Synthesis and Reactivity of Photochromic 2*H*-Chromenes based on 3-Carboxylated Coumarins

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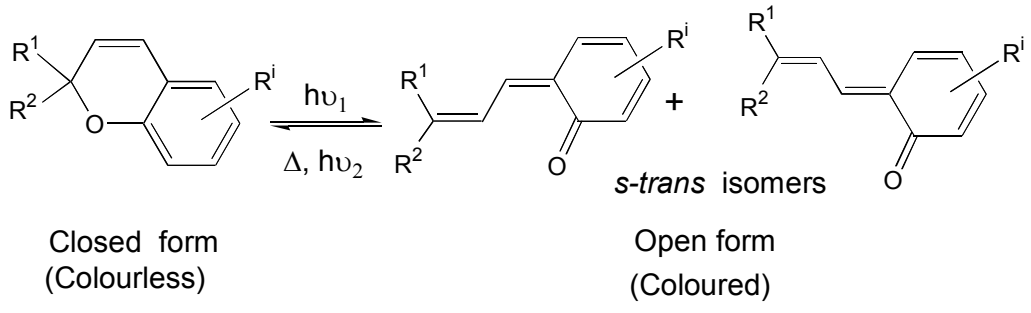
Abstract: New photochromic 2*H*-chromenes including a 3-carboxylated coumarin nucleus were synthesised from hydroxycoumarins, and, in one case, the corrresponding trimethoxysilylcarboxamide was prepared. The photochromic behaviour was studied under flash photolysis conditions. The introduction of electron-withdrawing substituents in this position of the coumarin nucleus led to a global and significant bathochromic shift in the spectra of the open forms and to an interesting intensification in the colorability.

1. Introduction. - Photochromic systems based on 2*H*-1-benzopyrans (=2*H*-chromenes) constitute an important research field to which, in the last decade, intense research efforts have been devoted due to their applications in variable optical transmission materials and to some potential applications in optical switches and memories [1] [2].

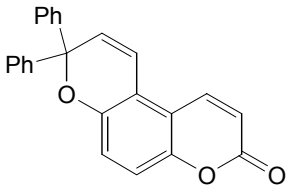
Their photochromic behaviour is based on a reversible pyran ring opening induced upon near UV irradiation that converts a colourless form into a set of *quasi*-planar forms (scheme 1), constituting a system with a distinct absorption spectrum. The back reaction may occur through a thermal process or irradiation with visible light.

Scheme 1

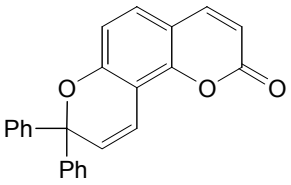


For applications in the field of variable transmission materials, the molecules involved should be incorporated in convenient host matrices in a stable manner. This can be achieved either by dispersing the photochrome in or covalently coupling the photochrome to the matrix, provided that the photochromic entity is not destroyed and the photochromic characteristics are not lost.

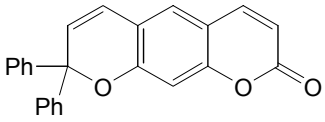
In the course of the search for new photochromic molecules [3-5], it was decided to study new *2H*-chromenes, which contain a coumarin nucleus. In our previous work on photochromic compounds based on the coumarin system [6], it was found that some *2H*-chromenes, namely compounds **Ref 1** and especially **Ref 2** and **Ref 3**, exhibited an interesting colouration efficiencies, and their open forms showed an extended absorption range in the visible region that could be useful for applications in the field of variable optical transmission materials.



Ref 1



Ref 2



Ref 3

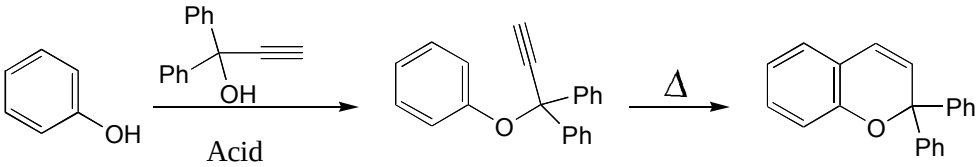
The coumarin moiety can be built with different substitution patterns, namely with ester substituents in the 3-position, offering a way to form further covalent bonds to various polymeric matrices (for example, through an ester or an amide linkage) allowing the build-up of supramolecular systems containing a photoreactive entity. Here we describe the synthesis and the photochromic properties of ethoxycarbonyl-substituted 2*H*-chromenes of this type, in order to verify the validity of this approach.

The ethoxycarbonyl substituent has been chosen not only for its electronic effects, but also because of its synthetic potential. The latter aspect was tested through the preparation of an amide containing a silylated side chain according to the method described by Karkkainen *et al.* for organic light emitting devices including coumarin dyes covalently bound to a siloxane matrix [7].

The spectrokinetic parameters, in solution, of the novel compounds were determined in order to evaluate the effects of the substitution on the photochromic behaviour.

