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Aldol reaction of β-*C*-glycosylic ketones: synthesis of *C*-(*E*)-cinnamoyl glycosylic compounds as precursors for new biologically active C-glycosides☆

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Abstract—A series of β-*C*-glycosylic ketones were prepared starting from D-glucose, D-xylose, D-mannose, and cellobiose. The β-*C*-glycosylic ketones on aldol condensation with different aromatic aldehydes in the presence of a suitable organocatalyst led to the formation of respective *C*-(*E*)-cinnamoyl glycosides stereoselectively in good yields as precursors for the synthesis of biologically active compounds.
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Keywords: Glycosylic ketones; Aldol reaction; *C*-Cinnamoyl glycosides

1. Introduction

The synthesis of *C*-glycosylic compounds (commonly termed 'C-glycosides') has received considerable attention in recent years due to their occurrence in a variety of natural products endowed with numerous biological activities.[1–7] The C-glycosides act as non-hydrolyzable mimics of glycosyl amines (often termed N-glycosides) and O-glycosides and are, therefore, useful in designing new chemotherapeutics and biological tools.[8–12] The most common method for C–C bond formation at the anomeric center involves nucleophilic attack on this naturally electrophilic carbon atom.[13–20] Very recently a few reports have appeared where reactions of several D-glycoses with β-keto esters or ketones led to the formation of β-*C*-glycosylic ketones in moderate to good yields.[21,22]

These glycosylic ketones may serve as intermediates for the synthesis of several *C*-cinnamoyl glycosides. The latter have great application in organic synthesis and biochemistry as the 1-*O*-cinnamoyl glucose derivatives **A** and **B** (Fig. 1) have recently been isolated as natural products and are reported to possess plant growth-inhibitory activity.[23] Further, α,β-unsaturated ketones serve as the core moiety in several natural ligands for covalent bonding with many receptors.[24] Encouraged with this report we were prompted to synthesize such β-*C*-glycosylic ketones and determine their scope in various other C–C bond forming reactions to access a library of different C-glycosides. In the first instance of its application, the aldol condensation of β-*C*-glycosylic ketones were successfully carried out to give respective *C*-cinnamoyl glycosides having the *E* geometry at the double bond. The cinnamoyl glycosides can be utilized in the synthesis of a library of organic compounds by chemical manipulations of the double bond[25–27] and carbonyl group[28] of the aglycon portion

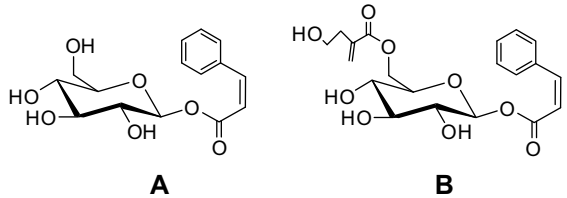

Figure 1. Plant growth-inhibitory 1-*O*-cinnamoyl glucose derivatives.

☆ The term 'C-glycoside' is commonly used for the correct terminology, '*C*-glycosylic compound'.

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and the hydroxyl functionalities of the sugar part. We have carried out all the reactions under ambient conditions with a view to find the most environment friendly and economical method.

2. Results and discussion

1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyl)-, 1-(2′,3′,4′-tri-*O*-acetyl-β-D-xylopyranosyl)-, 1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-mannopyranosyl)-, and 1-(2′,3′,6′,2″,3″,4″,6″-hepta-*O*-acetyl-β-cellobiosyl)-propan-2-ones were prepared by the Knoevenagel condensation of 2,4-pentanediones with D-glucose, D-xylose, D-mannose, and cellobiose, respectively, followed by acetylation of the hydroxyl groups present in the molecule following the earlier protocol.[29] The structures of all the β-*C*-glycosylic ketones were in accord with their spectroscopic data and microanalyses.[22,29] Aldol condensation of the above β-D-glucopyranosyl propanone (**1**) with different aromatic aldehydes, viz. benzaldehyde, 3-nitro-, 4-methoxy-, 3,4-dimethoxy-, 4-chlorobenzaldehydes, 2-naphthaldehyde, and pyridine-3-carboxaldehyde was carried out separately at ambient temperature in the presence of catalytic amount of pyrrolidine (20 mol %). To optimize the reaction conditions, the condensation of 1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-propan-2-one (**1**) in different organic solvents and water under the influence of various catalysts at ambient temperature was carried out to get the desired (*E*)-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-phenylbut-3-en-2-one (**2**) in varying yields (Scheme 1). Among the solvents used, CH_2Cl_2 in the presence of pyrrolidine (20 mol %) was found to be the most suitable combination to afford the maximum yield (74%) of the desired compound **2**. Minor products (TLC) formed during the reaction could not be isolated in pure form. The structure of (*E*)-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-phenylbut-3-en-2-one (**2**) was established on the basis of its NMR spectroscopic data and HRMS.

Similarly, condensation of the above β-D-glucosyl ketone **1** with different aldehydes, viz. 3-nitro-, 4-methoxy-, 3,4-dimethoxy-, 4-chlorobenzaldehydes, 2-naphthaldehyde, and pyridine-3-carboxaldehyde under the above optimum reaction conditions (Table 1 entry **6**) led to the formation of respective 1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-propan-2-ones (**3**–**8**) in good yields (Table 2, entries **1**–**7**). The structures of all the products were established on the basis of their spectroscopic data and analyses.

Table 1. Optimization of the aldol reaction of β-D-glucopyransoyl ketone **1** with benzaldehyde at ambient temperature

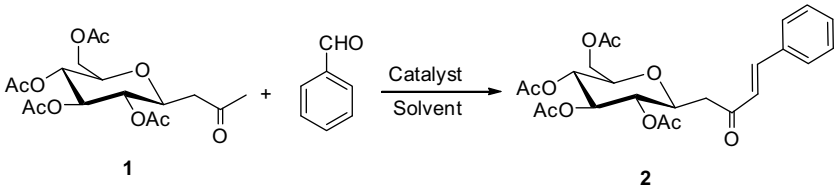
Entry	Solvent	Catalyst (20 mol %)	Reaction time (h)	Yield (%)
1	MeOH	Pyrrolidine	24	57
2	EtOH	Pyrrolidine	24	54
3	*n*-BuOH	Pyrrolidine	24	5
4	H_2O	Pyrrolidine	24	No reaction
5	DMSO	Pyrrolidine	10	58
6	CH_2Cl_2	Pyrrolidine	8	74
7	$CH_2Cl_2 + H_2O$	Pyrrolidine	24	5
8	CH_2Cl_2	DBU	8	No reaction
9	CH_2Cl_2	Piperidine	8	5
10	CH_2Cl_2	L-Proline	8	30
11	CH_2Cl_2	Et_3N	8	No reaction

To see the scope of this aldol condensation with other sugars, the condensation of 1-(2′,3′,4′-tri-*O*-acetyl-β-D-xylopyranosyl)-propan-2-one (**9**) with benzaldehyde, 3-nitrobenzaldehyde, and 4-methoxybenzaldehyde separately led to the formation of respective (*E*)-1-(2′,3′,4′-tri-*O*-acetyl-β-D-xylopyranosyl)-4-phenylbut-3-en-2-ones (**10**–**12**) in good yields (Table 2, entries 8–10). However, the aldol reaction of 1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-mannopyranosyl)-propan-2-one (**13**) was carried out only with 3-nitrobenzaldehyde to give the respective (*E*)-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-mannopyranosyl)-4-(3-nitrophenyl)but-3-en-2-one (**14**) in 70% yield (Table 2, entry **11**). The structures of compounds **10**–**12** and **14** were in accord with their spectroscopic data and microanalyses.

