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Article

Photochemistry of 3-Alkoxychromones: Photocyclisation of 2-Aryl-6-chloro-3-{(thiophen-2-yl)methoxy}chromones

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1,4-Biradicais gerados da fotoirradiação de cromonos 2-aril-3-[(tiofen-2-il)metóxi] produziram compostos tetraciclicos angulares contendo grupos tienil. A dehidrogenação e contração do anel dos produtos foram também observadas dependendo da densidade elétrica no anel 2-aril.

1,4-Biradicals generated upon photo-irradiation of 2-aryl-3-{(thiophen-2-yl)methoxy} chromones produced angular tetracyclic products bearing the thienyl group. The dehydrogenation and ring contraction products were also observed depending upon the electron density on the 2-aryl ring.

Keywords: alkoxychromone, type-II reaction, 1,4-biradical, ring contraction, angular tetracyclic

Introduction

Conjugated enones bearing the alkoxy and/or alkyl group at C-3, on photoirradiation with UV light undergo γ-hydrogen abstractions.[1-4] The products obtained, depend upon the nature of the substituents present in the substrates, for example, 2-alkyl-3-arylcyclohex-2-enones[5] and 3-alkoxy-2-phenyl-4-oxo-4*H*-1-benzopyran,[6-8] afforded the photocyclised angular products whereas 3-methoxy-2-methylchromones[9] have been found to furnish the novel dimeric oxetanol. In 3-alkoxy-2-arylchromones, the synthetic applications of these γ-hydrogen abstractions include the formation of vinyl ethers,[10] spiropyrans,[11] pyranopyrones,[12] pyranoalcohols,[13] angular tetracyclics[14] etc. In these phototransformations, the primary reaction is the n-π^* excitation of the C=O group that subsequently abstracts hydrogen from the 3-alkoxy group leading to the formation of the 1,4-biradical.[5-8] The nature of the 3-alkoxy group has been found to have a profound effect on the fate of 1,4-biradical[10,13] to form the mesomeric biradicals. To examine the effect of (thiophen-2-yl)methoxy group at 3-position of the chromones with different 2-aryl groups and also to study the possibility of photo-transposition[15] reactions of the thiophene when tied to the chromones, in this work we report the synthesis and the photolytic behavior of the chromones **2**(**a**-**g**).

Results and Discussion

The 2-aryl-3-{(thiophen-2-yl)methoxy}chromones **2**(**a-g**) were obtained by reacting 3-hydroxybenzopyrans[16-17] **1**(**a-g**) with 2-(chloromethyl)thiophene[18] using anhydrous K_2CO_3/n-$Bu_4N^+I^-$ in anhydrous acetone as the solvent as shown in Scheme 1.

The structures of the benzopyrans **2**(**a-g**) were derived from their spectral data (IR, ^{1}H, ^{13}C NMR, Experimental section).

The photoirradiation of the methanolic solution of **2**(**a-d**) with pyrex filtered UV light from a 125W Hg vapour lamp under the nitrogen atmosphere (Scheme 2) produced the photoproducts **3**(**a-d**) and **4a**, **4c**. In spite of our best efforts, the compound **4a** could not be isolated in the pure form and its structure was derived from the NMR data of the reaction mixture enriched in **4a** by the repeated crystallization of **3a**.

The other chromones **2e** and **2f** under the similar photolytic conditions produced the photoproducts **3e**, **4e** and **3f**, **3f'**, **4f**, **4f'** respectively in 10-35% yields (Scheme 3).

The photoirradiation of **2g**, a regio-isomer of **2e**, in the methanolic solution (0.001mol L^{-1}) with pyrex

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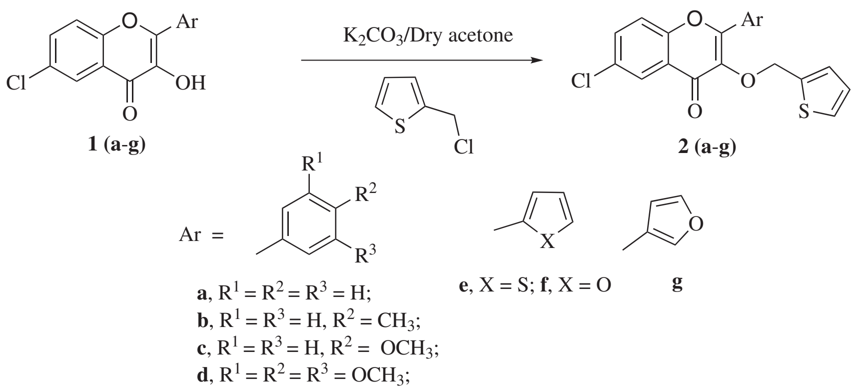
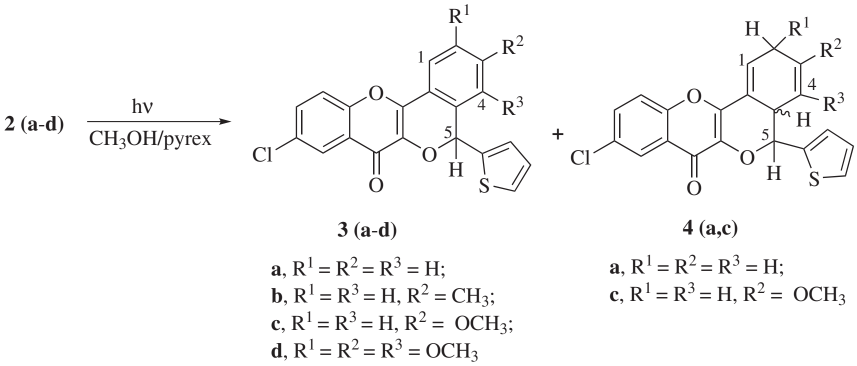
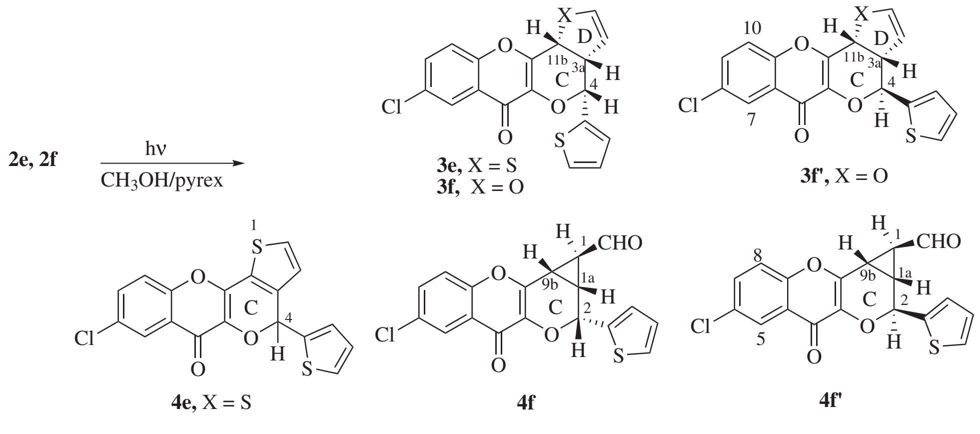


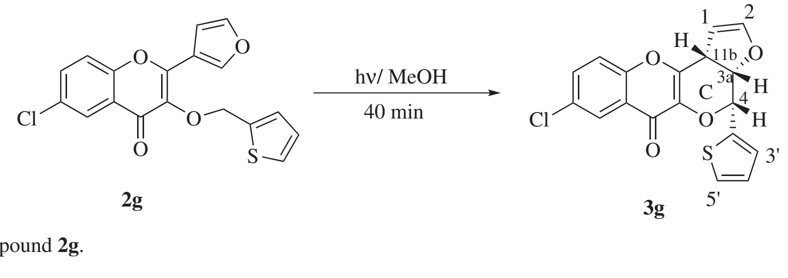
Scheme 1. Synthesis of 2-aryl-3-{(thiophen-2-yl)methoxy}chromones **2**(**a**-**g**).



