

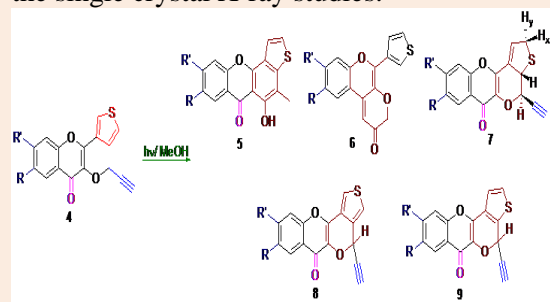
Research Article

Some Novel Photo-transformations in 4*H*-chromen-4-ones: Photolysis of 3-Propynyloxy -2-(thiophen-3-yl)-4*H*-chromen-4-onesRamesh C. Kamboj^{*1}, Pooja Jindal¹, Rita Arora¹, Ashu Chaudhary¹, Sadhika Khullar² and Sanjay K. Mandal²¹Department of Chemistry, Kurukshetra University, Kurukshetra-136119, Haryana (INDIA)²Department of Chemical Sciences, Indian Institute of Science Education and Research, Mohali, Sector 81, Manauli PO, S.A.S. Nagar, Mohali 140306, Punjab (INDIA)**Abstract**

Phototransformation of 2-(thiophen-3-yl)-4*H*-chromen-4-ones bearing propynyloxy moiety at 3-position has been described. These chromenones on photolysis by the pyrex filtered UV-light produced a diverse array of novel angular tri- and tetracyclic photoproducts; xanthenones through the tandem sigmatropic shifts and cyclization, pyranochromenones through intramolecular Paterno-Buchi reaction and oxa-xanthenones by the H-abstractions pathways in a diverging mode in one shot. This study revealed the considerable complexity of the mechanism where the presence of single structural construct, the acetylenic moiety, leads to different products by different reaction pathways.

Keywords: Cyclization, photoirradiation, 3-propynyloxy chromenones, pyranochromenones, xanthenones.

The structures of these photoproducts formed have been determined by the spectral data and the single crystal X-ray studies.

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Introduction

Photochemical processes like isomerisation [1], cyclizations [2], sigmatropic shifts [3], C-C bond cleavages [4], H-abstractions [5], etc., in a variety of organic molecules afforded, of course, in eco-friendly approach, an enormous range of simple to complex organic compounds which are otherwise difficult to obtain through thermal means. The photochemistry of acetylene and its derivatives, such as acetylene decarboxylate [6], diaryl acetylenes [7], conjugated acetylenes [8], ethoxy acetylenes [9] and acyclic acetylenic di- π -methanes [10] etc. has been of great interest. The photoinduced [2+2] cycloaddition of an olefin to a carbonyl center – the Paterno-Buchi reaction [11] - provides a facile and versatile access for oxetane [12] preparation with high regio- and stereoselectivities. [13] The ring opening reactions of oxetanes has been found to be very useful in synthetic chemistry [14]. Insect pheromones, asteltoxin [15] (a potent inhibitor of ATP synthesis) and (+)-Preussin [15] (an antifungal agent) can also be synthesized by Paterno-Buchi reaction followed by ring opening. The photoinduced [2+2] cycloaddition of acetylene with carbonyl compounds leads to the formation of 1,4-biradical which on cyclization leads to labile oxetene [16]. Acetylenes also have unveiled potential to exhibit prototropic acetylene-allene isomerization and participate in intramolecular reactions proceeding *via* six-membered cyclic transition states. Prototropic acetylene-allene isomerization has gained increasing importance as a versatile tool in synthetic organic chemistry [17]. Recently, alkoxy-1,2-dienes [18] synthesized by the prototropic isomerization of propargyl ethers are expedient building blocks for the synthesis of pyrroles, dihydropyridines, and other heterocycles with heteroatomic substituents. A comprehensive insight into the mechanism of prototropic acetylene-allene isomerization has laid the theoretical foundations of the chemistry of dicoordinated carbon and favors the wider use of this reaction in organic synthesis.

In our laboratory, a program on photochemistry of chromones has been initiated [3,5,19] whereupon these differently substituted chromones offered interesting polycyclic compounds for their further use in synthetic chemistry. Chromones [20] constitute one of the leading modules of oxygenated heterocyclic compounds occurring in the vegetal kingdom [21] and have attracted the major attention of the organic chemists because of their diverse biological activities such as anti-inflammatory [22], antitumor [23], antioxidant [24], antiulcer [25] and biocidal activities [26]. In the recent past, a preliminary study in our laboratory on the photochemical transformation of chromenones [19,27], functionalized with a propynyloxy group at 3-position demonstrated that the photoproducts were obtained mainly through the H-abstraction followed by cyclization. But, the 3-propynyloxy chromenones consists of an additional photochemically active chromophore i.e. acetylenic system alongwith a C=O group having γ -hydrogen. So, the molecular framework of these propargyloxy chromones unrelentingly prompted us to further explore their photochemistry concerning to acetylene pendant. In our continued efforts on the photochemistry of these molecules and also on the basis of preliminary reports [19,27-29] on the formation of some interesting photoproducts from the photoirradiation of these types of chromenones, herein, in addition to the products from H-abstraction route we report a complete study of photolytic behavior of 3-propynyloxy-2-(thiophen-3-yl)-4H-chromen-4-ones of being transformed simultaneously to many complex molecules- thienoxanthenones, thienooxaxanthenones and angular pyranochromenones in a divergent mode. Xanthenones derivatives have gained the enormous attention due to their antibilharzial, antitumor and antischistosomal activities [30]. Similarly, the pyranochromenones may mimic the activities (antineoplastic [31], antimicrobial [32], anti-cancer [33], anti-HIV [34], etc.) elicited by the coumarin derived pyranochromenones.

Experimental

General

Melting points were determined in open capillaries and are thus uncorrected. The photoirradiation was carried out with a 125W Hg lamp using a pyrex filter. The ^1H NMR spectra were recorded on 400 MHz and 300 MHz (75.4 MHz for ^{13}C NMR) using TMS as an internal standard. IR spectra were recorded on a MB3000 FT-IR spectrophotometer using KBr pellets. Mass spectra were recorded at 3500 eV as (ESI +Q1 mode). TLC plates were coated with silica gel G (suspended in CHCl_3 -MeOH) and iodine vapors were used as visualizing agent. The columns for purification were packed with Silica gel 100-200 mesh in pet. ether and left overnight before use. The elution was carried out with increasing proportion of benzene in pet. ether-benzene mixture. The yields reported are based on the amount of isolated photoproducts and are calculated by excluding the recovered starting substrates.

Single Crystal X-ray Diffraction Studies

X-ray diffraction data sets were collected on a Bruker AXS Kappa APEX II diffractometer equipped with a CCD detector (with the crystal-to-detector distance fixed at 60 mm) using sealed-tube monochromated Mo-K radiation (0.71073 Å) at the specified temperature. The crystal centering, unit cell determination, refinement of the cell parameters and data collection was controlled through the program APEX2 [35]. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS) [35]. The structure was solved by direct methods using SHELXS-97 and refined against F^2 using SHELXL-97 [36]. All calculations were performed using the SHELXTL V 11.0 suite of programs [36]. There were no residual peaks for all structures $> 1 \text{ e}/\text{Å}^3$. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. All figures were drawn using Mercury V 3.0 [37]. The final positional and thermal parameters of the non-hydrogen atoms for all structures are listed in the CIF files.

General method for the synthesis of chalcones 2

To the well-stirred suspension of powdered NaOH (0.02mol) in EtOH at 0 °C were added 2-hydroxyacetophenone **1** (0.01mol) and thiophene-3-carbaldehyde (0.011mol). The reaction mixture, which became deep red in color after 30

min, was stirred further for 3h. Thereafter, it was poured over ice and neutralized with dil. HCl to obtain acrylophenone, which was crystallized from EtOH to give the yellowish-orange needles of **2**.

1-(2-Hydroxyphenyl)-3-(thiophen-3-yl)prop-2-en-1-one 2a: Yield 1.81g (79%), orange-yellow solid, mp 66-68 °C; ν_{\max} (cm⁻¹): 3400 (OH), 1643 (C=O); δ_{H} (CDCl₃): 12.9 (1H, br s, OH), 7.94 (1H, d, $J_{3,2} = 15.6$ Hz, H-3), 7.91 (1H, dd, $J_o = 7.8$ Hz, $J_m = 1.5$ Hz, H-6'), 7.69 (1H, dd, $J_{2',4''} = 3.0$ Hz, $J_{2',5''} = 1.2$ Hz, H-2''), 7.52 (1H, td, $J_o = 7.8$ Hz, $J_m = 1.5$ Hz, H-4'), 7.50-7.46 (2H, m, H-2, 5''), 7.42 (1H, dd, $J_{4'',5''} = 5.1$ Hz, $J_{4'',2''} = 3.0$ Hz, H-4''), 7.05 (1H, dd, $J_o = 7.8$ Hz, $J_m = 1.5$ Hz, H-3'), 6.97 (1H, td, $J_o = 7.8$ Hz, $J_m = 1.5$ Hz, H-5'); $\delta_{13\text{C}}$ (CDCl₃): 192.38 (C-1), 159.73, 138.62, 137.22, 135.92, 130.97, 129.47, 126.59, 126.19, 124.53, 120.56, 117.93; Mass (m/z, +Q1): 231.1 (M⁺, 100%); Anal. Calcd. for C₁₃H₁₀O₂S: C, 67.80; H, 4.38. Found: C, 67.91; H, 4.84.

1-(2-Hydroxy-5-methylphenyl)-3-(thiophen-3-yl)prop-2-en-1-one 2b: Yield 1.73g (70.9%), yellow solid, mp 70 °C; ν_{\max} (cm⁻¹): 3350 (OH), 1641 (C=O); δ_{H} (CDCl₃): 12.7 (1H, br s, OH), 7.92 (1H, d, $J_{3,2} = 15.3$ Hz, H-3), 7.68-7.65 (2H, m, H-6', 2''), 7.52-7.46 (2H, m, H-5'', 2), 7.43-7.40 (1H, m, H-4''), 7.33 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.7$ Hz, H-4'), 6.95 (1H, d, $J_o = 9.0$ Hz, H-3'), 2.42 (3H, s, 5'-CH₃); $\delta_{13\text{C}}$ (CDCl₃): 190.58 (C-1), 153.61, 138.67, 137.13, 134.72, 133.99, 128.99, 126.83, 126.77, 120.19, 119.94, 103.32, 20.86 (5'-CH₃); Mass (m/z, +Q1): 245.1 (M⁺, 100%); Anal. Calcd. for C₁₄H₁₂O₂S: C, 68.83; H, 4.95. Found: C, 68.74; H, 4.89.

