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New Method for Regioselective Glycosylation Employing Saccharide Oxyanions

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Dedicated to Prof. Dr. Dr. Gerhard Bringmann on the occasion of his 60th birthday

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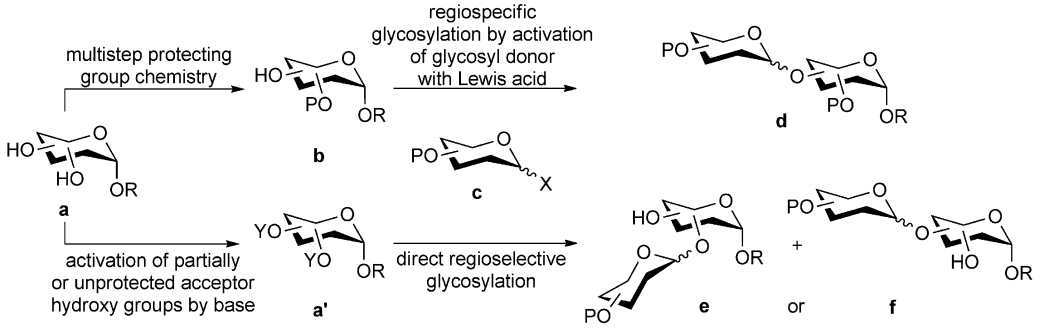
As an alternative concept for glycosylation, the prior activation of acceptor hydroxy groups for selective glycosidic bond formation, was investigated to give complex oligosaccharides. Oxyanions obtained from partially protected saccharides were glycosylated by employing glycopyranosyl halides, and the regiochemical results were studied. Initially, partially methylated methyl-α-D-glucopyranosides were used as a model system to study the underlying mechanistic principles of base-promoted glycosylation. High regioselectivities and stereospecific glycosidic bond formations were achieved, and the scope of the methodology was extended with different perbenzylated glycosyl donors.

Introduction

Carbohydrates play essential roles in almost all biological processes.[1] In order to explore the specific functions of carbohydrates and carbohydrate conjugates the development of efficient methods for the chemical synthesis of pure and well-defined samples is of major concern. A plethora of achievements have been made for regio- and stereoselective glycosidic bond formations in the last decades, however, the synthesis of oligosaccharides does not present a routine process due to their structural diversity and still requires solution on a case by case basis.[2]

The control of regioselectivity is one of the most important tasks in synthetic carbohydrate chemistry and is conventionally accomplished by extended protecting group chemistry. Thus, acceptor **a** has to be transformed into **b** containing one selectively unblocked hydroxy group. Subsequent attachment of a fully protected and (Lewis) acid-activated glycosyl donor **c** to acceptor **b** affords the glycosylation product **d** with strict regiocontrol (Scheme 1). The main drawback is that the protecting group chemistry implies tedious multistep protection and deprotection step. In addition, the lack of a general and absolute stereoselective



Scheme 1. Comparison of the commonly used Lewis acid mediated and base-promoted glycosylation methodology (P = protecting group, OY = activated OH group, X = leaving group).

glycosylation protocol enhances the complexity of glycosidic bond formation.[2]

Besides solution-phase chemistry, solid state attempts have been developed to assemble oligosaccharides.[3] Whereas the advantage in solid-state synthesis is highlighted in the facilitation of the time-consuming workup

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and purification, the main drawback is the need for a large number of differently protected building blocks in large amounts for the coupling reactions in the solid state, that is, even here extensive protecting group chemistry has to be utilized. Thus, other approaches to access carbohydrate components are of particular interest.

As a potential alternative, glycosylation of unprotected or partially protected acceptor derivatives (sometimes termed "open" glycosylation)[4] should offer shorter routes to oligosaccharides essentially decreasing the step economy of the overall process.

Regioselective glycosylation of partially protected acceptor glycosides has been reported;[5] however, due to the fact that in the majority of cases acceptor OH groups exhibit only slight differences in their reactivities, it is difficult to predict which hydroxy groups will be accessed, for example, the regioselectivity is strongly dependent on the functionalization of the acceptor.[6]

Regiochemical control could be solved by prior activation of the acceptor hydroxy groups leading to more distinct reactivity differences. To date only a few studies have been directed towards regioselective coupling with unprotected or partially protected and activated acceptor OH groups.[7] Boron and tin reagents have been applied to complexation-induced activation of particular OH groups.[8] A further possibility for activation of acceptor OH groups is their deprotonation to give oxyanions, which could lead to direct and selective glycosylation on partially protected or unprotected sugars, respectively (Scheme 1).[9] The advantages of this approach are twofold: reduction of the number of protection/deprotection steps and omitting the promoter. Thus, the idea was to activate acceptor **a** by base leading to acceptor **a**′. Afterwards, donor **c** will be attached directly to **a**′ and the ratio of the possible products **e** and **f** analysed.

To date, efforts have not been made to clarify and understand the relative reactivities of acceptor saccharide oxyanions in glycosylation reactions. Thus, these studies were started with a systematic survey initially using partially methylated methyl-α-D-glucopyranosides as model systems. Recently, the first results with a set of partially methylated derivatives showed that deprotonation led to more distinct reactivity differences of the competing hydroxy groups/oxyanions and achievements of high regioselectivities.[10] For a more profound understanding our research on base-promoted glycosylation was subsequently extended employing all partially methylated glucopyranosyl acceptors as well as the use of other glycopyranosyl donors, base promoters and protecting groups.

Defining oxyanion reactivities in partially protected acceptor units could give specific access to distinct oligosaccharides elaborating the base-promoted version into an alternative glycosylation method.

Results and Discussion

Donor and Acceptor Building Blocks

The study started with a systematic survey using partially methylated methyl-α-D-glucopyranosides as a model system (Figure 1). All partially methylated derivatives **1**–**14** were synthesized, including four trimethylated methyl-α-D-glucopyranosides **1**–**4**, six dimethylated derivatives of which three each exhibit separated (i.e., **5**–**7**) and adjacent (i.e., **8**–**10**) diols as well as four monomethylated compounds **11**–**14** showing different triol structures.

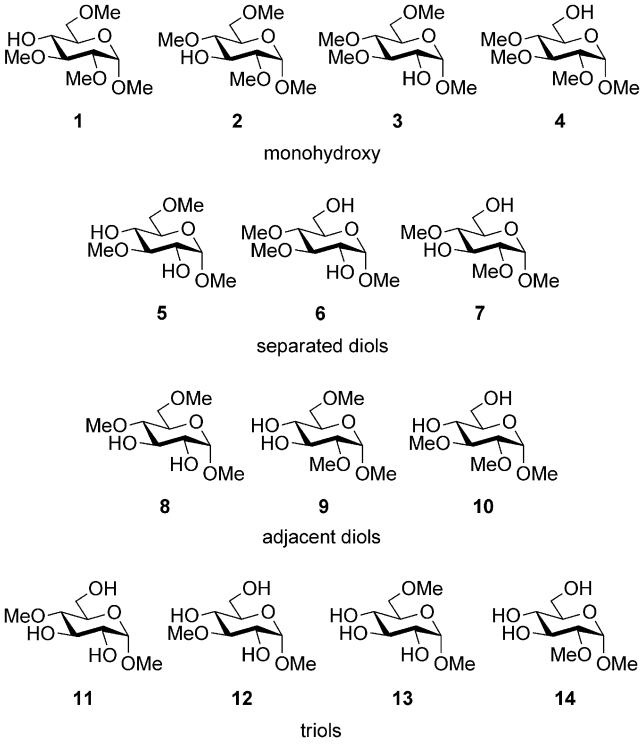


Figure 1. Partially methylated methyl-α-D-glucopyranosides **1**–**14** as model acceptors for initial studies on oxyanion reactivities in base-promoted glycosylations.

Whereas methyl-protected saccharides show only very limited synthetic utility in preparative organic synthesis, their use is advantageous for these first fundamental studies on oxyanion reactivities. Methyl groups are small, chemically inert protecting groups and the ^{1}H NMR signals do not interfere with the anomeric proton signals and thus determination of disaccharide distributions could be performed by simple integration (Figure 3).

Accordingly, the donors initially used in base-promoted glycosylations were also permethylated (i.e., **15**–**17**; Figure 2). Thereafter, donors **15**–**17** were replaced by perben-

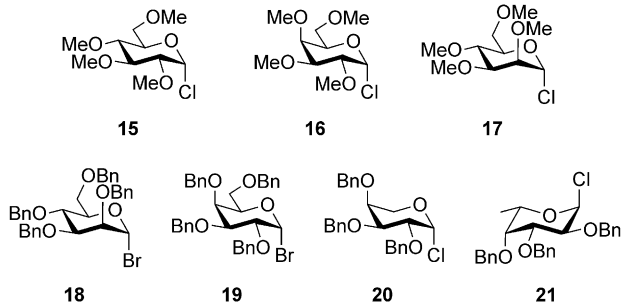


Figure 2. Methylated and benzylated donors **15**–**21** used in base-promoted glycosylations.

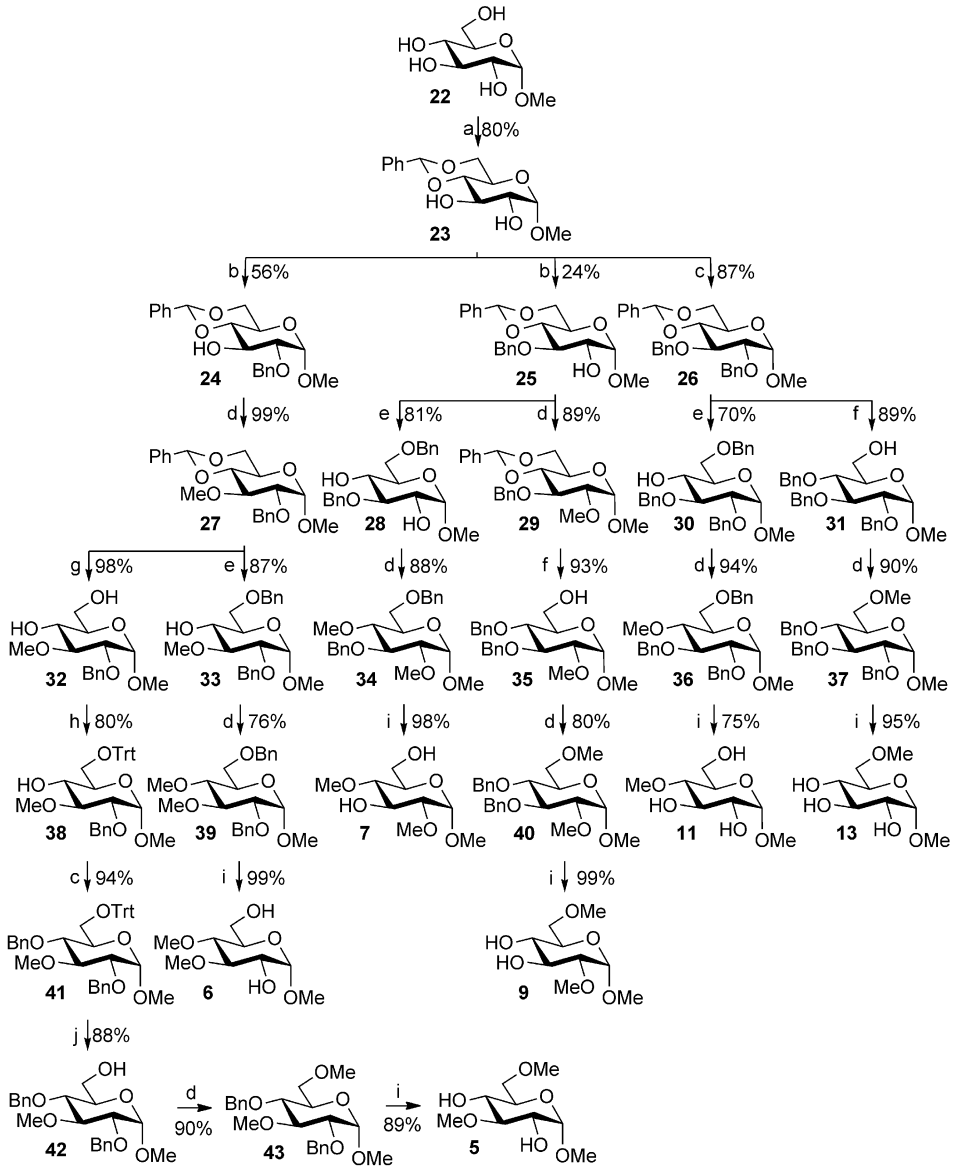
zylated halide donors **18**–**21** (Figure 2) to leave the model system stepwise and test the regiochemical outcomes after base-promoted glycosylation with removable protecting groups.

Acceptors **1**–**14** were synthesized employing standard protecting group chemistry (Scheme 2). The preparations of **1**–**4**, **8**, **10**, **12** and **14** were described previously,[10] and synthesis of the remainder is depicted in Scheme 2.

The precursor for **5**–**7**, **9**, **11** and **13** was the benzylidenated derivative **23**,[11] which was obtained from commercially available methyl-α-D-glucopyranoside (**22**). Derivative **23** was monobenzylated by phase-transfer catalysis furnishing **24** and **25** and dibenzylated **26**.[12] Intermediates **24**–**26** were subsequently converted into **28**, **30**, **31** (one step), **33** and **35** (two steps with a preceding methylation) by reductive cleavage of the benzylidene group.[13]

Methylation with NaH and MeI in *N*,*N*-dimethylformamide (DMF) and debenzylation by hydrogenolysis afforded acceptors **6**, **7**, **9**, **11** and **13** in high yields.

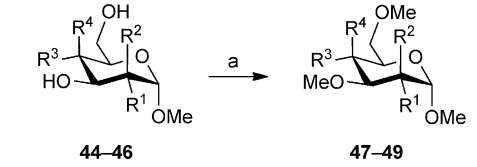
For the preparation of **5**, compound **24** was first converted into **27** by methylation. Subsequent removal of the benzylidene group afforded compound **32** following tritylation of **32**, benzylation of **38** and detritylation which finally yielded in intermediate **42**. Faster access to **42** would



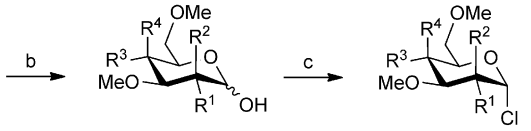
Scheme 2. Synthesis of partially methylated methyl-α-D-glucopyranosides **5**–**7**, **9**, **11** and **13**. Reagents and conditions: (a) benzaldehyde dimethyl acetal (BADMA), camphorsulfonic acid (CSA), CH_3CN, 80 °C, 20 min; (b) BnBr, $Bu_4N^+HSO_4^-$, 5% NaOH (aq.), DCM, reflux, 72 h; (c) 1. NaH (2 equiv. each OH), DMF, 0–5 °C, 1 h; 2. BnBr (2 equiv. each OH), DMF, 0 °C to r.t., 24 h; (d) 1. NaH (2 equiv. each OH), DMF, 0–5 °C, 1 h; 2. MeI (2 equiv. each OH), DMF, 0 °C to r.t., 24 h; (e) $NaCNBH_3$, F_3CSO_3H, THF, 0–5 °C, 1 h; (f) $LiAlH_4$, $AlCl_3$, DCM/Et_2O = 1:1, 50 °C, 2 h; (g) 1 N HCl, H_2O, MeOH, 60 °C, 3 h; (h) trityl chloride, cat. 4-*N*,*N*-dimethylaminopyridine (DMAP), Py, 60 °C, 72 h; (i) H_2, Pd/C, MeOH, r.t., 72 h; (j) trifluoroacetic acid (TFA, 90%), r.t., 5 min.

be the reductive cleavage of **27**; however, attempts for opening the benzylidene group using $LiAlH_4/AlCl_3$[14] gave poor regioselectivity most likely caused by the methyl group at C-3 and reductive opening with BH_3·THF and $Sc(OTf)_3$ failed.[15] Further, **42** was methylated to give **43** and deprotection was achieved by hydrogenolysis, which led to **5**.

Formation of donors **15**–**17** started with the permethylation of the corresponding methyl-α-D-glycopyranosides **44**–**46** in very high yields (Scheme 3). The next step was the acidic hydrolysis[16] of the glycosidic bond, which gave **50**–**52** as anomeric mixtures. Finally, the glycopyranosyl chlorides were prepared using oxalyl chloride and catalytic amounts of DMF.[17]



	R^1	R^2	R^3	R^4
44	OH	H	OH	H
45	OH	H	H	OH
46	H	OH	OH	H

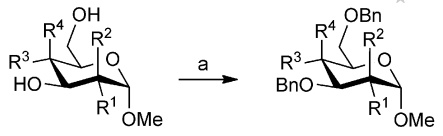


	R^1	R^2	R^3	R^4
47 (81%), **50** (60%), **15** (48%)	OMe	H	OMe	H
48 (99%), **51** (81%), **16** (92%)	OMe	H	H	OMe
49 (98%), **52** (77%), **17** (74%)	H	OMe	OMe	H

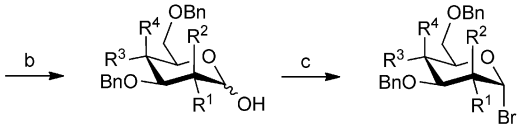
Scheme 3. Synthesis of permethylated glycopyranosyl chlorides **15**–**17**. Reagents and conditions: (a) 1. NaH (1.25 equiv. each OH), DMF, 0–5 °C, 1 h; 2. MeI (1.25 equiv. each OH), DMF, 0 °C to r.t., 24 h; (b) 0.5 M HCl (aq.), 100 °C, 48 h; (c) $(COCl)_2$, DMF, DCM, r.t., 1 h.

For construction of donors **18** and **19** a three-step synthesis was performed employing perbenzylation of the starting materials **45** and **46** to compounds **53** and **54**, acidic hydrolysis of the methylglycoside and bromination using oxalyl bromide in high yields (Scheme 4).[18]

The synthesis of the L-arabino- and L-fucopyranosyl chlorides **20** and **21** started with tetraacetates **57** and **62**, which were converted into the corresponding thioglycosides **58** and **63** using BF_3·Et_2O/thiophenol or trimethylsilyltrifluoromethanesulfonate (TMSOTf)/methylthiotrimethylsilane as reagents (Schemes 5 and 6).[19] Subsequent deacetylation and benzylation furnished **60** and **65** following treatment with *N*-bromosuccinimide (NBS) in acetone/water to cleave the thioglycosidic bonds.[20] Lastly, **61** and **66** were chlorinated to give the desired perbenzylated donors **20** and **21**.

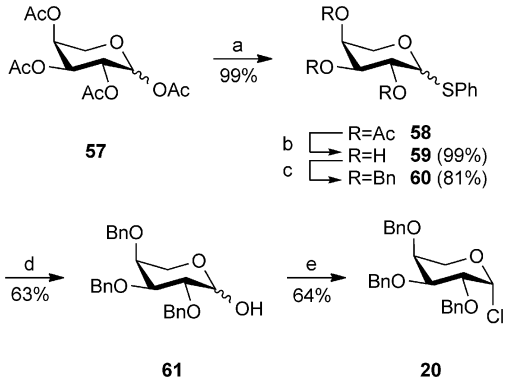


	R^1	R^2	R^3	R^4
46	H	OH	OH	H
45	OH	H	H	OH

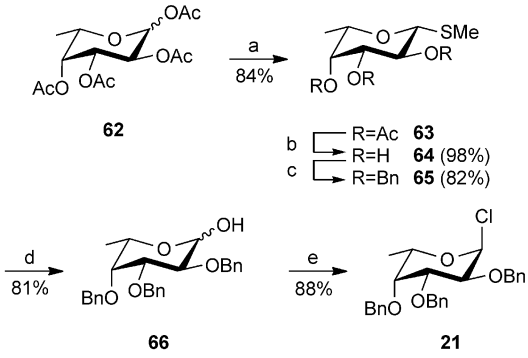


	R^1	R^2	R^3	R^4
53 (86%), **55** (54%), **18** (79%)	H	OBn	OBn	H
54 (84%), **56** (60%), **19** (83%)	OBn	H	H	OBn

Scheme 4. Synthesis of perbenzylated glycopyranosyl bromides **18** and **19**. Reagents and conditions: (a) 1. NaH (1.25 equiv. each OH), DMF, 0–5 °C, 1 h; 2. BnBr (1.25 equiv. each OH), DMF, 0 °C to r.t., 24 h; (b) AcOH, 2 N H_2SO_4, 100 °C, 24 h; (c) $(COBr)_2$, DCM, r.t., 1 h.



