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Photocyclisation of 3-alkoxy-6-chloro-2-(3-methylthiophen-2-yl)-4*H*-chromen-4-ones

Ramesh C. Kamboj *, Geeta Sharma, Dinesh Kumar, Rita Arora

Department of Chemistry, Kurukshetra University, Kurukshetra, 136119, India

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ABSTRACT

Photocyclisation of 3-alkoxy-6-chloro-2-(3-methylthiophen-2-yl)-4*H*-chromen-4-ones in methanol with pyrex filtered UV-light lead to the formation of tetracyclic compounds through intramolecular γ-hydrogen abstraction. The methyl group on the thiophenyl ring does not interfere in the photocyclisation although it does effect the product formation.

1. Introduction

Chromones [1] and their derivatives are the naturally occurring compounds ubiquitously found in the plant kingdom, and therefore are present in representative amounts in normal human diet. These phytochemicals possess a wide spectrum of biological activities such as anti-inflammatory [2], antimicrobial [3], anticancer and antitumour [4] and antioxidant [5] properties. In fact, the chromone moiety is an important element of the pharmacophores of many biologically active molecules displaying diverse medicinal applications [2].

Intramolecular H-abstraction [6–9] in 3-alkoxy-2-arylchromones is of considerable significance. These chromones on photo-irradiation undergo cyclisation via γ-H abstraction to yield the angular tetracyclic products and the product formation depends upon the nature of 3-alkoxy group. The 3-alkoxy-2-thiophenyl-4*H*-chromen-4-ones on photo-irradiation produced cyclized dihydro and dehydrogenated photoproducts [10,11]. From these, the cyclized dihydro photoproducts were formed via 1,5-sigmatropic H-shift whereas the cyclized dehydrogenated products are formed by the expulsion of H_2 during ketonisation directly. In the present study, we report the results of our investigation on the photoreactions of 3-alkoxy-6-chloro-2-(3-methylthiophen-2-yl)-4*H*-chromen-4-ones. The main objectives are:

- how does the methyl group at 3'-position effect the product formation through its steric/inductive effect;
- does the demethylation occurs leading to the formation of cyclized aromatic products as represented earlier or simple cyclisation occurs without its expulsion giving cyclized photoproducts analogous to dihydro-photoproduct having angular methyl group during photocyclisation;
- to unravel the effect of different groups at C-3 on the product formation/distribution.

* Corresponding author.
E-mail address: rckamboj@rediffmail.com (R.C. Kamboj).

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2. Results and discussion

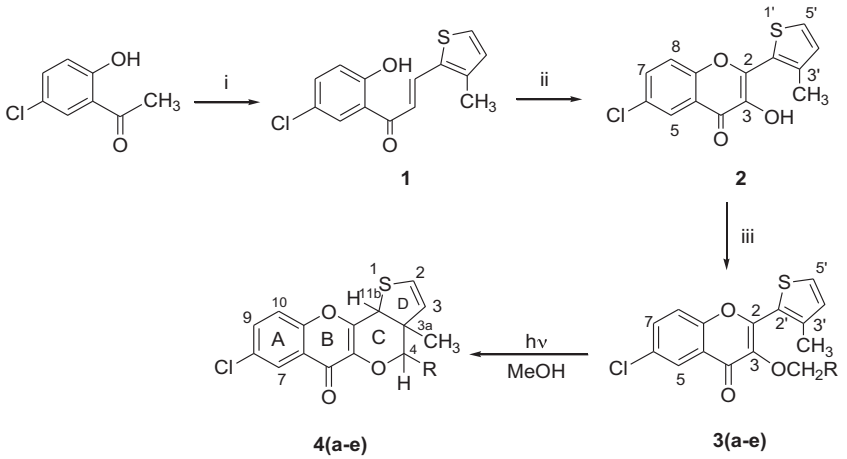
The required substrates, 3-alkoxy-2-(3-methylthiophen-2-yl)-4*H*-chromen-4-ones **3(a–e)** were synthesized by the alkylation of 3-hydroxychromen-4-one **2** that was obtained by the condensation of 5-chloro-2-hydroxyacetophenone with 3-methylthiophene-2-carboxaldehyde in the presence of NaOH/EtOH [12] to give chalcone **1**, followed by the treatment with $H_2O_2/^-OH$ under AFO conditions [13] (Scheme 1).

