Fluka*, *NovaBiochem*, *Riedel-de Haën*, or *Sigma-Aldrich* in at least synthesis-grade quality. Solvents and alcohols for reactions performed under anh. conditions were dried according to standard methods, and stored under Ar in the presence of activated molecular sieves (3 or 4 Å). CH_2Cl_2 and DMF used for peptide couplings were obtained from *Biosolve* in peptide-synthesis grade. Glycosidation reactions were carried out under anh. conditions under Ar atmosphere. Reactions were monitored by TLC (pre-coated silica gel plates; *Merck 60 F_{254}*). Chromatographic separations were performed on flash silica gel *32–63* (60 Å; *ICN Biomedicals*). CD Spectra were recorded in MeOH (*Uvasol*; *Merck*) at sample concentrations of 0.4 mM (**28**, **29**) or 0.075 mM (**35**) on a *Jasco J-715* apparatus in the range of 190–300 nm; $\Delta\varepsilon$ values were converted to molar ellipticity [Θ] with the *Jasco Spectra Analysis V1.0* software. NMR Spectra were recorded on *Bruker DPX-200* (200.13 (^{1}H) or 50.33 MHz (^{13}C)), *Bruker DRX-400* (400.13 or 100.61 MHz, resp.), and *Bruker DRX-600* (600.13 or 150.90 MHz, resp.) in

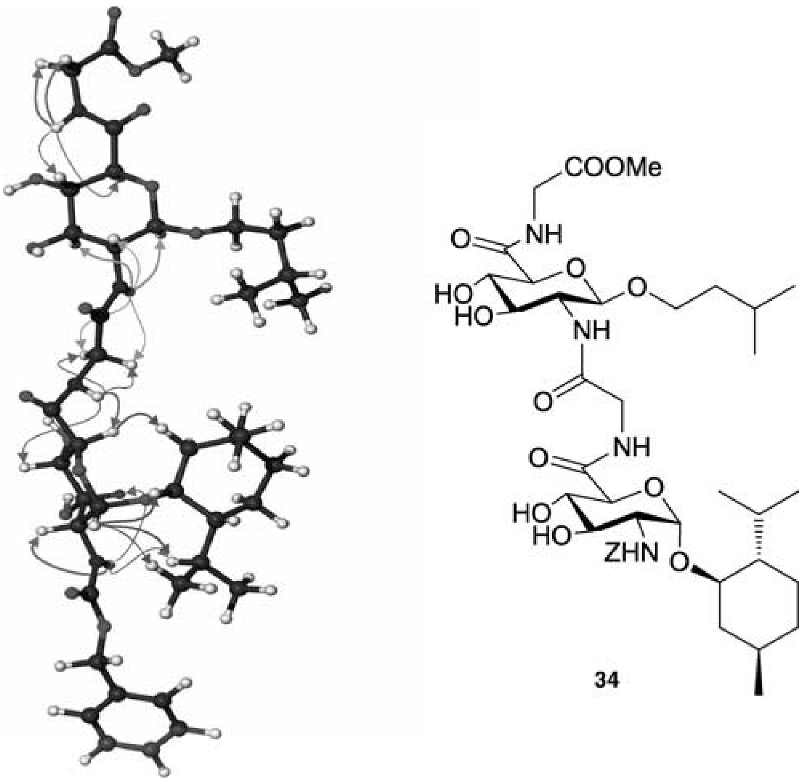
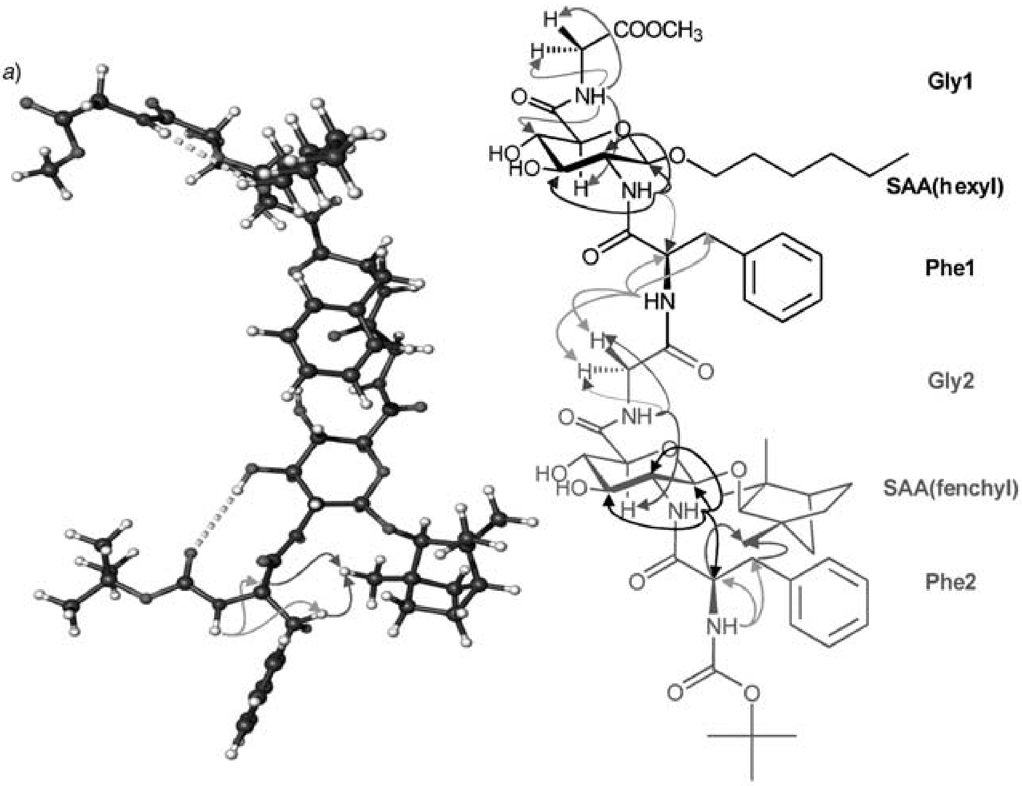


Fig. 3. *Calculated conformation of* **34**. NOEs used as geometrical restraints are depicted as arrows, their intensities being represented in arrow thickness.

$CDCl_3$, CD_3CN, or $(D_6)DMSO$; δ in ppm, J in Hz. Mass spectra (FAB) were recorded on a *VG Instruments Autospec* mass spectrometer, in *m/z*. Elemental analyses were carried out on a *Vario EL* (*Elementar/Hanau*).

2. *General Procedures.* 2.1. *Glycosidation Reactions* (*GP 1*). Glycosidation reactions were performed under strictly anh. conditions. Compound **2** and 1.1 – 5.0 equiv. of glycosyl acceptor were dissolved in anh. CH_2Cl_2 in the presence of ground *Drierite* and ground molecular sieves (3 Å), and stirred at r.t. for *ca.* 30 min. under continuous Ar flow. Then, 1.1 – 1.5 equiv. of TMSTf were added dropwise *via* a *Teflon* septum. The mixture was stirred for 30 – 60 min (TLC control), passed through a bed of *Celite*, and diluted with AcOEt. The filtrate was extracted with sat. $NaHCO_3$ soln., washed with brine, and dried (Na_2SO_4). After removal of the drying reagent and concentration under reduced pressure, the crude product was either crystallized from a suitable solvent (EtOH, AcOEt/hexanes, Et_2O) or subjected to column chromatography (CC).

2.2. *Oxidation Reactions* (*GP 2*). Deacetylation was carried out by adding a cat. amount of Na to a soln. or suspension of the respective acetylated glycoside in anh. MeOH. After a reaction time of 30 – 180 min (TLC control) at r.t., the resulting clear soln. was neutralized with *Dowex 50 WX4-100* (H^+ form), filtered, and evaporated to dryness. The crude product was usually very pure by NMR and FAB-MS (data not shown) and was, therefore, processed without further purification. The deacetylation product was dissolved in a 1 : 1 mixture of MeCN and *Borax* buffer (pH 9.0; at least 5 ml of MeCN per mmol of starting material) in the presence of TEMPO (15 mg). Oxidation solns. *A* (2.2 equiv. of $NaClO_2$ in 15 ml H_2O per mmol starting material) and *B* (9 ml bleach soln. + 2 ml sat. $NaHCO_3$ soln. + 4 ml brine) were simultaneously added dropwise at 4° (ice bath) and vigorous stirring. After completed addition, stirring was continued for *ca.* 30 min. Then, the pH of the soln. was raised to *ca.* 12 by adding 0.1M aq. NaOH soln. The mixture was extracted with Et_2O, and the org. phase was washed with 0.1M aq. NaOH soln (2 ×). The aq. layers were combined, carefully acidified to pH 1.5 – 2.0, and a)



35

b)

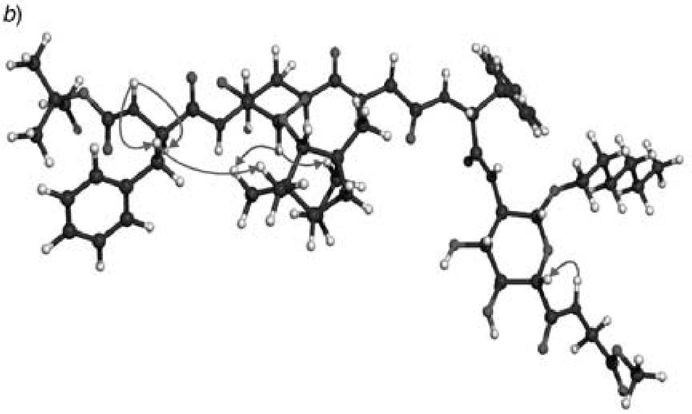


Fig. 4. *Calculated major* (a) *and minor* (b) *conformations of* **35**. Arrows indicate backbone NOEs used as geometrical restraints for MD simulations, which were equivalent for both the major and minor form. In the MD structures, individual NOEs of the major and minor form are indicated, their intensities being represented in arrow thickness.

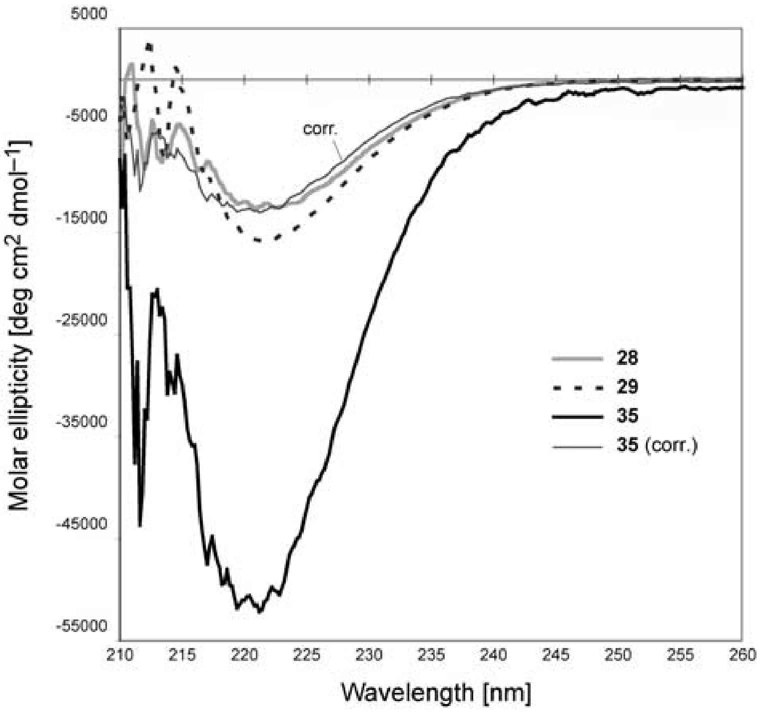


Fig. 5. *CD Spectra of* **35** *and the parent trimeric type-***IV** *building blocks* **28** *and* **29**. The corrected (corr.) curve of **35** represents that of **35** divided by the number of amide bonds adjacent to stereogenic centers (*i.e.*, four).

repeatedly extracted with AcOEt. The org. phase was dried (Na_2SO_4) and evaporated under reduced pressure to afford the crude products (intensively smelling glassy films), which were precipitated from ether/hexanes.

2.3. *Solution-Phase Peptide Coupling.* 2.3.1. *With EDC/HOBt* (*GP 3a*). The carboxy component (1 equiv.) and the amino component (1.0 – 1.3 equiv.) were dissolved in CH_2Cl_2 in the presence of HOBt (1.5 equiv.) and EDC hydrochloride (1.5 equiv.). After addition of Et(i-Pr)$_2$N or Et_3N, the mixture was stirred at r.t. for 3 – 12 h, concentrated to dryness under reduced pressure, and suspended in AcOEt. The crude product was precipitated from Et_2O or Et_2O/hexanes.

2.3.2. *With EEDQ* (*GP 3b*). The carboxy component (1.0 equiv.) and the amino component (1.0 – 1.3 equiv.) were dissolved in CH_2Cl_2 and treated with EEDQ (1.2 – 1.5 equiv.). After stirring at r.t. for 12 – 36 h, the mixture was concentrated under reduced pressure, suspended in AcOEt, and extracted with 10% (*w*/*v*) aq. citric acid soln., sat. $NaHCO_3$ soln., and brine. The org. layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure, and the remaining crude product was precipitated from Et_2O or Et_2O/ hexanes.

3. *Synthesis of the Glycosyl Donor* **2**. 3.1. *2-Deoxy-2-{[(4-methoxyphenyl)methylidene]amino}-*D*-glucopyranose.* Glucosamine hydrochloride (**1**; 20 g, 92.77 mmol) was dissolved in 5N aq. NaOH soln. (20.4 ml, 102.05 mmol; 1.1 equiv.) and treated with anisaldehyde (11.28 ml, 92.77 mmol, 1.0 equiv.). After brief shaking, the soln. solidified and was kept at 4° overnight. The crystalline slurry was suction-filtered, and rinsed with H_2O and small portions of Et_2O/hexanes 2 : 1 to afford, after drying, a creamy colorless solid (26.64 g, 89.6 mmol) in 97% yield. ^{1}H-NMR (400 MHz, (D_6)DMSO): 8.11 (*s*, ArC*H*=N); 7.69 (*d*, *J* = 8.5, 2 arom. H); 6.99 (*d*, *J* = 8.5, 2 arom. H); 6.51 (*d*, *J* = 6.5, 1-OH); 4.90 (*d*, *J* = 5.0, 4-OH); 4.79 (*d*, *J* = 6.0, 3-OH); 4.70 (*dd*, *J* = 7.3, 7.3, H–C(1)); 4.53 (*dd*, *J* = 5.8, 5.8, 6-OH); 3.79 (*s*, MeO); 3.74 (*ddd*, *J* = 11.5, 5.5, 2.0, H–C(6)); 3.47 (*ddd*, *J* = 11.5, 6.3, 6.3, H′–C(6)); 3.41 (*dd*, *J* = 9.5, 9.0, H–C(3)); 3.23 (*ddd*, *J* = 9.2, 6.3, 2.0, H–C(5)); 3.14 (*ddd*, *J* = 9.0, 9.2, 5.0, H–C(4)); 2.80 (*dd*, *J* = 8.5, 9.5, H–C(2)). ^{13}C-NMR (100 MHz, (D_6)DMSO): 161.43 (Ar–*C*H=N); 161.23, 129.80, 129.28, 114.07 (arom.); 95.91 (C(1)); 78.34 (C(2)); 77.03 (C(5)); 74.78 (C(3)); 70.56 (C(4)); 61.48

(C(6)); 55.45 (MeO). FAB-MS: 298.1 ([$M+H]^+$), 280.1 ([$M-H_2O]^+$). Anal. calc. for $C_{14}H_{19}NO_6$: C 56.56, H 6.44, N 4.46; found: C 55.93, H 6.25, N 4.49.

