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Reinvestigation of prototropic photochromism: 3-benzoyl-2-benzylchromones

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Abstract—The synthesis of a series of new nine 3-benzoyl-2-benzylchromones is developed through a classical and an optimized Kostanecki–Robinson method involving an *o*-hydroxyphenyl-β-diketone and an acid anhydride. The different spectrokinetic studies carried out in solution and in polymer matrixes have highlighted the main structure/photochromic parameters relationships and the influence of the medium on the photochromic properties.

1. Introduction

The recent marketing of variable optical transmission glasses based on thermoreversible organic photochromes involving electrocyclisation reactions such as spirooxazines and chromenes has known growing success.[1,2] The two main limitations of these compounds, regarding their applications, arise from the high dependency of the photochromic properties of these molecules to the temperature and also their relatively low fatigue resistance.[2,3]

In order to by-pass these disadvantages, the conception of new systems involving hydrogen transfer has been undertaken. In such systems the reversible hydrogen shift between two centers of the molecule induces a modification of the electronic structure and then a change in absorption spectra. The principal advantages of these prototropic systems are: (i) they are thermally and/or photochemicaly reversible and they could probably present a good resistance to the fatigue;[4] (ii) they do not involve important structural modification: then lower activation energy for the thermal decoloration could be expected compared to systems involving electrocyclisation which induce important molecular motion. On the other hand, this limited molecular reorganization makes the prototropic system able to work as well in constrained medium (rigid polymeric matrix, solid state) or not constrained medium (solution, flexible polymeric matrix).

Among the prototropic photochromic systems, compounds such as 3-benzoyl-2-benzylchromones, described in a specific way about 30 years ago,[5] but not developed thereafter, seem to be promising by a broad range of possible structural variations and potential photochromic properties (Scheme 1).[6]

This work presents a synthetic approach to a series of such chromones and a preliminary study of their photochromic properties under continuous irradiation conditions.

2. Results and discussion

2.1. Synthesis

To prepare 3-benzoyl-2-benzylchromones, the Kostanecki–Robinson method[7–13] has been chosen (Way 1, Scheme 2). This old and efficient method involving the Baker–Venkataraman rearrangement allows introduction of a large range of substituents. The two main precursors for this approach are the *o*-hydroxyphenyl-β-diketones and an acid anhydride. Nevertheless, this reaction leads to undesirable by-products. For instance the cyclisation of the *o*-acyl intermediate gives a coumarine (Way 2, Scheme 2), while the tricarbonylated intermediate leads to various flavones substituted or not in 3-position[14] (Ways 3 and 4, Scheme 2).

Most of the *o*-hydroxyphenyl-β-diketones are obtained using a traditional method involving a reaction between *o*-hydroxy acetophenone and acid chloride,[15] followed by a Baker–Venkataraman rearrangement[16,17] (Scheme 3). A diethylamino group has been introduced using a thermal condensation between a β-ketonic ester and a conveniently substituted phenol[18,19] (Scheme 4). Finally the Claisen condensation[20] between the *o*-hydroxy acetophenone and

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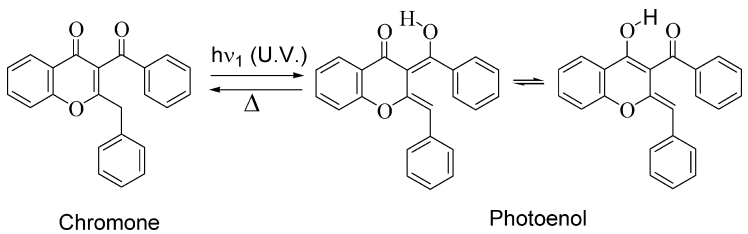


Scheme 1.

the ethylpicolinate allowed the introduction of a pyridine ring (Scheme 5).

Among the synthesized β-diketones **1**–**9**, compounds **2**, **7** and **8** are new.

The homoveratric anhydride prepared from the reaction of dicyclohexylcarbodiimide (DCC) with the corresponding acid has been used to perform the Kostanecki–Robinson reaction (Scheme 6), methoxy groups on the B-cycle improving the photochromic response of the 3-benzoyl-2-benzylchromones.

