

## Photocyclisations of some 3-alkoxychromones: Substituent control on photoreactivity

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The photochemical transformation of some 3-alkoxy-2-phenylchromones bearing various stabilizing substituents on the 3-alkoxy group have been described. In these studies, photoreactions occur through the 1,4-biradicals that yield angular tetracyclic products. The yield and distribution of the photoproducts are dictated by the nature of substituents of 3-alkoxy moieties.

**Keywords:** Photocyclisation, H-abstraction, alkoxychromones, photoreactivity

The past few decades have witnessed tremendous excitement among synthetic organic chemists working in the area of preparation of cyclic systems by the nonionic processes, particularly photocycloadditions<sup>1</sup> and biradical recombinations<sup>2</sup>. The latter are generated chiefly from the intramolecular H-abstraction by the photoexcited carbonyl chromophores. These H-abstractions occur preferably from  $\gamma$  (Ref. 3) and  $\delta$  (Ref. 4) positions to give 1,4- and 1,5-biradicals, which finally lead to numerous exotic photoproducts. 2-Aryl-3-alkoxychromones<sup>5</sup> are such substrates that undergo easy photo H-abstraction from  $\gamma$ -position. This photoreaction provides pyran ring from the cyclisation of 1,4-biradical with 2-aryl group. Earlier, some results on the photolysis of 3-alkoxy<sup>6</sup> and allyloxy<sup>7</sup> chromones have been reported where products were formed from 1,4- and 1,6-biradicals respectively. To investigate the detailed behaviour of these intermediate biradicals, photocyclisations had been attempted upon chromones **4a-c**, **5a-c** and **6a-c**. The major impetus behind this study was to investigate the effect of various stabilizing substituents (like ester, vinyl and naphthalene) of 3-alkoxy moieties on the intramolecular H-abstraction and thus, the product formation and their distribution in the photoreactions.

### Results and Discussion

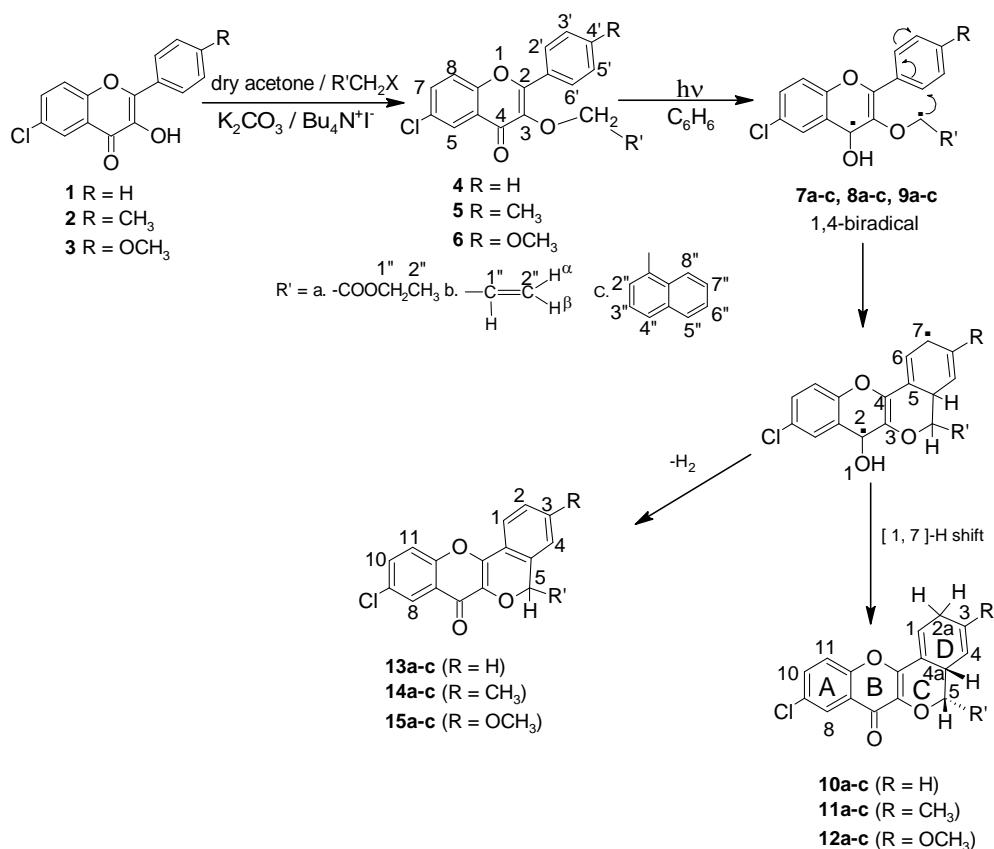
The chromones **4a-c**, **5a-c** and **6a-c** required for this study were obtained from the O-alkylation of the 3-hydroxy compounds<sup>5d</sup> **1-3** with an appropriate alkylating agent (like bromoethylacetate, allylbromide

and 1-chloromethylnaphthalene) in the presence of freshly ignited  $K_2CO_3$ /dry acetone and  $Bu_4N^+I^-$  as phase transfer catalyst (PTC). The use of PTC in these syntheses not only decreased the reaction time but also improved the yields of 3-alkoxychromones. The structures of these compounds were ascertained from the rigorous analysis of their spectral characterization data (UV-Vis, IR,  $^1H$  NMR) (see Experimental Section).

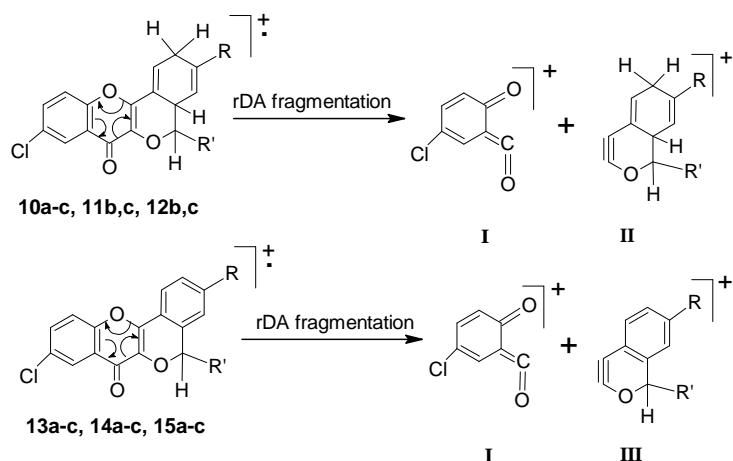
The deoxygenated benzene solutions of these chromones were irradiated with pyrex filtered light from the 125 W mercury arc lamp. The progress of these photoreactions was monitored by TLC. The column chromatographic work up of the photolysates yielded dihydrocyclised **10a-c**, **11b,c** and **12b,c** and dehydrogenated cyclised **13a-c**, **14a-c** and **15a-c** products (**Scheme I**). The structures of these photoproducts could be assigned from their spectral characterization (see Experimental Section).

The mass spectra of the photoproducts proved very helpful in the corroboration of their structures. All the compounds provided rDA fragments (**Scheme II**) in their spectra which are the characteristic fragments of the chromone moieties<sup>8</sup> (**Table I**).

