CHAPTER-II

Synthesis of O-containing Heterocyclic Compounds by Photo-irradiation of 3-Propargyloxy-2-(furan-3-yl)-4H-chromen-4-ones

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2.1 Introduction

Heterocyclic compounds have been the subject of the considerable chemical interest in the last decades. Various types of oxygen containing heterocyclic compounds with conjugated double bond structure play a significant role in both natural and artificial systems due to their photochemical and photophysical properties. Chromones\(^1\), which are ubiquitous in nature especially in plants and are responsible for photochemical transformations occurring during photosynthesis, are important class of oxygenated heterocyclic compounds with benzoannelated $\gamma$-pyrone ring (4\(H\)-1-benzopyran-4-one)\(^2\). This ring system is the core fragment of several flavanoids, such as flavones \(^2\) and isoflavones \(^3\).

\[ \text{2.1} \]
\[ \text{2.2} \]
\[ \text{2.3} \]

The structural diversity found in chromones led to their roughly division into different categories: simple chromones and fused chromones (pyrano and furochromones). Peucenin\(^2\) \(\text{2.4}\), eugenin\(^3\) \(\text{2.5}\), eugenitol\(^4\) \(\text{2.6}\) and isoeugenitol\(^5\) \(\text{2.7}\) are the examples of some commonly occurring simple chromones. In these, initially peucenin was identified which was isolated from rhizome of the masterwort, \textit{Peucedanum ostruthium}\(^6\).

\[ \text{2.4} \]
\[ \text{2.5} \]
\[ \text{2.6} \]
\[ \text{2.7} \]

This rigid bicyclic fragment of chromones has been classified as a privileged structure in drug discovery and the compounds encompassing it have a wide variety of pharmacologically activities such as antioxidant\(^7\), anti-HIV\(^8\), anticancer\(^9\).
wound healing\textsuperscript{10}, anti-inflammatory\textsuperscript{11}, anti-estrogens\textsuperscript{12}, antidiabetic\textsuperscript{13}, antiplatelet\textsuperscript{14}, astroprotective\textsuperscript{15} and anti-ulcer\textsuperscript{16}. Aloe-vera, an herb extensively used in pharmaceutical and cosmetic industry contains chromones aloesin \textbf{2.8} and isoaloesin \textbf{2.9} as their major consituents\textsuperscript{17}.

Barbigerone \textbf{2.10}, a naturally occurring pyranoisoflavone isolated from seeds of \textit{Tephrosia barbigeria}, exhibits various pharmacological properties such as antiplasmodic, antioxidant, 1,5-lipoxygenase inhibitory activity\textsuperscript{18-19} and also inhibits proliferation of several cancer lines by inducing apoptosis\textsuperscript{20}.

In addition to medicinal importance, the chromones have also found applications in dye industry. For example, pentahydroxy chromone, quercetin\textsuperscript{21} \textbf{2.11} has been used as a yellow dye for long. Chromones also exhibit very promising linear and non-linear optical properties\textsuperscript{22} \textbf{2.12} for optical interconnect applications (using GaAs laser as light source).
As chromones are bichromophoric substrates that contain double bond as well as C=O group as the chromophoric units which can undergo photo-excitation either in isolation or in conjugation. This makes them the very useful photochemically-active candidates and has led to the generation of some exotic heterocyclic compounds.\textsuperscript{23} Chromones are known to undergo photocycloaddition,\textsuperscript{24,25} photodimerisation,\textsuperscript{26,27} photoisomerisation,\textsuperscript{28,29} photorearangement\textsuperscript{30} and photooxidation-reduction\textsuperscript{31-35} reactions involving both n→π* and π→π* transitions.

Photocycloaddition reactions of chromones with different olefins and related compounds are known to provide products through both [3+2]π and [2+2]π cycloaddition reactions. Hannifin and Cohen\textsuperscript{24} have reported [2+2]π photocycloaddition reactions of chromones. Photolysis of solution of chromone \textsuperscript{2.13} with 1,1-dimethoxyethylene \textsuperscript{2.14} have led to formation of \textsuperscript{2.15}, the latter is secondary photolysis product \textsuperscript{2.16} of Paterno-Buchi reaction obtained by further reaction of \textsuperscript{2.14} on interaction with \textsuperscript{2.15}.

\begin{center}
\includegraphics[width=\textwidth]{diagram.png}
\end{center}

Photolysis of chromone-2-carboxamides \textsuperscript{2.17} with chiral auxiliary centre undergo diastereoselective product formation of C\textsubscript{2}-chiral anti-HH dimer scaffold \textsuperscript{2.18} \textsuperscript{36}.

The Diels-Alder \textsuperscript{2.21(a-c)} adduct of substituted chromones like \textsuperscript{2.19} go through clean and quantitative intramolecular [2+2]π alkene-arene photocyclization\textsuperscript{37} resulting into formation of polycyclic dienes upon irradiation with a broadband UV source with k = 350 ± 50 nm. This is first example of such type of photocyclisation in chromone series.
Synthesis of Xanthenones

The investigation on photochemical reduction of chromones 2.22 by Ohara et al. resulted into formation of products 2.23 and 2.24 by photoreduction of 2,3-double bond and C=O group respectively.

Chromones are prone to undergo photo-oxidation that lead to diverse array of products. Rotenone 2.25, a naturally occurring insecticide is a modified flavonoid that on photooxygenation has been reported to give rotenanone 2.26. This provides an example of a biogenetic type of synthesis.

Furan and its derivatives exhibit interesting photochemistry and have been the oldest and most extensively studied over past decades. The first report on gas-phase photolysis of furan came into sight in 1967. The photochemistry of furan 2.27 and some methyl-substituted derivatives has been demonstrated by Srinivasan. The product formation is always complex and markedly dependent on pressure. At low pressure, only dissociation takes place whereas at high pressure various adducts 2.28-2.30 between furan and primary products are formed.
Hiraoka et al have studied the photochemical isomerization\textsuperscript{42,43} of 2-methylfuran to 3-methylfuran. Mercury sensitized photochemistry of 2-methylfuran 2.31 resulted into 3-methylfuran 2.32 in addition to CO, 3-methylcyclopropene 2.33 and 1,3-butadiene in vapor phase.

The 2-phenyl-3-furylacrylic acid 2.34 was irradiated to obtain several types of photoproducts. In aerobic conditions the most prominent photochemically induced reaction was dehydrocyclization, a potentially useful method for preparation of substituted naphtho[2,1-b]furan-8-carboxylic acid 2.37. However in several instances lactonization of it into 2.36 was also observed\textsuperscript{44}. 

\[ \text{2.31} \xrightarrow{\text{hv, Hg}} \text{2.32} + \text{2.33} \]

\[ \text{2.34} \xrightarrow{\text{hv}} \text{2.35} \]

\[ \text{2.37} \xrightarrow{\text{hv/O}_2, -2\text{H}} \text{2.36} \]
Furyl and furochromones have attracted the attention of chemists due to their wide range of applications. Fumarin 2.38, a derivative of furyl chromone is used as rodenticide. Khellin 2.39 was the first furochromone isolated from *Ammi visnaga* used as a diuretic to relieve renal colic, in treatment of vitiligo, a pigmentation disorder and as a muscle relaxant. A large number of other furochromones khellin 2.40, visnagin 2.41, karanjin 2.42 etc. exist in nature and are of medicinal importance.

![Structures](image)

Solution phase photolysis of karanjin 2.42 shows a phototransformation into a pentacyclic compound by γ-hydrogen abstraction 2.43.

![Reaction](image)

It has been observed that furan analogues of flavones show biological activity, effective on living organisms similar to that of khellin a natural furochromone, which exhibit strong antispasmodic action. Also furan analogues of isofavones showed heart regulatory activity. Observed highest fish toxicity of furyl chromone, 7-methoxy-3-methyl-2-(2-furyl)-chromone as compared to karanjin, a furochromone demonstrates about physiological activity of the furyl chromones.

Huffman *et al.* carried out photochemical rearrangement of 3-aryloyl-2(2-furyl)chromones 2.44 which resulted into isomerised products 1-arylfuro-[3,4-b]-acrolein 2.45.
A number of examples (2.46, 2.50, 2.54, 2.57 & 2.59) on extensive study of photoirradiation of furyl chromones\textsuperscript{54-58} from our laboratory have been reported in recent years showing interesting photochemistry of furyl group. These chromones on irradiation by the pyrex filtered UV-light go through regioselective photocyclisation to produce many novel angular polycyclic photoproducts \textit{via} formation of 1,4-biradical, ring contraction and dealkoxylation.
Synthesis of Xanthenones

Triple bond has played important role in organic synthesis because of its participation in wide variety of reactions. In the past few years, photochemistry of acetylenes received a lot of attention for their biological activity point of view. Due to the prevalence of interesting results of acetylene irradiation, the photochemistry of the molecules containing acetylenic moiety continues to be subject of considerable interest. Also, Agosta and Margaretha have investigated the 1,5-cyclization of alkyl propargyl-1,4-biradicals and have been able to obtain products through the mesomerization of propargyl radical.
The photochemistry of 2.64 was very attractive and intriguing, where the expected hydrogen abstraction yielded triplet alkyl propargyl biradical 2.65. In the event, 2.65 was photochemically transformed into indanone 2.66, indicating that the biradical had efficiently cyclized in a 1,5-fashion to 2.67.62,63

Irradiation of solution of 2.68 in pentane afforded products in 3:1 mixture of diastereomeric 5-ethylidene cyclopentenes 2.69 and 2.70. Propargyl-alkyl biradical generated by decarbonylation of substrate rearranges to 5-ethylidene cyclopentene, which rearranges to 2.69 and 2.70.64.
De Jong developed an elegant synthesis\textsuperscript{65} of (alkylthio)thiophenes 2.73 by the addition of unsaturated carbon ions 2.71 from acetylenic precursors to carbon disulphide.

\[
\text{2.71} \quad \text{S} \quad \text{2.72} \quad \text{S} \quad \text{2.73}
\]

In our laboratory, the photoirradiation of variously substituted chromones and acetophenones (2.74, 2.76, 2.79, 2.82 & 2.87) with acetylenic pendant has been carried out, resulting into interesting outcomes of mechanistic and synthetic importance\textsuperscript{66-70}.
In the recent past, the photochemical transformation of 3-alkoxy/allyloxy-2-(thiophen-3-yl)chromenones produced a diverse array of the thienoxanthenone photoproducts via the Dewar thiophene type intermediates and 1,4-biradicals. But, the phototransformation of 3-proparaglyoxy-2-(thiophen-3-yl)chromenones gave some novel xanthones through C-skeleton reorganisation via the intramolecular Paterno-Buchi and isomerisation.

