Photochemistry of 3-alkoxychromones I — Photocyclisation of 6-chloro-3-alkoxy-2-(furan-3-yl)-4*H*-chromen-4-ones

Ramesh C. Kamboj, Urmila Berar, Surinder Berar, Mandeep Thakur, Rita Arora, and Satish C. Gupta

Abstract: 3-Alkoxy/allyloxy-6-chloro-2-(furan-3-yl)-4*H*-chromen-4-ones yield angular tetracyclic products involving the 2-furyl group on photoirradiation through the intermediacy of 1,4-biradicals. The nature of the 3-alkoxy/allyloxy group influenced the photoproduct distribution. The stereochemical dispositions of the products have been established using the J/Φ relationship and were corroborated by MM2 calculations.

Key words: furylchromone, type-II reaction, 1,5-sigmatropic shift.

Résumé : La photoirradiation des 3-alkoxy/allyloxy-6-chloro-2-(furan-3-yl)-4*H*-chroménones conduit à des produits tétracycliques angulaires impliquant le groupe 2-furyle par l'intermédiaire de biradicaux-1,4. La nature du groupe 3-alkoxy/allyloxy influence la distribution des photoproduits. Les dispositions stéréochimiques des produits ont été déterminées à l'aide de la relation J/Φ et elles ont été corroborées par des calculs théoriques MM2.

Mots-clés : furylchromone, réaction de type II, déplacement sigmatropique 1,5.

[Traduit par la Rédaction]

Introduction

In photochemical transformations of 3-alkoxy-2-aryl-4*H*-chromen-4-one,[1] the products formed depend upon the nature of substituents at C-2 and C-3. The 2-methyl-3-methoxy derivatives produced dimeric oxetanols and underwent demethoxylation.[2] The photolysis of 3-alkoxy-2-(phenyl/furyl/thienyl)-4*H*-chromen-4-one[3] produced angular tetracyclics, whereas 2-styryl[4] derivatives provided linear tricyclics. The photochemical reaction in these substrates are basically γ-H abstractions[1,5] and have provided interesting mechanistic and structural studies as well as synthetic utility.[6] We now report the results of our investigations on the photoreactions of 3-alkoxy/allyloxy-6-chloro-2-(furan-3-yl)-4*H*-chromen-4-ones. The study was aimed at the effect of different 3-alkoxy groups on the product distribution and stereochemistry when the furyl group is tethered to the chromone through its 3-position instead of 2-position.[3]

Results and discussion

The targets, 2-(furan-3-yl)-4*H*-chromen-4-ones (**3a–3j**), were synthesized commencing with the condensation of 5-chloro-2-hydroxyacetophenone with furan-3-carbaldehyde as per Scheme 1.

The structures of compounds **3a–3j** were found to be consistent with their spectral parameters (IR, ^{1}H-^{13}C NMR, Experimental secion).

The photolysis of the methanolic solution of **3a–3j** with pyrex filtered UV light, under nitrogen atmosphere produced the photoproducts **4a–4j**, **4b′**, **4h′**, **5g**, and **6g**. The structures of these photoproducts (Fig. 1) were confirmed by their spectral parameters(IR,^{1}H-^{13}C NMR) and elemental analysis.

Here, the interesting feature in the photoproducts isolated is the stereochemistry of ring C, which is in a half chair conformation (Fig. 2). In the photoproducts, **4a–4j**, **4b′**, **5g**, and **4h′**, the stereochemistry of the C/D ring junction is cis, as the trans-fusion of a five-membered ring will result in higher conformational strain as calculated by the MM2 energy minimizations program.[7] This is further borne out by the fact that $J_{3a,11b}$ = ~9.0 Hz, which correlates with calculated values of $\Phi_{3a,11b}$ (karplus rule) with cis-fusion of these protons (Table 1) and also from literature references.[8] Now assuming the C/D ring fusion as cis, the orientation of H-4 can be cis to H-3a or trans to H-3a. Here again, regarding the relative stereochemical disposition of H-3a and H-4, the use of the J/Φ relationship[9] and MM2 program has been invoked. The correlation of $\Phi_{3a,4}$ values obtained from two possible MM2 energy minimized 3D conformations,[7] **A** (H-4 trans to H-3a) and **B** (H-4 cis to H-3a), with $J_{3a,4}$ observed from ^{1}H NMR is shown in Table 1. In compound **4a** and **4c** both conformation are equivalent as substituents at C-4 are the same. A look at Table 1 demonstrates the trans disposition of H-3a and H-4 in compounds **4b**, **4d–4f**, and **4h**, whereas it is a cis disposition in compounds **4g**, **4i**, **4j**, **4b′**, **4h′**, and **5g**, which are in accordance with karplus rule.[9] This has given the stereocentre at C-4 - a *R* configuration in compounds **4b**, **4d–4f**, and **4h** and a *S* configuration in com-

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R.C. Kamboj,[1] U. Berar, S. Berar, M. Thakur, R. Arora, and S.C. Gupta. Department of Chemistry, Kurukshetra University, Kurukshetra 136 119, India.

[1] Corresponding author (e-mail: rckamboj@rediffmail.com).

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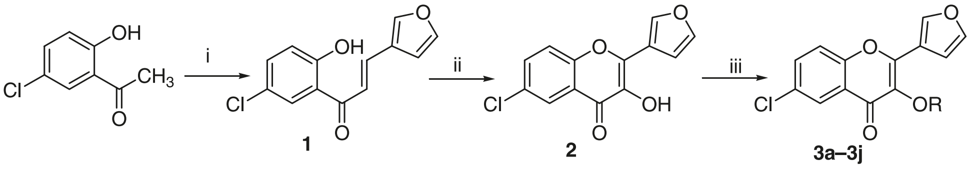
Scheme 1. Synthesis of furylchromones **3a–3j**.



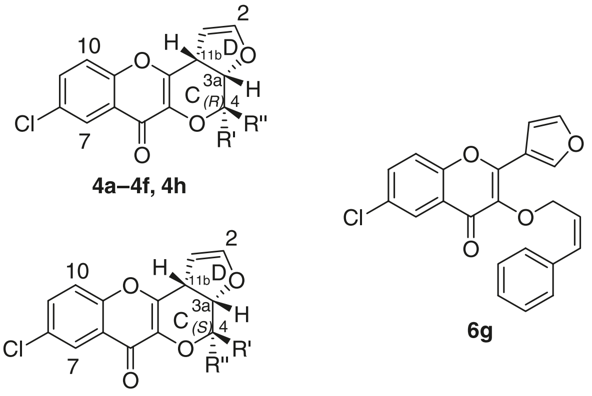
i: 3-Furaldehyde, C_2H_5OH, anhy·$Ba(OH)_2$, reflux
ii: KOH, H_2O_2(30%), 0°C
iii: K_2CO_3, CH_3COCH_3, $Bu_4N^+I^-$, RX

RX = CH_3I	**3a**, R = CH_3	80%
CH_3CH_2I	**3b**, R = CH_2CH_3	82%
$(CH_3)_2CHBr$	**3c**, R = $CH(CH_3)_2$	70%
H_2CCHCH_2Br	**3d**, R = CH_2CHCH_2	85%
$H_2CC(CH_3)CH_2Cl$	**3e**, R = $CH_2C(CH_3)CH_2$	72%
$(CH_3)_2CCHCH_2Br$	**3f**, R = $CH_2CHC(CH_3)_2$	70%
$C_6H_5CHCHCH_2Cl$	**3g**, R = $CH_2CHCHC_6H_5$	68%
$HCCCH_2Br$	**3h**, R = CH_2CCH	88%
$C_6H_5CH_2Cl$	**3i**, R = $CH_2C_6H_5$	70%
(p)$CH_3OC_6H_4CH_2Cl$	**3j**, R = $CH_2C_6H_4OCH_3$(p)	58%

Fig. 1. Structures of photoproducts.

4a; R'' = H
4b, **4b'**; R'' = CH_3
4d; R'' = $CHCH_2$
4e; R'' = $C(CH_3)CH_2$
4f; R'' = $CHC(CH_3)_2$
4g; R'' = CHCH(E)-Ph
4h, **4h'**; R'' = CCH
4i; R'' = CH_2Ph
4j; R'' = CH_2PhOCH_3(p)
5g; R'' = CHCH(Z)-Ph
R' = H

4c; R' = R'' = CH_3

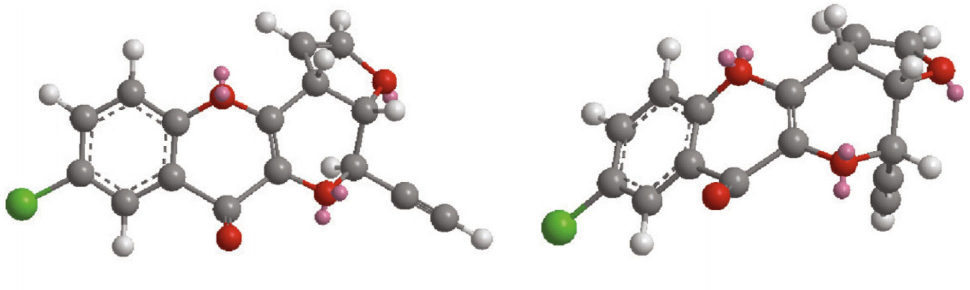


4a–4f, 4h

4g, 4i, 4j, 4b', 4h', 5g

6g

Fig. 2. MM2 energy minimized structures of compound **4h** and **4h'**.



