1,2-Diacetals in Synthesis: Total Synthesis of a Glycosylphosphatidylinositol Anchor of *Trypanosoma brucei*

Daniel K. Baeschlin, André R. Chaperon, Luke G. Green, Michael G. Hahn, Stuart J. Ince and Steven V. Ley*[a]

Abstract: A full account on a total synthesis of GPI anchor **1** employing butanediacetal (BDA) groups and a chiral bis(dihydropyran) is presented. The reactivity of selenium and thio glycosides was tuned by the use of BDA groups. This allowed the assembly of an appropriately protected GPI anchor precursor **2** in just six steps from the six building blocks **5**–**10** including only one protecting group manipulation (see Scheme 1). *myo*-Inositol was desymmetrised with the bis(dihydropyran) derivative **15** and appropriately protected to give inositol acceptor **21** in nine steps and 17% overall yield (see Scheme 3). The use of common starting materials and BDA-protections give efficient access to building blocks **5**, **6**, **7** and **8** (see Scheme 5). A new and improved synthesis of the glucosamine donor **28** is included. In summary, a highly convergent and efficient synthesis of GPI anchor **1**, which is clearly adaptable to other GPI anchors, has been reported.

Keywords: 1,2-diacetals · glycosylations · GPI anchors · inositols · oligosaccharides

Introduction

The demand for synthetic oligosaccharides and glycolipids has been fuelled by the constantly increasing interest in the role of carbohydrates in biological recognition processes.[1] Highly complex carbohydrates have been synthesised and many useful applications of these materials in biological experiments have been reported. Despite this, a vast amount of research is still directed towards the development of new and improved methods for the synthesis of oligosaccharides, which is an indication of the challenge still posed by these complex structures.[2] Our laboratory has shown that bis(dihydropyran)s form the corresponding dispiroketals with 1,2-diols[3] and subsequently demonstrated the synthetic potential of several variations of these systems as stereoselective protecting groups,[4] desymmetrising agents[5] and chiral auxiliaries[6] for natural product synthesis. As a logical extension of this work we showed that diacetal groups are also convenient protecting group for sugar building blocks and moreover are useful in controlling their reactivity in glycosidation reactions.[7] The glycosylphosphatidylinositol (GPI) anchor **1**[8] was chosen as a suitably challenging target to test these methods for the synthesis of GPI anchors in general and also their derivatives for biosynthetic studies (Scheme 1).

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GPI anchors attach proteins to membranes via a phosphoethanolamine unit linked to a trimannose–glucosamine–inositol backbone and a hydrophobic lipid that anchors the system in the membrane.[9] The carbohydrate backbone is conserved in all GPI anchors described to date. Nevertheless, various species specific carbohydrate side chains are observed alongside additional phosphoethanolamine units and variations in the lipid unit.[10] GPI anchors are ubiquitous in all eukaryotes and attach various types of proteins to membranes, acting as an alternative to transmembrane protein helices.[11]

Intensive efforts have been undertaken in the last decade to elucidate the biosynthesis of GPI anchors and a pathway, starting from phosphatidylinositol, is now generally accepted.[9, 12] At present the biosynthetic intermediates and the enzymes involved are being investigated with attention focused on any species dependent specificity, since this could reveal possible drug targets in some parasitic and fungal diseases.[13] Protozoan parasites are the cause of several devastating diseases such as malaria (*Plasmodium*), sleeping sickness (*Trypanosoma brucei*), Chagas disease (*Trypanosoma cruzi*) and leishmaniasis (*Leishmania*).[14] Treatment and prevention of these diseases is still very unsatisfactory. All these parasites exhibit an extraordinary high content of GPI-anchored molecules on their cell surface, which is essential for virulence and survival of these parasites in the host.[10] Efficient synthetic access to GPI anchors and particularly their analogues will help the further elucidation of the key biological processes. Four total syntheses of GPI anchors have been reported[15] along with the syntheses of various partial

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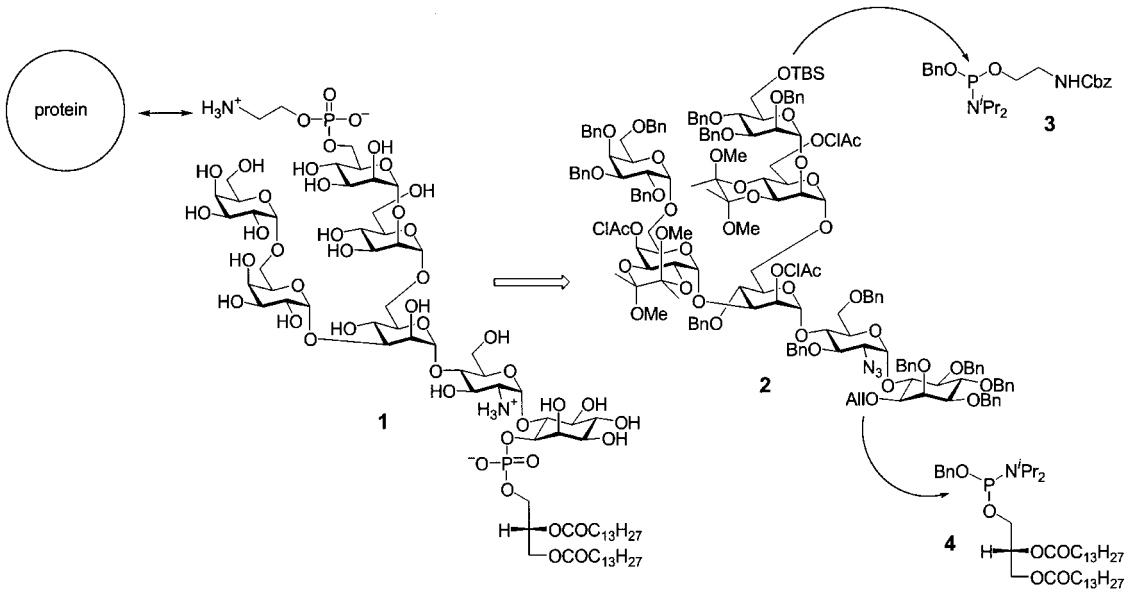


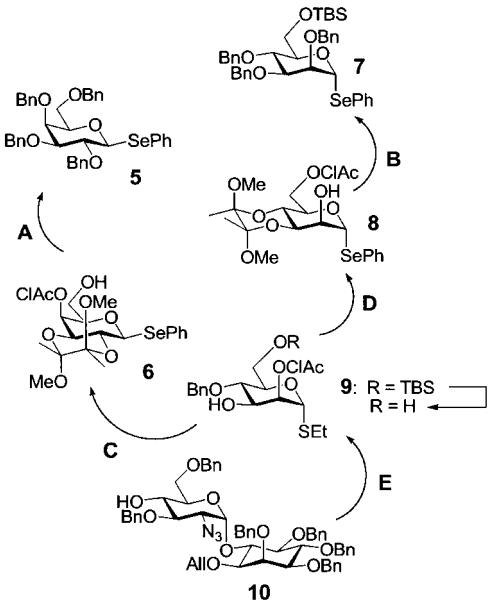
Scheme 1. Structure and retrosynthesis of GPI anchor **1** of *T. brucei*.

structures.[4, 16] A full account of the synthesis of GPI anchor **1** employing butanediacetal (BDA) groups and chiral bis(dihydropyran)s as efficient tools in its synthesis is reported here.[17] This work includes also a new and more efficient route to the glucosamine building block and a further improvement in the desymmetrisation of *myo*-inositol compared with our previous communication.

Results and Discussion

The noncarbohydrate side chains of GPI anchor **1** are linked by phosphodiesters as in all known GPI anchor structures (Scheme 1). This and the fact that the required phosphorylation chemistry[18] is well established, favours a late stage phosphorylation strategy. Such an approach would also facilitate the introduction of other side chains in other GPIs and preparation of further analogues. However, this strategy demands an appropriately protected carbohydrate core, such as **2**, which can be site specifically deprotected and phosphorylated at the appropriate stage.

The most efficient assembly of the carbohydrate core should be convergent and contain as few manipulations of the growing oligosaccharide as possible. Protecting groups influence the reactivity of glycosyl donors[19] and it has been shown that this effect can be used to assemble oligosaccharides without the need for protecting group manipulations.[20] Diacetal groups have proven particularly useful as reactivity tuning elements operating through torsional effects.[4, 7c, 21] It was anticipated that the use of BDA groups and appropriate anomeric leaving groups should allow the assembly of the core **2** in just six steps from the six building blocks **5**–**10**, including only one protecting group manipulation (Scheme 2). In the couplings **A** and **B** selective activation of the donor's selenium leaving group should be possible because of the deactivating effect of the BDA and chloroacetate groups in the acceptor, while in couplings **C** and **D** the higher reactivity of the anomeric selenium groups[22] in comparison with their sulfur equivalents should allow for selective activation. The strategy is also flexible: firstly, couplings **C**, **D** and **E** can be envisaged to proceed in any sequence in the event of steric mismatch, secondly the selenium and sulfur leaving groups could be transformed into a more reactive halide, should this prove necessary.

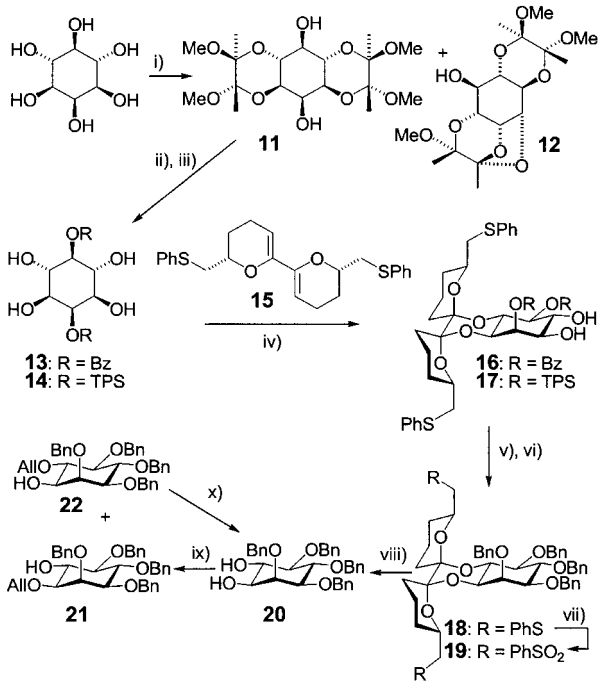


Scheme 2. Synthetic strategy: building blocks **5**–**10** allow the assembly of carbohydrate core **2** in only six steps.

Building block synthesis

The desymmetrisation of *myo*-inositol has remained a problem despite the tremendous interest in the biological role of inositolphosphates as second messengers.[23] Most syntheses of *myo*-inositols involve a chiral resolution or a low yielding desymmetrisation step.[15e, 24] We reported a new route to

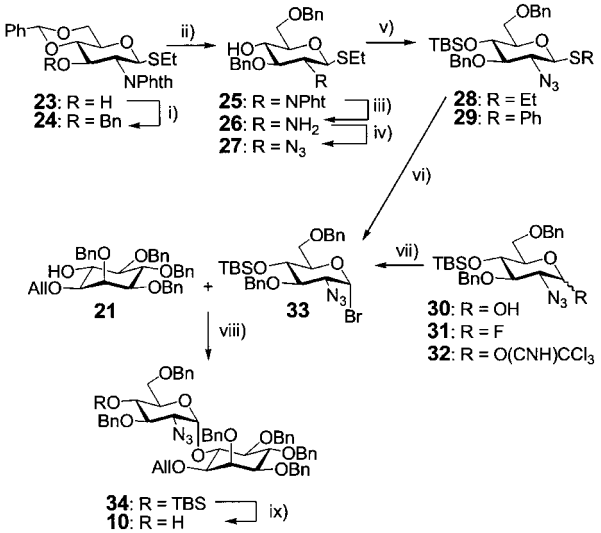
chiral L-*myo*-inositols employing the use of a chiral bis(dihydropyran).[5] A modification of this approach was used to provide access to D-*myo*-inositol **21** (Scheme 3). The symmetrical tetraol **13** is accessible in three steps from *myo*-inositol employing butane-2,3-dione as an economic alternative to 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane.[25] The



Scheme 3. Desymmetrisation of *myo*-inositol and elaboration to inositol building block **21**. i)[26a]; [**17**: ii) TPSCl, imidazole, DMF, 100 °C; iii) TFA/H_2O 9:1 92% over two steps; iv) **15**, $PPh_3 \cdot HBr$, $CHCl_3$, 81% (*de* 98%); v) TBAF, THF; vi) NaH, BnBr, DMF, 67% over two steps]; **16**: ii) BzCl, pyr; iii) TFA/H_2O 9:1, 99% over two steps; iv) **15**, $PPh_3 \cdot HBr$, $CHCl_3$, Δ, 71% (*de* 98%); v) K_2CO_3 (aq), MeOH; vi) NaH, BnBr, DMF, 70% over two steps; vii) *m*CPBA, CH_2Cl_2, 93%; viii) $LiN(TMS)_2$, THF, 0 °C, 93%; ix) $Bu_2Sn(OMe)_2$, toluene, Δ, then allylbromide, tetrabutylammonium iodide (TBAI), 65% (**22**: 21%); or NaH, THF, then allylbromide, 44% (**22**: 6%), x) $[(Ph_3P)_4RuH_2]$, EtOH, Δ, then *para*-toluenesulfonic acid, 76%.

reported BDA protection of *myo*-inositol is low yielding on large scale (28% at 277 mmol) but produces analytically pure product **11** without need for purification.[26] Alternatively, with butane-2,3-dione[27] and longer reaction times[26a] yields 81% of a 3:1 mixture of **11** and side product **12**, which can be removed by simple recrystallisation from CH_2Cl_2/MeOH.[28] Benzoylation of tetraacetal **11** followed by deprotection with trifluoroacetic acid (TFA)/water gave tetraol **13** in excellent yield. Tetraol **13** was then desymmetrised with bis(dihydropyran)[29] **15** furnishing **16** as a single diastereoisomer in 71% yield. The more soluble *tert*-butyldiphenylsilyl (TPS) protected tetraol **14** may be desymmetrised in an improved yield, providing **17** in 81%. Debenzoylation of **16** or desilylation of **17** followed by benzylation, oxidation and removal of the dispiroketal furnished diol **20**. Selective allylation via the tin acetal gave the desired alcohol **21** in 65% yield. The undesired isomer **22** (21%) was deprotected[30] and recycled. A 7:1 ratio[31] in favour of **21** can be obtained by precipitation of, presumably, the mono sodium anion of **20** with NaH in THF followed by alkylation.

Our previously reported synthesis of bromide **33** relied on a low yielding azidonitration step and the transformation of the anomeric alcohol **30** to the corresponding bromide.[4, 17] A more efficient synthesis of this building block is reported here (Scheme 4). Readily available phthalimide **23**[30] was transformed into alcohol **25** by benzylation and reductive benzylidene ring opening. The amine was deprotected with



Scheme 4. Synthesis of pseudodisaccharide **10**. i) BnBr, NaH, TBAI, DMF, 83%; ii) triethylsilane, TFA, CH_2Cl_2, 71%; iii) $H_2NNH_2 \cdot H_2O$, EtOH, Δ, 94%; iv) TfN_3, 4-(dimethylamino)pyridine (DMAP), CH_3CN, 98%; v) TBSCl, KHMDS, THF $-78\,^{\circ}C \rightarrow$RT, 93%; vi) Br_2, CH_2Cl_2, 0 °C to RT; vii) **30**, $SOBr_2$, imidazole, THF; viii) **33** (1.5 equiv), TBABr, CH_2Cl_2, molecular sieves (MS) 4 Å, three days, 65%; xi) TBAF, THF, 95%.

hydrazine, transformed into the azide with triflic azide (TfN_3) as first described by Vasella et al.[32] and the alcohol silylated to give building block **28** in excellent yield.[33] The anomeric sulfide **28** was readily transformed into bromide **33**. Crude bromide **33** was then coupled to inositol **21** with Leumieux's inversion protocol[34] to give the desired α-linked product **34** with excellent selectivity. Desilylation with tetrabutylammonium fluoride (TBAF) furnished pseudodisaccharide **10**.[35] Also investigated was the alternative use of the corresponding anomeric fluoride **31** as well as the trichloroacetimidate **32** as donor in this glycosidation due to encouraging literature reports,[15c, 15g] but in our hands only low yields and unsatisfactory selectivities were observed under a variety of conditions.

Readily available galactoside **35**[36] was protected as butanediacetal in 67% yield. Subsequent silylation, acylation and desilylation gave acceptor **6** (Scheme 5). Benzylation of the same starting material **35** gave galactoside donor **5**.[36b] Mannosides **7** and **8** were synthesised in analogous fashion from phenylselenide **39**.[21a] BDA protection gave diol **40** in 80%, which was treated with chloroacetic anhydride after tin acetal formation to produce acceptor **8**. The same starting material **39** was first silylated at the primary alcohol and then benzylated to give donor **6**.

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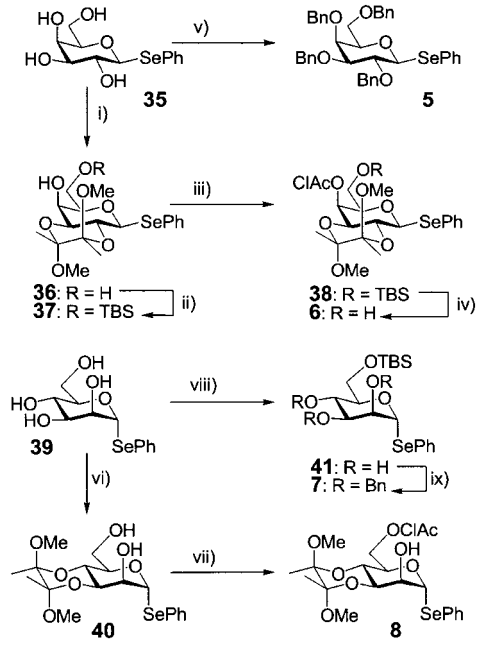
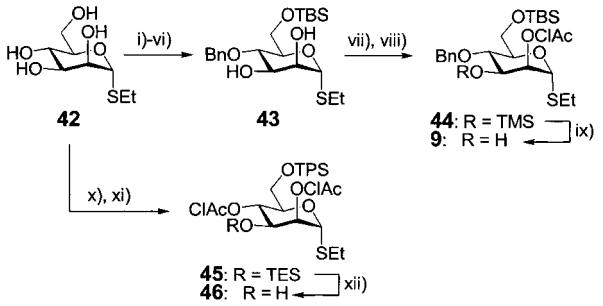


Scheme 5. Synthesis of building blocks **5**–**8**. i) butane-2,3-dione, $HC(OCH_3)_3$, CSA, MeOH, Δ, 67%; ii) TBSCl, imidazole, THF; iii) $(ClAc)_2O$, pyridine, CH_2Cl_2, 0 °C, 80% over two steps; iv) 48% HF (aq), CH_3CN, 95%; v) BnBr, NaH, DMF, 75%; vi) butane-2,3-dione, $HC(OCH_3)_3$, CSA, MeOH, Δ, 80%; vii) $(Bu_3Sn)_2O$, toluene, Δ, then $(ClAc)_2O$, CH_2Cl_2, O °C, 96%; viii) TBSCl, imidazole, THF, 82%; ix) BnBr, NaH, DMF, 91%.

