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## Phototransformation of 3-alkoxychromenones: regioselective photocyclisation and dealkoxylation†

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The phototransformation of some 2-(3-methoxyphenyl)-4*H*-chromen-4-ones bearing a propynyloxy moiety at the 3-position has been described. On photolysis with pyrex-filtered UV light from a Hg lamp (125 W), these chromenones 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 regioselective ring closure at the 6'-position of the 2-(3'-methoxy)phenyl moiety of the initially formed 1,4-biradical *via* a  $\gamma$ -H abstraction mechanism. No product whatsoever was observed through ring closure at the 2'-position. This behaviour has been found to be in accordance with the directive influence observed in free radical aromatic substitutions. This regioselective photocyclisation is further supported by calculations made from 3D structures (MM2 program). In addition, during the irradiation of these substrates, 2-(3-methoxyphenyl)-4*H*-chromen-4-ones were also realised through dealkoxylation. The structures of the substrates and photoproduct(s) have been determined by their spectroscopic (IR, NMR, mass spectrometry) studies.

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## Introduction

Photochemical intramolecular H abstractions in carbonyl compounds have found several synthetic applications<sup>1–11</sup> including the synthesis of numerous exotic carbocyclic and heterocyclic scaffolds that are otherwise very difficult to obtain under thermal conditions. The exceptional behaviour of the propargyl 1,4-biradical in forming photoproducts *via* unsaturated carbenes<sup>12,13</sup> has been investigated by Agosta and Margaretha,<sup>14</sup> and has encouraged us to study the photochemistry of chromenones containing the propargyl group.<sup>15–17</sup> In these studies, it was observed that the propynyloxy group behaved in many ways, such as 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<sup>18</sup> and are utilized as leuco-dyes, pH-sensitive fluorescent materials for tracking biomolecules and in laser technologies.<sup>19–22</sup> The reactive chromene core in the xanthenone moiety is responsible for a wide range of biological activities ranging from anti-cancer, anti-viral, diuretic, spasmolytic, anti-coagulant, and anti-anaphylactic to cognitive enhancement for the treatment of neuro-

degenerative impairments including Parkinson's disease, Alzheimer's disease, Down's syndrome, HIV-associated dementia and schizophrenia.<sup>23–29</sup> In view of these and our continuous effort in developing the photochemistry of such molecules, in the present paper we wish to report the results of our investigations on the photolysis of some 4*H*-chromen-4-ones bearing the propynyloxy moiety at the 3-position and the 3-methoxyphenyl moiety at the 2-position, with the motive to determine the regioselective photocyclisation and other reactions, as elicited earlier in other similar molecules.<sup>15–17,30–32</sup>

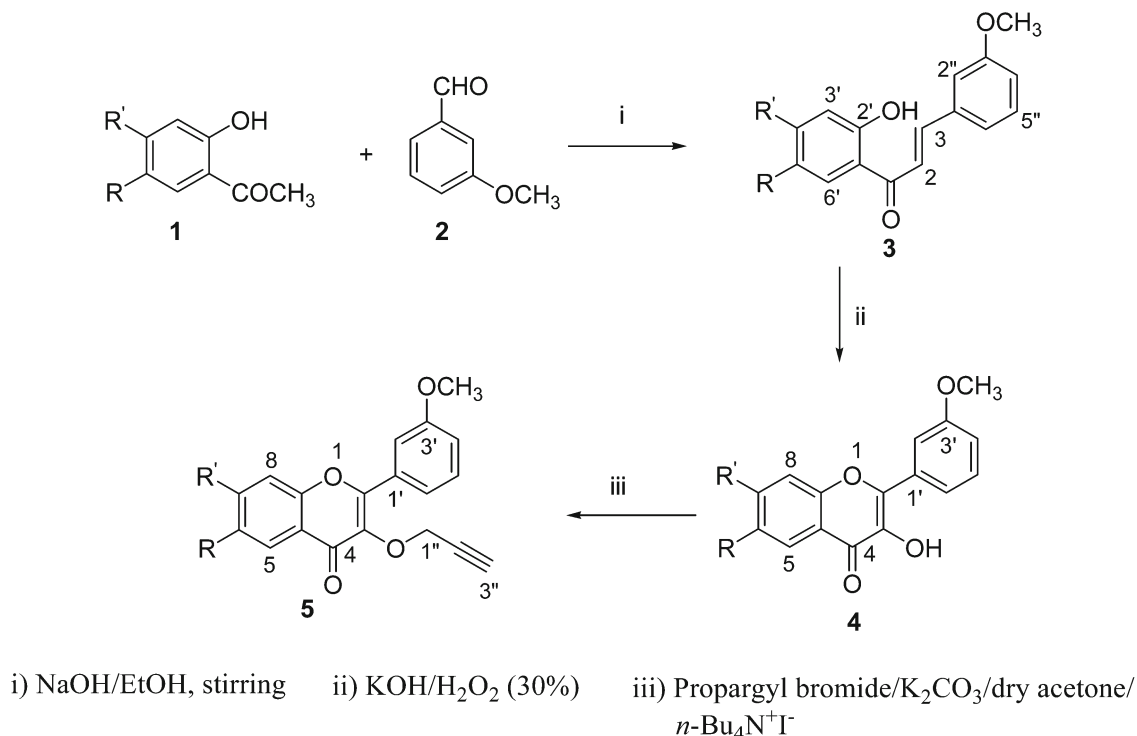
## Results and discussion

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 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 Algar–Flynn–Oyamada<sup>33,34</sup> reaction conditions, and (iii) subsequent alkylation of the latter with propargyl bromide in the presence of dry acetone, freshly dried K<sub>2</sub>CO<sub>3</sub> and tetra-*n*-butyl ammonium iodide (Scheme 1). The structures of compounds **3**, **4** and **5**<sup>30</sup> were confirmed by their spectroscopic data (*vide* experimental).

