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Iterative Synthesis of Spacered Glycodendrons as Oligomannoside Mimetics and Evaluation of Their Antiadhesive Properties

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Abstract: Dendrimer chemistry is an attractive concept for mimicry of the highly branched character of the bioactive carbohydrates found as part of a cell's sugar coat, called the glycocalyx. Glycodendrimers have thus been used to study biological processes occurring on cell surfaces, such as bacterial adhesion. This paper details a new approach in glycodendrimer synthesis, in which a 3,6-diallylated carbohydrate is utilised as core molecule, hydroboration–oxidation is the activating step, and glycosylation with branched and unbranched sugar trichloroacetimidates is used for dendritic growth. To obtain pure dendritic pseudo-tri- and -heptasaccharides in good yields, radical addition of mercaptoethanol to peripheral double bonds was also evaluated with great success. A collection of six new hyperbranched glycodendrons was tested for their potential as inhibitors of type 1 fimbriae-mediated bacterial adhesion in an ELISA and the results were interpreted with regard to sugar valency and spacer characteristics.

Keywords: bacterial adhesion · carbohydrates · dendrimers · mannosylation

Introduction

Every cell is surrounded by a nanodimensional macromolecular assembly of complex, highly branched glycoconjugates, which is referred to as a cell's glycocalyx. Interactions with the glycocalyx are essential for many biological processes such as cell–cell recognition, microbial adhesion, immunological response and fertilisation, as well as metastasis, inflammation and other disease states of a cell or tissue.[1] To study the structural and functional aspects of the various glycoconjugates in cellular biology, synthetic oligosaccharides and glycoconjugates are required.[2] They can be designed either according to the natural example structures or as so-called glycomimetics, which have been shown to serve as valuable tools in glycobiology[3] and glycomics.[4]

To mimic the highly branched character of the biologically active saccharides, dendrimer chemistry has been employed to achieve dendritic growth of so-called glycodendrimers, which have been designed according to a variety of architectures.[5] In addition to the use of hyperbranched noncarbohydrate core structures and their peripheral functionalisation with carbohydrates, glycodendrimers have been made by use of carbohydrate derivatives as branching elements with the aid of, for example, reductive amination[6] or peptide chemistry.[7] In order to allow a simple synthesis of glycosidically linked hyperbranched glycomimetics, we have recently reported on the synthesis and biological testing of carbohydrate-centred oligomannoside mimetics in which a uniformly spacer-modified carbohydrate core had been glycosylated with terminal sugar units.[8] Here, it has been our goal to establish a fractal geometry of dendritic glycosides, as outlined in Figure 1.

According to this model, a bifunctional glycoside capable of being activated as a glycosyl acceptor serves as the core molecule for the glycodendron synthesis, while a similarly bifunctional glycosyl donor acts as the branching element in the second iterative step of this dendrimer synthesis. We have designed the branching unit as di-*O*-allylated, because di-*O*-allylated glycosides can be conveniently synthesised, and in addition can be converted into the corresponding glycosyl acceptor diols for subsequent glycosylation steps in a number of ways. Glycosylation with a standard glycosyl donor stops dendritic growth, while still leading to interesting hyperbranched oligosaccharide mimetics. Glycosylation with a more elaborated glycosyl donor bearing the same bifunctionalisation as the core glycoside, on the other hand, allows further dendritic growth of the glycosylation product.

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Selected ^{1}H and ^{13}C NMR spectra.

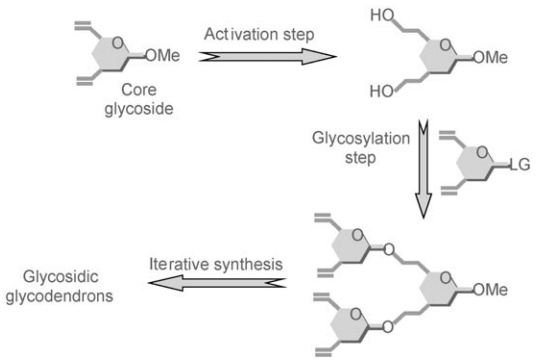


Figure 1. Synthesis of fractal glycosidic glycodendrimers starts with a bifunctional core glycoside, which in the first iterative step is activated into a dihydroxy derivative. In the second iterative step of this dendrimer synthesis, this diol then serves as glycosyl acceptor with the employment of a suited glycosyl donor that exhibits the same bifunctional character as the starting core glycoside.

Thus, dendritic growth should arise from iterative repetition of allyl group activation and glycosylation with a similarly di-*O*-allylated glycosyl donor.

Particular challenges of this project have been to establish a suitable branching glycosyl donor and to achieve dendritic pseudo-oligosaccharides in good amounts and yields and without structural defects.

To test our idea we chose to make dendritic oligomannoside mimetics, because we are interested in the investigation of their antiadhesive potency in mannose-specific bacterial adhesion[9] (see below).

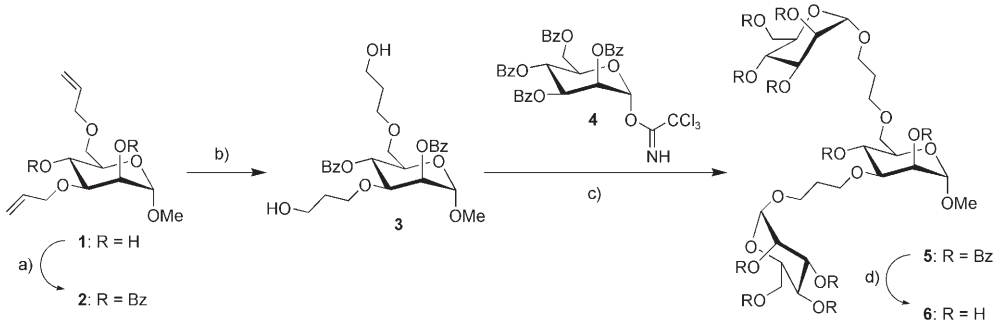
Results and Discussion

Synthesis: For the preparation of mannoside **3**, which was used as the core molecule for glycodendron synthesis, we started from methyl 3,6-di-*O*-allyl-α-D-mannopyranoside[10] (**1**; Scheme 1). The substitution pattern of **1** can be conveniently established through bis(tributyltin)oxide chemistry,[11] allowing regioselective 3,6-di-*O*-alkylation of mannosides in one-pot fashion. The free hydroxy groups of **1** were then benzoylated to yield mannoside **2**. Hydroboration–oxidation of the two allylic double bonds in **2** gave the spacered diol **3**, which served as glycosyl acceptor in the following syntheses. Firstly, both hydroxy groups in **3** were mannosylated with the perbenzoylated mannosyl trichloroacetimidate **4**[12] with TMSOTf (trimethylsilyl triflate) as Lewis acid catalyst to give the protected dendron **5** in very good yield. Deprotection of **5** under Zemplén conditions[13] gave the deprotected glycodendron **6**.

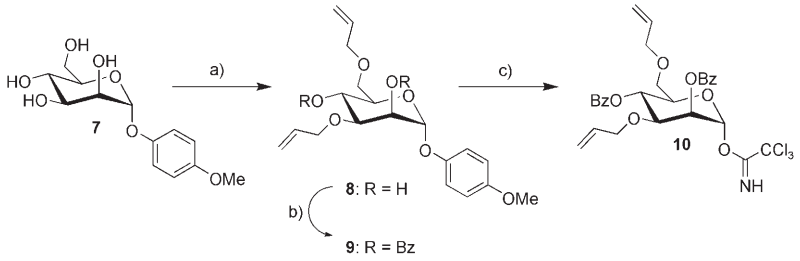
Glycodendron **6** can be regarded as a new trimannoside mimetic, which is of interest for its biological activity (see below). However, its substitution pattern does not allow its structural architecture to be further extended towards higher dendron generations. To enable dendritic growth of pseudo-oligomannosides, the core diol **3** has to be glycosylated with a "fractal" glycosyl donor that carries the same 3,6-*O*-substitution pattern as the core, rather than with the uniformly protected trichloroacetimidate **4**. After extensive investigations and evaluation of a number of different glycosyl donors, we finally selected *p*-methoxyphenyl (PMP) mannosides to allow the synthesis of a 3,6-*O*-diallyl-protected mannosyl donor. We started from *p*-methoxyphenyl mannoside **7**, which was regioselectively allylated in positions 3 and 6,[14] with subsequent benzoylation of the remaining hydroxy groups to give mannoside **9**, in analogy to the procedure used for the synthesis of **3** (Scheme 2). Removal of the PMP aglycon of **9** was accomplished with ceric ammonium nitrate (CAN), and the resulting reducing sugar could be directly converted into the trichloroacetimidate **10**. This mannosyl donor serves as a novel AB_2-type branching unit for the glycodendron synthesis, nicely utilising the special reactivity of the anomeric centre.

Next, mannosylation of diol **3** with this new branching glycosyl donor **10** had to be elaborated. A threefold excess of glycosyl donor per hydroxy group and a catalytic amount of TMSOTf proved sufficient to provide tetraene **11** in good yield (Scheme 3). A hydroboration–oxidation sequence then furnished the desired tetraol **12** in a moderate yield of 40%.

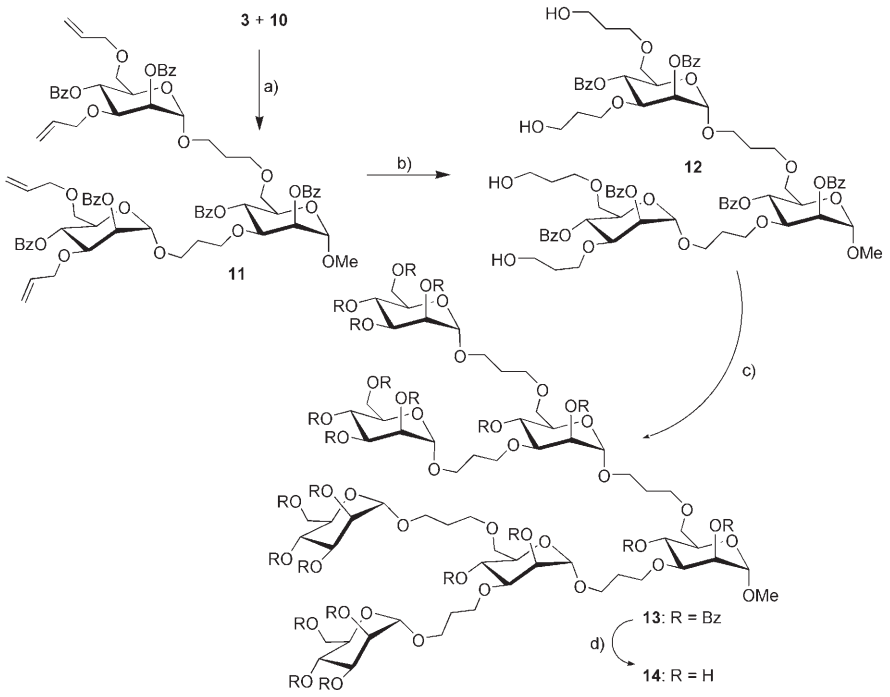
Although this synthetic scheme allows dendritic growth through repetitive glycosylation with **10**, in the production of a heptasaccharide dendron from **12** and the pseudo-pentadecasaccharide in the following generation, such high-molecular-weight glycodendrons could not be obtained in pure



Scheme 1. Synthesis of the pseudo-trisaccharide glycodendron **6**. a) BzCl, pyridine, 0°C→RT, overnight, 72%; b) i) 9-BBN, THF, reflux, 1 h; ii) 3 M NaOAc (aq.), H_2O_2 (30%), 0°C→RT, overnight, 69%; c) TMSOTf, CH_2Cl_2, RT, overnight, 92%; d) NaOMe, MeOH, RT, 86%.



Scheme 2. Synthesis of the allylated mannosyl donor **10**. a) i) Bis(tributyltin)oxide, toluene, reflux, 4 h; ii) AllBr, TBABr, 80 °C, 7 d, 51 %; b) BzCl, pyridine, 0 °C→RT, overnight, quant.; c) i) CAN, MeCN/H_2O (4:1), 0 °C→RT, 3 h; ii) trichloroacetonitrile, CH_2Cl_2, DBU, 0 °C→RT, 1 h, 53 % (over two steps).



Scheme 3. Synthesis of the pseudo-heptasaccharide glycodendron **14**. a) TMSOTf, CH_2Cl_2, RT, overnight, 79 %; b) i) 9-BBN, THF, reflux, 1 h; ii) 3 M NaOAc (aq.), H_2O_2 (30 %), 0 °C→RT, overnight, 40 %; c) **4**, TMSOTf, CH_2Cl_2, RT, overnight, 54 %; d) NaOMe, MeOH, RT, 88 %.

form, as our methodology suffers from two drawbacks: i) the hydroboration–oxidation sequence reaction becomes increasingly inconvenient when carried out on a multifunctional molecule, due to huge amounts of side products, and ii) the isolation procedures for the resulting polyols are difficult and yields in these reaction steps are not satisfactory.

We thus decided to perform tetra-*O*-glycosylation of **12** with trichloroacetimidate **4**, which allowed the preparation of the pure heptasaccharidic glycodendron **13** in a rather pleasing yield of 54 %. Deprotection then afforded **14** in 88 % yield (Scheme 3).

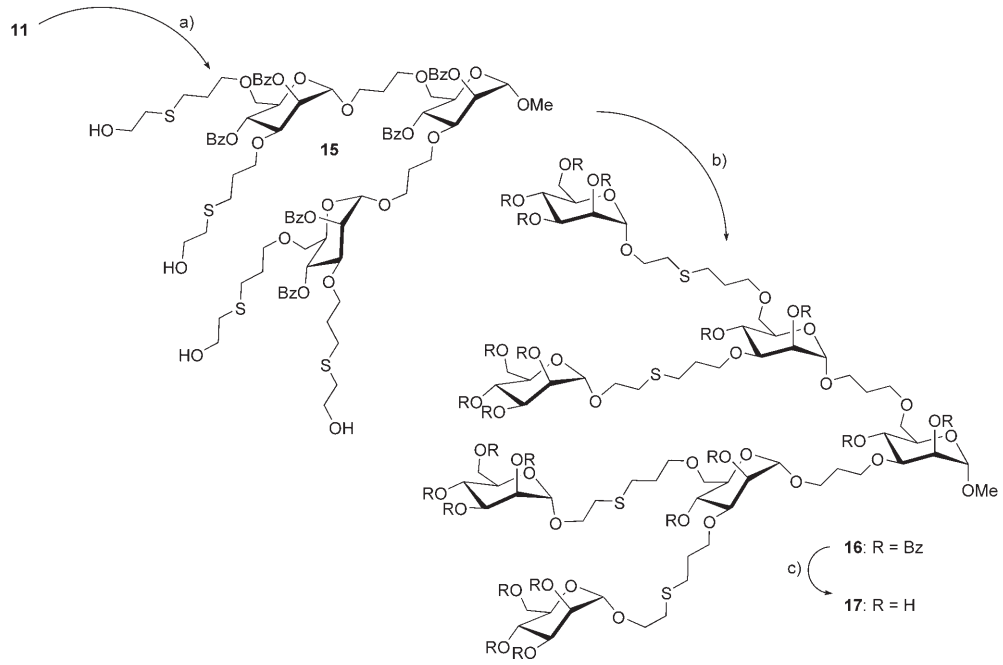
Interestingly, no partially mannosylated products of the glycosylation reaction, which had led to **13** being produced together with products with other structural defects, could be detected either on TLC or by MALDI-TOF-MS analysis. On the other hand, the starting material, acceptor alcohol **12**, was completely consumed during the reaction and only a base line spot was detectable by TLC besides the desired product.

