Wittig reactions of chromone-3-carboxaldehydes with benzylidenetriphenyl phosphoranes: a new synthesis of 3-styrylchromones

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An efficient route to 3-styrylchromones has been developed and applied to syntheses of several new derivatives. Wittig reactions of chromone-3-carboxaldehydes with some benzylic ylides gave a diastereomeric mixture of (*E*) and (*Z*)-3-styrylchromones that are separable by thin layer chromatography. The (*Z*)-isomers were the most abundant diastereomers independent of having electron-withdrawing or electron-donating substituents on the phenyl ring. Stereochemistry of the obtained diastereomers was established using NOESY experiments.

Introduction

Styrylchromones constitute a small group of oxygen heterocyclic compounds which have shown significant biological activities.[1] The synthesis of 2-styrylchromones have been extensively studied,[2] whereas to our knowledge only a few synthetic methods are available for the preparation of their isomers, 3-styrylchromones.[3–7] One of them involves the Heck reaction of 3-bromochromone with styrene, in the presence of palladium acetate, tri-*o*-tolylphosphine and triethylamine in DMF, and has only been used for the formation of unsubstituted (*E*)-3-styrylchromone.[3] The application of this procedure to polybrominated chromone derivatives would lead to the coupling of several alkenes to the chromone system at the halogenated sites. Another synthetic possibility was used to prepare (*E*)-2-methyl-3-(3′,5′-dihydroxystyryl)chromone from the Wittig reaction of an appropriate phosphonium salt with a benzaldehyde derivative.[4] The preparation of the required phosphonium salt involves a selective monobromination of 3-methylchromones, a procedure that often gives by-products. A third synthetic method consists in the condensation of chromone-3-carboxaldehydes with 2,4-dinitrotoluene in pyridine.[5] New and simple (*E*)-3-styrylchromones have been obtained, in moderate yields (45–58%), with this synthetic procedure. Some 3-styrylchromone type-compounds have been obtained from the condensation of chromone-3-carboxaldehydes with 6,8-dimethylcoumarin 4-acetic acid in pyridine.[6] The structural characterisation of the obtained chromones showed that the carboxyl group was missing, suggesting that a decarboxylation took place during the condensation of the active methylene group. The last synthetic method consists in the oxidative rearrangement of (*E*,*E*)-γ-alkyl-2′-hydroxycinnamylideneacetophenones, with thallium(III) trinitrate, into the corresponding acetal derivatives, 3-alkyl-4-aryl-1-(2-hydroxyphenyl)-2-(dimethoxymethyl)-3-buten-1-ones, which cyclise into the corresponding (*E*)-3-(α-alkylstyryl)chromones by treatment with hydrochloric acid.[7] This method has been developed in our laboratory and gave rise stereoselectively to the (*E*)-isomers, but it also has some limitations. It uses very toxic reagents, such as thallium trinitrate(III), and only 3-(α-alkylstyryl)chromones could be obtained. Furthermore, in an attempt to prepare 3-styrylchromones unsubstituted at the vinylic system Cα=Cβ, very complex mixtures were obtained.

Taking into account the potential uses of 3-styrylchromones and the need for having efficient synthetic methodologies for their syntheses, we report here work carried out on syntheses of these compounds from the Wittig reaction of chromone-3-carboxaldehyde derivatives with benzylic ylides.

The use of chromone-3-carboxaldehydes in the synthesis of heterocyclic systems has attracted the attention of many researchers, since their convenient synthesis was reported in the 1970's.[8] Much of the synthetic utility of this type of compounds derives from the reactivity of its electron deficient centres at C-2, C-4 and 3-formyl group. Chromone-3-carboxaldehydes can act as Michael acceptors, but also they can be used as heterodienes or dienophiles in cycloaddition reactions.[8,9] We have studied their reactivity in Wittig reactions with benzylic ylides (semi-stabilised ylides), and as a result, the establishment of a new synthetic method for (*E*)- and (*Z*)-3-styrylchromones has been set up. The influence of the substituents of the benzylic ylides and the chromone nucleus on reaction yields and (*E* : *Z*) isomeric ratios will also be discussed.

Results and discussion

Chemistry

Initial experiments considered the reaction of benzylidenetriphenylphosphorane **2a** with chromone-3-carboxaldehyde **1a**. Thus a THF suspension of benzyl triphenylphosphonium chloride was treated with a molar equivalent of sodium hydride; the solution became orange in colour (2 h), suggesting ylide formation. After the addition of a molar equivalent of chromone-3-carboxaldehyde **1a** to this ylide, and refluxing the reaction mixture for 24 h, it became yellow in colour. Thin layer chromatography (TLC) analysis of this reaction mixture revealed the presence of starting material and of two new products. Spectroscopic evidence of such compounds led us to assign its structure as (*E*)-3-styrylchromone **3a** (2%) and (*Z*)-3-styrylchromone **4a** (30%). Since that yield was not satisfactory, certain changes were made in the experimental

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procedure including time for the ylide formation and the molar quantity of base used (Table 1). We found that better conditions are those described in entry 5 of Table 1: 3 h for ylide formation, 1 equiv. of sodium hydride as base and 40 h for the reaction of the formed ylide with the carbonyl compound. Both (*E* and *Z*) diastereomers, **3a** and **4a**, were obtained in all the assays described in Table 1, the (*Z*) isomer being the most abundant, as expected for the reaction of semi-stabilised ylides with steric crowded carbonyl compounds[10] (Scheme 1).

After the establishment of optimised experimental conditions for the reaction of **1a** with **2a** (last entry of Table 1), we carried out the Wittig reaction of chromone-3-carboxaldehydes **1a–c** with ylides **2a–d**, obtaining a diastereomeric mixture of 3-styrylchromones, **3a–l** and **4a–l** (Table 2, Scheme 1). The (*Z*) isomer was the most abundant diastereomer independently of the starting ylide structure and of the carbonyl compound.

Our results suggest that the formation of ylide **2d**, bearing electron-donating substituents on the phenyl ring, is much faster than the others since the solution became orange in colour 5 min after the addition of base. Longer reaction times led to the decomposition of such an ylide, an observation based on the decoloration of the reaction medium. These data can be explained taking into account that ylides **2a–c**, bearing electron-neutral or electron-withdrawing groups on the phenyl ring, are more stable than ylide **2d**, allowing us to predict their quantitative formation. In the case of ylide **2d**, this is not possible due to the higher reactivity. Thus, the addition of chromone-3-carboxaldehydes **1a–c** must be done as soon as it is formed (but not in a quantitative way).

Wittig reactions of ylides **2a–d** and chromone-3-carboxaldehydes **1a,b** have also been carried out using n-butyllithium instead of sodium hydride in the formation of ylides (*Vide experimental*). The obtained results were more or less the same with a diastereomeric mixture of 3-styrylchromones **3a,b,d,e,g,h,j,k** and **4a,b,d,e,g,h,j,k** attained in approximately the same yield as that when sodium hydride was used as base and with the (*Z*) isomer being the most abundant one.

NMR spectroscopy

Most important features of the ^{1}H NMR spectra of 3-styrylchromones **3a–l** and **4a–l** are the resonances of their vinylic protons. In the case of (*E*)-isomers **3a–l** these resonances appear at $\delta = 6.85$–7.32 (H-α), 7.50–7.94 (H-β) and 7.94–8.14[11] (H-2). The coupling constant values of $^3J_{H\alpha-H\beta} = 16.1$–$16.4$ Hz indicate a *trans* configuration of these vinylic systems. The intense NOE cross peaks between H-2 and H-α and H-β observed in their 2D NOESY experiments demonstrate the existence of a free rotation around the C3–Cα bond.

In the ^{1}H NMR spectra of (*Z*)-3-styrylchromones **4a–l**, the proton resonances of H-α, H-β, and H-2, appear at δ 6.40–6.71, 6.67–6.90 and 7.47–7.80,[11] respectively. The coupling constant values of $^3J_{H\alpha-H\beta} = 12.0$–$12.1$ Hz indicate a *cis* configuration of these vinylic systems. The stereochemistry of these compounds **4a–l** was also established by 2D NOESY experiments. Strong NOE cross peaks were observed between H-α and H-β and also between H-β and H-2′,6′, while a weak cross peak between H-2 and H-2′,6′ was also observed. These results allowed us to confirm the *cis* configuration of the Cα=Cβ double bonds and also to establish the conformation of the styryl moiety relative to the chromone nucleus as depicted in Scheme 1. The coupling constant value $^4J_{H2\text{-}H\alpha} = 0.9$–$1.2$ Hz suggests a *Z-(sE)-Z* geometry for this moiety of the molecule.

