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Synthesis of some benzofurooxepines' derivatives *via* [3+2] cycloaddition of epoxide with tethered alkyne: A photochemical approach

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ABSTRACT

A novel, environmentally benign and single-step synthesis of 8-chloro-2-arylbenzo[*b*]furo[2,3-*e*]oxepin-10(4*H*)-ones by the photochemical irradiation of 2-{5-chloro-2-(prop-2-ynyloxy)benzoyl}-3-aryloxiranes has been developed. Some of these substrates also furnished hydroxyalkenones alongside. The formation of oxepinones as major products from these substrates has been envisioned to occur through the heterolytic C—C bond cleavage of epoxide, the oxirane ring giving carbonyl ylide intermediates followed by the furo-oxepinone ring formation *via* [3+2] cycloaddition while the hydroxyalkenones' formation as minor products takes place through the initial β-H abstraction followed by oxirane ring opening.

1. Introduction

Epoxy ketones are among the most versatile building blocks in organic synthesis as both the ketone [1] and epoxide [2] moieties can be further functionalized to afford interesting intermediates that are ultimate building blocks of numerous biomolecules. This invoked an ever-growing interest in the chemistry of epoxy ketones. A fascinating range of transformations has been developed and proved progressively more valuable for the synthesis of natural products and biologically active compounds such as the SK&F 104353 [3] (leukotriene antagonist), diltiazem [4] (potent blood pressure lowering agent), taxol [5] (anticancer-drug) and (+)-decursin [6] (novel protein kinase C activator), *etc.* The epoxy ketones have also been transformed to the oxepines, seven-membered heterocycles on photoirradiation [7] through γ-hydrogen abstraction. Seven-membered heterocyclic motifs are frequently present in the wide array of biologically active molecules [8]. An ample range of recent chemical review literature contributes to synthesis and transformation of seven-membered rings [9–12]. An incredible diversity of natural products such as janoxepin [13], oxepinamide C [14], and bauhiniastatin [15] contains oxepine ring in their molecular architecture. The oxepines and their derivatives (fused and substituted) constitute an important class of heterocyclic compounds and are known to possess many biological activities like antileishmanial [16], antiallergic [17], antidepressant [18], antipsychotic [19], anti-inflammatory [20] and antifungal [21] activities. From a chemical perspective, the intricacies of the structures have made them the objectives of enhanced attention by synthetic chemists. Numerous methods have been developed for their formation [22].

Keeping in view the motivating reactions and important uses elicited by epoxy ketones and also by oxepines, herein, an attempt has been made to photoirradiate the epoxy ketones (propynyloxy benzoyloxiranes) which offered benzofurooxepinone derivatives. To the best of our knowledge, there is no such method available for the synthesis of this type of tricyclic compounds *i.e.* benzofurooxepinones. The structural constructs of these molecules may be used in the development of medication for the treatment of urinary-incontinence [23].

2. Results and discussion

The required epoxy ketones (benzoyl oxiranes) **4(a–f)** were synthesized from 5-chloro-2-hydroxyacetophenone through the following sequence of reactions (Scheme 1):

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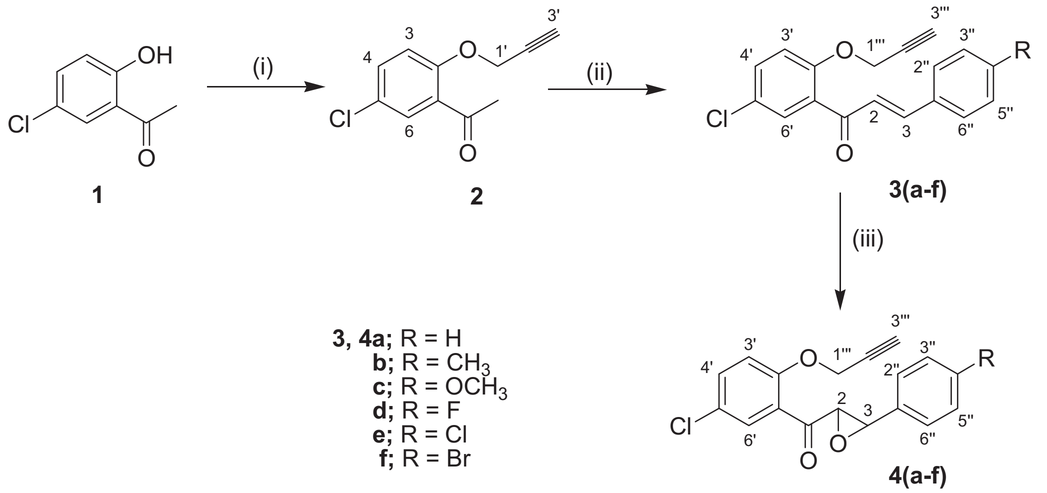


Scheme 1. Synthesis of benzoyl oxiranes **4(a–f)**. (i) Dry acetone/K_2CO_3/Propargyl Bromide, heat (ii) ArCHO, KOH/MeOH (iii) THF/MeOH/KOH, 0 °C, 50% H_2O_2.

The structures of the chalcones **3(a–f)** and benzoyl oxiranes **4(a–f)** were ascertained from their spectral parameters (*vide* experimental). The yields of all these compounds were in the range of 82–89%.

Regarding the structure of compound **3b** (mp 81–83 °C), its IR spectrum showed the strong absorption band at 1643 cm^{-1} and a weak absorption band at 2127 cm^{-1} due to C=O and C≡C groups, respectively. In the ^1H NMR spectrum of **3b**, three benzenoid protons appeared at δ 7.608 (1H, d, J_m = 2.7 Hz, H-6′), δ 7.456 (1H, dd, J_0 = 8.7 Hz, J_m = 2.7 Hz, H-4′) and δ 7.103 (1H, d, J_0 = 8.7 Hz, H-3′). The two-alkenyl protons had *trans* relationship as they showed resonances at δ 7.646 (1H, d, H-3) and δ 7.344 (1H, d, H-2) with coupling constant of 15.3 Hz. The NMR spectrum also exhibited two doublets at δ 7.531 (2H, d, J_0 = 7.5 Hz, H-2″, 6″) and δ 7.240 (2H, d, J_0 = 7.5 Hz, H-3″, 5″), respectively. The propargyl group protons H-1‴ and H-3‴ were present as doublets at δ 4.784 and δ 2.467, respectively, with $J_{allylic}$ = 2.1 Hz. The NMR spectrum also displayed a sharp singlet at δ 2.408 for methyl group protons.