Scheme 5. Synthesis of **20**. Reagents and conditions: (a) PhSH, BF_3·OEt_2, DCM, r.t., 2 h; (b) NaOMe, MeOH, r.t., 24 h; (c) 1. NaH (2 equiv. each OH), DMF, 0–5 °C, 1 h; 2. BnBr (2 equiv. each OH), DMF, 0 °C to r.t., 24 h; (d) NBS, acetone/H_2O = 9:1, r.t., 3 h; (e) $(COCl)_2$, DMF, DCM, r.t., 1 h.



Scheme 6. Synthesis of **21**. Reagents and conditions: (a) $H_3CCSSiMe_3$, TMSOTf, DCM, r.t., 15 h; (b) NaOMe, MeOH, r.t., 24 h; (c) 1. NaH (2 equiv. each OH), DMF, 0–5 °C, 1 h; 2. BnBr (2 equiv. each OH), DMF, 0 °C to r.t., 24 h; (d) NBS, acetone/H_2O = 9:1, r.t., 3 h; (e) $(COCl)_2$, DMF, DCM, r.t., 1 h.

Glycosylation Results

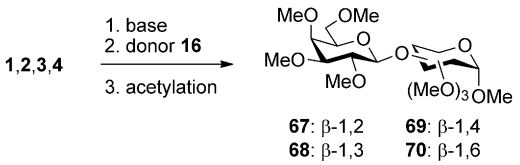
Base-promoted glycosylation was performed by initial deprotonation of the acceptor hydroxy groups **1**–**14** with NaH or *t*BuOK in DMF at room temperature. Subsequently, permethylated galactopyranosyl chloride **16** was added. After 4 h the reaction was quenched by addition of methanol. Acetylation of the remaining free hydroxy groups and purification by column chromatography afforded the corresponding disaccharide mixtures **71**–**87** (Table 2). In contrast to Lewis acid activated glycosylation this approach required only simple conditions (room temperature, absence of Lewis acid and molecular sieves), which led to successful glycosidic bond formation. In some cases, concomitant formation of higher glycosylated branched products were observed, however, their absolute yield was negligible.

In order to establish a reactivity arrangement for the oxyanions of trimethylated methyl-α-D-glucopyranosides **1**–**4** it was advantageous to apply them as an equimolar mixture. After reaction with **16** disaccharides **67**–**70** were obtained in different ratios (Table 1).

Relative yields of the disaccharide mixtures were determined by integration of the ^{1}H NMR signals of the anomeric or other well-separated protons. The assignment was facilitated enormously by the stereospecific β-galactopyranoside formation (Figure 3).

The uniform β-stereoselectivity is attributed to an S_N2-like reaction by inversion of configuration at the anomeric centre of donor **16**.[10]

Table 1. Glycosylation results for acceptors **1**–**4** with NaH and *t*BuOK as bases and **16** as the donor.[a]



Entry	Base	Yield [%]	Relative yield [%][b] β-1,2	β-1,3	β-1,4	β-1,6
1	NaH[c]	20	40	11	26	23
2	*t*BuOK	35	39	16	28	17

[a] General reaction conditions: NaH or *t*BuOK (3–4 equiv.), DMF, r.t., 1 h, then donor **16** (3–4 equiv.), r.t., 4 h, then Py, Ac_2O, r.t., 18 h. [b] Ratio determined by ^{1}H NMR spectroscopy. [c] Ref.[10]

Tables 1 and 2 show the results of all partially methylated methyl-α-D-glucopyranosides **1**–**14** with NaH and *t*BuOK as base promoter and **16** as donor. As glycosylations were conducted under the same conditions, product compositions can be compared. The regiochemical results observed after base-promoted glycosylation of acceptors **1**–**4** (trimethylated derivatives; Table 1) and **5**–**7** (dimethylated derivatives with isolated hydroxy groups; Table 2, Entries 1–3) activated (deprotonated) 2-OH groups were found to be most reactive for glycosylation with permethylated donor **16** and both bases. Thus β-1,2-linked disaccharides were the

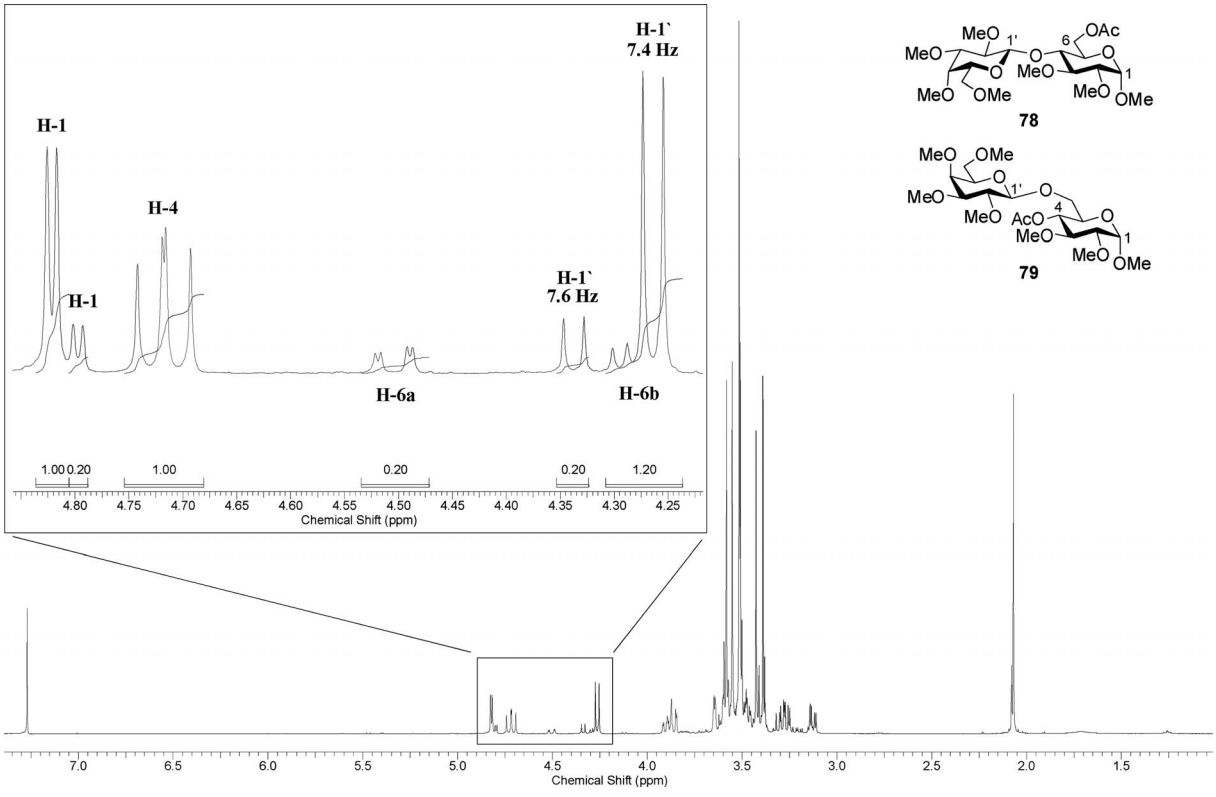
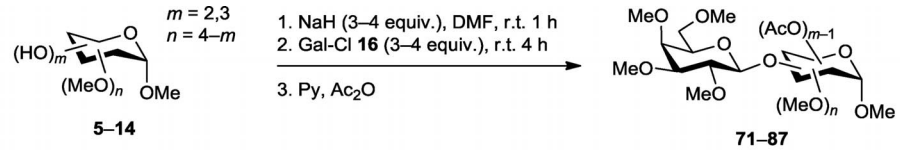
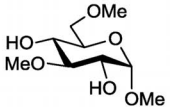
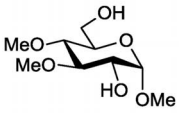
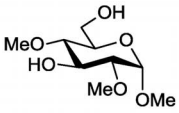
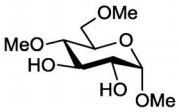
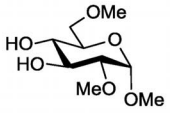
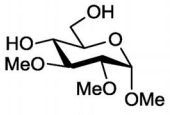
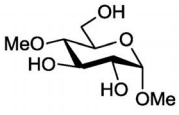
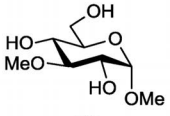
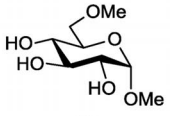
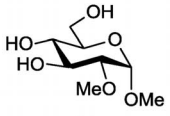


Figure 3. ^{1}H NMR spectrum of the disaccharide mixture **78** and **79**. Exclusively β-linked glycosylation products allowed determination of the relative yields by integration of the anomeric or other well-separated proton signals.

Table 2. Glycosylation results for acceptors **5**–**14** with NaH and *t*BuOK as bases and **16** as donor.[a]



5–14 **71–87**

Entry	Acceptor	Products	Base	Yield [%]	Relative yield [%][b] β-1,2	β-1,3	β-1,4	β-1,6
1	 **5**	**71** (β-1,2) **72** (β-1,4)	NaH *t*BuOK	31 11	86 61	×[c] ×	61 39	× ×
2	 **6**	**73** (β-1,2) **74** (β-1,6)	NaH *t*BuOK	29 20	91 72	× ×	× ×	9 28
3	 **7**	**75** (β-1,3) **76** (β-1,6)	NaH *t*BuOK	23 15	× ×	55 57	× ×	45 43
4	 **8**	**77** (β-1,2)	NaH[d] *t*BuOK	17 22	100 100	– –	× ×	× ×
5	 **9**	none	NaH *t*BuOK	– –	× ×	– –	– –	× ×
6	 **10**	**78** (β-1,4) **79** (β-1,6)	NaH[d] *t*BuOK	62 75	× ×	× ×	20 17	80 83
7	 **11**	**80** (β-1,2) **81** (β-1,3) **82** (β-1,6)	NaH *t*BuOK	26 26	63 64	9 17	× ×	28 19
8	 **12**	**83** (β-1,2) **84** (β-1,4) **85** (β-1,6)	NaH[d] *t*BuOK	40 52	32 3	× ×	10 15	58 82
9	 **13**	none	NaH *t*BuOK	– –	– –	– –	– –	× ×
10	 **14**	**86** (β-1,4) **87** (β-1,6)	NaH[d] *t*BuOK	30 44	× ×	– –	39 79	61 21

[a] General reaction conditions: NaH or *t*BuOK (3–4 equiv.), DMF, r.t., 1 h, then donor **16** (3–4 equiv.), r.t., 4 h, then Py, Ac_2O, r.t., 18 h. [b] Ratio determined by ^1H NMR spectroscopy. [c] ×: Methylated position, no linkage possible. [d] Ref.[10]

major regioisomers found after base-promoted glycosylation as observed in the results of 2,4-diol **5** and 2,6-diol **6** obtaining disaccharides **71** and **73** in high selectivity. The 4-OH group was ascertained as the secondary reactive position. The reactivity of the activated 3-OH and 6-OH groups is almost equal in the glycosylations of **7** (Table 2, Entry 3) and **1**–**4** (Table 1) with *t*BuOK; however, using NaH as the base for glycosylation of **1**–**4**, the 6-position was found to be more reactive. The latter observation recurred in the regiochemical outcomes of **11** (Table 2, Entry 7). Thus, the reactivity arrangement of isolated and activated OH groups can be exposed as follows:

2-OH > 4-OH > 6-OH ≥ 3-OH

The product distribution after treatment of dimethylated methyl-α-D-glucopyranosides **8** and **10** and monomethylated compounds **11**, **12** and **14** with base and donor **16** differed to some extent from those of derivatives **1**–**7** with isolated hydroxy groups (Table 2, Entries 4–10). Reaction of the 2,3-diol acceptor **8** with **16** led to a regiospecific formation of only β-1,2-linked disaccharide **77** in the presence of two hydroxy groups. Glycosylation of the 4,6-diol acceptor **10** with **16** provided disaccharides **78** and **79** in high yields. The disaccharide distribution of **78** and **79** showed high regioselectivity towards the 6-position, which was contrary to expectation by comparison with the reactivity order of isolated 4- and 6-oxyanions (Table 2, Entry 6).

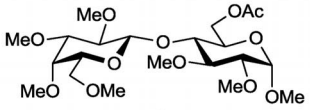
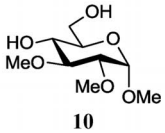
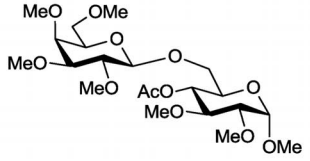
Base-promoted glycosylation of 2,4,6-triol **12** and 2,3,6-triol **11** with **16** provided disaccharides **80**–**85**, whose distribution clearly showed that activated diol structures were more reactive than isolated hydroxy groups. In the presence of a 4,6-diol (Table 2, Entry 8; acceptor **12**), glycosylation occurred preferentially at the 6-position as already observed for 4,6-diol **10**, and in a 2,3-diol structure (Table 2, Entry 7; acceptor **11**) β-1,2 was the favoured linkage as observed for acceptor **8** (2,3-diol). Although the variation of the base used for acceptors **8**, **10** and **11** did not have a significant influence on the product distribution, appreciable effects were found in the reactions of **12** and **14** with **16** (Table 2, Entries 8 and 10).

The results obtained after glycosylation of 3,4,6-triol **14** (Table 2, Entry 10) showed reverse regioselectivity by variation of the base. With regard to the observation of **10**, the regiochemical outcome with NaH as base was anticipated; however, the unexpected outcome for **14** using *t*BuOK can not be explained using our concept and is a matter of conjecture. In the case of 2,4,6-triol **12** the formation of the β-1,2-linked disaccharide was remarkably suppressed using *t*BuOK instead of NaH (Table 2, Entry 8). As the hydroxy groups were deprotonated irreversibly with NaH, deprotonation with *t*BuOK represented an equilibrium reaction. Consequently, a given alcoholate dispersion was present; in the case of **12** a predominant deprotonation most likely occurred at the diol structure rather than at the isolated hydroxy group.

After conversion of **9** and **14** with NaH and **16**, glycosylation products could not be detected. Hence, the nature of the glycosyl acceptors affects the outcome of glycosyl coupling suggesting elimination of **16** to give the corresponding glycal in the dominant side reaction, most probably on acceptors exhibiting a 3,4-diol structure.

Acceptor diols **8**, **10**, **11** and **12** and triol **14** are assumed to be partially deprotonated. Accordingly, unreacted hydroxy group(s) and oxyanion(s) delocalize the negative charge by hydrogen bonding.[10] This assumption was confirmed by the observation that the relative disaccharide distribution was independent of the amount of base added, clearly demonstrated by a set of experiments in which the concentration of base (*t*BuOK) and **16** were varied (Table 3). Apparently, the simultaneous increase of base and **16** led to higher overall yields of **78** and **79** along with the possible trisaccharide. However, no significant influence on the disaccharide product distribution was observed. The ratio of disaccharides **78** (β-1,4) and **79** (β-1,6) was about 1:4, varying the acceptor to base/donor ratio from 1:1 to 1:3. Obviously, deprotonation ceases at a particular point, in diol structures most likely after the first proton abstraction. After formation of disaccharides **78** and **79** with ratio 1:4, deprotonation continued on isolated OH-4 and OH-6,

Table 3. Glycosylation results for **10** by variation of base (*t*BuOK) and concentration of **16**.[a]

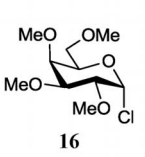
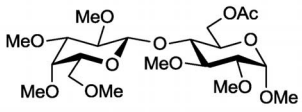
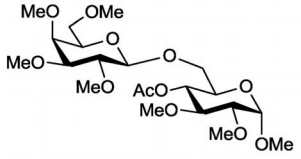
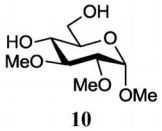
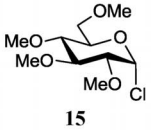
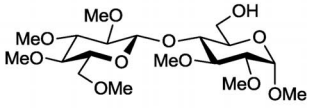
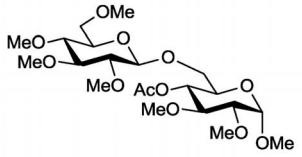
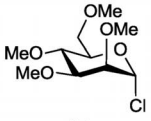
Entry	Acceptor	*t*BuOK [equiv.]	Donor **16** [equiv.]	Products	Yield [%][b]	Relative yield [%][d] β-1,4	β-1,6
1		1.0	1.0	 **78**	34	17	83
2	 **10**	2.0	2.0	 **79**	75[b] (11)[c]	17	83
3		3.0	3.0		68[b] (24)[c]	22	78

[a] *t*BuOK (1–3 equiv.), DMF, r.t., 1 h, then donor **16** (1–3 equiv.), r.t., 4 h, then Py, Ac_2O, r.t., 18 h. [b] Yield of disaccharides **78** and **79**. [c] Yield of the simultaneous formation of trisaccharide. [d] Ratio determined by ^1H NMR spectroscopy.

respectively, which finally led to branched trisaccharide side products. Additionally, the enhanced reactivity of the vicinal hydroxy groups provided strong support that the incorporation of an unreacted adjacent OH group by hydrogen bonding disperses the negative charge and decreases the basicity of the oxyanion initially formed.

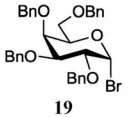
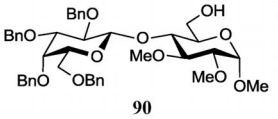
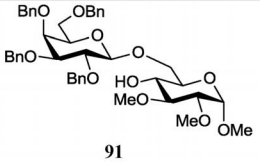
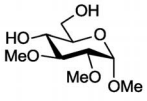
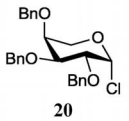
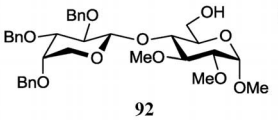
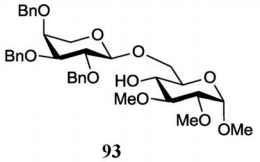
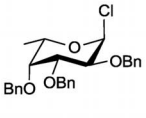
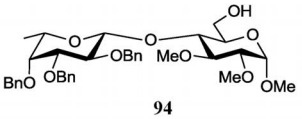
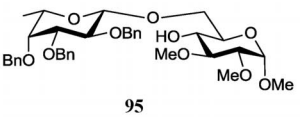
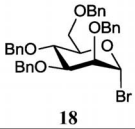
Furthermore, base-promoted glycosylation was investigated using different donor substrates. First of all, permethylated glycopyranosyl chlorides **15**–**17** were treated with deprotonated acceptor **10** (Table 4). Interestingly, comparing the glycosylation results of the galactopyranosyl donor **16** with donors possessing the *gluco* and *manno* configurations,

Table 4. Base-promoted glycosylations of **10** with various permethylated glycopyranosyl halides.[a]

Entry	Acceptor	Donor	Products	Yield [%][b]	Relative yield [%][c] β-1,4	β-1,6
1		 **16**	 **78**  **79**	62	20	80
2	 **10**	 **15**	 **88**  **89**	4	50	50
3		 **17**	no reaction	–	–	–

[a] NaH (3 equiv.), DMF, r.t., 1 h, then donor **15**, **16** or **17** (3 equiv.), r.t, 2–90 h, then Py, Ac_2O, r.t., 18 h. [b] Total yield of the two possible disaccharide regioisomers. [c] Ratio determined by ^1H NMR spectroscopy.

Table 5. Base-promoted glycosylations of **10** with perbenzylated glycopyranosyl halides **18**–**21**.[a]

Entry	Acceptor	Donor	Products	Yield [%][b]	Relative yield [%][c] β-1,4	β-1,6
1		 **19**	 **90**  **91**	20	25	75
2	 **10**	 **20**	 **92**  **93**	47	23	77
3		 **21**	 **94**  **95**	54	25	75
4		 **18**	no reaction	–	–	–

[a] NaH (3 equiv.), DMF, r.t., 1 h, then donor **18**, **19**, **20** or **21** (3 equiv.), r.t, 4–20 h. [b] Total yield of the two possible disaccharide regioisomers. [c] After separation by column chromatography.

respectively, the latter two are obviously less reactive than **16**. Employing glucopyranosyl donor **15** the two possible disaccharides **88** and **89** were formed in only 4% yield, and glycosylation with the mannopyranosyl donor **17** did not furnish disaccharides.

