Photochemical Study of Chalconoid-like Compounds: Synthesis of 4-Flavanoids

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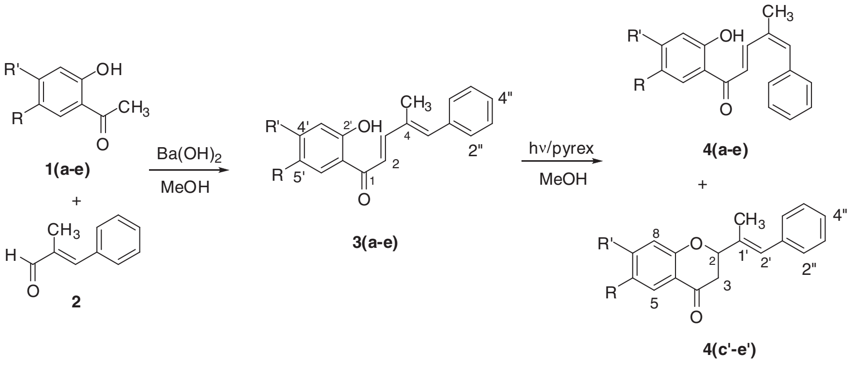

a) R = R' = H; **b**) R = CH3, R' = H; **c**) R = H, R' = OCH3; **d**) R = Cl, R' = CH3; **e**) R = Cl, R' = H

The photo-irradiation of chalconoid-like compounds; (*2E,4E*)-1-(2-hydroxyaryl)-4-methyl-5-phenylpenta-2,4-dien-1-ones to 4-flavanoids in solution phase has been described. The molecular scaffold of the probed substrates is responsive to intramolecular cyclization as well as *cis-trans* isomerizations and photoproducts corresponding to both of reactions have been realized also. The formation of photoproducts has been explained on the basis of excited state intramolecular proton transfer that further depends upon the different substituents present on the phenolic moiety.

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INTRODUCTION

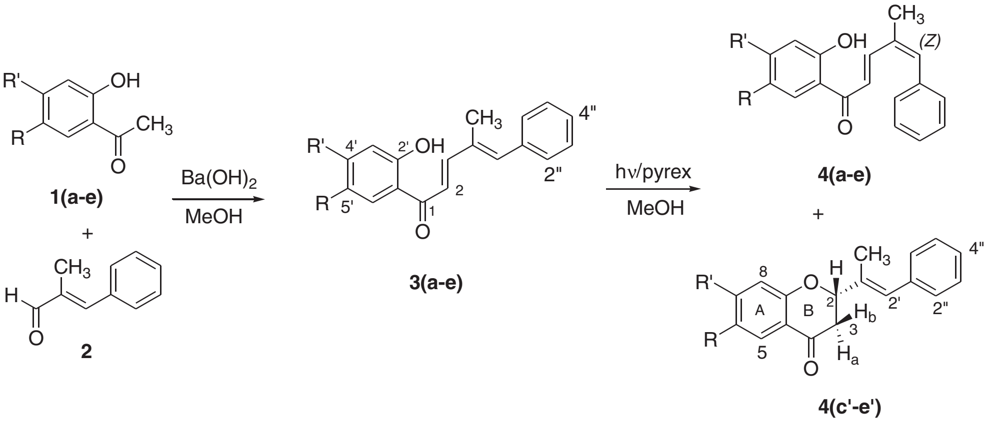
Chalcones ((*2E*)-1,3-diarylprop-2-en-1-ones), the bichromophoric molecules, considered as the precursors of flavonoids and isoflavonoids, are abundant in fruits, vegetables, spices, tea, and soy-based foodstuff and have been shown to display a diverse array of pharmacological activities [1–5]. These bichromophoric systems are good models for study of the photo-induced electron transfer process [6]. In addition, chalcones find various applications as organic brightening additives [7], potential nonlinear optical properties [8], and fluorescent probes for micellar solutions [9]. Photochemically, the chalconoids are known to undergo cycloadditions [10–13] and *cis-trans* isomerizations [14]. The 2′-hydroxychalcones are extensively studied photochemically and they are known to undergo photo-oxygenations [15] and excited state intramolecular proton transfers (ESIPT) [16–20] instead of cycloadditions. In the present study, we report the solution phase photoreactions of the chalconoid-like compounds having extended conjugation, (*2E,4E*)-1-(2-hydroxyaryl)-4-methyl-5-phenylpenta-2,4-dien-1-ones and also the effect of various substituents on the formation and distribution of the photoproducts arising through ESIPT.

