A Novel and Efficient Synthetic Method of Benzo[*f*]chromen-1-ones and Phenyl-4*H*-chromen-4-one through Photooxidative Cyclization of 6-[(*E*)-2-Arylvinyl]-4*H*-pyran-4-ones and 6-[(1*E*,3E)-4-Phenylbuta-1,3-dien-1-yl]-4*H*-pyran-4-one

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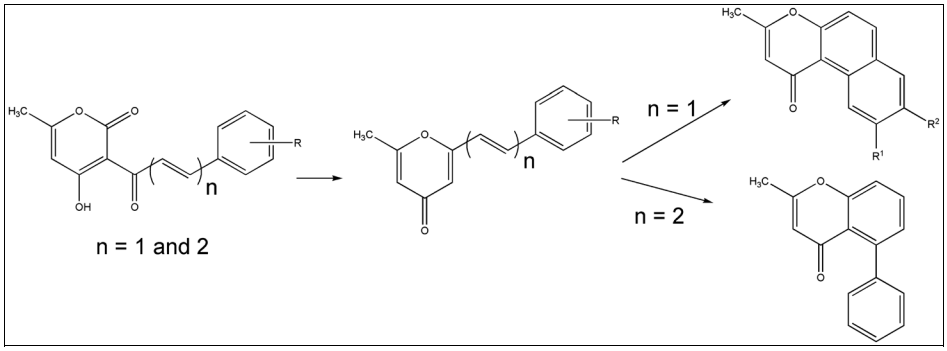

A rapid and efficient microwave-assisted transformation of 2-pyrones into 4-pyrones is reported. Then, a new photocatalytic oxidative cyclization of 6-[(*E*)-2-arylvinyl]-2-methyl-4*H*-pyran-4-ones and 2-methyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]-4*H*-pyran-4-one with UV light in the presence of a catalytic amount of $CuAlO_2$ is described. We obtained new 3-methyl-1*H*-benzo[*f*]chromen-1-ones and 2-methyl-5-phenyl-4*H*-chromen-4-one that were fully characterized by spectroscopic techniques.

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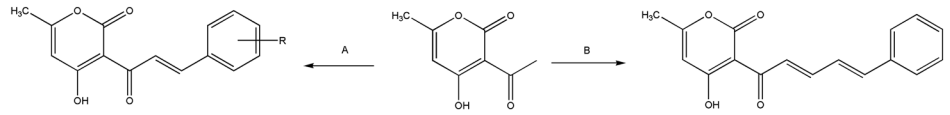
INTRODUCTION

Chromone derivatives constitute a large family of naturally occurring heterocyclic compounds. Their synthesis as well as their biological and pharmacological activities have deserved a great attention during the last decades [1]. Besides, dehydroacetic acid (DHAA) **1** (3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one) is often investigated because of its use for the synthesis of important organic compounds used as food additives, antihypertensive, antimicrobial, insecticidal, and cosmetics [2–5]. Recently, we have reported a simple procedure for the synthesis of substituted alkenes by microwave-assisted Knoevenagel condensation of DHAA **1** with benzaldehydes [6]. This method offers important advantages over conventional heating conditions, because it is a solvent free process, with shorter reaction times, better yields, lower costs, and environmentally friendly. Scheme 1 presents the reported general procedure for the formation of 4-hydroxy-6-methyl-3-[(2*E*)-3-phenylprop-2-enoyl]-2*H*-pyran-2-one **2a–f** and 4-hydroxy-6-methyl-3-[(2*E*,4*E*)-5-phenylpenta-2,4-dienoyl]-2*H*-pyran-2-one **3** by a Knoevenagel condensation.

The conversion of 2-pyrones (**2** and **3**) into 4-pyrones (**4** and **5**) (Scheme 2) has already been reported in the literature [7–9] by a conventional reflux of 2-pyrones in a 1:1 mixture of acetic acid/HCl for at least 8 h. A sequence of hydrolysis, decarboxylation, and cyclization reactions was proposed by Birch *et al.* to explain this transformation [8].

Taking into account our interest and knowledge on the use of compound **2** as starting material in several early studies [6,10,11] and on the photooxidative cyclization of (*E*)-2-styrylchromones into benzo[*a*]xanthene-12-ones [12,13], we decided to study the transformation of 2-pyrones **2a–f** and **3** into 4-pyrones **4a–f** and **5**, under microwave irradiation and to compare these results with those using conventional reflux. Finally, we developed a new synthetic method of 3-methyl-1*H*-benzo[*f*]chromen-1-ones **6a–f** and 2-methyl-5-phenyl-4*H*-chromen-4-one **7** by photocatalytic oxidative cyclization of 6-[(*E*)-2-arylvinyl]-2-methyl-4*H*-pyran-4-ones