Finally, the aldol condensation of a disaccharide-derived β-glycosylic ketone, 1-(2′,3′,6′,2″,3″,4″,6″-hepta-*O*-acetyl-β-cellobiosyl)propan-2-one (**15**) with benzaldehyde, 3,4-dimethoxybenzaldehyde, and naphthaldehyde under the above experimental conditions led to the formation of respective (*E*)-1-(2′,3′,6′,2″,3″,4″,6″-hepta-*O*-acetyl-β-cellobiosyl)-4-phenylbut-3-en-2-ones (**16**–**18**) in good yields (Table 2, entries **12**–**14**).

3. Conclusions

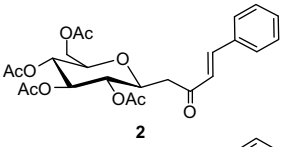
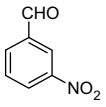
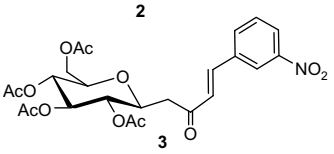
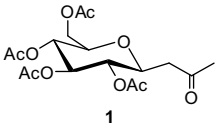
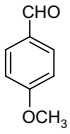
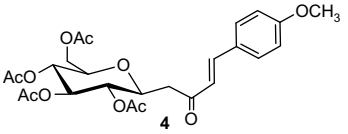
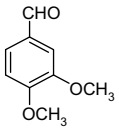
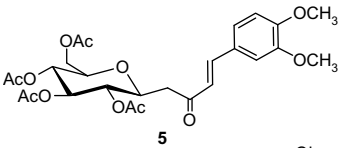
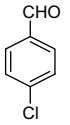
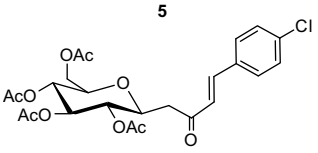
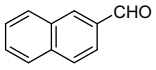
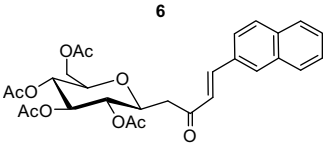
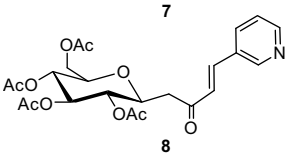
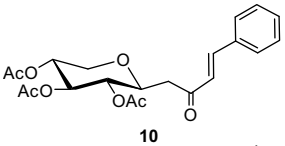
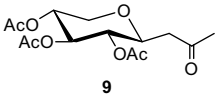
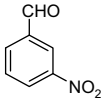
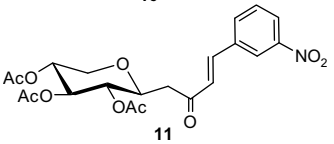
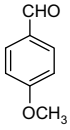
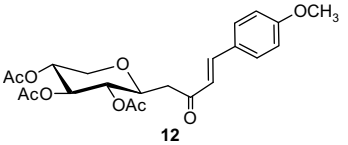
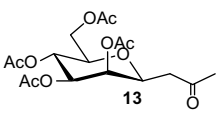
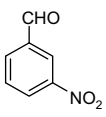
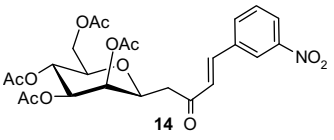
We have prepared β-*C*-glycosylic ketones of D-glucose, D-xylose, D-mannose, and D-cellobiose. The β-*C*-glycosylic ketones on aldol reaction with different aldehydes under ambient reaction conditions resulted in



1 2

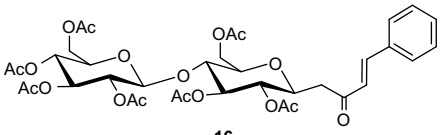
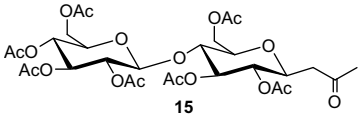
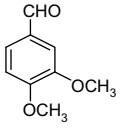
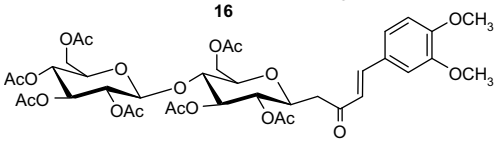
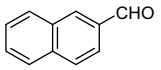
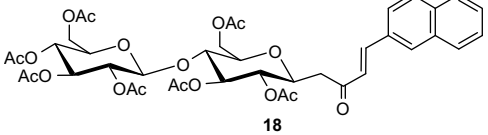
Scheme 1. Aldol reaction of β-*C*-glycosylic ketone **1** in the presence of various solvents.

Table 2. Synthesis of *C*-glycosylic phenylbutenones by reaction of glycosylic ketones **1**, **9**, **13** and **15** with different aldehydes

Entry	Substrate		Reaction time (h)	Product	% Yield
	Glycosylic ketone	Aldehyde			
1			8	 **2**	74
2			7	 **3**	70
3	 **1**		9	 **4**	69
4			10	 **5**	73
5			9	 **6**	66
6			11	 **7**	73
7			10	 **8**	71
8			9	 **10**	70
9	 **9**		8	 **11**	70
10			9	 **12**	75
11	 **13**		8	 **14**	70

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate		Reaction time (h)	Product	% Yield
	Glycosylic ketone	Aldehyde			
12			10	 **16**	71
13	 **15**		11	 **17**	70
14			9	 **18**	67

the respective (*E*)-1-(glycopyranosyl)-4-phenylbut-3-en-2-ones stereoselectively in good yields. The synthesized *C*-cinnamoyl glycoside congeners are being used as precursors for the synthesis of a library of potentially biologically active compounds.

4. Experimental

4.1. General methods

Commercially available reagent grade chemicals were used as received. All reactions were followed by TLC on E. Merck Kieselgel 60 F_{254}, with detection by UV light, spraying 20% aq $KMnO_4$ solution and/or spraying 4% ethanolic H_2SO_4. Column chromatography was performed on Silica Gel (60–120 mesh and 100–200 mesh, E. Merck). IR spectra were recorded as thin films or in KBr solution with a Perkin–Elmer Spectrum RX-1 (4000–450 cm^{-1}) spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Bruker DRX 300-MHz and 75-MHz instruments, respectively, in $CDCl_3$. Chemical shift values are reported in ppm relative to TMS (tetramethylsilane) as the internal reference, unless otherwise stated; s (singlet), d (doublet), t (triplet), m (multiplet); *J* in Hertz. FAB mass spectra were performed using a Jeol SX-102 mass spectrometer and ESI mass spectra were performed using a Quattro II (Micromass) instrument. Optical rotations were measured in a 1.0-dm tube with a Rudolf Autopol III polarimeter in $CHCl_3$. Excess of solvent was evaporated under reduced pressure at a bath temperature of 55 and 60 °C.