The observations mentioned above were revealed similarly in base-promoted glycosylations of **10** with perbenzylated donors **18**–**21** (Table 5). Again, no linkage products were found using a donor with the *manno* configuration (Table 5, Entry 4); however, employing galacto-, arabino- and fucopyranosyl donors **19**–**21** disaccharides **90**–**95** were isolated in up to 54% overall yield (Table 5, Entries 1–3). All three entries revealed that the relative yields were close to each other. As already observed for the permethylated donor **16**, position 6 was glycosylated preferentially.

Summarizing the results of the perbenzylated and permethylated donors, it is particularly noticeable that high conversion was only observed with donors with an axial ether group at C-4. Obviously, evidence suggests that the stereochemistry of C-4 affects predominantly the reactivity of the donor. This occurrence and the clarification of whether the stereochemistry at C-2 has influence on the reactivity are the subjects of ongoing investigations.

Conclusions

In this contribution an alternative methodology for the assembly of di- and oligosaccharides was investigated in which glycosidic linkages were made accessible by reaction of partially protected acceptor oxyanions and glycosyl halides without the use of a promoter. Our main focus was on the analysis of the relative disaccharide distribution in order to reveal preferred positions for glycosylation with the aim to omit protecting group schemes. Initially, experiments were performed in detail using model donor and acceptor systems. High regioselectivities were achieved due to prior deprotonation and the resulting wide reactivity differences of the competing oxyanions. It is notable that the applied glycosylation methodology selectively gave rise to β-glycopyranosides in absence of a participating group at C-2. In addition to hydrogen bond networks based on partial deprotonation of vicinal hydroxy groups, the base promoter seems to influence the relative oxyanion reactivities. Furthermore, the outcome of base-promoted glycosylation is strongly dependent of the donor configuration.

Further studies focussing on the synthetic scope of the base-promoted glycosylation methodology are currently in progress.

Experimental Section

General: All reagents were purchased from commercial sources and used as received. Sodium hydride (NaH) was used as 60% suspension in paraffin. TLC was performed on Merck silica gel 60 F_{254} plates. Compounds were detected by UV and/or by treatment with $EtOH/H_2SO_4$ (9:1) and subsequent heating. Column chromatography was performed with Merck/Fluka silica gel 60 (230–400 mesh). Solvents for column chromatography were distilled prior to use. ^1H and ^{13}C NMR spectra were recorded with Bruker AMX-400 or Bruker AV-400 spectrometers (400 MHz for ^1H, 101 MHz for ^{13}C) and calibrated using the solvent residual peak. Melting points were measured with an Apotec melting point apparatus. Optical rotations were obtained using a Krüss Optronic P8000 polarimeter (589 nm, 25 °C). HRMS (ESI) were recorded with a Thermo Finnigan MAT 95XL mass spectrometer. MS (MALDI-TOF) were recorded with a Bruker Biflex II (positive reflection mode, matrix: 2,5-dihydroxybenzoic acid). Relative yields of disaccharide mixtures were determined by integration of the signals in the ^1H NMR spectra of the anomeric or other well-separated protons. Preparation and characterization of compounds **1**–**4**, **8**, **10**, **12**, **16**, **21** was reported previously. Compounds **23**–**26** were prepared as reported.[11,12] Characterization data for **67**–**70**, **77**–**79**, **83**–**85**, **86** and **87** have been published previously.[10]

General Procedure A1

Methylation/Benzylation of Hydroxy Groups: To a stirring solution of the starting material (1 mmol) in anhydrous DMF (10 mL) was added sodium hydride (2–2.5 equiv. per OH group) at 0 °C. After 1 h, MeI/BnBr (2–2.5 equiv. per OH group) was added at 0 °C, and the mixture was warmed to ambient temperature and stirred for 12–18 h. Subsequently, the reaction was quenched by addition of methanol (5 mL), the solvents were removed under reduced pressure and the residue was taken up in H_2O/DCM (1:1). The product in the aqueous layer was extracted twice into DCM. The organic phase was washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash column chromatography [gradient petroleum ether (PE)/ethyl acetate] to yield the corresponding methylated/benzylated derivatives.

General Procedure A2

Permethylation/Perbenzylation: To a stirring solution of the methylglycoside (1 mmol) in anhydrous DMF (10 mL) was added sodium hydride (1.25–1.5 equiv. per OH group) at 0 °C. After 1 h, MeI/BnBr (1.25–1.5 equiv. per OH group) was added at 0 °C, and the mixture was warmed to ambient temperature and stirred for 12–18 h. Workup and purification was performed as described in general procedure A1.

General Procedure B1

Reductive Cleavage of the Benzylidene Group with $LiAlH_4/AlCl_3$: The starting material (1 mmol) was dissolved in anhydrous Et_2O/DCM (1:1, 7 mL) and $LiAlH_4$ (7.0 equiv.) added. The suspension was heated to 50 °C and $AlCl_3$ (4.5 equiv.) was added. After 2 h at 50 °C the mixture was diluted with Et_2O (200 mL) and treated with ethyl acetate (20 mL) and water (30 mL). The aqueous layer was extracted twice into Et_2O, and the combined organic layers were washed with water (2×) and brine, dried (Na_2SO_4) and concentrated. Subsequent purification by flash column chromatography (gradient PE/ethyl acetate) furnished the 6-OH free and 4-benzylated compounds.

General Procedure B2

Reductive Cleavage of the Benzylidene Group with $NaCNBH_3$/F_3CSO_3H: To a cooled solution (0 °C) of the benzylidene protected intermediate (1 mmol) in anhydrous THF (15 mL) was added $NaCNBH_3$ (7.0 equiv.) followed by dropwise addition of F_3CSO_3H (7.0 equiv.). After stirring for 15 min at 0 °C the mixture was poured into ice water. DCM was added and the aqueous phase extracted once into DCM. The combined organic layers were washed with saturated $NaHCO_3$ solution, dried and concentrated. Purification by flash column chromatography (gradient PE/ethyl acetate) afforded the 4-OH free and 6-benzylated compounds.

General Procedure C1

Hydrolysis of Permethylated Methyl Glycosides: The starting material (1 mmol) was stirred in 0.5 M HCl solution (6 mL) with heating to reflux for 48 h. After cooling, the solution was neutralized with $NaHCO_3$ solution and concentrated. The residue was purified by flash column chromatography (gradient PE/ethyl acetate).

General Procedure C2

Hydrolysis of Perbenzylated Methyl Glycosides: The perbenzylated methylglycoside (1 mmol) was dissolved in glacial acetic acid (10 mL) and 1 N H_2SO_4 (5 mL) and stirred with heating to reflux for 48 h. After cooling, the mixture was poured into ice water and extracted into DCM (3×). The organic layer was washed with saturated $NaHCO_3$ solution, dried and concentrated. The residue was purified by flash column chromatography (gradient PE/ethyl acetate).

General Procedure D

Cleavage of the Benzyl Group: To a solution of the benzylated intermediate (1 mmol) in distilled methanol (20 mL) was added Pd(10%)/C (30 mg) and the mixture stirred under an atmosphere of hydrogen at room temperature for 24–96 h. The catalyst was filtered off, the solvents removed under reduced pressure and the residue purified by flash silica gel chromatography (gradient PE/ethyl acetate).

General Procedure E

Chlorination: To a mixture of the starting material (1 mmol) and anhydrous DMF (0.3 equiv.) in anhydrous DCM (3 mL) was added oxalyl chloride (2.6 equiv.) in anhydrous DCM (3 mL) dropwise. The mixture was stirred at room temperature for 1 h, concentrated and the residue was filtered quickly through silica gel (gradient PE/ethyl acetate).

General Procedure F

Bromination: To a solution of the starting material (1 mmol) in anhydrous DCM (10 mL) was added oxalyl bromide (1.25 equiv.). After stirring for 1 h at room temperature the mixture was diluted with DCM (40 mL), filtered quickly through Celite and concentrated.

General Procedure G1

Base-promoted Glycosylation with Permethylated Glycosyl Donors: The acceptor (0.1 mmol) was dissolved in anhydrous DMF (2.0 mL), treated with the specified amount of base (2–4 equiv.) and stirred for 1 h. The donor (2–4 equiv.) in anhydrous DMF (2.0 mL) was added, and the mixture was stirred for 2–90 h. The reaction was quenched by addition of methanol (1 mL), and the solvents were removed under reduced pressure. The remaining syrup was taken up in pyridine and acetic anhydride (2:1 v/v, 6 mL) and stirred for 18 h. Pyridine was removed under reduced pressure and by co-distilling with toluene. The residue was purified by column chromatography (gradient PE/ethyl acetate) to give the disaccharide mixtures the relative yield of which was determined by ^1H NMR spectroscopy.

General Procedure G2

Base-promoted Glycosylation with Perbenzylated Glycosyl Donors: Glycosylation reactions were performed as described above (general procedure G1) without subsequent acetylation. Products were separated and purified by column chromatography.

Methyl 3,6-Di-*O*-methyl-α-D-glucopyranoside (5): Prepared according to procedure D. Compound **43** (2.26 g, 5.63 mmol), Pd(10%)/C (204 mg), MeOH (40 mL). Yield: 89% (1.12 g, 5.02 mmol), colourless solid, R_f = 0.15 [ethyl acetate (EA)], m.p. 68–70 °C, $[\alpha]_D^{25}$ = +127.9 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.76 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 3.74–3.70 (m, 1 H, 5-H), 3.67–3.58 (m, 3 H, 6-H, 2-H), 3.54 (dd, $^3J_{3,4}$ = 9.2 Hz, $^3J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.35 (dd, $^3J_{2,3}$ = 9.3 Hz, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.68. 3.45, 3.42 (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 99.6 (C-1), 84.2 (C-3), 72.4 (C-2), 72.2 (C-6), 70.7 (C-4), 69.8 (C-5), 60.8, 59.5, 55.4 (OCH_3) ppm. HRMS (ESI): calcd. for $C_9H_{18}O_6$ [M + Na]$^+$ 245.0996; found 245.0988.

Methyl 3,4-Di-*O*-methyl-α-D-glucopyranoside (6): Prepared according to procedure D. Compound **39** (1.33 g, 3.30 mmol), Pd(10%)/C (149 mg), MeOH (30 mL). Yield: 99% (720 mg, 3.25 mmol), colourless solid, R_f = 0.19 (EA), m.p. 53 °C, $[\alpha]_D^{25}$ = +166.0 (c = 0.2, $CHCl_3$) {ref.[21] $[\alpha]_D^{25}$ = +176.6 (c = 0.48, $CHCl_3$)}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.74 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 3.87–3.81 (m, 1 H, 6a-H), 3.73–3.71 (m, 1 H, 6b-H), 3.61–3.50 (m, 2 H, 2-H, 5-H), 3.38 (dd, $^3J_{2,3}$ = 9.3 Hz, $^3J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 3.17 (dd, $^3J_{3,4}$ = 8.8 Hz, $^3J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 3.66, 3.56, 3.42 (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 99.3 (C-1), 84.3 (C-3) 79.5 (C-4), 72.5 (C-2) 71.0 (C-5) 61.8 (C-6), 60.9, 60.4, 55.3 (OCH_3) ppm. HRMS (ESI): calcd. for $C_9H_{18}O_6$ [M + Na]$^+$ 245.0996; found 245.0996.

Methyl 2,4-Di-*O*-methyl-α-D-glucopyranoside (7): Prepared according to procedure D. Compound **39** (2.08 g, 5.17 mmol), Pd(10%)/C (250 mg), MeOH (50 mL). Yield: 98% (1.13 g, 5.06 mmol), colourless solid, R_f = 0.16 (EA), m.p. 78 °C, $[\alpha]_D^{25}$ = +156.2 (c = 0.83, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.87 (d, $^3J_{1,2}$ = 3.4 Hz, 1 H, 1-H), 3.94 (dd, $^3J_{2,3}$ = 9.2 Hz, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.85 (dd, $^3J_{5,6a}$ = 2.9 Hz, $^2J_{6a,6b}$ = 11.8 Hz, 1 H, 6a-H), 3.76 (dd, $^3J_{5,6b}$ = 4.0 Hz, $^2J_{6a,6b}$ = 11.8 Hz, 1 H, 6b-H), 3.61–3.55 (m, 1 H, 5-H), 3.22 (dd, $^3J_{3,4}$ = 9.2 Hz, $^3J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.16 (dd, $^3J_{1,2}$ = 3.4 Hz, $^3J_{2,3}$ = 9.2 Hz, 1 H, 2-H), 3.60, 3.51, 3.41 (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 96.7 (C-1), 81.4 (C-2), 79.3 (C-4), 73.1 (C-3), 70.4 (C-5), 62.0 (C-6), 60.6, 58.5, 55.3 (OCH_3) ppm. HRMS (ESI): calcd. for $C_9H_{18}O_6$ [M + Na]$^+$ 245.0996; found 245.0992.

Methyl 2,6-Di-*O*-methyl-α-D-glucopyranoside (9): Prepared according to procedure D. Compound **40** (820 mg, 2.04 mmol), Pd(10%)/C (200 mg), MeOH (40 mL). Yield: quant. (453 mg, 2.04 mmol), colourless syrup, R_f = 0.18 (PE/EA, 1:1), $[\alpha]_D^{25}$ = +149.7 (c = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.91 (d, $^3J_{1,2}$ = 3.3 Hz, 1 H, 1-H), 3.86 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.73–3.61 (m, 3 H, 5-H, 6a-H, 6b-H), 3.61–3.56 (m, 1 H, 4-H), 3.21 (dd, $^3J_{1,2}$ = 3.3 Hz, $^3J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 3.50, 3.44, 3.44 (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 96.9 (C-1), 80.9 (C-2), 73.0 (C-3), 72.0 (C-6), 70.9 (C-4), 69.5 (C-5), 59.5, 58.3, 55.3 (OCH_3) ppm. HRMS (ESI): calcd. for $C_9H_{18}O_6$ [M + Na]$^+$ 245.0996; found 245.0985.

Methyl 4-*O*-Methyl-α-D-glucopyranoside (11): Prepared according to procedure D. Compound **36** (631 mg, 1.32 mmol), Pd(10%)/C (202 mg), MeOH (50 mL). Yield: 75% (209 mg, 0.989 mmol), colourless solid, R_f = 0.06 (EA), m.p. 97 °C (ref.[22] m.p. 98 °C), $[\alpha]_D^{25}$ = +197.3 (c = 0.48, EtOH) {ref.[22] $[\alpha]_D^{25}$ = +191 (EtOH)}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.75 (d, $^3J_{1,2}$ = 4.1 Hz, 1 H, 1-H), 3.86 (dd, $^3J_{5,6a}$ = 2.8 Hz, $^2J_{6a,6b}$ = 12.1 Hz, 1 H, 6a-H), 3.78 (dd, $^3J_{2,3}$ = 9.5 Hz, $^3J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 3.76 (dd, $^3J_{5,6b}$ = 4.6 Hz, $^2J_{6a,6b}$ = 12.1 Hz, 1 H, 6b-H), 3.59, 3.42 (s, 3 H, OCH_3), 3.58–3.54 (m, 1 H, 5-H), 3.50 (dd, $^3J_{1,2}$ = 4.1 Hz, $^3J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 3.18 (dd, $^3J_{3,4}$ = 9.1 Hz, $^3J_{4,5}$ = 9.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 99.0 (C-1), 79.2 (C-4), 74.8 (C-3), 72.7 (C-2), 70.8 (C-5), 61.9 (C-6), 60.7, 55.4 (OCH_3) ppm. HRMS (ESI): calcd. for $C_8H_{16}O_6$ [M + Na]$^+$ calcd. 245.0839; found 231.0844.

Methyl 6-*O*-Methyl-α-D-glucopyranoside (13): Prepared according to procedure D. Compound **37** (1.14 g, 2.38 mmol), Pd(10%)/C (110 mg), MeOH (50 mL). Yield: 95% (470 mg, 2.26 mmol), colourless syrup, R_f = 0.07 (EA), $[\alpha]_D^{25}$ = +145.5 (c = 0.2, H_2O) {ref.[23] $[\alpha]_D$ = +128 (H_2O)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.78 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 3.75 (dd, $^3J_{2,3}$ = 9.2 Hz, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.70–3.60 (m, 3 H, 5-H, 6-H), 3.57–3.49 (m, 2 H, 2-H, 4-H), 3.43, 3.42 (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 99.5 (C-1), 75.1 (C-3), 72.5 (C-2), 72.4 (C-6), 71.3 (C-4), 69.9 (C-5), 59.7, 55.6 (OCH$_3$) ppm. HRMS (ESI): calcd. for $C_8H_{16}O_6$ [M + Na]$^+$ 245.0839; found 231.0838.

2,3,4,6-Tetra-*O*-methyl-α-D-glucopyranosyl Chloride (15): Prepared according to procedure E. Compound **50** (500 mg, 2.12 mmol), DMF (50 μL, 0.64 mmol), oxalyl chloride (500 μL, 5.71 mmol), DCM (10 mL). Yield: 48% (259 mg, 1.02 mmol), yellow liquid, R_f = 0.55 (EA), $[\alpha]_D^{25}$ = +182.7 (c = 0.99, $CHCl_3$) {ref.[24] $[\alpha]_D^{25}$ = +205.3 (c = 1.0, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.20 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 3.94 (ddd, $^3J_{4,5}$ = 10.0 Hz, $^3J_{5,6a}$ = 3.8 Hz, $^3J_{5,6b}$ = 2.0 Hz, 1 H, 5-H), 3.65 (dd, $^3J_{5,6a}$ = 3.8 Hz, $^2J_{6a,6b}$ = 10.8 Hz, 1 H, 6a-H), 3.59 (dd, $^3J_{5,6b}$ = 2.0 Hz, $^2J_{6a,6b}$ = 10.8 Hz, 1 H, 6b-H), 3.55 (dd, $^3J_{2,3}$ = 9.3 Hz, $^3J_{3,4}$ = 9.0 Hz, 1 H, 3-H), 3.38 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.30 (dd, $^3J_{3,4}$ = 9.0 Hz, $^3J_{4,5}$ = 10.0 Hz, 1 H, 4-H), 3.65, 3.56, 3.51, 3.42, (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 92.9 (C-1), 82.8 (C-3), 81.9 (C-2), 78.2 (C-4), 73.2 (C-5), 70.4 (C-6), 61.0, 60.6, 59.2, 58.5 (OCH$_3$) ppm.

2,3,4,6-Tetra-*O*-methyl-α-D-mannopyranosyl Chloride (17): Prepared according to procedure E. Compound **52** (214 mg, 0.907 mmol), DMF (20 μL, 0.26 mmol), oxalyl chloride (200 μL, 2.33 mmol), DCM (8 mL). Yield: 74% (171 mg, 0.671 mmol), yellow liquid, R_f = 0.40 (PE/EA, 1:1), $[\alpha]_D^{25}$ = +124.0 (c = 0.2, $CHCl_3$) {ref.[24] $[\alpha]_D^{25}$ = +99.2 (c = 1.0, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.19 (d, $^3J_{1,2}$ = 1.7 Hz, 1 H, 1-H), 3.88 (ddd, $^3J_{4,5}$ = 9.9 Hz, $^3J_{5,6a}$ = 4.3 Hz, $^3J_{5,6b}$ = 2.1 Hz, 1 H, 5-H), 3.81 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 3.74 (dd, $^3J_{1,2}$ = 1.7 Hz, $^3J_{2,3}$ = 3.3 Hz, 1 H, 2-H), 3.65 (dd, $^3J_{5,6a}$ = 4.3 Hz, $^2J_{6a,6b}$ = 10.8 Hz, 1 H, 6a-H), 3.60 (dd, $^3J_{5,6b}$ = 2.1 Hz, $^2J_{6a,6b}$ = 10.8 Hz, 1 H, 6b-H), 3.55 (dd, $^3J_{3,4}$ = 9.4 Hz, $^3J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 3.55, 3.53, 3.51, 3.40 (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 90.7 (C-1), 80.2 (C-2), 79.8 (C-3), 75.7 (C-4), 74.1 (C-5), 70.8 (C-6), 60.7, 59.2, 59.1, 58.0 (OCH$_3$) ppm.