It is evident from the studies mentioned above that the photochemistry of chromenones and furans has been investigated extensively. But little attention has been emphasized on phototransformations of furyl chromenones having acetylene pendant. Bearing in mind the photochemical behavior of furan and acetylene, we extended our plan to include the chromenones having 3-furyl as the substituent and acetylene pendant at 2- and
3-positions in our ongoing programme on the photochemical behavior of substituted chromenones. The investigation of photochemistry of 2-(furan-3-yl)chromenones having abstractable hydrogen adjacent to acetylene system may be fruitful area of research and may have numerous applications and also may provide a variety of mechanistic manifestations.

**Figure 1:** The 3-propargyloxy chromenones 2.99(a-d) (→) the probable photochemical pathways

Main objectives of our study are:

(i) To investigate the photochemistry of furylchromenones containing the propargyloxy group.

(ii) To see the product distribution and stereochemistry when furyl group is tethered to chromenone through its 3-position instead of 2-position *vis-a-vis* regio-selectivity - the clipping of the radical may take place at two sites i.e. 2- and 4-positions of the furan leading to the various angular polycyclic compounds.

(iii) There can happen some reactions pertaining to furan ring in isolation i.e. transpositions etc.
2.2 Results and Discussion

These substrates chromenones 2.99(a-d) needed for photochemical studies were synthesized by initial condensation of 2-hydroxyacetophenones 2.96(a-d) with furan-3-carbaldehyde in the presence of NaOH in ethanol to yield chalcones 2.97(a-d) which on subsequent cyclization under Algar-Flynn-Oyamada conditions produced 3-hydroxy-2-(furan-3-yl)-4H-chromen-4-ones 2.98(a-d). These 3-hydroxychromenones were then converted into respective propargyl ether 2.99(a-d) by reaction with propargyl bromide in the presence of dry acetone, freshly dried K$_2$CO$_3$ and n-Bu$_4$N$^+$I$^-$ as a phase transfer catalyst (Scheme 1). The structures of these photo-labile substrates 2.99(a-d) were found to be consistent with their spectral parameters (IR, $^1$H/$^13$C NMR, vide experimental).

Scheme 1: Synthesis of 2-(3-furyl)-3-(propargyloxy)-4H-chromen-4-ones 2.99(a-d)

In the electronic absorption spectral studies these chromenones 2.99(a-d) showed $\lambda_{\text{max}}$ in the range of 311-316 nm (Table 1), thus a pyrex filtered UV-light was used for the photoirradiation of methanolic solution of these chromenones.
Table 1: The electronic absorption spectral data (Observed $\lambda_{\text{max}}$) of the chromenones 2.99(a-d)

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Chromenone</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.99a</td>
<td>314.00</td>
</tr>
<tr>
<td>2</td>
<td>2.99b</td>
<td>311.50</td>
</tr>
<tr>
<td>3</td>
<td>2.99c</td>
<td>314.50</td>
</tr>
<tr>
<td>4</td>
<td>2.99d</td>
<td>316.00</td>
</tr>
</tbody>
</table>

The irradiation of methanolic solution of these chromenones 2.99(a-d) with pyrex filtered UV-light using a 125W Hg lamp, under nitrogen atmosphere produced a diverse array of photoproducts 2.100(a-d), 2.101(a,b,c) and 2.102(a,d) (Scheme 2). The structures of all the photoproducts were confirmed by their spectral parameters (IR, $^1$H/$^{13}$C NMR) and mass spectral analysis. In addition, the angular tricyclic photoproduct, the pyranochromenones 2.103(a-d) were also formed which were identified with $^1$H NMR spectral studies (a singlet at $\delta$ 6.52 and a singlet at $\delta$ 4.13 due to –OCH$_2$) of chromatographic fractions of photolysate. These were formed in traces and these could not be isolated inspite of our best efforts.

Scheme 2: Photochemical transformation of chromenones 2.99(a-d)
For more clarity about the product formation and their structures, the characterization of substrates and products has been discussed here.

6-Chloro-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99a:

The chromone 2.99a in the functional group region of IR spectrum had absorption band at 1605 cm\(^{-1}\) due to C=O stretch and at 2106 cm\(^{-1}\) due to C≡C stretch. In its \(^1\)H NMR spectrum, the furyl protons H-2', H-5' and H-4' appeared at \(\delta\) 8.41 (1H, dd, \(J_{2,5'} = 1.2\) Hz, \(J_{2,4'} = 0.6\) Hz), 8.05 (1H, d, \(J_{5,4} = 1.8\) Hz, \(J_{2,4'} = 0.6\) Hz) and 7.05 (1H, d, \(J_{4,5} = 1.8\) Hz) respectively. The benzenoid protons H-5, H-7 and H-8 gave signal at \(\delta\) 8.20 (1H, s), 7.60 (1H, dd, \(J_m = 2.4\) Hz, \(J_o = 9.0\) Hz) and 7.47 (1H, d, \(J_o = 9.0\) Hz). Two propargylenic protons H-1" and H-3" appeared at \(\delta\) 5.10 (2H, d, \(J_{1',3'} = 2.4\) Hz) and 2.45 (1H, d, \(J_{3',1''} = 2.4\) Hz) respectively. A proton decoupled \(^13\)C NMR showed 16 peaks corresponding to 16 carbons (vide experimental).

Photolysis of 6-chloro-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99a:

A deoxygenated solution of compound 2.99a (1.0 mM) in dry methanol was photolysed with a pyrex filtered light from 125 W mercury lamp under nitrogen atmosphere for 50 min. The progress of reaction was monitored by TLC. The solvent was distilled off and a red gummy mass was obtained which was chromatographed over a column of silica gel eluted in increasing proportion of petroleum ether-ethylacetate system to obtain 2.100a, 2.101a and 2.102a.

8-Chloro-5-hydroxy-4-methyl-6H-furo[2,3-c]xanthen-6-one 2.100a:

The shining yellow crystals of xanthenone 2.100a (mp 187-189 °C) exhibited IR absorption at 1651 cm\(^{-1}\) that may be assigned to the C=O of pyrone moiety. The signal due to absorption of C≡C stretch at 2106 cm\(^{-1}\) in 2.99a was not seen in IR spectrum of 2.100a which indicates the involvement of acetylene group in photoproduct formation. The structure of photoproduct 2.100a was further ascertained by \(^1\)H NMR, \(^13\)C NMR and
mass spectral data. The benzenoid protons H-7, H-9 and H-10 resonated at δ 8.21 (1H, d, J = 2.2 Hz), 7.66 (1H, dd, J_m = 2.2 Hz, J_o = 8.0 Hz) and 7.55 (1H, d, J_o = 8.0 Hz) respectively. The –OH proton signal appeared as singlet at δ 12.89, disappeared on D_2O shake. The methyl group showed their signal as a singlet at δ 2.59. The two furyl protons appeared as doublets at δ 7.69 (1H, J = 2.2 Hz, H-2) and at δ 7.15 (1H, J = 2.2Hz, H-1). These assignments in the ^1H NMR spectrum are in consistent to structure of 2.100a.

The carbon skeleton of photoproduct was in conformity with their observed proton decoupled ^13C NMR spectra with 16 peaks (vide experimental). The molecular ion peak for 2.100a in its mass spectrum was seen at m/z 300.8/302.9 (alike to 2.99a), this indicates that the photoproduct 2.100a is obtained from 2.99a through reorganization.

The photoproducts 2.101a (8-Chloro-4-ethynyl-3a,11b-dihydro-5-oxa-furo[2,3-c]xanthen-6-one) and 2.102a 8-Chloro-4-ethynyl-3a,11b-dihydro-5-oxa-furo[2,3-c]xanthen-6-one)

These two photoproducts 2.101a and 2.102a were very close in TLC examination. The comparison of ^1H NMR spectra of reactant 2.99a and the photoproduct 2.101a and 2.102a showed that the peak due to -OCH_2- at δ 5.10 (in 2.99a) was found absent in photoproducts. This indicates the participation of -OCH_2- in product formation. The benzenoid protons (H-7, H-9 and H-10) in 2.101a were found at their usual positions at δ 8.16 (1H, d, J_m = 2.2 Hz), 8.01 (1H, dd, J_m = 2.2 Hz, J_o = 7.6 Hz) and 7.72 (1H, d, J_o = 7.6 Hz). Protons H-3a, H-4 and H-11b showed resonances at δ 5.16 (1H, dd, J_3a,4 = 2.08 Hz, J_3a,11b = 10.0 Hz), 5.00 (1H, dd, J_4,4' = 2.2 Hz, J_4,3a = 2.0 Hz) and 4.22 (1H, dt, J_11b,1 = 2.1 Hz, J_11b,2 = 2.6 Hz, J_11b,3a = 10.0 Hz) respectively. The H-2 and H-1 protons appeared at δ 6.61 (1H, t, J_2,1 = 2.6 Hz) and 5.29 (1H, t, J_1,2 = 2.6 Hz). The acetylene proton gave signal at δ 3.51(1H, d, J_2,4 = 2.2 Hz). The structure was further corroborated by ^13C NMR and mass spectra (vide experimental).