4.2. General procedure for (*E*)-1-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-phenylbut-3-en-2-one (2)

To a solution of β-glycosylic ketone **1** (2.0 g, 5.15 mmol) in dry CH_2Cl_2 were added pyrrolidine (0.085 mL, 1.03 mmol) and benzaldehyde (0.60 mL, 5.66 mmol). After stirring at room temperature for given the time, the reaction mixture was evaporated under reduced pressure and extracted by EtOAc–water. The EtOAc layer was dried by Na_2SO_4 and concentrated. The product was purified by column chromatography on silica gel (60–120 mesh) using 4:6 EtOAc–hexane as eluent to give compound **1** as a colorless solid: mp 101–102 °C; yield 1.8 g (74%); R_f 0.5 (6:4 hexane–EtOAc); $[\alpha]_D^{25}$ −18 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2925, 1747, 1652; ^1H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 7.57–7.52 (m, 3H, ArH, H-4), 7.41–7.39 (m, 3H, Ar-H), 6.70 (d, 1H, *J* 16.2 Hz, H-3), 5.22 (t, 1H, *J* 9.3 Hz, H-4′), 5.06 (t, 1H, *J* 9.5 Hz, H-2′), 4.98 (t, 1H, *J* 9.5 Hz, H-3′), 4.26 (dd, 1H, $J_{5',6'b}$ 4.8 Hz, $J_{6'a,6'b}$ 12.3 Hz, H-6′b), 4.12 (ddd, 1H, $J_{1',2'}$ 11.5 Hz, $J_{1',1a}$ 8.4 Hz, $J_{1b,1'}$ 3.3 Hz, H-1′), 4.00 (dd, 1H, $J_{6'a,5'}$ 1.9 Hz, $J_{6'b,6'a}$ 12.3 Hz, H-6′a), 3.71 (ddd, 1H, $J_{4',5'}$ 9.9 Hz, $J_{5',6'a}$ 4.7 Hz, $J_{5',6'b}$ 2.1 Hz, H-5′), 3.00 (dd, 1H, $J_{1',1b}$ 8.3 Hz, $J_{1a,1b}$ 16.2 Hz, H-1b), 2.70 (dd, 1H, $J_{1b,1}$ 3.2 Hz $J_{1a,1b}$ 16.2 Hz, H-1a) 2.03, 2.02, 2.01, 1.98 (s, 12H, –$OCOCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 196.0 (C=O), 170.6, 170.3, 170.1, 169.6, (4 × –$OCOCH_3$), 145.2 (Ar-C), 143.9 (C-4), 131.0 (C-3), 129.7, 129.6, 129.3, 129.0, 128.7, (ArCH), 75.2 (C-5′), 74.5 (C-1′), 72.2 (C-3′), 70.3 (C-2′), 68.9 (C-4′), 62.3 (C-6′), 43.1 (C-1), 21.04 and 20.9 (4 × –$OCOCH_3$); ESIMS: *m*/*z* 477 $(M+H)^+$; HRMS *m*/*z*: calcd for $C_{24}H_{28}O_{10}$, 476.1682; found, 476.1678.

4.2.1. (*E*)-1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyl)-4-(3-nitrophenyl)-but-3-en-2-one (3). Compound **3** was obtained by the reaction of β-glycosylic ketone **1** (1.5 g, 3.86 mmol) and 3-nitrobenzaldehyde (0.64 g, 3.91 mmol) as a colorless solid: mp 71–72 °C; yield 1.4 g (70%); R_f 0.4 (7:3 hexane–EtOAc); $[\alpha]_D^{25}$ −30 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2926, 1751, 1666; ^1H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 8.41 (s,1H, Ar-

H), 8.24 (d, 1H, *J* 7.7 Hz, Ar-H), 7.84 (d, 1H, *J* 7.7 Hz, Ar-H), 7.62–7.54 (m, 2H, Ar-H, H-4), 6.85 (d, 1H, *J* 16.2 Hz H-3) 5.20 (t, 1H, *J* 9.3 Hz, H-4′), 5.05 (t, 1H, *J* 9.7 Hz, H-2′), 4.95 (t, 1H, *J* 9.5 Hz, H-3′), 4.25 (dd, 1H, $J_{5',6'b}$ 4.7 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6′b), 4.09 (ddd, 1H, $J_{1',2'}$ 11.6 Hz, $J_{1a,1'}$ 8.8 Hz, $J_{1b,1'}$ 3.0 Hz, H-1′), 4.00 (dd, 1H, $J_{6'a,5'}$ 1.8 Hz, $J_{6'b,6'a}$ 12.3 Hz, H-6′a), 3.70 (ddd, 1H, $J_{4',5'}$ 9.9 Hz, $J_{5',6'a}$ 4.5 Hz, $J_{5',6'b}$ 2.1 Hz, H-5′), 3.02 (dd, 1H, $J_{1b,1'}$ 8.4 Hz, $J_{1a,1b}$ 16.3 Hz, H-1b), 2.68 (dd, 1H, $J_{1a,1'}$ 3.1 Hz $J_{1a,1b}$ 16.3 Hz, H-1a), 2.02–1.98 (4s, 12H, 4 × –OCOCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 193.0 (C═O, C-2), 168.8 and 167.9, (4 × –OCOCH$_3$), 147.5, 139, 134, 132, 128, 127, 123, 121, 75.8 (C-5′), 74.6 (C-1′), 72.7 (C-3′), 70.3 (C-2′), 67 (C-4′), 60 (C-6′), 41.8 (C-1), 21.02 and 20.9 (4 × –OCOCH$_3$); ESIMS: *m*/*z* 544 (M+Na)$^+$; HRMS *m*/*z*: calcd for $C_{24}H_{27}NO_{12}$, 521.1533; found, 521.1550.

