Cationic Lipids for Gene Therapy, Part III[+]

Synthesis of High-Mannose Type Neoglycolipids: Active Targeting of Liposomes to Macrophages in Gene Therapy

Arno Düffels,[a] Luke G. Green,[a] Steven V. Ley,*[a] and Andrew D. Miller[b]

Abstract: The concise synthesis of five biantennary oligomannose neoglycolipids is presented. Employing a strategy based on the principles of reactivity tuning and orthogonal activation, the oligomannose moieties, isolated from the glycoprotein 63 of the parasite *Leishmania mexicana amazonensis*, were rapidly assembled taking advantage of common structural motifs found in these N-glycans. Deprotection of all structures was achieved in high yield by hydrogenolysis. The deprotected glycoconjugates were subsequently coupled to a cholesteroldiamine derivative using diethylsquarate as a linker. The resulting neoglycolipids will be used as additives to cationic liposome formulations in the active targeting of liposomes to macrophages.

Keywords: cationic liposomes · gene therapy · glycosidation · neoglycolipids · synthesis design

Introduction

While a great number of therapeutic agents are discovered every year, the clinical application of these is often limited by their failure to reach the site of action. A further problem is the toxicity of drugs at non-target sites. Selective drug targeting would not only reduce systemic toxicity but would also potentiate drug action by concentrating the drug in target cells or tissues. The delivery of active drug moieties specifically to their site of action is therefore of great interest in pharmaceutical science.

Gene therapy is a novel form of drug delivery that enlists the synthetic machinery of the patient's cells to produce a therapeutic agent.[1] An important advantage in gene therapy is that DNA need not be delivered to target tissues at a very high concentration since each gene can potentially express multiple copies of its polypeptide product. However, to employ their full potential as therapeutic agents, genes have to be delivered in a very specific and efficient way to their cellular targets. Both viral and non-viral approaches are being developed to achieve this.[2] Of the current range of non-viral vectors, cationic liposomes show particular promise and potential as clinically useful vector systems for the delivery of therapeutic nucleic acids to patients.[3] Previously it has been demonstrated that cationic liposomes formulated from 3β-[*N*-(*N*′,*N*′-dimethylaminoethane)carbamoyl]-cholesterol (DC-Chol) and the neutral phospholipid dioleyl L-α-phosphatidylethanolamine (DOPE) were able to transfect the lungs of mice in vivo.[4] In continuation of this work novel polyamine analogues of DC-Chol were synthesised that in formulations with DOPE were 100 times more efficient than DC-Chol/DOPE liposomes at gene delivery in vivo.[5] As part of a research program concerning the cell-specific delivery of liposome/DNA complexes we became interested in the targeting of macrophages with cationic liposomes.

It is known that liposomes injected into the bloodstream do not mediate active targeting but instead are readily recognized as foreign particles by reticuloendothelial cells (e.g. macrophages).[6] This characteristic can be used for the treatment of certain parasitic infections in macrophages like *Leishmaniasis*.[7] However, active targeting can be accomplished by attaching ligands to the surface of liposomes that mediate cell–cell recognition.[8] It has been shown that mannosylation of polylysine/DNA complexes resulted in an increase in macrophage uptake;[9] this suggests that molecular recognition of mannose residues by the well characterized macrophage mannosyl/fucosyl receptor[10] may occur prior to endocytosis. It was therefore anticipated that high-mannoside derived glycolipids, as part of cationic liposome formulation, should lead to an increase in cell-specific delivery of liposome/DNA complexes. For this reason we became interested in the mannosides of gp 63, the major surface glycoprotein of *Leishmania mexicana amazonensis* as means for the active targeting of macrophages with cationic liposomes (Figure 1).[11]

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[+] Part II: R. G. Cooper, R. P. Herbottle, H. Schneider, C. Coutelle, A. D. Miller, *Angew. Chem.* **1999**, *111*, 2128–2132; *Angew. Chem. Int. Ed.* **1999**, *38*, 1949–1952.

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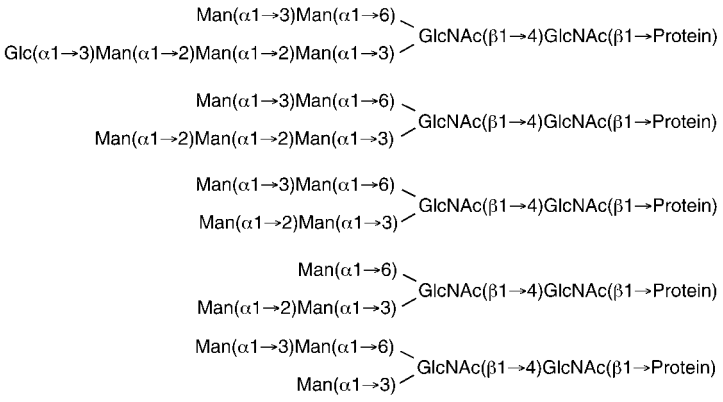


Figure 1. The N-glycans of gp 63 of *Leishmania mexicana amazonensis*.

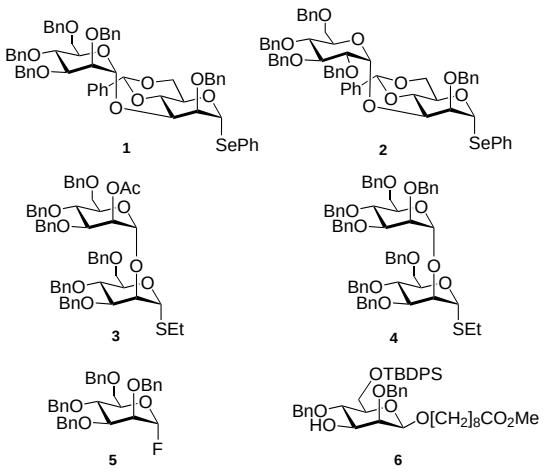


Figure 2. The building blocks **1**–**6**.

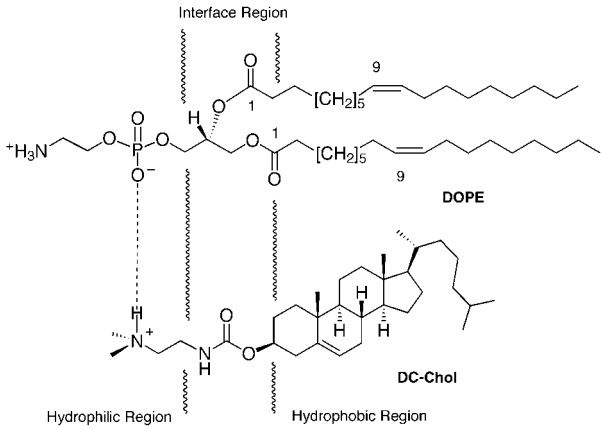


Figure 3. Putative alignment of DC-Chol and DOPE in cationic liposome bilayer.

Leishmania are digenetic parasites that are transmitted to man as a flagellated extracellular single-cell organism by the vector sandfly. Once inside the host the parasite loses its flagellum and becomes resident within macrophages.[12] Evidence exists that cell-surface oligosaccharides of this parasite play a role in the infection of human macrophages by *Leishmania* promastigotes, presumably by interaction with the macrophage mannosyl receptor.[13] To mimic this interaction and thereby increase the cellular uptake of cationic liposomes by macrophages was the aim of this project.

Synthetic strategy

In order to test the gp 63 derived high mannosides in the active targeting of macrophages it was decided to synthesise a new class of cholesterol-based neoglycolipids. Since the di-*N*-acetylchitobiose (GlcNAcβ(1→4)GlcNAc) moiety of the natural occurring N-glycans was not considered important for the binding to the macrophage mannose receptor it was replaced by a β-linked spacer.[14]

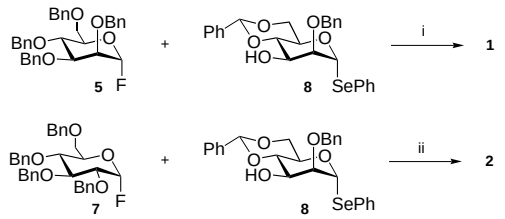
Seleno[15] and thio glycosides[16] have proven to be versatile building blocks for the stereoselective construction of complex mannosides as has been demonstrated in the synthesis of a high-mannose type nonasaccharide of the glycoprotein gp 120 of HIV by our group.[17] Based on this result and our continuing work in the area of protecting group mediated reactivity tuning in oligosaccharide synthesis,[18] the synthesis of the high-mannose glycoconjugates was addressed by stepwise addition of the respective mono- and disaccharide precursors **1**–**5** to the central β-mannoside **6**[19] (Figure 2). This convergent approach allowed the rapid assembly of the complete set of biantennary target molecules in a minimum number of steps from a common set of building blocks.[20] The resulting 8-methoxycarbonyloctyl glycosides were to be converted to primary amines by reaction with neat ethylenediamine and then coupled to a cholesterol amine using diethylsquarate as the linker, a method that has been introduced by Tietze et al. for the coupling of amines,[21] and that was further successfully employed by Hindsgaul et al. in the synthesis of neoglycoproteins.[22]

The design of the cholesterol amine was based upon the known behaviour of cholesterol in bilayer membranes[23] and a liposome model for DC-Chol/DOPE liposomes proposed by Felgner et al. (Figure 3).[24] According to this model, carbon atoms C1 to C9 of the oleoyl side chains of DOPE pack against the four fused cholesterol rings of DC-Chol so that the phosphate ester group of DOPE and the protonated tertiary amine functionality of DC-Chol are aligned and neutralise each other. The positive charge of the liposome then derives from the protonated ethanolamine side chain of DC-Chol. The model indicates that the methylene-group spacing between carbamoyl and the first amine functional group of a given DC-Chol polyamine analogue should be two or three carbon atoms to maintain charge complementation with DOPE.

Synthesis of the building blocks

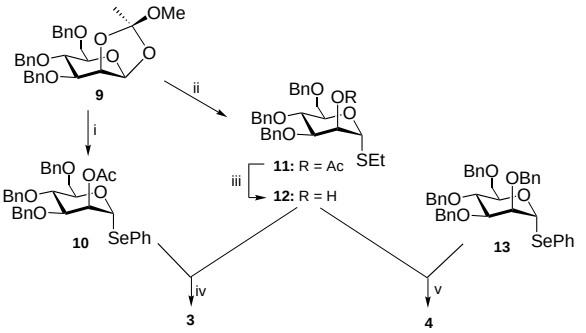
The disaccharides **1**–**4** were synthesised in single steps from known precursors employing the principles of orthogonal activation and reactivity tuning (Scheme 1). Orthogonal activation of mannopyranosyl fluoride **5**[25] and glucopyranosyl fluoride **7**[25] employing $HfCp_2Cl_2/AgClO_4$ as the activation system in the presence of alcohol **8**[26] gave the α-1,3-linked disaccharides **1** (74%) and **2** (72%) as single anomers.

The α-1,2-linked disaccharides **3** and **4** were prepared using the selectively acetylated seleno and thio mannosides **10** and



Scheme 1. i) $AgClO_4$, $HfCp_2Cl_2$, 4 Å MS, Et_2O, 74%; ii) $AgClO_4$, $HfCp_2Cl_2$, 4 Å MS, Et_2O, 72%.

12, derived from the known orthoester precursor **9**[27] (Scheme 2). Following a protocol of Sinaÿ et al.[28] orthoester **9** reacted with phenylselenol or ethanethiol in the presence of catalytic amounts of $HgBr_2$ to yield the seleno and thio mannosides **10** and **11** in excellent 96% and 94% yield,



Scheme 2. i) $HgBr_2$ (cat.), PhSeH, MeCN, 4 Å MS, 5 Å MS, 60 °C, 96%; ii) $HgBr_2$ (cat.), EtSH, MeCN, 4 Å MS, 5 Å MS, 60 °C, 94%; iii) K_2CO_3, MeOH, 85%; iv) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 75%; v) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 78%.

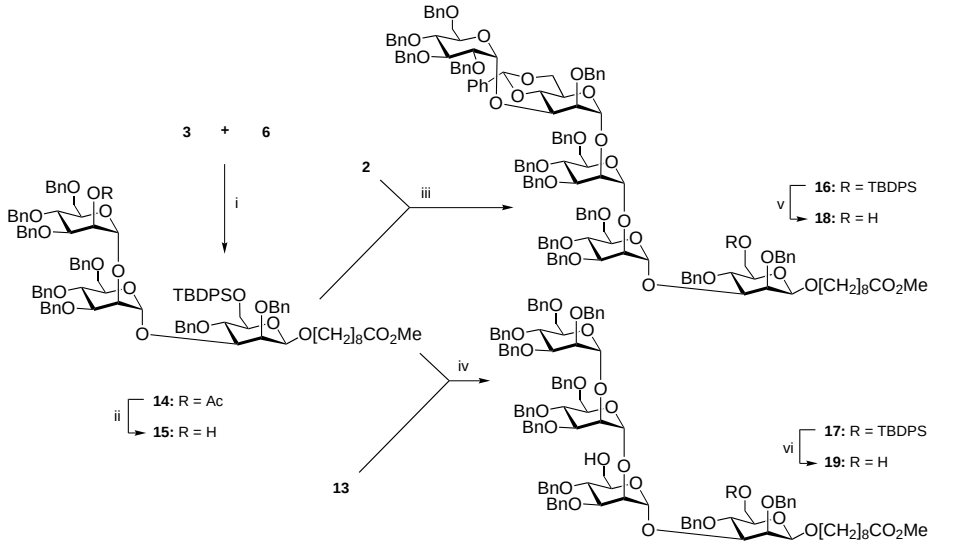
respectively. Deacetylation of **11** under standard conditions furnished the glycosyl acceptor **12** which was subsequently reacted with the selenoglycosyl donors **10** and **13** using NIS/TfOH activation conditions.[29] Owing to their inherent higher reactivity[15] the selenoglycosyl donors **10** and **13** were selectively activated in the presence of the thioglycosyl donor **12** resulting in the stereoselective formation of the disaccharides **3** and **4** in 75% and 78% yield, respectively.

Coupling of the fragments

With building blocks **1**–**6** in hand the target high-mannose oligosacchrides were prepared in four to six steps. Synthesis of heptasaccharide **20** and hexasaccharide **21** was accomplished via the common intermediary trisaccharide **15**. According to Scheme 3 the dimannoside **3** reacted with the selectively protected central β-mannoside **6** under NIS/TfOH activation conditions to give the fully protected product trisaccharide **14** in 81% yield on a gram scale. Standard deacetylation of **14** gave the desired glycosyl acceptor **15**. Glycosidation of the acceptor saccharide **15** with the seleno glycosides **2** and **13** under NIS/TfOH conditions yielded the desired penta- and tetrasaccharides **16** and **17** in 81% and 83%, respectively and completed the construction of the 3-antenna of the target compounds **20** and **21** (Scheme 3). Desilylation of the fully protected glycoconjugates **16** and **17** with buffered tetrabutylammonium fluoride (TBAF) in THF proceeded smoothly and was followed by the coupling of the resulting glycosyl acceptors **18** and **19** with seleno glycoside **1** to complete the synthesis of the fully protected target molecules **20** and **21** (Scheme 4).

As for the preparation of the hepta- and hexasaccharide **20** and **21**, a common trisaccharide intermediate was chosen in the synthesis of the high-mannose type saccharides **24** and **25**, taking advantage of the common structural motifs in both target molecules (Scheme 5). Thus, stereoselective glycosidation of the central β-mannoside **6** with the α-1,2-linked seleno glycoside **4** under NIS-TfOH conditions gave trimannoside **22** in 68% yield. Subsequent desilylation with TBAF in THF gave the key glycosyl acceptor **23** which underwent glycosidation reactions with seleno dimannoside **1** and fluoro mannoside **5**. The resulting high mannosides **24** and **25** were isolated as single anomers in 70% and 67% yield, respectively. When the perbenzylated seleno mannoside **13** reacted with the primary alcohol of trisaccharide **23** an anomeric mixture at the newly formed glycosidic linkage was observed.

The synthesis of the N-glycans of *Leishmania mexicana amazonensis* was completed with the three-step preparation of tetramannoside **28** (Scheme 6). Thus NIS/TfOH-mediated coupling of the perbenzylated seleno mannoside **13** with the free secondary alcohol of the central β-mannoside **6** resulted in the α-stereoselective formation of dimannoside **26** in 84% yield. Standard desilylation followed by glycosidation of



Scheme 3. i) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 81%; ii) K_2CO_3, MeOH, 88%; iii) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 81%; iv) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 83%; v) TBAF/3% AcOH, THF, 88%; vi) TBAF/3% AcOH, THF, 92%.

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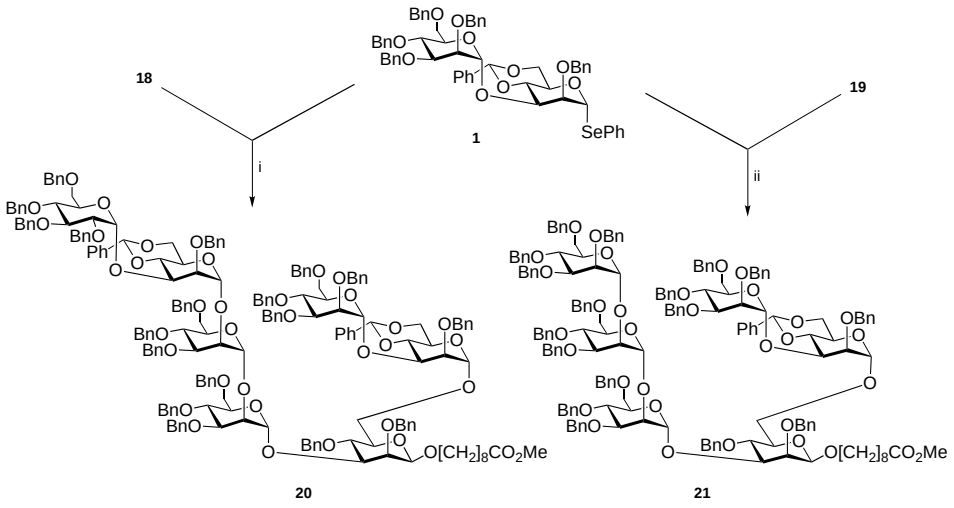
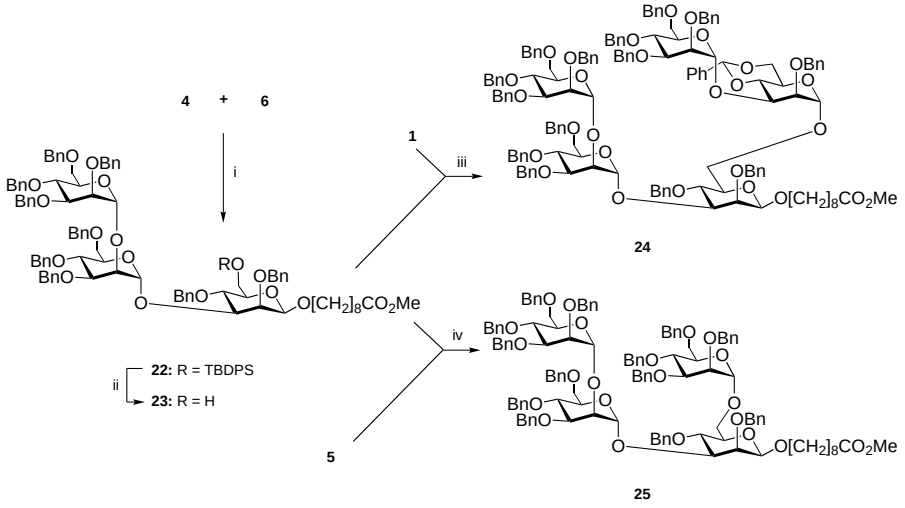
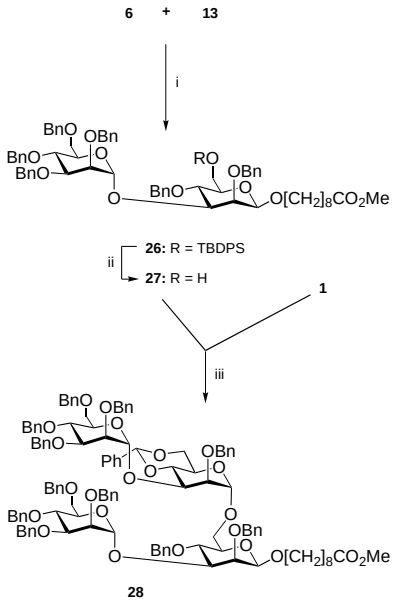


Scheme 4. i) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 51%; ii) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 53%.



Scheme 5. i) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 68%; ii) TBAF/3% AcOH, THF, 92%; iii) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 70%; iv) $AgClO_4$, $HfCp_2Cl_2$, 4 Å MS, Et_2O, 67%.



Scheme 6. i) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 84%; ii) TBAF/3% AcOH, THF, 95%; iii) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 1:1, 64%.

the resulting primary alcohol with the α-1,3-linked dimannoside **1** furnished the fully protected tetrasaccharide **28** in 64% yield.

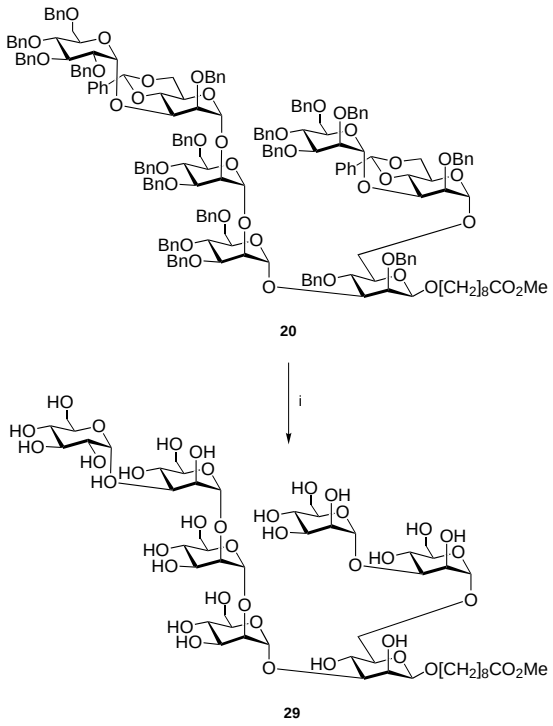
Deprotection

The saccharides **20**, **21**, **24**, **25** and **28** were deprotected by hydrogenation in a homogeneous mixture of dichloromethane, methanol and water (3:3:1) using $Pd(OH)_2/C$ as a catalyst as shown for heptamannoside **20** (Scheme 7).[30] The solvent system was chosen to keep both the starting material and the product in solution. The deprotections were carried out on a 150 mg scale and the resulting saccharides were isolated as colourless amorphous solids after size-exclusion chromatography on Sephadex G-15 (H_2O/*n*PrOH 95:5) in between 84% and 99% yield (Table 1).