3.2. *1,3,4,6-Tetra*-O-*acetyl-2-deoxy-2-{[(4-methoxyphenyl)methylidene]amino}*-D-*glucopyranose.* The above (*Sect. 3.1*) compound (26.6 g, 89.47 mmol) was dissolved in anh. pyridine (150 ml) and cooled in an ice bath, and Ac_2O (75 ml) was added in small portions under continuous stirring. The cooling bath was removed, and the mixture was stirred at r.t. for 2–4 h. After adding toluene, the solvents were removed under reduced pressure, the remaining oil being repeatedly co-evaporated with toluene. The resulting yellowish solid was crystallized from EtOH to afford the title compound (31 g, 66.6 mmol) in 72% yield. ^{1}H-NMR (400 MHz, (D_6)DMSO): 8.27 (*s*, Ar–C*H*=N); 7.64 (*d*, *J* = 8.5, 2 arom. H); 6.98 (*d*, *J* = 8.5, 2 arom. H); 6.05 (*d*, *J* = 8.0, H–C(1)); 5.43 (*dd*, *J* = 9.8, 9.8, H–C(3)); 4.96 (*dd*, *J* = 9.5, 9.5, H–C(4)); 4.26 (*m*, H–C(5), H–C(6)); 4.01 (*dd*, *J* = 12, 2, H'–C(6)); 3.78 (*s*, MeO of Ar); 3.43 (*dd*, *J* = 9.8, 8.0, H–C(2)); 3.28 (*s*, Ac); 2.01 (*s*, 2 Ac); 1.97 (*s*, Ac). ^{13}C-NMR (100 MHz, (D_6)DMSO): 170.14 (6-O*C*OMe); 169.54 (4-O*C*OMe); 169.08 (3-O*C*OMe); 168.68 (1-O*C*OMe); 164.57 (Ar–*C*H=N); 161.98, 130.03, 128.41, 114.34 (arom.); 92.69 (C(1)); 72.51 (C(3)); 72.37 (C(2)); 71.69 (C(5)); 68.00 (C(4)); 61.81 (C(6)); 55.51 (MeO of Ar); 20.64 (OCO*Me*); 20.57 (2 OCO*Me*); 20.31 (OCO*Me*). FAB-MS: 488.0 ([$M+Na]^+$), 466.0 ([$M+H]^+$), 406.0 ([$M-Ac]^+$), 346.0 ([$M-2Ac]^+$), 286.0 ([$M-3Ac]^+$). Anal. calc. for $C_{22}H_{27}NO_{11}$: C 56.77, H 5.85, N 3.01; found: C 56.53, H 5.89, N 2.89.

3.3. *1,3,4,6-Tetra*-O-*acetyl-β*-D-*glucosamine Hydrochloride.* The above (*Sect. 3.2*) compound (20 g, 42.97 mmol) was dissolved in hot acetone, and treated with conc. HCl (3.8 ml, 1.1 equiv.) under vigorous stirring. The immediately solidifying mass was cooled to r.t., stirred with Et_2O/hexanes, and kept overnight at 4°. After suction-filtration, the crystalline mass was washed with cold Et_2O/hexanes and then hexanes to yield a colorless solid (16.5 g, 42.90 mmol) in nearly quant. yield. ^{1}H-NMR (400 MHz, (D_6)DMSO): 5.54 (*d*, *J* = 8.5, H–C(1)); 5.04 (*dd*, *J* = 9.8, 9.8, H–C(3)); 4.80 (*dd*, *J* = 9.5, 9.5, H–C(4)); 4.14 (*dd*, *J* = 12.8, 5.3, H–C(6)); 3.94 (*m*, H'–C(6), H–C(5)); 2.77 (*dd*, *J* = 10.0, 8.5, H–C(2)); 2.10 (*s*, Ac); 1.98 (*s*, 2 Ac); 1.95 (*s*, Ac); the signal of the NH_2 group was broadened due to exchange with water. ^{13}C-NMR (100 MHz, (D_6)DMSO): 94.7 (C(1)); 74.56 (C(3)); 71.53 (C(5)); 68.49 (C(4)); 62.43 (C(6)); 55.12 (C(2)); 20.84 (OCO*Me*); 20.62 (2 OCO*Me*); 20.53 (OCO*Me*). FAB-MS: 384.3 ([$M+H]^+$), 348.2 ([$M-Cl]^+$), 370.2 ([$M-Cl+Na]^+$), 289.1 ([$M-Cl-Ac]^+$). Anal. calc. for $C_{14}H_{22}ClNO_9$: C 43.81, H 5.78, N 2.91; found: C 40.94, H 6.33, N 4.29.

3.4. *1,3,4,6-Tetra*-O-*acetyl-2-{[(benzyloxy)carbonyl]amino}-2-deoxy-β*-D-*glucopyranose* (**2**). The above (*Sect. 3.3*) compound (7.7 g, 20 mmol) was dissolved in $CHCl_3$ (40 ml) and H_2O (80 ml) in the presence of solid $NaHCO_3$ (2.5 equiv.) and benzylchlorocarbonate (ZCl; 1.5 equiv.). The mixture was stirred for 3–24 h, while maintaining the pH at 8.0, until TLC showed the disappearance of the starting material. The mixture was acidified to pH 1.5–2.0, and then extracted several times with $CHCl_3$. The combined org. layers were washed with diluted HCl, sat. $NaHCO_3$ soln., and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The remaining creamy-colorless product was crystallized from cyclohexane to yield **2** as a colorless solid (8.03 g) in 83% yield. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.44 (*d*, *J* = 8.7, NH); 7.34 (*m*, 2 arom H of Z); 7.28 (*m*, 3 arom. H of Z); 5.69 (*d*, *J* = 8.5, H–C(1)); 5.16 (*dd*, *J* = 9.7, 9.5, H–C(3)); 5.03 (*d*, *J* = 12.6, CH_2 of Z); 4.88 (*dd*, *J* = 9.7, 9.7, H–C(4)); 4.19 (*dd*, *J* = 12.3, 4.3, H–C(6)); 3.98 (*d*, *J* = 12.3, H'–C(6)); 3.67 (*m*, H–C(5)); 3.67 (*m*, H–C(2)); 1.99 (*s*, 2 Ac); 1.96 (*s*, Ac); 1.86 (*s*, Ac). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.03 (O*C*OMe); 169.52 (O*C*OMe); 169.28 (O*C*OMe); 155.92 (C=O of Z); 137.19, 128.40, 127.85, 127.47 (arom.); 91.98 (C(1)); 72.42 (C(3)); 71.67 (C(5)); 68.25 (C(4)); 65.49 (CH_2 of Z); 61.58 (C(6)); 54.31 (C(2)); 20.51 (OCO*Me*); 20.50 (OCO*Me*); 20.43 (OCO*Me*); 20.30 (OCO*Me*). FAB-MS: 504.2 ([$M+Na]^+$), 481.2 (M^+), 422.2 ([$M-Ac]^+$). Anal. calc. for $C_{22}H_{27}NO_{11}$: C 54.88, H 5.65, N 2.91; found: C 54.68, H 5.75, N 2.85.

4. *Preparation of Glycosides* **3**–**16**. 4.1. *3-Methylbutyl 3,4,6-Tri*-O-*acetyl-2-{[(benzyloxy)carbonyl]amino}-2-deoxy-β*-D-*glucopyranoside* (**3**). Compound **2** (2.006 g, 4.17 mmol) was treated with isoamyl alcohol (2.27 ml, 20.8 mmol, 5 equiv.) according to *GP 1*. The crude product was crystallized from EtOH to yield **3** (2.002 g) in 94.4% yield as a colorless solid. ^{1}H-NMR (400 MHz, (D_6)DMSO): 7.25 (*m*, 5 arom H); 4.94 (*m*, CH_2 of Z, H–C(5)); 4.74 (*dd*, *J* = 9.5, 9.5, H–C(4)); 4.47 (*d*, *J* = 8.0, H–C(1)); 4.10 (*dd*, *J* = 12.1, 4.5, H–C(6)); 3.93 (*dd*, *J* = 12.1, 2.0, H'–C(6)); 3.67 (*m*, H–C(3), 1 H of isoamyl); 3.37 (*m*, H–C(2), 1 H of isoamyl)); 1.93 (*s*, Ac); 1.88 (*s*, Ac); 1.78 (*s*, Ac); 1.54 (*dq*, *J* = 20, 6.7, 1 H of isoamyl); 1.28 (*ddd*, *J* = 20, 13, 7, 2 H of isoamyl); 0.75 (2*d*, *J* = 6.7, 2 Me of isoamyl). ^{13}C-NMR (100 MHz, (D_6)DMSO): 170.15 (O*C*OMe); 169.66 (O*C*OMe); 169.40 (O*C*OMe); 156.00 (N*C*OOBn); 137.33, 128.40, 127.83, 127.46 (arom.); 100.62 (C(1)); 72.88 (C(5)); 70.80 (C(3)); 68.86 (C(4)); 67.53 (1 C of isoamyl); 65.31 (CH_2 of Z); 61.97 (C(6)); 55.39 (C(2)); 37.89 (1 C of isoamyl); 24.35 (1 C of isoamyl); 22.54, 22.36 (2 Me of isoamyl); 20.60 (OCO*Me*); 20.51 (OCO*Me*); 20.40 (OCO*Me*). FAB-MS: 532.2 ([$M+Na]^+$), 510.2 ([$M+H]^+$), 422.1 ([$M-isoamyl]^+$). Anal. calc. for $C_{25}H_{35}NO_{10}$: C 58.93, H 6.92, N 2.75; found: C 58.65, H 7.14, N 2.71.

4.2. *Prop-2-enyl 3,4,6-Tri-*O*-acetyl-2-{[(benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranoside* (**4**). Compound **2** (1.0 g, 2.08 mmol) was treated with allyl alcohol (355 µl, 5.2 mmol, 2.5 equiv.) according to *GP 1*. The crude product was precipitated from Et_2O to yield **4** (896.5 mg) as a colorless solid in 90% yield. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.34 (*m*, NH, 2 arom H of Z); 7.29 (*m*, 3 arom. H of Z); 5.83 (*ddd*, *J* = 17.1, 10.5, 5.2, 1 H of allyl); 5.22 (*dd*, *J* = 17.1, 1.5, 1 H of allyl); 5.10 (*dd*, *J* = 10.5, 1.1, 1 H of allyl); 5.05 (*m*, 1 H of CH_2 of Z, H−C(3)); 4.99 (*d*, *J* = 12.5, 1 H of CH_2 of Z); 4.82 (*dd*, *J* = 9.7, 7.6, H−C(4)); 4.60 (*d*, *J* = 8.0, H−C(1)); 4.21 (*dd*, *J* = 13.2, 5.2, 1 H of allyl); 4.17 (br. *d*, *J* = 12.3, H−C(6)); 4.02 (*m*, 1 H of allyl, H′−C(6)); 3.75 (*m*, H−C(5)); 3.50 (*dd*, *J* = 9, 9, 8, H−C(2)); 2.01 (*s*, Ac); 1.95 (*s*, Ac); 1.85 (*s*, Ac). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.13 (O*C*OMe); 169.62 (O*C*OMe); 169.37 (O*C*OMe); 155.90 (C=O of Z); 137.32 (arom.), 134.33 (allyl); 128.39, 127.81, 127.48 (arom.); 116.70 (allyl); 100.00 (C(1)); 72.84 (C(3)); 70.85 (C(5)); 69.42 (C(6)); 68.83 (C(4)); 65.33 (CH_2 of Z); 61.92 (allyl); 55.41 (C(2)); 20.59 (OCO*Me*); 20.49 (OCO*Me*); 20.37 (OCO*Me*). FAB-MS: 502.2 ($[M+Na]^+$), 480.2 ($[M+H]^+$), 422.2 ($[M-\text{allyl}]^+$).

4.3. *2-Phenylethyl 3,4,6-Tri-*O*-acetyl-2-{[(benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranoside* (**5**). Compound **2** (2.5 g, 5.2 mmol) was reacted with 2-phenylethanol (653 µl, 5.45 mmol = 1.05 equiv.) according to *GP 1* for 15 min. Standard workup and crystallization from i-PrOH yielded **5** (1.2 g) in 43% yield as a colorless solid. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.40–7.26 (*m*, 5 arom. H of Z, NH); 7.26–7.13 (*m*, 5 arom. H of phenethyl); 5.07 (*m*, 1 H of CH_2 of Z, H−C(3)); 4.97 (*d*, *J* = 12.6, 1 H of CH_2 of Z); 4.82 (*dd*, *J* = 9.7, 9.3, H−C(4)); 4.63 (*d*, *J* = 7.9, H−C(1)); 4.17 (*dd*, *J* = 12.3, 4.7, H−C(6)); 4.03 (*dd*, *J* = 12.3, 1.7, H′−C(6)); 3.89 (*ddd*, *J* = 9.8, 6.9, 1 H of phenethyl); 3.77 (br. *d*, H−C(5)); 3.67 (*m*, *J* = 9.8, 6.9, 1 H of phenethyl); 3.49 (*ddd*, *J* = 9.3, 7.9, H−C(2)); 2.79 (*ddd*, *J* = 10, 6.9, 6.9, 2 H of phenethyl); 2.0 (*s*, OCO*Me*); 1.95 (*s*, OCO*Me*); 1.84 (*s*, OCO*Me*). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.9 (O*C*OMe); 170.4 (O*C*OMe); 170.1 (O*C*OMe); 156.7 (C=O of Z); 139.5, 138.1, 129.7, 129.2, 129.0, 128.6, 128.2, 126.9 (arom.); 101.1 (C(1)); 73.7 (C(3)); 71.9 (C(5)); 71.3 (CH_2 of phenethyl); 69.5 (C(4)); 66.1 (CH_2 of Z); 63.1 (C(6)); 56.1 (C(5)); 36.2 (CH_2 of phenethyl); 21.4 (3 OCO*Me*). FAB-MS: 566.2 ($[M+Na]^+$), 544.3 ($[M+H]^+$), 422.2 ($[M-\text{phenethyl}]^+$). Anal. calc. for $C_{28}H_{33}NO_{10}$: C 61.87, H 6.12, N 2.58; found: C 61.85, H 6.86, N 2.50.

4.4. *Hexyl 3,4,6-Tri-*O*-acetyl-2-{[(benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranoside* (**6**). Compound **2** (2.5 g, 5.2 mmol) was reacted with hexan-1-ol (973 µl, 7.8 mmol, 1.5 equiv.) according to *GP 1* for 30 min. Workup furnished a colorless solid, which was crystallized from EtOH to yield the title compound (1.57 g) in 60.4% yield. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.4–7.3 (*m*, NH, 2 arom. H of Z); 7.29 (br. *dd*, 2 arom. H of Z); 5.06 (*dd*, *J* = 10, 10, H−C(3)); 5.04 (*d*, *J* = 12.8, 1 H of CH_2 of Z); 4.96 (*d*, *J* = 12.8, 1 H of CH_2 of Z); 4.81 (*dd*, *J* = 10, 10, H−C(4)); 4.54 (*d*, *J* = 8.3, H−C(1)); 4.16 (*dd*, *J* = 12, 5, H−C(6)); 4.0 (*dd*, *J* = 12, 1.5, H′−C(6)); 3.75 (br. *m*, H−C(5)); 3.69 (*ddd*, *J* = 9.8, 6.5, 6.5, 1 H of hexyl); 3.45 (br. *ddd*, *J* = 9.2, 9.2, 8.3, H−C(2)); 3.42 (*ddd*, *J* = 9.8, 6.5, 6.5, 1 H of hexyl); 2.00 (*s*, Ac); 1.95 (*s*, Ac); 1.85 (*s*, Ac); 1.45 (*ddd*, *J* = 14, 7, 6.5, CH_2 of hexyl); 1.23 (br. *m*, 6 H of hexyl); 0.83 (*dd*, *J* = 7, 7, Me of hexyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.1, 169.6, 169.4 (3 O*C*OMe); 155.9 (C=O of Z); 137.3, 128.4, 127.8, 127.4 (arom. C of Z); 100.6 (C(1)); 72.9 (C(3)); 70.8 (C(5)); 69.1, (CH_2 of hexyl); 68.9 (C(4)); 65.3 (CH_2 of Z); 62.0 (C(6)); 55.4 (C(2)); 31.0, 29.0, 25.0, 22.1 (4 CH_2 of hexyl); 20.6, 20.5, 20.4 (3 OCO*Me*); 14.0 (Me of hexyl). FAB-MS: 546.2 ($[M+Na]^+$), 524.2 ($[M+H]^+$), 422.1 ($[M-\text{hexyl}]^+$). Anal. calc. for $C_{26}H_{37}NO_{10}$: C 59.64, H 7.12, N 2.68; found: C 59.35, H 7.41, N 2.60.

