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Aldol reaction of β-C-glycosidic ketones: synthesis of *E*- cinnamoyl glycosides as precursors for new biologically active C-glycosides

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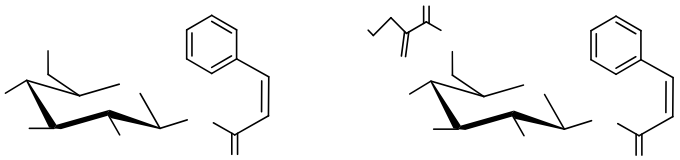
Abstract: A series of β-C-glycosidic ketones were prepared starting from D-glucose, D-xylose sugars, D-mannose and D-cellobiose. The β-C-glycosidic ketones on aldol condensation with different aromatic aldehydes in presence of a suitable organocatalyst led to the formation of respective *E*- cinnamoyl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

Keywords: Glycosidic ketones; Aldol reaction; Cinnamoyl glycosides.

1. Introduction:

The synthesis of C- glycosides has received considerable importance 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-hydrolysable mimics of *N*- 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 centre involves nucleophilic attack on this naturally electrophilic carbon atom.[13-20] Different reactions used to get the desired C-glycosides are; (i) nucleophilic substitution of glycosyl halides, lactones, glycals, and 1,2-anhydrosugars using carbanion reagents, including Lewis acid catalyzed alkylations with stannane and silane reagents to *O*-glycosides or 1-*O*-acetates; (ii) electrophilic substitution of anomeric anionic intermediates; (iii) radical alkylations activated by *Sm*, *Sn*, or other reagents; and (iv) the de novo synthesis. Very recently few reports have appeared where reactions of several D-glycoses with β-keto esters or ketones led to the formation of β-C-glycosidic ketones in moderate to good yields.[21,22]

Encouraged with this report we were prompted to synthesize such β-C-glycosidic ketones and see 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 aldol condensation of β-C-glycosidic ketones were successfully carried out to give respective *C*-cinnamoyl glycosides having *E* geometry of double bond. The latter have great application in organic synthesis and biochemistry as the cinnamyl glycosides **I** and **II** (Figure 1) has recently been isolated from natural product and reported to possess plant growth inhibitory activity.[23] The cinnamoyl glycosides can be utilized in the synthesis of library of organic compounds by chemical manipulations of double bond and carbonyl group of the aglycon portion and hydroxyl functionalities of the sugar part. We have carried out all the reactions under ambient conditions with a view to find the 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)-propan-2-ones, 1 - (2′, 3′, 4′, 6′- tetra-*O*-acetyl-*β*-D-mannopyranosyl)-, and 1-(2′, 3′, 6′, 2", 3", 4", 6"-hepta-O-acetyl-*β* cello-biosyl)- were prepared by the Knoevenagel condensation of 2, 4-pentan diones with D-glucose, D-xylose, D-mannose and D-cellobiose respectively followed by acetylation of the hydroxyl groups present in the molecule following the earlier protocol.[22] The structure of all the β-C-glycosidic ketones were in accordance with their spectroscopic data and microanalyses.[22,24] Aldol

