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Photo-transformations of 6-chloro-3-propargyloxy-2-aryl-4-oxo-4*H*-1-benzopyran: 1,4-hydrogen abstraction in propargylethers

Mandeep Thakur, Surinder Berar, Urmila Berar, Surinder Arora,
Satish C. Gupta, Ramesh C. Kamboj *

Department of Chemistry, Kurukshetra University, Kurukshetra 136 119, Haryana, India

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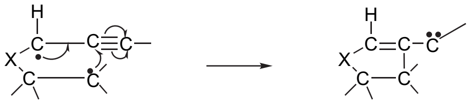
ABSTRACT

1,4-Biradicals generated in the Norrish type-II reactions of 3-propargyloxy-2-arylchromones lead to cyclic products involving the 2-aryl group. The formation and distribution of products varied with the nature of 2-aryl group.

1. Introduction

Intramolecular hydrogen-abstractions by the photoexcited C=O group have found several synthetic applications[1,2] including synthesis of many exotic molecules, which otherwise would not have been possible to obtain through thermal modes. Vinyl ethers,[3] spiropyrans,[4] both linear and angular polycyclics,[5,6] lactams and many other systems have been synthesised using this method. 3-Alkoxy-2-aryl(phenyl/thiophene/furan)chromones on photoirradiation undergo cyclisation to angular tetracyclic products. The product formation depends upon the nature of 3-alkoxy group and occurs through the formation of 1,4-biradical[7,8] via type-II H-abstraction process from the 3-alkoxy moiety by the photoexcited C=O group. Recently, Agosta and Margaretha[9] have investigated the 1,5-cyclisation of alkylpropargyl-1,4-biradicals and have been able to obtain products of sufficient chemical and mechanistic importance. The exceptional behaviour of propargyl 1,4-biradicals to form photoproducts via unsaturated carbenes[10,11] (Scheme 1) has prompted us to investigate the photochemistry of chromones containing propargyl group.



Scheme 1. Cyclisation of triplet alkylpropargyl biradical.

In the present article, we report the results of our investigations on the photoreactions of 3-propargyloxychromones bearing phenyl/thienyl/furyl at C-2 position. The purpose of work is threefold: (i) to determine the potential utility of the photoinduced intramolecular hydrogen transfer for the synthesis of polycyclics; (ii) to learn more about the fate of propargyl radical specially in comparison to that of allyl and benzyl radical already studied[3,12] and (iii) to study the exceptional behaviour of propargyl 1,4-biradicals to form photoproducts via unsaturated carbenes in the chromone systems.

2. Results and discussion

The propargylethers **2**(**a**–**f**) were obtained by reacting 3-hydroxybenzopyrans[12] **1**(**a**–**f**) with propargyl bromide in dry acetone as solvent (Scheme 2).

The propargyloxychromones **2a** and **2b** on photoirradiation with Pyrex filtered light from a 125 W Hg lamp in dry benzene furnished cyclised products **3a**, **4a** and **3b**, **4b** (Scheme 3), respectively. Inspite of our best efforts, compound **3a** could not be isolated in pure form and its structure was derived from the NMR data of the reaction mixture enriched in **3a**.

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* Corresponding author. Tel.: +91 1744 238466; fax: +91 1744 238277.
E-mail address: rckamboj@rediffmail.com (R.C. Kamboj).

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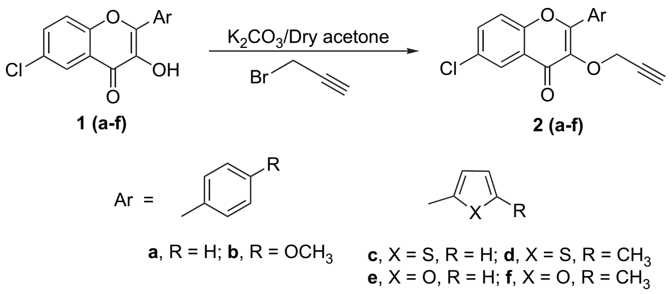
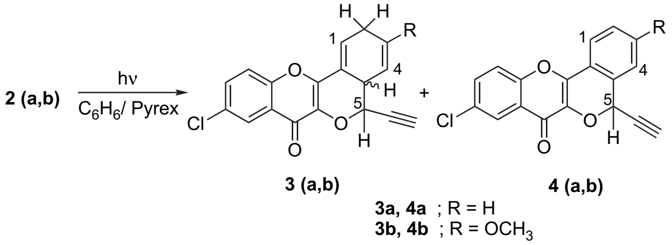
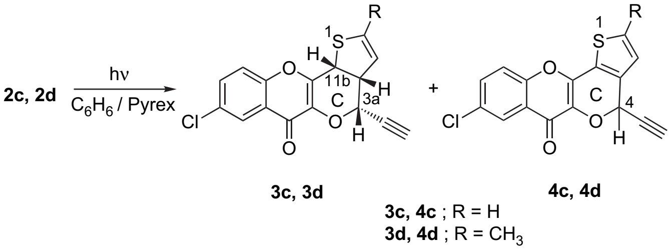


Scheme 2. Synthesis of propargylethers **2**(**a**–**f**).



Scheme 3. Photolysis of compounds **2a** and **2b**.

The other chromones **2c** and **2d** under similar photolytic conditions produced **3c**, **4c** and **3d**, **4d**, respectively, in 20–40% yields (Scheme 4).



Scheme 4. Photolysis of compounds **2c** and **2d**.

