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# D-Galactose-derived D-galacturonic acid derivatives suitable as glycosyl acceptors*

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ABSTRACT

Allyl (**1a**) and benzyl (**1b**) β-D-galactopyranosides were converted into methyl [allyl (and benzyl) 2-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranosid]uronates, (**6a** and **6b**) by three different routes. The carboxyl group was introduced by Jones oxidation of suitably protected precursors and esterified directly. The chemical behaviour of 6-*O*-trityl-, 6-*O*-(4,4′-dimethoxytrityl)-, and 6-*O*-(2-methoxypropane-2-yl)-derivatives was investigated. The overall yields obtained were strongly influenced by the protecting groups used, in particular their stability in acidic solution.

## INTRODUCTION

A previous paper[1] described the synthesis of potential galactopyranosyluronic donors, starting from isopropylidenated or acetylated galactose derivatives. Herein we describe synthesis of potential glycosyl acceptors (**6a** and **6b**), starting from the corresponding β-D-galactopyranosides.

Tritylated 1,2-*O*-(1-cyano)ethylidene derivatives of mono-, di-, and oligo-saccharides are used as monomers in polycondensation reactions to furnish polysaccharides having regular structures[2]. To prepare such monomers containing galacturonic acid, several differently blocked derivatives thereof were needed.

The current aim was to synthesize galactopyranosiduronic derivatives having protecting groups in various positions that differ markedly in their chemical behaviour, to enable the deprotection of one or other of the OH groups for subsequent direct glycosidation or for tritylation. Compounds **6a** and **6b** fulfilled these expectations, and three different routes for their preparation were investigated. By using galactopyranosides as starting materials instead of galacturonic acid, the formation of furanose isomers[3] could be avoided.

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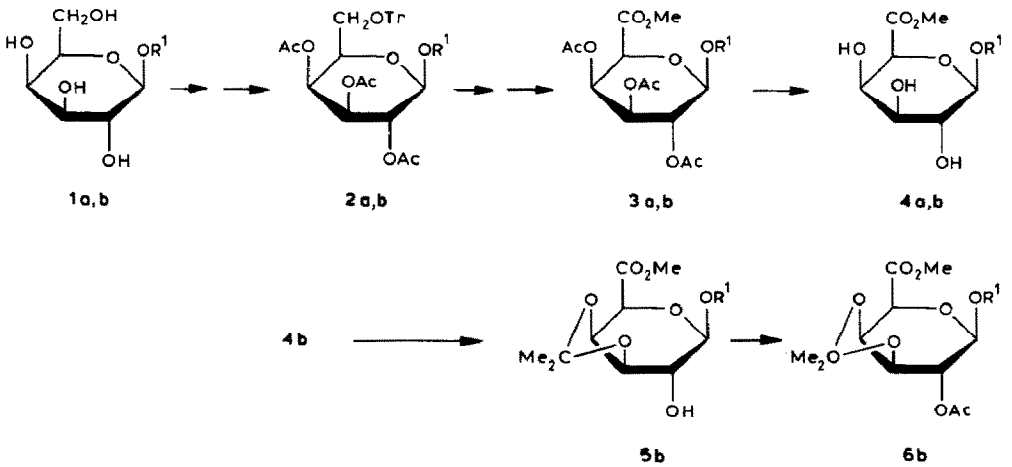
RESULTS AND DISCUSSION

Allyl[4] and benzyl[5] galactopyranosides were of particular interest because the anomeric centre may be deprotected by mild procedures. Both galactosides were prepared via 2,3,4,6-tetra-*O*-acetyl-*α*-D-galactosyl bromide[6]. This method is superior to the classical syntheses, because the cumbersome separation of the *α*,*β* anomers is avoided. In the syntheses of the glycosyl bromide according to the literature[6], the amount of water used to hydrolyze the excess of phosphorus tribromide should be decreased to increase the yield.

The first route **6a** and **6b** required the tritylation and subsequent acetylation of the galactosides **1a** and **1b**. A one-pot procedure afforded good yields of allyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-*β*-D-galactopyranoside (**2a**) and the corresponding benzyl galactoside (**2b**). Jones oxidation[7] of both these products did not require deprotection of the 6-position, as acidic conditions of the oxidation were sufficient to cleave off the trityl group. The resulting oxidation product was not isolated, but was immediately treated with methyl iodide under phase-transfer conditions to give the acetylated methyl (alkyl *β*-D-galactopyranosid)uronates **3a** and **3b**. Deacetylation of these fully protected compounds was achieved in an acidic medium. The classical Zemplén procedure was not employed, because the *β*-elimination typical for uronic acid derivatives might have occured under such conditions. The resulting methyl (allyl *β*-D-galactopyranosid)-uronate (**4a**) was obtained as syrup, wereas methyl (benzyl *β*-D-galactopyranosid)-uronate (**4b**) crystallized. The latter has already been synthesized directyl from galact-uronic acid[8]. Because **4b** was easier to handle, we utilized this compound exclusively to prepare **6b**. (Compound **6a** was obtained by a secound route, as outlined in a later chart). Treatment of **4b** with 2,2-dimethoxypropane afforded methyl (benzyl 3,4-*O*-

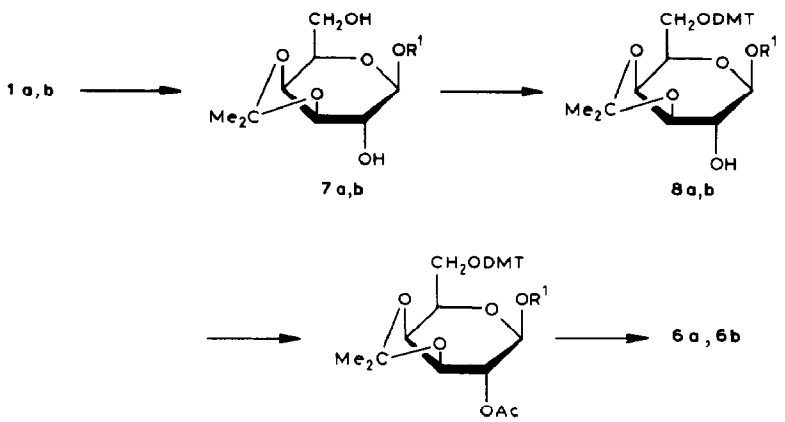



Tr = $Ph_3C$ , Ac = $CH_3CO$
in formulas a: $R^1$ = $CH_2{=}CHCH_2$
in formulas b: $R^1$ = $PhCH_2$

isopropylidene-β-D-galactopyranosid)uronate[8] (**5b**), acetylation of which furnished the final key intermediate, methyl (benzyl 2-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranosid)uronate (**6b**).

