

Photolysis of some 2-butenyl/butynylbischromones: Effect of solvent polarity

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Abstract: Photochemistry of some 2-butenyl/butynyl-bischromones has been investigated in benzene and isopropanol-THF (1:1). The photoreactions are initiated through the intramolecular H-abstraction that leads to the formation of tetracyclic derivatives and vinyl bischromones. Photolytic conversion of the bischromones is found to be dependent upon the nature of the intermediate spacer and H-donating capability of the solvent.

Keywords: 1,4-biradicals; bischromones; chromophores; photolytic conversion; intermediate spacer.

1. Introduction

Photochemical reactions have been utilized as an exciting synthetic tool by the organic chemist in the past decades.¹⁻¹¹ These reactions often produce such products which are inaccessible by thermal reactions and proceed along the excited state pathways.¹²⁻¹³ Photoreactions of the bichromophoric organic molecules have been studied in detail in the past¹⁴⁻²⁰ and their photochemical behaviour is influenced by the nature of the intervening carbon chain. In our previous studies on the bischromones,²¹⁻²⁴ the photolytic routes were dictated by the flexibility of intervening carbon units.²¹⁻²⁴ Further to study the impact of intermediate spacer on the course of photoreaction; we have focussed our attention on the synthesis of bischromones **1a-3a** & **1b-3b** built around trans-2-butene and 2-butyne. The main impetus behind this study was to investigate the effect of solvent polarity and the fixed geometry of the intermediate spacer upon the photoproducts formation and their distribution.

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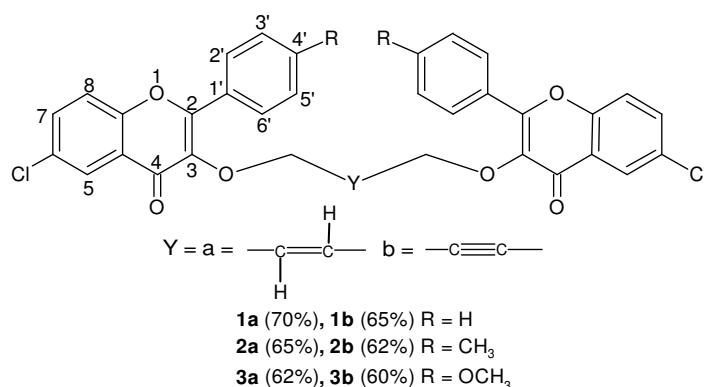


Figure 1. Bischromones

2. Results and Discussion

The bischromones **1a-3a** & **1b-3b** required for this photochemical study were synthesized by reacting 2-aryl-6-chloro-3-hydroxy-4-oxo-4*H*-1-benzopyran²⁵⁻²⁷ with an appropriate alkylating agent (like trans-1,4-dibromo-2-butene & 1,4-dichloro-2-butyne) in presence of anhydrous K₂CO₃ and Bu₄N⁺I (Phase Transfer Catalyst-PTC) in dry acetone. The monoalkylated chromones formed in the reaction mixtures were removed by the column chromatography (60-120 mesh). The reactions conducted in the absence of PTC (Bu₄N⁺I) provided very poor yields of the bischromones and also involved very long reaction times. The structures of the bischromones **1a-3a** & **1b-3b** were determined from the rigorous analysis of their IR, ¹H NMR (400 MHz) and mass spectral data (see experimental).

Table 1. Showing the PMR δ values of 3 -OCH₂- group in bischromones

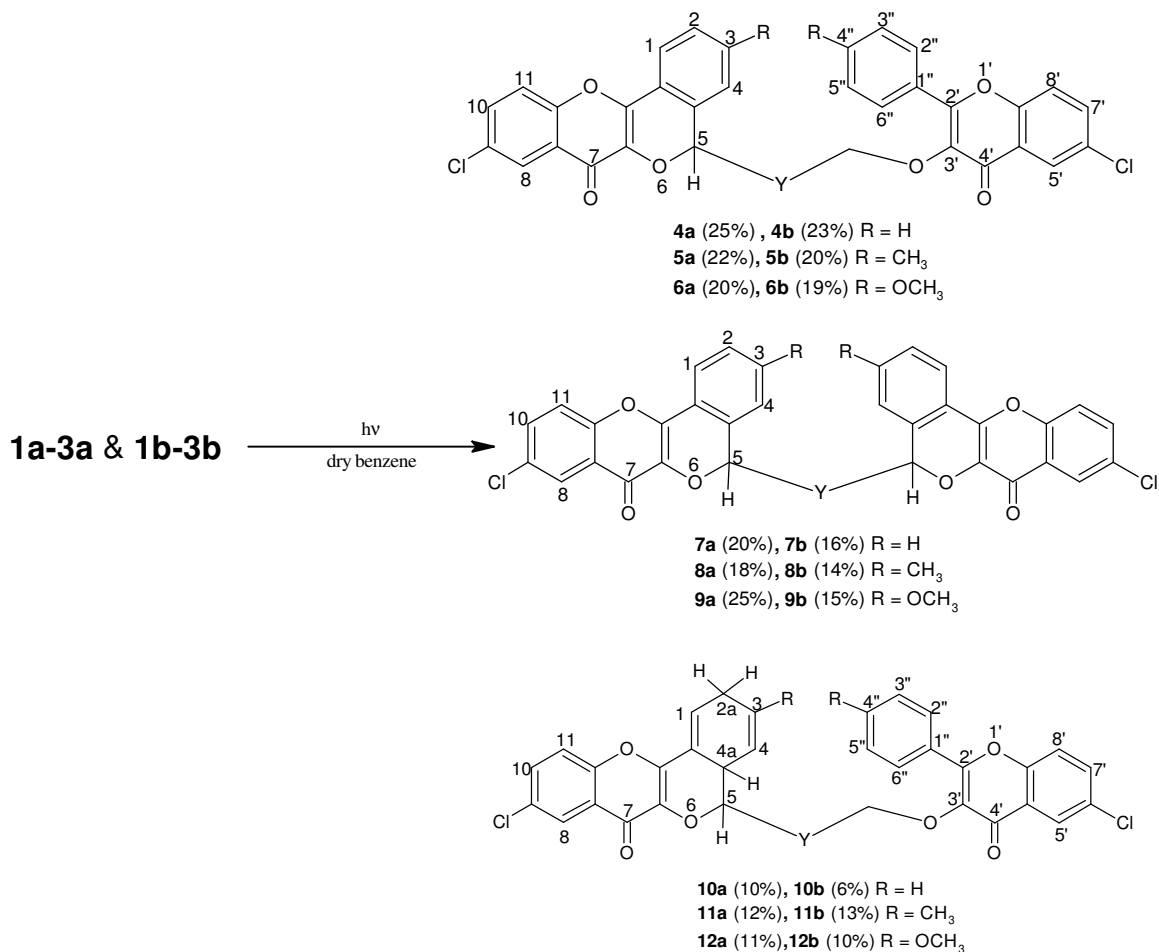
Compound	1a	1b	2a	2b	3a	3b
δ (OCH ₂)	4.53	4.92	4.52	4.91	4.56	4.94

The downfield resonance of 3-OCH₂- hydrogens in bischromones **1b-3b** as compared to **1a-3a** could be ascribed to the more electronegative character of the adjacent triple bond than double bond.

The photo irradiation of the bischromones **1a-3a** & **1b-3b** was carried out in dry benzene with Pyrex filtered light from a 125W Hg lamp. The photolysates thus obtained were subjected to extensive column chromatography (100-200 mesh) and repeated crystallizations to yield **4-12**. The structures of these photoproducts were characterized by the comparison of their ¹H NMR (400 MHz) spectra with those of starting materials **1a-3a** & **1b-3b** (see experimental).