The IR spectrum of compound **4b** (mp 140–142 °C) exhibited a strong absorption band at 1674 cm^{-1} due to C=O stretch and at 2129 cm^{-1} due to C≡C stretch. In the NMR spectrum of the **4b**, was seen a doublet at δ 7.814 (J_m = 2.4 Hz) for H-6′. The other two-benzenoid protons of benzoyl group showed the resonances at δ 7.504 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-4′) and at δ 7.056 (1H, d, J_0 = 8.4 Hz, H-3′). The NMR spectrum also showed two doublets at δ 7.352 (2H, J_0 = 8.4 Hz, H-2″, 6″) and at δ 6.945 (2H, J_0 = 8.4 Hz, H-3″, 5″), respectively. The two protons of oxirane ring were appeared as two distinct singlets at δ 4.332 (1H, s, H-2) and at δ 4.003 (1H, s, H-3). The propargyl group protons resonated at δ 4.489 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴) and δ 2.516 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴). The methyl group protons appeared as a sharp singlet at δ 2.394.

The structural scaffolding (Fig. 1) of these molecules **4(a–f)** inherently has propensity to offer the varied type of photochemistry through the δ- and β-hydrogen abstractions [24], direct cleavage of the oxirane ring [25] and inter-molecular cycloaddition reactions [26]. The electronic absorption spectra of these benzoyl oxiranes **4(a–f)** showed λ_{max} in the range of 315–320 nm (Fig. 2).

Therefore, the photolysis (Scheme 2) of the benzoyl oxiranes **4(a–f)** in dry benzene with pyrex filtered UV-light from 125W Hg lamp under nitrogen atmosphere was carried out which furnished the novel benzofurooxepinones **5(a–f)** in 67–81% yields. Also in some cases the hydroxyalkenones' derivatives **6(a, b, d, f)** were produced but the similar photoproducts from **4c** and **4e** could not be realized for these may have been produced in such minute amounts which escaped isolation in our hands. The photolysis of these substrates in THF furnished the photoproducts **5(a–f)** in 35–40% yields while in methanol no photoproduct was obtained.

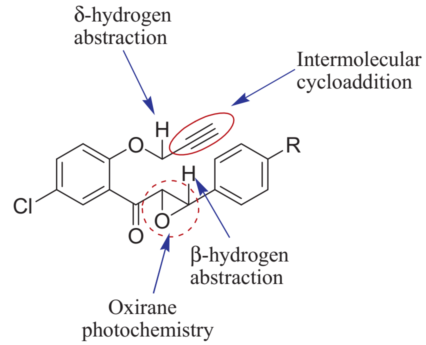


Fig. 1. Probable photochemical pathways of the substrates **4(a–f)**.

The structures of all the photoproducts formed were confirmed by the support of their spectral data (IR, ^1H NMR, ^{13}C NMR and mass, *etc.*). The compound **5b** (mp 218–219 °C) was white crystalline solid and showed IR absorption at 1612 cm^{-1} that may be assigned to the

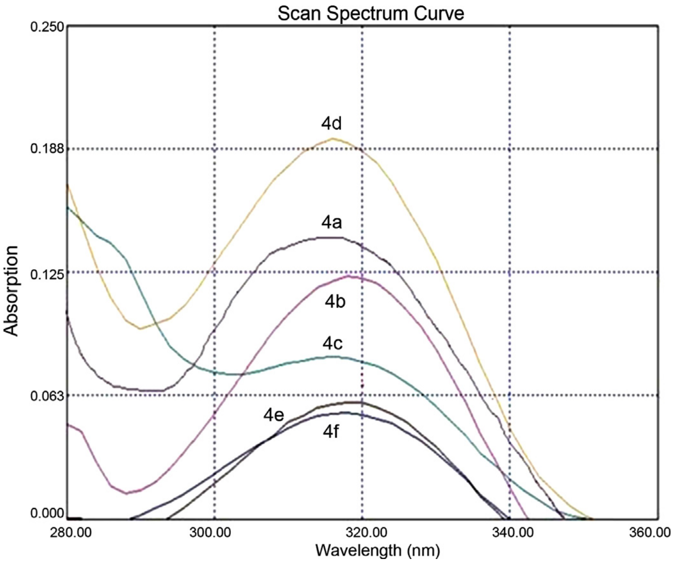
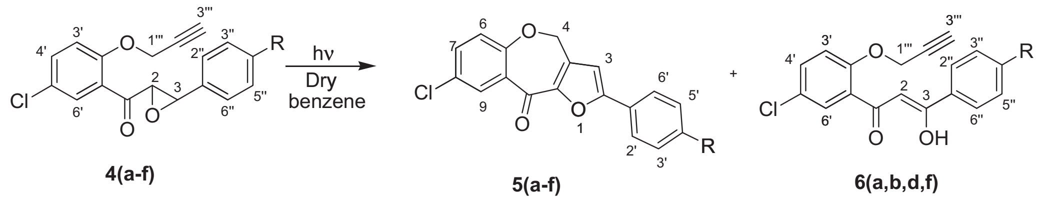


Fig. 2. Electronic absorption spectra of the substrates **4(a–f)**.



Scheme 2. Photolysis of benzoyl oxiranes **4(a–f)**.

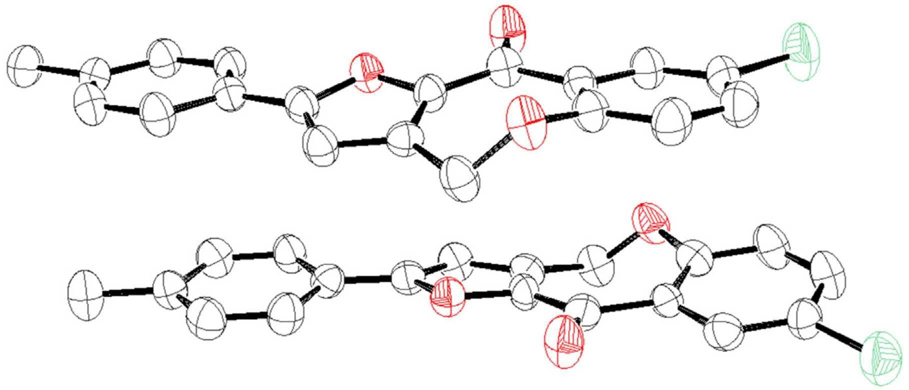


Fig. 3. Crystal structure of **5b** as determined by single crystal X-ray crystallography.

