Selective acylation and sulfonylation of 4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose

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Dedicated to Jhillu Singh Yadav to mark his outstanding contributions to synthetic organic chemistry

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Abstract
Selective acylation and sulfonylation of 4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose were systematically studied by introducing different electrophiles under the action of catalysts DMAP or Ag_2O. As a result, 18 novel mono-protected compounds at the 2- or 3-position of the *C*-glucoside were prepared and their structures were confirmed by ^{1}H-NMR, ^{13}C-NMR, 2D NOEs and HRMS analysis. The results showed that electrophiles play a significant role in determining the product distribution.

Keywords: Acylation, sulfonylation, regioselectivity, *C*-glucoside

Introduction

Considerable efforts have been devoted to the synthesis of *C*-glycosyl compounds owing to their natural occurrence, biological interest, and synthetic utility.[1] *C*-Glycosides are of special interest because of their conformational differences compared to *O*-glycosides or *N*-glycosides; they are resistant to enzymatic and acidic hydrolysis since the anomeric center has been transformed from acetal to ether.[2]

In the past few decades, the regioselective manipulation of carbohydrate hydroxyl groups has been addressed with challenging strategies. The presence of multiple reactive sites on saccharide molecules means the synthesis of carbohydrate derivatives often relies on extensive protecting group manipulations or bio-enzyme methods[3]. Oligosaccharides with 1-2 and/or 1-3 linkages are abundant in nature[4,5] such as SLeX analogs,[6] Globo-H,[7] and other bioactive oligosaccharides.[8,9] Appropriate protected glycosides with one free hydroxyl group at the 2- or 3-position are very

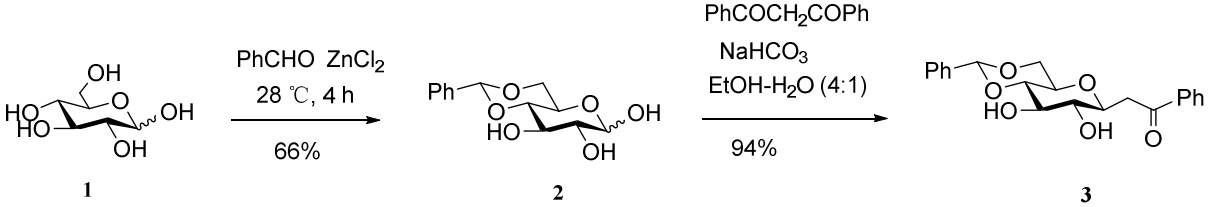
useful building blocks for the synthesis of bioactive oligosaccharide. Therefore we studied the regioselective protection of 2- or 3-position which have similar reactivity in carbohydrate derivatives with great interest. Nevertheless, small differences between the reactivity of 2- or 3-position can be utilized to achieve the desired protection pattern in one or a few steps.[10] Most studies had been focused on changing the hydrogen bond to an activated hydroxyl group at specific sites,[11] such as, methods employing DMAP[12,13] or functionalized DMAP,[14] organoboron,[15] organotin,[16] organosilicon,[17] The procedure also involves the use of inorganic catalysts like Ag_2O,[18] metal salts[19] and chiral copper(II) complex[20]. However, such strategies are, for the most part, dependent on *O*-glycosides, regioselective strategies for *C*-glycosides are very limited in the literature. The accessibility of new building blocks by an efficient and simple way represents an outstanding challenge in glycochemistry. Therefore, the preparation of selectively protected monosaccharide units bearing a single strategically positioned free hydroxyl group (a nucleophilic acceptor) symbolizes a breakthrough in carbohydrate synthesis together with the stereoselective glycosylation[21,22].

Our team has been engaged in the exploration of using simple sugar to synthesize corresponding drug intermediates, such as the synthesis of natural product D-mannoheptulose,[23] the stereocontrolled formation of protected aminodeoxyalditols,[24] synthesis of topiramate[25] and asymmetric catalyst derived from D-fructose.[26] Originally we reported the efficient synthesis of aryl ketone *β*-*C*-glycosides,[27] studying the regioselectivity of such compounds could make ways for the synthesis of bioactive oligosaccharides which can expand their application range. In this paper, we chose two different catalysts, DMAP and Ag_2O, due to their lower toxicity and easy availability. We reasoned that electrophilic reagents with different steric and electronic effects could modulate the reactivity of the secondary hydroxyl groups which is an important method to evaluate the regioselectivity using these two catalysts under mild conditions.

Results and Discussion

Synthesis of the substrate

Benzylidene, as widely used in carbohydrate chemistry, was chosen as the 4,6-*O* protecting group to selectively mask the C-4 and C-6 hydroxy groups. The selective cleavage of the 4,6-*O*-benzylidene group with various reagents allows entry into three types of structure.[28] The scheme used to prepare the benzylidene derivatives **3** is shown in Scheme 1, the approach is based on reported produres.[27,29]

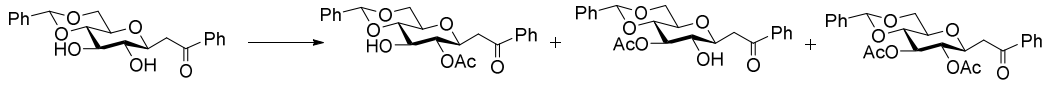


Scheme 1. General synthetic scheme to prepare target *C*-glycoside **3** from D-glucose **1**

Acetylation as a model reaction

First, the relative reactivity of the free hydroxyl groups of partially protected D-glucose derivatives was assessed using acetylation as a model reaction. The parameters that can affect the regioselectivity of the reaction are the reaction conditions and the chemical nature of the protecting groups. Solvents like CH_2Cl_2, THF, CH_3CN and $CHCl_3$, widely used for glycosylation reaction that we wish to model, were chosen. As a result, acylation of the compound **3** gave a mixture of monosubstituted and fully substituted products in which the 3-*O* functionalized derivatives predominated. The data summarized in Table 1 clearly indicates that the solvent effect were negligible since similar regioselectivities were achieved. There's no improvement to the regioselectivity when increase the polarity of the solvent. By comparison of the results in entry 1 with the others in Table 1, dichloromethane appeared to be the most suitable solvent.

Table 1. Optimization of solvent for acetylation reaction



3 **3a** **3b** **3c**

Entry	Solvent	Catalyst[a]	**3a**(%)[b]	**3b**(%)	**3c**(%)	**3a**: **3b**: **3c**
1	CH_2Cl_2	DMAP	45	54	1	1: 1.2: 0.02
2	THF	DMAP	47	48	5	1: 1.0: 0.11
3	$CHCl_3$	DMAP	32	35	33	1: 1.1: 1.0
4	CH_3CN	DMAP	32	38	30	1: 1.2: 0.94

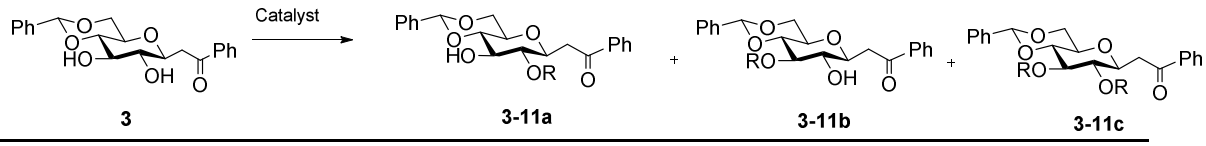
[a] Condition A: DMAP (10 mol%), AcCl(1.1 equiv), K_2CO_3(10 equiv) , solvent(50 mL), 25 ºC.; [b] isolated yield, based on reacted material **3**.