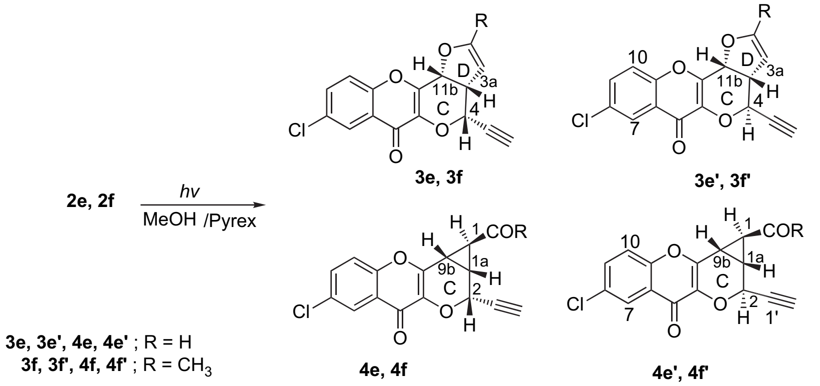
The photolysis of **2e** in methanolic solution (0.001 M) with Pyrex filtered UV light exhibited the complete disappearance (TLC) of **2e** in 40 min. A chromatographic separation produced two compounds **3e** and **4e** along with their stereoisomers **3e′** and **4e′**. Similarly tetracyclics **3f**, **4f** and **3f′**, **4f′** were the result of photolysis of compound **2f** (Scheme 5).

Regarding mechanistic considerations the primary photochemical process can be rationalised as the γ-H abstraction from propargyl group by the excited C=O group of the pyrone moiety to produce 1,4-biradical as analogously reported in earlier reports[12] (Scheme 6). The formation of **3c**, **3d**, **3e**, **3e′**, **3f**, **3f′** is through coupling of biradical followed by 1,5-H migration whereas in case of **3a**, **3b** it is 1,7-H migration. The fact that the photoproducts **4b** and **4d** are formed independently[8,13] from **2c** and **2d** and not via **3c** and **3d** was confirmed from the photoirradiation of **3c** when only polymeric products were obtained.

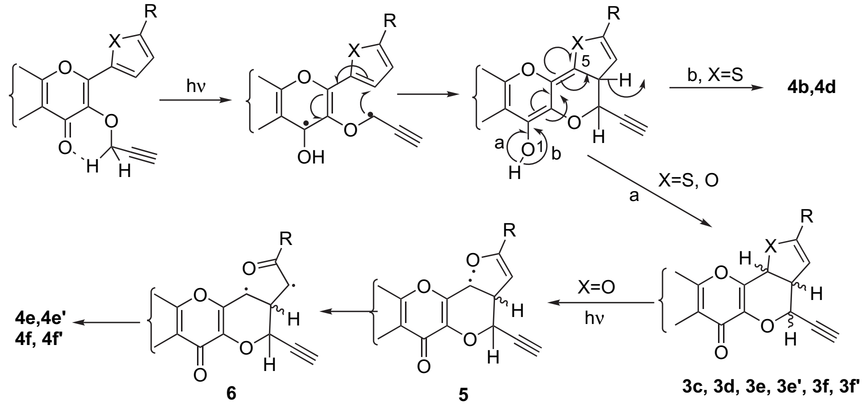
The primary photoproducts **3e** and **3e′** obtained from compound **2e** under the photolytic conditions may then undergo a ring contraction–ring expansion process[14] to produce biradical intermediate **5**, which through the intervention of mesomeric biradical **6** can give the cyclopropanecarboxaldehydes **4e** and **4e′**. Such a conversion was also supported by the further photolysis of pure isolated **3f** under the reaction conditions, which produced **4f**. The proposed mechanism obtains support from a similar observation of Francis and Sherwood[15] and Scribe and co-workers.[16] Here, no photoproduct via unsaturated carbene intermediate[10,11] could be realised possibly because of the more favourable coupling of the initially formed propargyl radical with the 2-aryl moiety present in the chromone.

The structures of benzopyrans **2**(**a**–**f**) and their photoproducts were found to be consistent with their spectral parameters (vide Section 4). Wherever needed the ^{1}H NMR assignments were brought out by decoupling experiments and stereo-chemical elucidations by J/Φ relationships. The C/D ring junction is cis-fused in **3c**, **3d**, **3e**, **3e′**, **3f** and **3f′**, is born out by the fact that $J_{3a,11b}$ is 8.0 Hz (**3c**),[17] which shows cis orientation of these protons. In the investigations on many naturally occurring *N*-heterocycles, Wooten and co-workers[18] in their exhaustive studies using various spectral techniques found bridgehead protons to be cis with J=7.0 Hz. In compounds **3c**, **3d**, **3e** and **3f**, $J_{3a,4}$=8.0 Hz for H-3a and H-4 protons show them to be cis, which is in accordance with the earlier observations,[12] thus placing the –C≡CH group in Ψ-equatorial conformation on half chair conformation of ring C. Further in photoproducts **3e′** and **3f′**, the orientation of H-3a, H-4 is trans ($J_{3a,4}$=4.2 Hz) with –C≡CH group in Ψ-axial conformation showing stereoisomeric relationship with **3e** and **3e′**. The MM2 energy minimised structures of compounds **3e** and **3e′** are shown in Figure 1, which also corroborate the above findings about the stereochemistry.