The structures of compounds **3(a–e)** were found to be consistent with their spectral parameters (IR, $^1H/^{13}C$ NMR). The yields of all these compounds were in the range of 80–98%.

The photolysis of methanolic solution of **3(a–e)** with pyrex filtered UV-light, under nitrogen atmosphere produced photoproducts **4(a–e)**, and the structures of these photoproducts (Scheme 2) were confirmed by their spectral data (IR, $^1H/^{13}C$-NMR) and elemental analysis.

In all these photoproducts, the ring *C* has half chair conformation and evidently, the *C*/*D* ring fusion is *cis*. For example in **4c**, the *trans*-fusion of five-membered ring will result in higher conformational strain as calculated by MM2 energy minimizations programme [14] than the *cis*-fusion and this is in accordance with the earlier findings in case of the naturally occurring pterocarpans [15–18] and N-heterocycles [19]. Now assuming the *C*/*D* ring fusion as *cis*, the orientation of H-4 can be *cis* or *trans* with respect to $-CH_3$ at C-3a. So, four possible 3D conformations **I, II** (H-4 *cis* to CH_3-3a) and **III, IV** (H-4 *trans* to CH_3-3a) were derived from MM2 energy minimizations programme which are shown in Fig. 1.

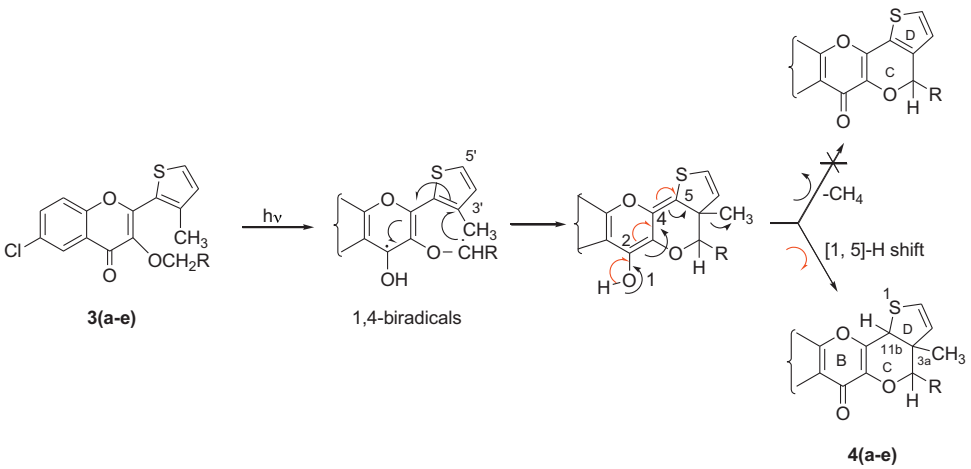
From the above four conformations, the one which has minimum energy i.e. conformation **I**, could be the possible



a, R = -H; **b**, R = -CCH; **c**, R = -$CHCH_2$; **d**, R = -$C(CH_3)CH_2$; **e**, R = -C_6H_5

i) 3-Methyl thiophene-2-carboxaldehyde/C_2H_5OH/NaOH; ii) KOH/H_2O_2(30%)/ 0°C
iii) K_2CO_3/dry CH_3COCH_3/$Bu_4N^+I^-$/RCH_2X

Scheme 1. Synthesis and photolysis of chromenones **3(a–e)**.



Scheme 2. Mechanism of photocyclisation of **3(a–e)**.

