Synthesis of Glycans from the Glycodelins: Two Undeca-, Two Deca-, Three Nona-, an Octa- and a Heptasaccharide

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Abstract: The concise synthesis of nine diantennary oligosaccharides by chemical and chemoenzymatic protocols is presented. The compounds display Lewis X, Lewis Y, sialyl Lewis X and T-antigen epitopes supported on a 3,6-branched trimannose core. A chemical approach was adopted for the synthesis of the unsymmetrically decorated structures and those that could not be accessed by enzymatic decoration of a core heptasaccharide.

Keywords: carbohydrates · glycosylations · sialyl Lewis Y · oligosaccharides · protecting groups

Introduction

Glycodelin-A (GdA), also known as placental protein 14 or progesterone-associated endometrial protein,[1] and glycodelin-S (GdS) are human glycoproteins isolated from amniotic fluid and seminal plasma, respectively.[2] While both display immunosuppressive activities, potentially serving to induce regiospecific immune protection to the foetus (GdA) or to sperm (GdS) from the female immune response,[3] GdA acts as a potent contraceptive, inhibiting human sperm binding to the outer covering of the egg (zona pelucida) under assay conditions (hemizona assay).[4] By contrast, GdS stimulates human sperm-zona pelucida binding in the same assay. It has been found that the two glycoproteins share essentially the same protein core but differ completely in their glycan structures,[5] furthering the belief that the decorating oligosaccharides may be responsible for the differences in the biological activities of the two glycoconjugates.

Before the structures of the GdS/GdA glycans were elucidated, evidence indicated that the same carbohydrate sequences that blocked selectin-mediated adhesions also inhibited human sperm–egg binding.[6] The demonstration that GdA carried a known selectin-binding sequence (GalNAcβ1 $\rightarrow$4[Fucα1 $\rightarrow$3]GlcNAc) was entirely consistent with this overlap in specificity.[5a, 7] However, both genetic and immunological analyses indicate that the human sperm lectin(s) that mediates binding to the zona pellucida is not a selectin.[5b] As part of a collaborative investigation into the glycodelins the following array of compounds has been assembled in order to probe the nature of their biological responses (Figure 1).

Compounds **1–6**, **9–11** derive from the GdS glycans and the remainder derive from GdA glycans (**7**) or are known selectin binders having been prepared previously[8] (**8**, **12–14**). Although all the compounds isolated from GdS/GdA are diantennary, the monovalent ligands were prepared as it was of interest to see if the trimannose core served a presentational role and acted as a means of polyvalent expression or merely served as a "spacer", potentially simplifying future investigations.

Central to the success of any "library" generation is the requirement that the chemistry employed must be general and readily transferable to a variety of substrates. In this regard chemical synthesis of oligosaccharides is notoriously unreliable for large structures where small, seemingly remote changes in substrate can have detrimental effects on coupling yields.[9] Hence, where possible, enzymes were employed, limiting only in their commercial availability and in the difficulty in forming the unsymmetrical structures.

Results and Discussion

The synthesis of diantennary *N*-glycans has received much attention with both chemical and enzymatic approaches providing successful outcomes.[10] However, compounds with the asymmetry or high degree of fucosylation present in the GdS glycans have not been prepared previously and there was

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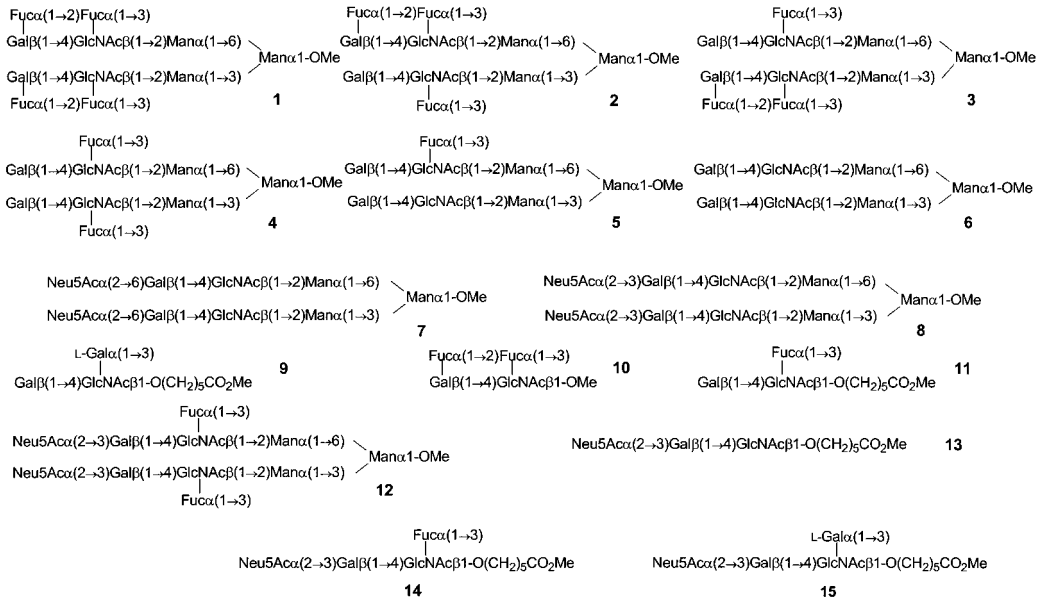


Figure 1. Glycans of GdS and GdA and related selectin binders.

evidence to suggest this would introduce problems (vide supra). An added criteria was the desire to synthesise all the compounds with a single strategy, thus reducing the amount of optimisation required. The following retrosynthetic routes presented themselves (Figure 2).

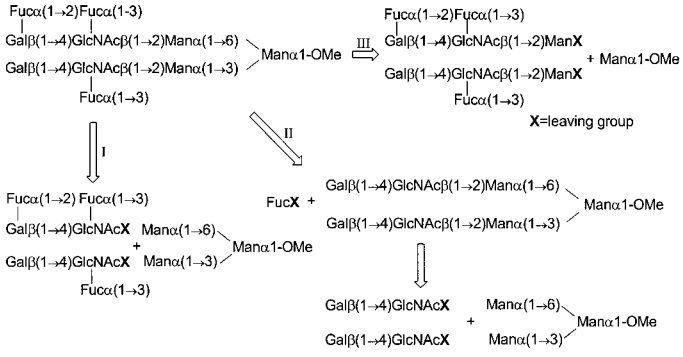
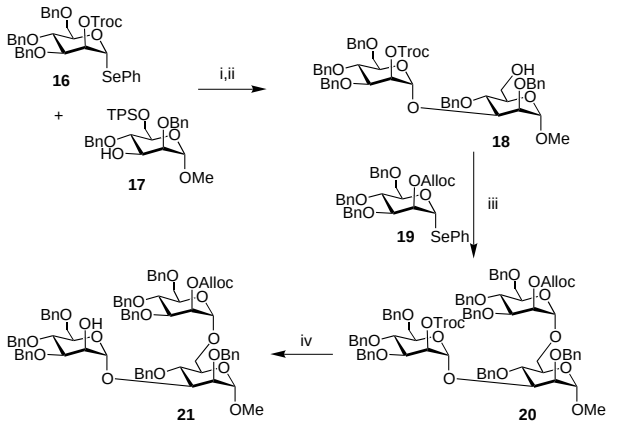


Figure 2. Retrosyntheses of the diantennary glycans.

The most convergent route I relied on block couplings of the individual epitopes Lewis X/Y onto a trimannose core, a route precedented by Lönn's synthesis of a derivative of nonasaccharide **4**.[11] However, Sinaÿ et al. later attempted this route without success prompting the suggestion that the coupling was impossible on grounds of "steric mismatch".[12] This forced them to adopt a linear strategy culminating in a block coupling akin to route III, a strategy which did not seem very amenable to the synthesis of a whole class of compounds. The alternative convergent strategy II, which involved coupling of lactosamine onto the trimannose core followed by late stage fucosylation, was discarded because of fears about purification of the final coupling product.

Attracted by the convergent efficiency of route I and the hope that the problems encountered in this route were specific to nonasaccharide **4** (which was to be prepared enzymatically) this route was evaluated.

Trimannose cores: The trimannose core for the unsymmetrical compounds **2**, **3** and **5** required that the terminal mannosyl-C2 hydroxyls be distinguished by two different protecting groups that could be selectively removed in the presence of any protecting groups on the Lewis X/Y precursors. In addition the chosen protecting groups would have to be directing (anchimerically) to encourage α-selectivity on coupling to the central mannoside **17**. To this end the orthogonal set of carbonates allyloxycarbonyl (Alloc) and 2′,2′,2′-trichloroethyloxycarbonyl (Troc) were selected (Scheme 1).

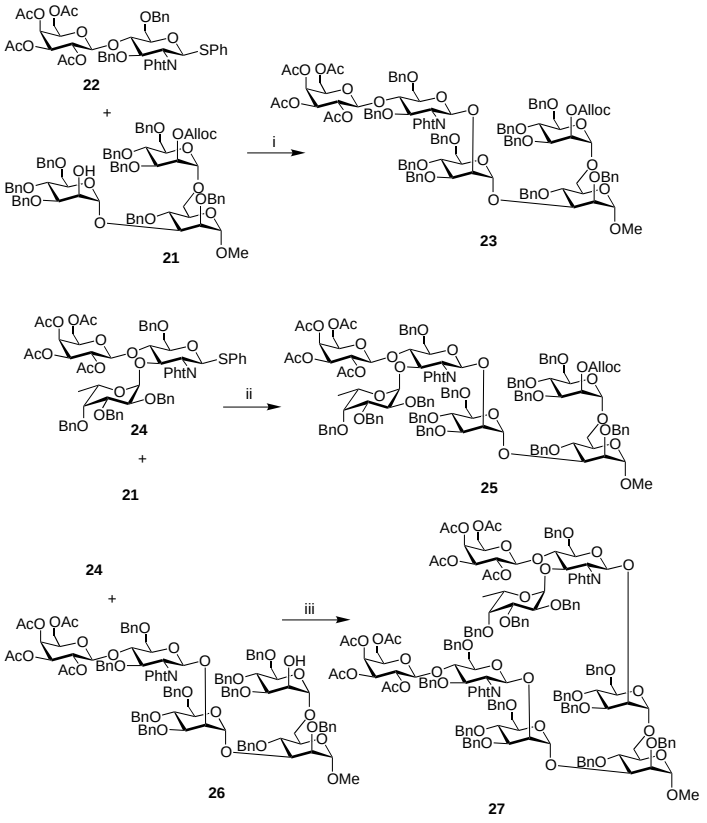


Scheme 1. i) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 2:1, 86%; ii) HF/pyridine, THF, 97%; iii) NIS, TfOH (cat.), 4 Å MS, CH_2Cl_2/Et_2O 2:1, 92%; iv) Zn, AcOH, 80%.

Troc-directed glycosylation of selenide **16** onto mannoside **17** and subsequent removal of the C6 *tert*-butyldiphenylsilyl (TBDPS) group with HF/pyridine afforded solely the α-1,3-linked disaccharide **18** in 83% overall yield. Alloc-directed glycosylation of selenide **19** onto acceptor **18** furnished the α-1,6-linkage in 92% yield, thus providing a trisaccharide **20** with two orthogonally protected alcohols, allowing extension from either branch. The glycosylation had to be performed in

this order because the Troc group was not as efficient a directing group as the Alloc group, owing to the electron deficient trichloroethoxy substituent, and in coupling to the more nucleophilic primary hydroxyl group significant amounts of β-linked product was detected. The Troc group was removed first, purely out of prejudice towards acidic conditions, affording alcohol **21** in 80% yield.[13]

Coupling studies: Initial coupling studies on the trimannose core centered on the simplest unsymmetrical structure octasaccharide **5**. Glycosylation of trimannose **21** with lactosamine donor (prepared by coupling of 2,3,4,6-tetra-*O*-acetyl-α-D-galactosyl bromide with phenyl 2-deoxy-3,6-di-*O*-benzyl-2-phthalimido-1-thio-β-D-glucopyranoside)[14] under AgOTf/NIS[15] activation afforded pentasaccharide **23** in 86% yield but, unusually, as a mixture of anomers, estimated as 15:1 β:α from the ^{1}H spectra (Scheme 2).



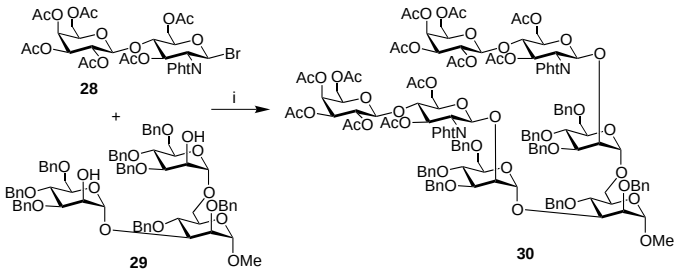
Scheme 2. i) NIS, AgOTf, 4 Å MS, CH_2Cl_2/toluene 2:1, $-50\,^\circ C \rightarrow -30\,^\circ C$, 86%; ii) a) Br_2, CH_2Cl_2, $-40\,^\circ C$ then cyclohexene; b) AgOTf, 2,6-lutidine, CH_2Cl_2/toluene 3:1, $-70\,^\circ C \rightarrow -40\,^\circ C$, 35%; iii) as for ii) 30%.

The α-linked product could only be generated if the anchimeric assistance of the phthalimido-carbonyl was overridden. Such failures of neighbouring group participation have been noted in the past and usually arise from steric impedance preventing attack on the dioxonium ion species.[16] Attack therefore occurs on the incipient oxonium ion (triflate ion pair)[17] from the sterically preferred face.

Hence, when the more sterically demanding Lewis X donor **24**[18] was reacted under the same conditions with acceptor **21**, the steric repulsion was great enough to prevent coupling occurring before elimination or hydrolysis took place. Converting the sulfide to the bromide (this allowed controlled activation at lower temperatures thus prolonging the lifetime of the active glycosylation species) permitted some coupling product **27** to form, albeit in poor yield (Scheme 2). A similar Lewis X donor is known to react readily with phenyl 3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside[12] implying that the steric clash is brought about by conformational restrictions within the trimannoside and the donor. Unfortunately this problem still exists in pentasaccharide **26** with a comparable yield of 30% obtained on coupling with **24**. Interestingly double coupling of the Lewis X bromide onto trimannose **29** does afford a 10% yield of a protected form of nonasaccharide **4**; this demonstrates that the coupling is not impossible, but certainly is very sensitive to the conditions employed (perhaps explaining the discrepancy between Lönn and Sinaÿ's results). Such a capricious reaction was not going to make for a reliable strategy, it was therefore abandoned in favour of route II.

Route II: In order to improve the selectivity of the lactosaminylation it was necessary to reduce the reactivity of the lactosamine donor, thereby destabilising the incipient oxonium ion in relation to the dioxonium ion. This would require that the benzyl groups on the glucosamine be replaced with ester functions, a protecting group pattern that precluded a successful coupling with a galactosyl donor.[19] Recourse was therefore made to the acetylated lactosamine donor **28** first prepared by Lönngren.[10b]

AgOTf-mediated double coupling of lactosamine donor **28** with trimannosyl diol **29**[20] afforded heptasaccharide **30** (Scheme 3) in an acceptable 64% yield as seemingly a single compound (deprotection revealed that the compound in fact existed as a 30:1 β:α mixture of anomers).



Scheme 3. i) AgOTf, 2,6-lutidine, 4Å MS, CH_2Cl_2/toluene 5:1, $-50\,^\circ C$, 64%.

Fortunately the lactosamine coupling proved to be very tolerant providing access to all the heptasaccharide cores (Table 1) of which **35**, the precursor to decasaccharide **2**, is given as an example (Scheme 4). Bromide **31** (prepared by derivatisation of lactosamine **28**)[21] was coupled with unsymmetrical trimannoside **21**. Buffered AgOTf was employed as the activator furnishing pentasaccharide **32** in 71% yield. Alloc removal with $[Pd(PPh_3)_4]$/dimedone[22] (88% yield) and further glycosylation with lactosamine **34** under identical conditions gave heptasaccharide **35** in 76% yield (again

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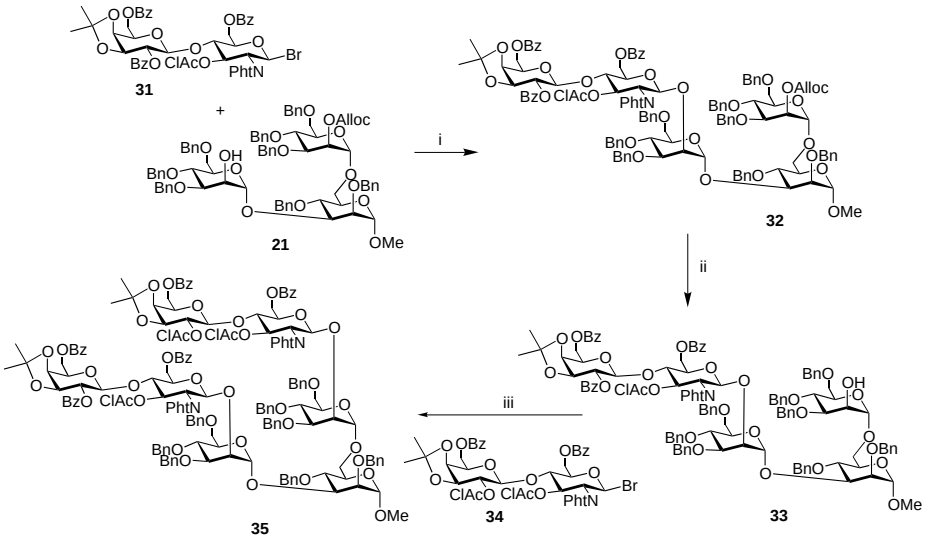
Table 1. Heptasaccharide syntheses.[a]

First donor	Trimannose acceptor	Pentasaccharide	Alloc deprotection	Second donor	Heptasaccharide
28 (3 equiv)	**29**	–	–	–	**30** 64
28 (1.5 equiv)	**21**	53	93	**31** (2 equiv)	**36** 71
31 (2 equiv)	**21**	71	88	**34** (2 equiv)	**35** 76
34 (2 equiv)	**21**	86	92	**31** (2 equiv)	**37** 60
34 (3 equiv)	**29**	–	–	–	**38** 71

[a] Yield for each step is given in %.

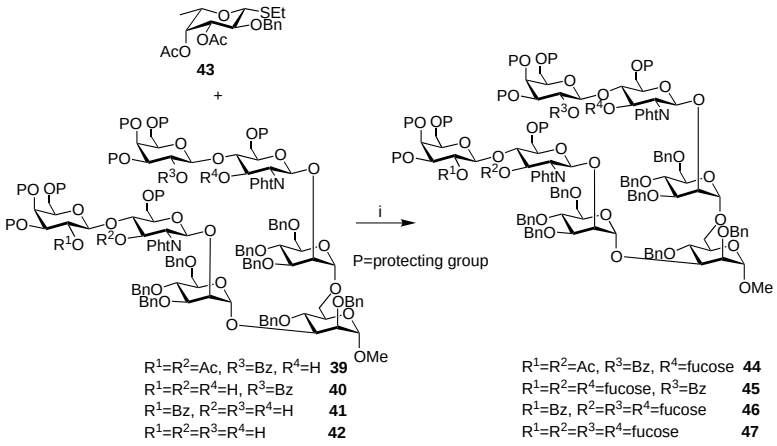


Scheme 4. i) AgOTf, 2,6-lutidine, 4 Å MS, CH_2Cl_2/toluene 5:1, −50 °C, 74 %; ii) $[Pd(PPh_3)_4]$, dimedone, THF, 88 %; iii) AgOTf, 2,6-lutidine, 4 Å MS, CH_2Cl_2/toluene 5:1, −50 °C, 76 %.

Heptasaccharide **39** was thus fucosylated with **43** by activation with MeOTf to yield octasaccharide **44** in 97 % yield (Scheme 5, Table 3). However, in fucosylating the other heptasaccharides 2,6-di-*tert*-butyl-4-methylpyridine was required as a buffer to protect the acid sensitive acetonides. Another feature of the fucosylation of these later structures is the lower yield, a result of incomplete glycosylation and concomitant difficulties in purification of the desired product. Resubjecting the mixture of oligosaccharides to the reaction conditions did not result in the conversion of the lower oligomers to more desired product. Analysis of the by-product from the synthesis of Lewis Y tetrasaccharide **49** indicated the mass balance was made up by the formation of the H-antigen trisaccharide **50**

deprotection revealed that the compound existed as a 30:1 β:α-mixture of anomers).

Selective removal of the chloroacetates was achieved by treatment of the various heptasaccharides with thiourea in a mixture of 2,6-lutidine/THF/MeOH or acetone affording alcohols **39**–**42** in good yields; this corresponds to approximately 90 % per chloroacetate (Table 2).[23]



Scheme 5. i) MeOTf, 2,6-di-*tert*-butyl-4-methylpyridine, 4 Å MS, CH_2Cl_2/Et_2O 2:1.

