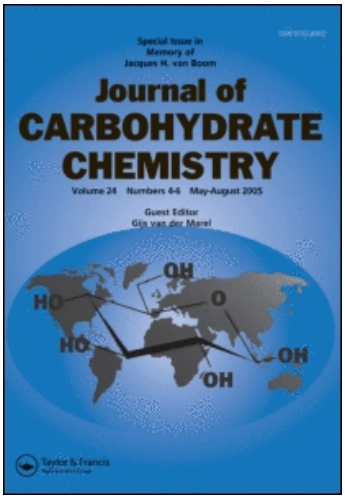

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Thomas Ziegler[a]; Guido Pantkowski[a]
[a] Institute of Organic Chemistry, University of Stuttgart Pfaffenwaldring 55, Stuttgart, Germany

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PREPARATION OF 1-*O*-ACYL-D-GLYCOPYRANOSES *VIA* CHLOROACETYLATED GLYCOPYRANOSYL DONORS

Thomas Ziegler * and Guido Pantkowski

Institute of Organic Chemistry, University of Stuttgart
Pfaffenwaldring 55, D-W-7000 Stuttgart 80, Germany

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ABSTRACT

Various 2,3,4,6-tetra-*O*-chloroacetyl-D-glucopyranosyl donors **2** were coupled to cinnamic acid (**3a**) and silver cinnamate (**4a**) to give the corresponding chloroacetylated 1-*O*-cinnamoyl-glucopyranose **5a** in good yields. The highest α-selectivity (α/β = 87:13) was achieved by coupling of the α-fluoride **2c** with **3a** under boron trifluoride catalysis whereas the α-bromide **2g** afforded exclusively **β-5a** upon treatment with **4a**. Thus, the D-glucosyl donors **2c** and **2g** and 2,3,4,6-tetra-*O*-chloroacetyl-α-D-galactopyranosyl bromide (**6**) were condensed with a series of acids **3a-e** (cinnamic, 2-methyl-4-pentenoic, 3,4,5-trimethoxybenzoic, oleic, and 4-chloroacetoxy cinnamic acid, respectively) and silver salts **4a-d** thereof. From α/β-mixtures **5a-c** and **5e** obtained from **2c** and the respective acid **3**, the α-products were isolated in moderate yield. Selected examples of thus prepared 1-*O*-acyl-D-glucoses **5** and D-galactoses **7** were dechloroacetylated using 1-piperidinethiocarbamide to give the corresponding unblocked 1-*O*-acyl monosaccharides **8** and **9** in 52-64% yield.

INTRODUCTION

Recently, we applied easily accessible fully chloroacetylated D-glycopyranosyl bromides for the convenient preparation of some base and hydrogenolysis-sensitive D-glycosides.[1] The use of chloroacetyl groups for the temporary protection of these derivatives is promising because dechloroacetylation can be done under essentially neutral

conditions,[1,2] leaving labile aglycons intact. Especially for the preparation of the title compounds this synthetic approach *via* chloroacetylated glycosyl halides appeared particularly useful. Since 1-*O*-acyl-D-glycopyranoses are widespread naturally occurring sugars (for example tannins) that also embrace derivatives with significant physiological properties,[3] several methods have been developed so far for their preparation. Most notably, 1-*O*-acyl-glycoses were prepared by regioselective acylation of the anomeric position of unprotected mono and disaccharides.[4,5] Other, less generally applicable, methods used partially trifluoroacetyl[6] and triethylsilyl[7] protected derivatives, respectively for the introduction of an acyl substituent at the anomeric position and the following hydrolytic deblocking. A gibberellin-β-D-glucosyl ester was obtained by enzymatic saponification of its synthetic peracetylated precursor, however, in poor yield and thus, seemed not to be generally suitable for preparative purposes. Recently, 2,3,4,6-tetra-*O*-chloroacetyl-D-glycopyranoses have been esterified at the anomeric hydroxyl by a Mitsunobu protocol followed by dechloroacetylation to give the corresponding 1-*O*-acyl derivatives,[8] however, with rather low α/β-selectivity. We have extended our previous approach *via* chloroacetylated glycopyranosyl halides for the preparation of various 1-*O*-acyl glycoses, since we expected this method to provide the title compounds with high diastereoselectivity.

RESULTS AND DISCUSSION

In order to determine the stereoselectivity of the formation of 1-*O*-acyl glycopyranoses, various 2,3,4,6-tetra-*O*-chloroacetyl-D-glycopyranosyl donors **2** and **6** were prepared as follows, and were tested in reactions with cinnamic acid **3a** and the silver salt **4a** thereof. The donors **2a-c** were obtained by chloroacetylation of the corresponding glucosides **1a-c** using chloroacetic anhydride.[1,9] The trichloroacetimidate **2f** was prepared *via* accordingly synthesized[1,10] benzyl 2,3,4,6-tetra-*O*-chloroacetyl-β-D-glucopyranoside (**2d**), hydrogenolysis of which afforded first 2,3,4,6-tetra-*O*-chloroacetyl-D-glucopyranose (**2e**). The latter compound, also conveniently available[8] by treatment of 1,2,3,4,6-penta-*O*-chloroacetyl-α-D-glucopyranose[1,8] with hydrazine acetate, afforded the trichloroacetimidate **2f** upon reaction with trichloroacetonitrile. The bromides **2g** and **6** were prepared as described previously.[1] Table 1 summarizes the results of the condensation of the donors **2** with cinnamic acid **3a** (for **2a-c** and **2f**) and its silver salt **4a** (for **2g** and **6**), respectively. In all cases, the previous finding[1,11] that chloroacetyl groups present in glycosyl donors decrease their reactivity towards nucleophiles was also evident here. For example, all chloroacetylated donors **2** needed several hours at room temperature in order to give a complete reaction. The phenyl 1-thio-D-glucoside (**2a**) did not react at all. Only

Table 1. Reaction of various 2,3,4,6-tetra-*O*-chloroacetyl-D-glycopyranosyl donors **2** and **6** with cinnamic acid **3a** and the silver salt **4a** thereof at room temperature.

