Stannylene Activation in Glycoside Synthesis: Regioselective Glycosidations at the Primary Position of Galactopyranosides Unprotected in the 2-, 3-, 4-, and 6-Positions

Per J. Garegg,* Jean-Luc Maloisel, Stefan Oscarson
Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden
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Stannylene activation with dibutyltin oxide of methyl D-galactopyranosides and of methyl β-D-glucopyranoside, respectively, followed by glycosidation with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide promoted by tetrabutylammonium iodide, or followed by glycosidation with ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside, or ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside, or ethyl 3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside, or ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside, the latter four glycosyl donors being promoted by dimethyl(methylthio)sulfonium trifluoromethanesulfonate (DMTST), led to regioselective glycosidation at the 6-OH of the stannylene glycosyl acceptors. This selectivity was not observed in the absence of stannylene activation.

In oligosaccharide synthesis two aspects have to be mastered. The first of these is stereoselective or, preferably, stereospecific glycosidation. The second one is protecting group manipulation in order to make sure that only specific hydroxy groups are glycosidated. Normally this means that all hydroxy groups *not* to be glycosidated have to be suitably protected. This in turn tends to make the synthesis paths lengthy and time-consuming. So-called "open" glycosidations, in which two or several hydroxy groups are free and in which one hydroxy group is glycosidated in preference to the other(s) may offer shorter routes to oligosaccharides.

Hydroxy group activation to electrophilic attack by way of tin activation has been proven useful in carbohydrate chemistry. The subject has been reviewed.[1,2] Two main avenues are open, either the use of bis(trialkyltin) oxide to form carbohydrate *O*-stannyl ethers, or the use of dialkyltin oxide to form carbohydrate *O*-stannylene acetals. In the pyranoside series, alkylation of such acetals bridging vicinal equatorial/axial oxygens leads predominantly to the equatorial monoether.[3-5]

The use of tin activation has also been examined in glycoside synthesis. In early studies, Ogawa and Matsui examined activation by means of tributyltin derivatives. In disaccharide syntheses, using participating groups in the 2-position, ortho esters were produced, which then could be transformed with Lewis acid into the corresponding disaccharides in moderate yields.[6,7] In a synthesis of the blood group B antigenic determinant, Augé and Veyrières used activation via dibutylstannylene intermediates to obtain monosubstitution of the parent diol. However, the same regioselective monosubstitution was observed in the absence of stannylene activation.[8] Martin-Lomas et al. used the tributylstannylene derivative of methyl β-lactoside in a halide-assisted glycosidation to obtain the α-(1→6′)-linked trisaccharide as the main product (58%), both the tributyl- and the dibutylstannylene derivatives of 1,6-anhydrogalactopyranoside were also glycosidated.[9]

In alkylation of galactopyranosides, the stannylene derivatives obtained upon treatment with dibutyltin oxide react to give preferential substitution in the 3-position.[3,4] Thus, treatment of the stannylene derivative obtained from methyl β-D-galactopyranoside with benzyl bromide gave the 3-*O*-benzyl ether (95%).[5] Equilibria between various structures including oligomeric ones are present in stannylene derivatives formed from partially protected hexopyranosides.[10] This can explain the apparent exceptions to the above results described in a recent study on *tert*-butyldimethylsilylation of the dibutylstannylene derivative of methyl 1-thio-β-lactoside. The 6′-ether instead of the expected 3′-ether was obtained.[11] The result was ascribed to the bulkiness of the silyl group.

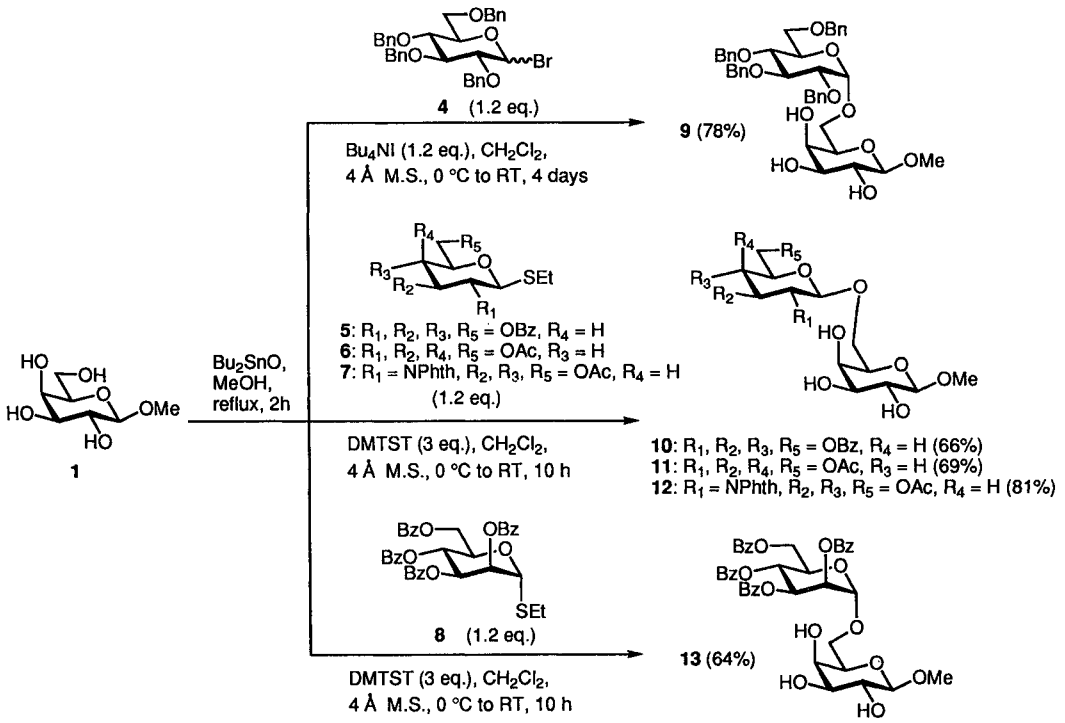
In the present communication, we describe glycosidations of *totally unprotected* methyl galactopyranosides and one instance of glycosidation of methyl β-D-glucopyranoside which in the form of their dibutylstannylene derivatives give regioselective glycosidation to form (1→6)-links in yields of 44–81%. We have examined glycosyl bromides and thioglycosides as glycosyl donors and stannylene derivatives of methyl α- and β-D-galactopyranoside and methyl β-D-glucopyranosides as glycosyl acceptors. The various compounds made are shown in Schemes 1 and 2 and the results of the various glycosidation reactions are outlined in Table 1.

Table 1.