4.2.2. (*E*)-1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyl)-4-(4-methoxyphenyl)but-3-en-2-one (4). Compound **4** was obtained by the reaction of β-glycosylic ketone **1** (2.0 g, 5.15 mmol) and 4-methoxybenzaldehyde (0.958 g, 5.15 mmol) as a colorless solid: mp 158–160 °C; yield 1.8 g (69%); R_f 0.4 (7:3 hexane–EtOAc); $[\alpha]_D^{25}$ −39 (*c* 0.1, CHCl$_3$); IR (KBr) ν_{max} cm^{-1}: 3022, 2953, 1748, 1598; ^{1}H NMR (300 MHz, CDCl$_3$ + CCl$_4$): δ 7.52–7.47 (m, 3H, Ar-H, H-4), 6.89 (d, 2H, *J* 8.6 Hz, Ar-H), 6.59 (d, 1H, *J* 16.2 Hz, H-3), 5.19 (t, 1H, *J* 9.3 Hz, H-4′), 5.06 (t, 1H, *J* 9.6 Hz, H-2′), 4.96 (t, 1H, *J* 9.5 Hz, H-3′), 4.25 (dd, 1H, $J_{5',6'b}$ 4.8 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6′b), 4.10 (ddd, 1H, $J_{1',2'}$ 11.4 Hz, $J_{1b,1}$ 3.1 Hz, H-1′), 4.00 (dd, 1H, $J_{6'a,5'}$ 1.3 Hz, $J_{6'b,6'a}$ 12.3 Hz, H-6′a), 3.83 (s, 3H, –OCH$_3$) 3.70 (ddd, 1H, $J_{5',6'a}$ 4.5 Hz, $J_{5',6'b}$ 2.7 Hz, H-5′), 2.99 (dd, 1H, $J_{1b,1'}$ 8.3 Hz, $J_{1a,1b}$ 16.1 Hz, H-1b), 2.64 (dd, 1H, $J_{1a,1'}$ 3.1 Hz $J_{1a,1b}$ 16.2 Hz, H-1a) 2.04–2.00 (4s, 12H, 4 × –OCOCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 196.1 (C═O, C-2), 170.7, 170.4, 170.1, 169.7, (4 × –OCOCH$_3$), 143.8, 130.5, 127.2, 124.4, 114.8, 76.1 (C-5′), 74.6 (C-1′), 72.1 (C-3′), 70.5 (C-2′), 68.8 (C-4′), 62.3 (C-6′), 55.6 (OCH$_3$), 42.8 (C-1), 21.05 and 20.9 (4 × –OCOCH$_3$); ESIMS: *m*/*z* 529 (M+Na)$^+$, HRMS *m*/*z*: calcd for $C_{25}H_{30}O_{11}$, 506.1789; found, 506.1786.

4.2.3. (*E*)-1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyl)-4-(3,4-dimethoxyphenyl)but-3-en-2-one (5). Compound **5** was obtained by the reaction of β-glycosylic ketone **1** (1.5 g, 3.86 mmol) and 3,4-dimethoxybenzldehyde (0.64 g, 3.86 mmol) as a colorless solid: mp 147–148 °C; yield 1.3 g (73%); R_f 0.3 (5:5 hexane–EtOAc); $[\alpha]_D^{25}$ −25 (*c* 0.1, CHCl$_3$); IR (KBr) ν_{max} cm^{-1}: 3020, 2945, 1747, 1652; ^{1}H NMR (300 MHz, CDCl$_3$ + CCl$_4$): δ 7.40 (d, 1H, *J* 16.1 Hz, H-4), 7.10–7.01 (m, 2H, Ar-H), 6.81 (d, 2H, *J* 8.3 Hz, Ar-H), 6.54 (d, 1H, *J* 16.1 Hz, H-3), 5.15 (t, 1H, *J* 9.3 Hz, H-4′), 4.99 (t, 1H, *J* 9.6 Hz, H-2′), 4.91 (t, 1H, *J* 9.4 Hz, H-3′), 4.23 (dd, 1H, $J_{5',6'b}$ 4.7 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6′b), 4.01 (ddd, 1H, $J_{1a,1}$ 8.3 Hz, $J_{1b,1}$ 3.2 Hz, H-1′), 3.98 (dd, 1H, $J_{6'a,5'}$ 1.7 Hz, H-6′a), 3.87 (s, 6H, –OCH$_3$X2), 3.66 (ddd, 1H, $J_{5',4'}$ 9.7 Hz, $J_{5',6'a}$ 4.4 Hz, $J_{5',6'b}$ 1.9 Hz, H-5′), 2.95 (dd, 1H, $J_{1b,1}$ 8.3 Hz, $J_{1a,1b}$ 16.1 Hz, H-1b), 2.58 (dd, 1H, $J_{1a,1'}$ 3.1 Hz $J_{1a,1b}$ 16.2 Hz, H-1a), 2.04–2.00 (4s, 12H, 4 × –OCOCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 196.1 (C═O, C-2), 171.8 and 170.2 (4 × –OCOCH$_3$), 152.1, 149.8, 143.8, 127.8, 124.8, 123.6, 111.8, 110.1, 75.8 (C-5′), 75.6 (C-1′), 74.9 (C-3′), 72.1 (C-2′), 68.8 (C-4′), 62.2 (C-6′), 56.2 (OCH$_3$), 56.1 (OCH$_3$) 42.8 (C-1), 21.04 and 20.9 (4 × –OCOCH$_3$); ESIMS: *m*/*z* 559 (M+Na)$^+$, HRMS *m*/*z*: calcd for $C_{26}H_{32}O_{12}$, 5.1894; found, 536.1891.

4.2.4. (*E*)-1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyl)-4-(4-chlorophenyl)but-3-en-2-one (6). Compound **6** was obtained by the reaction of β-glycosylic ketone **1** (1.5 g, 3.86 mmol) and 4-chlorobenzaldehyde (0.54 g, 3.86 mmol) as a colorless solid: mp 151–152 °C; yield 1.3 g (66%); R_f 0.5 (7:3 hexane–EtOAc); $[\alpha]_D^{25}$ −18 (*c* 0.1, CHCl$_3$); IR (KBr) ν_{max} cm^{-1}: 2943, 2877, 1748, 1598; ^{1}H NMR (300 MHz, CDCl$_3$ + CCl$_4$): δ 7.50–7.42 (m, 3H, Ar-H, H-4), 7.34 (d, 2H, *J* 8.5 Hz, Ar-H), 6.66 (d, 1H, *J* 16.2 Hz, H-3), 5.18 (t, 1H, *J* 9.2 Hz, H-4′), 5.02 (t, 1H, *J* 9.6 Hz, H-2′), 4.92 (t, 1H, *J* 9.4 Hz, H-3′), 4.27 (dd, 1H, $J_{5',6'b}$ 4.7 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6′b), 4.06 (ddd, 1H, $J_{1',2'}$ 11.5 Hz, $J_{1b,1'}$ 3.2 Hz, $J_{1a,1'}$ 8.5 Hz, H-1′), 3.97 (dd, 1H, $J_{6'a,5'}$ 1.9 Hz, $J_{6'b,6'a}$ 12.4 Hz, H-6′a), 3.67 (ddd, 1H, $J_{5',4'}$ 9.7 Hz, $J_{5',6'a}$ 4.3 Hz, $J_{5',6'b}$ 2.0 Hz, H-5′), 2.97 (dd, 1H, $J_{1b,1'}$ 8.4 Hz, $J_{1a,1b}$ 16.3 Hz, H-1b), 2.63 (dd, 1H, $J_{1a,1'}$ 3.1 Hz $J_{1a,1b}$ 16.3 Hz, H-1a) 2.00–1.70 (4s, 12H, –OCOCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 195.8 (C═O, C-2), 170.5, 170.2, 170.0, 169.6, (4 × –OCOCH$_3$), 142.3, 137.1, 133.1, 129.8, 129.7, 127.0, 76.2 (C-5′), 74.54 (C-1′), 74.51 (C-3′), 72.0 (C-2′), 68.8 (C-4′), 62.3 (C-6′), 43.2 (C-1), 21.03 and 20.94 (4 × –OCOCH$_3$); ESIMS: *m*/*z* 533 (M+Na)$^+$, HRMS *m*/*z*: calcd for $C_{24}H_{27}ClO_{10}$, 510.1292; found, 510.1291.