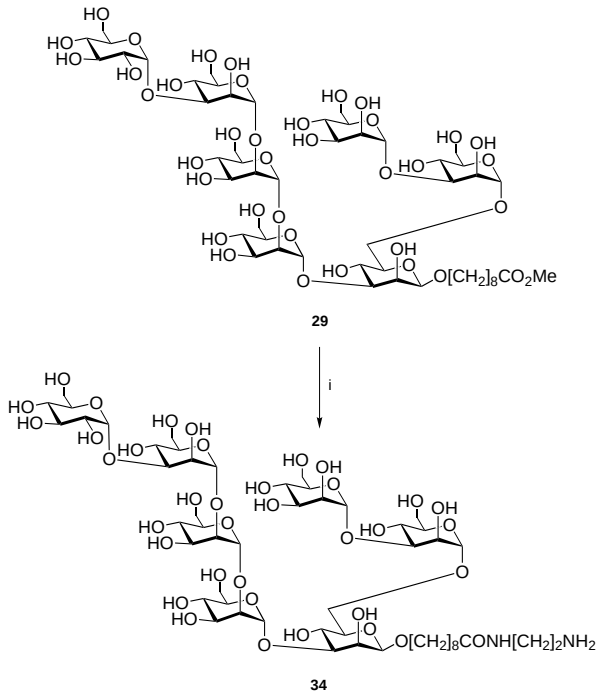
Synthesis of the cholesterol-based neoglycolipids

The synthetic high mannosides used in our neoglycolipid synthesis contained the 8-methoxycarbonyloctyl aglycone introduced by Lemieux as a linking arm for the attachment to proteins and solid supports.[14b] Couplings of oligosaccharides to proteins have previously been achieved by a sequence of reactions involving the reaction with hydrazine to form acyl hydrazides which were then oxidized by nitrous acid,[14b] or more conveniently, N_2O_4[31] to give the labile acyl azides. The acyl azides couple to proteins by acylation of amino groups, typically lysine residues. These procedures are effective for large scales, but on smaller scales it is difficult to obtain reproducible coupling yields.[31] The diethyl squarate method employed by Hindsgaul et al. on the other hand has been shown to be reliable for the coupling of very small amounts of oligosaccharides to proteins.[21] In accordance with this method the high mannosides **29**–**33** were dissolved in anhydrous ethylenediamine and heated at 70 °C for two days as shown for heptamannoside **29** (Scheme 8). The resulting amine amides were purified by size-exclusion chromatography on a Sephadex G-15 column (Table 2).

The high yielding synthesis of a diamine analogue of DC-Chol is shown in Scheme 9. In the first step cholesteryl chloroformate **39** was reacted with ethanolamine.[5] The resulting alcohol was mesylated to give the protected amino alcohol **41**. Displacing the mesylate with butanolamine and



Scheme 7. i) $Pd(OH)_2/C$, 1 atm H_2, CH_2Cl_2/MeOH/H_2O 3:3:1, 24 h, 84%.



Scheme 8. i) Ethylenediamine, 70°C, 2 d, 96%.

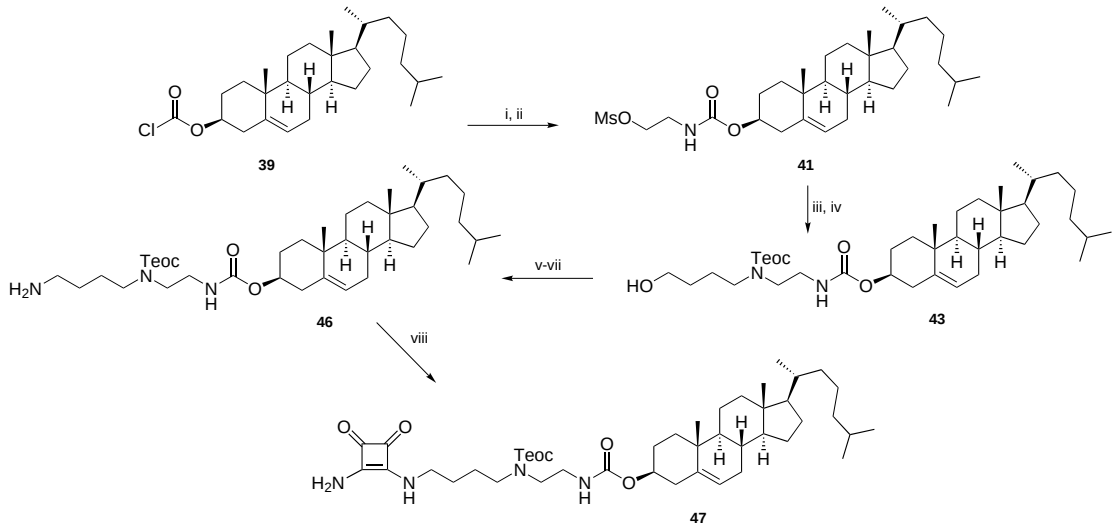
Table 1. Deprotection of high mannosides.

Starting material	Reaction product	Yield [%]
20	**29**	84
21	**30**	98
24	**31**	99
25	**32**	98
28	**33**	96

Table 2. Synthesis of high-mannoside amines.

Starting material	Reaction product	Yield [%]
29	**34**	96
30	**35**	89
31	**36**	99
32	**37**	96
33	**38**	97

(trimethylsilyl)ethoxycarbonyl (Teoc) protection of the secondary amine formed gave intermediate **43** in 64% yield over four steps. Transformation of the primary alcohol to an amine was achieved in three steps via mesylation, displacement of the mesylate with NaN_3 and Staudinger reduction of the resulting azide to give diamine **46** which in turn was transformed to the corresponding squaric acid amide ester **47** by reaction with diethyl squarate in CH_2Cl_2/MeOH (1:1).



Scheme 9. i) Ethanolamine, CH_2Cl_2, 0°C to rt, 90%; ii) $MeSO_2Cl$, NEt_3, CH_2Cl_2; iii) butanolamine, NaI, DMF, 76% over two steps; iv) Teoc-Suc, NEt_3, dioxane, 93%; v) $MeSO_2Cl$, NEt_3, CH_2Cl_2; vi) NaN_3, NaI, DMF, 86% over two steps; vii) PPh_3, THF, 95%; viii) diethyl squarate, CH_2Cl_2/MeOH, 87%.

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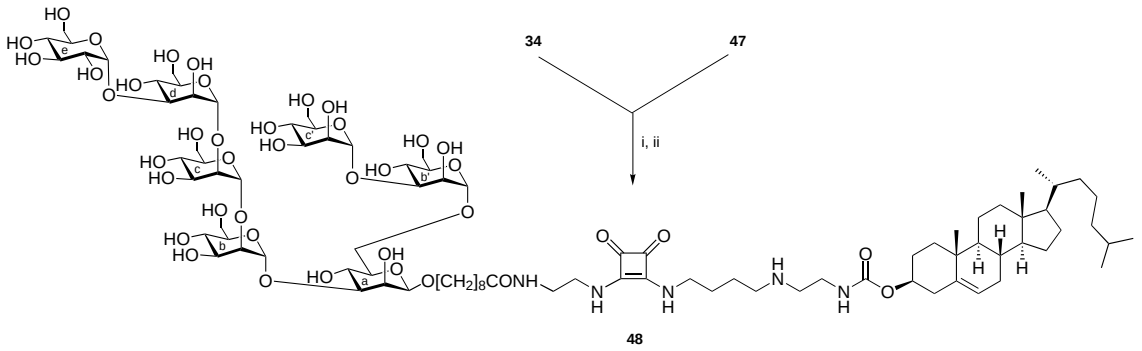

Scheme 10. i) CH_2Cl_2/MeOH/H_2O 3:3:1; ii) HF (48% in H_2O), CH_3CN.

Coupling of cholesterol squarate **47** with the deprotected high-mannoside amines **34**–**38** was achieved in a homogenous mixture of CH_2Cl_2, MeOH and H_2O (Scheme 10 and Table 3). Reactions were monitored by MALDI-TOF spectrometry and concentrated upon completion. In a final step deprotection of the Teoc-protected amine functionality was achieved by treatment of a suspension of the crude coupling product in CH_3CN with aqueous HF.

Table 3. Synthesis of neoglycolipids. The yields of the coupling reactions were estimated to be >90% prior to purification.

High mannoside	Reaction product	Yield [%]
34	**48**	78
35	**49**	65
36	**50**	52
37	**51**	42
38	**52**	53

Biological uses of the cholesterol-based neoglycolipids

The neoglycolipids, whose synthesis has been described above, are currently being incorporated into cationic liposome systems to facilitate targeted gene delivery into macrophages as part of our ongoing gene therapy stragtegy for the treatment of rheumatoid arthritis (RA). Although the aetiology of RA is unknown, it is evident that macrophages are critical for the development of RA in animal disease models such as the collagen induced arthritis (CIA) mouse model. Therefore, the targeting of therapeutic genes to active macrophages represents a potentially useful therapeutic aproach for the treatment of RA.

In our first set of in vivo experiments using CIA mice, we found that cationic liposomes containing 3-aza-N^1-cholesteryloxycarbonylhexane-1,6-diamine (ACHx), which are formulated ACHx/DC-Chol/DOPE (4.5:1.5:4 *w*/*w*/*w*) (0.72 mg per animal), we were able to mediate the partial transfection of macrophages with a human IL-10 expression plasmid (0.3 mg per animal), when the cationic liposome/DNA complex mixture was introduced by intra-peritoneal (i/p) administration.[34] Furthermore, this was followed by the distal delivery of IL-10 gene to the arthritic limbs of the animals resulting in up to 30 d suppression of CIA disease activity in these same affected areas. These results suggested that treatment of CIA by gene therapy could be viable provided that IL-10 plasmid could be more specifically targeted to the active macrophages involved. Consequently, specific experiments are now ongoing to incorporate the neoglycolipids into ACHx/DC-Chol/DOPE cationic liposomes for the targeted transfection of macrophages with the human IL-10 expressing plasmid. Provided that neoglycolipid targeting will lower the required dose of plasmid by two or more orders of magnitude whilst still maintaining the therapeutic effect, then the clinical treatment of RA by gene therapy should become a very real possibility.

Experimental Section

^{1}H-NMR spectra were recorded in $CDCl_3$, CD_3OD or D_2O on a Bruker DRX-600, DRX-500 and AC-400 spectrometers at 300 K. Residual protic solvent $CHCl_3$ ($\delta_H = 7.26$) was used as the internal reference. ^{13}C-NMR spectra were recorded in $CDCl_3$, CD_3OD or D_2O at 150, or 100 MHz on Bruker DRX-600 and AC400 spectrometers, respectively using the central resonance of $CDCl_3$ ($\delta_C = 77.0$) as the internal reference. DQF-COSY, HMQC, decoupled-HMQC, HMBC, TOCSY and 1-D TOCSY experiments were used to assist assignment of the products. NMR assignments are as indicated in Scheme 10. Mass spectra were obtained on Micromass Platfrom LC-MS and Q-Tof, Kratos MS890MS and Kompact 4, Bruker Daltonics Bio-Apex II (FT-ICR) spectrometers at the Department of Chemistry, University of Cambridge and on a Voyager STR spectrometer at M-Scan, Silwood Park, Ascot.

Flash column chromatography was carried out using Merck Kieselgel (230–400 mesh). Analytical thin-layer chromatography (tlc) and preparative tlc was performed using silica gel precoated glass-backed plates (Merck Kieselgel 60 F254) and visualised by UV and acidic ammonium molybdate (IV). PE refers to petroleum ether b.p. 40–60 °C, which was distilled prior to use.

All reactions were carried out under an argon atmosphere in oven-dried glassware unless otherwise stated. Diethyl ether was distilled from sodium benzophenone ketyl; dichloromethane and toluene from calcium hydride. Other reagents and solvents were purified using standard procedures. Aqueous solutions are saturated unless otherwise specified.

General procedure for the glycosidation of glycosyl fluorides

Glycosyl donor, glycosyl acceptor and $AgClO_4 \times H_2O$ were dried separately by azeotropic distillation with toluene and left under vacuum for 18 h prior to use. $HfCp_2Cl_2$ was dried under vacuum for 18 h. A suspension of $AgClO_4$ and 4 Å molecular sieves in Et_2O was stirred for 40 min. $HfCp_2Cl_2$ was added followed by a mixture of glycosyl donor and glycosyl acceptor. Upon completion of the reaction, as judged by tlc, the reaction mixture was diluted with Et_2O, filtered through Celite and washed with $NaHCO_3$. The organic phase was dried ($MgSO_4$), concentrated and the residue was purified by column chromatography.

General procedure for the glycosidation with glycosyl sulfides and glycosyl selenides

Glycosyl donor and glycosyl acceptor were dried separately by azeotropic distillation with toluene and left under vacuum for 18 h. A suspension of glycosyl donor, glycosyl acceptor and powdered 4 Å molecular sieves in CH_2Cl_2/Et_2O (1:1) was stirred for 30 min. A suspension of NIS in CH_2Cl_2/Et_2O (1:1) activated by a rapid addition of a 10 μL solution of 10 μL TfOH in CH_2Cl_2 (1 mL). Upon completion of the reaction, as judged by tlc, it was diluted with Et_2O, filtered through Celite, washed with $Na_2S_2O_3$ and $NaHCO_3$, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography.

General procedure for the desilylation

The TBDPS-ether was treated with TBAF (1M in THF containing 3% AcOH). Upon completion of the reaction, as judged by tlc, the mixture was partitioned between $NaHCO_3$ and CH_2Cl_2. The organic layer was separated and dried ($MgSO_4$). It was concentrated and purified by column chromatography.

General procedure for the debenzylation

The fully protected saccharide was dissolved in CH_2Cl_2/MeOH/H_2O (3:3:1). After addition of $Pd(OH)_2$/C the reaction flask was flushed with hydrogen (10 ×) and the reaction mixture was stirred under an atmosphere of hydrogen. Upon completion of the reaction as judged by MALDI-TOF the mixture was centrifuged and decanted. The concentrate (2 mL) was purified on Sephadex G-15 gel (H_2O/*n*PrOH 95:5). The column fractions were analysed by MALDI-TOF spectrometry and the product containing fractions were lyophilised.

General procedure for the amidation of methyl esters with ethylenediamine

The deprotected saccharide was stirred in dry ethylenediamine at 70 °C for 48 h. The reaction mixture was cooled to room temperature, diluted with water (3 mL), placed in an ice bath and concentrated in vacuo until 0.5 mL solvent was left. The concentrate was purified on Sephadex G-15 (H_2O/*n*PrOH/NH_3 94:5:1). The column fractions were analysed by MALDI-TOF spectrometry and the product containing fractions were lyophilised.

General procedure for the coupling of neoglycolipids and their final deprotection

A mixture of high-mannose amine and cholesterol squarate was dissolved in CH_2Cl_2, MeOH and H_20 under sonication. The reaction mixture was stirred at room temperature and concentrated upon completion of the reaction, as judged by MALDI-TOF. The concentrate was suspended in CH_3CN (1 mL) containing HF (0.1 mL, 48% in H_2O) and stirred for 16 h. Upon completion of the reaction as judged by MALDI-TOF the reaction mixture was azeotroped with methanol (5 ×) and concentrated. The reaction product was purified by repeated suspension in CH_2Cl_2 and decanting of the organic solvent.

Phenyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-1-seleno-α-D-mannopyranoside (1): This compound was synthesised according to the general procedure for the glycosidation of glycosyl fluorides. Activation of glycosyl donor **5** (500 mg, 1.08 mmol) with $AgClO_4$ (691 mg, 3.07 mmol) and $HfCp_2Cl_2$ (582 mg, 1.53 mmol) in the presence of glycosyl acceptor **8** (363 mg, 900 μmol) in Et_2O (20 mL) gave seleno dimannoside **1** as a colourless oil (696 mg, 670 μmol, 74%). $R_f = 0.30$ (PE/Et_2O 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 3.75-3.78$ (m, 3H, H-5_b, 2H-6_b), 3.88–3.94 (m, 3H, H$_a$-6_a, H-2_b, H-3_b), 3.98 (t, 1H, $J = 9.2$ Hz, H-4_b), 4.18 (d, 1H, $J = 2.1$ Hz, H-2_a), 4.23–4.29 (m, 3H, H-4_a, H-5_a, H$_b$-6_a), 4.38–4.43 (m, 2H, H-3_a, CH_2Ph), 4.52–4.70 (m, 8H, CH_2Ph), 4.94 (d, 1H, $J =$ 11.0 Hz, CH_2Ph), 5.47 (d, 1H, $J = 1.3$ Hz, H-1_b), 5.63 (s, 1H, C*H*Ph), 5.80 (s, 1H, H-1_a), 7.12–7.56 (m, 35H, H_{arom}); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta =$ 67.0 (C-5_a), 68.4 (C-6_a), 69.4 (C-6_b), [271.8, 72.7, 73.4, 75.0 (*C*H$_2$Ph)], 72.6 (C-5_b), 73.4 (C-3_a), 74.0 (C-2_b), 74.9 (C-4_b), 79.1 (C-4_a), 79.7 (C-3_b), 79.9 (C-2_a), 84.6 (C-1_a), 98.8 (C-1_b), 102.0 (*C*HPh), [126.3, 127.4, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.6, 129.3, 134.0, 137.5, 138.4, 138.5, 138.7 (C_{arom})]; *m*/*z* (FAB): found $[M+Na]^+$ 1043.3283; $C_{60}H_{60}O_{10}Se$ calcd for $[M+Na]^+$ 1043.3249.

Phenyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-1-seleno-α-D-mannopyranoside (2): This compound was synthesised according to the general procedure for the glycosidation of glycosyl fluorides. Activation of glycosyl donor **7** (500 mg, 1.08 mmol) with $AgClO_4$ (691 mg, 3.07 mmol) and $HfCp_2Cl_2$ (582 mg, 1.53 mmol) in the presence of glycosyl acceptor **8** (363 mg, 900 μmol) in Et_2O (20 mL) gave seleno dimannoside **2** as a colourless oil (677 mg, 650 μmol, 72%). $R_f = 0.28$ (PE/Et_2O 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 3.54-3.62$ (m, 2H, H-2_b, H-4_b), 3.68 (s, 2H, 2H-6_b), 3.77–3.81 (m, 1H, H-5_b), 3.92 (t, 1H, $J =$ 10.0 Hz, H$_a$-6_a), 4.02 (t, 1H, $J = 9.1$ Hz, H-3_b), 4.20 (s, 1H, H-2_a), 4.22–4.30 (m, 2H, H-5_a, H$_b$-6_a), 4.36 (d, 1H, $J = 12.3$ Hz, CH_2Ph), 4.42–4.50 (m, 3H, H-3_a, H-4_a, CH_2Ph), 4.53 (d, 1H, $J = 12.1$ Hz, CH_2Ph), 4.62 (d, 1H, $J =$ 12.3 Hz, CH_2Ph), 4.65 (d, 1H, $J = 12.1$ Hz, CH_2Ph), 4.76–4.89 (m, 4H, CH_2Ph), 5.01 (d, 1H, $J = 10.9$ Hz, CH_2Ph), 5.53 (1s, H, C*H*Ph), 5.55 (s, 1H, H-1_b), 5.85 (s, 1H, H-1_a), 7.02–7.54 (m, 35H, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 67.1$ (C-5_a), 68.5 (C-6_a), 68.6 (C-6_b), [70.7, 73.1, 73.5, 75.1. 75.6 (*C*H$_2$Ph)], 71.0 (C-5_b), 73.1 (C-4_a), 77.4 (C-4_b), 78.8 (C-2_b), 79.4 (C-3_a), 79.9 (C-2_a), 81.4 (C-3_b), 85.1 (C-1_a), 97.1 (C-1_b), 102.5 (*C*HPh), [126.5, 127.3, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2 128.3, 128.4, 128.6, 129.3, 133.9, 137.4, 137.7, 138.0, 138.2, 138.5 (C_{arom})]; *m*/*z* (FAB): found $[M+Na]^+$ 1043.3318, $C_{60}H_{60}O_{10}Se$ calcd for $[M+Na]^+$ 1043.3249.

Ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside (3): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyl donor **10** (1.38 g, 2.18 mmol) with NIS (490 mg, 2.18 mmol) in CH_2Cl_2/Et_2O (14 mL:14 mL) in the presence of glycosyl acceptor **12** (978 mg, 1.98 mmol) in CH_2Cl_2/Et_2O (11 mL:11 mL) gave thio dimannoside **3** as a colourless oil (1.44 g, 1.49 mmol, 75%). $R_f =$ 0.46 (PE/Et_2O 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.24$ (t, 3H, $J =$ 7.3 Hz, SCH_2CH_3), 2.17 (s, 3H, OC(O)CH_3), 2.55 (m, 2H, SCH_2CH_3), 3.72 (dd, 1H, $J = 1.3$, 11.0 Hz, H$_a$-6_b), 3.75 (dd, 1H, $J = 1.7$, 10.7 Hz, H$_a$-6_a), 3.81 (dd, 1H, $J = 4.9$ 10.7 Hz, H$_b$-6_a), 3.84 (dd, 1H, $J = 4.6$ 11.0 Hz, H$_b$-6_b), 3.86–4.84 (m, 2H, H-4_a, H-3_b), 3.93 (t, 1H, $J = 9.4$ Hz, H-4_b), 4.03 (dd, 1H, $J = 3.3$ 9.3 Hz, H-3_a), 4.04–4.07 (m, 1H, H-5_a), 4.09–4.11 (m, 1H, H-2_b), 4.13–4.17 (m, 1H, H-5_b), 4.44 (d, 1H, $J = 10.8$ Hz, CH_2Ph), 4.49 (d, 1H, $J =$ 10.8 Hz, CH_2Ph), 4.54 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 4.55 (d, 1H, $J =$ 12.2 Hz, CH_2Ph), 4.60 (d, 1H, $J = 10.8$ Hz, CH_2Ph), 4.67–4.73 (m, 5H, CH_2Ph), 4.87 (d, 1H, $J = 10.8$ Hz, CH_2Ph), 4.89 (d, 1H, $J = 10.8$ Hz, CH_2Ph), 5.09 (s, 1H, H-1_a), 5.43 (s, 1H, H-1_b), 5.56–5.58 (m, 1H, H-2_a), 7.17–7.40 (m, 30H, H_{arom}); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 15.0$ (SCH_2CH_3), 21.2 (OC(O)CH_3), 25.5 (SCH_2CH_3), 68.8 (C-2_a), 69.1 (C-6_a), 69.2 (C-6_b), [71.9, 72.1, 73.2, 73.4, 75.1, 75.2 (*C*H$_2$Ph)], 72.0 (C-5_a), 72.2 (C-5_b), 74.4 (C-4_a), 74.8 (C-4_b), 77.0 (C-2_b), 78.1 (C-3_a), 80.1 (C-3_b), 83.6 (C-1_b), 99.7 (C-1_a), [127.4, 127.5, 127.6, 127.7, 127.8, 128.0, 128.2, 128.3, 128.5, 138.0, 138.2, 138.5, 138.6 (C_{arom})], 170.2 (C=O); *m*/*z* (FAB): found $[M+Na]^+$ 991.4078, $C_{58}H_{65}O_{11}S$ calcd for $[M+Na]^+$ 991.4062.

Ethyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside (4): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyl donor **13** (796 mg, 1.17 mmol) with NIS (263 mg, 1.17 mmol) in CH_2Cl_2/Et_2O (8.0 mL:8.0 mL) in the presence of glycosyl acceptor **12** (570 mg, 1.06 mmol) in CH_2Cl_2/Et_2O (7.0 mL:7.0 mL) gave dimannoside **4** as a colourless oil (780 mg, 827 μmol, 78%). $R_f = 0.32$ (PE/Et_2O 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.22$ (t, 3H, $J = 7.4$ Hz, CH_2CH_3), 2.48–2.60 (m, 2H, CH_2CH$_3$), 3.70 (d, 1H, $J = 10.9$ Hz, H$_a$-6_b), 3.78 (d, 2H, $J = 3.5$ Hz, H-6_a), 3.81–3.88 (m, 4H, H-3_a, H-2_b, H-4_b, H$_b$-6_b), 3.92–3.96 (m, 2H, H-4_a, H-3_b), 3.98–4.04 (m, 1H, H-5_a), 4.10–4.17 (m, 2H, H-2_a, H-5_b), 4.49–4.72 (m, 12H, CH_2Ph), 4.84–4.90 (m, 2H, CH_2Ph), 5.18 (s, 1H, H-1_b), 5.42 (s, 1H, H-1_a), 7.17–7.40 (m, 35H, H_{arom}); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 15.0$ (SCH_2CH_3), 25.6 (SCH_2CH_3), 69.3 (C-6_b), 69.6 (C-6_a), 72.3 (C-5_a, C-5_b), [72.3, 72.5, 73.3, 75.0 (*C*H$_2$Ph)], [75.1, 80.4 (C-3_a, C-2_b, C-4_b)], 75.2 (C-4_a), 76.5 (C-2_a), 79.8 (C-3_b), 83.9 (C-1_a), 99.8 (C-1_b), [127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 128.5 (C_{arom})]; *m*/*z* (FAB): found $[M+Na]^+$ 1039.4442, $C_{63}H_{68}O_{10}S$ calcd for $[M+Na]^+$ 1039.4425.

Phenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-seleno-α-D-mannopyranoside (10): Orthoester **9** (5.06 g, 10.0 mmol) was dissolved in dry MeCN (35 mL) and powdered molecular sieves were added (4 Å, 3.0 g; 5 Å, 3.0 g). The mixture was stirred for 60 min before phenylselenol (5.20 mL, 33.0 mmol) and $HgBr_2$ (180 mg, 500 μmol) were added. The suspension was stirred at 60 °C for 6 h, diluted with CH_2Cl_2, filtered through Celite, washed with 5% NaOH, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (PE/Et_2O 3:1) to give **10** as a colourless oil (6.05 g, 9.60 mmol, 96%). $R_f = 0.43$ (PE/Et_2O 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.14$ (s, 3H, OC(O)CH_3), 3.72 (dd, 1H, $J = 1.1$, 10.9 Hz, H$_a$-6), 3.88 (dd, 1H, $J = 4.3$, 10.9 Hz, H$_b$-6), 3.91 (dd, 1H, $J = 3.1$, 9.4 Hz, H-3), 3.99 (t, 1H,

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J = 9.4 Hz, H-4), 4.23 (dd, 1H, J = 3.0, 9.5 Hz, H-5), 4.48 (d, 1H, J = 12.0 Hz, CH_2Ph), 4.52 (d, 1H, J = 10.6 Hz, CH_2Ph), 4.57 (d, 1H, J = 11.1 Hz, CH_2Ph), 4.67 (d, 1H, J = 12.0 Hz, CH_2Ph), 4.73 (d, 1H, J = 11.1 Hz, CH_2Ph), 4.89 (d, 1H, J = 10.6 Hz, CH_2Ph), 5.68 (m, 1H, H-2), 5.81 (s, 1H, H-1), 7.18–7.60 (m, 20H, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1 (OC(O)CH_3), 68.8 (C-6), [71.1, 74.3, 74.4 (C-3, C-4, C-5)], [71.9, 73.4, 75.4 (*C*H$_2$Ph)], 78.9 (C-2), 83.8 (C-1), [127.6, 127.8, 128.0, 128.2, 128.3, 128.4, 128.5, 129.2, 134.0, 127.6, 138.2, 138.3 (C_{arom})], 170.3 (C=O); m/z (FAB): found $[M+Na]^+$ 655.1554, $C_{35}H_{36}O_6Se$ calcd for $[M+Na]^+$ 655.1569.

Ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (11): Orthoester **9** (2.80 g, 5.53 mmol) was dissolved in dry MeCN (20 mL) and powdered molecular sieves were added (4 Å, 2.0 g; 5 Å, 2.0 g). The mixture was stirred for 60 min before ethanethiol (1.35 mL, 18.2 mmol) and $HgBr_2$ (100 mg, 265 μmol) were added. The suspension was stirred at 60 °C for 24 h, diluted with CH_2Cl_2, filtered through Celite, washed with 5% NaOH, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (PE/Et_2O 3:1) to give **11** as a colourless oil (2.78 g, 5.20 mmol, 94%). R_f = 0.35 (PE/Et_2O 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, 3H, J = 7.3 Hz, CH_2CH_3), 2.15 (s, 3H, OC(O)CH_3), 2.52–2.70 (m, 2H, CH_2CH_3), 3.68 (dd, 1H, J = 2.4, 12.6 Hz, H_a-6), 3.84 (dd, 1H, J = 4.1, 10.8 Hz, H_b-6), 3.89–3.98 (m, 2H, H-3, H-4), 4.13–4.18 (m, 1H, H-5), 4.44–4.54 (m, 3H, CH_2Ph), 4.68 (m, 2H, CH_2Ph), 4.85 (d, 1H, J = 10.8 Hz, CH_2Ph), 5.32 (s, 1H, H-1), 5.44 (d, 1H, J = 1.5 Hz, H-2), 7.12–7.38 (m, 15H, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9 (CH_2CH_3), 21.2 (OC(O)CH_3), 25.5 (CH_2CH_3), 68.9 (C-6), [70.6, 71.8, 74.6 (C-3, C-4, C-5)], [71.9, 73.4, 75.2 (*C*H$_2$Ph)], 78.6 (C-2), 82.5 (C-1), [127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.5, 137.7, 138.2, 138.4, (C_{arom})], 170.5 C=O); m/z (FAB): found $[M+Na]^+$ 559.2135, $C_{31}H_{36}O_6S$ calcd for $[M+Na]^+$ 559.2125.

Ethyl 3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (12): Thiomannoside **11** (1.02 g, 1.90 mmol) was dissolved in MeOH (15 mL) and K_2CO_3 (cat.) was added. After 2 h the reaction mixture was filtered, concentrated and purified by column chromatography (PE/Et_2O 1:2) to give **12** as a colourless oil (795 mg, 1.62 mmol, 85%). R_f = 0.49 (PE/Et_2O 1:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, 3H, J = 7.4 Hz, CH_2CH_3), 2.50–2.71 (m, 3H, CH_2CH_3, O*H*), 3.67 (dd, 1H, J = 1.9, 10.8 Hz, H_a-6), 3.79 (dd, 1H, J = 4.5 10.8 Hz, H_b-6), 3.84 (dd, 1H, J = 3.1, 9.2 Hz, H-3), 3.90 (t, 1H, J = 9.2 Hz, H-4), 4.09 (m, 1H, H-2), 4.16 (ddd, 1H, J = 1.9, 4.5, 9.2 Hz, H-5), 4.50 (d, 2H, J = 11.4 Hz CH_2Ph), 4.65 (m, 3H, CH_2Ph), 4.82 (d, 1H, J = 10.9 Hz, CH_2Ph), 5.39 (d, 1H, J = 1.1 Hz, H-1), 7.14–7.30 (m, 15H, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8 (CH_2CH_3), 24.9 (CH_2CH_3), 68.9 (C-6), [69.9, 71.5, 74.6 (C-3, C-4, C-5)], [72.1, 73.4, 75.1 (*C*H$_2$Ph)], 80.5 (C-2), 83.4 (C-1), [127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.6, 137.7, 138.3, 138.4 (C_{arom})]; m/z (FAB): found $[M+Na]^+$ 517.2026, $C_{29}H_{34}O_5S$ calcd for $[M+Na]^+$ 517.2019.

8-Methoxycarbonyloctyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside (14): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyl donor **3** (474 mg, 488 μmol) with NIS (150 mg, 666 μmol) in CH_2Cl_2/Et_2O (6.0 mL:6.0 mL) in the presence of glycosyl acceptor **6** (341 mg, 443 μmol) in CH_2Cl_2/Et_2O (11 mL:11 mL) gave the trimannoside **14** as a colourless oil (160 mg, 359 μmol, 81%). R_f = 0.41 (PE/Et_2O 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.04 (s, 9H, C[CH_3]$_3$), 1.28–1.38 (m, 8H, CH_2-linker), 1.58–1.65 (m, 4H, CH_2-linker), 2.14 (s, 3H, OC(O)CH_3), 2.29 (t, 2H, J = 7.5 Hz, $CH_2CO_2CH_3$), 3.19–3.24 (m, 1H, H-5$_a$), 3.36 (dt, 1H, J = 6.8 Hz, 15.5, CH_aH$_b$-linker), 3.45 (d, 1H, J = 10.7 Hz, H_a-6$_c$), 3.64–3.70 (m, 7H, $CH_2CO_2CH_3$, H-3$_a$, 2H-6$_b$, H_b-6$_c$), 3.81 (t, 1H, J = 9.5 Hz, H-4$_b$), 3.84–3.95 (m, 6H, OCH_aH$_b$-linker, 2H-6$_a$, H-5$_b$, H-4$_c$, H-5$_c$), 3.96–4.00 (m, 4H, H-2$_a$, H-2$_b$, H-3$_b$, H-3$_c$), 4.02 (t, 1H, J = 9.6 Hz, H-4$_a$), 4.32 (d, 1H, J = 10.9 Hz, CH_2Ph), 4.34 (s, 1H, H-1$_a$), 4.41 (d, 1H, J = 10.9 Hz, CH_2Ph), 4.45 (d, 1H, J = 10.9 Hz, CH_2Ph), 4.49–4.75 (m, 10H, CH_2Ph), 4.83 (d, 1H, J = 10.9 Hz, CH_2Ph), 4.87 (d, 1H, J = 11.7 Hz, CH_2Ph), 5.02 (s, 1H, H-1$_c$), 5.09 (d, 1H, J = 11.7 Hz, CH_2Ph), 5.21 (s, 1H, H-1$_b$), 5.52 (s, 1H, H-2$_c$), 7.13–7.79 (m, 50H, H_{arom}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 19.3 (*C*[CH_3]$_3$), 21.1 (OC(O)CH_3), [24.9, 26.2, 29.1, 29.2, 29.3, 29.8 (*C*H_2-linker)], 26.7 (C[CH_3]$_3$), 34.1 ($CH_2CO_2CH_3$), 51.4 ($CH_2CO_2CH_3$), 63.1 (C-6$_a$), 68.7 (C-2$_c$), 68.8 (C-6$_c$), 69.4 (OCH_2-linker), 69.5 (C-6$_b$), [71.8, 72.3, 73.2, 73.3, 74.0, 74.7, 75.0 (*C*H$_2$Ph)], 72.0 (C-5$_c$), 72.5 (C-5$_b$), 74.0 (C-4$_c$), 74.6 (C-4$_b$), 74.9 (C-4$_a$), 75.6 (C-2$_b$), 76.6 (C-5$_a$), [78.1, 78.2 (C-2$_a$, C-3$_c$)], 79.4 (C-3$_b$), 81.9 (C-3$_a$), 99.4 (C-1$_c$), 101.0 (C-1$_b$), 101.6 (C-1$_a$), [126.9, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 129.4, 133.4, 134.0, 135.6, 135. 9, 138.1, 138.3, 138.4, 138.5, 138.6, 138.7, 139.4 (C_{arom})], 170.1 (C=O), 174.2 (C=O); m/z (FAB): found $[M+Na]^+$ 1697.7787, $C_{102}H_{118}O_{19}Si$ calcd for $[M+Na]^+$ 1697.7929.

8-Methoxycarbonyloctyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside (15): Trimannoside **14** (1.08 g, 645 μmol) was dissolved in dry MeOH/CH_2Cl_2 (40 mL:10 mL) and K_2CO_3 (cat.) was added. After 12 h the reaction mixture was filtered, concentrated and purified by column chromatography (PE/Et_2O 1:1) to give **15** as a colourless oil (925 mg, 567 μmol, 88%). R_f = 0.42 (PE/Et_2O 1:2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.07 (s, 9H, C[CH_3]$_3$), 1.30–1.39 (m, 8H, CH_2-linker), 1.60–1.65 (m, 4H, CH_2-linker), 2.32 (t, 2H, J = 7.6 Hz, $CH_2CO_2CH_3$), 3.20–3.24 (m, 1H, H-5$_a$), 3.35–3.40 (m, 1H, CH_aH$_b$-linker), 3.52 (d, 1H, J = 10.2 Hz, H_a-6$_c$), 3.64 (dd, 1H, J = 4.0, 10.2 Hz, H_b-6$_c$), 3.67–3.71 (m, 6H, $CH_2CO_2CH_3$, H-3$_a$, 2H-6$_b$), 3.82 (t, 1H, J = 9.2 Hz, H-4$_b$), 3.86–3.97 (m, 7H, OCH_aH$_b$-linker, 2H-6$_a$, H-5$_b$, H-3$_c$, H-4$_c$, H-5$_c$), 3.97–3.99 (m, 3H, H-2$_a$, H-2$_b$, H-3$_b$), 4.03 (t, 1H, J = 9.6 Hz, H-4$_a$), 4.13 (s, 1H, H-2$_c$), 4.35 (s, 1H, H-1$_a$), 4.38 (d, 1H, J = 12.2 Hz, CH_2Ph), 4.48–4.66 (m, 10H, CH_2Ph), 4.71 (d, 1H, J = 12.2 Hz, CH_2Ph), 4.74 (d, 1H, J = 11.2 Hz, CH_2Ph), 4.82 (d, 1H, J = 11.2 Hz, CH_2Ph), 4.87 (d, 1H, J = 11.2 Hz, CH_2Ph), 5.09 (s, 1H, H-1$_c$), 5.12 (d, 1H, J = 12.2 Hz, CH_2Ph), 5.25 (s, 1H, H-1$_b$), 7.15–7.80 (m, 50H, H_{arom}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 19.3 (*C*[CH_3]$_3$), [24.9, 26.2, 29.1, 29.2, 29.3, 29.8 (*C*H_2-linker)], 26.7 (C[CH_3]$_3$), 34.1 ($CH_2CO_2CH_3$), 51.4 ($CH_2CO_2CH_3$), 63.1 (C-6$_a$), 68.7 (C-2$_c$), 68.8 (C-6$_c$), 69.4 (OCH_2-linker), 69.5 (C-6$_b$), [71.8, 72.3, 73.2, 73.3, 74.0, 74.7, 75.0 (*C*H$_2$Ph)], 72.0 (C-5$_c$), 72.5 (C-5$_b$), 74.0 (C-4$_c$), 74.6 (C-4$_b$), 74.9 (C-4$_a$), 75.6 (C-2$_b$), 76.6 (C-5$_a$), [78.1, 78.2 (C-2$_a$, C-3$_c$)], 79.4 (C-3$_b$), 81.9 (C-3$_a$), 99.4 (C-1$_c$), 101.0 (C-1$_b$), 101.6 (C-1$_a$), [126.9, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128,4, 129.4, 133.4, 134.0, 135.6, 135. 9, 138.1, 138.3, 138.4, 138.5, 138.6, 138.7, 139.4 (C_{arom})], 170.4 (C=O); m/z (FAB): found $[M+Na]^+$ 1632.7930, $C_{100}H_{116}O_{18}Si$ calcd for $[M+Na]^+$ 1632.7046.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside (16): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyl donor **2** (174 mg, 171 μmol) with NIS (53 mg, 233 μmol) in CH_2Cl_2/Et_2O (2.0 mL:2.0 mL) in the presence of glycosyl acceptor **15** (254 mg, 156 μmol) in CH_2Cl_2/Et_2O (11 mL:11 mL) gave pentasaccharide **16** as a colourless oil (315 mg, 126 μmol, 81%). R_f = 0.39 (PE/Et_2O 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.06 (s, 9H, C[CH_3]$_3$), 1.28–1.39 (m, 8H, CH_2-linker), 1.58–1.66 (m, 4H, CH_2-linker), 2.32 (t, 2H, J = 7.5 Hz, $CH_2CO_2CH_3$), 3.17 (d, 1H, J = 7.9 Hz, H-5$_a$), 3.33–3.38 (m, 1H, OCH_aH$_b$-linker), 3.51 (d, 1H, J = 10.3 Hz, H_a-6$_e$), 3.56–3.57 (m, 1H, H-2$_c$), 3.59–3.61 (m, 2H, 2H-6$_c$), 3.63–3.67 (m, 3H, H-3$_a$, H_a-6$_b$, H_b-6$_e$), 3.69 (s, 3H, $CH_2CO_2CH_3$), 3.70–3.71 (m, 1H, H_b-6$_b$), 3.72–3.78 (m, 2H, H-4$_e$, H-5$_e$), 3.79–3.85 (m, 3H, H-4$_b$, H-4$_c$, H_a-6$_d$), 3.86–3.95 (m, 6H, OCH_aH$_b$-linker, 2H-6$_a$, H-2$_b$, H-3$_c$, H-2$_d$), 3.95–4.00 (m, 5H, H-2$_a$, H-4$_a$, H-3$_b$, H-5$_b$, H-5$_c$), 4.03 (t, 1H, J = 9.2 Hz, H-3$_e$), 4.05–4.10 (m, 1H, H-5$_d$), 4.12–4.16 (m, 1H, H_b-6$_d$), 4.18 (d, 1H, J = 12.2 Hz, CH_2Ph), 4.21 (s, 1H, H-2$_c$), 4.28 (s, 1H, H-1$_a$), 4.36 (d, 1H, J = 12.2 Hz, CH_2Ph), 4.38–4.43 (m, 2H, CH_2Ph, H-4$_d$), 4.45–4.70 (m, 18H, CH_2Ph, H-3$_d$), 4.75–4.81 (m, 3H, CH_2Ph), 4.86 (d, 1H, J = 10.9 Hz, CH_2Ph), 5.00 (d, 1H, J = 10.9 Hz, CH_2Ph), 5.10 (d, 1H, J = 11.1 Hz, CH_2Ph), 5.16 (s, 1H, H-1$_c$), 5.24 (s, 1H, H-1$_d$), 5.28 (s, 1H, H-1$_b$), 5.48 (s, 1H, C*H*Ph), 5.63 (s, 1H, H-1$_e$), 7.06–7.80 (m, 80H, H_{arom}); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 19.3 (*C*[CH_3]$_3$), [25.0, 26.2, 29.1, 29.3, 29.4, 29.8 (*C*H_2-linker)], 26.7 (C[CH_3]$_3$), 34.1 ($CH_2CO_2CH_3$), 51.5 ($CH_2CO_2CH_3$), 63.1 (C-6$_a$), 64.6 (C-5$_d$), 68.1 (C-6$_e$), 68.8 (C-6$_d$), 69.3 (C-6$_c$), 69.4 (OCH_2-linker, C-6$_b$), [70.7, 72.4, 72.6, 73.1, 73.6, 73.9, 74.6, 74.9, 75.0, 75.5 (*C*H$_2$Ph)], 70.8 (C-5$_e$), 72.2 (C-5$_c$), 72.3 (C-3$_d$), 72.5 (C-5$_b$), 74.5 (C-4$_a$), 74.7 (C-4$_b$, C-2$_c$), 75.1 (C-4$_c$), 76.3 (C-2$_b$), 76.5 (C-5$_a$), 77.1 (C-4$_e$), 77.7 (C-2$_d$), 78.1 (C-3$_b$), 78.8 (C-2$_a$), 79.0 (C-2$_e$), 79.8 (C-4$_d$), 79.9 (C-3$_c$), 81.4 (C-3$_e$), 82.7 (C-3$_a$), 96.8 (C-1$_e$), 100.6 (C-1$_d$), 100.9 (C-1$_c$), 101.1 (C-1$_b$), 101.5 (C-1$_a$), 102.4 (*C*HPh), [126.5, 126.8, 127.3, 127.4, 127.5, 127.6, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 129.1, 129.5, 133.4, 134.0, 135.6, 136.0, 137.5, 137. 9, 138.0, 138.1, 138.3, 138.4, 138.5, 138.6, 139.5 (C_{arom})], 174.4 (C=O); m/z (FAB): found $[M+Na]^+$ 2518.1515, $C_{154}H_{170}O_{28}Si$ calcd for $[M+Na]^+$ 2518.1540.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-