For purification of the prepared glycodendrons, we took advantage of their relatively high molecular masses. All the protected compounds were purified by size-exclusion chromatography on Sephadex LH-20 with methanol/CH_2Cl_2 as the eluent in addition to purification on silica gel. In this manner, glycodendrons free of any structural defects could be obtained in pure form. The deprotected compounds were also purified in this way, with methanol as eluent.

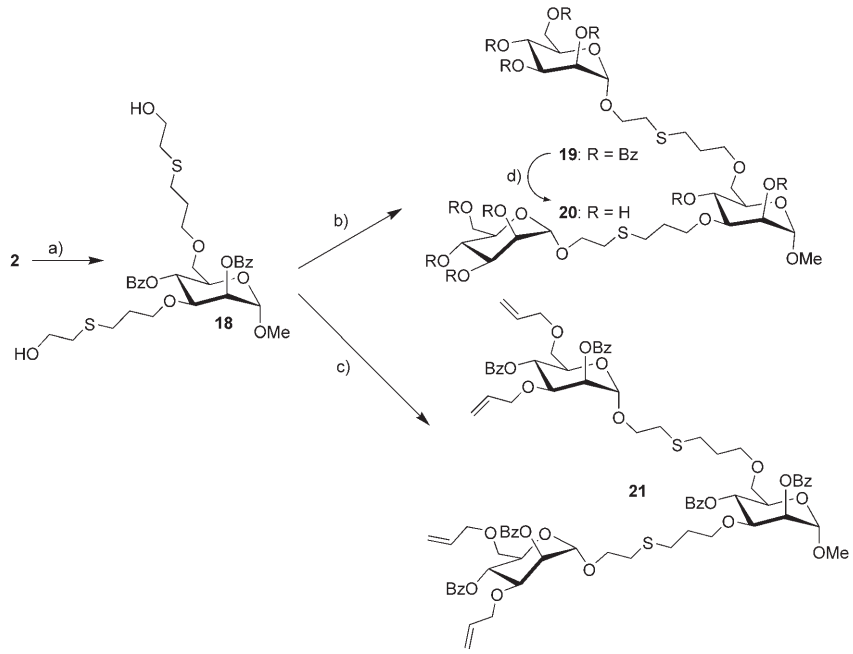
It has been our goal to compare the differently sized pseudo-oligomannosides **6** and **14** for their antiadhesive activities in mannose-mediated bacterial adhesion[9] (see below). In addition, we were keen to alter the spacer characteristics of these oligomannoside mimetics, both for biological and for chemical reasons.

As the hydroboration–oxidation step in our dendrimer synthesis suffers from the disadvantages described above, we tested different reactions that looked promising in terms of yields and reaction conditions to substitute the oxidation of allyl groups. We thus selected the radical addition of mercaptoethanol to double bonds,[15] a mild and generally high-yielding reaction from which any excess of reagent can be removed easily, due to its volatility.

We first tested the reaction with the tetraene **11**, which (after treatment with mercaptoethanol and AIBN) gave tetraol **15** in an excellent yield of 91 % (Scheme 4). Subsequent glycosylation with **4** and deprotection resulted in the unprotected heptasaccharidic glycodendron **17**. After this promising result, the same reaction was performed with the branched core mannoside **2**, affording the spacered diol **18** in 90 % yield (Scheme 5). This could either be di-*O*-glycosylated with **4**, to give the trisaccharidic glycodendron **19** in 61 % yield and unprotected **20** after debenzoylation, or bisglycosylated with the branching trichloroacetimidate **10** to



Scheme 4. Synthesis of glycodendron **17** with 4-thiahexyl spacers. a) $HS(CH_2)_2OH$, AIBN, dioxane, 75 °C, 4 h, 91 %; b) **4**, TMSOTf, CH_2Cl_2, RT, overnight, 31 %; c) NaOMe, MeOH, RT, 86 %.



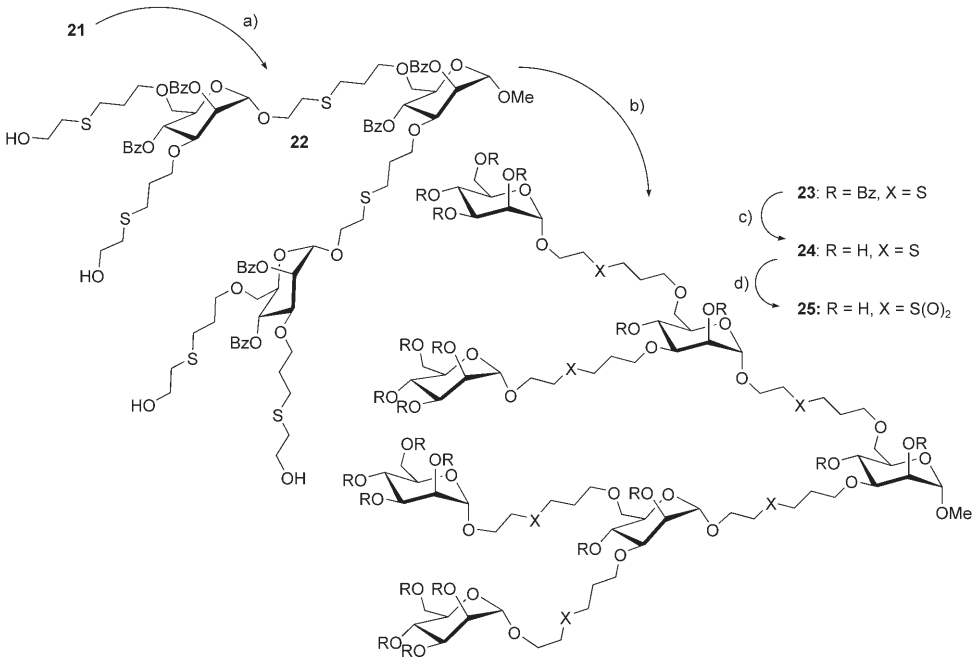
Scheme 5. Synthesis of glycodendrons **20** and **21**. a) $HS(CH_2)_2OH$, AIBN, dioxane, 75 °C, 4 h, 90 %; b) **4**, TMSOTf, CH_2Cl_2, RT, overnight, 61 %; c) **10**, TMSOTf, CH_2Cl_2, RT, overnight, 65 %; d) NaOMe, MeOH, RT, quant.

allow the synthesis of tetraene **21** in comparable yield (Scheme 5).

Subsequent addition of thioethanol again proceeded easily and gave tetraol **22** in 94 % yield (Scheme 6). This could in turn be glycosylated with **4**, providing the protected pseudo-heptasaccharide **23** in a satisfying 55 % yield, and its deprotection gave the heptasaccharidic glycodendron **24**. Again, as found in case of the synthesis of **13**, no partially glycosylated products could be detected.

Finally, we explored an interesting feature of these thiahexyl-spacered glycodendrons. As sulfides can exist in different oxidation states, we reasoned that this should have an influence on the overall three-dimensional structure of the dendron, as well as on the lipophilicity of the spacers. Both of these characteristics might be reflected in the biological activity of the molecule. To test this, we oxidised the deprotected dendron **24** with an excess of MMPP (magnesium monoperoxyphthalate) to give the corresponding sulfone **25** (Scheme 6).

Biological activity: The unprotected glycodendrons **6**, **14**, **17**, **20**, **24** and **25**, synthesised by the methodology described above, form a series of branched oligomannoside mimetics differing with regard both to their carbohydrate content and to their spacer characteristics. They were designed as mimetics of cell surface oligosaccharides of the high-mannose



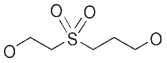
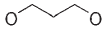
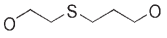
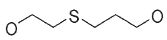
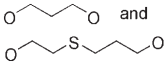
Scheme 6. Glycodendron synthesis with mercaptoethanol addition. a) $HS(CH_2)_2OH$, AIBN, dioxane, 75 °C, 4 h, 94 %; b) **4**, TMSOTf, CH_2Cl_2, RT, overnight, 55 %; c) NaOMe, MeOH/MeCN, RT, 68 %; d) MMPP, H_2O/MeOH overnight, RT, 67 %.

type, which are part of the glycocalyx. Many, if not all, biological processes occurring at cell surfaces are dependent on interactions with the glycocalyx. One of these processes is the adhesion of bacteria to their host cells,[9] which might trigger inflammation,[16] apoptosis[17] or peptic ulcer,[18] or might initiate other disease states of a cell.[19] Bacteria utilise proteinogenous appendages, so-called fimbriae or pili, to adhere to the host cell glycocalyx. These molecular interactions, which are assumed to be essential for this adhesion event, involve the interaction of fimbrial lectin domains with specific host cell saccharides. *Escherichia coli* possess so-called type 1 fimbriae, amongst others, which display specificity for α-D-mannosides, due to a mannose-specific protein called FimH located at the tips of these adhesive bacterial organelles. To understand the molecular interactions of type 1 fimbriated bacteria with cell surface oligosaccharides, on the one hand the molecular details of the interaction of FimH with α-D-mannosides have to be considered, while on the other, multivalency effects that may depend on molecular mechanisms other than just binding of α-D-mannosyl units to the adhesin FimH have been observed. Recently we have suggested a "macromolecular effect" to explain bacterial adhesion, a hypothesis that awaits further investigation.[8] Here, the multivalent oligomannoside mimetics prepared were tested for their potential as inhibitors of the type 1 fimbriae-mediated adhesion of *E. coli* to the polysaccharide mannan from *Saccharomyces cerevisiae* by use of an ELISA (enzyme-linked immunosorbent assay) formate. This assay allows the measurement of IC_{50} values for the inhibition of *E. coli* adhesion, which reflect the inhibitor concentrations that will cause 50 % inhibition of bacterial binding to mannan. Duplicate results were used for the construction of the inhibition curves.

The IC_{50} values determined were compared to the IC_{50} value of methyl α-D-mannoside (MeMan) as a standard inhibitor of mannose-specific bacterial adhesion. Relative inhibitory potencies (RIP values) based on the inhibitory potency of MeMan—which was set to 1—were calculated.

The ELISA results are summarised in Table 1, in which the tested compounds are ranked by their inhibitory potency. All of the synthesised glycodendrons perform better in the ELISA than the monovalent MeMan as inhibitors of the adhesion of type 1 fimbriated *E. coli* to mannan. The synthetic glycodendrons exceed the inhibitory potency of MeMan by one or two orders of magnitude. The small glycodendron **6**, consisting of three α-D-mannosyl units, showed the weakest inhibitory potency of all tested compounds. Glycodendrons containing seven α-D-mannosyl moieties were expected to perform better than their smaller counterparts, and this indeed holds true for **24** and **17**. With respect to the influence of sugar content, the small glycodendron **20**, in which two α-D-mannoside units are exposed on thiahexyl spacers, performs un-

Table 1. Inhibitory potencies of the prepared glycodendrons as inhibitors of mannose-specific adhesion of *E. coli* as determined by ELISA.[a]

Cmpd. ranked according to increasing inhibitory potency	Number of α-D-mannosyl units	Spacer characteristics	IC_{50} [mmol] (s.d.)	RIP (s.d.)
MeMan	one		5.9 (0.60)	1 –
6	three		0.58 (0.044)	10 (0.28)
25	seven		0.23 (0.003)	25 (2.9)
14	seven		0.14 (0.021)	42 (1.9)
20	three		0.089 (0.019)	67 (7.8)
24	seven		0.055 (0.017)	110 (23)
17	seven		0.031 (0.014)	200 (71)

[a] IC_{50} values are listed together with their standard deviations (s.d.s). So-called relative inhibitory potencies (RIPs) are relative to the IC_{50} value measured for methyl α-D-mannopyranoside (MeMan); the inhibitory potency of MeMan has thus been defined as RIP = 1. All RIP values are listed together with their standard deviations.

expectedly well, as it shows a medium inhibitory potency that exceeds that of the larger glycodendron **14**, in which the carbohydrate moieties are spacered by propyl units.

Thus, with regard to the influence of the spacer characteristics of the tested compounds, it can be concluded that glycodendrons with the longer thiahexyl spacers (such as **24**) showed increased inhibitory potencies in relation to their counterparts bearing propyl spacers (such as **14**, the shorter analogue of **24**). This might be due to increased conformational flexibility and availability of the spacered mannosyl residues. The lipophilic properties of the spacers might also promote the inhibitory potency of a given glycoconjugate; this consideration receives some backing from the finding that oxidation of the sulfide groups in **24** to afford the more hydrophilic sulfone spacers in **25** has a pronounced negative effect on the inhibitory potency of **25**.

With allowance for the accuracy of the measured data, reflected in the determined standard deviations (s.d.s; see Table 1), the tested compounds might be best classified into three groups of inhibitors. The two best inhibitors are the conformationally highly flexible glycodendrons **24** and **17**, both of which have the four exterior mannosyl moieties displayed on thiahexyl spacers. In addition, the rather small glycodendron **20**, exposing only two α-mannosyl moieties on similarly long spacers, performs relatively well as an inhibitor of bacterial adhesion in the applied ELISA and receives a middle ranking together with the larger, but more narrowly spacered, glycodendron **14** consisting of seven mannosyl moieties. Finally, glycodendron **25**, with sulfone spacers, and the smallest molecule **6** are the poorest inhibitors of the tested series. The spacered trimannoside mimetic **6** performs very similarly to the naturally occurring branching mannotrioside 3,6-di-*O*-(α-D-mannosyl)-α-D-mannoside, which was tested previously.[8,20]

Conclusion

In this study we have demonstrated a combination of sugar and dendrimer chemistry for the preparation of glycodendrons. With a 3,6-diallylated carbohydrate as the core molecule, hydroboration–oxidation as the activating step and glycosylation with branched and unbranched sugar trichloroacetimidates for the dendritic growth, a tri- and a heptasaccharidic glycodendron could be obtained in good yields. The use of the radical addition of mercaptoethanol to double bonds as the activating step was evaluated for dendron synthesis and enabled us to synthesise glycodendrons in much better yields. Whereas the hydroboration–oxidation sequence allowed conversion of the tetraene **11** in yields of about 40% (yielding **12**), radical addition of mercaptoethanol conveniently converted **11** into **15** in over 90% yield. Tetrakis-glycosylations could then be performed in yields of around 55% to obtain heptasaccharidic glycodendrons. To the best of our knowledge, this is the first example of the use of both mercaptoethanol addition and glycosylation as a repetitive reaction sequence in dendrimer synthesis.

As the deprotected glycodendrons are mimics of high-mannose-type oligosaccharides, they were tested as inhibitors of the mannose-specific adhesion of *E. coli* in an ELISA. All of the glycodendrons proved to be better inhibitors than MeMan. The chosen assay formate allows the measured data to be interpreted from two different points of view. On one hand, the interaction of the type 1 fimbrial lectin domain FimH with the α-D-mannosyl units, which are exposed by the tested glycodendrons in different densities, is likely to determine the measured IC_{50} value. On the other hand, the tested glycodendrons might also interfere with the macromolecular interaction of type 1 fimbriated *E. coli* with the polysaccharide mannan, which coats the ELISA plate. The obtained inhibitory potency of each tested compound could thus arise from a combination of a rather precisely defined ligand–receptor interaction and a more supramolecular effect. This scenario could also provide a clue for understanding of the influence of spacer characteristics, which were shown to be of importance in the tested series. The thiahexyl-spacered glycodendrons were generally better inhibitors than the propyl-spacered ones, probably due to increased conformational flexibility and enhanced lipophilicity of the spacers. Oxidation of the sulfides into less lipophilic sulfones diminished the inhibitory potency of the corresponding compound by approximately one order of magnitude. Further research to study the interaction of spacered glycosides with mannan is currently going on in our laboratory.

