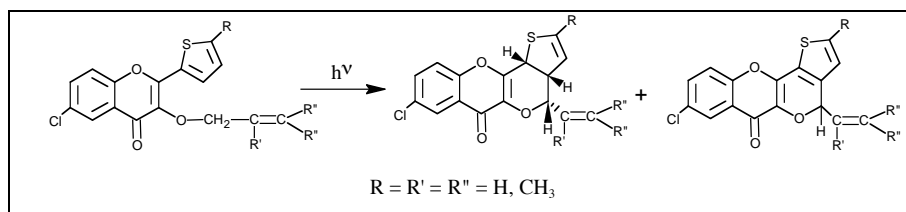


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Photoreorganisations of some 3-allyloxy-2-thienylchromones have been described. The photoreactions are initiated through the intramolecular H-abstraction to provide angular tetracyclic compounds. These chromones yield good chemical efficiency due to the involvement of highly stabilized allylic 1,4-biradicals.

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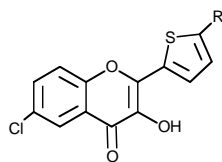
INTRODUCTION

Photochemical H-abstraction in the carbonyl substrates has been proved an exciting synthetic tool for the generation of numerous exotic carbocyclic and heterocyclic compounds [1-11]. 3-Alkoxy-2-arylchromones [12-16] undergo intramolecular photo-H-abstraction to provide the tetracyclic products. Earlier, we have reported some results upon the phototransformations of 3-alkoxy [17-26] and crotyloxy chromones [27]. The former give photoproducts through the cyclisation of 1,4-biradical, while the latter yields vinyl ether through the involvement of 1,6-biradical [27]. To investigate the detailed behavior of these biradicals, the researches have been focused on the 3-allyloxychromones **3a-3c** and **4a-4c**. The major interest in this study was twofold:

(i) How the allyloxy group at C-3 in place of methoxy and benzyloxy affects the course of photoreaction.

(ii) How the electron donating (methyl) substituent on the allyloxy group and thiophene ring affects the photoproducts formation and their distribution.

RESULTS AND DISCUSSION



1. R = H
2. R = CH₃

Figure 1

The 2-thienylchromones **3a-3c** and **4a-4c** required for this study were synthesized by reacting the 3-

hydroxychromones [25], **1** and **2** with an appropriate allylhalide in the presence of freshly ignited K₂CO₃, dry acetone and Bu₄N⁺I⁻ as phase transfer catalyst (PTC). The usual work up of the reaction mixtures provided yellow solids that were percolated through the columns of silica gel (60-120 mesh) and crystallized from EtOH to furnish the colorless needles of **3a-3c** and **4a-4c**. The structures of these chromones were deduced from the rigorous analysis of their spectral data (see experimental)

The benzene solutions of chromones **3a-3c** and **4a-4c** under N₂ atmosphere were irradiated with pyrex filtered light from a 125 W mercury arc lamp. The tlc of the photolytic mixture generally exhibited two major spots below the starting material and some unidentifiable polymeric material at the bottom in the form of tailing. The column chromatographic separation of the photolysates yielded dihydrocyclised **5a-5c**, **7a** and **7c** and dehydrocyclised **6a-6c** and **8a-8c** compounds.

The mass spectra of the photo products proved very instrumental in the interpretation of their structures. The dihydrocyclised compounds **5a-5c**, **7a** and **7c** exhibited the molecular ions at the value similar to starting chromones, indicating that during the photo conversion only reorganization has occurred. The retention of the benzopyrone moiety in these compounds was confirmed by the appearance of ions at m/z 154/156 as this fragment becomes available only through the retro Diels Alder (rDA) mode of cleavage of benzopyrone ring [28-30] (Scheme 2 and Table 1).

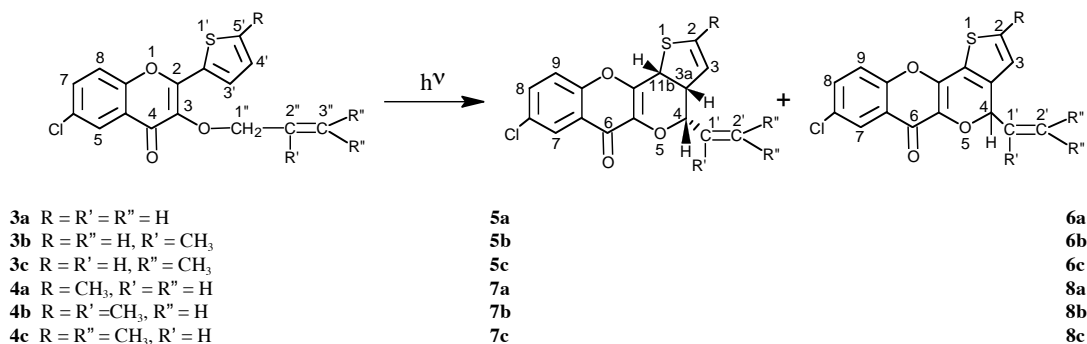
The dehydrocyclised products **6a-6c** and **8a-8c** displayed highest mass peaks that are two mass units less than their starting materials indicating the loss of a hydrogen molecule during the photo conversion. Again rDA fragment at m/z 154/156 confirmed the retention of benzopyrone moiety [28-30] (Scheme 2 and Table 1).

Further IR and ^1H NMR (300 MHz) spectra of the photoproducts corroborated their structures (see experimental).