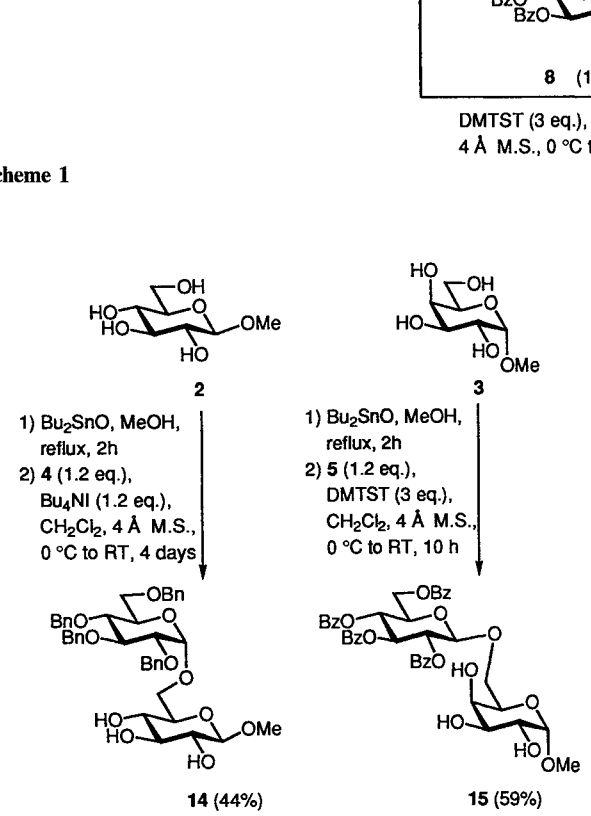
Acceptor	Donor	Method[a]	Product	(Yield, %)	
			Disaccharide	Trisacch.	Tetrasacch.
1	**4**	A	**9** (80)[b]	–	–
1	**4**	C	**9** (7)[c]	(6)[e]	–
1	**5**	B	**10** (66)	(10)[e]	–
1	**6**	B	**11** (69)	(12)[e]	–
1	**7**	B	**12** (81)	–	–
1	**8**	B	**13** (64)	(11)[e]	–
1	**7**	D	–	**18** (17)	**16** (14) **17** (7)
2	**4**	A	**14** (44)[d]	–	–
3	**5**	B	**15** (59)	(15)[e]	–

[a] A: (i) Bu_2SnO, MeOH, reflux, 2 h; (ii) Donor, Bu_4NI, CH_2Cl_2, 4 Å M.S., 0°C to r.t., 4 d. B: (i) Bu_2SnO, MeOH, reflux, 2 h; (ii) Donor, DMTST, CH_2Cl_2, 4 Å M.S., 0°C to r.t., 10 h. C: Bu_4NI, CH_2Cl_2, 4 Å M.S., 0°C to r.t., 4 d. D: DMTST, CH_2Cl_2, 4 Å M.S., 0°C to r.t., 10 h.
[b] α/β 97 : 3.
[c] 61% of **1** was recovered.
[d] α/β 96 : 4, 45% of **2** were recovered.
[e] Complex mixture.

The main product obtained when methyl β-D-galactopyranoside **(1)** was treated first with dibutyltin oxide and then reacted with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyran-



Scheme 1



Scheme 2

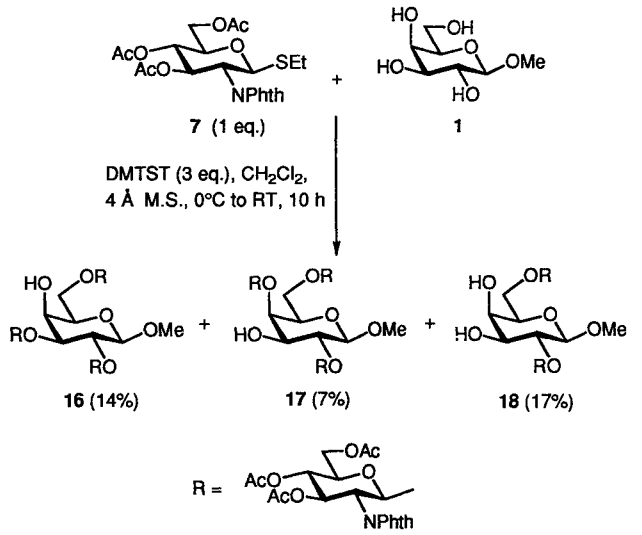
osyl bromide (**4**) in the presence of tetrabutylammonium iodide[12] was the α-(1-6)-linked disaccharide **9** (78%), a regioselectivity in agreement with the silylation of lactose mentioned above. Glycosylation of the same stannylene derivative with thioglycoside donors **5**–**8**, all with participating groups in the 2-positions, in the presence of dimethyl(methylthio)sulfonium triflate (DMTST) as the thiophilic promoter,[13] similarly gave (1–6)-linked disaccharides as major products. Due to participation of the 2-substituent, the glycosyl linkages formed in the products **10**–**12** had the expected β-configuration and analogously the α-configuration in the product **13**. Ortho esters were not observed as products in these reactions.

Changing the anomeric configuration of the glycosyl acceptor did not alter the preponderance of (1–6)-linkage in the product (compare **1** + **5** with **3** + **5**, Table 1). The stannylene derivative of methyl β-D-glucopyranoside (**2**) upon glycosidation with the glycosyl donor **4** also produced the (1–6)-linked disaccharide **14** although in a lower yield than that observed with the galactopyranoside acceptors (Scheme 2). This most probably is due to instability of the stannylene derivative of **2** as compared to those of the galactosides **1** and **3**, since 45% of unreacted **2** was recovered from the reaction mixture. In three instances (Table 1) mixtures of trisaccharides (10–15%) were formed as byproducts. The various disaccharide products were characterized from their NMR spectra (Table 2). The disaccharides were deprotected to the known unprotected disaccharide glycosides (see experimental part). Since the unprotected derivative **23** of **13** is not known, further characterization of **13** and **23** was performed. In order to further confirm the linkages of the disaccharides **9**–**18**, these were also fully acetylated or benzoylated and NMR spectra recorded (Table 2).

In order to ascertain that the results obtained indeed were due to stannylene activation, methyl β-D-galactopyranoside (**1**) was glycosidated in two separate experiments with the glucosyl bromide **4** and tetrabutylammonium iodide as promoter, and also with the thioglycoside donor **7** and DMTST as promoter in the *absence* of stannylene activation (Table 1). Under halide assisted glycosidation conditions almost no reaction occurred, whereas with the thioglycoside **7** a mixture of tri- and tetrasaccharides was formed from these heterogeneous reactions. (Table 1 and Scheme 3).

