# Synthesis and Biological Evaluation of a Backbone-Modified Phytoalexin Elicitor

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**Abstract**: Two suitably protected building blocks (**11** and **33**) for the preparation of amide-linked heptaglucoside mimetic **2**, an analogue of the naturally occurring phytoalexin elicitor **1a**, were readily accessible by glycal chemistry. Sequential elongation of terminal glucuronide **21** with laminaribiosyl hemiaminal **33** and anomeric amine **11** by EDC/HOBt-catalyzed condensation and two-step conversion of the C6-OTr moiety into the corresponding carboxylate function afforded homogeneous carbopeptoid **2** in high overall yield. It was found that replacement of the acetal linkages by the more rigid amide bonds destroys the phytoalexin-elicitor activity.

**Keywords**
bioorganic chemistry · carbohydrates · glycosides · peptide bonds · phytochemistry

## Introduction

More than ten years ago, Albersheim et al. reported that the branched β-D-glucohexaosyl glucitol **1a** (Figure 1),[1] isolated from the mycelial walls of *Phytophtora megasperma* (*f.sp. glycinea*), showed phytoalexin-elicitor activity[2] in soybean. Studies in our laboratory revealed that the synthetically prepared α-methyl $3^2,3^4$-di-β-D-glucopyranosylgentiopentaoside (**1b**) exhibits the same phytoalexin-elicitor activity[4] as naturally occurring **1a**.[3] Structure–activity studies showed[5] that the glucosyl units C, C′ and E are essential for maximum elicitor activity. However, the biopotency was reduced considerably if the two side-chain glucosyl units C and C′ were attached to adjacent backbone glucosyl residues (i.e. the isomer $3^3,3^4$-di-β-D-glucopyranosylgentiopentaose).[6] The outcome of the latter structure–activity studies implies that the biopotency of **1a** is more or less governed by a defined spatial alignment of the glucopyranosyl units along the linear sugar backbone. In this context, it was of interest to find out whether restriction of the conformational freedom of the β-(1 → 6) backbone linkages would impair the phytoalexin-elicitor activity. Thus far, several approaches dealing with the synthesis of carbohydrate mimics containing peptide instead of the natural interglycosidic bonds have been published.[7] The ease of introduction of an amide function, which is more rigid than a glycosidic bond, prompted us to prepare the amide–saccharide hybrid **2**, the backbone of which consists of a β-(1 → 6)-linked glucuronosylamide chain.

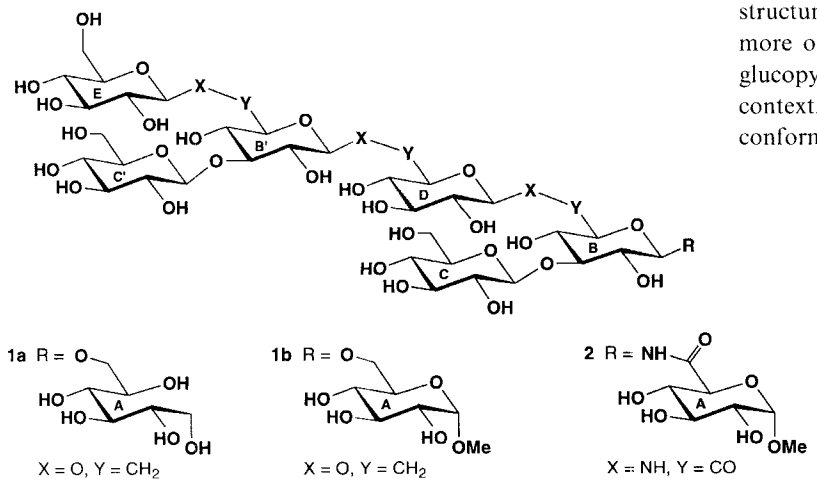


Figure 1. Structures of the naturally occuring phytoalexin elicitor **1a**, methyl heptaglucoside (**1b**) and carbopeptoid **2**.

## Results and Discussion

Prior to the preparation of target compound **2**, efforts were focused on the assembly of the linear β-(1 → 6)-amide-linked gentiotetraose[8] analogue **29**. It was envisaged that the (9*H*-fluoren-9-ylmethoxy)carbonyl (Fmoc) strategy, as followed earlier for the preparation of carbopeptoids,[7] could be adopted for the introduction of the requisite β-(1 → 6)-amide bonds. To this end, the condensation of the terminal β-glucosylamine **10** with

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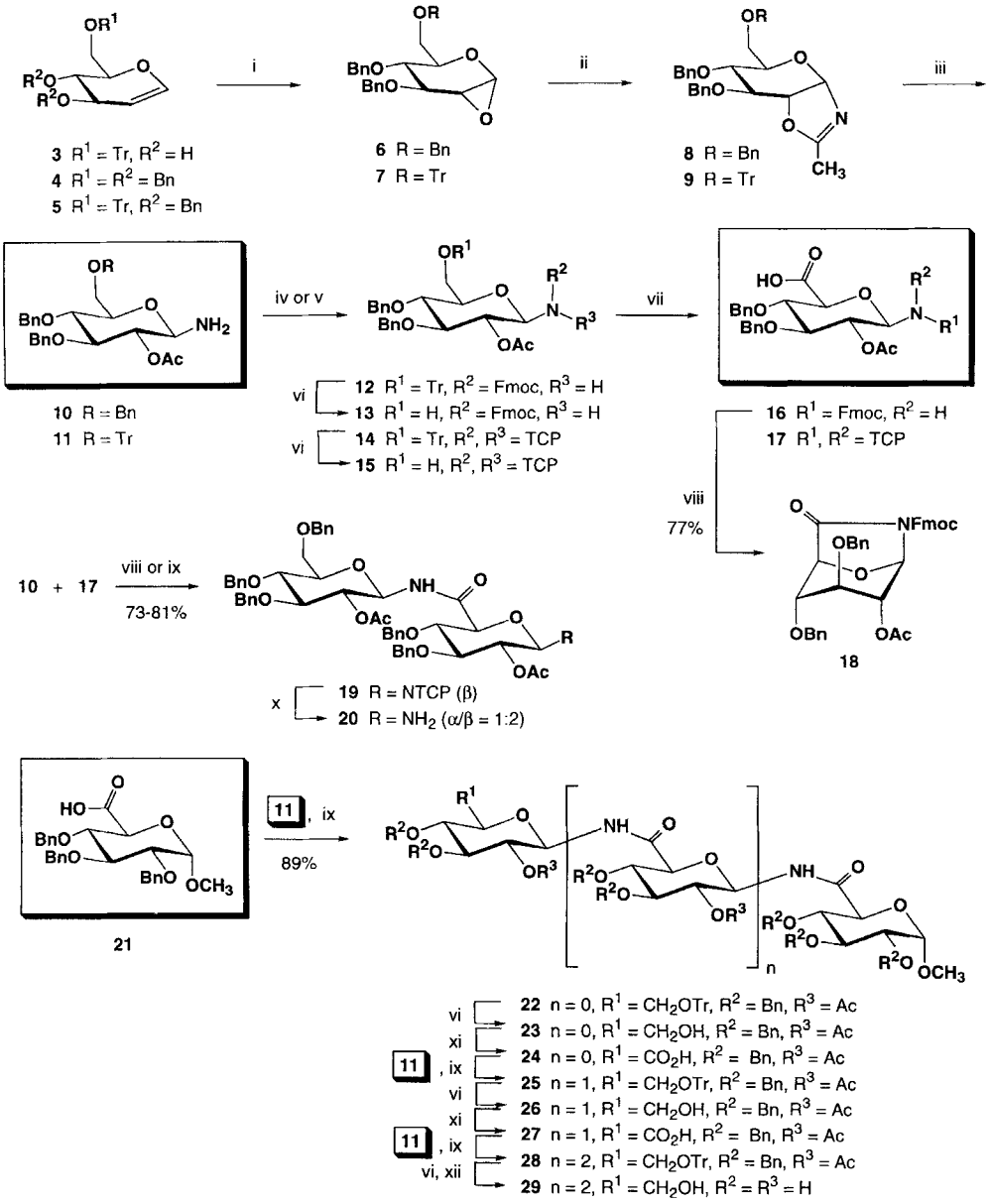


Scheme 1. i) 3,3-dimethyldioxirane, $CH_2Cl_2$/acetone, 0 °C, 5 min, quant.; ii) $CH_3CN$, $ZnCl_2$, 2 h, **8**: 65%, **9**: 63%; iii) 0.1 equiv $H_2SO_4$, THF/$H_2O$ (5:1, v/v), 15 min, quant.; iv) FmocOSu, $NaHCO_3$, $Na_2CO_3$, dioxane/$H_2O$ (1:1, v/v), 3 h, 87%; v) a: TCPO, $NEt_3$, $CH_2Cl_2$, 1 h; b: $Ac_2O$, pyr, 12 h, 69%; vi) 4% *p*-TsOH, $CH_2Cl_2$/MeOH (1:1, v/v), 2 h, **13**: 96%, **15**: 89%, **23**: 94%, **26**: 92%; vii) cat. TEMPO, NaOCl, $NaHCO_3$, NaCl, KBr, $Bu_4NCl$, $CH_2Cl_2/H_2O$ (1:1, v/v), 30 min, **16**: 84%, **17**: 81%; viii) BOP, *DIPEA*, $CH_2Cl_2$, 1 h; ix) EDC, HOBt, THF, 10 h, **25**: 84%, **28**: 78%; x) ethylenediamine, $CH_3CN$/EtOH/THF (2:1:1, v/v/v), 20 °C, 10 min, 88%; xi) a: vii; b: $NaClO_2$, $NaH_2PO_4$, 2-methyl-2-butene, *t*BuOH/$H_2O$ (1:1, v/v), 1 h, **24**: 84%, **27**: 81%; xii) a: cat. KO*t*Bu, MeOH/$CH_2Cl_2$ (2:1, v/v), 30 min; b: 3 atm. $H_2$, Pd/C, $CH_2Cl_2$/MeOH/$H_2O$ (1:2:1, v/v/v), 12 h, **28** → **29**: 72%.

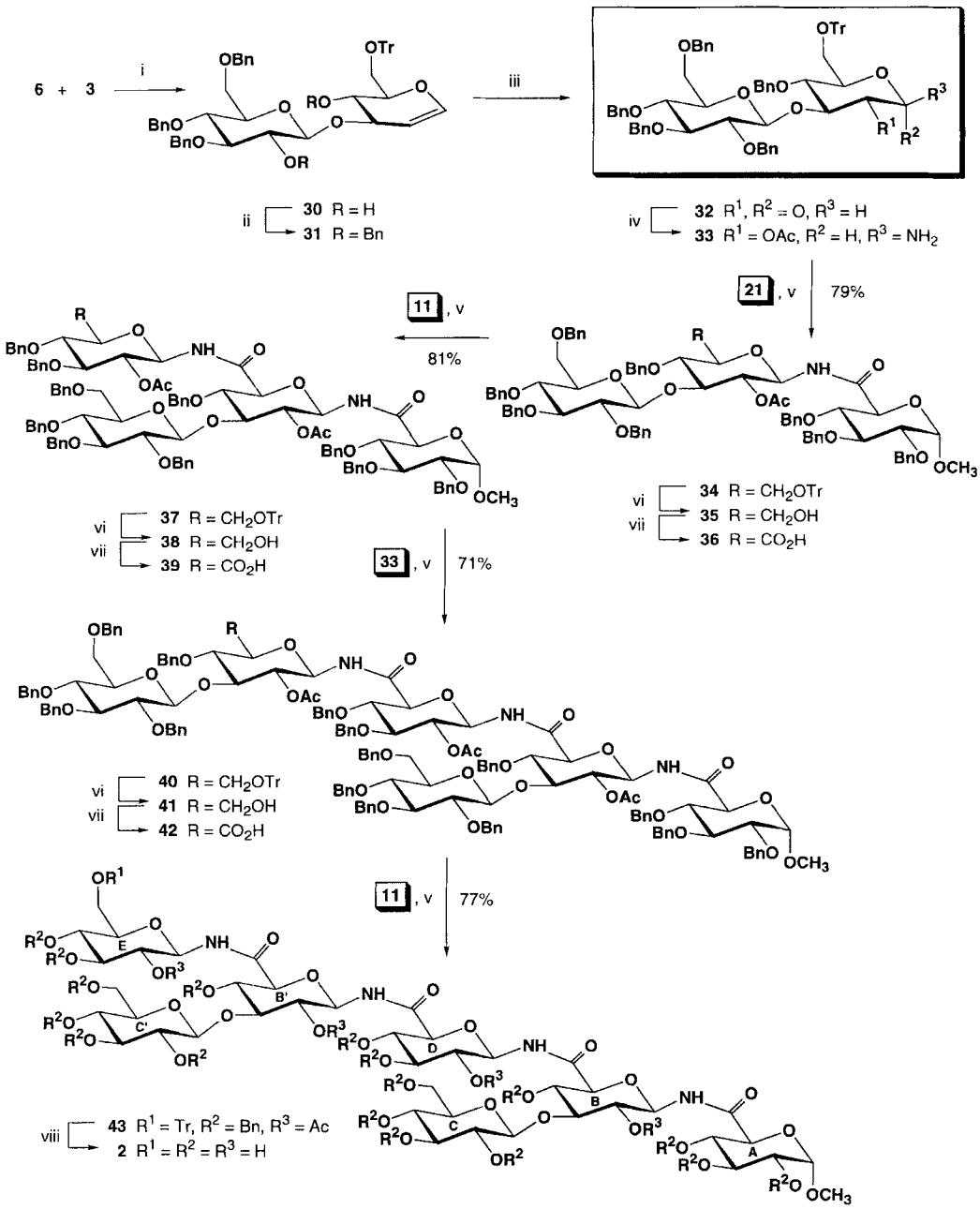
the Fmoc-protected nonterminal glucuronosylamine unit **16** was examined (see Scheme 1).

