Photo-reorganization of 3-alkoxy-6-chloro-2-(thiophen-3-yl)-4H-chromen-4-ones: Regioselective cyclization via γ-hydrogen abstraction

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ABSTRACT

Regioselective photocyclization of 3-alkoxy-6-chloro-4H-chromen-4-ones bearing thiophen-3-yl moiety at 2-position has been described. These chromenones on irradiation by the pyrex filtered UV-light produced a diverse array of novel angular tetracyclic photoproducts. Of these, mostly the cyclic dihydro and dehydrogenated photoproducts had the gem-dihydro functionality and exocyclic double bonds onto the fused pyran ring respectively, which is unprecedent in these chromenones.

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1. Introduction

Intramolecular H-abstractions [1–7] by the excited carbonyl group are the interesting tools for the synthesis of many exotic molecules, that are usually unobtainable through thermal modes. The spirocyclics [1,2], polycyclics [4–7] (both linear and angular), vinyl ethers [3], lactams [8,9] etc. have been synthesized by using this method. 3-Alkoxy-2-(phenyl/thienyl/furyl)chromones [4–7] and 2-alkoxy/alkyl-3-aryl-2-cyclohexenones [10] on photoirradiation lead to angular polycyclic products. Although the basic skeleton of the substrates is same, the products formed are quite different as well as interesting and their distribution has been found to depend upon the nature of substituents at C-2 and C-3 in chromones [4–7]. Many research efforts have been directed to obtain regioselective photocyclized products [11–13]. In most cases, since several types of photoproducts were produced, controlling the selectivity of the product is very hard. In our earlier study, an attempt was made to study the regioselective photocyclization of 3-alkoxy-chromones bearing a 3-furyl [14] group at C-2, possessing two sites (C-2′ and C-4′) for clipping of the initially formed 1,4-biradical, the photoproducts were afforded only by clipping at C-2′ with no photoproducts by clipping at C-4′ (Fig. 1).

To further explore the possibility of regioselective photocyclisation, in the present study, we report our investigations on the photoreactions of 3-alkoxy/allyloxy-6-chloro-4H-chromen-4-ones bearing thiophen-3-yl moiety at 2-position in place of furan moiety. Our objectives are: (i) how a thiophene moiety tethered to the chromenone through its C-3 position instead of C-2 position [15] effects the product formation/distribution, (ii) whether phototranspositions [16] – a route common in the photolysis of substituted thiophenes will occur in these photoreactions, (iii) whether photoproduct formation involves the Dewar thiophene [17,18], a valence bond isomer that may be formed in situ through the photoisomerization of thiophene and (iv) the prospect of the oxetane [19] – the cyclobutyl product formation.

2. Results and discussion

The targets, 2-(thiophen-3-yl)-4H-chromen-4-ones **3(a–f)** were synthesized by the condensation of 5-chloro-2-hydroxyacetophenone with thiophene-3-carbaldehyde in the presence of NaOH/EtOH, followed by reacting the resulting chalcones with 50% H_2O_2/OH$^-$ under AFO conditions [20] and subsequent alkylation (Scheme 1) of the 3-hydroxychromenones with suitable alkyl halide in the presence of dry acetone, freshly dried K_2CO_3 and n-Bu$_4$N$^+$I$^-$.

The structures of these photo-labile substrates **3(a–f)** were found to be consistent with their spectral parameters (IR, ^{1}H/^{13}C NMR, vide experimental).

In electronic absorption spectra, the chromenones **3(a–f)** showed λ_{max} in the range of 244–358 nm (Fig. 2), thus, a pyrex filtered UV-light was used for their photoirradiation.

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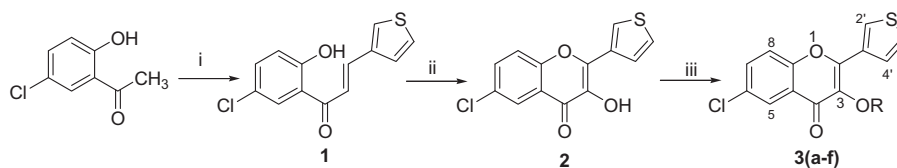
i; Thiophene-3-carbaldehyde/C$_2$H$_5$OH/NaOH/room temp.
ii; 50%H$_2$O$_2$/OH$^-$/0°C; iii; K$_2$CO$_3$/CH$_3$COCH$_3$/Bu$_4$N$^+$I$^-$/RX

RX =			
(CH$_3$)$_2$SO$_4$	**3a**, R =	-CH$_3$	80%
(H)C=C(CH$_2$Br)(H)(H)	**3b**, R =	^{a}H C=C ^{b}H, CH$_2$- H	81%
(H)C=C(CH$_2$Cl)(H)(CH$_3$)	**3c**, R =	^{a}H C=C ^{b}H, CH$_2$- CH$_3$	88%
(H$_3$C)C=C(CH$_2$Br)(H$_3$C)(H)	**3d**, R =	H$_3$C^a C=C H$_3$C^b, CH$_2$- H	72%
(H)C=C(CH$_2$Cl)(Ph)(H)	**3e**, R =	H C=C Ph, CH$_2$- H	85%
HC≡C−CH$_2$Br	**3f**, R =	HC≡C−CH$_2$-	86%

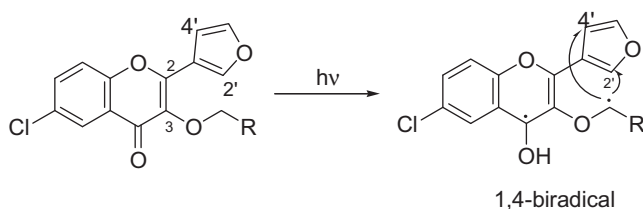**Scheme 1.** Synthesis of thienylchromenones **3(a–f)**.

Fig. 1. Possible sites for clipping at furyl group with 1,4-biradical.

The photoirradiation of methanolic solution of the chromenones **3(a–f)** with pyrex filtered UV-light using a 125 W Hg lamp, under nitrogen atmosphere produced the photoproducts **4(a–f)** and **4(a′–f′)**. The photoproducts **4(a–f)** were obtained in the single stereoisomeric forms. In addition to these, photolysis of **3a** produced **4a″** and that of **3b**, **3c** and **3f** produced **4b″**, **4c″** and **4f″**, respectively; no such products were obtained on irradiation of **3d**. The structures of these photoproducts (Scheme 2) were confirmed
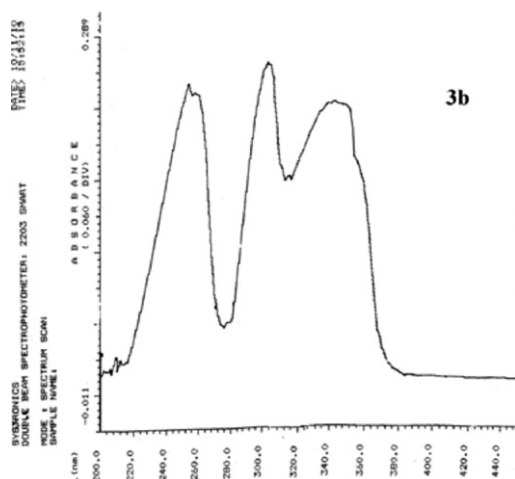

Fig. 2. Electronic absorption spectra of the substrate 3b.

by their spectral parameters (IR, ^{1}H/^{13}C NMR) and elemental analysis.

The compound **4b** in its IR spectrum exhibited a strong absorption band at 1628 cm^{-1} that may be assigned to the C=O of pyrone moiety. The two diastereotopic protons (H$_x$ and H$_y$) at C-3 resonated at different δ values (Fig. 3) with J_{gem} = 16.5 Hz (bond angle = 109.66°). The proton H$_x$-3 appeared downfield as it falls in deshielding zone of vinyl group and showed resonance at δ 4.04 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hx,3a}$ = 4.7 Hz, $J_{3Hx,1}$ = 2.4 Hz) with gauche conformation giving approximately a cis-disposition with respect to the H-3a (dihedral angle = 54.97°). The H$_y$-3 resonated at δ 3.86 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hy,3a}$ = 5.0 Hz, $J_{3Hy,1}$ = 3.7 Hz) indicating a near trans-disposition to H-3a with the dihedral angle of 120°. The proton H-1 was located at δ 6.62 (dt/ddd, $J_{1,3Hy}$ = 3.6 Hz, $J_{1,3Hx}$ = 2.4 Hz, $J_{1,3a}$ = 2.4 Hz). The protons H-1, H$_x$-3 and H$_y$-3 belonging to the modified thiophene moiety in **4b** were found to be up-field as compared to H-2′ and H-5′ in **3b**, which indicated the loss of aromatic character of the thiophene moiety in **4b**. The ring junction proton H-3a was seen at δ 4.49 (dtd/dddd, $J_{3a,4}$ = 10.8 Hz, $J_{3a,3Hy}$ = 5.0 Hz, $J_{3a,3Hx}$ = 4.7 Hz, $J_{3a,1}$ = 2.2 Hz). The pyran proton H-4 gave a dd at δ 4.37 ($J_{4,3a}$ = 10.8 Hz, J_{vic} = 6.9 Hz).

