ELSEVIER

www.elsevier.nl/locate/carres

Carbohydrate Research 332 (2001) 157–166

CARBOHYDRATE RESEARCH

Regioselective C-3-O-acylation and O-methylation of 4,6-*O*-benzylidene-β-D-gluco- and galactopyranosides displaying a range of anomeric substituents

Helen M.I. Osborn,* Victoria A. Brome, Laurence M. Harwood, William G. Suthers

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

Received 29 November 2000; accepted 20 February 2001

Abstract

The regioselective C-3-O-acylation and O-methylation of a range of 4,6-*O*-benzylidene-β-D-gluco- and galactopyranosides has been studied. Regioselectivity is achieved by forming the copper chelate of the 2,3-diol using either sodium hydride and copper(II) chloride, or copper(II) acetylacetanoate, or copper(II) acetate, prior to introduction of the acylating or methylating agent.

Keywords: Regioselective acylation; Copper chelate; Methylation; One-pot synthesis

1. Introduction

As our understanding of the vital roles of oligosaccharides as mediators of biological events increases, so does our need for efficient methods for their total syntheses.[1] As a consequence, a whole range of new oligosaccharide assembly strategies have been developed which allow efficient one-pot synthesis of oligosaccharides.[2] If access to individual isomers of biologically important oligosaccharides is to be possible, then orthogonally protected hermaphrodites (molecules which can act as donors or acceptors depending on the reaction conditions) must be available.[3] Such differentially protected hermaphrodites are generally accessible for manno- and galactopyranosides,[4] but are more elusive for glucopyranosides. For example, although it is generally possible to access glucopyranoside hermaphrodites with a free hydroxyl group at C-3, access to the isomeric hermaphrodites with a free hydroxyl group at C-2 is more difficult. Thus, despite the ubiquitous nature of glucopyranoside units within important oligosaccharides, the selective activation of the C-3 hydroxyl group remains a difficult challenge that still sanctions attention. This is in contrast to results obtained with isomeric monosaccharide counterparts, for which largely successful strategies have now been established.[4]

Both chemical[5] and enzymatic[6] methods are available for the regioselective protection of the C-3 hydroxyl group of methyl 4,6-*O*-benzylidene-β-D-glycopyranosides, to afford C-2 acceptors in good yields. However, until recently, the regioselective protection of the C-3 hydroxyl group of 4,6-*O*-benzylidene-β-D-glycopyranosides displaying more versatile anomeric substituents had been less widely

* Corresponding author. Tel.: +44-1189-875123; fax: +44-1189-316331.

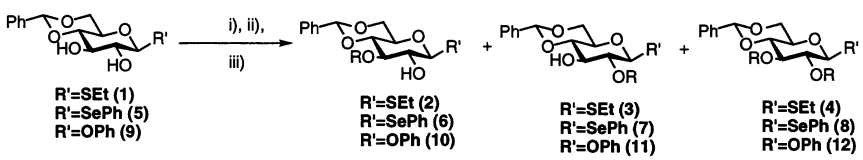
E-mail address: h.m.i.osborn@reading.ac.uk (H.M.I. Osborn).

0008-6215/01/$ - see front matter
PII: S0008-6215(01)00063-5

studied. Thus we have recently diverted our attention to this area of research and have developed two complimentary methods which permit efficient, regioselective entry to the desired targets.[7,8] Regioselective protection of the C-3 hydroxyl group is either achieved using lipase enzymes[7,9] or by performing copper chelates of the benzylidene protected glucopyranoside diols.[8] In the former case *Pseudomonas fluorescens* lipase (PFL), *Pseudomonas cepacia* lipase (Lipase P) and *Candida cylindracea* lipase (CCL) have been utilised within an enzymatic regioselective protection strategy. This has facilitated the incorporation of acetyl, pivaloyl or formyl esters in excellent yield and with excellent regioselectivity at C-3 of some 4,6-*O*-benzylidene-β-D-glucopyranosides.[7] In this paper we wish to provide a full report of an alternative copper mediated protection strategy,[8] discuss its applicability for the regioselective C-3 protection of 4,6-*O*-benzylidene-β-D-galactopyranosides and also outline the use of alternative copper species in the protection protocol.

2. Results and discussion

It has previously been reported[5] that copper chelates of methyl 4,6-*O*-benzylidene glycopyranoside dianions can react regioselectively with alkylating and acylating agents to afford C-3 alkylated/acylated products in good yields. It has been postulated that the carbohydrate dianions are deactivated by the formation of the copper(II) salt, and that as a result a regioselective reaction occurs at the C-3 hydroxyl group. Disubstitution is virtually suppressed under these reaction conditions. We have now demonstrated that dianions of 4,6-*O*-benzylidene glucopyranosides displaying a range of anomeric groups are also regioselectively protected under these reaction conditions. Hence access to orthogonally protected hermaphrodites has been achieved. This method involves treating a solution of the carbohydrate 2,3-diol in dry THF with two equivalents of sodium hydride prior to the addition of one equivalent of freshly prepared and rigorously dried copper(II) chloride. A range of acylating agents can then be added,

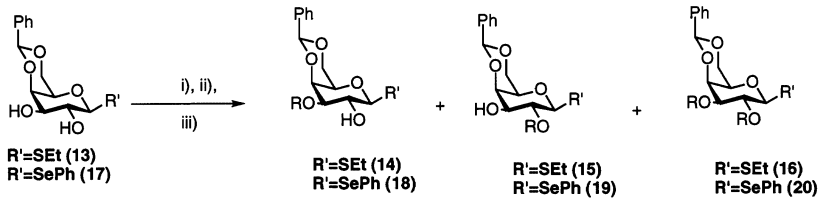


Reagents : i) NaH (2 eq.), THF; ii) $CuCl_2$ (1 eq.); iii) Alkylating or acylating agent

Alkylating or acylating reagent	R'	(2), (6) or (10) (%)[a]	(3), (7) or (11) (%)[a]	(4), (8) or (12) (%)[a]	(1), (5) or (9) (%)[a]
BzCl (a)	SEt	51 (48)	0	9 (7)	39 (37)
BzCl (a)	SePh	68 (65)	0	4	27 (25)
BzCl (a)	OPh	61	19	8 (7)	11 (9)
PivCl (b)	SEt	41	3	0	54 (53)
PivCl (b)	SePh	41 (39)	0	0	58 (55)
PivCl (b)	OPh	59	17	9 (8)	14 (11)
AcCl (c)	SEt	76 (74)	0	23 (21)	1 (1)
AcCl (c)	SePh	86 (81)	0	3 (3)	11 (10)
AcCl (c)	OPh	62	19	0	18 (15)
MeI (d)	SEt	6	0	0	94 (90)
MeI (d)	SePh	77 (75)	0	0	23 (21)
MeI (d)	OPh	64	23	0	13 (10)

[a] Ratios estimated from the ^1H nmr spectra of the crude reaction mixtures; isolated yields in brackets

Scheme 1.



Reagents : i) NaH (2 eq.), THF; ii) $CuCl_2$ (1 eq.); iii) Acylating agent (1.2 eq.)