To elucidate the stereochemistry of **5a-5c**, **7a** and **7c**, the correlation between dihedral angle (Φ) and coupling constant (J) was invoked. The vicinal coupling (3J) between H-3a and H-11b was found to be 8.1 Hz that reflects the *cis* fusion of ring C and D. Such a notion is in

concordance with the naturally occurring pterocarpan [31-37] and our earlier results [17-25]. The interrelationship between H-4 and H-3a in these products ($^3J = 10\text{Hz}$) indicates them to be *cis*, which is not without precedent [38]. The vinyl group at C-4 on pyran ring C, is placed in Ψ -equatorial conformation and such a view is in conformity with the literature [38] that the larger group always prefers equatorial position in cyclohexane.

Scheme 1



Scheme 2

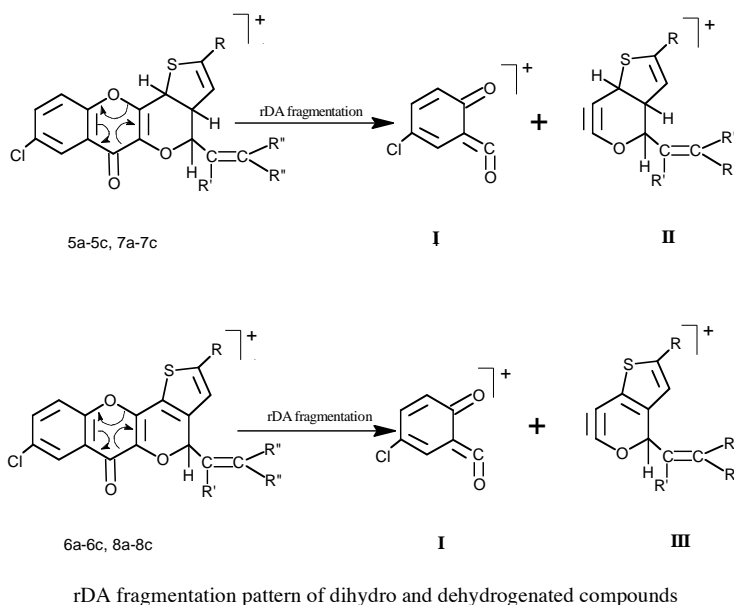


Table 1

rDA fragments of the photoproducts.									
Entry	Compound	Molecular ion(m/z)	rDA fragments(m/z)		Entry	Compound	Molecular ion(m/z)	rDA fragments(m/z)	
			I	II				I	III
1	5a	318/320	154/156	164	6	6a	316/318	154/156	162
2	5b	332/334	154/156	178	7	6b	330/332	154/156	176
3	5c	346/348	154/156	192	8	6c	344/346	154/156	190
4	7a	332/334	154/156	178	9	8a	330/332	154/156	176
5	7c	360/362	154/156	206	10	8b	344/346	154/156	190
					11	8c	358/360	154/156	204

Mechanistically, the phototransformations described above can be visualized as having occurred through an initial H-abstraction from C₃-OCH₂- group by the photoexcited carbonyl chromophore of the pyrone moiety to provide 1,4-biradical that further undergoes cyclization to give dihydrocyclic **5a-5c** and **7a-7c** and dehydrocyclic **6a-6c** and **8a-8c** photoproducts, as shown in Scheme 3.

Here, easy H-abstraction may be the result of a six membered cyclic transition state. The formation of the dihydrothiophene seems to be the result of keto-enol tautomerisation reaction. In our opinion, the dehydrocyclic photoproducts **6a-6c** and **8a-8c** are formed independently from the intermediate 1,4-biradicals **9a-9c** and not the oxidation products of their dihydro derivatives **5a-5c**, **7a** and **7c**. To confirm this view, the dihydrocyclic compounds were irradiated in benzene and MeOH resulting in polymeric material only and no detectable oxidized product. The photolysis of chromone **4b** in addition to photoproduct **8b** could have produced the product similar to **7b**. The possibility of

formation of this photoproduct can not be excluded completely, as it might be formed in the extremely low yield that its isolation had remained unsuccessful.

These photoreorganisations yield the products only through the involvement of 1,4-biradicals **9a-9c**. Even in the case of chromones **3c** and **4c**, the products could not be isolated through the tertiary 1,6-biradicals **10**. Thus, two methyl groups at end of the allyloxy chain are not sufficient to generate the 1,6-biradicals. This phenomenon may be ascribed from the view that 1,4-biradical in the present chromones preferably undergoes cyclisation with thienyl ring at C-2. But, involvement of 1,6-biradical occurs in chromones bearing the electron withdrawing (-COOEt) substituent at the distal end of 3-allyloxy group [27].

It is worth mentioning here that the phototransformations of chromones **3a-3c** and **4a-4c** presented better chemical efficiency in comparison to the similar photolysis of 3-benzyloxy and methoxy chromones [25].