The glaring spectrum of proton H-1 in **4b** described above was also supported by its 2D NOESY spectrum where three spots below H-1 corresponds to the H-3a, H$_x$-3 and H$_y$-3 protons confirmed that the H-1 shows allylic coupling with H-3a and through space coupling with H$_x$-3 and H$_y$-3.

Moreover, the 2D HSQC spectra further confirmed the presence of the C-3 bearing two hydrogens in the structure of **4b** as the spots aroused below H$_x$-3 and H$_y$-3 corresponds to the negative signal at δ 39.03 which became available due to C-3 (Fig. 4).

Likewise, the structures of other cyclic dihydro photoproducts **4a** and **4(c–f)** were confirmed by their spectral data.

Another feature worth revealing in the photoproducts isolated is the stereochemistry of ring C; which is in half-chair conformation. Regarding the relative stereochemical disposition of H-3a and H-4, which can be cis or trans, the use of J/Φ relationship [21–23] and MM2 programme [12] adequately indicated these to be in trans ($\Phi_{3a,4}$ = 152.80°) relationship, thus placing the bulkier groups, i.e. vinyl and acetylenyl groups in a pseudo-equatorial position. Such

Scheme 2. Photoirradiation of thienylchromenones **3(a–f)** and distribution of the photoproducts.

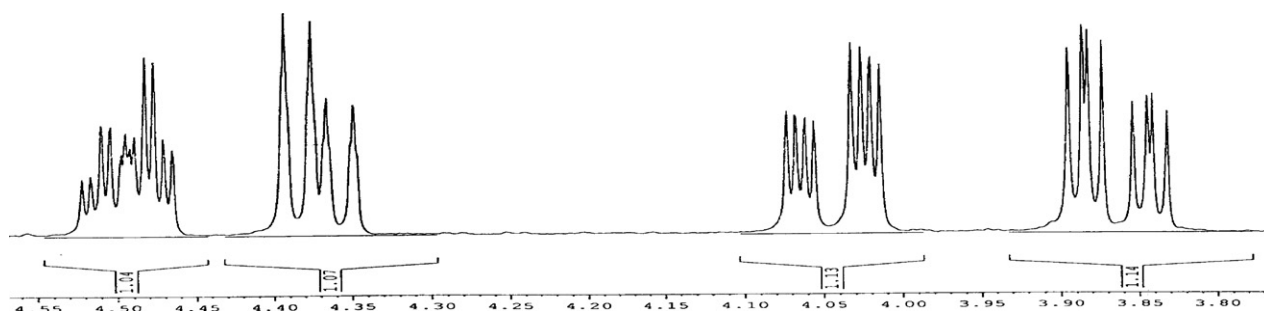| -R	Photoproduct	Yield (%)	Photoproduct	Yield (%)	Photoproduct	Yield (%)
-H	**4a**	30	**4a'**	35	**4a"**	20
(vinyl, CH=CH₂)	**4b**	29	**4b'**	36	**4b"**	10
(propenyl, CH=CH-CH₃)	**4c**	35	**4c'**	38	**4c"**	12
(isobutenyl, (H₃C)₂C=CH)	**4d**	20	**4d'**	21	---	---
(styryl, Ph-CH=CH (E))	**4e**	10#	**4e'**	45	---	---
HC≡C—	**4f**	36	**4f'**	8#	**4f"**	10#

yield caculated from ^{1}H NMR

Fig. 3. Partial 400MHz ^{1}H NMR spectrum of H-3a, H-4, H_x-3 and H_y-3 in **4b**.

a contention was further corroborated from the observation that H-3a in **4(b–f)** appeared down field than the equivalent proton in **4a** (R = –H) by 0.45–0.83 ppm (Table 1).

It may be argued that in **4b** the only pseudo-equatorially placed vinyl group at C-4 would deshield the H-3a in conformation **I** (Fig. 5). The proton H-3a would not experience such deshielding in the other possible conformation **II**. This has made the stereocentre C-4 to have *R*-configuration and stereocentre C-3a to have *S* configuration. The steric energy (E_{kcal}) calculations [24] also showed that

Table 1
Chemical shift of proton H-3a in 4(a-f).

Compound	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**
δ_{H-3a}	3.92	4.52	4.64	4.37	4.51	4.75
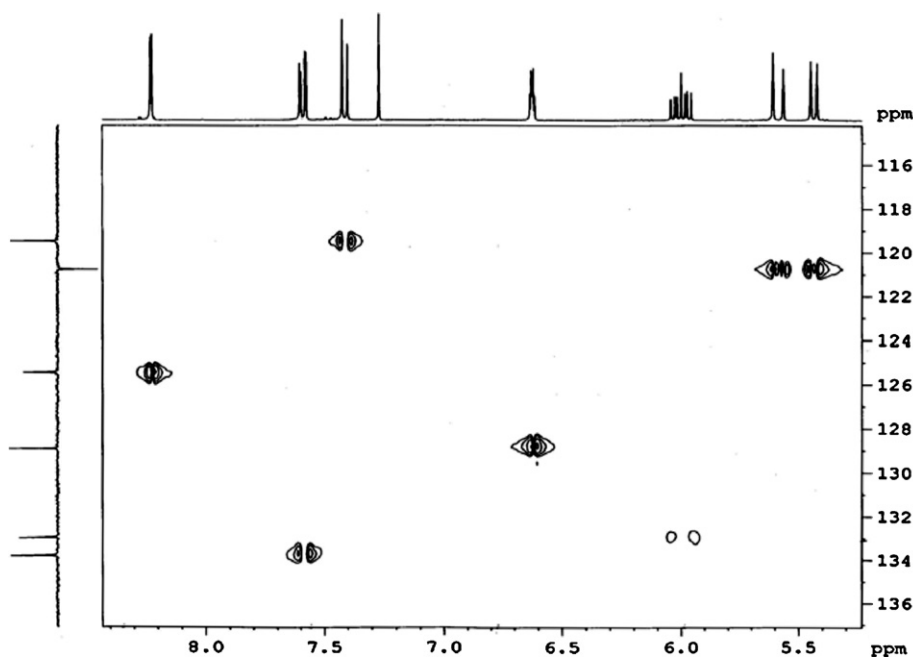
Fig. 4. ^{1}H/^{13}C 2D HSQC spectrum of **4b**.

(conformation I)
allyl ψ-equatorial

(conformation II)
allyl ψ-axial
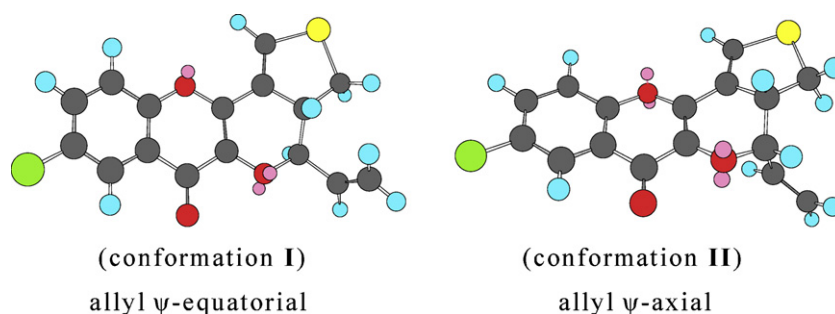
Fig. 5. MM2 energy minimized structures of expected conformations of compound **4b**.

the lower energy conformation (conformation **I**) is the one that explain the observed J/Φ relationship (Table 2).

