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Solid-Phase Oligosaccharide Synthesis of a Small Library of N-Glycans

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Abstract: Solid-phase oligosaccharide synthesis is based on a hydroxymethylbenzyl benzoate spacer linker which is connected to the Merrifield resin (**1P**). Glycosylation was performed with O-glycosyl trichloroacetimidates of glucosamine, mannose, and galactose permitting chain extension (**2**^{e}, **5**^{e}), branching (**4**^{b}, **7**^{b}, **8**^{b}), and chain termination (**3**^{t}, **6**^{t}, **9**^{t}) with the use of O-benzyl, O-benzoyl, and N-dimethylmaleoyl as permanent and O-fluorenylmethoxycarbonyl (Fmoc) and O-phenoxyacetyl (PA) as temporary protecting groups. The steps required on solid phase are i) glycosylation under TMSOTf catalysis, ii) selective cleavage of the temporary protecting groups, Fmoc with NEt_3 and PA with 0.5 equivalents of NaOMe in CH_2Cl_2/MeOH, and iii) product cleavage from the resin with 4.0 equivalents of NaOMe in CH_2Cl_2/MeOH and following O-acetylation for convenient product isolation. Thus a highly successful synthesis of a small library of seventeen N-glycan structures was made possible comprising the N-glycan pentasaccharide core structure **53** and two further chain extended hexa- and heptasaccharide N-glycans with a glucosamine or a lactosamine residue, respectively, which is attached to one of the mannose residues of the core structure (**56** and **59**).

Keywords: carbohydrates · glycoproteins · oligosaccharides · protecting groups · solid-phase synthesis

Introduction

Oligosaccharides play an important role in various biological processes; therefore the general interest in these compounds, particularly as constituents of glycoconjugates has greatly increased in recent years.[1–4] As a consequence, oligosaccharide synthesis has become an important issue.[5–10] Recently, successful solid-phase oligosaccharide syntheses (SPOS) have been developed by several research groups,[11–22] which exhibit the inherent advantages over solution phase synthesis, such as i) higher reaction yields due to the use of excess building blocks and/or reagents, ii) shorter reaction times for the completion of the syntheses, and iii) convenient purification procedures. In addition, methods to avoid undesired byproducts in the synthesis of the target molecule have been introduced.[23–26] However, no generally accepted strategy has yet appeared for the efficient construction of various complex oligosaccharides on polymer supports, thus limiting the commercialisation of automated synthesizers. To this end, still some improvement of the SPOS methodology is required.

With our ester based SPOS design (see below) very good results have already been obtained.[27] However, to cope with complex oligosaccharide synthesis, besides the linker–spacer system, three types of building blocks for controlled chain extension, branching, and termination are required: i) glycosyl donors for linear chain extension (suffix **e**) having one temporary protecting group at the subsequent ligation site which is orthogonal to the permanent protecting groups; ii) glycosyl donors for branching (suffix **b**) having at least two temporary protecting groups which are ideally orthogonal to each other and to the permanent protecting groups, and iii) glycosyl donors for chain termination (suffix **t**) having only permanent protecting groups, thus supporting controlled branching. An efficient solution to these requirements is presented herein.

Another problem, which has not been solved until today, is the selection of a versatile N-protecting group for glucosamine because overall yields and product purity were thus far dramatically dependent on glycosylation results of glucosamine acceptors.[25,28] In this paper, a simple and unexpected solution also to this problem is offered, thus permitting the synthesis of a small library of N-glycans in excellent overall yields. This approach emphasizes the overall versatility of our ester based SPOS design.

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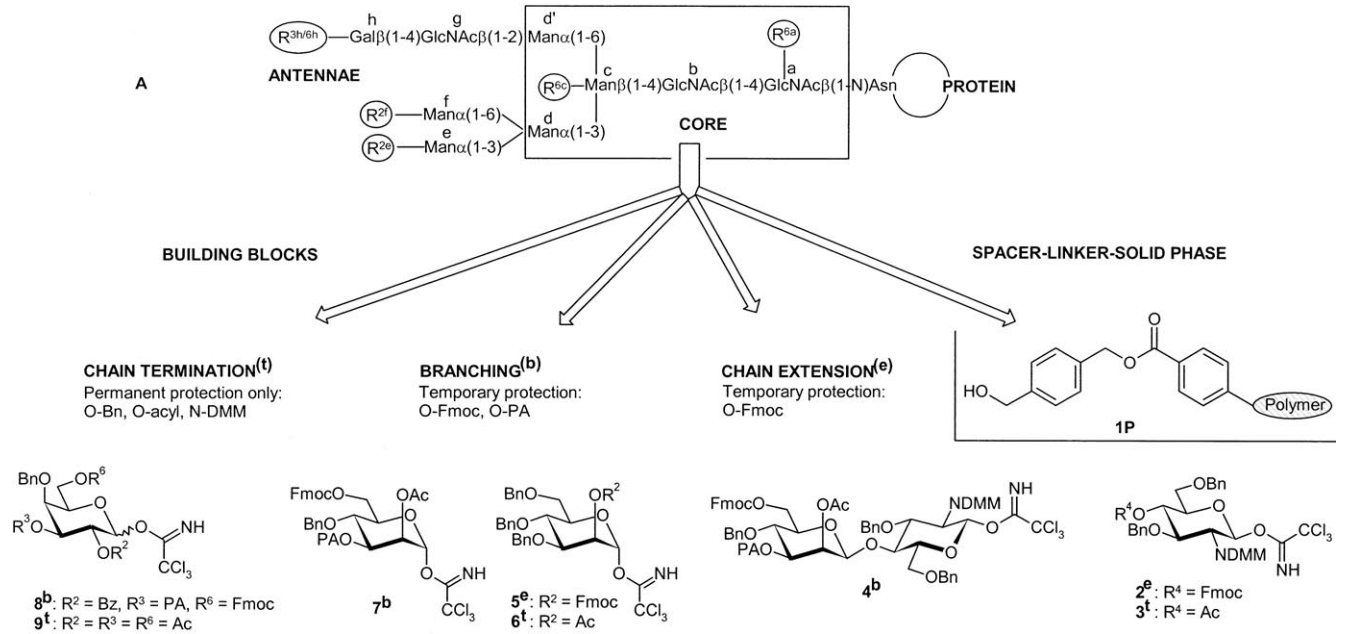
Results and Discussion

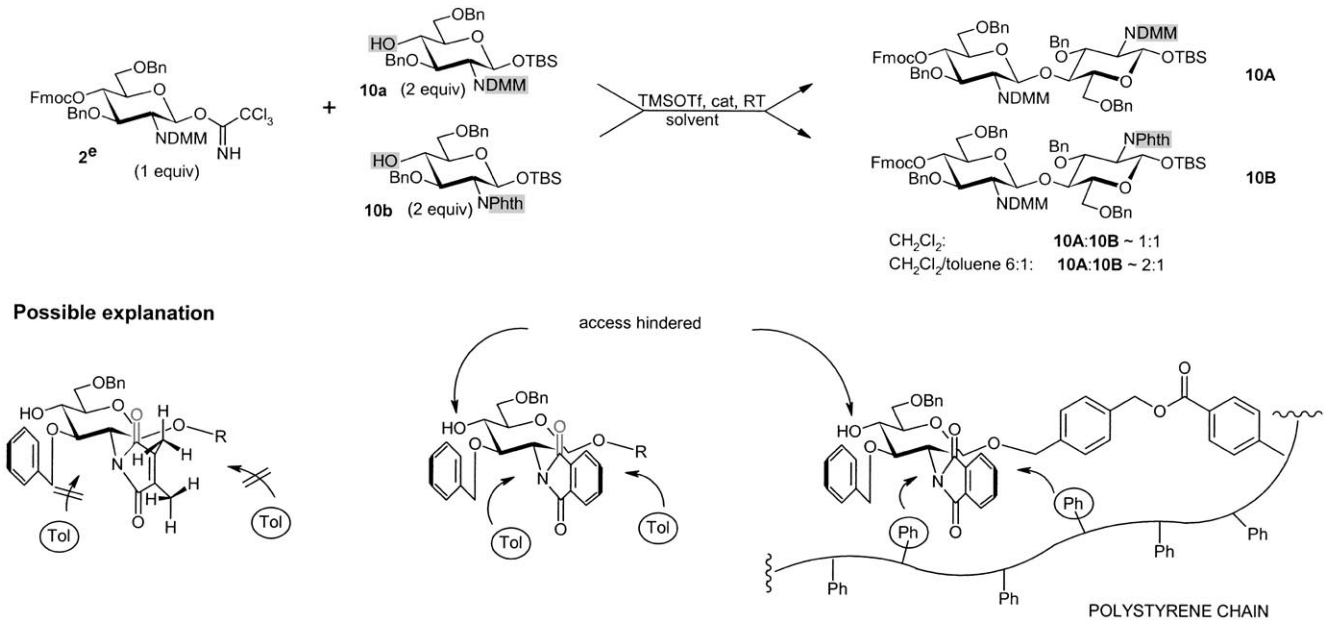
Retrosynthesis of branched N-glycans: The ester based SPOS methodology (Scheme 1) comprises i) different types of esters, that is, the benzoate group as a linker and for chain termination and the Fmoc and PA (phenoxyacetyl) group as temporary protecting groups for chain extension and branching which can be chemoselectively cleaved (in the sequence Fmoc and then PA); ii) the benzyl group for permanent O-protection and for the spacer between the anomeric centre at the reducing end sugar, thus providing after final product cleavage from the resin a structurally defined target molecule; iii) O-glycosyl trichloroacetimidates of type **e**, **b**, or **t** (for chain extension, branching or termination) as powerful glycosyl donors, which can be readily activated by catalytic amounts of (Lewis) acid; and iv) benzoic acid residues on the Merrifield resin for the linkage of the hydroxymethylbenzyl spacer. Hence, retrosynthesis of a typical N-glycan molecule **A** containing the core pentasaccharide and some antennae leads to spacer-linker connected Merrifield resin **1P** and to glycosyl donors **2**–**9** which can be selectively converted into acceptors on resin (**e** and **b**-type donor building blocks). Thus, as indicated in Scheme 1, only four simple procedures are required for successful SPOS: a) glycosidation under TMSOTf catalysis; b) product cleavage under transesterification conditions; c) selective Fmoc cleavage under basic conditions; and d) selective PA cleavage under milder transesterification conditions.

The dimethylmaleoyl (DMM) N-protecting group: One of the problems encountered in SPOS containing glucosamine residues is the low reactivity of the previously employed N-phthaloyl protected 4-O-unprotected glucosamine residues as acceptors, particularly when they are positioned at the reducing end next to the resin. Therefore, in our most recent approaches for the synthesis of N-glycan, lactosamine, and oligolactosamine oligosaccharides we have introduced a novel capping procedure to overcome this problem.[25] Alternatively, a reactivity increase of the acceptor moiety by introducing an azido group as latent amino functionality was investigated.[28] Both procedures worked well. However, capping does not increase the overall yield; in addition in the case of the azido group the nitrile effect[29] was found to be less efficient in anomeric stereocontrol on solid phase than in solution.[28]

Reinvestigation of the relative reactivity of N-phthaloyl (Phth) and N-dimethylmaleoyl (DMM) protected glucosamine acceptors **10a**, **b**[14] with N-DMM protected glucosamine donor **2**[e][13] (Scheme 2) revealed a difference in reactivity in different solvents: for instance, in CH_2Cl_2 the reactivity of **10a**, **b** was practically identical; however, upon addition of toluene to the reaction mixture, thus mimicking phenyl groups of the polystyrene, N-Phth protected acceptor **10b** exhibited lower reactivity than DMM protected acceptor **10a** (CH_2Cl_2: reaction rate **10a**/**10b** ≈1:1; CH_2Cl_2/toluene 6:1: reaction rate **10a**/**10b** ≈2:1). This difference in reactivity between these two acceptors was also found on Merrifield resin as shown below (see SPOS of compound **56** and ref. [27]). Hence, the N-DMM protected acceptors do not seem to have this loss in reactivity compared with the N-Phth protected acceptors. This is presumably due to interaction of polystyrene phenyl groups with the electron deficient planar phthaloyl residue eventually leading to limited access to the 4-hydroxy group. The two methyl groups of the



Scheme 1. Solid-phase synthesis of high-mannose, complex, and hybrid-type N-glycans: retrosynthesis scheme. Reactions on the solid phase: a) glycosidation: O-glycosyl trichloroacetimidates, TMSOTf (cat.), CH_2Cl_2, RT →−40 °C; b) product cleavage: NaOMe (4 equiv), CH_2Cl_2/MeOH 8:1; Ac_2O, Pyr; c) Fmoc cleavage: NEt_3/CH_2Cl_2 1:6; d) PA cleavage: NaOMe (0.5 equiv), CH_2Cl_2/MeOH 8:1; for c) and d) UV monitoring possible.

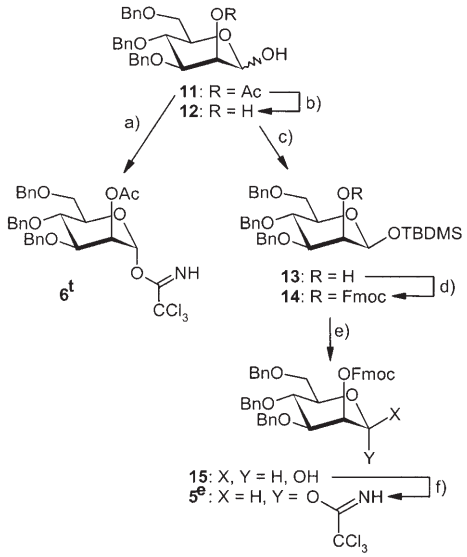


Scheme 2. Relative reactivity of N-DMM versus N-Phth protected glucosamine acceptors.

DMM residue seem to preclude this interaction and hence the 4-hydroxy group is more readily accessible. Excellent results with N-DMM protected building blocks in some preliminary studies were reason enough to demonstrate the efficiency of this SPOS design in the elaboration of a small library containing typical high-mannose, complex, and hybrid-type N-glycan constituents (see Scheme 1).

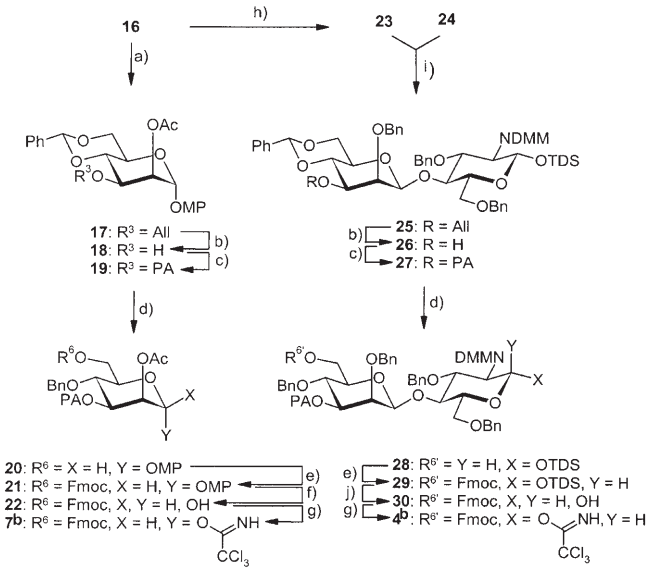
Building block synthesis of e-, b-, and t-type: The synthesis of glucosamine building blocks **2**^{e} and **3**^{t} followed known procedures. Mannosyl donors **5**^{e} and **6**^{t}[30] were readily obtained from known mannose derivative **11**[31] (Scheme 3). O-Deacetylation with NaOMe in methanol (→ **12**), regioselective 1-O-silylation with *tert*-butyl-dimethylsilyl (TBDMS) chloride in the presence of imidazole (→ **13**, only β), treatment with Fmoc-Cl in the presence of pyridine (→ **14**), and then selective 1-O-desilylation with the HF·pyridine complex in THF (→ **15**), and treatment with trichloroacetonitrile in the presence of sodium hydride as base afforded **5**^{e}[30] in very high overall yield. From **11**, following a known procedure also **6**^{t} was obtained.[32]

Mannosyl donor **7**^{b} required for branching via 3-O and 6-O was readily prepared from known mannose derivative **16**[33] (Scheme 4). 2-O-Acetylation (→ **17**) and 3-O-deallylation with *trans*-$[PdCl_2(NH_3)_2]$ complex in *tert*-butanol[34] (→ **18**) and then treatment with PA-Cl in pyridine afforded fully protected intermediate **19** in very high yield. Benzylidene ring opening with BH_3·THF as reducing agent in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as catalyst[35] afforded 6-O-unprotected intermediate **20**. Treatment with Fmoc-Cl in pyridine (→ **21**), cleavage of the methoxyphenyl (MP) group with ceric(IV) ammonium nitrate (CAN) in acetonitrile/water[36] afforded 1-O-unprotected intermediate **22** which on treatment with trichloroacetonitrile in the presence of sodium hydride afforded the desired trichloroacetimidate **7**^{b} in very good overall yield.

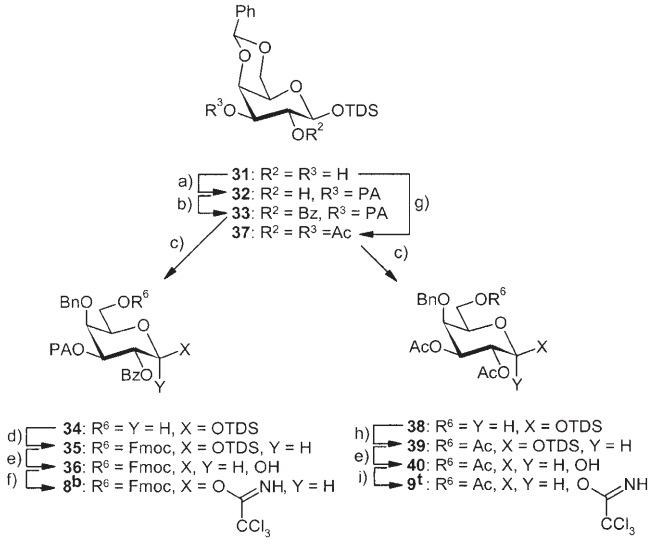


Scheme 3. Synthesis of building blocks **5**^{e} and **6**^{t}. a) CCl_3-CN, DBU, CH_2Cl_2, 0 °C (93 %); b) NaOMe, MeOH (quant); c) TBDMS-Cl, Im (77 %); d) Fmoc-Cl, Pyr (83 %); e) HF·Pyr, THF (90 %); f) CCl_3-CN, NaH, DMF (91 %).

The lack of highly β-selective mannosyl donors[27] necessitated the synthesis of the Manβ(1→4)GlcN-linked disaccharide donor **4**^{b}. To this end, a variation of the Crich procedure was employed with O-mannosyl trichloroacetimidate **23** as donor, which is readily available as previously reported.[33] Mannosylation of known 4-O-unprotected N-DMM protected glucosamine acceptor **24**[37] with donor **23** afforded disaccharide **25** in 71 % yield in a 4:1 β/α ratio.[33] Separation



Scheme 4. Synthesis of mannosyl donor $\mathbf{7^b}$ and disaccharide donor $\mathbf{4^b}$. a) Ac_2O, Pyr (quant); b) *trans*-$[PdCl_2(NH_3)_2]$, *t*BuOH (**18**: 81%; **26**: 79%); c) PA-Cl, Pyr (**19**: 91%; **27**: quant); d) BH_3·THF, TMSOTf (**20**: 73%; **28**: 77%); e) Fmoc-Cl, Pyr (**21**: 81%; **29**: 86%); f) CAN, MeCN, H_2O (**22**: 77%); g) CCl_3-CN, NaH, CH_2Cl_2 ($\mathbf{7^b}$: 95%; $\mathbf{4^b}$: 90%); h) BnBr, NaH, DMF (97%); CAN, MeOH, H_2O (69%); CCl_3-CN, DBU, CH_2Cl_2 (95%); i) TMSOTf, CH_2Cl_2, −50 °C, inverse procedure (71%, β/α 4:1); j) HF·Pyr, THF (86%).