1-(2-Hydroxy-5-methoxyphenyl)-3-(thiophen-3-yl)prop-2-en-1-one 2c: Yield 1.66g (63.8%), yellow solid, mp 80 °C; ν_{\max} (cm⁻¹): 3210 (OH), 1639 (C=O); δ_{H} (CDCl₃): 12.8 (1H, br s, OH), 7.94 (1H, d, $J_{3,2} = 15.3$ Hz, H-3), 7.73 (1H, dd, $J_{2',4''} = 3.0$ Hz, $J_{2',5''} = 1.2$ Hz, H-2''), 7.52 (1H, d, $J_m = 2.7$ Hz, H-6'), 7.44-7.38 (2H, m, H-5'', 2), 7.33 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.7$ Hz, H-4'), 7.25 (1H, dd, $J_{4'',5''} = 5.1$ Hz, $J_{4'',5''} = 3.0$ Hz, H-4''), 6.96 (1H, d, $J_o = 9.0$ Hz, H-3'), 3.82 (3H, s, 5'-OCH₃); $\delta_{13\text{C}}$ (CDCl₃): 192.10 (C-1), 159.52, 153.57, 138.31, 137.28, 134.44, 131.20, 126.64, 120.55, 124.83, 117.90, 103.35, 60.84 (5'-OCH₃); Mass (m/z, +Q1): 261.1 (M⁺, 100%); Anal. Calcd. for C₁₄H₁₂O₃S: C, 64.60; H, 4.65. Found: C, 64.67; H, 4.69.

1-(5-Chloro-2-hydroxy-4-methylphenyl)-3-(thiophen-3-yl)prop-2-en-1-one 2d: Yield 2.17g (78%), yellow solid, mp 150-152 °C; ν_{\max} (cm⁻¹): 3101 (OH), 1643 (C=O); δ_{H} (CDCl₃): 12.8 (1H, br s, OH), 7.94 (1H, d, $J_{3,2} = 15.3$ Hz, H-3), 7.85 (1H, s, H-6'), 7.70 (1H, dd, $J_{2',4''} = 3.0$ Hz, $J_{2',5''} = 1.2$ Hz, H-2''), 7.49 (1H, dd, $J_{5'',4''} = 5.1$ Hz, $J_{5'',2''} = 1.2$ Hz, H-5''), 7.43 (1H, dd, $J_{4'',5''} = 5.1$ Hz, $J_{4'',5''} = 3.0$ Hz, H-4''), 7.38 (1H, d, $J_{2,3} = 15.3$ Hz, H-2), 6.94 (1H, s, H-3'), 2.42 (3H, s, 4'-CH₃); $\delta_{13\text{C}}$ (CDCl₃): 192.24 (C-1), 162.02, 144.24, 137.26, 135.96, 134.25, 131.66, 128.75, 128.62, 123.47, 120.62, 120.17, 117.06, 14.38 (4'-CH₃); Mass (m/z, +Q1): 279.1/281.1 (M⁺, 100%); Anal. Calcd. for C₁₄H₁₁ClO₂S: C, 60.32; H, 3.98. Found: C, 60.23; H, 3.88.

1-(5-Chloro-2-hydroxyphenyl)-3-(thiophen-3-yl)prop-2-en-1-one 2e: Yield 11.4g (86%), yellow solid, mp 90 °C; ν_{\max} (cm⁻¹): 1643 (C=O), 3405 (OH); δ_{H} (CDCl₃): 7.96 (1H, d, $J_{3,2} = 15.3$ Hz, H-3), 7.86 (1H, d, $J_m = 2.7$ Hz, H-6'), 7.73 (1H, dd, $J_{2',4''} = 3.0$ Hz, $J_{2',5''} = 1.2$ Hz, H-2''), 7.50 (1H, dd, $J_{5'',4''} = 5.1$ Hz, $J_{5'',2''} = 1.2$ Hz, H-5''), 7.46 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.7$ Hz, H-4'), 7.44 (1H, dd, $J_{4'',5''} = 5.1$ Hz, $J_{4'',5''} = 3.0$ Hz, H-4''), 7.40 (1H, d, $J_{2,3} = 15.3$ Hz, H-2), 7.01 (1H, d, $J_o = 9.0$ Hz, H-3'); $\delta_{13\text{C}}$ (CDCl₃): 190.83 (C-1), 159.85, 145.19, 138.81, 135.48, 129.62, 127.80, 126.71, 126.17, 124.12, 120.21, 119.97; Mass (m/z, +Q1): 265.1/267.1 (M⁺, 100%); Anal. Calcd. for C₁₃H₉ClO₂S: C, 58.98; H, 3.43. Found: C, 59.07; H, 3.39.

General method for the synthesis of 2-(thiophen-3-yl)chromenones **3**

To the well stirred suspension of compound **2** (0.005mol) in methanol was added 10.0ml of 20% aq. KOH and cooled to 0 °C. To this dark red solution was added H₂O₂ (30%) drop-wise till the color changed to yellow and the stirring was continued for 2h. 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 **3**.

3-Hydroxy-2-(thiophen-3-yl)-4H-chromen-4-one 3a: Yield 1.01g (82.8%), light yellow solid, mp 186 °C; ν_{\max} (cm⁻¹): 3178 (OH), 1597 (C=O); δ_{H} (CDCl₃): 8.30 (1H, dd, $J_{2,4'} = 3.0$ Hz, $J_{2,5'} = 1.2$ Hz, H-2'), 8.23 (1H, dd, $J_o = 7.8$ Hz, $J_m =$

1.5 Hz, H-5), 7.86 (1H, d, $J_{5,4'} = 5.1$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.66 (1H, td, $J_o = 8.1$ Hz, $J_m = 1.5$ Hz, H-7), 7.55 (1H, d, $J_o = 8.4$ Hz, H-8), 7.43 (1H, dd, $J_{4,5'} = 5.1$ Hz, $J_{4,2'} = 3.0$ Hz, H-4'), 7.36 (1H, td, $J_o = 7.8$ Hz, $J_m = 1.5$ Hz, H-6), 6.94 (1H, s, OH); δ_{13C} (CDCl₃): 184.37, 152.87, 148.85, 136.18, 131.71, 131.35, 131.28, 131.05, 128.01, 126.43, 124.19, 116.62; Mass (m/z, +Q1): 245 (M⁺, 100%); Anal. Calcd. for C₁₃H₈O₃S: C, 63.92; H, 3.30. Found: C, 63.87; H, 3.35.

3-Hydroxy-6-methyl-2-(thiophen-3-yl)-4H-chromen-4-one 3b: Yield 1.11g (86%), light yellow solid, mp 184 °C; ν_{max} (cm⁻¹): 3240 (OH), 1605 (C=O); δ_H (CDCl₃): 8.32 (1H, dd, $J_{2,4'} = 3.0$ Hz, $J_{2,5'} = 1.2$ Hz, H-2'), 8.04 (1H, d, $J_m = 2.4$ Hz, H-5), 7.89 (1H, dd, $J_{5,4'} = 5.1$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.54-7.47 (3H, m, H-7, 8, 4'), 6.96 (1H, s, OH), 2.50 (3H, s, 6-CH₃); δ_{13C} (CDCl₃): 184.56, 152.83, 148.23, 136.62, 133.07, 132.14, 131.58, 131.31, 130.14, 129.20, 127.59, 127.33, 120.98, 21.36 (6-CH₃); Mass (m/z, +Q1): 259 (M⁺, 100%); Anal. Calcd. for C₁₄H₁₀O₃S: C, 65.10; H, 3.90. Found: C, 65.17; H, 3.86.

3-Hydroxy-6-methoxy-2-(thiophen-3-yl)-4H-chromen-4-one 3c: Yield 1.03g (75%), pale yellow solid, mp 188 °C; ν_{max} (cm⁻¹): 3194 (OH), 1597 (C=O); δ_H (CDCl₃): 8.33 (1H, dd, $J_{2,4'} = 3.0$ Hz, $J_{2,5'} = 1.2$ Hz, H-2'), 7.89 (1H, d, $J_m = 2.4$ Hz, H-5), 7.58 (1H, dd, $J_{5,4'} = 5.1$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.51-7.48 (2H, m, H-7, 8), 7.34-7.30 (1H, m, H-4'), 6.93 (1H, s, OH), 3.94 (3H, s, 6-OCH₃); δ_{13C} (CDCl₃): 184.87, 152.56, 149.65, 131.73, 131.13, 130.89, 130.46, 129.32, 128.64, 125.53, 124.24, 116.57, 54.67; Mass (m/z, +Q1): 275 (M⁺, 100%); Anal. Calcd. for C₁₄H₁₀O₄S: C, 61.30; H, 3.67. Found: C, 61.22; H, 3.63.

6-Chloro-3-hydroxy-7-methyl-2-(thiophen-3-yl)-4H-chromen-4-one 3d: Yield 1.3g (89%), pale yellow solid, mp 206-208 °C; ν_{max} (cm⁻¹): 3279 (OH), 1605 (C=O); δ_H (CDCl₃): 8.31 (1H, dd, $J_{2,4'} = 3.0$ Hz, $J_{2,5'} = 1.2$ Hz, H-2'), 8.20 (1H, d, $J_m = 2.4$ Hz, H-5), 7.85 (1H, dd, $J_{5,4'} = 5.1$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.48 (2H, m, H-4', 8), 6.93 (1H, s, OH), 2.42 (3H, s, 7-CH₃); δ_{13C} (CDCl₃): 185.65, 152.93, 148.81, 137.72, 136.68, 132.64, 129.96, 129.69, 128.46, 128.31, 126.17, 121.08, 21.20 (7-CH₃); Mass (m/z, +Q1): 293/295 (M⁺, 100%); Anal. Calcd. for C₁₄H₉ClO₃S: C, 57.44; H, 3.10. Found: C, 57.40; H, 3.03.

6-Chloro-3-hydroxy-2-(thiophen-3-yl)-4H-chromen-4-one 3e: Yield 2.2g (81%), pale yellow solid, mp 208-210 °C; ν_{max} (cm⁻¹): 1605 (C=O), 3248 (OH); δ_H (CDCl₃): 8.34 (1H, dd, $J_{2,4'} = 3.0$ Hz, $J_{2,5'} = 1.2$ Hz, H-2'), 8.23 (1H, d, $J_m = 2.4$ Hz, H-5), 7.88 (1H, dd, $J_{5,4'} = 5.1$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.66 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-7), 7.55 (1H, d, $J_o = 9.0$ Hz, H-8), 7.49 (1H, dd, $J_{4,5'} = 5.1$ Hz, $J_{4,2'} = 3.0$ Hz, H-4'), 6.9 (1H, s, OH); δ_{13C} (CDCl₃): 184.37, 152.87, 148.85, 130.18, 131.71, 131.35, 131.28, 131.05, 128.01, 126.43, 124.19, 116.62; Mass (m/z, +Q1): 279/281 (M⁺, 100%); Anal. Calcd. for C₁₃H₇ClO₃S: C, 56.02; H, 2.53. Found: C, 56.11; H, 2.47.

General method for the synthesis of 3-propargyloxy-2-(thiophen-3-yl)-chromenones 4

To a suspension of respective compound, **3** (0.001mol) and freshly dried K₂CO₃ (0.005mol) in dry acetone was added propargyl bromide (0.001mol), and tetra-*n*-butylammonium iodide (0.050g). 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 **4**.