A 300 MHz ^{1}H NMR spectrum of **4e** showed resonances at δ 9.82 (1H, d, J=2.4 Hz, C*H*O), 3.15 (1H, d{dd}, H-1), 2.84 (1H, d{dd}, H-1a) and 2.76 (1H, dd, H-9b). Decoupling of the doublet at δ 9.82 converted d{dd} at δ 3.15 (H-1) into quartet (J=3.6, 4.8 Hz) and conversely, irradiation of the signal at δ 3.15 converted the d{dd} due to H-1a to a quartet (J=1.8, 9.0 Hz) and the dd due to H-9b to a doublet (J=9.0 Hz). The coupling $J_{1,9b}$=3.6 Hz, $J_{1,1a}$=4.8 Hz and $J_{9b,1a}$=9.0 Hz values established that H-9b and H-1a are cis to each other and that H-1 is trans to both H-9b and H-1a. These findings correlate well with the studies made by Dauben and Wipke.[19] The upfield shift (~0.55 ppm) in δ value of H-1 than that observed by



Scheme 5. Photolysis of compounds **2e** and **2f**.



Scheme 6. Mechanism of photoproduct formation.

Padwa and Koehn[20] in cyclopropanecarboxaldehydes fused to cyclohexanes (δ_H 2.60) has brought out boat conformation of pyran ring C with minimal separation between H-1 and one of the sp^3 orbitals of oxygen (of pyran). The signal at δ 4.75, which could be assigned to H-2 has $J_{2,1a}=1.8$ Hz implying $\Phi_{2,1a}\sim60°$ and Ψ-equatorial position of –C≡CH[12] (Fig 2).

Of principal significance here was that compound **4e**′ has H-2 proton of pyran ring at much downfield (δ 5.22) and there was absence of $J_{2,1a}$ ($\Phi_{2,1a}\sim90°$). Both these observations support that –C≡CH is Ψ-axial with H-2 in its deshielding zone. The carbon skeleton of compounds **3e**, **3e**′, **4e**, **4e**′, **4f** and **4f**′ was further confirmed from their fully proton decoupled ^{13}C NMR spectra (see Section 4).

Regarding the effect of substituent at C-2 of the pyran ring in **2**(**a**–**f**) in product formation/distribution, an examination of Table 1 shows that in case of furyl chromones **2e** and **2f** only the photocyclised products are obtained. In others (phenyl, thiophene) the photocyclised (**A**) and photodehydrogenated (**B**) products are formed. For such difference, the only assignable reason could be the difference in electron density on the ring moiety at C-2. As the electron density on the ring at C-2 decreases from furyl to phenyl, the formation of cyclodehydrogenated product becomes prominent. It is possible that as shown in scheme, the transfer of hydrogen to the ring junction (at 11b) is assisted and this becomes faster than cleavage of H-3a leading to dehydrogenated products. An alternative explanation may be the different degree of aromaticity. The aromatic character increases from furan via thiophene to benzene. Consequently, the gain in energy by dehydrogenation is higher in the case of **4a** and **4b**, which may explain the predominant formation of these products. The dehydrogenation re-establishes aromaticity. Since the aromatic character is less expressed in the case of thiophene, the dehydrogenation is less dominant in these cases (**4c**, **4d**). Obviously, the low aromatic character of furan is insufficient to favour formation of dehydrogenation products.

Table 1

Compound	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
Ratio of **A**/**B**[a]	1:2	1:2	1:1.5	1:1.2	1:0	1:0

[a] Ratio calculated from isolated yields.

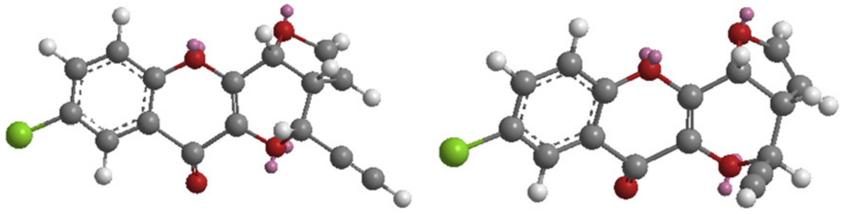

3e **3e'**

Figure 1. MM2 energy minimised structure of compounds **3e** and **3e**′.

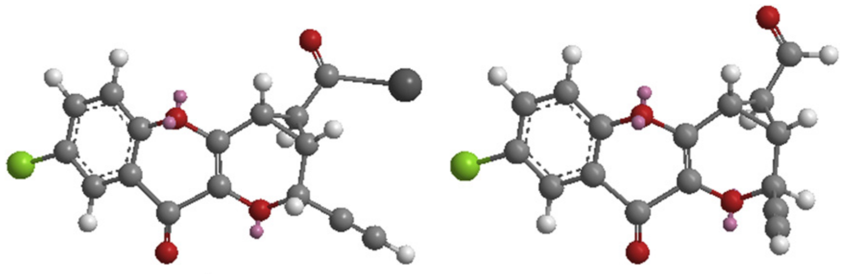

4e **4e'**

Figure 2. MM2 energy minimised structure of compounds **4e** and **4e**′.

3. Conclusion

Hydrogen abstraction from the 3-propargyloxy group by the C=O is the preferred reaction pathway for the formation of photoproducts and it is concluded that the formation and distribution of the tetracyclic products from 6-chloro-3-propargyloxy-2-aryl-4-oxo-4*H*-1-benzopyrans depend upon the 2-aryl moiety. The propargyl radical undergoes only cyclisation similar to allyl and benzyl radicals and no photoproduct formation through unsaturated carbene occurred.