RESULTS AND DISCUSSION

The substituted dienones **3(a–e)**, chalconoid-like compounds in the present study, were synthesized by the condensation of suitable acetophenone with an α-methylcinnamaldehyde using $Ba(OH)_2$ as base (Scheme 1). Their structures were ascertained from their spectral parameters (*vide* experimental). The compound **3d** in its IR spectrum (KBr) exhibited strong absorption band at $1632\,cm^{-1}$ that may be assigned to C=O of enone moiety. Its ^1H NMR (300 MHz, $CDCl_3$) spectrum had a broad singlet at δ 12.79 because of 2′-**OH** that disappears on D_2O shake. The protons H-3′ and H-6′ were revealed at δ 7.04 (1H, s) and 7.81 (1H, s), respectively. The resonances because of H-2 and H-3 appeared as doublets at δ 7.07 and 7.36, respectively, with *J* value of 15.0 Hz indicating *(E)*-configuration at C_2–C_3 double bond. The five protons because of phenyl ring were placed as a multiplet between δ 7.31–7.42. The ^1H NMR spectrum also showed the presence of two methyl groups at δ 2.20 (s, C_4–$\mathbf{CH_3}$) and 3.40 (s, $C_{4'}$–$\mathbf{CH_3}$).

Similarly, the ^1H NMR assignments of other compounds **3(a–c)** and **3e** were found to be consistent with their structures.

Scheme 1. Synthesis and photo-irradiation of chalconoids **3(a–e)**.



-R	-R'	Photoproduct	Yield (%)[a]	Photoproduct	Yield (%)[b]
-H	-H	**4a**	36	**4a'**	------
-CH_3	-H	**4b**	41	**4b'**	------
-H	-OCH_3	**4c**	32	**4c'**	25
-Cl	-CH_3	**4d**	29	**4d'**	45
-Cl	-H	**4e**	28	**4e'**	39

a - yield calculated from ^{1}H NMR; b - isolated yield

The photo-irradiation of these chalconoids **3(a–e)** in dry methanol (1.0 mM) for 90 min with pyrex filtered light using 125 W medium pressure mercury lamp under N_2 atm. produced the respective *seq cis*-isomers **4(a–e)** and the flavanoids **4(c′–e′)** as shown in Scheme 1. The structures of these photoproducts were confirmed by their spectral data (*vide* experimental). In the IR spectrum of photoproduct **4d′**, the absorption band for C=O group shifted towards higher value (1687 cm^{-1}) that indicated the lack of conjugation to C=O group in the flavanoid **4d′**. Also, in the ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of the photoproduct **4d′**, the resonances because of H-2, H_a-3, and H_b-3 protons were placed at δ 4.95 (1H, dd, $J_{2,3Hb} = 2.7$ Hz, $J_{2,3Ha} = 12.9$ Hz), 2.99 (1H, dd, $J_{3Ha,2} = 12.9$, $J_{3Ha,3Hb} = 16.8$ Hz), and δ 2.76 (1H, dd, $J_{3Hb,2} = 2.7$, $J_{3Hb,3Ha} = 16.8$ Hz), respectively. The two methyl resonated at δ 2.01 (3H, s, C_7–$\mathbf{CH_3}$) and 2.39 (3H, s, C_1–$\mathbf{CH_3}$). The three singlets at δ 6.68, 6.95, and 7.86 were assigned to the H-2′, H-8, and H-5, respectively. The five protons (H-2"–H-6") of the phenyl ring resonated in the aromatic region as an unresolved multiplet δ 7.092–7.39. The similar ^{1}H NMR patterns were displayed by the other photoproducts **4(c'–e')**.