The two building units **10** and **16** were readily accessible[9] starting from commercially available 3,4,6-tri-*O*-benzyl-D-glucal (**4**) and known 3,4-di-*O*-benzyl-6-*O*-trityl-D-glucal (**5**).[3c] Treatment of **4** with 3,3-dimethyldioxirane (DMD)[10] afforded the α-1,2-epoxide **6**,[11] which was converted with acetonitrile in the presence of $ZnCl_2$ into the α-oxazoline **8** in an overall yield of 65%. Ring-opening of oxazoline **8** with catalytic sulfuric acid[12] in THF/$H_2O$ furnished β-glucosylamine **10** in a quantitative yield. In a similar way, glucal **5** was transformed into hemiaminal **11**. Treatment of anomeric amine **11** with Fmoc-oxysuccinimide (FmocOSu) under Schotten–Baumann conditions gave fully protected derivative **12**. *p*-Toluenesulfonic acid (*p*-TsOH)-mediated detritylation of **12**, followed by oxidation[13] of the resulting primary alcohol **13** with 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) and sodium hypochlorite (NaOCl) under phase-transfer conditions, afforded the Fmoc-protected glucuronosylamine unit **16** in a yield of 81% based on **12**.

At this stage, the anomeric amine in **10** was condensed with the carboxylic acid derivative **16** by means of the coupling agent benzotriazol-1-yloxytris(dimethylamino)-phosphonium hexafluorophosphate (BOP) in the presence of *N*,*N*-diisopropylethylamine (DIPEA) to give the desired dimer fragment **19** (R = NHFmoc) in a yield of 10%. The spectroscopic data of the major product formed in the condensation were in full accordance with the β-(1 → 6)-amide-linked derivative **18**, indicating that the intramolecular amide bond formation proceeds faster than the corresponding intermolecular process.

It occurred to us that protection of the 1-amino function in **11** with the recently devised[14] tetrachlorophthaloyl (TCP) group presented an attractive alternative. Thus, glucosylamine **11** was converted into glucosylimide **14** following the recently reported procedure of Fraser-Reid et al.[15] Detritylation of **14** and TEMPO-mediated oxidation of the free primary alcohol in **15** gave TCP-protected 1-amino-1-deoxy glucuronic acid **17** in a high yield. Subsequent condensation of glucosylamine **10** with glucuronide **17** under the agency of BOP and DIPEA proceeded smoothly to give dimer **19** in a yield of 73%. It is of interest to note that the coupling efficiency of **10** with **17** to give **19** could be enhanced (73 → 81%) by use of the known peptide coupling agent 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) in the presence of the nucleophilic catalyst 1-hydroxybenzotriazole (HOBt). It was established that removal of the TCP moiety in **19** with ethylenediamine led to an epimeric mixture of **20** ($\alpha/\beta = 1:2$). Unfortunately, subjection of **19** to different reaction conditions (THF,

$T = 0-60\,^{\circ}C$, 1–3 equiv ethylenediamine, 5–60 min) did not suppress the anomerisation. Moreover, attempts to convert the α-anomer of **20** into the corresponding β-anomer with catalytic amounts (0.1–1.0 equiv) of $H_2SO_4$ in $THF/H_2O$ met with little success. In order to circumvent anomerisation during deprotection of the TCP group, hemiaminal **11** was now condensed with the known methyl glucuronide **21**[16] under the influence of EDC/HOBt. Work-up and purification gave the fully protected disaccharide analogue **22**, detritylation of which furnished dimer **23** in an overall yield of 84% from **11**. Elongation of the amide chain was effected by oxidation of **23** and subsequent condensation of the newly formed carboxylic acid function in **24** with the nonterminal unit **11**. TEMPO/NaOCl-mediated oxidation of **23** afforded an inseparable mixture of the desired carboxylate **24**, the corresponding aldehyde and its hydrate. Nevertheless, treatment of the crude mixture with $NaClO_2$ in the presence of the radical scavenger 2-methyl-2-butene resulted in complete oxidation to **24** in a yield of 84%.[17] Condensation of **24** with hemiaminal **11** proceeded smoothly to furnish fully protected trisaccharide mimetic **25**. Repetition of the sequence of reactions described above (i.e., two-step conversion of **25** into **27** followed by coupling with **11**) gave tetramer **28**. Deprotection of **28** by detritylation, deacetylation and hydrogenolysis yielded the gentiotetraose mimetic **29**, the homogeneity and identity of which was firmly established by mass spectrometry as well as $^{13}C$ and $^{1}H$ NMR spectroscopy (see Figure 2).




Scheme 2. i) $ZnCl_2$, THF, 0 °C, 15 min, 58%; ii) BnBr, NaH, DMF, 2 h, 87%; iii) 3,3-dimethyldioxirane, $CH_2Cl_2$/acetone, 0 °C, 5 min, 95%; iv) a: $CH_3CN$, $ZnCl_2$, 2 h; b: 0.1 equiv $H_2SO_4$, $THF/H_2O$ (5:1, v/v), 15 min, 59%; v) EDC, HOBt, THF, 10 h; vi) 4% *p*-TsOH, $CH_2Cl_2$/MeOH (1:1, v/v), 2 h, **35**: 91%, **38**: 92%, **41**: 89%; vii) a: cat. TEMPO, NaOCl, $NaHCO_3$, NaCl, KBr, $Bu_4NCl$, $CH_2Cl_2/H_2O$ (1:1, v/v), 30 min; b: $NaClO_2$, $NaH_2PO_4$, 2-methyl-2-butene, *t*BuOH/$H_2O$ (1:1, v/v), 1 h, **36**: 78%, **39**: 77%, **42**: 74%; viii) a: 4% *p*-TsOH, $CH_2Cl_2$/MeOH (1:1, v/v), 2 h; b: cat. KO*t*Bu, MeOH/$CH_2Cl_2$ (2:1, v/v), 30 min; c: 3 atm. $H_2$, Pd/C, $CH_2Cl_2$/MeOH/$H_2O$ (1:2:1, v/v/v), 12 h, 70%.

The crucial transformation of the C6-OTr into the corresponding carboxylate (**22** → **24**) thus being solved, it is evident that the assembly of target heptamer **2** can be accomplished (see Scheme 2) starting from the bifunctional laminaribiosyl unit **33**. The key dimeric hemiaminal **33** was prepared by regioselective condensation of α-1,2-epoxide **6** with 6-*O*-trityl-D-glucal[18] (**3**) yielding dimer glucal **30**,[19] which was subsequently benzylated to afford fully protected glucal **31**. DMD-mediated oxidation of **31** to give α-1,2-oxirane **32**, followed by $ZnCl_2$-mediated reaction with $CH_3CN$ and subsequent ring-opening of the intermediate oxazoline, led to the exclusive formation of the β-oriented laminaribiosyl hemiaminal **33** in 56% yield. EDC/HOBt-assisted condensation of the anomeric amino function in **33** with the methyl glucuronide **21** gave branched trimer **34** in 79% yield. Removal of the trityl group in **34** with *p*-TsOH and two-step oxidation (TEMPO/NaOCl then $NaClO_2$) of the $CH_2OH$ function in **35** yielded trimeric carboxylate **36**. Extension of **36** to the



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fully protected tetrameric unit **37** was accomplished by EDC/HOBt-induced coupling with the core building block **11**. Tetramer **37** was converted into the corresponding carboxylate **39** by detritylation (**37** → **38**) and oxidation. Coupling of **39** with 1-amino disaccharide **33** furnished the fully protected hexasaccharide **40**. Finally, after acidic removal of the trityl group in **40** and oxidation of alcohol **41** to hexasaccharide carboxylate **42**, the terminal residue **11** was introduced by the agency of EDC/HOBt to give the heptasaccharide analogue **43** in 77% yield. Treatment of the doubly branched heptamer **43** with *p*-TsOH followed by Zemplén deacylation of the 2-*O*-acetyl groups and then hydrogenolysis of the benzyl groups over Pd/C furnished target heptasaccharide mimetic **2** in 70% yield. The structure of **2** was unambiguously confirmed by mass spectrometry and NMR spectroscopy (600 MHz $^1$H TOCSY, HH-COSY and CH-COSY). For example, the coupling constants and chemical shifts of the set of four distinct doublets in the $^1$H NMR spectrum (see Figure 2, spectrum I) of the tetrameric fragment **29** are

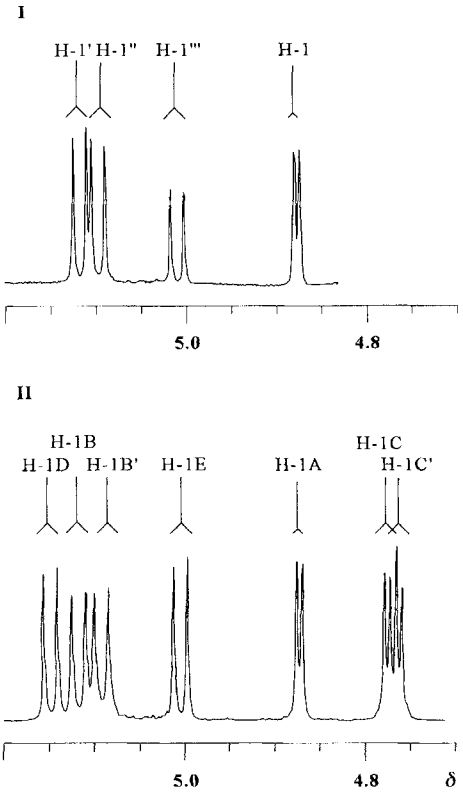


Figure 2. Anomeric regions of the 600 MHz $^1$H NMR spectra of tetramer **29** (I) and heptamer **2** (II).

characteristic for the presence of three $\beta$-(1 → 6)-amide linkages and one $\alpha$-linked methoxy group ($H_1$ corresponds to the glucuronide residue at the reducing end of **29** and $H_{1'''}$ to the glucosylamine unit at the nonreducing end). Three additional doublets, which arise from one $\beta$-(1 → 6)-amide and two $\beta$-(1 → 3)-glucosidic bonds, are observed in the corresponding spectrum (II) of the heptameric fragment **2**.

Preliminary biological studies[20] revealed that the amide-linked analogue **2** does not induce phytoalexin accumulation in soybean.

