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Phototransformations of some 3-alkoxy-6-chloro-2-{(*E*)-1′-methyl-2′-phenylvinyl}chromones: A study of type-II and triene bichromophoric system

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ABSTRACT

Irradiation of a methanolic solution of 3-alkoxy-6-chloro-2-{(*E*)-1′-methyl-2′-phenylvinyl}-4-oxo-4*H*-1-benzopyrans yielded 12*H*-benzo[a]xanthen-12-one, pyranopyrones, oxetanopyrananones and 7-chloro-3-methyl-2-phenyl-1,4-dioxa-cyclopenta-[b]naphthalene-9-one depending upon the structure of 3-alkoxy group (methoxy, benzyloxy, and allyloxy). The methyl group on the styryl moiety has been found to have a profound effect on the product formation due to the variation of energy gap between the π–π^* excited state of triene system as compared to the n–π^* state of the C=O group.

1. Introduction

3-Alkoxy-2-styrylchromones consist of two different photochemically active chromophores, i.e. a 6πe-triene system and a C=O group having γ-hydrogen. Intramolecular hydrogen abstractions by the excited carbonyl group occurring through the 1,4-biradical in 3-alkoxy-2-arylchromones are well established for the synthesis of various polycyclic and spirocyclic [1,2] products. These chromones consisted of 2-aryl groups, viz., furan [3], thiophene [4], phenyl [5,6] and a variety of alkoxy groups at 3-position. In these phototransformations, it is the n–π^* excited state of C=O which abstracts hydrogen from the γ-position to form the 1,4-biradical [7–9]. In few cases involving the 3-allyloxy groups, the isomerisation of the 1,4-biradical to 1,6-biradical is reported [10] giving rise to the entirely different products. On the other hand photocyclodehydrogenation of stilbenes [11] and their analogous 2-styrylchromones [12] is an extensively studied method for the formation of polycyclic aromatic compounds. In recent past, an attempt was made to study the triene and type-II system together in 3-alkoxy-2-styrylchromones [13] and the results reported showed products only arising by more facile H-abstractions. As a part of our continuing interest in the photochemistry of 3-alkoxychromones in the present article we report the detailed investigation on photolysis of 3-alkoxy-6-chloro-2-{(*E*)-1′-methyl-2′-phenylvinyl}chromones. In these substrates, the disposition of methyl group on styryl double bond can have steric influence as well as electronic effect by its electron releasing inductive effect on excitation energy of chromophores.

2. Results and discussion

The 3-alkoxy-6-chloro-2-{(*E*)-1′-methyl-2′-phenylvinyl}chromones **5–8** were synthesized by the condensation of 5-chloro-2-hydroxyacetophenone with α-methylcinnamaldehyde in the presence of $Ba(OH)_2$/EtOH, followed by reacting under AFO (50% H_2O_2/OH^-) conditions [14–16] and subsequent alkylation (Scheme 1) with suitable alkyl halide in the presence of dry acetone, freshly dried K_2CO_3 and n-$Bu_4N^+I^-$.

The photoirradiation of the chromones **5–8** for 2 h with Pyrex filtered UV light under N_2 atm. furnished products as shown in Scheme 2.

The photoproduct **9** was isolated in varied yields (6–10%) from photolysis of all chromones **5–8**. In the mass spectrum, the compound **9** showed the molecular ion at *m*/*z* 294 (100%) and the fragment peaks at 293 (M^+-1), 279 (M^+-CH_3) and 155 (rDA). IR spectrum showed the carbonyl absorption band at 1645 cm^{-1} indicating a highly delocalized system. ^1H NMR spectrum of **9** has much downfield peak at δ 9.95 (J = 9.0 Hz), which may be caused by the deshielding effect of carbonyl group [17] at C-12 and has been assigned to C_1–H. From the detailed ^1H NMR, ^{13}C NMR and elemental analysis, compound **9** was determined to be 10-chloro-6-methyl-12*H*-benzo[a]xanthen-12-one [12].

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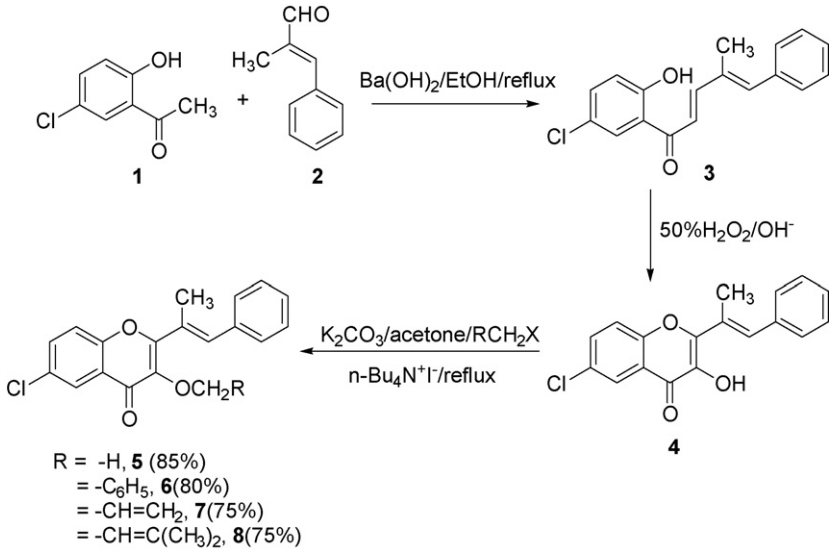
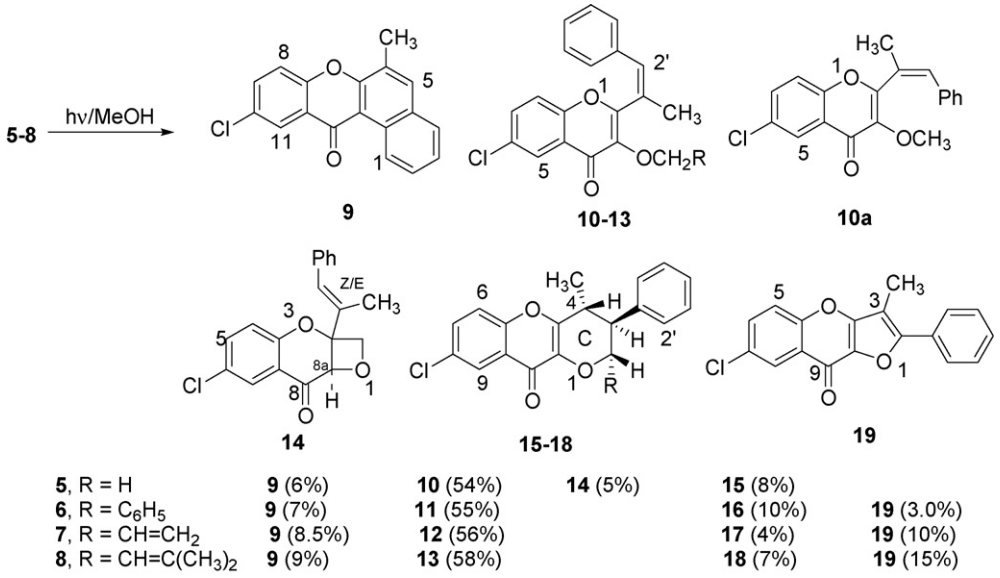


Scheme 1. Synthesis of benzopyrans **5**–**8**.