The connectivities found in the HMBC spectra of 3-styrylchromones **3a–l** and **4a–l** allowed an unequivocal assignment of quaternary carbon resonances and confirmation of protonated carbons ones, which were assigned from the correlations found in their HSQC spectra. The connectivities found in these HMBC spectra for H-2 and H-5 (for 5-unsubstituted compounds) played an important role in the assignment of carbon resonances of C-3, C-9 and C-α (and indirectly of the H-α proton resonance, from the HSQC spectra), (Fig. 1). The connectivities found for H-α (with C-2, C-4, C-1′ and C-β) and H-β (with C-3 and C-2′,6′) also support the assignment of these proton resonances.

Table 1 Wittig reaction of chromone-3-carboxaldehyde **1a** with benzylic ylide **2a**

Entry	Reaction time before the addition of **1a**	Equiv molar of NaH	Reaction time after the addition of **1a**	Yield[a] (%) (*E*/*Z*)
1	2 h	1 equiv.	24 h	2/30
2	2 h	1 equiv.	40 h	6/35
3	3 h	1 equiv.	24 h	6/38
4	3 h	1.5 equiv.	24h	3/46
5	3 h	1 equiv.	40 h	4/50

[a] Yields and (*E* : *Z*) ratios are based on preparative TLC isolated amounts.

Conclusion

Wittig reactions of chromone-3-carboxaldehydes with several benzylic ylides have been investigated and a new synthetic procedure for the synthesis of 3-styrylchromones has been established. These reactions led to a diasteromeric mixture of (*E*)- and (*Z*)-3-styrylchromones with the (*Z*)-isomers being the most abundant ones. The stereochemistry of these isomers was also established.

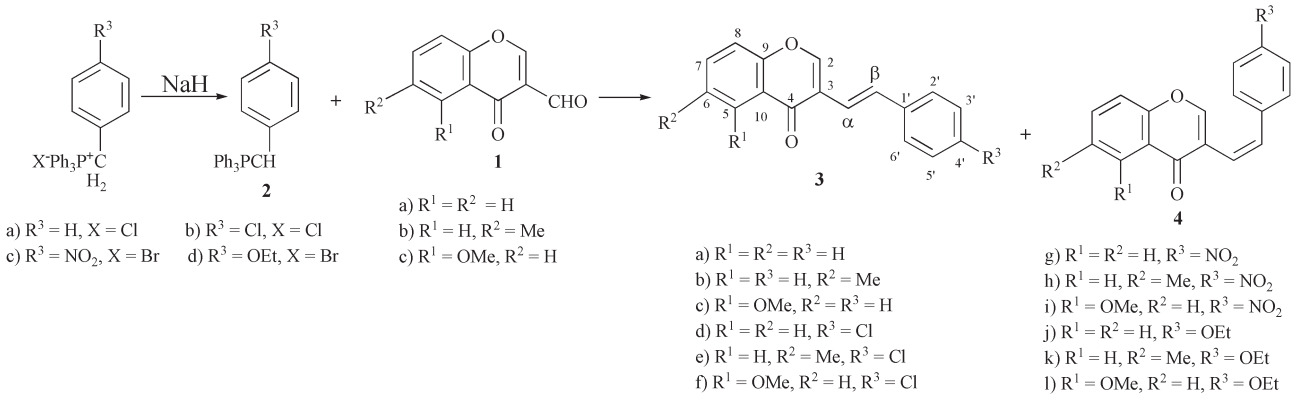
Experimental

Melting points were determined on a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. NMR spectra were recorded on Bruker DRX 300 spectrometer (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C), with $CDCl_3$ as solvent if not stated otherwise. 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 NOESY (mixing time of 800 ms) experiments, while ^{13}C assignments were made using 2D *g*HSQC and *g*HMBC experiments (long range C/H coupling constants were optimised to 7 Hz). Mass spectra (EI, 70 eV) were measured on a VG Autospec Q and M mass spectrometers. IR spectra were obtained in KBr pellets on a MATTSON 7000 FTIR spectrometer. Elemental analyses were obtained with a LECO 932 CHN analyser (University of Aveiro). Preparative thin layer chromatography was carried out with Riedel silica gel 60 DGF_{254}, and column chromatography using Merck silica gel 60, 70–230 mesh.

3-Formylchromones **1a,b** were obtained from Sigma-Aldrich while 3-formyl-5-methoxychromone **1c** was obtained as described in the literature.[12] All other chemicals and solvents used were obtained from commercial sources and used as received or dried using standard procedures.

Wittig reactions: general procedure for the synthesis of 3-styrylchromones (3a–l and 4a–l)

Method A–using sodium hydride. Sodium hydride (25 mg, 1.04 mmol) was added to a suspension of the appropriate phosphonium halide (1.04 mmol) in dry THF (25 mL), under nitrogen, and the reaction mixture was refluxed with stirring for the adequate time (as mentioned in Table 2). The



Scheme 1 Synthesis of (*E*)- and (*Z*)-3-styrylchromones.

appearance of orange colour and the disappearance of the suspension of phosphonium salts indicated the ylide formation. After that period, the appropriate chromone-3-carboxaldehydes **1a–c** (1.04 mmol) were added and the reaction mixture refluxed for the appropriate time, as mentioned in Table 2. The solvent was removed and the residue dissolved in dichloromethane (20 mL) and analysed by thin-layer chromatography. The TLC plates were eluted several times with mixtures of light petroleum:dichloromethane, leading to the isolation of two main spots, in each case. The component of high R_f spot was identified as being (*E*)-3-styrylchromones **3a–l**, whereas the other spot was constituted by (*Z*)-3-styrylchromone **4a–l** (total yields in Table 1). These compounds were recrystallised from ethanol.

Method B–using n-butyllithium. A cyclohexane solution of n-butyllithium (0.61 mL, 1.25 mmol) was added to a suspension of the appropriate phosphonium halide (1.04 mmol) in dry THF (25 mL) and kept under nitrogen at −60 °C. The reaction mixture was stirred at this temperature until the appearance of an intense orange colour, and the disappearance of the suspension of phosphonium salts (30 min to 1 h for ylides **2a–c** and 15 min for ylide **2d**) and the temperature allowed rising to room temperature. After this period, chromone-3-carboxaldehydes **1a,b** (1.04 mmol) were added and the reaction mixture refluxed for 24 h. The solvent was removed and the residue was dissolved in dichloromethane (20 mL) and analysed by thin-layer chromatography. The TLC plates were eluted several times with mixtures of light petroleum–dichloromethane, leading to the isolation of two main spots, in each case. The component of high R_f spot was identified as being (*E*)-3-styrylchromones **3a,b,d,e,g,h,j,k** (5–18%), whereas the other spot was constituted by (*Z*)-3-styrylchromone **4a,b,d,e,g,h,j,k** (45–64%). These compounds were recrystallised from ethanol.

Table 2 Wittig reactions of chromone-3-carboxaldehydes **1a–c** with ylides **2a–d**

Ylide	Chromone-3-carboxaldehydes	Time of ylide formation	Reaction time after the addition of chromone-3-carboxaldehydes	Yield[a] (%) (*E*/*Z*)
2a	**1a**	3 h	40 h	4/50
	1b	3 h	40 h	7/68
	1c	3 h	40 h	5/52
2b	**1a**	3 h	24 h	5/56
	1b	3 h	24 h	5/57
	1c	3 h	24 h	7/54
2c	**1a**	3 h	24 h	8/67
	1b	3 h	24 h	5/68
	1c	3 h	40 h	4/67
2d	**1a**	5 min	24 h	6/66
	1b	5 min	24 h	4/70
	1c	5 min	24 h	8/58

[a] Yields and (*E* : *Z*) ratios are based on preparative TLC isolated amounts.