Experimental Section

General remarks: All solvents were distilled prior to use: MeOH from Mg, toluene from Na/benzophenone, CH_2Cl_2 from P_4O_{10}, pyridine from CaH, and THF from Na/K/benzophenone. Dioxane was filtered through a column filled with basic aluminium oxide and stored under argon. Commercially available starting materials and reagents were used without further purification. Methyl 3,6-di-*O*-allyl-α-D-mannopyranoside (**1**),[10] *O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl) trichloroacetimidate (**4**)[12] and *p*-methoxyphenyl α-D-mannopyranoside (**7**)[14] were prepared according to the literature. Silica gel 60 (0.040–0.063 mm, Merck) was used for flash chromatography. All reactions were monitored by TLC on silica gel 60 F_{254} on aluminium foil (Merck) with detection by UV light and charring with $EtOH/H_2O/H_2SO_4$ (conc.) (14:10:1). Gel permeation chromatography was carried out on Sephadex LH-20 from Pharmacia-Biotech. NMR spectra were recorded on Bruker ARX 300 or DRX 500 instruments. NMR spectra were calibrated with respect to the solvent peak ($CDCl_3$: internal TMS ($\delta = 0.000$ ppm) for ^1H and $\delta = 77.000$ ppm for ^{13}C; [D_4]MeOH: $\delta = 3.310$ ppm for ^1H and $\delta = 49.050$ ppm for ^{13}C). Selected ^1H and ^{13}C NMR spectra are depicted in the Supporting Information. 2D NMR techniques ($^1H,^1H$ COSY and $^1H,^{13}C$ HSQC) were used for full assignment of the spectra. In case of the dendritic oligosaccharides, the protons and carbon atoms of the core molecule are labelled with c, those of the outer carbohydrate units with s (e.g., H-1c, H-4s), if assignment was possible. ESI-MS measurements were performed on a Mariner (Part-No. V800600) instrument. MALDI-TOF mass spectra were recorded on a Bruker Biflex III 19 kV instrument with CCA as matrix. EI/CI mass spectra were recorded on a Finnegan MAT 8230 instrument. Optical rotation was measured on a Perkin–Elmer Polarimeter 341. IR spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. Methyl α-D-mannopyranoside was purchased from Fluka, F-shaped 96-well microtiter plates from Sarstedt. Mannan from

Saccharomyces cerevisiae was purchased from Sigma and was used in aq. Na_2CO_3 (50 mM, 1 mg mL^{-1}, pH 9.6). The peroxidase-conjugated goat anti-rabbit antibody (IgG, H+L) was purchased from Dianova. Skimmed milk was from Ulzena, Tween 20 from Roth, ABTS [2,2-azidobis-(3-ethylbenzothiazoline-6-sulfonic acid)] from Fluka, and thimerosal [2-(ethylmercuriothio)benzoic acid sodium salt] was from Merck. A recombinant type 1 fimbriated *E. coli* strain—*E. coli* HB101 (pPKl4)[21]—was used and cultured as described earlier.[22] PBS (phosphate-buffered saline) was prepared by dissolving NaCl (8 g), KCl (0.2 g), $Na_2HPO_4{\cdot}2H_2O$ (1.44 g) and KH_2PO_4 (0.2 g) in doubly distilled water (pH 7.2, 1000 mL). PBSE was PBS buffer+thimerosal (100 mg L^{-1}), PBSET was PBSE buffer+Tween 20 (200 μL L^{-1}). Substrate buffer was sodium citrate dihydrate (0.1 M), adjusted to pH 4.5 with citric acid. For preparation of the ABTS solution, ABTS (1 mg) was dissolved in substrate buffer (1 mL), and H_2O_2 (0.1 %, 25 μL mL^{-1}) was added.

ELISA: To determine the potencies of the glycodendrons as inhibitors of type 1 fimbriae-mediated adhesion of *E. coli*, an ELISA was used as published earlier.[8,22] Polystyrene microtiter plates were coated with mannan solution (100 μL per well) and dried overnight at 37 °C. The plates were blocked once with skimmed milk in PBSE (5 %) for 30 min at 37 °C. The wells were washed with PBSE (150 μL), and then PBSE (50 μL) and inhibitor solutions (50 μL) were added. Inhibitor solutions were serially diluted twofold in PBSE. Bacterial suspension (50 μL per well) was added and the plate was left at 37 °C for 1 h to allow sedimentation of the bacteria. Then each well was washed four times with PBSE (150 μL) and the first antibody (anti-fimA antibody, solution as optimised prior to the experiments) in skimmed milk (2 %, 50 μL) was added. The plates were incubated for 30 min and then washed twice with PBSET, and then the second antibody (50 μL) was added. The plates were incubated for 30 min and then washed three times with PBSET and once with PBSE and substrate buffer. ABTS solution (50 μL) was added, and the system was incubated for 60 min at 37 °C. For ELISA controls, bacterial adhesion to blocked, uncoated microtiter plates was checked, and the reaction of the employed antibodies with yeast mannan was tested and found to be negligible. The low background was subtracted when the IC_{50} values were calculated. The percentage inhibition was calculated as $OD(nI)-OD(I)\times 100\times[OD(nI)]^{-1}$ (nI: no inhibitor, I: with inhibitor). IC_{50} values are average values from two independent assays. Relative inhibitory potencies (RIPs) are based on the IC_{50} value of methyl α-D-mannopyranoside (MeMan), with RIP (MeMan) = 1.

General procedures

General procedure 1—*O*-Benzoylation of hydroxy groups: Benzoyl chloride (2 equiv per OH group) was added dropwise under cooling with an ice bath to a solution of the appropriate sugar in dry pyridine (approx. 10 mL pyridine per g substance). The reaction mixture was allowed to warm to room temperature and stirred overnight. H_2O was then added (the same volume as pyridine) and phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3×), and the combined organic layers were subsequently washed with sat. $NaHCO_3$ solution, HCl (1 M) and brine, dried over $MgSO_4$ and filtered. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel.

General procedure 2—Hydroboration–oxidation of allyl groups: A solution of the appropriate allylated sugar in dry THF (approx. 100 mL per g substance) was treated under argon with 9-BBN (0.5 M in THF, 2 equiv per allyl group) and the system was heated under reflux for 1 h. Excess 9-BBN was destroyed by addition of H_2O (0.1 mL) with ice bath cooling, followed by the dropwise and simultaneous addition of equal volumes of a NaOAc solution (3 M) and hydrogen peroxide (30 %; combined the same volume as 9-BBN). The reaction mixture was then stirred overnight at room temperature. After saturation of the aqueous phase by addition of solid K_2CO_3 and phase separation, the aqueous phase was extracted three times with *tert*-butyl methyl ether. The combined organic layers were dried over $MgSO_4$, the solvent was evaporated in vacuo, and the crude product was purified by column chromatography.

General procedure 3—Radical addition of mercaptoethanol to allyl groups: The unsaturated compound was dissolved under argon in dry dioxane (1 mL per mL mercaptoethanol), mercaptoethanol (15 equiv per allyl group) and AIBN (20 mg) were added, and the reaction mixture was stirred at 75 °C (preheated oil bath) for 2 h. After addition of another portion of AIBN (20 mg), the mixture was heated for another 2 h, the solvent and the thiol were removed in vacuo, and the crude product was purified by column chromatography.

General procedure 4—Glycosylation with trichloroacetimidates: The acceptor and the trichloroacetimidate donor were dissolved under argon in a small volume of dry CH_2Cl_2 (approx. 1 mL CH_2Cl_2 per g imidate). The reaction was initiated by addition of TMSOTf (2–3 drops), and the solution was stirred at room temperature overnight. The reaction was then quenched with an excess of solid $NaHCO_3$, and the mixture was diluted with CH_2Cl_2 and filtered. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography.

General procedure 5—Debenzoylation under Zemplén conditions: The protected substance was either dissolved or suspended in dry MeOH, solid NaOMe was added until pH had reached approx. 10, and the mixture was stirred at room temperature. The dendritic heptasaccharides required the addition of a small amount of *tert*-butyl methyl ether, due to the insolubility of the compounds in pure MeOH. The *tert*-butyl methyl ether was removed in vacuo at room temperature after the compound had dissolved completely. After completion of the reaction, acidic ion-exchange resin (Amberlite IR-120, H^+ form) was added for neutralisation. Filtration and removal of the solvent in vacuo yielded the crude product, which could be purified by column chromatography on Sephadex LH-20 if necessary.

Methyl 3,6-di-*O*-allyl-2,4-di-*O*-benzoyl-α-D-mannopyranoside (2): Compound **2** was synthesised by GP 1 from methyl 3,6-di-*O*-allyl-α-D-mannopyranoside (**1**, 965 mg, 3.52 mmol) and benzoyl chloride (0.85 mL, 7.3 mmol). The crude product was purified by column chromatography (silica, pentane/ethyl acetate 4:1). Yield: 1.22 g (72 %) as a colourless syrup; $[\alpha]_D^{20}=-44$ ($c=0.89$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.12$–8.10 (m, 2H; 2×$H_{o\text{-}Ar}$), 8.08–8.05 (m, 2H; 2×$H_{o\text{-}Ar}$), 7.58 (m, 2H; 2×$H_{p\text{-}Ar}$), 7.46 (m, 4H; 4×$H_{m\text{-}Ar}$), 5.85 (dddd, $^3J=17.2$ Hz, $^3J=10.5$ Hz, $^3J=5.6$ Hz, $^3J=5.6$ Hz, 1H; manOCH$_2$C*H*=CH$_2$), 5.67 (dddd, $^3J=17.2$ Hz, $^3J=10.4$ Hz, $^3J=6.1$ Hz, $^3J=5.2$ Hz, 1H; manOCH$_2$C*H*=CH$_2$), 5.59 (dd≈t, $^3J=9.9$ Hz, 1H; H-4), 5.55 (dd, $^3J=1.9$ Hz, $^3J=3.4$ Hz, 1H; H-2), 5.23 (dddd, $^3J=17.2$ Hz, $^4J=1.7$ Hz, $^4J=1.7$ Hz, $^2J=1.7$ Hz, 1H; manOCH$_2$CH=C*H*$_{trans}$H), 5.15 (dddd, $^3J=17.2$ Hz, $^4J=1.6$ Hz, $^4J=1.6$ Hz, $^2J=1.6$ Hz, 1H; manOCH$_2$CH=C*H*$_{trans}$H), 5.10 (dddd, $^3J=10.4$ Hz, $^2J=1.8$ Hz, $^4J=1.3$ Hz, $^4J=1.3$ Hz, 1H; manOCH$_2$CH=C*H*$_{cis}$H), 5.02 (dddd, $^3J=10.4$ Hz, $^2J=1.3$ Hz, $^4J=1.3$ Hz, $^4J=1.3$ Hz, 1H; manOCH$_2$CH=C*H*$_{cis}$H), 4.91 (d, $^3J=1.8$ Hz, 1H; H-1), 4.11–4.05 (m, 2H; manOC*H*HCH=CH$_2$, H-5), 4.09 (dd, $^3J=9.9$ Hz, $^3J=3.4$ Hz, 1H; H-3), 4.01 (ddd, $^3J=5.6$ Hz, $^4J=1.4$ Hz, $^4J=1.4$ Hz, 2H; manOC*HH*CH=CH$_2$), 3.96 (m, 1H; manOC*H*HCH=CH$_2$), 3.67–3.63 (m, 2H; H-6, H-6′), 3.47 ppm (s, 3H; CH_3); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta=165.78$, 165.48 (2×C=O), 134.40, 134.24 (2×manOCH$_2$*C*H=CH$_2$), 133.19, 133.11 (2×$C_{p\text{-}Ar}$), 129.94 (2×$C_{o\text{-}Ar}$), 129.78 ($C_{Ar\text{-}q}$), 129.68 (2×$C_{o\text{-}Ar}$), 129.60 ($C_{Ar\text{-}q}$), 128.36 (2×$C_{m\text{-}Ar}$), 128.35 (2×$C_{m\text{-}Ar}$), 117.31, 116.87 (2×manOCH$_2$CH=*C*H$_2$), 98.72 (C-1), 74.43 (C-3), 72.46, 70.61 (2×manO*C*H$_2$CH=CH$_2$), 70.08 (C-5), 69.50 (C-6), 69.17 (C-2), 68.97 (C-4), 55.20 ppm (CH_3); IR (KBr): $\tilde{\nu}_{max}=2915$, 1726, 1323, 1266, 1111, 1069, 1027, 712 cm^{-1}; MS (CI/70 kV): *m*/*z* (%): 483.0 (75) $[M+H]^+$, 450.9 (100) $[M-OMe]^+$, 425.0 (1) $[M-HOAll]^+$, 361.0 (16) $[M-OBz]^+$; HRMS (ESI): *m*/*z*: calcd for $C_{27}H_{30}NaO_8$: 505.1833; found: 505.1857 $[M+Na]^+$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(3-hydroxypropyl)-α-D-mannopyranoside (3): Compound **3** was synthesised by GP 2 from mannoside **2** (234 mg, 0.485 mmol). The crude product was purified by column chromatography (silica, pentane/ethyl acetate 1:3). Yield: 174 mg (69 %) as a colourless syrup; $[\alpha]_D^{20}=-64$ ($c=0.88$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=8.12$ (m, 2H; 2×$H_{o\text{-}Ar}$), 8.06 (m, 2H; 2×$H_{o\text{-}Ar}$), 7.63–7.43 (m, 6H; 4×$H_{m\text{-}Ar}$, 2×$H_{p\text{-}Ar}$), 5.65 (dd≈t, $^3J=9.9$ Hz, 1H; H-4), 5.63 (dd, $^3J=3.4$ Hz, $^3J=1.9$ Hz, 1H; H-2), 4.94 (d, $^3J=1.9$ Hz, 1H; H-1), 4.03 (dd, $^3J=9.9$ Hz, $^3J=3.4$ Hz, 1H; H-3), 4.02 (m, 1H; H-5), 3.96–3.50 (m, 8H; 2×manOC*HH*CH$_2$C*HH*OH), 3.48 (s, 3H; CH_3), 3.42–3.38 (m, 2H; H-6, H-6′), 2.38–2.15 ppm (m, 4H; 2×manOCH$_2$C*HH*CH$_2$OH); ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta=166.16$, 165.86 (2×C=O), 133.54, 133.50, 129.97, 129.73, 128.56, 128.55 (4×$C_{o\text{-}Ar}$, 4×$C_{m\text{-}Ar}$, 2×$C_{p\text{-}Ar}$), 129.40,