2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl Bromide (18): Prepared according to procedure F. Compound **55** (932 mg, 1.72 mmol), oxalyl bromide (200 μL, 2.16 mmol), DCM (15 mL). Yield: 79% (820 mg, 1.36 mmol), yellow liquid, R_f = 0.81 (DCM/EA, 9:1), too labile for $[\alpha]_D^{25}$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.17 (m, 20 H, $H_{arom.}$), 6.48 (d, $^3J_{1,2}$ = 1.0 Hz, 1 H, 1-H), 4.92 (d, $^2J_{A,A'}$ = 10.8 Hz, 1 H, OCH_2Ph-A), 4.73–4.63 (m, 4 H, OCH_2Ph-B, C, D, D′), 4.61 (d, $^2J_{B,B'}$ = 11.8 Hz, 1 H, OCH_2Ph-B′), 4.56 (d, $^2J_{A,A'}$ = 10.8 Hz, 1 H, OCH_2Ph-A′), 4.52 (d, $^2J_{C,C'}$ = 12.3 Hz, 1 H, OCH_2Ph-C′), 4.32 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 4.13 (dd, $^3J_{3,4}$ = 9.5 Hz, $^3J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 3.99–3.94 (m, 2 H, 2-H, 5-H), 3.84 (dd, $^3J_{5,6a}$ = 4.3 Hz, $^2J_{6a,6b}$ = 11.3 Hz, 1 H, 6a-H), 3.71 (dd, $^3J_{5,6b}$ = 1.8, $^2J_{6a,6b}$ = 11.3 Hz, 1 H, 6b-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.2 138.0, 137.6 ($C_{arom.}$), 128.9, 128.8, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5 (CH$_{arom.}$), 88.2 (C-1), 78.6 (C-5), 78.4 (C-3), 76.1 (C-2), 75.3 (OCH$_2$Ph-A), 74.0 (C-4), 73.4 (OCH$_2$Ph-D), 72.9 (OCH$_2$Ph-B), 72.5 (OCH$_2$Ph-C), 69.0 (C-6) ppm.

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl Bromide (19): Prepared according to procedure F. Compound **56** (835 mg, 1.54 mmol), oxalyl bromide (185 μL, 1.98 mmol), DCM (15 mL). Yield: 83% (771 mg, 1.28 mmol), yellow liquid, R_f = 0.70 (PE/EA, 1:2), too labile for $[\alpha]_D^{25}$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.23 (m, 20 H, $H_{arom.}$), 6.53 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.96 (d, $^2J_{A,A'}$ = 11.5 Hz, 1 H, OCH_2Ph-A), 4.87 (d, $^2J_{B,B'}$ = 11.7 Hz, 1 H, OCH_2Ph-B), 4.79 (d, $^2J_{C,C'}$ = 11.9 Hz, 1 H, OCH_2Ph-C), 4.76 (d, $^2J_{B,B'}$ = 11.7 Hz, 1 H, OCH_2Ph-B′), 4.73 (d, $^2J_{C,C'}$ = 11.9 Hz, 1 H, OCH_2Ph-C′), 4.57 (d, $^2J_{A,A'}$ = 11.5 Hz, 1 H, OCH_2Ph-A′), 4.50 (d, $^2J_{D,D'}$ = 12.0 Hz, 1 H, OCH_2Ph-D), 4.42 (d, $^2J_{D,D'}$ = 12.0 Hz, 1 H, OCH_2Ph-D′), 4.27–4.22 (m, 1 H, 5-H), 4.22 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 4.01 (dd, $^3J_{3,4}$ = 2.8 Hz, $^3J_{4,5}$ = 1.0 Hz, 1 H, 4-H), 3.98 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{3,4}$ = 2.8 Hz, 1 H, 3-H), 3.57 (dd, $^3J_{5,6a}$ = 6.9 Hz, $^2J_{6a,6b}$ = 9.4 Hz, 1 H, 6a-H), 3.54 (dd, $^3J_{5,6b}$ = 6.1 Hz, $^2J_{6a,6b}$ = 9.4 Hz, 1 H, 6b-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 138.3, 137.8, 137.7 ($C_{arom.}$), 128.4, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5 (CH$_{arom.}$), 94.9 (C-1), 78.4 (C-3), 76.2 (C-2), 75.0 (OCH$_2$Ph-A), 74.4 (C-4), 73.5 (OCH$_2$Ph-D), 73.4 (OCH$_2$Ph-B), 73.1 (OCH$_2$Ph-C), 72.4 (C-5), 68.0 (C-6) ppm.

2,3,4-Tri-*O*-benzyl-β-L-arabinopyranosyl Chloride (20): To a solution of **57** (10.5 g, 33.0 mmol) in anhydrous DCM (100 mL) was added thiophenole (3.73 mL, 36.3 mmol) and BF_3·OEt_2 (4.60 mL, 36.3 mmol). The reaction mixture was stirred for 18 h, diluted with DCM, washed with saturated $NaHCO_3$ solution, dried and concentrated to yield 99% of **58** (11.5 g, 32.6 mmol), R_f = 0.54 (PE/EA, 1:1), which was used in the next step without further purification. Compound **58** (11.5 g, 32.6 mmol) was dissolved in anhydrous MeOH (150 mL), 0.1 M NaOMe solution was added to reach pH 8–9 and the mixture was stirred for 4 h. Subsequently, the solution was neutralized with Amberlite IR-120 (H^+) resin, filtered and concentrated. 99% **59** (7.8 g, 32.2 mmol) was obtained with R_f = 0.21 (DCM/MeOH, 10:1), which was benzylated according to procedure A1: **59** (7.8 g, 32.2 mmol), NaH (7.73 g, 193 mmol), BnBr (23.1 mL, 193 mmol), DMF (70 mL). Yield: 91% (16.0 g, 29.3 mmol) of **60**, R_f = 0.54 (PE/EA, 1:1), which was stirred with NBS (15.6 g, 87.8 mmol) in acetone/water (9:1) for 3 h at room temperature. Subsequently, ethyl acetate and water were added, the organic layer was washed with sat. $NaHCO_3$ solution, dried and concentrated. The residue was purified by column chromatography (petroleum ether ether/ethyl acetate). Yield of **61**: 63% (7.73 g, 18.4 mmol), in the furanose R_f = 0.36 (PE/EA, 2:1) and pyranose R_f = 0.22 (PE/EA, 2:1) forms. Finally, **20** was prepared according to procedure E. Compound **61** (500 mg, 1.19 mmol), DMF (18 μL, 0.35 mmol), oxalyl chloride (270 μL, 3.09 mmol), DCM (20 mL). Yield: 64% (336 mg, 0.765 mmol), colourless liquid, R_f = 0.75 (PE/EA, 1:1), $[\alpha]_D^{25}$ = +126.0 (c = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 15 H, $H_{arom.}$), 6.17 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.84 (d, $^2J_{A,A'}$ = 12.0 Hz, 1 H, OCH_2Ph-A), 4.80 (d, $^2J_{B,B'}$ = 11.8 Hz, 1 H, OCH_2Ph-B), 4.80–4.70 (m, 3 H, OCH_2Ph-C, C′, A′), 4.67 (d, $^2J_{B,B'}$ = 11.8 Hz, 1 H, OCH_2Ph-B′), 4.23 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.8 Hz, 1 H, 2-H), 3.98–3.91 (m, 2 H, 3-H, 5a-H), 3.87 (dd, $^3J_{4,5b}$ = 1.9 Hz, $^2J_{5a,5b}$ = 12.8 Hz, 1 H, 5b-H), 3.83–3.79 (m, 1 H, 4-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.4, 138.0, 138.0 ($C_{arom.}$), 128.4, 128.4, 128.4, 127.9, 127.9, 127.9, 127.8, 127.6 (CH$_{arom.}$), 95.7 (C-1), 76.8 (C-3), 76.2 (C-2), 73.4 (C-4), 73.2 (OCH$_2$Ph-A), 73.0 (OCH$_2$Ph-B), 72.1 (OCH$_2$Ph-C), 63.3 (C-5) ppm.

Methyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-methyl-α-D-glucopyranoside (27): Prepared according to procedure A1. Compound **24**[12] (6.1 g, 16 mmol), NaH (1.3 g, 33 mmol), MeI (2.1 mL, 34 mmol), DMF (70 mL). Yield: 99% (6.18 g, 16.0 mmol), colourless solid, R_f = 0.57 (PE/EA, 2:1), m.p. 97 °C (ref.[25] m.p. 97–98 °C), $[\alpha]_D^{25}$ = +29.8 (c = 0.5, $CHCl_3$) {ref.[25] $[\alpha]_D^{25}$ = +21.0 (c = 0.98, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.48 (m, 2 H, $H_{arom.}$), 7.42–

7.28 (m, 8 H, $H_{arom.}$), 5.53 (s, 1 H, PhC*H*OO), 4.86 (d, $^2J_{A,A'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-A), 4.69 (d, $^2J_{A,A'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-A′), 4.56 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.26 (dd, $^3J_{5,6a}$ = 4.8 Hz, $^2J_{6a,6b}$ = 10.2 Hz, 1 H, 6a-H), 3.82 (ddd, $^3J_{4,5}$ = 9.9 Hz, $^3J_{5,6a}$ = 4.8 Hz, $^3J_{5,6b}$ = 10.2 Hz, 1 H, 5-H), 3.77 (dd, $^3J_{2,3}$ = 9.2 Hz, $^3J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 3.71 (dd, $^3J_{5,6b}$ = 10.2 Hz, $^2J_{6a,6b}$ = 10.2 Hz, 1 H, 6b-H), 3.51 (dd, $^3J_{3,4}$ = 9.4 Hz, $^3J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 3.47 (dd, $^3J_{1,2}$ = 3.8, $^3J_{2,3}$ = 9.2 Hz, 1 H, 2-H), 3.65, 3.40 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.2, 137.4 ($C_{arom.}$), 128.9, 128.4, 128.2, 128.1, 127.9, 126.1 (*C*H$_{arom.}$), 101.4 (Ph*C*HOO), 99.2 (C-1), 82.1 (C-4), 80.0 (C-3), 79.0 (C-2), 73.7 (O*C*H$_2$Ph-A), 69.0 (C-6), 62.2 (C-5), 61.2, 55.3 (O*C*H$_3$) ppm. MS (MALDI-TOF): *m*/*z* = 409.3 $C_{22}H_{26}O_6$ [M + Na]$^+$ (calcd. 409.2).

Methyl 3,6-Di-*O*-benzyl-α-D-glucopyranoside (28): Prepared according to procedure B2. Compound **25**[12] (3.07 g, 8.25 mmol), $NaCNBH_3$ (3.62 g, 57.6 mmol), F_3CSO_3H (5.1 mL, 58.5 mmol), THF (75 mL). Yield: 81% (2.49 g, 6.65 mmol), colourless oil, R_f = 0.25 (PE/EA, 1:1), $[\alpha]_D^{25}$ = +65.2 (*c* = 0.71, $CHCl_3$) {ref.[21] $[\alpha]_D^{25}$ = +79.2 (*c* = 3.5, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 10 H, $H_{arom.}$), 4.97 (d, $^2J_{A,A'}$ = 11.5 Hz, 1 H, OC*H*$_2$Ph-A), 4.79 (d, $^2J_{A,A'}$ = 11.5 Hz, 1 H, OC*H*$_2$Ph-A′), 4.78 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.62 (d, $^2J_{B,B'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-B), 4.56 (d, $^2J_{B,B'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-B′), 3.76–3.72 (m, 1 H, 5-H), 3.72–3.70 (m, 2 H, 6-H), 3.70–3.66 (m, 1 H, 2-H), 3.65–3.61 (m, 1 H, 4-H), 3.59 (dd, $^3J_{2,3}$ = 8.7, $^3J_{3,4}$ = 8.9 Hz, 1 H, 3-H), 3.44 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.7, 137.9 ($C_{arom.}$), 128.3, 127.9, 127.7, 127.6, 127.5 (*C*Harom.), 99.5 (C-1), 82.7 (C-3), 74.9 (O*C*H$_2$Ph-A), 73.7 (O*C*H$_2$Ph-B), 72.6 (C-2), 71.0 (C-4), 70.0 (C-5), 69.8 (C-6), 55.3 (O*C*H$_3$) ppm. MS (MALDI-TOF): *m*/*z* = 397.6 $C_{21}H_{26}O_6$ [M + Na]$^+$ (calcd. 397.2).

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-methyl-α-D-glucopyranoside (29): Prepared according to procedure A1. Compound **25**[12] (2.19 g, 5.85 mmol), NaH (470 mg, 11.8 mmol), MeI (6.0 mL, 12 mmol, 2 M solution in MTBE), DMF (30 mL). Yield: 89% (2.03 g, 5.26 mmol), colourless solid, R_f = 0.38 (PE/EA, 2:1), m.p. 110 °C, $[\alpha]_D^{25}$ = +61.0 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.48 (m, 2 H, $H_{arom.}$), 7.42–7.34 (m, 3 H, $H_{arom.}$), 7.33–7.24 (m, 5 H, $H_{arom.}$), 5.57 (s, 1 H, PhC*H*OO), 4.89 (d, $^2J_{A,A'}$ = 11.5 Hz, 1 H, OC*H*$_2$Ph-A), 4.88 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.81 (d, $^2J_{A,A'}$ = 11.5 Hz, 1 H, OC*H*$_2$Ph-A′), 4.30 (dd, $^3J_{5,6a}$ = 4.7 Hz, $^2J_{6a,6b}$ = 10.1 Hz, 1 H, 6a-H), 3.99 (dd, $^3J_{2,3}$ = 9.2 Hz, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.84 (ddd, $^3J_{4,5}$ = 9.4 Hz, $^3J_{5,6a}$ = 4.7 Hz, $^3J_{5,6b}$ = 10.1 Hz, 1 H, 5-H), 3.75 (dd, $^3J_{5,6b}$ = 10.1 Hz, $^2J_{6a,6b}$ = 10.1 Hz, 1 H, 6b-H), 3.63 (dd, $^3J_{3,4}$ = 9.2 Hz, $^3J_{4,5}$ = 9.4 Hz, 1 H, 4-H), 3.59, 3.46 (s, 3 H, OC*H*$_3$), 3.39 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.7, 137.4 ($C_{arom.}$), 128.9, 128.3, 128.2, 127.9, 127.5, 126.0 (*C*H$_{arom.}$), 101.3 (Ph*C*HOO), 98.6 (C-1), 82.0 (C-4), 81.8 (C-2), 78.5 (C-3), 75.1 (O*C*H$_2$Ph-A), 69.1 (C-6), 62.3 (C-5), 59.8, 55.3 (O*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_{22}H_{26}O_6$ [M + Na]$^+$ 409.1622; found 409.1624.

Methyl 2,3,6-Tri-*O*-benzyl-α-D-glucopyranoside (30): Prepared according to procedure B2. Compound **26**[12] (1.01 g, 2.18 mmol), $NaCNBH_3$ (0.96 g, 15 mmol), F_3CSO_3H (1.3 mL, 15 mmol), THF (50 mL). Yield: 70% (717 mg, 1.54 mmol), colourless syrup, R_f = 0.59 (PE/EA, 1:1), $[\alpha]_D^{25}$ = +12.5 (*c* = 1.0, $CHCl_3$) {ref.[26] $[\alpha]_D^{23}$ = +11.9 (*c* = 2.67, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 15 H, H_{arom}), 5.01 (d, $^2J_{A,A'}$ = 11.4 Hz, 1 H, OC*H*$_2$Ph-A), 4.78 (d, $^2J_{B,B'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-B), 4.75 (d, $^2J_{A,A'}$ = 11.4 Hz, 1 H, OC*H*$_2$Ph-A′), 4.67 (d, $^2J_{B,B'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-B′), 4.64 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H) 4.60 (d, $^2J_{C,C'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-C), 4.55 (d, $^2J_{C,C'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-C′), 3.80 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.75–3.66 (m, 3 H, 5-H, 6-H), 3.61 (dd, $^3J_{3,4}$ = 9.2 Hz, $^3J_{4,5}$ = 9.1 Hz, 1 H, 4-H), 3.55 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 3.40 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.8, 138.0, 138.0 ($C_{arom.}$), 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.6 (*C*H$_{arom.}$), 98.2 (C-1), 81.4 (C-3), 79.6 (C-2), 75.4 (O*C*H$_2$Ph-A), 73.6 (O*C*H$_2$Ph-C), 73.2 (O*C*H$_2$Ph-B), 70.7 (C-4), 69.9 (C-5), 69.5 (C-6), 55.2 (O*C*H$_3$) ppm. MS (MALDI-TOF): *m*/*z* = 488.0 $C_{28}H_{32}O_6$ [M + Na]$^+$ (calcd. 487.2).

Methyl 2,3,4-Tri-*O*-benzyl-α-D-glucopyranoside (31): Prepared according to procedure B1. Compound **26**[12] (4.02 g, 8.69 mmol), $LiAlH_4$ (2.31 g, 60.8 mmol), $AlCl_3$ (5.2 g, 39 mmol), DCM (40 mL), Et_2O (40 mL). Yield: 89% (3.60 g, 7.75 mmol), colourless syrup, R_f = 0.12 (PE/EA, 2:1), $[\alpha]_D^{25}$ = +29.0 (*c* = 1.0, $CHCl_3$) {ref.[26] $[\alpha]_D^{23}$ = +24 (*c* = 1.01, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 15 H, $H_{arom.}$), 5.01 (d, $^2J_{A,A'}$ = 10.9 Hz, 1 H, OC*H*$_2$Ph-A), 4.90 (d, $^2J_{B,B'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-B), 4.85 (d, $^2J_{A,A'}$ = 10.9 Hz, 1 H, OC*H*$_2$Ph-A′), 4.82 (d, $^2J_{C,C'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-C), 4.68 (d, $^2J_{C,C'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-C′), 4.66 (d, $^2J_{B,B'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-B′), 4.59 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.03 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 3.79 (dd, $^3J_{5,6a}$ = 2.5 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1 H, 6a-H), 3.71 (dd, $^3J_{5,6b}$ = 3.8 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1 H, 6b-H), 3.71–3.64 (m, 1 H, 5-H), 3.54 (dd, $^3J_{3,4}$ = 9.3 Hz, $^3J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.52 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 3.38 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.8, 138.2 ($C_{arom.}$), 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 127.6 (*C*H$_{arom.}$), 98.2 (C-1), 82.0 (C-3), 80.0 (C-2), 77.5 (C-4), 75.7 (O*C*H$_2$Ph-A), 75.0 (O*C*H$_2$Ph-B), 73.4 (O*C*H$_2$Ph-C), 70.7 (C-5), 61.9 (C-6), 55.2 (O*C*H$_3$) ppm.

Methyl 2-*O*-Benzyl-3-*O*-methyl-α-D-glucopyranoside (32): Compound **27** (4.00 g, 10.4 mmol) was suspended in distilled methanol (80 mL) and treated with H_2O (8 mL) and 1 N HCl (1 mL). The mixture was stirred for 3 h at 55 °C and neutralized by addition of $NaHCO_3$ solution. Solvents were removed under reduced pressure, co-distilling with toluene, and the residue purified by flash silica gel chromatography (gradient PE/ethyl acetate). Yield: 98% (3.05 g, 10.2 mmol), colourless syrup, R_f = 0.09 (PE/EA, 2:1), $[\alpha]_D^{25}$ = +63.3 (*c* = 0.53, $CHCl_3$) {ref.[25] $[\alpha]_D^{24}$ = +59.0 (*c* = 0.98, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 5 H, $H_{arom.}$), 4.76 (d, $^2J_{A,A'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-A), 4.63 (d, $^2J_{A,A'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-A′), 4.58 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 3.85–3.76 (m, 2 H, 6-H), 3.66–3.60 (m, 1 H, 5-H), 3.55 (dd, $^3J_{2,3}$ = 9.4 Hz, $^3J_{3,4}$ = 8.9 Hz, 1 H, 3-H), 3.49 (dd, $^3J_{3,4}$ = 8.9 Hz, $^3J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.41 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.4 Hz, 1 H, 2-H), 3.69, 3.38 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.0 ($C_{arom.}$), 128.5, 128.0, 127.9 (*C*H$_{arom.}$), 98.2 (C-1), 82.9 (C-3), 79.7 (C-2), 73.0 (O*C*H$_2$Ph-A), 70.7 (C-5), 70.4 (C-4), 62.3 (C-6), 61.4, 55.2 (O*C*H$_3$) ppm.