Alkylating or acylating reagent	R'	(14) or (18) (%)[a]	(15) or (19) (%)[a]	(16) or (20) (%)[a]	(13) or (17) (%)[a]
BzCl	SEt	56 (50)	0	23 (22)	21
BzCl	SePh	71 (34)	0	0	29
PivCl	SEt	79 (40)	0	11 (10)	10
PivCl	SePh	64 (35)	0	0	36
AcCl	SEt	37	40	14	8
AcCl	SePh	74 (45)	2	13	10

[a] Ratios estimated from the ^{1}H nmr spectra of the crude reaction mixtures; isolated yields in brackets

Scheme 2.

to afford a predominance of the C-3 protected hermaphrodites as shown in Scheme 1.

For all of the acylated products, the signal for the H-3 proton in the ^{1}H NMR spectrum is shifted downfield for the C-3 acylated regioisomer, whilst the signal for the H-2 proton is shifted downfield for the C-2 acylated regioisomer. From these observations, and the integration of the peaks representing the benzylidene PhC*H* proton, it is possible to determine the ratio of regioisomers obtained in the crude reaction mixtures. Whenever possible, the isomeric products are separated by column chromatography on silica gel to provide accurate conversion yields. For alkylation experiments, extensive NMR correlation experiments are required to determine the isomeric composition of the product mixtures. In our hands, the alkylation reactions have proved more capricious than the acylation reactions, and at present, are restricted to regioselective methylation reactions.

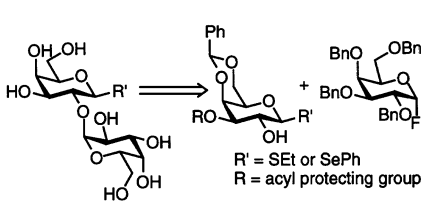
The copper- and enzyme-mediated protection methods provide complimentary methods for synthesising orthogonally protected glucopyranosides with a free hydroxyl group at C-2. Thus, whilst the yields and regioselectivities of the enzyme-mediated reactions often exceed those obtained chemically, a wider range of acyl groups can be introduced using the chemical method. Moreover, unlike the chemical method, the enzyme-mediated reactions provide no scope for regioselective alkylation. In the majority of cases, the chemical reactions are complete in much shorter reaction times than for the enzyme-mediated reactions.

In our previous enzyme studies we had investigated the regioselective protection of the C-3 hydroxyl group of 4,6-*O*-benzylidene-β-D-galactopyranosides. Although excellent regioselectivity could be achieved, the overall yields of conversion rendered the reaction of little synthetic use.[7] For example, ethyl 4,6-*O*-benzylidene - 1 - thio - β - D - galactopyranoside could be converted to the C-3 acetylated derivative with no trace of the C-2 acetylated isomer, but in only 10% yield, using PFL and vinyl acetate. Hence, we were keen to establish whether the copper-mediated protection protocol could be extended to encompass 4,6-*O*-benzylidene-β-D-galactopyranosides. The galactopyranoside diols required for the copper-mediated protection strategy were prepared according to literature procedures.[10] The diols were then treated with two equivalents of sodium hydride in anhydrous THF to form the di-alkoxide, according to our standard protocol. One equivalent of freshly prepared anhydrous copper(II) chloride was then added, following by 1.2 equivalents of the acylating agent. After work-up, analysis of the ^{1}H NMR spectrum of the crude reaction mixture allowed an estimation of the regioselectivity of the reaction. Whenever possible, the results were further verified by isolating the individual regioisomers by column chro-

matography. The results obtained in this way are highlighted in Scheme 2.

Hence regioselective protection in favour of the required C-3 protected regioisomer is possible for a range of galactopyranosides. The regioselectivity is enhanced significantly compared with the isomeric glucopyranoside derivatives. Moreover, although the isolated yields are generally lower than the glucopyranoside analogues, the process is still synthetically useful. For example, this method is currently being utilised in our laboratory for the large-scale synthesis of 2″-monoglycosylated-β-galactosyl donors for the synthesis of non-natural glycosylceramides (Scheme 3).

Preformation of the benzylidene di-alkoxide using sodium hydride is currently a prerequisite for efficient copper chelation in our synthetic protocol, and this may possibly hamper the extension of this work to incorporate the regioselective protection of fully deprotected monosaccharide derivatives, or disaccharide derivatives. Hence, to further extend the utility of this approach we were keen to determine whether alternative copper compounds could be utilised in the reaction, to effect chelation of the diol. In particular, we wished to establish a procedure that would allow efficient chelation of the diol without the need for alkoxide generation, using sodium hydride. Comprehensive reviews[11] have highlighted the necessary criteria for effective complexation of metals with polyols and have demonstrated that both the conformation of the polyol[12] and the ionic radius of the cation[13] influence the strength of the complexation. In general, the optimum ionic radius of the cation for complexing is 100–110 pm as illustrated by Na^+, Ca^{2+} and La^{3+}. Both larger and smaller cations complex somewhat less strongly and often necessitate prior polyol anion formation to allow effective complex formation. This is indeed the case for complexation of Cu^{2+}, with a cationic radius of 72 pm, to benzylidene protected glucopyranosides. Interestingly, $Cu(OAc)_2$ has been shown to complex strongly to polyols,[14] presumably via the $Cu(OAc)^+$ cation, without the need for prior polyol anion formation. This is in contrast to $Cu(NO_3)_2$ and $CuCl_2$, for which the enthalpy of interaction with non-deprotonated glycosides is small.[15] Hence the next stage of our research programme involved a study of the efficiency of $Cu(OAc)_2$ or $Cu(AcAc)_2$ to effect regioselective protection of ethyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside without prior anion formation. Good regioselectivity could be obtained using either complexing agent, and the selectivity could be further optimised by elevating the temperature to 55 °C and adding triethylamine as a base. In contrast, at a low temperature (−15 °C), no appreciable reaction took place. It also proved possible to perform the reaction in either THF or DME as the solvent, and to use acetyl chloride or acetic anhydride as the acylating agent. The optimum results obtained in this way with ethyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside are highlighted in Scheme 4.

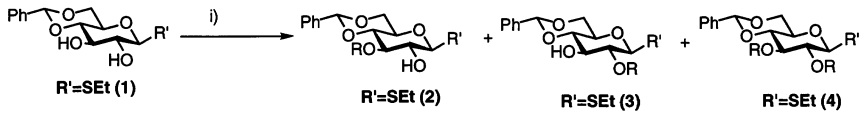


Scheme 3.

The full scope of this reaction and its application to the synthesis of oligosaccharides of biological importance is currently being investigated in our laboratory.