Table 2 shows that total photolytic conversion furnished by 3-allyloxychromones (entry 1-6) has been up to an extent of 1.5 times greater than the 3-benzyloxychromone

Scheme 3

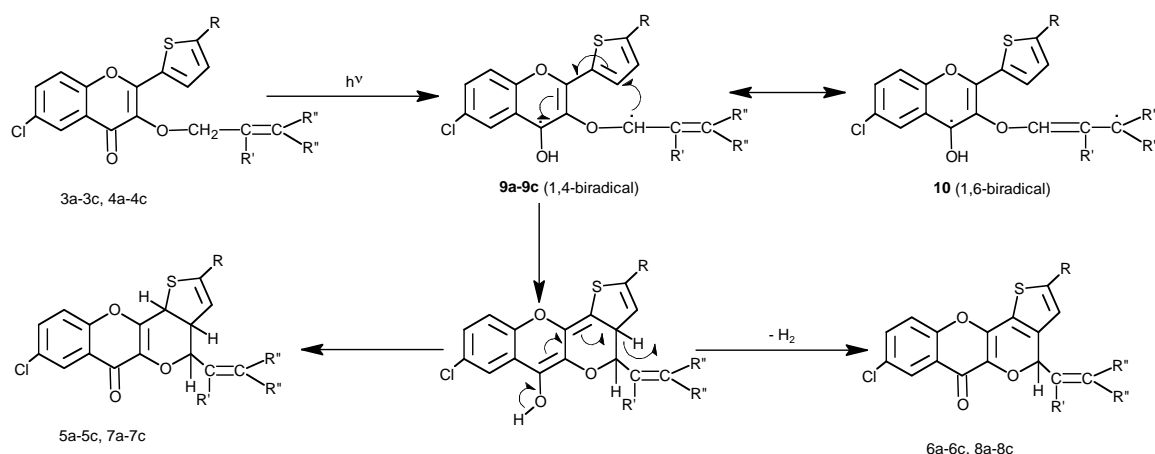


Table 2

Yield and distribution of the photoproducts

Entry					zTotal conversion (%)		
	R	R'	compound	Yield (%)		compound	Yield (%)
1	H	CH=CH ₂	5a	30	6a	10	40
2	H	C(CH ₃)=CH ₂	5b	30	6b	15	45
3	H	CH=C(CH ₃) ₂	5c	30	6c	10	40
4	CH ₃	CH=CH ₂	7a	30	8a	10	40
5	CH ₃	C(CH ₃)=CH ₂	7b	-	8b	38	38
6	CH ₃	CH=C(CH ₃) ₂	7c	32	8c	12	44
7 ²⁰	H	C ₆ H ₅	-	25	-	5	30
8 ²⁰	CH ₃	H	-	-	-	20	20

(entry 7) and almost double that of the 3-methoxychromone (entry 8). These results may be ascribed to the relative stabilities of the 1,4-biradicals involved in the photoreactions. It is well documented in literature that allylic radicals **9a-9c** are better stabilized than benzyl radicals that are more stabilized than alkyl radicals [39-42].

CONCLUSION

It may be concluded that the photolysis of 3-allyloxychromones provide good yield and distribution of the dihydrocyclised and dehydrocyclised compounds. Here, photoproducts are obtained only through the intermediacy of 1,4-biradicals. Introduction of methyl groups on the 2-thienyl and 3-allyloxy positions did not exhibit any significant effect upon the course of the photoreactions.

EXPERIMENTAL

Melting points reported are uncorrected. IR spectra were recorded on a Buck Scientific 500 Spectrophotometer using KBr pellets and UV spectra on U-2000 Hitachi-Spectrophotometer. ¹H NMR spectra were recorded on a 300 MHz Bruker spectrometer using TMS as internal standard. The mass spectra were recorded on 70 eV. TLC plates were coated with silica gel G suspended in MeOH-CHCl₃. Silica gel (100-200 mesh) was used for column chromatography.

3-Allyloxy-6-chloro-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (3a). A suspension of 6-chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran [25] **1** (2.8 g, 0.01 mol), allyl bromide (1.2 g, 0.01 mol), freshly ignited K₂CO₃ (1.0 g) and tetrabutylammonium iodide (1.0 g) in dry acetone (25 mL) was heated at reflux for 1h with stirring. A subsequent filtration of the reaction mixture followed by distillation of the solvent yielded a yellow solid product that was percolated through a column of silica-gel (60-120 mesh) using petroleum ether-benzene (1:1) as eluent and the resulting compound was further crystallized from EtOH to afford **3a**.

3a: Yield (85%), colourless needles, mp 113-115 °C; ir (ν_{max}, KBr): 1647 (C=O) cm⁻¹; λ_{max} THF 343 nm (15600), 328 nm (11200), 260 nm (12000 nm); ¹H nmr (300 MHz, CDCl₃) δ 8.19 (1H, d, J_m=2.4Hz, H-5), 7.96 (1H, dd, J_{3,5}=1.4Hz, J_{3,4}=3.7Hz, H-3'), 7.64 (1H, d, J_{5,4}=5.1Hz, J_{5,3}=1.4Hz, H-5'), 7.61 (1H, dd, J_{m,6}=2.4Hz, 8.9Hz, H-7), 7.49 (1H, d, J₆=8.9Hz, H-8), 7.22 (1H, dd, J_{4,5}=5.1Hz, J_{4,3}=3.7Hz, H-4'), 6.12 (1H, d{dd}, J_{2,1}=7.0Hz, J_{2,α}=10.3Hz, J_{2,β}=16.9Hz, H-2'') 5.42 (1H, d{dd}, J_{allyl}=1.3Hz, J_{β,α}=2.5Hz, J_{β,2'}=16.9Hz, H-β), 5.26 (1H, dd, J_{α,2'}=10.3Hz, J_{α,β}=2.5Hz, H-α), 4.86 (2H, dd, J_{allyl}=1.3Hz, J_{11''}=7.0Hz, H-1''); ms: m/z 318 (M⁺, 100); Anal. Calcd. For C₁₆H₁₁O₃ClS C, 60.38; H, 3.46. Found: C, 60.42; H, 3.50.

