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Synthesis and biological activities of new 7-*O*-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-chromones

K M Hatzade[1,2], V S Taile[1], P K Gaidhane[1], V D Umare[1], A G M Haldar[1] & V N Ingle*[1]

[1]Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur 440 033, India

[2]Department of Applied Chemistry, SVSS College of Engineering & Research, Wanadongri, Hingna Road, Nagpur 441 110, India

E-mail: g_kishor2000@yahoo.co.in

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A convenient route to synthesize some new medicinally important 7-hydroxy-3-(3-oxo-3-arylprop-1-enyl)-chromones **2** is described by the interaction of 7-hydroxy-3-formyl chromone **1** with various substituted acetophenones which on condensation with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide affords 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones **3**. Later on deacetylation with anhydrous zinc acetate in methanol gives 7-*O*-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones **4**. These compounds are evaluated for their *in vitro* antimicrobial and antioxidant activity. The structures of these newly synthesized compounds are established by IR, NMR, mass spectra, elemental analysis and chemical analysis.

Keywords: Chromones, α, β-unsaturated carbonyl compounds, glucosylation, *O*-β-D-glucosides, biological activity

In the last few years, glycobiology[1] has gained much attention because the oligosaccharide part of glycol-lipids, glycoproteins and other glycoconjugates are responsible for their function in various biological processes[2-10]. Although a large number of synthetic methods for glycoside formation have been developed[11-14], but not all problems are well solved. The stereo- and regioselectivity increases by intramolecular *O*-glycoside bond formation[15]. In continuation of this work[16], we report in this paper an efficient synthesis of α, β-unsaturated carbonyl compounds (chalcone) derived from 7-hydroxy-3-formyl-4*H*-chromen-4-one and substituted aceto-phenones and their *O*-glucosylation reaction in the absence of heavy metal salts but in the presence of DTMAB as a phase transfer catalyst leading to *O*-glucosides. Literature survey reveals the importance of chalcones as they possess antiinflammatory[17], antibacterial[18], antiviral[19], insecticidal[20], antimicro-bial[21], gastric protectant[22] and antipicorhenovirus activities[23]. Similarly, several therapeutically interest-ing biological activities of chromones have been reported including anticancer[24-29], anti-HIV[30-32] and antioxidant properties[33-35]. The remarkable biological properties of these categories of heterocycles oriented our attention to the synthesis of series of new heterocyclic derivatives combining chromonylidene acetophenone and carbohydrate moiety in one molecular frame as new possible biological active compounds. Herein, the synthesis of chalcones of hydroxy chromone and their *O*-glucosides starting from 7-hydroxy-3-formyl-4*H*-chromen-4-one is reported, together with the results on their biological activities.

Results and Discussion

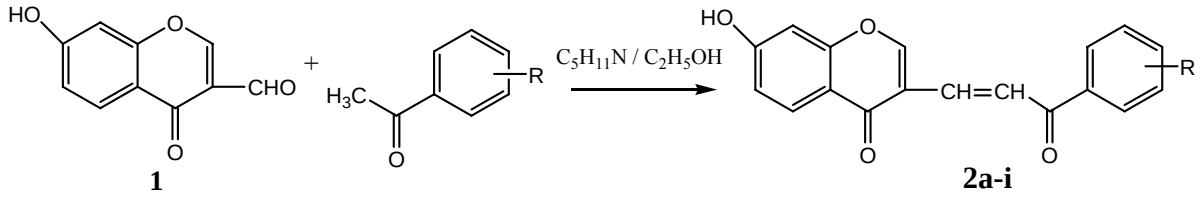
During the course of the present investigation, the starting compound 7-hydroxy-3-formyl-4*H*-chromen-4-one **1** required was synthesized by Vilsmeier-Haack reaction from resacetophenone[36]. The condensation[37] of **1** with substituted acetophenones in the presence of freshly distilled piperidine in dry absolute alcohol for about 2-3 hr has resulted in the formation of 7-hydroxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones **2**. The IR spectrum of **2a** showed a broad peak at 3348 cm^{-1} due to the OH stretch. The peaks at 3077, 2361 cm^{-1} were appeared due to Ar–CH stretch. A strong absorption at 1695 cm^{-1} was attributed due to α, β-unsaturated carbonyl C=O stretch. The peak at 1656 cm^{-1} was assigned to C=O stretching in γ-pyrone. The peaks at 1458 and 1090 cm^{-1} were due to

asymmetric stretch in α, β-unsaturated compound and C–O–C ether linkage stretch respectively. The ^{1}H NMR spectrum of the said compound showed the peaks at δ 7.70 (d, 1H, CH), 7.14 (s, 1H, OH), 6.1 (d, 1H, CH), 6.34-7.78 (m, 8H, Ar-H), 4.98 (s, 2-H, CH). There was no peak due to –CHO group. In the ^{13}C NMR spectrum, C-3′ (CO) and C-4 (C=O) resonated at δ 188.8 and 178.1 respectively while C-1′ and C-2′ resonated at δ 142.4 and 129.5 respectively consistent with formation of **2a** (**Scheme I**).