condensation of the above *β*-D-glucopyranosyl propanone **(1)** with different aromatic aldehydes viz. benzaldehyde, 3-nitro-, 4-methoxy-, 3,4-dimethoxy-, 4-chlorobenz-aldehydes, 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 condition 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. Among the solvents used CH_2Cl_2 in presence of pyrrolidine (20 mol %) was found to be the most suitable combination to afford the maximum yield (74%) of the desired compound **2**. The minor products (TLC) formed during reaction could not be isolated in pure forms. 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 spectroscopic data and HRMS. ESIMS of compounds **2** displayed $(M+H)^+$ peak at 477 amu. The IR spectrum of **2** showed the characteristic carbonyl frequencies of butenoyl ketone and acetate moiety at 1747 and 1652 cm^{-1} respectively. In ^{1}H-NMR spectrum the anomeric proton H-1′of the pyranose ring appeared at δ 4.12 (ddd, 1H, $J_{1',2'}$ 11.5 Hz, $J_{1',1a}$ 8.4 Hz, $J_{1b,1'}$ 3.3 Hz), while H-1a and H-1b of the aglycone portion appeared at δ 2.70 (dd, 1H, $J_{1a,1}$ 3.2 Hz $J_{1a,1b}$ 16.2 Hz) and δ 3.00 (dd, 1H, $J_{1',1b}$ 8.3 Hz, $J_{1a,1b}$ 16.2 Hz) respectively. H-5′ of the pyranose ring appeared at δ 3.71 (ddd, 1H, $J_{4',5'}$ 9.9 Hz, $J_{5',6'a}$ 4.7 Hz, $J_{5',6'b}$ 2.1 Hz) while *dd* of H-2′, H-3′ and H-4′ appearing as a three distinct triplets at δ 5.06 (*J* 9.5 Hz), δ 4.98 (*J* 9.5 Hz) and δ 5.22 (*J* 9.3 Hz) respectively. The two methylene protons (H-6′a and H-6′b) appeared as two *dd* at δ 4.00 ($J_{6'a,\,5'}$ 1.9 Hz, $J_{6'a,\,6'b}$ 12.3 Hz), and δ 4.26 ($J_{5',\,6'b}$ 4.8 Hz, $J_{6'a,\,6'b}$ 12.3 Hz) respectively. Out of the two olefinic protons, H-3 appeared as *d* at δ 6.70 (*J* 16.2 Hz) while H-4 was mixed with the multiplet of aromatic protons at δ 7.57-7.52. In ^{13}C-NMR spectrum C-1′ appeared at δ 74.5, while C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′, C-6′ appeared at δ 196.0, 131.0, 143.9, 70.3, 72.2, 68.9, 75.2, 62.3 respectively and C-1 appeared at δ 43.1.

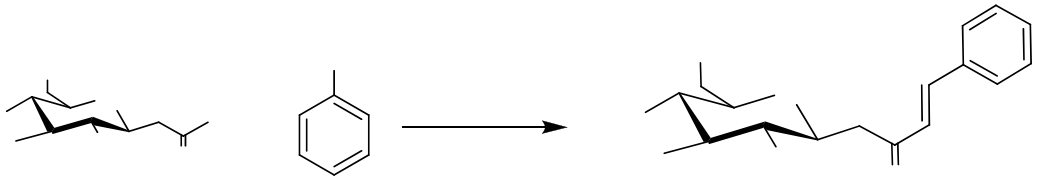
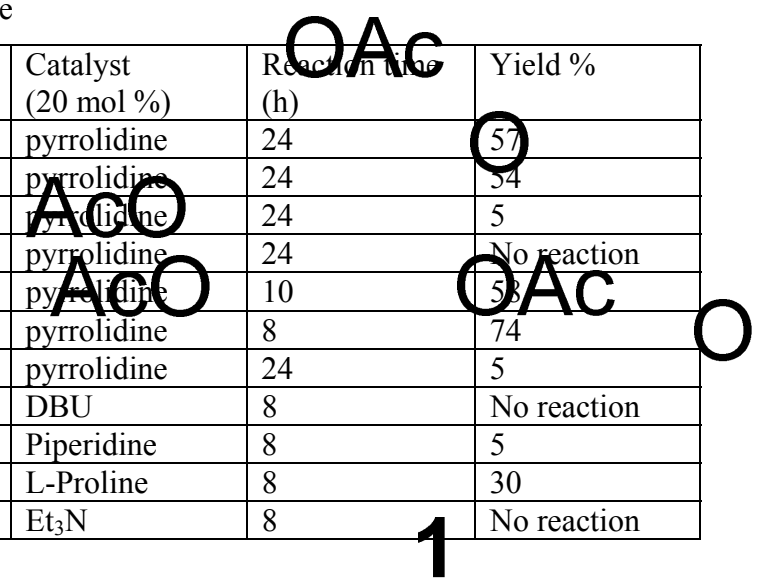


Table 1: Optimization of Aldol reaction of β-glucopyransoyl ketone **1** with benzaldehyde at ambient temperature