Scheme 2. Photolysis of compounds **2**(**a**-**d**).



Scheme 3. Photolysis of compounds **2e** and **2f**.



Scheme 4. Photolysis of compound **2g**.

filtered UV light for 40 min gave **3g** (50%, Scheme 4). No secondary photoproducts corresponding to **4f** and **4f**' were furnished.[31]

The structures of all the photoproducts were confirmed by the comparison of their spectral parameters (IR, ^{1}H, ^{13}C NMR) with those of the starting substrates **2**(**a-g**) and also from their elemental analysis. The photoproducts **3**(**a-d**) showed the IR absorption between 1630-1650 cm^{-1} for the pyrone C=O group. In their ^{1}H NMR spectra, the proton H-5 was found almost in the aromatic region of spectrum between δ 6.58-6.80 whereas in **4a** and **4c** it had the upfield resonance at δ *ca.* 5.00.

Regarding the stereochemistry of photoproducts **3f**, **3f**', **3e** and **3g**, the conformation of ring C is a half-chair. The protons H-11b and H-3a are in the *cis*-disposition (*cis* C/D ring junction) which has been derived from the observation that the $J_{3a,11b}$ = 8.1-10.5 Hz which is in accordance with J/Φ relationships[19,20](karplus rule) and the earlier studies.[21] In compounds **3f**, **3e** and **3g**, the coupling constant $J_{3a,4}$ *ca.* 8.4 Hz for H-3a and H-4 protons places them in a *cis*-orientation, which finds support from the literature studies[16] thus positioning the 4-thienyl group in Ψ-equatorial position on the half-chair conformation of the ring C (Figure 1). Further, in the photoproduct **3f**' (stereoisomer of **3f**), the orientation of H-3a and H-4 is *trans* ($J_{3a,4}$ = 2.1 Hz) with thienyl group in Ψ-axial conformation. This has made the stereocentre at C-4 to have a *R* configuration in the compounds **3e**, **3f** and **3g** and a *S* configuration in the compound **3f**'. The absolute configuration at C-11b and C-3a is *R* and *S* respectively in **3f**, **3e**, **3g** and **3f**'. The MM2 energy minimized structures of the compounds **3f** and **3f**' are shown in Figure 1 and their J/Φ data has been given in Table 1 which also confirms the above findings about the stereochemistry of the photoproducts.

Table 1. Relationship between coupling constant and dihedral angle (Φ)

Compound	$J_{11b,3a}$ (Hz)	$\Phi_{11b,3a}$	$J_{3a,4}$ (Hz)	$\Phi_{3a,4}$
3f	10.5	4.01°	8.4	27.76°
3f'	8.1	29.70°	2.1	91.58°
3e	9.6	12.60°	8.1	30.63°
3g	9.6	11.60°	6.6	37.26°

In the secondary photoproducts **4f** and **4f'** obtained from the photolysis of **2f**, the cyclopropyl protons[22] H-1a and H-9b are *cis* (*J* = 9.0 Hz) placed to each other and the H-1 is *trans* to both H-1a ($J_{1,1a}$ = 4.2/3.3 Hz) and H-9b ($J_{1,9b}$ = 3.6/3.9 Hz); the –CHO group is *exo* to the pyran ring C. In **4f,** the H-2 has been observed as doublet ($J_{2,1a}$ = 2.4 Hz), inferring that the plane containing H-1a and H-2 possesses $\Phi_{2,1a}$ *ca.* 50° (Figure 2) whereas its isomeric compound **4f'** has been found to possess different stereochemistry at C-2 with $\Phi_{2,1a}$ *ca.* 75° (*J* 1.2 Hz). The thienyl group at C-2 is

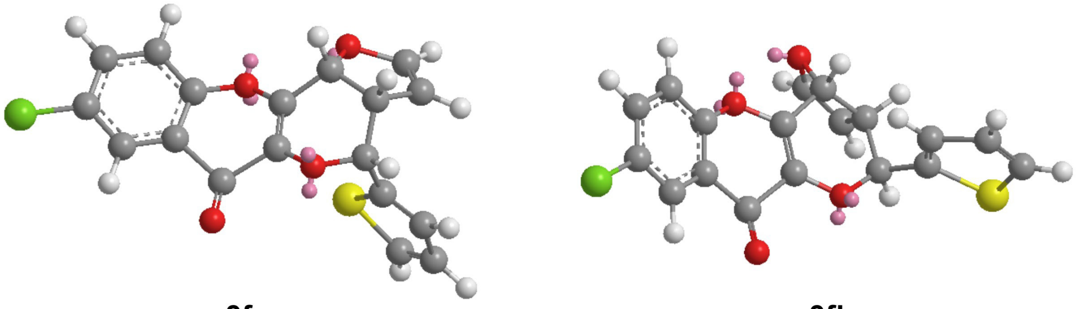

3f **3f'**

Figure 1. MM2 energy minimized structure of compounds **3f** and **3f**'.