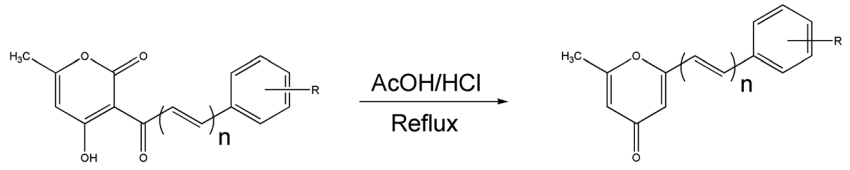
Scheme 1



2 **1** **3**

A: Benzaldehydes; B: Cinnamaldehyde
For compounds **2**:
a) R = H; b) R = 4-CH_3; c) R = 4-Cl; d) 4-NO_2; e) R = 3-CH_3; f) R = 3-NO_2

Scheme 2



2, n = 1
3, n = 2

4, n = 1
5, n = 2

4a–f and 2-methyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]-4*H*-pyran-4-one **5**, using $CuAlO_2$ and catalyst.

RESULTS AND DISCUSSION

According to Scheme 2, we carried out the acid-catalyzed transformation of compounds **2a–f** and **3** into **4a–f** and **5** through conventional reflux heating conditions and microwave-based procedures (the main reaction data are presented in Table 1). From the results presented in Table 1, one can conclude that synthesis of **4a–f** was carried out under microwave irradiation that provided increase in yield (0–17%), but the most important aspect to notice is the huge reduction on the reaction time (from 4–5 h to 8–10 min). It is also noteworthy that we performed the rapid (8 min) and efficient (90% of yield) synthesis of **5** under microwave-assisted transformation of **3**.

The structure of products **4a–f** and **5** were confirmed by mass spectrometry, ^{1}H and ^{13}C NMR, UV, and IR spectroscopy. Mass spectra of **4a–f** confirm the decarboxylation of compound **2**. From the ^{1}H NMR spectra, one can assign the signals corresponding to the resonances of H-5 (as doublet) and H-3 (as double quartet) at respectively δH 6.21–6.37 ppm ($^4J_{H5–H3} = 2.3$ Hz) and δH 6.10–6.12 ($^4J_{H3–CH3} = 0.7$ Hz). The resonances of H-1′ and H-2′ appear as doublets at δH 7.00–7.24 and 7.53–7.95 ppm (in some

Table 1

Comparison of conventional heating and microwave-based conversion of 2-pyrones **2a–f** and **3**–4-pyrones **4a–f** and **5**.

Products	Substituent R	Procedures	Reaction time (min)	Yield (%)	T (°C)[c]
4a	H	A[a]	240	62	–
		B[b]	10	70	134
4b	4-CH_3	A[a]	300	70	–
		B[b]	10	70	134
4c	4-Cl	A[a]	300	68	–
		B[b]	10	75	135
4d	4-NO_2	A[a]	300	74	–
		B[b]	10	80	134
4e	3-CH_3	A[a]	300	65	–
		B[b]	10	82	135
4f	3-NO_2	A[a]	300	83	–
		B[b]	10	90	135
5	H	A[a]	240	86	–
		B[b]	8	90	130

[a]Reaction mixture submitted to the thermal reflux, using acetic acid/HCl (50%/50%) as solvent. [b]Reaction mixture irradiated in a MW oven dedicated to organic synthesis at 200 W, using acetic acid/HCl (75%/25%) as solvent. [c]Temperature at the end of the reaction.

cases H-2′ appears under a multiplet corresponding to the resonances of the aromatic compounds). The coupling constant value $^3J_{H1'-H2'} = 16.0–16.3$ Hz suggests a *trans* configuration for this vinylic group. The same holds for the two vinylic groups C1′ = C2′ and C3′ = C4′ of compound **5**, which are also, according to the coupling constants ($^3J_{H1'-H2'} = 16.2$ Hz, $^3J_{H3'-H4'} = 16.0$ Hz and $^3J_{H2'-H3'} = 11.0$ Hz), in the *trans-s-trans* configuration [13]. Overall, the data confirm that the compounds obtained are those expected and that the proposed sequence of hydrolysis, decarboxylation, and cyclization reactions occurred [8].

The next step in our study was the cyclization of **4a–f** and **5** according to the conditions described by previous reports [12,13]; that is exposition of chloroform or ethanol solutions of these compounds to daylight and UV irradiation. The progress of the reactions was followed by ^{1}H NMR for 2 weeks but no change had been detected. This result prompted us to use a known photocatalytic oxidative cyclization using delafossite as catalyst. The delafossite family has attracted much attention because of their technological importance for catalytic, photocatalytic and more recently environment-friendly properties [14].

The photooxidative cyclization of **4a–f** and **5** was performed in ethanol using $CuAlO_2$ (10% of the mass of subtract) previously prepared from CuO, $Al(NO_3)_3$, and HNO_3 [15] (Scheme 3). The mixture was maintained in a double-walled pyrex reactor and exposed to UV light for 24 h, and in each case, one pure product has been isolated in a high yield (averaging 90–95%).