2	3,4	conditions[a]	yield	product	α/β-ratio[b]
2a	**3a**	NIS, 10 mol-% TfOH, 3 d	traces	**5a**	-
2b	**3a**	NIS, 10 mol-% TfOH, 2 h	77%	**5a**	30:70
2c	**3a**	5 equiv. BF_3OEt_2, 32 h	58%	**5a**	81:19[c]
2f	**3a**	10 mol-%, TMSOTf, 1.5 h	75%	**5a**	8:92
2g	**4a**	CH_2Cl_2, 30 h	71%	**5a**	0:100
6	**4a**	CH_2Cl_2, 30 h	70%	**7a**	0:100

a. NIS: *N*-iodosuccinimide, TfOH: trifluoromethanesulfonic acid, TMSOTf: trimethylsilyl trifluoromethanesulfonate. b. Determined by ^1H NMR. c. **α-5a** was isolated from the mixture in 39% yield.

traces of product **5a** could be detected on TLC. Aryl 1-thio-glycosides are usually less reactive under thiophilic activation than alkyl 1-thio-glycosides. However, phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside does react well with nucleophiles when activated with NIS/TfOH.[12] Obviously, the chloroacetyl groups present in **2a** deactivated this donor to such an extent that no reaction with **3a** occurred, whereas **2b** was reactive enough to give **5a** in a good yield. Even the imidate **2f** showed a low reactivity although imidates are usually rather reactive donors. Nevertheless, yields of chloroacetylated 1-*O*-acyl-D-glycosides **5a** and **7a** were good when prolonged reaction times were applied.

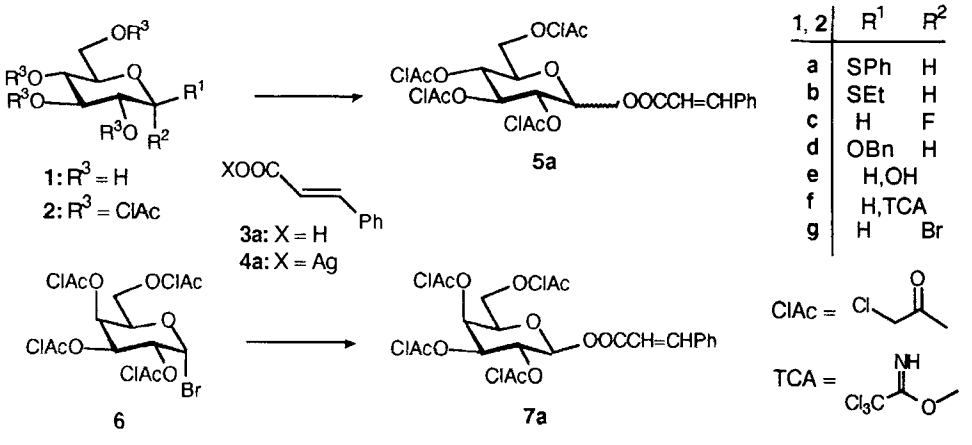
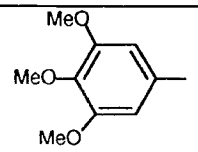
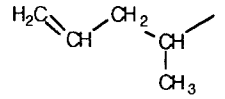
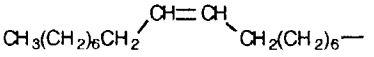
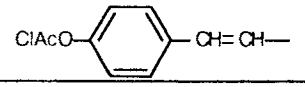


Table 2. Reaction of 2,3,4,6-tetra-*O*-chloroacetyl-α-D-glycopyranosyl halides **2c**, **2g**, and **6** with various carboxylic acids **3** and silver salts **4** thereof.

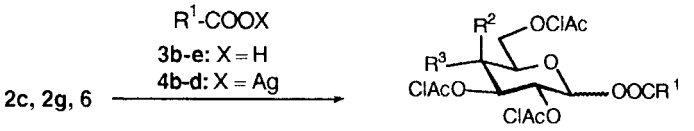
2,6	3,4	R^1	yield	product	α/β-ratio[a]
2c	**3b**		52%	**5b**	90:10[b]
2g	**4b**		64%	**5b**	0:100
6	**4b**		56%	**7b**	0:100
2c	**3c**		60%	**5c**	72:28[b]
2g	**4c**		70%	**5c**	0:100
6	**4c**		55%	**7c**	0:100
2c	**4d**		[c]	**5d**	[c]
2g	**4d**		75%	**5d**	0:100
6	**4d**		69%	**7d**	0:100
2c	**3e**		51%	**5e**	77:23[b]

a. Determined by ^{1}H NMR. b. From anomeric mixtures **α-5** was isolated in the following yields: **α-5b** (36%), **α-5c** (34%), **α-5e** (27%). c. Decomposition of compound **4d**.

The stereoselective outcome of the condensation depended strongly on the particular donor and the promotor used for its activation. The heterogenous reactions of the bromides **2g** and **6** with silver cinnamate **4a** in dichloromethane resulted expectedly[1] in the exclusive formation of the chloroacetylated 1-*O*-cinnamoyl-β-D-glycopyranoses **5a** and **7a**, respectively. Other solvents were not suitable because reaction of the chloroacetyl groups can occur.[1] In contrast, under homogenous conditions (*i.e.*, in reactions where the free acid **3a** was applied) a significant amount of the α-anomer of **5a** was formed. Since these condensations were performed under acidic and rather thermodynamic conditions due to the relatively long reaction times it is likely that the β-anomers were formed initially[1] with subsequent anomerisation to give the corresponding α-anomers. For preparative purposes, however, a high α/β-ratio was desirable because chromatographic separation of the anomers was difficult and a low β-content faciliated the purification of the α-anomers. The content of the α-anomer and of the yield of **5a** could not be increased by using other solvents or other Lewis acids (no further details). Therefore, we applied the glucosyl fluoride **2c** under BF_3-catalysis and the bromides **2g** and **6** in dichloromethane for further preparations of chloroacetylated 1-*O*-acyl-D-glycopyranoses (Table 2).

Table 3. Deblocking of selected 1-*O*-acyl-2,3,4,6-tetra-*O*-chloroacetyl-D-glycopyranoses **5** and **7** with 1-piperidinylthiocarbamide.

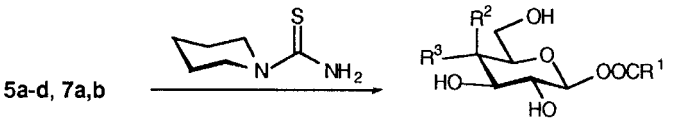
5, 7	β-5a	β-5b	β-5c	β-5d	β-7a	β-7b
yield	58%	61%	56%	52%	64%	55%
product	**8a**	**8b**	**8c**	**8d**	**9a**	**9b**



5b-e: R^2 = H, R^3 = ClAcO
7b,c: R^2 = ClAcO, R^3 = H

for the meaning of R^1 see Table 2.