***(E)*-3-Styrylchromone (3a).** Mp 168–169 °C (recrystallised from ethanol, lit.[3] 170–171 °C). IR ν = 1644 (C=O), 1615 (C=C), 1560, 1465, 1408, 1358, 1312, 1182, 972, 749, 695. ^{1}H NMR δ = 7.00 (d, 1 H, J = 16.3 Hz, H-α), 7.24–7.29 (m, 1 H, H-4′), 7.36 (t, 2 H, J = 7.4 Hz, H-3′,5′), 7.43 (ddd, 1 H, J = 8.0, 7.1 and 0.8 Hz, H-6), 7.47 (d, 1 H, J = 8.7 Hz, H-8), 7.53 (d, 2 H, J = 7.4 Hz, H-2′,6′), 7.64 (d, 1 H, J = 16.3 Hz, H-β), 7.68 (ddd, 1 H, J = 8.7, 7.1 and 1.6 Hz, H-7), 8.12 (s, 1 H, H-2), 8.31 (dd, 1 H, J = 8.0 and 1.6 Hz, H-5). ^{13}C NMR δ = 118.0 (C-8), 119.0 (C-α), 121.8 (C-3), 124.1 (C-10), 125.2 (C-6), 126.2 (C-5), 126.6 (C-2′,6′), 127.8 (C-4′), 128.6 (C-3′,5′), 131.7 (C-β), 133.5 (C-7), 137.3 (C-1′), 153.0 (C-2), 155.8 (C-9), 176.6 (C-4). EI-MS: m/z (rel. int.) 249 [(M + 1)$^+$, 21], 248 (M$^{+\bullet}$, 100), 247 [(M − 1)$^+$, 82], 231 (15), 219 (10), 171 (24), 155 (11), 128 (43), 127 (14), 124 (8), 121 (17), 120 (9), 105 (19), 102 (7), 92 (12), 85 (9), 83 (13), 77 (14). EI-HRMS ($C_{17}H_{12}O_2$ [M$^{+\bullet}$]), calcd. 248.0837; found: 248.0838.

***(Z)*-3-Styrylchromone (4a).** Mp 129–130 °C (recrystallised from ethanol). IR ν = 1639 (C=O), 1613 (C=C), 1569, 1465, 1413, 1374, 1353, 1321, 1216, 1188, 1133, 925, 846, 754, 699. ^{1}H NMR δ = 6.55 (dd, 1 H, J = 12.1 and 0.9 Hz, H-α), 6.81 (d, 1 H, J = 12.1 Hz, H-β), 7.21–7.32 (m, 5 H, H-2′,3′,4′,5′,6′), 7.40 (d, 1 H, J = 8.4 Hz, H-8), 7.42 (ddd, 1 H, J = 8.1, 7.1 and 0.9 Hz, H-6), 7.66 (ddd, 1 H, J = 8.4, 7.1 and 1.5 Hz, H-7), 7.73 (d, 1 H, J = 0.9 Hz, H-2), 8.29 (dd, 1 H, J = 8.1 and 1.5 Hz, H-5). ^{13}C NMR δ = 118.1 (C-8), 120.2 (C-α), 121.1 (C-3), 124.0 (C-10), 125.2 (C-6), 126.0 (C-5), 127.3 (C-4′), 128.5 and 128.6 (C-3′,5′ and C-2′,6′), 132.6 (C-β), 133.6 (C-7), 136.6 (C-1′), 154.1 (C-2), 156.1 (C-9), 177.2 (C-4). EI-MS: m/z (rel. int.) 249 [(M + 1)$^+$, 28], 248 (M$^{+\bullet}$, 100), 247 [(M − 1)$^+$, 86], 231 (23), 219 (19), 191 (10), 189 (11), 171

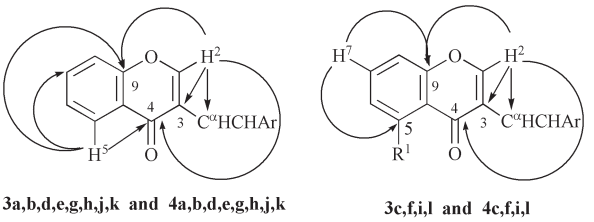


Fig. 1 Important connectivities found in the HMBC spectra of 3-styrylchromones **3a–l** and **4a–l**.

(41), 155 (22), 129 (12), 128 (64), 127 (29), 126 (9), 124 (8), 121 (24), 120 (16), 110 (15), 102 (18), 92 (28), 77 (15). Anal. calcd. for $C_{17}H_{12}O_2$: C 82.25, H 4.87; found: C 82.35, H 4.79%.

***(E)*-6-Methyl-3-styrylchromone (3b).** Mp 151–152 °C (recrystallised from ethanol). IR ν = 3020, 1641 (C=O), 1615 (C=C), 1563, 1484, 1349, 1311, 1301, 1267, 1162, 980, 972, 832, 747, 688. ^{1}H NMR δ = 2.47 (s, 3 H, 6-CH_3), 7.00 (dd, 1 H, J = 16.2 and 0.6 Hz, H-α), 7.24-7.29 (m, 1 H, H-4′), 7.35 (d, 2 H, J = 7.3 Hz, H-3′,5′), 7.36 (d, 1 H, J = 8.6 Hz, H-8), 7.48 (dd, 1 H, J = 8.6 and 2.2 Hz, H-7), 7.53 (d, 2 H, J = 7.3 Hz, H-2′,6′), 7.60 (d, 1 H, J = 16.2 Hz, H-β), 8.07 (d, 1 H, J = 2.2 Hz, H-5), 8.10 (s br, 1 H, H-2). ^{13}C NMR δ = 21.0 (6-*C*H$_3$), 117.8 (C-8), 119.1 (C-α), 121.6 (C-3), 123.7 (C-10), 125.5 (C-5), 126.6 (C-2′,6′), 127.8 (C-4′), 128.6 (C-3′,5′), 131.3 (C-β), 134.8 (C-7), 135.2 (C-6), 137.4 (C-1′), 152.9 (C-2), 154.1 (C-9), 176.7 (C-4). EI-MS: m/z (rel. int.) = 263 [(M + 1)$^+$, 28], 262 (M$^{+\bullet}$, 100), 261 [(M − 1)$^+$, 80], 245 (22), 233 (13), 185 (41), 155 (16), 135 (22), 134 (35), 131 (14), 128 (46), 127 (22), 115 (11), 106 (18), 105 (15), 103 (14), 89 (10), 78 (28), 77 (24). Anal. calcd. for $C_{18}H_{14}O_2$: C 82.42, H 5.38; found: C 82.16, H 5.21%.

***(Z)*-6-Methyl-3-styrylchromone (4b).** Mp 60–62 °C (recrystallised from ethanol). IR ν = 3015, 1637 (C=O), 1616 (C=C), 1571, 1485, 1443, 1405, 1360, 1340, 1321, 1227, 1182, 1134, 925, 817, 798, 758, 699. ^{1}H NMR δ = 2.44 (s, 3 H, 6-CH_3), 6.54 (dd, 1 H, J = 12.1 and 1.0 Hz, H-α), 6.78 (d, 1 H, J = 12.1 Hz, H-β), 7.19–7.31 (m, 5 H, H-2′,3′,4′,5′,6′), 7.27 (d, 1 H, J = 8.5 Hz, H-8), 7.44 (dd, 1 H, J = 8.5 and 2.2 Hz, H-7), 7.69 (d, 1 H, J = 1.0 Hz, H-2), 8.05 (d, 1 H, J = 2.2 Hz, H-5). ^{13}C NMR δ = 20.8 (6-*C*H$_3$), 117.8 (C-8), 120.3 (C-α), 120.8 (C-3), 123.5 (C-10), 125.2 (C-5), 127.2 (C-4′), 128.5 (C-2′,3′,5′,6′), 132.3 (C-β), 134.7 (C-7), 135.1 (C-6), 136.6 (C-1′), 153.9 (C-2), 154.3 (C-9), 177.1 (C-4). EI-MS: m/z (rel. int.) = 263 [(M + 1)$^+$, 24], 262 (M$^{+\bullet}$, 100), 261 [(M − 1)$^+$, 81], 245 (20), 233 (11), 185 (39), 155 (12), 135 (17), 134 (29), 128 (42), 127 (19), 115 (8), 106 (15), 105 (12), 103 (10), 89 (7), 78 (25), 77 (18). Anal. calcd. for $C_{18}H_{14}O_2$: C 82.42, H 5.38; found: C 82.20, H 5.42%.

