

Differently Glycosidated 2-Amino-2-deoxy-D-glucofuranosiduronic Acids as Building Blocks in Peptide Synthesis¹⁾

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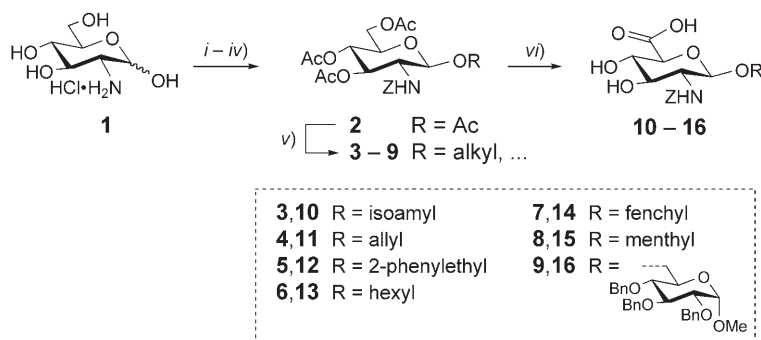
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Seven differently glycosidated sugar amino acids (SSAs) derived from glucosamine have been prepared. Following standard solution-phase peptide-coupling procedures, the glycosidated 2-amino-2-deoxy-D-glucofuranosiduronic acids were condensed with natural 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-glucofuranosiduronic acids (see *Table* below), and demonstrates their use in the synthesis of artificial peptides.

Results and Discussion. – The synthetic approach to alkyl 2-[(benzyloxy)carbonylamino]-2-deoxy- β -D-glucofuranosiduronic acids is summarized in the *Scheme* below. Starting from glucosamine hydrochloride (**1**), 1,3,4,6-tetra-*O*-acetyl-2-[(benzyloxy)carbonylamino]-2-deoxy- β -D-glucofuranose (**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

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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*) Ac₂O, pyridine, r.t., 2–4 h. *iii*) acetone, HCl (1.1 equiv.), reflux. *iv*) ZCl (1.5 equiv.), NaHCO₃ (2.5 equiv.), CHCl₃/H₂O 1:2, r.t., 3–24 h. *v*) R–OH, TMSTf, mol. sieves, anh. CH₂Cl₂, 4°, 15–46 min. *vi*) 1. Na (s), MeOH, 0.5–3 h; 2. *Dowex WX4-100* (H⁺), evaporation; 3. TEMPO (cat.), NaClO, NaClO₂, MeCN/*Borax* (pH 9.0) 1:1.

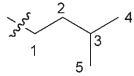
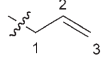
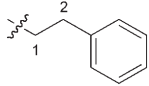
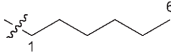
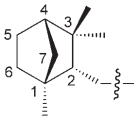
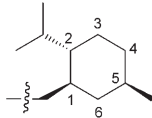
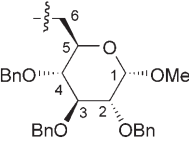
trichloroacetimidates, or other glycosyl donors, and can be used directly as a glycosyl donor in *Lewis* acid catalyzed glycosidation reactions.

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/NaClO₂ 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 NH₂ 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

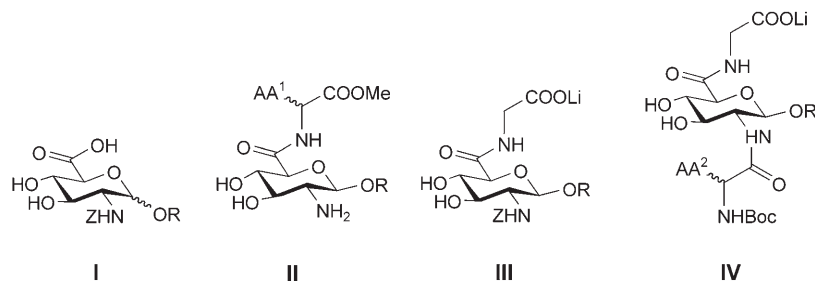
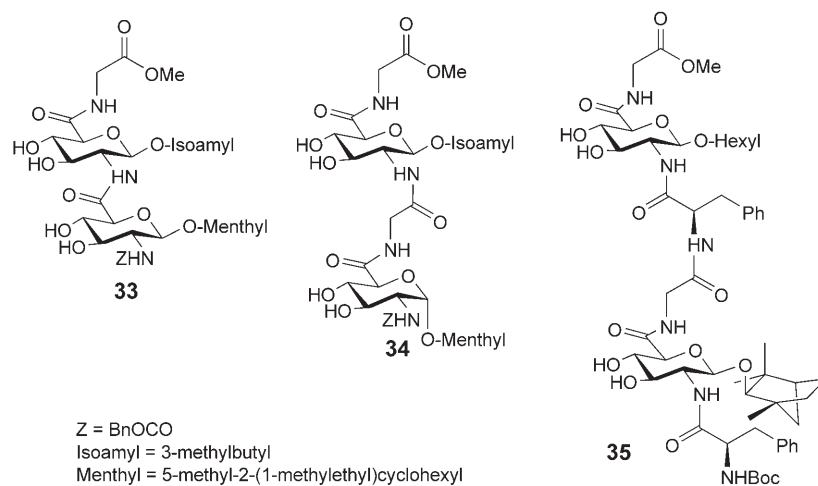


Fig. 1. Types of building blocks used for solution-phase peptide synthesis. All compounds are derived from the uronic acids **10**–**16** (type **I**). Saponification or *N*-deprotection (*Z* group) of **17**–**25** yields the dimeric building blocks **II** and **III**. Coupling of **II** with Boc-protected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