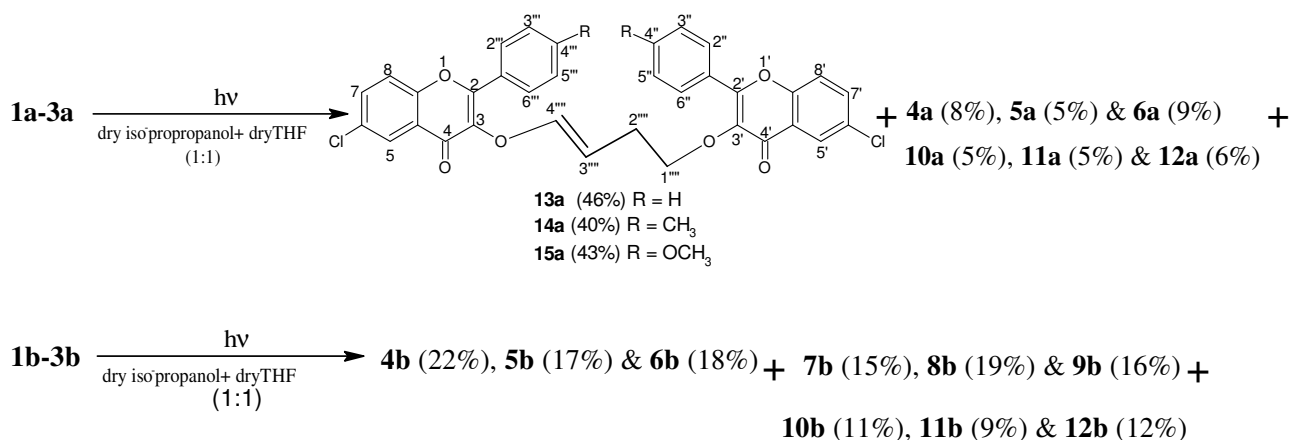
The IR spectra of the photoproducts also proved very helpful in their structural analysis. Photoproducts **4a** (1644, 1635 cm⁻¹), **4b** (1648, 1631 cm⁻¹), **5a** (1641, 1630 cm⁻¹), **5b** (1642, 1632 cm⁻¹), **6a** (1649, 1631 cm⁻¹), **6b** (1641, 1635 cm⁻¹), **10a** (1659, 1633 cm⁻¹), **10b** (1657, 1635 cm⁻¹), **11a** (1655, 1636 cm⁻¹), **11b** (1656, 1631 cm⁻¹), **12a** (1655, 1632 cm⁻¹) & **12b** (1653, 1631 cm⁻¹) could arise from the reaction of only one chromophoric unit which is evident from the two IR absorptions in their carbonyl group region while both chromophores undergo photoreaction to provide products **7a** (1643 cm⁻¹), **7b** (1641 cm⁻¹), **8a** (1643 cm⁻¹), **8b** (1644 cm⁻¹), **9a** (1640 cm⁻¹) & **9b** (1644 cm⁻¹) that exhibited only one intense absorption in their carbonyl region. Mass spectra of these compounds further corroborated their structure (see experimental).

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Scheme 1. Photolysis of the bischromones **1a-3a** & **1b-3b**

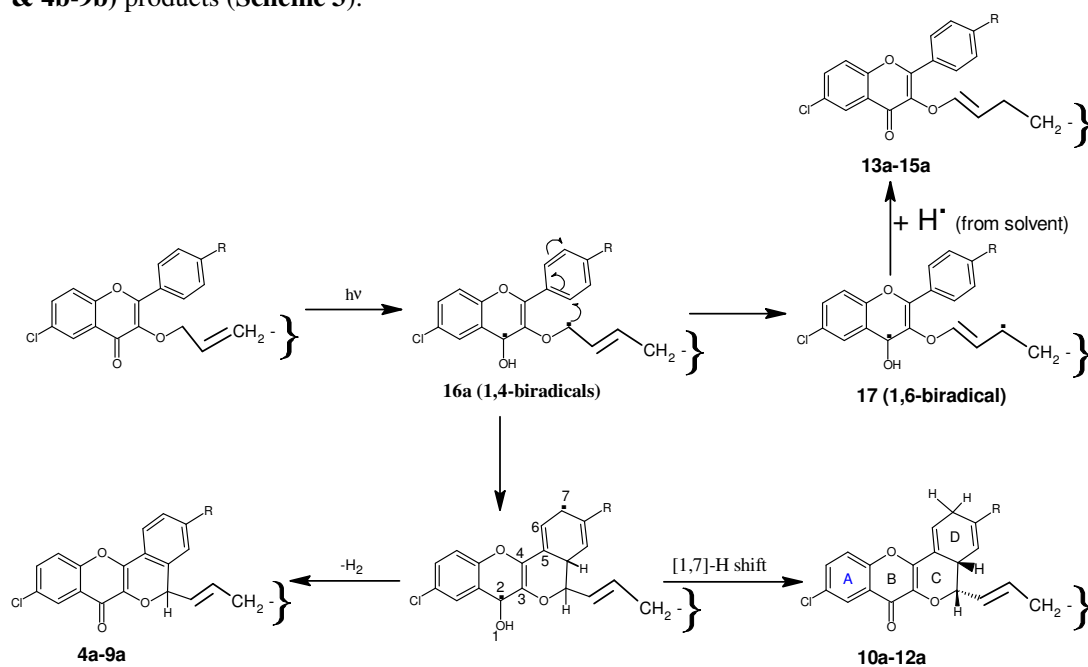
The stereochemical disposition of hydrogens at C-4a and C-5 in the photo-products **10a-12a** & **10b-12b** were ascertained from J and ϕ parameters. Both the hydrogens (C-4a, & 5) are present on the same side and it is evident from $J_{4a,5} = 10$ Hz ($\phi=0^\circ$).²⁸⁻³⁵ The heavier alkyl group at C-5 is present in the preferred *pseudo-equatorial* conformation and ring C in the half chair form.^{21,22}

To study the effect of the solvent polarity upon these photoreactions, the bischromones **1a-3a** were irradiated in isopropanol / THF (1:1) under the nitrogen atmosphere. The column chromatographic separation of their photolysates provided isomerized ethers **13a-15a** (as major products) along with the minor amount of cyclized compounds **4a-6a** & **10a-12a** (characterized by TLC, mp and mmp).



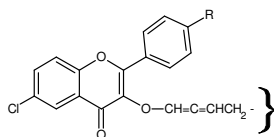
Scheme 2. Photolysis of the bischromones **1a-3a** & **1b-3b** in THF-isopropanol (1:1).

From the photolysis of **1b-3b** under the polar conditions, we could not obtain any product similar to **13a-15a** but photoreactions yielded only dihydrocyclized **10b-12b** and dehydrogenated cyclised compounds **4b-9b** (**Scheme 2**, analyzed by TLC, mp and mmp). Even the 400 MHz ¹H-NMR spectra of their crude photolysates did not exhibit the presence of such products. These results may be ascribed by considering the isomerization of intermediate 1,4-biradical **16a** to 1,6-biradical **17a** that further captures hydrogen atom from the solvent molecule (isopropanol) and subsequently undergoes keto-enol tautomerization reaction to give **13a-15a** (**Scheme 3**). But, the initially formed 1,4-biradical **16a** in **1b-3b** is reluctant to provide 1,6-biradical, because such an isomerization would have yielded an unstable allenic ether **21**. Thus, in bischromones **1b-3b** major photoproducts are obtained through the cyclization of 1,4-biradical under the polar protic and nonpolar aprotic conditions. Mechanistically, the photoreactions of bischromones **1a-3a** & **1b-3b** can be visualized as having occurred through an initial H-abstraction from the $-\text{OCH}_2-$ group by the photo excited carbonyl chromophore of the pyrone moiety to produce 1,4-biradical **16** that further undergoes cyclization^{21,22,25,27} to yield various dihydrocyclized (**10a-12a** & **10b-12b**) and dehydrocyclized (**4a-9a** & **4b-9b**) products (**Scheme 3**).



