Carbohydrate Research 359 (2012) 111–119

Contents lists available at SciVerse ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Note

Regioselective benzoylation of glycopyranosides by benzoic anhydride in the presence of $Cu(CF_3COO)_2$

Evgeny V. Evtushenko *

G.B. Elyakov Pacific Institute of Bioorganic Chemistry, Far-East Branch, Russian Academy of Sciences, Vladivostok 690022, Russian Federation

ARTICLE INFO

Article history:
Received 10 April 2012
Received in revised form 22 June 2012
Accepted 30 June 2012
Available online 9 July 2012

Keywords:
Glycopyranosides
Regioselective benzoylation
Copper(II) trifluoroacetate

ABSTRACT

Benzoylation of methyl and benzyl glycopyranosides by benzoic anhydride in acetonitrile in the presence of copper(II) trifluoroacetate as a promoter has given monobenzoates with a good yield and high regioselectivity. The composition of monobenzoates depended both on a configuration of hydroxyl groups and on a configuration of aglycone. The simple syntheses of the monobenzoates of some glycosides are offered.

© 2012 Elsevier Ltd. All rights reserved.

Carbohydrates and glycoconjugates are abundant in nature and often play an important role in live processes. Their study demands synthetic oligosaccharides. Synthesis of oligosaccharides usually involves the strategy based on blocking and deblocking of hydroxyl groups that demands multistages and time. Regioselective introduction of protective groups in carbohydrates could become an alternative approach for getting intermediates in oligosaccharide synthesis. Earlier for regioselective acylation of carbohydrates both enzymic[1] and chemical approaches[2–24] were used. Among the latter copper,[2–5] mercury,[3] nickel,[6] platinum[6] and zinc[6] chelates, tin-organic,[7–18] organoboron[19] and organosilicon[20] compounds, amines,[21–24] organocatalysts[25,26] and TMS ethers[27–29] were used.

However, despite certain advances in this area, regioselective protection of hydroxyl groups in sugars is still a challenge in organic synthesis.

Carbohydrates are known to form complexes with transition metals generally in water solutions.[30–32] No doubt that nucleophilicity of hydroxyl groups involved in complexation will depend both on the metal and on the geometry of the intermediate complex.

Recently we have found that selective substitution OH-3 in glycopyranosides under acetylation[33] and benzoylation[34] is easily achieved when molybdenum(V, VI) salts are used as catalysts, this probably is determined by formation of an intermediate complex of molybdenum atom with three hydroxyl groups of glycoside molecule.[33] Earlier Angyal[35] has found that copper(II) ions form strong complexes with some polyols at pH >5, presumably because of formation of binuclear copper ions.

In the present work we wanted to study the effect of complexation of carbohydrates with transition metals and in particular with copper(II) in aprotic solvents on relative reactivity of hydroxyl groups of carbohydrates in benzoylation.

It is of interest to note that salts of transition metals as catalysts were not active in benzoylation of glycosides by benzoic anhydride. However, the use of a little surplus of the salts in comparison with stoichiometric quantities often showed their efficiency in benzoylation (Table 1).

Table 1 shows that zinc(II), nickel(II), cobalt(II) and gadolinium(III) salts (entries 14–17) moderately activate the benzoylation of methyl α-L-rhamnopyranoside **1** and do not lead to the considerable distinctions in amounts of 2- and 3-benzoates in reaction mixtures. However, the use of trifluoroacetate (entry 4), triflate (entry 10) and perchlorate (entry 11) of copper(II) showed formation of 2-benzoate with high yield and regioselectivity in this reaction. Acetonitrile as solvent (entry 4 vs 5, 6, and 7) and collidine as base (entry 4 vs 8 and 9) were preferable in this reaction. The benzoylation of methyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranoside and methyl 2,4-di-*O*-methyl-β-D-xylopyranoside in these conditions gave 45% and 12% of benzoates, respectively. This indicates difficulty in substitution of isolated hydroxyl group especially at secondary carbon atom.

High differences in the reactivity of secondary hydroxyl groups of glycopyranosides in this reaction (Table 2) can be explained by accepting the existence of an intermediate chelate of copper(II) ion with *cis-vicinal* hydroxyl groups or with hydroxyl and methoxyl groups (Scheme 1), in which only one hydroxyl group is predominantly ionized and the second hydroxyl group is coordinated with copper(II) ion without ionization. The ionization of hydroxyl group should essentially raise its nucleophilicity. Thus usually small

* Tel.: +7 4232 311430; fax: +7 4232 314050.
E-mail address: evt@piboc.dvo.ru

0008-6215/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carres.2012.06.020

Table 1
Regioselective benzoylation of methyl α-L-rhamnopyranoside **1** by benzoic anhydride in the presence transition metal salts and 2,4,6-collidine[a]

Entry	Promoter	Solvent	Parent glycoside	Benzoates[b] (%)			
				HO-2	HO-3	HO-4	Di- + Tri-
1	—	CH_3CN[c]	92	2	6		
2	—	CH_3CN	66	4	26	4	
3	$Cu(CF_3COO)_2$	CH_3CN[c]	24	63	10	3	
4	$Cu(CF_3COO)_2$	CH_3CN		90	2	2	6
5	$Cu(CF_3COO)_2$	Dioxane	15	78	3	1	3
6	$Cu(CF_3COO)_2$	EtAc	13	75	4	3	5
7	$Cu(CF_3COO)_2$	THF	9	86	3	2	
8	$Cu(CF_3COO)_2$	CH_3CN[d]	75	17	3	1	4
9	$Cu(CF_3COO)_2$	CH_3CN[e]	4	83	6	3	4
10	$Cu(TfO)_2$	CH_3CN	4	85	3	5	3
11	$Cu(ClO_4)_2$	CH_3CN	2	81	4	6	7
12	$Cu(CCl_3COO)_2$	CH_3CN	7	74	10	3	6
13	$Cu(BzO)_2$	CH_3CN	44	33	16	2	5
14	$Zn(CF_3COO)_2$	CH_3CN	42	29	21	2	6
15	$Ni(CF_3COO)_2$	CH_3CN	78	10	8	4	
16	$Co(CF_3COO)_2$	CH_3CN	55	29	13	3	
17	$Gd(CF_3COO)_3$	CH_3CN	32	31	31	2	4

[a] Reaction conditions: methyl α-L-rhamnopyranoside (0.5 mmol), Bz_2O (0.65 mmol), promoter (0.65 mmol), base (0.65 mmol) in solvent (4 mL), 6 h, rt.
[b] Determined by ^1H NMR.
[c] Reaction was executed without base.
[d] Pyridine was used as base.
[e] Triethylamine was used as base.

differences in the reactivity of hydroxyl groups of sugars in acylation reactions can become considerable ones after forming chelates with copper(II) atoms.

In general, both steric factors and factors, favoring the stabilization of intermediate anions and increasing their nucleophilicity, play an important role in the reactivity of the hydroxyl groups of carbohydrates. They include, in particular, electron-withdrawing adjacent groups, the adjacent methylene group, intermolecular hydrogen bonding,[36–38] and stereoelectronic effects.[39] The complexation of carbohydrates can change the ratio of these factors, and as a consequence, the reactivity of the hydroxyl groups, that seems interesting from a synthetic point of view.

As a result, methyl and benzyl β-L-arabinopyranosides **8** and **9** (entries 8 and 9) having two couples of neighboring oxygen atoms, O-3 and O-4 and O-2 and O-1 (Scheme 2, a) gave in this reaction 2- and 4-benzoates in significant amounts. At the same time methyl and benzyl α-L-arabinopyranosides **6** and **7** (entries 6 and 7) having only one couple contiguous oxygen atoms, O-3 and O-4 (Scheme 2, b) gave basically 4-benzoates.

The results of benzoylation of D-xylopyranosides were similar to the above-mentioned ones. While the benzoylation of α-D-xylopyranoside **11** (entry 11) has given an equal mixture of 2- and 4-benzoates, the benzoylation of methyl (**13**) (entry 13) and benzyl (**14**) (entry 14) β-D-xylopyranosides has demonstrated exceptionally high regioselectivity in substitution of OH-4, which can be explained by the adjacency of the hydroxyl group to a methylene site at C-5 (Scheme 3, a and b). Similar results of the benzoylation of D-xylopyranosides and L-arabinopyranosides with using organo tin compounds were observed earlier.[8,16,17]

For better understanding the character of the interaction of copper(II) ion with molecule of β-D-xylopyranoside, methyl ethers of this glycoside were used. Methyl 2-*O*-methyl-β-D-xylopyranoside **15** (entry15) gave in this reaction practically one 2,4-di-*O*-methyl β-D-xylopyranoside confirming non participation of O-2 in the complexation of the parent glycoside.