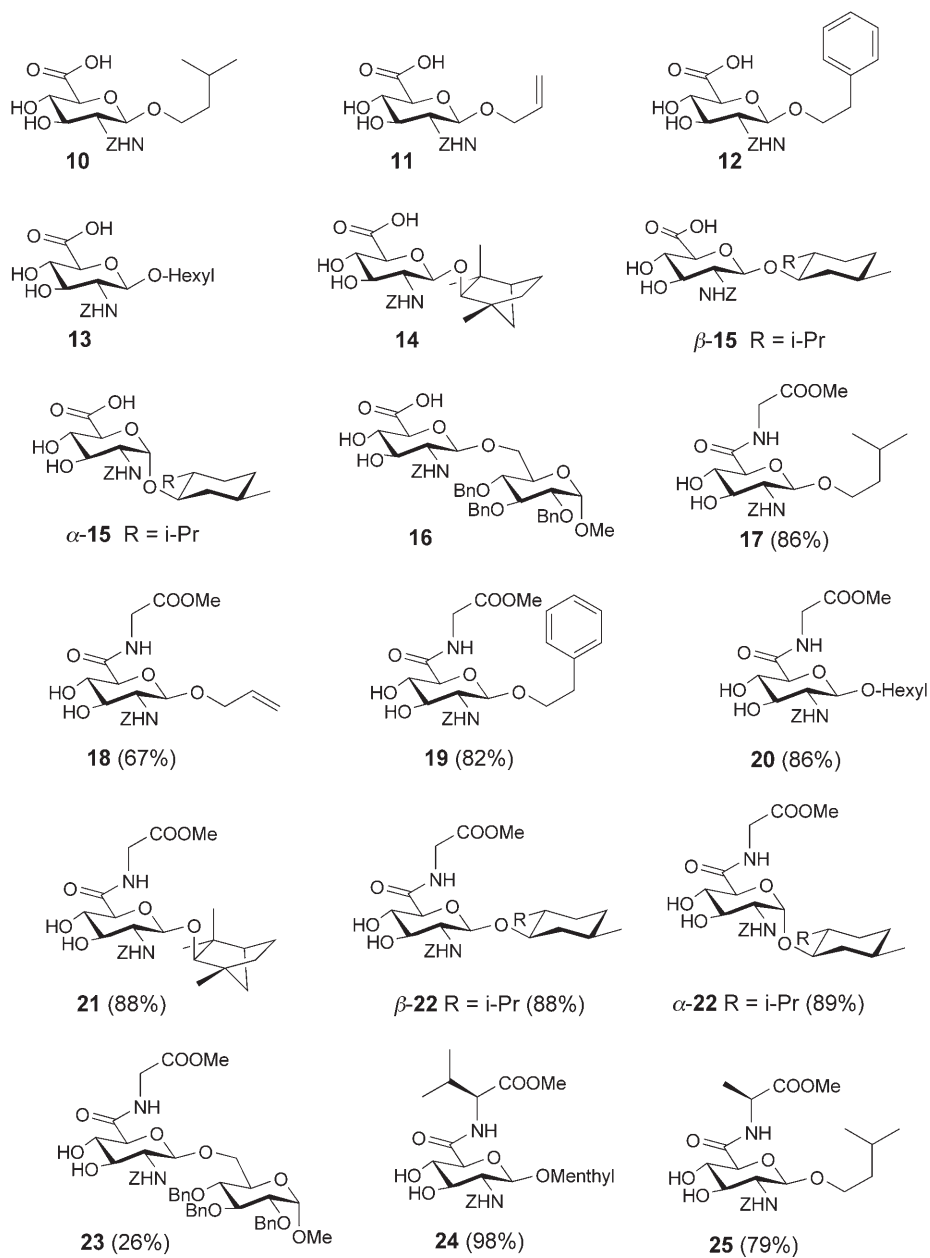


Fig. 2. Structures and yields of heterodimeric and heterotrimeric building blocks derived from the corresponding sugar amino acids

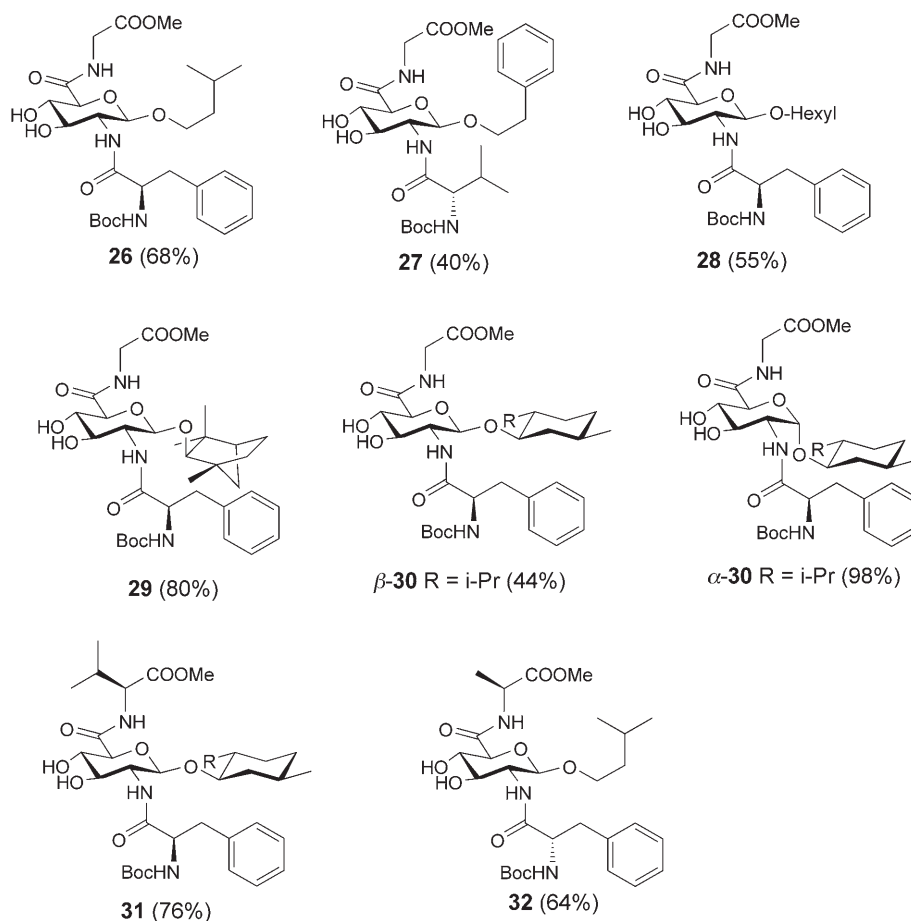


Fig. 2 (cont.)

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 F₂₅₄*). 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; $\Delta\epsilon$ values were converted to molar ellipticity $[\theta]$ with the *Jasco Spectra Analysis V1.0* software. NMR Spectra were recorded on *Bruker DPX-200* (200.13 (^1H) 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

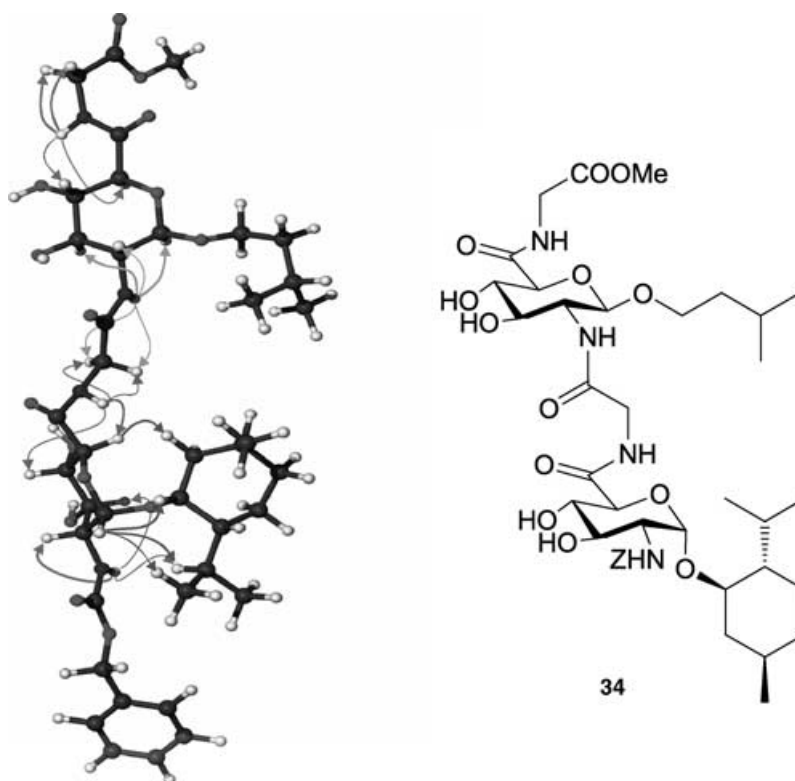


Fig. 3. Calculated conformation of **34**. NOEs used as geometrical restraints are depicted as arrows, their intensities being represented in arrow thickness.

