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Bromination and Azidation Reactions of 2-Styrylchromones. New Syntheses of 4(5)-Aryl-5(4)-(2-chromonyl)-1,2,3-triazoles

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Summary. The bromination of 2-styrylchromones, bearing electron neutral substituents, with two molar equivalents of piridinium tribromide gave 2-(2-aryl-1,2-dibromoethyl)chromones and 3-bromo-2-(2-aryl-1,2-dibromoethyl)chromones. The presence of electron-donating substituents on their B ring led to a mixture of compounds due to the higher reactivity of their C(2)=C(3) and C_α=C_β double bonds, whereas the strongly electron-withdrawing group hindered the bromination. The dehydrobromination of 2-(2-aryl-1,2-dibromoethyl)chromones with triethylamine gave a diastereomeric mixture of (*E*)- and (*Z*)-2-(α-bromostyryl)chromones. Some novel 4(5)-aryl-5(4)-(2-chromonyl)-1,2,3-triazoles have been obtained from the reactions of 2-(2-aryl-1,2-dibromoethyl)chromones, 2-(α-bromostyryl)chromones, and 2-styrylchromones with sodium azide. The reactions of 2-styrylchromones with sodium azide are more efficient, general, and constitute a one-pot synthetic method of 4(5)-aryl-5(4)-(2-chromonyl)-1,2,3-triazoles allowing the preparation of 1,2,3-triazoles bearing either electron-donating or electron-withdrawing substituents in their aryl ring. The structure of all new compounds was established by extensive NMR spectroscopic studies.

Keywords. 2-Styrylchromones; Bromination; Dehydrobromination; Azidation; 1,2,3-Triazoles.

Introduction

1,2,3-Triazoles are widely studied nitrogen heterocycles [1] with numerous applications in organic synthesis and with extensive biological and agrochemical activities [1, 2]. However, very little is known about the synthesis and chemical and biological properties of compounds having both chromone and 1,2,3-triazole moieties. To our best knowledge, only a limited number of reports have been published on the synthesis of 2-chromone-1,2,3-triazoles. The reaction of 2-cyanochromones

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with diazomethane has resulted in the formation of mixtures of isomeric derivatives with the predominance of 2-methyl-4-(2-chromonyl)-1,2,3-triazoles [3–5]. French authors reported on anti-inflammatory, anticonvulsive, neurotoxic, and anti-allergic effects of these compounds [5]. Recently *Liu et al.* published on the synthesis of 2-phenyl-4-(substituted 2-chromonyl)-1,2,3-triazoles by the *Baker-Venkataraman* rearrangement of 1,3-diketones obtained from 2′-hydroxyacetophenones and 2-phenyl-1,2,3-triazole-4-carboxylic acid [6].

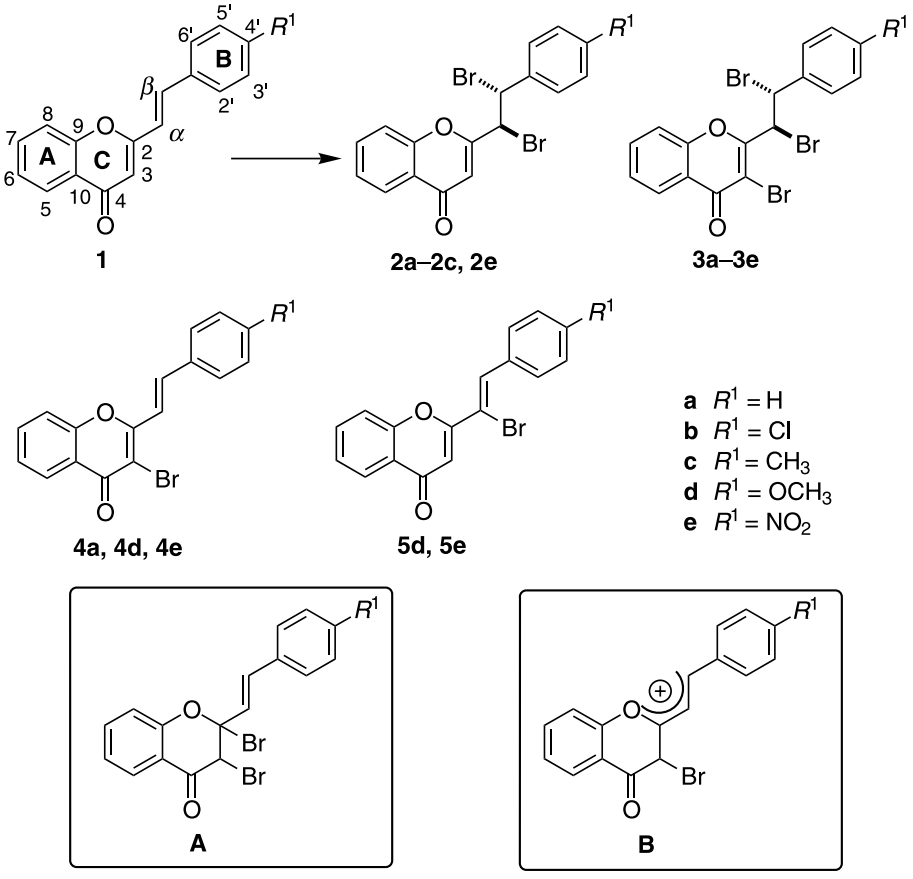
Synthetic methods affording 1,2,3-triazoles are well documented and reviewed [1, 7]. A widely used approach is based on one bond formation between nitrogen atoms, *e.g.*, the reaction of α-diazoketones with amines gives 1-substituted 1,2,3-triazoles while oxidative ring-closure of osazone-type compounds results in the formation of 1-amino-1,2,3-triazole derivatives. The base-catalysed condensation of compounds with activated methylene groups and azides provides another route. However, the most popular method undoubtedly consists of the 1,3-dipolar cycloaddition of azide to alkynes which is usually exploited to prepare 1-alkylated or arylated derivatives [1, 7–9]. Synthesis of 1*H*-1,2,3-triazoles requires the addition of hydrazoic acid what is somewhat dangerous and needs an activation by an electron-withdrawing group. Using benzyl, trimethylsilyl, or tributyltin azide and deprotecting the formed intermediate can avoid this drawback. The addition of azide ion as anionic dipole to alkynes may also offer a safer approach. Oxidative aromatisation of 1,2,3-triazolines also leads to 1,2,3-triazoles but the formation of 1,2,3-triazolines by 1,3-dipolar cycloaddition of azides to alkenes is usually a very slow reaction unless electron-withdrawing group or ring strain activates the double bond. Alternatively, addition of azides to enol ethers or enamines followed by the elimination of alcohols or secondary amines also provides an entry to 1,2,3-triazoles. A further version utilising the addition of aryl and vinyl azides to α-keto phosphorus ylides and an immediate elimination of triphenylphosphine oxide from the triazoline intermediates was published by *L'abbé et al.* [10].

Several papers reported on the *intramolecular* dipolar cyloaddition in an electron-deficient vinyl azide [11]. Based on the fact the chromone nucleus acts as a strongly electron-withdrawing moiety and that we have demonstrated the capability of the styryl double bond of 2-stryrylchromones **1** to react with diazomethane in a 1,3-dipolar cycloaddition [12], the intramolecular ring-closure of 2-(α- or β-azidostyryl)chromones seemed to be a promising way to prepare the hitherto unknown 4(5)-aryl-5(4)-(2-chromonyl)-1,2,3-triazoles. In accordance with our earlier studies [13] we deemed the needed azides available from various brominated species of 2-stryrylchromones **1**. In this paper we wish to report our results in the field of bromination and azidation of 2-stryrylchromones [14].

Results and Discussion

Synthesis

Our first synthetic approach to synthesise 1,2,3-triazoles **7** was based on the reaction of 2-(α-bromostyryl)chromones **5** and **6** with sodium azide. To prepare the desired starting materials, 2-styrylchromone **1a** was treated with pyridinium tribromide (*PTB*) (1 equiv.) in acetic acid at room temperature (Scheme 1). Preparative TLC of the obtained mixture afforded 3-bromo-2-styrylchromone (**4a**), 2-(1,2-dibromo-2-phenylethyl)chromone (**2a**), and 3-bromo-2-(1,2-dibromo-2-phenylethyl)chromone (**3a**) in low yields and with poor mass balance ($\sim$40%) (Table 1, Entry 1). Using two molar equivalents of *PTB* followed by silica gel



Scheme 1

Table 1. Conditions and yields of the bromination of 2-styrylchromones **1a**–**1f**

Entry	Starting material	Temp. °C	*PTB* equiv.	Yield*/%			
				2	**3**	**4**	**5**
1	**1a**	RT	1	10	15	16	–
2	**1a**	RT	2	44	41	–	–
3	**1b**	RT	2	41	24	–	–
4	**1c**	RT	2	33	42	–	–
5	**1d**	RT	2	–	15	10	32
6	**1e****	RT	2	–	–	15	–
7	**1e**	70	2	30	16	–	26

* Yields refer to pure isolated material; ** 70% of **1e** was recovered

column chromatography only the two brominated products **2a** (44%) and **3a** (41%) were obtained (Table 1, Entry 2). When this procedure was applied to 2-styrylchromones **1b** and **1c** the dibrominated chromones **2b** and **2c** and tribrominated compounds **3b** and **3c** were obtained again in good yields (Table 1, Entries 3, 4). These results demonstrate that the reactivity of double bonds C(2)=C(3) and

C_α=C_β is quite similar and their bromine addition takes place competitively leading to dibromides **2** and **A**. However, dibromides **A** lose HBr very smoothly, presumably in a reaction of E1 mechanism due to the evolvement of the highly stabilized carbocation **B**. This elimination results in the formation of the 3-brominated product **4**. Tribrominated chromone **3** may arise from either dibromide **2** or 3-bromochromone **4**. The $^3J_{\text{H-1}'\text{-H-2}'}$ values in bromides **2** and **3** verified their *erythro* relative configuration.