The compound 2.102a was found to be an isomer of 2.101a as detected by comparison of their ^1H NMR spectral data. The three benzenoid protons (H-7, H-9 and H-10) and furyl protons (H-2 and H-1) were found similarly placed as found in 2.101a (vide experimental). The chemical shifts and splitting pattern of H-3a, H-4 and H-11b at δ 5.15 (1H, dd, J_3a,4 = 6.8 Hz, J_3a,11b = 10.0 Hz), 4.97 (1H, dd, J_4,4' = 2.2 Hz) and 4.18 (1H, dt, J_11b,1 = 2.2 Hz, J_11b,2 = 2.6 Hz, J_11b,3a = 10.0 Hz) was same as in 2.101a with the change of coupling constant value of H-3a and H-4 which was found here 6.8 Hz. The furyl protons H-2 and H-1 resonated at δ 6.60 (1H, d, J_2,1 = 2.7 Hz) and 5.27 (1H, d, J_1,2 = 2.7 Hz). The acetylenic proton appeared as doublet at δ 3.49.
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To generalize these photo-reorganizations, the investigations were extended to include other derivatives namely 6-methyl-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99b, 6-chloro-7-methyl-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99c and 3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99d which were prepared by the similar procedure as used for 2.99a preparation.

6-Methyl-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99b:

The white colored propargyl ether 2.99b in functional group region of its IR spectrum exhibited adsorption at 1612 cm\(^{-1}\) due to C=O stretch and at 2101 cm\(^{-1}\) due to C≡C stretch. In \(^1\)H NMR spectrum, the furyl protons H-2' and H-4' and H-5' gave peaks at δ 8.39 (1H, d, \(J_{2',4'} = 1.2\) Hz), 7.41-7.28 (2H, m) respectively. The benzenoid protons H-5, H-7 and H-8 resonated at δ 8.18 (1H, d, \(J_m = 2.4\) Hz), 7.58 (1H, dd, \(J_m = 2.4\) Hz, \(J_o = 9.0\) Hz) and 7.02 (1H, d, \(J_o = 9.0\) Hz) respectively. The propargyl group protons H-1'' and H-3'' resonated at δ 5.09 (2H, d, \(J_{1',3'} = 2.4\) Hz) and 2.44 (1H, t, \(J_{3',1'} = 2.4\) Hz). The methyl protons resonated at δ 2.52 (3H, s, C\(_7\)-CH\(_3\)) as a singlet. A proton decoupled \(^{13}\)C NMR showed 17 peaks corresponding to 17 carbons (vide experimental).

Photolysis of 6-methyl-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99b:

A solution of chromenone derivative 2.99b (1.0 mM) in dry methanol was irradiated with pyrex filtered light from a 125 W Hg vapor lamp under nitrogen atmosphere for 50 min. Which upon chromatographic analysis (TLC) indicated appearance of 3 new spots. The reaction mixture after usual work up and chromatographic separation gave two new products (2.100b and 2.101b). Third product was formed in traces and couldn’t be isolated inspite of best efforts.

5-Hydroxy-4,8-dimethyl-6H-furo[2,3-c]xanthen-6-one 2.100b:

The structure elucidation of shining yellow crystals of the photoproduct 2.100b (mp 202-203 °C) was done from its various spectral parameters. The IR spectra confirmed the presence of C=O in benzopyrone entity (1651 cm\(^{-1}\)). The peak due to absorption for C≡C stretch at 2101 cm\(^{-1}\) present in IR spectrum of 2.99b disappeared in 2.100b showing the involvement of acetylene group in photoproduct formation. In its \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\)), 5 protons appeared in aromatic region. A doublet was seen for H-7 at δ 8.11 (\(J = 1.2\) Hz). Other two benzenoid protons H-9 and H-10 appeared as doublet of doublet at δ 7.57 (\(J_o = 8.4\) Hz, \(J_m = 2.2\) Hz) and a doublet at δ 7.45 (\(J = 8.5\) Hz) respectively. The two furyl protons appeared as doublets at δ 7.60 (\(J = 2.2\) Hz, H-2) and
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at δ 7.05 (J = 2.2 Hz, H-1). The other two sharp singlets integrating for three protons each at δ 2.49 and δ 2.45 may be ascribed to 4-CH₃ and 8-CH₃ groups respectively. The –OH proton resonated as a singlet at δ 12.98. The presence of –OH group was confirmed by D₂O shake. The ¹³C NMR spectrum of photoproduct displayed 17 peaks that further ascertained the intended structure (vide experimental). In mass spectrum, the base peak was at m/z 280.9 (same as that of 2.99b), this indicates the photoproduct 2.100a was formed from 2.99a by some reorganization with no fragmentation.

4-Ethynyl-3a,11b-dihydro-8-methyl-5-oxa-furo[2,3-c]xanthen-6-one 2.101b:
The compound 2.101b was a white crystalline solid and exhibited IR adsorption at 1643 cm⁻¹ which is for C=O of pyrone moiety. The acetylenic group remained intact during photochemical transformation which was ascertained by a peak at 2122 cm⁻¹. The structure of this photoproduct was further confirmed by ¹H NMR, ¹³C NMR and mass spectral parameters. The systematic analysis of spectral data of 2.101b specified the features that prove instrumental in arriving at the structural expression intended. In ¹H NMR of the photoproduct 2.101b, the protons of ring A were found to be similarly placed as in 2.99b. The three benzenoid protons gave signals at δ 8.07 (1H, d, Jₘ = 2.4 Hz, H-7), δ 7.46 (1H, dd, Jₘ = 2.4 Hz, J₀ = 8.7 Hz, H-9) and δ 7.36 (1H, d, J = 8.7 Hz, H-10). The protons H-2 and H-1 were found at δ 6.51 (1H, d, J₂,₁ = 2.4 Hz) and 5.32 (1H, d, J₁,₂ = 2.4 Hz) respectively. The protons H-3a, H-4 and H-11b resonated at δ 5.16 (1H, dd, J₃a,4 = 2.7 Hz, J₃a,11b = 10.2 Hz), 4.86 (1H, J₄,2 = 2.7 Hz) and 4.15 (1H, d, J₁₁b,3a = 10.2 Hz) respectively. The acetylenic proton was seen at δ 2.61 and methyl protons were observed as a singlet at δ 2.46. The ¹³C NMR spectrum of this compound showed 16 peaks which were for 16 C-atoms present in the molecule (vide experimental).

6-Chloro-7-methyl-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99c:
The structure of compound 2.99c rests upon following spectral parameters. The absorbance at 2110 cm⁻¹ and 1612 cm⁻¹ in the IR spectrum of the compound confirmed the presence of C≡C and C=O group respectively. The ¹H NMR spectrum displayed the resonance at δ 8.40 (1H, dd, J₂,₅ = 1.2 Hz, J₂,₄ = 0.6 Hz) and 7.55-7.42 (2H, m) which were assigned to H-2' and H-5' and H-4'. The benzenoid proton H-5 was revealed at δ 8.02 as a singlet, whereas H-8 showed a singlet at δ 7.07. The three protons belonging to propargyl group (H-1" and H-3") exhibited the expected pattern of coupling constants and δ values in aliphatic region at δ 5.27 (2H, d, J₁"₃" = 2.1 Hz, H-1") and δ 2.41 (1H, t, J₃",₁" = 2.1 Hz, H-3") respectively. The three protons of methyl group at position-7 gave a
Singlet at δ 2.46. A proton decoupled $^{13}$C NMR spectrum showed 17 peaks (vide experimental).

**Photolysis of 6-chloro-7-methyl-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99c:**
The deoxygenated methanolic solution of furyl chromenone 2.99c was irradiated with UV-light from 125W Hg vapor lamp in a pyrex glass vessel under nitrogen atmosphere. A TLC examination of the photolysate showed no more consumption after 50 min. The photolysate was reduced under reduced pressure to obtain a reddish brown gummy mass which was chromatographed over column to provide two products 2.101c and 2.102c.

**8-Chloro-5-hydroxy-4,9-dimethyl-6H-furo[2,3-c]xanthen-6-one 2.100c:**
The compound 2.99c (mp 176-178 °C) was yellow crystalline solid and had an absorption at 1659 cm$^{-1}$ (C=O) in its IR spectrum. The peak due to absorption for C≡C stretch at 2110 cm$^{-1}$ present in IR spectrum of 2.99c disappeared in IR spectrum of 2.100c which indicates the association of acetylene group in photoproduct formation. The structure of the compound was elucidated from $^1$H NMR and $^{13}$C NMR spectra. The benzenoid protons showed resonances at δ 8.25 (1H, s, H-7) and δ 7.45 (1H, s, H-10). The two furyl protons showed doublets at δ 7.61 (H-2) and δ 7.03 (H-1) with coupling constant of 2.2 Hz. Two methyl protons appeared as singlet at δ 2.54 and 2.40. The –OH proton appeared as a singlet at δ 12.77. A proton decoupled $^{13}$C NMR spectra showed 17 peaks (vide experimental). The mass spectra (m/z = 314.8/316.9) is also in favor of structure elucidated.