4. Experimental

4.1. General

IR spectra were recorded on a Buck Scientific 500 spectrophotometer using KBr pellets. ^{1}H NMR spectra were recorded on a 300 MHz Bruker spectrometer using TMS as internal standard. Mass spectra were recorded at 70 eV. Elemental analysis was carried on Perkin Elmer 2400 instrument. Melting points were determined in open capillaries and are thus uncorrected. TLC plates were coated with silica gel G (suspended in $CHCl_3$–MeOH) and iodine vapours were used as visualising agent. The columns for purification were packed with Silica gel 100–200 mesh in pet. ether–benzene (9:1) and left overnight before use. The elution was carried out with increasing proportion of benzene in pet. ether–benzene mixture. The yields reported are calculated by excluding the recovered starting compound.

4.2. General method for the synthesis of 6-chloro-3-propargyloxy-2-phenyl-4-oxo-4*H*-1-benzopyran, 2a

The 3-hydroxychromone, **1a** (2.50 g, 0.01 mol), propargyl bromide (1.2 g, 0.01 mol), dry K_2CO_3 (1.0 g) and tetra-*n*-butylammonium iodide (100 mg) were refluxed in dry acetone (50 ml) for 2 h. Filtration, evaporation of solvent and crystallisation of the residue from methanol gave **2a**.

The other ethers **2**(**b**–**f**) were synthesised by using this procedure starting from compounds **1**(**b**–**f**), respectively.

4.2.1. Compound **2a**

Yield 80%, white solid; mp 112–114 °C; ν_{max} (cm^{-1}) 2112 (C≡C), 1630 (C=O); δ_H ($CDCl_3$) 8.22 (1H, d, J_m=2.4 Hz, H-5), 8.11 (2H, m, H-2′, 6′), 7.62 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-7), 7.54–7.49 (4H, m, H-3′, 4′, 5′, 8), 4.99 (2H, d, J=2.7 Hz, H-1″), 2.32 (1H, t, J=2.7 Hz, H-3″). Anal. Calcd for $C_{18}H_{11}ClO_3$: C, 69.58; H, 3.57. Found: C, 69.47; H, 3.55.

4.2.2. Compound **2b**

Yield 78%, white solid; mp 116–118 °C; ν_{max} (cm^{-1}) 2110 (C≡C), 1626 (C=O); δ_H ($CDCl_3$) 8.20 (1H, d, J_m=2.4 Hz, H-5), 8.14 (2H, t{d}, J=2.4, 8.1 Hz, H-2′, 6′), 7.60 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-7), 7.48 (1H, d, J_o=9.0 Hz, H-8), 7.02 (2H, t{d}, J=2.4, 8.1 Hz, H-3′, 5′), 4.97 (2H, d, J=2.4 Hz, H-1″), 3.90 (3H, s, 4′-OCH_3), 2.33 (1H, t, J=2.4 Hz, H-3″). Anal. Calcd for $C_{19}H_{13}ClO_4$: C, 66.97; H, 3.85. Found: C, 66.79; H, 3.80.

4.2.3. Compound **2c**

Yield 80%, white solid; mp 138–140 °C; ν_{max} (cm^{-1}) 2114 (C≡C), 1644 (C=O); δ_H ($CDCl_3$) 8.18 (1H, d, J_m=2.4 Hz, H-5), 8.01 (1H, dd, $J_{3',5'}$=1.2 Hz, $J_{3',4'}$=3.6 Hz, H-3′), 7.66 (1H, dd, $J_{5',3'}$=1.2 Hz, $J_{5',4'}$=5.1 Hz, H-5′), 7.61 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-7), 7.50 (1H, d, J_o=9.0 Hz, H-8), 7.22 (1H, dd, $J_{4',3'}$=3.6 Hz, $J_{4',5'}$=5.1 Hz, H-4′), 5.17 (2H, d, J=2.4 Hz, H-1″), 2.41 (1H, t, J=2.4 Hz, H-3″). Anal. Calcd for $C_{16}H_9ClO_3S$: C, 60.67; H, 2.86. Found: C, 60.75; H, 2.87.

4.2.4. Compound **2d**

Yield 70%, white solid; mp 142–144 °C; ν_{max} (cm^{-1}) 2112 (C≡C), 1628 (C=O); δ_H ($CDCl_3$) 8.18 (1H, d, J_m=2.4 Hz, H-5), 7.83 (1H, d, $J_{3',4'}$=3.9 Hz, H-3′), 7.59 (1H, dd, $J_{m,o}$=2.4, 8.7 Hz, H-7), 7.47 (1H, d, J_o=8.7 Hz, H-8), 6.89 (1H, d, $J_{4',3'}$=3.9 Hz, H-4′), 5.14 (2H, d, J=2.1 Hz, H-1″), 2.59 (3H, s, 5′-CH_3), 2.41 (1H, t, J=2.1 Hz, H-3″). Anal. Calcd for $C_{17}H_{11}ClO_3S$: C, 61.73; H, 3.35. Found: C, 61.65; H, 3.33.