$C{=}O$ group of benzofurooxepinones. The peak due to absorption for $C{\equiv}C$ stretch at 2129 cm^{-1} present in the IR spectrum of **4b** was not be seen in IR spectrum of **5b** which indicates the involvement of the acetylene group in the photoproduct formation. In the ^{1}H NMR spectrum, three benzenoid protons were appeared at δ 8.185 (1H, d, $J_m = 2.4$ Hz, H-9), δ 7.471 (1H, dd, $J_0 = 8.1$ Hz, $J_m = 2.4$ Hz, H-7) and at δ 7.156 (1H, d, $J_0 = 8.1$ Hz, H-6). The two-oxepinone ring protons resonated at δ 5.140 (2H, s, H-4). The NMR spectrum also showed two doublets at δ 7.793 (2H, d, $J_0 = 7.8$ Hz, H-2′, 6′) and at δ 7.022 (2H, d, $J_0 = 7.8$ Hz, H-3′, 5′). A singlet at δ 6.703 may be well ascribed to the H-3 furyl proton. A three protons sharp singlet appeared at δ 2.422 for methyl group. The ^{13}C NMR spectrum of this photoproduct also corroborated the structure proposed. In order to firmly establish the structure of **5b**, it was further examined through single crystal X-ray crystallography [27]. There are two independent molecules in the asymmetric unit (Fig. 3).

The compound **6b** (mp 128–129 °C) was white crystalline solid and showed IR absorption at 3432 ($-$OH), 2150 ($C{\equiv}C$), 1713 ($C{=}O$) and 1605 ($C{=}C$). The acetylenic group remained intact during photolysis which was ascertained by the peak at 2150 cm^{-1}. The ^{1}H NMR spectrum showed three benzenoid protons at δ 7.900 (1H, d, $J_m = 2.4$ Hz, H-6′), δ 7.446 (1H, dd, $J_0 = 8.7$ Hz, $J_m = 2.4$ Hz, H-4′) and δ 7.184 (1H, d, $J_0 = 8.7$ Hz, H-3′). Two doublets were appeared at δ 7.959 (2H, d, $J_0 = 8.7$ Hz, H-2″, 6″) and δ 7.061 (2H, d, $J_0 = 8.7$ Hz, H-3″, 5″). The propargyl group protons resonated at δ 4.829 (2H, d, $J_{\text{allylic}} = 2.1$ Hz, H-1‴) and δ 2.448 (1H, d, $J_{\text{allylic}} = 2.1$ Hz, H-3‴). The alkenyl proton H-2 exhibited a singlet at δ 7.308. The methyl group protons appeared as a sharp singlet at δ 2.379.

The oxirane ring being 3-membered is highly strained and its photochemical cleavage has been observed earlier [28]. Therefore, its participation has been envisioned for the formation of photoproducts **5** and **6** from 2-{5-chloro-2-(prop-2-ynyloxy)benzoyl}-3-aryloxiranes. In the formation of **5**, it has been envisioned that the heterolytic C—C bond cleavage of the oxirane ring produces the carbonyl ylide intermediate **A** (see Scheme 3) that then cyclizes through [3+2] cycloaddition with ethynyl group to furnish **B**. Dehydrogenation of **B** *in situ* furnishes the oxepinones, the driving force being the formation of aromatic furan ring system. For the hydroxyalkenones **6**, the β-hydrogen abstraction by the carbonyl group of benzoyl moiety competes with C—C bond scission of the oxirane ring and generates the 1,3-biradical, **C**. This 1,3-biradical undergoes epoxide ring opening and affords 1,4-biradical, **D** which ultimately endowed us with the hydroxyalkenones **6(a, c, d, f)**.

The photolysis of these benzoyl oxiranes **4(a–f)** did not furnish the benzofurans and its derivatives like **7** and **8** expected through δ-hydrogen abstraction (Scheme 4) as were obtained from the photolysis of 1,5-bis(alkoxy)-2,4-dibenzoylbenzenes [29].

This may be because of the fact that the δ-hydrogen in **4(a–f)** is far away (5.078 Å, the average distance as R=H, CH_3, OCH_3, F, Cl, Br) from the carbonyl oxygen as is shown in energy-minimized MM2 structure (Fig. 4) and does not fall in the nodal plane of the carbonyl group, a prerequisite for H-abstraction. The products of inter-molecular cycloadditions were not obtained either.

This single-step process of benzofurooxepinones' synthesis appears to be very interesting as these products are obtained in good yields without the use of additional reagent (catalysts, *etc.*) and is thus novel and environmentally benign. The involvement of ethynyl in such an act of 7-membered heterocyclic ring formation is unprecedented. Our study shows the substantial complexity of the mechanism yielding different products. This process and its further exploration can lay a foundation for a clean route to synthesize many heterocyclic compounds which may simulate [23] the pharmaceutical activities.