4h (conformation **A**) **4h'** (conformation **B**)

pounds **4g**, **4i**, **4j**, **4b'**, **4h'**, and **5g**. A correlation of steric energy (E_{kcal}) also shows that in most cases the lower energy conformations are the ones that explain the observed J/Φ relationship (Table 1).

Here it is worth mentioning that in photolysis of chromones **3b** and **3h**, both photoproducts with conformation **A** and **B** were isolated, whereas in all other chromones only one product was isolated (either conformation **A** or **B**). The reason for this behaviour could be from the steric influence of the C-4 substituent, where the second isomer is either not formed or formed in such low concentrations that it escaped isolation. The 3-cinnamyloxychromone, **3g**, along with cyclisation to yield **4g** also underwent isomerization of the cinnamyl double bond to yield two new products, **5g** and **6g**, where the cinnamyl double bond is cis (J = 11.7 Hz).

The phototransformations (Scheme 2) described above can be visualized as having occurred through the formation of the 1,4 biradical intermediate[1] **7**. The products have been expected to be formed through a bond formation between the -CH- and the C-2 atom of the furan ring, which

Table 1. J/Φ correlation of conformations of photoproducts.

Comp.	Coupling constant		Conformation **A**			Conformation **B**		
	$J_{3a,11b}$ (Hz)	$J_{3a,4}$ (Hz)	$\Phi_{3a,11b}$	$\Phi_{3a,4}$	E_{kcal}	$\Phi_{3a,11b}$	$\Phi_{3a,4}$	E_{kcal}
4a	10.2	9.0	16.84	167.0	11.40	16.84	167.0	11.40
4b*	7.8	8.4	15.00	167.0	11.66			
4b′	9.9	1.2				13.75	43.24	11.91
4c	9.3	—	13.77	—	12.38	13.77	—	12.38
4d	9.6	6.9	15.30	169.0	11.67	15.47	44.35	12.18
4e	9.3	7.5	19.36	175.0	12.90	8.12	32.63	13.56
4f	9.0	7.2	13.96	171.0	12.89	14.10	43.01	14.05
4g	9.6	7.2	1.90	90.50	13.93	13.81	14.28	14.24
4h*	9.9	6.9	16.33	167.0	11.13			
4h′	9.9	2.7				16.51	48.21	11.17
4i	9.6	8.1	3.97	85.59	15.87	3.60	19.70	15.19
4j	9.9	8.4	5.40	86.51	20.47	8.72	3.65	16.67
5g	9.0	7.2	19.97	66.97	13.88	15.98	8.0	14.44

*Isomeric compounds with both conformations were isolated.

is followed by ketonisation and H-migration to C-11b (1,5-H migration). The furyl group at C-2 also possesses a 5-carbon for clipping of the 3-alkoxy radical but here, the 1,5-sigmatropic shift is not feasible.

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

The radical at C-11b in **8** (obtained in photolysis of 2′-furyl chromones) is stabilized by pyrone moiety and thus the C–O bond becomes prone to cleavage. There is no such stabilization available to the radical (at C-3a) in **9** for its formation and for the formation of ring contracted secondary photoproducts.

Conclusion

3-Alkoxy/allyloxy-6-chloro-2-(furan-3-yl)-4*H*-chromen-4-ones upon photoirradiation yielded angular tetracyclic products through the 1,4-biradical furnished through γ-H abstraction. No ring contracted secondary photoproduct formation was observed.

Experimental

General

Melting points were determined in open capillaries and are thus uncorrected. ^{1}H NMR spectra were recorded on a 300 MHz Bruker spectrometer using TMS as the internal standard. IR spectra were recorded on a Buck Scientific 500 spectrophotometer using KBr pellets. Mass spectra were recorded at 70 eV. Elemental analysis was carried out on a Perkin Elmer 2400 instrument. TLC plates were coated with silica gel G (suspended in $CHCl_3$-MeOH) and iodine vapours were used as the visualizing agent. The columns for purification were packed with Silica gel 100–200 mesh in petroleum ether/benzene (9:1) and left overnight before use. The elution was carried out with increasing proportions of benzene in the petroleum ether–benzene mixture. The yields reported are based on the amount of isolated photoproducts and are calculated by excluding the recovered substrates.

Fig. 3. Structures of proposed radicals.

8 **9**

Synthesis of chromones 3a–3j

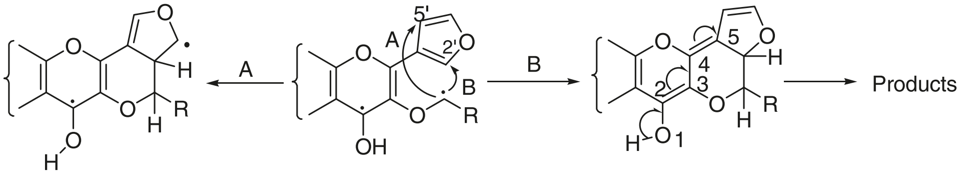
1-(5-Chloro-2-hydroxyphenyl)-3-(furan-3-yl)prop-2-en-1-one (1)

A solution of 5-chloro-2-hydroxyacetophenone (17.0 g, 0.1 mol) and 3-furaldehyde (9.6 g, 0.1 mol) in absolute ethanol and dehydrated S-200 barium hydroxide (dried at 200 °C for 2 h, 20.0 g) were refluxed in a water bath for 20 min. The dark red mixture was cooled and poured on ice-HCl to obtain **1** (17.36 g, 70%) as a yellow solid, crystallized from EtOH, mp 110–113 °C. IR ν_{max} (cm^{-1}): 1648.0 (C=O), 3405(OH). ^{1}H NMR ($CDCl_3$) δ: 12.72 (1H, s, OH), 7.85 (1H, d, $J_{3,2}$ = 15.0 Hz, H-3), 7.80 (1H, d, J_m = 2.7 Hz, H-6′), 7.79 (1H, br s, H-2″), 7.49 (1H, d, $J_{5'',4''}$ = 2.4 Hz, H-5″), 7.42 (1H, dd, J_m = 2.7 Hz, J_o = 9.0 Hz, H-4′), 7.25 (1H, d, $J_{2,3}$ = 15.0 Hz, H-2), 6.96 (1H, d, J_o = 9.0 Hz, H-3′), 6.75 (1H, d, $J_{4'',5''}$ = 2.4 Hz, H-4″). Anal. calcd. for $C_{13}H_9ClO_3$: C 62.79, H 3.65; found: C 62.70, H 3.61.

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

A solution of compound **1** (2.48 g, 0.01 mol) in EtOH at 0 °C was mixed with 12.0 mL 20% aq. NaOH by stirring. To this dark red solution was added H_2O_2 (30%) dropwise until the colour changed to yellow and the stirring was continued for 4 h. The reaction mixture was neutralized with ice-HCl to give creamy white precipitates, crystallized (chloroform-ethanol) to creamy white crystals (2.37 g, 90%), mp 206–208 °C. IR ν_{max} (cm^{-1}): 1615.0 (C=O), 3400(OH). ^{1}H NMR ($CDCl_3$) δ: 8.31 (1H, br s, H-2′), 8.21

Scheme 2. Cyclisation and 1,5-H shift of 1,4-biradical.



1,4-biradical, **7**

(1H, d, J_{m} = 2.4 Hz, H-5), 7.63 (1H, dd, J_{m} = 2.4 Hz, J_{o} = 9.0 Hz, H-7), 7.58 (1H, t, $J_{5',2'}$ = 1.5 Hz, $J_{5',4'}$ = 1.8 Hz, H-5′), 7.51 (1H, d, J_{o} = 9.0 Hz, H-8), 7.05 (1H, dd, $J_{4',2'}$ = 0.3 Hz, $J_{4',5'}$ = 1.8 Hz, H-4′). Anal. calcd. for $C_{13}H_7ClO_4$: C 59.45, H 2.69; found: C 59.31, H 2.69.