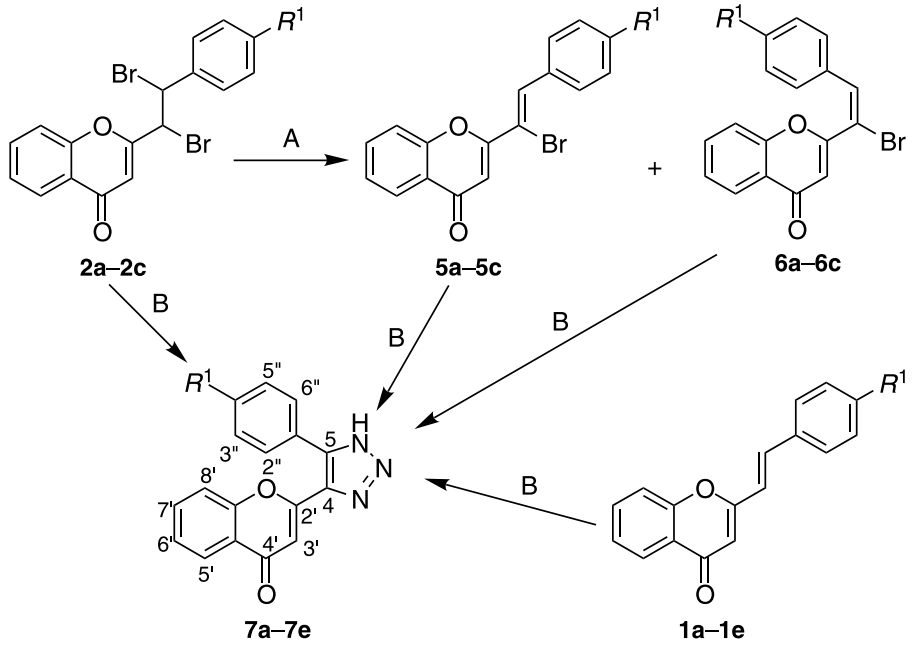
On the contrary, the bromination of 4′-methoxy-2-styrylchromone **1d** failed to give any expected dibrominated product **2d**, but 3-bromo-4′-methoxy-2-styrylchromone (**4d**, 10%), (*Z*)-4′-methoxy-2-(α-bromostyryl)chromone (**5d**, 32%) together with 3-bromo-2-[1,2-dibromo-2-(4-methoxyphenyl)ethyl]chromone (**3d**, 15%) were obtained instead (Table 1, Entry 5). Other tested bromination methods (Br_2 in CCl_4; *NBS* and benzoyl peroxide in CCl_4) gave similar results. This data indicate that in the presence of an electron-donating substituent in the B ring of 2-styrylchromones both C(2)=C(3) and C_α=C_β double bonds became more reactive. Moreover, the enhanced cation-stabilizing capability of the methoxy substituent facilitates the HBr elimination from intermediate **2d**.

The bromination of 4′-nitro-2-styrylchromone (**1e**) with two molar equivalents of *PTB* at room temperature for 10 days gave 3-bromo-4′-nitro-2-styrylchromone (**4e**) in 15% yield only while 70% of the unreacted starting material **1e** was recovered (Table 1, Entry 6). This indicates that C(2)=C(3) and C_α=C_β double bonds of 2-styrylchromones bearing electron-withdrawing substituents in their B ring became less reactive in consequence of the decreased π-electron density. When the bromination of **1e** was repeated at 70°C for 7 hours 2-[1,2-dibromo-2-(4-nitrophenyl)ethyl]chromone (**2e**, 30%), 3-bromo-2-[1,2-dibromo-2-(4-nitrophenyl) ethyl]chromone (**3e**, 16%), and (*Z*)-4′-nitro-2-(α-bromostyryl)chromone (**5e**, 26%) were obtained (Table 1, Entry 7).

The attempted bromination of 5-benzyloxy-2-styrylchromone (**1f**) with two molar equivalents of *PTB* at room temperature for 9 days gave a mixture of brominated 2-styrylchromone derivatives (*vide* Experimental). The benzyloxy group was cleaved probably by the HBr formed in the elimination reaction and the positions 6 and/or 8 activated by the hydroxy group have been brominated. Similar nuclear bromination of an activated ring A is well-documented [15].

The next step in our first approach to 1,2,3-triazoles **7** was the dehydrobromination of 2-(2-aryl-1,2-dibromoethyl)chromones **2**. The treatment of **2a**–**2c** with a high excess of triethylamine in refluxing toluene gave both (*Z*)-2-(α-bromostyryl) chromones **5a**–**5c** and (*E*)-2-(α-bromostyryl)chromones **6a**–**6c**, the more stable (*Z*)-isomers being the major products (65–89%) in each case (Scheme 2). The formation of both diastereomers in such elimination is not an unprecedented reaction, elimination from compounds with analogous structure such as *erythro*-chalcone dibromides [16], methyl *erythro*-2,3-dibromo-3-phenylpropanoate [17], or 2-bromo-3-methoxy-1,3-diphenylpropan-1-ones [18] led to a similar E/Z mixture *via* a likely E1cB mechanism.

In the third step the treatment of (*Z*)-2-(α-bromostyryl)chromones **5a**–**5c** with an excess of sodium azide in *DMF* at 120°C followed by acidic work-up afforded the expected 4(5)-aryl-5(4)-(2-chromonyl)-1,2,3-triazoles **7a**–**7c** (61–83%) (Scheme 2). 1,2,3-Triazole **7a** was also obtained from the diastereomeric (*E*)-2-(α-bromostyryl)chromone (**6a**) under the same conditions.



Scheme 2

This synthetic protocol to prepare 1,2,3-triazoles **7a**–**7c** constitutes an improvement to the previous one disclosed in our preliminary communication where the treatment of bromides **5** with sodium azide in refluxing *DMF* was reported to give 1,2,3-triazoles **7** in poorer (38–40%) yields and contaminated with tetrazole derivatives (10–12%) [14]. By decreasing the reaction temperature (153°C → 120°C) and increasing the excess of sodium azide (from 2 to 5 molar equivalents) the formation of by-products was completely eliminated and the desired 1,2,3-triazoles **7a**–**7c** are now available in better yields. The formation of these compounds must involve the transformation of bromides **5** into α- and β-azidovinyl compounds, by the well-documented addition-substitution-elimination pathway [19], which may cyclize to the obtained triazoles **7a**–**7c**. Our attempts to detect some intermediates, by performing the synthesis of triazole **7a** at lower temperatures, were unsuccessful.

Taking into account the nucleophilic character of the azide ion, the mechanism of the dehydrobromination and also the problems arising from the formation of both (*E*)- and (*Z*)-diastereomers in these reactions we tried to react 2-(2-aryl-1,2-dibromoethyl)chromones **2a**–**2c** with sodium azide in *DMF* at 120°C. These reactions followed by an acidic work-up yielded the expected triazoles **7a**–**7c** in good yields (54–73%) as well, which was comparable with those of the treatment of α-bromostyryl compounds **5**. Treatment of 2-(1,2-dibromo-2-phenylethyl)chromone **2a** with sodium azide in *DMF* at lower temperature (∼60°C) gave mainly (*Z*)-2-(α-bromostyryl)chromone **5a**. This indicates that the reaction involves the transformation of dibromo derivatives **2** into α-bromostyryl compounds **5**, by the elimination

of hydrogen bromide assisted by azide ion, which are transformed in the obtained 1,2,3-triazoles **7** by the reaction with sodium azide (*vide supra*).

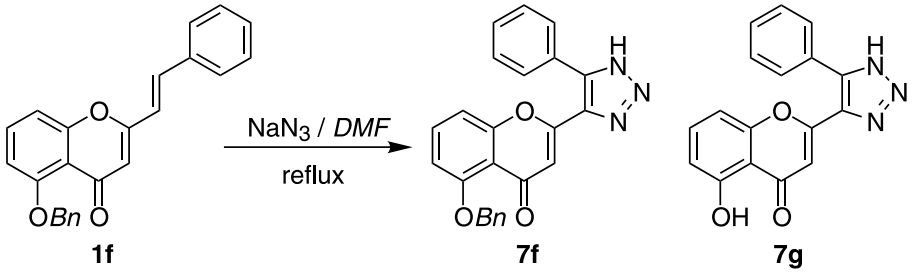
Due to the mesomeric effect of the carbonyl group $C_\alpha{=}C_\beta$ double bond of 2-styrylchromones could be considered as an ''activated'' double bond to participate in a cycloaddition reaction as a dipolarophile [1]. It was also pointed out that sluggish addition of azide to alkenes could be greatly improved by using protic or dipolar aprotic media [9]. Moreover, cycloadditions with participation of anionic dipoles were found to be greatly influenced by the polarity of the solvent. The increased reactivity of the anions poorly solvated in dipolar aprotic media considerably accelerates the cycloadditions [9]. Keeping these facts in mind, we essayed the reaction of 2-styrylchromones **1a**–**1e** with sodium azide in *DMF* at 120°C followed by treatment with acid. We found that these reactions gave directly 4(5)-aryl-5(4)-(2-chromonyl)-1,2,3-triazoles **7a**–**7e** in good yields (47–65%), *i.e.* not only 1,3-dipolar cycloaddition but spontaneous oxidation of the triazoline intermediate took place in a one-pot reaction (Scheme 2). This procedure renders possible to prepare 1,2,3-triazoles **7a**–**7e** bearing either electron-withdrawing or electron-donating substituents in the aryl ring of their styryl unit in one step. By comparing the yields of products **7**, this direct approach seems to be more effective in the case of chromones with electron-withdrawing groups in position 4′. The reaction of 2-styrylchromone **1a** with sodium azide in *DMF* at lower temperatures (60–80°C) also gave 1,2,3-triazole **7a** but in lower yields, no intermediates were detected.

When 5-benzyloxy-2-styrylchromone **1f** was reacted with sodium azide in *DMF* at 120°C followed by treatment with hydrochloric acid 1,2,3-triazoles **7f** (21%) and **7g** (25%) were obtained (Scheme 3). The formation of **7g** can be explained in terms of the cleavage of the benzyloxy group by hydrochloric acid during work-up.