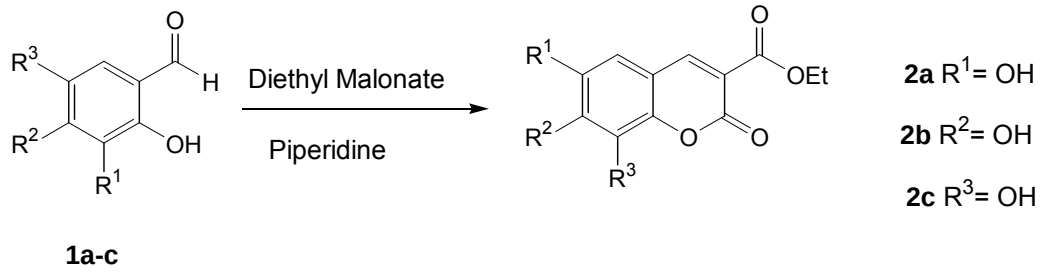
2. Results and Discussion. - 2.1. *Synthesis.* 2*H*-Chromenes can be easily prepared from phenolic precursors. The most versatile method is based on a one-pot reaction of a phenol with an alkynol under acidic catalysis. The reaction is considered to proceed *via* a Claisen rearrangement of aryl propargyl ethers, formed by phenol *O*-alkylation, followed by enolization, [1,5] H-migration and finally electrocyclic ring closure (Scheme 2). Alternatively, a $Ti(OEt)_4$ catalyzed condensation with α,β-unsaturated carbonyl compounds can be used [3].

Scheme 2



6-, 7- and 8- Hydroxycoumarins **2a-2c** containing an ester group in 3-position were prepared through the *Knoevenagel* condensation of the corresponding *ortho*-hydroxybenzaldehydes **1a-1c** with diethyl malonate [8] in high yield (*Scheme 3)*.

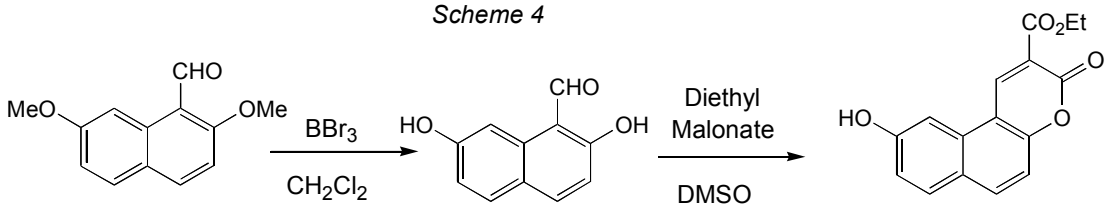
Scheme 3



1a-c

Hydroxybenzocoumarin **5** was prepared in 4 steps from 2,7-dihydroxynaphthalene. Methylation of 2,7-dihydroxynaphthalene gave the corresponding 2,7-dimethoxynaphthalene which was subsequently formylated using DMF/$POCl_3$, to give the naphthaldeyde-1-carbaldehyde **3** in 50% yield. Demethylation of **3** with BBr_3 gave 2,7-dihydroxynaphthaldehyde (**4** ; 52%), which was then converted in good yield (80%) to the corresponding coumarin as reported before (*Scheme 4*).

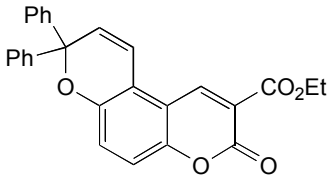
Scheme 4



3 **4** **5**

Our previous results [6] on the synthesis of 2*H*-chromenes from hydroxycoumarins indicate that, for these type of molecules, the cyclisation using the propynol method gives better yields, compared to the α, β-unsaturated aldehyde/$Ti(OEt)_4$ method.

Condensation of 3-ethoxycarbonyl hydroxycoumarins **2a, 2b** and **5** with 1,1-diphenylpropyn-1-ol using *p*-toluenesulfonic acid (APTS) as catalyst gave *2H*-chromenes **6-9** in low yields. Different solvents were used depending on the solubility of the starting material. The reaction of coumarin **2a** and **5** with 1,1-diphenylpropyn-1-ol was completely regiospecific, providing respectively the chromenes **6** and **9**, respectively, as the only isomers. A similar reaction applied to hydroxycoumarin **2b** gave a mixture of the linear chromene **7**, as the major product, together with a minor amount of the angular compound **8**. No reaction was observed with the hydroxycoumarin **2c** either by the propynol method or the $Ti(OEt)_4$ method. This result was somehow expected in view of what was observed before [6] with 8-hydroxycoumarin, where only traces of the final chromene were detected.