The benzoylation of methyl 3-*O*-methyl-β-D-xylopyranoside **16** (entry 16), however, gave approximately equal ratio of 2- and 4-benzoates, that is, possibly, determined by another type of an intermediate complex of the glycoside with Cu(II) ion (Scheme 3, c).

Methyl α-D-fucopyranoside **4** (entry 4) has a configuration of hydroxyl groups similar to methyl β-L-arabinopyranoside **8**, but it also has the substitute at C-5, which evidently hinders attack of the benzoylating agent, and does not contribute to stability of O-4 anion, and as a result the content of 2-benzoate and 3-benzoate in a reaction mixture was 80% and 9%, respectively. The latter was probably formed owing to the reaction of a complex of Cu(II) atom and O-3 and O-4 with benzoic anhydride (Scheme 4, a).

Methyl β-D-fucopyranoside **5** (entry 5) is likely to form only one intermediate complex with involvement of O-3 and O-4 (Scheme 4, b) and as a result, the content of 3-benzoate in reaction mixture was 83% and 95% from monobenzoate fraction.

The benzoylation of methyl (**1**) and especially benzyl (**2**) α-L-rhamnopyranoside (entries 1 and 2, respectively) in fact gave one 2-benzoate, possibly, due to the proximity of O-2 anion to the anomeric center (Scheme 5, a and b). While the benzoylation of β-anomer (**3**) (entry 3) gave almost exceptionally 3-benzoate, 92% from total mixture and 98% from monobenzoate fraction. Probably, stereoelectronic factor plays a main role in this case, destabilizing anion O-2 (Scheme 5, c). The interesting fact is that the benzoylation of these anomers in the presence of $MoO_2(acac)_2$ as catalyst demonstrated inverse dependence.[34]

Acylation of methyl α-L-rhamnopyranoside **1** by anhydrides of acetic, propionic and butyric acids (entries 23, 24, 25, respectively) in these conditions gave similar results with larger selectivity for butyric anhydride.

Earlier[8] it has been observed that the benzoylation of methyl glycosides α- and β-D-glucose and α-D-galactose using $(Bu_3Sn)_2O$ method gave 6-benzoates, but the benzoylation of methyl glycosides β-D-galactose and α-D-mannose led to mixtures of 3- and 6-benzoates.

We have found that benzoylation of glycosides bearing free HO-6, methyl α- and β-D-glucopyranosides **24** and **25** (entries 27 and 28, respectively), benzyl β-D-glucopyranoside **26** (entry 30), benzyl β-D-galactopyranoside **27** (entry 32) and methyl 2-acetamido-2-deoxy-α-D-glucopyranoside **23** (entry 26) gave 6-benzoates with average yield and full regioselectivity.

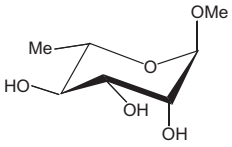
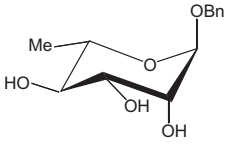
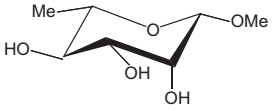
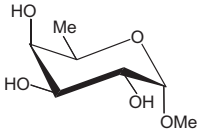
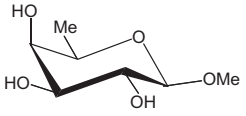
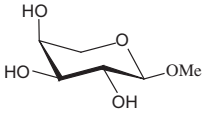
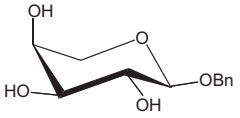
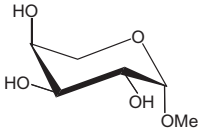
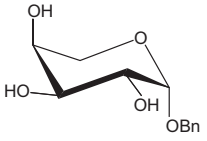
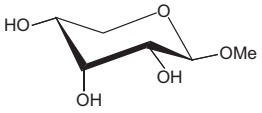
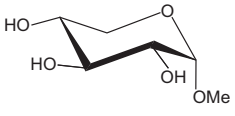
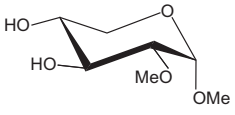
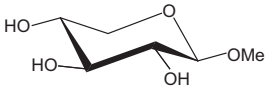
Benzoylation and butyration of methyl α-D-glucopyranoside **24** with 2.5 equiv of reagents gave 2,6-dibenzoate and 2,6-dibutyrate with yields of 74% and 70%, respectively, (entries 33 and 34), (Scheme 6). The similar result was received earlier[18] at benzoylation of methyl α-D-glucopyranoside using $(Bu_3Sn)_2O$ method.

It is known,[9] that benzoylation in the presence of tributyltin ethers and dialkylstannylene acetals of 6-O-protected glycosides demonstrated replacement of O-3 for α-D-galactose, O-2 for α-D-glucose, but for the glycosides of α-D-mannose high regioselectivity was not observed. We have found that the benzoylation of methyl (**17**) and benzyl (**18**) glycosides of 6-*O*-trityl-α-D-galactopyranose (entries 17 and 18, respectively), methyl 6-*O*-trityl-α-D-glucopyranoside (**20**) (entry 20) and methyl (**21**) and benzyl (**22**) glycosides of 6-*O*-trityl-α-D-mannopyranose (entries 21 and 22, respectively) gave 2-benzoates with good yield and high regioselectivity.

This result can be explained by the deprotonation of OH-2 in intermediate copper(II) complex due to the proximity to the anomeric center with more electron-withdrawing capacity (Scheme 7). The benzoylation of methyl 6-*O*-trityl-β-D-galactopyranoside **19** (entry 19) gave 3-benzoate with high yield and it was similar to the result for methyl β-D-fucopyranoside **5** (entry 5).

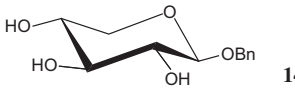
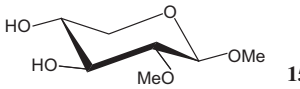
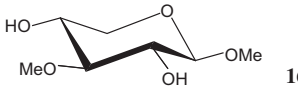
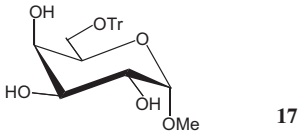
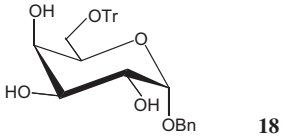
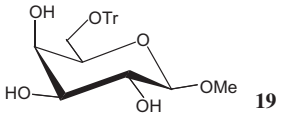
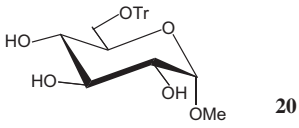
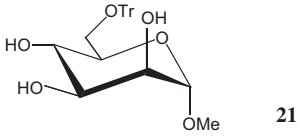
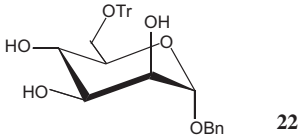
In conclusion, we have developed a simple and effective method for regioselective protection of hydroxyl groups in glycopyranosides. The regioselectivity is a consequence of formation of intermediate complexes of glycosides with copper(II) ions. The reaction of the latter with benzoic anhydride leads to selective replacement. As a consequence, replacement of OH-2 is reached for glycosides with the configurations of α-Rha, α-Fuc, and 6-O-trityl ethers of

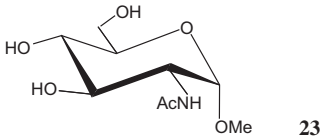
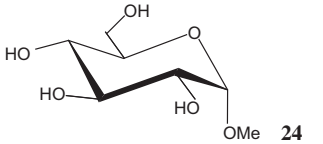
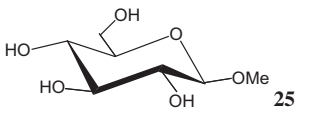
Table 2
Regioselective benzoylation of methyl and benzyl glycosides by benzoic anhydride in acetonitrile in the presence $Cu(CF_3COO)_2$ and 2,4,6-collidine

