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Synthesis of a Photochromic Fused 2*H*-Chromene Capable of Generating a Single Coloured Species

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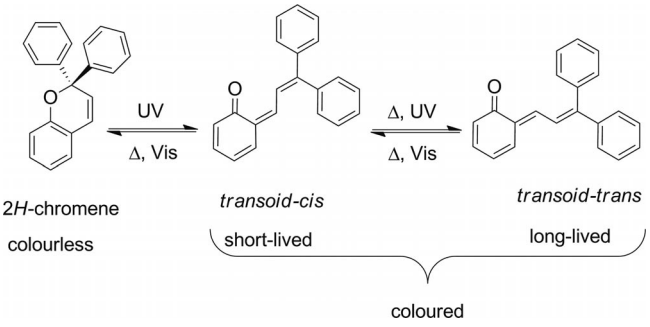
A new photochromic fused 2*H*-chromene that has a dehydropyran bridge between the pyran double bond and the benzene ring was prepared. Unlike standard 2*H*-chromenes that give rise to two coloured species (one short- and one long-lived) under UV irradiation, flash photolysis studies on this particular 2*H*-chromene show that the opening of the pyran ring led to the formation of a single, coloured, open species that bleaches to the uncoloured initial form in <1 ms. The design of this fused 2*H*-chromene avoids the formation of the undesirable long-lived, *transoid–trans*, coloured, open form; therefore, the colour fades very quickly, according to monoexponential kinetics, without the persistence of any residual colour commonly observed in 2*H*-chromenes. Acid treatment of 4-[(ethoxycarbonyl)methyl]-2*H*-chromenes led to the formation of lactones.

Introduction

Diaryl-substituted benzopyrans (2*H*-chromenes) and naphthopyrans are photochromic, colourless molecules that acquire colour under exposure to UV light. This phenomenon is due to a UV-promoted electrocyclic pyran ring-opening reaction, which leads to a mixture of two highly conjugated, coloured species that, in the absence of light, returns thermally to the uncoloured initial form (Scheme 1).[1] The incorporation of these substances, particularly the related naphthopyrans, in glass and polymer-based lenses led to the production of commercial plastic photochromic lenses, which present rapid colour changes in sunlight over a wide temperature range (0–40 °C).[2]

The two coloured, open forms, the *transoid–cis* (TC, major product) and *transoid–trans* isomers (TT, minor product; Scheme 1), have similar visible absorption spectra but very different thermal stability. Therefore, when the light source is removed, the system returns to the original colourless state (CF) according to a biexponential kinetic decay law. Initially, there is a fast colour decay due to the TC → CF conversion, followed by a slow colour decay due to the TT → TC double-bond isomerisation and TC → CF thermal ring-closure reactions.[3] As a result, significant residual colour remains for several minutes/hours depending on the structure of the photochromic molecule (Figure 1).[4–7]



Scheme 1. Photochromic equilibrium for 2,2-diphenyl-2*H*-chromene.

To improve the photochromic properties of 2*H*-chromenes and the parent naphthopyrans, many structural modifications have been tried, in particular, annelation at the *f*,*g*,*h* faces of the benzopyran and the introduction of substituents at the 5- and 6-positions or at the aryl groups located at the sp^3 pyran carbon atom.[8–17] However, after UV excitation, two photoisomers, in variable relative amounts, are always formed, and after an initial fast colour decay, they all show the slow bleaching of the more stable TT isomer (Figure 1).[18–24] One way to prevent the formation of this long-lived TT photoisomer, and therefore to avoid the persistence of residual colour, is to connect the pyran double bond to the benzene core. We have recently

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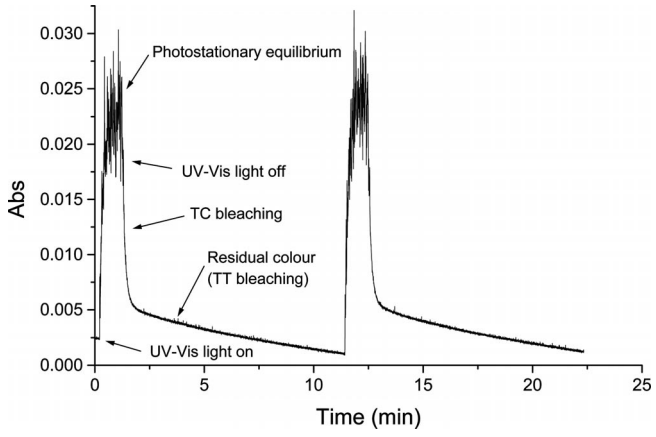
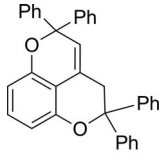