In summary, the present method gives immediate access to (1–6)-linked disaccharides with a galactosyl or glucos-

yl acceptor residue with the 2,3,4-positions open for further protecting group manipulations. The examples described include formation of α- as well as of β-linkages, and glycosidations with galactosyl, glucosyl, mannosyl, and 2-deoxy-2-phthalimidoglucosyl donors. The method thus gives rapid entry into (1–6)-linked branched oligosaccharides.



Scheme 3

General methods were the same as those described before.[14] Acetate and benzoate derivatives of the disaccharides **9–18** were prepared for NMR identification purposes only and were therefore not further characterized.

Dibutylstannylene Derivatives:
A suspension of the aglycone and 1.5 equiv of dibutyltin oxide in MeOH (0.1 mL/mg aglycone) was boiled under reflux until a clear solution was obtained. Reflux was then continued for 2 h. Evaporation of the solvent gave the crude stannylene derivative, which was used without further purification.

Method A; Glycosidation with 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl Bromide:
Tetrabutylammonium iodide (1.2 equiv) was added at 0°C to a suspension of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide (1.2 equiv), the stannylene derivative, and 4 Å molecular sieves in CH_2Cl_2 (0.05 mL/mg glycosyl bromide). The mixture was then stirred in the dark at r.t. for 4 d. After dilution with EtOAc (40 mL/mmol) and removal of molecular sieves the solution was evaporated and purified by flash chromatography.

Method B; Glycosidation with Thioglycoside Donors:
DMTST (3 equiv) was added at 0°C to a suspension of the thioglycoside (1.2 equiv), the stannylene derivative (1 equiv), and 4 Å molecular sieves in CH_2Cl_2 (0.05 mL/mg thioglycoside). The mixture was then allowed to warm up to r.t. and was stirred for an additional 10 h. The mixture was neutralized with NEt_3. After dilution with EtOAc (40 mL/mmol) and removal of molecular sieves, the solution was evaporated and purified by flash chromatography.

Methyl 6-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-galactopyranoside (9):
Methyl β-D-galactopyranoside **(1)** (50 mg, 0.26 mmol) was treated with Bu_2SnO (97 mg, 0.39 mmol) in MeOH (5 mL). The stannylene derivative was then reacted with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide[12] **(4)** (187 mg, 0.31 mmol) and tetrabutylammonium iodide (114 mg, 0.31 mmol) (Method A). Flash chromatography ($CHCl_3$/MeOH, 98.5:1.5 to 95:5) gave **9** (150 mg, 80%, contaminated by the β anomer, α/β 97:3) as a colourless oil. $R_f = 0.19$ ($CHCl_3$/MeOH, 95:5). $[\alpha]_D^{22} = +52.8°$ ($c = 1$, MeOH).

A portion was acetylated with Ac_2O/pyridine at r.t. overnight to give **9Ac** after conventional workup and flash chromatography (toluene/EtOAc, 5:1).

Methyl 6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-β-D-galactopyranoside (10):
Compound **1** (50 mg, 0.26 mmol) was treated with Bu_2SnO (97 mg, 0.39 mmol) in MeOH (5 mL). The stannylene derivative was then reacted with ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside[15] **(5)** (200 mg, 0.31 mmol) and DMTST (200 mg, 0.78 mmol) (Method B). Flash chromatography ($CHCl_3$/MeOH, 94:6) gave **10** (133 mg, 66%) as a white foam and a complex mixture of trisaccharides (20 mg, 10%). Compound **10**: $R_f = 0.15$ ($CHCl_3$/MeOH, 95:5). $[\alpha]_D^{22} = +8.6°$ ($c = 1$, MeOH).

A portion was acetylated with Ac_2O/pyridine at r.t. overnight to give **10Ac** after conventional workup and flash chromatography (toluene/EtOAc, 8:1).

Methyl 6-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (11):
Compound **1** (50 mg, 0.26 mmol) was treated with Bu_2SnO (97 mg, 0.39 mmol) in MeOH (5 mL). The stannylene derivative was then reacted with ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside[16] **(6)** (123 mg, 0.31 mmol) and DMTST (200 mg, 0.78 mmol) (Method B). Flash chromatography ($CHCl_3$/MeOH, 94:6) gave **11** (94 mg, 69%) as a transparent oil and a complex mixture of trisaccharides (20 mg, 10%). Compound **11**: $R_f = 0.14$ ($CHCl_3$/MeOH, 95:5). $[\alpha]_D^{22} = -12.0°$ ($c = 1$, MeOH).

A portion was benzoylated with benzoyl chloride/pyridine at r.t. overnight to give **11Bz** after conventional workup and flash chromatography (toluene/EtOAc, 6:1).

Methyl 6-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-β-D-galactopyranoside (12):
Compound **1** (50 mg, 0.26 mmol) was treated with Bu_2SnO (97 mg, 0.39 mmol) in MeOH (5 mL). The stannylene derivative was then reacted with ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[17] **(7)** (150 mg, 0.31 mmol) and DMTST (200 mg, 0.78 mmol) (Method B). Flash chromatography ($CHCl_3$/MeOH, 95:5) gave **12** (129 mg, 81%) as a transparent oil. $R_f = 0.16$ ($CHCl_3$/MeOH, 95:5). $[\alpha]_D^{22} = +12.2°$ ($c = 1$, MeOH).

A portion was acetylated with Ac_2O/pyridine at r.t. overnight to give **12Ac** after conventional workup and flash chromatography (toluene/EtOAc, 6:1).

Methyl 6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl)-β-D-galactopyranoside (13):
Compound **1** (50 mg, 0.26 mmol) was treated with Bu_2SnO (97 mg, 0.39 mmol) in MeOH (5 mL). The stannylene derivative was then reacted with ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside[15] **(8)** (200 mg, 0.31 mmol) and DMTST (200 mg, 0.78 mmol) (Method B). Flash chromatography ($CHCl_3$/MeOH, 95:5) gave **13** (129 mg, 64%) as a white foam and a complex mixture of trisaccharides (22 mg, 11%). $R_f = 0.17$ ($CHCl_3$/MeOH, 95:5). $[\alpha]_D^{22} = -50.7°$ ($c = 1$, $CHCl_3$).

$C_{41}H_{40}O_{15}$	calc.	C 63.73	H 5.22
(772.8)	found	63.52	5.26

A portion was acetylated with Ac_2O/pyridine at r.t. overnight to give **13Ac** after conventional workup and flash chromatography (toluene/EtOAc, 8:1).

