MOLYBDENUM-CATALYZED ALLYLIC SUBSTITUTION IN GLYCALS: A C–C BOND-FORMING FERRIER-TYPE REACTION

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Received October 30, 2001
Accepted November 20, 2001

Dedicated to the memory of Dr Václav Černý, an unforgettable mentor of one of us (P. K.).

The mild, Lewis-acidic complexes $[Mo(CO)_4Br_2]_2$, $(MeCN)_2Mo(CO)_3(SnCl_3)Cl$, and $(acac)_2Mo(OTf)_2$ have been found to catalyze the C(1)-specific *C*-glycosylation reaction of glycal acetates **1**–**3** with silyl enol ethers **4a**–**4c** and electron-rich aromatics **5a**, **5b** (PhOMe, PhOH). While silyl enol ethers produce predominantly α-*C*-glycopyranosides (with 2 : 1 to 4 : 1 selectivity), aromatics tend to afford mainly β-*C*-glycopyranosides (2 : 1 to 3 : 1) in a thermodynamically controlled process.

Keywords: *C*-Glycosides; Carbohydrates; Glycals; Allylic substitutions; Lewis acids; Stereoselective reactions; Molybdenum complexes.

Glycals are versatile building blocks in carbohydrate chemistry[1]; of particular importance is their application as starting materials in the synthesis of *C*-glycosides and oligosaccharides[2,3]. Being effectively allylic acetates (with a corollary of further substituents), glycals are known to undergo allylic substitution in the presence of either Lewis acids[1,4–6] or palladium(0) complexes[7]. As a rule, glycals afford C-1 substituted products on Lewis acid-catalyzed reactions[1,2,4,5]; formation of their C-3 isomers has only been observed in several instances[1,6]. On the other hand, organometallics have been shown to be capable of judicious controlling the C-1/C-3 selectivity. Thus, for instance, organozinc reagents tend to afford C-1 alkylated prod-

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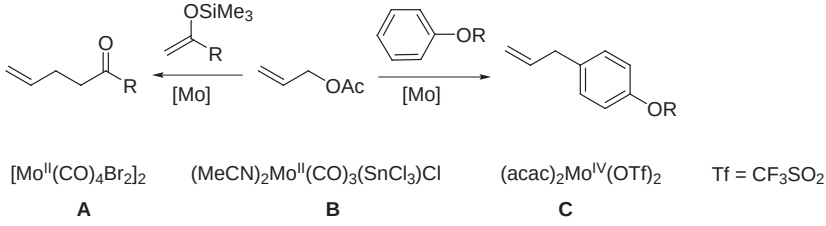
doi:10.1135/cccc20011735

ucts (in the presence of $BF_3{\cdot}OEt_2$ or Me_3SiOTf)[7], whereas Cu/Zn reagents prefer the reaction at C-3 under similar conditions[8]. Heck addition and Pd(0)-catalyzed allylic substitution give C-1 products[9,10], although the regioselectivity of the latter reaction can be altered, to some extent, by electronic and steric effects of the substituents surrounding the intermediate π-allyl complex[10].

We have recently reported on the Mo(II)- and Mo(IV)-catalyzed allylic substitution with a variety of *C*-nucleophiles, such as silyl enol ethers of simple ketones and electron-rich aromatics and heteroaromatics[11,12] (Scheme 1). We have also demonstrated that the Mo(II) and Mo(IV) complexes **A**–C act as very mild Lewis-acidic catalysts[11,12], which is in sharp contrast to Mo(0)- and Pd(0)-complexes, known to react *via* η^3-coordinated intermediates[13,14]. In view of the ready availability of the Mo(II) (refs[11e,11h,15]) and Mo(IV) (refs[12,16]) catalysts and their compatibility with various nucleophiles, it was of interest to extend this methodology to the carbohydrate realm with a view of developing a simple, non-expensive route to various *C*-glycosides, based on the Mo-catalyzed allylic substitution in the glycal molecule.