The observed ^3J values found in the present case for **4b** are in accordance with the $J^\dagger$ values calculated for the conformation **I**, in which the protons H-3a and H-4 are *trans* to each other and dihydrothiophene ring is *exo* to the ψ-chair pyran ring.

In the ^{1}H NMR of photoproduct **4b′**, the two thienyl protons H-1 and H-3 showed no coupling with each other and were located as singlet at δ 7.44. The pyran proton H-4 appeared as doublet at δ 6.05 ($J_{4,1'}$ = 6.3 Hz) which illustrate the absence of proton corresponding to H-3a. The structure of photoproduct **4b′** has been further corroborated by its mass spectrum, which showed retro-Diels Alder (rDA) fragmentation mode (Scheme 3), thereby indicating the presence of chromenone moiety in the **4b′**. The structures of the other photoproducts **4a′** and **4(c′–f′)** were also confirmed by their spectral data.

The mass spectrum of third photoproduct **4b″** also showed the m/z 317 as base peak as that of **4b′** but in its ^{1}H NMR spectrum the two thienyl protons appeared as doublets at δ 7.44 ($J_{2,1}$ = 5.1 Hz, H-2) and δ 7.35 ($J_{1,2}$ = 5.1 Hz, H-1) that made it differ from **4b′**. Likewise, the structures of **4c″** and **4f″** were confirmed by their spectral data.

The demethoxylated product **4a″** showed in its ^{1}H NMR spectrum a signal at δ 6.69, characteristic of H-3 proton in chromones [25]. The identity of photoproduct **4a″** was further confirmed by the synthesizing an authentic sample of the compound through the cyclization of compound **1**.
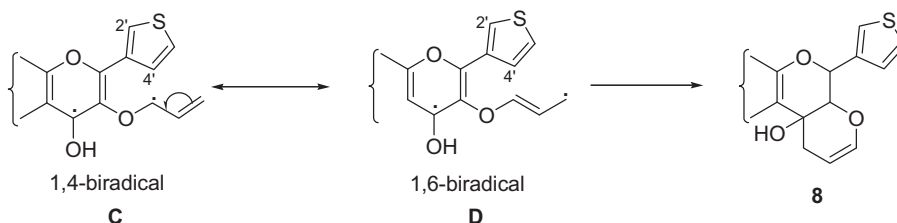
The photocyclization of **3(a–f)**, to furnish the dehydrogenated photoproducts **4(b″–c″)** and **4f″**, takes place simply through the coupling of 1,4-biradical 5X with C-2′-position of the thiophene ring as reported in our earlier studies [1–3,14] (Scheme 4).

Table 2
Expected coupling constants for the two conformations of **4b**.

Coupling protons	Conformation **I**			Conformation **II**			Observed
	Φ	$J^\dagger$	$E_{(kcal/mol)}$	Φ	$J^\dagger$	$E_{(kcal/mol)}$	J
H-3a and H-4	−175.17	12.9 Hz	16.616	−56.09	4.7 Hz	18.123	10.8 Hz

† Expected value.

Scheme 3. Mass fragmentation pattern of **4b′**.

Fig. 6. Resonance in 1,4-biradical of **3b**.
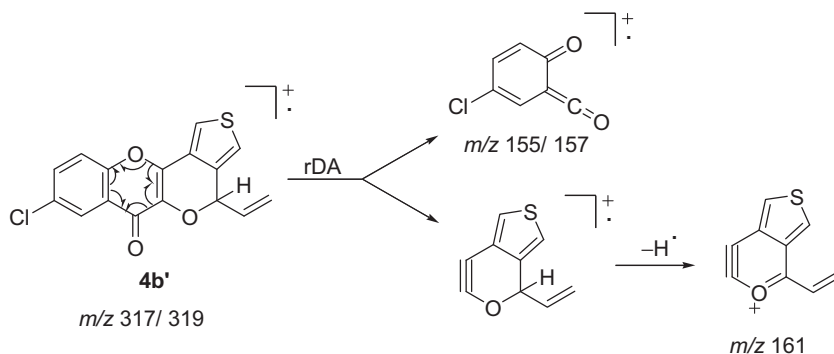
But the formation of photoproducts **4(a–f)** and **4(a′–f′)** can not be explained by the above route and there is no other favorable path except one (Scheme 5). According to this path the initially formed 1,4-biradical [1–3,26–28] 5Y may mesomerizes to C-4′ position and then clipped to give Dewar type structure 7 which furnished the photoproducts consequently.

The photocyclised products **4(a–f)** were formed from 7 via ketonisation and 1,7-H shift (Scheme 5). The cyclodehydrogenated photoproducts **4(a′–f′)** formed independently from 7 through the expulsion of H₂ not via dihydro photoproduct **4(a–f)**. This was confirmed by the fact that further irradiation of isolated **4(a–f)** yielded no product corresponding to **4(a′–f′)**.

Even though we have not isolated any Dewar type moiety but the proposed mechanism (Scheme 5) can also be supported by the fact that the photoirradiation of the chromenones, substituted with the 3-furyl group [14] at C-2 which have the same possibility (i.e. two possible sites (C-2′ and C-4′) for clipping of the initially formed 1,4-biradical) as that of the chromenones under study, afforded photoproducts only by clipping at C-2′. No photoproducts similar to **4(a–f)** and **4(a′–f′)** were produced by clipping at C-4′ as they need the involvement of the Dewar furan type structure which could not have been possible in those furan-3-yl chromenones probably due to high energy requirements. So, the intermediacy of Dewar type moiety in the phoirradiation of the thienylchromenones has been invoked. Since the energy of Dewar thiophene (S_o energy = 65 kcal mol^{-1}) is lower than that of Dewar furan (S_o energy = 78 kcal mol^{-1}) [29]. Therefore, it may be safely concluded that the formation of products **4(a–f)** and **4(a′–f′)** occurs via the low energy Dewar type intermediate **7** and the high level of regioselectivity achieved over here may be credited to some hidden electronic factors.

The chromenones **3(a–f)** can also undergo phototransposition reactions, but no products originating through such mode were realized. This observation is supported by the fact that carbonyl and olefinic substituents inhibit this type of rearrangement [30–38].

In case of **3a** (R = –CH₃), the formation of demethoxylated product **4a″** can be explained as earlier due to the cyclisation of –O–ĊH– radical at C-2 followed by the ketonisation and then ejection of HCHO from the oxetane [25,39,40]. No such type of photoproduct has been isolated when R = allyls. The only assignable reason to this behavior could be the steric factor which disfavors cyclization [19] of the bulky allyl radicals at C-2.

In the photolysis of allyloxy ethers **3(b–e)**, the allyl radical **C** at C-1″ may also mesomerises to give 1,6-biradical D [41] (Fig. 6) which may cyclise to give angular tricyclic photoproducts **8**. Such photoproducts were not obtained in the present study.