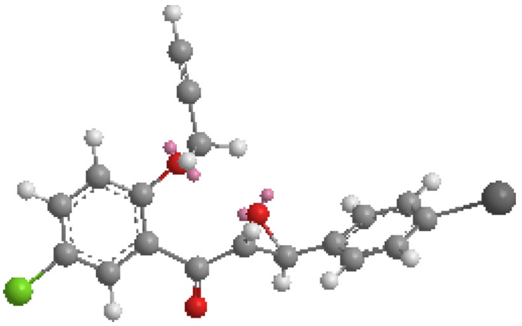
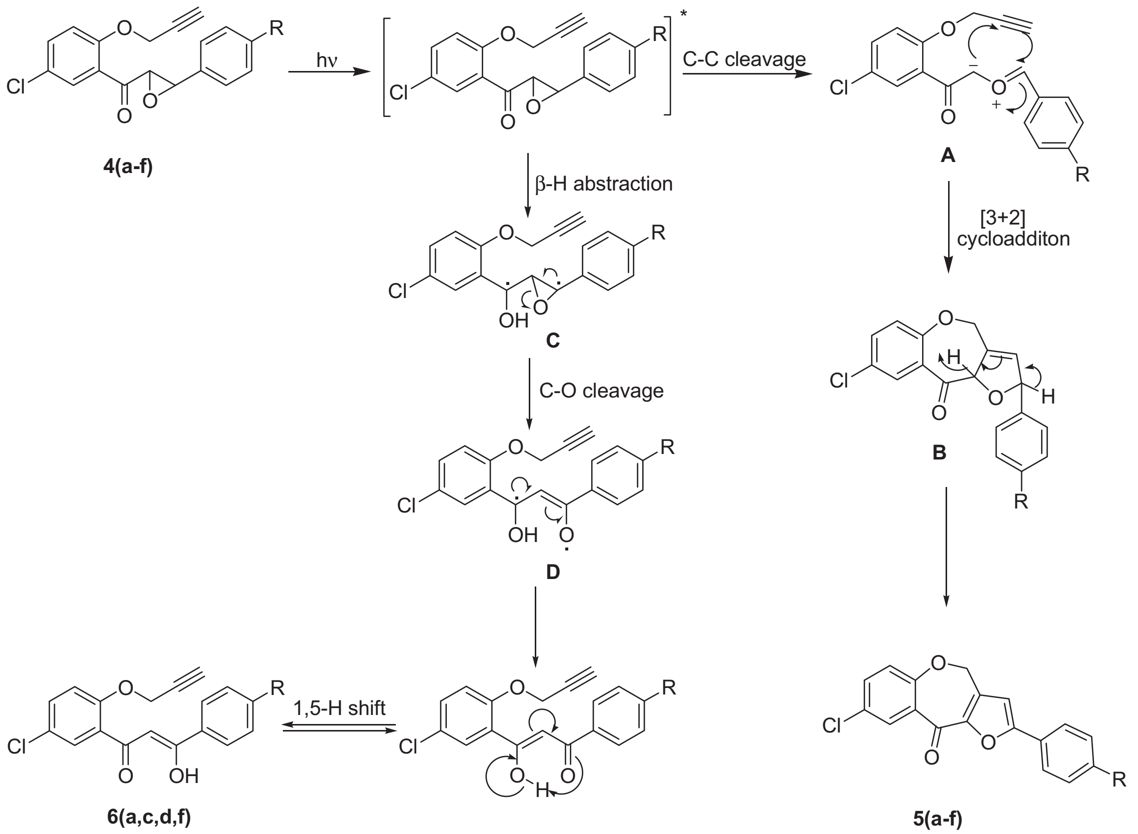
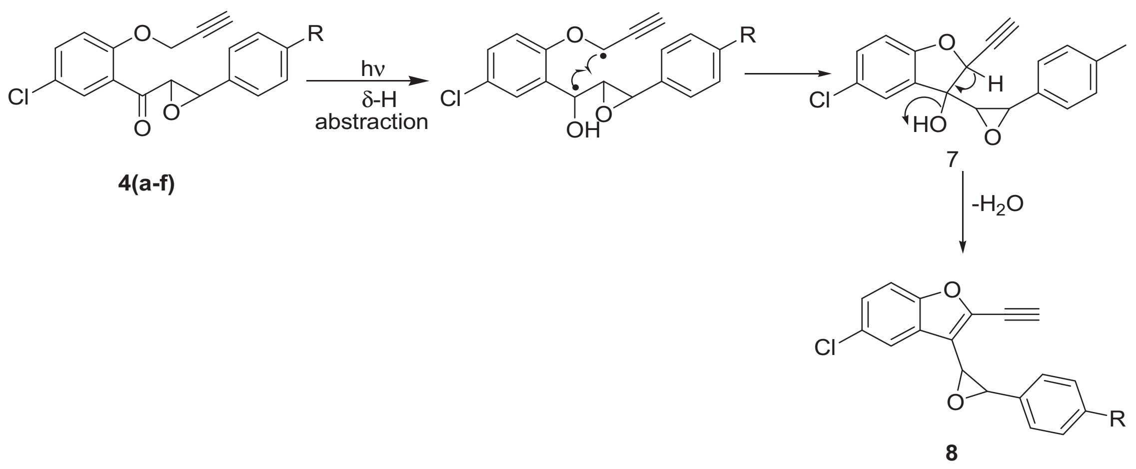


Fig. 4. Energy-minimized MM2 structure of benzoyl oxirane.



Scheme 3. Mechanism of photoproducts formation from benzoyl oxiranes.



Scheme 4.

3. Conclusion

In conclusion, the 2-{5-chloro-2-(prop-2-ynyloxy)benzoyl}-3-aryloxiranes were synthesized in high chemical yields and their photochemistry was investigated. Irradiation of these benzoyl oxiranes resulted in the development of a facile and new efficient synthesis of benzofurooxepine derivatives, which are structurally similar to some known pharmaceutically important compounds and thus may contribute immensely to the chemistry of heterocyclic compounds.

4. Experimental

4.1. General

The nuclear magnetic resonance ^{1}H NMR (300 MHz) and proton-decoupled ^{13}C NMR (75.4 MHz) spectra were recorded on Bruker spectrometer using TMS as internal standard. The infrared (IR) spectra were scanned in KBr pellets on a MB3000 FT-IR with HORIZON MB^{TM} FTIR software from ABB Bomen. The mass spectral data were obtained on WATERS, Q-TOF MICROMASS (LC–MS) spectrometer. Melting points were determined in open capillaries and are uncorrected. The photoirradiation of the deaerated solution of substrates was carried out using a pyrex filter under nitrogen atmosphere from 125 W Hg lamp. The columns for chromatographic separation were packed in pet. ether with silica gel and were eluted with pet. ether and ethyl acetate mixture (99:1). The X-ray crystallographic structure was collected on a Bruker Kappa APEX II diffractometer equipped with CCDC detector and sealed-tube monochromated Mo$K\alpha$ radiation using the program APEX2.

*4.2. General method for the synthesis of 5-chloro-2-(prop-2-ynyloxy)acetophenone **2***

The 5-chloro-2-hydroxyacetophenone **1** (0.01 mol), propargylbromide (0.01 mol), dry K_2CO_3 (1.0 g) and tetra-*n*-butylammonium iodide (50 mg) were refluxed in dry acetone (25 ml) for 3 h during which the color of reaction mixture changed from yellowish-brown to white. Filtration, evaporation of solvent and crystallization of the residue (MeOH) delivered **2**.

*4.2.1. 5-Chloro-2-(prop-2-ynyloxy)acetophenone **2***

Yield 87%, white solid, mp 58–60 °C; $\nu_{max}(cm^{-1})$: 2122 (C≡C), 1674 (C=O); $\delta_H(CDCl_3)$: 7.734 (1H, d, J_m = 2.4 Hz, H-6), 7.455 (1H, dd, J_0 = 8.7 Hz, J_m = 2.4 Hz, H-4), 7.061 (1H, d, J_0 = 8.7 Hz, H-3), 4.819 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1′), 2.579 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3′), 2.645 (3H, s, CH_3).

*4.3. General method for the synthesis of chalcones **3(a–f)***

To the well-stirred suspension of KOH (0.02 mol) in MeOH at 0 °C were added 5-chloro-2(prop-2-ynyloxy)acetophenone **2** (0.01 mol) and appropriate aldehyde (0.011 mol). The reaction mixture turned deep red in color after 30 min, and allowed to stir further for 3 h. Thereafter, it was poured over ice and neutralized with diluted HCl to obtain corresponding chalcone, which was crystallized from EtOH to give the shining needles.

4.3.1. 1-{5-Chloro-2-(prop-2-ynyloxy)phenyl}3-phenylprop-2-en-1-one

3a

Yield 88%, white solid, mp 92–93; $\nu_{max}(cm^{-1})$: 2126 (C≡C), 1643 (C=O); $\delta_H(CDCl_3)$: 7.648 (1H, d, J_{32} = 15.3 Hz, H-3), 7.617 (1H, d, J_m = 2.4 Hz, H-6′), 7.538 (2H, d, J_0 = 7.5 Hz, H-2″, 6″), 7.461 (1H, dd, J_0 = 8.7 Hz, J_m = 2.4 Hz, H-4′), 7.349 (1H, d, J_{23} = 15.3 Hz, H-2), 7.246 (3H, m, H-3″, 4″, 5″), 7.122 (1H, d, J_0 = 8.7 Hz, H-3′), 4.792 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 2.473 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴).