Scheme 3. A general mechanism of photo-reorganisation of bischromones

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Table 2. Total photolytic conversion of bischromones

Compound photolysed	1a	1b	2a	2b	3a	3b
Total photolytic conversion (%) in benzene	55	45	52	47	56	44
Total photolytic conversion (%) in (1:1)THF:isopropanol	59	48	50	45	58	46

It is evident from **table 2** that total photolytic conversions furnished by bischromones **1a-3a** have been greater than bischromones **1b-3b**. These results can be explained on the basis of the relative stabilities of the 1,4-biradicals involved in their photoreactions. It is well known that allylic radicals are more stabilised than propargylic radicals.³⁶⁻³⁸ **Table 2** also informs that use of polar and non polar solvent did not have any major influence upon the total photolytic conversions of the bischromones but only have affected the course of photoproduct formation.

In conclusion, it may be concluded that photolysis of 2-butenylbischromones gives better chemical efficiency than their corresponding 2-butynyl derivatives. The solvent polarity shows significant effect upon the nature of photoproducts formation and their distribution. These photoreactions provide a versatile tool for the synthesis of some exotic molecules (bistetracyclic derivatives & vinyl substituted bischromones) without using any specific reagent.

3. Experimental

Melting points reported are uncorrected. IR spectra were recorded on a Perkin Elmer spectrophotometer using KBr pellets and UV spectra on Elico SL-164 spectrophotometer. ¹H NMR spectra were recorded on a 400 MHz Bruker spectrometer using TMS as internal standard. The mass spectra were recorded on Shimadzu QP-5000. All photochemical reactions were conducted under the nitrogen (99.9%) atmosphere. Any trace of oxygen and moisture from the procured nitrogen were removed by passing through alkaline pyrogallol solution and concentrated sulfuric respectively. TLC Plates were coated with silica gel G suspended in MeOH-CHCl₃. Silica gel (100-200 mesh) was used for column chromatography.

Synthesis of 1a-3a and 1b-3b

Compound 1a: A suspension of 6-chloro-3-hydroxy-2-phenyl-4*H*-chromen-4-one²⁵ (2.7 g, 0.01 mol), trans-1,4-dibromo-2-butene (1.1 g, 0.005 mol), freshly ignited K₂CO₃ (1.0 g) and tetrabutylammonium iodide (1.0 g) in dry acetone (25 ml) was refluxed for 1h with stirring. A subsequent filtration of the reaction mixture followed by distillation of the solvent yielded a light yellow solid that was percolated through a column of silica gel (60-120 mesh) using petroleum ether-benzene (1:1) as eluent and further crystallized from EtOH to afford **1a**.

1a: Yield (2.1 g, 70%), white solid, mp. 130-131 °C; UV (THF) λ_{max} 340, 324 nm; IR (KBr) ν_{max} cm⁻¹ 1635 (C=O); ¹H-NMR (CDCl₃, 400 MHz) δ 8.18 (2H, d, J_m=2.5 Hz, H-5), 7.90 (4H, m, H-2', H-6'), 7.65 (2H, dd, J_{m,o}=2.4, 8.8 Hz, H-7), 7.45 (2H, d, J_o=8.8 Hz, H-8), 7.25 (6H, m, H-3', H-4', H-5'),

5.81 (2H, quasi quintet, $J_{vic}=6.8$ Hz, $OCH_2CH=CHCH_2O$), 4.53 (4H, d, $J_{vic}=6.9$ Hz, $OCH_2CH=CHCH_2O$); m/z 597 (M^+ , 100.0), 326 (23.4), 272 (12.9), 271 (90.0), 243 (35.0), 215 (54.7), 154 (32.0), 118 (12.2); Anal. Calcd. for $C_{34}H_{22}O_6Cl_2$: C, 68.35; H 3.71. Found: C, 68.40; H, 3.64%.

Compound 2a: Prepared using the procedure similar to **1a**, by taking 6-chloro-3-hydroxy-2-(4-methylphenyl)-4H-chromen-4-one²⁵ (2.9 g, 0.01 mol) and trans-1,4-dibromo-2-butene (1.1 g, 0.005 mol).

2a: Yield (2g, 65%), white solid, mp. 135-136 °C; UV (THF) λ_{max} 330, 326 nm; IR (KBr) ν_{max} cm^{-1} 1634 (C=O); ¹H-NMR ($CDCl_3$, 400 MHz) δ 8.17 (2H, d, $J_m=2.6$ Hz, H-5), 7.91 (4H, m, H-2', H-6'), 7.60 (2H, dd, $J_{m,o}=2.6, 8.9$ Hz, H-7), 7.48 (2H, d, $J_o=8.9$ Hz, H-8), 7.24 (4H, d, $J_o=8.1$ Hz, H-3', H5'), 5.81 (2H, quasi quintet, $J_{vic}=6.9$ Hz, $OCH_2CH=CHCH_2O$), 4.52 (4H, d, $J_{vic}=6.7$ Hz, $OCH_2CH=CHCH_2O$), 2.42 (6H, s, C_4-CH_3); m/z 625 (M^+ , 100.0), 340 (75.5), 286 (43.3), 285 (62.2), 257 (48.8), 229 (16.1), 154 (83.7), 132 (21.1); Anal. Calcd. for $C_{36}H_{26}O_6Cl_2$: C, 69.13; H 4.19. Found: C, 69.19; H, 4.11%.

Compound 3a: Prepared using the procedure similar to **1a**, by taking 6-chloro-3-hydroxy-2-(4-methoxyphenyl)-4H-chromen-4-one²⁵ (3.0 g, 0.01 mol) and trans-1,4-dibromo-2-butene (1.1 g, 0.005 mol).

3a: Yield (2g, 62%), white solid, mp. 139-140 °C; UV (THF) λ_{max} 346, 333 nm; IR (KBr) ν_{max} cm^{-1} 1637 (C=O); ¹H-NMR ($CDCl_3$, 400 MHz) δ 8.19 (2H, d, $J_m=2.5$ Hz, H-5), 7.91 (4H, m, H-2', H-6'), 7.60 (2H, dd, $J_{m,o}=2.5, 8.9$ Hz, H-7), 7.47 (2H, d, $J_o=8.9$ Hz, H-8), 7.26 (4H, d, $J_o=8.7$ Hz, H-3', H-5'), 5.83 (2H, quasi quintet, $J_{vic}=7.0$ Hz, $OCH_2CH=CHCH_2O$), 4.56 (4H, d, $J_{vic}=6.9$ Hz, $OCH_2CH=CHCH_2O$), 3.84 (6H, s, C_4-OCH_3); m/z 657 (M^+ , 100.0), 356 (33.1), 302 (75.8), 301 (19.6), 273 (90.4), 245 (60.0), 154 (61.8), 148 (27.4); Anal. Calcd. for $C_{36}H_{26}O_8Cl_2$: C, 65.76; H 3.99. Found: C, 65.89; H, 4.05%.

Compound 1b: Prepared using the procedure similar to **1a**, by taking 6-chloro-3-hydroxy-2-phenyl-4H-chromen-4-one²⁵ (2.7 g, 0.01 mol) and 1,4-dichloro-2-butyne (0.7 g, 0.005 mol).

1b: Yield (1.9g, 65%), white solid, mp. 128-130 °C; UV (THF) λ_{max} 347, 331 nm; IR (KBr) ν_{max} cm^{-1} 1635 (C=O); ¹H-NMR ($CDCl_3$, 400 MHz) δ 8.10 (2H, d, $J_m=2.5$ Hz, H-5), 7.74 (4H, m, H-2', H-6'), 7.52 (2H, dd, $J_{m,o}=2.6, 8.8$ Hz, H-7), 7.40 (2H, d, $J_o=8.9$ Hz, H-8), 7.11 (6H, m, H-3', H-4', H-5'), 4.92 (4H, s, C_3-OCH_2); m/z 595 (M^+ , 100.0), 324 (16.3), 272 (33.9), 271 (49.0), 243 (55.7), 215 (72.2), 154 (62.2), 118 (53.2); Anal. Calcd. for $C_{34}H_{20}O_6Cl_2$: C, 68.58; H 3.39. Found: C, 68.64; H, 3.33%.