Scheme 4. Photocyclization through coupling at C-2′ position of thienylchromenones.
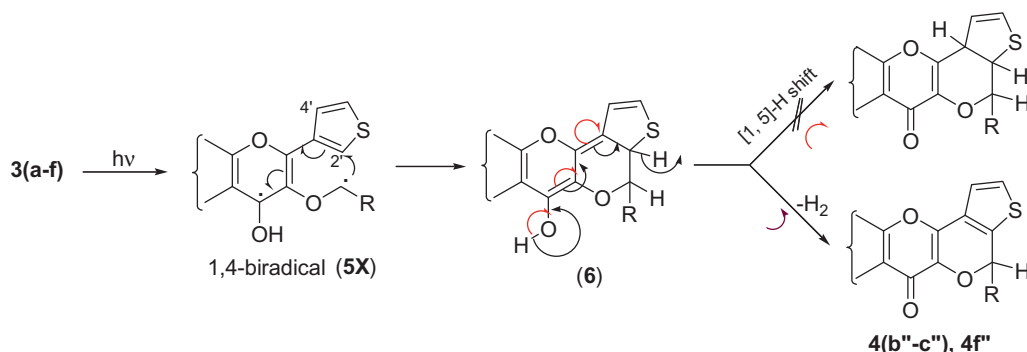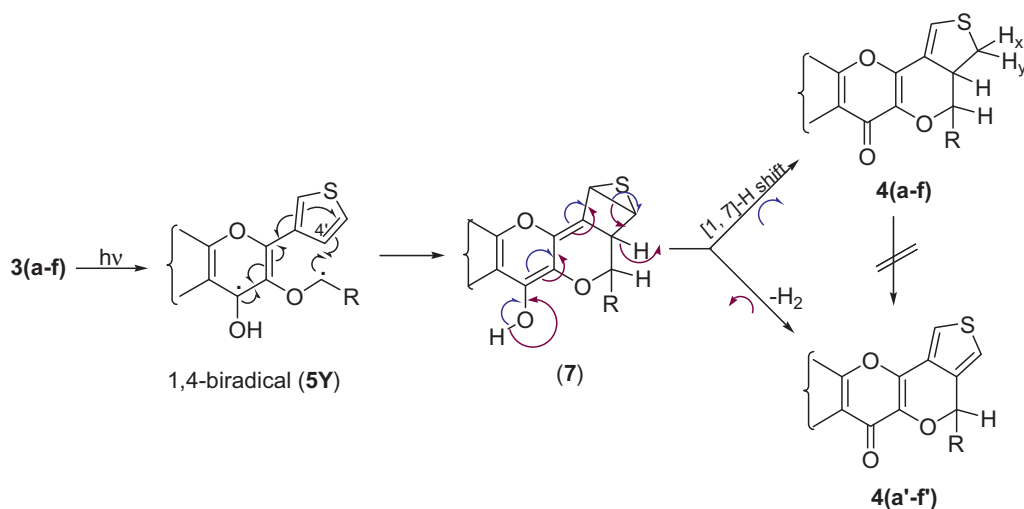
Scheme 5. Photocyclization through coupling at C-4′ position of thienylchromones.
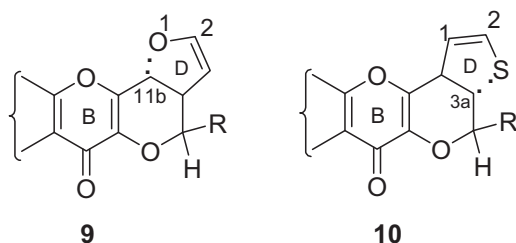
Fig. 7. Structures of proposed radicals.

The secondary ring contraction products observed by cleavage of ring D as isolated in our earlier work on 3-alkoxy-2-(2′-furyl) chromones [42–44], are altogether absent here and were not even observed by further photolysis of pure photoproducts. The reason attributed to such diversity may be the stabilty of biradicals (**9** and **10**) formed by cleavage of ring D which determines the ease of C–O bond cleavage (Fig. 7).

The radical at C-11b in **9** (obtained in photolysis of 2′-furyl chromones) is stabilized by pyrone moiety and thus C–O bond becomes prone to cleavage. But there is no such stabilization available to radical at C-3a in **10** (possible intermediate which can be formed from photoproduct obtained here) for its formation and hence no ring contracted secondary photoproducts were formed. These findings correlate well with the studies made by Maurizio D'Auria [29] on the photochemical isomerization reactions of furan and thiophene derivatives. On the basis of semiempirical calculations it has been shown that furan can give ring contraction product, i.e. the cyclopropenyl derivative because its triplet state can give the biradical intermediate, whereas thiophene can not be converted into the biradical intermediate as this intermediate is of higher energy (69 kcal mol^{-1}) than the excited triplet state (62 kcal mol^{-1}) of thiophene, thus preventing the formation of the cyclopropenyl derivatives.

3. Conclusion

3-Alkoxy-6-chloro-4H-chromen-4-ones bearing thiophen-3-yl moiety at 2-position on irradiation with the pyrex filtered UV light produced many novel dihydro and dehydrogenated angular tetracyclic photoproducts via 1,4-biradical furnished through γ-H abstraction. Most of these photoproducts were probably originated from the Dewar type moiety generated *in situ* through the photocyclization. No phototransposition, secondary ring contraction of thiophene and oxetane formation occurred in these substrates upon photoirradiation.

4. Experimental

4.1. General

Melting points were determined in open capillaries and are thus uncorrected. The photoirradiation was carried out with a 125 W Hg lamp using a pyrex filter. The ^{1}H NMR were recorded on 400 MHz Bruker spectrometer and 300 MHz (75.4 MHz for ^{13}C NMR) Bruker spectrometer using TMS as internal standard. IR spectra were recorded on a MB3000 FT-IR with HORIZON MB^{TM} FTIR software from ABB Bomen using KBr pellets. Mass spectra were recorded at 3500 eV as (ESI +Q1 mode). Elemental analysis was carried on Perkin Elmer 2400 instrument. TLC plates were coated with silica gel G (suspended in CHCl$_3$–MeOH) and iodine vapours were used as visualizing agent. The columns for purification were packed with Silica gel 100–200 mesh in pet.ether and left overnight before use. The elution was carried out with increasing proportion of benzene in pet.ether–benzene mixture. The yields reported are based on the amount of isolated photoproducts and are calculated by excluding the recovered starting substrates.

4.2. Synthesis of chromones **3(a–f)**

4.2.1. 1-(5-Chloro-2-hydroxyphenyl)-3-(thiophen-3-yl)prop-2-en-1-one, **1**

To the well-stirred suspension of powdered NaOH (0.8 g, 0.02 mol) in EtOH at 0 °C were added 5-chloro-2-hydroxyacetophenone (1.71 g, 0.01 mol) and thiophene-3-carbaldehyde (1.24 g, 0.011 mol). The reaction mixture, which became deep red in color after 30 min, was stirred further for 3 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 (86%), mp 90 °C; ν_{max} (cm^{-1}) 1643.0 (C=O), 3405 (OH); δ_H (CDCl$_3$) 7.96 (1H, d, $J_{3,2}$ = 15.3 Hz, H-3), 7.86 (1H, d, J_m = 2.7 Hz, H-6′), 7.73 (1H, dd, $J_{2″,4″}$ = 3.0 Hz, $J_{2″,5″}$ = 1.2 Hz, H-2″), 7.50 (1H, dd, $J_{5″,4″}$ = 5.1 Hz, $J_{5″,2″}$ = 1.2 Hz,

H-5″), 7.46 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.7$ Hz, H-4′), 7.44 (1H, dd, $J_{4″,5″} = 5.1$ Hz, $J_{4″,5″} = 3.0$ Hz, H-4″), 7.40 (1H, d, $J_{2,3} = 15.3$ Hz, H-2), 7.01 (1H, d, $J_o = 9.0$ Hz, H-3′).

4.2.2.
6-Chloro-3-hydroxy-2-(thiophen-3-yl)-4H-chromen-4-one, 2

To the well stirred suspension of compound 1 (2.64 g, 0.01 mol) in methanol was added 10.0 ml of 20% aq. KOH and cooled to 0 °C. To this dark red solution was added H_2O_2 (30%) drop-wise till the color changed to yellow and the stirring was continued for 4 h. The reaction mixture was neutralized with ice–HCl to give light yellow precipitates which were crystallized (CHCl$_3$–MeOH) to light yellow crystals (81%), mp 208–210 °C; ν_{max} (cm^{-1}) 1605.0 (C=O), 3248 (OH); δ_H (CDCl$_3$) 8.34 (1H, dd, $J_{2′,4′} = 3.0$ Hz, $J_{2′,5′} = 1.2$ Hz, H-2′), 8.23 (1H, d, $J_m = 2.4$ Hz, H-5), 7.88 (1H, dd, $J_{5′,4′} = 5.1$ Hz, $J_{5′,2′} = 1.2$ Hz, H-5′), 7.66 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-7), 7.55 (1H, d, $J_o = 9.0$ Hz, H-8), 7.49 (1H, dd, $J_{4′,5′} = 5.1$ Hz, $J_{4′,2′} = 3.0$ Hz, H-4′), 6.9 (1H, s, OH); Mass (m/z, +Q1): 279 (M$^+$, 100%).