NMR Spectroscopy

2-Styrylchromones and Intermediates

The main features of the NMR spectra of 2-(2-aryl-1,2-dibromoethyl)chromone **2a**–**2c** are the proton and carbon resonances of their ethylenic bridge. C-1′ and C-2′ resonances were assigned by 1D selective INEPT [20]: upon irradiation of H-3 (a singlet at $\delta = 6.51$ ppm) the resonances of C-10 ($\delta = 123.9$–124.0 ppm), C-2 ($\delta = 162.3$–162.7 ppm), and C-2′ ($\delta = 50.4$–50.6 ppm) were observed. The reso-



Scheme 3

nance at $\delta = 50.6–50.7$ ppm was then attributed to C-1′. The analysis of the HETCOR spectra allowed the assignment of H-1′ and H-2′ at $\delta = 5.20–5.25$ and 5.53–5.56 ppm.

The ^{1}H NMR spectra of 2-(2-aryl-1,2-dibromoethyl)-3-bromochromones **3a**–**3e** present two doublets at $\delta = 6.03–6.10$ and 5.58–5.67 ppm, corresponding to H-1′ and H-2′. Comparing the spectra of **3a**–**3e** with those of **2a**–**2c** one can conclude on the bromination at C-3, since their typical H-3 singlet is absent. The confirmation of the H-1′ and H-2′ resonances and the assignments of some quaternary carbons were also made by 1D selective INEPT [20]: upon irradiation of H-1′ the signals of C-1″, C-3, and C-2′ were observed, whereas the irradiation of H-2′ led to the appearance of C-2, C-1″, and C-2″,6″.

The NMR spectra of both 2-(α-bromostyryl)chromone diastereomers **5a**–**5c** and **6a**–**6c** are similar, but there are some important differences in the chemical shifts of H_β and C_β. In the case of the (*E*)-isomers **6a**–**6c** ring B and chromone moiety are not coplanar anymore due to steric hindrance. As a consequence of this there is no (or only limited) conjugation between the $\alpha,\beta,\gamma,\delta$-unsaturated system and ring B, hence the resonance of their C_β atoms appear at higher frequency values ($\delta = 138.7–140.1$ ppm) than those of the (*Z*) diastereomers **5a**–**5c** ($\delta = 132.8–135.2$ ppm). Due to the referred non-coplanarity both H_β ($\delta = 7.40–7.46$ ppm) and H-3 ($\delta = 6.42–6.44$ ppm) of (*E*)-isomers **6a**–**6c** appear at lower frequency values than those of the (*Z*)-isomers **5a**–**5c** (H_β, $\delta = 8.05–8.12$ ppm; H-3, $\delta = 6.98–7.01$ ppm).

The assignments of the other 2-styrylchromone derivatives proton and carbon resonances were based on the analysis of HSQC (or HETCOR in some cases) and HMBC spectra and also on our experience with the structural characterisation of this type of compounds [22].

1,2,3-Triazole Derivatives

The NMR spectra of 4(5)-aryl-5(4)-(2-chromonyl)-1,2,3-triazoles **7a**–**7e** were recorded in *DMSO*-d_6 with some drops of trifluoroacetic acid in order to accelerate the prototropy. In the absence of acid these spectra showed a mixture of tautomers. Comparing the NMR spectra of 1,2,3-triazoles **7a**–**7e** with those of the 2-styrylchromone precursors it was possible to observe the disappearance of their vinylic protons, whereas H-3′ resonance still appeared as a singlet at $\delta = 6.60–6.84$ ppm. The assignments of the carbon atoms of the 1,2,3-triazole ring of **7a**–**7e** were based on the analysis of their HMBC spectra; there is correlation between H-3′ and the signals of C-4 ($\delta = 134.7–136.8$ ppm) and also between H-2″,6″ and C-5 ($\delta = 141.6–149.6$ ppm).

Conclusion

The bromination of 2-styrylchromones with *PTB* was studied and revealed to be quite sensitive to the substituents of their A and B rings. The presence of electron-donating substituents on their B ring led to a mixture of compounds due to the higher reactivity of their C(2)=C(3) and C_α=C_β double bonds, whereas the strongly electron-withdrawing group hindered the bromination.

The reactions of 2-(2-aryl-1,2-dibromoethyl)chromones **2a**–**2c**, 2-(α-bromostyryl)chromones **5a**–**5c** and **6a**–**6c** with sodium azide were found to give some novel 4(5)-aryl-5(4)-(2-chromonyl)-1,2,3-triazoles **7a**–**7c**. However, the reaction of 2-styrylchromones **1a**–**1f** with sodium azide proved to be the more efficient, general, and one-pot synthetic method of 4(5)-aryl-5(4)-(2-chromonyl)-1,2,3-triazoles **7a**–**7g** allowing the preparation of 1,2,3-triazoles bearing either electron-donating or electron-withdrawing substituents in their aryl ring.

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; 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 (or HETCOR) and *g*HMBC experiments (long range C/H coupling constants were optimised to 7 Hz). Mass spectra (EI, 70 eV) were measured on VG Autospec Q and M mass spectrometers. Elemental analyses were obtained with a LECO 932 CHN analyser; the results were in accord with the calculated values, as well as the high resolution MS. 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.

*Halogenation of 2-Styrylchromones **1a–1f***

Method A. 5.15 g of *PTB* (16.1 mmol) were added to a solution of the appropriate 2-styrylchromone **1a**–**1f** [12, 21] (8.06 mmol) in 500 cm^3 of acetic acid. The mixture was stirred at room temperature (**1a**–**1c**: 32 h, **1d**: 1 wk, **1e**: 10 d, **1f**: 9 d) then poured into 200 cm^3 of H_2O and 100 g of ice. The obtained solid was filtered off and taken up in 100 cm^3 of $CHCl_3$. The organic layer was washed with H_2O (2×200 cm^3), dried (Na_2SO_4), and evaporated.

When starting with chromones **1a**–**1c** the obtained residue was purified by silica gel column chromatography (using a 1:9 mixture of light petroleum:CH_2Cl_2 as eluent). The first compound eluted was 2-(2-aryl-1,2-dibromoethyl)-3-bromochromone **3a**–**3c** (24–42%) followed by 2-(2-aryl-1,2-dibromoethyl)chromone **2a**–**2c** (33–44%).

When starting with **1d** the obtained residue was purified by preparative thin layer chromatography (using a 1:1 mixture of light petroleum:CH_2Cl_2 as eluent). After several elutions, four very close spots were collected; the first one was **3d** (15%), followed by **4d** (10%), and **5d** (32%). After removal of the solvent each residue was recrystallised from ethanol.

When starting with **1e** the obtained crude product was purified by column chromatography (using CH_2Cl_2 as eluent). The compound eluted first was the starting material **1e** (70%), followed by **4e** (15%). After removal of the solvent each residue was recrystallised from ethanol.

When starting with **1f**, the obtained residue was purified by preparative thin layer chromatography (using a 1:1 mixture of light petroleum:CH_2Cl_2 as eluent). After several elutions, four very close spots were collected; the first one was 6,8-dibromo-5-hydroxy-2-styrylchromone (59%), followed by 8-bromo-5-hydroxy-2-styrylchromone (4%), 6-bromo-5-hydroxy-2-styrylchromone (2%), and 3,8-dibromo-2-(1,2-dibromo-2-phenylethyl)-5-hydroxychromone (10%). After removal of the solvent each residue was recrystallised from ethanol.

Method B – (*only for 4′-nitro-2-styrylchromone* **1e**). 0.68 g of *PTB* (2.13 mmol) were added to a solution of 0.31 g of **1e** (1.07 mmol) in 200 cm^3 of acetic acid. The mixture was heated (70°C) for 7 hours and then poured into 200 cm^3 of H_2O and 100 g of ice. The obtained solid was filtered off and taken up in 100 cm^3 of chloroform. The organic layer was washed with H_2O (2×200 cm^3), dried (Na_2SO_4), and then evaporated. The obtained residue was purified by thin layer chromatography (using

CH_2Cl_2 as eluent). After several elutions, three very close spots were collected; the first one **3e** (181 mg, 16%), followed by **5e** (206 mg, 26%), and **2e** (290 mg, 30%). After removal of the solvent each residue was recrystallised from ethanol.

2-(1,2-Dibromo-2-phenylethyl)chromone (**2a**, $C_{17}H_{12}Br_2O_2$)

Yield: 1.45 g (44%); mp 159–161°C (*Et*OH); ^{1}H NMR: $\delta = 5.25$ (d, $J = 11.6$ Hz, H-1′), 5.56 (d, $J = 11.6$ Hz, H-2′), 6.51 (s, H-3), 7.40–7.54 (m, H-6 and H-2″,3″,4″,5″,6″), 7.61 (d, $J = 7.8$ Hz, H-8), 7.76 (dt, $J = 1.7$ and 7.8 Hz, H-7), 8.23 (dd, $J = 1.7$ and 7.8 Hz, H-5) ppm; ^{13}C NMR: $\delta = 50.4$ (C-2′), 50.6 (C-1′), 111.6 (C-3), 118.2 (C-8), 123.9 (C-10), 125.7 (C-6), 125.8 (C-5), 127.9 (C-2″,6″), 129.5 (C-3″,5″), 129.0 (C-4″), 134.3 (C-7), 138.1 (C-1″), 156.2 (C-9), 162.6 (C-2), 178.0 (C-4) ppm; EI-MS: m/z (%) = [410 (1), 408 (3), 406 (1), $M^{+\bullet}$], 329 (74), 327 (78), 326 (77), 325 (65), 311 (29), 247 (100), 218 (21), 189 (24), 127 (35), 121 (36), 109 (17), 92 (36), 77 (28).