Compound 2b: Prepared using the procedure similar to **1a**, by taking 6-chloro-3-hydroxy-2-(4-methylphenyl)-4H-chromen-4-one²⁵ (2.9 g, 0.01 mol) and 1,4-dichloro-2-butyne (0.7 g, 0.005 mol).

2b: Yield (1.9g, 62%), white solid, mp. 139-141 °C; UV (THF) λ_{max} 341, 321 nm; IR (KBr) ν_{max} cm^{-1} 1638 (C=O); ¹H-NMR ($CDCl_3$, 400 MHz) δ 8.11 (2H, d, $J_m=2.7$ Hz, H-5), 7.67 (4H, m, H-2', H-6'), 7.46 (2H, dd, $J_{m,o}=2.5, 8.8$ Hz, H-7), 7.41 (2H, d, $J_o=8.9$ Hz, H-8), 7.10 (4H, d, $J_o=8.2$ Hz, H-3', H-5'), 4.91 (4H, s, C_3-OCH_2), 2.39 (6H, s, C_4-CH_3); m/z 623 (M^+ , 100.0), 338 (12.3), 286 (79.0), 285 (45.4), 257 (73.3), 229 (32.0), 154 (52.8), 132 (43.6); Anal. Calcd. for $C_{36}H_{24}O_6Cl_2$: C, 69.35; H 3.88. Found: C, 69.39; H, 3.94%.

Compound 3b: Prepared using the procedure similar to **1a**, by taking 6-chloro-3-hydroxy-2-(4-methylphenyl)-4H-chromen-4-one²⁵ (3.0 g, 0.01 mol) and 1,4-dichloro-2-butyne (0.7 g, 0.005 mol).

3b: Yield (1.95g, 60%), white solid, mp. 142-144 °C; UV (THF) λ_{max} 342, 326 nm; IR (KBr) ν_{max} cm^{-1} 1640 (C=O); ¹H NMR ($CDCl_3$, 400 MHz) δ 8.09 (2H, d, $J_m=2.7$ Hz, H-5), 7.75 (4H, m, H-2', H-6'), 7.55 (2H, dd, $J_{m,o}=2.6, 9.0$ Hz, H-7), 7.39 (2H, d, $J_o=8.9$ Hz, H-8), 7.10 (4H, d, $J_o=8.5$ Hz, H-3', H-5'),

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4.94 (4H, s, C₃-OCH₂), 3.80 (6H, s, C₄-OCH₃); m/z 655 (M⁺, 100.0), 354 (71.1), 302 (52.2), 301 (17.1), 273 (39.1), 245 (42.4), 154 (81.1), 148 (30.0); Anal. Calcd. for C₃₆H₂₄O₈Cl₂: C, 65.96; H 3.69. Found: C, 66.05; H, 3.76%.

Photoirradiation of 1a-3a and 1b-3b

Photoirradiation of 1a: A deoxygenated solution of **1a** (100 mg, 0.00017 mol) in dry benzene (100 ml) was photolysed with light from a 125 W mercury arc lamp in pyrex reactor under pure N₂ atmosphere for 50 min. The progress of reaction was monitored by tlc. The photolysate on chromatographic work up over a column of silica gel (100-200 mesh), packed in petroleum ether-benzene (2:1) and eluted with benzene-EtOAc (3:1), furnished starting compound **1a** (35%, co-tlc & mmp) and three new compounds **4a**, **7a** and **10a**.

4a: Yield: (25mg, 25%), brown solid, mp. 160-161 °C; UV (THF) λ_{max} 315, 306 nm; IR (KBr) ν_{max} cm⁻¹ 1644 (C=O), 1635 (C=O); ¹H NMR (CDCl₃, 400 MHz) δ 8.27 (1H, d, J_m=2.6 Hz, H-8), 8.21 (1H, d, J_m=2.6 Hz, H-5'), 8.07 (2H, m, H-2'', H-6''), 7.86 (1H, dd, J=2.5, 8.0 Hz, H-1), 7.61 (1H, dd, J_{m,o}=2.6, 8.9 Hz, H-10), 7.60 (1H, dd, J_{m,o}=2.6, 8.9 Hz, H-7'), 7.49 (7H, m, H-2, H-3, H-11, H-8'', H-3'', H-4'', H-5''), 7.16 (1H, dd, J=2.4, 6.0 Hz, H-4), 5.92 (1H, ddt, J_{allyl,vic,trans}=1.1, 7.2, 16.1 Hz, CH=CHCH₂), 5.82 (1H, dt, J_{vic,trans}=6.8, 16.2 Hz, CH=CHCH₂O), 5.72 (1H, dd, J_{allyl,vic}=1.2, 6.8 Hz, H-5), 4.56 (2H, dd, J_{allyl,vic}=1.1, 6.5 Hz, CH=CHCH₂O), m/z 595 (M⁺, 100.0), 324 (50.0), 283 (21.4), 272 (62.8), 271 (14.4), 243 (56.4), 215 (80.4), 154 (21.2), 118 (41.1); Anal. Calcd. for C₃₄H₂₀O₆Cl₂: C, 68.58; H 3.39. Found: C, 68.63; H, 3.45%.

7a: Yield: (20mg, 20%), pale yellow solid, mp. 170-172 °C; UV (THF) λ_{max} 352, 316, 247 nm; IR (KBr) ν_{max} cm⁻¹ 1643 (C=O); ¹H NMR (CDCl₃, 400 MHz) δ 8.26 (2H, d, J_m=2.4 Hz, H-8), 7.84 (2H, dd, J_{m,o}=2.1, 9.6 Hz, H-1), 7.60 (2H, dd, J_{m,o}=2.4, 9.0 Hz, H-10), 7.52 (2H, d, J_o=9.0 Hz, H-11), 7.44 (4H, m, H-2, H-3), 7.17 (2H, dd, J=2.2, 6.0 Hz, H-4), 5.94 (2H, quasi d, J_{vic}=6.7 Hz, CH=CH), 5.74 (2H, d, J_{vic}=6.8 Hz, H-5), m/z 593 (M⁺, 85.0), 309 (19.8), 283 (100.0), 154 (38.5), 129 (34.4); Anal. Calcd. for C₃₄H₁₈O₆Cl₂: C, 68.82; H 3.06. Found: C, 68.89; H, 3.13%.

10a: Yield: (10mg, 10%), brown solid, mp. 126-128 °C; UV (THF) λ_{max} 317, 246 nm; IR (KBr) ν_{max} cm⁻¹: 1659 (C=O), 1633 (C=O); ¹H NMR (CDCl₃, 400 MHz) δ 8.23 (1H, d, J_m=2.6 Hz, H-8), 8.20 (1H, d, J_m=2.5 Hz, H-5'), 8.10 (2H, dd, J_{m,o}=2.2, 7.9 Hz, H-2'', 6''), 7.64 (2H, dd, J_{m,o}=2.4, 8.7 Hz, H-10, H-7'), 7.50 (3H, m, H-3'', H-4'', H-5''), 7.38 (2H, d, J_o=8.8 Hz, H-11, H-8'), 6.65 (1H, d, J_{1,2a}=2.0 Hz, H-1), 5.98 (1H, dd, J_{3,2a}=2.0 Hz, J_{3,4}=11.8 Hz, H-3), 5.90 (1H, ddt, J_{allyl,vic,trans}=1.1, 6.8, 16.0 Hz, CH=CHCH₂O), 5.81 (1H, dd, J_{vic,trans}=6.5, 15.9 Hz, CH=CHCH₂), 5.75 (1H, dd, J_{4,3}=11.6 Hz, J_{4,4a}=3.2 Hz, H-4), 4.45 (2H, dd, J_{allyl,vic}=1.2, 7.0 Hz, CH=CHCH₂O), 3.91 (1H, dd, J_{vic}=6.5 Hz, J_{5,4a}=11.1 Hz, H-5), 3.32 (1H, m, H-4a), 2.93 (brs, 2H, H-2a), m/z 597 (M⁺, 82.0), 326 (100.0), 285 (45.5), 272 (24.4), 215 (76.6), 154 (62.2), 118 (19.0); Anal. Calcd. for C₃₄H₂₂O₆Cl₂: C, 68.35; H 3.71. Found: C, 68.24; H, 3.67%.

