Protecting Group and Solvent Effects in Electrochemical Glycosylation

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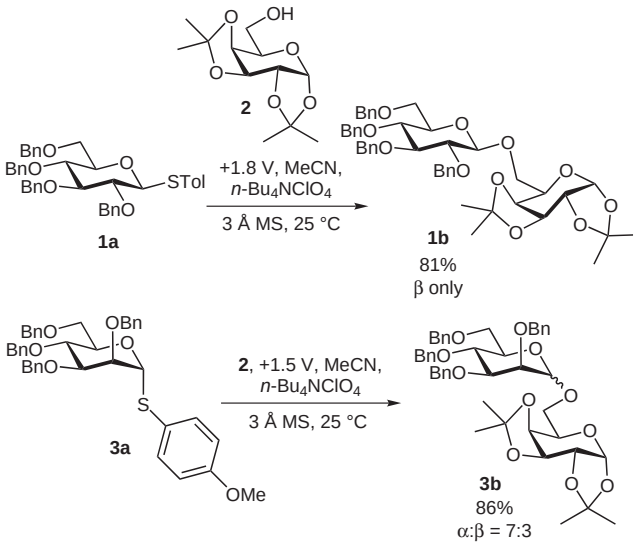
Abstract: An investigation is undertaken into the roles of protecting groups and the solvent in the electrochemical-mediated glycosylation of *manno* thioglycosides. Herein notable differences are observed between electrochemical and chemical glycosylation.

Key words: carbohydrates, glycosylations, electrochemistry, solvent effects, neighbouring-group effects

The structural complexity of oligosaccharides makes them extremely challenging synthetic targets.[1] Despite considerable synthetic efforts over the preceding decades the synthesis of a particular oligosaccharide target still remains an extremely time-consuming exercise.[2] However, recently the pioneering work of Fraser-Reid,[3] Ley,[4] and Wong[5] has stimulated several research groups to develop new techniques to allow the rapid assembly of oligosaccharides from preformed building blocks using the concept of reactivity tuning which allows selective chemical activation of one glycosyl donor in the presence of another, permitting multiple sequential glycosylations to be performed in one pot.

Inspired by the early work on electrochemical glycosylation of Noyori,[6] and Sinaÿ and Amatore,[7] we became intrigued as to whether a similar selective type of reactivity tuning approach would be possible for electrochemical glycosylation. Herein we envisaged using variation of cell potential to effect selective activation[8] of one glycosyl donor in the presence of a donor/acceptor which could then itself be later activated to act as a donor at a higher potential. We subsequently undertook[9] the synthesis and electrochemical investigation of a variety of differentially protected seleno-, thio- and *O*-glycosides as glycosyl donors for use in electrochemical glycosylation reactions and investigated their applications for the one-pot assembly of oligosaccharides. However, besides the ability to selectively activate one donor in the presence of another, a second prerequisite for the development of efficient one-pot oligosaccharide synthesis is that of achieving a high level of stereocontrol during each glycosylation reaction. In previous studies, good β-selectivity had been achieved for electrochemical-mediated glycosylation of *gluco* donors.[9] For example thiotolylglucoside **1a** was cleanly glycosylated with diacetone galactose **2** in acetonitrile at +1.8 V to give disaccharide **1b** in 81% yield as the pure β-anomer (Scheme 1). However, α-mannose-containing oligosaccharides are perhaps more relevant synthetic targets, particularly as they are major components of *N*-glycan oligosaccharides, and therefore attention turned to the potential uses of electrochemical glycosylation for the rapid assembly of α-oligomannose structures. Unfortunately in this case only low levels of stereocontrol were observed; for example whilst glycosylation[10] of perbenzylated donor thiomannoside **3a** with diacetone galactose at +1.5 V in acetonitrile did produce disaccharide **3b** in good yield, a considerable amount of the undesired β-anomer was produced (α/β = 7:3; Scheme 1).



Scheme 1 Contrasting stereochemical outcomes in the electrochemical glycosylation of perbenzylated *gluco* and *manno* thioglycosides

Perhaps the most straightforward method of achieving high stereocontrol during a glycosylation reaction is to use classical neighbouring-group participation of a 2-*O*-acyl-protected glycosyl donor.[11] However, previous reports, particularly from Lubineau[12] and co-workers, on the use of peracetylated donors for electrochemical glycosylation reactions indicated that such processes are low-yielding. There were therefore two objectives of an investigation into the use of a variety of *manno* thioglycoside donors that possessed different protecting groups at the 2-position in electrochemical glycosylation processes: first, to try and improve the stereocontrol of glycosylation, and second, to investigate protecting group effects on the yield of electrochemical glycosylation (Table 1). To these

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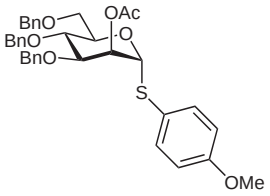
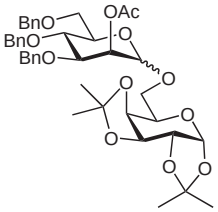
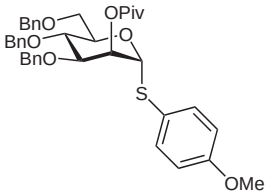
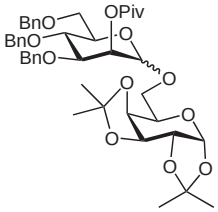
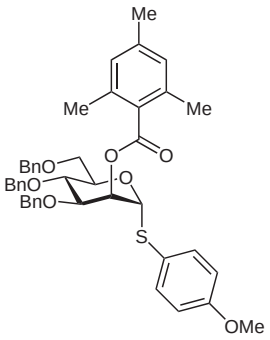
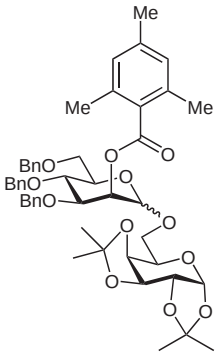
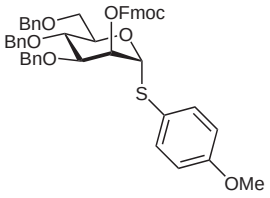
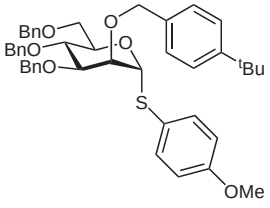
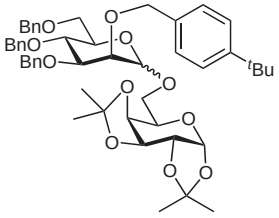
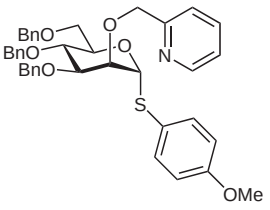
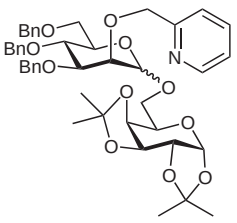
Table 1 Electrochemical Glycosylation of Thioglycoside Donors with Diacetone Galactose in Acetonitrile at +1.5 V