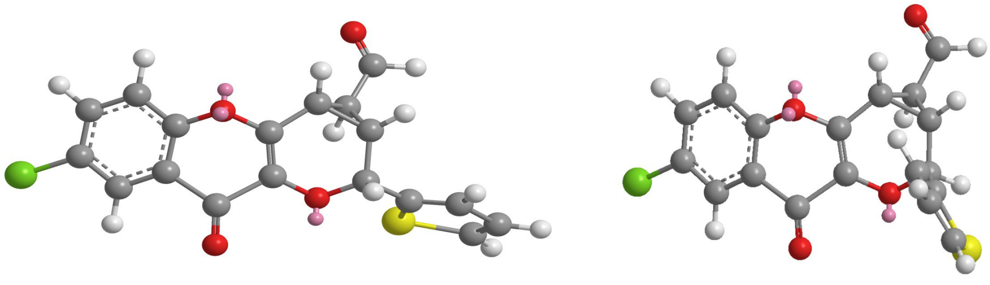

4f' **4f'**

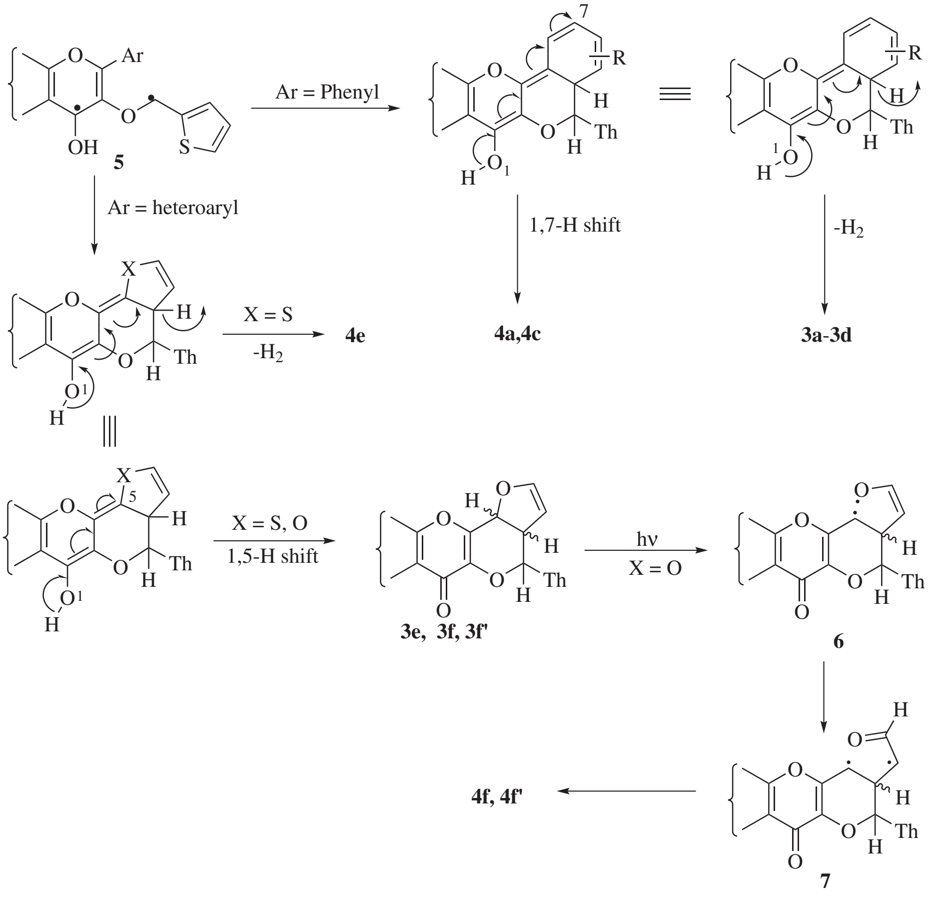
Figure 2. MM2 energy minimized structure of compounds **4f** and **4f**'.

below the plane in **4f** and above the plane in **4f'** (Figure 2). The difference in chemical shift of H-1 (0.4 ppm) in **4f** and **4f'** is because of the proximity to the pyran oxygen (ring C). The distance between H-1 and one of the sp^3 orbital of pyran oxygen is 2.25 A° in **4f** whereas in **4f'** it is 2.35A° leading to extra deshielding in the former. A similar explanation can be given to explain the observed downfield shift in δ value of H-1 (*ca.* 0.65 ppm) as compared to that reported in literature[23] for cyclopropane carboxaldehyde (δ 2.60) fused to the cyclohexane ring.

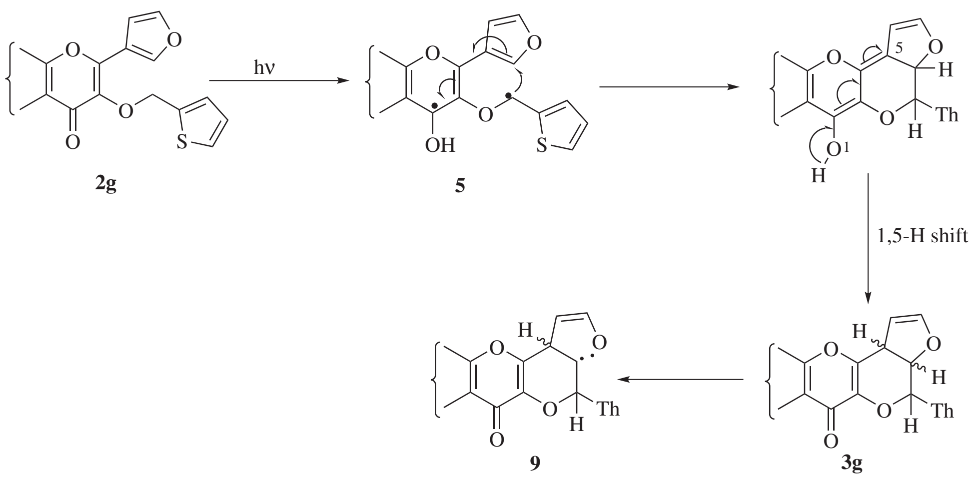
The carbon skeleton of photoproducts **3b**, **4c**, **3c**, **3d**, **3e**, **4e** and **3g** was further confirmed from their fully proton decoupled ^{13}C NMR spectra (Experimental section).

Regarding the effect of substituent at 2-position of the chromones **2**(**a-g**) on the product formation/distribution, it has been observed that in the case of furyl chromones **2f** and **2g** only the cyclised products are obtained. From the others substrates **2a-2e** (phenyl, thiophene), the photodehydrogenated cyclised products along with the cyclised products are also formed. For such difference, the assignable reason could be the different degree of aromaticity of the C-2 ring moiety. The aromatic character increases from furan *via* thiophene to benzene. So, the gain in energy by dehydrogenation is higher in **3a-3d** leading to the predominant formation of these aromatized photoproducts. The dehydrogenation re-establishes aromaticity. Since the aromatic character is less expressed in the case of thiophene, the dehydrogenation is less dominant here (**4e**). Obviously, the low aromatic character of furan is insufficient to favour formation of dehydrogenation products and hence only the cyclised products are furnished.

A possible mechanism involving the 1,4-biradical intermediate (Scheme 5) formed by the γ-hydrogen abstraction from $-OCH_2-$ by the photo-excited C=O akin to some earlier reports[6-8] may be envisioned for these phototransformations. The 1,4-biradical expectedly undergoes bond formation between the –CH– and the carbon atom of aryl ring at C-2 followed by product formation **3f**, **3f'**, **3e**, **3g** and **4a**, **4c** through 1,5- and 1,7-H-shifts respectively. The dehydrogenated products **3a-3d** and **4e** are formed directly by the expulsion of H_2 during the cyclisation and not by the dehydrogenation of their respective dihydroderivatives[6,8] as confirmed by the photolysis of pure isolated dihydrocompounds when no aromatization could be detected; only polymeric products



Scheme 5. Mechanism of photoproduct formation.