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

The compound **2** (2.50 g, 0.01 mol), CH_3I (1.2 g, 0.01 mol), dry K_2CO_3 (1.0 g), and tetra-*n*-butylammonium iodide (100 mg) were refluxed in dry acetone (50 mL) for 2 h. Filtration, evaporation of the solvent, and crystallization of the residue (MeOH) gave **3a** (80%), a light brown solid, mp 114–117 °C. IR $\nu_{\max}$ (cm^{-1}): 1655.0 (C=O). ^{1}H NMR (CDCl$_3$) δ: 8.30 (1H, br s, H-2′), 8.23 (1H, d, J_{m} = 2.4 Hz, H-5), 7.62 (1H, dd, J_{m} = 2.4 Hz, J_{o} = 9.0 Hz, H-7), 7.59 (1H, dd, $J_{5',2'}$ = 1.2 Hz, $J_{5',4'}$ = 1.5 Hz, H-5′), 7.48 (1H, d, J_{o} = 9.0 Hz, H-8), 7.02 (1H, dd, $J_{4',2'}$ = 0.3 Hz, $J_{4',5'}$ = 1.5 Hz, H-4′), 4.03 (3H, s, OC*H*$_3$). ^{13}C NMR (CDCl$_3$) δ: 172.83 (C-4), 153.24 (C-8a), 151.74 (C-2), 145.37 (C-5′), 143.75 (C-2′), 139.31 (C-4a), 133.44 (C-7), 130.67 (C-6), 125.33 (C-3), 125.15 (C-5), 119.50 (C-8), 117.71 (C-3′), 108.61 (C-4′), 59.53 (3-O*C*H$_3$). Anal. calcd. for $C_{14}H_9ClO_4$: C 60.78, H 3.28; found: C 63.65, H 3.31.

The other ethers (**3b**–**3j**) were synthesized by reacting 3-hydroxychromone (**2**) with ethyl iodide, isopropyl bromide, allyl bromide, methyl allyl chloride, dimethyl allyl bromide, cinnamyl chloride, propargyl bromide, benzyl chloride, and para methoxy benzyl chloride, respectively, by the procedure as described for compound **3a**.

*6-Chloro-3-ethoxy-2-(furan-3-yl)-4*H*-chromen-4-one (3b)*

Yield 82%, colourless solid; mp 104–106 °C (MeOH). IR $\nu_{\max}$ (cm^{-1}): 1635.0 (C=O). ^{1}H NMR (CDCl$_3$) δ: 8.33 (1H, br s, H-2′), 8.20 (1H, d, J_{m} = 2.1 Hz, H-5), 7.60 (1H, dd, J_{m} = 2.1 Hz, J_{o} = 9.0 Hz, H-7), 7.57 (1H, t, $J_{5',2'}$ = 1.2 Hz, $J_{5',4'}$ = 1.5 Hz, H-5′), 7.46 (1H, d, J_{o} = 9.0 Hz, H-8), 7.02 (1H, dd, $J_{4',2'}$ = 0.3 Hz, $J_{4',5'}$ = 1.5 Hz, H-4′), 4.31 (2H, q, J_{vic} = 7.2 Hz, H-1″), 1.44 (3H, t, J_{vic} = 7.2 Hz, H-2″). ^{13}C NMR (CDCl$_3$) δ: 172.98 (C-4), 153.19 (C-8a), 151.70 (C-2), 145.27 (C-5′), 143.62 (C-2′), 139.09 (C-4a), 133.38 (C-7), 130.59 (C-6), 125.29 (C-3), 125.15 (C-5), 119.50 (C-8), 117.91 (C-1′), 108.71 (C-4′), 67.89 (C-1″), 15.71 (C-2″). Anal. calcd. for $C_{15}H_{11}ClO_4$: C 61.98, H 3.81; found: C 61.88, H 3.78.

*6-Chloro-3-isopropyloxy-2-(furan-3-yl)-4*H*-chromen-4-one (3c)*

Yield 70%, colourless solid; mp 95–97 °C (MeOH); IR $\nu_{\max}$ (cm^{-1}): 1639.2 (C=O). ^{1}H NMR (CDCl$_3$) δ: 8.36 (1H, d, J = 0.9 Hz, H-2′), 8.19 (1H, d, J_{m} = 2.7 Hz, H-5), 7.59 (1H, dd, J_{m} = 2.7 Hz, J_{o} = 9.0 Hz, H-7), 7.55 (1H, t, $J_{5',2'}$ = 1.5 Hz, $J_{5',4'}$ = 1.8 Hz, H-5′), 7.46 (1H, d, J_{o} = 9.0 Hz, H-8), 7.04 (1H, d, $J_{4',5'}$ = 1.8 Hz, H-4′), 5.15 (1H, septet, J_{vic} = 6.3 Hz, H-1″), 1.32 (6H, d, J_{vic} = 6.3 Hz, C$_{1''}$-C*H*$_3$). ^{13}C NMR (CDCl$_3$) δ: 173.07 (C-4), 153.12 (C-8a), 151.79 (C-2), 145.73 (C-5′), 143.32 (C-2′), 137.00 (C-4a), 133.26 (C-7), 130.49 (C-6), 125.13 (C-5), 125.00 (C-3), 119.44 (C-8), 118.13 (C-1′), 108.92 (C-4′), 73.98 (C-1″), 22.49 (C$_{1''}$-*C*H$_3$). Anal. calcd. for $C_{16}H_{13}ClO_4$: C 63.06, H 4.30; found: C 62.97, H 4.27.

*3-Allyloxy-6-chloro-2-(furan-3-yl)-4*H*-chromen-4-one (3d)*

Yield 85%, light brown solid; mp 93–95 °C(MeOH). IR $\nu_{\max}$ (cm^{-1}): 1641 (C=O), 1613 (C=C). ^{1}H NMR (CDCl$_3$) δ: 8.33 (1H, br s, H-2′), 8.20 (1H, d, J_{m} = 2.4 Hz, H-5), 7.60 (1H, dd, J_{m} = 2.4 Hz, J_{o} = 9.0 Hz, H-7), 7.56 (1H, dd, $J_{5',2'}$ = 0.9 Hz, $J_{5',4'}$ = 1.8 Hz, H-5′), 7.47 (1H, d, J_{o} = 9.0 Hz, H-8), 7.02 (1H, dd, $J_{4',2'}$ = 0.3 Hz, $J_{4',5'}$ = 1.8 Hz, H-4′), 6.08 (1H, tdd, J_{vic} = 6.3 Hz, J_{trans} = 17.4 Hz, J_{cis} = 10.2 Hz, H-2″), 5.39 (1H, td, J_{allyl} = 1.5 Hz, J_{trans} = 17.4 Hz, H-3″b), 5.26 (1H, d, J_{cis} = 10.2 Hz, H-3″a), 4.80 (2H, dd, J_{vic} = 6.3 Hz, J_{allyl} = 1.5 Hz, H-1″). ^{13}C NMR (CDCl$_3$) δ: 171.00 (C-4), 153.10 (C-8a), 153.00 (C-2), 145.50 (C-5′), 143.62 (C-2′), 139.09 (C-4a), 133.45 (C-7), 133.30(C-2″), 130.60 (C-6), 123.14 (C-3), 123.34 (C-5), 119.83(C-3″), 119.10 (C-8), 117.84 (C-3′), 108.70 (C-4′), 72.69 (C-1″). Anal. calcd. for $C_{16}H_{11}ClO_4$: C 63.48, H 3.66; found: C 63.33, H 3.65.

*6-Chloro-2-(furan-3-yl)-3-(2-methylallyloxy)-4*H*-chromen-4-one (3e)*

Yield 72%, creamy white solid; mp 90–92 °C (MeOH). IR $\nu_{\max}$ (cm^{-1}): 1637 (C=O), 1619 (C=C). ^{1}H NMR (CDCl$_3$) δ: 8.32 (1H, dd, J_{m} = 0.9 Hz, H-2′), 8.20 (1H, d, J_{m} = 2.7 Hz, H-5), 7.59 (1H, dd, J_{m} = 2.7 Hz, J_{o} = 9.0 Hz, H-7), 7.56 (1H, t, $J_{5',2'}$ = 0.9 Hz, $J_{5',4'}$ = 1.8 Hz, H-5′), 7.46 (1H, d, J_{o} = 9.0 Hz, H-8), 7.01 (1H, dd, $J_{4',2'}$ = 0.9 Hz, $J_{4',5'}$ = 1.8 Hz, H-4′), 5.15 (1H, s, H-3″b), 5.01 (1H, s, H-3″a), 4.67 (2H, s, H-1″), 1.87 (3H, s, 2″-CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 172.78 (C-4), 153.18 (C-8a), 151.65 (C-2), 145.44 (C-5′), 143.64 (C-2′),141.18 (C-2″), 138.80 (C-4a), 133.37 (C-7), 130.63 (C-6), 125.29 (C-3), 125.12 (C-5), 119.48 (C-8), 117.76 (C-1′),113.80 (C-3″), 108.68 (C-4′), 75.13 (C-1″), 19.79 (2″-*C*H$_3$). Anal. calcd. for $C_{17}H_{13}ClO_4$: C 64.46, H 4.14; found: C 64.30, H 4.11.