The $^1$H- and $^{13}$C-n.m.r. spectra of **4a**, **4b** and **6b** were fully consistent with the assigned structures. The β stereochemistry of the glycosidic likages was evident from the large coupling (8.0 ±0.1 Hz) of the H-1 doublet in the $^1$H-n.m.r. spectra of compounds **2a**, **2b**, **3a**, and **3b**. Signals for C-1 of the β-linked products appeared in the anomeric region at 99.8 ±0.4 p.p.m. The three-bond coupling constants within the pyranose ring vary only slightly throughout the whole series and amount to 10.4 ±0.2 ($J_{2,3}$), 3.3 ±0.1 ($J_{3,4}$), and 1.2 ±0.2 Hz ($J_{4,5}$). The *J*-values indicate the anticipated $^4C_1$ conformation of the six-membered ring. The conversion of **2a** and **2b** into **3a** and **3b**, respectively, is also evident from the signals at 52.4 and 52.5 p.p.m. ($CO_2CH_3$) in the $^{13}$C-n.m.r. spectra of **3a** and **3b**, and from the strong downfield shift of the C-6 signal (61.0 to 166.3 and 166.4 p.p.m. respectively) as a result of oxidation of the primary alcohol to the carboxyl function.

The second approach to the key intermediates **6a** and **6b** required initial isopropylidenation of the glycosides **1a** and **1b** to furnish the 3,4-*O*-isopropylidenegalactosides **7a** and **7b**. Unfortunately, these desired products were always accompanied by the 4,6-*O*-isopropylidene isomers, which could not be suppressed even by use of a variety of published procedures[9–13]. Separation by column chromatography proved necessary in each case, and yields did not exceed 70%. Because of the similar acid lability of *O*-isopropylidene and *O*-tritylgroups, bis(4-methoxyphenyl)chlorophenylmethane was used as the reagent to protect the 6-position instead of chlorotriphenylmethane, affording **8a** and **8b** from **7a** and **7b**. Conventional acetylation of **8a** furnished allyl 2-*O*-acetyl-3,4-*O*-isopropylidene-6-*O*-(4,4'-dimethoxytrityl)-β-*D*-galactopyranoside (**9a**) as an oil; the




DMT = $(4\text{-}MeOC_6H_4)_2PhC$ , Ac = $CH_3CO$

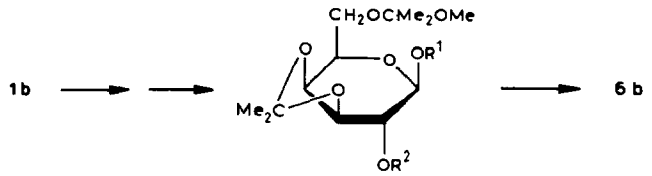
in formulas a: $R^1 = CH_2{=}CHCH_2$

in formulas b: $R^1 = PhCH_2$

corresponding benzyl glycoside **9b** crystallized. Jones oxidation of **9a** and **9b** with subsequent methylation led to methyl (allyl 2-*O*-acetyl-3,4-*O*-isopropylidene-β-D-galactopyranosid)uronate (**6a**) and again the corresponding benzyl derivative **6b**, already obtained by the first route. The low yields in the oxidation step (35 and 40%, respectively) confirm our findings that the Jones oxidation is not very satisfactory when applied to sugars having acid-labile protecting groups in positions other than the one to be oxidized. We showed earlier that 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-α,β-D-galactopyranoside also gave low yields of product on Jones oxidation; the anomeric acetoxy group was simultaneously attacked. In contrast to these results are the yields of 71% when methyl galactopyranoside derivatives corresponding to **9a** and **9b** were oxidized by the same procedure[14].

The third route to compound **6b** proved very straightforward. Lipták *et al.*[15] noted the value of open-chain acetals of acetone in the carbohydrate field. Later on the formation of such compounds, including derivatives of galactosides, was investigated systematically by Catelani *et al.*[16]. Thus benzyl β-D-galactopyranoside (**1b**) on reaction with 2,2-dimethoxypropane with rigorous exclusion of moisture led to benzyl 3,4-*O*-isopropylidene-6-*O*-(2-methoxypropane-2-yl)-β-D-galactopyranoside (**10b**), which was acetylated at O-2 to yield **11b**. This, from our point of view, seemed to be an ideal substrate for oxidation by the standard procedure used in this work, and this proved to be correct. Subsequent methylation of the (non-isolated) oxidation product gave **6b** in excellent overall yield (83%). When applied to the corresponding allyl β-D-galactopyranoside (**1a**), problems were encountered that are still under investigation.

When compared with the overall yield obtained in the first route (39% of **6b** over seven steps) and in the second route (23% of **6a** and 24% of **6b** in five steps), this third route just presented is the method of choice to prepare the standardized intermediate **6b** for glycoside synthesis with galacturonic acid derivatives.