The mass spectra of compounds **6a–f** and **7** [15] confirmed that a dehydrogenation reaction occurred because the molecular ions indicate the loss of 2 Da peaks relatively to those of the starting materials **2a–f** and **3**, respectively. From the analysis of the ^{1}H NMR spectra and HSQC experiments of all compounds **6a–f** and **7**, one can assign the resonance of H-3 (**6a–f**) and H-2 (**7**) as a quartet ($^4J \sim 0.7$ Hz) at δH 6.01–6.10 ppm and confirm the absence of the resonance due to H-5 of the starting materials **2a–f** and **3**. In the ^{13}C NMR of 4-pyranones **4a–f** and **5**, the signals corresponding to the resonance of protonated C-3 appear at δC 113–115 ppm; however, the resonance of the new non-protonated C-10b of **6a–f** and C-4a of **7** appear at δC 121.7–129.9 ppm.

In the case of the compounds **4e** and **4f** bearing *meta*-CH_3 and -NO_2 substituents, we can consider two possibilities of cyclization give rise to structures **I** or **II** (Figure 1). The analysis of the HMBC spectra of **6e** and **6f** confirmed the cyclization on the *para*-position relatively to the substituent, because a connectivity between the proton H-10 and the carbon C-10b of the pyran ring was observed (Figure 1). This finding and some other connectivities observed in the HMBC spectra of compounds **6a–f** are in perfect agreement with the structure **II**.

For the formation of compounds **6a–e** and **7**, one can envisage the photochemical excitation of the enone system followed by oxidative cyclization (Scheme 4). $CuAlO_2$ has been elaborated through the nitrate route in order to obtain a large surface to volume ratio and to shorten the traveled carriers' path [15]. It crystallizes in the delafossite structure and absorbs over the whole solar spectrum. In addition to being inexpensive, $CuAlO_2$ also shows an excellent chemical stability over the whole pH range and can be easily recovered at the end of the reaction. The proposal mechanism for the formation of **6a–f** and **7** may involve a *trans* → *cis* isomerisation of the vinylic system, which facilitates the cyclization by photocatalytic oxidative cyclization according to the reaction sequence depicted in Scheme 4.

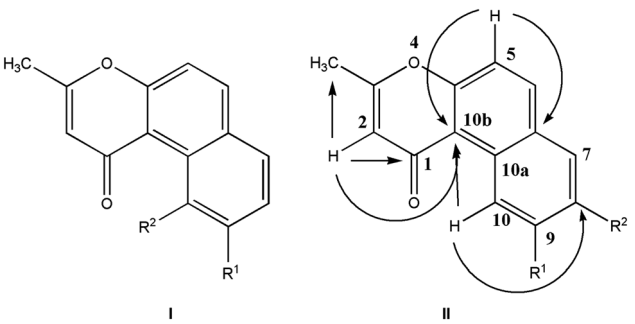
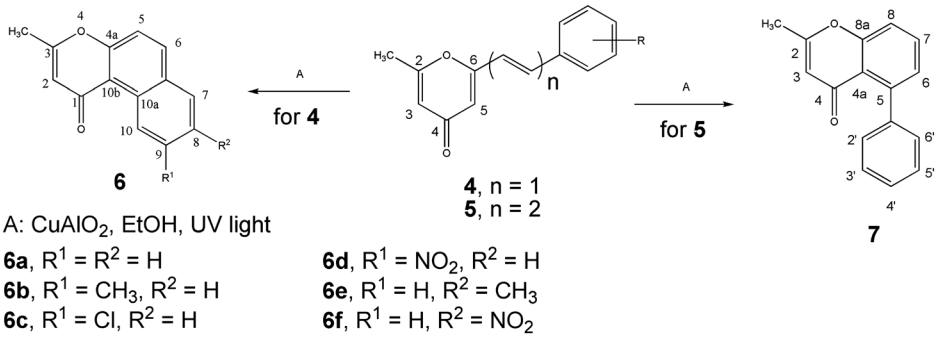
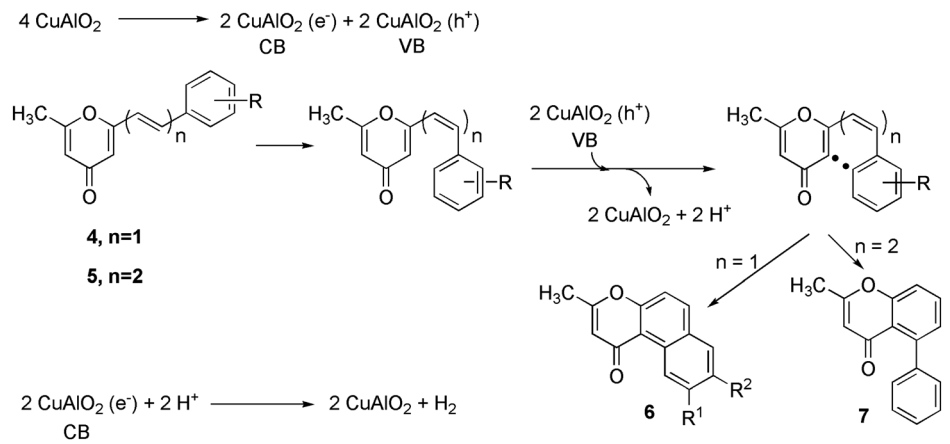


Figure 1. Two possibilities of cyclization give rise to structures **I** or **II**.