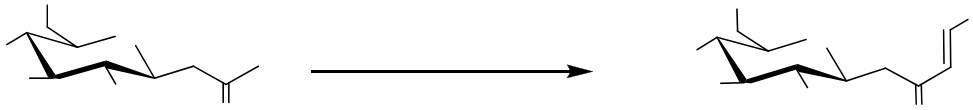
Entry	Solvent	Catalyst (20 mol %)	Reaction time (h)	Yield %
1	MeOH	pyrrolidine	24	57
2	EtOH	pyrrolidine	24	54
3	*n*-BuOH	pyrrolidine	24	5
4	H_2O	pyrrolidine	24	No reaction
5	DMSO	pyrrolidine	10	58
6	CH_2Cl_2	pyrrolidine	8	74
7	$CH_2Cl_2 + H_2O$	pyrrolidine	24	5
8	CH_2Cl_2	DBU	8	No reaction
9	CH_2Cl_2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



Similarly, condensation of the above β-C-glucosidic ketone **1** with different aldehydes, *viz*. 3-nitro-, 4-methoxy-, 3,4-dimethoxy-, 4-chloro-benzaldehydes, 2-naphthaldehyde and pyridine-3-carboxaldehyde under the above optimum reaction condition (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 as shown in Scheme **2**. The structures of all the products were established on the basis of their spectroscopic data and analyses. The IR spectrum of the compounds (**3-8**) exhibited the absorption band at around 1745 and 1650 cm^{-1} indicating the carbonyl group of acetate and butanone moieties. In ESIMS the above compounds (**3-8**) showed $[M+Na]^+$ peaks corresponding to their molecular formulae. In ^1H NMR and ^{13}C NMR spectra of the above compounds the

Scheme 1: Aldol reacti

protons and carbons pertaining to glucopyranose sugar ring and its acetyl substituents were observed at their usual chemical shifts and with similar multiplicities as in compound **2**. The protons and carbons of the linker (buten-3-one) also appeared as usual, the only difference was in the multiplicities of the aromatic protons and the appearance of proton and carbon signals due to substitutents on the aromatic ring.



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 - methoxy benzaldehyde separately led to the formation of respective (*E)* 1 - (2′, 3′, 4′- *tri* - *O* - acetyl - β - D - xylopyranosyl) - 4 - phenyl but-3-en-2-ones (**10**-**13**) in good yields (Scheme 2). However, the aldol reaction of 1 - (2′, 3′, 4′, 6′- tetra-*O*-acetyl-*β*-D-manno-pyranosyl)- propan-2-one (**11**) was carried out with the only aromatic aldehyde 3-nitrobenzaldehyde to give the respective (*E)* 1 - (2′, 3′, 4′, 6′-*tetra*-*O*-acetyl-β-D-mannopyranosyl) -4-(3-nitro phenyl) but-3-en-2-one (**14**) in 70 % yield. The structures of compounds **10**-**13** and **14** were in accordance with their spectroscopic data and microanalyses.