The central mannoside required a chloroacetate group at the 2-position to allow for anchimeric assistance and differentiation of the 3- and 6-position for regioselective glycosidation (Scheme 6). Treatment of thioethyl mannoside **42** with two equivalents of *tert*-butyldimethylsilyl chloride and imidazole in DMF gave selectively the 3-,6-disilylated compound in 68% yield. Disilylation of **42** followed by acylation and desilylation gave acceptor **46** in analogous fashion. Trial experiments indicated that the two chloroacetate groups in **45** might deactivate the anomeric leaving group too strongly for use in glycosidations. This suspicion was later confirmed (vide infra) and made synthetic access to **44**, with an activating benzyl group in the 4-position, very desirable. Selective



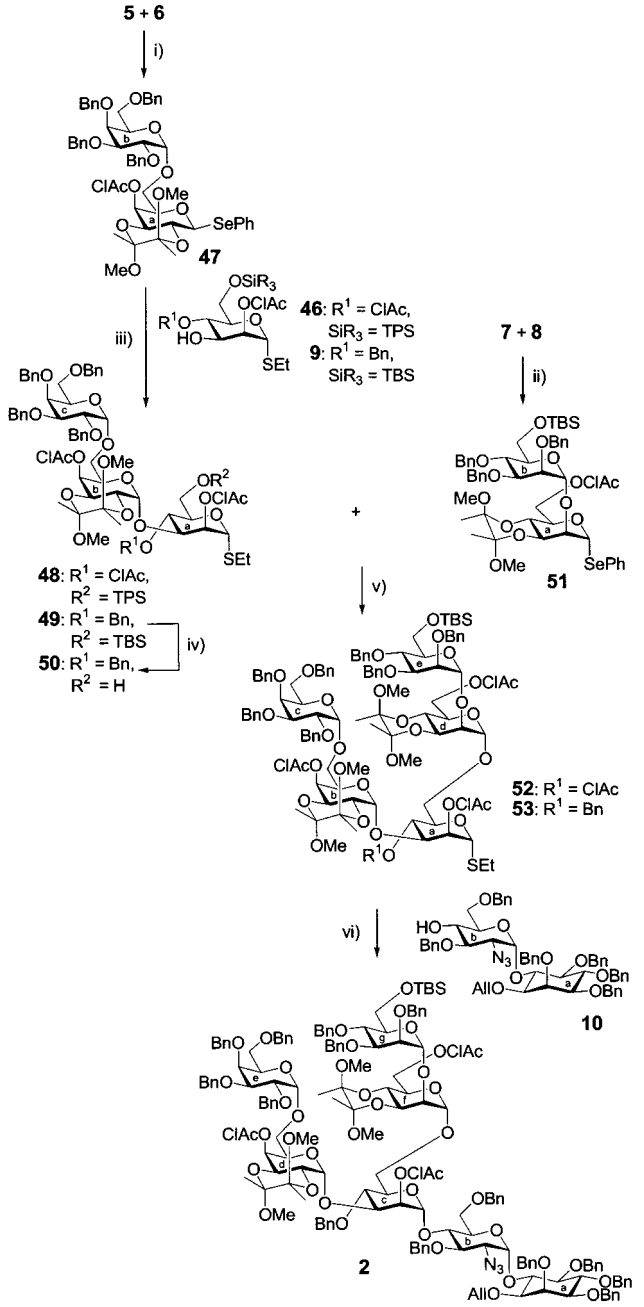
Scheme 6. Synthesis of building blocks **9** and **46**. i) TPSCl, imidazole, DMF; ii) $(CH_3)_2C(OCH_3)_2$, acetone, PPTS; iii) BnBr, NaH, DMF; iv) acetic acid/H_2O 4:1, 80 °C; v) TBAF, THF; vi) TBSCl, imidazole, THF, 65% over six steps; vii) TMSCl, TEA, CH_2Cl_2; viii) $(ClAc)_2O$, pyridine, CH_2Cl_2, 0 °C, 79% over two steps; ix) 48% HF (aq), CH_3CN, 95%; x) TPSCl (1 equiv), imidazole, DMF, then TESCl (1 equiv), 0 °C; xi) $(ClAc)_2O$, pyridine, CH_2Cl_2, 0 °C; xii) 48% HF (aq), CH_3CN, 33% over three steps.

introduction of a benzyl group on the 4-position of **42** required a longer sequence of reactions since reductive ring opening of a benzylidene acetal onto the 4-position of thioethyl mannose proceeded only in very low yields.[37] The following sequence was then chosen because of its reliability, high yield and the minimal purification required. Tetraol **42** was silylated, acetonide protected, benzylated, desilylated, treated with acid to remove the acetonide and protected with *tert*-butyldimethylsilyl chloride (TBSCl) to give diol **43** in 65% yield after one final purification on silica gel. Treatment with one equivalent of trimethylsilyl chloride (TMSCl) and triethylamine (TEA) led to selective silylation of the 3-position and, followed by acylation and desilylation, furnished the central building block **9**.

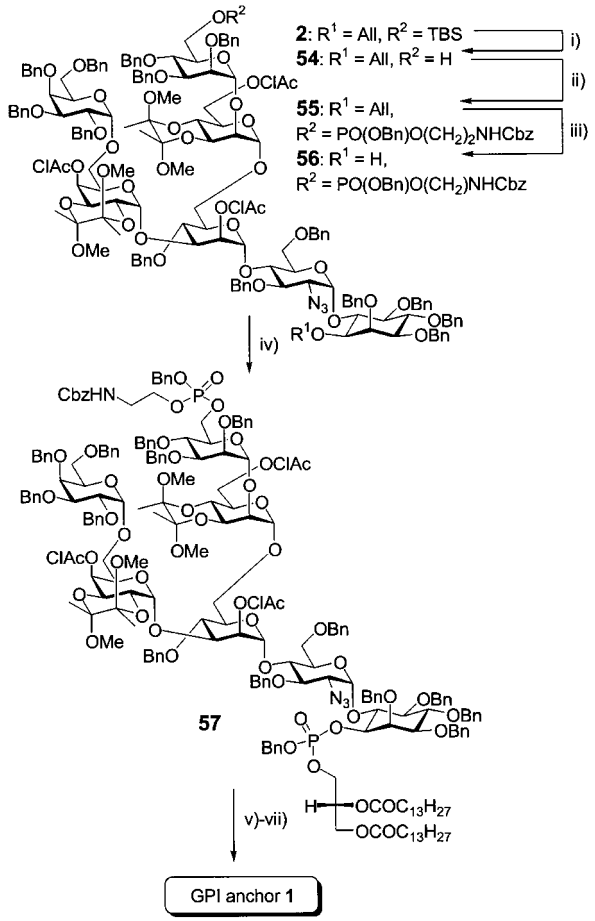
Oligosaccharide assembly

With all building blocks in hand the carbohydrate core was then assembled (Scheme 7). Fully benzylated galactoside **5** was selectively activated with *N*-iodosuccinimide (NIS) and catalytic amounts of triflic acid (TfOH) or trimethylsilyltriflate (TMSOTf)[38] in the presence of acceptor **6** to furnish the desired α-linked digalactoside **47** in 71% yield accompanied by the separable β-linked isomer (15%). Prior investigations had shown that the combined deactivating effects of the BDA and the chloroacetate group in **6** are required to prevent any homocoupling. In analogous fashion dimannoside **51** was obtained as one diastereoisomer in 87% yield from donor **7** and acceptor **8** under NIS/TMSOTf activation. The central mannoside **9**[39] was then 3-*O*-glycosylated with digalactoside **47**. Preliminary investigations with acceptor **46** had shown that NIS/TfOH activation of selenide **47** led to formation of the corresponding trisaccharide **48** in low yield with the anomeric succinimide of **47** as the main side product.[40] Activation with iodonium dicollidine perchlorate[41] or benzeneselenyl triflate[42] was also unsatisfactory; the former leading to incomplete turnover while the latter led to decomposition. Methyl triflate (MeOTf), first introduced by Lönn,[43] turned out to be a more efficient activating agent resulting in the formation of the desired trisaccharide **48** in good yield. The same reaction conditions were also applicable to the coupling of digalactoside **47** to acceptor **9** and trisaccharide **49** was obtained in 75% yield. The suspicion that trisaccharide **48** might be too deactivated by the two chloroacetate groups for synthetic use was confirmed by trial experiments: trisaccharide **48**[44] had to be converted into the corresponding bromide to disaccharide **10**, while the corresponding branched pentasaccharide **52**[45] could not be coupled to **10** nor transformed into the corresponding anomeric bromide without decomposition predominating.

As a result of these observations the trisaccharide **49** was chosen as the key intermediate for further assembly of the carbohydrate core. TBS deprotection with aqueous hydrogen fluoride in acetonitrile gave alcohol **50** in good yield. Glycosidation with selenophenyl donor **51** under MeOTf activation produced the pentasaccharide **53** in 75% yield. An excess of donor **51** (4 equiv), which was fully recovered, and high reaction concentration were used to suppress formation of the anhydrosugar of **50** arising from intramolecular



Scheme 7. Assembly of the carbohydrate core **2**. i) NIS (1 equiv), TMSOTf (cat.), Et_2O/CH_2Cl_2 1:1, MS 4 Å, 71%; ii) NIS (1 equiv), TMSOTf (cat.), Et_2O/CH_2Cl_2 1:1, MS 4 Å, 87%; iii) **9**, MeOTf (5 equiv), Et_2O, MS 4 Å, 75%; iv) 48% HF (aq), CH_3CN, 89%; v) **50**, **51** (5 equiv), MeOTf (5 equiv), CH_2Cl_2, MS 4 Å, 12 h, 75%; vi) **53** (1.4 equiv), NIS, TfOH (cat.), Et_2O/CH_2Cl_2 2:1, MS 4 Å, 50%.



Scheme 8. Phosphorylations and final deprotections. i) 48% HF (aq), CH_3CN, 81%; ii) **3** (10 equiv), tetrazole (20 equiv), CH_3CN/CH_2Cl_2 1:1, then *m*CPBA (−40→25 °C), 89%; iii) $PdCl_2$, NaOAc, HOAc/H_2O 19:1, 67% (81% based on recovered starting material); iv) **4** (10 equiv), tetrazole (20 equiv), CH_3CN/CH_2Cl_2 1:1, then *m*CPBA (−40→25 °C), 81%; v) Pd/C, H_2, $CHCl_3$/MeOH/H_2O 3:3:1; vi) $H_2NNHC(S)SH$, 2,6-lutidine/AcOH 3:1, vii) TFA/H_2O 9:1, 2 min, 90% over three steps.

glycosidation of the 6-hydroxyl group. The branched pentasaccharide **53** was coupled to disaccharide **10** under NIS/TfOH activation in 50% yield. The TfOH concentration and the amount and type of molecular sieves used turned out to be crucial in this final block coupling.

The carbohydrate core **2** was elaborated to the fully protected GPI anchor by using phosphoramidite chemistry, which had been successfully applied in other GPI syntheses (Scheme 8).[15d, 15g, 18] After desilylation the ethanolamine linker was introduced by phosphorylation with phosphoramidite **3** followed by oxidation with *meta*-chloroperbenzoic acid (*m*CPBA). Deallylation with $PdCl_2$[46] followed by phosphorylation with **4** and oxidation furnished the fully protected GPI anchor **57** as a mixture of four diastereoisomers. A final deprotection sequence involving hydrogenation, deacylation and deacetalisation was planned. Studies on the deprotection of diacetals had shown that the hydrolysis of BDA groups gave better results if performed after debenzylation. Hydrogenation of **57** with Pd/C removed the benzyl ethers, the benzyloxycarbonyl (Cbz) group and transformed the azide into the amine. Treatment with hydrazine dithiocarbonate[47] allowed the selective deacylation of the chloroacetates, whilst leaving the alkyl esters intact. Final rapid hydrolysis of the BDA groups with aqueous trifluoroacetic acid gave the GPI anchor **1** in 90% yield over the three steps. The final product was characterised by ^1H, ^{31}P NMR and MALDI-TOF MS. The ^1H NMR spectra was recorded in $[D_6]DMSO/D_2O$ (50:1) at 60 °C and the ^{31}P NMR spectra in CD_3CN/D_2O (3:1) at 50 °C. This was due to the low solubility of GPI anchor **1** in water and its tendency to form aggregates, leading to broad NMR signals.

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Conclusion

In summary, a highly convergent and efficient synthesis of GPI anchor **1** has been reported here. The use of bis(dihyropyran)s to desymmetrise *myo*-inositol and the use of BDA groups to conveniently protect monomers and to tune the reactivity of the resulting glycosyl donors proved to be especially effective. This strategy is clearly adaptable to other GPI anchors and a project directed towards the syntheses of other biologically interesting GPI anchor derivatives is underway.

Experimental Section

Dry toluene, acetonitrile, dichloroethane and dichloromethane were distilled from calcium hydride; methanol was distilled from magnesium; dry Et_2O and tetrahydrofuran were distilled from sodium/benzophenone. NaH was a 60% dispersion in mineral oil. Molecular sieves (4 Å, powdered) were predried in the oven and activated for 10 min under vacuum at 300 °C. Water was distilled. All aqueous (aq) solutions were saturated unless otherwise stated. Solvents for chromatography and reaction work up were distilled. Petrol is 40–60 °C petroleum ether, ether is diethylether. Reactions were carried out at RT under argon in predried glassware unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded at 27 °C on Bruker AM400, Bruker DRX200, DRX400, DRX500 and DRX600 spectrometers with $CHCl_3$ ($\delta = 7.26$) and $CDCl_3$ ($\delta = 77.0$) as internal reference signals unless otherwise stated. Signals were assigned by means of APT, DEPT, 1D TOCSY and 2D spectra (COSY, HMQC, HMBC). The assignment of ^{1}H and ^{13}C NMR signals of the saccharide units correlates with the lettering in Scheme 7. Infrared 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 Platform LC-MS, Micromass Q-Tof, Kratos MS890MS and Bruker Daltonics Bio-Apex II (FTICR) spectrometers by the MS-service of the Department of Chemistry, University of Cambridge, on a Voyager STR spectrometer by Dr. A. Reason at M-Scan, Silwood Park, Ascot and on a Kratos Kompact 4. Microanalyses were determined in the microanalytical laboratories at the Department of Chemistry, University of Cambridge. 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}. Column chromatography was carried out under pressure with Merck silica gel (230–400 mesh) or BDH florosil (200 US mesh, 0.075 mm). Analytical and preparative thin-layer chromatography (TLC) was performed by using precoated, glass backed plates (Merck silica gel 60 F_{254}) and visualised by ultra-violet radiation (254 nm) or acidic ammonium molybdate (IV).

2,4-*O*-Benzoyl-*myo*-inositol (13): BzCl (1.4 mL, 12 mmol) and dry pyridine (10 mL) were added to diol **11** (1.67 g, 4 mmol) and DMAP (spatula tip, cat.). The resulting solution was stirred for 5 h, before it was diluted with CH_2Cl_2, washed subsequently with aq 5% HCl and aq $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was dissolved in TFA/H_2O 9:1 (10 mL) and stirred for 10 min before the solvents were removed under reduced pressure. This process was repeated and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5 →85:15) to furnish tetraol **13** (1.55 g, 3.9 mmol, 99%) as a white solid: ^{1}H NMR (600 MHz, CD_3OD): $\delta = 3.81$ (dd, 2H, $J = 9.7$, 2.7 Hz, H-1/3), 4.00 (t, 2H, $J = 9.7$ Hz, H-4/6), 5.15 (t, 1H, $J = 9.7$ Hz, H-5), 5.76 (s, 1H, H-2), 7.48–7.53 (m, 4H, ArH), 7.59–7.64 (m, 2H, ArH), 8.07 (d, 2H, $J = 7.7$ Hz, ArH), 8.13 (d, 2H, $J = 7.7$ Hz, ArH); ^{13}C NMR (CD_3OD, 150 MHz): $\delta = 70.5$ (CH-1/3/4/6), 71.6 (CH-1/3/4/6), 74.7 (CH-2/5), 76.9 (CH-2/5), [128.0, 128.1, 129.3, 129.4 (CH-Ar)], [130.5, 132.7 (C_q-Ar)], [166.4, 166.6 (CO)]; HR-MS (FAB): *m/z*: 389.1242 $[M+H]^+$, $C_{20}H_{20}O_8$ requires $[M+H]^+$ 389.1236.

(2′*R*,2″*R*,6′*S*,6″*S*) 2,5-*O*-Dibenzoyl-1,6-*O*-(6′,6″-diphenylthiomethyl-3′,3″,4′,4″,5′,5″,6′,6″-octahydro-2′,2″-bis-2*H*-pyran-2′,2″-diyl)-D-*myo*-inositol (16): Bis(dihydropyran) **15** (634 mg, 1.54 mmol) and $Ph_3P \cdot HBr$ (250 mg, 0.782 mmol) were added to a suspension of inositol **13** (500 mg, 1.29 mmol) in dry $CHCl_3$ (20 mL). The mixture was refluxed for 19 h, before it was cooled to RT, diluted with EtOAc and washed with water. The aqueous phase was extracted with EtOAc (3×), the combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (SiO_2, Et_2O/petrol 3:1 →5:1) to give dispiroketal **16** (730 mg, 0.91 mmol, 71%): $[\alpha]_D^{19} = +12.2$ ($c = 1.8$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.05$–1.75 (m, 12H, CH_2-dispoke), 2.71–3.05 (m, 6H, CH_2SPh, 2 × OH), 3.75–3.89 (m, 3H, H-3, H-6′, H-6″), 3.94 (dd, 1H, $J = 10.0$, 2.8 Hz, H-1), 4.09 (m, 1H, H-4), 4.54 (t, 1H, $J = 10.0$ Hz, H-6), 5.24 (t, 1H, $J = 10.0$ Hz, H-5), 5.55 (t, 1H, $J = 2.8$ Hz, H-2), 7.10–7.55 (m, 16H, ArH), 7.91 (m, 2H, 2ArH), 8.15 (m, 2H, 2ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = [18.0, 18.1, 27.6, 27.7, 29.9, 30.1$ (CH_2-dispoke)], [39.4, 40.0 (CH_2SPh)], [66.0, 66.5, 69.7, 69.8, 71.4, 72.2, 73.2, 74.4 (CH)], [97.3, 98.0 (C_q-2′, C_q-2″)], [126.0, 126.1, 128.4, 128.9, 129.0, 129.1, 129.5, 129.9, 130.1, 133.2, 136.5, 137.0 (C_q-Ar, CH-Ar)], [166.8, 167.0 (CO)]; HR-MS (FAB): *m/z*: 821.2408 $[M+Na]^+$, $C_{44}H_{46}O_{10}S_2$ requires $[M+Na]^+$ 821.2430; $C_{44}H_{46}O_{10}S_2$: calcd C 66.15, H 5.8; found C 65.47, H 5.79.

2,5-*O*-Di-(*tert*-butyldiphenylsilyl)-*myo*-inositol (14): TPSCl (0.51 mL, 1.96 mmol) and dry DMF (0.5 mL) were added to diol **11** (200 mg, 0.46 mmol) and imidazole (200 mg, 2.94 mmol). The resulting slurry was stirred at 100 °C for 48 h. The mixture was diluted with CH_2Cl_2, washed with H_2O (3×) and dried over $MgSO_4$. The residue was dissolved in TFA/H_2O 9:1 and stirred for 5 min before the solvents were removed under reduced pressure. This process was once repeated and the residue was purified by column chromatography (SiO_2, petrol/EtOAc 3:1 →1:1) to furnish silyl ether **14** (305 mg, 0.48 mmol, 92%) as a white foam: $R_f = 0.7$ (petrol/EtOAc 3:2); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.12$ (s, 9H, CH_3-*t*Bu), 1.15 (s, 9H, CH_3-*t*Bu), 3.16 (dd, 2H, $J = 9.7$, 2.3 Hz, H-1/3), 3.46 (t, 1H, $J = 9.3$ Hz, H-5), 3.96 (t, 2H, $J = 8.9$ Hz, H-4/6), 4.17 (s, 1H, H-2), 7.38–7.48 (m, 12H, ArH),7.74 (d, 4H, $J = 6.7$ Hz, ArH), 7.79 (d, 4H, $J = 6.7$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = [19.7, 19.9$ (C_q-*t*Bu)], [27.1, 27.3 (CH_3-*t*Bu)], 72.2 (CH-1/3), 73.9 (CH-2), 74.3 (CH-4/6), 78.0 (CH-5), [127.7, 127.9, 129.9, 130.0 (CH-Ar)], [133.3, 133.7 (C_q-Ar)], [135.7, 136.3 (CH-Ar)]; HR-MS (FAB): *m/z*: 679.2909 $[M+Na]^+$, $C_{38}H_{48}O_6Si_2$ requires $[M+Na]^+$ 679.2887.