Fucosylation: Fucosylation was best achieved employing ethyl 2-*O*-benzyl-3,4-di-*O*-acetyl-1-thio-β-L-fucopyranoside[24] as donor in preference to 2,3,4-tri-*O*-benzyl-fucopyranoside derivatives. The deactivating effects of the two acetyl groups in **43** enhanced the α-selectivity of the reaction;[25] the tri-*O*-benzyl-fucopyranosides achieved only ratios of 15:1 α:β under optimised conditions.[26]

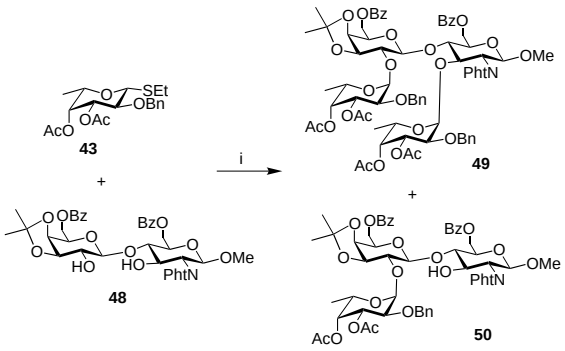
Table 2. Chloroacetate deprotection of the heptasaccharides **35**–**38**.

Substrate	Alcohol	Yield [%]
36	**39**	88
37	**40**	72
35	**41**	80
38	**42**	72

Table 3. Fucosylation of heptasaccharides **39**–**42** and **48**.

Alcohol	Fucosylated product	Yield [%]
39	**44**	97
40	**45**	48 (78 % per fucose)
41	**46**	46 (76 % per fucose)
42	**47**	44 (81 % per fucose)
48	**49**	69 (83 % per fucose)

(Scheme 6). This indicates perhaps that fucosylation of the galactose residue inhibits fucosylation of the glucosamine residue.



Scheme 6. i) MeOTf, 2,6-di-*tert*-butyl-4-methylpyridine, 4 Å MS, CH_2Cl_2/Et_2O 2:1, **49** 69%, **50** 26%.

Deprotection: Routine deprotection afforded the free oligosaccharides in good yields (Table 4). Unfortunately during the hydrogenation a small proportion of a unique benzyl group was reduced to the cyclohexylmethyl ether, a proportion which increased with greater size of the oligosaccharide. This by-product could be removed by reversed-phase chromatography but given its scarcity (<4%) was, in general, not separated.

Table 4. Deprotection of oligosaccharides.

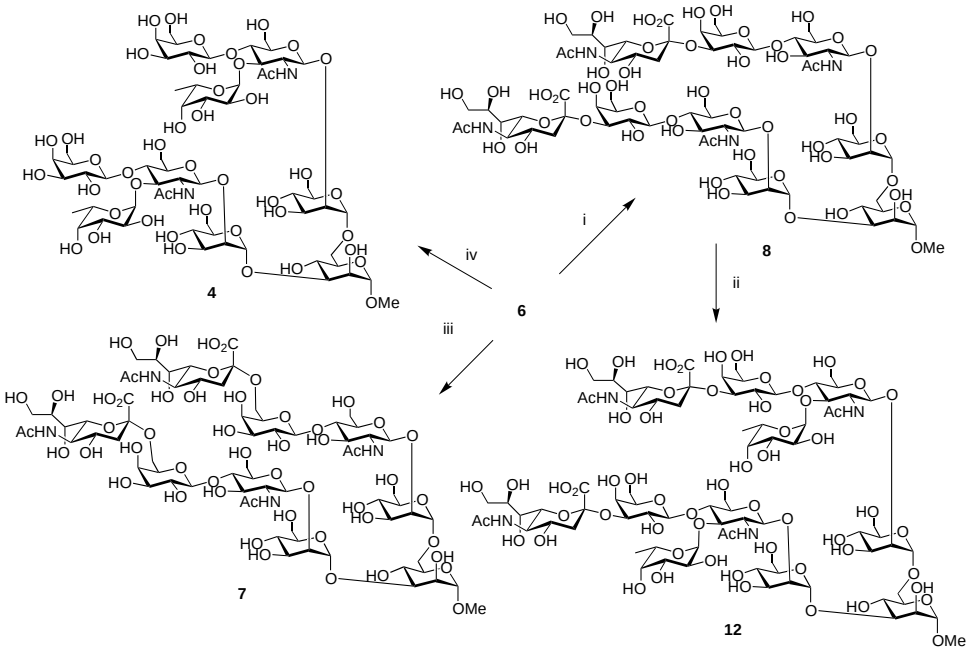
Substrate	Deprotected oligosaccharide	Yield [%]
30	**6**	80
44	**5**	63
45	**3**	95
46	**2**	95
47	**1**	94
49	**10**	95

Enzymatic elaboration: The introduction of glycosyl transferases has greatly ameliorated the synthesis of complex oligosaccharides with work in this area focusing particularly on the synthesis of selectin binding molecules.[27] α-Sialyltransferases in particular circumvent the problems associated with the chemical synthesis of sialyloligosaccharides, namely complications arising from both poor yields and selectivities.[28] The synthesis of four structurally diverse oligosaccharides **4**, **7**, **8** and **12** in high yields by one- and two-step protocols from heptasaccharide **6** illustrates the synthetic versatility of enzymatic glycosylation (Scheme 7). Bis-sialyl Lewis X undecasaccharide **12** was prepared by first incubating heptasaccharide **6** with α-2,3-sialyltransferase and CMP-sialic acid[29] in the presence of alkaline phosphatase[30] to give the bis-sialylated nonasaccharide **8** in 98% yield after size-exclusion chromatography. (The presence of a fucose on the C-3 position of glucosamine inhibits sialyl transfer[31] hence enzymatic sialylation has to be carried prior to fucosylation.) Further elaboration of nonasaccharide **8** was performed by fucosylation with GDP-L-fucose catalysed by human α-1,3-fucosyltransferase V affording undecasaccharide **12** in 69% yield. Nonasaccharides **4** and **7** were similarly prepared from heptasaccharide **6** in good yields without complication; this highlights the flexibility of the enzymatic approach.

The syntheses of the monovalent ligands **9**, **11** and **13**–**15** are based on the enzymatic decoration of *N*-acetyl lactosamine **52**, which was prepared by β-galactosidase-catalysed glycosidation of the *N*-acetyl glucosamine acceptor **51** employing lactose monohydrate as donor (Scheme 8).[7a]

Fucosylation of **52**, again employing the human α-1,3-fucosyltransferase V and the natural substrate GDP-L-fucose, afforded the Lewis X trisaccharide **11** in 72% yield. The same enzyme was also used to transfer the unnatural substrate GDP-L-galactose, affording the Lewis X derivative **9** in 70% yield. A prolonged reaction time was observed for the latter transformation; this is in agreement with kinetic data for the L-galactosylation of a similar disaccharide acceptor with the human milk α-1,3/4-fucosyltransferase reported by Hindsgaul.[32]

Sialylation of **52** was performed with α-2,3-sialyltransferase in a multienzyme system with in situ regeneration of CMP-



Scheme 7. i) α-2,3-sialytransferase, CMP-NeuAc, $MnCl_2$, $MgCl_2$, alkaline phosphatase, BSA, HEPES (200 mM, pH 7.5), 98%; ii) α-1,3-fucosyltransferase, GDP-L-fucose, $MnCl_2$, alkaline phosphatase, BSA, MES (50 mM, pH 6.0), 69%; iii) α-2,6-sialyltransferase, CMP-NeuAc, alkaline phosphatase, BSA, HEPES (50 mM, pH 7.0), 56%; iv) α-1,3-fucosyltransferase, GDP-L-fucose, $MnCl_2$, alkaline phosphatase, BSA, MES (50 mM, pH 6.0), 59%.

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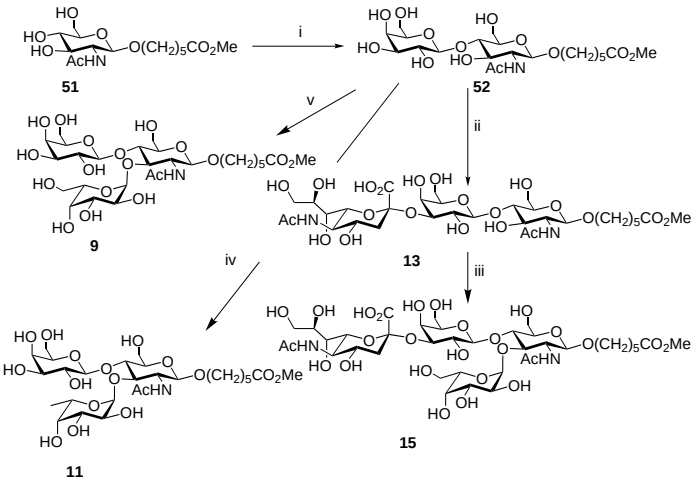

Scheme 8. i) α-lactose $\cdot H_2O$, galactosidase from *Bacillus circlans*, phosphate buffer pH 7.0, MeCN, 10%; ii) NeuAc, Pep $\cdot$ 3Na, $MgCl_2$, KCl, CTP, ATP, mercaptoethanol, NMK, PK, PPase, CMP-NeuAc-synthetase, α-2,3-sialyltransferase, BSA, HEPES (200 mM, pH 7.5), 73%; iii) α-1,3-fucosyltransferase, GDP-L-galactose, $MnCl_2$, alkaline phosphatase, BSA, MES (50 mM, pH 6.0), 64%; iv) α-1,3-fucosyltransferase, GDP-L-fucose, $MnCl_2$, alkaline phosphatase, BSA, MES (50 mM, pH 6.0), 72%; v) as for iii) 70%.

sialic acid,[33] which provided trisaccharide **13**[7a] in 73% yield. Fucosylation of **13** gave sialyl Lewis X tetrasaccharide **14**[7a] and incubation of **13** with the unnatural donor sugar nucleotide GDP-L-galactose and human α-1,3-fucosyltransferase V yielded the hydroxylated sialyl Lewis X derivative **15** in 64% yield completing the list of target compounds.

Conclusion

This controlled synthesis of a biologically relevant array serves as a testament to the maturity of oligosaccharide synthesis. By understanding the effects of various protecting groups on donor and acceptor reactivity a chemical route could be devised that maximised the yield of the desired product.[25] However, we still cannot predict when synthetic couplings will be adversely affected by steric factors, a feature of the bimolecular nature of the reaction.[34] Glycosyltransferases readily circumvent this problem but they too have their limitations. Although the combined, almost perfunctory approach detailed fulfilled the requirements of this investigation, it does not represent a general solution. Herein lies the true challenge to progress in oligosaccharide synthesis.

Experimental Section

^1H NMR spectra were recorded in $CDCl_3$ or D_2O on a Bruker DRX600, DRX500 and DPX200 spectrometers at 300 K. Residual protic solvent $CHCl_3$ ($\delta_H = 7.26$) was used as the external reference. ^{13}C NMR spectra were recorded in $CDCl_3$ or D_2O at 150 or 100 MHz on Bruker DRX600 and AC400 spectrometers, respectively, with the central resonance of $CDCl_3$ ($\delta_C = 77.0$) as the external reference. DQF-COSY, HMQC, coupled-HMQC, HMBC, TOCSY and 1D TOCSY experiments were used to assist assignment of the products. NMR assignments are as indicated in Figure 3. IR spectra were recorded as thin films between sodium chloride plates, deposited from chloroform solution on a FT-IR 1620 spectrometer. Mass spectra were obtained on Micromass Platfrom LC-MS and Q-Tof; Kratos MS890MS and Kompact 4; Bruker Daltonics Bio-Apex II (FTICR) spectrometers at the Department of Chemistry, University of Cambridge and on a Voyager STR spectrometer at M-Scan, Silwood Park, Ascot. Microanalyses were determined in the microanalytical laboratories at the University of Cambridge. Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. Optical rotations were measured with an Optical Activity AA-1000 polarimeter and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

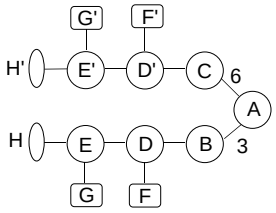

Figure 3. NMR assignment-residue labels.

Flash column chromatography was carried out with Merck Kieselgel (230–400 mesh). Analytical thin-layer chromatography (TLC) and preparative TLC was performed by using precoated glass-backed plates (Merck Kieselgel 60 F254) and visualised by UV and acidic ammonium molybdate(IV). Petrol 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.

α-1,3-Fucosyltransferase V, α-2,3-sialyltransferase and α-2,6-sialyltransferase were purchased from Calbiochem. CMP-Sialic acid, GDP-fucose and GDP-galactose were purchased from Calbiochem or synthesised by using published protocols.[35] **Abbreviations**: ATP adenosine 5′-triphosphate, BSA bovine serum albumim, CMP-NeuAc cytidine 5′-monophospho-*N*-acetylneuraminic acid, GDP guanidine 5′-diphosphate, HEPES *N*-2-hydroxylethylpiperazine-*N*′-2-ethane sulfonic acid, MES 2-(*N*-morpholine)ethane sulfonic acid, MK myokinase, NMK nucleoside monophosphate kinase, PEP phosphoenol pyruvate, PK pyruvate kinase, PPase inorganic pyrophosphorylase.

Methyl 2,4-di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside (17): Methyl 2,4-di-*O*-benzyl-α-D-mannopyranoside[36] (5.50 g, 14.7 mmol) was dissolved in pyridine (20 mL) and cooled to 0 °C. TBDPS-Cl (4.2 mL, 16.2 mmol) was added and the mixture was stirred for 12 h, allowing the reaction to reach ambient temperature. After removal of the solvent in vacuo, the residue was coevaporated with toluene (2×20 mL), dissolved in Et_2O and washed successively with 2% aqueous HCl (250 mL), $NaHCO_3$ (150 mL) and brine (100 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Flash column chromatography (petrol/Et_2O 2:1) afforded **17** as a colourless gum (7.87 g, 87%). $[\alpha]_D^{30} = +130.0$ ($c = 1.00$, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 1.10$ (s, 9H; $(CH_3)_3C$), 2.41 (d, $J = 9.3$ Hz, 1H; 3-OH), 3.36 (s, 3H; OCH_3), 3.65 (dt, $J = 3.2$, 9.3 Hz, 1H; H-5), 3.77 (m, 2H; H-2, H-4), 3.97 (m, 2H; H-6), 4.02 (td, $J = 3.8$, 9.3 Hz, 1H; H-3), 4.61 (d, $J = 11.1$ Hz, 1H; OCH_2Ph), 4.64 (d, $J = 11.8$ Hz, 1H; OCH_2Ph), 4.79 (d, $J = 11.8$ Hz, 1H; OCH_2Ph), 4.85 (s, 1H; H-1), 4.91 (d, $J = 11.1$ Hz, 1H; OCH_2Ph), 7.26–7.81 (m, 20H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 19.3$ ($(CH_3)_3C$), 26.8 ($(CH_3)_3C$), 54.5 (OCH_3), 63.3 (C-6), 71.9 (C-3), 72.1 (C-5), [72.8, 74.8 (OCH_2Ph)], 76.6 (C-4), 78.7 (C-2), 97.7 (C-1) [127.5, 127.6, 127.7, 127.8, 128.3, 128.5, 129.5 (CH)], [133.4, 133.9 (C)], [135.6, 135.9 (CH)], [137.9, 138.5 (C)]; IR (film): $\tilde{\nu} = 3454$ (OH), 3069, 2931, 1112, 1062, 700 cm^{-1}; MS (ES): m/z (%): 630 (100) $[M + NH_4]^+$; $C_{37}H_{44}O_6Si$ (612): calcd C 72.51, H 7.24; found: C 72.28, H 7.13.

Phenyl 3,4,6-tri-*O*-benzyl-1-seleno-α-D-mannopyranoside: 3,4,6-Tri-*O*-benzyl-1,2-*O*-(methoxyethylidene)-β-D-mannopyranose[37] (4.90 g, 9.67 mmol) was dissolved in MeCN (20 mL) and stirred over powdered molecular sieves (1.5 g of a mixure of 4 and 5 Å) for 1 h before the addition of phenylselenol (1.23 mL, 11.6 mmol) and mercury(II) bromide (50 mg, 0.1 mmol). The mixture was then heated at 60 °C for 2 h. On cooling, the mixture was diluted with Et_2O (80 mL), filtered through Celite and the filtrate washed with 5% aqueous NaOH (50 mL), water (50 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue purified by flash column chromatography (petrol/Et_2O 3:1) affording phenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-seleno-α-D-mannopyranoside (5.58 g, 91%) as a yellow amorphous solid. $[\alpha]_D^{30} = +140.2$ ($c = 1.00$, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 2.13$ (s, 3H; CH_3CO), 3.72 (dd, $J = 1.4$, 11.0 Hz, 1H; H-6a), 3.86 (dd, $J = 4.5$, 11.0 Hz, 1H; H-6b), 3.91 (dd, $J = 3.1$,

9.3 Hz, 1H; H-3), 3.98 (t, $J = 9.3$ Hz, 1H; H-4), 4.22 (m, 1H; H-5), 4.48 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.53 (d, $J = 10.7$ Hz, 1H; OCH_2Ph), 4.57 (d, $J = 11.2$ Hz, 1H; OCH_2Ph), 4.67 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.72 (d, $J = 11.2$ Hz, 1H; OCH_2Ph), 4.89 (d, $J = 10.7$ Hz, 1H; OCH_2Ph), 5.67 (dd, $J = 0.6$, 3.1 Hz, 1H; H-2), 5.80 (d, $J = 0.6$ Hz, 1H; H-1), 7.21–7.58 (m, 20H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 21.1$ (*C*H_3CO), 68.8 (C-6), [71.9, 73.4, 75.4 (C-2, 3, 4)], 78.9 (C-5), 83.8 (C-1), [127.6, 127.8, 128.0, 128.2, 128.3, 128.4, 128.5, 129.2, 134.0 (CH)], [137.6, 138.2, 138.3 (C)], 170.3 (C=O); IR (film): $\tilde{\nu} =$ 3029, 2867, 1743(C=O), 1605, 1578, 1496, 1454, 1098 cm^{-1}; MS (FAB): *m*/*z* (%): 573 (42) $[M - \mathrm{OAc}]^+$, 475 (68), $[M - \mathrm{SePh}]^+$, 181 (100); HRMS calcd for $C_{29}H_{31}O_6$: 475.1210; found 475.2139.

Phenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-seleno-α-D-mannopyranoside (5.54 g, 8.77 mmol) was dissolved in methanol (40 mL) to which was added K_2CO_3 (50 mg) and the reaction stirred for 3 h at ambient temperature. The reaction was neutralised with Amberlite IR-120 (plus), filtered and concentrated in vacuo to give clean phenyl 3,4,6-tri-*O*-benzyl-1-seleno-α-D-mannopyranoside (5.4 g, quant.) as a yellow oil without need for purification. $[\alpha]_D^{30} = +173.4$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 2.70$ (s, 1H; 2-OH), 3.69 (d, $J = 10.7$ Hz, 1H; H-6a), 3.82 (dd, $J = 4.4$, 10.7 Hz, 1H; H-6b), 3.88 (dd, $J = 2.9$, 9.5 Hz, 1H; H-3), 3.97 (t, $J = 9.5$ Hz, 1H; H-4), 4.20 (dd, $J = 4.4$, 9.5, 9.7 Hz, 1H; H-5), 4.32 (s, 1H; H-2), 4.47 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.56 (d, $J = 10.8$ Hz, 1H; OCH_2Ph), 4.63 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.72 (s, 2H; OCH_2Ph), 4.86 (d, $J = 10.8$ Hz, 1H; OCH_2Ph), 5.89 (s, 1H; H-1), 7.21–7.58 (m, 20H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 68.7$ (C-6), 70.5 (C-2), [72.1, 73.4 (O*C*H_2Ph)], 74.1 (C-5), 74.3 (C-4), 75.3 (O*C*H_2Ph), 80.6 (C-3), 85.4 (C-1), [127.6, 127.8, 128.0, 128.1, 128.2, 128.4, 128.7, 129.2, 134.0 (CH)], [137.6, 138.1, 138.2 (C)]; IR (film): $\tilde{\nu} = 3424$ (OH), 3030, 2868, 1605, 1579, 1496, 1455, 1055 cm^{-1}; MS (ES): *m*/*z* (%): 613 (100) $[M + \mathrm{Na}]^+$; $C_{33}H_{34}O_5Se$ (613): calcd C 67.23, H 5.84; found: C 67.02, H 5.84.