3-Propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one 4a: Yield 0.24g (85%), white solid, mp 98 °C; ν_{max} (cm⁻¹): 2106 (C≡C), 1605 (C=O); δ_H (CDCl₃): 8.43 (1H, dd, $J_{2,4'} = 3.0$ Hz, $J_{2,5'} = 1.2$ Hz, H-2'), 8.26 (1H, dd, $J_o = 7.8$ Hz, $J_m = 1.5$ Hz, H-5), 7.91 (1H, dd, $J_{5,4'} = 5.1$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.71 (1H, td, $J_o = 8.4$ Hz, $J_m = 1.5$ Hz, H-7), 7.55 (1H, dd, $J_o = 8.4$ Hz, $J_m = 1.5$ Hz, H-8), 7.46 (1H, dd, $J_{4,5'} = 5.1$ Hz, $J_{4,2'} = 3.0$ Hz, H-4'), 7.42 (1H, td, $J_o = 7.8$ Hz, $J_m = 1.5$ Hz, H-6), 5.10 (2H, d, $J_{1,3''} = 2.4$ Hz, H-1''), 2.42 (1H, t, $J_{3,1''} = 2.4$ Hz, H-3''); δ_C (CDCl₃): 174.60 (C-4), 154.91, 152.95, 137.46, 133.51, 133.35, 131.92, 129.66, 127.37, 125.70, 124.76, 123.99, 117.91, 78.68 (C-2''), 76.20 (C-3''), 59.12 (C-1''); Mass (m/z, +Q1): 283 (M⁺, 100%); Anal. Calcd. for C₁₆H₁₀O₃S: C, 68.07; H, 3.57. Found: C, 68.01; H, 3.53.

6-Methyl-3-propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one 4b: Yield 0.23g (77.7%), white solid, mp 112-114 °C; ν_{max} (cm⁻¹): 2129 (C≡C), 1612 (C=O); δ_H (CDCl₃): 8.41 (1H, dd, $J_{2,4'} = 3.0$ Hz, $J_{2,5'} = 1.2$ Hz, H-2'), 8.03 (1H, d, $J_m =$

2.4 Hz, H-5), 7.90 (1H, dd, $J_{5,4'} = 5.1$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.50 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-7), 7.46-7.43 (2H, m, H-8, H-4'), 5.09 (2H, d, $J_{1'',3''} = 2.4$ Hz, H-1''), 2.48 (3H, s, C₆-CH₃), 2.41 (1H, t, $J_{3'',1''} = 2.4$ Hz, H-3''); δ_C (CDCl₃): 174.59 (C-4), 153.22, 152.81, 137.45, 134.79, 134.71, 132.06, 129.46, 127.37, 125.57, 124.95, 123.70, 117.64, 78.74, 76.08, 59.09, 20.90 (C₆-CH₃); Mass (m/z, +Q1): 297 (M⁺, 100%); Anal. Calcd. for C₁₇H₁₂O₃S: C, 68.90; H, 4.08. Found: C, 68.87; H, 4.13.

6-Methoxy-3-propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one 4c: Yield 0.25g (81%), off-white solid, mp 124 °C; ν_{\max} (cm⁻¹): 2122 (C≡C), 1612 (C=O); δ_H (CDCl₃): 8.41 (1H, dd, $J_{2',4'} = 3.0$ Hz, $J_{2',5'} = 1.2$ Hz, H-2'), 7.89 (1H, d, $J_m = 2.4$ Hz, H-5), 7.61 (1H, dd, $J_{5,4'} = 5.1$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.47-7.28 (3H, m, H-7, 8, 4'), 5.10 (2H, d, $J_{1'',3''} = 2.4$ Hz, H-1''), 4.01 (3H, s, OCH₃), 2.42 (1H, t, $J_{3'',1''} = 2.4$ Hz, H-3''); δ_C (CDCl₃): 174.28 (C-4), 156.71, 152.74, 149.80, 137.14, 132.03, 129.42, 127.32, 125.59, 124.63, 123.98, 123.79, 119.32, 104.57, 78.73, 59.08, 55.91; Mass (m/z, +Q1): 313 (M⁺, 100%); Anal. Calcd. for C₁₇H₁₂O₄S: C, 65.37; H, 3.87. Found: C, 65.40; H, 3.89.

6-Chloro-7-methyl-3-propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one 4d: Yield 0.24g (73%), white solid, mp 136-138 °C; ν_{\max} (cm⁻¹): 2106 (C≡C), 1612 (C=O); δ_H (CDCl₃): 8.40 (1H, dd, $J_{2',4'} = 3.0$ Hz, $J_{2',5'} = 1.2$ Hz, H-2'), 8.20 (1H, s, H-5), 7.87 (1H, dd, $J_{5,4'} = 5.1$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.46-7.44 (2H, m, H-8, H-4'), 5.08 (2H, d, $J_{1'',3''} = 2.4$ Hz, H-1''), 2.53 (3H, s, C₇-CH₃), 2.42 (1H, t, $J_{3'',1''} = 2.4$ Hz, H-3''); δ_C (CDCl₃): 173.47 (C-4), 153.20, 152.97, 142.76, 137.32, 131.76, 131.58, 129.73, 127.28, 125.74, 125.30, 123.08, 119.69, 78.53, 76.25, 59.15, 20.85(C₇-CH₃); Mass (m/z, +Q1): 331/333 (M⁺, 100%); Anal. Calcd. for C₁₇H₁₁ClO₃S: C, 61.73; H, 3.35. Found: C, 61.67; H, 3.42.

6-Chloro-3-propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one 4e: Yield 0.27g (85%), white solid, mp 148-150 °C; ν_{\max} (cm⁻¹): 2129 (C≡C), 1636 (C=O); δ_H (CDCl₃): 8.42 (1H, dd, $J_{2',4'} = 3.0$ Hz, $J_{2',5'} = 1.2$ Hz, H-2'), 8.22 (1H, d, $J_m = 2.4$ Hz, H-5), 7.89 (1H, dd, $J_{5,4'} = 5.1$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.64 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-7), 7.52 (1H, d, $J_o = 9.0$ Hz, H-8), 7.46 (1H, d, $J_{4',5'} = 5.1$ Hz, $J_{4',2'} = 3.0$ Hz, H-4'), 5.10 (2H, d, $J_{1'',3''} = 2.4$ Hz, H-1''), 2.42 (1H, t, $J_{3'',1''} = 2.4$ Hz, H-3''); δ_C (CDCl₃): 173.66 (C-4), 153.21, 152.71, 138.62, 133.57, 133.35, 131.84, 130.63, 129.44, 127.09, 125.97, 125.10, 119.59, 119.10, 77.23, 72.92; Mass (m/z, +Q1): 317/319 (M⁺, 100%); Anal. Calcd. for C₁₆H₉ClO₃S: C, 60.67; H, 2.86. Found: C, 60.74; H, 2.88.

Photolysis of 3-propargyloxy-2-(thiophen-3-yl)-chromenones 4

Photolysis of 3-propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one 4a

A deoxygenated 1.0 mM methanolic solution of chromone **4a** contained in a pyrex glass vessel was purged with nitrogen for 30 min and then irradiated under nitrogen with light from a 125 W Hg vapor lamp for 30 min. The removal of solvent under reduced pressure yielded a gummy mass that was chromatographed over a column of silica gel. The column was eluted with increasing proportion of benzene in benzene-petroleum ether mixture yielding photoproducts **5a**, **6a**, **7a** and **8a**.

5-Hydroxy-4-methyl-6H-thieno[2,3-c]xanthen-6-one 5a: Yield 0.059g (21%), shining yellow crystals, mp. 189 °C; ν_{\max} (cm⁻¹): 1682 (C=O); δ_H (CDCl₃): 12.74 (1H, s, -OH), 8.37-8.35 (1H, dd, $J_o = 8.0$ Hz, $J_m = 1.68$ Hz, H-7), 7.82-7.78 (1H, ddd, $J_o = 8.0$ Hz, $J_m = 1.68$ Hz, H-8), 7.75-7.74 (1H, d, $J = 5.6$ Hz, H-2), 7.62-7.60 (1H, d, $J_o = 8.0$ Hz, H-10), 7.47-7.43 (1H, ddd, $J_o = 8.0$ Hz, $J_m = 2.16$ Hz, H-9), 7.34-7.33 (1H, d, $J = 5.6$ Hz, H-1), 2.47 (3H, s, 4-CH₃); δ_C (CDCl₃): 178.42, 153.36, 152.29, 150.12, 135.47, 134.19, 124.78, 122.36, 120.71, 120.53, 119.77, 116.62, 110.89, 107.36, 98.73, 14.66; HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₆H₁₀O₃S 283.0351; Found 283.0395; Anal. Calcd. for C₁₆H₁₀O₃S: C, 68.07; H, 3.57. Found: C, 68.00; H, 3.56.

5-(Thiophen-3-yl)pyrano[2,3-c]chromen-2(3H)-one 6a: Yield 0.079g (28%), Greenish yellow solid; mp 84 °C; ν_{\max} (cm⁻¹): 1643 (C=O); δ_H (CDCl₃): 8.22-8.20 (1H, dd, $J_{2',5'} = 3.0$ Hz, $J_{2',4'} = 1.2$ Hz, H-2'), 8.04-8.03 (1H, dd, $J_{5,4'} = 5.2$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.78-7.77 (1H, dd, $J_m = 1.64$ Hz, $J_o = 8.4$ Hz, H-10), 7.71-7.69 (1H, dd, $J_{4',5'} = 5.2$ Hz and $J_{4',2'} = 1.2$ Hz, H-4'), 7.56-7.54 (1H, d, $J_o = 8.4$ Hz, H-9), 7.49-7.46 (1H, dd, $J_o = 8.4$ Hz, $J_m = 1.64$ Hz, H-8), 7.36-7.35 (1H, d, $J_o = 8.4$ Hz, $J_m = 1.64$ Hz, H-7), 6.33 (1H, s, H-1), 4.73 (2H, s, H-3); δ_C (CDCl₃): 170.39, 152.23, 145.78,

142.01, 138.76, 133.42, 132.86, 131.77, 130.22, 128.26, 125.37, 124.12, 120.26, 119.38, 80.61; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{10}O_3S$ 283.0351; Found 283.0891; Anal. Calcd. for $C_{16}H_{10}O_3S$: C, 68.07; H, 3.57. Found: C, 67.96; H, 3.48.