129.31 (2×$C_{Ar\text{-}quart}$), 98.91 (C-1), 76.06, 69.88, 68.74, 68.60 (C-2, C-3, C-4, C-5), 69.66, 69.54, 67.51, 60.52, 59.69 (2×manO*C*H_2CH_2CH_2OH, 2×manOCH$_2$CH_2*C*H_2OH, C-6), 55.39 (CH_3), 32.25, 32.09 ppm (2×manOCH$_2$*C*H_2CH_2OH); IR(KBr): $\tilde{\nu}_{max}$=3434, 2927, 1725, 1452, 1323, 1267, 1114, 1070, 1027, 713 cm^{-1}; MS (CI, 70 kV): *m*/*z* (%): 487.3 (6) [*M*−OMe]$^+$, 413.2 (2) [*M*−OMe−HO(CH$_2$)$_3$OH]$^+$, 289.2 (4) [*M*−OMe−HO(CH$_2$)$_3$OH−OBz]$^+$; HRMS (ESI): *m*/*z*: calcd for $C_{27}H_{34}NaO_{10}$: 541.2044; found: 541.2004 [*M*+Na]$^+$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(3-{2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyloxy}-propyl)-α-D-mannopyranoside (5): The acceptor alcohol **3** (316 mg, 0.609 mmol) was glycosylated with donor **4** (4.51 g, 6.09 mmol) by GP 4. For purification, the crude product was chromatographed first on silica (toluene/EtOAc 9:1) and then on Sephadex LH-20 (acetone). Yield: 940 mg (92%) as a white foam; $[\alpha]_D^{20}=-54$ (c=1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=8.11–8.02 (m, 12H; 12×$H_{o\text{-}Ar}$), 7.95–7.91 (m, 4H; 4×$H_{o\text{-}Ar}$), 7.83–7.80 (m, 4H; 4×$H_{o\text{-}Ar}$), 7.61–7.45 (m, 7H; 7×$H_{p\text{-}Ar}$), 7.45–7.30 (m, 19H; 3×$H_{p\text{-}Ar}$, 16×$H_{m\text{-}Ar}$), 7.25 (m, 4H; 4×$H_{m\text{-}Ar}$), 6.10 (dd≈t, ^3J=10.1 Hz, 1H; H-4), 6.02 (dd≈t, ^3J=10.1 Hz, 1H; H-4), 5.89 (dd, ^3J=10.1 Hz, ^3J=3.3 Hz, 1H; H-3), 5.79 (dd, ^3J=10.1 Hz, ^3J=3.3 Hz, 1H; H-3), 5.69 (dd, ^3J=3.3 Hz, ^3J=1.8 Hz, 1H; H-2), 5.65 (dd≈t, ^3J=9.9 Hz, 1H; H-4c), 5.62 (dd, ^3J=3.2 Hz, ^3J=2.0 Hz, 1H; H-2c), 5.61 (dd, ^3J=3.3 Hz, ^3J=1.8 Hz, 1H; H-2), 5.08 (d, ^3J=1.7 Hz, 1H; H-1), 4.92 (d, ^3J=1.7 Hz, 1H; H-1c), 4.74 (d, ^3J=1.7 Hz, 1H; H-1), 4.67 (dd, ^2J=12.1 Hz, ^3J=2.5 Hz, 1H; H-6′), 4.50 (dd, ^2J=12.2 Hz, ^3J=2.6 Hz, 1H; H-6′), 4.46 (dd, ^2J=12.2 Hz, ^3J=4.2 Hz, 1H; H-6), 4.41–4.35 (m, 2H; H-5, H-6), 4.18 (m, 1H; H-5), 4.08 (m, 1H; H-5c), 4.06 (dd, ^3J=9.7 Hz, ^3J=3.2 Hz, 1H; H-3c), 3.92 (m, 1H; OC*H*H), 3.82 (m, 1H; OC*H*H), 3.73–3.54 (m, 6H; H-6c, H-6c′, 4×OC*H*H), 3.50–3.44 (m, 1H; OC*H*H), 3.48 (s, 3H; OCH_3), 3.40 (m, 1H; OC*H*H), 1.97 (m, 2H; OCH$_2$C*H*$_2$CH$_2$O), 1.75 ppm (m, 2H; OCH$_2$C*H*$_2$CH$_2$O); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ=166.09, 166.04, 165.61, 165.46, 165.43, 165.40, 165.38, 165.27, 165.13 (10×C=O), 133.35, 133.34, 133.31, 133.29, 133.16, 133.07, 133.02, 132.96 (10×$C_{p\text{-}Ar}$), 129.91, 129.88, 129.80, 129.74, 129.68, 129.66 (20×$C_{o\text{-}Ar}$), 129.58, 129.47, 129.36, 129.15, 129.10, 129.03, 128.98 (10×$C_{Ar\text{-}quart}$), 128.51, 128.44, 128.40, 128.39, 128.35, 128.23, 128.21 (20×$C_{m\text{-}Ar}$), 98.87 (C-1c), 97.58, 97.46 (2×C-1), 76.12 (C-3c), 70.45, 70.37 (2×C-2), 70.18 (C-6c), 70.08, 69.98 (2×C-3, C-5c), 68.91, 68.82, 68.71, 68.55 (C-2c, C-4c, 2×C-5), 68.08 (CH_2), 66.91, 66.90 (2×C-4), 66.60, 65.29, 65.27 (3×CH_2), 62.84, 62.74 (2×C-6), 55.30 (OCH_3), 29.78, 29.59 ppm (2×OCH$_2$CH_2CH$_2$O); IR (KBr): $\tilde{\nu}_{max}$=3063, 2924, 1728, 1602, 1584, 1492, 1451, 1315, 1266, 1177, 1110, 1069, 1027, 974, 709 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{95}H_{86}NaO_{28}$: 1697.5198; found: 1697.5121 [*M*+Na]$^+$.

Methyl 3,6-di-*O*-(3-{α-D-mannopyranosyloxy}-propyl)-α-D-mannopyranoside (6): Deprotection of compound **5** (298 mg, 0.178 mmol) was accomplished by GP 5. For purification, the crude product was chromatographed on Sephadex LH-20 (MeOH), dissolved in H_2O and lyophilised. Yield: 97.3 mg (86%) as a colourless foam; $[\alpha]_D^{20}=+70$ (c=0.64, MeOH); ^{1}H NMR (500 MHz, [D$_4$]MeOH): δ=4.79 (d, ^3J=1.6 Hz, 1H; H-1), 4.78 (d, ^3J=1.5 Hz, 1H; H-1), 4.67 (d, ^3J=1.7 Hz, 1H; H-1c), 3.97 (dd, ^3J=3.2 Hz, ^3J=1.8 Hz, 1H; H-2c), 3.93–3.53 (m, 24H; H-4c, H-5c, H-6c, H-6c′, 2×H-2, 2×H-3, 2×H-4, 2×H-5, 2×H-6, 2×H-6′, 2×OC*H*$_2$CH$_2$C*H*$_2$O), 3.45 (dd, ^3J=9.2 Hz, ^3J=3.3 Hz, 1H; H-3c), 3.41 (s, 3H; CH_3), 1.95–1.86 ppm (m, 4H; 2×OCH$_2$C*H*$_2$CH$_2$O); ^{13}C NMR (125.76 MHz, [D$_4$]MeOH): δ=102.66 (C-1c), 101.58, 101.50 (2×C-1), 80.98 (C-3c), 74.52, 74.64, 73.50, 72.69, 72.22 (5×CH), 71.60, 69.42 (2×CH_2), 68.94 (C-2c), 68.77, 68.69 (2×CH), 67.76 (CH_2), 67.66 (CH), 65.41, 65.39, 63.01, 62.94 (4×CH_2), 55.35 (CH_3), 31.09, 30.84 ppm (2×OCH$_2$CH_2CH$_2$O); IR (KBr): $\tilde{\nu}_{max}$=3440 (br), 2926, 1637, 1135, 1103, 1055, 974, 812 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{25}H_{46}NaO_{18}$: 657.2576; found: 657.2534 [*M*+Na]$^+$.

***p*-Methoxyphenyl 3,6-di-*O*-allyl-α-D-mannopyranoside (8)**: A suspension of *p*-methoxyphenyl α-D-mannopyranoside (**7**, 9.50 g, 33.2 mmol) in dry toluene (300 mL) was treated under argon with bis(tributyltin)oxide (25.4 mL, 49.8 mmol) and heated under reflux for 4 h on a Dean–Stark separator. After the mixture had cooled to room temperature, allyl bromide (28.1 mL, 332 mmol) and tetrabutylammonium bromide (3.21 g, 9.96 mmol) were added to the resulting clear solution and the mixture was stirred for 7 d at 80°C. Evaporation of the solvent in vacuo yielded an oily residue, which was taken up in EtOAc (300 mL). After addition of sat. aqueous KF solution (30 mL), the mixture was stirred vigorously for 2 h, the white precipitate was removed by filtration and washed with EtOAc, and the organic phases were combined. After phase separation, the organic phase was dried over $MgSO_4$ and filtered, the solvent was removed in vacuo, and the crude product was purified by column chromatography on silica (toluene/EtOAc 1:1). Yield: 6.15 g (51%) as a colourless oil; $[\alpha]_D^{20}=+87$ (c=2.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=7.01 (d, ^3J=9.1 Hz, 2H; 2×H_{Ar}), 6.82 (d, ^3J=9.1 Hz, 2H; 2×H_{Ar}), 6.00 (dddd, ^3J=17.0 Hz, ^3J=10.4 Hz, ^3J=5.8 Hz, ^3J=5.8 Hz, 1H; C*H*=CH$_2$), 5.87 (dddd, ^3J=17.2 Hz, ^3J=10.4 Hz, ^3J=5.6 Hz, ^3J=5.6 Hz, 1H; C*H*=CH$_2$), 5.49 (d, ^3J=1.7 Hz, 1H; H-1), 5.37 (dddd, ^3J=17.2 Hz, ^2J=1.5 Hz, ^4J=1.5 Hz, ^4J=1.5 Hz, 1H; CH=C*H*$_{trans}$H), 5.27–5.24 (m, 1H; CH=C*H*$_{cis}$H), 5.24 (dddd, ^3J=17.2 Hz, ^2J=1.6 Hz, ^4J=1.6 Hz, ^4J=1.6 Hz, 1H; CH=C*H*$_{trans}$H), 5.16 (dddd, ^3J=10.4 Hz, ^2J=1.5 Hz, ^4J=1.4 Hz, ^4J=1.4 Hz, 1H; CH=C*H*$_{cis}$H), 4.28 (dddd, ^2J=12.6 Hz, ^3J=5.7 Hz, ^4J=1.3 Hz, ^4J=1.3 Hz, 1H; C*H*HCH=CH$_2$), 4.22 (dddd, ^2J=12.6 Hz, ^3J=5.8 Hz, ^4J=1.3 Hz, ^4J=1.3 Hz, 1H; C*H*HCH=CH$_2$), 4.19 (dd, ^3J=3.3 Hz, ^3J=1.8 Hz, 1H; H-2), 4.03 (dddd, ^2J=12.8 Hz, ^3J=5.6 Hz, ^4J=1.4 Hz, ^4J=1.4 Hz, 1H; C*H*HCH=CH$_2$), 4.01–3.98 (m, 1H; C*H*HCH=CH$_2$), 3.99 (dd≈t, ^3J=9.5 Hz, 1H; H-4), 3.88 (ddd, ^3J=9.4 Hz, ^3J=4.5 Hz, ^3J=4.5 Hz, 1H; H-5), 3.81 (dd, ^3J=9.2 Hz, ^3J=3.4 Hz, 1H; H-3), 3.77 (s, 3H; OCH_3), 3.72 (dd, ^2J=10.4 Hz, ^3J=4.6 Hz, 1H; H-6), 3.67 (dd, ^2J=10.4 Hz, ^3J=4.4 Hz, 1H; H-6′), 2.84 (brs, 1H; OH), 2.61 ppm (brs, 1H; OH); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ=155.00, 150.13 (2×$C_{Ar\text{-}quart}$), 134.37, 134.30 (2×*C*H=CH$_2$), 117.81 (CH=*C*H$_2$), 117.80 (C_{Ar}), 117.16 (CH=CH$_2$), 114.58 (2×C_{Ar}), 98.43 (C-1), 78.78 (C-3), 72.46, 70.93 (2×*C*H$_2$CH=CH$_2$), 70.65 (C-5), 70.20 (C-6), 67.98, 67.83 (C-2, C-4), 55.61 ppm (OCH_3); IR (KBr): $\tilde{\nu}_{max}$=3432 (br), 2928, 1508, 1218, 1105, 1036, 928, 829, 751 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{19}H_{26}NaO_7$: 389.1571; found: 389.1575 [*M*+Na]$^+$.

***p*-Methoxyphenyl 3,6-di-*O*-allyl-2,4-di-*O*-benzoyl-α-D-mannopyranoside (9)**: Mannoside **8** (6.15 g, 16.8 mmol) was benzoylated by GP 1. The crude product was purified by chromatography on silica (cyclohexane/EtOAc 3:1). Yield: 9.64 g (quant.) as a colourless oil; $[\alpha]_D^{20}=+8$ (c=1.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=8.13 (m, 2H; 2×$H_{o\text{-}Ar}$), 8.08 (m, 2H; 2×$H_{o\text{-}Ar}$), 7.59 (m, 2H; 2×$H_{p\text{-}Ar}$), 7.51–7.42 (m, 4H; 4×$H_{m\text{-}Ar}$), 7.11 (m, 2H; 4×H_{Ar}), 6.84 (m, 2H; 4×H_{Ar}), 5.89–5.66 (m, 4H; H-2, H-4, 2×C*H*=CH$_2$), 5.59 (d, ^3J=1.9 Hz, 1H; H-1), 5.20 (dddd, ^3J=17.3 Hz, ^2J=1.6 Hz, ^4J=1.6 Hz, ^4J=1.6 Hz, 2H; 2×CH=C*H*$_{trans}$H), 5.07 (m, 2H; 2×CH=C*H*$_{cis}$H), 4.30 (dd, ^3J=9.6 Hz, ^3J=3.3 Hz, 1H; H-3), 4.27 (m, 1H; H-5), 4.17 (dddd≈ddt, ^3J=13.1 Hz, ^3J=5.2 Hz, ^4J=1.5 Hz, ^4J=1.5 Hz, 1H; C*H*HCH=CH$_2$), 4.04 (dddd≈ddt, ^2J=13.1 Hz, ^3J=5.9 Hz, ^4J=1.4 Hz, ^4J=1.4 Hz, 1H; C*H*HCH=CH$_2$), 3.97 (m, 2H; CH_2CH=CH$_2$), 3.78 (s, 3H; OCH_3), 3.69–3.60 ppm (m, 2H; H-6, H-6′); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ=165.79, 165.45 (2×C=O), 155.34, 150.18 (2×$C_{Ar\text{-}quart}$), 134.39, 134.23 (2×*C*H=CH$_2$), 133.33, 133.18 (2×$C_{p\text{-}Bz}$), 130.02, 129.74 (4×$C_{o\text{-}Bz}$), 129.48 (2×$C_{Bz\text{-}quart}$), 128.45, 128.40 (4×$C_{m\text{-}Bz}$), 118.25 (2×C_{Ar}), 117.45, 116.79 (2×CH=*C*H$_2$), 114.59 (2×C_{Ar}), 97.31 (C-1), 74.38 (C-3), 72.38, 70.79 (2×*C*H$_2$CH=CH$_2$), 70.73 (C-5), 69.20 (C-2, C-6), 68.75 (C-4), 55.61 ppm (OCH_3); IR (KBr): $\tilde{\nu}_{max}$=2910, 1727, 1602, 1507, 1452, 1360, 1265, 1215, 1108, 1027, 927, 827, 711 cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{33}H_{34}NaO_9$: 597.2095; found: 597.2064 [*M*+Na]$^+$.