For the dechloroacetylation of sugar derivatives thiourea[1,10] and hydrazinedithiocarbonate[1,2,8] are usually applied. However, since we previously encountered some problems when using these reagents for the deblocking of fully chloroacetylated glycosides, due to difficulties in removing excess of deblocking reagent,[1] we here tested several *N*,*N*-dialkyl thiourea derivatives for the final preparation of 1-*O*-acyl-glycopyranoses. It turned out that best results with respect to yield and ease of purification of the deblocked compounds were obtained with 1-piperidinethiocarbamide.[13] The latter thiourea derivative has been successfully applied for the high-yielding removal of *N*-chloroacetyl protective groups in amino acids.[14] Table 3 shows some representative results for the dechloroacetylation of selected derivatives **5** and **7** to give the title compounds **8** and **9** in moderate to good yield. A particular advantage of 1-piperidinethiocarbamide was that the reagent and the pseudothiohydantoin formed from the latter and the chloroacetic esters could be conveniently removed by a single chromatography.



8a-d: R^2 = H, R^3 = OH
9a,b: R^2 = OH, R^3 = H

for the meaning of R^1 see Table 2.

EXPERIMENTAL

General Methods. NMR data were extracted from spectra measured in solutions of $CDCl_3$ for blocked compounds and of CD_3OD for deblocked compounds (with TMS as an internal standard) at 25 °C with a Bruker AC 250F spectrometer. Proton-signal assignments were made by first order analysis of the spectra. Of the two magnetically non-equivalent geminal protons at C-6 of the monosaccharides, the one resonating at lower field was donated H6a and the one resonating at higher field was donated H6b. Carbon-signal assignments were made by mutual comparison of the spectra and by comparison with spectra of related compounds.[1,8,10] Optical rotations were measured at 25 °C with a Perkin-Elmer automatic polarimeter, Model 241. Melting points were measured with a Büchi apparatus, Model SMP-20. Thin-layer chromatography (TLC) was performed on precoated plastic sheets, Polygram SIL UV_{254}, 40 x 80 mm (Macherey-Nagel) using appropriately adjusted mixtures of carbon tetrachloride-acetone, dichloromethane-methanol and toluene-acetone, respectively for the developing. Detection was effected with UV light, where applicable, by iodine, and by charring with 5% sulfuric acid in ethanol. Preparative chromatography was performed by elution from columns of Silica Gel 60 (Merck) using solvent mixture *A*, carbon tetrachloride-acetone and *B*, dichloromethane-methanol. For the chromatography of the deblocked compds **8** and **9** the silica gel was successively prewashed with water, methanol, acetone and *n*-hexane and dried at 120 °C. Solutions in organic solvents were dried with anhydrous sodium sulfate, and concentrated at 2 kPa, ≤40 °C. Silver salts **4a-d**, were prepared by adding an equimolar amount of aqueous silver nitrate solution to a solution of the corresponding acids **3a-d** and an equimolar amount of sodium hydroxide in water. The precipitated silver salts were collected by filtration, washed with ice-cold water and dried in *vacuo*.

Phenyl 2,3,4,6-Tetra-*O*-chloroacetyl-1-thio-β-D-glucopyranoside (2a). Sodium hydrogen carbonate (2.4 g, 28.6 mmol) was added at room temp to a stirred solution of phenyl 1-thio-β-D-glucopyranoside (6.0 g, 22.0 mmol; prepared by deacetylation[15] of the corresponding acetylated derivative[16]) and chloroacetic anhydride (23.0 g, 0.134 mol) in DMF (40 mL). The mixture was stirred for 3 h and poured into water (250 mL). The solid that separated was collected by filtration, washed with water and dried in *vacuo*. Crystallisation from acetone/*n*-hexane gave **2a** (11.4 g, 89%), mp 130 °C, $[\alpha]_D$ -10.0° (*c* 1.0, $CHCl_3$). ^1H NMR δ 5.36 (t, 1 H, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3), 5.12 (t, 1 H, $J_{4,5} = 9.7$ Hz, H-4), 5.02 (dd, 1 H, $J_{1,2} = 10.0$ Hz, H-2), 4.76 (d, 1 H, H-1), 4.42-4.26 (m, 2 H, H-6a,6b), 4.09, 4.08, 4.01, 3.97 (s, 3 x d, 4 x 2 H, CH_2Cl), 3.86 (ddd, 1 H, $J_{5,6a} = 4.3$ Hz, $J_{5,6b} = 2.8$ Hz, H-5); ^{13}C NMR δ 85.1 (C-1), 75.2, 75.0 (C-5,3), 70.9 (C-2), 69.3 (C-4), 63.2 (C-6), 40.6, 40.4, 40.3, 40.2 (CH_2Cl).

Anal. Calcd for $C_{20}H_{20}Cl_4O_9S$: C, 41.54; H, 3.49; Cl, 24.52; S, 5.55. Found: C, 41.61; H, 3.48; Cl, 24.77; S, 5.81.

Ethyl 2,3,4,6-Tetra-*O*-chloroacetyl-1-thio-β-D-glucopyranoside (2b). Sodium hydrogen carbonate (6.0 g, 71.5 mmol) was added at room temp to a stirred solution of ethyl 1-thio-β-D-glucopyranoside (1.7 g, 7.6 mmol; prepared by deacetylation of the corresponding acetylated derivative[17]) and chloroacetic anhydride (6.8 g, 40.0 mmol) in DMF (50 mL). The mixture was stirred for 2 h, poured into water (250 mL) and extracted with dichloromethane. The combined organic layers were washed with water and concentrated. Chromatography (solvent *A*, 5:1) of the residue gave **2b** (3.47 g, 86%) as a colourless oil, $[\alpha]_D$ -16.6° (*c* 1.3, chloroform). ^{1}H NMR δ 5.37 (t, 1 H, $J_{3,4}$= $J_{4,5}$ = 9.4 Hz, H-4), 5.81 (bt, 1 H, $J_{1,2}$ = 10.1 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.12 (t, 1 H, H-3), 4.58 (d, 1 H, H-1), 4.36-4.34 (m, 2 H, H-6a,6b), 4.03, 4.12, 4.06, 4.00 (3 x s, d, 4 x 2 H, CH_2Cl), 3.98-3.81 (m, 1 H, H-5), 2.83-2.26 (m, 2 H, SCH_2CH_3), 1.28 (t, *J* = 7.5 Hz, 3 H, SCH_2CH_3); ^{13}C NMR δ 83.2 (C-1), 75.3, 74.9, 70.9, 69.5 (C-2,3,4,5), 63.3 (C-6), 40.6, 40.4, 40.2 (2 x 1 C, 2 C, CH_2Cl), 24.3 (SCH_2CH_3), 14.8 (SCH_2CH_3).