(3a*S*,4*R*)-4-Ethynyl-5-oxa-2*H*-thieno[2,3-*c*]xanthen-6(3a*H*)-one **7a**: Yield 0.099g (35%), light brown solid, mp 242 °C; ν_{\max} (cm^{-1}): 2122 (C≡C), 1628 (C=O); δ_H ($CDCl_3$): 8.30 (1H, dd, $J_o = 8.1$ Hz, $J_m = 2.0$ Hz, H-7), 7.71 (1H, ddd, $J_o = 8.1$ Hz, $J_m = 2.0$ Hz, H-8), 7.47 (1H, d, $J_o = 8.1$ Hz, H-10), 7.42 (1H, ddd, $J_o = 8.1$ Hz, $J_m = 2.0$ Hz, H-9), 6.66 (1H, m, $J_{1,2Hy} = 4.44$ Hz, $J_{1,2Hx} = 3.76$ Hz, $J_{1,3a} = 2.16$ Hz, H-1), 4.76 (1H, m, $J_{3a,4} = 10.8$ Hz, $J_{3a,2Hx} = 4.92$ Hz, $J_{3a,2Hy} = 2.36$ Hz, $J_{3a,1} = 2.16$ Hz, H-3a), 4.65 (1H, dd, $J_{4,3a} = 10.8$ Hz, $J_{4,2'} = 2.04$ Hz, H-4), 4.13 (1H, ddd, $J_{gem} = 16.5$ Hz, $J_{2Hy,1} = 4.44$ Hz, $J_{2Hy,3a} = 2.36$ Hz, H_y-2), 3.94 (1H, m, $J_{gem} = 16.5$ Hz, $J_{2Hx,3a} = 4.92$ Hz, $J_{2Hx,1} = 3.76$ Hz, H_x-2), 2.72 (1H, d, $J_{2,4} = 2.04$ Hz, H-2'); δ_C ($CDCl_3$): 171.34 (C-6), 154.65, 142.47, 138.27, 133.76 (C-9), 131.51, 129.46, 126.31 (C-1), 124.60 (C-7), 123.89, 117.74 (C-10), 77.94, 77.21 (C-2'), 72.68 (C-4), 54.38 (C-3a), 38.98 (C-2); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{10}O_3S$ 283.0351; Found 283.0351; Anal. Calcd. for $C_{16}H_{10}O_3S$: C, 68.07; H, 3.57. Found: C, 68.14; H, 3.51.

(4*R*)-4-Ethynyl-5-oxa-thieno[4,3-*c*]xanthen-6-one **8a**: Yield 0.04g (14%), dark brown solid, mp 146 °C; ν_{\max} (cm^{-1}): 2106 (C≡C), 1612 (C=O); δ_H ($CDCl_3$): 8.32 (1H, dd, $J_o = 8.1$ Hz, $J_m = 1.5$ Hz, H-7), 7.68 (1H, td, $J_o = 7.8$ Hz, $J_m = 1.5$ Hz, H-9), 7.55 (1H, d, $J_o = 8.7$ Hz, H-10), 7.45 (2H, s, H-1, H-3), 7.41 (1H, td, $J_o = 8.1$ Hz, $J_m = 1.5$ Hz, H-8), 6.28 (1H, brs, H-4), 2.73 (1H, d, $J_{2',4} = 1.8$ Hz, H-2'); δ_C ($CDCl_3$): 173.66, 153.21, 152.71, 138.62, 133.57, 133.35, 131.83, 130.63, 129.44, 127.09, 125.97, 125.10, 119.59, 119.10, 78.32, 65.98; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_8O_3S$ 281.0194; Found 281.0351; Anal. Calcd. for $C_{16}H_8O_3S$: C, 68.56; H, 2.88. Found: C, 68.45; H, 2.98.

Photolysis of 6-methyl-3-propargyloxy-2-(thiophen-3-yl)-4*H*-chromen-4-one 4b: A 1.0mM methanolic solution of **4b** on photolysis for 30 min furnished **5b**, **6b** and **7b**.

5-Hydroxy-4,8-dimethyl-6*H*-thieno[2,3-*c*]xanthen-6-one **5b**: Yield 0.086g (29%), shining yellow crystals, mp. 210 °C; ν_{\max} (cm^{-1}): 1682 (C=O); δ_H ($CDCl_3$): 12.78 (1H, s, -OH), 8.1 (1H, d, $J = 1.28$ Hz, H-7), 7.60-7.58 (1H, dd, $J_o = 8.4$ Hz, $J_m = 2.16$ Hz, H-9), 7.50-7.48 (1H, d, $J_o = 8.4$ Hz, H-10), 7.72-7.71 (1H, d, $J = 5.6$ Hz, H-2), 7.32-7.30 (1H, d, $J = 5.6$ Hz, H-1), 2.49 (3H, s, 4-CH₃), 2.45 (3H, s, 8-CH₃); δ_C ($CDCl_3$): 182.07, 154.00, 153.59, 150.11, 136.48, 134.27, 125.33, 123.34, 120.95, 120.66, 120.34, 117.64, 111.46, 106.45, 98.62, 20.94, 12.79; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{12}O_3S$ 297.0507; Found 297.1612; Anal. Calcd. for $C_{17}H_{12}O_3S$: C, 68.90; H, 4.08. Found: C, 68.82; H, 4.00.

9-Methyl-5-(thiophen-3-yl)pyrano[2,3-*c*]chromen-2(3*H*)-one **6b**: Yield 0.095g (32%), Greenish yellow solid; mp 76 °C; ν_{\max} (cm^{-1}): 1643 (C=O); δ_H ($CDCl_3$): 8.22-8.21 (1H, dd, $J_{2',5'} = 3.0$ Hz, $J_{2',4'} = 1.2$ Hz, H-2'), 7.78-7.77 (1H, dd, $J_{5',4'} = 5.2$ Hz, $J_{5',2'} = 1.2$ Hz, H-5'), 7.71 (1H, d, $J = 1.64$ Hz, H-10), 7.54-7.52 (1H, dd, $J_{4',5'} = 5.2$ Hz, $J_{4',2'} = 1.2$ Hz, H-4'), 7.45-7.42 (1H, dd, $J_o = 8.4$ Hz, $J_m = 1.64$ Hz, H-8), 7.39-7.37 (1H, d, $J_o = 8.4$ Hz, H-7), 6.33 (1H, s, H-1), 4.68 (2H, s, H-3), 2.46 (3H, s, 9-CH₃); δ_C ($CDCl_3$): 170.29, 152.52, 146.56, 141.90, 138.98, 134.38, 133.14, 127.54, 126.88, 125.61, 125.43, 121.82, 119.57, 116.26, 79.75, 18.09; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{12}O_3S$ 297.0507; Found 297.0804; Anal. Calcd. for $C_{17}H_{12}O_3S$: C, 68.90; H, 4.08. Found: C, 68.87; H, 4.11.

(3a*S*,4*R*)-4-Ethynyl-8-methyl-5-oxa-2*H*-thieno[2,3-*c*]xanthen-6(3a*H*)-one **7b**: Yield 0.1g (34%), brownish-white solid, mp 230 °C; ν_{\max} (cm^{-1}): 2122 (C≡C), 1628 (C=O). δ_H ($CDCl_3$): 8.04 (1H, d, $J_m = 2.0$ Hz, H-7), 7.47 (1H, dd, $J_o = 8.6$ Hz, $J_m = 2.0$ Hz, H-9), 7.34 (1H, d, $J_o = 8.6$ Hz, H-10), 6.63-6.61 (1H, m, $J_{1,2Hy} = 4.44$ Hz, $J_{1,2Hx} = 3.76$ Hz, $J_{1,3a} = 2.16$ Hz, H-1), 4.72 (1H, m, $J_{3a,4} = 10.92$ Hz, $J_{3a,2Hx} = 4.92$ Hz, $J_{3a,2Hy} = 2.36$ Hz, $J_{3a,1} = 2.16$ Hz, H-3a), 4.62 (1H, dd, $J_{4,3a} = 10.92$ Hz, $J_{4,2'} = 2.04$ Hz, H-4), 4.09 (1H, ddd, $J_{gem} = 16.4$ Hz, $J_{2Hy,1} = 4.44$ Hz, $J_{2Hy,3a} = 2.36$ Hz, H_y-2), 3.90 (1H, ddd, $J_{gem} = 16.4$ Hz, $J_{2Hx,3a} = 4.92$ Hz, $J_{2Hx,1} = 3.76$ Hz, H_x-2), 2.71 (1H, d, $J_{2',4} = 2.04$ Hz, H-2'), 2.44 (3H, s, C₈-CH₃); δ_C ($CDCl_3$): 170.63 (C-6), 152.92, 142.82, 139.67, 138.63, 133.74, 132.33, 130.41, 128.71, 125.45, 119.48, 84.00, 82.50, 82.30, 51.62(C-3a), 38.97 (C-2), 17.52(-CH₃); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{12}O_3S$ 297.0507; Found 297.0042; Anal. Calcd. for $C_{17}H_{12}O_3S$: C, 68.90; H, 4.08. Found: C, 68.82; H, 3.97.

Photolysis of 6-methoxy-3-propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one 4c: A 1.0mM methanolic solution of **4d** on photolysis for 30 min yielded **5c**, **6c** and **7c**.

4.6.3.1. 5-Hydroxy-8-methoxy-4-methyl-6H-thieno[2,3-c]xanthen-6-one 5c: Yield 0.068g (22%), shining yellow crystals, mp. 202 °C; ν_{\max} (cm⁻¹): 1682 (C=O); δ_{H} (CDCl₃): 12.64 (1H, s, -OH), 8.31 (1H, d, $J = 1.28$ Hz, H-7), 7.73-7.71 (1H, dd, $J_o = 8.4$ Hz, $J_m = 2.16$ Hz, H-9), 7.52 (1H, d, $J = 5.6$ Hz, H-2), 7.37-7.35 (1H, m, H-10, 1), 2.58 (3H, s, 4-CH₃), 3.96 (3H, s, 8-OCH₃); δ_{C} (CDCl₃): 180.79, 155.32, 153.73, 150.26, 136.75, 134.22, 125.65, 123.50, 120.86, 120.78, 119.93, 117.74, 112.21, 105.43, 99.97, 55.65, 19.63; HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₇H₁₂O₄S 313.0456; Found 313.0016; Anal. Calcd. for C₁₇H₁₂O₄S: C, 65.37; H, 3.87. Found: C, 65.31; H, 3.89.

9-Methoxy-5-(thiophen-3-yl)pyranol[2,3-c]chromen-2(3H)-one 6c: Yield 0.097g (31%), Greenish yellow solid; mp 107 °C; ν_{\max} (cm⁻¹): 1643 (C=O); δ_{H} (CDCl₃): 8.20-8.19 (1H, dd, $J_{2,5'} = 3.0$ Hz, $J_{2,4'} = 1.2$ Hz, H-2'), 8.05 (1H, dd, $J_{5,4'} = 5.2$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.77 (1H, d, $J = 1.64$ Hz, H-10), 7.66-7.62 (1H, dd, $J_{4,5'} = 5.2$ Hz and $J_{4,2'} = 1.2$ Hz, H-4'), 7.52-7.47 (2H, m, H-8, 7), 6.69 (1H, s, H-1), 4.63(2H, s, H-3), 4.05 (3H, s, 9-OCH₃); δ_{C} (CDCl₃): 170.68, 152.96, 142.93, 138.33, 133.82, 133.00, 132.02, 130.49, 128.93, 125.48, 124.81, 120.79, 119.51, 83.63, 53.44; HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₇H₁₂O₄S 313.0456; Found 313.0179; Anal. Calcd. for C₁₇H₁₂O₄S: C, 65.37; H, 3.87. Found: C, 65.39; H, 3.70.