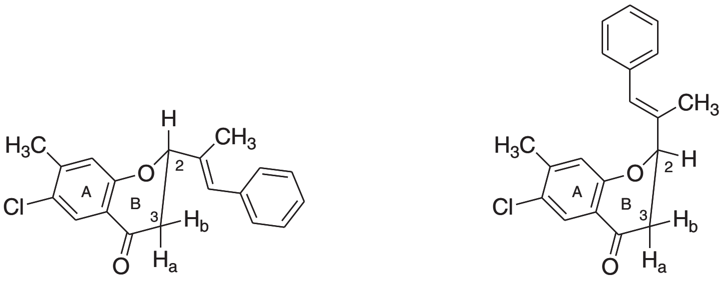
As far as stereochemical features concern, generally, the half-chair conformation is favored for chroman ring that mainly arises from the restricted rotation imposed by the benzene ring [21–23]. The MM2 minimized energy calculations (Table 1) showed that the energy differences between the two possible conformers **X** and **Y** (Fig. 1) of flavanoid **4d′** is small; therefore, the two conformers may exist in equilibrium. This ambiguity was resolved by ^{1}H NMR spectroscopy where $J_{2,3}$ coupling constants are informative to address the conformational aspects of the ring B, and it has been widely applied in analogous studies [21–23]. The relatively large $J_{2,3Ha}$ value (12.9 Hz) in compound **4d′** confirms the preferred pseudo-diaxial conformation of H-2 and H_a-3, thus placing the bulkier styryl group in pseudo-equatorial orientation (conformation **X**; Fig. 1). In order to support the preference of conformation **X** over the

Table 1

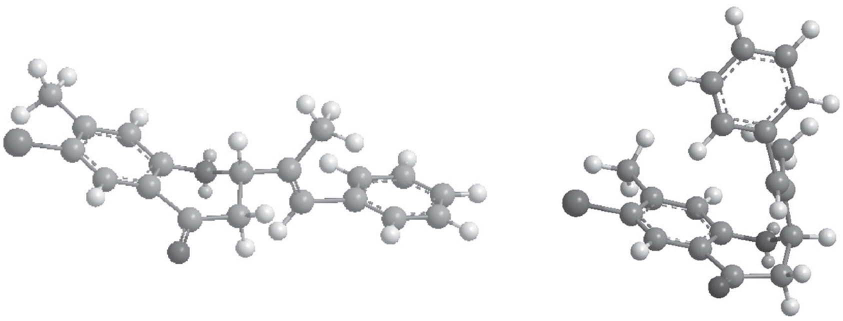
Expected coupling constants for the two conformations of **4d′**.

	Conformation **X**		Conformation **Y**		
	($E_{kcal/mol} = 9.090$)		($E_{kcal/mol} = 9.234$)		
Coupling protons	*Φ*	*J* (Hz)[a]	*Φ*	*J* (Hz)[a]	Observed *J* (Hz)
H-2 and H_a-3	177.11	12.9	57.89	4.2	12.9
H-2 and H_b-3	61.53	3.8	60.77	4.3	2.7

[a]Expected value.



(Conformation **X**) (Conformation **Y**)



(Conformation **X**)
styryl pseudo-equatorial
ring B half-chair

(Conformation **Y**)
styryl pseudo-axial
ring B half-chair

Figure 1. MM2 energy minimized structures of expected conformations of compound **4d′**.

conformation **Y**, the dihedral angles (*Φ*) and the expected *J* values along with the steric energies are calculated [24] with Chem3D Ultra 8.0 (PerkinElmer, Melville, NY) software (Table 1).

The observed ^3J values found in the present case for **4d′** are in accordance with the $J^{\dagger}$ values calculated (Table 1) for conformation **X**, where H-2 and H_a-3 are in pseudo-diaxial orientation and styryl group in pseudo-equatorial position (Fig. 1).