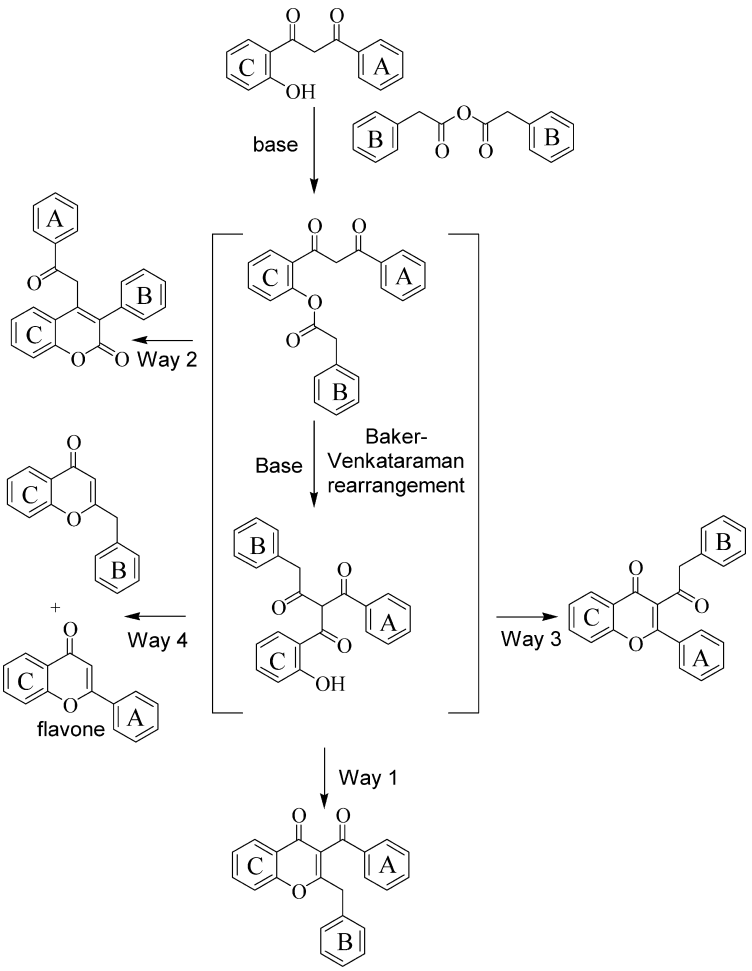
In this last reaction the sodium salt of the acid is generally added (method (a), Scheme 7). Sodium hydride[6] has been used also as base (method (b), Scheme 7) in order to favour the formation of the expected chromone instead of by-products (especially flavones[15] which are often the major products of the reaction, Scheme 2).

Nine new chromones have been prepared. Table 1 shows that, in the cases where methods (a) and (b) have been compared, the last one is the most efficient.

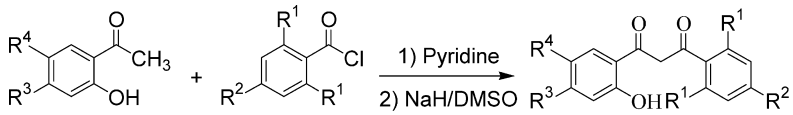
2.2. Photochromic behaviour

When they are submitted to UV irradiation, the chromones undergo a thermally reversible colour change due to a benzylic proton transfer towards the carbonyl group of the benzoyl substituent (Scheme 8).

The photochromic behaviour of the new 3-benzoyl-2-benzylchromones has been evaluated under continuous irradiation (xenon lamp) at room temperature using toluene

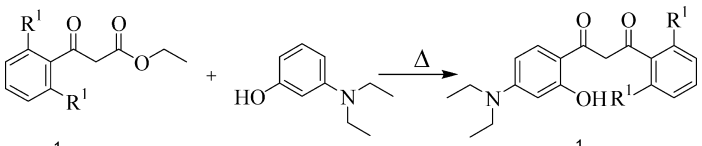


Scheme 2.



$R^1=R^2=R^3=R^4=H$: **1**
$R^1=F$; $R^2=R^3=R^4=H$: **2**
$R^1=R^2=CH_3$; $R^3=R^4=H$: **3**
$R^1=R^2=R^4=H$; $R^3=OCH_3$: **4**
$R^1=R^2=H$; $R^3=CH_3$; $R^4=Cl$: **5**
$R^1=R^2=R^3=H$; $R^4=CH_3$: **6**

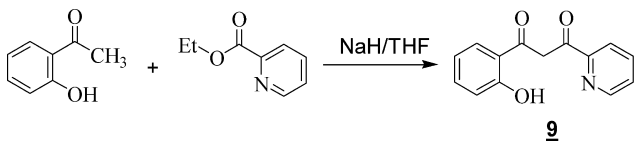
Scheme 3.



R^1 = H : **7a**
R^1 = F : **8a**

R^1 = H : **7**
R^1 = F : **8**

Scheme 4.



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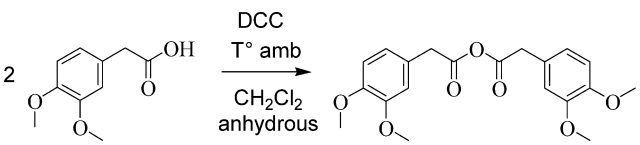
Scheme 5.



Scheme 6.