The stereochemical features of the dihydrophenyl compounds **10a-c**, **11b,c** and **12b,c** were deduced from the correlation between dihedral angle ( $\phi$ ) and coupling constant<sup>9</sup> ( $J$ ). The hydrogen atoms at C-4a and C-5 in **10a,b**, **11b** and **12b** were disposed *cis* to each other ( $J_{4a,5}=11$ Hz,  $\phi\sim 0^\circ$ ). The coupling constant between the same hydrogens (H-4a and 5) was found to be about 8.5-9.0Hz ( $\phi\sim 20^\circ$ ) in **10c**, **11c** and **12c**



Scheme I



Scheme II

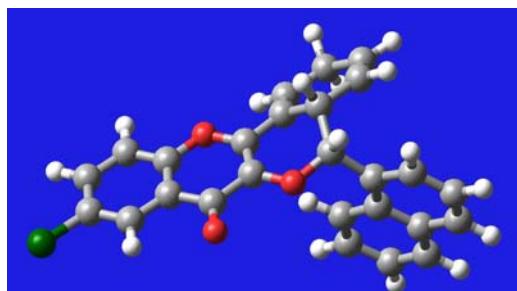
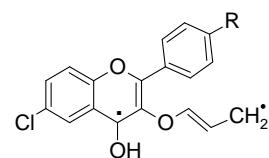
which also reflects their *cis* relationship. Here, pyran ring C is present in the pseudo chair form and R' group at C-5 occupies pseudo equatorial disposition which is not without precedent because the heavier group always prefers equatorial disposition in cyclohexane<sup>10</sup>. In these molecules, ring D being 'exo' to pyran ring C and H-4a and H-5 are above the plane of molecule. The energy-minimized structure<sup>11</sup> of compound **10c** has been shown in **Figure 1**.

Inspite of repeated and best efforts, it was not possible to isolate dihydrocyclised products similar to **10a** from the irradiation of chromones **5a** and **6a**. Although the TLC of their photolysates exhibited the formation of such products, these were formed in such extremely low yields that their isolation in pure state had always remained unsuccessful.

Mechanistically, these phototransformations could be ascribed to the easy intramolecular H-abstraction

**Table I** — rDA fragments of the photoproducts

Entry	Compd	Molecular ion ( <i>m/z</i> )	rDA fragments ( <i>m/z</i> )		Entry	Compd	Molecular ion ( <i>m/z</i> )	rDA fragments ( <i>m/z</i> )	
			I	II				I	III
1	<b>10a</b>	358	154/156	204	8	<b>13a</b>	356	154/156	202
2	<b>10b</b>	312	154/156	158	9	<b>14a</b>	370	154/156	216
3	<b>11b</b>	326	154/156	172	10	<b>15a</b>	386	154/156	232
4	<b>12b</b>	342	154/156	188	11	<b>13b</b>	310	154/156	156
5	<b>10c</b>	412	154/156	258	12	<b>14b</b>	324	154/156	170
6	<b>11c</b>	426	154/156	272	13	<b>15b</b>	340	154/156	186
7	<b>12c</b>	442	154/156	288	14	<b>13c</b>	410	154/156	256
					15	<b>14c</b>	424	154/156	270
					16	<b>15c</b>	440	154/156	286

**Figure 1****16****Figure 2****Table II** — Yield and distribution of photoproducts

Compd photolysed	Dihydro product yield (%)	Oxidized product yield (%)	Total photolytic conversion
<b>4a</b>	7	9	16
<b>5a</b>	-	12	12
<b>6a</b>	-	10	10
<b>4b</b>	10	30	40
<b>5b</b>	12	24	36
<b>6b</b>	12	20	32
<b>4c</b>	20	49	69
<b>5c</b>	22	42	64
<b>6c</b>	20	40	60

It is worth mentioning here that these photoreactions provided greater yields of oxidized products **13a-c**, **14a-c** and **15a-c** than their dihydroderivatives **10a-c**, **11b,c** and **12b,c**. During photoconversions, the phenyl ring at C-2 retains its aromaticity and thus stability in the former compounds, while the latter products contain dihydrophenyl ring, which is evidently nonaromatic and thus less stable.

The phototransformations of chromones **4c-6c** provided better chemical efficiency than **4b-6b** and **4a-6a**.

**Table II** shows that the total photolytic conversion, furnished by chromones **4c-6c**, has been upto an extent of four times as compared to **4a-6a** and almost

from  $C_3-OCH_2-$  groups by the photoexcited carbonyl chromophores through the six membered cyclic transition state that produced 1,4-biradicals **7a-c**, **8a-c** and **9a-c**. These intermediates further underwent cyclisation followed by [1,7]-H migration to yield dihydrocyclised products **10a-c**, **11b,c** and **12b,c** while loss of  $H_2$  molecule resulted in the dehydrogenated cyclised products **13a-c**, **14a-c** and **15a-c** (**Scheme I**). The latter were not the oxidation products of their former derivatives as further photoirradiation of the dihydro products did not provide any oxidized compound but had yielded only some unidentifiable polymeric material. So, both photoproducts were formed independently from biradical intermediates **7a-c**, **8a-c** and **9a-c**. The polarity of solvents (MeOH, THF and benzene) did not have any noticeable effect upon these photoreactions which clearly suggested the involvement of intramolecular H-abstraction.

In the case of chromones **4b-6b**, the intermediate 1,4-biradicals **7b-9b** had the opportunity to mesomerize to 1,6-biradical **16**, but that did not happen. But when ester ( $-COOEt$ ) moiety is present at the distal end of  $C_3$ -allyloxy chain, the initially formed 1,4-biradical mesomerizes to vinyl ether<sup>7</sup> (**Figure 2**).

double than **4b-6b**. These results may be ascribed to the relative stabilities of 1,4-biradicals **7a-c**, **8a-c** and **9a-c** involved in these photoreactions. Although allylic radicals<sup>12</sup> are more stable than benzylic radicals, in this case, however, naphthalene moiety provides greater delocalization to biradicals **7c-9c** that suggests their higher stability as compared to **7b-9b**. Although, ester group ( $-\text{COOEt}$ ) provides the possibility to the 1,4-biradicals **7a-9a** to mesomerize, but in this case it appears that electron withdrawing inductive effect may offset this behavior<sup>13</sup>, thus generating the least stable biradicals **7a-9a**.

## Experimental Section

Melting points reported are uncorrected. IR spectra were recorded on a Perkin Elmer spectrometer using KBr pellets and UV-Vis spectra on Elico SL-164 spectrometer.  $^1\text{H}$  NMR spectra were recorded on a 400 MHz Bruker spectrometer using TMS as internal standard. The mass spectra were recorded on Shimadzu QP-5000. TLC plates were coated with silica gel G suspended in MeOH-CHCl<sub>3</sub>. Silica gel (100-200 mesh) was used for column chromatography.

### Synthesis of chromones **4a-c**, **5a-c** and **6a-c**

**Ethyl[(6-chloro-4-oxo-2-phenyl-4H-chromen-3-yl)oxy]acetate, 4a:** A suspension of 6-chloro-3-hydroxy-2-phenyl-4H-chromen-4-one<sup>5d</sup> **1** (2.7 g, 0.01 mol), bromoethyl acetate (1.65 g, 0.01 mol), freshly ignited K<sub>2</sub>CO<sub>3</sub> (1.0 g) and tetrabutylammonium iodide (1.0 g) in dry acetone (25 mL) was refluxed for 1hr with stirring. A subsequent filtration of the reaction mixture followed by distillation of the solvent yielded a light yellow solid product that was percolated through a column of silica-gel (60-120 mesh) using petroleum ether-benzene (1:1) as eluent and that was further purified by recrystallization from EtOH to afford **4a**.