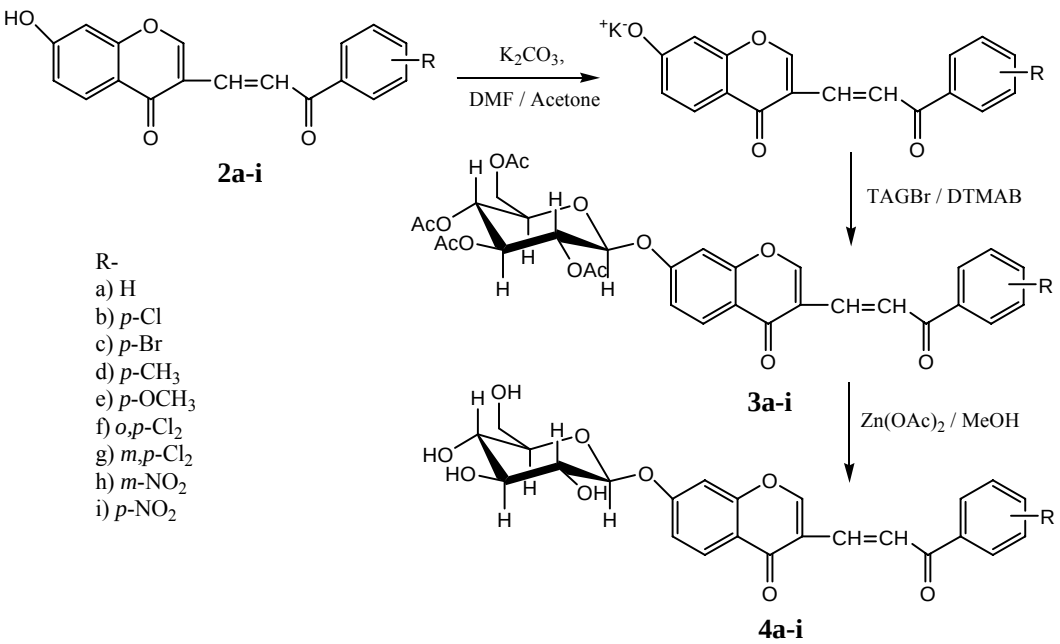
Glucosydation[38] reaction of **2** (*via* its potassium salt) has been carried out under anhydrous condition using 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (TAGBr) as a glucosyl donor which was prepared from glucose pentacetate in the crystalline form. This reaction was carried out using anhydrous K_2CO_3 in the presence of dodecyltrimethylammonium bromide (DTMAB) as a phase transfer catalyst in mixture of dry acetone and DMF. This gives rise to 2,3,4,6-tetra-*O*-acetyl-7-*O*-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones **3a-i**. The main advantage of this reaction was that the distereoselectivity was high in favour of β-anomer, improves the overall yield and regioselectivity. Only 10% of α-anomer was separated by column chromatography. The absence of IR band due to OH stretch at 3100-3500 cm^{-1} was indicating the formation of product **3a**. Also, the sharp peaks at 2363 and 2854 cm^{-1} were assigned to the –CH and glucosidic–CH stretches respectively. The C=O stretch peak was found to be shifted to 1722 cm^{-1}. A strong absorption at 1761 cm^{-1} was assigned to C=O stretch of *O*-acetyl groups of glucose moiety. The peaks at 1450, 1121 cm^{-1} were attributed to the CH=CH and C–O–C stretches. The β-anomer of acetylated **3a** is confirmed by ^{1}H NMR spectrum, the anomeric proton 1-H resonated as a doublet at δ 4.86, with the coupling constant $J_{1\text{-}2}$ = 4.2 Hz establishing the β-stereochemistry of the glycosidic bond. Also in ^{13}C NMR spectrum, C-1′ resonated downfield of the other glycosyl carbon at δ 101.8 consistent with the formation of acetylated β-glucosides **3a-i**. Deacetylation of **3a-i** with anhydrous zinc acetate in methanol affords the desired 7-*O*-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones **4a-i** in good yield (**Scheme II**). The IR spectrum showed the presence of characteristic absorption peaks at 3412 (br, OH peak of carbohydrate residue), 2858 (glucosidic–CH), 1718 (C=O), 1652 (C=O, γ-pyrone), 1466 (CH=CH), 1072 (C-O-C), 683 cm^{-1} (benzene monosubstituted), indicating the formation of **4a**. This was also confirmed by its ^{1}H and ^{13}C NMR and EI-MS data. In particular, in the ^{1}H NMR spectrum, the anomeric proton H-1 appeared as a doublet at δ 5.77 with a coupling constant $J_{1\text{-}2}$ = 7.2 Hz confirming the β-stereochemistry of the glycosidic bond. Thus, confirming the trans-diaxial relation between H-1 and H-2 of the sugar. Signals due to protons of the carbohydrate of the hydroxyl groups were not observed in the spectrum because of the fast exchange of all non-hydrogen bonded OH groups, and the acidic phenolic functions. Similarly in ^{13}C NMR spectrum, C-1′ resonated downfield of the other glycosyl carbon at δ 104.7 consistent with the formation of *O*-β-glucosides **4a-i**. In EI-MS studies, the molecular ion peak at *m*/*z* 454 $(M)^+$ was dominated by *m*/*z* 391 (100%) with the loss of *m*/*z* 163 corresponding to the loss of an intact anhydro-sugar moiety. This fragmentation pattern is characteristics for *O*-glucosidically linked sugar. Also the molecular ion at *m*/*z* 454 $(M)^+$ confirms the molecular formula $C_{24}H_{22}O_9$ of compound **4a**.

Biological activities

The synthesized compounds were evaluated for their *in vitro* antibacterial activity against *Escherichia coli, Klebisilla aerogens, Staphylococcus aureus* and *Bacillus substilis* and *in vitro* antifungal activity against *Aspergillus niger* and *Candida albicans* fungi by the cup plate diffusion method. The comparative study of 7-*O*-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones have been observed by using standard drugs ciprofloxacin, sulphacetamide for bacteria and gentamycin,



Scheme I — Synthesis of 7-hydroxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones **2a-i**



Scheme II — Synthesis of 7-*O*-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones **4a-i**

clotrimazole (100 ppm) for fungi. The test compounds were dissolved in DMSO at a concentration of 100 ppm. Most of the compounds exhibited mild to moderate antibacterial activity as well as antifungal activity against all the microbes tested. Similarly, *in vitro* free radical scavenging activities of glucosides were evaluated by DPPH assay method and most of the compounds were found active at 1 mg/mL concentration. Percentage scavenging of DPPH radical was calculated using the formula:

$$\% \text{ Scavenging of DPPH} = \left[\frac{(\text{Control Test})}{\text{Control}}\right] \times 100.$$

The results of antimicrobial (antibacterial and anti-fungal) activity and antioxidant activity are shown in **Table I**.

Conclusion

In the present work, *O*-β-D-glucosides of 7-hydroxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones were synthesized and evaluated their *in vitro* antimicrobial and anti-oxidant activity. Biological results indicated that the new glucosides of 7-hydroxy-chromonylidene chromones show greater pharmacological significance. Hence the compounds **4a-i** might be promising new antimicrobial as well as anti-oxidant agents.

Experimental Section

Melting points were determined on a liquid paraffin-bath in open capillary tube and were uncorrected. FT-IR spectra were recorded using (KBr) on a Perkin-Elmer FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300F (300 Hz) NMR spectrometer, using tetramethylsilane as an internal standard in DMSO-d_6 as solvent. Mass spectra were determined on a Hitachi Perkin-Elmer RMU 6D mass spectrometer. Elemental analyses were determined using the Perkin-Elmer 2400 CHN analyzer. Purity of the compounds was checked on silica gel plates using iodine vapour as visualizing agent.

7-Hydroxy-3-formyl chromone 1

In dry DMF (121 mL) in three necked flask, $POCl_3$ (75 mL, 0.49 mole) was added slowly with vigorous stirring at 50°C. Heating and stirring was continued for 2 hr at 45-55°C. The solution of resacetophenone (18.24 g, 0.12 mole) in DMF (25 mL) was then slowly added with stirring at 50°C and the stirring was continued for 2 hr. After cooling the mixture was kept overnight at RT and diluted slowly by adding ice-cold water (500 mL) and stirred again for 6 hr. The red crystalline product obtained was filtered off and recrystallised from alcohol, yield 45 g (78%), m.p. 269°C. Its alcoholic solution gives violet coloration with neutral $FeCl_3$. IR (KBr): 3428 (phenolic OH), 2363 (Ar-CH), 2773 (CH, CHO), 1685 (C=O), 1614 (C=C), 1093 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 9.59 (s, 1H, CHO), 8.82 (s, 1H, OH), 6.8-8.0 (m, 3H,

Table I — Biological activity of 7-*O*-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones **4a-i**