Entry	Glycosyl donor	Disaccharide	Yield	Ratio α/β[a]
1	 **4a**	 **4b**	15%	4:1
2	 **5a**	 **5b**	60%	9:1[b]
3	 **6a**	 **6b**	28%	7:3
4	 **7a**	not observed	–	–
5	 **8a**	 **8b**	65%	7:3
6[c]	 **9a**	 **9b**	16%	4:1

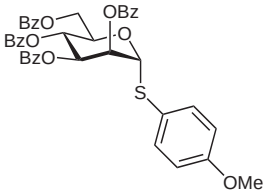
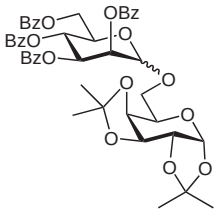
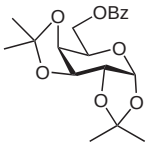
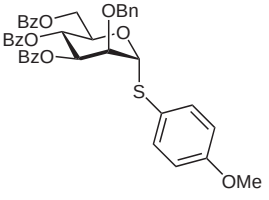
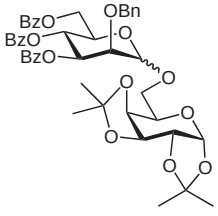
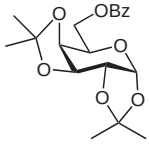
[a] Ratios determined by ^{1}H NMR of the crude mixture.
[b] Performing this electrochemical glycosylation at –20 °C did not alter the stereochemical outcome of the reaction.
[c] Glycosylation was carried out at +2.2 V.

ends, a series of thioglycosides **4a**–**9a** was synthesized in which the 3-, 4- and 6-hydroxyls were protected as benzyl ethers, and the protection of the 2-hydroxyl was varied. Glycosylation of the 2-*O*-acetate-protected donor **4a** with diacetone galactose **2** as a model glycosyl acceptor produced the desired disaccharide **4b**[13] in a very poor 15% yield, in line with the observations of Lubineau,[12] and in contrast with the earliest report by Noyori.[6] Interestingly, the ester protection did not result in complete control of anomeric stereochemistry; (α/β = 4:1; Table 1, entry 1) which contrasts with reports by Sinaÿ et al. on the use of 2-*O*-acylated *gluco* donors,[7c] but is in line with reports from the same group on the use of a 2-*O*-acylated *ido* donor.[7d] Reasoning that nucleophilic cleavage of the ester protection may be responsible for the reduced product yield glycosylation of the more robust pivaloyl-protected donor **5a** was undertaken. In line with the increased resistance to hydrolysis the yield of glycosylated product **5b**[14] was increased to a respectable 60% (Table 1, entry 2). However, once again stereocontrol, although higher than for the acetate ester, was not complete (α/β = 9:1) and in fact when this reaction was repeated at –20 °C in order to try and improve this α selectivity, the stereochemical outcome was found to be the same (Table 1, entry 2, footnote b).

Continuing the theme of steric retardation of hydrolysis the mesitoate-protected donor **6a** was synthesised. However, the yield of electrochemical-mediated glycosylation of **6a** was considerably lower than for the pivaloate **5a**, and disaccharide **6b**[15] was only isolated in a modest 28% yield perhaps indicating an acid-catalysed cleavage mechanism, and again with low stereocontrol (α/β = 7:3). Since the more acid-stable Fmoc protecting group has recently found increasingly useful application in oligosaccharide synthesis,[16] Fmoc-protected donor **7a** was synthesised and glycosylated under similar conditions. However, in this case, complete decomposition was observed, indicating that Fmoc protection is not compatible with electrochemical glycosylation. In an attempt to move away from participating protection and to simply increase the steric bulk of the 2-hydroxyl protecting group to try and favour formation of the desired α-disaccharide, the *p*-*tert*-butyl benzyl ether **8a** was synthesised. Glycosylation of **8a** with diacetone galactose under similar conditions produced disaccharide **8b**[17] in 65% yield, but with no improvement in stereocontrol (α/β = 7:3) compared to the normal benzyl ether. Finally the potential use of 2-*O*-picolyl protection, which was recently reported[18] as an arming participating protecting group for chemical glycosylation, was investigated. Thus picolyl-protected donor **9a** was synthesised and glycosylated with acceptor **2** at a slightly higher potential of +2.2 V. Disaccharide **9b** was produced only in a poor 16% yield, although the stereochemical outcome (α/β = 4:1) was slightly better than for the other non-ester protecting groups. These results indicate that ester protection of the 2-position is disadvantageous in terms of yield of electrochemical glycosylation, and does not invariably provide the high level of stereocontrol that is usually observed in more conventional glycosylation reactions. The fact that the use of nonparticipating protection at the 2-position does not lead to satisfactorily high levels of stereocontrol exacerbates the problem. This having been said, the use of the pivaloyl group for protection of the 2-position does appear to produce acceptable results.

It was next decided to investigate more precisely why the low levels of glycosylation product were observed for ester-protected glycosyl donors, and in particular whether this was because of ester protection specifically of the 2-position of the donor, which could result in a potential hydrolysis pathway via orthoester formation. The per-benzoylated thioglycoside **10a** was synthesised, and subjected to electrochemical glycosylation with acceptor **2** at +2.2 V in acetonitrile. In this case (Table 2, entry 1) the desired disaccharide **10b**[19] was produced in 49% yield as an anomeric mixture (α/β = 4:1). However, careful analysis of the reaction mixture revealed that the benzoylated acceptor **11** had also been produced in 30% yield. Clearly

Table 2 Electrochemical Glycosylation of Benzoyl-Protected Donors with Diacetone Galactose

Entry	Donor	Disaccharide	Yield	Ratio α/β	Transesterification product	Yield
1	**10a** 	**10b** 	49%	4:1	**11** 	30%
2	**12a** 	**12b** 	41%	6:1	**11** 	30%

this indicates that transesterification of the glycosyl acceptor is a competing side reaction, which is no doubt in part responsible for the lower yield of glycosylation using ester-protected donors. In order to investigate whether this transesterification had arisen because of the neighbouring-group participation, donor **12a**, which possesses benzyl protection at the 2-position but benzoyl protection at the 3-, 4-, and 6-hydroxyls, was synthesised. Electrochemical glycosylation of donor **12a** was then undertaken, to produce disaccharide **12b**[20] in 41% yield again as an anomeric mixture (α/β = 6:1), and indeed benzoylated acceptor **11** was again produced in 30% yield (Table 2, entry 2).

Two conclusions can be drawn from these experiments. First, since the anomeric ratios of disaccharide products are roughly equal (in fact glycosylation of the 2-*O*-benzyl donor **12a** is actually more α-selective), this provides further evidence that a neighbouring-group-participation mechanism is not operating exclusively. Second, since the esterified acceptor **11** was isolated in the same amount in both cases, the transesterification process does not necessarily result via a neighbouring-group-participation/orthoester-formation mechanism[21] since this is not possible in the case of 2-*O*-benzyl donor **12a**.