**10b, 11b**

In formulas **a**: $R^1 = CH_2{=}CHCH_2$
In formulas **b**: $R^1 = PhCH_2$
**10b**: $R^2 = H$, **11b**: $R^2 = Ac$

The $^{13}C$-n.m.r. spectra of **7b**, **8a**, **9a**, **5b**, and **6b** showed the presence of a *cis*-fused 1,3-dioxolane ring by the acetal carbon signal at 110.6 ± 0.5 p.p.m., a range in excellent accord with previous observations[17]. However, acetylation of **5b** and **8a** caused an unexpected upfield shift of the C-2 signal (73.6 and 73.8 p.p.m. to 72.3 and 73.3 p.p.m.,

respectively). In agreement with the β-shift effect of the 2-*O*-acetyl group, the signals of C-1 and C-3 appeared 1.8 ±0.1 p.p.m. upfield for **9a** and **6b** in comparison with the corresponding signals of **8a** and **5b**. It is reasonable to assume that the observed "inverse-α-shift-effect" of the 2-OAc group for **9a** and **6b** is attributable to the 3,4-fusion of the pyranose ring with the 1,3-dioxolane ring. The $^1$H-n.m.r. spectrum of **5b**, when interpreted in comparison with that of the corresponding derivative **4b**, indicates a distorted chair conformation, deformed towards a half-chair ($^1C_4 \rightarrow {}^3H_4$)[18]. Thus, the vicinal coupling constants within the pyranose ring exhibit significant differences between **4b** and **5b** to give 7.7 → 8.3 Hz ($J_{1,2}$), 9.9 → 7.3 Hz ($J_{2,3}$), 3.4 → 5.4 Hz ($J_{3,4}$), and 1.4 → 2.4 Hz ($J_{4,5}$). It seems possible that the acetylation to **6b** causes an additional change within the fused pyranose–dioxolane system of **5b**, resulting in an upfield shift of the C-2 signal, whereas a downfield shift was expected. Further investigation is necessary for verification of this hypothesis.

## EXPERIMENTAL

*General methods.* — Melting points were determined with Boetius micro apparatus BHMK05 (VEB Rapido, Dresden) and are corrected. Optical rotations were measured for solutions in a 1-dm cell with an automatic polarimeter "Polamat A" (VEB C.Zeiss, Jena). N.m.r. spectra were recorded at room temperature with a Bruker spectrometer model WM-250 at 250 MHz for $^1$H, and 62.89 MHz for $^{13}$C. Chemical shifts are given relative to the signal of internal tetramethylsilane. Key $^1$H resonances were assigned by selective homonuclear resonance, and $^{13}$C resonance by selective heteronuclear resonance. Thin-layer chromatography (t.l.c.) on precoated plates of silica gel (Merck, Prod. No. 5721) was performed with the following solvent-systems (v/v): ($A_1$) 1:1, ($A_2$) 2:1, ($A_3$) 3:1, and ($A_4$) 5:1 PhMe–EtOAc, (*B*) 3:1 EtOAc–2-propanol, ($C_1$) 1:1, ($C_2$) 3:1 PhMe–$Me_2CO$, (*D*) 1:1:1:0.1 PhMe–$Me_2CO$–2-propanol–$HCO_2H$, (*E*) 4:2:2:1 PhMe–EtOAc–EtOH–AcOH, ($F_1$) 6:1, ($F_2$) 10:1 $CHCl_3$–MeOH, (*G*) 1:1:0.1 PhMe–$Me_2CO$–EtOH. Detection was effected by spraying with a mixture of MeOH (40 mL), water (40 mL), conc. $H_2SO_4$ (20 mL), $H_2MoO_4$ (1 g), and $Ce(SO_4)_2$ (1 g). The spots were made visible by charring for 3–5 min at 150°. Preparative column chromatography was performed by gradient elution from columns of slurry-packed Silica Gel 60 (Merck No. 7754, 0.063–0.2 mm, or No. 9385, 0.040–0.063 mm). Dichloromethane, $CHCl_3$, PhMe, benzene, $Et_2O$, MeCN, allyl alcohol, pyridine and *sym*-collidine were dried by heating with $CaH_2$ under reflux and then distilled. Acetone was dried by $P_2O_5$ and then distilled from $KMnO_4$, and $Ac_2O$ was freshly distilled before use. Organic solutions were dried by filtration through cotton and then evaporated *in vacuo* at <40°.

*Allyl β-*D*-galactopyranoside* (**1a**). — A suspension of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide[5] (41.12 g, 0.1 mol), Drierite (100 g), $Hg(CN)_2$ (13.04 g, 52 mmol), and $HgBr_2$ (1.44 g, 4 mmol) in dry allyl alcohol (250 mL) was stirred for 7 h at ambient temperature (t.l.c., solvent $A_3$). The mixture was concentrated *in vacuo*, diluted with $CHCl_3$ (400 mL), and filtered. The filtrate was washed with aq. 10% KBr (3 × 150 mL) and water (2 × 150 mL), dried, and evaporated. The syrupy residue was dried *in*

*vacuo* to give allyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (35.70 g, 92%) not totally free of mercuric salts but pure enough for deacetylation. The syrup was dissolved in dry MeOH (200 mL) and treated with 0.5M methanolic NaOMe (4 mL). Within 2 h at ambient temperature, the reaction was complete (t.l.c., solvent *B*). The solution was made neutral with 0.05M methanolic AcOH (~ 40 mL), filtered, and evaporated. Addition of EtOH (4 mL) caused the residue to crystallize, giving the title compound (18.55 g, 84% overall yield), m.p. 100–101°, $[\alpha]_D^{20}$ −10.9° (*c* 0.9, $H_2O$); lit.[4], m.p. 102–103°, $[\alpha]_D^{25}$ −10.9° (*c* 3.4, $H_2O$).

*Benzyl β-D-galactopyranoside* (**1b**). — To a suspension of $PhCH_2OH$ (40 mL), Drierite (40 g), $Hg(CN)_2$ (25.78, 102 mmol), and $HgBr_2$ (3.60 g, 10 mmol) a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide[6] (41.12 g, 100 mmol) in dry MeCN (60 mL) was added during 1 h with stirring. Stirring was continued for 24 h (t.l.c., solvent $C_2$) at room temperature with the exclusion of atmospheric moisture. Chloroform (250 mL) was added, the mixture was filtered, the solids were washed with $CHCl_3$ (3 × 50 mL), and filtrate and washings were shaken with aq. KBr (3 × 150 mL) and water (2 × 150 mL). The organic phase was dried, evaporated, and the residue heated under high vacuum at 95° to remove the excess of $PhCH_2OH$ to give chromatographically homogeneous benzyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (38.84 g, 89%) as a syrup. The compound was dissolved in $CHCl_3$ (300 mL), and reconcentrated to a volume of ~70 mL. Dry MeOH (1 L) and MgO (100 g) were added and the suspension was stirred for 48 h at ambient temperature (t.l.c., solvent $C_2$). The MgO was centrifuged off and the resulting solution was evaporated to dryness. Crystallization from MeOH–$Et_2O$ gave the desired product **1b** (21.90 g, 81% overall yield), m.p. 103–104°, sufficiently pure for the next step. Recrystallization from MeOH–$Et_2O$ (twice) gave an analytical sample of **1b**, m.p. 125°, $[\alpha]_D^{20}$ −25.0° (*c* 1.0, $H_2O$); lit.[5] m.p. 125°, $[\alpha]_D^{27}$ −25.3° (*c* 1.2, $H_2O$).

