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Syntheses of (*E*)- and (*Z*)-3-styrylchromones

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Abstract Several (*E*)- and (*Z*)-3-styrylchromones were prepared by two different methodologies, the *Wittig* reaction of chromone-3-carboxaldehyde with benzylic ylides and the *Knoevenagel* condensation of chromone-3-carboxaldehyde with phenylacetic acids in the presence of potassium *tert*-butoxide under microwave irradiation. The *Knoevenagel* reaction followed by a decarboxylation offered an efficient and diastereoselective method for preparing (*E*)-3-styrylchromones in a shorter reaction time. It was also demonstrated that phenylacetic acid can also be substituted with success by phenylmalonic acid. The stereochemistry of all products was assigned by NMR experiments.

Keywords Chromone-3-carboxaldehyde; 3-Styrylchromones; *Wittig* reaction; *Knoevenagel* condensation; Microwave irradiation.

Introduction

Styrylchromones constitute a significant subgroup of oxygen heterocyclic compounds presenting important biological activities [1–4]. The only two known naturally occurring 2-styrylchromones are exceptionally cytotoxic *in vitro* to human leukemia cell lines [2]. Synthetic 2-styrylchromone derivatives exhibit potent cytotoxic, anti-allergic, antiviral, and anticancer activity [3]. More recently, we have shown that certain polyhydroxy-2-styrylchromones are potent inhibitors of xanthine oxidase, potent hepatoprotectors against *tert*-butylhydroperoxide, and potent inhibitors of the Cu(II)-induced peroxidation of LDLs [4]. Despite the relationship of 3-styrylchromones with the well-studied 2-styrylchromones very little is known about their biological activities; only antifungal (*A. niger* and *A. teniussiama*) and antibacterial (*E. coli* and *S. albus*) activities have been reported [5].

The synthesis of 2-styrylchromones has been extensively studied [6] while studies on synthesis routes for 3-styrylchromones are not abundant [5, 7–14]. The first two methods involve the *Heck* reaction of 3-bromochromone with styrene [7] and the *Wittig* reaction of an appropriate phosphonium salt with a benzaldehyde derivative [8]; each one of them was used for the synthesis of only one derivative. The third method consists in the oxidative rearrangement of (*E,E*)-γ-alkyl-2′-hydroxycinnamylideneacetophenones with thallium(III) nitrate followed by cyclisation into the corresponding (*E*)-3-(α-alkylstyryl)chromones by treatment with hydrochloric acid [9]. This method is selective for (*E*)-isomers and is the only known strategy which does not use a chromone as starting material. Its drawback is the use of the very toxic reagent like thallium(III) nitrate, and only 3-styrylchromones bearing α-alkyl

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substituents could be obtained. In the last decade, the reactivity of the electrophilic 3-formyl group of chromone-3-carboxaldehydes was successfully exploited in the synthesis of 3-styrylchromones. Some 3-styrylchromones have been obtained in moderate yields, from the condensation of chromone-3-carboxaldehyde with 6,8-dimethylcoumarin-4-acetic acid [10], involving a *Knoevenagel* condensation and a decarboxylation reaction. The condensation of chromone-3-carboxaldehydes with 2,4-dinitrotoluene or 4-nitrophenylacetic acid in pyridine afforded several nitrated (*E*)-3-styrylchromones in moderate yields [5, 11]. A modification of this method developed by our group involves the condensation of chromone-3-carboxaldehydes with phenylacetic acids followed by a decarboxylation reaction, under conventional heating or microwave (MW) irradiation and allowing a diastereoselective synthesis of new (*E*)-3-stryrylchromones [12]. We studied the alternative *Wittig* approach, namely the reaction of chromone-3-carboxaldehydes with benzylic ylides and this new variant gave a diastereomeric mixture of (*E*)- and (*Z*)-3-styrylchromones, the (*Z*) isomer being the more abundant one [13]. More recently, we have disclosed a new solvent-free MW protocol using chromone-3-carboxaldehydes and phenylmalonic acid on sodium acetate support affording (*E*)-3-styrylchromones in moderate-to-good yields, with complete diastereoselectivity [14]. Taking into consideration all of our recent work on the synthesis of 3-styrylchromones, we decided to carry out a systematic study on the three referred methods in order to evaluate their generality and to compare their yields.

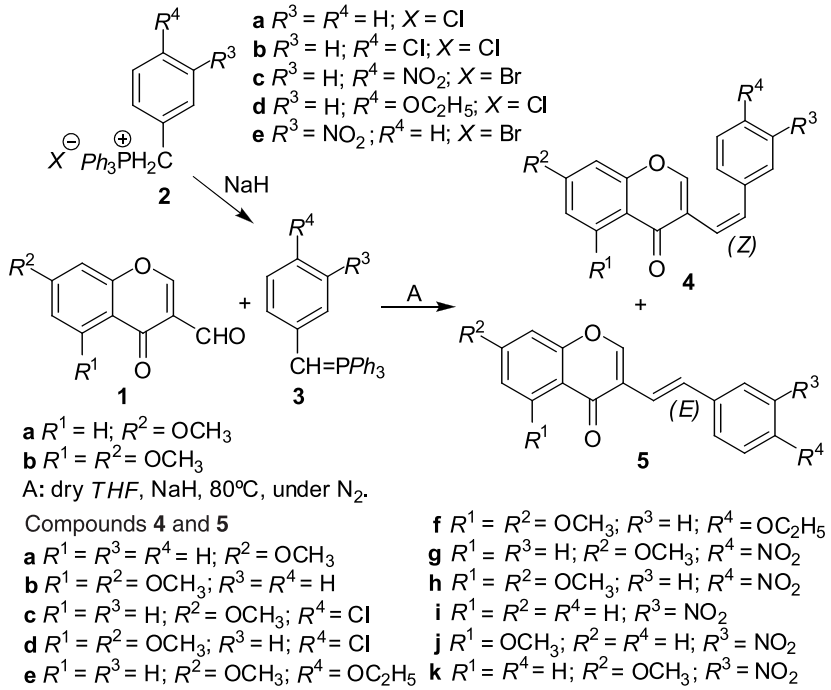
Results and discussion

Synthesis

In the *Wittig* reaction, a *THF* suspension of the appropriate benzyl triphenylphosphonium halides **2a**–**2e** was treated with a molar equivalent of sodium hydride; the solutions with the exception of 4-ethoxyphenylphosphonium bromide (**2d**) became orange after 3 h due to the formation of semi-stabilised ylides **3a**–**3e** (Table 1). After the addition of a molar equivalent of chromone-3-carboxaldehyde **1a** and **1b** and refluxing the mixture for a period given in Table 1 it became yellow in colour. *Wittig* reactions resulted in diastereomeric mixtures of (*Z*)- and (*E*)-3-styrylchromones **4a**–**4k** and **5a**–**5k** that were separable by thin layer chromatography (Scheme 1). In accordance with our previous observations [13] the (*Z*)-isomers **4a**–**4k** were the preferred diastereomers independently of having electron-withdrawing or electron-donating substituents on the phenyl ring (Table 1). This stereochemical outcome could be expected for the reaction of semi-stabilised ylides with steric crowded carbonyl compounds [15]. Comparison of the yields of (*Z*)-3-styrylchromones **4a**–**4h**, **4j**, and **4k** with those of previously synthesized analogs without 5- or 7-methoxy or 3′- or 4′-nitro substituents revealed that the incorporation of the electron-withdrawing nitro group did not alter the efficiency of the coupling. The effect of methoxy substituent is ambiguous, the yields decreased in 10–20% in four cases (**4a**, **4b**, **4e**, **4h**), but remained essentially the same for derivatives **4c**, **4d**, **4f**, and **4g**. In summary, we can conclude that this synthetic