4.5. *1,3,3-Trimethylbicyclo[2.2.1]hept-2-yl 3,4,6-Tri-*O*-acetyl-2-{[(benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranoside* (**7**). Compound **2** (1.62 g, 3.37 mmol) was reacted with (1*R*)-*endo*-(+)-fenchol (624 mg, 4.05 mmol, 1.2 equiv.) according to *GP 1* for 45 min. Crystallization from EtOH yielded **7** (1.14 g) in 58.6% yield as colorless needles. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.35 (*m*, 2 arom. H of Z, NH); 7.28 (*m*, 3 arom. H of Z); 5.11 (*dd*, *J* = 10.1, 10.1, H−C(3)); 4.99 (*s*, CH_2 of Z); 4.77 (*dd*, *J* = 9.6, 9.6, H−C(4)); 4.41 (*d*, *J* = 8.1, H−C(1)); 4.07 (*s*, CH_2(6)); 3.71 (br. *m*, H−C(5)); 3.48 (*ddd*, *J* = 10, 10, 8.1, H−C(2)); 3.01 (*s*, 1 H of fenchyl); 1.98, 1.96, 1.88 (3*s*, 3 Ac); 1.59 (*s*, 1 H of fenchyl); 1.54 (br. *d*, 2 H of fenchyl); 1.40 (*d*, 1 H of fenchyl); 1.31 (*m*, 1 H of fenchyl); 1.01 (*d*, 1 H of fenchyl); 0.97, 0.94 (2*s*, 2 Me of fenchyl); 0.82 (*m*, 1 H of fenchyl); 0.76 (*s*, Me of fenchyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.07, 169.67, 169.52 (3 O*C*OMe); 155.98 (C=O of Z), 137.25, 128.39, 127.91, 127.58 (arom.); 102.75 (C(1)); 93.75 (C(2) of fenchyl); 72.52 (C(3)); 70.54 (C(5)); 69.33 (C(4)); 65.36 (CH_2 of Z); 62.38 (C(6)); 55.76 (C(2)); 48.80 (C(4) of fenchyl); 47.62 (C(1) of fenchyl); 40.24 (C(7) of fenchyl); 29.53 (3-Me of fenchyl); 25.84 (C(5) of fenchyl); 25.40 (C(6) of fenchyl); 21.58 (1-Me of fenchyl); 20.62, 20.56, 20.49 (3 OCO*Me*); 19.31 (3-Me of fenchyl). FAB-MS: 598.3 ($[M+Na]^+$), 576.3 ($[M+H]^+$), 422.2 ($[M-\text{fenchyl}]^+$). Anal. calc. for $C_{30}H_{41}NP_{10}$: C 62.59, H 7.18, N 2.43; found: C 65.52, H 7.64, N 2.38.

4.6. *(1*S*,2*S*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 3,4,6-Tri-*O*-acetyl-2-{[(benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranoside* (**8**). Compound **2** (3 g, 6.22 mmol) was reacted with (2.917 g, 18.67 mmol, 3 equiv.) of (−)-menthol and TMSTf (1.2 equiv.)[2]) according to *GP 1* for 45 min. Crystallization from EtOH yielded **8** (3.28 g) in 91% yield. ^{1}H-NMR (400 MHz, (D_6)DMSO): 7.31 (*m*, 4 arom. H of Z, NH); 5.10 (*dd*, *J* = 9.8, 9.8, H−C(3)); 5.01 (*s*, CH_2 of Z); 4.78 (*dd*, *J* = 9.8, 9.8, H−C(4)); 4.62 (*d*, *J* = 8.0, H−C(1)); 4.09 (*dd*, *J* = 12, 5.5, H−C(6)); 3.99 (*dd*, *J* = 12, 2.3, H′−C(6)); 3.72 (*ddd*, *J* = 9.8, 5.5, 2.3, H−C(5)); 3.38 (*dd*, *J* = 8.0, 9.8, H−C(2)); 3.31 (*m*, 1 H of menthyl); 2.15 (*m*, 1 H of menthyl); 2.03 (br. *d*, 1 H of menthyl); 1.97, 1.95, 1.85 (3*s*, 3 Ac); 1.56 (br. *dt*, 2 H of menthyl); 1.29 (br. *m*, 1 H of menthyl), 1.06 (br. *dd*, 1 H of menthyl); 0.91 (*m*, 1 H of menthyl); 0.82 (br. *d*, 2 Me of menthyl); 0.69 (*d*, Me of menthyl). ^{13}C-NMR (100 MHz, (D_6)DMSO): 170.09, 169.66, 169.47 (3 O*C*OMe); 155.95 (C=O of Z); 137.42, 128.37, 127.81, 127.50 (arom.); 98.83 (C(1)); 78.20 (C(1) of menthyl); 72.85 (C(3)); 70.58 (C(5)); 69.26 (C(4)); 65.21 (CH_2 of Z); 62.41 (C(6)); 55.56 (C(2)); 47.30 (C(2) of menthyl); 40.34 (C(6) of menthyl); 33.98 (C(4) of menthyl); 30.94 (C(5) of menthyl); 24.70 (Me_2*C*H); 22.71 (C(3) of menthyl); 22.26 (Me of menthyl); 20.91 (Me of menthyl); 20.55 (2 OCO*Me*); 20.44 (OCO*Me*); 15.47 (Me of menthyl). FAB-MS: 578.2 ($[M+H]^+$), 600.2 ($[M+Na]^+$), 422.1 ($[M-\text{menthyl}]^+$), 156 (menthyl$^+$). Anal. calc. for $C_{30}H_{43}NO_{10}$: C 62.38, H 7.5, N 2.42; found: C 62.14, H 7.7, N 2.31.

4.7. *Methyl 6-*O*-(3,4,6-Tri-*O*-acetyl-2-{[(benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-*D*-glucopyranoside* (**9**). Compound **2** (523 mg, 1.09 mmol) was reacted with methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (505 mg) and TMSTf (1.5 equiv.) according to *GP 1* for 60 min. The crude product was subjected to CC (SiO_2), but the fractions still showed trace impurities of methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside. To obtain an anal. sample, a part of the purified material was recrystallized from i-PrOH/pentane to afford **9** (141 mg) in 14.6% yield as a colorless solid. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.49 (*d*, *J* = 9.4, 2′-NH); 7.39–7.17 (*m*, 18 arom. H); 7.13 (*m*, 2 arom. H); 5.10 (*dd*, *J* = 9.9, 9.9, H−C(3′)); 4.98 (*d*, *J* = 12.5, 1 H of CH_2 of Z); 4.84 (*dd*, *J* = 9.5, 9.5, H−C(4′)); 4.81 (*d*, *J* = 11.2, 1 H of CH_2 of Bn); 4.77 (*m*, H−C(1), 1 H of CH_2 of Z); 4.68 (*d*, *J* = 11.2, 1 H of CH_2 of Bn); 4.65 (*m*, 3 H of 2 CH_2 of Bn); 4.60 (*d*, *J* = 8.3, H−C(1′)); 4.56 (*d*, *J* = 10.8, 1 H of CH_2 of Bn); 4.2 (*dd*, *J* = 12, 4.3, H−C(6′)); 3.98 (*d*, *J* = 12, H′−C(6′)); 3.95 (*d*, *J* = 10.4, H−C(6)); 3.77 (*m*, H−C(5′)); 3.72, (*dd*, *J* = 9.3, 9.3, H−C(3)); 3.64 (*dd*, *J* = 10.4, 3.6, H′−C(6)); 3.58 (*m*, H−C(5)); 3.53 (*ddd*, *J* = 9.5, 9.5, 8.5, H−C(2′)); 3.43 (*m*, H−C(2), H−C(4)); 3.25 (*s*, 1-MeO); 1.99, 1.95, 1.86 (3*s*, 3 Ac); ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.2, 169.7, 169.4 (3 O*C*OMe); 155.9 (C=O of Bn); 139.0, 138.7, 138.6 (3 arom. C of Bn); 136.9 (arom. C of Z); 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.4 (8 arom. C); 100.9 (C(1′)); 97.0 (C(1)); 81.3 (C(3)); 79.9 (C(2)); 77.1 (C(4)); 74.7, 74.2 (2 CH_2 of Bn); 72.7 (C(3′)); 71.6 (CH_2 of Bn); 70.8 (C(5′)); 69.3 (C(5)); 68.7 (C(4′)); 67.8 (C(6)); 65.6 (CH_2 of Z); 61.9 (C(6′)); 55.4 (C(2′)); 54.7 (1-MeO); 20.7, 20.6, 20.5 (3 OCO*Me*). FAB-MS: 908.3 ($[M+Na]^+$), 886.3 ($[M+H]^+$), 854.3 ($[M-\text{MeO}]^+$), 746.2 ($[M-\text{MeO}-\text{BnO}]^+$), 663.1 ($[M-\text{MeO}-2\text{BnO}+\text{Na}]^+$), 639.1 ($[M-\text{MeO}-2\text{BnO}]^+$), 422.1. Anal. calc. for $C_{48}H_{55}NO_{15} \cdot H_2O$: C 64.04, H 6.58, N 1.52; found: C 64.60, H 6.42, N 1.56.

5. *Preparation of Pyranosiduronic Acids* **10**–**16**. 5.1. *3-Methylbutyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranosiduronic Acid* (**10**). Compound **3** (1.03 g) was oxidized with TEMPO according to *GP 2*. The remaining crude glassy film became crystalline after prolonged standing at r.t. or by trituration with Et_2O/pentane. Yield of **10**: 1.057 g (92%). ^{1}H-NMR (400 MHz, (D_6)DMSO): 7.3 (*m*, 5 arom. H); 7.07 (*d*, *J* = 8.5, NH); 4.98 (*d*, *J* = 12.3, CH_2 of Z); 4.29 (*d*, *J* = 8.0, H−C(1)); 3.72 (*ddd*, *J* = 9.4, 6.4, 6.4, 1 H of isoamyl); 3.53 (*d*, *J* = 9.0, H−C(5)); 3.37 (*ddd*, *J* = 9.4, 6.4, 6.4, 1 H of isoamyl); 3.33 (*dd*, *J* = 9.0, 9.0, H−C(4)); 3.30 (*dd*, *J* = 9.0, 8.5, H−C(3)); 1.62 (*ddd*, *J* = 6.4, 6.4, 6.4, 1 H of isoamyl); 1.33 (*dddd*, *J* = 13.6, 6.5, 6.5, 6.5, CH_2 of isoamyl); 0.82 (*d*, *J* = 6.5, Me of isoamyl); 0.81 (*d*, *J* = 6.5, Me of isoamyl). ^{13}C-NMR (100 MHz, (D_6)DMSO): 170.35 (COOH); 156.09 (C=O of Z); 137.31 (arom. C); 128.20 (3 arom. C); 127.59 (2 arom. C); 101.83 (C(1)); 75.73 (C(5)); 73.49 (C(3)); 72.21 (C(4)); 67.31 (CH_2 of Z); 65.15 (C(1) of isoamyl); 57.13 (C(2)); 37.96 (C(2) of isoamyl); 24.29 (C(3) of isoamyl); 22.54 (Me of isoamyl); 22.25 (Me of isoamyl). FAB-MS: 420.1 ($[M+Na]^+$), 398.1 ($[M+H]^+$), 310.1 ($[M-\text{isoamyl}]^+$). Anal. calc. for $C_{19}H_{27}NO_8$: C 57.42, H 6.85, N 3.52; found: C 56.37, H 6.83, N 3.49.

5.2. *Prop-2-enyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranosiduronic Acid* (**11**). Compound **4** (421.4 mg, 1.2 mmol) was oxidized according to *GP 2*. Extractive workup and removal of solvents under reduced pressure yielded **11** (415 mg) in 94% yield as a colorless solid. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.34 (br. *m*, 4 arom. H of Z); 7.29 (*m*, 1 arom H of Z); 7.1 (br. *m*, NH); 5.8 (*ddd*, *J* = 17.4, 10.4, 5.2, 1 H of allyl)); 5.22 (*dd*, *J* = 17.4, 1.5, 1 H of allyl); 5.1–4.9 (br. *m*, 4 H, 2 H of allyl, CH_2 of Z); 4.35 (*d*, *J* = 7.5, H−C(1)); 4.18 (*dd*, *J* = 13.6, 4.9, 1 H of allyl); 3.96 (*dd*, *J* = 13.6, 5.2, 2 H of allyl); 3.54 (*d*, *J* = 9, H−C(5)); 3.36 (*dd*, *J* = 9, 9, H−C(4)); 3.3 (br. *m*, H_2O, H−C(3), H−C(2)). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.01 (C(6)); 156.08 (C=O

[2]) With 2.0 equiv. of TMSTf of a freshly opened (and, therefore, probably more-reactive) batch, and after prolonged reaction time (3 h), the *α*-epimer of **8** was isolated quantitatively (data not shown).

of Z); 137.40 (arom. C); 134.52 (C(2) of allyl); 128.28, 128.25, 127.61 (3 arom. C); 116.13 (C(3) of allyl); 101.22 (C(1)); 75.84 (C(5)); 73.42 (C(3)); 72.13 (C(4)); 69.12 (C(1) of allyl); 65.08 (CH_2 of Z); 57.10 (C(2)). FAB-MS: 368.4 ([*M* + H]$^+$), 390.4 ([*M* + Na]$^+$), 310.3 ([*M* − allyl]$^+$).

5.3. *2-Phenylethyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranosiduronic Acid* (**12**). Compound **5** (839.1 mg, 2.01 mmol) was oxidized according to *GP 2*. An anal. sample was precipitated from Et_2O to afford **12** (339 mg) in 39% yield (first crop). Repeated crystallization of the mother liquor afforded two more crops, amounting to 60% overall yield. ^{1}H-NMR (600 MHz, (D_6)DMSO): 12.6 (br. *s*, COOH); 7.44 – 6.98 (m_c, 5 arom H of phenethyl, 5 arom. H of Z, NH); 5.23 (br. *s*, OH); 5.02 (*s*, OH, CH_2 of Z); 4.38 (*d*, *J* = 7.4, H−C(1)); 3.86 (*ddd*, *J* = 9.5, 7, 7, 1 H of phenethyl); 3.59 (*ddd*, *J* = 9.5, 7, 7, 1 H of phenethyl); 3.56 (*d*, *J* = 9.3, H−C(5)); 3.36 (*dd*, *J* = 9.3, 9.3, H−C(4)); 3.29 (*m*, H−C(3)); 3.25 (br. *s*, H_2O, H−C(2)); 2.75 (*ddd*, *J* = 13.9, 7, 7, 2 H of phenethyl). ^{13}C-(NMR) (150 MHz, (D_6)DMSO): 170.2 (C(6)); 156.2 (C=O of Z); 138.9 (arom. C of phenethyl); 137.4 (arom. C of Z); 129.4, 129.0, 128.7, 128.4, 128.2, 127.7, 126.7, 126.1 (8 arom. C); 101.6 (C(1)); 76.0 (C(5)); 73.6 (C(3)); 72.2 (C(4)); 69.6 (CH_2 of phenethyl); 65.2 (CH_2 of Z); 57.1 (C(2)); 35.5 (CH_2 of phenethyl). FAB-MS: 454.1 ([*M* + Na]$^+$), 432.1 ([*M* + H]$^+$), 298.1 ([*M* − Z]$^+$), 310.1 ([*M* − phenethyl]$^+$). Anal. calc. for $C_{22}H_{25}NO_8 \cdot H_2O$: C 58.79, H 6.06, N 3.12; found: C 59.59, H 6.03, N 3.15.