Scheme 2. Photolysis of benzopyrans **5**–**8**.

The photoproduct **10** is an isomer of **5** was established by *m*/*z* at 326 (M^+, 100), ^{1}H NMR shift pattern, ^{13}C NMR and the elemental analysis (Section 4). Further photolysis of pure **10** showed it to be a *Z*-isomer of **5** w.r.t 1′–2′ double bond. The compound **10** can have two conformations **10** and **10a**. A minimum energy calculation (Fig. 1) by the MM2 programme showed that **10** which has steric energy 4.37 kcal mol^{-1} is more stable than **10a** having the steric energy 41.72 kcal mol^{-1}.

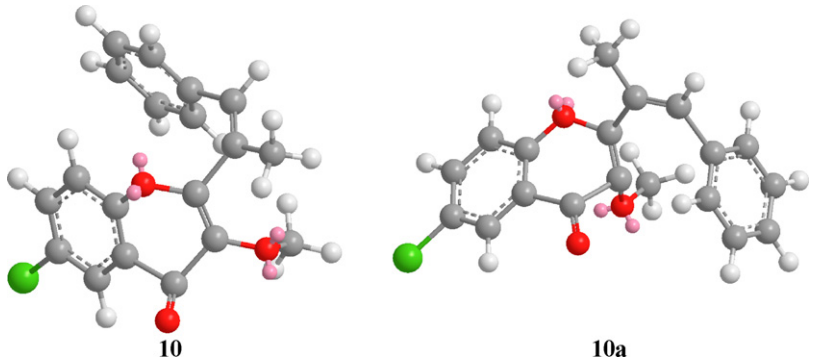


Fig. 1. MM2 Energy minimized 3D structures of compound **10** and **10a**.

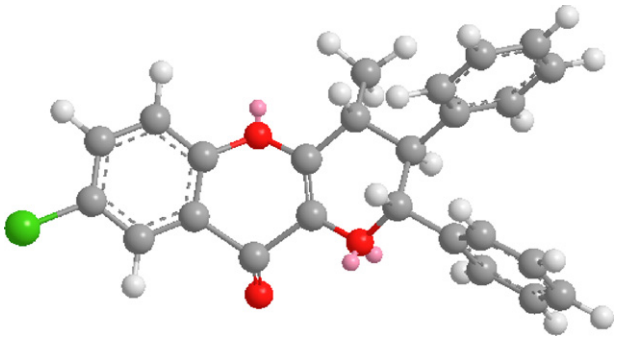


Fig. 2. MM2 Energy minimized 3D structure of compound **16**.

The other styryl chromones **6**, **7** and **8** behaved similarly and furnished products **11**, **12** and **13** (50–60%), respectively corresponding to product **10** with lower energy conformations similar to that of **10**.

The oxetane **14** (C=O, 1694 cm^{-1}) has the base peak at *m*/*z* 296 (M^+-30) in its mass spectrum, showing loss of CH_2O from the molecular ion at *m*/*z* 326 (58%). The ^1H NMR data has H-8a at δ 5.13 (d) and H-2a/H-2b at δ 5.01/4.90 ($J_{2a,2b}$ = 7.5 Hz) further confirming the presence of oxetane ring in **14**. The compound **14** was a mixture of *E*- and *Z*-isomers (1:1) w.r.t. styryl double bond as analyzed by the ^1H NMR shift pattern and the attempt to separate the isomers by column chromatography were unsuccessful.

The structures of the photoproducts **15–18** were established as linear tricyclic pyranopyrones corresponding to the chromones **5–8**, respectively by comparison with the similar photoproducts obtained in our earlier study [10]. In compound **16** the stereochemical disposition of two phenyl rings present at C-2 and C-3 was assumed to be *trans* and is confirmed by $J_{2,3}$ = 10.5 Hz. Such *J* values have also been observed [13] in our earlier studies on related compounds. The C-4 methyl group and C-3 phenyl were also *trans* to each other as indicated by $J_{4,3}$ = 10.5 Hz. An MM2 energy minimized structure [18] of compound **16** showed ring C in half chair conformation (Fig. 2) with $\Phi_{H2,H3}$ = 178° and $\Phi_{H3,H4}$ = 165° which are in accordance with observed coupling constants.

The stereochemical dispositions of the ring C in compounds **17** and **18** were also in agreement with compound **16**.

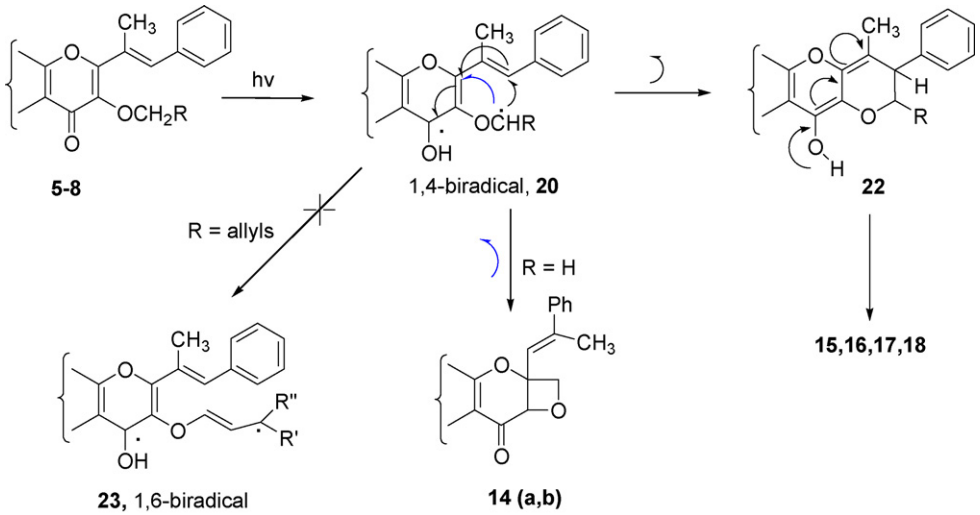
The compound **19** obtained from photoirradiation of **6** showed the carbonyl stretch at 1661 cm^{-1} in its IR spectrum and ^1H NMR spectra exhibited no signal in aliphatic region except for $-CH_3$ (δ 2.42, s). The mass spectrum showed the highest ion at *m*/*z* 310 (100%) and the presence of rDA fragment at 155 (15%) confirmed the presence of intact benzopyran moiety. The elemental analysis and the proton decoupled ^{13}C NMR assignments proved the structure to be the 7-chloro-3-methyl-2-phenyl-1,4-dioxacyclopenta[b]naphthalene-9-one. This product was also isolated from the photolysis of chromones **7** and **8**; no such product was obtained from compound **5**.

