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# Phototransformation of 3-alkoxychromenones: Regioselective photocyclisation and Dealkoxylation

Radhika Khanna, Aarti Dalal, Ramesh Kumar and Ramesh C Kamboj*

Department of Chemistry, Kurukshetra University, Kurukshetra-136119, Haryana

## Abstract:

Phototransformation of some 2-(3-methoxyphenyl)-4*H*-chromen-4-ones bearing propynyloxy moiety at 3-position has been described. These chromenones on photolysis by the pyrex filtered UV-light from Hg-lamp (125W) produced a major amount of 5-ethynyl-2-methoxy-6-oxa-benzo[5,6-*c*]xanthen-7-ones consisting of an exotic tetracyclic scaffold. These photoproducts have been envisioned to be produced through the regioselective ring closure at 6'-position of the 2-(3'-methoxy)phenyl moiety of the initially formed 1,4-biradical via γ-H abstraction mechanism. No product, whatsoever, was observed through ring closure at 2'-position. This behaviour has been found to be in accordance with directive influence observed in free radical aromatic substitutions. This regioselective photocyclisation was further supported by the calculations made from 3D-structures (MM2 programme). In addition, during the irradiation of these substrates, 2-(3-methoxyphenyl)-4*H*-chromen-4-ones through dealkoxylation were also realised. The structures of the substrates and photoproduct(s) have been determined by their spectroscopic (IR, NMR, Mass) studies.

**Keywords:** Chromenones, irradiation, Xanthenones, H-abstraction.

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*Corresponding author. Tel. :+91-9466650266; Fax :+91-1744-238277

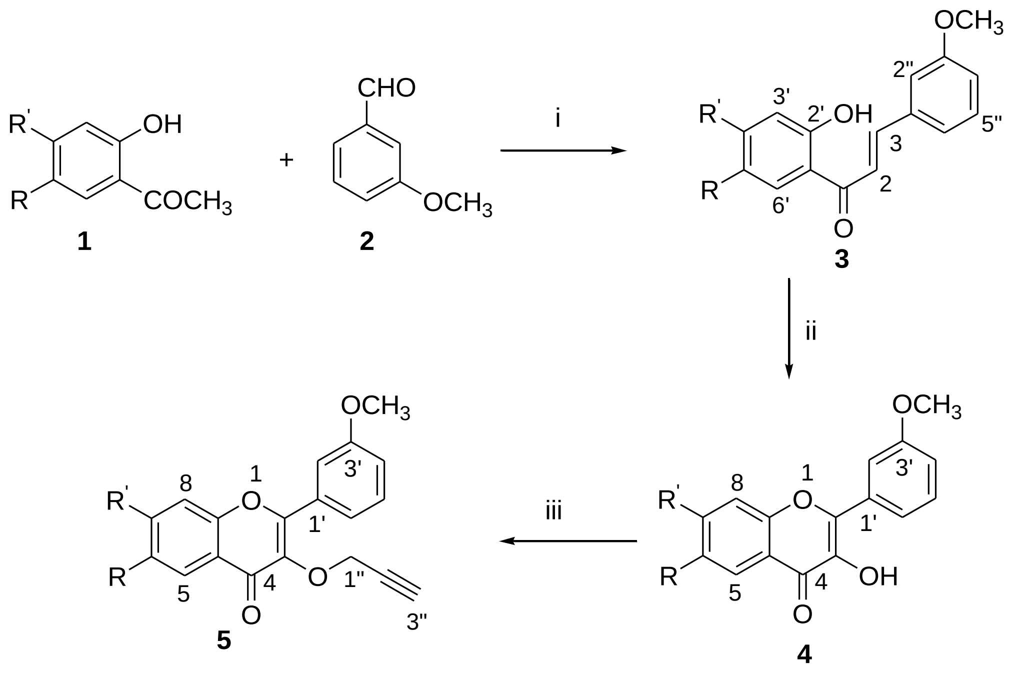
Email : rckamboj@hotmail.com (R. C. Kamboj)

## Introduction:

The photochemical intramolecular H-abstractions in the carbonyl compounds have elicited several synthetic applications [1-11] including the synthesis of numerous exotic carbocyclics and heterocyclic scaffolds which are otherwise very difficult to obtain under thermal conditions. The exceptional behaviour of propargyl 1,4-biradical to form photoproducts via unsaturated carbene [12-13] have been investigated by Agosta and Margaretha [14] which has intrigued us to study the photochemistry of chromenones containing propargyl group [15-17]. In these studies, it was observed that the propynyloxy group behaved in many ways i.e. as a suitable candidate for H-abstraction followed by ring closure, in tandem electrocyclisation and rearrangement, and in intramolecular Paterno-Buchi cyclisation. In most of these reactions, xanthenones are the main photoproducts. Xanthenones are secondary metabolites occurring in higher plants, fungi and lichens [18] and utilized as leuco-dyes, pH-sensitive fluorescent materials for tracking biomolecules and in laser technologies [19-22]. The reactive chromene core in xanthenones moiety is responsible for wide range of biological activities ranging from anti-cancer, anti-viral, diuretic, spasmolytic, anti-coagulant, anti-anaphylactic to cognitive enhancers for the treatment of neuro-degenerative impairments including Parkinson's disease, Alzheimer's disease, Down's syndrome, AIDS-assisted dementia and schizophrenia [23-29]. In view of these and our continuous effort on the photochemistry of such molecules, in the present communication, we wish to report the results of our investigations on the photolysis of some 4*H*-chromen-4-ones bearing the propynyloxy moiety at 3-position and 3-methoxyphenyl moiety at 2-position with the motive to determine the regioselective photocylisation and other reactions as elicited earlier in other similar molecules [15-17, 30-32].

