Synthesis of a New Type of Glycosidic Linkage: Acetal-Linked Disaccharides and Trisaccharides of Acyclic and Cyclic Sugars[‡]

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Dedicated to Professor Robert A. Field, University of East Anglia, U.K.

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New types of di- and trisaccharides related to a unique trisaccharide present in the cell walls of *Proteus* have been synthesized by coupling of acyclic sugar dithioacetals and di- and monohydroxy cyclic sugars. In this class of compounds an acyclic sugar is linked to a cyclic sugar through an acetal linkage. The formation of these acetal-linked pseudodi- and -trisaccharides has been achieved by a generalized reaction procedure mediated by 1,3-dibromo-5,5-dimethylhydantoin under mild, metal-free and neutral conditions. Sixteen protected and twelve deprotected di- and trisaccharides related to the trisaccharide found in the *Proteus* cell wall have been synthesized.

Introduction

Modern biochemistry and biology depend on structural knowledge of naturally occurring biologically important molecules such as oligosaccharides and glycoconjugates.[1–3] Sugars in nature exist as polysaccharides, glycoconjugates (glycoproteins and glycolipids) or glycosides in which monosaccharide units in cyclic form (pyranose or furanose) are joined together through O-glycosidic or C-glycosidic bonds. Several biosynthetic pathways for the formation of naturally occurring glycoconjugates have been explained on this basis, by consideration of the involvement of several glycosyltransferase enzymes in the biosynthesis.[4–8] According to the generally accepted and well supported mechanism for the synthesis of polysaccharides, it is believed that a glycosyltransferase enzyme stereospecifically joins the cyclic pyranose or furanose sugar to another sugar residue by using required cyclic sugar nucleotides.[9–12] In contrast with generally accepted knowledge, Vinogradov and Bock[13,14] discovered a new type of linkage between monosaccharides found in the core part of cell wall lipopolysaccharides (LPS) from two serotypes of *Proteus*. This is the first example of a new type of sugar–sugar linkage in bacterial polysaccharides, in which an open-chain sugar is linked to a cyclic sugar through acetal bond formation (Figure 1). After the discovery of such a type of glycosylidene glycosides in the bacterial cell wall, it has yet to be established whether this type of glycosides has any role in important biological functions or is able to stabilize the cell wall, to function as a cell-wall antigen or to act as a virulence factor. The existence of this type of glycosides indicated the existence of a new class of enzymes for their biosynthesis; these would certainly have to be different from the existing glycosyltransferases as these use cyclic sugar nucleotides for their action. In order to study the biological roles of this class of compounds in detail, it is essential to synthesize them chemically, as the natural source cannot provide them in good quantity. Prompted by the report of this new type of bacterial cell wall oligosaccharides, we found it interesting to synthesize such oligosaccharides, and here we disclose the synthesis of several disaccharides and trisaccharides in which an open-chain sugar is linked with the cyclic sugar through an acetal linkage. Although syntheses and isolations of several oligosaccharides containing acetal linkages have appeared in the literature,[15–23] most of these are cyclic monosaccharides linked to cyclic sugars through acetal linkages, these classes of compounds generally having been derived from cyclic sugar lactones. Some earlier reports deal with the formation

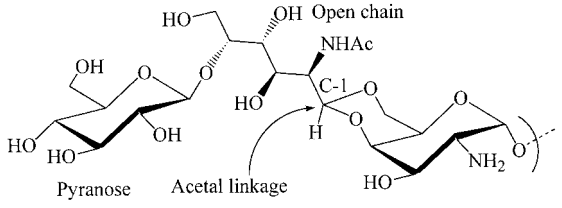

Figure 1. A new type of glycosyl linkage found in the cell wall of *Proteus* bacteria.

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of glycosylidene acetals derived from C-glycosyl aldehydes.[24] Recently, the formation of glycosylidene acetals and their selective reduction for the formation of coyolosa, a 6,6′-ether linked disaccharide natural product, has been reported.[25]

Results and Discussion

It has been emphasized that a series of acyclic glycosyl dithioacetal derivatives (Figure 2) could serve as a stable glycosyl donors to form glycosylidene acetals with mono- or dihydroxy cyclic sugar derivatives in order to synthesize the target molecules. Acyclic sugar dithioacetals were first prepared by E. Fischer[26] and as such represent some of the oldest known sugar derivatives.

Cyclic sugar derivatives for use as acceptors (Figure 3) were prepared by procedures reported elsewhere.[27–31] 4,6-Unprotected sugar derivatives **6**–**10** were prepared from the corresponding methyl glycosides by reaction sequences consisting of 4,6-*O*-benzylidene acetal formation, 2,3-di-*O*-benzylation or benzoylation and subsequent acid hydrolysis of the benzylidene acetal. The xylofuranose derivative **11**[32] was prepared from 1,2-*O*-isopropylidenexylofuranose by 5-*O*-tritylation, 3-*O*-benzylation and detritylation, whilst the 6-unprotected glucopyranoside derivative **12**[33] was prepared from the methyl glucopyranoside by 6-*O*-tritylation, 2,3,4-tri-*O*-benzylation and subsequent removal of the trityl group. All steps afforded excellent yields for the preparation of mono- and diunprotected cyclic sugar acceptors.

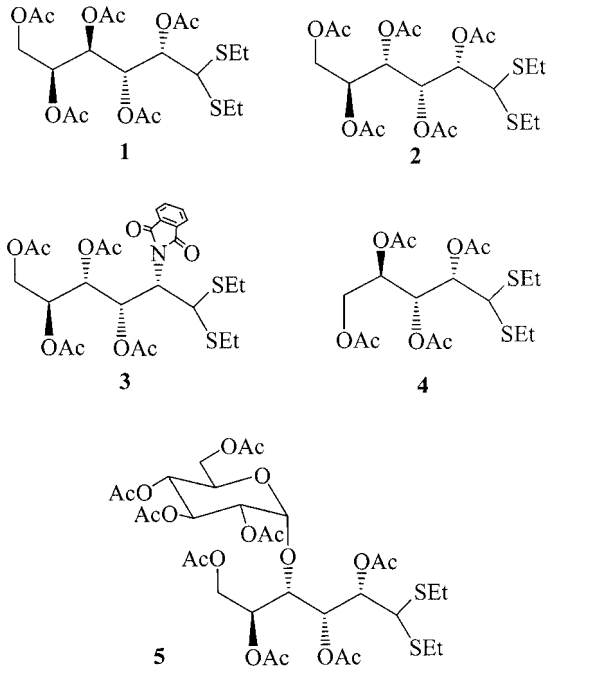


Figure 2. Acyclic glycosyl dithioacetals as glycosyl donors.

Access to the acyclic sugar donors (Figure 2) and cyclic sugar acceptors (Figure 3) having been achieved, several trial attempts were made to couple them successfully through acetal linkages. For this purpose, a series of thiophilic activators reported in the literature, such as *N*-bromosuccinimide,[34,35] *N*-iodosuccinimide,[36,37] molecular bromine[38,39] etc., were tested, but hydrolysed acyclic sugar donors and unreacted acceptors were isolated in all cases. We had recently found that 1,3-dibromo-5,5-dimethylhydantoin (DBDH) was able to act as a thiophilic activator to convert acyclic sugar dithioacetals into the alkyl glycofuranosides[40] and envisioned that DBDH, a cheap source for in situ generation of bromonium ion, might be a useful catalyst for the activation of sulfide to activate the dithioacetals in the presence of cyclic glycosyl acceptors towards the formation of acyclic glycosylidene acetals. DBDH has so far been utilized mainly as a free radical brominating agent[41] and as a source of bromonium ion, exploited in aromatic ring brominations,[42,43] but the full versatility of this reagent has not been well investigated. After a series of experiments regarding the quantity of activator, reaction solvent and other conditions, it was established that the use of 1.5 equivalent of DBDH was able to provide successful coupling of acyclic donors with the cyclic sugar derivatives through an acetal linkage at 0 °C in CH_3CN as solvent in a very short period of time and in excellent yields (Scheme 1, Table 1).

A series of di- and trisaccharides **14**–**31** (Figure 4 and Figure 5) were synthesized by this general procedure, through the coupling of a set of five peracetylated acyclic sugar dithioacetals **1**–**5** (Figure 2) with a set of eight suitably protected cyclic sugar derivatives **6**–**12** (Figure 3) in which the acyclic sugar was linked to the cyclic sugar through an acetal linkage. Use of an acyclic amino sugar

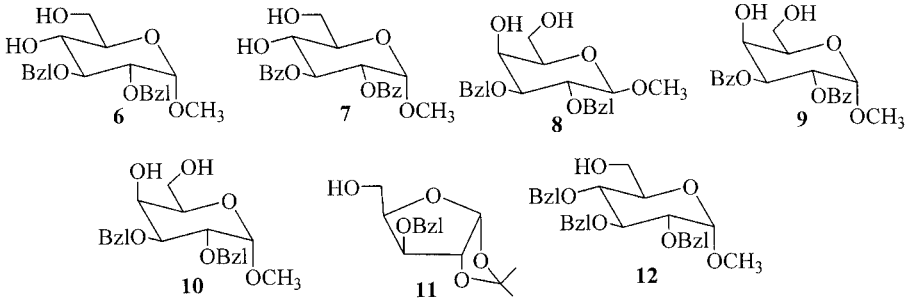
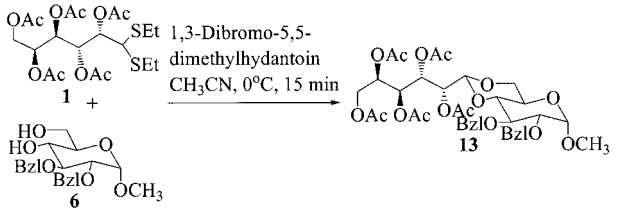


Figure 3. Cyclic mono- and dihydroxy sugar derivatives as glycosyl acceptors.