Methyl 6-*O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-glucopyranoside (14):
Methyl β-D-glucopyranoside **(2)** (50 mg, 0.26 mmol) was treated with Bu_2SnO (97 mg, 0.39 mmol) in MeOH (5 mL). The stannylene derivative was then reacted with **4** (187 mg, 0.31 mmol) and tetrabutylammonium iodide (114 mg, 0.31 mmol) (Method A). Flash

Table 2. NMR Data of Compounds[a] Prepared

	^{1}H NMR[b] δ, J (Hz)	^{13}C NMR[b] δ
9	3.33–3.66 (m, 11H), 3.82–3.90 (m, 4H), 4.07 (d, 1H, J_{1-2} = 7.3, H-1), 4.37–4.83 (m, 8H, 4 × CH_2Ph), 4.89 (d, 1H, $J_{1'2'}$ = 3.3, H-1'), 7.06–7.33 (m, 20H, ArH)	57.3 (OCH_3), 68.1, 69.8, 70.5, 71.4, 72.5, 73.9, 74.2, 74.6 (2C), 74.8, 75.8, 76.4, 79.0, 81.4, 82.9, 97.8 (C-1'), 105.7 (C-1), 128.6–129.4 (ArC), 139.3–140.1 (ArC)
9Ac	1.94, 2.01, 2.04 (3s, 9H, 3 × $COCH_3$), 3.40 (s, 3H, OMe), 3.38–3.90 (m, 9H), 4.31 (d, J_{1-2} = 8.1, H-1), 4.39–4.93 (m, 9H, 4 × CH_2Ph, H-1'), 4.98 (dd, 1H, J_{3-4} = 2.8, H-3), 5.15 (dd, 1H, J_{2-3} = 10.4, H-2), 5.39 (bd, 1H, H-4), 7.09–7.28 (m, 20H, ArH)	20.5, 20.6, 20.7 (3 × COCH_3), 57.0 (OCH_3), 66.0, 67.9, 68.4, 69.0, 70.2, 71.0, 71.9, 73.2, 73.3, 74.7, 75.6, 77.5, 79.7, 81.8, 97.0 (C-1'), 101.9 (C-1), 125.2–128.9 (ArC), 137.8–138.7 (ArC), 169.53, 169.91, 169.21 (3 × $COCH_3$)
10	3.21 (s, 3H, OCH_3), 3.34–3.44 (m, 2H), 3.64 (dd, 1H, J_{5-6} = 3.7, J_{5-6} = 7.1, H-5), 3.06 (d, 1H, J_{3-4} = 2.9, H-4), 3.93 (dd, 1H, J_{6-6} = 11.0, H-6), 3.98 (d, 1H, J_{1-2} = 7.4, H-1), 4.10 (d, 1H, H-6), 4.41 (m, 1H, H-5'), 4.54 (dd, 1H, $J_{5'-6'}$ = 3.7, $J_{6'-6'}$ = 12.1, H-6'), 4.69 (dd, 1H, $J_{5'-6'}$ = 2.3, H-6'), 5.19 (d, 1H, $J_{1'-2'}$ = 8.1, H-1'), 5.51 (dd, 1H, $J_{2'-3'}$ = 9.9, H-2'), 5.74, 6.03 (2t, 2H, H-3', H-4'), 7.28–8.06 (m, 20H, ArH)	57.0 (OCH_3), 64.0 (C-6'), 70.4, 70.8, 71.0, 72.3, 73.1, 73.5, 74.6, 74.7, 75.3, 102.5 (C-1'), 105.1 (C-1), 129.4–130.7 (ArC), 134.4–134.7 (ArC), 166.6, 166.7, 167.0, 167.5 (4 × COPh)
10Ac	1.94, 2.02, 2.05 (3s, 9H, 3 × COCH_3), 3.20 (s, 3H, OCH_3), 3.66–3.94 (m, 3H), 4.14 (m, 1H, H-5'), 4.21 (d, J_{1-2} = 7.7, H-1), 4.47 (dd, 1H, $J_{5'-6'}$ = 4.8, $J_{6'-6'}$ = 12.1, H-6'), 4.68 (dd, 1H, $J_{5'-6'}$ = 3.3, H-6'), 4.68 (dd, 1H, $J_{5'-6'}$ = 3.3, H-6'), 4.91 (d, 1H, $J_{1'-2'}$ = 7.8, H-1'), 4.96 (dd, 1H, J_{2-3} = 10.3, J_{3-4} = 3.3, H-3), 5.11 (dd, 1H, H-2), 5.35 (d, 1H, H-4), 5.51 (dd, 1H, $J_{2'-3'}$ = 9.9 Hz, H-2'), 5.68, 5.89 (2t, 2H), 7.22–8.04 (m, 20H, ArH)	20.5, 20.6, 20.7 (3C, 3 × COCH_3), 56.7 (OCH_3), 62.8 (C-6'), 67.9, 68.0, 69.0, 69.4, 70.9, 71.7, 72.2, 72.6, 72.8, 101.1 (C-1'), 101.8 (C-1), 128.2–129.7 (ArC), 133.2–133.4 (ArC), 164.9, 165.1, 165.7, 166.0 (4 × COPh), 169.5, 169.9, 170.0 (3 × $COCH_3$)
11	1.94, 2.01, 2.02, 2.11 (4s, 12H, 4 × $COCH_3$), 3.43–3.65 (m, 6H), 3.74 (m, 1H, H-4), 3.80 (dd, 1H, J_{5-6} = 7.3, J_{6-6} = 11.0, H-6), 3.94 (dd, 1H, J_{5-6} = 4.4, H-6), 4.08–4.15 (m, 4H), 4.72 (d, 1H, $J_{1'-2'}$ = 8.0, H-1'), 5.02–5.09 (m, 2H, H-2', H-3'), 5.36 (m, 1H, H-4')	20.5 (2C, 2 × COCH_3), 20.6, 20.8 (2 × COCH_3), 57.3 (OCH_3), 62.7 (C-6'), 68.9 (70.1, 70.4 (2C), 71.9, 72.4 (2C), 74.8, 75.4, 102.4 (C-1'), 105.9 (C-1), 171.3, 171.5, 171.9, 172.1 (4 × $COCH_3$)