*6-Chloro-2-(furan-3-yl)-3-(3-methylbut-2-enyloxy)-4*H*-chromen-4-one (3f)*

Yield 70%, off-white solid; mp 81–84 °C (MeOH). IR $\nu_{\max}$ (cm^{-1}): 1637.2 (C=O), 1608.6 (C=C). ^{1}H NMR (CDCl$_3$) δ: 8.33 (1H, d, $J_{2',5'}$ = 1.2 Hz, H-2′), 8.21 (1H, d, J_{m} = 2.4 Hz, H-5), 7.59 (1H, dd, J_{m} = 2.4 Hz, J_{o} = 9.0 Hz, H-7), 7.55 (1H, t, $J_{5',2'}$ = 1.2 Hz, $J_{5',4'}$ = 1.8 Hz, H-5′), 7.46 (1H, d, J_{o} = 9.0 Hz, H-8), 7.01 (1H, d, $J_{4',5'}$ = 1.8 Hz, H-4′), 5.53 (1H, tt, J_{vic} = 7.2 Hz, J_{allyl} = 1.5 Hz, H-2″), 4.78 (1H, d,

J_{vic} = 7.2 Hz, H-1″), 1.75 (3H, d, J_{allyl} = 1.5 Hz, H-4″), 1.73 (3H, s, $C_{3''}$-CH_3). ^{13}C NMR ($CDCl_3$) δ: 172.17 (C-4), 153.18 (C-8a), 152.79 (C-2), 145.63 (C-5′), 143.82 (C-2′), 137.90 (C-4a), 132.96 (C-7), 131.85 (C-3″), 130.42 (C-6), 124.23 (C-5), 123.50 (C-3), 120.80 (C-2″), 119.02 (C-8), 118.13 (C-3′), 108.62 (C-4′), 68.99 (C-1″), 18.05 (C-4″), 25.86 (3″-CH_3). Anal. calcd. for $C_{18}H_{15}ClO_4$: C 65.36, H 4.57; found: C 65.24, H 4.52.

*6-Chloro-2-(furan-3-yl)-3-(3-phenylallyloxy)-4*H*-chromen-4-one (3g)*

Yield 68%, light brown solid; mp 91–94 °C (EtOH). IR ν_{max} (cm^{-1}): 1648.4 (C=O), 1617(C=C). ^{1}H NMR ($CDCl_3$) δ: 8.36 (1H, t/dd, $J_{2',5'}$ = 1.5 Hz, $J_{2',4'}$ = 1.8 Hz, H-2′), 8.22 (1H, d, J_m = 2.4 Hz, H-5), 7.60 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-7), 7.56 (1H, t, $J_{5',2'}$ = 1.5 Hz, $J_{5',4'}$ = 1.8 Hz, H-5′), 7.46 (1H, d, J_o = 9.0 Hz, H-8), 7.29–7.35 (5H, m, H-2‴-6‴), 7.03 (1H, t, $J_{4',2'}$ = 1.8 Hz, $J_{4',5'}$ = 1.8 Hz, H-4′), 6.70 (1H, d, $J_{3',2'}$ = 15.9 Hz, H-3″), 6.44 (1H, td, $J_{2',3'}$ = 15.9 Hz, $J_{2',1'}$ = 6.6 Hz, H-2″), 4.96 (2H, d, $J_{1',2'}$ = 6.6 Hz, H-1″). ^{13}C NMR ($CDCl_3$) δ: 172.94 (C-4), 153.21 (C-8a), 152.03 (C-2), 145.50 (C-5′), 143.67 (C-2′), 136.26 (C-1‴), 134.61 (C-7), 133.44 (C-3″), 130.66(C-4‴), 128.57 (C-2‴, C-6‴), 128.05 (C-3), 126.70 (C-3‴, C-5‴), 125.26 (C-6), 125.14 (C-2″), 125.14 (C-4a), 124.29 (C-5), 119.54 (C-8), 117.91 (C-1′), 108.77 (C-4′), 72.48 (C-1″). Anal. calcd. for $C_{22}H_{15}ClO_4$: C 69.75, H 3.99; found: C 69.68, H 3.97.

*6-Chloro-2-(furan-3-yl)-3-propargyloxy-4*H*-chromen-4-one (3h)*

Yield 88%, light brown solid; mp 121–123 °C (MeOH). IR ν_{max} (cm^{-1}): 1634.3 (C=O), 2135(C≡C). ^{1}H NMR ($CDCl_3$) δ: 8.40 (1H, dd/t, $J_{2',5'}$ = 1.2 Hz, $J_{2',4'}$ = 0.6 Hz, H-2′), 8.20 (1H, d, J_m = 2.4 Hz, H-5), 7.61 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-7), 7.56 (1H, t, $J_{5',2'}$ = 1.2 Hz, $J_{5',4'}$ = 1.8 Hz, H-5′), 7.48 (1H, d, J_o = 9.0 Hz, H-8), 7.05 (1H, d, $J_{4',5'}$ = 1.8 Hz, $J_{4',2'}$ = 0.6 Hz, H-4′), 5.09 (2H, d, $J_{1',3'}$ = 2.4 Hz, H-1″), 2.44 (1H, d, $J_{3',1'}$ = 2.4 Hz, H-3″). ^{13}C NMR ($CDCl_3$) δ: 172.50 (C-4), 153.22 (C-2), 152.10 (C-8a), 145.96 (C-5′), 143.55 (C-2′), 138.50 (C-7), 133.60 (C-3), 130.82 (C-5), 128.42 (C-6), 125.11 (C-4a), 119.51 (C-8), 117.62 (C-1′), 108.83 (C-4′), 78.45 (C-2″), 76.27 (C-3″), 59.08 (C-1″). Anal. calcd. for $C_{16}H_9ClO_4$: C 63.91, H 3.02; found: C 63.72, H 3.00.

*3-Benzyloxy-6-chloro-2-(furan-3-yl)-4*H*-chromen-4-one (3i)*

Yield 70%, light yellow solid; mp 86–89 °C (MeOH). IR ν_{max} (cm^{-1}): 1643.3 (C=O). ^{1}H NMR ($CDCl_3$) δ: 8.23 (1H, d, J_m = 2.7 Hz, H-5), 8.20 (1H, d, $J_{2',5'}$ = 1.2 Hz, H-2′), 7.60 (1H, dd, J_m = 2.7 Hz, J_o = 9.0 Hz, H-7), 7.50 (1H, t, $J_{5',2'}$ = 1.2 Hz, $J_{5',4'}$ = 1.5 Hz, H-5′), 7.49 (1H, d, J_o = 9.0 Hz, H-8), 7.39–7.26 (5H, m, H-2″, 3″, 4″, 5″, 6″), 6.94 (1H, d, $J_{4',5'}$ = 1.5 Hz, H-4′), 5.30 (2H, s, -OCH_2-). ^{13}C NMR ($CDCl_3$) δ: 172.87 (C-4), 153.19 (C-2), 151.83 (C-8a), 145.57 (C-5′), 143.51 (C-2′), 138.74 (C-1″), 136.59 (C-7), 133.40 (C-3), 130.66 (C-4″), 128.85 (C-3″, C-5″), 128.50 (C-2″, C-6″), 128.42 (C-6), 125.28 (C-4a), 125.15 (C-5), 119.51 (C-8), 117.71 (C-1′), 108.69 (C-4′), 73.79 (-OCH_2-). Anal. calcd. for $C_{20}H_{13}ClO_4$: C 68.09, H 3.71; found: C 62.95, H 3.66.