***(E)*-5-Methoxy-3-styrylchromone (3c).** Mp 147–148 °C (recrystallised from ethanol). IR ν = 1649 (C=O), 1615 (C=C), 1598, 1567, 1474, 1450, 1432, 1372, 1347, 1289, 1270, 1070, 895, 804, 780, 684. ^{1}H NMR δ = 4.00 (s, 3 H, 5-OCH_3), 6.82 (d, 1 H, J = 8.4 Hz, 6-H), 6.95 (d, 1 H, J = 16.3 Hz, H-α), 7.01 (dd, 1 H, J = 8.4 and 0.7 Hz, H-8), 7.24-–7.28 (m, 1 H, H-4′), 7.34 (t, 2 H, J = 7.4 Hz, H-3′,5′), 7.50 (d, 2 H, J = 7.4 Hz, H-2′,6′), 7.54 (t, 1 H, J = 8.4 Hz, H-7), 7.63 (d, 1 H, J = 16.3 Hz, H-β), 7.97 (s, 1 H, 2-H). ^{13}C NMR δ = 56.4 (5-O*C*H$_3$), 106.4 (C-6), 110.0 (C-8), 114.7 (C-10), 119.1 (C-α), 122.7 (C-3), 126.5 (C-2′,6′), 127.7 (C-4′), 128.6 (C-3′,5′), 131.2 (C-β), 133.5 (C-7), 137.6 (C-1′), 151.1 (C-2), 157.8 (C-9), 160.2 (C-5), 176.3 (C-4). EI-MS: m/z (rel. int.) = 279 [(M + 1)$^+$, 29], 278 (M$^{+\bullet}$, 100), 277 [(M − 1)$^+$, 23], 262 (8), 250 (9), 249 (27), 247 (17), 231 (14), 201 (18), 171 (10), 160 (10), 159 (74), 150 (17), 139 (9), 128 (34), 127 (18), 122 (18), 121 (27), 115 (14), 107 (41), 102 (13), 92 (10), 91 (36), 77 (14). Anal. calcd. for $C_{18}H_{14}O_3$: C 77.68, H 5.07; found: C 77.30, H 4.98%.

***(Z)*-5-Methoxy-3-styrylchromone (4c).** Mp 83–84 °C (recrystallised from ethanol). IR ν = 1648 (C=O), 1616 (C=C), 1598, 1567, 1474, 1450, 1432, 1372, 1347, 1289, 1270, 1174, 895, 804, 780, 684. ^{1}H NMR δ = 3.91 (s, 3H, 5-OCH_3), 6.44 (dd, 1 H, J = 12.1 and 1.1 Hz, H-α), 6.67 (d, 1 H, J = 12.1 Hz, H-β), 6.72 (dd, 1 H, J = 8.3 and 0.7 Hz, H-6), 6.84 (dd, 1 H, J = 8.6 and 0.7 Hz, H-8), 7.11–7.21 (m, 5 H, H-2′,3′,4′,5′,6′), 7.42 (dd, 1 H, J = 8.6 and 8.3 Hz, H-7), 7.47 (d, 1 H, J = 1.1 Hz, H-2). ^{13}C NMR δ = 56.4 (5-O*C*H$_3$), 106.3 (C-6), 110.1 (C-8), 114.7 (C-10), 120.7 (C-α), 122.2 (C-3), 127.2 (C-4′), 128.6 (C-2′,3′,5′,6′), 132.1 (C-β), 133.6 (C-7), 136.8 (C-1′), 152.1 (C-2), 158.1 (C-9), 160.0 (C-5), 176.8 (C-4). EI-MS: m/z (rel. int.) = 279 [(M + 1)$^+$, 30], 278 (M$^{+\bullet}$, 100), 277 [(M − 1)$^+$, 26], 263 (71), 262 (10), 261 (6), 250 (8), 249 (25), 247 (20), 231 (16), 201 (21), 171 (11), 160 (12), 159 (72), 151 (9), 150 (17), 139 (12), 128 (30), 127 (18), 122 (16), 121 (24), 115 (13), 107 (33), 102 (11), 91 (32), 77 (11). EI-HRMS ($C_{18}H_{14}O_3$ [M$^{+\bullet}$]): calcd. 278.0943, found 278.0956.

***(E)*-4′-Chloro-3-styrylchromone (3d).** Mp 159–160 °C (recrystallised from ethanol). IR ν = 1642 (C=O), 1616 (C=C), 1612, 1561, 1489, 1467, 1408, 1361, 1308, 1289, 1161, 1094, 973, 861, 816, 758, 693. ^{1}H NMR δ = 6.93 (dd, 1 H, J = 16.2 and 0.7 Hz, H-α), 7.32 (d, 2 H, J = 8.4, Hz, H-3′,5′), 7.43 (dd, 1 H, J = 7.8 and 6.8 Hz, H-6), 7.45 (d, 2 H, J = 8.4 Hz, H-2′,6′), 7.47 (d, 1 H, J = 8.4 Hz, H-8), 7.64 (d, 1 H, J = 16.2 Hz, H-β), 7.68 (ddd, 1 H, J = 8.4, 6.8 and 1.7 Hz, H-7), 8.11 (s br, 1 H, H-2), 8.30 (dd, 1 H, J = 7.8 and 1.7 Hz, H-5). ^{13}C NMR δ = 118.0 (C-8), 119.7 (C-α), 121.5 (C-3), 124.1 (C-10), 125.3 (C-6), 126.2 (C-5), 127.7 (C-2′,6′), 128.8 (C-3′,5′), 130.5 (C-β), 133.4 (C-4′), 133.6 (C-7), 135.9 (C-1′), 153.3 (C-2), 155.8 (C-9), 176.6 (C-4). EI-MS: m/z (rel. int.) = 285 [(M + 1)$^+$, ^{37}Cl, 6], 284 (M$^{+\bullet}$, ^{37}Cl, 40), 283 [(M − 1)$^+$, ^{37}Cl, (M + 1)$^+$, ^{35}Cl, 41], 282 (M$^{+\bullet}$, ^{35}Cl, 100), 281 [(M − 1)$^+$, ^{35}Cl, 58], 265 (13), 247 (22), 218 (6), 189 (15), 171 (30), 164 (10), 162 (28), 127 (27), 126 (11), 123 (8), 121 (18), 120 (12), 92 (20), 85 (8), 83 (11), 77 (10). Anal. calcd. for $C_{17}H_{11}O_2Cl$: C 72.22, H 3.92; found: C 72.16, H 4.07%.

***(Z)*-4′-Chloro-3-styrylchromone (4d).** Mp 132–134 °C (recrystallised from ethanol). IR ν = 1640 (C=O), 1607 (C=C), 1569, 1488, 1463, 1375, 1350, 1319, 1211, 1186, 1136, 1086, 1012, 910, 852, 768, 685. ^{1}H NMR δ = 6.55 (dd, 1 H, J = 12.1 and 1.2 Hz, H-α), 6.75 (d, 1 H, J = 12.1 Hz, H-β), 7.24 (s, 4 H, H-2′,3′,5′,6′), 7.42 (d, 1 H, J = 7.6 Hz, H-8), 7.43 (ddd, 1 H, J = 7.7, 7.3 and 0.9 Hz, H-6), 7.68 (dd, 1 H, J = 7.6 and 7.3 Hz, H-7), 7.72 (d, 1 H, J = 1.2 Hz, H-2), 8.28 (d, 1 H, J = 7.7 Hz, H-5). ^{13}C NMR δ = 118.2 (C-8), 120.9 (C-3), 121.0 (C-α), 124.0 (C-10), 125.3 (C-6), 126.1 (C-5), 128.8 (C-3′,5′), 129.9 (C-2′,6′), 131.5 (C-β), 133.1 (C-4′), 133.7 (C-7), 135.0 (C-1′), 154.0 (C-2), 156.1 (C-9), 177.0 (C-4). EI-MS: m/z (rel. int.) = 285 [(M + 1)$^+$, ^{37}Cl, 12], 284 (M$^{+\bullet}$, ^{37}Cl, 47), 283 [(M − 1)$^+$, ^{37}Cl, (M + 1)$^+$, ^{35}Cl, 50], 282 (M$^{+\bullet}$, ^{35}Cl, 100), 281 [(M − 1)$^+$, ^{35}Cl, 66], 265 (20), 247 (31), 219 (11), 218 (13), 191 (13), 189 (28), 171 (43), 164 (18), 163 (11), 162 (40), 127 (43), 126 (22), 123 (12), 121 (30), 120 (22), 115 (10), 101 (10), 92 (38), 77 (13). Anal. calcd. for $C_{17}H_{11}O_2Cl$: C 72.22, H 3.92; found: C 72.56, H 4.07%.