CDCl_3 , CD_3CN , or $(\text{D}_6)\text{DMSO}$; 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 anhydrous conditions. Compound **2** and 1.1–5.0 equiv. of glycosyl acceptor were dissolved in anhydrous 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 catalytic amount of Na to a soln. or suspension of the respective acetylated glycoside in anhydrous 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

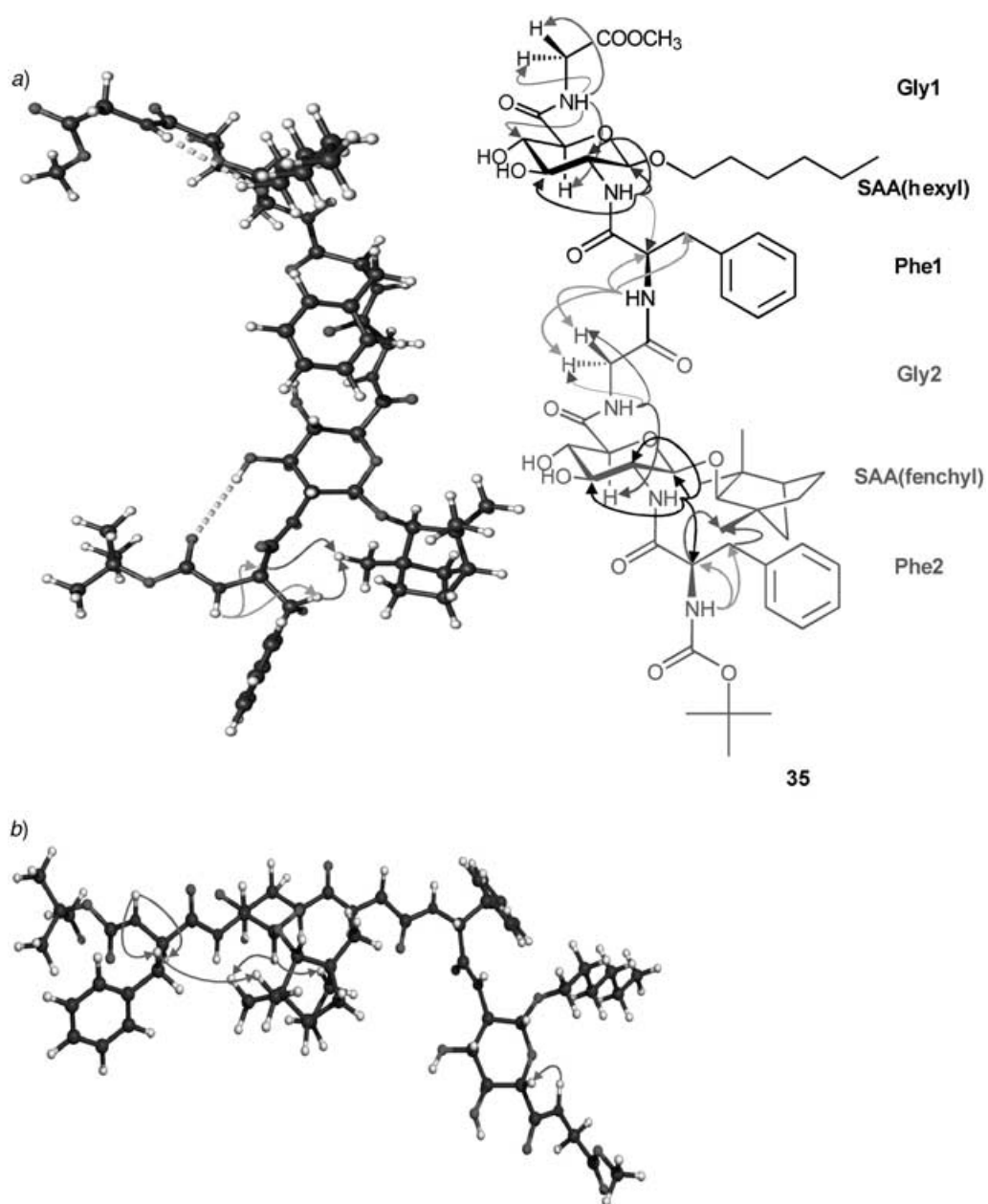


Fig. 4. Calculated major (a) and minor (b) conformations of **35**. Arrows indicate backbone NOEs used as geometrical restraints for MD simulations, which were equivalent for both the major and minor form. In the MD structures, individual NOEs of the major and minor form are indicated, their intensities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

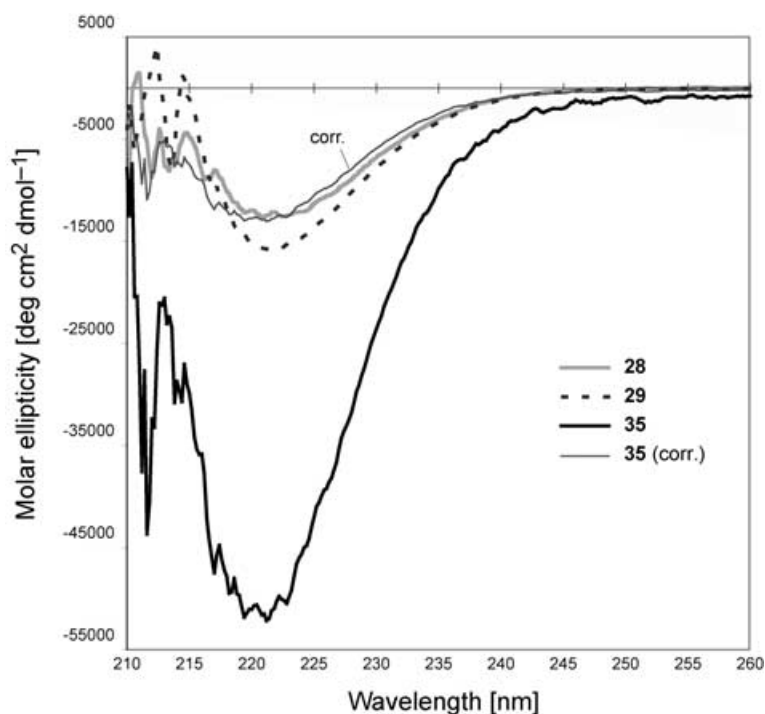


Fig. 5. CD Spectra of **35** and the parent trimeric type-IV building blocks **28** and **29**. The corrected (corr.) curve of **35** represents that of **35** divided by the number of amide bonds adjacent to stereogenic centers (*i.e.*, four).