Scheme 6. Mechanism of photoproduct **3g** formation

were formed. In the chromone **2f**, when the 2-aryl group is the furyl moiety, in addition to the dihydro products **3f** and **3f'**, the other photoproducts **4f** and **4f'** were also realized from the further photoisomerisation of **3f** and **3f'** where the dihydrofuran ring D undergoes ring contraction mechanism[24-27] to provide the cyclopropylaldehyde moiety. That the fused cyclopropylaldehyde **4f** and **4f'** are furnished from **3f** and **3f'** was confirmed by the observation that these on further irradiation under identical conditions provided **4f** and **4f'** along with some other minor products which escaped isolation. In this ring contraction mechanism, the biradical intermediate **6** is stabilized by the double bond of the pyrone moiety making the C–O bond amenable to cleavage. A similar ring contraction mechanism could not be observed in photolysis of **2g** which only yielded **3g** (Scheme 6).

Also, **3g** on further photoirradiation did not furnish any ring-contracted product similar to **4f**. This is probably due to the lack of stabilization of possible biradical[31] **9** (Scheme 6), which is not in conjugation with the double bond of the pyrone ring.

In all these chromones **2**(**a-g**), the often occurring phototransposition[15,28-30] reactions of alkyl/aryl thiophenes were not observed though they bear alkyl thiophene or both aryl and alkyl thiophene groups (**2e**).

Conclusions

Hydrogen abstraction from the 3-alkoxy group by the excited C=O is the preferred reaction pathway for the formation of photoproducts. The (thiophen-2-yl)methoxy radical generated undergoes cyclisation only similar to the allyl and benzyl radicals. No photo-transposition reactions of the thiophene ring were observed in these compounds.

Experimental

General

Melting points were determined in open capillaries and are thus uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300 MHz (for ^{13}C frequency = 75 MHz) Bruker spectrophotometer using TMS as the internal standard. IR spectra were recorded on a Buck Scientific 500 spectrophotometer using KBr pellets. Mass spectra recorded are either EI or FAB$^+$. 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 (9:2) and left overnight before use. The elution was carried out with increasing proportion of benzene in the petroleum ether-benzene mixture. The compounds **3f**, **3f'** and **4f**, **4f'** were separated by using silica gel of 200-400 mesh (ACROS Organics) for column chromatography. All photochemical reactions were conducted under a nitrogen (99.9%) atmosphere. Any trace of oxygen and moisture from the procured nitrogen was removed by passing through the alkaline pyragallol solution and concentrated sulfuric acid respectively.

*Synthesis of benzopyrans **2(a-g)***

*6-Chloro-2-phenyl-3-{(thiophen-2-yl)methoxy}-4-oxo-4***H***-1-benzopyran, **2a***: The 3-hydroxychromone, **1a** (2.72 g, 0.01 mol), 2-(chloromethyl)thiophene (1.32 g, 0.01 mol), anhydrous K_2CO_3 (1.0 g) and tetra-n-butylammonium iodide (100 mg) were refluxed in anhydrous acetone (50 mL) for 3 h. Filtration, evaporation of the solvent and crystallization of the residue from methanol gave **2a** (2.40 g, 65%), light brown solid; mp 86-89 °C; IR ν_{max}/cm^{-1}: 1645 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.26 (1H, d, J_m = 2.4 Hz, H-5), 8.00 (2H, m, H-2', H-6'), 7.63 (1H, dd, J_m = 2.4 Hz, J_o = 8.7 Hz, H-7), 7.49 (4H, m, H-8, H-3', H-4', H-5'), 7.22 (1H, dd, $J_{5'',3''}$ = 1.2 Hz, $J_{5'',4''}$ = 5.1 Hz, H-5″), 6.95 (1H, dd, $J_{3'',4''}$ = 3.6 Hz, H-3"), 6.87 (1H, dd, $J_{4'',3''}$ = 3.6 Hz, $J_{4'',5''}$ = 5.1 Hz, H-4"), 5.38 (2H, s, –OCH$_2$–); ^{13}C NMR (CDCl$_3$) δ 174.0 (C-4), 156.9 (C-8a), 153.6 (C-2), 139.1 (C-2″), 138.4 (C-3), 133.7 (C-7), 130.8 (C-5), 130.6 (C-1′), 128.9 (C-3′, C-5′), 128.5 (C-4′), 128.4 (C-6), 128.3 (C-2′, C-6′), 126.9 (C-4a), 126.5 (C-4″), 126.1 (C-3″), 125.1 (C-5″), 119.8 (C-8), 67.6 (–OCH$_2$–); Anal. Calc. for $C_{20}H_{13}ClO_3S$: C, 65.13; H, 3.55. Found: C, 65.02; H, 3.57.

The other ethers **2b-2g** were synthesized by using the above described procedure starting from the compounds **1b-1g** (0.01 mol each) respectively.

*6-Chloro-2-(4'-methylphenyl)-3-{(thiophen-2-yl) methoxy}-4-oxo-4***H***-1-benzo-pyran,* ***2b***: Yield 2.30 g (60%), light brown solid; mp 128-131 °C; IR ν_{max}/cm^{-1}: 1641 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.24 (1H, d, J_m = 2.4 Hz, H-5), 7.92 (2H, d, J_o = 8.4 Hz, H-2', H-6'), 7.60 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-7), 7.47 (1H, d, J_o = 9.0 Hz, H-8), 7.35 (2H, d, J_o = 8.4 Hz, H-3', H-5'), 7.22 (1H, dd, $J_{5'',4''}$ = 4.8 Hz, H-5"), 6.97 (1H, dd, $J_{3'',4''}$ = 3.0 Hz, H-3"), 6.87 (1H, m, H-4"), 5.36 (2H, s, –OCH$_2$–), 2.44 (3H, s, –CH$_3$); ^{13}C NMR (CDCl$_3$) δ 173.9 (C-4), 153.6 (C-8a), 141.4 (C-2), 138.6 (C-2"), 135.4 (C-4′), 133.8 (C-3), 133.6 (C-7), 130.7 (C-5), 129.4 (C-6), 129.1 (C-3′, C-5′), 128.8 (C-4″), 128.4 (C-5″), 127.7 (C-1′), 126.9 (C-3″), 126.5 (C-2′, C-6′), 125.1 (C-4a), 119.7 (C-8), 67.5 (–OCH$_2$–), 21.6 (4′–CH$_3$); Anal. Calc. for $C_{21}H_{15}ClO_3S$: C, 65.88; H, 3.95. Found: C, 65.73; H, 3.90.

*6-Chloro-2-(4'-methoxyphenyl)-3-{(thiophen-2-yl) methoxy}-4-oxo-4***H***-1-benzopyran,* ***2c***: Yield 2.57 g (65%), light brown solid; mp 118-120 °C; IR ν_{max}/cm^{-1}: 1639 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.24 (1H, d, J_m = 2.7 Hz, H-5), 8.02 (2H, d, J_o = 9.0 Hz, H-2', H-6'), 7.60 (1H, dd, J_m = 2.7 Hz, J_o = 9.0 Hz, H-7), 7.46 (1H, d, J_o = 9.0 Hz, H-8), 7.35 (2H, d, J_o = 8.4 Hz, H-3', H-5'), 7.22 (1H, dd, $J_{5'',4''}$ = 5.1 Hz, H-5"), 6.97 (3H, m, H-3", H-3', H-5'), 6.88 (1H, dd, $J_{4'',3''}$ = 3.6 Hz, $J_{4'',5''}$ = 5.1 Hz, H-4"), 5.36 (2H, s, –OCH$_2$–), 3.89 (3H, s, –OCH$_3$); Anal. Calc. for $C_{21}H_{15}ClO_4S$: C, 63.24; H, 3.79. Found: C, 63.13; H, 3.74.