Table 1 *Wittig* reaction of chromone-3-carboxaldehydes **1a** and **1b** with benzylic ylides **3a**–**3e** to yield **4a**–**4k** and **5a**–**5k**

Substituent	Ylide synthesis/h	Reaction with the chromone/h	Yield of (*Z*)-isomer **4**/%	Yield of (*E*)-isomer **5**/%
a $R^1 = R^3 = R^4 = H$; $R^2 = OCH_3$	3.00	48	39	5
b $R^1 = R^2 = OCH_3$; $R^3 = R^4 = H$	3.00	48	30	5
c $R^1 = R^3 = H$; $R^2 = OCH_3$; $R^4 = Cl$	3.00	48	57	5
d $R^1 = R^2 = OCH_3$; $R^3 = H$; $R^4 = Cl$	3.00	48	56	6
e $R^1 = R^3 = H$; $R^2 = OCH_3$; $R^4 = OC_2H_5$	0.08	48	47	6
f $R^1 = R^2 = OCH_3$; $R^3 = H$; $R^4 = OC_2H_5$	0.08	24	57	6
g $R^1 = R^3 = H$; $R^2 = OCH_3$; $R^4 = NO_2$	3.00	24	67	7
h $R^1 = R^2 = OCH_3$; $R^3 = H$; $R^4 = NO_2$	3.00	48	50	5
i $R^1 = R^2 = R^4 = H$; $R^3 = NO_2$	3.00	24	58	5
j $R^1 = OCH_3$; $R^2 = R^4 = H$; $R^3 = NO_2$	3.00	48	46	6
k $R^1 = R^4 = H$; $R^2 = OCH_3$; $R^3 = NO_2$	3.00	48	50	5

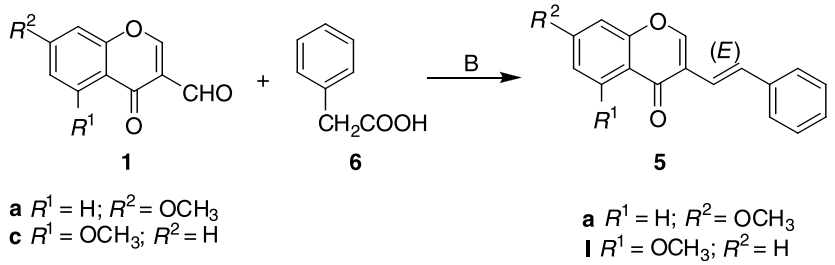


Scheme 1

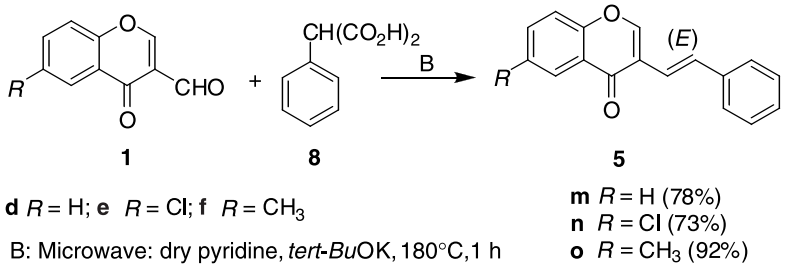
strategy is general and efficient for the preparation of (*Z*)-3-styrylchromones **4a**–**4k**.

The low yield obtained in the synthesis of (*E*)-3-styrylchromones by the *Wittig* reaction of chromone-3-carboxaldehydes with benzylic ylides led us to develop an alternative and diastereoselective methodology to obtain this isomer [12]. *Knoevenagel* condensation of chromone-3-carboxaldehyde with phenylacetic acids in refluxing pyridine and in the presence of potassium *tert*-butoxide gave (*E*)-3-styrylchromones in an efficient way (48–99%). These condensations under microwave irradiation gave the expected 3-styrylchromones in comparable yields (56–94%) but in a shorter reaction time [12]. In the present work 3-styrylchromones **5a** and **5l** were obtained by the latter method, but in lower yields (37–56%) (Scheme 2). These lower yields are probably due to decomposition of the starting chromone-3-carboxaldehydes **1a** and **1c** or of the obtained (*E*)-3-styrylchromones **5a** and **5l**, since the TLC from the reaction mixture allowed the identification of some phenylacetic acid derivative and a strongly brownish colour at the base line. These data seem to indicate that the incorporation of the electron-donating groups in the A ring of chromone-3-carboxaldehydes led to a decrease in the yield of the corresponding (*E*)-3-styrylchromone products.

We also extended our study to the condensation of chromone-3-carboxaldehydes **1d**–**1f** with phenylmalonic acid **8** (2.5 molar equivalents) under microwave irradiation using the conditions described above. (*E*)-3-Styrylchromones **5m**–**5o** were obtained in



Scheme 2



Scheme 3

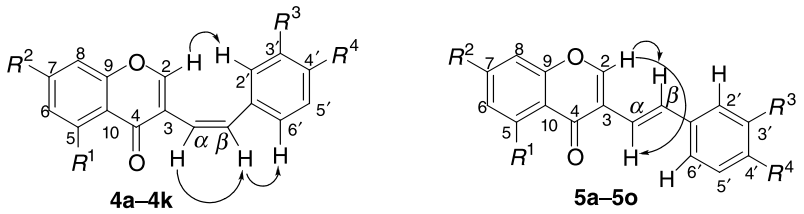


Fig. 1 Important cross peaks observed in the 2D N*O*ESY spectra of 3-styrylchromones **4a**–**4k** and **5a**–**5o**

very good yields (73–92%) and in a diastereoselective way, after one hour of irradiation at 180°C (Scheme 3). In that case two decarboxylations took place after a *Knoevenagel* condensation. This synthesis route is an improvement of our recent reported green protocol [14], since the (*E*)-3-styrylchromones were obtained in much better yields (73–92% when compared with the previous values 48–61%) independently of the electronic nature of the substituents in ring A and retaining the complete (*E*)-diastereoselectivity.

NMR spectroscopy

The most important features of the ^{1}H NMR spectra of 3-styrylchromones **4a**–**4k** and **5a**–**5o** are the resonances of their vinylic protons. The resonances assigned to H-β ($\delta_H = 6.67$–6.84 and 7.51–7.91 ppm) and C-β ($\delta_C = 129.1$–132.4 and 129.1–132.1 ppm) appeared at higher frequency values than those of H-α ($\delta_H = 6.39$–6.70 and 6.80–7.08 ppm) and C-α ($\delta_C = 118.6$–124.8 and 116.7–124.1 ppm). The coupling constant values of $^3J_{\text{H-}\alpha\text{-H-}\beta} \sim 12$ Hz in the case of **4a**–**4k** indicate a *cis* configuration for their vinylic system. The stereochemistry of these compounds was also confirmed by 2D N*O*ESY experiment. Strong N*O*E cross peaks were observed between the signals of H-α and H-β and also between that of H-β and H-2′,6′, while a weak cross peak between that of H-2 and H-2′,6′ was also found. These results confirm the *cis* configuration of the C-α = C-β double bond and also the conformation of the styryl moiety relative to the chromone nucleus (Fig. 1). The coupling constant values $^3J_{\text{H-}\alpha\text{-H-}\beta} \sim 16$–$17$ Hz in the case of compounds **5a**–**5o** establish a *trans* configuration for their vinylic moiety. The intense N*O*E cross peaks between the signals of H-2 and those of H-α and H-β, observed in the 2D N*O*ESY experiment, suggests a free rotation around the C-3-C-α bond (Fig. 1). It is also important to report from the ^{1}H NMR spectra of compounds **4a**–**4k** and **5a**–**5o** the singlet of H-2 at $\delta_H = 7.41$–7.71 and 7.63–8.16 ppm. In some cases this proton resonance appears as a doublet due to the long-range coupling with H-α ($^4J \sim 0.6$–1.4 Hz).