5.4. *Hexyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranosiduronic Acid* (**13**). Compound **6** (1.54 g) was deacetylated according to standard procedures (85% yield; data not shown), and the resulting product (1.06 g) was oxidized according to *GP 2*. The org. extract of the acidified aq. layer furnished **13** (1.085 g) in 98% yield as an off-white foam. ^{1}H-NMR (600 MHz, (D_6)DMSO): 12.6 (br. *s*, COOH); 7.33 (*m*, 4 arom. H of Z); 7.29 (*m*, 1 arom H. of Z); 7.08 (br. *d*, NH); 5.01 (br. *m*, 2 OH, CH_2 of Z); 4.3 (*d*, *J* = 7, H−C(1)); 3.67 (*ddd*, *J* = 9.6, 6, 6, 1 H of hexyl); 3.53 (*d*, *J* = 9.4, H−C(5)); 3.34 (*m*, H−C(4), 1 H of hexyl); 3.29 (br. *dd*, H−C(3)); 3.19 (br. *m*, H−C(2)); 1.42 (*ddd*, *J* = 13.7, 6.8, 6.8, 2 H of hexyl); 1.32 – 1.13 (*m*, 6 H of hexyl); 0.83 (*dd*, *J* = 6.8, 6.8, Me of hexyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.1 (C(6)); 156.1 (C=O of Z); 137.4, 128.3, 127.7, 127.6 (arom. C of Z); 101.8 (C(1)); 75.9 (C(5)); 73.5 (C(3)); 72.2 (C(4)); 68.9 (CH_2 of hexyl); 65.1 (CH_2 of Z); 57.2 (C(2)); 31.0, 29.1, 25.0, 22.1, 13.9 (4 CH_2 and 1 Me of hexyl)). FAB-MS: 412.2 ([*M* + H]$^+$), 434.2 ([*M* + Na]$^+$), 310.1 ([*M* − hexyl]$^+$). Anal. calc. for $C_{20}H_{29}NO_8 \cdot H_2O$: C 55.93, H 7.28, N 3.26; found: C 57.15, H 6.88, N 3.29.

5.5. *1,3,3-Trimethylbicyclo[2.2.1]hept-2-yl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranosiduronic Acid* (**14**). Compound **7** (753 mg, 1.675 mmol) was oxidized according to *GP 2*. Extractive workup yielded **14** (0.412 g) in 53% yield. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.32 (*m*, 4 arom. H of Z); 7.29 (*m*, 1 arom H of Z); 7.12 (*d*, *J* = 9.3, NH); 5.23 (br. *s*, OH); 5.04 (*d*, *J* = 12.5, 1 H of CH_2 of Z); 4.99 (br. *s*, OH); 4.93 (*d*, *J* = 12.5, 1 H of CH_2 of Z); 4.15 (*d*, *J* = 8.3, H−C(1)); 3.49 (*d*, *J* = 9.5, H−C(5)); 3.36 (*dd*, *J* = 9.2, 9.2, H−C(4)); 3.30 (br. *m*, H_2O, H−C(3)); 3.23 (*m*, H−C(2)); 2.95 (*s*, 1 H of fenchyl); 1.60 (br. *m*, 1 H of fenchyl); 1.57 (br. *m*, 1 H of fenchyl); 1.53 (br. *m*, 1 H of fenchyl); 1.39 (*d*, *J* = 9.4, 1 H of fenchyl); 1.30 (br. *m*, 1 H of fenchyl); 1.00 (*m*, 1 H of fenchyl); 0.98 (*s*, Me of fenchyl); 0.89 (*s*, Me of fenchyl); 0.80 (br. *m*, 1 H of fenchyl); 0.75 (*s*, Me of fenchyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.2 (C(6)); 156.1 (C=O of Z); 137.5, 128.3, 127.7, 125.4 (4 arom. C); 104.0 (C(1)); 93.2 (C(2) of fenchyl); 75.7 (C(5)); 73.3 (C(3)); 72.2 (C(4)); 65.1 (CH_2 of Z); 57.6 (C(5)); 48.8 (C(4) of fenchyl); 47.6 (C(1) of fenchyl); 40.6 (C(7) of fenchyl); 29.6 (Me of fenchyl); 25.9 (C(6) of fenchyl); 25.3 (C(5) of fenchyl); 21.7 (Me of fenchyl); 19.4 (Me of fenchyl). FAB-MS: 464.1 ([*M* + H]$^+$), 486.1 ([*M* + Na]$^+$), 310.0 ([*M* − fenchyl]$^+$). Anal. calc. for $C_{24}H_{33}NO_8 \cdot H_2O$: C 59.61, H 7.71, N 2.90; found: C 59.93, H 8.04, N 2.84.

5.6. *(1S,2S,5S)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranosiduronic Acid (β-**15**)*. Compound **8** (455.3 mg) was oxidized according to *GP 2*. Both the Et_2O extract of the basified aq. phase and the AcOEt extract of the acidified aq. phase contained, as the single product, the title compound. Yield: 463.5 mg (97%). Colorless foam. ^{1}H-NMR (400 MHz, (D_6)DMSO): 12.6 (br. *s*, COOH); 7.3 (*m*, 5 arom. H of Z); 7.09 (*d*, *J* = 9.5, NH); 5.09 (*d*, *J* = 12.5, 1 H of CH_2 of Z); 5.05 (br. *s*, OH); 4.92 (*d*, *J* = 12.5, 1 H of CH_2 of Z); 4.39 (*d*, *J* = 8.0, H−C(1)); 3.50 (*d*, *J* = 9.5, H−C(5)); 3.3 (br. *m*, H_2O, H−C(3), H−C(4), 1 H of menthyl); 3.09 (*m*, H−C(2))); 2.1 (*m*, 1 H of menthyl); 1.98 (br. *d*, *J* = 12, 1 H of menthyl); 1.55 (br. *d*, *J* = 12.8, 2 H of menthyl); 1.3 (*m*, 1 H of menthyl); 1.04 (*m*, 1 H of menthyl); 0.9 (*dd*, *J* = 12.7, 1 H of menthyl); 0.81 (br. *d*, 2 Me of menthyl); 0.74 (*m*, 1 H of menthyl); 0.65 (*d*, *J* = 7, Me of menthyl); 0.63 (br. *d*, *J* = 12, 1 H of menthyl). ^{13}C-NMR (100 MHz, (D_6)DMSO): 170.2 (C(6)); 156.2 (C=O of Z); 137.7, 128.3, 127.7, 127.6 (4 arom. C); 99.8 (C(1)); 77.7 (C(1) of menthyl); 75.9 (C(5)); 73.6 (C(4)); 72.2 (C(3)); 64.9 (CH_2 of Z); 57.5 (C(2)); 47.5 (C(2) of menthyl); 40.4 (C(6) of menthyl); 34.1 (C(4) of menthyl): 30.9 (C(5) of menthyl); 24.7 (Me_2*C*H of menthyl); 23.2 (C(3) of menthyl); 22.7 (Me of menthyl); 22.3 (Me of menthyl); 15.6 (Me of menthyl). FAB-MS: 510.0 ([*M* + 2Na]$^+$), 488.0 ([*M* + Na]$^+$), [*M* − menthyl]$^+$), 310.0. Anal. calc. for $C_{24}H_{35}NO_8 \cdot H_2O$: C 59.61, H 7.71, N 2.90; found: C 59.93, H 8.05, N 2.84.

5.7. *(1*S*,2*S*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-α-*D*-glucopyranosiduronic Acid* (α-**15**). Compound α-**8** (2.043 g, 4.523 mmol) was oxidized according to *GP 2*. Extractive workup yielded the title compound (1.9 g) in 90.5% yield. ^{1}H-NMR (600 MHz, (D_6)DMSO): 12.45 (br. *s*, COOH); 7.35 (*m*, 4 arom. H of Z); 7.31 (*m*, 1 arom. H of Z); 7.01 (*d*, *J* = 7.2, NH); 5.24 (br. *s*, OH); 5.02 (*d*, *J* = 12.5, 1 H of CH_2 of Z); 4.98 (*d*, *J* = 12.5, 1 H of CH_2 of Z); 4.89 (*d*, *J* = 3.2, H−C(1)); 4.73 (br. *s*, OH); 3.93 (*d*, *J* = 9, H−C(5)); 3.47 (*dd*, *J* = 9, 9, H−C(3)); 3.38 (*dd*, *J* = 9, 9, H−C(4)); 3.34 (*m*, H−C(2)); 3.20 (*m*, 1 H of menthyl); 2.26 (*dt*, *J* = 6.8, 1 H of menthyl); 2.07 (br. *d*, *J* = 12.3, 1 H of menthyl); 1.58 (br. *d*, *J* = 11.3, 1 H of menthyl); 1.53 (br. *d*, *J* = 12.7, 1 H of menthyl); 1.35 (*m*, 1 H of menthyl); 1.18 (*m*, 1 H of menthyl); 0.95 (*d*, *J* = 12.3, 1 H of menthyl); 0.88 (*m*, *J* = 12.7, 1 H of menthyl); 0.83 (*d*, *J* = 6.8, Me of menthyl); 0.77 (*d*, *J* = 7, Me of menthyl); 0.74 (*m*, 1 H of menthyl); 0.59 (*d*, *J* = 7; Me of menthyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.9 (C(6)); 156.0 (C=O of Z); 137.1 (arom. C); 128.4 (arom. CH); 127.9 (arom. CH); 127.9 (arom. CH); 99.3 (C(1)); 80.9 (C(1) of menthyl); 72.2 (C(5)); 72.2 (C(4)); 69.8 (C(3)); 65.5 (CH_2 of Z); 56.5 (C(2)); 48.4 (C(2) of menthyl); 42.8 (C(6) of menthyl); 39.9 (C(4) of menthyl); 31.1 (C(5) of menthyl); 24.2 (CH of menthyl); 22.3 (Me of menthyl); 21.2 (C(3) of menthyl); 21.1, 15.6 (2 Me of menthyl). FAB-MS: 510.0 ([*M* + 2Na]$^+$), 488.0 ([*M* + Na]$^+$), 310.0 ([*M* − menthyl]$^+$).

5.8. *Methyl 6-*O*-(2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranuronosyl)-2,3,4-tri-*O*-benzyl-α-*D*-glucopyranoside* (**16**). Compound **9** (269.4 mg, 304 μmol) was deacetylated according to standard procedures. An anal. sample (data not shown) was purified by precipitation from Et_2O/pentane. The deacetylated product (230 mg, 303 μmol) was oxidized according to *GP 2*. The org. extract of the acidified aq. layer furnished the title compound as a colorless solid (170 mg crude), which was precipitated from ether/pentane to yield **16** (95 mg) in 41% yield. ^{1}H-NMR (600 MHz, CD_3CN): 7.7 – 6.9 (*m*, 20 arom. H); 5.72 (br. *d*, NH); 5.01 (*d*, *J* = 11.7, 1 H of CH_2 of Z); 4.88 (*m*, 1 H of CH_2 of Z, 1 H of CH_2 of Bn); 4.78 (*d*, *J* = 3, H−C(1)); 4.74 (*d*, *J* = 11, 1 H of CH_2 of Bn); 4.72 (*d*, *J* = 10.8, 1 H of CH_2 of Bn); 4.66 (*s*, CH_2 of Bn); 4.57 (*d*, *J* = 10.8, 1 H of CH_2 of Bn); 4.45 (*d*, *J* = 8.1, H−C(1′)); 4.02 (*d*, *J* = 10.8, H−C(6)); 3.77 (*m*, H−C(5′), H−C(3)); 3.69 (*dd*, *J* = 10.8, 3.4, H′−C(6)); 3.63 (br. *d*, H−C(5)); 3.53 (*dd*, *J* = 9, 9, H−C(4′)); 3.51 (*dd*, *J* = 9.4, 9.4, H−C(4)); 3.45 (*m*, H−C(3′), H−C(2)); 3.39 (*m*, H−C(2′)); 3.31 (*s*, MeO). ^{13}C-NMR (150 MHz, CD_3CN): 170.3 (C(6′)), 157.3 (C=O of Z); 140.2, 139.8, 139.7 (3 arom. C of Bn); 137.9 (1 arom. C of Bn); 129.4, 129.3, 129.25, 129.2, 128.9, 128.8, 128.6, 128.5, 128.4 (9 arom. C); 102.8 (C(1′)); 98.6 (C(1)); 82.5 (C(3)); 81.2 (C(2)); 78.4 (C(4)); 75.9 (CH_2 of Bn); 75.5 (CH_2 of Bn); 75.2 (C(5′)); 74.5 (C(3′)); 73.2 (CH_2 of Bn); 73.1 (C(4′)); 70.5 (C(5)); 68.9 (C(6)); 67.3 (CH_2 of Z); 58.3 (C(2′)); 55.5 (MeO). FAB-MS: 818.3 ([*M* + 2Na]$^+$), 796.3 ([*M* + Na]$^+$), 758.9 ([*M* − MeO + H_2O]$^+$), 487.2, 310.1.

6. *Syntheses of Heterodimeric Building Blocks* **17** – **25**. 6.1. *3-Methylbutyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-*N*-{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (**17**). Compound **10** (1.695 g, 4.26 mmol) and glycine methylester hydrochloride (1.34 g, 10.66 mmol, 2.5 equiv.) were subjected to EDC coupling according to *GP 3a*. The resulting colorless solid was precipitated to afford **17** (1.71 g) in 86% yield. ^{1}H-NMR (600 MHz, CD_3CN): 7.39 – 7.30 (*m*, 5 arom. H); 7.28 (*m*, NH of Gly); 5.63 (br. *s*, 2-NH); 5.05 (*d*, *J* = 12.7, CH_2 of Z); 4.46 (*d*, *J* = 8.1, H−C(1)); 4.33 (*s*, 4-OH); 3.96 (*d*, *J* = 6, NCH_2); 3.90 (*ddd*, *J* = 9.8, 6.4, 6.4, 1 H of isoamyl); 3.73 (*d*, *J* = 9.4, H−C(5)); 3.69 (*s*, MeO); 3.52 (*ddd*, *J* = 9.8, 6.4, 1 H of isoamyl); 3.44, (br. *m*, H−C(3), H−C(4), 3-OH); 3.32 (*ddd*, *J* = 9, 9, 8, H−C(2)); 1.67 (*ddd*, *J* = 6.8, 6.4, 6.4, 1 H of isoamyl); 1.42 (*dddd*, *J* = 13.5, 6.8, 6.8, 6.8, CH_2 of isoamyl); 0.88 (*d*, *J* = 6.4, Me of isoamyl); 0.87 (*d*, *J* = 6.4, Me of isoamyl)). ^{13}C-NMR (150 MHz, CD_3CN): 172.3 (6-CONH); 170.9 (*C*OOMe); 157.5 (C=O of Z); 138.4, 129.5, 128.9, 128.7 (4 arom C. of Z); 102.5 (C(1)); 74.9 (C(3)); 74.0 (C(5)); 73.9 (C(4)); 69.1 (C(1) of isoamyl); 67.1 (CH_2 of Z); 58.2 (C(2)); 52.8 (COO*Me*); 41.4 (CH_2NH); 39.1 (C(2) of isoamyl); 25.7 (C(3) of isoamyl); 23.0 (C(4) of isoamyl); 22.7 (C(5) of isoamyl). FAB-MS: 859.4 ([2*M* + Na]$^+$), 491.2 ([*M* + Na]$^+$), 469.2 ([*M* + H]$^+$), 381.1 ([*M* − isoamyl]$^+$). Anal. calc. for $C_{22}H_{32}N_2O_9$: C 56.40, H 6.88, N 5.98; found: C 56.31, H 6.61, N 5.85.