3-Bromo-2-(1,2-dibromo-2-phenylethyl)chromone (**3a**, $C_{17}H_{11}Br_3O_2$)

Yield: 1.61 g (41%); mp 200–202°C (*Et*OH); ^{1}H NMR: $\delta = 5.61$ (d, $J = 11.6$ Hz, H-2′), 6.10 (d, $J = 11.6$ Hz, H-1′), 7.42–7.53 (m, H-6 and H-3″,4″,5″), 7.56 (dd, $J = 1.8$ and 8.0 Hz, H-2″,6″), 7.64 (d, $J = 8.0$ Hz, H-8), 7.80 (dt, $J = 1.6$ and 8.0 Hz, H-7), 8.28 (dd, $J = 1.6$ and 8.0 Hz, H-5) ppm; ^{13}C NMR: $\delta = 49.1$ (C-1′), 50.1 (C-2′), 110.9 (C-3), 117.9 (C-8), 121.9 (C-10), 126.2 (C-6), 126.6 (C-5), 128.0 (C-2″,6″), 129.1 (C-3″,5″), 129.6 (C-4″), 134.7 (C-7), 137.7 (C-1″), 155.1 (C-9), 159.8 (C-2), 172.4 (C-4) ppm; EI-MS: m/z (%) = [490 (3), 488 (7), 486 (7), 484 (3), $M^{+\bullet}$], 409 (28), 407 (38), 405 (27), 328 (30), 326 (30), 247 (93), 218 (18), 189 (23), 169 (19), 127 (34), 109 (17), 92 (20), 77 (19), 63 (21).

2-[1,2-Dibromo-2-(4-chlorophenyl)ethyl]chromone (**2b**, $C_{17}H_{11}Br_2ClO_2$)

Yield: 1.47 g (41%); mp 161–162°C (*Et*OH); ^{1}H NMR: $\delta = 5.20$ (d, $J = 11.6$ Hz, H-1′), 5.53 (d, $J = 11.6$ Hz, H-2′), 6.51 (s, H-3), 7.40–7.49 (m, H-6 and H-2″,3″,5″,6″), 7.59 (d, $J = 8.1$ Hz, H-8), 7.75 (ddd, $J = 1.6$, 7.8, and 8.1 Hz, H-7), 8.23 (dd, $J = 1.6$ and 7.9 Hz, H-5) ppm; ^{13}C NMR: $\delta = 50.4$ (C-2′), 50.6 (C-1′), 111.7 (C-3), 118.1 (C-8), 124.0 (C-10), 125.8 (C-6), 125.9 (C-5), 129.31 and 129.34 (C-2″,6″ and C-3″,5″), 134.3 (C-7), 135.4 (C-1″), 136.7 (C-4″), 156.2 (C-9), 162.3 (C-2), 177.9 (C-4) ppm; EI-MS: m/z (%) = [446 (1), 444 (5), 442 (8), 440 (3), $M^{+\bullet}$], 365 (43), 363 (79), 361 (73), 283 (71), 281 (100), 265 (73), 247 (53), 218 (31), 189 (38), 162 (66), 127 (67), 109 (62), 92 (59), 75 (26), 63 (37).

3-Bromo-2-[1,2-dibromo-2-(4-chlorophenyl)ethyl]chromone (**3b**, $C_{17}H_{10}Br_3ClO_2$)

Yield: 1.01 g (24%); mp 190–192°C (*Et*OH); ^{1}H NMR: $\delta = 5.58$ (d, $J = 11.6$ Hz, H-2′), 6.03 (d, $J = 11.6$ Hz, H-1′), 7.42–7.53 (m, H-6 and H-2″,3″,5″,6″), 7.62 (d, $J = 8.1$ Hz, H-8), 7.80 (dt, $J = 1.6$ and 8.1 Hz, H-7), 8.28 (dd, $J = 1.6$ and 8.0 Hz, H-5) ppm; ^{13}C NMR: $\delta = 49.0$ (C-1′), 49.1 (C-2′), 111.0 (C-3), 117.8 (C-8), 121.9 (C-10), 126.3 (C-6), 126.6 (C-5), 129.3 (C-3″,5″), 129.4 (C-2″,6″), 134.7 (C-7), 135.5 (C-4″), 136.3 (C-1″), 155.1 (C-9), 159.4 (C-2), 172.3 (C-4) ppm; EI-MS: m/z (%) = [526 (1), 524 (5), 522 (9), 520 (8), 518 (3), $M^{+\bullet}$], 445 (17), 443 (57), 441 (63), 439 (40), 364 (23), 362 (62), 360 (55), 283 (60), 281 (100), 245 (51), 218 (37), 205 (29), 189 (37), 161 (28), 126 (52), 109 (40), 92 (36), 75 (25), 63 (29).

2-[1,2-Dibromo-2-(4-methylphenyl)ethyl]chromone (**2c**, $C_{18}H_{14}Br_2O_2$)

Yield: 1.13 g (33%); mp 155–157°C (*Et*OH); ^{1}H NMR: $\delta = 2.40$ (s, 4″-CH_3), 5.25 (d, $J = 11.6$ Hz, H-1′), 5.55 (d, $J = 11.6$ Hz, H-2′), 6.51 (s, H-3), 7.25 (d, $J = 7.7$ Hz, H-3″,5″), 7.41 (d, $J = 7.7$ Hz,

H-2″,6″), 7.46 (ddd, $J = 1.0$, 7.6, and 7.8 Hz, 6-H), 7.60 (d, $J = 7.9$ Hz, 8-H), 7.75 (ddd, $J = 1.7$, 7.6, and 7.9 Hz, H-7), 8.23 (dd, $J = 1.7$ and 7.8 Hz, H-5) ppm; ^{13}C NMR: $\delta = 21.4$ (4″-*C*H$_3$), 50.6 (C-2′), 50.7 (C-1′), 111.6 (C-3), 118.2 (C-8), 124.0 (C-10), 125.7 (C-6), 125.9 (C-5), 127.8 (C-2″,6″), 129.8 (C-3″,5″), 134.3 (C-7), 135.2 (C-1″), 139.7 (C-4″), 156.2 (C-9), 162.7 (C-2), 178.0 (C-4) ppm; EI-MS: m/z (%) = [424 (5), 422 (10), 420 (5), M$^{+\bullet}$], 343 (61), 341 (62), 261 (100), 245 (44), 218 (21), 169 (21), 142 (44), 127 (5), 115 (35), 92 (25), 63 (25).

3-Bromo-2-[1,2-dibromo-2-(4-methylphenyl)ethyl]chromone (**3c**, $C_{18}H_{13}Br_3O_2$)

Yield: 1.70 g (42%); mp 193–195°C (*Et*OH); ^{1}H NMR: $\delta = 2.40$ (s, 4″-C*H*$_3$), 5.61 (d, $J = 11.6$ Hz, H-2′), 6.10 (d, $J = 11.6$ Hz, H-1′), 7.27 (d, $J = 8.0$ Hz, H-3″,5″), 7.44 (d, $J = 8.0$ Hz, H-2″,6″), 7.50 (t, $J = 7.8$ Hz, H-6), 7.63 (d, $J = 8.1$ Hz, H-8), 7.79 (ddd, $J = 1.4$, 7.8, and 8.1 Hz, H-7), 8.28 (dd, $J = 1.4$ and 7.8 Hz, H-5) ppm; ^{13}C NMR: $\delta = 21.4$ (4″-*C*H$_3$), 49.3 (C-1′), 50.3 (C-2′), 110.8 (C-3), 117.9 (C-8), 121.9 (C-10), 126.2 (C-6), 126.6 (C-5), 127.9 (C-2″,6″), 129.8 (C-3″,5″), 134.69 (C-7), 134.74 (C-1″), 139.8 (C-4″), 155.1 (C-9), 159.9 (C-2), 172.4 (C-4) ppm; EI-MS: m/z (%) = [502 (1), 500 (1), M$^{+\bullet}$], 342 (45), 340 (46), 261 (100), 246 (19), 218 (21), 189 (10), 139 (16), 115 (28), 92 (11), 63 (15).

3-Bromo-2-[1,2-dibromo-2-(4-methoxyphenyl)ethyl]chromone (**3d**, $C_{18}H_{13}Br_3O_3$)

Yield: 469 mg (15%); mp 173–175°C (*Et*OH); ^{1}H NMR: $\delta = 3.86$ (s, 4″-OC*H*$_3$), 5.61 (d, $J = 11.6$ Hz, H-2′), 6.09 (d, $J = 11.6$ Hz, H-1′), 6.98 (d, $J = 8.8$ Hz, H-3″,5″), 7.48 (d, $J = 8.8$ Hz, H-2″,6″), 7.50 (ddd, $J = 1.1$, 7.8, and 8.2 Hz, H-6), 7.63 (d, $J = 8.1$ Hz, H-8), 7.79 (ddd, $J = 1.6$, 7.8, and 8.1 Hz, H-7), 8.28 (dd, $J = 1.6$ and 8.2 Hz, H-5) ppm; ^{13}C NMR: $\delta = 49.5$ (C-1′), 50.5 (C-2′), 55.4 (4″-O*C*H$_3$), 110.8 (C-3), 114.4 (C-3″,5″), 117.9 (C-8), 121.9 (C-10), 126.2 (C-6), 126.6 (C-5), 129.4 (C-2″,6″), 129.7 (C-1″), 134.7 (C-7), 155.1 (C-9), 159.9 (C-2), 160.4 (C-4″), 172.4 (C-4) ppm; FAB$^+$-MS: m/z (%) = [518 (1), 516 (1), M$^{+\bullet}$], 460 (100), 443 (21), 357 (29), 348 (13).