Scheme 1.

Table 1. Coupling of acyclic sugar dithioacetals with cyclic sugar acceptors in the presence of 1,3-dibromo-5,5-dimethylhydantoin to produce acetal-linked disaccharide and trisaccharides between acyclic and cyclic sugars.

Entry	Acyclic sugar dithioacetal	Cyclic sugar acceptor	Time (min)	Product	Yield[a] (%)
a	**1**	**6**	20	**13**	72
b	**2**	**6**	20	**14**	74
c	**4**	**6**	25	**15**	69
d	**1**	**7**	15	**16**	75
e	**2**	**7**	20	**17**	78
f	**4**	**7**	20	**18**	70
g	**1**	**10**	25	**19**	73
h	**2**	**8**	25	**20**	72
i	**4**	**8**	30	**21**	67
j	**1**	**9**	30	**22**	73
k	**3**	**6**	40	**23**	62
l	**5**	**7**	40	**24**	65
m	**1**	**11**	20	**25**	76
n	**1**	**12**	20	**26**	75
o	**2**	**12**	25	**27**	72
p	**4**	**12**	25	**28**	77

[a] Isolated yield.

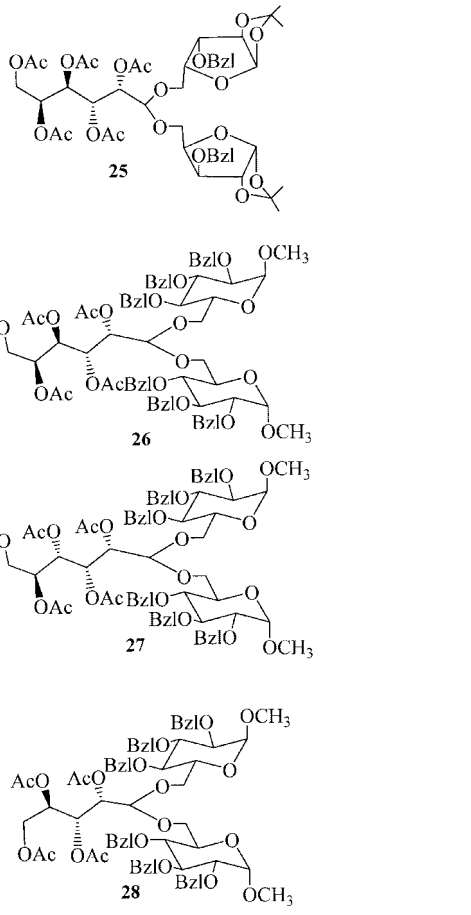


Figure 5. Synthesized acetal-linked acyclic–cyclic sugar trisaccharides.

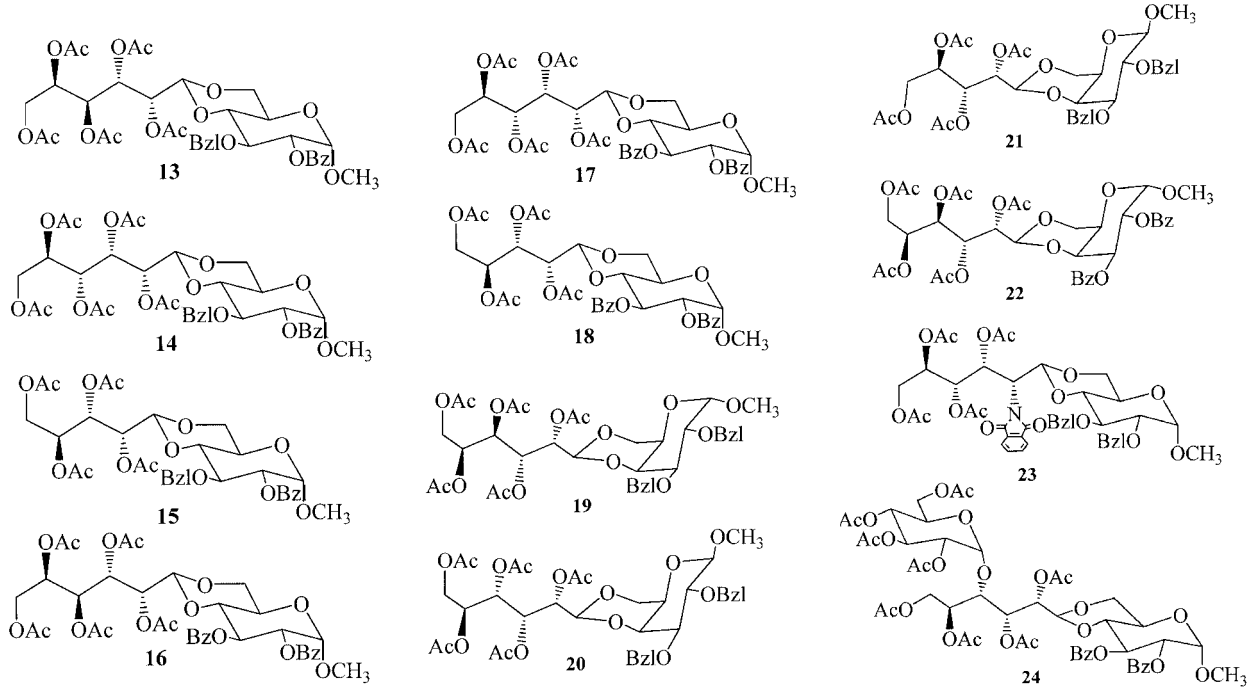


Figure 4. Synthesized acetal-linked acyclic–cyclic sugar disaccharides.

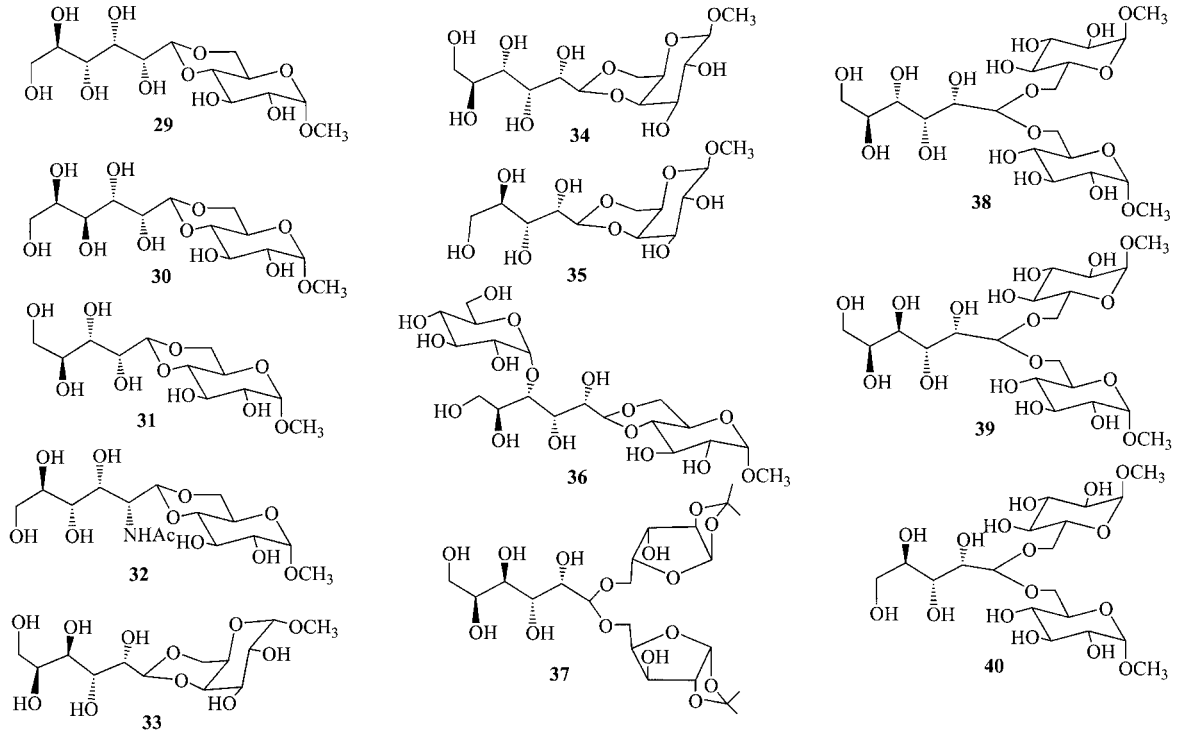


Figure 6. Deprotected di- and trisaccharides containing acetal linkages.

dithioacetal **3** and a disaccharide dithioacetal **5** also successfully produced the expected acetal-linked di- and trisaccharides respectively in very good yields.