Photoirradiation of 1a in isopropanol and THF (1:1): A deoxygenated solution of **1a** (100 mg, 0.00016 mol) in solvent mixture of isopropanol and THF (1:1, 100 ml) on photolysis for 1h furnished **4a** (8%), **10a** (5%) and **13a** (46%).

13a: Yield (46mg, 46%), white solid, mp. 136-137 °C; UV (THF) λ_{max} 341, 331 nm; IR (KBr) ν_{max} cm⁻¹ 1634 (C=O); ¹H NMR (400 MHz, CDCl₃) δ 8.21 (2H, d, J_m=2.5 Hz, H-5), δ 8.18 (1H, d, J_m=2.5 Hz, H-5'), 7.94 (2H, m, H-2'', H-6''), 7.91 (2H, m, H-2''', H-6'''), 7.65 (1H, dd, J_{m,o}=2.4, 8.9 Hz, H-7), 7.62 (1H, dd, J_{m,o}=2.5, 8.9 Hz, H-7'), 7.41 (1H, d, J=9.0 Hz, H-8), 7.38 (1H, d, J=8.8 Hz, H-8'), 7.23 (3H, d, J=8.3 Hz, H-3'', H-4'', H-5''), 7.21 (3H, d, J=8.3 Hz, H-3''', H-4''', H-5'''), 6.30 (1H, t{d}, J_{4'''',2'''}=1.3 Hz, J_{4'''',3'''}=12.8 Hz, H-4'''), 5.12 (1H, t{d}, J_{3'''',2'''}=7.2 Hz, J_{3'''',4'''}=12.9 Hz, H-3'''), 4.40 (2H, t, J_{vic}=6.8 Hz, H-1'''); m/z 597 (M⁺, 100.0), 326 (29.5), 272 (66.1), 271

(40.0), 243 (59.5), 215 (36.2), 154 (28.8), 118 (33.3); Anal. Calcd. for $C_{34}H_{22}O_6Cl_2$: C, 68.35; H 3.71. Found: C, 68.47; H, 3.67%.

Photoirradiation of 2a: A deoxygenated solution of **2a** (100 mg, 0.00016 mol) in dry benzene (100 ml) on photolysis for 1h yielded **5a**, **8a** and **11a**.

5a: Yield: (22mg, 22%), brown solid, mp. 164-165 °C; UV (THF) λ_{max} 320, 303 nm; IR (KBr) ν_{max} cm^{-1} 1641 (C=O); 1630 (C=O); 1H -NMR ($CDCl_3$, 400 MHz) δ 8.16 (1H, d, $J_m=2.6$ Hz, H-8), 8.03 (1H, d, $J_m=2.4$ Hz, H-5'), 7.74 (2H, m, H-2'', H-6''), 7.63 (1H, dd, $J_{m,o}=2.4$, 8.7 Hz, H-10), 7.56 (1H, dd, $J_{m,o}=2.4$, 8.4 Hz, H-7'), 7.55 (1H, d, $J_o=8.8$ Hz, H-11), 7.45 (1H, d, $J_o=8.9$ Hz, H-8'), 7.42 (1H, m, H-1), 7.22 (3H, m, H-3'', 5'', 2), 6.90 (1H, brs, H-4), 5.90 (1H, t{dd}, $J_{allyl,vic,trans}=1.2$, 7.1, 16.5 Hz, $CH=CHCH_2$), 5.82 (1H, dd, $J_{vic,trans}=6.2$, 16.8 Hz, $CH=CHCH_2O$), 5.75 (1H, dd, $J_{allyl,vic}=1.2$, 6.6 Hz, H-5), 4.57 (2H, dd, $J_{allyl,vic}=1.1$, 6.2 Hz, $CH=CHCH_2O$), 2.41 (3H, s, C_3-CH_3), 2.38 (3H, s, $C_4''-CH_3$); m/z 623 (M^+ , 95.0), 338 (52.4), 297 (100.0), 286 (20.9), 285 (79.6), 257 (45.3), 154 (12.3), 132 (38.8); Anal. Calcd. for $C_{36}H_{24}O_6Cl_2$: C, 69.35; H 3.88. Found: C, 69.43; H, 3.95%.

8a: Yield: (18mg, 18%), pale yellow solid, mp. 184-185 °C; UV (THF) λ_{max} 318, 309 nm; IR (KBr) ν_{max} cm^{-1} 1643 (C=O); 1H -NMR ($CDCl_3$, 400 MHz) δ 8.18 (2H, d, $J_m=2.4$ Hz, H-8), 7.60 (2H, dd, $J_{m,o}=2.4$, 8.6 Hz, H-10), 7.54 (2H, d, $J_o=8.6$ Hz, H-11), 7.41 (2H, m, H-1), 7.21 (2H, m, H-2), 6.91 (2H, brs, H-4), 5.91 (2H, d, $J_{vic}=6.2$ Hz, $CH=CH$), 5.72 (2H, d, $J_{vic}=6.8$ Hz, H-5), 2.42 (6H, s, C_3-CH_3); m/z 621 (M^+ , 90.0), 323 (33.5), 297 (100.0), 154 (83.3), 143 (30.0); Anal. Calcd. for $C_{36}H_{22}O_6Cl_2$: C, 69.52; H 3.57. Found: C, 69.44; H, 3.63%.

11a: Yield: (12mg, 12%), brown solid, mp. 131-133 °C; UV (THF) λ_{max} 315, 246 nm; IR (KBr) ν_{max} cm^{-1} 1655 (C=O), 1636 (C=O); 1H NMR ($CDCl_3$, 400 MHz) δ 8.21 (1H, d, $J_m=2.4$ Hz, H-8), 8.24 (1H, d, $J_m=2.6$ Hz, H-5'), 8.10 (2H, dd, $J_{m,o}=2.1$, 8.6 Hz, H-2'', 6''), 7.65 (2H, dd, $J_{m,o}=2.6$, 9.1 Hz, H-10, H-7'), 7.50 (2H, m, H-3'', H-5''), 7.36 (2H, d, $J_o=8.8$ Hz, H-11, 8'), 6.60 (1H, d, $J_{1,2a}=2.0$ Hz, H-1), 5.91 (1H, t{dd}, $J_{allyl,vic,trans}=1.3$, 6.6, 16.5 Hz, $CH=CHCH_2O$), 5.81 (1H, dd, $J_{vic,trans}=6.3$, 16.4 Hz, $CH=CHCH_2$), 5.71 (1H, dd, $J_{4,3}=11.8$ Hz, $J_{4,4a}=3.0$ Hz, H-4), 4.48 (2H, dd, $J_{allyl,vic}=1.2$, 6.8 Hz, $CH=CHCH_2O$), 3.94 (1H, dd, $J_{vic}=6.1$ Hz, $J_{5,4a}=11.3$ Hz, H-5), 3.32 (1H, m, H-4a), 2.95 (2H, brs, H-2a), 2.39 (3H, s, C_3-CH_3), 2.35 (3H, s, $C_4''-CH_3$), m/z 625 (M^+ , 80.0), 340 (45.5), 299 (31.4), 286 (53.3), 229 (100.0), 154 (24.4), 132 (67.7); Anal. Calcd. for $C_{36}H_{26}O_6Cl_2$: C, 69.13; H 4.19. Found: C, 69.18; H, 4.28%.