These chromenones **5** (absorption maxima,  $\lambda_{\max}$ , between 350–357 nm in MeOH) were tailored and designed with the objectives; (i) to illustrate regioselectivity, because these have a propensity for cyclisation at two possible sites, *i.e.* the 2'- and

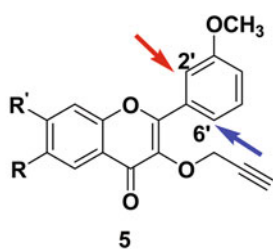
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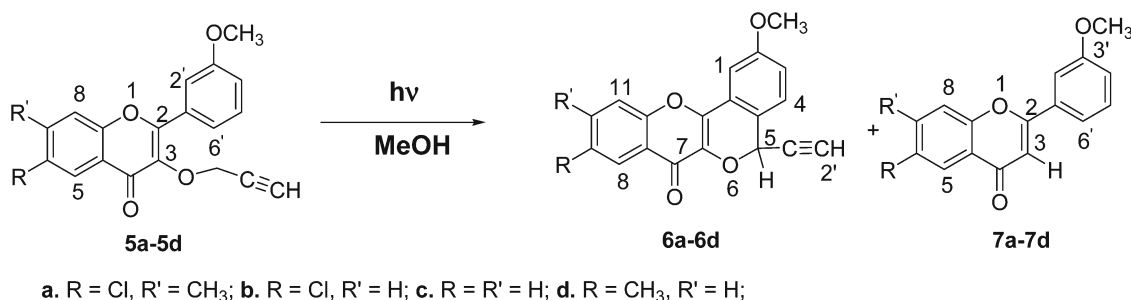
**Scheme 1** Synthesis of 2-(3-methoxyphenyl)-3-(prop-2-ynoxy)-4H-chromen-4-one 5.

6'-positions of the methoxyphenyl moiety, and (ii) to observe the effect of the propynyloxy group on photoproduct formation in comparison to other functionalities.<sup>31</sup>



" → ", the possible sites for photocyclization with -O-CH<sub>2</sub>-

Irradiation of 5(a-d) in methanol with pyrex-filtered light from a 125 W Hg UV lamp under an N<sub>2</sub> 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 the chromatographic separation of photolysate with increasing proportions of ethyl acetate in ethyl acetate-petroleum ether yielded the xanthenones 6 (35–45%) and the dealkoxylated chromenones 7 (20–24%) as the photoproducts, approximately in the ratio 2:1, respectively. The product composition remained the 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  $\delta$  8.3–7.9 ppm ( $J_m = 2.4$  Hz) for proton



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

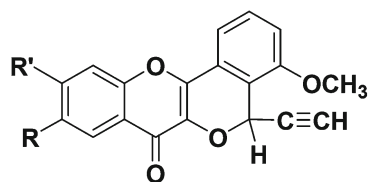
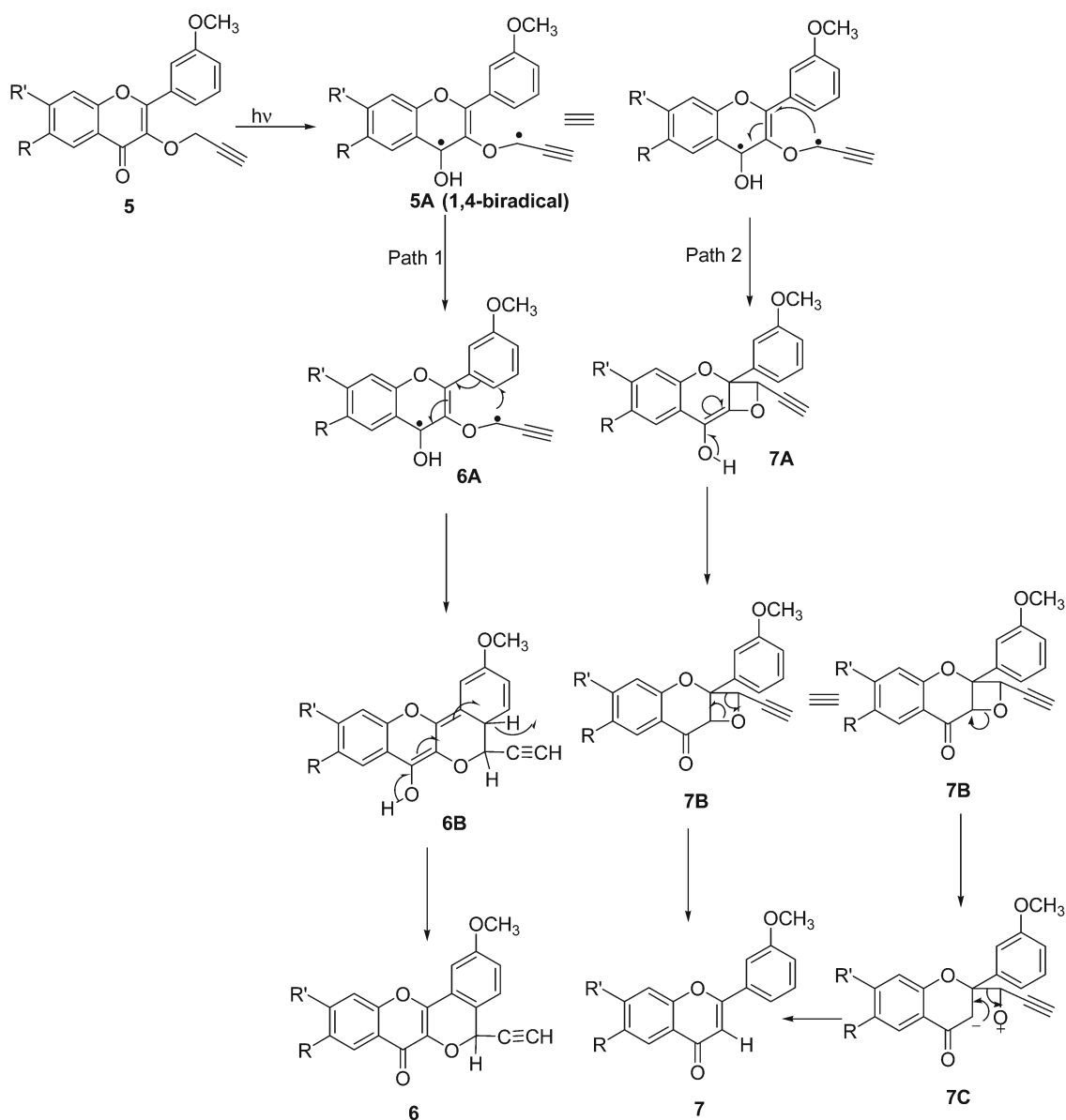