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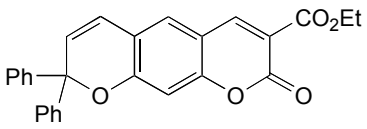

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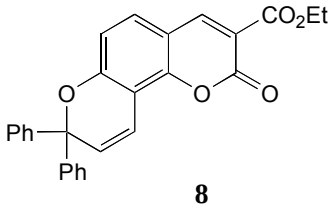

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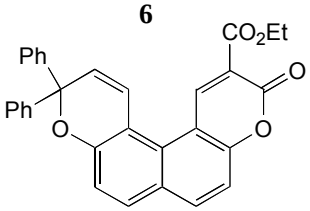

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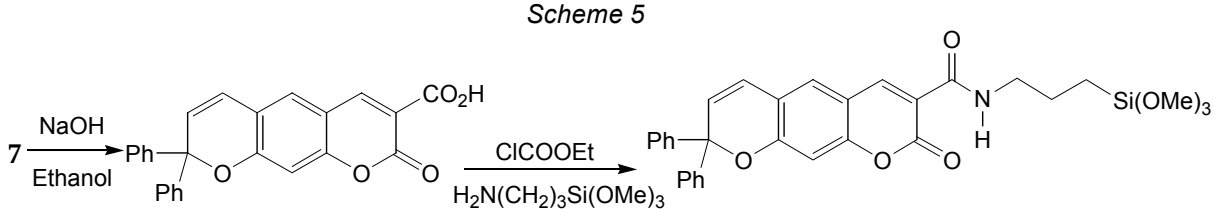
Basic hydrolysis of chromene **7** in ethanol gave the acid **10** which was then converted in 89% yield to its (3-trimethoxysilylpropyl)carboxamide **11** by the mixed anhydride method (ethyl chloroformate / 3-aminopropyltrimethoxysilane) in 89% [9] (Scheme 5).

Scheme 5

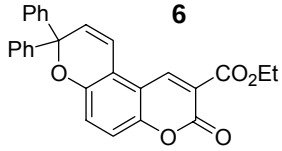
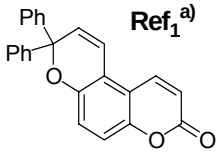
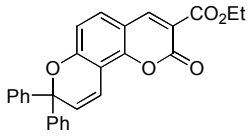
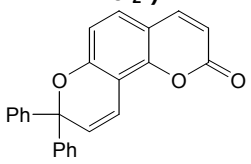
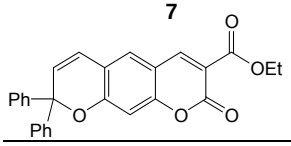
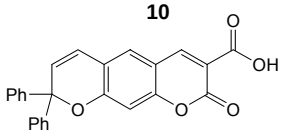
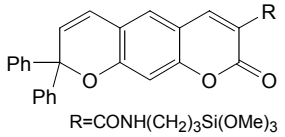
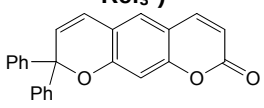
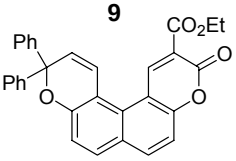


10 **11**

2.2. *Photochromic Properties*. The photochromic characteristics of the compounds were determined by the flash irradiation technique coupled to a rapid spectrometer. Details of the procedure are described in the experimental section. Results obtained for the new compounds are summarized in *Table 1* where the parent coumarins (Ref_1, Ref_2 and Ref_3) are also included for comparison. The values of $k\Delta$ are given for the wavelength at which A_0 is maximum (λ_1 in all cases). Calculations give similar values when compounds have two wavelengths of absorption. As an example, for compound **10,** the spectrum of the closed form and a set of spectra of the open form are also shown (Figs. 1 and 2, respectively). Calculations of $k\Delta$ at both wavelengths (λ_1 and λ_2) are given in *Table 2*.

The photochromic parameters, which have been taken into account, are: absorption wavelengths of the open forms, rate constants of thermal bleaching (k_Δ) and colouration ability or "colorability" (measured as the absorbance A_o immediately after the flash irradiation). A_0 is expressed by: $A_o = \varepsilon_{OF} \cdot \Phi_{col} \cdot k \cdot [CF]_0$, (at low concentration), where k depends on experimental conditions, ε_{OF} is the molar absorptivity of the open form at λ_{max}, Φ_{col} is the photocolouration quantum yield, and $[CF]_0$ is the initial concentration of the closed form [10].

Table 1. Spectrokinetic properties of **6-11** under Flash-Irradiation conditions (25μM in toluene at 25ºC)

Structure- Compound	Type of annellation	λ (closed form)	λ_1 [nm]	A_{01}	λ_2 [nm]	A_{02}	kΔ (amplitude) (s^{-1}) (%)	χ^2 x10^6
6 	5,6	321 392	500	1.2	-	-	2.60 (16) 0.05 (17) 0.02 (66)	9.0
Ref$_1$[a)] 	5,6	302	491	1.05	-	-	2.20 (69) 0.02 (31)	2.6
8 	5,6	354	441	0.37	590	0.22	49.00 (62) 0.02 (38)	4.9
Ref$_2$[b)] 	5,6	330 347	429	0.26	562	0.11	20.00 (91) 0.03 (9)	4.2
7 	6,7	328 367	445	3.3	597	1.8	13.00 (51) 0.50 (11) 0.03 (38)	3.7
10 	6,7	349	448	2.1	615	1.4	72 (43) 11.90 (18) 0.29 (15) 0.04 (24)	0.82
11  R=CONH$(CH_2)_3$Si$(OMe)_3$	6,7	-	447	0.31	604	0.18	18.00 (52) 0.35 (13) 0.03 (35)	1.1
Ref$_3$[c)] 	6,7	339 347	432	0.95	563	0.45	4.50 (53) 0.03 (47)	2.0
9 	5,6	414	462	0.37	-	-	15.65 (71) 0.02 (29)	3.8

