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First intramolecular Diels–Alder reactions using chromone derivatives: synthesis of chromeno-[3,4-*b*]xanthones and 2-(benzo[*c*]chromenyl)-chromones†

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A series of novel (*E*)-2-(2-propargyloxystyryl)chromones and (*E*,*E*)-2-[4-(2-propargyloxyphenyl)buta-1,3-dien-1-yl]chromones were designed and synthesized *via* aldol condensation of 2-methylchromones with 2-propargyloxy(benzaldehyde and cinnamaldehyde), respectively. Both chromone derivatives were used as substrates in microwave-assisted intramolecular Diels–Alder reactions, affording chromeno[3,4-*b*]-xanthones and 2-(benzo[*c*]chromenyl)chromones. This is the first report involving chromone derivatives in intramolecular Diels–Alder reactions for the synthesis of new oxygen heterocycles, namely xanthone- and flavone-type compounds.

Introduction

Chromone (or 4*H*-chromen-4-one), a natural occurring 6-*O*-membered heterocycle, is widely found as the basic core in a large variety of compounds that exhibits important biological properties.[1,2] This ring system is also a useful substrate for further functionalization, which can be achieved through oxidation, condensation, conjugate addition or Diels–Alder (DA) reactions.[3,4] In fact, a DA reaction is one of the most powerful cycloaddition reactions in organic synthesis and particularly, in the construction of 6-membered rings, combining dienes and dienophiles with different substitution patterns.[5,6] There are countless examples of natural products and other complex structures synthesized through this approach, with an outstanding degree of control and a high level of predictability for this process.[7] Inspired by the versatility of an intermolecular DA reaction, intramolecular DA reactions has also been employed in the total synthesis of several polycyclic natural products, using one or multiple step strategies.[8] Although some chromone derivatives such as 2- or 3-styrylcromones have been involved in DA reactions, either as dienes or dienophiles,[9–12] to the best of our knowledge, there are no reports involving chromone derivatives in intramolecular DA reactions. Thus, following our previous reports dealing with the reactivity of (*E*)-2-(4-arylbut-1-en-3-yn-1-yl)chromones and (*E*,*E*)-2-(4-arylbuta-1,3-dien-1-yl)chromones in DA reactions,[13,14] herein we envisaged the synthesis of novel propargyloxychromone derivatives to be used as substrates in intramolecular DA reactions. This is the first report involving chromone derivatives in intramolecular DA reactions under microwave (MW) irradiation, allowing the synthesis of chromeno[3,4-*b*]xanthones and 2-(benzo[*c*]chromenyl)chromones. Moreover, the prepared compounds can present enhanced biological properties since they combine the xanthone and chromene nucleus, and the benzochromene and chromone moieties in the same molecules (hybrid drug concept).[15–18]

Results and discussion

Synthesis of the starting chromones

The starting (*E*)-2′-propargyloxy-2-styrylchromones **4a–d** were prepared in good yields (73–86%) through base-catalyzed aldol condensation of the appropriate 2-methylchromone **2a–d** with *ortho*-propargyloxybenzaldehyde **3** [Scheme 1(ii)]. The required benzaldehyde **3** was obtained by propargylation of the commercially available salicylaldehyde **1** with propargyl bromide in the presence of potassium carbonate in refluxing acetone [Scheme 1(i)].

The main features in the ^{1}H NMR spectra of (*E*)-2′-propargyloxy-2-styrylchromones **4a–d** are the presence of: (i) two doublets at δ 6.81–6.91 and 7.81–7.94 ppm assigned to vinylic protons H-α and H-β, respectively, in a *trans* configuration ($^3J_{H\alpha-H\beta}$ 16.2 Hz); (ii) a singlet at δ 6.19–6.35 ppm assigned to proton H-3; and (iii) a doublet and a triplet at δ 4.83–4.85 and 2.58 ppm assigned to protons H-1″ and H-3″, respectively (see Scheme 1 for numbering).

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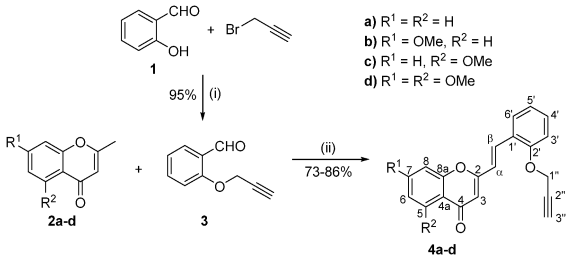
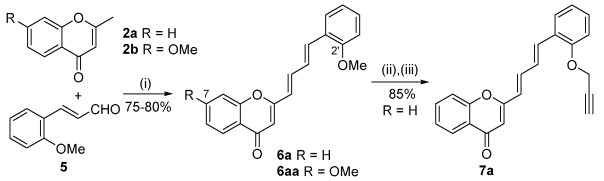


Scheme 1 Synthesis of (*E*)-2′-propargyloxy-2-styrylchromones **4a–d**. *Reagents and conditions*: (i) K_2CO_3, acetone, reflux, 2 h; (ii) Na, EtOH, r.t., 3–6 h.

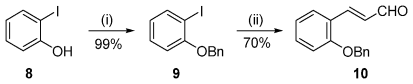


Scheme 2 Synthesis of chromones **6a**, **6aa** and **7a**. *Reagents and conditions*: (i) Na, EtOH, r.t., 2–3 h; (ii) BBr_3, CH_2Cl_2, r.t., 2 h; (iii) K_2CO_3, propargyl bromide, acetone, reflux, 5 h.

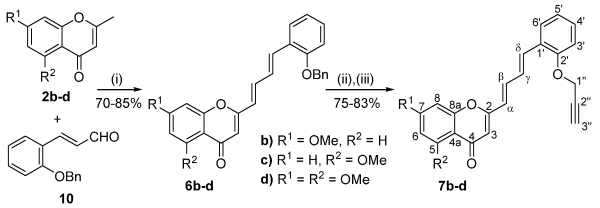
The synthesis of (*E*,*E*)-2-[4-(2-propargyloxyphenyl)buta-1,3-dien-1-yl]chromones was not straightforward. The initial strategy involved the base-catalyzed aldol condensation of 2-methylchromone **2a** with the commercially available *ortho*-methoxycinnamaldehyde **5**, affording the methoxy substituted chromone **6a** in good yield [Scheme 2(i)]. Then, the methyl group was cleaved with boron tribromide and the propargylation was accomplished with propargyl bromide in the presence of potassium carbonate as a base, giving the desired *O*-propargyl-2-butadienylchromone **7a** with a good overall yield (85%) [Scheme 2(ii) and (iii)]. This strategy was applied to the 2-methylchromone derivative **2b**, however, the demethylation step led to the undesired cleavage of both methyl groups (2′-OMe and 7-OMe). The analysis of the ^{1}H NMR spectrum of the crude product of the reaction with boron tribromide showed the presence of two singlets corresponding to protons 2′-O*H* and 7-O*H*, as well as another singlet corresponding to 7-OCH_3. The existence of a 7-OH group of the chromone moiety creates another undesired propargylation site, avoiding the selective propargylation of 2′-OH. Therefore, it was necessary to employ a different strategy for the synthesis of chromones **7b–d**.

The new strategy relied on the preparation of a specific cinnamaldehyde **10** with an appropriate *ortho* protecting group, which could be selectively cleaved using less harsh conditions (Scheme 3). Having this in mind, 2-iodophenol **8** was benzylated with benzyl bromide (BnBr) in the presence of potassium carbonate, affording the aryl iodide **9** in an almost quantitative yield [Scheme 3(i)]. Then, the desired cinnamaldehyde **10** was obtained through the palladium-catalyzed cross-coupling reaction of aryl iodide **9** with acrolein diethyl acetal, following a previously reported procedure[19] [Scheme 3(ii)].

The base-catalyzed aldol condensation of 2-methylchromones **2b–d** with cinnamaldehyde **10** afforded the desired chromones



Scheme 3 Synthesis of *ortho*-benzyloxycinnamaldehyde **10**. *Reagents and conditions*: (i) K_2CO_3, BnBr, acetone, reflux, 16 h; (ii) Acrolein diethyl acetal, $^nBu_4NOAc$, K_2CO_3, $Pd(OAc)_2$, DMF, 90 °C, 16 h.



Scheme 4 Synthesis of chromones **7b–d**. *Reagents and conditions*: (i) Na, EtOH, r.t., 4–6 h; (ii) AcOH/HCl (10% v/v), 100 °C, 16 h; (iii) K_2CO_3, propargyl bromide, acetone, reflux, 5 h.

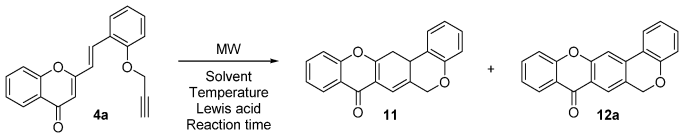
6b–d in good yields [Scheme 4(i)]. The next step of this strategy involved the selective cleavage of the benzyl group using a mixture of AcOH/HCl (37%) (10% v/v), followed by propargylation with propargyl bromide, which afforded the desired chromones **7b–d** in overall good yields [Scheme 4(ii) and (iii)].

The main structural features found in the ^{1}H NMR spectra of chromones **7a–d** are: (i) a doublet and a triplet at δ 4.78–4.80 and 2.56–2.57 ppm assigned to protons H-1″ and H-3″, respectively; (ii) a doublet at δ 6.27–6.36 ppm assigned to proton H-α in a *trans* configuration ($^3J_{H\alpha-H\beta}$ = 15.2 Hz); and (iii) a doublet at δ 7.26–7.31 ppm assigned to proton H-δ, in a *trans* configuration as well ($^3J_{H\alpha-H\beta}$ ∼ 15.5–16.1 Hz) (see Scheme 4 for numbering).