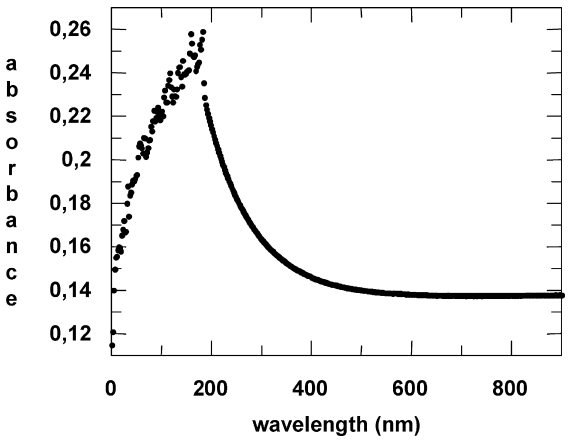


Figure 1. Kinetics of **10** in toluene and 0.4% of DABCO (5×10^{-3} M, 25°C, 150 W Xenon lamp). Absorbance is measured at 474 nm (λ_{max} of the coloured form).

and acetonitrile as solvents. The photostationary state is reached, when possible, after several tens of minutes of irradiation. In order to avoid degradation reaction occurring generally after a long period of illumination, the irradiation has been performed only for 3 min. An example of kinetic behaviour is given on Figure 1 for compound **10**.

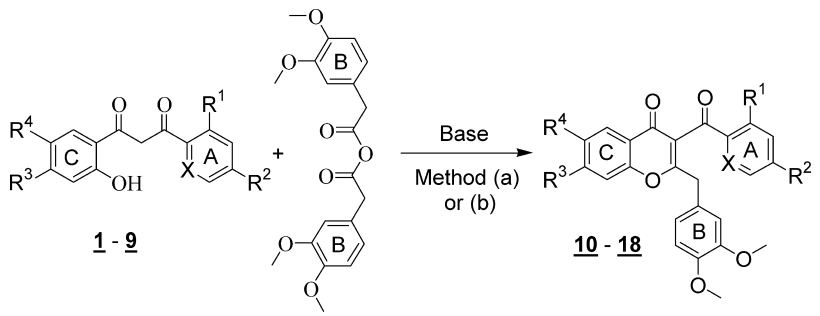
The detail of the experimental conditions is given in Section 4.

Spectrokinetic data are summarized in Table 2 and compared with those obtained with the unsubstitued 3-benzoyl-2-benzylchromone (**19**) (Scheme 9) taken as reference.

Three parameters are considered in order to characterize the coloured form: (i) the maximum wavelength of absorption (λ_{max}); (j) the thermal decolouration rate (k_Δ); (k) the

Table 1. Structure and preparation of 3-benzoyl-2-benzylchromones

Compounds	R^1	R^2	R^3	R^4	X	Yield (%) method (a)	Yield (%) method (b)	Precursors
10	H	H	H	H	CR^1	31	43	**1**
11	F	H	H	H	CR^1	26	67	**2**
12	CH_3	CH_3	H	H	CR^1	44	62	**3**
13	H	H	OCH_3	H	CR^1	–	25	**4**
14	H	H	CH_3	Cl	CR^1	–	28	**5**
15	H	H	H	CH_3	CR^1	–	31	**6**
16	H	H	$N(Et)_2$	H	CR^1	13	40	**7**
17	F	H	$N(Et)_2$	H	CR^1	–	53	**8**
18	H	H	H	H	N	–	19	**9**

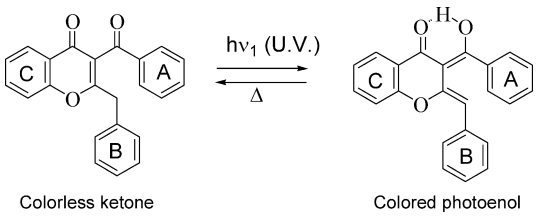


Scheme 7.

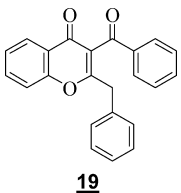
Table 2. Photochromic parameters obtained under continuous irradiation in toluene and acetonitrile solutions (150 W Xenon lamp, 25°C)

Compounds	Toluene			Acetonitrile
	λ_{max} (nm)	$A_{3'}$	k_Δ (s^{-1})	λ_{max} (nm)
10	474	0.61	$<10^{-5}$	443
11	461	0.35	1.3×10^{-2}	440
12	458	0.15	0	446
13	454	0.9	$<10^{-5}$	432
14	474	0.75	$<10^{-5}$	450
15	478	0.62	$<10^{-5}$	450
16	450	1.4[a]	$<10^{-5}$	No photochromism
17	440	1.8[a]	$<10^{-5}$	No photochromism
18	471	0.21	2.3×10^{-3}	447
19	460	0.32	$<10^{-5}$	430

[a] At a concentration of 10^{-3} mol/l and irradiation flux=800 W/m^2.



Scheme 8.



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Scheme 9.

colorability $A_{3'}$ which is the absorbance measured after 3 min of irradiation.