Photoirradiation of 2a in isopropanol and THF (1:1): A deoxygenated solution of **2a** (100 mg, 0.00016 mol) in solvent mixture of isopropanol and THF (1:1, 100 ml) on photolysis for 1h provided **5a** (5%), **11a** (5%) and **14a** (40%).

14a: Yield (40mg, 40%), white solid, mp. 139-140 °C; UV (THF) λ_{max} 342, 327 nm; IR (KBr) ν_{max} cm^{-1} 1637 (C=O); 1H -NMR ($CDCl_3$, 400 MHz) δ 8.20 (1H, d, $J_m=2.4$ Hz, H-5), δ 8.15 (1H, d, $J_m=2.6$ Hz, H-5'), 7.92 (2H, m, H-2'', H-6''), 7.90 (2H, m, H-2''', H-6'''), 7.65 (1H, dd, $J_{m,o}=2.4$, 8.9 Hz, H-7), 7.61 (1H, dd, $J_{m,o}=2.4$, 8.9 Hz, H-7'), 7.41 (1H, d, $J=9.0$ Hz, H-8), 7.36 (1H, d, $J=8.7$ Hz, H-8'), 7.24 (2H, d, $J=8.3$ Hz, H-3'', 5''), 7.20 (2H, d, $J=8.5$ Hz, H-3''', 5'''), 6.31 (1H, dt, $J_{4''',2'''}=1.4$ Hz, $J_{4''',3'''}=12.9$ Hz, H-4'''), 5.10 (1H, dt, $J_{3''',2'''}=7.4$ Hz, $J_{3''',4'''}=12.7$ Hz, H-3'''), 4.43 (2H, t, $J_{vic}=6.6$ Hz, H-1'''), 2.40 (2H, m, H-2'''), 2.34 (3H, s, $C_4''-CH_3$), 2.30 (3H, s, $C_4'''-CH_3$); m/z 625 (M^+ , 100.0), 340 (39.5), 286 (31.0), 257 (52.5), 229 (87.8), 154 (45.3), 132 (56.6); Anal. Calcd. for $C_{36}H_{26}O_6Cl_2$: C, 69.13; H 4.19. Found: C, 69.21; H, 4.24%.

Photoirradiation of 3a: A deoxygenated solution of **3a** (100 mg, 0.00015 mol) in dry benzene (100 ml) on photolysis for 1h gave **6a**, **9a** and **12a**.

6a: Yield: (20mg, 20%), brown solid, mp. 138-140 °C; UV (THF) λ_{max} THF 319, 311 nm; IR (KBr) ν_{max} cm^{-1} 1649 (C=O), 1631 (C=O); 1H -NMR ($CDCl_3$, 400 MHz) δ 8.17 (1H, d, $J_m=2.6$ Hz, H-8), 8.10 (1H, d, $J_m=2.4$ Hz, H-5'), 7.81 (2H, m, H-2'', H-6''), 7.60 (1H, dd, $J_{m,o}=2.5$, 8.8 Hz, H-10), 7.59 (1H,

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dd, $J_{m,o}=2.5, 9.1$ Hz, H-7'), 7.55 (1H, d, $J_o=8.9$ Hz, H-11), 7.45 (1H, d, $J_o=8.7$ Hz, H-8'), 7.41 (1H, m, H-1), 7.10 (3H, m, H-3'', 5'', 2), 6.92 (1H, br-s, H-4), 5.91 (1H, t{dd}, $J_{allyl,vic,trans}=1.0, 7.0, 16.4$ Hz, CH=CHCH₂), 5.82 (1H, dd, $J_{vic,trans}=6.8, 16.5$ Hz, CH=CHCH₂O), 5.71 (1H, dd, $J_{allyl,vic}=1.2, 6.5$ Hz, H-5) 4.54 (2H, dd, $J_{allyl,vic}=1.2, 6.6$ Hz, CH=CHCH₂O), 3.80 (3H, s, C₃-OCH₃), 3.73 (3H, s, C₄-OCH₃); m/z 655 (M⁺, 88.0), 354 (100.0), 313 (32.1), 302 (16.6), 273 (28.9), 245 (76.6), 154 (48.6), 148 (33.7); Anal. Calcd. for C₃₆H₂₄O₈Cl₂: C, 65.96; H 3.69. Found: C, 66.05; H, 3.62%.

9a: Yield: (25mg, 25%), pale yellow solid, mp. 190-192 °C; UV (THF) λ_{max} THF 322, 302 nm; IR (KBr) ν_{max} cm⁻¹ 1640 (C=O); ¹H-NMR (CDCl₃, 400 MHz) δ 8.17 (2H, d, $J_m=2.5$ Hz, H-8), 7.64 (2H, dd, $J_{m,o}=2.3, 8.9$ Hz, H-10), 7.59 (2H, d, $J_o=8.7$ Hz, H-11), 7.42 (2H, m, H-1), 7.21 (2H, m, H-2), 6.91 (2H, brs, H-4), 5.90 (2H, d, $J_{vic}=6.9$ Hz, CH=CH), 5.72 (2H, d, $J_{vic}=6.5$ Hz, H-5), 3.82 (6H, s, C₃-OCH₃); m/z 653 (M⁺, 100.0), 339 (42.6), 313 (11.5), 154 (75.5), 159 (60.0); Anal. Calcd. for C₃₆H₂₂O₈Cl₂: C, 66.17; H 3.39. Found: C, 66.25; H, 3.43%.

12a: Yield: (11mg, 11%), brown solid, mp. 133-134 °C; UV (THF) λ_{max} 315, 246 nm; IR (KBr) ν_{max} cm⁻¹: 1655 (C=O), 1632 (C=O); ¹H NMR (CDCl₃, 400 MHz) δ 8.24 (1H, d, $J_m=2.5$ Hz, H-8), 8.20 (1H, d, $J_m=2.5$ Hz, H-5'), 8.03 (2H, dd, $J_{m,o}=2.2, 7.9$ Hz, H-2'', H-6''), 7.60 (2H, dd, $J_{m,o}=2.4, 8.9$ Hz, H-10, H-7'), 7.50 (2H, m, H-3'', H-5''), 7.35 (2H, d, $J_o=8.9$ Hz, H-11, H-8'), 6.67 (1H, d, $J_{1,2a}=2.0$ Hz, H-1), 5.92 (1H, t{dd}, $J_{allyl,vic,trans}=1.1, 6.8, 16.5$ Hz, CH=CHCH₂O), 5.82 (1H, dd, $J_{vic,trans}=6.9, 16.4$ Hz, CH=CHCH₂), 5.71 (1H, dd, $J_{4,3}=11.8$ Hz, $J_{4,4a}=3.2$ Hz, H-4), 4.48 (2H, dd, $J_{allyl,vic}=1.1, 6.8$ Hz, CH=CHCH₂O), 3.92 (1H, dd, $J_{vic}=6.4$ Hz, $J_{5,4a}=11.2$ Hz, H-5), 3.79 (3H, s, C₃-OCH₃), 3.75 (3H, s, C₄-OCH₃), 3.31 (1H, m, H-4a), 2.94 (2H, brs, H-2a), m/z 657 (M⁺, 95.0), 356 (56.5), 315 (28.8), 302 (100.0), 245 (39.6), 154 (76.7), 148 (88.8); Anal. Calcd. for C₃₆H₂₆O₈Cl₂: C, 65.76; H 3.99. Found: C, 65.84; H, 4.04%.

Photoirradiation of 3a in isopropanol and THF (1:1): A deoxygenated solution of **3a** (100 mg, 0.00016 mol) in solvent mixture of isopropanol and THF (1:1, 100 ml) on photolysis for 1h furnished **6a** (9%), **12a** (6%) and **15a** (43%).