*6-Chloro-2-(furan-3-yl)-3-(4-methoxybenzyloxy)-4*H*-chromen-4-one (3j)*

Yield 58%, light yellow solid; mp 89–92 °C (MeOH). IR ν_{max} (cm^{-1}): 1650.4 (C=O). ^{1}H NMR ($CDCl_3$) δ: 8.16 (1H, d, J_m = 2.7 Hz, H-5), 8.13 (1H, br s, H-2′), 7.52 (1H, dd, J_m = 2.7 Hz, J_o = 9.0 Hz, H-7), 7.44 (1H, t, $J_{5',2'}$ = 1.5 Hz, $J_{5',4'}$ = 1.8 Hz, H-5′), 7.38 (1H, d, J_o = 9.0 Hz, H-8), 7.33 (2H, d, J_o = 8.4 Hz, H-2″, H-6″), 6.87 (1H, d, $J_{4',5'}$ = 1.8 Hz, H-4′), 6.79 (2H, d, J_o = 8.4 Hz, H-3″, H-5″), 5.18 (2H, s, -OCH_2-), 3.73 (3H, s, $C_{4''}$-OCH_3). ^{13}C NMR($CDCl_3$) δ: 171.49 (C-4), 158.31 (C-4″), 151.71 (C-8a), 150.39 (C-2), 144.12 (C-5′), 142.00 (C-2′), 137.19 (C-1″), 131.90 (C-7), 129.19 (C-2″, C-6″), 129.00 (C-3), 126.26 (C-6), 123.79 (C-4a), 123.65 (C-5), 118.06 (C-8), 116.31 (C-1′), 112.39 (C-3″, C-5″), 107.25 (C-4′), 72.00 (OCH_2), 53.79 ($C_{4''}$-OCH_3). Anal. calcd. for $C_{21}H_{15}ClO_4$: C 65.89, H 3.95; found: C 65.68, H 3.91.

Photoirradiation of chromones 3a–3j

*Photolysis of 6-chloro-2-(furan-3-yl)-3-methoxy-4*H*-chromen-4-one (3a)*

A methanolic solution (150 mL) of chromone **3a** (200 mg, 0.72 mmol) was irradiated with light from a 125 W Hg vapor lamp in a pyrex reactor under nitrogen atmosphere for 45 min. The removal of the solvent left a gummy solid, which was chromatographed to yield **4a**.

Compound **4a**

Yield 45%, white solid; mp 185–188 °C (EtOH). IR ν_{max} (cm^{-1}): 1649.7 (C=O). ^{1}H NMR ($CDCl_3$) δ: 8.23 (1H, d, J_m = 2.4 Hz, H-7), 7.58 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.40 (1H, d, J_o = 9.0 Hz, H-10), 6.46 (1H, dd/t, $J_{2,11b}$ = 2.1 Hz, $J_{2,1}$ = 2.4 Hz, H-2), 5.28 (1H, dd/t, $J_{1,2}$ = 2.4 Hz, $J_{1,11b}$ = 2.7 Hz, H-1), 5.10 (1H, d{dd}, $J_{3a,4a}$ = 2.4 Hz, $J_{3a,4b}$ = 9.0 Hz, $J_{3a,11b}$ = 10.2 Hz, H-3a), 4.34 (1H, dd, $J_{11b,1}$ = 2.7 Hz, $J_{11b,3a}$ = 10.2 Hz, H-11b), 4.14–4.07 (2H, m, H-4a, H-4b). ^{13}C NMR ($CDCl_3$) δ: 170.52 (C-6), 153.58 (C-10a), 151.94 (C-11a), 148.39 (C-2), 138.83 (C-6a), 133.47 (C-9), 130.57 (C-8), 125.45 (C-7), 124.73 (C-5a), 119.48 (C-10), 100.60 (C-1), 78.73 (C-4), 65.88 (C-3a), 40.83 (C-11b). Anal. calcd. for $C_{14}H_9ClO_4$: C 60.78, H 3.28; found: C 63.58, H 3.34. Mass (*m/z*): 276 (M$^+$, 100%).

*Photolysis of 6-chloro-3-ethoxy-2-(furan-3-yl)-4*H*-chromen-4-one (3b)*

A methanolic solution of **3b** (0.20 g, 0.7 mmol) on photolysis for 45 min furnished **4b** and **4b′**. These isomeric photoproducts were separated from the starting substrate **3b** by column chromatography. They were further separated from each other by preparative TLC.

Compound **4b**

Yield 22%, white solid; mp 174–176 °C (EtOH). IR ν_{max} (cm^{-1}): 1651.0 (C=O). ^{1}H NMR ($CDCl_3$) δ: 8.24 (1H, d, J_m = 2.4 Hz, H-7), 7.58 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7. 41 (1H, d, J_o = 9.0 Hz, H-10), 6.44 (1H, d, $J_{2,1}$ = 2.7 Hz, H-2), 5.36 (1H, dd/t, $J_{1,2}$ = 2.7 Hz, $J_{1,11b}$ = 2.7 Hz, H-1), 4.63 (1H, dd, $J_{3a,11b}$ = 7.8 Hz, $J_{3a,4}$ = 8.4 Hz, H-3a), 4.23 (1H, dd, $J_{11b,1}$ = 2.7 Hz, $J_{11b,3a}$ = 7.8 Hz, H-11b), 3.88 (1H, q{d}, J_{vic} = 6.6 Hz, $J_{4,3a}$ = 8.4 Hz, H-4), 1.65 (3H, d, J_{vic} = 6.6 Hz, C_4-CH_3). ^{13}C NMR ($CDCl_3$) δ: 171.10 (C-6), 153.63 (C-10a), 151.11 (C-11a), 147.27 (C-2), 138.22 (C-6a), 133.43 (C-9), 130.51 (C-8), 125.49 (C-7), 124.79 (C-5a), 119.46 (C-10), 100.69 (C-1), 80.69 (C-4), 71.72 (C-3a), 41.78 (C-11b), 17.69 (C_4-CH_3). Anal. calcd. for $C_{15}H_{11}ClO_4$: C 61.98, H 3.81; found: C 61.90, H 3.80. Mass (*m/z*): 290 (M^+, 100%).

Compound **4b′**

Yield 11%, white solid; mp 160–162 °C (EtOH). IR $\nu_{max.}$ (cm^{-1}): 1652.0 (C=O). ^1H NMR ($CDCl_3$) δ: 8.22 (1H, d, J_m = 2.4 Hz, H-7), 7.56 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.38 (1H, d, J_o = 9.0 Hz, H-10), 6.44 (1H, d, $J_{2,1}$ = 2.7 Hz, H-2), 5.25 (1H, d, $J_{1,2}$ = 2.7 Hz, H-1), 4.91 (1H, d, $J_{3a,11b}$ = 9.9 Hz, H-3a), 4.15 (1H, q, J_{vic} = 6.3 Hz, H-4), 4.05 (1H, d, $J_{11b,3a}$ = 9.9 Hz, H-11b), 1.55 (3H, d, J_{vic} = 6.3 Hz, C_4-CH_3). Anal. calcd. for $C_{15}H_{11}ClO_4$: C 61.98, H 3.81; found: C 61.87, H 3.78. Mass (*m/z*): 290 (M^+, 100%).

*Photolysis of 6-chloro-2-(furan-3-yl)-3-isopropyloxy-4*H*-chromen-4-one (3c)*

A methanolic solution of **3c** (0.20 g, 0.66 mmol) on photolysis for 45 min furnished **4c**.

Compound **4c**

Yield 48%, white solid; mp 165–167 °C ($CHCl_3$-EtOH). IR ν_{max} (cm^{-1}): 1655.8 (C=O). ^1H NMR ($CDCl_3$) δ: 8.23 (1H, d, J_m = 2.7 Hz, H-7), 7.56 (1H, dd, J_m = 2.7 Hz, J_o = 9.0 Hz, H-9), 7.38 (1H, d, J_o = 9.0 Hz, H-10), 6.43 (1H, dd, $J_{2,11b}$ = 1.8 Hz, $J_{2,1}$ = 3.0 Hz, H-2), 5.30 (1H, dd/t, $J_{1,2}$ = 3.0 Hz, $J_{1,11b}$ = 3.0 Hz, H-1), 4.64 (1H, d, $J_{3a,11b}$ = 9.3 Hz, H-3a), 3.95 (1H, dd{d}/m, $J_{11b,2}$ = 1.8 Hz, $J_{11b,1}$ = 3.0 Hz, $J_{11b,3a}$ = 9.3 Hz, H-11b), 1.62 (3H, s, C_4-CH_3b), 1.39 (3H, s, C_4-CH_3a). ^{13}C NMR ($CDCl_3$) δ: 173.00 (C-6), 159.00 (C-10a), 152.00 (C-11a), 148.20 (C-2), 135.00 (C-6a), 133.18 (C-9), 130.00 (C-8), 125.47 (C-7), 125.00 (C-5a), 119.39 (C-10), 100.49 (C-1), 85.99 (C-3a), 75.37 (C-4), 39.73 (C-11b), 23.94 (C_4-CH_3b), 23.38 (C_4-CH_3a). Anal. calcd. for $C_{16}H_{13}ClO_4$: C 63.06, H 4.30; found: C 63.01, H 4.25. Mass (*m/z*): 304/306 (M^+, 100%).