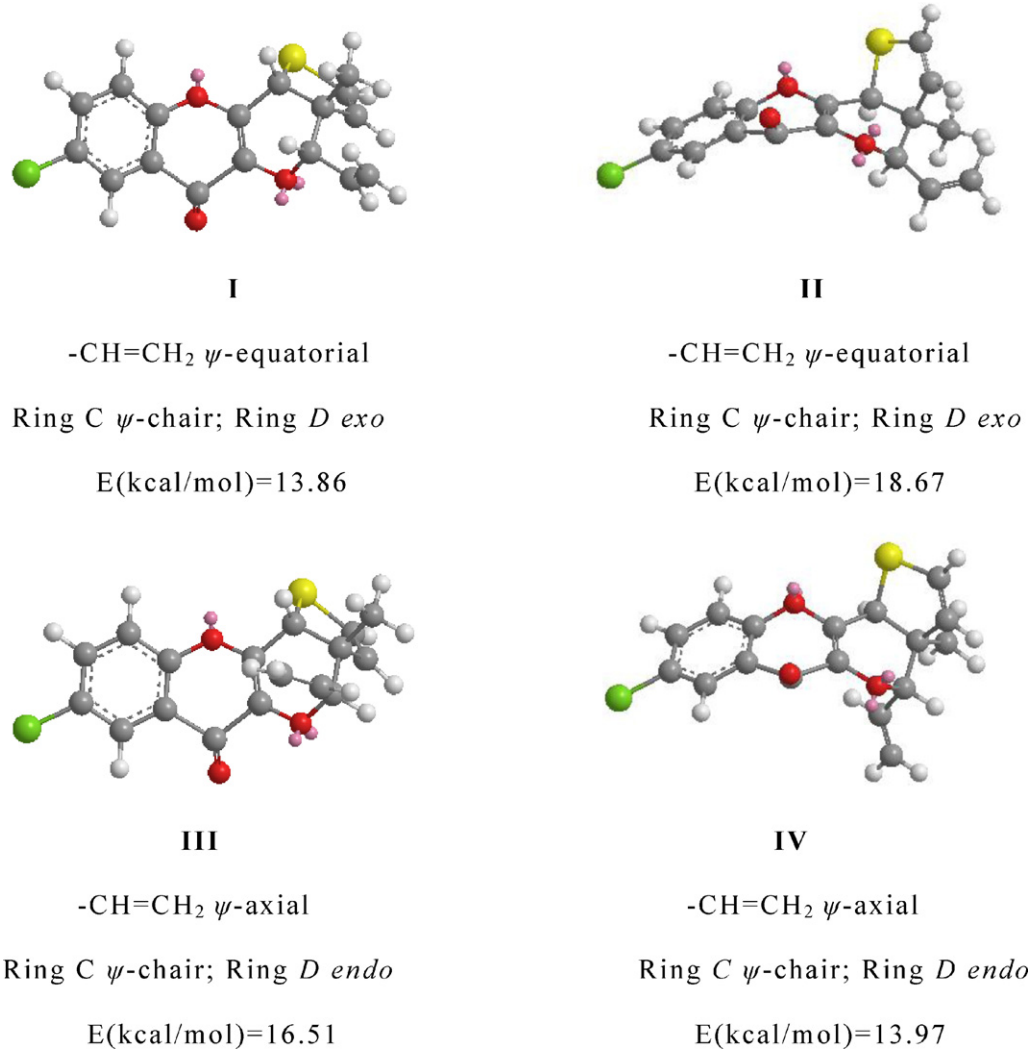


Fig. 1. Possible energy minimized conformations of photoproduct **4c**.

conformation for the photoproduct **4c** in which H-4 is *cis* to 3a-CH_3 group and bulkier vinyl group is at ψ-equatorial position. Such a view is in conformity with the literature [20] where the heavier group at equatorial position in cyclohexane is always preferred.

The thiophen-2-yl chromenones having same basic skeleton similar to **3(a–e)** with no 3–CH_3 group at thiophenyl group furnished cyclised dihydro and cyclised dehydrogenated aromatic photoproducts [10,11]. The cyclised dihydro photoproducts were formed via 1,5-sigmatropic H-shift whereas the cyclised dehyderogenated aromatic products were formed by the expulsion of H_2 during ketonisation directly. But, in the present study, the thiophen-2-yl chromenones **3(a–e)** having a –CH_3 group as a substituent at C-3 of thiophenyl, the formation of only cyclised dihydro type photoproducts **4(a–e)** through 1,5-sigmatropic H-shift is favored. No demethylation leading to the formation of aromatic photoproducts was observed as the energy required to break C–C bond is higher than that required to break a C–H bond.

Table 1
Yields of the photoproducts (**4a–4e**).

Photoproduct	4a	4b	4c	4d	4e
R	–H	–CCH	$-CHCH_2$	$-C(CH_3)CH_2$	C_6H_5
Yield (%)	24	38	46	71	87

The phototransformations (Scheme 2) described above can be visualized to occur through the formation of 1,4-biradical intermediate. The products have been expected to be formed through a bond formation between –$\dot{C}$H– radical and the C-3 atom of thiophene ring followed by ketonisation and H-migration to C-11b (1,5-H shift). The thiophenyl moiety at C-2 possesses only 3'-carbon available for clipping of 1,4-biradical.