Fig. 1 Possible product via cyclisation at 2'-position.

H8. Proton H11 resonated between  $\delta$  7.4 and 7.5 ppm (d,  $J_o = 8.8$  Hz) and proton H10, as in **6b–6d**, was observed between 7.7 and 7.6 ppm (dd,  $J_o = 8.8$  Hz and  $J_m = 2.4$  Hz). The acetylenic proton gave a signal at nearly  $\delta$  2.4 ppm (d,  $J_m = 2.4$  Hz), which showed allylic coupling with proton H5, which resonated as a

doublet at around  $\delta$  6.4 ppm ( $J_m = 2.4$  Hz). The rest of the protons, *i.e.* H1, H3 and H4, were observed at  $\delta$  7.5–7.4 ppm (d,  $J_m = 1.6$  Hz), 7.0 ppm (dd,  $J_o = 7.6$  Hz and  $J_m = 1.6$  Hz) and 7.48 ppm (d,  $J_o = 7.6$  Hz) respectively. This splitting and coupling pattern of H1, H3 and H4 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 formed (**7**) was confirmed by comparing its NMR spectrum with the substrate (**5**), where the former showed the presence of singlet at 6.8 ppm for H3 and the disappearance of doublets at  $\delta$  5.0 and 2.3 ppm (*vide* experimental) present in the <sup>1</sup>H NMR spectrum of **5**.

This structure of **6** was further confirmed by 2D COSY of **6b**, where it was clearly observed that H8 was interacting with H10, which was also correlating with H11, and the acetylenic

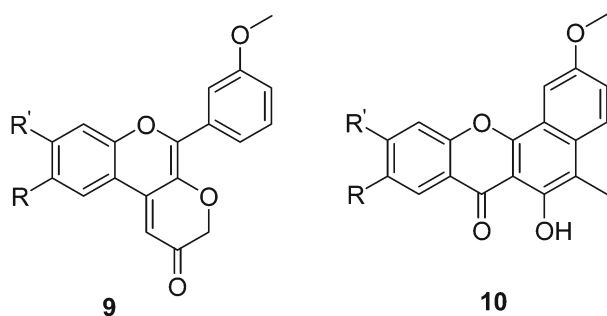


Scheme 3 Suggested mechanism for the formation of products (**6** & **7**) from 2-(3-methoxyphenyl)-3-(prop-2-ynoxy)-4H-chromen-4-ones **5** by photolysis.

proton was correlating with H5. The interactions of H3 with H1 and H4 were also observed.

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

The <sup>1</sup>H NMR spectral analysis of the photolysate also indicated the formation of a trace amount of pyranochromenones **9** (singlet at  $\delta$  6.8 ppm and doublet at  $\delta$  5.3 ppm), with no formation of xanthenones **10**, similar to those obtained from the photolytic studies<sup>15,17,35</sup> on 3-(prop-2nyloxy)-2-(thiophen-3-yl)-4*H*-chromen-4-ones. However, these products, being in trace amounts, could not be isolated in spite of our best efforts. Even the change of solvent from methanol to benzene had no effect on the product formation and isolation.