SCHEME 1

RESULTS AND DISCUSSION

D-Glucal triacetate (**1**) was selected as the pilot model compound to explore the glycosylation reactivity and to establish suitable reaction conditions (Chart 1). With the silyl enol ether derived from acetophenone (**4a**) and complex **A** (2 mole %) as catalyst in CH_2Cl_2 at room temperature, a ≈2 : 1 mixture of α- and β-*C*-glycopyranosides[17] **6a** and **7a** (Scheme 2) was obtained in good yield (Table I, entry 1) as the result of a remarkably fast reaction (≤5 min). Similarly fast reactions were observed for the remaining two catalysts **B** and C, showing little difference in the reactivity, product ratios, and yields (entries 2 and 3). With the silyl enol ethers **4b** and **4c** (derived from acetone and methyl isobutyrate, respectively), slightly higher α/β anomeric ratios of the products **6** and **7** (≈3 : 1) were obtained (entries 4–9).

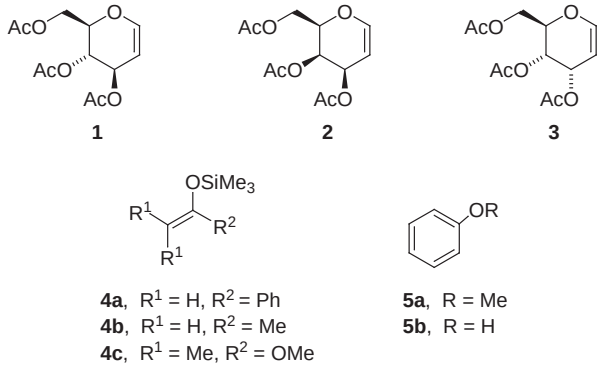


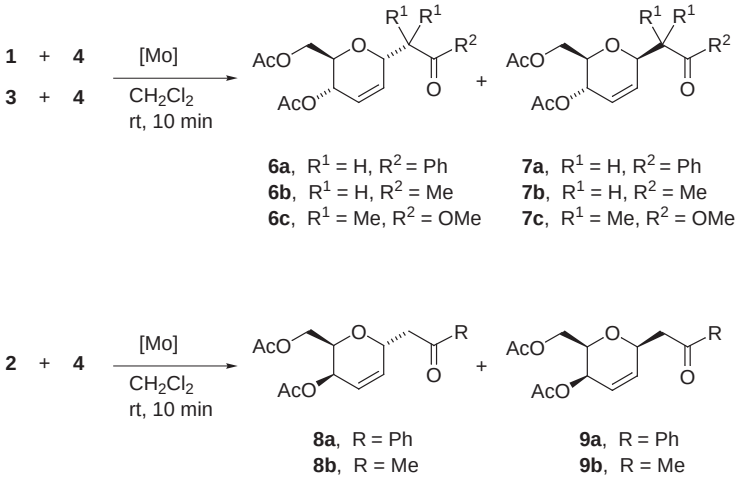
CHART 1

In the D-galactal series **2** (with the inverted configuration at 4-position), similar reactivities and preferences have been observed (entries 10–18), indicating that the change of configuration in the vicinity of the allylic system has little influence on the reaction course. Interestingly, the highest α/β ratios were observed for **4c**, the most sterically hindered nucleophile (up to 4 : 1; entries 16–18). The configurational change within the allylic system itself, as in D-allal triacetate **3**, again did not affect the reaction significantly (entry 19), suggesting a common reaction intermediate in the case of **1** and **3**. The Mo(IV) complex C appears to be the catalyst of choice as it gave consistently higher yields than **A** or **B** in each series (entries 3, 6, 9, 12, 15, and 18).