4.2.5. (*E*)-1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyl)-4-(2-napthyl)but-3-en-2-one (7). Compound **7** was obtained by the reaction of β-glycosylic ketone **1** (2.0 g, 5.91 mmol) and 2-napthaldehyde (0.93 g, 3.86 mmol) as a colorless solid: mp 158–160 °C; yield 2.0 g (73%); R_f 0.4 (6:4 hexane–EtOAc); $[\alpha]_D^{25}$ −34 (*c* 0.1, CHCl$_3$); IR (KBr) ν_{max} cm^{-1}: 2954, 1744, 1653; ^{1}H NMR (300 MHz, CDCl$_3$ + CCl$_4$): δ 7.94 (s,1H, Ar-H), 7.83–7.79 (m, 3H, Ar-H, H-4), 7.66–7.63 (m, 2H, Ar-H), 7.52–7.47 (m, 2H, Ar-H) 5.16 (t, 1H, *J* 9.2 Hz, H-4′), 5.02 (t, 1H, *J* 9.6 Hz, H-2′), 4.97 (t, 1H, *J* 9.5 Hz, H-3′), 4.26 (dd, 1H, $J_{5',6'b}$ 4.7 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6′b), 4.10 (ddd, 1H, $J_{1',2'}$ 11.5 Hz, $J_{1b,1'}$ 3.2 Hz, H-1′), 4.00 (dd, 1H, $J_{6'b,5'}$ 1.8 Hz, $J_{6'b,6'a}$ 12.3 Hz, H-6′a), 3.70 (ddd, 1H, $J_{4',5'}$ 9.3 Hz, $J_{5',6'a}$ 4.5 Hz, $J_{5',6'b}$ 2.1 Hz, H-5′), 3.02 (dd, 1H, $J_{1b,1'}$ 8.3 Hz, $J_{1a,1b}$ 16.3 Hz, H-1b), 2.64 (dd, 1H, $J_{1a,1}$ 3.1 Hz $J_{1a,1b}$

16.2 Hz, H-1a), 2.01–1.99 (4s, 12H, 4 × –OCOCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 196.0 (C=O, C-2), 169.6 and 170.6, (4 × –OCOCH$_3$), 144.0, 134.8, 133.7, 132.1, 131.1, 129.2, 129.0, 128.2, 127.8, 127.2, 126.7, 123.8, 76.7 (C-5′), 76.2 (C-1′), 74.6 (C-3′), 72.1 (C-2′), 68.8 (C-4′), 62.3 (C-6′), 43.1 (C-1), 21.0 and 20.9 (4 × –OCOCH$_3$); ESIMS: *m*/*z* 449 (M+Na)$^+$, HRMS *m*/*z*: calcd for $C_{28}H_{30}O_{10}$, 526.1839; found, 526.1845.

4.2.6. (*E*)-1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-glucopyranosyl)-4-(3-pyridyl)but-3-en-2-one (8). Compound **8** was obtained by the reaction of β-glycosylic ketone **1** (1.5 g, 3.86 mmol) and pyridine-3-carboxyaledehyde (0.36 mL, 3.86 mmol) as a colorless solid: mp 140–141 °C; yield 1.27 g (71%); R_f 0.3 (5:5 hexane–EtOAc); $[\alpha]_D^{25}$ −26 (*c* 0.1, CHCl$_3$); IR (KBr) ν_{max} cm^{-1}: 2941, 2880, 1747, 1691, 1616; ^{1}H NMR (300 MHz, CDCl$_3$ + CCl$_4$): δ 8.75 (s, 1H, Ar-H), 8.60 (d, 1H, *J* 3.6 Hz, Ar-H), 7.84 (d, 1H, *J* 7.9 Hz, Ar-H), 7.52 (d, 1H, *J* 16.3 Hz, H-4), 7.35–7.30 (m, 1H, Ar-H), 6.76 (d, 1H, *J* 16.3 Hz, H-3), 5.19 (t, 1H, *J* 9.3 Hz, H-4′), 5.04 (t, 1H, *J* 9.8 Hz, H-2′), 4.942 (t, 1H, *J* 9.7 Hz, H-3′), 4.23 (dd, 1H, $J_{5',6'b}$ 4.8 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6′b), 4.09 (ddd, 1H, $J_{1',2'}$ 11.5 Hz, $J_{1b,1'}$ 3.1 Hz, $J_{1a,1'}$ 8.8 Hz, H-1′), 3.98 (dd, 1H, $J_{6'a,5'}$ 1.7 Hz, $J_{6'b,6'a}$ 12.4 Hz, H-6′a), 3.69 (ddd, 1H, $J_{5',4'}$ 9.9 Hz, $J_{5',6'a}$ 4.5 Hz, $J_{5',6'b}$ 2.0 Hz, H-5′), 3.00 (dd, 1H, $J_{1b,1'}$ 8.5 Hz, $J_{1a,1b}$ 16.3 Hz, H-1b), 2.63 (dd, 1H, $J_{1a,1'}$ 3.1 Hz $J_{1a,1b}$ 16.3 Hz, H-1a) 2.03, 2.01, 1.996, 1.990 (4s, 12H, 4 × –OCOCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 195.3 (C=O, C-2), 170.2, 169.9, 169.7, 169.2, (4 × –OCOCH$_3$), 151.3, 150.0, 139.6, 134.2, 130.0, 127.8, 123.7, 75.8 (C-5′), 74.08 (C-1′), 74.03 (C-3′), 71.6 (C-2′), 68.3 (C-4′), 61.8 (C-6′), 42.8 (C-1), 20.63 and 20.53 (4 × –OCOCH$_3$); ESIMS: *m*/*z* 500 (M+Na)$^+$, HRMS *m*/*z*: calcd for $C_{23}H_{27}NO_{10}$, 477.1634; found, 477.1640.

4.3. (*E*)-1-(2′,3′,4′-Tri-*O*-β-D-xylopyranosyl)-4-phenylbut-3-en-2-one (10)

Compound **10** was obtained by the reaction of β-glycosylic ketone **9** (0.5 g, 1.58 mmol) and benzaldehyde (0.163 mL, 1.58 mmol) as a colorless solid: mp 112–116 °C; yield 0.45 g (70%); R_f 0.4 (7:3 hexane–EtOAc); $[\alpha]_D^{25}$ −62 (*c* 0.1, CHCl$_3$); IR (KBr) ν_{max} cm^{-1}: 3021, 2361, 1747, 1600; ^{1}H NMR (300 MHz, CDCl$_3$ + CCl$_4$): δ 7.54–7.38 (m, 3H, Ar-H and H-3), 7.38–7.27 (m, 3H, Ar-H), 6.73 (d, 1H, *J* 16.2 Hz, H-4), 5.19 (t, 1H, *J* 9.3 Hz, H-5′b), 4.99–4.90 (m, 1H, H-1′), 4.87 (t, 1H, *J* 9.6 Hz, H-5′a), 4.05–3.96 (m, 2H, H-3′, H-4′), 3.34 (t, 1H, *J* 10.8 Hz, H-2′), 2.98 (dd, 1H, $J_{1b,1'}$ 8.5 Hz, $J_{1a,1b}$ 16.0 Hz, H-1b), 2.62 (dd, 1H, $J_{1a,1'}$ 3.1 Hz, $J_{1a,1b}$ 16.0 Hz, H-1a), 2.02–2.01 (ts, 9H, 3 × –OCOCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 195.8 (C=O), 169.9, 169.8, 169.5 (3 × –OCOCH$_3$), 143.7 (Ar-C and C-4), 134.7 (C-3), 130.9, 129.3, 128.7, 126.7 (ArCH), 75.2 (C-5′), 74.1 (C-1′), 72.3 (C-3′), 69.6 (C-2′), 67.1 (C-4′), 43.0 (C-1), 31.1 and 20.9 (3 × –OCOCH$_3$); ESIMS: *m*/*z* 427 (M+Na)$^+$, HRMS *m*/*z*: calcd for $C_{22}H_{26}O_9$, 404.1515; found, 404.1471.