(2′*R*,2″*R*,6′*S*,6″*S*)-2,5-*O*-Di-(*tert*-butyldiphenylsilyl)-1,6-*O*-(6′,6″-diphenylthiomethyl-3′,3″,4′,4″,5′,5″,6′,6″-octahydro-2′,2″-bis-2*H*-pyran-2′,2″-diyl)-D-*myo*-inositol (17): Bis(dihydropyran) **15** (29 mg, 70 μmol) and $Ph_3P \cdot HBr$ (11 mg, 33 μmol) were added to a solution of inositol **14** (39 mg, 59 μmol) in dry $CHCl_3$ (2 mL). The mixture was stirred at RT for 4 h, before it was diluted with EtOAc and washed with water. The aqueous phase was extracted with EtOAc (3×), the combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (SiO_2, Et_2O/petrol 1:2) to give dispiroketal **17** (51 mg, 48 μmol, 81%): $R_f = 0.38$ (petrol/Et_2O 2:1); $[\alpha]_D^{27} = +9.8$ ($c = 1.35$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.05$ (s, 9H, CH_3-*t*Bu), 1.14 (s, 9H, CH_3-*t*Bu), 1.21–1.23 (m, 1H, H-3′/3″), 1.41–1.46 (m, 4H, H-4′/4″/5′/5″), 1.56–1.58 (m, 2H, H-4′/4″), 1.65–1.68 (m, 4H, H-3′/3″/5′/5″), 1.76–1.81 (s, 2H, 2 × OH), 1.86–1.90 (m, 1H, H-5′/5″), 2.88–2.92 (m, 3H, H-7′/7″, H-1/3), 2.97–3.00 (m, 1H, H-7′/7″), 3.25–3.27 (m, 1H, H-7′/7″), 3.35 (d, 1H, $J = 10.2$ Hz, H-1/3), 3.48–3.52 (m, 1H, H-6′/6″), 3.72 (d, 1H, $J = 8.8$ Hz, H-5), 3.82–3.87 (m, 2H, H-2, H-4/6), 4.18–4.21 (m, 1H, H-6′/6″), 4.32 (t, 1H, $J = 9.8$ Hz, H-4/6), 7.04–7.41 (m, 22H, ArH), 7.70 (t, 4H, $J = 7.2$ Hz, ArH), 7.83 (t, 4H, $J = 8.3$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = [17.3, 18.3$ (CH_2-4′, CH_2-4″)], [19.0, 19.8 (C_q-*t*Bu)], [27.2, 27.3 (CH_3-*t*Bu)], [27.7, 27.9 (CH_2-5′, CH_2-5″)], [29.5, 29.9 (CH_2-3′, CH_2-3″)], [39.0, 39.6 (CH_2SPh)], 67.6 (CH-1/3), 68.4 (CH-6′/6″), 68.6 (CH-4/6), 68.6 (CH-6′/6″), 72.6 (CH-2/4/6), 72.6 (CH-1/3), 75.1 (CH-2/4/6), 75.9 (CH-5), [97.1, 97.7 (C_q-2′, C_q-2′)], [127.3, 127.5, 127.5, 127.7, 128.0, 128.7, 128.8, 129.2, 129.4, 129.6, 129.7 (CH-Ar)], [132.8, 134.1, 134.4, 134.6 (C_q-Ar)], [135.9, 135.9, 136.1, 136.8 (CH-Ar)], [136.8, 137.5 (C_q-Ar)]; HR-MS (ESI): *m/z*: 1089.4182 $[M+Na]^+$, $C_{62}H_{74}O_8S_2Si_2$ requires $[M+Na]^+$ 1089.4256.

(2′*R*,2″*R*,6′*S*,6″*S*)-2,3,4,5-*O*-Tetrabenzyl-1,6-*O*-(6′,6″-diphenylthiomethyl-3′,3″,4′,4″,5′,5″,6′,6″-octahydro-2′,2″-bis-2*H*-pyran-2′,2″-diyl)-D-*myo*-inositol (18): *From* ***16***: A mixture of aq K_2CO_3 (6.4 mL, 6.4 mmol, 1M), dispiroketal **16** (2.42 g, 3.03 mmol) and MeOH (110 mL) was stirred for 2 h before aq NH_4Cl was added and extracted with $CHCl_3$ (6×).The combined organic phases were dried over $MgSO_4$ and concentrated. The obtained white solid (1.65 g) was dissolved in dry DMF (60 mL) and NaH (650 mg, 15.4 mmol) was added cautiously. The mixture was diluted with THF (60 mL) before benzyl bromide (1.66 mL, 14 mmol) was added dropwise. The mixture was stirred at RT for 16 h before aq NH_4Cl was added

cautiously at RT followed by water and it was extracted with ether (3 ×). The combined organic phases were washed with water, brine, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (SiO_2, Et_2O/petrol 1:8) to give benzyl ether **18** (2.0 g, 2.1 mmol, 70 %).

From ***17***: TBAF (270 μL, 0.27 μmol, 1M in THF) was added to dispiroketal **17** (97.3 mg, 90 μmol) in THF (1.5 mL). The solution was stirred for 12 h before the reaction mixture was filtered through a silica pad (CH_2Cl_2/MeOH 95:5) and concentrated. The obtained white solid (40 mg) was dissolved in dry DMF (1.5 mL) and NaH (16 mg, 0.45 mmol) was added. The mixture was diluted with THF (1.5 mL) before benzyl bromide (45 μL, 3.8 mmol) was added. The mixture was stirred at RT for 16 h before aq NH_4Cl was added at RT followed by water and it was extracted with ether (3 ×). The combined organic phases were washed with water, brine, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (SiO_2, Et_2O/petrol 1:8) to give benzyl ether **18** (54.3 mg, 0.06 mmol, 67 %); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.09-1.23$ (m, 12H, CH_2-dispoke), 2.96 (dd, 1H, $J = 13.6$, 4.7 Hz, CH_2SPh), 3.01–3.07 (m, 3H, CH_2SPh), 3.44 (dd, 1H, $J = 9.7$, 2.6 Hz, H-1), 3.50 (t, 1H, $J = 9.2$ Hz, H-5), 3.65 (dd, 1H, $J = 10.3$, 1.8 Hz, H-3), 3.80 (m, 1H, H-6′/6″), 3.92 (t, 1H, $J = 2.0$ Hz, H-2), 4.00 (t, 1H, $J = 9.3$ Hz, H-4/6), 4.05 (m, 1H, H-6′/6″), 4.44 (t, 1H, $J = 9.9$ Hz, H-4/6), 4.62 (m, 2H, CH_2Ph), 4.75–4.98 (m, 6H, CH_2Ph), 7.05–7.50 (m, 30H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = [18.5, 18.5, 27.9, 28.1, 29.6, 30.2 (CH_2-dispoke)], [39.4, 39.6 (CH_2SPh)], [68.4, 68.7, 69.2, 70.0 (CH)], [72.4, 73.7 (CH_2Ph)], 74.2 (CH), [75.2, 76.2 (CH_2Ph)], [81.0, 81.7, 82.0 (CH)], [96.9, 97.4 (C_q-2′, C_q-2″)], [125.5, 125.8, 127.2, 127.3, 127.4, 127.5, 127.6, 127.6, 127.9, 128.1, 128.2, 128.3, 128.4, 128.7, 128.8, 128.8, 129.0, 129.2 (CH-Ar)], [137.2, 137.3, 138.6, 139.1, 139.2, 139.3 (C_q-Ar)]; HR-MS (ESI): *m/z*: 973.3817 $[M + Na]^+$, $C_{58}H_{62}O_8S_2$ requires $[M + Na]^+$ 973.3778; $C_{58}H_{62}O_8S_2$: calcd C 73.23, H 6.54; found C 72.97, H 6.59.

(2′*R*,2″*R*,6′*S*,6″*S*)-2,3,4,5-*O*-Tetrabenzyl-1,6-*O*-(6′,6″-diphenylsulfonylmethyl-3′,3″,4′,4″,5′,5″,6′,6″-octahydro-2′,2″-bis-2*H*-pyran-2′,2″-diyl)-D-*myo*-inositol (19): *m*-Chloroperbenzoic acid (2.95 g, 8.55 mmol, 50 %) was added to a solution of sulfide **18** (1.81 g, 1.9 mmol) in dry CH_2Cl_2 (95 mL) at 0 °C. The mixture was stirred for 3 h at RT before aq $Na_2S_2O_3$ was added at 0 °C followed by extraction with CH_2Cl_2 (3 ×). The combined organic phases were washed with aq $NaHCO_3$, brine, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (SiO_2, Et_2O/petrol 3:1) to give sulfone **19** (1.8 g, 1.77 mmol, 93 %): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.04-2.02$ (m, 12H, CH_2-dispoke), 3.20 (dd, 1H, $J = 15.0$, 2.7 Hz, CH_2SO_2Ph), 3.24 (dd, 1H, $J = 15.0$, 7.4 Hz, CH_2-SO_2Ph), 3.35–3.42 (m, 2H, CH_2SO_2Ph), 3.53 (t, 1H, $J = 9.1$ Hz, H-5), 3.61 (dd, 1H, $J = 9.8$, 1.9 Hz, H-3), 3.79 (t, 1H, $J = 9.4$ Hz, H-4), 3.91 (t, 1H, $J = 9.8$ Hz, H-6), 4.04 (m, 2H, H-1, H-2), 4.12 (m, 1H, H-6′), 4.36 (m, 1H, H-6′), 4.67 (m, 2H, CH_2Ph), 4.79–4.85 (m, 4H, CH_2Ph), 4.90 (d, 1H, $J = 10.6$ Hz, CH_2Ph), 4.94 (d, 1H, $J = 10.6$ Hz, CH_2Ph), 7.15 (m, 2H, 2ArH), 7.25–7.44 (m, 23H, 23ArH), 7.51 (m, 1H, ArH), 7.64 (m, 2H, 2ArH), 8.02 (m, 2H, 2ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = [17.9, 27.5, 27.9, 29.8, 30.7 (CH_2-dispoke)], [61.7, 62.0 (CH_2-SO_2Ph)], 64.8 (CH-6″), 65.5 (CH-6′), 68.1 (CH-1), 69.1 (CH-6), [72.9, 74.1 (CH_2Ph)], 75.0 (CH-2), [75.7, 76.0 (CH_2Ph)], 81.2 (CH-5), 81.6 (CH-3), 81.8 (CH-4), [96.9, 97.4 (C_q-2′, C_q-2″)], [127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.4, 128.7, 129.3, 133.1, 133.2 (CH-Ar)], [138.5, 138.9, 139.1, 139.3, 141.3 (C_q-Ar)]; MS (FAB): *m/z*: 1037.7 $[M + Na]^+$, $C_{58}H_{62}O_{12}S_2$: calcd C 68.62, H 6.16; found C 68.25, H 6.12.

2,3,4,5-*O*-Tetrabenzyl-D-*myo*-inositol (20): *From* ***19***: LHMDS (5.78 mL, 5.78 mmol, 1M in THF) was added to a solution of sulfone **19** (1.68 g, 1.65 mmol) in dry THF (55 mL) at 0 °C. The mixture was stirred for 1.5 h at 0 °C before aq NH_4Cl was added followed by extraction with EtOAc (4 ×). The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (SiO_2, Et_2O/EtOAc 1:0 →5:1) to give diol **20** (0.83 g, 1.53 mmol, 93 %).

From ***22***: $[(Ph_3P)_4RuH_2]$ (70 mg, 62 μmol) and allyl ether **22** (562 mg, 0.97 mmol) were dissolved in ethanol (1 mL). The mixture was refluxed for 6.5 h before it was cooled to RT and *para*-toluenesulfonic acid (50 mg) was added. The reaction was stirred at RT for 2 h before Et_3N (5 drops) was added. The solvent was removed under vacuum and the residue was purified by column chromatography (SiO_2, petrol/Et_2O 1:1) to furnish diol **20** (397 mg, 0.73 mmol, 76 %); $[\alpha]_D^{19} = +13.8$ ($c = 0.86$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.27$ (s, 1H, OH), 3.32 (t, 1H, $J = 9.2$ Hz, H-5), 3.37 (m, 1H, H-2), 3.48 (dd, 1H, $J = 9.8$, 2.4 Hz, H-1), 3.82 (t, 1H, $J = 9.4$ Hz, H-6), 4.02 (m, 2H, H-3, H-4), 4.66–5.06 (m, 8H, CH_2Ph), 7.28–7.35 (m, 20H, 20ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 72.2$ (CH), 73.2 (CH_2Ph), 74.0 (CH), [74.9, 75.4, 75.8 (CH_2Ph)], [81.4, 81.5, 83.0 (CH)], [127.7, 127.7, 127.8, 127.8, 127.9, 128.1, 128.4, 128.5, 128.5, 128.6 (CH-Ar)], [138.2, 138.6, 138.6 (C_q-Ar)]; HR-MS (ESI): *m/z*: 563.2425 $[M + Na]^+$, $C_{34}H_{36}O_6$ requires $[M + Na]^+$ 563.2404; $C_{34}H_{36}O_6$: calcd C 75.21, H 6.57; found C 75.52, H 6.72.

1-*O*-Allyl-2,3,4,5-*O*-tetrabenzyl-D-*myo*-inositol (21): **A)** Inositol **20** (301 mg, 0.56 mmol) was dissolved in dry toluene (15 mL). Half the solvent was distilled off in a Dean–Stark apparatus, then $Bu_2Sn(OCH_3)_2$ (166 μL, 0.72 mmol) was added by syringe and the remaining solvent was distilled off. The obtained oil was dried under vacuum before allyl bromide (5 mL) and TBAI (206 mg, 0.56 mmol) were added and the mixture was refluxed for 3 h. The allyl bromide was removed under vacuum and the residue was purified by column chromatography (SiO_2, petrol/EtOAc 9:2 →7:2) to furnish allyl ether **21** (214 mg, 0.37 mmol, 66 %) and its regioisomer **22** (72 mg, 0.12 mmol, 22 %); **B)** NaH (14 mg, 0.35 mmol) was added to inositol **20** in dry THF (2 mL) and stirred for 30 min by which time a precipitate had formed. Allyl bromide (36 μL, 0.42 mmol) was added and the mixture was stirred for 14 h before aq NH_4Cl (10 mL) was added and it was extracted with ether (5 ×). The combined organic phases were dried over $MgSO_4$ and concentrated to obtain a crude mixture (113 mg, 56 %) of allyl ethers **21** and **22** in a 7:1 ratio as determined by HPLC.[31] The product mixture was purified by column chromatography (SiO_2, petrol/EtOAc 9:2 →7:2) to give allyl ether **21** (82 mg, 0.14 mmol, 40 %) and a mixed fraction (19 mg); **21**: $R_f = 0.30$ (petrol/EtOAc 3:1); **22**: $R_f = 0.19$ (petrol/EtOAc 3:1); $[\alpha]_D^{22} = -10.6$ ($c = 1.87$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.46$ (s, 1H, HO-6), 3.10 (dd, 1H, $J = 9.9$, 2.1 Hz, H-1), 3.38 (t, 1H, $J = 9.9$ Hz, H-5), 3.40 (dd, 1H, $J = 9.9$, 2.3 Hz, H-3), 3.99 (dd, 1H, $J = 5.7$, 12.7 Hz, CH_2-All), 4.04 (s, 1H, H-2), 4.04–4.08 (m, 2H, CH_2-All, H-4), 4.12 (t, 1H, $J = 9.4$ Hz, H-6), 4.64 (d, 1H, $J = 11.7$ Hz, CH_2Ph), 4.70 (d, 1H, $J = 11.7$ Hz, CH_2Ph), 4.80–4.93 (m, 6H, CH_2Ph), 5.18 (dd, 1H, $J = 10.4$, 1.0 Hz, =CH_2-All), 5.27 (dd, 1H, $J = 17.2$, 1.4 Hz, =CH_2-All), 5.85–5.92 (m, 1H, =CH-All), 7.27–7.40 (m, 20H, ArH); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 71.1 (CH_2-All), 72.7 (CH-6), 72.9 (CH_2Ph), 73.5 (C-2), 74.1 (CH_2Ph), 75.3 (CH_2Ph), 75.8 (CH_2Ph), 79.8 (C-1), 81.1 (C-3), 81.4 (C-4), 83.5 (C-5), 117.3 (=CH_2-All), 127.4–128.4 (CH-Ar), 134.5 (=CH-All), [138.4, 138.8, 138.9 (C_q-Ar)], 133.8 (CH-Ar); MS (CI) *m/z* (%): 457, 373, 316 (100), 289, 288, 270, 229; HR-MS (FAB): *m/z*: 581.2895 $[M + H]^+$, $C_{37}H_{40}O_6$ requires $[M + H]^+$ 581.2903. (*ee* 98 %; the enatiomeric excess was calculated by integration of the ^{19}F NMR of the di(α-methoxy-α-trifluoromethylphenylacetate) ester (diMTPA ester) of **21**. A sample of the diMTPA ester of the enantiomer of **21** was synthesised for comparison.)[48]

Ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (24): Glucosamine **23** (6.08 g, 13.8 mmol), benzyl bromide (2.5 mL, 20.7 mmol) and TBAI (spatula tip) were stirred in DMF (70 mL) at 0 °C and NaH (0.6 g, 17.9 mmol) was added portionwise. Once the addition was complete the reaction was removed from the cooling bath and stirred for a further 6 h. The reaction was then diluted with ether followed by the addition of aq NH_4Cl (10 mL). The organic phase was washed with water (3 ×), dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (Et_2O/petrol 1:9 →3:1) yielding **24** as a white foam (6.07 g, 11.4 mmol, 83 %); $[\alpha]_D^{32} = +122.5$ ($c = 1.00$ in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.17$ (t, 3H, $J = 7.4$ Hz, CH_3-SEt), 2.60–2.71 (m, 2H, CH_2-SEt), 3.69–3.73 (m, 1H, H-5), 3.81–3.86 (m, 2H, H-4, H-6), 4.31 (t, 1H, $J = 10.3$ Hz, H-2), 4.42 (dd, 1H, $J = 10.5$, 4.9 Hz, H-6), 4.46 (t, 1H, $J = 9.4$ Hz, H-3), 4.51 (d, 1H, $J = 12.3$ Hz, CH_2Ph), 4.79 (d, 1H, $J = 12.3$ Hz, CH_2Ph), 5.34 (d, 1H, $J = 10.6$ Hz, H-1), 5.63 (s, 1H, CHPh), 6.87–6.94 (m, 3H, 3ArH), 7.00 (d, 2H, $J = 7.1$ Hz, 2ArH), 7.38–7.42 (m, 3H, 3ArH), 7.53 (d, 2H, $J = 6.8$ Hz, 2ArH), 7.64–7.74 (m, 3H, 3ArH), 7.85 (d, 1H, $J = 6.8$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = 14.8$ (CH_3-SEt), 24.1 (CH_2-SEt), 54.7 (CH-2), 68.7 (CH_2-6), 70.4 (CH-5), 74.2 (CH_2Ph), 75.4 (CH-3), 82.8 (CH-4), 83.0 (CH-1), 101.3 (CHPh), [123.3, 123.6 (CH-Pht)], [126.0, 127.4, 128.0, 128.1, 128.3, 129.0 (CH-Ar)], [131.6, 131.6 (C_q-Ar)], [133.8, 133.9 (CH-Pht)], [137.3, 137.8 (C_q-Ar)], [167.3, 167.7 (CO)]; HR-MS (ESI): *m/z*: 554.1599 $[M + Na]^+$, $C_{30}H_{29}NO_6S$ requires $[M + Na]^+$ 554.1608; $C_{30}H_{29}NO_6S$: calcd C 67.78, H 5.5, N 2.63; found C 67.86, H 5.59, N 2.60.

Ethyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (25): Benzylidene acetal **24** (2.7 g, 5.08 mmol) was dried by azeotropic distillation with toluene before being dissolved in dry CH_2Cl_2 (12 mL) and triethylsilane (3.7 mL, 23 mmol). The reaction was cooled to 0 °C and anhydrous CF_3COOH (1.8 mL, 23 mmol) was added dropwise to the

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stirring reaction. On completion of the addition the reaction was removed from the cooling bath and stirred for a further 10 h. The reaction was then diluted with CH_2Cl_2 (60 mL) and poured onto aq $NaHCO_3$ (20 mL). The organic layer was separated, dried over $MgSO_4$ and concentrated. The resulting residue was purified by column chromatography (Et_2O/petrol 1:4 →2:1) to yield benzyl ether **25** (1.91 g, 3.6 mmol, 71 %) as a white foam; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.16$ (t, 3H, $J = 7.4$ Hz, CH_3-SEt), 2.56–2.69 (m, 2H, CH_2-SEt), 2.98 (s, 1H, OH-4), 3.67–3.70 (m, 1H, H-5), 3.76–3.79 (m, 1H, H-4), 3.82–3.86 (m, 2H, H-6), 4.22–4.30 (m, 2H, H-2, H-3), 4.54 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 4.59 (d, 1H, $J = 11.9$ Hz, CH_2Ph), 4.63 (d, 1H, $J = 11.9$ Hz, CH_2Ph), 4.75 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 5.27 (d, 1H, $J = 10.1$ Hz, H-1), 6.95–7.38 (m, 10H, ArH), 7.68–7.82 (m, 4H, PhtH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = 14.9$ (CH_3-SEt), 23.9 (CH_2-SEt), 54.4 (CH-2), 70.9 (CH_2-6), 73.8 (CH_2Ph), 74.4 (CH-4), 74.5 (CH_2Ph), 77.6 (CH-5), 79.6 (CH-3), 81.1 (CH-1), [123.2, 122.5 (CH-Pht)], [127.4, 127.8, 127.9, 128.1, 128.5 (CH-Ar)], 131.6 (CH-Ar), [133.8, 133.9 (CH-Pht)], [137.6, 138.1 (C_q-Ar)], [167.5, 168.1 (CO)]; HR-MS (ESI): *m/z*: 556.1754 [M + Na]$^+$, $C_{30}H_{31}NO_6S$ requires [M + Na]$^+$ 556.1764; $C_{30}H_{31}NO_6S$: calcd C 67.52, H 5.86, N 2.62; found C 67.42, H 5.93, N 2.67.