(3aS,4R)-4-Ethynyl-8-methoxy-5-oxa-2H-thieno[2,3-c]xanthen-6(3aH)-one 7c: Yield 0.11g (36%), brownish white solid, mp 240-242 °C; ν_{\max} (cm⁻¹): 2122 (C≡C), 1636 (C=O); δ_{H} (CDCl₃): 7.58 (1H, d, $J_m = 2.1$ Hz, H-7), 7.37 (1H, d, $J_o = 9.0$ Hz, H-10), 7.26 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.1$ Hz, H-9), 6.62 (1H, m, $J_{1,2\text{Hy}} = 4.44$ Hz, $J_{1,2\text{Hx}} = 3.76$ Hz, $J_{1,3a} = 2.16$ Hz, H-1), 4.72 (1H, m, $J_{3a,4} = 10.92$ Hz, $J_{3a,2\text{Hx}} = 4.92$ Hz, $J_{3a,2\text{Hy}} = 2.36$ Hz, $J_{3a,1} = 2.16$ Hz, H-3a), 4.62 (1H, dd, $J_{4,3a} = 10.92$ Hz, $J_{4,2'} = 2.04$ Hz, H-4), 4.09 (1H, ddd, $J_{\text{gem}} = 16.4$ Hz, $J_{2\text{Hy},1} = 4.44$ Hz, $J_{2\text{Hy},3a} = 2.36$ Hz, H_y-2), 3.92 (1H, ddd, $J_{\text{gem}} = 16.4$ Hz, $J_{2\text{Hx},3a} = 4.92$ Hz, $J_{2\text{Hx},1} = 3.76$ Hz, H_x-2), 2.72 (1H, d, $J_{2,4} = 2.04$ Hz, H-2'), 3.90 (3H, s, C₉-OCH₃); δ_{C} (CDCl₃): 171.01 (C-6), 156.50, 149.51, 142.32, 137.33, 131.48, 129.32 (C-1), 124.41, 124.19 (C-9), 119.18 (C-10), 104.95 (C-7), 78.00, 77.36 (C-2'), 72.66 (C-4), 56.02 (C₉-OCH₃), 54.37(C-3a), 38.99 (C-2); HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₇H₁₂O₄S 313.0456; Found 313.0016; Anal. Calcd. for C₁₇H₁₂O₄S: C, 65.37; H, 3.87. Found: C, 65.71; H, 3.81.

Photolysis of 6-chloro-7-methyl-3-propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one 4d: A 1.0mM methanolic solution of **4d** on photolysis for 30 min yielded **5d**, **6d**, **7d** and **8d**.

8-Chloro-5-hydroxy-4,9-dimethyl-6H-thieno[2,3-c]xanthen-6-one 5d: Yield 0.09g (26%), shining yellow crystals, mp. 162 °C; ν_{\max} (cm⁻¹): 1682 (C=O); δ_{H} (CDCl₃): 12.60 (1H, s, -OH), 8.29 (1H, s, H-7), 7.72-7.70 (1H, d, $J = 5.6$ Hz, H-2), 7.52 (1H, s, H-10), 7.35-7.34 (1H, d, $J = 5.6$ Hz, H-1), 2.57 (3H, s, 4-CH₃), 2.47 (3H, s, 9-CH₃); δ_{C} (CDCl₃): 173.58, 153.18, 152.51, 141.15, 133.53, 131.86, 131.76, 130.60, 129.37, 127.07, 125.97, 125.16, 125.08, 119.51, 113.90, 29.71, 19.82; HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₇H₁₁ClO₃S 331.0117, 332.0088; Found 331.2223, 333.2344; Anal. Calcd. for C₁₇H₁₁ClO₃S: C, 61.73; H, 3.35. Found: C, 61.67; H, 3.31.

9-Chloro-8-methyl-5-(thiophen-3-yl)pyranol[2,3-c]chromen-2(3H)-one 6d: Yield 0.073g (22%), Greenish yellow solid; mp 65 °C; ν_{\max} (cm⁻¹): 1643 (C=O); δ_{H} (CDCl₃): 8.18-8.17 (1H, dd, $J_{2,5'} = 3.0$ Hz, $J_{2,4'} = 1.2$ Hz, H-2'), 7.77 (1H, dd, $J_{5,4'} = 5.2$ Hz, $J_{5,2'} = 1.2$ Hz, H-5'), 7.49-7.45 (2H, m, H-10, 4'), 7.32 (1H, s, H-7), 6.67 (1H, s, H-1), 4.74 (2H, s, H-3), 2.41 (3H, s, 10-CH₃); δ_{C} (CDCl₃): 171.13, 152.78, 146.35, 142.12, 138.73, 134.36, 132.33, 132.07, 130.69, 128.36, 124.82, 124.39, 121.73, 118.60, 82.47, 20.24; HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₇H₁₁ClO₃S 331.0117, 332.0088; Found 331.1102, 333.1014; Anal. Calcd. for C₁₇H₁₁ClO₃S: C, 61.73; H, 3.35. Found: C, 61.78; H, 3.39.

(3aS,4R)-8-Chloro-4-ethynyl-9-methyl-5-oxa-2H-thieno[2,3-c]xanthen-6(3aH)-one 7d: Yield 0.1g (31%), off white solid, mp 234 °C. ν_{\max} (cm⁻¹): 2129 (C≡C), 1636 (C=O). δ_{H} (CDCl₃): 8.23 (1H, s, H-7), 7.37 (1H, s, H-10), 6.66 (1H,

m, $J_{1,2\text{Hy}} = 4.44$ Hz, $J_{1,2\text{Hx}} = 3.76$ Hz, $J_{1,3a} = 2.16$ Hz, H-1), 4.75-4.72 (1H, m, $J_{3a,4} = 10.92$ Hz, $J_{3a,2\text{Hx}} = 4.92$ Hz, $J_{3a,2\text{Hy}} = 2.36$ Hz, $J_{3a,1} = 2.16$ Hz, H-3a), 4.64 (1H, dd, $J_{4,3a} = 10.92$ Hz, $J_{4,2'} = 2.04$ Hz, H-4), 4.12 (1H, ddd, $J_{\text{gem}} = 16.4$ Hz, $J_{2\text{Hy},1} = 4.44$ Hz, $J_{2\text{Hy},3a} = 2.36$ Hz, H_y-2), 3.93 (1H, ddd, $J_{\text{gem}} = 16.4$ Hz, $J_{2\text{Hx},3a} = 4.92$ Hz, $J_{2\text{Hx},1} = 3.76$ Hz, H_x-2), 2.72 (1H, d, $J_{2',4} = 2.04$ Hz, H-2'), 2.51 (3H, s, C₉-CH₃). δ_{C} (CDCl₃): 170.11 (C-6), 152.86, 143.11, 142.52, 137.49, 131.43 (C-9), 131.19, 129.79, 125.58, 122.81, 119.54, 77.84, 77.17, 72.62, 54.25, 38.95 (C-2), 20.75 (9-CH₃); HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₇H₁₁ClO₃S 331.0117, 332.0088; Found 331.0018, 333.0004; Anal. Calcd. for C₁₇H₁₁ClO₃S: C, 61.73; H, 3.35. Found: C, 61.93; H, 3.41.

(4*R*)-8-Chloro-4-ethynyl-9-methyl-5-oxa-thieno[4,3-*c*]xanthen-6-one **8d**: Yield 0.056g (17%), light brown solid, mp 202 °C; ν_{max} (cm⁻¹): 2122 (C≡C), 1612 (C=O); δ_{H} (CDCl₃): 8.29 (1H, s, H-7), 7.45 (2H, s, H-1, H-3), 7.38 (1H, s, H-10), 6.28 (1H, s, H-4), 2.74 (1H, s, H-2'), 2.53 (3H, s, C₉-CH₃); δ_{C} (CDCl₃): 169.87, 152.60, 146.49, 142.49, 136.00, 133.41 (C-9), 131.72, 128.32, 127.36, 127.15, 125.74, 123.69, 121.86, 119.70, 78.40, 65.17, 20.76; HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₇H₉ClO₃S 328.9961, 330.9931; Found 329.2116, 331.2233; Anal. Calcd. for C₁₇H₉ClO₃S: C, 62.10; H, 2.76. Found: C, 62.08; H, 2.79.

Photolysis of 6-chloro-3-propargyloxy-2-(thiophen-3-yl)-4H-chromen-4-one 4e: A 1.0mM methanolic solution of **4e** on photolysis for 30 min yielded **5e**, **6e**, **7e**, **8e** and **9e**.

8-Chloro-5-hydroxy-4-methyl-6H-thieno[2,3-*c*]xanthen-6-one **5e**: Yield 0.073g (23%), shining yellow crystals, mp. 185 °C; ν_{max} (cm⁻¹): 1682 (C=O); δ_{H} (CDCl₃): 12.52 (1H, s, -OH), 8.32-8.31 (1H, d, $J_{\text{m}} = 2.20$ Hz, H-7), 7.75-7.72 (2H, m, H-9, 2), 7.59-7.57 (1H, d, $J_{\text{o}} = 9.0$ Hz, H-10), 7.36-7.35 (1H, d, $J = 5.6$ Hz, H-1), 2.47 (3H, s, 4-CH₃); δ_{C} (CDCl₃): 179.51, 153.93, 143.41, 141.68, 133.78, 130.81, 126.91, 126.05, 125.56, 125.14, 124.95, 119.87, 115.64, 108.92, 97.31, 21.61; HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₆H₉ClO₃S 316.9961, 318.9931; Found 317.0079, 319.0032; Anal. Calcd. for C₁₆H₉ClO₃S: C, 60.67; H, 2.86. Found: C, 60.73; H, 2.96.

9-Chloro-5-(thiophen-3-yl)pyran[2,3-*c*]chromen-2(3H)-one **6e**: Yield 0.076g (24%), Greenish yellow solid; mp 94 °C; ν_{max} (cm⁻¹): 1643 (C=O); δ_{H} (CDCl₃): 8.18-8.17 (1H, dd, $J_{2',5'} = 3.0$ Hz, $J_{2',4'} = 1.2$ Hz, H-2'), 8.03 (1H, dd, $J_{5',4'} = 5.2$ Hz, $J_{5',2'} = 1.2$ Hz, H-5'), 7.76 (1H, d, $J = 1.64$ Hz, H-10), 7.64-7.62 (1H, dd, $J_{4',5'} = 5.2$ Hz, $J_{4',2'} = 1.2$ Hz, H-4'), 7.52-7.46 (2H, m, H-8, 7), 6.69 (1H, s, H-1), 4.73 (2H, s, H-3); δ_{C} (CDCl₃): 171.32, 153.78, 146.47, 142.39, 138.36, 133.71, 132.92, 132.36, 130.18, 128.17, 124.89, 124.56, 121.78, 119.54, 82.74; HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₆H₉ClO₃S 316.9961, 318.9931; Found 317.0138, 319.0084; Anal. Calcd. for C₁₆H₉ClO₃S: C, 60.67; H, 2.86. Found: C, 60.77; H, 2.91.