Effect of different electrophilic reagents

The effect of various electrophilic reagents was another factor we considered and the results were summarized in Table 2. All reactions proceeded effectively under the same conditions: at 25 ºC catalyzed by either DMAP or Ag_2O. Conversion rates between 70 to 95% were observed. The data summarized in Table 2 clearly indicated the differentiation of the reactivity of each hydroxyl, as well as the existence of steric and electronic effects of the electrophiles. To our surprise, these electrophiles showed a higher preference for position 3 except for tosylation, using DMAP or Ag_2O as the catalyst. In the case of tosylation, the C-2-protected product was predominant and no fully protected product was formed (Table 2, entries 15, 16). Accordingly, we presume that steric hindrance was involved. To verify the guess, we tried mesylation, which has relative lower steric hindrance. As a result, C-3, as expected, was preferentially protected and the fully protected product arose (Table 2, entries 17, 18), which was different from tosylation. Then we further studied introduction of the benzenesulfonyl group; the result was the same as *p*-toluenesulfonylation with C-2-protected product predominant; data are not reported in Table 2. Thus we came to the conclusion that sulfonylation with higher steric hindrance, such as

tosylation, may preferentially generate the C-2 substituted compound, after which the C-3 position was more difficult to substitute, and thus no fully protected products were generated.

Table 2. Acylation and sulfonylation of 4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose with various electrophile catalyzed by DMAP or Ag_2O



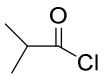
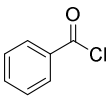
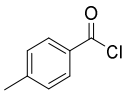
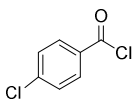
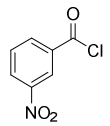
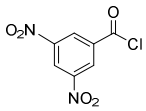
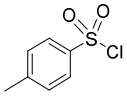
Entry	Reagent	Catalyst	Products	a(%)[b]	b(%)	c(%)	Ratio(a:b:c)	b/(a+b)(%)
1		DMAP	**3a, 3b, 3c**	45	54	1	1: 1.2: 0.02	55
2		Ag_2O[a]		29	55	16	1: 1.9: 0.55	65
3		DMAP	**4a, 4b, 4c**	27	63	10	1: 2.3: 0.37	70
4		Ag_2O		32	66	2	1: 2.1: 0.05	67
5		DMAP	**5a, 5b, 5c**	19	46	35	1: 2.4: 1.8	71
6		Ag_2O		24	65	11	1: 2.7: 0.46	73
7		DMAP	**6a, 6b, 6c**	15	52	33	1: 3.5: 2.2	77
8		Ag_2O		23	74	3	1: 3.2: 0.13	76
9		DMAP	**7a, 7b, 7c**	15	74	11	1: 4.9: 0.73	83
10		Ag_2O		18	74	8	1: 4.1: 0.44	80

Table 2 (continued)

Entry	Reagent	Catalyst	Products	a(%)b	b(%)	c(%)	Ratio(a:b:c)	b/(a+b)(%)
11		DMAP	**8a, 8b, 8c**	14	77	9	1: 5.5: 0.64	84
12		Ag_2O		13	69	18	1: 5.3: 1.4	84
13		DMAP	**9a, 9b, 9c**	11	79	10	1: 7.2: 0.91	88
14		Ag_2O		13	79	8	1: 6.1: 0.62	86
15		DMAP	**10a, 10b**	78	22	-[c]	3.5: 1 : 0	22
16		Ag_2O		74	26	-[c]	2.8: 1 : 0	26
17		DMAP	**11a, 11b, 11c**	21	59	20	1: 2.8: 0.95	74
18		Ag_2O		19	64	17	1: 3.4: 0.89	77

[a] Reaction conditions B: Ag_2O (1.5 equiv), KI (0.2 equiv), electrophile (1.1 equiv), CH_2Cl_2 (50 mL), 25 ºC. [b] Isolated yield, based on reacted material **3**. [c] Not detected.

The nature and position of substituents in the aromatic ring result in effects on the regioselectivity. The amount of C-3-protected products was slightly enhanced in the case of the substituted aromatic ring with the electron-withdrawing substituent groups (*i.e.*, *p*-chloro, *m*-nitro and 3,5-dinitro groups). Data collected in Table 2 also revealed that C-3-protected products increased or C-2- protected products decreased (the ratio of a/b decreased) with the increase of the steric hindrance in acylation. Eventually, results indicated that strong electron-withdrawing and higher steric hindrance lead regioselectivity product to 3-substituted ester in acylation.

Structure assignment

The mono-substituted products which are of comparable reactivity were evaluated by ^{1}H NMR. Changes in chemical shifts of crucial signals in starting materials and products were compared for structure characterization and product identification. NMR signal of H-2′ in regioselectivity product 2-*O*Ac (**3a**) was obviously shifted downfield from 3.50 ppm to 5.00 ppm, together with

the adjacent proton signals of H-1′ and H-3′ from 4.10 ppm to 4.30 ppm and 3.81 ppm to 4.00 ppm respectively. We also got the NOESY spectrum (500 MHz, $CDCl_3$) of products **8b** and **10a** for further confirmation. NOEs signals indicated spatial proximity of H-1′, H-3′ and H-5′ on one side of the ring and of H-2′ and H-4′ on the other side, respectively. We can see the NOE correlation at the same side. The significant nuclear NOE correlation between H-3′ (not H-2′) with H-5′ and H-3′ with H-1′ in **8b** and the downfield shifted signal of H-3′ indicated that compound **8b** were 3-*O*Ac (Figure 1), other NOE correlation can also be found. Similarly, a significant nuclear Overhauser effect between H-2′ with H-4′ can be observed in compound **10a** (Figure 2), and the other relevant signal can also be found, all of these indicated that compound **10a** was 2-*O*Ts not 3-*O*Ts.