3-Bromo-4′-methoxy-2-styrylchromone (**4d**, $C_{18}H_{13}BrO_3$)

Yield 287.7 mg (71%); mp 168–169°C (*Et*OH); ^{1}H NMR: $\delta = 3.87$ (s, 4′-OCH$_3$), 6.96 (d, $J = 8.8$ Hz, H-3′,5′), 7.35 (d, $J = 16.1$ Hz, H-α), 7.41 (ddd, $J = 0.9$, 7.5, and 7.8 Hz, H-6), 7.53 (d, $J = 8.0$ Hz, H-8), 7.61 (d, $J = 8.8$ Hz, H-2′,6′), 7.68 (d, $J = 16.1$ Hz, H-β), 7.70 (ddd, $J = 1.7$, 7.5, and 8.0 Hz, H-7), 8.23 (dd, $J = 1.7$ and 7.8 Hz, H-5) ppm; ^{13}C NMR: $\delta = 55.5$ (4′-OCH$_3$), 109.0 (C-3), 114.6 (C-3′,5′), 116.8 (C-α), 117.5 (C-8), 122.1 (C-10), 125.3 (C-6), 126.4 (C-5), 127.7 (C-1′), 129.8 (C-2′,6′), 134.0 (C-7), 139.4 (C-β), 154.9 (C-9), 158.9 (C-2), 161.5 (C-4′), 172.8 (C-4) ppm; EI-MS: m/z (%) = [358 (51), 356 (50), M$^{+\bullet}$], 277 (100), 262 (39), 234 (50), 205 (34), 193 (16), 178 (15), 127 (9), 114 (32), 92 (19), 63 (26).

(Z)-4′-Methoxy-2-(α-bromostyryl)chromone (**5d**, $C_{18}H_{13}BrO_3$)

Yield: 921 mg (32%); mp 147–149°C (*Et*OH); ^{1}H NMR: $\delta = 3.88$ (s, 4′-OC*H*$_3$), 6.98 (s, H-3), 6.99 (d, $J = 8.8$ Hz, H-3′,5′), 7.42 (ddd, $J = 0.9$, 7.4, and 8.0 Hz, H-6), 7.54 (dd, $J = 0.9$ and 8.1 Hz, H-8), 7.71 (ddd, $J = 1.7$, 7.4, and 8.1 Hz, H-7), 7.90 (d, $J = 8.8$ Hz, H-2′,6′), 8.05 (s, H-β), 8.21 (dd, $J = 1.7$ and 8.0 Hz, H-5) ppm; ^{13}C NMR: $\delta = 55.4$ (4′-O*C*H$_3$), 110.8 (C-α), 110.9 (C-3), 114.0 (C-3′,5′), 117.8 (C-8), 123.6 (C-10), 125.3 (C-6), 125.8 (C-5), 126.8 (C-1′), 132.2 (C-2′,6′), 134.1 (C-7), 134.7 (C-β), 156.0 (C-9), 160.7 (C-2), 160.9 (C-4′), 178.8 (C-4) ppm; EI-MS: m/z (%) = [358 (23), 356 (23), M$^{+\bullet}$], 318 (100), 293 (15), 277 (71), 262 (23), 249 (17), 234 (36), 137 (89), 121 (72), 109 (34), 92 (40), 77 (59), 63 (33).

2-[1,2-Dibromo-2-(4-nitrophenyl)ethyl]chromone (**2e**, $C_{17}H_{11}Br_2NO_4$)

Yield: 290 mg (30%); mp 216–218°C (*Et*OH); ^{1}H NMR: $\delta = 5.23$ (d, $J = 11.6$ Hz, H-1′), 5.62 (d, $J = 11.6$ Hz, H-2′), 6.54 (s, H-3), 7.48 (ddd, $J = 0.9$, 7.6, and 7.8 Hz, H-6), 7.60 (d, $J = 7.9$ Hz, H-8),

7.72 (d, $J = 8.8$ Hz, H-2″,6″), 7.77 (ddd, $J = 1.7$, 7.6, and 7.9 Hz, H-7), 8.24 (dd, $J = 1.7$ and 7.8 Hz, H-5), 8.32 (d, $J = 8.8$ Hz, H-3″,5″) ppm; ^{13}C NMR: $\delta = 48.0$ (C-2′), 49.6 (C-1′), 111.9 (C-3), 118.1 (C-8), 123.9 (C-10), 124.3 (C-3″,5″), 125.86 (C-6), 125.91 (C-5), 129.1 (C-2″,6″), 134.4 (C-7), 144.9 (C-1″), 148.2 (C-4″), 156.1 (C-9), 161.6 (C-2), 177.7 (C-4) ppm; EI-MS: m/z (%) = [455 (8), 453 (14), 451 (8), $M^{+\bullet}$], 374 (43), 372 (47), 356 (15), 292 (100), 276 (43), 246 (62), 218 (31), 189 (33), 121 (51), 92 (60).

3-Bromo-2-[1,2-dibromo-2-(4-nitrophenyl)ethyl]chromone (**3e**, $C_{17}H_{10}Br_3NO_4$)

Yield: 181 g (16%); mp 220–224°C (*Et*OH); ^{1}H NMR: $\delta = 5.67$ (d, $J = 11.6$ Hz, H-2′), 6.06 (d, $J = 11.6$ Hz, H-1′), 7.53 (ddd, $J = 1.0$, 7.4, and 8.1 Hz, H-6), 7.64 (d, $J = 8.1$ Hz, H-8), 7.75 (d, $J = 8.8$ Hz, H-2″,6″), 7.82 (ddd, $J = 1.7$, 7.4, and 8.1 Hz, H-7), 8.29 (dd, $J = 1.7$ and 8.1 Hz, H-5), 8.34 (d, $J = 8.8$ Hz, H-3″,5″) ppm; ^{13}C NMR: $\delta = 47.7$ (C-1′), 48.3 (C-2′), 111.3 (C-3), 117.8 (C-8), 121.9 (C-10), 124.3 (C-3″,5″), 126.4 (C-6), 126.7 (C-5), 129.2 (C-2″,6″), 134.8 (C-7), 144.5 (C-1″), 148.3 (C-4″), 155.1 (C-9), 158.8 (C-2), 172.1 (C-4) ppm; EI-MS: m/z (%) = [535 (2), 533 (6), 531 (6), 529 (2), $M^{+\bullet}$], 452 (16), 454 (10), 450 (10), 373 (59), 371 (59), 292 (73), 245 (100), 218 (40), 189 (44), 126 (33), 109 (12), 92 (41).

3-Bromo-4′-nitro-2-styrylchromone (**4e**, $C_{17}H_{10}BrNO_4$)

Yield: 59.7 mg (15%); mp 260–262°C (*Et*OH); ^{1}H NMR (35°C): $\delta = 7.47$ (ddd, $J = 0.9$, 7.2, and 8.0 Hz, H-6), 7.58 (d, $J = 8.0$ Hz, H-8), 7.65 (d, $J = 15.9$ Hz, H-α), 7.76 (ddd, $J = 1.6$, 7.2 and 8.0 Hz, H-7), 7.77 (d, $J = 15.9$ Hz, H-β), 7.81 (d, $J = 8.8$ Hz, H-2′,6′), 8.27 (dd, $J = 1.6$ and 8.0 Hz, H-5), 8.32 (d, $J = 8.8$ Hz, H-3′,5′) ppm; ^{13}C NMR (35°C): $\delta = 112.4$ (C-3), 117.6 (C-8), 122.1 (C-10), 123.6 (C-α), 124.4 (C-3′,5′), 125.7 (C-6), 126.6 (C-5), 128.5 (C-2′,6′), 134.4 (C-7), 136.4 (C-β), 141.0 (C-1′), 148.5 (C-4′), 154.9 (C-9), 157.2 (C-2), 172.6 (C-4) ppm; EI-MS: m/z (%) = [373 (55), 371 (55), $M^{+\bullet}$], 292 (73), 245 (100), 234 (15), 218 (41), 205 (15), 189 (40), 126 (34), 109 (9), 92 (41), 63 (18).

(Z)-4′-Nitro-2-(α-bromostyryl)chromone (**5e**, $C_{17}H_{10}BrNO_4$)

Yield: 206 mg (26%); mp 228–230°C (*Et*OH); ^{1}H NMR (35°C): $\delta = 7.01$ (s, H-3), 7.44 (ddd, $J = 1.0$, 7.7, and 7.8 Hz, H-6), 7.54 (d, $J = 7.8$ Hz, H-8), 7.73 (ddd, $J = 1.7$, 7.7, and 7.8 Hz, H-7), 7.94 (d, $J = 9.0$ Hz, H-2′,6′), 8.12 (s, H-β), 8.22 (dd, $J = 1.7$ and 7.8 Hz, H-5), 8.31 (d, $J = 9.0$ Hz, H-3′,5′) ppm; ^{13}C NMR (35°C): $\delta = 112.5$ (C-3), 117.7 (C-α), 117.8 (C-8), 123.7 (C-10), 123.7 (C-3′,5′), 125.7 (C-5), 125.9 (C-6), 130.6 (C-2′,6′), 132.8 (C-β), 134.4 (C-7), 140.8 (C-1″), 148.0 (C-4′), 156.0 (C-9), 159.3 (C-2), 178.3 (C-4) ppm; EI-MS: m/z (%) = [373 (14), 371 (14), $M^{+\bullet}$], 354 (27), 292 (100), 246 (66), 218 (22), 189 (33), 121 (41), 92 (44).

6,8-Dibromo-5-hydroxy-2-styrylchromone

Yield: 2.01 g (59%); mp 241–243°C (Ref. [15] 241–243°C).

8-Bromo-5-hydroxy-2-styrylchromone

Yield: 110.6 mg (4%); mp 175–177°C (Ref. [15] 175–178°C).

6-Bromo-5-hydroxy-2-styrylchromone

Yield: 56 mg (2%); mp 222–225°C (Ref. [15] 223–225°C).