3. Experimental

General methods.—TLC adsorption chromatography was carried out using silica gel (E. Merck): (a) 60 F_{254} 0.2 mm aluminium-backed plates; (b) column chromatography using 70–230 mesh silica gel (E. Merck). Visualisation of the TLC plates was by 254 nm UV light and by spray-head development using a 25:1 EtOH–H_2SO_4 reagent or an ammonium molybdate reagent (15 g ammonium molybdate in 150 mL of 10% H_2SO_4). Anhydrous THF and DME were prepared by distillation from a sodium wire. When denoted in the general method preparations, reactions were carried out under an inert atmosphere of Ar or N_2. Solvents were evaporated at aspirator vacuum at about 35 °C unless otherwise stated. Optical rotation measurements were



Reagents : i) See table

Copper reagent	Acylating agent	Solvent	Base	Temp (°C)	(2)	(3)	(4)	(1)
$Cu(acac)_2$	AcCl	THF		25	50	40	10	0
"	AcOAc	THF	TEA	25	64	21	15	0
"	AcOAc	THF	TEA	-15	0	0	0	100
"	AcOAc	DME	TEA	25	14	9	0	77
$Cu(OAc)_2$	AcCl	THF		25	30	40	30	0
"	AcOAc	THF	TEA	25	43	24	33	0
"	AcOAc	THF	TEA	-15	0	0	0	100
"	AcOAc	DME	TEA	25	20	5	0	75
"	AcCl	DME	TEA	25	56	5	5	34
"	AcOAc	DME	TEA	55	65	8	5	22
"	AcCl	DME	TEA	55	55	5	10	30

Scheme 4.

carried out at the sodium D line (589.3 nm) using a Perkin–Elmer 341 polarimeter. ^1H and ^{13}C NMR spectra were recorded at 400 or 250 MHz and 100 or 60 MHz, respectively, using Brucker AMX 400 and Brucker DPX 250 machines; mass spectroscopic analyses were obtain in the chemical ionisation mode using a Fisons VG Autospec.

General method for acylation reaction.—The 4,6-*O*-benzylidene derivative (1 equiv) was dissolved in anhyd THF (100 mg in 10 mL THF) and NaH in mineral oil (60%) (2 equiv) was added. The formation of the disodium alcoholate was complete in 1 h at rt to give a thick white slurry. Anhydrous copper(II) chloride (1 equiv) was added to the alcoholate slurry which went to dissolution as a dark green solution. To the green chelate solution was added an acylating reagent (1.2 equiv) and the reaction left to stir under N_2 at rt for 5 h. To the solution was added water (3 mL) and 3% aq NH_3 solution (3 mL) to give a dark blue solution. The organic layer was separated and the aq layer extracted with EtOAc (5×5 mL). The organic fractions were combined, dried ($MgSO_4$) and the excess solvent removed in vacuo to yield a pale yellow oil which when subjected to column chromatography (10:1 CH_2Cl_2–acetone, + 1% Et_3N) yielded the protected benzylidene derivatives.

Alkylation reaction.—The 4,6-*O*-benzylidene derivative (1 equiv) was dissolved in anhyd THF (100 mg in 10 mL THF) and NaH in mineral oil (60%) (2 equiv) was added. The formation of the disodium alcoholate was complete in 1 h at rt to give a thick white slurry. Anhydrous copper(II) (1 equiv) was added to the alcoholate slurry, which went to dissolution as a dark green solution. To the green chelate solution was added an alkylating reagent (5.0 equiv), the reaction was heated to reflux temperature and left to stir under N_2 for 24 h. The solution was cooled to rt, then water (3 mL) and 50% aq NH_3 solution (3 mL) were added to give a dark blue solution. The organic layer was separated and the aq layer extracted with EtOAc (5×5 mL). The organic fractions were combined, dried ($MgSO_4$) and the excess solvent removed in vacuo to yield a pale yellow oil which when subjected to column chromatography (10:1 CH_2Cl_2–acetone, + 1% Et_3N) yielded the protected benzylidene derivatives.

General method for copper acetylacetanoate reactions.—The 4,6-*O*-benzylidene protected glucose derivative (1 equiv) was dissolved in anhyd THF (100 mg in 10 mL) and copper acetoactanoate (1 equiv) added. The mixture was stirred for 1 h at rt to give a blue solution. To the blue chelate solution was added Ac_2O (1.2 equiv) and Et_3N (1.2 equiv) and the reaction was left to stir under N_2 at rt for 5 h. To the solution was added water (3 mL) and 50% aq NH_3 solution (3 mL) to give a dark blue solution. The organic layer was separated and

the aq layer extracted with EtOAc (5 × 5 mL). The organic fractions were combined, dried ($MgSO_4$) and the excess solvent removed in vacuo to yield a pale yellow oil which when subjected to column chromatography (10:1 CH_2Cl_2–acetone, + 1% Et_3N) yielded the protected benzylidene glucose derivatives.

General method for copper acetate reactions.—The 4,6-*O*-benzylidene protected glucose (1 equiv) was dissolved in anhyd DME (100 mg in 10 mL) and copper acetate (1 equiv) was added. The mixture was stirred for 1 h at rt to give a blue solution. To the blue chelate solution was added acetyl chloride (1.2 equiv) and Et_3N (1.2 equiv) and the reaction left to stir under nitrogen at rt for 5 h. To the solution was added water (3 mL) and 50% aq NH_3 solution (3 mL) to give a dark blue solution. The organic layer was separated and the aq layer extracted with EtOAc (5 × 5 mL). The organic fractions were combined, dried ($MgSO_4$) and the excess solvent removed in vacuo to yield a pale yellow oil which when subjected to column chromatography (10:1 CH_2Cl_2–acetone, + 1% Et_3N) yielded the protected benzylidene glucose derivatives.

*Ethyl 3-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-β-*D*-glucopyranoside* (**2a**).—Colourless oil (48%); $[\alpha]_D^{20}$ −67.0° (*c* 1.02 in $CHCl_3$), [lit.[16] $[\alpha]_D^{20}$ −122.9 (*c* 0.77 in $CHCl_3$)]; ν_{max} 3362 br (O–H), 2984 s (C–H), 2826 s (C–H), 1714 vs (C=O), 1446 s (C–H), 1374 vs (C–H), 1267 vs (C–O), 1082 s (C–O), 1024 s (C–O) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.25 (3 H, t, *J* 7.5, SCH_2CH_3), 2.68–2.71 (2 H, m, SCH_2CH_3), 2.78 (1 H, d, *J* 2.0, OH), 3.34–3.50 (2 H, m, H-2, H-5), 3.60–3.72 (2 H, m, H-4, H-6_a), 4.24 (1 H, dd, *J* 5.0, 10.5, H-6_b), 4.72 (1 H, d, *J* 10.0, H-1), 5.39–5.46 (2 H, m, H-3, Ph–C*H*), 7.23–7.42 (5 H, m, ArH); δ_C (60 MHz, $CDCl_3$) 15.25 (SCH_2CH_3), 24.92 (SCH_2CH_3), 67.50 (C-6), 71.48 (C-5), 73.09 (C-2), 75.74 (C-3), 77.32 (C-4), 88.12 (C-1), 101.42 (Ph*C*H), 126.11, 128.03, 128.21, 129.07, 130.45, 131.78 136.86 (Ar{C-1, C-2, C-3, C-4, C-5, C-6}), 158.9 (PhO{C-1}), 170.01 (CH_2CO_2); *m*/*z* (CI) 417 (M + H, 25%), 355 (27), 311 (24), 249 (37), 219 (100), 43 (59). (Found [M + H] 417.1361. $C_{22}H_{25}SO_6$ requires 417.1372.)