Oxygenated, electron-rich aromatics have traditionally been regarded as suitable substrates for glycosylation reactions. Indeed, our molybdenum catalysts proved to catalyze the glycosylation but the products of the reaction of glycals **1**–**3** with anisole (**5a**, Scheme 3) turned out be mainly the corresponding β-anomers **11a** and **13a**, respectively (Table II, entries 1–3 and 7–12), which contrasts with the predominant α-glycosylation in the case of silyl enol ethers (*vide supra*). Interestingly, phenol **5b** produced the corresponding *C*-glucoside, again predominantly as the β-anomer **11b** (Table II, entries 4–6), rather than the expected *O*-glycoside, which would be typical for other Lewis-acidic catalysts[1,18].

The reactivity of the aromatic donors raised the questions as to (i) the rationale for the formation of *C*-glycopyranosides **10b** and **11b** in the case of phenol (rather than the *O*-glycopyranosides) and (ii) the origin of the preference for β-anomeric products **11** and **13**.

Since PhO of the *O*-glycoside may, in principle, serve as a leaving group, we endeavored to establish whether this was the case with our Mo catalysts.



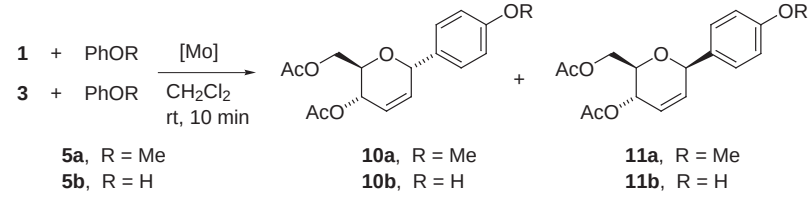
SCHEME 2

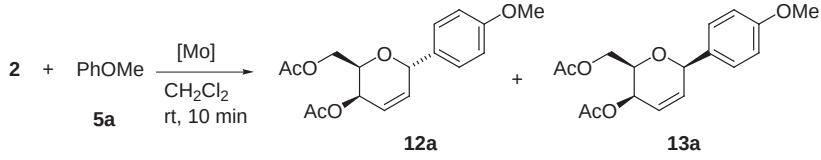
TABLE I
C-Glycosylation of **4a**–**4d** catalyzed by Mo complexes **A**, **B**, or C[a]

Entry	Carbohydrate	Nucleophile	Catalyst	Products	α/β ratio[b]	Yield, %
1	**1**	**4a**	**A**	**6a** + **7a**	63 : 37	61
2	**1**	**4a**	**B**	**6a** + **7a**	60 : 40	60
3	**1**	**4a**	**C**	**6a** + **7a**	65 : 35	64
4	**1**	**4b**	**A**	**6b** + **7b**	72 : 28	79
5	**1**	**4b**	**B**	**6b** + **7b**	71 : 29	83
6	**1**	**4b**	**C**	**6b** + **7b**	70 : 30	88
7	**1**	**4c**	**A**	**6c** + **7c**	73 : 27	63
8	**1**	**4c**	**B**	**6c** + **7c**	74 : 26	65
9	**1**	**4c**	**C**	**6c** + **7c**	75 : 25	68
10	**2**	**4a**	**A**	**8a** + **9a**	72 : 28	60
11	**2**	**4a**	**B**	**8a** + **9a**	73 : 27	63
12	**2**	**4a**	**C**	**8a** + **9a**	76 : 24	66
13	**2**	**4b**	**A**	**8b** + **9b**	71 : 29	79
14	**2**	**4b**	**B**	**8b** + **9b**	72 : 28	77
15	**2**	**4b**	**C**	**8b** + **9b**	71 : 29	85
16	**2**	**4c**	**A**	**8c** + **9c**	80 : 20	70
17	**2**	**4c**	**B**	**8c** + **9c**	78 : 22	69
18	**2**	**4c**	**C**	**8c** + **9c**	79 : 21	72
19	**3**	**4a**	**A**	**6a** + **7a**	64 : 36	75

[a] Conditions: catalyst (2 mole %), CH_2Cl_2, rt, 10 min (at 0.1 mmol scale). [b] Determined by the ^1H NMR spectrum of the crude product mixture.