Ethyl 2-amino-3,6-di-*O*-benzyl-2-deoxy-1-thio-*β*-D-glucopyranoside (26): Phthalimide **25** (380 mg, 0.71 mmol) and hydrazine hydrate (0.8 mL, 14.2 mmol) were refluxed in ethanol (17 mL) for 48 h before the solvent was removed under vacuum. The residue was taken up in aq 10 % NaOH/CH_2Cl_2 (40 mL:40 mL), the phases were separated and the aqueous phase was reextracted with CH_2Cl_2 (4 × 20 mL). The combined organic phases were washed with brine (40 mL), dried over $MgSO_4$ and concentrated to furnish amine **26** (270 mg, 0.67 mmol, 94 %): ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.29$ (t, 3H, $J = 7.4$ Hz, CH_3-SEt), 1.66 (br s, 2H, OH/NH_2), 2.65–2.75 (m, 2H, CH_2-SEt), 2.86 (t, 1H, $J = 9.6$ Hz, H-2), 3.09 (br s, 1H, OH/NH_2), 3.33 (t, 1H, $J = 9.0$ Hz, H-3), 3.48–3.51 (m, 1H, H-5), 3.71–3.80 (m, 3H, H-4, H-6), 4.30 (d, 1H, $J = 9.9$ Hz, H-1), 4.56 (d, 1H, $J = 11.9$ Hz, CH_2Ph), 4.59 (d, 1H, $J = 11.9$ Hz, CH_2Ph), 4.78 (d, 1H, $J = 11.5$ Hz, CH_2Ph), 4.98 (d, 1H, $J = 11.5$ Hz, CH_2Ph), 7.31–7.39 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = 15.3$ (CH_3-SEt), 24.4 (CH_2-SEt), 55.4 (CH-2), 71.2 (CH_2-6), 73.4 (CH-4), 73.8 (CH_2Ph), 75.0 (CH_2Ph), 77.6 (CH), 86.4 (CH), 86.9 (CH-1), [127.8, 127.8, 127.9, 127.9, 128.5, 128.6 (CH-Ar)], [137.6, 138.1 (C_q-Ar)]; HR-MS (ESI): *m/z*: 404.1878 [M + H]$^+$, $C_{22}H_{29}NO_4S$ requires [M + H]$^+$ 404.1890.

Ethyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-*β*-D-glucopyranoside (27): A freshly prepared solution of TfN_3[32a, 49] in CH_2Cl_2 (3.6 mL, 1.4 mmol, ca. 0.4 M) was added at RT to a solution of amine **26** (380 mg, 0.71 mmol) and DMAP (88 mg, 0.72 mmol) in acetonitrile (6 mL). The reaction mixture was stirred for 6 h before part of the solvent (ca. 6 mL) was removed under reduced pressure, the remaining solution was diluted with ether and successively washed with aq $NaHCO_3$, aq 5 % HCl, aq $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (petrol/Et_2O 1:1) to furnish azide **27** (276 mg, 0.64 mmol, 98 %) as an oil: $R_f = 0.30$ (petrol/Et_2O 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.32$ (t, 3H, $J = 7.5$ Hz, CH_3-SEt), 2.70–2.79 (m, 2H, CH_2-SEt), 3.35–3.45 (m, 3H, H-2, H-4, H-5), 3.66–3.76 (m, 3H, H-3, H-6), 4.31 (d, 1H, $J = 9.6$ Hz, H-1), 4.55 (d, 1H, $J = 11.9$ Hz, CH_2Ph), 4.60 (d, 1H, $J = 11.9$ Hz, CH_2Ph), 4.86 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 4.93 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 7.30–7.42 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = 15.0$ (CH_3-SEt), 24.7 (CH_2-SEt), 65.5 (CH-2), 70.4 (CH_2-6), 72.3 (CH-4), 73.7 (CH_2Ph), 75.3 (CH_2Ph), 77.8 (CH-5), 84.3 (CH-1), 84.5 (CH-3), [127.7, 127.9, 128.1, 128.2, 128.5, 128.6 (CH-Ar)], [137.6, 138.0 (C_q-Ar)]; HR-MS (ESI): *m/z*: 452.1604 [M + Na]$^+$, $C_{22}H_{27}N_3O_4S$ requires [M + Na]$^+$ 452.1614; $C_{22}H_{27}N_3O_4S$: calcd C 61.52, H 6.34, N 9.78; found C 61.70, H 6.36, N9.81.

Ethyl 2-azido-3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-1-thio-*β*-D-glucopyranoside (28): KHMDS (5.6 mL, 2.8 mmol, 0.5 M in toluene) was added to alcohol **27** (760 mg, 1.4 mmol) in dry THF (10 mL) at −78 °C, before TBSCl (640 mg, 4.2 mmol) in dry THF (2 mL) was added dropwise at −78 °C. The reaction mixture was warmed to RT and stirred 30 min before aq NH_4Cl was added, diluted with ether and washed with water. The aqueous phase was reextracted with ether and the combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (petrol/Et_2O 9:1) to furnish silyl ether **28** (706 mg, 1.3 mmol, 93 %): $R_f = 0.65$ (petrol/Et_2O 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.01$ (s, 3H, CH_3-TBS), 0.01 (s, 3H, CH_3-TBS), 0.86 (s, 9H, CH_3-*t*Bu), 1.35 (t, 3H, $J = 7.4$ Hz, CH_3-SEt), 2.71–2.82 (m, 2H, CH_2-SEt), 3.28 (t, 1H, $J = 8.9$ Hz, H-3), 3.37–3.42 (m, 2H, H-2, H-5), 3.57 (dd, 1H, $J = 10.8$, 6.3 Hz, H-6), 3.62 (t, 1H, $J = 9.1$ Hz, H-4), 3.74 (dd, 1H, $J = 10.7$, 1.8 Hz, H-6), 4.35 (d, 1H, $J = 10.2$ Hz, H-1), 4.51 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 4.65 (d, 1H, $J = 12.2$ Hz, CH_2Ph), 4.79 (d, 1H, $J = 11.2$, CH_2Ph), 4.91 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 7.26–7.38 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = -4.7$ (CH_3-TBS), −3.8 (CH_3-TBS), 15.1 (CH_3-SEt), 17.9 (C_q-*t*Bu), 24.6 (CH_2-SEt), 25.9 (CH_3-*t*Bu), 66.7 (CH-2), 69.3 (CH_2-6), 70.9 (CH-4), 73.3 (CH_2Ph), 75.4 (CH_2Ph), 80.7 (CH-5), 84.5 (CH-1), 85.4 (CH-3), [127.4, 127.5, 127.5, 128.3, 128.3 (CH-Ar)], [138.1, 138.3 (C_q-Ar)]; HR-MS (ESI): *m/z*: 566.2467 [M + Na]$^+$, $C_{28}H_{41}N_3O_4SSi$ requires [M + Na]$^+$ 566.2479; $C_{28}H_{41}N_3O_4SSi$: calcd C 61.84, H 7.60, N 7.73; found C 62.21, H 7.62, N 7.74.

1-Bromo-2-azido-3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*-D-glucopyranoside (33): *From **28***: Bromine (32 μL, 0.68 mmol) was added at 0 °C to a solution of **28** (340 mg, 0.63 mmol) in dry CH_2Cl_2 (4 mL). The reaction solution was stirred at RT for one hour, before it was diluted with ether, washed with aq $Na_2S_2O_3$, dried over Na_2SO_4 and concentrated to give bromide **33** as a yellow oil, which was immediately used in the next reaction.

*From **30***: A solution of hemiacetal **30**[4] (1.0 g, 2.0 mmol) in dry THF (6 mL) was added to a suspension of $SOBr_2$ (260 μL, 3.3 mmol) and imidazole (205 mg, 3.01 mmol) in dry THF (20 mL) at 0 °C. The resulting suspension was stirred for 30 min before it was diluted with dry ether, filtered over a pad of florisil and ground $Na_2S_2O_3$, and concentrated to furnish bromide **33** as a yellow oil, which was immediately used in the next reaction: $R_f = 0.37$ (petrol/Et_2O 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.01$ (s, 3H, CH_3-TBS), 0.05 (s, 3H, CH_3-TBS), 0.87 (s, 9H, CH_3-*t*Bu), 3.61 (dd, 1H, $J = 3.7$, 9.7 Hz, H-2), 3.65 (dd, 1H, $J = 2.0$, 11.0 Hz, H-6), 3.73 (dd, 1H, $J = 4.1$, 11.0 Hz, H-6), 3.78 (t, 1H, $J = 9$ Hz, H-3), 3.88 (t, 1H, $J = 9$ Hz, H-4), 3.98–4.02 (m, 1H, H-5), 4.48 (d, 1H, $J = 12.0$ Hz, CH_2Ph), 4.62 (d, 1H, $J = 12.0$ Hz, CH_2Ph), 4.81 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 4.91 (d, 2H, $J = 11.2$ Hz, CH_2Ph), 6.50 (d, 1H, $J = 3.6$ Hz, H-1), 7.24–7.38 (m, 10H, ArH).

1-*O*-Allyl-2,3,4,5-tetra-*O*-benzyl-6-*O*-(2-azido-3,6-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-*α*-D-glucopyranosyl)-D-*myo*-inositol (34): Alcohol **21** (650 mg, 1.34 mmol) was dried by azeotropic distillation with dry toluene and left under vacuum for 4 h. Molecular sieves (4 Å, 500 mg), TBABr (451 mg, 1.4 mmol) and dry CH_2Cl_2 (2 mL) were added. The resulting suspension was stirred for 4 h before a solution of freshly prepared bromide **33** (prepared from 2 mmol of **28**) in CH_2Cl_2 (3 mL) was added. The reaction mixture was partly concentrated by a dry argon flow (to ca. 3 mL) and stirred at RT in the dark. The solution was stirred for 24 h and was then diluted with ether, filtered through celite, washed with aq $NaHCO_3$, dried over $MgSO_4$ and concentrated. The brown residue was purified by column chromatography (petrol/Et_2O 4:1) to furnish disaccharide **34** (925 mg, 0.87 mmol, 65 %) as a yellow oil: $R_f = 0.40$ (petrol/Et_2O 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -0.04$ (s, 3H, CH_3-TBS), −0.02 (s, 3H, CH_3-TBS), 0.76 (s, 9H, CH_3-*t*Bu), 3.25 (dd, 1H, $J = 3.7$, 10.2 Hz, H-2_b), 3.32 (m, 2H, H-6_b), 3.40 (d, 2H, $J = 9.5$ Hz, H-1_a, H-3_a), 3.44 (t, 1H, $J = 9.3$ Hz, H-5_a), 3.76 (t, 1H, $J = 9.8$ Hz, H-3_b), 3.82 (t, 1H, $J = 9.0$ Hz, H-4_b), 3.98 (d, 1H, $J = 9.8$ Hz, H-5_b), 3.98–4.04 (m, 2H, CH_2-All), 4.06 (s, 1H, H-2_a), 4.14 (t, 1H, $J = 9.5$ Hz, H-4/6_a), 4.31 (t, 1H, $J = 9.5$ Hz, H-4/6_a), 4.39 (d, 1H, $J = 12.0$ Hz, CH_2Ph), 4.46 (d, 1H, $J = 12.0$ Hz, CH_2Ph), 4.62 (d, 1H, $J = 11.8$ Hz, CH_2Ph), 4.68 (d, 1H, $J = 11.8$ Hz, CH_2Ph), 4.73 (d, 1H, $J = 11.4$ Hz, CH_2Ph), 4.79 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 4.83 (d, 1H, $J = 11.6$ Hz, CH_2Ph), 4.88 (s, 2H, CH_2Ph), 4.93 (d, 2H, $J = 10.8$ Hz, CH_2Ph), 5.02 (d, 1H, $J = 11.5$ Hz, CH_2Ph), 5.18 (d, 1H, $J = 10.8$ Hz, =CH_2-All), 5.29 (d, 1H, $J = 17.2$ Hz, =CH_2-All), 5.78 (d, 1H, $J = 3.7$ Hz, H-1_b), 5.86–5.99 (m, 1H, =CH-All), 7.08–7.45 (m, 30H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = [-4.9, -3.8$ (CH_3-TBS)], 18.0 (C_q-*t*Bu), 26.1 (CH_3-*t*Bu), 63.9 (CH-2_b), 68.2 (CH_2-6_b), 70.6 (CH), 70.8 (CH_2-All), [71.5, 72.8 (CH)], [72.9, 73.1, 74.1, 74.4, 75.0 (CH_2Ph)], 75.6 (CH), 75.8 (CH_2Ph), [80.4, 80.9, 81.3, 81.9, 82.0 (CH)], 97.9 (CH-1_b), 117.0 (=CH_2-All), [126.8, 127.1, 127.3, 127.3, 127.5, 127.5, 127.7, 127.7, 127.9, 128.1, 128.2, 128.2, 128.2, 128.3, 128.5 (CH-Ar)], 134.3 (CH-All), [138.3, 138.5, 138.6, 138.7, 138.9 (C_q-Ar)].

1-*O*-Allyl-2,3,4,5-tetra-*O*-benzyl-6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-D-*myo*-inositol (10): TBAF (0.5 mL, 1 M in THF, 0.5 mmol) was added to a solution of silyl ether **34** (235 mg, 0.218 mmol) in THF (5 mL). The reaction mixture was stirred for 2 h before it was diluted with ether, washed with aq $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (SiO_2, petrol/Et_2O 2:1) to furnish disaccharide **10** (190 mg, 0.19 mmol, 88 %) as a yellow oil: $R_f = 0.16$ (petrol/Et_2O 2:1); $[\alpha]_D^{26} = +32.4$ ($c = 1.14$ in $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 2.02$ (d, 1H, $J = 3.7$ Hz, OH-4$_b$), 3.20 (dd, 1H, $J = 3.5$, 13.5 Hz, H-6$_b$), 3.23 (dd, 1H, $J = 3.7$, 10.2 Hz, H-2$_b$), 3.31 (dd, 1H, $J = 2.8$, 17.1 Hz, H-6$_b$), 3.37–3.43 (m, 2H, H-1$_a$, H-3$_a$), 3.44 (t, 1H, $J = 9.3$ Hz, H-5$_a$), 3.71–3.76 (m, 1H, H-4$_b$), 3.81 (t, 1H, $J = 9.9$ Hz, H-3$_b$), 3.97–4.08 (m, 4H, CH_2-All, H-2$_a$, H-5$_b$), 4.16 (t, 1H, $J = 9.5$ Hz, H-4$_a$/6$_a$), 4.23 (t, 1H, $J = 9.6$ Hz, H-4$_a$/6$_a$), 4.24 (d, 1H, $J = 12.0$ Hz, CH_2Ph), 4.42 (d, 1H, $J = 12.0$ Hz, CH_2Ph), 4.62 (d, 1H, $J = 11.8$ Hz, CH_2Ph), 4.68 (d, 1H, $J = 11.8$ Hz, CH_2Ph), 4.71 (d, 1H, $J = 11.1$ Hz, CH_2Ph), 4.81 (d, 1H, $J = 10.6$ Hz, CH_2Ph), 4.85 (s, 2H, CH_2Ph), 4.89 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 4.91 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 4.99 (d, 1H, $J = 10.6$ Hz, CH_2Ph), 5.06 (d, 1H, $J = 11.1$ Hz, CH_2Ph), 5.20 (d, 1H, $J = 10.4$ Hz, =CH_2-All), 5.30 (dd, 1H, $J = 1.2$, 17.2 Hz, =CH_2-All), 5.72 (d, 1H, $J = 3.6$ Hz, H-1$_b$), 5.91–5.99 (m, 1H, =CH-All), 7.16–7.45 (m, 30H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 62.9$ (CH-2$_b$), 69.1 (CH_2-6$_b$), 69.4 (CH-5$_b$), 70.9 (CH_2-All), 72.2 (CH-4$_b$), 72.8 (CH_2Ph), 73.0 (CH-2$_a$), [73.4, 74.1, 74.8 (CH_2Ph)], 75.1 (CH-4$_a$), [75.5, 75.6 (CH_2Ph)], 79.4 (CH-3$_b$), 80.9 (CH-1$_a$), 81.5 (CH-5$_a$), 81.9 (CH-3$_a$), 82.0 (CH-6$_a$), 97.6 (CH-1$_b$), 117.1 (=CH_2-All), 127.4–128.5 (CH-Ar), 134.3 (=CH-All), 138.0–138.8 (C_q-Ar); IR (film): $\tilde{\nu} = 3029$ cm^{-1}, 2866, 2105 (N_3), 1604, 1496, 1453, 1358, 1208, 1051, 735, 697; HR-MS (FAB): *m/z*: 970.4196 $[M + Na]^+$, $C_{57}H_{61}O_{10}N_3$ requires $[M + Na]^+$ 970.4254.

(2′*R*,3′*R*) Phenyl 2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-1-seleno-β-D-galactopyranoside (36): Galactoside **35** (21 g, 65.7 mmol), butane-2,3-dione (6.9 mL, 78.8 mmol), trimethylorthoformate (23 mL, 197 mmol) and camphorsulfonic acid (1.5 g, 6.5 mmol) were stirred under reflux in MeOH (200 mL) for 16 h. Triethylamine (2 mL) was added at RT and the solution was concentrated. The residue was purified by column chromatography (SiO_2, EtOAc/petrol 3:2 →3:1) to furnish diol **36** (19.2 g, 44.3 mmol, 67%) as a white foam: $R_f = 0.28$ (EtOAc/petrol 3:2); $[\alpha]_D^{26} = -147.1$ ($c = 0.94$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.30$ (s, 3H, CH_3-BDA), 1.31 (s, 3H, CH_3-BDA), 3.17 (s, 3H, OCH_3-BDA), 3.25 (s, 3H, OCH_3-BDA), 3.58 (t, 1H, $J = 5.5$ Hz, H-5), 3.74 (dd, 1H, $J = 2.9$, 9.7 Hz, H-3), 3.77 (dd, 1H, $J = 4.6$, 11.8 Hz, H-6), 3.93 (dd, 1H, $J = 6.7$, 11.8 Hz, H-6), 4.00 (d, 1H, $J = 2.1$ Hz, H-4), 4.10 (t, 1H, $J = 10$ Hz, H-2), 4.95 (d, 1H, $J = 10$ Hz, H-1), 7.21–7.31 (m, 3H, ArH), 7.59–7.71 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 17.5$ (CH_3-BDA), 17.7 (CH_3-BDA), 48.1 (OCH_3-BDA), 50.3 (OCH_3-BDA), 62.6 (CH_2-6), 66.2 (CH), 68.4 (CH), 71.7 CH), 80.1 (CH), 81.4 (CH-1), 100.5 (C_q-BDA), 128.1 (CH-Ar), 128.5 (C_q-Ar), 129.0 (CH-Ar), 134.1 (CH-Ar); IR (film): $\tilde{\nu} = 3419$ cm^{-1}, 2947, 1579, 1377, 1120, 1048; MS (FAB): *m/z* (%): 434 (2) $[M + H]^+$, 403 (70) $[M - OCH_3]^+$, 371 (8) $[M - (OCH_3)_2]^+$, 307 (15), 245 (60), 213 (65), 154 (100); $C_{18}H_{26}O_7Se$: calcd C 49.89, H 6.05; found C 49.55, H 6.01.