**4a:** Yield (2.9 g, 83%); white needles; m.p. 104-05°C; IR (KBr): 1745, 1630 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 343 (15600), 328 (11200), 260 (12000);  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  8.20 (1H, d,  $J_{\text{m}}=2.4\text{Hz}$ , H-5), 8.15 (1H, m, H-2', 6'), 7.62 (1H, d,  $J_{\text{m},0}=2.6$ , 8.9Hz, H-7), 7.53 (3H, m, H-3', 4', 5'), 7.51 (1H, d,  $J_{\text{o}}=8.9\text{Hz}$ , H-8), 4.88 (2H, s, C<sub>3</sub>-OCH<sub>2</sub>), 4.17 (2H, q,  $J_{\text{vic}}=8.1\text{Hz}$ , H-1''), 1.23 (3H, t,  $J_{\text{vic}}=8.1\text{Hz}$ , H-2''); MS:  $m/z$  358 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>19</sub>H<sub>15</sub>O<sub>5</sub>Cl: C, 63.69; H 4.19. Found: C, 63.73; H, 4.23%.

**Ethyl[(6-chloro-4-oxo-2(4-methylphenyl)-4H-chromen-3-yl)oxy]acetate, 5a:** The chromone **5a** was synthesized by reacting **2<sup>5d</sup>** (2.85 g, 0.01 mol) with

bromoethyl acetate (1.65 g, 0.01 mol) under similar conditions as used for **4a**.

**5a:** Yield (3.0 g, 81%); white needles; m.p. 124-25°C; IR (KBr): 1745, 1630 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 345 (15300), 320 (11800), 260 (13100);  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  8.21 (1H, d,  $J_{\text{m}}=2.6\text{Hz}$ , H-5), 8.10 (1H, d,  $J_{\text{t}}=2.0$ , 7.5Hz, H-2', 6'), 7.63 (1H, dd,  $J_{\text{m},0}=2.6$ , 8.9Hz, H-7), 7.34 (2H, d,  $J_{\text{o}}=8.9\text{Hz}$ , H-3', 5'), 7.22 (1H, d,  $J_{\text{o}}=8.9\text{Hz}$ , H-8), 4.88 (2H, s, C<sub>3</sub>-OCH<sub>2</sub>), 4.19 (2H, q,  $J_{\text{vic}}=7.5\text{Hz}$ , H-1''), 2.46 (3H, s, C<sub>4'</sub>-CH<sub>3</sub>), 1.24 (3H, t,  $J_{\text{vic}}=7.5\text{Hz}$ , H-2''); MS:  $m/z$  372 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>19</sub>H<sub>15</sub>O<sub>5</sub>Cl: C, 64.52; H, 4.57. Found: C, 64.50; H, 4.55%.

**Ethyl [{6-chloro-4-oxo- 2 (4-methoxyphenyl)-4H-chromen-3-yl}oxy]acetate, 6a:** The chromone **6a** was synthesized by reacting **3<sup>5d</sup>** (3.0 g, 0.01 mol) with bromoethyl acetate (1.65 g, 0.01 mol) under similar conditions as applied for **4a**.

**6a:** Yield (2.9 g, 75%); white needles; m.p. 109-10°C; IR (KBr): 1732, 1634 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 340 (17300), 325 (10400), 258 (15000);  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  8.20 (1H, d,  $J_{\text{m}}=2.5\text{Hz}$ , H-5), 8.18 (2H, m, H-2', 6'), 7.60 (1H, dd,  $J_{\text{m},0}=2.5$ , 8.9Hz, H-7), 7.50 (1H, dd,  $J_{\text{o}}=8.9\text{Hz}$ , H-8), 7.02 (2H, d,  $J_{\text{t}}=2.0$ , 7.5Hz, H-3', 5'), 4.85 (2H, s, C<sub>3</sub>-OCH<sub>2</sub>), 4.21 (2H, q,  $J_{\text{vic}}=7.2\text{Hz}$ , H-1''), 3.89 (3H, s, C<sub>4'</sub>-OCH<sub>3</sub>), 1.23 (3H, t,  $J_{\text{vic}}=7.2\text{Hz}$ , H-2''); MS:  $m/z$  388 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>19</sub>H<sub>15</sub>O<sub>5</sub>C: C, 61.86; H, 4.38. Found: C, 61.82; H, 4.39%.

**3-(Allyloxy)-6-chloro-2-phenyl-4H-chromen-4-one, 4b:** The chromone **4b** was synthesized by reacting **1<sup>5d</sup>** (2.7 g, 0.01 mol) with allyl bromide (1.2 g, 0.01 mol) under similar conditions as applied for **4a**.

**4b:** Yield (2.7 g, 87%); white powder; m.p. 86-87°C; IR (KBr): 1641 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 343 (15100), 320 (13300), 250 (11500);  $^1\text{H}$  NMR (CDCl<sub>3</sub>):  $\delta$  8.21 (1H, d,  $J_{\text{m}}=2.6\text{Hz}$ , H-5), 8.10 (2H, m, H-2', 6'), 7.62 (1H, dd,  $J_{\text{m},0}=2.6$ , 8.9Hz, H-7), 7.53 (1H, m, H-3', 4', 5'), 7.51 (1H,  $J_{\text{o}}=8.9\text{Hz}$ , H-8), 5.98 (1H, dd,  $J_{1'',\alpha}=10.3\text{Hz}$ ,  $J_{1'',\beta}=17.1\text{Hz}$ , H-1''), 5.28 (1H, dd,  $J_{\text{allyl}}=1.4\text{Hz}$ ,  $J_{\beta,1''}=17.1\text{Hz}$ , H- $\beta$ ), 5.17 (1H, dd,  $J_{\text{allyl}}=1.4\text{Hz}$ ,  $J_{\alpha,1''}=10.3\text{Hz}$ , H- $\alpha$ ), 4.63 (2H, d,  $J_{\text{dd}}=1.2\text{Hz}$ ,  $J_{\text{vic}}=6.1\text{Hz}$ , C<sub>3</sub>-OCH<sub>2</sub>); MS:  $m/z$  312 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>18</sub>H<sub>13</sub>O<sub>3</sub>Cl: C, 69.23; H, 4.17. Found: C, 69.20; H, 4.19%.

**3-(Allyloxy)-6-chloro- 2(4-methylphenyl)-4H-chromen-4-one, 5b:** The chromone **5b** was synthesized by reacting **2** (Ref. 5d) (2.85 g, 0.01 mol) with allyl bromide (1.2 g, 0.01 mol) under similar conditions as used for **4a**.