To this end, *O*-glycoside **14** was prepared from **1** *via* Ferrier reaction, according to the known procedure[18] (Scheme 4), and submitted to the reaction conditions (2 mole % of C at room temperature). Within 5 min, TLC analysis demonstrated a quantitative conversion of **14** into a 31 : 69 mix-





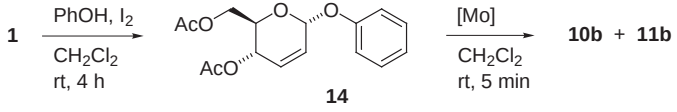
SCHEME 3

TABLE II
C-Glycosylation of aromatics catalyzed by Mo complexes **A**, **B**, or C[a]

Entry	Carbohydrate	Nucleophile	Catalyst	Product(s)	α/β ratio[b]	Yield, %
1	**1**	PhOMe	**A**	**10a** + **11a**	25 : 75	40
2	**1**	PhOMe	**B**	**10a** + **11a**	27 : 73	42
3	**1**	PhOMe	**C**	**10a** + **11a**	28 : 72	45
4	**1**	PhOH	**A**	**10b** + **11b**	35 : 65	45
5	**1**	PhOH	**B**	**10b** + **11b**	33 : 67	47
6	**1**	PhOH	**C**	**10b** + **11b**	34 : 66	45
7	**2**	PhOMe	**A**	**12a** + **13a**	35 : 65	39
8	**2**	PhOMe	**B**	**12a** + **13a**	33 : 67	43
9	**2**	PhOMe	**C**	**12a** + **13a**	32 : 68	46
10	**3**	PhOMe	**A**	**10a** + **11a**	24 : 76	51
11	**3**	PhOMe	**B**	**10a** + **11a**	27 : 73	48
12	**3**	PhOMe	**A**	**10a** + **11a**	26 : 74	54

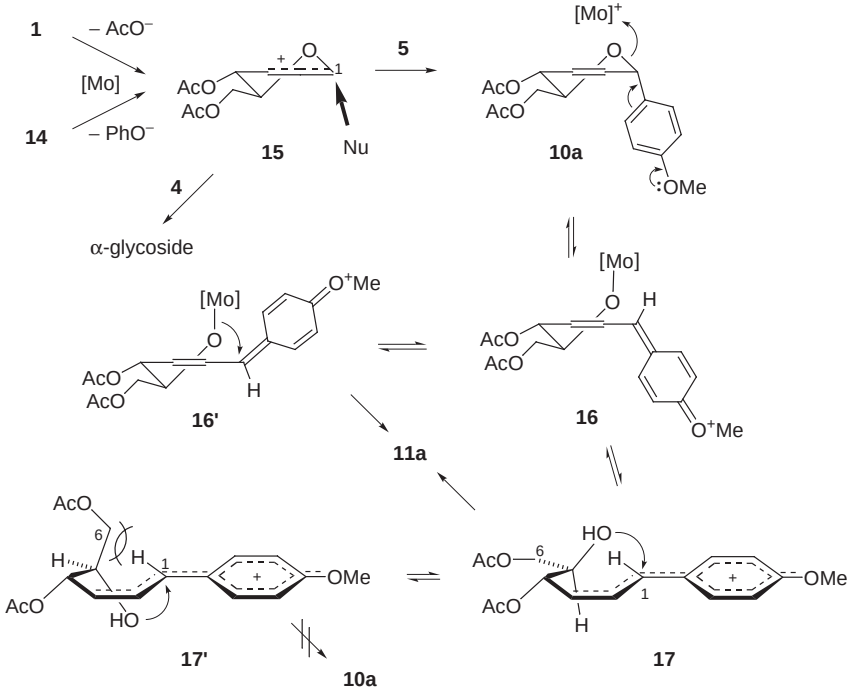
[a] Conditions: catalyst (2 mole %), CH_2Cl_2, rt, 10 min (at 0.1 mmol scale). [b] Determined by the ^1H NMR spectrum of the crude product mixture.