Phenyl 3,4,6-tri-*O*-benzyl-1-seleno-2-*O*-(2′,2′,2′-trichloroethoxycarbonyl)-α-D-mannopyranoside (16): Phenyl 3,4,6-tri-*O*-benzyl-1-seleno-α-D-mannopyranoside (3.12 g, 5.3 mmol) and 4-dimethylaminopyridine (1.30 g, 10.6 mmol) were dissolved in CH_2Cl_2 (20 mL) and 2′,2′,2′-trichloroethyl chloroformate (1.8 mL, 13.2 mmol) was added dropwise to the stirring mixture. The reaction was stirred for a further 6 h at ambient temperature after which time it was passed through a plug of silica, eluting with Et_2O/CH_2Cl_2 1:1 (3 × 10 mL). The filrate was concentrated under reduced pressure and the residue purified by flash column chromatograpy (petrol/Et_2O 7:1) affording **16** (3.99 g, 98%) as colourless oil. $[\alpha]_D^{30} = +152.0$ ($c = 0.35$ $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 3.74$ (dd, $J = 2.0$, 11.0 Hz, 1H; H-6a), 3.86 (dd, $J = 4.6$, 11.0 Hz, 1H; H-6b), 3.94–3.96 (m, 1H; H-3), 4.00 (t, $J = 9.2$ Hz, 1H; H-4), 4.20–4.28 (m, 1H; H-5), 4.48 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.54 (d, $J = 10.8$ Hz, 1H; OCH_2Ph), 4.63 (d, $J = 11.5$ Hz, 1H; OCH_2Ph), 4.66 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.75 (d, $J = 11.5$ Hz, 1H; OCH_2Ph), 4.76 (s, 2H; OCH_2CCl$_3$), 4.89 (d, $J = 10.8$ Hz, 1H; OCH_2Ph), 5.51 (d, $J = 2.6$ Hz, 1H; H-2), 5.89 (s, 1H; H-1), 7.18–7.61 (m, 20H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 68.8$ (C-6), [72.1, 73.4 (O*C*H_2Ph)], 74.3 (C-4), 74.6 (C-5), 75.3 (O*C*H_2Ph), 76.1 (C-2), 77.0 (O*C*H_2CCl$_3$), 78.8 (C-3), 83.0 (C-1), 94.3 (OCH$_2$*C*Cl$_3$), [127.5, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5 (CH)], 128.9 (C), [129.3, 134.1 (CH)], [137.5, 138.2 (C)], 153.6 (C=O); IR (film): $\tilde{\nu} =$ 3030, 2867, 1758 (C=O), 1452, 1370, 1097, 1022 cm^{-1}; MS (FAB): *m*/*z* (%): 765 (52) $[M]^+$, 764 (51) $[M - 1]^+$, 181 (100); HRMS calcd for $C_{35}H_{35}O_7Cl_3Se$: 765.0692; found 765.0697.

Phenyl 3,4,6-tri-*O*-benzyl-1-seleno-2-*O*-allyloxycarbonyl-α-D-mannopyranoside (19): Phenyl 3,4,6-tri-*O*-benzyl-1-seleno-α-D-mannopyranoside (5.12 g, 8.7 mmol) and 4-dimethylaminopyridine (1.60 g, 13.1 mmol) were dissolved in CH_2Cl_2 (25 mL) and allyl chloroformate (2.4 mL, 22.6 mmol) was added dropwise. The reaction was stirred for 12 h at ambient temperature after which time it was passed through a plug of silica, eluting with Et_2O/CH_2Cl_2 1:1 (3 × 10 mL). The filtrate was concentrated under reduced pressure and the residue purified by flash column chromatography (petrol/Et_2O 5:1) affording **19** (5.74 g, 98%) as a yellow oil. $[\alpha]_D^{30} = +117.3$ ($c = 1.44$, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): $\delta = 3.73$ (dd, $J = 2.0$, 10.9 Hz, 1H; H-6a), 3.85 (dd, $J = 4.6$, 10.9 Hz, 1H; H-6b), 3.90–3.95 (m, 1H; H-3), 3.98 (t, $J = 9.2$ Hz, 1H; H-4), 4.21–4.23 (m, 1H; H-5), 4.48 (d, $J = 12.1$ Hz, 1H; OCH_2Ph), 4.53 (d, $J = 10.8$ Hz, 1H; OCH_2Ph), 4.62 (d, $J = 11.4$ Hz, 1H; OCH_2Ph), 4.63 (d, $J = 5.7$ Hz, 1H; OCH_2allyl), 4.66 (d, $J = 12.1$ Hz, 1H; OCH_2Ph), 4.77 (d, $J = 11.4$ Hz, 1H; OCH_2Ph), 4.90 (d, $J = 10.8$ Hz, 1H; OCH_2Ph), 5.26 (ddd, $J = 1.3$, 3.0, 10.4 Hz, 1H; CH=CH_2), 5.36 (ddd, $J = 1.3$, 3.0, 17.2 Hz, 1H; CH=CH_2), 5.48 (d, $J = 2.5$ Hz, 1H; H-2), 5.89 (s, 1H; H-1), 5.83–6.03 (m, 1H; C*H*=CH$_2$), 7.18–7.61 (m, 20H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 68.8$ (*C*H$_2$allyl, C-6), [72.0, 73.4 (O*C*H$_2$Ph)], 74.5 (C-4, 5), 74.9 (C-2), 75.4 (O*C*H$_2$Ph), 78.8 (C-3), 83.4 (C-1), 119.1 (CH=*C*H$_2$allyl), [127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4 (CH)], 129.1 (C), 131.4 (*C*H=CH$_2$allyl), 134.1 (CH), [137.6, 138.3 (C)], 155.9 (C=O); IR (film): $\tilde{\nu} = 3030$, 2867, 1745 (C=O), 1454, 1368, 1098, 1024 cm^{-1}; MS (FIB): *m*/*z* (%): 673 (24) $[M - 1]^+$, 181 (100); HRMS calcd for $C_{37}H_{37}O_7Se$: 673.1705; found 673.1654.

Methyl 2,4-di-*O*-benzyl-3-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(2′,2′,2′-trichloroethoxycarbonyl)-α-D-mannopyranosyl]-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside (18a): Selenide **16** (0.50 g, 654 μmol) and acceptor **17** (0.33 g, 545 μmol) were coevaporated with toluene (3 × 5 mL) before being stirred over 4 Å powdered sieves (0.80 g) in CH_2Cl_2/Et_2O (1:1 4 mL) for 4 h. *N*-Iodosuccinimide (NIS) (0.18 g, 817 μmol), dried by coevaporation with toluene (3 × 3 mL) and storage in vacuo, was suspended in CH_2Cl_2 (1 mL) and sonicated until generation of a fine suspension. Catalytic triflic acid (50 μL of a stock solution of 50 μL of triflic acid in 1 mL of CH_2Cl_2) was added to the suspension and the mixture immediately transferred by syringe to the vigorously stirring mixture of sugars. After 0.5 h the reaction was diluted with Et_2O (20 mL), filtered through Celite, washed with 10% aqueous $Na_2S_2O_3$ (10 mL), and dried ($MgSO_4$). The solvents were removed in vacuo and the residue purified by flash column chromatography (petrol/Et_2O 5:1) furnishing the titled dimannoside (0.57 g, 86%) as a colourless gum. $[\alpha]_D^{30} = +8.9$ ($c = 1.13$ CH_2Cl_2); ^{1}H NMR ($CDCl_3$): $\delta = 1.06$ (s, 9H; (CH$_3$)$_3$C)), 3.26 (s, 3H; OCH$_3$), 3.59–3.62 (m, 1H; H-5A), 3.68–3.72 (m, 2H; H-6B), 3.84 (t, $J = 9.6$ Hz, 1H; H-4B), 3.87 (s, 1H; H-2A), 3.88 (dd, $J = 1.0$, 11.3 Hz, 1H; H-6Aa), 3.93 (dd, $J = 4.5$, 11.3 Hz, 1H; H-6Ab), 3.99 (ddd, $J = 3.0$, 4.0, 9.6 Hz, 1H; H-5B), 4.05 (dd, $J = 3.8$, 9.6 Hz, 1H; H-3B), 4.06 (t, $J = 9.6$ Hz, 1H; H-4A), 4.17 (dd, $J = 3.1$, 9.6 Hz, 1H; H-3A), 4.51 (d, $J = 11.9$ Hz, 1H; OCH_2Ph), 4.52 (d, $J = 10.8$ Hz, 1H; OCH_2Ph), 4.54 (d, $J = 11.1$ Hz, 1H; OCH_2CCl$_3$), 4.57 (d, $J = 11.2$ Hz, 1H; OCH_2Ph), 4.61 (d, $J = 11.9$ Hz, 1H; OCH_2Ph), 4.64 (d, $J = 12.1$ Hz, 1H; OCH_2Ph), 4.67 (m, 2H; OCH_2Ph and OCH_2CCl$_3$), 4.68 (d, $J = 12.1$ Hz, 1H; OCH_2Ph), 4.72 (s, 1H; H-1A), 4.73 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.75 (d, $J = 11.2$ Hz, 1H; OCH_2Ph), 4.87 (d, $J = 10.8$ Hz, 1H; OCH_2Ph), 5.30 (d, $J = 2.8$ Hz, 1H; H-2B), 5.31 (s, 1H; H-1B), 7.17–7.75 (m, 35H; Ph); ^{13}C NMR ($CDCl_3$): $\delta =$ 19.4 (CH$_3$)$_3$*C*)), 26.8 (*C*H$_3$)$_3$C)), 54.6 (OCH$_3$), 63.1 (C-6A), 69.3 (C-6B), 72.1 (*C*H$_2$CCl$_3$), 72.4 (O*C*H$_2$Ph), 72.5 (C-5B), 72.9 (C-5A), 73.6 (O*C*H$_2$Ph), 74.0 (C-2B), 74.4 (C-4B), 74.9 (C-4A), [75.0, 75.1, 76.9 (O*C*H$_2$Ph)], 78.0 (C-2A, C-3B), 78.8 (C-3A), 94.4 (CH$_2$*C*Cl$_3$), 98.3 (C-1A), 99.2 (C-1B), [127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.3, 128.4, 129.6, (CH)], [133.4, 133.9 (C)], [135.5, 136.0 (C)], [137.9, 138.2, 138.3, 138.4, 138.6 (C)], 153.7 (C=O); IR (film): $\tilde{\nu} =$ 3062, 3019, 2928, 2844, 1761 (C=O), 1452, 1137, 1103, 1061, 1022 cm^{-1}; MS (ES): *m*/*z* (%): 1238 (100) $[M + \mathrm{NH_4}]^+$; $C_{67}H_{73}O_{13}SiCl_3$ (1220): calcd C 65.99, H 6.04; found: C 66.03, H 6.03.

Methyl 2,4-di-*O*-benzyl-3-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(2′,2′,2′-trichloroethoxycarbonyl)-α-D-mannopyranosyl]-α-D-mannopyranoside (18): Mannoside **18a** (0.57 g, 467 μmol) was dissolved in a solution of HF · pyridine in THF (8 mL 2.4 M solution) and stirred for 5 h at ambient temperature. The reaction was then diluted with Et_2O (30 mL) and washed with 1N HCl (10 mL) and $NaHCO_3$ (2 × 20 mL) and dried ($MgSO_4$). After evaporation of the solvents under reduced pressure the crude product was purified by flash column chromatography (petrol/Et_2O 1:1) affording desilylated dimannoside **18** (0.47 g, 97%) as a colourless foam. $[\alpha]_D^{30} = +9.9$ ($c = 2.70$, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): $\delta = 2.01$ (s, 1H; 6B-OH), 3.27 (s, 3H; OCH$_3$), 3.61 (dt, $J = 3.2$, 9.5 Hz, 1H; H-5A), 3.68–3.72 (m, 2H; H-6B), 3.72–3.77 (m, 1H; H-6Aa), 3.81–3.86 (m, 3H; 2A, 4B, H-6Ab), 3.94 (dt, $J = 3.3$, 9.7 Hz, 1H; H-5B), 4.00 (t, $J = 9.5$ Hz, 1H; H-4A), 4.03 (dd, $J = 3.2$, 9.1 Hz, 1H; H-3B), 4.19 (dd, $J = 2.9$, 9.5 Hz, 1H; H-3A), 4.51 (d, $J = 11.9$ Hz, 1H; OCH_2Ph), 4.52 (d, $J = 11.0$ Hz, 1H; OCH_2Ph), 4.55 (d, $J = 11.9$ Hz, 1H; OCH_2CCl$_3$), 4.60 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.61 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.65 (d, $J = 11.0$ Hz, 1H; OCH_2Ph), 4.66 (s, 1H; H-1A), 4.69 (m, 3H; OCH_2CCl$_3$ and OCH_2Ph), 4.74 (d, $J = 11.8$ Hz, 1H; OCH_2Ph), 4.82 (d, $J = 11.1$ Hz, 1H; OCH_2Ph), 4.89 (d, $J =$ 11.1 Hz, 1H; OCH_2Ph), 5.31 (m, 1H; H-2B), 5.35 (s, 1H; H-1B), 7.19–7.35 (m, 25H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 54.9$ (OCH$_3$), 62.0 (C-6A), 69.2 (C-6B), 72.0 (O*C*H$_2$CCl$_3$), 72.1 (C-5A), 72.5 (C-5B), [72.6, 73.5 (O*C*H$_2$Ph)], 73.8 (C-2B), 74.2 (C-4B), 74.9 (C-4A), [75.0, 75.1, 76.9 (O*C*H$_2$Ph)], 77.4 (C-2A), 77.8 (C-3B), 78.3 (C-3A), 94.3 (OCH$_2$*C*Cl$_3$), 98.6 (C-1A), 99.1 (C-1B), [127.5, 127.7, 127.8, 127.9, 128.3, 128.4, 128.5 (CH)], [137.7, 138.0, 138.1, 138.3, 138.4 (C)], 153.7 (C=O); IR (film): $\tilde{\nu} = 2929$, 1762 (C=O), 1457, 1376, 1137, 1064 cm^{-1}; MS

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(FIB): *m/z* (%): 1115 (81) $[M+Cs]^+$, 1005 (40), $[M+Na]^+$, 517 (100); HRMS calcd for $C_{51}H_{55}O_{13}Cl_3Na$: 1003.2606; found 1003.2606.

Methyl 2,4-di-*O*-benzyl-3-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(2′,2′,2′-trichloroethoxycarbonyl)-α-D-mannopyranosyl]-6-*O*-(2-*O*-allyloxycarbonyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (20): Selenide **19** (0.19 g, 280 μmol) and dimannoside **18** (0.22 g, 224 μmol) were coevaporated with toluene (2 × 6 mL) prior to stirring over powdered 4 Å sieves in CH_2Cl_2/Et_2O (1:1 3 mL) for 2 h. *N*-Iodosuccinimide (75 mg, 336 μmol), dried by coevaporation with toluene (3 × 2 mL) and storage in vacuo, was suspended in CH_2Cl_2 (1 mL) and sonicated until generation of a fine suspension. Catalytic triflic acid (40 μL of a stock solution of 50 μL of triflic acid in 1 mL of CH_2Cl_2) was added to the suspension and the mixture immediately transferred by syringe to the vigorously stirring mixture of sugars. After 15 min the reaction was diluted with Et_2O (20 mL), filtered through Celite, washed with 10% aqueous $Na_2S_2O_3$ (10 mL), and dried ($MgSO_4$). The solvents were removed in vacuo and the residue purified by flash column chromatography (petrol/Et_2O 1:1) furnishing trisaccharide **20** (0.31 g, 92%) as a colourless foam. $[\alpha]_D^{30} = +29.5$ ($c = 1.41$, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): $\delta = 3.25$ (s, 3H; OCH_3), 3.65 (dd, $J =$ 10.8 Hz, 1H; H-6Ca), 3.69–3.75 (m, 5H; H-5A, 5A, 6Ab, 6B), 3.80–3.82 (m, 1H; H-5C), 3.83–3.95 (m, 5H; H-2A, 4A, 4B, 4C, 6Aa), 3.98–4.01 (m, 2H; H-3C, 5B), 4.09 (dd, $J =$ 2.8, 9.3 Hz, 1H; H-3B), 4.20 (dd, $J = 3.0$, 9.5 Hz, 1H; H-3A), 4.49–4.51 (m, 3H; OCH_2Ph), 4.52 (d, $J = 11.4$ Hz, 1H, OCH_2Ph), 4.53 (d, $J =$ 12.1 Hz, 1H; OCH_2Ph), 4.55 (d, $J = 11.4$ Hz, 1H; OCH_2Ph), 4.57 (d, $J = 11.2$ Hz, 1H; OCH_2Ph), 4.62 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.65 (d, $J = 12.1$ Hz, 1H; OCH_2Ph), 4.65–4.67 (m, 4H; OCH_2CCl_3, OCH_2allyl), 4.69 (s, 1H; H-1A), 4.70 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.71 (d, $J = 11.2$ Hz, 1H; OCH_2Ph), 4.72 (d, $J =$ 11.4 Hz, 1H; OCH_2Ph), 4.74 (d, $J = 12.0$ Hz, 1H; OCH_2Ph), 4.77 (d, $J = 11.3$ Hz, 1H; OCH_2Ph), 4.89 (d, $J = 11.4$ Hz, 1H; OCH_2Ph), 4.91 (d, $J = 11.3$ Hz, 1H; OCH_2Ph), 5.10 (s, 1H; H-1C), 5.29 (dd, $J = 1.4$, 10.5 Hz, 1H; $CH{=}CH_2$), 5.31 (t, $J = 2.5$ Hz, 1H; H-2C), 5.33–5.35 (m, 2H; H-1B, 2B), 5.40 (dd, $J =$ 1.4, 17.2 Hz, 1H; $CH{=}CH_2$), 5.96 (ddt, $J = 6.0$, 10.5, 17.2 Hz, 1H; $CH{=}CH_2$), 7.17–7.36 (m, 40H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 54.8$ (OCH_3), 66.5 (C-6B), 68.7 (OCH_2allyl), 68.9 (C-6A), 69.5 (C-6C), 71.1 (C-5B), 71.4 (OCH_2Ph), 71.7 (C-5C), 72.1 (OCH_2Ph), 72.3 (C-2C, OCH_2CCl_3), 72.5 (C-3B), [73.4, 73.6 (OCH_2Ph)], 73.9 (C-2B), 74.3 (C-4C, C-4B), 75.0 (C-4A), [75.1, 75.2, 76.9 (OCH_2Ph)], 77.5 (C-2A, C-3C), 78.0 (C-3C), 78.7 (C-3A), 94.4 (OCH_2CCl_3), 97.8 (C-1C), 98.1 (C-1A), 99.2 (C-1B), 118.9 ($CH{=}CH_2$), [127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4 (CH)], 131.6 ($CH{=}CH_2$), [137.9, 138.1, 138.3, 138.4, 138.5 (C)], [153.7, 154.5 (C=O)]; IR (film): $\tilde{\nu} = 3030$, 2921, 1750 (C=O), 1453, 1364, 1232, 1136, 1099, 1052, 1028, 697 cm^{-1}; MS (MALDI): *m/z* (%): 1522 (100) $[M+Na]^+$; $C_{82}H_{87}O_{20}Cl_3$ (1499): calcd C 65.75, H 5.86; found: C 65.91, H 5.84.

Methyl 2,4-di-*O*-benzyl-3-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-6-*O*-(2-*O*-allyloxycarbonyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (21): Trimannose **20** (0.55 g, 367 μmol) was dissolved in AcOH (8 mL) and zinc dust (0.2 g, 3.16 mmol) was added. The reaction was stirred for 3 h at ambient temperature after which time the reaction was diluted with Et_2O (20 mL) and filtered through Celite. The solvents were removed in vacuo and the residue coevaporated with toluene (3 × 10 mL) before purification by flash column chromatography (petrol/Et_2O 3:2) affording **21** (0.39 g, 80%) as a colourless glass. $[\alpha]_D^{30} = +36.1$ ($c = 0.96$, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): $\delta = 2.34$ (s, 1H; 2C-OH), 3.21 (s, 3H; OCH_3), 3.60 (dd, $J = 1.0$, 10.8 Hz, 1H; H-6Ca), 3.64–3.69 (m, 5H; H-5A, 6Aa, 6B, 6Cb), 3.77–3.80 (m, 2H; H-4B, 5C), 3.83–3.95 (m, 7H; H-2A, 3B, 3C, 4A, 4C, 5B, 6Ab), 4.01 (s, 1H; H-2B), 4.11 (dd, $J = 3.0$, 9.4 Hz, 1H; H-3A), 4.43–4.56 (m, 7H; OCH_2Ph), 4.63–4.68 (m, 10H; 7 × OCH_2Ph, 2 × OCH_2allyl, H-1A), 4.84 (m, 2H; OCH_2Ph), 5.06 (s, 1H; H-1C), 5.22 (s, 1H; H-1B), 5.25 (dd, $J = 1.2$, 10.5 Hz, 1H; $CH{=}CH_2$), 5.26 (s, 1H; H-2C), 5.36 (dd, $J = 1.2$, 17.2 Hz, 1H; $CH{=}CH_2$), 5.93 (ddt, $J = 6.0$, 10.5, 17.2 Hz, 1H; $CH{=}CH_2$), 7.11–7.32 (m, 40H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 54.8$ (OCH_3), 66.5 (C-6A), 68.7 (C-2B), 68.8 (OCH_2allyl), 68.9 (C-6C), 69.4 (C-6B), 71.0 (C-5A), 71.4 (OCH_2Ph), 71.7 (C-5C), 72.0 (C-5B), [72.1, 72.4 (OCH_2Ph)], 72.5 (C-2C), 74.3 (C-4C), [73.4, 73.5 (OCH_2Ph)], 74.6 (C-4B), [74.8, 75.0 (OCH_2Ph)], 75.1 (C-4A), 75.2 (OCH_2Ph), 77.6 (C-3C), 77.7 (C-2A), 78.4 (C-3A), 80.1 (C-3B), 97.8 (C-1C), 98.2 (C-1A), 101.4 (C-1B), 118.9 ($CH{=}CH_2$), [127.5, 127.6, 127.7, 127.8 (CH)], [137.9, 138.1, 138.3, 138.4, 138.5, 138.6 (C)], 154.7 (C=O); IR (film): $\tilde{\nu} = 3030$, 2921, 1749 (C=O), 1496, 1453, 1364, 1232, 1136, 1098, 1062, 1028 cm^{-1}; MS (FIB): *m/z* (%): 1456 (38) $[M+Cs]^+$, 1345 (81), $[M+Na]^+$, 517 (100); HRMS calcd for $C_{79}H_{86}O_{18}Na$: 1345.5712; found 1345.5685.