Sr. No.	Zone of Inhibition (mm) (Activity Index) [std]						% Inhibition Antioxidant activity
	Antibacterial Activity				Antifungal Activity		
	Gram-positive		Gram-negative				
	S. aureus	*B. substilis*	*E. coli*	*K. aerogens*	*C. albicans*	*A. niger*	DPPH
4a	23 (0.68)* (0.74)#	17 (0.59)* (0.65)#	35 (1.00)* (1.21)#	20 (0.91)* (0.95)#	32 (1.52)* (1.39)#	21 (0.84)* (0.88)#	81.01 (0.83)*
4b	19 (0.56)* (0.61)#	25 (0.86)* (0.96)#	33 (0.94)* (1.14)#	17 (0.77)* (0.81)#	25 (1.19)* (1.09)#	23 (0.92)* (0.96)#	78.25 (0.80)*
4c	22 (0.65)* (0.71)#	15 (0.52)* (0.58)#	21 (0.60)* (0.72)#	23 (1.04)* (1.10)#	30 (1.43)* (1.30)#	24 (0.96)* (1.00)#	88.47 (0.90)*
4d	23 (0.68)* (0.74)#	15 (0.52)* (0.58)#	24 (0.69)* (0.83)#	18 (0.81)* (0.86)#	24 (1.14)* (1.04)#	26 (1.04)* (1.08)#	74.69 (076)*
4e	22 (0.65)* (0.71)#	21 (0.72)* (0.81)#	21 (0.60)* (0.72)#	20 (0.91)* (0.95)#	24 (1.14)* (1.04)#	22 (0.88)* (0.92)#	87.93 (0.90)*
4f	29 (0.85)* (0.94)#	22 (0.76)* (0.85)#	23 (0.66)* (0.79)#	20 (0.91)* (0.95)#	26 (1.24)* (1.13)#	20 (0.80)* (0.83)#	80.94 (0.83)*
4g	30 (0.88)* (0.97)#	24 (0.83)* (0.92)#	21 (0.60)* (0.72)#	24 (1.09)* (1.14)#	22 (1.05)* (0.96)#	26 (1.04)* (1.08)#	89.78 (0.92)*
4h	28 (0.84)* (0.90)#	26 (0.90)* (1.00)#	28 (0.80)* (0.97)#	21 (0.95)* (1.00)#	27 (1.29)* (1.17)#	19 (0.76)* (0.79)#	87.45 (0.89)*
4i	23 (0.68)* (0.74)#	20 (0.69)* (0.77)#	21 (0.60)* (0.72)#	21 (0.95)* (1.00)#	18 (0.85)* (0.78)#	22 (0.88)* (0.92)#	90.12 (0.92)*
Std.1	34	29	35	22	21	25	98.03
Std. 2	31	26	29	21	23	24	

(Activity index) = Inhibition zone of the sample/Inhibition zone of the standard, * = Activity index against Std. 1, # = Activity index against Std. 2. For antibacterial activity: Std. 1 = Ciprofloxacin and Std. 2 = Sulphacetamide; for antifungal activity: Std. 1 = Gentamycin and Std. 2 = Clotrimazole; for anti-oxidant activity: Std. 1= Ascorbic Acid.

Ar-H), 4.95 (s, 2-H, CH); ^{13}C NMR (DMSO-d_6): δ 188.1 (s, CHO of C-3), 174.9 (s, C-4, C=O), 171.0 (s, C-2), 161.2 (s, C-7), 157.9 (s, C-9), 131.4 (s, C-5), 115.7 (s, C-3, C-CHO), 114.0 (s, C-10), 109.4 (s, C-6), 104.8 (s, C-8).

General procedure for 7-hydroxy-3-(3-aryl-3-oxo-prop-1-enyl)-4H-chromen-4-one 2a-i

A mixture of 7-hydroxy-3-formyl-4*H*-chromen-4-one (0.01 mole), substituted acetophenone (0.012 mole), ethyl alcohol (100 mL) and one drop of piperidine were warmed for 2-3 hr (monitored by TLC). It was cooled to 0°C; the light yellow solid obtained was filtered, washed with distilled water, dried and crystallized from benzene/ethanol. It gave red colour with Conc. H_2SO_4.

2a: Yield 80%; m.p. 221°C (ethanol); Found: C, 73.93; H, 4.10. $C_{18}H_{12}O_4$ requires C, 73.97; H, 4.14%; IR (KBr): 3348 (br, OH), 3077, 2361 (Ar-CH), 1656 (C=O, γ-pyrone), 1695 (C=O), 1458 (CH=CH), 1090 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.70 (d, 1H, CH), 7.14 (s, 1H, OH), 6.1 (d, 1H, CH), 6.34-7.78 (m, 8H, Ar-H), 4.98 (s, 2-H, CH); ^{13}C NMR (DMSO-d_6): δ 188.8 (s, C-3′, CO), 178.1 (s, C-4, C=O), 164.8 (s, C-7), 157.8 (s, C-9), 149.0 (s, C-2), 142.4 (s, C-1′, CH), 138.0 (s, C-1″), 135.1 (s, C-4″), 131.8 (s, C-5), 130.2 (s, C-2″, C-6″), 129.5 (s, C-2′, CH), 128.9 (s, C-3″, C-5″), 118.9 (s, C-3), 116.1 (s, C-10), 111.4 (s, C-6), 104.8 (s, C-8).

2b: Yield 81%; m.p. 218°C (benzene); Found: C, 66.15; H, 3.35. $C_{18}H_{11}ClO_4$ requires C, 66.17; H, 3.39%; IR (KBr): 3411 (br, OH), 3081, 2364 (Ar-CH), 1647 (C=O, γ-pyrone), 1691 (C=O), 1457 (CH=CH), 1089 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.71 (d, 1H, CH), 7.25 (d, 1H, CH), 7.19 (s, 1H, OH), 6.37-7.89 (m, 7H, Ar-H), 4.92 (s, 2-H, CH); ^{13}C NMR (DMSO-d_6): δ 190.1 (s, C-3′, CO), 177.1 (s, C-4, C=O), 165.1 (s, C-7), 159.2 (s, C-9), 150.0 (s, C-2), 142.9 (s, C-1′, CH), 141.0 (s, C-4″, C-Cl), 135.8 (s, C-1″), 132.1 (s, C-2″, C-6″), 131.8 (s, C-5), 130.1 (s, C-3″, C-5″), 128.7 (s, C-2′, CH), 120.1 (s, C-3), 117.4 (s, C-10), 110.1 (s, C-6), 106.4 (s, C-8).

2c: Yield 81%; m.p. 230°C (benzene); Found: C, 58.21; H, 2.96. $C_{18}H_{11}BrO_4$ requires C, 58.24; H, 2.99%; IR (KBr): 3381 (br, OH), 3085, 2366 (Ar-CH), 1645 (C=O, γ-pyrone), 1686 (C=O), 1459

(CH=CH), 1090 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.71 (d, 1H, CH), 7.20 (s, 1H, OH), 7.20 (d, 1H, CH), 6.38-7.74 (m, 7H, Ar-H), 5.01 (s, 2-H, CH); ^{13}C NMR (DMSO-d_6): δ 188.8 (s, C-3′, CO), 176.9 (s, C-4, C=O), 165.1 (s, C-7), 159.1 (s, C-9), 148.5 (s, C-2), 143.6 (s, C-1′, CH), 137.1 (s, C-1″), 132.8 (s, C-3″, C-5″), 132.0 (s, C-2″, C-6″), 131.5 (s, C-5), 129.0 (s, C-4″, C-Br), 128.9 (s, C-2′, CH), 119.1 (s, C-3), 116.0 (s, C-10), 110.1 (s, C-6), 104.9 (s, C-8).

2d: Yield 82%; m.p. 215°C (ethanol); Found: C, 74.47; H, 4.57. $C_{19}H_{14}O_4$ requires C, 74.50; H, 4.61%; IR (KBr): 3412 (br, OH), 3083, 2364 (Ar-CH), 1642 (C=O, γ-pyrone), 1684 (C=O), 1458 (CH=CH), 1094 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.71 (d, 1H, CH), 7.21 (d, 1H, CH), 7.19 (s, 1H, OH), 6.39-7.71 (m, 7H, Ar-H), 5.03 (s, 2-H, CH), 2.31 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6): δ 188.6 (s, C-3′, CO), 176.5 (s, C-4, C=O), 165.4 (s, C-7), 158.4 (s, C-9), 150.1 (s, C-2), 144.4 (s, C-1′, CH), 143.8 (s, C-4″, C-CH_3), 135.1 (s, C-1″), 132.4 (s, C-5), 129.4 (s, C-2″, C-6″), 129.1 (s, C-2′, CH), 129.0 (s, C-3″, C-5″), 118.8 (s, C-3), 117.0 (s, C-10), 111.1 (s, C-6), 105.0 (s, C-8), 24.0 (s, CH_3 of C-4″).