6-Chloro-3-(2'-methylprop-1'-enyloxy)-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (3b). The chromone **3b** was synthesized by reacting **1** (2.8 g, 0.01 mol) with 3-chloro-2-methylpropene (0.9 g, 0.01 mol) under the similar conditions as used for **3a**.

3b: Yield (80%), colourless needles, mp 98-100 °C; ir (ν_{max}, KBr): 1640 (C=O) cm⁻¹; λ_{max} THF 345 nm (17000), 329 nm (13000), 261 nm (15000 nm); ¹H nmr (300 MHz, CDCl₃) δ 8.19 (1H, d, J_m=2.5Hz, H-5), 7.98 (1H, dd, J_{3,5}=1.3Hz, J_{3,4}=3.7Hz, H-3'), 7.63 (1H, d, J_{5,4}=5.0Hz, H-5'), 7.61 (1H, dd, J_{m,6}=2.5Hz,

8.9Hz, H-7), 7.49 (1H, d, J₆=8.9Hz, H-8), 7.22 (1H, dd, J_{4,5}=3.7Hz, J_{4,3}=5.0Hz, H-4'), 5.20 (1H, br s, H-β) 5.03 (1H, H-α), 4.71 (2H, s, H-1''), 1.91 (3H, s, C₂-CH₃); ms: m/z 332 (M⁺, 100); Anal. Calcd. For C₁₇H₁₃O₃ClS C, 61.45; H, 3.92. Found: C, 61.42; H, 3.94.

6-Chloro-3-(3'-methylbut-2'-enyloxy)-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (3c). The chromone **3a** was synthesized by treating **1** (2.8 g, 0.01 mol) with 1-chloro-3-methylbutene (0.9 g, 0.01 mol) under the similar conditions as applied for **3a**.

3c: Yield (70%), colourless needles, mp 125-127 °C; ir (ν_{max}, KBr): 1636 (C=O) cm⁻¹; λ_{max} THF 344 nm (15400), 329 nm (12000), 260 nm (17300 nm); ¹H nmr (300 MHz, CDCl₃) δ 8.20 (1H, d, J_m=2.4Hz, H-5), 7.96 (1H, dd, J_{3,5}=1.1Hz, J_{3,4}=3.8Hz, H-3'), 7.63 (1H, d, J_{5,4}=5.0Hz, J_{5,3}=1.1Hz, H-5'), 7.60 (1H, dd, J_{m,6}=2.4Hz, 8.9Hz, H-7), 7.48 (1H, d, J₆=8.9Hz, H-8), 7.21 (1H, dd, J_{4,5}=5.0Hz, J_{4,3}=3.8Hz, H-4'), 5.61 (1H, dd, J_{allyl}=1.2Hz, J_{vic}=7.0Hz, H-2'') 4.85 (2H, d, J_{vic}=7.4Hz, H-1''), 1.76 (6H, br s, C_{3'}-(CH₃)₂); ms: m/z 346 (M⁺, 100); Anal. Calcd. For C₁₈H₁₅O₃ClS C, 62.43; H, 4.34. Found: C, 62.40; H, 4.32.

Photolysis of 3-Allyloxy-6-chloro-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (3a). A deoxygenated solution of **3a** (200 mg, 0.00063 mol) in dry benzene (100 mL) was photolysed with light from a 125 W mercury lamp in pyrex reactor under N₂ atmosphere for 50 min. The progress of reaction was monitored by tlc. The solvent was removed by distillation 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 (9.5:0.5) gave starting compound **3a** (30%, c-tlc & mmp.), and the two new compounds **5a** and **6a**.

5a: Yield (30%), pale yellow solid, mp 168-170 °C; ir (ν_{max}, KBr): 1665 (C=O) cm⁻¹; λ_{max} THF 325 nm (13100), 283 nm (12200), 239 nm (21000 nm); ¹H nmr (300 MHz, CDCl₃) δ 8.23 (1H, d, J_m=2.6Hz, H-7), 7.58 (1H, dd, J_{m,6}=2.6Hz, 9.0Hz, H-9), 7.41 (1H, d, J₆=9.0Hz, H-10), 6.40 (1H, dd, J_{2,3a}=1.0Hz, J_{2,3}=6.3Hz, H-2), 5.97 (1H, d{dd}, J_{1,4}=6.9Hz, J_{1,α}=10.3Hz, J_{1,β}=17.0Hz, H-1'), 5.56 (1H, dd, J_{3,3a}=3.0Hz, J_{3,2}=6.3Hz, H-3), 5.45 (1H, d, J_{β,1}=17.0Hz, H-β) 5.41 (1H, d, J_{α,1}=10.3Hz, H-α), 4.98 (1H, d, J_{1,β,3α}=8.4Hz, H-11b), 4.34 (1H, dd, J_{4,1}=6.9Hz, J_{4,3a}=10.0Hz, H-4), 3.27 (1H, d{dd}, J_{3a,3}=3.0Hz, J_{3a,11b}=8.4, J_{3a,4}=10.0Hz, H-3a); ms: m/z 318 (M⁺, 100); Anal. Calcd. For C₁₆H₁₁O₃ClS C, 60.38; H, 3.46. Found: C, 60.35; H, 3.49.