*Ethyl 3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-β-*D*-glucopyranoside* (**2b**).—Brown viscous oil (41%); $[\alpha]_D^{20}$ −66.9° (*c* 1.02 in $CHCl_3$), [lit[7a] $[\alpha]_D^{20}$ −67.0 (*c* 1.02 in $CHCl_3$)]; ν_{max} 3492 br (O–H), 3067 w and 3037 w (C–H), 2981 s (C–H), 1737 vs and 1715 vs (C=O), 1481 s and 1397 s (C–H), 1282 s and 1079 s and 1019 s (C–O), 751 s and 698 s (Ar), 653 w (S–C) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.16 (9 H, s, $(CH_3)_3CO$), 1.25 (3 H, t, *J* 7.5, SCH_2CH_3), 2.68–2.71 (2 H, m, SCH_2CH_3), 2.73 (1 H, d, *J* 2.0, OH), 3.45–353 (2 H, m, H-2, H-5), 3.61 (1 H, t, *J* 9.5, H-4), 3.70 (1 H, t, *J* 10.5, H-6_a), 4.29 (1 H, dd, *J* 5.0, 10.5, H-6_b), 4.44 (1 H, d, *J* 10.0, H-1), 5.12 (1 H, t, *J* 9.0, H-3) 5.45 (1 H, s, Ph–C*H*), 7.26–7.35 (5 H, m, ArH); δ_C (60 MHz, $CDCl_3$); 15.25 (SCH_2CH_3), 25.00 (SCH_2CH_3), 27.08 ($CH_3)_3C$) 38.97 ($(CH_3)_3CCO$) 68.56 (C-6), 70.64 (C-5), 72.32 (C-2), 74.87 (C-3), 78.43 (C-4), 87.23 (C-1), 101.07 (Ph*C*H), 125.85, 128.18, 128.34, 128.93, 129.02, 136.92 (Ar{C-1, C-2, C-3, C-4, C-5, C-6}), 178.78 ($(CH_3)_3CCO$); *m*/*z* (CI) 415 ($M + NH_4^+$, 24%), 397 (M + H, 80), 335 (72), 291 (100), 229 (64), 199 (48), 149 (61), 105 (63), 85 (48), 57 (53). (Found [M + H] 397.1705. $C_{20}H_{29}SO_6$ requires 397.1684.)

*Ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-*D*-glucopyranoside* (**2c**).—White solid (74%); m.p. 115–117 °C [lit.[9] 118–120 °C]; $[\alpha]_D^{20}$ −65.0° (*c* 1.0 in $CHCl_3$), [lit.[9] −67.3 (*c* 1.03 in $CHCl_3$)]; ν_{max} 3372 br (O–H), 2984 s (C–H), 2826 s (C–H), 1714 vs (C=O), 1446 s (C–H), 1374 vs (C–H), 1267 vs (C–O), 1082 s (C–O), 1024 s (C–O) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.25 (3 H, t, *J* 7.5, SCH_2CH_3), 2.06 (3 H, s, CH_3COO), 2.67–2.70 (2 H, m, SCH_2CH_3), 3.45–3.52 (2 H, m, H-2, H-5), 3.58 (1 H, app. t, *J* 9.0, 9.5, H-4), 3.69 (1 H, app. t, *J* 10.0, 10.5, H-6), 4.27 (1 H, dd, *J* 5.0, 10.5, H-6), 4.43 (1 H, d, *J* 10.0, H-1), 5.16 (1 H, app. t, *J* 9.0, 9.5, H-3) 5.42 (1 H, s, Ph–C*H*), 7.27–7.38 (5 H, m, ArH); δ_C (60 MHz; $CDCl_3$) 15.25 (SCH_2CH_3), 21.01 (CH_3COO), 24.92 (SCH_2CH_3), 68.50 (C-6), 70.48 (C-5), 72.09 (C-2), 74.74 (C-3), 78.32 (C-4), 87.12 (C-1), 101.42 (Ph*C*H), 126.11, 128.21, 129.07, 136.86 (Ar{C-1, C-2, C-3, C-4, C-5, C-6}), 171.01 (CH_3CO_2); *m*/*z* (CI) 355 (M + H, 24%), 293 (23), 249 (39), 187 (32),

105 (100), 43 (59). (Found [M + H] 355.1221. $C_{17}H_{23}O_6$ requires 355.1215.)

*Ethyl 3-*O*-methyl-4,6-*O*-benzylidene-1-thio-β-*D*-glucopyranoside* (**2d**).—Colourless oil (6%); m.p. 117–120 °C, [lit.[9] 134 °C]; $[\alpha]_D^{20}$ − 32.1° (*c* 1.03 in $CHCl_3$), [lit.[9] − 60 (*c* 1.46 in $CHCl_3$)]; ν_{max} 3372 br (O–H), 2984 s (C–H), 2854 s (C–H), 1446 s (C–H), 1374 vs (C–H); δ_H (250 MHz, $CDCl_3$) 1.25 (3 H, t, *J* 7.5, SCH_2CH_3), 2.67–2.70 (2 H, m, SCH_2CH_3), 3.48 (3 H, s, CH_3O), 3.45–3.52 (2 H, m, H-2, H-5), 3.58 (1 H, app. t, *J* 9.0, 9.5, H-4), 3.69 (1 H, app. t, *J* 10.0, 10.5, H-6_a), 4.27 (1 H, dd, *J* 5.0, 10.5, H-6_b), 4.43 (1 H, d, *J* 10.0, H-1), 5.16 (1 H, app. t, *J* 9.0, 9.5, H-3) 5.42 (1 H, s, Ph–C*H*), 7.27–7.38 (5 H, m, ArH); δ_C (60 MHz, $CDCl_3$) 15.25 (SCH_2CH_3), 16.01 (CH_3O), 24.92 (SCH_2CH_3), 68.50 (C-6), 70.48 (C-5), 72.09 (C-2), 74.74 (C-3), 78.32 (C-4), 87.12 (C-1), 101.42 (Ph*C*H), 126.11, 128.21, 129.07, 136.86 (Ar{C-1, C-2, C-3, C-4, C-5, C-6}); *m*/*z* (CI) 327 (M + H, 23%), 265 (24), 221 (37), 159 (33), 105 (100), 43 (43). (Found [M + H] 327.1259. $C_{16}H_{23}SO_5$ requires 327.1266.)