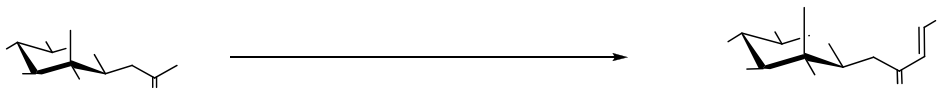
OAc

O

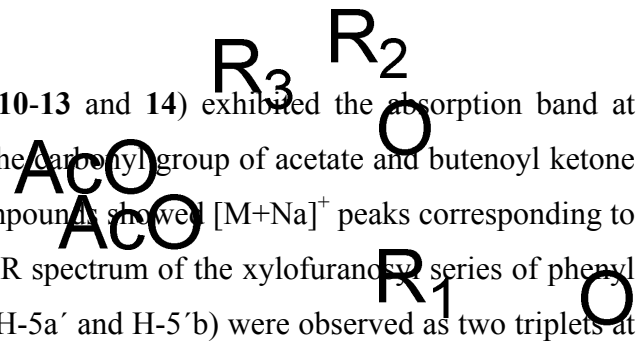
AcO

AcO

OAc



The IR spectrum of the compounds (**10**-**13** and **14**) exhibited the absorption band at around 1742 and 1636 cm^{-1} indicating the carbonyl group of acetate and butenoyl ketone moieties. In ESIMS all of the above compounds showed $[M+Na]^+$ peaks corresponding to their molecular formulae. In the ^1H NMR spectrum of the xylofuranosyl series of phenyl butenones (**10**-**13**), two protons at C-5 (H-5a′ and H-5′b) were observed as two triplets at around δ 5.15 and 4.88 respectively. The *ddd* of anomeric proton (H-1′) was mixed with the one of the above triplets at δ 4.88 and appeared as *m* at around δ 4.92. Other proton and carbon signals of the sugar ring and its substituents were observed as usual. The chemical shifts and multiplicities of the aglycone protons were similar to those of glucopyranosyl series. In ^{1}HNMR spectrum of compound **14**, H-1′and H-6′ were observed as a *m* at δ 5.39-5.10, while H-3′ and H-4′ appeared as *m* at δ 4.32-4.01. The H-5′ of the mannopyranosyl ring was observed as *d* at δ 3.80 (J= 12.2 Hz). The two methylene protons at C-1 (H-1a and H-1b) were observed at δ 2.68 (dd, 1H, $J_{1a,1'}$ 4.6 Hz $J_{1a,1b}$ 16.8 Hz) and 3.02 (dd, 1H, $J_{1b,1'}$ 7.5 Hz, $J_{1a,1b}$ 16.8 Hz) respectively. One of the alkenyl protons, H-3 appeared as *d* at δ 6.70 (J 16.2 Hz) while H-4 was merged with the *m* of aromatic protons at δ 7.57-7.52 (m, 3H, Ar-H & H-4). In ^{13} C-NMR spectrum C-1′ appeared at δ 73.3, while C-2, C-3, C-4, C-2′, C-3′, C-4′, C-5′, C-6′ appeared at δ 195.0, 134, 140, 70.4, 72.5, 66.3, 75.8, 62.9 respectively and C-1 appeared at δ 42.5.

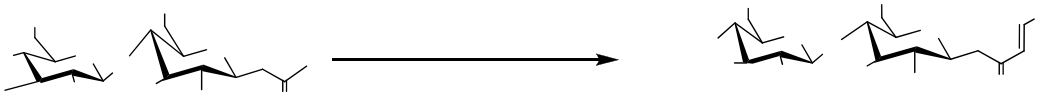


9, R_1= OAc, R_2= H, R_3= H
13, R_1= H, R_2= OAc, R_3=

Scheme 3: Synthesis of (*E*)
but-3-en-2-one an

Finally, aldol condensation of a disaccharide derived β-glycosidic ketone, 1-(2′, 3′, 6′, 2", 3", 4", 6"-hepta-O-acetyl-*β* cellobiosyl)-propan-2-one (**15**) with benzaldehyde, 3,4-

dimethoxy benzaldehyde and naphthaldehyde under the above experimental condition led to the formation 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 (Scheme 4). The IR spectrum of the compounds (**16-18**) exhibited the absorption band at around 1747 and 1654 cm^{-1} indicating the carbonyl group of acetate and butenoyl ketone moieties. In ESI mass spectra of the compounds showed the respective $[M+Na]^+$ peaks at m/z 787, 699 and 837 respectively. In the ^{1}H-NMR spectrum the anomeric proton of the pyranose ring H-1" as doublet at 4.49 δ (d, 1H, *J* 7.9 Hz) while H-1′ was merged with a multiplet of 6"a at δ 4.13- 4.02 (m, 3H), while the two protons (H-1a and H-1b) of the aglycone portion appeared at δ 2.65 (dd, 1H, $J_{1a,1'}$ 3.1 Hz $J_{1a,2b}$ 16.0) and 2.93 (dd, 1H, $J_{1b,1'}$ 8.4 Hz, $J_{1a,1b}$ 16.0 Hz). One of the alkenyl protons, H-3 appeared as *d* at δ 6.70 (*J* 16.2 Hz) while the other proton (H-4) appeared along with the multiplet of aromatic protons at δ 7.57-7.47 (m, 3H, Ar-H, H-4). The other hepta-*O*-acetyl-β-cellobiosyl ring and substituent protons were observed at their usual chemical shifts and multiplicities. In ^{13} C-NMR spectrum C-1', C-1" showed signals at δ 74.4, 101.0 respectively, while C-2, C-3, C-4, C-6′, C-6" appeared at δ 196.0, 131.0, 143.9, 62.5, 68.2 respectively. The methylene carbon (C-1) was observed at δ 43.1.