6a: Yield (10%), pale yellow solid, mp 197-199 °C; ir (ν_{max}, KBr): 1644 (C=O) cm⁻¹; λ_{max} THF 372 nm (16700), 323 nm (14000), 245 nm (23000 nm); ¹H nmr (300 MHz, CDCl₃) δ 8.27 (1H, d, J_m=2.5Hz, H-7), 7.62 (1H, d, J_{2,3}=5.1Hz, H-2), 7.60 (1H, dd, J_{m,6}=2.5Hz, 9.0Hz, H-9), 7.48 (1H, d, J₆=9.0Hz, H-10), 6.97 (1H, d, J_{3,2}=5.1Hz, H-3), 6.09 (1H, d{dd}, J_{1,4}=5.7Hz, J_{1,α}=10.2Hz, J_{1,β}=16.5Hz, H-1'), 6.01 (1H, d, J_{4,1}=5.7Hz, H-4), 5.35 (1H, d, J_{α,1}=10.2Hz, H-α) 5.28 (1H, d, J_{β,1}=16.5Hz, H-β); ms: m/z 318 (M⁺, 75); Anal. Calcd. For C₁₆H₉O₃ClS C, 60.76; H, 2.85. Found: C, 60.80; H, 2.81.

Photolysis of 6-Chloro-3-(2'-methylprop-1'-enyloxy)-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (3b). The benzene solution of **3b** (200 mg, 0.00060 mol) was photolysed under the similar conditions as described for **3a**. The photolysate on chromatographic separation provided the two new compounds **5b** and **6b**.

5b: Yield (30%), pale yellow solid, mp 158-160 °C; ir (ν_{max}, KBr): 1659 (C=O) cm⁻¹; λ_{max} THF 324 nm (12800), 283 nm (11000), 238 nm (22000 nm); ¹H nmr (300 MHz, CDCl₃) δ 8.23 (1H, d, J_m=2.3Hz, H-7), 7.58 (1H, dd, J_{m,6}=2.3Hz, 9.0Hz, H-9),

7.41 (1H, d, $J_{\text{O}}=9.0\text{Hz}$, H-10), 6.38 (1H, d, $J_{2,3}=5.8\text{Hz}$, H-2), 5.47 (1H, dd, $J_{3,3a}=3.5\text{Hz}$, $J_{3,2}=5.8\text{Hz}$, H-3), 5.11 (1H, d, $J_{\text{allyl}}=1.4\text{Hz}$, H- β) 5.06 (1H, s, H- α), 5.01 (1H, d, $J_{11b,3a}=8.1\text{Hz}$, H-11b), 4.30 (1H, d, $J_{4,3a}=10.0\text{Hz}$, H-4), 3.42 (1H, d{dd}, $J_{3a,3}=3.5\text{Hz}$, $J_{3a,11b}=8.1\text{Hz}$, $J_{3a,4}=10.0\text{Hz}$, H-3a); 1.90 (3H, s, $\text{C}_1\text{-CH}_3$); ms: m/z 332 (M^+ , 100); Anal. Calcd. For $\text{C}_{17}\text{H}_{13}\text{O}_3\text{ClS}$ C, 61.45; H, 3.92. Found: C, 61.48; H, 3.96.

6b: Yield (15%), pale yellow solid, mp 188-190 °C; ir (ν_{max} , KBr): 1645 (C=O) cm^{-1} ; λ_{max} THF 371 nm (16500), 323 nm (14200); 255 nm (26000); ^1H nmr (300 MHz, CDCl_3) δ 8.26 (1H, d, $J_{\text{m}}=2.5\text{Hz}$, H-7), 7.60 (1H, d, $J_{2,3}=4.6\text{Hz}$, H-2), 7.58 (1H, dd, $J_{\text{m,o}}=2.5\text{Hz}$, 8.9Hz, H-9), 7.47 (1H, d, $J_{\text{O}}=8.9\text{Hz}$, H-10), 6.90 (1H, d, $J_{3,2}=4.6\text{Hz}$, H-3), 5.94 (1H, s, H-4), 5.07 (1H, d, $J_{\text{allyl}}=1.2\text{Hz}$, H- β) 4.90 (1H, s, H- α), 1.87 (3H, s, $\text{C}_1\text{-CH}_3$); ms: m/z 330 (M^+ , 60); Anal. Calcd. For $\text{C}_{17}\text{H}_{11}\text{O}_3\text{ClS}$ C, 61.82; H, 3.33. Found: C, 61.79; H, 3.37.

Photolysis of 6-Chloro-3-(3'-methylbut-2'-enyloxy)-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (3c). The photolysis of a benzene solution of **3c** (200 mg, 0.00058 mol) under the similar conditions as used for **3a** furnished the two new compounds **5c** and **6c**.