4.2.3.
6-Chloro-3-methoxy-2-(thiophen-3-yl)-4H-chromen-4-one, 3a

To a suspension of compound, 2 (0.556 g, 0.002 mol) and freshly ignited K$_2$CO$_3$ (1.38 g, 0.01 mol) in dry acetone was added dimethyl sulphate (0.277 g, 0.002 mol), and tetra-n-butylammonium iodide (0.050 g). The reaction mixture was refluxed for 4 h and the color of reaction mixture change from orange red to white. Filtration, evaporation of solvent and crystallization of the residue (MeOH) gave 3a (80%), white solid/colourless crystals, mp 142–143 °C; λ_{max} MeOH 351, 300, 252 nm; ν_{max} (cm^{-1}) 1636.0 (C=O); δ_H (CDCl$_3$) 8.33 (1H, dd, $J_{2′,4′} = 3.0$ Hz, $J_{2′,5′} = 1.2$ Hz, H-2′), 8.24 (1H, d, $J_m = 2.4$ Hz, H-5), 7.83 (1H, dd, $J_{5′,4′} = 5.1$ Hz, $J_{5′,2′} = 1.2$ Hz, H-5′), 7.63 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-7), 7.51 (1H, d, $J_o = 9.0$ Hz, H-8), 7.47 (1H, dd, $J_{4′,5′} = 5.1$ Hz, $J_{4′,2′} = 3.0$ Hz, H-4′), 4.01 (3H, s, OCH$_3$); δ^{13}C (CDCl$_3$) 173.62 (C-4), 153.23, 152.39, 140.16, 133.56, 131.72, 130.64, 129.26, 126.93, 126.13, 125.21, 125.10, 119.57, 59.75 (3-OCH$_3$); Mass (m/z, +Q1): 293 (M$^+$).

The other ethers 3(b–f) were synthesized by reacting 3-hydroxychromenone 2 with allyl bromide, methyl allyl chloride, dimethyl allyl bromide, cinnamyl chloride and propargyl bromide respectively by the procedure as used for compound 3a.

4.2.4. 3-Allyloxy-6-chloro-2-(thiophen-3-yl)-4H-chromen-4-one,
3b

Yield 81%, white solid; mp 102–104 °C (MeOH); λ_{max} MeOH 348, 302, 251 nm; ν_{max} (cm^{-1}) 1636 (C=O), 1605 (C=C); δ_H (CDCl$_3$) 8.37 (1H, dd, $J_{2′,4′} = 3.0$ Hz, $J_{2′,5′} = 1.2$ Hz, H-2′), 8.23 (1H, d, $J_m = 2.4$ Hz, H-5), 7.86 (1H, dd, $J_{5′,4′} = 5.1$ Hz, $J_{5′,2′} = 1.2$ Hz, H-5′), 7.63 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-7), 7.51 (1H, d, $J_o = 9.0$ Hz, H-8), 7.47 (1H, dd, $J_{4′,5′} = 5.1$ Hz, $J_{4′,2′} = 3.0$ Hz, H-4′), 6.08 (1H, ddt, $J_{trans} = 17.1$ Hz, $J_{cis} = 10.5$ Hz, $J_{vic} = 6.0$ Hz, H-2″), 5.39 (1H, dt, $J_{trans} = 17.1$ Hz, $J_{allyl} = 1.2$ Hz, H$_a$-3″), 5.26 (1H, d, $J_{cis} = 10.5$ Hz, H$_b$-3″), 4.78 (2H, dd, $J_{vic} = 6.0$ Hz, $J_{allyl} = 1.2$ Hz, H-1″); δ^{13}C (CDCl$_3$) 173.66 (C-4), 153.21, 152.71, 140.15, 138.62, 133.57, 133.35, 131.83, 130.63, 129.44, 127.09, 125.97, 125.10, 119.59, 119.10 (C-3″), 72.92 (C-1″); Mass (m/z, +Q1): 318.96 (M$^+$, 100%).

4.2.5. 6-Chloro-3-(2-methylallyloxy)-2-(thiophen-3-yl)-4H-
chromen-4-one,
3c

Yield 88%, white solid; mp 108–110 °C (MeOH); λ_{max} MeOH 358, 301, 244 nm; ν_{max} (cm^{-1}) 1636 (C=O), 1605 (C=C); δ_H (CDCl$_3$) 8.36 (1H, dd, $J_{2′,4′} = 3.0$ Hz, $J_{2′,5′} = 1.2$ Hz, H-2′), 8.22 (1H, d, $J_m = 2.7$ Hz, H-5), 7.84 (1H, dd, $J_{5′,4′} = 5.1$ Hz, $J_{5′,2′} = 1.2$ Hz, H-5′), 7.63 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.7$ Hz, H-7), 7.56 (1H, d, $J_o = 9.0$ Hz, H-8), 7.50 (1H, dd, $J_{4′,5′} = 5.1$ Hz, $J_{4′,2′} = 3.0$ Hz, H-4′), 5.15 (1H, s, H$_a$-3″), 5.01 (1H, s, H$_b$-3″), 4.66 (2H, s, H-1″), 1.86 (3H, s, 2″-CH$_3$); δ^{13}C (CDCl$_3$): 173.58

(C-4), 153.18, 152.51, 141.15, 138.86, 133.53, 131.76, 130.60, 129.37, 127.07, 125.97, 125.16, 125.08, 119.59, 113.90, 75.38 (C-1″), 19.82 (2″-CH$_3$); Mass (m/z, +Q1): 333 (M$^+$, 100%).

4.2.6. 6-Chloro-3-(3-methylbut-2-enyloxy)-2-(thiophen-3-yl)-
4H-chromen-4-one,
3d

Yield 72%, white solid; mp 103 °C (MeOH); λ_{max} MeOH 357, 300, 246 nm; ν_{max} (cm^{-1}) 1643 (C=O), 1605 (C=C); δ_H (CDCl$_3$) 8.36 (1H, dd, $J_{2′,4′} = 3.0$ Hz, $J_{2′,5′} = 1.2$ Hz, H-2′), 8.21 (1H, d, $J_m = 2.4$ Hz, H-5), 7.85 (1H, dd, $J_{5′,4′} = 5.1$ Hz, $J_{5′,2′} = 1.2$ Hz, H-5′), 7.61 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-7), 7.49 (1H, d, $J_o = 9.0$ Hz, H-8), 7.45 (1H, dd, $J_{4′,5′} = 5.1$ Hz, $J_{4′,2′} = 3.0$ Hz, H-4′), 5.53 (1H, t, $J_{vic} = 7.2$ Hz, H-2″), 4.75 (1H, d, $J_{vic} = 7.2$ Hz, H-1″), 1.75 (3H, s, C$_3$″-CH$_3$a), 1.72 (3H, s, C$_3$″-CH$_3$b); δ^{13}C (CDCl$_3$) 173.85 (C-4), 153.22, 152.71, 139.71, 138.96, 133.46, 132.01, 130.54, 129.28, 127.11, 125.79, 125.14, 125.10, 119.74, 119.58, 68.63 (C-1″), 25.81 (3″-CH$_3$a), 18.11 (3″-CH$_3$b); Mass (m/z, +Q1): 347 (M$^+$, 100%).

4.2.7. 6-Chloro-3-(3-phenylallyloxy)-2-(thiophen-3-yl)-4H-
chromen-4-one,
3e

Yield 85%, creamish solid; mp 102–104 °C (EtOH); λ_{max} MeOH 354, 308, 252 nm; ν_{max} (cm^{-1}) 1643 (C=O), 1605 (C=C); δ_H (CDCl$_3$) 8.38 (1H, dd, $J_{2′,4′} = 3.0$ Hz, $J_{2′,5′} = 1.2$ Hz, H-2′), 8.24 (1H, d, $J_m = 2.4$ Hz, H-5), 7.87 (1H, dd, $J_{5′,4′} = 5.1$ Hz, $J_{5′,2′} = 1.2$ Hz, H-5′), 7.62 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-7), 7.51–7.47 (2H, m, H-8, H-4′), 7.33–7.29 (5H, m, H-2‴–6‴), 6.69 (1H, d, $J_{3″,2″} = 15.6$ Hz, H-3″), 6.41 (1H, dt, $J_{2″,3″} = 15.6$ Hz, $J_{2″,1″} = 6.6$ Hz, H-2″), 4.94 (2H, d, $J_{1″,2″} = 6.6$ Hz, H-1″); δ^{13}C (CDCl$_3$) 173.74 (C-4), 153.24, 152.90, 139.23, 138.58, 136.31, 134.49, 133.59, 131.91, 130.64, 129.48, 128.57, 128.02, 127.19, 126.69, 126.03, 125.11, 124.40, 119.64, 72.73 (C-1″); Mass (m/z, +Q1): 395 (M$^+$, 100%).