Although it is believed that acetal-linked compounds might suffer from chemical instability under various reaction conditions, to our satisfaction all protected di- and trisaccharides containing acetal linkages were successfully deprotected by conventional deprotection techniques. Therefore, 12 deprotected di- and trisaccharides **29**–**40** with acetal linkages instead of glycosyl bonds were synthesized successfully (Figure 6). Compound **36** can be regarded as a close analogue of the unique trisaccharide present in the *Proteus* cell wall (Figure 1).

It is noteworthy that only single stereoisomers of the glycosylidene acetals were obtained as the coupled products, as confirmed by their masses and ^{1}H and ^{13}C NMR spectra, and also by NOE measurements and HPLC analysis. In an NOE study of compounds **13**–**24**, strong NOE enhancements between the H-1s in the acyclic sugar components and the H-4s and H-6s in the cyclic sugar moieties were observed, possible only if H-1 in the acyclic sugar moiety (acetal proton) is present in an axial orientation in compounds **13**–**18**, **23** and **24** and in an equatorial orientation in the cases of compounds **19**–**22**. Therefore, the C-1 atoms in the acyclic sugars in compounds **13**–**18**, **23** and **24** have (*R*) configurations, whereas C-1 in the acyclic sugars in compounds **19**–**22** has (*S*) configuration (Figure 7).

We presume that DBDH generates bromonium ion (Br^{+}) in situ, and that this is captured by the lone pair of sulfur to form a reactive bromosulfonium ion intermediate, facilitating the nucleophilic attack of the cyclic di- or monohydroxy acceptor to generate the target acetal-linked di- and trisaccharides (Scheme 2).

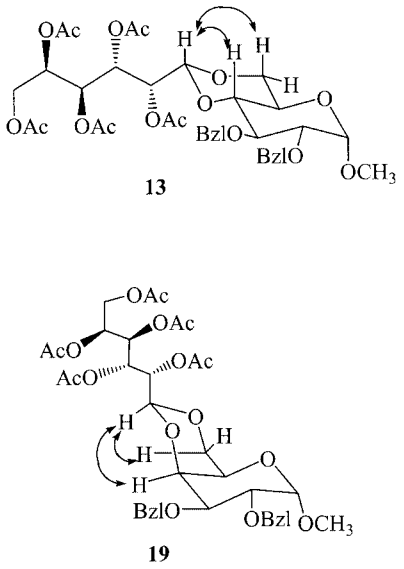
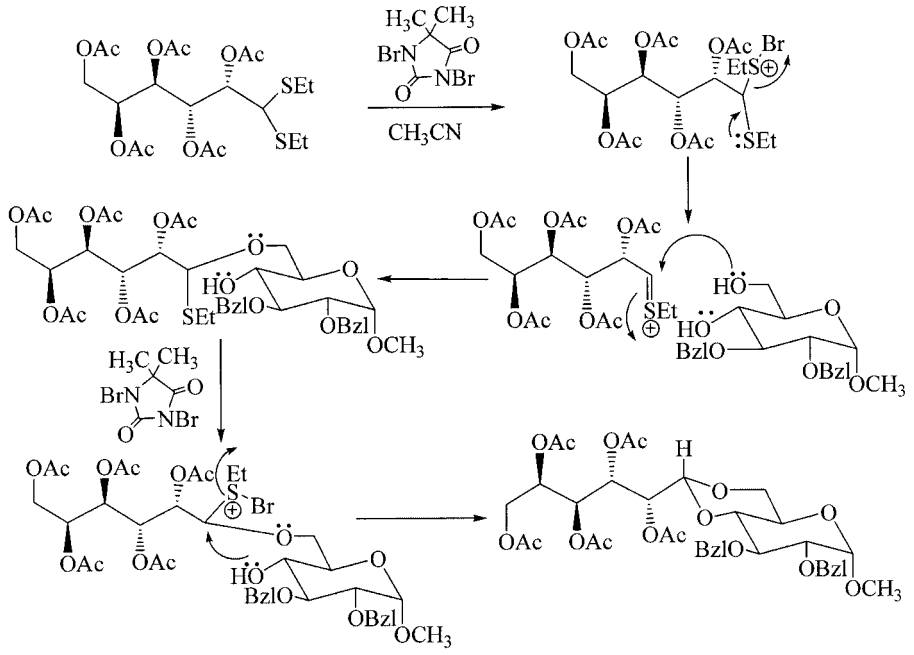


Figure 7. NOE enhancement observed between acyclic H-1 and H-4 and H-6 of cyclic sugars.

In summary, a new class of di- and trisaccharides has been synthesized by coupling of readily accessible acyclic glycosyldithioacetals with di- or monohydroxylated cyclic



Scheme 2. Plausible mechanism for the formation of acyclic glycosylidene glycoside.

sugar derivatives in the presence of DBDH, a thiophilic activator, in excellent yield. In all cases, single stereoisomers were obtained exclusively. These new sets of compounds (**29**–**40**) are analogues of a unique trisaccharide found in the cell wall of *Proteus*, and it is planned to evaluate their inhibitory activities against several glycosyltransferases and glycosidases. These new classes of compounds may open up new vistas in glycobiology involving the existence of a previously unknown class of enzymes used for the incorporation of these acceptors in cell wall biosynthesis. Studies on the further utilization of these compounds towards the formation of ether-linked disaccharides of acyclic and cyclic sugars by regioselective reduction of the acetal linkage are currently in progress in our laboratory.

Experimental Section

General Remarks: All the reactions were monitored by thin-layer chromatography over silica gel coated TLC plates. TLC spots were visualized by warming of ceric sulfate-sprayed (2% $CeSO_4$ in 2 N H_2SO_4) plates (hot plate at about 150 °C). Silica gel (100–200 mesh, SRL, India) was used for column chromatography. ESI-MS mass spectra were recorded on a Micromass Quattro II instrument. HPLC experiments were run on a Shimadzu LC 10 AD system with a Lichrocart chiral column and MeOH or CH_3CN/H_2O as an eluent. ^1H and ^{13}C NMR was recorded on a Bruker Advance DPX 200 MHz machine with TMS as internal reference. Chemical shift values are expressed in δ (ppm). Elementary analysis was carried out on a Carlo ERBA-1108 analyzer. Optical rotations were measured at 25 °C on a Rudolf Autopol III polarimeter. Commercially available grades of organic solvents of adequate purity were used in many reactions.

Typical Experimental Procedure for the Preparation of Acetal-Linked Di- and Trisaccharides 13–28: A solution of 2,3,4,5,6-penta-*O*-acetyl-D-glucose diethyl dithioacetal (**2**; 630.0 mg, 1.26 mmol) and methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (**6**; 295.0 mg, 0.84 mmol) in anhydrous acetonitrile (15.0 mL) was placed in an ice bath. 1,3-Dibromo-5,5-dimethylhydantoin (360.0 mg, 1.26 mmol) was added to the cooled reaction mixture, which was allowed to stir at 0 °C for the specified time as mentioned in Table 1. After complete disappearance of the starting material (as monitored by TLC), triethylamine (200 μL) was added and the solvent was removed under reduced pressure. The crude reaction mixture was dissolved in dichloromethane (25 mL). The organic layer was washed successively with 5% aq. $Na_2S_2O_3$, satd. aq. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated to dryness. Column chromatography of the crude mass over SiO_2 with hexane/EtOAc (4:1) as an eluent furnished pure methyl 2,3-di-*O*-benzyl-4,6-*O*-[(1*R*)-2,3,4,5,6-penta-*O*-acetyl-D-glucosylidene]-α-D-glucopyranoside (**14**; 465.0 mg, 74%). A series of di- and trisaccharides **13**–**28** was synthesized under similar reaction conditions.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-[(1*R*)-2,3,4,5,6-penta-*O*-acetyl-D-galactosylidene]-α-D-glucopyranoside (13): Yellowish oil (451.0 mg; 72%). $[\alpha]_D^{25}$ = +22.1 (*c* = 0.1, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.96, 2.00, 2.06, 2.11, 2.12 (5s, 15 H, 5 $COCH_3$), 3.34 (s, 3 H, OCH_3), 3.36–3.39 (m, 1 H), 3.42–3.49 (m, 2 H), 3.62–3.67 (m, 1 H), 3.80–3.91 (m, 2 H), 4.06–4.11 (dd, *J* = 10.0, 5.4 Hz, 1 H), 4.25–4.31 (dd, *J* = 12.0, 4.6 Hz, 1 H), 4.50 (d, *J* = 3.4 Hz, 1 H), 4.57 (d, *J* = 5.2 Hz, 1 H), 4.65 (d, *J* = 12 Hz, 1 H), 4.77–4.83 (dd, *J* = 11.9 Hz, 2 H), 4.99 (d, *J* = 11.2 Hz, 1 H), 5.12–5.15 (dd, *J* = 5.3, 1.6 Hz, 1 H), 5.25–5.32 (m, 2 H), 5.57–5.62 (dd, *J* = 9.6, 1.6 Hz, 1 H), 7.27–7.48 (10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (2 C), 21.1 (3 C), 55.7, 62.1, 62.7, 67.1, 68.1 (2 C), 69.0, 69.1, 74.2, 75.3, 78.5, 79.5, 82.4, 99.1, 99.5, 127.0–139.18 (aromatic C), 169.7, 170.2, 170.3, 170.6, 178.4 ppm. IR (neat): $\tilde{\nu}$ = 3020, 2931, 2874, 1755, 1496, 1453, 1372, 1218, 1053,