Scheme 3



Scheme 4



CONCLUSION

We have demonstrated that the conversion of 4-hydroxy-6-methyl-3-[(2*E*)-3-arylprop-2-enoyl]-2*H*-pyran-2-ones **2a–f** and 4-hydroxy-6-methyl-3-[(2*E*,4*E*)-5-phenylpenta-2,4-dienoyl]-2*H*-pyran-2-one **3** into 2-methyl-6-[(*E*)-2-arylvinyl]-4*H*-pyran-4-ones **4a–f** and 2-methyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]-4 *H*-pyran-4-one **5** is greatly facilitated by microwave irradiation. Moreover, the reaction times are dramatically reduced. Further, we have shown that compounds **4a–f** and **5** undergo an efficient photocatalytic oxidative cyclization, using $CuAlO_2$ as catalyst, to give 3-methyl-1*H*-benzo[*f*]chromen-1-ones **6a–f** and 3-methyl-9-phenyl-1*H*-benzo[*f*]chromen-1-one **7**. Studies of the reactivity of these new compounds as well as their biological applications are in progress.

EXPERIMENTAL

The microwave-assisted organic reactions were performed in an Ethos SYNTH microwave (Milestone Inc., Shelton, CT) dedicated to the organic synthesis. The photooxidative cyclization was performed in a small-sized pyrex reactor (250 mL), with a double jacket connected to a thermostated bath, regulated at 30 ± 0.1 °C. The light source consisted of halogen lamp (500 W, OSRAM, Munich, Germany). Melting points were determined on a Stuart scientific SPM3 apparatus fitted with a microscope and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in DMSO solutions, on a Bruker Avance 300 spectrometer (Bruker Biospin SAS, Wissembourg, France), operating at 300.13 and 75.47 MHz, respectively; the chemical shifts are expressed in ppm (δ) and coupling constants (*J*) are giving in Hz. ^{1}H and ^{13}C NMR assignments were made by using HSQC and HMBC experiments. Electron impact mass spectra were obtained at 70 eV electron impact ionization using Nermag R 10-10 C quadruple mass spectrometer (Nermag SA, Rueil Malmaison, France). Infrared spectra were recorded on a Magna-IR 550 series II Nicolet apparatus, using potassium bromide pellets. UV spectra were recorded on Cary 50 Scan UV-Visible spectrometer (Agilent Technologies, Massy, France) in chloroform solutions(Spectralab Scientific Inc., Ontario, Canada). A (8/2 v/v) mixture of CH_2Cl_2/CH_3OH has been used for the TLC analysis.

$CuAlO_2$ has been synthesized by chemical co-precipitation [15]. Stoichiometric amounts of CuO (pre-fired at 400 °C) and $Al(NO_3)_3.9H_2O$ were dissolved in concentrated HNO_3 (6 N). The blue solution was dehydrated in a sand bath until dryness. Then, the amorphous powder was fired in an air oven at 700 °C. The reaction was completed usually after two thermal treatments at 950 °C. Unreacted Cu_2O was removed by soaking the powder in NH_4OH (5 N). The end product exhibits a blue color and the phase was confirmed by XRD using CuK_2 radiation.

General procedure for the synthesis of 2-methyl-6-[(*E*)-2-arylethenyl]-4*H*-pyran-4-ones 4a-f and 2-methyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-4*H*-pyran-4-one 5. A solution of 3-[(2*E*)-3-arylprop-2-enoyl]-4-hydroxy-6-methyl-2*H*-pyran-2-ones **2a–f** or 4-hydroxy-6-methyl-3-[(2*E*,4*E*)-5-phenylpenta-2,4-dienoyl]-2*H*-pyran-2-one **3** (5 mmol) in of acetic acid (10 mL) and of HCl (10 mL) was refluxed with stirring for 4–5 h. After extraction by chloroform (3×50 mL) and washing by diethyl ether, compounds **4a–f** and **5** were obtained without crystallization. The purity was then confirmed by thin layer chromatography.

2-Methyl-6-[(E)-2-phenylethenyl]-4H-pyran-4-one (4a). This compound was obtained as yellow powder. Yield: 66%; mp 121–122 °C.^{1}H NMR (DMSO-d_6): δ 2.33 (d, 3H, 2-CH_3, $J_{CH3\text{-}H3} = 0.7$ Hz), 6.11 (dq, 1H, H-3, $J_{H3–CH3} = 0.7$ Hz, $J_{H3–H5} = 2.3$ Hz), 6.30 (d, 1H, H-5, $J_{H5–H3} = 2.3$ Hz), 7.03 (d, 1`H, H-1′, $J_{H1'–H2'} = 16.3$ Hz), 7.55 (m, 6H, H-2′ and H-Ph); ^{13}C NMR (DMSO-d_6): δ 19.1 (2-*C*H_3), 113.0 (C-5), 113.4 (C-3), 120.0 (C-1′), 127.4 (C-5′,7′), 128.8 (C-4′,8′), 134.7 (C-3′), 129.4 (C-6′) 134.9 (C-2′), 161.3 (C-6), 165.3 (C-2), 178.1 (C-4); EIMS: *m/z* (rel. int.) 212 ($M^{+\cdot}$, 74); IR: (ν, cm^{-1}) 3050, 1668, 1612, 1392; UV: λ_{max} 334 (ε 152.100). *Anal.* Calcd for $C_{14}H_{12}O_2$: C 79.22, H 5.70. Found: C 79.15, H 5.38%.