The dynamic behaviour of the amide-linked gentiobiose carbopeptoid **45** (see Figure 3) was simulated by a 10 ns molecular

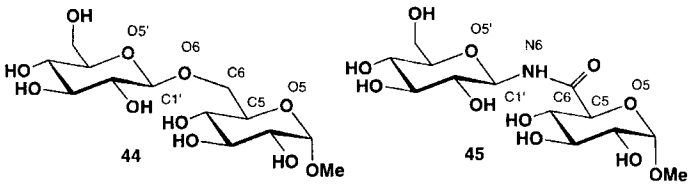


Figure 3. Structures of $\alpha$-methyl gentiobioside **44** and carbopeptoid **45**.

dynamics run at a constant temperature of 300 K, using the recently developed CHEAT95 force field[21] for hydrated oligosaccharides. For comparison, the acetal-linked $\alpha$-methyl gentiobioside **44** (Table 1) was also simulated under the same conditions. The most important difference between gentiobioside **44** and its amide-linked analogue **45** in the simulations is the flexibility of the linkage. The former compound shows many transitions between different conformers, while the latter stays in the same conformation for more than 8 ns. After that, a few transitions to a second conformation can be observed. The average values of the dihedral angles around the linkages of the most significant conformations observed in the simulations are listed in Table 1 and the preferred conformations are shown in Figure 4. It is not excluded that the binding of the flexible acetal-

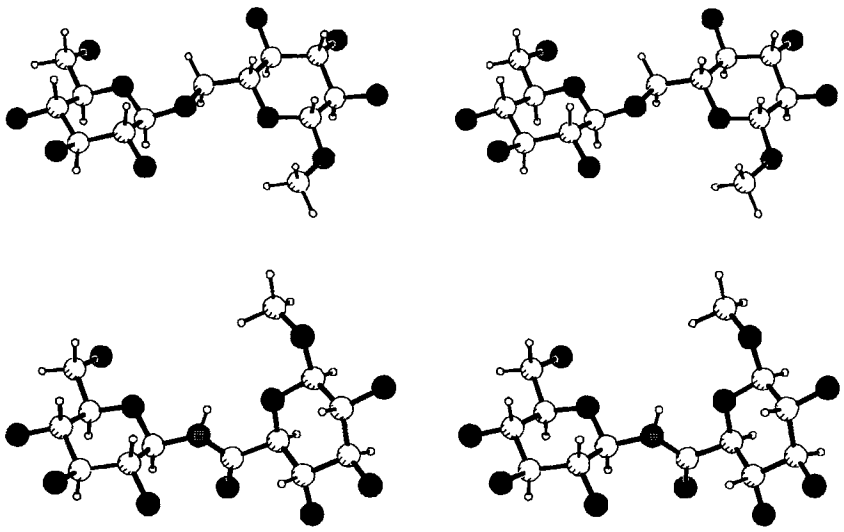

Figure 4. Stereoviews of the preferred conformations of $\alpha$-methyl gentiobioside **44** (above) and carbopeptoid **45** (below).

Table 1. Average torsion angles (degrees) and relative occurrence (%) for the most significant conformations of **44** and **45** in the 10 ns MD simulations.

Acetal-linked $\alpha$-methyl gentiobioside **44**

| O5'-C1'-O6-C6 | C1'-O6-C6-C5 | O6-C6-C5-O5 | % |
|---|---|---|---|
| −50 | −170 | 60 | 55 |
| −40 | 180 | −60 | 25 |
| −60 | −90 | 50 | 5 |
| −50 | 180 | 170 | 5 |
| −40 | 90 | 50 | 5 |

Amide-linked $\alpha$-methyl gentiobioside **45**

| O5'-C1'-N6-C6 | C1'-N6-C6-C5 | N6-C6-C5-O5 | % |
|---|---|---|---|
| −130 | 180 | −10 | 95 |
| 60 | 180 | −20 | 5 |

linked phytoalexin elicitor **1b** to the plant cell receptor proceeds by an induced-fit mechanism. However, the presence of the amide linkages in the conformationally restrained heptaglucoside analogue **2** may prevent such a mode of binding to the receptor, accounting for its lack of activity.

## Conclusion

The results presented in this paper show that elongation of a terminal glucuronide (e.g. **21**) with a suitably protected anomeric amine (e.g. **11** or **33**) and subsequent two-step conversion of the $CH_2OTr$ function in the growing chain into the corresponding carboxylate presents a convenient approach towards $\beta$-(1 → 6)-glucuronosylamide carbopeptoids (e.g. **2** and **29**). Moreover, it is also apparent that replacement of the $\beta$-(1 → 6)-acetal linkages in **1b** by the more rigid amide bonds completely ruins the phytoalexin-elicitor activity. It may therefore be concluded that incorporation of an amide instead of a natural glycosidic bond into oligosaccharides has a detrimental effect on the molecular geometry and hydrogen-bonding potential.

## Experimental Section

$^1H$ and $^{13}C$ NMR spectra were recorded with a Jeol JNM-FX-200 (200/50.1 MHz), a Bruker WM-300 (300/75.1 MHz) or a Bruker DMX-600 spectrometer (600/150.3 MHz). Chemical shifts ($\delta$) are given relative to tetramethylsilane as internal standard. Mass spectra were recorded with a Finnigan MAT TSQ70 triple quadropole mass spectrometer. Optical rotations were measured on a Propol automatic polarimeter. Dichloromethane ($CH_2Cl_2$), pyridine and toluene were heated under reflux with $CaH_2$ for 3 h, distilled and stored over molecular sieves (4 Å). *N,N*-Diisopropylethylamine (DIPEA) was subsequently distilled from KOH, ninhydrin and $CaH_2$. Triethylamine was distilled from $CaH_2$. Acetone (Boom Chemicals, c.p.), acetonitrile (Rathburn, HPLC grade), 1,2-dichloroethane (Biosolvent, HPLC grade), *N,N*-dimethylformamide (DMF, Baker, p.a.), 1,4-dioxane (Baker, p.a.), ethanol (Baker, p.a.) and tetrahydrofuran (THF, Biosolvent, HPLC grade) were stored over molecular sieves (4 Å). Methanol (Rathburn, HPLC grade) was stored over molecular sieves (3 Å). Zinc chloride (Merck, p.a.) was dissolved in THF (1.0 M solution) and stored over molecular sieves (3 Å). Acetic anhydride (Baker, p.a.), benzotriazol-1-yloxytris(dimethylamino)-phosphonium hexafluorophosphate (BOP, Richelieu), benzyl bromide (Merck), *tert*-butanol (Baker, p.a.), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, Acros), ethylenediamine (Acros, p.a.), 1-hydroxybenzotriazole (HOBt, Aldrich), 9-fluorenylmethoxycarbonyloxysuccinimide (FmocOSu, Nova Biochem), 2-methyl-2-butene (Aldrich), Oxone® (Aldrich), palladium on carbon (10%, Acros), potassium *tert*-butoxide (Aldrich), sodium chlorite (Acros), sodium hydride (Acros, 60% dispersion in mineral oil), sodium hypochlorite (13% active chlorine solution, Acros), tetra-*n*-butylammonium chloride, tetrachlorophthalic anhydride (TCPO, Acros), 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO, Aldrich), *p*-toluenesulfonic acid monohydrate (Aldrich) and trityl chloride (TrCl, Merck) were used as received. Column chromatography was performed on Baker silica gel (0.063–0.200 mm). Gel permeation chromatography was accomplished on HW-40 column material (Pharmacia). TLC analysis was carried out on prepared plates from Schleicher & Schüll (F1500, LS254) with detection by UV absorption (254 nm) where applicable and charring with 20% $H_2SO_4$ in MeOH or ammonium molybdate (25 g $L^{-1}$) and ceric ammonium sulfate (10 g $L^{-1}$) in 10% aq. $H_2SO_4$. Reactions were run at ambient temperature, unless otherwise stated. Prior to reactions that required anhydrous conditions, traces of water in the glycosides were removed by coevaporation with 1,2-dichloroethane, pyridine or toluene.

**(3a*S*,5*R*,6*R*,7*S*,7a*R*)-6,7-Bis(benzyloxy)-5-(trityloxymethyl)-2-methyl-5*H*-pyrano[2,3-*d*]oxazole (9)**: Under a continuous stream of dry nitrogen, $ZnCl_2$ (1.0 M solution in THF, 30 mL) was added to a stirred solution of epoxide **7** (11.7 g, 20 mmol) in $CH_3CN$ (100 mL). The reaction mixture was stirred for 2 h, subsequently diluted with EtOAc (400 mL) and washed with sat. aq. NaCl (2 × 100 mL) and aq. $NaHCO_3$ (1.0 M, 100 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by silica gel chromatography (20–50% EtOAc/light petroleum) afforded oxazoline **9** as a white foam (7.9 g, 12.6 mmol, 63%). $^1H$ NMR ($CDCl_3$): $\delta$ = 7.52–6.89 (m, 25H, $H_{arom}$), 5.99 (d, 1H, H1, $J_{1,2}$ = 8.1 Hz), 4.85 (dd, 1H, H2, $J_{2,3}$ = 8.4 Hz), 4.70 (AB, 2H, $CH_2$ Bn), 4.54 (AB, 2H, $CH_2$ Bn), 3.81–3.79 (m, 2H, H3/H4), 3.60 (m, 2H, H5/H6), 3.28 (m, 1H, H6′), 2.03 (s, 3H, $CH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 168.0 (C=N), 143.6 ($C_q$ Tr), 137.6, 137.5 ($C_q$ Bn), 128.5–126.7 ($C_{arom}$), 93.1 (C1, $J_{C,H}$ = 168.5 Hz), 86.3 ($C_q$ Tr), 80.0, 79.8, 74.5, 71.5 (C2/C3/C4/C5), 73.4, 72.1 ($CH_2$ Bn), 62.9 (C6), 14.0 ($CH_3$).

**2-*O*-Acetyl-3,4-di-*O*-benzyl-6-*O*-trityl-$\beta$-D-glucopyranosylamine (11)**: To a stirred solution of oxazoline **9** (7.9 g, 12.6 mmol) in THF/$H_2O$ (100 mL, 5:1, v/v) was added aq. $H_2SO_4$ (1.0 M, 1.26 mL). After 30 min, the reaction mixture was quenched by addition of aq. $NaHCO_3$ (1.0 M, 50 mL). The neutralised mixture was extracted with EtOAc (2 × 200 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting colourless oil was purified by flash chromatography over silica gel (50% EtOAc/light petroleum) to furnish glucosylamine **11** as a white solid in quantitative yield (8.1 g, 12.6 mmol). $[\alpha]_D$ = +12.6 ($c$ = 1, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ = 7.52–6.84 (m, 25H, $H_{arom}$), 4.90 (dd, 1H, H2, $J_{1,2}$ = 8.8 Hz, $J_{2,3}$ = 9.6 Hz), 4.67 (AB, 2H, $CH_2$ Bn), 4.60 (AB, 2H, $CH_2$ Bn), 4.07 (d, 1H, H1), 3.86 (dd, 1H, H3, $J_{3,4}$ = 9.4 Hz), 3.69–3.42 (m, 3H, H4/H5/H6), 3.21 (dd, 1H, H6′, $J_{5,6'}$ = 3.6 Hz, $J_{6,6'}$ = 10.1 Hz), 2.03 (s, 3H, $CH_3$ Ac), 1.80 (brs, 2H, $NH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 170.2 (C=O Ac), 143.5 ($C_q$ Tr), 138.0, 137.5 ($C_q$ Bn), 128.5–126.7 ($C_{arom}$), 86.1 ($C_q$ Tr), 84.3 (C1, $J_{C,H}$ = 158.2 Hz), 83.3, 78.0, 75.5, 74.2 (C2/C3/C4/C5), 75.0, 74.6 ($CH_2$ Bn), 62.2 (C6), 20.8 ($CH_3$ Ac); $C_{41}H_{41}NO_6$ (643.3): calcd. C 76.49, H 6.42, N 2.18; found C 76.35, H 6.20, N 2.09.

***N*-(Fluoren-9-ylmethoxycarbonyl)-2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-trityl-$\beta$-D-glucopyranosylamine (12)**: To a stirred mixture of glucosylamine **11** (3.22 g, 5.0 mmol), dioxane (25 mL) and $H_2O$ (25 mL) containing $NaHCO_3$ (1.68 g, 20.0 mmol) and $Na_2CO_3$ (1.06 g, 10.0 mmol) was added FmocOSu (2.02 g, 6.0 mmol). After 3 h, the reaction mixture was extracted with EtOAc (2 × 100 mL) and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The resulting pale yellow oil was purified by silica gel chromatography (0–25% EtOAc/light petroleum) to furnish carbamate **12** as a white foam (3.77 g, 4.4 mmol, 87%). $^1H$ NMR ($CDCl_3$): $\delta$ = 7.87–6.93 (m, 33H, $H_{arom}$), 5.81 (d, 1H, NH, $J_{1,NH}$ = 6.6 Hz), 5.07 (dd, 1H, H1, $J_{1,2}$ = 6.8 Hz), 4.76 (AB, 2H, $CH_2$ Bn), 4.69 (AB, 2H, $CH_2$ Bn), 4.46 (d, 2H, $CH_2$ Fmoc), 4.33 (t, 1H, CH Fmoc), 4.08 (dd, 1H, H2, $J_{2,3}$ = 9.6 Hz), 3.78–3.62 (m, 4H, H3/H4/H5/H6), 3.25 (dd, 1H, H6′, $J_{5,6'}$ = 2.8 Hz, $J_{6,6'}$ = 10.1 Hz), 2.07 (s, 3H, $CH_3$ Ac); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 171.4 (C=O Ac), 156.2 (C=O Fmoc), 144.9, 141.7 ($C_q$ Fmoc), 144.2 ($C_q$ Tr), 138.6, 138.1 ($C_q$ Bn), 129.2–120.3 ($C_{arom}$), 86.8 ($C_q$ Tr), 83.5 (C1), 81.3, 78.2, 76.7, 73.3 (C2/C3/C4/C5), 74.8, 74.5 ($CH_2$ Bn), 65.4 ($CH_2$ Fmoc), 62.5 (C6), 47.3 (CH Fmoc), 21.2 ($CH_3$ Ac); $C_{56}H_{51}NO_8$ (865.4): calcd. C 77.67, H 5.94, N 1.62; found C 77.70, H 5.98, N 1.51.