909, 854, 762, 700, 667, 604 cm^{-1}. ESI-MS: *m/z* = 764.5 [*M* + NH_4]$^+$. $C_{37}H_{46}O_{16}$ (746): calcd. C 59.51, H 6.21; found C 59.35, H 6.40.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-[(1*R*)-2,3,4,5,6-penta-*O*-acetyl-D-glucosylidene]-α-D-glucopyranoside (14): Yellowish oil (465.0 mg; 74%). $[\alpha]_D^{25}$ = +29.1 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.89, 1.96, 1.99, 2.01, 2.02 (5s, 15 H, 5 COCH_3), 3.27–3.34 (m, 1 H), 3.38 (s, 3 H, OCH_3), 3.41–3.51 (m, 2 H), 3.64–3.71 (m, 1 H), 3.89–3.99 (t, *J* = 9.4 Hz each, 1 H), 4.03–4.12 (m, 2 H), 4.18–4.26 (dd, *J* = 14.0, 4.0 Hz, 1 H), 4.56 (d, *J* = 3.6 Hz, 1 H), 4.68–4.69 (dd, *J* = 10.0 Hz, 2 H), 4.79 (m, 1 H), 4.75–4.92 (dd, *J* = 11.6, 12.0 Hz, 2 H), 5.05–5.16 (m, 2 H), 5.47–5.51 (dd, *J* = 7.6, 3.2 Hz, 1 H), 5.62–5.67 (dd, *J* = 6.8, 2.0 Hz, 1 H), 7.19–7.38 (m, 10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9 (3 C), 21.1 (2 C), 55.9, 62.1, 62.3, 68.3, 68.9, 69.1, 69.6, 71.2, 74.1, 75.8, 78.9, 79.3, 82.1, 99.3, 99.6, 128.0–138.9 (aromatic C), 169.9 (2 C), 170.9 (3C) ppm. IR (neat): ṽ = 2926, 1750, 1449, 1371, 1219, 1052, 754, 700, 605 cm^{-1}. ESI-MS: *m/z* = 764.4 [*M* + NH_4]$^+$. $C_{37}H_{46}O_{16}$ (746): calcd. C 59.51, H 6.21; found C 59.36, H 6.40.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-[(1*R*)-2,3,4,5-tetra-*O*-acetyl-D-arabinosylidene]-α-D-glucopyranoside (15): Yellowish oil (391.0 mg; 69%). $[\alpha]_D^{25}$ = +3.3 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.96, 2.03, 2.04, 2.10 (4s, 12 H, 4 COCH_3), 3.32–3.34 (m, 1 H), 3.36 (s, 3 H, OCH_3), 3.42–3.46 (m, 1 H), 3.47–3.49 (dd, *J* = 10.0, 2.0 Hz, 1 H), 3.68–3.70 (m, 1 H), 3.95 (t, *J* = 8.2 Hz each, 1 H), 4.10–4.21 (m, 3 H), 4.52–4.54 (m, 2 H), 4.61 (d, *J* = 12 Hz, 1 H), 4.75 (s, 2 H, PhCH_2), 4.82 (d, *J* = 11.8 Hz, 1 H), 5.20 (m, 1 H), 5.26–5.28 (m, 1 H), 5.51–5.54 (dd, *J* = 7.6, 3.0 Hz, 1 H), 7.30–7.39 (m, 10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (4 C), 55.8, 63.2 (2 C), 68.2 (2 C), 68.6, 69.5, 73.0, 74.8, 78.2, 79.0, 80.5, 99.7, 99.9, 127.9–138.2 (aromatic C), 170.1, 170.5, 171.2, 171.6 ppm. IR (neat): ṽ = 2926, 2857, 1750, 1457, 1374, 1220, 1162, 1076, 858, 756, 701, 666, 606 cm^{-1}. ESI-MS: *m/z* = 692.4 [*M* + NH_4]$^+$. $C_{34}H_{42}O_{14}$ (674): calcd. C 60.53, H 6.27; found C 60.35, H 6.50.

Methyl 2,3-Di-*O*-benzoyl-4,6-*O*-[(1*R*)-2,3,4,5,6-penta-*O*-acetyl-D-galactosylidene]-α-D-glucopyranoside (16): Yellowish oil (488.0 mg; 75%). $[\alpha]_D^{25}$ = +76.6 (*c* = 0.01, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.57, 1.96, 2.03, 2.09, 2.17 (5s, 15 H, 5 COCH_3), 3.38 (s, 3 H, OCH_3), 3.50–3.63 (m, 2 H), 3.70–3.79 (dd, *J* = 8.0, 3.6 Hz, 1 H), 3.87–4.00 (m, 1 H), 4.19–4.29 (m, 2 H), 4.54 (d, *J* = 6.4 Hz, 1 H), 5.06–5.17 (m, 4 H), 5.21–5.23 (dd, *J* = 10.0, 2.0 Hz, 1 H), 5.40–5.46 (dd, *J* = 10.0, 1.2 Hz, 1 H), 5.87–5.96 (t, 1 H), 7.31–8.04 (m, 10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5 (2 C), 20.9 (3 C), 55.8, 62.5 (2 C), 66.6, 67.8 (2 C), 68.9, 69.2, 69.4, 72.9, 79.4, 98.1, 99.2, 126.9–133.7 (aromatic C), 166.1, 166.3, 168.9–170.7 (5C) ppm. IR (neat): ṽ = 3022, 2979, 2933, 1754, 1753, 1451, 1372, 1277, 1213, 1105, 1048, 764, 713, 668, 599 cm^{-1}. ESI-MS: *m/z* = 792.4 [*M* + NH_4]$^+$. $C_{37}H_{42}O_{18}$ (774): calcd. C 57.36, H 5.46; found C 57.55, H 6.70.

Methyl 2,3-Di-*O*-benzoyl-4,6-*O*-[(1*R*)-2,3,4,5,6-penta-*O*-acetyl-D-glucosylidene]-α-D-glucopyranoside (17): Yellowish oil (507.0 mg; 78%). $[\alpha]_D^{25}$ = +98.3 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.78, 1.91, 1.95, 1.98, 2.01 (5s, 15 H, 5 COCH_3), 3.33 (s, 3 H, OCH_3), 3.52–3.57 (m, 2 H), 3.85–3.87 (m, 1 H), 4.01–4.03 (m, 1 H), 4.10–4.16 (m, 2 H), 4.63 (d, *J* = 4.2 Hz, 1 H), 4.99–5.02 (m, 1 H), 5.12–5.16 (m, 2 H), 5.20 (d, *J* = 3.7 Hz, 1 H), 5.39–5.48 (m, 2 H), 5.87–5.96 (t, 1 H), 7.27–7.91 (m, 10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (2 C), 21.0 (3 C), 55.9, 62.1, 62.4, 67.8, 68.8 (2 C), 69.6, 69.8, 70.7, 72.6, 79.4, 98.2, 99.6, 125.7–133.8 (aromatic C), 165.8, 166.3, 169.7, 170.1, 170.2, 170.3, 170.9 ppm. IR (neat): ṽ = 2927, 2856, 1753, 1451, 1372, 1220, 1105, 1050, 758, 713 cm^{-1}. ESI-MS: *m/z* = 792.3 [*M* + NH_4]$^+$. $C_{37}H_{42}O_{18}$ (774): calcd. C 57.36, H 5.46; found C 57.15, H 5.59.