*Allyl 2,3,4-tri-O-acetyl-6-O-trityl-β-D-galactopyranoside* (**2a**). — To a solution of **1a** (11.01 g, 50 mmol) and 4-dimethylaminopyridine (1.10 g, 9 mmol) in dry pyridine (85 mL) $Ph_3CCl$ (25.10 g, 90 mmol) was added. After stirring for 20 h at ambient temperature (t.l.c., solvent *D*), a mixture of $Ac_2O$ (80 mL) and pyridine (240 mL) was added, and the solution was stirred for another 20 h at room temperature (t.l.c., solvent $A_3$). The mixture was cooled to 0° and EtOH (30 mL) added dropwise to decompose the excess of $Ac_2O$. After 1 h the solution was poured into ice–water (1.5 L). The aqueous layer was extracted with $CHCl_3$ (3 × 100 mL), and heptane (600 mL) was added to the extract. The organic solution was washed succesively with ice–water (250 mL), cold aq. 15% $NaHSO_4$ (3 × 250 mL), ice–water (250 mL), cold aq. $NaHCO_3$ (3 × 250 mL) and water (2 × 250 mL), dried, and evaporated. The crude material was purified by column chromatography (EtOAc gradient 20% → 67% in heptane) to yield **2a** (21.9 g, 75%), m.p. 155° (from EtOAc–heptane), $[\alpha]_D^{20}$ −24.6° (*c* 0.94, $Me_2CO$); $^1$H-n.m.r.($CDCl_3$): δ 1.92, 2.01, 2.09 (3 s, 3 × 3 H, OAc), 3.11 (dd, 1 H, $J_{6,6'}$ 9.0 $J_{5,6'}$ 8.1 Hz, H-6'), 3.41 (dd, 1 H, $J_{6,6'}$ 9.0, $J_{5,6}$ 5.7 Hz, H-6), 3.82 (m, 1 H, H-5), 4.09 (m, 1 H, $OCH_2CH=CH_2$), 4.34 (m, 1 H, $OCH_2CH=CH_2$), 4.51 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 5.07 (dd, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 5.19 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2), 5.20, 5.30 (2 m, 1 H, $OCH_2CH=CH_2$), 5.58 (dd, 1 H, $J_{4,5}$ 1.0

Hz, H-4), 5.84 (m, 1 H, $OCH_2CH=CH_2$), and 7.3 (m, 15 H, Ph); $^{13}$C-n.m.r. ($CDCl_3$): $\delta$ 20.6, 20.7, 20.8 ($CH_3CO$), 61.0 (C-6), 67.5 (C-4), 69.3 (C-2), 70.0 ($OCH_2CH=CH_2$), 71.3 (C-3), 72.3 (C-5), 86.4 ($CPh_3$), 100.2 (C-1), 117.5 ($OCH_2CH=CH_2$), 127.3, 128.0, 128.7, 143.4 (Ph), 133.5 ($OCH_2CH=CH_2$), 169.5, 170.1, and 170.3 ($CH_3CO$).

*Anal.* Calc. for $C_{34}H_{36}O_9$ (588.7): C, 69.37; H, 6.16. Found: C, 69.50; H, 6.01.

*Benzyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-*D*-galactopyranoside* (**2b**). — Compound **1b** (13.52 g, 50 mmol) was processed as described for the synthesis of **2a** to furnish 22.35 g (70%) of **2b**; m.p. 68° (from EtOAc–heptane), $[\alpha]_D^{28}$ −60.5° (*c* 1.96, $CHCl_3$); $^1$H-n.m.r. ($CDCl_3$); $\delta$ 1.92, 2.00, 2.03 (3 s, 3 × 3 H, OAc), 3.14 (dd, 1 H, $J_{6,6'}$ 9.2 Hz, $J_{5,6'}$ 7.9 Hz, H-6'), 3.44 (dd, 1 H, $J_{6,6'}$ 9.2 Hz, $J_{5,6}$ 5.8 Hz, H-6), 3.80 (m, 1 H, H-5), 4.50 (d, $J_{1,2}$ 8.0 Hz, H-1), 4.63 (d, 1 H, *J* 12.5 Hz, $CH_2Ph$), 4.90 (d, 1 H, *J* 12.5 Hz, $CH_2Ph$), 5.04 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 5.24 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2), 5.56 (dd, 1 H, $J_{4,5}$ 1.0 Hz, H-4), 7.26, and 7.46 (2 m, 20 H, Ph);$^{13}$C-n.m.r. ($CDCl_3$): $\delta$ 20.6, 20.8 (3 C, $CH_3CO$), 61.0 (C-6), 67.5 (C-4), 69.2 (C-2), 70.6 ($CH_2Ph$), 71.2 (C-3), 72.3 (C-5), 86.9 ($CPh_3$), 99.7 (C-1), 127.3, 127.7, 128.0, 128.5, 128.7, 129.1, 136.9, 143.4 (Ph), 169.5, 170.1, and 170.3 ($CH_3CO$).

*Anal.* Calc. for $C_{38}H_{38}O_9$ (638.7): C, 71.46; H, 6.00. Found: C, 71.80; H, 6.22.