Although the mechanism of this reaction is not established yet, the formation of **6** (path 1) and **7** (path 2) from **5** can be envisioned (Scheme 3) to occur through the initial formation of a 1,4-biradical *via* a  $\gamma$ -H abstraction mechanism,<sup>30</sup> followed by ring closure by coupling of the  $-O-\dot{C}H-$  radical with the 6'-position of the 2-(3'-methoxyphenyl) moiety regioselectively. Photoproduct **7** has been conceived to be formed through the formation of oxetane **7B**, followed by its fragmentation (concerted or stepwise), as observed earlier<sup>36</sup> in the 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 (Fig. 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** could 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 pyrillium ring system.<sup>37</sup> A ring oxygen in the 3-position would certainly support its formation, as would a carbonyl oxygen next to it.

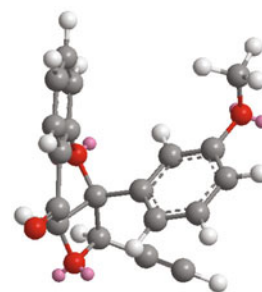
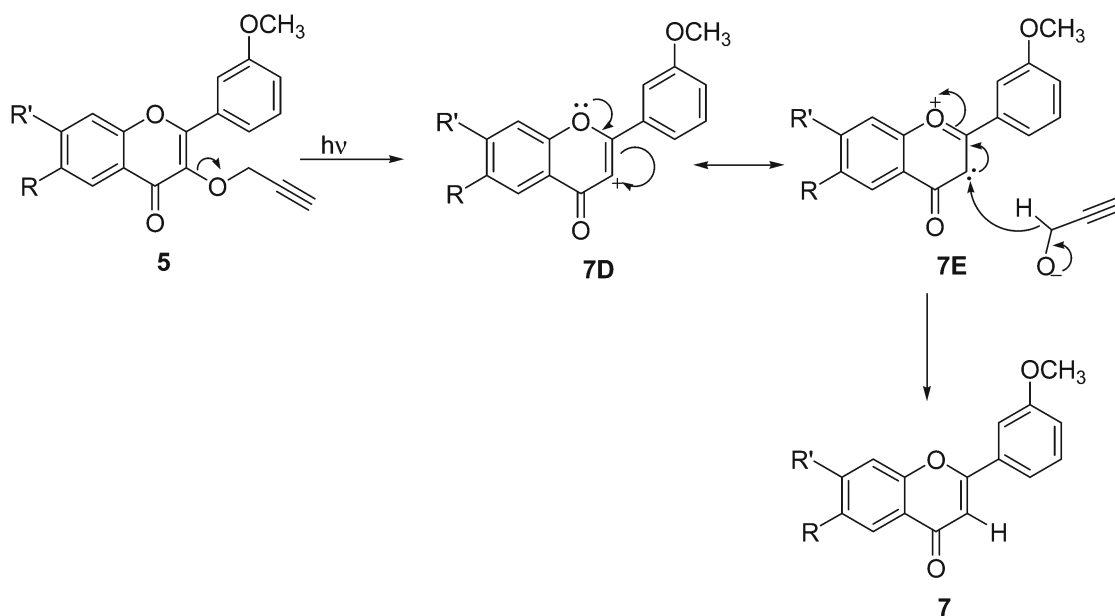


Fig. 2 MM2 energy-minimized 3D structure of tentative oxetane **7B** – a folded conformation (a representative case).



Scheme 4 Alternate plausible mechanism for the formation of **7**.

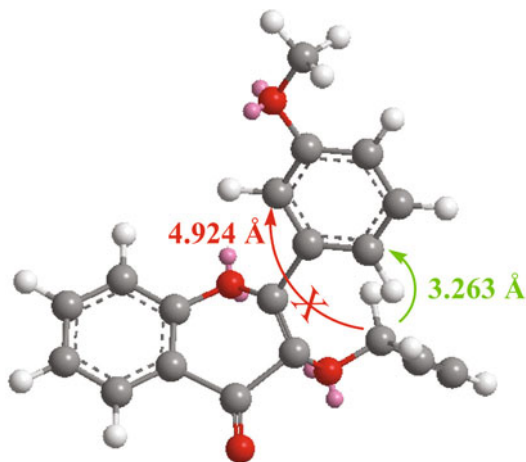


Fig. 3 MM2 energy-minimized 3D structure of compound 5.

This photocyclisation is in accordance<sup>38</sup> with the directive influence observed in free radical aromatic substitution (*o*- and *p*-directing). In this case, regioselectivity for ring formation exclusively at the 6'-position (*p*- to methoxy and *o*- to the chromenyl group) with no ring formation at the 2'-position has been observed, which can be explained by the steric hindrance experienced at the 2'-position from the 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  $-O-CH_2-$  and the 6'-position (the two clipping atoms for ring formation) have been observed in close proximity; the contact averaged at 3.263 Å, which is quite a bit shorter than the close contact (average 4.924 Å) between  $-O-CH_2-$  and the 2'-position of the methoxyphenyl ring at the 2-position (Fig. 3).