The nature of the reaction solvent is known to play a major role in determining the stereochemical outcome of chemical glycosylation reactions. In particular the use of acetonitrile has been demonstrated to increase the proportion of β-glycosides produced by the intermediacy of α-nitrilium ions.[22] In order to more definitively investigate the stereochemical outcome of electrochemical glycosylation reactions, a third series of experiments was undertaken. Herein the any possible solvent effects were investigated by performing glycosylations in both acetonitrile and dichloromethane as the solvent. Moreover, a series of oxidative chemical glycosylations of the same donor/acceptor pairs were performed in parallel using the one-electron oxidizing agent tris(4-bromophenyl)amminium hexachloroantimonate [$(BrC_6H_4)_3NSbCl_6$][23] as the promoter, and the stereochemical results of these experiments were compared (Table 3).

Glycosylation of perbenzylated thiomannoside **3a** with acceptor **2** at +2.2 V in acetonitrile gave the expected disaccharide **3b** in 80% yield as an approximate 8:3 α/β mixture (Table 3, entry 1). Performing the same reaction at a slightly lower potential (+1.9 V) at low temperature (–40 °C) did not significantly change the stereochemical outcome of the reaction (Table 3, entry 2). Moreover, changing the solvent to CH_2Cl_2 and performing the reaction at this slightly lower potential gave disaccharide **3b** in an improved 96% yield, but again as a 7:3 α/β mixture (Table 3, entry 3). However, using $(BrC_6H_4)_3NSbCl_6$ as a one-electron oxidant activator in acetonitrile as solvent gave disaccharide **3b** in 64% yield as a 1:1 mixture of anomers (Table 3, entry 4), whilst in contrast the use of $(BrC_6H_4)_3NSbCl_6$ in CH_2Cl_2 gave **3b** in only 49% yield as a 7:3 mixture of anomers (Table 3, entry 5). These results indicate that whilst the nature of the solvent plays a significant role in determining the stereochemical outcome of the chemical glycosylation, considerably more β-disaccharide being formed in acetonitrile, a similar effect is not observed for the electrochemical glycosylation. In this case the stereochemical outcome of the reaction appears to be largely solvent-independent. Finally both electrochemical and chemical glycosylation of the 2-*O*-pivaloyl-protected donor **5a** were undertaken in acetonitrile. Electrochemical glycosylation resulted in the formation of disaccharide **5b** in a modest 55% yield as a 9:2 α/β mixture of anomers (Table 3, entry 6). However, chemical glycosylation produced disaccharide **5b** in a much improved 96% yield, as an approximate ca. 7:1 α/β mixture of anomers (Table 3, entry 7). Taken together, these two final results indicate that not only is chemical glycosylation of ester-protected donors more efficient than electrochemical glycosylation in terms of yield, but also that higher levels of stereocontrol can be achieved chemically since it appears that neighbouring-group participation is not the predominant process in the latter case.

Table 3 Solvent Effects in Electrochemical and One-Electron-Oxidation-Mediated Glycosylation[24] of Donors **3a** and **5a**

Entry	Donor[a]	Activation Method[b]	Solvent	Product (yield)	Anomeric ratio
1	**3a**	+2.2 V	MeCN	**3b** (80%)	8:3
2	**3a**	+1.9 V at –40 °C	MeCN	**3b** (89%)	7:3
3	**3a**	+1.9 V	CH_2Cl_2	**3b** (96%)	7:3
4	**3a**	$(BrC_6H_4)_3NSbCl_6$	MeCN	**3b** (64%)	1:1
5	**3a**	$(BrC_6H_4)_3NSbCl_6$	CH_2Cl_2	**3b** (49%)	7:3
6	**5a**	+2.2 V	MeCN	**5b** (55%)	9:2
7	**5a**	$(BrC_6H_4)_3NSbCl_6$	MeCN	**5b** (96%)	7:1

[a] The acceptor was in all cases diacetone galactose **2**.
[b] All glycosylations were performed at r.t. unless otherwise stated

In summary, it is clear that there are subtle yet important differences between chemical and electrochemical glycosylation reactions. One primary disadvantage of electrochemical glycosylation processes is the poor compatibility with ester protecting groups on the donor, the use of which, unless hindered pivaloate esters are employed, results in considerably reduced yields of glycosylated product. One competing process herein is transesterification of the glycosyl acceptor, and it is clear that this process does not necessarily happen because of neighbouring-group participation/orthoester formation since esters at positions other then the 2-hydroxyl are also transferred with equal ease. Finally neighbouring-group participation and solvent effects, both of which are well-established methods for achieving increased stereocontrol of glycosylation, do not appear to affect the stereochemical outcome of electrochemical glycosylation reactions in nearly as significant a manner as for more standard chemical glycosylation processes. These observations, combined with the fact that the reaction temperature also does

not seem to alter the stereochemical outcome of electrochemical glycosylation, underline the contrasts in chemistry which can occur between solution-phase species and those adsorbed on electrode surfaces.

Further investigations into the potential uses of electrochemical glycosylation techniques for the rapid assembly of oligosaccharide structures are currently in progress, and the results will be reported in due course.