3,8-Dibromo-2-(1,2-dibromo-2-phenylethyl)-5-hydroxychromone ($C_{17}H_{10}Br_4O_3$)

Yield: 469 mg (44%); mp 155–157°C (*Et*OH); ^{1}H NMR: $\delta = 5.67$ (d, $J = 11.5$ Hz, H-2′), 6.00 (d, $J = 11.5$ Hz, H-1′), 6.87 (d, $J = 8.8$ Hz, H-6), 7.43–7.50 (m, H-3′,4′,5′), 7.56 (dd, $J = 1.6$ and 7.7 Hz, H-2′,6′), 7.84 (d, $J = 8.8$ Hz, H-7), 11.95 (s, 5-O*H*) ppm; ^{13}C NMR: $\delta = 48.4$ (C-1′), 50.1 (C-2′), 98.3 (C-8), 108.5 (C-3), 110.4 (C-10), 113.6 (C-6), 128.2 (C-2′,6′), 129.1 (C-3′,5′), 129.8 (C-4′), 137.3 (C-1′), 139.3 (C-7), 151.2 (C-9), 159.8 (C-5), 161.4 (C-2), 177.3 (C-4) ppm; EI-MS: m/z (%) = [586 (3), 584 (4), 582 (4), 580 (4), 578 (4)], 502 (8), 422 (100), 343 (60), 263 (36), 234 (11), 205 (13), 171 (14), 127 (55), 77 (23).

Dehydrobromination of 2-(2-aryl-1,2-dibromoethyl)chromone ***2a–2c***

Triethylamine (25.9 cm^3, 0.187 mol) was added to a solution of the appropriate 2-(2-aryl-1,2-dibromoethyl)chromone **2a**–**2c** (3.98 mmol) in 50 cm^3 of toluene and the resulting mixture was stirred at reflux, for 2 h. After cooling to room temperature the formed solid triethylammonium bromide was filtered off and the filtrate was taken up in 150 cm^3 of $CHCl_3$. The organic layer was washed with H_2O (2×150 cm^3), dried (Na_2SO_4) and then evaporated. The residue in each case was recrystallised from ethanol allowing the separation of the solid (*Z*)-2-(α-bromostyryl)chromones **5a**–**5c** from the oil of (*E*)-2-(α-bromostyryl)chromones **6a**–**6c**.

(Z)-2-(α-Bromostyryl)chromone (**5a**, $C_{17}H_{11}BrO_2$)

Yield: 846 mg (65%); mp 117–120°C (*Et*OH); ^{1}H NMR: $\delta = 7.00$ (s, H-3), 7.40–7.50 (m, H-6 and H-3′,4′,5′), 7.55 (d, $J = 8.2$ Hz, H-8), 7.72 (ddd, $J = 1.6$, 7.8, and 8.2 Hz, H-7), 7.84 (dd, $J = 1.9$ and 7.6 Hz, H-2′,6′), 8.10 (s, H-β), 8.21 (dd, $J = 1.6$ and 8.0 Hz, H-5) ppm; ^{13}C NMR: $\delta = 111.5$ (C-3), 113.5 (C-α), 117.8 (C-8), 123.5 (C-10), 125.4 (C-6), 125.7 (C-5), 128.5 (C-3′,5′), 130.1 (C-2′,6′), 129.8 (C-4′), 134.2 (C-7), 134.3 (C-1′), 135.2 (C-β), 156.0 (C-9), 160.3 (C-2), 178.7 (C-4) ppm; EI-MS: m/z (%) = [328 (19), 326 (18), $M^{+\bullet}$], 311 (17), 247 (100), 218 (13), 189 (13), 127 (19), 92 (15), 77 (12).

(E)-2-(α-Bromostyryl)chromone (**6a**, $C_{17}H_{11}BrO_2$)

Yield: 417 mg (32%); yellowish oil; ^{1}H NMR: $\delta = 6.46$ (s, H-3), 7.17–7.29 (m, H-8 and H-2′,3′,4′,5′,6′), 7.40 (ddd, $J = 1.0$, 7.7, and 8.1 Hz, H-6), 7.46 (s, H-β), 7.64 (ddd, $J = 1.7$, 7.6, and 8.1 Hz, H-7), 8.16 (dd, $J = 1.7$ and 7.7 Hz, H-5) ppm; ^{13}C NMR: $\delta = 112.1$ (C-α), 112.9 (C-3), 118.1 (C-8), 123.7 (C-10), 125.4 (C-6), 125.5 (C-5), 128.2 (C-3′,5′), 128.5 (C-2′,6′), 128.9 (C-4′), 134.0 (C-7), 134.8 (C-1′), 140.1 (C-β), 155.9 (C-9), 160.8 (C-2), 177.9 (C-4) ppm; EI-MS: m/z (%) = [328 (9), 326 (9), $M^{+\bullet}$], 309 (12), 247 (100), 218 (12), 189 (13), 127 (23), 92 (17), 77 (15).

(Z)-4′-Chloro-2-(α-bromostyryl)chromone (**5b**, $C_{17}H_{10}BrClO_2$)

Yield: 1.28 g (89%); mp 181–182°C (*Et*OH); ^{1}H NMR: $\delta = 6.99$ (s, H-3), 7.41 (dt, $J = 7.9$ and 8.1 Hz, H-6), 7.44 (d, $J = 8.5$ Hz, H-3′,5′), 7.54 (d, $J = 8.1$ Hz, H-8), 7.72 (dt, $J = 1.5$ and 8.1 Hz, H-7), 7.79 (d, $J = 8.5$ Hz, H-2′,6′), 8.05 (s, H-β), 8.21 (dd, $J = 1.5$ and 7.9 Hz, H-5) ppm; ^{13}C NMR: $\delta = 111.7$ (C-3), 114.3 (C-α), 117.8 (C-8), 123.6 (C-10), 125.5 (C-6), 125.8 (C-5), 128.8 (C-3′,5′), 131.3 (C-2′,6′), 132.8 (C-1′), 133.9 (C-β), 134.3 (C-7), 135.8 (C-4′), 156.0 (C-9), 160.0 (C-2), 178.6 (C-4) ppm; EI-MS: m/z (%) = [364 (9), 362 (21), 360 (18), $M^{+\bullet}$], 345 (26), 281 (100), 246 (26), 218 (25), 189 (15), 121 (29), 109 (26), 92 (29), 63 (20).

(E)-4′-Chloro-2-(α-bromostyryl)chromone (**6b**, $C_{17}H_{10}BrClO_2$)

Yield: 58 mg (4%); yellowish oil; ^{1}H NMR: $\delta = 6.47$ (s, H-3), 7.13 (d, $J = 8.5$ Hz, H-3′,5′), 7.24 (d, $J = 8.5$ Hz, H-2′,6′), 7.26 (dd, $J = 1.0$ and 8.1 Hz, H-8), 7.40 (s, H-β), 7.42 (ddd, $J = 1.0$, 7.6, and

8.0 Hz, H-6), 7.67 (ddd, $J = 1.6$, 7.6, and 8.1 Hz, H-7), 8.17 (dd, $J = 1.6$ and 8.0 Hz, H-5) ppm; ^{13}C NMR: $\delta = 112.9$ (C-α), 113.1 (C-3), 118.1 (C-8), 123.8 (C-10), 125.6 (C-5), 125.6 (C-6), 128.9 (C-2′,6′), 129.6 (C-3′,5′), 133.3 (C-1′), 134.3 (C-7), 134.9 (C-4′), 138.7 (C-β), 156.0 (C-9), 160.5 (C-2), 177.9 (C-4) ppm; EI-MS: m/z (%) = [364 (7), 362 (22), 360 (18), $M^{+\bullet}$] 345 (28), 281 (100), 246 (28), 218 (27), 189 (21), 161 (17), 126 (38), 121 (43), 109 (22), 92 (35), 75 (18), 63 (20).

(Z)-4′-Methyl-2-(α-bromostyryl)chromone (**5c**, $C_{18}H_{13}BrO_2$)

Yield: 964 mg (71%); mp 124–126°C (*Et*OH); ^{1}H NMR: $\delta = 2.41$ (s, 4′-CH_3), 6.99 (s, H-3), 7.28 (d, $J = 8.3$ Hz, H-3′,5′), 7.43 (ddd, $J = 1.1$, 7.6, and 7.8 Hz, H-6), 7.55 (d, $J = 7.8$ Hz, H-8), 7.72 (ddd, $J = 1.7$, 7.6, and 7.8 Hz, H-7), 7.78 (d, $J = 8.3$ Hz, H-2′,6′), 8.08 (s, H-β), 8.21 (dd, $J = 1.7$ and 7.8 Hz, H-5) ppm; ^{13}C NMR: $\delta = 21.6$ (4′-*C*H_3), 111.3 (C-3), 112.5 (C-α), 117.9 (C-8), 123.6 (C-10), 125.4 (C-6), 125.8 (C-5), 129.3 (C-3′,5′), 130.2 (C-2′,6′), 131.5 (C-1′), 134.1 (C-7), 135.2 (C-β), 140.4 (C-4′), 156.0 (C-9), 160.5 (C-2), 178.8 (C-4) ppm; EI-MS: m/z (%) = [342 (15), 340 (15), $M^{+\bullet}$], 325 (21), 261 (100), 246 (15), 218 (19), 141 (19), 115 (23), 92 (16), 63 (18).

(E)-4′-Methyl-2-(α-bromostyryl)chromone (**6c**, $C_{18}H_{13}BrO_2$)

Yield: 41 mg (3%); yellowish oil; ^{1}H NMR: $\delta = 2.30$ (s, 4′-CH_3), 6.44 (s, H-3), 7.04–7.10 (m, H-2′,3′,5′,6′), 7.34 (d, $J = 7.9$ Hz, H-8), 7.42 (s, H-β), 7.42 (ddd, $J = 0.9$, 7.6, and 7.9 Hz, H-6), 7.68 (ddd, $J = 1.7$, 7.6, and 7.9 Hz, H-7), 8.18 (dd, $J = 1.7$ and 7.9 Hz, H-5) ppm; ^{13}C NMR: $\delta = 21.3$ (4′-*C*H_3), 111.1 (C-α), 112.9 (C-3), 118.3 (C-8), 123.9 (C-10), 125.5 (C-6), 125.6 (C-5), 128.3 (C-2′,6′), 129.4 (C-3′,5′), 131.9 (C-1′), 134.1 (C-7), 139.3 (C-4′), 140.1 (C-β), 156.2 (C-9), 161.2 (C-2), 178.1 (C-4) ppm; EI-MS: m/z (%) = [342 (11), 340 (11), $M^{+\bullet}$], 325 (20), 261 (100), 246 (14), 218 (18), 189 (8), 139 (14), 115 (23), 97 (21).