4.2.5. Compound **2e**

Yield 63%, white solid; mp 151–152 °C; ν_{max} (cm^{-1}) 2127 (C≡C), 1656 (C=O); δ_H ($CDCl_3$) 8.19 (1H, d, J_m=2.4 Hz, H-5), 7.72 (1H, d, $J_{5',4'}$=1.8 Hz, H-5′), 7.62 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-7), 7.53 (1H, d, J_o=9.0 Hz, H-8), 7.44 (1H, d, $J_{3',4'}$=3.6 Hz, H-3′), 6.64 (1H, dd, $J_{4',5'}$=1.8 Hz, $J_{4',3'}$=3.6 Hz, H-4′), 5.10 (2H, d, J=2.4 Hz, H-1″), 2.42 (1H, t, J=2.4 Hz, H-3″). Anal. Calcd for $C_{16}H_9ClO_4$: C, 63.91; H, 3.02. Found: C, 63.79; H, 3.00.

4.2.6. Compound **2f**

Yield 70%, white solid; mp 154–156 °C; ν_{max} (cm^{-1}) 2113 (C≡C), 1628 (C=O); δ_H ($CDCl_3$) 8.18 (1H, d, J_m=2.4 Hz, H-5), 7.60 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-7), 7.53 (1H, d, J_o=9.0 Hz, H-8), 7.44 (1H, d, $J_{3',4'}$=3.6 Hz, H-3′), 6.25 (1H, d, $J_{4',3'}$=3.6 Hz, H-4′), 5.06 (2H, d, J=2.4 Hz, H-1″), 2.42 (1H, t, J=2.4 Hz, H-3″), 2.40 (3H, s, 5′-CH_3). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.88; H, 3.52. Found: C, 64.87; H, 3.55.

4.3. Photolysis of 6-chloro-3-propargyloxy-2-phenyl-4-oxo-4*H*-1-benzopyran, 2a

General procedure: A deoxygenated solution of chromone **2a** (200 mg) in dry thiophene free benzene (150 ml) was refluxed for 5 min. The solution was out-gassed with nitrogen for 1 h and then irradiated in a Pyrex reactor under nitrogen atmosphere for 40 min with a 125 W Hg vapour lamp. The removal of solvent under reduced pressure yielded a red gummy mass that was chromatographed over a column of silica gel to yield **3a** and **4a**.

Other compounds **2b**, **2c** and **2d** were also photolysed by following the same procedure to yield respective products. The compounds **2e** and **2f** were photolysed in magnesium-dried methanol solvent with rest of conditions being the same.

4.3.1. Compound **3a**

Yield 20% (calculated from NMR spectrum of mixture); R_f 0.59 (2% ethyl acetate in benzene); ν_{max} (cm^{-1}) 2112 (C≡C), 1640 (C=O); δ_H ($CDCl_3$) 8.23 (1H, d, J_m=2.7 Hz, H-8), 7.61 (1H, dd, $J_{m,o}$=2.7, 8.7 Hz, H-10), 7.42 (1H, d, J_o=8.7 Hz, H-11), 6.67 (1H, br s, H-1), 6.01 (2H, br s, H-3, 4), 4.45 (1H, dd, J=2.1, 11.1 Hz, H-5), 3.31 (1H, m, H-4a), 3.02 (2H, m, H-2), 2.65 (1H, d, J=2.1 Hz, H-2′).

4.3.2. Compound **4a**

Yield 35%, white solid; R_f 0.59 (2% ethyl acetate in benzene); mp 238–240 °C; ν_{max} (cm^{-1}) 2120 (C≡C), 1640 (C=O); δ_H ($CDCl_3$) 8.29 (1H, d, J_m=2.7 Hz, H-8), 7.91 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-1), 7.65 (1H, dd, $J_{m,o}$=2.7, 8.7 Hz, H-10), 7.59 (2H, m, H-2, 3), 7.47 (1H, d, J=8.7 Hz, H-11), 7.41 (1H, dd, $J_{m,o}$=2.7, 8.7 Hz, H-4), 4.46 (1H, d, J=2.1 Hz, H-5), 2.65 (1H, d, J=2.1 Hz, H-2′). Anal. Calcd for $C_{18}H_9ClO_3$: C, 70.03; H, 2.94. Found: C, 69.88; H, 2.98; *m*/*z* 308 (M$^+$, 100%).

4.3.3. Compound **3b**

Yield 16%, white solid; R_f 0.51 (2% ethyl acetate in benzene); mp 182–184 °C; ν_{max} (cm^{-1}) 2112 (C≡C), 1630 (C=O); δ_H ($CDCl_3$) 8.20 (1H, d, J_m=2.7 Hz, H-8), 7.61 (1H, dd, $J_{m,o}$=2.7, 9.0 Hz, H-10), 7.35 (1H, d, J_o=9.0 Hz, H-11), 6.63 (1H, br s, H-1), 4.85 (1H, s, H-4), 4.35 (1H, dd, J=2.1, 11.1 Hz, H-5), 3.64 (3H, s, 3-OCH_3), 3.38 (1H, m, H-4a), 2.97 (2H, m, H-2), 2.69 (1H, J=2.1 Hz, H-2′). Anal. Calcd for $C_{19}H_{13}ClO_4$: C, 66.97; H, 3.85. Found: C, 66.94; H, 3.81; *m*/*z* 340 (M$^+$, 100%).