Methyl 2,6-Di-*O*-benzyl-3-*O*-methyl-α-D-glucopyranoside (33): Prepared according to procedure B2. Compound **27** (1.50 g, 3.88 mmol), $NaCNBH_3$ (1.71 g, 27.2 mmol), F_3CSO_3H (2.36 mL, 27.2 mmol), THF (50 mL). Yield: 87% (1.32 g, 3.40 mmol), colourless oil, R_f = 0.29 (PE/EA, 1:1), $[\alpha]_D^{25}$ = +64.2 (*c* = 1.0, HCl_3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.25 (m, 10 H, $H_{arom.}$), 4.76 (d, $^2J_{A,A'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-A), 4.63 (d, $^2J_{A,A'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-A′), 4.61 (d, $^2J_{B,B'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-B), 4.61 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.55 (d, $^2J_{B,B'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-B′), 3.75–3.65 (m, 3 H, 4-H, 6-H), 3.59–3.49 (m, 2 H, 5-H, 3-H), 3.48–3.40 (m, 1 H, 2-H), 3.67, 3.36 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.1, 137.9 ($C_{arom.}$), 128.4, 128.3, 128.0, 127.8, 127.6, 127.6 (*C*H$_{arom.}$), 98.2 (C-1), 82.9 (C-3), 79.5 (C-2), 73.5 (O*C*H$_2$Ph-B), 73.0 (O*C*H$_2$Ph-A), 70.9 (C-5), 69.7

(C-4), 69.5 (C-6), 61.3, 55.2 (O*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_{22}H_{28}O_6$ [M + Na]$^+$ 411.1778; found 411.1777.

Methyl 3,6-Di-*O*-benzyl-2,4-di-*O*-methyl-α-D-glucopyranoside (34): Prepared according to procedure A1. Compound **28** (2.22 g, 5.93 mmol), NaH (1.24 g, 31.0 mmol), MeI (1.8 mL, 29 mmol), DMF (50 mL). Yield: 88% (6.18 g, 16.0 mmol), yellow oil, R_f = 0.49 (PE/EA, 1:1), $[a]_D^{25}$ = +81.6 (c = 0.63, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.25 (m, 10 H, H$_{arom.}$), 4.89 (d, $^2J_{A,A'}$ = 11.4 Hz, 1 H, OC*H*$_2$Ph-A), 4.87 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.77 (d, $^2J_{A,A'}$ = 11.4 Hz, 1 H, OC*H*$_2$Ph-A′), 4.67 (d, $^2J_{B,B'}$ = 12.1 Hz, 1 H, OC*H*$_2$Ph-B), 4.55 (d, $^2J_{B,B'}$ = 12.1 Hz, 1 H, OC*H*$_2$Ph-B′), 3.81 (dd, $^3J_{2,3}$ = 9.3 Hz, $^3J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 3.75–3.71 (m, 1 H, 6a-H), 3.70–3.62 (m, 2 H, 6b-H, 5-H), 3.35 (dd, $^3J_{3,4}$ = 9.4 Hz, $^3J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.33 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.54, 3.47, 3.44 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.0, 138.1 (C$_{arom.}$), 128.3, 127.9, 127.7, 127.6, 127.5 (*C*H$_{arom.}$), 97.6 (C-1), 82.1 (C-2), 82.1 (C-3), 79.4 (C-4), 75.5 (O*C*H$_2$Ph-A), 73.5 (O*C*H$_2$Ph-B), 70.3 (C-5), 68.7 (C-6), 60.7, 59.2, 55.2 (O*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_{23}H_{30}O_6$ [M + Na]$^+$ 425.1935; found 425.1933.

Methyl 3,4-Di-*O*-benzyl-2-*O*-methyl-α-D-glucopyranoside (35): Prepared according to procedure B1. Compound **29** (1.31 g, 3.39 mmol), $LiAlH_4$ (914 mg, 24.1 mmol), $AlCl_3$ (1.81 g, 13.6 mmol), DCM (30 mL), Et_2O (30 mL). Yield: 93% (1.23 g, 3.17 mmol), colourless syrup, R_f = 0.37 (PE/EA, 1:2), $[a]_D^{25}$ = +95.0 (c = 0.2, $CHCl_3$) {ref.[25] $[a]_D^{23}$ = +77.0 (c = 1.0, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 10 H, H$_{arom}$), 4.94 (d, $^2J_{A,A'}$ = 10.9 Hz, 1 H, OC*H*$_2$Ph-A), 4.90 (d, $^2J_{B,B'}$ = 11.2 Hz, 1 H, OC*H*$_2$Ph-B), 4.86 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.81 (d, $^2J_{A,A'}$ = 10.9 Hz, 1 H, OC*H*$_2$Ph-A′), 4.66 (d, $^2J_{B,B'}$ = 11.2 Hz, 1 H, OC*H*$_2$Ph-B′), 3.95 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.82 (dd, $^3J_{5,6a}$ = 2.8 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1 H, 6a-H), 3.73 (dd, $^3J_{5,6b}$ = 4.0 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1 H, 6b-H), 3.67 (ddd, $^3J_{4,5}$ = 9.7 Hz, $^3J_{5,6a}$ = 2.8 Hz, $^3J_{5,6b}$ = 4.0 Hz, 1 H, 5-H), 3.55 (dd, $^3J_{3,4}$ = 9.2 Hz, $^3J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 3.33 (d, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 3.56, 3.43 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.7, 138.1 (C$_{arom.}$), 128.5, 128.4, 128.0, 127.9, 127.9, 127.6 (*C*H$_{arom.}$), 97.5 (C-1), 82.4 (C-2), 81.9 (C-3), 77.2 (C-4), 75.6 (O*C*H$_2$Ph-A), 75.0 (O*C*H$_2$Ph-B), 70.7 (C-5), 61.9 (C-6), 59.2, 55.1 (O*C*H$_3$) ppm.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-methyl-α-D-glucopyranoside (36): Prepared according to procedure A1. Compound **30** (681 mg, 1.47 mmol), NaH (128 mg, 3.23 mmol), MeI [1.6 mL, 3.2 mmol, 2 M solution in methyl *t*-butyl ether (MTBE)], DMF (40 mL). Yield: 94% (661 mg, 1.38 mmol), colourless syrup, R_f = 0.21 (PE/EA, 4:1), $[a]_D^{25}$ = +39.0 (c = 1.06, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.27 (m, 15 H, H$_{arom.}$), 4.95 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-A), 4.81 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-A′), 4.79 (d, $^2J_{B,B'}$ = 12.3 Hz, 1 H, OC*H*$_2$Ph-B), 4.66 (d, $^2J_{B,B'}$ = 12.3 Hz, 1 H, OC*H*$_2$Ph-B′), 4.64 (d, $^2J_{C,C'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-C), 4.61 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.53 (d, $^2J_{C,C'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-C′), 3.87 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 3.70 (dd, $^3J_{5,6a}$ = 3.8 Hz, $^2J_{6a,6b}$ = 10.6 Hz, 1 H, 6a-H), 3.67–3.63 (m, 2 H, 5-H, 6b-H), 3.52 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 3.47, 3.38 (s, 3 H, OC*H*$_3$) 3.34 (dd, $^3J_{3,4}$ = 9.4 Hz, $^3J_{4,5}$ = 9.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.9, 138.2, 138.0 (C$_{arom.}$), 128.4, 128.3, 128.3, 128.1, 128.0, 127.8, 127.8, 127.6, 127.6 (*C*H$_{arom.}$), 98.2 (C-1), 82.1 (C-3), 79.6 (C-2), 79.4 (C-4), 75.6 (O*C*H$_2$Ph-A), 73.4 (O*C*H$_2$Ph-B), 73.4 (O*C*H$_2$Ph-C), 70.1 (C-5), 68.6 (C-6), 60.7, 55.4 (O*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_{29}H_{34}O_6$ [M + Na]$^+$ 501.2248; found 501.2253.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-methyl-α-D-glucopyranoside (37): Prepared according to procedure A1. Compound **31** (1.32 g, 2.84 mmol), NaH (266 mg, 6.65 mmol), MeI (400 μL, 6.43 mmol), DMF (25 mL). Yield: 90% (1.22 g, 2.56 mmol), yellow oil, R_f = 0.27 (PE/EA, 3:1), $[a]_D^{25}$ = +15.2 (c = 0.5, $CHCl_3$) {ref.[14] $[a]_D^{23}$ = +8 (c = 0.71, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.24 (m, 15 H, H$_{arom}$), 4.99 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-A), 4.88 (d, $^2J_{B,B'}$ = 11.1 Hz, 1 H, OC*H*$_2$Ph-B), 4.84 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-A′), 4.80 (d, $^2J_{C,C'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-C), 4.66 (d, $^2J_{C,C'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-C′), 4.61 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.60 (d, $^2J_{B,B'}$ = 11.1 Hz, 1 H, OC*H*$_2$Ph-B′), 3.99 (dd, $^3J_{2,3}$ = 9.7 Hz, $^3J_{3,4}$ = 9.0 Hz, 1 H, 3-H), 3.72 (ddd, $^3J_{4,5}$ = 10.1 Hz, $^3J_{5,6a}$ = 3.9 Hz, $^3J_{5,6b}$ = 2.3 Hz, 1 H, 5-H), 3.61 (dd, $^3J_{5,6a}$ = 3.9 Hz, $^2J_{6a,6b}$ = 10.5 Hz, 1 H, 6a-H), 3.60 (dd, $^3J_{3,4}$ = 9.0 Hz, $^3J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 3.55 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 3.54 (dd, $^3J_{5,6b}$ = 2.3 Hz, $^3J_{6a,6b}$ = 10.5 Hz, 1 H, 6b-H), 3.38, 3.35 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.9, 138.4, 138.2 (C$_{arom.}$), 128.4, 128.4, 128.3, 128.2, 127.9, 127.9, 127.7, 127.5 (*C*H$_{arom.}$), 98.3 (C-1), 82.1 (C-3), 79.8 (C-2), 77.6 (C-4), 75.7 (O*C*H$_2$Ph-A), 75.0 (O*C*H$_2$Ph-B), 73.4 (O*C*H$_2$Ph-C), 71.0 (C-6), 69.9 (C-5), 59.1, 55.2 (O*C*H$_3$) ppm. MS (MALDI-TOF): m/z = 501.8 $C_{29}H_{34}O_6$ [M + Na]$^+$ (calcd. 501.2).

Methyl 2-*O*-Benzyl-3-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (38): Compound **32** (3.05 g, 10.2 mmol) and chlorotriphenylmethane (3.0 g, 11 mmol) were dissolved in anhydrous pyridine (30 mL) and a catalytic amount (20 mg) of DMAP was added. The mixture was stirred at 60 °C for 72 h, evaporated in vacuo, co-distilling with toluene, and purified by flash silica gel chromatography (gradient PE/ethyl acetate). Yield: 80% (4.48 g, 8.28 mmol), colourless solid, R_f = 0.53 (PE/EA, 1:1), m.p. 144–145 °C (ref.[25] m.p. 146–147 °C), $[a]_D^{25}$ = +30.3 (c = 0.21, $CHCl_3$) {ref.[25] $[a]_D^{25}$ = +37.0 (c = 1.0, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.20 (m, 20 H, H$_{arom.}$), 4.78 (d, $^2J_{A,A'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-A), 4.66 (d, $^2J_{A,A'}$ = 12.2 Hz, OC*H*$_2$Ph-A′), 4.65 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 3.73–3.67 (m, 1 H, 5-H), 3.56–3.46 (m, 2 H, 3-H, 4-H), 3.43 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.4 Hz, 1 H, 2-H), 3.37 (dd, $^3J_{5,6a}$ = 4.1 Hz, $^2J_{6a,6b}$ = 9.9 Hz, 1 H, 6a-H), 3.33 (dd, $^3J_{5,6b}$ = 5.1 Hz, $^2J_{6a,6b}$ = 9.9 Hz, 1 H, 6b-H), 3.68, 3.40 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.8, 143.7, 138.2 (C$_{arom.}$), 128.6, 128.4, 128.4, 128.0, 127.9, 127.9, 127.8, 127.2, 127.0 (*C*H$_{arom.}$), 98.2 (C-1), 86.9 (Ph$_3$*C*O), 82.9 (C-3), 79.7 (C-2), 73.0 (O*C*H$_2$Ph-A), 71.9 (C-4), 69.6 (C-5), 64.1 (C-6), 61.4, 55.1 (O*C*H$_3$) ppm. MS (MALDI-TOF): m/z = 564.0 $C_{34}H_{36}O_6$ [M + Na]$^+$ (calcd. 563.2).

Methyl 2,6-Di-*O*-benzyl-3,4-di-*O*-methyl-α-D-glucopyranoside (39): Prepared according to procedure A1. Compound **33** (1.73 g, 4.45 mmol), NaH (400 mg, 10.0 mmol), MeI (5.0 mL, 10 mmol, 2 M solution in MTBE), DMF (40 mL). Yield: 76% (1.36 g, 3.31 mmol), yellow syrup, R_f = 0.56 (PE/EA, 1:1), $[a]_D^{25}$ = +65.0 (c = 0.3, $CHCl_3$) {ref.[21] $[a]_D^{23}$ = +52.0 (c = 0.54, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.27 (m, 10 H, H$_{arom.}$), 4.79 (d, $^2J_{A,A'}$ = 12.3 Hz, 1 H, OC*H*$_2$Ph-A), 4.67–4.61 (m, 2 H, OC*H*$_2$Ph-A′, OC*H*$_2$Ph-B), 4.58 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.52 (d, $^2J_{B,B'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-B′), 3.70–3.55 (m, 4 H, 3-H, 5-H, 6-H), 3.41 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 3.24 (dd, $^3J_{3,4}$ = 8.9 Hz, $^3J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 3.67, 3.48, 3.36 (s, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.3, 138.1 (C$_{arom.}$), 128.4, 128.3, 128.0, 127.8, 127.8, 127.6 (*C*H$_{arom.}$), 98.2 (C-1), 83.8 (C-3), 79.4 (C-4), 79.4 (C-2), 73.4 (OC*H*$_2$Ph-B), 73.3 (OC*H*$_2$Ph-A) 69.9 (C-5), 68.5 (C-6), 61.0, 60.4, 55.1 (O*C*H$_3$) ppm. MS (MALDI-TOF): m/z = 425.2 $C_{23}H_{30}O_6$ [M + Na]$^+$ (calcd. 425.2).

Methyl 3,4-Di-*O*-benzyl-2,6-di-*O*-methyl-α-D-glucopyranoside (40): Prepared according to procedure A1. Compound **35** (1.11 g,

2.86 mmol), NaH (170 mg, 7.08 mmol), MeI (3.5 mL, 7.0 mmol, 2 M solution in MTBE), DMF (50 mL). Yield: 80% (920 mg, 2.29 mmol), yellow syrup, R_f = 0.36 (PE/EA, 1:1), $[\alpha]_D^{25}$ = +74.9 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.24 (m, 10 H, $H_{arom.}$), 4.93 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-A), 4.88 (d, $^2J_{B,B'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-B), 4.88 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.80 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-A′), 4.61 (d, $^2J_{B,B'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-B′), 3.93 (dd, $^3J_{2,3}$ = 9.0 Hz, $^2J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.73 (ddd, $^3J_{4,5}$ = 10.0 Hz, $^3J_{5,6a}$ = 1.3 Hz, $^3J_{5,6b}$ = 6.0 Hz, 1 H, 5-H), 3.65–3.60 (m, 2 H, 6a-H, 6b-H), 3.60–3.55 (m, 1 H, 4-H), 3.40–3.34 (m, 1 H, 2-H), 3.54, 3.44, 3.37 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.9, 138.3 ($C_{arom.}$), 128.4, 128.3, 127.9, 127.7, 127.5 (*C*H$_{arom.}$), 97.6 (C-1), 82.3 (C-2), 82.0 (C-3), 77.4 (C-4), 75.5 (O*C*H$_2$Ph-A), 75.1 (O*C*H$_2$Ph-B), 71.0 (C-6), 69.9 (C-5), 59.2, 59.2, 55.1 (O*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_{23}H_{30}O_6$ [M + Na]$^+$ 425.1935; found 425.1933.

Methyl 2,4-Di-*O*-benzyl-3-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (41): Prepared according to procedure A1. Compound **38** (4.42 g, 8.17 mmol), NaH (653 mg, 16.3 mmol), BnBr (2.0 mL, 17 mmol), DMF (40 mL). Yield: 94% (4.84 g, 7.67 mmol), colourless solid, R_f = 0.46 (PE/EA, 4:1), m.p. 63–65 °C, $[\alpha]_D^{25}$ = +45.2 (*c* = 0.2, $CHCl_3$) {ref.[25] $[\alpha]_D^{23}$ = +43.0 (*c* = 1.2, $CHCl_3$)}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.15 (m, 23 H, $H_{arom.}$), 6.98–6.92 (m, 2 H, $H_{arom.}$), 4.86–4.81 (m, 1 H, 1-H), 4.75 (d, $^2J_{A,A'}$ = 11.8 Hz, 1 H, OCH_2Ph-A), 4.70 (d, $^2J_{A,A'}$ = 11.8 Hz, 1 H, OCH_2Ph-A′), 4.67 (d, $^2J_{B,B'}$ = 10.8 Hz, 1 H, OCH_2Ph-B), 4.28 (d, $^2J_{B,B'}$ = 10.8 Hz, 1 H, OCH_2Ph-B′), 3.70 (ddd, $^3J_{4,5}$ = 9.8 Hz, $^3J_{5,6a}$ = 1.5 Hz, $^3J_{5,6b}$ = 5.3 Hz, 1 H, 5-H), 3.57–3.52 (m, 2 H, 3-H, 2-H), 3.50–3.42 (m, 2 H, 4-H, 6a-H), 3.13 (dd, $^3J_{5,6b}$ = 5.3 Hz, $^2J_{6a,6b}$ = 10.0 Hz, 1 H, 6b-H), 3.61, 3.43 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.5, 139.9, 139.6 ($C_{arom.}$), 130.1, 129.6, 129.3, 129.2, 129.0, 128.9, 128.7, 128.2 (*C*H$_{arom.}$), 99.2 (C-1), 87.9 (Ph_3CO), 85.2 (C-3), 81.7 (C-2), 79.5 (C-4), 75.9 (O*C*H$_2$Ph-B), 74.2 (O*C*H$_2$Ph-A), 71.7 (C-5), 64.2 (C-6), 61.6, 55.5 (O*C*H$_3$) ppm. MS (MALDI-TOF): *m*/*z* = 653.4 $C_{41}H_{42}O_6$ [M + Na]$^+$ (calcd. 653.3).

Methyl 2,4-Di-*O*-benzyl-3-*O*-methyl-α-D-glucopyranoside (42): Compound **41** (4.77 g, 7.57 mmol) was stirred in TFA (15 mL, 90%) for 5 min. The mixture was diluted with DCM, neutralized by washing with sat. $NaHCO_3$, dried and concentrated in vacuo. The residue was purified by flash column chromatography (gradient PE/ethyl acetate). Yield: 88% (2.56 g, 6.58 mmol), yellow oil, R_f = 0.29 (PE/EA, 1:1), $[\alpha]_D^{25}$ = +73.9 (*c* = 0.2, $CHCl_3$) {ref.[25] $[\alpha]_D^{23}$ = +62.0 (*c* = 1.2, $CHCl_3$)}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.28 (m, 10 H, $H_{arom.}$), 4.90 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OCH_2Ph-A), 4.82 (d, $^2J_{B,B'}$ = 12.1 Hz, 1 H, OCH_2Ph-B), 4.67 (d, $^2J_{B,B'}$ = 12.1 Hz, 1 H, OCH_2Ph-B′), 4.66 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OCH_2Ph-A′), 4.56 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 3.77 (dd, $^3J_{5,6a}$ = 2.9 Hz, $^2J_{6a,6b}$ = 11.8 Hz, 1 H, 6a-H), 3.74–3.69 (m, 1 H, 3-H), 3.69 (dd, $^3J_{5,6b}$ = 3.9 Hz, $^2J_{6a,6b}$ = 11.8 Hz, 1 H, 6b-H), 3.62 (ddd, $^3J_{4,5}$ = 9.6 Hz, $^3J_{5,6a}$ = 2.9 Hz, $^3J_{5,6b}$ = 3.9 Hz, 1 H, 5-H), 3.43 (dd, $^3J_{3,4}$ = 8.8 Hz, $^3J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.40 (dd, $^3J_{1,2}$ = 3.5 Hz, $^3J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 3.71, 3.35 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.2 ($C_{arom.}$), 128.4, 128.4, 128.0, 127.9, 127.8, 127.8 (*C*H$_{arom.}$), 98.2 (C-1), 83.7 (C-3), 79.8 (C-2), 77.4 (C-4), 74.8 (O*C*H$_2$Ph-A), 73.3 (O*C*H$_2$Ph-B), 70.5 (C-5), 61.9 (C-6), 61.1, 55.1 (O*C*H$_3$) ppm. MS (MALDI-TOF): *m*/*z* = 411.1 $C_{22}H_{28}O_6$ [M + Na]$^+$ (calcd. 411.2).