*Phenyl 3-*O*-benzoyl-4,6-*O*-benzylidene-1-seleno-β-*D*-glucopyranoside* (**6a**).—Clear gum (65%); $[\alpha]_D^{20}$ − 73.5° (*c* 1.02 in $CHCl_3$); ν_{max} 3424 br (O–H), 2930 w, 2880 s (C–H), 1740 vs (C=O), 1600 s (C=C), 1590 w (C=C) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 3.44–3.79 (4 H, m, H-2, H-4, H-5, H-6_a), 4.39 (1 H, dd, *J* 4.5, 9.0, H-6_b), 4.85 (1 H, d, *J* 9.0, H-1), 5.39 (1 H, t, *J* 9.0, H-3), 5.43 (1 H, s, Ph–C*H*), 7.19–7.60 (15 H, m, ArH);); δ_C (60 MHz; $CDCl_3$) 67.50 (C-6), 73.09 (C-2), 75.74 (C-3), 77.32 (C-4), 78.48 (C-5), 87.12 (C-1), 101.42 (Ph*C*H), 117.46, 118.67, 119.36, 120.68, 126.11, 126.89, 127.56, 128.43, 128.45, 129.12, 130.56, 131.28 136.79 (SeAr, Ar{C-1, C-2, C-3, C-4, C-5, C-6}), 158.5 (PhO{C-1}, 170.89 (CH_3CO_2). *m*/*z* (CI) 513 (M + H, 23%), 406 (29), 355 (69), 312 (32), 148 (35), 127 (49), 105 (100), 71 (87), 43 (75). (Found [M + H] 513.0809. $C_{26}H_{25}O_6Se$ requires 513.0816.)

*Phenyl 3-*O*-pivaloyl-4,6-*O*-benzylidene-1-seleno-β-*D*-glucopyranoside* (**6b**).—Clear gum (39%); $[\alpha]_D^{20}$ − 64.0° (*c* 1.02 in $CHCl_3$); ν_{max} 3424 br (O–H), 3057 w, 3042 w, 2930 w, 2880 s (C–H), 1745 vs (C=O), 1600 s (C=C), 1590 w (C=C), 1497 s (C=C) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.22 (9 H, s, $(CH_3)_3CCO$), 3.39–3.52 (2 H, m, H-2, H-5), 3.68–3.73 (2 H, m, H-5, H-6_a), 4.28–4.33 (1 H, m, H-6_b), 4.84 (1 H, d, *J* 10.2, H-1), 5.09 (1 H, t, *J* 9.1, H-3), 5.44 (1 H, s, Ph–C*H*), 7.24–7.59 (10 H, m, ArH); δ_C (60 MHz, $CDCl_3$) 27.29 ($(CH_3)_3CCOO$), 39.31 ($(CH_3)_3CCOO$), 67.50 (C-6), 73.09 (C-2), 75.74 (C-3), 77.32 (C-4), 78.48 (C-5), 87.12 (C-1), 101.42 (Ph*C*H), 126.11, 127.11, 127.76, 128.03, 128.21, 129.07, 130.45, 131.78 136.86 (SeAr, Ar{C-1, C-2, C-3, C-4, C-5, C-6}), 158.9 (PhO{C-1}, 170.01 (CCO_2); *m*/*z* (CI) 493 (M + H, 24%), 386 (32), 335 (67), 292 (31), 275 (59), 148 (41), 127 (53), 105 (100), 78 (85), 43 (71). (Found [M + H] 493.1121. $C_{24}H_{29}O_6Se$ requires 493.1129.)

*Phenyl 3-*O*-acetyl-4,6-*O*-benzylidene-1-seleno-β-*D*-glucopyranoside* (**6c**).—White solid (81%); m.p. 156–159 °C; $[\alpha]_D^{27}$ − 18.7° (*c* 0.15 in $CHCl_3$); ν_{max} 3465 br (O–H), 2954 w, 2885 s (C–H), 1740 s (C=O), 1600 s (C=C), 1591 w (C=C), 1495 s (C=C) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.11 (3 H, s, CH_3COO) 3.51–3.58 (3 H, m, H-2, H-4, H-5), 3.76 (1 H, app. t, *J* 10.5, 9.5, H-6_a), 4.40 (1 H, app. t, *J* 4.5, 10.5, H-6_b), 4.87 (1 H, d, *J* 10.0, H-1), 5.20 (1 H, t, *J* 9.0, H-3), 5.48 (1 H, s, Ph–C*H*), 7.31–7.66 (10 H, m, ArH); δ_C (60 MHz, $CDCl_3$) 20.98 (CH_3COO), 68.51 (C-6), 71.89, 72.24, 74.60, 78.20 (C-5, C-2, C-3, C-4), 85.43 (C-1), 101.50 (Ph*C*H), 126.12, 128.24, 128.73, 129.13, 129.26, 131.49, 135.41, 136.80 (Ar ArSe{C-1, C-2, C-3, C-4, C-5, C-6}), 171.07 (CH_3CO_2); *m*/*z* (CI) 451 (M + H, 18%), 390 (5), 344 (36), 293 (71), 250 (36), 233 (55), 187 (30), 148 (44), 127 (51), 105 (100), 78 (82), 43 (72). (Found [M + H] 451.0649. $C_{21}H_{23}O_6Se$ requires 451.0659.)

*Phenyl 3-*O*-methyl-4,6-*O*-benzylidene-1-seleno-β-*D*-glucopyranoside* (**6d**).—Colourless oil (75%); $[\alpha]_D^{20}$ − 24.0° (*c* 1.01 in $CHCl_3$), [lit.[17] $[\alpha]_D^{20}$ − 38° (*c* 1.0 in $CHCl_3$)]; ν_{max} 3334 br (O–H), 2980 s (C–H), 2854 s (C–H), 1445 s (C–H), 1372 vs (C–H) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.68 (1 H, d, *J* 2.0 Hz, OH), 3.40 (3 H, s, C-3OCH_3), 3.47–3.49 (2 H, m, H-2, H-5), 3.57–3.59 (1 H, m, H-4), 3.62 (3 H, s, C-1), 3.66 (1 H, t, *J* 9.8 Hz, H-6), 3.72–3.78 (1 H, m, H-3), 4.19–4.23 (1 H, dd, *J* 5.0, 9.8 Hz, H-6), 4.94 (1 H, d, *J* 2.5 Hz, H-1), 5.47 (1 H, s, Ph–C*H*), 7.28–7.44 (10 H, m, ArH); δ_C (60

MHz; $CDCl_3$) 67.50 (C-5), 69.75 (C-6), 80.10 (C-2), 80.85 (C-3), 85.35 (C-2), 94.26 (C-1), 100.15 (PhCH), 124.45, 124.65, 127.32, 127.43, 127.55, 127.85, 128.25 (Ar, PhO{C-2, C-3, C-4, C-5, C-6}), 134.78 (Ar{C-1}), 168.15 (PhO{C-1); *m/z* (CI) 423 (M + H, 21%), 362 (7), 317 (29), 265 (65), 222 (39), 205 (57), 190 (44), 159 (34), 127 (46), 105 (100), 78 (74), 43 (67). (Found [M + H] 423.0701. $C_{20}H_{23}O_5Se$ requires 423.0711.)

*Phenyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**10a**).—White solid (61%). m.p. 201–204 °C; [lit.[18] 207 °C]; $[\alpha]_D^{27}$ −67.6° (*c* 1.02 in $CHCl_3$), [lit.[18] $[\alpha]_D^{20}$ −72° (*c* 1 in $CHCl_3$)]; ν_{max} 3362 br (O–H), 2984 s (C–H), 2826 s (C–H), 1714 vs (C=O), 1446 s (C–H), 1374 vs (C–H), 1267 vs (C–O), 1082 s (C–O), 1024 s (C–O) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 3.45–3.57 (3 H, m, H-2, H-4, H-6_a), 3.89–4.01 (1 H, m, H-5), 4.34–4.56 (1 H, app. dd, *J* 4.5, 9.5, H-6_b), 5.16 (1 H, d, *J* 7.5, H-1), 5.38 (1 H, t, *J* 9.5, H-3), 5.51 (1 H, s, Ph–C*H*), 6.78–7.32 (15 H, m, Ar); δ_C (60 MHz, $CDCl_3$) 64.40 (C-5), 69.06 (C-6), 72.28 (C-2), 74.18 (C-3), 82.19 (C-4), 96.69 (C-1), 102.36 (PhCH), 117.83, 123.59, 127.29, 128.75, 129.59, 130.47 (Ar, PhO{C-2, C-3, C-4, C-5, C-6}), 138.92 (Ar{C-1}), 157.90 (PhO{C-1); *m/z* (CI) 449 (M + H, 35%), 355 (100), 347 (15), 249 (21), 149 (22), 129 (9), 105 (35), 94 (19), 57 (29), 39 (5).

*Phenyl 3-*O*-pivaloyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**10b**).—Brown viscous oil (59%); $[\alpha]_D^{27}$ −64.1° (*c* 1.01 in $CHCl_3$); ν_{max} 3362 br (O–H), 2984 s (C–H), 2826 s (C–H), 1714 vs (C=O), 1446 s (C–H), 1374 vs (C–H), 1267 vs (C–O), 1082 s (C–O), 1024 s (C–O) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.14 (9 H, s, $(CH_3)_3CCOO$), 3.58–3.69 (3 H, m, H-2, H-4, H-6_a), 3.94–4.00 (1 H, m, H-5), 4.15–4.19 (1 H, app. dd, *J* 4.5, 9.5, H-6_b), 5.07 (1 H, d, *J* 7.5, H-1), 5.35 (1 H, t, *J* 9.5, H-3), 5.50 (1 H, s, Ph–C*H*), 6.95–7.42 (10 H, m, Ar); δ_C (60 MHz, C_3D_6O) 27.29 ($(CH_3)_3CCOO$), 39.31 ($(CH_3)_3CCOO$), 64.40 (C-5), 69.06 (C-6), 72.28 (C-2), 74.18 (C-3), 82.19 (C-2), 96.69 (C-1), 102.36 (PhCH), 117.83, 123.59, 127.29, 128.75, 129.59, 130.47 (Ar, PhO{C-2, C-3, C-4, C-5, C-6}), 138.92 (Ar{C-1}), 157.90 (PhO{C-1); *m/z* (CI) 429 (M + H, 37%), 335 (M–OPh, 100), 327 (17), 317 (7), 229 (21), 211 (11), 162 (7), 149 (28), 129 (9), 105 (37), 94 (20), 91 (12), 77 (8), 66 (8), 65 (8), 57 (27), 43 (8), 39 (6). (Found [M + H] 429.1564. $C_{23}H_{28}O_6$ requires 429.1913.)

*Phenyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**10c**).—White solid (62%); m.p. 205–209 °C; $[\alpha]_D^{20}$ −66.5° (*c* 1.02 in $CHCl_3$); ν_{max} 3424 br (O–H), 3057 w, 3042 w, 2930 w, 2880 s (C–H), 1745 vs (C=O), 1600 s (C=C), 1590 w (C=C), 1497 s (C=C) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.16 (3 H, s, CH_3COO), 3.55–3.91 (4 H, m, H-2, H-5, H-4, H-6_a), 4.36–4.43 (1 H, m, H-6_b), 5.11 (1 H, d, *J* 7.5, H-1), 5.31 (1 H, t, *J* 9.5, H-3), 5.52 (1 H, s, Ph–C*H*), 6.99–7.51 (10 H, m, Ar); δ_C (60 MHz, $CDCl_3$) 25.29 (CH_3COO), 66.30 (C-6), 71.75 (C-5), 73.25 (C-2), 75.82 (C-3), 81.93 (C-4), 95.92 (C-1), 101.35 (PhCH), 117.63, 123.82, 127.28, 128.55, 129.25, 130.88, 137.28 (ArC), 161.68 (CH_3COO); *m/z* (CI) 387 (M + H, 21%), 293 (M–OPh, 97), 233 (14), 187 (30), 149 (38), 127 (25), 105 (23), 94 (28), 92 (68), 91 (81), 77 (19), 58 (21), 43 (100), 39 (14). (Found [M + H] 387.1444. $C_{21}H_{22}O_7$ requires 387.1443.)

*Phenyl 3-*O*-methyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**10d**).—Colourless solid (64%); m.p. 203–206 °C [lit.[19] 211 °C]; $[\alpha]_D^{20}$ −43.2° (*c* 1.04 in $CHCl_3$), [lit.[19] $[\alpha]_D^{20}$ −46.2° (*c* 1 in $CHCl_3$)]; ν_{max} 3369 br (O–H), 2982 s (C–H), 2854 s (C–H), 1445 s (C–H), 1372 vs (C–H) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.73 (1 H, d, *J* 2.0, OH), 3.38 (2 H, s, C-3–OCH_3), 3.47–3.49 (2 H, m, H-2, H-5), 3.55–3.57 (1 H, m, H-4), 3.58 (3 H, s, C-1–O–CH_3), 3.66 (1 H, t, *J* 9.8, H-6), 3.72–3.78 (1 H, m, H-3), 4.19–4.23 (1 H, dd, *J* 5.0, 9.8, H-6), 4.72 (1 H, d, *J* 2.5, H-1), 5.47 (1 H, s, Ph–C*H*), 7.28–7.44 (10 H, m, ArH); δ_C (60 MHz, $CDCl_3$) 67.50 (C-5), 69.75 (C-6), 80.20 (C-2), 80.95 (C-3), 85.45 (C-2), 96.56 (C-1), 100.15 (PhCH), 124.85, 124.95, 127.25, 127.35, 127.4, 127.95, 128.80 (Ar, PhO{C-2, C-3, C-4, C-5, C-6}), 136.20 (Ar{C-1}), 164.75 (PhO{C-1}); *m/z* (CI) 359 (M + H, 24%), 265 (92), 205 (17), 159 (29), 149 (34), 127 (29), 105 (21), 94 (23), 92 (71), 91 (78), 43 (100). (Found [M + H] 359.1487. $C_{20}H_{23}O_6$ requires 359.1495.)