Scheme 5. Synthesis of galactosyl donors $\mathbf{8^b}$ and $\mathbf{9^t}$. a) PA-Cl, Pyr, −15 °C (92%); b) BzCN, NEt_3, MeCN (93%); c) BH_3·THF, TMSOTf (**34**: 76%; **38**: 73%); d) Fmoc-Cl, Pyr (84%); e) HF·Pyr, THF (**36**: 88%; **40**: 94%); f) CCl_3-CN, NaH, CH_2Cl_2 (88%); g) Ac_2O, Pyr (91%); h) Ac_2O, Pyr (quant); i) CCl_3-CN, DBU, CH_2Cl_2 (88%).

of the β-anomer and O-deallylation as described above furnished 3b-O-unprotected intermediate **26** which gave fully protected **27** with PA-Cl in pyridine. The transformation of **27** into donor $\mathbf{4^b}$ via reductive benzylidene ring opening (→ **28**), introduction of the Fmoc group (→ **29**), 1a-O-desilylation (→ **30**), and reaction with trichloroacetonitrile followed standard procedures.

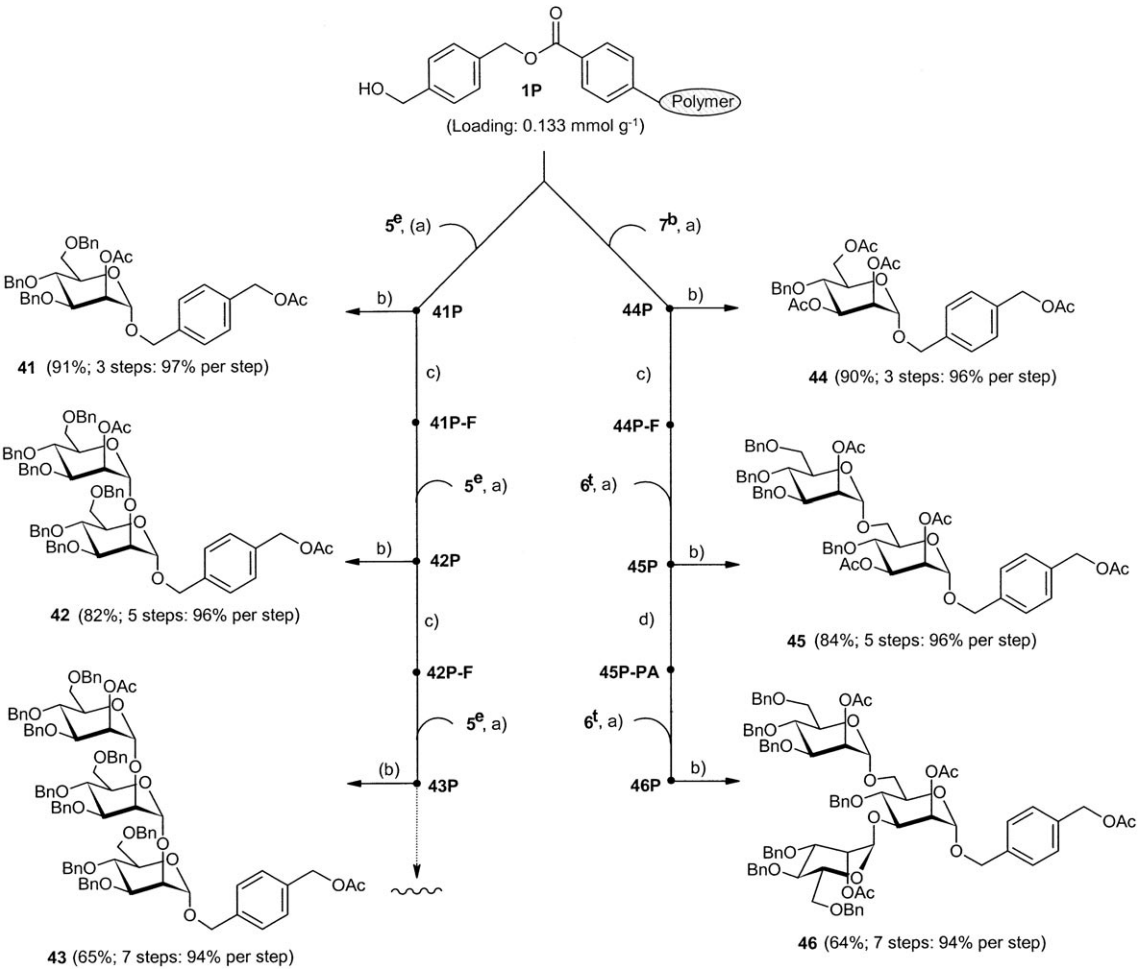
The galactosyl donors $\mathbf{8^b}$ and $\mathbf{9^t}$ were obtained from readily accessible 4,6-*O*-benzylidenegalactopyranoside **31** (Scheme 5).[38] Regioselective phenoxyacetylation with PA-Cl in pyridine at −15 °C afforded 3-O-PA protected **32** in high yield; ensuing 2-O-benzoylation with benzoyl cyanide in the presence of triethylamine led to intermediate **33**; under these conditions no PA migration was observed. Obviously, transformation of **33** into donor $\mathbf{8^b}$ via **34**, **35** and **36** followed the same procedures as described for the transformation of **27** into $\mathbf{4^b}$.

For the synthesis of galactosyl donor $\mathbf{9^t}$ compound **31** was fully O-acetylated affording known **37**.[38] Reductive ring opening as described gave 6-O-unprotected intermediate **38** which on O-acetylation (→ **39**) and then desilylation (→ **40**) and reaction with trichloroacetonitrile (with DBU as base) furnished trichloroacetimidate $\mathbf{9^t}$ in high overall yield.

SPOS with glycosyl donors 2–9: In order to probe the efficiency and versatility of the designed glycosyl donors firstly the synthesis of some α-connected high mannose constituents of N-glycans was investigated, because glycosylation with donors of type **5** and **6** gives generally good results.[30] Thus, reaction of spacer-linker loaded resin **1P**, obtained as previously described,[13] (loading 0.133 mmol g^{-1}) with donor $\mathbf{5^e}$ in the presence of TMSOTf as catalyst under standard conditions gave polymer **41P** (Scheme 6). Product cleavage under standard conditions and O-acetylation gave α-linked mannopyranoside **41** in 91% yield. Selective cleavage of the Fmoc group from **41P** under standard conditions (→ **41P–F**) and reaction with donor $\mathbf{5^e}$ gave **42P**; this was confirmed by cleavage of the product from the resin yielding α-linked disaccharide **42** and by structural assignment by NMR and MS data. Repetition of this sequence of reactions with **42P** led to **42P-F** and after glycosylation with donor $\mathbf{5^e}$ to **43P** which on product cleavage from the resin afforded α-linked trimannoside **43** after seven steps in 65% overall yield (94% per step).

This excellent result encouraged us to synthesize the corresponding branched trisaccharide **46** via the same procedure. Reaction of **1P** with mannosyl donor $\mathbf{7^b}$ led to **44P**, as shown after cleavage and O-acetylation affording glycoside **44** in 90% yield. For the branching first the Fmoc group was removed by treatment with triethylamine (→ **44P-F**) and then mannosylation with the terminating mannosyl donor $\mathbf{6^t}$ was performed (→ **45P**) which gave on cleavage from the resin and acetylation disaccharide **45**. Phenoxyacetyl cleavage from **45P** under treatment with NaOMe (0.5 equiv) in CH_2Cl_2/MeOH 8:1 (standard conditions) led to **45P-PA**. On mannosylation with $\mathbf{6^t}$ (→ **46P**) and cleavage from the resin and O-acetylation the desired branched trisaccharide **46** was obtained, again in high overall yield (64%, seven steps, 94% per step).

Another important part of complex type N-glycans is the LacNAcβ(1→2)Man trisaccharide moiety (Schemes 1 and 7). In order to investigate its synthesis from **41P** (Schemes 6 and 7) transformation into **41P-F** is again required. Subse-

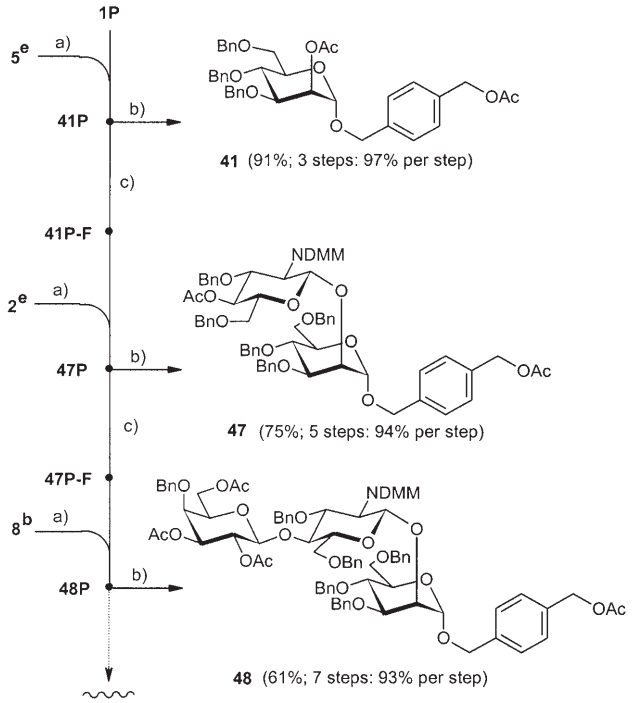


Scheme 6. Synthesis of N-glycan constituents **41**–**46**. For reagents and conditions see Scheme 1.

quent glycosylation with N-DMM protected glucosamine donor **2**^{e}[13] afforded **47P** as shown by product cleavage from the resin and O-acetylation, which furnished β-linked disaccharide **47**. Fmoc cleavage from **47P** (→ **47P-F**) and glycosylation with galactosyl donor **8**^{b} (reaction with **9**^{t} worked as well) led to **48P**. Product cleavage from the resin as described led cleanly to the target trisaccharide **48** in 61% overall yield (seven steps, 93% per step), hence in almost the same yield as obtained for the mannosylations yielding trisaccharide **43**.

With these excellent results, the synthesis of the N-glycan core structure and of branched N-glycans was undertaken (Scheme 8). To this end, **1P** was first glycosylated with N-DMM protected glucosamine donor **2**^{e} to afford polymer **49P** which after resin cleavage and O-acetylation afforded β-linked glycoside **49** in high yield. Fmoc cleavage from **49P** (→ **49P-F**), glycosylation with **2**^{e} (→ **50P**), and finally product cleavage from the resin gave chitobioside **50** in 65% overall yield. Reaction of **49P-F** with disaccharide donor **4**^{b} furnished resin bound trisaccharide **51P** again in very good yield, as demonstrated by product cleavage from the resin and per-O-acetylation affording trisaccharide **51**. Fmoc cleavage from **51P** gave **51P-F**, which was used for two purposes. Mannosylation with chain terminating mannosyl donor **6**^{t} led to **52P** as proven by product **52**. PA cleavage from **52P** (→ **52P-PA**) and mannosylation with **6**^{t} (→ **53P**) led in the usual manner to the N-glycan pentasaccharide core structure **53** after nine steps in 39% yield (90% per step).

For further chain extension and branching **51P-F** was glycosylated with mannosyl donor **5**^{e} affording **54P** which also gave **52** after cleavage of the product from the resin and per-O-acetylation in practically the same yield as obtained via **52P**. Fmoc cleavage from **54P** (→ **54P-F**) and subsequent glycosylation with chain terminating glucosamine donor **3**^{t}[36] led to **55P** which gave pentasaccharide **55** in the usual manner. Selective cleavage of the PA group from **55P** (→ **55P-PA**) and then glycosylation with mannosyl donor **5**^{e} furnished **56P**; from the latter the N-DMM protected branched hexasaccharide **56** was obtained after 11 steps in 30% overall yield (90% per step). The previously reported SPOS of an N-Phth protected analogue of **56** was obtained in only 19% overall yield,[27] thus exhibiting the reactivity difference between the two N-protecting groups. Reaction of **54P-F** with glucosamine donor **2**^{e} permitting chain extension yielded **57P** which after cleavage of the product from



Scheme 7. Synthesis of N-glycan constituents **41**, **47**, and **48**. For reagents and conditions see Scheme 1.

the resin and per-O-acetylation also gave **55** with simlar yields as obtained via **55P**. Fmoc cleavage from **57P** (→ **57P-F**) and then galactosylation with the chain terminating galactosyl donor $\mathbf{9^t}$ provided **58P**; after standard cleavage conditions the linear hexasaccharide **58** was obtained. Phenoxyacetyl group removal from resin **58P** (→ **58P-PA**) and subsequent mannosylation with donor $\mathbf{5^e}$ led to resin bound heptasaccharide **59P** and finally, after 13 steps on the resin, to branched target molecule **59** in 22% overall isolated yield (89% per step). All seventeen acyloxymethylbenzyl glycosides obtained after cleavage of the product from the resin and per-O-acetylation (i.e., **41**–**53**, **55**, **56**, **58**, **59**) required essentially only one chromatographic step by flash chromatography or medium pressure chromatography for purification; this demonstrates the efficiency and versatility of this straightforward approach to solid-phase oligosaccharide synthesis. The structural assignments are based on NMR and MS data. N-DMM and O-benzyl deprotection in similar types of compounds has already been performed successfully.[39]

Conclusion

The solid-phase oligosaccharide synthesis based on differently cleavable esters—for the linker benzoate, for temporary protection of the glycosyl donors Fmoc and PA with additional orthogonal permanent protection (O-benzyl, O-benzoyl, and N-DMM), and a Merrifield resin as solid support–exhibited excellent results during all stages of the assembly: i) The required O-glycosyl trichloroacetimidate glycosyl donors were generally readily available by standard procedures; ii) all glycosylations, including those with N-DMM protected glycosyl donors, gave high yields; iii) the methodology presented herein shows the desired versatility in terms of efficient chain extension and branching requiring only two standard (in one direction) orthogonal protecting groups; iv) cleavage of the product from the resin was feasible leading to stable 1-O-benzyl type products with only benzyl, DMM and, after acetylation, acetyl protection; v) the crude products were already of high purity; therefore, standard silica gel chromatography and MPLC were sufficient for purification; vi) yields of isolated products were high, ranging from 97% per step (after three steps) to 89% per step (after 13 steps) on solid phase; vii) the methodology is technically simple, thus lending itself available to automation. Thus further process and hence yield optimisation will be possible, adding to the overall power of this highly efficient methodology for solid phase supported oligosaccharide synthesis. The very positive characteristics as outlined here should make this method attractive for general acceptance.

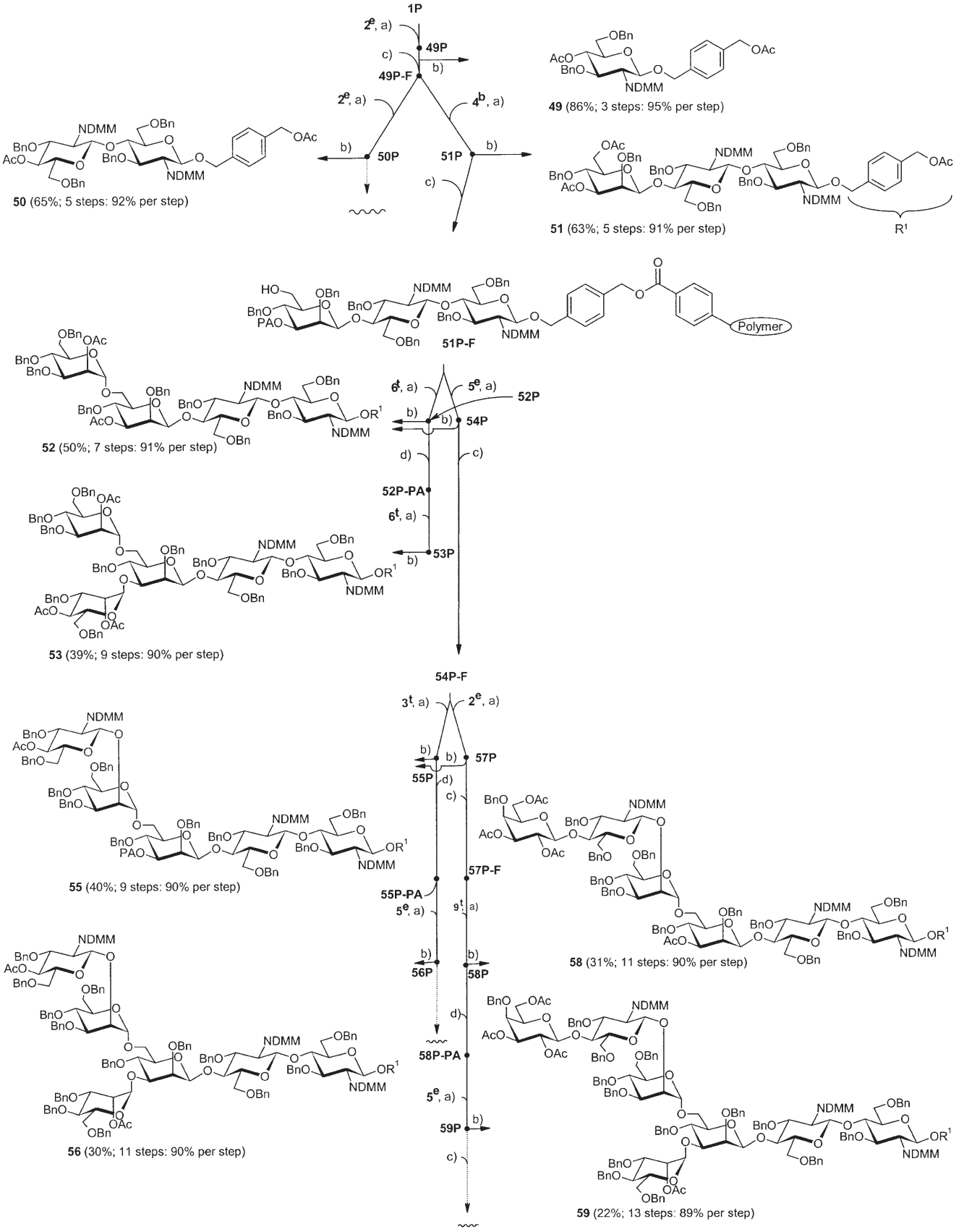
Experimental Section

General remarks: Each solvent was purified and dried in the usual manner. All reactions were performed by using dry solvents and under argon unless otherwise stated. TLC was performed on plastic plates of silica gel 60 F_{254}. Detection was achieved by treatment with a solution of ammonium molybdate (20 g) and cerium(IV) sulfate (0.4 g) in 10% H_2SO_4 (400 mL), or with 15% H_2SO_4, and then heating at 150 °C. Flash chromatography was carried out on silica gel (Baker 30–60 mm). Adsorption of crude reaction products was performed using silica gel (Baker 60–200 mm). Petroleum ether was used in the boiling range 35–70 °C; toluene, CH_2Cl_2, MeOH, and EtOAc were distilled. Optical rotations were determined at 21 °C by using a Perkin-Elmer 241/MC polarimeter (1 dm cell). NMR spectra were recorded by using Bruker 600 DRX instruments; tetramethylsilane was internal standard. MS spectra were recorded using a MALDI-kompakt (Kratos) instrument operating in the positive mode; 2,5-dihydroxybenzoic acid (DHB) in THF was the matrix. Microanalyses were performed in the microanalysis unit at the Fachbereich Chemie, Universität Konstanz.

General procedure for the glycosylation on solid phase (GP 1): The dry resin with the acceptor was treated with a solution of the donor (3 equiv) in dry CH_2Cl_2 (15 mL g^{-1} resin) under argon atmosphere. After shaking under argon atmosphere for 10 min at the temperature given for each reaction (see below) a freshly prepared solution of TMSOTf (0.5 mol L^{-1}) in CH_2Cl_2 was added and this mixture was shaken for another 30 min. After filtration the resin was washed alternating with THF and CH_2Cl_2 (15 mL g^{-1} resin each). Shaking was performed with the IKA-VIBRAX-VXR instrument of Janke and Kunkel GmbH, Germany. The temperature was controlled by a thermostat.