## Results and discussion:

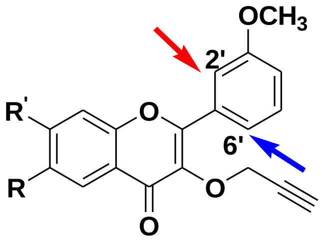
The chromenones, 2-(3-methoxyphenyl)-3-(prop-2-ynyloxy)-4*H*-chromen-4-ones **5** consisting of an acetylenic pendant, were synthesized by (i) condensing the acetophenones **1** with 3-methoxybenzaldehyde **2** in the presence of NaOH/EtOH (ii) followed by the cyclisation of chalcones **3** to 3-hydroxychromenones **4** under the Algar-Flynn-Oyamada [33-34] reaction conditions and (iii) subsequent alkylation of the latter with propargyl bromide in the presence of dry acetone, freshly dried $K_2CO_3$ and tetra-*n*-butyl ammonium iodide (Scheme 1). The structures of the compounds **3**, **4** and **5** [30] were confirmed by their spectroscopic data (*vide* experimental).



i) NaOH/EtOH, stirring ii) KOH/$H_2O_2$ (30%) iii) Propargyl bromide/$K_2CO_3$/dry acetone/ $n$-$Bu_4N^+I^-$

**Scheme 1:** Synthesis of 2-(3-methoxyphenyl)-3-(prop-2-ynyloxy)-4*H*-chromen-4-ones **5**.

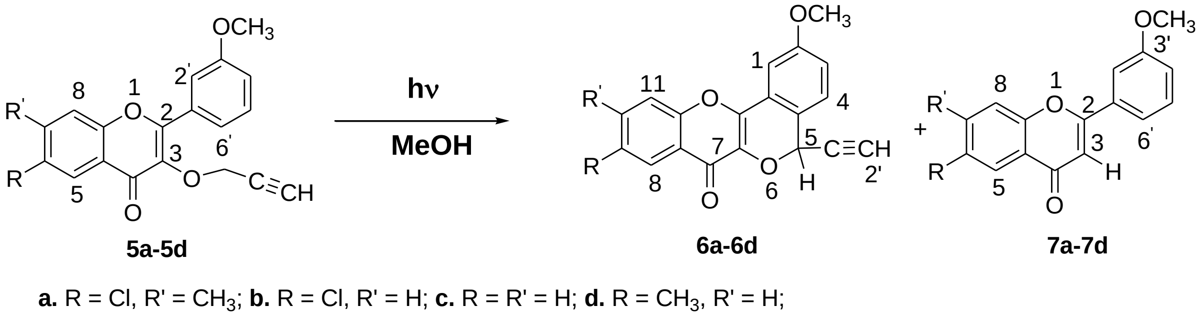
These chromenones **5** (the absorption maxima, $\lambda_{max,}$ between 350-357 nm in MeOH) were tailored and designed with the objectives; (i) to illustrate regioselectivity because these have the propensity of cyclisation at the two possible sites i.e. 2'- and 6'-position of the methoxyphenyl moiety and (ii) to observe the effect of propynyloxy group on the photoproduct formation in comparison to other functionalities [31].



**5**

**" ⟶", the possible sites for photocyclistion with -O-<u>C</u>$H_2$-**

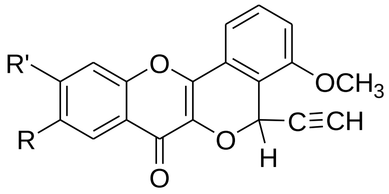
An irradiation of **5 (a-d)** in methanol with pyrex filtered light from 125W Hg UV lamp under $N_2$ atmosphere, furnished two new compounds **6(a-d)** and **7(a-d)** in each case as indicated by the thin layer chromatographic examination of their reaction mixtures (Scheme 2). The removal of solvent under reduced pressure and chromatographic separation of photolysate with increasing proportion of ethylacetate in ethylacetate-petroleum ether yielded the xanthenones **6** (35-45%) and the dealkoxylated chromenones **7** **(**20-24%) as the photoproducts approximately in the ratio of 2:1, respectively. The product composition remained same when benzene was used as the solvent instead of methanol. The structures of these photoproducts were obtained by their spectroscopic studies. In the NMR spectrum of product **6**, a doublet was observed at δ 8.3-7.9 ($J_m$ = 2.4 Hz) for the proton H-8. The proton H-11 resonated between δ7.4-7.5 (d, $J_o$ = 8.8 Hz) and the proton H-10 as in **6b-6d** was observed between 7.7-7.6 (dd, $J_o$ = 8.8 Hz and $J_m$ = 2.4 Hz). The acetylenic proton gave the signal nearly at δ 2.4 (d, $J_m$ = 2.4 Hz) which showed allylic coupling with H-5 proton which resonated as a doublet at around δ 6.4 ($J_m$ = 2.4 Hz). Rest of the protons i.e. H-1, H-3 and H-4 were observed at δ 7.5-7.4 (d, $J_m$ = 1.6 Hz), 7.0 (dd, $J_o$ = 7.6 Hz and $J_m$ = 1.6 Hz) and 7.48 (d, $J_o$ = 7.6 Hz) respectively. This splitting and coupling pattern of the H-1, H-3 and H-4 is in agreement with the proposed structure i.e. **6(a-d)** not with the structures **8(a-d).** The structure of the dealkoxylated product **7** formed was confirmed by comparing its NMR spectrum with the substrate **5** where the former showed the presence of singlet at 6.8 for H-3 and disappearance of doublet at δ 5.0 and 2.3 (*vide* experimental) present in the $^1$H NMR spectrum of **5**.



**Scheme 2:** Conversion of **5** to **6** *via* photochemical transformation.

This structure of **6** was further confirmed by 2D-COSY of **6b** where it was clearly observed that H-8 was interacting with H-10 which was also correlating with H-11. And acetylenic proton was correlating with H-5. The interactions of H-3 with H-1 and H-4 were also observed.

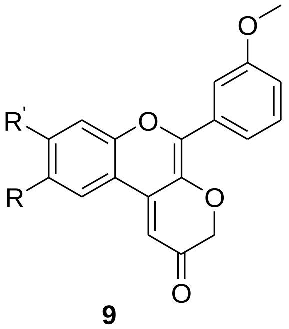
The perusal of the structures of the xanthenones **6(a-d)** obtained here showed that these have been produced through the regioselective cyclisation at 6'-position of the 2-(3'-methoxyphenyl) moiety. No photoproduct similar to **8** (Figure 1) through the regioselective cyclisation at 2'-position was realised which is having a fair probability as observed earlier with alkoxy group [30] other than the propargyloxy group. Also no dihydro product i.e. 5-ethynyl-4a,5-dihydro-4-methoxyisochromeno[4,3-b]chromen-7(2*H*)-one similar to **4** in [31] was realised.



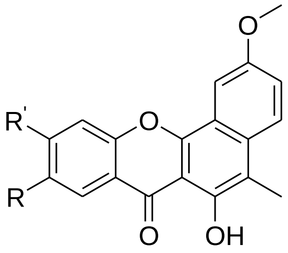
**8**

**Fig. 1**

The $^1$H NMR spectral analysis of the photolysate also indicated the formation of the trace amount of photoproducts pyranochromenones **9** ( singlet at δ 6.8 and doublet at δ 5.3) with no formation of xanthenones **10** similar to those obtained from the photolytic studies [15, 17, 34] on 3-(prop-2nyloxy)-2-(thiophen-3-yl)-4*H*-chromen-4-ones. But, these products being in trace amounts could not be isolated inspite of our best efforts. Even the change of solvent from methanol to benzene had no effect on the product formation and isolation.