**9-Chloro-4-ethynyl-3a,11b-dihydro-8-methyl-5-oxa-furo[2,3-c]xanthen-6-one 2.101c:**
The compound 2.101c (mp 128-130 °C) was a white crystalline solid and showed a peak at 1643 cm$^{-1}$ due to IR absorption of C=O group of chromenone ring. And a peak at 2129 cm$^{-1}$ pointed that the C≡C remained as such during phototransformation. A detailed analysis of $^1$H NMR spectral data of 2.101c indicated the features that lend support to the proposed structure. The benzenoid protons resonated as singlet for both H-10 and H-7 at δ 8.21 and δ 7.26 respectively. The protons belonging to modified furan moiety in 2.101c were found to be upfield as compared to H-2' and H-5' as in 2.98c pointing toward the loss of aromatic character of furan moiety in 2.101c. The protons H-3a, H-4 and H-11b were found at δ 5.14 (1H, dd, $J_{3a,11b} = 10.1$ Hz, $J_{3a,4} = 2.7$ Hz), 4.85 (1H, d, $J_{4,3a} = 2.7$ Hz) and 4.12(dt, $J_{11b,3a} = 10.1$ Hz, $J_{11b,1} = 2.6$ Hz, $J_{11b,2} = 2.2$ Hz) respectively. The acetylenic proton H-2' appeared as a doublet at δ 2.61 ($J_{2',4} = 2.1$ Hz) whereas the methyl proton
appeared as singlet at $\delta$ 2.48. The $^{13}$C NMR (18 peaks) and mass (m/z = 314.9/316.9) further corroborated the structure.

3-Propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99d:

The structure of the chromenone 2.99d has been established from their IR, $^1$H NMR and $^{13}$C NMR (vide experimental) spectral data. The presence of a strong carbonyl band (1605 cm$^{-1}$) and propargyl band (2105 cm$^{-1}$) in IR spectra was a characteristic feature of this chromenone. In $^1$H NMR spectrum (300 MHz, CDCl$_3$), the absorption at $\delta$ 8.09 (1H, d, $J_\alpha$ = 9.2 Hz), 7.51 (1H, dd, $J_\alpha$ = 9.2 Hz, $J_m$ = 2.4 Hz), 6.95 (1H, dd, $J_\alpha$ = 9.2 Hz) and 6.72 (1H, d, $J_\alpha$ = 9.2 Hz, H-6) were due to H-5, H-7, H-8 and H-6 protons respectively. The furyl protons H-2’, H-5’ and H-4’ were seen at $\delta$ 8.31 (1H, dd, $J_{2',4'}$ = 1.5 Hz, $J_{2',5'}$ = 1.2 Hz), 7.94 (1H, dd, $J_{5',2'}$ = 1.2 Hz, $J_{5',4'}$ = 1.8 Hz) and 7.39 (1H, d, $J_{4',5'}$ = 1.8 Hz) respectively. The peak for –OCH$_2$ group appeared as a doublet at $\delta$ 5.00 and another proton of acetylene group gave signal at $\delta$ 2.35 as a triplet.

Photolysis of 3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99d:

A deoxygenated methanolic solution of chromenone 2.99d (1.0 mM) contained in a pyrex glass vessel was purged with nitrogen for 30 min and then irradiated under nitrogen atmosphere with light from a 125 W Hg vapor lamp for 50 min. A TLC examination of photolysate showed no more consumption of starting compound after 50 min. The removal of solvent under reduced pressure yielded a gummy mass that was chromatographed over a column of silica gel (100-200 mesh). The column was eluted with increasing proportion of ethylacetate in petroleum ether to obtain photoproducts 2.100d and 2.102d.

5-Hydroxy-4-methyl-6H-furo[2,3-c]xanthen-6-one 2.100d:

The xanthenone 2.100d was a crystalline compound (mp 181-183 °C) and had a strong absorption at 1651 cm$^{-1}$ in IR spectrum due to C=O stretch. The nonexistence of peak at 2105 cm$^{-1}$ due to C≡C stretch in the IR spectrum of 2.100d points towards the participation of acetylene group in photoproduct formation. The structure of compound 2.100d has been further confirmed through spectral studies ($^1$H NMR, $^{13}$C NMR and mass). The four benzeniod protons showed resonances at $\delta$ 8.33 (1H, d, $J_\alpha$ = 8.0 Hz, H-7), 7.74 (1H, ddd, $J_\alpha$ = 8.0 Hz, $J_m$ = 1.68 Hz, H-8), 7.60 (1H, d, $J_\alpha$ = 8.0 Hz, H-10) and 7.50 (1H, ddd, $J_\alpha$ = 8.0 Hz, $J_m$ = 2.16 Hz, H-9) respectively. The two furyl protons gave signals at $\delta$ 7.66 (1H, d, $J$ = 2.2 Hz, H-2) and 7.38 (1H, d, $J$ = 2.2 Hz, H-1). The –OH
proton, disappeared on D$_2$O shake, appeared as singlet at 12.94. A proton decoupled $^{13}$C NMR showed 16 peaks matching to 16 carbons (vide experimental) which also authenticate the structure of 2.100d. The mass spectrum exhibited the molecular ion peak at m/z 266.1 (same as observed for 2.99d) representing that only reorganization has occurred in 2.99d.

4-Ethynyl-3a,11b-dihydro-5-oxa-furo[2,3-c]xanthen-6-one 2.102d:

The structure of new tetracyclic product was corroborated as follow: The compound 2.102d in its IR spectrum revealed strong absorption band at 1641 cm$^{-1}$ that may be assigned to benzopyrone moiety. The peak at 2130 cm$^{-1}$ascertained that the acetylenic pendant remained intact during photolysis. The comparison of $^1$H NMR spectra of 2.99d and 2.102d exhibited that the resonance at 5.10 (-OCH$_2$) and 8.31 (H-2') present in former were found missing in the latter thereby representing the association of these protons in photoconversion. The three benzenoid protons H-7, H-9 and H-10 in 2.102d were found to be likewise located at H-5, H-7 and H-8 protons in 2.99d. The protons belonging to furan moiety in H-1 and H-2 were sited at $\delta$ 6.73 and 5.52 upfield in contrast to H-4' and H-5', which indicated the loss of aromatic character of furan moiety. The ring junction protons H-3a, H-4 and H-11b were seen at $\delta$ 5.36, 5.05 and 4.35 respectively. The two protons H-3a and H-11b were seen to have coupling constant $J_{\text{vic}}$ = 10.2 Hz. The $^{13}$C NMR and mass spectral data (vide experimental) further confirmed this structure.

**Stereochemistry of photoproducts 2.101(a,b,c) and 2.102(a,d)**

Photoproduct 2.102a was found to be isomer of 2.101a by comparison of $^1$H NMR spectra of 2.101a and 2.102a as observed earlier in our lab$^{70}$. To elucidate the stereochemical features of these tetracyclic photoproducts, the correlation between dihedral angle ($\Phi$) and coupling constant (J) was invoked. In photoproducts 2.101a, 2.101b, 2.101c and 2.102a, 2.102d the stereochemistry of C/D ring junction is cis, as the trans-ring junction of five-membered ring will place it highly strained as calculated by MM2 energy minimization program$^{70}$ (Figure 1). Now assuming the C/D ring fusion cis, the orientation of H-4 to H-3a can be cis or trans. The J/$\Phi$ relationship and MM2 program was used to confirm the relative stereochemical disposition of H-3a and H-4. The correlation of $\Phi_{3a,4}$ values obtained from two possible MM2 energy minimized 3D configurations I (H-4 cis to H-3a) and II (H-4 trans to H-3a) with $J_{3a,4}$ observed from $^1$H NMR is shown in Table 2. A glance at Table 2 demonstrates the trans-disposition of
H-3a and H-4 protons in compounds 2.101a, 2.102b, 2.102c and cis-disposition in compounds 2.102a and 2.102d which are in accordance with Karplus rule.

![Cis-configuration I](image1)  
![Trans-configuration II](image2)

**Figure1:** Energy minimized MM2 structures of 2.101a and 2.102a

Table 2: Expected coupling constants for the two configurations.

<table>
<thead>
<tr>
<th>Comp</th>
<th>Coupling protons</th>
<th>Configuration I</th>
<th>Configuration II</th>
<th>Observed J(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Phi$ (Hz)</td>
<td>$J'$ (Hz)</td>
<td>E(Kcal/mol)</td>
</tr>
<tr>
<td>2.101a*</td>
<td>H-3a &amp; H-4</td>
<td>-</td>
<td>73.03</td>
<td>3.2</td>
</tr>
<tr>
<td>2.101b</td>
<td>H-3a &amp; H-4</td>
<td>-168</td>
<td>11.5</td>
<td>11.43</td>
</tr>
<tr>
<td>2.101c</td>
<td>H-3a &amp; H-4</td>
<td>-168</td>
<td>11.5</td>
<td>12.04</td>
</tr>
<tr>
<td>2.102a*</td>
<td>H-3a &amp; H-4</td>
<td>-47.4</td>
<td>5.6</td>
<td>11.07</td>
</tr>
<tr>
<td>2.102d</td>
<td>H-3a &amp; H-4</td>
<td>-48.7</td>
<td>5.8</td>
<td>11.16</td>
</tr>
</tbody>
</table>

$J'$: Expected value. *Isomeric compounds with both configurations were isolated.

In these photoconversions, the regioselectivity for ring formation exclusively at 2'-position (furyl moiety) with no ring formation at 4'-position has been observed. The reason for this may be that the clipping at C-4' requires the involvement of the Dewar furan type moiety which is not possible probably due to high energy requirements ($S_o$ energy = 78 kcal mol$^{-1}$)$^{76}$, but this type of ring formation has been observed in case of photoirradiation of the thienylchromenones with the intermediacy of Dewar thiopene ($S_o$ energy = 65 kcal mol$^{-1}$)$^{71}$. The clipping at 2'-position is also supported by the calculations made from 3D-structure (MM2 programme) for the furylchromenones substrates. The $-\text{O}--\text{CH}_2--$ and the 2'-position (the two clipping atoms for ring formation) have been observed in close proximity (Figure 2) with contact averaged at 3.449Å as compared to 5.090 Å for clipping of $-\text{O}--\text{CH}_2--$ and the 4'-position.
Mechanistic considerations

The formation of product 2.100 from chromones 2.99 can be envisioned to occur through the initial photochemical sigmatropic 1,3-H shift in chromone to furnish allenyloxy chromone 2.99A which cyclizes to 2.100A. The support for formation of allenyloxy chromone intermediate 2.99A can be derived from the former interpretation made in conjugated acetylenic carbonyl compounds\textsuperscript{77,78} where the acetylenic compounds have been rearranged to the allenes photochemically. The intermediate 2.100A is converted to 2.100B by sigmatropic 1,5-H shift that subsequently gives 2.100 (through 1,3-H) (Scheme 3).