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(10) **Typical Procedure for Electrochemical Glycosylation**: Electrochemical glycosylation was carried out using galvanostatic system with Pt as auxiliary and working electrodes, and Ag as the reference electrode. Under an atmosphere of argon, glycosyl donor (ca. 70–150 mg, 1 equiv), glycosyl acceptor (ca. 30–70 mg, 1.2 equiv), *n*-Bu_4NClO_4 (ca. 650 mg), and 3 Å MS were suspended in anhyd MeCN (or CH_2Cl_2, 20 mL) and the reaction mixture was stirred at 25 °C for 30 min prior to commencing electrolysis. Electrolysis was then performed at the required potential (+1.5 V to +2.2 V depending on the donor) until the necessary charge was reached (typically 2.5 F·mol^{-1}). At this point the mixture was filtered through Celite®, the filtrate was concentrated under reduced pressure, and the residue was taken up into Et_2O. Any remaining solid was removed by filtration through Celite,® and the filtrate was again concentrated under reduced pressure. Finally purification by flash column chromatography (typically eluting with PE–EtOAc, 9:1) afforded the desired disaccharide as colourless oil.
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(13) Selected data for **4b** (α-anomer only): $[\alpha]_D^{22}$ +10 (*c* = 0.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, Me), 1.34 (s, 3 H, Me), 1.43 (s, 3 H, Me), 1.52 (s, 3 H, Me), 2.15 (s, 3 H, MeCO), 3.68–3.71 (m, 2 H, H-6a, H-6b), 3.76–3.84 (m, 3 H, H-6′a, H-6′b, H-5a), 3.91–3.95 (m, 2 H, H-4b, H-5b), 3.99 (dd, $J_{2b,3b}$ = 3.0 Hz, $J_{3b,4b}$ = 9.5 Hz, 1 H, H-3b), 4.22 (dd, $J_{3a,4a}$ = 8.0 Hz, $J_{4a,5a}$ = 1.5 Hz, 1 H, H-4a), 4.30 (dd, $J_{1a,2a}$ = 5.0 Hz, $J_{2a,3a}$ = 2.5 Hz, 1 H, H-2a), 4.47 (d, *J* = 10.5 Hz, 1 H, CH_2 of Bn), 4.49 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.53 (d, *J* = 11.0 Hz, 1 H, CH_2 of Bn), 4.60 (dd, $J_{2a,3a}$ = 2.5 Hz, $J_{3a,4a}$ = 8.0 Hz, 1 H, H-3a), 4.69 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.70 (d, *J* = 11.0 Hz, 1 H, CH_2 of Bn), 4.87 (d, *J* = 10.5 Hz, 1 H, CH_2 of Bn), 4.90 (d, $J_{1b,2b}$ = 1.5 Hz, 1 H, H-1b), 5.40 (dd, $J_{1b,2b}$ = 2.0 Hz, $J_{2b,3b}$ = 3.0 Hz, 1 H, H-2b), 5.50 (d, $J_{1a,2a}$ = 5.0 Hz, 1 H, H-1a), 7.10–7.36 (m, 15 H, 15 × ArH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 21.1 (MeCO), 24.5 (Me), 24.9 (Me), 25.9 (Me), 26.1 (Me), 65.9 (C-4b), 66.1 (C-6), 68.6 (C-6), 68.7 (C-2b), 70.5 (C-3a), 70.6 (C-2a), 70.8 (C-4a), 71.5 (C-5a), 71.8 (CH_2), 73.4 (CH_2), 74.2 (C-5b), 75.1 (CH_2), 78.1 (C-3b), 96.2 (C-1a), 97.9 (C-1b), 108.6 (Cqx), 109.3 (Cqy), 127.5 (ArCH), 127.6 (ArCH), 127.7 (ArCH), 127.8 (2 × ArCH), 127.9 (2 × ArCH), 128.0 (2 × ArCH), 128.3 (4 × ArCH), 128.3 (2 × ArCH), 138.0 (ArC), 138.2 (ArC), 138.4 (ArC), 170.4 (C=O). HRMS (ESI$^+$): *m*/*z* [M + NH_4^+] calcd for $C_{41}H_{54}NO_{12}$: 752.3641; found: 752.3649.
(14) Selected data for **5b** (α-anomer): $[\alpha]_D^{20}$ –6 (*c* = 1.2 $CHCl_3$). IR (film): 1732 (s, C=O), 1371 (s, CO) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.21 (s, 9 H, *t*-Bu), 1.33 (s, 3 H, Me), 1.35 (s, 3 H, Me), 1.43 (s, 3 H, Me), 1.52 (s, 3 H, Me), 3.72 (dd, $J_{5a,6a}$ = 6.5 Hz, $J_{6a,6'a}$ = 10.5 Hz, 1 H, H-6a), 3.72–3.74 (m, 1 H, H-6b), 3.80 (dd, $J_{5,6'a}$ = 6.5 Hz, $J_{6a,6'a}$ = 10.5 Hz, 1 H, H-6′a), 3.78–3.82 (m, 1 H, H-6′b), 3.83–3.87 (m, 1 H, H-5b), 3.91 (app t, $J_{3b,4b}$ = 9.5 Hz, $J_{4b,5b}$ = 9.5 Hz, 1 H, H-4b), 3.95 (d app t, $J_{4a,5a}$ = 1.5 Hz, $J_{5a,6a}$ = 6.5 Hz, $J_{5a,6'a}$ = 6.5 Hz, 1 H, H-5a), 3.99 (dd, $J_{2b,3b}$ = 3.0 Hz, $J_{3b,4b}$ = 9.5 Hz, 1 H, H-3b), 4.22 (dd, $J_{3a,4a}$ = 8.0 Hz, $J_{4a,5a}$ = 1.5 Hz, 1 H, H-4a), 4.31 (dd, $J_{1a,2a}$ = 5.0 Hz, $J_{2a,3a}$ = 2.5 Hz, 1 H, H-2a), 4.49 (d, *J* = 11.0 Hz, 1 H, CH_2 of Bn), 4.50 (d, *J* = 11.0 Hz, 1 H, CH_2 of Bn), 4.51 (d, *J* = 13.0 Hz, 1 H, CH_2 of Bn), 4.60 (dd, $J_{2a,3a}$ = 2.5 Hz, $J_{3a,4a}$ = 8.0 Hz, 1 H, H-3a), 4.68 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.69 (d, *J* = 11.0 Hz, 1 H, CH_2 of Bn), 4.82 (d, *J* = 11.0 Hz, 1 H, CH_2 of Bn), 4.88 (d, $J_{1b,2b}$ = 2.0 Hz, 1 H, H-1b), 5.40 (dd, $J_{1b,2b}$ = 2.0 Hz, $J_{2b,3b}$ = 3.0 Hz, 1 H, H-2b), 5.51 (d, $J_{1a,2a}$ = 5.0 Hz, 1 H, H-1a), 7.15–7.36 (m, 15 H, 15 × ArH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 24.5 (Me), 24.9 (Me), 25.0 (Me), 26.1 (Me), 27.1 (*t*-Bu), 38.9 (CqPiv), 65.8 (C-5a), 65.9 (C-6), 68.1 (C-2b), 68.8 (C-6), 70.6 (C-3a), 70.7 (C-2a), 70.8 (C-4a), 71,4 (CH_2 of Bn), 71.5 (C-5b), 73.1 (CH_2 of Bn), 74.1 (C-4b), 75.1 (CH_2 of Bn), 78.3 (C-3b), 96.3 (C-1a), 97.8 (C-1b), 108.6 (Cq), 109.3 (Cq), 107.4