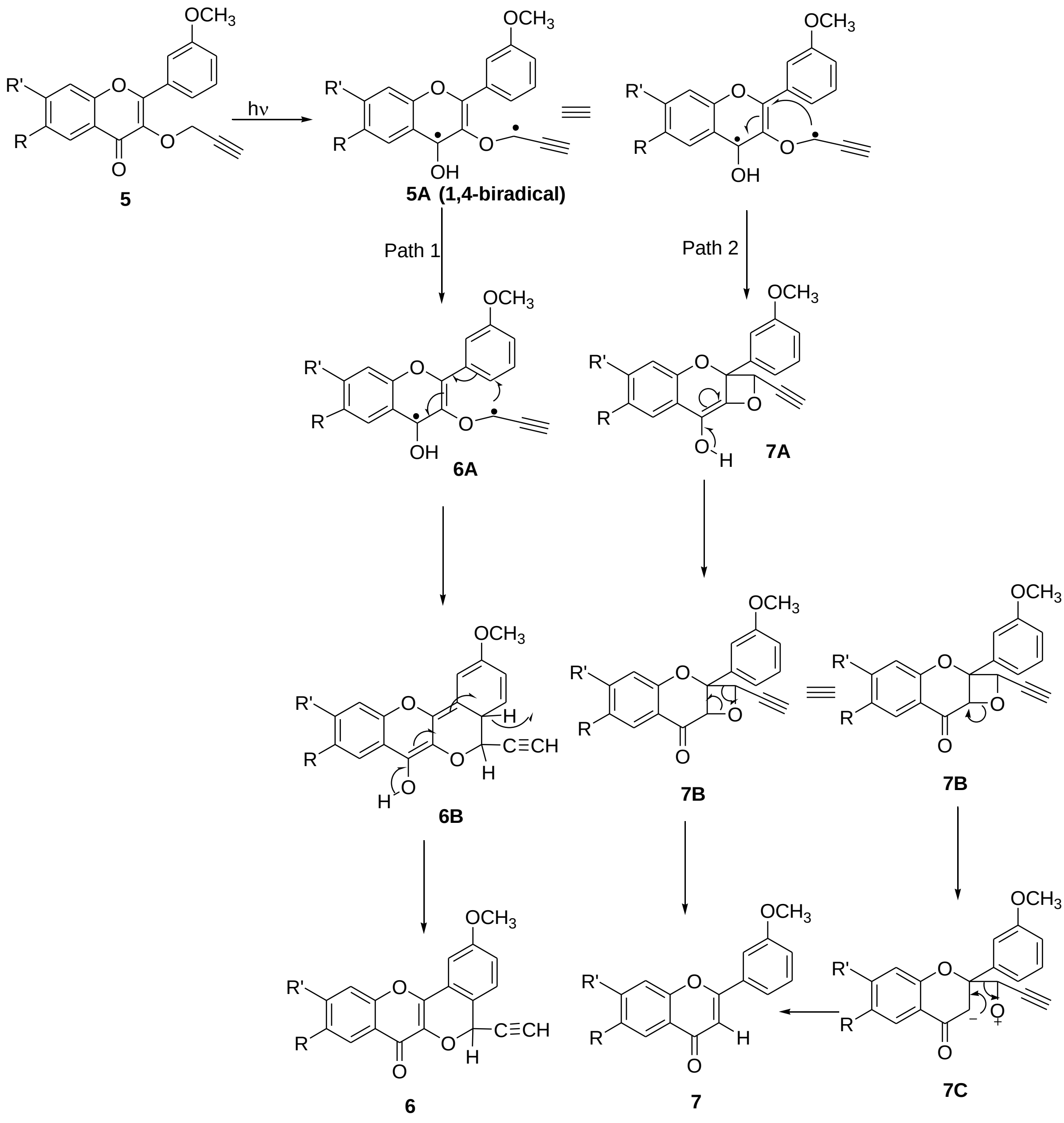


**9**



**10**

Though the mechanism of this reaction is not established yet but the formation of **6** (path 1) and **7** (path 2) from **5** can be envisioned (Scheme 3) to occur through the initial formation of 1,4-biradical via γ-H abstraction mechanism [30] followed by ring closure by coupling of **-O-ĊH-** radical with the 6'-position of the 2-(3'-methoxyphenyl) moiety regioselectively. The photoproduct **7** has been conceived to be formed through the formation of oxetane **7B** followed by its fragmentation (concerted or stepwise) as observed earlier [36] in photochemical cycloreversion of oxetane dyads. Further, the higher reactivity of oxetane **7B** formed *in situ* toward fragmentation may probably be related to its folded conformations (Figure 2) and also to the presence of the electron-donating methoxyphenyl chromophore and the electron-withdrawing carbonyl group in the chromenone moiety. The formation of **7** can also be through the heterolytic mechanism (Scheme 4) involving the formation of alkoxide plus a chromenone cation **7D** which would be like a 2-oxocyclohexadienyl carbene **7E** being part of the pyrrilium ring system [37]. A ring oxygen in 3-position would certainly support its formation as would a carbonyl oxygen next to it.



**Scheme 3:** Suggested mechanism of products (**6** & **7**) formation from 2-(3-methoxyphenyl)-3-(prop-2-ynyloxy)-4*H*-chromen-4-ones **5** by photolysis.