***N*-(Fluoren-9-ylmethoxycarbonyl)-2-*O*-acetyl-3,4-di-*O*-benzyl-$\beta$-D-glucopyranosylamine (13)**: A solution of *p*-TsOH (4%, 4.0 g) in MeOH/$CH_2Cl_2$ (100 mL, 1:1, v/v) was added to a stirred solution of compound **12** (3.77 g, 4.4 mmol) in $CH_2Cl_2$ (4 mL). After 2 h, the reaction mixture was neutralised by addition of aq. $NaHCO_3$ (1.0 M, 50 mL) and extracted with EtOAc (2 × 100 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure, and the resulting pale yellow oil was subjected to silica gel chromatography (20–50% EtOAc/light petroleum) to afford alcohol **13** as a white solid (2.60 g, 4.2 mmol, 96%). $^1H$ NMR ($CDCl_3$): $\delta$ = 7.78–7.30 (m, 18H, $H_{arom}$), 6.68 (d, 1H, NH, $J_{1,NH}$ = 6.4 Hz), 4.85 (dd, 1H, H1, $J_{1,2}$ = 7.1 Hz), 4.82 (AB, 2H, $CH_2$ Bn), 4.72 (AB, 2H, $CH_2$ Bn), 4.37 (m, 3H, $CH_2$ Fmoc, H2), 4.25 (t, 1H, CH Fmoc), 3.90–3.70 (m, 3H, H3/H4/H5), 3.62 (m, 2H, H6/H6′), 1.95 (s, 3H, $CH_3$ Ac); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 170.8 (C=O Ac), 155.7 (C=O Fmoc), 143.6, 141.2 ($C_q$ Fmoc), 138.1, 137.9 ($C_q$ Bn), 128.3–119.9 ($C_{arom}$), 83.0 (C1), 80.8, 77.2, 77.1, 72.7 (C2/C3/C4/C5), 75.2, 75.0 ($CH_2$ Bn), 65.7 ($CH_2$ Fmoc), 61.0 (C6), 46.8 (CH Fmoc), 20.7 ($CH_3$ Ac); $C_{37}H_{37}NO_8$ (623.3): calcd. C 71.25, H 5.98, N 2.25; found C 71.35, H 6.03, N 2.16.



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***N,N*-Tetrachlorophthaloyl-2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-trityl-β-D-glucopyranosylamine (14)**: Tetrachlorophthalic anhydride (1.72 g, 6.0 mmol) was added to a stirred solution of glucosylamine **11** (3.22 g, 5.0 mmol) in $CH_2Cl_2$ (25 mL) containing triethylamine (0.84 mL, 6.0 mmol). The reaction mixture was stirred for 1 h and concentrated in vacuo, and the resulting slurry was dissolved in pyridine (15 mL). Acetic anhydride (1.42 mL, 15 mmol) was added to the latter solution and the reaction mixture was stirred for 12 h and subsequently concentrated under reduced pressure. The residue was dissolved in EtOAc (100 mL), washed with aq. $NaHCO_3$ (2 × 50 mL), dried ($MgSO_4$) and concentrated in vacuo. Traces of pyridine were removed by coevaporation with toluene (3 × 50 mL). Purification was accomplished by silica gel chromatography (0–30% EtOAc/light petroleum) to afford glucosylimide **14** as a white foam (3.15 g, 3.5 mmol, 69%). $^1$H NMR ($CDCl_3$): $\delta$ = 7.51–6.94 (m, 25H, $H_{arom}$), 5.88 (dd, 1H, H2, $J_{1,2}$ = 9.4 Hz, $J_{2,3}$ = 9.2 Hz), 5.30 (d, 1H, H1), 4.73 (AB, 2H, $CH_2$ Bn), 4.67 (AB, 2H, $CH_2$ Bn), 4.07 (dd, 1H, H3, $J_{3,4}$ = 9.6 Hz), 3.76 (dd, 1H, H4, $J_{4,5}$ = 9.2 Hz), 3.62 (dd, 1H, H6, $J_{5,6}$ = 2.1 Hz, $J_{6,6'}$ = 11.0 Hz), 3.55 (m, 1H, H5), 3.25 (dd, 1H, H6′, $J_{5,6'}$ = 4.1 Hz), 1.81 (s, 3H, $CH_3$ Ac); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 170.0 (C=O Ac), 161.6 (C=OTCP), 143.9 ($C_q$ Tr), 140.5, 130.1, 127.3 ($C_q$ TCP), 138.3, 137.8 ($C_q$ Bn), 128.9–127.0 ($C_{arom}$), 86.8 ($C_q$ Tr), 83.7 (C1), 78.9, 77.8, 77.4, 71.1 (C2/C3/C4/C5), 75.5, 75.2 ($CH_2$ Bn), 63.0 (C6), 20.7 ($CH_3$ Ac); $C_{49}H_{39}Cl_4NO_8$ (909.1): calcd. C 64.56, H 4.31, N 1.54; found C 64.55, H 4.29, N 1.55.

***N,N*-Tetrachlorophthaloyl-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucopyranosylamine (15)**: Compound **14** (3.15 g, 3.5 mmol) was detritylated as described for the preparation of **13** from **12** and subsequently subjected to silica gel chromatography (20–50% EtOAc/light petroleum) to give alcohol **15** as a white solid (2.06 g, 3.1 mmol, 89%). $^1$H NMR ($CDCl_3$): $\delta$ = 7.45–7.39 (m, 10H, $H_{arom}$), 5.91 (dd, 1H, H2, $J_{1,2}$ = 9.2 Hz, $J_{2,3}$ = 7.7 Hz), 5.44 (dd, 1H, H1, $J_{1,3}$ = 1.5 Hz), 4.96 (AB, 2H, $CH_2$ Bn), 4.87 (AB, 2H, $CH_2$ Bn), 4.02–3.84 (m, 4H, H3/H4/H6/H6′), 3.70 (m, 1H, H5), 1.93 (s, 3H, $CH_3$ Ac); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 169.9 (C=O Ac), 161.7 (C=O TCP), 140.2, 129.9, 126.9 ($C_q$ TCP), 138.2, 137.9 ($C_q$ Bn), 128.3–127.6 ($C_{arom}$), 83.4 (C1), 78.6, 78.5, 76.9, 70.7 (C2/C3/C4/C5), 75.2, 75.1 ($CH_2$ Bn), 61.3 (C6), 20.6 ($CH_3$ Ac); $C_{30}H_{25}Cl_4NO_8$ (667.0): calcd. C 53.83, H 3.76, N 2.09; found C 53.70, H 3.84, N 2.09.

***N*-(Fluoren-9-ylmethoxycarbonyl)-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucuronopyranosylamine (16)**: Alcohol **13** (2.60 g, 4.2 mmol) was dissolved in $CH_2Cl_2$ (20 mL). To this solution was added TEMPO (10 mg, 64 μmol), sat. aq. $NaHCO_3$ (10 mL), KBr (50 mg, 0.42 mmol) and $(n$Bu$)_4$NCl (60 mg). The heterogeneous mixture was cooled (0 °C), after which a solution of aq. NaOCl (13% active chlorine, 8 mL), sat. aq. $NaHCO_3$ (5 mL) and sat. aq. NaCl (10 mL) was added dropwise over 15 min under vigourous stirring. 15 min after the final addition the reaction mixture was acidified with aq. HCl (0.5 M, 20 mL) and extracted with EtOAc. The combined organic phase was dried ($MgSO_4$) and concentrated under reduced pressure, and the resulting pale yellow oil was subjected to silica gel chromatography (0–3% MeOH/$CH_2Cl_2$) to afford carboxylic acid **16** as a white solid (2.23 g, 3.5 mmol, 84%). $^1$H NMR ($CDCl_3$): $\delta$ = 7.76–7.28 (m, 18H, $H_{arom}$), 6.91 (d, 1H, NH, $J_{1,NH}$ = 5.8 Hz), 4.98 (dd, 1H, H1, $J_{1,2}$ = 8.8 Hz), 4.84 (AB, 2H, $CH_2$ Bn), 4.68 (AB, 2H, $CH_2$ Bn), 4.58 (dd, 1H, H2, $J_{2,3}$ = 8.1 Hz), 4.41 (d, 1H, H5, $J_{4,5}$ = 7.9 Hz), 4.36–4.22 (m, 3H, $CH_2$ Fmoc, H4), 4.19 (t, 1H, CH Fmoc), 3.96 (dd, 1H, H3, $J_{3,4}$ = 9.2 Hz), 2.01 (s, 3H, $CH_3$ Ac); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 171.4, 170.7 (C=O Ac, C6), 155.6 (C=O Fmoc), 143.4, 140.9 ($C_q$ Fmoc), 137.8, 137.4 ($C_q$ Bn), 128.2–119.7 ($C_{arom}$), 81.9 (C1), 80.6, 79.5, 75.7, 71.9 (C2/C3/C4/C5), 75.2, 74.7 ($CH_2$ Bn), 67.5 ($CH_2$ Fmoc), 46.5 (CH Fmoc), 20.6 ($CH_3$ Ac); MS (ESI): $m/z$ = 638 ($M$+H$^+$), 655 ($M$+NH$_4^+$), 660 ($M$+Na$^+$); $C_{37}H_{35}NO_9$ (637.2): calcd. C 69.69, H 5.53, N 2.20; found C 69.52, H 5.57, N 2.18.

***N,N*-Tetrachlorophthaloyl-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucuronopyranosylamine (17)**: Alcohol **15** (2.06 g, 3.1 mmol) was oxidised with TEMPO/NaOCl as described for the synthesis of **16** from **13** and the resulting pale yellow oil was subjected to silica gel chromatography (0–3% MeOH/$CH_2Cl_2$) to afford carboxylic acid **17** as a white solid (1.70 g, 2.5 mmol, 81%). $^1$H NMR ($CDCl_3$): $\delta$ = 7.42–7.37 (m, 10H, $H_{arom}$), 6.03 (dd, 1H, H2, $J_{1,2}$ = 9.4 Hz, $J_{2,3}$ = 7.5 Hz), 5.60 (d, 1H, H1), 4.96–4.77 (m, 4H, 2 × $CH_2$ Bn), 4.36 (d, 1H, H5, $J_{4,5}$ = 7.9 Hz), 4.19 (dd, 1H, H4, $J_{3,4}$ = 9.0 Hz), 3.94 (dd, 1H, H3), 1.95 (s, 3H, $CH_3$ Ac); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 169.6, 168.9 (C6, C=O Ac), 161.3 (C=O TCP), 140.1, 129.7, 126.6 ($C_q$ TCP), 137.6, 137.1 ($C_q$ Bn), 127.9–127.3 ($C_{arom}$), 82.4 (C1), 78.6, 78.0, 76.1, 69.5 (C2/C3/C4/C5), 77.3, 76.6 ($CH_2$ Bn), 19.9 ($CH_3$ Ac); MS (ESI): $m/z$ = 682 ($M$+H$^+$), 699 ($M$+NH$_4^+$); $C_{30}H_{23}Cl_4NO_9$ (681.0): calcd. C 52.73, H 3.39, N 2.05; found C 52.70, H 3.42, N 2.05.