(3*aS*,4*R*)-8-Chloro-4-ethynyl-5-oxa-2H-thieno[2,3-*c*]xanthen-6(3*aH*)-one **7e**: Yield 0.091g (29%), off white solid, mp 224-226 °C; ν_{max} (cm⁻¹): 2129 (C≡C), 1628 (C=O); δ_{H} (CDCl₃): 8.04 (1H, d, $J_{\text{m}} = 2.1$ Hz, H-7), 7.62 (1H, dd, $J_{\text{o}} = 9.0$ Hz, $J_{\text{m}} = 2.1$ Hz, H-9), 7.43 (1H, d, $J_{\text{o}} = 9.0$ Hz, H-10), 6.66 (1H, m, $J_{1,2\text{Hy}} = 4.44$ Hz, $J_{1,2\text{Hx}} = 3.76$ Hz, $J_{1,3a} = 2.16$ Hz, H-1), 4.76 (1H, m, $J_{3a,4} = 10.92$ Hz, $J_{3a,2\text{Hx}} = 4.92$ Hz, $J_{3a,2\text{Hy}} = 2.36$ Hz, $J_{3a,1} = 2.16$ Hz, H-3a), 4.65 (1H, dd, $J_{4,3a} = 10.92$ Hz, $J_{4,2'} = 2.04$ Hz, H-4), 4.13 (1H, ddd, $J_{\text{gem}} = 16.4$ Hz, $J_{2\text{Hy},1} = 4.44$ Hz, $J_{2\text{Hy},3a} = 2.36$ Hz, H_y-2), 3.95 (1H, ddd, $J_{\text{gem}} = 16.4$ Hz, $J_{2\text{Hx},3a} = 4.92$ Hz, $J_{2\text{Hx},1} = 3.76$ Hz, H_x-2), 2.73 (1H, d, $J_{2',4} = 2.04$ Hz, H-2'). δ_{C} (CDCl₃): 170.15 (C-6), 152.95, 142.73, 137.70, 133.98 (C-9), 131.19, 130.70, 130.06 (C-1), 125.53 (C-7), 124.77, 119.48 (C-10), 90.82, 77.75 (C-2'), 72.72 (C-4), 54.27 (C-3a), 39.02 (C-2); HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd. for C₁₆H₉ClO₃S 316.9961, 318.9931; Found 317.0085, 319.0031; Anal. Calcd. for C₁₆H₉ClO₃S: C, 60.67; H, 2.86. Found: C, 60.62; H, 2.89.

(4*R*)-8-Chloro-4-ethynyl-5-oxa-thieno[4,3-*c*]xanthen-6-one **8e**: (Data from mixture ¹H NMR/IR of **8e** and **9e**), Yield 8% (NMR yield); ν_{max} (cm⁻¹): 2128 (C≡C), 1628 (C=O); δ_{H} (CDCl₃): 8.27 (1H, d, $J_{\text{m}} = 2.4$ Hz, H-7), 7.63 (1H, dd, $J_{\text{o}} = 9.0$ Hz, $J_{\text{m}} = 2.4$ Hz, H-9), 7.52 (1H, d, $J_{\text{o}} = 9.0$ Hz, H-10), 7.47 (2H, s, H-1, H-3), 6.76 (1H, d, $J_{4,2'} = 2.4$ Hz, H-4), 2.48 (1H, d, $J_{2',4} = 2.4$ Hz, H-2').

(4*R*)-8-Chloro-4-ethynyl-5-oxa-thieno[2,3-*c*]xanthen-6-one **9e**: (Data from mixture ¹H NMR/IR of **8e** and **9e**), Yield 10% (NMR yield); ν_{\max} (cm⁻¹): 1643 (C=O); δ_{H} (CDCl₃): 8.32 (1H, d, $J_{\text{m}} = 2.4$ Hz, H-7), 7.63 (1H, dd, $J_{\text{o}} = 9.0$ Hz, $J_{\text{m}} = 2.4$ Hz, H-9), 7.52 (1H, d, $J_{\text{o}} = 9.0$ Hz, H-10), 7.48 (1H, d, $J_{2,1} = 5.1$ Hz, H-2), 7.44 (1H, d, $J_{1,2} = 5.1$ Hz, H-1), 6.30 (1H, d, $J_{4,2'} = 2.4$ Hz, H-4), 2.75 (1H, d, $J_{2',4} = 2.4$ Hz, H-2').

Results and Discussion

Agosta and Margaretha [38] 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. Correspondingly, the propargyl radical generated through γ -H abstraction in the target compounds, 3-propargyloxy-2-(thiophen-3-yl)chromenones **4** may give attractive and intriguing photochemistry. The *prima facie* of the structural construct of the molecules also indicates the possibility of many other photochemical processes like regioselective photocyclization, phototransposition, ring contraction, cycloadditions encompassing the acetylenic moiety, intramolecular paterno-buchi reaction, electrocyclicization, sigmatropic shifts etc. and these possibilities (**Figure 1**) prompted us to continue and further explore the photochemistry of the 2-(thiophen-3-yl)-4*H*-chromen-4-ones bearing propargyloxy moiety at 3-position.

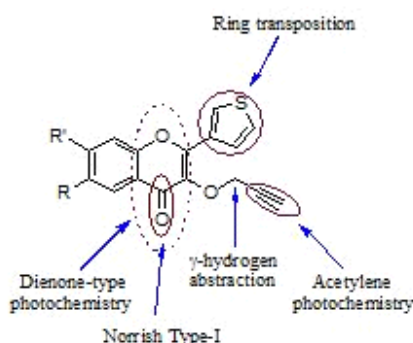
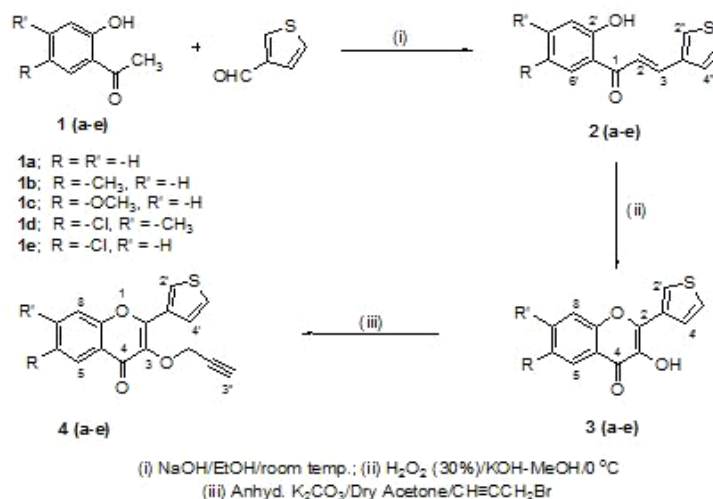


Figure 1 Probable photochemical pathways of the substrates **4(a-e)**



Scheme 1 Synthesis of chromenones **4(a-e)**

These substrates were produced by an initial condensation of 2-hydroxyacetophenones **1(a-e)** with thiophene-3-carbaldehyde in the presence of NaOH in ethanol to yield chalcones **2(a-e)** which on subsequent cyclization under Algar-Flynn-Oyamada conditions [39] produced 3-hydroxy-2-(thiophen-3-yl)-4*H*-chromen-4-ones **3(a-e)**. These

3-hydroxychromones were then converted into respective propargyl ether **4 (a-e)** by reaction with propargyl bromide in the presence of dry acetone, freshly dried K_2CO_3 and tetra-*n*-butylammonium iodide (**Scheme 1**). The structures of these photo-labile substrates **4 (a-e)** were found to be consistent with their spectral data (IR, $^1H/^{13}C$ NMR, *vide experimental*).

In electronic absorption spectra, the chromenones **4 (a-e)** showed λ_{max} in the range of 316-320 nm (**Figure 2**), thus, a pyrex filtered UV-light was used for their photoirradiation.

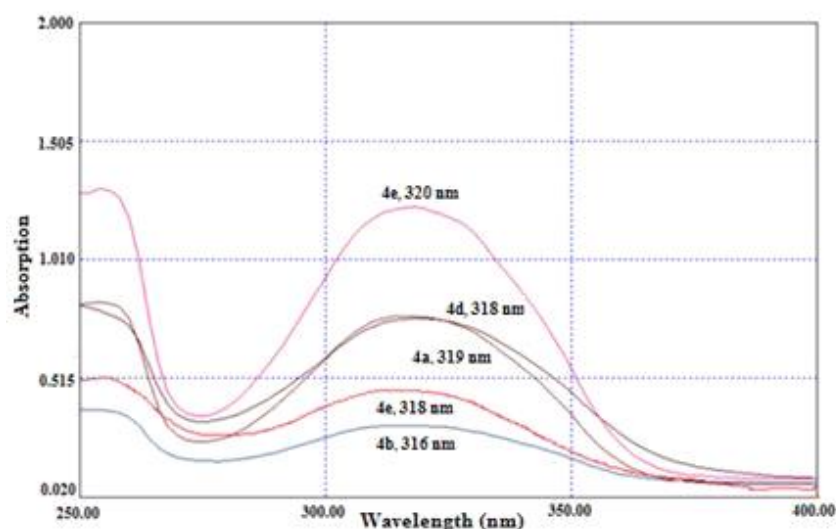
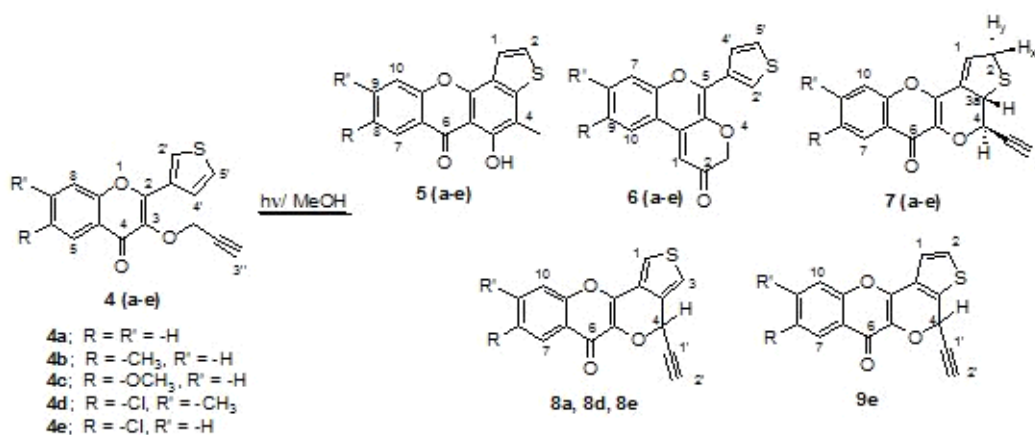


Figure 2 Electronic spectra of the substrates.4

The photoirradiation of methanolic solution (1.0 mM) of these chromenones **4 (a-e)** with pyrex filtered UV light using a 125W Hg lamp, under nitrogen atmosphere produced a diverse array of photoproducts **5, 6, 7, 8** and **9 (Scheme 2)**. The structures of all the photoproducts were confirmed by their spectral parameters (IR, $^1H/^{13}C$ NMR) and elemental analysis. The photoproducts **8a** and **8d** were isolated in pure form while, in spite of our best efforts, the other photoproducts **8 (b & c)** and **9 (a-d)** could not be detected and isolated (**Table 1**). The photoproduct **8e** had contamination of **9e** and their structures were derived from the analysis of 1H NMR spectrum of their mixture.