Entry	Glycoside	Benzoates[a] (%)			
		HO-2	HO-3	HO-4	Di- + tri-
1	 **1**	90 (83)	2	2	6
2	 **2**	92 (84)	1		7
3	 **3**		92 (84)	2	6
4	 **4**	80 (70)	9		11
5	 **5**	4	83 (72)		13
6	 **6**		8	80 (71)	12
7	 **7**		6	85 (75)	9
8	 **8**	43	3	42	12
9	 **9**	28	11	52	9
10	 **10**	52	25	13	10
11	 **11**	45		45	10
12	 **12**			84 (73)	16
13	 **13**			95 (86)	5

(*continued on next page*)

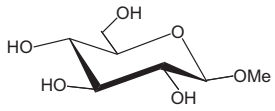
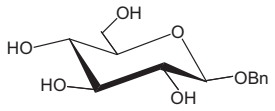
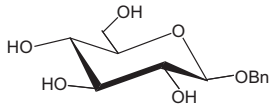
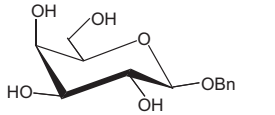
Table 2 (*continued*)

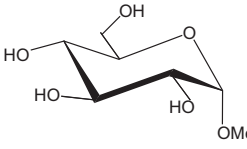
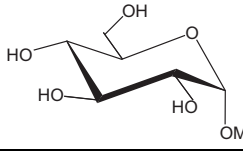
Entry	Glycoside	Benzoates[a] (%)			
		HO-2	HO-3	HO-4	Di- + tri-
14	 **14**			98 (87)	2
15	 **15**			96 (83)	4
16	 **16**	51		43	6
17	 **17**	81 (70)	6		13
18	 **18**	88 (78)	4		8
19	 **19**	4	86 (75)		10
20	 **20**	85 (74)	5		10
21	 **21**	85 (76)	6		9
22	 **22**	88 (77)	5		7
23	**1**+ Ac_2O	80	11	1	8
24	**1**+ $(EtCO)_2O$	75	14	2	9
25	**1**+ $(PrCO)_2O$	85	13		2

Entry	Parent glycoside	Benzoates[a] (%)				
		HO-2	HO-3	HO-4	HO-6	Di- + tri-
26	 **23**	4			91 (83)	5
27	 **24**	3			72 (65)	25
28	 **25**	9			82 (72)	9

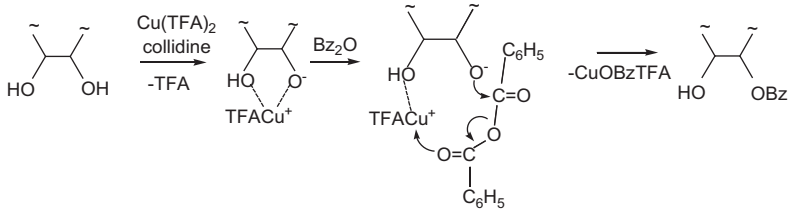
(*continued on next page*)

Table 2 (*continued*)

		Parent glycoside	Benzoates[a] (%)				
			HO-2	HO-3	HO-4	HO-6	Di- + tri-
29	 **25**[b]	10				75 (68)	15
30	 **26**	6				77 (69)	17
31	 **26**[b]	5				77 (67)	18
32	 **27**	8				80 (70)	12

		Benzoates[a] (%)				
		HO-2	HO-3	HO-4	HO-6	2,6-di-Bz
33	 **24**				13	87 (74)
34	 **24**[b]				16	84 (70)

[a] Determined by ^{1}H NMR, isolated yields in brackets.
[b] Butyrates.



Scheme 1. The proposed mechanism of regioselective benzoylation of diols in the presence of $Cu(CF_3COO)_2$.

α-Glc, α-Gal, and α-Man; replacement of OH-3 for glycosides with the configurations of β-Rha, β-Fuc, and β-Gal; replacement of OH-4 for glycosides with the configurations of β-Xyl and α-Ara; replacement of OH-6 for fully unprotected glycosides with the configurations of α-NAcGlc, α-Glc, β-Glc, and β-Gal. The simple syntheses of the monobenzoates of some glycosides are offered.

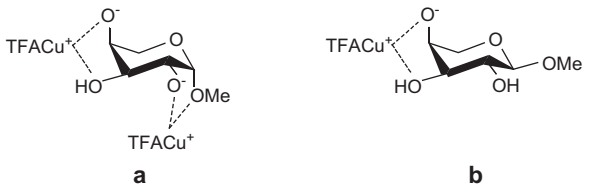
1. Experimental

1.1. General methods

Melting points were determined on Boethius micro hot-stage apparatus and were uncorrected. Optical rotations were measured with a Perkin–Elmer model 141. Spectra ^{1}H and ^{13}C NMR were registered on Bruker DPX-300 (^{1}H at 300 MHz and ^{13}C at 75 MHz). Chemical shifts (δ) are reported in ppm related to Me_4Si. (+)HR LSI mass spectra were obtained on an Agilent Technology 6510 Q_TOF LC/MS mass spectrometer (USA). The samples were dissolved in methanol (*c* 0.01 mg/mL). TLC was performed on Silica Gel L (5–40 μm; Chemapol) with hexane–acetone 7:3 (A), and with $CHCl_3$–MeOH 20:1 (B). For detection 10% sulfuric acid in ethanol at 130° was used. Column chromatography was performed on Silica Gel (100–160 μm; Chemapol).

1.2. General procedure for the monoacylation of glycosides 1–27 and for the dibenzoylation and dibutyration of methyl α-D-glucopyranoside 24

The solution of glycopyranoside (0.5 mmol), anhydride (0.65 mmol), a promoter (0.65 mmol), and 2,4,6-collidine (0.65 mmol) in a solvent (4 ml) was stirred at room temperature



Scheme 2. The proposed coordination of methyl β- (a) and α- (b) L-arabinopyranosides by $Cu^+(CF_3COO)$.

for 6 h. The dibenzoylation and the dibutyration of methyl α-D-glucopyranoside **24** were done with 2.5 equiv surplus of reagents. The reaction was monitoring by TLC. For the treatment of monobenzoates of glycosides **1**–**22**, 2,6-dibenzoate and 2,6-dibutyrate of **24** chloroform (30 mL) was added to the reaction mixture. The organic layer was washed with 2 M HCl (2 mL), aq $NaHCO_3$ (1 mL) and water (1 mL) and was concentrated to small volume under reduced pressure at room temperature. The products were isolated by flash chromatography on a column of silica gel using gradient acetone in hexane. For the treatment of monobenzoates of methyl α-L-rhamnopyranoside **1**, 6-monobenzoates and 6-monobutyrates of glycosides **23**–**27** aq sodium thiosulfate (2 mmol) was added to the reaction mixture until discoloration. The solution was concentrated to small volume under reduced pressure at room temperature. The products were isolated by flash chromatography on a column of silica gel using gradient methanol in chloroform.

1.3. Methyl 2-*O*-benzoyl-α-L-rhamnopyranoside (1a)

Yield from **1** 117 mg, 83%. R_f 0.41 (A). $[\alpha]_D^{20}$ +2.8 (*c* 0.6, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.12–8.04 (m, 2H, Ar), 7.64–7.57 (m, 1H, Ar), 7.49–7.43 (m, 2H, Ar), 5.34 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 4,78 (d, 1H, H-1), 4,06 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 3,74 (dd, 1H, $J_{5,6}$ = 6.1 Hz, H-5), 3,61 (t, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 3,42 (s, 3H, OCH_3), 1,39 (d, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 133.3, 129.8, 129.4, 128.3, 98.5, 73.5, 72.8, 70.5, 67.8, 54.9, 17.5. HRMS (ESI) calcd for $C_{14}H_{18}O_6Na$ *m/z* $(M+Na)^+$: 305.0996. Found: 305.1004.