Moreover, the yields of the photoproducts **4(a–e)** formed depended upon the nature of the alkoxy group at C-3 position of the substrates (**3a**–**3e**). As the stability of the 1,4-biradicals generated *in situ* from **3a** (R = –H) to **3e** (R = $-C_6H_5$) increases (Scheme 2), yield of the corresponding photoproduct also increases (Table 1).

3. Conclusion

The 3-alkoxy-6-chloro-2-(3-methylthiophen-2-yl)-4*H*-chromen-4-ones upon photo-irradiation yielded angular tetracyclic products through 1,4-biradical furnished by γ-H abstraction, no demethylation occurred and therefore no cyclised aromatic photoproduct was realized.

4. Experimental

4.1. Materials and methods

Melting points were determined in open capillaries and are thus uncorrected. $^1H/^{13}C$ NMR spectra were recorded at 300 MHz (75.4 MHz for ^{13}C NMR) on a 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 2500 eV (ESI-Source) using a Water's Q-TOF micro instrument. Elemental analysis was carried on Perkin Elmer 2400 instrument. TLC plates were coated with silica gel G (suspended in $CHCl_3$–MeOH) and iodine vapors 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 substrates.

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

*1-(5-Chloro-2-hydroxyphenyl)-3-(3-methylthiophen-2-yl)prop-2-en-1-one (**1**)*

A solution of 5-chloro-2-hydroxyacetophenone (1.70 g, 1.0 eq.) and 3-methylthiophene-2-carboxaldehyde (1.38 g, 1.1 eq.) in absolute ethanol and sodium hydroxide (2.0 eq.) were stirred for 4 h. The dark red mixture was poured on ice-HCl to obtain **1** as yellow solid, crystallized from EtOH (1.90 g, 68.44%), m.p. 110–112 °C; IR ν_{max} (cm^{-1}): 1628.0 (C = O), 3405 (OH); ^1H NMR ($CDCl_3$, 300 MHz): δ 12.90 (1H, s, OH), 8.19 (1H, d, $J_{3,2}$ = 15.0 Hz, H-3), 7.84 (1H, d, $J_{6',4'}$ = 2.4 Hz, H-6'), 7.45 (1H, dd, $J_{4',6'}$ = 2.4 Hz, $J_{4',3'}$ = 9.0 Hz, H-4'), 7.42 (1H, d, $J_{5'',4''}$ = 5.4 Hz, H-5''), 7.28 (1H, d, $J_{2,3}$ = 15.0 Hz, H-2), 7.00 (1H, d, $J_{3',4'}$ = 9.0 Hz, H-3'), 6.97 (1H, d, $J_{4'',5''}$ = 5.4 Hz, H-4''), 2.46 (3H, s, 3''–C**H**$_3$); ^{13}C NMR ($CDCl_3$): δ 192.24 (C-1), 162.02, 144.24, 137.26, 135.96, 134.25, 131.66, 128.75, 128.62, 123.47, 120.62, 120.17, 117.06, 14.38; Anal. Calcd. for $C_{14}H_{11}ClO_2S$: C, 60.32; H, 3.98. Found: C, 60.30; H, 3.94.

*6-Chloro-3-hydroxy-2-(3-methylthiophen-2-yl)-4H-chromen-4-one (**2**)*

To a well stirred suspension of compound **1** (1.0 g, 0.003 mol) in MeOH was added aq. KOH (10 ml, 20%). This mixture was cooled to 0 °C. To this dark red solution was added H_2O_2 (30%) drop-wise till the colour changed to yellow and the stirring was continued for 4 h. The reaction mixture was neutralized with ice-HCl to give light yellow precipitates, crystallized (chloroform-ethanol) to light yellow solid (0.74 g, 70%), m.p. 190 °C; IR ν_{max} (cm^{-1}): 1597 (C = O), 3232 (OH); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.23 (1H, d, $J_{5,7}$ = 2.4 Hz, H-5), 7.66 (1H, dd, $J_{7,5}$ = 2.4 Hz, $J_{7,8}$ = 9.0 Hz, H-7), 7.56 (1H, d, $J_{5',4'}$ = 5.1 Hz, H-5'), 7.51 (1H, d, $J_{8,7}$ = 9.0 Hz, H-8), 7.01 (1H, d, $J_{4',5'}$ = 5.1 Hz, H-4'), 2.60 (3H, s, 3'–C**H**$_3$); ^{13}C NMR ($CDCl_3$): δ 172.23 (C-3), 153.52, 144.02, 140.84, 137.12, 133.70, 131.44, 130.57, 129.44, 125.39, 124.72, 121.94, 119.73, 16.79 (3'–C**H**$_3$); Anal. Calcd. for $C_{14}H_9ClO_3S$: C, 57.44; H, 3.10. Found: C, 57.39; H, 3.07.