The photoconversion of the chalconoids **3(c–e)** into flavanoids **4(c′–e′)** described earlier (Scheme 1) can be visualized to occur through π–π^* excitation [20] of carbonyl group that resulted in ESIPT. In the ground state structure, the strong intramolecular hydrogen bonding between the phenolic proton and the carbonyl oxygen of these compounds **3(a–e)** leads to a six-membered cyclic transition state **I** (Scheme 2) that is supported well by the ^{1}H NMR spectra ($\delta_{OH} \sim 12.79$ for **3d**). The photo-irradiation of chalconoids resulted in intramolecular proton transfer to give the enol (**II**) in *seq trans* configuration (Scheme 2), which in turn produced **III** that cyclized to give **IV** *via* a thermal 6π-electrocyclic ring-closure. The intermediate **IV** subsequently tautomerizes to yield 4-flavanoids. The cyclization of **III–IV** is likely to be highly favorable because of the restoration of aromatic character of the phenyl ring ensuring the stability and proceeds effectively *via* a thermal 6π-electrocyclic process. It has been studied [25] that the photochemical rearrangement of 3-chromanone derivatives takes place *via* enolization and a similar mechanism has been proposed for the photochemical ring opening reaction of substituted 4-flavanones [26]. The calculation of heat of formation (ΔH_f) by MOPAC-PM3 program for the transition states **I–IV** of compound **3d** is tabulated in Table 2.

A closer look of Table 2 shows that the conversion of **I** → **II** → **III** is an endothermic process and thus requires the photochemical energy. The conversion **III** → **IV** is exothermic and can proceed well with the dissipation of energy. In the photocyclization of the chalconoids (Scheme 2), the first step is the transfer of phenolic proton to the carbonyl oxygen to form enol-**II**. The ease of hydrogen transfer is related to the type and energy of excited state of carbonyl group involved and the acidity of the phenolic proton that further depends upon the different substitution. The electron-releasing groups ($-OCH_3$ and $-CH_3$ in **3c** and **3d**, respectively) at *para* position to the carbonyl chromophore make it more basic [27] by lowering the energy of its π–π^* excited state and enhancing the ESIPT for photocyclization. Also, the electron-withdrawing group ($-$Cl in **3d** and **3e**) *para* to the phenolic oxygen

Scheme 2. Photoconversion of chalconoids **3(a–e)**.

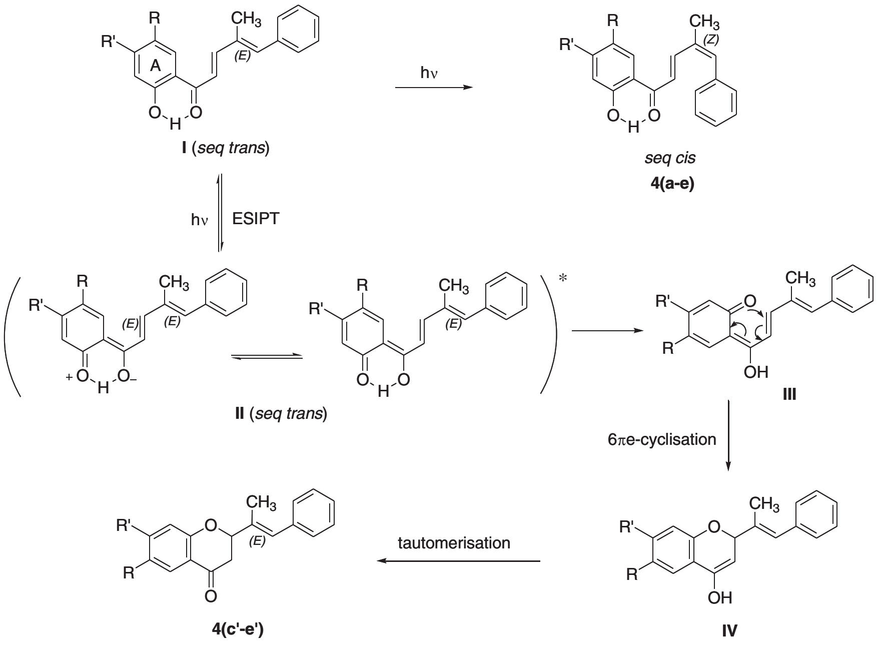


Table 2

ΔH_f for the transition states of compound **3d** leading to the formation of **4d′**.

State	I	II	III	IV
$\Delta H_{f\ \text{(kcal/mol)}}$	−18.80	−15.34	3.21	−12.41

increases the acidity of phenolic proton and make its transfer to carbonyl more facile. Therefore, the chalconoids **3c, 3d**, and **3e** furnished cyclised photoproducts (**4c′, 4d′**, and **4e′**, respectively) in addition to the products arising through *cis-trans* isomerization (**4c, 4d**, and **4e**, respectively), whereas chalconoids **3a** and **3b** produced only the *seq cis* isomeric products (**4a** and **4b**, respectively) with no formation of cyclised product corresponding to **4d′** (Scheme 1).