(2′*R*,3′*R*) Phenyl 6-*O*-*tert*-butyldimethylsilyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-1-seleno-β-D-galactopyranoside (37): Diol **36** (5.03 g, 11.6 mmol) and imidazole (1.19 g, 17.4 mmol) were dissolved in dry THF (100 mL) and TBSCl (1.92 g, 12.76 mmol) in dry THF (15 mL) was added at 0 °C. After the solution was stirred for 5 h at RT, MeOH (5 mL) was added, the reaction mixture was filtered over a florisil pad and the solvents were removed under vacuum. The residue was purified by column chromatography (SiO_2, petrol/EtOAc 9:1 →4:1) to furnish silyl ether **37** (4.95 g, 9.76 mmol, 84%) as a white foam: $R_f = 0.27$ (petrol/EtOAc 11:2); $[\alpha]_D^{26} = -117.9$ ($c = 0.95$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.07$ (s, 3H, CH_3-TBS), 0.09 (s, 3H, CH_3-TBS), 0.90 (s, 9H, CH_3-*t*Bu), 1.30 (m, 3H, CH_3-BDA), 1.34 (s, 3H, CH_3-BDA), 2.69 (s, 1H, OH-4), 3.15 (s, 3H, OCH_3-BDA), 3.26 (s, 3H, OCH_3-BDA), 3.54 (t, 1H, $J = 5.6$ Hz, H-5), 3.72 (dd, 1H, $J = 2.9$, 9.8 Hz, H-3), 3.84 (dd, 1H, $J = 5.1$, 10.4 Hz, H-6), 3.93 (dd, 1H, $J = 6.3$, 10.4 Hz, H-6), 4.05 (s, 1H, H-4), 4.12 (t, 1H, $J = 9.9$ Hz, H-2), 4.94 (d, 1H, $J = 10.1$ Hz, H-1), 7.20–7.31 (m, 3H, ArH), 7.60–7.71 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -5.4$ (CH_3-TBS), [17.6, 17.8 (CH_3-BDA)], 18.3 (C_q-*t*Bu), 25.9 (CH_3-*t*Bu), [48.0, 48.1 (OCH_3-BDA)], 62.6 (CH_2-6), [66.1, 67.8, 72.0, 80.0 (CH)], 82.0 (CH-1), 100.4 (C_q-BDA), [127.4, 128.8 (CH-Ar)], 129.0 (C_q-Ar), 133.8 (CH-Ar); IR (film): $\tilde{\nu} = 3458$ cm^{-1}, 2951, 2855, 1580, 1472, 1377, 1253, 1142, 1120, 1050; MS (FAB): *m/z* (%): 547.3 (2) $[M + H]^+$, 517 (6) $[M - OCH_3]^+$, 485 (5) $[M - (OCH_3)_2]^+$, 399 (5), 359 (100) $[M - SePh - OCH_3]^+$, 327 (10); $C_{24}H_{40}O_7SeSi$: calcd C 52.64, H 7.34; found C 52.38, H 7.40.

(2′*R*,3′*R*) Phenyl 6-*O*-*tert*-butyldimethylsilyl-4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-1-seleno-β-D-galactopyranoside (38): Galactoside **37** (670 mg, 1.32 mmol) and dry pyridine (0.5 mL, 6.2 mmol) were dissolved in dry CH_2Cl_2 (10 mL) and $(ClAc)_2O$ (1.6 mL, 1M in CH_2Cl_2, 1.6 mmol) was added at 0 °C. The solution was stirred for one hour at 0 °C before water (1 mL) was added. The reaction mixture was diluted with ether, washed with aq 10% HCl, aq $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (SiO_2, petrol/Et_2O 4:1) to furnish fully protected galactoside **38** (655 mg, 1.05 mmol, 79%) as a white foam: $R_f = 0.39$ (petrol/Et_2O 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.02$ (s, 6H, CH_3-TBS), 0.86 (s, 9H, CH_3-*t*Bu), 1.21 (s, 3H, CH_3-BDA), 1.28 (s, 3H, CH_3-BDA), 3.12 (s, 3H, OCH_3-BDA), 3.24 (s, 3H, OCH_3-BDA), 3.62 (dd, 1H, $J = 7.0$, 9.0 Hz, H-6), 3.70–3.75 (m, 2H, H-5, H-6), 3.86 (dd, 1H, $J = 3.1$, 10.1 Hz, H-3), 4.00 (t, 1H, $J = 10.1$ Hz, H-2), 4.13 (s, 2H, ClAc), 4.98 (d, 1H, $J = 10.1$ Hz, H-1), 5.47 (d, 1H, $J = 2.0$ Hz, H-4), 7.24–7.26 (m, 3H, ArH), 7.63 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -5.5$ (CH_3-TBS), [17.4, 17.7 (CH_3-BDA)], 18.2 (C_q-*t*Bu), 25.7 (CH_3-*t*Bu), 40.8 (CH_2-ClAc), [48.0, 48.2 (OCH_3-BDA)], 61.0 (CH_2-6), [66.3, 69.7, 70.3, 79.2 (CH)], 82.0 (CH-1), [100.2, 100.4 (C_q-BDA)], 127.6 (CH-Ar), 128.7 (C_q-Ar), [128.9, 133.8 (CH-Ar)], 166.4 (CO-ClAc); HR-MS (ESI): *m/z*: 663.1 $[M + K]^+$, 647.1337 $[M + Na]^+$; $C_{26}H_{41}O_8SeSiCl$ requires $[M + Na]^+$ 647.1424; $C_{26}H_{41}O_8SeSiCl$: calcd C 50.04, H 6.62; found C 49.94, H 6.58.

(2′*R*,3′*R*) Phenyl 4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-1-seleno-β-D-galactopyranoside (6): Galactoside **38** (870 mg, 1.39 mmol) was dissolved in CH_3CN (10 mL) and aq HF (100 μL, 48% in H_2O, 2.8 mmol) was added. The solution was stirred for 2 h at RT before it was diluted with CH_2Cl_2, washed with aq $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was dried under vacuum to furnish crude alcohol **6** (>90%) as a white foam which was used for the next reaction step without purification: $R_f = 0.25$ (Et_2O/petrol 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.24$ (s, 3H, CH_3-BDA), 1.29 (s, 3H, CH_3-BDA), 2.15 (s, 1H, OH-6), 3.17 (s, 3H, OCH_3-BDA), 3.24 (s, 3H, OCH_3-BDA), 3.52 (m, 1H, H-6), 3.65–3.78 (m, 2H, H-5, H-6), 3.86 (dd, 1H, $J = 3.0$, 10.0 Hz, H-3), 4.03 (t, 1H, $J = 10.0$ Hz, H-2), 4.18 (s, 2H, ClAc), 4.98 (d, 1H, $J = 10.0$ Hz, H-1), 5.35 (d, 1H, $J = 2.0$ Hz, H-4), 7.23–7.30 (m, 3H, ArH), 7.61–7.67 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = [17.4, 17.7$ (CH_3-BDA)], 40.9 (CH_2-ClAc), 48.2 (2OCH_3-BDA), 60.8 (CH_2-6), [66.4, 69.8, 70.6, 79.2 (CH)], 81.5 (CH-1), 100.5 (C_q-BDA), 127.9 (CH-Ar), 128.1 (C_q-Ar), [129.0, 134.2 (CH-Ar)], 168.1 (CO-ClAc); HR-MS (ESI): *m/z*: 1043.16 $[2M + Na]^+$, 533.0484 $[M + Na]^+$; $C_{20}H_{27}O_8SeCl$ requires $[M + Na]^+$ 533.0457.

(2′*S*,3′*S*) Phenyl 3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-1-seleno-α-D-mannopyranoside (40): Mannoside **39** (3.97 g, 12.4 mmol), butane-2,3-dione (1.3 mL, 14.9 mmol), trimethylorthoformate (4.2 mL, 37 mmol) and camphorsulfonic acid (800 mg, 3.4 mmol) were stirred under reflux in MeOH (100 mL) for 8 h. Triethylamine (1 mL) was added at RT and the solution was concentrated. The residue was crystallised from MeOH to furnish pure diol **40** (3.78 g, 8.7 mmol, 71%) as white crystals and crude product (1.0 g): $R_f = 0.39$ (EtOAc/petrol 3:2); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.31$ (s, 3H, CH_3-BDA), 1.33 (s, 3H, CH_3-BDA), 1.89 (t, 1H, $J = 6.3$ Hz, OH-6), 2.74 (s, 1H, OH-2), 3.25 (s, 3H, OCH_3-BDA), 3.31 (s, 3H, OCH_3-BDA), 3.74–3.82 (m, 2H, H-6), 4.03 (dd, 1H, $J = 2.6$, 9.5 Hz, H-4), 4.13–4.20 (m, 2H, H-3, H-5), 4.26 (s, 1H, H-2), 5.80 (s, 1H, H-1), 7.25–7.32 (m, 3H, ArH), 7.55–7.59 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = [17.7, 17.8$ (CH_3-BDA)], [48.0, 48.2 (OCH_3-BDA)], 61.1 (CH_2-6), [63.1, 69.0, 71.7, 73.2 (CH)], 85.5 (CH-1), [99.9, 100.5 (C_q-BDA)], 128.0 (CH-Ar), 128.9 (C_q-Ar), [129.3, 134.3 (CH-Ar)]; HR-MS (ESI): *m/z*: 457.0732 $[M + Na]^+$; $C_{18}H_{26}O_7Se$ requires $[M + Na]^+$ 457.0741; $C_{18}H_{26}O_7Se$: calcd C 49.89, H 6.05; found C 49.80, H 5.98.

(2′*S*,3′*S*) Phenyl 6-*O*-chloroacetyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-1-seleno-α-D-mannopyranoside (8): Diol **40** (510 mg, 1.18 mmol) and $(Bu_3Sn)_2O$ (0.68 mL, 1.3 mmol) were stirred under reflux and Dean–Stark conditions in dry toluene (30 mL) for 16 h. Toluene was partly removed under vacuum (to ca. 6 mL), molecular sieves (4 Å, 500 mg) were added and $(ClAc)_2O$ (1.3 mL, 1M in toluene, 1.3 mmol) was added at 0 °C. The reaction mixture was warmed to RT and stirred for one hour before it was diluted with CH_2Cl_2, filtered through celite and concentrated. The residue was purified by column chromatography (SiO_2, Et_2O/petrol 2:1) to furnish alcohol **8** (670 mg, 1.13 mmol, 96%) as a white foam: $R_f = 0.24$ (Et_2O/petrol 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.30$ (s, 3H, CH_3-BDA), 1.33 (s, 3H, CH_3-BDA), 2.63 (s, 1H, OH-2), 3.22 (s, 3H, OCH_3-BDA), 3.30 (s, 3H, OCH_3-BDA), 3.95–4.02 (m, 3H, H-3, ClAc), 4.11 (t, 1H, $J = 10.0$ Hz, H-4), 4.26 (d, 1H, $J = 2.3$ Hz, H-2), 4.35 (dd, 1H, $J = 5.9$, 11.6 Hz, H-6), 4.38–4.41 (m, 1H, H-5), 4.45 (dd, 1H, $J = 1.6$, 11.6 Hz, H-6), 5.83 (s, 1H, H-1), 7.27–7.30 (m, 3H, ArH), 7.56–7.58 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 17.7$ (CH_3-BDA), 40.1 (CH_2-ClAc), [48.1, 48.2 (OCH_3-BDA)], 63.4 (CH), 64.0 (CH_2-6), [69.1, 70.7, 71.5 (CH)], 85.4

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(CH-1), [100.1, 100.6 (C_q-BDA)], 128.0 (CH-Ar), 128.9 (C_q-Ar), [129.3, 134.0 (CH-Ar)], 167.1 (CO-ClAc); HR-MS (ESI): *m/z*: 533.0452 $[M+Na]^+$; $C_{20}H_{27}O_8SeCl$ requires $[M+Na]^+$ 533.0457; $C_{20}H_{27}O_8SeCl$ calcd C 47.12, H 5.34; found C 46.86, H 5.25.

Phenyl 6-*O*-*tert*-butyldimethylsilyl-1-seleno-α-D-mannopyranoside (41): Mannoside **39** (5 g, 15.7 mmol) and imidazole (1.9 g, 28.2 mmol) were dissolved in dry THF (100 mL) and TBSCl (3.3 g, 21.9 mmol) in dry THF (15 mL) was added. After the solutin was stirred for 30 min the reaction mixture was filtered through silica and the solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, $CHCl_3$/MeOH 9:1) to furnish silyl ether **41** (5.6 g, 12.9 mmol, 82 %) as a white foam: $[\alpha]_D^{30} = +238$ ($c = 0.85$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.09$ (s, 6H, CH_3-TBS), 0.90 (s, 9H, CH_3-*t*Bu), 3.00 (s, 1H, OH), 3.29 (s, 1H, OH), 3.63 (s, 1H, OH), 3.80 (m, 4H), 4.02 (m, 1H), 4.27 (s, 1H), 5.79 (s, 1H, H-1), 7.22–7.30 (m, 3H, ArH), 7.52–7.62 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -5.5$ (CH_3-TBS), 18.3 (C_q-TBS), 25.9 (CH_3-*t*Bu), 64.9 (CH_2-6), [71.0, 72.4, 72.9 (CH)], 85.6 (CH-1), [127.8, 129.2 (CH-Ar)], 129.3 (C_q-Ar), 133.8 (CH-Ar); MS (FAB): *m/z*: 377 $[M-t\mathrm{Bu}]^+$, 359, 277, 259, 201, 158, 156; $C_{18}H_{30}O_5SeSi$: calcd C 49.88, H 6.98; found C 49.56, H 6.90.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-1-seleno-α-D-mannopyranoside (7): Triol **41** (5.3 g, 12.2 mmol) and benzyl bromide (7.3 mL, 61 mmol) were dissolved in dry DMF (50 mL). NaH (1.17 g, 50 mmol) was added slowly at 0 °C and the reaction mixture was stirred at RT for 16 h. Aq NH_4Cl was added slowly at 0 °C before the reaction mixture was diluted with ether and washed with water. The aqueous phase was reextracted with ether (4×) and the combined organic phases were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (SiO_2, petrol/EtOAc 98:2 →97:3) to furnish mannoside **7** (7.8 g, 11.1 mmol, 91 %); $[\alpha]_D^{30} = +97.5$ ($c = 0.96$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.05$ (s, 3H, CH_3-TBS), 0.06 (s, 3H, CH_3-TBS), 0.89 (s, 9H, CH_3-*t*Bu), 3.80–4.10 (m, 6H), 4.57–4.65 (m, 4H, CH_2Ph), 4.67 (d, 1H, $J = 10.8$ Hz, CH_2Ph), 4.95 (d, 1H, $J = 10.8$ Hz, CH_2Ph), 5.85 (d, 1H, $J = 1.2$ Hz, H-1), 7.20–7.38 (m, 18H, ArH), 7.48–7.53 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = [-5.3, -5.1$ (CH_3-TBS)], 18.4 (C_q-*t*Bu), 26.0 (CH_3-*t*Bu), 62.6 (CH_2-6), [72.1, 72.1 (CH_2Ph)], 74.7 (CH-4), 75.3 (CH_2Ph), 76.0 (CH-5), 77.1 (CH-2), 80.5 (CH-3), 84.1 (CH-1), 127.6–129.1 (CH-Ar), 130.1 (C_q-Ar), 133.8 (CH-Ar), [138.1, 138.3, 138.7 (C_q-Ar)]; MS (FAB): *m/z*: 647 $[M-t\mathrm{Bu}]^+$, 547, 431, 381, 331, 271, 219, 181, 158; HR-MS (FAB): *m/z*: 647.1741 $[M-t\mathrm{Bu}]^+$, $C_{39}H_{48}O_5SeSi$ requires $[M-t\mathrm{Bu}]^+$ 647.1731.

Ethyl 4-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (43): TBDPSCl (17.9 mL, 67.5 mmol) was added dropwise to a solution of tetraol **42** (15 g, 66.87 mmol) and imidazole (6.8 g, 100 mmol) in dry DMF (70 mL). The solution was stirred for 4 h, MeOH (2 mL) was added, the mixture was concentrated (to ca. 30 mL), diluted with ether, washed with water (3×), dried over $MgSO_4$ and concentrated. The residue, 2-dimethoxypropane (60 mL) and PPTS (800 mg) were dissolved in acetone (200 mL) and stirred for 24 h. Triethylamine (1 mL) was added and the solution was concentrated. The residue and benzyl bromide (11.8 mL, 100 mmol) were dissolved in dry DMF. NaH (4 g, 100 mmol) was added portionwise at 0 °C. The reaction mixture was stirred at RT for 12 h, before MeOH (3 mL) was added and the solvent partly removed under vacuum. The remaining mixture was diluted with ether, washed with water (2×), dried over $MgSO_4$ and concentrated. The residue and TBAF (70 mL, 1M in THF, 70 mmol) were dissolved in THF (100 mL) and stirred for 12 h. The solvent was removed under vacuum. The residue was dissolved in toluene, filtered through a silica pad (petrol/Et_2O 1:1) and concentrated. The remaining oil was taken up in AcOH/water (4:1, 375 mL) and stirred at 60 °C for 6 h. The reaction mixture was poured onto ice water (1 L), neutralised with solid Na_2CO_3, extracted with EtOAc (2×), dried over $MgSO_4$ and concentrated. The residue and imidazole (6 g, 87 mmol) were dissolved in dry THF (50 mL) and TBSCl (9.01 g, 58 mmol) in dry THF (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred at RT for 2 h, filtered through a silica pad and concentrated. The residue was purified by column chromatography (SiO_2, petrol/EtOAc 3:1 →2:1) to furnish diol **43** (18.6 g, 43.4 mmol, 65 %): $R_f = 0.25$ (petrol/EtOAc 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.07$ (s, 3H, CH_3-TBS), 0.09 (s, 3H, CH_3-TBS), 0.92 (s, 9H, CH_3-*t*Bu), 1.28 (t, 3H, $J = 7.4$ Hz, CH_3-SEt), 2.40 (d, 1H, $J = 5.6$ Hz, OH-3), 2.48 (d, 1H, $J = 4.8$ Hz, OH-2), 2.52–2.59 (m, 1H, CH_2-SEt), 2.61–2.68 (m, 1H, CH_2-SEt), 3.69 (t, 1H, $J = 9.3$ Hz, H-4), 3.83–3.94 (m, 3H, H-3, 2×H-6), 3.96–4.03 (m, 2H, H-2, H-5), 4.73 (d, 1H, $J = 11.3$ Hz, CH_2Ph), 4.77 (d, 1H, $J = 11.3$ Hz, CH_2Ph), 5.28 (s, 1H, H-1), 7.28–7.40 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = [-5.3, -5.2$ (CH_3-TBS)], 14.1 (CH_3-SEt), 18.3 (C_q-*t*Bu), 24.7 (CH_2-SEt), 25.9 (CH_3-*t*Bu), 62.4 (CH_2-6), [72.1, 72.4, 72.5 (CH)], 74.5 (CH_2Ph), 76.1 (CH), 83.5 (CH-1), [127.9, 128.6 (CH-Ar)], 138.4 (C_q-Ar); MS (ESI): *m/z* (%): 874 (50) $[2M+NH_4]^+$, 446 (100) $[M+NH_4]^+$, 429 (80) $[M+H]^+$, 367 (75) $[M-SEt]^+$; $C_{21}H_{36}O_5SSi$: calcd C 58.84, H 8.47; found C 58.85, H 8.41.

Ethyl 4-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-3-*O*-trimethylsilyl-1-thio-α-D-mannopyranoside (44): TMSCl (3.0 mL, 23.2 mmol) was added dropwise to a solution of diol **43** (9.9 g, 23 mmol) and triethylamine (6.6 mL, 47.1 mmol) in dry CH_2Cl_2 (70 mL) at −78 °C. The solution was warmed to RT over 2 h and stirred for one hour at RT. The reaction mixture was concentrated, diluted with ether, filtered through a florosil pad and concentrated. The residue and anhydrous pyridine (5.57 mL, 69 mmol) were dissolved in dry CH_2Cl_2 (100 mL), a solution of $ClAc_2O$ (7.9 g, 46 mmol) in dry CH_2Cl_2 (10 mL) was added at −5 °C and the reaction mixture was stirred at −5 °C for one hour. The reaction mixture was washed with $CuSO_4$ (2×), water, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (florosil, petrol/Et_2O 98:2 →96:4) to furnish silyl ether **44** (10.6 g, 18.3 mmol, 79 %): $R_f = 0.45$ (petrol/Et_2O 9:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.05$ (s, 3H, CH_3-TBS), 0.07 (s, 3H, CH_3-TBS), 0.16 (s, 9H, CH_3-TMS), 0.91 (s, 9H, CH_3-*t*Bu), 1.24 (t, 3H, $J = 7.0$, CH_3-SEt), 2.57–2.76 (2m, H, CH_2-SEt), 3.76 (t, 1H, $J = 9.2$ Hz, H-4), 3.78 (dd, 1H, $J = 22.0$, 1.4 Hz, H-6), 3.87 (dd, 1H, $J = 22.0$, 4.0 Hz, H-6), 3.96 (ddd, 1H, $J = 9.0$, 4.0, 1.5 Hz, H-5), 4.11 (dd, 1H, $J = 8.9$, 2.8 Hz, H-3), 4.13 (d, 1H, $J = 14.6$ Hz, ClAc), 4.17 (d, 1H, $J = 14.6$ Hz, ClAc), 4.61 (d, 1H, $J = 11.0$ Hz, CH_2Ph), 4.82 (d, 1H, $J = 11.0$ Hz, CH_2Ph), 5.19 (dd, 1H, $J = 2.8$, 1.1 Hz, CH-2), 5.21 (s, 1H, H-1), 7.32–7.39 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = -5.4$ (CH_3-TBS), −5.2 (CH_3-TBS), −0.05 (CH_3-TMS), 14.8 (CH_3-SEt), 18.3 (C_q-*t*Bu), 25.4 (CH_2-SEt), 25.9 (CH_3-*t*Bu), 40.9 (CH_2-ClAc), 62.2 (CH_2-6), 71.6 (CH-3), 73.3 (CH-5), 75.2 (CH_2Ph), 75.5 (CH-4), 76.4 (CH-2), 81.8 (CH-1), [127.6, 127.8, 128.3 (CH-Ar)], 138.5 (C_q-Ar), 166.8 (CO-ClAc); MS (ESI): *m/z* (%): 599.2 $[M+Na]^+$ (100), 523.23 $[M-SEt]^+$ (50), 505.2 (70), 451.2 (80); $C_{26}H_{45}O_6SSi_2Cl$: calcd C 54.09, H 7.86; found C 54.31, H 7.82.