**5b:** Yield (2.7 g, 84%); white powder; m.p. 82-83°C; IR (KBr): 1634 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 338 (16300), 315 (10200), 254 (13200); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.20 (1H, d,  $J_{m}=2.6$ Hz, H-5), 8.00 (2H, q,  $J_{p,o}=1.0$ , 6.6Hz, H-2', 6'), 7.61 (1H, dd,  $J_{m,o}=2.6$ , 8.9Hz, H-7), 7.50 (1H, d,  $J_o=8.9$  Hz, H-8), 7.33 (2H, d,  $J_o=8.0$ Hz, H-3', 5'), 5.97 (1H, dd,  $J_{1'',\alpha}=10.3$ Hz,  $J_{1'',\beta}=17.1$ Hz, H-1''), 5.30 (1H, dd,  $J_{allyl}=1.4$ Hz,  $J_{\beta,1''}=17.1$ Hz, H-β), 5.17 (1H, dd,  $J_{allyl}=1.4$ Hz,  $J_{\alpha,1''}=10.3$ Hz, H-α), 4.63 (2H, d{dd},  $J_{allyl}=1.3$ Hz,  $J_{vic}=6.0$ Hz, C<sub>2</sub>-OCH<sub>2</sub>), 2.44 (3H, s, C<sub>4'</sub>-CH<sub>3</sub>); MS: *m/z* 326 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>19</sub>H<sub>15</sub>O<sub>3</sub>Cl: C, 69.94; H, 4.60. Found: C, 69.91; H, 4.62%.

**3-(Allyloxy)-6-chloro-2(4-methoxyphenyl)-4H-chromen-4-one, 6b:** The chromone **6b** was synthesized by reacting **3** (Ref. 5d) (3.0 g, 0.01 mol) with allyl bromide (1.2 g, 0.01 mol) under similar conditions as used for **4a**.

**6b:** Yield (2.9 g, 85%); white powder; m.p. 98-99°C; IR (KBr): 1634 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 345 (16600), 325 (13100), 259 (13900); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.21 (1H, d,  $J_{m}=2.6$ Hz, H-5), 8.12 (2H, dd,  $J_{p,o}=1.2$ , 6.9Hz, H-2', 6'), 7.60 (1H, dd,  $J_{m,o}=2.6$ , 8.9Hz, H-7), 7.5 (1H, d,  $J_o=9.0$ Hz, H-8), 7.03 (2H, dd,  $J_{m,o}=2.6$ , 7.5Hz, H-3', 5'), 5.98 (1H, dd,  $J_{1'',\alpha}=10.3$ Hz,  $J_{1'',\beta}=17.1$ Hz, H-1''), 5.31 (1H, dd,  $J_{allyl}=1.5$ Hz,  $J_{\beta,1''}=17.1$ Hz, H-β), 5.18 (1H, d{dd},  $J_{allyl}=1.1$ Hz,  $J_{\alpha,1''}=10.4$ Hz, H-α), 4.64 (2H, dd,  $J_{allyl}=1.2$ Hz,  $J_{vic}=6.2$ Hz, C<sub>3</sub>-OCH<sub>2</sub>), 3.90 (3H, s, C<sub>4'</sub>-OCH<sub>3</sub>); MS: *m/z* 342 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>19</sub>H<sub>15</sub>O<sub>4</sub>Cl: C, 66.67; H 4.39. Found: C, 66.70; H, 4.36%.

**6-Chloro-3-(1-naphthylmethoxy)-2-phenyl-4H-chromen-4-one, 4c:** The chromone **4c** was synthesized by reacting **1** (Ref. 5d) (2.7 g, 0.01 mol) with 1-chloromethylnaphthalene (1.75 g, 0.01 mol) under similar conditions as applied for **4a**.

**4c:** Yield (3 g, 74%); white needles; m.p. 126-27°C; IR (KBr): 1640 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 340 (14300), 322 (12100), 245 (13000); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.35 (1H, m, H-8''), 8.33 (1H, d,  $J_{m}=2.5$ Hz, H-5), 7.88 (2H, m, H-2', 6'), 7.81 (2H, m, H-7'', 6''), 7.65 (1H, dd,  $J_{m,o}=2.5$ , 8.9Hz, H-7), 7.50 (1H, d,  $J_o=8.9$ Hz, H-8), 7.48 (3H, m, H-3', 4', 5'), 7.40 (2H, m, H-2'', 3''), 7.32 (2H, m, H-4'', 5''), 5.57 (2H, s, C<sub>3</sub>-OCH<sub>2</sub>); MS: *m/z* 412 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>26</sub>H<sub>17</sub>O<sub>3</sub>Cl: C, 75.73; H, 4.13. Found: C, 75.71; H, 4.17%.

**6-Chloro-3-(1-naphthylmethoxy)-2 (4-methylphenyl)-4H-chromen-4-one, 5c:** The chromone **5c** was

synthesized by reacting **2** (Ref. 5d) (2.85 g, 0.01 mol) with 1-chloromethylnaphthalene (1.75 g, 0.01 mol) under similar conditions as used for **4a**.

**5c:** Yield (3.1 g, 73%); white needles; m.p. 142-43°C; IR (KBr): 1634 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 330 (16500), 320 (12100), 251 (17000); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.40 (1H, m, H-8''), 8.32 (1H, d,  $J_{m}=2.6$ Hz, H-5), 7.80 (4H, m, H-2', 6', 6'', 7''), 7.65 (1H, dd,  $J_o=8.9$ Hz,  $J_{m}=2.8$ Hz, H-7), 7.51 (1H, d,  $J_o=8.9$ Hz, H-8), 7.49 (2H, m, H-3', 5'), 7.40 (2H, m, H-2'', 3''), 7.10 (2H, d,  $J_o=8.2$ Hz, H-4'', 5''), 5.55 (2H, s, C<sub>3</sub>-OCH<sub>2</sub>), 2.38 (3H, s, C<sub>4'</sub>-CH<sub>3</sub>); MS: *m/z* 426 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>27</sub>H<sub>19</sub>O<sub>3</sub>Cl: C, 76.06; H, 4.46. Found: C, 76.08; H, 4.49%.

**6-Chloro-3-(1-naphthylmethoxy)-2(4-methoxyphenyl)-4H-chromen-4-one, 6c:** The chromone **6c** was synthesized by reacting **3** (Ref. 5d) (3.0 g, 0.01 mol) with 1-chloromethylnaphthalene (1.75 g, 0.01 mol) under similar conditions as used for **4a**.

**6c:** Yield (3.3 g, 76%); white needles; m.p. 146-47°C; IR (KBr): 1634 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 335 (14600), 322 (12100), 260 (16600); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.45 (1H, dd,  $J_{p,o}=1.0$ , 8.2Hz, H-8''), 8.30 (1H, d,  $J_{m}=2.6$ Hz, H-5), 7.89 (2H, m, H-2', 6'), 7.82 (2H, dd,  $J=6.4$ Hz,  $J=7.8$ Hz, H-6'', 7''), 7.61 (1H, dd,  $J_{m,o}=2.6$ , 8.9Hz, H-7), 7.46 (5H, m, H-8, 2'', 3'', 4'', 5''), 6.80 (2H, t{d},  $J_{m,o}=3.0$ , 9.0Hz, H-3', 5'), 5.54 (2H, s, C<sub>3</sub>-OCH<sub>2</sub>), 3.84 (3H, s, C<sub>4'</sub>-OCH<sub>3</sub>); MS: *m/z* 442 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>27</sub>H<sub>19</sub>O<sub>4</sub>Cl: C, 73.30; H, 4.30. Found: C, 73.28; H, 4.32%.