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 $\text{Et}(\text{i-Pr})_2\text{N}$ 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. $^1\text{H-NMR}$ (400 MHz, (D_6) DMSO): 8.11 (s, ArCH=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)). $^{13}\text{C-NMR}$ (100 MHz, (D_6) DMSO): 161.43 (Ar-CH=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 anhyd. 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. 1H -NMR (400 MHz, (D_6) DMSO): 8.27 (s, Ar-CH=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-OCOMe); 169.54 (4-OCOMe); 169.08 (3-OCOMe); 168.68 (1-OCOMe); 164.57 (Ar-CH=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 (OCOMe); 20.57 (2 OCOMe); 20.31 (OCOMe). 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. 1H -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 (OCOMe); 20.62 (2 OCOMe); 20.53 (OCOMe). 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. 1H -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 (OCOMe); 169.52 (OCOMe); 169.28 (OCOMe); 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 (OCOMe); 20.50 (OCOMe); 20.43 (OCOMe); 20.30 (OCOMe). 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. 1H -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 (2d, $J = 6.7$, 2 Me of isoamyl). ^{13}C -NMR (100 MHz, (D_6) DMSO): 170.15 (OCOMe); 169.66 (OCOMe); 169.40 (OCOMe); 156.00 (NCOOBn); 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 (OCOMe); 20.51 (OCOMe); 20.40 (OCOMe). 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)carbonylamino]-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 I*. The crude product was precipitated from Et₂O to yield **4** (896.5 mg) as a colorless solid in 90% yield. ¹H-NMR (600 MHz, (D₆)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 CH₂ of Z, H-C(3)); 4.99 (*d*, *J* = 12.5, 1 H of CH₂ 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). ¹³C-NMR (150 MHz, (D₆)DMSO): 170.13 (OCOMe); 169.62 (OCOMe); 169.37 (OCOMe); 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 (CH₂ of Z); 61.92 (allyl); 55.41 (C(2)); 20.59 (OCOMe); 20.49 (OCOMe); 20.37 (OCOMe). FAB-MS: 502.2 ([*M* + Na]⁺), 480.2 ([*M* + H]⁺), 422.2 ([*M* - allyl]⁺).

4.3. *2-Phenylethyl 3,4,6-Tri-O-acetyl-2-[(benzyloxy)carbonylamino]-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 I* for 15 min. Standard workup and crystallization from *i*-PrOH yielded **5** (1.2 g) in 43% yield as a colorless solid. ¹H-NMR (600 MHz, (D₆)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 CH₂ of Z, H-C(3)); 4.97 (*d*, *J* = 12.6, 1 H of CH₂ 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*, OCOMe); 1.95 (*s*, OCOMe); 1.84 (*s*, OCOMe). ¹³C-NMR (150 MHz, (D₆)DMSO): 170.9 (OCOMe); 170.4 (OCOMe); 170.1 (OCOMe); 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 (CH₂ of phenethyl); 69.5 (C(4)); 66.1 (CH₂ of Z); 63.1 (C(6)); 56.1 (C(5)); 36.2 (CH₂ of phenethyl); 21.4 (3 OCOMe). FAB-MS: 566.2 ([*M* + Na]⁺), 544.3 ([*M* + H]⁺), 422.2 ([*M* - phenethyl]⁺). Anal. calc. for C₂₈H₃₃NO₁₀: 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)carbonylamino]-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 I* 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. ¹H-NMR (600 MHz, (D₆)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 CH₂ of Z); 4.96 (*d*, *J* = 12.8, 1 H of CH₂ 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, CH₂ of hexyl); 1.23 (*br. m*, 6 H of hexyl); 0.83 (*dd*, *J* = 7, 7, Me of hexyl). ¹³C-NMR (150 MHz, (D₆)DMSO): 170.1, 169.6, 169.4 (3 OCOMe); 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, (CH₂ of hexyl); 68.9 (C(4)); 65.3 (CH₂ of Z); 62.0 (C(6)); 55.4 (C(2)); 31.0, 29.0, 25.0, 22.1 (4 CH₂ of hexyl); 20.6, 20.5, 20.4 (3 OCOMe); 14.0 (Me of hexyl). FAB-MS: 546.2 ([*M* + Na]⁺), 524.2 ([*M* + H]⁺), 422.1 ([*M* - hexyl]⁺). Anal. calc. for C₂₆H₃₇NO₁₀: 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)carbonylamino]-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 I* for 45 min. Crystallization from EtOH yielded **7** (1.14 g) in 58.6% yield as colorless needles. ¹H-NMR (600 MHz, (D₆)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*, CH₂ 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*, CH₂(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). ¹³C-NMR (150 MHz, (D₆)DMSO): 170.07, 169.67, 169.52 (3 OCOMe); 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 (CH₂ 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 OCOMe); 19.31 (3-Me of fenchyl). FAB-MS: 598.3 ([*M* + Na]⁺), 576.3 ([*M* + H]⁺), 422.2 ([*M* - fenchyl]⁺). Anal. calc. for C₃₀H₄₁NP₁₀: 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)carbonylamino]-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. ¹H-NMR (400 MHz, (D₆)DMSO): 7.31 (*m*, 4 arom. H of Z, NH); 5.10 (*dd*, *J* = 9.8, 9.8, H–C(3)); 5.01 (*s*, CH₂ 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). ¹³C-NMR (100 MHz, (D₆)DMSO): 170.09, 169.66, 169.47 (3 OCOMe); 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 (CH₂ 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 (Me₂CH); 22.71 (C(3) of menthyl); 22.26 (Me of menthyl); 20.91 (Me of menthyl); 20.55 (2 OCOMe); 20.44 (OCOMe); 15.47 (Me of menthyl). FAB-MS: 578.2 ([*M* + H]⁺), 600.2 ([*M* + Na]⁺), 422.1 ([*M* – menthyl]⁺), 156 (menthyl⁺). Anal. calc. for C₃₀H₄₃NO₁₀: 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 (SiO₂), 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. ¹H-NMR (600 MHz, (D₆)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 CH₂ of Z); 4.84 (*dd*, *J* = 9.5, 9.5, H–C(4')); 4.81 (*d*, *J* = 11.2, 1 H of CH₂ of Bn); 4.77 (*m*, H–C(1), 1 H of CH₂ of Z); 4.68 (*d*, *J* = 11.2, 1 H of CH₂ of Bn); 4.65 (*m*, 3 H of 2 CH₂ of Bn); 4.60 (*d*, *J* = 8.3, H–C(1')); 4.56 (*d*, *J* = 10.8, 1 H of CH₂ 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); ¹³C-NMR (150 MHz, (D₆)DMSO): 170.2, 169.7, 169.4 (3 OCOMe); 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 CH₂ of Bn); 72.7 (C(3')); 71.6 (CH₂ of Bn); 70.8 (C(5')); 69.3 (C(5)); 68.7 (C(4')); 67.8 (C(6)); 65.6 (CH₂ of Z); 61.9 (C(6')); 55.4 (C(2')); 54.7 (1-MeO); 20.7, 20.6, 20.5 (3 OCOMe). FAB-MS: 908.3 ([*M* + Na]⁺), 886.3 ([*M* + H]⁺), 854.3 ([*M* – MeO]⁺), 746.2 ([*M* – MeO – BnO]⁺), 663.1 ([*M* – MeO – 2BnO + Na]⁺), 639.1 ([*M* – MeO – 2BnO]⁺), 422.1. Anal. calc. for C₄₈H₅₅NO₁₅ · H₂O: 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 Et₂O/pentane. Yield of **10**: 1.057 g (92%). ¹H-NMR (400 MHz, (D₆)DMSO): 7.3 (*m*, 5 arom. H); 7.07 (*d*, *J* = 8.5, NH); 4.98 (*d*, *J* = 12.3, CH₂ 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, CH₂ of isoamyl); 0.82 (*d*, *J* = 6.5, Me of isoamyl); 0.81 (*d*, *J* = 6.5, Me of isoamyl). ¹³C-NMR (100 MHz, (D₆)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 (CH₂ 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* – isoamyl]⁺). Anal. calc. for C₁₉H₂₇NO₈: 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. ¹H-NMR (600 MHz, (D₆)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, CH₂ 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*, H₂O, H–C(3), H–C(2)). ¹³C-NMR (150 MHz, (D₆)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 (CH₂ 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)carbonylamino]-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 Et₂O 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. ¹H-NMR (600 MHz, (D₆)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, CH₂ 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, H₂O, H–C(2)); 2.75 (*ddd*, *J* = 13.9, 7, 7, 2 H of phenethyl). ¹³C-NMR (150 MHz, (D₆)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 (CH₂ of phenethyl); 65.2 (CH₂ of Z); 57.1 (C(2)); 35.5 (CH₂ of phenethyl). FAB-MS: 454.1 ([M + Na]⁺), 432.1 ([M + H]⁺), 298.1 ([M – Z]⁺), 310.1 ([M – phenethyl]⁺). Anal. calc. for C₂₂H₂₅NO₈ · H₂O: C 58.79, H 6.06, N 3.12; found: C 59.59, H 6.03, N 3.15.