[a]) *3,8-Dihydro-8,8-diphenylpyrano[3,2-f][1]benzopyran-3-one*
[b]) *2,8-Dihydro-8,8-diphenylpyrano[2,3-f][1]benzopyran-2-one*
[c]) *2,8-Dihydro-2,2-diphenylpyrano[3,2-g][1]benzopyran-8-one*

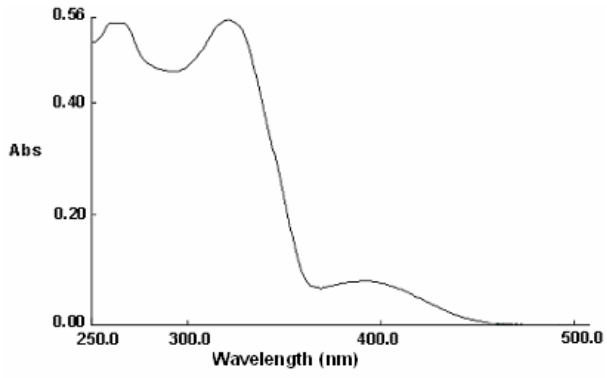


Figure 1. UV Absorption spectrum of compound **10** (closed form)

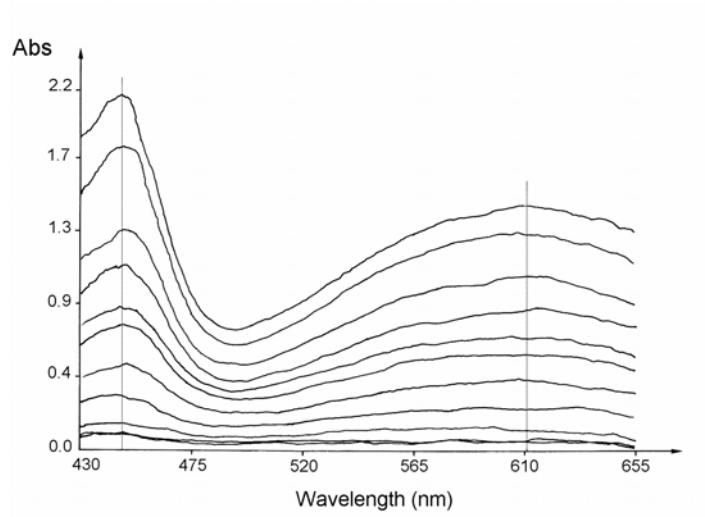


Figure 2. Set of decreasing absorption spectra of compound **10 (**open form) after flash irradiation

All the compounds described exhibit photochromic behavior, at room temperature in toluene solution. Irradiation of compounds **7**, **8**, **10**, and **11** led to open forms with broad visible absorption spectra.

Table 2. Calculations of the rate constants of thermal ring closure for compound **10**.

λ [nm]	A_0	kΔ [s^{-1}]	Amplitude [%]	χ^2
448	2.1	72± 4 11.9±0.7 0.29±0.03 0.040±0.002	43 18 15 24	$8.2x10^{-7}$
615	1.4	71± 4 12.2±0.8 0.33±0.02 0.041±0.002	38 18 16 28	$5.0x10^{-7}$

From a general point of view, compared to the parent reference coumarins without substituents, the introduction of electron-withdrawing substituents with π-electrons, located on C(3)

of the coumarin moiety (ethoxycarbonyl group in compounds **6**-**8**, carboxylic acid group in compound **10** and carboxamide group in compound **11**) led to a global and significant bathochromic shift in the spectra of the open forms, without the loss of the visible absorption spectra pattern.

Besides this interesting feature, the colorability intensification observed (except for compound **11**) due to the presence of the carboethoxy group, particularly in compounds having the coumarin nucleus fused in the 6,7-positions of the 2*H*-1-benzopyran entity, is also noteworthy.

This effect is particularly interesting, considering the appreciable thermal instability of all the open forms, indicated by the very fast thermal bleaching rates. Fast bleaching kinetics is normally accompanied by modest colorabilities, as the formation of coloured species in a reasonable yield is hindered. This improvement is apparently lost when the ester substituent is converted to the silylated carboxamide. The loss of photochromic properties, mainly colorability, for photochrome moieties chemically bonded to a silane link has been addressed several times in the literature[11]. It is currently accepted that, during irradiation, a part of UV light is dissipated through the silyl link. It is likely that the same process occurs for compound **11**, leading to the poor colorability observed in this case.