*Methyl (allyl 2,3,4-tri-*O*-acetyl-β-*D*-galactopyranosid)uronate* (**3a**). — To a solution of **2a** (2.94 g, 5 mmol) in $Me_2CO$ (16 mL) and $CH_2Cl_2$ (11 mL) was added dropwise, during 30 min, at ~0°, a solution of $CrO_3$ (2.50 g, 25 mmol) in 3.5M $H_2SO_4$ (10 mL). After an additional 30 min the chilling was terminated and the mixture stirred for 1.5 h (t.l.c., solvent *E*). Ethanol (20 mL) was then added at 0°, and, after 30 min, the solid separated was filtered off, thoroughly washed with $Me_2CO$, and the combined organic phases were concentrated to 100 mL. To the concentrate $NaHCO_3$ (4 g) was added in small portions, and the suspension evaporated. For esterification of the carboxylic group, the residue was partitioned between $CH_2Cl_2$ (30 mL) and water (20 mL), $Bu_4NBr$ (1.60 g) and MeI (2.60 mL) were added, and the suspension was stirred vigorously for 20 h at ambient temperature (t.l.c., solvent $A_2$). Water (30 mL) was then added, the phases were separated, and the aqueous phase was extracted with $CHCl_3$ (3 × 20 mL), dried, and evaporated. The syrupy residue was dissolved in a minimum of $CH_2Cl_2$, and $Et_2O$ was added, whereupon the ammonium salts precipitated. The filtrate was evaporated and processed by column chromatography (EtOAc gradient 9 → 12% in PhMe; t.l.c., solvent $A_4$) to yield 1.36 g (73%) of **3a**; m.p. 98–99° (from EtOAc–heptane), $[\alpha]_D^{20}$ 0° (*c* 1.0, $CHCl_3$); $^1$H-n.m.r. ($CDCl_3$): $\delta$ 2.02, 2.07, 2.13 (3 s, 3 × 3 H, OAc), 3.78 (s, 3 H, $CO_2Me$), 4.16 (m, 1 H, $OCH_2CH=CH_2$), 4.36 (d, 1 H, $J_{4,5}$ 1.3 Hz, H-5), 4.44 (m, 1 H, $OCH_2CH=CH_2$), 4.58 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.10 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 5.25 (m, 1 H, $OCH_2CH=CH_2$), 5.29 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2), 5.73 (dd, 1 H, $J_{4,5}$ 1.3 Hz, H-4), and 5.87 (m, 1 H, $OCH_2CH=CH_2$); $^{13}$C-n.m.r. ($CDCl_3$): $\delta$ 20.3, 20.5 (3 C, $CH_3CO$), 52.4 (OMe), 68.3 (C-4), 68.6 (C-2), 69.9 $OCH_2CH=CH_2$), 70.6 (C-3), 72.3 (C-5), 99.9 (C-1), 117.4, 133.3 $OCH_2CH=CH_2$), 166.3 (C-6), 169.0, 169.6, and 169.7 ($CH_3CO$).

*Anal.* Calc. for $C_{16}H_{22}O_{10}$ (374.4): C, 51.34; H, 5.92. Found: C, 51.56; H, 6.20.

*Methyl (benzyl 2,3,4-tri-*O*-acetyl-β-*D*-galactopyranosid)uronate* (**3b**). — The galactoside **2b** (3.19 g, 5 mmol) was processed as already described to yield **3b** (1.37 g, 65%), m.p. 108–110° (from EtOAc–heptane), $[\alpha]_D^{27}$ −32.3° (c 1.04, $CHCl_3$); lit.[8], m.p.

108.5–109.5°, $[\alpha]_D^{20}$ −12° (*c* 0.5, MeOH); $^1$H-n.m.r. ($CDCl_3$): δ 1.94, 1.97, 2.08 (3 s, 3 × 3H, OAc), 3.73 (s, 3 H, $CO_2Me$), 4.30 (d, 1 H, $J_{4,5}$ 1.4 Hz, H-5), 4.53 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.63, 4.95 (dd, 2 H, *J* 12.3 Hz, $CH_2Ph$), 5.01 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 5.29 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2), 5.67 (dd, 1 H, $J_{4,5}$ 1.4 Hz, H-4), and 7.28 (m, 5 H, Ph); $^{13}$C-n.m.r. ($CDCl_3$): δ 20.4, 20.5 (3 C, $CH_3CO$), 52.5 (OMe), 68.2 (C-4), 68.4 (C-2), 70.4 (C-3), 70.6 ($CH_2Ph$), 72.2 (C-5), 99.4 (C-1), 127.6, 127.8, 128.2, 136.6 (Ph), 166.4 (C-6), 169.0, 169.6, and 169.8 (3 C, $CH_3CO$).

*Anal.* Calc. for $C_{20}H_{22}O_{10}$ (422.4): C, 56.87; H, 5.25. Found: C, 56.75; H, 5.30.

*Methyl (allyl β-*D*-galactopyranosid)uronate* (**4a**). — To methanolic 1% HCl (prepared by adding of 7.3 mL of AcCl to 360 mL of ice-cold dry MeOH) was added **3a** (3.74 g, 10 mmol) with stirring and the mixture kept for 24 h at ambient temperature (t.l.c., solvent $F_1$). The solution was made neutral by addition of $Pb(CO_3)_2 \cdot Pb(OH)_2$ (30 g). After stirring for 2 h, the lead salts were centrifuged off, washed with MeOH, and the filtrate and washings were combined and concentrated. The residue was applied to a column of silica gel (10:1 $CHCl_3$–MeOH) to give **4a** (2.22 g, 90%) as a syrup, $[\alpha]_D^{22}$ −62.9° (*c* 1.0, $Me_2CO$).

*Anal.* Calc. for $C_{10}H_{16}O_7$ (246.2); C, 48.78; H, 6.55. Found: C, 48.65; H, 6.70.

*Methyl (benzyl β-*D*-galactopyranosid)uronate* (**4b**). — Compound **3b** (4.22 g, 10 mmol) was deacetylated as described for the synthesis of **4a** to furnish **4b** (2.77 g, 93%), m.p. 166° (from EtOAc–heptane), $[\alpha]_D^{28}$ −66.1° (*c* 1.5, MeOH), lit.[8], m.p. 167–168°, $[\alpha]_D^{20}$ −71° (*c* 0.5, MeOH); $^1$H-n.m.r. ($CDCl_3$ + $D_2O$): δ 3.48 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 3.57 (dd, 1 H, $J_{4,5}$ 1.4 Hz, H-4), 3.57 (dd, 1 H, $J_{2,3}$ 9.9Hz, H-2), 3.75 (s, 3 H, OMe), 4.03 (d, 1 H, H-5), 4.24 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.57, 4.91 (dd, 2 H, *J* 11.8 Hz, $CH_2Ph$), and 7.3 (m, 5 H, Ph); $^{13}$C-n.m.r. ($CDCl_3$ + $D_2O$ + $CD_3OD$): δ 52.2 (OMe), 69.7 (C-4), 70.5 (C-2); 71.0 ($CH_2Ph$), 72.8 (C-3), 74.1 (C-5), 101.8 (C-1), 127.8, 128.1, 128.2, 136.9 (Ph), and 168.8 (C-6).