ture of α- and β-*C*-glycopyranosides **10b**/**11b** (86%), which is practically identical with the results of the glycosylation reaction of phenol **5b** with **1** (Table II, entry 6). Similarly, catalyst **A** afforded a ≈1 : 1 mixture (76%) and **B** furnished a ≈1 : 2 mixture (95%) of **10b** and **11b**. This behavior has not been reported for other Lewis-acidic catalysts, which demonstrates the unusual properties of the Mo(II) and Mo(IV) catalysts.



SCHEME 4

The differences in the stereochemical outcome of the glycosylation of **4** *versus* **5** can be understood as follows: the preferred attack by the nucleophile at the allylic cation **15**, generated by the removal of AcO^- (Scheme 5), should be pseudoaxial, owing to the stereoelectronic effects. Hence, glycosylation should primarily produce the α-anomer, as in the case of the silyl enol ethers **4a**–**4c**. However, unlike *O*-glycosides, the α-anomers



SCHEME 5

of *C*-glycosides are not stabilized by the stereoelectronic effect (owing to the higher level of the $LUMO_{C(1)–C}$ as compared with the $LUMO_{C(1)–O}$), leaving space for the $\alpha \rightarrow \beta$ equilibration. In fact, with the aromatic *C*-glycosides, the endocyclic oxygen can, in principle, serve as a leaving group, generating benzylic cation **16** that can undergo a C–C bond rotation to **16′**, whose cyclization would produce β-anomer **11a**. However, cation **16**/**16′** is likely to be further stabilized by conjugation with the allylic double bond, which would dictate that the aromatic ring and the four carbons C(1) to C(4) be in the same plane, as in **17** and **17′**. Cyclization of the delocalized cation **17** will produce β-anomer **11a**, whereas its conformational isomer **17′** would cyclize to give α-anomer **10a**. The latter ring closure, however, would proceed *via* a higher-energy transition state owing to the clash of C-6 with 1-H, thereby favoring the **17** → **11a** pathway. Treatment of the pure α-*C*-glucoside **10a** with catalyst C resulted in the formation of a 1 : 2 mixture of **10a** and **11a**, which supports this equilibration mechanism.

In conclusion, we have developed a protocol for mild, C(1)-specific glycosylation of silyl enol ethers and aromatics with glycals (*e.g.*, **1** + **4** → **6** and **1** + **5** → **11**), catalyzed by Lewis-acidic complexes $[Mo(CO)_4Br_2]_2$, $(MeCN)_2Mo(CO)_3(SnCl_3)Cl$, and $(acac)_2Mo(OTf)_2$. While silyl enol ethers produced predominantly α-*C*-glycopyranosides (with 2 : 1 to 4 : 1 selectivity), aromatics afforded mainly β-*C*-glycopyranosides (2 : 1 to 3 : 1) in a thermodynamically controlled isomerization process.