***O*-(3,6-Di-*O*-allyl-2,4-di-*O*-benzoyl-α-D-mannopyranosyl) trichloroacetimidate (10)**: Mannoside **9** (16.5 g, 28.7 mmol) was dissolved in MeCN/H_2O (4:1, 190 mL), the solution was cooled to 0°C, and CAN (47.2 g, 86.1 mmol, 3 equiv) was added. After stirring for 3 h at room temperature, the mixture was diluted with EtOAc (400 mL). The phases were separated, the organic layer was washed successively with H_2O (100 mL), sat. $NaHCO_3$ solution (100 mL) and H_2O (100 mL), dried over $MgSO_4$ and filtered, and the solvent was evaporated in vacuo. The residue was purified by chromatography on silica (cyclohexane/EtOAc 3:1), and the fraction containing the intermediate 3,6-di-*O*-allyl-2,4-di-*O*-benzoyl-D-mannopyranose was collected as a dark red solid (9.14 g). This was dissolved under argon together with trichloroacetonitrile (19.6 mL, 195 mmol) in dry CH_2Cl_2 (90 mL), the solution was cooled to 0°C, and the reaction was initiated by addition of DBU (0.2 mL). After 1 h stirring at room temperature, all volatiles were evaporated in vacuo without

heating and the crude product was purified by column chromatography on silica (cyclohexane/EtOAc 4:1). Yield: 9.27 g (53%, over 2 steps) as a colourless syrup; $[\alpha]_D^{20}=-26$ ($c=0.52$, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.79$ (s, 1H; NH), 8.13 (m, 2H; 2×$H_{o\text{-}Ar}$), 8.07 (m, 2H; 2×$H_{o\text{-}Ar}$), 7.62–7.58 (m, 2H; $H_{p\text{-}Ar}$), 7.50–7.45 (m, 4H; 4×$H_{m\text{-}Ar}$), 6.48 (d, $^3J=2.1$ Hz, 1H; H-1), 5.82 (dddd, $^3J=17.2$ Hz, $^3J=10.4$ Hz, $^3J=5.6$ Hz, $^3J=5.6$ Hz, 1H; C*H*=CH_2), 5.75 (dd≈t, $^3J=10.0$ Hz, 1H; H-4), 5.74 (dd, $^3J=3.3$ Hz, $^3J=2.2$ Hz, 1H; H-2), 5.70 (dddd, $^3J=17.2$ Hz, $^3J=10.3$ Hz, $^3J=6.3$ Hz, $^3J=5.4$ Hz, 1H; C*H*=CH_2), 5.21 (dddd, $^3J=17.3$ Hz, $^2J=1.7$ Hz, $^4J=1.7$ Hz, $^4J=1.7$ Hz, 1H; CH=CH_{trans}H), 5.16 (dddd, $^3J=17.2$ Hz, $^2J=1.6$ Hz, $^4J=1.6$ Hz, $^4J=1.6$ Hz, 1H; CH=CH_{trans}H), 5.10–5.05 (m, 2H; 2×CH=CH_{cis}H), 4.29 (ddd, $^3J=10.1$ Hz, $^3J=4.0$ Hz, $^3J=4.0$ Hz, 1H; H-5), 4.20 (dd, $^3J=9.8$ Hz, $^3J=3.3$ Hz, 1H; H-3), 4.14–4.09 (m, 1H; C*H*HCH=CH_2), 4.03–3.98 (m, 3H; 3×C*H*HCH=CH_2), 3.67 ppm (m, 2H; H-6, H-6′); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta=165.52$, 165.39 (2×C=O), 159.79 (C=NH), 134.39, 134.00 (2×*C*H=CH_2), 133.46, 133.25 (2×$C_{p\text{-}Ar}$), 130.10, 129.77 (4×$C_{o\text{-}Ar}$), 129.66, 129.27 (2×$C_{Ar\text{-}quart}$), 128.50, 128.43 (4×$C_{m\text{-}Ar}$), 118.05, 117.00 (2×CH=*C*H_2), 95.18 (C-1), 90.83 (CCl_3), 73.99 (C-3), 73.16 (C-5), 72.50, 70.95 (2×*C*H_2CH=CH_2), 69.14 (C-6), 68.22, 67.67 ppm (C-2, C-4); IR (KBr): $\tilde{\nu}_{max}=3447$, 2921, 1729, 1676, 1452, 1320, 1264, 1107, 1069, 1028, 975, 934, 840, 796, 710, 644 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{28}H_{28}Cl_3NNaO_8$: 634.0773; found: 634.0757 $[M+Na]^+$.

Methyl 3,6-di-*O*-(3-{3,6-di-*O*-allyl-2,4-di-*O*-benzoyl-α-D-mannopyranosyloxy}-propyl)-2,4-di-*O*-benzoyl-α-D-mannopyranoside (11): The acceptor alcohol **3** (478 mg, 0.921 mmol) was glycosylated with donor **10** (3.75 g, 6.12 mmol) by GP 4. For purification, the crude product was chromatographed on silica (toluene/EtOAc 8:1). Yield: 1.03 g (79%) as a colourless foam; $[\alpha]_D^{20}=-68$ ($c=0.51$, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.12$–8.04 (m, 12H; 12×$H_{o\text{-}Ar}$), 7.59–7.47 (m, 6H; 6×$H_{p\text{-}Ar}$), 7.47–7.39 (m, 12H; 12×$H_{m\text{-}Ar}$), 5.81 (m, 2H; 2×C*H*=CH_2), 5.66 (m, 2H; 2×C*H*=CH_2), 5.61 (dd≈t, $^3J=9.9$ Hz, 1H; H-4), 5.61 (m, 1H; H-2), 5.58 (dd≈t, $^3J=10.1$ Hz, 1H; H-4), 5.53 (dd≈t, $^3J=9.9$ Hz, 1H; H-4), 5.51 (m, 1H; H-2), 5.44 (dd, $^3J=3.3$ Hz, $^3J=1.9$ Hz, 1H; H-2), 5.20 (dddd, $^3J=17.3$ Hz, $^2J=1.7$ Hz, $^4J=1.7$ Hz, $^4J=1.7$ Hz, 1H; CH=CH_{trans}H), 5.19 (dddd, $^3J=17.3$ Hz, $^2J=1.7$ Hz, $^4J=1.7$ Hz, $^4J=1.7$ Hz, 1H; CH=CH_{trans}H), 5.11 (m, 2H; 2×CH=CH_{trans}H), 5.07 (m, 2H; 2×CH=CH_{cis}H), 4.98 (m, 2H; 2×CH=CH_{cis}H), 4.97 (d, $^3J=2.0$ Hz, 1H; H-1), 4.92 (d, $^3J=1.9$ Hz, 1H; H-1), 4.67 (d, $^3J=1.9$ Hz, 1H; H-1), 4.10–3.88 (m, 14H; 3×H-3, 3×H-5, 8×OC*H*HCH=CH_2), 3.80 (m, 2H; 2×OC*H*HCH_2), 3.69 (dd, $^2J=10.7$ Hz, $^3J=3.0$ Hz, 1H; H-6′), 3.65 (dd, $^2J=10.7$ Hz, $^3J=5.5$ Hz, 1H; H-6), 3.63–3.51 (m, 8H; 4×H-6, 4×OC*H*HCH_2), 3.50–3.43 (m, 1H; OC*H*HCH_2), 3.47 (s, 3H; OCH_3), 3.36 (m, 1H; OC*H*HCH_2), 1.90 (m, 2H; $OCH_2CH_2CH_2O$), 1.72 ppm (m, 2H; $OCH_2CH_2CH_2O$); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta=165.82$, 165.73, 165.63, 165.57, 165.55 (6×C=O), 134.56, 134.54, 134.39, 134.36 (4×*C*H=CH_2), 133.33, 133.26, 133.24, 133.17, 133.16, 133.11 (6×$C_{p\text{-}Ar}$), 130.03, 130.01 ($C_{o\text{-}Ar}$), 129.93, 129.85 ($C_{Ar\text{-}quart}$), 129.78 ($C_{o\text{-}Ar}$), 129.75 ($C_{Ar\text{-}quart}$), 129.73 ($C_{o\text{-}Ar}$), 129.67 ($C_{Ar\text{-}quart}$), 128.54, 128.51, 128.44, 128.43, 128.40 (12×$C_{m\text{-}Ar}$), 117.23, 117.18, 116.89, 116.85 (4×CH=*C*H_2), 98.88, 97.72, 97.70 (3×C-1), 75.88, 74.69, 74.65 (3×C-3), 72.54, 72.50, 70.67, 70.60 (4×*C*H_2CH=CH_2), 70.38 (C-6), 70.27, 70.17, 70.09 (3×C-5), 69.58, 69.48 (2×C-6), 69.36, 69.22 (2×C-2), 69.11, 69.07, 68.91 (C-2, 3×C-4), 68.54, 66.76, 65.06, 64.96 (4×OCH_2CH_2), 55.35 (CH_3), 29.80, 29.75 ppm (2×$OCH_2CH_2CH_2O$); IR (KBr): $\tilde{\nu}_{max}=2918$, 1725, 1451, 1265, 1110, 1069, 1027, 711 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{79}H_{86}NaO_{24}$: 1441.5401; found: 1441.5416 $[M+Na]^+$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(3-{2,4-di-*O*-benzoyl-3,6-di-*O*-[3-hydroxypropyl]-α-D-mannopyranosyloxy}-propyl)-α-D-mannopyranoside (12): Compound **12** was synthesised from mannoside **11** (216 mg, 0.152 mmol) by GP 2. The crude product was purified by column chromatography on silica (EtOAc) and then on Sephadex LH-20 (CH_2Cl_2/MeOH 1:1). Yield: 91 mg (40%) as a sticky white foam; $[\alpha]_D^{20}=-74$ ($c=4.2$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=8.14$–8.00 (m, 12H; 12×$H_{o\text{-}Ar}$), 7.64–7.50 (m, 6H; 6×$H_{p\text{-}Ar}$), 7.50–7.37 (m, 12H; 12×$H_{m\text{-}Ar}$), 5.68–5.53 (m, 5H; 2×H-2, 3×H-4), 5.51 (dd, $^3J=3.1$ Hz, $^3J=1.9$ Hz, 1H; H-2), 5.00 (d, $^3J=1.7$ Hz, 1H; H-1), 4.91 (d, $^3J=1.7$ Hz, 1H; H-1), 4.69 (d, $^3J=1.7$ Hz, 1H; H-1), 4.10–4.02 (m, 1H; H-5), 4.05 (dd, $^3J=9.7$ Hz, $^3J=3.3$ Hz, 1H; H-3), 4.02–3.94 (m, 1H; H-5), 3.99 (dd, $^3J=9.7$ Hz, $^3J=3.3$ Hz, 1H; H-3), 3.94–3.30 (m, 32H; H-3, H-5, 3×H-6, 3×H-6′, 2×OC*H*$_2$CH$_2$C*H*$_2$O, 4×OC*H*$_2$CH$_2$C*H*$_2$OH), 3.47 (s, 3H; OCH_3), 2.85 (br, 2H; 2×OH), 2.10 (br, 2H; 2×OH), 1.91 (m, 2H; $OCH_2CH_2CH_2O$), 1.85–1.70 (m, 6H; $OCH_2CH_2CH_2O$, 2×$OCH_2CH_2CH_2OH$), 1.61–1.50 ppm (m, 4H; 2×$OCH_2CH_2CH_2OH$); ^{13}C NMR (76.47 MHz, $CDCl_3$): $\delta=166.15$, 166.02, 165.83, 165.69, 165.49 (6×C=O), 133.50, 133.44, 133.41, 133.33, 133.27 (6×$C_{p\text{-}Ar}$), 129.94, 129.92, 129.72, 129.71 (10×$C_{o\text{-}Ar}$), 129.70 ($C_{Ar\text{-}quart}$), 129.66 (2×$C_{o\text{-}Ar}$), 129.52, 129.46, 129.42, 129.40, 129.32 (5×$C_{Ar\text{-}quart}$), 128.56–128.43 (12×$C_{m\text{-}Ar}$), 98.82, 97.77, 97.73 (3×C-1), 76.21, 76.13, 75.80 (3×C-3), 70.20 (OCH_2), 69.98, 69.96, 69.84 (3×C-5), 69.46 (2×OCH_2), 69.31 (2×OCH_2), 68.97, 68.85, 68.80, 68.77, 68.62, 68.56 (3×C-2, 3×C-4), 68.36, 67.46, 67.36, 66.57, 65.08, 64.95 (6×OCH_2), 60.35, 60.26, 59.70, 59.66 (4×$OCH_2CH_2CH_2OH$), 55.32 (OCH_3), 32.27, 32.25, 32.10, 32.09 (4×$OCH_2CH_2CH_2OH$), 29.72, 29.66 ppm (2×$CH_2CH_2CH_2O$); IR (KBr): $\tilde{\nu}_{max}=3434$, 2926, 2881, 1724, 1601, 1451, 1358, 1322, 1267, 1113, 1070, 1027, 712 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{79}H_{94}NaO_{28}$: 1513.5824; found: 1513.5883 $[M+Na]^+$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(3-{2,4-di-*O*-benzoyl-3,6-di-*O*-[3-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)-propyl]-α-D-mannopyranosyloxy}-propyl)-α-D-mannopyranoside (13): The acceptor tetraol **12** (76 mg, 51 μmol) was glycosylated with donor **4** (758 mg, 1.02 mmol) by GP 4. For purification, the crude product was first chromatographed on silica (toluene/EtOAc 8:1) and then on Sephadex LH-20 (CH_2Cl_2/MeOH 1:1). Yield: 105 mg (54%) as a white foam; $[\alpha]_D^{20}=-70$ ($c=1.6$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.10$–8.01 (m, 28H; 28×$H_{o\text{-}Ar}$), 7.94–7.90 (m, 8H; 8×$H_{o\text{-}Ar}$), 7.83–7.78 (m, 8H; 8×$H_{o\text{-}Ar}$), 7.61–7.22 (m, 66H; 66×H_{Ar}), 6.09 (dd≈t, $^3J=10.1$ Hz, 2H; 2×H-4), 6.01 (dd≈t, $^3J=10.1$ Hz, 1H; H-4), 6.00 (dd≈t, $^3J=10.1$ Hz, 1H; H-4), 5.87 (dd, $^3J=10.1$ Hz, $^3J=3.3$ Hz, 2H; 2×H-3), 5.76 (2×dd≈m_c, 2H; 2×H-3), 5.68 (dd, $^3J=3.3$ Hz, $^3J=1.8$ Hz, 2H; 2×H-2), 5.67 (dd≈t, $^3J=9.9$ Hz, 1H; H-4), 5.63–5.56 (m, 6H; 4×H-2, 2×H-4), 5.50 (dd, $^3J=3.1$ Hz, $^3J=1.9$ Hz, 1H; H-2), 5.06 (d, $^3J=1.6$ Hz, 2H; 2×H-1), 4.99 (d, $^3J=1.7$ Hz, 1H; H-1), 4.89 (d, $^3J=1.7$ Hz, 1H; H-1), 4.71 (d, $^3J=1.7$ Hz, 1H; H-1), 4.70 (d, $^3J=1.7$ Hz, 2H; 2×H-1), 4.65 (m, 2H; 2×H-6), 4.49–4.42 (m, 4H; 4×H-6), 4.40–4.31 (m, 4H; 2×H-5, 2×H-6), 4.15 (m, 2H; 2×H-5), 4.08–3.98, 3.92–3.85 (2×m, 8H; 3×H-3, 3×H-5, 2×OC*H*HCH$_2$CH$_2$O), 3.84–3.76 (m, 4H; 4×OC$_H$HCH$_2$CH$_2$O), 3.71–3.33 (m, 24H; 6×H-6, 18 OC*H*HCH$_2$CH$_2$O), 3.44 (s, 3H; OCH_3), 1.97–1.87 (m, 6H; 3×$OCH_2CH_2CH_2O$), 1.80–1.66 ppm (m, 6H; 3×$OCH_2CH_2CH_2O$); ^{13}C NMR (125.47 MHz, $CDCl_3$): $\delta=166.09$, 166.04, 165.65, 165.58, 165.51, 165.42, 165.39, 165.36, 165.26, 165.13 (22×C=O), 133.33, 133.30, 133.23, 133.12, 133.06, 133.03, 133.02, 132.95 (22×$C_{p\text{-}Ar}$), 129.91, 129.81, 129.75, 129.69, 129.66 (44×$C_{o\text{-}Ar}$), 129.49, 129.40, 129.18, 129.15, 129.05, 129.00 (22×$C_{Ar\text{-}quart}$), 128.60–128.30, 128.23, 128.21 (44×$C_{m\text{-}Ar}$), 98.80, 97.82, 97.80 (3×C-1), 97.58 (2×C-1), 97.44 (2×C-1), 76.21, 76.13, 75.83 (3×C-3), 70.44, 70.38, 70.25, 70.11, 70.04, 69.99, 69.85, 69.11, 68.88, 68.83, 68.78, 68.70, 68.49 (7×C-2, 4×C-3, 3×C-4, 7×C-5), 70.02, 69.91 (3×C-6), 68.47, 68.15, 68.11 (3×CH_2), 66.90 (4×C-4), 66.72, 66.56, 66.53, 65.48, 65.34, 65.13, 65.00 (9×CH_2), 62.85 (2×C-6), 62.71 (2×C-6), 55.24 (OCH_3), 29.77, 29.71, 29.61 ppm (6×$OCH_2CH_2CH_2O$); IR (KBr): $\tilde{\nu}_{max}=2958$, 1727, 1602, 1584, 1451, 1316, 1266, 1177, 1109, 1068, 1026, 709 cm^{-1}; MALDI-TOF-MS: m/z: calcd for $C_{215}H_{198}NaO_{64}$: 3826.21; found: 3826.41 $[M+Na]^+$, 3842.38 $[M+K]^+$.