3. Conclusion:

We have prepared β-*C*-glycosidic ketones of D-glucose, D-xylose, D-mannose and D-cellobiose. The β-*C*-glycosidic ketones on aldol reaction with different aldehydes at ambient reaction condition resulted in the respective (*E)*1-(glycopyranosyl) -4-phenylbut-3-en-2-one stereoselectively in good yields. The synthesized *C*-cinnamoyl

glycoside congeners are being used as precursors for the synthesis a library of biologically active compounds.

4. Experimental

4.1. General methods

Commercially available reagent grade chemicals were used as received. All reaction was followed by TLC on E. Merck Kieselgel 60 F_{254}, with detection by UV light, spraying a 20% $KMnO_4$ aq solution and / or spraying a 4% H_2SO_4 ethanolic solution. Column chromatography was performed on silica gel (60-120 mesh& 100-200 mesh, E. Merck). IR spectra were recorded as thin films or in KBr soln with a Perkin Elmer Spectrum RX-1 (4000-450 cm^{-1}) spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Brucker DRX -300 in $CDCl_3$. chemical shift values are reported in ppm relative to TMS (tetra methyl silane) as internal reference, unless otherwise stated; s (singlet), d (doublet), t (triplet), m (multiplet); *J* in hertz. FAB mass spectra were performed using a mass Spectrometer Jeol SX-102 and ESI mass spectra were performed using Quattro II (Micromass). Elemental analyses were performed on a Perkin–Elmer 2400 II elemental analyzer. Optical rotations were measured in a 1.0 dm tube with a Rudolf Autopol III polarimeter in $CHCl_3$.

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

To a solution of β- glycosidic ketone **1** (2.0 g, 5.15 mmol) in dry CH_2Cl_2 was added pyrrolidine (0.085 mL, 1.03 mmol) and benzaldehyde (0.60 mL 5.66 mmol).After stirring at room temperature for given time, reaction mixture was evaporated under reduced pressure and extracted by ethyl acetate / water. The ethyl acetate layer was dried by sodium sulphate (Na_2SO_4) and concentrated. The product was purified by column chromatography on silica gel (60-120 mesh) using ethyl acetate: hexane (4:6) as eluent to give compound 1 as colorless solid, mp 101-102 °C; yield 1.8 g, 74 %; R_f 0.5 (6:4 hexane-EtOAc); $[\alpha]^{25}_D$ -18 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2925, 1747, 1652; ^1H-NMR (300MHz, $CDCl_3$ + 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 x -$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 477 $(M+H)^+$, HRMS: Calcd for $C_{24}H_{28}O_{10}$: 476.1682; found: m/z 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):

Was obtained by the reaction of β- glycosidic 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); $[\alpha]^{25}_D$ - 30 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2926, 1751, 1666; ^{1}H-NMR (300MHz, $CDCl_3$ + 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 x -$OCOCH_3$). ^{13} C NMR (50 MHz, $CDCl_3$): δ 193.0 (C=O, C-2), 168.8 and 167.9, (4 x-$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 544 $(M+Na)^+$; HRMS: Calcd for $C_{24}H_{27}O_{12}N$: 521.1533; found: m/z 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*):

Was obtained by the reaction of β- glycosidic 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); $[\alpha]^{25}_D$ - 39 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3022, 2953, 1748, 1598; ^{1}H NMR (300MHz, $CDCl_3$ + 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 x -$OCOCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 196.1 (C=O, C-2), 170.7, 170.4, 170.1, 169.7, (4 x -$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 529 $(M+Na)^+$, HRMS: Calcd for $C_{25}H_{30}O_{11}$: 506.1789; found: m/z 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*):

Was obtained by the reaction of β- glycosidic 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); $[\alpha]^{25}_D$ - 25 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3020, 2945, 1747, 1652; ^{1}H-NMR (300MHz, $CDCl_3$ + 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_3X2), 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 x -$OCOCH_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 196.1 (C=O, C-2), 171.8 and 170.2 (4 x -$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 559(M+ Na)$^+$, HRMS: Calcd for $C_{26}H_{32}O_{12}$: 5.1894; found: m/z 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*):