*6-Chloro-3-{(thiophen-2-yl)methoxy}-2-(3',4',5'-trimethoxyphenyl)-4-oxo-4***H***-1-benzopyran,* ***2d***: Yield 2.60 g (57%), pale yellow solid; mp 129-131 °C; IR ν_{max}/cm^{-1}: 1643 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.17 (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), 7.42 (1H, d, J_o = 9.0 Hz, H-8), 7.15 (1H, dd, $J_{5'',4''}$ = 5.1 Hz, H-5"), 6.90 (1H, d, $J_{3'',4''}$ = 3.3 Hz, H-3"), 6.81 (1H, dd, $J_{4'',3''}$ = 3.3 Hz, $J_{4'',5''}$ = 5.1 Hz, H-4"), 5.27 (2H, s, –CH$_2$–), 3.86 (3H, s, C$_{4'}$–OCH$_3$), 3.77 (6H, s, C$_{3'}$ & C$_{5'}$–OCH$_3$); ^{13}C NMR (CDCl$_3$) δ 173.8 (C-4), 156.4 (C-8a), 153.5 (C-2), 152.9 (C-3′, C-5′), 140.6 (C-4′), 139.3 (C-2″), 138.6 (C-3), 133.7 (C-7), 130.8 (C-5), 128.3 (C-6), 127.0 (C-4″), 126.6 (C-5″), 125.5 (C-1′), 125.2 (C-3″), 125.0 (C-4a), 119.7 (C-8), 106.7 (C-2′, C-6′), 68.0 (–OCH$_2$–), 61.0 (4′–OCH$_3$), 56.3 (3′, 5′–OCH$_3$); Anal. Calc. for $C_{23}H_{19}ClO_6S$: C, 60.20; H, 4.17. Found: C, 60.12; H, 4.18.

*6-Chloro-2-(2'-thienyl)-3-{(thiophen-2-yl)methoxy}-4-oxo-4***H***-1-benzopyran,* ***2e***: Yield 2.98 g (80%), pale yellow solid; mp 122-124 °C; IR ν_{max}/cm^{-1}: 1639 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.24 (1H, d, J_m = 2.4 Hz, H-5), 7.96 (1H, dd, $J_{3',5'}$ = 0.9 Hz, $J_{3',4'}$ = 3.6 Hz, H-3'), 7.65 (1H, dd, $J_{5',3'}$ = 0.9 Hz, $J_{5',4'}$ = 4.8 Hz, H-5'), 7.63 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-7), 7.47 (1H, d, J_o = 9.0 Hz, H-8), 7.29 (1H, dd, $J_{3'',5''}$ = 0.9 Hz, H-3"), 7.20 (1H, dd, $J_{4',3'}$ = 3.9 Hz, $J_{4',5'}$ = 4.8 Hz, H-4'), 7.17 (1H, d, H-5"), 6.95 (1H, dd, $J_{4'',3''}$ = 3.3 Hz, $J_{4'',5''}$ = 5.1 Hz, H-4"), 5.64 (2H, s, –OCH$_2$–); ^{13}C NMR (CDCl$_3$) δ 174.1 (C-4), 153.0 (C-8a), 149.8 (C-2), 138.0 (C-4a), 133.5 (C-7), 132.5 (C-2′), 131.8 (C-2″), 130.1 (C-6), 129.9 (C-5′), 129.1 (C-4″), 127.9 (C-4′), 127.4 (C-3″), 126.6 (C-5″), 125.6 (C-3), 125.1 (C-5), 124.5 (C-3′), 119.5 (C-8), 67.0 (–OCH$_2$–); Anal. Calc. for $C_{18}H_{11}ClO_3S_2$: C, 57.67; H, 2.96. Found: C, 57.48; H, 2.92.

*6-Chloro-2-(2'-furyl)-3-{(thiophen-2-yl)methoxy}-4-oxo-4***H***-1-benzopyran,* ***2f***: Yield 2.15 g (60%), pale yellow solid; mp 114-115 °C; IR ν_{max}/cm^{-1}: 1640 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.22 (1H, d, J_m = 2.4 Hz, H-5), 7.67 (1H, m, H-5'), 7.61 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-7), 7.50 (1H, d, J_o = 9.0 Hz, H-8), 7.36 (1H, dd, $J_{3',5'}$ = 1.8 Hz, $J_{3',4'}$ = 3.3 Hz, H-3'), 7.28 (1H, dd, $J_{5'',3''}$ = 1.8 Hz, $J_{5'',4''}$ = 5.1 Hz, H-5''), 7.11 (1H, dd, $J_{3'',5''}$ = 1.8 Hz, $J_{3'',4''}$ = 3.0 Hz, H-3"), 6.93 (1H, dd, $J_{4'',3''}$ = 3.0 Hz, $J_{4'',5''}$ = 5.1 Hz, H-4"), 6.60 (1H, dd, $J_{4',5'}$ = 1.8 Hz, $J_{4',3'}$ = 3.3 Hz, H-4'), 5.57 (2H, s, –OCH$_2$–); ^{13}C NMR (CDCl$_3$) δ 172.2 (C-4), 154.2 (C-8a), 151.5 (C-2), 145.3 (C-5′), 144.2 (C-2'), 138.4 (C-4a), 137.1 (C-2"), 132.9 (C-7), 130.5 (C-6), 127.8 (C-4"), 127.0 (C-3"), 126.3 (C-5''), 125.2 (C-5), 124.9 (C-3), 119.7 (C-8), 110.1 (C-4'), 109.2 (C-3'), 67.2 (–OCH$_2$–); Anal. Calc. for $C_{18}H_{11}ClO_4S$: C, 60.26; H, 3.09. Found: C, 60.11; H, 3.11.

*6-Chloro-2-(3'-furyl)-3-{(thiophen-2-yl)methoxy}-4-oxo-4***H***-1-benzopyran,* ***2g***: Yield 2.43 g (68%), light brown solid; mp 126-128 °C; IR ν_{max}/cm^{-1}: 1646 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.27 (1H, t, $J_{2',4'}$ = 0.6 Hz, H-2'), 8.24 (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), 7.52 (1H, t, $J_{5',2'}$ = 1.5 Hz, $J_{5',4'}$ = 1.8 Hz, H-5'), 7.45 (1H, d, J_o = 9.0 Hz, H-8), 7.29 (1H, dd, $J_{5'',3''}$ = 1.2 Hz, $J_{5'',4''}$=5.1 Hz, H-5"), 7.12 (1H, d, $J_{3'',4''}$= 3.3 Hz, H-3"), 6.96 (2H, m, H-4", H-4'), 5.58 (2H, s, –OCH$_2$–); ^{13}C NMR (CDCl$_3$) δ 172.8 (C-4), 153.2 (C-8a), 152.0 (C-2), 145.7 (C-5′), 143.4 (C-2'), 138.5 (C-4a), 138.0 (C-2"), 133.4 (C-7), 130.7 (C-6), 128.6 (C-4"), 127.0 (C-3"), 126.8 (C-5"), 125.2 (C-3), 125.1 (C-5), 119.5 (C-8), 117.7 (C-3'), 108.7 (C-4'), 67.2 (–OCH$_2$–); Anal. Calc. for $C_{18}H_{11}ClO_4S$: C, 60.26; H, 3.09. Found: C, 60.21; H, 3.05.