Regarding the mechanistic considerations, the formation of products **9–19** can be well envisaged to occur through the competitive photo-excitation of C=O and triene system. The substrates **5–8** consist of two photochemically active chromophores: the triene and the C=O group. The former can undergo π–π^* excitation whereas the later can undergo both π–π^* and n–π^* excitation. The n–π^* excited state of pyrone C=O group can undergo γ-H abstraction from the 3-alkoxy group thus producing a 1,4-biradical **20**. The products **15**, **16**, **17** and **18** are formed by the clipping of this alkoxy radical at the 2′-position of the styryl moiety followed by the 1,5-sigmatropic H-shift (Scheme 3).

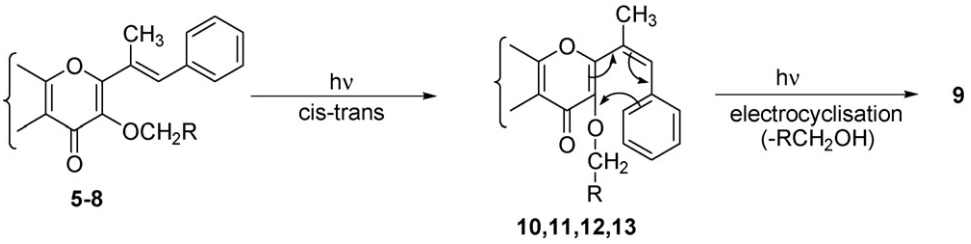
In case of **5** (R = H) the product corresponding to the cyclisation (oxetane **14)** of alkoxy radical at C-2 followed by ketonisation has also been observed. No such photoproduct has been isolated when R = Ph and allyls. The only assignable reason to this behaviour could be the steric factor which disfavours the cyclisation of the bulky benzyl/allyl radical at C-2.

The photolysis of allyloxy ethers **7** and **8** may offer an interesting situation. In addition to cyclisation, the allyloxy radical at C-2′ may also isomerise to a 1,6-biradical **23** [10]. The products corresponding to the isomerisation of the allyloxy radical were not formed in the present study. The reason to this may be the low concentration of radical formed by H-abstraction as the other pathways (*cis*–*trans* isomerisation, electrocyclisation) of reaction and the dealkylation to 3-hydroxy chromone gets preferred due to lowering of π–π^* excitation energy of triene system as compared to n–π^* transition of C=O group. The other aspect may be the fast union of allyloxy radical **20** to C-2′ position favoured by the greater stability of the enol **22** due to positive inductive effect of the methyl group present at the styryl double bond.

In addition to the products **14**–**18** obtained by type-II reactions, the compounds **5**–**8** also experienced isomerisation of the styryl (1′–2′) double bond to give products **10**–**13**, respectively as the major reaction. The isomerisation was a reversible process as found by the photolysis of pure *Z*-isomer (isolated from photolysis). The



Scheme 3. Mechanism of photoproduct formation through 1,4-biradical.



Scheme 4. Mechanism of the photoproduct formation through isomerisation and electrocyclisation.

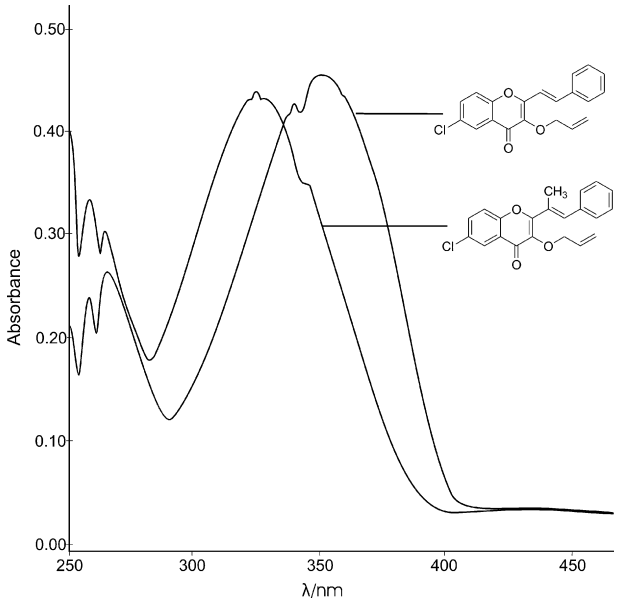


Fig. 3. UV absorption spectrum of compounds **7** and **21**.

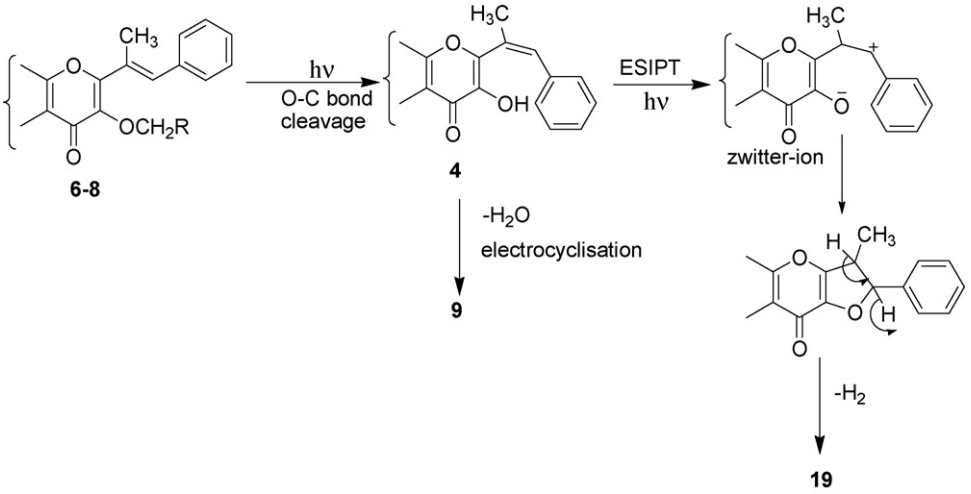
equilibrium of reaction was time dependent as observed by the ^{1}H NMR integral ratio at different time intervals and *Z*-isomer was the major product (>50%) after the reaction time of 2 h.