1.4. Benzyl 2-*O*-benzoyl-α-L-rhamnopyranoside (2a)

Yield from **2** 150 mg, 84%. R_f 0.52 (A). mp 126–127 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ −53.5 (*c* 0.6, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.09–8.04 (m, 2H, Ar), 7.64–7.57 (m, 1H, Ar), 7.47–7.30 (m, 7H, Ar), 5.42 (dd, 1H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.5 Hz, H-2), 5.01 (d, 1H, H-1), 4.78 (d, 1H, J_{gem} = 11.8 Hz, CH_2Ph), 4.58 (d, 1H, CH_2Ph), 4.15 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 3.84 (dd, 1H, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 6.1 Hz, H-5), 3.65 (t, 1H, H-4), 1.39 (d, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 136.9, 133.4, 129.8, 129.3, 128.4, 128.3, 127.9, 96.9, 73.6, 72.9, 70.6, 69.4, 68.2, 17.5. HRMS (ESI) calcd for $C_{20}H_{22}O_6Na$ *m/z* $(M+Na)^+$: 381.1309. Found: 381.1305.

1.5. Methyl 3-*O*-benzoyl-β-L-rhamnopyranoside (3a)

Yield from **3** 118 mg, 84%. R_f 0.48 (A). mp 104–105 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ +92.0 (*c* 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.12–8.08 (m, 2H, Ar), 7.62–7.55 (m, 1H, Ar), 7.47–7.40 (m, 2H, Ar), 4.98 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 4.50 (d, 1H, $J_{1,2}$ = 1.0 Hz, H-1), 4.23 (dd, 1H, H-2), 3.87 (t, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 3.56 (s, 3H, OCH_3), 3.43 (dd, 1H, $J_{5,6}$ = 6.1 Hz, H-5), 1.41 (d, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 133.3, 129.8, 129.4, 128.4, 100.2, 76.6, 72.2, 70.5, 69.4, 56.8, 17.5. HRMS (ESI) calcd for $C_{14}H_{18}O_6Na$ *m/z* $(M+Na)^+$: 305.0996. Found: 305.1001.

1.6. Methyl 2-*O*-benzoyl-α-D-fucopyranoside (4a)

Yield from **4** 99 mg, 70%. R_f 0.45 (A). mp 176–177 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ +188.4 (*c* 0.4, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.11–8.08 (m, 2H, Ar), 7.61–7.51 (m, 1H, Ar), 7.49–7.43 (m, 2H, Ar), 5.20 (dd, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 4.99 (d, 1H, H-1), 4.18 (ddd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{3,OH-3}$ = 6.6 Hz, H-3), 4.06 (m, 1H, H-5), 3.88 (t, 1H, $J_{4,5}$ = 3.4 Hz, H-4), 3.39 (s, 3H, OCH_3), 2.84 (d, 1H, OH-3), 2.46 (d, 1H, $J_{4,OH-4}$ = 4.6 Hz, OH-4), 1.35 (d, 3H, $J_{5,CH3}$ = 6.7 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 133.3, 129.9, 129.5, 128.4, 97.5, 72.4, 72.3, 68.8, 65.4, 55.4, 16.1. HRMS (ESI) calcd for $C_{14}H_{18}O_6Na$ *m/z* $(M+Na)^+$: 305.0996. Found: 305.0998.

1.7. Methyl 3-*O*-benzoyl-β-D-fucopyranoside (5a)

Yield from **5** 101 mg, 72%. The properties are as according to the literature data.[34]

1.8. Methyl 4-*O*-benzoyl-α-L-arabinopyranoside (6a)

Yield from **6** 95 mg, 71%. R_f 0.24 (A). $[\alpha]_D^{20}$ +29.0 (*c* 0.7, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.09–8.06 (m, 2H, Ar), 7.62–7.54 (m, 1H, Ar), 7.47–7.42 (m, 2H, Ar), 5,39 (td, 1H, $J_{3,4}$ = 3.5 Hz, $J_{4,5a}$ = 2.8 Hz, $J_{4,5b}$ = 1.7 Hz, H-4), 4,23 (d, 1H, $J_{1,2}$ = 6.8 Hz, H-1), 4.18 (dd, 1H, $J_{5a,5b}$ = 13.2 Hz, H-5a), 3.92 (dd, 1H, $J_{2,3}$ = 9.0 Hz, H-3), 3,83 (dd, 1H, H-2), 3,70 (dd, 1H, H-5b), 3,58 (s, 3H, CH_3O). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 133.2, 129.8, 129.6, 128.3, 103.9, 71.9, 71.6, 70.7, 63.7, 57.0. HRMS (ESI) calcd for $C_{13}H_{16}O_6Na$ *m/z* $(M+Na)^+$: 291.0839. Found: 291.0837.

1.9. Benzyl 4-*O*-benzoyl-α-L-arabinopyranoside (7a)

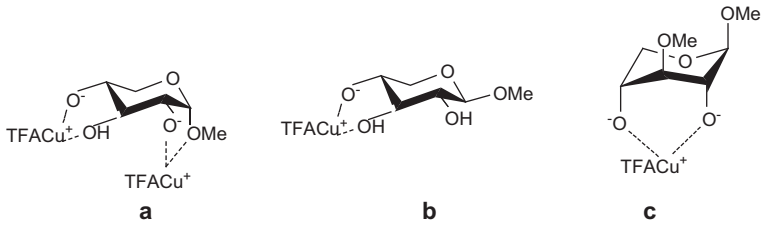
Yield from **7** 129 mg, 75%. R_f 0.33 (A). mp 137–138 °C (from EtOAc–hexane), $[\alpha]_D^{20}$ +8.4 (*c* 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.12–8.05 (m, 2H, Ar), 7.60–7.53 (m, 1H, Ar), 7.47–7.29 (m, 7H, Ar), 5.38 (m, 1H, H-4), 4.95 (d, 1H, J_{gem} = 11.6 Hz, CH_2Ph), 4.62 (d, 1H, CH_2Ph), 4.40 (d, 1H, H-1), 4.20 (dd, 1H, $J_{4,5a}$ = 2.8 Hz, $J_{5a,5b}$ = 13.2 Hz, H-5_a), 3.89 (m, 2H, H-2, H-3), 3.69 (dd, 1H, $J_{4,5b}$ = 1.5 Hz, H-5_b). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 136.7, 133.2, 129.8, 128.5, 128.3, 128.2, 128.1, 101.8, 72.0, 71.6, 71.0, 70.5, 63.7. HRMS (ESI) calcd for $C_{19}H_{20}O_6Na$ *m/z* $(M+Na)^+$: 367.1152. Found: 367.1151.

1.10. Methyl 4-*O*-benzoyl-2-*O*-methyl-α-D-xylopyranoside (12a)

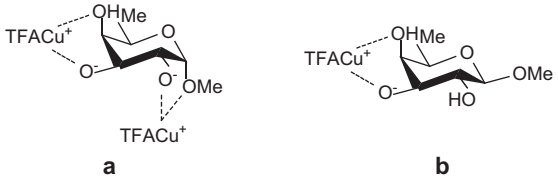
Yield from **12** 103 mg, 73%. R_f 0.47 (A). mp 107–108 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ +71.3 (*c* 0.4, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.08–8.04 (m, 2H, Ar), 7.61–7.54 (m, 1H, Ar), 7.48–7.41 (m, 2H, Ar), 5.10 (m, 1H, H-4), 4.91 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 4.15 (t, 1H, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.89 (dd, 1H, $J_{4,5a}$ = 5.9 Hz, $J_{5a,5b}$ = 10.8 Hz, H-5_a), 3.61 (t, $J_{4,5b}$ = 10.8 Hz, H-5_b), 3.55 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 3.30 (dd, 1H, H-2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 133.3, 129.8, 129.5, 128.4, 96.9, 81.4, 71.9, 70.7, 58.7, 58.4, 55.5. HRMS (ESI) calcd for $C_{14}H_{18}O_6Na$ *m/z* $(M+Na)^+$: 305.0996. Found: 305.0992.

1.11. Methyl 4-*O*-benzoyl-β-D-xylopyranoside (13a)

Yield from **13** 115 mg, 86%. R_f 0.30 (A). mp 118–119 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ −101.8 (*c* 0.4, $CHCl_3$). Lit. data:[8] mp 125–126 °C. Lit. data:[16] mp 84–85 °C, $[\alpha]_D^{20}$ −81.4 ($CHCl_3$). Lit. data:[17] mp 122.5–123.5 °C, $[\alpha]_D$ −92.3 (CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$) δ 8.08–8.02, (m, 2H, Ar), 7.62–7.56 (m, 1H, Ar), 7.48–7.43 (m, 2H, Ar), 5.09 (td, 1H, $J_{3,4}$ = 7.4 Hz, $J_{4,5a}$ = 4.5 Hz, $J_{4,5b}$ = 7.4 Hz, H-4),



Scheme 3. The proposed coordination of methyl α- (a), β- (b) and 3-*O*-methyl β- (c) D-xylopyranosides by $Cu^+(CF_3COO)$.