α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside (17): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyl donor **13** (126 mg, 186 μmol) with NIS (52.0 mg, 232 μmol) in CH_2Cl_2/Et_2O (2.0 mL:2.0 mL) in the presence of glycosyl acceptor **15** (253 mg, 156 μmol) in CH_2Cl_2/Et_2O (2.0 mL:2.0 mL) gave tetramannoside **17** as a colourless oil (277 mg, 129 μmol, 83%). $R_f = 0.50$ (PE/Et_2O 1:1); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 1.08$ (s, 9H, C[CH_3]$_3$), 1.32–1.40 (m, 8H, CH_2-linker), 1.60–1.68 (m, 4H, CH_2-linker), 2.33 (t, 2H, $J = 7.6$ Hz, $CH_2CO_2CH_3$), 3.21–3.25 (m, 1H, H-5$_a$), 3.37–3.42 (m, 1H, OCH_aH$_b$-linker), 3.53 (d, 1H, $J = 10.2$ Hz, H$_a$-6$_c$), 3.56 (d, 1H, $J = 9.2$ Hz, H$_a$-6$_d$), 3.66–3.73 (m, 8H, $CH_2CO_2CH_3$, H-3$_a$, 2H-6$_b$, H$_b$-6$_c$, H$_b$-6$_d$), 3.82 (t, 1H, $J = 9.6$ Hz, H-4$_b$), 3.84–3.88 (m, 2H, H-4$_c$, H-2$_d$), 3.89–3.98 (m, 9H, OCH$_a$$H_b$-linker, 2H-6$_a$, H-3$_b$, H-5$_b$, H-3$_c$, H-5$_c$, H-3$_d$, H-5$_d$), 3.98–4.01 (m, 3H, H-2$_a$, H-4$_a$, H-2$_b$), 4.10 (t, 1H, $J = 9.6$ Hz, H-4$_d$), 4.19 (s, 1H, H-2$_c$), 4.33 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 4.35 (s, 1H, H-1$_a$), 4.36 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 4.46–4.60 (m, 15H, CH_2Ph), 4.65 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 4.72–4.78 (m, 2H, CH_2Ph), 4.84–4.94 (m, 3H, CH_2Ph), 5.12 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 5.21 (s, 1H, H-1$_c$), 5.24 (s, 1H, H-1$_d$), 5.31 (s, 1H, H-1$_b$), 7.10–7.81 (m, 70H, H$_{arom}$); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 19.3$ (C[CH_3]$_3$), [25.0, 26.2, 29.1, 29.3, 29.4, 29.8 (OCH_2-linker)], 26.8 (C[CH_3]$_3$), 34.1 ($CH_2CO_2CH_3$), 51.4 ($CH_2CO_2CH_3$), 63.2 (C-6$_a$), 69.2 (C-6$_d$), 69.4 (OCH_2-linker, C-6$_b$), 69.5 (C-6$_c$), [72.1, 72.4, 73.2, 73.4, 74.0, 74.4, 75.1, 75.2 (CH_2Ph)], [72.5, 72.6 (C-5$_b$, C-5$_c$, C-5$_d$)], [74.9, 75.0, 75.1 (C-4$_a$, C-4$_b$, C-2$_c$, C-4$_c$, C-2$_d$, C-4$_d$)], 76.0 (C-2$_b$), 76.6 (C-5$_a$), 78.2 (C-2$_a$), 79.2 (C-3$_b$), 79.8 (C-3$_d$), 79.9 (C-3$_c$), 82.1 (C-3$_a$), 99.5 (C-1$_d$), 101.0 (C-1$_c$), 101.1 (C-1$_b$), 101.6 (C-1$_a$), [127.4, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128,4, 134.1, 135.6, 136.0, 138.3, 138.4, 138.6, 138.7, 138.8 (C$_{arom}$)], 174.2 (C=O); m/z (FAB): found $[M+Na]^+$ 2178.0255, $C_{134}H_{150}O_{23}Si$ calcd for $[M+Na]^+$ 2178.0229.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-D-mannopyranoside (18): This compound was synthesised according to the general procedure for the desilylation. Treatment of silylether **16** (740 mg, 297 μmol) with TBAF/AcOH (3%) (3.6 mL) gave pentasaccharide **18** as a colourless oil (590 mg, 261 μmol, 88%). $R_f = 0.27$ (PE/Et_2O 1:2); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 1.27–1.36$ m, (m, 8H, CH_2-linker), 1.56–1.66 (m, 4H, CH_2-linker), 2.30 (2t, H, $J = 7.6$ Hz, $CH_2CO_2CH_3$), 3.11–3.15 (m, 1H, H-5$_a$), 3.29–3.34 (m, 1H, OCH_aH$_b$-linker), 3.47–3.51 (m, 1H, H$_a$-6$_c$), 3.55 (dd, 1H, $J = 3.6$, 9.7 Hz H-2$_e$), 3.58–3.66 (m, 7H, H-3$_a$, H$_a$-6$_a$, 2H-6$_b$, 2H-6$_c$, H$_b$-6$_c$), 3.68 (s, 3H, $CH_2CO_2CH_3$), 3.70 (t, 1H, $J = 8.9$ Hz, H-4$_e$), 3.73–3.79 (m, 4H, H$_b$-6$_a$, H-4$_b$, H-4$_c$, H-5$_e$), 3.80–3.85 (m, 4H, OCH$_a$$H_b$-linker, H-4$_a$, H-5$_b$, H$_a-6_d$), 3.89–3.93 (m, 5H, H-2$_a$, H-2$_b$, H-3$_b$, H-3$_c$, H-2$_d$), 3.94–3.98 (m, 1H, H-5$_c$), 4.01 (t, 1H, $J = 9.2$ Hz, H-3$_e$), 4.03–4.07 (m, H, H-5$_d$), 4.12 (dd, 1H, $J = 4.8$, 10.0 Hz, H$_b$-6$_d$), 4.17 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 4.20 (s, 1H, H-2$_c$), 4.26 (s, 1H, H-1$_a$), 4.33–4.63 (m, 18H, CH_2Ph, H-3$_d$, H-4$_d$), 4.67–4.86 (m, 7H, CH_2Ph), 4.89 (d, 1H, $J = 10.9$ Hz, CH_2Ph), 4.99 (d, 1H, $J = 12.4$ Hz, CH_2Ph), 5.15 (s, 1H, H-1$_c$), 5.23 (s, 1H, H-1$_d$), 5.28 (s, 1H, H-1$_b$), 5.48 (s, 1H, CHPh), 5.62 (d, 1H, $J = 3.5$ Hz, H-1$_e$), 7.04–7.42 (m, 70H, H$_{arom}$); ^{13}C NMR (150 MHz, $CDCl_3$): δ = [24.9, 26.0, 29.1, 29.2, 29.3, 29.7 (CH_2-linker)], 34.1 ($CH_2CO_2CH_3$), 51.2 ($CH_2CO_2CH_3$), 63.3 (C-6$_a$), 64.6 (C-5$_d$), 68.1 (C-6$_e$), 68.7 (C-6$_d$), 69.4 (C-6$_b$, C-6$_c$), 70.2 (OCH_2-linker), [70.7, 72.1, 72.2, 72.6, 73.1, 73.2, 73.3, 73.6, 74.1, 74.7, 74.9, 75.1, 75.5 (CH_2Ph)], 70.8 (C-5$_e$), 72.3 (C-5$_c$), 72.5 (C-5$_b$), 74.4 (C-4$_a$), 74.5 (C-3$_d$), 74.6 (C-2$_c$), [74.8, 75.0 (C-4$_b$, C-4$_c$)], 75.6 (C-5$_a$), 75.9 (C-2$_b$), 77.1 (C-4$_e$), [77.6, 77.9, 78.7 (C-2$_a$, C-3$_b$, C-2$_d$)], 79.0 (C-2$_e$), 79.8 (C-3$_c$, C-4$_d$), 81.4 (C-3$_a$, C-3$_e$), 96.7 (C-1$_e$), 100.6 (C-1$_d$), 100.8 (C-1$_c$), 101.0 (C-1$_b$), 101.1 (C-1$_a$), 102.4 (CHPh), [127.2, 127.4, 127.6, 127.8, 127.8, 128.1, 138.0, 138.3, 138.6, 138.8 (C$_{arom}$)], 174.3 (C=O); m/z (FAB): found $[M+Na]^+$ 2280.0284, $C_{138}H_{152}O_{28}$ calcd for $[M+Na]^+$ 2280.0362.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-D-mannopyranoside (19): This compound was synthesised according to the general procedure for the desilylation. Treatment of silylether **17** (472 mg, 219 μmol) with TBAF/AcOH (3%) (1.4 mL) gave tetramannoside **19** as a colourless oil (385 mg, 200 μmol, 92%). $R_f = 0.37$ (PE/Et_2O 1:2); ^1H NMR (600 MHz, $CDCl_3$): δ = 1.28–1.35 (m, 8H, CH_2-linker), 1.56–1.65 (m, 4H, CH_2-linker), 2.30 (t, 1H, $J = 7.6$ Hz, $CH_2CO_2CH_3$), 3.13–3.17 (m, 1H, H-5$_a$), 3.30–3.34 (m, 1H, OCH_aH$_b$-linker), 3.49–3.53 (m, 2H, H$_a$-6$_b$, H$_a$-6$_d$), 3.58–3.70 (m, 9H, CO_2CH_3, H-3$_a$, H$_a$-6$_a$, H$_b$-6$_b$, 2H-6$_c$, H$_b$-6$_d$), 3.72–3.76 (m, 2H, H$_b$-6$_a$, H-4$_c$), 3.78–3.94 (m, 11H, OCH_aH$_b$-linker, H-2$_a$, H-4$_a$, H-3$_b$, H-4$_b$, H-5$_b$, H-3$_c$, H-5$_c$, H-2$_d$, H-3$_d$, H-5$_d$), 4.02 (s, 1H, H-2$_c$), 4.06 (t, 1H, $J = 9.6$ Hz, H-4$_d$), 4.16 (s, 1H, H-2$_b$), 4.28–4.31 (m, 2H, H-1$_a$, CH_2Ph), 4.35 (d, 1H, J = 12.4 Hz, CH_2Ph), 4.43–4.57 (m, 16H, CH_2Ph), 4.70 (d, 1H, $J = 12.4$ Hz, CH_2Ph), 4.75 (d, 1H, $J = 11.5$ Hz, CH_2Ph), 4.81–4.90 (m, 3H, CH_2Ph), 4.98 (d, 1H, $J = 12.4$ Hz, CH_2Ph), 5.17 (s, 1H, H-1$_b$), 5.19 (s, 1H, H-1$_d$), 5.28 (s, 1H, H-1$_c$), 7.12–7.38 (m, 60H, H$_{arom}$); ^{13}C NMR (150 MHz, $CDCl_3$): δ = [24.9, 26.0, 29.0, 29.1, 29.2, 29.7 (OCH_2-linker)], 34.1 ($CH_2CO_2CH_3$), 51.4 (CO_2CH_3), 62.3 (C-6$_a$), [69.1, 69.5 (C-6$_b$, C-6$_c$, C-6$_d$)], [72.0, 72.1, 72.3, 73.1, 73.2, 74.2, 74.6, 74.7 (CH_2Ph)], [72.4, 72.5 (C-5$_b$, C-5$_c$, C-5$_d$)], [74.8, 74.9, 75.0, 75.1 (C-4$_a$, C-2$_b$, C-4$_b$, C-4$_c$, C-2$_d$, C-4$_d$)], 75.6 (C-5$_a$), 75.7 (C-2$_c$), 77.9 (C-2$_a$), [79.0, 79.7, 79.8 (C-3$_b$, C-3$_c$, C-3$_d$)], 81.4 (C-3$_a$), 99.4 (C-1$_d$), 101.0 (C-1$_b$, C-1$_c$), 101.6, (C-1$_a$), [127.3, 127.4, 127.5, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 138.3, 138.5, 138.6, 138.7 (C$_{arom}$)], 174.2 (C=O); m/z (FAB): found $[M+Na]^+$ 1939.9042, $C_{118}H_{132}O_{23}$ calcd for $[M+Na]^+$ 1939.9052.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranoside (20): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyl donor **1** (107 mg, 105 μmol) with NIS (36 mg, 158 μmol) in CH_2Cl_2/Et_2O (1.0 mL:1.0 mL) in the presence of glycosyl acceptor **18** (198 mg, 87.7 μmol) in CH_2Cl_2/Et_2O (2.0 mL:2.0 mL) gave heptasaccharide **20** as a colourless oil (140 mg, 45.2 μmol, 51%). $R_f = 0.29$ (PE/Et_2O 1:1); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 1.24–1.29$ (m, 8H, CH_2-linker), 1.45–1.50 (m, 2H, CH_2-linker), 1.54 (t, 2H, $J = 7.2$ Hz, CH_2-linker), 2.25 (t, 2H, $J = 7.6$ Hz, $CH_2CO_2CH_3$), 3.14–3.17 (m, 1H, H-5$_a$), 3.27–3.32 (m, 1H, OCH_aH$_b$-linker), 3.47 (d, 1H, $J = 10.0$ Hz, H$_a$-6$_e$), 3.53–3.82 (m, 23H, $CH_2CO_2CH_3$, H-3$_a$, H-4$_a$, 2H-6$_a$, H-4$_b$, 2H-6$_b$, H-4$_c$, 2H-6$_c$, H$_a$-6$_d$, H-2$_e$, H-4$_e$, H-5$_e$, H$_b$-6$_e$, H-2$_{b'}$, H$_a$-6$_{b'}$, H-5$_{c'}$, 2H-6$_{c'}$), 3.84–3.95 (m, 11H, OCH$_a$$H_b$-linker, H-2$_a$, H-2$_b$, H-3$_b$, H-5$_b$, H-3$_c$, H-5$_c$, H-2$_d$, H-5$_{b'}$, H-2$_{c'}$, H-3$_{c'}$), 3.97–4.04 (m, 3H, H-3$_e$, H-5$_d$, H-4$_{c'}$), 4.07–4.11 (m, 2H, H$_b-6_d$, H-4$_{b'}$), 4.13–4.20 (m, 4H, C$H_2$Ph, H-1$_a$, H-2$_c$, H$_b-6_{b'}$), 4.25–4.39 (m, 6H, C$H_2$Ph, H-4$_d$, H-3$_{b'}$), 4.41–5.02 (m, 33H, C$H_2$Ph, H-3$_d$, H-1$_{b'}$), 5.13 (s, 1H, H-1$_c$), 5.20 (s, 1H, H-1$_d$), 5.27 (s, 1H, H-1$_b$), 5.39 (s, H-1$_{c'}$), 5.46 (s, 1H, C$H$Ph), 5.55 (s, 1H, C$H$Ph), 5.60 (d, 1H, $J = 3.3$ Hz, H-1$_e$), 7.02–7.45 (m, 100H, H$_{arom}$); ^{13}C NMR (150 MHz, $CDCl_3$): δ = [25.0, 26.1, 29.2, 29.4, 29.7, 29.8 (CH_2-linker)], 34.1 ($CH_2CO_2CH_3$), 51.5 ($CH_2CO_2CH_3$), 63.8 (C-5$_{b'}$), 65.6 (C-5$_d$), 66.4 (C-6$_a$), 68.1 (C-6$_e$), 68.7 (C-6$_d$), 68.8 (C-6$_{b'}$), [69.1, 69.4, 69.9 (C-6$_b$, C-6$_c$, C-6$_{c'}$)], 70.7 (OCH_2-linker), 70.8 (C-5$_{c'}$), [71.6, 71.7, 72.3, 72.6, 73.2, 73.3, 73.4, 73.6, 73.9, 74.9, 75.0, 75.5 (CH_2Ph)], [72.2, 72.4, 72.5 (C-5$_b$, C-5$_c$, C-5$_e$)], 73.7 (C-3$_d$), [74.3, 74.6, 74.7, 75.1 (C-4$_a$, C-5$_a$, C-2$_c$, C-2$_{b'}$, C-2$_{c'}$, C-4$_{c'}$)], 76.0 (C-2$_b$), 77.1 (C-4$_e$), [77.3, 77.7, 77.8, 77.9 (C-2$_a$, C-4$_b$, C-4$_c$, C-2$_d$)], 79.0 (C-3$_b$, C-2$_e$), 79.4 (C-4$_{b'}$), 79.6 (C-3$_{c'}$), 79.8 (C-3$_c$, C-4$_d$), 81.4 (C-3$_e$), 82.5 (C-3$_a$), 96.6 (C-1$_e$), 98.5 (C-1$_{b'}$), 98.6 (C-1$_{c'}$), 100.5 (C-1$_d$), 100.8 (C-1$_c$), 101.1 (C-1$_b$), 101.3 (C-1$_a$), 101.9 (CHPh), 102.4 (CHPh), [126.3, 126.5, 127.1, 127.3, 127.4, 127.5, 127.6, 127.8, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 129.1, 129.2, 137.9, 138.0, 138.3, 138.4, 138.5, 138.7, 138.9, 139.0 (C$_{arom}$)] 174.3 (C=O); m/z (FAB): found $[M+Na]^+$ 3142.4056. $C_{192}H_{206}O_{38}Na$ calcd for $[M+Na]$, 3142.4079.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranoside (21): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyl donor **1** (191 mg, 207 μmol) with NIS (70.0 mg, 310 μmol) in CH_2Cl_2/Et_2O (2.0 mL:2.0 mL) in the presence of glycosyl acceptor **19** (198 mg, 103 μmol) in CH_2Cl_2/Et_2O (2.0 mL:2.0 mL) gave hexamannoside **21** as a colourless oil (152 mg, 54.6 μmol, 53%). $R_f = 0.29$ (PE/Et_2O 1:1); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 1.18–1.26$ (m, 8H, CH_2-linker), 1.46–1.54 (m, 4H, CH_2-linker), 2.24 (t, 2H, $J = 7.6$ Hz, $CH_2CO_2CH_3$), 3.15–3.19 (m, 1H, H-5$_a$), 3.27–3.31 (m, 1H, OCH_aH$_b$-linker), 3.47 (d, 1H, $J = 10.6$ Hz H$_a$-6$_d$), 3.49 (d, 1H, $J = 10.9$ Hz, H$_a$-6$_c$), 3.54–3.69 (m, 12H, CO_2CH_3, H-3$_a$, H-4$_a$, 2H-6$_a$, 2H-6$_b$, H$_b$-6$_c$, H$_b$-6$_d$, H$_a$-6$_{c'}$), 3.71–3.92 (m, 18H, OCH$_a$$H_b$-linker, H-2$_a$, H-3$_b$, H-4$_b$, H-5$_b$, H-3$_c$,