## Conclusion

It may be concluded that 2-(3-methoxyphenyl)-3-(prop-2-ynyloxy)-4-*H*-chromen-4-ones yield tetracyclic product(s) 5-ethynyl-2-methoxy-6-oxa-benzo[5,6-*c*]xanthen-7-ones on phototransformation, through  $\gamma$ -H abstraction followed by regioselective cyclisation at 6-position, which has been found to be controlled by the steric influence. Further, these angular tetracyclics, the benzoxanthenones, have been produced by an environmentally benign green method without using any toxic reagents. 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. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in

CDCl<sub>3</sub> on a 300 MHz/400 MHz Bruker spectrometer using TMS as an internal standard. Mass spectra were recorded on a LC-MS Spectrometer Model Q-ToF Micro Waters source in ES<sup>+</sup> 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–ethyl acetate mixture. The yields reported are based on the amount of isolated photoproduct 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 a well-stirred suspension of powdered NaOH (0.1 mol) in EtOH at 0 °C were added substituted 2-hydroxyacetophenone (0.05 mol) and 3-methoxybenzaldehyde (0.055 mol). The reaction mixture, which became deep red in color after 3 h, was stirred for 7–8 h. Thereafter, it was poured over ice and was neutralized with dil. HCl to obtain acrylophenone, which was crystallized from EtOH to give yellow needles of 3.

**3a** – Orange solid in 77% yield, mp 91–94 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 3405 (–OH), 1645 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 12.67 (1H, s, OH), 7.90 (1H, s, H6'), 7.86 (1H, d,  $J_{3,2} = 15.2$  Hz, H3), 7.51 (1H, d,  $J_{2,3} = 15.2$  Hz, H2), 7.38 (1H, t,  $J_o = 8.0$  Hz,  $J_m = 7.2$  Hz, H5''), 7.28 (1H, dd,  $J_o = 8.0$  Hz,  $J_m = 2.0$  Hz, H6''), 7.17 (1H, d,  $J_m = 2.0$  Hz, H2''), 7.01 (1H, td,  $J_o = 8.0$  Hz,  $J_m = 2.0$  Hz, H4''), 6.91 (1H, s, H3'), 3.88 (3H, s, OCH<sub>3</sub>), 2.39 ppm (3H, s, CH<sub>3</sub>).

**3b** – Orange solid in 78% yield, mp 88–92 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 3415 (–OH), 1641 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 12.76 (1H, s, OH), 7.96 (1H, d,  $J_m = 2.8$  Hz, H6'), 7.84 (1H, d,  $J_{3,2} = 15.2$  Hz, H3), 7.56 (1H, d,  $J_{2,3} = 15.2$  Hz, H2), 7.52 (1H, d,  $J_o = 6.8$  Hz,  $J_m = 2.8$  Hz, H4'), 7.32 (1H, dd,  $J_o = 8.0$  Hz, H5''), 7.11 (1H, d,  $J_m = 2.4$  Hz, H2''), 7.04 (2H, m, H4'', 6''), 6.91 (1H, d,  $J_o = 6.8$  Hz, H6'), 3.90 ppm (3H, s, OCH<sub>3</sub>).

**3c** – Orange solid in 75% yield, mp 78–81 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 3445 (–OH), 1643 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 12.79 (1H, s, OH), 7.93 (1H, dd,  $J_o = 6.8$  Hz,  $J_m = 2.8$  Hz, H6'), 7.86 (1H, d,  $J_{3,2} = 15.6$  Hz, H3), 7.65 (1H, d,  $J_{2,3} = 15.6$  Hz, H2), 7.52 (1H, td,  $J_o = 6.8$  Hz,  $J_m = 1.6$  Hz, H4'), 7.37 (1H, td,  $J_o = 6.8$  Hz,  $J_m = 2.8$  Hz, H5'), 7.29 (1H, dd,  $J_o = 8.0$  Hz, H5''), 7.17 (1H, d,  $J_m = 1.6$  Hz, H2''), 7.04 (1H, td,  $J_o = 8.0$  Hz,  $J_m = 2.4$ , H6''), 7.00 (1H, td,  $J_o = 8.0$  Hz,  $J_m = 2.4$  and 1.6 Hz, H4''), 6.92 (1H, dd,  $J_o = 6.8$  Hz,  $J_m = 2.8$  Hz, H3'), 3.84 ppm (3H, s, OCH<sub>3</sub>).

**3d** – Orange solid in 71% yield, mp 79–83 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 3405 (–OH), 1645 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 12.76 (1H, s, OH), 7.93 (1H, d,  $J_m = 2.8$  Hz, H6'), 7.88 (1H, d,  $J_{3,2} = 15.2$  Hz, H3), 7.56 (1H, d,  $J_{2,3} = 15.2$  Hz, H2), 7.50 (1H, dd,  $J_o = 8.4$  Hz,  $J_m = 2.8$  Hz, H4'), 7.41 (1H, dd,  $J_o = 8.0$  Hz, H5''), 7.11 (1H, d,  $J_m = 2.0$  Hz, H2''), 7.04 (2H, m, H4'', 6''), 6.90 (1H, d,  $J_o = 8.4$  Hz, H3'), 3.90 (3H, s, OCH<sub>3</sub>), 2.53 ppm (3H, s, 5'-CH<sub>3</sub>).

**Synthesis of 3-hydroxy-2(3-methoxyphenyl)-4H-chromen-4-ones (4a–4d).** To a suspension of chalcone (0.01 mol) in methanol was added 10.0 ml of 20% aq. KOH, and this

mixture was cooled to 0 °C. To this dark red well-stirred solution was added H<sub>2</sub>O<sub>2</sub> (30%) dropwise until the color changed to yellow, and the stirring was continued for 1 h. The reaction mixture was neutralized with ice-HCl to give light yellow precipitates. The solid was filtered, dried and crystallized (CHCl<sub>3</sub>-MeOH) to give yellow crystals of 3-hydroxychromenones **4**.