***(E)*-4′-Chloro-6-methyl-3-styrylchromone (3e).** Mp 162–164 °C (recrystallised from ethanol). IR ν = 3053, 1632 (C=O), 1618 (C=C), 1575, 1483, 1431, 1336, 1324, 1133, 1088, 850, 837, 811, 794, 778. ^{1}H NMR δ = 2.46 (s, 3 H, 6-CH_3), 6.92 (dd, 1 H, J = 16.3 and 0.5 Hz, H-α), 7.30 (d, 2 H, J = 8.5 Hz, H-3′,5′), 7.35 (d, 1 H, J = 8.6 Hz, H-8), 7.43 (d, 2 H, J = 8.5 Hz, H-2′,6′), 7.47 (dd, 1 H, J = 8.6 and 2.2 Hz, H-7), 7.58 (d, 1 H, J = 16.3 Hz, H-β), 8.06 (d, 1 H, J = 2.2 Hz, H-5), 8.07 (s br, 1 H, H-2). ^{13}C NMR δ = 21.0 (6-*C*H$_3$), 117.8 (C-8), 119.8 (C-α), 121.2 (C-3), 123.7 (C-10), 125.4 (C-5), 127.7 (C-2′,6′), 128.8 (C-3′,5′), 130.1 (C-β), 133.3 (C-4′), 134.8 (C-7), 135.3 (C-6), 135.9 (C-1′), 153.2 (C-2), 154.0 (C-9), 176.6 (C-4). EI-MS: m/z (rel. int.) = 299, [(M + 1)$^+$ ^{37}Cl, 10], 298 (M$^{+\bullet}$, ^{37}Cl, 46), 297 [(M − 1)$^+$, ^{37}Cl, (M + 1)$^+$, ^{35}Cl, 49], 296 (M$^{+\bullet}$, ^{35}Cl, 100), 295 [(M − 1)$^+$, ^{35}Cl, 64], 279 (16), 261 (17), 189 (12), 185 (40), 162 (18), 148 (7), 135 (25), 134 (39), 127 (24), 126 (11), 106 (15), 105 (11), 78 (29), 77 (15). Anal. calcd. for $C_{18}H_{13}ClO_2$: C 72.85, H 4.42; found: C 72.71, H 4.03%.

***(Z)*-4′-Chloro-6-methyl-3-styrylchromone (4e).** Mp 119–120 °C (recrystallised from ethanol). IR ν = 3053, 1632 (C=O), 1618 (C=C), 1580, 1426, 1363, 1323, 1133, 1088, 1011, 837, 811, 794, 778. ^{1}H NMR δ = 2.46 (s, 3 H, 6-CH_3), 6.54 (dd, 1 H, J = 12.1 and 1.0 Hz, H-α), 6.72 (d, 1 H, J = 12.1 Hz, H-β), 7.22 (s, 4 H, H-2′,3′,5′,6′), 7.29 (d, 1 H, J = 8.5 Hz, H-8), 7.47 (dd, 1 H, J = 8.5 and 2.2 Hz, H-7), 7.69 (d, 1 H, J = 1.0 Hz, H-2), 8.04 (d, 1 H, J = 2.2 Hz, H-5). ^{13}C NMR δ = 20.9 (6-*C*H$_3$), 117.8 (C-8), 120.7 (C-3), 121.1 (C-α), 123.5 (C-10), 125.2 (C-5), 128.7 (C-3′,5′), 129.9 (C-2′,6′), 131.2 (C-β), 132.9 (C-4′), 134.9 (C-7), 135.0 and 135.2 (C-1′ and C-6), 153.8 (C-2), 154.3 (C-9), 176.9 (C-4). EI-MS: m/z (rel. int.) = 299, [(M + 1)$^+$ ^{37}Cl, 7], 298 (M$^{+\bullet}$, ^{37}Cl, 37), 297 [(M − 1)$^+$, ^{37}Cl, (M + 1)$^+$, ^{35}Cl, 41], 296 (M$^{+\bullet}$,^{35}Cl, 100), 295 [(M − 1)$^+$, ^{35}Cl, 60], 279 (14), 261 (15), 189 (10), 185 (43), 162 (18), 135 (24), 134 (41), 130 (10), 127 (21), 126 (10), 106 (14), 105 (9), 78 (19), 77 (15). Anal. calcd. for $C_{18}H_{13}ClO_2$: C 72.85, H 4.42; found: C 73.12, H 4.34%.

***(E)*-4′-Chloro-5-methoxy-3-styrylchromone (3f).** Mp 161–162 °C (recrystallised from ethanol). IR ν = 1644 (C=O), 1609 (C=C), 1571, 1487, 1475, 1435, 1373, 1355, 1295, 1267, 1188, 1141, 1087, 1010, 918, 861, 818, 802, 774, 752, 684. ^{1}H NMR δ = 4.01 (s, 3 H, OCH_3), 6.83 (d, 1 H, J = 8.3, Hz, H-6), 6.89 (d, 1 H, J = 16.4 Hz, H-α), 7.02 (dd, 1 H, J = 8.3 and 0.7 Hz, H-8), 7.30 (d, 2 H, J = 8.4 Hz, H-3′,5′), 7.42 (d, 2 H, J = 8.4 Hz, H-2′,6′), 7.55 (t, 1 H, J = 8.3 Hz, H-7), 7.64 (d, 1 H, J = 16.4 Hz, H-β), 7.96 (s, 1 H, H-2). ^{13}C NMR δ = 56.4 (O*C*H$_3$), 106.4 (C-6), 110.0 (C-8), 114.7 (C-10), 119.7 (C-α), 122.4 (C-3), 127.6 (C-2′,6′), 128.6 (C-3′,5′), 130.0 (C-β), 133.2 (C-4′), 133.6 (C-7), 136.1 (C-1′), 151.5 (C-2), 157.8 (C-9), 160.2 (C-5), 176.3 (C-4). EI-MS: m/z (rel. int.) = 314 (M$^{+\bullet}$, ^{37}Cl, 13), 313, [(M − 1)$^+$ ^{37}Cl, (M + 1)$^+$, ^{35}Cl, 12], 312 (M$^{+\bullet}$, ^{35}Cl, 34), 311, [(M − 1)$^+$, ^{35}Cl, 41), 296 (5), 279 (4), 278 (11), 277 (22), 250 (4), 248 (7), 220 (10), 218 (14), 205 (10), 192 (22), 189 (10), 183 (19), 178 (15), 177 (59), 176 (14), 158 (16), 156 (44), 152 (17), 151 (89), 150 (62), 149 (35), 141 (41), 139 (100), 122 (25), 113 (16), 111 (44), 107 (46), 97 (16). Anal. calcd. for $C_{18}H_{13}O_3Cl$: C 69.13, H 4.19; found: C 69.14, H 4.19%.

***(Z)*-4′-Chloro-5-methoxy-3-styrylchromone (4f).** Mp 124–126 °C (recrystallised from ethanol). IR ν = 1644 (C=O), 1609 (C=C), 1571, 1475, 1435, 1376, 1355, 1295, 1267, 1188, 1141, 1087, 1010, 918, 818, 802, 774, 752, 684. ^{1}H NMR δ = 3.99 (s, 3 H, OCH_3), 6.53 (dd, 1 H, J = 12.1 and 1.0 Hz, H-α), 6.69 (d, 1 H, J = 12.1 Hz, H-β), 6.82 (d, 1 H, J = 8.3 Hz, H-6), 6.95 (d, 1 H, J = 8.3 Hz, H-8), 7.23 (s, 4 H, H-2′,3′,5′,6′), 7.53 (d, 1 H, J = 1.0 Hz, H-2), 7.54 (t, 1 H, J = 8.3 Hz, H-7). ^{13}C NMR δ = 56.4 (O*C*H$_3$), 106.3 (C-6), 110.1 (C-8), 114.6 (C-10), 121.5 (C-α), 122.1 (C-3), 128.7 (C-3′,5′), 129.9 (C-2′,6′), 130.9 (C-β), 132.8 (C-4′), 133.7 (C-7), 135.2 (C-1′), 152.0 (C-2), 158.1 (C-9), 160.0 (C-5), 176.7 (C-4). EI-MS: m/z (rel. int.) = 315 [(M + 1)$^+$, ^{37}Cl, 4], 314 (M$^{+\bullet}$, ^{37}Cl, 23), 313 [(M − 1)$^+$, ^{37}Cl, (M + 1)$^+$, ^{35}Cl, 17], 312 (M$^{+\bullet}$, ^{35}Cl, 66), 311 [(M − 1)$^+$, ^{35}Cl, 16], 283 (10), 281 (8), 201 (10), 189 (6), 187 (5), 171 (7), 162 (9), 160 (12), 159 (100), 151 (8), 150 (13), 149 (7), 127 (25), 126 (11), 125 (30), 122 (13), 121 (14), 107 (30), 77 (7). Anal. calcd. for $C_{18}H_{13}O_3Cl$: C 69.13, H 4.19; found: C 69.13, H 4.21%.