Intramolecular Diels–Alder reactions

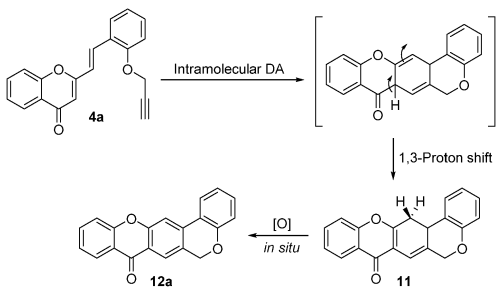
Once we achieved the synthesis of the propargyloxychromone derivatives **4a–d** and **7a–d**, they were used as templates for MW-assisted intramolecular DA reactions. The (*E*)-2′-propargyloxy-2-styrylchromone **4a** was used as a model substrate to prepare chromeno[3,4-*b*]xanthone derivatives. A careful optimization of the reaction conditions under MW irradiation was performed. Several attempts were carried out by varying the solvents, temperatures, reaction times and Lewis acid activation (Table 1). Chromeno[3,4-*b*]xanthone **12a** was obtained in fair to good yields (38–60%) using *N*-methyl-2-pyrrolidone (NMP) or 1,2,4-trichlorobenzene (1,2,4-TCB) as solvents, at an increased temperature (Table 1, entries 3–5). At a lower temperature and using DMF as the solvent xanthone **12a** was obtained in very low yield (Table 1, entries 3–5). The formation of this compound could be explained on the basis of a sequence of reactions involving firstly an intramolecular DA reaction, followed by olefin migration and *in situ* oxidation to afford chromeno[3,4-*b*]xanthone **12a** (Scheme 5). To prove this concept, derivative **11** was isolated in low yields (Table 1, entries 2–5, 7, 9 and 10) and its formation follows the same sequence of reactions without the *in situ* oxidation step (Scheme 5). In order to push the reaction towards the oxidized product, oxidizing agents such as 1,4-benzoquinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and chloranil were added to the crude reaction (Table 1, entries 6–8) and the best results were achieved

Table 1 MW-assisted intramolecular DA reaction using (*E*)-2′-propargyloxy-2-styrylchromone (**4a**)

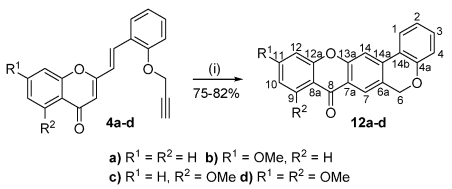


Entry	Solvent	Lewis acid[b]	T (°C)	Time (min)	**12a** yield[a] (%)	**11** yield[a] (%)	**4a** recovered[a] (%)
1	DMF	—	165	40	4	—	93
2	DMF	—	200	40	4	26	66
3	NMP	—	200	40	38	20	33
4	1,2,4-TCB	—	200	40	54	21	23
5	1,2,4-TCB	—	200	60	60	10	20
6[c]	1,2,4-TCB	—	200	60	10	—	—
7[d]	1,2,4-TCB	—	200	60	50	11	Traces
8[e]	1,2,4-TCB	—	200	60	75	—	Traces
9	1,2,4-TCB	—	200	80	60	8	15
10	1,2,4-TCB	—	220	60	50	8	14
11	1,2,4-TCB	$Sc(OTf)_3$	200	60	10	—	—
12	1,2,4-TCB	$Sc(OTf)_3$	165	40	7	Traces	92
13	1,2,4-TCB	$SnCl_2$	200	60	8	Traces	—
14	1,2,4-TCB	$AlCl_3$	200	60	10	Traces	—
15	—	$Sc(OTf)_3$	165	40	3	—	91
16	—	AuCl	200	40	6	—	—
17	—	—	200	40	29	—	51
18	—	—	200	80	37	—	40

[a] Isolated yield. [b] 0.5 equiv. of Lewis acid. [c] Addition of 0.1 equiv. of DDQ to the crude mixture. Heating for 30 min at 100 °C under MW irradiation. [d] Addition of 0.1 equiv. of 1,4-benzoquinone to the crude mixture. Heating for 30 min at 50 °C under MW irradiation. [e] Addition of 0.1 equiv. of chloranil to the crude mixture. Heating for 30 min at 80 °C under MW irradiation. DMF = dimethylformamide; NMP = *N*-methyl-2-pyrrolidone; 1,2,4-TCB = 1,2,4-trichlorobenzene.



Scheme 5 Proposed mechanism for the formation of compounds **11** and **12a**.



Scheme 6 MW-assisted synthesis of chromeno[3,4-*b*]xanthones **12a–d**. *Reagents and conditions*: (i) 1,2,4-TCB, MW, 200 °C, 60 min. Chloranil, MW, 80 °C, 30 min.

in the presence of chloranil, being the chromeno[3,4-*b*]xanthone **12a** obtained as the only product in a 75% yield (Table 1, entry 8).

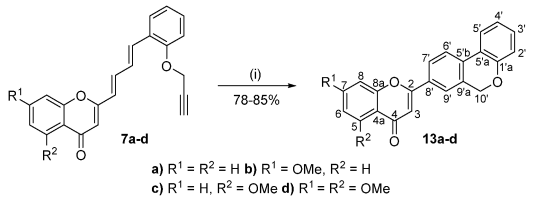
The effect of the addition of a series of Lewis acids was evaluated in solvent and solvent-free conditions, however, in all cases, the chromeno[3,4-*b*]xanthone **12a** was only obtained in low yields (Table 1, entries 11–16). Attempts to perform the reaction in solvent-free conditions were not advantageous affording compound **12a** in only 29–37% yield (Table 1, entries 17 and 18).

The best reaction conditions obtained for chromone derivative **4a** were applied to derivatives **4b–d**, affording the corresponding chromeno[3,4-*b*]xanthones **12b–d** in good yields (Scheme 6).

The chromeno[3,4-*b*]xanthones **12a–d** were easily distinguished from their chromone precursors **4a–d** by the analysis of their ^{1}H NMR spectra. The absence of the signals of the vinylic protons H-α and H-β, as well as the signal of proton H-3, and the presence of three singlets at δ 8.04–8.12; 7.61–7.76 and 5.20–5.23 ppm assigned to protons H-7, H-14 and H-6, respectively (see Scheme 6 for numbering), confirmed the structure of compounds **12a–d.**

In the case of chromones **7a–d**, the presence of two dienes may lead to distinct intramolecular-DA products (reaction on diene-3,2:α,β or diene-α,β:γ,δ – see Scheme 4 for numbering). Previous work on MW-assisted DA reactions of similar butadienyl-chromones with *N*-methylmaleimide as dienophile, showed that the reaction is selective towards the most reactive diene-α,β:γ,δ in the presence of scandium triflate as a Lewis acid.[14] Therefore, the intramolecular DA reaction of chromones **7a–d** was carried out using the optimized reaction conditions obtained for chromones **4a–d** (Scheme 7). Interestingly, the (benzo[*c*]chromenyl)chromones **13a–d** were obtained as the only product in good yields (78–85%) (Scheme 7).

The main features observed in the ^{1}H NMR spectra of 2-(benzo[*c*]chromenyl)chromones **13a–d** are the presence of: (i) a singlet at δ 5.19–5.23 ppm assigned to protons H-10′; (ii) a doublet at δ 7.78–7.84 ppm assigned to proton H-6′; and (iii) a double of doublets at δ 7.86–7.94 ppm assigned to proton H-7′.



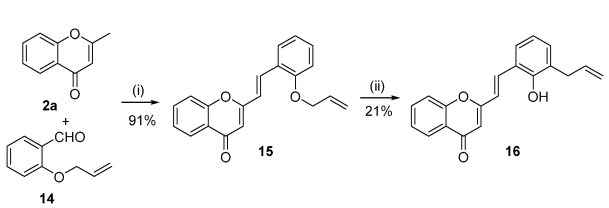
Scheme 7 MW-assisted synthesis of 2-(benzo[*c*]chromenyl)chromones **13a–d**. *Reagents and conditions*: (i) 1,2,4-TCB, MW, 200 °C, 60 min and then chloranil, MW, 80 °C, 30 min.

Concerning the signal of proton H-9′, it was observed as a doublet at δ 7.66–7.71 ppm for derivatives **13b–d**, and as a multiplet at δ 7.69–7.75 ppm for derivative **13a** (see Scheme 7 for numbering). The absence of the signals corresponding to the vinylic protons H-α, H-β, H-γ and H-δ, as well as the remaining presence of the singlet assigned to proton H-3, clearly indicates that the intramolecular DA reaction occurred in the diene-α,β:γ,δ, followed by *in situ* dehydrogenation of the formed adduct.

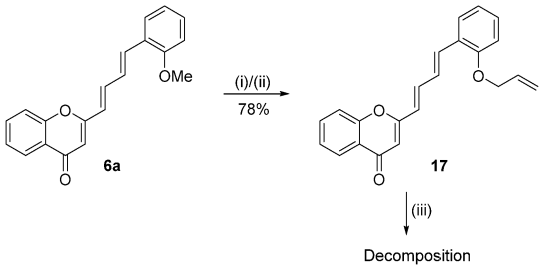
So far, the reactivity of a terminal alkyne as the dienophile in an intramolecular DA reaction was addressed in good overall yields (75–85%). In addition, we decided to further evaluate the same kind of reaction with a terminal alkene as dienophile. Thus, the intramolecular DA reaction was also attempted in the allyloxy-substituted chromone derivative **15**.

Compound **15** was prepared as described for propargyloxychromone **4a**, using the commercially available 2-(allyloxy)benzaldehyde **14** [Scheme 8(i)]. Concerning the intramolecular DA reaction on compound **15**, two reaction attempts were carried out. When the reaction was performed in DMF under MW irradiation at 165 °C, compound **16** was obtained in 21% yield, which results from the Claisen rearrangement of compound **15** [Scheme 8(ii)]. Increasing the reaction temperature to 200 °C also under MW irradiation and using 1,2,4-TCB as a solvent, complete degradation of the starting material was observed, and several unidentified byproducts were obtained. This suggests that the allyloxy substituent was not reactive as dienophile in intramolecular DA reactions when compared to the propargyloxy substituent.

The chromone derivative **17** was prepared through deprotection of **6a**, followed by allylation of the formed hydroxychromone [Scheme 9(i)/(ii)]. Despite the unsuccessful intramolecular DA reaction on compound **15**, we also attempted it in compound **17** using the same reaction conditions used for its analogue **7a** [Scheme 9(iii)]. Unfortunately, the reaction afforded several unidentified byproducts and no intramolecular DA product was observed.



Scheme 8 Synthesis and Claisen rearrangement of chromone **15**. *Reagents and conditions*: (i) Na, EtOH, r.t., 2 h; (ii) DMF, MW, 165 °C, 40 min.