2e: Yield 79%; m.p. 218°C (benzene); Found: C, 70.78; H, 4.30. $C_{19}H_{14}O_5$ requires C, 70.80; H, 4.38%; IR (KBr): 3412 (br, OH), 3083, 2366 (Ar-CH), 1658 (C=O, γ-pyrone), 1696 (C=O), 1464 (CH=CH), 1090 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.71 (d, 1H, CH), 7.26 (d, 1H, CH), 7.23 (s, 1H, OH), 6.34-7.73 (m, 7H, Ar-H), 4.98 (s, 2-H, CH), 3.73 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6): δ 190.1 (s, C-3′, CO), 176.6 (s, C-4, C=O), 166.1 (s, C-7), 165.7 (s, C-4″, C-CH_3), 157.9 (s, C-9), 148.7 (s, C-2), 143.0 (s, C-1′, CH), 132.4 (s, C-5), 131.0 (s, C-2″, C-6″), 129.8 (s, C-1″), 128.7 (s, C-2′, CH), 118.6 (s, C-3), 115.8 (s, C-10), 115.0 (s, C-3″, C-5″), 111.0 (s, C-6), 106.1 (s, C-8), 56.1 (s, OCH_3 of C-4″).

2f: Yield 85%; m.p. 205°C (ethanol); Found: C, 59.85; H, 2.75. $C_{18}H_{10}Cl_2O_4$ requires C, 59.86; H, 2.79%; IR (KBr): 3388 (br, OH), 3045, 2361 (Ar-CH), 1659 (C=O, γ-pyrone), 1689 (C=O), 1460 (CH=CH), 1093 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.79 (d, 1H, CH), 7.21 (d, 1H, CH), 7.19 (s, 1H, OH), 6.36-7.67 (m, 6H, Ar-H), 5.11 (s, 2-H, CH); ^{13}C NMR (DMSO-d_6): δ 189.0 (s, C-3′, CO), 177.1 (s, C-4, C=O), 165.1 (s, C-7), 159.1 (s, C-9), 149.0 (s, C-2), 142.8 (s, C-1′, CH), 142.0 (s, C-4″, C-Cl), 135.4 (s, C-2″, C-Cl), 134.6 (s, C-1″), 132.1 (s, C-6″), 131.7 (s, C-5), 130.0 (s, C-3″), 128.4 (s, C-2′, CH), 127.1 (s, C-5″), 120.0 (s, C-3), 117.0 (s, C-10), 109.6 (s, C-6), 104.8 (s, C-8).

2g: Yield 78%; m.p. 209°C (ethanol); Found: C, 59.85; H, 2.75. $C_{18}H_{10}Cl_2O_4$ requires C, 59.86; H, 2.79%; IR (KBr): 3356 (br, OH), 3081, 2361 (Ar-CH), 1649 (C=O, γ-pyrone), 1683 (C=O), 1461 (CH=CH), 1093 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.68 (d, 1H, CH), 7.19 (d, 1H, CH), 7.17 (s, 1H, OH), 6.36-7.79 (m, 6H, Ar-H), 5.01 (s, 2-H, CH); ^{13}C NMR (DMSO-d_6): δ 190.4 (s, C-3′, CO), 176.8 (s, C-4, C=O), 164.5 (s, C-7), 157.8 (s, C-9), 150.0 (s, C-2), 143.0 (s, C-1′, CH), 139.0 (s, C-4″, C-Cl), 137.1 (s, C-1″), 134.2 (s, C-3″, C-Cl), 131.5 (s, C-5), 131.0 (s, C-5″), 130.8 (s, C-2″), 130.1 (s, C-6″), 128.9 (s, C-2′, CH), 119.1 (s, C-3), 116.0 (s, C-10), 109.9 (s, C-6), 104.5 (s, C-8).

2h: Yield 83%; m.p. 220°C (benzene); Found: C, 64.08; H, 3.25; N, 4.13. $C_{18}H_{11}NO_6$ requires C, 64.10; H, 3.29; N, 4.15%; IR (KBr): 3445 (br, OH), 3081, 2366 (Ar-CH), 1650 (C=O, γ-pyrone), 1688 (C=O), 1461 (CH=CH), 1098 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.80 (d, 1H, CH), 7.25 (d, 1H, CH), 7.24 (s, 1H, OH), 6.35-8.78 (m, 7H, Ar-H), 4.87 (s, 2-H, CH); ^{13}C NMR (DMSO-d_6): δ 189.1 (s, C-3′, CO), 177.8 (s, C-4, C=O), 165.0 (s, C-7), 157.6 (s, C-9), 147.6 (s, C-2), 147.2 (s, C-3″, C-NO_2), 143.2 (s, C-1′, CH), 138.0 (s, C-1″), 135.4 (s, C-6″), 131.0 (s, C-5), 129.6 (s, C-5″), 129.4 (s, C-2′, CH), 126.3 (s, C-4″) 124.5 (s, C-2″), 119.8 (s, C-3), 116.0 (s, C-10), 110.1 (s, C-6), 105.1 (s, C-8).

2i: Yield 80%; m.p. 280°C (benzene); Found: C, 64.08; H, 3.25; N, 4.13. $C_{18}H_{11}NO_6$ requires C, 64.10; H, 3.29; N, 4.15%; IR (KBr): 3422 (br, OH), 3076, 2362 (Ar-CH), 1642 (C=O, γ-pyrone), 1681 (C=O), 1466 (CH=CH), 1075 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.70 (d, 1H, CH), 7.20 (d, 1H, CH), 7.18 (s, 1H, OH), 6.34-8.30 (m, 7H, Ar-H), 4.99 (s, 2-H, CH); ^{13}C NMR (DMSO-d_6): δ 188.5 (s, C-3′, CO), 177.0 (s, C-4, C=O), 165.5 (s, C-7), 159.1 (s, C-9), 155.0 (s, C-4″, C-NO_2), 149.0 (s, C-2), 144.4 (s, C-1″), 142.8 (s, C-1′, CH), 132.4 (s, C-5), 130.1 (s, C-6″), 131.0 (s, C-5″), 130.0 (s, C-2″), 129.4 (s, C-2′, CH), 120.7 (s, C-3″), 119.1 (s, C-3), 115.4 (s, C-10), 109.9 (s, C-6), 104.9 (s, C-8).

General procedure for 2,3,4,6-tetra-*O*-acetyl-7-*O*-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones 3a-i

In a 25 mL round-bottomed flask, anhydrous K_2CO_3 (6.3 mmole) was added to the mixture of DMF (9 mL) and acetone (6 mL), then 7-hydroxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones (**2a-i**, 0.30

mmole), DTMAB (10 mg) and α-acetylbromoglucose (0.60 mmole) were added under stirring, the reaction-mixture was refluxed for 5-6 hr (monitored by TLC). Then acetone was removed under vacuum, water (20 mL) was added to the flask. The mixture was extracted with ethyl acetate (5 × 10 mL), the organic layer was washed by 20 mL water and brine, dried over anhydrous $MgSO_4$, then removed the solvent to give the residue which was purified by silica gel flash chromatography (ethyl acetate : petroleum ether 1 : 2 v/v) to give a brown coloured semisolid.