Methyl 3,6-di-*O*-(3-{3,6-di-*O*-[3-(α-D-mannopyranosyloxy)-propyl]-α-D-mannopyranosyloxy}-propyl)-α-D-mannopyranoside (14): Deprotection of compound **13** (89 mg, 23 μmol) was accomplished by GP 5. For purification, the crude product was chromatographed on Sephadex LH-20 (MeOH), dissolved in H_2O and lyophilised. Yield: 31 mg (88%) as a colourless amorphous solid; $[\alpha]_D^{20}=+70$ ($c=0.98$, MeOH); ^{1}H NMR (500 MHz, [D$_4$]MeOH): $\delta=4.78$–4.75 (m, 6H; 6×H-1), 4.66 (d, $^3J=1.6$ Hz, 1H; H-1), 3.98–3.94 (m, 3H; 3×H-2), 3.91–3.49 (m, 60H; 4×H-2, 4×H-3, 7×H-4, 7×H-5, 14×H-6, 24×OC*H*H), 3.47–3.41 (m, 3H; 3×H-3), 3.39 (s, 3H; OCH_3), 1.96–1.83 ppm (m, 12H; 6×$OCH_2CH_2CH_2O$); ^{13}C NMR (125.76 MHz, [D$_4$]MeOH): $\delta=102.70$, 101.66 (2×C-1), 101.62 (2×C-1), 101.54 (3×C-1), 81.10, 81.09, 81.02 (3×C-3), 74.58 (2×C-5), 74.51 (2×C-5), 73.62, 73.55, 73.52 (3×C-5), 72.71 (4×C-3), 72.25 (4×C-2), 71.72, 71.64, 71.57, 69.56, 69.49 (CH_2), 69.10, 68.92 (CH), 68.80 (2×C-4), 68.71 (2×C-4), 67.90, 67.80 (CH_2), 67.76, 67.71 (CH), 65.77, 65.72, 65.42 (CH_2), 63.06 (2×C-6), 63.00 (2×C-6), 55.43 (OCH_3), 31.15 (2×$OCH_2CH_2CH_2O$), 31.08 ($OCH_2CH_2CH_2O$), 30.88 (2×$OCH_2CH_2CH_2O$), 30.84 ppm ($OCH_2CH_2CH_2O$); IR (KBr): $\tilde{\nu}_{max}=3435$, 2925, 1637, 1136,

1105, 1054, 974, 810 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{61}H_{110}NaO_{42}$: 1537.6364; found: 1537.6402 $[M+Na]^+$, 780.3149 $[M+Na]^{2+}$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(3-{2,4-di-*O*-benzoyl-3,6-di-*O*-[6-hydroxy-4-thiahexyl]-α-D-mannopyranosyloxy}-propyl)-α-D-mannopyranoside (15): The unsaturated compound **11** (238 mg, 0.168 mmol) was treated with mercaptoethanol (0.70 mL, 10 mmol) by GP 3. The crude product was purified by column chromatography on Sephadex LH-20 (MeOH). Yield: 265 mg (91%) as a colourless, glassy solid; $[\alpha]_D^{20}=-61$ ($c=1.8$, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.12$–8.03 (m, 12H; 12×$H_{o\text{-}Ar}$), 7.61–7.40 (m, 18H; 18×H_{Ar}), 5.65–5.55 (m, 4H; H-2c, 3×H-4), 5.54 (dd, $^3J=3.1$ Hz, $^3J=1.9$ Hz, 1H; H-2), 5.46 (dd, $^3J=3.1$ Hz, $^3J=1.9$ Hz, 1H; H-2), 4.97 (d, $^3J=1.6$ Hz, 1H; H-1), 4.92 (d, $^3J=1.5$ Hz, 1H; H-1c), 4.68 (d, $^3J=1.6$ Hz, 1H; H-1), 4.09–4.04 (m, 1H; H-5), 4.06 (dd, $^3J=9.7$ Hz, $^3J=3.3$ Hz, 1H; H-3), 4.01–3.97 (m, 1H; H-5), 3.96 (dd, $^3J=9.7$ Hz, $^3J=3.3$ Hz, 1H; H-3), 3.88–3.83 (m, 1H; H-5), 3.86 (dd, $^3J=9.7$ Hz, $^3J=3.3$ Hz, 1H; H-3), 3.82–3.34 (m, 30H; 3×H-6, 3×H-6′, 8×OC*H*HCH$_2$CH$_2$O, 8×OC*H*HCH$_2$CH$_2$S, 8×SCH$_2$C*H*HOH), 3.48 (s, 3H; OCH_3), 2.65 (m, 4H; 4×SC*H*HCH$_2$OH), 2.59 (m, 4H; 4×SC*H*HCH$_2$CH$_2$O), 2.40–2.33 (m, 4H; 4×SC*H*HCH$_2$OH), 2.33–2.19 (m, 4H; 4×SC*H*HCH$_2$CH$_2$O), 1.91 (m, 2H; 2×OCH$_2$C*H*HCH$_2$O), 1.87–1.68 (m, 6H; 4×SCH$_2$C*H*HCH$_2$O, 2×OCH$_2$C*H*HCH$_2$O), 1.66–1.52 ppm (m, 4H; 4×SCH$_2$C*H*HCH$_2$O); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta=165.67$, 165.50 (6×C=O), 133.33, 133.30, 133.27 (6×$C_{p\text{-}Ar}$), 129.91, 129.88, 129.65 ($C_{o\text{-}Ar}$), 129.59, 129.54 ($C_{Ar\text{-}quart}$), 128.49, 128.47 (12×$C_{m\text{-}Ar}$), 98.81 (C-1c), 97.74, 97.70 (2×C-1), 76.09, 76.03, 75.81 (3×C-3), 70.24 (OCH_2), 69.99 (3×C-5), 69.96, 69.93, 69.91, 69.80, 69.69 (OCH_2), 69.01, 68.96, 68.86, 68.84, 68.77, 68.72 (3×C-2, 3×C-4), 68.42, 68.10, 68.07 (2×C-6, OCH_2), 66.63 (C-6), 65.05, 64.89, 60.42, 60.00 (OCH_2), 55.31 (OCH_3), 35.13, 34.84, 34.83 (4×SCH$_2$CH$_2$OH), 29.91, 29.84, 29.81, 29.72, 29.67 (2×OCH$_2$CH$_2$CH$_2$O, 4×SCH$_2$CH$_2$CH$_2$O), 28.25, 27.75 ppm (2×SCH$_2$CH$_2$CH$_2$O); IR (KBr): $\tilde{\nu}_{max}=3447$ (br), 2920, 1724, 1601, 1451, 1323, 1266, 1112, 1069, 1026, 802, 712 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{87}H_{110}NaO_{28}S_4$: 1753.5959; found: 1753.5939 $[M+Na]^+$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(3-{2,4-di-*O*-benzoyl-3,6-di-*O*-[6-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)-4-thiahexyl]-α-D-mannopyranosyloxy}-propyl)-α-D-mannopyranoside (16): The acceptor tetraol **15** (202 mg, 0.116 mmol) was glycosylated with donor **4** (1.72 g, 2.32 mmol) by GP 4. For purification, the crude product was chromatographed on silica (toluene/EtOAc 8:1). Yield: 146 mg (31%) as a yellowish amorphous solid; $[\alpha]_D^{20}=-54$ ($c=1.1$, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$, TMS): $\delta=8.14$–7.99 (m, 28H; 28×$H_{o\text{-}Ar}$), 7.98–7.90 (m, 8H; 8×$H_{o\text{-}Ar}$), 7.86–7.79 (m, 8H; 8×$H_{o\text{-}Ar}$), 7.62–7.14 (m, 66H; 66×H_{Ar}), 6.17–6.04 (m, 4H; 4×H-4), 5.93–5.83 (m, 4H; 4×H-3), 5.69 (m, 2H; 2×H-2), 5.66 (dd, $^3J=3.3$ Hz, $^3J=1.8$ Hz, 2H; 2×H-2), 5.64–5.50 (m, 5H; 2×H-2, 3×H-4), 5.49 (dd, $^3J=3.0$ Hz, $^3J=1.9$ Hz, 1H; H-2), 5.10 (br, 2H; 2×H-1), 5.00 (d, $^3J=1.6$ Hz, 2H; 2×H-1), 4.99 (d, $^3J=1.4$ Hz, 1H; H-1), 4.91 (d, $^3J=1.5$ Hz, 1H; H-1), 4.73–4.60 (m, 5H; H-1, 4×H-6), 4.55–4.38 (m, 8H; 4×H-5, 4×H-6), 4.11–3.31 (m, 36H; 3×H-3, 3×H-5, 3×H-6, 3×H-6′, 12×OCH_2), 3.46 (s, 3H; OCH_3), 2.77 (2×ddd≈t, $^3J=6.8$ Hz, 4H; 2×SCH_2CH$_2$O), 2.63 (m, 4H; 2×SCH_2CH$_2$CH$_2$O), 2.44 (m, 4H; 2×SCH_2CH$_2$O), 2.31 (m, 4H; 2×SCH_2CH$_2$CH$_2$O), 1.99–1.50 ppm (m, 12H; 2×OCH$_2$CH_2CH$_2$O, 4×SCH$_2$CH_2CH$_2$O); ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta=166.06$, 165.64, 165.62, 165.46, 165.42, 165.36, 165.31 (22×C=O), 133.42, 133.38, 133.28, 133.26, 133.10, 133.02, 133.00 (22×$C_{p\text{-}Ar}$), 129.90, 129.79, 129.76, 129.68 (44×$C_{o\text{-}Ar}$), 129.56, 129.27, 129.25, 129.04, 129.03, 128.91 (22×$C_{Ar\text{-}quart}$), 128.62–128.31, 128.24 (44×$C_{m\text{-}Ar}$), 98.79, 97.74, 97.71 (3×C-1), 97.64 (2×C-1), 97.52 (2×C-1), 76.02, 75.97, 75.81 (3×C-3), 70.39 (4×C-2), 70.32, 70.10, 70.06 (3×C-6), 69.99, 69.81 (4×C-3, 3×C-4, 3×C-5), 69.02, 68.93, 68.87–68.72 (3×C-2, 4×C-5), 68.45, 68.17, 68.06, 68.03, 67.81 (OCH_2), 66.84–66.70 (4×C-4), 66.64, 65.06, 64.87 (OCH_2), 62.76 (4×C-6), 55.27 (OCH_3), 31.21 (2×SCH$_2$CH$_2$O), 30.98 (2×SCH$_2$CH$_2$O), 29.84, 29.74, 29.67, 29.57, 29.56 (2×OCH$_2$CH$_2$CH$_2$O, 4×OCH$_2$CH$_2$CH$_2$S), 29.24 (2×SCH$_2$CH$_2$CH$_2$O), 28.97 ppm (2×SCH$_2$CH$_2$CH$_2$O); IR (KBr): $\tilde{\nu}_{max}=3063$, 2923, 1727, 1602, 1451, 1316, 1266, 1177, 1109, 1069, 1026, 709 cm^{-1}; MALDI-TOF-MS: m/z: calcd for $C_{223}H_{214}NaO_{64}S_4$: 4069.36; found: 4068.89 $[M+Na]^+$, 4085.17 $[M+K]^+$.