In acetonitrile as solvent an average hypsochromic shift of 25 nm is observed compared to that in toluene. Moreover, if the thermal decolouration rates are very slow in toluene, they become extremely fast in acetonitrile and are not evaluable, the absorbances obtained after 3 min of irradiation being very weak (0.02–0.10). Then the following discussion is related to results obtained in toluene.

Concerning the wavelength of absorption of the coloured form (λ_{max}), from a general point of view the introduction of two methoxy groups on the B cycle induces a bathochromic shift when compared to the compound **19**. In contrast, the introduction of electrondonor groups on the C cycle gives a high hypsochromic shift.

All the new compounds described show a very slow thermal decolouration due to the high stability of the photoenolic coloured forms in non polar solvent. However, in the case of compounds **11** and **18**, the introduction of substituents in the *ortho* position of the A-cycle or the presence of a heteroatom in place of a carbon atom in the *ortho* position in the same cycle induces a clear acceleration of the rate constants.

The studied chromones being very sensitive to the nature of the medium, supplementary experiments were carried out in solution in the presence of additives but also in polymer matrix. Then, the addition of amino base (DABCO) in the toluenic solution (0.4% compared to the photochrome concentration) increases the thermal decolouration rate significantly (10 to 10^3 times depending on the considered compound). On the contrary, the addition of nickel salt in acetonitrile (20%) allows a better observation of the photochromism by decreasing the thermal decolouration rate. The study realized in polyurethane (PU) and polymethylmethacrylate (PMMA) polymer matrixes with compounds **10** and **18** shows that the nature of the polymer plays a significant role on the spectrokinetic parameters. Then changing PU (T_g=−20°C) by PMMA (T_g=+125°C) leads to an hypsochromic shift of the absorption of the coloured form ($\Delta\lambda_{max}$=−10 and −20 nm, respectively, for **10** and **18**) and to a decrease in the thermal fading rates (×0.16 and ×0.08, respectively, for **10** and **18**).

3. Conclusion

The synthesis of a series of nine new 3-benzoyl-2-benzylchromones has been performed through an optimized Kostanecki–Robinson method. A structure/photochromic parameters relationship has been established for these compounds for which the photochromism involves a photoenolisation reaction.

Complementary studies carried out in solution and in polymer matrixes showed also the influence of the medium on

the photochromic properties. Structure variation and modification of the medium allow to improve the photochromic behaviour and especially the thermal stability of the photoenol form, regarding applications for variable optical transmission materials. The main limitations in this aim is nevertheless the weaker photosensibility (10 to 10^2 times) towards conventional photochromic pigments involving electrocyclisation reaction (spirooxazines, naphthopyranes).

4. Experimental

4.1. Materials and methods

Solvents (Carlo Erba) were used without further purification other than drying over molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker BM 250 spectrometer (250 and 62.5 MHz, respectively, for ^{1}H and ^{13}C) using tetramethylsilane as internal standard. Chemical shifts are given in ppm and coupling constants in Hz. Melting points (°C), measured in capillary tubes on a Buchi 510 apparatus, are uncorrected. Column chromatography was performed on silica gel Merck 60 (70–230 mesh). Elemental analysis was performed by the Microanalytical Center of the CNRS. The reported compounds identification was made by ^{1}H NMR.

Photochromic measurements were performed in toluene solutions of spectrometric grade (Aldrich) at 20°C (±0.2°), at a concentration of 5×10^{-3} mol/l and a irradiation flux=1000 W/m^2. The analysis cell (optical pathlength 10 mm) was placed in a thermostated copper block inside the sample chamber of a Cary 50 spectrometer. An Oriel 150 W high pressure Xe lamp was used for irradiation.

4.2. Starting materials

Homoveratric acid (Aldrich), sodium hydride (Aldrich), DBU (Lancaster), **5** (Aldrich), **6** (Aldrich) were commercially available. Compounds **1**,[5] **3**,[21] **4**,[22] **9**[23] and the homoveratric anhydride[24] were prepared according to previously described methods.

4.2.1. 3-(2,6-Difluorophenyl)-1-(2-hydroxyphenyl)propane-1,3-dione (2). 6.8 g (50 mmol) of 2′-hydroxyacetophenone and 11.2 g (70 mmol) of 2,6-difluorobenzoyl chloride were solubilized in 10 ml of pyridine. The mixture was stirred at ambient temperature during 30 min. The solution was carefully acidified with a cold solution (1N) of hydrochloric acid, and the precipitate was collected by filtration, washed repeatedly with water and dried. The *ortho*-acylated derivative formed was solubilized in 20 ml of dried DMSO, and the solution was added slowly to a stirred suspension of 1.5 g (60 mmol) of sodium hydride powder in 50 ml of dried DMSO. After 1 h, at ambient temperature, the mixture was slowly carried out in a icy satured solution of oxalic acid. The precipitate was collected by filtration, washed repeatedly with water and dried to give **2** as a yellow powder. Crystallisation gave a yellow solid, yield 65%, mp 126 (from methanol). ^{1}H NMR ($CDCl_3$): 100% enolic form; 6.58 (1H, s); 6.90 (1H, dd, J=8.0 Hz); 6.98–7.04 (3H, m); 7.37–7.51 (2H, m); 7.68 (1H, d, J=8.1 Hz); 11.92 (1H, s); 15.09 (1H, s).