Anal. Calcd for $C_{16}H_{20}Cl_4O_9S$: C, 36.25; H, 3.80; Cl, 26.75; S, 6.05. Found: C, 36.36; H, 3.88; Cl, 26.93; S, 5.95.

2,3,4,6-Tetra-*O*-chloroacetyl-α-D-glucopyranosyl Fluoride (2c). Sodium hydrogen carbonate (2.4 g, 28.6 mmol) was added at room temp to a stirred solution of α-D-glucopyranosyl fluoride (4.0 g, 22.0 mmol) and chloroacetic anhydride (21.0 g, 0.123 mol) in DMF (40 mL). The mixture was stirred for 1 h and poured into water (250 mL). The solid that separated was collected by filtration, washed with water and dried in *vacuo*. Crystallisation from acetone/diethyl ether gave **2c** (8.25 g, 80%), mp 122 °C, $[\alpha]_D$ +69.6° (*c* 1.0, $CHCl_3$). ^{1}H NMR δ 5.80 (dd, 1 H, $J_{1,2}$ = 2.7 Hz, $J_{1,F}$ = 52.6 Hz, H-1), 5.60 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz, H-3), 5.25 (t, 1 H, $J_{4,5}$ = 9.8 Hz, H-4), 5.06 (ddd, 1 H, $J_{2,F}$ = 23.5 Hz, H-2), 4.43-4.26 (m, 3 H, H-5,6a,6b), 4.13, 4.10, 4.03, 4.00 (2 x s, 2 x d, 4 x 2 H, CH_2Cl); ^{13}C NMR δ 103.2 (d, $J_{C,F}$ = 231.0 Hz, C-1), 71.2 (d, $J_{C,F}$ = 24.7 Hz, C-2), 70.6 (C-3), 69.3 (d, $J_{C,F}$ = 4.3 Hz, C-5), 68.4 (C-4), 62.4 (C-6), 40.5, 40.24, 40.21, 40.17 (CH_2Cl).

Anal. Calcd for $C_{14}H_{15}Cl_4FO_9$: C, 34.45; H, 3.10; Cl, 29.06. Found: C, 34.61; H, 3.16; Cl, 29.02.

2,3,4,6-Tetra-*O*-chloroacetyl-D-glucopyranosyl Trichloroacetimidate (2f). A mixture of **2e** (2.43 g, 5.0 mmol; prepared from compound **2d** as described[1,10]), trichloroacetonitrile (2.0 mL) and potassium carbonate (2.0 g) in dichloromethane (15 mL) was stirred at room temp for 4 h and filtered through a layer of Celite. Concentration and chromatography (solvent *A*, 5:1) of the residue gave a 2.6:1 α/β-mixture (^{1}H NMR) of **2f** (1.89 g, 60%) as a colourless foam, $[\alpha]_D$ +54.8° (*c* 0.5, chloroform). ^{1}H NMR

(significant peaks) **α-2f**: δ 6.60 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1), 5.68 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.8 Hz, H-3), 5.26 (dd, 1 H, H-2); **β-2f**: δ 6.01 (d, 1 H, $J_{1,2}$ = 5.5 Hz, H-1), 5.25 (dd, 1 H, $J_{2,3}$ = 9.6 Hz, H-2), 4.76 (ddd, 1 H, $J_{5,6a}$ = 5.3 Hz, $J_{5,6b}$ = 3.0 Hz, H-5); ^{13}C NMR **α-2f**: δ 160.5 (C=NH), 116.0 (CCl_3), 92.3 (C-1), 73.5, 71.1, 70.8 (C-2,3,5), 68.9 (C-4), 63.5 (C-6), 40.6, 40.5, 40.4, 40.3 (CH_2Cl); **β-2f**: δ 161.7 (C=NH), 116.4 (CCl_3), 100.5 (C-1), 77.4 (C-5), 72.1, 71.3 (C-2,3), 68.2 (C-4), 64.1 (C-6), 40.7, 40.6 (2 x 2 C, CH_2Cl).

Anal. Calcd for $C_{16}H_{16}Cl_7NO_{10}$: C, 30.48; H, 2.56; Cl, 39.36; N, 2.22. Found: C, 30.28; H, 2.56; Cl, 39.24; N, 2.47.

4-Chloroacetoxycinnamic Acid (3e). Chloroacetyl chloride (7.5 g, 66.4 mmol) was added at 0 °C to a stirred solution of *p*-coumaric acid (4.0 g, 24.4 mmol) in aqueous sodium hydroxide solution (3 N, 35 mL) and the resulting suspension was stirred for 5 min. After addition of aqueous HCl solution, the material that separated was collected by filtration and washed with ice-cold water. Crystallisation from acetone/*n*-hexane gave **3e** (3.96 g, 68%), mp 186-187 °C. ^{1}H NMR (d_6-acetone) δ 7.79-7.75, 7.29-7.26 (2 x m, 2 x 2 H, $H_{arom.}$), 7.70 (d, 1 H, *J* = -16.0 Hz, *CH*=CHCOO), 6.54 (d, 1 H, CH=C*H*COO), 4.59 (s, 2 H, CH_2Cl).

Anal. Calcd for $C_{11}H_9ClO_4$: C, 54.90; H, 3.77; Cl, 14.73. Found: C, 55.09; H, 3.78; Cl, 14.50.

2,3,4,6-Tetra-*O*-chloroacetyl-1-*O*-cinnamoyl-D-glucopyranose (5a). (a) A mixture of **2a** (1.33 g, 2.3 mmol), **3a** (0.37 g, 2.5 mmol), *N*-iodosuccinimide (0.67 g, 3.4 mmol) and trifluoromethanesulfonic acid (60 µL, 0.7 mmol) in dichloromethane (20 mL) was stirred at room temp for 3 d. TLC (solvent *A*, 5:1) revealed the formation of traces of **5a**.

(b) A mixture of **2b** (392.4 mg, 1.0 mmol), **3a** (177.8 mg, 1.2 mmol), *N*-iodosuccinimide (270.0 mg, 1.2 mmol) and trifluoromethanesulfonic acid (10 µL, 0.1 mmol) in dichloromethane (5 mL) was treated as described for (a). After stirring at room temp for 2 h the mixture was washed with aqueous sodium hydrogen carbonate and sodium thiosulfate solution. Concentration and filtration over a short column of silica gel gave a 30:70 α/β-mixture (^{1}H NMR) of **5a** (370 mg, 77%) as a colourless foam.