The other most important product was the tetra cyclic compound **9**, which was isolated during the photolysis of all the chromones **5–8**. The mechanism of formation of this compound must involve the conrotatory photocyclisation of the 6πe-triene system, which is favoured due to the lowering of π–π* transition energy of 6πe-triene system by the electron releasing inductive effect of the methyl group (Scheme 4).

A close look of the UV absorption spectrum (MeOH) of 3-allyloxy-6-chloro-2-{(*E*)-1′-methyl-2′-phenylvinyl}-4-oxo-4*H*-1-benzopyran **7** and 3-allyloxy-6-chloro-2-{(*E*)-2′-phenylvinyl}-4-oxo-4*H*-1-benzopyran [10] **21** clearly reveal the role of methyl group on photochemical transition energy (Fig. 3). In compound **7**, absorption band corresponding to n–π* (325 nm) excitation of C=O is higher in energy than that of **21** (352 nm). This change in energy of n–π* excitation makes the π–π* transition in **7** more preferable and hence favours the photoproduct formation corresponding to this transition.

Further it is important to mention here that photolysis of 3-allyloxy-6-chloro-2-{(*E*)-2′-phenylvinyl}-4-oxo-4*H*-1-benzopyran neither yield *Z*-isomer nor the product corresponding to **9**.

The formation of compound **19** involved the dealkylation of C_3-alkoxy group and the cyclisation to give five-membered furan ring. It was formed in the photolysis of the chromones **6**–**8** and the yield of cyclised product was in the order benzyl < allyl < 3-methylbut-2-enyl < hydrogen. Its formation is explained by the dealkylation of 3-alkoxy group followed by the excited state intramolecular proton transfer (ESIPT) from the 3-hydroxy group through the π–π* excited triene chromophore (Scheme 5). The ESIPT would lead to the formation of the zwitterionic intermediate which photocyclises to the five-membered ring followed by expulsion of H_2 leading to the creation of aromatic product. The dealkylation of **6**–**8** to produce the 3-hydroxy compound is favoured by the increased delocalization of alkoxy radical (benzyl < allyl < 3-methylbut-2-enyl) and hence the yield of compound



Scheme 5. Mechanism of photoproduct formation through dealkylation and excited state intramolecular proton transfer.

19 follows the same order. The presence of the intermediate **4** in the reaction was observed by the ^{1}H NMR data of the reaction mixture. The formation of **19** through the 3-hydroxy intermediate was established by the photolysis of pure **4** to give **19** and **9**. This mechanism finds further support from the formation of benzofuran derivatives by the cyclisation from *o*-allylphenols [19,20] and *o*-hydroxystyrenes [21–25] involving the ESIPT mechanism.

The quenching of C=O (n–π*) excitation in **5** by I_2 during photolysis rendered photoproducts **9** and **10** only, confirming the involvement of both chromophores (carbonyl and triene) in phototransformation and the formation of **9** and **10** through the π–π* excited state. Further it was also found that the photolysis of **10** provided the mixture of **5**, **9**, **10**, **14** and **15**; the ratio of **5** and **10** depended upon the irradiation time (vide ^{1}H NMR). The styryl chromones [10,13] without the methyl group on the styryl C=C, did not yield the products corresponding to **9**, **10** and **19**.

3. Conclusions

It may be concluded that due to the inclusion of the electron releasing methyl group on the triene system of 3-alkoxy-2-styrylchromes, the facile formation of the 1,4-biradical by photo-excitation of the C=O group is in competition with the 6πe-electrocyclisation and isomerisation of π–π* excited triene system. Though the 3-alkoxy-2-styrylchromones [10] are known to yield pyranopyrones, oxetanopyrananones and pyranoalcohols but to our best knowledge this is the first case where their photochemical reaction could lead to the formation of the substituted 1,4-dioxa-cyclopenta[b]naphthalene-9-one.

4. Experimental

Melting points were taken in the open capillaries and are uncorrected. IR spectra were recorded in KBr pellets on a Buck Scientific spectrometer. ^{1}H NMR and proton decoupled ^{13}C NMR spectra were taken on 300 MHz (for ^{13}C frequency is 75.5 MHz) Brucker spectrometer in $CDCl_3$ solvent using TMS as the internal standard. Mass spectra recorded are either EI or FAB$^+$. TLC plates were coated with the silica gel G (suspended in $CHCl_3$–MeOH) and iodine vapours were used as the visualizing agent. Columns were packed in silica gel (100–200 mesh) in pet ether–benzene (9:1) and left overnight before use. The elution was carried out with increasing proportion of benzene in pet ether–benzene mixture. All photochemical reactions were conducted under a nitrogen (99.9%) atmosphere. Any trace of oxygen and moisture from the procured nitrogen was removed by passing it through alkaline pyragallol solution and concentrated sulphuric acid, respectively. The percentage yields reported in the photochemical reactions are calculated by excluding the recovered starting substrates.

4.1. Synthesis of chromones *5*–*8*

4.1.1. 1-(5′-Chloro-2′-hydroxyphenyl)-4-methyl-5-phenyl-penta-2,4-dien-1-one, *3*

A solution of 5-chloro-2-hydroxyacetophenone (17 g, 0.1 mol) and α-methylcinnamaldehyde (14.6 g, 0.1 mol) in ethanol and dehydrated S-200 barium hydroxide [26] (20 g) was refluxed on water bath for 20 min. The resulting mixture was cooled and poured into ice-HCl to give compound **3** (23.8 g, 79%) as yellow solid, crystallized from ethanol, m.p. 96–98 °C; ν_{max} (cm^{-1}) 1630 (C=O), 3315 (OH); δ_H ($CDCl_3$) 12.83 (1H, s, 2′-O*H*), 7.83 (1H, d, J_m = 2.7 Hz, H-6′), 7.78 (1H, d, $J_{3,2}$ = 15.0 Hz, H-3), 7.44 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-4′), 7.42–7.30 (5H, m, H-2″–6″), 7.09 (1H, d, $J_{2,3}$ = 15.0 Hz, H-2), 7.06 (1H, t, J_{allyl} = 0.9 Hz, H-5), 6.98 (1H, d, J_o = 9.0 Hz, H-3′), 2.21 (3H, d, J_{allyl} = 0.9 Hz, 4-C*H*$_3$).