Scheme 9 Synthesis of chromone derivative **17**. *Reagents and conditions*: (i) BBr_3, CH_2Cl_2, r.t., 2 h; (ii) K_2CO_3, allyl bromide, acetone, reflux, 4 h; (iii) 1,2,4-TCB, MW, 200 °C, 60 min.

Conclusions

In conclusion, we prepared in good yields a series of novel (*E*)-2′-[propargyloxy-2-styryl]chromones and (*E*,*E*)-2-[4-[2-(propargyloxyphenyl)buta-1,3-dien-1-yl]]chromones through base-catalyzed aldol condensation of 2-methylchromones with the appropriate salicylaldehyde and *ortho*-(methoxy/benzyloxy)-cinnamaldehyde (in the latter case cleavage of the protecting groups and propargylation steps were necessary), which were further used as substrates in intramolecular DA reactions. Chromeno[3,4-*b*]xanthones and 2-(benzo[*c*]chromenyl)chromones were obtained *via* an MW-assisted intramolecular DA reaction, followed by *in situ* dehydrogenation. 2′-Allyloxy-2-styrylchromone and 2′-allyloxy-2-(4-arylbuta-1,3-dien-1-yl)chromone derivatives were also prepared and considered for intramolecular DA reactions. However, in the first case, a Claisen rearrangement product was obtained instead of the expected intramolecular DA product; in the later case, the intramolecular DA reaction did not occur due to the thermal decomposition of the chromone reagent.

Experimental

Materials and methods

Melting points were measured with a Büchi B-540 apparatus. NMR spectra were recorded with a Bruker Avance 300 (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C) and 500 (500.13 MHz for ^{1}H and 125.77 MHz for ^{13}C) spectrometers. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz; the internal standard was TMS. Unequivocal ^{13}C assignments were made with the aid of 2D *g*HSQC and *g*HMBC (delays for one-bond-long range $J_{C/H}$ couplings were optimized for 145 and 7 Hz, respectively) experiments. Positive-ion ESI mass spectra were acquired with a QTOF 2 instrument [dilution of 1 μL] of the sample in chloroform solution (*ca.* 10–5 m) in 200 μL of 0.1% trifluoroacetic acid/methanol solution. Nitrogen was used as the nebuliser gas and argon as the collision gas. The needle voltage was set at 3000 V, with the ion source at 80 °C and the desolvation temperature at 150 °C. The cone voltage was 35 V. Other low- and high-resolution mass spectra (EI, 70 eV) were measured with VG Autospec Q and M spectrometers. Preparative thin-layer chromatography was performed with Merck silica gel (60 DGF254). All chemicals and solvents used were obtained from commercial sources and used as received or dried using standard procedures.

MW-assisted reactions were carried out in a CEM Discover SP apparatus.

Synthetic procedures

General procedure for the synthesis of 2-methyl-4*H*-chromen-4-ones 2a–d. The 2-methylchromones **2a–d** were synthesized according to procedures previously described in the literature and showed identical spectroscopic and analytical data.[20]

General procedure for the synthesis of 2-(prop-2-yn-1-yloxy)-benzaldehyde 3. K_2CO_3 (6.84 g, 49.5 mmol) and propargyl bromide (3.22 mL, 36.3 mmol) were added to a solution of salicylaldehyde (4.0 g, 33 mmol) in acetone (100 mL). The resulting mixture was refluxed for 2 h. After that period, the reaction mixture was poured into ice (100 g) and water (100 mL) and the pH adjusted to 4 with dilute HCl (10%). The precipitate was recovered *via* filtration and washed with water (50 mL). White solid; yield 5.0 g (95%); m.p. 68–70 °C (Lit. 69–70 °C).[21] ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.58 (t, 1H, H-3′, *J* 2.4 Hz), 4.84 (d, 2H, H-1′, *J* 2.4 Hz), 7.07–7.14 (m, 2H, H-3, H-5), 7,58 (ddd, 1H, H-4, *J* 8.3; 7.3; 1.8 Hz), 7.87 (dd, 1H, H-6, *J* 7.7; 1.8 Hz), 10.49 (s, 1H, C*H*O) ppm.

General procedure for the synthesis of (*E*)-2-[2-(prop-2-yn-1-yloxy)styryl]chromones 4a–d. To a mixture of sodium (110 mg, 5 mmol) in ethanol (5 mL) was added the appropriate 2-methylchromone **2a–d** (1.25 mmol) and the *O*-propargylbenzaldehyde 3 (250 mg, 1.56 mmol). The resulting mixture was stirred at room temperature for 3–6 h. After that period, the mixture was poured into ice (20 g) and water (30 mL) and the pH was adjusted to 4 with dilute HCl (10%). The precipitate was removed *via* filtration, taken in CH_2Cl_2 and purified using silica gel column chromatography using CH_2Cl_2 as the eluent.

*(E)-2-[2-(Prop-2-yn-1-yloxy)styryl]chromone (**4a**).* Light green solid; yield 325 mg (86%); m.p. 137–138 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.58 (t, 1H, H-3″, *J* 2.4 Hz), 4.85 (d, 2H, H-1″, *J* 2.4 Hz), 6.35 (s, 1H, H-3), 6.91 (d, 1H, H-α, *J* 16.2 Hz), 7.07 (ddd, 1H, H-5′ *J* 7.6; 7.4; 1.0 Hz), 7.09 (dd, 1H, H-3′, *J* 8.6; 1.0 Hz), 7.37 (ddd, 1H, H-4′, *J* 8.6; 7.4; 1.7 Hz), 7.40 (ddd, 1H, H-6, *J* 8.0; 7.1; 1.1 Hz), 7.57 (dd, 1H, H-8, *J* 8.5; 1.1 Hz), 7.62 (dd, 1H, H-6′, *J* 7.6; 1.7 Hz), 7.69 (ddd, 1H, H-7, *J* 8.5; 7.1; 1.7 Hz), 7.94 (d, 1H, H-β, *J* 16.2 Hz), 8.20 (dd, 1H, H-5, *J* 8.0; 1.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.3 (C-1″), 76.1 (C-3″), 78.2 (C-2″), 110.5 (C-3), 112.8 (C-3′), 118.0 (C-8), 121.2 (C-α), 121.9 (C-5′), 124.2 (C-4a), 124.7 (C-1′), 124.9 (C-6), 125.7 (C-5), 128.3 (C-6′), 130.9 (C-4′), 132.0 (C-β), 133.7 (C-7), 155.9 (C-2′), 156.1 (C-8a), 162.3 (C-2), 178.6 (C-4) ppm. HRMS (ESI$^+$): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{15}O_3$: 303.1021; found 303.1011.

*(E)-7-Methoxy-2-[2-(prop-2-yn-1-yloxy)styryl]chromone (**4b**).* Light yellow solid; yield 303 mg (73%); m.p. 151–153 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.58 (t, 1H, H-3″, *J* 2.4 Hz), 3.95 (s, 3H, 7-OCH_3), 4.85 (d, 2H, H-1″, *J* 2.4 Hz), 6.28 (s, 1H, H-3), 6.88 (d, 1H, H-α, *J* 16.2 Hz), 6.95-6.98 (m, 2H, H-6, H-8), 7.05-7.10 (m, 2H, H-3′, H-5′), 7.37 (ddd, 1H, H-4′, *J* 8.3; 7.3; 1.7 Hz), 7.61 (dd, 1H, H-6′, *J* 7.7; 1.7 Hz), 7.89 (d, 1H, H-β, *J* 16.2 Hz), 8.10 (d, 1H, H-5, *J* 9.2 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.9 (C-1″), 56.3 (7-O*C*H$_3$), 76.1 (C-3″), 78.2 (C-2″), 100.4 (C-8), 110.5 (C-3), 112.8 (C-3′), 114.1 (C-6), 118.1 (C-4a), 121.3 (C-α), 121.9 (C-5′), 124.8 (C-1′), 127.0 (C-5), 128.2 (C-6′), 130.7 (C-4′), 131.4 (C-β), 155.8 (C-2′), 157.8 (C-8a), 161.9 (C-2), 164.1 (C-7), 178.0 (C-4) ppm. HRMS (ESI$^+$): *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{17}O_4$: 333.1121; found 333.1123.

*(E)-5-Methoxy-2-[2-(prop-2-yn-1-yloxy)styryl]chromone (**4c**).* Light yellow solid; yield 311 mg (75%); m.p. 180–182 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.58 (t, 1H, H-3″, *J* 2.3 Hz), 3.99 (s, 3H, 5-OCH_3), 4.83 (d, 2H, H-1″, *J* 2.3 Hz), 6.26 (s, 1H, H-3), 6.80 (d, 1H, H-6, *J* 8.3 Hz), 6.83 (d, 1H, H-α, *J* 16.2 Hz), 7.06 (dt, 1H, H-5′, *J* 7.5; 0.9 Hz), 7.07 (dd, 1H, H-3′, *J* 8.5; 0.9 Hz), 7.13 (dd, 1H, H-8, *J* 8.3; 0.9 Hz), 7.36 (ddd, 1H, H-4′, *J* 8.5; 7.5; 0.9 Hz), 7.56 (t, 1H, H-7, *J* 8.3 Hz), 7.59 (dd, 1H, H-6′, *J* 7.5; 1.7 Hz), 7.85 (d, 1H, H-β, *J* 16.2 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.3 (C-1″), 56.5 (5-O*C*H$_3$), 76.1 (C-3″), 78.2 (C-2″), 106.2 (C-6), 110.2 (C-8), 112.1 (C-3), 112.8 (C-3′), 114.8 (C-4a), 120.9 (C-α), 121.8 (C-5′), 124.8 (C-1′), 128.2 (C-6′), 130.6 (C-4′), 131.4 (C-β), 133.6 (C-7), 155.8 (C-2′), 158.1 (C-8a), 159.7 (C-5), 160.1 (C-2), 178.5 (C-4) ppm. HRMS (ESI$^+$): *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{17}O_4$: 333.1121; found 333.1129.