Scheme 4. The proposed coordination of methyl α- (a) and β- (b) D-fucopyranosides by $Cu^+(CF_3COO)$.

4.40 (d, 1H, $J_{1,2}$ = 5.9 Hz, H-1), 4.23 (dd, 1H, $J_{5a,5b}$ = 12.1 Hz, H-5_a), 3,91 (dt, 1H, $J_{2,3}$ = 7.4 Hz, $J_{3,OH-3}$ = 3.9 Hz, H-3), 3.63–3.49 (m, 2H, H-2, H-5_b), 3.56 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 133.4, 129.7, 129.3, 128.4, 103.4, 72.7, 72.5, 71.8, 61.7, 56.8. HRMS (ESI) calcd for $C_{13}H_{16}O_6Na$ *m/z* $(M+Na)^+$: 291.0839. Found: 291.0843.

1.12. Benzyl 4-*O*-benzoyl-β-D-xylopyranoside (14a)

Yield from **14** 150 mg, 87%. R_f 0.44 (A). mp 142–143 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ −53.6 (*c* 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.05–8.02 (m, 2H, Ar), 7.63–7.56 (m, 1H, Ar), 7.49–7.30 (m, 7H, Ar), 5.11 (dt, 1H, $J_{3,4}$ = 7.3 Hz, $J_{4,5a}$ = 4.4 Hz, $J_{4,5b}$ = 7.3 Hz, H-4), 4.91 (d, 1H, J_{gem} = 11.6 Hz, CH_2Ph), 4.64 (d, 1H, CH_2Ph), 4.58 (d, 1H, $J_{1,2}$ = 5.8 Hz, H-1), 4.26 (dd, 1H, $J_{5a,5b}$ = 12.2 Hz, H-5_a), 3.90 (dt, 1H, $J_{2,3}$ = 7.4 Hz, H-3), 3.64 (dt, 1H, H-2), 3.55 (dd, 1H, H-5_b), 3.10, (d, 1H, $J_{OH,H}$ = 5.3 Hz, OH), 2.72 (d, 1H, $J_{OH,H}$ = 5.1 Hz, OH) ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 133.2, 132.8, 129.6, 128.3, 128.2, 128.1, 128.0, 127.9, 102.0, 73.1 × 2, 71.9, 70.8, 62.4. HRMS (ESI) calcd for $C_{19}H_{20}O_6Na$ *m/z* $(M+Na)^+$: 367.1152. Found: 367.1150.

1.13. Methyl 4-*O*-benzoyl-2-*O*-methyl-β-D-xylopyranoside (15a)

Yield from **15** 117 mg, 83%. R_f 0.52 (A). mp 135–136 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ −133.8 (*c* 0.4, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.09–8.04 (m, 2H, Ar), 7.61–7.54 (m, 1H, Ar), 7.48–7.41 (m, 2H, Ar), 5,08 (td, 1H, $J_{3,4}$ = 7.9 Hz, $J_{4,5a}$ = 4.8 Hz, $J_{4,5b}$ = 7.9 Hz, H-4), 4,40 (d, 1H, $J_{1,2}$ = 6.1 Hz, H-1), 4,21 (dd, 1H, $J_{5a,5b}$ = 12.0 Hz, H-5_a), 3,89 (td, 1H, $J_{2,3}$ = 7.9 Hz, $J_{3,OH-3}$ = 3.0 Hz, H-3), 3,59 (s, 3H, OCH_3), 3,54 (s, 3H, OCH_3), 3,47 (dd, 1H, H-5_b), 3,16 (dd, 1H, H-2), 2,97 (d, 1H, OH-3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 133.2, 129.7, 129.5, 128.3, 103.5, 81.5, 71.7 × 2, 61.6, 60.0, 56.4. HRMS (ESI) calcd for $C_{14}H_{18}O_6Na$ *m/z* $(M+Na)^+$: 305.0996. Found: 305.0993.

1.14. Methyl 2-*O*-benzoyl-6-*O*-trityl-α-D-galactopyranoside (17a)

Yield from **17** 189 mg, 70%. R_f 0.48 (A). mp 144–146 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ +90.0 (*c* 0.4, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.15–8.10 (m, 2H, Ar), 7.87–7.83 (m, 1H, Ar), 7.64–7.47 (m, 9H, Ar), 7.39–7.28 (m, 8H, Ar), 5,28 (dd, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 5,09 (d, 1H, H-1), 4.28–4.12 (m, 2H, H-3, H-4), 3,97 (bt, 1H, $J_{5,6}$ = 5.8 Hz, H-5), 3.54–3.46 (m, 2H, H-6a, H-6b), 3,44 (s, 3H, OCH_3), 2.79 (d, 1H, $J_{H,OH}$ = 3.2 Hz, OH), 2.76 (d, 1H, $J_{H,OH}$ = 7.7 Hz, OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 143.6, 133.2, 132.0, 129.9, 129.6, 128.5, 128.3, 127.9, 127.3, 127.1, 97.5, 72.3, 70.3, 68.5 × 2, 63.3, 55.3. HRMS (ESI) calcd for $C_{33}H_{32}O_7Na$ *m/z* $(M+Na)^+$: 563.2040. Found: 563.2036.

1.15. Benzyl 2-*O*-benzoyl-6-*O*-trityl-α-D-galactopyranoside (18a)

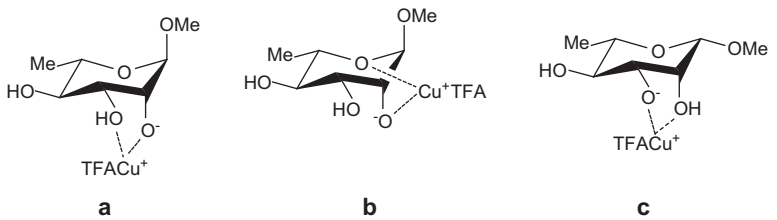
Yield from **18** 240 mg, 78%. R_f 0.46 (A). mp 67–68 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ +94.8 (*c* 0.6, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.12–8.06 (m, 2H, Ar), 7.64–7.56 (m, 1H, Ar), 7.52–7.44 (m, 8H, Ar), 7.37–7.24 (m, 14H, Ar), 5,28 (dd, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 10.0 Hz, H-2), 5,23 (d, 1H, H-1), 4,77 (d, 1H, J_{gem} = 12.3 Hz, CH_2Ph), 4,57 (d, 1H, CH_2Ph), 4,19 (m, 1H, H-3), 4,11 (m, 1H, H-4), 4,03 (td, 1H, $J_{4,5}$ = 1.0 Hz, $J_{5,6a}$ = 5.7, $J_{5,6b}$ = 5.7 Hz, H-5), 3,46 (dd, 1H, $J_{6a,6b}$ = 9.9 Hz, H-6a), 3,39 (dd, 1H, H-6b), 2.77 (dd, 1H, $J_{H,OH}$ = 3.3 Hz, OH) 2.73 (dd, 1H, $J_{H,OH}$ = 7.8 Hz, OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 143.6, 137.2, 133.2, 129.8, 129.6, 128.6, 128.3, 127.9, 127.7, 127.5, 127.1, 95.7, 72.3, 70.3, 69.4, 69.0, 68.6, 63.4. HRMS (ESI) calcd for $C_{39}H_{36}O_7Na$ *m/z* $(M+Na)^+$: 639.2353. Found: 639.2358.