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H-4$_c$, H-5$_c$, H-2$_d$, H-3$_d$, H-5$_d$, H-2$_{b'}$, H-5$_{b'}$, H$_a$-6$_{b'}$, H-2$_{c'}$, H-3$_{c'}$, H-5$_{c'}$, H$_b$-6$_{c'}$), 4.00–4.06 (m, 3H, H-2$_b$, H-4$_d$, H-4$_{c'}$), 4.09 (t, 1H, J = 9.8 Hz, H-4$_{b'}$), 4.14 (s, 1H, H-2$_c$), 4.17–4.21 (m, 2H, H-1$_a$, H$_b$-6$_{b'}$), 4.25–4.70 (m, 29H, CH_2Ph, H-3$_{b'}$), 4.76–4.90 (m, 6H, CH_2Ph, H-1$_{b'}$), 4.99 (d, 1H, J = 12.5 Hz, CH_2Ph), 5.15 (s, 1H, H-1$_c$), 5.19 (s, 1H, H-1$_d$), 5.26 (s, 1H, H-1$_b$), 5.28 (s, 1H, H-1$_{c'}$), 5.55 (s, 1H, CHPh), 7.04–7.42 (m, 90H, H$_{arom}$); ^{13}C NMR (150 MHz, $CDCl_3$): δ = [24.9, 26.1, 29.1, 29.3, 29.7, 29.8 (CH_2-linker)], 34.1 (CH_2CO$_2$CH$_3$), 51.4 (CO$_2$CH_3), 63.7 (C-5$_{b'}$), 66.4 (C-6$_a$), [66.8, 68.9, 69.0, 69.1, 69.4 (C-6$_b$, C-6$_c$, C-6$_d$, C-6$_{b'}$, C-6$_{c'}$)], 69.9 (OCH_2-linker), [71.6, 71.7, 72.0, 72.1, 72.6, 73.1, 73.2, 73.3, 73.4, 74.0, 74.9, 75.1, 75.2 (CH_2Ph)], [72.3, 72.4, 72.5 (C-5$_b$, C-5$_c$, C-5$_d$, C-5$_{c'}$)], 73.6 (C-3$_{b'}$), [74.4, 74.5, 74.6, 74.7, 74.8, 75.0 (C-4$_a$, C-5$_a$, C-2$_b$, C-4$_b$, C-2$_c$, C-4$_c$, C-4$_d$, C-4$_{c'}$)], 77.8 (C-2$_a$, C-2$_{b'}$), [79.2, 79.3, 79.6, 79.7, 79.8 (C-3$_b$, C-3$_c$, C-2$_d$, C-3$_d$, C-4$_{b'}$, C-2$_{c'}$, C-3$_{c'}$)], 81.9 (C-3$_a$), 98.7 (C-1$_{b'}$), 98.8 (C-1$_{c'}$), 99.3 (C-1$_d$), 100.9 (C-1$_c$), 101.2 (C-1$_b$), 101.4, (C-1$_a$), 101.9 (CHPh), [127.4. 127.5, 127.6, 127.8, 128.0, 128.1, 128.2, 128.3, 138.0, 138.3, 138.4, 138.5, 138.7 (C$_{arom}$)], 174.2 (C=O); m/z (FAB): found $[M+2\mathrm{Na}]^{2+}$ 1412.6225, $C_{172}H_{186}O_{33}Na$ calcd for ½$[M+2\mathrm{Na}]$ 1412.6336.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside (22): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyl donor **4** (515 mg, 507 μmol) with NIS (132 mg, 585 μmol) in CH_2Cl_2/Et_2O (2.5 mL:2.5 mL) in the presence of glycosyl acceptor **6** (300 mg, 390 μmol) in CH_2Cl_2/Et_2O (5.0 mL:5.0 mL) gave trimannoside **22** as a colourless oil (457 mg, 345 μmol, 68%). R_f = 0.50 (PE/Et$_2$O 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (s, 9H, C[CH_3]$_3$), 1.37–1.50 (m, 8H, CH_2-linker), 1.68–1.75 (m, 4H, CH_2-linker), 2.38 (t, 2H, J = 7.6 Hz, CH_2CO$_2$CH$_3$), 3.27–3.32 (m, 1H, H-5$_a$), 3.46 (dt, 1H, J = 9.2, 6.5 Hz, OCH_aH$_b$-linker), 3.62 (d, 1H, J = 10.0 Hz, H$_a$-6$_c$), 3.73–3.80 (m, 7H, CH$_2$CO$_2$CH_3, H-3$_a$, 2H-6$_b$, H$_b$-6$_c$), 3.84 (t, 1H, J = 9.6 Hz, H-4$_b$), 3.93 (m, 1H, H-2$_c$), 3.96–4.04 (m, 5H, OCH$_a$$H_b$-linker, 2H-6$_a$, H-5$_c$, H-3$_c$), 4.05 (m, 2H, H-3$_b$, H-5$_b$), 4.09 (d, 1H, J = 2.7 Hz, H-2$_a$), 4.10–4.15 (3m, H, H-4$_a$, H-2$_b$, H-4$_c$), 4.42 (s, 1H, H-1$_a$), 4.46 (d, 1H, J = 12.2 Hz, CH$_2$Ph), 4.57–4.73 (m, 12H, CH_2Ph), 4.82 (d, 1H, J = 12.2 Hz, CH_2Ph), 4.88 (d, 1H, J = 11.3 Hz, CH_2Ph), 4.94 (d, 1H, J = 11.3 Hz, CH_2Ph), 4.97 (d, 1H, J = 11.3 Hz, CH_2Ph), 5.21 (d, 1H, J = 12.2 Hz, CH_2Ph), 5.24 (s, 1H, H-1$_c$), 5.34 (s, 1H, H-1$_b$), 7.24–7.88 (m, 55H, H$_{arom}$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.4 (C[CH$_3$]$_3$), [25.0, 26.3, 29.2, 29.3, 29.4, 29.9 (CH_2-linker)], 26.8 (C[CH_3]$_3$), 34.2 (CH_2CO$_2$CH$_3$), 51.5 (CH$_2$CO$_2$CH_3), 63.2 (C-6$_a$), [69.3, 69.5, 69.6 (OCH_2-linker, C-6$_b$, C-6$_c$)], [72.3, 72.5 (C-5$_b$, C-5$_c$)], [72.3, 72.7, 73.3, 73.5, 74.1, 75.0, 75.1 (CH_2Ph)], 75.0 (C-2$_b$, C-4$_b$, C-2$_c$), 75.1 (C-4$_a$, C-4$_c$), 76.7 (C-5$_a$), 78.3 (C-2$_a$), 79.8 (C-3$_b$, C-3$_c$), 82.2 (C-3$_a$), 99.7 (C-1$_c$), 101.3 (C-1$_b$), 101.7 (C-1$_a$), [127.0, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6, 129.6, 133.6, 134.1, 135.7, 136.1, 138.4, 138.6, 138.7, 138.8 (C$_{arom}$)], 174.2 (C=O); m/z (FAB): found $[M+\mathrm{Na}]^+$ 1723.8516. $C_{107}H_{122}O_{18}Si$ calcd for $[M+\mathrm{Na}]^+$ 1723.8473.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-D-mannopyranoside (23): This compound was synthesised according to the general procedure for the desilylation. Treatment of silylether **22** (1.66 g, 964 μmol) with TBAF/AcOH (3%) (3.0 mL) gave the trimannoside **23** as a colourless oil (1.32 g, 887 μmol, 92%). R_f = 0.34 (PE/Et$_2$O 1:2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27–1.35 (m, 8H, CH_2-linker), 1.55–1.65 (m, 4H, CH_2-linker), 2.04 (t, 1H, J = 6.7 Hz, OH), 2.28 (t, 2H, J = 7.5 Hz, CH_2CO$_2$CH$_3$), 3.13–3.19 (m, 1H, H-5$_a$), 3.29–3.37 (m, 1H, OCH_aH$_b$-linker), 3.51 (d, 1H, J = 10.5 Hz, H$_a$-6$_b$), 3.57–3.62 (m, 3H, H$_a$-6$_a$, H$_b$-6$_b$, H$_a$-6$_c$), 3.63–3.69 (m, 6H, CH$_2$CO$_2$CH_3, H-3$_a$, H-4$_b$, H$_b$-6$_c$), 3.72–3.77 (m, 1H, H$_b$-6$_a$), 3.78–3.83 (m, 3H, OCH$_a$$H_b$-linker, H-5$_b$, H-2$_c$), 3.83–3.89 (m, 4H, H-4$_a$, H-3$_b$, H-3$_c$, H-5$_c$), 3.90 (d, 1H, J = 2.5 Hz, H-2$_a$), 3.97–4.02 (m, 2H, H-2$_b$, H-4$_c$), 4.30 (s, 1H, H-1$_a$), 4.37 (d, 1H, J = 12.3 Hz, CH$_2$Ph), 4.45–4.58 (m, 12H, CH$_2$Ph), 4.69 (d, 1H, J = 12.3 Hz, CH$_2$Ph), 4.76–4.86 (m, 3H, CH$_2$Ph), 4.99 (d, 1H, J = 12.3 Hz, CH$_2$Ph), 5.12 (1s, H, H-1$_c$), 5.23 (s, 1H, H-1$_b$), 7.15–7.39 (m, 45H, H$_{arom}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = [25.0, 26.1, 29.1, 29.2, 29.3, 29.7 (CH_2-linker)], 34.1 (CH_2CO$_2$CH$_3$), 51.5 (CH$_2$CO$_2$CH_3), 63.3 (C-6$_a$), [69.3, 69.5 (C-6$_b$, C-6$_c$)], 70.2 (OCH_2-linker), [72.2, 72.5, 73.2, 73.3, 74.3, 74.7, 74.9 (CH_2Ph)], 72.4 (C-5$_c$), 72.7 (C-5$_b$), 74.8 (C-4$_a$, C-4$_b$, C-2$_c$), 75.2 (C-2$_b$, C-4$_c$), 75.7 (C-5$_a$), 78.0 (C-2$_a$), 79.7 (C-3$_b$, C-3$_c$), 81.4 (C-3$_a$), 99.6 (C-1$_c$), 101.1 (C-1$_b$), 101.7 (C-1$_a$), [127.2, 127.4, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.3, 128.5, 128.6, 133.6, 138.2, 138.5, 138.6, 138.8, 138.9 (C$_{arom}$)], 174.3 (C=O); m/z (FAB): found $[M+\mathrm{Na}]^+$ 1507.7076, $C_{91}H_{104}O_{18}$ calcd for $[M+\mathrm{Na}]^+$ 1507.7115.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranoside (24): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyl donor **1** (92.0 mg, 90.5 μmol) with NIS (31.0 mg, 136 μmol) in CH_2Cl_2/Et_2O (1.0 mL:1.0 mL) in the presence of glycosyl acceptor **23** (112 mg, 75.4 μmol) in CH_2Cl_2/Et_2O (2.0 mL:2.0 mL) gave pentamannoside **24** as a colourless oil (124 mg, 52.8 μmol, 70%). R_f = 0.33 (PE/Et$_2$O 1:1); ^{1}H NMR (500 MHz, $CDCl_3$: δ = 1.20–1.35 (m, 8H, CH_2-linker), 1.50–1.63 (m, 4H, CH_2-linker), 2.30 (t, 2H, J = 7.6 Hz, CH_2CO$_2$CH$_3$), 3.21–3.26 (m, 1H, H-5$_a$), 3.31–3.37 (m, 1H, OCH_aH$_b$-linker), 3.52 (d, 1H, J = 10.5 Hz, H$_a$-6$_c$), 3.58–3.63 (m, 3H, H$_a$-6$_a$, 2H-6$_b$), 3.64–3.74 (m, 8H, CH$_2$CO$_2$CH_3, H-3$_a$, H$_b$-6$_a$, H-4$_b$, H$_b$-6$_c$, H$_a$-6$_{c'}$), 3.75–3.79 (m, 3H, H-4$_a$, H-5$_{c'}$, H$_b$-6$_{c'}$), 3.80–3.82 (m, 2H, H$_a$-6$_{b'}$, H-2$_c$), 3.83–3.85 (m, 2H, H-5$_b$, H-2$_{b'}$), 3.87–3.93 (m, 8H, OCH$_a$$H_b$-linker, H-2$_a$, H-3$_b$, H-5$_{b'}$, H-3$_c$, H-5$_c$, H-2$_{c'}$, H-3$_{c'}$), 4.01–4.10 (3m, H, H-2$_b$, H-4$_c$, H-4$_{c'}$), 4.12 (t, 1H, J = 9.6 Hz, H-4$_{b'}$), 4.20–4.25 (m, 2H, H-1$_a$, H$_b$-6$_{b'}$), 4.31–4.35 (m, 2H, H-3$_{b'}$, CH$_2$Ph), 4.40 (m, 2H, CH_2Ph), 4.47–4.66 (m, 19H, CH_2Ph), 4.74 (d, 1H, J = 12.4 Hz, CH_2Ph), 4.84–4.94 (m, 5H, H-1$_{b'}$, CH_2Ph), 5.03 (d, 1H, J = 12.4 Hz, CH_2Ph), 5.15 (s, 1H, H-1$_c$), 5.27 (s, 1H, H-1$_b$), 5.43 (s, 1H, H-1$_{c'}$), 5.59 (s, 1H, CHPh), 7.06–7.50 (m, 75H, H$_{arom}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = [25.0, 26.2, 29.2, 29.4, 29.8, 29.9 (CH_2-linker)], 34.2 (CH_2CO$_2$CH$_3$), 51.5 (CH$_2$CO$_2$CH_3), 63.8 (C-5$_{b'}$), 66.3 (C-6$_a$), 68.9 (C-6$_{b'}$), 69.1 (C-6$_{c'}$), 69.2 (C-6$_c$), 69.5 (C-6$_b$), 70.0 (OCH_2-linker), [71.6, 71.8, 72.2, 73.4, 74.1, 74.7, 75.0, (CH_2Ph)], 72.4, (C-5$_c$, C-5$_{c'}$), 72.5 (C-5$_b$), 73.6 (C-3$_b$), 74.3 (C-2$_{c'}$), 74.6 (C-4$_{c'}$), 74.8 (C-4$_a$, C-4$_b$), 74.9 (C-2$_c$), 75.1 (C-5$_a$), 75.2 (C-2$_b$, C-4$_c$), 77.8 (C-2$_a$, C-2$_{b'}$), 79.4 (C-4$_{b'}$), [79.5, 79.6 (C-3$_c$, C-3$_{c'}$)], 79.8 (C-3$_{b'}$), 81.8 (C-3$_a$), 98.8 (C-1$_{b'}$,1$_{c'}$), 99.6 (C-1$_c$), 101.2 (C-1$_b$), 101.5 (C-1$_a$), 102.0 (CHPh), [126.3, 127.2, 127.3, 127.5, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 129.2, 137.8, 138.0, 138.2, 138.3, 138.4, 138.5, 138.6, 138.7, 138.9, 139.0 (C$_{arom}$)], 174.4 (C=O); m/z (FAB): found $[M+\mathrm{Na}]^+$ 2370.0888, $C_{145}H_{158}O_{28}$ calcd for $[M+\mathrm{Na}]^+$ 2370.0832.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranoside (25): This compound was synthesised according to the general procedure for the glycosidation of glycosyl fluorides. Activation of glycosyl donor **5** (60.1 mg, 114 μmol) with $AgClO_4$ (67.2 mg, 298 μmol) and $HfCp_2Cl_2$ (57.1 mg, 149 μmol) in the presence of glycosyl acceptor **23** (130 mg, 87.6 μmol) in Et$_2$O (20 mL) gave the tetramannoside **25** as a colourless oil (118 mg, 76.4 μmol, 67%). R_f = 0.38 (PE/Et$_2$O 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24–1.34 (8m, H, CH_2-linker), 1.50–1.56 (m, 2H, CH_2-linker), 1.59–1.66 (2m, H, CH_2-linker), 2.30 (t, 1H, J = 7.6 Hz, CH_2CO$_2$CH$_3$), 3.18–3.22 (m, 1H, H-5$_a$), 3.28–3.33 (m, 1H, OCH_aH$_b$-linker), 3.50 (d, 1H, J = 10.6 Hz, H$_a$-6$_c$), 3.62–3.73 (m, 9H, CH$_2$CO$_2$CH_3, H-3$_a$, H$_a$-6$_a$, 2H-6$_b$, H$_b$-6$_c$, H$_a$-6$_{b'}$), 3.74–3.78 (m, 3H, H-4$_b$, H-5$_{b'}$, H$_b$-6$_{b'}$), 3.80–3.85 (m, 3H, OCH$_a$$H_b$-linker, H$_b-6_a$, H-2$_c$), 3.87–3.95 (m, 5H, H-4$_a$, H-5$_b$, H-3$_c$, H-5$_c$, H-3$_{b'}$), 3.96–3.99 (m, 3H, H-2$_a$, H-3$_b$, H-2$_{b'}$), 4.02–4.07 (m, 2H, H-4$_c$, H-4$_{b'}$), 4.10 (s, 1H, H-2$_b$), 4.29 (s, 1H, H-1$_a$), 4.41 (d, 1H, J = 12.2 Hz, CH_2Ph), 4.44 (d, 1H, J = 12.2 Hz, CH_2Ph), 4.47–4.79 (m, 20H, CH_2Ph), 4.84–4.95 (m, 3H, CH_2Ph), 5.08 (d, 1H, J = 12.2 Hz, CH_2Ph), 5.14 (s, 1H, H-1$_{b'}$), 5.17 (s, 1H, H-1$_c$), 5.18 (s, 1H, H-1$_b$), 7.17–7.45 (m, 65H, H$_{arom}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = [25.0, 26.1, 29.1, 29.2, 29.8, 29.9 (CH_2-linker)], 34.1 (CH_2CO$_2$CH$_3$), 51.5 (CH$_2$CO$_2$CH_3), 66.2 (C-6$_a$), 69.2 (C-6$_c$, C-6$_{b'}$), 69.4 (C-6$_b$), 70.0, (OCH_2-linker), [71.1, 72.1, 72.2, 72.3, 72.5, 73.2, 73.3, 73.4, 74.7, 75.0, 75.1 (CH_2Ph)], 71.7 (C-5$_{b'}$), 72.4 (C-5$_c$), 72.7 (C-5$_b$), 74.5 (C-4$_a$), 74.7 (C-4$_b$), 74.8 (C-2$_c$, C-4$_c$, C-2$_{b'}$, C-4$_{b'}$), 75.1 (C-2$_b$), 75.3 (C-5$_a$), 78.3 (C-2$_a$), 79.1 (C-3$_{b'}$), 79.6 (C-3$_c$), 79.9 (C-3$_b$), 82.0 (C-3$_a$), 98.4 (C-1$_{b'}$), 99.5 (C-1$_c$), 101.2 (C-1$_b$), 101.7 (C-1$_a$), [127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 128.0, 128.2, 128.3, 128.4, 128.5, 128.9, 138.1, 138.3, 138.4, 138.5, 138.7, 138.8, 139.1 (C$_{arom}$)], 174.3 (C=O); m/z (FAB): found $[M+\mathrm{Na}]^+$ 2029.9477, $C_{125}H_{138}O_{23}$ calcd for $[M+\mathrm{Na}]^+$ 2029.9521.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside (26): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyl donor **13** (326 mg, 480 μmol) with NIS (124 mg, 554 μmol) in CH_2Cl_2/Et_2O (2.0 mL:2.0 mL) in the presence of glycosyl acceptor **6** (284 mg, 369 μmol) in CH_2Cl_2/Et_2O (4.0 mL:4.0 mL) gave the thio dimannoside **26** as a colourless oil (400 mg, 310 μmol, 84%). R_f = 0.54 (PE/Et$_2$O 1:1); ^{1}H NMR

(500 MHz, $CDCl_3$): $\delta = 1.05$ (s, 9H, C[CH_3]$_3$), 1.28 – 1.40 (m, 8H, CH_2-linker), 1.58 – 1.66 (m, 4H, CH_2-linker), 2.30 (t, 2H, $J = 7.6$ Hz, $CH_2CO_2CH_3$), 3.27 – 3.31 (m, 1H, H-5$_a$), 3.38 (dt, 1H, $J = 9.1$, 6.6 Hz, OCH_aH$_b$-linker), 3.67 (s, 3H, $CH_2CO_2CH_3$), 3.68 – 3.70 (m, 2H, 2H-6$_b$), 3.74 (s, 1H, H-2$_b$), 3.78 (dd, 1H, $J = 2.6$, 9.7 Hz, H-3$_a$), 3.87 – 3.97 (m, 7H, OCH$_a$$H_b$-linker, H-2$_a$, 2H-6$_a$, H-3$_b$, H-4$_b$, H-5$_b$), 4.04 (t, 1H, $J = 9.6$ Hz, C-4$_a$), 4.40 (s, 1H, H-1$_a$), 4.41 – 4.66 (m, 9H, CH_2Ph), 4.78 (d, 1H, $J =$ 12.2 Hz, CH_2Ph), 4.91 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 5.05 (d, 1H, $J =$ 12.2 Hz, CH_2Ph), 5.24 (s, 1H, H-1$_b$), 7.13 – 7.79 (m, 40H, H$_{arom}$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.4$ (C[CH_3]$_3$), [25.0, 26.2, 29.2, 29.3, 29.4, 29.8 (CH_2-linker)], 26.8 (C[CH_3]$_3$), 34.1 ($CH_2CO_2CH_3$), 51.5 ($CH_2CO_2CH_3$), 63.1 (C-6$_a$), 69.5 (OCH_2-linker, C-6$_b$), [72.5, 73.4, 74.0, 74.7 (CH_2Ph)], [72.6, 75.0, 78.0, 80.0 (C-2$_a$, C-3$_b$, C-4$_b$, C-5$_b$)], 75.2 (C-4$_a$), 75.9 (C-2$_b$), 76.8 (C-5$_a$), 80.7 (C-3$_a$), 100.1 (C-1$_b$), 101.7 (C-1$_a$), [127.0, 127.1, 127.3, 127.4, 127.5, 127.6, 127.7, 127.9, 128.0, 128.2, 128.3, 128.4, 129.5, 133.4, 134.0, 135.6, 136.0, 138.5, 138.6, 138.9, 139.3 (C$_{arom}$)], 174.3 (C=O); *m*/*z* (FAB): found [*M*+Na]$^+$ 1313.6343, $C_{80}H_{94}O_{13}Si$ calcd for [*M*+Na]$^+$ 1313.6356.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-D-mannopyranoside (27): This compound was synthesised according to the general procedure for the desilylation. Treatment of silylether **26** (795 mg, 629 μmol) with TBAF/AcOH (3%) (1.9 mL) gave the dimannoside **27** as a colourless oil (619 mg, 598 μmol, 95%). $R_f = 0.30$ (PE/Et_2O 1:2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.28 – 1.40$ (m, 8H, CH_2-linker), 1.58 – 1.67 (m, 4H, CH_2-linker), 2.11 – 2.15 (s, 1H, OH), 2.30 (t, 2H, $J = 7.6$ Hz, $CH_2CO_2CH_3$), 3.28 – 3.33 (m, 1H, H-5$_a$), 3.37 (dt, 1H, $J = 9.1$, 6.6 Hz, OCH_aH$_b$-linker), 3.65 – 3.68 (m, 5H, $CH_2CO_2CH_3$, 2H-6$_a$), 3.70 – 3.74 (m, 1H, H$_a$-6$_b$), 3.75 – 3.77 (m, 1H, H-2$_b$), 3.78 – 3.85 (m, 3H, H-3$_a$, H-4$_b$, H$_b$-6$_b$), 3.85 – 3.88 (m, 1H, OCH$_a$$H_b$-linker), 3.90 – 3.92 (m, 3H, H-2$_a$, H-3$_b$, H-5$_b$), 3.93 (t, 1H, $J = 9.6$ Hz, H-4$_a$), 4.40 – 4.67 (m, 9H, CH_2Ph), 4.42 (s, 1H, H-1$_a$), 4.78 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 4.90 (d, 1H, $J = 12.4$ Hz, CH_2Ph), 4.97 (d, 1H, $J = 12.4$ Hz, CH_2Ph), 5.27 (d, 1H, $J = 1.2$ Hz, H-1$_b$), 7.15 – 7.44 (m, 30H, H$_{arom}$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ [25.0, 26.1, 29.1, 29.2, 29.3, 29.7 (CH_2-linker)], 34.1 ($CH_2CO_2CH_3$), 51.5 ($CH_2CO_2CH_3$), 62.2 (C-6$_a$), 70.2 (OCH_2-linker, C-6$_b$), [72.4, 72.5, 73.3, 74.3, 74.7, 74.8 (CH_2Ph)], 72.6 (C-4$_b$), [75.0, 75.3 77.7, 79.9 (C-2$_a$, C-4$_a$, C-3$_b$, C-5$_b$)], 75.7 (C-2$_b$), 75.9 (C-5$_a$), 80.1 (C-3$_a$), 100.1 (C-1$_b$), 101.7 (C-1$_a$), [127.2, 127.5, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 128.5, 138.1, 138.3 138.4, 138.5, 138.7, 138.8 (C$_{arom}$)], 174.3 (C=O); *m*/*z* (FAB): found [*M*+Na]$^+$ 1075.5189. $C_{64}H_{76}O_{13}$ calcd for [*M*+Na]$^+$ 1075.5178.