One can notice also the appearance of several rate constants (2 to 4) for the thermal fading of the new compounds. This phenomenon is probably due to the stabilization of different *s-trans* and *s-cis* open-form isomers during the photochromic process of such systems. . Compounds **7**, **10,** and **11,** which are derived from compound **Ref$_3$** by different substitutions at C(3), have a similar kinetics behavior. Indeed, except the very fast rate constant in compound **10** (72 s^{-1}), these three compounds behave similarly with three corresponding rate constants, which are of the same order of magnitude. It is likely that, in **7** and **11**, the fourth fastest component is not detected in our experimental conditions, due to poor amplitude, which falls within the flash excitation. On the other hand, the unsubstituted compound **Ref$_3$** is clearly different from those substituted at C(3) both in the thermal fading, which can only be described in the reference compound by a two step decay, and in the spectroscopic characteristics (*ca*. 430 nm *vs. ca*. 450 nm).

Compound **9** was synthesised in order to minimize the influence of the coumarin moiety in the thermal instability of the open forms. Compared to the reference 2*H*-chromenes, no improvement in the photochromic behavior was achieved through the fusion of an additional benzene ring between the coumarin and the 2*H*-1-benzopyran moieties.

3. Conclusions.

Four new hetero-[6,7]-annellated 2*H*-chromenes have been synthesized in a series for which very few compounds are found in the literature.

The synthesis of 2*H*-chromenes fused with a pyranone ring possessing an ester substituent was achieved by standard methods. This kind of substitution opens the possibility of further modifications in the molecules and constitutes a potentially interesting way to bind covalently photochromic molecules to convenient polymeric matrices. No lost of the relevant spectral features was observed, and the new compounds exhibit a marked intensification in the

coloration efficiency. The conversion of the ester group to silylated carboxamide group led, however, to a significant decrease in the colourability.

Experimental Part

1. *General*. Petroleum ether: b.p. 40-60º. Column chromatography (CC): *Silica gel 60* (*70-230 mesh*). M.p.: uncorrected. UV-Spectra: in EtOH on a *JASCO 7850*; λ_{max} (log ε [dm^3 mol^{-1} cm^{-1}]). FT-IR Spectra: *Bomem*, *MB Series*; in cm^{-1}. ^{1}H-NMR Spectra: in $CDCl_3$ (if not stated otherwise) on a *Varian Unity Plus* (300 MHz); δ in ppm rel. to Me_4Si (= 0 ppm), *J* in Hz. ^{1}H-NMR assignments were based on irradiation experiments.^{13}C-NMR Spectra: in $CDCl_3$ on a *Varian Unity Plus* (75.4 MHz). MS: *AutoSpecE Spectrometer*; *m/z* (%). Elemental analyses: *LECO 932 CHNS Analyser.* HR-FABMS: *VG AutoSpec M spectrometer.*

2. *Spectrokinetic measurements***.** For the determination at 25°C of λ_1 and λ_2, A_{01} and A_{02}, and k_Δ, 25μM of **6**-**11** in toluene were used. The flash photolysis apparatus was coupled to a *Warner and Swasey* rapid spectrometer, to allow recording of absorption spectra of the coloured forms in the visible 400-700 nm range (acquisition time: 1 ms, repetitively: 1.25 ms) [12-13]. Flashes (duration: 50 μs) were generated by two xenon tubes with a quartz envelope. The energy of the flashes was 60 J for the whole polychromatic emission spectrum. For measurements, thermostated (25°C) 100-mm cells were used. The light from the analysis lamp (50 W, quartz-iodine) was filtered using a *Schott GG400* high-pass filter. In a preliminary experiment, both the visible absorption spectrum, and λ_1 and λ_2 of the open form were determined. In a second experiment, the initial absorbances A_{01} and A_{02} were measured, followed by the decrease in absorbance with time. The rate constants were calculated using a multi-exponential model designed to minimize the χ^2 (residual quadratic error). The χ^2 for each fitting is reported in *Table 1*.

3. *Synthesis. - General Procedure for the Synthesis of Coumarins* **2a-2c**: A mixture of dihydroxybenzaldehyde (5.00 g, 36.2 mmol), diethyl malonate (7.12 ml, 47.0 mmol) and ethanol (50 ml) was placed in a round bottom flask and a few drops of piperidine and glacial acetic acid were added. After 4h, 5h, 4 h reflux respectively for **2a**, **2b**, **2c**, the soln. was cooled and water (50 ml) was added. The precipitate was collected by filtration, washed with a soln. of ethanol (40 ml) and water (60 ml) and air dried.