Methyl 2,4-Di-*O*-benzyl-3,6-di-*O*-methyl-α-D-glucopyranoside (43): Prepared according to procedure A1. Compound **42** (2.47 g, 6.36 mmol), NaH (508 mg, 12.7 mmol), MeI (0.79 mL, 12.7 mmol), DMF (25 mL). Yield: 90% (2.32 g, 5.76 mmol), yellow oil, R_f = 0.25 (PE/EA, 4:1), $[\alpha]_D^{25}$ = +69.3 (*c* = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 10 H, $H_{arom.}$), 4.88 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-A), 4.81 (d, $^2J_{B,B'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-B), 4.65 (d, $^2J_{B,B'}$ = 12.2 Hz, 1 H, OC*H*$_2$Ph-B′), 4.61 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OC*H*$_2$Ph-A′), 4.57 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 3.72–3.64 (m, 2 H, 3-H, 5-H), 3.59 (dd, $^3J_{5,6a}$ = 3.6 Hz, $^2J_{6a,6b}$ = 10.4 Hz, 1 H, 6a-H), 3.53 (dd, $^3J_{5,6b}$ = 2.3 Hz, $^2J_{6a,6b}$ = 10.4 Hz, 1 H, 6b-H), 3.50 (dd, $^3J_{3,4}$ = 9.6 Hz, $^3J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.44 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.7 Hz, 1 H, 2-H), 3.70, 3.36, 3.34 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 138.3 ($C_{arom.}$), 128.4, 128.0, 127.9, 127.8, 127.7 (*C*H$_{arom.}$), 98.3 (C-1), 83.8 (C-3), 79.6 (C-2), 77.5 (C-4), 74.9 (O*C*H$_2$Ph-A), 73.3 (O*C*H$_2$Ph-B), 70.9 (C-6), 69.7 (C-5), 61.2, 59.1, 55.1 (O*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_{23}H_{30}O_6$ [M + Na]$^+$ 425.1935; found 425.1937.

Methyl 2,3,4,6-Tetra-*O*-methyl-α-D-glucopyranoside (47): Prepared according to procedure A2. Compound **44** (10.0 g, 51.5 mmol), NaH (10.3 g, 256 mmol), MeI (16.0 mL, 257 mmol), DMF (250 mL). Yield: 81% (10.5 g, 42.0 mmol), yellow oil, R_f = 0.33 (EA), $[\alpha]_D^{25}$ = +130.6 (*c* = 1.45, H_2O) {ref.[24] $[\alpha]_D^{23}$ = +158.0 (*c* = 1.45, H_2O)}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.82 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 3.61–3.55 (m, 3 H, 5-H, 6-H), 3.50 (dd, $^3J_{2,3}$ = 9.6 Hz, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.21 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 3.22–3.16 (m, 1 H, 4-H), 3.62, 3.54, 3.51, 3.42, 3.41 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 97.6 (C-1), 83.5 (C-3), 81.7 (C-2), 79.4 (C-4), 71.1 (C-6), 69.9 (C-5), 60.8, 60.4, 59.2, 59.0, 55.1 (O*C*H$_3$) ppm.

Methyl 2,3,4,6-Tetra-*O*-methyl-α-D-galactopyranoside (48): Prepared according to procedure A2. Compound **45** (8.02 g, 41.3 mmol), NaH (8.26 g, 207 mmol), MeI (12.9 mL, 207 mmol), DMF (200 mL). Yield: 99% (10.2 g, 40.8 mmol), colourless oil, R_f = 0.33 (EA), $[\alpha]_D^{25}$ = +142.8 (*c* = 1.00, $CHCl_3$) {ref.[27] $[\alpha]_D$ = +143.3 (*c* = 1.45, H_2O)}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.87 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 3.88–3.82 (m, 1 H, 5-H), 3.69 (dd, $^3J_{3,4}$ = 2.8 Hz, $^3J_{4,5}$ = 1.0 Hz, 1 H, 4-H), 3.63 (dd, $^3J_{1,2}$ = 3.5 Hz, $^3J_{2,3}$ = 10.2 Hz, 1 H, 2-H), 3.59–3.49 (m, 3 H, 6a-H, 3-H, 6b-H), 3.57, 3.51, 3.51, 3.41, 3.40 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 98.0 (C-1), 80.4 (C-3), 77.9 (C-2), 76.3 (C-4), 71.2 (C-6), 68.9 (C-5), 61.3, 59.1, 58.9, 58.2, 55.3 (O*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_{11}H_{22}O_6$ [M + Na]$^+$ 273.1309; found 273.1317.

Methyl-2,3,4,6-tetra-*O*-methyl-α-D-mannopyranoside (49): Prepared according to procedure A2. Compound **46** (2.0 g, 10.3 mmol), NaH (2.07 g, 51.8 mmol), MeI (3.20 mL, 51.4 mmol), DMF (70 mL). Yield: 98% (2.53 g, 10.1 mmol), yellow oil, R_f = 0.40 (EA), $[\alpha]_D^{25}$ = +57.8 (*c* = 0.4, $CHCl_3$) {ref.[24] $[\alpha]_D^{23}$ = +71.0 (*c* = 1.26, $CHCl_3$)}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.76 (d, $^3J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 3.58–3.55 (m, 2 H, 6-H), 3.55–3.50 (m, 2 H, 5-H, 2-H), 3.48–3.44 (m, 1 H, 3-H), 3.38 (dd, $^3J_{3,4}$ = 9.3 Hz, $^3J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.48, 3.45, 3.44, 3.39, 3.37 (s, je 3 H, OC*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 98.0 (C-1), 81.2 (C-3), 77.1 (C-2), 76.4 (C-4), 71.7 (C-6), 71.2 (C-5), 60.5, 59.1, 58.9, 57.6, 54.8 (O*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_{11}H_{22}O_6$ [M + Na]$^+$ 273.1309; found 273.1310.

2,3,4,6-Tetra-*O*-methyl-α/β-D-glucopyranose (50): Prepared according to procedure C1. Compound **47** (10.5 g, 42.0 mmol), 0.5 M HCl (150 mL). Yield: 59% (5.8 g, 25 mmol), α/β ratio = 2.9:1, colourless solid, R_f = 0.16 (EA), $[\alpha]_D^{25}$ = +76.8 (*c* = 1.01, H_2O) {ref.[16] $[\alpha]_D^{23}$ = +78.5 (*c* = 2.8, H_2O)}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.34–5.30 (m, 1 H, 1α-H), 4.61–4.55 (m, 1 H, 1β-H), 3.89 (ddd, 1 H, 5α-H), 3.65–3.55 (m, 4 H, 6α-H, 6β-H), 3.53–3.47 (m, 1 H, 3α-H), 3.36 (ddd, $^3J_{4\beta,5\beta}$ = 9.8 Hz, $^3J_{5\beta,6a\beta}$ = 2.1 Hz, $^3J_{5\beta,6b\beta}$ = 5.6 Hz, 1 H, 5β-H), 3.20 (dd, $^3J_{1\alpha,2\alpha}$ = 3.6 Hz, $^3J_{2\alpha,3\alpha}$ = 9.3 Hz, 1 H, 2α-H), 3.21–3.15 (m, 1 H, 3β-H), 3.16 (dd, $^3J_{3\alpha,4\alpha}$ = 9.3 Hz, $^3J_{4\alpha,5\alpha}$ = 10.3 Hz, 1 H, 4α-H), 3.10 (dd, $^3J_{3\beta,4\beta}$ = 8.8 Hz, $^3J_{4\beta,5\beta}$ = 9.8 Hz, 1 H, 4β-

H), 2.96 (dd, $^3J_{1\beta,2\beta}$ = 7.6 Hz, $^3J_{2\beta,3\beta}$ = 8.9 Hz, 1 H, 2β-H), 3.63, 3.54, 3.52, 3.40 (s, 3 H, OCH_3-α), 3.63, 3.61, 3.52, 3.40 (s, 3 H, OCH_3-β) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 97.1 (C-1β), 90.7 (C-1α), 86.4 (C-3β), 84.8 (C-2β), 83.1 (C-3α), 82.0 (C-2α), 79.6 (C-4β), 79.5 (C-4α), 74.4 (C-5β), 71.6 (C-6β), 71.3 (C-6α), 70.0 (C-5α), 60.8, 60.4, 59.1, 58.8 (OCH_3-α), 60.7, 60.4, 60.3, 59.2 (OCH_3-β) ppm.

2,3,4,6-Tetra-*O*-methyl-α/β-D-galactopyranose (51): Prepared according to procedure C1. Compound **48** (7.49 g, 29.9 mmol), 0.5 M HCl (200 mL). Yield: 81% (5.8 g, 25 mmol), α/β ratio = 3.2:1, colourless oil, R_f = 0.16 (EA), $[\alpha]_D^{25}$ = +113.0 (*c* = 0.26, H_2O) {ref.[28] $[\alpha]_D^{23}$ = +118.0 (*c* = 1.9, H_2O)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.40 (d, $^3J_{1\alpha,2\alpha}$ = 3.8 Hz, 1 H, 1α-H), 4.55 (d, $^3J_{1\beta,2\beta}$ = 7.6 Hz, 1 H, 1β-H), 4.16–4.10 (m, 1 H, 5α-H), 3.71–3.69 (m, 1 H, 4α-H), 3.66–3.59 (m, 2 H, 2α-H, 4β-H), 3.58–3.50 (m, 6 H, 5β-H, 3α-H, 6α-H, 6β-H), 3.29 (dd, $^3J_{1\beta,2\beta}$ = 7.6 Hz, $^3J_{2\beta,3\beta}$ = 9.9 Hz, 1 H, 2β-H), 3.17 (dd, $^3J_{2\beta,3\beta}$ = 9.9 Hz, $^3J_{3\beta,4\beta}$ = 3.1 Hz, 1 H, 3β-H), 3.57, 3.53, 3.52, 3.39 (s, 3 H, OCH_3-α), 3.63, 3.55, 3.50, 3.39 (s, 3 H, OCH_3-β) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 97.6 (C-1β), 91.1 (C-1α), 84.0 (C-3β), 82.0 (C-2β), 80.0 (C-3α), 78.1 (C-2α), 76.0 (C-4α), 75.1 (C-4β), 73.3 (C-5β), 71.4 (C-6α), 71.1 (C-6β), 69.1 (C-5α), 61.2, 60.8, 59.1, 58.2 (OCH_3-β), 61.2, 59.1, 58.9, 58.0 (OCH_3-α) ppm. HRMS (ESI): calcd. for $C_{10}H_{20}O_6$ [M + Na]$^+$ 425.1152; found 259.1157.

2,3,4,6-Tetra-*O*-methyl-α/β-D-mannopyranose (52): Prepared according to procedure C1. Compound **49** (2.25 g, 9.00 mmol), 0.5 M HCl (50 mL). Yield: 77% (1.65 g, 6.97 mmol), α/β ratio = 5:1, colourless oil, R_f = 0.11 (EA), $[\alpha]_D^{25}$ = +12.0 (*c* = 0.2, H_2O). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (d, $^3J_{1\alpha,2\alpha}$ = 1.3 Hz, 1 H, 1α-H), 4.67 (d, $^3J_{1\beta,2\beta}$ = 1.3 Hz, 1 H, 1β-H), 3.91 (ddd, $^3J_{4\alpha,5\alpha}$ = 9.5 Hz, $^3J_{5\alpha,6a\alpha}$ = 2.3 Hz, $^3J_{5\alpha,6b\alpha}$ = 6.9 Hz, 1 H, 5α-H), 3.64–3.59 (m, 6 H, 2α-H, 3α-H, 6aα-H, 6β-H, 2β-H), 3.57 (dd, $^3J_{5\alpha,6b\alpha}$ = 6.9 Hz, $^2J_{6a\alpha,6b\alpha}$ = 10.0 Hz, 1 H, 6bα-H), 3.44 (dd, $^3J_{3\beta,4\beta}$ = 9.4 Hz, $^3J_{4\beta,5\beta}$ = 9.5 Hz, 1 H, 4β-H), 3.36–3.29 (m, 1 H, 4α-H), 3.28 (ddd, $^3J_{4\beta,5\beta}$ = 9.5 Hz, $^3J_{5\beta,6a\beta}$ = 5.0 Hz, $^3J_{5\beta,6b\beta}$ = 2.3 Hz, 1 H, 5β-H), 3.23 (dd, $^3J_{2\beta,3\beta}$ = 3.0 Hz, $^3J_{3\beta,4\beta}$ = 9.4 Hz, 1 H, 3β-H) 3.65, 3.53, 3.52, 3.39 (s, OCH_3-β), 3.51, 3.50, 3.49, 3.38 (s, 3 H, OCH_3-α) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 93.9 (C-1β), 91.2 (C-1α), 85.0 (C-3β), 80.8 (C-3α), 78.0 (C-2β), 77.4 (C-2α), 77.0 (C-4α), 76.0 (C-4β), 74.8 (C-5β), 72.2 (C-6α), 71.4 (C-6β), 70.8 (C-5α), 60.6, 59.1, 59.0, 57.7 (OCH_3-α), 61.6, 60.5, 59.2, 58.1 (OCH_3-β) ppm. HRMS (ESI): calcd. for $C_{10}H_{20}O_6$ [M + Na]$^+$ 259.1152; found 259.1161.

Methyl 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranoside (53): Prepared according to procedure A2. Compound **46** (5.00 g, 25.7 mmol), NaH (5.63 g, 141 mmol), BnBr (17.2 mL, 141 mmol), DMF (90 mL). Yield: 86% (12.3 g, 22.2 mmol), colourless oil, R_f = 0.43 (PE/EA, 2:1), $[\alpha]_D^{25}$ = +43.2 (*c* = 0.5, $CHCl_3$) {ref.[29] $[\alpha]_D^{23}$ = +23.4 (*c* = 1.0, CH_2Cl_2)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.15 (m, 20 H, $H_{arom.}$), 4.91 (d, $^2J_{A,A'}$ = 10.8 Hz, 1 H, OCH_2Ph-A), 4.80 (d, $^3J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 4.78–4.72 (m, 2 H, OCH_2Ph-B, D), 4.72–4.61 (m, 3 H, OCH_2Ph-C, B′, D′), 4.58 (d, $^2J_{C,C'}$ = 12.0 Hz, 1 H, OCH_2Ph-C′), 4.53 (d, $^2J_{A,A'}$ = 10.8 Hz, 1 H, OCH_2Ph-A′), 4.03–3.97 (m, 1 H, 4-H), 3.92 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 3.84–3.74 (m, 4 H, 2-H, 5-H, 6-H), 3.35 (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 138.5, 138.4, 138.3 ($C_{arom.}$), 128.3, 128.3, 128.3, 127.9, 127.8, 127.7, 127.6, 127.4 ($CH_{arom.}$), 98.9 (C-1), 80.2 (C-3), 75.0 (OCH_2Ph-A), 74.9 (C-4), 74.5 (C-5), 73.3 (OCH_2Ph-C), 72.5 (OCH_2Ph-B), 72.1 (OCH_2Ph-D), 71.7 (C-2), 69.3 (C-6), 54.7 (OCH_3) ppm.

Methyl 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranoside (54): Prepared according to procedure A2. Compound **45** (4.02 g, 20.7 mmol), NaH (4.60 g, 115 mmol), BnBr (14.0 mL, 115 mmol), DMF (80 mL). Yield: 84% (9.66 g, 17.4 mmol), colourless oil, R_f = 0.23 (PE/EA, 4:1), $[\alpha]_D^{25}$ = +29.2 (*c* = 0.5, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.21 (m, 20 H, $H_{arom.}$), 4.94 (d, $^2J_{A,A'}$ = 11.5 Hz, 1 H, OCH_2Ph-A), 4.84 (d, $^2J_{B,B'}$ = 11.9 Hz, 1 H, OCH_2Ph-B), 4.83 (d, $^2J_{C,C'}$ = 12.2 Hz, 1 H, OCH_2Ph-C), 4.72 (d, $^2J_{B,B'}$ = 11.9 Hz, 1 H, OCH_2Ph-B′), 4.68 (d, $^2J_{C,C'}$ = 12.2 Hz, 1 H, OCH_2Ph-C′), 4.68 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.56 (d, $^2J_{A,A'}$ = 11.5 Hz, 1 H, OCH_2Ph-A′), 4.47 (d, $^2J_{D,D'}$ = 11.7 Hz, 1 H, OCH_2Ph-D), 4.38 (d, $^2J_{D,D'}$ = 11.7 Hz, 1 H, OCH_2Ph-D′), 4.03 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 10.9 Hz, 1 H, 2-H), 3.95–3.86 (m, 3 H, 3-H, 4-H, 5-H), 3.54–3.47 (m, 2 H, 6-H), 3.36 (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.8, 138.6, 138.5, 138.0 ($C_{arom.}$), 128.4, 128.3, 128.2, 128.2, 128.1, 127.7, 127.7, 127.7, 127.6, 127.5 ($CH_{arom.}$), 98.8 (C-1), 79.1 (C-3), 76.4 (C-2), 75.1 (C-4), 74.7 (OCH_2Ph-A), 73.6 (OCH_2Ph-B), 73.5 (OCH_2Ph-D), 73.3 (OCH_2Ph-C), 69.2 (C-5), 69.1 (C-6) ppm. HRMS (ESI): calcd. for $C_{35}H_{38}O_6$ [M + Na]$^+$ 577.2561; found 577.2579.

2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranose (55): Prepared according to procedure C2. Compound **53** (5.31 g, 9.57 mmol), glacial acetic acid (85 mL), 1 N H_2SO_4 (42 mL). Yield: 54% (2.79 g, 5.16 mmol), α/β ratio: 3:1, yellow oil, R_f = 0.52 (DCM/MeOH, 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.25 (m, 36 H, $H_{arom.}$), 7.25–7.13 (m, 4 H, $H_{arom.}$), 5.29 (d, $^3J_{1\alpha,2\alpha}$ = 0.5 Hz, 1 H, 1α-H), 5.13 (d, $^2J_{A\alpha,A'\alpha}$ = 11.7 Hz, 1 H, OCH_2Ph-Aα), 4.95–4.46 (m, 16 H, 1β-H, OCH_2Ph-A′α, Bα, B′α, Cα, C′α, Dα, D′α, Aβ, A′β, Bβ, B′β, Cβ, C′β, Dβ, D′β), 4.09–4.02 (m, 1 H, 5α-H), 4.02–3.94 (m, 2 H, 3α-H, 4β-H), 3.94–3.85 (m, 2 H, 4α-H, 2β-H), 3.84 (dd, $^3J_{1\alpha,2\alpha}$ = 0.5 Hz, $^3J_{2\alpha,3\alpha}$ = 3.1 Hz, 1 H, 2α-H), 3.80–3.75 (m, 2 H, 6aβ-H, 6bβ-H), 3.75–3.68 (m, 3 H, 6aα-H, 6bα-H, 2β-H), 3.64 (dd, $^3J_{2\beta,3\beta}$ = 2.8 Hz, $^3J_{3\beta,4\beta}$ = 9.4 Hz, 1 H, 3β-H), 3.51–3.45 (m, 1 H, 5β-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 138.4, 138.3, 138.2, 138.1 ($C_{arom.}$ α,β), 128.5, 128.3, 127.9, 127.8, 127.6, 127.6 ($CH_{arom.}$ α,β), 93.7 (C-1β), 92.8 (C-1α), 83.1 (C-3β), 79.7 (C-4α), 76.0 (C-2β), 75.2 (C-5β), 75.2 (C-2α), 75.0 (OCH_2Ph-α), 74.7 (C-5α), 74.6 (OCH_2Ph-β), 74.3 (C-4β), 73.5 (OCH_2Ph-β), 73.4 (OCH_2Ph-α), 72.9 (OCH_2Ph-β), 72.7(OCH_2Ph-α), 72.2 (OCH_2Ph-α), 71.7 (C-3α), 69.6 (C-6α), 69.0 (C-6β) ppm. HRMS (ESI): calcd. for $C_{34}H_{36}O_6$ [M + Na]$^+$ 563.2404; found 563.2407.