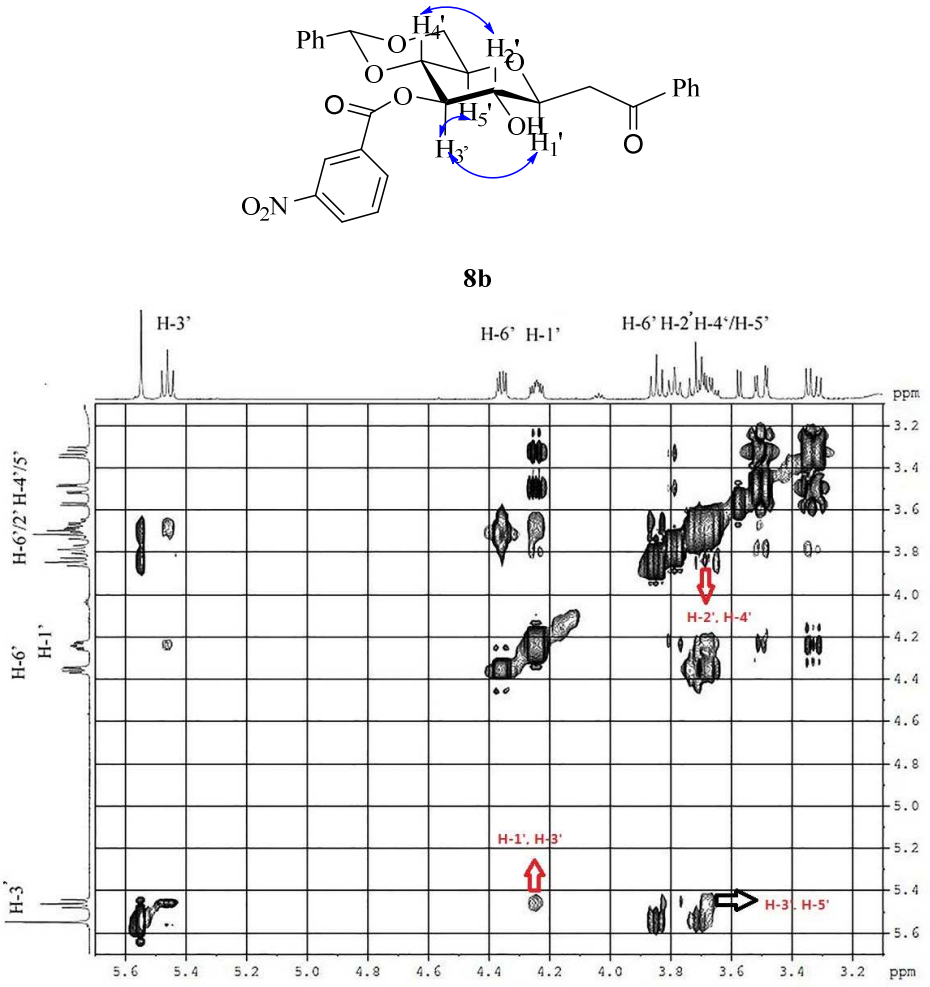


Figure 1. Nuclear Overhauser effect observed in **8b.**

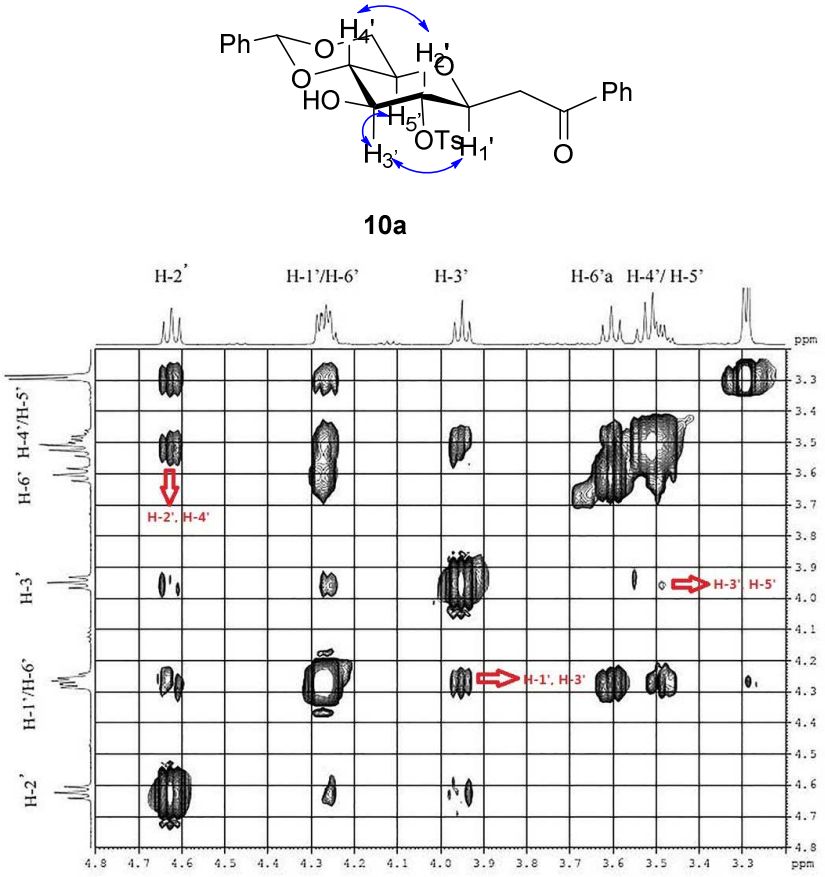


Figure 2. Nuclear Overhauser effect observed in **10a.**

Conclusions

In conclusion, the regioselectivity of 2- or 3-position in 4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose was investigated in this paper. Several electrophilic reagents were employed to study the differentiated selectivity of 2- or 3-position in the presence of catalyst DMAP or Ag_2O. Steric and electronic effects on the regioselectivity were elaborated, and other factors like solvents were considered. Eventually, several conclusions were obtained as follows: dichloromethane was the better solvent; protecting group with stronger electron-withdrawing and larger steric hindrance tended to occupy C-3 in acylation and C-2 in sulfonylation. The synthesized 26 compounds with 18 mono-protected compounds were obtained and reported for the first time, which can fulfil the need of the building block of bioactive *C*-glycosides with 1-2 and/or 1-3 linkages.

Experimental Section

General. Melting points were determined in open glass capillaries using a Griffin melting point apparatus. Solvents were distilled and dried by standard methods. All commercially available reagents were used without further purification. The progress of the reactions was monitored by thin-layer chromatography (TLC) over silica gel, and spots were visualized with UV light or iodine. ^{1}H, ^{13}C NMR and NOESY spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance III 500MHz spectrometer. Proton chemical shifts are reported in ppm relative to the internal standard tetramethylsilane (δ_{TMS} = 0 ppm) or solvents (δ_{DMSO} = 2.50 ppm), and carbon chemical shifts are reported in ppm relative to the solvents (δ_{CDCl_3} = 77.00, δ_{DMSO} = 39.7). Data were recorded and evaluated using TOPSPIN 3.1 (Bruker Biospin). All chemical shifts are given in ppm relative to tetramethylsilane. The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), or combinations of these. HRMS spectra analyses were performed on an Agilent 6540Q-TOF MS.

General procedure catalyzed by Ag_2O. To a stirred solution of 4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose **3** (92 mg, 0.25 mmol) in dichloromethane (50 mL) was added fresh Ag_2O (87 mg, 0.375 mmol), KI (8 mg, 0.05 mmol), electrophile RCl (0.275 mmol). The reaction mixture was stirred for 8 h at 25 ºC, filtered through a small pad of silica gel, and washed with dichloromethane. Evaporation of the solvent followed by column chromatography (petroleum ether/ethyl acetate 8:1 to 2:1) gave the products white crystals.

General procedure catalyzed by DMAP. To a solution of 4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose **3** (92 mg, 0.25 mmol) in CH_2Cl_2 (50 mL) was added K_2CO_3 (345 mg, 2.5 mmol) then DMAP (10 mol%) and RCl (0.275 mmol). After stirring for 8 h at 25 ºC, the solution was filtrated on a silica gel pad and concentrated *in vacuo*. The products were purified by column chromatography (petroleum ether/ethyl acetate 8:1 to 2:1).

4,6-*O*-Benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (3). Dry $ZnCl_2$ (30 g, 0.22 mmol) was added to a solution of **1** (20 g, 0.11 mmol) in dry PhCHO (120 mL) at 28 ºC. The mixture was stirred for 4 h and cooled to room temperature, then poured into 600 mL cool water. The resulting crystalline mass was filtered off after 0.5 h at 0 ºC and washed first with cold water (2 × 50 mL) and then with pentane (2 × 50 mL). Dried in the air to afford protected compound **2** (19.54 g, 65.61%, white powder). To a solution of **2** (2 g, 7.46 mmol) in 30 mL EtOH-H_2O (4:1) was added $NaHCO_3$ (1.4 g, 16.67 mmol) then dibenzoylmethane (3 g, 13.38 mmol). The reaction mixture was stirred at 90 ºC overnight. The solutions were allowed to cool to room temperature and the product was recrystallized as white crystals. Purification of the residues was performed by recrystallization from EtOH-H_2O. The overall yields reached up to 94%. White solid, mp 147-149 ºC, R_f (petroleum ether/EtOAc, 1:4) = 0.80, ^{1}H NMR (500 MHz, $CDCl_3$) 7.98 (2H, d, *J* 7.3 Hz, Ar *H*), 7.58 (1H, t, *J* 7.4 Hz, Ar *H*), 7.48 (4H, t, *J* 7.6 Hz, Ar *H*), 7.38 (3H, dd, *J* 8.5, 3.1 Hz, Ar *H*), 5.51 (1H, s, Ph-CH-), 4.29 (1H, dd, *J* 10.4, 4.5 Hz, H-6′a), 4.14-4.06 (1H, m, H-1′), 3.81 (td, *J* 8.7, 2.0 Hz, H-3′), 3.64 (t, *J* 10.0 Hz, H-6′b), 3.48-3.54 (3H,

m, H-4′, H-2′, H-5′), 3.48-3.39 (1H, m, H-1′a), 3.26 (1H, dd, *J* 16.6, 7.8 Hz, H-1′b), 2.83 (2H, d, *J* 10.6 Hz, OH). ^{13}C NMR (125 MHz, $CDCl_3$, DMSO-d_6) 202.6, 142.5, 141.9, 137.9, 133.2, 131.4, 106.3, 86.2, 81.7, 79.5, 79.3, 75.3, 73.5, 45.2.HRMS (ESI): calcd for $C_{21}H_{22}O_6Na$: *m/z* 393.1309 $[M + Na]^+$; found 393.1309.