Preparation of Lewis X/Y precursors

Ethyl 3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside: $BF_3 \cdot OEt_2$ (0.84 mL, 6.8 mmol) was added at 0 °C to a stirred solution of 1,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranose[10b] (3.5 g, 4.6 mmol) and EtSH (1.50 mL, 20.3 mmol) in CH_2Cl_2. On completion of the addition the cooling bath was removed and the reaction stirred for a further 12 h. The reaction was quenched by addition of Et_3N (1.11 mL), diluted with CH_2Cl_2 (50 mL), washed with water (25 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue purified by flash column chromatography (petrol/Et_2O 4:1) yielding the titled sulfide (3.00 g, 85%) as fine white needles (Et_2O). M.p. 229–231 °C; $[\alpha]_D^{30} = +12.4$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 1.20$ (t, $J = 7.5$ Hz, 3H; SCH_2CH_3), 1.89 (s, 3H; CH_3CO), 1.96 (s, 3H; CH_3CO), 2.04 (s, 3H; CH_3CO), 2.06 (s, 3H; CH_3CO), 2.12 (s, 6H; CH_3CO), 2.58–2.69 (m, 2H; SCH_2CH_3), 3.81–3.87 (m, 3H; H-4D, 5D, 5E), 4.04 (dd, $J = 7.6$, 11.2 Hz, 1H; H-6Ea), 4.09 (dd, $J = 6.2$, 11.2 Hz, 1H; H-6Eb), 4.15 (dd, $J = 5.2$, 11.9 Hz, 1H; H-6Da), 4.27 (t, $J = 10.3$ Hz, 1H; H-2D), 4.50 (d, $J = 11.9$ Hz, 1H; H-6Db), 4.53 (d, $J = 8.0$ Hz, 1H; H-1E), 4.96 (dd, $J = 3.2$, 10.4 Hz, 1H; H-3E), 5.12 (dd, $J = 8.0$, 10.4 Hz, 1H; H-2E), 5.33 (d, $J = 3.2$ Hz, 1H; H-4E), 5.48 (d, $J = 10.3$ Hz, 1H; H-1D), 5.77 (dd, $J = 10.0$, 10.3 Hz, 1H; H-3D), 7.70–7.80 (m, 4H; Phth); ^{13}C NMR ($CDCl_3$): $\delta = 15.0$ (SCH_2CH_3), [20.5, 20.6, 20.8 (CH_3CO)], 24.6 (SCH_2CH_3), 54.0 (C-2D), 60.7 (C-6E), 62.5 (C-6D), 66.6 (C-4E), 69.1 (C-2E), 70.6 (C-5E), 71.0 (C-3E), 71.9 (C-3B), 76.6 (C-4D, C-5D), 81.1 (C-1D), 101.1 (C-1E), [123.6, 123.7 (CH)], [131.2, 131.7 (C)], [134.1, 134.4 (CH)], [167.4, 167.6 (NC=O)], [169.1, 169.7, 170.0, 170.1, 170.3, 170.4 (CH_3CO)]; IR (film): $\tilde{\nu} = 2974$, 1749 (C=O), 1717 (C=O), 1371, 1222, 1036 cm^{-1}; MS (ES): *m/z* (%): 785 (100) $[M+NH_4]^+$; $C_{34}H_{41}O_{17}NS$ (767): calcd C 53.18, H 5.39, N 1.83; found: C 53.00, H 5.30, N 1.64.

Ethyl 4-*O*-(3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside: Ethyl 3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (3.00 g, 3.9 mmol) was dissolved in MeOH/THF (2:1 75 mL). K_2CO_3 (50 mg) was added and the reaction was stirred for 40 min. The reaction was neutralised by addition of Amberlite IR-120 (plus) causing the product to precipitate. The suspension was decanted off the resin by repeated washing with MeOH and the combined washings concentrated to yield ethyl 4-*O*-(β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (2.04 g, quant.) as an amorphous white powder which was used without further purification. Ethyl 4-*O*-(β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (1.00 g, 1.94 mmol) and dry *p*-toluenesulfonic acid (0.25 g, 1.31 mmol) were dissolved in DMSO (10 mL). 2,2-Dimethoxypropane (0.48 mL, 3.9 mmol) was added and the reaction stirred for 12 h after which time the reaction was quenched by addition of Et_3N (0.5 mL). The solvent was removed in vacuo and the residue purified by flash column chromatography (EtOAc) affording the titled compound (0.95 g, 88%) as a white foam. $[\alpha]_D^{30} = +35.1$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 1.17$ (t, $J = 7.5$ Hz, 3H; SCH_2CH_3), 1.31 (s, 3H; $(CH_3)_2C$), 1.48 (s, 3H; $(CH_3)_2C$), 2.60–2.70 (m, 2H; SCH_2CH_3), 3.14 (m, 1H; 6E-OH), 3.46 (s, 1H; 6D-OH), 3.58–3.63 (m, 2H; H-2E, 5D), 3.74 (t, $J = 9.5$ Hz, 1H; H-4D), 3.79–3.87 (m, 2H; H-6E), 3.92–3.98 (m, 4H; H-5E, 6D, 2E-OH), 4.15–4.19 (m, 3H; H-2D, 3E, 4E), 4.45 (d, $J = 8.0$ Hz, 1H; H-1E), 4.49 (t, $J = 9.5$ Hz, 1H; H-3D), 4.64 (s, 1H; 3D-OH), 5.34 (d, $J = 10.5$ Hz, 1H; H-1D), 7.71–7.86 (m, 4H; Phth); ^{13}C NMR ($CDCl_3$): $\delta =$ 14.9 (SCH_2CH_3), 24.2 (SCH_2CH_3), [27.0, 31.4 (CH_3)], 55.4 (C-2D), 62.0 (C-6D, 6E), 70.8 (C-3D), 73.4 (C-2E), 73.8 (C-4E), 74.0 (C-5E), 78.6 (C-5D), 79.2 (C-3E), 81.3 (C-1D), 82.0 (C-4D), 98.7 (C-1E), 110.5 ($(CH_3)_2CO_2$), [123.1, 123.7 (CH)], [131.7, 131.8 (C)], 134.1 (CH), [167.9, 168.2 (NC=O)]; IR (film): $\tilde{\nu} = 3407$, 2926, 1717, 1654, 1388, 1075 cm^{-1}; HRMS (ES) calcd for $C_{25}H_{33}O_{11}SNa$: 578.1672; found 578.1674.

Ethyl 6-*O*-benzoyl-4-*O*-(6-*O*-benzoyl-3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside: Ethyl 4-*O*-(3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (0.92 g, 1.66 mmol) was stirred in THF (16 mL) and Et_3N (2.3 mL) at −80 °C. Benzoyl chloride (1.4 mL, 12 mmol) was added dropwise and the reaction stirred for 22 h allowing the temperature to warm to −45 °C. The reaction was then quenched by addition of MeOH (1 mL) and warmed to ambient temperature. The reaction was diluted with

CH_2Cl_2 (50 mL) and washed with water (20 mL), dried ($NaSO_4$), and concentrated under reduced pressure. The residue was purified by flash column chromatography (petrol/Et_2O gradient 1:1 →1:4) furnishing the title compound (1.09 g, 86%) as a white foam. $[\alpha]_D^{30} = +54.7$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 1.21$ (t, J 7.3 Hz, 3H; SCH_2CH_3), 1.35 (s, 3H; $(CH_3)_2C$), 1.54 (s, 3H; $CH_3)_2C$), 2.63 – 2.73 (m, 2H; SCH_2CH_3), 3.51 (t, $J =$ 9.5 Hz, 1H; H-4D), 3.56 (d, $J = 2.0$ Hz, 1H; 2E-OH), 3.69 – 3.73 (m, 1H; H-5E), 3.84 – 3.88 (m, 1H; H-5D), 4.11 – 4.16 (m, 2H; H-3E, 4E), 4.18 (dd, $J = 2.0$, 5.5 Hz, 1H; H-2E), 4.19 – 4.36 (m, 3H; H-1E, 2D, 6Ea), 4.45 (dd, $J = 5.4$, 11.9 Hz, 1H; H-6Da), 4.52 (t, $J = 9.5$ Hz, 1H; H-3D), 4.67 (s, 1H; 3D-OH), 4.78 (dd, $J = 2.3$, 12.3 Hz, 1H; H-6Eb), 4.92 (d, $J = 11.9$ Hz, 1H; H-6Db), 5.38 (d, $J = 10.5$ Hz, 1H; H-1D), 7.30 – 8.08 (m, 14H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 15.0$ (SCH_2CH_3), 24.2 (SCH_2CH_3), [26.3, 28.0 (CH_3)], 54.7 (C-2D), 63.9 (C-6D), 64.4 (C-6E), 71.0 (C-3D), 72.0 (C-4E), 73.2 (C-3E), 73.3 (C-5E), 77.6 (C-5D), 78.9 (C-2E), 81.2 (C-1D), 83.6 (C-4D), 103.7 (C-1E), 110.8 ($(CH_3)_2CO_2$), [123.3, 123.5, 128.3, 128.5 (CH)], [129.2, 129.6 (C)], 129.8 (CH), [131.7, 131.8 (C)], [133.0, 133.4, 133.9, 134.1 (CH)], [166.4, 166.8 (C=O)], [167.6, 168.0 (NC=O)]; IR (film): $\tilde{\nu} = 3446$, 2927, 1750 (C=O), 1714 (C=O), 1382, 1270, 1036, 714 cm^{-1}; MS (ES): m/z (%): 808 (100) $[M + CO_2]^-$, $C_{39}H_{41}O_{13}NS$ (764): calcd C 61.33, H 5.41, N 1.83; found: C 60.60, H 5.35, N 1.79.

Ethyl 6-*O*-benzoyl-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-*β*-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside: Ethyl 6-*O*-benzoyl-4-*O*-(6-*O*-benzoyl-3:4-*O*-isopropylidene-*β*-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (0.83 g, 1.09 mmol) was heated at reflux under Dean – Stark conditions in toluene (15 mL) with dibutyltin dimethoxide (0.32 mL, 1.4 mmol) for 1.5 h. The solvent volume was then reduced to approximately 5 mL (by distillation) and the reaction allowed to cool. Beaded 4 Å sieves (1 g) were added, followed by BzCl (0.64 mL, 5.5 mmol) and the reaction stirred for 3 d. The supernatant was then decanted and concentrated under reduced pressure. The resulting residue was partitioned between petrol and MeCN. The MeCN fraction was collected, concentrated and the residue purified by flash column chromatography (petrol/Et_2O gradient 1:1 →1:4) yielding the title compound (0.93 g, 98%) as a white foam. $[\alpha]_D^{30} = +44.6$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 1.12$ (t, J 7.5, 3H; SCH_2CH_3), 1.34 (s, 3H; $(CH_3)_2C$), 1.63 (s, 3H; $(CH_3)_2C$), 2.53 – 2.63 (m, 2H; SCH_2CH_3), 3.66 (t, $J = 9.7$ Hz, 1H; H-4D), 3.81 – 3.83 (m, 1H; H-5D), 4.42 – 4.40 (m, 7H; H-2D, 3E, 4E, 5E, 6D, 6Ea), 4.56 (t, $J = 9.7$ Hz, 1H; H-3D), 4.60 (s, 1H; 3D-OH), 4.65 (d, $J =$ 8.1 Hz, 1H; H-1E), 4.85 (dd, $J = 2.5$, 12.3 Hz, 1H; H-6Eb), 5.34 – 5.37 (m, 2H; H-1D, 2E), 7.28 – 8.09 (m, 19H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 14.9$ (SCH_2CH_3), 24.1 (SCH_2CH_3), [26.8, 27.8 (CH_3)], 54.9 (C-2D), 63.1 (C-6D), 63.7 (C-6E), 70.8 (C-3D), 72.1 (C-5E), 73.0 (C-1D), 73.4 (C-4E), 76.0 (C-5D), 77.0 (C-3E), 81.1 (C-2E), 83.2 (C-4D), 101.5 (C-1E), 111.3 ($(CH_3)_2CO_2$), [123.3, 123.5, 128.3, 128.4 (CH)], [128.9, 129.2 (C)], 129.6 (CH), 129.8 (C), 129.9 (CH), [131.7, 131.9 (C)], [133.0, 133.1, 133.3, 133.9, 134.0 (CH)], [165.2, 165.6, 166.4 (C=O)], [167.6, 167.9 (NC=O)]; IR (film): $\tilde{\nu} = 3460$, 2988, 1775 (C=O), 1714 (C=O), 1602, 1367, 1271, 1109, 1071, 710 cm^{-1}; HRMS (ES) calcd for $C_{46}H_{45}O_{14}NSNa$: 890.2458; found 890.2449.

Ethyl 6-*O*-benzoyl-3-*O*-chloroacetyl-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-*β*-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (31): Ethyl 6-*O*-benzoyl-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-*β*-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (0.91 g, 1.01 mmol) and $ClAc_2O$ (0.32 g, 1.89 mmol) were stirred in CH_2Cl_2 (10 mL) at 0 °C and pyridine (0.25 mL, 3.15 mmol) was added. The cooling bath was removed and the reaction stirred for a further 12 h. The reaction was then diluted with in CH_2Cl_2 (50 mL), washed successively with 0.1M HCl (2 × 20 mL), $NaHCO_3$ (20 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue purified filtration through a plug of silica (Et_2O) affording **31** (0.89 g, 90%) as a white foam. $[\alpha]_D^{30} = +33.2$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta =$ 1.12 (3H, t, $J = 7.4$ Hz, SCH_2CH_3), 1.32 (3H, s, $(CH_3)_2C$), 1.59 (3H, s, $(CH_3)_2C$), 2.51 – 2.62 (2H, m, SCH_2CH_3), 3.84 – 3.86 (1H, m, H-5D), 3.95 – 3.99 (3H, m, H-4D, 5E, CH_2Cl), 4.08 (1H, d, $J = 14.7$ Hz, CH_2Cl), 4.20 (1H, dd, $J = 1.9$, 7.8 Hz, H-4E), 4.29 (1H, t, $J = 7.8$ Hz, H-3E), 4.34 (1H, t, $J =$ 10.5 Hz, H-2D), 4.44 – 4.48 (2H, m, H-6Da, 6Ea), 4.54 (1H, d, $J = 11.2$ Hz, H-6Db), 4.58 (1H, d, $J = 7.8$ Hz, H-1E), 4.77 (1H, dd, $J = 4.1$, 11.9 Hz, H-6E), 5.17 (1H, t, $J = 7.8$ Hz, H-2E), 5.45 (1H, d, $J = 10.5$ Hz, H-1D), 5.92 (1H, t, $J = 9.9$ Hz, H-3D), 7.36 – 8.14 (19H, m, Ar); ^{13}C NMR ($CDCl_3$): $\delta =$ 14.9 (SCH_2CH_3), 24.5 (SCH_2CH_3), [26.2, 27.5 (CH_3)], 40.4 (CH_2Cl), 53.8 (C-2D), 62.8 (C-6D), 63.3 (C-6E), 71.6 (C-4D), 72.9 (C-3D), 73.2 (C-4E), 73.4 (C-2E), 76.2 (C-5E), 76.8 (C-5D), 77.1 (C-3E), 81.1 (C-1D), 100.6 (C-1E), 111.1 ($(CH_3)_2CO_2$), [123.7, 123.8, 128.4, 128.5, 128.8 (CH)], 129.2 (C), 129.5 (CH), [129.6, 129.7 (C)], [129.8, 131.2, 131.5, 133.2 (CH)], [134.2, 134.4 (CH)], [164.8, 165.8, 166.2, 166.6 (C=O)], [167.6, 167.6 NC=O)]; IR (film): $\tilde{\nu} = 2987$, 1770 (C=O), 1722 (C=O), 1601, 1384, 1272, 1110, 1070, 1027, 710 cm^{-1}; MS (ES): m/z (%): 962 (100) $[M + NH_4]^+$; $C_{48}H_{46}O_{15}NSCl$ (944): calcd C 61.05, H 74.91, N 1.48; found: C 60.77, H 4.84, N 1.39.

Ethyl 6-*O*-benzoyl-3-*O*-chloroacetyl-4-*O*-(6-*O*-benzoyl-2-*O*-chloroacetyl-3:4-*O*-isopropylidene-*β*-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (34): Ethyl 6-*O*-benzoyl-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-*β*-D-galactopyranosyl)-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (0.26 g, 0.3 mmol) and $ClAc_2O$ (0.18 g, 1.1 mmol) were stirred in CH_2Cl_2 (3 mL) at 0 °C and pyridine (0.17 mL, 2.0 mmol) was added. The cooling bath was removed and the reaction stirred for a futher 12 h. The reaction was then diluted with CH_2Cl_2 (40 mL), washed successively with 0.1M HCl (2 × 10 mL), $NaHCO_3$ (15 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue purified by flash column chromatography (petrol/Et_2O gradient 1:1 →2:3) affording **34** (0.29 g, 94%) as a white foam. $[\alpha]_D^{30} = +54.7$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 1.16$ (3H, t, $J = 7.4$ Hz, SCH_2CH_3), 1.31 (s, 3H; $(CH_3)_2C$), 1.54 (s, 3H; $(CH_3)_2C$), 2.55 – 2.67 (m, 2H; SCH_2CH_3), 3.93 – 4.00 (m, 4H; H-4D, 5D, 5E, CH_2Cl), 4.08 (d, $J = 14.7$ Hz, 5H; H-3E, 4E, CH_2Cl), 4.35 (t, $J = 10.5$ Hz, 1H; H-2D), 4.41 – 4.45 (m, 3H; H-1E, 6Ea, 6Da), 4.71 – 4.75 (m, 2H; H-6Db, 6Eb), 4.94 (t, $J = 7.3$ Hz, 1H; H-2E), 5.50 (d, $J = 10.5$ Hz, 1H; H-1D), 5.93 (t, $J = 10.5$ Hz, 1H; H-3D), 7.38 – 8.12 (m, 14H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 15.6$ (SCH_2CH_3), 26.2 (SCH_2CH_3), [27.4, 29.0 (CH_3)], 40.4 (C-6D), 40.6 (C-6E), 53.8 (C-D), 62.9 (CH_2Cl), 63.1 (CH_2Cl), 71.6 (C-5E), 72.9 (C-3D), 73.2 (C-4E), 74.7 (C-2E), 76.1 (C-4D), 76.9 (C-3E, 5D), 81.2 (C-1D), 99.9 (C-1E), 111.3 ($(CH_3)_2CO_2$), [123.7, 123.8, 128.5, 128.8, 129.5, 129.6 (CH)], [131.2, 131.5 (C)], [133.4, 133.6, 134.3, 134.4 (CH)], [165.8, 165.9, 166.2, 166.6 (C=O)], [167.2, 167.6 (NC=O)]; IR (film): $\tilde{\nu} = 3446$, 2927, 1750 (C=O), 1714 (C=O), 1382, 1270, 1036, 714 cm^{-1}; MS (ES): m/z (%): 961 (100) $[M + CO_2]^-$, $C_{43}H_{43}O_{15}NSCl_2$ (917): calcd C 56.38, H 4.74, N 1.53; found: C 56.10, H 4.56, N 1.45.

Preparation of lactosamine bromides from sulfides: The lactosamine sulfide was dissolved in CH_2Cl_2 at 0 °C and Br_2 (typically 10 μL) was added until a reddish colour persisted. The reaction was stirred for 0.5 h after which time it was diluted with CH_2Cl_2 (30 mL), washed with 20% aqueous $Na_2S_2O_3$ (8 mL), dried ($NaSO_4$), and concentrated under reduced pressure. The resulting bromide was used without further purification.