11Bz	1.96, 1.98, 2.06, 2.14 (4s, 12H, 4 × $COCH_3$), 3.60 (s, 3H, OCH_3), 3.81–4.19 (m, 6H), 4.55, 4.69 (2d, 2H, J_{1-2} and $J_{1'-2'}$ = 7.7, H-1, H-1')', 4.98 (dd, 1H, $J_{2'-3'}$ = 10.6, J_{3d-4d} = 3.3, H-3'), 5.21 (dd, 1H, H-2'), 5.36 (br d, H-4'), 5.54 (dd, 1H, J_{2-3} = 10.3, J_{3-4} = 3.3, H-3), 5.75 (dd, 1H, H-2), 5.85 (bd, 1H, H-4), 7.20–8.08 (m, 20H, ArH)	20.6 (3C, 3 × COCH_3), 20.71 (2C, 2 × COCH_3), 57.2 (OCH_3), 61.1 (C-6'), 67.0, 67.7, 68.5, 68.7, 69.7, 70.7, 70.9, 71.8,. 73.0, 100.9 and 102.4 (C-1 and C-1'), 128.2–133.6 (ArC), 165.3, 165.4, 165.5 (3C, 3 × COPh), 169.3, 170.1, 170.2, 170.3 (4 × $COCH_3$)
12	1.87, 2.04, 2.11, (3s, 9H, 3 × $COCH_3$), 3.12 (s, 3H, OCH_3), 3.35–3.76 (m, 4H), 3.94–4.38 (m, 7H), 5.13 (t, 1H, H-4'), 5.52 (d, 1H, $J_{1'-2'}$ = 8.4, H-1'), 5.80 (t, 1H, H-3'), 7.85–7.87 (m, 4H, ArH)	21.1, 21.1, 21.5 (3 × COCH_3), 55.9 (C-2'), 56.7 (OCH_3), 63.1 (C-6'), 70.2, 70.4, 70.6, 71.9, 72.2, 73.0, 74.5, 75.0, 99.4 (C-1'), 105.4 (C-1), 124.5–135.8 (ArC), 168.9, 169.0, 171.2, 171.6, 172.3 (5 × CO)
12Ac	1.86, 1.92, 2.02, 2.04, 2.10, 2.13 (6s, 18H, $COCH_3$), 3.23 (s, 3H, OCH_3), 3.66–3.88 (m, 4H), 4.18–4.36 (m, 4H), 4.93 (dd, 1H, J_{2-3} = 10.4, J_{3-4} = 3.3, H-3), 5.09 (dd, 1H, J_{1-2} = 7.9, H-2), 5.18 (t, 1H, H-4'), 5.27 (d, 1H, $J_{1'-2'}$ = 8.4 Hz, H-1'), 5.76 (dd, $J_{2'-3'}$ = 10.6, $J_{3'-4'}$ = 9.1, H-3'), 7.72–7.87 (m, 4H, ArH)	20.4, 20.5 (2C, 2 × COCH_3), 20.6 (2C, 2 × COCH_3), 20.7 (2 × COCH_3), 54.4 (C-2'), 56.5 (OCH_3), 61.8 (C-6'), 67.5, 67.7, 68.7, 68.9, 70.6, 70.8, 71.9, 72.2, 97.7 (C-1'), 101.7 (C-1), 123.6, 131.3, 134.3 (ArC), 168.4–170.6 (CO)
13	3.48–3.88 (m, 8H), 4.12 (m, 1H), 4.22 (d, 1H, J_{1-2} = 7.6, H-1), 4.45 (dd, 1H, $J_{5'-6'}$ = 2.9, $J_{6'-6'}$ = 2.9, H-6'), 4.62–4.74 (m, 2H), 5.14 (d, 1H, $J_{1'-2'}$ = 1.8, H-1'), 5.68 (dd, 1H, $J_{2'-3'}$ = 3.3, H-2'), 5.85 (dd, 1H, $J_{3'-4'}$ = 10.2, H-3'), 6.09 (t, H-4'), 7.19–8.09 (m, 20H, ArH)	57.4 (OCH_3), 63.7 (C-6'), 68.1, 68.2, 70.0, 70.5, 71.6, 71.8, 72.5, 74.7, 74.9, 98.5 (C-1'), 106.0 (C-1), 129.5–134.7 (ArC), 166.7, 166.8, 166.91, 167.5 (4 × COPh)
13Ac	2.00, 2.04, 2.08 (3s, 9H, 3 × $COCH_3$), 3.62–4.07 (m, 6H), 4.50–4.58 (m, 3H), 4.71 (m, 1H), 5.08 (d, 1H, $J_{1'-2'}$ = 1.8, H-1'), 5.11 (dd, 1H, J_{2-3} = 10.5, J_{3-4} = 3.3, H-3), 5.27 (dd, 1H, J_{1-2} = 7.9, H-2), 5.47 (d, 1H, H-4), 5.68 (dd, 1H, $J_{2'-3'}$ = 3.3, H-2'), 5.91 (dd, 1H, $J_{3'-4'}$ = 10.3, H-3'), 6.11 (t, 1H, H-4'), 7.24–8.15 (m, 20H, ArH)	20.5 (2C, 2 × COCH_3), 20.8 ($COCH_3$), 57.0 (OCH_3), 62.7 (C-6'), 66.4, 66.7, 67.8, 68.9, 69.1, 69.8, 70.1, 70.9, 71.9, 97.2 (C-1'), 102.0 (C-1), 128.2–133.4 (ArC), 165.2, 165.3, 165.4, 166.1 (4 × COPh), 169.5, 170.0, 170.2 (3 × $COCH_3$)
14	3.33–91 (m, 15H), 4.16 (d, 1H, J_{1-2} = 8.1, H-1), 4.41–4.86 (m, 8H, 4 × CH_2Ph), 4.97 (d, 1H, $J_{1'-2'}$ = 3.3, H-1'), 7.08–7.37 (m, 20H, ArH)	57.4 (OCH_3), 67.3 (C-6'), 69.9, 71.2, 71.7, 73.5, 74.1, 75.0, 75.8, 76.4, 76.4 (2C), 78.1, 79.1, 81.4, 82.9, 97.5 (C-1'), 105.3 (C-1), 128.5–140.1 (ArC)
14Ac	1.99, 2.01, 2.04 (3s, 9H, 3 × $COCH_3$), 3.39 (s, 3H, OCH_3), 3.49–3.99 (m, 9H), 4.37 (d, 1H, J_{1-2} = 8.1, H-1), 4.42–4.60 (m, 4H, 4 × CH_2Ph), 4.64–5.00 (m, 7H), 5.19 (t, 1H), 7.07–7.41 (m, 20H, ArH)	20.6 (COCH_3), 20.7 (2C, 2 × COCH_3), 57.0 (OCH_3), 66.3 (C-6'), 68.4, 69.5, 70.1, 71.4, 72.7, 73.0, 73.2, 73.4, 74.8, 75.6, 76.5, 77.2, 79.8, 81.8, 96.8 (C-1'), 101.3 (C-1), 127.5–128.4 (ArC), 137.8–138.7 (ArC), 169.4, 169.5, 170.3 (3 × $COCH_3$)