3a: Yield 85%; $[\alpha]_D^{25}$ = - 21.2 (*c* 0.1 in DMSO); Found: C, 61.71; H, 4.84. $C_{32}H_{30}O_{13}$ requires C, 61.73; H, 4.86%; IR (KBr): 3042, 2363 (Ar-CH), 2854 (glucosidic-CH), 1761 (C=O of *O*-acetyl gps of glycone moiety), 1722 (C=O), 1450 (CH=CH), 1121 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.70 (d, 1H, CH), 7.26 (s, 2-H, CH), 7.20 (d, 1H, CH), 6.44-7.89 (m, 8H, Ar-H), 4.84-5.05 (m, 3H, 2′,3′,4′-H), 4.86 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 4.2), 4.34 (dd, 1H, 5′-H), 3.80-4.29 (m, 2H, 6′-H), 2.01, 1.95, 1.99, 2.05 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): δ 176.0 (s, C-4, C=O), 169.6 (s, C-atoms of acetyl C=O), 163.9 (s, C-7), 148.9 (s, C-2), 157.4 (s, C-9), 143.5 (s, CH-C-3), 130.8 (s, C-5), 129.1 (s, CH=CH), 127.1-134.6 (s, aromatic 6C-atom), 118.1 (s, C-3), 115.5 (s, C-10), 108.9 (s, C-6), 103.4 (s, C-8), 101.8 (s, C-1′, anomeric C-atom), 74.8 (s, C-5′), 72.1 (s, C-2′), 70.8 (s, C-4′), 70.5 (s, C-3′), 64.9 (s, C-6′), 20.4 (s, C-atom, CH_3 of acetyl group).

3b: Yield 88%; $[\alpha]_D^{25}$ =-25.7 (*c* 0.1 in DMSO); Found: C, 58.47; H, 4.40. $C_{32}H_{29}ClO_{13}$ requires C, 58.50; H, 4.45%; IR (KBr): 3044, 2365 (Ar-CH), 2857 (glucosidic-CH), 1754 (C=O of *O*-acetyl gps of glycone moiety), 1723 (C=O), 1455 (CH=CH), 1079 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.72 (d, 1H, CH), 7.24 (s, 2-H, CH), 7.19 (d, 1H, CH), 6.42-7.59 (m, 7H, Ar-H), 4.75-4.99 (m, 3H, 2′,3′,4′-H), 4.79 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 4.1), 4.34 (dd, 1H, 5′-H), 3.98-4.32 (m, 2H, 6′-H), 2.02, 1.96, 1.94, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): δ 176.1 (s, C-4, C=O), 170.3 (s, C-atoms of acetyl C=O), 164.2 (s, C-7), 159.0 (s, C-2), 157.6 (s, C-9), 142.9 (s, CH-C-3), 130.8 (s, C-5), 129.6 (s, CH=CH), 128.5-134.9 (s, aromatic 6C-atom), 119.0 (s, C-3), 116.1 (s, C-10), 109.0 (s, C-6), 103.6 (s, C-8), 102.4 (s, C-1′, anomeric C-atom), 75.2 (s, C-5′), 72.2 (s, C-2′), 71.4 (s, C-4′), 71.0 (s, C-3′), 66.1 (s, C-6′), 20.5 (s, C-atom, CH_3 of acetyl group).

3c: Yield 82%; $[\alpha]_D^{25}$ =-18.1 (*c* 0.1 in DMSO); Found: C, 54.70; H, 4.14. $C_{32}H_{29}BrO_{13}$ requires C, 54.79; H, 4.17%; IR (KBr): 3041, 2361 (Ar-CH), 2852 (glucosidic-CH), 1765 (C=O of *O*-acetyl gps of glycone moiety), 1724 (C=O), 1466 (CH=CH), 1049 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.74 (d, 1H, CH), 7.31 (s, 2-H, CH), 7.28 (d, 1H, CH), 6.44-7.56 (m, 7H, Ar-H), 4.78-5.05 (m, 3H, 2′,3′,4′-H), 4.78 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 4.0), 4.41 (dd, 1H, 5′-H), 3.89-4.29 (m, 2H, 6′-H), 1.99, 1.94, 1.98, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): δ 176.0 (s, C-4, C=O), 170.0 (s, C-atoms of acetyl C=O), 163.8 (s, C-7), 158.9 (s, C-2), 158.1 (s, C-9), 142.7 (s, CH-C-3), 131.0 (s, C-5), 128.6 (s, CH=CH), 123.5-132.9 (s, aromatic 6C-atom), 118.1 (s, C-3), 115.0 (s, C-10), 108.9 (s, C-6), 103.4 (s, C-8), 102.5 (s, C-1′, anomeric C-atom), 75.4 (s, C-5′), 72.3 (s, C-2′), 71.0 (s, C-4′), 70.9 (s, C-3′), 66.1 (s, C-6′), 21.1 (s, C-atom, CH_3 of acetyl group).

3d: Yield 90%; $[\alpha]_D^{25}$ =-22.6 (*c* 0.1 in DMSO); Found: C, 62.22; H, 5.04. $C_{33}H_{32}O_{13}$ requires C, 62.26; H, 5.07%; IR (KBr): 3042, 2362 (Ar-CH), 2857 (glucosidic-CH), 1761 (C=O of *O*-acetyl gps of glycone moiety), 1726 (C=O), 1460 (CH=CH), 1079 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.68 (d, 1H, CH), 7.44 (s, 2-H, CH), 7.24 (d, 1H, CH), 6.41-7.58 (m, 7H, Ar-H), 4.72-5.11 (m, 3H, 2′,3′,4′-H), 4.89 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 4.2), 4.49 (dd, 1H, 5′-H), 3.75-4.29 (m, 2H, 6′-H), 2.37 (s, 3H, CH_3), 2.02, 1.94, 1.98, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): δ 176.0 (s, C-4, C=O), 170.6 (s, C-atoms of acetyl C=O), 164.7 (s, C-7), 159.0 (s, C-2), 157.4 (s, C-9), 143.1 (s, CH-C-3), 130.6 (s, C-5), 129.0 (s, CH=CH), 127.1-138.9 (s, aromatic 6C-atom), 118.1 (s, C-3), 115.0 (s, C-10), 108.8 (s, C-6), 103.4 (s, C-8), 102.6 (s, C-1′, anomeric C-atom), 75.4 (s, C-5′), 72.1 (s, C-2′), 71.1 (s, C-4′), 71.0 (s, C-3′), 65.7 (s, C-6′), 23.7 (s, C-atom, CH_3), 20.7 (s, C-atom, CH_3 of acetyl group).

3e: Yield 87%; $[\alpha]_D^{25}$ =-20.7 (*c* 0.1 in DMSO); Found: C, 60.73; H, 4.90. $C_{33}H_{32}O_{14}$ requires C, 60.73; H, 4.94%; IR (KBr): 3037, 2368 (Ar-CH), 2862 (glucosidic-CH), 1755 (C=O of *O*-acetyl gps of glycone moiety), 1728 (C=O), 1446 (CH=CH), 1100 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.72 (d, 1H, CH), 7.45 (s, 2-H, CH), 7.17 (d, 1H, CH), 6.39-7.61 (m, 7H, Ar-H), 4.89 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 4.1), 4.71-5.05 (m, 3H, 2′,3′,4′-H), 4.48 (dd, 1H, 5′-H), 3.74-4.29 (m, 2H, 6′-H), 3.65 (s, 3H, OCH_3), 1.97, 1.98, 1.97, 2.00 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): δ 174.8 (s, C-4, C=O), 170.4 (s, C-atoms of acetyl C=O), 163.9 (s, C-7), 159.0 (s, C-2), 157.4

(s, C-9), 143.4 (s, CH-C-3), 130.7 (s, C-5), 128.2 (s, CH=CH), 113.5-161.5 (s, aromatic 6C-atom), 119.1 (s, C-3), 115.0 (s, C-10), 108.7 (s, C-6), 103.4 (s, C-8), 101.7 (s, C-1′, anomeric C-atom), 74.7 (s, C-5′), 72.1 (s, C-2′), 70.9 (s, C-4′), 70.4 (s, C-3′), 66.1 (s, C-6′), 56.2 (s, C-atom, OCH_3), 20.7 (s, C-atom, CH_3 of acetyl group).