4.3.1. (*E*)-1-(2′,3′,4′-Tri-*O*-acetyl-β-D-xylopyranosyl)-4-(3-nitrophenyl)but-3-en-2-one (11). Compound **11** was obtained by the reaction of β-glycosylic ketone **9** (0.5 g, 1.58 mmol) and 3-nitrobenaldehyde (0.238 g, 1.58 mmol) as a colorless solid: mp 110–114 °C; yield 0.53 g (75%); R_f 0.4 (7:3 hexane–EtOAc); $[\alpha]_D^{25}$ −40 (*c* 0.1, CHCl$_3$); IR (KBr) ν_{max} cm^{-1}: 2920, 2361, 1747, 1532; ^{1}H NMR (300 MHz, CDCl$_3$ + CCl$_4$): δ 8.40 (s, 1H, Ar-H), 8.24 (d, 1H, *J* 5.4 Hz, Ar-H), 7.84 (d, 1H, *J* 5.1 Hz, Ar-H), 7.62–7.55 (m, 2H, Ar-H, H-3), 6.87 (d, 1H, *J* 10.7 Hz, H-4), 5.19 (t, 1H, *J* 9.3 Hz, H-5′b), 4.97–4.92 (m, 2H, H-1′), 4.89 (t, 1H, *J* 9.5 Hz, H-5′a), 4.07–4.01 (m, 2H, H-3′, H-4′), 3.31 (t, 1H, *J* 10.8 Hz, H-2′), 3.02 (dd, 1H, $J_{1b,1'}$ 8.7 Hz, $J_{1a,1b}$ 16.3 Hz, H-1b), 2.69 (dd, 1H, $J_{1a,1'}$ 2.97 Hz, $J_{1a,1b}$ 16.1 Hz, H-1a), 2.03–2.02 (ts, 9H, 3 × –OCOCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 195.8 (C=O), 170.2, 170.0, 169.8 (3 × –OCOCH$_3$), 149.2, 140.7, (Ar-C and C-4), 136.5 (C-3), 134.1, 130.3, 129.0, 125.1, 123.0 (ArCH), 75.1 (C-5′), 74.0 (C-1′), 72.2 (C-3′), 69.5 (C-2′), 67.1 (C-4′), 43.4 (C-1), 31.2 and 21.0 (3 × –OCOCH$_3$); ESIMS: *m*/*z* 472 (M+Na)$^+$; HRMS *m*/*z*: calcd for $C_{21}H_{23}NO_{10}$, 449.1321; found, 449.1312.

4.3.2. (*E*)-1-(2′,3′,4′-Tri-*O*-acetyl-β-D-xylopyranosyl)-4-(4-methoxyphenyl)but-3-en-2-one (12). Compound **12** was obtained by the reaction of β-glycosylic ketone **9** (0.5 g, 1.58 mmol) and 4-methoxybenzaldehyde (0.21 mL, 1.58 mmol) as a colorless solid: mp 140–145 °C; yield 0.48 g (70%); R_f 0.4 (7:3 hexane–EtOAc); $[\alpha]_D^{25}$ −52 (*c* 0.1, CHCl$_3$); IR (KBr) ν_{max} cm^{-1}: 2928, 2361, 1739, 1530; ^{1}H NMR (300 MHz, CDCl$_3$ + CCl$_4$): δ 7.51–7.48 (m, 3H, Ar-H and H-3), 6.92 (d, 2H, *J* 8.73 Hz, Ar-H), 6.64 (d, 1H, *J* 16.1 Hz, H-4), 5.19 (t, 1H, *J* 9.3 Hz, H-5′b), 4.99–4.94 (m, 2H, H-1), 4.91 (t, 1H, *J* 9.5 Hz, H-5′a), 4.07–4.02 (m, 2H, H-3′, H-4′), 3.85 (s, 1H, –OCH$_3$), 3.32 (t, 1H, *J* 10.8 Hz, H-2′), 2.98 (dd, 1H, $J_{1b,1'}$ 8.5 Hz, $J_{1a,1b}$ 15.9 Hz, H-1a), 2.63 (dd, 1H, $J_{1a,1'}$ 3.1 Hz, $J_{1a,1b}$ 15.9 Hz, H-1a), 2.03–2.02 (ts, 9H, 3 × –OCOCH$_3$). ^{13}C NMR (50 MHz, CDCl$_3$): δ 196.0 (C=O), 170.2, 170.0, 169.7 (3 × –OCOCH$_3$), 162.1, 143.7, (Ar-C and C-4), 127.3 (C-3), 130.5, 124.5, 114.8 (ArCH), 75.3 (C-5′), 74.2 (C-1′), 72.4 (C-3′), 69.7 (C-2′), 67.1 (C-4′), 55.6 (OCH$_3$), 42.9 (C-1), 21.0 (3 × –OCOCH$_3$); ESIMS: *m*/*z* 457 (M+Na)$^+$, HRMS *m*/*z*: calcd for $C_{22}H_{26}O_9$, 434.1577; found, 434.1543.

4.4. (*E*)-1-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-mannopyranosyl)-4-(3-nitrophenyl)but-3-en-2-one (14)

Compound **14** was obtained by the reaction of β-glycosylic ketone **13** (1.5 g, 3.86 mmol) and 3-nitrobenalde-