Figure 1. Absorbance evolution during UV/Vis irradiation and darkness for 2,2-diphenyl-2*H*-chromene.

reported the photochromic properties of a new type of fused dehydropyrano[2,3,4-*de*]benzopyran where the rotation of the double bond, which produces the long-lived TT isomer, is impossible due to the presence of a pyran bridge that links the double bond to the benzene ring. UV irradiation of this compound generated one coloured species that faded completely to the closed form in a few milliseconds according to a monoexponential decay law.[25] However, it was observed that, in $CDCl_3$, this unsymmetrical molecule established an equilibrium between two different pyran compounds due to the migration of the double bond, and therefore one might consider that, in solution and under UV irradiation, the opening of both pyran rings may occur with the formation of two different, coloured, short-lived, open forms.

To overcome this problem, we designed a new symmetrical fused 2*H*-chromene with two pyran rings substituted by the same phenyl groups (Scheme 2). Due to this symmetrical pattern, even if the double bond migrates, the ring opening will lead to the same molecule. In this paper, we describe the synthesis of this new, symmetrical, fused 2*H*-chromene and its photochromic behaviour under laser flash photolysis conditions.



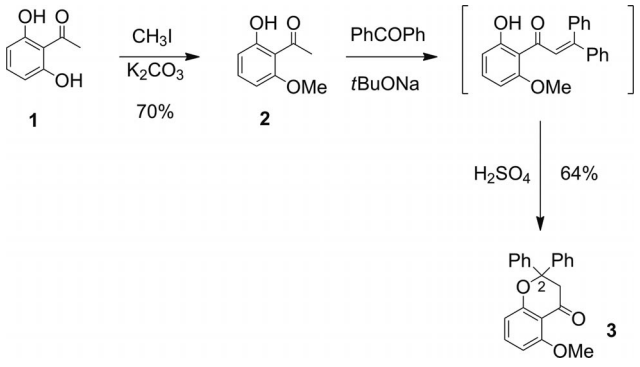
10

Scheme 2. New, symmetrical, fused 2*H*-chromene **10**.

Results and Discussion

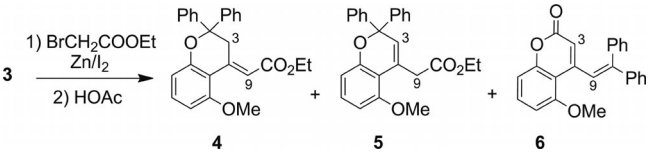
Synthesis

The synthesis of the target benzopyran **10** was more complicated than expected. 2*H*-Chromenes are usually prepared by the condensation of phenols with 1,1-diarylprop-2-yn-1-ol, which affords double-bond-unsubstituted benzopyrans in good yield. To prepare this fused benzopyran, we chose the condensation of 2′-hydroxyacetophenones with benzophenones, which is known to produce benzopyranones, a good precursor of benzopyrans, and an intermediate with a carbonyl group, which would allow the building of the second dihydropyran ring.[26] However, the reaction of the 2′,6′-dihydroxyacetophenone (**1**) with benzophenone in a basic medium did not afforded the expected hydroxybenzopyran, and a new aurone dye was isolated instead.[27] As the presence of the second hydroxy group seemed to inhibit the formation of the benzopyranone, we methylated one hydroxy group[28] and then performed the condensation of methoxyacetophenone **2** with benzophenone in the presence of *t*BuONa to give an intermediate, yellow, conjugated dye, which was treated with H_2SO_4 at 0 °C to afford 5-methoxybenzopyranone (**3**, Scheme 3). The ^{1}H NMR spectrum of **3** displayed two singlets at δ = 3.82 (3 H) and 3.47 (2 H) ppm, assigned to the methoxy and methylene protons, and a characteristic signal in the ^{13}C NMR spectrum at δ = 85.08 ppm for C-2.



Scheme 3. Synthesis of **3**.