4.3.4. Compound **4b**

Yield 30%, white solid; R_f 0.48 (2% ethyl acetate in benzene); mp 240–242 °C; ν_{max} (cm^{-1}) 2120 (C≡C), 1640 (C=O); δ_H ($CDCl_3$) 8.27

(1H, d, J_m=2.4 Hz, H-8), 7.78 (1H, d, J_o=8.7 Hz, H-10), 7.48 (1H, d, J_o=8.7 Hz, H-11), 7.00 (1H, dd, $J_{m,o}$=2.1, 8.7 Hz, H-2), 6.93 (1H, d, J_m=2.1 Hz, H-4), 5.95 (1H, s, H-5), 3.91 (3H, s, 3-OCH_3), 2.62 (1H, d, J=1.8 Hz, H-2′). Anal. Calcd for $C_{19}H_{11}ClO_4$: C, 67.37; H, 3.27. Found: C, 67.20; H, 3.26; *m*/*z* 338 (M$^+$, 100%).

4.3.5. Compound **3c**

Yield 20%, white solid; R_f 0.45 (5% ethyl acetate in benzene); mp 158–160 °C; ν_{max} (cm^{-1}) 2112 (C≡C), 1653 (C=O); δ_H (CDCl$_3$) 8.23 (1H, d, J_m=2.4 Hz, H-7), 7.60 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-9), 7.41 (1H, d, J_o=9.0 Hz, H-10), 6.40 (1H, dd, J=1.2, 6.0 Hz, H-2), 5.69 (1H, dd, J=2.7, 6.0 Hz, H-3), 4.94 (1H, d, J=8.4 Hz, H-11b), 4.77 (1H, dd, J=2.1, 8.1 Hz, H-4), 3.63 (1H, m, H-3a), 2.59 (1H, d, J=2.1 Hz, H-2′). Anal. Calcd for $C_{16}H_9ClO_3S$: C, 60.67; H, 2.86. Found: C, 60.70; H, 2.83; *m*/*z* 316 (M$^+$, 100%), 262 (M$^+$−54, 49).

4.3.6. Compound **4c**

Yield 30%, white solid; R_f 0.25 (5% ethyl acetate in benzene); mp 188–190 °C; ν_{max} (cm^{-1}) 2112 (C≡C), 1641 (C=O); δ_H (CDCl$_3$) 8.29 (1H, d, J_m=2.4 Hz, H-7), 7.64 (1H, d, J=4.8 Hz, H-2), 7.60 (1H, dd, $J_{m,o}$= 2.4, 9.0 Hz, H-9), 7.49 (1H, d, J_o=9.0 Hz, H-10), 7.10 (1H, d, J=4.8 Hz, H-3), 6.23 (1H, br s, H-4), 2.68 (1H, br s, H-2′). Anal. Calcd for $C_{16}H_7ClO_3S$: C, 61.06; H, 2.24. Found: C, 61.00; H, 2.21; *m*/*z* 314 (M$^+$, 100%).

4.3.7. Compound **3d**

Yield 25%, white solid; R_f 0.47 (5% ethyl acetate in benzene); mp 130–132 °C; ν_{max} (cm^{-1}) 2123 (C≡C), 1657 (C=O); δ_H (CDCl$_3$) 8.23 (1H, d, J_m=2.4 Hz, H-7), 7.58 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-9), 7.41 (1H, d, J_o=9.0 Hz, H-10), 5.33 (1H, br s, H-3), 4.98 (1H, d, J=8.4 Hz, H-11b), 4.78 (1H, dd, J=2.1, 8.4 Hz, H-4), 3.60 (1H, m, H-3a), 2.55 (1H, d, J=2.1 Hz, H-2′), 1.94 (3H, br s, –CH_3). . Anal. Calcd for $C_{17}H_{11}ClO_3S$: C, 61.73; H, 3.35. Found: C, 61.73; H, 3.30; *m*/*z* 330 (M$^+$, 100%), 276 (M$^+$−54, 37).

4.3.8. Compound **4d**

Yield 30%, white solid; R_f 0.28 (5% ethyl acetate in benzene); mp 174–176 °C; ν_{max} (cm^{-1}) 2120 (C≡C), 1646 (C=O); δ_H (CDCl$_3$) 8.28 (1H, d, J_m=2.4 Hz, H-7), 7.58 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-9), 7.46 (1H, d, J_o=9.0 Hz, H-10), 6.77 (1H, br s, H-3), 6.13 (1H, d, J=2.1 Hz, H-4), 2.66 (1H, J=2.1 Hz, H-2′), 2.60 (3H, br s, 2-CH_3). Anal. Calcd for $C_{17}H_9ClO_3S$: C, 62.10; H, 2.76. Found: C, 61.98; H, 2.75; *m*/*z* 328 (M$^+$, 100%).

4.3.9. Compound **3e**

Yield 15%, white solid; R_f 0.61 (3% ethyl acetate in benzene); mp 242–243 °C; ν_{max} (cm^{-1}) 2132 (C≡C), 1650 (C=O); δ_H (CDCl$_3$) 8.25 (1H, d, J_m=2.4 Hz, H-7), 7.62 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-9), 7.48 (1H, d, J_o=9.0 Hz, H-10), 6.58–6.57 (1H, m, H-2), 5.27 (1H, m, H-3), 5.24 (1H, d, J=9.6 Hz, H-11b), 4.28 (1H, dd, J=2.1, 9.6 Hz, H-4), 3.47–3.39 (1H, m, H-3a), 2.62 (1H, d, J=2.1 Hz, H-2′); δ_C 47.03 (C-3a), 66.68 (C-4), 73.19 (C-2′), 75.86 (C-11b), 77.84 (C-1′), 99.79 (C-3), 119.93 (C-10), 124.60 (C-6a), 125.40 (C-5a), 130.79 (C-8), 134.08 (C-9), 138.91 (C-7), 147.32 (C-11a), 148.28 (C-2), 153.77 (C-10a), 170.81 (C-6). Anal. Calcd for $C_{16}H_9ClO_4$: C, 63.91; H, 3.02. Found: C, 63.98; H, 2.99; *m*/*z* 300 (M$^+$, 100%).