Ethyl 4-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-*O*-chloroacetyl-1-thio-α-D-mannopyranoside (9): Silyl ether **44** (325 mg, 0.56 mmol) was dissolved in CH_3CN (5.6 mL) and aq HF (23.3 μL, 48 % in H_2O, 0.57 mmol) in CH_3CN (210 μL) was added. The solution was stirred for 30 min at RT before it was concentrated. The residue was dried under vacuum to furnish crude alcohol **9** (>95 %) which was immediately used in the next reaction without purification: $R_f = 0.28$ (petrol/Et_2O 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta =$ 0.08 (s, 3H, CH_3-TBS), 0.10 (s, 3H, CH_3-TBS), 0.93 (s, 9H, CH_3-*t*Bu), 1.28 (t, 3H, $J = 5.8$, CH_3-SEt), 2.55–2.68 (m, 2H, CH_2-SEt), 3.77–3.87 (m, 2H, H-4, H-6), 3.93–3.99 (m, 2H, H-5, H-6), 4.07–4.11 (m, 1H, H-3), 4.09 (d, 1H, $J = 14.6$ Hz, ClAc), 4.14 (d, 1H, $J = 14.6$ Hz, ClAc), 4.75 (s, 2H, CH_2Ph), 5.26 (d, 1H, $J = 3.0$ Hz, CH-2), 5.27 (s, 1H, H-1), 7.28–7.40 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = [-5.4, -5.1$ (CH_3-TBS)], 14.8 (CH_3-SEt), 18.3 (C_q-*t*Bu), 25.5 (CH_2-SEt), 25.8 (CH_3-*t*Bu), 40.8 (CH_2-ClAc), 62.1 (CH_2-6), [70.6, 72.9 (CH)], 74.8 (CH_2Ph), [75.6, 75.9 (CH)], 81.7 (CH-1), [127.9, 128.0, 128.6 (CH-Ar)], 138.3 (C_q-Ar), 167.0 (CO-ClAc).

(2′*R*,3′*R*) Phenyl 4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-1-seleno-β-D-galactopyranoside (47): A mixture of galactosyl donor **5** (992 mg, 1.42 mmol) and galactosyl acceptor **6** (677 mg, 1.33 mmol) was dried by azeotropic distillation with dry toluene and left under vacuum for 4 h. Molecular sieves (4 Å, 500 mg) and dry CH_2Cl_2/Et_2O (7 mL:7 mL) were added. The resulting suspension was stirred for 15 min before a freshly prepared mixture of NIS (334 mg, 1.46 mmol) and TMSOTf (50 μL of a solution of 50 μL TMSOTf in 1 mL dry CH_2Cl_2) in dry CH_2Cl_2/Et_2O (7 mL:7 mL) was added rapidly. The reaction mixture turned dark brown immediately. After the solution was stirred for one hour, the mixture was diluted with ether, filtered through celite, washed with aq $NaHCO_3$, aq $Na_2S_2O_3$, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (SiO_2, petrol/Et_2O 3:2) to furnish digalactoside **47** (0.977 mg, 0.944 mmol, 71 %) and its β anomer (15 %): $R_f = 0.29$ (α anomer) and 0.26 (β anomer) (Et_2O/petrol 1:1); ^{1}H NMR (600 MHz, $CDCl_3$, α anomer): $\delta = 1.24$ (s, 3H, CH_3-BDA), 1.32 (s, 3H, CH_3-BDA), 3.17 (s, 3H, OCH_3-BDA), 3.24 (s, 3H, OCH_3-BDA), 3.49 (m, 1H, H-6_b), 3.54–3.59 (m, 2H, H-6_b, H-6_a), 3.75 (dd, 1H, $J = 6.2$, 10.5 Hz, H-6_a), 3.84 (dd, 1H, $J = 2.7$,

10.1 Hz, H-3$_b$), 3.87 (dd, 1H, J = 3.1, 9.8 Hz, H-3$_a$), 3.91 (s, 1H, H-4$_b$), 3.94 (t, 1H, J = 5.6 Hz, H-5$_a$), 3.97 (t, 1H, J = 6.5 Hz, H-5$_b$), 4.01 – 4.04 (m, 3H, CH$_2$-ClAc, H-2$_a$, H-2$_b$), 4.06 (d, 1H, J = 15.1 Hz, CH$_2$-ClAc), 4.43 (d, 1H, J = 11.8 Hz, CH$_2$Ph), 4.46 (d, 1H, J = 11.8 Hz, CH$_2$Ph), 4.56 (d, 1H, J = 11.0 Hz, CH$_2$Ph), 4.70 – 4.77 (m, 3H, CH$_2$Ph), 4.81 – 4.85 (m, 2H, CH$_2$Ph, H-1$_b$), 4.94 (d, 1H, J = 11.0 Hz, CH$_2$Ph), 5.01 (d, 1H, J = 10.0 Hz, H-1$_a$), 5.44 (d, 1H, J = 2.7 Hz, H-4$_a$), 7.16 – 7.43 (m, 23H, ArH), 7.60 – 7.63 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = [17.4, 17.7 (CH$_3$-BDA)], 40.8 (CH$_2$-ClAc), [48.1, 48.1 (OCH$_3$-BDA)], 66.36 (CH-2$_a$), 66.65 (CH$_2$-6$_a$), 69.1 (CH$_2$-6$_b$), 69.4 (CH-5$_b$), 70.0 (CH-3$_a$), 70.5 (CH-4$_a$), [73.2, 73.3, 73.4, 73.7 (CH$_2$Ph)], 75.0 (CH-4$_b$), 76.6 (CH-2$_b$), 77.5 (CH-5$_a$), 79.0 (CH-3$_b$), 81.6 (CH-1$_a$), 98.0 (CH-1$_b$), [100.3, 100.5 (C$_q$-BDA)], [127.3, 127.4, 127.5, 127.6, 127.7, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3 (CH-Ar)], 128.6 (C$_q$-Ar), [128.9, 133.9 (CH-Ar)], [138.2, 138.4, 138.7, 138.9 (C$_q$-Ar)], 167.0 (CO-ClAc); HR-MS (ESI): m/z: 1071.2645 [M + K]$^+$, 1055.2904 [M + Na]$^+$, 1039.31959; $C_{54}H_{61}O_{13}SeCl$ requires [M + Na]$^+$ 1055.2863; $C_{54}H_{61}O_{13}SeCl$: calcd C 62.82, H 5.96; found C 62.75, H 5.90.

(2′*S*,3′*S*) Phenyl 6-*O*-chloroacetyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranosyl)-1-seleno-α-D-mannopyranoside (51): A mixture of donor **7** (83 mg, 0.12 mmol) and acceptor **8** (53 mg, 0.104 mmol) was dried by azeotropic distillation with dry toluene and left under vacuum for 4 h. Molecular sieves (4 Å, 200 mg) and dry CH_2Cl_2/Et_2O (1 mL:1 mL) were added. The resulting suspension was stirred for 30 min before NIS (122 mg, 0.54 mmol) and TMSOTf (10 μL of a solution of 50 μL TMSOTf in 1 mL dry CH_2Cl_2) were added sequentially. The reaction mixture turned dark brown immediately and was stirred for one hour before triethylamine (0.1 mL) was added. The mixture was diluted with ether, filtered through celite, washed with aq $NaHCO_3$, aq $Na_2S_2O_4$, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (SiO_2, petrol/Et_2O 3:1 →2:1) to furnish dimannoside **51** (96 mg, 0.098 mmol, 87 %): R_f = 0.55 (Et_2O/petrol 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.02 (s, 6H, CH$_3$-TBS), 0.90 (s, 9H, CH$_3$-*t*Bu), 1.32 (s, 6H, CH$_3$-BDA), 3.22 (s, 3H, OCH$_3$-BDA), 3.33 (s, 3H, OCH$_3$-BDA), 3.63 – 3.68 (m, 1H, H-5$_b$), 3.75 (d, 1H, J = 10.4 Hz, H-6$_b$), 3.83 (dd, 1H, J = 10.9, 4.3 Hz, H-6$_b$), 3.88 (d, 1H, J = 14.7 Hz, ClAc), 3.92 – 3.99 (m, 4H, ClAc, H-2$_b$, H-3$_b$, H-4$_b$), 4.01 (dd, 1H, J = 9.9, 1.9 Hz, H-3$_a$), 4.07 – 4.13 (m, 1H, H-4$_a$), 4.30 (s, 1H, H-2$_a$), 4.31 – 4.36 (m, 2H, H-5$_a$, H-6$_a$), 4.44 (d, 1H, J = 9.5 Hz, H-6$_a$), 4.57 – 4.64 (m, 4H, CH$_2$Ph), 4.70 (d, 1H, J = 12 Hz, CH$_2$Ph), 4.91 (d, 1H, J = 10.5 Hz, CH$_2$Ph), 5.33 (s, 1H, H-1$_b$), 5.79 (s, 1H, H-1$_a$), 7.22 – 7.35 (m, 16H, ArH), 7.40 (d, 2H, J = 3.3 Hz, ArH), 7.55 (d, 2H, J = 2.8 Hz, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = [−5.3, −5.11 (CH$_3$-TBS)], [17.7, 17.8 (CH$_3$-BDA)], 18.3 (C$_q$-*t*Bu), 26.0 (CH$_3$-*t*Bu), 40.6 (CH$_2$-ClAc), [48.1, 48.1 (OCH$_3$-BDA)], 62.7 (CH$_2$-6$_b$), 63.5 (CH-4$_a$), 63.8 (CH$_2$-6$_a$), 69.7 (CH-3$_a$), 70.8 (CH-5$_a$), [72.0, 72.1 (CH$_2$Ph)], 73.7 (CH-5$_b$), 74.7 (CH-2/3/4$_b$), 75.1 (CH-2/3/4$_b$, CH$_2$Ph), 76.2 (CH-2$_a$), 79.8 (CH-2/3/4$_b$), 85.1 (CH-1$_a$), 98.6 (CH-1$_b$), [99.8, 100.0 (C$_q$-BDA)], [127.3, 127.5, 127.6, 127.7, 127.8, 128.0, 128.2, 128.3, 129.2 (CH-Ar)], 129.4 (C$_q$-Ar), 133.5 (CH-Ar), [138.6, 138.7, 138.7 (C$_q$-Ar)], 167.1 (CO-ClAc); HR-MS (ESI): m/z: 1079.3251 [M + Na]$^+$; $C_{53}H_{69}O_{13}SiSeCl$ requires [M + Na]$^+$ 1079.3258; $C_{53}H_{69}O_{13}SiSeCl$: calcd C 60.25, H 6.58; found C 60.23, H 6.76.

(2′*R*,3′*R*) Ethyl 4-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-*O*-chloroacetyl-3-*O*-(4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-galactopyranosyl)-1-thio-α-D-mannopyranoside (49): A mixture of galactosyl donor **47** (805 mg, 0.78 mmol) and acceptor **9** (freshly prepared from 0.75 mmol of **44**) was dried by azeotropic distillation with dry toluene and left under vacuum for 4 h. Molecular sieves (4 Å, 3 g) and dry ether (15 mL) were added. The resulting suspension was stirred for 30 min before MeOTf (420 μL, 3.75 mmol) was added dropwise. The reaction mixture was stirred for 4 h before triethylamine (1 mL) was added and it was diluted with ether and concentrated. The residue was purified by column chromatography (SiO_2, petrol/Et_2O 2:1 →3:2) to furnish trisaccharide **49** (794 mg, 0.575 mmol, 76 %): R_f = 0.46 (Et_2O/petrol 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.05 (s, 3H, CH$_3$-TBS), 0.07 (s, 3H, CH$_3$-TBS), 0.92 (s, 9H, CH$_3$-*t*Bu), 1.11 (s, 3H, CH$_3$-BDA), 1.18 (s, 3H, CH$_3$-BDA), 1.20 (t, 3H, J = 7.3 Hz, CH$_3$-SEt), 2.45 – 2.62 (m, 2H, CH$_2$-SEt), 3.01 (s, 3H, OCH$_3$-BDA), 3.22 (s, 3H, OCH$_3$-BDA), 3.56 (d, 2H, J = 6.5 Hz, H-6$_c$), 3.58 – 3.64 (m, 2H, H-6$_b$), 3.72 – 3.78 (m, 2H, H-6$_a$), 3.84 (t, 1H, J = 9.3 Hz, H-4$_a$), 3.93 – 3.97 (m, 1H, H-5$_a$), 3.97 – 4.06 (m, 5H, H-2$_b$, H-2$_c$, H-3$_c$, H-4$_c$, ClAc), 4.07 – 4.14 (m, 4H, H-3$_b$, H-5$_c$, 2 × ClAc), 4.15 – 4.22 (m, 2H, H-3$_a$, ClAc), 4.23 (t, 1H, J = 5.8 Hz, H-5$_b$), 4.42 (d, 1H, J = 11.2 Hz, CH$_2$Ph), 4.52 (d, 1H, J = 11.2 Hz, CH$_2$Ph), 4.56 (d, 1H, J = 11.2 Hz, CH$_2$Ph), 4.61 (d, 1H, J = 11.2 Hz, CH$_2$Ph), 4.73 (m, 2H, CH$_2$Ph), 4.76 (d, 1H, J = 11.3 Hz, CH$_2$Ph), 4.84 (d, 1H, J = 2.7 Hz, H-1$_c$), 4.89 (d, 1H, J = 11.2 Hz, CH$_2$Ph), 4.93 (d, 1H, J = 11.3 Hz, CH$_2$Ph), 5.10 (d, 1H, J = 11.2 Hz, CH$_2$Ph), 5.21 (s, 1H, H-1$_a$), 5.22 (d, 1H, J = 3.4 Hz, H-1$_b$), 5.29 (s, 1H, H-2$_a$), 5.43 (s, 1H, H-4$_b$), 7.19 – 7.42 (m, 25H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = [−5.4, −5.2 (CH$_3$-TBS)], 14.7 (CH$_3$-SEt), [17.4, 17.6 (CH$_3$-BDA)], 18.3 (C$_q$-*t*Bu), 25.2 (CH$_2$-SEt), 25.8 (CH$_3$-*t*Bu), [40.8, 40.9 (CH$_2$-ClAc)], [47.7, 48.1 (OCH$_3$-BDA)], 62.0 (CH$_2$-6$_a$), 64.1 (CH-3$_b$), 65.0 (CH-2$_b$), 67.2 (CH$_2$-6$_b$), 68.9 (CH$_2$-6$_c$), 69.3 (CH-5$_b$), 69.4 (CH-5$_c$), 70.9 (CH-4$_b$), [73.0, 73.0 (CH$_2$Ph)], 73.1 (CH-5$_a$), 73.1 (CH$_2$Ph), 74.4 (CH-4$_a$), [74.5, 74.7 (CH$_2$Ph)], 75.1 (CH-2/3/4$_c$), 75.6 (CH-2$_a$), 76.8 (CH-2/3/4$_c$), 77.7 (CH-3$_a$), 78.8 (CH-2/3/4$_c$), 81.3 (CH-1$_a$), 98.6 (CH-1$_c$), 99.5 (CH-1$_b$), 99.8 (C$_q$-BDA), [127.2, 127.3, 127.4, 127.4, 127.4, 127.5, 127.6, 128.0, 128.1, 128.1, 128.2, 128.2, 128.3 (CH-Ar)], [138.3, 138.7, 138.8, 138.9, 139.2 (C$_q$-Ar)], [166.8, 166.9 (CO-ClAc)]; HR-MS (ESI): m/z: 1401.4943 [M + Na]$^+$, $C_{71}H_{92}O_{19}SiSCl_2$ requires [M + Na]$^+$ 1401.4997; $C_{71}H_{92}O_{19}SiSCl_2$: calcd C 61.77, H 6.72; found C 61.57, H 6.69.

(2′*R*,3′*R*) Ethyl 4-*O*-benzyl-2-*O*-chloroacetyl-3-*O*-(4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-galactopyranosyl)-1-thio-α-D-mannopyranoside (50): Silyl ether **49** (1.91 g, 1.24 mmol) was dissolved in CH_3CN (15 mL) and aq HF (445 μL, 48 % in H_2O, 12.3 mmol) was added. The solution was stirred for one hour at RT before methoxytrimethylsilane (TMSOMe) (excess) was added and the solvent was partly evaporated (to ca. 5 mL). The remaining solution was diluted with ether, washed with $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (SiO_2, Et_2O/petrol 3:1) to give alcohol **50** (1.39 g, 1.1 mmol, 89 %): R_f = 0.26 (petrol/Et_2O 1:2); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.11 (s, 3H, CH$_3$-BDA), 1.17 (s, 3H, CH$_3$-BDA), 1.21 (t, 3H, J = 7.3 Hz, CH$_3$-SEt), 1.73 (s, 1H, OH-6$_a$), 2.48 – 2.56 (m, 2H, CH$_2$-SEt), 3.02 (s, 3H, OCH$_3$-BDA), 3.22 (s, 3H, OCH$_3$-BDA), 3.58 (d, 2H, J = 6.6 Hz, H-6$_c$), 3.61 – 3.66 (m, 2H, H-6$_b$), 3.66 – 3.75 (m, 2H, H-6$_a$), 3.91 (t, 1H, J = 9.5 Hz, H-4$_a$), 3.97 – 4.06 (m, 6H, H-5$_a$, H-2$_b$, H-2$_c$, H-3$_c$, H-4$_c$, ClAc), 4.08 – 4.13 (m, 3H, H-3$_b$, H-5$_c$, ClAc), 4.17 (d, 1H, J = 15.0 Hz, ClAc), 4.18 (dd, 1H, J = 3.1, 9.1 Hz, H-3$_a$), 4.23 (d, 1H, J = 15.0 Hz, ClAc), 4.28 (t, 1H, J = 5.7 Hz, H-5$_b$), 4.44 (d, 1H, J = 11.5 Hz, CH$_2$Ph), 4.52 (d, 1H, J = 11.5 Hz, CH$_2$Ph), 4.57 (d, 1H, J = 11.5 Hz, CH$_2$Ph), 4.69 (d, 1H, J = 11.5 Hz, CH$_2$Ph), 4.74 (s, 2H, CH$_2$Ph), 4.77 (d, 1H, J = 11.5 Hz, CH$_2$Ph), 4.87 (d, 1H, J = 2.7 Hz, H-1$_c$), 4.89 (d, 1H, J = 11.5 Hz, CH$_2$Ph), 4.93 (d, 1H, J = 11.5 Hz, CH$_2$Ph), 5.10 (d, 1H, J = 11.5 Hz, CH$_2$Ph), 5.20 (s, 1H, H-1$_a$), 5.25 (d, 1H, J = 3.3 Hz, H-1$_b$), 5.32 (s, 1H, H-2$_a$), 5.48 (s, 1H, H-4$_b$), 7.23 – 7.45 (m, 25H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 14.7 (CH$_3$-SEt), [17.5, 17.6 (CH$_3$-BDA)], 25.4 (CH$_2$-SEt), [40.8, 40.9 (CH$_2$-ClAc)], [47.7, 48.1 (OCH$_3$-BDA)], 61.6 (CH$_2$-6$_a$), 64.0 (CH-3$_b$), 65.0 (CH-2$_b$), 67.3 (CH$_2$-6$_b$), 68.9 (CH$_2$-6$_c$), 69.4 (CH-5$_b$), 69.5 (CH-5$_c$), 70.8 (CH-4$_b$), 72.3 (CH-5$_a$), [73.0, 73.1, 73.2 (CH$_2$Ph)], 73.6 (CH-4$_a$), [74.5, 74.7 (CH$_2$Ph)], 75.1 (CH-2/3/4$_c$), 75.4 (CH-2$_a$), 76.8 (CH-2/3/4$_c$), 77.6 (CH-3$_a$), 78.8 (CH-2/3/4$_c$), 81.7 (CH-1$_a$), 98.7 (CH-1$_c$), 99.5 (CH-1$_b$), 99.8 (C$_q$-BDA), [127.3, 127.4, 127.5, 127.5, 127.6, 127.7, 128.0, 128.1, 128.3, 128.3, 128.3, 128.3 (CH-Ar)], [138.3, 138.5, 138.7, 138.8, 139.2 (C$_q$-Ar)], [166.8, 166.9 (CO-ClAc)]; HR-MS (ESI): m/z: 1287.4130 [M + Na]$^+$, $C_{65}H_{78}O_{19}SCl_2$ requires [M + Na]$^+$ 1287.4133; $C_{65}H_{78}O_{19}SCl_2$: calcd C 61.65, H 6.21; found C 61.38, H 6.12.