4.2.2. 1-(4-Diethylamino-2-hydroxyphenyl)-3-phenylpropane-1,3-dione (7). A mixture of 7.71 g (43.4 mmol) of 2-(diethylamino)phenol and 6.95 g (36.23 mmol) of ethylbenzoylacetate was heated at 200°C in an erlenmeyer. After cooling, the residue was purified by column chromatography, eluent pentane/Et_2O (80/20). Crystallisation gave a yellow solid, yield 28%, mp 129 (from ethanol). ^{1}H NMR ($CDCl_3$): 100% enolic form; 1.21 (6H, t, J=7.1 Hz); 3.40 (4H, q, J=7.1 Hz); 6.10 (1H, s); 6.23 (1H, d, J=9.1 Hz); 6.64 (1H, s); 7.45–7.50 (3H, m); 7.59 (1H, d, J=9.1 Hz); 7.90 (2H, d, J=7.5 Hz); 12.70 (1H, s); 15.40 (1H, s).

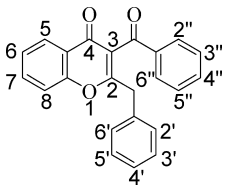
4.2.3. (2,6-Difluorobenzoyl) ethylacetate (8a). Under argon atmosphere, 36.8 g (0.36 mol) of Et_3N and 42.5 g (0.45 mol) of $MgCl_2$ were added to a solution cooled at 10–15°C of 62.8 g (0.37 mol) of potassium monoethylmalonate in 550 ml of CH_3CN. The mixture was stirred 2.5 h at ambient temperature, then cooled to 0°C. 31.2 g (0.18 mol) of 2,6-difluorobenzoyl chloride were added slowly and 3.6 g (0.04 mol) of Et_3N were again added. After stirring at ambient temperature, the solvent was evaporated and 300 ml of toluene was added to the residue. The mixture was cooled to 10–15°C and hydrolized with 250 ml of a solution of hydrochloric acid (12%). The organic layer was separated, washed two times with 65 ml of solution of HCl (12%) and water. The solvent was evaporated and the residue was purified by column chromatography, eluent CH_2Cl_2 to give colorless liquid. Yield 31%. ^{1}H NMR ($CDCl_3$): 1.23 (3H, t, J=6.9 Hz); 3.91 (2H, s, J=6.9 Hz); 4.19 (2H, q); 7.28–7.32 (3H, m).

4.2.4. 1-(4-Diethylamino-2-hydroxyphenyl)-3-(2,6-difluorophenyl)propane-1,3-dione (8). 0.86 g (5.21 mmol) of 2-(diethylamino)phenol and 1 g (4.34 mmol) of **8a** were heated in an erlenmeyer at 160°C. After cooling, the residue was purified by column chromatography, eluent pentane/Et_2O (80/20). Crystallisation gave a yellow solid, yield 37%, mp 78 (from ethanol). ^{1}H NMR ($CDCl_3$): 100% enolic form; 1.20 (6H, t, J=7.1 Hz); 3.39 (4H, q, J=7.1 Hz); 6.10 (1H, s); 6.20 (1H, d, J=9.2 Hz); 6.34 (1H, s); 6.97 (2H, dd, J=8.3 Hz); 7.38 (1H, dd, J=8.3 Hz); 7.45 (1H, d, J=9.2 Hz); 12.55 (1H, s); 15.08 (1H, s).

4.3. General methods for the synthesis of chromones

Method A. 2.08 mmol of the diketone, 4.16 mmol of the homoveratric acid anhydride and 4.16 mmol of sodium salt of homoveratric acid were heated at 160°C during 4 h. After cooling, the mixture was solubilized in CH_2Cl_2. The organic layer was washed three times with a saturated solution of $NaHCO_3$, dried with $MgSO_4$ and evaporated. The residue was purified by column chromatography, eluent CH_2Cl_2/-Et_2O (90/10).

Method B. 2 mmol of the diketone, 3 mmol of the homoveratric acid anhydride and 3.4 mmol of sodium hydride were refluxed 4 h in 6 ml of toluene. After cooling, CH_2Cl_2 was added to the mixture. The organic layer was washed three times with a solution of $NaHCO_3$ (10%), dried with $MgSO_4$ and evaporated. The residue was purified by column chromatography, eluent CH_2Cl_2/Et_2O (90/10).