Syntheses of 4(5)-aryl-5(4)-(2-chromonyl)-1,2,3-triazoles ***7a–7e***

Method A – From (Z)-2-(α-bromostyryl)chromones **5a–5c**. 0.293 g of NaN_3 (4.51 mmol) were added to a solution of the appropriate (*Z*)–2-(α-bromostyryl)chromone **5a–5c** (0.902 mmol) in 25 cm^3 of dry *DMF*. The reaction mixture was heated (120°C) with stirring for 24 h then poured into 200 cm^3 of H_2O, ice (100 g), and HCl (*pH* adjusted to 3). The obtained solid was filtered, washed with water, and taken up in 100 cm^3 of acetone. The organic layer was dried (Na_2SO_4) and then evaporated. The residue in each case was recrystallised from a mixture of dichloromethane:methanol = 9:1 giving the corresponding 4(5)-aryl-5(4)-(2-chromonyl)-1,2,3-triazoles (**7a**, 80%, 209 mg), (**7b**, 83%, 243 mg), and (**7c**, 61%, 167 mg).

Method B – From 2-(2-aryl-1,2-dibromoethyl)chromones **2a–2c**. When 2-(2-aryl-1,2-dibromoethyl)chromones **2a–2c** were treated with NaN_3 and worked up according to the experimental procedure of Method A 4(5)-aryl-(4)-(2-chromonyl)-1,2,3-triazoles (**7a**, 73%, 191 mg), (**7b**, 69%, 201 mg), and (**7c**, 54%, 148 mg) were obtained.

Method C – From 2-styrylchromones **1a–1e**. The reaction of 2-styrylchromones **1a–1e** with NaN_3 according to the experimental procedure of Method A resulted in the corresponding 4(5)-aryl-(4)-(2-chromonyl)-1,2,3-triazoles (**7a**, 55%, 144 mg), (**7b**, 59%, 172 mg), (**7c**, 48%, 131 mg), (**7d**, 47%, 135 mg), and (**7e**, 65%, 196 mg).

5(4)-(2-Chromonyl)-4(5)-phenyl-1,2,3-triazole (**7a**, $C_{17}H_{11}N_3O_2$)

Mp 233–235°C (*Et*OH). ^{1}H NMR (*DMSO*-d_6 + *TFA*): $\delta = 6.78$ (s, H-3′), 7.17 (d, $J = 8.4$ Hz, H-8′), 7.45 (t, $J = 7.7$ Hz, H-6′), 7.52–7.54 (m, H-3″,4″,5″), 7.68–7.76 (m, H-7′ and H-2″,6″), 8.03 (dd, $J = 1.3$ and 7.7 Hz, H-5′) ppm; ^{13}C NMR (*DMSO*-d_6 + *TFA*): $\delta = 108.4$ (C-3′), 118.1 (C-8′), 124.0 (C-

10′), 125.2 (C-5′), 125.9 (C-6′), 128.5 (C-1″), 128.7 (C-3″,5″), 129.5 (C-2″,6″), 129.8 (C-4″), 134.6 (C-7′), 135.4 (C-4), 142.1 (C-5), 155.7 (C-9′), 157.8 (C-2′), 176.8 (C-4′) ppm; EI-MS: $m/z(\%) = 289$ (37) [$M^{+\bullet}$], 288 (100) [M-H]$^+$, 272 (8), 169 (10), 121 (28), 92 (26).

4(5)-(4-Chlorophenyl)-5(4)-(2-chromonyl)-1,2,3-triazole (**7b**, $C_{17}H_{10}ClN_3O_2$)

Mp 299–301°C (*Et*OH); ^{1}H NMR (*DMSO*-d_6 + *TFA*): $\delta = 6.78$ (s, H-3′), 7.22 (d, $J = 8.0$ Hz, H-8′), 7.45 (ddd, $J = 0.7$, 7.6, and 7.8 Hz, H-6′), 7.59 (d, $J = 8.5$ Hz, H-3″,5″), 7.63 (d, $J = 8.5$ Hz, H-2″,6″), 7.74 (ddd, $J = 1.6$, 7.6, and 8.0 Hz, H-7′), 8.03 (dd, $J = 1.6$ and 7.8 Hz, H-5′) ppm; ^{13}C NMR (*DMSO*-d_6 + *TFA*): $\delta = 108.6$ (C-3′), 118.3 (C-8′), 124.0 (C-10′), 125.2. (C-5′), 125.9 (C-6′), 127.7 (C-1″), 128.8 (C-3″,5″), 131.3 (C-2″,6″), 134.7 (C-7′ and C-4), 135.6 (C-4″), 141.6 (C-5), 155.7 (C-9′), 157.8 (C-2′), 176.8 (C-4′) ppm; EI-MS: m/z (%) = [325 (4), 323 (16), $M^{+\bullet}$], 322 (41), 161 (34), 131 (100), 121 (24), 103 (36), 92 (24).

5(4)-(2-Chromonyl)-4(5)-(4-methylphenyl)-1,2,3-triazole (**7c**, $C_{18}H_{13}N_3O_2$)

Mp 258–260°C (*Et*OH); ^{1}H NMR (*DMSO*-d_6 + *TFA*): $\delta = 2.39$ (s, 4″-CH_3), 6.76 (s, H-3′), 7.24 (d, $J = 8.1$ Hz, H-8′), 7.35 (d, $J = 8.0$ Hz, H-3″,5″), 7.46 (t, $J = 7.7$ Hz, H-6′), 7.59 (d, $J = 8.0$ Hz, H-2″,6″), 7.75 (ddd, $J = 1.6$, 7.7, and 8.1 Hz, H-7′), 8.03 (dd, $J = 1.6$ and 7.7 Hz, H-5′) ppm; ^{13}C NMR (*DMSO*-d_6 + *TFA*): $\delta = 21.0$ (4″-CH_3), 108.2 (C-3′), 118.1 (C-8′), 120.9 (C-1″), 123.9 (C-10′), 125.1 (C-5′), 125.8 (C-6′), 129.2 (C-2″,6″ and C-3″,5″), 134.5 (C-7′), 135.0 (C-4), 139.4 (C-4″), 141.6 (C-5), 155.6 (C-9′), 157.8 (C-2′), 176.6 (C-4′) ppm; EI-MS: m/z (%) = 303 (52) [$M^{+\bullet}$], 302 (100) [M-H]$^+$, 275 (9), 247 (11), 121 (33), 103 (9), 92 (22).

5(4)-(2-Chromonyl)-4(5)-(4-methoxyphenyl)-1,2,3-triazole (**7d**, $C_{18}H_{13}N_3O_3$)

Mp 261–263°C (*Et*OH); ^{1}H NMR (*DMSO*-d_6 + *TFA*): $\delta = 3.85$ (s, 4″-OCH_3), 6.77 (s, H-3′), 7.12 (d, $J = 8.8$ Hz, H-3″,5″), 7.30 (d, $J = 8.4$ Hz, H-8′), 7.49 (t, $J = 7.6$ Hz, H-6′), 7.67 (d, $J = 8.8$ Hz, H-2″,6″), 7.79 (ddd, $J = 1.6$, 7.6, and 8.4 Hz, H-7′), 8.05 (dd, $J = 1.6$ and 7.6 Hz, H-5′) ppm; ^{13}C NMR (*DMSO*-d_6 + *TFA*): $\delta = 55.9$ (4″-OCH_3), 108.9 (C-3′), 114.8 (C-3″,5″), 118.6 (C-8′), 121.1 (C-1″), 124.9 (C-10′), 126.0 (C-5′), 126.4 (C-6′), 131.7 (C-2″,6″), 135.1 (C-7′), 135.7 (C-4), 142.2 (C-5), 156.6 (C-9′), 159.0 (C-2′), 161.5 (C-4″), 177.8 (C-4′) ppm; EI-MS: $m/z(\%) = 319$ (43) [$M^{+\bullet}$], 318 (39) [M-H]$^+$, 161 (59), 131 (100), 121 (23), 103 (35), 92 (18), 78 (41), 63 (62).

5(4)-(2-Chromonyl)-4(5)-(4-nitrophenyl)-1,2,3-triazole (**7e**, $C_{17}H_{10}N_4O_4$)

Mp > 300°C (*Et*OH); ^{1}H NMR (*DMSO*-d_6 + *TFA*): $\delta = 6.84$ (s, H-3′), 7.29 (d, $J = 8.0$ Hz, H-8′) 7.51 (t, $J = 7.7$ Hz, H-6′), 7.78 (dt, $J = 1.6$ and 8.0 Hz, H-7′), 8.04 (d, $J = 8.7$ Hz, H-2″,6″), 8.04 (dd, $J = 1.6$ and 7.7 Hz, H-5′), 8.39 (d, $J = 8.7$ Hz, H-3″,5″) ppm; ^{13}C NMR (*DMSO*-d_6 + *TFA*): $\delta = 109.5$ (C-3′), 118.7 (C-8′), 124.2 (C-3″,5), 124.6 (C-10′), 125.7 (C-5′), 126.3 (C-6′), 131.1 (C-2″,6″), 135.0 (C-7′), 136.6 (C-1″), 136.8 (C-4), 142.5 (C-5), 148.6 (C-4″), 156.3 (C-9′), 157.6 (C-2′), 177.4 (C-4′) ppm; EI-MS: m/z (%) = 334 (36) [$M^{+\bullet}$], 333 (100) [M-H]$^+$, 317 (10), 287 (7), 259 (7), 205 (8), 120 (25), 92 (41).

Synthesis of 5(4)-[5-(benzyloxy and hydroxy)-2-chromonyl]-4(5)-phenyl-1,2,3-triazoles ***7f, 7g***

NaN_3 (14 g, 02.11 mmol) was added to a solution of 0.15 g of 5-benzyloxy-2-styrylchromone **1f** (0.42 mmol) in 25 cm^3 of dry *DMF*. The reaction mixture was heated with stirring at 120°C under N_2 for 5 days then poured into a mixture of 200 cm^3 of H_2O, ice (100 g), and HCl (*pH* adjusted to 3).