6.2. *Prop-2-enyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-*N*-{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (**18**). Compound **11** (280 mg) and glycine methylester hydrochloride (143 mg, 1.14 mmol, 1.5 equiv.) were condensed according to *GP 3a* to afford a glassy solid. Yield: 219.4 mg (66.5%) of **18**. ^{1}H-NMR (400 MHz, (D_6)DMSO): 8.35 (*t*, *J* = 5.8, NH of Gly); 7.43 – 7.22 (*m*, 5 arom. H of Z); 7.17 (*d*, *J* = 8.5, 2-NH); 5.82 (*dddd*, *J* = 17, 10, 5, 5, 1 H of allyl)); 5.23 (br. *d*, *J* = 17, 1 H of allyl); 5.16 – 4.92 (*m*, 1 H of allyl, CH_2 of Z, 3-OH, 4-OH); 4.37 (*d*, *J* = 8, H−C(1)); 4.24 (*dd*, *J* = 13.5, 5, 1 H of allyl); 3.98 (*dd*, *J* = 13.5, 5, 1 H of allyl); 3.88 (*d*, *J* = 5.8, NCH_2); 3.63 (*s*, MeO); 3.3 (br. *m*, H_2O, H−C(2), H−C(3), H−C(4)). ^{13}C-NMR (100 MHz, (D_6)DMSO): 170.2 (C(6)); 169.3 (*C*OOMe); 156.2 (C=O of Z); 137.5 (arom. C of Z); 134.6 (C(2) of allyl); 128.5, 128.4, 127.8, 127.7 (4 arom. C. of Z); 116.2 (C(3) of allyl); 101.1 (C(1)); 75.2 (C(5)); 73.6 (C(3)); 72.3 (C(4)); 69.1 (C(1) of allyl); 65.2 (CH_2 of Z); 57.1 (C(2)); 51.9 (COO*Me*); 40.6 (NCH_2). FAB-MS: 461.2 ([*M* + Na]$^+$), 381.1 ([*M* − allyl]$^+$).

6.3. *2-Phenylethyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy*-N-*{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (**19**). Compound **12** (318.3 mg, 738 μmol) and glycine methylester hydrochloride (185 mg, 1.475 mmol, 2.0 equiv.) were coupled according to *GP 3a* to furnish a crude product, which was purified by precipitation from Et_2O/hexanes to afford **19** (307 mg) in 82% yield as a colorless solid. ^{1}H-NMR (600 MHz, (D_6)DMSO): 8.27 (*t*, *J* = 6, NH of Gly); 7.35 (*m*, 4 arom. H); 7.29 (*d*, 1 arom. H); 7.22 (*m*, 4 arom. H); 7.16 (*m*, 1 arom. H); 7.11 (br. *d*, 2-NH); 5.02 (br. *s*, CH_2 of Z, 3-OH); 4.96 (*d*, *J* = 4, 4-OH); 4.41 (*d*, *J* = 7.6, H−C(1)); 3.92 (*m*, *J* = 9.7, 7, 1 H of phenethyl); 3.88 (*d*, *J* = 6, NCH_2); 3.61 (*m*, MeO, H−C(5), 1 H of phenethyl); 3.35 (*ddd*, *J* = 8.5, 8.5, 4, H−C(4)); 3.32 (*m*, H−C(3)); 3.27 (br. *m*, H−C(2)); 2.77 (*m*, *J* = 14, 7, 1 H of phenethyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.0 (C(6)); 169.3 (*C*OOMe); 156.1 (C=O of Z); 138.8 (arom. C of phenethyl); 137.4 (arom. C of Z); 128.9, 128.3, 128.2, 127.7, 126.0 (5 arom. C); 101.4 (C(1)); 75.2 (C(5)); 73.7 (C(3)); 72.2 (C(4)); 69.4 (CH_2 of phenethyl); 65.2 (CH_2 of Z); 51.7 (C(2)); 40.6 (NCH_2); 35.5 (CH_2 of phenethyl). FAB-MS: 525.2 ([*M* + Na]$^+$), 503.2 ([*M* + H]$^+$), 381.1 ([*M* − 2(phenethyl)]$^+$). Anal. calc. for $C_{25}H_{30}N_2O_9 \cdot H_2O$: C 57.80, H 6.01, N 5.39; found: C 57.94, H 5.66, N 5.25.

6.4. *Hexyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy*-N-*{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (**20**). Compound **13** (1.076 g, 2.42 mmol) and glycine methylester hydrochloride (608 mg, 4.84 mmol, 2.0 equiv.) were coupled according to *GP 3a* to afford, after precipitation from Et_2O, **20** (998.4 mg) in 86% yield as a colorless solid. ^{1}H-NMR (400 MHz, (D_6)DMSO): 8.32 (*t*, *J* = 6, NH of Gly); 7.33 (*m*, 5 arom. H of Z); 7.12 (*d*, *J* = 9, 2-NH); 5.06 (*m*, 3-OH); 5.01 (*m*, CH_2 of Z, 4-OH); 4.32 (*d*, *J* = 8.5, H−C(1)); 3.87 (*dd*, *J* = 6, 2, NCH_2); 3.73 (*ddd*, *J* = 9.7, 6.4, 6.4, 1 H of hexyl); 3.63 (*s*, MeO); 3.59 (*d*, *J* = 9, H−C(5)); 3.4 – 3.3 (*m*, 1 H of hexyl, H−C(4), H−C(3)); 3.21 (*dd*, *J* = 9, 9, 8.5, H−C(2)); 1.44 (*m*, 2 H of hexyl); 1.2 (br. *m*, 6 H of hexyl); 0.83 (*t*, *J* = 6.8, Me of hexyl). ^{13}C-NMR (100 MHz, (D_6)DMSO): 170.2 (C(6)); 169.4 (*C*OOMe); 156.2 (C=O of Z); 137.5, 128.4, 127.8, 127.7 (4 arom. C of Z); 101.7 (C(1)); 75.3 (C(5)); 73.6 (C(3)); 72.3 (C(4)); 68.9 (CH_2 of hexyl); 65.2 (CH_2 of Z); 57.1 (C(2)); 51.8 (COO*Me*); 40.6 (NCH_2); 31.2, 29.1, 25.1, 22.2 (4 CH_2 of hexyl); 14.0 (Me of hexyl). FAB-MS: 505.2 ([*M* + Na]$^+$), 483.1 ([*M* + H]$^+$), 381.1 ([*M* − hexyl]$^+$), 349.1 ([*M* + 2 − COOBn]$^+$). Anal. calc. for $C_{23}H_{34}N_2O_9$: C 57.25, H 7.10, N 5.81; found: C 56.04, H 6.70, N 5.47.

6.5. *1,3,3-Trimethylbicyclo[2.2.1]hept-2-yl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy*-N-*{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (**21**). Compound **14** (891.2 mg, 1.92 mmol) and glycine methylester hydrochloride (353 mg) were coupled according to *GP 3a* to afford **21** (903 mg) in 88% yield as a colorless solid. ^{1}H-NMR (600 MHz, (D_6)DMSO): 8.09 (br. *t*, *J* = 5.5, NH of Gly); 7.44 – 7.25 (*m*, 5 arom. H of Z); 7.07 (*d*, *J* = 8.7, 2-NH); 5.1 – 4.8 (*m*, CH_2 of Z, 3-OH, 4-OH); 4.19 (*d*, *J* = 8, H−C(1)); 3.95 – 3.85 (*dd*, *J* = 17, 5.5, NCH_2); 3.61 (*s*, MeO); 3.55 (*d*, *J* = 9, H−C(5)); 3.42 (br. *m*, H−C(4)); 3.38 (br. *m*, H−C(3)); 3.25 (*ddd*, *J* = 9, 9, 8, H−C(2)); 3.01 (*s*, 1 H of fenchyl); 1.61 (br. *m*, 1 H of fenchyl); 1.57 (*s*, 1 H of fenchyl); 1.55 (br. *m*, 1 H of fenchyl); 1.40 (*d*, 1 H of fenchyl); 1.30 (br. *m*, 1 H of fenchyl); 1.00 (*s*, Me and 1 H of fenchyl); 0.92 (*s*, Me of fenchyl), 0.81 (br. *m*, 1 H of fenchyl); 0.78 (*s*, Me of fenchyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 169.9 (C(6)); 169.2 (*C*OOMe); 156.0 (C=O of Z); 137.4, 128.2, 127.6 (3 arom. C of Z); 103.8 (C(1)); 93.1 (C(2) of fenchyl); 75.5 (C(5)); 73.4 (C(3)); 72.0 (C(4)); 65.0 (CH_2 of Z); 57.5 (C(2)); 51.6 (COO*Me*); 48.8 (C(1) of fenchyl); 48.7 (C(3) of fenchyl); 47.6 (C(4) of fenchyl); 40.6 (C(7) of fenchyl); 38.8 (NCH_2); 29.6 (Me of fenchyl); 25.8 (C(6) of fenchyl); 25.3 (C(5) of fenchyl); 21.6, 19.4 (2 Me of fenchyl). FAB-MS: 557.2 ([*M* + Na]$^+$), 535.2 ([*M* + H]$^+$), 381.1 ([M − fenchyl]$^+$). Anal. calc. for $C_{27}H_{38}N_2O_9 \cdot EtOH$: C 59.98, H 7.64, N 4.82; found: C 60.15, H 7.01, N 4.44.

6.6. *(1*S*,2*S*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy*-N-*{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (*β*-**22**). Compound *β*-**15** (336 mg, 722 μmol) and glycine methylester hydrochloride (145 mg, 1.23 mmol, 1.7 equiv.) were coupled according to *GP 3a* to afford *β*-**22** (345.8 mg) in 89% yield as a colorless solid. ^{1}H-NMR (600 MHz, (D_6)DMSO): 8.12 (*m*, NH of Gly); 7.39 (*s*, 4 arom. H of Z); 7.25 (*m*, 1 arom. H of Z); 7.09 (*d*, *J* = 9, 2-NH); 5.09 (*d*, *J* = 12.7, 1 H of CH_2 of Z); 5.02 (*d*, *J* = 3, 4-OH); 4.97 (*d*, *J* = 3, 3-OH); 4.93 (*d*, *J* = 12.7, 1 H of CH_2 of Z); 4.40 (*d*, *J* = 8.5, H−C(1)); 3.87 (*m*, NCH_2); 3.61 (*s*, MeO); 3.55 (*d*, *J* = 9, H−C(5)); 3.35 (br. *m*, H−C(4), H−C(3)); 3.31 (br. *m*, 1 H of menthyl); 3.11 (*ddd*, *J* = 9, 9, 8.5, H−C(2)); 2.19 (*m*, 1 H of menthyl); 2.00 (br. *d*, *J* = 11.7, 1 H of menthyl); 1.56 (br. *m*, 2 H of menthyl); 1.29 (br. *s*, 1 H of menthyl); 1.04 (*m*, 1 H of menthyl); 0.90 (*m*, *J* = 12, 1 H of menthyl); 0.81 (*d*, 2 Me of menthyl); 0.75 (*m*, *J* = 12, 1 H of menthyl); 0.67 (*m*, 1 Me and 1 H of menthyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.0 (C(6)); 168.9 (*C*OOMe); 156.1 (C=O of Z); 137.6, 128.3, 127.7, 127.6 (4 arom. C. of Z); 99.7 (C(1)); 77.7 (C(1) of menthyl); 75.5 (C(5)); 73.7 (C(4)); 72.1 (C(3)); 64.9 (CH_2 of Z); 57.3 (C(2)); 52.0 (COO*Me*); 47.5 (C(2) of menthyl); 40.4 (NCH_2); 40.2 (C(6) of menthyl); 34.1 (C(4) of menthyl); 30.9 (C(6) of menthyl); 24.7 (C(7) of menthyl); 22.6 (C(3) of menthyl); 22.3 (Me of menthyl); 21.1 (Me of menthyl); 15.6

(Me of menthyl). FAB-MS: 582.2 ($[M+2Na]^+$), 559.2 ($[M+Na]^+$), 537.2 ($[M+H]^+$), 381.2 ($[M-\text{menthyl}]^+$). Anal. calc. for $C_{27}H_{40}N_2O_9$: C 60.43, H 7.51, N 5.22; found: C 60.11, H 7.52, N 5.16.

6.7. *(1S,2S,5S)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-N-{[(methoxy)carbonyl]methyl}-α-D-glucopyranosiduronamide* (α-**22**). Compound α-**15** (1.43 g, 3.07 mmol) and glycine methylester hydrochloride (771 mg, 5.14 mmol, 2.0 equiv.) were coupled according to *GP 3a* to furnish, after precipitation from Et_2O/hexanes, α-**22** as a colorless solid in 88% yield. ^{1}H-NMR (600 MHz, (D_6)DMSO): 8.27 (*t*, *J* = 6, NH of Gly); 7.35 (*m*, 4 arom. H of Z); 7.31 (*m*, 1 arom. H of Z); 6.96 (*d*, *J* = 7, 2-NH); 5.00 (*d*, *J* = 12.8, CH_2 of Z); 4.97 (*d*, *J* = 4.3, 4-OH); 4.94 (*d*, *J* = 3.6, H−(1)); 4.73 (*d*, *J* = 3.6, 3-OH); 3.93 (*d*, *J* = 9.8, H−C(5)); 3.86 (*dd*, *J* = 17, 6, NCH_2); 3.62 (*s*, MeO); 3.51 (*m*, H−C(3)); 3.38 (*ddd*, *J* = 7, 9, 3.5, H−C(2)); 3.35 (*dd*, *J* = 9, 9, 4.3, H−C(4)); 3.20 (*m*, 1 H of menthyl); 2.28 (*m*, 1 H of menthyl); 2.05 (br. *d*, *J* = 11.9, 1 H of menthyl); 1.59 (br. *d*, *J* = 12.3, 1 H of menthyl); 1.54 (br. *d*, *J* = 13, 1 H of menthyl); 1.34 (br. *m*, 1 H of menthyl); 1.20 (*m*, 1 H of menthyl); 0.99 (*m*, *J* = 11.9, 1 H of menthyl); 0.90 (*m*, 1 H of menthyl); 0.85 (*d*, *J* = 6.8, Me of menthyl); 0.79 (br. *d*, *J* = 7, Me and 1 H of menthyl); 0.60 (*d*, *J* = 6.8, Me of menthyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.1 (C(6)); 170.0 (*C*OOMe); 156.1 (C=O of Z); 137.0, 128.3, 127.9, 127.8 (4 arom. C. of Z); 99.1 (C(1)); 81.1 (C(1) of menthyl); 72.7 (C(4)); 71.6 (C(5)); 69.8 (C(3)); 65.5 (CH_2 of Z); 56.3 (C(2)); 51.7 (COO*Me*); 48.3 (C(2) of menthyl); 42.5 (C(6) of menthyl); 40.5 (NCH_2); 33.9 (C(4) of menthyl); 31.2 (C(2) of menthyl); 24.2 (1 C of menthyl); 22.3 (C(3) of menthyl); 22.1, 21.2, 15.5 (3 Me of menthyl). FAB-MS: 582.2 ($[M+2Na]^+$), 559.2 ($[M+Na]^+$), 537.2 ($[M+H]^+$), 381.2 ($[M-\text{menthyl}]^+$). Anal. calc. for $C_{27}H_{40}N_2O_9$: C 60.43, H 7.51, N 5.22; found: C 60.11, H 7.52, N 5.16.

6.8. *Methyl 6-O-((5S)-2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-5-[({[(methoxy)carbonyl]methyl}amino)carbonyl]-β-D-xylopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside* (**23**). Compound **16** (161.2 mg, 0.208 mmol) and glycine methylester hydrochloride (78.5 mg, 0.625 mmol, 3.0 equiv.) were coupled according to *GP 3a*. The crude product was precipitated from Et_2O to yield **23** (48 mg) in 27% yield as a colorless solid. FAB-MS: 867.4 ($[M+Na]^+$), 845.4 ($[M+H]^+$), 734.3 ($[M-Z+Na]^+$), 711.3 ($[M-Z]^+$), 662.3 ($[M-2(\text{benzyl})]^+$), 634.4 ($[M+3-2(\text{benzyl})-\text{MeO}]^+$), 487.2, 464.2, 381.3.