*(E)-5,7-Dimethoxy-2-[2-(prop-2-yn-1-yloxy)styryl]chromone (**4d**).* White solid; yield 331 mg (73%); m.p. 190–193 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.58 (t, 1H, H-3″, *J* 2.4 Hz), 3.93 (s, 3H, 7-OCH_3), 3.95 (s, 3H, 5-OCH_3), 4.84 (d, 2H, H-1″, *J* 2.4 Hz), 6.19 (s, 1H, H-3), 6.36 (d, 1H, H-6, *J* 2.3 Hz), 6.58 (d, 1H, H-8, *J* 2.3 Hz), 6.81 (d, 1H, H-α, *J* 16.2 Hz), 7.04–7.07 (m, 1H, H-5′), 7.08 (dd, 1H, H-3′, *J* 8.4; 1.0 Hz), 7.35 (ddd, 1H, H-4′, *J* 8.4; 7.3; 1.7 Hz), 7.59 (dd, 1H, H-6′, *J* 7.7; 1.7 Hz), 7.81 (d, 1H, H-β, *J* 16.2 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8 (7-O*C*H$_3$), 56.2 (C-1″), 56.4 (5-O*C*H$_3$), 76.1 (C-3″), 78.2 (C-2″), 92.9 (C-8), 96.0 (C-6), 109.8 (C-4a), 112.1 (C-3), 112.8 (C-3′), 121.0 (C-5′), 121.9 (C-α), 124.9 (C-1′), 128.2 (C-6′), 130.5 (C-4′), 130.8 (C-β), 155.8 (C-2′), 159.6 and 159.7 (C-2 and C-8a), 160.9 (C-5), 164.0 (C-7), 177.8 (C-4) ppm. HRMS (ESI$^+$): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{19}O_5$: 363.1227; found 363.1229.

Synthesis of (*E*,*E*)-2-[4-(2-methoxyphenyl)buta-1,3-dien-1-yl]-chromone (6a) and (*E*,*E*)-7-methoxy-2-[4-(2-methoxyphenyl)buta-1,3-dien-1-yl]chromone (6aa). To a mixture of sodium (110 mg, 5 mmol) in ethanol (5 mL) was added the appropriate 2-methylchromone **2a** and **2b** (1.15 mmol) and the *ortho*-methoxycinnamaldehyde 5 (253 mg, 1.56 mmol). The resulting mixture was stirred at room temperature for 2–3 h. After that period, the mixture was poured into ice (20 g) and water (30 mL) and the pH was adjusted to 4 with dilute HCl (10%). The precipitate was removed *via* filtration, taken in CH_2Cl_2 and purified using silica gel column chromatography using CH_2Cl_2 as the eluent.

*(E,E)-2-[4-(2-Methoxyphenyl)buta-1,3-dien-1-yl]chromone (**6a**).* Yellow solid; yield 285 mg (75%); m.p. 103–105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 3H, 2′-OCH_3), 6.25 (s, 1H, H-3), 6.35 (d, 1H, H-α, *J* 15.3 Hz), 6.92 (dd, 1H, H-3′, *J* 8.3; 1.0 Hz), 6.98 (dt, 1H, H-5′, *J* 7.6; 1.0 Hz), 6.98–7.07 (m, 1H, H-γ), 7.27–7.32 (m, 2H, H-4′, H-δ), 7.38 (ddd, 1H, H-6, *J* 8.0; 7.1; 1.1 Hz), 7.42–7.51 (m, 1H, H-β), 7.49 (dd, 1H, H-8, *J* 8.7; 1.1 Hz), 7.54 (dd, 1H, H-6′, *J* 7.6; 1.7 Hz), 7.67 (ddd, 1H, H-7, *J* 8.7; 7.1; 1.7 Hz), 8.19 (dd, 1H, H-5, *J* 8.0; 1.7 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$):

δ 55.5 (2′-OCH$_3$), 110.1 (C-3), 111.1 (C-3′), 117.8 (C-8), 120.8 (C-5′), 122.9 (C-α), 124.2 (C-4a), 124.9 (C-6), 125.2 (C-1′), 125.7 (C-5), 127.3 (C-6′), 127.7 (C-γ), 130.1 (C-4′), 133.6 (C-7), 134.4 (C-δ), 138.5 (C-β), 156.0 (C-8a), 157.4 (C-2′), 162.1 (C-2), 178.4 (C-4) ppm. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{20}H_{17}O_3$: 305.1178; found 305.1170.

*(E,E)-7-Methoxy-2-[4-(2-methoxyphenyl)buta-1,3-dien-1-yl]chromone (**6aa**).* Yellow solid; yield 308 mg (80%); m.p. 129–131 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.90 (s, 3H, 2′-OCH$_3$), 3.93 (s, 3H, 7-OCH$_3$), 6.19 (s, 1H, H-3), 6.33 (d, 1H, H-α, *J* 15.2 Hz), 6.90 (d, 1H, H-8, *J* 2.4 Hz), 6.90–6.92 (m, 1H, H-3′), 6.95 (dd, 1H, H-6, *J* 8.8; 2.4 Hz), 6.96–6.99 (m, 1H, H-5′), 7.02 (ddd, 1H, H-γ, *J* 15.7; 11.0; 0.8 Hz), 7.26–7.29 (m, 1H, H-δ), 7.29 (ddd, 1H, H-4′, *J* 8.2; 7.4; 1.7 Hz), 7.43 (ddd, 1H, H-β, *J* 15.2; 11.0; 0.8 Hz), 7.53 (dd, 1H, H-6′, *J* 7.7; 1.7 Hz), 8.09 (d, 1H, H-5, *J* 8.8 Hz) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 55.5 (2′-OCH$_3$), 55.8 (7-OCH$_3$), 100.2 (C-8), 110.0 (C-3), 111.1 (C-3′), 113.9 (C-6), 118.0 (C-4a), 120.8 (C-5′), 122.9 (C-α), 125.3 (C-1′), 127.0 (C-5), 127.2 (C-6′), 127.7 (C-γ), 130.0 (C-4′), 134.0 (C-δ), 137.9 (C-β), 157.3 (C-2′), 157.7 (C-8a), 161.7 (C-2), 164.1 (C-7), 177.9 (C-4) ppm.

Synthesis of (*E*,*E*)-2-{4-[2-(prop-2-yn-1-yloxy)phenyl]buta-1,3-dien-1-yl}chromone (7a). A solution of BBr_3 in CH_2Cl_2 1M (1.64 mL) was added to a solution of chromone derivative **6a** (200 mg, 0.657 mmol) in CH_2Cl_2 (5 mL) under a nitrogen atmosphere. The resulting mixture was stirred at room temperature for 2 h. After that period, the mixture was poured into ice (5 g) and water (15 mL) and the slurry was stirred until the formation of a precipitate was achieved. The precipitate was removed *via* filtration and washed with water (100 mL) and ethyl ether (50 mL). To a stirring mixture of the precipitate in acetone (30 mL) was added K_2CO_3 (136 mg, 1.5 equiv.) and propargyl bromide 80% m/m in xylene (0.2 mL; 3 equiv.). The resulting mixture was stirred at reflux for 5 h. After that period, the mixture was poured into ice (5 g) and water (15 mL) and the pH was adjusted to 4 with dilute HCl (10%). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), dried over anhydrous Na_2SO_4 and the solvent evaporated to dryness. The residue was purified using preparative TLC using CH_2Cl_2/EtOAc (5 : 1) as the eluent.

Orange solid; yield 183 mg (85%); m.p. 160–162 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.57 (t, 1H, H-3″, *J* 2.4 Hz), 4.80 (d, 2H, H-1″, *J* 2.4 Hz), 6.26 (s, 1H, H-3), 6.36 (d, 1H, H-α, *J* 15.2 Hz), 6.97-7.06 (m, 3H, H-3′, H-5′, H-γ), 7.28–7.34 (m, 1H, H-4′), 7.31 (d, 1H, H-δ, *J* 15.7 Hz), 7.39 (ddd, 1H, H-6, *J* 7.9; 7.1; 0.8 Hz), 7.43-7.52 (m, 1H, H-β), 7.51 (dd, 1H, H-8, *J* 8.5; 0.8 Hz), 7.57 (dd, 1H, H-6′, *J* 7.9; 1.6 Hz), 7.68 (ddd, 1H, H-7, *J* 8.5; 7.1; 1.7 Hz), 8.19 (dd, 1H, H-5, *J* 7.9; 1.7 Hz) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 56.3 (C-1″), 75.9 (C-3″), 78.3 (C-2″), 110.2 (C-3), 112.7 (C-3′), 117.8 (C-8), 121.8 (C-5′), 123.2 (C-α), 124.2 (C-4a), 124.9 (C-6), 125.7 (C-5), 125.9 (C-1′), 127.2 (C-6′), 127.9 (C-γ), 129.9 (C-4′), 133.7 (C-7), 133.9 (C-δ), 138.3 (C-β), 155.3 (C-2′), 156.0 (C-8a), 162.0 (C-2), 178.5 (C-4) ppm. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{22}H_{17}O_3$: 329.1172; found 329.1175.

General procedure for the synthesis of (*E*,*E*)-2-{4-[2-(benzyloxy)phenyl]buta-1,3-dien-1-yl}chromones 6b–d. To a mixture of sodium (110 mg, 5 mmol) in ethanol (5 mL) was added the appropriate 2-methylchromone **2b–d** (1.25 mmol) and the *ortho*-benzyloxycinnamaldehyde **10** (372 mg, 1.56 mmol). The resulting mixture was stirred at room temperature for 4–6 h. After that period, the mixture was poured into ice (20 g) and water (30 mL) and the pH was adjusted to 4 with dilute HCl (10%). The precipitate was removed *via* filtration, taken in CH_2Cl_2 and purified using silica gel column chromatography using CH_2Cl_2 as the eluent.