3f: Yield 89%; $[\alpha]_D^{25}$ =-19.0 (*c* 0.1 in DMSO); Found: C, 55.52; H, 4.05. $C_{32}H_{28}Cl_2O_{13}$ requires C, 55.58; H, 4.08%; IR (KBr): 3045, 2361 (Ar-CH), 2852 (glucosidic-CH), 1762 (C=O of *O*-acetyl gps of glycone moiety), 1701 (C=O), 1454 (CH=CH), 1078 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.66 (d, 1H, CH), 7.28 (s, 2-H, CH), 7.19 (d, 1H, CH), 6.35-7.64 (m, 6H, Ar-H), 4.78-4.99 (m, 3H, 2′,3′,4′-H), 4.79 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 4.0), 4.44 (dd, 1H, 5′-H), 3.78-4.27 (m, 2H, 6′-H), 1.97, 1.98, 1.99, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): δ 174.8 (s, C-4, C=O), 171.0 (s, C-atoms of acetyl C=O), 163.8 (s, C-7), 159.7 (s, C-2), 158.1 (s, C-9), 142.7 (s, CH-C-3), 130.8 (s, C-5), 128.5 (s, CH=CH), 126.8-135.9 (s, aromatic 6C-atom), 117.9 (s, C-3), 115.0 (s, C-10), 108.7 (s, C-6), 103.4 (s, C-8), 101.7 (s, C-1′, anomeric C-atom), 75.4 (s, C-5′), 72.1 (s, C-2′), 71.7 (s, C-4′), 71.4 (s, C-3′), 66.4 (s, C-6′), 21.8 (s, C-atom, CH_3 of acetyl group).

3g: Yield 90%; $[\alpha]_D^{25}$ =-22.9 (*c* 0.1 in DMSO); Found: C, 55.52; H, 4.05. $C_{32}H_{28}Cl_2O_{13}$ requires C, 55.58; H, 4.08%; IR (KBr): 3054, 2368 (Ar-CH), 2858 (glucosidic-CH), 1766 (C=O of *O*-acetyl gps of glycone moiety), 1718 (C=O), 1461 (CH=CH), 1078 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.75 (d, 1H, CH), 7.27 (s, 2-H, CH), 7.23 (d, 1H, CH), 6.38-7.58 (m, 6H, Ar-H), 4.75-5.05 (m, 3H, 2′,3′,4′-H), 4.68 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 4.2), 4.47 (dd, 1H, 5′-H), 3.76-4.34 (m, 2H, 6′-H), 2.02, 1.98, 1.94, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): δ 176.6 (s, C-4, C=O), 171.0 (s, C-atoms of acetyl C=O), 163.7 (s, C-7), 159.4 (s, C-2), 158.5 (s, C-9), 143.1 (s, CH-C-3), 130.8 (s, C-5), 129.6 (s, CH=CH), 127.4-134.5 (s, aromatic 6C-atom), 119.1 (s, C-3), 116.4 (s, C-10), 109.4 (s, C-6), 104.5 (s, C-8), 101.7 (s, C-1′, anomeric C-atom), 74.7 (s, C-5′), 72.1 (s, C-2′), 71.2 (s, C-4′), 71.0 (s, C-3′), 66.0 (s, C-6′), 20.4 (s, C-atom, CH_3 of acetyl group).

3h: Yield 85%; $[\alpha]_D^{25}$ =-16 (*c* 0.1 in DMSO); Found: C, 57.54; H, 4.25; N, 2.13. $C_{32}H_{29}NO_{15}$ requires C, 57.57; H, 4.38; N, 2.10%; IR (KBr): 3045, 2360 (Ar-CH), 2852 (glucosidic-CH), 1764 (C=O of *O*-acetyl gps of glycone moiety), 1709 (C=O), 1467 (CH=CH), 1048 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.77 (d, 1H, CH), 7.29 (s, 2-H, CH), 7.19 (d, 1H, CH), 6.40-8.45 (m, 7H, Ar-H), 4.78-5.01 (m, 3H, 2′,3′,4′-H), 4.81 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 4.1), 4.40 (dd, 1H, 5′-H), 3.78-4.29 (m, 2H, 6′-H), 1.98, 1.97, 1.99, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): δ 174.7 (s, C-4, C=O), 170.0 (s, C-atoms of acetyl C=O), 163.7 (s, C-7), 158.7 (s, C-2), 157.4 (s, C-9), 142.9 (s, CH-C-3),, 130.8 (s, C-5), 129.3 (s, CH=CH), 121.5-149.4 (s, aromatic 6C-atom), 117.5 (s, C-3), 114.8 (s, C-10), 108.6 (s, C-6), 103.4 (s, C-8), 101.7 (s, C-1′, anomeric C-atom), 75.4 (s, C-5′), 72.1 (s, C-2′), 71.1 (s, C-4′), 70.8 (s, C-3′), 65.1 (s, C-6′), 21.8 (s, C-atom, CH_3 of acetyl group).

3i: Yield 88%; $[\alpha]_D^{25}$ =-19.5 (*c* 0.1 in DMSO); Found: C, 57.54; H, 4.25; N, 2.13. $C_{32}H_{29}NO_{15}$ requires C, 57.57; H, 4.38; N, 2.10%; IR (KBr): 3033, 2363 (Ar-CH), 2852 (glucosidic-CH), 1760 (C=O of *O*-acetyl gps of glycone moiety), 1715 (C=O), 1452 (CH=CH), 1088 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.69 (d, 1H, CH), 7.24 (s, 2-H, CH), 7.22 (d, 1H, CH), 6.40-8.30 (m, 7H, Ar-H), 4.80-5.05 (m, 3H, 2′,3′,4′-H), 4.77 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 4.2), 4.45 (dd, 1H, 5′-H), 3.78-4.29 (m, 2H, 6′-H), 2.00, 1.97, 1.96, 2.01 (s, 3H, OAc); ^{13}C NMR (DMSO-d_6): δ 176.1 (s, C-4, C=O), 170.0 (s, C-atoms of acetyl C=O), 164.4 (s, C-7), 158.7 (s, C-2), 157.4 (s, C-9), 143.2 (s, CH-C-3), 131.0 (s, C-5), 128.6 (s, CH=CH), 121.5-149.0 (s, aromatic 6C-atom), 119.4 (s, C-3), 116.4 (s, C-10), 109.5 (s, C-6), 103.4 (s, C-8), 102.5 (s, C-1′, anomeric C-atom), 75.2 (s, C-5′), 72.2 (s, C-2′), 71.1 (s, C-4′), 71.0 (s, C-3′), 65.4 (s, C-6′), 20.8 (s, C-atom, CH_3 of acetyl group).

General procedure for 7-*O*-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones 4a-i

The mixture of 2,3,4,6-tetra-*O*-acetyl-7-*O*-β-D-glucopyranosyloxy-3-(3-oxo-3-arylprop-1-enyl)-4*H*-chromen-4-ones (0.109 mmole), dry methanol (2 mL) and anhydrous zinc acetate (0.126 mmole) was refluxed for 7 hr. After cooled down at RT, it was filtered through cation exchanged resin; the solvent was removed under vacuum. The residue was purified by silica gel chromatography ($CHCl_3$, MeOH, 12:1 v/v) to get the brown coloured semisolid.