*Photolysis of benzopyrans **2a**-**2g***

General procedure: A deoxygenated solution of chromone **2a** (200 mg) in magnesium dried methanol (150 mL) was refluxed for 5 min. The solution was degassed with nitrogen for 1 h and then irradiated in a pyrex vessel under nitrogen atmosphere for 40 min with a 125W Hg vapour lamp. The removal of the solvent under reduced pressure left a red gummy mass that was chromatographed over a column of silica gel to yield **3a** and **4a.**

Other compounds **2b-2g** (200 mg each) were also photolysed by following the same procedure to yield the respective products. In all these cases the yield of the photoproducts ranges between 20-50%. The rest of the material was a mixture of unidentifiable polymeric products and starting chromone.

*Compound **3a***: Yield 52 mg (26%), off-white solid; mp 180-182 °C; R$_f$ 0.68 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1640 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.26 (1H, d, J_m = 2.1 Hz, H-8), 7.97 (1H, m, H-1), 7.64 (1H, dd, J_m = 2.1 Hz, J_o = 9.0 Hz, H-10), 7.57 (2H, m, H-2, H-3), 7.52 (1H, d, J_o = 9.0 Hz, H-11), 7.42 (1H, m, H-4), 7.23 (1H, d, $J_{5',4'}$ = 5.1 Hz, H-5'), 6.90 (2H, m, H-4', H-3'), 6.65 (1H, s, H-5); *m/z* 366 (M$^+$, 100%); Anal. Calc. for $C_{20}H_{11}ClO_3S$: C, 65.49; H, 3.02. Found: C, 65.31; H, 2.99.

*Compound **4a***: Yield 20% (calculated from ^{1}H NMR spectrum of mixture); R$_f$ 0.68 (5% ethyl acetate in benzene); ^{1}H NMR (CDCl$_3$) δ 8.24 (1H, d, J_m = 2.4 Hz, H-8), 7.60 (1H, dd, J_m = 2.4 Hz, J_o = 8.7 Hz, H-10), 7.44 (1H, d, J_o = 8.7 Hz, H-11), 7.18 (1H, d, $J_{5',4'}$ = 3.3 Hz, H-5'), 7.06 (1H, d, $J_{4',3'}$ = 3.6 Hz, H-4'), 6.90 (1H, d, $J_{3',4'}$ = 3.6 Hz, H-3'), 6.80 (1H, br s, H-1), 5.88 (1H, m, H-3), 5.39 (1H, d, J = 9.9 Hz, H-4), 5.00 (1H, d, $J_{5,4a}$ = 11.1 Hz, H-5), 3.46 (1H, m, H-4a), 3.03 (2H, m, H-2).

*Compound **3b***: Yield 60mg (30%), off-white solid; mp 207-209 °C; R$_f$ 0.67 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1635 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.23 (1H, d, J_m = 2.4 Hz, H-8), 7.82 (1H, d, J_o = 7.8 Hz, H-1), 7.58 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-10), 7.49 (1H, d, J_o = 9.0 Hz, H-11), 7.36 (2H, m, H-3', H-5'), 7.08 (1H, dd, H-2), 6.88 (2H, m, H-4', H-4), 6.58 (1H, s, H-5), 2.45 (3H, s, –CH$_3$); ^{13}C NMR (CDCl$_3$) δ 173.0 (C-7), 153.5 (C-11a), 151.0 (C-13), 149.8 (C-2′), 135.3 (C-3), 134.0 (C-6a), 133.0 (C-10), 130.0 (C-8), 127.9 (C-4), 127.3 (C-2), 126.9 (C-4′), 126.6 (C-11), 125.9 (C-9), 125.7 (C-3′), 125.2 (C-5′), 124.0 (C-4a), 122.3 (C-12b), 119.6 (C-11), 74.7 (C-5), 22.0 (3–CH$_3$); *m/z* 380 (M$^+$, 100%); Anal. Calc. for $C_{21}H_{13}ClO_3S$: C, 66.23; H, 3.44. Found: C, 66.25; H, 3.36.

*Compound **3c***: Yield 44 mg (22%), light brown solid; mp 140-142 °C; R$_f$ 0.54 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1637 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.25 (1H, d, J_m = 2.4 Hz, H-8), 7.89 (1H, d, J_o = 8.4 Hz, H-1), 7.58 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-10), 7.49 (1H, d, J_o = 9.0 Hz, H-11), 7.37 (1H, s, H-5'), 7.09 (1H, dd, $J_{2,4}$ = 2.1 Hz, $J_{2,1}$ = 8.4 Hz, H-2), 6.90 (2H, m, H-3', H-4'), 6.79 (1H, d, $J_{4,2}$ = 2.4 Hz, H-4), 6.58 (1H, s, H-5), 3.97 (3H, s, –OCH$_3$); ^{13}C NMR (CDCl$_3$) δ 170.3 (C-7), 162.6 (C-3), 154.0 (C-11a), 152.0 (C-12a), 148.7 (C-2′), 135.8 (C-6a), 133.1 (C-10), 130.6 (C-8), 128.3 (C-9), 128.0 (C-7a), 127.3 (C-1), 126.9 (C-4″), 126.6 (C-3″), 125.4 (C-5″), 125.0 (C-4a), 124.3 (C-12b), 119.5 (C-11), 114.8 (C-2), 111.7 (C-4), 74.8 (C-5), 55.7 (3–OCH$_3$); *m/z* 396 (M$^+$, 100%); Anal. Calc. for $C_{21}H_{13}ClO_4S$: C, 63.56; H, 3.30. Found: C, 63.21; H, 3.34.

*Compound **4c***: Yield 59 mg (30%), white solid; mp 163-166 °C; R$_f$ 0.58 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1648 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.22 (1H, d, J_m = 2.7 Hz, H-8), 7.56 (1H, dd, J_m = 2.7 Hz, J_o = 8.7 Hz, H-10), 7.39 (2H, m, H-11, H-5'), 7.14 (1H, d, H-3'), 7.02 (1H, m, H-4'), 6.86 (1H, br s, H-1), 5.20 (2H, m, H-4, H-5), 3.67 (3H, s, –OCH$_3$), 3.38 (1H, m, H-4a), 2.38 (1H, m, H-2a), 1.98 (1H, m, H-2b); ^{13}C NMR (CDCl$_3$) δ 170.6 (C-7), 152.9 (C-11a), 144.6 (C-3), 139.4 (C-6a), 138.4 (C-2′), 133.9 (C-10), 133.0 (C-12b), 130.5 (C-8), 128.8 (C-12a), 127.9 (C-9), 127.1 (C-7a), 126.8 (C-4′), 125.5 (C-3′), 124.7 (C-5′), 123.9 (C-1), 120.2 (C-4), 119.4 (C-11), 79.0 (C-5), 40.9 (4–OCH$_3$), 40.8 (C-4a), 39.9 (C-2); *m/z* 398 (M$^+$, 100%); Anal. Calc. for $C_{21}H_{15}ClO_4S$: C, 63.24; H, 3.79. Found: C, 63.19; H, 3.78.