*(E,E)-2-{4-[2-(Benzyloxy)phenyl]buta-1,3-dien-1-yl}-7-methoxychromone (**6b**).* Yellow solid; yield 436 mg (85%); m.p. 139–142 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.91 (s, 3H, 7-OCH$_3$), 5.14 (s, 2H, 2′-OCH$_2$C$_6$H$_5$), 6.16 (s, 1H, H-3), 6.27 (d, 1H, H-α, *J* 15.2 Hz), 6.90 (d, 1H, H-8, *J* 2.3 Hz), 6.93 (dd, 1H, H-6, *J* 8.8; 2.3 Hz), 6.96–7.04 (m, 3H, H-γ, H-3′, H-5′), 7.27 (ddd, 1H, H-4′, *J* 8.2; 7.4; 1.6 Hz), 7.32 (d, 1H, H-δ, *J* 15.7 Hz), 7.37–7.49 (m, 6H, H-β, 2′-OCH$_2$C$_6$H$_5$), 7.57 (dd, 1H, H-6′, *J* 7.7; 1.6 Hz), 8.08 (d, 1H, H-5, *J* 8.8 Hz) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 55.9 (7-OCH$_3$), 70.4 (2′-OCH$_2$C$_6$H$_5$), 100.2 (C-8), 110.1 (C-3), 112.5 (C-3′), 114.1 (C-6), 118.0 (C-4a), 121.2 (C-5′), 123.1 (C-α), 125.6 (C-1′), 127.0 (C-5), 127.1 (C-6′), 127.6 (C-2,6 of 2′-OCH$_2$C$_6$H$_5$), 127.8 (C-γ), 128.2 (C-4 of 2′-OCH$_2$C$_6$H$_5$), 128.7 (C-3,5 of 2′-OCH$_2$C$_6$H$_5$), 130.0 (C-4′), 133.7 (C-δ), 136.8 (C-1 of 2′-OCH$_2$C$_6$H$_5$), 137.8 (C-β), 156.5 (C-2′), 157.8 (C-8a), 161.6 (C-2), 164.1 (C-7), 177.9 (C-4) ppm. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{27}H_{23}O_4$: 411.1591; found 411.1601.

*(E,E)-2-{4-[2-(Benzyloxy)phenyl]buta-1,3-dien-1-yl}-5-methoxychromone (**6c**).* Yellow solid; yield 410 mg (80%); m.p. 125–127 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.98 (s, 3H, 5-OCH$_3$), 5.15 (s, 2H, 2′-OCH$_2$C$_6$H$_5$), 6.15 (s, 1H, H-3), 6.23 (d, 1H, H-α, *J* 15.3 Hz), 6.79 (dd, 1H, H-6, *J* 8.4; 0.9 Hz), 6.97 (dd, 1H, H-3′, *J* 8.4; 1.0 Hz), 6.97–7.05 (m, 2H, H-γ, H-5′), 7.07 (dd, 1H, H-8, *J* 8.4; 0.9 Hz), 7.25–7.28 (m, 1H, H-4′), 7.30 (d, 1H, H-δ, *J* 15.7 Hz), 7.34–7.49 (m, 6H, H-β, 2′-OCH$_2$C$_6$H$_5$), 7.53 (t, 1H, H-7, *J* 8.4 Hz), 7.56 (dd, 1H, H-6′, *J* 7.6; 1.5 Hz) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 56.5 (5-OCH$_3$), 70.4 (2′-OCH$_2$C$_6$H$_5$), 106.2 (C-6), 110.0 (C-8), 111.7 (C-3), 112.5 (C-3′), 114.7 (C-4a), 121.1 (C-5′), 122.6 (C-α), 125.7 (C-1′), 127.2 (C-6′), 127.6 (C-2,6 of 2′-OCH$_2$C$_6$H$_5$), 127.9 (C-γ), 128.1 (C-4 of 2′-OCH$_2$C$_6$H$_5$), 128.7 (C-3,5 of 2′-OCH$_2$C$_6$H$_5$), 129.9 (C-4′), 133.6 and 133.7 (C-δ and C-7), 136.8 (C-1 of 2′-OCH$_2$C$_6$H$_5$), 137.8 (C-β), 156.5 (C-2′), 158.1 (C-8a), 159.7 and 159.9 (C-2 and C-5), 178.4 (C-4) ppm. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{27}H_{23}O_4$: 411.1591; found 411.1596.

*(E,E)-2-{4-[2-(Benzyloxy)phenyl]buta-1,3-dien-1-yl}-5,7-dimethoxychromone (**6d**).* Yellow solid; yield 385 mg (70%); m.p. 180–183 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.90 (s, 3H, 7-OCH$_3$), 3.93 (s, 3H, 5-OCH$_3$), 5.14 (s, 2H, 2′-OCH$_2$C$_6$H$_5$), 6.09 (s, 1H, H-3), 6.21 (d, 1H, H-α, *J* 15.3 Hz), 6.34 (d, 1H, H-6, *J* 2.3 Hz), 6.52 (d, 1H, H-8, *J* 2.3 Hz), 6.96-7.03 (m, 3H, H-3′, H-5′, H-γ), 7.25–7.28 (m, 1H, H-4′), 7.29 (d, 1H, H-δ, *J* 15.8 Hz), 7.33–7.49 (m, 6H, H-β, 2′-OCH$_2$C$_6$H$_5$), 7.56 (dd, 1H, H-6′, *J* 7.7; 1.7 Hz) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 55.8 (7-OCH$_3$), 56.4 (5-OCH$_3$), 70.4 (2′-OCH$_2$C$_6$H$_5$), 92.7 (C-8), 96.0 (C-6), 109.4 (C-4a), 111.8 (C-3), 112.5 (C-3′), 121.1 (C-5′), 122.7 (C-α), 125.7 (C-1′), 127.1 (C-6′), 127.6 (C-2,6 of 2′-OCH$_2$C$_6$H$_5$), 127.9 (C-γ), 128.2 (C-4 of 2′-OCH$_2$C$_6$H$_5$), 128.7 (C-3,5 of 2′-OCH$_2$C$_6$H$_5$), 129.9 (C-4′), 133.2 (C-δ), 136.8 (C-1 of 2′-OCH$_2$C$_6$H$_5$), 137.2 (C-β), 156.5 (C-2′), 159.4 (C-2), 159.7 (C-8a), 160.9 (C-5), 164.0 (C-7),

177.7 (C-4) ppm. HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{28}H_{25}O_5$: 441.1697; found 441.1714.

General procedure for the synthesis of (*E*,*E*)-2-{4-[2-(prop-2-yn-1-yloxy)phenyl]buta-1,3-dien-1-yl}chromones 7b–d. To a stirring mixture of AcOH/HCl 37% (10% v/v) (10 mL) was added the appropriate chromone derivative **6b–d** (0.487 mmol). The resulting mixture was stirred at 100 °C for 16 h. After that period, the mixture was poured into ice (5 g) and water (15 mL), the aqueous layer was extracted with EtOAc (3 × 50 mL), dried over anhydrous Na_2SO_4 and the solvent evaporated to dryness. To a stirring mixture of the residue in acetone (30 mL) was added K_2CO_3 (101 mg, 1.5 equiv.) and propargyl bromide 80% m/m in xylene (0.13 mL, 3 equiv.). The mixture was refluxed for 5 h. After that period, the mixture was poured into ice (5 g) and water (15 mL) and the pH was adjusted to 4 with dilute HCl (10%). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), dried over anhydrous Na_2SO_4 and the solvent evaporated to dryness. The residue was purified *via* preparative TLC using CH_2Cl_2/EtOAc (5 : 1) as the eluent.

*(E,E)-7-Methoxy-2-{4-[2-(prop-2-yn-1-yloxy)phenyl]buta-1,3-dien-1-yl}chromone (**7b**).* Yellow solid; yield 145 mg (83%); m.p. 137–139 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.57 (t, 1H, H-3″, *J* 2.4 Hz), 3.93 (s, 3H, 7-OC*H*$_3$), 4.79 (d, 2H, H-1″, *J* 2.4 Hz), 6.19 (s, 1H, H-3), 6.33 (d, 1H, H-α, *J* 15.2 Hz), 6.91-7.05 (m, 5H, H-6, H-8, H-3′, H-5′, H-γ), 7.29 (d, 1H, H-δ, *J* 16.1 Hz), 7.26–7.33 (m, 1H, H-4′), 7.43 (dd, 1H, H-β, *J* 15.2; 10.9 Hz), 7.56 (dd, 1H, H-6′, *J* 7.9; 1.7 Hz), 8.09 (d, 1H, H-5, *J* 8.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8 (7-O*C*H$_3$), 56.3 (C-1″), 75.8 (C-3″), 78.4 (C-2″), 100.2 (C-8), 110.2 (C-3), 112.7 (C-3′), 114.0 (C-6), 118.0 (C-4a), 121.8 (C-5′), 123.2 (C-α), 125.9 (C-1′), 127.0 (C-5), 127.2 (C-6′), 127.9 (C-γ), 129.8 (C-4′), 133.5 (C-δ), 137.7 (C-β), 155.3 (C-2′), 157.7 (C-8a), 161.6 (C-2), 164.1 (C-7), 177.9 (C-4) ppm. HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{23}H_{19}O_4$: 359.1278; found 359.1285.

*(E,E)-5-Methoxy-2-{4-[2-(prop-2-yn-1-yloxy)phenyl]buta-1,3-dien-1-yl}chromone (**7c**).* Yellow solid; yield 140 mg (80%); m.p. 103–105 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.56 (t, 1H, H-3″, *J* 2.4 Hz), 3.98 (s, 3H, 5-OC*H*$_3$), 4.79 (d, 2H, H-1″, *J* 2.4 Hz), 6.17 (s, 1H, H-3), 6.29 (d, 1H, H-α, *J* 15.2 Hz), 6.80 (dd, 1H, H-6, *J* 8.4; 1.0 Hz), 6.97–7.04 (m, 3H, H-3′, H-5′, H-γ), 7.07 (dd, 1H, H-8, *J* 8.4; 1.0 Hz), 7.27 (d, 1H, H-δ, *J* 15.5 Hz), 7.28–7.31 (m, 1H, H-4′), 7.39 (ddd, 1H, H-β, *J* 15.2; 11.0; 0.9 Hz), 7.55 (t, 1H, H-7, *J* 8.4 Hz), 7.56 (dd, 1H, H-6′, *J* 7.9; 1.7 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.3 (C-1″), 56.5 (5-O*C*H$_3$), 75.8 (C-3″), 78.4 (C-2″), 106.2 (C-6), 110.0 (C-8), 111.8 (C-3), 112.7 (C-3′), 114.7 (C-4a), 121.8 (C-5′), 122.8 (C-α), 126.0 (C-1′), 127.2 (C-6′), 128.0 (C-γ), 129.8 (C-4′), 133.3 (C-δ), 133.6 (C-7), 137.6 (C-β), 155.2 (C-2′), 158.1 (C-8a), 159.8 (C-2 and C-5), 178.4 (C-4) ppm. HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{23}H_{19}O_4$: 359.1278; found 359.1285.