Scheme 2 Photolysis of chromenones **4 (a-e)**

Table 1 Distribution of the photoproducts

5	Yield (%)	6	Yield (%)	7	Yield (%)	8	Yield (%)	9	Yield (%)
5a	21	6a	28	7a	35	8a	14	9a	-
5b	29	6b	32	7b	34	8b	-	9b	-
5c	22	6c	31	7c	36	8c	-	9c	-
5d	26	6d	22	7d	31	8d	17	9d	-
5e	23	6e	24	7e	29	8e	8	9e	10

The FTIR spectrum of **5a** shows a strong absorption band at 1682 cm^{-1} that may be assigned to the C=O group of the pyrone moiety. In the NMR spectrum of the photoproduct **5a**, was seen a doublet of doublet between δ 8.37-8.35 ($J_o = 8.0\text{ Hz}$ and $J_m = 1.68\text{ Hz}$) for H-7. The other three benzenoid protons showed the resonances between δ 7.82-7.78 (1H, ddd, $J_o = 8.0\text{ Hz}$, $J_m = 1.68\text{ Hz}$, H-8), δ 7.62-7.60 (1H, d, $J_o = 8.0\text{ Hz}$, H-10) and between δ 7.47-7.43 (1H, ddd, $J_o = 8.0\text{ Hz}$, $J_m = 2.16\text{ Hz}$, H-9). The two thienyl protons gave the signals as the doublets between δ 7.75-7.74 (H-2) and 7.34-7.33 (H-1) with the usual characteristic thienyl coupling of $J = 5.6\text{ Hz}$. The -OH proton absorption disappearing on D_2O shake appeared as singlet at δ 12.74. The methyl protons appeared as a singlet at δ 2.47 (4- CH_3). These assignments in the NMR spectrum are consistent with the structure of **5a**. The structure of **5a** was further confirmed on the basis of the structure of **5b** which was ascertained by its 2D-COSY spectrum and single crystal X-ray analysis [29]. The product **5** formation may be rationalized [29] through the initial photochemical sigmatropic 1,3-H shift in chromenone to furnish the allenylloxy chromenone followed by cyclization and further sigmatropic 1,3-H shift. The support for the formation of allenylloxy chromenone has been derived from the earlier observations made in conjugated acetylenic carbonyl compounds [17,18,40] where the acetylenic compounds have been rearranged to the allenes photochemically.

The FTIR spectrum of **6a** showed a strong absorption band at 1643 cm^{-1} that may be assigned to the C=O of the pyrone moiety. In the NMR spectrum of **6a**, a dd between δ 7.78-7.77 ($J_m = 1.64\text{ Hz}$ and $J_o = 8.4\text{ Hz}$) for H-10 was observed. For the other benzenoid protons, resonances between δ 7.56-7.54 (1H, d, $J_o = 8.4\text{ Hz}$, H-9), 7.49-7.46 (1H, dd, $J_o = 8.4\text{ Hz}$, $J_m = 1.64\text{ Hz}$, H-8) and between δ 7.36-7.35 (1H, d, $J_o = 8.4\text{ Hz}$, $J_m = 1.64\text{ Hz}$, H-7) were observed. The three thienyl protons gave their resonances as the doublet of doublets between δ 8.22-8.20 ($J_{2,5'} = 3.0\text{ Hz}$ and $J_{2,4'} = 1.2\text{ Hz}$, H-2'), δ 8.04-8.03 ($J_{5,4'} = 5.2\text{ Hz}$ and $J_{5,2'} = 1.2\text{ Hz}$, H-5') and between δ 7.71-7.69 ($J_{4,5'} = 5.2\text{ Hz}$ and $J_{4,2'} = 1.2\text{ Hz}$, H-4'). This shows that during photo-irradiation the thienyl ring remained intact. The H-1 proton absorption appeared as a singlet at δ 6.33. The -O- CH_2 -protons exhibited a singlet at δ 4.73. This structure of **6a** was further corroborated by the structure of **6b** which was confirmed by its 2D COSY and single X-ray crystal data [28]. The formation of **6** from the chromenones has been envisioned to occur through the intramolecular Paterno-Buchi reaction [28] involving the initial formation of a 1,4-biradical which cyclizes to an oxetene which being highly strained [16,41] easily isomerizes to **6**.

The FTIR spectrum of **7b** shows a strong absorption band at 2122 cm^{-1} for the $-\text{C}\equiv\text{CH}$ group and 1628 cm^{-1} for C=O group of the pyrone moiety. In the NMR spectrum of the photoproduct **7b**, the benzenoid proton H-7 was seen as a doublet at δ 8.04 ($J_m = 2.0\text{ Hz}$). The other two protons showed the resonances at δ 7.47 (dd, $J_o = 8.6\text{ Hz}$, $J_m = 2.0\text{ Hz}$, H-9) and at δ 7.34 (d, $J_o = 8.6\text{ Hz}$, H-10). The proton H-1 resonated as a multiplet between δ 6.63-6.61. The H-3a proton present at the ring junction appeared as a multiplet at 4.72 ($J_{3a,4} = 10.92\text{ Hz}$, $J_{3a,2\text{Hx}} = 4.92\text{ Hz}$, $J_{3a,2\text{Hy}} = 2.36\text{ Hz}$, $J_{3a,1} = 2.16\text{ Hz}$). The pyran proton H-4 was found to couple with H-3a and H-2' as it gave a dd at δ 4.62 (1H, dd, $J_{4,3a} = 10.92\text{ Hz}$, $J_{4,2'} = 2.04\text{ Hz}$, H-4). The enantiotopic methylene protons H_x -2 and H_y -2 showed two distinct signals at δ 4.09 (1H, ddd, $J_{\text{gem}} = 16.4\text{ Hz}$, $J_{2\text{Hy},1} = 4.44\text{ Hz}$, $J_{2\text{Hy},3a} = 2.36\text{ Hz}$, H_y -2) and 3.90 (1H, ddd, $J_{\text{gem}} = 16.4\text{ Hz}$, $J_{2\text{Hx},3a}$

4.92 Hz, $J_{2H_{x,1}} = 3.76$ Hz, H_{x-2}) as these are coupling to H-1 and H-3a protons. The doublet at δ 2.71 was ascribed to the acetylenic proton H-2'. The methyl groups' protons appeared as a singlet at δ 2.44 (8-CH₃).

To elucidate the stereochemical feature of the photoproduct **7b**, the use of J/Φ relationship and MM2 programme was invoked. The observed 3J values found in the present case for **7b** are in accordance with the J^\ddagger values calculated (Table 2) for the conformation I, in which the protons H-3a and H-4 are *trans* to each other and dihydrothiophene ring is *exo* to the *psuedo*-chair pyran ring. It may be argued that in **7b** only the pseudo-equatorially placed acetylene group at C-4 would deshield the H-3a (Figure 3). The proton H-3a would not experience such deshielding in the other possible conformation II. Therefore, the stereocentres C-4 and C-3a have been assigned the *R*- and *S*-configurations respectively. It is clear from energy minimized 3D-MM2 structures (Figure 3) of **7b** that the proton H-3a is closer to H_{x-2} than H_{y-2} as the close contact between H-3a and H_{x-2} is 3.707 and between H-3a and H_{y-2} is 4.355 Å. Thus, it can be affirmed that H_{x-2} is above while H_{y-2} is below the plane.

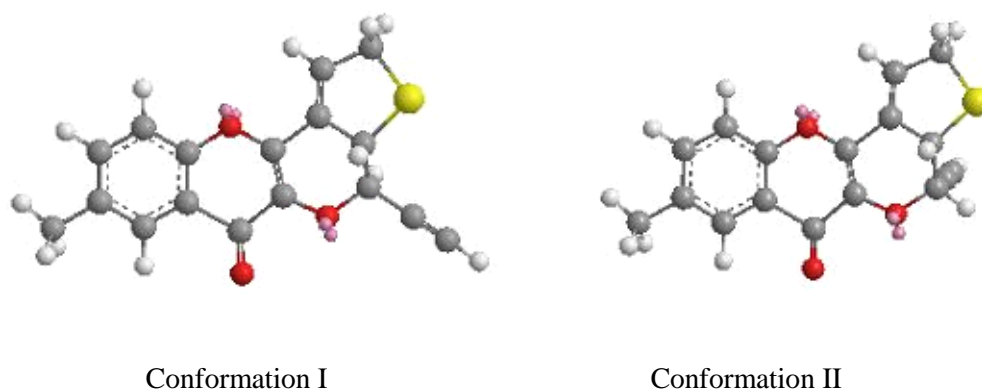


Figure 3 Energy minimized MM2 structures of **7b**

Table 2 Expected coupling constants for the two conformations of **7b**

Coupling protons	Conformation I			Conformation II			Observed J
	Φ	J^\ddagger	E(Kcal/mol)	Φ	J^\ddagger	E(Kcal/mol)	
H-3a and H-4	-179	12.99Hz	12.039	-59.25	4.11Hz	12.293	10.8Hz

J^\ddagger Expected value

For further confirmation of these ^1H NMR assignments to the different protons in **7b**, its 2D COSY (Figure 4) was recorded. It can be seen in Figure 4, H-1 is directly interacting with H_{x-2} , H_{y-2} and H-3a that is the reason that it appeared as multiplet between δ 6.63-6.61. The H-3a is in close vicinity with H-4 and also with H_{x-2} and H_{y-2} and these enantiotopic protons are also interacting with each other. The acetylenic proton H-2' is showing interaction with H-4. The benzenoid protons H-9 and H-10 are correlating to each other as well as to H-7. Moreover, in DEPT-135 spectra of **7b**, the negative signal at δ 39.01 showed the presence of carbon containing two protons. In its 2D-HSQC spectrum, spots arising due to H_{x-2} and H_{y-2} of C-2 corresponded to the negative signal at δ 39.01 and thus confirmed the presence of C-2 bearing two hydrogens. The structure of **7b** was further corroborated (Figure 4 and 5) by its single X-ray structure analysis [42]. On this basis, this structure of **7e** obtained from the photolysis **4e** differs from our earlier reported structure **4f** [27] which was not based upon the X-ray data and only a single chromenone bearing acetylene moiety was photolysed.