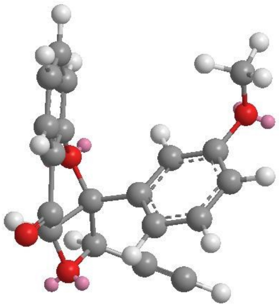
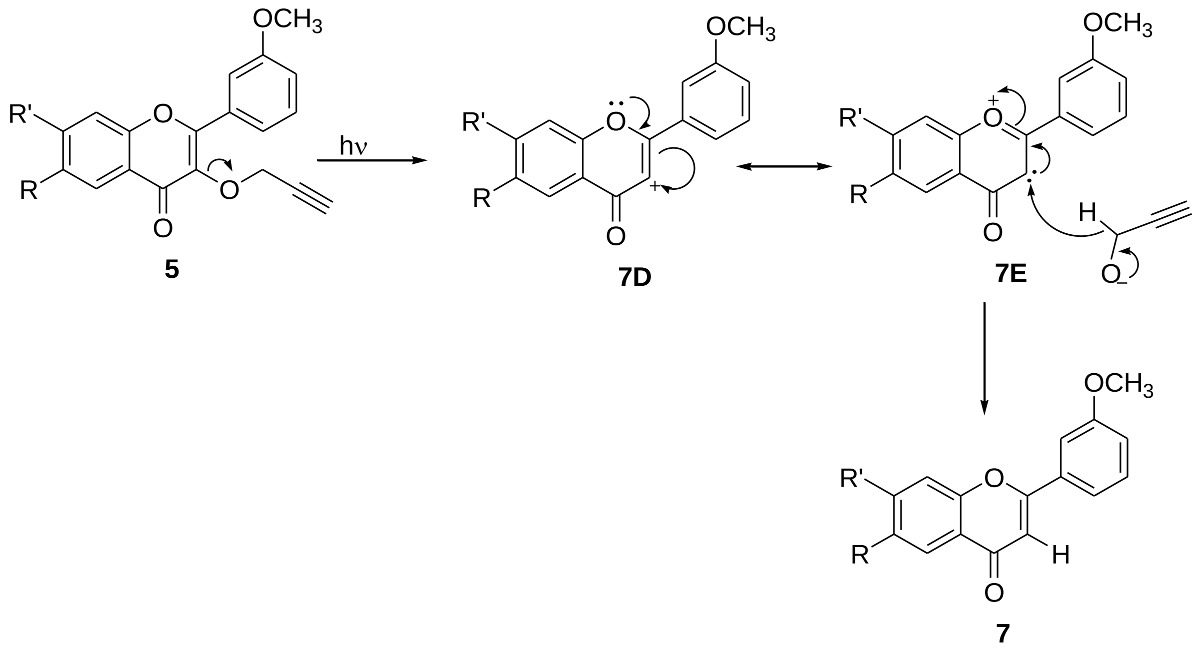


**Fig. 2:** MM2 energy minimized 3D-structure of tentative Oxetane **7B** - A Folded conformation (a representative case)



**Scheme 4:** Alternate plausible mechanism of formation of **7**

This photocyclisation is in accordance [38] with directive influence observed in free radical aromatic substitution (*o*- and *p*-directing). In this case, regioselectivity for ring formation exclusively at 6'-position (*p*- to methoxy and *o*- to the chromenyl group) with no ring formation at 2'-position has been observed which can explained by the steric hindrance experienced at 2'-position from methoxy and chromenyl groups tethered to the phenyl moiety at the 3'- and 1'-positions respectively. This regioselectivity for photocyclisation was further substantiated by the proximity effect as revealed by the calculations made from 3D-structures (MM2 programme) for the substrates **5**. The -O-$\underline{C}H_2$- and the 6'-position (the two clipping atoms for ring formation) have been observed in close proximity as close contact averaged at

3.263 Å which is quite shorter than the close contact (average 4.924Å) between -O-<u>C</u>$H_2$- and the 2'-position of the methoxyphenyl ring at 2-position (Figure 3).

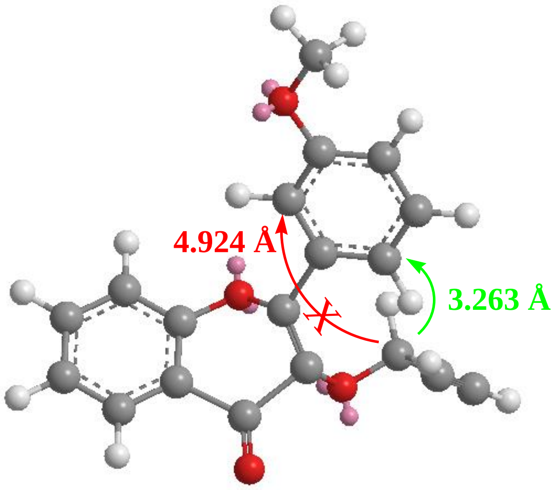


**Fig. 3:** MM2 energy minimized 3D-structure of compound 5.

## Conclusion:

It may be concluded that 2-(3-methoxyphenyl)-3-(prop-2-ynyloxy)-4-*H*-chromen-4-ones on phototransformation yielded tetracyclic product(s) 5-ethynyl-2-methoxy-6-oxa-benzo[5,6-*c*]xanthen-7-ones through γ-H abstraction followed by the regioselective cyclisation at 6-position that has been found to be controlled by the steric influence. Further, these angular tetracyclics, the benzoxanthenones have been produced by the environmentally benign green method without using any specific and toxic reagent. And also the solvents used in the study for purification and other purposes have been recovered substantially and reused.

## Experimental:

### General

Melting points recorded are uncorrected and taken in open capillaries. IR spectra were recorded on a Perkin-Elmer IR spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ on a 300 MHz/400MHz Bruker spectrometer using TMS as an internal standard. Mass spectra were recorded on LC-MS Spectrometer Model Q-ToF Micro Waters source in $ES^+$ mode. The columns for purification were packed with Silica gel 100-200 mesh in petroleum ether/ethyl acetate (9:1) and left overnight before use. The elution was carried out with increasing proportions of ethyl acetate in the petroleum ether-ethylacetate mixture. The yields reported are based on the amount of isolated photoproducts and are calculated by excluding the recovered substrates. The solvents used in the study for purification and other purposes have been recovered.

**Synthesis of 1-(2-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-ones (3a-3d):**

To the well-stirred suspension of powdered NaOH (0.1mol) in EtOH at 0 $^{o}$C were added substituted 2-hydroxyacetophenone (0.05mol) and 3-methoxybenzaldehyde (0.055mol). The reaction mixture, which became deep red in color after 3h, was stirred further for 7-8h. Thereafter, it was poured over ice and was neutralized with dil. HCl to obtain acrylophenone that was crystallized from EtOH to give yellow needles as **3**.

**3a -** Orange solid in 77% yield, mp 91-94 $^{o}$C; $\nu_{max}$ (cm$^{-1}$): 3405 (-OH), 1645 (C=O); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 12.67 (1H, s, OH), 7.90 (1H, s, H-6'), 7.86 (1H, d, $J_{3,2}$ = 15.2 Hz, H-3), 7.51 (1H, d, $J_{2,3}$ = 15.2 Hz, H-2), 7.38 (1H, t, $J_o$ = 8.0 Hz, $J_o$ = 7.2 Hz, H-5''), 7.28 (1H, dd, $J_o$ = 8.0 Hz, $J_m$ = 2.0 Hz, H-6''), 7.17 (1H, d, $J_m$ = 2.0 Hz, H-2''), 7.01 (1H, td, $J_o$ = 8.0 Hz, $J_m$ = 2.0 Hz, H-4''), 6.91 (1H, s, H-3'), 3.88 (3H, s, $OCH_3$), 2.39 (3H, s, $CH_3$).