General procedure for the cleavage of the Fmoc group of a resin-bound compound (GP 2): CH_2Cl_2 (12 mL g^{-1} resin) was added to the dry resin with the resin-bound compound and the reaction vessel was shaken for 10 min at room temperature under argon atmosphere. Then NEt_3 (2 mL g^{-1} resin) was added and the mixture was shaken for 2 h. After filtration the resin was washed alternately with THF and CH_2Cl_2. This step was carried out until no UV-active methylidenefluorene was detectable in the washings. Finally the resin was washed alternating with THF and CH_2Cl_2 and dried in high vacuum.

General procedure for the cleavage of the phenoxyacetyl group of a resin-bound compound (GP 3): The dry resin with the resin-bound com-



Scheme 8. Synthesis of N-glycan constituents **49**–**53**, **55**, **56**, **58**, and **59**. For reagents and conditions see Scheme 1.

pound was treated with CH_2Cl_2/methanol 4:1 (12 mL g^{-1} resin). After the reaction vessel was shaking for 10 min at room temperature under argon atmosphere a NaOMe solution in methanol (0.5 equiv, dissolved in 10% of the total volume) was added and shaken for 20 min. Then the resin was filtered. This step was carried out until no UV-active phenoxyacetylmethylester was detectable in the washings. Finally the resin was washed alternately with THF and CH_2Cl_2 and dried in high vacuum.

General procedure for the analytical cleavage of the compound (GP 4): The resin (5 mg) with the resin-bound compound was treated with CH_2Cl_2/methanol 4:1 (12 mL g^{-1} resin). After the reaction vessel was shaken for 10 min at room temperature a NaOMe solution in methanol (5 equiv, dissolved in 10% of the total volume) was added and shaken for 30 min.

General procedure for cleavage of the compound from the resin (GP 5): The dry resin with the resin-bound compound was treated with CH_2Cl_2/methanol 4:1 (12 mL g^{-1} resin) and the reaction vessel was shaken for 10 min at RT under argon atmosphere. Then a NaOMe solution in methanol (5 equiv, dissolved in 10% of the total volume) was added, the mixture was shaken for 1 h and then was filtered. This procedure was carried out for three times. Finally the resin was washed alternately with THF and CH_2Cl_2, the combined solutions were neutralized with acidic ion-exchange resin (Amberlite IR120, H^+ form); the resin was filtered off and the solvents were evaporated under reduced pressure.

3,4,6-Tri-*O*-benzyl-α/β-D-mannopyranose (12): A NaOMe solution (410 μL, $c = 0.1$ mol L^{-1}) was added to a solution of compound **11**[31] (2.0 g, 4.06 mmol) in dry methanol. After 5 h the solution was neutralized with ion-exchange resin (Amberlite IR120, H^+ form), the ion-exchange resin filtered off and the solvent evaporated in vacuo. Flash chromatography (petroleum ether/ethyl acetate 1:1) gave compound **12** (1.83 g, quant) as colourless oil. $R_f = 0.22$ (petroleum ether/ethyl acetate 1:1); $[\alpha]_D = +21.3°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.58$ (br s, 1H, 2-OH), 3.36–3.42 (m, $^1/_2$H, 5β-H), 3.51–3.85 (m, $4 \times {}^1/_2$H, 3β-H, 4α-H, 4β-H, 6α-H, 6α′-H, 6β-H, 6β′-H, 1-OH), 3.92 (dd, $^3J_{3\alpha,2\alpha} = 3.2$, $^3J_{3\alpha,4\alpha} = 9.1$ Hz, $^1/_2$H, 3α-H), 4.00–4.08 (m, $1 \times {}^1/_2$H, 2α-H, 2β-H, 5α-H), 4.45–4.67 (m, $5 \times {}^1/_2$H, 1β-H, 5 OC*H*HPh), 4.82 (d, $J_{gem} = 10.9$ Hz, $^1/_2$H, OC*H*HPh), 4.84 (d, $J_{gem} = 10.8$ Hz, $^1/_2$H, OC*H*HPh), 5.26 (br s, $^1/_2$H, 1α-H), 7.12–7.35 (m, 15H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 68.5$, 68.9, 69.3, 70.8, 71.7, 72.0, 73.4, 73.5, 74.5, 74.7, 75.0, 79.7, 81.6, 93.9, 94.2, 127.7, 127.85, 127.90, 127.95, 127.99, 128.04, 128.3, 128.5, 137.7, 137.89, 137.92, 138.2; MALDI MS (positive mode): m/z: 473.2 $[M+Na]^+$, 489.2 $[M+K]^+$; elemental analysis calcd (%) for $C_{27}H_{30}O_6$ (450.5): C 71.98, H 6.71; found: C 71.74, H 6.44.

***tert*-Butyldimethylsilyl 3,4,6-tri-*O*-benzyl-β-D-mannopyranoside (13)**: Imidazole (304 mg, 3.73 mmol) was added to a solution of compound **12** (1.6 g, 3.55 mmol) in dry CH_2Cl_2 (20 mL). After 5 min *tert*-butyldimethylchlorosilane (536 mg, 3.55 mmol) was added and stirred for 4 h. The precipitation was filtered off and the solvent evaporated in vacuo. Flash chromatography (toluene/ethyl acetate 6:1) gave compound **13** (1.54 g, 2.74 mmol, 77%) as colourless oil. $R_f = 0.53$ (toluene/ethyl acetate 3:1); $[\alpha]_D = -1.4°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.13$ (s, 3H, CH_3), 0.17 (s, 3H, CH_3), 0.91 (s, 9H, C(CH_3)$_3$), 2.44 (br s, 1H, 2-OH), 3.40 (ddd, $^3J_{5,4} = 9.6$, $^3J_{5,6} = 2.9$, $^3J_{5,6'} = 4.3$ Hz, 1H, 5-H), 3.56 (dd, $^3J_{3,2} = 3.1$, $^3J_{3,4} = 9.1$ Hz, 1H, 3-H), 3.65–3.71 (m, 2H, 6-H, 6′-H), 3.85–3.93 (t, 1H, 4-H), 3.99–4.00 (m, 1H, 2-H), 4.53 (d, $J_{gem} = 12.2$ Hz, 1H, OC*H*HPh), 4.56 (d, $J_{gem} = 10.9$ Hz, 1H, OC*H*HPh), 4.62 (d, $J_{gem} = 12.2$ Hz, 1H, OC*H*HPh), 4.68 (d, $J_{gem} = 12.0$ Hz, 1H, OC*H*HPh), 4.71–4.72 (m, 1H, 1-H), 4.81 (d, $J_{gem} = 11.9$ Hz, 1H, OC*H*HPh), 4.92 (d, $J_{gem} = 10.9$ Hz, 1H, OC*H*HPh), 7.21–7.41 (m, 15H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = -5.3$, −4.1, 18.0, 25.7, 69.4, 69.6, 71.2, 73.4, 74.1, 75.1, 75.2, 81.6, 95.0, 127.4, 127.6, 127.7, 127.8, 128.0, 128.2, 128.3, 128.4, 138.1, 138.4, $^1J_{1\text{-}C,1\text{-}H} = 156.3$ Hz; MALDI MS (positive mode): m/z: 586.9 $[M+Na]^+$, 602.9 $[M+K]^+$; elemental analysis calcd (%) for $C_{33}H_{44}O_6Si$ (564.8): C 70.18, H 7.85; found: C 70.07, H 7.91.

***tert*-Butyldimethylsilyl 3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenylmethoxycarbonyl)-β-D-mannopyranoside (14)**: Fmoc-Cl (1.90 g, 7.43 mmol) was added to a solution of compound **13** (1.4 g, 2.48 mmol) in dry pyridine (15 mL) and the reaction mixture was stirred overnight (12 h) at RT. The solvent was evaporated in vacuo and coevaporated with toluene (3× 15 mL). Flash chromatography (toluene/ethyl acetate 10:1 → 4:1) gave compound **14** (1.62 g, 2.06 mmol, 83%) as a white foam. $R_f = 0.78$ (toluene/ethyl acetate 3:1); $[\alpha]_D = +2.6°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.12$ (s, 3H, COCH_3), 0.17 (s, 3H, COCH_3), 0.86 (s, 9H, 3CH_3), 3.50 (m, $^3J_{5,4} = 9.6$, $^3J_{5,6} = 3.7$, $^3J_{5,6'} = 7.3$ Hz, 1H, 5-H), 3.72 (dd, $^3J_{3,2} = 3.2$, $^3J_{3,4} = 9.3$ Hz, 1H, 3-H), 3.78–3.89 (m, 3H, 4-H, 6-H, 6′-H), 4.26–4.41 (m, 3H, 9-H (Fmoc), 2C*H*H (Fmoc)), 4.55–4.63 (m, 3H, 3OC*H*HPh), 4.70 (d, $J_{gem} = 12.0$ Hz, 1H, OC*H*HPh), 4.81 (d, $J_{gem} = 11.5$ Hz, 1H, OC*H*HPh), 4.86 (s, 1H, 1-H), 4.92 (d, $J_{gem} = 10.9$ Hz, 1H, OC*H*HPh), 5.34–5.36 (m, 1H, 2-H), 7.22–7.78 (m, 23H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 17.9$, 25.6, 46.7, 69.5, 70.2, 71.4, 73.5, 73.8, 74.3, 75.2, 75.6, 80.1, 94.0, 119.9, 125.4, 127.1, 127.5, 127.7, 127.9, 128.0, 128.31, 128.34, 137.7, 138.3, 141.2, 143.6, 155.4; FAB-MS (positive mode): m/z: 808.7 $[M+Na]^+$; elemental analysis calcd (%) for $C_{48}H_{54}O_8Si$ (787.0): C 73.25, H 6.92; found: C 73.15, H 7.01.

3,4,6-Tri-*O*-benzyl-2-*O*-(9-fluorenylmethoxycarbonyl)-α/β-D-mannopyranose (15): HF·pyridine (2.79 mL, 19.1 mmol) was added at RT to a solution of compound **14** (1.50 g, 1.91 mmol) in dry THF (10 mL) and the reaction mixture was stirred overnight (12 h). The solution was diluted with ethyl acetate (15 mL) and neutralized with a saturated $NaHCO_3$ solution. The organic layer was separated, the aqueous layer was extracted three times with ethyl acetate (50 mL) and the combined organic layers were concentrated in vacuo. Flash chromatography (toluene/ethyl acetate 3:1) gave compound **15** (1.16 g, 1.71 mmol, 90%) as a white foam. Compound **15** was immediately used in the next reaction step. $R_f(\beta) = 0.31$, $R_f(\alpha) = 0.17$ (toluene/ethyl acetate 3:1); $[\alpha]_D = +12.8°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ (α compound) = 3.51 (d, $^3J_{1\text{-}OH,1} = 3.2$ Hz, 1H, 1-O*H*), 3.70–3.84 (m, 3H, 4-H, 6-H, 6′-H), 4.07 (dd, $^3J_{3,2} = 3.1$, $^3J_{3,4} = 9.5$ Hz, 1H, 3-H), 4.11–4.15 (m, 1H, 5-H), 4.21–4.65 (m, 7H, 2OC*H*H (Fmoc), 9-H (Fmoc), 4 OC*H*HPh), 4.76 (d, $J_{gem} = 11.4$ Hz, 1H, OC*H*HPh), 4.90 (d, $J_{gem} = 10.9$ Hz, 1H, OC*H*HPh), 5.23 (dd, $^3J_{2,1} = 1.8$, $^3J_{2,3} = 3.1$ Hz, 1H, 2-H), 5.35 (m, 1H, 1-H), 7.14–7.78 (m, 23H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 46.6$, 69.4, 70.2, 71.1, 71.8, 72.9, 73.4, 74.6, 75.2, 77.7, 92.2, 119.9, 120.0, 125.2, 125.4, 127.1, 127.6, 127.65, 127.71, 127.77, 127.81, 127.87, 127.95, 128.0, 128.2, 128.3, 128.4, 128.6, 129.0, 137.8, 137.9, 138.2, 141.17, 141.24, 143.3, 143.5, 154.8, 176.9, 178.4; MALDI MS (positive mode): m/z: calcd for $C_{42}H_{40}O_8$: 672.8; found: 694.7 $[M+Na]^+$, 710.7 $[M+K]^+$.

***O*-[3,4,6-Tri-*O*-benzyl-2-*O*-(9-fluorenylmethoxycarbonyl)-α-D-mannopyranosyl]-trichloroacetimidate (5^e)**: Trichloroacetonitrile (0.79 mL, 7.45 mmol) and NaH (5 mg) were added to a solution of compound **15** (1.0 g, 1.49 mmol) in dry CH_2Cl_2 (3 mL). After stirring at RT for 30 min, the reaction mixture was neutralized with silica gel. Flash chromatography (petroleum ether/ethyl acetate 3:1) gave compound **5^e** (1.12 g, 1.37 mmol, 92%) as colourless oil. Compound **5^e** was immediately used for the next reaction step. $R_f = 0.47$ (toluene/ethyl acetate 3:1); $[\alpha]_D = +17.1°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 3.75$ (dd, $^3J_{5,6} = 1.6$, $^3J_{6,6'} = 11.2$ Hz, 1H, 6-H), 3.87 (dd, $^3J_{5,6'} = 3.9$, $^3J_{6',6} = 11.2$ Hz, 1H, 6′-H), 4.05–4.51 (m, 6H, CH_2 (Fmoc), 9-H (Fmoc), 3-H, 4-H, 5-H), 4.52–4.67 (m, 3H, 3OC*H*HPh), 4.72 (d, $J_{gem} = 12.0$ Hz, 1H, OC*H*HPh), 4.78 (d, $J_{gem} = 11.4$ Hz, 1H, OC*H*HPh), 4.92 (d, $J_{gem} = 10.6$ Hz, 1H, OC*H*HPh), 5.33–5.35 (m, 1H, 2-H), 6.45 (d, $^3J_{1,2} = 1.9$ Hz, 1H, 1-H), 7.18–7.79 (m, 23H, Ph), 8.71 (s, 1H, N*H*); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 46.6$, 68.5, 70.5, 71.3, 72.1, 73.5, 73.7, 74.6, 75.5, 77.3, 90.7, 95.2, 120.0, 125.2, 125.4, 127.2, 127.6, 127.8, 127.9, 128.1, 128.3, 128.4, 137.5, 138.1, 138.2, 141.2, 141.3, 143.2, 143.4, 154.6, 160.0.

4-Methoxyphenyl 2-*O*-acetyl-3-*O*-allyl-4,6-*O*-benzylidene-α-D-mannopyranoside (17): Ac_2O (1.70 mL, 18.2 mmol) was added to a solution of compound **16** (1.5 g, 3.62 mmol) in dry pyridine (20 mL). After 12 h the solvent was evaporated in vacuo and three times coevaporated with toluene (20 mL). Flash chromatography (petroleum ether/ethyl acetate 4:1) gave compound **17** (1.65 g, 3.62 mmol, quant.) as colourless oil. $R_f = 0.60$ (petroleum ether/ethyl acetate 3:1); $[\alpha]_D = +73.1°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.19$ (s, 3H, CH_3), 3.77–3.86 (m, 4H, 5-H, OCH_3), 3.99–4.28 (m, 6H, 3-H, 4-H, 6-H, 6′-H, OCH_2-CH=CH$_2$), 5.17 (m, 2H, OCH$_2$-CH=CH_2), 5.39 (d, $^3J_{1,2} = 1.7$ Hz, 1H, 1-H), 5.51 (dd, $^3J_{2,1} = 1.7$, $^3J_{2,3} = 2.8$ Hz, 1H, 2-H), 5.63 (s, 1H, C*H*Ph), 5.83–5.99 (m, 1H, OCH$_2$-C*H*=CH$_2$), 6.80–7.51 (m, 9H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$):

δ = 20.9, 55.6, 64.4, 68.5, 69.9, 71.4, 73.3, 78.3, 97.7, 101.6, 114.6, 117.2, 117.9, 126.0, 128.1, 128.9, 134.3, 137.3, 149.6, 155.3, 170.0; MALDI MS (positive mode): *m/z*: 478.9 $[M+Na]^+$, 494.8 $[M+K]^+$; elemental analysis calcd (%) for $C_{25}H_{28}O_8$ (456.5): C 65.78, H 6.18; found: C 65.89, H 6.08.

4-Methoxyphenyl 2-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranoside (18): A solution of compound **17** (1.2 g, 2.63 mmol) in *tert*-butanol (15 mL) and *trans*-$[Pd(NH_3)_2Cl_2]$ (108 mg, 0.526 mmol) as a catalyst was heated under reflux overnight (12 h). After cooling to RT the solution was filtered and the solvent was evaporated in vacuo. Flash chromatography (toluene/ethyl acetate 5:1) gave compound **18** (887 mg, 2.12 mmol, 81%) as a white foam. Compound **18** was immediately used for the next reaction step. R_f = 0.25 (toluene/ethyl acetate 3:1); $[\alpha]_D = +62.7°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.22 (s, 3H, CH_3), 2.43 (d, $^3J_{3\text{-}OH,3}$ = 4.1 Hz, 1H, 3-OH), 3.78–3.86 (m, 4H, 5-H, OCH_3), 3.99–4.05 (m, 2H, 4-H, 6-H), 4.23 (dd, $^3J_{6',5}$ = 4.2, J_{gem} = 10.1 Hz, 1H, 6′-H), 4.43–4.46 (m, 1H, 3-H), 5.40–5.42 (m, 2H, 1-H, 2-H), 5.62 (s, 1H, C*H*Ph), 6.82–7.52 (m, 9H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.0, 55.7, 64.0, 67.2, 68.6, 72.0, 78.9, 97.5, 102.3, 114.7, 117.9, 126.3, 128.4, 129.0, 129.3, 137.1, 155.4, 170.4; MALDI MS (positive mode): *m/z*: calcd for $C_{22}H_{24}O_8$: 416.4; found: 438.7 $[M+Na]^+$; FAB-MS (positive mode): *m/z*: 439.2 $[M+Na]^+$.

4-Methoxyphenyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-phenoxyacetyl-α-D-mannopyranoside (19): Phenoxyacetyl chloride (322 μL, 2.30 mmol) was added dropwise at 0°C to a solution of compound **18** (0.8 g, 1.92 mmol) in dry pyridine (12 mL). After 30 min the reaction was quenched with methanol (1 mL). The reaction mixture was evaporated in vacuo and co-evaporated three times with toluene (10 mL). Flash chromatography (petroleum ether/ethyl acetate 8:1 → 2:1) gave compound **19** (960 mg, 1.74 mmol, 91%) as a white foam. R_f = 0.17 (petroleum ether/ethyl acetate 3:1); $[\alpha]_D = +35.2°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.14 (s, 3H, CH_3), 3.78–3.88 (m, 4H, OCH_3, 5-H), 4.11–4.16 (m, 2H, 4-H, 6-H), 4.22–4.27 (m, 1H, 6′-H), 4.60 (d, J_{gem} = 16.4 Hz, 1H, COC*H*-HOPh), 4.68 (d, J_{gem} = 16.4 Hz, 1H, COC*H*HOPh), 5.39 (d, $^3J_{1,2}$ = 1.7 Hz, 1H, 1-H), 5.54 (dd, $^3J_{2,1}$ = 1.7, $^3J_{2,3}$ = 3.6 Hz, 1H, 2-H), 5.57 (s, 1H, C*H*Ph), 5.78 (dd, $^3J_{3,2}$ = 3.6, $^3J_{3,4}$ = 10.1 Hz, 1H, 3-H), 6.80–7.46 (m, 14H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.8, 55.7, 64.4, 65.2, 68.5, 68.9, 70.0, 75.9, 97.5, 102.0, 114.6, 114.7, 117.8, 121.7, 126.2, 128.3, 129.2, 129.5, 136.9, 149.6, 155.4, 157.8, 169.8; MALDI MS (positive mode): *m/z*: 573.2 $[M+Na]^+$; elemental analysis calcd (%) for $C_{30}H_{30}O_{10}$ (550.6): C 65.45, H 5.49; found: C 65.74, H 5.67.