Conclusion

We studied the *Wittig* reactions of chromone-3-carboxaldehydes **1a** and **1b** with benzylic ylides **3a**–**3e** giving both (*Z*)- and (*E*)-3-styrylchromones **4a**–**4k** and **5a**–**5k**, but the (*E*)-isomers were minor products in all cases. No significant substituent effect was found. Studies on the *Knoevenagel* condensation of chromone-3-carboxaldehydes **1a** and **1c**–**1f** and phenylacetic acid **6** or phenylmalonic acid **8**, followed by decarboxylation under classical heating or microwave irradiation, proved the generality of this approach although the incorporation of electron-donating methoxy groups in the ring A resulted in

lower product yields. The beneficial effect of microwave irradiation was the shortening of the reaction time compared to the reactions under conventional heating conditions.

Experimental

Melting points were determined on a Reichert Thermovar apparatus fitted with a microscope. NMR spectra were recorded on Bruker Avance 300 (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C) and Bruker Avance 500 (500.13 MHz for ^{1}H and 125.76 MHz for ^{13}C) spectrometers, with $CDCl_3$ as solvent. Chemical shifts (δ) are reported in ppm values and coupling constants (J) in Hz. The internal standard was *TMS*. ^{1}H assignments were made using 2D *g*COSY and N*O*ESY (mixing time of 800 ms) experiments, while ^{13}C assignments were made using 2D *g*HSQC and *g*HMBC (long-range C/H coupling constants were optimised to 7 Hz) experiments. Electron impact (EI, 70 eV) and FAB$^+$ mass spectra were measured on a VG Autospec Q and M mass spectrometer [HRMS were in good agreement ($\pm$0.5 ppm) with the calculated values], while electrospray mass spectra (positive mode, ES$^+$) were measured on a Micromass Q-TOF-2TH spectrometer. Elemental analyses were obtained with a LECO 932 CHN analyser (University of Aveiro) and the results were in good agreement ($\pm$0.4%) with the calculated values. Preparative thin layer chromatography was carried out with Riedel silica gel 60 DGF_{254}, and column chromatography using Merk silica gel 60, 70–230 mesh. Chromone-3-carboxaldehyde and benzyltriphenylphosphonium salts are commercial reagents and were obtained from Sigma-Aldrich. 3-(Nitrobenzyl)triphenylphosphonium bromide was synthesised following the procedure reported by *Russell et al.* [16]. All other chemicals and solvents used were obtained from commercial sources and used as received or dried using standard procedures.

*General experimental procedure for the synthesis of 3-styrylchromones **4a–4k** and **5a–5k** by using Wittig reactions*

Sodium hydride (25 mg, 1.04 mmol) was added to a suspension of the appropriate phosphonium halide (1.04 mmol) in 25 cm^3 dry *THF* under nitrogen, and the reaction mixture was refluxed with stirring for the adequate time (see Table 1). The appearance of an orange colour and the disappearance of the suspension of phosphonium salts indicated the ylide formation. After that period, the appropriate chromone-3-carboxaldehyde **1a**, **1b** (1.04 mmol) was added and the reaction mixture refluxed for the time given in Table 1. Then the mixture was poured into 50 cm^3 H_2O and 30 g ice and acidified at *pH* 3 using HCl (20%). The organic layer was extracted with 3×30 cm^3 $CHCl_3$ and the solvent was evaporated to dryness. The residue was taken in 20 cm^3 CH_2Cl_2 and purified by thin layer chromatography using CH_2Cl_2 as eluent, leading to the isolation of two main spots, in each case. The component of higher R_f value was identified in each case as (*E*)-3-styrylchromones **5a–5k** whereas the other was the (*Z*)-3-styrylchromones **4a–4k** (the main compounds). These compounds were recrystallised from ethanol (**4a**, 112.9 mg, 39%; **5a**, 14.5 mg, 5%; **4b**, 77.4 mg, 30%; **5b**, 12.9 mg, 5%; **4c**, 185.4 mg, 57%; **5c**, 16.3 mg, 5%; **4d**, 199.7 mg, 56%; **5d**, 21.4 mg, 6%; **4e**, 157.6 mg, 47%; **5e**, 20.1 mg, 6%; **4f**, 208.9 mg, 57%; **5f**, 22.0 mg, 6%; **4g**, 225.2 mg, 67%; **5g**, 23.6 mg, 7%; **4h**, 183.7 mg, 50%; **5h**, 18.3 mg, 5%; **4i**, 176.9 mg, 58%; **5i**, 15.3 mg, 5%; **4j**, 154.7 mg, 46%; **5j**, 20.2 mg, 6%; **4k**, 168.1 mg, 50%; **5k**, 16.8 mg, 5%).

*General experimental procedure for the synthesis of (E)-3-styrylchromones **5a**, **5l** by using Knoevenagel condensation under microwave irradiation*

A mixture of chromone-3-carboxaldehydes **1a**, **1c** (0.574 mmol), 390 mg phenylacetic acid **6** (2.87 mmol) and 0.10 g *tert-Bu*OK (0.86 mmol) in 15 cm^3 dry pyridine was irradiated in a 100 cm^3 *PFA* sealed vessel of a high-pressure rotor segment in an Ethos SYNTH microwave (Milestone Inc), at a maximum temperature of 180°C for 1 h (maximum power of 800 W). After that period the reaction mixture was cooled to room temperature and poured into 25 cm^3 H_2O and 20 g ice and the *pH* adjusted to 2 with a solution of HCl (10%). The pale yellow precipitate was separated by filtration, washed with H_2O, and purified by thin layer chromatography with a 7:3 mixture of CH_2Cl_2-light petroleum as eluent. The obtained residue was crystallised from ethanol giving (*E*)-3-styrylchromones **5a**, **5l** in moderate yields (**5a**, 89.4 mg, 56%; **5l**, 59.1 mg, 37%).

*General experimental procedure for the synthesis of (E)-3-styrylchromones **5m–5o** by using Knoevenagel condensation under microwave irradiation*

A mixture of chromone-3-carboxaldehydes **1d–1f** (0.574 mmol), 0.26 g phenylmalonic acid **8** (1.44 mmol), and 0.10 g *tert-Bu*OK (0.86 mmol) in 15 cm^3 dry pyridine was irradiated in a 100 cm^3 *PFA* sealed vessel of a high-pressure rotor segment in an Ethos SYNTH microwave (Milestone Inc), at a maximum temperature of 180°C for 1 h (maximum power of 800 W). After that period the reaction mixture was cooled to room temperature and poured into 25 cm^3 H_2O and 20 g ice and the *pH* adjusted to 2 with a solution of HCl (10%). The pale yellow precipitate was separated by filtration, washed with H_2O, and purified by thin layer chromatography with a 7:3 mixture of CH_2Cl_2-light petroleum as eluent. The obtained residue was crystallised from ethanol giving (*E*)-3-styrylchromones **5m–5o** in good yields (**5m**, 111.1 mg, 78%; **5n**, 118.5 mg, 73%; **5o**, 138.6 mg, 92%).