1.16. Methyl 3-*O*-benzoyl-6-*O*-trityl-β-D-galactopyranoside (19a)

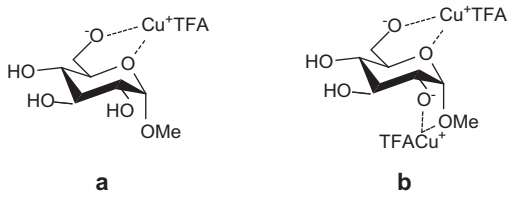
Yield from **19** 202 mg, 75%. The properties are as according to the literature data.[34]

1.17. Methyl 2-*O*-benzoyl-6-*O*-trityl-α-D-glucopyranoside (20a)

Yield from **20** 200 mg, 74%. R_f 0.46 (A). mp 83–85 °C (from EtOAc–hexane), $[\alpha]_D^{20}$ +70.1 (*c* 0.4, $CHCl_3$). Lit data:[40] 85–86 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.11–8.08 (m, 2H, PhH), 7.60–7.54 (m,



Scheme 5. The proposed coordination of methyl α- I type (a), α- II type (b) and β- (c) L-rhamnopyranosides by $Cu^+(CF_3COO)$.



Scheme 6. The proposed coordination of methyl α-D-glucopyranoside by $Cu^+(CF_3COO)$, (a)—with 1.3 equiv, (b)—with 2.5 equiv of promoter.

1H, PhH), 7.50–7.44 (m,7H, PhH), 7.35–7.22 (m, 10H, PhH), 5.03 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.95 (dd, 1H, $J_{2,3}$ 9.9 Hz, H-2), 4.10 (t, 1H, $J_{3,4}$ 8.6 Hz, H-3), 3.74 (m, 1H, H-5), 3.66 (dd, 1H, $J_{4,5}$ 9.6 Hz, H-4), 3,49–3.42 (m, 2H, H-6a, H-6b), 3.38 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 143.6, 133.4, 133.2, 129.9, 128.6, 128.3, 127.6, 127.1, 97.0, 73.7, 72.4, 71.7, 69.5, 63.9, 55.1. HRMS (ESI) calcd for $C_{33}H_{32}O_7Na$ *m/z* $(M+Na)^+$: 563.2040. Found: 563.2038.

1.18. Methyl 2-*O*-benzoyl-6-*O*-trityl-α-D-mannopyranoside (21a)

Yield from **21** 205 mg, 76%. R_f 0.43 (A). mp 74–76 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ +11.1 (*c* 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.10–8.06 (m, 2H, Ar), 7.63–7.43 (m, 9H, Ar), 7.35–7.27 (m, 9H, Ar), 5,36 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 2.8 Hz, H-2), 4,86 (d, 1H, H-1), 4,10–3.98 (m, 2H, H-3, H-4), 3,68 (m, 1H, H-5), 3,54 (dd, $J_{5,6a}$ = 3.9 Hz, $J_{6a,6b}$ = 10.2 Hz, H-6a), 3,46 (dd, 1H, $J_{5,6b}$ = 4.5 Hz, H-6b), 3,40 (s, 3H, OCH_3), 2.38 (d, 1H, $J_{H,OH}$ = 2.6 Hz, OH), 2.28 (d, 1H, $J_{H,OH}$ = 4.7 Hz, OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 143.7, 133.3, 129.8, 129.5, 128.6, 128.4, 127.8, 127.0, 98.6, 72.3, 70.6, 70.2, 69.4, 63.5, 55.0. HRMS (ESI) calcd for $C_{33}H_{32}O_7Na$ *m/z* $(M+Na)^+$: 563.2040. Found: 563.2045.

1.19. Benzyl 2-*O*-benzoyl-6-*O*-trityl-α-D-mannopyranoside (22a)

Yield from **22** 237 mg, 77%. R_f 0.37 (A). mp 62–64 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ +21.4 (*c* 0.4, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 8.10–8.05 (m, 2H, Ar), 7.83–7.79 (m, 1H, Ar), 7.60–7.40 (m, 10H, Ar), 7.36–7.27 (m, 12H, Ar) 5.43 (dd, 1H, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.07 (d, 1H, H-1), 4.76 and 4.56 (2d, 2H, J_{gem} = 11.8 Hz, CH_2Ph), 4.15 (m, 1H, H-3), 4.05 (t, 1H, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.4 Hz, H-4), 3.78 (m, 1H, H-5), 3.52 (dd, 1H, $J_{5,6a}$ = 3.8 Hz, $J_{6a,6b}$ = 10.1 Hz, H-6a), 3,44 (dd, 1H, $J_{5,6b}$ = 4.6 Hz, H-6b), 2.39 (d, 1H, $J_{H,OH}$ = 2.2 Hz, OH), 2.34 (d, 1H, $J_{H,OH}$ = 3.9 Hz, OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 143.8, 136.9, 133.2, 131.9, 129.8, 129.6, 128.6, 128.5, 128.4, 127.8, 127.3, 127.0, 96.9, 72.4, 71.2, 70.4, 69.3, 69.2, 63.4. HRMS (ESI) calcd for $C_{39}H_{36}O_7Na$ *m/z* $(M+Na)^+$: 639.2353. Found: 639.2357.

1.20. Methyl 6-*O*-benzoyl-2-acetamido-2-deoxy-α-D-glucopyranoside (23a)

Yield from **23** 141 mg, 83%. R_f 0.17 (B). mp 194–195 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ +44.0 (*c* 0.6, $CHCl_3$). ^1H NMR (300 MHz, CD_3OD) δ 8,08–8,00 (m, 2H, Ar), 7,63–7,57 (m, 1H, Ar), 7,50–7,44 (m, 2H, Ar), 4,67 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4,64 (dd, 1H, $J_{5,6a}$ = 2.1 Hz, $J_{6a,6b}$ = 11.8 Hz, H-6a), 4,45 (dd, 1H, $J_{5,6b}$ = 5.8 Hz, H-6b), 4.02 (dd, 1H, $J_{2,3}$ = 10.6 Hz, H-2), 3.86 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, H-5), 3,67 (dd, 1H, $J_{3,4}$ = 8.9 Hz, H-3), 3.48 (t, 1H, H-4), 3.37 (s, 3H, OCH_3), 1.98 (s, 3H, CH_3CO). ^{13}C NMR (75 MHz, CD_3OD) δ 174.3, 168.5, 134.9, 132.0, 131.1, 130.2, 100.5, 73.5, 73.0, 71.9, 65.9, 56.1, 55.9, 23.2. HRMS (ESI) calcd for $C_{16}H_{21}O_7NNa$ *m/z* $(M+Na)^+$: 362.1210. Found: 362.1205.

1.21. Methyl 6-*O*-benzoyl-α-D-glucopyranoside (24a)

Yield from **24** 97 mg, 65%. R_f 0.21 (B). mp 126–128 °C (from EtOAc–hexane), $[\alpha]_D^{20}$ +92.7 (*c* 0.5, $CHCl_3$). Lit. data:[41] mp 127–129 °C, Lit. data:[18] $[\alpha]_D$ +91.0 ($CHCl_3$). ^1H NMR (300 MHz, CD_3OD) δ 8.09–8.04 (m, 2H, Ar), 7.67–7.62 (m, 1H, Ar), 7.55–7.48 (m, 2H, Ar), 4.72 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.66 (dd, 1H, $J_{5,6a}$ = 2.1 Hz, $J_{6a,6b}$ = 11.8 Hz, H-6a), 4.47 (dd, 1H, $J_{5,6b}$ = 6.0 Hz, H-6b), 3.88 (ddd, 1H, $J_{4,5}$ = 9.8 Hz, H-5), 3.69 (t, 1H, $J_{2,3}$ = $J_{3,4}$ 9.3 Hz, H-3), 3.47–3.37 (m, 2H, H-2, H-4), 3.44 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, CD_3OD) δ 168.5, 134.9 132.0, 131.1, 130.2, 101.9, 75.7, 74.1, 72.6, 71.8, 66.0, 56.2. HRMS (ESI) calcd for $C_{14}H_{18}O_7Na$ *m/z* $(M+Na)^+$: 321.0945. Found: 321.0949.