Typical protocol for lactosamine coupling: The lactosamine bromide [x mol] and acceptor [x/(1.5 – 3) mol] were combined and dried by coevaporation with toluene (2 × 3 mL) and storage in vacuo. Beaded 4 Å sieves (0.5 g) were added to the residue, followed by CH_2Cl_2 (1 mL) and the mixture stirred in the absence of light for 3 h. The temperature was lowered to −50 °C and a solution of dried AgOTf [(x + 0.5) mol], dried by coevaporation with toluene (2 × 1 mL) and storage in vacuo, and 2,6-lutidine [(x + 0.5) mol] in a mixture of CH_2Cl_2/toluene (3:1 1.5 mL) was added, by syringe, dropwise over a period of 20 min. (It is recommended that this solution be prepared immediately prior to use as the AgOTf/2,6-lutidine complex slowly precipitates on standing.) The reaction was then stirred for a further 1 h after which time it was quenched by addition of Et_3N (0.1 mL), diluted with CH_2Cl_2 (40 mL), washed with 20% aqueous $Na_2S_2O_3$ (8 mL) and dried ($MgSO_4$). The solvents were removed under reduced pressure and the residue purified as indicated.

Methyl 2,4-di-*O*-benzyl-3,6-di-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl]-*α*-D-mannopyranosyl}-*α*-D-mannopyranoside (30): Bromide **28** (200 mg, 261 μmol) was reacted with trimannose **29** (108 mg, 87 μmol) in accordance with the general procedure. The product was purified by flash column chromatography (EtOAc/petrol 2:3) to yield heptasaccharide **30** (147 mg, 64%) as a white foam. ^{1}H NMR ($CDCl_3$): $\delta =$ 1.88 (s, 3H; $(CH_3)_2C$), 1.91 (s, 3H; $(CH_3)_2C$), 1.93 (s, 3H; CH_3CO), 1.97 (s, 3H; CH_3CO), 1.98 (s, 3H; CH_3CO), 1.99 (s, 3H; CH_3CO), 2.05 (s, 6H; CH_3CO), 2.06 (s, 3H; CH_3CO), 2.10 (s, 3H; CH_3CO), 2.06 (s, 3H; CH_3CO), 2.14 (s, 3H; CH_3CO), 2.15 (s, 3H; CH_3CO), 2.40 – 2.42 (m, 1H; H-5D), 2.79 (dd, $J = 6.1$, 11.7 Hz, 1H; H-6Ba), 3.00 (dd, $J = 6.1$, 11.9 Hz, 1H; H-6Ca), 3.19 (d, $J = 11.9$ Hz, 1H; H-6Cb), 3.24 (s, 3H; OCH_3), 3.44 – 3.49 (m, 3H; H-5C, 6Ab, 6Bb), 3.59 (t, $J = 9.6$ Hz, 1H; H-4C), 3.61 – 4.86 (m, 43H), 4.90 – 4.95 (m, 2H; H-3E, 3E′), 4.98 (s, 1H; H-1B), 5.05 – 5.16 (m, 3H; H-2E, 2E′, OCH_2Ph), 5.33 (s, 2H; H-4E, 4E′), 5.50 (d, $J = 8.6$ Hz, 1H;

0947-6539/99/0511-3334 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 11

H-1D′), 5.54 (t, $J = 9.9$ Hz, 1H; H-3D), 5.57 (dd, $J = 8.7$, 10.7 Hz, 1H; H-3D′), 7.35–7.87 (m, 48H; Ar); ^{13}C NMR ($CDCl_3$): δ = [20.5, 20.6, 20.7 (CH_3CO)], 54.5 (C-2D), 54.7 (C-2D′), 54.8 (OCH_3), [60.7, 60.8 (C-6E, 6E′)], 61.6 (C-6D), 62.5 (C-6D′), 65.9 (C-6A), 66.6 (C-4E, 4E′), 69.1 (C-2E, 2E′), 69.4 (C-6C), 70.1 (C-6B), 70.2 (OCH_2Ph), 70.5–70.7 (C-3D′, 5A, 5E, 5E′), 70.8 (OCH_2Ph), 71.0–71.2 (C-3D, 3E, 3E′), 71.5 (C-4B), 72.5 (OCH_2Ph), 71.8 (C-5D), 72.6 (C-5B, 5D′), 72.9 (OCH_2Ph), 73.0 (C-2B), 73.2 (C-2C), 73.8 (OCH_2Ph), 74.2 (C-5C), 74.3 (C-4C), 74.4 (C-4A), [74.8, 75.1 (OCH_2Ph)], 76.8 (C-4D′), 77.0 (C-4D), 77.3 (C-3C), 77.5 (C-2A), 77.9 (C-3B), 79.0 (C-3A), 95.7 (C-1D), 96.6 (C-1D′), 97.1 (C-1C), 98.7 (C-1A), 98.8 (C-1B), 101.1 (C-1E′), 101.3 (C-1E), [123.2, 123.3, 123.5, 123.9, 126.0, 127.2, 127.3, 127.4, 127.5, 127.5, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.5 (CH)], [131.2, 131.6 (C)], [133.9, 134.2 (CH)], [137.8, 137.9, 138.0, 138.2, 138.4, 138.5, 138.6 (C)], [167.3, 167.4, 168.0, 168.3, 169.0, 169.3, 169.9, 170.3, 170.5 (C=O)]; IR (film): $\tilde{\nu} = 2923$, 1749 (C=O), 1718 (C=O), 1451, 1386, 1367, 1222, 1073 cm^{-1}; HRMS (ES) calcd for $C_{139}H_{152}O_{50}N_2Na$: 2671.9305; found 2671.9280.

General protocol for Alloc deprotection: The oligosaccharide (x mol) and 5,5-dimethyl-1,3-cyclohexanedione (5x mol) were dissolved in THF to which was added [$Pd(PPh_3)_4$] (5 mg) and the mixture stirred in the absence of light for 4 h. The solvent was then removed under reduced pressure and the residue purified by size-exclusion chromatography on Sephadex LH-20 ($MeOH/CH_2Cl_2$ 1:1).

Methyl 2,4-di-*O*-benzyl-3-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[6-*O*-benzoyl-3-chloroacetyl-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-6-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[6-*O*-benzoyl-3-chloroacetyl-4-*O*-(6-*O*-benzoyl-2-*O*-chloroacetyl-3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]}-α-D-mannopyranoside (35): Bromide **31** (143 mg, 151 μmol) was reacted with trimannose **21** (100 mg, 75 μmol) in accordance with the general procedure to yield a pentasaccharide (125 mg, 74%) after purification by size-exclusion chromatography on Sephadex LH-20 ($MeOH:CH_2Cl_2$ 1:1) followed by preparative TLC ($petrol/Et_2O$ 9:1). The Alloc group was removed in accordance with the general procedure (88%). The resulting alcohol (101 mg, 47 μmol) was subsequently glycosylated with bromide **34** (86 mg, 94 μmol) in accordance with the general procedure to afford heptasaccharide **35** (106 mg, 76%) after purification by size-exclusion chromatography on Sephadex LH-20 ($MeOH/CH_2Cl_2$ 1:1) followed by preparative TLC ($petrol/Et_2O$ 3:2) as a white glass. ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 3H; $(CH_3)_2C$), 1.32 (s, 3H; $(CH_3)_2C$), 1.56 (s, 6H; $(CH_3)_2C$), 2.73 (dd, $J = 7.0$, 10.8 Hz, 1H; H-5D′), 2.98 (dd, $J = 5.8$, 11.1 Hz, 1H; H-6Ca), 3.17–3.19 (m, 4H; H-6Cb, OCH_3), 3.36–4.98 (m, 69H), 5.21 (t, $J = 7.7$ Hz, 1H; H-2E′), 5.51 (d, $J = 8.4$ Hz, 1H; H-1D), 5.66 (t, $J = 10.7$ Hz, 1H; H-3D′), 5.91 (t, $J = 9.1$ Hz, 1H; H-3D), 6.89–8.18 (m, 68H; Ar); ^{13}C NMR ($CDCl_3$): δ = [26.2, 26.3, 27.4, 27.5 (CH_3)], [40.5, 40.6 (CH_2Cl)], 54.2 (C-2D′), 54.4 (C-2D), 54.8 (OCH_3), 62.3 (C-6D′), 62.7 (C-6D), 63.2 (C-6E), 63.3 (C-6E′), 65.8 (C-6A), 69.5 (C-6C), 70.2 (C-6B), 70.3 (OCH_2Ph), 70.7 (OCH_2Ph, C-5A), 71.4 (C-5C), 71.6 (C-5E′), 71.7 (C-3D′, 5E), 71.8 (C-5D′), 72.1 (C-3D), [72.5, 72.6 (OCH_2Ph)], 72.7 (C-5B), 72.9 (OCH_2Ph, C-5D), 73.0 (C-2B), 73.3 (C-4E′), 73.4 (C-4E), 73.5 (OCH_2Ph, C-2C), 73.6 (C-2E′), 74.2 (C-4B), 74.3 (C-4C), 74.6 (C-2E′, 4A), 76.0 (C-4D′), 76.4 (C-4D), 76.9 (C-3E), 77.4 (C-3C), 77.5 (C-2A), 77.6 (C-3E′), 77.7 (C-3B), 78.7 (C-3A), 95.9 (C-1D′), 98.9 (C-1D, 1C), 98.7 (C-1B, 1A), 100.2 (C-1E), 100.7 (C-1E′), [111.2, 111.3 ($(CH_3)_2CO_2$)], [123.2, 123.4, 123.9, 125.5, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.4, 128.5, 128.6, 128.7 (CH)], 128.8 (C), [128.9, 129.4, 129.5, 129.6, 130.0 (CH)], [131.3, 131.7 (C)], [133.4, 133.5, 133.6, 133.7, 133.8, 134.0, 134.2 (CH)], [137.8, 137.9, 138.2, 138.5, 138.6, 138.7 (C)], [164.8, 165.7, 165.8, 166.3, 166.6, 166.7, 168.0, 168.2 (C=O)]; IR (film): $\tilde{\nu} = 2929$, 1777 (C=O), 1721 (C=O), 1453, 1386, 1273, 1110, 1069, 712 cm^{-1}; MS (ES): m/z (%): 2973 (5) $[M + Na]^+$, 2844 (100) $[M - 2 \times ClAc + Na]^+$, 2768 (10) $[M - 3 \times ClAc + Na]^+$; HRMS (ES) calcd for $[C_{158}H_{155}O_{44}N_2ClNa_2]^{2+}$: 1433.4791; found 1433.4810.

Methyl 2,4-di-*O*-benzyl-3-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-6-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[6-*O*-benzoyl-3-chloroacetyl-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-α-D-mannopyranoside (36): Bromide **28** (178 mg, 226 μmol) was reacted with trimannose **21** (200 mg, 152 μmol) in accordance with the general procedure to yield a pentasaccharide (169 mg, 53%) after purification by flash column chromatography (EtOAc/petrol 1:1) and size-exclusion chromatography on Sephadex LH-20 ($MeOH/CH_2Cl_2$ 1:1). The Alloc group was removed in accordance with the general procedure (93%). The resulting alcohol (50 mg, 26 μmol) was subsequently glycosylated with bromide **31** (49 mg, 52 μmol) in accordance with the general procedure to afford heptasaccharide **36** (63 mg, 86%) after purification by preparative TLC (EtOAc/petrol 1:1) as a white glass. ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 3H; $(CH_3)_2C$), 1.61 (s, 3H; $(CH_3)_2C$), 1.89 (s, 3H; CH_3CO), 1.93 (s, 3H; CH_3CO), 1.99 (s, 3H; CH_3CO), 2.06 (s, 3H; CH_3CO), 2.11 (s, 3H; CH_3CO), 2.15 (s, 3H; CH_3CO), 2.43 (m, 1H; H-5D), 2.79 (dd, $J = 6.7$, 10.8 Hz, 1H; H-6Ba), 3.00 (dd, $J = 5.8$ Hz, 11.1, 1H; H-6Ca), 3.19–3.22 (m, 4H; H-6Aa, OCH_3), 3.36–3.46 (m, 4H), 3.54 (1H, t, $J = 9.4$ Hz, H-4C), 3.57–3.59 (m, 1H; H-5A), 3.64–5.16 (m, 52H), 5.18 (t, $J = 7.2$ Hz, 1H; H-3E′), 5.34 (d, $J = 3.1$ Hz, 1H; H-4E), 5.44 (d, $J = 8.4$ Hz, 1H; H-1D′), 5.56 (t, $J = 9.1$ Hz, 1H; H-3D), 5.90 (t, $J = 9.1$ Hz, 1H; H-3D′), 6.98–8.13 (m, 63H; Ar); ^{13}C NMR ($CDCl_3$): δ = [20.5, 20.6, 20.7 (CH_3CO)], [26.1, 27.4 (CH_3)], 40.5 (CH_2Cl), 54.4 (C-2D′), 54.6 (C-2D), 54.8 (OCH_3), 60.8 (C-6E), 61.6 (C-6D), 62.6 (C-6D′), 63.4 (C-6E′), 65.8 (C-6A), 66.6 (C-4E), 69.1 (C-2E), 69.5 (C-6C), 70.1 (C-6B), 70.2 (OCH_2Ph), 70.5 (C-5E), 70.7 (C-3D), 70.8 (OCH_2Ph, C-5A), 71.2 (C-3E), 71.4 (C-5C), 71.7 (C-5E′), 71.8 (C-5D), 72.2 (C-3D′), [72.4, 72.5 (OCH_2Ph)], 72.6 (C-5B), 72.8 (C-5D′), 72.9 (OCH_2Ph), 73.1 (C-4E′), 73.2 (C-2B), 73.3 (C-2C, 2E′), 73.8 (OCH_2Ph), 74.3 (C-4B), 74.5 (C-4C), 74.7 (OCH_2Ph), 76.4 (C-4D′), 76.87 (C-4D), 77.2 (C-3E′), 77.3 (C-3C), 77.6 (C-2A), 77.9 (C-3B), 78.2 (C-3A), 95.7 (C-1D), 96.8 (C-1D′), 97.0 (C-1C), 98.5 (C-1A), 98.8 (C-1B), 100.9 (C-1E), 101.3 (C-1E′), 111.1 ($(CH_3)_2CO_2$), [123.1, 123.5, 126.0, 126.7, 126.9, 127.0, 127.1, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 128.8, 129.9 (CH)], [129.2, 129.4 (C)], [129.5 (CH)], 129.6 (C), 129.8 (CH), 131.5 (C), [133.3, 133.54, 134.0 (CH)], [137.8, 138.0, 138.2, 138.3, 138.4, 138.5, 138.6, 138.7 (C)] and [164.8, 165.8, 166.3, 166.6, 168.9, 169.7, 170.1, 170.2, 170.3 (C=O)]; IR (film): $\tilde{\nu} = 2933$, 1748 (C=O), 1720 (C=O), 1453, 1386, 1268, 1107, 1070, 715 cm^{-1}; HRMS (ES) calcd for $[C_{153}H_{157}O_{48}N_2ClNa_2]^{2+}$: 1435.4689; found 1435.4742.

Methyl 2,4-di-*O*-benzyl-3-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[6-*O*-benzoyl-3-chloroacetyl-4-*O*-(6-*O*-benzoyl-2-*O*-chloroacetyl-3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]}-6-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[6-*O*-benzoyl-3-chloroacetyl-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-α-D-mannopyranoside (37): Bromide **34** (90 mg, 98 μmol) was reacted with trimannose **21** (65 mg, 49 μmol) in accordance with the general procedure to yield a pentasaccharide (92 mg, 86%) after purification by size-exclusion chromatography on Sephadex LH-20 ($MeOH/CH_2Cl_2$ 1:1). The Alloc group was removed in accordance with the general procedure (92%). The resulting alcohol (67 mg, 32 μmol) was subsequently glycosylated with bromide **31** (72 mg, 77 μmol) in accordance with the general procedure to afford heptasaccharide **37** (57 mg, 60%) after purification by by size-exclusion chromatography on Sephadex LH-20 ($MeOH/CH_2Cl_2$ 1:1) followed by preparative TLC (EtOAc/petrol 3:2) as a white glass. ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 3H; $(CH_3)_2C$), 1.38 (s, 3H; $(CH_3)_2C$), 1.60 (s, 3H; $(CH_3)_2C$), 1.61 (s, 3H; $(CH_3)_2C$), 2.87–2.90 (m, 2H; H-5D, 6Ba), 3.00 (dd, $J = 5.8$, 11.1 Hz, 1H; H-6Ca), 3.13 (s, 3H; OCH_3), 3.23 (d, $J = 11.1$ Hz, 1H; H-6Cb), 3.37–4.80 (m, 61H), 4.88 (d, $J = 11.3$ Hz, 1H; H-6E′b), 4.93 (s, 1H; H-1B), 5.01 (d, $J = 8.4$ Hz, 1H; H-1D), 5.19 (t, $J = 7.2$ Hz, 1H; H-2E), 5.41 (d, $J = 8.4$ Hz, 1H; H-1D′), 5.90 (dd, $J = 9.1$, 10.7 Hz, 1H; H-3D′), 6.99–8.14 (m, 73H; Ar); ^{13}C NMR ($CDCl_3$): δ = [26.1, 26.2, 27.5, 28.1 (CH_3)], 40.5 (CH_2Cl), 54.4 (C-2D′), 54.7 (OCH_3), 55.3 (C-2D), 62.6 (C-6D′), 63.4 (C-6E), 63.9 (C-6E′), 64.0 (C-6D), 65.0 (C-6A), 69.5 (C-6C), 69.6 (C-3D), 70.2 (OCH_2Ph), 70.3 (C-6B), 70.7 (OCH_2Ph), 70.9 (C-5A), 71.4 (C-5C), 71.7 (C-5E), 72.0 (C-5E′), 72.2 (C-3D′), [72.3, 72.5 (OCH_2Ph)], 72.6 (C-5B), 72.8 (C-5D′), 73.0 (OCH_2Ph), 73.2 (C-4E, 4E′), 73.3 (C-3E), 73.4 (C-5D), 73.5 (C-2B, 2C, 2E, 2E′), 73.8 (OCH_2Ph), 74.3 (C-4C), 74.5 (C-4A, 4B), [74.7, 74.9 (OCH_2Ph)], 76.4 (C-4D′), 77.1 (C-3E′), 77.3 (C-3C), 77.6 (C-2A), 77.8 (C-3B, 3E′), 78.9 (C-3A), 83.5 (C-4D), 96.3 (C-1D), 96.8 (C-1D′), 97.0 (C-1C), 98.4 (C-1A), 99.2 (C-1B), 100.9 (C-1E), 103.7 (C-1E′), [110.8, 111.1 ($(CH_3)_2CO_2$)], [123.1, 123.4, 123.6, 125.8, 127.3, 127.4, 127.6, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8 (CH)], [128.9, 129.0, 129.2 (C)]. [129.4, 129.5 (CH)], 129.6 (C), 129.7 (CH), 129.3 (C), [129.9, 130.0 (CH)], 131.9 (C), [133.0, 133.1, 133.4, 133.6, 133.8, 133.9, 134.0 (CH)], [137.8, 138.1, 138.2, 138.3, 138.4, 138.5, 138.6, 138.8 (C)], [164.8, 135.8, 166.3, 166.5, 166.6, 167.2, 167.6, 168.2, 168.4 (C=O)]; IR (film): $\tilde{\nu} = 2930$, 1777 (C=O), 1722

(C=O), 1594, 1389, 1273, 1110, 1070, 712 cm^{-1}; HRMS (ES) calcd for $[C_{162}H_{159}O_{48}N_2Cl_3Na_2]^{2+}$: 1509.4507; found 1509.4519.