(c) A solution of **2c** (1.29 g, 2.63 mmol), **3a** (0.48 g, 3.21 mmol) and boron trifluoride etherate (0.4 mL, 13.2 mmol) in dichloromethane (15 mL) was stirred at room temp for 32 h, washed with aqueous sodium hydrogen carbonate, concentrated and filtered through a short column of silica gel to give a 81:19 α/β-mixture (^{1}H NMR) of **5a** (0.94 g, 58%) as a colourless foam. Chromatography (solvent *A*, 5:1) gave **α-5a** (0.64 g, 39%), $[\alpha]_D$ +109.3° (*c* 1.0, chloroform). ^{1}H NMR δ 7.81 (d, 1 H, *J* = -16.0 Hz, *CH*=CHCOO), 6.53 (d, 1 H, CH=C*H*COO), 6.50 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 5.69 (t, 1

H, $J_{2,3} = J_{3,4} = 9.8$ Hz, H-3), 5.28 (t, 1 H, $J_{4,5} = 9.8$ Hz, H-4), 5.27 (dd, 1 H, H-2), 4.40 (dd, 1 H, $J_{5,6a} = 4.4$ Hz, $J_{6a,6b} = -12.9$ Hz, H-6a), 4.34-4.29 (m, 2 H, H-5,6b), 4.02, 4.05, 4.02, 4.01 (d, 3 x s, 4 x 2 H, CH_2Cl); ^{13}C NMR δ 148.0 (*C*H=CHCOO), 115.8 (CH=*C*HCOO), 88.6 (C-1), 71.2, 70.4, 69.4, 69.2 (C-2,3,4,5), 62.8 (C-6), 40.5, 40.2 (2 x 2 C, CH_2Cl).

Anal. Calcd for $C_{23}H_{22}Cl_4O_{11}$: C, 44.83; H, 3.60; Cl, 23.01. Found: C, 45.40; H, 3.71; Cl, 22.31.

(d) Trimethylsilyl trifluoromethanesulfonate (18 μL, 0.1 mmol) was added at -20 °C to a solution of **2f** (630.5 mg, 1.0 mmol) and **3a** (177.8 mg, 1.2 mmol) in dichloromethane (5 mL). The solution was stirred at room temp for 1.5 h and washed with aqueous sodium hydrogen carbonate solution. Concentration and filtration over a short column of silica gel gave a 8:92 α/β-mixture (^1H NMR) of **5a** (360 mg, 75%) as a colourless foam.

(e) A suspension of **2g** (887.0 mg, 1.62 mmol) and **4a** (603.4 mg, 2.37 mmol) in dichloromethane (8 mL) was stirred at room temp for 30 h. The mixture was filtered through a layer of Celite and the filtrate was washed with aqueous sodium thiosulfate solution. Concentration and chromatography (solvent *A*, 5:1) of the residue gave **β-5a** (711.4 mg, 71%) as a colourless foam, $[\alpha]_D$ -4.4° (*c* 0.9, chloroform). ^1H NMR δ 7.76 (d, 1 H, $J = -16.0$ Hz, PhC*H*=CH-), 6.41 (d, 1 H, PhCH=C*H*-), 5.93 (d, 1 H, $J_{1,2} = 8.1$ Hz, H-1), 5.46 (t, 1 H, $J_{3,4} = J_{4,5} = 9.4$ Hz, H-4), 5.34 (dd, 1 H, $J_{2,3} = 9.3$ Hz, H-2), 5.27 (t, 1 H, H-3), 4.43 (dd, 1 H, $J_{5,6a} = 4.2$ Hz, $J_{6a,6b} = -12.6$ Hz, H-6a), 4.32 (dd, 1 H, $J_{5,6b} = 2.3$ Hz, H-6b), 4.27-4.06 (m, 1 H, H-5), 4.05, 4.13, 4.03, 4.02 (d, 3 x s, 4 x 1 H, CH_2Cl); ^{13}C NMR δ 148.1 (*C*H=CHCOO), 115.7 (CH=*C*HCOO), 91.4 (C-1), 73.8, 72.1, 71.4 (C-2,3,5), 69.1 (C-4), 62.8 (C-6), 40.6, 40.2 (1 C, 3 C, CH_2Cl).

Anal. Calcd for $C_{23}H_{22}Cl_4O_{11}$: C, 44.83; H, 3.60; Cl, 23.01. Found: C, 44.57; H, 3.59; Cl, 23.22.

2,3,4,6-Tetra-*O*-chloroacetyl-1-*O*-(3,4,5-trimethoxybenzoyl)-D-glucopyranose (5b). (a) A solution of **2c** (1.09 g, 2.23 mmol), **3b** (0.62 g, 2.9 mmol) and boron trifluoride etherate (0.38 mL, 3.03 mmol) in dichloromethane (15 mL) was stirred at room temp for 30 h. Work up as described for **5a** (c) gave a 90:10 α/β-mixture (^1H NMR) of **5b** (0.79 g, 52%). Chromatography (solvent *A*, 5:1) gave **α-5b** (0.54 g, 36%) as a colourless glass, $[\alpha]_D$ +51.8° (*c* 1.0, chloroform). ^1H NMR δ 6.55 (d, 1 H, $J_{1,2} = 3.4$ Hz, H-1), 5.80 (t, 1 H, $J_{2,3} = J_{3,4} = 9.9$ Hz, H-3), 5.30 (dd, 1 H, H-2), 5.26 (t, 1 H, $J_{4,5} = 9.9$ Hz, H-4), 4.40 (dd, 1 H, $J_{5,6a} = 2.6$ Hz, $J_{6a,6b} = -12.8$ Hz, H-6a), 4.32 (dd, 1 H, $J_{5,6b} = 2.4$ Hz, H-6b), 4.24-4.19 (m, 1 H, H-5), 4.13, 4.04, 4.00, 4.06 (3 x s, d, 4 x 2 H, CH_2Cl), 3.96, 3.95 (2 x s, 6 H, 3 H, OCH_3); ^{13}C NMR δ 89.3 (C-1), 70.9, 70.6, 69.4, 69.3 (C-2,3,4,5), 62.8 (C-6), 61.0, 56.5 (1 C, 2 C, OCH_3), 40.5, 40.2 (2 x 2 C, CH_2Cl).

Anal. Calcd for $C_{24}H_{26}Cl_4O_{14}$: C, 42.37; H, 3.85; Cl, 20.85. Found: C, 42.58; H, 4.04; Cl, 20.79.