5c: Yield (30%), pale yellow solid, mp 170-172 °C; ir (ν_{max} , KBr): 1651 (C=O) cm^{-1} ; λ_{max} THF 324 nm (12800), 283 nm (11000), 238 nm (22000 nm); ^1H nmr (300 MHz, CDCl_3) δ 8.23 (1H, d, $J_{\text{m}}=2.4\text{Hz}$, H-7), 7.57 (1H, dd, $J_{\text{m,o}}=2.4\text{Hz}$, 8.9Hz, H-9), 7.39 (1H, d, $J_{\text{O}}=8.9\text{Hz}$, H-10), 6.36 (1H, d, $J_{2,3}=5.8\text{Hz}$, H-2), 5.48 (1H, dd, $J_{3,3a}=3.1\text{Hz}$, $J_{3,2}=6.0\text{Hz}$, H-3), 5.35 (1H, dd, $J_{\text{allyl}}=1.1\text{Hz}$, $J_{1,4}=8.9\text{Hz}$, H-1'), 4.99 (1H, d, $J_{11b,3a}=8.0\text{Hz}$, H-11b), 4.55 (1H, dd, $J_{4,3a}=10.0\text{Hz}$, $J_{4,1}=8.9\text{Hz}$, H-4), 3.23 (1H, d{dd}, $J_{3a,3}=3.1\text{Hz}$, $J_{3a,11b}=8.0\text{Hz}$, $J_{3a,4}=10.0\text{Hz}$, H-3a); 1.79 (3H, s, $\text{C}_2\text{-CH}_3\text{-}\beta$), 1.69 (3H, s, $\text{C}_2\text{-CH}_3\text{-}\alpha$); ms: m/z 346 (M^+ , 100); Anal. Calcd. For $\text{C}_{18}\text{H}_{15}\text{O}_3\text{ClS}$ C, 62.43; H, 4.34. Found: C, 62.46; H, 4.38.

6c: Yield (10%), pale yellow solid, mp 196-198 °C; ir (ν_{max} , KBr): 1643 (C=O), 1606 (C=O) cm^{-1} ; λ_{max} THF 371 nm (16500), 323 nm (14200); 255 nm (26000); ^1H nmr (300 MHz, CDCl_3) δ 8.26 (1H, d, $J_{\text{m}}=2.4\text{Hz}$, H-7), 7.56 (1H, dd, $J_{\text{m,o}}=2.4\text{Hz}$, 8.9Hz, H-9), 7.55 (1H, d, $J_{2,3}=4.7\text{Hz}$, H-2), 7.46 (1H, d, $J_{\text{O}}=8.9\text{Hz}$, H-10), 6.84 (1H, d, $J_{3,2}=4.7\text{Hz}$, H-3), 6.15 (1H, d, $J_{1,4}=9.0\text{Hz}$, H-1'), 5.64 (1H, d, $J_{4,1}=9.0\text{Hz}$, H-4) 1.83 (3H, s, $\text{C}_2\text{-CH}_3\text{-}\beta$), 1.80 (3H, s, $\text{C}_2\text{-CH}_3\text{-}\alpha$); ms: m/z 344 (M^+ , 50); Anal. Calcd. For $\text{C}_{18}\text{H}_{13}\text{O}_3\text{ClS}$ C, 62.79; H, 3.78. Found: C, 62.76; H, 3.82.

3-Allyloxy-6-chloro-2-(5'-methyl-2'-thienyl)-4-oxo-4H-1-benzopyran (4a). A suspension of 6-chloro-3-hydroxy-2-(5'-methyl-2'-thienyl)-4-oxo-4H-1-benzopyran [25] **2** (2.9 g, 0.01 mol) was treated with allylbromide (0.9 g, 0.01 mol) under the similar conditions as used for **3a**.

4a: Yield (85%), colourless solid, mp 140-142 °C; ir (ν_{max} , KBr): 1639 (C=O) cm^{-1} ; λ_{max} THF 353 nm (19300), 263 nm (12200); ^1H nmr (300 MHz, CDCl_3) δ 8.18 (1H, d, $J_{\text{m}}=2.7\text{Hz}$, H-5), 7.79 (1H, d, $J_{3,4}=3.7\text{Hz}$, H-3'), 7.58 (1H, dd, $J_{\text{m,o}}=2.7\text{Hz}$, 8.9Hz, H-7), 7.46 (1H, d, $J_{\text{O}}=8.9\text{Hz}$, H-8), 6.88 (1H, dd, $J_{4,3}=3.7\text{Hz}$, $J_{\text{allyl}}=1.1\text{Hz}$, H-4'), 6.14 (1H, t{dd}, $J_{2,1}=6.1\text{Hz}$, $J_{2,\alpha}=10.3\text{Hz}$, $J_{2,\beta}=16.0\text{Hz}$, H-2'') 5.41 (1H, d{dd}, $J_{\beta,\alpha}=2.6\text{Hz}$, $J_{\text{allyl}}=1.1\text{Hz}$, $J_{\beta,2}=16.0\text{Hz}$, H- β) 5.26 (1H, dd, $J_{\text{allyl}}=1.1\text{Hz}$, $J_{\alpha,2}=10.3\text{Hz}$, H- α), 4.84 (2H, d, $J_{1,2}=6.2\text{Hz}$, H-1''), 2.58 (3H, s, $\text{C}_5\text{-CH}_3$); ms: m/z 332 (M^+ , 100.0); Anal. Calcd. For $\text{C}_{17}\text{H}_{13}\text{O}_3\text{ClS}$ C, 61.45; H, 3.92. Found: C, 61.42; H, 3.96.

6-Chloro-3-(2"-methylprop-1"-enyloxy)-2-(5'-methyl-2'-thienyl)-4-oxo-4H-1-benzopyran (4b). The chromone **4b** was synthesized by reacting **2** (2.9 g, 0.01 mol) with 3-chloro-2-methylpropene (0.9 g, 0.01 mol) under the similar conditions as applied for **3a**.