Methyl 2,4-di-*O*-benzyl-3,6-di-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[6-*O*-benzoyl-3-chloroacetyl-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-α-D-mannopyranoside (38): Bromide **34** (140 mg, 153 μmol) was reacted with trimannose **29** (63 mg, 50 μmol) in accordance with the general procedure. The product was purified by size-exclusion chromatography on Sephadex LH-20 (MeOH/CH_2Cl_2 1:1) to yield heptasaccharide **38** (107 mg, 71%) as a white glass. ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 6H; $(CH_3)_2$C), 1.56 (s, 3H; $(CH_3)_2$C), 1.58 (s, 3H; $(CH_3)_2$C), 2.53 – 2.55 (m, 1H; H-5D), 2.78 (dd, $J =$ 6.9, 10.3 Hz, 1H; H-6Ba), 3.00 (dd, $J = 5.6$, 10.8 Hz, 1H; H-Ca), 3.21 (s, H-6Aa, 4H; OCH_3), 3.41 – 5.00 (m, 64H), 5.01 (s, 1H; H-1B), 5.13 (d, $J =$ 8.3 Hz, 1H; H-1D), 5.53 (d, $J = 8.3$ Hz, 1H; H-1D′), 5.71 (t, $J = 9.6$ Hz, 1H; H-3D), 5.92 (t, $J = 9.5$ Hz, 1H; H-3D′), 6.95 – 8.12 (m, 68H; Ar); ^{13}C NMR ($CDCl_3$): $\delta =$ [26.1, 26.2, 27.4 (CH_3)], [40.4, 40.6, 40.8 (CH_2Cl)], 54.3 (C-2D), 54.4 (C-2D′), 54.8 (OCH_3), 62.3 (C-6D), 63.0 (C-6D′), 63.2 (C-6E, 6E′), 65.9 (C-6A), 69.4 (C-6C), 70.1 (C-6B), 70.3 (OCH_2Ph), 70.6 (C-5A), 70.7 (OCH_2Ph), 71.4 (C-5C), 71.6 (C-5E), 71.7 (C-5E′), 71.8 (C-3D), 72.0 (C-5D), 72.1 (C-3D′), 72.5 (OCH_2Ph), 72.6 (C-5B), 72.8 (OCH_2Ph), 72.9 (C-5D′), 73.1 (C-2B), 73.2 (C-4E), 73.3 (C-4E′), 73.4 (C-2C), 73.8 (OCH_2Ph), 74.2 (C-4B), 74.3 (C-4C), 74.6 (C-2E′, 4A), 74.7 (C-2E), [74.8, 75.0 (OCH_2Ph)], 76.3 (C-4D′), 76.6 (C-4D), 76.9 (C-3E′), 77.2 (C-3E), 77.5 (C-2A, 3C), 77.8 (C-3B), 78.5 (C-3A), 95.9 (C-1D), 96.8 (C-1D′), 97.0 (C-1C), 98.7 (C-1A, 1B), 100.1 (C-1E′), 100.5 (C-1E), 111.3 ($(CH_3)_2CO_2$), [123.2, 123.5, 123.9, 126.1, 127.2, 127.3, 127.4, 127.5, 127.6, 127.9, 128.0, 128.1, 128.2, 128.4, 128.6, 128.9 (CH)], 129.4 (C), 129.5 (CH), 129.6 (CH), [131.4, 131.5 (C)], [133.4, 133.5, 133.6, 133.7, 133.8, 134.0, 134.2, 137.8, 137.9, 138.2, 138.4, 138.5, 138.6, 138.7 (C)], [165.7, 165.8, 165.9, 166.1, 166.2, 166.3, 166.6, 167.2, 168.0, 168.2 (C=O)]; IR (film): $\tilde{\nu} = 2929$, 1777 (C=O), 1721 (C=O), 1453, 1386, 1273, 1110, 1069, 712 cm^{-1}; HRMS (ES) calcd for $[C_{157}H_{156}O_{46}N_2Cl_2Na_2]^{2+}$: 1495.4234; found 1495.4192.

General procedure for dechloracetylation: The oligosaccharide (x mol), thiourea (10x mol) and 2,6-lutidine (10x mol) were stirred in a mixture of MeOH/(THF or acetone) (3:1 0.5 mL) for a period of typically 7 d. The reaction was monitored by ^{1}H NMR of reaction aliquots, using the OCH_3 signal as a guide to reaction progress. On completion the reaction was diluted with CH_2Cl_2 (30 mL), washed with 0.3M HCl (10 mL) and dried ($NaSO_4$). The solvents were removed under reduced pressure and the residue purified by preparative TLC (petrol/EtOAc 2:3).

General protocol for fucosylation: The oligosaccharide, fucoside **43** (4 equiv per glycosylation site, x mol) and 2,6-di-*tert*-butyl-4-methylpyridine (3x mol) were coevaporated with toluene (2 × 3 mL) before addition of beaded 4 sieves (1.0 g). A mixture of CH_2Cl_2/Et_2O (2:1 1 mL) was added and the reaction stirred for 3 h before addition of MeOTf (3x mol). The reaction was stirred for a further 12 h before it was diluted with CH_2Cl_2 (30 mL), washed with $NaHCO_3$ (5 mL) and dried ($NaSO_4$). The solvents were removed under reduced pressure and the residue purified by preparative TLC.

Methyl 2,4-di-*O*-benzyl-3-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-6-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[6-*O*-benzoyl-3-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-α-D-mannopyranoside (44): Heptasaccharide **36** (106 mg, 37 μmol) was dechloroacetylated in accordance with the general procedure furnishing alcohol **39** (91 mg, 88%). Alcohol **39** (89 mg, 32 μmol) was subsequently fucosylated with sulfide **43** (49 mg, 129 μmol) in accordance with the general procedure (without addition of base) to afford octasaccharide **44** (95 mg, 97%) as a white glass after purification by preparative TLC (EtOAc/petrol 1:1). ^{1}H NMR ($CDCl_3$): $\delta = 1.26 – 1.27$ (m, 6H; H-6F, $(CH_3)_2$C), 1.31 (s, 3H; $(CH_3)_2$C), 1.68 (s, 3H; $(CH_3)_2$C), 1.89 (s, 3H; CH_3CO), 1.93 (s, 3H; CH_3CO), 1.97 (s, 3H; CH_3CO), 1.99 (s, 3H; CH_3CO), 2.05 (s, 3H; CH_3CO), 2.11 (s, 3H; CH_3CO), 2.44 – 2.46 (m, 1H; H-5D), 2.75 – 2.81 (m, 2H; H-6Ba, 6Ca), 3.16 (s, 3H; OCH_3), 3.21 (d, $J = 10.2$ Hz, 1H; H-6Cb), 3.30 (d, $J = 10.2$ Hz, 1H; H-6Aa), 3.34 – 3.72 (m, 4H), 3.76 (dd, $J = 2.2$, 9.4 Hz, 1H; H-3C), 3.77 – 3.90 (m, 7H), 3.94 (dd, $J = 2.7$, 9.5 Hz, 1H; H-3A), 3.95 – 5.34 (m, 56H), 5.55 (dd, $J = 9.0$, 10.6 Hz, 1H; H-2E′), 6.83 – 8.20 (m, 68H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 16.1$ (C-6F) [20.5, 20.6, 20.7 (CH_3CO)], [26.1, 27.7 (CH_3)], 54.6 (C-2D), 54.7 (OCH_3), 56.2 (C-2D′), 60.8 (C-6E), 61.6 (C-6D), 62.6 (C-D′), 62.8 (C-6E′), 64.6 (C-5F), 65.9 (C-6A), 66.6 (C-4E), 69.2 (C-2E), 69.9 (C-6C), 70.1 (C-6B), 70.5 (C-3F), 70.6 (C-5E′, 5E), 70.7 (C-3D), 70.8 (C-5A, OCH_2Ph), 71.1 (C-5C), 71.2 (C-3E), 71.8 (C-5D), 72.1 (C-4F), 72.2 (C-2F), [72.4, 72.5 (OCH_2Ph)], 72.6 (C-5B), 72.7 (C-3D′), 72.8 (C-2C), 72.9 (OCH_2Ph), 73.0 (C-2B), 73.3 (C-2E′, 5D′), 73.5 (C-4E′), 73.8 (OCH_2Ph), 74.3 (C-4B), 74.4 (C-4C), 74.5 (C-4A), [74.8, 75.0 (OCH_2Ph)], 75.9 (C-4D′), 76.8 (C-3C), 77.2 (C-4D), 77.5 (C-2A), 77.6 (C-3E′), 77.9 (C-3B), 78.8 (C-3A), 95.7 (C-1D), 96.8 (C-1D′), 97.0 (C-1C), 97.5 (C-1F), 98.5 (C-1A), 98.7 (C-1B), 100.2 (C-1E′), 101.3 (C-1E), 110.9 ($(CH_3)_2CO_2$), [123.1, 123.3, 123.5, 123.7, 125.7, 126.8, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8 (CH)], [129.2, 129.3 (C)], [129.5, 129.8, 129.9 (CH)], 130.1 (C), [131.3, 131.7, 133.2, 133.3, 133.5, 133.7 (CH)], [137.9, 138.2, 138.4, 138.5, 138.7 (C)], [164.9, 166.0, 166.4, 166.8, 167.4, 167.9, 168.9, 169.2, 169.3, 169.8, 170.1, 170.4 (C=O)]; IR (film): $\tilde{\nu} = 2934$, 1748 (C=O), 1716 (C=O), 1454, 1386, 1223, 1071, 720 cm^{-1}; HRMS (ES) calcd for $C_{168}H_{176}O_{53}N_2Na$: 3092.1030; found 3092.1192.

Methyl 2,4-di-*O*-benzyl-3-*O*-(3,4,6-tri-*O*-benzyl-2-*O*-{6-*O*-benzoyl-3-*O*-[3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl]-4-*O*-[6-*O*-benzoyl-3:4-*O*-isopropylidene-2-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl]-2-deoxy-2-phthalimido-β-D-glucopyranosyl}-α-D-mannopyranosyl)-6-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[6-*O*-benzoyl-3-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-α-D-mannopyranoside (45): Heptasaccharide **37** (54 mg, 18 μmol) was dechloroacetylated in accordance with the general procedure furnishing alcohol **40** (36 mg, 72%). Alcohol **40** (36 mg, 13 μmol) was subsequently fucosylated with sulfide **43** (60 mg, 157 μmol) in accordance with the general procedure to afford decasaccharide **45** (23 mg, 48%) as a white glass after purification by preparative TLC (EtOAc/petrol 2:3 triple elution). ^{1}H NMR ($CDCl_3$): $\delta = 1.16$ (d, $J = 6.2$ Hz, 3H; H-6F′), 1.22 (d, $J =$ 6.3 Hz, 3H; H-6G), 1.26 (d, $J = 6.3$ Hz, 3H; H-6F), 1.31 (s, 6H; $(CH_3)_2$C), 1.48 (s, 3H; $(CH_3)_2$C), 1.58 (s, 3H; $(CH_3)_2$C), 1.63 (s, 3H; CH_3CO), 1.68 (s, 3H; CH_3CO), 1.89 (s, 3H; CH_3CO), 1.95 (s, 3H; CH_3CO), 1.97 (s, 3H; CH_3CO), 2.15 (s, 3H; CH_3CO), 2.71 – 2.80 (m, 1H; H-6Ba), 2.81 – 2.88 (m, 1H; H-6Ca), 3.13 (s, 3H; OCH_3), 3.24 – 4.90 (m, 74H), 5.00 – 5.03 (m, 1H; H-5F′), 5.24 (s, 1H; H-4F′), 5.25 – 5.36 (m, 6H), 5.42 (s, 1H; H-4G), 5.49 (d, $J = 3.2$ Hz, 1H; H-1G), 6.84 – 8.21 (m, 88H; Ar); ^{13}C NMR ($CDCl_3$): $\delta =$ 15.9 (C-6F), 16.1 (C-6G), 16.3 (C-6F′), [20.5, 20.6, 20.7 (CH_3CO)], [26.0, 26.3, 27.7, 27.9 (CH_3)], 54.6 (C-2D′), 56.6 (C-2D), 62.3 (C-6D′), 62.6 (C-6D), 62.8 (C-6E′), 62.9 (C-6E), 64.4 (C-5F′), 64.5 (C-5F), 65.0 (C-5G), 65.8 (C-6A), 69.5 (C-3G), 69.8 (OCH_2Ph), 69.9 (C-6C), 70.4 (C-3F), 70.5 (C-3F′), 70.7 (C-6B), 71.0 (C-5C), 71.1 (C-5A), 71.7 (OCH_2Ph), 71.9 (C-4G), 72.1 – 72.2 (C-2F, 2G, 4F, 5B, 4F′, 5E, 5E′), 72.3 (OCH_2Ph), 72.4 (C-2F′, 2B, 3D, 4A), [72.5, 72.6, 72.8 (OCH_2Ph)], 73.2 (C-2C), 73.3 (C-2E′, 5D), 73.4 (C-5D′), 73.5 (C-4E′), 73.6 (C-4E), 73.7 (C-3D′), 74.3 (C-4C), 74.4 (C-4B, OCH_2Ph), [74.5, 74.6 (OCH_2Ph)], 75.3 (C-4D′), 75.9 (C-4D), 77.0 (C-2E), 77.2 (C-3C), 77.4 (C-3B), 77.5 (C-2A), 77.6 (C-3E′), 79.4 (C-3E), 80.1 (C-3A), 96.2 (C-1G, 1D′), 96.9 (C-1C), 97.0 (C-1D), 97.5 (C-1F), 97.9 (C-1A), 98.2 (C-1F′), 99.0 (C-1B), 100.2 (C-1E, 1E′), [110.3, 110.9 ($(CH_3)_2CO_2$)], [123.4, 127.1, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 128.4, 128.5, 128.7, 128.8 (CH)], [129.1, 129.3 (C)], 129.4 (C), 129.5 (C), [129.6, 129.8, 129.9, 130.1 (CH)], [130.3, 131.6, 132.1, 132.1 (C)], [133.1, 133.2, 133.3, 133.5, 133.9 (CH)], [137.9, 138.0, 138.1, 138.2, 138.4, 138.6, 138.8 (C)], [164.9, 165.3, 166.0, 166.4, 166.5, 166.7, 169.1, 169.2, 169.3, 169.4, 170.1, 170.3, 170.4 (C=O)]; IR (film): $\tilde{\nu} = 3030$, 1722 (C=O), 1601, 1453, 1385, 1251, 1097, 713 cm^{-1}; HRMS (ES) calcd for $[C_{207}H_{216}O_{61}N_2Na_2]^{2+}$: 1875.6823; found 1875.6879.

Methyl 2,4-di-*O*-benzyl-3-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[6-*O*-benzoyl-3-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-(2,6-di-*O*-benzoyl-3:4-*O*-isopropylidene-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-6-*O*-(3,4,6-tri-*O*-benzyl-2-*O*-{6-*O*-benzoyl-3-*O*-[3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl]-4-*O*-[6-*O*-benzoyl-3:4-*O*-isopropylidene-2-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl]-2-deoxy-2-phthalimido-β-D-glucopyranosyl}-α-D-mannopyranosyl)-α-D-mannopyranoside (46): Heptasaccharide **35** (104 mg, 35 μmol) was dechloroacetylated in accordance with the general procedure furnishing alcohol **41** (77 mg, 80%). Alcohol **41** (77 mg, 28 μmol) was subsequently fucosylated with sulfide **43** (128 mg, 335 μmol) in accordance with the general procedure to afford decasaccharide **46** (48 mg, 46%) as a white glass after purification by flash column chromatography (EtOAc/petrol gradient 3:2 →5:1) followed by prepara-

0947-6539/99/0511-3336 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 11

tive TLC (acetone/CH_2Cl_2 5:95). ^{1}H NMR ($CDCl_3$): $\delta = 1.14$ (d, $J = 6.2$ Hz, 3H; H-6F′), 1.26 (d, $J = 6.2$ Hz, 3H; H-6G′), 1.31 (s, (3H; CH_3)$_2$C), 1.32 (s, 3H; (CH_3)$_2$C), 1.33 (d, $J = 6.6$ Hz, 3H; H-6F), 1.48 (s, 3H; (CH_3)$_2$C), 1.60 (s, (3H; CH_3)$_2$C), 1.65 (s, 3H; CH_3CO), 1.68 (s, 3H; CH_3CO), 1.94 (s, 3H; CH_3CO), 1.95 (s, 3H; CH_3CO), 2.00 (s, 3H; CH_3CO), 2.16 (s, 3H; CH_3CO), 2.44–2.48 (m, 1H; H-6Ba), 2.64–2.65 (m, 1H; H-6Ca), 3.10 (s, 3H; OCH$_3$), 3.17 (d, $J = 10.6$ Hz, 1H; H-6Cb), 3.24 (t, $J = 9.4$ Hz, 1H; H-4B), 3.30–3.33 (m, 2H; H-4C, 6Aa), 3.38 (d, $J = 10.3$ Hz, 1H; H-6Bb), 3.44–3.47 (m, 1H; H-5B), 3.54–3.74 (m, 14H), 3.80–3.81 (m, 1H; H-5E), 3.86 (m, 44H), 4.90 (d, $J = 3.3$ Hz, 1H; H-1F), 4.92–5.10 (m, 6H), 5.15 (d, $J = 12.0$ Hz, 1H; H-6D′b), 5.25–5.94 (m, 9H), 5.44 (s, 1H; H-4G), 5.49 (d, $J = 3.3$ Hz, 1H; H-1G), 6.77–8.26 (m, 88H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 15.8$ (C-6G), 16.2 (C-6F), 16.3 (C-6F′), [20.5, 20.7 (*C*H$_3$CO)], [26.0, 26.1, 27.7, 28.0 (CH$_3$)], 54.7 (OCH$_3$), 56.1 (C-2D), 56.4 (C-2D′), 62.2 (C-6D′), 62.4 (C-6D), 62.8 (C-6E), 62.9 (C-6E′), 64.4 (C-5F′), 64.5 (C-5F), 65.0 (C-5G′), 66.3 (C-6A), 69.5 (C-3G′), 69.7 (O*C*H$_2$Ph), 70.1 (C-6C), 70.3 (O*C*H$_2$Ph), 70.4 (C-3F, 5A), 70.5 (C-3F′), 70.7 (C-6B), 71.0 (C-5C), 71.9 (C-4G′), 72.2 (C-2F, 2F′, 3D, 4F, 4F′, 5B, 5D, 5E, 5E′, O*C*H$_2$Ph), 72.4 (O*C*H$_2$Ph), 72.5 (C-2C), 72.6 (O*C*H$_2$Ph), 72.7 (C-2B), 72.8 (O*C*H$_2$Ph), 73.1 (C-2G′), 73.3 (C-2E), 73.4 (O*C*H$_2$Ph), 73.5 (C-3D′), 73.6 (C-5D′), 73.7 (C-4E), 74.1 (C-4B), 74.2 (C-4C), 74.6 (C-4E′, O*C*H$_2$Ph), 74.8 (C-4A), 75.5 (C-4D′), 75.9 (C-4D), 76.8 (C-2E′), 77.0 (C-3C), 77.4 (C-2A), 77.6 (C-3B), 77.8 (C-3E), 78.6 (C-3A), 79.4 (C-3E′), 96.0 (C-1D), 96.2 (C-1G′), 96.8 (C-1C, 1D′), 97.5 (C-1F), 97.9 (C-1F′), 98.5 (C-1A), 99.7 (C-1B), 100.1 (C-1E), 100.2 (C-1E′), [110.3, 111.0 ((CH$_3$)$_2$*C*O$_2$)], [123.4, 123.6, 125.5, 127.1, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 128.8, 128.9 (CH)], 129.3 (C), [129.4, 129.5 (CH)], 129.6 (C), 130.1 (C), 130.2 (CH), [131.8, 132.1 (C)], [133.1, 133.2, 133.54, 133.7, 133.9 (CH)], [137.9, 138.0, 138.1, 138.3, 138.4, 138.6, 138.7 (C)], [164.9, 165.3, 165.9, 166.5, 166.7, 166.8, 168.9, 169.1, 169.3, 170.3, 170.4 (C=O)]; IR (film): $\tilde{\nu} = 2922$, 1744 (C=O), 1716 (C=O), 1602, 1453, 1386, 1246, 1161, 1103, 1069, 714 cm^{-1}; HRMS (ES) calcd for $[C_{207}H_{216}O_{61}N_2Na_2]^{2+}$: 1875.6823; found 1875.6879.