(b) A suspension of **2g** (912.0 mg, 1.66 mmol) and **4b** (811.9 mg, 2.54 mmol) in dichloromethane (8 mL) was stirred at room temp for 3 h. Work up as described for **5a** (e) gave **β-5b** (723.4 mg, 64%) as a colourless foam, $[\alpha]_D$ -26.2° (*c* 1.0, chloroform). ^1H NMR δ 5.91 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H-1), 5.55-5.41 (m, 2 H, H-2,3), 5.29 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 4.45 (dd, 1 H, $J_{5,6a}$ = 4.2 Hz, $J_{6a,6b}$ = -12.5 Hz, H-6a), 4.34 (dd, 1 H, $J_{5,6b}$ = 2.1 Hz, H-6b), 4.12, 4.03 (2 x s, 2 x 2 H, CH_2Cl), 4.05, 4.00 (2 x d, 2 x 2 H, CH_2Cl), 3.92, 3.91 (2 x s, 3 H, 6 H, OCH_3), 3.88-3.78 (m, 1 H, H-5); ^{13}C NMR δ 92.0 (C-1), 73.4, 72.2, 71.3 (C-2,3,5), 69.2 (C-4), 62.7 (C-6), 61.0 (OCH_3), 56.3 (2 C, OCH_3), 40.5, 40.2 (1 C, 3 C, CH_2Cl).

Anal. Calcd for $C_{24}H_{26}Cl_4O_{14}$: C, 42.37; H, 3.85; Cl, 20.85. Found: C, 42.66; H, 4.03; Cl, 20.67.

2,3,4,6-Tetra-*O*-chloroacetyl-1-*O*-(2-methyl-4-pentenoyl)-D-gluco-pyranose (5c). (a) A solution of **2c** (1.02 g, 2.08 mmol), **3c** (0.3 g, 2.59 mmol) and boron trifluoride etherate (0.4 mL, 3.18 mmol) in dichloromethane (16 mL) was stirred at room temp for 24 h. Work up as described for **5a** (c) gave a 72:28 α/β-mixture (^1H NMR) of **5c** (0.73 g, 60%). Chromatography (solvent *A*, 5:1) gave **α-5c** (0.41 g, 34%) as a colourless foam, $[\alpha]_D$ +73.2° (*c* 1.3, chloroform). ^1H NMR δ 6.38 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1), 5.86-5.69 (m, 1 H, H_2C=C*H*), 5.59 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz, H-3), 5.24 (t, 1 H, $J_{4,5}$ = 9.8 Hz, H-4), 5.22-4.93 (m, 3 H, H-2, H_2C=CH), 4.37 (dd, 1 H, $J_{5,6a}$ = 4.1 Hz, $J_{6a,6b}$ = -12.5 Hz, H-6a), 4.32-4.17 (m, 2 H, H-5,6b), 4.12, 4.02, 4.05, 3.98 (2 x s, 2 x d, 4 x 2 H, CH_2Cl); ^{13}C NMR δ 134.6 (H_2C=*C*H), 117.6 (H_2*C*=CH), 88.4 (C-1), 71.0, 70.5, 69.5, 69.1 (C-2,3,4,5), 62.8 (C-6), 40.5, 40.3, 40.2, 40.1 (CH_2Cl), 39.1 (*C*H-CH_3), 37.4 (CH_2), 16.5 (CH-*C*H_3).

Anal. Calcd for $C_{20}H_{24}Cl_4O_{11}$: C, 41.26; H, 4.15; Cl, 24.36. Found: C, 41.03; H, 4.18; Cl, 23.94.

(b) A suspension of **2g** (685.0 mg, 1.25 mmol) and **4c** (465.3 mg, 2.11 mmol) in dichloromethane (20 mL) was stirred at room temp for 24 h. Work up as described for **5a** (e) gave **β-5c** (508.4 mg, 70%) as a colourless foam, $[\alpha]_D$ +6.8° (*c* 1.0, chloroform). ^1H NMR δ 5.82 (d, 1 H, $J_{1,2}$ = 8.3 Hz, H-1), 5.74-5.62 (m, 1 H, H_2C=C*H*), 5.40 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz, H-3), 5.28-5.19 (m, 2 H, H-2,4), 5.10-5.07, 5.04-5.03 (2 x m, 2 x 1 H, H_2C=CH), 4.41 (dd, 1 H, $J_{5,6a}$ = 4.3 Hz, $J_{6a,6b}$ = -12.5 Hz, H-6a), 4.30 (dd, 1 H, $J_{5,6b}$ = 2.3 Hz, H-6b), 4.12, 4.00, 3.99, 4.03 (3 x s, d, 4 x 2 H, CH_2Cl), 3.97-3.93 (m, 1 H, H-5); ^{13}C NMR δ 134.5 (H_2C=*C*H), 117.5 (H_2*C*=CH), 91.1 (C-1), 73.8, 72.1, 71.3 (C-2,3,5), 69.1 (C-4), 62.7 (C-6), 40.5, 40.2 (1 C, 3 C, CH_2Cl), 39.0 (*C*H-CH_3), 37.2 (CH_2), 16.2 (CH-*C*H_3).

Anal. Calcd for $C_{20}H_{24}Cl_4O_{11}$: C, 41.26; H, 4.15; Cl, 24.36. Found: C, 40.92; H, 4.19; Cl, 23.62.

2,3,4,6-Tetra-*O*-chloroacetyl-1-*O*-oleoyl-β-D-glucopyranose (5d). A suspension of **2g** (1.45 g, 2.64 mmol) and **4d** (1.27 g, 3.26 mmol) in dichloromethane (50 mL) was stirred at room temp for 72 h. Work up as described for **5a** (e) and chromatography (solvent *A*, 10:1) gave **5d** (1.50 g, 75%) as a wax like solid, $[\alpha]_D$ -8.7° (*c* 1.0, chloroform). ^{1}H NMR δ 5.79 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1), 5.54 (d, 2 H, *J* = 7.9 Hz, C*H*=C*H*), 5.41-5.30 (m, 2 H, H-2,3), 5.22 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.4 Hz, H-4), 4.51-4.39 (m, 1 H, H-6a), 4.30 (dd, 1 H, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = -12.4 Hz, H-6b), 4.15, 4.12, 4.03, 4.00 (4 x s, 4 x 2 H, CH_2Cl), 3.96-3.75 (m, 1 H, H-5); ^{13}C NMR δ 130.1, 129.7 (*C*H=*C*H), 93.6 (C-1), 73.9, 72.5, 71.3, 69.8 (C-2,3,4,5), 62.7 (C-6), 40.9, 40.5, 40.2 (2 x 1 C, 2 C, CH_2Cl).