(ArCH), 127.4 (2 × ArCH), 127.6 (ArCH), 127.9 (2 × ArCH), 128.1 (2 × ArCH), 128.2 (2 × ArCH), 128.2 (2 × ArCH), 128.3 (2 × ArCH), 138.3, 138.3, 138.4 (ArC), 138.4 (ArCH), 177.6 (C=O). HRMS (ESI$^+$): *m*/*z* [M + Na$^+$] calcd for $C_{44}H_{56}NaO_{12}$: 799.3664; found: 799.3662. Selected data for **5b** (β-anomer): $[\alpha]_D^{20}$ –39 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 9 H, *t*-Bu), 1.29 (s, 3 H, Me), 1.32 (s, 3 H, Me), 1.42 (s, 3 H, Me), 1.52 (s, 3 H, Me), 3.46 (d app t, $J_{4,5}$ = 3.5 Hz, $J_{5,6}$ = 3.5 Hz, $J_{5,6'}$ = 9.5 Hz, 1 H, H-5b), 3.65 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz, 1 H, H-3b), 3.69 (dd, $J_{5,6}$ = 10.5 Hz, $J_{6,6'}$ = 4.0 Hz, 1 H, H-6a), 3.74–3.79 (m, 3 H, H-6b, H-6′b, H-6′a), 3.97 (ddd, $J_{4,5}$ = 1.5 Hz, $J_{5,6}$ = 10.5 Hz, $J_{5,6'}$ = 4.0 Hz, 1 H, H-5a), 4.02 (dd, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 3.5 Hz, 1 H, H-4b), 4.20 (dd, $J_{3,4}$ = 8.0 Hz, $J_{4,5}$ = 1.5 Hz, 1 H, H-4a), 4.28 (dd, $J_{1,2}$ = 5.0 Hz, $J_{2,3}$ = 2.5 Hz, 1 H, H-2a), 4.46 (d, *J* = 11.5 Hz, 1 H, CH_2 of Bn), 4.50 (d, *J* = 10.5 Hz, 1 H, CH_2 of Bn), 4.55 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.56 (dd, $J_{2,3}$ = 2.5 Hz, $J_{3,4}$ = 8.0 Hz, 1 H, H-3a), 4.63 (br s, 1 H, H-1b), 4.68 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.74 (d, *J* = 11.5 Hz, 1 H, CH_2 of Bn), 4.83 (d, *J* = 11.0 Hz, 1 H, CH_2 of Bn), 5.50 (d, $J_{1,2}$ = 5.0 Hz, 1 H, H-1a), 5.61 (d, $J_{2,3}$ = 3.0 Hz, 1 H, H-2b), 7.10–7.40 (m, 15 H, 15 × ArH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.3 (Me), 25.0 (Me), 25.9 (Me), 26.0 (Me), 27.2 (*t*-Bu), 39.0 (CqPiv), 67.5 (C-2b), 67.8 (CH), 68.8 (C-6), 69.0 (C-6), 70.5 (C-3a), 70.6 (C-2a), 70.9 (CH_2 of Bn), 71.2 (C-4a), 73.2 (CH_2 of Bn), 74.2 (CH), 75.1 (CH_2 of Bn), 75.4 (CH), 80.3 (C-3b), 96.2 (C-1a), 99.3 (C-1b), 108.7 (Cq), 109.2 (Cq), 127.4 (ArCH), 127.6 (2 × ArCH), 127.6 (ArCH), 127.6 (ArCH), 128.0 (2 × ArCH), 128.1 (2 × ArCH), 128.2 (2 × ArCH), 128.2 (2 × ArCH), 128.3 (2 × ArCH), 176.6 (C=O), 137.9 (ArC), 138.5 (2 × ArC).

(15) Selected data for **6b** (α-anomer only): $[\alpha]_D^{20}$ –38 (*c* = 0.3, $CHCl_3$). IR (film): 3031 (CHAr), 2921 (CH), 1729 (s, C=O), 1497 (s, CH), 1072, 1260 (s, CO) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (s, 3 H, Me), 1.35 (s, 3 H, Me), 1.44 (s, 3 H, Me), 1.53 (s, 3 H, Me), 2.28 (s, 2 × 3 H, 2 × $Me_{mesitoyl}$), 2.29 (s, 3 H, $Me_{mesitoyl}$), 3.69 (br d, $J_{6b,6'b}$ = 10.5 Hz, 1 H, H-6b), 3.75 (d, $J_{5a,6a}$ = 6.5 Hz, $J_{6a,6'a}$ = 10.5 Hz, 1 H, H-6a), 3.76 (dd, $J_{5b,6'b}$ = 3.0 Hz, $J_{6b,6'b}$ = 10.5 Hz, 1 H, H-6′b), 3.83 (dd, $J_{5a,6'a}$ = 6.5 Hz, $J_{6a,6'a}$ = 10.5 Hz, 1 H, H-6′a), 3.87–3.90 (m, 2 H, H-4b, H-5b), 3.98 (d app t, $J_{4a,5a}$ = 1.5 Hz, $J_{5a,6a}$ = 6.5 Hz, $J_{5a,6'a}$ = 6.5 Hz, 1 H, H-5a), 4.08–4.10 (dd, $J_{2b,3b}$ = 3.0 Hz, $J_{3b,4b}$ = 9.0 Hz, 1 H, H-3b), 4.25 (dd, $J_{3a,4a}$ = 8.0 Hz, $J_{4a,5a}$ = 1.5 Hz, 1 H, H-4a), 4.31 (dd, $J_{1a,2a}$ = 5.0 Hz, $J_{2a,3a}$ = 2.5 Hz, 1 H, H-2a), 4.45 (d, *J* = 11.5 Hz, 1 H, CH_2 of Bn), 4.47 (d, *J* = 12.5 Hz, 1 H, CH_2 of Bn), 4.60 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.62 (d, *J* = 11.0 Hz, 1 H, CH_2 of Bn), 4.63 (dd, $J_{2a,3a}$ = 2.5 Hz, $J_{3a,4a}$ = 8.0 Hz, 1 H, H-3a), 4.81 (d, *J* = 11.0 Hz, 2 H, 2 × CH_2 of Bn), 5.05 (d, $J_{1b,2b}$ = 2.0 Hz, 1 H, H-1b), 5.52 (d, $J_{1a,2a}$ = 5.0 Hz, 1 H, H-1a), 5.65 (dd, $J_{1b,2b}$ = 2.0 Hz, $J_{2b,3b}$ = 3.0 Hz, 1 H, H-2b), 6.82 (s, 2 H, 2 × ArH), 7.13–7.16 (m, 2 H, 2 × ArH), 7.23–7.40 (m, 13 H, 13 × ArH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.0 (2 × Me), 21.1 (Me), 24.5 (Me), 24.9 (Me), 26.0 (Me), 26.2 (Me), 65.8 (C-5a), 66.0 (C-6a), 68.8 (C-6b), 69.3 (C-2b), 70.6 (C-3a, C-2a), 70.9 (C-4a), 71.8 (C-5b), 71.9 (CH_2 of Bn), 73.2 (CH_2 of Bn), 74.5 (C-4b), 75.2 (CH_2 of Bn), 76.2 (C-3b), 96.3 (C-1a), 97.6 (C-1b), 108.6 (Cq), 109.4 (Cq), 127.4 (ArCH), 127.5 (ArCH), 127.6 (ArCH), 127.7 (2 × ArCH), 127.9 (2 × ArCH), 128.0 (2 × ArCH), 128.2 (2 × ArCH), 128.2 (2 × ArCH), 128.3 (2 × ArCH), 128.3 (2 × ArCH), 130.6 (Cq), 135.6 (2 × Cq), 138.1 (Cq), 138.3 (Cq), 138.3 (Cq), 139.3 (Cq), 139.3 (Cq), 169.3 (C=O). HRMS (ESI$^+$): *m*/*z* [M + Na$^+$] calcd for $C_{49}H_{58}NaO_{12}$: 861.3820; found: 861.3818. Anal. Calcd for $C_{49}H_{58}O_{12}$: C, 70.15; H, 6.97. Found: C, 69.76; H, 6.59.

(16) (a) Zhu, T.; Boons, G.-J. *Tetrahedron: Asymmetry* **2000**, *11*, 199. (b) Roussel, F.; Knerr, L.; Grathwohl, M.; Schmidt, R. R. *Org. Lett.* **2000**, *2*, 3043.