Methyl 2,4-di-*O*-benzyl-3,6-di-*O*-(3,4,6-tri-*O*-benzyl-2-*O*-{6-*O*-benzoyl-3-*O*-[3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl]-4-*O*-[6-*O*-benzoyl-3:4-*O*-isopropylidene-2-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl]-2-deoxy-2-phthalimido-β-D-glucopyranosyl}-α-D-mannopyranosyl)-α-D-mannopyranoside (47): Heptasaccharide **38** (107 mg, 36 μmol) was dechloroacetylated in accordance with the general procedure furnishing alcohol **42** (69 mg, 72%). Alcohol **42** (69 mg, 26 μmol) was subsequently fucosylated with sulfide **43** (160 mg, 418 μmol) in accordance with the general procedure to afford undecasaccharide **47** (45 mg, 44%) as a white glass after purification by repeated preparative TLC (elution: 1. EtOAc/petrol 45:55, triple elution 2. acetone/CH_2Cl_2 5:95). (Due to signal overlap fucoside-G could not be distinguished from fucoside-G′ and signals originating from the residues are thus both identified as H- or C-G.) ^{1}H NMR ($CDCl_3$): $\delta = 1.10–1.15$ (m, 6H; H-6F, 6F′), 1.23 (d, $J = 6.4$ Hz, 3H; H-6G), 1.26 1 (d, $J = 6.6$ Hz, 3H; H-6G), 1.31 (s, 3H; (CH_3)$_2$C), 1.32 (s, 3H; CH_3)$_2$C), 1.45 (s, 3H; (CH_3)$_2$C), 1.63 (s, 3H; CH_3CO), 1.65 (s, 3H; CH_3CO), 1.90 (s, 3H; CH_3CO), 1.93 (s, 3H; CH_3CO), 1.95 (s, 6H; CH_3CO), 2.74–2.79 (m, 1H; H-6Ca), 2.80–2.85 (m, 1H; H-6Ba), 3.12 (s, 3H; OCH$_3$), 3.23 (d, $J = 10.3$ Hz, 1H; H-6Cb), 3.31 (d, $J = 9.8$ Hz, 1H; H-6Aa), 3.34–4.96 (m, 83H), 5.00–5.03 (m, 1H; H-5F), 5.08–5.10 (m, 2H; H-1D, 5F′), 5.14 (d, $J = 11.6$ Hz, 1H; H-6D′), 5.23–5.38 (m, 7H), 5.44–5.45 (m, 2H; H-4G), 5.48 (s, 2H; H-1G), 6.82–8.21 (m, 88H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = [15.8, 15.9$ (C-6G)], 16.2 (C-6F), 16.3 (C-6F′), [20.5, 20.7 (*C*H$_3$CO)], [26.0, 26.1, 27.9, 28.0 (CH$_3$)], 54.6 (OCH$_3$), 56.4 (C-2D), 56.7 (C-2D′), 62.3 (C-6D′), 62.4 (C-6D), 62.9 (C-6E, 6E′), 64.3 (C-5F′), 64.5 (C-5F), 65.0 (C-5G), 66.3 (C-6A), 69.5 (C-3G), [69.7, 69.8 (O*C*H$_2$Ph), 70.0 (C-6C), 70.4 (C-3F′), 70.5 (C-5A), 70.6 (C-3F), 70.8 (C-6B), 71.0 (C-5C), 71.8 (O*C*H$_2$Ph), 71.9 (C-4G), 72.1–72.4 (C-2B, 2C, 2F, 2F′, 2G, 4A, 4F, 4F′, 5B, 5E, 5E′, O*C*H$_2$Ph), [72.6, 72.8 (O*C*H$_2$Ph), 73.1 (C-5D′), 73.3 (C-5D), 73.4 (C-3D′), 73.5 (C-4E′), 73.6 (C-4E), 73.7 (C-3D), 74.1 (C-4B, 4C), [74.5, 74.6 (O*C*H$_2$Ph)], 75.4 (C-4D), 75.5 (C-4D′), 76.8 (C-2E), 76.9 (C-2E′), 77.0 (C-3C), 77.3 (C-2A), 77.5 (C-3B), 79.4 (C-3E′), 79.5 (C-3E), 80.3 (C-3A), 96.2 (C-1G), 96.7 (C-1C, 1D), 96.9 (C-1D′), 97.9 (C-1A), 98.0 (C-1F′), 98.2 (C-1F), 99.0 (C-1B), 100.1 (C-1E′), 100.2 (C-1E), [110.2, 110.3 ((CH$_3$)$_2$*C*O$_2$)], [123.4, 127.0, 127.1, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 128.5, 128.8, 129.5, 129.6 (CH)], 129.7 (C), 129.8 (CH), [130.1, 131.7, 132.0, 132.3 (C)], [133.1, 133.2, 133.7, 133.9 (CH)], [138.0, 138.1, 138.2, 138.3, 138.4, 138.5, 138.6, 138.7, 138.9 (C)], [165.4, 166.5, 169.2, 169.3, 169.6, 170.3, 170.4 (C=O)]; IR (film): $\tilde{\nu} = 2920$, 2843, 1745 (C=O), 1714 (C=O), 1452, 1378, 1246, 1069, 714 cm^{-1}; HRMS (ES) calcd for $[C_{217}H_{232}O_{66}N_2Na_2]^{2+}$: 1983.7322; found 1983.7280.

Methyl 6-*O*-benzoyl-3-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-[6-*O*-benzoyl-3:4-*O*-isopropylidene-2-*O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl]-2-deoxy-2-phthalimido-β-D-glucopyranoside (49): Disaccharide **48** (36 mg, 53 μmol), prepared by methanolysis of **34**, was reacted with sulfide **43** (161 mg, 42 μmol) under conditions outlined in the general procedure to afford tetrasaccharide **49** (43 mg, 69%) as a white glass after purification by flash column chromatography (petrol/Et_2O gradient 1:1 → 3:7) followed by preparative TLC (acetone/CH_2Cl_2 4:96 double elution). $[\alpha]_D^{30} = -45.2$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR ($CDCl_3$): $\delta = 1.10$ (d, $J = 6.5$ Hz, 3H; H-6F), 1.23 (d, $J = 6.5$ Hz, 3H; H-6G), 1.30 (s, 3H; (CH_3)$_2$C), 1.46 (s, 3H; (CH_3)$_2$C), 1.63 (s, 3H; CH_3CO), 1.94 (s, 3H; CH_3CO), 1.99 (s, 3H; CH_3CO), 2.14 (s, 3H; CH_3CO), 3.34 (s, 3H; OCH$_3$), 3.59 (dd, $J = 3.7$, 10.8 Hz, 1H; H-2F), 3.68 (t, $J = 8.0$ Hz, 1H; H-2E), 3.81–3.83 (m, 1H; H-5D), 3.86–3.89 (m, 2H; H-2G, 5E), 4.03–4.09 (m, 3H; H-3E, 4E, OC*H*$_2$Ph), 4.20 (t, $J = 9.6$ Hz, 1H; H-4D), 4.26 (d, $J = 12.6$ Hz, 1H; OC*H*$_2$Ph), 4.37 (dd, $J = 8.6$, 9.6 Hz, 1H; H-2D), 4.48–4.70 (m, 6H; H-1E, 5G, 6Da, 6Ea, OC*H*$_2$Ph), 4.79 (t, $J = 9.6$ Hz, 1H; H-3D), 4.88–4.92 (m, 2H; H-1F, 6Eb), 5.01 (d, $J = 8.6$ Hz, 1H; H-1D), 5.06–5.07 (m, 2H; H-5F, 6Db), 5.23 (s, 1H; H-4F), 5.28 (dd, $J = 3.1$, 10.7 Hz, 1H; H-3G), 5.32 (dd, $J = 3.1$, 10.8 Hz, 1H; H-3F), 5.42 (d, $J = 3.1$ Hz, 1H; H-4G), 5.47 (d, $J = 3.5$ Hz, 1H; H-1G), 6.82–8.20 (m, 24H; Ar); ^{13}C NMR ($CDCl_3$): $\delta = 15.7$ (C-6G), 16.3 (C-6F), [20.5, 20.7, 20.8 (*C*H$_3$CO)], [26.0, 28.0 (CH$_3$)], 56.4 (C-2D), 56.9 (OCH$_3$), 62.2 (C-6D), 62.8 (C-6E), 64.4 (C-5F), 64.9 (C-5G), 69.7 (C-3G), 70.6 (C-3F), 71.8 (C-4G), 72.1 (C-4F, 5E), 72.3 (O*C*H$_2$Ph), 72.4 (C-2F), 72.9 (O*C*H$_2$Ph), 73.0 (C-2G), 73.5 (C-3D), 73.6 (C-4E, 5D), 75.5 (C-4D), 76.6 (C-2E), 79.4 (C-3E), 96.0 (C-1G), 98.0 (C-1F), 99.5 (C-1D), 100.0 (C-1E), 110.1 ((CH$_3$)$_2$*C*O$_2$), [123.6, 127.3, 127.5, 127.6, 127.7, 127.9, 128.2, 128.8, 129.4 (CH)], 129.7 (C), 129.8 (CH), [130.1, 131.8 (CH)], [133.1, 133.2, 134.1 (CH)], [137.9, 138.3 (C)], [165.5, 166.4, 167.9, 169.3, 169.9, 170.3, 170.6 (C=O)]; IR (film): $\tilde{\nu} = 2940$, 1744 (C=O), 1717 (C=O), 1453, 1379, 1241, 1098, 1043, 717 cm^{-1}; HRMS (ES) calcd for $C_{72}H_{79}O_{26}NNa$: 1396.4782; found 1396.4763.

General protocol for deprotection:

1. Acetonide removal:
   The oligosaccharide (x mol) was dissolved in CH_2Cl_2 (0.26 μmol mL^{-1}) and a 50% aqueous solution of trifluoroacetic acid (9x L) was added. The mixture was stirred vigorously for 2 d before the reaction was quenched by addition of Et_3N (0.1 mL) and the solvent removed under reduced pressure.
2. Phthalimide/debenzoylation removal and global acetylation:
   The oligosaccharide (x mol) and hydrazine monohydrate (2000x mol) were heated at reflux in EtOH (4 mL) for 12 h. After the reaction had cooled the solvent was removed under reduced pressure and the residue coevaporated with toluene (2 × 10 mL). The residue was then dissolved in pyridine (1 mL) and Ac_2O (1 mL) was added dropwise and the mixture stirred for 12 h. The reaction was then concentrated under reduced pressure and the residue again coevaporated with toluene (2 × 10 mL) before purification on Sephadex LH-20 (MeOH/CH_2Cl_2 1:1).
3. O-Deactylation and debenzylation:
   The oligosaccharide was dissolved in MeOH and K_2CO_3 (10 mg) was added. The reaction was stirred for 12 h before it was diluted with MeOH (20 mL), quenched by addition of Amberlite IR-120 (plus), and filtered washing with MeOH (20 mL). The solvent was removed under reduced pressure. The resulting residue was redissolved in MeOH (2 mL), 20% wt Pd(OH)$_2$/C (50 mg) added and the reaction stirred under a H_2 atmosphere for a period of 7 d, the reaction being monitored by MALDI-TOF mass spectral analysis. Further catalyst (50 mg) was added every 2 d. On completion the reaction was filtered through a glass sinter and the catalyst washed with MeOH (50 mL). The solvent was removed under reduced pressure and the residue purified by size-exclusion chromatography on Sephadex G-15 (H_2O) and dried by lyophilisation.

Methyl 3,6-di-*O*-(2-*O*-{3-*O*-[α-L-fucopyranosyl]-4-*O*-[2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl]-2-deoxy-2-acetamido-β-D-glucopyranosyl}-α-D-mannopyranosyl)-α-D-mannopyranoside (1): Undecasaccharide **47** (41 mg, 10 μmol) was deprotected under the conditions outlined in the general protocol to furnish **1** (18 mg, 94%) as an amorphous white powder. (Due to signal overlap fucosides-F and G could not be distinguished from fucosides-F′ and G′, likewise for glucosamine D and D′ and galactose E and

E′ hence signals originating from these residues are thus both identified as H- or C-D, E, F and G, respectively.) ^{1}H NMR (D_2O): $\delta = 1.16$ (d, $J =$ 7.1 Hz, 3H; H-6F), 1.17 (d, $J = 6.8$ Hz, 3H; H-6F), 1.18 (d, $J = 6.6$ Hz, 3H; H-6G), 1.19 (d, $J = 6.8$ Hz, 3H; H-6G), 1.98 (s, 3H; CH_3CO), 1.99 (s, 3H; CH_3CO), 3.33 – 3.35 (s, 4H; H-5D, OCH_3), 3.41 – 4.01 (m, 49H), 3.98 – 4.01 (m, 2H; H-2A, 6Ab), 4.05 (s, 1H; H-2C), 4.09 (s, 1H; H-2B), 4.15 – 4.20 (m, 2H; H-5G), 4.43 (d, $J = 7.6$ Hz, 2H; H-1E), 4.48 – 4.52 (m, 2H; H-1D), 4.68 (s, 1H; H-1A), 4.79 – 4.81 (m, 2H; H-5F), 4.83 (s, 1H, H-1C), 5.04 – 5.06 (3H, m, H-1B, 1F), 5.20 – 5.21 (2H, m, H-1G); selected ^{13}C NMR (D_2O): $\delta =$ [15.4, 15.5 (6-F,G)], 22.5 (CH_3CO), 54.9 (OCH_3), 65.3 (C-6A), 66.7 (C-5F), 66.9 (C-5G), 69.5 (C-2A), 75.6 (C-5D), 76.4 (C-2C), 76.5 (C-2B), 96.7 (C-1C), 98.5 (C-1F), 99.2 (C-1D), 99.3 (C-1B), 99.5 (C-1G), 100.2 (C-1E), 101.1 (C-1A), 101.2 (C-1E); HRMS (MALDI) calcd for $C_{71}H_{120}O_{52}N_2Na$: 1855.6704; found 1855.6765.

Methyl 3-*O*-{2-*O*-[3-*O*-(α-L-fucopyranosyl)-4-*O*-(β-D-galactopyranosyl)-2-deoxy-2-acetamido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-6-*O*-(2-*O*-{3-*O*-[α-L-fucopyranosyl]-4-*O*-[2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl]-2-deoxy-2-acetamido-β-D-glucopyranosyl}-α-D-mannopyranosyl)-α-D-mannopyranoside (2): Decasaccharide **46** (44 mg, 12 μmol) was deprotected under the conditions outlined in the general protocol to furnish **2** (19 mg, 95 %) as an amorphous white powder. (Due to signal overlap fucoside-F could not be distinguished from fucoside-F′, likewise for glucosamine D and D′, and signals originating from these residues are thus both identified as H- or C-F and H- or C-D, respectively.) ^{1}H NMR (D_2O): $\delta = 1.10$ (d, $J = 6.6$ Hz, 3H; H-6F), 1.16 (d, $J = 6.6$ Hz, 3H; H-6F), 1.20 (d, $J = 6.6$ Hz, 3H; H-6G), 2.05 (s, 3H; CH_3CO), 2.06 (s, 3H; CH_3CO), 3.35 (s, 4H; H-5D, OCH_3), 3.41 – 3.95 (m, 46H), 4.00 (dd, $J = 7.5$ Hz, 11.2, 1H; H-6Ab), 4.02 (s, 1H; H-2A), 4.05 (s, 1H; H-2C), 4.11 (s, 1H; H-2B), 4.17 – 4.19 (m, 1H; H-5G′), 4.37 (d, $J = 7.8$ Hz, 1H; H-1E), 4.43 (d, $J =$ 7.8 Hz, 1H; H-1E′), 4.47 – 4.50 (m, 2H; H-1D), 4.68 (s, 1H; H-1A), 4.75 – 4.80 (m, 2H; 2 × H-5F), 4.83 (s, 1H; H-1C), 5.03 (s, 1H; H-1B), 5.05 (s, 2H; H-1F), 5.21 (s, 1H; H-1G′); selected ^{13}C NMR (D_2O): $\delta =$ [15.3, 15.4, 15.5 (6-F,G)], [22.4, 22.5 (CH_3CO)], 54.8 (OCH_3), 65.4 (C-6A), 66.7 (C-5F), 66.8 (C-5G′), 69.5 (C-2A), 75.6 (C-5D), 76.3 (C-2C), 76.4 (C-2B), 96.8 (C-1C), 98.5 (C-1F), 99.3 (C-1D), 99.4 (C-1B), 99.5 (C-1G′), 100.2 (C-1E′), 101.0 (C-1A), 101.8 (C-1E); MALDI-MS: calcd for $C_{65}H_{110}O_{48}N_2Na$: 1709.6125; found 1709.6077.

Methyl 3-*O*-(2-*O*-{3-*O*-[α-L-fucopyranosyl]-4-*O*-[2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl]-2-deoxy-2-acetamido-β-D-glucopyranosyl}-α-D-mannopyranosyl)-6-*O*-{2-*O*-[3-*O*-(α-L-fucopyranosyl)-4-*O*-(β-D-galactopyranosyl)-2-deoxy-2-acetamido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-α-D-mannopyranoside (3): Decasaccharide **45** (23 mg, 6 μmol) was deprotected under the conditions outlined in the general protocol to furnish **3** (10 mg, 95 %) as an amorphous white powder. (Due to signal overlap fucoside-F could not be distinguished from fucoside-F′, likewise for glucosamine D and D′, and signals originating from these residues are thus both identified as H- or C-F and H- or C-D, respectively.) ^{1}H NMR (D_2O): $\delta = 1.11$ (d, $J = 6.2$ Hz, 3H; H-6F), 1.16 (d, $J = 6.1$ Hz, 3H; H-6F), 1.19 (d, $J = 6.0$ Hz, 3H; H-6G), 1.97 (s, 3H; CH_3CO), 1.98 (s, 3H; CH_3CO), 3.34 (s, 4H; H-5D, OCH_3), 3.41 – 3.95 (m, 46H), 3.98 (d, $J = 10.8$ Hz, 1H; H-6Ab), 4.02 (s, 1H; H-2A), 4.06 (s, 1H; H-2C), 4.08 (s, 1H; H-2B), 4.17 – 4.18 (m, 1H; H-5G), 4.38 (d, $J = 7.6$ Hz, 1H; H-1E), 4.42 (d, $J = 7.5$ Hz, 1H; H-1E′), 4.49 (d, $J = 7.9$ Hz, 1H; H-1D), 4.54 (d, $J = 8.0$ Hz, 1H; H-1D), 4.68 (s, 1H; H-1A), 4.76 – 4.80 (m, 2H; H-5F), 4.85 (s, 1H; H-1C), 5.04 (s, 2H; H-1B, 1F), 5.06 (s, 1H; H-1F), 5.19 (s, 1H; H-1G); selected ^{13}C NMR (D_2O): $\delta =$ [15.3, 15.4, 15.5 (6-F,G)], 22.5 (CH_3CO), 54.8 (OCH_3), 65.2 (C-6A), 66.7 (C-5F), 66.9 (C-5G), 69.5 (C-2A), 75.6 (C-5D), 76.3 (C-2C), 76.5 (C-2B), 96.7 (C-1C), 98.5 (C-1F), 99.2 (C-1D), 99.3 (C-1B), 99.5 (C-1G), 100.2 (C-1E′), 101.2 (C-1A), 101.8 (C-1E); MALDI-MS calcd for $C_{65}H_{110}O_{48}N_2Na$ 1709.6125; found 1709.6016.

Methyl 3-*O*-{2-*O*-[4-*O*-(β-D-galactopyranosyl)-2-deoxy-2-acetamido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-6-*O*-{2-*O*-[3-*O*-(L-fucopyranosyl)-4-*O*-(β-D-galactopyranosyl)-2-deoxy-2-acetamido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-α-D-mannopyranoside (5): Octasaccharide **44** (81 mg, 26 μmol) was deprotected under the conditions outlined in the general protocol to furnish **5** (23 mg, 63 %) as an amorphous white powder. ^{1}H NMR (D_2O): $\delta = 1.11$ (d, $J = 6.4$ Hz, 3H; H-6F), 1.98 (s, 6H; CH_3CO), 3.35 (s, 3H; OCH_3), 3.41 – 3.96 (m, 41H), 3.99 (dd, $J = 3.9$, 11.3 Hz, 1H; H-6Ab), 4.03 (s, 1H; H-2A), 4.07 (s, 1H; H-2C), 4.12 (s, 1H; H-2B), 4.38 (d, $J = 7.7$ Hz, 1H; H-1E′), 4.40 (d, $J = 8.2$ Hz, 1H; H-1E), 4.51 (d, $J = 7.2$ Hz, 1H; H-1D), 4.54 (d, $J = 7.7$ Hz, 1H; H-1D′), 4.68 (s, 1H; H-1A), 4.77 (q, $J =$ 6.4 Hz, 1H; H-5F), 4.85 (s, 1H; H-1C), 5.05 (s, 1H; H-1B), 5.07 (d, $J =$ 4.0 Hz, 1H; H-1F); selected ^{13}C NMR (D_2O): $\delta = 15.3$ (6-F), [22.3, 22.4 (CH_3CO)], 54.8 (OCH_3), 65.4 (C-6A), 66.7 (C-5F), 69.4 (C-2A), 76.2 (C-2C), 76.5 (C-2B), 96.7 (C-1C), 98.6 (C-1F), 99.2 (C-1D′), 99.4 (C-1B), 99.5 (C-1D), 101.0 (C-1A), 101.8 (C-1E′), 102.9 (C-1E); MALDI: calcd for $C_{53}H_{90}O_{40}N_2Na$: 1417.4976; found 1417.4924.

Methyl 3,6-di-*O*-{2-*O*-[4-*O*-(β-D-galactopyranosyl)-2-deoxy-2-acetamido-β-D-glucopyranosyl]-α-D-mannopyranosyl}-α-D-mannopyranoside (6): Heptasaccharide **30** (170 mg, 64 μmol) was deprotected under the conditions outlined in the general protocol to furnish **6** (64 mg, 80 %) as an amorphous white powder. ^{1}H NMR (D_2O): $\delta = 1.98$ (s, 3H; CH_3CO), 1.99 (s, 6H; CH_3CO), 3.34 (s, 3H; OCH_3), 3.42 – 3.87 (m, 33H), 3.90 (d, $J =$ 11.7 Hz, 2H; H-6Db, 6D′b), 3.98 (d, $J = 11.1$ Hz, 1H; H-6Ab), 4.02 (s, 1H; H-2A), 4.06 (s, 1H; H-2C), 4.11 (s, 1H; H-2B), 4.40 (d, $J = 7.8$ Hz, 2H; H-1E, 1E′), 4.51 (d, $J = 7.5$ Hz, 1H; H-1D), 4.53 (d, $J = 7.7$ Hz, 1H; H-1D′), 4.66 (s, 1H; H-1A), 4.86 (s, 1H; H-1C), 5.04 (s, 1H; H-1B); selected ^{13}C NMR (D_2O): $\delta = 22.3$ (CH_3CO), 54.9 (OCH_3), 60.0 (C-6D, 6D′), 65.4 (C-6A), 69.5 (C-2A), 76.3 (C-2C), 76.5 (C-2B), 96.8 (C-1C), 99.4 (C-1B, 1D′), 99.5 (C-1D), 101.0 (C-1A), 102.9 (C-1E, 1E′); MALDI: calcd for $C_{47}H_{80}O_{26}N_2Na$: 1271.4388; found 1271.4355.