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranose (56): Prepared according to procedure C2. Compound **54** (6.02 g, 10.8 mmol), glacial acetic acid (105 mL), 1 N H_2SO_4 (52 mL). Yield: 60% (3.51 g, 6.50 mmol), α/β ratio: 2.5:1, colourless solid, R_f = 0.54 (DCM/MeOH, 6:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.25 (m, 40 H, $H_{arom.}$), 5.29 (d, $^3J_{1\alpha,2\alpha}$ = 3.6 Hz, 1 H, H-1α), 4.98–4.91 (m, 2 H, OCH_2Ph-Aβ, Bβ), 4.95 (d, $^2J_{A\alpha,A'\alpha}$ = 11.5 Hz, 1 H, OCH_2Ph-Aα), 4.86–4.70 (m, 7 H, H-1α, OCH_2Ph-Bα, B′α, Cα, C′α, A′β, B′β, Cβ), 4.67 (d, $^3J_{1\beta,2\beta}$ = 7.4 Hz, 1 H, H-1β), 4.62 (d, $^2J_{C\beta,C'\beta}$ = 11.7 Hz, 1 H, OCH_2Ph-C′β), 4.60 (d, $^2J_{A\alpha,A'\alpha}$ = 11.5 Hz, 1 H, OCH_2Ph-A′α), 4.51–4.40 (m, 2 H, OCH_2Ph-Dβ, D′β), 4.49 (d, $^2J_{D\alpha,D'\alpha}$ = 12.0 Hz, 1 H, OCH_2Ph-Dα), 4.42 (d, $^2J_{D\alpha,D'\alpha}$ = 12.0 Hz, 1 H, OCH_2Ph-D′α), 4.20–4.13 (m, 1 H, H-5α), 4.05 (dd, $^3J_{1\alpha,2\alpha}$ = 3.6 Hz, $^3J_{2\alpha,3\alpha}$ = 9.7 Hz, 1 H, H-2α), 3.99–3.96 (m, 1 H, H-4α), 3.93 (dd, $^3J_{2\alpha,3\alpha}$ = 9.7 Hz, $^3J_{3\alpha,4\alpha}$ = 2.8 Hz, 1 H, H-3α), 3.91–3.89 (m, 1 H, H-4β), 3.78 (dd, $^3J_{1\beta,2\beta}$ = 7.4 Hz, $^3J_{2\beta,3\beta}$ = 9.7 Hz, 1 H, H-2β), 3.65–3.57 (m, 2 H, H-5β, H-6aβ), 3.58–3.46 (m, 4 H, H-6α, H-6bβ, H-3β) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.6, 138.5, 138.2, 137.8 ($C_{arom.}$,α), 138.5, 138.4, 138.3, 137.7 ($C_{arom.}$,β), 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5 ($CH_{arom.}$ α,β), 97.8 (C-1β), 91.9 (C-1α), 82.2 (C-3β), 80.7 (C-2β), 78.7 (C-3α), 76.6 (C-2α), 75.1, 74.5, 72.9 (OCH_2Ph-β), 74.6, 73.5, 73.4, 72.9 (OCH_2Ph-α), 74.6 (C-4α), 73.6 (C-4β), 73.6 (C-5β), 69.5 (C-5α), 69.0 (C-6α), 68.9 (C-6β) ppm.

HRMS (ESI): calcd. for $C_{34}H_{36}O_6$ [M + Na]$^+$ 563.2404; found 563.2404.

Methyl 2,3,4-Tri-*O*-acetyl-1-thio-β-L-fucopyranoside (63): To a solution of **62** (9.58 g, 28.8 mmol) in anhydrous DCM (160 mL) were added methylthiotrimethylsilane (4.40 mL, 31.1 mmol) and TMSOTf (5.18 mL, 26.8 mmol). The reaction mixture was stirred for 15 h, diluted with DCM, washed with saturated $NaHCO_3$ solution, dried and concentrated. The product was purified by column chromatography (petroleum ether ether/ethyl acetate). Yield: 84% (7.77 g, 24.3 mmol), colourless solid, R_f = 0.34 (PE/EA, 2:1), m.p. 145 °C (ref.[30] m.p. 139–141 °C), $[\alpha]_D^{25}$ = +3.4 (*c* = 1.0, $CHCl_3$) {ref.[30] $[\alpha]_D^{23}$ = –0.7 (*c* = 1.0, $CHCl_3$)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.27 (dd, $^3J_{3,4}$ = 3.3 Hz, $^3J_{4,5}$ = 1.0 Hz, 1 H, 4-H), 5.24 (dd, $^3J_{1,2}$ = 9.8 Hz, $^3J_{2,3}$ = 10.0 Hz, 1 H, 2-H), 5.05 (dd, $^3J_{2,3}$ = 10.0 Hz, $^3J_{3,4}$ = 3.3 Hz, 1 H, 3-H), 4.35 (d, $^3J_{1,2}$ = 9.8 Hz, 1 H, 1-H), 3.85 (dq, $^3J_{4,5}$ = 1.0 Hz, $^3J_{5,6}$ = 6.3 Hz, 1 H, 5-H), 2.19 (s, 3 H, SC*H*$_3$), 2.17, 2.07, 1.98 (s, 3 H, C*H*$_3$-OAc), 1.22 (d, $^3J_{5,6}$ = 6.3 Hz, 3 H, 6-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6, 170.1, 169.7 (C=O), 83.1 (C-1), 73.2 (C-5), 72.3 (C-3), 70.5 (C-4), 66.6 (C-2), 20.8, 20.6, 20.6 (C*H*$_3$-OAc), 16.3 (C-6), 11.5 (S*C*H$_3$) ppm.

Methyl 1-Thio-β-L-fucopyranoside (64): Compound **63** (5.39 g, 16.8 mmol) was dissolved in anhydrous MeOH (100 mL), 0.1 M NaOMe solution was added to reach pH 8–9 and the mixture was stirred for 24 h. Subsequently, the solution was neutralized with Amberlite IR-120 (H$^+$) resin, filtered and concentrated. The product was purified by column chromatography (gradient ethyl acetate/methanol). Yield: 98% (3.21 g, 16.5 mmol), colourless solid, R_f = 0.60 (DCM/MeOH, 5:1), m.p. 102 °C, $[\alpha]_D^{25}$ = +20.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.43 (d, $^3J_{3,OH\text{-}3}$ = 4.6 Hz, 1 H, O*H*-3), 4.25 (d, $^3J_{1,2}$ = 9.4 Hz, 1 H, 1-H), 4.00 (s, 1 H, O*H*-4), 3.84–3.79 (m, 1 H, 4-H), 3.75–3.60 (m, 3 H, 2-H, 3-H, 5-H), 3.52 (d, $^3J_{2,OH\text{-}2}$ = 5.3 Hz, 1 H, O*H*-2), 2.23 (s, 3 H, SC*H*$_3$), 1.32 (d, $^3J_{5,6}$ = 6.3 Hz, 3 H, 6-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 86.1 (C-1), 75.2 (C-5), 74.8 (C-3), 71.9 (C-4), 69.8 (C-2), 16.6 (C-6), 12.2 (S*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_7H_{14}O_4S$ [M + Na]$^+$ 217.0505; found 217.0501.

Methyl 2,3,4-Tri-*O*-benzyl-1-thio-β-L-fucopyranoside (65): Prepared according to procedure A1. Compound **64** (2.51 g, 12.9 mmol), NaH (3.15 g, 78.8 mmol), BnBr (9.3 mL, 78.3 mmol), DMF (50 mL). Yield: 82% (4.84 g, 10.4 mmol), colourless syrup, R_f = 0.27 (PE/EA, 2:1), $[\alpha]_D^{25}$ = –44.0 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 15 H, H$_{arom.}$), 5.02 (d, $^2J_{A,A'}$ = 11.7 Hz, 1 H, OC*H*$_2$Ph-A), 4.90 (d, $^2J_{B,B'}$ = 10.1 Hz, 1 H, OC*H*$_2$Ph-B), 4.84 (d, $^2J_{B,B'}$ = 10.1 Hz, 1 H, OC*H*$_2$Ph-B′), 4.79 (d, $^2J_{C,C'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-C), 4.75 (d, $^2J_{C,C'}$ = 12.0 Hz, 1 H, OC*H*$_2$Ph-C′), 4.71 (d, $^2J_{A,A'}$ = 11.7 Hz, 1 H, OC*H*$_2$Ph-A′), 4.32 (d, $^3J_{1,2}$ = 9.5 Hz, 1 H, 1-H), 3.86 (dd, $^3J_{1,2}$ = 9.5 Hz, $^3J_{2,3}$ = 9.2 Hz, 1 H, 2-H), 3.64 (d, $^2J_{3,4}$ = 2.8 Hz, 1 H, 4-H), 3.59 (dd, $^3J_{2,3}$ = 9.2 Hz, $^3J_{3,4}$ = 2.8 Hz, 1 H, 3-H), 3.52 (q, $^3J_{5,6}$ = 6.3 Hz, 1 H, 5-H), 2.23 (s, 3 H, SC*H*$_3$), 1.23 (d, $^3J_{5,6}$ = 6.3 Hz, 3 H, 6-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.7, 138.4, 138.3 (C$_{arom.}$), 128.4, 128.3, 128.1, 128.1, 127.7, 127.6, 127.5, 127.5 (*C*H$_{arom.}$), 85.3 (C-1), 84.4 (C-3), 77.8 (C-2), 76.5 (C-4), 75.6 (O*C*H$_2$Ph-B), 74.5 (C-5), 74.5 (O*C*H$_2$Ph-A), 72.8 (O*C*H$_2$Ph-C), 17.2 (C-6), 12.7 (S*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_{28}H_{32}O_4S$ [M + Na]$^+$ 487.1914; found 487.1909.

2,3,4-Tri-*O*-benzyl-α/β-L-fucopyranose (66): Compound **65** (3.99 g, 8.59 mmol) and NBS (4.61 g, 25.8 mmol) were stirred in an acetone/water, 9:1 mixture for 3 h at room temperature. Subsequently, ethyl acetate and water were added, the organic layer was washed with sat. $NaHCO_3$ solution, dried, and concentrated. The residue was purified by column chromatography (PE/ethyl acetate). Yield: 81% (3.03 g, 6.97 mmol), colourless solid, R_f = 0.43 (PE/EA, 1:1), α/β ratio: 1.4:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.27 (m, 30 H, H$_{arom.}$), 5.28 (s, 1 H, 1α-H), 5.05–4.60 (m, 13 H, OC*H*$_2$Ph-α,β, 1β-H), 4.15–4.08 (m, 1 H, 5α-H), 4.05 (dd, $^3J_{1\alpha,2\alpha}$ = 3.3 Hz, $J_{2\alpha,3\alpha}$ = 9.9 Hz, 1 H, 2α-H), 3.94–3.88 (m, 1 H, 3α-H), 3.78–3.72 (m, 1 H, 2β-H), 3.70–3.66 (m, 1 H, 4α-H), 3.62–3.51 (m, 3 H, 3β-H, 4β-H, 5β-H), 3.09 (d, $^3J_{1\beta,OH\text{-}1}$ = 6.6 Hz, 1 H, O*H*-1β), 2.91 (s, 1 H, O*H*-1α), 1.21 (d, $^3J_{5\beta,6\beta}$ = 6.3 Hz, 3 H, 6β-H), 1.16 (d, $^3J_{5\alpha,6\alpha}$ = 6.6 Hz, 3 H, 6α-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.6, 138.5, 138.2 (C$_{arom.}$,α), 138.6, 138.4, 138.4 (C$_{arom.}$,β), 128.4, 128.3, 128.2, 128.2, 128.0, 127.8, 127.6, 127.6, 127.6, 127.5, (*C*H$_{arom.}$ α,β), 97.7 (C-1β), 91.9 (C-1α), 82.5 (C-3β), 80.7 (C-2β), 79.1 (C-3α), 77.3 (C-4α), 76.5 (C-2α), 76.3 (C-4β), 75.0, 74.7, 73.1 (O*C*H$_2$Ph-β), 74.7, 73.5, 73.0 (O*C*H$_2$Ph-α), 70.8 (C-5β), 66.7 (C-5α), 16.9 (C-6β), 16.7 (C-6α) ppm. HRMS (ESI): calcd. for $C_{27}H_{30}O_5$ [M + Na]$^+$ 457.1985; found 457.1993.

Methyl 4-*O*-Acetyl-3,6-di-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (71) and Methyl 2-*O*-Acetyl-3,6-di-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (72): Prepared according to procedure G1. Compound **5** (50.5 mg, 0.227 mmol), NaH (27.5 g, 0.688 mmol), **16** (173 mg, 0.680 mmol), DMF (10 mL). Yield: 31% (34.5 mg, 0.0715 mmol), colourless solid, relative yield **71/72** = 84:16 (^{1}H NMR), R_f = 0.23 (EA). Data for **71**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.90 (dd, $^3J_{3,4}$ = 8.9 Hz, $^3J_{4,5}$ = 10.3 Hz, 1 H, 4-H), 4.86 (d, $^3J_{1,2}$ = 3.0 Hz, 1 H, 1-H), 4.41 (d, $^3J_{1',2'}$ = 7.8 Hz, 1 H, 1′-H), 3.80 (ddd, $^3J_{4,5}$ = 10.3 Hz, $^3J_{5,6a}$ = 3.0 Hz, $^3J_{5,6b}$ = 5.5 Hz, 1 H, 5-H), 3.71–3.54 (m, 4 H, 3-H, 2-H, 4′-H, 6a′-H, 6b′-H), 3.49–3.31 (m, 5 H, 5′-H, 6b′-H, 6-H, 2′-H), 3.12 (dd, $^3J_{2',3'}$ = 9.7 Hz, $^3J_{3',4'}$ = 3.2 Hz, 1 H, 3′-H), 3.59, 3.55, 3.51, 3.51, 3.39, 3.36, 3.35 (s, 3 H, OC*H*$_3$), 2.10 (s, 3 H, C*H*$_3$-OAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8 (C=O), 104.8 (C-1′), 99.5 (C-1), 84.1 (C-3′), 80.3 (C-2′), 80.2 (C-3), 78.7 (C-2), 74.9 (C-4′), 72.9 (C-5′), 71.6 (C-6), 71.1 (C-4), 70.6 (C-6′), 68.3 (C-5), 61.3, 60.7, 60.3, 59.4, 59.1, 58.3, 55.3 (O*C*H$_3$), 20.9 (*C*H$_3$-OAc) ppm. Data for **72**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.88–4.84 (m, 1 H, 1-H), 4.74 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 4.30 (d, $^3J_{1',2'}$ = 7.8 Hz, 1 H, 1′-H), 3.80–3.31 (m, 30 H, 6a-H, 5-H, 4-H, 3-H, 6b-H, 4′-H, 5′-H, 6′-H, 7× OC*H*$_3$), 3.26 (dd, $^3J_{1',2'}$ = 7.8 Hz, $^3J_{2',3'}$ = 9.5 Hz, 1 H, 2′-H), 3.15–3.09 (m, 1 H, 3′-H), 2.12 (s, 3 H, C*H*$_3$-OAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 103.9 (C-1′), 96.9 (C-1), 84.5 (C-3′), 80.9 (C-2′), 79.6 (C-3), 78.3 (C-4), 74.5 (C-4′), 73.0 (C-5′), 72.8 (C-2), 70.4 (C-6), 70.3 (C-6′), 69.9 (C-5), 61.2, 60.9, 59.1, 59.0, 58.1, 55.1 (O*C*H$_3$), 21.0 (*C*H$_3$-OAc) ppm. HRMS (ESI): calcd. for $C_{21}H_{38}O_{12}$ [M + Na]$^+$ 505.2255; found 505.2258.

Methyl 6-*O*-Acetyl-3,4-di-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (73) and Methyl 2-*O*-Acetyl-3,4-di-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (74): Prepared according to procedure G1. Compound **6** (52.0 mg, 0.234 mmol), NaH (27.7 g, 0.693 mmol), **16** (176 mg, 0.691 mmol), DMF (10 mL). Yield: 27% (30.2 mg, 0.0626 mmol), colourless solid, relative yield **73/74** = 92:8 (^{1}H NMR), R_f = 0.23 (EA). Disaccharide **73** was fully characterized by NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.81 (d, $^3J_{1,2}$ = 3.2 Hz, 1 H, 1-H), 4.38 (d, $^3J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.30–4.23 (m, 2 H, 6a-H, 6b-H), 3.71 (ddd, $^3J_{4,5}$ = 10.1 Hz, $^3J_{5,6a}$ = 3.5 Hz, $^3J_{5,6b}$ = 3.5 Hz, 1 H, 5-H), 3.67–3.42 (m, 6 H, 4′-H, 3-H, 6a′-H, 2-H, 6b′-H, 5′-H), 3.40–3.13 (m, 1 H, 2′-H), 3.13 (dd, $^3J_{2',3'}$ = 9.8 Hz, $^3J_{3',4'}$ = 3.2 Hz, 1 H, 3′-H), 3.07 (dd, $^3J_{3,4}$ = 8.8 Hz, $^3J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 3.63, 3.61, 3.55, 3.52, 3.51, 3.36, 3.35 (s, 3 H, OC*H*$_3$), 2.10 (s, 3 H, C*H*$_3$-OAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.8 (C=O), 105.0 (C-1′), 99.5 (C-1), 84.2 (C-3′), 82.9 (C-3), 80.2 (C-4), 80.1 (C-2′), 79.6 (C-2), 74.8 (C-4′), 72.9 (C-5′), 70.7 (C-6′),

68.3 (C-5), 63.2 (C-6), 61.3, 60.8, 60.8, 60.5, 59.1, 58.3, 55.1 (O*C*H$_3$), 20.8 (*C*H$_3$-OAc) ppm. HRMS (ESI): calcd. for $C_{21}H_{38}O_{12}$ [M + Na]$^+$ 505.2255; found 505.2255.

Methyl 6-*O*-Acetyl-2,4-di-*O*-methyl-3-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (75) and Methyl 3-*O*-Acetyl-2,4-di-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (76): Prepared according to procedure G1. Compound **7** (50.0 mg, 0.225 mmol), NaH (27.2 g, 0.680 mmol), **16** (172 mg, 0.675 mmol), DMF (10 mL). Yield: 23% (25.2 mg, 0.0510 mmol), colourless solid, relative yield **75/76** = 55:45 (^{1}H NMR), R_f = 0.22 (EA). Data for **75**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.82 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.67 (d, $^3J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.33–4.24 (m, 2 H, 6-H), 4.08 (dd, $^3J_{2,3}$ = 9.5 Hz, $^3J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 3.80–3.42 (m, 5 H, 5-H, 4′-H, 6′-H, 5′-H), 3.30–3.21 (m, 2 H, 2-H, 2′-H), 3.16–3.09 (m, 2 H, 3′-H, 4-H), 3.61, 3.54, 3.53, 3.51, 3.41, 3.40, 3.37 (s, 3 H, OC*H*$_3$), 2.10 (s, 3 H, C*H*$_3$-OAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.8 (C=O), 103.3 (C-1′), 96.9 (C-1), 83.7 (C-3′), 82.4 (C-2), 81.0 (C-2′), 78.2 (C-3), 78.2 (C-4), 74.6 (C-4′), 72.3 (C-5′), 70.3 (C-6′), 68.3 (C-5), 63.5 (C-6), 61.2, 60.5, 60.5, 59.1, 58.7, 58.1, 55.1 (O*C*H$_3$), 20.8 (*C*H$_3$-OAc) ppm. Data for **76**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.37 (dd, $^3J_{2,3}$ = 9.8 Hz, $^3J_{3,4}$ = 9.8 Hz, 1 H, 3-H), 4.85 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.27 (d, $^3J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 4.14–4.10 (m, 1 H, 6a-H), 3.80–3.35 (m, 6 H, 5-H, 6b-H, 4′-H, 6′-H, 5′-H, 2′-H), 3.30–3.21 (m, 2 H, 2-H, 4-H), 3.16–3.09 (m, 1 H, 3′-H), 3.62, 3.55, 3.52, 3.50, 3.41, 3.41, 3.40 (s, 3 H, OC*H*$_3$), 2.11 (s, 3 H, C*H*$_3$-OAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.8 (C=O), 104.1 (C-1′), 97.0 (C-1), 84.0 (C-3′), 80.5 (C-2′), 79.6 (C-2), 77.8 (C-4), 74.8 (C-4′), 73.5 (C-3), 73.2 (C-5′), 70.8 (C-6′), 69.5 (C-5), 68.3 (C-6), 61.1, 60.9, 59.3, 59.2, 58.6, 58.3, 55.1 (O*C*H$_3$), 21.1 (*C*H$_3$-OAc) ppm. HRMS (ESI): calcd. for $C_{21}H_{38}O_{12}$ [M + Na]$^+$ 505.2255; found 505.2258.