*Ethyl 3-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-β-*D*-galactopyranoside* (**14a**).—Colourless solid (50%); m.p. 127–128.5 °C, [lit.[16]

129.5–130.5 °C]; $[\alpha]_D^{20}$ + 52.1° (*c* 1.0, $CHCl_3$), [lit.[16] + 57.9°, *c* 1.0, $CHCl_3$)]; ν_{max} ($CHCl_3$) 3480 (O–H), 1720 (C=O), 1450 (C–H) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.38 (3 H, t, *J* 7.5, SCH_2CH_3) 2.78–2.91 (2 H, m, SCH_2CH_3), 3.66 (1 H, d, *J* 1.4, H-5), 4.07 (1 H, dd, *J* 1.4, *J′* 12.5, H-6), 4.26 (1 H, app. t, *J* 9.6, H-2), 4.39 (1 H, dd, *J* 1.4, *J′* 12.5, H-6), 4.52 (1 H, d, *J* 9.6, H-1), 4.55 (1 H, dd, *J* 1.4, *J′* 3.5, H-4), 5.19 (1 H, dd, *J* 3.5, *J′* 9.6, H-3), 5.53 (1 H, s, PhC*H*), 7.36–7.59 (8 H, m, Ph–H), 8.09–8.13 (2 H, m, Ph–H); δ_C (60 MHz, $CDCl_3$) 15.7 (SCH_2CH_3), 23.8 (SCH_2CH_3), 67.1 (C-2), 69.6 (C-6), 70.4 (C-5), 74.4 (C-4), 75.7 (C-3), 86.4 (C-1), 101.3 (Ph*C*H), 126.6, 128.5, 128.8, 129.3, 130.1, 130.4, 133.7, 138.2, (Ar–C), 166.8 (C=O); *m*/*z* (CI) 417 (M + H, 8%), 355 (63), 311 (30), 149 (27), 105 (100). (Found [M + H] 417.1389. $C_{22}H_{25}O_6S$ requires 417.1389.)

*Ethyl 3-*O*-pivaloyl-4,6-*O*-benzylidene-1-thio-β-*D*-galactopyranoside* (**14b**).—Colourless solid (40%), m.p. 106.5–108 °C; $[\alpha]_D^{20}$ 48.5° (*c* 1.0, $CHCl_3$); ν_{max} ($CHCl_3$) 3480 (O–H), 2970 (C–H), 1730 (C=O) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.17 (9 H, s, $C(CH_3)_3$) 1.24 (3 H, t, *J* 7.4, SCH_2CH_3), 2.63–2.76 (SCH_2CH_3), 3.48 (1 H, d, *J* 1.6, H-5), 3.92 (1 H, dd, *J* 1.6, *J′* 12.5, H-6), 4.00 (1 H, d, *J* 9.6, H-2), 4.25 (1 H, dd, *J* 1.6, *J′* 12.5, H-6), 4.32–4.36 (2 H, m, H-1, H-4), 4.77 (1 H. dd, *J* 3.6, *J′* 9.6, H-3), 5.41 (1 H, s, PhC*H*), 7.25–7.30 (3 H, m, Ph–H), 7.37–7.41 (2 H, m, Ph–H); δ_C (60 MHz, $CDCl_3$) 15.7 (SCH_2CH_3) 23.9 (SCH_2CH_3), 27.5 ($C(CH_3)$), 39.4 ($C(CH_3)$), 67.0 (C-2), 69.6 (C-6), 70.3 (C-5), 74.1 (C-4), 75.1 (C-3), 86.3 (C-1), 101.0 (Ph*C*H), 126.4, 126.8, 128.5, 128.7, 129.2, 138.2 (Ar–C), 178.8 (C=O); *m*/*z* (CI) 397 (M + H, 17%), 335 (100), 291 (54), 247 (65), 149 (70), 57 (66). (Found [M + H] 397.1691. $C_{20}H_{29}O_6S$ requires 397.1702.)

*Ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-*D*-galactopyranoside* (**14c**).—δ_H (250 MHz, $CDCl_3$) 1.23 (3 H, t, *J* 7.5, SCH_2CH_3), 2.07 (3 H, s, $COOCH_3$), 2.55–2.79 (2 H, m, SCH_2CH_3), 3.45–3.47 (1 H, m, H-5), 3.94 (1 H, dd, *J* 1.8, 12.5, H-6), 3.96 (1 H, dd, *J* 1.8, 12.5, H-6), 3.99 (1 H, app. t, *J* 9.6, H-2), 4.33 (1 H, dd, *J* 1.0, 3.5, H-4), 4.34 (1 H, d, *J* 9.6, H-1), 4.81 (1 H, dd, *J* 3.5, 9.6, H-3), 5.42 (1 H, s, PhC*H*), 7.28–7.43 (5 H, m, Ph–H); δ_C (60 MHz, $CDCl_3$) 15.3 (SCH_2CH_3), 21.5 ($COOCH_3$), 23.4 (SCH_2CH_3), 66.8 (C-2), 69.6 (C-6), 70.3 (C-5), 72.9 (C-4), 75.3 (C-3), 82.9 (C-1), 126.7, 128.6, 129.5, 137.8 (ArC), 170.9 (C=O); *m*/*z* (CI) 355 (M + H, 23%), 293 (100), 249 (31), 187 (20), 149 (15), 105 (12).

*Phenyl 3-*O*-benzoyl-4,6-*O*-benzylidene-1-seleno-β-*D*-galactopyranoside* (**18a**).—Colourless solid (34%); m.p. 60.5–62.0 °C; $[\alpha]_D^{20}$ + 3.8° (*c* 1.0, $CHCl_3$); ν_{max} ($CHCl_3$) 3480 (O–H), 3060 (Ph–H), 2860 (C–H), 1720 (C=O) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 3.55 (1 H, d, *J* 1.0, H-5), 3.93 (1 H, dd, *J* 1.7, 12.5, H-6), 4.08 (1 H, dt, *J* 2.3, *J′* 9.7, H-2), 4.30 (1 H, dd, *J* 1.0, *J′* 12.4, H-6), 4.40 (1 H, dd, *J* 1.0, *J′* 3.4, H-4), 4.80 (1 H, d, *J* 9.7, H-1), 5.08 (1 H, dd, *J* 3.4, *J′* 9.7, H-3), 5.39 (1 H, s, PhC*H*), 7.10–7.32 (11 H, m, Ph–H), 7.66–7.70 (2 H, m, Ph–H), 7.91–7.96 (2 H, m, Ph–H); δ_C (60 MHz, $CDCl_3$) 67.0 (C-2), 69.5 (C-6), 71.3 (C-5), 74.4 (C-4), 75.3 (C-3), 84.9 (C-1), 101.1 (Ph*C*H), 126.6, 126.8, 127.0, 128.5, 128.6, 128.8, 129.4, 129.6, 130.0, 130.1, 130.6, 133.3, 133.7, 135.6, 138.2 (Ar–C), 166.8 (C=O); *m*/*z* (CI) (M + H, 4%), 407 (45), 355 (100), 248 (19), 148 (38), 105 (96). (Found [M + H] 513.0826. $C_{26}H_{25}O_6Se$ requires 513.0816.)