**4a** - cream solid in 72% yield, mp 112–116 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 3202 (-OH), 1610 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>,  $\delta$  (ppm), 400 MHz]: 8.20 (1H, s, H5), 7.87 (1H, dd,  $J_o = 7.2$  Hz, H5'), 6.96 (4H, m, H8, 2', 4' and 6'), 3.80 (3H, s, OCH<sub>3</sub>), 2.53 (3H, s, CH<sub>3</sub>).

**4b** - cream solid in 76% yield, mp 108–110 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 3210 (-OH), 1605 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 8.02 (1H, d,  $J_m = 1.6$  Hz, H5), 7.88 (1H, dd,  $J_o = 8.4$  Hz,  $J_m = 1.6$  Hz, H7), 7.74 (1H, dd,  $J_o = 6.8$  Hz,  $J_m = 1.6$  Hz, H6'), 7.56 (1H, d,  $J_o = 8.4$  Hz, H5'), 7.44 (2H, m, H2' and 8), 7.10 (1H, td,  $J_o = 8.4$  Hz,  $J_m = 1.6$  Hz, H4'), 3.90 (3H, s, OCH<sub>3</sub>).

**4c** - cream solid in 71% yield, mp 101–103 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 3205 (-OH), 1615 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 8.27 (1H, dd,  $J_o = 8.0$  Hz,  $J_m = 1.6$  Hz, H5), 7.73 (1H, td,  $J_o = 6.8$  Hz,  $J_m = 1.6$  Hz, H6), 7.70 (1H, td,  $J_o = 6.8$  Hz,  $J_m = 1.6$  Hz, H7), 7.68 (1H, d,  $J_m = 1.6$  Hz, H2'), 7.56 (1H, dd,  $J_o = 8.0$  Hz, H5'), 7.45 (1H, dd,  $J_o = 8.8$  Hz,  $J_m = 2.8$  Hz, H8), 7.42 (1H, dd,  $J_o = 6.8$  Hz,  $J_m = 1.6$  Hz, H6'), 7.08 (1H, td,  $J_o = 8.0$  Hz,  $J_m = 1.6$  Hz, H4'), 3.90 (3H, s, OCH<sub>3</sub>).

**4d** - cream solid in 69% yield, mp 110–113 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 3232 (-OH), 1605 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 7.96 (1H, d,  $J_m = 2.0$  Hz, H5), 7.78 (1H, dd,  $J_o = 8.4$  Hz,  $J_m = 2.0$  Hz, H7), 7.74 (1H, dd,  $J_o = 7.6$  Hz,  $J_m = 1.6$  Hz, H6'), 7.64 (1H, dd,  $J_o = 7.6$  Hz, and 8.4 Hz, H5'), 7.51 (2H, m, H2' and 8), 7.03 (1H, d,  $J_o = 8.4$  Hz,  $J_m = 1.6$  Hz, H4'), 3.90 (3H, s, OCH<sub>3</sub>), 2.54 (3H, s, CH<sub>3</sub>).

**Synthesis of 2-(3-methoxyphenyl)-3-(prop-2-ynyl)-4H-chromen-4-ones (5a–5d)**. To a suspension of compound **4** (0.001mol) and freshly dried K<sub>2</sub>CO<sub>3</sub> (0.005mol) in dry acetone was added propargyl bromide (0.001 mol) and tetra-*n*-butylammonium iodide (0.050 g). The reaction mixture was refluxed for 4 h 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;  $\nu_{\max}$  (cm<sup>-1</sup>): 2124 (C≡C), 1621 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 8.20 (1H, s, H5), 7.70 (1H, dd,  $J_o = 8.4$  Hz,  $J_m = 1.6$  Hz, H6'), 7.45 (1H, dd,  $J_o = 8.4$  Hz, H5'), 7.07 (2H, m, H2' and 4'), 6.98 (1H, s, H8), 4.98 (2H, d,  $J_{1',3''} = 2.4$  Hz, H1''), 3.89 (3H, s, OCH<sub>3</sub>), 2.52 (3H, s, CH<sub>3</sub>), 2.37 (1H, t,  $J_{3'',1''} = 2.4$  Hz, H3''); <sup>13</sup>C NMR [CDCl<sub>3</sub>,  $\delta$  (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;  $\nu_{\max}$  (cm<sup>-1</sup>): 2128 (C≡C), 1615 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 8.08 (1H, d,  $J_m = 2.8$  Hz, H5), 7.70 (2H, m, H7, 5'), 7.62 (1H, dd,  $J_o = 8.8$  Hz, H6'), 7.32 (2H, m, H2' and 8), 7.10 (1H, td,  $J_o = 8.8$  Hz,  $J_m = 1.6$  Hz, H4'), 4.98 (2H, d,  $J_{1',3''} = 2.4$  Hz, H1''), 3.90 (3H, s, OCH<sub>3</sub>), 2.35 (1H, t,  $J_{3'',1''} = 2.4$  Hz, H3''); <sup>13</sup>C NMR [CDCl<sub>3</sub>,  $\delta$  (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, 118.4, 116.8, 116.2, 78.3, 76.4, 58.1, 55.0.