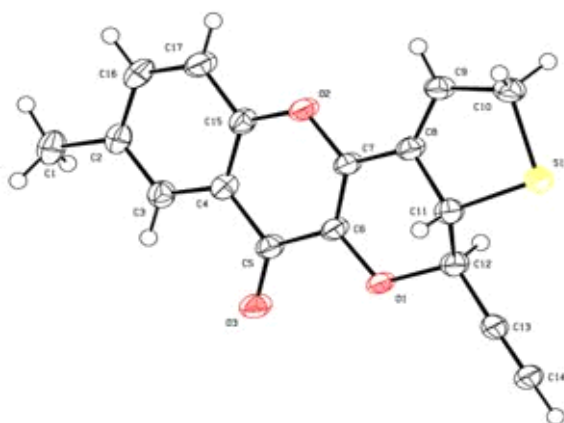


Figure 4 Structure of **7b** determined by single crystal X-ray analysis

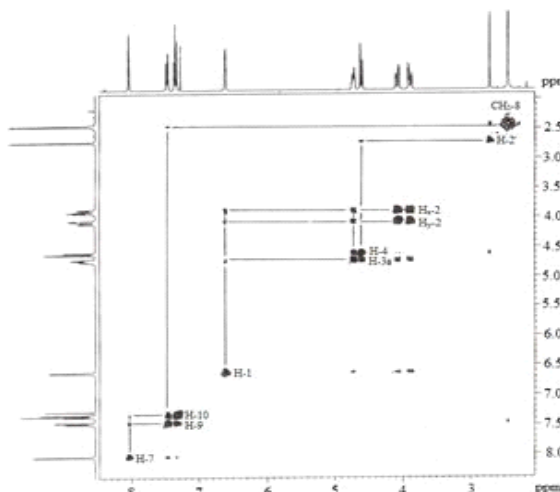
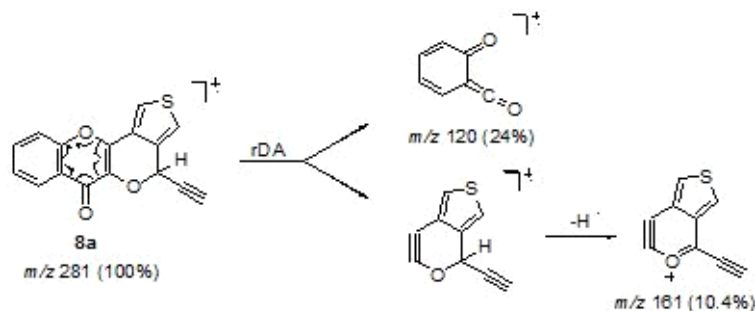


Figure 5 2D-COSY spectrum of **7b**

The photocyclization of **4** to furnish the dihydrophotoproducts **7** has been envisioned to take place simply through the coupling of 1,4-biradical **C** with C-2' position of the thiophene ring as reported in our earlier studies [19,27] (**Scheme 4**) to give **D** *in situ* followed by 1,7-H shift.

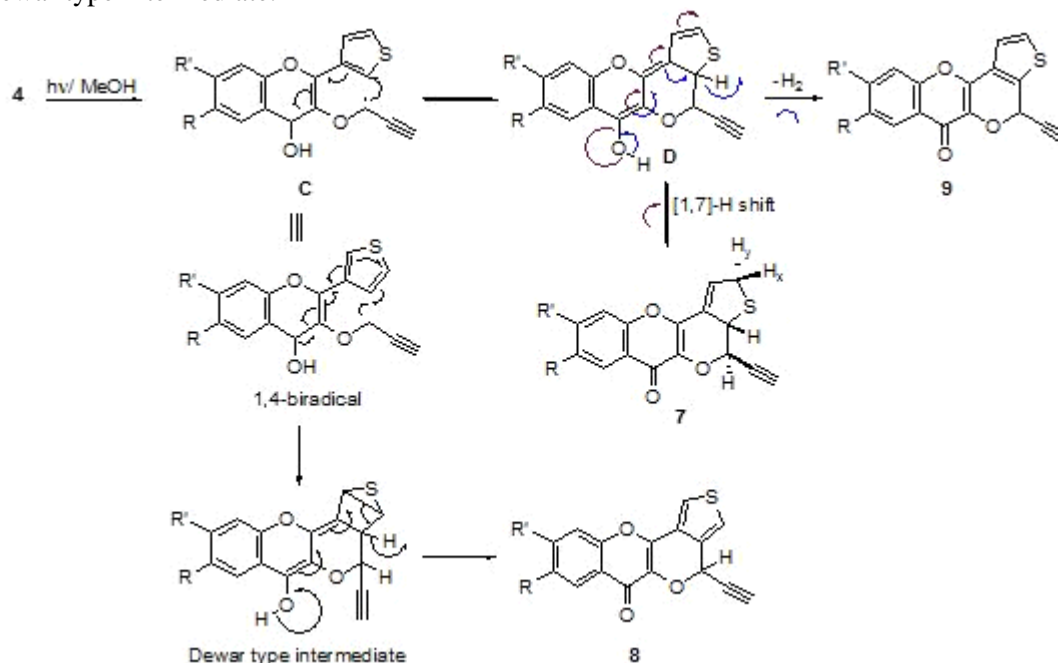
In IR spectrum of **8a**, a strong absorption for the carbonyl group was observed at 1612 cm^{-1} , which indicated the presence of benzopyrone moiety. In addition, one more absorption was observed at 2106 cm^{-1} which was assigned to the acetylene group. In ^1H NMR spectrum (300 MHz, CDCl_3) the benzenoid protons displayed resonances at their usual places i.e. δ 8.32 (1H, dd, $J_o = 8.1\text{ Hz}$, $J_m = 1.5\text{ Hz}$, H-7), 7.68 (1H, td, $J_o = 7.8\text{ Hz}$, $J_m = 1.5\text{ Hz}$, H-9), 7.55 (1H, d, $J_o = 8.7\text{ Hz}$, H-10) and 7.41 (1H, td, $J_o = 8.1\text{ Hz}$, $J_m = 1.5\text{ Hz}$, H-8). The signal for ring D protons (H-1 and H-3) was found to be placed at δ 7.45 (2H, s). The H-4 proton appeared at δ 6.28 as broad singlet. The proton of the acetylene group at C-4 resonated at δ 2.73 doublet ($J_{2',4} = 1.8\text{ Hz}$). The carbon skeleton of photoproduct was in agreement with their observed proton decoupled ^{13}C NMR spectra (*vide* experimental). The mass spectrum (**Scheme 3**) exhibited the molecular ion peak at m/z 281, indicating that two mass units have been lost from the starting compound **4a** and showed retro-Diels Alder (rDA) fragmentation mode thereby illustrating the presence of chromenone moiety.



Scheme 3 Mass fragmentation pattern of **8a**

The formation (**Scheme 4**) of photoproducts **8** may only be explained by coupling [43] of initially formed 1,4-biradical **C** with C-4 position of the thiophene to give Dewar type intermediate which consequently furnishes the photoproducts upon dehydrogenation. This Dewar type intermediate could not be isolated but the proposed mechanism (**Scheme 4**) gets support from the fact that the photoirradiation of the chromenones, substituted with the 3-furyl group [44] at C-2 which have the same possibility (i.e. two possible sites (C-2' and C-4') for clipping of the initially formed 1,4-biradical) as that of the chromenones under study, afforded photoproducts only by clipping at

C-2'. No photoproducts similar to **8** were produced by clipping at C-4' as they need the involvement of the Dewar furan type structure which could not have been possible in those furan-3-yl chromenones probably due to high energy requirements. So, the intermediacy of Dewar type moiety in the photoirradiation of the thienylchromenones has been invoked. Since the energy of Dewar thiophene (S_0 energy = 65 kcal mol⁻¹) is lower than that of Dewar furan (S_0 energy = 78 kcal mol⁻¹) [45]. Therefore, it may be safely concluded that the formation of products **8** occurs *via* the low energy Dewar type intermediate.



Scheme 4 A proposed mechanism of the formation of **7**, **8** and **9**

The structure of tetracyclic photoproduct **9e** rests upon the IR and NMR spectral data. The compound **9e** in the functional group region of its IR spectrum had strong absorption band at 1643 cm⁻¹, a characteristic of benzopyrone moiety. In its ¹H NMR spectrum, the protons of ring A were found to be placed at δ 8.32 (1H, d, $J_m = 2.4$ Hz, H-7), 7.63 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-9) and 7.52 (1H, d, $J_o = 9.0$ Hz, H-10). The two protons belonging to the 3-thienyl moiety were upfield and appeared as doublets at δ 7.48 (1H, $J_{2,1} = 5.1$ Hz, H-2) and δ 7.44 (1H, $J_{1,2} = 5.1$ Hz, H-1). The proton H-4 belonging to ring C was seen at δ 6.30 (d, $J_{4,2'} = 2.4$ Hz). The acetylenic proton H-2' appeared as doublet at δ 2.75. The formation of **9** may be rationalised through the dehydrogenation of **D** (**Scheme 4**).

As observed in the earlier work on 3-alkoxy-2-(2-furyl) chromones [46], the secondary ring contraction products observed by cleavage of thiophene ring are altogether absent here and were not even realized by further photolysis of pure photoproducts. These findings correlate well with the studies made by Maurizio D'Auria on the photochemical isomerization reactions of furan [45] and thiophene derivatives and also with our earlier studies [27]. It has been shown by the semiempirical calculations that furan can give ring contraction product, i.e. the cyclopropenyl derivative for its triplet state can give the biradical intermediate, whereas thiophene cannot be converted into the biradical intermediate as this intermediate is of higher energy (69 kcal mol⁻¹) than the excited triplet state (62 kcal mol⁻¹) of thiophene, thus preventing the formation of the cyclopropenyl derivatives. Also, no photoproducts concerning to the phototransposition and oxetane formation processes were obtained in these substrates upon photoirradiation.

Conclusions

It may be concluded that the inclusion of the acetylene moiety at the 3-position of 2-(thiophen-3-yl)chromenones, brings the facile formation of the 1,4-biradical by photo-excitation of the C=O group in competition with the

acetylene-allene isomerization and photoinduced [2+2] cycloaddition of chromenone carbonyl with acetylene group. To the best of our knowledge, this is the first case where the synthesis of various exotic novel photoproducts i.e. xanthenones, pyranochromenones, oxaxanthenones bearing gem-dihydro functionality and dehydrogenated oxaxanthenones takes place in a diverging mode in one shot and is unprecedented in these chromenones. The exploration of this intriguing photochemistry in chromenones encouraged us to continue travelling on this productive road. Expansion of the scope of this photoreaction, further elucidation of the reaction mechanism, and the application to other aromatic systems are ongoing in our laboratory.

Acknowledgements

The one of the authors (P.J.) wishes to express her gratitude to the University Grant commission (UGC), New Delhi for the financial assistance as JRF for the accomplishment of this work. The X-ray facility at IISER, Mohali, is gratefully acknowledged.

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Publication History

Received 4th June 2014
Accepted 8th June 2014
Online 29th June 2014