6-Methyl-2-[(E)-2-(4-methyphenyl)ethenyl]-4H-pyran-4-one (4b). This compound was obtained as yellow powder. Yield 70%; mp. 120–121 °C; ^{1}H NMR (DMSO-d_6): δ 2.31 (d, 3H, 2-CH_3, $J_{CH3–H3} = 0.7$ Hz), 2.31 (s, 3H, 6′-CH_3), 6.12 (dq, 1H, H-3, $J_{H3\text{-}CH3} = 0.7$ Hz, $J_{H3–H5} = 2.4$ Hz), 6.21 (d, 1H, H-5, $J_{H5–H3} = 2.3$ Hz), 7.05 (d, 1H, H-1′, $J_{H1'–H2'} = 16.0$ Hz), 7.54 (m, 5H, H-2′ and C_6H_4); ^{13}C NMR (DMSO-d_6): δ 19.1 (2-CH_3), 21.3 (6′-CH_3), 113.1 (C-5), 113.6 (C-3), 119.8 (C-1′), 127.3 (C-3′), 130.1 (C-5′,7′), 128.1 (C-4′,8′), 125.3 (C-2′), 160.4 (C-6′), 161.8 (C-6), 165.1 (C-2), 178.0 (C-4); EIMS: *m/z* (rel. int.) 242 ($M^{+\cdot}$, 53); IR: (ν, cm^{-1}) 3000, 1662, 1618, 1381; UV: λ_{max} 333 (ε 156.100). *Anal.* Calcd for $C_{15}H_{14}O_2$: C 79.62, H 6.24. Found: C 79.48, H 6.10%.

2-[(E)-2-(4-Chlorophenyl)ethenyl]-6-methyl-4H-pyran-4-one (4c). This compound was obtained as yellow small crystals. Yield 72%; mp 110–111 °C; ^{1}H NMR (DMSO-d_6): δ 2.31 (d, 3H, 2-CH_3, $J_{CH3–H3}$ = 0.8 Hz), 6.10 (dq, 1H, H-3, $J_{H3–CH3}$ = 0.8 Hz, $J_{H3–H5}$ = 2.3 Hz), 6.29 (d, 1H, H-5, $J_{H5–H3}$ = 2.3 Hz), 7.03 (d, 1H, H-1′, $J_{H1′–H2′}$ = 16.2 Hz), 7.53 (m, 5H, H-2′ and C_6H_4); ^{13}C NMR (DMSO-d_6): δ 19.1 (2-CH_3), 113.2 (C-5), 113.5 (C-3), 120.8 (C-1′), 133.3 (C-3′), 128.6 (C-5′,7′), 129.1 (C-4′,8′), 133.6 (C-2′), 133.9 (C-6′), 161.6 (C-6), 165.3 (C-2), 178.6 (C-4); EIMS: *m/z* (rel. int.) 246 ($M^{+\cdot}$, 80); IR: (ν, cm^{-1}) 3000, 1678, 1612, 1386;UV: λ_{max} 335 (ε 148.900). *Anal*. Calcd for $C_{14}H_{11}ClO_2$: C 68.16, H 4.49. Found: C 68.02, H, 4.36%.

2-[(E)-2-(4-Nitrophenyl)ethenyl]-6-methyl-4H-pyran-4-one (4d). This compound was obtained as colored powder. Yield: 81%; mp. 208–209 °C; ^{1}H NMR (DMSO-d_6): δ 2.33 (d, 3H, 2-CH_3, $J_{CH3–H3}$ = 0.7 Hz), 6.11 (dq, 1H, H-3, $J_{H3–CH3}$ = 0.7 Hz, $J_{H3–H5}$ = 2.3 Hz), 6.37 (d, 1H, H-5, $J_{H5–H3}$ = 2.3 Hz), 7.24 (d, 1H, H-1′, $J_{H1′-H2′}$ = 16.2 Hz), 7.95 (m, 5H, H-2′ and C_6H_4); ^{13}C NMR (DMSO-d_6): δ 19.1 (2-CH_3), 113.6 (C-5), 114.6 (C-3), 124.4 (C-1′), 141.5 (C-3′),123.9 (C-5′,7′), 128.4 (C-4′,8′), 132.2 (C-2′), 129.4 (C-6′), 160.5 (C-6), 165.5 (C-2), 178.6 (C-4); EIMS: *m/z* (rel. int.) 257($M^{+\cdot}$, 100); IR: (ν, cm^{-1}) 3040, 1676, 1601,1389; UV: λ_{max} 331 (ε 148.200). *Anal*. Calcd for $C_{14}H_{11}NO_4$: C 65.37, H 4.31. Found: C 65.20, H 4.27%.