**3b** – Orange solid in 78% yield, mp 88-92 $^{o}$C; $\nu_{max}$ (cm$^{-1}$): 3415 (-OH), 1641 (C=O); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 12.76 (1H, s, OH), 7.96 (1H, d, $J_m$ = 2.8 Hz , H-6'), 7.84 (1H, d, $J_{3,2}$ = 15.2 Hz, H-3), 7.56 (1H, d, $J_{2,3}$ = 15.2 Hz, H-2), 7.52 (1H, d, $J_o$ = 6.8 Hz, $J_m$ = 2.8 Hz, H-4'), 7.32 (1H, dd, $J_o$ = 8.0 Hz, H-5''), 7.11 (1H, d, $J_m$ = 2.4 Hz, H-2''), 7.04 (2H, m, H-4'', 6'' ), 6.91 (1H, d, $J_o$ = 6.8 Hz, H-6'), 3.90 (3H, s, $OCH_3$).

**3c** – Orange solid in 75% yield, mp 78-81 $^{o}$C; $\nu_{max}$ (cm$^{-1}$): 3445 (-OH), 1643 (C=O); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 12.79 (1H, s, OH), 7.93 (1H, dd, $J_o$ = 6.8 Hz, $J_m$ = 2.8 Hz H-6'), 7.86 (1H, d, $J_{3,2}$ = 15.6 Hz, H-3), 7.65 (1H, d, $J_{2,3}$ = 15.6 Hz, H-2), 7.52 (1H, td, $J_o$ = 6.8 Hz, $J_m$ = 1.6 Hz, H-4'), 7.37 (1H, td, $J_o$ = 6.8 Hz, $J_m$ = 2.8 Hz, H-5'), 7.29 (1H, dd, $J_o$ = 8.0 Hz, H-5''), 7.17 (1H, d, $J_m$ = 1.6 Hz, H-2''), 7.04 (1H, td, $J_o$ = 8.0 Hz, $J_m$ = 2.4, H-6''), 7.00 (1H, td, $J_o$ = 8.0 Hz, $J_m$ = 2.4 and 1.6 Hz, H-4''), 6.92 (1H, dd, $J_o$ = 6.8 Hz, $J_m$ = 2.8 Hz, H-3'), 3.84 (3H, s, $OCH_3$).

**3d** – Orange solid in 71 % yield, mp 79-83 $^{o}$C; $\nu_{max}$ (cm$^{-1}$): 3405 (-OH), 1645 (C=O); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 12.76 (1H, s, OH), 7.93 (1H,d, $J_m$ = 2.8 Hz ,H-6'), 7.88 (1H, d, $J_{3,2}$ = 15.2 Hz, H-3), 7.56 (1H, d, $J_{2,3}$ = 15.2 Hz, H-2), 7.50 (1H, dd, $J_o$ = 8.4 Hz, $J_m$ = 2.8 Hz, H-4'), 7.41 (1H, dd, $J_o$ = 8.0 Hz, H-5''), 7.11 (1H, d, $J_m$ = 2.0 Hz, H-2''), 7.04 (2H, m, H- 4'', 6'' ), 6.90 (1H, d, $J_o$ = 8.4 Hz, H-3'), 3.90 (3H, s, $OCH_3$), 2.53 (3H, s, 5'-$CH_3$).

**Synthesis of 3-hydroxy-2(3-methoxyphenyl)-4*H*-chromen-4-ones (4a-4d):**

To the suspension of chalcone (0.01mol) in methanol was added 10.0 ml of 20% aq. KOH and this mixture was cooled to 0 $^oC$. To this dark red well stirred solution was added $H_2O_2$ (30%) drop-wise till the color changed to yellow and the stirring was continued for 1h. The reaction mixture was neutralized with ice-HCl to give light yellow precipitates. The solid was filtered, dried and crystallized ($CHCl_3$-MeOH) to give yellow crystals of 3-hydroxychromenones as **4**.

**4a** – cream solid in 72% yield, mp 112-116 $^oC$; $\boldsymbol{\nu}_{\mathbf{max}}$ ($cm^{-1}$): 3202 (-OH), 1610 (C=O); $^1H$ NMR [$CDCl_3$, δ (ppm), 400 MHz]: 8.20 (1H, s, H-5), 7.87 (1H, dd, $J_o$ = 7.2 Hz, H-5'), 6.96 (4H, m, H-8,2',4' and 6'), 3.80 (3H, s, $OCH_3$), 2.53 (3H, s, $CH_3$).

**4b** – cream solid in 76% yield, mp 108-110 $^oC$; $\boldsymbol{\nu}_{\mathbf{max}}$ ($cm^{-1}$): 3210 (-OH), 1605 (C=O); $^1H$ NMR [$CDCl_3$, δ (ppm), 400 MHz]: 8.02 (1H, d, $J_m$ = 1.6 Hz, H-5), 7.88 (1H, dd, $J_o$ = 8.4 Hz, $J_m$ = 1.6 Hz, H- 7), 7.74 (1H, dd, $J_o$ = 6.8 Hz, $J_m$ = 1.6 Hz, H-6'), 7.56 (1H, d, $J_o$ = 8.4 Hz, H-5'), 7.44 ( 2H, m, H-2' and 8), 7.10 (1H, td, $J_o$ = 8.4 Hz, $J_m$ = 1.6 Hz, H-4'), 3.90 (3H, s, $OCH_3$).

**4c** – cream solid in 71% yield, mp 101-103 $^oC$; $\boldsymbol{\nu}_{\mathbf{max}}$ ($cm^{-1}$): 3205 (-OH), 1615 (C=O); $^1H$ NMR [$CDCl_3$, δ (ppm), 400 MHz]: 8.27 (1H, dd, $J_o$ = 8.0 Hz, $J_m$ = 1.6 Hz, H-5), 7.73 (1H, td, $J_o$ = 6.8 Hz, $J_m$ = 1.6 Hz, H-6), 7.70 (1H, td, $J_o$ = 6.8 Hz, $J_m$ = 1.6 Hz, H-7), 7.68 (1H, d, $J_m$ = 1.6 Hz, H-2'), 7.56 (1H, dd, $J_o$ = 8.0 Hz, H-5'), 7.45 (1H, dd, $J_o$ = 8.8 Hz, $J_m$ = 2.8 Hz, H-8), 7.42 (1H, dd, $J_o$ = 6.8 Hz, $J_m$ = 1.6 Hz, H-6'), 7.08 (1H, td, $J_o$ = 8.0 Hz, $J_m$ = 1.6 Hz, H-4'), 3.90 (3H, s, $OCH_3$).