(Z)-7-Methoxy-3-styrylchromone (**4a**, $C_{18}H_{14}O_3$)

Mp 106–107°C; ^{1}H NMR (300.13 MHz): $\delta = 3.88$ (s, 7-OC*H*$_3$), 6.53 (dd, $J = 12.0$, 0.9 Hz, H-α), 6.76 (d, $J = 2.4$ Hz, H-8), 6.76 (d, $J = 12.0$ Hz, H-β), 6.98 (dd, $J = 8.9$, 2.4 Hz, H-6), 7.20–7.32 (m, H-2′,3′,4′,5′,6′), 7.65 (d, $J = 0.9$ Hz, H-2), 8.18 (d, $J = 8.9$ Hz, H-5) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.8$ (7-O*C*H$_3$), 100.1 (C-8), 114.6 (C-6), 117.9 (C-10), 120.3 (C-α), 120.9 (C-3,4′), 127.2 and 127.4 (C-2′,6′,3′,5′), 132.4 (C-β), 136.7 (C-1′), 153.5 (C-2), 157.8 (C-9), 163.9 (C-7), 176.5 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 279 [(M + H)$^+$, 24], 278 (M$^{+\bullet}$, 100), 277 [(M − H)$^+$, 91], 261 (13), 249 [(M–HCO)$^+$, 10], 234 (4), 218 (2), 201 [(M–

$C_6H_5)^+$, 30], 189 (3), 178 (6), 158 (3), 151 (27), 139 (7), 128 (39), 122 (16), 115 (8), 107 (15), 102 (10), 92 (4), 85 (6), 77 (11), 63 (9), 57 (6).

(E)-7-Methoxy-3-styrylchromone (**5a**, $C_{18}H_{14}O_3$)
Mp 123–125°C; ^{1}H NMR (300.13 MHz): $\delta = 3.91$ (s, 7-OC*H*$_3$), 6.85 (d, $J = 2.4$ Hz, H-8), 6.98 (dd, $J = 16.6$, 0.7 Hz, H-α), 7.00 (dd, $J = 8.9$, 2.4 Hz, H-6), 7.26–7.29 (m, H-4′), 7.36 (t, $J = 7.4$ Hz, H-3′,5′), 7.52 (d, $J = 7.4$ Hz, H-2′,6′), 7.61 (d, $J = 16.6$ Hz, H-β), 8.05 (s, H-2), 8.20 (d, $J = 8.9$ Hz, H-5) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.8$ (7-O*C*H$_3$), 100.1 (C-8), 114.7 (C-6), 118.0 (C-10), 119.1 (C-α), 121.7 (C-3), 126.6 (C-2′,6′), 127.6 (C-5), 127.8 (C-4′), 128.7 (C-3′,5′), 131.4 (C-β), 137.4 (C-1′), 152.5 (C-2), 157.6 (C-9), 163.9 (C-7), 176.1 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 279 [(M + H)$^+$, 26], 278 (M$^{+\bullet}$, 100), 277 [(M − H)$^+$, 88], 261 [(M–OH)$^+$, 16], 249 [(M–HCO)$^+$, 11], 234 (5), 218 (2), 207 (2), 201 (37), 189 (3), 178 (4), 161 (3), 151 (34), 139 (12), 128 (39), 122 (14), 107 (15), 94 (3), 89 (8), 83 (5), 77 (19), 63 (13).

(Z)-5,7-Dimethoxy-3-styrylchromone (**4b**, $C_{19}H_{16}O_4$)
Mp 135–137°C; ^{1}H NMR (300.13 MHz): $\delta = 3.83$ (s, 7-OC*H*$_3$), 3.93 (s, 5-OC*H*$_3$), 6.32 (d, $J = 2.3$ Hz, H-8), 6.34 (d, $J = 2.3$ Hz, H-6), 6.50 (dd, $J = 12.1$, 0.9 Hz, H-α), 6.73 (d, $J = 12.1$ Hz, H-β), 7.18–7.31 (m, H-2′,3′,4′,5′,6′), 7.46 (d, $J = 0.9$ Hz, H-2) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.6$ (7-O*C*H$_3$), 56.2 (5-O*C*H$_3$), 92.4 (C-8), 96.0 (C-6), 109.3 (C-10), 120.7 (C-α), 121.9 (C-3), 127.0 (C-4′), 128.4 (C-2′,6′), 128.5 (C-3′,5′), 131.8 (C-β), 136.7 (C-1′), 151.4 (C-2), 159.6 (C-9), 161.0 (C-5), 163.7 (C-7), 175.9 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 309 [(M + H)$^+$, 308 (M$^{+\bullet}$, 100), 28], 307 [(M − H)$^+$, 30], 291 [(M–OH)$^+$, 6], 280 [(M–CO)$^+$, 11], 279 (36), 277 [(M–OCH$_3$)$^+$, 21], 261 (9), 249 (5), 231 [(M–$C_6H_5)^+$, 23], 217 (3), 203 (11), 201 (12), 190 (13), 189 (78), 181 (11), 180 (17), 176 (11), 165 (7), 151 (32), 152 (21), 154 (12), 138 (5), 137 (31), 128 (30), 127 (15), 115 (16), 109 (9), 102 (11), 91 (15), 77 (16), 69 (12), 63 (16).

(E)-5,7-Dimethoxy-3-styrylchromone (**5b**, $C_{19}H_{16}O_4$)
Mp 152–155°C; ^{1}H NMR (300.13 MHz): $\delta = 3.91$ (s, 7-OC*H*$_3$), 3.99 (s, 5-OC*H*$_3$), 6.40 (d, $J = 2.3$ Hz, H-8), 6.46 (d, $J = 2.3$ Hz, H-6), 6.96 (d, $J = 16.4$ Hz, H-α), 7.24–7.28 (m, H-4′), 7.33–7.38 (m, H-3′,5′), 7.52 (d, $J = 8.6$ Hz, H-2′,6′), 7.64 (d, $J = 16.4$ Hz, H-β), 7.92 (s, H-2) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.7$ (7-O*C*H$_3$), 56.3 (5-O*C*H$_3$), 92.5 (C-8), 96.2 (C-6), 109.3 (C-10), 119.2 (C-α), 122.6 (C-3), 126.5 (C-2′,6′), 127.6 (C-4′), 128.6 (C-3′,5′), 131.0 (C-β), 137.6 (C-1′), 150.6 (C-2), 159.4 (C-9), 161.4 (C-5), 163.8 (C-7), 175.6 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 308 (M$^{+\bullet}$, 100), 307 [(M − H)$^+$, 34], 291 [(M–OH)$^+$, 6], 279 [(M–HCO)$^+$, 32], 277 [(M–OCH$_3$)$^+$, 16], 261 (7), 249 (4), 231 [(M–$C_6H_5)^+$, 19], 217 (3), 201 (9), 189 (69), 181 (13), 165 (6), 151 (27), 137 (26), 128 (23), 115 (12), 102 (7), 91 (12), 78 (6), 69 (9).

(Z)-4′-Chloro-7-methoxy-3-styrylchromone (**4c**, $C_{18}H_{13}ClO_3$)
Mp 156–158°C; ^{1}H NMR (300.13 MHz): $\delta = 3.88$ (s, 7-OC*H*$_3$), 6.53 (dd, $J = 12.1$, 1.2 Hz, H-α), 6.72 (d, $J = 12.1$ Hz, H-β), 6.77 (d, $J = 2.4$ Hz, H-8), 6.98 (dd, $J = 8.9$, 2.4 Hz, H-6), 7.23 (AB, $J = 8.0$ Hz, H-2′,3′,5′,6′), 7.63 (d, $J = 1.2$ Hz, H-2), 8.16 (d, $J = 8.9$ Hz, H-5) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.7$ (7-O*C*H$_3$), 100.1 (C-8), 114.7 (C-6), 117.8 (C-10), 120.7 (C-3), 121.1 (C-α), 127.3 (C-5), 128.7 (C-3′,5′), 129.9 (C-2′,6′), 131.2 (C-β), 132.9 (C-4′), 135.0 (C-1′), 153.4 (C-2), 157.8 (C-9), 164.0 (C-7), 176.3 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 314 [(M$^{+\bullet}$,^{37}Cl), 44], 313 [(M + H)$^+$, 46], 312 [(M$^{+\bullet}$,^{35}Cl), 100], 311 [(M − H)$^+$, 65], 295 [(M–OH)$^+$, 15], 283 [(M–HCO)$^+$, 9], 277 [(M–Cl)$^+$, 14], 268 (5), 201 [(M–$C_6H_4Cl)^+$, 41], 189 (8), 176 [(M–$C_8H_5Cl)^+$, 5], 162 (23), 151 (44), 138 (9), 127 (24), 122 (20), 115 (4), 107 (15), 79 (11), 63 (12).