![Scheme 3: A proposed mechanism for the formation of 2.100](image)

The formation of 2.101 and 2.102 from 2.99 can be visualized to occur through the formation of 1,4-biradical via γ-hydrogen abstraction mechanism\textsuperscript{70} (Scheme 4). The products formed may be rationalized through bond formation between –O-CH- radical
with the 2'-position of the furan ring regioselectively, which is followed by ketonization and H-migration to C-11b (1,5-H migration).

Scheme 4: Mechanism for formation of 2.101 and 2.102

In our earlier work on 3-alkoxy-2-(2'-furyl)chromenones 2.50\textsuperscript{79-82} the secondary product 2.52 with ring contraction were observed and isolated; the reason attributed to such diversity may be the stabilization of radical (2.104) by pyrone moiety at C-11b furnished by photo-irradiation of 2'-furylchromenones, whereas, no such stabilization is offered in radical 2.105 at C-3a for formation of ring contracted secondary products.

It may be concluded that the novel angular tetracyclic furoxanthone derivatives have been synthesized by the photo-reorganisation of 2-(3-furyl)-3-(propargyloxy)-4H-
Synthesis of Xanthenones

chromen-4-ones. This transformation took place by acetylene-allene isomerisation via tandem sigmatropic shift and Norrish Type-II reaction i.e. γ-hydrogen abstraction. In this case, ring closure at C-2' of furan ring of the initially generated –O-CH- radical has been observed regioselectively with no ring closure whatsoever at C-4' position.
2.3 Experimental

Synthesis of 1-(5-chloro-2-hydroxyphenyl)-3-(furan-3-yl)prop-2-en-1-one 2.97a:

To the well-stirred suspension of NaOH (4.0 g, 0.1 mol) in EtOH at 0 °C, added 5-chloro-2-hydroxyacetophenone 2.96a (8.5 g, 0.05 mol) and furan-3-carbaldehyde (5.28 g, 0.055 mol). The reaction mixture, which became deep red in color after 30 min, was stirred further for 4h. Thereafter, it was poured over ice and was neutralized with dil. HCl to obtain acrylophenone that was crystallized from EtOH to give yellow needles 2.97a.

Yield 84%, yellow solid, mp 110-112 °C;

ν_{max} (cm^{-1}): 3415 (OH), 1638 (C=O);

^1^H NMR (300 MHz, δ (ppm), CDCl₃): 12.72 (1H, s, OH), 8.73 (1H, d, Jₘ = 2.7 Hz, H-6'), 8.17 (1H, d, J₃,₂ = 14.7 Hz, H-3), 8.00 (1H, s, H-2''), 7.87 (1H, d, J₂,₃ = 14.7 Hz, H-2), 7.78 (1H, d, J₅',₄' = 2.4 Hz, H-5''), 7.50 (1H, dd, Jₘ = 2.7 Hz, J₀ = 9.0 Hz, H-4'), 7.33 (1H, d, J₀ = 9.0 Hz, H-3'), 6.99 (1H, d, J₄',₅' = 2.4 Hz, H-4'');

^1^C NMR (CDCl₃, δ (ppm)): 192.22 (C=O), 160.24, 146.25, 145.45, 143.97, 136.18, 129.00, 124.52, 122.12, 120.58, 119.55, 117.87, 107.46.

Synthesis of 6-chloro-3-hydroxy-2-(furan-3-yl)-4H-chromen-4-one 2.98a:

To the suspension of chalcone 2.97a (2.48 g, 0.01 mol) in methanol was added 10.0 ml of 20% aq. KOH and cooled to 0 °C. To this dark red well stirred solution H₂O₂ (30%) was added drop-wise till the color changed to yellow and the stirring was continued for 1h. The reaction mixture was neutralized with ice-HCl to give light yellow precipitates. The solid was filtered, dried and crystallized (CHCl₃-MeOH) to give yellow crystals of benzopyrone 2.98a.
Yield 83%, yellow solid, mp 205-208 °C;

ν_{max} (cm^{-1}): 3210 (OH), 1615 (C=O);

^{1}H NMR (300 MHz, δ (ppm), CDCl₃): 8.40 (1H, s, H-2'), 8.14 (1H, d, J_{m} = 2.4 Hz, H-5), 7.89 (1H, dd, J_{m} = 2.4 Hz, J_{o} = 9.0 Hz, H-7), 7.67 (1H, d, J_{5';4'} = 1.8 Hz, H-5'), 7.59 (1H, d, J_{o} = 9.0 Hz, H-8), 7.05 (1H, d, J_{4';5'} = 1.8 Hz, H-4');

^{13}C NMR (CDCl₃, δ (ppm)): 178.27 (C=O), 160.18, 157.21, 144.42, 142.63, 139.17, 135.36, 130.61, 124.01, 123.51, 119.91, 117.73, 108.20.

**Synthesis of 6-chloro-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99a:**

Propargyl bromide (0.131 g, 0.001 mol) was added to a suspension of compound, 2.98a (0.246 g, 0.001 mol), freshly dried K₂CO₃ (0.69 g, 0.005 mol) and tetra-n-butylammonium iodide (0.050 g) in dry acetone. The reaction mixture was refluxed for 4h and the color of reaction mixture turned to white from orange red. Filtration, evaporation of solvent and crystallization of the residue (MeOH) gave 2.99a.

Yield 81%, white solid, mp 150-152 °C;

ν_{max} (cm^{-1}): 2106 (C=C), 1605 (C=O);

^{1}H NMR (300 MHz, δ (ppm), CDCl₃): 8.41 (1H, dd, J_{2';5'} = 1.2 Hz, J_{2';4'} = 0.6 Hz, H-2'), 8.20 (1H, s, H-5), 8.05 (1H, d, J_{5';4'} = 1.8 Hz, H-5'), 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), 7.05 (1H, d, J_{4';5'} = 1.8 Hz, H-4'), 5.10 (2H, d, J_{1';3'} = 2.4 Hz, H-1''), 2.45 (1H, d, J_{3';1'} = 2.4 Hz, H-3'');
Synthesis of Xanthenones

$^{13}$C NMR (CDCl$_3$, δ (ppm)): 172.62 (C=O), 153.23, 152.49, 145.94, 143.54, 137.47, 133.56, 130.82, 128.42, 125.11, 119.53, 117.64, 108.84, 78.50, 76.24, 59.09 (-OCH$_2$).

Photolysis of 6-chloro-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99a:

A deoxygenated methanolic solution (150.0 ml) of the 2.99a (0.0001 mol, 20 mg) was irradiated with light from a 125W Hg vapor lamp in a pyrex reactor under nitrogen atmosphere for 50 min. This protocol was repeated a number of times for irradiation of 900mg of 2.98a and all the photolysates so obtained were pooled together. The removal of the solvent from the photolysate left a gummy solid, which was chromatographed over a column of silica gel. The column was eluted with increasing proportion of ethyl acetate in ethyl acetate-pet ether mixture to yield, the photoproducts 2.100a, 2.101a and 2.102a.

![Diagram of photolysis reaction]

8-Chloro-5-hydroxy-4-methyl-6H-furo[2,3-c]xanthen-6-one 2.100a:

Yield 22%, yellow solid, mp 187-189 °C;

$\nu_{\text{max}}$ (cm$^{-1}$): 1651 (C=O);

$^1$H NMR (400 MHz, δ (ppm), CDCl$_3$): 12.89 (1H, s, OH), 8.21 (1H, d, $J = 2.2$ Hz, H-7), 7.69 (1H, d, $J = 2.2$ Hz, H-2), 7.66 (1H, dd, $J_m = 2.2$ Hz, $J_o = 8.0$ Hz, H-9), 7.55 (1H, d, $J_o = 8.0$ Hz, H-10), 7.15 (1H, d, $J = 2.2$ Hz, H-1), 2.59 (3H, s, 4-CH$_3$);

$^{13}$C NMR (CDCl$_3$, δ (ppm)): 182.30 (C=O), 156.55, 153.24, 144.35, 144.47, 142.49, 136.20, 126.74, 126.40, 119.97, 119.49, 109.69, 105.20, 104.49, 104.06, 21.41 (C$_4$-CH$_3$);

Mass (m/z): 300.8/302.9 (M, M+2).
8-Chloro-4-ethynyl-3a,11b-dihydro-5-oxa-furo[2,3-c]xanthen-6-one 2.101a:
Yield 25%, white solid, mp 142-144 °C;
ν_{max} \text{ (cm}^{-1}\text{): } 1641 \text{ (C=O), 2130 (C≡C)};
^1H \text{ NMR (400 MHz, } \delta \text{ (ppm), CDCl}_3\text{): } 8.16 \text{ (1H, d, } J_m = 2.2 \text{ Hz, H-7}), 8.01 \text{ (1H, dd, } J_m = 2.2 \text{ Hz, } J_o = 7.6 \text{ Hz, H-9}), 7.72 \text{ (1H, d, } J_o = 7.6 \text{ Hz, H-10}), 6.61 \text{ (1H, d, } J_{2,1} = 2.6 \text{ Hz, H-2}), 5.29 \text{ (1H, t, } J_{1,2} = 2.6 \text{ Hz, H-1}), 5.16 \text{ (1H, dd, } J_{3a,4} = 2.0 \text{ Hz, } J_{3a,11b} = 10.0 \text{ Hz, H-3a}), 5.00 \text{ (1H, dd, } J_{4,2'} = 2.2 \text{ Hz, } J_{4,3a} = 2.0 \text{ Hz, H-4}), 4.22 \text{ (1H, dt, } J_{11b,1} = 2.1 \text{ Hz, } J_{11b,2} = 2.6 \text{ Hz, } J_{11b,3a} = 10.0 \text{ Hz, H-11b}), 3.51 \text{ (1H, d, } J_{2',4} = 2.2 \text{ Hz, H-2')};
^{13}C \text{ NMR (CDCl}_3\text{, } \delta \text{ (ppm): } 169.30 \text{ (C=O), 153.33, 148.29, 147.96, 135.08, 133.51, 129.71, 124.29, 120.26, 100.59 (C-1), 81.79 (C-1'), 78.98 (C-3a), 77.52 (C-2'), 66.40 (C-4), 40.64 (C-11b)};
\text{Mass (m/z): } 300.8/302.9 (M, M+2).