(2′*R*,3′*R*,2″*S*,3″*S*) Ethyl 4-*O*-benzyl-2-*O*-chloroacetyl-3-*O*-(4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-galactopyranosyl)-6-*O*-(6-*O*-chloroacetyl-3,4-*O*-(2″,3″-dimethoxybutane-2″,3″-diyl)-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl)-α-D-mannopyranosyl)-1-thio-α-D-mannopyranoside (53): A mixture of mannosyl donor **51** (81 mg, 77 μmol) and acceptor **50** (20 mg, 16 μmol) was dried by azeotropic distillation with dry toluene and left under vacuum for 4 h. Molecular sieves (4 Å, 250 mg) and dry CH_2Cl_2 (0.8 mL) were added. The resulting suspension was stirred for one hour before MeOTf (8 μL, 72 μmol) was added dropwise. The reaction mixture was stirred for 24 hours before triethylamine (1 mL) was added and it was diluted with ether, filtered through celite and concentrated. The residue was purified by preparative TLC (SiO_2, petrol/Et_2O 2:3) to furnish pentasaccharide **53** (26 mg, 12 μmol, 75 %): R_f = 0.64 (Et_2O/petrol 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.04 (s, 6H, CH$_3$-TBS), 0.86 (s, 9H, CH$_3$-*t*Bu), 1.02 (s, 3H, CH$_3$-BDA), 1.15 (s, 3H, CH$_3$-BDA), 1.22 (t, 3H, J = 7.3 Hz, CH$_3$-SEt), 1.26 (s, 3H, CH$_3$-BDA), 1.32 (s, 3H, CH$_3$-BDA), 2.44 – 2.52 (m, 1H, CH$_2$-SEt), 2.54 – 2.61 (m, 1H, CH$_2$-SEt), 2.93 (s, 3H,

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OCH_3-BDA), 3.19 (s, 3H, OCH_3-BDA), 3.21 (s, 3H, OCH_3-BDA), 3.23 (s, 3H, OCH_3-BDA), 3.56 (d, 1H, $J = 10.4$ Hz, H-6_a), 3.58–3.63 (m, 3H, H-6_b, 2 × H-6_c), 3.65–3.69 (m, 2H, H-6_b, H-5_e), 3.71–3.78 (m, 2H, H-5_a, H-6_a), 3.80–3.85 (m, 2H, H-5_d, H-6_e), 3.86–3.90 (m, 2H, ClAc, H-6_e), 3.92–3.97 (m, 5H, ClAc, H-4_d, H-2_e, H-3_e, H-4_e), 3.98–4.02 (m, 4H, ClAc, H-2_b, H-2_d, H-3_d), 4.03–4.06 (m, 3H, H-2_c, H-3_c, H-4_c), 4.07–4.14 (m, 4H, ClAc, H-3_b, H-5_c, H-6_d), 4.14–4.23 (m, 4H, 2 × ClAc, H-4_a, H-3_a), 4.28 (t, 1H, $J =$ 5.8 Hz, H-5_b), 4.38 (d, 1H, $J = 10.5$ Hz, H-6_d), 4.46 (d, 1H, $J = 11.9$ Hz, CH_2Ph), 4.53–4.71 (m, 8H, CH_2Ph), 4.79 (s, 1H, H-1_d), 4.74–4.80 (m, 3H, CH_2Ph), 4.88 (d, 1H, $J = 2.8$ Hz, H-1_c), 4.90–4.96 (m, 3H, CH_2Ph), 5.20 (s, 1H, H-1_a), 5.24 (s, 1H, H-1_b), 5.25 (d, 1H, $J = 11.3$ Hz, CH_2Ph), 5.33 (s, 2H, H-2_a, H-1_e), 5.47 (s, 1H, H-4_b), 7.20–7.43 (m, 40H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ [−5.3, −5.1 (CH_3-TBS)], 14.6 (CH_3-SEt), [17.3, 17.5 , 17.7, 17.9 (CH_3-BDA)], 18.3 (C_q-*t*Bu), 25.0 (CH_2-SEt), 25.9 (CH_3-*t*Bu), [40.7, 40.9 (CH_2-ClAc)], [47.6, 47.8, 48.0, 48.1 (OCH_3-BDA)], 62.7 (CH_2-6_e), 63.1 (CH-4_d), 63.8 (CH_2-6_d), 64.0 (CH-3_b), 64.9 (CH-2_b), 66.3 (CH_2-6_a), 67.3 (CH_2-6_b), 68.6 (CH-2/3/4_c), 68.8 (CH-5_d), 68.9 (CH_2-6_c), 69.4 (CH-5_b), 69.4 (CH-5_c), 70.8 (CH-4_b), 71.2 (CH-4_a), [71.8, 72.1, 73.0, 73.2 (CH_2Ph)], 73.6 (CH-5_e), 74.4 (CH-2/3_d), 74.5 (CH_2Ph), 74.6 (CH-5_a, CH-2/3/4_e), [74.8, 75.0 (CH_2Ph)], [75.1, 75.2 (CH-2/3/4_c, CH-2/3/4_e], 75.4 (CH-2_a), 76.8 (CH-2/3_d), 77.8 (CH-3_a), 78.8 (CH-2/3/4_c), 79.8 (CH-2/3/4_e), 81.0 (CH-1_a), 98.6 (CH-1_c), 98.6 (CH-1_e), 99.5 (CH-1_d), 99.6 (CH-1_b), [99.6, 99.8, 99.9 (C_q-BDA)], [127.0, 127.3, 127.5, 127.5, 127.6, 127.6, 128.0, 128.0, 128.1, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3 (CH-Ar)], [138.3, 138.5, 138.6, 138.7, 138.7, 138.8, 138.8, 139.2 (C_q-Ar)], [166.7, 166.8, 167.1 (CO-ClAc)]; MS (MALDI-TOF): *m/z*: 2189 $[M + Na]^+$; $C_{112}H_{141}O_{32}SiSCl_3$: calcd C 62.11, H 6.56; found C 61.96, H 6.43.

(2′*R*,3′*R*,2″*S*,3″*S*) 1-*O*-Allyl-2,3,4,5-tetra-*O*-benzyl-6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-((4-*O*-benzyl-2-*O*-chloroacetyl-3-*O*-(4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-galactopyranosyl)-6-*O*-(6-*O*-chloroacetyl-3,4-*O*-(2″,3″-dimethoxybutane-2″,3″-diyl)-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranosyl)-α-D-mannopyranosyl)-α-D-mannopyranosyl))-α-D-glucopyranosyl)-D-*myo*-inositol (2): Two mixtures of donor **53** (2 × 70 mg, 2 × 32 μmol) and acceptor **10** (2 × 20 mg, 2 × 21 μmol) were dried by azeotropic distillation with dry toluene and left under vacuum for 4 h. Molecular sieves (4 Å, 2 × 250 mg, beads) and dry Et_2O/CH_2Cl_2 (2 × 0.8 mL:2 × 0.4 mL) were added to each mixture separately. The resulting mixtures were stirred for 2 h before they were cooled to 0 °C. NIS (2 × 15 mg, 2 × 63 μmol) was added and the mixtures were stirred for another hour at 0 °C. TfOH (2 × 40 μL of a solution of 2 × 30 μL TfOH in 2 × 2 mL dry CH_2Cl_2) was added at −10 °C and the reaction mixtures were immediately warmed to 0 °C and stirred for 20 min before additional TfOH (2 × 20 μL of a solution of 2 × 30 μL TfOH in 2 × 2 mL dry CH_2Cl_2) was added at −10 °C followed immediately by warming to 0 °C. The reaction mixtures were stirred for another 10 min at 0 °C before triethylamine (2 × 3 drops) was added. The two reaction mixtures were combined and diluted with ether, washed with aq $Na_2S_2O_3$, dried over $MgSO_4$ and concentrated. The residue was purified by preparative TLC (SiO_2, petrol/Et_2O 60:45) to furnish heptasaccharide **2** (64 mg, 21 μmol, 50%): $R_f = 0.42$ (Et_2O/petrol 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.04$ (s, 3H, CH_3-TBS), 0.05 (s, 3H, CH_3-TBS), 0.87 (s, 9H, CH_3-*t*Bu), 0.99 (s, 3H, CH_3-BDA), 1.17 (s, 3H, CH_3-BDA), 1.28 (s, 3H, CH_3-BDA), 1.29 (s, 3H, CH_3-BDA), 3.03 (s, 3H, OCH_3-BDA), 3.02–3.08 (m, 1H, H-6_b), 3.17 (s, 3H, OCH_3-BDA), 3.22 (s, 3H, OCH_3-BDA), 3.25 (s, 3H, OCH_3-BDA), 3.17–3.29 (m, 2H, H-6_b, H-6_c), 3.32 (dd, 1H, $J = 3.6$, 9.8 Hz, H-2_b), 3.40–3.43 (m, 2H, H-1_a, H-3_a), 3.46 (t, 1H, $J = 9.3$ Hz, H-5_a), 3.53 (d, 2H, $J = 6.7$ Hz, 2 × H-6_e), 3.59–3.62 (m, 1H, H-6_c), 3.65–3.70 (m, 4H, H-5_c, H-6_d, H-5_f, H-3/4/5_g), 3.71–3.88 (m, 7H, 2 × ClAc, H-4_c, H-6_d, H-6_g, H-2_f, H-6_f), 3.90–4.13 (m, 23H, 4 × ClAc, 2 × CH_2-All, H-2_a, H-3_b, H-4_b, H-5_b, H-3_c, H-2_d, H-2_e, H-3_e, H-4_e, H-5_e, H-3_f, H-4_f, H-6_f, H-3/4/5_g, H-3/4/5_g, H-2_g, H-6_g), 4.15–4.20 (m, 2H, H-4_a, H-3_d), 4.26 (t, 1H, $J = 9.6$ Hz, H-6_a), 4.28–4.30 (m, 1H, H-5_d), 4.31 (d, 1H, $J =$ 11.9 Hz, CH_2Ph), 4.38 (d, 1H, $J = 11.9$ Hz, CH_2Ph), 4.41 (d, 1H, $J =$ 12.0 Hz, CH_2Ph), 4.49 (d, 1H, $J = 12.0$ Hz, CH_2Ph), 4.54–4.59 (m, 2H, CH_2Ph), 4.58 (s, 1H, H-1_f), 4.61–4.84 (m, 14H, CH_2Ph), 4.85–4.90 (m, 4H, CH_2Ph, H-1_e), 4.92–4.95 (m, 2H, CH_2Ph), 5.00 (d, 1H, $J = 10.8$ Hz, CH_2Ph), 5.11 (d, 1H, $J = 11.3$ Hz, CH_2Ph), 5.19 (s, 1H, H-1_d), 5.20 (d, 1H, $J = 10.7$ Hz, =CH_2-All), 5.27 (s, 1H, H-1_g), 5.30 (s, 1H, H-2_c), 5.31 (d, 1H, $J = 5.8$ Hz, =CH_2-All), 5.42 (s, 1H, H-1_c), 5.48 (d, 1H, $J = 12.1$ Hz, CH_2Ph), 5.57 (s, 1H, H-4_d), 5.70 (d, 1H, $J = 3.7$ Hz, H-1_b), 5.93–6.00 (m, 1H, =CH-All), 7.18–7.46 (m, 70H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ [−5.3, −5.1 (CH_3-TBS)], [17.3, 17.5, 17.7, 18.0 (CH_3-BDA)], 18.3 (C_q-*t*Bu), 25.9 (CH_3-*t*Bu), [40.6, 40.6, 41.0 (CH_2-ClAc)], [47.7, 47.8, 47.9, 48.0 (OCH_3-BDA)], 62.6 (CH_2-6_g), 62.9 (CH-3/4_f), 63.5 (CH-2_b), 63.6 (CH_2-6_f), 64.2 (CH-3_d), 65.1 (CH-2_d), 66.2 (CH_2-6_c), 66.6 (CH_2-6_d), 68.1 (CH_2-6_b), 68.6 (CH), 68.6 (CH-5_f), 68.8 (CH_2-6_e), 69.1 (CH-5_d), 69.6 (CH-3/5_b), 69.8 (CH-2/3/$4/5_e$), 70.2 (CH-4_d), 70.7 (CH_2-All), 71.0 (CH-5_c), [71.8, 72.1 (CH_2Ph)], 72.8 (CH-4_b), 72.9 (CH_2Ph), 73.0 (CH), [73.0, 73.2, 73.3, 73.3 (CH_2Ph)], 73.4 (CH-2/3/4/5_g), 73.6 (CH-2/4_c), 73.7 (CH-2/4_c), [74.2, 74.3, 74.4 (CH_2Ph)], 74.5 (CH), 74.7 (CH_2Ph), 74.8 (CH-2_f), 74.9 (CH), [75.1, 75.2 (CH_2Ph)], 75.4 (CH), 75.7 (CH_2Ph), 75.7 (CH-6_a), 76.8 (CH), 78.8 (CH-2/3/4/5_e), 79.0 (CH-3_c), 80.0 (CH-2/3/4/5_g), 80.8 (CH-3/5_b), 80.9 (CH-1/3_a), 81.1 (CH-5_a), 81.7 (CH-1/3_a), 82.0 (CH-4_a), 96.9 (CH-1_c), 97.7 (CH-1_b), 98.7 (CH-1_g), 98.9 (CH-1_e), 99.2 (CH-1_f), [99.6, 99.7, 99.8, 99.9 (C_q-BDA)], 100.0 (CH-1_d), 116.9 (=CH_2-All), [126.7, 127.4, 127.5, 127.5, 127.7, 127.8, 128.0, 128.1, 128.1, 128.1, 128.1, 128.1, 128.2, 128.2, 128.3, 128.4, 128.4 (CH-Ar)], 134.3 (=CH-All), [137.6, 138.1, 138.2, 128.6, 138.6, 138.8, 138.8, 138.9, 139.1, 139.2 (C_q-Ar)], [166.6, 166.7, 166.8 (CO-ClAc)]; MS [(+)-MALDI-TOF]: *m/z*: 3086; $C_{167}H_{196}O_{42}N_3SiCl_3$ requires $[M + Na]^+$ 3071; $C_{167}H_{196}O_{42}N_3SiCl_3$: calcd C 65.73, H 6.47, N 1.38; found C 65.48, H 6.56, N 1.34.

(2′*R*,3′*R*,2″*S*,3″*S*) 1-*O*-Allyl-2,3,4,5-tetra-*O*-benzyl-6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-((4-*O*-benzyl-2-*O*-chloroacetyl-3-*O*-(4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-galactopyranosyl)-6-*O*-(6-*O*-chloroacetyl-3,4-*O*-(2″,3″-dimethoxybutane-2″,3″-diyl)-2-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranosyl)-α-D-mannopyranosyl))-α-D-glucopyranosyl)-D-*myo*-inositol (54): Silyl ether **2** (122 mg, 40 μmol) was dissolved in CH_3CN (1.5 mL) and aq HF (30 μL, 48% in H_2O, 0.8 mmol) was added. The reaction mixture was stirred for 20 min at RT before TMSOMe (excess) was added. The solution was diluted with CH_2Cl_2, washed with aq $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (Et_2O/petrol 1:1 → 3:2) to give alcohol **54** (96 mg, 32 μmol, 81%): $R_f = 0.42$ (Et_2O/petrol 3:2); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.02$ (s, 3H, CH_3-BDA), 1.16 (s, 3H, CH_3-BDA), 1.28 (s, 3H, CH_3-BDA), 1.29 (s, 3H, CH_3-BDA), 3.01 (s, 4H, OCH_3-BDA, H-6_b), 3.15–3.17 (m, 4H, OCH_3-BDA, H-6_b), 3.21 (s, 3H, OCH_3-BDA), 3.26 (s, 3H, OCH_3-BDA), 3.27–3.32 (m, 2H, H-2_b, H-6_c), 3.39 (d, 2H, $J = 9.8$ Hz, H-1_a, H-3_a), 3.44 (d, 1H, $J = 9.3$ Hz, H-5_a), 3.50–3.56 (m, 2H, H-6_e), 3.58–3.63 (m, 3H, H-5_c, H-6_c, H-6_g), 3.63–3.69 (m, 4H, H-6_d, H-5_g, H-6_g, H-5_f), 3.71 (d, 1H, $J = 9.0$ Hz, H-6_d), 3.74–3.80 (m, 2H, ClAc, H-4_c), 3.82 (d, 1H, $J = 14.8$ Hz, ClAc), 3.85 (s, 1H, H-2_f), 3.88–4.08 (m, 21H, 3 × ClAc, 2 × CH_2-All, H-2_a, H-3_b, H-4_b, H-5_b, H-3_c, H-2_d, H-2_e, H-3_e, H-4_e, H-5_e, H-3_f, H-4_f, H-6_f, H-2_g, H-3_g, H-4_g), 4.10–4.17 (m, 4H, ClAc, H-4_a, H-3_d, H-6_f), 4.23 (t, 1H, $J = 9.6$ Hz, H-6_a), 4.27 (d, 1H, $J = 12.1$ Hz, CH_2Ph), 4.28–4.32 (m, 1H, H-5_d), 4.38 (d, 2H, $J = 12.3$ Hz, CH_2Ph), 4.46 (d, 1H, $J = 12.0$ Hz, CH_2Ph), 4.53 (d, 2H, $J = 11.6$ Hz, CH_2Ph), 4.56–4.62 (m, 5H, CH_2Ph), 4.64–4.67 (m, 4H, 3 × CH_2Ph, H-1_f), 4.67–4.74 (m, 3H, CH_2Ph), 4.77 (d, 1H, $J =$ 10.8 Hz, CH_2Ph), 4.81 (d, 1H, $J = 11.8$ Hz, CH_2Ph), 4.83–4.92 (m, 7H, 6 × CH_2Ph, H-1_e), 4.98 (d, 1H, $J = 10.8$ Hz, CH_2Ph), 5.10 (d, 1H, $J = 11.2$ Hz, CH_2Ph), 5.19 (d, 1H, $J = 10.2$ Hz, =CH_2-All), 5.20 (s, 1H, H-1_d), 5.24 (s, 1H, H-1_g), 5.28 (s, 1H, H-2_c), 5.29 (d, 1H, $J = 17.1$ Hz, =CH_2-All), 5.38 (d, 1H, $J = 11.8$ Hz, CH_2Ph), 5.40 (s, 1H, H-1_c), 5.55 (s, 1H, H-4_d), 5.67 (d, 1H, $J = 3.7$ Hz, H-1_b), 5.92–5.99 (m, 1H, =CH-All), 7.13–7.45 (m, 70H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta =$ [17.3, 17.5, 17.7, 17.9 (CH_3-BDA)], [40.6, 40.7, 41.0 (CH_2-ClAc)], [47.7, 47.8, 47.9, 48.0 (OCH_3-BDA)], 62.2 (CH_2-6_g), 62.9 (CH-2/3_f), 63.5 (CH-2_b), 63.6 (CH_2-6_f), 64.1 (CH-3_d), 65.1 (CH-2_d), 66.1 (CH_2-6_c), 66.6 (CH_2-6_d), 68.1 (CH_2-6_b), 68.4 (CH), 68.6 (CH-5_f), 68.7 (CH_2-6_e), 69.0 (CH-5_d), 69.6 (CH-5_b), 69.8 (CH-5_e), 70.2 (CH-4_d), 70.7 (CH_2-All), 71.5 (CH-5_c), [71.8, 72.4 (CH_2Ph)], 72.6 (CH-5_g), 72.8 (CH_2Ph), 72.9 (CH), 73.0 (CH-4_b), [73.0, 73.1, 73.2, 73.4 (CH_2Ph)], 73.5 (CH-2/4_c), 73.6 (CH-2/4_c), [74.1, 74.3, 74.4, 74.7 (CH_2Ph)], [74.8, 74.9 (CH)], 75.0 (CH-2_f), [75.1, 75.2 (CH_2Ph)], 75.2 (CH), 75.6 (CH_2Ph), 75.7 (CH-6_a), 76.8 (CH), 78.4 (CH-3_c), 78.8 (CH-2/3/4_e), 79.8 (CH-2/3/4_g), 80.8 (CH-3_b), 80.9 (CH-1/3_a), 81.1 (CH-5_a), 81.7 (CH-1/3_a), 82.0 (CH-4_a), 97.1 (CH-1_c), 97.8 (CH-1_b), 98.8 (CH-1_e), 99.0 (CH-1_g), 99.6 (CH-1_f), [99.6, 99.7, 99.8, 99.8 (C_q-BDA)], 99.8 (CH-1_d), 117.0 (=CH_2-All), [126.9, 127.4, 127.5, 127.5, 127.6, 127.7, 127.7, 128.1, 128.1, 128.1, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4 (CH-Ar)], 134.3 (=CH-All), [137.6, 138.1, 138.2, 138.3, 138.4, 138.5, 138.6, 138.6, 138.8, 139.1 (C_q-Ar)], [166.7, 166.8, 166.9 (CO-ClAc)]; MS [(+)-MALDI-TOF]: *m/z*: 2962; $C_{161}H_{182}O_{42}N_3Cl_3$ requires $[M + Na]^+$ 2957; $C_{161}H_{182}O_{42}N_3Cl_3$: calcd C 65.83, H 6.24, N 1.43; found C 65.88, H 6.36, N 1.32.