Table 2. (continued)

	^{1}H NMR[b] δ, J (Hz)	^{13}C NMR[b] δ
15	2.97 (s, 3 H, OCH_3), 3.56 (dd, J_{5-6} = 3.3 Hz, J_{6-6} = 10.3, H-6), 3.65 (dd, J_{5-6} = 3.7, H-6), 3.73–4.05 (m, 4 H), 4.35 (m, 1 H, H-5'), 4.42 (d, 1 H, J_{1-2} = 3.7, H-1), 4.48 (dd, 1 H, $J_{5'-6'}$ = 4.8, $J_{6'-6'}$ = 12.1, H-6'), 4.62 (dd, $J_{5'-6'}$ = 3.3, H-6'), 5.12 (d, $J_{1'-2'}$ = 7.7, H-1'), 5.47 (dd, $J_{2'-3}$ = 9.9, H-2'), 5.68 (t, 1 H), 5.98 (t, 1 H), 7.20–7.99 (m, 20 H, ArH)	55.3 (OCH_3), 64.1 (C-6'), 70.1, 70.9, 71.1, 71.2 (2 C), 71.7, 73.1, 73.6, 74.6, 101.1 (C-1), 102.8 (C-1'), 129.4–134.7 (ArC), 166.6, 166.7, 167.0, 167.5 (4 × $COPh$)
15Ac	1.90, 1.99, 2.00 (3 s, 9 H, 3 × $COCH_3$), 2.97 (s, 3 H, OCH_3), 3.60 (dd, 1 H, J_{5-6} = 8.4, J_{6-6} = 10.9, H-6), 3.84 (dd, 1 H, J_{5-6} = 3.3, H-6), 4.07–4.13 (m, 2 H), 4.44 (dd, 1 H, $J_{5'-6'}$ = 4.8, $J_{6'-6'}$ = 12.1, H-6'), 4.59 (dd, 1 H, $J_{5'-6'}$ = 3.2, H-6'), 4.71 (d, 1 H, J_{1-2} = 3.3, H-1), 4.86 (d, 1 H, $J_{1'-2'}$ = 8.1, H-1'), 5.01 (dd, 1 H, J_{2-3} = 11.0, H-2), 5.23 (dd, 1 H, J_{3-4} = 3.1, H-1), 5.34 (bd, 1 H, H-4), 5.47 (dd, 1 H, $J_{2'-3'}$ = 9.9, H-2'), 5.62, 5.84 (2 t, 2 H, H-3', H-4'), 7.16–7.98 (m, 20 H, ArH)	20.6 (2 C, 2 × $COCH_3$), 20.8 ($COCH_3$), 54.9 (OCH_3), 62.9 (C-6'), 67.5, 67.8, 68.2, 68.6, 68.9, 69.6, 71.8, 72.2, 72.8, 96.7 (C-1), 101.3 (C-1'), 125.3–133.4 (ArC), 165, 165.1, 165.8, 166.1 (4 × $COPh$), 169.7, 170.0, 170.4 (3 × $COCH_3$)

[a] Compounds **9, 10,** and **12–15** were acetylated to give, respectively, **9Ac, 10Ac, 12Ac, 13Ac, 14Ac,** and **15Ac**. Compound **11** was benzoylated to **11Bz**.

[b] CD_3OD/TMS for compounds **9–15**, $CDCl_3$/TMS for compounds **9Ac, 10Ac, 11Bz, 12Ac, 13Ac, 14Ac,** and **15Ac**.

chromatography ($CHCl_3$/MeOH, 98.5:1.5 to 90:10) gave **14** (82 mg, 44%, contaminated by the β anomer, α/β 96:4) as a colourless oil and unreacted **2** (22.5 mg, 45%). Compound **14**: R_f = 0.20 ($CHCl_3$/MeOH, 95:5). $[\alpha]_D^{22}$ = + 24.9° (c = 1, MeOH).

A portion was acetylated with Ac_2O/pyridine at r.t. overnight to give **14Ac** after conventional workup and flash chromatography (toluene/EtOAc, 5:1).

Methyl 6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-galactopyranoside (15):

Methyl α-D-galactopyranoside **(3)** (50 mg, 0.26 mmol) was treated with Bu_2SnO (97 mg, 0.39 mmol) in MeOH (5 mL). The stannylene derivative was then reacted with **5** (200 mg, 0.31 mmol) and DMTST (200 mg, 0.78 mmol) (Method B). Flash chromatography ($CHCl_3$/MeOH, 94:6) gave **15** (119 mg, 59%) as a white foam and a complex mixture of trisaccharides (30 mg, 15%). Compound **15**: R_f = 0.15 ($CHCl_3$/MeOH, 95:5). $[\alpha]_D^{22}$ = + 38.6° (c = 1, MeOH).

A portion was acetylated with Ac_2O/pyridine at r.t. overnight to give **15Ac** after conventional workup and flash chromatography (toluene/EtOAc, 8:1).

Glycosidations of Methyl β-D-galactopyranoside Without Bu_2SnO:

(a) With 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl Bromide[12] **(4)**:

Tetrabutylammonium iodide (228 mg, 0.62 mmol) was added at 0 °C to a suspension of **4** (374 mg, 0.62 mmol), **1** (100 mg, 0.515 mmol), and 4 Å molecular sieves in CH_2Cl_2 (10 mL). The mixture was then stirred in the dark at r.t. for 4 d. After dilution with EtOAc and removal of molecular sieves the solution was evaporated. Flash chromatography ($CHCl_3$/MeOH, 99:1 to 95:5) gave a complex mixture of trisaccharides (39 mg, 6%), **9** (26 mg, 7%), and unreacted **1** (61 mg, 61%).

(b) With Ethyl 3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[17] **(7)**:

DMTST (396 mg, 1.545 mmol) was added at 0 °C to a suspension of **7** (297 mg, 0.618 mmol), **1** (100 mg, 0.515 mmol), and 4 Å molecular sieves in CH_2Cl_2 (10 mL). The mixture was then allowed to warm up to r.t. and was stirred for an additional 10 h. The mixture was neutralized with NEt_3. After dilution with EtOAc and removal of molecular sieves the solution was evaporated. Flash chromatography (toluene/EtOAc, 1:1 to 1:3) gave first pure **16** (31 mg, 4%), then a mixture of **16** and **17** (**16/17**, 10:7, 126 mg, 17%), and finally **18** (90 mg, 17%). For analytical purpose a fraction of **17** was purified by preparative TLC ($CHCl_3$/MeOH, 95:5).