**4d** – cream solid in 69 % yield, mp 110-113 $^oC$; $\boldsymbol{\nu}_{\mathbf{max}}$ ($cm^{-1}$): 3232 (-OH), 1605 (C=O); $^1H$ NMR [$CDCl_3$, δ (ppm), 400 MHz]: 7.96 (1H, d $J_m$ = 2.0 Hz, H-5), 7.78 (1H, dd, $J_o$ = 8.4 Hz, $J_m$ = 2.0 Hz, H- 7), 7.74 (1H, dd, $J_o$ = 7.6 Hz, $J_m$ = 1.6 Hz, H-6'), 7.64 (1H, dd, $J_o$ = 7.6 Hz, and 8.4 Hz, H-5'), 7.51 ( 2H, m, H-2' and 8), 7.03 (1H, d, $J_o$ = 8.4 Hz, $J_m$ = 1.6 Hz, H-4'), 3.90 (3H, s, $OCH_3$), 2.54 (3H, s, $CH_3$).

**Synthesis of 2-(3-methoxyphenyl)-3-(prop-2-ynyloxy)-4*H*-chromen-4-ones (5a-5d):**

To a suspension of compound, **4** (0.001mol) and freshly dried $K_2CO_3$ (0.005mol) in dry acetone was added propargyl bromide (0.001mol) and tetra-*n*-butylammonium iodide (0.050g). The reaction mixture was refluxed for 4h and the color of the reaction mixture changed from reddish-orange to white. Filtration, evaporation of solvent and crystallization of the residue (MeOH) gave **5**.

**5a** –White solid in 72% yield, mp 101-104 °C; $\lambda_{max}$ (MeOH): 351 nm; $\boldsymbol{\nu}_{\mathbf{max}}$ (cm$^{-1}$): 2124 (C≡C), 1621 (C=O); $^1$H NMR [$CDCl_3$, δ (ppm), 400 MHz]: 8.20 (1H, s, H-5), 7.70 (1H, dd, $J_o$ = 8.4 Hz, $J_m$ = 1.6 Hz H-6'), 7.45 (1H, dd, $J_o$ = 8.4 Hz, H-5'), 7.07 (2H, m, H-2' and 4'), 6.98 (1H, s, H-8), 4.98 (2H, d, $J_{1'',3''}$ = 2.4 Hz, H-1''), 3.89 (3H, s, $OCH_3$), 2.52 (3H, s, $CH_3$), 2.37 (1H, t, $J_{3'',1''}$ = 2.4 Hz, H-3''); $^{13}$C NMR [$CDCl_3$, δ (ppm)]: 160.5, 154.3, 153.0, 142.7, 142.6, 131.5, 130.1, 126.4, 125.7, 123.3, 120.4, 119.7, 117.4, 114.4, 113.9, 107.4, 77.3, 61.9, 55.9, 20.8.

**5b** – White solid in 85% yield, mp 98-102 °C; $\lambda_{max}$ (MeOH): 343 nm; $\boldsymbol{\nu}_{\mathbf{max}}$ (cm$^{-1}$): 2128 (C≡C), 1615 (C=O); $^1$H NMR [$CDCl_3$, δ (ppm), 400 MHz]: 8.08 (1H, d, $J_m$ = 2.8 Hz, H-5), 7.70 (2H, m, H-7, 5'), 7.62 (1H, dd, $J_o$ = 8.8 Hz, H-6'), 7.32 (2H, m, H-2' and 8), 7.10 (1H, td, $J_o$ = 8.8 Hz, $J_m$ = 1.6 Hz, H-4'), 4.98 (2H, d, $J_{1'',3''}$ = 2.4 Hz, H-1''), 3.90 (3H, s, $OCH_3$), 2.35 (1H, t, $J_{3'',1''}$ = 2.4 Hz, H-3''); $^{13}$C NMR [$CDCl_3$, δ (ppm)]: 173.2, 158.4, 157.1, 141.6, 135.7, 127.9, 127.0, 125.3, 123.5, 122.0, 121.7, 119.6, 116.8, 116.2, 78.3, 58.1, 55.0.

**5c** – White solid in 74% yield, mp 110-112 °C; $\lambda_{max}$ (MeOH): 353 nm; $\boldsymbol{\nu}_{\mathbf{max}}$ (cm$^{-1}$): 2132 (C≡C), 1625 (C=O); $^1$H NMR [$CDCl_3$, δ (ppm), 400 MHz]: 8.28 (1H, dd, $J_o$ = 8.0 Hz, $J_m$ = 1.6 Hz, H-5), 7.73 (1H, td, $J_o$ = 8.0 Hz, $J_m$ = 1.6 Hz, H-6), 7.72 (1H, dd, $J_o$ = 8.4 Hz, $J_m$ = 1.6 Hz, H-6') 7.70 (1H, td, $J_o$ = 8.0 Hz, $J_m$ = 1.6 Hz, H-7), 7.61 (1H, dd, $J_o$ = 8.8 Hz, H-5'), 7.45 (2H, m, H-2' and 8), 7.08 (1H, td, $J_o$ = 8.0 Hz, $J_m$ = 1.6 Hz, H-4'), 5.00 (2H, d, $J_{1'',3''}$ = 2.4 Hz, H-1''), 3.90 (3H, s, $OCH_3$), 2.36 (1H, t, $J_{3'',1''}$ = 2.4 Hz, H-3''); $^{13}$C NMR [$CDCl_3$, δ (ppm)]:174.9, 159.4, 155.3, 133.6, 132.1, 129.9, 129.4, 125.8, 124.8, 124.0, 121.3, 118.0, 116.8, 114.2, 78.6, 59.2, 55.0.