(E)-4′-Chloro-7-methoxy-3-styrylchromone (**5c**, $C_{18}H_{13}ClO_3$)
Mp 165–166°C; ^{1}H NMR (300.13 MHz): $\delta = 3.91$ (s, 7-OC*H*$_3$), 6.84 (d, $J = 2.4$ Hz, H-8), 6.91 (dd, $J = 16.3$, 1.4 Hz, H-α), 6.99 (dd, $J = 8.9$, 2.4 Hz, H-6), 7.31 (d, $J = 8.5$ Hz, H-3′,5′), 7.43 (d, $J = 8.5$ Hz, H-2′,6′), 7.60 (d, $J = 16.3$ Hz, H-β), 7.63 (d, $J = 1.4$ Hz, H-2), 8.16 (d, $J = 8.9$ Hz, H-5) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.8$ (7-O*C*H$_3$), 100.1 (C-8), 114.7 (C-6), 117.9 (C-10), 119.8 (C-α), 121.3 (C-3), 127.6 (C-5), 127.7 (C-2′,6′), 128.8 (C-3′,5′), 130.2 (C-β), 133.3 (C-4′), 135.9 (C-1′), 152.9 (C-2), 157.5 (C-9), 164.0 (C-7), 176.0 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 314 [(M$^{+\bullet}$,^{37}Cl), 47], 313 [(M + H)$^+$, 49], 312 [(M$^{+\bullet}$,^{35}Cl), 100], 311 [(M − H)$^+$, 64], 295 [(M–OH)$^+$, 15], 283 [(M–HCO)$^+$, 9], 277 [(M–^{35}Cl)$^+$, 14], 268 (5), 201 [(M–$C_6H_4Cl)^+$, 44], 189 (8), 176 [(M–$C_8H_5Cl)^+$, 5], 162 (26), 156 (7), 151 (52), 150 (29), 138 (9), 127 (27), 122 (24), 115 (5), 107 (17), 79 (12), 63 (15).

(Z)-4′-Chloro-5,7-dimethoxy-3-styrylchromone
(**4d**, $C_{19}H_{15}ClO_4$)
Mp 150–151°C; ^{1}H NMR (300.13 MHz): $\delta = 3.87$ (s, 7-OC*H*$_3$), 3.96 (s, 5-OC*H*$_3$), 6.36 (s, H-6,8), 6.51 (dd, $J = 12.1$, 0.9 Hz, H-α), 6.68 (d, $J = 12.1$ Hz, H-β), 7.23 (AB, $J = 8.2$ Hz, H-2′,3′,5′,6′), 7.45 (d, $J = 0.9$ Hz, H-2) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.7$ (7-O*C*H$_3$), 56.3 (5-O*C*H$_3$), 92.6 (C-8), 96.2 (C-6), 109.4 (C-10), 121.7 (C-α), 121.9 (C-3), 128.7 (C-3′,5′), 130.0 (C-2′,6′), 130.8 (C-β), 132.8 (C-4′), 135.3 (C-1′), 151.4 (C-2), 159.7 (C-9), 161.1 (C-5), 164.0 (C-7), 175.9 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 344 [(M$^{+\bullet}$, ^{37}Cl), 37] 343 [(M + H)$^+$, 35], 342 [(M$^{+\bullet}$, ^{35}Cl), 100], 341 [(M − H)$^+$, 41], 329 (2), 325 [(M–OH)$^+$, 7], 313 [(M–HCO)$^+$, 23], 297 (6), 283 (3), 249 (2), 235 (10), 217 (4), 208 (2), 201 (11), 189 (100), 181 (30), 162 (14), 151 (25), 137 (33), 127 (25), 109 (10), 95 (7), 77 (9), 69 (12).

(E)-4′-Chloro-5,7-dimethoxy-3-styrylchromone
(**5d**, $C_{19}H_{15}ClO_4$)
Mp 182–183°C; ^{1}H NMR (300.13 MHz): $\delta = 3.89$ (s, 7-OC*H*$_3$), 3.97 (s, 5-OC*H*$_3$), 6.38 (d, $J = 2.3$ Hz, H-8), 6.45 (d, $J = 2.3$ Hz, H-6), 6.88 (d, $J = 16.6$ Hz, H-α), 7.30 (d, $J = 8.6$ Hz, H-3′,5′), 7.41 (d, $J = 8.6$ Hz, H-2′,6′), 7.64 (d, $J = 16.6$ Hz, H-β), 7.89 (s, H-2) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.7$ (5-O*C*H$_3$), 56.3 (5-O*C*H$_3$), 92.6 (C-8), 96.2 (C-6), 109.4 (C-10), 121.7 (C-α), 121.9 (C-3), 128.7 (C-3′,5′),

130.0 (C-2′,6′), 130.8 (C-β), 132.8 (C-4′), 135.3 (C-1′), 151.4 (C-2), 159.7 (C-9), 161.1 (C-5), 164.0 (C-7), 175.9 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 344 [($M^{+\bullet}$, ^{37}Cl), 28], 343 [(M + H)$^+$, 20], 342 [($M^{+\bullet}$, ^{35}Cl), 77], 341 [(M-H)$^+$, 12], 325 [(M–OH)$^+$, 2], 313 [(M–HCO)$^+$, 17], 311 [(M–OCH_3)$^+$, 8], 297 (4), 231 [(M–C_6H_4Cl)$^+$, 10], 217 (2), 201 (7), 189 (100), 180 (9), 162 (7), 151 (17), 137 (20), 125 (24), 109 (5), 91 (4), 77 (5), 63 (6).

(Z)-4′-Ethoxy-7-methoxy-3-styrylchromone (**4e**, $C_{20}H_{18}O_4$) Mp 90–92°C; ^{1}H NMR (300.13 MHz): δ = 1.39 (t, J = 7.0 Hz, 4′-OCH$_2$CH_3), 3.88 (s, 7-OCH_3), 4.00 (q, J = 7.0 Hz, 4′-OCH_2CH$_3$), 6.40 (dd, J = 12.0, 1.2 Hz, H-α), 6.70 (d, J = 12.0 Hz, H-β), 6.76 (d, J = 2.4 Hz, H-8), 6.78 (d, J = 8.8 Hz, H-3′,5′), 6.96 (dd, J = 8.9, 2.4 Hz, H-6), 7.71 (d, J = 1.2 Hz, H-2), 7.23 (d, J = 8.8 Hz, H-2′,6′), 8.17 (d, J = 8.9 Hz, H-5) ppm; ^{13}C NMR (75.47 MHz): δ = 14.7 (4′-OCH$_2$CH_3), 55.7 (7-OCH_3), 63.3 (4′-OCH_2CH$_3$), 100.1 (C-8), 114.4 (C-3′,5′), 114.5 (C-6), 117.9 (C-10), 118.6 (C-α), 121.2 (C-3), 127.3 (C-5), 128.8 (C-1′), 129.8 (C-2′,6′), 132.1 (C-β), 153.4 (C-2), 157.8 (C-9), 158.0 (C-4′), 163.9 (C-7), 176.5 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 322 ($M^{+\bullet}$, 100), 305 [(M–OH)$^+$, 6], 293 [(M–HCO)$^+$, 60], 277 [(M–OCH_2CH_3)$^+$, 9], 265 (7), 250 (8), 237 (2), 222 (3), 201 (8), 194 (2), 176 (24), 171 (2), 165 (5), 158 (2), 151 (25), 144 (15), 134 (7), 122 (11), 115 (36), 107 (14), 95 (3), 94 (3), 89 (8), 79 (11), 69 (3), 63 (26).