Methyl 3,6-Di-*O*-acetyl-4-*O*-methyl-2-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (80), Methyl 2,6-Di-*O*-acetyl-4-*O*-methyl-3-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-gluco-pyranoside (81) and Methyl 2,3-Di-*O*-acetyl-4-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (82): Prepared according to procedure G1. Compound **11** (46.3 mg, 0.222 mmol), NaH (37.2 g, 0.930 mmol), **16** (214 mg, 0.840 mmol), DMF (10 mL). Yield: 26% (39.7 mg, 0.0778 mmol), yellow syrup, relative yield **80/81/82** = 63:9:28 (^{1}H NMR), R_f = 0.25 (EA). Disaccharide **80** was fully characterized by NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.50 (dd, $^3J_{2,3}$ = 10.0 Hz, $^3J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 4.87 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.29–4.27 (m, 2 H, 6-H), 4.21 (d, $^3J_{1',2'}$ = 7.8 Hz, 1 H, 1′-H), 3.87–3.83 (m, 1 H, 5-H), 3.62–3.42 (m, 5 H, 4′-H, 2-H, 6′-H, 5′-H), 3.27–3.25 (m, 1 H, 2′-H), 3.23–3.20 (m, 1 H, 4-H), 3.06 (dd, $^3J_{2',3'}$ = 9.7 Hz, $^3J_{3',4'}$ = 3.1 Hz, 1 H, 3′-H), 3.54, 3.50, 3.48, 3.39, 3.37, 3.37 (s, 3 H, OC*H*$_3$), 2.11, 2.11 (s, 3 H, C*H*$_3$-OAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.7, 169.7 (C=O), 105.6 (C-1′), 99.4 (C-1), 84.2 (C-3′), 79.9 (C-2′), 78.4 (C-2), 78.3 (C-4), 74.9 (C-4′), 73.2 (C-5′), 72.6 (C-3), 70.9 (C-6′), 67.9 (C-5), 63.1 (C-6), 61.2, 61.0, 59.4, 59.1, 58.3, 55.2 (O*C*H$_3$), 21.1, 20.8 (*C*H$_3$-OAc) ppm. HRMS (ESI): calcd. for $C_{22}H_{38}O_{13}$ [M + Na]$^+$ 533.2205; found 533.2200.

Methyl 6-*O*-Acetyl-2,3-di-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-glucopyranosyl)-α-D-glucopyranoside (88) and Methyl 4-*O*-Acetyl-2,3-di-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-methyl-β-D-glucopyranosyl)-α-D-glucopyranoside (89): Prepared according to procedure G1. Compound **5** (102.3 mg, 0.459 mmol), NaH (36.7 g, 0.918 mmol), **15** (234 mg, 0.919 mmol), DMF (10 mL). Yield: 4% (8.9 mg, 0.018 mmol), yellow syrup, relative yield **88/89** = 50:50 (^{1}H NMR), R_f = 0.34/0.27 (EA). Disaccharide **89** was fully characterized by NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.85 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.79 (dd, $^3J_{3,4}$ = 9.5 Hz, $^3J_{4,5}$ = 10.0 Hz, 1 H, 4-H), 4.26 (d, $^3J_{1',2'}$ = 7.9 Hz, 1 H, 1′-H), 3.93–3.84 (m, 2 H, 5-H, 6a-H), 3.65–3.48 (m, 4 H, 3-H, 6b-H, 6′-H), 3.28 (dd, $^3J_{1,2}$ = 3.5 Hz, $^3J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 3.27–3.22 (m, 1 H, 5′-H), 3.19–3.11 (m, 2 H, 3′-H, 4′-H), 3.03–2.96 (m, 1 H, 2′-H), 3.62, 3.58, 3.53, 3.53, 3.53, 3.45, 3.39 (s, 3 H, OC*H*$_3$), 2.10 (s, 3 H, C*H*$_3$-OAc) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 103.7 (C-1′), 97.2 (C-1), 86.3 (C-3′), 83.7 (C-2′), 81.4 (C-2), 80.9 (C-3), 79.2 (C-4′), 74.5 (C-5′), 71.2 (C-6′), 70.7 (C-4), 68.9 (C-5), 68.7 (C-6), 60.8, 60.8, 60.5, 60.4, 59.3, 59.2, 55.2 (O*C*H$_3$), 20.7 (*C*H$_3$-OAc) ppm.

Methyl 2,3-Di-*O*-methyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-D-glucopyranoside (90) and Methyl 2,3-Di-*O*-methyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-α-D-glucopyranoside (91): Prepared according to procedure G2. Compound **5** (100 mg, 0.450 mmol), NaH (40.0 g, 1.00 mmol), **19** (337 mg, 0.558 mmol), DMF (20 mL). Data for **90**: Yield: 5% (17.0 mg, 0.0228 mmol), yellow syrup, R_f = 0.07 (EA), $[\alpha]_D^{25}$ = +30.7 (c = 0.02, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.24 (m, 20 H, H$_{arom.}$), 4.96 (d, $^2J_{A,A'}$ = 11.7 Hz, 1 H, OC*H*$_2$Ph-A), 4.90 (d, $^2J_{B,B'}$ = 11.3 Hz, 1 H, OC*H*$_2$Ph-B), 4.79 (d, $^2J_{B,B'}$ = 11.3 Hz, 1 H, OC*H*$_2$Ph-B′), 4.78 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.73 (d, $^2J_{C,C'}$ = 11.8 Hz, 1 H, OC*H*$_2$Ph-C), 4.67 (d, $^2J_{C,C'}$ = 11.8 Hz, 1 H, OC*H*$_2$Ph-C′), 4.60 (d, $^2J_{A,A'}$ = 11.7 Hz, 1 H, OC*H*$_2$Ph-A′), 4.53 (d, $^3J_{1',2'}$ = 7.8 Hz, 1 H, 1′-H), 4.49 (d, $^2J_{D,D'}$ = 11.9 Hz, 1 H, OC*H*$_2$Ph-D), 4.43 (d, $^2J_{D,D'}$ = 11.9 Hz, 1 H, OC*H*$_2$Ph-D′), 3.96–3.93 (m, 1 H, 4′-H), 3.83–3.77 (m, 1 H, 6a-H), 3.79 (dd, $^3J_{1',2'}$ = 7.8 Hz, $^3J_{2',3'}$ = 9.7 Hz, 1 H, 2′-H), 3.73–3.68 (m, 1 H, 6b-H), 3.68–3.63 (m, 4 H, 4-H, 5-H, 6′-H), 3.63–3.53 (m, 3 H, 5′-H, 3-H, 3′-H), 3.58, 3.52, 3.40 (s, 3 H, OC*H*$_3$), 3.16 (dd, $^3J_{1,2}$ = 3.6, $^3J_{2,3}$ = 9.4 Hz, 1 H, 2-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.9, 138.6, 138.3, 138.0 (C$_{arom.}$), 128.4, 128.4, 128.2, 128.1, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4 (*C*H$_{arom.}$), 103.4 (C-1′), 97.5 (C-1), 82.8 (C-3′), 81.6 (C-3), 81.5 (C-2), 79.8 (C-4), 77.9 (C-2′), 75.2 (O*C*H$_2$Ph-B), 74.4 (O*C*H$_2$Ph-A), 73.5 (O*C*H$_2$Ph-D), 73.5 (C-4′), 73.2 (C-5′), 72.6 (O*C*H$_2$Ph-C), 70.6 (C-5), 68.5 (C-6′), 61.3 (C-6), 61.0, 59.2, 55.2 (O*C*H$_3$) ppm. Data for **91**: Yield: 15% (51.0 mg, 0.0685 mmol), colourless syrup, R_f = 0.12 (EA), $[\alpha]_D^{25}$ = +21.2 (c = 0.02, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.25 (m, 20 H, H$_{arom.}$), 4.96 (d, $^2J_{A,A'}$ = 10.9 Hz, 1 H, OC*H*$_2$Ph-A), 4.94 (d, $^2J_{B,B'}$ = 11.6 Hz, 1 H, OC*H*$_2$Ph-B), 4.83 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.78 (d, $^2J_{A,A'}$ = 10.9 Hz, 1 H, OC*H*$_2$Ph-A′), 4.75 (d, $^2J_{C,C'}$ = 11.9 Hz, 1 H, OC*H*$_2$Ph-C), 4.72 (d, $^2J_{C,C'}$ = 11.9 Hz, 1 H, OC*H*$_2$Ph-C′), 4.60 (d, $^2J_{B,B'}$ = 11.6 Hz, 1 H, OC*H*$_2$Ph-B′), 4.48 (d, $^2J_{D,D'}$ = 11.8 Hz, 1 H, OC*H*$_2$Ph-D), 4.44 (d, $^3J_{1',2'}$ = 7.5 Hz, 1 H, 1′-H), 4.43 (d, $^2J_{D,D'}$ = 11.8 Hz, 1 H, OC*H*$_2$Ph-D′), 4.15 (dd, $^3J_{5,6a}$ = 5.5 Hz, $^2J_{6a,6b}$ = 13.3 Hz, 1 H, 6a-H), 3.92–3.89 (m, 1 H, 4′-H), 3.86 (dd, $^3J_{1',2'}$ = 7.5 Hz, $^3J_{2',3'}$ = 9.8 Hz, 1 H, 2′-H), 3.82–3.75 (m, 2 H, 5-H, 6b-H), 3.65–3.56 (m, 3 H, 5′,H-6′-H), 3.54 (dd, $^3J_{2',3'}$ = 9.8 Hz, $^3J_{3',4'}$ = 2.9 Hz, 1 H, 3′-H), 3.54–3.49 (m, 1 H, 4-H), 3.45 (dd, $^3J_{2,3}$ = 9.2, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.62, 3.48, 3.38 (s, 3 H, OC*H*$_3$), 3.20 (dd, $^3J_{1,2}$ = 3.8 Hz, $^3J_{2,3}$ = 9.2 Hz, 1 H, 2-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.7, 138.6, 138.4, 137.9 (C$_{arom.}$), 128.4, 128.3, 128.3, 128.1, 128.1, 128.1, 127.9, 127.8, 127.5, 127.5, 127.5 (*C*H$_{arom.}$), 104.2 (C-1′), 94.9 (C-1), 82.7 (C-3), 82.2 (C-3′), 81.7 (C-2), 79.3 (C-2′), 75.1 (O*C*H$_2$Ph-A), 74.5 (O*C*H$_2$Ph-B), 73.5 (O*C*H$_2$Ph-D), 73.5 (C-5′), 73.4 (C-4′), 72.9 (O*C*H$_2$Ph-C), 70.8 (C-4), 70.0 (C-5), 69.2 (C-6), 68.7 (C-6′), 61.1, 58.4, 55.2 (O*C*H$_3$) ppm. HRMS (ESI): calcd. for $C_{43}H_{52}O_{11}$ [M + Na]$^+$ 767.3402; found 767.3410.

Methyl 2,3-Di-*O*-methyl-4-*O*-(2,3,4-tri-*O*-benzyl-α-L-arabinopyranosyl)-α-D-glucopyranoside (92) and Methyl 2,3-Di-*O*-methyl-6-

***O*-(2,3,4-tri-*O*-benzyl-α-L-arabinopyranosyl)-α-D-glucopyranoside (93):** Prepared according to procedure G2. Compound **5** (100 mg, 0.450 mmol), NaH (35.0 g, 0.900 mmol), **20** (296 mg, 0.675 mmol), DMF (10 mL). Data for **92**: Yield: 11% (30.0 mg, 0.0480 mmol), yellow syrup, R_f = 0.37 (EA), $[\alpha]_D^{25}$ = +176.0 (c = 0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 15 H, $H_{arom.}$), 4.84 (d, $^2J_{A,A'}$ = 11.1 Hz, 1 H, OCH_2Ph-A), 4.78 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 4.75 (d, $^2J_{A,A'}$ = 11.1 Hz, 1 H, OCH_2Ph-A′), 4.71 (d, $^2J_{B,B'}$ = 12.5 Hz, 1 H, OCH_2Ph-B), 4.65 (d, $^2J_{B,B'}$ = 12.5 Hz, 1 H, OCH_2Ph-B′), 4.64 (d, $^2J_{C,C'}$ = 12.1 Hz, 1 H, OCH_2Ph-C), 4.61 (d, $^2J_{C,C'}$ = 12.1 Hz, 1 H, OCH_2Ph-C′), 4.46 (d, $^3J_{1',2'}$ = 6.8 Hz, 1 H, 1′-H), 4.12 (dd, $^3J_{4',5a'}$ = 3.3 Hz, $^2J_{5a',5b'}$ = 12.9 Hz, 1 H, 5a′-H), 3.78 (dd, $^3J_{5,6a}$ = 3.3 Hz, $^2J_{6a,6b}$ = 11.9 Hz, 1 H, 6a-H), 3.76 (dd, $^3J_{1',2'}$ = 6.8 Hz, $^3J_{2',3'}$ = 8.8 Hz, 1 H, 2′-H), 3.72–3.62 (m, 3 H, 4′-H, 6b-H, 4-H), 3.59–3.51 (m, 3 H, 3-H, 3′-H, 5-H), 3.27 (dd, $^3J_{4',5b'}$ = 1.3 Hz, $^2J_{5a',5b'}$ = 12.9 Hz, 1 H, 5b′-H), 3.18 (dd, $^3J_{1,2}$ = 3.8, $^3J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.65, 3.54, 3.41 (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.6, 138.3, 138.3 ($C_{arom.}$), 128.3, 128.3, 128.3, 127.9, 127.8, 127.8, 127.6, 127.6, 127.6 ($CH_{arom.}$), 103.1 (C-1′), 97.8 (C-1), 81.9 (C-3), 81.6 (C-2), 80.1 (C-3′), 79.3 (C-2′), 77.2 (C-4), 75.0 (OCH_2Ph-A), 72.5 (C-4′),72.1 (OCH_2Ph-C), 70.9 (OCH_2Ph-B), 70.7 (C-5), 62.3 (C-5′), 61.2 (C-6), 61.3, 59.5, 55.2 (OCH_3) ppm. Data for **93**: Yield: 36% (102 mg, 0.163 mmol), colourless solid, R_f = 0.49 (EA), m.p. 115 °C, $[\alpha]_D^{25}$ = +85.0 (c = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.25 (m, 15 H, $H_{arom.}$), 4.83 (d, $^2J_{A,A'}$ = 11.0 Hz, 1 H, OCH_2Ph-A), 4.83 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.75–4.69 (m, 2 H, OCH_2Ph-B, OCH_2Ph-A′), 4.67–4.60 (m, 3 H, OCH_2Ph-B′, OCH_2Ph-C, OCH_2Ph-C′), 4.42 (d, $^3J_{1',2'}$ = 6.3 Hz, 1 H, 1′-H), 4.10–4.01 (m, 2 H, 6a-H, 5a′-H), 3.82–3.70 (m, 4 H, 2′-H, 5-H, 6b-H, 4′-H), 3.56 (dd, $^3J_{2',3'}$ = 8.3, $^3J_{3',4'}$ = 3.0 Hz, 1 H, 3′-H), 3.56–3.51 (m, 1 H, 4-H), 3.46 (dd, $^3J_{2,3}$ = 9.3 Hz, $^3J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 3.33 (dd, $^3J_{4',5b'}$ = 1.5 Hz, $^2J_{5a',5b'}$ = 12.3 Hz, 1 H, 5b′-H), 3.20 (dd, $^3J_{1,2}$ = 3.5 Hz, $^3J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.62, 3.48, 3.39 (s, 3 H, OCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 138.3 ($C_{arom.}$), 128.4, 128.3, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6 ($CH_{arom.}$), 103.1 (C-1′), 97.4 (C-1), 82.6 (C-3), 81.6 (C-2), 78.7 (C-3′), 78.4 (C-2′), 74.6 (OCH_2Ph-A), 72.5 (OCH_2Ph-C), 72.3 (C-4′), 71.6 (C-4), 71.3 (OCH_2Ph-B), 69.6 (C-5), 69.0 (C-6), 62.0 (C-5′), 61.1, 58.6, 55.2 (OCH_3) ppm. HRMS (ESI): calcd. for $C_{35}H_{44}O_{10}$ [M + Na]$^+$ 647.2827; found 647.2830.

Methyl 2,3-Di-*O*-methyl-4-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (94) and Methyl 2,3-Di-*O*-methyl-6-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (95): Prepared according to procedure G2. Compound **5** (66.6 mg, 0.300 mmol), NaH (24.0 g, 0.600 mmol), **21** (292 mg, 0.645 mmol), DMF (10 mL). Yield: 54% (104 mg, 0.163 mmol), colourless syrup, relative yield **94/95** = 25:75 (^1H NMR), R_f = 0.44/0.37 (EA). Disaccharide **95** was fully characterized by NMR spectroscopy. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 15 H, $H_{arom.}$), 4.97 (d, $^2J_{A,A'}$ = 11.3 Hz, 1 H, OCH_2Ph-A), 4.95 (d, $^2J_{B,B'}$ = 10.7 Hz, 1 H, OCH_2Ph-B), 4.79 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.78 (d, $^2J_{C,C'}$ = 11.6 Hz, 1 H, OCH_2Ph-C), 4.76 (d, $^2J_{B,B'}$ = 10.7 Hz, 1 H, OCH_2Ph-B′), 4.71 (d, $^2J_{C,C'}$ = 11.6 Hz, 1 H, OCH_2Ph-C′), 4.69 (d, $^2J_{A,A'}$ = 11.3 Hz, 1 H, OCH_2Ph-A′), 4.38 (d, $^3J_{1',2'}$ = 7.8 Hz, 1 H, 1′-H), 4.13 (dd, $^3J_{5,6a}$ = 5.9 Hz, $^2J_{6a,6b}$ = 11.3 Hz, 1 H, 6a-H), 3.82 (dd, $^3J_{1',2'}$ = 7.8 Hz, $^3J_{2',3'}$ = 9.6 Hz, 1 H, 2′-H), 3.80 (dd, $^3J_{5,6b}$ = 1.5 Hz, $^2J_{6a,6b}$ = 11.3 Hz, 1 H, 6b-H), 3.68–3.61 (m, 2 H, 4-H, 5-H), 3.56–3.42 (m, 4 H, 4′-H, 3-H, 3′-H, 5′-H), 3.63, 3.46, 3.38 (s, 3 H, OCH_3), 3.16 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 1.18 (d, $^3J_{5',6'}$ = 6.5 Hz, 3 H, 6′-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.8, 138.5, 138.5 ($C_{arom.}$), 128.4, 128.3, 128.2, 128.1, 128.1, 127.6, 127.4 ($CH_{arom.}$), 104.2 (C-1′), 97.5 (C-1), 82.5 (C-3′), 82.4 (C-3), 81.6 (C-2), 79.2 (C-2′), 76.3 (C-4′), 75.0 (OCH_2Ph-B), 74.6 (OCH_2Ph-A), 73.2 (OCH_2Ph-C), 70.5 (C-5′), 70.4, 70.2 (C-4, C-5), 68.8 (C-6), 61.0, 58.6, 55.1 (OCH_3), 16.8 (C-6′) ppm. HRMS (ESI): calcd. for $C_{41}H_{48}O_{10}$ [M + Na]$^+$ 723.3140; found 723.3135.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H and ^{13}C NMR spectra of all new compounds.

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