(17) Selected data for **8b** (α-anomer): $[\alpha]_D^{20}$ –6 (*c* = 0.7, $CHCl_3$). IR (film): 3050 (CHAr), 2962 (CH), 1600–2000 (CHAr), 1497 (w, CH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (s, 9 H, *t*-Bu), 1.34 (s, 2 × 3 H, 2 × Me), 1.44 (s, 3 H, Me), 1.52 (s, 3 H, Me), 3.69–3.81 (m, 5 H, H-6a, H-6′a, H-6b, H-6′b, H-2b), 3.84–3.85 (m, 1 H, H-5b), 3.90 (dd, $J_{2b,3b}$ = 3.0 Hz, $J_{3b,4b}$ = 9.5 Hz, 1 H, H-3b), 3.97 (d app t, $J_{4a,5a}$ = 1.5 Hz, $J_{5a,6a}$ = 6.5 Hz, $J_{5a,6'a}$ = 6.5 Hz, 1 H, H-5a), 4.02 (app t, $J_{3b,4b}$ = 9.5 Hz, $J_{4b,5b}$ = 9.5 Hz, 1 H, H-4b), 4.17 (dd, $J_{3a,4a}$ = 8.0 Hz, $J_{4a,5a}$ = 1.5 Hz, 1 H, H-4a), 4.32 (dd, $J_{1a,2a}$ = 5.0 Hz, $J_{2a,3a}$ = 2.5 Hz, 1 H, H-2a), 4.50 (d, *J* = 10.5 Hz, 1 H, CH_2 of Bn), 4.54–4.58 (m, 3 H, CH_2 of Bn), 4.60 (dd, $J_{2a,3a}$ = 2.5 Hz, $J_{3a,4a}$ = 8.0 Hz, 1 H, H-3a), 4.67 (d, *J* = 12.5 Hz, 1 H, CH_2 of Bn), 4.69 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.74 (d, *J* = 12.5 Hz, 1 H, CH_2 of Bn), 4.87 (d, *J* = 10.5 Hz, 1 H, CH_2 of Bn), 5.04 (d, $J_{1b,2b}$ = 1.5 Hz, 1 H, H-1b), 5.53 (d, $J_{1a,2a}$ = 5.0 Hz, 1 H, H-1a), 7.15–7.37 (m, 19 H, 19 × ArH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.6 (Me), 25.1 (Me), 26.2 (Me), 26.3 (Me), 34.7 (Cq), 65.3 (C-5a), 65.5 (C-6), 69.3 (C-6), 70.8 (C-3a), 70.9 (C-2a), 71.2 (C-4a), 72.1 (CH_2), 72.2 (CH_2), 72.3 (C-2b), 73.5 (CH_2), 74.3 (C-5b), 75.0 (C-4b), 75.3 (CH_2), 80.2 (C-3b), 96.5 (C-1a), 97.3 (C-1b), 108.8 (Cq), 109.5 (Cq), 125.5 (2 × ArCH), 127.5 (2 × ArCH), 127.6 (ArCH), 127.7 (2 × ArCH), 127.8 (2 × ArCH), 127.9 (2 × ArCH), 128.1 (2 × ArCH), 128.3 (4 × ArCH), 128.4 (2 × ArCH), 135.5 (ArC), 138.6 (ArC), 138.7 (ArC), 138.8 (ArC), 150.7 (ArC). HRMS (ESI$^+$): *m*/*z* [M + Na$^+$] calcd for $C_{50}H_{62}NaO_{11}$: 861.4184; found: 861.4162. Selected data for **8b** (β-anomer): $[\alpha]_D^{20}$ –48 (*c* = 0.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (s, 9 H, *t*-Bu), 1.33 (s, 3 H, Me), 1.34 (s, 3 H, Me), 1.44 (s, 3 H, Me), 1.50 (s, 3 H, Me), 3.41 (ddd, $J_{4b,5b}$ = 9.5 Hz, $J_{5b,6b}$ = 5.0 Hz, $J_{5b,6'b}$ = 2.0 Hz, 1 H, H-5b), 3.44 (dd, $J_{2b,3b}$ = 3.0 Hz, $J_{3b,4b}$ = 9.5 Hz, 1 H, H-3b), 3.62 (dd, $J_{5a,6a}$ = 10.5 Hz, $J_{6a,6'a}$ = 9.5 Hz, 1 H, H-6a), 3.75 (dd, $J_{5b,6b}$ = 5.0 Hz, $J_{6b,6'b}$ = 10.5 Hz, 1 H, H-6b), 3.79 (dd, $J_{5b,6'b}$ = 2.0 Hz, $J_{6b,6'b}$ = 10.5 Hz, 1 H, H-6′b), 3.89 (app t, $J_{3b,4b}$ = 9.5 Hz, $J_{4b,5b}$ = 9.5 Hz, 1 H, H-4b), 4.00 (d, $J_{2b,3b}$ = 3.0 Hz, 1 H, H-2b), 4.13 (br d, 1 H, H-5a), 4.22 (dd, $J_{5a,6'a}$ = 2.0 Hz, $J_{6a,6'a}$ = 9.5 Hz, 1 H, H-6′a), 4.23 (dd, $J_{3a,4a}$ = 9.0 Hz, $J_{4a,5a}$ = 1.5 Hz, 1 H, H-4a), 4.29 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.34 (dd, $J_{1a,2a}$ = 5.0 Hz, $J_{2a,3a}$ = 2.5 Hz, 1 H, H-2a), 4.40 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.45 (s, 1 H, H-1b), 4.50 (d, *J* = 10.5 Hz, 1 H, CH_2 of Bn), 4.56 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.62 (dd, $J_{2a,3a}$ = 2.5 Hz, $J_{3a,4a}$ = 9.0 Hz, 1 H, H-3a), 4.63 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.90 (d, *J* = 10.5 Hz, 1 H, CH_2 of Bn), 4.91 (d, *J* = 12.5 Hz, 1 H, CH_2 of Bn), 4.98 (d, *J* = 12.5 Hz, 1 H, CH_2 of Bn), 5.61 (d, $J_{1a,2a}$ = 5.0 Hz, 1 H, H-1a), 7.15–7.45 (m, 19 H, 19 × ArH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 24.4 (Me), 25.1 (Me), 26.0 (Me), 26.1 (Me), 31.4 (*t*-Bu), 34.5 (Cq), 68.0 (C-5a), 69.6 (C-6b), 69.9 (C-6a), 70.5 (CH), 70.8 (CH), 70.9 (CH_2), 71.7 (CH), 71.9 (CH), 73.1 (CH_2), 73.4 (CH_2), 74.8 (C-4b), 75.1 (CH_2), 75.8 (CH), 81.9 (CH), 96.4 (C-1a), 102.4 (C-1b), 108.7 (Cq), 109.5 (Cq), 125.1 (2 × ArCH), 127.4 (ArCH), 127.5 (ArCH), 127.5 (2 × ArCH), 127.6 (ArCH), 127.9 (2 × ArCH), 128.0 (2 × ArCH), 128.2 (4 × ArCH), 128.3 (2 × ArCH), 128.6 (2 × ArCH), 135.5 (ArC), 138.1 (ArC), 138.4 (2 × ArC), 150.2 (ArC). HRMS (ESI$^+$): *m*/*z* [M + Na$^+$] calcd for $C_{50}H_{62}NaO_{11}$: 861.4184; found: 861.4192.