2-*O*-Acetyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (3a). White solid, mp 138-140 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.29, ^{1}H NMR (500 MHz, $CDCl_3$, DMSO), 7.99-7.92 (2H, m, Ar *H*), 7.59 (1H, d, *J* 7.4 Hz, Ar *H*), 7.49 (4H, m, Ar *H*), 7.44-7.33 (3H, m, Ar *H*), 5.54 (1H, s, Ph-CH-), 4.99 (1H, t, *J* 9.4 Hz, H-2′), 4.30 (2H, dd, *J* 10.3, 4.3 Hz, H-1′, H-6′a), 3.97 (1H, d, *J* 2.4 Hz, H-3′), 3.64 (1H, d, *J* 10.1 Hz, H-6′b), 3.56 (2H, m, H-4′, H-5′), 3.33 (1H, dd, *J* 16.7, 8.3 Hz, H-1′a), 2.96 (1H, dd, *J* 16.7, 3.0 Hz, H-1′b), 2.09 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) 196.7, 170.9, 136.9, 136.8, 133.5, 129.4, 128.7, 128.3, 126.3, 102.0, 81.4, 74.4, 74.3, 73.2, 70.2, 68.6, 40.8, 21.0.HRMS (ESI): calcd for $C_{23}H_{24}O_7Na$: *m/z* 435.1414 $[M + Na]^+$; found 435.1414.

3-*O*-Acetyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (3b). White solid, mp 181-183 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.21, ^{1}H NMR (500 MHz, DMSO-d_6) 8.03-7.83 (2H, m, Ar *H*), 7.64 (1H, t, *J* 7.4 Hz, Ar *H*), 7.52 (2H, t, *J* 7.7 Hz, Ar *H*), 7.34(1H, s, Ar *H*), 5.56 (1H, s, Ph-CH-), 5.05 (1H, t, *J* 9.3 Hz, H-3′), 4.11 (1H, dd, *J* 10.2, 4.9 Hz, H-6′a), 4.03-3.99 (1H, m, H-1′), 3.66-3.52 (2H, m, H-6′b, H-4′), 3.51-3.39 (2H, m, H-5′, H-2′), 3.35-3.33(1H, m, H-1′a) 3.22 (1H, dd, *J* 7.3 16.6, H-1′b), 2.03 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 172.6, 137.0, 136.9, 133.4, 129.1, 128.6, 128.4, 128.3, 126.2, 101.5, 78.6, 77.3, 77.0, 73.9, 70.7, 68.8, 41.1, 21.0.HRMS (ESI): calcd for $C_{23}H_{24}O_7Na$: *m/z* 435.1414 $[M + Na]^+$; found 435.1413.

2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (3c). White solid, mp 150-152 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.56, ^{1}H NMR (500 MHz, DMSO-d_6) 7.97-7.84 (2H, m, Ar *H*), 7.63 (1H, d, *J* 7.3 Hz, Ar *H*), 7.52 (2H, t, *J* 7.7 Hz, Ar *H*), 7.35 (5H, m, Ar *H*), 5.61 (1H, s, Ph-CH-), 5.30 (1H, t, *J* 9.4 Hz, H-2′), 4.93 (1H, t, *J* 9.5 Hz, H-3′), 4.37-4.27 (1H, m, H-1′), 4.14 (1H, m, H-6′a), 3.77 (1H, t, *J* 9.2Hz, H-6′b), 3.65 (2H, m, H-4′, H-5′), 3.38-3.26(1H, m, H-1′a), 3.15-3.09 (1H, m, H-1′b), 1.97 (3H, s, CH_3), 1.92 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) 196.2, 170.3, 170.2, 136.9, 136.7, 133.5, 129.1, 128.5, 128.2, 126.2, 101.5, 78.8, 74.6, 73.0, 72.6, 70.6, 68.6, 40.7, 20.9, 20.7.HRMS (ESI): calcd for $C_{25}H_{26}O_8Na$: *m/z* 477.1520 $[M + Na]^+$; found 477.1521.

2-*O*-Isobutyryl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (4a). White solid, mp 152-154 ºC, R_f (petroleum ether/EtOAc, 4:1) = 0.23, ^{1}H NMR (500 MHz, $CDCl_3$) 7.95 (2H, d, *J* 7.5 Hz, Ar *H*), 7.59 (1H, t, *J* 7.4 Hz, Ar *H*), 7.49 (4H, m, Ar *H*), 7.39 (3H, dd, *J* 8.2, 2.9 Hz, Ar *H*), 5.54 (1H, s, Ph-CH-), 4.98 (1H, t, *J* 9.4 Hz, H-2′), 4.38-4.20 (2H, m, H-1, H-6′a), 3.97 (1H, t, *J* 8.8 Hz, H-3′), 3.65 (1H, t, *J* 9.9 Hz, H-6′b), 3.56 (2H, dt, *J* 8.9, 6.8 Hz, H-5′, H-4′), 3.33 (1H, dd, *J* 16.8, 8.5 Hz, H-1′a), 2.92 (1H, dd, *J* 16.8, 2.8 Hz, H-1′b), 2.66-2.51 (1H, m, H-5′), 1.19 (3H, d, *J* 7.0 Hz, CH_3), 1.14 (3H, d, *J* 7.0 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) 195.5, 175.8, 135.6, 132.3, 128.2, 127.5, 127.2, 127.1, 125.1, 100.7, 80.2, 76.44, 73.3,

72.5, 69.1, 67.5, 39.5, 32.9, 17.8, 17.6.HRMS (ESI): calcd for $C_{25}H_{28}O_7Na$: *m/z* 463.1727 [M + Na]$^+$; found 463.1729.

3-*O*-Isobutyryl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (4b). White solid, mp 185-187 ºC, R_f (petroleum ether/EtOAc, 4:1) = 0.15, ^{1}H NMR (500 MHz, $CDCl_3$) 7.98 (2H, d, *J* 7.5 Hz, Ar *H*), 7.58 (1H, t, *J* 7.4 Hz, Ar *H*), 7.50-7.42 (4H, m, Ar *H*), 7.41-7.31 (3H, m, Ar *H*), 5.52 (1H, s, Ph-CH-), 5.16 (1H, t, *J* 9.2 Hz, H-3′), 4.30 (1H, dd, *J* 10.3, 4.7 Hz, H-6′a), 4.18 (1H, td, *J* 9.7, 2.8 Hz, H-1′), 3.66 (2H, td, *J* 9.8, 4.7 Hz, H-6′b, H-2′), 3.61-3.56 (2H, m, H-4′, H-5′), 3.49 (1H, dd, *J* 16.6, 2.8 Hz, H-1′a), 3.24 (1H, dd, *J* 16.6, 8.2 Hz, H-1′b), 2.67 (1H, dt, *J* 13.9, 7.0 Hz, CH), 1.22 (3H, d, *J* 7.0, CH_3), 1.21(3H, d, *J* 7.0, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) 196.5, 177.6, 135.9, 135.7, 132.2, 127.8, 127.5, 127.2, 127.1, 124.8, 100.0, 77.6, 76.1, 74.8, 72.7, 69.4, 67.6, 39.9, 33.0, 17.9, 17.7.HRMS (ESI): calcd for $C_{25}H_{28}O_7Na$: *m/z* 463.1727 [M + Na]$^+$; found 463.1729.

2,3-Di-*O*-isobutyryl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (4c). White solid, mp 163-165 ºC, R_f (petroleum ether/EtOAc, 4:1) = 0.56, ^{1}H NMR (500 MHz, $CDCl_3$) 7.94 (2H, d, *J* 7.4 Hz, Ar *H*), 7.59 (1H, d, *J* 7.4 Hz, Ar *H*), 7.49 (2H, t, *J* 7.7 Hz, Ar *H*), 7.42 (2H, dd, *J* 6.6, 2.7 Hz, Ar *H*), 7.40-7.29 (3H, m, Ar *H*), 5.51 (1H, s, Ph-CH-), 5.43 (1H, t, *J* 9.3 Hz, H-3′), 5.11 (1H, t, *J* 9.6 Hz, H-2′), 4.44-4.33 (1H, m, H-1′), 4.32 (1H, dd, *J* 9.7, 4.1 Hz, H-6′a), 3.71-3.61 (3H, m, H-6′b, H-4′, H-5′), 3.31 (1H, dd, *J* 16.7, 8.5 Hz, H-1′a), 2.89 (1H, dd, *J* 16.7, 2.8 Hz, H-1′b), 2.69-2.42 (2H, m, CH), 1.15-1.09 (12H, m, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) 195.1, 175.0, 174.9, 135.8, 132.3, 127.8, 127.5, 127.1, 127.0, 124.8, 100.1, 78.0 (s), 73.6, 71.0, 69.4, 67.5, 39.43, 32.8, 17.9, 17.8, 17.7, 17.6.HRMS (ESI): calcd for $C_{29}H_{34}O_8Na$: *m/z* 533.2146 [M + Na]$^+$; found 533.2145.