2-Methyl-6-[(E)-2-(3-methylphenyl)ethenyl]-4H-pyran-4-one (4e). This compound was obtained as colored powder. Yield: 74% mp 113–114 °C; ^{1}H NMR (DMSO-d_6): δ 2.31 (d, 3H, 2-CH_3, $J_{CH3–H3}$ = 0.7 Hz), 2.33 (s, 3H, 5′-CH_3) 6.12 (dq, 1H, H-3, $J_{H3–CH3}$ = 0.7 Hz, $J_{H3–H5}$ = 2.3 Hz), 6.28 (d, 1H, H-5, J_{H5-H3} = 2.3 Hz), 7.00 (d, 1H, H-1′, $J_{H1′–H2′}$ = 16.1 Hz), 7.95 (m, 5H, H-2′ and C_6H_4); ^{13}C NMR (DMSO-d_6): δ 19.8 (2-CH_3), 21.3 (5′-CH_3), 114.1 (C-5), 113.3 (C-3), 119.3 (C-1′), 124.7 (C-8′), 128.1 (C-7′), 128.8 (C-4′), 130.5 (C-6′), 134.8 (C-2′ and C-3′), 138.6 (C-5′), 161.9 (C-6), 165.0 (C-2), 180.3 (C-4); EIMS: *m/z* (rel. int.) 226 ($M^{+\cdot}$, 100); IR: (ν, cm^{-1}) 3063, 1675, 1607, 1379; UV: λ_{max} 334 (ε 172.800). *Anal*. Calcd for $C_{15}H_{14}O_2$: C 79.62, H 6.24. Found: C 79.48, H 6.12%.

2-[(E)-2-(3-Nitrophenyl)ethenyl]-6-methyl-4H-pyran-4-one (4f). This compound was obtained as yellow powder. Yield: 90%; mp. 181–182 °C; ^{1}H NMR (DMSO-d_6): δ 2.32 (s, 3H, 2-CH_3), 6.12 (s, 1H, H-3), 6.37 (d, 1H, H-5, $J_{H5–H3}$ = 2.0 Hz), 7.08 (d, 1H, H-1′, $J_{H1′–H2′}$ = 16.0 Hz), 7.80 (m, 5H, H-2′ and C_6H_4); ^{13}C NMR (DMSO-d_6): δ 19.1 (2-CH_3), 114.4 (C-5), 115.0 (C-3), 124.4 (C-1′), 130.0 (C-3′), 124.9 (C-4′), 133.6 (C-6′), 148.3 (C-3′), 128.5 (C-4′), 130.9 (C-2′), 130.9 (C-5′), 160.7 (C-6), 165.5 (C-2), 180.1 (C-4); EIMS: *m/z* (rel. int.) 257 ($M^{+\cdot}$, 67); IR: (ν, cm^{-1}) 3030, 1673, 1611, 1378; UV: λ_{max} 332 (ε 135.000). *Anal*. Calcd for $C_{14}H_{11}NO_4$: C 65.37, H 4.31. Found: C 65.20, H 4.10%.

2-Methyl-6-[(1E,3E)-4-phenylbuta-1,3-dienyl]-4H-pyran-4-one (5). This compound was obtained as yellow small crystals. Yield 91%; mp 140–141 °C; ^{1}H NMR (DMSO-d_6): δ 2.32 (d, 3H, 2-CH3, $J_{CH3–H3}$ = 0.7 Hz), 6.12 (dq, 1H, H-3, $J_{H3–CH3}$ = 0.7 Hz, $J_{H3–H5}$ = 2.3 Hz), 6.36 (d, 1H, H-5, $J_{H5–H3}$ = 2.3 Hz), 6.93 (d, 1H, H-1′, $J_{H1′–H2′}$ = 16.2 Hz), 7.12 (dd, 1H, H-2′, $J_{H2′–H1′}$ = 16.2 Hz, $^3J_{H2′–H3′}$ = 11.0 Hz), 7.40 (dd, 1H, H-3′, $^3J_{H3′–H2′}$ = 11.0 Hz, $J_{H3′–H4′}$ = 16.0 Hz), 7.58 (m, 6H, H-4′, H-Ph); ^{13}C NMR (DMSO-d_6): δ 19.1 (2-CH_3), 113.0 (C-5), 113.5 (C-3), 120.1 (C-1′), 125.5 (C-3′), 127.5 (C-5′,7′), 129.2 (C-4′,8′), 128.8 (C-4′), 131.1 (C-2′), 134.7 (C-3′),129.4 (C-5′), 161.3 (C-6), 165.2 (C-2), 178.0 (C-4); EIMS: *m/z* (rel. int.) 238 ($M^{+\cdot}$, 59); IR: (ν, cm^{-1}) 3023, 1666, 1604, 1349; UV: λ_{max} 323 (ε 126.000). *Anal*. Calcd for $C_{16}H_{14}O_2$: C 80.65, H 5.92. Found: C 80.48, H 5.87%.