4b: Yield (85%), colourless needles, mp 117-119 °C; ir (ν_{max} , KBr): 1649 (C=O) cm^{-1} ; λ_{max} THF 354 nm (19100), 264 nm (12700); ^1H nmr (300 MHz, CDCl_3) δ 8.18 (1H, d, $J_{\text{m}}=2.7\text{Hz}$, H-5), 7.79 (1H, d, $J_{3,4}=3.7\text{Hz}$, H-3'), 7.58 (1H, dd, $J_{\text{m,o}}=2.7\text{Hz}$, 8.9Hz, H-7), 7.45 (1H, d, $J_{\text{O}}=8.9\text{Hz}$, H-8), 6.88 (1H, dd, $J_{4,3}=3.7\text{Hz}$, $J_{\text{allyl}}=1.2\text{Hz}$, H-4'), 5.19 (1H, br s, H- β) 5.02 (1H, s, H- α), 4.69 (2H, s, H-1''), 2.57 (3H, s, $\text{C}_5\text{-CH}_3$) 1.91 (3H, s, $\text{C}_2\text{-CH}_3$); ms: m/z 346 (M^+ , 85); Anal. Calcd. For $\text{C}_{18}\text{H}_{15}\text{O}_3\text{ClS}$ C, 62.33; H, 4.36. Found: C, 62.30; H, 4.40.

6-Chloro-3-(3"-methylbut-2"-enyloxy)-2-(5'-methyl-2'-thienyl)-4-oxo-4H-1-benzopyran (4c). The chromone **4c** was synthesized by treating **1** (2.9 g, 0.01 mol) with 1-chloro-3-methylbutene (0.9 g, 0.01 mol) under the similar conditions as applied for **3a**.

4c: Yield (85%), colourless needles, mp 130-132 °C; ir (ν_{max} , KBr): 1643 (C=O) cm^{-1} ; λ_{max} THF 354 nm (19100), 264 nm (12700); ^1H nmr (300 MHz, CDCl_3) δ 8.19 (1H, d, $J_{\text{m}}=2.4\text{Hz}$, H-5), 7.78 (1H, dd, $J_{3,4}=3.8\text{Hz}$, H-3'), 7.58 (1H, dd, $J_{\text{m,o}}=2.4\text{Hz}$, 8.9Hz, H-7), 7.45 (1H, d, $J_{\text{O}}=8.9\text{Hz}$, H-8), 6.88 (1H, dd, $J_{4,3}=3.8\text{Hz}$, $J_{\text{allyl}}=1.1\text{Hz}$, H-4'), 5.60 (1H, t, $J_{\text{vic}}=7.2\text{Hz}$, H-2'') 4.82 (2H, d, $J_{\text{vic}}=7.2\text{Hz}$, H-1''), 2.58 (3H, s, $\text{C}_5\text{-CH}_3$), 1.76 (6H, br s, $\text{C}_3\text{-}(\text{CH}_3)_2$); ms: m/z 360 (M^+ , 80); Anal. Calcd. For $\text{C}_{19}\text{H}_{17}\text{O}_3\text{ClS}$ C, 61.45; H, 3.92. Found: C, 61.41; H, 3.90.

Photolysis of 3-Allyloxy-6-chloro-2-(5'-methyl-2'-thienyl)-4-oxo-4H-1-benzopyran (4a). The photolysis of a benzene solution of **4a** (200 mg, 0.00060 mol) under the similar condition as applied for **3a**, furnished the two new compounds **7a** and **8a**.

7a: Yield (30%), pale yellow solid, mp 168-170 °C; ir (ν_{max} , KBr): 1659 (C=O) cm^{-1} ; λ_{max} THF 325 nm (14000), 283 nm (10200), 236 nm (22800 nm); ^1H nmr (300 MHz, CDCl_3) δ 8.22 (1H, d, $J_{\text{m}}=2.4\text{Hz}$, H-7), 7.58 (1H, dd, $J_{\text{m,o}}=2.4\text{Hz}$, 8.9Hz, H-9), 7.40 (1H, d, $J_{\text{O}}=8.9\text{Hz}$, H-10), 5.93 (1H, d{dd}, $J_{1,4}=6.9\text{Hz}$, $J_{1,\alpha}=10.3\text{Hz}$, $J_{1,\beta}=17.0\text{Hz}$, H-1'), 5.46 (1H, d, $J_{\beta,1}=17.0\text{Hz}$, H- β) 5.38 (1H, d, $J_{\alpha,1}=10.5\text{Hz}$, H- α), 5.20 (1H, dd, $J_{3,3a}=2.9\text{Hz}$, H-3), 5.01 (1H, d, $J_{11b,3a}=7.8\text{Hz}$, H-11b), 4.40 (1H, dd, $J_{4,1}=6.7\text{Hz}$, $J_{4,3a}=9.6\text{Hz}$, H-4), 3.23 (1H, m, H-3a), 2.00 (3H, s, $\text{C}_2\text{-CH}_3$); ms: m/z 332 (M^+ , 90); Anal. Calcd. For $\text{C}_{17}\text{H}_{13}\text{O}_3\text{ClS}$ C, 61.45; H, 3.92. Found: C, 61.48; H, 3.89.