4.1.2. 6-Chloro-3-hydroxy-2-{(*E*)-1′-methyl-2′-phenylvinyl}-4-oxo-4H-1-benzopyran, *4*

To a solution of **3** (2.98 g, 0.01 mol) in MeOH was mixed powdered NaOH (1.4 g, 0.35 mol) at 0 °C. To this dark red solution was added H_2O_2 (50%) drop wise till the colour changes to yellow. This reaction mixture was then warmed to 40 °C for 10 min and poured into ice-HCl to give light yellow precipitates which were crystallized ($CHCl_3$–EtOH) to give greenish yellow needles (1.31 g, 42%), m.p. 138–140 °C; ν_{max} (cm^{-1}) 1612 (C=O), 3308 (OH); δ_H ($CDCl_3$) 8.20 (1H, d, J_m = 2.4 Hz, H-5), 7.70 (1H, t, J_{allyl} = 0.9 Hz, H-2′), 7.62 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.50 (1H, d, J_o = 9.0 Hz, H-8), 7.46–7.30 (5H, m, H-2″, 3″, 4″, 5″, 6″), 6.90 (1H, s, 3-O*H*), 2.38 (3H, d, J_{allyl} = 0.9 Hz, 1′-C*H*$_3$).

4.1.3. 6-Chloro-3-methoxy-2-{(*E*)-1′-methyl-2′-phenylvinyl}-4-oxo-4H-1-benzopyran, *5*

Compound **4** (3.12 g, 0.01 mol), K_2CO_3 (2.76 g) and CH_3I (1.5 g, 0.01 mol) were refluxed in dry acetone for 3 h with 50 mg of tetra-n-butylammonium iodide (n-$Bu_4N^+I^-$) till the colour changes from red to colourless. The subsequent decomposition in ice-HCl followed by the filtration and the recrystallization in methanol provided ether **5** (2.71 g, 85%) as colourless crystals, R_f 0.62 (3% ethyl acetate in benzene); m.p. 90–92 °C; [Found: C, 69.84; H, 4.63. $C_{19}H_{15}ClO_3$ requires C, 69.62; H, 4.67]; λ_{max} MeOH 345, 324, 262 nm; ν_{max} (cm^{-1}) 1655 (C=O), 1609 (C=C); δ_H ($CDCl_3$) 8.23 (1H, d, J_m = 2.7 Hz, H-5), 7.62 (1H, dd, $J_{m,o}$ = 2.4, 9.0 Hz, H-7), 7.47 (1H, d, J_o = 9.0 Hz, H-8), 7.46-7.36 (6H, m, H-2′, 2″–6″), 3.95 (3H, s, 3-OC*H*$_3$), 2.35 (3H, d, J_{allyl} = 1.2 Hz, 1′-C*H*$_3$); δ_C ($CDCl_3$) 173.90, 159.19, 153.33, 141.27, 139.32, 136.24, 136.20, 133.55, 130.53, 129.49, 128.42, 128.12, 128.00, 125.08, 119.65, 60.37, 16.17; *m*/*z* 326 (M$^+$, 100%).

The chromones **6**–**8** were synthesized from compound **4** using benzyl chloride, allyl bromide and 3-methylbut-2-enylbromide by the procedure used for the compound **5**.

4.1.4. 3-Benzyloxy-6-chloro-2-{(*E*)-1′-methyl-2′-phenylvinyl}-4-oxo-4H-1-benzopyran, *6*

Colourless crystals (3.2 g, 80%), R_f 0.63 (3% ethyl acetate in benzene); m.p. 72–74 °C; [Found: C, 74.43; H, 4.71. $C_{25}H_{19}ClO_3$ requires C, 74.53; H, 4.75]; λ_{max} MeOH 342, 322, 258 nm; ν_{max} (cm^{-1}) 1632 (C=O), 1609 (C=C); δ_H ($CDCl_3$) 8.17 (1H, d, J_m = 2.4 Hz, H-5), 7.53 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.38 (1H, d, J_o = 9.0 Hz, H-8), 7.36–7.21 (11H, m, H-2′, 2″–6″, 2‴–6‴), 5.12 (2H, s, 3-OCH_2–), 2.05 (3H, d, J_{allyl} = 1.2 Hz, 1′-C*H*$_3$); δ_C ($CDCl_3$) 173.96, 160.39, 153.33, 142.15, 139.25, 136.89, 136.60, 136.15, 133.55, 130.56, 129.43, 129.13, 128.35, 128.34, 128.26, 127.93, 127.82, 125.07, 119.71, 74.24, 16.07; *m*/*z* 402 (M$^+$, 100%).

4.1.5. 3-Allyloxy-6-chloro-2-{(*E*)-1′-methyl-2′-phenylvinyl}-4-oxo-4H-1-benzopyran, *7*

Colourless crystals (2.65 g, 75%), R_f 0.61 (3% ethyl acetate in benzene); m.p. 62–63 °C; [Found: C, 71.33; H, 4.85. $C_{21}H_{17}ClO_3$ requires C, 71.49; H, 4.86]; λ_{max} MeOH 345, 325, 261 nm; ν_{max} (cm^{-1}) 1644 (C=O), 1611 (C=C); δ_H ($CDCl_3$) 8.22 (1H, d, J_m = 2.4 Hz, H-5), 7.62 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.49–7.33 (7H, m, H-8, H-2′, 2″–6″), 6.07 (1H, tdd, $J_{2‴,1‴}$ = 6.0 Hz, $J_{2‴,3‴a}$ = 17.4 Hz, $J_{2‴,3‴b}$ = 10.5 Hz, H-2‴), 5.35 (1H, dd, J_{allyl} = 0.9 Hz, $J_{3‴a,2‴}$ = 17.4 Hz, H-3‴a), 5.24 (1H, d, $J_{3‴b,2‴}$ = 10.5 Hz, H-3‴b), 4.68 (2H, dd, J_{allyl} = 0.9 Hz, $J_{1‴,2‴}$ = 6.0 Hz, H-1‴), 2.34 (d, J_{allyl} = 0.9 Hz, 1′-C*H*$_3$); δ_C ($CDCl_3$) 173.90, 159.79, 153.31, 139.63, 136.67, 136.23, 133.51, 130.53, 129.44, 128.42, 128.02, 127.97, 125.08, 125.08, 125.05, 119.65, 118.62, 73.46, 16.29; *m*/*z* 352 (M$^+$, 100%).