To build the second dihydropyran ring, we performed a Reformatsky reaction of **3** with ethyl bromoacetate in the presence of zinc and iodine followed by reflux in acetic acid, which gave a mixture of three compounds that were separated by column chromatography: the dehydrobenzopyran **4** and the expected benzopyran **5** (major compound), both formed by nucleophilic addition followed by acid-catalysed dehydration, and the unexpected coumarin **6** (Scheme 4).

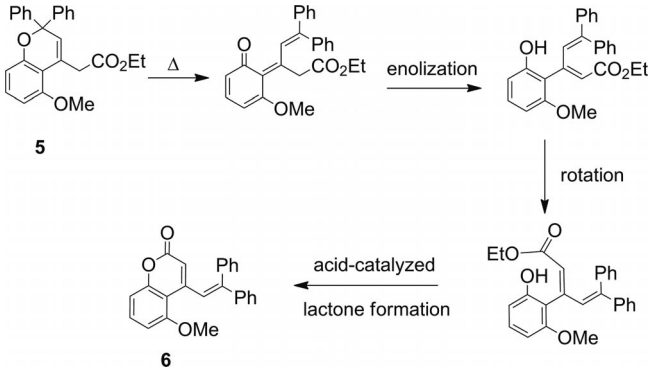


Scheme 4. Reformatsky reaction of **3**.

The ^{1}H NMR spectra of **4** and **5** are very similar, the main differences being the chemical shifts of the signals of protons 3 and 9. For **4**, the methylene 3-H signal is at δ = 4.27 ppm, and the ethylene 9-H signal is at δ = 7.03 ppm, whereas the ^{1}H NMR spectrum of **5** displayed a singlet for

allylic 9-H at δ = 3.57 ppm and a characteristic singlet at δ = 5.89 ppm for pyran 3-H. The (*E*) configuration of the double bond of **4** was established by 2D NOESY, which showed a dipolar correlation between 9-H and the protons of the methoxy group. The ^{1}H NMR spectrum of **6** shows the absence of the methylene protons and the terminal ester ethoxy group and displayed two doublets at δ = 5.84 and 7.26 ppm, coupled through ^4J = 1.4 Hz, assigned to the ethylene protons 3-H and 9-H. ^{13}C NMR spectroscopy supported the assignment of the structure by the presence of a low-field signal at δ = 160.7 ppm for the lactone C=O group. The structure of this compound was unambiguously established by 2D NMR experiments: The ^{1}H-^{13}C HMBC experiment displayed a long-range correlation between the lactone quaternary carbon atom and ethylene 3-H at δ = 5.84 ppm. In addition, NOESY underlined the dipolar correlation between the methoxy group (δ = 3.87 ppm) and proton 9-H (δ = 7.26 ppm), which confirmed the structure of **6**.

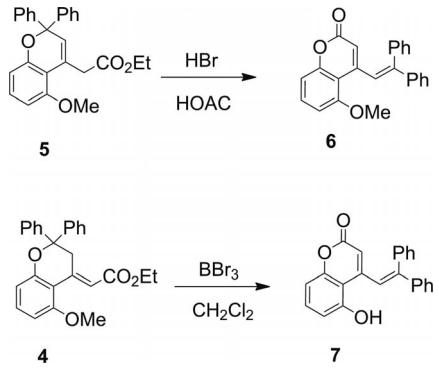
The lactone **6** was probably formed from **5** by thermal pyran ring opening followed by enolisation, rotation and acid-catalysed lactone formation as observed previously in naphthopyrans (Scheme 5).[29]



Scheme 5. Mechanism for the formation of **6**.

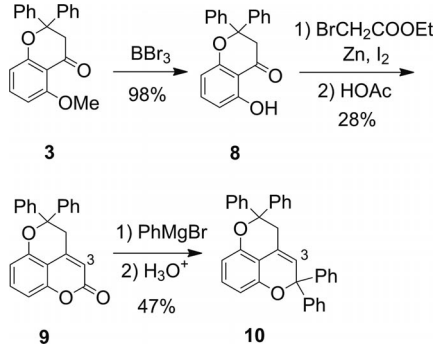
In order to form the pyranone ring, **5** was heated to reflux in a mixture of HBr/HOAc (1:1), a reagent known to promote the cleavage of the methoxy group, but the reaction led only to **6**, which confirms that this compound, observed in the Reformatsky reaction of **3** with ethyl bromoacetate/Zn/I_2, is formed after acidic treatment. An attempt to cleave the methoxy group of **4** by using BBr_3/CH_2Cl_2 led to a similar result: the reaction afforded the lactone **7** formed by a similar rearrangement to **6** followed by the deprotection of the methoxy group (Scheme 6).