*6-Chloro-3-methoxy-2-(3-methylthiophen-2-yl)-4H-chromen-4-one (**3a**)*

The compound, **2** (2.92 g, 1.0 eq.), $(CH_3)_2SO_4$ (1.38 g, 1.1 eq.), dry K_2CO_3 (1.1 eq.) and tetra-n-butylammonium iodide (100 mg, 3.0 mol%) were refluxed in dry acetone (20 ml) for 4 h. Filtration, evaporation of solvent and crystallization of the residue (EtOH) gave **3a** (80%) as a creamish solid, m.p. 136–138 °C; λ_{max} (MeOH) 297, 264 nm; IR ν_{max} (cm^{-1}): 1643.0 (C = O); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.24 (1H, d, $J_{5,7}$ = 2.4 Hz, H-5), 7.62 (1H, dd, $J_{7,5}$ = 2.4 Hz, $J_{7,8}$ = 9.0 Hz, H-7), 7.53 (1H, d, $J_{5',4'}$ = 5.1 Hz, H-5'), 7.46 (1H, d, $J_{8,7}$ = 9.0 Hz, H-8), 7.00 (1H, d, $J_{4',5'}$ = 5.1 Hz, H-4'), 3.99 (3H, s, –OC**H**$_3$), 2.66 (3H, s, 3'–C**H**$_3$); ^{13}C NMR ($CDCl_3$): δ 172.84 (C-4), 153.14, 141.83, 139.46, 133.46, 131.66, 130.74, 130.12, 125.33, 125.16, 124.57, 119.28, 77.19, 59.96 (3-O**C**H$_3$), 17.33 (3'–C**H**$_3$); Mass *(m/z)*: 307 (**M + 1**, 88%); Anal. Calcd. for $C_{15}H_{11}ClO_3S$: C, 58.73; H, 3.61. Found: C, 58.78; H, 3.63.

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

*6-Chloro-2-(3-methylthiophen-2-yl)-3-propargyloxy-4H-chromen-4-one (**3b**)*

Yield 88%, light yellow solid; m.p. 156–158 °C; λ_{max} (MeOH) 294, 263 nm; IR ν_{max} (cm^{-1}): 1636.3 (C = O); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.23 (1H, d, $J_{5,7}$ = 2.7 Hz, H-5), 7.63 (1H, dd, $J_{7,5}$ = 2.7 Hz, $J_{7,8}$ = 9.0 Hz, H-7), 7.55 (1H, d, $J_{5',4'}$ = 5.1 Hz, H-5'), 7.48 (1H, d, $J_{8,7}$ = 9.0 Hz, H-8), 7.00 (1H, d, $J_{4',5'}$ = 5.1 Hz, H-4'), 5.07 (2H, d, $J_{1'',3''}$ = 2.4 Hz, H-1''), 2.65 (3H, s, 3'–C**H**$_3$), 2.40 (1H, t, $J_{3'',1''}$ = 2.4 Hz, H-3''); ^{13}C NMR ($CDCl_3$): δ 172.50 (C-4), 153.22, 152.10, 142.10, 141.00, 133.62, 131.47, 130.87, 130.27, 129.80, 125.15, 124.78, 119.36, 76.59, 76.33, 59.03 (C-1''), 17.39 (3''–C**H**$_3$); Mass *(m/z)*: 331 (**M + 1**, 36%); Anal. Calcd. for $C_{17}H_{11}ClO_3S$: C, 61.73; H, 3.35. Found: C, 61.78; H, 3.37.