2-*O*-Benzoyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (5a). White solid, mp 51-53 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.49, ^{1}H NMR (500 MHz, $CDCl_3$) 8.05 (2H, d, *J* 7.3 Hz, Ar *H*), 7.91 (2H, d, *J* 7.3 Hz, Ar *H*), 7.59 (2H, t, *J* 7.4 Hz, Ar *H*), 7.57-7.49 (3H, m, Ar *H*), 7.49-7.42 (3H, m, Ar *H*), 7.40 (3H, dt, *J* 4.4, 3.3 Hz, Ar *H*), 5.58 (1H, s, Ph-CH-), 5.26 (1H, t, *J* 9.4 Hz, H-2′), 4.47(1H, td, *J* 9.9, 2.7 Hz, H-1′), 4.35 (1H, dd, *J* 10.1, 4.2 Hz, H-6′a), 4.15 (1H, t, *J* 8.7 Hz, H-3′), 3.76-3.58 (3H, m, H-6′b, H-4′, H-5′), 3.41 (1H, dd, *J* 16.8, 8.6 Hz, H-1′a), 3.02 (1H, dd, *J* 16.8, 2.8 Hz, H-1′b), 2.69 (1H, s, OH). ^{13}C NMR (125 MHz, $CDCl_3$) 195.2, 165.1, 123.6, 129.0, 128.3, 128.1, 127.6, 127.5, 127.4, 127.2, 125.3, 101.0, 80.5, 73.8, 72.5, 69.5, 69.4, 67.7, 35.1.HRMS (ESI): calcd for $C_{28}H_{26}O_7Na$: *m/z* 497.1571 [M + Na]$^+$; found 497.1573.

3-*O*-Benzoyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (5b). White solid, mp 182-184 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.40, ^{1}H NMR (500 MHz, $CDCl_3$) 8.17-8.06 (2H, m, Ar *H*), 8.01-7.93 (2H, m, Ar *H*), 7.61-7.58 (2H, m, Ar *H*), 7.55-7.39 (6H, m, Ar *H*), 7.39-7.29 (3H, m, Ar *H*), 5.56 (1H, s, Ph-CH), 5.37 (1H, t, *J* 9.2 Hz, H-3′), 4.36 (1H, dd, *J* 10.0, 4.5 Hz, H-6′a), 4.24 (1H, ddd, *J* 9.6, 8.3, 3.0 Hz, H-1′), 3.84 (1H, t, *J* 9.3 Hz, H-2′), 3.80-3.69 (2H, m, H-5′, H-4′), 3.66 (1H, dd, *J* 9.2, 4.5 Hz, H-6′b), 3.53 (1H, dd, *J* 16.6, 3.0 Hz, H-1′a), 3.39 (1H, d, *J* 4.6 Hz, OH), 3.27 (1H, dd, *J* 16.6, 8.1 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 192.8, 163.1, 132.2, 132.1, 128.7, 128.5, 125.2, 124.6, 124.2, 123.8, 123.6, 123.5,

123.4, 121.3, 96.6, 74.0, 72.6, 72.5, 69.1, 65.9, 64.0, 36.3.HRMS (ESI): calcd for $C_{28}H_{26}O_7Na$: *m/z* 497.1571 $[M + Na]^+$; found 497.1572.

2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (5c). White solid, mp 116-118 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.60, ^{1}H NMR (500 MHz, $CDCl_3$) 7.99-7.86 (6H, m, Ar *H*), 7.56 (1H, t, *J* 7.4 Hz, Ar *H*), 7.54-7.47 (2H, m, Ar *H*), 7.47-7.40 (4H, m, Ar *H*), 7.37 (4H, m, Ar *H*), 7.34-7.29 (3H, m, Ar *H*), 5.86 (1H, t, *J* 9.5 Hz, H-2′), 5.55(1H, s, Ph-CH), 5.52 (1H, t, *J* 16.3, 6.7 Hz, H-3′), 4.59 (1H, td, *J* 9.9, 2.8 Hz, H-1′), 4.39 (1H, dd, *J* 9.5, 3.9 Hz, H-6′a), 3.92 (1H, t, *J* 9.3 Hz, H-4′), 3.85-3.69 (2H, m, H-5′, H-6′b), 3.44 (1H, dd, *J* 16.8, 8.7 Hz, H-1′a), 3.05 (1H, dd, *J* 16.8, 2.8 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 191.4, 161.0, 132.0, 131.9, 128.6, 128.2, 125.1, 124.9, 124.7, 124.2, 123.8, 123.6, 123.4, 121.3, 96.6, 74.5, 70.20, 68.5, 67.9, 66.1, 63.9, 35.8.HRMS (ESI): calcd for $C_{35}H_{30}O_8Na$: *m/z* 601.1833 $[M + Na]^+$; found 601.1834.

2-*O*-(4-Methylbenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (6a). White solid, mp 55-57 ºC, R_f (petroleum ether/EtOAc, 4:1) = 0.24, ^{1}H NMR (500 MHz, $CDCl_3$) 7.99 (1H, s, Ar *H*), 7.96-7.87 (3H, m, Ar *H*), 7.55 (t, *J* 7.4 Hz, Ar *H*), 7.53-7.47 (2H, m, Ar *H*), 7.43 (2H, t, *J* 7.8 Hz, Ar *H*), 7.39 (3H, td, *J* 4.8, 2.4 Hz, Ar *H*), 7.25 (2H, d, *J* 8.1 Hz, Ar *H*), 5.57 (1H, s, Ph-CH), 5.23 (1H, t, *J* 9.6, H-2′), 4.46 (1H, td, *J* 9.9, 2.6. H-1′), 4.34 (1H, dd, *J* 10.1, 4.2 Hz, H-6′a), 4.13 (1H, t, *J* 8.8 Hz, H-3′), 3.75-3.59 (3H, m, H-4′, H-5′, H-6′b), 3.40 (1H, dd, *J* 16.9, 8.8 Hz, H-1′a), 3.00 (1H, dd, *J* 16.8, 2.6 Hz, H-1′b), 2.41 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) 195.5, 165.2, 143.3, 135.8, 132.2, 128.9, 128.2, 128.1, 127.4, 127.2, 127.1, 125.1, 100.8, 80.3, 73.4, 72.3, 69.1, 67.5, 39.5, 20.6.HRMS (ESI): calcd for $C_{29}H_{28}O_7Na$: *m/z* 511.1727 $[M + Na]^+$; found 511.1727.

3-*O*-(4-Methylbenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (6b). White solid, mp 135-137 ºC, R_f (petroleum ether/EtOAc, 4:1) = 0.17, ^{1}H NMR (500 MHz, $CDCl_3$) 7.99 (4H, t, *J* 7.3 Hz, Ar *H*), 7.62-7.56 (1H, m, Ar *H*), 7.51-7.46 (2H, m, Ar *H*), 7.46-7.41 (2H, m, Ar *H*), 7.34-7.29 (3H, m, Ar *H*), 7.28-7.23 (2H, m, Ar *H*), 5.56 (1H, s, Ph-CH), 5.36 (1H, t, *J* 9.2 Hz, H-3′), 4.34 (1H, dd, *J* 10.2, 4.6 Hz, H-6′a), 4.23 (1H, td, *J* 9.6, 2.8 Hz, H-1′), 3.82 (1H, t, *J* 9.4 Hz, H-6′b), 3.77-3.68 (2H, m, H-4′, H-2′), 3.64 (1H, td, *J* 9.7, 4.6 Hz, H-5′), 3.53 (1H, dd, *J* 16.5, 2.8 Hz, H-1′a), 3.25 (1H, dd, *J* 16.6, 8.3 Hz, H-1′b), 2.42 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) 196.4, 167.0, 143.2, 135.8, 135.7, 132.1, 128.9, 128.0, 127.8, 127.5, 127.2, 127.1, 125.3, 124.9, 100.2, 77.6, 76.2, 75.6, 72.76, 69.54, 67.64, 39.97, 20.58).HRMS (ESI): calcd for $C_{29}H_{28}O_7Na$: *m/z* 511.1727 $[M + Na]^+$; found 511.1729.