**5d** – White solid in 73% yield, mp 91-94 °C; $\lambda_{max}$ (MeOH): 357 nm; $\boldsymbol{\nu}_{\mathbf{max}}$ (cm$^{-1}$): 2128 (C≡C), 1622 (C=O); $^1$H NMR [$CDCl_3$, δ (ppm), 400 MHz]: 8.27 (1H, d, $J_m$ = 2.4 Hz, H-5), 7.79 (1H, dd, $J_o$ = 8.4 Hz, $J_m$ = 2.4 Hz, H-7, ), 7.54 (1H, dd, $J_o$ = 8.1 Hz, H-5'), 7.32 (3H, m, H-2', 6' and 8), 7.01 (1H, dd, $J_o$ = 8.0 Hz, $J_m$ = 1.6 Hz, H-4'), 4.99 (2H, d, $J_{1'',3''}$ = 2.4 Hz, H-1''), 3.90 (3H, s, $OCH_3$), 2.43 (3H, s, $CH_3$), 2.33 (1H, t, $J_{3'',1''}$ = 2.4 Hz, H-3''); $^{13}$C NMR [$CDCl_3$, δ (ppm)]:169.7, 159.1, 158.1, 138.1, 133.6, 131.1, 129.9, 126.1, 124.0, 122.8, 121.1, 118.9, 115.8, 114.6, 76.6, 59.6 55.8, 20.4.

**Photolysis of 2-(3-methoxyphenyl)-3-(prop-2-ynyloxy)-4*H*-chromen-4-ones (5a-5d):**

A deoxygenated 1.0 mM methanolic solution of chromenone **5** contained in a pyrex glass vessel was purged with nitrogen for 30 min and then irradiated under nitrogen with light from a 125 W Hg vapor lamp for 45 min. The removal of solvent under reduced pressure yielded a gummy mass that was chromatographed over a column of silica gel. The column was eluted with increasing proportion of ethylacetate in ethylacetate-petroleum ether mixture yielding photoproducts **6** and **7**.

9-Chloro-5-ethynyl-2-methoxy-10-methyl-6-oxa-benzo[5,6-c]xanthen-7-one **6a** :

White solid in 37% yield, mp 202-204 $^{o}$C; $\boldsymbol{\nu}_{\mathbf{max}}$ (cm$^{-1}$): 2128 (C≡C), 1628 (C=O); $^{1}$H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 8.27 (1H, s, H-8), 7.48 (2H, m, H-1 and 11), 7.36 (1H, d, $J_o$ = 8.0 Hz, H-4), 7.08 (1H, dd, $J_o$ = 8.0 Hz, $J_m$ = 2.8 Hz H-3), 6.39 (1H, d, $J_{5,2'}$ = 2.4 Hz, H-5), 3.94 (3H, s, OCH$_3$), 2.52 (3H, s, CH$_3$), 2.39 (1H, d, $J_{2',5}$ = 2.4 Hz, H-2'); $^{13}$C NMR [CDCl$_3$, δ (ppm)]: 160.5, 154.3, 153.0, 142.7, 142.6, 131.5, 130.1, 126.4, 125.7, 123.3, 120.4, 119.7, 117.4, 114.4, 113.9, 107.4, 77.3, 61.9, 55.9, 20.8; Mass (m/z): 352.0 (M+, 100%).

9-Chloro-5-ethynyl-2-methoxy-6-oxa-benzo[5,6-c]xanthen-7-one **6b** :

White solid in 34% yield, mp 180-185 $^{o}$C; $\boldsymbol{\nu}_{\mathbf{max}}$ (cm$^{-1}$): 2125 (C≡C), 1621 (C=O); $^{1}$H NMR [CDCl$_3$, δ (ppm), 400 MHz]:8.30 (1H, d, $J_m$ = 2.4 Hz, H-8), 7.64 (1H, dd, $J_o$ = 8.8 Hz, $J_m$ = 2.4 Hz, H-10), 7.55 (1H, d, $J_o$ = 8.8 Hz, H-11), 7.51 (1H, d, $J_m$ = 1.6 Hz, H-1), 7.49 (1H, d, $J_o$ = 7.6 Hz, H-4), 7.09 (1H, dd, $J_o$ = 7.6 Hz, $J_m$ = 1.6 Hz, H-3), 6.40 (1H, d, $J_{5,2'}$ = 2.4 Hz, H-5), 3.94 (3H, s, OCH$_3$), 2.40 (1H, d, $J_{2',5}$ = 2.4 Hz, H-2'); $^{13}$C NMR [CDCl$_3$, δ (ppm),]:170.8, 154.4, 153.1, 147.4, 135.1, 133.6, 130.7, 130.2, 125.5, 124.4, 120.5, 119.7, 114.6, 114.0, 79.6, 74.4, 61.9, 56.0, 22.7; Mass (m/z): 338.9 (M+, 100%).

5-Ethynyl-2-methoxy-6-oxa-benzo[5,6-c]xanthen-7-one **6c :**

White solid in 41% yield, mp 192-194 $^{o}$C; $\boldsymbol{\nu}_{\mathbf{max}}$ (cm$^{-1}$): 2115 (C≡C), 1628 (C=O); $^{1}$H NMR [CDCl$_3$, δ (ppm), 400 MHz]:7.93 (1H, dd, $J_o$ = 6.8 Hz, $J_m$ = 2.8 Hz, H-8), 7.65 (1H, td, $J_o$ = 6.8 Hz, $J_m$ = 2.8 Hz, H-10), 7.52 (1H, dd, $J_o$ = 6.8 Hz, $J_m$ = 1.8 Hz, H-11), 7.48 (1H, d, $J_m$ = 2.0 Hz, H-1), 7.37 (1H, d, $J_o$ = 7.6 Hz, H-4), 7.17 (1H, m, H-9), 7.04 (1H, dd, $J_o$ = 7.6 Hz, $J_m$ = 2.0 Hz, H-3), 6.41 (1H, d, $J_{5,2'}$ = 2.4 Hz, H-5), 3.90 (3H, s, OCH$_3$), 2.35 (1H, d, $J_{2',5}$ = 2.4 Hz, H-2'); $^{13}$C NMR [CDCl$_3$, δ (ppm)]: 169.3, 159.5, 157.3, 136.1, 135.3, 135.1, 130.9, 130.4, 128.4, 127.6, 124.2, 121.5, 116.4, 113.2, 110.7, 84.7, 76.4, 65.2, 55.9; Mass (m/z): 304.0 (M+, 100%).