Methyl 3-*O*-(α-L-fucopyranosyl)-4-*O*-[2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl]-2-deoxy-2-acetamido-β-D-glucopyranoside (10):[38] Tetrasaccharide **49** (39 mg, 29 μmol) was deprotected under the conditions outlined in the general protocol to furnish **10** (19 mg, 95 %) as an amorphous white powder, spectroscopically identical to that prepared by Lemieux.

Methyl 3,6-di-*O*-(2-*O*-[-2-acetamido-2-deoxy-3-*O*-{α-L-fucopyranosyl}-4-*O*-{β-D-galactopyranosyl}-β-D-glucopyranosyl]-α-D-mannopyranosyl)-α-D-mannopyranoside (4): α-1,3-Fucosyltransferase V (30 mU, 60 μL) was added to a solution of the heptasaccharide **6** (5.0 mg, 4.0 μmol) and GDP-L-fucose (5.4 mg, 8.2 μmol) in MES buffer (1.0 mL, 50 mM, pH 6.0) containing 1 mg BSA, 7 U alkaline phosphatase and $MnCl_2 \cdot 4H_2O$ (25 μL of a 1M solution). The mixture was shaken at 37 °C for 8 d (additions of identical amounts of GDP-L-fucose, α-1,3-fucosyltransferase V and alkaline phosphatase were repeated after 2 d, 4 d and 6 d). The reaction mixture was centrifuged, the supernatant was concentrated and purified with Bio Gel P-4 (aq. 50 mM NH_4HCO_3) to give **4** (3.7 mg, 59 %) as a white solid after lyophilisation. (Due to signal overlap residues-D, E and F could not be distinguished from residues-D′, E′ and F′. Therefore signals originating from these residues are thus both identified as H- or C-D, E and F.) ^{1}H NMR (D_2O): $\delta = 1.09 – 1.13$ (s, 6H; H-6F), 1.97 (s, 3H; CH_3CO), 1.98 (s, 3H; CH_3CO), 3.35 (s, 3H; OCH_3), 3.40 – 3.95 (m, 44H), 3.96 – 4.00 (m, 1H; H-6A), 4.02 (s, 1H; H-2A), 4.06 (s, 1H; H-2C), 4.11 (s, 1H; H-2B), 4.36 – 4.39 (m, 2H; H-1E), 4.50 – 4.55 (m, 2H; H-1D), 4.68 (s, 1H; H-1A), 4.74 – 4.78 (m, 2H; H-5F), 4.85 (s, 1H; H-1C), 5.04 (s, 1H; H-1B), 5.05 – 5.07 (m, 2H; H-1F); selected ^{13}C NMR (HMQC, D_2O): $\delta = 15.2$ (C-6F), 22.4 (CH_3CO), 54.9 (C-6A), 66.6 (C-5F), 69.4 (C-2A), 76.3 (C-2C), 76.5 (C-2B), 96.6 (C-1C), 98.5 (C-1F), 99.2 (C-1D), 99.4 (C-1B), 101.0 (C-1A), 101.8 (C-1E), 101.9 (C-1E); MS (MALDI) calcd for $C_{69}H_{116}N_4O_{44}$: 1563.5546; found 1563.5521.

Methyl 3,6-di-*O*-(2-*O*-[2-acetamido-2-deoxy-4-*O*-{6-*O*-(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulo-pyranuronic acid)-β-D-galactopyranosyl}-β-D-glucopyranosyl]-α-D-mannopyranosyl)-α-D-mannopyranoside (7): α-2,6-Sialyltransferase (30 mU, 30 μL) was added to a solution of the heptasaccharide **6** (5.0 mg, 4.0 μmol) and CMP-sialic acid (5.0 mg, 8.0 μmol) in HEPES buffer (1.0 mL, 50 mM, pH 7.0) containing 1 mg BSA, and 7 U alkaline phosphatase. The mixture was shaken at 37 °C for 3 d (additions of identical amounts of CMP-sialic acid, α-2,6-sialyltransferase and alkaline phosphatase were repeated after 2 d, 4 d, and 7 d). The reaction mixture was centrifuged, the supernatant was concentrated and purified with Bio Gel P-4 (100 mM NH_4HCO_3) to give **7** (4.1 mg, 56 %) as a white solid after lyophilisation. (Due to signal overlap residues-D, E and H could not be distinguished from residues-D′, E′ and H′, hence signals originating from these residues are thus both identified as H- or C-D, E and H, respectively.) ^{1}H NMR (D_2O): $\delta = 1.65$ (t, $J = 11.7$ Hz, 2H; H-3H_{ax}), 1.96 (s, 6H; CH_3CO), 1.99 (s, 3H; CH_3CO), 2.00 (s, 3H; CH_3CO), 2.59 (dd, $J =$ 4.4, 11.6 Hz, 2H; H-3H_{eq}), 3.36 (s, 3H; OCH_3), 3.43 – 3.95 (m, 52H), 3.97 – 4.00 (m, 1H; H-6A), 4.02 (s, 1H; H-2A), 4.07 (s, 1H; H-2C), 4.12 (s, 1H; H-2B), 4.36 – 4.39 (m, 2H; H-1E), 4.52 – 4.57 (m, 2H; H-1D), 4.68 (s, 1H; H-1A), 4.90 (s, 1H; H-1C), 5.08 (s, 1H; H-1B); selected ^{13}C NMR (HMQC, D_2O): $\delta =$ [22.0, 22.4 (CH_3CO)], 40.1 (C-3H), 54.8 (OCH_3), 65.4 (C-6A),

0947-6539/99/0511-3338 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 11

69.5 (C-2A), 76.4 (C-2C), 76.5 (C-2B), 96.7 (C-1C), 99.3 (C-1D), 99.4 (C-1B), 101.0 (C-1A), 103.6 (C-1E); MS (MALDI): The $[M]^+$ ions were not stable to spectrometric analysis, however, global methylation allowed for some analysis: calcd for $C_{101}H_{178}N_4O_{52}Na$ 2303.48, found 2304.86.

Methyl 3,6-di-*O*-(2-*O*-[2-acetamido-2-deoxy-4-*O*-{3-*O*-(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulo-pyranuronic acid)-β-D-galacto-pyranosyl}-β-D-glucopyranosyl]-α-D-mannopyranosyl)-α-D-mannopyranoside (8): α-2,3-Sialyltransferase (60 mU, 60 μL) was added to a solution of the heptasaccharide **6** (10.0 mg, 8.0 μmol) and CMP-sialic acid (10.0 mg, 16.0 μmol) in HEPES buffer (2.0 mL, 100 mM, pH 7.5) containing 4 mg BSA, 14 U alkaline phosphatase, $MnCl_2 \cdot 4H_2O$ (10 mL of a 1 M solution), and $MgCl_2$ (40 μL 1 M solution). The mixture was shaken at 37 °C for 9 d (additions of identical amounts of CMP-sialic acid, α-2,3-sialyltransferase and alkaline phosphatase were repeated after 2 d, 4 d and 7 d). It was centrifuged, the supernatant was concentrated and purified with Bio Gel P-4 (aq. 150 mM NH_4HCO_3) to give **8** (14.7 mg, 98 %) as a white solid after lyophilisation. (Due to signal overlap residue-H could not be distinguished from residue-H′ hence signals originating from these residues are thus both identified as H- or C-H.) ^{1}H NMR (D_2O): $\delta = 1.73$ (t, $J = 12.2$ Hz, 2H; H-3H$_{ax}$), 1.96 (s, 6H; CH_3CO), 1.98 (s, 3H; CH_3CO), 1.99 (s, 3H; CH_3CO), 2.69 (dd, $J = 4.4$, 12.2 Hz, 2H; H-3H$_{eq}$), 3.34 (s, 3H; OCH_3), 3.43–3.96 (m, 50H), 3.97–3.99 (m, 1H; H-6A), 4.02–4.08 (m, 4H; H-2A, 2C, 3E, 3E′), 4.11 (s, 1H; H-2B), 4.46–4.49 (m, 2H; H-1E, 1E′), 4.50 (d, $J = 7.9$ Hz, 1H; H-1D), 4.52 (d, $J = 7.9$ Hz, 1H; H-1D′), 4.67 (s, 1H; H-1A), 4.86 (s, 1H; H-1C), 5.05 (s, 1H; H-1B); selected ^{13}C NMR (HMQC, D_2O): δ = [22.1, 22.3 (CH_3CO)], 39.6 (C-3H), 54.7 (OCH_3), 65.4 (C-6A), [69.6, 75.5, 75.6, 76.4 (C-2A, 2C, 3E, 3E′)], 76.6 (C-2B), 96.7 (C-1C), 99.3 (C-1B), 99.4 (C-1D′), 99.6 (C-1D), 101.0 (C-1A), [102.6, 102.7 (C-1E, 1E′)]; MS (MALDI): The $[M]^+$ ions were not stable to spectrometric analysis, however, global methylation allowed for some analysis: calcd for $C_{101}H_{178}N_4O_{52}Na$ 2303.48, found 2304.80.

5-Methoxycarbonylhexyl 2-acetamido-2-deoxy-3-*O*-(α-L-galactopyranosyl)-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (9): A solution of α-1,3-fucosyltransferase V (46 mU, 92 μL) was added to a solution of **52** (10.0 mg, 19.5 μmol) and GDP-L-galactose (12.0 mg, 19.5 μmol) in MES buffer (2.0 mL, 50 mM, pH 6.0) containing 4 mg BSA, 20 U alkaline phosphatase and $MnCl_2 \cdot 4H_2O$ (40 μL of a 1 M solution). The mixture was shaken at 37 °C for 6 d. (Addition of identical amounts of α-1,3-fucosyltransferase V, GDP-L-galactose and alkaline phosphatase was repeated after 48 h and 96 h) It was centrifuged, the supernatant was concentrated and purified with Bio Gel P-2 (aq. 50 mM NH_4HCO_3) to give **9** (9.2 mg, 70 %) as a white solid after lyophilisation. ^{1}H NMR (D_2O): δ = 1.23–1.29 (m, 2H; CH_2linker), 1.46–1.57 (m, 4H; CH_2linker), 1.95 (s, 3H; CH_3CO), 2.32 (t, $J = 7.4$ Hz, 2H; CH_2CO), 3.44–3.95 (m, 22H), 4.39 (d, J = 7.7 Hz, 1H; H-1D), 4.45 (d, $J = 8.2$ Hz, 1H; H-1E), 4.71 (t, $J = 6.4$ Hz, 1H, H-5F), 5.11 (d, $J = 3.6$ Hz, 1H; H-1F); selected ^{13}C NMR (D_2O): $\delta = 22.3$ (CH_3CO), [23.9, 24.7, 28.2 (CH_2linker)], 33.6 (CH_2CO), 69.8 (C-5F), 98.5 (C-1F), 100.9 (C-1D), 102.2 (C-1E); HRMS (FAB): calcd for $C_{27}H_{47}NO_{17}Na$: 696.2685; found 696.2677.

5-Methoxycarbonylhexyl 2-acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (11): A solution of α-1,3-fucosyltransferase V (46 mU, 92 μL) was added to a solution of **52** (15.7 mg, 30.1 μmol) and GDP-L-fucose (30.0 mg, 45.0 μmol) in MES buffer (4.0 mL, 50 mM, pH 6.0) containing 4 mg BSA, 30 U alkaline phosphatase and $MnCl_2 \cdot 4H_2O$ (80 μL of a 1 M solution). The mixture was shaken at 37 °C for 2 d. The reaction mixture was centrifuged, the supernatant was concentrated and purified with Bio Gel P-2 (aq. 50 mM NH_4HCO_3) to give **11** (14.5 mg, 72 %) as a white solid after lyophilisation. ^{1}H NMR (D_2O): $\delta = 1.15$ (d, $J = 6.5$ Hz, 3H; H-6F), 1.27–1.35 (m, 2H; CH_2linker), 1.5–1.64 (m, 4H; CH_2linker), 2.00 (s, 3H; OCH_3), 2.37 (t, J = 7.3 Hz, 2H; CH_2CO), 3.26–4.00 (m, 21H), 4.43 (d, $J = 7.8$ Hz, 1H; H-1E), 4.50 (d, $J = 7.6$ Hz, 1H; H-1D), 5.08 (d, $J = 3.5$ Hz, 1H; H-1F); selected ^{13}C NMR (D_2O): $\delta = 17.8$ (C-6F), 24.7 (CH_3CO), [26.4, 27.1, 30.7 (CH_2linker)], 36.1 (CH_2CO), 101.1 (C-1D), 103.4 (C-1E), 104.3 (C-1F); HRMS (FAB): calcd for $C_{27}H_{47}NO_{17}Cs$: 790.1898; found 790.1872.

Methyl 3,6-di-*O*-(2-*O*-[2-acetamido-2-deoxy-3-*O*-{α-L-fucopyranosyl}-4-*O*-(3-*O*-[5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulo-pyranuronic acid]-β-D-galactopyranosyl)-β-D-glucopyranosyl]-α-D-mannopyranosyl)-α-D-mannopyranoside (12): α-1,3-Fucosyltransferase V (30 mU, 60 μL) was added to a solution of **8** (5.1 mg, 2.8 μmol) and GDP-L-fucose (4.0 mg, 6.5 μmol) in MES buffer (1.0 mL, 50 mM, pH 6.0) containing 1 mg BSA, 7 U alkaline phosphatase and $MnCl_2 \cdot 4H_2O$ (20 μL of a 1 M solution). The mixture was shaken at 37 °C for 8 d (the addition of identical amounts of GDP-L-fucose, α-1,3-fucosyltransferase V and alkaline phosphatase was repeated after 2 d and 4 d). The reaction mixture was centrifuged, the supernatant was concentrated and purified with Bio Gel P-4 (aq. 150 mM NH_4HCO_3) to give **12** (4.1 mg, 69 %) as a white solid after lyophilisation. (Due to signal overlap residues-D, E, F and H could not be distinguished from residues-D′, E′, F′ and H′ hence signals originating from these residues are thus both identified as H- or C-D, E, F or H, respectively.) ^{1}H NMR (D_2O): $\delta = 1.10$ (d, $J = 1.9$ Hz, 3H; H-6F), 1.12 (d, $J = 1.9$ Hz, 3H; H-6F), 1.73 (t, $J = 12.2$ Hz, 2H; H-3H$_{ax}$), 1.96 (s, 6H; CH_3CO), 1.97 (s, 3H; CH_3CO), 1.98 (s, 3H; CH_3CO), 2.69 (dd, $J = 4.5$, 12.2 Hz, 2H; H-3H$_{eq}$), 3.35 (s, 3H; OCH_3), 3.42–3.95 (m, 57H), 4.00–4.04 (m, 3H; H-2A, H-3E), 4.07 (s, 1H; H-2C), 4.11 (m, 1H; H-2B), 4.43–4.47 (m, 2H; H-1E), 4.50–4.56 (m, 2H; H-1D), 4.67 (s, 1H; H-1A), 4.73–4.77 (m, 2H; H-5F), 4.85 (s, 1H; H-1C), 5.03 (s, 1H; H-1B), 5.04–5.07 (m, 2H; H-1F); selected ^{13}C NMR (HMQC, D_2O): $\delta = 15.2$ (C-6F), [22.0, 22.5 (CH_3CO)], 39.8 (C-3H), 54.8 (OCH_3), 66.6 (C-5F), [69.6, 75.6, 75.7, 76.4 (C-2B, 2C, 3E)], 96.7 (C-1C), 98.5 (C-1F), 99.3 (C-1D), 99.4 (C-1B), 101.0 (C-1A), 101.6 (C-1E); MS (MALDI): The $[M]^+$ ions were not stable to spectrometric analysis, however, global methylation allowed for some analysis: calcd for $C_{117}H_{208}N_4O_{60}Na$ 2651.87, found 2652.92.

5-Methoxycarbonylhexyl 2-acetamido-2-deoxy-4-*O*-(β-D-galactopyranosyl-3-*O*-[5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulo-pyranuronic acid])-β-D-glucopyranoside (13): A solution of the lactosamine derivative **52** (100 mg, 196 μmol), neuraminic acid (72 mg, 235 μmol), PEP · 3Na (138 mg, 587 μmol), $MgCl_2 \cdot 6H_2O$ (19 mg, 78 μmol), $MnCl_2 \cdot 4H_2O$ (4 mg, 12 μmol), KCl (7 mg, 78 μmol), CTP (12 mg, 23 μmol), ATP (1.25 mg, 2 μmol) and mercaptoethanol (3 μL) in HEPES buffer (200 mM, pH 7.5, 2.5 mL) was adjusted with 1 N NaOH to pH 7.5 and the enzymes NMK (2.5 U), PK (80 U), PPase (8 U), CMP-NeuAc synthetase (0.3 U) and α-2,3-sialyltransferase (0.8 U) were added to the solution. The mixture was left at ambient temperature for 5 d. It was concentrated, and the residue was puridied by flash column chromatography (EtOAc/MeOH/0.02 % $CaCl_2$ 5:2:1) to give the title compound as a colourless solid (114 mg, 73 %) which was spectroscopically identical to that reported previously.[7a]

5-Methoxycarbonylhexyl 2-acetamido-2-deoxy-3-*O*-(α-L-fucopyranosyl)-4-*O*-(3-*O*-[5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulo-pyranuronic acid]-β-D-galactopyranosyl)-β-D-glucopyranoside (14): α-1,3-Fucosyltransferase V (46 mU, 92 μL) was added to a solution of **13** (15.7 mg, 30.1 μmol) and GDP-L-fucose (30.0 mg, 45.0 μmol) in MES buffer (4.0 mL, 50 mM, pH 6.0) containing 4 mg BSA, 30 U alkaline phosphatase and $MnCl_2 \cdot 4H_2O$ (80 μL 1 M solution). The mixture was shaken at 37 °C for 24 h. The reaction mixture was centrifuged, the supernatant was concentrated and purified with Bio Gel P-2 (aq. 50 mM NH_4HCO_3) to give a white solid after lyophilisation (20.6 mg, 71 %) spectroscopically identical to that reported previously.[7a]

5-Methoxycarbonylhexyl 2-acetamido-2-deoxy-3-*O*-(α-L-galactopyranosyl)-4-*O*-(3-*O*-[5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulo-pyranuronic acid]-β-D-galactopyranosyl)-β-D-glucopyranoside (15): α-1,3-Fucosyltransferase V (46 mU, 92 μL) was added to a solution of **13** (18.5 mg, 23.0 μmol) and GDP-L-galactose (22.5 mg, 37.2 μmol) in MES buffer (3.0 mL, 50 mM, pH 6.0) containing 3 mg BSA, 20 U alkaline phosphatase and $MnCl_2 \cdot 4H_2O$ (60 μL of a 1 M solution). The mixture was shaken at 37 °C for 5 d. It was centrifuged, the supernatant was concentrated and purified with Bio Gel P-2 (aq. 50 mM NH_4HCO_3) to give **15** (14.2 mg, 64 %) as a white solid after lyophilisation. ^{1}H NMR (D_2O): δ = 1.25–1.30 (m, 2H; CH_2linker), 1.46–1.59 (m, 4H; CH_2linker), 1.75 (t, J = 12.1 Hz, 1H; H-3H$_{eq}$), 1.97 (s, 3H; CH_3CO), 1.98 (s, 3H; CH_3CO), 2.34 (t, $J = 7.6$ Hz, 2H; CH_2CO), 2.71 (dd, $J = 4.8$, 12.5 Hz, 1H; H-3H$_{ax}$), 3.49–3.98 (m, 28H), 4.04 (dd, $J = 3.3$, 9.9 Hz, 1H; H-3E), 4.45–4.48 (m, 2H; H-1D, 1E), 4.68–4.71 (m, 1H, H-5F), 5.13 (d, $J = 4.1$ Hz, 1H; H-1F); selected ^{13}C NMR (D_2O): δ = [24.5, 24.7 (CH_3CO)], [26.4, 27.1, 30.7 (CH_2linker)], 36.1 (CH_2CO), 69.9 (C-5F), 70.5 (C-3E), 100.8 (C-1D), 102.0 (C-1E), 103.4 (C-1F); HRMS (ESI): calcd for $C_{38}H_{64}N_2O_{26}Na$: 987.3639; found 987.3660.

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