2,3-Di-*O*-(4-Methylbenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (6c). White solid, mp 81-83 ºC, R_f (petroleum ether/EtOAc, 4:1) = 0.46, ^{1}H NMR (500 MHz, $CDCl_3$) 7.91 (2H, d, *J* 7.4 Hz, Ar *H*), 7.83 (4H, dd, *J* 14.3, 8.2 Hz, Ar *H*), 7.56 (1H, t, *J* 7.4 Hz, Ar *H*), 7.51-7.39 (4H, m, Ar *H*), 7.39-7.28 (3H, m, Ar *H*), 7.16 (4H, dd, *J* 8.1, 1.7 Hz, Ar *H*), 5.84 (1H, t, *J* 9.5 Hz, H-3′), 5.54 (1H, s, Ph-CH), 5.49 (1H, t, *J* 9.6 Hz, H-2′), 4.56 (1H, td, *J* 9.7, 2.5 Hz, H-1′), 4.38 (1H, dd, *J* 9.4, 3.8 Hz, H-6′a), 3.90 (1H, t, *J* 9.2 Hz, H-6′b), 3.80 3.72(2H, m, H-5′, H-4′), 3.43 (1H, dd, *J* 16.8, 8.9 Hz, H-1′a), 3.02 (1H, dd, *J* 16.8, 2.5 Hz, H-1′b), 2.35 (d, *J* 1.5 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) 195.2, 164.7, 164.5, 143.2, 142.5, 135.7, 135.6,

132.2, 128.8, 128.6, 128.0, 127.8, 127.4, 127.1, 127.0, 125.6, 124.9, 124.8, 100.3, 78.2, 73.9, 71.9, 71.4, 69.7, 67.56, 39.3, 20.5. HRMS (ESI): calcd for $C_{37}H_{34}O_8Na$: *m/z* 629.2146 $[M + Na]^+$; found 629.2147.

2-*O*-(4-Chlorobenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (7a). White solid, mp 81-83 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.56, ^{1}H NMR (500 MHz, $CDCl_3$) 7.96-7.90 (2H, m, Ar *H*), 7.89-7.83 (2H m, Ar *H*), 7.52 (1H, t, *J* 7.4 Hz, Ar *H*), 7.49 (2H, m, Ar *H*), 7.44-7.32 (7H, m, Ar *H*), 5.55 (1H, s, Ph-CH), 5.22 (1H, t, *J* 9.7, H-2′), 4.43 (1H, ddd, *J* 10.0, 8.4, 3.2 Hz, H-1′), 4.32 (1H, dd, *J* 10.2, 4.3 Hz, H-6′a), 4.10 (1H, t, *J* 8.8 Hz, H-3′), 3.72-3.54 (3H, m, H-6′b, H-4′, H-5′), 3.36 (1H, dd, *J* 16.8, 8.3 Hz, H-1′a), 2.99 (1H, dd, *J* 16.8, 3.1 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 195.3, 164.2, 138.9, 135.8, 135.6, 132.2, 130.1, 128.2, 127.7, 127.4, 127.2, 127.1, 126.4, 125.1, 100.8, 80.3, 73.9, 73.4, 72.3, 69.2, 67.5, 39.6, 28.5.HRMS (ESI): calcd for $C_{28}H_{25}ClO_7Na$: *m/z* 531.1181 $[M + Na]^+$; found 531.1182.

3-*O*-(4-Chlorobenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (7b). White solid, mp 172-174 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.61, ^{1}H NMR (500 MHz, $CDCl_3$) 8.00 (4H, dd, *J* 11.7, 8.2 Hz, Ar *H*), 7.59 (1H, t, *J* 7.3 Hz, Ar *H*), 7.49 (2H, t, *J* 7.6 Hz, Ar *H*), 7.45-7.38 (4H, m, Ar *H*), 7.38-7.29 (3H, m, Ar *H*), 5.54 (1H, s, Ph-CH), 5.40 (1H, t, *J* 9.2 Hz, H-3′), 4.35 (1H, dd, *J* 10.0, 4.4 Hz, H-6′a), 4.30-4.18 (1H, m, H-1′), 3.81 (1H, t, *J* 9.3 Hz, H-6′b), 3.78-3.64(3H, m, H-4, H-2′, H-5′), 3.52 (1H, dd, *J* 16.6, 2.9 Hz, H-1′a), 3.28 (1H, dd, *J* 16.6, 7.9 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 196.5, 165.8, 138.8, 135.7, 132.2, 130.2, 127.9, 127.7, 127.5, 127.2, 127.1, 126.7, 124.9, 100.3, 77.6, 76.4, 76.1, 72.7, 69.6, 67.6, 40.0.HRMS (ESI): calcd for $C_{28}H_{25}ClO_7Na$: *m/z* 531.1181 $[M + Na]^+$; found 531.1182.

2,3-Di-*O*-(4-Chlorobenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (7c). White solid, mp 117-119 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.72, ^{1}H NMR (500 MHz, $CDCl_3$) 7.88 (4H, dd, *J* 13.7, 8.0 Hz, Ar *H*), 7.83 (2H, d, *J* 8.6 Hz, Ar *H*), 7.56 (1H, t, *J* 7.4 Hz, Ar *H*), 7.47-7.38 (4H, m, Ar *H*), 7.33 (7H, dd, *J* 9.5, 5.6 Hz, Ar *H*), 5.80 (1H, t, *J* 9.5 Hz, H-2′), 5.54 (1H, s, Ph-CH), 5.47 (1H, t, *J* 9.6 Hz, H-3′), 4.64-4.51 (1H, m, H-1′), 4.39 (1H, dd, *J* 8.5, 2.8 Hz, H-6′a), 3.91 (1H, t, *J* 9.2 Hz, H-6′b), 3.83-3.68 (2H, m, H-4′, H-5′), 3.42 (1H, dd, *J* 16.8, 8.3 Hz, H-1′a), 3.04 (1H, dd, *J* 16.8, 3.0 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 194.9, 163.8, 163.7, 135.6, 135.4, 132.3, 130.1, 130.0, 127.9, 127.7, 127.5, 127.1, 126.6, 125.8, 125.0, 100.4, 77.9, 73.7, 72.5, 71.9, 69.8, 67.5, 39.4.HRMS (ESI): calcd for $C_{35}H_{28}Cl_2O_8Na$: *m/z* 669.1053 $[M + Na]^+$; found 669.1056.

2-*O*-(3-Nitrobenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (8a). White solid, mp 124-126 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.35, ^{1}H NMR (500 MHz, $CDCl_3$) 9.01-8.84 (1H, m, Ar *H*), 8.52-8.37 (2H, m, Ar *H*), 8.05-7.95 (2H, m, Ar *H*), 7.70-7.63 (1H, m, Ar *H*), 7.60 (1H, t, *J* 7.4 Hz, Ar *H*), 7.49 (2H, t, *J* 7.7 Hz, Ar *H*), 7.42 (2H, dd, *J* 6.6, 3.1 Hz, Ar *H*), 7.35-7.29 (3H, m, Ar *H*), 5.55 (1H, s, Ph-CH), 5.48 (1H, t, *J* 9.3 Hz, H-2′), 4.36 (1H, dd, *J* 9.7, 4.1 Hz, H-6′a), 4.31-4.19 (1H, m, H-1′), 3.86 (1H, d, *J* 9.1 Hz, H-6′b), 3.80 (1H, t, *J* 9.3 Hz, H-3′), 3.70 (2H, ddd, *J* 13.1, 9.6, 5.0 Hz, H-4′, H-5′), 3.51 (1H, dd, *J* 16.7, 3.6 Hz, H-1′a), 3.34 (1H, dd, *J* 16.6, 7.4 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 195.1, 162.9, 147.1, 134.4, 132.3, 128.6, 128.3, 127.5, 127.3, 127.1, 126.7, 125.1, 123.7, 100.9, 80.2, 74.4,

73.3, 72.1, 69.2, 67.5, 39.7.HRMS (ESI): calcd for $C_{28}H_{25}NO_9Na$: *m/z* 542.1422 $[M + Na]^+$; found 542.1421.