5-Ethynyl-2-methoxy-9-methyl-6-oxa-benzo[5,6-c]xanthen-7-one **6d :**

White solid in 46% yield, mp 201-203 °C; ***ν*max** (cm$^{-1}$): 2138 (C≡C), 1625 (C=O); $^1$H NMR [CDCl$_3$, δ (ppm), 400 MHz]:8.27 (1H, d, $J_m$ = 1.6 Hz, H-8), 7.72 (1H, dd, $J_o$ = 8.4 Hz, $J_m$ = 1.6 Hz, H-10), 7.61 (2H, m, H-1 and11), 7.48 (1H, d, $J_o$ = 8.0 Hz, H-4), 7.04 (1H, dd, $J_o$ = 7.6 Hz, $J_m$ = 2.0 Hz, H-3), 6.40 (1H, d, $J_{5,2'}$ = 2.4 Hz, H-5), 3.93 (3H, s, OCH$_3$), 2.50 (3H, s, CH$_3$), 2.35 (1H, d, $J_{2',5}$ = 2.4 Hz, H-2'); $^{13}$C NMR [CDCl$_3$, δ (ppm)]: 170.4, 156.1, 153.2, 136.7, 135.6, 130.9, 129.8, 127.4, 126.1, 124.4, 122.6, 118.2, 113.5, 110.6, 108.5, 83.6, 76.2, 65.3, 55.9, 21.2; Mass (m/z): 318.4 (M+, 100%).

6-Chloro-2-(3-methoxyphenyl)-7-methyl-4*H*-chromen-4-one **7a:**

White solid in 21% yield, mp 118-121 °C; ***ν*max** (cm$^{-1}$): 1628 (C=O); $^1$H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 8.18 (1H, s, H-5), 7.47 (4H, m, H-2', 5', 6' and 8), 7.12 (1H, d, $J_m$ = 1.6 Hz, H-4'), 6.79 (1H, s, H-3), 3.90 (3H, s, OCH$_3$), 2.53 (3H, s, -CH$_3$); $^{13}$C NMR [CDCl$_3$, δ (ppm)]: 189.8, 177.4, 166.7, 162.1, 156.5, 144.4, 134.6, 133.8, 127.4, 121.1, 118.0, 117.9, 117.0, 107.1, 101.7, 56.2, 29.7; Mass (m/z): 302.03 (M+, 100%).

6-Chloro-2-(3-methoxyphenyl)-4*H*-chromen-4-one **7b:**

White solid in 24% yield, mp 110-112 °C; ***ν*max** (cm$^{-1}$): 1622 (C=O); $^1$H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 8.20 (1H, d, $J_m$ = 2.4 Hz, H-5), 7.66 (1H, dd, $J_o$ = 8.0 Hz, $J_m$ = 2.4 Hz, H-7), 7.55 ( 4H, m, H-2', 5', 6' and 8), 7.11 (1H, d, $J_o$ = 8.0 Hz, $J_m$ = 2.0 Hz, H-4'), 6.82 (1H, s, H-3), 3.90 (3H, s, OCH$_3$); $^{13}$C NMR [CDCl$_3$, δ (ppm)]: 190.8, 177.1, 163.7, 160.0, 154.5, 134.0, 132.7, 131.2, 130.2, 125.2, 119.8, 118.7, 117.4, 111.8, 107.7, 55.2; Mass (m/z): 288.0 (M+, 100%).

2-(3-Methoxyphenyl)-4*H*-chromen-4-one **7c:**

White solid in 20% yield, mp 121-125 °C; ***ν*max** (cm$^{-1}$): 1625 (C=O); $^1$H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 8.25 (1H, dd, $J_o$ = 8.0 Hz, $J_m$ = 1.6 Hz, H-5), 7.73 (1H, td, $J_o$ = 8.0 Hz, $J_m$ = 1.6 Hz, H-7), 7.69 (1H, d, $J_m$ = 2.4 Hz, H-2'), 7.59 ( 1H, dd, $J_o$ = 8.0 Hz, $J_m$ = 1.6 Hz, H-6),7.46 (3H, m, H-8, 5' and 6'), 7.10 (1H, dd, $J_o$ = 8.8 Hz, $J_m$ = 2.4 Hz, H-4'), 6.83 (1H, s, H-3), 3.90 (3H, s, OCH$_3$); $^{13}$C NMR [CDCl$_3$, δ (ppm)]:190.1, 175.1, 161.0, 160.0, 154.1, 144.8, 132.5, 131.1, 130.0, 127.2, 121.1, 118.0, 115.4, 110.8, 105.0, 57.4; Mass (m/z): 253.05 (M+, 100%).

2-(3-Methoxyphenyl)-6-methyl-4*H*-chromen-4-one **7d:**

White solid in 20% yield, mp 104-108 °C; $\boldsymbol{\nu}_{\mathbf{max}}$ (cm$^{-1}$): 1628 (C=O); $^1$H NMR [CDCl$_3$, δ (ppm), 400 MHz]: 8.18 (1H, d, $J_m$ = 2.4 Hz, H-5), 7.67 (1H, d, $J_m$ = 2.0 Hz ,H-2'), 7.52 (1H, dd, $J_m$ = 8.0 Hz, $J_m$ = 2.4 Hz, H-7), 7.42 (3H, m, H-8, 5' and 6'), 7.15 (1H, dd, $J_o$ = 8.4 Hz, $J_m$ = 2.0 Hz, H-4'), 6.80 (1H, s, H-3), 3.90 (3H, s, OCH$_3$), 2.53 (3H, s, -CH$_3$); $^{13}$C NMR [CDCl$_3$, δ (ppm)]: 189.4, 177.8, 167.0, 160.0, 154.0, 142.8, 132.7, 131.1, 129.0, 125.2, 120.4, 118.8, 117.4, 111.0, 107.2, 55.6, 27.4; Mass (m/z): 267.06 (M+, 100%).

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# Phototransformation of 3-alkoxychromenones: Regioselective photocyclisation and Dealkoxylation

Radhika Khanna, Aarti Dalal, Ramesh Kumar and Ramesh C Kamboj*

Department of Chemistry, Kurukshetra University, Kurukshetra-136119, Haryana

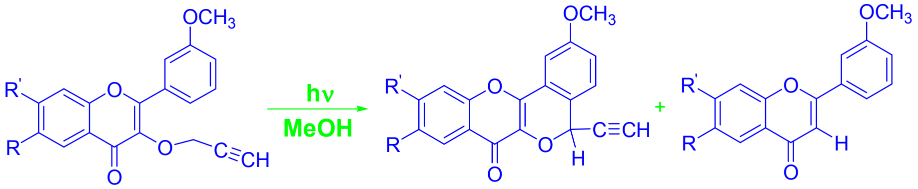

Photo-transformation of some 2-(3-methoxyphenyl)-4*H*-chromen-4-ones bearing propynyloxy moiety at 3-position into 5-ethynyl-2-methoxy-6-oxa-benzo[5,6-*c*]xanthen-7-ones and 2-(3-methoxyphenyl)-4*H*-chromen-4-ones via regioselective cyclisation and dealkoxylation, respectively has been described.