8-Chloro-4-ethynyl-3a,11b-dihydro-5-oxa-furo[2,3-c]xanthen-6-one 2.102a:
Yield 29%, white solid, mp 124-126 °C;
ν_{max} \text{ (cm}^{-1}\text{): } 2129 \text{ (C≡C), 1643 (C=O)};
^1H \text{ NMR (400 MHz, } \delta \text{ (ppm), CDCl}_3\text{): } 8.14 \text{ (1H, s, } J_m = 2.2 \text{ Hz, H-7}), 8.00 \text{ (1H, dd, } J_m = 2.2 \text{ Hz, } J_o = 7.6 \text{ Hz, H-9}), 7.71 \text{ (1H, d, } J_o = 7.6 \text{ Hz, H-10}), 6.60 \text{ (1H, d, } J_{2,1} = 2.7 \text{ Hz, H-2}), 5.27 \text{ (1H, d, } J_{1,2} = 2.7 \text{ Hz, H-1}), 5.15 \text{ (1H, dd, } J_{3a,4} = 6.8 \text{ Hz, } J_{3a,11b} = 10.0 \text{ Hz, H-3a}), 4.97 \text{ (1H, dd, } J_{4,2'} = 2.2 \text{ Hz, H-4}), 4.18 \text{ (1H, t, } J_{11b,1} = 2.2 \text{ Hz, } J_{11b,2} = 2.6 \text{ Hz, } J_{11b,3a} = 10.0 \text{ Hz, H-11b}), 3.49 \text{ (1H, d, } J_{2',4} = 2.2 \text{ Hz, H-2')};
^{13}C \text{ NMR (CDCl}_3\text{, } \delta \text{ (ppm): } 169.21 \text{ (C=O), 153.27, 152.26, 148.46, 136.21, 135.28, 133.33, 129.57, 124.11, 120.06, 104.40 (C-1), 81.82 (C-1'), 78.41 (C-3a), 77.32 (C-2'), 65.75 (C-4), 40.02 (C-11b)};
\text{Mass (m/z): } 300.8/302.9 (M, M+2).

Synthesis of 1-(2-hydroxy-5-methylphenyl)-3-(furan-3-yl)prop-2-en-1-one 2.97b:
The acrylophenone was obtained by condensing 2-hydroxy-5-methylacetophenone 2.96b (1.50 g, 0.01 mol) and furan-3-carbeldehyde (1.05 g, 0.011 mol) using the same procedure as described for compound 2.97a.
Synthesis of Xanthenones

Yield 76%, yellow solid, mp 130-132 °C;

$\nu_{\text{max}}$ (cm$^{-1}$): 3340(OH), 1628 (C=O);

$^1$H NMR (300 MHz, δ (ppm), CDCl$_3$): 12.70 (1H, s, OH), 7.86 (1H, d, $J_{3,2} = 15.0$ Hz, H-3), 7.79 (1H, d, $J_m = 2.7$ Hz, H-6'), 7.64 (1H, s, H-2''), 7.50 (1H, d, $J_{5',4'} = 2.4$ Hz, H-5''), 7.40 (1H, dd, $J_m = 2.7$ Hz, $J_o = 9.0$ Hz, H-4'), 7.30 (1H, d, $J_{2,3} = 15.0$ Hz, H-2), 6.95 (1H, d, $J_o = 9.0$ Hz, H-3'), 6.75 (1H, d, $J_{4',5'} = 2.4$ Hz, H-4''), 2.44 (3H, s, CH$_3$);

$^{13}$C NMR (CDCl$_3$, δ (ppm)): 189.91 (C=O), 158.88, 147.24, 146.85, 144.37, 136.08, 131.19, 126.11, 124.52, 120.88, 119.80, 116.47, 108.86, 20.85 (C$_5$-CH$_3$).

Synthesis of 3-hydroxy-6-methyl-2-(furan-3-yl)-4H-chromen-4-one 2.98b:

The hydroxychromone 2.98b was obtained from acrylophenone (1.14 g, 0.005 mol) by Algar-Flynn-Oyamada cyclization as described previously for the compound 2.98a.

Yield 83%, creamish white solid, mp 220-222 °C.

$\nu_{\text{max}}$ (cm$^{-1}$): 3205(OH), 1612 (C=O);

$^1$H NMR (300 MHz, δ (ppm), CDCl$_3$): 8.31 (1H, s, H-2'), 8.03 (1H, d, $J_m = 2.4$ Hz, H-5), 7.73 (1H, d, $J_o = 9.0$ Hz, H-7), 7.58 (1H, d, $J_{5',4'} = 1.8$ Hz, H-5'), 7.49 (1H, t, $J_o = 9.0$ Hz, H-8), 6.95 (1H, d, $J_{4',5'} = 1.8$ Hz, H-4'), 2.41 (3H, s, CH$_3$);

$^{13}$C NMR (CDCl$_3$, δ (ppm)): 178.37 (C=O), 160.15, 157.24, 144.41, 142.53, 139.12, 135.32, 130.57, 124.10, 123.47, 119.87, 117.63, 108.10, 21.34 (C$_6$-CH$_3$).
Synthesis of 6-methyl-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99b:

Propargyl bromide (0.131 g, 0.001 mol) was added to a suspension of compound, 2.98b (0.226 g, 0.001 mol) and freshly dried K₂CO₃ (0.69 g, 0.005 mol) in dry acetone, followed by addition of phase transfer catalyst tetra-n-butylammonium iodide (0.050 g). The reaction mixture was refluxed for 4h and the color of the reaction mixture changed from reddish-orange to white. Filtration, evaporation of solvent and crystallization of the residue (MeOH) gave 2.99b.

Yield 78%, white solid, mp 120-122 °C;

ν<sub>max</sub> (cm⁻¹): 2101 (C=O), 1612 (C=O);

¹H NMR (300 MHz, δ (ppm), CDCl₃): 8.39 (1H, dd, J₂,₄ = 1.8 Hz, J₂,₅ = 1.2 Hz, H-2'), 8.18 (1H, d, J₃ = 2.4 Hz, H-5), 7.58 (1H, dd, J₃ = 2.4 Hz, J₀ = 9.0 Hz, H-7), 7.41-7.28 (2H, m, H-5', H-4'), 7.02 (1H, d, J₀ = 9.0 Hz, H-8), 5.09 (2H, d, J₁',₃' = 2.4 Hz, H-1''), 2.52 (3H, s, C₇-CH₃), 2.44 (1H, t, J₃',₁' = 2.4 Hz, H-3'');

¹³C NMR (CDCl₃, δ (ppm): 173.50 (C=O), 154.21, 152.51, 144.94, 143.50, 138.47, 133.53, 130.39, 128.11, 125.01, 119.94, 117.60, 108.84, 78.40, 76.21, 59.08, 21.84 (C₆-CH₃).

Photolysis of 6-methyl-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99b:

A deoxygenated solution of 2.99b in dry methanol was irradiated in a pyrex glass vessel under nitrogen atmosphere for 50 min with a 125 W Hg vapor lamp. Progress of reaction was monitored by TLC. To produce enough of product for structural analysis, a total of 1000 mg of 2.99b was irradiated in a number of batches (20 mg in 150 ml). The removal of solvent under reduced pressure yielded a gummy mass that was chromatographed over a column of silica gel (100-200 mesh). The column was eluted with increasing proportion of ethylacetate in petroleum ether-ethylacetate as eluting system mixture to yield photoproducts 2.100b and 2.101b.
**Synthesis of Xanthenones**

*5-Hydroxy-4,8-dimethyl-6H-furo[2,3-c]xanthen-6-one 2.100b:*

Yield 22%, shining yellow crystals, mp. 202-203 °C;

\[ \nu_{\text{max}} \ (\text{cm}^{-1}) : 1651 \ (\text{C}=\text{O}); \]

\[ ^1\text{H} \text{ NMR (400 MHz, } \delta \text{ (ppm), CDCl}_3): 12.98 \ (1\text{H, s, OH}), 8.11 \ (1\text{H, d, } J = 1.2 \text{ Hz, H-7}), \]

7.60 (1H, d, \( J = 2.2 \text{ Hz, H-2} \)), 7.57 (1H, dd, \( J_o = 8.4 \text{ Hz, } J_m = 2.2 \text{ Hz, H-9} \)), 7.45 (1H, d, \( J = 8.5 \text{ Hz, H-10} \)), 7.05 (1H, d, \( J = 2.2 \text{ Hz, H-1} \)), 2.49 (3H, s, 4-CH\(_3\)), 2.45 (3H, s, 8-CH\(_3\));

\[ ^13\text{C} \text{ NMR (CDCl}_3, \delta \text{ (ppm)}: 181.88 \ (\text{C}=\text{O}), 159.51, 156.55, 153.95, 148.18, 136.81, \]

135.66, 134.12, 125.74, 120.55, 107.62, 105.44, 105.10, 103.67, 103.21, 28.64 (C\(_8\)-CH\(_3\)), 13.42 (C\(_4\)-CH\(_3\));

Mass (m/z): 280.8 (M\(^+\), 100%).