*3-Allyloxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-one (**3c**)*

Yield 95%, creamish solid; m.p. 130–132 °C; λ_{max} (MeOH) 296, 266 nm; IR ν_{max} (cm^{-1}): 1643 (C = O), 1605 (C = C); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.23 (1H, d, $J_{5,7}$ = 2.4 Hz, H-5), 7.61 (1H, dd, $J_{7,5}$ = 2.4 Hz, $J_{7,8}$ = 9.0 Hz, H-7), 7.52 (1H, d, $J_{5',4'}$ = 5.1 Hz, H-5'), 7.46 (1H, d, $J_{8,7}$ = 9.0 Hz, H-8), 7.00 (1H, d, $J_{4',5'}$= 5.1 Hz, H-4'), 6.07 (1H, ddt, $J_{2'',1''}$ = 6.6 Hz, $J_{2'',3''a}$ = 17.4 Hz, $J_{2'',3''b}$ = 10.8 Hz, H-2''), 5.37 (1H, dd, $J_{3''a,1''}$ = 1.5 Hz, $J_{3''a,2''}$ = 17.4 Hz, H-3''a), 5.23 (1H, dd, $J_{3''b,2''}$ = 10.5 Hz, $J_{3''b,1''}$ = 1.2 Hz, H-3''b), 4.76 (2H, d, $J_{1'',2''}$ = 6.6 Hz, H-1''), 2.64 (3H, s, 3'–C**H**$_3$); ^{13}C NMR ($CDCl_3$): δ 172.87 (C-4), 154.07, 153.12, 141.83, 137.87, 133.44, 133.21, 131.54, 130.69, 129.99, 125.20, 125.12, 124.76, 119.31, 119.18, 72.99, 17.36 (3'–C**H**$_3$); Mass *(m/z)*: 333 (**M + 1**, 3%); Anal. Calcd. for $C_{17}H_{13}ClO_3S$: C, 61.35; H, 3.94. Found: C, 61.33; H, 3.92.

*6-Chloro-2-(3-methylthiophen-2-yl)-3-(2-methylallyloxy)-4H-chromen-4-one (**3d**)*

Yield 95%, light yellow solid; m.p. 98–100 °C; λ_{max} (MeOH) 297, 263 nm; IR ν_{max} (cm^{-1}): 1636 (C = O), 1605 (C = C); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.19 (1H, d, $J_{5,7}$ = 2.7 Hz, H-5), 7.62 (1H, dd, $J_{7,5}$ = 2.7 Hz, $J_{7,8}$ = 7.8 Hz, H-7), 7.52 (1H, d, $J_{5',4'}$ = 4.8 Hz, H-5'), 7.46 (1H, d, $J_{8,7}$ = 7.8 Hz, H-8), 6.98 (1H, d, $J_{4',5'}$ = 4.8 Hz, H-4'), 5.09 (1H, s, H-3''b), 5.03 (1H, s, H-3''a), 4.72 (2H, s, H-1''), 1.80 (3H, s, 2''–CH_3), 1.58 (3H, s, 3'–C**H**$_3$); ^{13}C ($CDCl_3$): δ 172.88 (C-4), 154.02, 153.21, 141.76, 141.00, 138.46, 133.45, 131.33, 130.69, 129.87, 125.30, 125.15, 124.86, 119.35, 114.08, 75.67 (C-1''), 19.67, 17.10 (3'–C**H**$_3$); Mass *(m/z)*: 347 (**M + 1**, 8%); Anal. Calcd. for $C_{18}H_{15}ClO_3S$: C, 62.33; H, 4.36. Found: C, 62.30; H, 4.31.

*3-Benzyloxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-one (**3e**)*

Yield 95%, light yellow solid; m.p. 132–134 °C; λ_{max} (MeOH) 297, 263 nm; IR ν_{max} (cm^{-1}): 1628.0 (C = O); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.26 (1H, d, $J_{5,7}$ = 2.4 Hz, H-5), 7.62 (1H, dd, $J_{7,5}$ = 2.4 Hz, $J_{7,8}$ = 8.7 Hz, H-7), 7.42–7.46 (3H, m, H-8, 3'', 7''), 7.49 (1H, d, $J_{5',4'}$ = 5.1 Hz, H-5'), 7.39–7.28 (3H, m, H-4'', 5'', 6''), 6.93 (1H, d, $J_{4',5'}$ = 5.1 Hz, H-4'), 5.22 (2H, s, –OC**H**$_2$–), 2.55 (3H, s, 3'–C**H**$_3$); ^{13}C ($CDCl_3$): δ 172.95 (C-4), 154.14, 153.21, 141.82, 138.13, 136.40, 133.48, 131.32, 130.73, 129.91, 128.95, 128.22, 125.27, 125.12, 124.83, 119.38, 73.75 (–OCH$_2$–), 17.11 (3'–C**H**$_3$); Mass *(m/z)*: 383 (**M + 1**, 4%); Anal. Calcd. for $C_{21}H_{15}ClO_3S$: C, 65.88; H, 3.95. Found: C, 65.79; H, 3.88.