Methyl 2,3-Di-*O*-benzoyl-4,6-*O*-[(1*R*)-2,3,4,5-tetra-*O*-acetyl-D-arabinosylidene]-α-D-glucopyranoside (18): Yellowish oil (414.0 mg; 70%). $[\alpha]_D^{25}$ = +62.5 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.64, 1.97, 2.02, 2.08 (4s, 12 H, 4 COCH_3), 3.40 (s, 3 H, OCH_3), 3.53–3.58 (m, 2 H), 4.01–4.05 (m, 1 H), 4.12–4.16 (m, 2 H), 4.19 (m, 1 H), 4.28–4.32 (m, 1 H), 4.53 (d, *J* = 6.4 Hz, 1 H), 5.10–5.12 (m, 2 H), 5.23–5.29 (m, 1 H), 5.51–5.54 (dd, *J* = 7.6, 2.0 Hz, 1 H), 5.95 (t, 1 H), 7.33–7.98 (m, 10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3 (2 C), 21.1 (2 C), 55.9, 62.2, 62.5, 68.5 (2 C), 68.9, 69.6 (2 C), 72.4, 79.7, 98.3, 99.4, 128.7–133.8 (aromatic C), 165.5, 166.4, 169.6 (2 C), 170.3, 171.1 ppm. IR (neat): ṽ = 3020, 2927, 2856, 1733, 1454, 1372, 1275, 1219, 1103, 1052, 759, 713, 668 cm^{-1}. ESI-MS: *m/z* = 720.3 [*M* + NH_4]$^+$. $C_{34}H_{38}O_{16}$ (702): calcd. C 58.12, H 5.45; found C 57.90, H 5.70.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-[(1*S*)-2,3,4,5,6-penta-*O*-acetyl-D-galactosylidene]-α-D-galactopyranoside (19): Yellowish oil (458.0 mg; 73%). $[\alpha]_D^{25}$ = +40.1 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.01, 2.03, 2.05, 2.07, 2.10 (5s, 15 H, 5 COCH_3), 3.33 (s, 3 H, OCH_3), 3.62 (br. s, 1 H), 3.62–3.68 (dd, *J* = 12.0, 3.0 Hz, 1 H), 3.83–3.90 (m, 3 H), 4.00–4.08 (m, 2 H), 4.23–4.31 (dd, *J* = 11.6, 4.5 Hz, 1 H), 4.56 (d, *J* = 5.6 Hz, 1 H), 4.62 (m, 1 H), 4.68–4.86 (2dd, 4 H, 2PhCH_2), 5.18–5.21 (m, 2 H), 5.26–5.32 (dd, *J* = 10.0, 4.0 Hz, 1 H), 5.64–5.70 (dd, *J* = 9.8, 1.2 Hz, 1 H), 7.26–7.40 (m, 10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (2 C), 21.2 (3 C), 55.9, 62.7, 62.9, 66.9, 67.9, 68.0, 69.4, 69.5, 72.5, 74.3, 74.8, 75.8, 76.1, 98.3, 99.9, 127.7–139.1 (aromatic C), 169.7, 170.3, 170.7 (2 C), 170.8 ppm. IR (neat): ṽ = 3298, 3026, 2926, 2859, 1730, 1451, 1373, 1223, 1050, 756, 701, 601 cm^{-1}. ESI-MS: *m/z* = 764.4 [*M* + NH_4]$^+$. $C_{37}H_{46}O_{16}$ (746): calcd. C 59.51, H 6.21; found C 59.35, H 6.42.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-[(1*S*)-2,3,4,5,6-penta-*O*-acetyl-D-glucosylidene]-β-D-galactopyranoside (20): Yellowish oil (452.0 mg; 72%). $[\alpha]_D^{25}$ = +19.5 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.98, 2.01, 2.04, 2.05, 2.08 (5s, 15 H, 5 COCH_3), 3.54 (s, 3 H, OCH_3), 3.80–3.84 (dd, *J* = 10.0, 9.6 Hz, 1 H), 3.90–3.94 (m, 2 H), 4.16–4.20 (m, 4 H), 4.26–4.28 (d, *J* = 7.6 Hz, 1 H), 4.66 (br. s, 2 H, PhCH_2), 4.70 (d, *J* = 2.0 Hz, 1 H), 4.82–4.89 (dd, *J* = 11.6, 12.0 Hz, 2 H, PhCH_2), 5.20–5.29 (m, 3 H), 5.40–5.46 (m, 1 H), 5.70–5.73 (m, 1 H), 7.28–7.39 (m, 10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.0 (5 C), 57.1, 60.7, 62.3, 66.6, 68.1, 69.4, 70.5, 71.2, 72.1, 74.2, 75.5, 78.1, 79.5, 98.9, 105.1, 127.84–139.5 (aromatic C), 170.0, 170.3 (2 C), 171.0, 171.6 ppm. IR (neat): ṽ = 3466, 2927, 1748, 1373, 1222, 1054, 758, 700 cm^{-1}. ESI-MS: *m/z* = 764.4 [*M* + NH_4]$^+$. $C_{37}H_{46}O_{16}$ (746): calcd. C 59.51, H 6.21; found C 59.33, H 6.45.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-[(1*S*)-2,3,4,5-tetra-*O*-acetyl-D-arabinosylidene]-β-D-galactopyranoside (21): Yellowish oil (380.0 mg; 67%). $[\alpha]_D^{25}$ = +2.7 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.97, 2.02, 2.06, 2.09 (4s, 12 H, 4 COCH_3), 3.24 (br. s, 1 H), 3.43–3.45 (m, 1 H), 3.48–3.50 (dd, *J* = 9.6, 3.6 Hz, 1 H), 3.54 (s, 3 H, OCH_3), 3.74 (d, *J* = 7.6 Hz, 1 H), 3.78–3.80 (dd, *J* = 6.9, 1.2 Hz, 1 H), 3.96 (d, *J* = 3.6 Hz, 1 H), 4.21–4.33 (m, 3 H), 4.56–4.62 (d, *J* = 12.0 Hz, 1 H), 4.63 (d, *J* = 4.0 Hz, 1 H), 4.79–4.92 (3d, *J* = 12.0 Hz, 3 H, PhCH_2), 5.18–5.21 (m, 1 H), 5.27–5.31 (dd, *J* = 5.4, 2.8 Hz, 1 H), 5.56–5.62 (dd, *J* = 8.0, 2.2 Hz, 1 H), 7.31–7.40 (m, 10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (5 C), 57.3, 62.4, 66.7, 68.7, 68.9, 69.3, 70.2, 71.6, 73.7, 75.4, 78.4, 79.3, 99.2, 104.9, 127.8–139.3 (aromatic C), 169.8, 170.0, 170.3, 171.0 ppm. IR (neat): ṽ = 3466, 3020, 2928, 2867, 1745, 1452, 1373,

1223, 1058, 760 cm^{-1}. ESI-MS: m/z = 692.3 [M + NH_4]$^+$. $C_{34}H_{42}O_{14}$ (674): calcd. C 60.53, H 6.27; found C 60.35, H 6.50.

Methyl 2,3-Di-*O*-benzoyl-4,6-*O*-[(1*S*)-2,3,4,5,6-penta-*O*-acetyl-D-galactosylidene]-α-D-galactopyranoside (22): Yellowish oil (475.0 mg; 73%). $[\alpha]_D^{25}$ = +62.5 (c = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.72, 1.97, 2.08, 2.11, 2.17 (5s, 15 H, 5 COCH_3), 3.43 (s, 3 H, OCH_3), 3.73–3.78 (m, 2 H), 3.81–3.87 (dd, J = 7.2 Hz each, 1 H), 4.18–4.31 (m, 2 H), 4.40 (d, J = 2.0 Hz, 1 H), 4.48 (d, J = 7.0 Hz, 1 H), 5.14–5.29 (m, 4 H), 5.61–5.67 (m, 3 H), 7.32–8.00 (m, 10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6 (2 C), 21.0 (3 C), 54.3, 62.4, 62.7, 67.2, 67.8, 68.0, 68.8, 69.3, 69.5 (2 C), 73.9, 98.5, 98.6, 128.7–133.7 (aromatic C), 166.0, 166.3, 169.4, 169.6, 170.4, 170.9 (2C) ppm. IR (neat): $\tilde{\nu}$ = 3277, 3022, 2939, 2933, 1729, 1451, 1372, 1219, 1106, 1048, 764, 713, 669 cm^{-1}. ESI-MS: m/z = 792.4 [M + NH_4]$^+$. $C_{37}H_{42}O_{18}$ (774): calcd. C 57.36, H 5.46; found C 57.20, H 6.70.

Methyl 2,3-Di-*O*-benzyl-4,6-*O*-[(1*R*)-3,4,5,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-D-glucosylidene]-α-D-glucopyranoside (23): Yellowish oil (435.0 mg; 62%). $[\alpha]_D^{25}$ = +3.2 (c = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86, 2.03, 2.09, 2.10 (4s, 12 H, 4 COCH_3), 3.14 (s, 3 H, OCH_3), 3.25–3.29 (dd, J = 7.6, 2.5 Hz, 1 H), 3.34–3.41 (m, 2 H), 3.56–3.61 (m, 2 H), 3.76–3.80 (m, 1 H), 4.09–4.13 (dd, J = 8.0, 1.2 Hz, 1 H), 4.21–4.25 (m, 1 H), 4.28–4.34 (m, 3 H), 4.49–4.68 (3dd, J = 12.0 Hz each, 3 H, PhCH_2), 4.88 (d, J = 12.0 Hz, 1 H, PhCH_2), 5.20 (t, J = 9.8 Hz each, 1 H), 5.39 (d, J = 9.8 Hz, 1 H), 5.78 (dd, J = 9.0 Hz each, 1 H), 7.27–7.34 (m, 14 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.81, 20.97 (2 C), 21.1, 55.2, 60.6, 62.4, 69.4, 69.9, 70.2, 70.3, 71.1, 72.3, 73.4, 75.6, 80.0, 81.6, 98.2, 99.3, 123.8–139.2 (aromatic C), 156.9, 168.1, 169.9, 170.5, 171.2, 175.6 ppm. IR (neat): $\tilde{\nu}$ = 3337, 3018, 2931, 1724, 1669, 1499, 1454, 1388, 1228, 1049, 917, 764, 701, 667 cm^{-1}. ESI-MS: m/z = 851.3 [M + NH_4]$^+$. $C_{43}H_{47}NO_{16}$ (833): calcd. C 61.94, H 5.68; found C 62.18, H 5.90.