4.1.6. 6-Chloro-3-(3‴-methyl)but-2-enyloxy-2-{(E)-1′-methyl-2′-phenylvinyl}-4-oxo-4H-1-benzopyran, ***8***

Colourless crystals (2.85 g, 75%), R_f 0.60 (3% ethyl acetate in benzene); m.p. 38–39 °C; [Found: C, 71.30; H, 4.88. $C_{23}H_{21}ClO_3$ requires C, 72.53; H, 5.56]; λ_{max} MeOH 346, 324, 260 nm; ν_{max} (cm^{-1}) 1641 (C=O), 1611 (C=C); δ_H ($CDCl_3$) 8.22 (1H, d, J_m = 2.4 Hz, H-5), 7.62 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.49–7.33 (7H, m, H-8, H-2′, H-2″–6″), 5.37 (1H, tt, J_{allyl} = 1.5 Hz, $J_{2‴,1‴}$ = 6.6 Hz, H-2‴), 4.49 (2H, d, $J_{1‴,2‴}$ = 6.6 Hz, H-1‴), 2.30 (3H, d, J_{allyl} = 1.5 Hz, 1′-CH_3), 1.69 (3H, s, H-4‴), 1.66 (3H, s, 3‴-CH_3); δ_C ($CDCl_3$) 174.15, 159.92, 153.33, 139.76, 139.42, 136.46, 136.31, 133.47, 130.46, 129.44, 128.39, 128.23, 127.92, 125.06, 125.02, 119.89, 119.67, 68.91, 25.86, 18.05, 16.28; *m*/*z* 380 (M^+, 100%).

4.2. Photoirradiation of chromones ***5–8***

4.2.1. Photolysis of 6-Chloro-3-methoxy-2-{(E)-1′-methyl-2′-phenylvinyl}-4-oxo-4H-1-benzopyran, ***5***

A deoxygenated solution of **5** (350 mg) in magnesium dried MeOH (200 ml) was irradiated in a Pyrex glass reactor under N_2 atm. with 125 W Hg vapour lamp for 2 h. The yellow-red gummy mass obtained after the evaporation of solvent under reduced pressure was chromatographed over column of silica gel yielding compounds **9**, **14**, **10** and **15** in order of their decreasing R_f values (elution with benzene–pet ether).

Compound **9**. Creamy solid (6%), R_f 0.84 (3% ethyl acetate in benzene); m.p. 140–142 °C; [Found: C, 73.21; H, 3.72. $C_{18}H_{11}ClO_2$ requires C, 73.35; H, 3.76]; ν_{max} (cm^{-1}) 1645 (C=O); δ_H ($CDCl_3$) 9.95 (1H, d, J_o = 9.0 Hz, H-1), 8.36 (1H, d, J_m = 2.7 Hz, H-11), 7.94 (1H, s, H-5), 7.75 (1H, dd, $J_{m,o}$ = 2.1 Hz, 8.1 Hz, H-4), 7.67 (1H, dt, $J_{m,o}$ = 2.1 Hz, 8.1 Hz, H-2), 7.62 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-9), 7.53 (1H, dt, $J_{m,o}$ = 2.1 Hz, 8.1 Hz, H-3), 7.51 (1H, d, J_o = 9.0 Hz, H-8), 2.62 (3H, s, 6-CH_3); δ_C ($CDCl_3$) 177.44, 156.77, 152.79, 146.05, 136.51, 133.92, 130.14, 129.93, 128.74, 127.58, 126.68, 126.54, 126.29, 125.96, 125.96, 124.21, 119.30, 16.77; *m*/*z* 294 (M^+, 100%).

Compound **10**. Colourless crystals (54%), R_f 0.68 (3% ethyl acetate in benzene); m.p. 120–122 °C; [Found: C, 69.71; H, 4.62. $C_{19}H_{15}ClO_3$ requires C, 69.84; H, 4.63]; ν_{max} (cm^{-1}) 1651 (C=O), 1604 (C=C); δ_H ($CDCl_3$) 8.21 (1H, d, J_m = 2.7 Hz, H-5), 7.57 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-7), 7.28 (1H, d, J_o = 9.0 Hz, H-8), 7.23–7.11 (5H, m, H-2″–6″), 6.82 (1H, t, J_{allyl} = 1.5 Hz, H-2′), 3.64 (3H, s, 3-OCH_3), 2.28 (3H, d, J_{allyl} = 1.5 Hz, 1′-CH_3); δ_C ($CDCl_3$) 173.48, 158.61, 153.74, 140.78, 136.24, 134.55, 133.52, 130.67, 128.38, 127.98, 127.80, 127.46, 125.52, 125.09, 119.78, 60.02, 22.96; *m*/*z* 326 (M^+, 100%).

Compound **14**. Creamy semisolid (5%), R_f 0.75 (3% ethyl acetate in benzene); ν_{max} (cm^{-1}) 1694 (C=O), 1604 (C=C); δ_H ($CDCl_3$), *E-isomer* 7.85 (1H, d, J_m = 2.7 Hz, H-7), 7.46 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-5), 6.99 (1H, d, J_o = 9.0 Hz, H-4), 6.75 (1H, t, J_{allyl} = 1.5 Hz, H-2′), 7.35–7.17 (5H, m, H-2″–6″), 5.13 (1H, d, $J_{8a,2b}$ = 0.6 Hz, H-8a), 5.01 (1H, d, $J_{2a,2b}$ = 7.5 Hz, H-2a), 4.90 (1H, dd, $J_{2b,8a}$ = 0.6 Hz, $J_{2b,2a}$ = 7.5 Hz, H-2b), 1.98 (3H, d, J_{allyl} = 1.5 Hz, 1′-CH_3); δ_H ($CDCl_3$), *Z-isomer* 7.78 (1H, d, J_m = 2.7 Hz, H-7), 7.47 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-5), 7.03 (1H, d, J_o = 9.0 Hz, H-4), 6.69 (1H, t, J_{allyl} = 1.2 Hz, H-2′), 7.02–7.35 (5H, m, H-2″–6″), 4.77 (1H, d, $J_{8a,2b}$ = 0.6 Hz, H-8a), 4.47 (1H, d, $J_{2a,2b}$ = 8.1 Hz, H-2a), 4.51 (1H, dd, $J_{2b,2a}$ = 8.1 Hz, $J_{2b,8a}$ = 0.6 Hz, H-2b), 1.98 (3H, d, J_{allyl} = 1.2 Hz, 1′-CH_3); *m*/*z* 326 (M^+, 57.7%), 296 (M^+−30, 100%).