1.22. Methyl 6-*O*-benzoyl-β-D-glucopyranoside (25a)

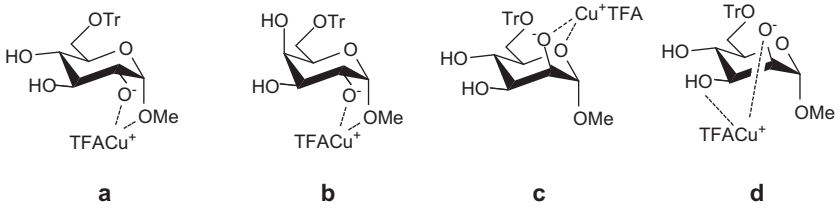
Yield from **25** 107 mg, 72%. R_f 0.19 (B). mp 132–133 °C (from EtOAc–hexane), $[\alpha]_D^{20}$ −18.5 (*c* 0.5, $CHCl_3$). Lit. data:[8] mp 136–138 °C. Lit. data:[41] mp 131–132 °C, $[\alpha]_D^{27}$ −24.2 (water). ^1H NMR (300 MHz, CD_3OD) δ 8.10–8.06 (m, 2H, Ar), 7.67–7.62 (m, 1H, Ar), 7.55–7.49 (m, 2H, Ar), 4.69 (dd, 1H, $J_{5,6a}$ = 2.2 Hz, $J_{6a,6b}$ = 11.9 Hz, H-6a), 4.49 (dd, 1H, $J_{5,6b}$ = 5.7 Hz, H-6b), 4.26 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 3.63 (ddd, 1H, $J_{4,5}$ = 9.5 Hz, H-5), 3.52 (s, 3H, OMe), 3.45 (m, 2H, H-3, H-4), 3.24 (dd, 1H, $J_{2,3}$ = 8.9, H-2). ^{13}C NMR (75 MHz, CD_3OD) δ 168.5, 134.9, 132.0, 131.2, 130.2, 106.0, 78.5, 76.0, 75.6, 72.4, 65.8, 57.8. HRMS (ESI) calcd for $C_{14}H_{18}O_7Na$ *m/z* $(M+Na)^+$: 321.0945. Found: 321.0942.

1.23. Methyl 6-*O*-butyryl-β-D-glucopyranoside (25b)

Yield from **25** 90 mg, 68%. R_f 0.21 (B). mp 104–106 °C (from EtOAc–hexane), $[\alpha]_D^{20}$ −20.4 (*c* 0.4, $CHCl_3$). ^1H NMR (300 MHz, CD_3OD) δ 4.45 (dd, 1H, $J_{5,6a}$ = 2.1 Hz, $J_{6a,6b}$ = 11.8 Hz, H-6a), 4.24 (dd, 1H, $J_{5,6b}$ = 5.8 Hz, H-6b), 4.20 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 3.52 (s, 3H, OCH_3), 3.50–3.37 (m, 2H), 3.30 (m, 1H), 3.14 (t, 1H, *J* = 8.4 Hz), 2.37 (t, 2H, *J* = 7.3 Hz, CH_2CO), 1.68 (dt, 2H, *J* = 7.2 Hz, CH_2CH_3), 0.99 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C NMR (75 MHz, CD_3OD) δ 175.8, 106.0, 78.5, 75.9, 75.6, 72.2, 65.1, 57.8, 37.4, 20.0, 14.5. HRMS (ESI) calcd for $C_{11}H_{20}O_7Na$ *m/z* $(M+Na)^+$: 287.1101. Found: 287.1096.

1.24. Benzyl 6-*O*-benzoyl-β-D-glucopyranoside (26a)

Yield from **26** 129 mg, 69%. R_f 0.33 (B). mp 118–119 °C (from EtOAc–hexane), $[\alpha]_D^{20}$ −51.2 (*c* 0.7, $CHCl_3$). ^1H NMR (300 MHz,



Scheme 7. The proposed coordination of 6-*O*-trityl ethers of methyl α-D-glucopyranoside (a), methyl α-D-galactopyranoside (b), methyl α-D-mannopyranoside, I type (c) and methyl α-D-mannopyranoside, II type (d) by $Cu^+(CF_3COO)$.

CD_3OD) δ 8.08–8.04 (m, 2H, Ar), 7.65–7.58 (m, 1H, Ar), 7.52–7.45 (m, 2H, Ar), 7.35–7.22 (m, 5H, Ar), 4.80 (d, 1H, J_{gem} = 11.9 Hz, CH_2), 4.67 (dd, 1H, $J_{5,6a}$ = 2.1 Hz, $J_{6a,6b}$ = 11.8 Hz, H-6a), 4.62 (d, 1H, CH_2), 4.48 (dd, 1H, $J_{5,6b}$ = 6.1, H-6b), 4.37 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 3.57 (ddd, 1H, $J_{4,5}$ = 9.4 Hz, H-5), 3.43 (t, 1H, J = 8.5 Hz), 3.37 (t, 1H, J = 8.5 Hz), 3.27 (m, 1H). ^{13}C NMR (75 MHz, CD_3OD) δ 168.5, 139.3, 135.0, 132.0, 131.2, 130.2, 129.9, 129.8, 129.3, 103.7, 78.6, 76.0, 75.7, 72.5, 72.4, 65.8. HRMS (ESI) calcd for $C_{20}H_{22}O_7Na$ m/z $(M+Na)^+$: 397.1258. Found: 397.1252.

1.25. Benzyl 6-*O*-butyryl-β-D-glucopyranoside (26b)

Yield from **26** 114 mg, 67%. R_f 0.36 (B). mp 54–56 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ −56.7 (*c* 0.4, $CHCl_3$). Lit. data:[42] mp 65 °C $[\alpha]_D^{23}$ −55.7° ($CHCl_3$). ^{1}H NMR (300 MHz, CD_3OD) δ 7.50–7.25 (m, 5H, Ar), 4.63(d, 1H, J_{gem} = 11.8 Hz, CH_2), 4.44 (dd, 1H, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 11.8 Hz, H-6a), 4.34 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-2), 4.22 (dd, 1H, $J_{5,6b}$ = 5.8 Hz, H-6b), 3.44 (ddd, 1H, $J_{4,5}$ = 9.1 Hz, H-5), 3.35–3.30 (m, 2H), 3.24 (dd, 1H, $J_{2,3}$ = 9.3 Hz, H-3), 2.35 (t, 2H, J = 7.2 Hz, CH_2CO), 1.66 (dt, 2H, J = 7.4 Hz, CH_2CH_3), 0.96 (t, 3H, J = 7.4 Hz, CH_3). ^{13}C NMR (75 MHz, CD_3OD) δ 175.8, 139.5, 129.9, 129.8, 129.3. 103.8, 78.5, 76.0, 75.6, 72.4, 72.3, 65.1, 37.5, 20.0, 14.6. HRMS (ESI) calcd for $C_{17}H_{24}O_7Na$ m/z $(M+Na)^+$: 363.1414. Found: 363.1419.

1.26. Benzyl 6-*O*-benzoyl-β-D-galactopyranoside (27a)

Yield from **27** 131 mg, 70%. R_f 0.28 (B). mp 93–94 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ −25.0 (*c* 0.7, $CHCl_3$). Lit. data:[43] mp 92–94 °C $[\alpha]_D^{25}$ −22.5 (methanol). ^{1}H NMR (300 MHz, CD_3OD) δ 8.07–7.99 (m, 2H, Ar), 7.63–7.54 (m, 1H, Ar), 7.52–7.45 (m, 2H, Ar), 7.37–7.22 (m, 5H, Ar), 4.82 (d, 1H, PhCH_2), 4.64 (d, 1H, J_{gem} = 11.9 Hz, PhCH_2), 4.60 (dd, 1H, $J_{5,6a}$ = 7.7 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6a), 4.47 (dd, 1H, $J_{5,6b}$ = 4.8 Hz, H-6b), 4.31 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 3.89 (d, 1H, $J_{3,4}$ = 3.1 Hz, H-4), 3.85 (m, 1H, H-5), 3.62 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.50 (dd, 1H, H-3). ^{13}C NMR (75 MHz, CD_3OD) δ 168.4, 139.4, 135.0, 134.6, 131.9, 131.2, 130.2, 129.9, 129.8, 129.3, 104.1, 75.3, 74.7, 73.0, 72.2, 71.0, 65.8. HRMS (ESI) calcd for $C_{20}H_{22}O_7Na$ m/z $(M+Na)^+$: 397.1258. Found: 397.1255.