*Anal.* Calc. for $C_{14}H_{18}O_7$ (298.3): C, 56.37; H, 6.08. Found: C, 56.10; H, 6.20.

*Methyl (benzyl 3,4-*O*-isopropylidene-β-*D*-galactopyranosid)uronate* (**5b**). — To a suspension of **4b** (2.98 g, 10 mmol) in dry $Me_2CO$ (80 mL) and 2,2-dimethoxypropane (20 mL), was added TsOH (400 mg), and the mixture was stirred for 24 h at ambient temperature (t.l.c., solvent $F_2$). The mixture was then passed through a layer of alkaline aluminia (2 × 3 cm), the eluate evaporated, and the residue was crystallized from EtOAc–heptane to give **5b** (3.25 g, 96%), m.p. 119°, $[\alpha]_D^{20}$ −46.2° (*c* 1.03, $CHCl_3$); lit.[8], m.p. 116.5–117.5°, $[\alpha]_D^{20}$ −36° (*c* 0.56, MeOH); $^1$H-n.m.r. ($CDCl_3$ + $D_2O$): δ 1.35, 1.52 (2 s, 2 × 3 H, $Me_2C$), 3.68 (dd, 1 H, $J_{2,3}$ 7.3 Hz, H-2), 3.87 (s, 3 H, OMe), 4.12 (dd, 1 H, $J_{3,4}$ 5.4 Hz, H-3), 4.28 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1), 4.39 (d, 1 H, $J_{4,5}$ 2.5 Hz, H-5), 4.46 (dd, 1 H, H-4), 4.61, 5.01 (dd, 2 H, *J* 11.8 Hz, $CH_2Ph$), and 7.35 (m, 5 H, Ph); $^{13}$C-n.m.r. ($CDCl_3$): δ 26.3, 28.0 (2 C, $Me_2C$), 52.6 (OMe), 71.0 ($CH_2Ph$), 72.4 (C-5), 73.0 (C-4), 73.6 (C-2), 78.5 (C-3), 100.9 (C-1), 110.7 ($Me_2C$), 128.1, 128.3, 128.6, 136.7 (Ph), and 167.5 (C-6).

*Anal.* Calc. for $C_{17}H_{22}O_7$ (338.4): C, 60.35; H, 6.55. Found: C, 60.60; H, 6.81.

*Methyl (benzyl 2-*O*-acetyl-3,4-*O*-isopropylidene-β-*D*-galactopyranosid)uronate* (**6b**). — A solution of **5b** (3.38 g, 10 mmol) in dry pyridine (40 mL) was treated with $Ac_2O$ (20 mL) at 0° and kept for 24 h at this temperature (t.l.c., solvent $A_3$). Ethanol (10 mL)

was added dropwise at 0°. After 30 min the mixture was diluted with $CHCl_3$ (200 mL), and the organic layer was successively washed with ice–water (70 mL), cold aq. 15% $NaHSO_4$ (2 × 70 mL), ice–water (70 mL), cold aq. $NaHCO_3$ (2 × 70 mL), ice–water (70 mL), dried, and evaporated to give **6b** (3.7 g, 97%); m.p. 130–132° (from EtOAc–heptane), $[\alpha]_D^{20}$ −47.7° (*c* 0.92, $CHCl_3$).

*Anal.* Calc. for $C_{19}H_{24}O_8$ (380.4): C, 59.99; H, 6.36. Found: C, 60.21; H, 6.60.

*Allyl 3,4-O-isopropylidene-β-D-galactopyranoside* (**7a**). — To a stirred solution of **1a** (22.02 g, 100 mmol) in 2,2-dimethoxypropane (52 g, 500 mmol) was added TsOH (500 mg) at ambient temperature. The mixture was stirred for 24 h (t.l.c., solvent *G*), made neutral by addition of $NaHCO_3$ (1.0 g), filtered through Celite and evaporated. The residue was purified by column chromatography (1:1 PhMe–EtOAc) to give **7a** (18.22 g, 70%), m.p. 93–95° (from EtOAc–heptane), $[\alpha]_D^{20}$ +1.8° (*c* 1.0, $Me_2CO$); lit.[9] m.p. 91–92°, $[\alpha]_D^{22}$ +10° (*c* 2.0, $CHCl_3$).

*Anal.* Calc. for $C_{12}H_{20}O_6$ (260.3): C, 55.37; H, 7.74. Found: C, 55.60; H, 8.10.

*Benzyl 3,4-O-isopropylidene-β-D-galactopyranoside* (**7b**). — Compound **1b** (27.03 g, 100 mmol) was treated exactly as described for the preparation of **7a** to yield **7b** (21.11 g, 68%), m.p. 118–119° (from EtOAc–heptane), $[\alpha]_D^{23}$ −7.1° (*c* 1.0, $CHCl_3$), lit.[5] m.p. 113–115°, $[\alpha]_D^{25}$ −1.47° (*c* 1.12, $CHCl_3$); $^1$H-n.m.r. ($CDCl_3$): δ 1.35, 1.53 (2 s, 2 × 3 H, $Me_2C$), 2.23 (dd, 1 H, $J_{OH,6} = J_{OH,6'}$ 3.5 Hz, OH-6), 2.70 (d, 1 H, $J_{OH,2}$ 2.5 Hz, OH-2), 3.61 (m, 1 H, $J_{2,3}$ 6.9 Hz, $J_{2,OH}$ 2.5 Hz, H-2), 3.83 (m, 1 H, $J_{5,6'}$ 10.4, $J_{6,6'}$ 12.4 Hz, H-6'), 3.83 (m, 1 H, $J_{5,6}$ 8.3 Hz, H-5), 3.98 (m, 1 H, H-6), 4.08 (dd, 1 H, $J_{3,4}$ 5.5 Hz, H-3), 4.13 (dd, 1 H, $J_{4,5}$ 1.8 Hz, H-4), 4.28 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.65, 4.92 (dd, 2 H, *J* 11.9 Hz, $CH_2Ph$), and 7.37 (m, 5 H, Ph); $^{13}$C-n.m.r. ($CDCl_3$): δ 26.3, 28.1 [$C(CH_3)_2$], 62.3 (C-6), 71.2 ($CH_2Ph$), 73.6 (C-2, C-5), 73.9 (C-4), 79.0 (C-3), 101.4 (C-1), 110.4 [$C(CH_3)_2$], 128.1, 128.3, 128.5, and 137.0 (Ph).