hyde (0.64 g, 3.91 mmol), as a colorless solid: mp 130–132 °C; yield 1.4 g (70%); R_f 0.4 (1:1 hexane–EtOAc); $[\alpha]_D^{25}$ −28 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1} 2926, 1742, 1636; ^1H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 8.40 (s,1H, Ar-H), 8.23 (d, 1H, *J* 7.7 Hz, Ar-H), 7.85 (d, 1H, *J* 7.7 Hz, Ar-H), 7.62–7.54 (m, 2H, Ar-H, H-4), 6.83 (d, 1H, *J* 16.2 Hz H-3), 5.35 (d, 1H, *J* 3.0 Hz, H-4′), 5.21–5.10 (m, 2H, H-2′, H-3′), 4.32–4.24 (m, 2H, H-1′, H-6′b), 4.03 (d, *J* 12.3 Hz, H-6′a), 3.70 (ddd, 1H, $J_{4',5'}$ 9.9 Hz, $J_{5',6'a}$ 4.5 Hz, $J_{5',6'b}$ 2.1 Hz, H-5′), 3.02 (dd, 1H, $J_{1b,1'}$ 7.5 Hz, $J_{1a,1b}$ 16.8 Hz, H-1b), 2.68 (dd, 1H, $J_{1a,1'}$ 4.6 Hz $J_{1a,1b}$ 16.8 Hz, H-1a), 2.02–1.98 (4s, 12H, 4 × –$OCOCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 195.3 (C═O, C-2), 170.7 and 169.9 (4 × –$OCOCH_3$), 149, 140, 136, 134, 130, 128, 125, 122, 75.8 (C-5′), 73.3 (C-1′), 72.5 (C-3′), 70.4 (C-2′), 66.3 (C-4′), 62.9 (C-6′), 42.5 (C-1), 21.02 and 20.9 (4 × –$OCOCH_3$); ESIMS: *m*/*z* 544 $(M+Na)^+$; HRMS *m*/*z*: calcd for $C_{24}H_{27}NO_{12}$, 521.1533; found, 521.1541.

4.5. (*E*)-1-(2′,3′,6′,2″,3″,4″,6″-Hepta-*O*-acetyl-β-cellobiosyl)-4-phenylbut-3-en-2-one (16)

Compound **16** was obtained by the reaction of β-glycosylic ketone **15** (1.5 g, 2.22 mmol) and benzaldehyde (0.228 mL, 2.22 mmol) as a colorless solid: mp 164–165 °C; yield 1.2 g (71%); R_f 0.5 (3:2 hexane–EtOAc); $[\alpha]_D^{25}$ −20 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2959, 1747, 1684, 1611; ^1H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 7.57–7.47 (m, 3H, Ar-H, H-4), 7.40–7.37 (m, 3H, Ar-H), 6.70 (d, 1H, *J* 16.2 Hz, H-3), 5.20 (t, 1H, *J* 9.2 Hz, H-3′), 5.09 (t, 1H, *J* 9.0 Hz, H-3″), 5.05 (t, 1H, *J* 9.4 Hz, H-4″), 4.95–4.87 (m, 2H, H-2′, H-2″), 4.49 (d, 1H, *J* 7.9 Hz, H-1″), 4.42–4.34 (m, 2H, H-6′b, H-6′a), 4.13–4.02 (m, 3H, H-6″b,H-6″a, H-1′), 3.75 (t, 1H, *J* 9.7 Hz, H-4′), 3.67–3.63 (m, 2H, H-5″, H-5′), 2.93 (dd, 1H, $J_{1b,1'}$ 8.4 Hz, $J_{1a,1b}$ 16.0 Hz, H-1b), 2.65 (dd, 1H, $J_{1a,1'}$ 3.1 Hz $J_{1a,2b}$ 16.0 Hz, H-1a), 2.08–1.96 (7s, 21H, 7 × –$OCOCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 196.0 (C═O, C-2), 170.9 and 169.4, (7 × –$OCOCH_3$), 143.9 (C-4), 134.6 (Ar-C) 131.0 (C-3), 129.9 and 126.6, (5 × ArCH), 101.0 (C-1″), 77.4, 77.2, 77.1, 74.4, 74.2, 73.4, 72.3, 71.9, 68.2, 62.5 (C-6″), 62.0 (C-6′), 43.1 (C-1), 21.04 and 20.9 (7 × –$OCOCH_3$); ESIMS: *m*/*z* 787 $(M+Na)^+$; HRMS *m*/*z*: calcd for $C_{36}H_{45}O_{18}$, 765.26059; found, 765.26519.

4.5.1. (*E*)-1-(2′,3′,6′,2″,3″,4″,6″-Hepta-*O*-acetyl-β-cellobiosyl)-4-(3,4-dimethoxyphenyl)but-3-en-2-one (17).

Compound **17** was obtained by the reaction of β-glycosylic ketone **15** (1 g, 1.47 mmol) and 3,4-dimethoxybenzaldehyde (0.245 g, 1.47 mmol) as a colorless solid: mp 160–161°C; yield 0.9 g (67%); R_f 0.4 (2:3 hexane–EtOAc); $[\alpha]_D^{25}$ −25 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2929, 1749, 1641; ^1H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 7.45 (d, 1H, *J* 16.0 Hz, H-4), 7.09 (d, 1H, *J* 8.2 Hz, Ar-H), 7.05 (s, 1H, Ar-H), 6.83 (d, 1H, *J* 8.2 Hz, Ar-H), 6.57 (d, 1H, *J* 16.0 Hz, H-3), 5.15 (t, 1H, *J* 9.2 Hz, H-3′), 5.08–5.00 (m, 2H, H-3″, H-4″), 4.90–4.79 (m, 2H, H-2′, H-2″), 4.51 (d, 1H, *J* 8.4 Hz, H-1″), 4.39–4.33 (m, 2H, H-6′b, H-6′a), 4.14–3.98 (m, 3H, H-6″b, H-6″a, H-1′), 3.91 (s, 6H, 2 × –OCH_3), 3.73–3.62 (m, 3H, H-5″, H-5′, H-4′), 2.86 (dd, 1H, $J_{1b,1'}$ 8.4 Hz, $J_{1a,1b}$ 16.0 Hz, H-1b), 2.62 (dd, 1H, $J_{1a,1'}$ 3.1 Hz $J_{1a,2b}$ 16.0 Hz, H-1a), 2.10–2.00 (7s, 21H, 7 × –$OCOCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 194.9 (C═O, C-2), 169.8 and 168.4, (7 × –$OCOCH_3$), 151.5, 149.3, 143.2 (C-4), 127.2, 124.1, 123.1, 111.0, 109.8, 100.7 (C-1″), 76.7, 76.6, 74.1, 73.8, 73.6, 72.9, 71.9, 71.6, 67.7 (9 × –CH), 62.0 (C-6″), 61.4 (C-6′), 55.7 (2 × –OCH_3), 42.6 (C-1), 20.7 and 20.4 (7 × –$OCOCH_3$); ESIMS: *m*/*z* 699 $(M+Na)^+$; HRMS *m*/*z*: calcd for $C_{40}H_{47}O_{18}$, 815.27624; found, 815.28032.

4.5.2. (*E*)-1-(2′,3′,6′,2″,3″,4″,6″-Hepta-*O*-acetyl-β-cellobiosyl)-4-(2-napthyl)but-3-en-2-one (18).