4.3.1. 3-Benzoyl-2-(3,4-dimethoxybenzyl)[4*H*-1]benzopyran-4-one (10). Method A: 31%, Method B: 43% yield. Crystallisation gave a white solid, mp 135 (from methanol). ^{1}H NMR ($CDCl_3$): 3.70 (3H, s, OCH_3); 3.81 (3H, s, OCH_3); 3.88 (2H, s, CH_2); 6.72 (1H, d, J=8.2 Hz, H-5′); 6.75 (1H, s, H-2′); 6.86 (1H, d, J=8.2 Hz, H-6′); 7.36–7.47 (4H, m, H-8, H-3″, H-4″ and H-5″); 7.57 (1H, dd,J=7.5, 7.9 Hz, H-6); 7.68 (1H, dd, J=7.5, 7.6 Hz, H-7); 7.87 (2H, d, J=7.2 Hz, H-2″ and H-6″); 8.15 (1H, d, J=7.9 Hz, H-5); ^{13}C NMR ($CDCl_3$): 38.2 (t); 55.6 (q); 55.8 (q); 111.2 (d); 112.3 (d); 117.9 (d); 121.5 (d); 122.9 (s); 123.3 (s); 125.4 (d); 125.9 (d); 127.1 (s); 128.6 (2*d); 129.4 (2*d); 133.7 (d); 134.1 (d); 137.1 (s); 148.2 (s); 148.9 (s); 155.9 (s); 166.3 (s); 176.2 (s); 193.9 (s). Anal. calcd for $C_{25}H_{20}O_5$: C, 74.99; H, 5.03; found: C, 74.89, H, 5.07.

4.3.2. 3-(2,6-Difluorobenzoyl)-2-(3,4-dimethoxybenzyl)[4*H*-1]benzopyran-4-one (11). Method A: 26%, Method B: 67% yield. Crystallisation gave a pink solid, mp 150 (from methanol). ^{1}H NMR ($CDCl_3$): 3.85 (3H, s, OCH_3); 3.88 (3H, s, OCH_3); 4.16 (2H, s, CH_2); 6.82 (1H, d, J=7.9 Hz, H-5′); 6.93 (2H, dd, J=8.2 Hz, H-3″ and H-5″); 7.00 (1H, d, J=8.0 Hz, H-6′); 7.04 (1H, s, H-2′); 7.32–7.42 (3H, m, H-6, H-8 and H-4″); 7.62 (1H, dd, J=7.1 Hz, H-7); 8.07 (1H, d, J=7.9 Hz, H-5); ^{13}C NMR ($CDCl_3$): 37.8 (t); 55.8 (q); 55.9 (q); 111.2 (d); 111.7 (2*d, J_{CF}=24.4 Hz); 112.5 (d); 117.9 (d); 121.7 (d); 123.4 (s); 123.7 (s); 125.7 (d); 125.8 (d); 127.4 (s); 132.7 (d, J_{CF}=10.3 Hz); 134.3 (d); 148.3 (s); 149.0 (s); 155.6 (s); 158.4 (2*s, J_{CF}=242.9 Hz); 170.4 (s); 175.9 (s); 187.8 (s). Anal. calcd for $C_{25}H_{18}O_5F_2$: C, 68.80; H, 4.16; F, 8.71; found: C, 68.82, H, 4.21; F, 8.67.

4.3.3. 2-(3,4-Dimethoxybenzyl)-3-(2,4,6-trimethylbenzoyl)[4*H*-1]benzopyran-4-one (12). Method A: 44%, Method B: 62% yield. Crystallisation gave a beige solid, mp 135 (from methanol). ^{1}H NMR ($CDCl_3$): 2.23 (6H, s, CH_3); 2.28 (3H, s, CH_3); 3.86 (3H, s, OCH_3); 3.89 (3H, s, OCH_3); 4.20 (2H, s, CH_2); 6.82 (2H, s, H-3″ and H-5″); 6.83 (1H, d, J=8.2 Hz, H-5′); 7.03 (1H, d, J=8.3 Hz, H-6′); 7.06 (1H, s, H-2′); 7.33 (1H, dd, J=7.7, 7.8 Hz, H-6); 7.39 (1H, d, J=7.5 Hz, H-8); 7.63 (1H, dd, J=7.5, 7.7 Hz, H-7); 8.07 (1H, d, J=7.8 Hz, H-5). ^{13}C NMR ($CDCl_3$): 20.3 (2*q); 21.3 (q); 38.1 (t); 56.0 (2*q); 111.4 (s); 112.9 (d); 117.8 (d); 121.9 (d); 123.9 (s); 124.2 (s); 125.7 (d); 126.3 (d); 127.6 (s); 129.2 (2*d); 134.2 (d); 134.7 (2*s); 138.9 (s); 139.2 (s); 148.5 (s); 149.1 (s); 155.6 (s); 170.4 (s); 175.6 (s); 197.3 (s). Anal. calcd for $C_{28}H_{26}O_5$: C, 76.00; H, 5.92; found: C, 75.87, H, 6.00.