Methyl 3,6-di-*O*-(3-{3,6-di-*O*-[6-α-D-mannopyranosyloxy)-4-thiahexyl]-α-D-mannopyranosyloxy}-propyl)-α-D-mannopyranoside (17): Deprotection of compound **16** (126 mg, 0.116 mmol) was accomplished by GP 5. For purification, the crude product was chromatographed on Sephadex LH-20 (MeOH), dissolved in H_2O with a small amount of acetonitrile and lyophilised. Yield: 47 mg (86%) as a white fluffy solid; $[\alpha]_D^{20}=+65$ ($c=1.4$, MeOH); ^1H NMR (500 MHz, [D$_4$]MeOH): $\delta=4.81$–4.79 (m, 4H; 4×H-1), 4.78 (d, $^3J=1.7$ Hz, 1H; H-1), 4.77 (d, $^3J=1.7$ Hz, 1H; H-1), 4.67 (d, $^3J=1.5$ Hz, 1H; H-1), 4.00–3.94 (m, 3H; 3×H-2), 3.92–3.52 (m, 60H; 4×H-2, 4×H-3, 7×H-4, 7×H-5, 14×H-6, 24×OC*H*H), 3.47–3.41 (m, 3H; 3×H-3), 3.39 (s, 3H; OCH_3), 2.77–2.70 (m, 12H; 4×SCH_2CH$_2$O, 4×SC*H*HCH$_2$CH$_2$O), 2.68 (m, 4H; 4×SC*H*HCH$_2$CH$_2$O), 1.96–1.82 ppm (m, 12H; 2×OCH$_2$CH_2CH$_2$O, 4×SCH$_2$CH_2CH$_2$O); ^{13}C NMR (125.76 MHz, [D$_4$]MeOH): $\delta=102.68$ (C-1), 101.69 (4×C-1), 101.64, 101.53 (2×C-1), 81.13, 81.09, 81.03 (3×C-3), 74.83, 74.80, 73.56, 73.51, 73.49, 72.63, 72.17 (CH), 71.76, 71.67, 71.60, 71.09, 71.07, 69.56, 69.38 (CH_2), 68.93, 68.91, 68.67, 68.65 (CH), 68.58, 68.56, 67.89 (CH_2), 67.72, 67.70, 67.65 (CH), 65.72, 65.71, 63.00, 62.97 (CH_2), 55.46 (OCH_3), 32.51 (2×SCH$_2$CH$_2$O), 32.45 (2×SCH$_2$CH$_2$O), 31.21, 31.10, 31.07, 30.91 (2×OCH$_2$CH$_2$CH$_2$O, 4×OCH$_2$CH$_2$CH$_2$S), 30.18, 30.07, 30.06 ppm (4×SCH$_2$CH$_2$CH$_2$O); IR (KBr): $\tilde{\nu}_{max}=3423$, 2923, 1637, 1132, 1103, 1085, 1055, 976, 807 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{69}H_{126}NaO_{42}S_4$: 1777.6499; found: 1777.6474 $[M+Na]^+$, 900.3226 $[M+Na]^{2+}$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(6-hydroxy-4-thiahexyl)-α-D-mannopyranoside (18): Mannoside **2** (1.50 g, 3.11 mmol) was treated with mercaptoethanol (6.5 mL, 93 mmol) by GP 3. The crude product was purified by column chromatography on silica (EtOAc/cyclohexane 4:1). Yield: 1.79 g (90%) as a colourless oil; $[\alpha]_D^{20}=-54$ ($c=0.81$, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.11$ (m, 2H; 2×$H_{o\text{-}Ar}$), 8.06 (m, 2H; 2×$H_{o\text{-}Ar}$), 7.60 (m, 2H; 2×$H_{p\text{-}Ar}$), 7.48 (m, 4H; $H_{m\text{-}Ar}$), 5.64 (dd≈t, $^3J=9.9$ Hz, 1H; H-4), 5.57 (dd, $^3J=3.3$ Hz, $^3J=1.9$ Hz, 1H; H-2), 4.91 (d, $^3J=1.8$ Hz, 1H; H-1), 4.03 (ddd, $^3J=10.1$ Hz, $^3J=4.9$ Hz, $^3J=2.7$ Hz, 1H; H-5), 4.00 (dd, $^3J=9.7$ Hz, $^3J=3.3$ Hz, 1H; H-3), 3.74–3.57 (m, 6H; H-6, H-6′, 2×OC*H*HCH$_2$CH$_2$S, 2×HOC*H*HCH$_2$S), 3.51–3.45 (m, 1H; OC*H*HCH$_2$CH$_2$S), 3.48 (s, 3H; OCH_3), 3.45–3.38 (m, 3H; OC*H*HCH$_2$CH$_2$S, 2×HOC*H*HCH$_2$S), 2.68 (t, $^3J=6.0$ Hz, 1H; SC*H*HCH$_2$OH), 2.68 (t, $^3J=6.1$ Hz, 1H; SC*H*HCH$_2$OH), 2.62 (t, $^3J=7.3$ Hz, SCH_2CH$_2$CH$_2$O), 2.41–2.33 (m, 2H; SCH_2CH$_2$OH), 2.32–2.20 (m, 4H; SCH_2CH$_2$O, 2×OH), 1.84 (m, 2H; OCH$_2$CH_2CH$_2$S), 1.61 ppm (m, 2H; OCH$_2$CH_2CH$_2$S); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta=165.74$, 165.51 (2×C=O), 133.36, 133.33 (2×$C_{p\text{-}Ar}$), 129.90, 129.67 (4×$C_{o\text{-}Ar}$), 129.56 ($C_{Ar\text{-}quart}$), 128.53, 128.50 (4×$C_{m\text{-}Ar}$), 98.86 (C-1), 75.99 (C-3), 69.98, 69.88 (OCH$_2$CH$_2$CH$_2$S, C-5, C-6), 68.87, 68.76 (C-2, C-4), 68.13 (OCH$_2$CH$_2$CH$_2$S), 60.36, 60.00 (2×HOCH$_2$CH$_2$S), 55.30 (OCH_3), 35.21, 34.90 (2×SCH$_2$CH$_2$OH), 29.92, 29.80 (2×SCH$_2$CH$_2$CH$_2$O), 28.24, 27.77 ppm (2×SCH$_2$CH$_2$CH$_2$O); IR (KBr): $\tilde{\nu}_{max}=3432$, 2919, 1724, 1601, 1451, 1323, 1267, 1113, 1069, 1027, 713 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{31}H_{42}NaO_{10}S_2$: 661.2112; found: 661.2141 $[M+Na]^+$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(6-{2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyloxy}-4-thiahexyl)-α-D-mannopyranoside (19): The acceptor alcohol **18** (115 mg, 0.180 mmol) was glycosylated with donor **4** (977 mg, 1.32 mmol) by GP 4. For purification, the crude product was chromatographed on silica (cyclohexane/EtOAc 4:3) and then on Sephadex LH-20 (CH_2Cl_2/MeOH 1:1). Yield: 197 mg (61%) as a white foam; $[\alpha]_D^{20}=-54$ ($c=0.58$, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.13$–8.02 (m, 12H; 12×$H_{o\text{-}Ar}$), 7.96–7.92 (m, 4H; 4×$H_{o\text{-}Ar}$), 7.85–7.81 (m, 4H; $H_{o\text{-}Ar}$), 7.60–7.22 (m, 30H; 20×$H_{m\text{-}Ar}$, 10×$H_{p\text{-}Ar}$), 6.10 (m, 2H; 2×H-4), 5.89 (dd, $^3J=10.1$ Hz, $^3J=3.3$ Hz, 1H; H-3), 5.87 (dd, $^3J=10.1$ Hz, $^3J=3.3$ Hz, 1H; H-3), 5.69 (dd, $^3J=3.3$ Hz, $^3J=1.8$ Hz, 1H; H-2), 5.67 (dd, $^3J=3.3$ Hz, $^3J=1.8$ Hz, 1H; H-2), 5.61–5.56 (m, 2H; H-2c, H-4c), 5.10 (d, $^3J=1.7$ Hz, 1H; H-1), 5.02 (d, $^3J=1.7$ Hz, 1H; H-1), 4.90 (d, $^3J=1.7$ Hz, 1H; H-1c), 4.71–4.61 (m, 2H; 2×H-6), 4.53–4.41 (m, 4H; 2×H-5, 2×H-6), 4.07 (m, 1H; H-5c), 4.03 (dd, $^3J=9.8$ Hz, $^3J=3.4$ Hz, 1H; H-3c), 3.93 (ddd, $^3J=10.1$ Hz, $^3J=7.1$ Hz, $^3J=7.1$ Hz, 1H; OC*H*HCH$_2$S), 3.80–3.67 (m, 3H; OC*H*HCH$_2$CH$_2$S, 2×OC*H*HCH$_2$S), 3.66–3.62 (m, 2H; H-6c, H-6c′), 3.61–3.51 (m, 3H; 2×OC*H*HCH$_2$CH$_2$S, OC*H*HCH$_2$S), 3.50–3.49 (m, 1H; OC*H*HCH$_2$S), 3.46 (s, 3H; OCH_3), 2.79 (m, 2H; SCH_2CH$_2$O), 2.65 (m, 2H; SCH_2CH$_2$CH$_2$O), 2.47 (m, 2H; SCH_2CH$_2$O), 2.35 (m, 2H; SCH_2CH$_2$CH$_2$O), 1.84, 1.64 ppm (m, 2H; SCH$_2$CH_2CH$_2$O); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta=166.12$, 166.11, 166.10, 165.74, 165.46, 165.41, 165.36 (10×C=O), 133.46, 133.44, 133.40, 133.36, 133.14, 133.12, 133.05,

133.03 ($10\times C_{p\text{-Ar}}$), 129.95, 129.84, 129.80, 129.73 ($20\times C_{o\text{-Ar}}$), 129.33, 129.29, 129.11, 129.07, 128.99, 128.96 ($10\times C_{\text{Ar-quart}}$), 128.58, 128.52, 128.44, 128.43, 128.28 ($20\times C_{m\text{-Ar}}$), 98.82 (C-1c), 97.69, 97.58 (2×C-1), 75.93 (C-3c), 70.45 (2×C-2), 70.32 (C-6c), 70.09 (OCH_2), 70.02 (2×C-3), 69.98 (C-5c), 69.08, 68.99, 68.96, 68.93 (C-2c, C-4c, 2×C-5), 68.22, 68.16, 67.93 ($3\times OCH_2$), 66.86, 66.83 (2×C-4), 62.83 (2×C-6), 55.28 (OCH_3), 31.29, 31.08 ($2\times SCH_2CH_2O$), 29.94, 29.58 ($2\times OCH_2CH_2CH_2S$), 29.31, 29.04 ppm ($2\times SCH_2CH_2CH_2O$); IR (KBr): $\tilde{\nu}_{max}=3064$, 2925, 1727, 1602, 1451, 1315, 1266, 1109, 1069, 1026, 709 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{99}H_{94}NaO_{28}S_2$: 1817.5265; found: 1817.5260 $[M+Na]^+$.

Methyl 3,6-di-*O*-(6-{α-D-mannopyranosyloxy}-4-thiahexyl)-α-D-mannopyranoside (20): Deprotection of compound **19** (128 mg, 71.3 μmol) was accomplished by GP 5. For purification, the crude product was chromatographed on Sephadex LH-20 (MeOH), dissolved in H_2O and lyophilised. Yield: 53 mg (quant.) as a yellowish amorphous solid; $[\alpha]_D^{20}=+66$ ($c=1.1$, MeOH); ^{1}H NMR (300 MHz, [D$_4$]MeOH): $\delta=4.79$ (d, $^3J=1.7$ Hz, 2H; 2×H-1), 4.65 (d, $^3J=1.8$ Hz, 1H; H-1c), 3.96 (dd, $^3J=3.2$ Hz, $^3J=1.8$ Hz, 1H; H-2c), 3.93–3.55 (m, 24H; 2×H-2, 2×H-3, 3×H-4, 3×H-5, 3×H-6, 3×H-6′, 8×OC*H*H), 3.41 (dd, $^3J=9.0$ Hz, $^3J=3.3$ Hz, 1H; H-3c), 3.38 (s, 3H; OCH_3), 2.77–2.63 (m, 8H; $2\times CH_2SCH_2$), 1.87 ppm (m, 4H; $2\times OCH_2CH_2CH_2S$); ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta=102.70$ (C-1c), 101.69, 101.68 (2×C-1), 81.03 (C-3c), 74.84, 74.82, 73.46 (3×CH), 72.60 (2×CH), 72.17 (2×CH), 71.60, 71.02, 69.33 ($3\times CH_2$), 68.75, 68.65, 68.63 (C-2c, 2×CH), 68.57, 68.54 ($2\times CH_2$), 67.57 (CH), 63.00, 62.96 ($2\times CH_2$), 55.38 (OCH_3), 32.45, 32.40 ($2\times SCH_2CH_2O$), 31.18, 31.08 ($2\times OCH_2CH_2CH_2S$), 30.13, 30.01 ppm ($2\times SCH_2CH_2CH_2O$); IR (KBr): $\tilde{\nu}_{max}=3438$ (br), 2924, 1637, 1203, 1134, 1055, 973, 807 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{29}H_{54}NaO_{18}S_2$: 777.2644; found: 777.2657 $[M+Na]^+$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(6-{3,6-di-*O*-allyl-2,4-di-*O*-benzoyl-α-D-mannopyranosyloxy}-4-thiahexyl)-α-D-mannopyranoside (21): The acceptor alcohol **18** (200 mg, 0.313 mmol) was glycosylated with donor **10** (1.46 g, 2.38 mmol) by GP 4. For purification, the crude product was chromatographed on silica (toluene/EtOAc 8:1) and then on Sephadex LH-20 (CH_2Cl_2/MeOH 1:1). Yield: 309 mg (65%) as a white foam; $[\alpha]_D^{20}=-52$ ($c=1.9$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.12$–8.02 (m, 12H; $12\times H_{o\text{-Ar}}$), 7.57 (m, 6H; $6\times H_{p\text{-Ar}}$), 7.46 (m, 12H; $12\times H_{m\text{-Ar}}$), 5.82 (m, 2H; $2\times CH{=}CH_2$), 5.70–5.55 (m, 6H; $2\times CH{=}CH_2$, H-2, 3×H-4), 5.53 (dd, $^3J=3.2$ Hz, $^3J=1.9$ Hz, 1H; H-2), 5.50 (dd, $^3J=3.2$ Hz, $^3J=1.9$ Hz, 1H; H-2), 5.21 (dddd, $^3J=17.3$ Hz, $^2J=1.7$ Hz, $^4J=1.7$ Hz, $^4J=1.7$ Hz, 1H; CH=CH_{trans}H), 5.20 (dddd, $^3J=17.3$ Hz, $^2J=1.6$ Hz, $^4J=1.6$ Hz, $^4J=1.6$ Hz, 1H; CH=CH_{trans}H), 5.15–5.04 (m, 4H; 2×CH=CH_{trans}H, 2×CH=CH_{cis}H), 5.02 (d, $^3J=1.7$ Hz, 1H; H-1), 4.99 (m, 2H; 2×CH=CH_{cis}H), 4.93 (d, $^3J=1.7$ Hz, 1H; H-1), 4.91 (d, $^3J=1.6$ Hz, 1H; H-1), 4.13 (m, 1H; H-5), 4.11–3.91 (m, 13H; 3×H-3, 2×H-5, 8×OC*H*HCH=CH_2), 3.88 (ddd, $^2J=10.3$ Hz, $^3J=7.0$ Hz, $^3J=7.0$ Hz, 1H; OC*H*HCH$_2$S), 3.74 (ddd, $^2J=9.3$ Hz, $^3J=5.7$ Hz, $^3J=5.7$ Hz, 1H; OC*H*HCH$_2$CH$_2$S), 3.71–3.51 (m, 10H; 6×H-6, 2×OC*H*HCH$_2$S, 2×OC*H*HCH$_2$CH$_2$S), 3.50–3.43 (m, 2H; OC*H*HCH$_2$S, OC*H*HCH$_2$CH$_2$S), 3.47 (s, 3H; OCH_3), 2.74 (m, 2H; 2×C*H*HCH$_2$O), 2.64 (m, 2H; 2×SC*H*HCH$_2$CH$_2$O), 2.44 (m, 2H; 2×C*H*HCH$_2$O), 2.35 (m, 2H; 2×SC*H*HCH$_2$CH$_2$O), 1.86 (m, 2H; $OCH_2CH_2CH_2S$), 1.65 ppm (m, 2H; $OCH_2CH_2CH_2S$); ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta=165.78$, 165.75, 165.68, 165.49, 165.40 (6×C=O), 134.42, 134.40, 134.23 (4×*C*H=CH$_2$), 133.30, 133.26, 133.22, 133.20, 133.12, 133.11 ($6\times C_{p\text{-Ar}}$), 129.96, 129.91 ($C_{o\text{-Ar}}$), 129.81, 129.79, 129.74 ($C_{\text{Ar-quart}}$), 129.71 ($C_{o\text{-Ar}}$), 129.63, 129.60 ($C_{\text{Ar-quart}}$), 128.50, 128.46, 128.39, 128.37 ($12\times C_{m\text{-Ar}}$), 117.22, 116.93, 116.89 (4×CH=*C*H$_2$), 98.79, 97.79, 97.67 (3×C-1), 75.89, 74.53, 74.48 (3×C-3), 72.47, 72.44, 70.65, 70.62 (4×*C*H$_2$CH=CH$_2$), 70.40, 70.30 (2×C-5), 70.27, 70.12 ($2\times OCH_2$), 69.96 (C-5), 69.43, 69.39 ($2\times OCH_2$), 69.26, 69.23 (2×C-2), 68.92, 68.87 (C-2, 3×C-4), 68.14 (O*C*H$_2$CH$_2$CH$_2$S), 67.65, 67.44 ($2\times OCH_2$), 55.25 (OCH_3), 31.26, 31.15 ($2\times SCH_2CH_2O$), 29.85, 29.52 ($2\times OCH_2CH_2CH_2S$), 29.15, 28.95 ppm ($2\times SCH_2CH_2CH_2O$); IR (KBr): $\tilde{\nu}_{max}=2918$, 2866, 1724, 1451, 1265, 1110, 1070, 1026, 711 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{83}H_{94}NaO_{24}S_2$: 1561.5469; found: 1561.5418 $[M+Na]^+$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(6-{2,4-di-*O*-benzoyl-3,6-di-*O*-[6-hydroxy-4-thiahexyl]-α-D-mannopyranosyloxy}-4-thiahexyl)-α-D-mannopyranoside (22): The unsaturated compound **21** (211 mg, 0.137 mmol) was treated with mercaptoethanol (576 μL, 8.22 mmol) by GP 3. The crude product was purified by column chromatography on silica (EtOAc/cyclohexane 5:1) and then on Sephadex LH-20 (CH_2Cl_2/MeOH 1:1). Yield: 239 mg (94%) as a colourless foam; $[\alpha]_D^{20}=-44$ ($c=1.8$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta=8.14$–8.02 (m, 12H; $12\times H_{o\text{-Ar}}$), 7.64–7.55 (m, 6H; $6\times H_{p\text{-Ar}}$), 7.53–7.42 (m, 12H, $12\times H_{m\text{-Ar}}$), 5.65 (dd≈t, $^3J=10.0$ Hz, 1H; H-4), 5.63 (dd≈t, $^3J=10.0$ Hz, 1H; H-4), 5.60–5.54 (m, 3H; 2×H-2, H-4), 5.53 (dd, $^3J=3.2$ Hz, $^3J=1.9$ Hz, 1H; H-2), 5.02 (d, $^3J=1.8$ Hz, 1H; H-1), 4.93 (d, $^3J=1.7$ Hz, 1H; H-1), 4.91 (d, $^3J=1.6$ Hz, 1H; H-1), 4.14–3.92 (m, 6H; 3×H-3, 3×H-5), 3.87 (ddd, $^2J=10.5$ Hz, $^3J=7.0$ Hz, $^3J=7.0$ Hz, 1H; OC*H*HCH$_2$S), 3.79–3.36 (m, 29H; 3×H-6, 3×H-6′, $4\times CH_2OH$, $15\times OCHH$), 3.48 (s, 3H; OCH_3), 2.75 (t, $^3J=6.8$ Hz, 2H; SCH_2CH_2O), 2.69–2.55 (m, 12H; $10\times SCHH$, 2×OH), 2.46 (t, $^3J=6.7$ Hz, 2H; SCH_2CH_2O), 2.42–2.16 (m, 12H; $10\times SCHH$, 2×OH), 1.91–1.51 ppm (m, 12H; $6\times OCH_2CH_2CH_2S$); ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta=165.72$, 165.70, 165.53, 165.45 (6×C=O), 133.44–133.26 ($6\times C_{p\text{-Ar}}$), 129.91, 129.89, 129.73–129.64 ($12\times C_{o\text{-Ar}}$, $C_{\text{Ar-quart}}$), 129.63, 129.61, 129.56, 129.53, 129.50 ($5\times C_{\text{Ar-quart}}$), 128.59–128.45 ($12\times C_{m\text{-Ar}}$), 98.78, 97.88, 97.77 (3×C-1), 75.96, 75.93, 75.88 (3×C-3), 70.18 (OCH_2), 70.15 (C-5), 70.13 (OCH_2), 70.05 (C-5), 69.98, 69.95 ($2\times OCH_2$), 69.93 (C-5), 69.77, 69.73 ($2\times OCH_2$), 68.90, 69.88, 68.86, 68.64 (3×C-2, 3×C-4), 68.19, 68.12, 67.62, 67.43 ($5\times OCH_2$), 60.42 ($2\times CH_2OH$), 60.00 ($2\times CH_2OH$), 55.29 (OCH_3), 35.16, 35.15, 34.84, 34.83 ($4\times SCH_2CH_2OH$), 31.31, 31.17 ($2\times SCH_2CH_2O$), 29.90, 29.87, 29.78, 29.53 ($6\times OCH_2CH_2CH_2S$), 29.16, 28.95 ($2\times SCH_2CH_2CH_2O$), 28.26 ($2\times SCH_2CH_2CH_2O$), 27.73 ppm ($2\times SCH_2CH_2CH_2O$); IR (KBr): $\tilde{\nu}_{max}=3435$, 2920, 2870, 1724, 1322, 1266, 1112, 1070, 1027, 713 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{91}H_{118}NaO_{28}S_6$: 1873.6026; found: 1873.6035 $[M+Na]^+$.