Methyl 2,3-Di-*O*-benzoyl-4,6-*O*-[(1*R*)-2,3,5,6-tetra-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-D-glucosylidene]-α-D-glucopyranoside (24): Yellowish oil (580.0 mg; 65%). $[\alpha]_D^{25}$ = +25.1 (c = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.99, 2.00, 2.01, 2.03, 2.05, 2.06, 2.09, 2.10, (8 s, 24 H, 8 COCH_3), 3.42 (s, 3 H), 3.51–3.64 (m, 2 H), 3.83–3.88 (m, 2 H), 3.90–4.01 (m, 3 H), 4.08–4.33 (m, 4 H), 4.43–4.51 (dd, J = 9.0 and 3.5 Hz Hz, 1 H), 4.70 (d, J = 2.6 Hz, 1 H), 4.95 (br. s, 1 H), 5.06–5.11 (m, 2 H), 5.12–5.19 (m, 2 H), 5.36–5.46 (m, 1 H), 5.52–5.56 (m, 1 H), 5.81–5.90 (m, 1 H), 7.27–7.96 (10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (4 C), 21.0 (4 C), 56.2, 62.2, 62.3, 62.5, 68.4, 68.5, 68.7, 68.9, 69.6, 70.2, 70.4, 70.8, 71.5, 72.5, 76.8, 79.6, 97.7, 98.3, 100.1, 128.6–133.8 (aromatic C), 165.8, 166.3, 169.8, 169.9, 170.3 (3 C), 170.8, 170.9 (2 C) ppm. IR (neat): $\tilde{\nu}$ = 3488, 3023, 2933, 1745, 1452, 1372, 1226, 1045, 761, 700 cm^{-1}. ESI-MS: m/z = 1085.4 [M + Na]$^+$. $C_{49}H_{58}O_{26}$ (1062): calcd. C 55.37, H 5.50; found C 55.17, H 5.76.

5,5′-*O*-(2,3,4,5,6-*O*-Penta-*O*-acetyl-D-galactosylidene)bis(1,2-*O*-isopropylidene-3-*O*-benzyl-α-D-xylofuranose) (25): Yellowish oil (1.20 g; 76%). $[\alpha]_D^{25}$ = –5.3 (c = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.28, 1.30 (2s, 6 H, CH(CH_3)$_2$), 1.45, 148 (2s, 6 H, CH(CH_3)$_2$), 1.98, 2.00, 2.03, 2.06, 2.10 (5s, 15 H, 5 COCH_3), 3.55–3.60 (dd, J = 7.6, 4.0 Hz, 1 H), 3.74–3.80 (m, 2 H), 3.86–3.87 (m, 1 H), 3.89–4.00 (m, 3 H), 4.20–4.30 (m, 2 H), 4.38–4.39 (m, 2 H), 4.40–4.67 (m, 6 H), 5.15–5.25 (m, 3 H), 5.55–5.61 (dd, J = 8.0, 2.0 Hz, 1 H), 5.90 (d, J = 3.6 Hz, 2 H), 7.29–7.32 (m, 10 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0 (5 C), 26.7 (2 C), 27.2 (2 C), 62.7, 66.5, 67.3, 67.7, 68.1 (2 C), 68.9, 72.1, 72.5, 79.5, 79.9, 82.3, 82.4, 82.6, 82.7, 102.2, 105.5 (2 C), 112.1 (2 C), 127.9–137.9 (aromatic C), 169.4, 170.4 (2 C), 170.7, 170.8 ppm. IR (neat): $\tilde{\nu}$ = 3022, 2986, 2934, 1750, 1455, 1374, 1219, 1164, 1077, 857, 764, 699, 667 cm^{-1}. ESI-MS: m/z = 950.4 [M + NH_4]$^+$. $C_{46}H_{60}O_{20}$ (932): calcd. C 59.22, H 6.48; found C 58.92, H 6.75.

6,6′-*O*-(2,3,4,5,6-Penta-*O*-acetyl-D-galactosylidene)bis(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (26): Yellowish oil (1.64 g; 75%). $[\alpha]_D^{25}$ = +15.1 (c = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.82, 1.87, 1.89, 1.91, 1.93 (5s, 15 H, 5 COCH_3), 3.22, 3.26 (2s, 6 H, 2 OCH_3), 3.29–3.37 (m, 3 H), 3.39–3.43 (m, 2 H), 3.45–3.49 (m, 2 H), 3.56–3.77 (m, 4 H), 3.86 (t, J = 7.6 Hz, 2 H), 4.15–4.23 (dd, J = 7.6, 3.0 Hz, 1 H), 4.36–4.42 (m, 3 H), 4.46–4.51 (m, 3 H), 4.54 (d, J = 4.0 Hz, 1 H), 4.62–4.72 (m, 6 H), 4.84 (d, J = 12.0 Hz, 2 H), 5.07–5.15 (m, 3 H), 5.40 (dd, J = 7.0, 3.6 Hz, 1 H), 7.16–7.21 (m, 30 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 21.1 (2 C), 21.2 (2 C), 55.5 (2 C), 62.7 (2 C), 66.6, 67.2, 67.9 (2 C), 68.3 (2 C), 69.1, 70.3 (2 C), 73.7 (2 C), 75.1 (2 C), 76.0 (2 C), 80.2 (2 C), 82.4 (2 C), 98.4 (2 C), 101.6, 127.9–139.3 (aromatic C), 169.3, 170.0, 170.3, 170.7, 170.8 ppm. IR (neat): $\tilde{\nu}$ = 3025, 2930, 1752, 1455, 1369, 1225, 1062, 758, 700, 667 cm^{-1}. ESI-MS: m/z = 1318.6 [M + NH_4]$^+$. $C_{72}H_{84}O_{22}$ (1300): calcd. C 66.45, H 6.51; found C 66.65, H 6.78.

6,6′-*O*-(2,3,4,5,6-Penta-*O*-acetyl-D-glucosylidene)bis(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (27): Yellowish oil (1.57 g; 72%). $[\alpha]_D^{25}$ = +14.5 (c = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.91, 1.94, 1.97, 1.98, 2.04 (5s, 15 H, 5 COCH_3), 3.32, 3.35 (2s, 6 H, 2 OCH_3), 3.39–3.46 (m, 2 H), 3.51 (d, J = 4.0 Hz, 1 H), 3.55–3.59 (m, 2 H), 3.62–3.71 (m, 4 H), 3.79–3.85 (dd, J = 9.6, 3.0 Hz, 1 H), 3.90–3.99 (m, 4 H), 4.03–4.09 (dd, J = 9.0, 6.0 Hz, 1 H), 4.15–4.21 (dd, J = 7.6, 2.4 Hz, 1 H), 4.48 (d, J = 4.0 Hz, 1 H), 4.53–4.58 (m, 2 H), 4.61–4.64 (m, 2 H), 4.70 (d, J = 4.8 Hz, 1 H), 4.74 (m, 2 H), 4.79–4.84 (m, 3 H), 4.97 (d, J = 12.0 Hz, 2 H), 5.10–5.19 (m, 2 H), 5.38–5.42 (m, 2 H), 7.25–7.33 (aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (2 C), 21.1 (3 C), 55.5 (2 C), 62.3 (2 C), 66.7, 67.9, 68.9, 69.6, 70.0 (2 C), 70.4 (2 C), 73.6 (2 C), 75.1, 75.3, 76.0 (2 C), 78.4, 80.4 (2 C), 82.4 (2 C), 98.2, 98.5, 102.5, 127.9–139.3 (aromatic C), 169.8 (2 C), 170.2 (2 C), 170.8 ppm. IR (neat): $\tilde{\nu}$ = 3487, 3064, 3017, 2931, 1750, 1496, 1455, 1370, 1221, 1159, 1056, 915, 765, 700, 668 cm^{-1}. ESI-MS: m/z = 1318.5 [M + NH_4]$^+$. $C_{72}H_{84}O_{22}$ (1300): calcd. C 66.45, H 6.51; found C 66.26, H 6.70.

6,6′-*O*-(2,3,4,5-Tetra-*O*-acetyl-D-arabinosylidene)bis(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) (28): Yellowish oil (1.58 g; 77%). $[\alpha]_D^{25}$ = +19.2 (c = 0.1, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.90, 1.93, 1.97, 2.01 (4s, 12 H, 4 COCH_3), 3.31, 3.33 (2s, 6 H, 2 OCH_3), 3.38–3.50 (m, 4 H), 3.56–3.68 (m, 4 H), 3.79 (d, J = 2.0 Hz, 1 H), 3.84–3.99 (m, 4 H), 4.09 (d, J = 7.4 Hz, 1 H), 4.15–4.21 (dd, J = 7.6, 2.0 Hz, 1 H), 4.50–4.91 (m, 12 H), 4.91–4.98 (dd, J = 12.0 Hz, 2 H), 5.08–5.17 (m, 1 H), 5.22–5.26 (dd, J = 7.4, 3.0 Hz, 1 H), 5.51–5.56 (dd, J = 7.6, 2.0 Hz, 1 H), 7.29–7.30 (m, 30 H, aromatic H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (4 C), 55.5 (2 C), 62.6, 66.8, 67.9, 69.0 (2 C), 69.8, 70.3, 70.5, 73.7 (2 C), 75.1, 75.4, 76.0 (2 C), 78.2 (2 C), 80.4, 80.5, 82.4 (2 C), 98.3, 98.5, 102.0, 127.9–139.3 (m, aromatic C), 169.6, 170.0, 170.2, 170.9 ppm. IR (neat): $\tilde{\nu}$ = 3029, 2929, 1749, 1455, 1369, 1221, 1159, 1071, 752, 701 cm^{-1}. ESI-MS: m/z = 1246.5 [M + NH_4]$^+$. $C_{69}H_{80}O_{20}$ (1228): calcd. C 67.41, H 6.56; found C 67.20, H 6.75.