4-Methoxyphenyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-phenoxyacetyl-α-D-mannopyranoside (20): Compound **19** (0.9 g, 1.64 mmol) was dissolved in a BH_3·THF solution (c = 1 mol L^{-1}). At 0°C TMSOTf (0.31 mL, 1.72 mmol) was added dropwise. After 30 min the reaction mixture was stirred at RT for another 1.5 h. The solution was neutralized with NEt_3 (2 mL), methanol was added and after 15 min the solution was evaporated in vacuo and coevaporated three times with methanol (20 mL). Flash chromatography (toluene/ethyl acetate 8:1) gave compound **20** (657 mg, 1.20 mmol, 73%) as colourless oil. R_f = 0.27 (toluene/ethyl acetate 2:1); $[\alpha]_D = +40.8°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.78 (t, 1H, 6-OH), 3.76–3.82 (m, 5H, 6-H, 6′-H, OCH_3), 3.88–3.94 (m, 1H, 5-H), 4.05 (t, 1H, 4-H), 4.50 (d, J_{gem} = 16.3 Hz, 1H, COC*H*HOPh), 4.58 (d, J_{gem} = 16.3 Hz, 1H, COC*H*HOPh), 4.64 (s, 2H, 2OC*H*HPh), 5.37 (d, $^3J_{1,2}$ = 1.9 Hz, 1H, 1-H), 5.48 (dd, $^3J_{2,1}$ = 1.9, $^3J_{2,3}$ = 3.4 Hz, 1H, 2-H), 5.66 (dd, $^3J_{3,2}$ = 3.4, $^3J_{3,4}$ = 9.7 Hz, 1H, 3-H), 6.79–7.38 (m, 14H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.8, 55.6, 61.4, 65.2, 69.8, 72.1, 72.4, 72.7, 74.9, 96.8, 114.5, 114.7, 117.8, 121.7, 127.8, 128.0, 128.5, 129.6, 137.8, 149.7, 155.3, 157.8, 168.3, 170.0; MALDI MS (positive mode): *m/z*: 574.9 $[M+Na]^+$; elemental analysis calcd (%) for $C_{30}H_{32}O_{10}$ (552.5): C 65.21, H 5.84; found: C 65.17, H 6.22.

4-Methoxyphenyl 2-*O*-acetyl-4-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-α-D-mannopyranoside (21): Fmoc-Cl (696 mg, 2.71 mmol) was added to a solution of compound **20** (600 mg, 1.09 mmol) in dry pyridine (15 mL) and the reaction mixture was stirred overnight (12 h) at RT. The solvent was evaporated in vacuo and coevaporated (3× 25 mL) with toluene. Flash chromatography (toluene/ethyl acetate 10:1 → 6:1) gave compound **21** (684 mg, 0.882 mmol, 81%) as a white foam. R_f = 0.90 (toluene/ethyl acetate 3:1); $[\alpha]_D = +23.5°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.10 (s, 3H, CH_3), 3.72 (s, 3H, OCH_3), 4.00 (t, 1H, 4-H), 4.23 (ddd, $^3J_{5,4}$ = 9.9, $^3J_{5,6}$ = 2.9, $^3J_{5,6'}$ = 6.4 Hz, 1H, 5-H), 4.25 (t, ^3J = 7.4 Hz, 1H, 9-H (Fmoc)), 4.38–4.48 (m, 4H, 2 OC*H*H (Fmoc), 6-H, 6′-H), 4.55–4.66 (m, 4H, 2 OC*H*HPh, 2 COC*H*HOPh), 5.39 (d, $^3J_{1,2}$ = 1.9 Hz, 1H, 1-H), 5.49 (dd, $^3J_{2,1}$ = 1.9, $^3J_{2,3}$ = 3.4 Hz, 1H, 2-H), 5.68 (dd, $^3J_{3,2}$ = 3.4, $^3J_{3,4}$ = 9.4 Hz, 1H, 3-H), 6.78–7.79 (m, 22H, Ph); MALDI MS (positive mode): *m/z*: 797.6 $[M+Na]^+$, 813.7 $[M+K]^+$; elemental analysis calcd (%) for $C_{45}H_{42}O_{12}$ (774.8): C 69.76, H 5.46; found: C 69.76, H 5.72.

2-*O*-Acetyl-4-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-α-D-mannopyranose (22): Compound **21** (620 mg, 0.80 mmol) was dissolved in acetonitrile/water 4:1. At 0°C CAN (1.10 g, 2.00 mmol) was added, diluted with ethyl acetate after 15 min and then neutralized with saturated $NaHCO_3$ solution. The aqueous layer was extracted with ethyl acetate (3×35 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was evaporated in vacuo. Flash chromatography (toluene/ethyl acetate 5:1 → 2:1) gave compound **22** (409 mg, 0.616 mmol, 77%) as colourless oil. Compound **22** was immediately used in the next reaction step. R_f = 0.17 (petroleum ether/ethyl acetate 2:1); $[\alpha]_D = +6.8°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.05 (s, 3H, CH_3), 3.26 (d, $^3J_{1\text{-}OH,1\text{-}H}$ = 4.0 Hz, 1H, 1-O*H*), 3.89 (t, 1H, 4-H), 4.19–4.58 (m, 9-H, 5-H, 6-H, 6′-H, 9-H (Fmoc), 2 C*H*H (Fmoc), OC*H*HPh, 2 COC*H*HOPh), 4.63 (d, J_{gem} = 11.3 Hz, 1H, OC*H*HPh), 5.20 (dd, $^3J_{1\text{-}H,1\text{-}OH}$ = 4.0, $^3J_{1,2}$ = 1.9 Hz, 1H, 1-H), 5.33 (dd, $^3J_{2,1}$ = 1.9, $^3J_{2,3}$ = 3.3 Hz, 1H, 2-H), 5.55 (dd, $^3J_{3,2}$ = 3.3, $^3J_{2\text{-}H,4\text{-}OH}$ = 9.7 Hz, 1H, 3-H), 6.85–7.78 (m, 18H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.8, 46.7, 65.2, 66.5, 69.7, 70.0, 70.1, 72.6, 74.8, 92.2, 114.5, 120.1, 121.7, 125.07, 125.1, 127.1, 127.8, 127.9, 128.0, 128.5, 129.6, 137.5, 141.3, 143.2, 143.3, 155.0, 157.7, 168.2, 170.1; MALDI MS (positive mode): *m/z*: calcd for $C_{38}H_{36}O_{11}$: 668.7; found: 691.3 $[M+Na]^+$, 707.1 $[M+K]^+$; FAB-MS (positive mode): *m/z*: 690.5 $[M+Na]^+$.

***O*-[2-*O*-Acetyl-4-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-α-D-mannopyranosyl]-trichloroacetimidate (7^b)**: Trichloroacetonitrile (0.28 mL, 2.63 mmol) and NaH (5 mg) were added to a solution of compound **22** (350 mg, 0.525 mmol) in dry CH_2Cl_2 (3 mL). After stirring for 30 min at RT, the reaction mixture was neutralized with silica gel. Flash chromatography (petroleum ether/ethyl acetate 2:1) gave compound **7^b** (403 mg, 0.497 mmol, 95%) as colourless oil. Compound **7^b** was immediately used in the next reaction step. R_f = 0.61 (toluene/ethyl acetate 3:1); $[\alpha]_D = +24.6°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.11 (s, 3H, CH_3), 4.03 (t, 1H, 4-H), 4.15–4.29 (m, 2H, 9-H (Fmoc), 5-H), 4.37–4.61 (m, 7H, 6-H, 6′-H, 2 C*H*H (Fmoc), OC*H*HPh, 2 COC*H*-HOPh), 4.65 (d, J_{gem} = 11.1 Hz, 1H, OC*H*HPh), 5.51–5.56 (m, 2H, 2-H, 3-H), 6.28 (d, $^3J_{1,2}$ = 1.6 Hz, 1H, 1-H), 6.87–7.79 (m, 18H, Ph), 8.73 (s, 1H, N*H*); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.7, 46.0, 65.8, 70.1, 71.9, 72.3, 72.8, 75.1, 90.5, 94.6, 114.4, 120.1, 121.8, 125.1, 127.1, 127.9, 128.0, 128.2, 128.6, 129.7, 137.2, 141.3, 143.3, 154.8, 168.1, 169.7.

Thexyldimethylsilyl *O*-(2-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (26): A solution of compound **25** (1.35 g, 1.36 mmol) in *tert*-butanol (20 mL) and *trans*-$[Pd(NH_3)_2Cl_2]$ (56 mg, 0.27 mmol) as a catalyst was heated under reflux overnight (12 h). After cooling to RT the solution was filtered and the solvent evaporated in vacuo. Flash chromatography (toluene/ethyl acetate 8:1) gave compound **26** (1.02 g, 1.07 mmol, 79%) as a white foam. R_f = 0.37 (toluene/ethyl acetate 5:1); $[\alpha]_D = -3.5°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.13 (s, 3H, CH_3), 0.26 (s, 3H, CH_3), 0.83–0.89 (m, 12H, 4 CH_3), 1.60–1.63 (m, 1H, $(CH_3)_2CH$), 1.93 (m, 6H, 2 CH_3), 2.50 (br s, 1H, 3b-OH), 3.31–3.32 (m, 1H, 5b-H), 3.62–3.69 (m, 2H, 5a-H, 6b-H), 3.74–3.75 (m, 1H, 3b-H), 3.79–3.87 (m, 4H, 2b-H, 4b-H, 6a-H, 6a′-H), 4.04 (dd, $^3J_{2a,1a}$ = 8.2, $^3J_{2a,3a}$ = 10.6 Hz, 1H, 2a-H), 4.15 (t, 1H, 4a-H), 4.26 (dd, $^3J_{3a,2a}$ = 10.6, $^3J_{3a,4a}$ = 8.9 Hz, 1H, 3a-H), 4.32 (dd, $^3J_{6'b,5b}$ = 4.8, J_{gem} = 10.4 Hz, 1H, 6b′-H), 4.57 (d, J_{gem} = 12.4 Hz, 1H, OC*H*HPh), 4.66 (d, J_{gem} = 12.1 Hz, 1H, OC*H*HPh), 4.80–4.82 (m, 2H, 1b-H, OC*H*HPh), 4.86 (d, J_{gem} = 12.1 Hz, 1H, OC*H*HPh), 5.03 (d, J_{gem} = 12.4 Hz, 1H, OC*H*HPh), 5.16 (d, J_{gem} = 11.6 Hz, 1H, OC*H*HPh), 5.32 (d, $^3J_{1a,2a}$ = 8.2 Hz, 1H, 1a-H), 5.58 (s, 1H, C*H*Ph), 7.21–7.60 (m, 20H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): δ = −3.8, −1.8, 18.3, 18.4, 19.8, 19.9, 24.5, 34.0, 57.5 (C-2a), 66.9 (C-5b), 68.5 (C-6b), 68.6 (C-6a), 70.9 (C-3b), 73.7, 74.3, 74.7 (C-5a), 75.6, 77.2 (C-3a), 78.8 (C-2b),

79.2 (C-4b), 79.6 (C-4a), 93.5 (C-1a), 101.9 (*C*HPh), 102.1 (C-1b), 126.3, 127.0, 127.88, 127.93, 127.97, 128.2, 128.48, 128.55, 129.1, 137.2, 137.8, 138.1, 139.2; $^{1}J_{1a\text{-}C,1a\text{-}H}=163.3$, $^{1}J_{1b\text{-}C,1b\text{-}H}=158.4$ Hz; MALDI MS (positive mode): *m/z*: 972.6 $[M+Na]^+$, 988.6 $[M+K]^+$: elemental analysis calcd (%) for $C_{54}H_{67}NO_{12}Si$ (950.2): C 68.26, H 7.11, N 1.47; found: C 68.28, H 7.13, N 1.67.

Thexyldimethylsilyl *O*-(2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-phenoxyacetyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (27): Phenoxyacetyl chloride (169 μL, 1.20 mmol) was added dropwise at 0 °C to a solution of compound **26** (0.95 g, 1.00 mmol) in dry pyridine (10 mL). After 1 h the reaction was quenched with methanol (1 mL). The reaction mixture was evaporated in vacuo and coevaporated with toluene (3×10 mL). Flash chromatography (petroleum ether/ethyl acetate 6:1 → 2:1) gave compound **27** (1.07 g, 0.988 mmol, 99 %) as a white foam. $R_f=0.69$ (toluene/ethyl acetate 3:1); $[\alpha]_D=-14.0°$ ($c=1.0$, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=-0.01$ (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.69–0.77 (m, 12H, 4 CH_3), 1.46–1.49 (m, 1H, $(CH_3)_2CH$), 1.76–1.83 (m, 6H, 2 CH_3), 3.22–3.26 (m, 1H, 5b-H), 3.46–3.48 (d, 1H, 5a-H), 3.56 (t, 1H, 6b-H), 3.67 (br s, 2H, 6a-H, 6a′-H), 3.89 (dd, $^{3}J_{2a,1a}=8.2$, $^{3}J_{2a,3a}=10.6$ Hz, 1H, 2a-H), 3.97 (d, 1H, 2b-H), 4.00–4.05 (m, 2H, 4a-H, 4b-H), 4.12 (t, 1H, 3a-H), 4.17–4.19 (m, 1H, 6b′H), 4.41 (d, $J_{gem}=16.2$ Hz, 1H, COC*H*HOPh), 4.43 (d, $J_{gem}=12.4$ Hz, 1H, OC*H*HPh), 4.53–4.58 (m, 2H, OC*H*HPh, COC*H*HOPh), 4.61 (d, $J_{gem}=12.0$ Hz, 1H, OC*H*HPh), 4.71 (d, $J_{gem}=12.1$ Hz, 1H, OC*H*HPh), 4.73 (s, 1H, 1b-H), 4.87 (d, $J_{gem}=12.0$ Hz, 1H, OC*H*HPh), 4.88 (d, $J_{gem}=12.4$ Hz, 1H, OC*H*HPh), 4.99 (dd, $^{3}J_{3b,2b}=3.1$, $^{3}J_{3b,4b}=10.3$ Hz, 1H, 3b-H), 5.17 (d, $^{3}J_{1a,2a}=8.2$ Hz, 1H, 1a-H), 5.43 (s, 1H, C*H*Ph), 6.80–7.32 (m, 25H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta=-3.8$, −1.8, 18.3, 18.4, 19.8, 19.9, 24.5, 34.0, 57.5 (C-2a), 64.9, 67.0 (C-5b), 68.5 (C-6b), 68.6 (C-6a), 73.0 (C-3b), 73.6, 74.3, 74.7 (C-5a), 75.4 (C-4b), 75.7, 76.6 (C-2b), 77.0 (C-3a), 77.2, 79.2 (C-4a), 93.5 (C-1a), 101.3 (C-1b), 101.6 (*C*HPh), 114.6, 121.7, 122.1, 126.2, 126.9, 127.8, 127.9, 127.97, 128.04, 128.3, 128.4, 128.6, 129.1, 129.5, 137.8, 138.1, 139.2, 157.6, 168.4; $^{1}J_{1a\text{-}C,1a\text{-}H}=163.3$, $^{1}J_{1b\text{-}C,1b\text{-}H}=158.9$ Hz; MALDI MS (positive mode): *m/z*: 1105.6 $[M+Na]^+$, 1121.6 $[M+K]^+$; elemental analysis calcd (%) for $C_{62}H_{73}NO_{14}Si$ (1084.3): C 68.68, H 6.79, N 1.29; found: C 68.62, H 6.91, N 1.29.

Thexyldimethylsilyl *O*-(2,4-di-*O*-benzyl-3-*O*-phenoxyacetyl-β-D-mannopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (28): Compound **27** (0.9 g, 0.830 mmol) was dissolved in a BH_3·THF solution ($c=1$ mol L^{-1}). At 0 °C TMSOTf (0.18 mL, 1.0 mmol) was added dropwise. After 30 min the reaction mixture was stirred at RT for an additional 1.5 h. The solution was neutralized with NEt_3 (1 mL), methanol was added and after 15 min the solution was evaporated in vacuo and coevaporated three times with methanol (30 mL). Flash chromatography (toluene/ethyl acetate 7:1) gave compound **28** (693 mg, 0.639 mmol, 77 %) as colourless oil. $R_f=0.45$ (toluene/ethyl acetate 3:1); $[\alpha]_D=-16.1°$ ($c=1.0$, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=0.00$ (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.69–0.77 (m, 12H, 4 CH_3), 1.47–1.50 (m, 1H, $(CH_3)_2CH$), 1.78–1.85 (m, 6H, 2 CH_3), 3.19–3.22 (m, 1H, 5b-H), 3.46–3.52 (m, 2H, 5a-H, 6b-H), 3.65–3.71 (m, 3H, 6a-H, 6a′-H, 6b′-H), 3.88–3.95 (m, 3H, 2a-H, 2b-H, 4b-H), 4.01 (t, 1H, 4a-H), 4.14 (dd, $^{3}J_{3a,2a}=10.7$, $^{3}J_{3a,4a}=8.8$ Hz, 1H, 3a-H), 4.31 (br s, 2H, COC*H*HOPh), 4.42 (d, $J_{gem}=12.3$ Hz, 1H, OC*H*HPh), 4.53–4.59 (m, 4H, 4 OC*H*HPh), 4.67–4.69 (m, 2H, 1b-H, OC*H*HPh), 4.85–4.87 (m, 2H, 3b-H, OC*H*HPh), 4.95 (d, $J_{gem}=12.3$ Hz, 1H, OC*H*HPh), 5.18 (d, $^{3}J_{1a,2a}=8.1$ Hz, 1H, 1a-H), 6.79–7.36 (m, 25H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta=-3.8$, −1.8, 18.3, 18.4, 19.8, 19.9, 24.5, 34.0, 57.5 (C-2a), 61.8 (C-6b), 64.9, 68.4 (C-6a), 72.8 (C-4b), 73.5, 74.0, 74.8 (C-5a), 74.9, 75.4 (C-5b), 76.1 (C-2b), 76.7 (C-3b), 77.0 (C-3a), 78.5 (C-4a), 93.5 (C-1a), 100.2 (C-1b), 114.5, 121.8, 122.1, 127.1, 127.3, 127.69, 127.73, 127.83, 128.17, 128.33, 128.43, 128.52, 129.6, 137.8, 138.0, 138.3, 139.0, 157.0, 168.3, $^{1}J_{1a\text{-}C,1a\text{-}H}=163.3$, $^{1}J_{1b\text{-}C,1b\text{-}H}=158.3$ Hz; MALDI MS (positive mode): *m/z*: calcd for: 1086.3; found: 1107.8 $[M+Na]^+$, 1123.8 $[M+K]^+$; elemental analysis calcd (%) for $C_{62}H_{75}NO_{14}$: C 68.55, H 6.96, N 1.29; found: C 68.61, H 7.02, N 1.30.