6.9. *(1S,2S,5S)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-N-{(S)-[(methoxy)carbonyl](1-methylethyl)methyl}-β-D-glucopyranosiduronamide* (**24**). Compound β-**15** (310.6 mg, 667 μmol) and valine methylester hydrochloride (134 mg, 800 μmol, 1.2 equiv.) were coupled according to *GP 3b* to yield **24** (373.5 mg) in 97% yield as a colorless solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.32 (*m*, 4 arom. H of Z); 7.30 (*m*, 1 arom. H of Z); 6.97 (*d*, *J* = 9, NH of Val); 5.17 (*d*, *J* = 5, 2-NH); 5.09, 5.03 (2*d*, *J* = 11 each, CH_2 of Z); 4.78 (*d*, *J* = 7.2, H−C(1)); 4.54 (*dd*, *J* = 9, 5, α-H of Val); 4.00 (br. *m*, H−C(3)); 3.76 (*d*, *J* = 9, H−C(5)); 3.71 (*s*, MeO); 3.55 (*dd*, *J* = 9, 9, H−C(4)); 3.43 (br. *m*, 1 H of menthyl); 3.21 (*m*, *J* = 7.2, H−C(2)); 2.23 (*m*, 1 H of menthyl); 2.16 (*m*, β-H of Val); 1.92 (*m*, 1 H of menthyl); 1.61 (*d*, 2 × 1 H of menthyl); 1.30 (br. *m*, 1 H of menthyl); 0.94 (*m*, 1 H of menthyl); 0.91 (*d*, *J* = 9.8, Me of Val); 0.88 (*d*, *J* = 6.8, Me of Val); 0.87 (*d*, *J* = 7.2, Me of menthyl); 0.84 (*d*, *J* = 6.6, Me of menthyl); 0.81 (*d*, *J* = 7, Me of menthyl); 0.78 (br. *m*, 2 × 1 H of menthyl). ^{13}C-NMR (150 MHz, $CDCl_3$): 171.4 (C(6)); 170.9 (*C*OOMe); 156.2 (C=O of Z); 136.1, 128.5, 128.2, 128.1 (4 arom. C of Z); 98.0 (C(1)); 78.5 (C(1) of menthyl); 73.1 (C(4)); 72.3 (C(3)); 71.9 (C(5)); 66.9 (CH_2 of Z); 57.3 (C(2)); 56.4 (α-H of Val); 52.3 (COO*Me*); 47.2 (C(2) of menthyl); 40.2 (C(6) of menthyl); 34.0 (C(4) of menthyl); 31.2 (C(5) of menthyl); 31.1 (β-H of Val); 25.2 (CH of menthyl); 22.8 (C(3) of menthyl); 22.2, 20.8 (2 Me of menthyl); 18.9, 17.5 (2 Me of Val); 16.0 (Me of menthyl). FAB-MS: 601.2 ($[M+Na]^+$), 579.2 ($[M+H]^+$), 423.1 ($[M-\text{menthyl}]^+$).

6.10. *3-Methylbutyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-N-{(S)-[(methoxy)carbonyl](methyl)methyl}-β-D-glucopyranosiduronamide* (**25**). Compound **10** (513.0 mg, 1.3 mmol) and alanine methylester hydrochloride (270.3 mg) were coupled according to *GP 3a* to afford **25** (492 mg) as a colorless solid in 79% yield. ^{1}H-NMR (400 MHz, (D_6)DMSO): 8.30 (*d*, *J* = 7, NH of Ala); 7.41 – 7.23 (*m*, 5 arom. H of Z); 7.11 (*d*, *J* = 9, 2-NH); 5.26 – 4.83 (br. *m*, CH_2 of Z); 4.34 (*dq*, *J* = 7, 7, α-H of Ala); 4.29 (*d*, *J* = 8.0, H−C(1)); 3.73 (*m*, *J* = 9.8, 8.0, 1 H of isoamyl); 3.62 (*s*, MeO); 3.56 (*d*, *J* = 9.5, H−C(5)); 3.39 (*m*, *J* = 9.8, 6.8, 1 H of isoamyl); 3.38 (*dd*, *J* = 9.5, 9.5, H−C(4)); 3.3 (br. *m*, H_2O, H−C(3)); 3.22 (*ddd*, *J* = 9, 9, H−C(2)); 1.62 (*m*, 1 H of isoamyl); 1.36 (*m*, 2 H of isoamyl); 1.29 (*d*, *J* = 7, α-Me of Ala); 0 81 (*d*, 6 H of isoamyl). ^{13}C-NMR (100 MHz, (D_6)DMSO): 172.9 (C(6)); 168.4 (*C*OOMe); 156.2 (C=O of Z); 137.5, 128.4, 127.8, 127.7 (4 arom. C of Z); 101.9 (C(1)): 75.7 (C(5)); 73.7 (C(3)); 72.0 (C(4)); 67.3 (C(1) of isoamyl); 65.1 (CH_2 of Z); 57.1 (C(2)); 52.0 (COO*Me*); 47.5 (α-*C* of Ala); 38.0 (C(2) of isoamyl); 24.3 (C(3) of isoamyl); 22.6 (C(4) of isoamyl); 22.4 (C(5) of isoamyl); 17.3 (α-Me of Ala). FAB-MS: 505.1 ($[M+Na]^+$), 483.1 ($[M+H]^+$), 395.1 ($[M-\text{isoamyl}]^+$).

7. *Preparation of Heterotrimeric Compounds.* All heterodimers were used in the amino-deprotected form obtained by hydrogenolytic cleavage of the Z group in the presence of 10% Pd/C in EtOH or MeOH under 1 atm of H_2 for 3 – 12 h. After filtration and removal of the solvent under reduced pressure, the desired

deprotected compounds were obtained mostly in quant. yields, and were used in the subsequent coupling without further purification. The amino-deprotected heterodimers were characterized by NMR and MS (data not shown).

7.1. *3-Methylbutyl 2-{[*N*-(*tert*-Butoxycarbonyl)-*D*-phenylalanyl]amino}-2-deoxy-*N*-{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (**26**). *N*-Deprotected **17** (605 mg, 1.81 mmol) was coupled with Boc-D-Phe-OH (600 mg) according to *GP 3b*. After extractive workup and removal of solvents, the remaining residue was precipitated from Et_2O/hexanes to afford **26** (710 mg) in 68% yield as a colorless solid. ^{1}H-NMR (400 MHz, (D_6)DMSO): 8.36 (*t*, *J* = 5.8, NH of Gly); 7.93 (*d*, *J* = 9, 2-NH); 7.25 (2*d*, 4 arom. H of Phe); 7.17 (*m*, 1 arom. H of Phe); 6.68 (*d*, *J* = 9, NH of Phe); 5.09 (*d*, *J* = 3.5, 4-OH); 4.94 (*d*, *J* = 4.5, 3-OH); 4.41 (*d*, *J* = 8.5, H−C(1)); 4.17 (*dt*, *J* = 9, 9, 3.5, α-H of Phe); 3.88 (*d*, *J* = 5.8, α-CH_2 of Gly); 3.75 (*m*, *J* = 9.5, 6.5, 1 H of isoamyl); 3.67 (*d*, *J* = 9, H−C(5)); 3.63 (*s*, MeO); 3.50 (*ddd*, *J* = 9, 9, 8.5, H−C(2)); 3.44–3.34 (br. *m*, 3 H of isoamyl); 2.96 (*dd*, *J* = 13.5, 3.5, 1 β-H of Phe); 2.70 (*ddd*, *J* = 13.5, 9, 9, 1 β-H of Phe); 1.62 (*m*, 1 H of isoamyl); 1.26 (*s*, *t*-BuO), 0.80 (*d*, *J* = 6.5, 2 Me of isoamyl). ^{13}C-NMR (100 MHz, (D_6)DMSO): 171.8 (CONH of Phe); 170.3 (C(6)); 169.5 (*C*OOMe); 155.3 (*C*OO^{t}Bu); 138.5, 129.4, 128.1, 126.3 (4 arom. C of Phe); 101.5 (C(1)); 78.0 (O*C*Me_3); 75.4 (C(5)); 73.8 (C(3)); 72.3 (C(4)); 67.3 (C(1) of isoamyl); 55.8 (α-C of Phe); 55.4 (C(2)); 51.9 (COO*Me*); 40.7 (α-C of Gly); 38.3 (β-C of Phe); 38.1 (C(2) of isoamyl); 28.3 (OC*Me*$_3$); 24.4 (C(3) of isoamyl); 22.7 (C(4) of isoamyl); 22.5 (C(5) of isoamyl). FAB-MS: 1185.7 ([2*M* + Na]$^+$), 604.3 ([*M* + Na]$^+$), 582.3 ([*M* + H]$^+$), 504.3 ([*M* − Boc + Na]$^+$), 494.3 ([*M* − isoamyl]$^+$). Anal. calc. for $C_{28}H_{43}N_3O_{10} \cdot H_2O$: C 56.08, H 7.56, N 7.01; found: C 56.54, H 7.39, N 6.89.

7.2. *2-Phenylethyl 2-{[*N*-(*tert*-Butoxycarbonyl)-*L*-valinyl]amino}-2-deoxy-*N*-{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (**27**). *N*-Deprotected **19** (300 mg, 815 μmol) and Boc-L-Val-OH (253 mg) were coupled according to *GP 3b*. The crude product was precipitated from Et_2O/hexanes to afford **27** (180 mg) in 40% yield. ^{1}H-NMR (600 MHz, CD_3CN): 7.28 (*m*, 2 arom. H of phenethyl, NH of Gly); 7.23 (*d*, 2 arom. H of phenethyl): 7.19 (*m*, 1 arom. H of phenethyl); 6.66 (*d*, *J* = 8.9, 2-NH); 5.49 (*d*, *J* = 5.7, NH of Val); 4.61 (*d*, *J* = 8.5, H−C(1)); 4.03 (*ddd*, *J* = 9.6, 7.4, 1 H of phenethyl); 3.94 (*d*, *J* = 6, α-CH_2 of Gly); 3.83 (*dd*, *J* = 8, 5.7, α-H of Val); 3.74 (*m*, 2 H of phenethyl); 3.68 (*s*, MeO); 3.60 (*dd*, *J* = 8.9, 8.5, H−C(2)); 3.57 (*d*, *J* = 3.0, 3-OH); 3.52 (*dd*, *J* = 8.9, 8.9, H−C(3)); 3.44 (*dd*, *J* = 8.9, 8.9, H−C(4)); 2.85 (br. *dd*, *J* = 7.4, 6.9, 2 H of phenethyl); 2.02 (*m*, β-H of Val); 1.41 (*s*, *t*-BuO); 0.93, 0.87 (2*d*, *J* = 6.8 each, 2 Me of Val). ^{13}C-NMR (150 MHz, CD_3CN): 173.0 (CONH of Val); 172.2 (C(6)); 170.8 (*C*OOMe); 157.1 (*C*OO^{t}Bu); 139.8, 130.0, 129.4, 127.2 (4 arom. C of phenethyl); 101.8 (C(1)); 80.0 (COO*C*Me_3); 75.1 (C(3)); 73.9 (C(5)); 73.8 (C(4)); 71.2 (C(1) of phenethyl); 61.3 (α-C of Val); 56.3 (C(2)); 52.8 (COO*Me*); 41.3 (α-C of Gly); 36.8 (C(2) of phenethyl); 31.7 (β-C of Val); 28.6 (OC*Me*$_3$); 19.6, 18.1 (2 Me of Val). FAB-MS: 590.3 ([*M* + Na]$^+$), 568.3 ([*M* + H]$^+$), 468.2 ([*M* + 2 − Boc]$^+$), 446.2 ([*M* − 2(phenethyl)]$^+$). Anal. calc. for $C_{27}H_{41}N_3O_{10} \cdot H_2O$: C 55.47, H 7.28, N 7.19; found: C 55.65, H 7.13, N 6.93.

7.3. *Hexyl 2-{[*N*-(*tert*-Butoxycarbonyl)-*D*-phenylalanyl]amino}-2-deoxy-*N*-{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (**28**). *N*-Deprotected **20** (667.6 mg, 1.996 mmol) and Boc-D-Phe-OH (635.6 mg, 2.39 mmol, 1.2 equiv.) were coupled according to *GP 3b* to afford **28** (1.04 g) in 87% yield as a colorless solid. ^{1}H-NMR (600 MHz, (D_6)DMSO): 8.31 (*t*, *J* = 5.5, NH of Gly); 7.91 (*d*, *J* = 8.7, 2-NH); 7.24 (*m*, 4 arom. H of Phe); 7.17 (*m*, 1 arom. H of Phe); 6.61 (*d*, *J* = 9, NH of Phe); 5.04 (*d*, *J* = 3.8, 4-OH); 4.90 (*d*, *J* = 4.7, 3-OH); 4.42 (*d*, *J* = 8.5, H−C(1)); 4.18 (br. *ddd*, *J* = 10, 9, 3, α-H of Phe); 3.90, 3.87 (2*dd*, *J* = 17 and 5.5 each, α-CH_2 of Gly); 3.71 (br. *m*, 1 H of hexyl); 3.67 (*d*, *J* = 9, H−C(5)); 3.63 (*s*, COOMe); 3.51 (*ddd*, *J* = 9, 9, 8.5, H−C(2)); 3.38 (br. *m*, H−C(3), H−C(4), 1 H of hexyl); 2.97 (*dd*, *J* = 13.5, 3, 1 H of CH_2 of Phe); 2.72 (*dd*, *J* = 13.5, 10, 1 H of CH_2 of Phe); 1.44 (br. *m*, 2 H of hexyl); 1.33–1.12 (br. *m*, *t*-BuO, 6 H of hexyl); 0.78 (*t*, *J* = 6.7, Me of hexyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 171.7 (*C*ONH of Phe); 170.1 (C(6)); 169.4 (*C*OOMe); 155.1 (*C*OO^{t}Bu); 138.4, 129.3, 128.0, 126.2 (4 arom. C of Phe); 101.3 (C(1)); 77.9 (O*C*Me_3); 75.3 (C(5)); 73.8 (C(3)); 72.3 (C(4)); 68.9 (C(1) of hexyl); 55.7 (α-C of Phe); 55.3 (C(2)); 51.8 (COO*Me*); 40.6 (α-C of Gly); 38.2 (β-C of Phe); 31.2 (C(4) of hexyl); 29.2 (C(2) of hexyl); 28.2 (OC*Me*$_3$); 25.2 (C(3) of hexyl); 22.1 (C(5) of hexyl); 14.0 (C(6) of hexyl). FAB-MS: 618.3 ([*M* + Na]$^+$), 1213.6 ([2*M* + Na]$^+$), 495.3 ([*M* + 1 − Boc]$^+$), 518.3 ([*M* − Boc + Na]$^+$). Anal. calc. for $C_{29}H_{45}N_3O_{10} \cdot 4\,H_2O$: C 52.48, H 7.44, N 6.33; found: C 53.14, H 6.95, N 6.40.