(E)-4′-Ethoxy-7-methoxy-3-styrylchromone (**5e**, $C_{20}H_{18}O_4$) Mp 147–148°C; ^{1}H NMR (500.13 MHz): δ = 1.43 (t, J = 7.0 Hz, 4′-OCH$_2$CH_3), 3.91 (s, 7-OCH_3), 4.06 (q, J = 7.0 Hz, 4′-OCH_2CH$_3$), 6.84 (d, J = 2.4 Hz, H-8), 6.85 (d, J = 16.4 Hz, H-α), 6.88 (d, J = 8.7 Hz, H-3′,5′), 6.99 (dd, J = 8.9, 2.4 Hz, H-6), 7.45 (d, J = 8.7 Hz, H-2′,6′), 7.51 (d, J = 16.4 Hz, H-β), 8.03 (s, H-2), 8.20 (d, J = 8.9 Hz, H-5) ppm; ^{13}C NMR (125.76 MHz): δ = 14.8 (4′-OCH$_2$CH_3), 55.8 (7-OCH_3), 63.4 (4′-OCH_2CH$_3$), 100.0 (C-8), 114.6 (C-6 and C-3′,5′), 116.7 (C-α), 117.6 (C-10), 121.9 (C-3), 127.8 (C-5 and C-2′,6′), 130.0 (C-1′), 131.0 (C-β), 152.0 (C-2), 157.2 (C-4′), 158.8 (C-9), 163.9 (C-7), 176.1 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 322 ($M^{+\bullet}$, 100), 305 [(M–OH)$^+$, 7], 293 [(M–HCO)$^+$, 62] or [(M–C_2H_5)$^+$, 62], 277 [(M–C_2H_5O)$^+$, 11], 265 (8), 250 (8), 237 (2), 222 (3), 201 [(M–C_8H_9O)$^+$, 10], 176 (7), 165 (4), 158 (1), 151 (29), 144 (14), 135 (4), 122 (6), 115 (29), 107 (9), 94 (2), 89 (6), 77 (6), 63 (11).

(Z)-4′-Ethoxy-5,7-dimethoxy-3-styrylchromone (**4f**, $C_{21}H_{20}O_5$) Mp 147–149°C; ^{1}H NMR (300.13 MHz): δ = 1.40 (t, J = 7.0 Hz, 4′-OCH$_2$CH_3), 3.86 (s, 7-OCH_3), 3.95 (s, 5-OCH_3), 4.01 (q, J = 7.0 Hz, 4′-OCH_2CH$_3$), 6.36 (s, 2H, H-6,8), 6.39 (dd, J = 12.1, 1.2 Hz, H-α), 6.67 (d, J = 12.1 Hz, H-β), 6.79 (d, J = 8.7 Hz, H-3′,5′), 7.22 (d, J = 8.7 Hz, H-2′,6′), 7.54 (d, J = 1.2 Hz, H-2) ppm; ^{13}C NMR (75.47 MHz): δ = 14.8 (4′-OCH$_2$CH_3), 55.7 (7-OCH_3), 56.3 (5-OCH_3), 63.3 (4′-OCH_2CH$_3$), 92.6 (C-8), 96.1 (C-6), 109.5 (C-10), 114.4 (C-3′,5′), 119.4 (C-α), 122.4 (C-3), 129.1 (C-β), 129.9 (C-2′,6′), 131.6 (C-1′), 151.5 (C-2), 158.0 (C-4′), 159.7 (C-9), 161.2 (C-5), 163.8 (C-7), 176.1 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 353 [(M + H)$^+$, 34], 352 ($M^{+\bullet}$, 100), 351 [(M − H)$^+$, 29], 335 [(M–OH)$^+$, 7], 323 [(M–HCO)$^+$, 27] or 323 [(M–C_2H_5)$^+$, 27], 309 (17), 293 (12), 277 (5), 265 (4), 250 (2), 237 (2), 231 [(M–C_8H_9O)$^+$, 9], 221 (1), 209 (1), 201 (3), 189 (3), 181 (15), 172 (11), 162 (16), 152 (11), 144 (18), 135 (52), 122 (6), 116 (8), 107 (33), 89 (7), 81 (3), 75 (5), 69 (8), 63 (11).

(E)-4′-Ethoxy-5,7-dimethoxy-3-styrylchromone (**5f**, $C_{21}H_{20}O_5$) ^{1}H NMR (300.13 MHz): δ = 1.41 (t, J = 7.0 Hz, 4′-OCH$_2$-CH_3), 3.87 (s, 7-OCH_3), 3.95 (s, 5-OCH_3), 4.02 (q, J = 7.0 Hz, 4′-OCH_2CH$_3$), 6.36 (d, J = 2.2 Hz, H-8), 6.42 (d, J = 2.2 Hz, H-6), 6.80 (d, J = 16.2 Hz, H-α), 6.86 (d, J = 8.7 Hz, H-3′,5′), 7.41 (d, J = 8.7 Hz, H-2′,6′), 7.53 (d, J = 16.2 Hz, H-β), 7.86 (s, H-2) ppm; ^{13}C NMR (75.47 MHz): δ = 14.8 (4′-OCH$_2$CH_3), 55.7 (7-OCH_3), 56.3 (5-OCH_3), 63.4 (4′-OCH_2CH$_3$), 92.5 (C-8), 96.1 (C-6), 109.4 (C-10), 114.5 (C-3′,5′), 116.8 (C-α), 122.8 (C-3), 127.7 (C-2′,6′), 130.2 (C-1′), 130.5 (C-β), 150.0 (C-2), 158.6 (C-4′), 159.4 (C-9), 161.3 (C-5), 163.7 (C-7), 175.6 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 353 [(M + H)$^+$, 23], 352 ($M^{+\bullet}$, 100), 351 [(M − H)$^+$, 16], 335 [(M–OH)$^+$, 3], 323 [(M–HCO)$^+$, 14] or 323 [(M–C_2H_5)$^+$, 14], 309 (8), 293 (5), 277 (3), 265 (1), 231 [(M–C_8H_9O)$^+$, 5], 219 (2), 201 (1), 190 (7), 181 (9), 172 (4), 162 (11), 151 (5), 144 (12), 135 (35), 122 (2), 115 (14), 107 (19), 89 (3), 83 (9), 77 (5), 69 (15), 63 (4).

(Z)-7-Methoxy-4′-nitro-3-styrylchromone (**4g**, $C_{18}H_{13}NO_5$) Mp 171–174°C; ^{1}H NMR (300.13 MHz): δ = 3.90 (s, 7-OCH_3), 6.70 (dd, J = 12.2, 1.2 Hz, H-α), 6.80 (d, J = 2.4 Hz, H-8), 6.82 (d, J = 12.2 Hz, H-β), 7.01 (dd, J = 8.9, 2.4 Hz, H-6), 7.46 (d, J = 8.7 Hz, H-2′,6′), 7.60 (d, J = 1.2 Hz, H-2), 8.14 (d, J = 8.7 Hz, H-3′,5′), 8.17 (d, J = 8.9 Hz, H-5) ppm; ^{13}C NMR (75.47 MHz): δ = 55.9 (7-OCH_3), 100.3 (C-8), 115.0 (C-6), 117.8 (C-10), 120.5 (C-3), 123.9 (C-2′,6′), 124.1 (C-α), 127.4 (C-5), 129.4 (C-3′,5′), 130.6 (C-β), 143.6 (C-1′), 146.6 (C-4′), 153.6 (C-2), 157.9 (C-9), 164.3 (C-7), 176.0 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 323 ($M^{+\bullet}$, 100), 306 [(M–OH)$^+$, 8], 293 [(M–NO)$^+$, 9], 276 (21), 260 (3), 248 (6), 234 (4), 201 [(M–$C_6H_4NO_2$)$^+$, 61], 189 (3), 176 (5), 158 (3), 151 (40), 135 (3), 122 (23), 115 (9), 107 (17), 92 (4), 79 (12), 63 (17).