*Compound **3d***: Yield 40 mg (20%), light brown solid; mp 200-203 °C; R$_f$ 0.47 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1636 (C=O); ^{1}H NMR (CDCl$_3$) δ 8.15 (1H, d, J_m = 2.1 Hz, H-8), 7.50 (1H, dd, J_m = 2.1 Hz, J_o = 9.0 Hz, H-10), 7.43 (1H, d, J_o = 9.0 Hz, H-11), 7.11 (2H, m, H-1, H-5'), 6.78 (3H, m, H-3', H-4', H-5), 3.95 (3H, s, C$_4$–OCH$_3$), 3.88 (3H, s, C_3–OCH_3), 3.77 (3H, s, C_2–OCH_3); ^{13}C NMR ($CDCl_3$) δ 172.8 (C-7), 154.6 (C-11a), 152.9 (C-12a), 149.4 (C-2′), 145.0 (C-4), 142.8 (C-2), 136.2 (C-3), 134.4 (C-6a), 133.2 (C-10), 130.6 (C-8), 126.8 (C-9), 126.6 (C-4′), 126.4 (C-5′), 125.4 (C-3′), 125.3 (C-7a), 121.0 (C-12b), 119.5 (C-4a), 119.5 (C-11), 101.1 (C-1), 69.7 (C-50), 61.1 (4–OCH_3), 61.1 (3–OCH_3), 56.4 (2–OCH_3); *m/z* 456 (M^+, 100%); Anal. Calc. for $C_{23}H_{17}ClO_6S$: C, 60.46; H, 3.75. Found: C, 66.31; H, 3.74.

Compound ***3e***: Yield 42 mg (21%), off-white solid; mp 179-182 °C; R_f 0.48 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1655 (C=O); ^{1}H NMR ($CDCl_3$) δ 8.16 (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), 7.34 (1H, d, J_o = 9.0 Hz, H-10), 7.28 (1H, m, H-5’), 7.07 (1H, d, $J_{3',4'}$ = 3.3 Hz, H-3’), 6.94 (1H, dd, $J_{4',3'}$ = 3.3 Hz, $J_{4',5'}$ = 4.8 Hz, H-4’), 6.33 (1H, d, $J_{2,3}$ = 6.3 Hz, H-2), 5.30 (1H, dd, $J_{3,3a}$ = 3.0 Hz, $J_{3,2}$ = 6.3 Hz, H-3), 5.08 (1H, d, $J_{4,3a}$ = 9.6 Hz, H-4), 4.98 (1H, d, $J_{11b,3a}$ = 8.1 Hz, H-11b), 3.60 (1H, m, $J_{3a,3}$ = 3.0 Hz, $J_{3a,4}$ = 9.6 Hz, H-3a); ^{13}C NMR ($CDCl_3$) δ 170.4 (C-6), 153.5 (C-10a), 148.6 (C-11a), 139.6 (C-2′), 138.6 (C-6a), 134.7 (C-9), 130.6 (C-8), 128.3 (C-2), 127.4 (C-4′), 126.8 (C-3′), 126.4 (C-4), 125.5 (C-7), 124.7 (C-5a), 121.6 (C-5′), 119.6 (C-10), 72.5 (C-4), 51.5 (C-3a), 46.2 (C-11b); *m/z* 374 (M^+, 100%), 320 (M^+-54, 39%); Anal. Calc. for $C_{18}H_{11}ClO_3S_2$: C, 57.67; H, 2.96. Found: C, 57.45; H, 2.94.

Compound ***4e***: Yield 40 mg (20%), light brown solid; mp 122-125 °C; R_f 0.34 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1642 (C=O); ^{1}H NMR ($CDCl_3$) δ 8.16 (1H, d, J_m = 2.4 Hz, H-7), 7.56 (1H, d, $J_{2,3}$ = 5.1 Hz, H-2), 7.50 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.39 (1H, d, J_o = 9.0 Hz, H-10), 7.28 (1H, m, H-5’), 7.22 (1H, dd, $J_{3',5'}$ = 1.2 Hz, $J_{3',4'}$ = 5.1 Hz, H-3’), 6.91 (1H, d, $J_{3,2}$ = 5.1 Hz, H-3), 6.86 (1H, dd, $J_{4',5'}$ = 3.6 Hz, $J_{4',3'}$ = 5.1 Hz, H-4’), 6.74 (1H, s, H-4); ^{13}C NMR ($CDCl_3$) δ 172.2 (C-6), 153.0 (C-10a), 147.9 (C-11a), 145.1 (C-3a), 139.4 (C-2′), 139.0 (C-6a), 134.9 (C-11b), 133.2 (C-9), 130.8 (C-8), 129.5 (C-2), 127.2 (C-4), 126.9 (C-3′), 126.8 (C-3), 125.7 (C-7), 125.5 (C-5a), 122.6 (C-5′), 119.4 (C-10), 74.0 (C-4); *m/z* 372 (M^+, 100%); Anal. Calc. for $C_{18}H_{11}ClO_3S_2$: C, 57.98; H, 2.43. Found: C, 58.00; H, 2.40.

Compound ***3f***: Yield 49 mg (25%), pale yellow solid; mp 188-191 °C; R_f 0.60 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1652 (C=O); ^{1}H NMR ($CDCl_3$) δ 8.24 (1H, d, J_m = 2.7 Hz, H-7), 7.63 (1H, dd, J_m = 2.7 Hz, J_o = 9.0 Hz, H-9), 7.50 (1H, d, J_o = 9.0 Hz, H-10), 7.38 (1H, d, $J_{5',4'}$ = 5.1 Hz, H-5’), 7.17 (1H, d, $J_{3',4'}$ = 3.0 Hz, H-3’), 7.04 (1H, dd, $J_{4',3'}$ = 3.0 Hz, $J_{4',5'}$ = 5.1 Hz, H-4’), 6.59 (1H, br s, H-2), 5.28 (1H, d, $J_{4,3a}$ = 8.4 Hz, H-4), 5.02 (1H, t, $J_{3,2}$ = 2.7 Hz, $J_{3,3a}$ = 2.7 Hz, H-3), 4.70 (1H, d, $J_{11b,3a}$ = 10.5 Hz, H-11b), 3.43 (1H, d{t}, $J_{3a,3}$ = 2.1 Hz, $J_{3a,4}$ = 8.4 Hz, $J_{3a,11b}$ = 10.5 Hz, H-3a). *m/z* 358 (M^+, 100%); Anal. Calc. for $C_{18}H_{11}ClO_4S$: C, 60.26; H, 3.09. Found: C, 60.10; H, 3.05.