The obtained solid was filtered off, washed with water, and taken up in 100 cm^3 of CH_2Cl_2. The organic layer was washed with H_2O ($2 \times 100\,cm^3$), dried (Na_2SO_4), and evaporated. The obtained residue was purified by TLC (using a 9:1 mixture of CH_2Cl_2:ethyl acetate as eluent). After several elutions, two spots were collected. The fraction of higher R_f value was **7g** followed by **7f**. After removal of the solvent, each residue was recrystallised from ethanol.

5(4)-(5-Benzyloxy-2-chromonyl)-4(5)-phenyl-1,2,3-triazole (**7f**, $C_{24}H_{17}N_3O_3$)

Yield: 34 mg (21%); mp 210–211°C (*Et*OH); ^{1}H NMR (*DMSO*-d_6 + *TFA*): $\delta = 5.25$ (s, 5′-OC*H*$_2$C$_6$H$_5$), 6.60 (s, H-3′), 6.70 (d, $J = 8.2$ Hz, H-6′), 7.07 (d, $J = 8.2$ Hz, H-8′), 7.29–7.43 (m, H-3,4,5 of 5′-OCH$_2$C$_6$*H*$_5$), 7.52–7.56 (m, H-3″,4″,5″), 7.60–7.63 (m, H-7′ and H-2,6 of 5′-OCH$_2$C$_6$*H*$_5$), 7.69 (dd, $J = 2.2$ and 7.5 Hz, H-2″,6″) ppm; ^{13}C NMR (*DMSO*-d_6 + *TFA*): $\delta = 70.4$ (5′-O*C*H$_2$C$_6$H$_5$), 109.2 (C-8′), 110.2 (C-3′), 110.2 (C-6′), 115.0 (C-10′), 127.3 (C-2,6 of 5′-OCH$_2$*C*$_6$H$_5$), 127.9 (C-4 of 5′-OCH$_2$*C*$_6$H$_5$), 128.7 (C-3,5 of 5′-OCH$_2$*C*$_6$H$_5$), 128.8 (C-3″,5″), 129.6 (C-2″,6″ and C-1″), 129.8 (C-4″), 134.7 (C-7′), 135.3 (C-4), 137.3 (C-1 of 5′-OCH$_2$*C*$_6$H$_5$), 142.1 (C-5), 155.7 (C-9′), 157.9 (C-5′), 158.5 (C-2′), 176.4 (C-4′) ppm; EI-MS: m/z (%) = 395 (18) [$M^{+\bullet}$], 305 (100), 289 (7), 276 (9), 196 (9), 170 (10), 137 (29), 108 (25), 84 (69).

5(4)-(5-Hydroxy-2-chromonyl)-4(5)-phenyl-1,2,3-triazole (**7g**, $C_{17}H_{11}N_3O_3$)

Yield: 32 mg (25%); mp 217–219°C (*Et*OH); ^{1}H NMR (*DMSO*-d_6 + *TFA*): $\delta = 6.60$ (d, $J = 8.3$ Hz, H-6′), 6.81 (d, $J = 8.3$ Hz, H-8′), 6.81 (s, H-3′), 7.53–7.57 (m, H-3″,4″,5″), 7.61 (t, $J = 8.3$ Hz, H-7′), 7.71 (dd, $J = 2.3$ and 7.5 Hz, H-2″,6″), 12.64 (s, 5′-O*H*) ppm; ^{13}C NMR (*DMSO*-d_6 + *TFA*): $\delta = 106.7$ (C-8′), 107.3 (C-6′), 111.5 (C-3′), 110.7 (C-10′), 128.1 (C-1″), 128.7 (C-3″,5″), 129.6 (C-2″,6″), 129.9 (C-4″), 135.0 (C-4), 136.2 (C-7′), 149.6 (C-5), 155.8 (C-9′), 159.3 (C-5′), 160.2 (C-2′), 182.9 (C-4′) ppm; EI-MS: m/z (%) = 305 (100) [$M^{+\bullet}$], 276 (6), 196 (11), 170 (11), 137 (33), 108 (27), 91 (12), 84 (24), 66 (32).

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References

[1] a) L'Abbé G (1969) Chem Rev **69**: 345; b) Gilchrist TL, Ghymer GE (1974) Adv Heterocycl Chem **16**: 33; c) Wamhoff H (1984) In: Katritzky AR, Rees CW, Potts KV (eds) Comprehensive Heterocyclic Chemistry, vol 4, Pergamon, Oxford, p 669; d) Dehne H (1994) In: Schaumann E (ed) Houben-Weyl, Hetarene III, Teil 4, Band E8d. Thieme, Stuttgart, p 305

[2] Some selected activities published recently: a) Brockunier LL, Parmee ER, Ok HO, Candelore MR, Cascieri MA, Colwell LF, Deng LF, Feeney WP, Forrest MJ, Hom GJ, McIntyre DE, Tota L, Wyvratt MJ, Fisher MH, Weber AE (2000) Bioorg Med Chem Lett **10**: 2111; b) Genin MJ, Allwine DA, Anderson DJ, Barbachyn MR, Emmert DE, Garmon SA, Graber DR, Grega KC, Hester JB, Hutchinson DK, Morris J, Reischer RJ, Ford CW, Zurenko GE, Hamel JC, Schaadt RD, Stapert D, Yagi BH (2000) J Med Chem **43**: 953; c) Sorbera LA, Leeson FA, Rabasseda X, Castaner J (2000) Drug Future **25**: 1145; d) Chen MD, Lu SJ, Yang YH, Du XL, Yuan GP, Yang SY (2001) Chinese J Org Chem **21**: 1147; e) Lazrek HB, Taourirte M, Oulih T, Barascut JL,

Imbach JL, Pannecouque C, Witrouw M, DeClerq E (2001) Nucleos Nucleot Nucleic Acids **20**: 1949; f) Himanshu TR, Olsen CE, Errington W, Parmar VS, Prasad AK (2002) Bioorg Med Chem **10**: 963

[3] Dean FM, Johnson RS (1981) J Chem Soc Perkin Trans 1: 224

[4] a) Mouysset G, Grassy G, Payard M, Commenges G, Carpy A, Couquelet J (1988) J Heterocycl Chem **25**: 1167; b) Danoun S, Baziard-Mouysset G, Stigliani JL, Commenges G, Carpy A, Payard M (1995) Bull Soc Chem Fr **132**: 943

[5] Mouysset G, Payard M, Couquelet J, Bastide P, Stenger A, Delhon A, Tisneversailles J (1990) Farmaco **45**: 847

[6] Liu FM, Yu JX, Wang M, Liu YT, Chen YZ (1998) Chem J Chinese Univ **19**: 1081

[7] Katritzky AR, Pozharskii AF (2000) Handbook of Heterocyclic Chemistry, 2nd ed. Pergamon, Amsterdam

[8] Bastide J, Hamelin J, Texier F, Quang YV (1973) Bull Soc Chim Fr 2555–2579 and 2871

[9] Kadaba K (1973) Synthesis: 71

[10] a) Ykman P, L'Abbé G, Smets G (1971) Tetrahedron **27**: 845; b) Ykman P, Mathys G, L'Abbé G, Smets G (1972) J Org Chem **37**: 3213

[11] a) Meek JS, Fowler JS (1967) J Am Chem Soc **89**: 1967; b) Wörner FP, Reimlinger H (1970) Chem Ber **103**: 1908; c) Khisatmudinov GH, Bondarenko OA, Kuprianova LA (1975) Zh Org Khim **11**: 2445

[12] Pinto DCGA, Silva AMS, Almeida LMPM, Cavaleiro JAS, Lévai A, Patonay T (1998) J Heterocycl Chem **35**: 217

[13] Patonay T, Bognár R, Litkei G (1984) Tetrahedron **40**: 2555

[14] The first results of this work has been reported in a preliminary communication: Silva AMS, Vieira JS, Cavaleiro JAS, Patonay T, Lévai A, Elguero J (1999) Heterocycles **51**: 481

[15] a) Pinto DCGA, Silva AMS, Cavaleiro JAS (1994) Tetrahedron Lett **35**: 9459; b) Pinto DCGA, Silva AMS, Cavaleiro JAS (1996) J Heterocycl Chem **33**: 1887

[16] a) Donnelly DJ, Donnelly JA, Keegan JR (1977) Tetrahedron **33**: 3289; b) Reddy NJ, Bokadia M, Sharma TC, Donnelly JA (1981) J Org Chem **46**: 638; c) Paranjape MV, Wadodkar KN (1981) Indian J Chem **20B**: 808; d) David SK, Main L, Old KB (1981) J Chem Soc Perkin Trans 2: 1367; e) Dhar DN (1981) The Chemistry of Chalcones and Related Compounds. Wiley-Interscience: New York

[17] Garay RO, Cabaleiro MC (1990) J Chem Res S: 166

[18] Cabaleiro MC, Garay RO (1984) J Chem Soc Perkin Trans 2: 179

[19] Hassner A (1984) In: Scriven EFV (ed) Azides and Nitrenes – Reactivity and Utility. Academic Press, Florida, p 35

[20] Bax A (1984) J Magn Reson **57**: 314

[21] a) Silva AMS, Pinto DCGA, Cavaleiro JAS (1994) Tetrahedron Lett **35**: 5899; b) Silva AMS, Pinto DCGA, Tavares HR, Cavaleiro JAS, Jimeno ML, Elguero J (1998) Eur J Org Chem: 2031; c) Pinto DCGA, Silva AMS, Cavaleiro JAS, Foces-Foces C, Llamas-Sainz A, Jagerovic N, Elguero J (1999) Tetrahedron **55**: 10187; d) Pinto DCGA, Silva AMS, Cavaleiro JAS (2000) New J Chem **24**: 85