4.2.8.
6-Chloro-3-propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one,
3f

Yield 86%, white solid; mp 148–150 °C (MeOH); λ_{max} MeOH 347, 306, 249 nm; ν_{max} (cm^{-1}) 1638 (C=O), 2135 (C≡C); δ_H (CDCl$_3$) 8.42 (1H, dd, $J_{2′,4′} = 3.0$ Hz, $J_{2′,5′} = 1.2$ Hz, H-2′), 8.22 (1H, d, $J_m = 2.4$ Hz, H-5), 7.89 (1H, dd, $J_{5′,4′} = 5.1$ Hz, $J_{5′,2′} = 1.2$ Hz, H-5′), 7.64 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-7), 7.52 (1H, d, $J_o = 9.0$ Hz, H-8), 7.46 (1H, d, $J_{4′,5′} = 5.1$ Hz, $J_{4′,2′} = 3.0$ Hz, H-4′), 5.10 (2H, d, $J_{1″,3″} = 2.4$ Hz, H-1″), 2.42 (1H, t, $J_{3″,1″} = 2.4$ Hz, H-3″); δ^{13}C (CDCl$_3$) 173.66 (C-4), 153.21, 152.71, 138.62, 133.57, 133.35, 131.84, 130.63, 129.44, 127.09, 125.97, 125.10, 119.59, 119.10, 77.23, 72.92 (C-1″); Mass (m/z, +Q1): 317 (M$^+$, 100%).

4.3. Photoirradiation of chromones 3(a-f)

4.3.1. Photolysis of
6-chloro-3-methoxy-2-(thiophen-3-yl)-4H-chromen-4-one, 3a

A 1.0 mM methanolic solution of chromone 3a 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 50 min. The removal of solvent left a gummy solid which was chromatographed to yield 4a, 4a′ and 4a″.

Compound 4a. Yield 30%, light yellow solid; mp 224–226 °C; ν_{max} (cm^{-1}) 1636 (C=O); δ_H (CDCl$_3$/400 MHz) 8.22 (1H, d, $J_m = 2.6$ Hz, H-7), 7.58 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.6$ Hz, H-9), 7.41 (1H, d, $J_o = 9.0$ Hz, H-10), 6.59 (1H, dt/ddd, $J_{1,3Hx} = 3.6$ Hz, $J_{1,3Hy} = 2.4$ Hz, $J_{1,3a} = 2.4$ Hz, H-1), 4.71–4.64 (2H, m, H$_a$-4, H$_b$-4), 4.09 (1H, ddd, $J_{3Hx,3Hy} = 16.4$ Hz, $J_{3Hx,3a} = 4.6$ Hz, $J_{3Hx,1} = 2.4$ Hz, H$_x$-3), 3.96–3.88 (2H, m, H$_y$-3, H-3a); δ^{13}C (CDCl$_3$) 170.76 (C-6), 152.95, 142.80, 138.07, 133.82 (C-9), 131.99, 130.49, 128.30 (C-1), 125.35 (C-7), 124.63, 119.51 (C-10), 71.75 (C-4), 48.09 (C-3a), 39.27 (C-3). Anal. Calcd. for C$_{14}$H$_9$ClO$_3$S:

C, 57.44; H, 3.10. Found: C, 57.04; H, 3.10; Mass (m/z, +Q1): 293/295 (M$^+$, 100%).

Compound **4a′**.Yield 35%, light yellow solid; mp 240–242 °C; ν_{max} (cm^{-1}) 1636 (C=O); δ_H (CDCl$_3$) 8.30 (1H, d, J_m = 2.4 Hz, H-7), 7.61 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.50 (1H, d, J_o = 9.0 Hz, H-10), 7.42 (2H, s, H-1, H-3), 5.51 (2H, s, H$_a$-4, H$_b$-4); δ^{13}C (CDCl$_3$) 169.82 (C-6), 152.59, 147.17, 135.92, 134.90, 133.24 (C-9), 130.80, 127.60, 126.20, 125.57 (C-7), 125.41, 121.70, 119.57 (C-10), 65.56 (C-4). Anal. Calcd. for C$_{14}$H$_7$ClO$_3$S: C, 57.84; H, 2.83. Found: C, 57.95; H, 2.86; Mass (m/z, +Q1): 291/293 (M$^+$, 100%).

Compound **4a″**.Yield 20%, white solid; mp 160 °C; ν_{max} (cm^{-1}) 1651 (C=O); δ_H (CDCl$_3$) 8.19 (1H, d, J_m = 2.7 Hz, H-5), 8.04 (1H, dd, $J_{2',4'}$ = 2.4 Hz, $J_{2',5'}$ = 1.5 Hz, H-2′), 7.64 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-7), 7.50 (3H, m, H-8, 4′, 5′), 6.69 (1H, s, H-3); δ^{13}C (CDCl$_3$) 177.11 (C-4), 159.77, 154.37, 133.86 (C-7), 131.15, 127.54, 127.15, 125.48 (C-5), 125.19, 125.02, 124.97, 119.66 (C-8), 107.04 (C-3). Anal. Calcd. for C$_{13}$H$_7$ClO$_2$S: C, 59.43; H, 2.69. Found: C, 59.43; H, 2.67; Mass (m/z, +Q1): 263/265 (M$^+$, 100%).

4.3.2. Photolysis of 3-allyloxy-6-chloro-2-(thiophen-3-yl)-4H-chromen-4-one, **3b**

A 1.0 mM methanolic solution of 3b on photolysis for 50 min furnished **4b**, **4b′** and **4b″**.

Compound **4b**. Yield 29%, white solid; mp 210–212 °C; ν_{max} (cm^{-1}) 1628 (C=O); δ_H (CDCl$_3$/400MHz) 8.23 (1H, d, J_m = 2.6 Hz, H-7), 7.59 (1H, dd, J_o = 9.0 Hz, J_m = 2.6 Hz, H-9), 7.41 (1H, d, J_o = 9.0 Hz, H-10), 6.62 (1H, dt/ddd, $J_{1,3Hy}$ = 3.6 Hz, $J_{1,3Hx}$ = 2.4 Hz, $J_{1,3a}$ = 2.4 Hz, H-1), 5.99 (1H, ddd, J_{trans} = 17.2 Hz, J_{cis} = 10.6 Hz, J_{vic} = 6.9 Hz, H-1′), 5.58 (1H, dd, J_{trans} = 17.2 Hz, $J_{2'a,4}$ = 0.9 Hz, H-2′a), 5.44 (1H, dd, J_{cis} = 10.6 Hz, $J_{2'b,4}$ = 0.9 Hz, H-2′b), 4.49 (1H, dtd/dddd, $J_{3a,4}$ = 10.8 Hz, $J_{3a,3Hy}$ = 5.0 Hz, $J_{3a,3Hx}$ = 4.8 Hz, $J_{3a,1}$ = 2.2 Hz, H-3a), 4.37 (1H, dd, $J_{4,3a}$ = 10.8 Hz, $J_{4,1'}$ = 6.9 Hz, H-4), 4.04 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3x,3a}$ = 4.8 Hz, $J_{3x,1}$ = 2.4 Hz, H$_x$-3), 3.86 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hy,3a}$ = 5.0 Hz, $J_{3Hy,1}$ = 3.7 Hz, H$_y$-3); δ^{13}C (CDCl$_3$) 170.66 (C-6), 152.96, 142.92, 138.33, 133.80 (C-9), 133.00(C-1′), 132.03, 130.48, 128.90 (C-1), 125.48 (C-7), 124.81, 120.75 (C-2′), 119.50 (C-10), 83.02 (C-4), 53.44 (C-3a), 39.02 (C-3). Anal. Calcd. for C$_{16}$H$_{11}$ClO$_3$S: C, 60.28; H, 3.48. Found: C, 60.46; H, 3.60; Mass (m/z, +Q1): 319/321 (M$^+$, 100%).

Compound **4b′**. Yield 36%, light yellow solid; mp 198–200 °C; ν_{max} (cm^{-1}) 1643 (C=O); δ_H (CDCl$_3$) 8.30 (1H, d, J_m = 2.4 Hz, H-7), 7.61 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.50 (1H, d, J_o = 9.0 Hz, H-10), 7.44 (2H, s, H-1, H-3), 6.18 (1H, ddd, J_{trans} = 17.1 Hz, J_{cis} = 10.5 Hz, J_{vic} = 6.3 Hz, H-1′), 6.05 (1H, d, J_{vic} = 6.3 Hz, H-4), 5.45-5.39 (2H, m, H-2′a, H-2′b); δ^{13}C (CDCl$_3$) 170.01 (C-6), 152.56, 146.74, 138.81, 134.02, 133.21 (C-9), 130.75, 128.34, 127.13, 126.89, 125.59, 125.45 (C-7), 121.96, 119.92, 119.58 (C-10), 76.30 (C-4). Anal. Calcd. for C$_{16}$H$_9$ClO$_3$S: C, 60.67; H, 2.86. Found: C, 61.46; H, 2.72; Mass (m/z, +Q1): 317/319 (M$^+$, 100%).