Methyl 2,4-di-*O*-benzoyl-3,6-di-*O*-(6-{2,4-di-*O*-benzoyl-3,6-di-*O*-[6-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyloxy)-4-thiahexyl]-α-D-mannopyranosyloxy}-4-thiahexyl)-α-D-mannopyranoside (23): The acceptor tetraol **22** (220 mg, 0.119 mmol) was glycosylated with donor **4** (1.76 g, 2.38 mmol) by GP 4. For purification, the crude product was chromatographed on silica (toluene/EtOAc 8:1) and then on Sephadex LH-20 (CH_2Cl_2/MeOH 1:1). Yield: 274 mg (55%) as a white foam; $[\alpha]_D^{20}=-47$ ($c=1.1$, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): $\delta=8.12$–8.03 (m, 28H; $28\times H_{o\text{-Ar}}$), 7.96–7.92 (m, 8H; $8\times H_{o\text{-Ar}}$), 7.84–7.80 (m, 8H; $8\times H_{o\text{-Ar}}$), 7.61–7.22 (m, 66H; $66\times H_{Ar}$), 6.13–6.06 (m, 4H; 4×H-4), 5.89 (dd, $^3J=10.1$ Hz, $^3J=3.3$ Hz, 2H; 2×H-3), 5.86 (dd, $^3J=10.1$ Hz, $^3J=3.3$ Hz, 2H; 2×H-3), 5.68 (m, 2H; 2×H-2), 5.66 (dd, $^3J=3.3$ Hz, $^3J=1.8$ Hz, 2H; 2×H-2), 5.63 (dd≈t, $^3J=9.9$ Hz, 1H; H-4), 5.62 (dd≈t, $^3J=9.9$ Hz, 1H; H-4), 5.58–5.52 (m, 4H; 3×H-2, H-4), 5.09 (br, 2H; 2×H-1), 5.02 (d, $^3J=1.7$ Hz, 1H; H-1), 5.00 (d, $^3J=1.5$ Hz, 2H; 2×H-1), 4.94 (d, $^3J=1.7$ Hz, 1H; H-1), 4.90 (d, $^3J=1.7$ Hz, 1H; H-1), 4.70–4.62 (m, 4H; 4×H-6), 4.53–4.41 (m, 8H; 4×H-5, 4×H-6), 4.11 (m, 1H; H-5), 4.08–3.99 (m, 4H; 2×H-3, 2×H-5), 3.97 (dd, $^3J=9.8$ Hz, $^3J=3.2$ Hz, 1H; H-3), 3.94–3.84 (m, 3H; 3×OC*H*HCH$_2$S), 3.78–3.41 (m, 27H; 6×H-6, 9×OC*H*HCH$_2$S, 12×OC*H*HCH$_2$CH$_2$S), 3.46 (s, 3H; OCH_3), 2.81–2.71 (m, 6H; 6×SC*H*HCH$_2$O), 2.68–2.59 (m, 6H; 6×SC*H*HCH$_2$CH$_2$O), 2.50–2.40 (m, 6H; 6×SC*H*HCH$_2$O), 2.40–2.25 (m, 6H; SC*H*HCH$_2$CH$_2$O), 1.85 (m, 6H; $6\times OCH_2CHHCH_2S$), 1.67–1.56 ppm (m, 6H; $6\times OCH_2CHHCH_2S$); ^{13}C NMR (150.90 MHz, $CDCl_3$): $\delta=166.06$, 165.66, 165.42, 165.37, 165.31 (22×C=O), 133.40, 133.36, 133.30, 133.09, 132.99 ($22\times C_{p\text{-Ar}}$), 129.89, 129.78, 129.74, 129.67 ($44\times C_{o\text{-Ar}}$), 129.60, 129.57, 129.28, 129.26, 129.06, 129.03, 128.93, 128.92 ($22\times C_{\text{Ar-quart}}$), 128.60–128.44, 128.40, 128.38, 128.23 ($44\times C_{m\text{-Ar}}$), 98.76, 97.87, 97.77 (3×C-1), 97.64 (2×C-1), 97.53 (2×C-1), 75.88 (3×C-3), 70.39 (4×C-2), 70.28 (C-6), 70.22, 70.16–69.90, 69.02, 68.94, 68.89, 68.75 (3×C-2, 4×C-3, 3×C-4, 7×C-5, 2×C-6), 68.17, 68.10, 67.83, 67.59, 67.40 ($12\times OCH_2$), 66.80 (2×C-4), 66.78 (2×C-4), 62.77 (4×C-6), 55.23 (OCH_3), 31.28 (SCH_2CH_2O), 31.23 ($2\times SCH_2CH_2O$), 31.14 (SCH_2CH_2O), 31.00 ($2\times SCH_2CH_2O$), 29.85, 29.55, 29.24, 29.12, 28.95, 28.91 ppm ($6\times OCH_2CH_2CH_2S$); IR (KBr): $\tilde{\nu}_{max}=2922$, 1727, 1602, 1451, 1316, 1266, 1109, 1069, 1026, 709 cm^{-1}; MALDI-TOF-MS: m/z: calcd for $C_{227}H_{222}NaO_{64}S_6$: 4186.23; found: 4186.44 $[M+Na]^+$, 4202.34 $[M+K]^+$.

Methyl 3,6-di-*O*-(6-{3,6-di-*O*-[6-(α-D-mannopyranosyloxy)-4-thiahexyl]-α-D-mannopyranosyloxy}-4-thiahexyl)-α-D-mannopyranoside (24): Deprotection of compound **23** (251 mg, 60 μmol) was accomplished by GP 5. For purification, the crude product was chromatographed on Sephadex LH-20 (MeOH), dissolved in H_2O with a small amount of MeCN and

lyophilised. Yield: 78 mg (68%) as a white fluffy solid; $[\alpha]_D^{20}=+67$ ($c=1.0$, MeOH); ^{1}H NMR (500 MHz, [D$_4$]MeOH): $\delta=4.81$–4.79 (m, 6H; 6×H-1), 4.66 (d, $^3J=1.7$ Hz, 1H; H-1), 3.98 (dd, $^3J=3.1$ Hz, $^3J=1.8$ Hz, 2H; 2×H-2), 3.97 (dd, $^3J=3.2$ Hz, $^3J=1.8$ Hz, 1H; H-2), 3.92–3.56 (m, 60H; 4×H-2, 4×H-3, 7×H-4, 7×H-5, 14×H-6, 24×OC*H*H), 3.47–3.41 (m, 3H; 3×H-3), 3.39 (s, 3H; OCH_3), 2.80–2.70 (m, 18H; 6×SCH_2CH$_2$O, 6×SC*H*HCH$_2$CH$_2$O), 2.68 (m, 6H; 6×SC*H*HCH$_2$CH$_2$O), 1.95–1.82 ppm (m, 12H; 6×SCH$_2$C*H*$_2$CH$_2$O); ^{13}C NMR (125.76 MHz, [D$_4$]MeOH): $\delta=$ 102.68 (C-1), 101.75–101.65 (6×C-1), 81.09 (C-3), 81.04 (2×C-3), 74.83 (2×C-5s), 74.80 (2×C-5s), 73.74 (2×C-5), 73.48 (C-5), 72.63, 72.62 (4×C-3s), 72.17 (4×C-2s), 71.72, 71.03, 69.40, 69.34 (CH_2), 68.84, 68.80, 68.67, 68.64 (CH), 68.58, 68.56 (CH_2), 67.66 (CH), 63.01 (2×C-6), 62.98 (2×C-6), 55.46 (OCH_3), 32.52 (2×S*C*H$_2$CH$_2$O), 32.50, 32.46 (2×S*C*H$_2$CH$_2$O), 32.44 (2×S*C*H$_2$CH$_2$O), 31.20, 31.14, 31.10 (6×OCH$_2$*C*H$_2$CH$_2$S), 30.17, 30.12, 30.10, 30.02 ppm (6×S*C*H$_2$CH$_2$CH$_2$O); IR (KBr): $\tilde{\nu}_{max}=3424$, 2923, 1636, 1132, 1105, 1086, 1056, 976 cm^{-1}; MALDI-TOF-MS: m/z: calcd for $C_{73}H_{134}NaO_{42}S_6$: 1897.66; found: 1897.04 $[M+Na]^+$.

Methyl 3,6-di-*O*-(6-{3,6-di-*O*-[6-(α-D-mannopyranosyloxy)-4,4-dioxo-4-thiahexyl]-α-D-mannopyranosyloxy}-4,4-dioxo-4-thiahexyl)-α-D-mannopyranoside (25): A solution of compound **24** (26.5 mg, 14.1 μmol) in a mixture of H$_2$O/MeOH (1:1, 2 mL) was treated with MMPP (85%, 49 mg, 85 μmol) and then stirred overnight at room temperature. After addition of more MMPP (13 mg, 21 μmol) the solution was diluted with H$_2$O (10 mL), frozen and lyophilised. The residue was chromatographed on Sephadex LH-20 (H$_2$O). Yield: 19.7 mg (67%) as a white fluffy solid; $[\alpha]_D^{20}=+39$ ($c=0.53$, H$_2$O); ^{1}H NMR (500 MHz, D$_2$O): $\delta=4.80$ (d, $^3J=$ 1.6 Hz, 2H; 2×H-1), 4.79 (d, $^3J=1.6$ Hz, 4H; 4×H-1), 4.65 (H-1c, under the H$_2$O peak), 4.07 (m, 6H; 6×OC*H*HCH$_2$SO$_2$), 4.03 (dd, $^3J=3.2$ Hz, $^3J=1.9$ Hz, 2H; 2×H-2), 4.00 (dd, $^3J=3.2$ Hz, $^3J=1.8$ Hz, 1H; H-2c), 3.85 (dd, $^3J=3.4$ Hz, $^3J=1.7$ Hz, 4H; 4×H-2s), 3.83 (m, 6H; 6×OC*H*HCH$_2$SO$_2$), 3.80–3.50 (m, 44H; 4×H-3, 7×H-4, 7×H-5, 14×H-6, 12×OC*H*HCH$_2$CH$_2$SO$_2$), 3.50–3.41 (m, 15H; 3×H-3, 12×OCH$_2$C*H*HSO$_2$), 3.30 (s, 3H; OCH_3), 3.27 (m, 12H; 12×OCH$_2$CH$_2$C*H*HSO$_2$), 2.08–1.97 ppm (m, 12H; 6×OCH$_2$C*H*$_2$CH$_2$SO$_2$); ^{13}C NMR (125.76 MHz, D$_2$O): $\delta=102.88$ (C-1c), 101.94 (6×C-1), 80.92 (C-3), 80.82 (2×C-3), 75.07, 73.74, 73.25, 72.58, 71.88 (CH), 71.57, 70.89, 70.83, 69.23, 69.16 (CH_2), 68.64, 67.78, 67.75 (CH), 62.91, 62.57, 62.53 (CH_2), 56.93 (OCH_3), 54.21, 54.10, 53.25, 53.22, 53.15, 53.12 (6×CH$_2$SO$_2$CH$_2$), 23.81, 23.48 ppm (6×OCH$_2$CH$_2$CH$_2$SO$_2$); IR (KBr): $\tilde{\nu}_{max}=$ 3425, 2925, 1637, 1313, 1276, 1128, 1086, 1056, 978 cm^{-1}; MALDI-TOF-MS: m/z: calcd for $C_{73}H_{134}NaO_{54}S_6$: 2089.60; found: 2089.34 $[M+Na]^+$.

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