***N*-Fluoren-9-ylmethoxycarbonyl-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucuronopyranosylamide (18)**: BOP (0.243 g, 0.55 mmol) was added to a stirred solution of glucosylamine **10** (0.246 g, 0.5 mmol), glucuronide **16** (0.319 g, 0.5 mmol) and DIPEA (0.26 mL, 1.5 mmol) in $CH_2Cl_2$ (3 mL). Stirring was continued for 1 h, after which the reaction mixture was diluted with EtOAc (50 mL) and washed with aq. phosphate buffer (pH = 7, 0.1 M, 2 × 10 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by silica gel chromatography (0–30% EtOAc/light petroleum) afforded glucuronosylamide **18** as a white foam (0.238 g, 0.39 mmol, 77%). When the reaction was carried out in the absence of **10**, the same yield of cyclisation product **18** was obtained. $^1$H NMR ($CDCl_3$): $\delta$ = 7.78–7.07 (m, 18H, $H_{arom}$), 5.69 (t, 1H, H2, $J_{1,2}$ = $J_{2,3}$ = 1.7 Hz), 4.94 (d, 1H, H1), 4.58 (d, 1H, H5, $J_{4,5}$ = 2.2 Hz), 4.53–4.32 (m, 6H, 2 × $CH_2$ Bn, $CH_2$ Fmoc), 4.18 (t, 1H, CH Fmoc), 3.72 (dd, 1H, H4, $J_{3,4}$ = 1.7 Hz), 3.65 (t, 1H, H3), 2.14 (s, 3H, $CH_3$ Ac); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 169.8, 166.8 (C=O Ac, C6), 149.2 (C=O Fmoc), 142.8, 141.1 ($C_q$ Fmoc), 136.8, 136.7 ($C_q$ Bn), 128.4–119.8 ($C_{arom}$), 86.5 (C1), 76.6, 73.6, 71.8, 65.3 (C2/C3/C4/C5), 71.9, 71.4 ($CH_2$ Bn), 68.8 ($CH_2$ Fmoc), 46.3 (CH Fmoc), 20.8 ($CH_3$ Ac); MS (ESI): $m/z$ = 620 ($M$+H$^+$), 637 ($M$+NH$_4^+$), 642 ($M$+Na$^+$), 658 ($M$+K$^+$); $C_{37}H_{33}NO_8$ (619.3): calcd. C 71.79, H 5.33, N 2.26; found C 71.76, H 5.35, N 2.19.

**6-*N*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-1-*N,N*-tetrachlorophthaloyl-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-amidoglucuronopyranosylamine (19)**:

*Method A*: BOP (0.243 g, 0.55 mmol) was added to a stirred solution of glucosylamine **10** (0.246 g, 0.5 mmol), glucuronide **17** (0.340 g, 0.5 mmol) and DIPEA (0.26 mL, 1.5 mmol) in $CH_2Cl_2$ (3 mL). Stirring was continued for 1 h, after which the reaction mixture was diluted with EtOAc (50 mL) and washed with aq. phosphate buffer (pH = 7, 0.1 M, 2 × 10 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue was effected by silica gel chromatography (10–30% EtOAc/light petroleum) to yield dimer **19** as a white foam (0.422 g, 0.37 mmol, 73%).

*Method B*: EDC (0.105 g, 0.55 mmol) was added to a solution of glucosylamine **10** (0.246 g, 0.5 mmol), glucuronide **17** (0.340 g, 0.5 mmol) and HOBt (0.068 g, 0.5 mmol) in THF (3 mL) and the solution was stirred for 10 h. Subsequently, the reaction mixture was diluted with EtOAc (50 mL), washed with aq. $NaHCO_3$ (1.0 M, 3 × 10 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue was accomplished by silica gel chromatography (10–30% EtOAc/light petroleum) to give dimer **19** as a white foam (0.468 g, 0.41 mmol, 81%). $^1$H NMR ($CDCl_3$): $\delta$ = 7.38–7.10 (m, 25H, $H_{arom}$), 7.14 (d, 1H, NH, $J_{NH,1'}$ = 7.4 Hz), 5.95 (dd, 1H, H2, $J_{1,2}$ = 9.4 Hz, $J_{2,3}$ = 8.5 Hz), 5.37 (d, 1H, H1), 5.07 (dd, 1H, H1′, $J_{1',2'}$ = 9.2 Hz), 4.85 (AB, 2H, $CH_2$ Bn), 4.76 (dd, 1H, H2′, $J_{2',3'}$ = 10.6 Hz), 4.72 (AB, 2H, $CH_2$ Bn), 4.63 (AB, 2H, $CH_2$ Bn), 4.56 (AB, 2H, $CH_2$ Bn), 4.45 (AB, 2H, $CH_2$ Bn), 4.07 (d, 1H, H5, $J_{4,5}$ = 8.7 Hz), 3.85 (dd, 1H, H4, $J_{3,4}$ = 8.3 Hz), 3.75 (dd, 1H, H3), 3.73–3.68 (m, 3H, H3′/H4′/H5′), 3.67 (dd, 1H, H6′A, $J_{5',6'A}$ = 2.9 Hz, $J_{6'A,6'B}$ = 9.2 Hz), 3.55 (dd, 1H, H6′B, $J_{5',6'B}$ = 4.6 Hz), 1.87, 1.80 (2 × s, 2 × 3H, 2$CH_3$ Ac); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 170.6, 169.4, 167.8 (C6, 2C=O Ac), 161.5 (C=O TCP), 140.3, 129.9, 126.9 ($C_q$ TCP), 138.0, 137.7, 137.7, 137.5, 137.4 ($C_q$ Bn), 128.1–127.5 ($C_{arom}$), 82.9, 82.4 (C1/C1′), 78.6, 77.8, 77.5, 77.3, 76.4, 76.1, 72.4, 69.2 (C2–C5, C2′–C5′), 75.2, 75.1, 74.9, 74.8, 73.3 ($CH_2$ Bn), 67.9 (C6′), 20.5, 20.4 ($CH_3$ Ac); MS (ESI): $m/z$ = 1155 ($M$+H$^+$), 1172 ($M$+NH$_4^+$); $C_{59}H_{54}Cl_4N_2O_{14}$ (1154.2): calcd. C 61.25, H 4.70, N 2.42; found C 61.24, H 4.76, N 2.43.

**6-*N*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2-*O*-acetyl-3,4-di-*O*-benzyl-α,β-D-amidoglucuronopyranosylamine (20)**: To a stirred solution of dimer **19** (0.578 g, 0.50 mmol) in $CH_3CN$/EtOH/THF (2:1:1, v/v/v, 4 mL) was added ethylenediamine (0.13 mL, 2.0 mmol). After 10 min, the reaction mixture was concentrated under reduced pressure at room temperature, suspended in $CH_2Cl_2$ (25 mL) and filtered through a bed of silica (2 g). The filtrate was concentrated in vacuo to afford anomeric mixture **20** as a white solid (0.391 g, 0.44 mmol, 88%, α/β = 1:2). α-Anomer: $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 172.0, 170.5, 169.3 (C6, 2C=O Ac), 138.1, 137.8, 137.7, 137.6, 137.5 ($C_q$ Bn), 128.3–127.6 ($C_{arom}$), 83.0, 82.1 (C1/C1′), 78.3, 77.4, 76.5, 75.1, 73.5, 72.5, 72.4, 71.0 (C2–C5, C2′–C5′), 75.0, 74.8, 73.5, 72.6, 72.1 ($CH_2$ Bn), 67.8 (C6′), 20.9, 20.3 ($CH_3$ Ac); β-Anomer: $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 171.0,

170.2, 169.4 (C6, 2C=O Ac), 138.1, 137.8, 137.7, 137.6, 137.5 ($C_q$ Bn), 128.3–127.6 ($C_{arom}$), 84.1, 83.1 (C1/C1'), 79.6, 77.9, 77.4, 76.5, 76.4, 75.2, 74.1, 72.9 (C2–C5, C2'–C5'), 75.3, 75.0, 74.8, 74.6, 73.5 ($CH_2$ Bn), 68.1 (C6'), 20.9, 20.8 ($CH_3$ Ac); $C_{51}H_{56}N_2O_{12}$ (888.4): calcd. C 68.90, H 6.35, N 3.15; found C 68.94, H 6.42, N 3.08.

**General procedure for amide bond formation**: EDC (0.210 g, 1.1 mmol) was added to a stirred solution of HOBt (0.135 g, 1.0 mmol), the appropriate glucosylamine (1.0 mmol) and glucuronic acid derivative (1.0 mmol) in THF (5 mL). When TLC analysis (40% EtOAc/light petroleum) indicated complete conversion of the starting materials (10 h), the reaction mixture was diluted with EtOAc (50 mL), washed with aq. $NaHCO_3$ (1.0 M, 3 × 10 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue was accomplished by silica gel chromatography (10–40% EtOAc/light petroleum) to afford the corresponding amide-linked oligomer as a white foam.

**Methyl 6-*N*-(2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-trityl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (22)**: Yield: 0.982 g, 0.89 mmol, 89%; $^1$H NMR ($CDCl_3$): δ = 7.47–6.86 (m, 40H, $H_{arom}$), 6.97 (d, 1H, NH, $J_{NH,1'}$ = 9.4 Hz), 5.23 (dd, 1H, H1', $J_{1',2'}$ = 9.6 Hz), 4.97 (dd, 1H, H2', $J_{2',3'}$ = 8.9 Hz), 4.91 (d, 1H, H1, $J_{1,2}$ = 3.8 Hz), 4.85–4.62 (m, 10H, 5$CH_2$ Bn), 4.39 (d, 1H, H5, $J_{4,5}$ = 10.5 Hz), 4.18 (dd, 1H, H4, $J_{3,4}$ = 8.7 Hz), 4.14 (dd, 1H, H3, $J_{2,3}$ = 9.4 Hz), 3.97 (dd, 1H, H3', $J_{3',4'}$ = 9.4 Hz), 3.72 (t, 1H, H4', $J_{4',5'}$ = 9.4 Hz), 3.68 (dd, 1H, H6'A, $J_{5',6'A}$ = 3.0 Hz, $J_{6'A,6'B}$ = 11.9 Hz), 3.62–3.50 (m, 2H, H2/H5'), 3.44 (s, 3H, OMe), 3.20 (dd, 1H, H6'B, $J_{5',6'B}$ = 4.1 Hz), 1.87 (s, 3H, $CH_3$ Ac); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 170.2, 169.0 (C6, C=O Ac), 143.3 ($C_q$ Tr), 138.1, 137.7, 137.5, 137.3, 137.2 ($C_q$ Bn), 128.2–126.5 ($C_{arom}$), 98.0 (C1), 85.9 ($C_q$ Tr), 82.7 (C1'), 80.8, 79.8, 79.0, 77.6, 77.4, 76.2, 72.7, 70.2 (C2–C5, C2'–C5'), 75.4, 75.0, 74.6, 74.5, 73.0 ($CH_2$ Bn), 61.6 (C6'), 55.2 (OMe), 20.2 ($CH_3$ Ac); MS (ESI): $m/z$ = 1104 ($M+H^+$), 1121 ($M+NH_4^+$), 1126 ($M+Na^+$); $C_{69}H_{69}NO_{12}$ (1103.5): calcd. C 75.05, H 6.30, N 1.27; found C 75.10, H 6.40, N 1.20.

**General procedure for detritylation**: A solution of *p*-TsOH (4%, 1.0 g) in $MeOH/CH_2Cl_2$ (25 mL, 1:1, v/v) was added to a stirred solution of the 6-*O*-tritylated oligomer (1.0 mmol) in $CH_2Cl_2$ (2 mL). After 2 h, the reaction mixture was neutralised by addition of aq. $NaHCO_3$ (1.0 M, 50 mL) and extracted with EtOAc (2 × 100 mL). The combined organic layers were concentrated under reduced pressure and the resulting pale yellow oil was subjected to silica gel chromatography (0–2% $MeOH/CH_2Cl_2$) to furnish the corresponding primary alcohol as a white solid.

**Methyl 6-*N*-(2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (23)**: Yield: 0.720 g, 0.84 mmol, 94%; $^1$H NMR ($CDCl_3$): δ = 7.33–7.25 (m, 25H, $H_{arom}$), 6.88 (d, 1H, NH, $J_{NH,1'}$ = 9.6 Hz), 5.17 (dd, 1H, H1', $J_{1',2'}$ = 9.2 Hz), 4.89 (dd, 1H, H2', $J_{2',3'}$ = 10.7 Hz), 4.82 (d, 1H, H1, $J_{1,2}$ = 4.5 Hz), 4.79–4.60 (m, 10H, 5$CH_2$ Bn), 4.03 (d, 1H, H5, $J_{4,5}$ = 9.9 Hz), 4.01 (dd, 1H, H4, $J_{3,4}$ = 6.7 Hz), 3.80 (dd, 1H, H3, $J_{2,3}$ = 8.8 Hz), 3.75 (dd, 1H, H6'A, $J_{5',6'A}$ = 3.1 Hz, $J_{6'A,6'B}$ = 7.1 Hz), 3.70–3.45 (m, 5H, H2/H3'/H4'/H5'/H6'B), 3.37 (s, 3H, OMe), 1.88 (s, 3H, $CH_3$ Ac), 1.78 (br s, 1H, OH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 171.0, 170.1 (C6, C=O Ac), 138.7, 138.6, 138.3, 138.1, 138.0 ($C_q$ Bn), 128.5–127.7 ($C_{arom}$), 98.7 (C1), 83.1 (C1'), 81.3, 80.0, 79.5, 78.0, 77.6, 77.4, 77.3, 70.8 (C2–C5, C2'–C5'), 75.9, 75.4, 75.1, 73.5, 73.4 ($CH_2$ Bn), 61.1 (C6'), 55.7 (OMe), 20.8 ($CH_3$ Ac); $C_{50}H_{55}NO_{12}$ (861.4): calcd. C 69.67, H 6.43, N 1.62; found C 69.50, H 6.46, N 1.63.