In all these compounds **3(a–e)**, no photoproduct through cycloaddition reaction was obtained although their basic skeleton seems to afford those.

CONCLUSION

It may be concluded that on photo-irradiation, the substituted (*2E*,*4E*)-1-(2-hydroxyaryl)-4-methyl-5-phenylpenta-2,4-dien-1-ones endured *cis-trans* isomerization and cyclization to 4-flavanoids. The cyclization efficiency of the investigated substrates depends upon the electron density on phenolic oxygen as well as on the carbonyl group. Although, the molecular structure of these substrates is consenting to the cycloadditions, but no photoproducts corresponding to those reactions under the conditions were realized here.

EXPERIMENTAL

General. Melting points were determined in open capillaries and are thus uncorrected. ^{1}H NMR spectra were recorded on a 300 MHz Bruker spectrometer using TMS as internal standard. IR spectra were recorded on a Buck Scientific 500 spectrophotometer using KBr pellets. 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 petroleum ether (60–80°C)-benzene and left overnight before use. The elution was carried out with increasing proportion of benzene in petroleum ether-benzene mixture. A total of 99.9% dry N_2 gas was continuously bubbled through the reaction solution to maintain inert atmosphere during photolysis.

Synthesis of chalconoids 3(a–e)

(2E,4E)-1-(2-Hydroxyphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (3a). A solution of 2-hydroxyacetophenone (1.36 g; 0.01 mol) and α-methyl cinnamaldehyde (1.46 g; 0.01 mol) in absolute methanol and dehydrated S200 barium hydroxide (0.02 mol) was refluxed on water bath for 20 min. The solution was cooled and poured onto crushed ice; it was then acidified with conc. HCl to give a yellow solid. The solid was filtered, washed with water, and crystallized from ethanol to give the yellow needles **3a**. Yield 78%; mp 116°C; UV–vis (MeOH) λ_{max}: 204, 247, 339 nm; IR ν_{max} (cm^{-1}): 1663 (C=O), 3320 (OH); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.83 (1H, s, OH), 7.99 (1H, dd, $J_m = 1.8$, $J_o = 8.7$ Hz, H-6′), 7.50 (1H, dt, $J_m = 1.5$ Hz, $J_o = 7.8$ Hz, H-5′), 7.58 (1H, dt, $J_m = 1.5$ Hz, $J_o = 8.4$ Hz, H-4′), 7.64 (1H, d, $J_{trans} = 15.3$ Hz, H-3), 7.06 (1H, d, $J_{trans} = 15.3$ Hz, H-2), 6.98 (1H, s, H-5), 7.26–7.40 (5H, m, Phenyl protons), 2.17 (3H, s, 4-CH_3).

The other substrates **3(b–e)** were synthesized by reacting substituted 2-hydroxyacetophenone **1(b–e)** with α-methylcinnamaldehyde **2** under the reaction conditions as used for compound **3a**.

(2E,4E)-1-(2-Hydroxy-5-methylphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (3b). Yield 73%; Yellow solid; mp 95°C; UV–vis (MeOH) λ_{max}: 204, 248, 337 nm; IR ν_{max} (cm^{-1}): 1634 (C=O), 3328 (OH); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 12.74 (1H, s, OH), 7.65 (1H, d, $J_m = 1.5$ Hz, H-6′), 7.31 (1H, dd, $J_m = 1.5$ Hz, $J_o = 8.4$ Hz, H-4′), 6.93 (1H, d, $J_o = 8.4$ Hz, H-3′), 7.75 (1H, d, $J_{trans} = 15.0$ Hz, H-3), 7.18 (1H, d, $J_{trans} = 15.0$ Hz, H-2), 7.03 (1H, s, H-5), 7.29–7.45 (5H, m, Phenyl protons), 2.36 (3H, s, 5′-CH$_3$), 2.21 (3H, s, 4-CH$_3$).