*Anal.* Calc. for $C_{16}H_{22}O_6$ (310.4): C, 61.92; H, 7.15. Found: C, 62.18; H, 7,31.

*Allyl 3,4-O-isopropylidene-6-O-(4,4'-dimethoxytrityl)-β-D-galactopyranoside* (**8a**). — To a stirred solution of **7a** (2.60 g, 10 mmol) in dry pyridine (40 mL) *sym*-collidine (4 mL) and bis(4-methoxyphenyl)chlorophenylmethan (6.10 g, 18 mmol) were added. Stirring was continued for 10 h at ambient temperature (t.l.c., solvent $A_3$). The mixture was then diluted with EtOAc (200 mL), filtered, concentrated to 1/3 volume, and 5:1 PhMe–EtOH (3 × 20 mL) was evaporated from the solution. The syrup obtained was purified by column chromatography (5:1 PhMe–EtOAc), to give syrupy **8a** (5.39 g, 95%), $[\alpha]_D^{20}$ −16.3° (*c* 1.0, $Me_2CO$); $^1$H-n.m.r. ($CDCl_3$): δ 1.37, 1.50 (2 s, 2 × 3 H, $Me_2C$), 3.46 (m, 2 H, $J_{6,6'}$ 9.1 Hz, H-6, H-6'), 3.59 (t, 1 H, $J_{2,3}$ 7.3 Hz, H-2), 3.79 (s, 6 H, 2 × OMe), 3.83 (m, 1 H, $J_{5,6}$ $J_{5,6'}$ = 6.1 Hz, H-5), 4.08 (dd, 1 H, $J_{3,4}$ 5.4 Hz, H-3), 4.16 (m, 1 H, $OCH_2CH=CH_2$), 4.23 (dd, 1 H, $J_{4,5}$ 2.0 Hz, H-4), 4.23 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.39 (m, 1 H, $OCH_2CH=CH_2$), 5.22, 5.32, 5.90 (3, m, 3 H, $OCH_2CH=CH_2$), and 6.84–7.50 (m, 13 H, Ph); $^{13}$C-n.m.r. ($CDCl_3$): δ 26.4, 28.2 [$C(CH_3)_2$], 55.3 (2 × OMe), 62.7 (C-6), 70.0 ($OCH_2CH=CH_2$), 72.7 (C-5), 73.8 (C-2), 73.9 (C-4), 79.0 (C-3), 86.3 ($CPh_3$), 101.4 (C-1), 110.1 [$C(CH_3)_2$], 113.2 (Ph), 118.0 ($OCH_2CH=CH_2$), 126.8, 127.8, 128.3, 129.2, 130.2 (Ph), 133.9 ($OCH_2CH=CH_2$), 136.3, 145.1, and 158.6 (Ph).

*Anal.* Calc. for $C_{33}H_{38}O_8$ (567.7): C, 70.44; H, 6.81. Found: C, 70.71; H, 7.02.

*Benzyl 3,4-O-isopropylidene-6-O-(4,4'-dimethoxytrityl)-β-D-galactopyranoside* (**8b**). — Processing of **7b** (3.10 g, 10 mmol) exactly as described for the preparation of **8a** afforded **8b** (5.63 g, 92%) as a syrup, $[\alpha]_D^{22}$ −26.1° (*c* 1.0, $CHCl_3$); $^{13}$C-n.m.r. ($CDCl_3$): δ 26.3, 28.1 [$C(CH_3)_2$], 55.2 (2 × OMe), 62.7 (C-6), 70.6 ($CH_2Ph$), 72.8 (C-5), 73.9 (C-2, C-4), 78.8 (C-3), 86.1 ($CPh_3$), 101.0 (C-1), 110.1 [$C(CH_3)_2$], 113.2, 126.8, 127.8, 128.1, 128.4, 128.5, 130.2, 136.2, 137.0, 145.0, and 158.5 (Ph).

*Anal.* Calc. for $C_{37}H_{20}O_8$ (612.7): C, 72.53; H, 6.58. Found: C, 72.73; H, 6.85.