**5c** - White solid in 74% yield, mp 110–112 °C;  $\lambda_{\max}$  (MeOH): 353 nm;  $\nu_{\max}$  (cm<sup>-1</sup>): 2132 (C≡C), 1625 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 8.28 (1H, dd,  $J_o = 8.0$  Hz,  $J_m = 1.6$  Hz, H5), 7.73 (1H, td,  $J_o = 8.0$  Hz,  $J_m = 1.6$  Hz, H6), 7.72 (1H, dd,  $J_o = 8.4$  Hz,  $J_m = 1.6$  Hz, H6'), 7.70 (1H, td,  $J_o = 8.0$  Hz,  $J_m = 1.6$  Hz, H7), 7.61 (1H, dd,  $J_o = 8.8$  Hz, H5'), 7.45 (2H, m, H2' and 8), 7.08 (1H, td,  $J_o = 8.0$  Hz,  $J_m = 1.6$  Hz, H4'), 5.00 (2H, d,  $J_{1',3''} = 2.4$  Hz, H1''), 3.90 (3H, s, OCH<sub>3</sub>), 2.36 (1H, t,  $J_{3'',1''} = 2.4$  Hz, H3''); <sup>13</sup>C NMR [CDCl<sub>3</sub>,  $\delta$  (ppm)]: 174.9, 159.4, 155.3, 133.6, 132.1, 129.9, 129.4, 125.8, 124.8, 124.0, 121.3, 119.3, 118.0, 116.8, 114.2, 78.6, 76.1, 59.2, 55.0.

**5d** - White solid in 73% yield, mp 91–94 °C;  $\lambda_{\max}$  (MeOH): 357 nm;  $\nu_{\max}$  (cm<sup>-1</sup>): 2128 (C≡C), 1622 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 8.27 (1H, d,  $J_m = 2.4$  Hz, H5), 7.79 (1H, dd,  $J_o = 8.4$  Hz,  $J_m = 2.4$  Hz, H7), 7.54 (1H, dd,  $J_o = 8.1$  Hz, H5'), 7.32 (3H, m, H2', 6' and 8), 7.01 (1H, dd,  $J_o = 8.0$  Hz,  $J_m = 1.6$  Hz, H4'), 4.99 (2H, d,  $J_{1',3''} = 2.4$  Hz, H1''), 3.90 (3H, s, OCH<sub>3</sub>), 2.43 (3H, s, CH<sub>3</sub>), 2.33 (1H, t,  $J_{3'',1''} = 2.4$  Hz, H3''); <sup>13</sup>C NMR [CDCl<sub>3</sub>,  $\delta$  (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, 116.4, 115.8, 114.6, 78.6, 76.6, 59.6, 55.8, 20.4.

**Photolysis of 2-(3-methoxyphenyl)-3-(prop-2-ynyl)-4H-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 proportions of ethyl acetate in an ethyl acetate-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 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 2128 (C≡C), 1628 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 8.27 (1H, s, H8), 7.48 (2H, m, H1 and 11), 7.36 (1H, d,  $J_o = 8.0$  Hz, H4), 7.08 (1H, dd,  $J_o = 8.0$  Hz,  $J_m = 2.8$  Hz, H3), 6.39 (1H, d,  $J_{5,2'} = 2.4$  Hz, H5), 3.94 (3H, s, OCH<sub>3</sub>), 2.52 (3H, s, CH<sub>3</sub>), 2.39 (1H, d,  $J_{2',5} = 2.4$  Hz, H2'); <sup>13</sup>C NMR [CDCl<sub>3</sub>,  $\delta$  (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<sup>+</sup>, 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 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 2125 (C≡C), 1621 (C=O); <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400 MHz,  $\delta$  (ppm)]: 8.30 (1H, d,  $J_m = 2.4$  Hz, H8), 7.64 (1H, dd,  $J_o = 8.8$  Hz,  $J_m = 2.4$  Hz, H10), 7.55 (1H, d,  $J_o = 8.8$  Hz, H11), 7.51 (1H, d,  $J_m = 1.6$  Hz, H1), 7.49 (1H, d,  $J_o = 7.6$  Hz, H4), 7.09 (1H, dd,  $J_o = 7.6$  Hz,  $J_m = 1.6$  Hz, H3), 6.40 (1H, d,  $J_{5,2'} = 2.4$  Hz, H5), 3.94 (3H, s, OCH<sub>3</sub>), 2.40 (1H, d,  $J_{2',5} = 2.4$  Hz, H2'); <sup>13</sup>C NMR [CDCl<sub>3</sub>,  $\delta$  (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<sup>+</sup>, 100%).