1.27. Methyl 2,6-di-*O*-benzoyl-α-D-glucopyranoside (24b)

Yield from **24** 149 mg, 74%. R_f 0.41 (A). mp 142–143 °C (from EtOAc–hexane) $[\alpha]_D^{20}$ +70.4 (*c* 0.6, $CHCl_3$). Lit. data:[18] mp 140–142 °C, $[\alpha]_D$ +66.1 ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11–8.07 (m, 4H, Ar), 7.63–7.55 (m, 2H, Ar), 7.49–7.43 (m, 4H, Ar), 5.06 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.95 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 4.83 (dd, 1H, $J_{5,6a}$ = 4.2 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.52 (dd, 1H, $J_{5,6b}$ = 2.2 Hz, H-6b), 4.19 (dt, 1H, J = 9.5 Hz), 3.95 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, H-5), 3.59 (dt, 1H, J = 9.6 Hz), 3.41 (s, 3H, OCH_3), 3.32 (d, 1H, $J_{H,OH}$ = 3.4 Hz, OH), 2.71 (d, 1H, $J_{H,OH}$ = 3.2 Hz, OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 166.4, 133.3, 133.0, 129.9, 129.8, 129.5, 129.4, 128.4, 128.3, 97.3, 73.7, 71.5, 70.6, 69.5, 63.6, 55.3. HRMS (ESI) calcd for $C_{21}H_{22}O_8Na$ m/z $(M+Na)^+$: 425.1207. Found: 425.1211.

1.28. Methyl 2,6-di-*O*-butyryl-α-D-glucopyranoside (24c)

Yield from **24** 117 mg, 70%. R_f 0.56 (A). $[\alpha]_D^{20}$ +84.5 (*c* 0.6, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.89 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.69 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2), 4.49 (dd, 1H, $J_{5,6a}$ = 4.4 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.26 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, H-6b), 3.95 (t, 1H, $J_{3,4}$ = 9.4 Hz,), 3.75 (ddd, 1H, $J_{4,5}$ = 10.0, H-5), 3.42 (m, 1H), 3.36 (s, 3H, OCH_3), 2.36 (m, 4H, CH_2CO), 1.66 (m, 4H, CH_2CH_3), 0.95 (m, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 173.5, 97.1, 72.8, 71.2, 70.4, 69.3, 62.8, 55.2, 35.9 × 2, 18.3 × 2, 13.5, 13.4. HRMS (ESI) calcd for $C_{15}H_{26}O_8Na$ m/z $(M+Na)^+$: 357.1520. Found: 357.1523.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2012.06.020.

References

1. Chang, S. W.; Shaw, J. F. *New Biotechnol.* **2009**, *26*, 109–116.
2. Avela, E. *Sucr. Belge.* **1973**, *92*, 337–344.
3. Eby, R.; Webster, K. T.; Schuerch, C. *Carbohydr. Res.* **1984**, *129*, 111–120.
4. Gridley, J. J.; Osborn, H. M. I.; Suthers, W. G. *Tetrahedron Lett.* **1999**, *40*, 6991–6994.
5. Osborn, H. M. I.; Brome, V. A.; Harwood, L. M.; Suthers, W. G. *Carbohydr. Res.* **2001**, *332*, 157–166.
6. Gangadharmath, U. B.; Demchenko, A. V. *Synlett* **2004**, 2191–2193.
7. David, S.; Hanessian, S. *Tetrahedron* **1985**, *41*, 643–663.
8. Tsuda, Y.; Haque, M. E.; Yoshimoto, K. *Chem. Pharm. Bull.* **1983**, *31*, 1612–1624.
9. Grindley, T. B. *Adv. Carbohydr. Chem. Biochem.* **1998**, *53*, 17–142.
10. Holzapfel, C. W.; Koekemoer, J. M.; Marais, C. F. *Afr. J. Chem.* **1984**, *37*, 9–26.
11. Herradon, B.; Morcuende, A.; Valverde, S. *Synlett* **1995**, 455–458.
12. Iwasaki, F.; Maki, T.; Onomura, O.; Nakashima, W.; Matsumura, Y. *J. Org. Chem.* **2000**, *65*, 996–1002.
13. Martinelly, M. J.; Vaidyanathan, R.; Pawlak, J. M.; Nayyar, N. K.; Dhokte, U. P.; Doecke, C. W.; Zollars, L. M. H.; Moher, E. D.; Khau, V. V.; Kosmrlj, B. *J. Am. Chem. Soc.* **2002**, *124*, 3578–3585.
14. Zhang, Z.; Wong, C.-H. *Tetrahedron* **2002**, *58*, 6513–6519.
15. Dong, H.; Pei, Z.; Bystrom, S.; Ramstrom, O. *J. Org. Chem.* **2007**, *72*, 1499–1502.
16. Demizu, Y.; Kubo, Y.; Miyoshi, H.; Maki, T.; Matsumura, Y.; Moriyama, N.; Onomura, O. *Org. Lett.* **2008**, *10*, 5075–5077.
17. Helm, R. F.; Ralph, J. *J. Org. Chem.* **1991**, *56*, 7015–7021.
18. Ogawa, T.; Matsui, M. *Tetrahedron* **1981**, *37*, 2363–2369.
19. Lee, D.; Taylor, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 3724–3727.
20. Zhou, Y.; Ramström, O.; Dong, H. *Chem. Commun.* **2012**, 5370–5372.
21. Hu, G.; Vasella, A. *Helv. Chim. Acta* **2003**, *86*, 4369–4391.
22. Lu, X.-A.; Chou, C.-H.; Wang, C.-C.; Hung, S.-C. *Synlett* **2003**, 1364–1366.
23. Kattnig, E.; Albert, M. *Org. Lett.* **2004**, *6*, 945–948.
24. Muramatsu, W.; Kawabata, T. *Tetrahedron Lett.* **2007**, *48*, 5031–5033.
25. Kawabata, T.; Furuta, T. *Chem. Lett.* **2009**, *38*, 640–647.
26. Muramatsu, W.; Mishiro, K.; Ueda, Y.; Furuta, T.; Kawabata, T. *Eur. J. Org. Chem.* **2010**, 827–831.
27. Wang, C.-C.; Lee, J.-C.; Luo, S.-Y.; Kulkarni, S. S.; Huang, Y.-W.; Lee, C.-C.; Chang, K.-L.; Hung, S.-C. *Nature* **2007**, *446*, 896–899.
28. Witschi, M. A.; Gervay-Hague, J. *Org. Lett.* **2010**, *12*, 4312–4315.
29. Joseph, A. A.; Verma, V. P.; Liu, X.-Y.; Wu, C.-H.; Dhurandhare, V. M.; Wang, C.-C. *Eur. J. Org. Chem.* **2012**, 744–753.
30. Alekseev, Y. E.; Garnovskii, A. D.; Zhdanov, Y. A. *Usp. Khim.* **1998**, *67*, 723–744.
31. Gyurcsik, B.; Nagy, L. *Coord. Chem. Rev.* **2000**, *203*, 81–149.
32. Zhdanov, Y. A.; Alekseev, Yu. E. *Usp. Khim.* **2002**, *71*, 1090–1102
33. Evtushenko, E. V. *Synth. Commun.* **2006**, *36*, 1593–1599.
34. Evtushenko, E. V. *J. Carbohydr. Chem.* **2010**, *29*, 369–378.
35. Angyal, S. J. *Carbohydr. Res.* **1990**, *200*, 181–188.
36. Kurahashi, T.; Mizutani, T.; Yoshida, J.-I. *J. Chem. Soc., Perkin Trans. 1* **1999**, 465.
37. Moitessier, N.; Englebienne, P.; Chapleur, Y. *Tetrahedron* **2005**, *61*, 6839–6853.
38. Matwiejuk, M.; Thiem, J. *Eur. J. Org. Chem.* **2012**, 2180–2187.
39. Dong, H.; Zhou, Y.; Pan, X.; Cui, F.; Liu, W.; Liu, J.; Ramström, O. *J. Org. Chem.* **2012**, *77*, 1457–1467.
40. Dalpozzo, R.; De Nino, A.; Maiuolo, L.; Procopio, A.; Sindona, G.; Tagarelli, A. *Synth. Commun.* **2004**, *34*, 4207–4217.
41. Bollenback, G. N.; Parrish, F. W. *Carbohydr. Res.* **1971**, *17*, 431–438.
42. Goncalves, P. M. L.; Roberts, S. M.; Wan, P. W. H. *Tetrahedron* **2004**, *60*, 927–932.
43. Levy, A.; Flowers, H. M.; Sharon, N. *Carbohydr. Res.* **1967**, *4*, 305–311.