*Ethyl 6-hydroxy-2-oxo-2*H-*[1]benzopyran-3-carboxylate* (**2a**): yellow solid (93%), M.p. 188-190º (ethanol). FT-IR: 3331, 1748 (C=O), 1672 (C=O). ^{1}H-NMR: 1.42 (*t*, J = 7.2, OEt); 4.42 (*q*, J = 7.2, OEt); 5.18 (*s*, OH); 7.03 (*d*, J = 2.7, H-C(5)); 7.15-7.18 (*dd*, J = 2.7 and 9, H-C(7)); 7.24-7.32 (*m*, H-C(8)); 8.44 (*s*, H-C(4)).

*Ethyl 7-hydroxy-2-oxo-2*H-*[1]benzopyran-3-carboxylate* (**2b**): light yellow solid (71%), M.p. 171-172º (ethanol). FT-IR: 3552, 3471, 3333, 1741 (C=O), 1681 (C=O). ^{1}H-NMR (acetone-d_6): 1.37 (*t*, J = 7.2, OEt); 4.35 (*q*, J = 7.2, OEt); 6.81 (*d*, J = 2.4, H-C(8));

6.93-6.97 (*dd*, J = 2.1 and 8.4, H-C(6)); 7.75 (*d*, J = 8.4, H-C(5)); 8.63 (*s*, H-C(4)). The signal due to OH was not observed.

*Ethyl 8-hydroxy-2-oxo-2*H-*[1]benzopyran-3-carboxylate* (**2c**): light yellow fluffy crystals (69%). M.p. 178-181º (ethanol). FT-IR: 3306, 1747 (C=O), 1696 (C=O). ^{1}H-NMR (acetone- d_6): 1.35 (*t*, J = 7.2, OEt); 4.38 (*q*, J = 7.2, OEt); 7.20-7.36 (*m*, H-C(5), H-C(6) and H-C(7)); 8.63 (*s*, H-C(4)); 9.30 (*br s*, OH).

2,7-Dihydroxynaphthalene-1-carbaldehyde (**4**): A solution of BBr_3 in CH_2Cl_2 **(**14 ml**)** was gradually syringed to a CH_2Cl_2 **(**10 ml) soln. of **3** 2,7-dimethoxynaphthene-1-carbaldehyde (1.00 g, 4.63 mmol**)** cooled at –55 ºC and maintained under an inert atmosphere. The mixture was left at room temperature with stirring for 24h. The soln. was treated with H_2O (40 ml), extracted with Et_2O (3×20 ml) and the organic layers were combined and dried (Na_2SO_4). Solvent evaporation gave a brown solid that was purified by column chromatography (light petroleum / diethyl ether), giving yellow crystals (52%). M.p.198-200 ºC [14]. FT-IR (Nujol): 3460 to 3097 (wide band), 1613. ^{1}H-NMR (DMSO-d_6): 6.90–6.98 (*m*, J = 8.7, H-C(3) and H-C(6)); 7.69 (*d*, J = 8.7 , H-C(4) or H-C(5)); 7.95 (*d*, J = 9.3, H-C(5) or H-C(4)); 8.32 (*d*, J = 2.1, H-C-(8)); 10 (*br s*, HO-C(7), this signal exchanged with D_2O); 10.69 (*s*, CHO); 11.71 (*s*, HO-C(2), this signal exchanged with D_2O).

*Ethyl 9-hydroxy-3-oxo-3*H-*benzo[f][1]benzopyran-2-carboxylate* (5): A mixture of 4 (0.500 g, 2.66 mmol) diethyl malonate (2.30 ml, 5.30 mmol), DMSO (10 ml), piperidine (3 ml) and glacial acetic acid (1 ml) was heated under reflux for 3h at 50 ºC. After cooling, H_2O (5 ml) was added. The precipitate was collected by filtration and washed with a solution of ethanol. The coumarin was obtained as a yellow solid (80%). M.p. 244–246º. FT-IR (Nujol) 3516, 1738 (C=O), 1682 (C=O), 1631. ^{1}H-NMR: 1.46 (*t*, J = 7.2, OEt); 4.48 (*q*, J = 7.2, OEt); 6.22 (*br s*, OH); 7.20 (*dd*, J = 2.7 and 9, H-C(8)); 7.30 (*d*, J = 9, H-C(5)); 7.66 (*d*, J = 2.7, H-C(10)); 7.83 (*d*, J = 9, H-C(7)); 8.01 (*d*, J = 9, H-C(6)); 9.24 (*s*, H-C(1)). MS: 285 (1.18, $[M+1]^+$), 284 (100, M^+), 256 (7), 239 (54), 228 (30), 210 (15), 212 (50), 184 (23), 155 (44), 126 (20), 77 (6). HR-MS: 284.068474 (M^+, $C_{27}H_{21}O_5$; calc. 284.068231).

General Procedure for the Synthesis of **6-9**: *p*-Toluenesulphonic acid (0.154 g, 0.89 mmol) and hydroxycoumarin (1.00 g, 6.17 mmol) were added to a solution of 1,1-diphenylprop-2-yn-1-ol (1.91 g, 9.26 mmol) in 50 ml of dry acetonitrile (compounds **6**, **9**) or dry toluene (compounds **7**,**8**). The suspension was refluxed for about 48 hours under an argon atmosphere and after cooling it was treated with water and extracted with chloroform (4×30 ml). The combined organic layers were washed with 10% NaOH solution (4×30 ml) and dried (Na_2SO_4). Solvent evaporation gave a yellow oil which was purified by column chromatography (petroleum ether / diethyl ether).