**General procedure for oxidation of primary alcohols to carboxylic acids**: To a solution of the primary alcohol (1.0 mmol) in $CH_2Cl_2$ (20 mL) was added TEMPO (2 mg, 13 μmol), sat. aq. $NaHCO_3$ (2 mL), KBr (10 mg, 0.08 mmol) and $(nBu)_4NCl$ (15 mg). This heterogeneous mixture was cooled (0 °C), after which a solution of aq. NaOCl (13% active chlorine, 2 mL), sat. aq. $NaHCO_3$ (1 mL) and sat. aq. NaCl (2 mL) was added dropwise over 15 min under vigorous stirring. 15 min after the last addition the reaction mixture was acidified with aq. HCl (0.5 M, 10 mL) and extracted with EtOAc (2 × 50 mL). The combined organic phase was dried ($MgSO_4$) and concentrated under reduced pressure, and the resulting pale yellow oil was dissolved in *t*BuOH (20 mL), 2-methyl-2-butene (5 mL) and $H_2O$ (20 mL). To this solution was subsequently added $NaH_2PO_4 \cdot H_2O$ (2.0 g, 14 mmol) and $NaClO_2$ (2.0 g, 22 mmol). The reaction mixture was stirred for 2 h and extracted with EtOAc (2 × 100 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure, and the resulting colourless oil was purified by silica gel chromatography (0–3% $MeOH/CH_2Cl_2$) to afford the corresponding carboxylic acid derivative as a white solid.

**Methyl 6-*N*-(2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucuronopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (24)**: Yield: 0.544 g, 0.62 mmol, 84%; $^1$H NMR ($CDCl_3$): δ = 7.36–7.23 (m, 25H, $H_{arom}$), 7.08 (d, 1H, NH, $J_{NH,1'}$ = 9.3 Hz), 5.13 (t, 1H, H1', $J_{1',2'}$ = 9.3 Hz), 4.90–4.65 (m, 10H, 5$CH_2$ Bn), 4.77 (dd, 1H, H2', $J_{2',3'}$ = 9.5 Hz), 4.58 (d, 1H, H1, $J_{1,2}$ = 4.6 Hz), 4.10 (d, 1H, H5', $J_{4',5'}$ = 9.2 Hz), 4.03 (d, 1H, H5, $J_{4,5}$ = 10.0 Hz), 3.97 (dd, 1H, H4, $J_{3,4}$ = 9.4 Hz), 3.78 (dd, 1H, H4', $J_{3',4'}$ = 8.7 Hz), 3.76 (dd, 1H, H3'), 3.49 (dd, 1H, H2, $J_{2,3}$ = 9.2 Hz), 3.46 (dd, 1H, H3), 3.34 (s, 3H, OMe), 1.86 (s, 3H, $CH_3$ Ac); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 171.1, 170.7, 170.3 (C6, C6', C=O Ac), 138.0, 137.4, 137.4, 137.1, 137.0 ($C_q$ Bn), 128.0–127.4 ($C_{arom}$), 98.1 (C1), 81.8 (C1'), 80.8, 79.4, 78.9, 78.8, 77.5, 75.6, 72.0, 70.1 (C2–C5, C2'–C5'), 75.4, 74.9, 74.8, 73.2, 73.1 ($CH_2$ Bn), 55.1 (OMe), 20.2 ($CH_3$ Ac); $C_{50}H_{53}NO_{13}$ (875.4): calcd. C 68.56, H 6.10, N 1.60; found C 68.54, H 6.25, N 1.54.

**Methyl 6-*N*-[6-*N*-(2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-trityl-β-D-glucopyranosyl)-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (25)**: Yield: 0.782 g, 0.52 mmol, 84%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 170.5, 170.3, 170.0, 168.8 (C6/C6', 2C=O Ac), 143.4 ($C_q$ Tr), 138.0, 137.7, 137.5, 137.4, 137.3, 137.2, 136.9 ($C_q$ Bn), 128.3–126.7 ($C_{arom}$), 97.8 (C1), 86.0 ($C_q$ Tr), 82.8, 81.7 (C1'/C1''), 80.7, 80.1, 79.4, 79.0, 77.4, 77.1, 76.9, 76.3, 76.1, 72.7, 71.9, 70.1 (C2–C5, C2'–C5', C2''–C5''), 75.6, 75.2, 75.0, 74.7, 74.6, 73.2, 73.1 ($CH_2$ Bn), 61.7 (C6''), 54.6 (OMe), 20.3, 20.2 ($CH_3$ Ac); MS (ESI): $m/z$ = 1502 ($M+H^+$), 1519 ($M+NH_4^+$), 1524 ($M+Na^+$); $C_{91}H_{92}N_2O_{18}$ (1500.6): calcd. C 72.78, H 6.17, N 1.87; found C 72.80, H 6.20, N 1.86.

**Methyl 6-*N*-[6-*N*-(2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl)-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (26)**: Yield: 0.602 g, 0.48 mmol, 92%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 170.8, 170.4, 169.7, 168.4 (C6/C6', 2C=O Ac), 138.3, 138.0, 137.7, 137.6, 137.6, 137.5, 137.4 ($C_q$ Bn), 128.2–127.4 ($C_{arom}$), 98.1 (C1), 82.8, 81.4 (C1'/C1''), 80.9, 80.0, 79.2, 79.1, 78.6, 77.8, 77.2, 77.1, 75.7, 72.7, 72.4, 70.3 (C2–C5, C2'–C5', C2''–C5''), 75.6, 74.9, 74.8, 74.6, 74.4, 73.2, 73.2 ($CH_2$ Bn), 60.9 (C6''), 55.5 (OMe), 20.5, 20.4 ($CH_3$ Ac); $C_{72}H_{78}N_2O_{18}$ (1258.5): calcd. C 68.67, H 6.24, N 2.22; found C 68.69, H 6.20, N 2.19.

**Methyl 6-*N*-[6-*N*-(2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucuronopyranosyl)-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (27)**: Yield: 0.391 g, 0.31 mmol, 81%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 171.0, 170.4, 169.9, 169.8, 169.2 (C6/C6'/C6'', 2C=O Ac), 138.3, 137.7, 137.6, 137.5, 137.4, 137.3, 137.1 ($C_q$ Bn), 128.2–127.5 ($C_{arom}$), 98.1 (C1), 81.8, 81.3 (C1'/C1''), 81.0, 80.2, 79.1, 79.1, 78.2, 77.9, 76.6, 75.5, 75.2, 72.6, 72.0, 70.3 (C2–C5, C2'–C5', C2''–C5''), 75.7, 75.0, 75.0, 74.9, 74.5, 74.3, 73.3 ($CH_2$ Bn), 55.6 (OMe), 20.6, 20.3 ($CH_3$ Ac); $C_{72}H_{76}N_2O_{19}$ (1272.5): calcd. C 67.91, H 6.02, N 2.20; found C 68.00, H 6.20, N 2.11.

**Methyl 6-*N*-[6-*N*-[6-*N*-(2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-trityl-β-D-glucopyranosyl)-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (28)**: Yield: 0.459 g, 0.24 mmol, 78%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 171.1, 171.0, 170.4, 169.6, 168.6, 168.1 (C6/C6'/C6'', 3C=O Ac), 143.7 ($C_q$ Tr), 138.5–137.3 ($C_q$ Bn), 128.7–126.9 ($C_{arom}$), 98.3 (C1), 86.4 ($C_q$ Tr), 83.2, 82.0, 81.4 (C1'/C1''/C1'''), 81.1, 80.4, 79.3, 79.1, 78.2, 78.2, 77.8, 77.7, 77.4, 76.6, 76.0, 75.7, 73.2, 72.8, 72.4, 70.4 (C2–C5, C2'–C5', C2''–C5'', C2'''–C5'''), 75.9–73.5 ($CH_2$ Bn), 62.3 (C6'''), 55.8 (OMe), 20.8, 20.7, 20.6 ($CH_3$ Ac); MS (ESI): $m/z$ = 1899 ($M+H^+$), 1916 ($M+NH_4^+$), 1921 ($M+Na^+$); $C_{113}H_{115}N_3O_{24}$ (1897.8): calcd. C 71.47, H 6.10, N 2.21; found C 71.28, H 6.19, N 2.18.

**General procedure for deblocking of the amide-linked oligomers**: The fully protected oligomer was detritylated as described in the general procedure to give the corresponding primary alcohol. To a stirred solution of the appropriate alcohol (0.10 mmol) in $MeOH/CH_2Cl_2$ (5 mL, 2:1, v/v) was added KO*t*Bu (11 mg, 0.10 mmol). After 30 min, the reaction was terminated by addition of DOWEX-$H^+$ (100 mg). The ion-exchange resin was filtered



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off and the filtrate was concentrated in vacuo. The resulting colourless oil was dissolved in $CH_2Cl_2$/MeOH/$H_2O$ (1:2:1, v/v/v, 4 mL), after which palladium on carbon (10%, 100 mg) was added. The heterogeneous mixture was hydrogenated at elevated pressure (3 atm) in a Parr apparatus for 12 h and subsequently filtered. The filtrate was concentrated under reduced pressure and subjected to Pharmacia HW-40 gel filtration (eluent: $H_2O$) and lyophilised to afford the corresponding unprotected amide-linked oligomer.

**Methyl 6-*N*-[6-*N*-[6-*N*-(β-D-glucopyranosyl)-β-D-amidoglucuronopyranosyl]-β-D-amidoglucuronopyranosyl]-α-D-amidoglucuronopyranoside (29)**: Yield: 124 mg, 0.17 mmol, 72%. $[\alpha]_D = +3.5°$ ($c = 0.4$, $H_2O$); $^1$H NMR ($D_2O$): $\delta = 5.11$ (d, 1H, H1′, $J_{1',2'} = 9.2$ Hz), 5.09 (d, 1H, H1″, $J_{1'',2''} = 9.2$ Hz), 5.00 (d, 1H, H1‴, $J1''',2''' = 9.2$ Hz), 4.86 (d, 1H, H1, $J_{1,2} = 3.7$ Hz), 4.11 (d, 1H, H5, $J_{4,5} = 7.2$ Hz), 4.08 (d, 1H, H5′, $J_{4',5'} = 9.8$ Hz), 4.03 (d, 1H, H5″, $J_{4'',5''} = 9.2$ Hz), 3.84 (dd, 1H, H6‴A, $J_{5''',6'''A} = 2.1$ Hz, $J_{6'''A,6'''B} = 12.4$ Hz), 3.77 (m, 1H, H5‴), 3.68 (dd, 1H, H6‴B, $J_{5''',6'''B} = 4.1$ Hz), 3.66 (dd, 1H, H3, $J_{2,3} = 9.0$ Hz, $J_{3,4} = 9.4$ Hz), 3.61–3.56 (m, 6H, H4/H3′/H4′/H3″/H4″/H4‴), 3.52 (t, 1H, H3‴, $J_{2''',3'''} = J_{3''',4'''} = 9.7$ Hz), 3.50–3.48 (m, 3H, H2/H2′/H2″), 3.42 (dd, 1H, H2‴), 3.41 (s, 3H, OMe); $^{13}$C{$^1$H} NMR ($D_2O$): $\delta = 173.3$, 172.3, 172.2 (C6/C6′/C6″), 100.5 (C1), 79.9 (C1″), 79.9 (C1′), 79.9 (C1‴), 78.5, 77.2, 76.7, 76.6, 72.4, 72.2, 71.9, 71.8, 71.6 (C2/C4/C2′/C3′/C4′/C2″/C3″/C4″/C4‴), 77.5 (C5), 73.3 (C5‴), 72.3 (C3‴), 71.9 (C5′), 71.8 (C5″), 71.6 (C3), 70.0 (C2‴), 61.3 (C6‴), 56.4 (OMe); MS (ESI): $m/z = 720$ ($M+H^+$), 737 ($M+NH_4^+$).

**1,5-Anhydro-3-*O*-(3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-6-*O*-trityl-2-deoxy-D-*arabino*-hex-1-enitol (30)**: Under a continuous stream of dry nitrogen, $ZnCl_2$ (1.0 M solution in THF, 10 mL) was added to a cooled (0 °C) and stirred solution of epoxide **6** (2.16 g, 5.0 mmol) and glucal **3** (2.91 g, 7.5 mmol) in THF (25 mL). After 15 min, the reaction mixture was diluted with EtOAc (100 mL) and washed with sat. aq. NaCl (2 × 50 mL) and aq. $NaHCO_3$ (1.0 M, 50 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by silica gel column chromatography (20–50% EtOAc/light petroleum) afforded dimer glucal **30** (2.38 g, 2.9 mmol, 58%) contaminated with ca. 0.5 mmol (0.4 g) of the corresponding β-(1→4)-linked disaccharide glucal.