*4-Ethynyl-3a,11b-dihydro-8-methyl-5-oxa-furo[2,3-c]xanthen-6-one 2.101b:*

Yield 27%, white solid, mp 134-136°C;

\[ \nu_{\text{max}} \ (\text{cm}^{-1}) : 2122 \ (\text{C}=\text{C}), 1643 \ (\text{C}=\text{O}) ; \]

\[ ^1\text{H} \text{ NMR (300 MHz, } \delta \text{ (ppm), CDCl}_3): 8.07 \ (1\text{H, d, } J_m = 2.4 \text{ Hz, H-7}), 7.46 \ (1\text{H, dd, } J_m = 2.4 \text{ Hz, } J_o = 8.7 \text{ Hz, H-9}), 7.36 \ (1\text{H, d, } J = 8.7 \text{ Hz, H-10} \)), 6.51 \ (1\text{H, d, } J_{2,1} = 2.4 \text{ Hz, H-2}), 5.32 \ (1\text{H, d, } J_{1,2} = 2.4 \text{ Hz, H-1} \), 5.16 \ (1\text{H, dd, } J_{3a,4} = 2.7 \text{ Hz, } J_{3a,11b} = 10.2 \text{ Hz, H-3a}), 4.86 \ (1\text{H, } J_{4,2}= 2.7 \text{ Hz, H-4}), 4.15 \ (1\text{H, d, } J_{11b,3a}=10.2 \text{ Hz, H-11b}), 2.61 \ (1\text{H, d, } J = 1.8 \text{ Hz, H-2}), 2.46 \ (1\text{H, s, CH}_3) ; \]

\[ ^13\text{C} \text{ NMR (CDCl}_3, \delta \text{ (ppm): 170.12 } (\text{C}=\text{O}), 153.20, 152.70, 148.33, 134.71, 128.35, \]

125.55, 123.57, 117.51, 100.74 (C-1), 81.22 (C-1'), 76.71 (C-3a), 76.09 (C-2'), 66.67 (C-4), 41.09 (C-11b), 20.85 (C\(_8\)-CH\(_3\));

Mass (m/z): 280.9 (M\(^+\), 100%).
Synthesis of 1-(5-chloro-2-hydroxy-4-methylphenyl)-3-(furan-3-yl)prop-2-en-1-one 2.97c:

The acrylophenone 2.97c was obtained by condensing 5-chloro-2-hydroxy-4-methylacetophenone 2.96c (1.84 g, 0.01 mol) and furan-3-carboxaldehyde (1.05 g, 0.011 mol) followed by same procedure as described previously for the compound 2.97a.

Yield 73%, yellow solid, mp 111-113 °C;

ν_max (cm⁻¹): 3418 (OH), 1636 (C=O);

¹H NMR (300 MHz, δ (ppm), CDCl₃): 12.72 (1H, s, OH), 7.88 (1H, s, H-2"), 7.81 (1H, d, J₇',₄'= 3.0 Hz, H-5"), 7.49 (1H, d, J₃,₂' = 15.0 Hz, H-3), 7.32 (1H, d, J₂,₃ = 15.0 Hz, H-2), 7.24 (1H, s, H-6'), 6.91 (1H, d, J₄',₅' = 3.0 Hz, H-4"), 6.77 (1H, s, H-3'), 2.50 (3H, s, CH₃);

¹³C NMR (CDCl₃, δ (ppm): 192.21 (C=O), 161.99, 146.24, 145.45, 144.77, 135.98, 129.09, 124.12, 123.12, 120.58, 119.50, 118.87, 107.46, 20.77 (C₄-CH₃).

Synthesis of 6-chloro-3-hydroxy-7-methyl-2-(furan-3-yl)-4H-chromen-4-one 2.98c:

The hydroxychromone 2.98c was obtained from acrylophenone (1.31 g, 0.005 mol) by Algar-Flynn-Oymada cyclization as described for the compound 2.98a.

Yield 84%, yellowish white solid, mp 224-226 °C;

ν_max (cm⁻¹): 3248 (OH), 1605 (C=O);

¹H NMR (300 MHz, δ (ppm), CDCl₃): 8.29 (1H, dd, J₂',₄'=1.2 Hz, J₂',₅' = 1.5 Hz, H-2"), 7.57 (1H, dd, J₅',₄' = 1.5 Hz, J₅',₄' = 1.8 Hz, H-5"), 7.35 (1H, s, H-5), 7.04 (1H, s, H-8), 6.59 (1H, dd, J₄',₂'=1.2 Hz, J₄',₅' = 1.8 Hz, H-4"), 2.50 (3H, s, CH₃);
Synthesis of 6-chloro-7-methyl-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99c:

To a suspension of compound, 2.98c (0.260 g, 0.001 mol) and freshly dried K₂CO₃ (0.69 g, 0.005 mol) in dry acetone propargyl bromide (0.131 g, 0.001 mol) and tetra-n-butylammonium iodide (0.050 g) was added. The reaction mixture was refluxed for 4h and the color of reaction mixture changed from reddish-orange to white. Filtration, evaporation of solvent and crystallization of the residue (MeOH) gave 2.99c.

Yield 87%, white solid, mp 142°C;

ν_max (cm⁻¹): 2110 (C=O), 1612 (C=O).

¹H NMR (300 MHz, δ (ppm), CDCl₃): 8.40 (1H, dd, J₂,₄ =0.6, J₂,₅ =1.2, H-2'), 8.02 (1H, s, H-5), 7.55-7.42 (2H, m, H-5', H-4'), 7.07 (1H, s, H-8), 5.27 (2H, d, J₁',₃'=2.1 Hz, H-1”), 2.46 (3H, s, C₇-CH₃), 2.41 (1H, t, J₃',₁'=2.1 Hz, H-3”);

¹³C NMR (CDCl₃, δ (ppm)): 178.23 (C=O), 156.56, 153.83, 148.03, 145.44, 143.04, 139.47, 132.55, 129.12, 124.11, 119.63, 117.94, 107.80, 78.80, 76.44, 56.89, 20.84 (C₇-CH₃).

Photolysis of 6-chloro-7-methyl-3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99c:

A deoxygenated solution of 2.99c in dry methanol was irradiated in a pyrex glass vessel under nitrogen atmosphere for 50 min with a 125 W Hg vapor lamp. Progress of reaction was monitored by TLC. To produce enough products for structural analysis, a total of 1000 mg of 2.99c was irradiated in a number of batches (20 mg in 150 ml). The removal of solvent under reduced pressure yielded a gummy mass that was chromatographed over a column of silica gel (100-200 mesh). The column was eluted with increasing proportion of ethylacetate in petroleum ether-ethylacetate as eluting system mixture yielding photoproducts 2.100c and 2.101c.
**Synthesis of Xanthenones**

![Chemical Structure](image)

**8-Chloro-5-hydroxy-4,9-dimethyl-6H-furo[2,3-c]xanthone-6-one 2.100c:**

Yield 24%, shining yellow crystals, mp 176-178 °C;

ν_max (cm⁻¹): 1659 (C=O);

¹H NMR (400 MHz, δ (ppm), CDCl₃): 12.77 (1H, s, OH), 8.25 (1H, s, H-7), 7.61 (1H, d, J₂₁ = 2.2 Hz, H-2), 7.45 (1H, s, H-10), 7.03 (1H, d, J₁₂ = 2.2 Hz, H-1), 2.54 (3H, s, 4-CH₃), 2.40 (3H, s, 9-CH₃);

¹³C NMR (CDCl₃, δ (ppm)): 180.61 (C=O), 156.52, 153.54, 144.35, 144.07, 143.83, 136.20, 125.74, 125.44, 119.97, 119.49, 107.73, 105.20, 104.02, 29.69 (C₉-CH₃), 14.08 (C₄-CH₃);

Mass (m/z): 314.8/316.9 (M, M+2).

**9-Chloro-4-ethynyl-3a,11b-dihydro-8-methyl-5-oxa-furo[2,3-c]xanthone-6-one 2.101c:**

Yield 29%, white solid, mp 128-130 °C;

ν_max (cm⁻¹): 2129 (C≡C), 1643 (C=O);

¹H NMR (400 MHz, δ (ppm), CDCl₃): 8.21 (1H, s, H-7), 7.32 (1H, d, J₂₁ = 2.4 Hz, H-2), 7.26 (1H, s, H-10), 5.28 (1H, t, J₁₂ = 2.4 Hz, H-1), 5.14 (1H, dd, J₃ₐ₁₁ₙ = 10.1 Hz, J₃ₐ₄ = 2.7 Hz, H-3a), 4.85 (1H, d, J₄₃ₐ = 2.7 Hz, H-4), 4.12(dt, J₁₁ₙ₃ₐ = 10.1 Hz, J₁₁ₙ₂ = 2.6 Hz, J₁₁ₙ₂ = 2.2 Hz, H-11b), 2.61 (1H, d, J₂₂₄ = 2.1 Hz, H-2'), 2.48 (3H, s, 9-CH₃);

¹³C NMR (CDCl₃, δ (ppm)): 169.15 (C=O), 153.29, 152.71, 137.01, 135.59, 135.48, 133.50, 129.57, 124.19, 120.17, 100.21 (C-1'), 81.57 (C-1'), 78.91 (C-3a), 77.51 (C-2'), 66.40 (C-4), 40.29 (C-11b), 20.84 (C₉-CH₃).