4.3.2. 1-{5-Chloro-2-(prop-2-ynyloxy)phenyl}-3-(p-tolyl)prop-2-en-1-one

3b

Yield 84%, white solid, mp 81–83 °C; $\nu_{max}(cm^{-1})$: 2127 (C≡C), 1643 (C=O); $\delta_H(CDCl_3)$: 7.646 (1H, d, J_{32} = 15.3 Hz, H-3), 7.608 (1H, d, J_m = 2.7 Hz, H-6′), 7.531 (2H, d, J_0 = 7.5 Hz, H-2″, 6″), 7.456 (1H, dd, J_0 = 8.7 Hz, J_m = 2.7 Hz, H-4′), 7.344 (1H, d, J_{23} = 15.3 Hz, H-2), 7.240 (2H, d, J_0 = 7.5 Hz, H-3″, 5″), 7.103 (1H, d, J_0 = 8.7 Hz, H-3′), 4.784 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 2.467 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴), 2.408 (3H, s, CH_3).

4.3.3. 1-{5-Chloro-2-(prop-2-ynyloxy)phenyl}-3-(4-methoxyphenyl)prop-2-en-1-one

3c

Yield 87%, creamish solid, mp 117–118 °C; $\nu_{max}(cm^{-1})$: 2126 (C≡C), 1643 (C=O); $\delta_H(CDCl_3)$: 7.628 (1H, d, J_{32} = 15.9 Hz, H-3), 7.603 (1H, d, J_m = 2.7 Hz, H-6′), 7.576 (2H, d, J_0 = 8.7 Hz, H-2″, 6″), 7.455 (1H, dd, J_0 = 8.7 Hz, J_m = 2.7 Hz, H-4′), 7.258 (1H, d, J_{23} = 15.9 Hz, H-2), 7.099 (1H, d, J_0 = 8.7 Hz, H-3′), 6.952 (2H, d, J_0 = 8.7 Hz, H-3″, 5″), 4.787 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 3.870 (3H, s, OCH_3), 2.555 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴).

4.3.4. 1-{5-Chloro-2-(prop-2-ynyloxy)phenyl}-3-(4-fluorophenyl)prop-2-en-1-one

3d

Yield 89%, white solid, mp 104–105 °C; $\nu_{max}(cm^{-1})$: 2150 (C≡C), 1651 (C=O); $\delta_H(CDCl_3)$: 7.631 (1H, d, J_{32} = 15.9 Hz, H-3), 7.592 (1H, d, J_m = 2.7 Hz, H-6′), 7.502 (2H, d, J_0 = 8.7 Hz, H-2″, 6″), 7.471 (1H, dd, J_0 = 8.7 Hz, J_m = 2.7 Hz, H-4′), 7.335 (1H, d, J_{23} = 15.9 Hz, H-2), 7.137 (1H, d, J_0 = 8.7 Hz, H-3′), 7.104 (2H, d, J_0 = 8.7 Hz, H-3″, 5″), 4.797 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 2.568 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴).

4.3.5. 1-{5-Chloro-2-(prop-2-ynyloxy)phenyl}-3-(4-chlorophenyl)prop-2-en-1-one

3e

Yield 87%, white solid, mp 101–103 °C; $\nu_{max}(cm^{-1})$: 2129 (C≡C),1643 (C=O); $\delta_H(CDCl_3)$: 7.634 (1H, d, J_{32} = 15.9 Hz, H-3), 7.568 (1H, d, J_m = 2.7 Hz, H-6′), 7.540 (2H, d, J_0 = 8.7 Hz, H-2″, 6″), 7.473 (1H, dd, J_0 = 8.7 Hz, J_m = 2.7 Hz, H-4′), 7.407 (1H, d, J_{23} = 15.9 Hz, H-2), 7.335 (1H, d, J_0 = 8.7 Hz, H-3′), 7.098 (2H, d, J_0 = 8.7 Hz, H-3″, 5″), 4.793 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 2.570 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴).

4.3.6. 1-{5-Chloro-2-(prop-2-ynyloxy)phenyl}-3-(4-bromophenyl)prop-2-en-1-one

3f

Yield 89%, white solid, mp 110–112 °C; $\nu_{max}(cm^{-1})$: 2150 (C≡C), 1651 (C=O); $\delta_H(CDCl_3)$: 7.637 (1H, d, J_{32} = 15.9 Hz, H-3), 7.562 (1H, d, J_m = 2.7 Hz, H-6′), 7.493 (1H, dd, J_0 = 8.7 Hz, J_m = 2.7 Hz, H-4′), 7.474 (2H, d, J_0 = 7.8 Hz, H-2″, 6″), 7.406 (1H, d, J_{23} = 15.9 Hz, H-2), 7.354 (1H, d, J_0 = 8.7 Hz, H-3′), 7.093 (2H, d, J_0 = 7.8 Hz, H-3″, 5″), 4.795 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 2.571 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴).

*4.4. General method for the synthesis of benzoyl oxiranes **4(a–f)***

To the well stirred suspension of compound **3** (0.005 mol) in methanol was added 10.0 ml of 20% aqueous KOH and cooled to 0 °C. To this mixture was added H_2O_2 (50%) drop-wise till a white solid began to appear. The reaction mixture was neutralized with ice-HCl to give white precipitates. The solid was filtered, dried and crystallized (EtOH) to give creamish crystals of benzoyl oxirane **4**.

4.4.1. 2-{5-Chloro-2-(prop-2-ynyloxy)benzoyl}-3-phenyloxirane

4a

Yield 84%, creamish white solid, mp 117–118; $\nu_{max}(cm^{-1})$: 2150 (C≡C), 1666 (C=O); $\delta_H(CDCl_3)$: 7.830 (1H, d, J_m = 2.4 Hz, H-6′), 7.505 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-4′), 7.236 (2H, d, J_0 = 8.4 Hz, H-2″, 6″), 7.036 (1H, d, J_0 = 8.4 Hz, H-3′), 7.019 (3H, m, H-3″, 4″, 5″), 4.478 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 4.343 (1H, s, H-2), 4.039 (1H, s, H-3), 2.367 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴); Anal. calcd. for $C_{18}H_{13}ClO_3$: C, 69.13; H, 4.19. Found: C, 69.06; H, 4.12.