8-Methoxycarbonyloctyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranoside (28): This compound was synthesised according to the general procedure for glycosyl sulfide and glycosyl selenide coupling. Activation of glycosyldonor **1** (201 mg, 197 μmol) with NIS (70.9 mg, 315 μmol) in CH_2Cl_2/Et_2O (1.6 mL, 1.6 mL) in the presence of glycosyl acceptor **27** (157 mg, 151 μmol) in CH_2Cl_2/Et_2O (2.2 mL:2.2 mL) gave the tetrasaccharide **28** as a colourles oil (189 mg, 96.6 μmol, 64%). $R_f = 0.30$ (PE/Et_2O 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.23 – 1.33$ (m, 8H, CH_2-linker), 1.53 – 1.63 (m, 4H, CH_2-linker), 2.28 (t, 2H, $J = 7.6$ Hz, $CH_2CO_2CH_3$), 3.30 – 3.34 (m, 1H, H-5$_a$), 3.37 (m, 1H, OCH_aH$_b$-linker), 3.67 – 3.71 (m, 7H, $CH_2CO_2CH_3$, H$_a$-6$_a$, H$_a$-6$_b$, 2H-6$_{c'}$), 3.77 – 3.85 (m, 8H, H-3$_a$, H-4$_a$, H$_b$-6$_a$, H-2$_b$, H-4$_b$, H$_b$-6$_b$, H$_a$-6$_{b'}$, H-5$_{c'}$), 3.87 – 3.95 (m, 8H, OCH$_a$$H_b$-linker, H-2$_a$, H-3$_b$, H-5$_b$, H-2$_{b'}$, H-5$_{b'}$, H-2$_{c'}$, H-3$_{c'}$), 4.05 (t, 1H, $J = 9.2$ Hz, H-4$_{c'}$), 4.15 (t, 1H, $J = 9.6$ Hz, H-4$_{b'}$), 4.24 (dd, H, $J = 4.5$, 10.0 Hz, H$_b$-6$_{b'}$), 4.32 (s, 1H, H-1$_a$), 4.35 (m, 1H, H-3$_{b'}$), 4.42 (d, 1H, $J = 11.5$ Hz, CH_2Ph), 4.46 – 4.67 (m, 16H, CH_2Ph), 4.71 (d, 1H, $J = 12.4$ Hz, CH_2Ph), 4.81 (d, 1H, $J = 12.4$ Hz, CH_2Ph), 4.89 – 5.01 (m, 3H, CH_2Ph), 4.97 (s, 1H, H-1$_{b'}$), 5.28 (s, 1H, H-1$_b$), 5.43 (s, 1H, H-1$_{c'}$), 5.59 (s, 1H, CHPh), 7.08 – 7.35 (m, 60H, H$_{arom}$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ [25.0, 26.2, 29.2, 29.4, 29.8, 29.9 (CH_2-linker)], 31.2 ($CH_2CO_2CH_3$), 51.5 ($CH_2CO_2CH_3$), 64.0 (C-5$_b$), 66.5 (C-6$_a$), 68.9 (C-6$_{b'}$), 69.2 (C-6$_b$), 69.5 (C-6$_{c'}$), 70.1 (OCH_2-linker), [71.7, 71.8, 72.4, 73.3, 74.1, 74.7, 74.8 (CH_2Ph)], 72.5 (C-4$_b$, C-5$_{c'}$), 73.6 (C-3$_{b'}$), 74.3 (C-2$_{b'}$), 74.6 (C-4$_{c'}$), 75.0, (C-5$_{b'}$), 75.3 (C-5$_a$), 75.6 (C-4$_a$), 75.8 (C-2$_b$), 77.4 (C-2$_a$), 77.9 (C-2$_{c'}$), 79.4 (C-4$_{b'}$), 79.7 (C-3$_{c'}$), 80.1 (C-3$_b$), 80.3 (C-3$_a$), 98.9 (C-1$_{c'}$), 99.0 (C-1$_{b'}$), 100.3 (C-1$_b$), 101.6 (C-1$_a$), 102.0 (CHPh), [126.3, 127.1, 127.3, 127.5, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 129.2, 137.8, 138.0, 138.1, 138.4, 138.6, 138.7, 138.8, 138.9 (C$_{arom}$)], 174.3 (C=O); *m*/*z* (FAB): found [*M*+2Na]$^{2+}$ 980.4382, $C_{118}H_{130}O_{23}$ calcd for ½[*M*+2Na] 980.4394.

8-Methoxycarbonyloctyl α-D-glucopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)]-β-D-mannopyranoside (29): This compound was synthesised according to the general procedure for the debenzylation. Treatment of the fully protected heptasaccharide **20** (152 mg, 48.0 μmol) with Pd(OH)$_2$/C (182 mg) in CH_2Cl_2/MeOH/H_2O (10 mL:10 mL:3.3 mL) under an atmosphere of hydrogen gave the heptasaccharide **29** as a colourless amorphous solid (53.9 mg, 40.3 μmol, 84%). ^{1}H NMR (600 MHz, D_2O): $\delta = 1.24 – 1.31$ (m, 8H, CH_2-linker), 1.48 – 1.55 (m, 4H, CH_2-linker), 2.32 (t, 2H, $J = 7.4$ Hz, $CH_2CO_2CH_3$), 3.33 (t, 1H, $J = 9.6$ Hz, H-4$_e$), 3.45 – 3.47 (m, 1H, H-5$_a$), 3.49 (dd, 1H, $J = 3.8$, 9.9 Hz, H-2$_e$), 3.55 – 3.84 (m, 33H, OCH_2-linker, $CH_2CO_2CH_3$, H-3$_a$, H-4$_a$, H$_a$-6$_a$, H-4$_b$, H-5$_b$, 2H-6$_b$, H-3$_c$, H-4$_c$, H-5$_c$, H$_a$-6$_c$, H-4$_d$, H-5$_d$, 2H-6$_d$, H-3$_e$, H-5$_e$, 2H-6$_e$, H-4$_{b'}$, H-5$_{b'}$, 2H-6$_{b'}$, H-3$_{c'}$, H-4$_{c'}$, H-5$_{c'}$, 2H-6$_{c'}$), 3.86 – 3.90 (m, 4H, H$_b$-6$_a$, H$_b$-6$_c$, H-3$_d$, H-3$_{b'}$), 3.94 (dd, 1H, $J = 3.1$, 9.7 Hz, H-3$_b$), 4.00 (s, 1H, H-2$_{c'}$), 4.02 (s, 1H, H-2$_b$), 4.04 – 4.06 (m, 2H, H-2$_a$, H-2$_c$), 4.07 (s, 1H, H-2$_{b'}$), 4.17 (s, 1H, H-2$_d$), 4.59 (s, 1H, H-1$_a$), 4.83 (s, 1H, H-1$_{b'}$), 4.97 (s, 1H, H-1$_d$), 5.08 (s, 1H, H-1$_c$), 5.20 (d, 1H, $J =$ 3.8 Hz, H-1$_e$), 5.23 (s, 1H, H-1$_c$), 5.28 (s, 1H, H-1$_b$); ^{13}C NMR (150 MHz, D_2O): $\delta =$ [24.3, 25.0, 28.2, 28.3, 28.6, 28.7 (CH_2-linker)], 33.7 ($CH_2CO_2CH_3$), 52.1 ($CH_2CO_2CH_3$), [60.7, 60.8, 60.9, 61.0 (C-6$_b$, C-6$_c$, C-6$_d$, C-6$_e$, C-6$_{b'}$, C-6$_{c'}$)], 65.7 (C-6$_a$), [66.0, 66.1 (C-4$_a$, C-4$_{b'}$, C-4$_d$)], [66.8, 66.9, 67.0 (C-4$_b$, C-4$_c$, C-4$_{c'}$)], 69.6 (C-2$_{b'}$), 69.7 (C-4$_e$), 69.8 (C-2$_d$), [70.0, 70.1, 70.4 (C-2$_a$, C-3$_b$, C-3$_c$, C-5$_e$, C-2$_{c'}$)], 70.2 (OCH_2-linker), 70.3 (C-3$_{c'}$), 71.8 (C-2$_e$), [72.4, 72.8, 72.9, 73.2, 73.3, 73.4 (C-5$_b$, C-5$_c$, C-5$_d$, C-3$_e$, C-5$_{b'}$, C-5$_{c'}$)], 74.2, (C-5$_a$), [78.2, 78.4 (C-3$_d$, C-3$_{b'}$)], 78.5 (C-2$_c$), 78.7 (C-2$_b$), 80.9 (C-3$_a$), 99.4 (C-1$_{b'}$), 99.8 (C-1$_a$), 100.4 (C-1$_e$), 100.6 (C-1$_b$, C-1$_c$), 102.1 (C-1$_d$), 102.2 (C-1$_{c'}$), 177.9 (C=O); *m*/*z* (FAB): found [*M*+Na]$^+$ 1345.4962, $C_{52}H_{90}O_{38}$ calcd for [*M*+Na]$^+$ 1345.5007.

8-Methoxycarbonyloctyl α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)]-β-D-mannopyranoside (30): This compound was synthesised according to the general procedure for the debenzylation. Treatment of the fully protected hexasaccharide **21** (150 mg, 53.9 μmol) with Pd(OH)$_2$/C (180 mg) in CH_2Cl_2/MeOH/H_2O (10 mL:10 mL:3.3 mL) under an atmosphere of hydrogen gave the hexasaccharide **30** as a colourless amorphous solid (61.5 mg, 52.8 μmol, 98%). ^{1}H NMR (600 MHz, D_2O): $\delta = 1.30 – 1.39$ (m, 8H, CH_2-linker), 1.57 – 1.62 (m, 4H, CH_2-linker), 2.30 (2t, H, $J = 7.4$ Hz, $CH_2CO_2CH_3$), 3.31 – 3.35 (m, 1H, H-5$_a$), 3.49 – 3.53 (m, 1H, OCH_aH$_b$-linker), 3.54 – 3.63 (m, 5H, H-3$_a$, H-4$_b$, H-4$_c$, H-4$_d$, H-4$_{c'}$), 3.64 (s, 3H, $CH_2CO_2CH_3$), 3.65 – 3.73 (m, 9H, H$_a$-6$_b$, H-5$_c$, H$_a$-6$_c$, H-5$_d$, 2H-6$_d$, H-5$_{b'}$, H$_a$-6$_{b'}$, H$_a$-6$_{c'}$), 3.74 – 3.83 (m, 7H, H-4$_a$, H$_a$-6$_a$, H-5$_b$, H-3$_c$, H-4$_{b'}$, H-5$_{c'}$, H$_b$-6$_{c'}$), 3.85 – 3.89 (m, 7H, OCH$_a$$H_b$-linker, H-3$_b$, H-3$_d$, H-3$_{b'}$, H$_b-6_{b'}$, H-3$_{c'}$), 3.91 – 3.96 (m, 2H, H$_b-6_a$, H$_b-6_b$), 3.97 (s, 2H, H-2$_d$, H-2$_{c'}$), 4.01 – 4.04 (m, 2H, H-2$_b$, H-2$_c$), 4.07 (d, 1H, $J = 2.7$ Hz, H-2$_a$), 4.09 (m, 1H, H-2$_{b'}$), 4.47 (s, 1H, H-1$_a$), 4.83 (s, 1H, H-1$_{b'}$), 4.98 (s, 1H, H-1$_d$), 5.08 (s, 1H, H-1$_{c'}$), 5.28 (s, 1H, H-1$_c$), 5.38 (s, 1H, H-1$_b$); ^{13}C NMR (150 MHz, D_2O): $\delta =$ [24.6, 25.7, 28.7, 28.9, 29.0, 29.3 (CH_2-linker)], 34.4 ($CH_2CO_2CH_3$), 50.6 ($CH_2CO_2CH_3$), [61.4, 61.5, 61.7, 61.8, 61.9 (C-6$_b$, C-6$_c$, C-6$_d$, C-6$_{b'}$, C-6$_{c'}$)], 65.9 (C-6$_a$), [66.1, 66.2 (C-4$_a$, C-4$_{b'}$)], [67.4, 67.5, 67.7 67.9 (C-4$_b$, C-4$_c$, C-4$_d$, C-4$_{c'}$)], 69.3 (OCH_2-linker), 69.9 (C-2$_{b'}$), 70.4 (C-2$_a$), [70.5, 70.6, 70.7, 71.0, 71.1, 73.2, 73.4, 73.5, 73.6 (C-3$_b$, C-5$_b$, C-3$_c$, C-5$_c$, C-2$_d$, C-3$_d$, C-5$_d$, C-5$_{b'}$, C-2$_{c'}$, C-3$_{c'}$, C-5$_{c'}$)], 75.5 (C-5$_a$), 78.7 (C-2$_c$), 78.9 (C-3$_{b'}$), 79.0 (C-2$_b$), 81.3 (C-3$_a$), 100.2 (C-1$_a$, C-1$_{b'}$), 100.6 (C-1$_b$), 101.0 (C-1$_c$), 102.3 (C-1$_{c'}$), 102.7 (C-1$_d$), 174.7 (C=O); *m*/*z* (FAB): found [*M*+Na]$^+$ 1183.4465. $C_{46}H_{80}O_{33}$ calcd for [*M*+Na]$^+$ 1183.4479.

8-Methoxycarbonyloctyl α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranoside (31): This compound was synthesised according to the general procedure for the debenzylation. Treatment of the fully protected pentasaccharide **24** (185 mg, 79.0 μmol) with Pd(OH)$_2$/C (222 mg) in CH_2Cl_2/MeOH/H_2O (12 mL:12 mL:4.0 mL) under an atmosphere of hydrogen gave the pentasaccharide **31** as a colourless amorphous solid (78.0 mg, 78.2 μmol, 99%). ^{1}H NMR (600 MHz, D_2O): $\delta = 1.28 – 1.40$ (m, 8H, CH_2-linker), 1.57 – 1.63 (m, 4H, CH_2-linker), 2.32 (t, 2H, $J = 7.4$ Hz, $CH_2CO_2CH_3$), 3.33 – 3.37 (m, 1H, H-5$_a$), 3.50 – 3.54 (m, 1H, OCH_aH$_b$-linker), 3.55 – 3.61 (m, 4H, H-3$_a$, H-4$_b$, H-4$_c$, H-4$_e$), 3.62 – 3.66 (s, 4H, $CH_2CO_2CH_3$, H$_a$-6$_b$), 3.67 – 3.76 (m, 6H, H$_a$-6$_{b'}$, H-5$_c$, 2H-6$_c$, H-5$_{b'}$, H$_a$-6$_{c'}$), 3.77 – 3.83 (m, 6H, H-4$_a$, H$_a$-6$_a$, H-5$_b$, H-4$_{b'}$, H-3$_{c'}$, H-5$_{c'}$), 3.84 – 3.89 (m, 6H, OCH$_a$$H_b$-linker, H-3$_b$, H-3$_c$, H-3$_{b'}$, H$_b-6_{b'}$, H$_b-6_{c'}$), 3.93 – 3.97 (m, 2H, H$_b-6_a$, H$_b-6_b$), 3.98 (s, 2H, H-2$_c$, H-2$_{c'}$), 4.03 (1s, H, H-2$_b$), 4.07 (s, 1H, H-2$_a$), 4.11 (s, 1H, H-2$_{b'}$), 4.49 (s, 1H, H-1$_a$), 4.89 (s, 1H, H-1$_{b'}$), 5.00 (s, 1H, H-1$_c$), 5.10 (s, 1H, H-1$_{c'}$), 5.48 (s, 1H, H-1$_b$); ^{13}C NMR (150 MHz, D_2O): $\delta =$ [24.6,

0947-6539/00/0608-1426 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 8

25.6, 28.7, 28.9, 29.0, 29.3 (CH_2-linker)], 34.4 ($CH_2CO_2CH_3$), 50.6 ($CH_2CO_2CH_3$), [61.4, 61.5, 61.8 (C-6_b, C-6_c, C-$6_{b'}$, C-$6_{c'}$)], 65.9 (C-6_a), [66.0, 66.2 (C-3_c, C-$4_{b'}$)], [67.3, 67.4, 67.9 (C-4_b, C-4_c, C-$4_{c'}$)], 69.3 (OCH_2-linker), 69.9 (C-$2_{b'}$), 70.4 (C-2_c), 70.5 (C-2_a), 70.6 (C-3_b), 70.7 (C-$2_{c'}$), [71.0, 73.2, 73.4, 73.6 (C-4_a, C-5_b, C-5_c, C-$5_{b'}$, C-$5_{c'}$)], 71.1 (C-$3_{c'}$), 75.4 (C-5_a), 78.7 (C-2_b), 78.9 (C-$3_{b'}$), 81.3 (C-3_a), 100.2 (C-$1_{b'}$), 100.3 (C-1_a), 100.8 (C-1_b), 102.3 (C-$1_{c'}$), 102.7 (C-1_c), 174.7 (C=O); *m/z* (FAB): found $[M+Na]^+$ 1021.3988, $C_{40}H_{70}O_{28}$ calcd for $[M+Na]^+$ 1021.3951.

8-Methoxycarbonyloctyl α-D-mannopyranosyl-(1→2)α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-β-D-mannopyranoside (32): This compound was synthesised according to the general procedure for the debenzylation. Treatment of the fully protected tetrasaccharide **25** (106 mg, 52.8 μmol) with $Pd(OH)_2$/C (127 mg) in CH_2Cl_2/MeOH/H_2O (7.0 mL:7.0 mL:2.3 mL) under an atmosphere of hydrogen gave the tetrasaccharide **32** as a colourless amorphous solid (43.2 mg, 51.7 μmol, 98%). ^{1}H NMR (600 MHz, D_2O): $\delta = 1.30-1.39$ (m, 8H, CH_2-linker), 1.56–1.63 (m, 4H, CH_2-linker), 2.30 (t, 2H, $J = 7.4$ Hz, $CH_2CO_2CH_3$), 3.31–3.35 (m, 1H, H-5_a), 3.49–3.53 (m, 1H, OCH_aH_b-linker), 3.55–3.58 (m, 3H, H-3_a, H-4_b, H-4_c), 3.63–3.80 (m, 14H, $CH_2CO_2CH_3$, H$_a$-6_a, H-5_b, H$_a$-6_b, H-5_c, 2H-6_c, H-$3_{b'}$, H-$4_{b'}$, H-$5_{b'}$, 2H-$6_{b'}$), 3.81–3.88 (m, 5H, OCH_aH_b-linker, H-4_a, H-3_b, H-3_c, H-$2_{b'}$), 3.90–3.93 (m, 2H, H$_b$-6_a, H$_b$-6_b), 3.97 (s, 1H, H-2_c), 4.03 (s, 1H, H-2_b), 4.06 (d, 1H, $J = 2.8$ Hz, H-2_a), 4.47 (s, 1H, H-1_a), 4.83 (s, 1H, H-$1_{b'}$), 4.99 (s, 1H, H-1_c), 5.37 (s, 1H, H-1_b); ^{13}C NMR (150 MHz, D_2O): $\delta = [24.6, 25.6, 28.7, 28.8, 28.9, 29.3$ (CH_2-linker)], 34.4 ($CH_2CO_2CH_3$), 50.7 ($CH_2CO_2CH_3$), [61.5, 61.7, 61.8 (C-6_b, C-6_c, C-$6_{b'}$)], 65.7 (C-4_a), 66.1 (C-6_a), [67.2, 67.3, 67.9 (C-4_b, C-4_c, C-$4_{b'}$)], 69.3 (OCH_2-linker), [70.4, 70.5, 70.6, 71.0, 71.2 (C-2_a, C-2_c, C-3_b, C-3_c, C-$2_{b'}$, C-$3_{b'}$)], [72.9, 73.6 (C-5_b, C-5_c, C-$5_{b'}$)], 75.4 (C-5_a), 78.7 (C-2_b), 81.4 (C-3_a), 100.0 (C-$1_{b'}$), 100.2 (C-1_a), 100.8 (C-1_b), 102.8 (C-1_c), 175.0 (C=O); *m/z* (FAB): found $[M+Na]^+$ 859.3452, $C_{34}H_{60}O_{23}$ calcd for $[M+Na]^+$ 859.3429.