Mass (m/z): 314.9/316.9 (M, M+2)
Synthesis of 1-(2-hydroxyphenyl)-3-(furan-3-yl)prop-2-en-1-one 2.97d:

To a well stirred suspension of powdered NaOH (0.8 g, 0.02 mol) in EtOH at 0 °C, 2-hydroxyacetophenone 2.96d (1.36 g, 0.01 mol) and furan-3-carbaldehyde (1.05 g, 0.011 mol) were added. The reaction mixture, which became deep red in color after 30 min, was stirred further for 4h. Thereafter, it was poured over ice and neutralized with dil. HCl to acquire acrylophenone, which was crystallized from EtOH to give the yellow needles of 2.97d.

![Synthesis of 1-(2-hydroxyphenyl)-3-(furan-3-yl)prop-2-en-1-one 2.97d](image)

Yield 75%, yellow solid, mp 94-96 °C;

ν_{max} (cm\(^{-1}\)): 3405 (OH), 1635 (C=O);

\(^1\)H NMR (300 MHz, δ (ppm), CDCl\(_3\)): 12.83 (1H, s, OH), 7.93 (1H, d, \(J_{3,2} = 15.0\) Hz, H-3), 7.90 (1H, d, \(J_m = 2.7\) Hz, \(J_o = 9.0\) Hz, H-6’), 7.85 (1H, s, H-2”), 7.55-7.49 (2H, m, H-5”, 5’), 7.43 (1H, d, \(J_{2,3} = 15.0\) Hz, H-2), 7.07 (1H, dd, \(J_m = 2.7\) Hz, \(J_o = 9.0\) Hz, H-4’), 6.70 (1H, d, \(J_m = 2.7\) Hz, \(J_o = 9.0\) Hz, H-3’), 6.77 (1H, d, \(J_{4',5'} = 2.4\) Hz, H-4’’);

\(^13\)C NMR (CDCl\(_3\), δ (ppm)): 190.71 (C=O), 161.89, 147.24, 145.25, 144.07, 136.08, 130.09, 125.12, 123.52, 121.58, 119.80, 117.47, 107.46

Synthesis of 3-hydroxy-2-(furan-3-yl)-4H-chromen-4-one 2.98d:

To a thoroughly stirred suspension of compound 2.97d (1.07 g, 0.005 mol) in methanol 10.0 ml of 20% aq. KOH was added and cooled the solution to 0 °C. Drop-wise H\(_2\)O\(_2\) (30%) was added to dark red solution till it changes to yellow color and continued stirring for 2h. The reaction was monitored by TLC. Then the reaction mixture was poured over ice and neutralized with HCl to obtain yellow coloured precipitates. The solid was filtered, dried and crystallized (CHCl\(_3\)-MeOH) to give yellow crystals of benzopyrane 2.98d.
Yield 80%, yellowish solid, mp 206-208 °C;

\( \nu_{\text{max}} \) (cm\(^{-1}\)): 3188 (OH), 1615 (C=O);

\(^1\)H NMR (300 MHz, \( \delta \) (ppm), CDCl\(_3\)): 8.40 (1H, s, H-2'), 8.14 (1H, dd, \( J_m = 2.4 \) Hz, \( J_o = 9.0 \) Hz, H-5), 7.89 (1H, d, \( J_m = 2.4 \) Hz, \( J_o = 9.0 \) Hz, H-7), 7.67 (1H, d, \( J_{5,8'} = 1.8 \) Hz, H-5'), 7.59 (1H, d, \( J_o = 9.0 \) Hz, H-8), 7.05 (1H, d, \( J_{4,5'} = 1.8 \) Hz, H-4'), 6.93 (1H, dd, \( J_o = 9.0 \) Hz, \( J_m = 2.4 \) Hz, H-6);

\(^{13}\)C NMR (CDCl\(_3\), \( \delta \) (ppm)): 178.27 (C=O), 160.18, 157.21, 144.42, 142.63, 139.17, 135.36, 130.61, 124.01, 123.51, 119.91, 117.73, 108.20.

**Synthesis of 3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99d:**

Propargyl bromide (0.131 g, 0.001 mol) was added to a suspension of 3-hydroxychromone 2.98d (0.212 g, 0.001 mol) and freshly dried K\(_2\)CO\(_3\) (0.69 g, 0.005 mol) in dry acetone containing tetra-n-butylammonium iodide (0.050g) as phase transfer catalyst. The reaction mixture was refluxed for 4h and during the refluxing the color of reaction mixture changed from orange red to white. The resulting solution was filtered and washed with acetone. The solvent was evaporated and crystallization of residue (MeOH) gave 2.99d.

Yield 81%, white solid, mp 96 °C

\( \nu_{\text{max}} \) (cm\(^{-1}\)): 2105 (C=C), 1605 (C=O).

\(^1\)H NMR (300 MHz, \( \delta \) (ppm), CDCl\(_3\)): 8.31 (1H, dd, \( J_{2,4'} = 1.5 \) Hz, \( J_{2,5'} = 1.2 \) Hz, H-2'), 8.09 (1H, d, \( J_o = 9.2 \) Hz, H-5), 7.94 (1H, dd, \( J_{5,2'} = 1.2 \) Hz, \( J_{5,4'} = 1.8 \) Hz, H-5'), 7.51 (1H, dd, \( J_o = 9.2 \) Hz, \( J_m = 2.4 \) Hz, H-7), 7.39 (1H, d, \( J_{4,5'} = 1.8 \) Hz, H-4'), 6.95 (1H, d, \( J_o = 9.2 \) Hz, H-8), 6.93 (1H, dd, \( J_o = 9.0 \) Hz, \( J_m = 2.4 \) Hz, H-6).
Synthesis of Xanthenones

Hz, H-8), 6.72 (1H, d, J_o = 9.2 Hz, H-6), 5.00 (2H, d, J_{1';3'} = 2.4 Hz, H-1'), 2.35 (1H, t, J_{5';1''} = 2.4 Hz, H-3').

^{13}C NMR (CDCl_3, \delta (ppm): 173.92 (C=O), 154.23, 152.44, 144.94, 143.50, 138.41, 133.52, 130.82, 125.51, 121.00, 117.84, 108.64, 106.43 78.57 (C-2'), 76.04 (C-3'), 59.69 (C-1').

Photolysis of 3-propargyloxy-2-(furan-3-yl)-4H-chromen-4-one 2.99d:

A deoxygenated solution of 2.99d (1.0 mM) in dry methanol was irradiated in a pyrex glass vessel under nitrogen atmosphere for 50 min with a 125 W Hg vapor lamp. Progress of reaction was monitored by TLC. To produce enough products for structural analysis, a total of 1000 mg of 2.99d was irradiated in a number of batches (40 mg in 150 ml). Solvent was removed under reduced pressure and a gummy mass was obtained which was directly chromatographed over a column of silica gel (100-200 mesh). The column was eluted with increasing proportion of ethylacetate in petroleum ether-ethylacetate as eluting system mixture to get photoproducts 2.100d and 2.102d.

5-Hydroxy-4-methyl-6H-furo[2,3-c]xanthen-6-one 2.100d:

Yield 18%, shining yellow crystals, mp 181-183 °C;

v_{max} (cm^{-1}): 1651 (C=O);

^{1}H NMR (400 MHz, \delta (ppm), CDCl_3): 12.94 (1H, s, OH), 8.33 (1H, d, J_o = 8.0 Hz, H-7), 7.74 (1H, ddd, J_o = 8.0 Hz, J_m = 1.6 Hz, H-8), 7.66 (1H, d, J = 2.4 Hz, H-2), 7.60 (1H, d, J_o = 8.0 Hz, H-10), 7.50 (1H, ddd, J_o = 8.0 Hz, J_m = 2.1 Hz, H-9), 7.38 (1H, d, J = 2.2 Hz, H-1), 2.41 (3H, s, 4-CH_3);

^{13}C NMR (CDCl_3, \delta (ppm): 177.21 (C=O), 156.54, 153.91, 148.11, 136.61, 135.66, 134.12, 125.51, 124.43, 119.87, 119.48, 107.61, 105.10, 104.31, 104.12, 14.21;

Mass (m/z): 266.1 (M^+, 100%).

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4-Ethynyl-3a,11b-dihydro-5-oxa-furo[2,3-c]xanthen-6-one 2.102d:

Yield 26%, white solid, mp 120-122 °C;

ν_{max} (cm^{-1}): 2130 (C≡C), 1641 (C=O);

^1H NMR (300 MHz, δ (ppm), CDCl_3): 8.27 (1H, d, J_o = 7.8 Hz, H-7), 7.66 (1H, dd, J_o = 8.1 Hz, J_m = 2.4 Hz, H-9), 7.57 (1H, d, J_o = 8.1 Hz, H-10), 7.46 (1H, d, J_o = 7.8 Hz, H-8), 6.73 (1H, dd, J_{2,11b} = 1.5 Hz, J_{2,1} = 2.4 Hz, H-2), 5.52 (1H, J_{1,2} = 2.4 Hz, H-1), 5.36 (1H, dd, J_{3a,4} = 6.9 Hz, J_{3a,11b} = 10.2 Hz, H-3a), 5.05 (1H, dd, J_{4,3a} = 6.9 Hz, H-4), 4.35 (1H, dd, J_{11b,3a} = 10.2 Hz, H-11b), 2.61 (1H, d, J_{2',4} = 2.1 Hz, H-2');

^13C NMR (CDCl_3, δ (ppm): 170.15 (C=O), 154.66, 152.74, 148.21, 137.43, 135.20, 133.47, 129.56, 124.41, 120.16, 100.31 (C-1), 80.14 (C-1'), 78.87 (C-3a), 77.52 (C-2'), 66.55 (C-4), 41.11 (C-11b);

Mass (m/z): 266.3 (M^+, 100%).
References


2. Spath, E.; Eiter, K. *Chem. Ber.* 1941, 74(B), 1851.


Synthesis of Xanthenones

Synthesis of Xanthenones