EXPERIMENTAL

General Methods

The NMR spectra were recorded in $CDCl_3$, ^1H at 250 MHz and ^{13}C at 62.9 MHz with chloroform-d_1 (δ 7.26, ^1H; δ 77.0, ^{13}C) as internal standard; chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz; 2D-techniques were used to establish the structures and to assign the signals. The IR spectra were recorded for a thin film between KBr plates unless otherwise stated. The mass spectra (EI and/or CI) were measured on a dual sector mass spectrometer using direct inlet and the lowest temperature enabling evaporation. All reactions were performed under an atmosphere of dry, oxygen-free nitrogen in oven-dried glassware. Solvents and solutions were transferred by syringe-septum and cannula techniques. The identity of the products prepared by different methods was checked by comparison of their NMR, IR, and MS data and by the TLC behavior. Most of the products are known compounds: **6a**[19], **6b**[19c,20], **6c**[5c], **7a**[19], **7b**[20c], **7c**[5c], **8a**[19b], **8b**[20c], **8c**[5c], **9a**[19b], **9b**[20c], **9c**[5c], **10a**[21], **11a**[21], **12a**[21a], **13a**[21a], and **14**[18]. The starting glycal triacetates **1–3** were prepared from the corresponding glycals, of which D-glucal and D-galactal are commercially available, while D-allal was synthesized according to the literature procedure[4b,22]. The silyl enol ethers were obtained in the same manner as reported in our previous paper[11h].

Dibromomolybdenum Tetracarbonyl Dimer (**A**)

A solution of bromine (1.36 g, 8.5 mmol) in dichloromethane (10 ml) was added to a suspension of the finely ground molybdenum hexacarbonyl (2.24 g, 8.5 mmol) in deoxygenated dichloromethane (60 ml) at –78 °C; the mixture gradually evolved carbon monoxide and the solid dissolved. The solution was maintained at –78 °C for 1 h and the solvent was then evaporated under reduced pressure at –78 °C to yield complex **A** as an orange, crystalline solid (3.03 g, 97%). Pure product, which could be stored in a freezer under nitrogen for several months, was obtained by recrystallization from MeCN. IR (CH_2Cl_2): ν(C≡O) 2 100 (s), 2 020 (m), 1 980 (m), 1 960 (m) cm^{-1} in accordance with the literature[15d,15e].

Bis(acetonitrile)tricarbonylchloro(trichlorostannyl)molybdenum (**B**)

A nitrogen-purged mixture of molybdenum hexacarbonyl (4.0 g, 15.4 mmol) and dry degassed acetonitrile (120 ml) was heated under reflux for 24 h to give a yellow/light brown solution. The solution was cooled to room temperature and tin(IV) chloride (3.18 g, 15.4 mmol) was added, the mixture was stirred for 10 min, and the solvent was removed in vacuum to give a dark red solid. The latter solid was redissolved in dry acetonitrile (30 ml) and filtered through a sintered glass filter, which removed a black tar residue and gave an orange/red filtrate. Removal of the solvent furnished complex **B** as a red/orange solid (6.39 g, 79%). IR (CH_2Cl_2): ν(C≡O) 2 027 (s), 1 990 (s), 1 953 (m), 1 915 (w); ν(C≡N) 2 320 (w), 2 285 (w) cm^{-1}. IR (Nujol): ν(C≡O) 2 030 (m), 1 955 (m), 1 920 (br); ν(C≡N) 2 310 (w), 2 295 (w) cm^{-1} in accordance with the literature[11,15].

Bis(pentane-2,4-dionato)molybdenum(IV) Ditriflate (C)

This complex was generated *in situ* by adding silver triflate (10 mg, 0.039 mmol) to a solution of $(acac)_2MoCl_2$ (5 mg, 0.014 mmol)[12,16] in dry CH_2Cl_2 (10 ml) prior to each reaction.

General Procedure for the Glycosylation Reactions Catalyzed by Complexes **A**–C

Catalyst **A**, **B**, or C (2 mole %) was added to a solution of glycal (150 mg, 0.55 mmol) and the nucleophile (0.65 mmol) in dichloromethane and the resultant mixture was stirred at room temperature for 5 min upon which time all starting materials had been consumed, as evidenced by TLC. The mixture was successively washed with water (2 × 50 ml) and saturated sodium hydrogen carbonate (2 × 50 ml). The organic layer was then separated and dried and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (5 g) with a petroleum ether–ether mixture (1 : 1) as eluent, to give a mixture of anomeric glycosides; for the ratios (determined by ^1H NMR with reference to the ratios of 6-H and selected other protons) and yields (isolated yields of the anomeric mixtures), see Table I. The mixture was then separated into α- and β-glycopyranosides by chromatography on silica gel (10 g) with a petroleum ether–ether mixture (90 : 10) for the purpose of characterization.