**5-Ethynyl-2-methoxy-6-oxa-benzo[5,6-*c*]xanthen-7-one 6c**. White solid in 41% yield, mp 192–194 °C;  $\nu_{\max}$  (cm<sup>-1</sup>): 2115

(C≡C), 1628 (C=O);  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz,  $\delta$  (ppm)]: 7.93 (1H, dd,  $J_o = 6.8$  Hz,  $J_m = 2.8$  Hz, H8), 7.65 (1H, td,  $J_o = 6.8$  Hz,  $J_m = 2.8$  Hz, H10), 7.52 (1H, dd,  $J_o = 6.8$  Hz,  $J_m = 1.8$  Hz, H11), 7.48 (1H, d,  $J_m = 2.0$  Hz, H1), 7.37 (1H, d,  $J_o = 7.6$  Hz, H4), 7.17 (1H, m, H9), 7.04 (1H, dd,  $J_o = 7.6$  Hz,  $J_m = 2.0$  Hz, H3), 6.41 (1H, d,  $J_{5,2'} = 2.4$  Hz, H5), 3.90 (3H, s, OCH<sub>3</sub>), 2.35 (1H, d,  $J_{2',5} = 2.4$  Hz, H2');  $^{13}\text{C}$  NMR [ $\text{CDCl}_3$ ,  $\delta$  (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 ( $\text{M}^+$ , 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;  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 2138 (C≡C), 1625 (C=O);  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz,  $\delta$  (ppm)]: 8.27 (1H, d,  $J_m = 1.6$  Hz, H8), 7.72 (1H, dd,  $J_o = 8.4$  Hz,  $J_m = 1.6$  Hz, H10), 7.61 (2H, m, H1 and 11), 7.48 (1H, d,  $J_o = 8.0$  Hz, H4), 7.04 (1H, dd,  $J_o = 7.6$  Hz,  $J_m = 2.0$  Hz, H3), 6.40 (1H, d,  $J_{5,2'} = 2.4$  Hz, H5), 3.93 (3H, s, OCH<sub>3</sub>), 2.50 (3H, s, CH<sub>3</sub>), 2.35 (1H, d,  $J_{2',5} = 2.4$  Hz, H2');  $^{13}\text{C}$  NMR [ $\text{CDCl}_3$ ,  $\delta$  (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 ( $\text{M}^+$ , 100%).

**6-Chloro-2-(3-methoxyphenyl)-7-methyl-4H-chromen-4-one 7a.** White solid in 21% yield, mp 118–121 °C;  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 1628 (C=O);  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz,  $\delta$  (ppm)]: 8.18 (1H, s, H5), 7.47 (4H, m, H2', 5', 6' and 8), 7.12 (1H, d,  $J_m = 1.6$  Hz, H4'), 6.79 (1H, s, H3), 3.90 (3H, s, OCH<sub>3</sub>), 2.53 (3H, s, -CH<sub>3</sub>);  $^{13}\text{C}$  NMR [ $\text{CDCl}_3$ ,  $\delta$  (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 ( $\text{M}^+$ , 100%).

**6-Chloro-2-(3-methoxyphenyl)-4H-chromen-4-one 7b.** White solid in 24% yield, mp 110–112 °C;  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 1622 (C=O);  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz,  $\delta$  (ppm)]: 8.20 (1H, d,  $J_m = 2.4$  Hz, H5), 7.66 (1H, dd,  $J_o = 8.0$  Hz,  $J_m = 2.4$  Hz, H7), 7.55 (4H, m, H2', 5', 6' and 8), 7.11 (1H, d,  $J_o = 8.0$  Hz,  $J_m = 2.0$  Hz, H4'), 6.82 (1H, s, H3), 3.90 (3H, s, OCH<sub>3</sub>);  $^{13}\text{C}$  NMR [ $\text{CDCl}_3$ ,  $\delta$  (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 ( $\text{M}^+$ , 100%).

**2-(3-Methoxyphenyl)-4H-chromen-4-one 7c.** White solid in 20% yield, mp 121–125 °C;  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 1625 (C=O);  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz,  $\delta$  (ppm)]: 8.25 (1H, dd,  $J_o = 8.0$  Hz,  $J_m = 1.6$  Hz, H5), 7.73 (1H, td,  $J_o = 8.0$  Hz,  $J_m = 1.6$  Hz, H7), 7.69 (1H, d,  $J_m = 2.4$  Hz, H2'), 7.59 (1H, dd,  $J_o = 8.0$  Hz,  $J_m = 1.6$  Hz, H6), 7.46 (3H, m, H8, 5' and 6'), 7.10 (1H, dd,  $J_o = 8.8$  Hz,  $J_m = 2.4$  Hz, H4'), 6.83 (1H, s, H3), 3.90 (3H, s, OCH<sub>3</sub>);  $^{13}\text{C}$  NMR [ $\text{CDCl}_3$ ,  $\delta$  (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 ( $\text{M}^+$ , 100%).

**2-(3-Methoxyphenyl)-6-methyl-4H-chromen-4-one 7d.** White solid in 20% yield, mp 104–108 °C;  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 1628 (C=O);  $^1\text{H}$  NMR [ $\text{CDCl}_3$ , 400 MHz,  $\delta$  (ppm)]: 8.18 (1H, d,  $J_m = 2.4$  Hz, H5), 7.67 (1H, d,  $J_m = 2.0$  Hz, H2'), 7.52 (1H, dd,  $J_m = 8.0$  Hz,  $J_m = 2.4$  Hz, H7), 7.42 (3H, m, H8, 5' and 6'), 7.15 (1H, dd,  $J_o = 8.4$  Hz,  $J_m = 2.0$  Hz, H4'), 6.80 (1H, s, H3), 3.90 (3H, s, OCH<sub>3</sub>), 2.53 (3H, s, -CH<sub>3</sub>);  $^{13}\text{C}$  NMR [ $\text{CDCl}_3$ ,  $\delta$  (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 ( $\text{M}^+$ , 100%).

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