5.4. *Hexyl 2-[(Benzyloxy)carbonylamino]-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. ¹H-NMR (600 MHz, (D₆)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, CH₂ 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). ¹³C-NMR (150 MHz, (D₆)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 (CH₂ of hexyl); 65.1 (CH₂ of Z); 57.2 (C(2)); 31.0, 29.1, 25.0, 22.1, 13.9 (4 CH₂ and 1 Me of hexyl). FAB-MS: 412.2 ([M + H]⁺), 434.2 ([M + Na]⁺), 310.1 ([M – hexyl]⁺). Anal. calc. for C₂₀H₂₉NO₈ · H₂O: 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)carbonylamino]-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. ¹H-NMR (600 MHz, (D₆)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 CH₂ of Z); 4.99 (br. s, OH); 4.93 (*d*, *J* = 12.5, 1 H of CH₂ 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*, H₂O, 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). ¹³C-NMR (150 MHz, (D₆)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 (CH₂ 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 C₂₄H₃₃NO₈ · H₂O: 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)carbonylamino]-2-deoxy-β-D-glucopyranosiduronic Acid (β-15)*. Compound **8** (455.3 mg) was oxidized according to GP 2. Both the Et₂O 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. ¹H-NMR (400 MHz, (D₆)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 CH₂ of Z); 5.05 (br. s, OH); 4.92 (*d*, *J* = 12.5, 1 H of CH₂ of Z); 4.39 (*d*, *J* = 8.0, H–C(1)); 3.50 (*d*, *J* = 9.5, H–C(5)); 3.3 (br. *m*, H₂O, 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). ¹³C-NMR (100 MHz, (D₆)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 (CH₂ 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 (Me₂CH 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 C₂₄H₃₃NO₈ · H₂O: 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)carbonylamino]-2-deoxy- α -D-glucopyranosiduronic Acid (**a-15**). Compound **a-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. ¹H-NMR (600 MHz, (D₆)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 CH₂ of Z); 4.98 (*d*, *J* = 12.5, 1 H of CH₂ 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). ¹³C-NMR (150 MHz, (D₆)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 (CH₂ 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)carbonylamino]-2-deoxy- β -D-glucopyranuronosyl]-2,3,4-tri-O-benzyl- α -D-glucopyranoside (**16**). Compound **9** (269.4 mg, 304 μ mol) was deacetylated according to standard procedures. An anal. sample (data not shown) was purified by precipitation from Et₂O/pentane. The deacetylated product (230 mg, 303 μ mol) 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. ¹H-NMR (600 MHz, CD₃CN): 7.7–6.9 (*m*, 20 arom. H); 5.72 (br. *d*, NH); 5.01 (*d*, *J* = 11.7, 1 H of CH₂ of Z); 4.88 (*m*, 1 H of CH₂ of Z, 1 H of CH₂ of Bn); 4.78 (*d*, *J* = 3, H–C(1)); 4.74 (*d*, *J* = 11, 1 H of CH₂ of Bn); 4.72 (*d*, *J* = 10.8, 1 H of CH₂ of Bn); 4.66 (*s*, CH₂ of Bn); 4.57 (*d*, *J* = 10.8, 1 H of CH₂ 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). ¹³C-NMR (150 MHz, CD₃CN): 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 (CH₂ of Bn); 75.5 (CH₂ of Bn); 75.2 (C(5')); 74.5 (C(3')); 73.2 (CH₂ of Bn); 73.1 (C(4')); 70.5 (C(5)); 68.9 (C(6)); 67.3 (CH₂ of Z); 58.3 (C(2')); 55.5 (MeO). FAB-MS: 818.3 ([*M* + 2Na]⁺), 796.3 ([*M* + Na]⁺), 758.9 ([*M* – MeO + H₂O]⁺), 487.2, 310.1.