***(E)*-4′-Nitro-3-styrylchromone (3g).** Mp 225–226 °C (recrystallised from ethanol). IR ν = 1643 (C=O), 1613 (C=C), 1594, 1561, 1509, 1461, 1342, 1318, 1276, 1210, 1183, 1108, 970, 869, 857, 770, 745, 700. ^{1}H NMR (DMSO-d$_6$) δ = 7.32 (d, 1 H, J = 16.3 Hz, H-α), 7.55 (ddd, 1 H, J = 8.0, 6.9 and 1.0 Hz, H-6), 7.72 (d, 1 H, J = 8.2 Hz, H-8), 7.81 (d, 2 H, J = 8.8 Hz, H-2′,6′), 7.85 (ddd, 1 H, J = 8.2, 6.9 and 1.6 Hz, H-7), 7.94 (d, 1 H, J = 16.3 Hz, H-β), 8.16 (dd, 1 H, J = 8.0 and 1.6 Hz, H-5), 8.24 (d, 2 H, J = 8.8 Hz, H-3′,5′), 8.77 (s, 1 H, H-2). ^{13}C NMR (DMSO-d$_6$) δ = 118.5 (C-8), 119.8 (C-3), 123.5 (C-10), 124.1 (C-3′,5′), 125.0 (C-α), 125.4 (C-5), 125.9 (C-6), 127.1 (C-2′,6′), 128.5 (C-β), 134.4 (C-7), 144.2 (C-1′), 146.3 (C-4′), 155.2 (C-2), 157.3 (C-9), 175.5 (C-4). EI-MS: m/z (rel. int.) = 294 [(M + 1)$^+$, 25], 293 (M$^{+\bullet}$, 100), 292 [(M − 1)$^+$, 49], 276 (8), 263 (12), 247 (10), 246 (27), 218 (12), 200 (6), 189 (14), 171 (51), 128 (11), 127 (12), 121 (25), 120 (24), 115 (11), 92 (30), 77 (12). Anal. calcd. for $C_{17}H_{11}NO_4$: C 69.62, H 3.78, N 4.78; found: C 69.54, H 3.92, N 4.76%.

***(Z)*-4′-Nitro-3-styrylchromone (4g).** Mp 151–152 °C (recrystallised from ethanol). IR ν = 1638 (C=O), 1612 (C=C), 1593, 1567, 1513, 1463, 1374, 1336, 1319, 1218, 1138, 1102, 926, 855, 764, 681. ^{1}H NMR (DMSO-d$_6$) δ = 6.59 (dd, 1 H, J = 12.1 and 0.9 Hz, H-α), 6.90 (d, 1 H, J = 12.1 Hz, H-β), 7.51 (ddd, 1 H, J = 8.0, 7.2 and 0.8 Hz, H-6), 7.57 (d, 2 H, J = 8.8 Hz, H-2′,6′), 7.63 (d, 1 H, J = 8.1 Hz, H-8), 7.81 (ddd, 1 H, J = 8.1, 7.2 and 1.5 Hz, H-7), 8.08 (dd, 1 H, J = 8.0 and 1.5 Hz, H-5), 8.12 (d, 2 H, J = 8.8 Hz, H-3′,5′), 8.20 (d, 1 H, J = 0.9 Hz, H-2). ^{13}C NMR (DMSO-d$_6$) δ = 118.5 (C-8), 120.2 (C-3), 123.4 (C-10), 123.7 (C-3′,5′), 123.9 (C-α), 125.2 (C-5), 125.7 (C-6), 129.7 (C-2′,6′), 130.9 (C-β), 134.3 (C-7), 143.6 (C-1′), 146.1 (C-4′), 155.2 (C-2), 155.7 (C-9), 175.3 (C-4). EI-MS: m/z (rel. int.) = 294 [(M + 1)$^+$, 29], 293 (M$^{+\bullet}$, 100), 292 [(M − 1)$^+$, 49], 276 (11), 263 (12), 247 (13), 246 (28), 218 (13), 200 (9), 189 (14), 171 (53), 146 (16), 127 (15), 126 (14), 121 (32), 120 (29), 115 (10), 92 (29), 78 (13), 77 (15). Anal. calcd. for $C_{17}H_{11}NO_4$: C 69.62, H 3.78, N 4.78; found: C 69.59, H 3.82, N 4.71%.

***(E)*-6-Methyl-4′-nitro-3-styrylchromone (3h).** Mp 225–227 °C (recrystallised from ethanol). IR ν = 3068, 1651 (C=O), 1615 (C=C), 1592, 1561, 1507, 1463, 1335, 1318, 1300, 1267, 1159, 1105, 969, 869, 857, 763, 745, 699. ^{1}H NMR δ = 2.49 (s, 3 H, 6-CH_3), 7.08 (dd, 1 H, J = 16.2 and 0.5 Hz, H-α), 7.39 (d, 1 H, J = 8.5 Hz, H-8), 7.51 (dd, 1 H, J = 8.5 and 2.2 Hz, H-7), 7.64 (d, 2 H, J = 8.8 Hz, H-2′,6′), 7.84 (d, 1 H, J = 16.2 Hz, H-β), 8.08 (d, 1 H, J = 2.2 Hz, H-5), 8.14 (s br, 1 H, H-2), 8.22 (d, 2 H, J = 8.8 Hz, H-3′,5′). ^{13}C NMR δ = 21.0 (6-*C*H$_3$), 117.9 (C-8), 120.6 (C-3), 123.5 (C-10), 124.1 (C-α,3′,5′), 125.5 (C-5), 126.9 (C-2′,6′), 129.3 (C-β), 135.1 (C-7), 135.7 (C-6), 144.1 (C-1′), 146.8 (C-4′), 154.0 (C-9), 154.6 (C-2), 176.4 (C-4). EI-MS: m/z (rel. int.) = 308 [(M + 1)$^+$, 27], 307 (M$^{+\bullet}$, 100), 306 [(M − 1)$^+$, 48], 209 (8), 277 (11), 260 (19), 232 (5), 186 (5), 185 (59), 135 (26), 134 (30), 127 (9), 126 (10), 115 (8), 106 (16), 105 (10), 78 (20), 77 (15). Anal. calcd. for $C_{18}H_{13}NO_4$: C 70.35, H 4.26, N 4.56; found: C 70.35, H 4.43, N 4.51%.

***(Z)*-6-Methyl-4′-nitro-3-styrylchromone (4h).** Mp 179–180 °C (recrystallised from ethanol). IR ν = 3066, 1651 (C=O), 1615 (C=C), 1592, 1561, 1504, 1463, 1335, 1318, 1307, 1276, 1159, 1105, 969, 869, 857, 763, 745, 699. ^{1}H NMR δ = 2.47 (s, 3 H, 6-CH_3), 6.71 (dd, 1 H, J = 12.1 and 1.1 Hz, H-α), 6.83 (d, 1 H, J = 12.1 Hz, H-β), 7.32 (d, 1 H, J = 8.7 Hz, H-8), 7.46 (d, 2 H, J = 8.7 Hz, H-2′,6′), 7.50 (dd, 1 H, J = 8.7 and 2.2 Hz, H-7), 7.68 (d, 1 H, J = 1.1 Hz, H-2), 8.04 (d, 1 H, J = 2.2 Hz, H-5), 8.13 (d, 2 H, J = 8.7 Hz, H-3′,5′). ^{13}C NMR δ = 20.9 (6-*C*H$_3$), 117.9 (C-8), 120.5 (C-3), 123.6 (C-10), 123.9 (C-3′,5′), 124.1 (C-α), 125.3 (C-5), 129.4 (C-2′,6′), 130.6 (C-β), 135.2 (C-7), 135.6 (C-6), 143.6 (C-1′), 146.6 (C-4′), 154.0 (C-2), 154.4 (C-9), 176.7 (C-4). EI-MS: m/z (rel. int.) = 308 [(M + 1)$^+$, 23], 307 (M$^{+\bullet}$, 100), 306 [(M − 1)$^+$, 49], 290 (7), 277 (8), 260 (18), 232 (5), 186 (5), 185 (52), 135 (17), 134 (22), 126 (5), 115 (5), 106 (10), 78 (14), 77 (13). Anal. calcd. for $C_{18}H_{13}NO_4$: C 70.35, H 4.26, N 4.56; found: C 70.06, H 4.24, N 4.49%.