4.3.4. 3-Benzoyl-2-(3,4-dimethoxybenzyl)-7-methoxy[4*H*-1]benzopyran-4-one (13). Method B: 25% yield. Crystallisation gave a beige solid, mp 178 (from methanol). ^{1}H NMR ($CDCl_3$): 3.84 (3H, s, OCH_3); 3.89 (3H, s,OCH_3); 3.95 (3H, s, OCH_3); 4.06 (2H, s, CH_2); 6.40–6.77 (4H, m, H-8, H-2′, H-5′ and H-6′); 6.85 (1H, d, J=8.9 Hz, H-6); 7.33 (2H, dd, J=7.7, 7.3 Hz, H-3″ and H-5″); 7.47 (1H, dd, J=7.3 Hz, H-4″); 7.80 (2H, d, J=7.3 Hz, H-2″ and H-6″); 7.95 (1H, d, J=7.4 Hz, H-5). ^{13}C NMR ($CDCl_3$)**:** 38.1 (t); 55.7 (2*q); 55.9 (q); 100.3 (d); 111.2 (d); 112.3 (d); 114.7 (d); 117.1 (s); 121.5 (d); 122.8 (s); 127.3 (d); 127.3 (s); 128.6 (2*d); 129.5 (2*d); 133.7 (d); 137.3 (s); 148.2 (s); 148.9 (s); 157.7 (s); 164.4 (s); 165.8 (s); 175.6 (s); 194.1 (s). Anal. calcd for $C_{26}H_{22}O_6$: C, 72.55; H, 5.15; found: C, 72.53, H, 5.17.

4.3.5. 3-Benzoyl-6-chloro-2-(3,4-dimethoxybenzyl)-7-methyl[4*H*-1]benzopyran-4-one(14). Method B: 28% yield. Crystallisation gave a yellow solid, mp 159 (from methanol). ^{1}H NMR ($CDCl_3$): 2.47 (3H, s, CH_3); 3.70 (3H, s, OCH_3); 3.80 (3H, s, OCH_3); 3.85 (2H, s, CH_2); 6.72–6.84 (3H, m, H-2′, H-5′ and H-6′); 7.34 (1H, s, H-8); 7.42 (2H, dd, J=7.2, 7.3 Hz, H-3″ and H-5″); 7.57 (1H, dd, J=7.3 Hz, H-4″); 7.85 (2H, d, J=7.2 Hz, H-2″ and H-6″); 8.08 (1H, s, H-5). ^{13}C NMR ($CDCl_3$): 21.1 (q); 38.5 (t); 55.9 (q); 56.1 (q); 111.5 (d); 112.6 (d); 120.1 (d); 121.8 (d); 122.6 (s); 123.1 (s); 125.7 (d); 127.3 (s); 128.9 (2*d); 129.7 (2*d); 132.4 (d); 134.5 (d); 137.3 (s); 143.8 (d); 148.6 (s); 149.2 (s); 154.9 (s); 166.7 (s); 174.3 (s); 193.9 (s). Anal. calcd for $C_{26}H_{21}O_5Cl$: C, 69.57; H, 4.72; Cl, 7.90; found: C, 69.52, H, 4.79; Cl, 7.85.

4.3.6. 3-Benzoyl-2-(3,4-dimethoxybenzyl)-6-methyl[4*H*-1]benzopyran-4-one (15). Method B: 31% yield. Crystallisation gave a white solid, mp 111 (from methanol). ^{1}H NMR ($CDCl_3$): 2.39 (3H, s, CH_3); 3.69 (3H, s, OCH_3); 3.78 (3H, s, OCH_3); 3.85 (2H, s, CH_2); 6.71–6.85 (3H, m, H-2′, H-5′ and H-6′); 7.35 (2H, dd, J=7.4, 8.5 Hz, H-3″ and H-5″); 7.40–7.45 (2H, m, H-7 and H-8); 7.54 (1H, dd, J=7.4 Hz, H-4″); 7.86–7.96 (3H, m, H-5, H-2″ and H-6″). ^{13}C NMR ($CDCl_3$): 20.9 (q); 39.1 (t); 55.6 (q); 55.8 (q); 110.9 (d); 112.3 (d); 119.4 (d); 122.1 (d); 122.9 (s); 123.4 (s); 126.1 (d); 126.2 (d); 127.5 (s); 129.1 (2*d); 130.1 (2*d); 133.3 (d); 133.9 (d); 137.6 (s); 148.5 (s); 148.9 (s); 155.5 (s); 168.9 (s); 175.2 (s); 193.4 (s). Anal. calcd for $C_{26}H_{22}O_5$: C, 75.35; H, 5.35; found: C, 75.29, H, 5.36.