6. Syntheses of Heterodimeric Building Blocks **17**–**25**. 6.1. 3-Methylbutyl 2-[[(Benzyloxy)carbonylamino]-2-deoxy-N-[[(methoxy)carbonylmethyl]- 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. ¹H-NMR (600 MHz, CD₃CN): 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, CH₂ of Z); 4.46 (*d*, *J* = 8.1, H–C(1)); 4.33 (*s*, 4-OH); 3.96 (*d*, *J* = 6, NCH₂); 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 (*ddd*, *J* = 13.5, 6.8, 6.8, 6.8, CH₂ of isoamyl); 0.88 (*d*, *J* = 6.4, Me of isoamyl); 0.87 (*d*, *J* = 6.4, Me of isoamyl). ¹³C-NMR (150 MHz, CD₃CN): 172.3 (6-CONH); 170.9 (COOMe); 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 (CH₂ of Z); 58.2 (C(2)); 52.8 (COOMe); 41.4 (CH₂NH); 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 C₂₂H₃₂N₂O₉: 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)carbonylamino]-2-deoxy-N-[[(methoxy)carbonylmethyl]- 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**. ¹H-NMR (400 MHz, (D₆)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 (*ddd*, *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, CH₂ 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, NCH₂); 3.63 (*s*, MeO); 3.3 (br. *m*, H₂O, H–C(2), H–C(3), H–C(4)). ¹³C-NMR (100 MHz, (D₆)DMSO): 170.2 (C(6)); 169.3 (COOMe); 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 (CH₂ of Z); 57.1 (C(2)); 51.9 (COOMe); 40.6 (NCH₂). 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 μ mol) 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 Et₂O/hexanes to afford **19** (307 mg) in 82% yield as a colorless solid. ¹H-NMR (600 MHz, (D₆)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*, CH₂ 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, NCH₂); 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). ¹³C-NMR (150 MHz, (D₆)DMSO): 170.0 (C(6)); 169.3 (COOMe); 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 (CH₂ of phenethyl); 65.2 (CH₂ of Z); 51.7 (C(2)); 40.6 (NCH₂); 35.5 (CH₂ of phenethyl). FAB-MS: 525.2 ([*M* + Na]⁺), 503.2 ([*M* + H]⁺), 381.1 ([*M* - 2(phenethyl)]⁺). Anal. calc. for C₂₅H₃₀N₂O₉ · H₂O: 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 Et₂O, **20** (998.4 mg) in 86% yield as a colorless solid. ¹H-NMR (400 MHz, (D₆)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*, CH₂ of Z, 4-OH); 4.32 (*d*, *J* = 8.5, H-C(1)); 3.87 (*dd*, *J* = 6, 2, NCH₂); 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, 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). ¹³C-NMR (100 MHz, (D₆)DMSO): 170.2 (C(6)); 169.4 (COOMe); 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 (CH₂ of hexyl); 65.2 (CH₂ of Z); 57.1 (C(2)); 51.8 (COOMe); 40.6 (NCH₂); 31.2, 29.1, 25.1, 22.2 (4 CH₂ 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 C₂₃H₃₄N₂O₉: 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. ¹H-NMR (600 MHz, (D₆)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*, CH₂ of Z, 3-OH, 4-OH); 4.19 (*d*, *J* = 8, H-C(1)); 3.95-3.85 (*dd*, *J* = 17, 5.5, NCH₂); 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 fenethyl); 1.61 (*br. m*, 1 H of fenethyl); 1.57 (*s*, 1 H of fenethyl); 1.55 (*br. m*, 1 H of fenethyl); 1.40 (*d*, 1 H of fenethyl); 1.30 (*br. m*, 1 H of fenethyl); 1.00 (*s*, Me and 1 H of fenethyl); 0.92 (*s*, Me of fenethyl), 0.81 (*br. m*, 1 H of fenethyl); 0.78 (*s*, Me of fenethyl). ¹³C-NMR (150 MHz, (D₆)DMSO): 169.9 (C(6)); 169.2 (COOMe); 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 fenethyl); 75.5 (C(5)); 73.4 (C(3)); 72.0 (C(4)); 65.0 (CH₂ of Z); 57.5 (C(2)); 51.6 (COOMe); 48.8 (C(1) of fenethyl); 48.7 (C(3) of fenethyl); 47.6 (C(4) of fenethyl); 40.6 (C(7) of fenethyl); 38.8 (NCH₂); 29.6 (Me of fenethyl); 25.8 (C(6) of fenethyl); 25.3 (C(5) of fenethyl); 21.6, 19.4 (2 Me of fenethyl). FAB-MS: 557.2 ([*M* + Na]⁺), 535.2 ([*M* + H]⁺), 381.1 ([*M* - fenethyl]⁺). Anal. calc. for C₂₇H₃₈N₂O₉ · 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 μ mol) 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. ¹H-NMR (600 MHz, (D₆)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 CH₂ 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 CH₂ of Z); 4.40 (*d*, *J* = 8.5, H-C(1)); 3.87 (*m*, NCH₂); 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). ¹³C-NMR (150 MHz, (D₆)DMSO): 170.0 (C(6)); 168.9 (COOMe); 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 (CH₂ of Z); 57.3 (C(2)); 52.0 (COOMe); 47.5 (C(2) of menthyl); 40.4 (NCH₂); 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. (1*S*,2*S*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-[[*(Benzyloxy)carbonylamino*]-2-deoxy-N-[[*(methoxy)carbonylmethyl*]- 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. 1H -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*, $J = 13.1$, 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 (COOMe); 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 (COOMe); 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-((5*S*)-2-[[*(Benzyloxy)carbonylamino*]-2-deoxy-5-[[*(methoxy)carbonylmethyl*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. (1*S*,2*S*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-[[*(Benzyloxy)carbonylamino*]-2-deoxy-N-[(*S*)-[(*methoxy)carbonylmethyl*]-1-methylethyl)methyl]- β -D-glucopyranosiduronamide (24). Compound β -15 (310.6 mg, 667 μ mol) and valine methylester hydrochloride (134 mg, 800 μ mol, 1.2 equiv.) were coupled according to *GP 3b* to yield 24 (373.5 mg) in 97% yield as a colorless solid. 1H -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*, $J = 9.9, 9$, 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 (COOMe); 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 (COOMe); 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)carbonylamino*]-2-deoxy-N-[(*S*)-[(*methoxy)carbonylmethyl*]-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. 1H -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*, $J = 9.9, 9$, 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 (COOMe); 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 (COOMe); 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 Et₂O/hexanes to afford **26** (710 mg) in 68% yield as a colorless solid. ¹H-NMR (400 MHz, (D₆)DMSO): 8.36 (*t*, *J* = 5.8, NH of Gly); 7.93 (*d*, *J* = 9, 2-NH); 7.25 (*2d*, 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 -CH₂ 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). ¹³C-NMR (100 MHz, (D₆)DMSO): 171.8 (CONH of Phe); 170.3 (C(6)); 169.5 (COOMe); 155.3 (COO^tBu); 138.5, 129.4, 128.1, 126.3 (4 arom. C of Phe); 101.5 (C(1)); 78.0 (OCMe₃); 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 (COOMe); 40.7 (α -C of Gly); 38.3 (β -C of Phe); 38.1 (C(2) of isoamyl); 28.3 (OCMe₃); 24.4 (C(3) of isoamyl); 22.7 (C(4) of isoamyl); 22.5 (C(5) of isoamyl). FAB-MS: 1185.7 ([*M* + Na]⁺), 604.3 ([*M* + Na]⁺), 582.3 ([*M* + H]⁺), 504.3 ([*M* – Boc + Na]⁺), 494.3 ([*M* – isoamyl]⁺). Anal. calc. for C₂₈H₄₃N₃O₁₀·H₂O: 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 μ mol) and Boc-L-Val-OH (253 mg) were coupled according to *GP 3b*. The crude product was precipitated from Et₂O/hexanes to afford **27** (180 mg) in 40% yield. ¹H-NMR (600 MHz, CD₃CN): 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 -CH₂ 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 (*2d*, *J* = 6.8 each, 2 Me of Val). ¹³C-NMR (150 MHz, CD₃CN): 173.0 (CONH of Val); 172.2 (C(6)); 170.8 (COOMe); 157.1 (COO^tBu); 139.8, 130.0, 129.4, 127.2 (4 arom. C of phenethyl); 101.8 (C(1)); 80.0 (COOCMe₃); 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 (COOMe); 41.3 (α -C of Gly); 36.8 (C(2) of phenethyl); 31.7 (β -C of Val); 28.6 (OCMe₃); 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 C₂₇H₄₁N₃O₁₀·H₂O: 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. ¹H-NMR (600 MHz, (D₆)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 (*2dd*, *J* = 17 and 5.5 each, α -CH₂ 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 CH₂ of Phe); 2.72 (*dd*, *J* = 13.5, 10, 1 H of CH₂ 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). ¹³C-NMR (150 MHz, (D₆)DMSO): 171.7 (CONH of Phe); 170.1 (C(6)); 169.4 (COOMe); 155.1 (COO^tBu); 138.4, 129.3, 128.0, 126.2 (4 arom. C of Phe); 101.3 (C(1)); 77.9 (OCMe₃); 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 (COOMe); 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 (OCMe₃); 25.2 (C(3) of hexyl); 22.1 (C(6) of hexyl); 14.0 (C(6) of hexyl). FAB-MS: 618.3 ([*M* + Na]⁺), 1213.6 ([*2M* + Na]⁺), 495.3 ([*M* + 1 – Boc]⁺), 518.3 ([*M* – Boc + Na]⁺). Anal. calc. for C₂₉H₄₅N₃O₁₀·4 H₂O: 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 Et₂O/hexanes to yield **29** (864.9 mg) in 79.8% yield as a colorless solid. ¹H-NMR (400 MHz, (D₆)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 (*2d*, *J* = 5.8 each, α -CH₂ 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*, $J = 12.5, 3, 1 \beta\text{-H}$ of Phe); 2.70 (*dd*, $J = 12.5, 12, 1 \beta\text{-H}$ 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*, $J = 9, 1 \text{H}$ 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). $^{13}\text{C-NMR}$ (100 MHz, $(\text{D}_6)\text{DMSO}$): 171.6 (CONH of Phe); 170.1 (C(6)); 168.8 (COOMe); 155.2 (COO'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 (OCMe₃); 75.6 (C(5)); 73.8 (C(3)); 72.1 (C(4)); 55.7 ($\alpha\text{-C}$ of Phe); 55.6 (C(2)); 51.8 ($\alpha\text{-C}$ 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 ($\alpha\text{-C}$ of Gly); 39.0 ($\beta\text{-C}$ of Phe); 29.5 (*endo*-Me of fenchyl); 28.3 (OCMe₃); 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 ($[2M + \text{Na}]^+$), 670.2 ($[M + \text{Na}]^+$), 648.2 ($[M + \text{H}]^+$), 570.2 ($[M - \text{Boc} + \text{H} + \text{Na}]^+$), 494.1 ($[M - \text{fenchyl}]^+$), 438.1 ($[M - \text{fenchyl} - \text{Boc} + 2\text{Na}]^+$).