*Phenyl 3-*O*-pivaolyl-4,6-*O*-benzylidene-1-seleno-β-*D*-galactopyranoside* (**18b**).—Colourless solid (35%); m.p. 146–148 °C; $[\alpha]_D^{20}$ + 12.7 (*c* 1.0, $CHCl_3$); ν_{max} ($CHCl_3$) 3480 (O–H), 2970 (C–H), 1730 (C=O) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.18 (9 H, s, ($C(CH_3)_3$)), 2.47 (1 H, br s, OH), 3.58 (1 H, app. d, *J* 1.2, H-5), 4.00 (1 H, dd, *J* 1.7, 12.5, H-6), 4.05 (1 H, app. t, *J* 9.7, H-2), 4.37 (1 H, dd, *J* 1.7, 12.5, H-6), 4.39 (1 H, dd, *J* 0.9, 3.5, H-4), 4.83 (1 H, d, *J* 9.7, H-1), 4.84 (1 H, dd, *J* 3.5, 9.7, H-3), 5.48 (1 H, s, PhC*H*), 7.13–7.42 (8 H, m, ArH), 7.72–7.74 (2 H, m, ArH); δ_C (60 MH, $CDCl_3$) 27.4 ($C(CH_3)$) 39.4 ($C(CH_3)$), 67.0 (C-2), 69.6, 71.2, 74.0, 74.6 (C-6), 85.2 (C-1), 100.8 (Ph*C*H), 126.5, 126.9, 128.5, 129.3, 129.5, 135.2, 138.3 (Ar–C), 178.8 (C=O); *m*/*z* (CI) 493 (M + H, 4%), 387 (32), 335 (100), 229 (20), 149 (70), 85 (17), 57 (29). (Found [M + H] 493.1125. $C_{24}H_{29}O_6Se$ requires 493.1129.)

*Phenyl 3-*O*-acetyl-4,6-*O*-benzylidene-1-seleno-β-*D*-galactopyranoside* (**18c**).—Colourless solid (45%); m.p. 66–67 °C; $[\alpha]_D^{20}$ + 9.2° (*c* 1.0, $CHCl_3$); ν_{max} ($CHCl_3$) 3460 (O–H), 2880

(C–H), 1735 (C=O) cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.01 (3 H, s, OCH_3), 3.52 (1 H, *J* 1.7, H-5), 3.91 (1 H, t, *J* 9.7, H-2), 3.94 (1 H, dd, *J* 1.7, *J′* 12.5, H-6), 4.27–4.33 (2 H, m, H-4, H-6), 4.75 (1 H, d, *J* 9.7, H-1), 4.82 (1 H, dd, *J* 3.4, *J′* 9.7, H-3), 5.39 (1 H, s, PhC*H*), 7.09–7.29 (8 H, m, Ph–H), 7.66–7.70 (2 H, m, Ph–H); δ_C (60 MHz, $CDCl_3$) 66.7 (C-5), 69.6 (C-6), 71.1 (C-2), 74.1 (C-4), 74.8 (C-3), 84.7 (C-1), 101.3 (Ph*C*H), 126.0, 126.8, 128.6, 128.7, 129.5, 129.6, 135.8, 138.1 (Ar–C), 171.4 (C=O); *m*/*z* (CI) 451 (M + H, 7%), 344 (34), 293 (100), 187 (28), 149 (25). (Found [M + H] 451.0660. $C_{21}H_{23}O_6Se$ requires 451.0660.)

Acknowledgements

We are grateful to the EPSRC (Fast track award to WGS), The University of Reading Research Endowment Trust Fund (studentship to VAB) and the Royal Society (Equipment grant) for financial support of this work.

References

[1] For example see (a) McAuliffe, J.; Hindsgaul, O. *Chem. Ind.* **1997**, 153. (b) Varki, A. *Glycobiology* **1993**, *3*, 97. (c) Sharon, N.; Lis, H. *Sci. Am.* **1993**, *268*, 84.
[2] For recent reviews in this area see (a) Boons, G. -J. *Contemp. Org. Synth.* **1996**, *3*, 173. (b) Boons, G. -J. *Tetrahedron* **1996**, *52*, 1095. (c) Danishefsky, S. J.; Roberge, J. Y. *Pure Appl. Chem.* **1995**, *67*, 1647.
[3] Barresi, F.; Hindsgaul, O. *J. Carbohydr. Chem.* **1995**, *14*, 1043.
[4] (a) Collins, P. M.; Ferrier, R. J. *Monosaccharides: Their Chemistry and their Roles in Natural Products*; Wiley: Chichester, 1995 Ch. 5;
(b) Haines, A. H. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 11.
[5] (a) Eby, R.; Schuerch, C. *Carbohydr. Res.* **1982**, *100*, C41;
(b) Eby, R.; Webster, K. T.; Schuerch, C. *Carbohydr. Res.* **1984**, *129*, 111;
(c) Avela, E.; Holmbom, B. *Acta Acad. Abstract Ser. B* **1971**, *14*, 31;
(d) Avela, E.; Melander, B.; Holmbom, B. *Acta. Acad. Abstracts Ser. B* **1971**, *15*, 31.
[6] (a) Chinn, M. J.; Iacazio, G.; Spackman, D. G.; Turner, N. J.; Roberts, S. M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 661;
(b) Iacazio, G.; Roberts, S. M. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1099;
(c) Panza, L.; Brasca, S.; Riva, S.; Russo, G. *Tetrahedron Asymmetry* **1993**, *4*, 931.
[7] (a) Gridley, J. J.; Hacking, A. J.; Osborn, H. M. I.; Spackman, D. G. *Synlett* **1997**, 1397;
(b) Gridley, J. J.; Hacking, A. J.; Osborn, H. M. I.; Spackman, D. G. *Tetrahedron* **1998**, *54*, 14925.
[8] Gridley, J. J.; Osborn, H. M. I.; Suthers, W. G. *Tetrahedron Lett.* **1999**, *40*, 6991.
[9] Matsuo, I.; Isomura, M.; Walton, R.; Ajisaka, K. *Tetrahedron Lett.* **1996**, *37*, 8795.
[10] Mallet, A.; Mallet, J.; Sinaÿ, P. *Tetrahedron Asymmetry* **1994**, *5*, 2593.
[11] (a) Angyal, S. J. *Adv. Carbohydr. Chem. Biochem.* **1989**, *47*, 1;
(b) Rendleman, Jr., J. A. *Adv. Carbohydr. Chem.* **1966**, *21*, 209;
(c) Rendleman, Jr., J. A. *J. Org. Chem.* **1966**, *31*, 1839.
[12] Angyal, S. J.; Davies, K. P. *J. Chem. Soc., Chem. Commun.* **1971**, 500.
[13] Angyal, S. J. *Aust. J. Chem.* **1972**, *25*, 1957.
[14] (a) Bourne, E. J.; Searle, F.; Weigel, H. *Carbohydr. Res.* **1971**, *16*, 185;
(b) Briggs, J.; Finch, P.; Matulewicz, M. C.; Weigel, H. *Carbohydr. Res.* **1981**, *97*, 181.
[15] Vesala, A.; Lönnberg, H.; Käppi, R.; Arpalahti, J. *Carbohydr. Res.* **1982**, *102*, 312.
[16] Garegg, P. J.; Kvarnström, I.; Niklasson, A.; Niklasson, G.; Svensson, S. C. T. *J. Carbohydr. Chem.* **1993**, *12*, 933.
[17] Helmboldt, A.; Mallet, J.-M.; Petitou, M.; Sinay, P. *Bull. Soc. Chim. Fr.* **1997**, *134*, 1057.
[18] Rivaille, S. *Bull. Soc. Chim. Fr.* **1963**, *716*, 718.
[19] Nanasi, L. *Acta Chim. Acad. Sci. Hung.* **1975**, *84*, 63.