#### Photoirradiation of chromones 4a-c, 5a-c and 6a-c

**Photolysis of ethyl[6-chloro-4-oxo-2-phenyl-4H-chromen-3-yl]oxy]acetate, 4a:** A deoxygenated solution of **4a** (200 mg, 0.00056 mol) in dry benzene (200 mL) was photolysed with light from a 125 W mercury lamp in a pyrex reactor under nitrogen atmosphere for 1 hr. The progress of reaction was monitored by TLC. The solvent was distilled out under reduced pressure to obtain a dark gummy viscous mass, which was chromatographed over a column of silica gel (100-200 mesh) packed in petroleum ether-benzene (2:3). Elution of column with benzene-EtOAc (3:1) gave starting compound **4a** (60%, co-TLC and m.m.p.), and two new compounds **10a** and **13a**.

**10a:** Yield (14 mg, 7%); light yellow powder; m.p. 168-70°C; IR (KBr): 1650 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 325 (13100), 283 (12200), 239 (21000); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.34 (1H, d,  $J_{m}=2.5$ Hz, H-8), 7.65 (1H, dd,  $J_{m,o}=2.6$ , 8.8Hz, H-10), 7.50 (1H, d,

$J_o=8.9$ Hz, H-11), 6.81 (1H, d,  $J_{1,2a}=2.0$ Hz, H-1), 5.90 (1H, dd,  $J_{3,2a}=2.0$ Hz,  $J_{3,4}=10.0$ Hz, H-3), 5.70 (1H, d,  $J_{4,3}=10.0$ Hz, H-4), 4.20 (1H, d,  $J_{4a5}=11.0$ Hz, H-5), 3.50 (1H, dd,  $J_{5,4a}=11.0$ Hz,  $J_{4a,3}=2.0$ Hz, H-4a), 3.0 (2H, br s, H-2a); MS:  $m/z$  358 ( $M^+$ , 40%). Anal. Calcd. for  $C_{19}H_{15}O_5Cl$ : C, 63.69; H, 4.19. Found: C, 63.66; H, 4.18%.

**13a:** Yield (18 mg, 9%); pale yellow powder; m.p. 200-01°C; IR (KBr): 1640  $\text{cm}^{-1}$  (C=O); UV-Vis (THF): nm 330 (11300), 290 (15200), 230 (20000);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.30 (1H, d,  $J_m=2.7$ Hz, H-8), 7.87 (2H, dd,  $J=4.6$ , 7.8Hz, H-1, 2), 7.63 (1H, d,  $J_{m,o}=2.7$ , 8.9Hz, H-10), 7.60 (1H, d,  $J_o=8.9$ Hz, H-11), 7.42 (2H, m, H-3, 4), 5.87 (1H, s, H-5), 4.19 (2H, q,  $J_{\text{vic}}=7.5$ Hz, H-1''), 1.18 (3H, t,  $J_{\text{vic}}'=7.5$ Hz, H-2''); MS:  $m/z$  356 ( $M^+$ , 100%). Anal. Calcd. for  $C_{19}H_{13}O_5Cl$ : C, 64.04; H, 3.63. Found: C, 64.01; H, 3.65%.

**Photolysis of ethyl{[-6-chloro-4-oxo-2(4-methyl-phenyl)-4H-chromen-3-yl]oxy}acetate, 5a:** The benzene solution of **5a** (200 mg, 0.00054 mol) was photolysed under similar conditions as described for **4a**. The photolysate on chromatographic separation provided one new compound **14a**.

**14a:** Yield (24 mg, 12%); light yellow powder; m.p. 208-10°C; IR (KBr): 1642  $\text{cm}^{-1}$  (C=O); UV-Vis (THF): nm 340 (13100), 290 (14400), 240 (19300);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.31 (1H, d,  $J_m=2.6$ Hz, H-8), 7.77 (1H, d,  $J_o=8.1$ Hz, H-1), 7.63 (1H, dd,  $J_{m,o}=2.6$ , 8.9Hz, H-10), 7.54 (1H, d,  $J_o=8.9$ Hz, H-11), 7.35 (1H, m, H-2), 7.25 (1H, d,  $J_m=2.3$ Hz, H-4), 5.84 (1H, s, H-5), 4.19 (2H, q,  $J_{\text{vic}}=7.5$ Hz, H-1''), 2.47 (3H, s,  $C_3-CH_3$ ), 1.22 (3H, t,  $J_{\text{vic}}=7.5$ Hz, H-2''); MS:  $m/z$  370 ( $M^+$ , 100%). Anal. Calcd. for  $C_{20}H_{15}O_5Cl$ : C, 64.86; H, 4.03. Found: C, 64.83; H, 4.00%.

**Photolysis of ethyl{[-6-chloro-4-oxo-2(4-methoxy-phenyl)-4H-chromen-3-yl]oxy}acetate, 6a:** The benzene solution of **6a** (200 mg, 0.00052 mol) was photolysed under similar conditions as described for **4a**. The photolysate on chromatographic separation furnished one new compound **15a**.

**15a:** Yield (20 mg, 10%); light yellow powder; m.p. 220-22°C; IR (KBr): 1643  $\text{cm}^{-1}$  (C=O); UV-Vis (THF): nm 345 (14100), 295 (12100), 251 (21600);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.32 (1H, d,  $J_m=2.6$ Hz, H-8), 7.82 (1H, d,  $J_o=8.6$ Hz, H-1), 7.61 (1H, dd,  $J_{m,o}=2.5$ , 8.9Hz, H-10), 7.51 (1H, d,  $J_o=8.9$ Hz, H-11), 7.05 (1H, dd,  $J_{m,o}=2.4$ , 8.6Hz, H-2), 6.94 (1H, d,  $J_m=2.3$ Hz, H-4), 5.84 (1H, s, H-5), 4.18 (2H, m,  $J_{\text{vic}}=7.1$ Hz, H-1''), 3.92 (3H, s,  $C_3-OCH_3$ ), 1.21 (3H, t,  $J_{\text{vic}}'=7.1$ Hz,

H-2''); MS:  $m/z$  386 ( $M^+$ , 100%). Anal. Calcd. for  $C_{20}H_{15}O_6Cl$ : C, 62.18; H, 3.89. Found: C, 62.16; H, 3.92%.

**Photolysis of 3-(allyloxy)-6-chloro-2-phenyl-4H-chromen-4-one, 4b:** The benzene solution of **4b** (200 mg, 0.00064 mol) was photolysed under similar conditions as described for **4a**. The chromatographic separation of photolysate yielded two new compounds **10b** and **13b**.