*Photolysis of 3-allyloxy-6-chloro-2-(furan-3-yl)-4*H*-chromen-4-one (3d)*

A methanolic solution of **3d** (0.20 g, 0.66 mmol) on photolysis for 45 min furnished **4d**.

Compound **4d**

Yield 29%, white solid; mp 145–146 °C (EtOH). IR ν_{max} (cm^{-1}): 1637(C=O). ^1H NMR ($CDCl_3$) δ: 8.17 (1H, d, J_m = 2.4 Hz, H-7), 7.51 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.34 (1H, d, J_o = 9.0 Hz, H-10), 6.40 (1H, d, $J_{2,1}$ = 2.7 Hz, H-2), 5.93 (1H, ddd, J_{vic} = 5.1 Hz, J_{trans} = 17.4 Hz, J_{cis} = 10.8 Hz, H-1′), 5.47 (1H, d, J_{trans} = 17.4 Hz, H-2′b), 5.35 (1H, d, J_{cis} = 10.8 Hz, H-2′a), 5.30 (1H, t, $J_{1,2}$ = 2.7 Hz, $J_{1,11b}$ = 2.7 Hz, H-1), 4.77 (1H, dd $J_{3a,4}$ = 6.9 Hz, $J_{3a,11b}$ = 9.6 Hz, H-3a), 4.10 (1H, dd, $J_{11b,1}$ = 2.7 Hz, $J_{11b,3a}$ = 9.6 Hz, H-11b), 4.40 (1H, dd, $J_{4,3a}$= 6.9 Hz, $J_{4,1'}$ = 5.1 Hz, H-4). ^{13}C NMR ($CDCl_3$) δ: 172.00 (C-6), 151.61 (C-10a), 149.35 (C-11a), 145.57 (C-2), 135.47 (C-6a), 131.49 (C-9), 130.76 (C-1′), 128.59 (C-8), 123.51 (C-7), 122.79 (C-5a), 117.67 (C-10), 117.50 (C-2′), 98.77 (C-1), 77.91 (C-4), 73.23 (C-3a), 39.11 (C-11b). Anal. calcd. for $C_{16}H_{11}ClO_4$: C 63.48, H 3.66; Found: C 63.46, H 3.60. Mass (*m/z*): 302 (M^+, 100%).

*Photolysis of 6-chloro-2-(furan-3-yl)-3-(2-methylallyloxy)-4*H*-chromen-4-one (3e)*

A methanolic solution of **3e** (0.20 g, 0.63 mmol) on photolysis for 45 min furnished **4e**.

Compound **4e**

Yield 24%, white solid; mp 196–200 °C ($CHCl_3$-EtOH). IR ν_{max} (cm^{-1}): 1641 (C=O). ^1H NMR ($CDCl_3$) δ: 8.22 (1H, d, J_m = 2.4 Hz, H-7), 7.59 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7. 41 (1H, d, J_o = 9.0 Hz, H-10), 6.47 (1H, d, $J_{2,1}$ = 2.7 Hz, H-2), 5.37 (1H, s, H-2′b), 5.17 (1H, s, H-2′a), 5.13 (1H, dd/t, $J_{1,2}$ = 2.7 Hz, $J_{1,11b}$ = 2.7 Hz, H-1), 4.63 (1H, dd, $J_{3a,11b}$ = 9.3 Hz, $J_{3a,4}$ = 7.5 Hz, H-3a), 4.31 (1H, q{d}, J_{vic} = 6.6 Hz, $J_{4,3a}$ = 7.5 Hz, H-4), 3.88 (1H, dd, $J_{11b,1}$ = 2.7 Hz, $J_{11b,3a}$ = 9.3 Hz, H-11b), 1.85 (3H, s, $C_{1'}$-CH_3). ^{13}C NMR ($CDCl_3$) δ: 171.80 (C-6), 152.68 (C-10a), 149.05 (C-11a), 146.27 (C-2), 135.82 (C-6a), 133.40 (C-9), 140.28 (C-1′), 129.51 (C-8), 126.49 (C-7), 122.70 (C-5a), 118.06 (C-10), 108.45 (C-2′), 99.69 (C-1), 80.10 (C-4), 72.70 (C-3a), 40.15 (C-11b), 18.69 (1′-CH_3). Anal. calcd. for $C_{17}H_{13}ClO_4$: C 64.46, H 4.14; found: C 64.34, H 4.12. Mass (*m/z*): 316 (M^+, 100%).

*Photolysis of 6-chloro-2-(furan-3-yl)-3-(3-methylbut-2-enyloxy)-4*H*-chromen-4-one (3f)*

A methanolic solution of **3f** (0.20 g, 0.6 mmol) on photolysis for 45 min furnished **4f**.

Compound **4f**

Yield 31%, light brown solid; mp 99–102 °C ($CHCl_3$-EtOH). IR ν_{max} (cm^{-1}): 1637.2 (C=O). ^1H NMR ($CDCl_3$) δ: 8.23 (1H, d, J_m = 2.4 Hz, H-7), 7.58 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.44 (1H, d, J_o = 9.0 Hz, H-10), 6.45 (1H, d, $J_{2,1}$ = 2.7 Hz, H-2), 5.49 (1H, dd/t, $J_{1,2}$ = 2.7 Hz, $J_{1,11b}$ = 3.0 Hz, H-1), 5.37 (1H, dd, $J_{1',4}$ = 5.7 Hz, J_{allyl} = 1.5 Hz, H-1′), 4.75 (1H, dd, $J_{3a,11b}$ = 9.0 Hz, $J_{3a,4}$ = 7.8 Hz, H-3a), 4.58 (1H, dd, $J_{4,3a}$ = 7.8 Hz, $J_{4,1'}$ = 5.7 Hz, H-4), 4.21 (1H, dd, $J_{11b,1}$ = 3.0 Hz, $J_{11b,3a}$ = 9.0 Hz, H-11b), 1.80 (3H, d, J_{allyl} = 1.5 Hz, $C_{2'}$-CH_3b), 1.76 (3H, s, $C_{2'}$-CH_3a). ^{13}C NMR ($CDCl_3$) δ: 172.50 (C-6), 153.41 (C-10a), 150.30 (C-11a), 144.28 (C-2), 135.00 (C-6a), 132.78 (C-9), 132.70 (C-2′), 128.00 (C-8), 123.20 (C-1′), 123.50 (C-7), 123.05 (C-5a), 119.19 (C-10), 101.79 (C-1), 79.80 (C-3a), 70.37 (C-4), 39.97 (C-11b), 25.20 (2′-CH_3b), 19.20 (2′-CH_3a). Anal. calcd. for $C_{18}H_{15}ClO_4$: C 65.36, H 4.57; found: C 65.28, H 4.51. Mass (*m/z*): 330 (M^+, 100%).

*Photolysis of 6-chloro-2-(furan-3-yl)-3-(3-phenylallyloxy)-4*H*-chromen-4-one (3g)*

A methanolic solution of **3g** (0.20 g, 0.53 mmol) on photolysis for 45 min furnished three photoproducts: **4g**, **5g**, and **6g**.

Compound **4g**

Yield 16%, light yellow solid; mp 155–157 °C ($CHCl_3$-EtOH). IR ν_{max} (cm^{-1}): 1639.6 (C=O). ^1H NMR ($CDCl_3$) δ: 8.25 (1H, d, J_m = 2.7 Hz, H-7), 7.58 (1H, dd, J_m = 2.7 Hz, J_o = 9.0 Hz, H-9), 7.41 (1H, d, J_o = 9.0 Hz, H-10), 7.28–7.36 (5H, m, H-2″-6″), 6.85 (1H, d, $J_{2',1'}$ = 16.5 Hz, H-2′), 6.50 (1H, dd/t, $J_{2,11b}$ = 2.1 Hz, $J_{2,1}$ = 2.4 Hz, H-2), 6.33 (1H, dd, $J_{1',4}$ = 6.0 Hz, $J_{1',2'}$ = 16.5 Hz, H-1′), 5.40 (1H, dd/t, $J_{1,11b}$ = 2.4 Hz, $J_{1,2}$ = 2.4 Hz, H-1), 4.91 (1H, dd, $J_{3a,4}$ = 7.2 Hz, $J_{3a,11b}$ = 9.6 Hz, H-3a), 4.58 (1H, t, $J_{4,3a}$ = 7.2 Hz, $J_{4,1'}$ = 6.0 Hz, H-4), 4.25 (1H, t{d}, $J_{11b,2}$ = 2.1 Hz, $J_{11b,1}$ = 2.4 Hz, $J_{11b,3a}$ = 9.6 Hz, H-11b). ^{13}C NMR (CDCl$_3$) δ: 172.13 (C-6), 154.05 (C-10a), 151.91 (C-11a), 144.50 (C-2), 138.44 (C-6a), 137.20 (C-1″), 130.78 (C-2′), 129.65 (C-9), 129.06 (C-3″, C-5″), 128.00 (C-4″), 127.77 (C-2″, C-6″), 126.02 (C-1′), 125.81 (C-7), 125.54 (C-8), 124.37 (C-5a), 118.06 (C-10), 98.88 (C-1), 77.56 (C-3a), 75.00 (C-4), 38.75 (C-11b). Anal. calcd. for $C_{22}H_{15}ClO_4$: C 69.75, H 3.99; found: C 69.60, H 3.95. Mass (*m/z*): 378 (M$^+$, 100%).