Compound **18** was obtained by the reaction of β-glycosylic ketone **15** (1 g, 1.47 mmol) and 2-napthaledehyde (0.23 g, 1.47 mmol) as a colorless solid: mp 220–222 °C; yield 0.85 g (70%); R_f 0.5 (3:2 hexane–EtOAc); $[\alpha]_D^{25}$ −24 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1} 3021, 2927, 1749, 1608; ^1H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 7.96 (s, 1H, Ar-H), 7.87–7.83 (m, 3H, Ar-H), 7.72–7.66 (m, 2H, Ar-H), 7.54–7.51 (m, 2H, Ar-H, H-4), 7.40–7.37 (m, 3H, Ar-H), 6.84 (d, 1H, *J* 16.1 Hz, H-3), 5.20 (t, 1H, *J* 9.2 Hz, H-3′), 5.15–5.06 (m, 2H, H-3″, H-4″), 4.95–4.88 (m, 2H, H-2′, H-2″), 4.53 (d, 1H, *J* 7.6 Hz, H-1″), 4.43–4.36 (m, 2H, H-6′b, H-6′a), 4.15–4.02 (m, 3H, H-6″b, H-6″a, H-1′), 3.77 (t, 1H, *J* 9.5 Hz, H-4′), 3.67–3.64 (m, 2H, H-5″, H-5′), 2.93 (dd, 1H, $J_{1b,1'}$ 8.4 Hz, $J_{1a,1b}$ 16.0 Hz, H-1b), 2.65 (dd, 1H, $J_{1a,1'}$ 3.1 Hz $J_{1a,2b}$ 16.0 Hz, H-1a), 2.09–2.02 (7s, 21H, 7 × –$OCOCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 195.9 (C═O, C-2), 170.6 and 169.1, (7 × –$OCOCH_3$), 143.8 (C-4), 134.6, 133.7, 132.1 (Ar-C), 131.0 (C-3), 129.2 and 123.8, (7 × –ArCH), 101.1 (C-1″), 78.6, 78.3, 78.2, 77.5, 77.4, 77.3, 77.1, 73.4, 72.3, 68.2, 62.5 (C-6″), 61.9 (C-6′), 43.2 (C-1), 21.04 and 20.9 (7 × –$OCOCH_3$); ESIMS: *m*/*z* 837 $(M+Na)^+$; HRMS *m*/*z*: calcd for $C_{38}H_{49}NO_{20}$, 825.28172; found, 825.28334.

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Supplementary data

Scanned HRMS, ESIMS, ^{1}H NMR and ^{13}C NMR spectra of the selected compounds are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.04.021.

References

1. Moore, R. E.; Scheuer, P. J. *Science* **1971**, *172*, 495–498.
2. Moore, R. E.; Bartolini, G. *J. Am. Chem. Soc.* **1981**, *103*, 2491–2494.
3. Usami, M.; Satake, M.; Ishida, S.; Inoue, A.; Kan, Y.; Yasumoto, T. *J. Am. Chem. Soc.* **1995**, *117*, 5389–5390.
4. Suh, E. M.; Kishi, Y. *J. Am. Chem. Soc.* **1994**, *116*, 11205–11206.
5. Hirata, Y.; Uemura, D. *Pure Appl. Chem.* **1986**, *58*, 701–710.
6. Litaudon, M.; Hickford, S. J. H.; Lill, R. E.; Lake, R. J.; Blunt, J. W.; Munro, M. H. G. *J. Org. Chem.* **1997**, *62*, 1868–1871.
7. Trefzer, A.; Hoffmeister, D.; Künzel, E.; Stockert, S.; Weitnauer, G.; Westrich, L.; Rix, U.; Fuchser, J.; Bindseil, K. U.; Rohr, J.; Bechthold, A. *Chem. Biol.* **2000**, *7*, 133–142 and references cited therein.
8. Sears, P.; Wang, C. H. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 12086–12093.
9. Witczak, Z. J. *Curr. Med. Chem.* **1995**, *1*, 392–405.
10. Beau, J. M.; Vauzeilles, B.; Skrydstrup, T. In *Glycoscience: Chemistry and Chemical Biology*; Fraser-Reid, B., Tatsuta, K., Thiem, J., Eds.; Springer: Heidelberg, 2001; Vol. 3, pp 2679–2724.
11. Jimenez-Barbero, J.; Espinosa, J. F.; Asensio, J. L.; Canada, F. J.; Poveda, A. *Adv. Carbohydr. Chem. Biochem.* **2001**, *56*, 235–284.
12. O'Leary, D. J.; Kishi, Y. *J. Org. Chem.* **1994**, *59*, 6629–6636 and references contained therein.
13. Vasella, A. *Pure Appl. Chem.* **1991**, *63*, 507–518.
14. Du, Y.; Linhardt, R. J.; Vlahov, I. R. *Tetrahedron* **1998**, *54*, 9913–9959.
15. Togo, H.; He, W.; Waki, Y.; Yokoyama, M. *Synlett* **1998**, 700–717.
16. Beau, J. M.; Gallagher, T. *Top. Curr. Chem.* **1997**, *187*, 1–54.
17. Nicotra, F. *Top. Curr. Chem.* **1997**, *187*, 55–583.
18. Praly, J. P. *Adv. Carbohydr. Chem. Biochem.* **2000**, *56*, 115–126.
19. Postema, M. H. D. *C-Glycoside Synthesis*; CRC Press: London, 1995.
20. (a) Levy, D. E.; Tang, C. In *The Chemistry of C-Glycosides*; Elsevier: Tarrytown, NY, 1995; Vol. 13; (b) Somsák, L. *Chem. Rev.* **2001**, *101*, 81–135; (c) *The Organic Chemistry of Sugars*; Levy, D. E., Fügedi, P., Eds.; CRC Press/Taylor & Francis: Boca Raton, 2006; p 928.
21. Wang, Z.; Shao, H.; Lacroix, E.; Wu, S. H.; Jennings, H. J.; Zou, W. *J. Org. Chem.* **2003**, *68*, 8097–8105.
22. Rodrigues, F.; Canac, Y.; Lubineau, A. *Chem. Commun.* **2000**, 2049–2050.
23. (a) Morita, S.; Hiradate, S.; Fujii, Y.; Harada, J. *Plant Growth Regul.* **2005**, *46*, 125–131; (b) Shao, H.; Wang, Z.; Lacroix, E.; Wu, S. H.; Jennings, H. J.; Zou, W. *J. Am. Chem. Soc.* **2002**, *124*, 2130–2131.
24. Shiraki, T.; Kamiya, N.; Shiki, S.; Kodama, T. S.; Kakizuka, A.; Jingami, H. *J. Biol. Chem.* **2005**, *280*, 14145–14153.
25. Geller, T.; Gerlach, A.; Kruger, C. M.; Militzer, H. C. *Tetrahedron Lett.* **2004**, *45*, 5065–5067.
26. Katiyar, D.; Tiwari, V. K.; Tewari, N.; Verma, S. S.; Sinha, S.; Gaikwad, A.; Srivastava, A.; Chaturvedi, V.; Srivastava, R.; Srivastava, B. S.; Tripathi, R. P. *Eur. J. Med. Chem.* **2005**, *40*, 351–360.
27. Tripathi, R. P.; Tripathi, R.; Tiwari, V. K.; Bala, L.; Sinha, S.; Srivastava, A.; Srivastava, R.; Srivastava, B. S. *Eur. J. Med. Chem.* **2002**, *37*, 773–781.
28. Yadav, J. S.; Reddy, B. V. S.; Reddy, M. S.; Prasad, A. R. *Tetrahedron Lett.* **2002**, *43*, 9703–9706.
29. Riemann, I.; Papadopoulos, M. A.; Knorst, M.; Fessner, W. D. *Aust. J. Chem.* **2002**, *55*, 147–154.