**10b:** Yield (20 mg, 10%); light yellow powder; m.p. 168-70°C; IR (KBr): 1657  $\text{cm}^{-1}$  (C=O); UV-Vis (THF): nm 335 (11300), 292 (22200), 260 (15000);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.20 (1H, d,  $J_m=2.5$ Hz, H-8), 7.60 (1H, dd,  $J_{m,o}=2.5$ , 8.9Hz, H-10), 7.50 (1H, d,  $J_o=8.9$ Hz, H-11), 6.85 (1H, br s, H-1), 6.0 (1H, d{dd},  $J_{1',5}=5.5$ Hz,  $J_{1',\alpha}=10.4$ Hz,  $J_{1',\beta}=16.0$ Hz, H-1''), 5.85 (1H, dd,  $J_{3,2a}=2.0$ Hz,  $J_{3,4}=10.0$ Hz, H-3), 5.70 (1H, d,  $J_{4,3}=10.0$ Hz, H-4), 5.20 (1H, d,  $J_{\alpha_1''}=10.3$ Hz, H- $\alpha$ ), 5.15 (1H, d,  $J_{\beta_1''}=17.7$ Hz, H- $\beta$ ), 4.50 (1H, d,  $J_{5,4a}'=11.0$ Hz, H-5), 3.60 (1H, d,  $J=11.0$ Hz, H-4a), 2.80 (2H, m, H-2a); MS:  $m/z$  312 ( $M^+$ , 60%). Anal. Calcd. for  $C_{18}H_{13}O_3Cl$ : C, 69.23; H, 4.17. Found: C, 69.20; H, 4.15%.

**13b:** Yield (60 mg, 30%); light yellow solid; m.p. 210-12°C; IR (KBr): 1640  $\text{cm}^{-1}$  (C=O); UV-Vis (THF): nm 342 (12100), 292 (16200), 240 (11700);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.24 (1H, d,  $J_m=2.6$ Hz, H-8), 8.00 (1H, d,  $J_{m,o}=2.3$ , 8.6Hz, H-1), 7.62 (1H, dd,  $J_m=2.4$ Hz,  $J_{m,o}=2.6$ , 8.9Hz, H-10), 7.57 (1H, d,  $J_o=8.9$ Hz, H-11), 7.5 (3H, m, H-2, 3, 4), 6.05 (1H, d{dd},  $J_{1',5}=5.5$ Hz,  $J_{1',\alpha}=10.5$ Hz,  $J_{1',\beta}=16.5$ Hz, H-1''), 5.30 (1H, d,  $J_{\alpha_1''}=10.4$ Hz, H- $\alpha$ ), 5.15 (1H, d,  $J_{\beta_1''}=17.2$ Hz, H- $\beta$ ), 4.85 (1H, d,  $J_{5,1}'=5.5$ Hz, H-5); MS:  $m/z$  310 ( $M^+$ , 50%). Anal. Calcd. for  $C_{18}H_{11}O_3Cl$  requires C, 69.68; H, 3.55. Found: C, 69.70; H, 3.53%.

**Photolysis of 3-(allyloxy)-6-chloro-2(4-methyl-phenyl)-4H-chromen-4-one, 5b:** The benzene solution of **5b** (200 mg, 0.00061 mol) was photolysed under similar conditions as described for **4a**. The photolysate on chromatographic separation afforded two new compounds **11b** and **14b**.

**11b:** Yield (24 mg, 12%); light yellow powder; m.p. 160-62°C; IR (KBr): 1651  $\text{cm}^{-1}$  (C=O); UV-Vis (THF): nm 330 (23100), 285 (15200), 250 (13000);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.23 (1H, d,  $J_m=2.5$ Hz, H-8), 7.65 (1H, dd,  $J_{m,o}=2.5$ , 8.9Hz, H-10), 7.51 (1H, d,  $J_o=8.9$ Hz, H-11), 6.80 (1H, br s, H-1), 5.50 (1H, br s, H-4), 6.00 (1H, d{dd},  $J_{1',5}=5.5$ Hz,  $J_{1',\alpha}=10.4$ Hz,  $J_{1',\beta}=16.0$ Hz, H-1''), 5.30 (1H, d,  $J_{\alpha_1''}=10.3$ Hz, H- $\alpha$ ),

5.21 (1H, d,  $J_{\beta 1}''=17.0$ Hz, H- $\beta$ ), 5.45 (1H, d,  $J_{5,4a}=11.0$ Hz, H-5), 3.50 (1H, d,  $J_{4a,5}=11.0$ Hz, H-4a), 3.50 (3H, s,  $C_3$ -OCH<sub>3</sub>), 2.90 (2H, m, H-2a); MS:  $m/z$  326 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>19</sub>H<sub>15</sub>O<sub>3</sub>Cl C, 69.94; H, 4.60. Found: C, 69.91; H, 4.58%.

**14b:** Yield (48 mg, 24%); light yellow powder; m.p. 200-02°C; IR (KBr): 1639 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 338 (12100), 274 (17200), 245 (20300); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.26 (1H, d,  $J_m=2.5$ Hz, H-8), 7.76 (1H, d,  $J_o=8.0$ Hz, H-1), 7.60 (1H, dd,  $J_{m,o}=2.5$ , 8.9Hz, H-10), 7.51 (1H, d,  $J_o=8.9$ Hz, H-11), 6.98 (2H, m, H-2, 4), 6.05 (1H, d{dd},  $J_{1',5}=5.5$ Hz,  $J_{1',\alpha}=10.5$ Hz,  $J_{1',\beta}=16.5$ Hz, H-1''), 5.32 (1H, d,  $J_{\alpha 1}''=10.3$ Hz, H- $\alpha$ ), 5.20 (1H, d,  $J_{\beta 1}''=17.2$ Hz, H- $\beta$ ), 5.00 (1H, d,  $J_{5,1}''=5.5$ Hz, H-5), 2.25 (3H, s,  $C_3$ -CH<sub>3</sub>); MS:  $m/z$  324 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>19</sub>H<sub>13</sub>O<sub>3</sub>Cl: C, 70.37; H, 4.01. Found: C, 70.35; H, 4.03%.

**Photolysis of 3-(allyloxy)-6-chloro-2(4-methoxy-phenyl)-4H-chromen-4-one, 6b:** The benzene solution of **6b** (200 mg, 0.00058 mol) was photolysed under similar conditions as described for **4a**. The chromatographic work up of photolysate provided the two new compounds **12b** and **15b**.

**12b:** Yield (24 mg, 12%); light yellow powder; m.p. 178-80°C; IR (KBr): 1654 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 335 (21500), 285 (13200), 253 (9000); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.23 (1H, d,  $J_m=2.5$ Hz, H-8), 7.55 (1H, dd,  $J_{m,o}=2.5$ , 8.9Hz, H-10), 7.45 (1H, d,  $J_o=8.9$ Hz, H-11), 6.71 (1H, br s, H-1), 6.10 (1H, d{dd},  $J_{1',5}=5.5$ Hz,  $J_{1',\alpha}=10.4$ Hz,  $J_{1',\beta}=16.0$ Hz, H-1''), 5.25 (1H, br s, H-4), 5.20 (1H, d,  $J_{\alpha 1}''=10.1$ Hz, H- $\alpha$ ), 5.11 (1H, d,  $J_{\beta 1}''=17.0$ Hz, H- $\beta$ ), 4.50 (1H, d,  $J_{5,4a}'=10.6$ Hz, H-5), 4.00 (1H, d,  $J_{4a,5}=11.0$ Hz, H-4a), 3.80 (3H, s,  $C_3$ -OCH<sub>3</sub>), 2.36 (2H, q,  $J_{\text{vic}}=2.0$ Hz, H-2a); MS:  $m/z$  342 (M<sup>+</sup>, 40%). Anal. Calcd. for C<sub>19</sub>H<sub>15</sub>O<sub>4</sub>Cl: C, 66.67; H, 4.39. Found: C, 66.70; H, 4.42%.