General procedure for the synthesis of 3-methyl-1H-benzo[*f*]chromen-1-ones 6a-f and 2-methyl-5-phenyl-4H-chromen-4-one 7. A mixture of 6-[(*E*)-2-arylethenyl]-2-methyl-4H-pyran-4-ones **4a–f** or 2-methyl-6-[(1*E*,3*E*)-4-phenylbuta-1,3-dienyl]-4H-pyran-4-one **5** (5 mmol) and $CuAlO_2$ (10% in mass of subtract) in ethanol (30 mL) was subjected to halogen lamp illumination with stirring for 24 h. After filtration and crystallization in ethanol, compounds **6a–f** and **7** were obtained.

3-Methyl-1H-benzo[f]chromen-1-one (6a). This compound was obtained as colored powder. Yield 94%; mp. 190–191 °C; ^{1}H NMR (DMSO-d_6): δ 2.10 (d, 3H, 3-CH_3), 6.01 (q, 1H, H-2), 7.41 (d, 1H, H-5), 7.64 (d, 1H, H-10), 7.70 (m, 1H, H-9), 7.76 (m, 1H, H-8), 7.91 (dd, 1H, H-7), 8.15 (dd, 1H, H-6); ^{13}C NMR (DMSO-d_6): δ 19.2 (3-CH_3), 113.3 (C-2), 117.1 (C-5), 122.6 (C-10b), 126.7 (C-8), 127.5 (C-10), 128.6 (C-9), 128.8 (C-6a), 130.1 (C-10a), 130.8 (C-7), 138.7 (C-6), 157.2 (C-4a), 166.1 (C-3), 179.8 (C-1); EIMS: *m/z* (rel. int.) 210 ($M^{+\cdot}$, 90); IR: (ν, cm^{-1}) 3030, 1643, 1629, 1315; UV: λ_{max} 322 (ε 123.900). *Anal*. Calcd for $C_{14}H_{10}O_2$: C 79.98, H 4.79. Found: C 79.72, H, 4.63%.

3,9-Dimethyl-1H-benzo[f]chromen-1-one (6b). This compound was obtained as colored small crystals. Yield 92%; mp. 194–195 °C; ^{1}H NMR (DMSO-d_6): δ 2.10 (d, 3H, 3-CH_3), 2.48 (d 3H, 9-CH_3), 6.04 (q, 1H, H-2), 7.41 (d, 1H, H-5), 7.68 (d, 1H, H-10), 7.74 (m, 1H, H-9), 8.10 (dd, 1H, H-7), 8.06 (dd, 1H, H-6); ^{13}C NMR (DMSO-d_6): δ 19.1 (3-CH_3), 21.2 (9-CH_3), 113.3 (C-2), 122.6 (C-10b), 117.0 (C-5),138.5 (C-6), 128.6 (C-6a), 135.3 (C-7), 120.1 (C-8), 140.0 (C-9), 122,8 (C-10), 133.1 (C-10a), 156.8 (C-4a), 166.1 (C-3), 179.8 (C-1); EIMS: *m/z* (rel. int.) 240 ($M^{+\cdot}$, 100); IR: (ν, cm^{-1}) 3024, 1644, 1623, 1360; UV: λ_{max} 322 (ε 127.100). *Anal*. Calcd for $C_{15}H_{12}O_2$. C 80.34, H 5.39. Found: C 80.07, H 5.20%.

9-Chloro-3-methyl-1H-benzo[f]chromen-1-one (6c). This compound was obtained as colored powder. Yield 90%; mp 201–202 °C; ^{1}H NMR (DMSO-d_6): δ 2.08 (d, 3H, 3-CH_3), 6.05 (q, 1H, H-2), 7.39 (d, 1H, H-5), 7.5 (d, 1H, H-10), 7.40 (m, 1H, H-8), 7.86 (m, 1H, H-7), 8.07 (m 1H, H-6); ^{13}C NMR (DMSO-d_6): δ 19.2 (3-CH_3), 113.3 (C-2), 117.1 (C-5), 120.0 (C-8), 121.7 (C-10b), 127.8 (C-6a), 132.5 (C-8), 133.0 (C-10a), 135.1 (C-7),138.9 (C-9 and C-6), 157.3 (C-4a), 166.1 (C-3), 179.7 (C-1); EIMS: *m/z* (rel. int.) 244 ($M^{+\cdot}$, 100); IR: (ν, cm^{-1}) 3019, 1648, 1623, 1360; UV: λ_{max} 323 (ε 113.000) . Anal. calcd for $C_{14}H_9ClO_2$: C 68.72, H 3.71. Found: C 68.47, H 3.59%.