4.3.7. 3-Benzoyl-7-diethylamino-2-(3,4-dimethoxybenzyl)[4*H*-1]benzopyran-4-one (16). Method A: 13% yield. Crystallisation gave a yellow solid, mp 132 (from methanol). ^{1}H NMR ($CDCl_3$): 1.19 (6H, t, J=6.9 Hz, CH_3); 3.39 (4H, q, J=6.9 Hz, NCH_2); 3.69 (3H, s, OCH_3); 3.80 (5H, s, CH_2 and OCH_3); 6.41 (1H, s, H-8); 6.65–6.86 (4H, m, H-6, H-2′, H-5′ and H-6′); 7.39 (2H, dd, J=7.5, 7.7 Hz, H-3″ and H-5″); 7.53 (1H, dd, J=7.5 Hz, H-4″); 7.88–7.93 (3H, m, H-5, H-2″ and H-6″). ^{13}C NMR ($CDCl_3$): 12.6 (q); 38.3 (t); 44.9 (t); 55.8 (q); 96.4 (d); 110.8 (d); 111.3 (d); 112.4 (s); 112.5 (d); 121.6 (d); 122.7 (s); 127.3 (d); 128.0 (s); 128.7 (2*d); 129.6 (2*d); 133.7 (d); 137.8 (s); 148.3 (s); 149.1 (s); 152.3 (d); 158.7 (s); 165.0 (s); 175.5 (s); 195.0 (s). Anal. calcd for $C_{29}H_{29}O_5N$: C, 73.87; H, 6.20; N, 2.97; found: C, 73.59, H, 6.22; N, 3.01.

4.3.8. 7-Diethylamino-3-(2,6-difluorobenzoyl)-2-(3,4-dimethoxybenzyl)[4*H*-1]benzopyran-4-one (17). Method B: 53% yield. Crystallisation gave a yellow solid, mp 168 (from methanol). ^{1}H NMR ($CDCl_3$): 1.18 (6H, t, J=7.0 Hz,

CH_3); 3.43 (4H, q, J=7.0 Hz, NCH_2); 3.85 (3H, s, OCH_3); 3.87 (3H, s, OCH_3); 4.12 (2H, s, CH_2); 6.35 (1H, s, H-8); 6.65 (1H, d, J=9.1 Hz, H-6); 6.83 (1H, d, J=8.2 Hz, H-5′); 6.91 (2H, dd, J=8.1 Hz, H-3″ and H-5″); 7.01 (1H, d, J=8.3 Hz, H-6′); 7.04 (1H, s, H-2′); 7.36 (1H, dd, J=8.1 Hz, H-4″); 7.85 (1H, d, J=9.1 Hz, H-5). ^{13}C NMR ($CDCl_3$): 12.2 (q); 37.5 (t); 44.5 (t); 55.7 (q); 96.0 (d); 110.6 (d); 111.1 (d); 111.5 (d); 111.9 (J_{CF}=24.8 Hz, 2*d); 112,4 (s); 119.5 (J_{CF}=16.3 Hz, s); 121.5 (d); 123.0 (s); 126.7 (s); 128.0 (s); 132.1 (J_{CF}=10.1 Hz, s); 148.0 (s); 148.8 (s); 152.1 (s); 157.9 (s); 158.2 (J_{CF}=240 Hz, 2*s); 166.2 (s); 174.6 (s); 188.4 (s). Anal. calcd for $C_{29}H_{27}O_5NF_2$: C, 68.63; H, 5.36; N, 2.76; F, 7.49; found: C, 68.71, H, 5.43; N, 2.82; F, 7.56.

4.3.9. 2-(3,4-Dimethoxybenzyl)-3-(2-pyridoyl)[4*H*-1]benzopyran-4-one (18). Method B: 19% yield. Crystallisation gave a beige solid, mp 151 (from methanol). ^{1}H NMR ($CDCl_3$): 3.70 (6H, s, OCH_3); 3.86 (2H, s, CH_2); 6.67 (1H, d, J=7.8 Hz, H-5′); 6.84 (1H, d, J=7.7 Hz, H-6′); 6.86 (1H, s, H-2′); 7.23–7.36 (3H, m, H-6, H-8 and H-4″); 7.54 (1H, dd, J=7.1 Hz, H-7); 7.78 (1H, dd, J=7.7 Hz, H-5″); 7.99–8.04 (2H, m, H-3″ and H-6″); 8.48 (1H, d, J=7.3 Hz, H-5). ^{13}C NMR ($CDCl_3$): 38.2 (t); 55.7 (q); 55.8 (q); 111.7 (d); 112.4 (d); 117.9 (d); 121.7 (d); 122.7 (d); 123.4 (s); 123.6 (s); 125.3 (d); 125.6 (d); 127.1 (d); 127.4 (s); 133.9 (d); 136.9 (d); 148.2 (s); 148.9 (s); 149.1 (d); 154.2 (s); 156.1 (s); 166.6 (s); 176.5 (s); 195.1 (s). Anal. calcd for $C_{24}H_{19}O_5N$: C, 71.81; H, 4.77; N, 3.49; found: C, 71.63, H, 4.92; N, 3.54.

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