4a: Yield 95%; $[\alpha]_D^{25}$ =-10.3 (*c* 0.1 in DMSO); Found: C, 63.40; H, 4.84. $C_{24}H_{22}O_9$ requires C, 63.43; H, 4.88%; IR (KBr): 3412 (br, OH peak of carbohydrate residue), 2858 (glucosidic-CH), 2362

(Ar-CH), 1718 (C=O), 1652 (C=O, γ-pyrone), 1466 (CH=CH), 1072 (C-O-C), 683 cm^{-1} (benzene monosubstituted); ^1H NMR (DMSO-d_6): δ 7.73 (d, 1H, CH), 7.27 (s, 2-H, CH), 7.22 (d, 1H, CH), 6.40-7.57 (m, 8H, Ar-H), 5.77 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 7.2), 3.47-3.99 (m, 3H, 2′,3′,4′-H), 3.71 (dd, 1H, 5′-H), 3.49-3.87 (m, 2H, 6′-H); ^{13}C NMR (DMSO-d_6): δ 189.2 (s, C=O), 176.0 (s, C-4, C=O), 163.7 (s, C-7), 160.1 (s, C-2), 158.2 (s, C-9), 143.2 (s, CH-C-3), 130.7 (s, C-5), 129.7 (s, CH=CH), 127.0-133.8 (s, aromatic 6 C-atom), 118.1 (s, C-3), 116.3 (s, C-10), 109.5 (s, C-6), 104.7 (s, C-1′, anomeric C-atom), 104.5 (s, C-8), 81.1 (s, C-5′), 77.3 (s, C-3′), 75.7 (s, C-2′), 73.0 (s, C-4′), 66.4 (s, C-6′); EI-MS *m*/*z* (%) 454 (M^+, 21), 391 (100), 187 (28), 163 (39), 161 (22), 131 (34), 105 (45), 77 (43).

4b: Yield 96%; $[\alpha]_D^{25}$ =-14.1 (*c* 0.1 in DMSO); Found: C, 58.91; H, 4.40. $C_{24}H_{21}ClO_9$ requires C, 58.96; H, 4.33%; IR (KBr): 3425 (br, OH peak of carbohydrate residue), 2846 (glucosidic-CH), 2361 (Ar-CH), 1713 (C=O), 1677 (C=O, γ-pyrone), 1458 (CH=CH), 1089 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.75 (d, 1H, CH), 7.27 (s, 2-H, CH), 7.18 (d, 1H, CH), 6.39-7.60 (m, 7H, Ar-H), 5.75 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 7.15), 3.45-3.94 (m, 3H, 2′,3′,4′-H), 3.88 (dd, 1H, 5′-H), 3.44-3.91 (m, 2H, 6′-H); ^{13}C NMR (DMSO-d_6): δ 189.5 (s, C=O), 175.7 (s, C-4, C=O), 163.5 (s, C-7), 159.8 (s, C-2), 158.2 (s, C-9), 143.9 (s, CH-C-3), 130.4 (s, C-5), 129.3 (s, CH=CH), 128.0-134.9 (s, aromatic 6C-atom), 117.8 (s, C-3), 115.1 (s, C-10), 108.7 (s, C-6), 106.1 (s, C-1′, anomeric C-atom), 104.5 (s, C-8), 82.0 (s, C-5′), 77.0 (s, C-3′), 75.2 (s, C-2′), 73.1 (s, C-4′), 64.8 (s, C-6′); EI-MS *m*/*z* (%) 489 (M^+, 21), 326 (100), 187 (50), 165 (34), 163 (30), 161 (29), 139 (32).

4c: Yield 91%; $[\alpha]_D^{25}$ =-12.4 (*c* 0.1 in DMSO); Found: C, 54.01; H, 3.95. $C_{24}H_{21}BrO_9$ requires C, 54.05; H, 3.97%; IR (KBr): 3399 (br, OH peak of carbohydrate residue), 2844 (glucosidic-CH), 2364 (Ar-CH), 1729 (C=O), 1687 (C=O, γ-pyrone), 1461 (CH=CH), 1092 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.73 (d, 1H, CH), 7.29 (s, 2-H, CH), 7.26 (d, 1H, CH), 6.40-7.58 (m, 7H, Ar-H), 3.48-3.98 (3H, m, 2′,3′,4′-H), 5.68 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 7.1), 3.84 (dd, 1H, 5′-H), 3.50-3.86 (m, 2H, 6′-H); ^{13}C NMR (DMSO-d_6): δ 189.3 (s, C=O), 175.1 (s, C-4, C=O), 163.8 (s, C-7), 158.9 (s, C-2), 158.1 (s, C-9), 143.1 (s, CH-C-3), 130.8 (s, C-5), 129.7 (s, CH=CH), 123.0-132.5 (s, aromatic 6C-atom), 117.6 (s, C-3), 114.8 (s, C-10), 109.8 (s, C-6), 106.2 (s, C-1′, anomeric C-atom), 103.0 (s, C-8), 82.2 (s, C-5′), 77.0 (s, C-3′), 75.0 (s, C-2′), 73.1 (s, C-4′), 64.6 (s, C-6′); EI-MS *m*/*z* (%) 533 (M^+, 10), 371 (100), 208 (14), 187 (18), 183 (28), 163 (33), 161(20).

4d: Yield 92%; $[\alpha]_D^{25}$ = −14.7 (*c* 0.1 in DMSO); Found: C, 64.04; H, 5.04. $C_{25}H_{24}O_9$ requires C, 64.10; H, 5.16%; IR (KBr): 3425 (br, OH peak of carbohydrate residue), 2859 (glucosidic-CH), 2361 (Ar-CH), 1728 (C=O), 1645 (C=O, γ-pyrone), 1459 (CH=CH), 1090 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.68 (d, 1H, CH), 7.21 (s, 2-H, CH), 7.20 (d, 1H, CH), 6.40-7.60 (m, 7H, Ar-H), 5.68 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 7.0), 3.49-3.97 (m, 3H, 2′,3′,4′-H), 3.88 (dd, 1H, 5′-H), 3.59-3.89 (m, 2H, 6′-H), 2.29 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6): δ 189.8 (s, C=O), 174.7 (s, C-4, C=O), 163.6 (s, C-7), 159.6 (s, C-2), 158.2 (s, C-9), 142.7 (s, CH-C-3), 130.4 (s, C-5), 129.4 (s, CH=CH), 127.5-138.9 (s, aromatic 6C-atom), 118.0 (s, C-3), 115.1 (s, C-10), 108.8 (s, C-6), 104.9 (s, C-1′, anomeric C-atom), 104.3 (s, C-8), 81.1 (s, C-5′), 77.8 (s, C-3′), 75.0 (s, C-2′), 73.1 (s, C-4′), 66.0 (s, C-6′), 23.7 (s, C-atom, CH_3); EI-MS *m*/*z* (%) 468 (M^+, 14), 305 (100), 187 (32), 163 (35), 161 (39), 145 (24), 119 (20).

4e: Yield 91%; $[\alpha]_D^{25}$ = −9.4 (*c* 0.1 in DMSO); Found: C, 60.95; H, 4.90. $C_{25}H_{24}O_{10}$ requires C, 60.98; H, 4.99%; IR (KBr): 3420 (br, OH peak of carbohydrate residue), 2850 (glucosidic-CH), 2363 (Ar-CH), 1700 (C=O), 1634 (C=O, γ-pyrone), 1449 (CH=CH), 1093 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6): δ 7.73 (d, 1H, CH), 7.35 (s, 2-H, CH), 7.28 (d, 1H, CH), 6.41-7.59 (m, 7H, Ar-H), 5.75 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 7.16), 3.35-3.92 (m, 3H, 2′,3′,4′-H), 3.90 (dd, 1H, 5′-H), 3.45-3.84 (m, 2H, 6′-H), 3.79 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6): δ 189.4 (s, C=O), 176.1 (s, C-4, C=O), 163.8 (s, C-7), 158.9 (s, C-2), 158.2 (s, C-9), 143.6 (s, CH-C-3), 132.4 (s, C-5), 128.8 (s, CH=CH), 115.0-161.5 (s, aromatic 6C-atom), 117.6 (s, C-3), 115.0 (s, C-10), 109.8 (s, C-6), 104.8 (s, C-1′, anomeric C-atom), 103.2 (s, C-8), 81.4 (s, C-5′), 77.2 (s, C-3′), 75.2 (s, C-2′), 73.1 (s, C-4′), 64.8 (s, C-6′), 56.1 (s, C-atom, OCH_3); EI-MS *m*/*z* (%) 484 (M^+, 19), 321 (100), 163 (22), 161 (31), 135 (27).