Compound **4b″**. Yield 10%, white solid; mp 178–180 °C; ν_{max} (cm^{-1}) 1637 (C=O); δ_H (CDCl$_3$) 8.26 (1H, d, J_m = 2.4 Hz, H-7), 7.63 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.47 (1H, d, J_o = 9.0 Hz, H-10), 7.44 (1H, d, $J_{2,1}$ = 5.1 Hz, H-2), 7.35 (1H, d, $J_{1,2}$ = 5.1 Hz, H-1), 6.60 (1H, ddd, J_{trans} = 17.1 Hz, J_{cis} = 10.5 Hz, J_{vic} = 6.3 Hz, H-1′), 6.03 (1H, d, J_{vic} = 6.3 Hz, H-4), 5.15–5.03 (2H, m, H-2′a, H-2′b); δ^{13}C (CDCl$_3$) 171.21 (C-6), 153.65, 143.74, 138.78, 133.78 (C-9), 133.01, 130.86, 129.34, 127.13, 126.94, 125.67, 125.51 (C-7), 125.04, 123.87, 119.85 (C-10), 74.30 (C-4). Anal. Calcd. for C$_{16}$H$_9$ClO$_3$S: C, 60.67; H, 2.86. Found: C, 60.67; H, 2.78; Mass (m/z, +Q1): 317/319 (M$^+$, 100%).

4.3.3. Photolysis of 6-chloro-3-(2-methylallyloxy)-2-(thiophen-3-yl)-4H-chromen-4-one, **3c**

A 1.0 mM methanolic solution of 3c on photolysis for 50 min furnished **4c**, **4c′** and **4c″**.

Compound **4c**. Yield 35%, light yellow solid; mp 210 °C; ν_{max} (cm^{-1}) 1636 (C=O); δ_H (CDCl$_3$/400MHz) 8.23 (1H, d, J_m = 2.6 Hz, H-7), 7.59 (1H, dd, J_o = 9.0 Hz, J_m = 2.6 Hz, H-9), 7.41 (1H, d, J_o = 9.0 Hz, H-10), 6.61 (1H, dt/ddd, $J_{1,3Hy}$ = 3.6 Hz, $J_{1,3Hx}$ = 2.4 Hz, $J_{1,3a}$ = 2.4 Hz, H-1), 5.19 (1H, s, H-2′b), 5.15 (1H, t, J = 1.4 Hz, H-2′a), 4.63 (1H, dtd/dddd, $J_{3a,4}$ = 10.8 Hz, $J_{3a,3Hy}$ = 5.0 Hz, $J_{3a,3Hx}$ = 4.8 Hz, $J_{3a,1}$ = 2.2 Hz, H-3a), 4.32 (1H, d, $J_{4,3a}$ = 10.8 Hz, H-4), 4.03 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hx,3a}$ = 4.8 Hz, $J_{3Hx,1}$ = 2.4 Hz, H$_x$-3), 3.85 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hy,3a}$ = 5.0 Hz, $J_{3Hy,1}$ = 3.7 Hz, H$_y$-3), 1.91 (3H, s, C$_{1'}$-CH$_3$); δ^{13}C (CDCl$_3$) 170.63 (C-6), 152.92, 142.82, 139.67 (C-1′), 138.63, 133.74 (C-9), 132.33, 130.41, 128.71 (C-1), 125.45 (C-7), 124.83, 119.48 (C-10), 117.54 (C-2′), 86.38 (C-4), 51.62 (C-3a), 38.97 (C-3), 17.52 (1′-CH$_3$). Anal. Calcd. for C$_{17}$H$_{13}$ClO$_3$S: C, 61.35; H, 3.94. Found: C, 60.84; H, 4.02; Mass (m/z, +Q1): 333/335 (M$^+$, 100%).

Compound **4c′**. Yield 38%, light yellow solid; mp 184 °C; ν_{max} (cm^{-1}) 1627 (C=O); δ_H (CDCl$_3$) 8.30 (1H, d, J_m = 2.4 Hz, H-7), 7.61 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.50 (1H, d, J_o = 9.0 Hz, H-10), 7.43 (2H, s, H-1,3), 6.04 (1H, s, H-4), 5.17 (1H, s, H-2′a), 5.02 (1H, s, H-2′b), 1.95 (3H, s, C$_{1'}$-CH$_3$); δ^{13}C (CDCl$_3$) 169.88 (C-6), 152.52, 146.56, 141.90, 138.98, 134.38, 133.14 (C-9), 130.69, 127.54, 126.88, 125.61, 125.43 (C-7), 121.82, 119.57 (C-10), 116.26, 79.75 (C-4), 18.09 (1′-CH$_3$). Anal. Calcd. for C$_{17}$H$_{11}$ClO$_3$S: C, 61.73; H, 3.35. Found: C, 61.73; H, 3.39; Mass (m/z, +Q1): 331/333(M$^+$, 100%).

Compound **4c″**. Yield 12%, off-white solid; mp 190–192 °C; ν_{max} (cm^{-1}) 1643 (C=O); δ_H (CDCl$_3$) 8.26 (1H, d, J_m = 2.4 Hz, H-7), 7.63 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.47 (1H, d, J_o = 9.0 Hz, H-10), 7.37 (1H, d, $J_{2,1}$ = 5.4 Hz, H-2), 7.31 (1H, d, $J_{1,2}$ = 5.4 Hz, H-1), 6.44 (1H, s, H-4), 4.89 (2H, s, H-2′a, 2′b), 1.85 (3H, s, C$_{1'}$-CH$_3$); δ^{13}C (CDCl$_3$) 171.80 (C-6), 153.93, 143.41, 141.68, 138.98, 133.78 (C-9), 130.81, 129.21, 126.91, 126.05, 125.56 (C-7), 125.14, 124.95, 119.87 (C-10), 115.64, 74.79 (C-4), 21.61 (1′-CH$_3$). Anal. Calcd. for C$_{17}$H$_{11}$ClO$_3$S: C, 61.73; H, 3.35. Found: C, 61.34; H, 3.12; Mass (m/z, +Q1): 331/333 (M$^+$, 100%).

4.3.4. Photolysis of 6-chloro-3-(3-methylbut-2-enyloxy)-2-(thiophen-3-yl)-4H-chromen-4-one, **3d**

A 1.0 mM methanolic solution of **3d** on photolysis for 50 min furnished **4d** and **4d′**.

Compound **4d**. Yield 20%, light brown solid; mp 212–214 °C; ν_{max} (cm^{-1}) 1637 (C=O); δ_H (CDCl$_3$) 8.23 (1H, d, J_m = 2.4 Hz, H-7), 7.59 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.41 (1H, d, J_o = 9.0 Hz, H-10), 6.64-6.61 (1H, m, H-1), 5.82 (1H, dd, $J_{1',4}$ = 6.6 Hz, J_{allyl} = 1.5 Hz, H-1′), 4.56 (1H, dtd/dddd, $J_{3a,4}$ = 10.8 Hz, $J_{3a,3Hy}$ = 5.0 Hz, $J_{3a,3Hx}$ = 4.8 Hz, $J_{3a,1}$ = 2.2 Hz, H-3a), 4.37 (1H, dd, $J_{4,3a}$ = 10.8 Hz, $J_{4,1'}$ = 6.6 Hz, H-4), 4.05 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hx,3a}$ = 4.8 Hz, $J_{3Hx,1}$ = 2.4 Hz, H$_x$-3), 3.87 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hy,3a}$ = 5.0 Hz, $J_{3Hy,1}$ = 3.7 Hz, H$_y$-3), 1.80 (3H, d, J_{allyl} = 1.5 Hz, C$_{2'}$-CH$_3$a), 1.76 (3H, s, C$_{2'}$-CH$_3$b); δ^{13}C (CDCl$_3$) 170.65 (C-6), 152.94, 142.86, 139.82, 138.00, 133.98 (C-9), 133.70, 130.42, 128.20 (C-1), 125.50 (C-7), 124.82, 121.52, 119.46 (C-10), 85.80(C-4), 50.37 (C-3a), 39.97 (C-3), 25.20 (2′-CH$_3$a), 19.20 (2′-CH$_3$b). Anal. Calcd. for C$_{18}$H$_{15}$ClO$_3$S: C, 62.33; H, 4.36. Found: C, 62.33; H, 4.36; Mass (m/z, +Q1): 347/349 (M$^+$, 100%).