15a: Yield (43mg, 43%), white solid, mp. 142-143 °C; UV (THF) λ_{max} 341, 328 nm; IR (KBr) ν_{max} cm⁻¹ 1635 (C=O); ¹H-NMR (CDCl₃, 400 MHz) δ 8.23 (1H, d, $J_m=2.4$ Hz, H-5), δ 8.20 (1H, d, $J_m=2.4$ Hz, H-5'), 7.90 (2H, m, H-2'', H-6''), 7.88 (2H, m, H-2''', H-6'''), 7.66 (1H, dd, $J_{m,o}=2.4, 9.0$ Hz, H-7), 7.63 (1H, dd, $J_{m,o}=2.5, 8.8$ Hz, H-7'), 7.41 (1H, d, $J=8.9$ Hz, H-8), 7.34 (1H, d, $J=8.9$ Hz, H-8'), 7.23 (2H, d, $J=8.6$ Hz, H-3'', H-5''), 7.21 (2H, d, $J=8.4$ Hz, H-3''', 5'''), 6.30 (1H, t{d}, $J_{4''', 2''''}=1.5$ Hz, $J_{4''', 3''''}=12.6$ Hz, H-4''''), 5.12 (1H, t{d}, $J_{3''''', 2''''}=7.7$ Hz, $J_{3''''', 4''''}=12.5$ Hz, H-3''''), 4.49 (2H, t, $J_{vic}=6.5$ Hz, H-1''''), 3.84 (3H, s, C₄-OCH₃), 3.81 (3H, s, C₄-OCH₃), 2.40 (2H, m, H-2'''''); m/z 657 (M⁺, 100.0), 356 (44.1), 302 (87.7), 301 (33.3), 273 (67.8), 154 (20.0), 148 (61.0); Anal. Calcd. for C₃₆H₂₆O₈Cl₂: C, 65.76; H 3.99. Found: C, 65.80; H, 4.04%.

Photoirradiation of 1b: A deoxygenated solution of **1b** (100 mg, 0.00017 mol) in dry benzene (100 ml) on photolysis for 1h yielded **4b,7b** and **10b**.

4b: Yield: (23mg, 23%), brown solid, mp. 167-169 °C; UV (THF) λ_{max} 315, 312 nm; IR (KBr) ν_{max} cm⁻¹ 1648 (C=O), 1631 (C=O); ¹H NMR (CDCl₃, 400 MHz) δ 8.22 (1H, d, $J_m=2.4$ Hz, H-8), 8.20 (1H, d, $J_m=2.5$ Hz, H-5'), 8.10 (2H, m, H-2'', H-6''), 7.89 (1H, dd, $J=2.3, 8.0$ Hz, H-1), 7.62 (1H, dd, $J_{m,o}=2.2, 9.0$ Hz, H-10), 7.60 (1H, dd, $J_{m,o}=2.5, 8.5$ Hz, H-7'), 7.39 (7H, m, H-2, H-3, H-11, H-8', H-3'', H-4'', H-5''), 7.20 (1H, dd, $J=2.4, 6.1$ Hz, H-4), 5.71 (1H, s, H-5), 4.91 (2H, s, OCH₂); m/z 593 (M⁺, 100.0), 322 (76.9), 283 (22.3), 272 (88.0), 271 (67.4), 215 (53.2), 154 (39.0), 118 (49.9); Anal. Calcd. for C₃₄H₁₈O₆Cl₂: C, 68.82; H 3.06. Found: C, 68.74; H, 2.94%.

7b: Yield: (16mg, 16%), pale yellow solid, mp. 180-182 °C; UV (THF) λ_{max} 352, 316 nm; IR (KBr) ν_{max} cm⁻¹ 1641 (C=O); ¹H NMR (CDCl₃, 400 MHz) δ 8.23 (2H, d, $J_m=2.5$ Hz, H-8), 7.81 (2H, dd, $J=2.3, 9.1$ Hz, H-1), 7.61 (2H, dd, $J_{m,o}=2.6, 9.0$ Hz, H-10), 7.51 (2H, d, $J_o=9.0$ Hz, H-11), 7.41 (4H, m, H-2, H-3), 7.15 (2H, dd, $J=2.2, 6.2$ Hz, H-4), 5.75 (2H, s, H-5), m/z 591 (M⁺, 100.0), 309 (55.3),

283 (17.5), 154 (89.5), 129 (62.2); Anal. Calcd. for $C_{34}H_{16}O_6Cl_2$: C, 69.05; H 2.73. Found: C, 69.16; H, 2.80%.

10b: Yield: (6mg, 6%), brown solid, mp. 135-137 °C; UV (THF) λ_{max} 319, 247 nm; IR (KBr) ν_{max} cm^{-1} 1657 (C=O), 1635 (C=O); 1H NMR ($CDCl_3$, 400 MHz) δ 8.27 (1H, d, $J_m=2.5$ Hz, H-8), 8.21 (1H, d, $J_m=2.5$ Hz, H-5'), 8.10 (2H, dd, $J_{m,o}=2.1$, 8.8 Hz, H-2'', H-6''), 7.60 (2H, dd, $J_{m,o}=2.5$, 8.9 Hz, H-10, H-7'), 7.51 (3H, m, H-3'', H-4'', H-5''), 7.41 (2H, d, $J_o=8.9$ Hz, H-11, H-8'), 6.71 (1H, d, $J_{1,2a}=2.0$ Hz, H-1), 5.91 (1H, dd, $J_{3,2a}=2.0$ Hz, $J_{3,4}=11.1$ Hz, H-3), 5.71 (1H, dd, $J_{4,3}=11.3$ Hz, $J_{4,4a}=3.0$ Hz, H-4), 4.82 (2H, s, OCH_2), 4.20 (1H, s, H-5), 3.30 (1H, m, H-4a), 2.91 (2H, brs, H-2a); m/z 595 (M^+ , 100.0), 324 (17.7), 285 (61.0), 272 (72.2), 215 (91.2), 154 (28.8), 118 (14.3); Anal. Calcd. for $C_{34}H_{20}O_6Cl_2$: C, 68.58; H 3.39. Found: C, 68.67; H, 3.47%.

Photoirradiation of 1b in isopropanol and THF (1:1): A deoxygenated solution of **1b** (100 mg, 0.00016 mol) in solvent mixture of isopropanol and THF (1:1, 100 ml) on photolysis for 1h provided **4b** (22%), **7b** (15%) and **10b** (11%).

Photoirradiation of 2b: A deoxygenated solution of **2b** (100 mg, 0.00016 mol) in dry benzene (100 ml) on photolysis for 1h gave **5b**, **8b** and **11b**.

5b: Yield: (20mg, 20%), pale yellow solid, mp. 160-162 °C; UV (THF) λ_{max} 318, 310 nm; IR (KBr) ν_{max} cm^{-1} : 1642 (C=O), 1632 (C=O); 1H -NMR ($CDCl_3$, 400 MHz) δ 8.18 (1H, d, $J_m=2.6$ Hz, H-8), 8.00 (1H, d, $J_m=2.5$ Hz, H-5'), 7.83 (2H, m, H-2'', H-6''), 7.60 (1H, dd, $J_{m,o}=2.5$, 8.9 Hz, H-10), 7.54 (1H, dd, $J_{m,o}=2.4$, 9.1 Hz, H-7'), 7.53 (1H, d, $J_o=8.8$ Hz, H-11), 7.43 (1H, d, $J_o=8.9$ Hz, H-8'), 7.40 (1H, m, H-1), 7.21 (3H, m, H-3'', H-5''), H-2), 6.90 (1H, br-s, H-4), 5.74 (1H, s, H-5), 4.95 (1H, s, OCH_2), 2.41 (3H, s, C_3-CH_3), 2.36 (3H, s, C_4-CH_3); m/z 621 (M^+ , 86.0), 336 (60.0), 297 (100.0), 286 (41.5), 285 (58.2), 257 (47.4), 229 (69.5), 154 (35.2), 132 (57.6); Anal. Calcd. for $C_{36}H_{22}O_6Cl_2$: C, 69.58; H 3.57. Found: C, 69.68; H, 3.64%.