*(E,E)-5,7-Dimethoxy-2-{4-[2-(prop-2-yn-1-yloxy)phenyl]buta-1,3-dien-1-yl}chromone (**7d**).* Yellow solid; yield 142 mg (75%); m.p. 95–98 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.56 (t, 1H, H-3″, *J* 2.4 Hz), 3.92 (s, 3H, 7-OC*H*$_3$), 3.94 (s, 3H, 5-OC*H*$_3$), 4.78 (d, 2H, H-1″, *J* 2.4 Hz), 6.11 (s, 1H, H-3), 6.27 (d, 1H, H-α, *J* 15.2 Hz), 6.35 (d, 1H, H-6, *J* 2.3 Hz), 6.52 (d, 1H, H-8, *J* 2.3 Hz), 6.96–7.02 (m, 3H, H-3′, H-5′, H-γ), 7.26 (d, 1H, H-δ, *J* 15.7 Hz), 7.27–7.31 (m, 1H, H-4′), 7.36 (ddd, 1H, H-β, *J* 15.2; 11.0; 0.9 Hz), 7.56 (dd, 1H, H-6′, *J* 8.0; 1.6 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.8 (7-O*C*H$_3$), 56.3 (C-1″), 56.4 (5-O*C*H$_3$), 75.8 (C-3″), 78.4 (C-2″), 92.7 (C-8), 96.0 (C-6), 109.4 (C-4a), 111.8 (C-3), 112.7 (C-3′), 121.8 (C-5′), 122.9 (C-α), 126.0 (C-1′), 127.1 (C-6′), 128.0 (C-γ), 129.7 (C-4′), 133.0 (C-δ), 137.1 (C-β), 155.2 (C-2′), 159.3 (C-2), 159.7 (C-8a), 160.9 (C-5), 164.0 (C-7), 177.7 (C-4) ppm. HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{24}H_{21}O_5$: 389.1384; found 389.1399.

Synthesis of 1-benzyloxy-2-iodobenzene (9). K_2CO_3 (1.89 g, 13.6 mmol) and benzyl bromide (1.19 mL, 10.0 mmol) were added to a solution of 2-iodophenol **8** (2 g, 9.1 mmol) in acetone (100 mL). The resulting mixture was stirred at reflux for 16 h. After that period, the mixture was poured into ice (100 g) and water (100 mL) and the pH was adjusted to 4 with dilute HCl (10%). The aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL), dried over anhydrous Na_2SO_4 and the solvent evaporated to dryness. Colorless oil; yield 2.80 g (99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.15 (s, 2H, 1-OC*H*$_2$C$_6$H$_5$), 6.72 (dt, 1H, H-4, *J* 7.6; 1.4 Hz), 6.86 (dd, 1H, H-6, *J* 8.2; 1.4 Hz), 7.27 (ddd, 1H, H-5, *J* 8.2; 7.6; 1.6 Hz), 7.32-7.51 (m, 5H, 1-OCH$_2$C$_6$*H*$_5$), 7.80 (dd, 1H, H-3, *J* 7.6; 1.6 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 70.8 (1-O*C*H$_2$C$_6$H$_5$), 86.8 (C-2), 112.7 (C-6), 122.8 (C-4), 127.0 (C-2,6 of 1-OCH$_2$*C*$_6$H$_5$), 127.9 (C-4 of 1-OCH$_2$*C*$_6$H$_5$), 128.6 (C-3,5 of 1-OCH$_2$*C*$_6$H$_5$), 129.4 (C-5), 136.5 (C-1 of 1-OCH$_2$*C*$_6$H$_5$), 139.6 (C-3), 157.2 (C-1) ppm. HRMS (ESI$^+$): *m/z* [M + H]$^+$ calcd for $C_{13}H_{12}IO$: 310.9933; found 310.9938.

Synthesis of (*E*)-3-[2-(benzyloxy)phenyl]acrylaldehyde (10). Acrolein diethyl acetal (4.1 mL, 27 mmol), ^{n}Bu$_4$NOAc (5.4 g, 18 mmol), K_2CO_3 (1.86 g, 13.5 mmol) and $Pd(OAc)_2$ (61 mg, 0.27 mmol) were added to a solution of 1-benzyloxy-2-iodobenzene **9** (2.80 g, 9 mmol) in DMF (10 mL). The mixture was stirred at 90 °C for 16 h. After that period, the mixture was poured into ice (50 g) and water (50 mL), the pH was adjusted to 1 with dilute HCl (10%), and the aqueous mixture was stirred at room temperature for 15 min. Then, it was extracted with Et_2O (3 × 100 mL), dried over anhydrous Na_2SO_4 and the solvent evaporated to dryness. The crude residue was purified using silica gel column chromatography using CH_2Cl_2 as the eluent. White solid; yield 1.50 g (70%); m.p. 56–58 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.16 (s, 2H, 2-OCH$_2$C$_6$H$_5$), 6.77 (dd, 1H, H-α, *J* 16.1; 7.9 Hz), 6.98–7.01 (m, 1H, H-5), 6.99 (d, 1H, H-3, *J* 7.9 Hz), 7.33–7.44 (m, 6H, 2-OCH$_2$C$_6$H$_5$, H-4), 7.58 (dd, 1H, H-6, *J* 8.1; 1.7 Hz), 7.90 (d, 1H, H-β, *J* 16.1 Hz), 9.66 (d, 1H, CHO, *J* 7.9 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 70.6 (2-O*C*H$_2$C$_6$H$_5$), 112.8 (C-3), 121.2 (C-5), 123.3 (C-1), 127.4 (C-2,6 of 2-OCH$_2$*C*$_6$H$_5$), 128.3 (C-4 of 2-OCH$_2$*C*$_6$H$_5$), 128.7 (C-6), 128.8 (C-3,5 of 2-OCH$_2$*C*$_6$H$_5$), 129.0 (C-α), 132.7 (C-4), 136.3 (C-1 of 2-OCH$_2$*C*$_6$H$_5$), 148.0 (C-β), 157.4 (C-2), 194.6 (*C*HO) ppm. HRMS (ESI$^+$): *m/z* [M + Na]$^+$ calcd for $C_{16}H_{14}O_2Na$: 261.0886; found 261.0890.

Synthesis of 14,14*a*-dihydro-6*H*,8*H*-chromeno[3,4-*b*]xanthen-8-one (11). This compound was isolated from the MW-assisted intramolecular DA reaction of chromone derivative **4a** (0.1 mmol, 30 mg) in DMF, NMP or 1,2,4-TCB as solvents (see Table 1). White solid; m.p. 215–217 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.89 (t, 1H, H-14, *J* 17.1 Hz), 3.27 (dd, 1H, H-14, *J* 17.1; 8.1 Hz), 4.09 (ddd, 1H, H-14a, *J* 17.1; 8.1; 3.2 Hz), 4.53 (dd, 1H, H-6, *J* 12.5; 1.8 Hz),

4.78 (d, 1H, H-6, *J* 12.5 Hz), 6.85 (dd, 1H, H-7, *J* 3.2; 1.8 Hz), 6.97 (dd, 1H, H-4, *J* 8.1; 1.2 Hz), 7.01 (dt, 1H, H-2, *J* 7.5; 1.2 Hz), 7.18-7.21 (m, 1H, H-3), 7.25-7.26 (m, 1H, H-1), 7.42 (ddd, 1H, H-10, *J* 8.0; 7.1; 1.1 Hz), 7.47 (dd, 1H, H-12, *J* 8.6; 1.1 Hz), 7.66 (ddd, 1H, H-11, *J* 8.6; 7.1; 1.7 Hz), 8.26 (dd, 1H, H-9, *J* 8.0; 1.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 33.5 (C-14a), 34.6 (C-14), 68.8 (C-6), 115.7 (C-7), 115.8 (C-7a), 117.7 (C-4), 118.0 (C-12), 121.7 (C-2), 123.9 (C-8a), 124.9 (C-14b), 125.2 (C-10), 126.2 (C-9), 128.06 and 128.13 (C-1 and C-3), 130.2 (C-6a), 133.4 (C-11), 154.6 (C-4a), 155.8 (C-12a), 164.2 (C-13a), 174.2 (C-8).

General procedure for the synthesis of 6*H*,8*H*-chromeno[3,4-*b*]xanthen-8-ones 12a–d. The appropriate (*E*)-2′-propargyloxy-2-styrylchromone **4a–d** (0.1 mmol) and 1,2,4-TCB (0.3 mL) were mixed in a closed glass vessel. The resulting mixture was heated under MW irradiation at 200 °C for 60 min. After that period, chloranil (10 μmol, 2.5 mg) was added to the crude mixture and it was heated under MW irradiation at 80 °C for 30 min. The resulting mixture was dissolved in CH_2Cl_2 (5 mL) and purified using preparative TLC using CH_2Cl_2 as the eluent.

*6H,8H-Chromeno[3,4-b]xanthen-8-one (**12a**).* White solid; yield 22 mg (75%); m.p. 209–211 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.23 (s, 2H, H-6), 7.05 (dd, 1H, H-4, *J* 8.1; 1.2 Hz), 7.13 (dt, 1H, H-2, *J* 7.7; 1.2 Hz), 7.35 (ddd, 1H, H-3, *J* 8.1; 7.7; 1.6 Hz), 7.39 (ddd, 1H, H-10, *J* 8.0; 7.1; 1.1 Hz), 7.51 (dd, 1H, H-12, *J* 8.4; 1.1 Hz), 7.74 (ddd, 1H, H-11, *J* 8.4; 7.1; 1.7 Hz), 7.76 (s, 1H, H-14), 7.81 (dd, 1H, H-1, *J* 7.7; 1.6 Hz), 8.12 (s, 1H, H-7), 8.34 (dd, 1H, H-9, *J* 8.0; 1.7 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.0 (C-6), 110.9 (C-14), 117.9 and 118.0 (C-4 and C-12), 120.7 (C-7a), 121.4 (C-14b), 121.9 (C-8a), 122.5 and 122.6 (C-2 and C-7), 124.1 (C-10), 124.4 (C-1), 126.7 (C-9), 127.6 (C-6a), 131.5 (C-3), 134.9 (C-11), 137.0 (C-14a), 155.6 (C-4a), 156.2 (C-12a), 156.5 (C-13a), 176.6 (C-8) ppm. HRMS (ESI$^+$): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{13}O_3$: 301.0859; found 301.0864.