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. $^1\text{H-NMR}$ (600 MHz, $(\text{D}_6)\text{DMSO}$): 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*, $\alpha\text{-H}$ of Phe); 3.88 (*d*, $J = 5.8$, $\alpha\text{-CH}_2$ 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 $\beta\text{-CH}_2$ of Phe); 2.71 (*dd*, $J = 10.3, 13.8$, 1 H of $\beta\text{-CH}_2$ of Phe); 2.20 (*m*, 1 H of menthyl); 2.04 (br. *d*, $J = 12$, 1 H of menthyl); 1.55 (*m*, $2 \times 1 \text{H}$ 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*, $2 \times 1 \text{H}$ of menthyl); 0.68 (*d*, $J = 7$, Me of menthyl). $^{13}\text{C-NMR}$ (150 MHz, $(\text{D}_6)\text{DMSO}$): 171.4 (CONH of Phe); 170.1 (C(6)); 169.0 (COOMe); 155.2 (COO'Bu); 138.5, 129.4, 128.0, 126.2 (4 arom. C of Phe); 98.9 (C(1)); 78.0 (OCMe₃); 77.1 (C(1) of menthyl); 75.7 (C(5)); 73.9 (C(4)); 72.1 (C(3)); 55.6 (C(2), $\alpha\text{-C}$ of Phe); 51.8 (COOMe); 47.5 (C(2) of menthyl); 40.7 (C(6) of menthyl); 40.6 ($\alpha\text{-C}$ of Gly); 38.3 ($\beta\text{-C}$ of Phe); 34.1 (C(4) of menthyl); 31.0 (C(5) of menthyl); 28.3 (OCMe₃); 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 ($[M + \text{H} + \text{Na}]^+$), 651.1 ($[M + 2\text{H}]^+$), 494.7 ($[M - \text{menthyl}]^+$), 395.3 ($[M + 2 - \text{Boc}]^+$). Anal. calc. for C₃₃H₅₁N₃O₁₀ · H₂O: 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 CH₂Cl₂/hexanes to afford α -**30** (635 mg) in 60% yield as a colorless solid. $^1\text{H-NMR}$ (600 MHz, $(\text{D}_6)\text{DMSO}$): 8.30 (*t*, $J = 6$, NH of Gly); 7.6 (*d*, $J = 7, 2\text{-NH}$); 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*, $J = 10.0, 9.3, 3.0$, $\alpha\text{-H}$ of Phe); 3.98 (*d*, $J = 9.8$, H–C(5)); 3.87 (*dd*, $J = 17, 6$, $\alpha\text{-CH}_2$ 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*, $J = 13.2, 3, 1 \text{H}$ of $\beta\text{-CH}_2$ of Phe); 2.69 (*dd*, $J = 13.2, 10, 1 \text{H}$ of $\beta\text{-CH}_2$ of Phe); 2.25 (*m*, $J = 6.9, 6.9, 1 \text{H}$ of menthyl); 2.08 (*d*, $J = 11.6, 1 \text{H}$ of menthyl); 1.58 (*d*, $J = 12, 1 \text{H}$ of menthyl); 1.54 (*d*, $J = 13, 1 \text{H}$ 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*, $J = 11.6, 1 \text{H}$ of menthyl); 0.91 (*m*, $J = 13, 1 \text{H}$ of menthyl); 0.86 (*d*, $J = 6$, Me of menthyl); 0.81 (*d*, $J = 6.9$, Me of menthyl); 0.76 (*dd*, $J = 12, 1 \text{H}$ of menthyl), 0.63 (*d*, $J = 6.9$, Me of menthyl). $^{13}\text{C-NMR}$ (150 MHz, $(\text{D}_6)\text{DMSO}$): 171.9 (CONH of Phe); 170.1 (C(6)); 170.0 (COOMe); 155.3 (COO'Bu); 138.3, 129.3, 128.0, 126.1 (4 arom. C of Phe); 98.7 (C(1)); 80.2 (OCMe₃); 78.1 (C(1) of menthyl); 72.8 (C(4)); 71.9 (C(5)); 70.1 (C(3)); 55.5 ($\alpha\text{-C}$ of Phe); 54.4 ($\beta\text{-C}$ of Phe); 51.7 (COOMe); 48.4 (C(2) of menthyl); 42.5 (C(6) of menthyl); 40.5 ($\alpha\text{-C}$ of Gly); 38.0 ($\beta\text{-C}$ of Phe); 33.9 (C(4) of menthyl); 31.2 (C(5) of menthyl); 28.2 (OCMe₃); 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 ($[M + \text{H} + \text{Na}]^+$), 651.1 ($[M + 2\text{H}]^+$), 494.7 ($[M - \text{menthyl}]^+$), 395.3 ($[M + 2\text{H} - \text{menthyl} - \text{Boc}]^+$). Anal. calc. for C₃₃H₅₁N₃O₁₀ · H₂O: 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 Et₂O to yield **31** (305 mg) in 75.6% yield. $^1\text{H-NMR}$ (600 MHz, $(\text{D}_6)\text{DMSO}$): 8.13 (*d*, $J = 8.7$, NH of Val); 7.94 (*d*, $J = 7.9, 2\text{-NH}$); 7.28–7.24 (*m*, 5 arom. H of Phe); 6.63 (*d*, $J = 8.7$, NH of Phe); 5.06 (*d*, $J = 5.1, 4\text{-OH}$); 4.85 (*d*, $J = 5.1, 3\text{-OH}$); 4.51 (*d*, $J = 7.8, \text{H-C}(1)$); 4.26 (*dd*, $J = 8.7, 6.3, \alpha\text{-H}$ of Val); 4.16 (*ddd*, $J = 9.4, 8.7, 3.5, \alpha\text{-H}$ of Phe); 3.70 (*d*, $J = 9.4, \text{H-C}(5)$); 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*, $J = 13.8, 3.5, 1 \text{H}$ of $\beta\text{-CH}_2$ of Phe); 2.71 (*dd*, $J = 13.8, 9.4, 1 \text{H}$ of $\beta\text{-CH}_2$ 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). $^{13}\text{C-NMR}$ (150 MHz, (D_6) DMSO): 171.9 (CONH of Ph); 171.4 (C(6)); 168.4 (COOMe); 155.2 (COO^tBu); 138.5, 129.7, 129.5, 128.3, 128.1 (4 arom. C of Phe); 99.2 (C(1)); 80.5 (OCMe₃); 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 (COOMe); 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 (OCMe₃); 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 ($[M + \text{Na}]^+$), 692.3 ($[M + \text{H}]^+$), 614.2 ($[M - \text{Boc} + \text{Na}]^+$), 536.2 ($[M - \text{menthyl}]^+$), 480.1 ($[M - \text{Boc} - \text{menthyl} + 2\text{Na}]^+$).