4.3.10. Compound **3e′**

Yield 13%, white solid; R_f 0.56 (3% ethyl acetate in benzene); mp 216–218 °C; ν_{max} (cm^{-1}) 2126 (C≡C), 1663 (C=O); δ_H (CDCl$_3$) 8.22 (1H, d, J_m=2.4 Hz, H-7), 7.60 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-9), 7.46 (1H, d, J_o=9.0 Hz, H-10), 6.53–6.52 (1H, m, H-2), 5.37 (1H, d, $J_{11b,3a}$=9.9 Hz, H-11b), 5.23 (1H, t, J=2.4 Hz, H-3), 4.97–4.94 (1H, dd, J=2.1, 4.2 Hz, H-4), 3.82–3.76 (1H, d{dd}, J=2.4, 4.2, 9.9 Hz, H-3a), 2.48 (1H, d, J=2.1 Hz, H-2′); δ_C 47.20 (C-3a), 66.08 (C-4), 73.29 (C-2′), 75.86 (C-11b), 76.89 (C-1′), 99.56 (C-3), 120.12 (C-10), 124.46 (C-6a), 125.64 (C-5a), 130.87 (C-8), 134.50 (C-9), 138.91 (C-7), 148.02 (C-11a), 148.45 (C-2), 153.27 (C-10a), 170.38 (C-6). Anal. Calcd for $C_{16}H_9ClO_4$: C, 63.91; H, 3.02. Found: C, 63.80; H, 3.00; *m*/*z* 300 (M$^+$, 100%).

4.3.11. Compound **4e**

Yield 18%, white solid; R_f 0.38 (3% ethyl acetate in benzene); mp 196–198 °C; ν_{max} (cm^{-1}) 2126 (C≡C), 1698 (–CHO), 1640 (C=O); δ_H (CDCl$_3$) 9.82 (1H, d, J=2.4 Hz, –C*H*O), 8.22 (1H, d, J_m=2.4 Hz, H-5), 7.58 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-7), 7.40 (1H, d, J_o=9.0 Hz, H-8), 4.75–4.73 (1H, dd, J =1.8, 2.1 Hz, H-2), 3.15 (1H, d{dd}, $J_{1,CHO}$=2.4 Hz, $J_{1,9b}$=3.6 Hz, $J_{1,1a}$=4.8 Hz, H-1), 2.84 (1H, d{dd}, $J_{1a,2}$=1.8 Hz, $J_{1a,1}$=4.8 Hz, $J_{1a,9b}$=9.0 Hz, H-1a), 2.76 (1H, dd, $J_{9b,1}$=3.6 Hz, $J_{9b,1a}$=9.0 Hz, H-9b), 2.67 (1H, d, J=2.1 Hz, H-2′). δ_C 22.47 (C-9b), 31.73 (C-1), 33.85 (C-1a), 62.29 (C-2′), 76.23 (C-2), 78.42 (C-1′), 119.40 (C-8), 125.14 (C-4a), 127.06 (C-7), 133.58 (C-6), 135.18 (C-5), 136.34 (C-3a), 151.86 (C-9a), 153.33 (C-8a), 168.94 (C-4), 195.74 (–*C*HO). Anal. Calcd for $C_{16}H_9ClO_4$: C, 63.91; H, 3.02. Found: C, 63.85; H, 2.98; *m*/*z* 300 (M$^+$, 32%), 271 (M$^+$−29, 100%).

4.3.12. Compound **4e′**

Yield 13%, white solid; R_f 0.34 (3% ethyl acetate in benzene); mp 164–166 °C; ν_{max} (cm^{-1}) 2130 (C≡C), 1714 (CHO), 1632 (C=O); δ_H (CDCl$_3$) 9.75 (1H, d, J=2.4 Hz, –C*H*O), 8.24 (1H, d, J_m=2.4 Hz, H-5), 7.60 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-7), 7.43 (1H, d, J_o=9.0 Hz, H-8), 5.22 (1H, d, J=2.1 Hz, H-2), 3.00 (1H, d{dd}, $J_{1,CHO}$=2.4 Hz, $J_{1,9b}$=3.6 Hz, $J_{1,1a}$=4.8 Hz, H-1), 2.81 (2H, m, H-1a, 9b), 2.45 (1H, d, J=2.1 Hz, H-2′). δ_C 21.68 (C-9b), 31.06 (C-1), 32.82 (C-1a), 62.44 (C-2′), 76.45 (C-2), 78.73 (C-1′), 116.42 (C-8), 124.57 (C-4a), 125.18 (C-7), 131.61 (C-6), 133.85 (C-5), 135.11 (C-3a) 152.08 (C-9a), 153.85 (C-8a), 169.09 (C-4), 196.81 (–*C*HO). Anal. Calcd for $C_{16}H_9ClO_4$: C, 63.91; H, 3.02. Found: C, 63.93; H, 3.04; *m*/*z* 300 (M$^+$, 30%), 271 (M$^+$−29, 100).