Rearrangement of *O*- to *C*-Glycoside

Catalyst **A**, **B**, or C (2 mole %) was added to a solution of *O*-glycopyranoside **14** (70 mg, 0.22 mmol) in dichloromethane (5 ml) and the mixture was stirred at room temperature for 5 min, whereupon completion of the reaction was observed by TLC. The resultant products

were purified by flash chromatography on silica gel (5 g) with a petroleum ether–ether mixture (1 : 1) as eluent to yield the rearranged *C*-glycopyranosides **10b** and **11b**; the resulting α/β ratios and yields are discussed in the text.

4-(4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)phenol (**10b**). ^{1}H NMR: 2.06 s, 3 H (AcO); 2.09 s, 3 H (AcO); 3.72 ddd, *J* = 5.9, 5.7, 3.1, 1 H (5′-H); 4.07 dd, *J* = 12.0, 3.1, 1 H (6′-H_a); 4.25 dd, *J* = 12.0, 5.7, 1 H (6′-H_b); 5.27 m, *W*/2 = 6.0, 1 H (1′-H); 5.28–5.38 m, 1 H (4′-H); 5.95 m, 1 H (3′-H); 6.15 m, 1 H (2′-H); 6.84 br d, *J* = 8.5, 2 H (arom.); 7.29 br d, *J* = 8.5, 2 H (arom.). ^{13}C NMR: 20.8 (q), 21.1 (q), 63.0 (t), 65.2 (d), 68.9 (d), 73.5 (d), 115.3 (d), 125.0 (d), 129.7 (d), 130.7 (s), 131.7 (d), 156.0 (s), 170.6 (s), 171.0 (s). EI HRMS: 307.11816 ($C_{16}H_{19}O_6$ requires MH^+, 307.11817).

4-(4,6-Di-O-acetyl-2,3-dideoxy-β-D-erythro-hex-2-enopyranosyl)phenol (**11b**). ^{1}H NMR: 2.00 s, 3 H (AcO); 2.04 s, 3 H (AcO); 3.95 ddd, *J* = 8.5, 5.7, 2.8, 1 H (5′-H); 4.12 dd, *J* = 12.2, 5.7, 1 H (6′-H_a); 4.21 dd, *J* = 12.2, 2.8, 1 H (6′-H_b); 5.08 m, *W*/2 = 6.5, 1 H (1′-H); 5.34 dp, *J* = 8.4, 1.5, 1 H (4′-H); 5.76 dt, *J* = 10.4, 1.8, 1 H (3′-H); 5.84 dt, *J* = 10.4, 1.3, 1 H (2′-H); 6.73 br d, *J* = 8.6, 2 H (arom.); 7.13 br d, *J* = 8.6, 2 H (arom.). ^{13}C NMR: 21.3 (q), 21.5 (q), 64.2 (t), 66.0 (d), 75.2 (d), 77.6 (d), 115.9 (d), 125.2 (d), 129.3 (d), 132.1 (s), 133.3 (d), 156.5 (s), 171.0 (s), 171.6 (s). IR: ν(OH) 3 590; ν(arom. C–H) 2 960, 2 930, 2 860; ν(C=O) 1 745, 1 740 cm^{-1}. EI MS (*m*/*z*, %): 307 (MH^+). EI HRMS: 307.11817 ($C_{16}H_{19}O_6$ requires MH^+, 307.11817).

We thank the EPSRC and Glaxo SmithKline for a CASE award to B. P. F.

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with the published data. In addition, NOE experiments (especially the occurrence *vs* absence of the effect between 1-H and 5-H), in conjunction with 2D techniques, were employed to confirm the assignment.

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