3-*O*-(3-Nitrobenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (8b). White solid, mp 108-110 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.23, ^{1}H NMR (500 MHz, $CDCl_3$) 8.78 (1H, s, Ar *H*), 8.52-8.24 (2H, m, Ar *H*), 7.87 (2H, d, *J* 7.3 Hz, Ar *H*), 7.63 (1H, t, *J* 8.0 Hz, Ar *H*), 7.56-7.46 (3H, m, Ar *H*), 7.46-7.29 (5H, m, Ar *H*), 5.55 (1H, s, Ph-CH), 5.28 (1H, t, *J* 9.4 Hz, H-3′), 4.46 (1H, ddd, *J* 10.2, 8.0, 3.5 Hz, H-1′), 4.34 (1H, dd, *J* 10.1, 3.7 Hz, H-6′a), 4.12 (1H, q, *J* 7.2 Hz, H-6′b), 3.78-3.52 (3H, m, H-5′, H-4′, H-2′), 3.38 (1H, dd, *J* 16.7, 7.9 Hz, H-1′a), 3.04 (1H, dd, *J* 16.7, 3.5 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 196.6, 164.1, 147.1, 135.7, 134.6, 128.6, 128.0, 127.5, 127.2, 127.1, 126.6, 125.0, 123.7, 100.4, 77.5, 75.8, 75.6, 72.6, 69.7, 67.6, 40.1.HRMS (ESI): calcd for $C_{28}H_{25}NO_9Na$: *m/z* 542.1422 $[M + Na]^+$; found 542.1418.

2,3-Di-*O*-(3-Nitrobenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (8c). White solid, mp 139-141 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.43, ^{1}H NMR (500 MHz, $CDCl_3$) 8.84-8.72 (1H, m, Ar *H*), 8.70-8.60 (1H, m, Ar *H*), 8.37 (2H, d, *J* 8.0 Hz, Ar *H*), 8.25 (1H, d, *J* 7.9 Hz, Ar *H*), 8.20 (1H, s, Ar *H*), 7.95-7.82 (2H, m, Ar *H*), 7.67-7.51 (3H, m, Ar *H*), 7.43 (4H, dd, *J* 10.0, 5.2 Hz, Ar *H*), 7.38-7.30 (3H, m, Ar *H*), 5.87 (1H, t, *J* 9.4 H-3′), 5.57 (1H, s, Ph-CH), 5.56(1H, t, *J* 9.4, H-2′) 4.71-4.59 (1H, m, H-1′), 4.42 (1H, dd, *J* 8.6, 2.9 Hz, H-6′a), 4.00 (1H, t, *J* 9.3 Hz, H-6′b), 3.89-3.72 (2H, m, H-4′, H-5′), 3.43 (1H, dd, *J* 16.6, 7.6 Hz, H-1′a), 3.11 (1H, dd, *J* 16.6, 3.8 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 194.6, 162.6, 147.1, 134.2, 134.1, 128.7, 128.5, 128.0, 127.5, 127.1, 126.8, 125.0, 123.7, 100.6, 77.6, 73.7, 73.3, 72.9, 69.8, 67.4, 39.6.HRMS (ESI): calcd for $C_{35}H_{28}N_2O_{12}Na$: *m/z* 691.1534 $[M + Na]^+$; found 691.1534.

2-*O*-(3,5-Dinitrobenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (9a). White solid, mp 178-180 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.51, ^{1}H NMR (500 MHz, $CDCl_3$) 9.22 (1H, t, *J* 2.1 Hz, Ar *H*), 9.08 (2H, d, *J* 2.1 Hz, Ar *H*), 7.92-7.79 (2H, m, Ar *H*), 7.62-7.45 (3H, m, Ar *H*), 7.45-7.34 (5H, m, Ar *H*), 5.58 (1H, s, Ph-CH), 5.33 (1H, t, *J* 9.5, H-2′), 4.60-4.47 (1H, m, H-1′), 4.38 (1H, dd, *J* 10.0, 3.7 Hz, H-6′a), 4.21 (t, *J* 9.0 Hz, H-3′), 3.77-3.69 (3H, m, H-5′, H-4′, H-6′b), 3.40 (1H, dd, *J* 16.6, 7.0 Hz, H-1′a), 3.11 (1H, dd, *J* 16.6, 4.4 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 191.2, 157.3, 143.7, 131.9, 131.5, 128.8, 124.8, 124.7, 123.9, 123.6, 123.4, 121.4, 117.9, 97.3, 76.4, 71.7, 69.5, 68.2, 65.5, 63.8, 36.2.HRMS (ESI): calcd for $C_{28}H_{24}N_2O_{11}Na$: *m/z* 587.1272 $[M + Na]^+$; found 587.1252.

3-*O*-(3,5-Dinitrobenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (9b). White solid, mp 179-181 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.37, ^{1}H NMR (500 MHz, $CDCl_3$) 9.22 (1H, t, *J* 2.1 Hz, Ar *H*), 9.19 (2H, d, *J* 2.1 Hz, Ar *H*), 7.99 (2H, dd, *J* 8.3, 1.1 Hz, Ar *H*), 7.66-7.57 (1H, m, Ar *H*), 7.50 (2H, t, *J* 7.7 Hz, Ar *H*), 7.45-7.36 (2H, m, Ar *H*), 7.35-7.29 (3H, m, Ar *H*), 5.63-5.48 (2H, m, H-3, Ph-CH), 4.38 (1H, dd, *J* 9.2, 3.6 Hz, H-6′a), 4.32-4.20 (1H, m, H-1′), 3.85 (2H, dt, *J* 18.5, 9.2 Hz, H-6′b, H-4′), 3.72 (2H dt, *J* 9.1, 7.2 Hz, H-5′, H-2′), 3.50 (1H, dd, *J* 16.8, 4.3 Hz, H-1′a), 3.40 (1H, dd, *J* 16.8, 6.6 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 193.3, 177.0, 158.1, 143.7, 131.8, 128.9, 128.5, 124.9, 124.4, 123.9, 123.6,

123.4, 121.3, 117.8, 96.8, 73.7, 73.6, 71.9, 68.8, 66.0, 63.8, 36.5.HRMS (ESI): calcd for $C_{28}H_{24}N_2O_{11}Na$: *m/z* 587.1272 $[M + Na]^+$; found 587.1273.

2,3-Di-*O*-(3,5-dinitrobenzoyl)-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (9c). White solid, mp 144-146 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.63, ^{1}H NMR (500 MHz, $CDCl_3$) 9.17 (1H, t, *J* 2.0 Hz, Ar *H*), 9.15 (1H, t, *J* 2.0 Hz, Ar *H*), 9.04 (2H, d, *J* 2.0 Hz, Ar *H*), 8.95 (2H, d, *J* 2.0 Hz, Ar *H*), 7.84 (2H, d, *J* 7.4 Hz, Ar *H*), 7.54 (1H, t, *J* 7.4 Hz, Ar *H*), 7.47-7.33 (4H, m, Ar *H*), 7.32-7.27 (3H, m, Ar *H*), 5.91 (1H, t, *J* 9.3 Hz, H-3′), 5.64-5.58 (1H, t, *J* 9.5, H-2′), 5.58 (1H, s, Ph-CH), 4.78-4.65 (1H, m, H-1′), 4.44 (1H, dd, *J* 10.1, 4.3 Hz, H-6′a), 4.14-4.02 (1H, t, *J* 9.4, H-4′), 3.85 (1H, dq, *J* 13.2, 4.4 Hz, H-5′), 3.80 (1H, t, *J* 10.1 Hz, H-6′b), 3.43 (1H, dd, *J* 16.5, 6.6 Hz, H-1′a), 3.18 (1H, dd, *J* 16.5, 4.7 Hz, H-1′b). ^{13}C NMR (125 MHz, $CDCl_3$) 190.6, 157.3, 157.2, 143.8, 129.0, 124.8, 124.7, 124.5, 124.0, 123.5, 123.4, 121.3, 118.2, 118.1, 97.1, 73.5, 70.8, 70.4, 69.8, 66.0, 63.7, 36.1.HRMS (ESI): calcd for $C_{35}H_{26}N_4O_{16}Na$: *m/z* 781.1236 $[M + Na]^+$; found 781.1468.