3-Methyl-9-nitro-1 H-benzo[f]chromen-1-one (6d). This compound was obtained as colored powder. Yield 93%; mp 220–221 °C; ^{1}H NMR (DMSO-d_6): δ 2.11 (d, 3H, 3-CH_3), 6.08 (q, 1H, H-2), 7.42 (d, 1H, H-5), 8.10 (m, 1H, H-6), 8.34 (d, 1H, H-10), 8.40 (1H, H-8), 8.42 (m, 1H, H-7); ^{13}C NMR (DMSO-d_6): δ 19.2 (3-CH_3), 112.9 (C-10), 113.3 (C-2), 114.9 (C-5), 121.8 (C-8), 127.1 (C-10b), 127.7 (C-7), 130.1 (C-6a), 130.2 (C-10a), 141.1 (C-6), 150.3 (C-9), 159.5 (C-4a), 166.2 (C-3), 179.8 (C-1); EIMS: *m/z* (rel. int.) 255 ($M^{+\cdot}$, 100); IR: (ν, cm^{-1}) 3023, 1650, 1629,1357; UV: λ_{max} 322 (ε 121.300). *Anal.* Calcd for $C_{14}H_9NO_4$: C 65.88, H 3.55. Found: C 65.72, H 3.47%.

3,8-Dimethyl-1H-benzo[f]chromen-1-one (6e). This compound was obtained as colored small crystals. Yield 92%; mp. 190–191 °C; ^{1}H NMR (DMSO-d_6): δ 2.10 (d, 3H, 3-CH_3), 2.48 (s, 3H, 8-CH_3), 6.04 (q, 1H, H-2), 7.41(d, 1H, H-5), 7.68 (d, 1H, H-10), 7.74 (m, 1H, H-9), 8.06 (dd, 1H, H-6), 8.10 (dd, 1H, H-7), ^{13}C NMR (DMSO-d_6): δ 19.2 (3-CH_3), 21.1 (8-CH_3),

113.3 (C-2), 116.2 (C-5), 121.9 (C-10b), 125.1 (C-10), 128.5 (C-10a), 128.8 (C-6a), 130.3 (C-9), 132.8 (C-6), 135.8 (C-7 and C-8), 157.3 (C-4a), 166.1 (C-3), 1 79.8 (C-1); EIMS: *m/z* (rel. int.) 224 ($M^{+\cdot}$, 75); IR: (ν, cm^{-1}) 3010, 1643, 1612, 1325; UV: λ_{max} 322 (ε 121.400). *Anal*. Calcd for $C_{15}H_{12}O_2$: C 80.34, H 5.39. Found: C 80.10, H 5.23%.

3-Methyl-8-nitro-1H-benzo[f]chromen-1-one (6f). This compound was obtained as colored small crystals. Yield 93%; mp 210–211 °C; ^{1}H NMR (DMSO-d_6): δ 2.09 (d, 3H, 3-CH_3), 6.08 (q, 1H, H-2), 7.62 (d, 1H, H-5), 7.70 (d, 1H, H-10), 8.20 (m, 1H, H-9), 8.36 (dd, 1H, H-6), 8.92 (dd, 1H, H-7); ^{13}C NMR (DMSO-d_6): δ 19.2 (3-CH_3), 113.3 (C-2), 125.0 (C-10b), 119.2 (C-5), 136.9 (C-6), 126.8 (C-6a), 131.1 (C-7), 147.9 (C-8), 124.6 (C-9), 126.9 (C-10), 132.2 (C-10a), 154.6 (C-4a), 166.2 (C-3), 180.1 (C-1); EIMS: *m/z* (rel. int.) 255 ($M^{+\cdot}$, 55); IR: (ν, cm^{-1}) 3010, 1642, 1622, 1358; UV: λ_{max} 322 (ε 117.200). *Anal*. Calcd. for $C_{14}H_9NO_4$: C 65.88, H 3.55. Found: C 65.72, H 3.49%.

2-Methyl-5-phenyl-4 H-chromen-4-one (7). This compound was obtained as colored powder. Yield 95%; mp 190–191 °C; ^{1}H NMR (DMSO-d_6): δ 2.12 (d, 3H, 2-CH_3), 6.10 (q, 1H, H-3), 6.72 (d, 1H, H-8), 6.89 (d, 1H, H-7), 7.52–7.79 (m, 6H, H-6, H-Ph); ^{13}C NMR (DMSO-d_6): δ 19.1 (2-CH_3), 111.2 (C-3), 124.2 (C-6), 125.2 (C-8), 127.9 (C-3′,5′), 128.6 (C-2′,6′), 129.9 (C-4a), 130.2 (C-4′), 133.8 (C-7), 140.1 (C-5), 153.7 (C-1′), 157.4 (C-8a), 164.7 (C-2), 179.4 (C-4); EIMS: *m/z* (rel. int.) 236 ($M^{+\cdot}$, 70); IR: (ν, cm^{-1}) 3001, 1649, 1623, 1376; UV: λ_{max} 321 (ε 123.000). Anal. calcd. for $C_{16}H_{12}O_2$: C 81.34, H 5.12. Found: C 81.22, H 4.95%.

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