Methyl 2,3,6-Tri-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-β-D-galactopyranoside (16):

R_f = 0.36 (toluene/EtOAc, 1:2). $[\alpha]_D^{22}$ = + 26.8° (c = 1, $CHCl_3$).

^{1}H NMR ($CDCl_3$, selected data): δ = 2.82 (s, 3 H, OCH_3), 4.87, 5.03, 5.16 (3 t, 3 H, H-4', H-4'', H-4'''), 5.36, 5.38 (2 d, 1 H, $J_{1'-2'}$ = 8.4 Hz, H-1', H-1''), 5.42 (d, $J_{1'''-2'''}$ = 8.4 Hz, H-1'''), 5.54 (dd, 1 H, $J_{2'-3'}$ = 9.2, $J_{3'-4'}$ = 10.6 Hz, H-3'), 5.74–5.83 (m, 2 H, H-3'', H-3'''), 7.66–8.04 (m, 12 H, arom. H).

^{13}C NMR ($CDCl_3$, selected data): δ = 54.30 (C-2'), 54.54 (2 C, C-2'', C-2'''), 54.95 (OCH_3), 61.79, 62.03, 62.46 (C-6', C-6'', C-6'''), 94.51 (C-1'), 97.99 (C-1'', C-1'''), 99.54 (C-1).

A portion was benzoylated with benzoyl chloride/pyridine at r.t. overnight to give **16Bz** after conventional workup and flash chromatography (toluene/EtOAc, 1:2).

^{1}H NMR ($CDCl_3$, selected data): δ = 2.69 (s, 3 H, OCH_3), 4.96–5.05 (m, 2 H, H-4', H-4''), 5.15 (dd, 1 H, $J_{3'''-4'''}$ = 9.2, $J_{4'''-5'''}$ = 10.3 Hz, H-4'''), 5.23 (dd, 1 H, J_{3-4} = 3.6, J_{4-5} = 2.2 Hz, H-4), 5.27 (d, $J_{1'-2'}$ = 8.4 Hz, H-1'), 5.45–5.50 (m, 2 H, H-1'', H-1'''), 5.61–5.82 (m, 3 H, H-3', H-3'', H-3''').

^{13}C NMR ($CDCl_3$, selected data): δ = 54.34 (C-2''), 54.53 (2 C, C-2'', C-2'''), 55.01 (OCH_3), 61.65, 61.81, 62.32 (C-6', C-6'', C-6'''), 95.24, 97.07, 97.94 (C-1', C-1'', C-1'''), 99.69 (C-1).

Methyl 2,4,6-Tri-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-β-D-galactopyranoside (17):

R_f = 0.33 (toluene/EtOAc 1:2). $[\alpha]_D^{22}$ = + 18.2° (c = 0.5, $CHCl_3$).

^{1}H NMR ($CDCl_3$, selected data): δ = 2.62 (s, 3 H, OCH_3), 4.94 (t, 1 H, H-4'), 5.07 (d, 1 H, $J_{1'-2'}$ = 8.4 Hz, H-1'), 5.09–5.21 (m, 2 H, H-4'', H-4'''), 5.31 (d, 1 H, $J_{1''-2''}$ = 8.4 Hz, H-1''), 5.37 (d, 1 H, $J_{1'''-2'''}$ = 8.4 Hz, H-1'''), 5.44 (dd, 1 H, $J_{2'-3'}$ = 8.8, $J_{3'-4'}$ = 10.6 Hz, H-3'), 5.76–5.84 (m, 2 H, H-3'', H-3'''), 7.69–8.01 (m, 12 H, arom. H).

^{13}C NMR ($CDCl_3$, selected data): δ = 53.72, 54.47, 54.63 (C-2', C-2'', C-2'''), 54.81 (OCH_3), 61.35, 61.62, 61.95 (C-6', C-6'', C-6'''), 95.97, 98.02, 99.50, 99.72 (4 C, C-1, C-1', C-1'', C-1''').

A portion was acetylated with Ac_2O/pyridine in the presence of 4-dimethylaminopyridine (DMAP) at r.t. overnight, to give **17Ac** after conventional workup and flash chromatography (toluene/EtOAc, 1:2).

^{1}H NMR ($CDCl_3$, selected data): δ = 2.91 (s, 3 H, OCH_3), 4.47 (dd, 1 H, J_{2-3} = 10.3, J_{3-4} = 2.9 Hz, H-3), 4.69 (d, 1 H, $J_{1'-2'}$ = 8.4 Hz, H-1'), 4.96–5.30 (m, 4 H, H-1'', H-4', H-4'', H-4'''),

5.38 (d, 1 H, $J_{1'''-2'''}$ = 8.4 Hz, H-1'''), 5.52 (dd, 1 H, $J_{2'-3'}$ = 9.2, $J_{3'-4'}$ = 10.6 Hz, H-3'), 5.73–5.83 (m, 2 H, H-3'', H-3''').

Methyl 2,6-Di-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-β-D-galactopyranoside (18):
R_f = 0.18 (toluene/EtOAc, 1:2). $[\alpha]_D^{22}$ = + 10.5° (*c* = 1, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.84, 1.85 (2 s, 6 H, 2 × $COCH_3$), 2.02 (s, 6 H, 2 × $COCH_3$), 2.08, 2.09 (2 s, 6 H, 2 × $COCH_3$), 2.58 (br s, 2 H, HO-3, HO-4), 3.06 (s, 3 H, OCH_3), 3.29–3.47 (m, 3 H), 3.59–3.90 (m, 6 H), 4.04 (d, J_{1-2} = 7.7 Hz, H-1), 4.16–4.37 (m, 6 H), 5.09–5.17 (m, 2 H, H-4', H-4''), 5.40 (d, 1 H, $J_{1'-2'}$ = 8.4 Hz, H-1'), 5.55 (d, 1 H, $J_{1''-2''}$ = 8.8 Hz, H-1''), 5.72–5.85 (m, 2 H, H-3', H-3''), 7.71–7.85 (m, 8 H, arom. H).

^{13}C NMR ($CDCl_3$): δ = 20.31, 20.41 (2 × $COCH_3$), 20.60 (2 × $COCH_3$), 20.73 (2 × $COCH_3$), 54.46 (C-2', C-2''), 56.08 (OCH_3), 61.89, 62.03 (C-6', C-6''), 68.03, 68.22, 68.87 (2 C), 70.49, 70.62, 71.81, 71.95 (2 C), 72.68, 80.35, 98.11 (C-1'), 98.27 (C-1''), 101.84 (C-1), 123.43–134.32 (arom. C), 167.40–170.72 (CO).