(2E,4E)-1-(2-Hydroxy-4-methoxyphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (3c). Yield 69%; Yellow solid; mp 104°C; UV–vis (MeOH) λ_{max}: 205, 256, 336 nm; IR ν_{max} (cm^{-1}): 1633 (C=O), 3320 (OH); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 13.53 (1H, s, OH), 7.18 (1H, d, $J_o = 9.0$ Hz, H-6′), 6.50 (1H, dd, $J_m = 2.4$ Hz, $J_o = 9.0$ Hz, H-5′), 6.50 (1H, d, $J_o = 2.4$ Hz, H-3′), 7.74 (1H, d, $J_{trans} = 15.0$ Hz, H-3), 7.13 (1H, d, $J_{trans} = 15.0$ Hz, H-2), 7.03 (1H, s, H-5), 7.28–7.43 (5H, m, Phenyl protons), 3.88 (3H, s, OCH$_3$), 2.20 (3H, s, 4-CH$_3$).

(2E,4E)-1-(5-Chloro-2-hydroxy-4-methylphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (3d). Yield 76%; Yellow solid; mp 92°C; UV–vis (MeOH) λ_{max}: 208, 258, 336 nm; IR ν_{max} (cm^{-1}): 1632 (C=O), 3317 (OH); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 12.79 (1H, s, OH), 7.81 (1H, s, H-6′), 7.04 (1H, s, H-3′), 7.36 (1H, d, $J_{trans} = 15.0$ Hz, H-3), 7.07 (1H, d, $J_{trans} = 15.0$ Hz, H-2), 6.91 (1H, s, H-5), 7.31–7.42 (5H, m, Phenyl protons), 3.40(3H, s, 4′-CH$_3$), 2.20 (3H, s, 4-CH$_3$).

(2E,4E)-1-(5-Chloro-2-hydroxyphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (3e) *[28].* Yield 83%; Yellow solid; mp 98°C; UV–vis (MeOH) λ_{max}: 204, 243, 343 nm; IR ν_{max} (cm^{-1}): 1630 (C=O), 3314 (OH); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 12.83 (1H, s, OH), 7.83 (1H, d, $J_m = 2.7$ Hz, H-6′), 7.44 (1H, dd, $J_m = 2.7$ Hz, $J_o = 9.0$ Hz, H-4′), 6.98 (1H, d, $J_o = 9.0$ Hz, H-3′), 7.78 (1H, d, $J_{trans} = 15.0$ Hz, H-2), 7.09 (1H, d, $J_{trans} = 15.0$ Hz, H-3), 7.06 (1H, s, H-5), 7.30–7.42 (5H, m, Phenyl protons), 2.21 (3H, s, 4-CH$_3$).

Photolysis of chalconoids 3(a–e)

Photolysis of (2E,4E)-1-(2-hydroxyphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (3a). A deoxygenated solution of the compound **3a** (1.0 mM) in dry methanol was irradiated with pyrex filtered light from 125 W medium pressure mercury lamp for 90 min. The color of the solution became light brown. Solvent was distilled off under reduced pressure, and a gummy mass was obtained which was then chromatographed over silica gel (100–200 mesh) using benzene-petroleum ether as an eluent. Elution of the column gave the starting compound and the isomeric photoproduct **4a**.

(2E,4Z)-1-(2-Hydroxyphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (4a). Yield 36%; IR ν_{max} (cm^{-1}): 1665 (C=O), 3319 (OH); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 12.95 (1H, s, OH), 7.96 (1H, dd, $J_m = 1.8$ Hz, $J_o = 8.7$ Hz, H-6′), 7.47 (1H, dt, $J_m = 1.2$ Hz, $J_o = 7.8$ Hz, H-5′), 7.58 (1H, dt, $J_m = 1.5$ Hz, $J_o = 8.4$ Hz, H-4′), 8.06 (1H, d, $J_{trans} = 15.0$ Hz, H-3), 7.09 (1H, d, $J_{trans} = 15.0$ Hz, H-2), 7.01 (1H, s, H-5), 7.26–7.40 (5H, m, Phenyl protons), 2.18 (3H, s, 4-CH$_3$).

Photolysis of (2E,4E)-1-(2-hydroxy-5-methylphenyl)-4-methyl-5-phenyl penta-2,4-dien-1-one (3b). Photo-irradiation of methanolic solution of **3b** (1.0 mM) produced **4b** in 90 min.