*4.4.2. 2-{5-Chloro-2-(prop-2-ynyloxy)benzoyl}-3-(p-tolyl)oxirane **4b***

Yield 84%, white solid, mp 140–142 °C; $\nu_{max}(cm^{-1})$: 2129 (C≡C), 1674 (C=O); $\delta_H(CDCl_3)$: 7.814 (1H, d, J_m = 2.4 Hz, H-6′), 7.504 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-4′), 7.352 (2H, d, J_0 = 8.4 Hz, H-2″, 6″), 7.056 (1H, d, J_0 = 8.4 Hz, H-3′), 6.945 (2H, d, J_0 = 8.4 Hz, H-3″, 5″), 4.489 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴) 4.332 (1H, s, H-2), 4.003 (1H, s, H-3), 2.516 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴), 2.394 (3H, s, CH_3); Anal. calcd. for $C_{19}H_{15}ClO_3$: C, 69.84; H, 4.63. Found: C, 69.81; H, 3.67.

4.4.3. 2-{5-Chloro-2-(prop-2-ynyloxy)benzoyl}-3-(4-methoxyphenyl)oxirane

4c

Yield 82%, white solid, mp 128–130 °C; ν_{max}(cm^{-1}): 2129 (C≡C), 1674 (C═O); δ_H(CDCl$_3$): 7.820 (1H, d, J_m = 2.4 Hz, H-6′), 7.510 (1H, dd, J_0 = 8.7 Hz, J_m = 2.4 Hz, H-4′), 7.336 (2H, d, J_0 = 8.4 Hz, H-2″, 6″), 7.058 (1H, d, J_0 = 8.7 Hz, H-3′), 6.953 (2H, d, J_0 = 8.4 Hz, H-3″, 5″), 4.502 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 4.335 (1H, s, H-2), 3.990 (1H, s, H-3), 3.851 (3H, s, OCH_3), 2.410 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴); Anal. calcd. for $C_{19}H_{15}ClO_4$: C, 66.58; H, 4.41. Found: C, 69.54; H, 4.38.

4.4.4. 2-{5-Chloro-2-(prop-2-ynyloxy)benzoyl}-3-(4-fluorophenyl)oxirane

4d

Yield 85%, white solid, mp 111–113 °C; ν_{max}(cm^{-1}): 2129 (C≡C), 1674 (C═O); δ_H(CDCl$_3$): 7.642 (1H, d, J_m = 2.4 Hz, H-6′), 7.464 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-4′), 7.379 (2H, d, J_0 = 8.7 Hz, H-2′, 6′), 6.965 (1H, d, J_0 = 8.4 Hz, H-3′), 6.940 (2H, d, J_0 = 8.7 Hz, H-3′, 5′), 4.367 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 4.186 (1H, s, H-2), 3.865 (1H, s, H-3), 2.556 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴), Anal. calcd. for $C_{18}H_{12}ClFO_3$: C, 65.37; H, 3.66. Found: C, 65.43; H, 3.61.

4.4.5. 2-{5-Chloro-2-(prop-2-ynyloxy)benzoyl}-3-(4-chlorophenyl)oxirane

4e

Yield 85%, white solid, mp 118–120 °C; ν_{max}(cm^{-1}): 2129 (C≡C), 1674 (C═O); δ_H(CDCl$_3$): 7.708 (1H, d, J_m = 2.4 Hz, H-6′), 7.625 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-4′), 7.434 (2H, d, J_0 = 8.7 Hz, H-2″, 6″), 7.218 (1H, d, J_0 = 8.4 Hz, H-3′), 6.985 (2H, d, J_0 = 8.7 Hz, H-3″, 5″), 4.433 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 4.229 (1H, s, H-2), 3.918 (1H, s, H-3), 2.516 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴); Anal. calcd. for $C_{18}H_{12}Cl_2O_3$: C, 62.27; H, 3.48. Found: C, 62.25; H, 3.44.

4.4.6. 2-{5-Chloro-2-(prop-2-ynyloxy)benzoyl}-3-(4-bromophenyl)oxirane

4f

Yield 85%, white solid, mp 138–140 °C; ν_{max}(cm^{-1}): 2127 (C≡C), 1682 (C═O); δ_H(CDCl$_3$): 7.553 (1H, d, J_m = 2.4 Hz, H-6′), 7.340 (1H, dd, J_0 = 7.8 Hz, J_m = 2.4 Hz, H-4′), 7.314 (2H, d, J_0 = 8.7 Hz, H-2″, 6″), 7.083 (1H, d, J_0 = 7.8 Hz, H-3′), 6.882 (2H, d, J_0 = 8.7 Hz, H-3″, 5″), 4.311 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 4.116 (1H, s, H-2), 3.772 (1H, s, H-3), 2.381 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴); Anal. calcd. for $C_{18}H_{12}BrClO_3$: C, 55.20; H, 3.09. Found: C, 55.16; H, 3.03.

*4.5. Photolysis of benzoyl oxiranes **4(a–f)***

*4.5.1. Photolysis of 2-{5-chloro-2-(prop-2-ynyloxy)benzoyl}-3-phenyloxirane **4a***

A deoxygenated 1.0 mM solution in dry benzene of the benzoyl oxirane **4a** contained in a pyrex glass vessel was purged with nitrogen for 30 min and then irradiated under nitrogen atmosphere with light from a 125W Hg vapor lamp for 45 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 ethyl-acetate in pet. ether–ethyl acetate mixture to obtain photoproducts **5a** and **6a**.

*4.5.1.1. 8-Chloro-2-phenylbenzo[b]furo[2,3-e]oxepin-10(4H)-one **5a**.* Yield 73%, white solid, mp 183–185; ν_{max}(cm^{-1}): 1612 (C═O); δ_H(CDCl$_3$): 8.194 (1H, d, J_m = 2.4 Hz, H-9), 7.899 (2H, d, J_0 = 8.7 Hz, H-2′, 6′), 7.481 (1H, dd, J_0 = 8.7 Hz, J_m = 2.4 Hz, H-7), 7.162 (1H, d, J_0 = 8.7 Hz, H-6), 7.456 (3H, m, H-3′, 4′, 5′), 6.757 (1H, s, H-3), 5.153 (2H, s, H-4). δ_C(CDCl$_3$): 66.87, 105.02, 123.82, 125.55, 129.68, 130.33, 130.52, 130.59, 134.06, 136.46, 140.21, 148.68, 156.43, 160.35, 176.65. MS(ES+) *m*/*z*: 311, 313; Anal. calcd. for $C_{18}H_{11}ClO_3$: C, 69.58; H, 3.57. Found: C, 69.51; H, 3.52.