Compound **4d′**. Yield 21%, light brown solid; mp 188 °C; ν_{max} (cm^{-1}) 1641 (C=O); δ_H (CDCl$_3$) 8.28 (1H, d, J_m = 2.4 Hz, H-7), 7.60 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.49 (1H, d, J_o = 9.0 Hz, H-10), 7.44 (2H, s, H-1, H-3), 6.01 (1H, dd, $J_{1',4}$ = 6.3 Hz, J_{allyl} = 1.5 Hz, H-1′), 5.86 (1H, d, $J_{4,1'}$ = 6.3 Hz, H-4), 1.81 (3H, d, J_{allyl} = 1.5 Hz, C$_{2'}$-CH$_3$a), 1.78 (3H, s, C$_{2'}$-CH$_3$b); δ^{13}C (CDCl$_3$) 170.23 (C-6), 152.54, 146.50, 138.87, 134.22, 133.16 (C-9), 130.71, 129.56, 127.34, 126.87, 125.60, 125.49 (C-7), 121.89, 119.58 (C-10), 118.65, 76.42 (C-4), 24.20 (2′-CH$_3$a), 18.09 (2′-CH$_3$b). Anal. Calcd. for C$_{18}$H$_{13}$ClO$_3$S: C, 62.70; H, 3.80. Found: C, 62.58; H, 3.80; Mass (m/z, +Q1): 345/347 (M$^+$, 100%).

4.3.5. Photolysis of 6-chloro-3-(3-phenylallyloxy)-2-(thiophen-3-yl)-4H-chromen-4-one, 3e

A 1.0 mM methanolic solution of 3e on photolysis for 50 min furnished three photoproducts **4e** and **4e′**.

Compound **4e**. (Data from mixture ^{1}H NMR/IR of **2** and **4e**) Yield 10%; ν_{max} (cm^{-1}) 1638 (C=O); δ_H (CDCl$_3$) 8.27 (1H, d, J_m = 2.4 Hz, H-7), 7.61 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.43 (1H, d, J_o = 9.0 Hz, H-10), 7.36–7.28 (5H, m, H-2″–6″), 6.84 (1H, d, $J_{2',1'}$ = 16.2 Hz, H-2′), 6.64 (1H, brs, H-1), 6.31 (1H, dd, $J_{1',2'}$ = 16.2 Hz, $J_{1',4}$ = 6.9 Hz, H-1′), 4.51 (1H, dtd/dddd, $J_{3a,4}$ = 10.8 Hz, $J_{3a,3Hy}$ = 5.0 Hz, $J_{3a,3Hx}$ = 4.8 Hz, $J_{3a,1}$ = 2.2 Hz, H-3a), 4.37 (1H, dd, $J_{4,3a}$ = 10.8 Hz, $J_{4,1'}$ = 6.9 Hz, H-4), 4.16 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hx,3a}$ = 4.8 Hz, $J_{3Hx,1}$ = 2.4 Hz, H$_x$-3), 3.88 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hy,3a}$ = 5.0 Hz, $J_{3Hy,1}$ = 3.7 Hz, H$_y$-3). *Compound* **4e′** Yield 45%, off white solid; mp 176–178 °C; ν_{max} (cm^{-1}) 1643 (C=O); δ_H (CDCl$_3$) 8.15 (1H, d, J_m = 2.1 Hz, H-7), 7.61 (1H, dd, J_o = 9.0 Hz, J_m = 2.1 Hz, H-9), 7.51 (1H, d, J_o = 9.0 Hz, H-10), 7.46 (2H, s, H-1, H-3), 7.42-7.31 (5H, m, H-2″–6″), 6.71 (1H, d, $J_{2',1'}$ = 15.9 Hz, H-2′), 6.51 (1H, dd, $J_{1',2'}$ = 15.9 Hz, $J_{1',4}$ = 6.6 Hz, H-1′), 6.23 (1H, d, $J_{4,1'}$ = 6.6 Hz, H-4); δ^{13}C (CDCl$_3$) 170.06 (C-6), 152.58, 146.72, 139.21, 135.36, 135.02, 134.20, 133.21 (C-9), 130.75, 128.66, 128.34, 127.19, 127.07, 126.99, 125.67, 125.47 (C-7), 124.83, 122.03, 119.58 (C-10), 75.76(C-4). Anal. Calcd. for C$_{22}$H$_{13}$ClO$_3$S: C, 67.26; H, 3.34. Found: C, 67.68; H, 3.23; Mass (m/z, +Q1): 393/395 (M$^+$, 100%).

4.3.6. Photolysis of 6-chloro-3-propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one, 3f

A 1.0 mM methanolic solution of 3f on photolysis for 50 min furnished **4f**, **4f′** and **4f″**. These photoproducts were separated from the starting substrate by column chromatography.

Compound **4f**. Yield 36%, light brown solid; mp 228–230 °C; ν_{max} (cm^{-1}) 1636 (C=O), 2129 (C≡C); δ_H (CDCl$_3$) 8.25 (1H, d, J_m = 2.4 Hz, H-7), 7.62 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.43 (1H, d, J_o = 9.0 Hz, H-10), 6.66 (1H, brs, H-1), 4.75 (1H, dtd/dddd, $J_{3a,4}$ = 10.8 Hz, $J_{3a,3Hy}$ = 5.0 Hz, $J_{3a,3Hx}$ = 4.8 Hz, $J_{3a,1}$ = 2.2 Hz, H-3a), 4.63 (1H, dd, $J_{4,3a}$ = 10.8 Hz, $J_{4,2'}$ = 1.8 Hz, H-4), 4.11 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hx,3a}$ = 4.8 Hz, $J_{3Hx,1}$ = 2.4 Hz, H$_x$-3), 3.92 (1H, ddd, J_{gem} = 16.5 Hz, $J_{3Hy,3a}$ = 5.0 Hz, $J_{3Hy,1}$ = 3.7 Hz, H$_y$-3), 2.74 (1H, d, $J_{2',4}$ = 1.8 Hz, H-2′); δ^{13}C (CDCl$_3$) 170.15 (C-6), 152.95, 142.73, 137.70, 133.98 (C-9), 131.19, 130.70, 130.06 (C-1), 125.53 (C-7), 124.77, 119.48 (C-10), 90.82, 77.75 (C-2′), 72.72 (C-4), 54.27 (C-3a), 39.02 (C-3). Anal. Calcd. for C$_{16}$H$_9$ClO$_3$S: C, 60.67; H, 2.86. Found: C, 60.67; H, 2.89; Mass (m/z, +Q1): 317/319 (M$^+$, 100%).

Compound **4f′**. (Data from mixture ^{1}H NMR/IR of **4f′** and **4f″**) Yield 8%; ν_{max} (cm^{-1}) 1628 (C=O), 2128 (C≡C); δ_H (CDCl$_3$) 8.27 (1H, d, J_m = 2.4 Hz, H-7), 7.63 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.52 (1H, d, J_o = 9.0 Hz, H-10), 7.47 (2H, s, H-1,3), 6.76 (1H, d, $J_{4,2'}$ = 2.4 Hz, H-4), 2.48 (1H, d, $J_{2',4}$ = 2.4 Hz, H-2′).

Compound **4f″**. Yield 10%; ν_{max} (cm^{-1}) 1643 (C=O), 2130 (C≡C); δ_H (CDCl$_3$) 8.32 (1H, d, J_m = 2.4 Hz, H-7), 7.63 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.52 (1H, d, J_o = 9.0 Hz, H-10), 7.48 (1H, d, $J_{2,1}$ = 5.1 Hz, H-2), 7.44 (1H, d, $J_{1,2}$ = 5.1 Hz, H-1), 6.30 (1H, d, $J_{4,2'}$ = 2.4 Hz, H-4), 2.75 (1H, d, $J_{2',4}$ = 2.4 Hz, H-2′).

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