*11-Methoxy-6H,8H-chromeno[3,4-b]xanthen-8-one (**12b**).* White solid; yield 27 mg (81%); m.p. 223–225 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.95 (s, 3H, 11-OC*H*$_3$), 5.21 (s, 2H, H-6), 6.89 (d, 1H, H-12, *J* 2.4 Hz), 6.95 (dd, 1H, H-10, *J* 8.9; 2.4 Hz), 7.04 (dd, 1H, H-4, *J* 8.2; 1.2 Hz), 7.12 (dt, 1H, H-2, *J* 7.6; 1.2 Hz), 7.34 (ddd, 1H, H-3, *J* 8.2; 7.6; 1.6 Hz), 7.71 (s, 1H, H-14), 7.79 (dd, 1H, H-1, *J* 7.6; 1.6 Hz), 8.09 (s, 1H, H-7), 8.24 (d, 1H, H-9, *J* 8.9 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.9 (11-O*C*H$_3$), 68.0 (C-6), 100.3 (C-12), 110.6 (C-14), 113.3 (C-10), 115.8 (C-8a), 118.0 (C-4), 120.8 (C-14b), 121.5 (C-7a), 122.5 and 122.6 (C-2 and C-7), 124.3 (C-1), 127.5 (C-6a), 128.3 (C-9), 131.3 (C-3), 136.5 (C-14a), 155.6 (C-4a), 156.5 (C-13a), 158.1 (C-12a), 165.1 (C-11), 175.7 (C-8) ppm. HRMS (ESI$^+$): *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{15}O_4$: 331.0965; found 331.0971.

*9-Methoxy-6H,8H-chromeno[3,4-b]xanthen-8-one (**12c**).* White solid; yield 27 mg (82%); m.p. 257–258 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.02 (s, 3H, 9-OC*H*$_3$), 5.20 (s, 2H, H-6), 6.80 (dd, 1H, H-10, *J* 8.3; 0.9 Hz), 7.03 (dd, 1H, H-4, *J* 8.1; 1.2 Hz), 7.06 (dd, 1H, H-12, *J* 8.3; 0.9 Hz), 7.10 (dt, 1H, H-2, *J* 7.5; 1.2 Hz), 7.33 (ddd, 1H, H-3, *J* 8.1; 7.5; 1.6 Hz), 7.60 (t, 1H, H-11, *J* 8.3 Hz), 7.66 (s, 1H, H-14), 7.77 (dd, 1H, H-1, *J* 7.5; 1.6 Hz), 8.06 (s, 1H, H-7) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.5 (9-O*C*H$_3$), 68.0 (C-6), 105.5 (C-10), 110.0 and 110.2 (C-12 and C-14), 112.5 (C-8a), 117.9 (C-4), 121.5 (C-14b), 121.9 (C-7a), 122.4 and 122.7 (C-2 and C-7), 124.3 (C-1), 127.5 (C-6a), 131.2 (C-3), 134.8 (C-11), 136.3 (C-14a), 155.3 (C-13a), 155.6 (C-4a), 158.2 (C-12a), 160.7 (C-9), 175.9 (C-8) ppm. HRMS (ESI$^+$): *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{15}O_4$: 331.0965; found 331.0971.

*9,11-Dimethoxy-6H,8H-chromeno[3,4-b]xanthen-8-one (**12d**).* White solid; yield 28 mg (78%); m.p. 249–250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.92 (s, 3H, 11-OC*H*$_3$), 3.98 (s, 3H, 9-OC*H*$_3$), 5.20 (s, 2H, H-6), 6.34 (d, 1H, H-10, *J* 2.3 Hz), 6.50 (d, 1H, H-12, *J* 2.3 Hz), 7.03 (dd, 1H, H-4, *J* 8.2; 1.2 Hz), 7.10 (dt, 1H, H-2, *J* 7.5; 1.2 Hz), 7.32 (ddd, 1H, H-3, *J* 8.2; 7.5; 1.6 Hz), 7.61 (s, 1H, H-14), 7.76 (dd, 1H, H-1, *J* 7.5; 1.6 Hz), 8.04 (s, 1H, H-7) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8 (11-O*C*H$_3$), 56.4 (9-OC*H*$_3$), 68.0 (C-6), 92.8 (C-12), 95.2 (C-10), 107.3 (C-8a), 109.9 (C-14), 117.9 (C-4), 121.6 (C-14b), 122.0 (C-7a), 122.4 and 122.7 (C-2 and C-7), 124.2 (C-1), 127.4 (C-6a), 131.1 (C-3), 135.8 (C-14a), 155.2 (C-13a), 155.5 (C-4a), 159.8 (C-12a), 162.0 (C-9), 164.9 (C-11), 174.8 (C-8) ppm. HRMS (ESI$^+$): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{17}O_5$: 361.1071; found 361.1076.

General procedure for the synthesis of 2-(6*H*-benzo[*c*]chromen-8-yl)-4*H*-chromen-4-ones 13a–d. The appropriate chromone derivative **7a–d** (0.1 mmol) and 1,2,4-TCB (0.3 mL) were mixed in a closed glass vessel. The resulting mixture was heated under MW irradiation at 200 °C for 60 min. After that period, chloranil (10 μmol, 2.5 mg) was added to the crude mixture and it was heated under MW irradiation at 80 °C for 30 min. After that period, the crude was dissolved in CH_2Cl_2 (5 mL) and purified using preparative TLC using hexane/EtOAc (9:7) as the eluent.

*2-(6H-Benzo[c]chromen-8-yl)-4H-chromen-4-one (**13a**).* White solid; yield 28 mg (85%); m.p. 229–232 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.23 (s, 2H, H-10′), 6.85 (s, 1H, H-3), 7.04 (dd, 1H, H-2′, *J* 8.1; 1.2 Hz), 7.11 (dt, 1H, H-4′, *J* 7.6; 1.2 Hz), 7.32 (ddd, 1H, H-3′, *J* 8.1; 7.6; 1.6 Hz), 7.44 (ddd, 1H, H-6, *J* 8.0; 7.1; 1.0 Hz), 7.60 (dd, 1H, H-8, *J* 8.7; 1.0 Hz), 7.69–7.75 (m, 2H, H-7, H-9′), 7.79 (dd, 1H, H-5′, *J* 7.6; 1.6 Hz), 7.84 (d, 1H, H-6′, *J* 8.2 Hz), 7.94 (dd, 1H, H-7′, *J* 8.2; 2.0 Hz), 8.25 (dd, 1H, H-5, *J* 8.0; 1.7 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.3 (C-10′), 107.4 (C-3), 117.7 (C-2′), 118.1 (C-8), 121.9 (C-5′a), 122.5; 122.6 and 122.7 (C-4′, C-6′ and C-9′), 123.8 (C-5′), 124.0 (C-4a), 125.3 (C-6), 125.8 (C-5), 126.4 (C-7′), 130.716 and 130.724 (C-3′ and C-8′), 132.0 (C-9′a), 133.5 (C-5′b), 133.9 (C-7), 155.2 (C-1′a), 156.2 (C-8a), 162.8 (C-2), 178.4 (C-4) ppm. HRMS (ESI$^+$): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{15}O_3$: 327.1016; found 327.1019.

*2-(6H-Benzo[c]chromen-8-yl)-7-methoxy-4H-chromen-4-one (**13b**).* White solid; yield 29 mg (81%); m.p. 184–187 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.95 (s, 3H, 7-OC*H*$_3$), 5.22 (s, 2H, H-10′), 6.78 (s, 1H, H-3), 6.99–7.05 (m, 3H, H-6, H-8, H-2′), 7.10 (dt, 1H, H-4′, *J* 7.6; 1.3 Hz), 7.31 (ddd, 1H, H-3′, *J* 8.1; 7.6; 1.6 Hz), 7.71 (d, 1H, H-9′, *J* 1.7 Hz), 7.78 (dd, 1H, H-5′, *J* 7.6; 1.6 Hz), 7.82 (d, 1H, H-6′, *J* 8.2 Hz), 7.91 (dd, 1H, H-7′, *J* 8.2; 1.7 Hz), 8.14 (d, 1H, H-5, *J* 9.5 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.9 (7-O*C*H$_3$), 68.3 (C-10′), 100.4 (C-8), 107.3 (C-3), 114.5 (C-6), 117.7 (C-2′), 117.9 (C-4a), 121.9 (C-5′a), 122.4; 122.5 and 122.6 (C-4′, C-6′ and C-9′),

123.8 (C-5′), 126.3 (C-7′), 127.1 (C-5), 130.6 (C-3′), 130.8 (C-8′), 132.0 (C-9′a), 133.3 (C-5′b), 155.1 (C-1′a), 158.0 (C-8a), 162.3 (C-2), 164.2 (C-7), 177.8 (C-4) ppm. HRMS (ESI^+): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{17}O_4$: 357.1121; found 357.1127.

*2-(6H-Benzo[c]chromen-8-yl)-5-methoxy-4H-chromen-4-one (**13c**).* White solid; yield 30 mg (85%); m.p. 227–229 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.00 (s, 3H, 5-OCH_3), 5.20 (s, 2H, H-10′), 6.75 (s, 1H, H-3), 6.83 (dd, 1H, H-6, *J* 8.4; 0.9 Hz), 7.02 (dd, 1H, H-2′, *J* 8.1; 1.2 Hz), 7.09 (dt, 1H, H-4′, *J* 7.5; 1.2 Hz), 7.15 (dd, 1H, H-8, *J* 8.4; 0.9 Hz), 7.27–7.33 (m, 1H, H-3′), 7.58 (t, 1H, H-7, *J* 8.4 Hz), 7.68 (d, 1H, H-9′, *J* 1.9 Hz), 7.75–7.81 (m, 1H, H-5′), 7.79 (d, 1H, H-6′, *J* 8.1 Hz), 7.88 (dd, 1H, H-7′, *J* 8.1; 1.9 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.5 (5-O*C*H$_3$), 68.3 (C-10′), 106.5 (C-6), 108.9 (C-3), 110.1 (C-8), 114.6 (C-4a), 117.6 (C-2′), 122.0 (C-5′a), 122.3; 122.4 and 122.5 (C-4′, C-6′ and C-9′), 123.7 (C-5′), 126.2 (C-7′), 130.4 (C-8′), 130.6 (C-3′), 131.9 (C-9′a), 133.2 (C-5′b), 133.8 (C-7), 155.1 (C-1′a), 158.2 (C-8a), 159.8 (C-5), 160.5 (C-2), 178.3 (C-4) ppm. HRMS (ESI^+): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{17}O_4$: 357.1121; found 357.1123.