(2E,4Z)-1-(2-Hydroxy-5-methylphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (4b). Yield 41%; IR ν_{max} (cm^{-1}): 1632 (C=O), 3328 (OH); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 12.63 (1H, s, OH), 7.63 (1H, d, $J_m = 1.5$ Hz, H-6′), 7.31(1H, dd, $J_m = 1.5$ Hz, $J_o = 8.4$ Hz, H-4′), 6.91 (1H, d, $J_o = 8.4$ Hz, H-3′), 8.04 (1H, d, $J_{trans} = 15.3$ Hz, H-3), 7.21 (1H, d, $J_{trans} = 15.3$ Hz, H-2), 6.79 (1H, s, H-5), 7.29–7.44 (5H, m, Phenyl protons), 2.35 (3H, s, 5′-CH$_3$), 2.20 (3H, s, 4-CH$_3$).

Photolysis of (2E,4E)-1-(2-hydroxy-4-methoxyphenyl)-4-methyl-5-phenyl penta-2,4-dien-1-one (3c). A methanolic solution of **3c** (1.0 mM) furnished **4c** and **4c**’ on photolysis for 90 min.

(2E,4Z)-1-(2-Hydroxy-4-methoxyphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (4c). Yield 32%; IR ν_{max} (cm^{-1}): 1630 (C=O), 3322 (OH); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 13.43 (1H, s, OH), 7.78 (1H, d, $J_o = 8.4$ Hz, H-6′), 6.49 (1H, dd, $J_m = 2.4$ Hz, $J_o = 8.4$ Hz, H-5′), 6.47 (1H, d, $J_o = 2.4$ Hz, H-3′), 8.02 (1H, d, $J_{trans} = 15.0$ Hz, H-3), 7.14 (1H, d, $J_{trans} = 15.0$ Hz, H-2), 6.94 (1H, s, H-5), 7.30–7.41 (5H, m, Phenyl protons), 3.85 (3H, s, OCH$_3$), 2.19 (3H, s, 4-CH$_3$).

2,3-Dihydro-7-methoxy-2-((E)-1-phenylprop-1-en-2yl)chromen-4-one (4c′). Yield 25%; White solid; mp 90°C; IR ν_{max} (cm^{-1}): 1680 (C=O); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.85 (1H, d, $J_m = 2.4$ Hz, H-5), 6.61 (1H, dd, $J_m = 2.4$ Hz, $J_o = 8.7$ Hz, H-6), 7.28–7.39 (5H, m, Phenyl protons), 6.50 (1H, d, $J_m = 2.4$ Hz, H-8), 6.69 (1H, s, H-2′), 4.98 (1H, dd, $J_{2,3Hb} = 2.4$, $J_{2,3Ha} = 13.2$ Hz, H-2), 3.85 (3H, s, OCH$_3$), 2.98 (1H, dd, $J_{3Ha,2} = 13.2$, $J_{3Ha,3Hb} = 16.8$ Hz, H$_a$-3), 2.62 (1H, dd, $J_{3Hb,2} = 2.4$, $J_{3Hb,3Ha} = 16.8$ Hz, H$_b$-3), 2.02 (3H, s, CH$_3$); ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ 190.99, 166.66, 163.60, 134.86, 129.08, 128.24, 128.70, 128.50, 127.08, 114.77, 110.14, 100.82, 83.36, 55.66, 41.64, 29.50, 13.88; Mass (m/z, +Q1): 329 ([M + 1]$^+$, 100); *Anal.* Calcd. for C$_{19}$H$_{17}$ClO$_3$: C, 69.41; H, 5.21. Found: C, 69.39; H, 5.13.

Photolysis of (2E,4E)-1-(5-Chloro-2-hydroxy-4-methylphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (3d). Photo-irradiation of methanolic solution of 3d (1.0 mM) delivered **4d** and **4d**′ in 90 min.

(2E,4Z)-1-(5-Chloro-2-hydroxy-4-methylphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (4d). Yield 29%; IR ν_{max} (cm^{-1}): 1633 (C=O), 3317 (OH); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 12.79 (1H, s, OH), 7.81 (1H, s, H-6′), 6.89 (1H, s, H-3′), 8.04 (1H, d, $J_{trans} = 15.0$ Hz, H-3), 7.10 (1H, d, $J_{trans} = 15.0$ Hz, H-2), 6.99 (1H, s, H-5), 7.26–7.43 (5H, m, Phenyl protons), 2.39 (3H, s, 4′-CH$_3$), 2.20 (3H, s, 4-CH$_3$).