*Allyl 2-O-acetyl-3,4-O-isopropylidene-6-O-(4,4'-dimethoxytrityl)-β-D-galactopyranoside* (**9a**). — To a stirred solution of **8a** (5.68 g, 10 mmol) in dry pyridine (30 mL) $Ac_2O$ (10 mL) was added at 0°. The mixture was kept for 5 h at room temperature (t.l.c., solvent $A_3$), then again cooled to 0°, and EtOH (4 mL) was added dropwise. After 30 min, the mixture was diluted with $CHCl_3$ (60 mL) and poured into ice-cold aq. $NaHCO_3$ (300 mL). The aqueous layer was extracted with $CHCl_3$ (2 × 70 mL), and the combined organic phases were washed with ice-cold aq. $NaHCO_3$ (2 × 100 mL), water (2 × 100 mL), dried, and evaporated. The residue was chromatographed 10:1 PhMe–EtOAc, containing 1% pyridine) to give **9a** (5.93 g, 98%) as syrup, $[\alpha]_D^{20}$ −18.9° (*c* 1.0, $Me_2CO$); $^1$H-n.m.r. ($CDCl_3$): δ 1.37, 1.56 (2 s, 2 × 3 H, $Me_2C$), 2.13 (s, 3 H, OAc), 3.42 (dd, 1 H, $J_{6,6'}$ 9.2 Hz, $J_{5,6'}$ 6.0 Hz, H-6'), 3.52 (dd, 1H, $J_{5,6}$ 6.4 Hz, H-6), 3.81 (s, 6 H, 2 × OMe), 3.83 (m, 1 H, H-5), 4.13 (m, 1 H, $OCH_2CH=CH_2$), 4.17 (dd, 1 H, $J_{3,4}$ 5.1 Hz, H-3), 4.24 (dd, 1 H, $J_{4,5}$ 1.8 Hz, H-4), 4.35 (m, 1 H, $OCH_2CH=CH_2$), 4.38 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 5.03 (dd, 1 H, $J_{2,3}$ 7.2 Hz, H-2), 5.20, 5.30, 5.90 (3 m, 3 H, $OCH_2CH=CH_2$), and 6.86–7.50 (m, 13 H, Ph); $^{13}$C-n.m.r. ($CDCl_3$): δ 21.0 ($CH_3CO$), 26.5, 27.8 [$C(CH_3)_2$], 55.3 (2 × OMe), 62.7 (C-6), 69.4 ($OCH_2CH=CH_2$), 72.6 (C-5), 73.3 (C-2), 74.1 (C-4), 77.3 (C-3), 86.4 ($CPh_3$), 99.5 (C-1), 110.5 [$C(CH_3)_2$], 113.3 (Ph), 117.2 ($OCH_2CH=CH_2$), 126.9, 127.9, 128.4, 129.3, 130.3 (Ph), 134.0 ($OCH_2CH=CH_2$), 136.3, 145.1, 158.7 (Ph), and 169.6 ($CH_3CO$).

*Anal.* Calc. for $C_{35}H_{40}O_9$ (604.7): C, 69.52; H, 6.67. Found: C, 69.30; H, 6.91.

*Benzyl 2-O-acetyl-3,4-O-isopropylidene-6-O-(4,4'-dimethoxytrityl)-β-D-galactopyranoside* (**9b**). — Processing of **8b** (6.13 g, 10 mmol) as described above yielded **9b** (6.22 g, 95%) as a syrup, $[\alpha]_D^{22}$ −24.4° (*c* 1.1, $CHCl_3$).

*Anal.* Calc. for $C_{39}H_{42}O_9$ (654.77): C, 71.54; H, 6.47. Found: C, 71.81; H, 6.56.

Methyl *(allyl 2-O-acetyl-3,4-O-isopropylidene-β-D-galactopyranosid)uronate* (**6a**). — A solution of **9a** (3.03 g, 5 mmol) in $Me_2CO$ (30 mL) and $CH_2Cl_2$ (20 mL) was treated with a solution of $CrO_3$ (1.10 g, 11 mmol) in 3.5M $H_2SO_4$ (5 mL) as described for the preparation of **3a**. After processing, the crude product was purified by column chromatography (EtOAc gradient 9 → 17% in PhMe) to yield **6a** (0.58 g, 35%), m.p. 98–101° (from EtOAc–heptane), $[\alpha]_D^{20}$ −21.3 (*c* 1.0, $Me_2CO$); $^1$H-n.m.r. ($CDCl_3$): δ 1.33, 1.56 (2s, 3 × 3H, $Me_2C$), 2.10 (s, 3H, OAc), 3.85 (s, 3H, $CO_2Me$), 4.09 (m, 1H, $OCH_2CH=CH_2$), 4.24 (dd, 1H, $J_{3,4}$ 5.4 Hz, H-3), 4.39 (m, 1 H, $OCH_2CH=CH_2$), 4.41 (d, 1 H, $J_{4,5}$ 2.4 Hz, H-5), 4.46 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.49 (dd, 1 H, H-4), 5.06 (t, 1 H, $J_{2,3}$ 6.9 Hz, H-2), 5.18, 5.29, and 5.84 (3 m, 3 H, $OCH_2CH=CH_2$); $^{13}$C-n.m.r ($CDCl_3$): δ 20.9 ($CH_3CO$), 26.3, 27.4 [$C(CH_3)_2$], 52.5 (OMe), 69.7 ($OCH_2CH=CH_2$), 72.2 (C-5), 72.3 (C-2), 73.9 (C-4), 76.7 (C-3), 99.3 (C-1), 111.1 [$C(CH_3)_2$], 117.4, 133.7 ($OCH_2CH=CH_2$), 167.4 (C-6), and 169.4 ($CH_3CO$).

*Anal.* Calc. for $C_{15}H_{22}O_8$ (330.3): C, 54.54; H, 6.71. Found: C, 54.31; H, 6.93.

*Methyl (benzyl 2-O-acetyl-3,4-O-isopropylidene-β-D-galactopyranosid)uronate* (**6b**). — *A. via* **9b**. The benzyl galactoside derivative **9b** (3.27 g, 5 mmol) was oxidized and subsequently esterificated as described for the synthesis of **6a** from **9a** to yield **6b** (0.75 g, 40%).

*B. via non isolated* **11b**. To an anhydrous solution of TsOH (42 mg, 0.22 mmol) in 2.2-dimethoxypropane (50 mL) was added **1b** (1.3 g, 5 mmol), and the mixture was stirred in an argon atmosphere for 48 h at room temperature, with the exclusion of atmospheric moisture. The completion of the reaction was monitored by t.l.c. (solvent $C_1$ with addition of 1% $Et_3N$). After adding $Et_3N$ (0.3 mL), the mixture was evaporated and the resulting residue dissolved in an ice-cold solution of dry pyridine (25 mL) and $Ac_2O$ (5 mL). After 24 h at 5°, EtOH was added dropwise, and, after 30 min, the mixture was poured into ice-cold aq. $NaHCO_3$ (100 mL) and extracted with $CHCl_3$ (2 × 60 mL). The organic layer was washed with ice-cold aq. $NaHCO_3$ (2 × 40 mL), ice–water (2 × 40 mL), dried, and evaporated with repeated addition of PhMe. The residue (crude **11b**) was dissolved in $Me_2CO$ (30 mL) and $CH_2Cl_2$ (20 mL), and oxidized, esterified and processed as described for the preparation of **6a** from **9a** to afford **6b** (1.58 g, 83%).

The physical parameters of **6b**, prepared *via* **9b** and **11b**, respectively, were fully consistent with those of the product obtained by acetylation of **5b** (see foregoing).

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