Anal. Calcd for $C_{32}H_{48}Cl_4O_{11}$: C, 51.21; H, 6.45; Cl, 18.89. Found: C, 51.00; H, 6.45; Cl, 18.39.

2,3,4,6-Tetra-*O*-chloroacetyl-1-*O*-(4-chloroacetoxycinnamoyl)-D-glucopyranose (5e). A solution of **2c** (557.3 mg, 1.14 mmol), **3e** (346.2 mg, 1.44 mmol) and boron trifluoride etherate (0.2 mL, 1.59 mmol) in dichloromethane (20 mL) was stirred at room temp for 56 h. Work up as described for **5a** (c) gave a 77:23 α/β-mixture (^{1}H NMR) of **5e** (429.5 mg, 51%). Chromatography (solvent *A*, 5:1) gave **α-5e** (219.7 mg, 27%) as a colourless oil, $[\alpha]_D$ +43.3° (*c* 0.7, chloroform). ^{1}H NMR δ 7.68 (d, 1 H, *J* = -16.5 Hz, C*H*=CHCOO), 6.28 (d, 1 H, CH=C*H*COO), 6.27 (d, 1 H, $J_{1,2}$ = 4.1 Hz, H-1), 5.68 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.8 Hz, H-3), 5.23 (t, 1 H, $J_{4,5}$ = 9.8 Hz, H-4), 5.15 (dd, 1 H, H-2), 4.76, 4.14, 4.13, 4.09, 4.08 (5 x s, 5 x 2 H, CH_2Cl), 4.45-4.16 (m, 3 H, H-5,6a,6b); ^{13}C NMR δ 146.3 (*C*H=CHCOO), 116.0 (CH=*C*HCOO), 89.1 (C-1), 72.1, 71.5, 70.0, 69.1 (C-2,3,4,5), 62.5 (C-6), 41.6, 40.6, 40.2 (1 C, 2 x 2 C, CH_2Cl).

Anal. Calcd for $C_{25}H_{23}Cl_5O_{13}$: C, 42.37; H, 3.27. Found: C, 42.69; H, 3.38.

2,3,4,6-Tetra-*O*-chloroacetyl-1-*O*-cinnamoyl-β-D-galactopyranose (7a). A suspension of **6** (1.03 g, 1.88 mmol) and **4a** (0.71 g, 2.8 mmol) in dichloromethane (20 mL) was stirred at room temp for 40 h. Work up as described for **5a** (e) gave **7a** (0.81 g, 70%) as a colourless foam, $[\alpha]_D$ -3.7° (*c* 1.0, chloroform). ^{1}H NMR δ 7.78 (d, 1 H, *J* = -16.0 Hz, C*H*=CHCOO), 6.42 (d, 1 H, CH=C*H*COO), 5.93 (d, 1 H, $J_{1,2}$ = 8.2 Hz, H-1), 5.57-5.48 (m, 2 H, H-2,4), 5.34 (dd, 1 H, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 3.4 Hz, H-3), 4.37-4.27 (m, 3 H, H-5,6a,6b), 4.22, 4.08, 4.02 (3 x s, 2 x 2 H, 4 H, CH_2Cl); ^{13}C NMR δ 148.1 (*C*H=CHCOO), 115.7 (CH=*C*HCOO), 91.7 (C-1), 72.0, 71.2, 69.1, 68.6 (C-2,3,4,5), 62.1 (C-6), 40.5, 40.3 (2 x 2 C, CH_2Cl).

Anal. Calcd for $C_{23}H_{22}Cl_4O_{11}$: C, 44.83; H, 3.60; Cl, 23.01. Found: C, 44.63; H, 3.60; Cl, 22.34.

2,3,4,6-Tetra-*O*-chloroacetyl-1-*O*-(3,4,5-trimethoxybenzoyl)-β-D-galactopyranose (7b). A suspension of **6** (911.6 mg, 1.66 mmol) and **4b** (638.2 mg, 2.00 mmol) in dichloromethane (20 mL) was stirred at room temp for 2 h. Work up as described for **5a** (e) gave **7b** (627.3 mg, 56%) as a colourless foam, $[\alpha]_D$ -16.4° (*c* 1.0, chloroform). ^{1}H NMR δ 5.89 (d, 1 H, $J_{1,2}$ = 8.3 Hz, H-1), 5.61-5.57 (m, 2 H, H-2,4), 5.37 (dd, 1 H, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.4 Hz, H-3), 4.39-4.26 (m, 3 H, H-5,6a,6b), 4.22, 4.08, 4.03, 4.00 (3 x s, d, 4 x 2 H, CH_2Cl), 3.93 (s, 9 H, OCH_3); ^{13}C NMR δ 92.4 (C-1), 71.6, 71.3, 69.0, 68.4 (C-2,3,4,5), 61.9 (C-6), 61.0, 56.3 (1 C, 2 C, OCH_3), 40.4, 40.3 (2 x 2 C, CH_2Cl).

Anal. Calcd for $C_{24}H_{26}Cl_4O_{14}$: C, 42.37; H, 3.85; Cl, 20.85. Found: C, 42.61; H, 3.84; Cl, 20.30.

2,3,4,6-Tetra-*O*-chloroacetyl-1-*O*-(2-methyl-4-pentenoyl)-β-D-galactopyranose (7c). A suspension of **6** (702.0 mg, 1.28 mmol) and **4c** (473.6 mg, 2.14 mmol) in dichloromethane (20 mL) was stirred at room temp for 24 h. Work up as described for **5a** (e) gave **7c** (410.8 mg, 55%) as a colourless foam, $[\alpha]_D$ +14.1° (*c* 1.0, chloroform). ^{1}H NMR δ 5.79 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1), 5.75-5.60 (m, 1 H, H_2C=C*H*), 5.53-5.48 (m, 1 H, H-4), 5.41 (dd, 1 H, $J_{2,3}$ = 10.3 Hz, H-2), 5.28 (dd, 1 H, $J_{3,4}$ = 3.3 Hz, H-3), 5.11-5.07, 5.04-5.03 (2 x m, 2 H, *H*$_2$C=CH), 4.38-4.25 (m, 3 H, H-5,6a,6b), 4.20, 4.07, 4.00, 4.01 (3 x s, d, 4 x 2 H, CH_2Cl); ^{13}C NMR δ 134.6 (H_2C=*C*H), 117.4 (H_2*C*=CH), 91.5 (C-1), 72.0, 71.1, 69.0, 68.5 (C-2,3,4,5), 62.0 (C-6), 40.4, 40.2 (2 x 2 C, CH_2Cl), 39.0 (*C*H-CH_3), 37.2 (CH_2), 16.2 (CH-*C*H$_3$).