Compound ***3f′***: Yield 34 mg (17%), pale yellow solid; mp 165-170 °C; R_f 0.56 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1652 (C=O); ^{1}H NMR ($CDCl_3$) δ 8.23 (1H, d, J_m = 2.4 Hz, H-7), 7.61 (1H, dd, J_m = 2.4 Hz, J_o = 9.0 Hz, H-9), 7.48 (1H, d, J_o = 9.0 Hz, H-10), 7.36 (1H, dd, $J_{5',4'}$ = 5.1 Hz, H-5’), 7.17 (1H, d, $J_{3',4'}$ = 3.0 Hz, H-3’), 7.04 (1H, dd, $J_{4',3'}$ = 3.0 Hz, $J_{4',5'}$ = 5.1 Hz, H-4’), 6.39 (1H, br s, H-2), 5.66 (1H, d, $J_{11b,3a}$ = 8.1 Hz, H-11b), 5.43 (1H, d, $J_{4,3a}$ = 2.1 Hz, H-4), 5.10 (1H, t, $J_{3,3a}$ = 2.1 Hz, $J_{3,2}$ = 2.1 Hz, H-3), 4.11 (1H, d{t}, $J_{3a,3}$ = 2.1 Hz, $J_{3a,4}$ = 2.1 Hz, $J_{3a,11b}$ = 8.1 Hz, H-3a). *m/z* 358 (M^+, 100%); Anal. Calc. for $C_{18}H_{11}ClO_4S$: C, 60.26; H, 3.09. Found: C, 60.02; H, 3.02.

Compound ***4f***: Yield 40 mg (20%), brown solid; mp 190-193 °C; R_f 0.41 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1707 (–CHO), 1660 (C=O); ^{1}H NMR ($CDCl_3$) δ 9.79 (1H, d, $J_{CHO,1}$ = 2.4 Hz, –CHO), 8.23 (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), 7.43 (1H, d, J_o = 9.0 Hz, H-8), 7.39 (1H, dd, $J_{5',3'}$ = 2.1 Hz, $J_{5',4'}$ = 5.1 Hz, H-5’), 7.22 (1H, dd, $J_{3',5'}$ = 2.1 Hz, $J_{3',4'}$ = 3.6 Hz, H-3’), 7.04 (1H, dd, $J_{4',3'}$ = 3.6 Hz, $J_{4',5'}$ = 5.1 Hz, H-4’), 5.27 (1H, d, $J_{2,1a}$ = 2.4 Hz, H-2), 3.27 (1H, d{dd}, $J_{1,CHO}$ = 2.4 Hz, $J_{1,9b}$ = 3.6 Hz, $J_{1,1a}$ = 4.2 Hz, H-1), 2.89 (1H, dd, $J_{9b,1}$ = 3.6 Hz, $J_{9b,1a}$ = 9.0 Hz, H-9b), 2.82 (1H, d{dd}, $J_{1a,2}$ = 2.4 Hz, $J_{1a,1}$ = 4.2 Hz, $J_{1a,9b}$ = 9.0 Hz, H-1a); *m/z* 358 (M^+, 44%), 329 (M^+-29, 100%); Anal. Calc. for $C_{18}H_{11}ClO_4S$: C, 60.26; H, 3.09. Found: C, 60.30; H, 3.00.

Compound ***4f′***: Yield 22mg (11%), light brown solid; mp 168-170 °C; R_f 0.35 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1705 (–CHO), 1657 (C=O); ^{1}H NMR ($CDCl_3$) δ 9.40 (1H, d, $J_{CHO,1}$ = 5.7 Hz, –CHO), 8.23 (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), 7.43 (1H, d, J_o = 9.0 Hz, H-8), 7.39 (1H, dd, $J_{5',3'}$ = 2.1 Hz, $J_{5',4'}$ = 5.1 Hz, H-5’), 7.22 (1H, dd, $J_{3',5'}$ = 2.1 Hz, $J_{3',4'}$ = 3.6 Hz, H-3’), 7.04 (1H, dd, $J_{4',3'}$ = 3.6 Hz, $J_{4',5'}$ = 5.1 Hz, H-4’), 5.46 (1H, d, $J_{2,1a}$ = 1.2 Hz, H-2), 2.87 (1H, d{dd}, $J_{1,1a}$ = 3.3 Hz, $J_{1,9b}$ = 3.9 Hz, $J_{1,CHO}$ = 5.7 Hz, H-1), 2.75 (1H, dd, $J_{9b,1}$ = 3.9 Hz, $J_{9b,1a}$ = 9.0 Hz, H-9b), 2.53 (1H, d{dd}, $J_{1a,2}$ = 1.2 Hz, $J_{1a,1}$ = 3.3 Hz, $J_{1a,9b}$ = 9.0 Hz, H-1a); *m/z* 358 (M^+, 38%), 329 (M^+-29, 100%); Anal. Calc. for $C_{18}H_{11}ClO_4S$: C, 60.26; H, 3.09. Found: C, 60.08; H, 3.10.

Compound ***3g***: Yield 100 mg (50%), off-white solid; mp 142-144 °C; R_f 0.62 (5% ethyl acetate in benzene); IR ν_{max}/cm^{-1}: 1645.0 (C=O); ^{1}H NMR ($CDCl_3$) δ 8.23 (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), 7.42 (1H, d, J_o = 9.0 Hz, H-10), 7.33 (1H, d, $J_{5',4'}$ = 5.1 Hz, H-5’), 7.20 (1H, d, $J_{3',4'}$ = 3.0 Hz, H-3’), 7.02 (1H, m, H-4’), 6.52 (1H, d, $J_{2,1}$ = 2.4 Hz, H-2), 5.41 (1H, t, $J_{1,2}$ = 2.4 Hz, $J_{1,11b}$ = 2.4 Hz, H-1), 5.30 (1H, d, $J_{4,3a}$ = 6.6 Hz, H-4), 5.20 (1H, dd, $J_{3a,4}$ = 6.6 Hz, $J_{3a,11b}$ = 9.6 Hz, H-3a), 4.27 (1H, dd, $J_{11b,3a}$ = 9.6 Hz, H-11b); ^{13}C NMR ($CDCl_3$) δ 170.4 (C-6), 153.6 (C-10a), 151.5 (C-11a), 147.7 (C-2), 138.9 (C-6a), 137.4 (C-2′), 133.5 (C-9), 130.6 (C-8), 126.9 (C-4′), 126.9 (C-3′), 125.5 (C-7), 124.8 (C-5a), 124.3 (C-5′), 119.5 (C-10), 100.8 (C-1), 81.2 (C-4), 73.1 (C-3a), 41.4 (C-11b); m/z 358 (M^+, 100%); Anal. Calc. for $C_{18}H_{11}ClO_4S$: C, 60.26; H, 3.09. Found: C, 60.35; H, 3.06.

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