Was obtained by the reaction of β- glycosidic 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); $[\alpha]^{25}_D$ - 18 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2943, 2877, 1748, 1598; ^{1}H-NMR (300MHz, $CDCl_3$ + 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 x -$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 533 (M+ Na)$^+$, HRMS: Calcd for $C_{24}H_{27}O_{10}Cl$: 510.1292; found: m/z 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):

Was obtained by the reaction of β- glycosidic 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); $[\alpha]^{25}_D$ - 34 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2954, 1744, 1653; ^{1}H-NMR (300MHz, $CDCl_3$ + 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 x -$OCOCH_3$). ^{13} C NMR (50 MHz, $CDCl_3$): δ 196.0 (C=O, C-2), 169.6 and 170.6, (4 x -$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 449 $(M+Na)^+$, HRMS: Calcd for $C_{28}H_{30}O_{10}$: 526.1839; found: m/z 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)*:

Was obtained by the reaction of β- glycosidic 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 1.27g, 71 %; R_f 0.3 (5:5 hexane-EtOAc); $[\alpha]^{25}_D$ - 26 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}:2941, 2880, 1747, 1691,1616; ^{1}H-NMR (300MHz, $CDCl_3$ + 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 x -$OCOCH_3$). ^{13} C NMR (50 MHz, $CDCl_3$): δ 195.3 (C=O, C-2), 170.2, 169.9, 169.7, 169.2, (4 x -$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 500 $(M+ Na)^+$, HRMS: Calcd for $C_{23}H_{27}O_{10}N$: 477.1634; found: m/z 477.1640.

4.3 (*E)* 1 - (2′, 3′, 4′- tri-*O*-β-D-xylopyranosyl) -4- phenyl but-3-en-2-one (*10*):

Was obtained by the reaction of β- glycosidic 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); $[\alpha]^{25}_D$ - 62 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 3021, 2361, 1747, 1600; ^{1}H NMR (300MHz, $CDCl_3$ + CCl_4): δ 7.54-7.38 (m, 3H, Ar-H & 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 x-$OCOCH_3$). ^{13} C NMR (50 MHz, $CDCl_3$): δ 195.8 (C=O), 169.9, 169.8, 169.5 (3 x -$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 427 $(M+Na)^+$, HRMS: Calcd for $C_{22}H_{26}O_9$: 404.1515; found: m/z 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*):

Was obtained by the reaction of β- glycosidic 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); $[\alpha]^{25}_D$ - 40 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2920, 2361, 1747, 1532; ^{1}H-NMR (300MHz, $CDCl_3$ + 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 x -$OCOCH_3$). ^{13} C NMR (50 MHz, $CDCl_3$): δ 195.8 (C=O), 170.2, 170.0, 169.8 (3 x -$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 472 $(M+Na)^+$; HRMS: Calcd for $C_{21}H_{23}O_{10}N$: 449.1321; found: m/z 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*):

Was obtained by the reaction of β- glycosidic ketone **9** (0.5 g, 1.58 mmol) and 4-methoxybenzaldehyde (.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); $[\alpha]^{25}_D$ - 52 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2928, 2361, 1739, 1530; ^{1}H NMR (300MHz, $CDCl_3$ + CCl_4): δ 7.51-7.48 (m, 3H, Ar-H & 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 x -$OCOCH_3$). ^{13} C NMR (50 MHz, $CDCl_3$): δ 196.0 (C=O), 170.2, 170.0, 169.7 (3 x -$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 457 $(M+ Na)^+$, HRMS: Calcd for $C_{22}H_{26}O_9$: 434.1577; found: m/z 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*):