Compound **15**. Creamy solid (8%), R_f 0.45 (3% ethyl acetate in benzene); m.p. 149–150 °C; [Found: C, 69.82; H, 4.59. $C_{19}H_{15}ClO_3$ requires C, 69.84; H, 4.63]; ν_{max} (cm^{-1}) 1657 (C=O); δ_H ($CDCl_3$) 8.20 (1H, d, J_m = 2.4 Hz, H-9), 7.51 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.34 (1H, d, J_o = 9.0 Hz, H-6), 7.30–7.15 (5H, m, H-2′–6′), 4.30 (1H, dd, $J_{2a,3}$ = 3.9 Hz, $J_{2a,2b}$ = 11.1 Hz, H-2a), 3.97 (1H, t, $J_{2b,3}$ = 10.6 Hz, $J_{2b,2a}$ = 11.1 Hz, H-2b), 3.15 (1H, qd, $J_{4,3}$ = 10.2 Hz, J_{vic} = 6.9 Hz, H-4), 2.92 (1H, dt/ddd, $J_{3,2a}$ = 3.9 Hz, $J_{3,2b}$ = 10.6 Hz, $J_{3,4}$ = 10.2 Hz, H-3), 1.26 (3H, d, J_{vic} = 6.9 Hz, 4-CH_3); δ_C ($CDCl_3$) 169.83, 152.51, 152.04, 137.51, 136.41, 132.30, 129.26, 128.10, 127.79, 126.78, 124.28, 123.27, 118.48, 68.92, 45.75, 35.52, 14.62; *m*/*z* 326 (M^+, 100%), 155 (25%).

4.2.2. Photolysis of 3-benzyloxy-6-chloro-2-{(E)-1′-methyl-2′-phenylvinyl}-4-oxo-4H-1-benzopyran, ***6***

A methanolic solution of **6** (350 mg) on photoirradiation for 2 h furnished **9** (7%), **11**, **16** and **19**.

Compound **11**. Light yellow solid (55%); R_f 0.68 (3% ethyl acetate in benzene); m.p. 52–54 °C; [Found: C, 74.49; H, 4.77. $C_{25}H_{19}ClO_3$ requires C, 74.53; H, 4.75]; ν_{max} (cm^{-1}) 1643 (C=O), 1608 (C=C); δ_H ($CDCl_3$) 8.14 (1H, d, J_m = 2.7 Hz, H-5), 7.45 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.22 (1H, d, J_o = 9.0 Hz, H-8), 7.36–6.88 (10H, m, H-2″–6″, 2‴–6‴), 6.65 (1H, t, J_{allyl} = 1.2 Hz, H-2′) 4.89 (2H, s, 3-OCH_2–), 2.09 (3H, d, J_{allyl} = 1.2 Hz, 1′-CH_3); δ_C ($CDCl_3$) 173.59, 159.11, 153.74, 139.57, 139.28, 136.99, 136.22, 134.59, 133.53, 130.69, 128.57, 128.31, 128.07, 127.94, 127.62, 127.33, 125.47, 125.00, 119.73, 73.58, 23.00; *m*/*z* 402 (M^+, 100%).

Compound **16**. Yellow solid (10%); R_f 0.47 (3% ethyl acetate in benzene); m.p. 175–177 °C; [Found: C, 74.35; H, 4.68. $C_{25}H_{19}ClO_3$ requires C, 74.53; H, 4.75]; ν_{max} (cm^{-1}) 1647 (C=O); δ_H ($CDCl_3$) 8.21 (1H, d, J_m = 2.7 Hz, H-9), 7.52 (1H, dd, $J_{m,o}$ = 2.7 Hz, 9.0 Hz, H-7), 7.36 (1H, d, J_o = 9.0 Hz, H-6), 7.15–6.89 (10H, m, H-2′–6′, 2″–6″), 4.90 (1H, d, $J_{2,3}$ = 10.5 Hz, H-2), 3.37 (1H, qd, J_{vic} = 6.6, $J_{4,3}$ = 10.2 Hz, H-4), 2.92 (1H, t, $J_{3,2}$ = 10.5 Hz, $J_{3,4}$ = 10.2 Hz, H-3), 1.23 (3H, d, J_{vic} = 6.6 Hz, 4-CH_3); δ_C ($CDCl_3$) 170.23, 153.06, 152.85, 138.30, 138.07, 137.28, 132.87, 129.85, 128.27, 128.04, 127.64, 127.53, 127.05, 126.87, 125.02, 124.10, 119.05, 82.40, 53.91, 37.20, 15.01; *m*/*z* 402 (M^+, 100%).

Compound **19**. Colourless crystalline solid (3%); R_f 0.55 (3% ethyl acetate in benzene); m.p. 165–167 °C; [Found: C, 69.44; H, 3.59. $C_{18}H_{11}ClO_3$ requires C, 69.58; H, 3.57]; ν_{max} (cm^{-1}) 1659 (C=O); δ_H ($CDCl_3$) 8.34 (1H, d, J_m = 2.4 Hz, H-8), 7.57 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-6), 7.49 (1H, d, J_o = 9.0 Hz, H-5), 7.82 (2H, dd, $J_{m,o}$ = 1.8 Hz, 8.4 Hz, H-2′, 6′), 7.39–7.45 (3H, m, H-3′, 4′, 5′) 2.42 (3H, s, 3-CH_3); δ_C ($CDCl_3$) 173.10, 163.80, 155.42, 155.33, 154.07, 134.86, 132.94, 130.49, 129.80, 129.56, 128.90, 126.95, 126.06, 119.56, 107.74, 7.96; *m*/*z* 310 (M^+, 100%).

4.2.3. Photolysis of 3-allyloxy-6-chloro-2-{(E)-1′-methyl-2′-phenylvinyl}-4-oxo-4H-1-benzopyran, ***7***

A methanolic solution of 7 (350 mg) on photoirradiation for 2 h furnished **9** (8.5%), **12**, **17** and **19** (10%).