**15b:** Yield (40 mg, 20%); light yellow powder; m.p. 218-20°C; IR (KBr): 1643 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 341 (17100), 276 (9200), 249 (19100); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.24 (1H, d,  $J_m=2.4$ Hz, H-8), 7.80 (1H, d,  $J_o=8.6$ Hz, H-1), 7.57 (1H, dd,  $J_{m,o}=2.5$ , 8.9Hz, H-10), 7.40 (1H, d,  $J_o=8.9$ Hz, H-11), 6.98 (1H, dd,  $J_{m,o}=2.4$ , 8.6Hz, H-2), 6.72 (1H, d,  $J_m=2.3$ Hz, H-4), 6.05 (1H, d{dd},  $J_{1',5}=5.5$ Hz,  $J_{1',\alpha}=10.5$ Hz,  $J_{1',\beta}=17.1$ Hz, H-1''), 5.33 (1H, d,  $J_{\alpha 1}''=10.3$ Hz, H- $\alpha$ ), 5.22 (1H, d,  $J_{\beta 1}''=17.2$ Hz, H- $\beta$ ), 5.00 (1H, d,  $J_{5,1}''=5.5$ Hz, H-5), 3.87 (3H, s,  $C_3$ -OCH<sub>3</sub>); MS:  $m/z$  340 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>19</sub>H<sub>13</sub>O<sub>4</sub>Cl: C, 67.06; H, 3.82. Found: C, 67.03; H, 3.85%.

**Photolysis of 6-chloro-3-(1-naphthylmethoxy)-2-phenyl-4H-chromen-4-one, 4c:** The benzene solution of **4c** (200 mg, 0.00048 mol) was photolysed under similar conditions as described for **4a**. The photolysate on chromatographic separation yielded two new compounds **10c** and **13c**.

**10c:** Yield (40 mg, 20%); pale yellow powder; m.p. 171-73°C; IR (KBr): 1650 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 340 (15700), 275 (11700), 245 (21000); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.30 (1H, m, H-8''), 8.20 (1H, d,  $J_m=2.5$ Hz, H-8), 7.80 (3H, m, H-5'', 6'', 7''), 7.68 (1H, dd,  $J_{m,o}=2.5$ , 8.9Hz, H-10), 7.56 (1H, d,  $J_o=8.9$ Hz, H-11), 7.50 (3H, m, H-2'', 3'', 4''), 6.60 (1H, br s, H-1), 5.90 (1H, d,  $J_{3,4}=11.0$ Hz, H-3), 5.56 (1H, dd,  $J_{4,3}=10.5$ Hz,  $J_{4,4a}=1.5$ Hz, H-4), 5.50 (1H, d,  $J_{5,4a}=8.5$ Hz, H-5), 3.80 (1H, d,  $J_{4a,5}=8.5$ Hz, H-4a), 2.80 (2H, m, H-2a); MS:  $m/z$  412 (M<sup>+</sup>, 70%). Anal. Calcd. for C<sub>26</sub>H<sub>17</sub>O<sub>3</sub>Cl: C, 75.73; H, 4.13. Found: C, 75.75; H, 4.15%.

**13c:** Yield (98 mg, 49%); pale yellow powder; m.p. 218-19°C; IR (KBr): 1640 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 345 (10900), 280 (15200), 250 (16000); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.30 (1H, m, H-8''), 8.23 (1H, d,  $J_m=2.5$ Hz, H-8), 8.02 (1H, d,  $J_o=8.5$ Hz, H-1), 7.92 (3H, m, H-5'', 6'', 7''), 7.62 (1H, dd,  $J_{m,o}=2.5$ , 9.0Hz, H-10), 7.58 (2H, m, H-2, 3), 7.51 (1H, d,  $J_o=8.9$ Hz, H-11), 7.48 (3H, m, H-2'', 3'', 4''), 7.0 (1H, m, H-4), 6.70 (1H, s, H-5); MS:  $m/z$  410 (M<sup>+</sup>, 100%). Anal. Calcd. for C<sub>26</sub>H<sub>15</sub>O<sub>3</sub>Cl C, 76.10; H, 3.66. Found: C, 76.12; H, 3.69%.

**Photolysis of 6-chloro-3-(1-naphthylmethoxy)-2(4-methylphenyl)-4H-chromen-4-one, 5c:** The benzene solution of **5c** (200 mg, 0.00047 mol) was photolysed under similar conditions as described for **4a**. The chromatographic separation of the photolysate furnished two new compounds **11c** and **14c**.

**11c:** Yield (44 mg, 22%); pale yellow powder; m.p. 178-80°C; IR (KBr): 1655 cm<sup>-1</sup> (C=O); UV-Vis (THF): nm 350 (9100), 290 (21200), 256 (11000); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.33 (1H, m, H-8''), 8.21 (1H, d,  $J_m=2.5$ Hz, H-8), 7.90 (3H, m, H-5'', 6'', 7''), 7.60 (1H, dd,  $J_{m,o}=2.5$ , 8.9Hz, H-10), 7.54 (1H, d,  $J_o=8.9$ Hz, H-11), 7.52 (3H, m, H-2'', 3'', 4''), 6.45 (1H, br s, H-1), 6.00 (1H, dd,  $J_{4,4a}=2.0$ Hz,  $J_{4,3}=10.0$ Hz, H-4), 5.50 (1H, d,  $J_{5,4a}=9.0$ Hz, H-5), 4.14 (1H, dd,  $J_{4a,4}=2.0$ Hz,  $J_{4a,5}=9.0$ Hz, H-4a), 3.00 (2H, m, H-2a), 2.29 (3H, s, H- C<sub>3</sub>-CH<sub>3</sub>); MS:  $m/z$  426 (M<sup>+</sup>, 30%). Anal. Calcd. for C<sub>27</sub>H<sub>19</sub>O<sub>3</sub>Cl: C, 76.06; H, 4.46. Found: C, 76.09; H, 4.48%.

**14c:** Yield (84 mg, 42%); pale yellow powder; m.p. 223-24°C; IR (KBr): 1638  $\text{cm}^{-1}$  (C=O); UV-Vis (THF): nm 353 (10100), 285 (11200), 240 (13500);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.32 (1H, m, H-8''), 8.22 (1H, d,  $J_m$ =2.4Hz, H-8), 8.00 (1H, d,  $J_o$ =8.5Hz, H-1), 7.90 (3H, m, H-5'', 6'', 7''), 7.65 (1H, dd,  $J_{m,o}$ =2.4, 9.0Hz, H-10), 7.53 (1H, m, H-2), 7.51 (1H, d,  $J_o$ =8.9Hz, H-11), 7.48 (3H, m, H-2'', 3'', 4''), 7.0 (1H, m, H-4), 6.40 (1H, s, H-5), 2.23 (3H, s,  $\text{C}_3\text{-CH}_3$ ); MS:  $m/z$  424 ( $\text{M}^+$ , 100%). Anal. Calcd. for  $\text{C}_{27}\text{H}_{17}\text{O}_3\text{Cl}$ : C, 76.42; H, 4.01. Found: C, 76.40; H, 4.04%.

**Photolysis of 6-chloro-3-(1-naphthylmethoxy)-2(4-methoxyphenyl)-4H-chromen-4-one, 6c:** The benzene solution of **6c** (200 mg, 0.00045 mol) was photolysed under similar conditions as described for **4a**. The photolysate on chromatographic work up afforded two new compounds **12c** and **15c**.