Anal. Calcd for $C_{20}H_{24}Cl_4O_{11}$: C, 41.26; H, 4.15. Found: C, 40.99; H, 4.17.

2,3,4,6-Tetra-*O*-chloroacetyl-1-*O*-oleoyl-β-D-galactopyranose (7d). A suspension of **6** (1.45 g, 2.63 mmol) and **4d** (1.28 g, 3.3 mmol) in dichloromethane (50 mL) was stirred at room temp for 72 h. Work up as described for **5a** (e) gave **7d** (1.36 g, 69%) as a highly viscous oil, $[\alpha]_D$ +9.6° (*c* 1.3, chloroform). ^{1}H NMR δ 5.79 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1), 5.52-5.49 (m, 1 H, H-4), 5.40 (dd, 1 H, $J_{2,3}$ = 10.3 Hz, H-2), 5.36-5.30 (m, 2 H, C*H*=C*H*), 5.26 (dd, 1 H, $J_{3,4}$ = 3.3 Hz, H-3), 4.37-4.22 (m, 3 H, H-5,6a,6b), 4.19, 4.06, 4.00, 3.99 (4 x s, 4 x 2 H, CH_2Cl); ^{13}C NMR δ 130.1, 129.7 (*C*H=*C*H), 91.4 (C-1), 72.0, 71.2, 69.1, 68.5 (C-2,3,4,5), 62.0 (C-6), 40.4, 40.2 (2 x 2 C, CH_2Cl).

Anal. Calcd for $C_{32}H_{48}Cl_4O_{11}$: C, 51.21; H, 6.45. Found: C, 51.27; H, 6.50.

1-*O*-Acyl-D-glycopyranoses (8, 9). General Procedure. A solution of **5** and **7**, respectively and 1-piperidinethiocarbamide[13] (2 equivalents per chloroacetyl group to be removed) in methanol/dichloromethane (1:1) for compd **5a** or methanol/chloroform (1:1) for all other compds was stirred at room temp for 18-24 h until all starting material had reacted (TLC, solvent *B*, 10:1). Concentration and chromatography (solvent *B*, 10:1) gave **8** and **9**, respectively.

1-*O*-Cinnamoyl-β-D-glucopyranose (8a). According to the General Procedure, **5a** (0.66 g, 1.38 mmol) afforded **8a** (0.25 g, 58%) as an amorphous solid, $[\alpha]_D$ -8.2° (*c* 0.9, methanol).^{13}C NMR δ 147.6 (*C*H=CHCOO), 118.2 (CH=*C*HCOO), 95.9 (C-1), 78.8, 77.9, 74.0, 71.0 (C-2,3,4,5), 62.3 (C-6).

Anal. Calcd for $C_{15}H_{18}O_7$: C, 58.06; H, 5.85. Found: C, 57.71; H, 6.12.

1-*O*-(3,4,5-Trimethoxybenzoyl)-β-D-glucopyranose (8b). According to the General Procedure, **β-5b** (313.5 mg, 0.46 mmol) afforded **8b** (104.8 mg, 61%) as a colourless glass, $[\alpha]_D$ -7.1° (*c* 0.9, methanol).^{13}C NMR δ 97.8 (C-1), 80.2, 79.3, 75.4, 72.4 (C-2,3,4,5), 63.7 (C-6), 62.6, 58.2 (1 C, 2 C, OCH_3).

DCI-MS (NH_3): m/z = 375 (MH^+), 392 (MH^++NH_3).

1-*O*-(2-Methyl-4-pentenoyl)-β-D-glucopyranose (8c). According to the General Procedure, **β-5c** (146.8 mg, 0.25 mmol) afforded **8c** (37.6 mg, 56%) as a colourless hygroscopic solid, $[\alpha]_D$ +9.2° (*c* 0.7, methanol). ^{13}C NMR δ 136.6 (H_2C=*C*H), 117.5 (H_2*C*=CH), 95.8 (C-1), 78.9, 78.1, 74.0, 71.1 (C-2,3,4,5), 62.4 (C-6), 40.3 (*C*H-CH_3), 38.5 (CH_2), 16.5 (CH-*C*H_3).

DCI-MS (NH_3): m/z = 276 (M^+), 277 (MH^+), 294 (MH^++NH_3).

1-*O*-Oleoyl-β-D-glucopyranose (8d). According to the General Procedure, **β-5d** (609.2 mg, 0.81 mmol) afforded **8d** (185.6 mg, 52%) as a colourless hygroscopic solid, $[\alpha]_D$ +15.4° (*c* 0.6, methanol). ^{13}C NMR δ 130.7, 130.6 (*C*H=*C*H), 98.1 (C-1), 77.9, 77.8, 76.2, 71.7 (C-2,3,4,5), 62.6 (C-6).

DCI-MS (NH_3): m/z = 444 (M^+).

1-*O*-Cinnamoyl-β-D-galactopyranose (9a). According to the General Procedure, **7a** (367.4 mg, 0.6 mmol) afforded **9a** (118.4 mg, 64%) as a colourless foam, $[\alpha]_D$ +17.8° (*c* 0.6, methanol). ^{13}C NMR δ 147.6 (*C*H=CHCOO), 119.7 (CH=*C*HCOO), 97.9 (C-1), 78.9, 76.2, 72.7, 71.5 (C-2,3,4,5), 63.6 (C-6).

Anal. Calcd for $C_{15}H_{18}O_7$: C, 58.06; H, 5.85. Found: C, 57.70; H, 5.98.

1-*O*-(3,4,5-Trimethoxybenzoyl)-β-D-galactopyranose (9b). According to the General Procedure, **7b** (146.3 mg, 0.22 mmol) afforded **9b** (45.3 mg, 55%) as a colourless hygroscopic solid, $[\alpha]_D$ +12.4° (*c* 0.6, methanol). ^{13}C NMR δ 96.8 (C-1), 78.8, 77.5, 73.7, 72.7 (C-2,3,4,5), 64.7 (C-6), 59.3, 54.8 (1 C, 2 C, OCH_3).

DCI-MS (CH_4): m/z = 374 (M^+), 375 (MH^+).

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