(2′*R*,3′*R*,2″*S*,3″*S*) 1-*O*-Allyl-2,3,4,5-tetra-*O*-benzyl-6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-((4-*O*-benzyl-2-*O*-chloroacetyl-3-*O*-(4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-galactopyranosyl)-6-*O*-(6-*O*-chloroacetyl-3,4-*O*-(2″,3″-dimethoxybutane-2″,3″-diyl)-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-(benzyl-*O*-(2-((*N*-benzyloxycarbonyl)amino)ethyl)phosphono)-α-D-mannopyranosyl)-α-D-mannopyranosyl)-α-D-mannopyranosyl))-α-D-glucopyranosyl)-D-*myo*-inositol (55): A mixture of alcohol **54** (54 mg, 18.4 μmol) and tetrazole (19.3 mg, 0.27 mmol) was co-evaporated with toluene, before the mixture was dissolved in dry CH_3CN (2.5 mL) and phosphoramidite **3** (80 mg, 0.18 mmol) in dry CH_2Cl_2 (2.5 mL) was added. The reaction mixture was stirred for 3.5 h at RT before *m*CPBA (71 mg, 0.37 mmol) was added at −40 °C. The reaction mixture was warmed to RT over 30 min and stirred at RT for 1 h. The solution was diluted with CH_2Cl_2, washed with aq $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was purified by preparative TLC (EtOAc/petrol 3:2) to give phosphotriester **55** (54 mg, 16.4 μmol, 89 %) as a mixture of two diastereoisomers (1:1): $R_f = 0.65$ (EtOAc/petrol 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.98$ (s, 3H, CH_3-BDA), 0.99 (s, 3H, CH_3-BDA), 1.16 (s, 6H, CH_3-BDA), 1.30 (s, 12H, CH_3-BDA), 3.01 (s, 6H, OCH_3-BDA), 3.04 (s, 2H), 3.17 (s, 6H, OCH_3-BDA), 3.20–3.34 (m, 24H), 3.41 (d, 4H, $J = 9.8$ Hz, H-1_a, H-3_a), 3.45 (d, 2H, $J = 9.3$ Hz, H-5_a), 3.53 (d, 2H, $J = 6.7$ Hz, H-6_e), 3.57–5.14 (m, 146H), 5.18–5.21 (m, 4H), 5.25–5.32 (m, 8H), 5.43 (s, 2H), 5.46–5.50 (m, 2H), 5.56 (s, 2H, H-4_d), 5.65–5.69 (m, 2H, H-1_b), 5.92–5.99 (m, 2H, =CH-All), 7.14–7.43 (m, 160H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = [17.3, 17.5, 17.6, 17.9 (CH_3-BDA)], [40.5, 40.6, 40.9, 41.2 (CH_2)], [47.7, 47.8, 47.8, 47.9 (OCH_3-BDA)], 62.7, 63.4, 63.5, 64.2, 64.6, 64.8, 65.1, 66.2, 66.2, 66.6, 66.8, 68.1, 68.6, 68.7, 69.1, 69.3, 69.3, 69.4, 69.4, 69.6, 69.6, 69.8, 70.2, 70.8, 70.9, 71.0, 71.1, 71.1, 71.7, 71.7, 72.5, 72.6, 72.9, 73.0, 73.2, 73.2, 73.3, 73.3, 73.6, 73.6, 73.7, 74.1, 74.3, 74.3, 74.7, 74.9, 75.1, 75.1, 75.1, 75.2, 75.6, 75.7, 75.8, 76.8, 77.2, 78.8, 78.9, 79.0, 79.8, 79.8, 80.9, 80.9, 81.1, 81.7, 82.0, [96.8, 97.8, 98.8, 98.8, 99.1 (CH)], [99.6, 99.6, 99.7, 99.8 (C_q)], 100.0 (CH), 117.0 (CH_2), [126.7, 126.7, 127.1, 127.2, 127.4–128.6 (CH-Ar)], 134.3 (=CH-All), [135.8, 135.8, 135.9, 135.9, 136.6, 137.6, 138.1, 138.2, 138.3, 138.3, 138.3, 138.3, 138.4, 138.6, 138.8, 138.9, 139.1, 139.2, 139.2 (C_q-Ar)], [156.3, 156.3 (OCONH)], [166.7, 166.7, 166.8 (CO-ClAc)]; ^{31}P NMR ($CDCl_3$, 243 MHz): $\delta = -0.09$, 0.03; MS (FAB): *m/z*: 3308 $[M + Na]^+$; $C_{178}H_{200}O_{47}N_4PCl_3$ requires $[M + Na]^+$ 3308.

(2′*R*,3′*R*,2″*S*,3″*S*) 2,3,4,5-Tetra-*O*-benzyl-6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-((4-*O*-benzyl-2-*O*-chloroacetyl-3-*O*-(4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-galactopyranosyl)-6-*O*-(6-*O*-chloroacetyl-3,4-*O*-(2″,3″-dimethoxybutane-2″,3″-diyl)-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-(benzyl-*O*-(2-((*N*-benzyloxycarbonyl)amino)ethyl)phosphono)-α-D-mannopyranosyl)-α-D-mannopyranosyl)-α-D-mannopyranosyl))-α-D-glucopyranosyl)-D-*myo*-inositol (56): A mixture of allyl ether **55** (21 mg, 6.4 μmol), $PdCl_2$ (23 mg, 0.13 mmol) and NaOAc (21 mg, 0.26 mmol) in acetic acid/H_2O (1 mL, 19:1) was stirred under argon for 48 h. The reaction mixture was diluted with EtOAc, filtered through celite, washed with aq $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (petrol/EtOAc 2:1 → 3:2) to give alcohol **56** (14 mg, 4.3 μmol, 67 %) and starting material **55** (5 mg, 1.5 μmol, 23 %): $R_f = 0.24$ (petrol/EtOAc 3:2); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.98$ (s, 3H, CH_3-BDA), 0.99 (s, 3H, CH_3-BDA), 1.15 (s, 6H, 2 × CH_3-BDA), 1.28 (s, 12H, 4 × CH_3-BDA), 2.98 (s, 8H, 2 × OCH_3-BDA, CH), 3.07–3.37 (m, 28H, 6 × OCH_3-BDA, 5 × CH), 3.40 (t, 2H, $J = 9.3$ Hz), 3.42–3.78 (m, 30H), 3.81–4.39 (m, 60H), 4.41 (d, 2H, $J = 12$ Hz), 4.48–5.07 (m, 58H), 5.17 (d, 2H, $J = 3.3$ Hz), 5.24–5.27 (m, 6H), 5.36–5.41 (m, 6H), 5.54 (s, 2H), 7.11–7.43 (m, 160H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = [17.3, 17.5, 17.6, 17.9 (CH_3-BDA)], [40.5, 40.6, 40.9 (CH_2Cl)], 41.2 (CH_2N), [47.7, 47.8, 48.0, 48.0 (OCH_3-BDA)], 62.8, 63.4, 64.1, 64.3, 65.0, 65.8, 66.4, 66.4, 66.6, 66.6, 66.8, 66.8, 68.1, 68.5, 68.5, 68.5, 68.9, 69.0, 69.3, 69.3, 69.4, 69.4, 69.8, 70.2, 70.5, 70.5, 71.1, 71.1, 71.7, 71.7, 71.8, 72.5, 72.6, 72.9, 73.0, 73.1, 73.2, 73.3, 73.4, 73.6, 73.7, 73.7, 74.4, 74.7, 74.7, 74.9, 74.9, 75.0, 75.1, 75.1, 75.2, 75.7, 76.8, 77.2, 78.6, 78.8, 79.9, 79.9, 80.9, 81.0, 81.3, 81.4, 82.0, 96.4, 98.5, 98.8, 98.8, 98.9, 99.0, 99.6, 99.6, 99.7, 99.8, 99.8, 100.0, [126.9, 126.9, 127.2–128.6 (CH-Ar)], [135.8, 135.8, 135.9, 135.9, 136.6, 137.2, 138.0–139.1 (C_q-Ar)], [156.2 (OCONH)], [166.7, 166.8 (CO-ClAc)]; ^{31}P NMR ($CDCl_3$, 243 MHz): $\delta = -0.07$, 0.04; MS (FAB): *m/z*: 3269 $[M + Na]^+$; $C_{175}H_{196}O_{47}N_4PCl_3$ requires $[M + Na]^+$ 3268.

(2′*R*,3′*R*,2″*S*,3″*S*) 2,3,4,5-Tetra-*O*-benzyl-1-*O*-((1,2-di-*O*-myristoyl-*sn*-glycerol-3-yl) benzyl phosphono)-6-*O*-(2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-((4-*O*-benzyl-2-*O*-chloroacetyl-3-*O*-(4-*O*-chloroacetyl-2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-α-D-galactopyranosyl)-6-*O*-(6-*O*-chloroacetyl-3,4-*O*-(2″,3″-dimethoxybutane-2″,3″-diyl)-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-((2-((*N*-benzyloxycarbonyl)amino)ethyl) benzyl phosphono)-α-D-mannopyranosyl)-α-D-mannopyranosyl)-α-D-mannopyranosyl))-α-D-glucopyranosyl)-D-*myo*-inositol (57): A mixture of alcohol **56** (54 mg, 16.5 μmol) and tetrazole (17.5 mg, 0.25 mmol) was co-evaporated with toluene, before it was dissolved in dry CH_3CN (2 mL) and phosphoramidite **4** (124 mg, 0.17 mmol) in dry CH_2Cl_2 (2 mL) was added. The reaction mixture was stirred for 12 h at RT before *m*CPBA (57 mg, 0.33 mmol) was added at −40 °C. The reaction mixture was warmed to RT over 30 min and stirred at RT for one hour. The solution was diluted with CH_2Cl_2, washed with aq $NaHCO_3$, dried over $MgSO_4$ and concentrated. The residue was purified by size-exclusion chromatography (Sephadex LH-20, CH_2Cl_2/MeOH 1:1) followed by column chromatography (SiO_2, petrol/EtOAc 2:1 → 1:3) to give phosphotriester **57** (13.3 μmol, 81 %) as two separable mixtures, each containing two diastereoisomers; **57_{a+b}** (16 mg, 4.1 μmol): $R_f = 0.29$ (petrol/EtOAc 3:2); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.84–0.93$ (m, 18H, 4 × CH_3, 2 × CH_3-BDA), 1.12 (s, 6H, 2 × CH_3-BDA), 1.20–1.30 (s, 92H, 40 × CH_2, 4 × CH_3-BDA), 1.53–1.58 (m, 8H, 4 × CH_2), 2.21–2.26 (m, 8H, 4 × CH_2), 2.97 (s, 3H, OCH_3-BDA), 2.97 (s, 3H, OCH_3-BDA), 3.13–3.30 (m, 28H, 6 × OCH_3-BDA, 10 × CH), 3.38–5.03 (m, 166H), 5.12–5.17 (m, 6H), 5.26 (s, 6H), 5.38–5.43 (m, 4H), 5.50 (s, 2H), 7.18–7.43 (m, 170H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz, selected signals only): $\delta = 14.1$ (CH_3), [17.2, 17.5, 17.7, 17.9 (CH_3-BDA)], [22.6, 24.8, 24.8, 29.0–29.7, 31.9, 34.0, 34.1 CH_2)], [40.5, 40.6, 41.0 (CH_2Cl)], 41.3 (CH_2N), [47.7, 47.8, 47.9, 48.0 (OCH_3-BDA)], 156.3 (OCONH), [166.8, 166.8 (CO-ClAc)], [172.9, 173.1 (CO-myristoyl)]; ^{31}P NMR ($CDCl_3$, 243 MHz): $\delta = -0.12$, 0.00, 6.88, 6.89; MS (FAB): *m/z* (%): 3912 (38) $[M + H]^+$, 3800.9 (100) $[M - Cbz + Na]^+$; MS [(+)-MALDI-TOF]: *m/z*: 3798 $[M - Cbz + Na]^+$; a mixed fraction, containing all four diastereoisomers **57_{a-d}** (7 mg, 1.8 μmol): MS [(+)-MALDI-TOF]: *m/z*: 3799 $[M - Cbz + Na]^+$; and **57_{c+d}** (29 mg, 7.4 μmol): $R_f = 0.19$ (petrol/EtOAc 3:2); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.83–0.94$ (18H, m, 4 × CH_3, 2 × CH_3-BDA), 1.13 (s, 6H, 2 × CH_3-BDA), 1.20–1.29 (s, 92H, 40 × CH_2, 4 × CH_3-BDA), 1.54–1.60 (m, 8H, 4 × CH_2), 2.25–2.29 (m, 8H, 4 × CH_2), 2.90–2.95 (m, 2H), 2.98 (s, 6H, 2 × OCH_3-BDA), 3.12–3.25 (m, 22H, 6 × OCH_3-BDA), 3.30–5.10 (m, 172H), 5.16 (s, 2H), 5.30 (s, 6H), 5.39–5.43 (m, 4H), 5.50 (s, 4H), 7.18–7.43 (m, 170H, ArH); ^{13}C NMR ($CDCl_3$, 150 MHz): $\delta = 14.1$ (CH_3), [17.2, 17.5, 17.7, 17.9 (CH_3-BDA)], [22.6, 24.8, 24.9, 29.7, 31.9, 34.0, 34.2 (CH_2)], [40.5, 40.7, 40.9 (CH_2Cl)], 41.2 (CH_2N), [47.7, 47.9, 47.9, 48.0, 48.0 (OCH_3-BDA)], 61.7, 62.9, 63.5, 64.1, 64.8, 64.8, 65.1, 65.8, 66.1, 66.6, 66.8, 68.1, 68.5, 68.6, 68.8, 68.9, 69.3, 69.3, 69.4, 69.5, 69.5, 69.8, 70.1, 70.1, 71.1, 71.3, 71.6, 71.7, 71.7, 72.0, 72.1, 72.2, 72.5, 72.6, 72.7, 73.0, 73.2, 73.5, 73.7, 74.5, 74.5, 74.7, 74.7, 74.9, 75.0, 75.2, 75.2, 75.5, 75.8, 75.9, 76.0, 78.8, 79.0, 79.1, 79.5, 79.8, 80.1, 80.9, 81.5, 82.9, 96.9, 98.7, 98.7, 98.9, 99.2, 99.2, 99.6, 99.6, 99.7, 99.8, 99.9, 100.2, 100.2, [126.8, 126.8, 127.2–129.1 (CH-Ar)], [135.8, 135.8, 135.8, 135.9, 135.9, 136.6, 137.5, 137.9–139.1 (C_q-Ar)], 156.2 (OCONH), [166.7, 166.8, 166.8 (CO-ClAc)], [172.7, 173.1 (CO-myristoyl)]; ^{31}P NMR ($CDCl_3$, 243 MHz): $\delta = -0.12$, −0.02, 7.79, 7.82; MS [(+)-MALDI-TOF]: *m/z*: 3799 $[M - Cbz + Na]^+$.

(2′*R*,3′*R*,2″*S*,3″*S*) 1-*O*-(1,2-Di-*O*-myristoyl-*sn*-glycerol-3-yl phosphono)-6-*O*-(2-amino-2-deoxy-4-*O*-(3-*O*-(2,3-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-(α-D-galactopyranosyl)-α-D-galactopyranosyl)-6-*O*-(3,4-*O*-(2″,3″-dimethoxybutane-2″,3″-diyl)-2-*O*-(6-*O*-(2-aminoethyl phosphono)-α-D-mannopyranosyl)-α-D-mannopyranosyl)-α-D-mannopyranosyl))-α-D-glucopyranosyl)-D-*myo*-inositol (58): A mixture of protected GPI anchor **57_{a+b}** (5.5 mg, 1.4 μmol) and Pd/C (15 mg, 10 %) in CH_3Cl/MeOH/H_2O (1.15 mL, 1:1:0.3) was stirred under a H_2 atmosphere for 8 h. The reaction mixture was filtered through celite, eluted with pyridine and concentrated. The residue was dissolved in lutidine/AcOH/MeOH (1 mL, 3:1:1) and a freshly prepared solution of HDTC[47] (0.2 mL, 0.4 M) was added at 0 °C. The reaction was stirred at 0 °C for 12 h before it was purified by size-exclusion chromatography (Sephadex G-25, H_2O:*n*-propanol 95:5) to give **58** (4.1 mg) as a brown solid: ^{1}H NMR (600 MHz, CD_3OD, selected signals only): $\delta = 0.82–0.99$ (m, 12H, 2 × CH_3, 2 × CH_3-BDA), 1.20–1.38 (m, 46H, 20 × CH_2, 2 × CH_3-BDA), 1.56–1.70 (m, 4H, 2 × CH_2), 2.25–2.40 (m, 4H, 2 × CH_2), 3.24 (s, 3H, OCH_3-BDA), 3.27 (s, 3H, OCH_3-BDA), 3.34 (s, 3H, OCH_3-BDA), 4.67 (s, 1H, H-1_{Man}), 4.83 (s, 1H, H-1_{Man}), 5.01 (s, 2H, 2 × H-1); 5.08 (s, 1H, H-1); 5.31 (s, 1H, H-1); 5.45 (s, 1H, H-1); ^{31}P NMR (CD_3OD, 243 MHz): $\delta = 1.55$, 9.46; MS [(−)-MALDI-TOF]: *m/z*: 2035 $[M - H]^-$.

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1-*O*-(1,2-Di-*O*-myristoyl-*sn*-glycerol-3-yl phosphono)-6-*O*-(2-amino-2-deoxy-4-*O*-(3-*O*-(6-*O*-(α-D-galactopyranosyl)-α-D-galactopyranosyl)-6-*O*-(2-*O*-(6-*O*-(2-aminoethyl phosphono)-α-D-mannopyranosyl)-α-D-mannopyranosyl)-α-D-mannopyranosyl))-α-D-glucopyranosyl)-D-*myo*-inositol (1): Crude product **58** (4.1 mg) was dissolved in TFA/H_2O (200 μL, 9:1) for 2 min before the solvent was removed under reduced pressure. The remaining solid was purified by size-exclusion chromatography (Sephadex G-25, H_2O/*n*-propanol 80:12), filtered (RP-18 silica, MeOH then pyridine) and lyophilised to give **1** (2.3 mg, 1.3 μmol, 90% over three steps) as a brown solid: ^{1}H NMR (600 MHz, [D_6]DMSO/D_2O 50:1, 60 °C, selected signals only): $\delta = 0.78-0.89$ (m, 6H, $2 \times CH_3$), 1.18–1.39 (m, 40H, $20 \times CH_2$), 1.44–1.56 (m, 4H, $2 \times CH_2$), 2.22–2.39 (m, 4H, $2 \times CH_2$), 4.67 (s, 1H, H-1_{Man}), 4.83 (s, 1H, H-1_{Man}), 4.87 (t, 1H, $J = 9.3$ Hz, H-1_{Gal}) 4.91 (t, 1H, $J = 3.5$ Hz, H-1_{Gal}), 4.94 (s, 1H, H-1_{Man}), 5.35 (s, 1H, H-1_{Glu}); ^{31}P NMR (243 MHz, CD_3CN/D_2O (3:1), 50 °C): $\delta = 9.24$, 1.36; MS [(+)-MALDI-TOF, only major isotope peaks]: *m/z* (%): 1932 (15), 1910 (15) $[M + Na + K - H]^+$, 1893 (20) $[M + 2Na - H]^+$, 1887 (40) $[M + K]^+$, 1871.93 (50) $[M + Na]^+$, 1849.93 (100) $[M + H]^+$, 1831.88 (25) $[M - OH]^+$; $C_{75}H_{138}N_2O_{45}P_2$ requires $[M + H]^+$ 1849.81.

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[49] **Caution**: TfN_3 is explosive and TfN_3 solutions should therefore never be evaporated to dryness!

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