Ethyl 3,8-dihydro-3-oxo-8,8-diphenylpyrano[3,2-f][1]benzopyran-2-carboxylate(**6**): light yellow solid (20%). M.p. 192-193º. FT-IR (Nujol): 1756 (C=O), 1739 (C=O), 1694. ^{1}H-NMR: 1.40 (*t*, J = 7, OEt); 4.42 (*q*, J = 7, OEt); 7.56 (*d*, J = 10, H-C(9)); 7.08 (*d*, J = 10,

H-C(10)); 7.12-7.50 (*m*, H-C(5), H-C(6)), 7.24-7.44 (*m*, 10 arom. H, Ph); 8.78 (*s*, H-C(1)). ^{13}C-NMR: 14.22 (CH_3), 62.06 (OCH_2), 82.77 (C(8)), 113.52, 117.05 (C(5) or C(6)), 117.66 (C(9) or C(10)), 117.96, 118.30, 123.50 (C(5) or C(6)), 126.87 (Ph), 127.93 (Ph), 128.26 (Ph), 132.68 (C(9) or C(10)), 143.6, 143.8 (C(1)), 148.84, 150.18, 156.56 (C=O), 163.37 (C=O). The signals for C (5), (6), (9) and (10) were assigned by HETCOR. MS: 425 (1.24, $[M+1]^+$), 424 (75, M^+), 379 (7, $[M\text{-OEt}]^+$), 368 (16), 348 (22), 347 (100, $[M\text{-Ph}]^+$), 310 (18). HR-MS: 424.131777 (M^+, $C_{27}H_{20}O_5$; calc. 424.131074). U.V. λ_{max} (log ε) 391.5 (4,513), 321.0 (4,264), 266.5 (4,744).

Ethyl 2-oxo-8,8-diphenyl-2H,8H-pyrano[3,2-g][1]benzopyran-3-carboxylate(**7**): light brown solid (26 %), M.p. 171-172º. FT-IR: 1770, 1715. ^{1}H-NMR: 1.40 (*t*, J = 7, OEt); 4.39 (*q*, J = 7, OEt); 6.29 (*d*, J = 10, H-C(7)); 6.67 (*d*, J = 10, H-C(6)); 6.88 (*s*, H-C(10)); 7.24 (*s*, H-C(5)); 7.28-7.42 (*m*, 10 arom. H, Ph); 8.44 (*s*, H-C(4)). ^{13}C-NMR: 14.19 (CH_3), 61.65 (OCH_2), 84.38 (C(8)), 104.26 (CH), 112.24, 114.35, 118.78, 121.28 (CH), 126.80 (CH), 128.01 (CH), 128.32 (CH), 129.67 (CH), 143.63, 148.63 (CH), 156.81, 157.07, 158.56 (C=O), 163.29 (C=O). MS: 425 (30, $[M+1]^+$), 424 (100, M^+), 396 (1, $[M\text{-CO}]^+$), 379 (7, $[M\text{-OEt}]^+$), 348 (20), 347 (86, $[M\text{-Ph}]^+$), 319 (3). Anal. Calc. for $C_{27}H_{20}O_5$: C 76.42, H 4.72; found C 76.37, H 4.94. U.V. λ_{max} (log ε) 366.4 (4,512), 328.5 (4,264), 266.5 (4,744).

Ethyl 2-oxo-8,8-diphenyl-2H,8H-pyrano[2,3-f][1]benzopyran-3-carboxylate (**8**): off white solid (12%). M.p. 185-186ºC (ethanol). FT-IR: 1771, 1717. ^{1}H-NMR: 1.40 (*t*, J = 7, OEt); 4.40 (*q*, J = 7, OEt); 6.29 (*d*, J = 10, H-C(9)); 6.92 (*d*, J = 8.4, H-C(6)); 7.20 (*d*, J = 10, H-C(10)); 7.28-7.44 (*m*, 10 arom. H and H-C(5)); 8.45 (*s*, H-C(4). ^{13}C-NMR: 14.19 (CH_3), 61.63 (OCH_2), 84.31 (C(8)), 108.99, 112.06, 113.89, 114.35 (CH), 115.80 (CH), 126.86 (CH), 128.13 (CH), 128.27 (CH), 129.07 (CH), 130.18 (CH), 143.67, 149.20 (CH), 151.55, 156.67, 157.91 (C=O), 163.25 (C=O). MS: 424 (9), 347 (8), 279 (5), 149 (23), 119 (24), 107 (73), 106 (100), 91 (30), 79 (43), 77 (34). Anal. Calc. for $C_{27}H_{20}O_5$: C 76.42, H 4.72; found: C 76.36, H 4.69. U.V. λ_{max} (log ε) 354.0 (4,929), 290.5 (4,830), 264.5 (4,848).