4f: Yield 88%; $[\alpha]_D^{25}$ = −10.2 (*c* 0.1 in DMSO); Found: C, 55.04; H, 3.84. $C_{24}H_{20}Cl_2O_9$ requires C, 55.08; H, 3.85%; IR (KBr): 3421 (br, OH peak of carbohydrate residue), 2852 (glucosidic-CH), 2364 (Ar-CH), 1702 (C=O), 1649 (C=O, γ-pyrone), 1456 (CH=CH), 1073 cm^{-1} (C-O-C); ^1H NMR (DMSO-d_6):

δ 7.71 (d, 1H, CH), 7.28 (s, 2-H, CH), 7.26 (d, 1H, CH), 6.39-7.58 (m, 6H, Ar-H), 3.39-3.90 (m, 3H, 2′,3′,4′-H), 5.71 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 7.05), 3.79 (dd, 1H, 5′-H), 3.47-3.94 (m, 2H, 6′-H); ^{13}C NMR (DMSO-d_6): δ 188.5 (s, C=O), 175.8 (s, C-4, C=O), 164.1 (s, C-7), 159.6 (s, C-2), 158.1 (s, C-9), 143.0 (s, CH-C-3), 131.4 (s, C-5), 129.0 (s, CH=CH), 127.5-135.9 (s, aromatic 6C-atom), 117.9 (s, C-3), 115.1 (s, C-10), 108.4 (s, C-6), 104.0 (s, C-1′, anomeric C-atom), 103.4 (s, C-8), 81.2 (s, C-5′), 77.2 (s, C-3′), 75.3 (s, C-2′), 73.2 (s, C-4′), 64.7 (s, C-6′); EI-MS *m*/*z* (%) 523 (M^+, 24), 360 (100), 200 (44), 187 (37), 174 (29), 163 (31), 161 (41).

4g: Yield 93%; $[\alpha]_D^{25} = -11.5$ (*c* 0.1 in DMSO); Found: C, 55.04; H, 3.84. $C_{24}H_{20}Cl_2O_9$ requires C, 55.08; H, 3.85%; IR (KBr): 3406 (br, OH peak of carbohydrate residue), 2363 (Ar-CH), 2858 (glucosidic-CH), 1712 (C=O), 1650 (C=O, γ-pyrone), 1461 (CH=CH), 1072 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.69 (d, 1H, CH), 7.26 (s, 2-H, CH), 7.23 (d, 1H, CH), 6.41-7.61 (m, 6H, Ar-H), 5.71 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 7.05), 3.35-3.87 (m, 3H, 2′,3′,4′-H), 3.88 (dd, 1H, 5′-H), 3.59-3.89 (m, 2H, 6′-H); ^{13}C NMR (DMSO-d_6): δ 189.0 (s, C=O), 174.6 (s, C-4, C=O), 163.5 (s, C-7), 158.1 (s, C-2), 157.3 (s, C-9), 143.8 (s, CH-C-3), 130.6 (s, C-5), 129.3 (s, CH=CH), 126.5-134.0 (s, aromatic 6C-atom), 119.0 (s, C-3), 114.8 (s, C-10), 109.5 (s, C-6), 104.8 (s, C-1′, anomeric C-atom), 104.2 (s, C-8), 81.4 (s, C-5′), 77.1 (s, C-3′), 75.1 (s, C-2′), 73.2 (s, C-4′), 64.8 (s, C-6′).

4h: Yield 88%; $[\alpha]_D^{25} = -10.9$ (*c* 0.1 in DMSO); Found: C, 57.54; H, 4.25; N, 2.75. $C_{24}H_{21}NO_{11}$ requires C, 57.72; H, 4.24, N, 2.80%; IR (KBr): 3428 (br, OH peak of carbohydrate residue), 2852 (glucosidic-CH), 2361 (Ar-CH), 1712 (C=O), 1642 (C=O, γ-pyrone), 1448 (CH=CH), 1090 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.77 (d, 1H, CH), 7.47 (s, 2-H, CH), 7.27 (d, 1H, CH), 6.48-8.49 (m, 7H, Ar-H), 5.77 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 7.1), 3.38-3.99 (m, 3H, 2′,3′,4′-H), 3.89 (dd, 1H, 5′-H), 3.38-3.75 (m, 2H, 6′-H); ^{13}C NMR (DMSO-d_6): δ 189.5 (s, C=O), 174.8 (s, C-4, C=O), 163.8 (s, C-7), 158.6 (s, C-2), 158.0 (s, C-9), 143.1 (s, CH-C-3), 130.8 (s, C-5), 129.3 (s, CH=CH), 120.5-149.5 (s, aromatic 6C-atom), 118.0 (s, C-3), 116.4 (s, C-10), 109.6 (s, C-6), 106.0 (s, C-1′, anomeric C-atom), 104.1 (s, C-8), 82.1 (s, C-5′), 77.3 (s, C-3′), 75.2 (s, C-2′), 73.0 (s, C-4′), 64.8 (s, C-6; EI-MS *m*/*z* (%) 500 (M^+, 14), 337 (100), 187 (27), 176 (31), 163 (30), 161 (28), 150 (21).

4i: Yield 90%; $[\alpha]_D^{25}$ =-8.8 (*c* 0.1 in DMSO); Found: C, 57.54; H, 4.25; N, 2.75. $C_{24}H_{21}NO_{11}$ requires C, 57.72; H, 4.24, N, 2.80%; IR (KBr): 3455 (br, OH peak of carbohydrate residue), 2850 (glucosidic-CH), 2360 (Ar-CH), 1720 (C=O), 1653 (C=O, γ-pyrone), 1463 (CH=CH), 1099 cm^{-1} (C-O-C); ^{1}H NMR (DMSO-d_6): δ 7.74 (d, 1H, CH), 7.43 (s, 2-H, CH), 7.21 (d, 1H, CH), 6.40-8.20 (m, 7H, Ar-H), 5.69 (d, 1H, 1′-H, anomeric proton, $J_{1\text{-}2}$ = 7.2), 3.35-4.10 (m, 3H, 2′,3′,4′-H), 3.64 (dd, 1H, 5′-H), 3.45-3.85 (m, 2H, 6′-H); ^{13}C NMR (DMSO-d_6): δ 188.8 (s, C=O), 174.4 (s, C-4, C=O), 163.9 (s, C-7), 160.2 (s, C-2), 158.1 (s, C-9), 143.0 (s, CH-C-3), 131.0 (s, C-5), 129.6 (s, CH=CH), 121.2-148.9 (s, aromatic 6C-atom), 118.7 (s, C-3), 115.1 (s, C-10), 110.0 (s, C-6), 104.6 (s, C-1′, anomeric C-atom), 104.2 (s, C-8), 81.4 (s, C-5′), 77.0 (s, C-3′), 75.3 (s, C-2′), 73.4 (s, C-4′), 66.6 (s, C-6′).

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