2-*O*-4-Tosyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (10a). White solid, mp 113-115 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.38, ^{1}H NMR (500 MHz, $CDCl_3$) 7.93 (2H, d, *J* 8.0 Hz, Ar *H*), 7.84 (2H, d, *J* 7.9 Hz, Ar *H*), 7.60 (1H, t, *J* 7.4 Hz, Ar *H*), 7.53-7.42 (4H, m, Ar *H*), 7.41-7.34 (3H, m, Ar *H*), 7.32 (2H, d, *J* 8.0 Hz, Ar *H*), 5.51 (1H, s, Ph-CH), 4.64 (1H, t, *J* 9.2 Hz, H-2′), 4.30-4.27 (2H, m, H-1′, H-6′a), 3.97 (1H, t, *J* 8.6 Hz, H-3′), 3.62 (1H, t, *J* 9.8 Hz, H-6′b), 3.54-3.51 (2H, m, H-4′, H-5′), 3.30 (d, *J* = 5.6 Hz, H-1′a, H-1′b), 2.42 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.2, 145.4, 136.7, 133.4, 129.8, 129.3, 128.7, 128.3, 128.2, 126.3, 101.9, 81.9, 80.8, 77.3, 77.1, 76.8, 74.1, 73.0, 70.2, 68.5, 40.2, 21.7.HRMS (ESI): calcd for $C_{38}H_{28}O_8SNa$: *m/z* 547.1397 $[M + Na]^+$; found 547.1398.

3-*O*-4-Tosyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (10b). White solid, mp 160-162 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.32, ^{1}H NMR (500 MHz, $CDCl_3$) 7.98 (2H, d, *J* 8.0 Hz, Ar *H*), 7.73 (2H, d, *J* 8.3 Hz, Ar *H*), 7.59 (1H, t, *J* 7.4 Hz, Ar *H*), 7.49 (2H, t, *J* 7.7 Hz, Ar *H*), 7.44-7.31 (3H, m, Ar *H*), 7.23 (2H, d, *J* 7.6 Hz, Ar *H*), 7.03 (2H, d, *J* 8.2 Hz, Ar *H*), 5.34 (1H, s, Ph-CH), 4.55 (1H, t, *J* 8.9 Hz, H-3′), 4.26 (1H, dd, *J* 10.6, 4.9 Hz, H-6′a), 4.20-4.09 (1H, m, H-1′), 3.78-3.75 (1H, t, *J* 8.7, H-4′), 3.62-3.55 (2H, m, H-2′, H-6′b), 3.52 (1H, dd, *J* 16.6, 2.6 Hz, H-1′a), 3.45 (1H, td, *J* 9.7, 4.9 Hz, H-5′), 3.24 (1H, dd, *J* 16.7, 8.5 Hz, H-1′b), 2.33 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) 195.9, 143.8, 135.7, 135.5, 133.8, 132.1, 130.5, 128.3, 127.9, 127.5, 127.2, 127.1, 126.9, 125.1, 100.4, 83.1, 77.0, 76.1, 75.8, 74.8, 74.0, 71.6, 69.3, 67.4, 39.9, 20.5. HRMS (ESI): calcd for $C_{38}H_{28}O_8SNa$: *m/z* 547.1397 $[M + Na]^+$; found 547.1399.

2-*O*-Mesyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (11a). White solid, mp 107-108 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.15, ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06-7.91 (2H, m, Ar *H*), 7.58 (1H, dd, *J* 10.5, 4.3 Hz, Ar *H*), 7.55-7.40 (4H, m, Ar *H*), 7.43-7.29 (3H, m, Ar *H*), 5.52 (1H, s, Ph-CH), 4.58 (1H, t, *J* 9.7 Hz, H-2′), 4.40-4.24 (2H, m, H-1, H-6′a), 4.06 (1H, t, *J* 8.5, H-3′), 3.62 (1H, t, *J* 10.1 Hz, H-6′b), 3.37-3.36 (2H, m, H-5′, H-4′), 3.42-3.29 (2H, m, H-1′a, H-1′b), 3.22 (3H, s, CH_3), 2.96 (d, *J* = 1.7 Hz, OH). ^{13}C NMR (125 MHz, $CDCl_3$) 196.2, 136.7, 133.3, 129.4, 128.6, 128.3, 128.2, 126.2, 102.0, 81.5, 81.1, 74.2,

73.2, 69.9, 68.5, 40.1, 38.8.HRMS (ESI): calcd for $C_{22}H_{24}O_8SNa$: *m/z* 471.1084 $[M + Na]^+$; found 471.1084.

3-*O*-Mesyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (11b). White solid, mp 152-154 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.25, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (2H, d, *J* 7.3 Hz, Ar *H*), 7.59 (1H, t, *J* 7.4 Hz, Ar *H*), 7.52-7.40 (4H, m, Ar *H*), 7.40-7.30 (3H, m, Ar *H*), 5.52 (1H, s, Ph-CH), 4.72 (1H, t, *J* 9.1 Hz, H-3′), 4.33 (1H, dd, *J* 10.4, 4.7 Hz, H-6′a), 4.22-4.05 (1H, m, H-1′), 3.80-3.61 (3H, m, H-6′b, H-4′, H-2′), 3.61-3.52 (1H, m, H-5′), 3.50 (1H, dd, *J* 16.7, 3.0 Hz, H-1′a), 3.33 (1H, d, *J* 4.2 Hz, OH), 3.27 (1H, dd, *J* 16.7, 8.0 Hz, H-1′b), 3.04 (3H, d, *J* 3.6 Hz, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) 197.2, 136.7, 136.6, 133.4, 129.3, 128.6, 128.3, 128.2, 126.0, 101.7, 84.5, 76.9, 76.7, 72.5, 70.6, 68.6, 41.1, 38.4.HRMS (ESI): calcd for $C_{22}H_{24}O_8SNa$: *m/z* 471.1084 $[M + Na]^+$; found 471.1086.

2,3-Di-*O*-mesyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-*β*-D-glucopyranose (11c). White solid, mp 95-97 ºC, R_f (petroleum ether/EtOAc, 2:1) = 0.35, ^{1}H NMR (500 MHz, $CDCl_3$) 7.95 (2H, d, *J* 7.9 Hz, Ar *H*), 7.58 (1H, s, Ar *H*), 7.48 (2H, t, *J* 7.6 Hz, Ar *H*), 7.45-7.40 (2H, m, Ar *H*), 7.40-7.33 (3H, m, Ar *H*), 5.53 (1H, s, Ph-CH), 4.94 (1H, t, *J* 9.3 Hz, H-2′), 4.78 (1H, t, *J* 9.4 Hz, H-3′), 4.36-4.34 (2H, m, H-1′, H-6′a), 3.77 (1H, t, *J* = 9.2 Hz, H-6′b), 3.71-3.58 (2H, m, H-4′, H-5′), 3.50 (1H, dd, *J* 1.5, 17.3 Hz, H-1′a), 3.39 (1H, dd, *J* 8.9, 17.3 Hz, H-1′b), 3.26 (3H, s, CH_3), 2.99 (3H, s, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) 195.6, 136.6, 126.1, 133.4, 129.6, 128.6, 128.5, 128.1, 126.0, 102.1, 80.9, 79.0, 76.7, 75.2, 70.5, 68.5, 40.0, 39.6, 39.6.HRMS (ESI): calcd for $C_{23}H_{26}O_{10}S_2Na$: *m/z* 549.0860 $[M + Na]^+$; found 549.0861.

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