*4.5.1.2. 1-{5-Chloro-2-(prop-2-ynyloxy)phenyl}-3-hydroxy-3-phenylprop-2-en-1-one **6a**.* Yield 25%, white solid, mp 140–142 °C; ν_{max}(cm^{-1}): 3418 (—OH), 2150 (C≡C), 1713 (C═O), 1605 (C = C); δ_H(CDCl$_3$): 8.026 (2H, d, J_0 = 8.1 Hz, H-2″, 6″), 7.973 (1H, d, J_m = 2.4 Hz, H-6′), 7.520 (3H, m, H-3″, 4″, 5″), 7.456 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-4′), 7.209 (1H, s, H-2), 7.071 (1H, d, J_0 = 8.4 Hz, H-3′), 4.841 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 2.630 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴). δ_C(CDCl$_3$): 57.13, 99.24, 115.09, 115.36, 121.89, 126.27, 127.42, 127.67, 129.58, 129.62, 130.12, 132.29, 133.54, 153.46, 154.87, 181.22, 186.64. MS (ES+) *m*/*z*: 313.1, 315.1. Anal. calcd. for $C_{18}H_{13}ClO_3$: C, 69.13; H, 4.19. Found: C, 69.08; H, 4.13.

*4.5.2. Photolysis of 2-{5-chloro-2-(prop-2-ynyloxy)benzoyl}-3-(p-tolyl)oxirane **4b***

A 1.0 mM solution of **4b** in dry benzene on photolysis for 45 min furnished **5b** and **6b**.

*4.5.2.1. 8-Chloro-2-(p-tolyl)benzo[b]furo[2,3-e]oxepin-10(4H)-one **5b**.* Yield 72%, white solid, mp 218–219 °C; ν_{max}(cm^{-1}): 1612 (C═O); δ_H(CDCl$_3$): 8.185 (1H, d, J_m = 2.4 Hz, H-9), 7.793 (2H, d, J_0 = 7.8 Hz, H-2′, 6′), 7.471 (1H, dd, J_0 = 8.1 Hz, J_m = 2.4 Hz, H-7), 7.156 (1H, d, J_0 = 8.1 Hz, H-6), 7.022 (2H, d, J_0 = 7.8 Hz, H-3′, 5′), 6.703 (1H, s, H-3), 5.140 (2H, s, H-4), 2.422 (3H, s, CH_3). δ_C(CDCl$_3$): 21.51, 66.94, 105.03, 123.93, 125.52, 126.01, 129.69, 130.10, 130.32, 130.67, 134.17, 136.58, 140.39, 148.50, 156.58, 160.53, 176.62. MS (ES+) *m*/*z*: 325, 327; Anal. calcd. for $C_{19}H_{13}ClO_3$: C, 70.27; H, 4.03. Found: C, 70.19; H, 4.01.

*4.5.2.2. 1-{5-Chloro-2-(prop-2-ynyloxy)phenyl}-3-hydroxy-3-p-tolylprop-2-en-1-one **6b**.* Yield 24%, white solid, mp 128–129 °C; ν_{max}(cm^{-1}): 3432 (—OH), 2150 (C≡C), 1713 (C═O), 1605 (C = C); δ_H(CDCl$_3$): 7.959 (2H, d, J_0 = 8.7 Hz, H-2″, 6″), 7.900 (1H, d, J_m = 2.4 Hz, H-6′), 7.446 (1H, dd, J_0 = 8.7 Hz, J_m = 2.4 Hz, H-4′), 7.308 (1H, s, H-2), 7.184 (1H, d, J_0 = 8.7 Hz, H-3′), 7.061 (2H, d, J_0 = 8.7 Hz, H-3″, 5″), 4.829 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 2.448 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴), 2.379 (3H, s, CH_3). δ_C(CDCl$_3$): 21.61, 57.08, 98.42, 114.90, 122.53, 127.19, 127.38, 127.46, 129.33, 129.65, 130.13, 132.15, 133.00, 143.29, 154.84, 181.19, 186.56. MS (ES+) *m*/*z*: 327.1, 329.1. Anal. calcd. for $C_{19}H_{15}ClO_3$: C, 69.84; H, 4.63. Found: C, 69.79; H, 4.58.

4.5.3. Photolysis of 2-{5-chloro-2-(prop-2-ynyloxy)benzoyl}-3-(4-methoxyphenyl)oxirane

4c

A 1.0 mM solution of **4c** in dry benzene on photolysis for 45 min furnished only one photoproduct **5c**.

*4.5.3.1. 8-Chloro-2-(4′-methoxyphenyl)benzo[b]furo[2,3-e]oxepin-10(4H)-one **5c**.* Yield 79%, white solid, mp 194–196 °C; ν_{max}(cm^{-1}): 1612 (C═O); δ_H(CDCl$_3$): 8.189 (1H, d, J_m = 2.4 Hz, H-9), 7.846 (2H, d, J_0 = 8.7 Hz, H-2′, 6′), 7.467 (1H, dd, J_0 = 8.7 Hz, J_m = 2.4 Hz, H-7), 7.155 (1H, d, J_0 = 8.7 Hz, H-6), 7.050 (2H, d, J_0 = 8.7 Hz, H-3′, 5′), 6.628 (1H, s, H-3), 5.136 (2H, s, H-4), 3.890 (3H, s, OCH_3). δ_C(CDCl$_3$): 55.42, 66.83, 105.52, 113.91, 114.47, 122.23, 123.28, 124.50, 127.25, 130.42, 130.66, 132.74, 139.80, 160.62, 161.21, 168.39, 173.98. MS (ES+) *m*/*z*: 341, 343. Anal. calcd. for $C_{19}H_{13}ClO_4$: C, 66.97; H, 3.85. Found: C, 66.92; H, 3.76.

4.5.4. Photolysis of 2-{5-chloro-2-(prop-2-ynyloxy)benzoyl}-3-(4-fluorophenyl)oxirane ***4d***

A 1.0 mM solution of **4d** in dry benzene on photolysis for 45 min yielded **5d** and **6d**.

*4.5.4.1. 8-Chloro-2-(4′-fluorophenyl)benzo[b]furo[2,3-e]oxepin-10(4H)-one **5d**.* Yield 67%, white solid, mp 178–180 °C; ν_{max}(cm^{-1}): 1612 (C=O) δ_H(CDCl$_3$): 8.189 (1H, d, J_m = 2.7 Hz, H-9), 7.969 (2H, d, J_0 = 8.4 Hz, H-2′, 6′), 7.872 (2H, d, J_0 = 8.4 Hz, H-3′, 5′), 7.487 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-7), 7.202 (1H, d, J_0 = 8.4 Hz, H-6), 6.765 (1H, s, H-3), 5.154 (2H, s, H-4). δ_C(CDCl$_3$): 66.91, 105.13, 123.15, 125.33, 126.21, 129.48, 129.57, 130.03, 130.58, 134.17, 136.58, 149.67, 149.22, 156.32, 160.33, 176.54. MS (ES+) *m/z*: 329, 331. Anal. calcd. for $C_{18}H_{10}ClFO_3$: C, 65.77; H, 3.07. Found: C, 65.71; H, 3.00.