8-Methoxycarbonyloctyl α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranoside (33): This compound was synthesised according to the general procedure for the debenzylation. Treatment of the fully protected tetrasaccharide **28** (104 mg, 54.1 μmol) with $Pd(OH)_2$/C (124 mg) in CH_2Cl_2/MeOH/H_2O (7.0 mL:7.0 mL:2.3 mL) under an atmosphere of hydrogen gave the tetrasaccharide **33** as a colourless amorphous solid (43.5 mg, 51.9 μmol, 96%). ^{1}H NMR (600 MHz, D_2O): $\delta = 1.30-1.40$ (m, 8H, CH_2-linker), 1.57–1.63 (m, 4H, CH_2-linker), 2.30 (t, 2H, $J = 7.4$ Hz, $CH_2CO_2CH_3$), 3.33–3.37 (m, 1H, H-5_a), 3.51–3.54 (m, 1H, OCH_aH_b-linker), 3.56–3.64 (m, 3H, H-3_a, H-4_b, H-4_c), 3.65 (s, 3H, $CH_2CO_2CH_3$), 3.67–3.75 (m, 4H, H$_a$-6_b, H-$5_{b'}$, H$_a$-$6_{b'}$, H$_a$-$6_{c'}$), 3.77–3.90 (m, 11H, OCH_aH_b-linker, H-4_a, H$_a$-6_a, H-3_b, H-5_b, H$_b$-6_b, H-$3_{b'}$, H-$4_{b'}$, H$_b$-$6_{b'}$, H-$3_{c'}$, H-$5_{c'}$, H$_b$-$6_{c'}$), 3.93 (dd, 1H, $J = 5.2$, 11.1 Hz, H$_b$-6_a), 3.97 (s, 1H, H-2_b), 3.98 (s, 1H, H-$2_{c'}$), 4.08–4.11 (m, 2H, H-2_a, H-$2_{b'}$), 4.49 (s, 1H, H-1_a), 4.83 (s, 1H, H-$1_{b'}$), 5.07 (s, 1H, H-1_b), 5.08 (s, 1H, H-$1_{c'}$); ^{13}C NMR (150 MHz, D_2O): $\delta = [24.6, 25.6, 28.7, 28.8, 28.9, 29.3$ (CH_2-linker)], 34.4 ($CH_2CO_2CH_3$), 50.6 ($CH_2CO_2CH_3$), [61.4, 61.5, 61.7 (C-6_b, C-$6_{b'}$, C-$6_{c'}$)], 65.9 (C-6_a), [66.0, 66.2 (C-4_a, C-$4_{b'}$)], [67.4, 67.5 (C-4_b, C-$4_{c'}$)], 69.3 (OCH_2-linker), 69.9 (C-$2_{b'}$), 70.5 (C-2_a), 70.6 (C-$2_{c'}$), 70.7 (C-2_b), [71.0, 71.1, 73.1, 73.8, 73.5 (C-3_b, C-5_b, C-$5_{b'}$, C-$3_{c'}$, C-$5_{c'}$)], 75.4 (C-5_a), 78.9 (C-$3_{b'}$), 81.4 (C-3_a), 100.1 (C-$1_{b'}$), 100.2 (C-1_a), 102.3 (C-$1_{c'}$), 102.5 (C-1_b), 174.7 (C=O); *m/z* (FAB): found $[M+Na]^+$ 859.3420, $C_{34}H_{60}O_{23}$ calcd for $[M+Na]^+$ 859.3423.

8-[N^1-Ethylen-1,2-diamino]-carbonyloctyl α-D-glucopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)]-β-D-mannopyranoside (34): This compound was synthesised according to the general procedure for the amidation of methyl esters with ethylenediamine. The fully deprotected heptasaccharide **29** (19.3 mg, 14.6 μmol) was reacted in dry ethylenediamine (1 mL) to give the amine **34** as a light brown amorphous solid (18.9 mg, 14.0 μmol, 96%). ^{1}H NMR (600 MHz, D_2O): $\delta = 1.20-1.28$ (m, 8H, CH_2-linker), 1.48–1.55 (m, 4H, CH_2-linker), 2.20 (t, 2H, $J = 7.4$ Hz, CH_2CONH), 3.04 (t, 2H, $J = 6.1$ Hz, CH_2NH_2), 3.41 (t, 2H, $J = 6.1$ Hz, $CONHCH_2$), 3.33 (t, 1H, $J = 9.6$ Hz, H-4_c), 3.45–3.50 (m, 2H, H-5_a, H-2_e), 3.55–3.84 (m, 30H, OCH_2-linker, H-3_a, H-4_a, H$_a$-6_a, H-4_b, H-5_b, 2H-6_b, H-3_c, H-4_c, H-5_c, H$_a$-6_c, H-4_d, H-5_d, 2H-6_d, H-3_e, H-5_e, 2H-6_e, H-$4_{b'}$, H-$5_{b'}$, 2H-$6_{b'}$, H-$3_{c'}$, H-$4_{c'}$, H-$5_{c'}$, 2H-$6_{c'}$), 3.85–3.90 (m, 4H, H$_b$-6_a, H$_b$-6_c, H-3_d, H-$3_{b'}$), 3.93 (dd, 1H, $J = 2.8$, 9.7 Hz, H-3_b), 4.00 (s, 1H, H-$2_{c'}$), 4.01 (s, 1H, H-2_b), 4.03–4.05 (m, 2H, H-2_a, H-2_c), 4.07 (s, 1H, H-$2_{b'}$), 4.16 (s, 1H, H-2_d), 4.59 (s, 1H, H-1_a), 4.82 (s, 1H, H-$1_{b'}$), 4.97 (s, 1H, H-1_d), 5.08 (s, 1H, H-$1_{c'}$), 5.18 (d, 1H, $J = 3.7$ Hz, H-1_e), 5.23 (s, 1H, H-1_c), 5.28 (s, 1H, H-1_b); ^{13}C NMR (150 MHz, D_2O): $\delta = [25.0, 25.1, 28.1, 28.3, 28.6$, ($CH_2$-linker)], 35.7 ($CH_2NH_2$), 37.2 ($CH_2CONH$), 39.2 ($CONHCH_2$), [60.7, 60.8, 60.9, 61.0 (C-6_b, C-6_c, C-6_d, C-6_e, C-$6_{b'}$, C-$6_{c'}$)], 65.7 (C-6_a), [65.9, 66.1 (C-4_a, C-$4_{b'}$, C-4_d)], [(66.8, 66.9, 67.0 (C-4_b, C-4_c, C-$4_{c'}$)], 69.5 (C-$2_{b'}$), 69.7 (C-4_e), 69.8 (C-2_d), [70.0, 70.1, 70.3, 70.4 (C-2_a, C-3_b, C-3_c, C-5_e, C-$2_{c'}$, C-$3_{c'}$)], 70.2 (OCH_2-linker), 71.8 (C-2_e), [72.3, 72.7, 72.8, 73.2, 73.3, 73.4 (C-5_b, C-5_c, C-5_d, C-3_e, C-$5_{b'}$, C-$5_{c'}$)], 74.2, (C-5_a), [78.2, 78.4 (C-3_d, C-$3_{b'}$)], 78.5 (C-2_c), 78.7 (C-2_b), 80.8 (C-3_a), 99.4 (C-$1_{b'}$), 99.7 (C-1_a), 100.4 (C-1_e), 100.6 (C-1_b, C-1_c), 102.1 (C-1_d), 102.2 (C-$1_{c'}$), 178.3 (C=O); *m/z* (FAB): found $[M+H]^+$ 1351.5652, $C_{53}H_{94}N_2O_{37}$ calcd for $[M+H]^+$ 1351.5614.

8-[N^1-Ethylen-1,2-diamino]-carbonyloctyl α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)]-β-D-mannopyranoside (35): This compound was synthesised according to the general procedure for the amidation of methyl esters with ethylenediamine. The fully deprotected hexasaccharide **30** (18.8 mg, 16.2 μmol) was reacted in dry ethylenediamine (1 mL) to give the amine **35** as a light brown amorphous solid (17.2 mg, 14.4 μmol, 89%). ^{1}H NMR (600 MHz, D_2O): $\delta = 1.21-1.29$ (m, 8H, CH_2-linker), 1.50–1.56 (m, 4H, CH_2-linker), 2.20 (t, 2H, $J = 6.4$ Hz, CH_2CONH), 2.97 (t, 2H, $J = 6.1$ Hz, CH_2NH_2), 3.37 (t, 2H, $J = 6.1$ Hz, $CONHCH_2$), 3.45–3.48 (m, 1H, H-5_a), 3.55–3.65 (m, 6H, OCH_aH_b-linker, H-3_a, H-4_b, H-4_c, H-4_d, H-$4_{c'}$), 3.67–3.74 (m, 12H, H-5_b, H$_a$-6_b, H-5_c, H$_a$-6_c, H-5_d, H$_a$-6_d, H-$4_{b'}$, H-$5_{b'}$, H$_a$-$6_{b'}$, H-$5_{c'}$, 2H-$6_{c'}$), 3.75–3.79 (m, 5H, H-4_a, H$_a$-6_a, H-3_c, H-3_d, H$_b$-6_d), 3.80–3.83 (m, 3H, H-3_b, H-$3_{b'}$, H-$3_{c'}$), 3.83–3.90 (m, 4H, OCH_aH_b-linker, H$_b$-6_a, H$_b$-6_c, H$_b$-$6_{b'}$), 3.93 (dd, 1H, $J = 3.3$, 9.8 Hz, H$_b$-6_b), 3.99–4.02 (m, 3H, H-2_b, H-2_d, H-$2_{c'}$), 4.03–4.05 (m, 2H, H-2_c, H-$2_{b'}$), 4.07 (s, 1H, H-2_a), 4.59 (s, 1H, H-1_a), 4.83 (s, 1H, H-$1_{b'}$), 4.97 (s, 1H, H-1_d), 5.07 (s, 1H, H-$1_{c'}$), 5.23 (s, 1H, H-1_c), 5.37 (s, 1H, H-1_b); ^{13}C NMR (150 MHz, D_2O): $\delta = [25.0, 25.1, 28.1, 28.3, 28.6$ (CH_2-linker)], 35.7 (CH_2NH_2), 37.8 (CH_2CONH), 39.3 ($CONHCH_2$), [60.9, 61.0, 61.1 (C-6_b, C-6_c, C-6_d, C-$6_{b'}$, C-$6_{c'}$)], 65.9 (C-6_a), [66.1, 66.2 (C-4_a, C-$4_{b'}$)], [66.7, 66.8, 66.9, 67.0 (C-4_b, C-4_c, C-4_d, C-$4_{c'}$)], 69.5 (C-2_a), [69.9, 70.0, 70.1, 70.3, 70.4 (C-3_b, C-3_c, C-2_d, C-3_d, C-$2_{b'}$, C-$2_{c'}$, C-$3_{c'}$)], 70.2 (OCH_2-linker), [72.8, 72.1, 73.2, 73.3, 73.4 (C-5_b, C-5_c, C-5_d, C-$5_{b'}$, C-$5_{c'}$)], 74.2 (C-5_a), 78.2 (C-$3_{b'}$), 78.5 (C-2_c), 78.7 (C-2_b), 80.9 (C-3_a), 99.4 (C-$1_{b'}$), 99.8 (C-1_a), 100.6 (C-1_b, C-1_c), 102.2 (C-1_d), 102.3 (C-$1_{c'}$), 178.2 (C=O); *m/z* (FAB): found $[M+H]^+$ 1189.5082, $C_{47}H_{84}N_2O_{32}$ calcd for $[M+H]^+$ 1189.5085.

8-[N^1-Ethylen-1,2-diamino]-carbonyloctyl α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranoside (36): This compound was synthesised according to the general procedure for the amidation of methyl esters with ethylenediamine. The fully deprotected pentasaccharide **31** (14.7 mg, 14.7 μmol) was reacted in dry ethylenediamine (1 mL) to give the amine **36** as a light brown amorphous solid (15.0 mg, 14.6 μmol, 99%). ^{1}H NMR (600 MHz, D_2O): $\delta = 1.20-1.28$ (m, 8H, CH_2-linker), 1.50–1.57 (m, 4H, CH_2-linker), 2.10 (t, 2H, $J = 7.4$ Hz, CH_2CONH), 2.84 (t, 2H, $J = 6.2$ Hz, CH_2NH_2), 3.31 (t, 2H, $J = 6.1$ Hz, $CONHCH_2$), 3.45–3.49 (m, 1H, H-5_a), 3.58–3.90 (m, 25H, OCH_2-linker, H-3_a, H-4_a, 2H-6_a, H-3_b, H-4_b, H-5_b, H$_a$-6_b, H-3_c, H-4_c, H-5_c, 2H-6_c, H-$3_{b'}$, H-$4_{b'}$, H-$5_{b'}$, 2H-$6_{b'}$, H-$3_{c'}$, H-$4_{c'}$, H-$5_{c'}$, 2H-$6_{c'}$), 3.92 (dd, 1H, $J = 3.1$, 9.6 Hz, H$_b$-6_b), 3.99–4.01 (m, 2H, H-2_c, H-$2_{c'}$), 4.03–4.08 (m, 3H, H-2_a, H-2_b, H-$2_{b'}$), 4.58 (s, 1H, H-1_a), 4.82 (s, 1H, H-$1_{b'}$), 4.98 (s, 1H, H-1_c), 5.07 (s, 1H, H-$1_{c'}$), 5.28 (s, 1H, H-1_b); ^{13}C NMR (150 MHz, D_2O): $\delta = [25.0, 25.1, 28.1, 28.3, 28.7$ (CH_2-linker)], 35.7 (CH_2CONH), 38.8 ($CONHCH_2$), 39.4 (CH_2NH_2), [60.9, 61.0, 61.8 (C-6_b, C-$6_{b'}$, C-6_c, C-$6_{c'}$)], 65.7 (C-6_a), [66.0, 66.1 (C-3_c, C-$4_{b'}$,)], [66.7, 66.8, 67.0 (C-4_b, C-4_c, C-$4_{c'}$)], 69.5 (OCH_2-linker), [69.9, 70.0, 70.1, 70.2, 70.3, 70.4, 72.8, 73.2, 73.3 (C-2_a, C-4_a, C-3_b, C-5_b, C-$2_{b'}$, C-$5_{b'}$, C-2_c, C-5_c, C-$2_{c'}$, C-$3_{c'}$, C-$5_{c'}$)], 74.2 (C-5_a), 78.2 (C-$3_{b'}$), 78.4 (C-2_b), 80.9 (C-3_a), 99.4 (C-$1_{b'}$), 99.8 (C-1_a), 100.7 (C-1_b), 102.2 (C-$1_{c'}$, C-1_c), 178.0 (C=O); *m/z* (FAB): found $[M+H]^+$ 1027.4581, $C_{41}H_{74}N_2O_{27}$ calcd for $[M+H]^+$ 1027.4557.

8-[N^1-Ethylen-1,2-diamino]-carbonyloctyl α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-β-D-mannopyranoside (37): This compound was synthesised according to the general procedure for the amidation of methyl esters with ethylenediamine. The fully deprotected tetrasaccharide **32** (25.7 mg, 30.7 μmol) was reacted in dry ethylenediamine (1 mL) to give the amine **37** as a light brown amorphous solid (26.0 mg, 29.5 μmol, 96%). ^{1}H NMR (600 MHz, D_2O): $\delta = 1.21-1.32$ (m, 8H, CH_2-linker), 1.50–1.57 (m, 4H, CH_2-linker), 2.19 (t, 2H, $J = 7.3$ Hz, CH_2CONH), 2.86 (t, 2H, $J = 6.1$ Hz, CH_2NH_2), 3.30 (t, 2H, $J = 6.1$ Hz, $CONHCH_2$), 3.45–3.49 (m, 1H, H-5_a), 3.56–3.60 (m, 3H, H-4_b, H-4_c, H-$4_{b'}$), 3.62–3.65 (m, 2H, H-3_a, H-$5_{b'}$), 3.67–3.73 (7m, H, H-4_a, H$_a$-

6_a, H-5_b, H_a-6_b, H-5_c, H_a-6_c, H_a-$6_{b'}$), 3.74 – 3.80 (m, 3H, H-3_c, H_b-6_c, H-$3_{b'}$), 3.81 – 3.84 (m, 2H, H-3_b, H_b-$6_{b'}$), 3.88 (dd, 1H, $J = 5.1$, 11.1 Hz, H_b-6_a), 3.92 – 3.95 (m, 2H, H_b-6_b, H-$2_{b'}$), 4.00 (s, 1H, H-2_c), 4.04 (s, 1H, H-2_b), 4.05 (d, 1H, $J = 3.0$ Hz, H-2_a), 4.59 (s, 1H, H-1_a), 4.84 (s, 1H, H-$1_{b'}$), 4.98 (s, 1H, H-1_c), 5.27 (s, 1H, H-1_b); ^{13}C NMR (150 MHz, D_2O): δ = [25.0, 25.2, 28.1, 28.2, 28.3, 28.6 (CH_2-linker)], 35.7 (CH_2NH_2), 39.1 (CONHCH_2), 39.5 (CH_2CONH), [60.9, 61.0 (C-6_b, C-6_c, C-$6_{b'}$)], 65.6 (C-6_a), 65.9 (C-4_a), [66.7, 67.0 (C-4_b, C-4_c, C-$4_{b'}$)], [69.9, 70.0, 70.1, 70.3, 70.6 (C-2_a, C-3_b, C-2_c, C-3_c, C-$2_{b'}$, C-$3_{b'}$)], 70.1 (OCH_2-linker), 72.7 (C-$5_{b'}$), [73.2, 73.3 (C-5_b, C-5_c)], 74.1 (C-5_a), 78.4 (C-2_b), 80.9 (C-3_a), 99.4 (C-$1_{b'}$), 99.8 (C-1_a), 100.7 (C-1_b), 102.3 (C-1_c), 178.0 (C=O); *m/z* (FAB): found $[M+Na]^+$ 887.3890, $C_{35}H_{64}N_2O_{22}$ calcd for $[M+Na]^+$ 887.3849.

8-[*N*^{1}-Ethylen-1,2-diamino]-carbonyloctyl α-D-mannopyranosyl-(1 $\rightarrow$3)-[α-D-mannopyranosyl-(1 $\rightarrow$3)-α-D-mannopyranosyl-(1 $\rightarrow$6)]-2,4-di-*O*-benzyl-β-D-mannopyranoside (38): This compound was synthesised according to the general procedure for the amidation of methyl esters with ethylenediamine. The fully deprotected tetrasaccharide **33** (21.2 mg, 25.4 μmol) was reacted in dry ethylenediamine (1 mL) to give the amine **38** as a light brown amorphous solid (21.3 mg, 22.9 μmol, 97%). ^{1}H NMR (600 MHz, D_2O): δ = 1.20 – 1.30 (m, 8H, CH_2-linker), 1.49 – 1.57 (m, 4H, CH_2-linker), 2.19 (t, 2H, $J = 7.3$ Hz, CH_2CONH), 2.86 (t, 2H, $J = 6.0$ Hz, CH_2NH$_2$), 3.31 (t, 2H, $J = 6.0$ Hz, CONHCH_2), 3.46 – 3.49 (m, 1H, H-5_a), 3.56 – 3.62 (m, 3H, OC$H_a$$H_b$-linker, H-$4_b$, H-$4_{c'}$), 3.65 – 3.79 (m, 10H, H-3_a, H-4_a, H_a-6_a, H-5_b, H_a-6_b, H-$4_{b'}$, H-$5_{b'}$, H_a-$6_{b'}$, H-$5_{c'}$, H_a-$6_{c'}$), 3.80 – 3.89 (m, 8H, OC$H_a$$H_b$-linker, H_b-6_a, H-3_b, H_b-6_b, H-$3_{b'}$, H_b-$6_{b'}$, H-$3_{c'}$, H_b-$6_{c'}$), 4.00 (s, 2H, H-2_b, H-$2_{c'}$), 4.07 (s, 2H, H-2_a, H-$2_{b'}$), 4.60 (s, 1H, H-1_a), 4.83 (s, 1H, H-$1_{b'}$), 5.03 (s, 1H, H-$1_{c'}$), 5.07 (s, 1H, H-1_b); ^{13}C NMR (150 MHz, D_2O): δ = [25.0, 25.2, 28.1, 28.2, 28.6 (CH_2-linker)], 35.7 (CH_2CONH), 39.1 (CONHCH_2), 39.5 (CH_2NH_2), [60.9, 61.0 (C-6_b, C-$6_{b'}$, C-$6_{c'}$)], 65.7 (C-6_a), 65.9 (C-4_a), 66.1 (C-$4_{b'}$), 66.8 (C-4_b, C-$4_{c'}$), 69.5 (C-2_a), [70.1, 70.3, 70.4, (C-2_b, C-3_b, C-$2_{b'}$, C-$2_{c'}$, C-$3_{c'}$)], 70.1 (OCH_2-linker), [72.8, 73.3 (C-5_b, C-$5_{b'}$, C-$5_{c'}$)], 74.2 (C-5_a), 78.2 (C-$3_{b'}$), 80.7 (C-3_a), 99.4 (C-$1_{b'}$), 99.8 (C-1_a), 102.2 (C-1_b), 102.3 (C-$1_{c'}$), 178.0 (C=O); *m/z* (FAB): found $[M+H]^+$ 865.4037, $C_{35}H_{64}N_2O_{22}$ calcd for $[M+H]^+$ 865.4029.

***N*^{1}-Cholesteryloxycarbonyl-1-amino-2-methylsulfonyl ethane (41)**: Alcohol **40** (2.00 g, 4.21 mmol) was dissolved in CH_2Cl_2 (12 mL) and cooled to 0 °C. After addition of NEt_3 (1.76 mL, 12.6 mmol), $MeSO_2Cl$ (846 μL, 10.5 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 60 min. It was quenched with ice water, extracted with Et_2O and the combined organic phases were washed with NH_4Cl, H_2O and brine. It was dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The crude product was used without further purification (2.31 g, quant.). $R_f = 0.50$ (Et_2O); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.67 (s, 3H, H-18′), 0.85 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.87 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.91 (d, 3H, $J = 6.5$ Hz, H-21′), 0.93 – 1.60 (m, 24H), 1.79 – 2.03 (m, 5H), 2.25 – 2.37 (m, 2H, H-4′), 3.03 (s, 3H, CH_3SO_3), 3.50 – 3.52 (m, 2H, H-2), 4.28 – 4.30 (m, 2H, H-1), 4.46 – 4.53 (m, 1H, H-3′), 5.01 (s, 1H, Chol-OC(O)NH), 5.35 – 5.37 (m, 1H, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.8 (C-18′), 18.7 (C-21′), 19.3 (C-19′), 21.0, [22.5, 22.8 (C-26′, C-27′)], 23.8, 24.3, 28.0, 28.1, 28.2, 31.8, 31.9, 35.7, 36.2, 36.5 (C_q), 36.9, 37.5 (CH_3SO_3), 38.4, 39.5, 39.7, 40.3 (C-2), 42.3 (C_q), 50.0, 56.1, 56.6, 68.7 (C-1), 74.9 (C-3′), 122.6 (C-6′), 139.6 (C-5′), 156.0 (C=O); *m/z* (ESI): found $[M+Na]^+$ 574.3564, $C_{31}H_{53}NO_5S$ calcd for $[M+Na]^+$ 574.3542.