8a: Yield (10%), pale yellow solid, mp 188-190 °C; ir (ν_{max} , KBr): 1643 (C=O) cm^{-1} ; λ_{max} THF 379 nm (12300), 325 nm (11000), 231 nm (20300 nm); ^1H nmr (300 MHz, CDCl_3) δ 8.26 (1H, d, $J_{\text{m}}=2.5\text{Hz}$, H-7), 7.56 (1H, dd, $J_{\text{m,o}}=2.5\text{Hz}$, 8.9Hz, H-9), 7.44 (1H, d, $J_{\text{O}}=8.9\text{Hz}$, H-10), 6.62 (1H, s H-3), 6.07 (1H, d{dd}, $J_{1,4}=6.0\text{Hz}$, $J_{1,\alpha}=10.6\text{Hz}$, $J_{1,\beta}=17.0\text{Hz}$, H-1'), 5.90 (1H, d, $J_{4,1}=6.0\text{Hz}$, H-4), 5.30 (1H, d, $J_{\beta,1}=17.0\text{Hz}$, H- β) 5.32 (1H, d, $J_{\alpha,1}=10.6\text{Hz}$, H- α), 2.58 (3H, s, $\text{C}_2\text{-CH}_3$); ms: m/z 330 (M^+ , 70); Anal. Calcd. For $\text{C}_{17}\text{H}_{11}\text{O}_3\text{ClS}$ C, 60.76; H, 2.85. Found: C, 60.79; H, 2.88.

Photolysis of 6-Chloro-3-(2"-methylprop-1"-enyloxy)-2-(5'-methyl-2'-thienyl)-4-oxo-4H-1-benzopyran (4b). The benzene solution of **4b** (200 mg, 0.00058 mol) was photolysed under the similar conditions as used for **3a**. The chromatographic separation of photolysate provided the only compound **8b**.

8b: Yield (38%), pale yellow solid, mp 189-191 °C; ir (ν_{max} , KBr): 1634 (C=O) cm^{-1} ; λ_{max} THF 357 nm (13200), 324 nm (15000), 232 nm (28000 nm); ^1H nmr (300 MHz, CDCl_3) δ 8.25 (1H, d, $J_{\text{m}}=2.7\text{Hz}$, H-7), 7.55 (1H, dd, $J_{\text{m,o}}=2.7\text{Hz}$, 8.9Hz, H-9), 7.44 (1H, d, $J_{\text{O}}=8.9\text{Hz}$, H-10), 6.57 (1H, s H-3), 5.84 (1H, s, H-4), 5.04 (1H, s, H- β) 4.92 (1H, s, H- α), 2.57 (3H, s, $\text{C}_2\text{-CH}_3$);

ms: m/z 344 (M⁺, 50); Anal. Calcd. For C₁₈H₁₃O₃ClS C, 62.79; H, 3.78. Found: C, 60.83; H, 3.81.

Photolysis of 6-Chloro-3-(3"-methylbut-2"-enyloxy)-2-(5'-methyl-2'-thienyl)-4-oxo-4H-1-benzopyran (4c). The photolysis of a benzene solution of **4c** (200 mg, 0.00056 mol) under the similar conditions, as applied for **3a**, yielded the two new compounds **7c** and **8c**.

7c: Yield (32%), pale yellow solid, mp 163-165 °C; ir (ν_{max}, KBr): 1651 (C=O) cm⁻¹; λ_{max} THF 357 nm (13200), 324 nm (15000), 232 nm (28000 nm); ¹H nmr (300 MHz, CDCl₃) δ 8.22 (1H, d, J_m=2.5Hz, H-7), 7.56 (1H, dd, J_{m,o}=2.5Hz, 8.9Hz, H-9), 7.38 (1H, d, J_o=8.9Hz, H-10), 5.33 (1H, dd, J_{allyl}=1.2Hz, J_{vic}=8.5Hz, H-1'), 5.12 (1H, dd, J_{allyl}=1.0Hz, J_{3,3a}=2.8Hz, H-3), 5.04 (1H, d, J_{11b,3a}=8.0Hz, H-11b), 4.61 (1H, dd, J_{vic}=8.5Hz, J_{4,3a}=9.7Hz, H-4), 3.18 (1H, d{dd}, J_{3a,3}=2.8Hz, J_{3a,11b}=8.0Hz, J_{3a,4}=9.7Hz, H-3a), 1.98 (3H, s, C₂-CH₃), 1.79 (3H, d, J_{allyl}=1.0Hz, C₂-CH₃-α), 1.69 (3H, d, J_{allyl}=1.0Hz, C₂-CH₃-β); ms: m/z 360 (M⁺, 75); Anal. Calcd. For C₁₉H₁₇O₃ClS C, 61.45; H, 3.92. Found: C, 61.49; H, 3.96.

8c: Yield (12%), pale yellow solid, mp 192-194 °C; ir (ν_{max}, KBr): 1642 (C=O), 1607 (C=O) cm⁻¹; λ_{max} THF 379 nm (12300), 325 nm (11000), 231 nm (20300 nm); ¹H nmr (300 MHz, CDCl₃) δ 8.27 (1H, d, J_m=2.5Hz, H-7), 7.55 (1H, dd, J_{m,o}=2.5Hz, 8.9Hz, H-9), 7.45 (1H, d, J_o=8.9Hz, H-10), 6.25 (1H, br s H-3), 6.07 (1H, d, H-1'), 5.61 (1H, d, J_{vic}=9.05Hz, H-4), 2.56 (3H, s, C₂-CH₃), 1.81 (3H, s, C₂-CH₃-α), 1.78 (3H, s, C₂-CH₃-β); ms: m/z 358 (M⁺, 63); Anal. Calcd. For C₁₉H₁₅O₃ClS C, 63.69; H, 4.19. Found: C, 63.65; H, 4.23.

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