(E)-7-Methoxy-4′-nitro-3-styrylchromone (**5g**, $C_{18}H_{13}NO_5$) Mp 173–174°C; ^{1}H NMR (300.13 MHz): δ = 3.95 (s, 7-OCH_3), 6.89 (d, J = 2.4 Hz, H-8), 7.05 (dd, J = 8.8, 2.4 Hz, H-6), 7.08 (d, J = 16.2 Hz, H-α), 7.66 (d, J = 8.8 Hz, H-2′,6′), 7.87 (d, J = 16.2 Hz, H-β), 8.10 (s, H-2), 8.23 (d, J = 8.8 Hz, H-5), 8.24 (d, J = 8.8 Hz, H-3′,5′) ppm; ^{13}C NMR (75.47 MHz): δ = 55.9 (7-OCH_3), 100.2 (C-8), 115.0 (C-6), 118.0 (C-10), 120.7 (C-3), 124.0 (C-α and C-2′,6′), 126.9 (C-3′,5′), 127.6 (C-5), 129.4 (C-β), 144.1 (C-1′), 146.8 (C-4′), 154.2 (C-2), 157.5 (C-9), 164.2 (C-7), 175.8 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 323 ($M^{+\bullet}$, 100), 306 [(M–OH)$^+$, 6], 293 [(M–NO)$^+$, 11], 276 (16), 260 (2), 248 (4), 234 (3), 201 [(M–$C_6H_4NO_2$)$^+$, 53], 189 (2), 176 (4), 158 (2), 151 (32), 143 (3), 122 (17), 115 (7), 107 (12), 92 (3), 79 (8), 63 (12), 57 (4).

(Z)-5,7-Dimethoxy-4′-nitro-3-styrylchromone (**4h**, $C_{19}H_{15}NO_6$) Mp 122–124°C; ^{1}H NMR (300.13 MHz): $\delta = 3.87$ (s, 7-OCH_3), 3.96 (s, 5-OCH_3), 6.37 (d, $J = 2.2$ Hz, H-8), 6.39 (d, $J = 2.2$ Hz, H-6), 6.69 (dd, $J = 12.1$, 1.0 Hz, H-α), 6.77 (d, $J = 12.1$ Hz, H-β), 7.41 (d, $J = 1.0$ Hz, H-2), 7.45 (d, $J = 8.7$ Hz, H-2′,6′), 8.13 (d, $J = 8.7$ Hz, H-3′,5′) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.8$ (7-OCH_3), 56.4 (5-OCH_3), 92.6 (C-8), 96.4 (C-6), 109.3 (C-10), 121.7 (C-3), 124.1 (C-3′,5′), 124.8 (C-α), 129.5 (C-2′,6′), 130.0 (C-β), 143.8 (C-1′), 146.6 (C-4′), 151.5 (C-2), 159.8 (C-9), 161.2 (C-5), 164.2 (C-7), 175.7 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 353 ($M^{+\bullet}$, 100), 352 [$(M-H)^+$, 18], 336 [$(M–OH)^+$, 98], 323 [$(M–NO)^+$, 19], 306 [$(M–HNO_2)^+$, 57], 292 (6), 277 (19), 261 (5), 249 (6), 231 (29), 201 (31), 189 (36), 181 (14), 165 (10), 152 (34), 143 (4), 137 (69), 126 (24), 115 (26), 109 (21), 95 (10), 77 (23), 69 (19), 63 (21).

(E)-5,7-Dimethoxy-4′-nitro-3-styrylchromone (**5h**, $C_{19}H_{15}NO_6$) Mp 210–212°C; ^{1}H NMR (300.13 MHz): $\delta = 3.90$ (s, 7-OCH_3), 3.98 (s, 5-OCH_3), 6.40 (d, $J = 2.3$ Hz, H-8), 6.46 (d, $J = 2.3$ Hz, H-6), 7.00 (d, $J = 16.6$ Hz, H-α), 7.59 (d, $J = 8.8$ Hz, H-2′,6′), 7.88 (d, $J = 16.6$ Hz, H-β), 7.93 (s, H-2), 8.19 (d, $J = 8.8$ Hz, H-3′,5′) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.8$ (7-OCH_3), 56.4 (5-OCH_3), 92.6 (C-6), 96.5 (C-8), 109.4 (C-10), 121.6 (C-3), 124.07 (C-3′,5′), 124.1 (C-α), 126.8 (C-2′,6′), 129.1 (C-β), 144.4 (C-1′), 146.7 (C-4′), 152.5 (C-2), 159.3 (C-9), 161.4 (C-5), 164.1 (C-7), 175.4 (C-4) ppm; MS (EI, 70 eV): m/z (%) = 353 ($M^{+\bullet}$, 100), 336 [$(M–OH)^+$, 91], 323 [$(M–NO)^+$, 16], 306 [$(M–HNO_2)^+$, 45], 292 (4), 277 (12), 249 (3), 231 [$(M–C_6H_4NO_2)^+$, 21], 201 (19), 189 (26), 180 (10), 165 (4), 151 (19), 137 (31), 127 (8), 115 (10), 109 (10), 89 (5), 77 (11), 63 (14).

(Z)-3′-Nitro-3-styrylchromone (**4i**, $C_{17}H_{11}NO_4$) Mp 94–96°C; ^{1}H NMR (300.13 MHz): $\delta = 6.69$ (dd, $J = 12.1$, 1.2 Hz, H-α), 6.84 (d, $J = 12.1$ Hz, H-β), 7.42 (d, $J = 8.6$ Hz, H-8), 7.45 (t, $J = 7.9$ Hz, H-5′), 7.40–7.47 (m, H-6), 7.60–7.65 (m, H-6′), 7.69 (ddd, $J = 7.6$, 8.6, 1.7 Hz, H-7), 7.71 (d, $J = 1.2$ Hz, H-2), 8.08 (ddd, $J = 7.9$, 2.1, 0.8 Hz, H-4′), 8.17 (t, $J = 2.1$ Hz, H-2′), 8.27 (dd, $J = 8.1$, 1.7 Hz, H-5) ppm; ^{13}C NMR (75.47 MHz): $\delta = 118.2$ (C-8), 120.6 (C-3), 122.2 (C-4′), 123.1 (C-α), 123.5 (C-2′), 123.9 (C-10), 125.5 (C-6), 126.1 (C-5), 129.6 (C-5′), 130.4 (C-β), 133.9 (C-7), 134.5 (C-6′), 138.4 (C-1′), 148.5 (C-3′), 154.0 (C-2), 156.1 (C-9), 176.7 (C-4) ppm; MS (ES^+): m/z (%) = 294 [$(M+H)^+$, 28], 316 [$(M+Na)^+$, 100], 609 [$(2M+Na)^+$, 15].

(E)-3′-Nitro-3-styrylchromone (**5i**, $C_{17}H_{11}NO_4$) Mp 178–180°C; ^{1}H NMR (300.13 MHz): $\delta = 7.05$ (d, $J = 16.3$ Hz, H-α), 7.47 (ddd, $J = 7.6$, 8.0, 1.1 Hz, H-6), 7.51 (d, $J = 8.1$ Hz, H-8), 7.53 (t, $J = 8.0$ Hz, H-5′), 7.71 (ddd, $J = 7.6$, 8.1, 1.6 Hz, H-7), 7.79–7.83 (m, H-6′), 7.88 (d, $J = 16.3$ Hz, H-β), 8.11 (ddd, $J = 8.0$, 2.1, 0.8 Hz, H-4′), 8.16 (s, H-2), 8.32 (dd, $J = 8.0$, 1.6 Hz, H-5), 8.39 (t, $J = 2.1$ Hz, H-2′) ppm; ^{13}C NMR (75.47 MHz): $\delta = 118.1$ (C-8), 120.7 (C-2′), 120.8 (C-3), 122.2 (C-4′), 122.4 (C-α), 124.1 (C-10), 125.6 (C-6), 126.3 (C-5), 129.6 (C-β,5′), 132.7 (C-6′), 133.8 (C-7),139.3 (C-1′), 148.3 (C-3′), 154.4 (C-2), 155.5 (C-9), 176.5 (C-4) ppm; MS (ES^+): m/z (%) = 294 [$(M+H)^+$, 60], 316 [$(M+Na)^+$, 84], 609 [$(2M+Na)^+$, 100], 902 [$(3M+Na)^+$, 12].