***(E)*-5-Methoxy-4′-nitro-3-styrylchromone (3i).** Mp 210–211 °C (recrystallised from ethanol). IR ν = 1655 (C=O),

1615 (C=C), 1595, 1567, 1509, 1475, 1337, 1326, 1297, 1270, 1165, 1105, 1083, 976, 872, 808, 774, 746, 700. ^{1}H NMR $\delta = 4.02$ (s, 3 H, OCH_3), 6.85 (dd, 1 H, $J = 8.4$ and 0.9 Hz, H-6), 7.01 (dd, 1 H, $J = 16.3$ and 0.5 Hz, H-α), 7.03 (dd, 1 H, $J = 8.4$ and 0.9 Hz, H-8), 7.57 (t, 1 H, $J = 8.4$ Hz, H-7), 7.60 (d, 2 H, $J = 8.8$ Hz, H-2′,6′), 7.89 (d, 1 H, $J = 16.3$ Hz, H-β), 8.00 (s br, 1 H, H-2), 8.18 (d, 2 H, $J = 8.8$ Hz, H-3′,5′). ^{13}C NMR $\delta = 56.4$ (OCH_3), 106.7 (C-6), 110.0 (C-8), 114.6 (C-10), 121.6 (C-3), 123.96 (C-α), 124.04 (C-3′,5′), 126.8 (C-2′,6′), 129.2 (C-β), 133.9 (C-7), 144.3 (C-1′), 146.7 (C-4′), 153.0 (C-2), 157.6 (C-9), 160.2 (C-5), 176.1 (C-4). EI-MS: m/z (rel. int.) = 324 [$(M+1)^+$, 24], 323 ($M^{+\bullet}$, 100), 322, [$(M-1)^+$ 11], 307 (27), 306 (87), 293 (12), 277 (12), 276 (42), 247 (19), 201 (17), 171 (17), 159 (29), 150 (13), 122 (15), 107 (35), 92 (8). Anal. calcd. for $C_{18}H_{13}NO_5$: C 66.87, H 4.05, N 4.33; found: C 67.01, H 3.95, N 4.26%.

***(Z)*-5-Methoxy-4′-nitro-3-styrylchromone (4i).** Mp 212–214 °C (recrystallised from ethanol). IR $\nu = 1642$ (C=O), 1606 (C=C), 1594, 1567, 1509, 1476, 1439, 1336, 1293, 1267, 1192, 1104, 1076, 920, 876, 859, 803, 779, 716, 679. ^{1}H NMR $\delta = 4.00$ (s, 3 H, OCH_3), 6.69 (dd, 1 H, $J = 12.0$ and 1.1 Hz, H-α), 6.78 (d, 1 H, $J = 12.0$ Hz, H-β), 6.84 (dd, 1 H, $J = 8.4$ and 0.8 Hz, H-6), 6.95 (dd, 1 H, $J = 8.4$ and 0.8 Hz, H-8), 7.45 (d, 2 H, $J = 8.7$ Hz, H-2′,6′), 7.49 (d, 1 H, $J = 1.1$ Hz, H-2), 7.56 (t, 1 H, $J = 8.4$ Hz, H-7), 8.13 (d, 2 H, $J = 8.7$ Hz, H-3′,5′). ^{13}C NMR $\delta = 56.4$ (OCH_3), 106.6 (C-6), 110.1 (C-8), 114.6 (C-10), 121.8 (C-3), 123.9 (C-3′,5′), 124.5 (C-α), 129.5 (C-2′,6′), 130.1 (C-β), 133.9 (C-7), 143.7 (C-1′), 146.6 (C-4′), 152.0 (C-2), 158.1 (C-9), 160.0 (C-5), 176.4 (C-4). EI-MS: m/z (rel. int.) = 324 [$(M+1)^+$, 21], 323 ($M^{+\bullet}$, 100), 322, [$(M-1)^+$ 10], 293 (11), 307 (19), 306 (85), 293 (11), 277 (10), 276 (35), 247 (17), 201 (14), 171 (14), 159 (22), 122 (14), 107 (34), 92 (7). Anal. calcd. for $C_{18}H_{13}NO_5$: C 66.87, H 4.05, N 4.33; found: C 66.86, H 4.02, N 4.29%.

***(E)*-4′-Ethoxy-3-styrylchromone (3j).** Mp 129–130 °C (recrystallised from ethanol). IR $\nu = 2980$, 2931, 1644 (C=O), 1612 (C=C), 1561, 1509, 1466, 1398, 1353, 1276, 1243, 1179, 1142, 1115, 1041, 977, 820, 758, 696. ^{1}H NMR $\delta = 1.44$ (t, 3 H, $J = 7.0$ Hz, CH_3), 4.07 (q, 2 H, $J = 7.0$ Hz, CH_2), 6.87 (d, 1 H, $J = 16.4$ Hz, H-α), 6.90 (d, 2 H, $J = 8.7$, Hz, H-3′,5′), 7.42 (dd, 1 H, $J = 7.8$ and 1.4 Hz, H-6), 7.47 (d, 2 H, $J = 8.7$ Hz, H-2′,6′), 7.48 (d, 1 H, $J = 8.5$ Hz, H-8), 7.56 (d, 1 H, $J = 16.4$ Hz, H-β), 7.68 (ddd, 1 H, $J = 8.5$, 7.8 and 1.4 Hz, H-7), 8.11 (s, 1 H, H-2), 8.32 (dd, 1 H, $J = 7.8$ and 1.4 Hz, H-5). ^{13}C NMR $\delta = 14.8$ (CH_3), 63.4 (CH_2), 114.6 (C-3′,5′), 116.6 (C-α), 118.0 (C-8), 122.1 (C-3), 124.0 (C-10), 125.1 (C-6), 126.2 (C-5), 127.8 (C-2′,6′), 130.0 (C-1′), 131.2 (C-β), 133.4 (C-7), 152.4 (C-2), 155.8 (C-9), 158.8 (C-4′), 176.7 (C-4). EI-MS: m/z (rel. int.) = 293 [$(M+1)^+$, 30], 292 ($M^{+\bullet}$, 100), 291 [$(M-1)^+$, 19], 275 (5), 264 (25), 263 (76), 247 (17), 235 (14), 219 (6), 218 (5), 207 (8), 205 (6), 189 (5), 178 (9), 172 (7), 171 (18), 144 (19), 143 (12), 132 (9), 121 (19), 116 (8), 115 (35), 92 (13), 89 (11), 77 (10). Anal. calcd. for $C_{19}H_{16}O_3Cl$: C 78.06, H, 5.52; found: C 77.68, H 5.51%.

***(Z)*-4′-Ethoxy-3-styrylchromone (4j).** Yellowish oil. IR $\nu = 2978$, 2929, 1644 (C=O), 1612 (C=C), 1571, 1509, 1465, 1396, 1352, 1244, 1177, 1143, 1115, 1043, 976, 820, 758, 695. ^{1}H NMR $\delta = 1.40$ (t, 3 H, $J = 7.0$ Hz, CH_3), 4.00 (q, 2 H, $J = 7.0$ Hz, CH_2), 6.42 (d, 1 H, $J = 12.1$, Hz, H-α), 6.73 (d, 1 H, $J = 12.1$ Hz, H-β), 6.79 (d, 2 H, $J = 8.7$ Hz, H-3′,5′), 7.23 (d, 2 H, $J = 8.7$ Hz, H-2′,6′), 7.4 (d, 1 H, $J = 8.0$ Hz, H-8), 7.41 (dd, 1 H, $J = 8.0$ and 7.3 Hz, H-6), 7.66 (ddd, 1 H, $J = 8.0$, 7.3 and 1.6 Hz, H-7), 7.80 (s, 1 H, 2-H), 8.28 (dd, 1 H, $J = 8.0$ and 1.6 Hz, H-5). ^{13}C NMR $\delta = 14.7$ (CH_3), 63.3 (CH_2), 114.4 (C-3′,5′), 118.1 (C-8), 118.5 (C-α), 121.4 (C-3), 124.0 (C-10), 125.1 (C-6), 126.0 (C-5), 128.7 (C-1′), 129.8 (C-2′,6′), 132.3 (C-β), 133.5 (C-7), 154.0 (C-2), 156.0 (C-9), 158.1 (C-4′), 177.1 (C-4). EI-MS: m/z (rel. int.) = 293 [$(M+1)^+$, 58], 292 ($M^{+\bullet}$, 100), 291 [$(M-1)^+$, 49], 275 (7), 265 (12), 264 (30), 263 (89), 247 (18), 235 (20), 218 (5), 207 (11), 189 (5), 178 (14), 171 (16), 149 (14), 144 (16), 143 (8), 121 (23), 116 (7), 115 (36), 92 (10), 89 (8), 77 (6). EI-HRMS ($C_{19}H_{16}O_3$ [$M^{+\bullet}$]): calcd. 292.1099, found 292.1111.