(18) Smoot, J. T.; Pornsuriyasak, P.; Demchenko, A. V. *Angew. Chem. Int. Ed.* **2005**, *44*, 7123.

(19) Selected data for **10b** (α-anomer only): $[\alpha]_D^{19}$ –61 (*c* = 0.3, $CHCl_3$). IR (film): 3010 (w, CHAr), 2988 (w, CH), 1728 (s, C=O), 1601, 1595, 1500, 1452 (m, C=CAr), 1263, 1060 (s,

CO) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.36 (s, 2 × 3 H, 2 × Me), 1.43 (s, 3 H, Me), 1.63 (s, 3 H, Me), 3.89 (dd, $J_{5a,6a}$ = 6.5 Hz, $J_{6a,6'a}$ = 11.0 Hz, 1 H, H-6a), 3.97 (dd, $J_{5a,6'a}$ = 6.5 Hz, $J_{6a,6'a}$ = 11.0 Hz, 1 H, H-6′a), 4.12 (d app t, $J_{4a,5a}$ = 2.0 Hz, $J_{5a,6a}$ = 6.5 Hz, $J_{5a,6'a}$ = 6.5 Hz, 1 H, H-5a), 4.34 (dd, $J_{3a,4a}$ = 8.0 Hz, $J_{4a,5a}$ = 2.0 Hz, 1 H, H-4a), 4.35 (dd, $J_{1a,2a}$ = 5.0 Hz, $J_{2a,3a}$ = 2.5 Hz, 1 H, H-3a), 4.50 (dd, $J_{5b,6b}$ = 3.0 Hz, $J_{6b,6'b}$ = 12.0 Hz, 1 H, H-6b), 4.59 (br d app t, $J_{4b,5b}$ = 10.0 Hz, $J_{5b,6b}$ = 3.0 Hz, $J_{5b,6'b}$ = 3.0 Hz, 1 H, H-5b), 4.67 (dd, $J_{2a,3a}$ = 2.0 Hz, $J_{3a,4a}$ = 8.0 Hz, 1 H, H-3a), 4.69 (dd, $J_{5b,6'b}$ = 3.0 Hz, $J_{6b,6'b}$ = 12.0 Hz, 1 H, H-6′b), 5.16 (d, $J_{1b,2b}$ = 2.0 Hz, 1 H, H-1b), 5.57 (d, $J_{1a,2a}$ = 5.0 Hz, 1 H, H-1a), 5.74 (dd, $J_{1b,2b}$ = 2.0 Hz, $J_{2b,3b}$ = 3.0 Hz, 1 H, H-2b), 5.91 (dd, $J_{2b,3b}$ = 3.0 Hz, $J_{3b,4b}$ = 10.0 Hz, 1 H, H-3b), 6.14 (app t, $J_{3b,4b}$ = 10.0 Hz, $J_{4b,5b}$ = 10.0 Hz, 1 H, H-4b), 7.25–7.28 (m, 2 H, 2 × ArH), 7.33–7.45 (m, 7 H, 7 × ArH), 7.48–7.53 (m, 1 H, ArH), 7.55–7.62 (m, 2 H, 2 × ArH), 7.84 (dd, $J_{A,B}$ = 8.5 Hz, $J_{A,X}$ = 1.5 Hz, 2 H, 2 × ArH), 7.96 (dd, $J_{A,B}$ = 8.5 Hz, $J_{A,X}$ = 1.5 Hz, 2 H, 2 × ArH), 8.06 (dd, $J_{A,B}$ = 8.5 Hz, $J_{A,X}$ = 1.5 Hz, 2 H, 2 × ArH), 8.12 (dd, $J_{A,B}$ = 8.5 Hz, $J_{A,X}$ = 1.5 Hz, 2 H, 2 × ArH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 24.6 (Me), 25.1 (Me), 26.1 (Me), 26.4 (Me), 63.0 (C-6b), 66.8 (C-5a), 67.0 (C-4b), 67.7 (C-6a), 69.0 (C-5b), 70.4 (C-3b), 70.5 (C-2b), 70.8 (C-3a), 71.0, 71.1 (C-2a, C-4a), 96.5 (C-1a), 98.0 (C-1b), 108.9 (Cq), 109.6 (Cq), 128.4 (2 × ArCH), 128.5 (2 × ArCH), 128.6 (2 × ArCH), 128.7 (2 × ArCH), 129.2 (ArC), 129.3 (ArC), 129.5 (ArC), 129.8 (2 × ArCH), 129.9 (2 × ArCH), 129.9 (2 × ArCH), 130.0 (2 × ArCH), 130.1 (ArC), 133.1 (ArCH), 133.3 (ArCH), 133.5 (ArCH), 133.6 (ArCH), 165.5 (C=O), 165.5 (C=O), 165.6 (C=O), 166.4 (C=O). HRMS (ESI$^+$): *m*/*z* [M + NH_4^+] calcd for $C_{46}H_{50}NO_{15}$: 856.3175; found: 856.3167).