6-Chloro-2,3-Dihydro-7-methyl-2-((E)-1-phenylprop-1-en-2yl) chromen-4-one (4d′). Yield 45%; White solid; mp 81°C; IR ν_{max} (cm^{-1}): 1687 (C=O); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.86 (1H, s, H-5), 6.95 (1H, s, H-8), 7.29–7.39 (5H, m, Phenyl protons), 6.68 (1H, s, H-2′), 4.95 (1H, dd, $J_{2,3Hb} = 2.7$, $J_{2,3Ha} = 12.9$ Hz, H-2), 2.39 (3H, s, CH3), 2.99 (1H, dd, $J_{3Ha,2} = 12.9$, $J_{3Ha,3Hb} = 16.8$ Hz, H$_a$-3), 2.76 (1H, dd, $J_{3Hb,2} = 2.7$, $J_{3Hb,3Ha} = 16.8$ Hz, H$_b$-3), 2.01 (3H, s, CH$_3$); ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ 189.23, 157.97, 143.30, 134.69, 132.68, 127.21, 126.41, 125.30, 126.84, 124.81, 118.28, 118.02, 81.23, 39.80, 29.09, 19.01, 12.05; Mass (*m/z*, +Q1): 313 ([M + 1]$^+$, 100); *Anal.* Calcd. for C$_{19}$H$_{17}$ClO$_2$: C, 72.96; H, 5.48. Found: C, 72.92; H, 5.40.

Photolysis of (2E,4E)-1-(5-chloro-2-hydroxyphenyl)-4-methyl-5-phenyl penta-2,4-dien-1-one (3e). A methanolic solution of **3e** (1.0 mM) furnished **4e** and **4e**′ on photolysis for 90 min.

(2E,4Z)-1-(5-Chloro-2-hydroxyphenyl)-4-methyl-5-phenylpenta-2,4-dien-1-one (4e). Yield 28%; IR ν_{max} (cm^{-1}): 1631 (C=O), 3315 (OH); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 12.71 (1H, s, OH), 8.70 (1H, d, $J = 18.4$ Hz, H-3), 7.89 (1H, d, $J_m = 2.4$ Hz, H-6′), 7.05 (1H, d, $J_{trans} = 18.4$ Hz, H-2), 7.15 (1H, s, H-5), 7.27–7.39 (7H, m, H-4′, 5′, Phenyl protons), 2.21 (3H, s, 4-CH$_3$).

6-Chloro-2,3-dihydro-2-((E)-1-phenylprop-1-en-2yl)chromen-4-one (4e′). Yield 39%; White solid; mp 84°C; IR ν_{max} (cm^{-1}): 1698 (C=O); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.79 (1H, d, $J_m = 2.7$ Hz, H-5), 7.36 (1H, dd, $J_m = 2.7$ Hz, $J_o = 9.0$ Hz, H-7), 7.05–7.30 (5H, m, Phenyl protons), 6.94 (1H, d, $J_o = 9.0$ Hz, H-8), 6.61

(1H, s, H-2′), 4.90 (1H, dd, $J_{2,3Hb} = 2.4$, $J_{2,3Ha} = 12.9$ Hz, H-2), 2.94 (1H, dd, $J_{3Ha,2} = 13.2$, $J_{3Ha,3Hb} = 16.8$ Hz, H_a-3), 2.62 (1H, dd, $J_{3Hb,2} = 2.4$, $J_{3Hb,3Ha} = 16.8$ Hz, H_b-3), 1.94 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 190.01, 157.83, 142.98, 135.01, 132.65, 127.26, 126.34, 125.31, 126.85, 124.76, 118.25, 117.97, 81.20, 40.18, 29.13, 12.02; Mass (m/z, +Q1): 299 ($[M+1]^+$, 100); *Anal.* Calcd. for $C_{18}H_{15}ClO_2$: C, 72.36; H, 5.06. Found: C, 72.25; H, 5.05.

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