Thexyldimethylsilyl *O*-[2,4-di-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (29): Fmoc-Cl (0.38 g, 1.50 mmol) was added to a solution of compound **28** (650 mg, 0.599 mmol) in dry pyridine (10 mL) and the reaction mixture stirred overnight (12 h) at RT. The solvent was evaporated in vacuo and coevaporated three times (15 mL) with toluene. Flash chromatography (toluene/ethyl acetate 12:1 → 6:1) gave compound **29** (0.676 g, 0.515 mmol, 86 %) as a white foam. $R_f=0.61$ (toluene/ethyl acetate 4:1); $[\alpha]_D=-3.1°$ ($c=1.0$, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=0.02$ (s, 3H, CH_3), 0.11 (s, 3H, CH_3), 0.68–0.74 (m, 12H, 4 CH_3), 1.46–1.48 (m, 1H, $(CH_3)_2CH$), 1.69–1.82 (m, 6H, 2 CH_3), 3.45–3.50 (m, 2H, 5a-H, 5b-H), 3.69 (br s, 2H, 6a-H, 6a′-H), 3.90 (dd, $^{3}J_{2a,1a}=8.3$, $^{3}J_{2a,3a}=10.5$ Hz, 1H, 2a-H), 3.99–4.02 (m, 2H, 2b-H, 4b-H), 4.06 (t, 1H, 4a-H), 4.11–4.16 (m, 2H, 3a-H, 9-H (Fmoc)), 4.26–4.41 (m, 6H, 6b-H, 6b′-H, 2 COC*H*HOPh, 2 OC*H*H (Fmoc)), 4.52 (d, $J_{gem}=12.9$ Hz, 1H, OCHHPh), 4.56–4.59 (m, 3H, 3 OC*H*HPh), 4.62 (d, $J_{gem}=12.1$ Hz, 1H, OC*H*HPh), 4.69 (d, $J_{gem}=12.2$ Hz, 1H, OC*H*HPh), 4.76 (s, 1H, 1b-H), 4.89 (dd, $^{3}J_{3b,2b}=2.9$, $^{3}J_{3b,4b}=9.7$ Hz, 1H, 3b-H), 4.92 (d, $J_{gem}=12.3$ Hz, 1H, OC*H*HPh), 4.95 (d, $J_{gem}=12.9$ Hz, 1H, OC*H*HPh), 5.16 (d, $^{3}J_{1a,2a}=8.3$ Hz, 1H, 1a-H), 6.81–7.73 (m, 33H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta=-3.9$, −1.9, 18.3, 18.4, 19.7, 19.9, 33.9, 46.5, 57.4 (C-2a), 64.9, 66.4 (C-6b), 68.6 (C-6a), 69.9, 72.9 (C-4b), 73.2 (C-5b), 73.5, 74.0, 74.6, 74.7 (C-5a), 74.8, 75.9 (C-2b), 76.8 (C-3b), 77.2 (C-3a), 79.2 (C-4a), 93.4 (C-1a), 100.9 (C-1b), 114.5, 119.9, 121.8, 125.25, 125.28, 126.8, 127.09, 127.12, 127.70, 127.74, 127.9, 128.26, 128.32, 128.47, 128.50, 129.6, 137.7, 137.9, 138.4, 139.4, 141.1, 141.2, 143.36, 143.49, 154.9, 168.3, $^{1}J_{1a\text{-}C,1a\text{-}H}=163.4$, $^{1}J_{1b\text{-}C,1b\text{-}H}=158.6$ Hz; MALDI MS (positive mode): *m/z*: calcd for: 1308.6; found: 1331.4 $[M+Na]^+$, 1346.3 $[M+K]^+$; elemental analysis calcd (%) for $C_{77}H_{85}NO_{16}Si$: C 70.67, H 6.55, N 1.07; found: C 70.32, H 6.68, N 0.87.

[2,4-Di-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-α/β-D-glucopyranose (30): HF·pyridine (0.76 mL, 4.81 mmol) was added at RT to a solution of compound **29** (0.63 g, 0.481 mmol) in dry THF (8 mL) and the reaction mixture was stirred overnight (12 h). The solution was diluted with ethyl acetate (15 mL) and neutralized with saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer extracted three times with ethyl acetate (30 mL) and the combined organic layers were concentrated in vacuo. Flash chromatography (toluene/ethyl acetate 4:1) gave compound **30** (485 mg, 0.414 mmol, 86 %) as a white foam. R_f (α) = 0.41, R_f (α) = 0.24 (toluene/ethyl acetate 2:1); $[\alpha]_D=+1.8°$ ($c=1.0$, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.73$ (br s, 6H, 2 CH_3), 2.81 (s, 1H, 1a-OH), 3.36–3.41 (m, 1H, 5b-H), 3.51–3.53 (m, $^1/_2$H, 5a-H), 3.64–3.73 (m, 2H, 6a-H, 6a′-H), 3.81 (dd, $^{3}J_{2a,1a}=8.7$, $^{3}J_{2a,3a}=10.5$ Hz, $^1/_2$H, 2a-H), 3.92–3.97 (m, 2H, 2b-H, 4b-H), 4.04–4.73 (m, $18\times{}^1/_2$H, 2a-H, 3a-H, 4a-H, 5a-H, 1b-H, 6b-H, 6b′-H, 9-H (Fmoc), 2 C*H*H (Fmoc), $7\times{}^1/_2$ OC*H*HPh, 2 COC*H*HOPh), 4.77–4.81 (m, 1H, 3b-H), 4.97 (d, $J_{gem}=12.9$ Hz, $^1/_2$H, OC*H*HPh), 5.11–5.13 (m, $^1/_2$H, 1a-H), 5.21 (t, $^1/_2$H, 1a-H), 6.80–7.38 (m, 33H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta=46.6$, 55.5 (C-2a,α), 57.4 (C-2a,β), 64.9 (C-6b,α), 66.4 (C-6b,β), 68.3 (C-6a,α; C-6a,β), 70.0 (C-5a,α), 72.8, 73.1 (C-4b,α; C-4b,β), 73.2 (C-5b,α; C-5b,β), 73.7, 74.4, 74.7 (C-5a,β), 74.8, 75.0, 75.9 (C-2b,α; C-2b,β), 76.8 (C-3b,α; C-3b,β), 77.0 (C-3a,α; C-3a,β), 78.8 (C-4a,β), 79.1 (C-4a,α), 92.8 (C-1a,α), 93.1 (C-1a,β), 100.6 (C-1b,α; C-1b,β), 114.5, 119.9, 121.8, 125.23, 125.28, 126.8, 127.1, 127.68, 127.76, 127.81, 127.95, 127.98, 128.05, 128.09, 128.33, 128.48, 128.67, 129.6, 136.8, 137.50, 137.75, 141.2, 143.3, 143.5, 157.5, 168.2, 171.6, $^{1}J_{1a(\alpha)\text{-}C,1a(\alpha)\text{-}H}=176.0$, $^{1}J_{1a(\beta)\text{-}C,1a(\beta)\text{-}H}=166.3$, $^{1}J_{1b\text{-}C,1b\text{-}H}=158.2$ Hz; MALDI MS (positive mode): *m/z*: calcd for 1202.3; found: 1188.1 $[M+Na]^+$, 1204.3 $[M+K]^+$; elemental analysis calcd (%) for $C_{69}H_{67}NO_{16}\cdot 2H_2O$: C 68.93, H 5.61, N 1.16; found: C 68.94, H 5.58, N 1.07.

***O*-{[2,4-Di-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl}-trichloroacetimidate (4^b)**: Trichloroacetonitrile (0.22 mL, 1.93 mmol) and NaH (5 mg) were added to a solution of compound **30** (0.45 g, 0.386 mmol) in dry CH_2Cl_2 (3 mL). After stirring for 30 min at RT, the reaction mixture was neutralized with silica gel. Flash chromatography (petroleum ether/ethyl acetate 3:1) gave compound $\mathbf{4^b}$ (454 mg, 0.347 mmol, 90 %) as colourless oil. Compound $\mathbf{4^b}$ was immediately used in the next reaction step. $R_f=0.56$ (toluene/ethyl acetate 3:1); $[\alpha]_D=+8.3°$ ($c=1.0$, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.71$ (s, 6H, 2 CH_3), 3.37–3.40 (m, 1H, 5b-H), 3.67–3.70 (m, 2H, 5a-H, 6a-H), 3.78–3.79 (m, 1H, 6a′-H), 3.95–3.99 (m, 2H, 2b-H, 4b-H), 4.13–

4.37 (m, 10H, 2a-H, 3a-H, 4a-H, 6b-H, 6b′-H, 9-H (Fmoc), 2 C*H*H (Fmoc), 2 OC*H*HPh), 4.48 (d, J_{gem} = 13.0 Hz, 1H, OC*H*HPh), 4.51 (d, J_{gem} = 12.1 Hz, 1H, OC*H*HPh), 4.57–4.71 (m, 5H, 1b-H, 2 COC*H*OPh, 2 OC*H*HPh), 4.81 (dd, $^3J_{3b,2b}$ = 3.0, $^3J_{3b,4b}$ = 9.7 Hz, 1H, 3b-H), 4.89 (d, J_{gem} = 12.3 Hz, 1H, OC*H*HPh), 4.98 (d, J_{gem} = 13.0 Hz, 1H, OC*H*HPh), 6.22 (d, $^3J_{1a,2a}$ = 8.4 Hz, 1H, 1a-H), 6.80–7.72 (m, 33H, Ph), 8.54 (s, 1H, N*H*); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 29.7, 46.6, 54.3 (C-2a), 64.9, 66.4 (C-6b), 68.0 (C-6a), 70.0, 72.9, 73.2 (C-4b), 73.5 (C-5b), 74.5, 74.8, 75.6, 75.9 (C-5a), 76.8 (C-2b), 77.0 (C-3b), 77.2 (C-3a), 78.5, 78.8 (C-4a), 90.1, 94.1 (C-1a), 100.6 (C-1b), 112.3, 114.5, 119.9, 121.8, 125.3, 127.1, 127.72, 127.78, 127.97, 128.02, 128.22, 128.36, 128.36, 128.50, 128.6, 129.6, 136.8, 141.2, $^1J_{1a\text{-}C,1a\text{-}H}$ = 172.8, $^1J_{1b\text{-}C,1b\text{-}H}$ = 158.2 Hz; M_w: calcd for $C_{71}H_{67}Cl_3N_2O_{16}$: 1310.7.

Thexyldimethylsilyl 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-phenoxyacetyl-β-D-galactopyranoside (34): Compound **33** (1.0 g, 1.54 mmol) was dissolved in a BH_3·THF solution (c = 1 mol L^{-1}). At 0 °C TMSOTf (0.29 mL, 1.62 mmol) was added dropwise. After 30 min the reaction mixture was stirred at RT for another 2 h. The solution was neutralized with NEt_3 (2 mL), methanol was added and after 15 min the solution was evaporated in vacuo and coevaporated three times with methanol (25 mL). Flash chromatography (toluene/ethyl acetate 6:1) gave compound **34** (760 mg, 1.33 mmol, 76%) as colourless oil. R_f = 0.35 (petroleum ether/ethyl acetate 2:1); $[\alpha]_D$ = −0.4° (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.02 (s, 3H, CH_3), 0.11 (s, 3H, CH_3), 0.66–0.69 (m, 12H, 4 CH_3), 1.41–1.52 (m, 1H, C-(CH$_3$)$_2$*H*), 3.50–3.64 (m, 2H, 5-H, 6-H), 3.76–3.84 (m, 1H, 6′-H), 3.93 (d, $^3J_{4,3}$ = 3.1 Hz, 1H, 4-H), 4.34 (d, J_{gem} = 16.4 Hz, 1H, COC*H*HOPh), 4.43 (d, J_{gem} = 16.4 Hz, 1H, COC*H*HOPh), 4.54 (d, J_{gem} = 12.0 Hz, 1H, OC*H*HPh), 4.72 (d, J_{gem} = 12.0 Hz, 1H, OC*H*HPh), 4.82 (d, $^3J_{1,2}$ = 7.5 Hz, 1H, 1-H), 5.27 (dd, $^3J_{3,2}$ = 10.5, $^3J_{3,4}$ = 3.1 Hz, 1H, 3-H), 5.61 (dd, $^3J_{2,1}$ = 7.5, $^3J_{2,3}$ = 10.5 Hz, 1H, 2-H), 6.64–8.00 (m, 15H, 15 Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ = −3.3, −1.7, 18.3, 19.7, 24.7, 33.7, 61.5, 64.8, 72.0, 73.8, 74.6, 75.0, 96.4, 114.4, 121.7, 128.2, 128.4, 128.5, 128.6, 129.5, 129.7, 133.1, 137.5, 157.4, 165.1, 168.5; MALDI MS (positive mode): m/z: calcd for: 650.83; found: 673.0 [M+Na]$^+$, 688.9 [M+K]$^+$; elemental analysis calcd (%) for $C_{36}H_{46}O_9Si$: C 66.44, H 7.12; found: C 66.45, H 7.15.

Thexyldimethylsilyl 2-*O*-benzoyl-4-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-β-D-galactopyranoside (35): Fmoc-Cl (694 g, 2.69 mmol) was added to a solution of compound **34** (700 mg, 1.08 mmol) in dry pyridine (10 mL) and the reaction mixture was stirred overnight (12 h) at RT. The solvent was evaporated in vacuo and coevaporated three times (20 mL) with toluene. Flash chromatography (toluene/ethyl acetate 10:1 → 6:1) gave compound **35** (791 mg, 0.903 mmol, 84%) as colourless oil. R_f = 0.39 (petroleum ether/ethyl acetate 4:1); $[\alpha]_D$ = +2.4° (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.05 (s, 3H, CH_3), 0.14 (s, 3H, CH_3), 0.67–0.71 (m, 12H, 4 CH_3), 1.42–1.53 (m, 1H, C(CH$_3$)$_2$*H*), 3.80–3.85 (t, 1H, 5-H), 3.96 (d, 1H, $^3J_{4,3}$ = 3.1 Hz, 1H, 4-H), 4.13 (dd, $^3J_{6,5}$ = 6.0, J_{gem} = 11.0 Hz, 1H, 6-H), 4.25 (t, ^3J = 7.2 Hz, 1H, 9-H (Fmoc)), 4.30–4.48 (m, 5H, 2 COC*H*HOPh, 2 OC*H*H (Fmoc), 6′-H), 4.59 (d, J_{gem} = 11.8 Hz, 1H, OC*H*HPh), 4.72 (d, J_{gem} = 11.8 Hz, 1H, OC*H*HPh), 4.82 (d, $^3J_{1,2}$ = 7.5 Hz, 1H, 1-H), 5.30 (dd, $^3J_{3,2}$ = 10.5, $^3J_{3,4}$ = 3.1 Hz, 1H, 3-H), 5.62 (dd, $^3J_{2,1}$ = 7.5, $^3J_{2,3}$ = 10.5 Hz, 1H, 2-H), 6.66–8.02 (m, 23H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ = −3.5, −1.8, 18.3, 19.78, 19.81, 24.7, 33.8, 46.7, 64.8, 65.8, 70.0, 71.8, 72.2, 74.1, 74.3, 75.1, 96.4, 114.4, 120.1, 121.7, 125.1, 125.13, 127.2, 127.9, 128.1, 128.4, 128.5, 129.5, 129.67, 129.72, 133.1, 137.4, 141.3, 143.2, 154.7, 165.1, 168.5; MALDI MS (positive mode): m/z: calcd for 873.1; found: 895.3 [M+Na]$^+$, 911.3 [M+K]$^+$; elemental analysis calcd (%) for $C_{51}H_{56}O_{11}Si$: C 70.16, H 6.47; found: C 69.87, H 6.88.

2-*O*-Benzoyl-4-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-α/β-D-galactopyranose (36): HF·pyridine (1.18 mL, 8.1 mmol) was added at RT to a solution of compound **35** (700 mg, 0.805 mmol) in dry THF (8 mL) and the reaction mixture was stirred overnight (12 h). The solution was diluted with ethyl acetate (15 mL) and neutralized with a saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted three times with ethyl acetate (35 mL) and the combined organic layers were concentrated in vacuo. Flash chromatography (toluene/ethyl acetate 4:1) gave compound **36** (518 mg, 0.707 mmol, 88%) as a white foam. $R_f(\alpha)$ = 0.74, $R_f(\beta)$ = 0.69 (petroleum ether/ethyl acetate 1:1); $[\alpha]_D$ = +52.7° (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ (α-compound) = 2.96–2.98 (m, 1H, 1-OH), 4.04 (d, $^3J_{4,3}$ = 2.6 Hz, 1H, 4-H), 4.12 (m, 8H, 5-H, 6-H, 6′-H, 9-H (Fmoc), 2 C*H*H (Fmoc), 2 COC*H*-HOPh), 4.54 (d, J_{gem} = 11.6 Hz, 1H, OC*H*HPh), 4.73 (d, J_{gem} = 11.5 Hz, 1H, OC*H*HPh), 5.51 (dd, $^3J_{2,1}$ = 2.9, $^3J_{2,3}$ = 10.7 Hz, 1H, 2-H), 5.68 (t, 1H, 1-H), 5.79 (dd, $^3J_{3,2}$ = 10.7, $^3J_{3,4}$ = 2.9 Hz, 1H, 3-H), 6.68–8.04 (m, 23H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 46.7, 65.0, 66.1, 68.0, 69.7, 70.0, 70.7, 75.1, 75.2, 90.8, 114.4, 120.1, 121.8, 125.05, 125.11, 127.2, 127.9, 128.1, 128.3, 128.4, 128.5, 128.6, 129.2, 129.5, 129.85, 129.93, 133.5, 137.4, 141.3, 143.2, 154.8, 157.5, 165.7, 168.5, 178.5; MALDI MS (positive mode): m/z: calcd for: 748.8; found: 752.9 [M+Na]$^+$, 768.9 [M+K]$^+$; elemental analysis calcd (%) for $C_{43}H_{48}O_{11}$·H_2O: C 68.97, H 5.38; found: C 68.92, H 5.34.

***O*-[2-*O*-Benzoyl-4-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-α-D-galactopyranosyl] trichloroacetimidate (8^b)**: Trichloroacetonitrile (0.32 mL, 3.00 mmol) and NaH (5 mg) were added to a solution of compound **36** (450 mg, 0.601 mmol) in dry CH_2Cl_2 (3 mL). After stirring for 30 min at RT, the reaction mixture was neutralized with silica gel. Flash chromatography (toluene/ethyl acetate 5:1) gave compound **8^b** (463 mg, 0.529 mmol, 88%) as a white foam. Compound **8^b** was immediately used in the next reaction step. R_f = 0.54 (toluene/ethyl acetate 3:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.15–4.56 (m, 8H, CH_2 (Fmoc), 9-H (Fmoc), OC*H*HPh, 4-H, 5-H, 6-H, 6′-H), 4.60 (d, J_{gem} = 11.6 Hz, 1H, OC*H*HPh), 4.74 (d, J_{gem} = 11.5 Hz, 1H, OC*H*HPh), 5.77 (dd, $^3J_{3,2}$ = 3.3, $^3J_{3,4}$ = 10.7 Hz, 1H, 3-H), 5.85 (dd, $^3J_{2,1}$ = 2.7, $^3J_{2,3}$ = 10.7 Hz, 1H, 2-H), 6.71–8.00 (m, 24H, 23 Ph, 1-H), 8.51 (s, 1H, N*H*); M_w: calcd for $C_{45}H_{38}Cl_3NO_{11}$: 875.1.

Thexyldimethylsilyl 2,3-di-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranoside (38): Compound **37** (2.0 g, 4.04 mmol) was dissolved in a BH_3·THF solution (c = 1 mol L^{-1}). At 0 °C TMSOTf (0.18 mL, 1.0 mmol) was added dropwise. After 1 h the reaction mixture was stirred at RT for another 2.5 h. The solution was neutralized with NEt_3 (3 mL), methanol was added and after 15 min the solution was evaporated in vacuo and coevaporated three times with methanol (40 mL). Flash chromatography (toluene/ethyl acetate 8:1) gave compound **38** (1.46 g, 2.94 mmol, 73%) as colourless oil. R_f = 0.29 (toluene/ethyl acetate 3:1); $[\alpha]_D$ = −4.3° (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.13 (s, 3H, CH_3), 0.15 (s, 3H, CH_3), 0.82–0.89 (m, 12H, 4 CH_3), 1.57–1.63 (m, 1H, (CH$_3$)$_2$C*H*), 2.03 (s, 6H, 2 CH_3), 3.47–3.57 (m, 2H, 6-H, 6′-H), 3.74–3.80 (m, 1H, 5-H), 3.89 (d, $^3J_{4,3}$ = 3.2 Hz, 1H, 4-H), 4.51 (d, J_{gem} = 11.8 Hz, 1H, OC*H*HPh), 4.68 (d, $^3J_{1,2}$ = 7.6 Hz, 1H, 1-H), 4.78 (d, J_{gem} = 11.8 Hz, 1H, OC*H*HPh), 4.93 (dd, $^3J_{3,2}$ = 10.5, $^3J_{3,4}$ = 3.2 Hz, 1H, 3-H), 5.33 (dd, $^3J_{2,1}$ = 7.6, $^3J_{2,3}$ = 10.5 Hz, 1H, 2-H), 7.26–7.38 (m, 5H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 18.5, 19.9, 20.8, 24.8, 33.9, 61.6, 71.6, 73.5, 74.1, 74.8, 74.9, 77.2, 96.3, 128.2, 128.5, 128.54, 137.5, 170.5; MALDI MS (positive mode): m/z: calcd for $C_{25}H_{40}O_8Si$: 496.7; found: 519.2 [M+Na]$^+$, 535.2 [M+K]$^+$.