7.4. *1,3,3-Trimethylbicyclo[2.2.1]hept-2-yl 2-{[*N*-(*tert*-Butoxycarbonyl)-*D*-phenylalanyl]amino}-2-deoxy-*N*-{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (**29**). *N*-Deprotected **21** (670.6 mg, 1.674 mmol) and Boc-D-Phe-OH (555.3 mg) were coupled according to *GP 3a*. The resulting crude product was precipitated from Et_2O/hexanes to yield **29** (864.9 mg) in 79.8% yield as a colorless solid. ^{1}H-NMR (400 MHz, (D_6)DMSO): 8.19 (*t*, *J* = 5.8, NH of Gly); 7.93 (*d*, *J* = 9, 2-NH); 7.23 (*m*, 4 arom. H of Phe); 7.16 (*m*, 1 arom. H of Phe); 6.70 (*d*, *J* = 8.8, NH of Phe); 5.08 (*d*, *J* = 5, 3-OH); 4.79 (*d*, *J* = 5, 4-OH); 4.29 (*d*, *J* = 8, H−C(1)); 4.19 (*m*, α-H of Phe); 3.89 (2*d*, *J* = 5.8 each, α-CH_2 of Gly); 3.65–3.55 (*m*, H−C(5), H−C(2), COOMe); 3.41 (*m*, H−C(3), H−C(4)); 3.04 (*s*, 1 H of fenchyl); 2.99 (*dd*, *J* = 12.5, 3, 1 β-H of Phe); 2.70 (*dd*, *J* = 12.5, 12, 1 β-H of Phe); 1.62 (br. *m*, 1 H of fenchyl); 1.56 (br. *s*, 1 H of fenchyl); 1.53 (br. *m*, 1 H of fenchyl); 1.39 (br. *d*, *J* = 9, 1 H of fenchyl); 1.30 (br. *m*, 1 H of fenchyl); 1.25 (*s*, *t*-BuO); 1.03 (*s*, Me of fenchyl); 0.99 (br. *m*, 1 H of fenchyl); 0.92 (*s*, *endo*-Me of fenchyl); 0.76 (*s*, 1 H and *exo*-Me of fenchyl). ^{13}C-NMR (100 MHz, (D_6)DMSO): 171.6 (CONH of Phe); 170.1 (C(6)); 168.8 (*C*OOMe); 155.2 (*C*OO^{t}Bu); 138.7, 129.4, 128.0, 126.1 (4 arom. C of Phe); 103.0 (C(1)); 91.7 (C(2) of fenchyl); 77.8 (O*C*Me$_3$); 75.6 (C(5)); 73.8 (C(3)); 72.1 (C(4)); 55.7 (α-C of Phe); 55.6 (C(2)); 51.8 (α-C of Gly); 48.8 (C(1) and C(3) of fenchyl); 47.5 (C(4) of fenchyl); 40.9 (C(7) of fenchyl); 40.7 (α-C of Gly); 39.0 (β-C of Phe); 29.5 (*endo*-Me of fenchyl); 28.3 (OC*Me*$_3$); 25.9 (C(5) of fenchyl); 25.5 (C(6) of fenchyl); 21.7 (*exo*-Me of fenchyl); 19.7 (Me of fenchyl). FAB-MS: 1317.2 ([2*M* + Na]$^+$), 670.2 ([*M* + Na]$^+$), 648.2 ([*M* + H]$^+$), 570.2 ([*M* − Boc + H + Na]$^+$), 494.1 ([*M* − fenchyl]$^+$), 438.1 ([*M* − fenchyl − Boc + 2Na]$^+$).

7.5. *(1*S*,2*S*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-{[*N*-(*tert*-Butoxycarbonyl)-*D*-phenylalanyl]amino}-2-deoxy-*N*-{[(methoxy)carbonyl]methyl}-β-*D*-glucopyranosiduronamide* (β-**30**). *N*-Deprotected β-**22** (551.6 mg, 1.37 mmol) and Boc-D-Phe-OH (472.5 mg, 1.78 mmol, 1.5 equiv.) were coupled according to *GP 3a* to furnish β-**30** (894.5 mg) in 98% yield as a yellow foam. ^{1}H-NMR (600 MHz, (D_6)DMSO): 8.16 (*t*, *J* = 5.8, NH of Gly); 7.91 (*d*, *J* = 6.6, 2-NH); 7.24 (*m*, 4 arom. H of Phe); 7.17 (*m*, 1 arom. H of Phe); 6.59 (*d*, *J* = 8.7, NH of Phe); 5.04 (*d*, *J* = 4.5, 3-OH); 4.87 (*d*, 4-OH); 4.53 (*d*, *J* = 7.2, H−C(1)); 4.17 (*m*, α-H of Phe); 3.88 (*d*, *J* = 5.8, α-CH$_2$ of Gly); 3.63 (*d*, *J* = 9.4, H−C(5)); 3.61 (*s*, COOMe); 3.44–3.34 (*m*, H−C(2), H−C(3), H−C(4), 1 H of menthyl); 3.01 (*dd*, *J* = 3.4, 13.8, 1 H of β-CH$_2$ of Phe); 2.71 (*dd*, *J* = 10.3, 13.8, 1 H of β-CH$_2$ of Phe); 2.20 (*m*, 1 H of menthyl); 2.04 (br. *d*, *J* = 12, 1 H of menthyl); 1.55 (*m*, 2 × 1 H of menthyl); 1.30 (br. *m*, 1 H of menthyl); 1.27 (*s*, *t*-BuO); 1.04 (*m*, 1 H of menthyl); 0.90 (*m*, *J* = 13, 1 H of menthyl); 0.81 (*d*, *J* = 10, Me of menthyl); 0.80 (*d*, *J* = 9.4, Me of menthyl); 0.72 (br. *m*, 2 × 1 H of menthyl); 0.68 (*d*, *J* = 7, Me of menthyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 171.4 (*C*ONH of Phe); 170.1 (C(6)); 169.0 (*C*OOMe); 155.2 (*C*OO^{t}Bu); 138.5, 129.4, 128.0, 126.2 (4 arom. C of Phe); 98.9 (C(1)); 78.0 (O*C*Me$_3$); 77.1 (C(1) of menthyl); 75.7 (C(5)); 73.9 (C(4)); 72.1 (C(3)); 55.6 (C(2), α-C of Phe); 51.8 (COO*Me*); 47.5 (C(2) of menthyl); 40.7 (C(6) of menthyl); 40.6 (α-C of Gly); 38.3 (β-C of Phe); 34.1 (C(4) of menthyl); 31.0 (C(5) of menthyl); 28.3 (OC*Me*$_3$); 24.6 (1 H of menthyl); 22.7 (C(3) of menthyl); 22.3, 21.1, 15.6 (3 Me of menthyl). FAB-MS: 673.1 ([*M* + H + Na]$^+$), 651.1 ([*M* + 2 H]$^+$), 494.7 ([*M* − menthyl]$^+$), 395.3 ([*M* + 2 − Boc]$^+$). Anal. calc. for $C_{33}H_{51}N_3O_{10} \cdot H_2O$: C 59.44, H 7.86, N 6.30; found: C 59.13, H 7.84, N 6.15.

7.6. *(1*S*,2*S*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-{[*N*-(*tert*-Butoxycarbonyl)-*D*-phenylalanyl]amino}-2-deoxy-*N*-{[(methoxy)carbonyl]methyl}-α-*D*-glucopyranosiduronamide* (α-**30**). *N*-Deprotected α-**22** (1.0604 g, 2.63 mmol) and Boc-D-Phe-OH (840 mg, 3.145 mmol, 1.2 equiv.) were coupled according to *GP 3a*. The crude product was purified by precipitation from CH_2Cl_2/hexanes to afford α-**30** (635 mg) in 60% yield as a colorless solid. ^{1}H-NMR (600 MHz, (D_6)DMSO): 8.30 (*t*, *J* = 6, NH of Gly); 7.6 (*d*, *J* = 7, 2-NH); 7.23 (*m*, 4 arom. H of Phe); 7.16 (*m*, 1 arom. H of Phe); 6.76 (*d*, *J* = 9.3, NH of Phe); 4.92 (*d*, *J* = 3.4, H−C(1)); 4.28 (*ddd*, *J* = 10.0, 9.3, 3.0, α-H of Phe); 3.98 (*d*, *J* = 9.8, H−C(5)); 3.87 (*dd*, *J* = 17, 6, α-CH$_2$ of Gly); 3.72 (br. *m*, H−C(2)); 3.62 (*s*, COOMe); 3.56 (br. *m*, H−C(3)); 3.41 (br. *m*, H−C(4)); 3.02 (*dd*, *J* = 13.2, 3, 1 H of β-CH$_2$ of Phe); 2.69 (*dd*, *J* = 13.2, 10, 1 H of β-CH$_2$ of Phe); 2.25 (*m*, *J* = 6.9, 6.9, 1 H of menthyl); 2.08 (*d*, *J* = 11.6, 1 H of menthyl); 1.58 (*d*, *J* = 12, 1 H of menthyl); 1.54 (*d*, *J* = 13, 1 H of menthyl); 1.34 (*m*, 1 H of menthyl); 1.25 (*s*, *t*-BuO); 1.13 (br. *s*, 1 H of menthyl); 1.01 (*m*, *J* = 11.6, 1 H of menthyl); 0.91 (*m*, *J* = 13, 1 H of menthyl); 0.86 (*d*, *J* = 6, Me of menthyl); 0.81 (*d*, *J* = 6.9, Me of menthyl); 0.76 (*dd*, *J* = 12, 1 H of menthyl), 0.63 (*d*, *J* = 6.9, Me of menthyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 171.9 (CONH of Phe); 170.1 (C(6)); 170.0 (*C*OOMe); 155.3 (*C*OO^{t}Bu); 138.3, 129.3, 128.0, 126.1 (4 arom. C of Phe); 98.7 (C(1)); 80.2 (O*C*Me$_3$); 78.1 (C(1) of menthyl); 72.8 (C(4)); 71.9 (C(5)); 70.1 (C(3)); 55.5 (α-C of Phe); 54.4 (β-C of Phe); 51.7 (COO*Me*); 48.4 (C(2) of menthyl); 42.5 (C(6) of menthyl); 40.5 (α-C of Gly); 38.0 (β-C of Phe); 33.9 (C(4) of menthyl); 31.2 (C(5) of menthyl); 28.2 (OC*Me*$_3$); 24.5 (1 C of menthyl); 22.4 (C(3) of menthyl); 22.1, 21.2, 15.7 (3 Me of menthyl). FAB-MS: 673.1 ([*M* + H + Na]$^+$), 651.1 ([*M* + 2 H]$^+$), 494.7 ([*M* − menthyl]$^+$), 395.3 ([*M* + 2 H − menthyl − Boc]$^+$). Anal. calc. for $C_{33}H_{51}N_3O_{10} \cdot H_2O$: C 59.44, H 7.86, N 6.30; found: C 59.13, H 7.84, N 6.15.

7.7. *(1*S*,2*S*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-{[*N*-(*tert*-Butoxycarbonyl)-*D*-phenylalanyl]amino}-2-deoxy-*N*-{(*S*)-[(methoxy)carbonyl](1-methylethyl)methyl}-β-*D*-glucopyranosiduronamide* (**31**). *N*-Deprotected **24** (259.6 mg, 585 μmol) and Boc-D-Phe-OH (233 mg, 878 μmol, 1.5 equiv.) were coupled according to *GP 3b*. The resulting crude product was purified by precipitation from Et_2O to yield **31** (305 mg) in 75.6% yield. ^{1}H-NMR (600 MHz, (D_6)DMSO): 8.13 (*d*, *J* = 8.7, NH of Val); 7.94 (*d*, *J* = 7.9, 2-NH); 7.28–7.24 (*m*, 5 arom. H of Phe); 6.63 (*d*, *J* = 8.7, NH of Phe); 5.06 (*d*, *J* = 5.1, 4-OH); 4.85 (*d*, *J* = 5.1, 3-OH); 4.51 (*d*, *J* = 7.8, H−C(1)); 4.26 (*dd*, *J* = 8.7, 6.3, α-H of Val); 4.16 (*ddd*, *J* = 9.4, 8.7, 3.5, α-H of Phe); 3.70 (*d*, *J* = 9.4, H−C(5)); 3.63 (*s*, COOMe); 3.46 (*m*, H−C(4)); 3.40 (*m*, H−C(3), H−C(2)); 3.35 (br. *m*, 1 H of menthyl); 3.01 (*dd*, *J* = 13.8, 3.5, 1 H of β-CH$_2$ of Phe); 2.71 (*dd*, *J* = 13.8, 9.4, 1 H of β-CH$_2$ of Phe); 2.15 (*m*, 1 H of menthyl); 2.05 (*m*, 1 H of menthyl); 2.01 (*m*, $J = 6.4$, 6.4, β-H of Val), 1.54 (*m*, 2×1 H of menthyl); 1.27 (br. *s*, 1 H of menthyl, *t*-BuO); 1.04 (*dd*, $J = 11$, 11, 1 H of menthyl); 0.88 (*m*, 1 H of menthyl); 0.85 (*d*, $J = 6.4$, 2 Me of Val); 0.80 (*m*, 2 Me of menthyl); 0.69 (*m*, 2×1 H of menthyl); 0.65 (*d*, Me of menthyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 171.9 (CONH of Ph); 171.4 (C(6)); 168.4 (COOMe); 155.2 (*C*OO^{t}Bu); 138.5, 129.7, 129.5, 128.3, 128.1 (4 arom. C of Phe); 99.2 (C(1)); 80.5 (O*C*Me$_3$); 77.1 (C(1) of menthyl); 75.6 (C(5)); 74.0 (C(3)); 71.4 (C(4)); 56.9 (α-C of Val); 55.5 (C(2)); 55.4 (α-C of Phe); 51.7 (COO*Me*); 47.3 (C(2) of menthyl); 40.5 (C(6) of menthyl); 38.2 (β-C of Phe); 34.0 (C(4) of menthyl); 30.9 (C(5) of menthyl); 30.5 (β-C of Val); 28.2 (OC*Me*$_3$); 24.6 (1 C of menthyl); 22.7 (C(3) of menthyl); 22.2, 20.9 (2 Me of menthyl); 18.9, 18.2 (2 Me of Val); 15.6 (Me of menthyl). FAB-MS: 714.3 ($[M + \mathrm{Na}]^+$), 692.3 ($[M + \mathrm{H}]^+$), 614.2 ($[M - \mathrm{Boc} + \mathrm{Na}]^+$), 536.2 ($[M - \mathrm{menthyl}]^+$), 480.1 ($[M - \mathrm{Boc} - \mathrm{menthyl} + 2\mathrm{Na}]^+$).

7.8. *3-Methylbutyl 2-{[*N*-(*tert*-Butoxycarbonyl)-*L*-phenylalanyl]amino}-2-deoxy-*N*-{(*S*)-[(methoxy)carbonyl](methyl)methyl}-β-*D*-glucopyranosiduronamide* (**32**). *N*-Deprotected **25** (315 mg, 905 µmol) and Boc-L-Phe-OH (290 mg, 1.09 mmol, 1.21 equiv.) were coupled according to *GP 3b*. The crude product (512 mg, 94.5%) showed residual traces of the EEDQ reagent and was, therefore, precipitated from Et_2O to afford **32** (343 mg) in a yield of 63.6% as a colorless solid. ^{1}H-NMR (600 MHz, $CDCl_3$): 7.28 (*m*, 2 arom. H of Phe); 7.23 (*m*, 1 arom. H of Phe); 7.20 (*m*, 2 arom. H of Phe); 7.12 (*d*, $J = 7.4$, NH of Ala); 6.44 (br. *s*, 2-NH); 5.17 (*d*, $J = 7.2$, NH of Phe); 4.69 (br. *m*, H–C(1), OH); 4.56 (*dq*, $J = 7.4$, 7.2, α-H of Ala); 4.28 (*dt*, $J = 7.2$, 7.2, α-H of Phe); 3.91 (*dd*, $J = 9.5$, 9.5, H–C(3)); 3.86 (*ddd*, $J = 15.7$, 6.8, 6.8, 1 H of isoamyl); 3.76 (*d*, $J = 9.3$, H–C(5)); 3.74 (*s*, COOMe); 3.56 (*dd*, $J = 9.3$, 9.3, H–C(4)); 3.45 (*m*, $J = 15.7$, 7.2, 1 H of isoamyl); 3.26 (*ddd*, $J = 9.5$, 9.5, 8.5, H–C(2)); 3.05 (*dd*, $J = 13.6$, 7.2, 1 H of β-CH_2 of Phe); 2.98 (*dd*, $J = 13.6$, 7.2, 1 H of β-CH_2 of Phe); 1.65 (*m*, 1 H of isoamyl); 1.44 (br. *s*, 2 H of isoamyl); 1.42 (*d*, $J = 7.2$, Me of Ala); 1.36 (*s*, *t*-BuO); 0.86 (*d*, $J = 6.3$, 2 Me of isoamyl). ^{13}C-NMR (150 MHz, $CDCl_3$): 172.7 (CONH of Phe); 172.1 (C(6)); 170.2 (*C*OOMe); 156.6 (*C*OO^{t}Bu); 136.5, 129.3, 128.7, 127.0 (4 arom. C of Phe); 100.0 (C(1)); 80.5 (O*C*Me$_3$); 72.5 (C(4)); 72.2 (C(3)); 72.1 (C(5)); 67.8 (C(1) of isoamyl); 57.6 (C(2)); 56.1 (α-C of Phe); 52.7 (MeO); 47.5 (α-C of Ala); 38.0 (C(2) of isoamyl, β-C of Phe); 28.2 (OC*Me*$_3$); 24.6 (C(3) of isoamyl); 22.5 (C(4) of isoamyl); 22.4 (C(5) of isoamyl); 18.1 (Me of Ala). FAB-MS: 618.3 ($[M + \mathrm{Na}]^+$), 596.3 ($[M + \mathrm{H}]^+$).