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 Et₂O to afford **32** (343 mg) in a yield of 63.6% as a colorless solid. $^1\text{H-NMR}$ (600 MHz, CDCl₃): 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 -CH₂ of Phe); 2.98 (*dd*, $J = 13.6, 7.2$, 1 H of β -CH₂ 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). $^{13}\text{C-NMR}$ (150 MHz, CDCl₃): 172.7 (CONH of Phe); 172.1 (C(6)); 170.2 (COOMe); 156.6 (COO^tBu); 136.5, 129.3, 128.7, 127.0 (4 arom. C of Phe); 100.0 (C(1)); 80.5 (OCMe₃); 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 (OCMe₃); 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 ($[M + \text{Na}]^+$), 596.3 ($[M + \text{H}]^+$).

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-[[[(1S,2S,5S)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-[(Benzyloxy)carbonyl]amino]-2-deoxy- β -D-glucopyranosiduronyl]amino]-2-deoxy- β -D-glucopyranosiduronyl]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 CH₂Cl₂ (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 Et₂O and then purified by gel filtration (*Sephadex LH-20*) to yield **33** (86.5 mg) as a colorless solid in 41.2% yield. $^1\text{H-NMR}$ (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 CH₂ of Z); 4.92 (br. *s*, 1 H of CH₂ 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 -CH₂ 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). $^{13}\text{C-NMR}$ (150 MHz, (D_6) DMSO): 169.9 (C(6), C(6')); 169.6 (COOMe); 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 (CH₂ of Z); 55.6 (C(2), C(2')); 54.5 (α -C of Gly); 47.3 (C(2) of menthyl); 40.4 (COOMe); 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 ($[M + \text{Na}]^+$), 782.2 ($[M + \text{H}]^+$), 670.4 ($[M - Z + \text{H} + \text{Na}]^+$). MALDI-MS (rel. to angiotensin): 804.4 ($[M + \text{Na}]^+$), 671.6 ($[M - Z + 2\text{H} + \text{Na}]^+$).

8.2. *[(3-Methylbutyl 2-[[[(1S,2S,5S)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-[(Benzyloxy)carbonyl]amino]-2-deoxy- α -D-glucopyranosiduronyl]glyciny]amino]-2-deoxy- β -D-glucopyranosiduronyl]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 (SiO₂; CHCl₃/MeOH 30:1) to afford **34** (53.9 mg) in 17% yield. $^1\text{H-NMR}$ (600 MHz, (D_6) DMSO): 8.31 (*t*, $J = 5.8$, NH of Gly¹); 7.88 (*t*, $J = 5.3$, NH of Gly²); 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*, CH₂ 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 -CH₂ of Gly¹); 3.77 (*dd*, *J* = 16, 5.3, α -CH₂ of Gly²); 3.74 (*m*, 1 H of isoamyl); 3.69 (*dd*, *J* = 16, 5.3, 1 H of CH₂ of Gly²); 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). ¹³C-NMR (150 MHz, (D₆)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 (CH₂ 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 Gly²); 40.6 (α -C of Gly¹); 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* – isoamyl]⁺), 595.2 ([*M* – isoamyl – menthyl]⁺). Anal. calc. for C₄₀H₆₂N₄O₁₅ · 6 H₂O: 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]glycinyloxy]-*D*-phenylalanyl]amino]-2-deoxy- β -*D*-glucopyranosid-uronol]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 Et₂O/pentane furnished a crude product (82 mg), which was purified by prep. RP-HPLC (*Si 60-10-C18*; MeCN/H₂O (pH 7) 60 : 40, isocratic) to afford **35** (48 mg) in 42% yield. ¹H-NMR (600 MHz, (D₆)DMSO)³): 8.32 (*t*, *J* = 5.7, NH of Gly¹); 8.12 (*d*, *J* = 9, NH of Phe¹); 8.03 (*d*, *J* = 9, 2-NH); 7.93 (*d*, *J* = 9.4, 2'-NH); 7.84 (*br. t*, NH of Gly²); 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 Phe² (major)); 6.18 (*br. d*, *J* = 8, 0.3 NH of Phe² (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 Phe¹); 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 Phe²); 3.89 (*m*, *J* = 5.7, α -CH₂ of Gly¹); 3.83 (*dd*, *J* = 16, 6, 1 H of α -CH₂ of Gly²); 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 CH₂ of Gly², 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 -CH₂ of Phe¹ and Phe², resp., 1 H of fenchyl); 2.74–2.65 (*br. m*, 1 H of β -CH₂ of Phe¹ and Phe², resp.), 1.61 (*br. m*, 1 H of fenchyl); 1.57–1.41 (*br. m*, 2 \times 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 OCMe₃ (major)); 1.12–1.05 (*br. s*, 3 H, OCMe₃ (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). ¹³C-NMR (150 MHz, (D₆)DMSO): 171.1, 170.2, 169.4, 168.7 (4 CONH); 167.9 (COOMe); 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 (OCMe₃); 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 Phe¹); 55.6 (α -C of Phe²); 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 Gly²); 40.9 (CH of fenchyl); 40.6 (α -C of Gly¹); 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 (OCMe₃); 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* – Boc]⁺). MALDI-MS (rel. to angiotensin): 1133 ([*M* + Na]⁺).

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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