(20) Selected data for **12b** (α-anomer): $[\alpha]_D^{24}$ –14 (*c* = 0.9, $CHCl_3$). IR (film): 3020 (w, CHAr), 2934 (w, CH), 1725 (s, C=O), 1601, 1598, 1500, 1452 (m, C=CAr), 1270, 1069 (s, CO), 711 (m, CH) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (s, 2 × 3 H, 2 × Me), 1.44 (s, 3 H, Me), 1.58 (s, 3 H, Me), 3.81 (dd, $J_{5a,6a}$ = 6.5 Hz, $J_{6a,6'a}$ = 10.5 Hz, 1 H, H-6a), 3.94 (dd, $J_{5a,6'a}$ = 6.5 Hz, $J_{6a,6'a}$ = 10.5 Hz, 1 H, H-6′a), 4.07 (d app t, $J_{4a,5a}$ = 1.5 Hz, $J_{5a,6a}$ = 6.5 Hz, $J_{5a,6'a}$ = 6.5 Hz, 1 H, H-5a), 4.13 (dd, $J_{1b,2b}$ = 1.5 Hz, $J_{2b,3b}$ = 3.0 Hz, 1 H, H-2b), 4.26 (dd, $J_{3a,4a}$ = 8.0 Hz, $J_{4a,5a}$ = 1.5 Hz, 1 H, H-4a), 4.34 (dd, $J_{1a,2a}$ = 5.0 Hz, $J_{2a,3a}$ = 2.5 Hz, 1 H, H-2a), 4.45 (dd, $J_{4b,5b}$ = 10.0 Hz, $J_{5b,6b}$ = 5.0 Hz, $J_{5b,6'b}$ = 2.5 Hz, 1 H, H-5b), 4.48 (dd, $J_{5b,6b}$ = 5.0 Hz, $J_{6b,6'b}$ = 12.0 Hz, 1 H, H-6b), 4.57 (dd, $J_{5b,6'b}$ = 2.5 Hz, $J_{6b,6'b}$ = 12.0 Hz, 1 H, H-6′b), 4.64 (dd, $J_{2a,3a}$ = 2.5 Hz, $J_{3a,4a}$ = 8.0 Hz, 1 H, H-3a), 4.65 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.69 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 5.11 (d, $J_{1b,2b}$ = 1.5 Hz, 1 H, H-1b), 5.55 (d, $J_{1a,2a}$ = 5.0 Hz, 1 H, H-1a), 5.69 (dd, $J_{2b,3b}$ = 3.0 Hz, $J_{3b,4b}$ = 10.0 Hz, 1 H, H-3b), 6.06 (app t, $J_{3b,4b}$ = 10.0 Hz, $J_{4b,5b}$ = 10.0 Hz, 1 H, H-4b), 7.15–7.38 (m, 11 H, 11 × ArH), 7.45–7.53 (m, 3 H, 3 × ArH), 7.92–8.10 (m, 6 H, 6 × ArH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 24.7 (Me), 25.1 (Me), 26.1 (Me), 26.2 (Me), 63.6 (C-6b), 66.2 (C-5a), 66.7 (C-6a), 67.4 (C-4b), 69.1 (C-5b), 70.7 (C-2a), 70.8 (C-3a), 71.1 (C-4a), 72.4 (C-3b), 73.1 (CH_2 of Bn), 75.7 (C-2b), 96.5 (C-1a), 97.9 (C-1b), 108.8 (Cq), 109.5 (Cq), 127.6, 128.4, 128.5, 129.9 (16 × ArCH), 127.7 (ArCH), 129.4 (ArC), 129.5 (ArC), 130.0 (ArC), 132.9 (ArCH), 133.3 (2 × ArCH), 137.8 (ArC), 165.5 (C=O), 165.9 (C=O), 166.4 (C=O). HRMS (ESI$^+$): *m*/*z* [M + NH_4^+] calcd for $C_{46}H_{52}NO_{14}$: 842.3382; found: 842.3422. Selected data for **12b** (β-anomer): $[\alpha]_D^{24}$ –7 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (s, 2 × 3 H, 2 × Me), 1.42 (s, 3 H, Me), 1.55 (s, 3 H, Me), 3.75 (dd, $J_{5a,6a}$ = 6.5 Hz, $J_{6a,6'a}$ = 10.5 Hz, 1 H, H-6a), 3.89 (dd, $J_{5a,6'a}$ = 6.5 Hz, $J_{6a,6'a}$ = 10.5 Hz, 1 H, H-6′a), 4.00 (dd, $J_{1b,2b}$ = 1.5 Hz, $J_{2b,3b}$ = 3.5 Hz, 1 H, H-2b), 4.02 (d app t, $J_{4a,5a}$ = 2.0 Hz, $J_{5a,6a}$ = 6.5 Hz, $J_{5a,6'a}$ = 6.5 Hz, 1 H, H-5a), 4.09 (ddd, $J_{4b,5b}$ = 10.0 Hz, $J_{5b,6b}$ = 2.0 Hz, $J_{5b,6'b}$ = 4.0 Hz, 1 H, H-5b), 4.23 (dd, $J_{3a,4a}$ = 8.0 Hz, $J_{4a,5a}$ = 2.0 Hz, 1 H, H-4a), 4.25 (app t, $J_{3b,4b}$ = 10.0 Hz, $J_{4b,5b}$ = 10.0 Hz, 1 H, H-4b), 4.32 (dd, $J_{1a,2a}$ = 5.0 Hz, $J_{2a,3a}$ = 2.5 Hz, 1 H, H-2a), 4.58 (dd, $J_{5b,6b}$ = 2.0 Hz, $J_{6b,6'b}$ = 12.0 Hz, 1 H, H-6b), 4.62 (dd, $J_{2a,3a}$ = 2.5 Hz, $J_{3a,4a}$ = 8.0 Hz, 1 H, H-3a), 4.63 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.68 (d, *J* = 12.0 Hz, 1 H, CH_2 of Bn), 4.79 (dd, $J_{5b,6b}$ = 4.0 Hz, $J_{6b,6'b}$ = 12.0 Hz, 1 H, H-6b), 5.05 (d, $J_{1b,2b}$ = 1.5 Hz, 1 H, H-1b), 5.43 (dd, $J_{2b,3b}$ = 3.5 Hz, $J_{3b,4b}$ = 10.0 Hz, 1 H, H-3b), 5.53 (d, $J_{1a,2a}$ = 5.0 Hz, 1 H, H-1a), 7.16–7.31 (m, 5 H, 5 × ArH), 7.36–7.47 (m, 6 H, 6 × ArH), 7.53–7.61 (m, 3 H, 3 × ArH), 8.01–8.11 (m, 6 H, 6 × ArH). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 24.7 (Me), 25.1 (Me), 26.1 (Me), 26.3 (Me), 64.1 (C-6b), 66.2 (C-5a), 66.2 (C-4b), 66.4 (C-6a), 70.7 (C-2a), 70.8 (C-3a), 71.1 (C-4a), 71.6 (C-5b), 73.1 (CH_2 of Bn), 74.7 (C-3b), 76.2 (C-2b), 96.5 (C-1a), 97.8 (C-1b), 108.9 (Cq), 109.5 (Cq), 127.6, 128.4, 128.5, 128.6, 130.0 (16 × ArCH), 127.8 (ArCH), 129.7 (2 × ArC), 130.0 (ArC), 133.2 (ArCH), 133.4 (2 × ArCH), 138.0 (ArC), 166.9 (C=O), 167.2 (2 × C=O).

(21) See for example: Ziegler, T.; Kovac, P.; Glaudemans, C. P. J. *Liebigs Ann. Chem.* **1990**, 613.

(22) (a) Braccini, I.; Derouet, C.; Esnault, J.; Hervé du Penhoat, C.; Mallet, J.-M.; Michon, V.; Sinaÿ, P. *Carbohydr. Res.* **1993**, *246*, 23. (b) Sinaÿ, P. *Pure Appl. Chem.* **1991**, *63*, 519. (c) Marra, A.; Esnault, J.; Veyrières, A.; Sinaÿ, P. *J. Am. Chem. Soc.* **1992**, *114*, 6354; and references contained therein.

(23) (a) Marra, A.; Mallet, J.-M.; Amatore, C.; Sinaÿ, P. *Synlett* **1990**, 572. (b) Mehta, S.; Pinto, B. M. *Carbohydr. Res.* **1998**, *310*, 43.

(24) **Typical Procedure for Chemical Glycosylation Mediated by (4-$BrC_6H_4)_3NSbCl_6$**: Under an atmosphere of argon, glycosyl donor (ca. 30–90 mg, 1 equiv), glycosyl acceptor (ca. 20–50 mg, 1.2 equiv) and 3 Å MS were suspended in anhyd MeCN (or CH_2Cl_2, 10 mL) and the reaction mixture was stirred at r.t. for 30 min prior to addition of (4-$BrC_6H_4)_3NSbCl_6$ (ca. 120–340 mg, 3 equiv). After 3 h, the mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was then purified by flash column chromatography (typically eluting with PE–EtOAc, 9:1) to afford the desired disaccharide as a colourless oil.