General Deprotection Methods

Typical Reaction Procedure for Deacetylation and Debenzoylation. Preparation of 16–18, 22, 24: Sodium methoxide in MeOH (0.1 M, 0.20 mL) was added to a solution of compound **16** (200.0 mg, 0.26 mmol) in dry MeOH (5.0 mL) and the reaction mixture was stirred for 5 h at room temperature. After completion of the reac-

tion as monitored by TLC, the solution was neutralized by addition of Amberlite IR 120 (H^+) resin, filtered and concentrated under reduced pressure to give the crude deprotected disaccharide, which was further purified through LH-20 with MeOH as eluent to furnish pure **30** (83.3 mg, 90%).

Typical Reaction Procedure for Debenzylation. Preparation of 13–15, 19–21, 23, 25–28: A solution of compound **13** (200.0 mg, 0.27 mmol) in degassed MeOH (5.0 mL) was hydrogenated in the presence of $Pd(OH)_2$-C (20% wet; 200 mg) for 24 h at room temperature. After completion of the reaction as monitored by TLC, the reaction mixture was filtered through a celite bed and concentrated under reduced pressure to furnish the partially deprotected disaccharide, which on further saponification produced the fully deprotected disaccharide.

Methyl 4,6-*O*-[(1*R*)-D-Glucosylidene]-α-D-glucopyranoside (29): Compound **29** was prepared either from compound **14** by hydrogenolysis followed by saponification or from **17** by saponification as described in the general deprotection procedure. White powder (78.6 mg; 85%). $[\alpha]_D^{25}$ = +73.6 (*c* = 0.3, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 3.14–3.23 (m, 2 H), 3.32 (s, 3 H), 3.36–3.43 (m, 2 H), 3.46–3.51 (m, 2 H), 3.56–3.72 (m, 4 H), 3.95–3.99 (m, 1 H), 4.05–4.09 (m, 1 H), 4.50 (br. s, 1 H), 4.61 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 57.4, 65.3, 66.2, 71.1 (2 C), 73.4, 74.4, 75.5, 75.7, 76.4, 83.8, 103.5, 104.2 ppm. IR (KBr): $\tilde{\nu}$ = 3403 (bs), 1594, 1351, 1061 cm^{-1}. ESI-MS: *m*/*z* = 374.1 $[M + NH_4]^+$. $C_{13}H_{24}O_{11}$ (356): calcd. C 43.82, H 6.79; found C 43.64, H 7.02.

Methyl 4,6-*O*-[(1*R*)-D-Galactosylidene]-α-D-glucopyranoside (30): Compound **30** was prepared either from compound **13** by hydrogenolysis followed by saponification or from **16** by saponification as described in the general deprotection procedure. White powder (83.3 mg; 90%). $[\alpha]_D^{25}$ = +94.7 (*c* = 0.3, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 3.39 (s, 3 H), 3.42–3.46 (m, 1 H), 3.59–3.64 (m, 2 H), 3.66–3.67 (m, 2 H), 3.69–3.75 (m, 2 H), 3.80–3.83 (m, 1 H), 3.85–3.89 (m, 2 H), 3.92–3.95 (m, 1 H), 4.20–4.26 (dd, *J* = 6.0 and 1.5 Hz Hz, 1 H), 4.79 (br. s, 1 H), 4.81 (d, *J* = 4.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 55.7, 62.8, 63.6, 68.2, 68.8, 69.4, 70.4 (3 C), 72.0, 80.5, 100.5, 101.8 ppm. IR (KBr): $\tilde{\nu}$ = 3426 (bs), 1595, 1349, 1034 cm^{-1}. ESI-MS: *m*/*z* = 374.1 $[M + NH_4]^+$. $C_{13}H_{24}O_{11}$ (356): calcd. C 43.82, H 6.79; found C 43.66, H 6.98.

Methyl 4,6-*O*-[(1*R*)-D-Arabinosylidene]-α-D-glucopyranoside (31): Compound **31** was prepared either from compound **15** by hydrogenolysis followed by saponification or from **18** by saponification as described in the general deprotection procedure. White powder (73.7 mg; 87%). $[\alpha]_D^{25}$ = +73.8 (*c* = 0.3, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 3.47 (s, 3 H), 3.51–3.55 (m, 1 H), 3.65–3.67 (m, 1 H), 3.69–3.72 (m, 1 H), 3.73–3.80 (m, 3 H), 3.82–3.86 (m, 1 H), 3.88–3.94 (m, 2 H), 4.26–4.31 (m, 1 H), 4.55 (br. s, 1 H), 4.84 (br. s, 1 H), 4.90 (d, *J* = 4.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 55.7, 62.7, 63.3, 68.2, 69.9, 70.4, 70.6, 70.9, 72.1, 80.4, 100.5, 101.6 ppm. IR (KBr): $\tilde{\nu}$ = 3420 (bs), 2362, 1596, 1352 cm^{-1}. ESI-MS: *m*/*z* = 344.1 $[M + NH_4]^+$. $C_{12}H_{22}O_{10}$ (326): calcd. C 44.17, H 6.80; found C 44.0, H 7.05.

Methyl 4,6-*O*-[(1*R*)-2-Acetamido-2-deoxy-D-glucosylidene]-α-D-glucopyranoside (32): Ethylenediamine (0.5 mL) was added to a solution of compound **23** (250.0 mg, 0.3 mmol) in *n*-butanol (5.0 mL) and the reaction mixture was heated at reflux for 12 h. The reaction mixture was concentrated under reduced pressure and the crude reaction product was acetylated with Ac_2O and pyridine. Hydrogenolysis of the resulting acetylated product and subsequent saponification gave compound **32**, which was purified over LH-20 with MeOH as eluent. White powder (97.0 mg; 82%). $[\alpha]_D^{25}$ = +51.2 (*c* = 0.2, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 1.97 (s, 3 H), 3.25–3.29 (m, 1 H), 3.32 (s, 3 H), 3.36–3.39 (m, 2 H), 3.43–3.49 (m, 2 H), 3.54–3.58 (m, 1 H), 3.60–3.66 (m, 2 H), 3.69–3.73 (m, 2 H), 3.83–3.90 (m, 1 H), 4.05–4.14 (m, 1 H), 4.42–4.47 (d, *J* = 8.2 Hz, 1 H), 4.70 (d, *J* = 4.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 22.6, 55.4, 55.9, 61.2, 68.9, 70.0, 70.4, 70.8, 71.6, 73.5, 74.2, 76.3, 99.7, 102.1, 174.9 ppm. IR (KBr): $\tilde{\nu}$ = 3446 (bs), 2933, 2364, 1593, 1380, 1351, 1048 cm^{-1}. ESI-MS: *m*/*z* = 420.1 $[M + Na]^+$. $C_{15}H_{27}O_{11}N$ (397): calcd. C 45.34, H 6.85; found C 45.13, H 7.04.

Methyl 4,6-*O*-[(1*S*)-D-Galactosylidene]-α-D-galactopyranoside (33): Compound **33** was prepared either from compound **19** by hydrogenolysis followed by saponification or from **22** by saponification as described in the general deprotection procedure. White powder (78.6 mg; 85%). $[\alpha]_D^{25}$ = +108 (*c* = 0.3, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 3.30–3.34 (m, 1 H), 3.39 (s, 3 H), 3.63–3.69 (m, 2 H), 3.71 (br. s, 1 H), 3.80–3.87 (m, 2 H), 3.88–3.90 (m, 2 H), 3.94–3.96 (m, 1 H), 4.0–4.02 (m, 1 H), 4.07–4.09 (m, 1 H), 4.54 (br. s, 1 H), 4.69–4.70 (m, 1 H), 4.74 (d, *J* = 4.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 55.9, 64.5, 65.0, 69.8 (2 C), 70.0 (2 C), 70.8, 71.7, 71.9, 77.4, 102.2, 102.4 ppm. IR (KBr): $\tilde{\nu}$ = 2363, 1219, 771 cm^{-1}. ESI-MS: *m*/*z* = 374.1 $[M + NH_4]^+$. $C_{13}H_{24}O_{11}$ (356): calcd. C 43.82, H 6.79; found C 43.62, H 7.0.

Methyl 4,6-*O*-[(1*S*)-D-Glucosylidene]-β-D-galactopyranoside (34): Compound **34** was prepared from compound **20** by hydrogenolysis followed by saponification as described in the general deprotection procedure. White powder (78.6 mg; 85%). $[\alpha]_D^{25}$ = +13.6 (*c* = 0.3, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 3.48–3.55 (m, 2 H), 3.59 (s, 3 H), 3.62–3.64 (m, 1 H), 3.70–3.78 (m, 2 H), 3.80–3.95 (m, 3 H), 4.01–4.08 (m, 2 H), 4.15–4.26 (m, 2 H), 4.40 (d, *J* = 7.2 Hz, 1 H), 4.87 (d, *J* = 4.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 57.6, 63.3, 67.2, 68.7 (2 C), 70.8, 71.4, 71.9 (2 C), 73.1, 75.8, 100.8, 103.9 ppm. IR (KBr): $\tilde{\nu}$ = 3448 (bs), 2927, 2365, 1657, 1598, 1219 cm^{-1}. ESI-MS: *m*/*z* = 374.1 $[M + NH_4]^+$. $C_{13}H_{24}O_{11}$ (356): calcd. C 43.82, H 6.79; found C 43.66, H 7.05.