8. *Fragment Condensations. N*-Deprotection was carried out as described above, and *C*-deprotection was achieved by saponification with sat. aq. LiOH soln. (1.1 equiv.) in EtOH for 3 h, followed by neutralization and lyophilization. The respective saponification products (Li carboxylates) were obtained in quant. yields. Complete saponification was ascertained by NMR and MS experiments (data not shown).

8.1. *[(3-Methylbutyl 2-{[((1*S*,2*S*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-β-*D*-glucopyranosid)uronyl]amino}-2-deoxy-β-*D*-glucopyranosid)uronyl]glycine Methyl Ester* (**33**). Compound β-**15** (124.6 mg, 267.6 µmol) was pre-activated with HOBt (55 mg, 403 µmol, 1.5 equiv.) and EDC · HCl (103 mg, 535.3 µmol, 2.0 equiv.) in CH_2Cl_2 (5 ml), and then reacted with *N*-deprotected **17** (92.0 mg, 275.1 µmol, 1.03 equiv.) according to *GP 3a*. Extractive workup after 48 h furnished a crude product, which was precipitated from Et_2O and then purified by gel filtration (*Sephadex LH-20*) to yield **33** (86.5 mg) as a colorless solid in 41.2% yield. ^{1}H-NMR (600 MHz, (D_6)DMSO): 7.83 (*m*, NH of Gly); 7.31 – 7.14 (*m*, 5 arom. H of Z); 6.73 (*m*, 2-NH, 2′-NH); 5.03 (br. *s*, 1 H of CH_2 of Z); 4.92 (br. *s*, 1 H of CH_2 of Z); 4.79 (br. *s*, 2 OH); 4.71 (br. *s*, 2 OH); 4.48 (br. *d*, $J = 8.1$, H–C(1), H–C(1′)); 3.92 (*m*, α-CH_2 of Gly); 3.87 – 3.82 (*m*, 1 H of isoamyl); 3.68 (br. *d*, H–C(5), H–C(5′)); 3.64 (*s*, MeO); 3.58 – 3.33 (br. *m*, H–C(3), H–C(3′), H–C(2), H–C(2′), H–C(4), H–C(4′), 1 H of isoamyl); 3.31 (*dt*, 1 H of menthyl); 2.23 (br. *m*, 1 H of menthyl); 1.56 – 1.47 (*m*, 1 H of isoamyl, 2×1 H of menthyl); 1.42 – 1.28 (*m*, 2 H of isoamyl); 1.25 (br. *m*, 1 H of menthyl); 1.09 (br. *m*, 1 H of menthyl); 0.91 – 0.54 (br. *m*, 5 Me, 3×1 H of menthyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 169.9 (C(6), C(6′)); 169.6 (*C*OOMe); 156.1 (C=O of Z); 137.3, 128.1, 127.5, 127.2 (4 arom. C of Z); 100.8 (C(1)); 99.3 (C(1′)); 77.7 (C(1) of menthyl); 74.7 (C(5), C(5′)); 73.7 (C(3), C(3′)); 72.1 (C(4), C(4′)); 67.3 (C(1) of isoamyl); 65.1 (CH_2 of Z); 55.6 (C(2), C(2′)); 54.5 (α-C of Gly); 47.3 (C(2) of menthyl); 40.4 (COO*Me*); 37.8 (C(6) of menthyl); 35.8 (C(2) of isoamyl); 33.9 (C(4) of menthyl); 30.9 (C(5) of menthyl); 24.6 (1 C of menthyl); 24.3 (C(3) of isoamyl); 22.6 (C(3) of menthyl); 22.4 (Me of menthyl); 22.0 (Me of isoamyl); 20.7 (Me of menthyl); 15.8 (Me of isoamyl, Me of menthyl). FAB-MS: 804.2 ($[M + \mathrm{Na}]^+$), 782.2 ($[M + \mathrm{H}]^+$), 670.4 ($[M - \mathrm{Z} + \mathrm{H} + \mathrm{Na}]^+$). MALDI-MS (rel. to angiotensin): 804.4 ($[M + \mathrm{Na}]^+$), 671.6 ($[M - \mathrm{Z} + 2\,\mathrm{H} + \mathrm{Na}]^+$).

8.2. *{[3-Methylbutyl 2-({[((1*S*,2*S*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-{[(Benzyloxy)carbonyl]amino}-2-deoxy-α-*D*-glucopyranosid)uronyl]glycinyl}amino)-2-deoxy-β-*D*-glucopyranosid]uronyl}glycine Methyl Ester* (**34**). Saponified α-**22** (Li salt; 200 mg, 378.4 µmol) was coupled with *N*-deprotected **17** (126.5 mg, 378.4 µmol, 1.0 equiv.) according to *GP 3b*. Extractive workup after 48 h furnished a crude product, which was subjected to CC (SiO_2; $CHCl_3$/MeOH 30 : 1) to afford **34** (53.9 mg) in 17% yield. ^{1}H-NMR (600 MHz, (D_6)DMSO): 8.31 (*t*, $J = 5.8$, NH of Gly^1); 7.88 (*t*, $J = 5.3$, NH of Gly^2); 7.76 (*d*, $J = 8.8$, 2-NH); 7.35 (*s*, 4 arom.

H of Z); 7.31 (*m*, 1 arom. H of Z); 7.04 (*d*, *J* = 7.2, 2′-NH); 5.18 (*d*, *J* = 3.8, 4′-OH); 5.04 (*d*, *J* = 3.4, 4-OH); 5.0 (*m*, CH_2 of Z, 3-OH); 4.93 (*d*, *J* = 3.6, H−C(1′)); 4.79 (*d*, *J* = 5.7, 3′-OH); 4.39 (*d*, *J* = 8.3, H−C(1)); 3.95 (*d*, *J* = 9.8, H−C(5′)); 3.88 (*d*, *J* = 5.8, α-CH_2 of Gly[1]); 3.77 (*dd*, *J* = 16, 5.3, α-CH_2 of Gly[2]); 3.74 (*m*, 1 H of isoamyl); 3.69 (*dd*, *J* = 16, 5.3, 1 H of CH_2 of Gly[2]); 3.66 (*d*, *J* = 9, H−C(5)); 3.63 (*s*, MeO); 3.51 (*ddd*, *J* = 9, 9, 5.7, H−C(3′)); 3.45 (*dd*, *J* = 9, 8.8, 8.3, H−C(2)); 3.42–3.32 (*m*, H−C(2′), H−C(4′), H−C(4), H−C(3), 1 H of isoamyl); 3.21 (*dt*, *J* = 10, 4, 1 H of menthyl); 2.28 (*m*, 1 H of menthyl); 2.02 (br. *d*, *J* = 11.9, 1 H of menthyl); 1.65–1.55 (*m*, Me of isoamyl, 1 H of menthyl); 1.53 (*m*, *J* = 13, 1 H of menthyl); 1.42–1.28 (*m*, 2 H of isoamyl, 1 H of menthyl); 1.18 (br. *dd*, *J* = 11, 11, 1 H of menthyl); 0.97 (*ddd*, *J* = 11.9, 11, 11, 1 H of menthyl); 0.89 (*m*, *J* = 13, 1 H of menthyl); 0.84–0.83 (*m*, 2 Me of isoamyl, Me of menthyl); 0.78 (*d*, *J* = 6.8, Me of menthyl); 0.74 (*m*, *J* = 13, 1 H of menthyl); 0.60 (*d*, *J* = 6.8, Me of menthyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 170.2, 169.6, 169.4, 168.3 (4 CONH); 156.1 (C=O of Z); 137.1, 128.4, 127.9 (3 arom C of Z); 101.2 (C(2)); 99.2 (C(1′)); 81.0 (C(1) of menthyl); 75.3 (C(5)); 73.6 (C(4′)); 73.0 (C(3)); 72.2 (C(4)); 71.8 (C(5′)); 69.7 (C(3′)); 67.3 (C(1) of isoamyl); 65.6 (CH_2 of Z); 56.3 (C(2′)); 55.5 (C(2)); 51.8 (COOMe); 48.4 (C(2) of menthyl); 42.7 (C(6) of menthyl); 41.9 (α-C of Gly[2]); 40.6 (α-C of Gly[1]); 37.9 (C(2) of isoamyl); 34.0 (C(4) of menthyl); 31.2 (C(5) of menthyl); 24.4 (C(3) of isoamyl); 24.2 (1 C of menthyl); 22.7 (C(3) of menthyl); 22.4 (1 C of menthyl); 22.3 (2 Me of isoamyl); 21.3, 15.6 (2 Me of menthyl). FAB-MS: 861.4 ($[M+Na]^+$), 751.4 ($[M-\text{isoamyl}]^+$), 595.2 ($[M-\text{isoamyl}-\text{menthyl}]^+$). Anal. calc. for $C_{40}H_{62}N_4O_{15} \cdot 6\,H_2O$: C 51.96, H 7.28, N 5.95; found: C 51.45, H 7.14, N 5.64.

8.3. *[(Hexyl 2-{[({[1,3,3-Trimethylbicyclo[2.2.1]hept-2-yl 2-Deoxy-2-({*N*-[(*tert*-Butoxy)carbonyl]-*D-phenylalanyl}amino)-β-*D*-glucopyranosid]uronyl}glycinyl)-*D*-phenylalanyl]amino}-2-deoxy-β-*D*-glucopyranosid)-uronyl]glycine Methyl Ester* (**35**). *C*-Deprotected **29** (Li carboxylate; 64 mg, 0.1 mmol) and *N*-deprotected **28** (53.5 mg, 0.1 mmol) were coupled according to *GP 3a*. Extractive workup after 3.5 d and precipitation from Et_2O/pentane furnished a crude product (82 mg), which was purified by prep. RP-HPLC (*Si 60-10-C18*; MeCN/H_2O (pH 7) 60:40, isocratic) to afford **35** (48 mg) in 42% yield. ^{1}H-NMR (600 MHz, (D_6)DMSO)[3]): 8.32 (*t*, *J* = 5.7, NH of Gly[1]); 8.12 (*d*, *J* = 9, NH of Phe[1]); 8.03 (*d*, *J* = 9, 2-NH); 7.93 (*d*, *J* = 9.4, 2′-NH); 7.84 (br. *t*, NH of Gly[2]); 7.22 (br. *s*, 8 arom. H of Phe); 7.16 (*m*, 2 arom. H of Phe); 6.68 (br. *d*, *J* = 10, 0.7 NH of Phe[2] (major)); 6.18 (br. *d*, *J* = 8, 0.3 NH of Phe[2] (minor)); 5.10 (br. *s*, 0.7 OH (major)); 5.06 (br. *s*, 1.3 OH); 5.00 (*m*, OH); 4.80 (*m*, OH); 4.58 (*dt*, *J* = 9, 3.5, α-H of Phe[1]); 4.45 (*d*, *J* = 7.8, 0.3 H−C(1′) (minor)); 4.36 (*d*, *J* = 8.5, H−C(1)); 4.29 (*d*, *J* = 8.3, 0.7 H−C(1′) (major)); 4.19 (br. *m*, α-H of Phe[2]); 3.89 (*m*, *J* = 5.7, α-CH_2 of Gly[1]); 3.83 (*dd*, *J* = 16, 6, 1 H of α-CH_2 of Gly[2]); 3.71 (*m*, *J* = 9.5, 6.8, 1 H of hexyl); 3.67 (*d*, *J* = 9, H−C(5)); 3.63 (*s*, MeO); 3.62 (*d*, *J* = 8, H−C(5′)); 3.58–3.55 (*m*, 1 H of CH_2 of Gly[2], H−C(2), H−C(2′)); 3.42–3.34 (br. *m*, H−C(3), H−C(3′), H−C(4), H−C(4′), 1 H of hexyl); 3.07–2.96 (br. *m*, 1 H of β-CH_2 of Phe[1] and Phe[2], resp., 1 H of fenchyl); 2.74–2.65 (br. *m*, 1 H of β-CH_2 of Phe[1] and Phe[2], resp.), 1.61 (br. *m*, 1 H of fenchyl); 1.57–1.41 (br. *m*, 2 × 1 H of fenchyl, 2 H of hexyl); 1.36 (br. *d*, 1 H of fenchyl); 1.33–1.14 (br. *m*, 13 H, 6 H of hexyl, 0.7 $OCMe_3$ (major)); 1.12–1.05 (br. *s*, 3 H, $OCMe_3$ (minor)); 1.02 (*s*, Me of fenchyl (major)); 0.99 (br. *s*, > 1 H, 1 H and Me of fenchyl (minor)); 0.93 (*s*, > 1 H, Me of fenchyl (minor)); 0.87 (*s*, Me of fenchyl (major)); 0.78 (br. *t*, 1 H of fenchyl, Me of hexyl); 0.74 (*s*, Me of fenchyl). ^{13}C-NMR (150 MHz, (D_6)DMSO): 171.1, 170.2, 169.4, 168.7 (4 CONH); 167.9 (*C*OOMe); 155.1 (C=O of Boc)); 138.0, 129.3, 128.1, 126.3, 126.1 (5 arom. C of Phe); 102.8 (H−C(1′) (major)); 101.5 (H−C(1)); 100.6 (H−C(1′) (minor)); 91.5 (C(2) of fenchyl (major)); 89.9 (C(2) of fenchyl (minor); 77.8 (O*C*Me₃); 75.6 (H−C(5)); 75.3 (H−C(5′)); 73.8 (H−C(3), H−C(3′)); 72.4 (H−C(4), H−C(4′)); 68.9 (C(1) of hexyl); 55.7 (α-C of Phe[1]); 55.6 (α-C of Phe[2]); 55.1 (H−C(2), H−C(2′)); 48.8 (C_q of fenchyl (major)); 48.6 (C_q of fenchyl (minor)); 47.5 (C_q of fenchyl (major)); 41.9 (α-C of Gly[2]); 40.9 (CH of fenchyl); 40.6 (α-C of Gly[1]); 39.0 (β-C of Phe); 31.4 (Me of fenchyl (major)); 31.3 (C(4) of hexyl); 29.7 (Me of fenchyl (major)); 29.3 (C(2) of hexyl); 28.3 ($OCMe_3$); 25.7 (C(5) of fenchyl); 25.4 (C(6) of fenchyl); 25.3 (C(3) of hexyl); 22.2 (C(5) of hexyl); 21.7 (Me of fenchyl (major)); 21.2 (Me of fenchyl (minor)); 19.7 (Me of fenchyl (major)); 19.6 (Me of fenchyl (minor)); 14.0 (Me of hexyl). FAB-MS: 1133.5 ($[M+Na]^+$), 1033.4 ($[M-\text{Boc}]^+$). MALDI-MS (rel. to angiotensin): 1133 ($[M+Na]^+$).

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[3]) NMR assignments include two subsets of signals in a ratio of *ca*. 0.7 to 0.3, with variation in the part of the fenchyl glycoside. Shift differences occurred in the region of the glycoside linkage and the adjacent Boc-D-Phe substituent. The two conformers are designated as *major* and *minor*, resp.

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