8b: Yield: (14mg, 14%), pale yellow solid, mp. 184-186 °C; UV (THF) λ_{max} 320, 306 nm; IR (KBr) ν_{max} cm^{-1} : 1644 (C=O); 1H NMR ($CDCl_3$, 400 MHz) δ 8.11 (2H, d, $J_m=2.6$ Hz, H-8), 7.60 (2H, dd, $J_{m,o}=2.4$, 8.9 Hz, H-10), 7.59 (2H, d, $J_o=8.9$ Hz, H-11), 7.40 (2H, m, H-1), 7.20 (2H, m, H-2), 6.92 (2H, brs, H-4), 5.73 (2H, s, H-5), 2.42 (6H, s, C_3-CH_3); m/z 619 (M^+ , 100.0), 323 (14.6), 297 (27.0), 154 (88.3), 143 (62.7); Anal. Calcd. for $C_{36}H_{20}O_6Cl_2$: C, 69.80; H 3.25. Found: C, 69.88; H, 3.29%.

11b: Yield: (13mg, 13%), brown solid, mp. 130-132 °C; UV (THF) λ_{max} 318, 246 nm; IR (KBr) ν_{max} cm^{-1} 1656 (C=O), 1631 (C=O); 1H NMR ($CDCl_3$, 400 MHz) δ 8.22 (1H, d, $J_m=2.1$ Hz, H-8), 8.18 (1H, d, $J_m=2.5$ Hz, H-5'), 8.11 (2H, dd, $J_{m,o}=2.0$, 8.5 Hz, H-2'', H-6''), 7.63 (2H, dd, $J_{m,o}=2.5$, 8.8 Hz, H-10, H-7'), 7.50 (2H, m, H-3'', H-5''), 7.40 (2H, d, $J_o=8.8$ Hz, H-11, H-8'), 6.68 (1H, d, $J_{1,2a}=2.1$ Hz, H-1), 5.73 (1H, dd, $J_{4,3}=11.6$ Hz, $J_{4,4a}=3.1$ Hz, H-4), 4.85 (2H, s, OCH_2), 4.25 (1H, s, H-5), 3.31 (1H, m, H-4a), 2.90 (2H, brs, H-2a), 2.43 (3H, s, C_3-CH_3), 2.40 (3H, s, C_4-CH_3); m/z 623 (M^+ , 92.0), 338 (100.0), 299 (53.3), 286 (46.4), 229 (22.9), 154 (51.1), 132 (59.6); Anal. Calcd. for $C_{36}H_{24}O_6Cl_2$: C, 69.35; H 3.88. Found: C, 69.43; H, 3.93%.

Photoirradiation of 2b in isopropanol and THF (1:1): A deoxygenated solution of **2b** (100 mg, 0.00016 mol) in solvent mixture of isopropanol and THF (1:1, 100 ml) on photolysis for 1h furnished **5b** (17%), **8b** (19%) and **11b** (9%).

Photoirradiation of 3b: A deoxygenated solution of **3b** (100 mg, 0.00015 mol) in dry benzene (100 ml) on photolysis for 1h yielded **6b**, **9b** and **12b**.

6b: Yield: (19mg, 19%), brown solid, mp. 162-164 °C; UV (THF) λ_{max} 317, 310 nm; IR (KBr) ν_{max} cm^{-1} 1641 (C=O), 1635 (C=O); 1H -NMR ($CDCl_3$, 400 MHz) δ 8.19 (1H, d, $J_m=2.6$ Hz, H-8), 8.05 (1H, d, $J_m=2.4$ Hz, H-5'), 7.87 (2H, m, H-2'', H-6''), 7.65 (1H, dd, $J_{m,o}=2.5$, 8.8 Hz, H-10), 7.60 (1H, dd,

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$J_{m,o}=2.6, 9.0$ Hz, H-7'), 7.57 (1H, d, $J_o=8.9$ Hz, H-11), 7.49 (1H, d, $J_o=8.9$ Hz, H-8'), 7.45 (1H, m, H-1), 7.21 (3H, m, H-3'', H-5'', H-2), 6.93 (1H, brs, H-4), 5.71 (1H, s, H-5), 4.95 (2H, s, OCH₂), 3.82 (3H, s, C₃-OCH₃), 3.77 (3H, s, C₄'-OCH₃); m/z 653 (M⁺, 100.0), 352 (44.2), 313 (73.3), 302 (40.0), 301 (68.3), 273 (56.6), 245 (19.2), 154 (42.2), 148 (14.4); Anal. Calcd. for C₃₆H₂₂O₈Cl₂: C, 66.17; H 3.39. Found: C, 66.29; H, 3.32%.

9b: Yield: (13mg, 13%), pale yellow solid, mp. 194-196 °C; UV (THF) λ_{max} 313, 303 nm; IR (KBr) ν_{max} cm⁻¹ 1644 (C=O); ¹H-NMR (CDCl₃, 400 MHz) δ 8.15 (2H, d, $J_m=2.4$ Hz, H-8), 7.62 (2H, dd, $J_{m,o}=2.5, 8.9$ Hz, H-10), 7.52 (2H, d, $J_o=8.8$ Hz, H-11), 7.45 (2H, m, H-1), 7.20 (2H, m, H-2), 6.92 (2H, brs, H-4), 5.74 (2H, s, H-5), 3.78 (6H, s, C₃-OCH₃); m/z 651 (M⁺, 100.0), 339 (33.2), 313 (56.4), 159 (19.7), 154 (70.0); Anal. Calcd. for C₃₆H₂₀O₈Cl₂: C, 66.37; H 3.09. Found: C, 66.46; H, 3.02%.

12b: Yield: (10mg, 10%), brown solid, mp. 142-143 °C; UV (THF) λ_{max} 325, 266 nm; IR (KBr) ν_{max} cm⁻¹ 1653 (C=O), 1631 (C=O); ¹H NMR (CDCl₃, 400 MHz) δ 8.23 (1H, d, $J_m=2.5$ Hz, H-8), 8.21 (1H, d, $J_m=2.5$ Hz, H-5'), 8.10 (2H, dd, $J_{m,o}=2.1, 7.8$ Hz, H-2'', H-6''), 7.61 (2H, dd, $J_{m,o}=2.5, 8.9$ Hz, H-10, H-7'), 7.51 (2H, m, H-3'', H-5''), 7.38 (2H, d, $J_o=8.9$ Hz, H-11, H-8'), 6.67 (1H, d, $J_{1,2a}=2.0$ Hz, H-1), 5.75 (1H, dd, $J_{4,3}=11.8$ Hz, $J_{4,4a}=3.3$ Hz, H-4), 4.83 (2H, s, OCH₂), 4.22 (1H, s, H-5), 3.78 (3H, s, C₃-OCH₃), 3.70 (3H, s, C₄'-OCH₃), 3.30 (1H, m, H-4a), 2.91 (2H, brs, H-2a), m/z 655 (M⁺, 90.0), 354 (49.6), 315 (71.7), 302 (100.0), 245 (87.0), 154 (43.3), 148 (26.6); Anal. Calcd. for C₃₆H₂₄O₈Cl₂: C, 65.96; H 3.69. Found: C, 65.86; H, 3.74%.

Photoirradiation of 3b in isopropanol and THF (1:1): A deoxygenated solution of **3b** (100 mg, 0.00016 mol) in solvent mixture of isopropanol and THF (1:1, 100 ml) on photolysis for 1h gave **6b** (18%), **9b** (16%) and **12b** (12%).

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