Compound **5g**

Yield 10%, light yellow solid; mp 181–182 °C (CHCl$_3$-EtOH). IR ν_{max} (cm^{-1}): 1642 (C=O). ^{1}H NMR (CDCl$_3$): 8.23 (1H, d, J_m = 2.7 Hz, H-7), 7.58 (1H, dd, J_m = 2.7 Hz, J_o = 9.0 Hz, H-9), 7.41 (1H, d, J_o = 9.0 Hz, H-10), 7.28–7.36 (5H, m, H-2″-6″), 6.93 (1H, d, $J_{2',1'}$ = 11.7 Hz, H-2′), 6.39 (1H, dd/t, $J_{2,11b}$ = 2.4 Hz, $J_{2,1}$ = 2.4 Hz, H-2), 5.83 (1H, dd, $J_{1',4}$ = 6.0 Hz, $J_{1',2'}$ = 11.7 Hz, H-1′), 5.35 (1H, dd/t, $J_{1,11b}$ = 2.4 Hz, $J_{1,2}$ = 2.4 Hz, H-1), 4.72 (1H, dd, $J_{3a,4}$ = 7.2 Hz, $J_{3a,11b}$ = 9.0 Hz, H-3a), 4.58 (1H, t, $J_{4,3a}$ = 7.2 Hz, $J_{4,1'}$ = 6.0 Hz, H-4), 4.25 (1H, t{d}, $J_{11b,2}$ = 2.4 Hz, $J_{11b,1}$ = 2.4 Hz, $J_{11b,3a}$ = 9.6 Hz, H-11b). ^{13}C NMR (CDCl$_3$) δ: 172.92 (C-6), 154.56 (C-10a), 151.21 (C-11a), 144.59 (C-2), 137.94 (C-6a), 138.88 (C-1″), 132.05 (C-2′), 129.42 (C-9), 129.86 (C-3″, C-5″), 128.05 (C-4″), 127.95 (C-2″, C-6″), 126.22 (C-1′), 126.01 (C-7), 125.54 (C-8), 124.72 (C-5a), 119.08 (C-10), 98.76 (C-1), 77.25 (C-3a), 75.84 (C-4), 39.08(C-11b). Anal. calcd. for $C_{22}H_{15}ClO_4$: C 69.75, H 3.99; found: C 69.65, H 3.93. Mass (*m/z*): 378 (M$^+$, 100%).

Compound **6g** *(data from a mixture of ^{1}H NMR/IR of* **3g** *and* **6g***)*

Yield 25%. IR ν_{max} (cm^{-1}): 1653 (C=O). ^{1}H NMR (CDCl$_3$) δ: 8.32 (1H, t, $J_{2',5'}$ = 1.8 Hz, $J_{2',4'}$ = 1.8 Hz, H-2′), 8.23 (1H, d, J_m = 2.4 Hz, H-5), 7.55 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-7), 7.55 (1H, t, $J_{5',2'}$ = 1.8 Hz, $J_{5',4'}$ = 1.8 Hz, H-5′), 7.44 (1H, d, J_o = 9.0 Hz, H-8), 7.20–7.28 (5H, m, H-2‴-6‴), 7.00 (1H, t, $J_{4',2'}$ = 1.8 Hz, $J_{4',5'}$ = 1.8 Hz, H-4′), 6.65 (1H, d, $J_{3',2'}$ = 11.4 Hz, H-3″), 6.35 (1H, td, $J_{2',3'}$ = 11.4 Hz, $J_{2',1'}$ = 6.6 Hz, H-2″), 4.93 (2H, d, $J_{1',2'}$ = 6.6 Hz, H-1″).

*Photolysis of 6-chloro-2-(furan-3-yl)-3-propargyloxy-4*H*-chromen-4-one (3h)*

A methanolic solution of **3h** (0.20 g, 0.66 mmol) on photolysis for 45 min furnished two isomeric products: **4h** and **4h′**. These photoproducts were separated from the starting substrate by column chromatography. They were further separated from each other by preparative TLC.

Compound **4h**

Yield 21%, white solid; mp 140–145 °C (CHCl$_3$-EtOH). IR ν_{max} (cm^{-1}): 1641.2 (C=O), 2130 (C≡C). ^{1}H NMR (CDCl$_3$): 8.24 (1H, d, J_m = 2.4 Hz, H-7), 7.58 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.42 (1H, d, J_o = 9.0 Hz, H-10), 6.51 (1H, dd, $J_{2,11b}$ = 1.5 Hz, $J_{2,1}$ = 2.4 Hz, H-2), 5.31 (1H, t, $J_{1,11b}$ = 2.1 Hz, $J_{1,2}$ = 2.4 Hz, H-1), 5.17 (1H, dd, $J_{3a,4}$ = 2.7 Hz, $J_{3a,11b}$ = 9.9 Hz, H-3a), 5.06 (1H, t, $J_{4,3a}$ = 2.7 Hz, $J_{4,2'}$ = 2.1 Hz, H-4), 4.16 (1H, t, $J_{11b,1}$ = 2.1 Hz, $J_{11b,2}$ = 1.5 Hz, $J_{11b,3a}$ = 9.9 Hz, H-11b), 2.63 (1H, d, $J_{2',4}$ = 2.1 Hz, H-2′). ^{13}C NMR (CDCl$_3$) δ: 172.08 (C-6), 153.06 (C-10a), 151.22 (C-11a), 145.32 (C-2), 136.12 (C-6a), 134.02 (C-9), 130.11 (C-8), 127.24 (C-7), 124.30 (C-5a), 119.00 (C-10), 101.68 (C-1), 77.44 (C-1′), 74.50 (C-3a), 73.78 (C-2′), 68.98 (C-4), 40.45 (C-11b). Anal. calcd. for $C_{16}H_9ClO_4$: C 63.91, H 3.02; found: C 63.83, H 3.06. Mass (*m/z*): 300 (M$^+$, 100%).

Compound **4h′**

Yield 20%, white solid; mp 121–122 °C (CHCl$_3$-EtOH). IR $\nu_{max.}$ (cm^{-1}): 1645 (C=O), 2128 (C≡C). ^{1}H NMR (CDCl$_3$) δ: 8.21 (1H, d, J_m = 2.4 Hz, H-7), 7.58 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.40 (1H, d, J_o = 9.0 Hz, H-10), 6.46 (1H, d, $J_{2,1}$ = 3.0 Hz, H-2), 5.31 (1H, d, $J_{1,2}$ = 3.0 Hz, H-1), 5.09 (1H, d, $J_{3a,11b}$ = 9.9 Hz, $J_{3a,4}$ = 6.9 Hz, H-3a), 4.86 (1H, q, $J_{4,3a}$ = 6.9 Hz, $J_{4,2'}$ = 2.1 Hz, H-4), 4.12 (1H, d, $J_{11b,3a}$ = 9.9 Hz, H-11b), 2.49 (1H, d, $J_{2',4}$ = 1.8 Hz, H-2′). ^{13}C NMR (CDCl$_3$) δ: 171.68 (C-6), 152.56 (C-10a), 152.92 (C-11a), 145.60 (C-2), 135.98 (C-6a), 134.44 (C-9), 130.19 (C-8), 127.22 (C-7), 124.54 (C-5a), 119.23 (C-10), 101.45 (C-1), 77.49 (C-1′), 74.67 (C-3a), 73.88 (C-2′), 68.38 (C-4), 40.15 (C-11b). Anal. calcd. for $C_{16}H_9ClO_4$: C 63.91, H 3.02; found: C 63.80, H 2.99. Mass (*m/z*): 300 (M$^+$, 100%).

*Photolysis of 3-benzyloxy-6-chloro-2-(furan-3-yl)-4*H*-chromen-4-one (3i)*

A methanolic solution of **3i** (0.20 g, 0.57 mmol) on photolysis for 45 min furnished **4i**.