***N*^{1}-Cholesteryloxycarbonyl-3-aza-1-aminoheptan-7-ol (42)**: Mesylate **41** (2.00 g, 3.62 mmol) was dissolved in DMF (20 mL) and NaI (543 mg, 3.62 mmol) and butanolamine (3.34 mL, 36.2 mmol) were added. The mixture was heated to 80 °C and stirred for 18 h. The reaction mixture was cooled to room temperature, diluted with Et_2O and washed with H_2O. The layers were separated and the aqueous layer extracted with Et_2O. The combined organic phases were washed with NH_4Cl, H_2O and brine, dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was purified by column chromatography to give **42** as a yellow amorphous solid (1.49 g, 2.75 mmol, 76%). $R_f = 0.16$ (CH_2Cl_2/MeOH/NH_3 92:7:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.66 (s, 3H, H-18′), 0.84 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.85 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.90 (d, 3H, $J = 5.9$ Hz, H-21′), 0.92 – 1.67 (m, 29H), 1.78 – 2.01 (m, 5H), 2.24 – 2.36 (m, 2H, H-4′), 2.64 (t, 2H, $J = 5.8$ Hz, H-4), 2.73 (t, 2H, $J = 5.5$ Hz, H-2), 3.24 – 3.30 (m, 2H, H-1), 3.57 (t, 2H, $J = 5.3$ Hz, H-7), 4.43 – 4.51 (m, 1H, H-3′), 5.19 (s, 1H, Chol-OC(O)NH), 5.35 – 5.38 (m, 1H, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.8 (C-18′), 18.7 (C-21′), 19.3 (C-19′), 21.0, [22.5, 22.8 (C-26′, C-27′)], 23.8, 24.3, 28.0, 28.1, 28.2, 28.3, 31.8, 31.9, 32.1, 35.8, 36.2, 36.5 (C_q), 37.0, 38.5, 39.5, 39.7, 40.4 (C-1), 42.3 (C_q), 48.9 (C-2), 49.3 (C-4), 50.0, 56.1, 56.7, 62.5 (C-7), 74.4 (C-3′), 122.4 (C-6′), 139.8 (C-5′), 156.4 (C=O); *m/z* (ESI): found $[M+H]^+$ 545.4655, $C_{34}H_{60}N_2O_3$ calcd for $[M+H]^+$ 545.4682.

***N*^{1}-Cholesteryloxycarbonyl-3-aza-*N*^{3}-trimethylsilylethoxycarbonyl-1-aminoheptan-7-ol (43)**: NEt_3 (242 μL, 1.74 mmol) and TeocSuc (321 mg, 1.24 mmol) was added at room temperature to a solution of amine **42** (743 mg, 1.36 mmol) in dioxane (10 mL)s and the resulting reaction mixture was stirred for 18 h. The reaction mixture was diluted with CH_2Cl_2, H_2O was added and the organic phase was washed with NH_4Cl, H_2O and brine, dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was purified by column chromatography to give **43** (817 mg, 1.27 mmol, 93%). $R_f = 0.28$ (Et_2O); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.04 (s, 9H, Si[CH_3]$_3$), 0.67 (s, 3H, H-18′), 0.85 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.86 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.90 (d, 3H, $J = 6.5$ Hz, H-21′), 0.91 – 1.68 (m, 28H), 1.78 – 2.01 (m, 6H), 2.22 – 2.35 (m, 2H, H-4′), 3.23 – 3.40 (m, 6H), 3.65 (t, 2H, $J = 6.0$ Hz), 4.16 (t, 2H, $J = 8.7$ Hz), 4.44 – 4.51 (m, 1H, H-3′), 5.17 (s, 1H, Chol-OC(O)NH), 5.37 (m, 1H, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$): δ = −1.5 (Si[CH_3]$_3$), 11.8 (C-18′), 17.9, 18.7 (C-21′), 19.3 (C-19′), 21.0 [22.5, 22.8 (C-26′, C-27′)], 23.8, 24.2, 24.8, 28.0, 28.1, 28.2, 29.6, 31.8, 31.9, 35.7, 36.1, 36.5 (C_q), 36.9, 38.5, 39.5, 39.7, 39.9, 42.3 (C_q), 46.6, 47.5, 50.0, 56.1, 56.6, 62.3, 63.7, 74.4 (C-3′), 122.4 (C-6′), 139.8 (C-5′), 156.3 (C=O), 156.4 (C=O); *m/z* (ESI): found $[M+Na]^+$ 711.5109, $C_{40}H_{72}N_2O_5Si$ calcd for $[M+Na]^+$ 711.5108.

***N*^{1}-Cholesteryloxycarbonyl-3-aza-*N*^{3}-trimethylsilylethoxycarbonyl-1-amino-7-methylsulfonyl heptane (44)**: Alcohol **43** (500 mg, 775 μmol) was dissolved in CH_2Cl_2 (3 mL) and cooled to 0 °C. After addition of NEt_3 (324 μL, 2.33 mmol), $MeSO_2Cl$ (156 μL, 1.94 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. It was quenched with ice water, extracted with Et_2O and the combined organic phases were washed with NH_4Cl, H_2O and brine. It was dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The crude product was used without further purification (558 mg, quant.). R_f = 0.53 (Et_2O); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.04 (s, 9H, Si[CH_3]$_3$), 0.67 (s, 3H, H-18′), 0.85 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.86 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.91 (d, 3H, $J = 6.5$ Hz, H-21′), 0.92 – 2.02 (m, 34H), 2.13 – 2.17 (m, 1H), 2.23 – 2.36 (m, 2H, H-4′), 3.01 (s, 3H, CH_3SO_3), 3.24 – 3.38 (m, 6H), 4.16 (t, 2H, $J = 8.7$ Hz), 4.22 – 4.27 (m, 2H), 4.43 – 4.51 (m, 1H, H-3′), 5.10 (s, 1H, Chol-OC(O)NH), 5.36 (m, 1H, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$): δ = −1.5 (Si[CH_3]$_3$), 11.8 (C-18′), 17.9, 18.7 (C-21′), 19.3 (C-19′), 21.0, [22.5, 22.8 (C-26′, C-27′)], 23.8, 24.2, 24.8, 26.3, 26.4, 28.0, 28.1, 28.2, 31.8, 31.9, 35.8, 36.2, 36.5 (C_q), 36.9, 37.3, 38.5, 39.5, 39.7, 42.3 (C_q), 46.7, 50.0, 56.1, 56.6, 63.8, 74.4 (C-3′), 122.5 (C-6′), 139.7 (C-5′), 156.2 (C=O), 156.4 (C=O); *m/z* (ESI): found $[M+Na]^+$ 789.4913, $C_{41}H_{74}N_2O_7SSi$ calcd for $[M+Na]^+$ 789.4884.

***N*^{1}-Cholesteryloxycarbonyl-3-aza-*N*^{3}-trimethylsilylethoxycarbonyl-1-amino-7-azido-heptane (45)**: Mesylate **44** (470 mg, 651 μmol) was dissolved in DMF (6 mL) and NaI (98 mg, 651 μmol) and NaN_3 (128 mg, 1.95 mmol) were added. It was slowly heated to 80 °C and stirred for 4 h. The reaction mixture was concentrated under reduced pressure and the residue was diluted with Et_2O, washed with $NaHCO_3$, the aqueous layer reextracted with Et_2O and the combined organic phases washed with $NaHCO_3$, H_2O and brine. The organic phase was dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by column chromatography gave **45** (380 mg, 560 mmol, 86%). $R_f = 0.30$ (PE/Et_2O 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.03 (s, 9H, Si[CH_3]$_3$), 0.66 (s, 3H, H-18′), 0.84 (d, 3H, J = 2.7 Hz, H-26′/H-27′), 0.85 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.88 (d, 3H, J = 6.5 Hz, H-21′), 0.90 – 1.63 (m, 30H), 1.79 – 2.01 (m, 5H), 2.22 – 2.36 (m, 2H, H-4′), 3.22 – 3.37 (m, 8H), 4.14 – 4.18 (m, 2H), 4.43 – 4.50 (m, 1H, H-3′), 5.12 (s, 1H, Chol-OC(O)NH), 5.36 (m, 1H, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$): = −1.6 (Si[CH_3]$_3$), 11.8 (C-18′), 17.9, 18.7 (C-21′), 19.3 (C-19′), 21.0, [22.5, 22.8 (C-26′, C-27′)], 23.8, 24.2, 25.6, 26.0, 28.0, 28.1, 28.2, 31.8, 31.9, 35.8, 36.1, 36.5 (C_q), 36.9, 38.5, 39.5, 39.7, 42.3 (C_q), 46.5, 47.1, 50.0, 51.1, 56.1, 56.6, 63.8, 74.4 (C-3′), 122.5 (C-6′), 139.8 (C-5′), 156.3 (C=O), 156.4 (C=O); *m/z* (ESI): found $[M - N_2+3H]^+$ 688.5492, $C_{40}H_{74}N_5O_4Si$ calcd for $[M - N_2+3H]$ 688.5448.

***N*^{1}-Cholesteryloxycarbonyl-3-aza-*N*^{3}-trimethylsilylethoxycarbonyl-1,7-diaminoheptane (46)**: A mixture of azide **45** (420 mg, 613 mmol) and PPh_3 (194 mg, 735 mmol) in THF (1.4 mL) was stirred at room temperature for 2 h after which time an additional PPh_3 (485 mg, 1.84 mmol) was added. After 12 h conc. NH_3 (0.4 mL) was added and the resulting mixture allowed stirring for 2 h. Extraction of the reaction mixture with CH_2Cl_2, washing

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with H_2O, concentration under reduced pressure and purification by column chromatography (CH_2Cl_2/MeOH/NH_3 92:7:1) gave amine **46** (400 mg, 582 mmol, 95%). $R_f = 0.41$ (CH_2Cl_2/MeOH/NH_3 92:7:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.04$ (s, 9H, Si[CH_3]$_3$), 0.67 (s, 3H, H-18′), 0.85 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.86 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.90 (d, 3H, $J = 6.5$ Hz, H-21′), 0.92–1.60 (m, 32H), 1.79–2.02 (m, 5H), 2.22–2.36 (m, 2H, H-4′), 3.20–3.38 (m, 6H), 4.14–4.18 (m, 2H), 4.44–4.52 (m, 1H, H-3′), 5.17 (s, 1H, Chol-OC(O)N*H*), 5.36 (m, 1H, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -1.5$ (Si[CH_3]$_3$), 11.8 (C-18′), 17.9, 18.7 (C-21′), 19.3 (C-19′), 21.0, [22.5, 22.8 (C-26′, C-27′)], 23.8, 24.2, 25.8, 28.0, 28.1, 28.2, 30.7, 31.8 31.9, 35.7, 36.1, 36.5 (C_q), 36.9, 38.5, 39.5, 39.7, 39.9, 41.8, 42.3 (C_q), 46.6, 47.5, 50.0, 51.1, 56.1, 56.6, 63.8, 74.4 (C-3′), 122.4 (C-6′), 139.8 (C-5′), 156.3 (C=O), 156.4 (C=O); *m/z* (ESI): found $[M+Na]^+$ 688.5416, $C_{40}H_{73}N_3O_4Si$ calcd for $[M+Na]^+$ 688.5448.

N^1-Cholesteryloxycarbonyl-3-aza-N^3-trimethylsilylethoxycarbonyl-N^7-2-ethoxy-3,4-dioxo-1-cyclobuten-1-yl-1,7-diaminoheptane (47): A solution of amine **46** (100 mg, 145 μmol) and diethylsquarate (27.2 mg, 160 μmol) in CH_2Cl_2/MeOH (0.3 mL, 0.3 mL) was stirred at room temperature for 12 h, concentrated under reduced pressure and purified by column chromatography to give **47** as a colourless amorphous solid (103 mg, 126 μmol, 87%). $R_f = 0.23$ (Et_2O); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.04$ (s, 9H, Si[CH_3]$_3$), 0.67 (s, 3H, H-18′), 0.86 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.87 (d, 3H, $J = 2.7$ Hz, H-26′/H-27′), 0.91 (d, 3H, $J = 6.5$ Hz, H-21′), 0.92–1.64 (m, 33H), 1.79–1.86 (m, 3H), 1.94–2.01 (m, 2H), 2.23–2.37 (m, 2H, H-4′), 3.23–3.51 (m, 7H), 4.14–4.19 (m, 2H), 4.43–4.48 (m, 1H, H-3′), 4.73–4.77 (m, 2H), 4.79 (s, 1H, N*H*-Teoc), 5.01 (s, 1H, Chol-OC(O)N*H*), 5.30 (m, 1H, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -1.5$ (Si[CH_3]$_3$), 11.8 (C-18′), 17.9, 18.7 (C-21′), 19.3 (C-19′), 21.0, [22.5, 22.8 (C-26′, C-27′)], 23.8, 24.3, 28.0, 28.1, 28.2, 29.6, 31.8 31.9, 35.8, 36.2, 36.5 (C_q), 36.9, 38.5, 39.5, 39.7, 39.9, 42.3 (C_q), 46.6, 47.5, 50.0, 56.7, 63.9, 69.6, 70.5, 74.4 (C-3′), 122.4 (C-6′), 139.8 (C-5′), 156.3 (C=O), 156.4 (C=O); *m/z* (ESI): found $[M+Na]^+$ 834.5416, $C_{46}H_{77}N_3O_7Si$ calcd for $[M+Na]^+$ 834.5429.

N^1-Cholesteryloxycarbonyl-3-aza-N^3-trimethylsilylethoxycarbonyl-N^7-2-(α-D-glucopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)]-β-D-mannopyranosyl-8-[N^1-ethylen-1,2-diamino]-carbonyloctyl)-3,4-dioxo-1-cyclobuten-1-yl-1,7-diaminoheptane (48): High-mannose amine **34** (17.0 mg, 12.6 μmol) and cholesterol squarate **47** (10.2 mg, 12.6 μmol) were stirred in CH_2Cl_2/MeOH/H_2O (0.4 mL, 0.4 mL, 0.2 mL) for 6 d. Deprotection gave the neoglycolipid **48** as a colourless amorphous solid (17.9 mg, 9.1 μmol,72%); ^{1}H NMR (600 MHz, MeOD, selected data): $\delta = 0.72$ (s, H-18′), 0.87 (d, $J = 2.0$ Hz, H-26′/H-27′), 0.88 (d, $J = 2.0$ Hz, H-26′/H-27′), 0.94 (d, $J = 6.5$ Hz, H-21′), 2.22 (t, $J = 7.5$ Hz, CH_2CONH), 4.22 (s, H-2), 4.47 (s, H-1), 4.81 (s, H-1), 4.96 (s, H-1), 5.08 (s, H-1), 5.14 (d, $J = 3.8$ Hz, H-1$_e$), 5.29 (s, H-1), 5.39 (H-1); ^{13}C NMR (150 MHz, MeOD, selected data according to HMQC): $\delta = 10.9$ (C-18′), 17.7 (C-21′), 21.5 (C-26′, C-27′), 35.4 (*C*H$_2$CONH), 69.6 (C-2), 100.1 (C-1), 100.2 (C-1), 100.3 (C-1), 100.6 (C-1), 100.9 (C-1), 102.3 (C-1), 102.7 (C-1); $C_{60}H_{60}O_{10}Se$ calcd for $[M+Na]^+$ 1043.3249; *m/z* (ESI): found $[M+Na]^+$ 1995.37, $C_{91}H_{153}N_5O_{41}$ calcd for $[M+Na]^+$ 1994.99.

N^1-Cholesteryloxycarbonyl-3-aza-N^3-trimethylsilylethoxycarbonyl-N^7-2-(α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)]-β-D-mannopyranosyl-8-[N^1-ethylen-1,2-diamino]-carbonyloctyl)-3,4-dioxo-1-cyclobuten-1-yl-1,7-diaminoheptane (49): High-mannose amine **35** (15.4 mg, 13.0 μmol) and cholesterol squarate **47** (10.5 mg, 13.0 μmol) were stirred in CH_2Cl_2/MeOH/H_2O (0.6 mL, 1.0 mL, 0.2 mL) for 7 d. Deprotection gave the neoglycolipid **49** as a colourless amorphous solid (16.0 mg, 8.8 μmol, 68%); ^{1}H NMR (600 MHz, MeOD, selected data): $\delta = 0.72$ (s, H-18′), 0.87 (s, H-26′/H-27′), 0.88 (s, H-26′/H-27′), 0.94 (d, $J = 6.0$ Hz, H-21′), 3.96 (s, H-2), 4.01 (s, H-2), 4.08 (s, H-2), 4.41 (s, H-3′), 4.48 (s, H-1), 4.83 (s, H-1), 4.97 (s, H-1), 5.08 (s, H-1), 5.28 (s, H-1), 5.39 (s, H-1, H-6′); ^{13}C NMR (125 MHz, MeOD, selected data according to HMQC): $\delta = 10.2$ (C-18′), 17.1 (C-21′), 20.9 (C-26′, C-27′), 37.6 (C-4′), 69.6 (C-2), 69.9 (C-2), 74.3 (C-3′), 78.3 (C-2), 99.5 (C-1), 99.6 (C-1), 99.9 (C-1), 100.3 (C-1), 101.8 (C-1), 103.1 (C-1), 121.6 (C-6′); *m/z* (ESI): found $[M+Na]^+$ 1833.57, $C_{85}H_{143}N_5O_{36}$ calcd for $[M+Na]^+$ 1832.94.

N^1-Cholesteryloxycarbonyl-3-aza-N^3-trimethylsilylethoxycarbonyl-N^7-2-(α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-8-[N^1-ethylen-1,2-diamino]-carbonyloctyl)-3,4-dioxo-1-cyclobuten-1-yl-1,7-diaminoheptane (50): High-mannose amine **36** (11.7 mg, 11.4 μmol) and cholesterol squarate **47** (9.3 mg, 11.4 μmol) were stirred in CH_2Cl_2/MeOH/H_2O (0.6 mL, 0.4 mL, 0.2 mL) for 5 d. Deprotection gave the neoglycolipid **50** as a colourless amorphous solid (9.8 mg, 5.9 μmol,52%); ^{1}H NMR (600 MHz, MeOD, selected data): $\delta = 0.70$ (s, H-18′), 0.85 (s, H-26′/H-27′), 0.86 (s, H-26′/H-27′), 0.92 (d, $J = 6.4$ Hz, H-21′), 4.51 (s, H-1), 4.74 (s, H-1), 4.83 (s, H-1), 4.99 (s, H-1), 5.11 (s, H-1), 5.37 (s, H-6′); ^{13}C NMR (125 MHz, MeOD): $\delta = 18.0$ (C-21′), 21.8 (C-26′, C-27′), 100.0 (C-1), 100.2 (C-1), 102.0 (C-1), 102.3 (C-1), 125.0 (C-6′); *m/z* (ESI): found $[M+Na]^+$ 1671.47, $C_{79}H_{133}N_5O_{31}$ calcd for $[M+Na]^+$ 1670.89.

N^1-Cholesteryloxycarbonyl-3-aza-N^3-trimethylsilylethoxycarbonyl-N^7-2-(α-D-mannopyranosyl-(1→2)α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-β-D-mannopyranosyl-8-[N^1-ethylen-1,2-diamino]-carbonyloctyl)-3,4-dioxo-1-cyclobuten-1-yl-1,7-diaminoheptane (51): High-mannose amine **37** (12.7 mg, 14.7 μmol) and cholesterol squarate **47** (11.9 mg, 14.7 μmol) were stirred in CH_2Cl_2/MeOH/H_2O (1.2 mL, 1.2 mL, 0.2 mL) for 7 d. Deprotection gave the neoglycolipid **51** as a colourless amorphous solid (9.3 mg, 6.2 μmol, 42%); ^{1}H NMR (600 MHz, MeOD, selected data): $\delta = 0.72$ (s, H-18′), 0.87 (s, H-26′/H-27′), 0.88 (s, H-26′/H-27′), 0.94 (d, $J = 6.0$ Hz, H-21′), 2.22 (t, $J = 7.5$ Hz, CH_2CONH), 2.33 (m, H-4′), 4.47 (d, $J = 6.2$ Hz, H-1$_a$), 4.82 (s, H-1), 4.98 (s, H-1), 5.36–5.38 (m, H-1, H-6′); ^{13}C NMR (125 MHz, MeOD, selected data according to HMQC): $\delta = 10.8$ (C-18′), 17.7 (C-21′), 21.6 (C-26′, C-27′), 35.4 (CH_2CONH), 38.1 (C-4′), 100.0 (C-1), 100.3 (C-1$_a$), 100.8 (C-1), 102.7 (C-1), 122.2 (C-6′); *m/z* (ESI): found $[M+Na]^+$ 1509.37, $C_{75}H_{123}N_5O_{26}$ calcd for $[M+Na]^+$ 1508.84.

N^1-Cholesteryloxycarbonyl-3-aza-N^3-trimethylsilylethoxycarbonyl-N^7-2-(α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→3)-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-8-[N^1-ethylen-1,2-diamino]-carbonyloctyl)-3,4-dioxo-1-cyclobuten-1-yl-1,7-diaminoheptane (52): High-mannose amine **38** (15.2 mg, 17.6 μmol) and cholesterol squarate **47** (14.3 mg, 17.6 μmol) were stirred in CH_2Cl_2/MeOH/H_2O (1.2 mL, 1.2 mL, 0.2 mL) for 7 d. Deprotection gave the neoglycolipid **52** as a colourless amorphous solid (14.1 mg, 9.3 μmol, 53%); ^{1}H NMR (600 MHz, MeOD, selected data) $\delta = 0.72$ (s, H-18′), 0.87 (s, H-26′/H-27′), 0.88 (s, H-26′/H-27′), 0.94 (d, $J = 6.5$ Hz, H-21′), 4.50 (s, H-1), 4.81 (s, H-1), 5.08 (s, 2H-1), 5.38 (s, H-6′); ^{13}C NMR (125 MHz, MeOD, selected data according to HMQC): $\delta = 10.8$ (C-18′), 17.8 (C-21′), 21.6 (C-26′, C-27′), 100.1 (C-1), 100.3 (C-1), 102.3 (C-1), 102.7 (C-1), 122.2 (C-6′); *m/z* (ESI): found $[M+Na]^+$ 1509.45, $C_{75}H_{123}N_5O_{26}$ calcd for $[M+Na]^+$ 1508.84.

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