Thexyldimethylsilyl 2,3,6-tri-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranoside (39): Compound **38** (1.30 g, 2.61 mmol) was dissolved in a mixture of pyridine (15 mL) and Ac_2O (7 mL). After 12 h the solvent was evaporated in vacuo and coevaporated with toluene. Flash chromatography (toluene/ethyl acetate 8:1) gave compound **39** (1.39 g, 2.60 mmol, quant) as colourless oil. R_f = 0.57 (toluene/ethyl acetate 3:1); $[\alpha]_D$ = −1.2° (c = 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.02 (s, 3H, SiCH_3), 0.00 (s, 3H, SiCH_3), 0.67–0.71 (m, 12H, 4 CH_3), 1.39–1.50 (m, 1H, C*H*(CH$_3$)$_2$), 1.84 (s, 3H, COCH_3), 1.87 (s, 3H, COCH_3), 1.88 (s, 3H, COCH_3), 3.51–3.56 (m, 1H, 5-H), 3.74–3.75 (m, 1H, 4-H), 3.87 (dd, $^3J_{6,5}$ = 6.0, J_{gem} = 11.1 Hz, 1H, 6-H), 4.09 (dd, $^3J_{6',5}$ = 7.0, J_{gem} = 11.1 Hz, 1H, 6′-H), 4.39 (d, J_{gem} = 11.8 Hz, 1H, OC*H*HPh), 4.50 (d, $^3J_{1,2}$ = 7.6 Hz, 1H, 1-H), 4.60 (d, J_{gem} = 11.8 Hz, 1H, OC*H*HPh), 4.78 (dd, $^3J_{3,2}$ = 10.5, $^3J_{3,4}$ = 3.1 Hz, 1H, 3-H), 5.17 (dd, $^3J_{2,1}$ = 7.6, $^3J_{2,3}$ = 10.5, 1H, 2-H), 7.13–7.21 (m, 5H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ = −3.6, −2.0, 18.4, 19.8, 19.9, 20.6, 20.7, 24.7, 33.8, 62.5, 71.4, 72.1, 73.6, 73.8, 74.8, 96.1, 127.9, 128.2, 128.3, 137.4, 169.1, 170.3, 170.4; MALDI MS (positive mode): m/z: calcd for: 538.7; found: 561.4 [M+Na]$^+$, 577.3 [M+K]$^+$; elemental analysis calcd (%) for $C_{27}H_{42}O_9Si$: C 60.20, H 7.86; found: C 60.20, H 7.87.

2,3,6-Tri-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranose (40): HF·pyridine (3.28 mL, 22.3 mmol) was added at RT to a solution of compound **39** (1.20 g, 2.23 mmol) in dry THF (10 mL) and the reaction mixture was stirred overnight (12 h). The solution was diluted with ethyl acetate

(20 mL) and neutralized with a saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer extracted three times with ethyl acetate (30 mL) and the combined organic layers were concentrated in vacuo. Flash chromatography (toluene/ethyl acetate 4:1) gave compound **40** (828 mg, 2.09 mmol, 94%) as a white foam. Compound **40** was immediately used in the next reaction step. $R_f = 0.22$ (toluene/ethyl acetate 3:2); $[\alpha]_D = +65.9°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.01$ (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 3.57 (d, $^3J_{4,3} = 3.1$ Hz, $^1/_2$H, 4-H), 3.73–3.78 (m, $^1/_2$H, 5-H), 3.94 (d, $^3J_{4,3} = 3.1$ Hz, $^1/_2$H, 4-H), 4.03–4.31 (m, $2 \times {}^1/_2$H, $^1/_2$ 5-H, 6-H, 6′-H), 4.51–4.63 (m, $1 \times {}^1/_2$H, $^1/_2$ 3-H, OC*H*HPh), 4.73 (d, $J_{gem} = 11.4$ Hz, 1H, OC*H*HPh), 4.99 (dd, $^3J_{3,2} = 3.1$, $^3J_{3,4} = 10.5$ Hz, $^1/_2$H, 3-H), 5.20–5.51 (m, 2H, 1-H, 2-H), 7.27–7.39 (m, 5H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 20.7$, 20.78, 20.82, 62.4, 62.7, 67.9, 68.9, 70.2, 71.7, 72.5, 73.2, 73.7, 74.8, 75.1, 90.6, 96.0, 128.0, 128.2, 128.3, 128.4, 128.5, 137.2, 137.4, 170.3, 170.4, 170.5, 171.1; MALDI MS (positive mode): m/z: calcd for $C_{19}H_{24}O_9$: 396.4; 418.9 $[M+Na]^+$, 434.9 $[M+K]^+$.

***O*-(2,3,6-Tri-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranosyl) trichloroacetimidate (9^t)**: Trichloroacetonitrile (1.11 mL, 9.45 mmol) and a catalytic amount of DBU were added to a solution of compound **40** (750 mg, 1.89 mmol) in dry CH_2Cl_2 (3 mL). After stirring for 30 min at RT, the reaction mixture was neutralized with silica. Flash chromatography (toluene/ethyl acetate 6:1) gave compound **9^{t}α** (720 mg, 1.34 mmol, 70%) and **9^{t}β** (180 mg, 0.333 mmol, 18%) as colourless oil. Compound **9^t** was immediately used in the next reaction step. **9^{t}α**: $R_f = 0.53$ (toluene/ethyl acetate 3:1); $[\alpha]_D = +64.4°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 1.99 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 4.07–4.30 (m, 4H, 4-H, 5-H, 6-H, 6′-H), 4.56 (d, $J_{gem} = 11.5$ Hz, 1H, OC*H*HPh), 4.74 (d, $J_{gem} = 11.4$ Hz, 1H, OC*H*HPh), 5.35 (dd, $^3J_{3,2} = 10.8$, $^3J_{3,4} = 2.9$ Hz, 1H, 3-H), 5.55 (dd, $^3J_{2,1} = 3.6$, $^3J_{2,3} = 10.8$ Hz, 1H, 2-H), 6.59 (d, $^3J_{1,2} = 3.6$ Hz, 1H, 1-H), 7.27–7.37 (m, 5H, Ph), 8.62 (s, 1H, N*H*); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 20.5$, 20.7, 20.9, 62.3, 67.5, 70.5, 70.7, 74.2, 75.3, 93.9, 128.2, 128.6, 137.2, 161.0, 170.0, 170.3; M_w: calcd for $C_{21}H_{24}Cl_3NO_9$: 540.8; **9^{t}β**: $R_f = 0.27$ (toluene/ethyl acetate 3:1); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.01$ (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 3.90–3.96 (m, 1H, 5-H), 4.01 (dd, $^3J_{4,3} = 3.0$, $^3J_{4,5} =$ 1.4 Hz, 1H, 4-H), 4.15 (dd, $^3J_{6,5} = 6.7$, $J_{gem} = 11.2$ Hz, 1H, 6-H), 4.30 (dd, $^3J_{6',5} = 6.3$, $J_{gem} = 11.2$ Hz, 1H, 6′-H), 4.58 (d, $J_{gem} = 11.6$ Hz, 1H, OC*H*HPh), 4.77 (d, $J_{gem} = 11.5$ Hz, 1H, OC*H*HPh), 5.07 (dd, $^3J_{3,2} = 10.0$, $^3J_{3,4} = 3.1$ Hz, 1H, 3-H), 5.63 (dd, $^3J_{2,1} = 7.9$, $^3J_{2,3} = 10.0$ Hz, 1H, 2-H), 5.81 (d, $^3J_{1,2} = 7.9$ Hz, 1H, 1-H), 7.26–7.38 (m, 5H, Ph), 8.66 (s, 1H, N*H*); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 20.7$, 20.8, 63.0, 68.4, 73.15, 73.18, 73.21, 75.0, 96.1, 128.2, 128.4, 128.5, 161.2, 169.0, 170.29, 170.32; M_w: calcd for $C_{21}H_{24}Cl_3NO_9$: 540.8.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl 3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenylmethoxycarbonyl)-α-D-mannopyranoside (41P): Polymer bound acceptor **1P** was treated with donor **5^e** according to GP 1 at RT (0.25 equiv TMSOTf). Compound **41P** was obtained.

4-(Acetoxymethyl)benzyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (41): According to GP 5 product of compound **41P** was cleavedn from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. Flash chromatography (toluene/ethyl acetate 6:1) gave compound **41** (16 mg) as colourless oil (91% yield over three reaction steps, corresponding to an average yield of 97% per step). $R_f = 0.83$ (petroleum ether/ethyl acetate 1:1); $[\alpha]_D = +30.0°$ ($c = 0.5$ $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.10$ (s, 3H, $COCH_3$), 2.14 (s, 3H, $COCH_3$), 3.67–3.94 (m, 4H, 4-H, 5-H, 6-H, 6′-H), 4.02 (dd, $^3J_{3,2} = 3.2$, $^3J_{3,4} = 8.6$ Hz, 1H, 3-H), 4.44–4.55 (m, 4H, 4 OC*H*HPh), 4.67–4.72 (m, 3H, 3 OC*H*HPh), 4.85 (d, $J_{gem} = 10.7$ Hz, 1H, OC*H*HPh), 4.93 (d, $^3J_{1,2} = 1.7$ Hz, 1H, 1-H), 5.10 (s, 2H, CH_2OAc), 5.41 (dd, $^3J_{2,1} = 1.7$, $^3J_{2,3} = 3.2$ Hz, 1H, 2-H), 7.12–7.38 (m, 19H, Ph); MALDI MS (positive mode): m/z: calcd for $C_{39}H_{42}O_9$: 654.8; found: 677.5 $[M+Na]^+$, 693.4 $[M+K]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (41P-F): The Fmoc group of compound **41P** was removed according to GP 2. The polymer bound trisaccharide **41P-F** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-[3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenylmethoxycarbonyl)-α-D-mannopyranosyl]-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (42P): According to GP 1 the polymer bound acceptor **41P-F** was treated with donor **5^e** at 0°C (0.25 equiv TMSOTf). Compound **42P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benyl-α-D-mannopyranoside (42): According to GP 5 the product of compound **42P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. MPLC (toluene/ethyl acetate 5:1) gave compound **42** (15 mg) as colourless oil (82% yield over five reaction steps, corresponding to an average yield of 96% per step). $R_f = 0.57$ (toluene/ethyl acetate 4:1); $[\alpha]_D = +36.5°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 2.08$ (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 3.60–3.61 (m, 1H, 6-H), 3.68–3.90 (m, 7H, 4a-H, 4b-H, 5a-H, 5b-H, 3 6-H), 3.94 (dd, $J_{3,2} = 2.6$, $J_{3,4} = 9.2$ Hz, 1H, 3a-H), 4.03 (s, 1H, 2a-H), 4.34 (d, $J_{gem} = 11.9$ Hz, 1H, OC*H*HPh), 4.41 (d, $J_{gem} = 10.9$ Hz, 1H, OC*H*HPh), 4.44–4.46 (m, 2H, 2 OC*H*HPh), 4.53–4.55 (m, 2H, 2 OC*H*HPh), 4.61–4.68 (m, 6H, 6 OC*H*HPh), 4.83–4.85 (m, 2H, 2 OC*H*HPh), 4.97 (s, 1H, 1a-H), 5.07 (s, 3H, 1b-H, CH_2OAc), 5.54 (s, 1H, 2b-H), 7.14–7.34 (m, 34H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta =$ 21.0, 21.1, 66.0, 68.6 (C-2b), 68.9 (C-6b), 69.2 (C-6a), 71.7 (C-5b), 71.9, 72.0 (C-5a), 72.1, 73.3, 73.4, 74.3 (C-4b), 74.6 (C-4a), 74.9 (C-2a), 75.1, 75.2, 78.1 (C-3b), 79.6 (C-3a), 98.1 (C-1a), 99.6 (C-1b), 127.41, 127.46, 127.49, 127.52, 127.58, 127.64, 127.75, 127.77, 127.98, 128.05, 128.14, 128.29, 128.36, 135.4, 137.4, 138.0, 138.3, 138.39, 138.43, 170.1, 170.8, $^1J_{1a\text{-}C,1a\text{-}H} = 171.2$, $^1J_{1b\text{-}C,1b\text{-}H} = 173.6$ Hz; MALDI MS (positive mode): m/z: 1109.7 $[M+Na]^+$, 1125.8 $[M+K]^+$; FAB-MS (positive mode): m/z: calcd for $C_{66}H_{17}O_{14}$: 1087.3; found: 1109.0 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (42P-F): The Fmoc group of compound **42P** was removed according to GP 2. The polymer bound disaccharide **42P-F** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-[3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenylmethoxycarbonyl)-α-D-mannopyranosyl]-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (43P): According to GP 1 the polymer bound acceptor **42P-F** was treated with donor **5^e** at RT (0.25 equiv TMSOTf). Compound **43P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (43): According to GP 5 the product of compound **43P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. Flash chromatography (toluene/ethyl acetate 12:1) gave compound **43** (16 mg) as colourless oil (65% yield over seven reaction steps, corresponding to an average yield of 94% per step). $R_f = 0.40$ (toluene/ethyl acetate 8:1); $[\alpha]_D = +28.5°$ ($c =$ 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 2.07$ (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 3.51–3.53 (m, 1H, 6-H), 3.63–3.72 (m, 4H, 4 6-H), 3.76–3.81 (m, 4H, 4a-H, 4b-H, 5-H, 6-H), 3.88–3.91 (m, 5H, 3a-H, 3b-H, 4c-H, 2 5-H), 3.98–4.01 (m, 2H, 2a-H, 3c-H), 4.10 (brs, 1H, 2b-H), 4.29 (d, $J_{gem} = 12.0$ Hz, 1H, OC*H*HPh), 4.30 (d, $J_{gem} = 12.2$ Hz, 1H, OC*H*HPh), 4.40–4.68 (m, 15H, 15 OC*H*HPh), 4.80–4.84 (m, 3H, 3 OC*H*HPh), 5.02 (brs, 1H, 1a-H), 5.05 (brs, 3H, 1c-H, CH_2OAc), 5.18 (brs, 1H, 1b-H), 5.53 (brs, 1H, 2c-H); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta = 21.0$, 21.2, 66.0, 68.66, 68.7 (C-2c), 68.7–69.4 (3 C-6), 71.9–72.0 (3 C-5), 72.1, 73.2, 73.3, 74.2, 74.7 (C-4a, C-4b), 74.8 (C-2b), 74.9 (C-2a), 75.1, 75.2, 78.1 (C-3c), 79.2 (C-3a, C-3b, C-4c), 98.3 (C-1a), 99.4 (C-1c), 100.7 (C-1b), 127.45, 127.50, 127.57, 127.63, 127.71, 127.74, 127.80, 127.97, 128.15, 128.21, 128.27, 128.30, 128.38, 137.5, 138.14, 138.29, 138.34, 138.40, 138.52, 170.1, 170.8, $^1J_{1a\text{-}C,1a\text{-}H} = 172.7$, $^1J_{1b\text{-}C,1b\text{-}H} = 173.6$, $^1J_{1c\text{-}C,1c\text{-}H} = 172.7$ Hz; MALDI MS (positive mode): m/z: calcd for $C_{93}H_{98}O_{19}$: 1519.8; found: 1541.7 $[M+Na]^+$, 1557.7 $[M+K]^+$; FAB-MS (positive mode): m/z: 1541.8 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl 2-*O*-acetyl-4-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-α-D-mannopyranoside (44P): According to GP 1 the polymer bound spacer

1P was treated with donor **7**[b] at 0°C (0.25 equiv TMSOTf). Compound **44P** was obtained.

4-(Acetoxymethyl)benzyl 2,3,6-tri-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (44): According to GP 5 the product of compound **44P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. Flash chromatography (toluene/ethyl acetate 8:1) gave compound **44** (13 mg) as colourless oil (90% over three steps, corresponding to an average yield of 96% per step). R_f=0.44 (toluene/ethyl acetate 3:2); $[\alpha]_D$=+62.1° (c=1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.98 (s, 3H, COCH_3), 2.11 (s, 6H, 2 COCH_3), 2.13 (s, 3H, COCH_3), 3.82 (t, 1H, 4-H), 3.96 (m, $^3J_{5,4}$=9.9, $^3J_{5,6}$=2.7, $^3J_{5,6'}$=4.4 Hz, 1H, 5-H), 4.30–4.33 (m, 2H, 6-H, 6′-H), 4.53 (d, J_{gem}=12.0 Hz, 1H, OCHHPh), 4.57 (d, J_{gem}=11.1 Hz, 1H, OCHHPh), 4.68 (d, J_{gem}=11.1 Hz, 1H, OCHHPh), 4.70 (d, J_{gem}=12.0 Hz, 1H, OCHHPh), 4.83 (d, $^3J_{1,2}$=1.8 Hz, 1H, 1-H), 5.10 (s, 2H, CH_2OAc), 5.29 (dd, $^3J_{2,1}$=1.8, $^3J_{2,3}$=3.5 Hz, 1H, 2-H), 5.39 (dd, $^3J_{3,2}$=3.5, $^3J_{3,4}$=9.4 Hz, 1H, 3-H), 7.24–7.38 (m, 9H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ=20.9, 63.1, 65.9, 69.1, 69.8, 70.0, 71.9, 73.1, 74.9, 77.2, 96.6, 127.8, 128.0, 128.3, 128.4, 128.5, 135.9, 136.5, 137.6, 169.7, 169.9, 170.6; MALDI MS (positive mode): m/z: calcd for $C_{29}H_{34}O_{11}$: 558.6; found: 582.0 $[M+Na]^+$, 598.0 $[M+K]^+$; FAB-MS (positive mode): m/z: 580.5 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl 2,3-di-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (44P-F): The Fmoc group of compound **44P** was removed according to GP 2. The polymer bound monosaccharide **44P-F** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2-*O*-acetyl-4-*O*-benzyl-3-*O*-phenoxyacetyl-α-D-mannopyranoside (45P): According to GP 1 the polymer bound acceptor **44P-F** was treated with donor **6**[t] at 0°C (0.25 equiv TMSOTf). Compound **45P** was obtained.