**12c:** Yield (40 mg, 20%); pale yellow powder; m.p. 185-87°C; IR (KBr): 1665  $\text{cm}^{-1}$  (C=O); UV-Vis (THF): nm 342 (12100), 274 (14400), 240 (9100);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.33 (1H, m, H-8''), 8.21 (1H, d,  $J_m$ =2.5Hz, H-8), 7.90 (3H, m, H-5'', 6'', 7''), 7.60 (1H, dd,  $J_{m,o}$ =2.5, 8.9Hz, H-10), 7.54 (1H, d,  $J_o$ =8.9Hz, H-11), 7.52 (3H, m, H-2'', 3'', 4''), 6.45 (1H, br s, H-1), 6.00 (1H, d,  $J_{4,3}$ =10.0Hz, H-4), 5.70 (1H, d,  $J_{5,4a}$ =8.5Hz, H-5), 4.14 (1H, dd,  $J_{4a,4}$ =2.0Hz,  $J_{4a,5}$ =8.5Hz, H-4a), 3.72 (3H, s,  $\text{C}_3\text{-OCH}_3$ ), 2.70 (2H, m, H-2a); MS:  $m/z$  442 ( $\text{M}^+$ , 50%). Anal. Calcd. for  $\text{C}_{27}\text{H}_{19}\text{O}_4\text{Cl}$ : C, 73.30; H, 4.30. Found: C, 73.32; H, 4.28%.

**15c:** Yield (80 mg, 40%); pale yellow powder; m.p. 228-30°C; IR (KBr): 1642  $\text{cm}^{-1}$  (C=O); UV-Vis (THF): nm 348 (10100), 285 (11100), 245 (19000);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.32 (1H, m, H-8''), 8.22 (1H, d,  $J_m$ =2.4Hz, H-8), 8.00 (1H, d,  $J_o$ =8.5Hz, H-1), 7.90 (3H, m, H-5'', 6'', 7''), 7.65 (1H, dd,  $J_{m,o}$ =2.4, 9.0Hz, H-10), 7.53 (1H, m, H-2), 7.51 (1H, d,  $J_o$ =8.9Hz, H-11), 7.48 (3H, m, H-2'', 3'', 4''), 7.00 (1H, m, H-4), 6.60 (1H, s, H-5), 3.72 (3H, s,  $\text{C}_3\text{-OCH}_3$ ); MS:  $m/z$  440 ( $\text{M}^+$ , 100%). Anal. Calcd. for  $\text{C}_{27}\text{H}_{17}\text{O}_4\text{Cl}$ : C, 73.64; H, 3.86. Found: C, 73.61; H, 3.89%.

## Conclusion

It may be concluded that the photoreactivity and thus the chemical efficiency of the chromones is dependent upon the nature of substituents of  $\text{C}_3\text{-OCH}_2$ - moiety. The chromones bearing naphthyl substituent yield the best chemical efficiency while the least efficiency is provided by ester containing

compounds. The vinyl substituted chromones present photoreactivity of an intermediate nature.

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## References

- 1 Wagner P J & Howbert J, *J Am Chem Soc*, 103, **1981**, 688.
- 2 (a) Hart D J & Tsai Y M, *J Am Chem Soc*, 104, **1982**, 1430; (b) Stark G & Blain N H, *J Am Chem Soc*, 104, **1982**, 2321.
- 3 (a) Scaiano J C, *Tetrahedron*, 38, **1982**, 819; (b) Yang N C & Yang D H, *J Am Chem Soc*, 80, **1958**, 2913; (c) Wagner P J, Kelso P A, Kemppainen A E, McGrath J M, Schott H N & Zepp R G, *J Am Chem Soc*, 94, **1972**, 7506; (d) Gagosian R B, Dalton J C & Turro N J, *J Am Chem Soc*, 92, **1970**, 4752; (e) Lewis F D & Hilliard T A, *J Am Chem Soc*, 94, **1972**, 3852.
- 4 (a) Coyle D J, Peterson R V & Heicklen J, *J Am Chem Soc*, 86, **1964**, 3850; (b) Yates P & Pal J M, *J Am Chem Soc*, 1970, 553; (c) Stephenson L M & Parlett J L, *J Org Chem*, 36, **1971**, 1093; (d) Pappas S P & Zehr R D, *J Am Chem Soc*, 93, **1971**, 7112; (e) Lappin G R, *J Org Chem*, 36, **1971**, 1805.
- 5 (a) Matsuura T, Matsushima H & Sakamoto H, *J Am Chem Soc*, 89, **1967**, 6370; (b) Matsuura T, Matsushima H & Nakashima R, *Tetrahedron*, 26, **1970**, 435; (c) Gupta S C & Mukerjee S M, *Tetrahedron Lett*, 51, **1973**, 5073; (d) Yadav N S, Dhawan S N & Gupta S C, *J Indian Chem Soc*, 67, **1990**, 770.
- 6 (a) Gupta S C, Sharma S, Yusuf M, Arora S, Saini A, Kamboj R C & Dhawan S N, *J Chem Res(s)*, **2002**, 165; (b) Gupta S C, Yusuf M, Arora S, Sharma S, Kamboj R C & Dhawan S N, *Tetrahedron*, 58, **2002**, 3095; (c) Gupta S C, Yusuf M, Arora S & Kamboj R C, *Tetrahedron*, 59, **2003**, 3609; (d) Gupta S C, Yusuf M, Sharma S, Saini A, Arora S & Kamboj R C, *Tetrahedron*, 60, **2004**, 8445; (e) Gupta S C, Yusuf M, Thakur M & Kamboj R C, *J Chem Res(s)*, **2005**, 741; (f) Kumar R & Yusuf M, *ARKIVOC*, XI, **2006**, 239; (g) Yusuf M, Kumar R & Gupta S C, *ARKIVOC*, XV, **2006**, 28.
- 7 Gupta S C, Yusuf M, Sharma S & Arora S, *Tetrahedron Lett*, 43, **2002**, 6875.
- 8 (a) Ellis G P, *Chromenes, Chromanones and Chromones*, edited by Weisberger E C A, (John Wiley and Sons, New York), **1977**, Ch VIII, p 481; (b) Porter Q N & Baldas J, *Mass Spectrometry of Heterocyclic Compounds*, (Wiley Interscience, New York), 168, **1971**, p 148; (c) Barker G & Ellis G P, *Org Mass Spectrom*, 5, **1971**, 857.
- 9 Banks S W, Steel M J, Ward D & Dewick P M, *J Chem Soc, Chem Commun* **1982**, 156.
- 10 Karplus K & Grant D M, *Proc Nat Acad Sci, USA*, 45, **1969**, 1269.
- 11 Macro Model Program V 9.0, MM3\* Force Field.
- 12 (a) Tsang W, *J Am Chem Soc*, 107, **1985**, 2872; (b) Holmes J L, Lossing F P & MacColl A, *J Am Chem Soc*, 110, **1988**, 7339; (c) Holmes J L & Lossing F P, *J Am Chem Soc*, 110, **1988**, 7343.
- 13 Wagner P J, *J Am Chem Soc*, **1970**, 4, 168.