(Z)-5-Methoxy-3′-nitro-3-styrylchromone (**4j**, $C_{18}H_{13}NO_5$) Mp 80–82°C; ^{1}H NMR (300.13 MHz): $\delta = 4.00$ (s, 5-OCH_3), 6.67 (dd, $J = 12.1$, 1.1 Hz, H-α), 6.78 (d, $J = 12.1$ Hz, H-β), 6.84 (d, $J = 8.2$ Hz, H-8), 6.95 (dd, $J = 8.2$, 0.9 Hz, H-6), 7.44 (t, $J = 8.2$ Hz, H-7), 7.51 (d, $J = 1.1$ Hz, H-2), 7.56 (t, $J = 8.3$ Hz, H-5′), 7.60–7.64 (m, H-6′), 8.07 (ddd, $J = 8.3$, 2.0, 1.0 Hz, H-4′), 8.16 (t, $J = 2.0$ Hz, H-2′) ppm; ^{13}C NMR (75.47 MHz): $\delta = 56.5$ (5-OCH_3), 106.6 (C-8), 110.1 (C-6), 114.6 (C-10), 121.7 (C-3), 122.1 (C-4′), 123.5 (C-2′), 123.7 (C-α), 129.5 (C-7), 129.8 (C-β), 134.0 (C-5′), 134.6 (C-6′), 138.5 (C-1′), 148.5 (C-3′), 151.9 (C-2), 158.1 (C-9), 160.0 (C-5), 176.5 (C-4) ppm; MS (ES^+): m/z (%) = 324 [$(M+H)^+$, 8], 346 [$(M+Na)^+$, 100], 669 [$(2M+Na)^+$, 56].

(E)-5-Methoxy-3′-nitro-3-styrylchromone (**5j**, $C_{18}H_{13}NO_5$) Mp 176–177°C; ^{1}H NMR (300.13 MHz): $\delta = 4.03$ (s, 5-OCH_3), 6.86 (d, $J = 8.2$ Hz, H-6), 6.99 (d, $J = 16.4$ Hz, H-α), 7.05 (dd, $J = 8.2$, 0.8 Hz, H-8), 7.51 (t, $J = 8.2$ Hz, H-7), 7.58 (t, $J = 8.3$ Hz, H-5′), 7.75–7.79 (m, H-6′), 7.91 (d, $J = 16.4$ Hz, H-β), 8.00 (s, H-2), 8.10 (ddd, $J = 8.3$, 2.1, 1.0 Hz, H-4′), 8.36 (t, $J = 2.1$ Hz, H-2′) ppm; ^{13}C NMR (75.47 MHz): $\delta = 56.5$ (5-OCH_3), 106.7 (C-8), 110.0 (C-6), 114.5 (C-10), 120.5 (C-2′), 121.7 (C-3), 122.1 (C-4′), 122.4 (C-α), 129.2 (C-β), 129.6 (C-7), 132.7 (C-6′), 133.9 (C-5′), 139.6 (C-1′), 145.4 (C-3′), 152.7 (C-2), 157.7 (C-9), 160.3 (C-5), 176.4 (C-4) ppm; MS (ES^+) (with *TFA*): m/z (%) = 324 [$(M+H)^+$, 37], 346 [$(M+Na)^+$, 54], 669 [$(2M+Na)^+$, 100], 992 [$(3M+Na)^+$, 22].

(Z)-7-Methoxy-3′-nitro-3-styrylchromone (**4k**, $C_{18}H_{13}NO_5$) Mp 92–93°C; ^{1}H NMR (300.13 MHz): $\delta = 3.90$ (s, 7-OCH_3), 6.67 (dd, $J = 12.3$, 1.2 Hz, H-α), 6.79 (d, $J = 2.4$ Hz, H-8), 6.81 (d, $J = 12.3$ Hz, H-β), 7.00 (dd, $J = 9.0$, 2.4 Hz, H-6), 7.44 (t, $J = 8.0$ Hz, H-5′), 7.60–7.64 (m, H-6′), 7.63 (d, $J = 1.2$ Hz, H-2), 8.07 (ddd, $J = 8.0$, 2.1, 1.0 Hz, H-4′), 8.17 (d, $J = 9.0$ Hz, H-5), 8.17 (t, $J = 2.1$ Hz, H-2′) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.9$ (7-OCH_3), 100.3 (C-8), 114.9 (C-6), 117.8 (C-10), 120.5 (C-3), 122.2 (C-4′), 123.3 (C-α), 123.5 (C-2′), 127.5 (C-5), 129.5 (C-5′), 130.3 (C-β), 134.6 (C-6′), 138.5 (C-1′), 148.5 (C-3′), 153.5 (C-2), 157.9 (C-9), 164.2 (C-7), 176.1 (C-4) ppm; MS (ES^+): m/z (%) = 324 [$(M+H)^+$, 24], 346 [$(M+Na)^+$, 100], 669 [$(2M+Na)^+$, 56].

(E)-7-Methoxy-3′-nitro-3-styrylchromone (**5k**, $C_{18}H_{13}NO_5$) Mp 198–200°C; ^{1}H NMR (300.13 MHz): $\delta = 3.93$ (s, 7-OCH_3), 6.87 (d, $J = 2.4$ Hz, H-8), 7.02 (dd, $J = 8.9$, 2.4 Hz, H-6), 7.03 (d, $J = 16.3$ Hz, H-α), 7.52 (t, $J = 8.0$ Hz, H-5′), 7.78–7.82 (m, H-6′), 7.85 (d, $J = 16.3$ Hz, H-β), 8.08 (s, H-2), 8.11 (ddd, $J = 8.2$, 1.8, 0.9 Hz, H-4′), 8.21 (d, $J = 8.9$ Hz, H-5), 8.38 (t, $J = 1.8$ Hz, H-2′) ppm; ^{13}C NMR (75.47 MHz): $\delta = 55.9$ (7-OCH_3), 100.2 (C-8), 114.9 (C-6), 120.6 (C-2′), 122.2 (C-4′), 122.5 (C-α), 127.6 (C-5), 129.4 (C-β), 129.6 (C-5′), 132.6 (C-6′), 139.4 (C-1′), 146.2 (C-3′), 153.9 (C-2), 157.5 (C-9), 166.3 (C-7), 175.1 (C-4) ppm; MS (ES^+):

m/z (%) = 324 [$(M+H)^+$, 73], 669 [$(2M+Na)^+$, 100], 992 [$(3M+Na)^+$, 35].

The following products have been reported in literature and in this work they were identified on the basis of their mps: (*Z*)-*5-Methoxy-3-styrylchromone* (**5l**, $C_{18}H_{14}O_3$), Mp 147–148°C (Ref. [13] 147–148°C); (*E*)-*3-Styrylchromone* (**5m**), mp 163–165°C (Ref. [13] 168–169°C); (*E*)-*6-Chloro-3-styrylchromone* (**5n**), mp 200–201°C (Ref. [14] 198–201°C); (*E*)-*6-Methyl-3-styrylchromone* (**5o**), mp 149–151°C (Ref. [13] 151–152°C).

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