*4.3. Photo-irradiation of chromenones **3(a–e)***

*4.3.1. Photolysis of compound (**3a**)*

A methanolic solution (150 ml) of chromenone **3a** (500 mg, 1.6 mmol) was irradiated with light from a 125 W Hg vapor lamp in a pyrex reactor under Nitrogen atmosphere for 90 min. The removal of solvent left a gummy solid which was chromatographed to yield **4a.**

Compound (**4a**): yield 24%, light yellow solid; m.p. 174–176 °C; IR ν_{max} (cm^{-1}): 1649.7 (C = O); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.25 (1H, d, $J_{7,9}$ = 2.1 Hz, H-7), 7.60 (1H, dd, $J_{9,7}$ = 2.4 Hz, $J_{9,10}$ = 9.0 Hz, H-9), 7.42 (1H, d, $J_{10,9}$ = 9.0 Hz, H-10), 6.27 (1H, d, $J_{2,3}$ = 6.6 Hz, H-2), 5.43 (1H, d, $J_{3,2}$ = 6.6 Hz, H-3), 4.44 (1H, s, H-11b), 4.08 (1H, d, H-4a), 3.88 (1H, d, H-4b), 1.36 (3H, s, 3a–C**H**$_3$); ^{13}C ($CDCl_3$): δ 170.52 (C-6), 153.58, 151.94, 148.39, 138.83, 133.47, 130.57, 125.45, 124.73, 119.48, 100.60, 78.73, 65.88, 40.83, 17.90 (3a–C**H**$_3$); Mass *(m/z)*: 307 (**M + 1**, 3%); Anal. Calcd. for $C_{15}H_{11}ClO_3S$: C, 58.73; H, 3.61. Found: C, 58.78; H, 3.64.

*4.3.2. Photolysis of compound (**3b**)*

A methanolic solution of **3b** (500 mg, 1.5 mmol) on photolysis for 45 min furnished **4b**.

Compound (**4b**): yield 38%, creamish white solid; m.p. 202–204 °C; IR ν_{max} (cm^{-1}): 1643 (C = O), 2114 (C≡C); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.25 (1H, d, $J_{7,9}$ = 2.7 Hz, H-7), 7.60 (1H, dd, $J_{9,7}$ = 2.7 Hz, $J_{9,10}$ = 9.0 Hz, H-9), 7.42 (1H, d, $J_{10,9}$ = 9.0 Hz, H-10), 6.30 (1H, d, $J_{2,3}$ = 6.0 Hz, H-2), 5.54 (1H, d, $J_{3,2}$ = 6.0 Hz, H-3), 4.83 (1H, d, $J_{4,2'}$ = 2.1 Hz, H-4), 4.54 (1H, s, H-11b), 2.58 (1H, d, $J_{2',4}$ = 2.1 Hz, H-2'), 1.46 (3H, s, 3a–C**H**$_3$); ^{13}C ($CDCl_3$): δ 170.39 (C-6), 153.66, 148.85, 137.21, 133.81, 130.67, 127.51, 127.11, 125.43, 124.55, 119.65, 76.63, 76.52, 68.40, 53.71, 51.54, 18.93 (3a–C**H**$_3$); Mass *(m/z)*: 331 (**M + 1**, 100%); Anal. Calcd. for $C_{17}H_{11}ClO_3S$: C, 61.73; H, 3.35. Found: C, 61.78; H, 3.31.

*4.3.3. Photolysis of compound (**3c**)*

A methanolic solution of **3c** (500 mg, 1.5 mmol) on photolysis for 45 min furnished **4c**.