Ethyl 3-oxo-10,10-diphenyl-3H,10H-pyrano[2´,3´:7,8]naphtho[2,1-b]pyran-2-carboxylate (**9**): red-brown solid (40 %). M.p. 232-234º. FT-IR (Nujol): 1752, 1694. ^{1}H-NMR: 1.50 (*t*, J = 7.2, OEt); 4.48 (*q*, J = 7.2, OEt); 6.31 (*d*, J = 9.6, H-C(11)); 7.23 (*d*, J = 9.6, H-C(12)); 7.24-7.40 (*m*, 6 arom. H and H-C(5) and H-C(8); 7.50-7.58 (*m*, 4 arom. H, Ph); 7.74 (*d*, J = 8.7, H-C(6)); 7.94 (*d*, J = 9, H-C(7)); 9.36 (*s*, H-C(1)). ^{13}C-NMR: 14.24 (CH_3), 61.85 (OCH_2), 82.72 (C(10)), 122.02, 113.65, 114.34 (CH), 115.51, 118.32 (CH),

123.41 (CH), 126.36, 126.91 (Ph), 127.09 (CH), 127.81 (Ph), 128.17 (Ph), 131.57(CH), 136.75 (CH), 143.82 (CH), 148.19 (CH), 154.67, 156.47, 157.91(C=O), 163.58 (C=O). MS: 476 (18, $[M+2]^+$), 475 (52, $[M+1]^+$), 474 (23, M^+), 429 (6). HR-MS: 475.154622 ($[M+1]^+$, $C_{31}H_{22}O_5$; calc. 475.154549). U.V. λ_{max} (log ε) 413.5 (3,439), 264.0 (4,604).

2-Oxo-8,8-diphenyl-2H,8H-pyrano[3,2-g][1]benzopyran-3-carboxylic (**10**): 1M NaOH (0.36 ml, 0.354 mmol) was added under stirring to a soln. of compound **7** (0.100 g, 0.236 mmol) in ethanol (10 ml) at room temperature. After stirring for 3 hours the mixture was cooled in an ice-water bath and acidified to pH=3 with 5M HCl. After storage in the cold for two hours the precipitate was collected on a filter, washed thoroughly with water and air dried to yield a light brown solid (40%). M.p. 180-183º. FT-IR (Nujol): 1949, 1759. ^{1}H-NMR: 6.35 (*d*, J = 10, H-C(7)); 6.72 (*d*, J = 10, H-C(6)); 6.98 (*s*, H-C(10)); 7.30-7.43 (*m*, 10 arom. H and H-C(5)); 8.79 (*s*, H-C(4)); 12.20 (*br s*, OH). ^{13}C-NMR: 85.01 (C(8)), 104.70 (CH), 111. 07, 112.93, 120.05, 120.92 (CH), 126.83 (CH), 127.58 (CH), 128.23 (CH), 128.45 (CH), 130.60 (CH), 143.31, 150.90 (CH), 156.51, 159.87, 163.05 (C=O), 164.27 (C=O). MS: 398 (28, $[M+2]^+$), 397 (100, $[M+1]^+$), 396 (45, M^+), 380 (16), 379 (54), 319 (17). HR-MS: 397.108271 ($[M+1]^+$, $C_{25}H_{16}O_5$; calc. 397.107599). U.V. λ_{max} (log ε) 349.0 (4,179), 263.5 (5,115144).

2-Oxo-8,8-diphenyl-N-[(3-trimethoxysilyl)propyl]-2H,8H-pyrano[3,2-g][1]benzopyran-7-carboxamide (**11**): Compound **10** (39.6 mg, 0.100 mmol) was dissolved in $CHCl_3$ (5 ml) and triethylamine (0.015 ml, 0.10 mmol) was added. The mixture was stirred and cooled to –5 ºC and ethylchloroformate (0.010 ml, 0.10 mmol) was added. The reaction mixture was kept at –5 ºC for 30 minutes, (3-aminopropyl)trimethoxysilane (0.017 ml, 0.10 mmol) was added and the stirring was kept overnight at room temperature. The reaction mixture was extracted with water, and the organic layer was collected and dried ($MgSO_4$). Solvent evaporation gave a yellow oil. (89%). FT-IR (Nujol): 2273, 1761, 1713. ^{1}H-NMR: 8.80 (*t*, J = 5.7, NH); 8.77 (*s*, H-C(4)); 7.41-7.27 (*m*, 10 arom. H and H-C(5)); 6.91 (*s*, H-(10)); 6.69 (*d*, J =9.9, H-C(6)); 6.30 (*d*, J = 9.9, H-C(7)); 3.58 (*s*, OCH_3); 3.48-3.41 (*m*, NCH_2); 1.77-1.70 (*m*, CH_2); 0.75-0.68 (*m*, $SiCH_2$). HR-MS: 558.19222 ($[M+1]^+$, $C_{31}H_{31}O_7NSi$; calc. 558.194806).

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