***(E)*-4′-Ethoxy-6-methyl-3-styrylchromone (3k).** Mp 158-159 °C (recrystallised from ethanol). IR $\nu = 3065$, 2978, 2932, 1641 (C=O), 1615 (C=C), 1562, 1509, 1485, 1478, 1431, 1390, 1350, 1274, 1244, 1178, 1156, 1114, 1046, 900, 856, 823, 810, 790. ^{1}H NMR $\delta = 1.42$ (t, 3 H, $J = 7.0$ Hz, CH_3), 2.46 (s, 3 H, 6-CH_3), 4.04 (q, 2 H, $J = 7.0$ Hz, CH_2), 6.85 (d, 1 H, $J = 16.4$ Hz, H-α), 6.87 (d, 2 H, $J = 8.7$ Hz, H-3′,5′), 6.34 (d, 1 H, $J = 8.7$ Hz, H-8), 7.44 (d, 2 H, $J = 8.7$ Hz, H-2′,6′), 7.45 (d, 1 H, $J = 8.7$ Hz, H-7), 7.50 (d, 1 H, $J = 16.4$ Hz, H-β), 8.05 (s, 1 H, H-2), 8.06 (s, 1 H, H-5). ^{13}C NMR $\delta = 14.8$ (CH_3), 20.9 (6-CH_3), 63.4 (CH_2), 114.5 (C-3′,5′), 116.7 (C-α), 117.7 (C-8), 121.8 (C-3), 123.6 (C-10), 125.4 (C-5), 127.8 (C-2′,6′), 130.0 (C-1′), 130.8 (C-β), 134.6 (C-7), 135.0 (C-6), 152.3 (C-2), 154.1 (C-9), 158.7 (C-4′), 176.7 (C-4). EI-MS: m/z (rel. int.) = 307 [$(M+1)^+$, 30], 306 ($M^{+\bullet}$, 100), 305 [$(M-1)^+$, 22], 289 (7), 278 (23), 277 (69), 261 (13), 249 (12), 185 (13), 172 (8), 171 (7), 144 (19), 143 (10), 139 (12), 135 (19), 134 (7), 116 (6), 115 (29), 106 (6), 89 (10), 78 (10), 77 (12). Anal. calcd. for $C_{20}H_{18}O_3$: C 78.41, H 5.92; found: C 78.02, H 5.82%.

***(Z)*-4′-Ethoxy-6-methyl-3-styrylchromone (4k).** Mp 110–112 °C (recrystallised from ethanol). IR $\nu = 3065$, 2978, 2923, 1643 (C=O), 1617 and 1605 (C=C), 1573, 1509, 1482, 1478, 1431, 1404, 1322, 1290, 1246, 1196, 1178, 1152, 1131, 1117, 1051, 907, 862, 830, 803, 773. ^{1}H NMR $\delta = 1.40$ (t, 3 H, $J = 7.0$ Hz, CH_3), 2.46 (s, 3 H, 6-CH_3), 4.00 (q, 2 H, $J = 7.0$ Hz, CH_2), 6.42 (dd, 1 H, $J = 12.1$ and 1.1 Hz, H-α), 6.72 (d, 1 H, $J = 12.1$ Hz, H-β), 6.78 (d, 2 H, $J = 8.7$ Hz, H-3′,5′), 7.22 (d, 2 H, $J = 8.7$ Hz, H-2′,6′), 7.30 (d, 1 H, $J = 8.5$ Hz, H-8), 7.46 (dd, 1 H, $J = 8.5$ and 1.9 Hz, H-7), 7.78 (d, 1 H, $J = 1.1$ Hz, H-2), 8.06 (d, 1 H, $J = 1.9$ Hz, H-5). ^{13}C NMR $\delta = 14.8$ (CH_3), 21.0 (6-CH_3), 63.3 (CH_2), 111.4 (C-3′,5′), 117.8 (C-8), 118.8 (C-α), 121.2 (C-3), 123.8 (C-10), 125.3 (C-5), 128.9 (C-1′), 129.9 (C-2′,6′), 132.2 (C-β), 134.7 (C-7), 135.1 (C-6), 153.9 (C-2), 154.4 (C-9), 158.1 (C-4′), 177.2 (C-4). EI-MS: m/z (rel. int.) = 307 [$(M+1)^+$, 30], 306 ($M^{+\bullet}$, 100), 305 [$(M-1)^+$, 15], 278 (20), 277 (68), 261 (10), 249 (12), 185 (9), 172 (8), 144 (17), 135 (16), 115 (26), 89 (6), 77 (6). Anal. calcd. for $C_{20}H_{18}O_3$: C 78.41, H 5.92, found C 78.47, H 6.16%.

***(E)*-4′-Ethoxy-5-methoxy-3-styrylchromone (3l).** Yellowish oil. IR $\nu = 3012$, 2937, 1643 (C=O), 1604 (C=C), 1568, 1511, 1475, 1431, 1392, 1299, 1268, 1249, 1174, 1114, 1074, 1043, 970, 921, 806, 732, 688. ^{1}H NMR $\delta = 1.42$ (t, 3 H, $J = 7.0$ Hz, CH_3), 4.01 (s, 3 H, OCH_3), 4.05 (q, 2 H, $J = 7.0$ Hz, OCH_2), 6.83 (d, 1 H, $J = 16.1$ Hz, H-α), 6.84 (d, 1 H, $J = 8.0$ Hz, H-6), 6.88 (d, 2 H, $J = 8.7$ Hz, H-3′,5′), 7.01 (d, 1 H, $J = 8.0$ Hz, H-8), 7.43 (d, 2 H, $J = 8.7$ Hz, H-2′,6′), 7.54 (t, 1 H, $J = 8.0$ Hz, H-7), 7.55 (d, 1 H, $J = 16.1$ Hz, H-β), 7.94 (s, 1 H, H-2). ^{13}C NMR: $\delta = 14.8$ (CH_3), 56.4 (OCH_3), 63.5 (OCH_2), 106.3 (C-6), 110.0 (C-8), 114.6 (C-3′,5′), 114.7 (C-10), 116.8 (C-α), 123.1 (C-3), 127.8 (C-2′,6′), 130.2 (C-1′), 130.8 (C-β), 133.4 (C-7), 150.6 (C-2), 157.9 (C-9), 158.7 (C-4′), 160.3 (C-5), 176.4 (C-4). EI-MS: m/z (rel. int.) = 322 ($M^{+\bullet}$, 100), 305 (5), 293 (29), 278 (20), 250 (8), 201 (8), 159 (13), 151 (15), 144 (16), 135 (53), 121 (10), 115 (41), 107 57), 89 (10), 77 (11), 63 (12). EI-HRMS ($C_{20}H_{18}O_4$ [$M^{+\bullet}$]): calcd. 322.1205, found 322.1212.

***(Z)*-4′-Ethoxy-5-methoxy-3-styrylchromone (4l).** Mp 107–108 °C (recrystallised from ethanol). IR ν = 3093, 2971, 2925, 1644 (C=O), 1602 (C=C), 1567, 1510, 1475, 1431, 1373, 1353, 1290, 1268, 1180, 1141, 1076, 1045, 852, 815, 773, 686. ^{1}H NMR δ = 1.40 (t, 3 H, J = 7.0 Hz, CH_3), 3.99 (s, 3 H, OCH_3), 4.00 (q, 2 H, J = 7.0 Hz, OCH_2), 6.40 (dd, 1 H, J = 12.1 and 1.2 Hz, H-α), 6.68 (d, 1 H, J = 12.1 Hz, H-β), 6.79 (d, 2 H, J = 8.7 Hz, H-3′,5′), 6.80 (dd, 1 H, J = 8.3 and 0.8 Hz, H-6), 6.94 (dd, 1 H, J = 8.3 and 0.8 Hz, H-8), 7.22 (d, 2 H, J = 8.7 Hz, H-2′,6′), 7.52 (t, 1 H, J = 8.3 Hz, H-7), 7.62 (d, 1 H, J = 1.2 Hz, H-2). ^{13}C NMR: δ = 14.7 (*C*H$_3$), 56.3 (O*C*H$_3$), 63.3 (O*C*H$_2$), 106.2 (C-6), 110.1 (C-8), 114.4 (C-3′,5′), 114.7 (C-10), 119.1 (C-α), 122.5 (C-3), 128.9 (C-1′), 129.8 (C-2′,6′), 131.7 (C-β), 133.5 (C-7), 152.0 (C-2), 158.0 and 158.1 (C-9 and C-4′), 159.9 (C-5), 176.8 (C-4). EI-MS: m/z (rel. int.) = 322 ($M^{+\bullet}$, 100), 321 (20), 305 (7), 293 (26), 278 (19), 263 (11), 250 (7), 201 (8), 172 (8), 160 (12), 151 (13), 144 (15), 135 (49), 121 (10), 115 (32), 107 (45), 89 (7), 77 (7), 65 (6). Anal. calcd. for $C_{20}H_{18}O_4$: C 74.52, H 5.63; found: C 74.32, H 5.86%.

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