*β-(1→3)-linked disaccharide glucal*: $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 145.8$ (C1), 144.2 ($C_q$ Tr), 138.6, 137.8, 137.6 ($C_q$ Bn), 128.9–127.0 ($C_{arom}$), 102.9 (C1′, $J_{C,H} = 158.9$ Hz), 100.2 (C2), 86.6 ($C_q$ Tr), 84.4, 81.9, 77.8, 77.7, 74.7, 74.6, 68.2 (C3–C5, C2′–C5′), 75.3, 75.1, 73.5 ($CH_2$ Bn), 69.0 (C6′), 63.1 (C6); MS (ESI): $m/z = 821$ ($M+H^+$), 838 ($M+NH_4^+$), 843 ($M+Na^+$).

*β-(1→4)-linked disaccharide glucal*: $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 145.8$ (C1), 144.2 ($C_q$ Tr), 138.7, 138.3, 137.6 ($C_q$ Bn), 128.9–127.0 ($C_{arom}$), 103.8 (C1′, $J_{C,H} = 161.2$ Hz), 100.1 (C2), 86.7 ($C_q$ Tr), 84.3, 82.2, 79.0, 77.8, 74.8, 74.5, 68.2 (C3–C5, C2′–C5′), 75.4, 75.3, 73.7 ($CH_2$ Bn), 68.8 (C6′), 63.2 (C6).

**1,5-Anhydro-4-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-6-*O*-trityl-2-deoxy-D-*arabino*-hex-1-enitol (31)**: NaH (0.24 g, 10 mmol) and benzyl bromide (1.2 mL, 10 mmol) were added to a stirred solution of dimer **30** (2.38 g, 2.9 mmol of β-(1→3)-linked disaccharide and 0.4 g, 0.5 mmol of β-(1→4)-linked dimer) in DMF (10 mL). The reaction mixture was quenched after 2 h by addition of MeOH (2 mL) and concentrated under reduced pressure. The residue was then dissolved in diethyl ether (50 mL), washed with $H_2O$ (2 × 25 mL), dried ($MgSO_4$) and purified by silica gel column chromatography (0–20% EtOAc/light petroleum) to furnish fully protected dimer glucal **31** (2.52 g, 2.5 mmol, 87%) as a colourless oil. $^1$H NMR ($CDCl_3$): $\delta = 7.50–7.05$ (m, 40H, $H_{arom}$), 6.49 (dd, 1H, H1, $J_{1,2} = 6.1$ Hz, $J_{1,3} = 0.6$ Hz), 4.87 (dd, 1H, H2, $J_{2,3} = 3.0$ Hz), 4.82 (AB, 2H, $CH_2$ Bn), 4.77 (AB, 2H, $CH_2$ Bn), 4.60 (AB, 2H, $CH_2$ Bn), 4.58 (AB, 2H, $CH_2$ Bn), 4.52 (AB, 2H, $CH_2$ Bn), 4.47 (d, 1H, H1′, $J_{1,2} = 7.8$ Hz), 4.39 (ddd, 1H, H3, $J_{3,4} = 7.8$ Hz), 4.11 (m, 1H, H5), 3.95 (dd, 1H, H4, $J_{4,5} = 5.5$ Hz), 3.65–3.54 (m, 4H, H3′/H4′/H5′/H6A), 3.46 (m, 2H, H6′A/H6′B), 3.38 (m, 1H, H6B), 3.35 (dd, 1H, H2′, $J_{2',3'} = 8.7$ Hz); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 144.6$ (C1), 143.7 ($C_q$ Tr), 138.4, 138.2, 138.1, 138.0, 137.9 ($C_q$ Bn), 128.5–126.7 ($C_{arom}$), 101.8 (C1′), 99.0 (C2), 86.2 ($C_q$ Tr), 84.4, 81.9, 77.5, 76.6, 74.5, 74.2, 74.2 (C3–C5, C2′–C5′), 75.2, 74.6, 74.4, 73.0, 72.6 ($CH_2$ Bn), 68.7 (C6′), 62.3 (C6); $C_{66}H_{64}O_9$ (1000.5): calcd. C 79.18, H 6.44; found C 79.16, H 6.46.

**1,2-Anhydro-4-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-6-*O*-trityl-β-D-glucopyranose (32)**: A solution of 3,3-dimethyldioxirane in acetone (0.080 M, 38 mL, 3.0 mmol) was added dropwise to a cooled (0 °C) and stirred solution of dimer glucal **31** (2.52 g, 2.5 mmol) in $CH_2Cl_2$ (10 mL). After the reaction mixture had been stirred for 5 min, the solvents were evaporated in vacuo to give 1,2-anhydro derivative **32** as a white foam (2.41 g, 2.4 mmol, 95%). $^1$H NMR ($CDCl_3$): $\delta = 7.51–6.85$ (m, 40H, $H_{arom}$), 5.09 (d, 1H, H1, $J_{1,2} = 2.4$ Hz), 4.79 (AB, 2H, $CH_2$ Bn), 4.71 (AB, 2H, $CH_2$ Bn), 4.63 (AB, 2H, $CH_2$ Bn), 4.59 (d, 1H, H1′, $J_{1',2'} = 7.8$ Hz), 4.58 (AB, 2H, $CH_2$ Bn), 4.52 (AB, 2H, $CH_2$ Bn), 4.19 (dd, 1H, H3, $J_{2,3} = 1.5$ Hz, $J_{3,4} = 7.5$ Hz), 3.95 (dd, 1H, H4, $J_{4,5} = 6.5$ Hz), 3.72 (m, 1H, H5), 3.70–3.52 (m, 4H, H3′/H4′/H5′/H6A), 3.41 (m, 2H, H6′A/H6′B), 3.31 (m, 1H, H6B), 3.29 (dd, 1H, H2′, $J_{2',3'} = 8.0$ Hz), 3.07 (dd, 1H, H2); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 143.6$ ($C_q$ Tr), 138.3, 138.1, 138.0, 137.8, 137.7 ($C_q$ Bn), 128.4–126.6 ($C_{arom}$), 101.0 (C1′), 86.0 ($C_q$ Tr), 84.5, 81.9, 81.8, 77.4, 76.6, 72.8, 72.7, 68.9 (C1/C3–C5, C2′–C5′), 75.2, 74.8, 74.5, 73.1, 73.0 ($CH_2$ Bn), 68.4 (C6′), 61.8 (C6), 51.8 (C2).

**2-*O*-Acetyl-4-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-6-*O*-trityl-β-D-glucopyranosylamine (33)**: Under a continuous stream of dry nitrogen, $ZnCl_2$ (1.0 M solution in THF, 3.6 mL) was added to a stirred solution of epoxide **32** (2.41 g, 2.4 mmol) in $CH_3CN$ (20 mL). The reaction mixture was stirred for 2 h, subsequently diluted with EtOAc (100 mL) and washed with sat. aq. NaCl (2 × 50 mL) and aq. $NaHCO_3$ (1.0 M, 50 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. To a stirred solution of residue in THF/$H_2O$ (15 mL, 5:1, v/v) was added aq. $H_2SO_4$ (1.0 M, 0.24 mL). After 15 min, the reaction mixture was quenched by addition of aq. $NaHCO_3$ (1.0 M, 10 mL). The neutralised mixture was extracted with EtOAc (2 × 50 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting colourless oil was purified by flash chromatography over silica gel (20–50% EtOAc/light petroleum) to furnish glucosylamine **33** as a white solid (1.52 g, 1.4 mmol, 59%). $[\alpha]_D = +13.0°$ ($c = 0.2$, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta = 7.55–6.90$ (m, 40H, $H_{arom}$), 4.91 (dd, 1H, H2, $J_{1,2} = 9.8$ Hz, $J_{2,3} = 8.9$ Hz), 4.81 (AB, 2H, $CH_2$ Bn), 4.72 (AB, 2H, $CH_2$ Bn), 4.67 (AB, 2H, $CH_2$ Bn), 4.60 (AB, 2H, $CH_2$ Bn), 4.57 (AB, 2H, $CH_2$ Bn), 4.52 (d, 1H, H1′, $J_{1',2'} = 10.8$ Hz), 4.04 (d, 1H, H1), 3.73 (dd, 1H, H6A, $J_{5,6A} = 1.7$ Hz, $J_{6A,6B} = 9.2$ Hz), 3.62 (dd, 1H, H3′, $J_{2',3'} = 8.9$ Hz, $J_{3',4'} = 7.8$ Hz), 3.59–3.45 (m, 7H, H3/H4/H5/H4′/H5′/H6′A/H6′B), 3.42 (dd, 1H, H2′), 3.19 (dd, 1H, H6B, $J_{5,6B} = 4.6$ Hz), 2.09 (s, 3H, $CH_3$ Ac), 1.61 (brs, 2H, $NH_2$); $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 170.1$ (C=O Ac), 143.8 ($C_q$ Tr), 138.3, 138.2, 138.1, 137.9, 137.8 ($C_q$ Bn), 128.6–126.7 ($C_{arom}$), 103.3 (C1′), 86.2 ($C_q$ Tr), 84.7 (C1), 84.4, 81.9, 80.3, 77.9, 77.8, 76.4, 75.6, 75.0 (C2–C5, C2′–C5′), 75.3, 74.6, 74.4, 73.1, 73.0 ($CH_2$ Bn), 69.0 (C6′), 63.1 (C6), 21.0 ($CH_3$ Ac); MS (ESI): $m/z = 1076$ ($M+H^+$), 1093 ($M+NH_4^+$); $C_{68}H_{69}NO_{11}$ (1075.5): calcd. C 75.89, H 6.46, N 1.30; found C 75.80, H 6.60, N 1.27.

**Methyl 6-*N*-[2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-6-*O*-trityl-β-D-glucopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (34)**: Yield: 1.21 g, 0.79 mmol, 79%; $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 170.6$, 169.1 (C6A, C=O Ac), 143.5 ($C_q$ Tr), 138.2–137.4 ($C_q$ Bn), 128.5–126.6 ($C_{arom}$), 103.3 (C1C), 98.1 (C1A), 86.1 ($C_q$ Tr), 84.7 (C1B), 81.8, 81.0, 80.1, 80.0, 79.0, 78.9, 77.8, 77.5, 76.8, 75.0, 73.6, 70.1 (C2A–C5A, C2B–C5B, C2C–C5C), 75.5–73.0 ($CH_2$ Bn), 68.7 (C6C), 62.4 (C6B), 55.4 (OMe), 20.6 ($CH_3$ Ac); MS (ESI): $m/z = 1537$ ($M+H^+$), 1554 ($M+NH_4^+$); $C_{96}H_{97}NO_{17}$ (1535.7): calcd. C 75.03, H 6.36, N 0.91; found C 75.02, H 6.40, N 0.89.

**Methyl 6-*N*-[2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (35)**: Yield: 0.934 g, 0.72 mmol, 91%; $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 170.6$, 169.1 (C6A, C=O Ac), 138.1–137.5 ($C_q$ Bn), 127.9–127.0 ($C_{arom}$), 103.2 (C1C), 98.0 (C1A), 84.5 (C1B), 81.8, 81.6, 80.7, 79.8, 79.7, 78.9, 77.3, 76.7, 74.9, 73.4, 70.2, 70.1 (C2A–C5A, C2B–C5B, C2C–C5C), 75.3–72.9 ($CH_2$ Bn), 68.7 (C6C), 61.0 (C6B), 55.2 (OMe), 20.5 ($CH_3$ Ac); $C_{77}H_{83}NO_{17}$ (1293.6): calcd. C 71.44, H 6.46, N 1.08; found C 71.60, H 6.61, N 1.02.

**Methyl 6-*N*-[2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (36)**: Yield: 0.734 g, 0.56 mmol, 78%; $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta = 170.8$, 170.2, 169.9 (C6A/C6B, C=O Ac), 138.3–137.4 ($C_q$ Bn), 128.2–127.3 ($C_{arom}$), 103.4 (C1C), 98.2 (C1A), 84.7 (C1B), 82.0, 81.1, 81.0, 79.8, 79.7, 79.1, 79.0, 77.8, 77.7, 76.8, 73.4, 70.1 (C2A–C5A, C2B–C5B, C2C–C5C), 75.4–73.2 ($CH_2$ Bn), 68.9 (C6C), 55.6 (OMe), 20.6 ($CH_3$ Ac);

$C_{77}H_{81}NO_{18}$ (1308.5): calcd. C 70.68, H 6.24, N 1.07; found C 70.59, H 6.30, N 1.10.