4.3.13. Compound **3f**

Yield 10%, white solid; R_f 0.64 (3% ethyl acetate in benzene); mp 209–210 °C; ν_{max} (cm^{-1}) 2130 (C≡C), 1647 (C=O); δ_H (CDCl$_3$) 8.24 (1H, d, J_m=2.4 Hz, H-7), 7.61 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-9), 7.48 (1H, d, J_o=9.0 Hz, H-10), 5.26 (1H, d, $J_{11b,3a}$=8.4 Hz, 11b), 4.88 (1H, s, H-3), 4.26 (1H, dd, $J_{4,2'}$=2.1 Hz, $J_{4,3a}$=9.6 Hz, H-4), 3.39–3.33 (1H, m, H-3a), 2.60 (1H, d, J=2.1 Hz, H-2′), 1.93 (3H, s, 2-CH_3). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.88; H, 3.52. Found: C, 64.69; H, 3.49; *m*/*z* 314 (M$^+$, 100%).

4.3.14. Compound **3f′**

Yield 5%, white solid; R_f 0.59 (3% ethyl acetate in benzene); mp 198–200 °C; ν_{max} (cm^{-1}) 2130 (C≡C), 1648 (C=O); δ_H (CDCl$_3$) 8.24 (1H, d, J_m=2.4 Hz, H-7), 7.62 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-9), 7.49 (1H, d, J_o=9.0 Hz, H-10), 5.36 (1H, d, $J_{11b,3a}$=8.7 Hz, H-11b), 4.88 (1H, s, H-3), 4.89 (1H, dd, $J_{4,2'}$=2.1 Hz, $J_{4,3a}$=3.9 Hz, H-4), 3.74–3.69 (1H, m, H-3a), 2.60 (1H, d, J=2.1 Hz, H-2′) 1.95 (3H, s, 3-CH_3). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.88; H, 3.52. Found: C, 64.75; H, 3.52; *m*/*z* 314 (M$^+$, 100%).

4.3.15. Compound **4f**

Yield 20%, white solid; R_f 0.40 (3% ethyl acetate in benzene); mp 161–162 °C; ν_{max} (cm^{-1}) 2130 (C≡C), 1700 (–COCH$_3$), 1644 (C=O); δ_H (CDCl$_3$) 8.16 (1H, d, J_m=2.4 Hz, H-5), 7.57 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-7), 7.40 (1H, d, J_o=9.0 Hz, H-8), 4.71–4.69 (1H, t, J=1.5, 2.1 Hz, H-2), 3.10 (1H, dd, $J_{1,9b}$=3.6 Hz, $J_{1,1a}$=4.8 Hz, H-1), 2.72 (1H, d{dd}, $J_{1a,2}$=1.5 Hz, $J_{1a,1}$=4.8 Hz, $J_{1a,9b}$=9.0 Hz, H-1a), 2.67 (1H, dd, $J_{9b,1}$=3.6 Hz, $J_{9b,1a}$=9.0 Hz, H-9b), 2.66 (1H, d, J=2.1 Hz, H-2′), 2.42 (3H, s, –COCH_3); δ_C 21.81 (C-9b), 31.26 (C-1), 32.74 (C –COCH$_3$), 34.42 (C-1a), 62.66 (C-2′), 75.51 (C-2), 78.80 (C-1′), 119.51 (C-8), 125.20 (C-4a), 130.95 (C-7), 133.05 (C-6), 133.28 (C-5), 138.76 (C-3a), 153.27 (C-9a), 153.40 (C-8a), 169.66 (C-4), 202.59 (–*C*OCH$_3$). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.88; H, 3.52. Found: C, 64.72; H, 3.53; *m*/*z* 314 (M$^+$, 36%), 271 (M$^+$−43, 100).

4.3.16. Compound ***4f′***

Yield 17%, white solid; R_f 0.34 (3% ethyl acetate in benzene); mp 254–256 °C; ν_{max} (cm^{-1}) 2112 (C≡C), 1707 (–COCH$_3$), 1631 (C=O); δ_H (CDCl$_3$) 8.24 (1H, d, J_m=2.4 Hz, H-5), 7.60 (1H, dd, $J_{m,o}$=2.4, 9.0 Hz, H-7), 7.43 (1H, d, J_o=9.0 Hz, H-8), 5.20–5.18 (1H, m, H-2), 2.92 (1H, dd, $J_{1,9b}$=3.6 Hz, $J_{1,1a}$=4.8 Hz, H-1), 2.72 (1H, d{dd}, $J_{1a,2}$=0.9 Hz, $J_{1a,1}$=4.8 Hz, $J_{1a,9b}$=9.0 Hz, H-1a), 2.66 (1H $J_{9b,1}$=3.6 Hz, $J_{9b,1a}$=9.0 Hz, H-9b), 2.42 (1H, d, J=2.1 Hz, H-2′), 2.37 (3H, s, –COCH_3); δ_C 22.84 (C-9b), 31.21 (C-1), 32.66 (C –COCH$_3$), 34.33 (C-1a), 61.35 (C-2′), 75.94 (C-2), 78.76 (C-1′), 119.40 (C-8), 125.09 (C-4a), 130.91 (C-7), 133.43 (C-6), 134.96 (C-5), 139.46 (C-3a), 152.73 (C-9a), 153.29 (C-8a), 168.87 (C-4), 202.88 (–COCH$_3$). Anal. Calcd for $C_{17}H_{11}ClO_4$: C, 64.88; H, 3.52. Found: C, 64.81; H, 3.50; *m*/*z* 314 (M$^+$, 33%), 271 (M$^+$−43, 100).

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