Compound **4i**

Yield 50%, white solid; mp 116–118 °C (CHCl$_3$-EtOH). IR ν_{max} (cm^{-1}): 1647.2 (C=O). ^{1}H NMR (CDCl$_3$) δ: 8.25 (1H, d, J_m = 2.4 Hz, H-7), 7.59 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.49–7.36 (6H, m, H-10, 2′, 3′, 4′, 5′, 6′), 6.51 (1H, dd, $J_{2,11b}$ = 1.8 Hz, $J_{2,1}$ = 2.4 Hz, H-2), 5.44 (1H, t, $J_{1,11b}$ = 2.1 Hz, $J_{1,2}$ = 2.4 Hz, H-1), 5.08 (1H, dd, $J_{3a,4}$ = 8.1 Hz, $J_{3a,11b}$ = 9.6 Hz, H-3a), 4.80 (1H, d, $J_{4,3a}$ = 8.1 Hz, H-4), 4.30 (1H, t, $J_{11b,1}$ = 2.1 Hz, $J_{11b,2}$ = 2.4 Hz, $J_{11b,3a}$ = 9.6 Hz, H-11b). ^{13}C NMR (CDCl$_3$) δ: 171.00 (C-6), 153.00 (C-10a), 150.78 (C-11a), 146.96 (C-2), 138.00 (C-6a), 136.42 (C-1′), 133.08 (C-9), 130.31 (C-8), 128.34 (C-4′), 128.20 (C-3′, C-5′), 126.83 (C-2′, C-6′) 125.14 (C-7), 124.00 (C-5a), 119.07 (C-10), 100.45 (C-1), 79.99 (C-4), 76.38 (C-3a), 41.75 (C-11b). Anal. calcd. for $C_{20}H_{13}ClO_4$: C 68.09, H 3.71; found: C 63.15, H 3.66. Mass (*m/z*): 352 (M$^+$, 100%).

*Photolysis of 6-chloro-2-(furan-3-yl)-3-(4″-methoxybenzyloxy)-4*H*-chromen-4-one (3j)*

A methanolic solution of **3j** (0.20 g, 0.52 mol) on photolysis for 45 min furnished **4j**.

Compound **4j**

Yield 37%, white solid; mp 172–174 °C (CHCl$_3$-EtOH). IR ν_{max} (cm^{-1}): 1644.6 (C=O). ^{1}H NMR (CDCl$_3$) δ: 8.17 (1H, d, J_m = 2.4 Hz, H-7), 7.52 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.35 (1H, d, J_o = 9.0 Hz, H-10), 7.34 (2H, d, J_o = 8.7 Hz, H-2′, H-6′), 6.86 (2H, d, J_o = 8.7 Hz, H-3′, H-5′), 6.43 (1H, dd, $J_{2,11b}$ = 2.1 Hz, $J_{2,1}$ = 3.6 Hz, H-2), 5.36

(1H, dd, $J_{1,11b}$ = 2.4 Hz, $J_{1,2}$ = 3.6 Hz, H-1), 5.00 (1H, dd, $J_{3a,4}$ = 8.4 Hz, $J_{3a,11b}$ = 9.9 Hz, H-3a), 4.75 (1H, d, $J_{4,3a}$ = 8.4 Hz, H-4), 4.24 (1H, t{d}, $J_{11b,2}$ = 2.1 Hz, $J_{11b,1}$ = 2.4 Hz, $J_{11b,3a}$ = 9.9 Hz, H-11b), 3.74 (3H, s, $C_{4'}$-OCH_3). ^{13}C NMR ($CDCl_3$) δ: 171.00 (C-6), 156.96 (C-4′), 154.00 (C-10a), 151.00 (C-11a), 144.37 (C-2), 138.00 (C-6a), 135.55 (C-1′), 130.47 (C-9), 125.84 (C-8), 125.66 (C-2′, C-6′), 124.00 (C-5a), 122.54 (C-7), 116.49 (C-10), 111.06 (C-3′, C-5′), 97.83 (C-1), 77.29 (C-3a), 74.00 (C-4), 39.25(C-11b), 52.31 ($C_{4'}$-OCH_3). Anal. calcd. for $C_{21}H_{15}ClO_4$: C 65.89, H 3.95; found: C 65.93, H 3.96. Mass (*m/z*): 382 (M^+, 100%).

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References

(1) (a) Waiss, A. C.; Corse, J. *J. Am. Chem. Soc.* **1965**, *87*, 2068 doi:10.1021/ja01087a051.; (b) Waiss, A. C.; Lundin, R. E.; Lee, A.; Corse, J. *J. Am. Chem. Soc.* **1967**, *89*, 6213 doi:10.1021/ja01000a039.; (c) Matsuura, T.; Matsushima, H. *Tetrahedron* **1968**, *24*, 6615 doi:10.1016/S0040-4020(01)96876-0.; (d) Gupta, S. C.; Mukerjee, S. K. *Indian J. Chem.* **1973**, *11*, 1263.

(2) (a) Gupta, S. C.; Mukerjee, S. K. *Tetrahedron Lett.* **1973**, *14*, 5073 doi:10.1016/S0040-4039(01)87390-1.; (b) Mandal, P.; Nath, A.; Venkateswaran, R. V. *Tetrahedron* **1996**, *52*, 7855. doi:10.1016/0040-4020(96)00356-0.

(3) (a) Gupta, S. C.; Saini, A.; Kumar, D.; Yadav, N. S.; Chand, K.; Mor, S.; Dhawan, S. N. *J. Chem. Soc. Perkin Trans. I* **1995**, 177 doi:10.1039/p19950000177.; (b) Gupta, S. C.; Sharma, S.; Saini, A.; Dhawan, S. N. *J. Chem. Soc. Perkin Trans. I* **1999**, 2391. doi:10.1039/a901090d.

(4) (a) Gupta, S. C.; Yusuf, M.; Sharma, S.; Saini, A.; Arora, S.; Kamboj, R. C. *Tetrahedron* **2004**, *60*, 8445 doi:10.1016/j.tet.2004.07.003.; (b) Berar, S.; Berar, U.; Thakur, M.; Gupta, S. C.; Kamboj, R. C. *J. Indian Chem. Soc.* **2008**, *85*, 1.

(5) (a) Feigenbaum, A.; Fort, Y.; Pete, J. P.; Scholler, D. *J. Org. Chem.* **1986**, *51*, 4424 doi:10.1021/jo00373a015.; (b) Gupta, S. C.; Yadav, N. S.; Dhawan, S. N. *Indian J. Chem., Sect. B* **1991**, *30*, 790.

(6) (a) Gupta, S. C.; Saini, A.; Sharma, S.; Dhawan, S. N.; Kapoor, M. *Tetrahedron Lett.* **1996**, *37*, 8913 doi:10.1016/S0040-4039(96)02046-1.; (b) Gupta, S. C.; Thakur, M.; Berar, S.; Berar, U.; Kamboj, R. C. *Beilstein J. Org. Chem.* **2007**, *3*, 14 doi:10.1186/1860-5397-3-14. PMID:17374172.; (c) Gupta, S. C.; Yusuf, M.; Sharma, S.; Arora, S. *Tetrahedron Lett.* **2002**, *43*, 6875. doi:10.1016/S0040-4039(02)01366-7.

(7) Minimize energy to a minimum RMS gradient of 0.100 by MM2 incorporated in Chem office 8.0 Chem 3D ultra 8.0.

(8) (a) Pachler, K. G. R.; Underwood, W. G. E. *Tetrahedron* **1967**, *23*, 1817 doi:10.1016/S0040-4020(01)82581-3.; (b) Banks, S. W.; Steele, M. J.; Ward, D.; Dewick, P. M. *J. Chem. Soc. Chem. Commun.* **1982**, 156; (c) Chavdarian, C. G.; Seeman, J. I.; Wooten, J. B. *J. Org. Chem.* **1983**, *48*, 492 doi:10.1021/jo00152a016.; (d) Harper, S. H.; Kemp, A. D.; Underwood, W. G. E. *J. Chem. Soc. Chem. Commun.* **1965**, 309; (e) Perrin, D. R.; Bottomley, W. *J. Am. Chem. Soc.* **1962**, *84*, 1919. doi:10.1021/ja00869a030.

(9) (a) Jackman, L. M.; Sternhell, S. *Applications of NMR Spectroscopy in Organic Chemistry,* 2nd ed.; Pergamon Press: NewYork, 1969; p. 281; (b) Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783. doi:10.1016/0040-4020(80)80155-4.

(10) (a) Van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129 doi:10.1021/ja00752a025.; (b) Van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1968**, *90*, 3894. doi:10.1021/ja01016a071.