4-(Acetoxymethyl)benzyl O-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2,3-di-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (45): According to GP 5 the product of compound **45P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. Flash chromatography (petroleum ether/ethyl acetate 2:1) gave compound **45** (14 mg) as colourless oil (84% yield over five reaction steps, corresponding to an average yield of 92% per step). R_f=0.33 (toluene/ethyl acetate 3:1); $[\alpha]_D$=+49.6° (c=0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ=1.98 (s, 3H, COCH_3), 2.09 (s, 3H, COCH_3), 2.11 (s, 3H, COCH_3), 2.17 (s, 3H, COCH_3), 3.64 (dd, $^3J_{6b,5b}$=1.3, J_{gem}=10.6 Hz, 1H, 6b-H), 3.71–3.75 (m, 2H, 6a-H, 6b′-H), 3.83–3.89 (m, 4H, 4a-H, 5a-H, 5b-H, 6a′-H), 3.92 (t, 1H, 4b-H), 3.99 (dd, $^3J_{3b,2b}$=3.0, $^3J_{3b,4b}$=9.3 Hz, 1H, 3b-H), 4.44–4.53 (m, 5H, 5 OCHHPh), 4.62–4.64 (m, 2H, 2 OCHHPh), 4.68 (d, J_{gem}=12.1 Hz, 1H, OCHHPh), 4.72 (d, J_{gem}=11.4 Hz, 1H, OCHHPh), 4.74 (d, 1H, 1a-H), 4.88 (d, J_{gem}=10.6 Hz, 1H, OCHHPh), 5.02 (d, 1H, 1b-H), 5.05 (s, 2H, CH_2OAc), 5.26 (dd, $^3J_{2a,1a}$=1.6, $^3J_{2a,3a}$=3.3 Hz, 1H, 2a-H), 5.39 (dd, $^3J_{3a,2a}$=3.3, $^3J_{3a,4a}$=9.3 Hz, 1H, 3a-H), 5.49 (dd, $^3J_{2b,1b}$=1.9, $^3J_{2b,3b}$=3.0 Hz, 1H, 2b-H), 7.23–7.31 (m, 24H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): δ=20.79, 20.85, 20.95, 21.08, 65.4 (C-6a), 65.9, 68.2 (C-2b), 68.4, 68.6 (C-6b), 70.0 (C-2a), 71.1 (C-5a), 71.4 (C-5b), 71.9 (C-3a), 73.0 (C-4a), 73.3, 74.2 (C-4b), 74.7, 75.2, 77.6 (C-3b), 95.9 (C-1a), 97.8 (C-1b), 127.33, 127.55, 127.59, 127.72, 127.76, 127.90, 128.06, 128.24, 128.35, 135.57, 136.4, 137.66, 137.74, 138.1, 138.3, 169.7, 170.0, 170.3, 170.8, $^1J_{1a\text{-}C,1a\text{-}H}$=172.2, $^1J_{1b\text{-}C,1b\text{-}H}$=172.2 Hz; MALDI MS (positive mode): m/z: calcd for $C_{56}H_{62}O_{16}$: 991.1; found: 1013.0 $[M+Na]^+$, 1029.0 $[M+K]^+$; FAB-MS (positive mode): m/z: 1013.0 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (45P-PA): The PA group of compound **45P** was removed according to GP 3. The polymer bound disaccharide **45P-PA** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)]-2-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (46P): According to GP 1 the polymer bound acceptor **45P-PA** was treated with donor **6**[t] at 0°C (0.25 equiv TMSOTf). Compound **46P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)]-2-*O*-acetyl-4-*O*-benzyl-α-D-mannopyranoside (46): According to GP 5 the product of compound **46P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. MPLC (petroleum ether/ethyl acetate 2:1) gave compound **46** (15 mg) as colourless oil (64% yield over seven reaction steps, corresponding to an average yield of 94% per step). R_f=0.49 (toluene/ethyl acetate 3:1); $[\alpha]_D$=+40.6° (c=0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ=2.05 (s, 3H, COCH_3), 2.09 (s, 6H, 2 COCH_3), 2.15 (s, 3H, COCH_3), 3.62–3.82 (m, 10H, 4a-H, 5a-H, 5b-H, 5c-H, 6a-H, 6a′-H, 6b-H, 6b′-H, 6c-H, 6c′-H), 3.90–3.98 (m, 4H, 3b-H, 3c-H, 4b-H, 4c-H), 4.24 (dd, $^3J_{3a,2a}$=3.2, $^3J_{3a,4a}$=9.8 Hz, 1H, 3a-H), 4.40–4.49 (m, 7H, 7 OCHHPh), 4.53 (d, J_{gem}=11.3 Hz, 1H, OCHHPh), 4.57–4.61 (m, 2H, 2 OCHHPh), 4.67 (d, J_{gem}=12.1 Hz, 1H, OCHHPh), 4.70 (d, J_{gem}=12.1 Hz, 1H, OCHHPh), 4.71 (d, J_{gem}=11.2 Hz, 1H, OCHHPh), 4.75 (d, J_{gem}=10.9 Hz, 1H, OCHHPh), 4.80 (s, 1H, 1a-H), 4.83 (d, J_{gem}=10.9 Hz, 1H, OCHHPh), 4.86 (d, J_{gem}=10.6 Hz, 1H, OCHHPh), 4.99 (s, 1H, 1b-H), 5.05 (s, 2H, OCH_2OAc), 5.15 (s, 1H, 1c-H), 5.17–5.18 (m, 1H, 2a-H), 5.43–5.45 (m, 1H, 2c-H), 5.46–5.47 (m, 1H, 2b-H), 7.10–7.33 (m, 39H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): δ=21.0, 21.1, 65.4 (C-6), 66.0 (CH_2OAc), 68.1 (C-2b), 68.3 (C-6), 68.4, 68.6 (C-6), 68.8 (C-2c), 71.2, 71.4, 71.6, 71.7 (C-2a), 72.4, 73.3, 73.4, 74.2, 75.0, 75.3, 77.75, 77.84, 77.9, 95.9 (C-1a), 97.9 (C-1b), 100.0 (C-1c), 127.48, 127.52, 127.64, 127.73, 127.80, 127.91, 127.93, 128.06, 128.12, 128.24, 128.29, 128.32, 128.37, 128.40, 128.48, 136.72, 137.63, 137.7, 138.4, 170.2, 170.3, $^1J_{1a\text{-}C,1a\text{-}H}$=174.1, $^1J_{1b\text{-}C,1b\text{-}H}$=173.5, $^1J_{1b\text{-}C,1b\text{-}H}$=172.4 Hz; MALDI MS (positive mode): m/z: calcd for $C_{83}H_{90}O_{21}$: 1423.6; found: 1446.1 $[M+Na]^+$, 1462.5 $[M+K]^+$; FAB-MS (positive mode): m/z: 1446.0 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-[3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranosyl]-(→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (47P): According to GP 1 the polymer bound acceptor **41P-F** was treated with donor **2**[e,13] at −15°C (0.30 equiv TMSOTf). Compound **47P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (47): According to GP 5 the product of compound **47P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. MPLC (toluene/ethyl acetate 7:2) gave compound **47** (20 mg) as colourless oil (75% yield over five reaction steps, corresponding to an average yield of 94% per step). R_f=0.5 (toluene/ethyl acetate 3:1); $[\alpha]_D$=+19.5° (c=1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ=1.73 (s, 6H, 2 CH_3), 1.94 (s, 3H, COCH_3), 2.10 (s, 3H, COCH_3), 3.31 (dd, $^3J_{6,5}$=7.0, J_{gem}=10.7 Hz, 1H, 6a-H), 3.49–3.63 (m, 4H, 4a-H, 6′a-H, 6b-H, 6′b-H), 3.68–3.73 (m, 2H, 5a-H, 5b-H), 3.84 (dd, $^3J_{3,2}$=2.9, $^3J_{3,4}$=8.9 Hz, 1H, 3a-H), 4.11 (brs, 1H, 2a-H), 4.18 (dd, $^3J_{2,1}$=8.6, $^3J_{2,3}$=10.6 Hz, 1H, 2b-H), 4.28–4.44 (m, 8H, 3b-H, 7 OCHHPh), 4.47 (d, 1H, J_{gem}=11.5 Hz, OCHHPh), 4.57 (brs, 1H, 1a-H), 4.60 (d, J_{gem}=11.7 Hz, 1H, OCHHPh), 4.62 (d, J_{gem}=12.0 Hz, 1H, COHHPh), 4.77 (d, J_{gem}=11.5 Hz, 1H, COHHPh), 4.81 (d, J_{gem}=10.8 Hz, 1H, COHHPh), 5.06–5.09 (m, 4H, 1b-H, 4b-H, CH_2OAc), 7.11–7.30 (m, 29H, 29 Ph); ^{13}C NMR (151 MHz, $CDCl_3$): δ=20.9, 21.0, 55.0, 55.5 (C-2b), 66.0, 68.7, 69.1, 70.0 (C-6a), 70.2 (C-6b), 70.8, 71.6 (C-5a), 72.3, 72.8, 73.4, 73.5 (C-4b), 73.6 (C-5b), 73.7 (C-2a), 74.5 (C-4a), 75.0, 77.2 (C-3b), 77.7 (C-3a), 96.8 (C-1a), 97.1 (C-1b), 127.45, 127.51, 127.70, 127.84, 127.95, 128.11, 128.21, 128.24, 128.27, 128.31, 128.34, 128.90, 135.4, 136.9, 137.2, 137.7, 138.1, 138.2, 138.3; MALDI MS (positive mode): m/z: calcd for $C_{65}H_{69}NO_{15}$: 1104.2; found: 1125.9 $[M+Na]^+$, 1141.9 $[M+K]^+$; FAB-MS (positive mode): m/z: 1126.1 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (47P-F): The Fmoc group of com-

pound **47P** was removed according to GP 2. The polymer bound disaccharide **47P-F** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-[2-*O*-benzoyl-4-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-β-D-galactopyranosyl]-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (48P): According to GP 1 the polymer bound acceptor **47P-F** was treated with donor **8**[b] at −20 °C (0.35 equiv TMSOTf). Compound **48P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(2,3,6-tri-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (48): According to GP 5 the product of compound **48P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. Flash chromatography (toluene/ethyl acetate 10:1 → 4:1) gave compound **48** (15 mg) as colourless oil (61% yield over seven reaction steps, corresponding to an average yield of 93% per step). R_f = 0.43 (toluene/acetone 6:1); $[\alpha]_D$ = +15.9° (c = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.69 (s, 6H, 2 CH_3), 1.97–1.98 (m, 6H, 2 COCH_3), 2.02 (s, 3H, COCH_3), 2.10 (s, 3H, COCH_3), 3.29–3.32 (dd, $^3J_{6a,5a}$ = 7.3, J_{gem} = 11.1 Hz, 1H, 6a-H), 3.49–3.53 (m, 3H, 4a-H, 5b-H, 5c-H), 3.57 (d, 1H, 6a′-H), 3.69–3.73 (m, 3H, 5a-H, 6b-H, 6b′-H), 3.82–3.85 (m, 2H, 3a-H, 4c-H), 3.91 (dd, $^3J_{6c,5c}$ = 6.8, J_{gem} = 12.8 Hz, 1H, 6c-H), 3.97 (t, 1H, 4b-H), 4.05–4.12 (m, 4H, 2a-H, 2b-H, 3b-H, 6c′-H), 4.32 (d, J_{gem} = 11.7 Hz, 1H, OCHHPh), 4.37 (d, J_{gem} = 10.8 Hz, 1H, OCHHPh), 4.38 (d, J_{gem} = 12.0 Hz, 1H, OCHHPh), 4.42–4.44 (m, 3H, 3 OCHHPh), 4.45 (d, J_{gem} = 11.7 Hz, 1H, OCHHPh), 4.48 (d, J_{gem} = 11.8 Hz, 1H, OCHHPh), 4.59–4.61 (m, 3H, 1a-H, 1c-H, OCHHPh), 4.64 (d, J_{gem} = 11.9 Hz, 1H, OCHHPh), 4.70 (d, J_{gem} = 11.7 Hz, 1H, OCHHPh), 4.77–4.83 (m, 4H, 3c-H, 3 OCHHPh), 5.05 (d, $^3J_{1b,2b}$ = 8.4 Hz, 1H, 1b-H), 5.08 (br s, 2H, CH_2OAc), 5.33 (dd, $^3J_{2c,1c}$ = 8.1, $^3J_{2c,3c}$ = 10.2 Hz, 1H, 2c-H), 7.11–7.31 (m, 34H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 20.8, 21.0, 55.3 (C-2b), 62.0 (C-6c), 66.0, 68.7 (C-6b), 70.0 (C-6a), 70.3 (C-2c), 70.6, 71.6 (C-5a), 72.0 (C-5c), 72.9 (C-4c), 73.6 (C-2a), 74.0, 74.3 (C-3c), 74.83 (C-4a), 74.88 (C-5b), 77.4 (C-3b), 78.0 (C-3a, C-4b), 96.9 (C-1a), 97.1 (C-1b), 100.5 (C-1c), 126.9, 127.41, 127.47, 127.74, 127.85, 127.98, 128.07, 128.13, 128.19, 128.26, 128.30, 128.33, 128.38, 128.46, 136.7, 137.3, 138.3, 138.4, 139.0, 169.2, 170.4, $^1J_{1a\text{-}C,1a\text{-}H}$ = 169.9, $^1J_{1b\text{-}C,1b\text{-}H}$ = 161.6, $^1J_{1c\text{-}C,1c\text{-}H}$ = 160.7 Hz; MALDI MS (positive mode): m/z: calcd for $C_{82}H_{89}NO_{22}$: 1440.6; found: 1462.8 $[M+Na]^+$, 1478.5 $[M+K]^+$; FAB-MS (positive mode): m/z: 1463.2 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl 3,6-di-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (49P): According to GP 1 the polymer bound spacer **1P** was treated with donor **2**[e] at −35 °C (0.25 equiv TMSOTf). Compound **49P** was obtained.

4-(Acetoxymethyl)benzyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (49): According to GP 5 the product of compound **49P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. Flash chromatography (petroleum ether/ethyl acetate 2:1) gave compound **49** (12 mg) as colourless oil (86% over three reaction steps, corresponding to an average yield of 95% per step). R_f = 0.28 (petroleum ether/ethyl acetate 2:1); $[\alpha]_D$ = +5.2° (c = 0.5, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.77 (br s, 6H, 2 CH_3), 1.94 (s, 3H, COCH_3), 2.09 (s, 3H, COCH_3), 3.59–3.61 (m, 2H, 6-H, 6′-H), 3.65–3.73 (m, 1H, 5-H), 4.07 (dd, $^3J_{2,1}$ = 8.5, $^3J_{2,3}$ = 8.4 Hz, 1H, 2-H), 4.27 (t, 1H, 3-H), 4.29 (d, J_{gem} = 12.1 Hz, 1H, OCHHPh), 4.48 (d, J_{gem} = 12.4 Hz, 1H, OCHHPh), 4.55 (s, 2H, 2 OCHHPh), 4.60 (d, J_{gem} = 12.1 Hz, 1H, OCHHPh), 4.82 (d, J_{gem} = 12.4 Hz, 1H, OCHHPh), 5.0 (d, $^3J_{1,2}$ = 8.5 Hz, 1H, 1-H), 5.05–5.12 (m, 3H, 4-H, CH_2OAc), 7.06–7.36 (m, 14H, Ph); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 8.5, 20.82, 20.85, 55.2, 65.9, 69.7, 70.3, 72.3, 73.5, 73.6, 73.7, 77.3, 97.5, 127.4, 127.7, 127.8, 128.1, 128.2, 128.4, 135.3, 136.9, 137.4, 137.9, 138.1, 169.6, 171.0; MALDI MS (positive mode): m/z: calcd for $C_{38}H_{41}NO_{10}$: 671.7; found: 694.7 $[M+Na]^+$, 710.7 $[M+K]^+$; FAB-MS (positive mode): m/z: 694 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl 3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (49P-F): The Fmoc group of compound **49P** was removed according GP 2. Compound **49P-F** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-[2,4-di-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (50P): The polymer bound acceptor **49P-F** was treated with donor **2**[e] according GP 1 at −30 °C (0.35 equiv TMSOTf). Compound **50P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (50): According to GP 5 the product of compound **50P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. Flash chromatography (toluene/ethyl acetate 8:1) gave compound **50** (12 mg) as colourless oil (65% yield over five reaction steps, corresponding to an average yield of 92% per step). R_f = 0.46 (toluene/ethyl acetate 3:1); $[\alpha]_D$ = +9.3° (c = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.62–1.90 (m, 12H, 4 CH_3), 1.91 (s, 3H, COCH_3), 2.07 (s, 3H, COCH_3), 3.33–3.35 (m, 1H, 5a-H), 3.38–3.43 (m, 2H, 6a-H, 6b-H), 3.48–3.57 (m, 3H, 5b-H, 6a′-H, 6b′-H), 3.94–3.96 (m, 1H, 2a-H), 4.00–4.04 (m, 2H, 2b-H, 3a-H), 4.07 (t, 1H, 4a-H), 4.27–4.31 (m, 2H, 3b-H, OCHHPh), 4.39–4.62 (m, 7H, 7 OCHHPh), 4.71 (d, J_{gem} = 12.5 Hz, 1H, OCHHPh), 4.82 (d, J_{gem} = 12.6 Hz, 1H, OCHHPh), 4.86 (d, $J_{1,2}$ = 8.5 Hz, 1H, 1a-H), 5.02 (s, 2H, CH_2OAc), 5.08 (d, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.3 Hz, 4b-H), 5.14 (d, $J_{1,2}$ = 8.4 Hz, 1H, 1b-H), 7.08–7.35 (m, 24H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 20.9, 21.0, 55.4 (C-2a), 54.7, 55.9 (C-2b), 66.0, 68.0 (C-6a), 69.3 (C-6b), 69.5, 70.0, 71.9 (C-4b), 72.4, 72.8, 73.3 (C-5b), 73.5, 73.66, 73.78, 74.3, 74.6 (C-5a), 76.0 (C-4a), 76.8, 77.0 (C-3a), 77.2 (C-3b), 77.3, 97.1 (C-1b), 97.3 (C-1a), 126.9, 127.32, 127.40, 127.44, 127.71, 127.74, 127.86, 128.0, 128.13, 128.22, 128.27, 128.29, 128.32, 135.13, 136.6, 137.6, 138.2, 138.3, 139.0, 169.6, 170.8, 171.3; FAB-MS (positive mode): m/z: calcd for $C_{64}H_{68}N_2O_{16}$: 1121.2; found: 1143.0 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-[2,4-di-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-β-D-mannopyranosyl]-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (51P): The polymer bound acceptor **49P-F** was treated with donor **4**[b] according to GP 1 at −25 °C (0.3 equiv TMSOTf). Compound **51P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-β-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (51): According to GP 5 the product of compound **51P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. MPLC (toluene/ethyl acetate 3:1) gave compound **51** (15 mg) as colourless oil (63% yield over five reaction steps, corresponding to an average yield of 92% per step). R_f = 0.35 (toluene/ethyl acetate 3:1); $[\alpha]_D$ = +2.2° (c = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.69–1.84 (m, 15H, 4 CH_3, COCH_3), 1.93 (s, 3H, COCH_3), 2.07 (s, 3H, COCH_3), 3.16 (d, 1H, 5b-H), 3.32–3.35 (m, 2H, 5a-H, 5c-H), 3.40 (dd, J_{gem} = 10.9, $^3J_{6a,5a}$ = 3.7 Hz, 1H, 6a-H), 3.46 (dd, J_{gem} = 11.2, $^3J_{6b,5b}$ = 2.5 Hz, 1H, 6b-H), 3.57 (d, 1H, 6a′-H), 3.63 (d, 1H, 6b′-H), 3.84 (t, 1H, 4c-H), 3.90 (br s, 1H, 2c-H), 3.91–4.10 (m, 6H, 2b-H, 3a-H, 4b-H, 3b-H, 4a-H, 2a-H), 4.20–4.21 (m, 2H, 6c-H, 6c′-H), 4.35 (d, J_{gem} = 12.8 Hz, OCHHPh), 4.39–4.55 (m, 7H, 7 OCHHPh), 4.62 (d, J_{gem} = 10.8 Hz, OCHHPh), 4.63 (d, J_{gem} = 12.0 Hz, OCHHPh), 4.67 (s, 1H, 1c-H), 4.72 (d, J_{gem} = 12.5 Hz, OCHHPh), 4.75 (dd, $^3J_{3c,2c}$ = 3.0, $^3J_{3c,4c}$ = 9.9 Hz, 1H, 3c-H), 4.84–4.87 (m, 3H, 1a-H, 2 OCHHPh), 4.95 (d, J_{gem} = 12.8 Hz, OCHHPh), 5.02 (br s, 2H, CH_2OAc), 5.07 (d, $^3J_{1,2}$ = 8.4 Hz, 1H, 1b-H), 7.00–7.34 (m, 34H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 20.6, 21.0, 38.0, 55.4 (C-2a), 56.3 (C-2b), 63.1 (C-6c), 66.0, 67.9 (C-6b), 68.2 (C-6a), 70.0, 72.8, 73.1 (C-4c, C-5c), 73.2, 74.4, 74.6 (C-5a, C-5b), 74.8, 75.7 (C-4a), 75.9 (C-2c), 76.0 (C-3c), 77.2 (C-3a), 77.8 (C-3b), 79.0 (C-4b), 97.1 (C-1b), 97.3 (C-1a), 100.9 (C-1c), 126.8, 127.27, 127.36, 127.61, 127.69,