A portion was benzoylated with benzoyl chloride/pyridine at r.t. overnight to give **18Bz** after conventional workup and flash chromatography (toluene/EtOAc, 1:2).

^{1}H NMR ($CDCl_3$, selected data): δ = 3.26 (s, 3 H, OCH_3), 3.92 (dd, 1 H, J_{1-2} = 7.5, J_{2-3} = 10.2 Hz, H-2), 4.38 (d, 1 H, H-1), 5.07–5.17 (m, 2 H, H-4', H-4''), 5.19 (dd, 1 H, J_{3-4} = 3.4 Hz, H-3), 5.38 (d, 1 H, $J_{1'-2'}$ = 8.8 Hz, H-1'), 5.45 (d, 1 H, H-4), 5.54 (d, 1 H, $J_{1''-2''}$ = 8.4 Hz, H-1''), 5.60–5.75 (m, 2 H, H-3', H-3'').

^{13}C NMR ($CDCl_3$, selected data): δ = 54.39, 54.69 (C-2', C-2''), 56.60 (OCH_3), 61.73, 61.84 (C-6', C-6''), 97.53, 97.69 (C-1', C-1''), 102.39 (C-1).

Deprotection of the Disaccharides:
All NMR data of the unprotected disaccharides were in agreement with the published data.[18-20]

Methyl 6-*O*-α-D-Glucopyranosyl-β-D-galactopyranoside (19):
A suspension of **9** (115 mg, 0.16 mmol) and Pd/C (10%, 100 mg) in AcOH (8 mL) was stirred for 14 h under H_2 (60 p.s.i.). The solids were filtered off and washed with H_2O. The combined solutions were concentrated and the residue purified by flash chromatography (EtOAc/MeOH/H_2O, 65:23:12) to yield **19** (49 mg, 85%, contaminated by the β anomer, α/β 97:3) as a transparent solid. R_f = 0.25 (EtOAc/MeOH/H_2O, 65:23:12). $[\alpha]_D^{22}$ = + 53° (*c* = 1, H_2O), (lit.[18] $[\alpha]_D$ = + 51°).

Methyl 6-*O*-β-D-Glucopyranosyl-β-D-galactopyranoside (20):
Compound **10** (110 mg, 0.142 mmol) was stirred overnight in presence of a 1 mM solution of NaOMe in MeOH (5 mL). The mixture was neutralized by addition of Dowex (H^+) ion exchange resin, diluted with H_2O (10 mL), filtered and evaporated. The residue was further purified by flash chromatography (EtOAc/MeOH/H_2O, 65:23:12) to yield **20** (48 mg, 95%) as a transparent amorphous solid. R_f = 0.22 (EtOAc/MeOH/H_2O, 65:23:12). $[\alpha]_D^{22}$ = − 27.5° (*c* = 1, H_2O), (lit.[18] $[\alpha]_D$ = − 28°).

Methyl 6-*O*-β-D-Galactopyranosyl-β-D-galactopyranoside (21):
Compound **11** (80 mg, 0.153 mmol) was deprotected as described for **10** to yield **21** (52 mg, 96%) as a white solid. Recrystallized from MeOH, mp 220–221 °C. $[\alpha]_D^{22}$ = − 9° (*c* = 0.5, H_2O), (lit.[19] mp 220–221 °C, $[\alpha]_D$ = − 9°). R_f = 0.18 (EtOAc/MeOH/H_2O, 65:23:12).

Methyl 6-*O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-β-D-galactopyranoside (22):
A solution of **12** (106 mg, 0.173 mmol) in MeOH (2 mL) and $MeNH_2$ (4 mL, 33% in EtOH) was heated at reflux. After 3 h the solvents were evaporated, and the residue was acetylated (pyridine/Ac_2O, 2:1) overnight. Conventional work up and flash chromatography (EtOAc) gave a product (95 mg; R_f = 0.45, EtOAc) which was dissolved in a 1 mM solution of NaOMe in MeOH (5 mL) and stirred overnight. The mixture was neutralized by addition of Dowex H^+) ion exchange resin, diluted with H_2 and filtered. Evaporation left a white residue which was further purified by flash chromatography (EtOAc/MeOH/H_2O, 65:23:12) to yield **22** (51 mg, 74%) as a white solid. Recrystallized from MeOH, mp 256–257 °C. $[\alpha]_D^{22}$ = − 27° (*c* = 1.1, H_2O/MeOH, 1:1), (lit.[20] mp 256–257 °C, $[\alpha]_D$ = − 26.9°). R_f = 0.18 (EtOAc/MeOH/H_2O, 65:23:12).

Methyl 6-*O*-α-D-Mannopyranosyl-β-D-galactopyranoside (23):
Compound **13** (105 mg, 0.136 mmol) was deprotected as described for **10** to yield **23** (44 mg, 91%) as a transparent solid. R_f = 0.23 (EtOAc/MeOH/H_2O, 65:23:12). $[\alpha]_D^{22}$ = + 48.2° (*c* = 1, H_2O).

$C_{13}H_{24}O_{11}$	calc.	C 43.82	H 6.74
(356.3)	found	43.72	6.67

^{1}H NMR (D_2O): δ = 3.46–3.94 (m, 15 H), 4.28 (d, 1 H, J_{1-2} = 7.7 Hz, H-1), 4.88 (d, 1 H, J_{1-2} = 1.8 Hz, H-1').

^{13}C NMR (D_2O): δ = 57.83 (OCH_3), 61.83 (C-6'), 67.02, 67.70, 69.67, 70.89, 71.48, 71.56, 73.70 (3 C), 100.51 (C-1'), 104.61 (C-1).

Methyl 6-*O*-α-D-Glucopyranosyl-β-D-glucopyranoside (24):
Compound **14** (60 mg, 0.084 mmol) was deprotected as described for **9** to yield **24** (24 mg, 81%, contaminated by the β anomer, α/β 96:4) as a transparent solid. R_f = 0.25 (EtOAc/MeOH/H_2O 65:23:12). $[\alpha]_D^{22}$ = + 89° (*c* = 1, H_2O), (lit.[18] $[\alpha]_D$ = + 87°).

Methyl 6-*O*-β-D-glucopyranosyl-α-D-galactopyranoside (25):
Compound **15** (92 mg, 0.119 mmol) was deprotected as described for **10** to yield **25** (40 mg, 94%) as a transparent solid. R_f = 0.22 (EtOAc/MeOH/H_2O, 65:23:12). $[\alpha]_D^{22}$ = + 72° (*c* = 1, H_2O), (lit.[18] $[\alpha]_D$ = + 72°).

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