**Methyl 6-*N*-[6-*N*-[2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-trityl-β-D-glucopyranosyl]-2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (37)**: Yield: 0.881 g, 0.45 mmol, 81%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 170.4, 170.2, 169.3, 167.6 (C6A/C6B, 2C=O Ac), 143.4 ($C_q$ Tr), 138.1–137.2 ($C_q$ Bn), 127.9–126.7 ($C_{arom}$), 103.2 (C1C), 97.6 (C1A), 85.9 ($C_q$ Tr), 84.5, 82.7 (C1B/C1D), 80.7–69.9 (C2A–C5A, C2B–C5B, C2C–C5C, C2D–C5D), 75.1–72.9 ($CH_2$ Bn), 68.7 (C6C), 61.5 (C6D), 54.5 (OMe), 20.4, 20.3 ($CH_3$ Ac); MS (ESI): $m/2z$ = 968 ($M+2H^+$); $C_{118}H_{120}N_2O_{23}$ (1932.8): calcd. C 73.27, H 6.25, N 1.45; found C 73.12, H 6.40, N 1.39.

**Methyl 6-*N*-[6-*N*-[2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl]-2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (38)**: Yield: 0.699 g, 0.41 mmol, 92%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 170.4, 170.0, 169.8, 168.0 (C6A/C6B, 2C=O Ac), 138.0–136.9 ($C_q$ Bn), 127.8–127.1 ($C_{arom}$), 103.0 (C1C), 97.9 (C1A), 84.2, 82.6 (C1B/C1D), 81.6–70.0 (C2A–C5A, C2B–C5B, C2C–C5C, C2D–C5D), 75.3–72.8 ($CH_2$ Bn), 68.6 (C6C), 60.5 (C6D), 55.1 (OMe), 20.3, 20.1 ($CH_3$ Ac); $C_{99}H_{106}N_2O_{23}$ (1690.7): calcd. C 70.28, H 6.31, N 1.66; found C 70.28, H 6.32, N 1.62.

**Methyl 6-*N*-[6-*N*-[2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucuronopyranosyl]-2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (39)**: Yield: 0.542 g, 0.32 mmol, 77%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 170.5, 170.2, 169.9, 169.7, 168.4 (C6A/C6B/C6D, 2C=O Ac), 138.2–137.3 ($C_q$ Bn), 128.5–127.1 ($C_{arom}$), 103.3 (C1C), 98.0 (C1A), 84.5, 81.9 (C1B/C1D), 80.8–70.0 (C2A–C5A, C2B–C5B, C2C–C5C, C2D–C5D), 75.5–73.1 ($CH_2$ Bn), 68.8 (C6C), 55.4 (OMe), 20.5, 20.4 ($CH_3$ Ac); $C_{99}H_{104}N_2O_{24}$ (1704.7): calcd. C 69.70, H 6.14, N 1.64; found C 69.54, H 6.28, N 1.57.

**Methyl 6-*N*-[6-*N*-[6-*N*-[2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-6-*O*-trityl-β-D-glucopyranosyl]-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (40)**: Yield 0.639 g, 0.23 mmol, 71%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 171.2, 171.0, 170.4, 170.0, 169.8, 168.4 (C6A/C6B/C6D, 3C=O Ac), 143.5 ($C_q$ Tr), 138.0–137.0 ($C_q$ Bn), 127.9–127.0 ($C_{arom}$), 103.1, 103.0 (C1C/C1C′), 98.0 (C1A), 86.1 ($C_q$ Tr), 84.5, 81.8, 81.7 (C1B/C1D/C1B′), 80.7–70.2 (C2A–C5A, C2B–C5B, C2C–C5C, C2D–C5D, C2B′–C5B′, C2C′–C5C′), 75.4–72.9 ($CH_2$ Bn), 68.8, 68.7 (C6C/C6C′), 62.7 (C6B′), 55.2 (OMe), 20.5, 20.4, 20.1 ($CH_3$ Ac); MS (ESI): $m/2z$ = 1382 ($M+2H^+$); $C_{167}H_{171}N_3O_{34}$ (2762.2): calcd. C 72.57, H 6.24, N 1.52; found C 72.54, H 6.28, N 1.50.

**Methyl 6-*N*-[6-*N*-[6-*N*-[2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl]-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (41)**: Yield: 0.523 g, 0.20 mmol, 89%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 171.4, 170.4, 170.3, 169.4, 168.2, 167.8 (C6A/C6B/C6D, 3C=O Ac), 138.3–137.2 ($C_q$ Bn), 128.3–127.1 ($C_{arom}$), 103.3, 103.2 (C1C/C1C′), 98.1 (C1A), 84.6, 81.9, 81.9 (C1B/C1D/C1B′), 80.9–70.1 (C2A–C5A, C2B–C5B, C2C–C5C, C2D–C5D, C2B′–C5B′, C2C′–C5C′), 75.5–73.1 ($CH_2$ Bn), 68.8, 68.7 (C6C/C6C′), 61.3 (C6B′), 55.5 (OMe), 20.7, 20.5, 20.4 ($CH_3$ Ac); $C_{148}H_{157}N_3O_{34}$ (2520.1): calcd. C 70.49, H 6.27, N 1.67; found C 70.12, H 6.39, N 1.57.

**Methyl 6-*N*-[6-*N*-[6-*N*-[2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucuronopyranosyl]-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (42)**: Yield: 0.376 g, 0.15 mmol, 74%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 171.7, 170.6, 170.2, 169.6, 169.5, 169.4, 167.9 (C6A/C6B/C6D/C6B′, 3C=O Ac), 138.3–137.0 ($C_q$ Bn), 128.1–127.2 ($C_{arom}$), 103.3, 103.2 (C1C/C1C′), 98.1 (C1A), 84.6, 81.9, 81.1 (C1B/C1D/C1B′), 80.9–70.2 (C2A–C5A, C2B–C5B, C2C–C5C, C2D–C5D, C2B′–C5B′, C2C′–C5C′), 75.6–73.1 ($CH_2$ Bn), 68.9, 68.8 (C6C/C6C′), 55.5 (OMe), 20.7, 20.6, 20.4 ($CH_3$ Ac); $C_{148}H_{155}N_3O_{35}$ (2534.0): calcd. C 70.10, H 6.16, N 1.66; found C 70.14, H 6.28, N 1.59.

**Methyl 6-*N*-[6-*N*-[6-*N*-[6-*N*-[2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-trityl-β-D-glucopyranosyl]-2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-amidoglucuronopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-amidoglucuronopyranoside (43)**: Yield: 0.357 g, 0.12 mmol, 77%; $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 171.6, 170.8, 170.6, 170.4, 170.3, 169.6, 168.5, 167.8 (C6A/C6B/C6D/C6B′, 4C=O Ac), 143.7 ($C_q$ Tr), 138.4, 138.3, 138.3, 138.2, 138.0, 138.0, 137.9, 137.9, 137.8, 137.8, 137.7, 137.7, 137.6, 137.6, 137.5, 137.4, 137.3 ($C_q$ Bn), 127.9–126.9 ($C_{arom}$), 103.4, 103.4 (C1C/C1C′), 98.2 (C1A), 86.3 ($C_q$ Tr), 84.7, 84.6, 83.5, 83.1 (C1B/C1D/C1B′/C1E), 82.0, 81.9, 81.4, 81.1, 80.2, 79.4, 79.3, 79.2, 78.2, 78.1, 77.9, 77.7, 77.3, 77.2, 76.8, 76.0, 75.8, 74.5, 74.5, 74.3, 73.6, 73.4, 73.2, 72.9, 72.8, 72.6, 71.7, 70.3 (C2A–C5A, C2B–C5B, C2C–C5C, C2D–C5D, C2B′–C5B′, C2C′–C5C′/C2E–C5E), 75.8, 75.8, 75.7, 75.6, 75.6, 75.4, 75.4, 75.4, 75.3, 75.3, 75.2, 75.1, 75.0, 75.0, 74.8, 74.8, 74.5 ($CH_2$ Bn), 69.0, 68.9 (C6C/C6C′), 62.4 (C6E), 55.7 (OMe), 20.9, 20.7, 20.6, 20.5 ($CH_3$ Ac); MS (ESI): $m/2z$ = 1581 ($M+2H^+$); $C_{189}H_{194}N_4O_{40}$ (3159.3): calcd. C 71.80, H 6.18, N 1.77; found C 71.99, H 6.40, N 1.65.

**Methyl 6-*N*-[6-*N*-[6-*N*-[6-*N*-[β-D-glucopyranosyl]-3-*O*-(β-D-glucopyranosyl)-β-D-amidoglucuronopyranosyl]-β-D-amidoglucuronopyranosyl]-3-*O*-(β-D-glucopyranosyl)-β-D-amidoglucuronopyranosyl]-α-D-amidoglucuronopyranoside (2)**: Compound **43** (357 mg, 0.12 mmol) was deprotected and purified as described in the general procedure to give **2** as a white fluffy solid (98 mg, 0.08 mmol, 70%). NMR data are given in Table 2. $[\alpha]_D$ = −2.0° ($c$ = 0.3, $H_2O$); MS (ESI): $m/2z$ = 610 ($M+2H^+$); $C_{43}H_{70}N_4O_{36}$ (1218.4): calcd. C 42.37, H 5.79, N 4.60; found C 42.31, H 5.93, N 4.53.

Table 2. $^{13}C\{^1H\}$ NMR ($D_2O$, 150.3 MHz) and $^1H$ NMR ($D_2O$, 600 MHz) data for heptamer **2** [a] obtained from CH-COSY, HH-COSY and TOCSY experiments.

| | 1 | 2 | 3 | 4 | 5 | 6 | 6′ |
|---|---|---|---|---|---|---|---|
| A | 4.87 [b] (d) [c] | 3.62 (dd) | 3.69 (dd) | 3.55 (dd) | 4.09 (d) | | |
| | (3.8) [d] | (3.8, 9.8) | (9.8, 10.0) | (10.0, 9.8) | (9.8) | | |
| | 100.5 [e] | 71.5 | 70.5 | 78.5 | 77.2 | [f] | |
| B | 5.15 (d) | 3.74 (t) | 3.89 (dd) | 3.69 (t) | 4.08 (d) | | |
| | (9.3) | (9.2) | (9.2, 9.9) | (9.9) | (9.9) | | |
| | 80.0 | 71.4 | 84.6 | 77.5 | 72.1 | [f] | |
| B′ | 5.12 (d) | 3.74 (t) | 3.89 (dd) | 3.69 (t) | 4.05 (d) | | |
| | (9.3) | (9.3) | (9.3, 9.9) | (9.9) | (9.9) | | |
| | 80.0 | 71.4 | 84.5 | 77.5 | 72.0 | [f] | |
| C | 4.77 (d) | 3.34 (dd) | 3.50 (dd) | 3.39 (t) | 3.46 (m) | 3.91 (dd) | 3.71 (dd) |
| | (7.9) | (7.9, 8.9) | (8.9, 8.6) | (8.6) | | (12.3, 2.3) | (12.3, 4.0) |
| | 103.5 | 74.3 | 76.4 | 70.1 | 77.3 | 61.6 | |
| C′ | 4.76 (d) | 3.35 (dd) | 3.51 (dd) | 3.38 (t) | 3.46 (m) | 3.90 (dd) | 3.70 (dd) |
| | (8.0) | (8.0, 8.9) | (8.9, 8.6) | (8.6) | | (12.3, 2.3) | (12.3, 4.1) |
| | 103.5 | 74.3 | 76.4 | 70.1 | 77.3 | 61.6 | |
| D | 5.10 (d) | 3.51 (dd) | 3.60 (t) | 3.59 (t) | 4.03 (d) | | |
| | (9.0) | (9.0, 9.2) | (9.2) | (9.3) | (9.3) | | |
| | 79.9 | 71.9 | 77.2 | 77.4 | 71.8 | [f] | |
| E | 5.01 (d) | 3.36 (t) | 3.43 (t) | 3.41 (dd) | 3.51 (m) | 3.85 (dd) | 3.68 (dd) |
| | (9.2) | (9.2) | (9.2) | (9.2, 8.9) | | (11.6, 2.5) | (11.6, 5.0) |
| | 79.8 | 73.4 | 72.5 | 71.3 | 77.0 | 61.4 | |

[a] OMe group: $\delta$ = 3.61 ($^1H$ NMR) and 56.4 ($^{13}C$ NMR). [b] Proton chemical shift. [c] Proton multiplicity. [d] Proton coupling constants (Hz). [e] $^{13}C$ chemical shift. [f] C6A/C6B/C6D/C6B′: 173.3, 172.4, 172.1, 171.9.

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