Methyl 4,6-*O*-[(1*S*)-D-Arabinosylidene]-β-D-galactopyranoside (35): Compound **35** was prepared from compound **21** by hydrogenolysis followed by saponification as described in the general deprotection procedure. White powder (72.0 mg; 85%). $[\alpha]_D^{25}$ = +30.2 (*c* = 0.3, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 3.46–3.50 (m, 1 H), 3.51 (s, 3 H), 3.55–3.59 (m, 1 H), 3.60–3.67 (m, 2 H), 3.68–3.73 (m, 1 H), 3.76–3.80 (m, 2 H), 3.83–3.90 (m, 2 H), 3.95–4.01 (m, 1 H), 4.06–4.11 (m, 2 H), 4.30 (d, *J* = 7.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 57.5, 63.4, 67.2, 68.7, 69.4, 70.7, 70.9, 72.0, 73.0, 75.7, 100.8, 103.9 ppm. IR (KBr): $\tilde{\nu}$ = 3399 (bs), 3021, 2365, 1216, 768 cm^{-1}. ESI-MS: *m*/*z* = 344.1 $[M + NH_4]^+$. $C_{12}H_{22}O_{10}$ (326): calcd. C 44.17, H 6.80; found C 43.95, H 7.0.

Methyl 4,6-*O*-[(1*R*)-α-D-Glucopyranosyl-(1→4)-D-glucosylidene]-α-D-glucopyranoside (36): Compound **36** was prepared from compound **24** by saponification as described in the general deprotection procedure. White powder (105.0 mg; 78%). $[\alpha]_D^{25}$ = +108.9 (*c* = 0.3, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 3.40 (s, 3 H), 3.45–3.50 (m, 4 H), 3.52–3.58 (m, 4 H), 3.60–3.68 (m, 6 H), 3.71–3.76 (m, 2 H), 3.88–3.91 (m, 1 H), 3.97–4.07 (m, 1 H), 4.40–4.45 (m, 1 H), 5.01 (d, *J* = 2.0 Hz, 1 H), 5.37 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 55.7, 60.8, 62.7, 66.9 (2 C), 69.8 (2 C), 71.6, 71.7, 72.0 (2 C), 72.8, 73.1, 73.2, 80.4, 81.8, 99.8, 100.5, 101.4 ppm. IR (KBr): $\tilde{\nu}$ = 3400 (bs), 3016, 2360, 1210, 778 cm^{-1}. ESI-MS: *m*/*z* = 536.2 $[M + NH_4]^+$. $C_{19}H_{34}O_{16}$ (518): calcd. C 44.02, H 6.61; found C 43.8, H 6.88.

5,5′-*O*-(D-Galactosylidene)bis(1,2-*O*-isopropylidene-α-D-xylofuranose) (37): Compound **37** was prepared from compound **25** by hydrogenolysis followed by saponification as described in the general de-

protection procedure. White powder (127.0 mg; 90%). $[\alpha]_D^{25}$ = –9.2 (c = 0.4, MeOH). ^{1}H NMR (200 MHz, CD_3OD): δ = 1.27 (s, 3 H), 1.32 (s, 3 H), 1.40 (s, 3 H), 1.48 (s, 3 H), 3.33–3.49 (m, 2 H), 3.50–3.55 (m, 1 H), 3.66–3.69 (m, 2 H), 3.77–3.87 (m, 3 H), 3.94–4.02 (m, 3 H), 4.18–4.21 (m, 2 H), 4.27–4.40 (m, 3 H), 4.51–4.52 (m, 2 H), 5.90–5.94 (t, J = 3.8 Hz each, 1 H) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 25.5 (2 C), 26.0 (2 C), 63.7, 65.9, 66.1, 69.1, 69.7 (2 C), 70.5, 74.4 (2 C), 79.9, 80.2, 85.0 (2 C), 104.1, 104.9 (2 C), 113.1 (2 C) ppm. IR (KBr): $\tilde{\nu}$ = 3433 (bs), 2364, 1596, 1352, 1086, 770 cm^{-1}. ESI-MS: m/z = 560.2 $[M + NH_4]^+$. $C_{22}H_{38}O_{15}$ (542): calcd. C 48.70, H 7.06; found C 48.48, H 7.22.

6,6′-*O*-(D-Glucosylidene)bis(methyl α-D-glucopyranoside) (38): Compound **38** was prepared from compound **27** by hydrogenolysis followed by saponification as described in the general deprotection procedure. White powder (122.0 mg; 85%). $[\alpha]_D^{25}$ = +96.6 (c = 0.3, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 3.50 (s, 3 H), 3.57 (s, 3 H), 3.63–3.65 (m, 1 H), 3.68–3.69 (m, 1 H), 3.70–3.72 (m, 3 H), 3.74–3.80 (m, 2 H), 3.81–3.82 (m, 2 H), 3.85–3.93 (m, 4 H), 3.96–3.99 (m, 2 H), 4.02–4.05 (m, 1 H), 4.06–4.09 (m, 2 H), 4.14 (br. s, 1 H), 4.52 (m, 1 H), 4.88 (d, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 55.5, 55.6, 61.0, 66.9, 67.3, 69.2, 69.8, 69.9, 70.9 (2 C), 71.4, 71.5 (2 C), 72.5, 72.8, 73.5 (2 C), 99.8 (2 C), 104.0 ppm. IR (KBr): $\tilde{\nu}$ = 3431 (bs), 2359, 1590, 1347, 1093 cm^{-1}. ESI-MS: m/z = 568.2 $[M + NH_4]^+$. $C_{20}H_{38}O_{17}$ (550): calcd. C 43.64, H 6.96; found C 43.46, H 7.18.

6,6′-*O*-(D-Galactosylidene)bis(methyl α-D-glucopyranoside) (39): Compound **39** was prepared from compound **26** by hydrogenolysis followed by saponification as described in the general deprotection procedure. White powder (124.0 mg; 87%). $[\alpha]_D^{25}$ = +97.6 (c = 0.3, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 3.38 (s, 3 H), 3.39 (s, 3 H), 3.40–3.42 (m, 1 H), 3.45–3.47 (m, 1 H), 3.49–3.51 (m, 2 H), 3.54–3.58 (m, 1 H), 3.59–3.61 (m, 2 H), 3.62–3.66 (m, 3 H), 3.71–3.73 (m, 1 H), 3.78–3.79 (m, 1 H), 3.82–3.90 (m, 4 H), 3.94–3.97 (m, 1 H), 4.0–4.02 (m, 2 H), 4.06–4.08 (m, 1 H), 4.76 (d, J = 4.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 55.5, 55.6, 63.7, 66.5, 66.9, 69.1, 69.6, 69.8 (2 C), 69.9, 70.4, 70.9, 71.0, 71.5 (2 C), 73.4 (2 C), 99.8 (2 C), 104.2 ppm. IR (KBr): $\tilde{\nu}$ = 3750 (bs), 2366, 1700, 1654, 1517, 1219, 769 cm^{-1}. ESI-MS: m/z = 568.2 $[M + NH_4]^+$. $C_{20}H_{38}O_{17}$ (550): calcd. C 43.64, H 6.96; found C 43.47, H 7.20.

6,6′-*O*-(D-Arabinosylidene)bis(methyl α-D-glucopyranoside) (40): Compound **40** was prepared from compound **28** by hydrogenolysis followed by saponification as described in the general deprotection procedure. White powder (108.0 mg; 80%). $[\alpha]_D^{25}$ = +78.5 (c = 0.3, MeOH). ^{1}H NMR (200 MHz, D_2O): δ = 3.43 (m, 1 H), 3.50 (s, 3 H), 3.51 (s, 3 H), 3.53 (br. s, 1 H), 3.56–3.58 (m, 1 H), 3.60–3.66 (m, 2 H), 3.67–3.71 (m, 2 H), 3.73–3.75 (m, 1 H), 3.78–3.83 (m, 4 H), 3.86–3.90 (m, 2 H), 3.91–3.92 (m, 1 H), 3.93–3.95 (m, 1 H), 4.0–4.07 (m, 2 H), 4.15–4.19 (m, 1 H), 4.80 (d, J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 55.6 (2 C), 63.4, 65.9, 67.2, 69.7, 69.8, 69.9, 70.1, 70.8 (2 C), 71.1, 71.6 (2 C), 73.4 (2 C), 99.7 (2 C), 103.8 ppm. IR (KBr): $\tilde{\nu}$ = 3455 (bs), 2925, 2364, 1695 cm^{-1}. ESI-MS: m/z = 538.2 $[M + NH_4]^+$. $C_{19}H_{36}O_{16}$ (520): calcd. C 43.84, H 6.97; found C 43.65, H 7.16.

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