Compound (**4c**): yield 46%, creamish solid; m.p. 176–178 °C; IR ν_{max} (cm^{-1}): 1651(C = O); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.26 (1H, d, $J_{7,9}$ = 2.4 Hz, H-7), 7.60 (1H, dd, $J_{9,7}$ = 2.4 Hz, $J_{9,10}$ = 9.0 Hz, H-9), 7.41 (1H, d, $J_{10,9}$ = 9.0 Hz, H-10), 6.37 (1H, d, $J_{2,3}$ = 6.0 Hz, H-2), 5.99 (1H, ddd, $J_{1',2'}$ = 6.6 Hz, $J_{1',2'a}$ = 17.4 Hz, $J_{1',2'b}$ = 10.8 Hz, H-1'), 5.47 (1H, d, $J_{2'a,1'}$ = 17.4 Hz, H-2'a), 5.35 (1H, d, $J_{2'b,1'}$ = 10.8 Hz, H-2'b), 5.40 (1H, d, $J_{2,3}$ = 6.0 Hz, H-3), 4.60 (1H, s, H-11b), 4.54 (1H, d, $J_{4,1'}$ = 6.6 Hz, H-4), 1.26 (3H, s, 3a–C**H**$_3$); ^{13}C ($CDCl_3$): δ 171.00 (C-6), 153.61, 148.15, 139.57, 138.47, 133.49, 130.76, 128.59, 126.51, 125.79, 124.68, 119.67, 116.50, 78.7, 54.10, 52.06, 18.97 (3a–C**H**$_3$); Mass *(m/z)*: 333 (**M + 1**, 88%); Anal. Calcd. for $C_{17}H_{13}ClO_3S$: C, 61.35; H, 3.94. Found: C, 61.30; H, 3.91.

*4.3.4. Photolysis of compound (**3d**)*

A methanolic solution of **3d** (500 mg, 1.4 mmol) on photolysis for 45 min furnished **4d**.

Compound (**4d**): yield 71%, creamish solid; m.p. 214 °C; IR ν_{max} (cm^{-1}): 1659 (C = O); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.24 (1H, d, $J_{7,9}$ = 2.7 Hz, H-7), 7.59 (1H, dd, $J_{9,7}$ = 2.7 Hz, $J_{9,10}$ = 9.0 Hz, H-9), 7.39 (1H, d, $J_{10,9}$ = 9.0 Hz, H-10), 6.36 (1H, d, $J_{2,3}$ = 6.0 Hz, H-2), 5.44 (1H, d, $J_{2,3}$ = 6.0 Hz, H-3), 5.16 (2H, d, $J_{4,3a}$ = 2.1, 2'–C**H**$_2$), 4.56 (1H, s, H-11b), 1.94 (3H, s, 1'–C**H**$_3$), 1.28 (3H, s, 3a–C**H**$_3$); ^{13}C ($CDCl_3$): δ 170.51 (C-6), 153.62, 147.96, 139.87, 138.35, 133.61, 130.47, 128.56, 126.42, 125.39, 124.67, 119.62, 116.57, 78.34, 54.05, 52.01, 21.42, 18.78 (3a–C**H**$_3$); Mass *(m/z)*: 347 (**M + 1**, 27%); Anal. Calcd. for $C_{18}H_{15}ClO_3S$: C, 62.33; H, 4.36. Found: C, 62.28; H, 4.31.

*4.3.5. Photolysis of compound (**3e**)*

A methanolic solution of **3e** (500 mg, 1.3 mmol) on photolysis for 45 min furnished **4e**.

Compound (**4e**): yield 87%, creamish solid; m.p. 186–188 °C; IR ν_{max} (cm^{-1}): 1651 (C = O); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.28 (1H, d, $J_{7,9}$ = 2.4 Hz, H-7), 7.62 (1H, dd, $J_{9,7}$ = 2.4 Hz, $J_{9,10}$ = 8.4 Hz, H-9), 7.28–7.47 (6H, m, H-10, 2', 3', 4', 5', 6'), 6.46 (1H, d, $J_{2,3}$ = 6.0 Hz, H-2), 5.16 (1H, d, $J_{3,2}$ = 6.0 Hz, H-3), 5.12 (1H, s, H-4), 4.74 (1H, s, H-11b), 1.60 (3H, s, 3a–C**H**$_3$); ^{13}C ($CDCl_3$): δ 170.51 (C-6), 153.68, 148.10, 138.72, 135.75, 133.70, 130.56, 128.23, 127.96, 127.85, 126.93, 125.48, 124.72, 119.64, 76.61, 53.57, 52.22, 17.77 (3a–C**H**$_3$); Mass *(m/z)*: 383 (**M + 1**, 44%); Anal. Calcd. for $C_{21}H_{15}ClO_3S$: C, 65.88; H, 3.95. Found: C, 65.91; H, 3.96.

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