Was obtained by the reaction of β- glycosidic ketone **13** (1.5 g, 3.86 mmol) and 3-nitrobenaldehyde (0.64 g, 3.91 mmol), as a colorless solid, mp 130-132 °C; yield 1.4 g, 70 %; R_f 0.4 (5:5 hexane-EtOAc); $[\alpha]^{25}_D$ - 28 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1} 2926, 1742, 1636; ^{1}H-NMR (300MHz, $CDCl_3$ + 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 x -$OCOCH_3$). ^{13} C NMR (50 MHz, $CDCl_3$): δ 195.3 (C=O, C-2), 170.7 and 169.9, (4 x -$OCOCH_3$), 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 x -$OCOCH_3$); ESIMS: m/z 544 $(M+Na)^+$; HRMS: Calcd for $C_{24}H_{27}O_{12}N$: 521.1533; found: m/z 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*):

Was obtained by the reaction of β- glycosidic 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 1.2g, 71 %; R_f 0.5 (6:4 hexane-EtOAc); $[\alpha]^{25}_D$ -20 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2959, 1747, 1684, 1611; ^{1}H-NMR (300MHz, $CDCl_3$ + 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 x -$OCOCH_3$). ^{13} C NMR (50 MHz, $CDCl_3$): δ 196.0 (C=O, C-2), 170.9 and 169.4, (7 x -$OCOCH_3$), 143.9 (C-4), 134.6 (Ar-C) 131.0 (C-3), 129.9 and 126.6, (5 x 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 x -$OCOCH_3$); ESIMS: m/z 787 $(M+Na)^+$; HRMS: Calcd for $C_{36}H_{45}O_{18}$: 765.26059; found: m/z . 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*):

Was obtained by the reaction of β- glycosidic ketone **15** (1 g, 1.47 mmol) and 3,4-dimetoxybenzaldehyde (0.245 g, 1.47 mmol) as a colorless solid, mp 160 -161°C; yield 0.9 g, 67 %; R_f 0.4 (4:6 hexane-EtOAc); $[\alpha]^{25}_D$ -25 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1}: 2929, 1749, 1641; ^{1}H-NMR (300MHz, $CDCl_3$ + 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 x -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 x -$OCOCH_3$). ^{13} C NMR (50 MHz, $CDCl_3$): δ 194.9 (C=O, C-2), 169.8 and 168.4, (7 x -$OCOCH_3$), 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 x -CH), 62.0 (C-6"), 61.4 (C-6´), 55.7 (2 x -OCH_3), 42.6 (C-1), 20.7 and 20.4 (7 x -$OCOCH_3$); ESIMS: m/z 699 $(M+Na)^+$; HRMS: Calcd for $C_{40}H_{47}O_{18}$: 815.27624; found: m/z 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*):

Was obtained by the reaction of β- glycosidic 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 (6:4 hexane-EtOAc); $[\alpha]^{25}_D$ -24 (c 0.1, $CHCl_3$); IR (KBr) ν_{max} cm^{-1} 3021, 2927, 1749, 1608; ^{1}H-NMR (300MHz, $CDCl_3$ + 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 x -$OCOCH_3$). ^{13} C NMR (50 MHz, $CDCl_3$): δ 195.9 (C=O, C-2), 170.6 and 169.1, (7 x -$OCOCH_3$), 143.8 (C-4), 134.6, 133.7, 132.1 (Ar-C), 131.0 (C-3), 129.2 and 123.8, (7 x -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 x -$OCOCH_3$); ESIMS: m/z 837 $(M+Na)^+$; HRMS: Calcd for $C_{38}H_{49}O_{20}N$: 825.28172; found: m/z 825.28334.

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References:

(1) Moore, R. E.; Scheuer, P. J. *Science* **1971**, *172*, 495-498.

(2) Moore, R. E.; Bartolini, G. J. *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. Polyether macrolides.

(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. Polyketides:

(7) Trefzer, A.; Hoffmeister, D.; Ku¨ nzel, 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 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. see:

(11) Jimenez-Barbero,J.; Espinosa, J. F.; Asensio, J. L.; Canada, F. J.; Poveda, A. *Adv. Carb. 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) Levy, D. E.; Tang, C. *The Chemistry of C-Glycosides*; Elsevier: Tarrytown, NY, 1995; Vol.13

(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 Regulation* **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) Riemann, I.; Papadopoulos, M. A.; Knorst, M.; Fessner, W. D. *Aust. J. Chem*. **2002,** *55*, 147-154.