Compound **12**. Light yellow solid (56%), R_f 0.66 (3% ethyl acetate in benzene); m.p. 48–52 °C; [Found: C, 71.42; H, 4.89. $C_{21}H_{17}ClO_3$ requires C, 71.49; H, 4.86]; ν_{max} (cm^{-1}) 1643 (C=O), 1608 (C=C); δ_H ($CDCl_3$) 8.20 (1H, d, J_m = 2.4 Hz, H-5), 7.55 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.25 (1H, d, J_o = 9.0 Hz, H-8), 7.48-7.11 (5H, m, H-2″–6″), 6.79 (1H, t, J_{allyl} = 0.6 Hz, H-2′), 5.92 (1H, tdd, $J_{2‴,1‴}$ = 6.0 Hz, $J_{2‴,3‴a}$ = 17.1 Hz, $J_{2‴,3‴b}$ = 10.2 Hz, H-2‴), 5.23 (1H, dd, J_{allyl} = 0.9 Hz, $J_{3‴a,2‴}$ = 17.1 Hz, H-3‴a), 5.13 (1H, d, $J_{3‴b,2‴}$ = 10.2 Hz, H-3‴b), 4.43 (2H, dd, J_{allyl} = 0.9 Hz, $J_{1‴,2‴}$ = 6.0 Hz, H-1‴), 2.29 (3H, d, J_{allyl} = 0.6 Hz, 1′-CH_3); *m*/*z* 352 (M^+, 100%).

Compound **17**. Yellow solid (4%); R_f 0.49 (3% ethyl acetate in benzene); m.p. 124–126 °C; [Found: C, 71.27; H, 4.81. $C_{21}H_{17}ClO_3$ requires C, 71.49; H, 4.86]; ν_{max} (cm^{-1}) 1646 (C=O); δ_H ($CDCl_3$) 8.18 (1H, d, J_m = 2.4 Hz, H-9), 7.50 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.32 (1H, d, J_o = 9.0 Hz, H-6), 7.28–7.08 (5H, m, H-2′–6′), 4.42 (1H, dd, $J_{2,1″}$ = 6.6 Hz, $J_{2,3}$ = 10.5 Hz, H-2), 3.19 (1H, qd, J_{vic} = 6.6 Hz, $J_{4,3}$ = 10.5 Hz, H-4), 2.65 (1H, t/dd, $J_{3,2}$ = 10.5 Hz, $J_{3,4}$ = 10.5 Hz, H-3), 5.56 (1H, ddd, $J_{1″,2}$ = 6.6 Hz, $J_{1″,2″b}$ = 10.5 Hz, $J_{1″,2″a}$ = 17.1 Hz, H-1″), 5.18 (1H, d, $J_{2″a,1″}$ = 17.1 Hz, H-2″a), 5.02 (1H, d, $J_{2″b,1″}$ = 10.5 Hz, H-2″b), 1.18 (3H, d, J_{vic} = 6.6 Hz, 4-CH_3); δ_C ($CDCl_3$) 174.52, 153.41, 153.19, 138.84, 138.09, 134.12, 133.23, 130.21, 129.00, 128.47, 127.61, 125.30, 120.45, 120.05, 119.48, 119.29, 80.42, 52.57, 37.60, 15.27; *m*/*z* 352 (M^+, 100%).

4.2.4. Photolysis of 6-Chloro-3-(3‴-methyl)but-2-enyloxy-2-{(E)-1′-methyl-2′-phenylvinyl}-4-oxo-4H-1-benzopyran, ***8***

A methanolic solution of **8** (1.0 g) on photoirradiation for 2 h gave **9** (9%), **13**, **18** and **19** (15%).

Compound **13**. Light yellow solid (58%); R_f 0.62 (3% ethyl acetate in benzene); m.p. 54–56 °C; [Found: C, 71.49; H, 4.86. $C_{23}H_{21}ClO_3$ requires C, 72.53; H, 5.56]; ν_{max} (cm^{-1}) 1631 (C=O), 1608 (C=C); δ_H ($CDCl_3$) 8.22 (1H, d, J_m = 2.4 Hz, H-5), 7.54 (1H, dd, $J_{m,o}$ = 2.4 Hz, 9.0 Hz, H-7), 7.50–7.00 (6H, m, H-8, 2″–6″), 6.77 (1H, t, J_{allyl} = 1.5 Hz, H-2′), 5.37 (1H, t, $J_{2‴,1‴}$ = 6.6 Hz, H-2‴), 4.49 (1H, d, $J_{1‴,2‴}$ = 6.6 Hz, H-1‴), 2.30 (3H, d, J_{allyl} = 1.5 Hz, 1′-CH_3), 1.69 (3H, s, H-4‴), 1.66 (3H, s, 3‴-CH_3); δ_C ($CDCl_3$) 174.26, 159.48, 154.1, 140.36, 139.59, 136.70, 134.77, 133.94, 132.10, 131.08, 128.80, 128.57, 128.33, 128.14, 125.53, 120.70, 120.24, 69.06, 26.27, 23.57, 18.49; *m*/*z* 380 (M^+, 100%).

Compound **18**. Yellow solid (50 mg, 7%); R_f 0.46 (3% ethyl acetate in benzene); m.p. 119–121 °C; [Found: C, 71.20; H, 4.79. $C_{23}H_{21}ClO_3$ requires C, 72.53; H, 5.56]; ν_{max} (cm^{-1}) 1646 (C=O); δ_H ($CDCl_3$) 8.20 (1H, d, J_m = 2.4 Hz, H-9), 7.49 (1H, dd, $J_{m,o}$ = 2.4 Hz, 8.7 Hz, H-7), 7.33 (1H, d, J_o = 8.7 Hz, H-6), 7.29–7.01 (5H, m, H-2′–6′), 5.08 (1H, d, $J_{1″,2}$ = 9.3 Hz, H-1″), 4.65 (1H, dd, $J_{2,1″}$ = 9.3 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 3.21 (1H, qd, J_{vic} = 6.9 Hz, $J_{4,3}$ = 10.2 Hz, H-4), 2.66 (1H, t/dd, $J_{3,4}$ = 10.2 Hz, $J_{3,2}$ = 10.2 Hz, H-3), 1.45 (3H, s, H-3″), 1.32 (3H, s, 2″-CH_3), 1.18 (3H, d, J_{vic} = 6.6 Hz, 4-CH_3); δ_C ($CDCl_3$) 173.40, 153.25, 152.90, 138.80, 138.25, 132.75, 128.25, 128.12, 126.92, 125.01, 130.10, 127.50, 122.10, 121.51, 119.03, 81.05, 52.00, 37.20, 25.50, 18.00, 15.09; *m*/*z* 380 (M^+, 100).

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