*4.5.4.2. 1-{5-Chloro-2-(prop-2-ynyloxy)phenyl}-3-hydroxy-3-(4′-fluorophenyl)prop-2-en-1-one **6d**.* Yield 29%, white solid, mp 121–122 °C; ν_{max}(cm^{-1}): 3418 (-OH), 2150 (C≡C), 1713 (C=O), 1605 (C = C); δ_H(CDCl$_3$): 8.029 (2H, d, J_0 = 8.7 Hz, H-2″, 6″), 7.972 (1H, d, J_m = 2.4 Hz, H-6′), 7.456 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-4′), 7.355 (1H, s, H-2), 7.176 (2H, d, J_0 = 8.7 Hz, H-3″, 5″), 7.064 (1H, d, J_0 = 8.4 Hz, H-3′), 4.839 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 2.637 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴). δ_C(CDCl$_3$): 57.21, 99.33, 115.34, 115.82, 127.22, 127.44, 127.78, 129.82, 129.91, 130.25, 132.32, 133.56, 154.35, 155.02, 181.47, 186.71. MS (ES+) *m/z*: 331.1, 333.1. Anal. calcd. for $C_{18}H_{12}ClFO_3$: C, 65.37; H, 3.66. Found: C, 65.32; H, 3.63.

4.5.5. Photolysis of 2-{5-chloro-2-(prop-2-ynyloxy)benzoyl}-3-(4-chlorophenyl)oxirane ***4e***

A 1.0 mM solution of **4e** in dry benzene on photolysis for 45 min gave only one photoproduct **5e**.

*4.5.5.1. 8-Chloro-2-(4′-chlorophenyl)benzo[b]furo[2,3-e]oxepin-10(4H)-one **5e**.* Yield 81%, white solid, mp 240–242 °C; ν_{max}(cm^{-1}): 1612 (C=O); δ_H(CDCl$_3$): 8.179 (1H, d, J_m = 2.4 Hz, H-9), 7.830 (2H, d, J_0 = 8.1 Hz, H-2′, 6′), 7.465 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-7), 7.444 (2H, d, J_0 = 8.1 Hz, H-3′, 5′), 7.164 (1H, d, J_0 = 8.4 Hz, H-6), 6.748 (1H, s, H-3), 5.148 (2H, s, H-4). δ_C(CDCl$_3$): 66.80, 105.90, 119.28, 123.97, 126.72, 126.87, 129.30, 129.62, 130.20, 130.53, 130.68, 134.37, 136.23, 159.13, 160.54, 177.47. MS (ES+) *m/z*: 345, 347, 349. Anal. calcd. for $C_{18}H_{10}ClFO_3$: C, 65.77; H, 3.07. Found: C, 65.71; H, 3.02.

4.5.6. Photolysis of 2-{5-chloro-2-(prop-2-ynyloxy)benzoyl}-3-(4-bromophenyl)oxirane ***4f***

A 1.0 mM solution of **4f** in dry benzene on photolysis for 45 min resulted in the formation of **5f** and **6f**.

*4.5.6.1. 8-Chloro-2-(4′-bromophenyl)benzo[b]furo[2,3-e]oxepin-10(4H)-one **5f**.* Yield 74%, white solid, mp 128–130 °C; ν_{max}(cm^{-1}): 1620 (C=O); δ_H(CDCl$_3$): 8.187 (1H, d, J_m = 2.7 Hz, H-9), 7.766 (2H, d, J_0 = 8.4 Hz, H-2′, 6′), 7.629 (2H, d, J_0 = 8.4 Hz, H-3′, 5′), 7.494 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-7), 7.165 (1H, d, J_0 = 8.4 Hz, H-6), 6.760 (1H, s, H-3), 5.150 (2H, s, H-4). δ_C(CDCl$_3$): 66.92, 105.94, 119.35, 124.57, 126.87, 127.65, 129.83, 130.02, 130.26, 131.12, 131.58, 134.68, 136.63, 159.52, 160.78, 178.31. MS (ES+) *m/z*: 389, 391, 393. Anal. calcd. for $C_{18}H_{10}BrClO_3$: C, 55.49; H, 2.59. Found: C, 55.41; H, 2.50.

*4.5.6.2. 1-{5-Chloro-2-(prop-2-ynyloxy)phenyl}-3-hydroxy-3-(4′-bromophenyl)prop-2-en-1-one **6f**.* Yield 21%, white solid, mp 76–78 °C; ν_{max}(cm^{-1}): 3479 (-OH), 2150 (C≡C), 1713 (C=O), 1605 (C=C); δ_H(CDCl$_3$): 7.604 (2H, d, J_0 = 8.1 Hz, H-2″, 6″), 7.500 (1H, d, J_m = 2.4 Hz, H-6′), 7.472 (2H, d, J_0 = 8.1 Hz, H-3″, 5″), 7.168 (1H, s, H-2), 6.938 (1H, dd, J_0 = 8.4 Hz, J_m = 2.4 Hz, H-4′), 6.721 (1H, d, J_0 = 8.4 Hz, H-3′), 4.787 (2H, d, $J_{allylic}$ = 2.1 Hz, H-1‴), 2.591 (1H, d, $J_{allylic}$ = 2.1 Hz, H-3‴). δ_C(CDCl$_3$): 57.13, 99.24, 115.09, 115.36, 121.89, 126.27, 127.42, 127.67, 129.58, 129.62, 130.12, 132.29, 133.54, 153.46, 154.87, 181.22, 186.64. MS (ES+) *m/z*: 391.0, 393.0, 395.0. Anal. calcd. for $C_{18}H_{12}BrClO_3$: C, 55.20; H, 3.09. Found: C, 55.16; H, 3.03.

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[27] The structure of **5b** was collected on a Bruker Kappa APEX II diffractometer equipped with CCDC detector and sealed-tube monochromated Mo$K\alpha$ radiation using the program APEX2. It crystallizes in the triclinic space group P-1 with cell dimensions a = 8.389(3) Å, b = 12.553(4) Å, c = 14.932(5) Å, α = 71.89(2)°, β = 83.41(2)°, γ = 87.82(2)°, Volume = 1484.7(8) Å^3, and Z = 4. A total of 18,377 reflections were measured to a maximum θ angle of 25.06° (0.84 Å resolution), of which 5128 were independent (R_{int} = 7.66%, R_{sig} = 10.73%) and 2404 were greater than $2\sigma(F^2)$. The structure was solved and refined using the Bruker SHELXTL Software Package, with final anisotropic full-matrix least-squares refinement on F^2 with 417 variables converging to R1 = 4.79%, for the observed data and wR2 = 9.24% for all data. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters. The goodness-of-fit was 0.884. The largest peak in the final difference electron density synthesis was 0.217 e$^-$/Å^3 and the largest hole was −0.271 e$^-$/Å^3. Crystallographic data for the structure of **5b** have been deposited in the Cambridge Crystallographic Data Centre (deposition number: CCDC 958448). Copies of these data can be obtained free of charge *via* the internet at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK. Fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk/).

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