*2-(6H-Benzo[c]chromen-8-yl)-5,7-dimethoxy-4H-chromen-4-one (**13d**).* White solid; yield 30 mg (78%); m.p. 178–181 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H, 7-OCH_3), 3.96 (s, 3H, 5-OCH_3), 5.19 (s, 2H, H-10′), 6.38 (d, 1H, H-6, *J* 2.3 Hz), 6.59 (d, 1H, H-8, *J* 2.3 Hz), 6.69 (s, 1H, H-3), 7.02 (dd, 1H, H-2′, *J* 8.1; 1.2 Hz), 7.09 (dt, 1H, H-4′, *J* 7.7; 1.2 Hz), 7.27–7.33 (m, 1H, H-3′), 7.66 (d, 1H, H-9′, *J* 1.6 Hz), 7.76 (dd, 1H, H-5′, *J* 7.7; 1.7 Hz), 7.78 (d, 1H, H-6′, *J* 8.2 Hz), 7.86 (dd, 1H, H-7′, *J* 8.2; 1.6 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8 (7-O*C*H$_3$), 56.4 (5-O*C*H$_3$), 68.3 (C-10′), 92.8 (C-8), 96.2 (C-6), 108.9 (C-3), 109.3 (C-4a), 117.6 (C-2′), 122.0 (C-5′a), 122.2 (C-9′), 122.4 and 122.5 (C-4′ and C-6′), 123.7 (C-5′), 126.0 (C-7′), 130.5 and 130.6 (C-8′ and C-3′), 131.9 (C-9′a), 133.0 (C-5′b), 155.1 (C-1′a), 159.8 and 160.0 (C-2 and C-8a), 160.9 (C-5), 164.1 (C-7), 177.5 (C-4) ppm. HRMS (ESI^+): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{19}O_5$: 387.1227; found 387.1233.

Synthesis of (*E*)-2-(2-allyloxystyryl)-4*H*-chromen-4-one (15). To a mixture of sodium (110 mg, 5 mmol) in ethanol (5 mL) was added the 2-methylchromone **2a** (200 mg, 1.25 mmol) and the *O*-allyloxybenzaldehyde **14** (253 mg, 1.56 mmol). The resulting mixture was stirred at room temperature for 2 h. After that period, the mixture was poured into ice (20 g) and water (30 mL) and the pH was adjusted to 4 with dilute HCl (10%). The precipitate was removed *via* filtration, taken in CH_2Cl_2 and purified using silica gel column chromatography using CH_2Cl_2 as the eluent. Yellow solid; yield 346 mg (91%); m.p. 109–111 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.68 (dt, 2H, H-1″, *J* 5.1; 1.6 Hz), 5.37 (dq, 1H, H-3″, *J* 10.6; 1.6 Hz), 5.50 (dq, 1H, H-3″, *J* 17.2; 1.6 Hz), 6.14 (ddt, 1H, H-2″, *J* 17.2; 10.5; 5.1 Hz), 6.34 (s, 1H, H-3), 6.93 (d, 1H, H-α, *J* 16.2 Hz), 6.95 (dd, 1H, H-3′, *J* 8.3; 1.0 Hz), 7.02 (dt, 1H, H-5′, *J* 7.5; 1.0 Hz), 7.34 (ddd, 1H, H-4′, *J* 8.3; 7.5; 1.7 Hz), 7.39 (ddd, 1H, H-6, *J* 8.0; 7.1; 1.1 Hz), 7.55 (dd, 1H, H-8, *J* 8.5; 1.1 Hz), 7.60 (dd, 1H, H-6′, *J* 7.5; 1.7 Hz), 7.68 (ddd, 1H, H-7, *J* 8.5; 7.1; 1.6 Hz), 7.97 (d, 1H, H-β, *J* 16.2 Hz), 8.20 (dd, 1H, H-5, *J* 8.0; 1.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.2 (C-1″), 110.3 (C-3), 112.6 (C-3′), 117.8 and 117.9 (C-8 and C-3″), 120.9 (C-α), 121.1 (C-5′), 124.2 and 124.3 (C-1′ and C-4a), 124.9 (C-6), 125.6 (C-5), 128.4 (C-6′), 131.0 (C-4′), 132.4 (C-β), 132.9 (C-2″), 133.6 (C-7), 156.1 (C-2′), 157.1 (C-8a), 162.5 (C-2), 178.6 (C-4).

Synthesis of (*E*)-2-(3-allyl-2-hydroxystyryl)-4*H*-chromen-4-one (16). The chromone derivative **15** (30 mg, 0.1 mmol) and 1,2,4-TCB (0.3 mL) were mixed in a closed glass vessel. The resulting mixture was heated under MW irradiation at 200 °C for 60 min. After that period, the crude mixture was dissolved in CH_2Cl_2 (5 mL) and purified *via* preparative TLC using hexane/EtOAc (9 : 7) as the eluent. Yellow solid; yield 6 mg (21%); m.p. 185–187 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.50 (dt, 1H, H-1″, *J* 6.3; 1.7 Hz), 5.28-5.32 (m, 2H, H-3″), 5.86 (s, 1H, 2′-O*H*), 6.06 (ddt, 1H, H-2″, *J* 15.9; 10.7; 6.2 Hz), 6.34 (s, 1H, H-3), 6.92 (d, 1H, H-α, *J* 16.1 Hz), 6.94–6.97 (t, 1H, H-5′, *J* 7.8 Hz), 7.14 (dd, 1H, H-4′, *J* 7.8; 1.6 Hz), 7.39 (ddd, 1H, H-6, *J* 8.0; 7.3; 1.0 Hz), 7.49 (dd, 1H, H-6′, *J* 7.8; 1.6 Hz), 7.53 (dd, 1H, H-8, *J* 8.4; 1.0 Hz), 7.67 (ddd, 1H, H-7; *J* 8.4; 7.3; 1.7 Hz), 7.93 (d, 1H, H-β, *J* 16.1 Hz), 8.20 (dd, 1H, H-5, *J* 8.0; 1.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.9 (C-1″), 110.3 (C-3), 117.8 and 117.9 (C-8 and C-3″), 121.07 and 121.10 (C-5′ and C-α), 123.1 (C-1′), 124.1 (C-4a), 124.9 (C-6), 125.4 (C-3′), 125.6 (C-5), 127.1 (C-6′), 132.0 (C-4′), 132.4 (C-β), 133.7 (C-7), 135.8 (C-2″), 153.7 (C-2′), 156.0 (C-8a), 162.4 (C-2), 178.6 (C-4).

Synthesis of (1*E*,3*E*)-2-[4-(2-allyloxyphenyl)buta-1,3-dien-1-yl]-4*H*-chromen-4-one (17). A solution of BBr_3 in CH_2Cl_2 1M (1.64 mL) was added to a solution of chromone derivative **6a** (200 mg, 0.657 mmol) in CH_2Cl_2 (5 mL) under a nitrogen atmosphere. The resulting mixture was stirred at room temperature for 2 h. After that period, the mixture was poured into ice (5 g) and water (15 mL) and the slurry was stirred until the formation of a precipitate was achieved. The precipitate was removed *via* filtration and washed with water (100 mL) and ethyl ether (50 mL). To a stirring mixture of the precipitate in acetone (30 mL) was added K_2CO_3 (136 mg, 1.5 equiv.) and allyl bromide (0.2 mL; 3 equiv.). The resulting mixture was stirred at reflux for 4 h. After that period, the mixture was poured into ice (5 g) and water (15 mL) and the pH was adjusted to 4 with dilute HCl (10%). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), dried over anhydrous Na_2SO_4 and the solvent evaporated to dryness. The residue was purified *via* preparative TLC using CH_2Cl_2/EtOAc (5 : 1) as the eluent. Yellow solid; yield 169 mg (78%); m.p. 120–122 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.63 (dt, 2H, H-1″, *J* 5.2; 1.5 Hz), 5.35 (dq, 1H, H-3″, *J* 10.5; 1.5 Hz), 5.47 (dq, 1H, H-3″, *J* 17.3; 1.5 Hz), 6.13 (ddt, 1H, H-2″, *J* 17.3; 10.5; 5.2 Hz), 6.25 (s, 1H, H-3), 6.35 (d, 1H, H-α, *J* 15.2 Hz), 6.91 (dd, 1H, H-3′, *J* 8.4; 1.0 Hz), 6.98 (dt, 1H, H-5′, *J* 7.6; 1.0 Hz), 7.03 (ddd, 1H, H-γ, *J* 15.7; 11.0; 0.7 Hz), 7.27–7.30 (m, 1H, H-4′), 7.34 (d, 1H, H-δ, *J* 15.7 Hz), 7.38 (ddd, 1H, H-6, *J* 7.9; 7.1; 1.1 Hz), 7.47 (ddd, 1H, H-β, *J* 15.2; 11.0; 0.8 Hz), 7.51 (dd, 1H, H-8, *J* 8.4; 1.1 Hz), 7.55 (dd, 1H, H-6′, *J* 7.6; 1.7 Hz), 7.67 (ddd, 1H, H-7; *J* 8.4; 7.1; 1.7 Hz), 8.19 (dd, 1H, H-5, *J* 7.9; 1.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.2 (C-1″), 110.1 (C-3), 112.5 (C-3′), 117.8 and 117.9 (C-8 and C-3″), 121.0 (C-5′), 122.9 (C-α), 124.2 (C-4a), 124.9 (C-6), 125.5 (C-1′), 125.6 (C-5), 127.2 (C-6′), 127.6 (C-γ), 130.0 (C-4′), 133.1 (C-2″), 133.6 (C-7), 134.2 (C-δ), 138.4 (C-β), 156.0 (C-2′), 156.4 (C-8a), 162.0 (C-2), 178.4 (C-4).

Conflicts of interest

There are no conflicts to declare.

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