127.75, 127.84, 127.97, 128.12, 128.20, 128.43, 128.50, 135.1, 136.6, 137.6, 137.8, 138.44, 138.51, 139.6, 170.1, 170.8, 171.3, $^1J_{1a\text{-}C,1a\text{-}H}$ = 165.4, $^1J_{1b\text{-}C,1b\text{-}H}$ = 168.3, $^1J_{1c\text{-}C,1c\text{-}H}$ = 158.6 Hz; MALDI MS (positive mode): *m/z*: calcd for $C_{86}H_{92}N_2O_{22}$: 1505.7; found: 1528.0 $[M+Na]^+$, 1543.8 $[M+K]^+$; FAB-MS (positive mode): *m/z*: 1528 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(2,4-di-*O*-benzyl-3-*O*-phenoxyacetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (51 P-F): The Fmoc group of compound **51 P** was removed according to GP 2. The polymer bound trisaccharide **51 P-F** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzyl-3-*O*-phenoxyacetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (52 P): According to GP 1 the polymer bound acceptor **51 P-F** was treated with donor **6^t** at 0 °C (0.25 equiv TMSOTf). Compound **52 P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(3-*O*-acetyl-2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (52): According to GP 5 the product of compound **52-P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo and coevaporated three times with toluene. MPLC (toluene/ethyl acetate 3:1) gave compound **52** (15 mg) as colourless oil (50 % over five steps, corresponding to an average yield of 92 % per step). R_f = 0.42 (toluene/ethyl acetate 3:1); $[\alpha]_D$ = +21° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.66–1.88 (m, 12 H, 4 CH_3), 1.93 (s, 3 H, $COCH_3$), 1.99 (s, 3 H, $COCH_3$), 2.14 (s, 3 H, $COCH_3$), 3.20 (d, 1 H, 5b-H), 3.31 (d, 1 H, 5c-H), 3.36–3.38 (m, 1 H, 5a-H), 3.41–3.44 (m, 1 H, 6a-H), 3.53–3.60 (m, 3 H, 6a′-H, 6b-H, 6d-H), 3.68–3.77 (m, 4 H, 5d-H, 6b′-H, 6c-H, 6d′-H), 3.86–4.09 (m, 11 H, 2a-H, 2b-H, 2c-H, 3a-H, 3b-H, 3d-H, 4a-H, 4b-H, 4c-H, 4d-H, 6c′-H), 4.32 (d, J_{gem} = 11.2 Hz, 1 H, OC*H*HPh), 4.42–4.64 (m, 13 H, 13 OC*H*HPh), 3.72–5.01 (m, 10 H, 1a-H, 1c-H, 1d-H, 3c-H, 6 OC*H*HPh), 5.09 (s, 2 H, CH_2OAc), 5.11 (d, $^3J_{1b,2b}$ = 8.4 Hz, 1 H, 1b-H), 5.43 (br s, 1 H, 2d-H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 20.8, 21.0, 55.4 (C-2a), 56.3 (C-2b), 66.0, 66.5 (C-6c), 67.9 (C-6b), 68.1 (C-2d), 68.2 (C-6a), 68.6 (C-6d), 70.0, 71.2, 71.7 (C-5d), 72.8 (C-3a), 73.2, 73.3, 74.0 (C-4d), 74.4 (C-5c), 74.6 (C-5a, C-5b), 75.0, 75.6 (C-4a), 75.9 (C-2c), 76.2 (C-3c), 77.0 (C-4c), 77.2 (C-3b), 77.7 (C-3d), 79.6 (C-4b), 97.0 (C-1b), 97.3 (C-1a), 98.3 (C-1d), 101.4 (C-1c), 127.1, 127.28, 127.47, 127.59, 127.70, 127.75, 127.87, 127.94, 128.03, 128.14, 128.20, 128.22, 128.30, 128.38, 128.48, 136.55, 137.9, 139.1, 169.8, 170.2, 171.3, $^1J_{1a\text{-}C,1a\text{-}H}$ = 167.3, $^1J_{1b\text{-}c,1b\text{-}H}$ = 164.9, $^1J_{1c\text{-}C,1c\text{-}H}$ = 173.1, $^1J_{1d\text{-}C,1d\text{-}H}$ = 156.7 Hz; MALDI MS (positive mode): *m/z*: calcd for $C_{113}H_{120}N_2O_{27}$: 1938.2; found: 1959.6 $[M+Na]^+$, 1975.6 $[M+K]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (52 P-PA): According to GP 3 the PA group of compound **52 P** was removed. Compound **52 P-PA** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)]-(2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (53 P): According to GP 1 the polymer bound acceptor **52 P-PA** was treated with donor **6^t** at 0 °C (0.25 equiv TMSOTf). Compound **53 P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)]-(2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (53): According to GP 5 the product of compound **53 P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo, coevaporated three times with toluene and precleaned by flash chromatography (petroleum ether/ethyl acetate 2:1). MPLC (toluene/ethyl acetate 3:1) gave compound **53** (13 mg) as colourless oil (39 % yield over nine reaction steps, corresponding to an average yield of 90 % per step). R_f = 0.55 (toluene/acetone 5:1); $[\alpha]_D$ = +28.3° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.63–1.80 (m, 12 H, 4 CH_3), 1.84 (s, 3 H, $COCH_3$), 2.06 (s, 3 H, $COCH_3$), 2.09 (s, 3 H, $COCH_3$), 3.07–3.15 (m, 2 H, 5b-H, 5c-H), 3.27–3.38 (m, 3 H, 5a-H, 6a-H, 6b-H), 3.48–3.68 (m, 9 H, 3c-H, 5e-H, 6a′-H, 6b′-H, 6c-H, 6d-H, 6d′-H, 6e-H, 6e′-H), 3.77–4.06 (m, 14 H, 2a-H, 2b-H, 2c-H, 3a-H, 3b-H, 3d-H, 3e-H, 4a-H, 4b-H, 4c-H, 4d-H, 4e-H, 5d-H, 6c′-H), 4.33–4.47 (m, 12 H, 12 OC*H*HPh), 4.52–4.61 (m, 6 H, 1c-H, 5 OC*H*HPh), 4.65–5.01 (m, 14 H, 1a-H, 1b-H, 1e-H, 11 OC*H*HPh), 5.13 (br s, 1 H, 1d-H), 5.32 (br s, 1 H, 2e-H), 5.48 (br s, 1 H, 2d-H), 6.99–7.32 (m, 64 H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 56.5 (C-2a), 57.5 (C-2b), 67.7 (C-6c), 68.8 (C-6b), 69.2 (C-2e), 69.3 (C-6a), 69.8 (C-2d, C-6e), 70.1 (C-6d), 72.9 (C-5e), 73.5 (C-3a), 73.6 (C-5d), 75.3 (C-3e, C-4e), 75.7 (C-4c, C-5c), 75.8 (C-5a, C-5b), 76.9 (C-4a), 78.6 (C-3d), 79.0 (C-4d), 79.1 (C-2c), 79.3 (C-3b), 79.4 (C-4b), 82.4 (C-3c), 98.2 (C-1b), 98.5 (C-1a), 99.6 (C-1e), 100.8 (C-1d), 103.2 (C-1c), $^1J_{1a\text{-}C,1a\text{-}H}$ = 164.6, $^1J_{1b\text{-}C,1b\text{-}H}$ = 168.1, $^1J_{1c\text{-}C,1c\text{-}H}$ = 158.2, $^1J_{1d\text{-}C,1d\text{-}H}$ = 174.4, $^1J_{1e\text{-}C,1e\text{-}H}$ = 173.4 Hz; MALDI MS (positive mode): *m/z*: calcd for $C_{140}H_{148}N_2O_{32}$: 2370.7; found: 2392.0 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-[3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenylmethoxycarbonyl)-α-D-mannopyranosyl]-(1→2)-(2,4-di-*O*-benzyl-3-*O*-phenoxy-acetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (54 P): According to GP 1 the polymer bound acceptor **51 P-F** was treated with donor **5^e** at 0 °C (0.25 equiv TMSOTf). Compound **54 P** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzyl-3-*O*-phenoxyacetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (54 P-F): The Fmoc group of compound **54 P** was removed according to GP 2. The polymer bound tetrasaccharide **54 P-F** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzyl-3-*O*-phenoxyacetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (55 P): According to GP 1 the polymer bound acceptor **54 P-F** was treated with donor **3^t**[36] at −20 °C (0.30 equiv TMSOTf). Compound **55 P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(3-*O*-acetyl-2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (55): According to GP 5 the product of compound **55 P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo, coevaporated three times with toluene and precleaned by flash chromatography (petroleum ether/ethyl acetate 2:1). MPLC (toluene/ethyl acetate 3:1) gave compound **55** (15 mg) as colourless oil (40 % yield over nine reaction steps, corresponding to an average yield of 90 % per step). R_f = 0.52 (petroleum ether/ethyl acetate 1:1); $[\alpha]_D$ = +8.3° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.61–1.85 (m, 24 H, 6 CH_3, 2 $COCH_3$), 2.06 (s, 3 H, $COCH_3$), 3.10–5.22 (m, 61 H, 1a-H, 1b-H, 1c-H, 1d-H, 1e-H, 2a-H, 2b-H, 2c-H, 2d-H, 2e-H, 3a-H, 3b-H, 3c-H, 3d-H, 3e-H, 4a-H, 4b-H, 4c-H, 4d-H, 4e-H, 5a-H, 5b-H, 5c-H, 5d-H, 5e-H, 6a-H, 6a′-H, 6b-H, 6b′-H, 6c-H, 6c′-H, 6d-H, 6d′-H, 6e-H, 6e′-H, 24 OC*H*HPh, CH_2OAc), 6.75–7.40 (m, 59 H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 20.8, 20.9, 21.0, 55.2, 55.4, 56.2, 65.9, 68.0, 69.9, 71.9, 72.3, 72.5, 72.6, 72.9, 73.3, 74.3, 74.5, 74.6, 74.9, 76.1, 76.8, 77.2, 77.8, 78.1, 81.0, 97.2, 97.8, 99.1, 100.1, 127.27, 127.31, 127.35, 127.5, 127.6, 127.7, 127.8, 128.0, 128.08, 128.12, 128.16, 128.2,

128.3, 128.4, 128.7, 137.7, 138.4, 138.6, 139.3, 171.3; MALDI MS (positive mode): m/z: calcd for $C_{139}H_{147}N_3O_{33}$: 2387.7; found: 2410.7 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (55P-PA): According to GP 3 the PA group of compound **55P** was removed. Compound **55P-PA** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)]-(2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (56P): According to GP 1 the polymer-bound acceptor **55P-PA** was treated with donor **5**^{e} at 0 °C (0.25 equiv TMSOTf). Compound **56P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)]-(2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (56): According to GP 5 the product of compound **56P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo, coevaporated three times with toluene and precleaned by flash chromatography (petroleum ether/ethyl acetate 2:1). MPLC (toluene/ethyl acetate 3:1) gave compound **56** (12 mg) as colourless oil (30% yield over eleven reaction steps, corresponding to an average yield of 90% per step). $R_f=0.61$ (toluene/ethyl acetate 2:1); $[\alpha]_D=+5.4°$ ($c=0.5$, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.63$–1.76 (m, 21H, 6 CH_3, COCH_3), 2.06 (s, 3H, COCH_3), 2.09 (s, 3H, COCH_3), 3.18–3.25 (m, 3H, 5a-H, 5b-H, 5e-H), 3.32–4.93 (m, 64H, 1b-H, 1c-H, 1e-H, 2a-H, 2b-H, 2c-H, 2e-H, 2f-H, 3a-H, 3b-H, 3c-H, 3d-H, 3e-H, 3f-H, 4a-H, 4b-H, 4c-H, 4d-H, 4e-H, 4f-H, 5c-H, 5d-H, 5f-H, 6a-H, 6a′-H, 6b-H, 6b′-H, 6c-H, 6c′-H, 6d-H, 6d′-H, 6e-H, 6e′-H, 6f-H, 6f′-H, 30 OCHHPh), 5.01 (br s, 2H, CH_2OAc), 5.09–5.12 (m, 2H, 1a-H, 1d-H), 5.21–5.23 (m, 2H, 1f-H, 4f-H), 5.43 (m, 1H, 2d-H), 6.80–7.47 (m, 74H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta=56.5$, 57.4, 67.2, 68.6, 68.7, 69.3, 69.5, 69.9, 71.0, 71.6, 73.0, 73.5, 73.6, 75.3, 75.7, 76.1, 78.0, 79.2, 79.3, 79.5, 82.3, 98.4, 99.1, 100.3, 100.7, 101.3, 101.8; MALDI MS (positive mode): m/z: calcd for $C_{166}H_{175}N_3O_{38}$:2820.2; found: 2841.4 $[M+Na]^+$.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-[3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranosyl]-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzyl-3-*O*-phenoxyacetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (57P): According to GP 1 the polymer bound acceptor **54P-F** was treated with donor **2**^{e} at 0 °C (0.3 equiv TMSOTf). Compound **57P** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(3,6-Di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzyl-3-*O*-phenoxyacetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (57P-F): The Fmoc group of compound **57P** was removed according to GP 2. The polymer bound heptasaccharide **57P-F** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(2,3,6-tri-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzyl-3-*O*-phenoxyacetyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (58P): According to GP 3 the polymer bound acceptor **57P-F** was treated with donor **9**^{t} at −20 °C (0.35 equiv TMSOTf). Compound **58P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(2,3,6-tri-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzyl-3-*O*-phenoxyacetyl-β-D-mannopyranosyl)-(1→2)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (58): According to GP 5 the product of compound **58P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo, coevaporated three times with toluene and precleaned by flash chromatography (petroleum ether/ethyl acetate 3:1). MPLC (toluene/ethyl acetate 3:1) gave compound **58** (13 mg) as colourless oil (31% yield over eleven reaction steps, corresponding to an average yield of 90% per step). $R_f=0.58$ (toluene/ethyl acetate 3:1); $[\alpha]_D=+8.1°$ ($c=0.5$, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.84$–2.07 (m, 33H, 5 COCH_3, 6 CH_3), 2.72 (m, 1H, 5-H), 3.11–3.17 (m, 3H, 5-H, 2 6-H), 3.19–3.21 (m, 1H, 5-H), 3.35–3.37 (m, 3H, 3 6-H), 3.44–3.48 (m, 6H, 2 5-H, 4 6-H), 3.52–3–54 (m, 1H, 6-H), 3.60–3.62 (m, 2H, 2 6-H), 3.73–5.04 (m, 51H, 1a-H, 1b-H, 1c-H, 1d-H, 1e-H, 1f-H, 2a-H, 2b-H, 2c-H, 2d-H, 2e-H, 3a-H, 3b-H, 3c-H, 3d-H, 3e-H, 3f-H, 4a-H, 4b-H, 4c-H, 4d-H, 4e-H, 4f-H, 26 OCHHPh, CH_2OAc), 5.34–5.37 (m, 1H, 2f-H), 7.04–7.32 (m, 64H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta=55.2$, 55.4, 56.3, 62.0, 66.0, 66.6, 68.4, 69.7, 70.3, 71.9, 73.8, 74.0, 74.2, 74.5, 74.6, 75.4, 76.2, 76.3, 76.8. 77.0, 77.2, 77.7, 78.0, 80.3, 96.8, 97.1, 97.3, 97.7, 100.5, 101.9, $^1J_{1a\text{-}C,1a\text{-}H}=166.6$, $^1J_{1b\text{-}C,1b\text{-}H}=162.4$, $^1J_{1c\text{-}C,1c\text{-}H}=157.4$, $^1J_{1d\text{-}C,1d\text{-}H}=168.3$, $^1J_{1e\text{-}C,1e\text{-}H}=164.1$, $^1J_{1f\text{-}C,1f\text{-}H}=164.1$ Hz; MALDI MS (positive mode): m/z: 2747.2 $[M+Na]^+$; M_w: calcd for $C_{156}H_{167}N_3O_{40}$: 2724.0.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(2,3,6-tri-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→2)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (58P-PA): According to GP 3 the PA group of compound **58P** was removed. Compound **58P-PA** was obtained.

4-(Polystyrene-divinylbenzene-carbonyloxymethyl)benzyl *O*-(2,3,6-tri-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-{[3,4,6-tri-*O*-benzyl-2-*O*-(9-fluorenylmethoxycarbonyl)-α-D-mannopyranosyl]-(1→3)}-(2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyrano-side (59P): According to GP 1 the polymer bound acceptor **58P-PA** was treated with donor **5**^{e} at 0 °C (0.25 equiv TMSOTf). Compound **59P** was obtained.

4-(Acetoxymethyl)benzyl *O*-(2,3,6-tri-*O*-acetyl-4-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)]-(2,4-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-(3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (59): According to GP 5 the product of compound **59P** was cleaved from the resin and treated with pyridine (1 mL) and Ac_2O (1 mL). After 12 h the solvent was evaporated in vacuo, coevaporated three times with toluene and precleaned by flash chromatography (petroleum ether/ethyl acetate 1:1). MPLC (toluene/ethyl acetate 5:2) gave compound **59** (10 mg) as colourless oil (22% yield over eleven steps, corresponding to an average yield of 89% per step). $R_f=0.51$ (toluene/ethyl acetate 2:1); $[\alpha]_D=+14.7°$ ($c=0.5$, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=1.64$–2–07 (m, 33H, 5 COCH_3, 6 CH_3), 2.65 (m, 1H, 5-H), 3.10–3.11 (m, 2H, 2 5-H), 3.25–3.35 (m, 3H, 5-H, 2 6-H), 3.40–3.46 (m, 5H, 3 5-H, 2 6-H), 3.52–3.75 (m, 7H, 7 6-H), 3.81–5.00 (m, 61H, 6 1-H, 2a-H, 2b-H, 2c-H, 2d-H, 2e-H, 2f-H, 3a-H, 3b-H, 3c-H, 3d-H, 3e-H, 3f-H, 3 g-H, 4a-H, 4b-H, 4c-H, 4d-H, 4e-H, 4f-H, 4 g-H, 3 6-H, 32 OCHHPh), 5.02 (s, 2H, CH_2OAc), 5.13 (s, 1H, 1-H), 5.34 (dd, $^3J_{2f,1f}=8.1$, $^3J_{2f,3f}=10.1$ Hz, 1H, 2f-H), 5.49 (br s, 1H, 2 g-H), 7.01–7.30 (m, 79H, Ph); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta=56.6$, 57.6, 63.3, 68.1,

68.8, 69.2, 69.3, 70.2, 70.8, 70.9, 71.0, 73.1, 73.6, 75.1, 75.7, 75.8, 78.1, 79.1, 79.2, 81.5, 82.4, 98.1, 98.3, 98.5, 99.1, 100.8, 101.7, 103.6, $^1J_{1a\text{-}C,1a\text{-}H}$ = 168.7, $^1J_{1b\text{-}C,1b\text{-}H}$ = 169.5, $^1J_{1c\text{-}C,1c\text{-}H}$ = 156.6, $^1J_{1d\text{-}C,1d\text{-}H}$ = 174.4, $^1J_{1e\text{-}C,1e\text{-}H}$ = 171.1, $^1J_{1f\text{-}C,1f\text{-}H}$ = 167.9, $^1J_{1g\text{-}C,1g\text{-}H}$ = 167.1 Hz; MALDI MS (positive mode): *m*/*z*: 3179.1 $[M+Na]^+$; M_w: calcd for $C_{183}H_{195}N_3O_{45}$: 3156.5.

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