As the acidic conditions needed to cleave the methoxy group promoted the rearrangement of **4** and **5** to **7** and **6**, we decided to deprotect the methoxy group of **3** before we performed the Reformatsky reaction, which was a better solution (Scheme 7). Thus, treatment of **3** with BBr_3/CH_2Cl_2 afforded after hydrolysis the 5-hydroxybenzopyranone **8** in quantitative yield. The ^{1}H NMR spectrum of **8** displayed a sharp singlet for the hydroxy proton at δ = 11.5 ppm, and a signal at δ = 197.1 ppm in the ^{13}C NMR spectrum due to the carbonyl group. Treatment of **8** with



Scheme 6. Rearrangement of **4** and **5** to **6** and **7**.

ethyl bromoacetate/Zn/I_2 followed by reflux in HOAc gave the fused dihydrobenzopyran **9** characterised by the disappearance of the hydroxy signal and the emergence of a singlet at δ = 6.20 ppm assigned to the ethylene lactone proton 3-H in the ^{1}H NMR spectrum. The change in the chemical shift of the carbonyl low-field signal from δ = 197.1 ppm to δ = 160.9 ppm confirmed the formation of the lactone ring. Finally, the reaction of **9** with the Grignard reagent PhMgBr gave, after acid hydrolysis, the target **10**. The ^{1}H NMR spectrum of **10** displayed an upfield shift of the 3-H proton signal from δ = 6.20 ppm to δ = 5.66 ppm indicative of the formation of the 2,2-diphenylpyran ring. This transformation was confirmed in the ^{13}C NMR spectrum by two signals at δ = 83.4 and 83.1 ppm, which are characteristic of the two pyran sp^3 C–O carbon atoms. The full NMR spectroscopic characterisation of this compound can be found in the Supporting Information. Thus, **10** was prepared in five steps from **1**.



Scheme 7. Synthesis of **10**.

Photochromic Behaviour

In acetonitrile solution, **10** is colourless with a maximum absorption at 283 nm (Figure 2). Laser irradiation at 266 nm of 10^{-4} M solutions of **10** in acetonitrile or methylcyclohexane (MCH) led to the fast development of a broad absorption band with two maxima at around 400 and 540 nm, which can be attributed to a highly conjugated benzopyran open form.

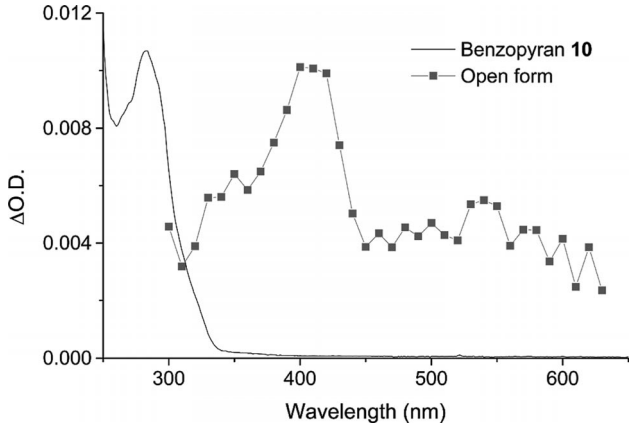


Figure 2. Normalised absorption spectra of **10** in 10^{-4} M degassed acetonitrile, collected before and after laser irradiation at 266 nm.

The time evolution of the absorbance at 400 and 540 nm indicates that the formation of the open form occurs within the laser pulse (ca. 20 ns), and no additional signals (in degassed solutions) were observed in the microsecond or millisecond time range, which could be attributed to the triplet state of the closed form (Table 1).

Table 1. Lifetimes τ [μs] for the coloured open form of **10** collected at 400 and 540 nm in MeCN and at 400 and 520 nm in MCH.

Solvent	τ at 400 nm	τ at 540 nm
MeCN	120	100
MeCN (degassed)	125	125
	τ at 400 nm	τ at 520 nm
MCH	105	110
MCH (degassed)	107	105

After the pulse, the absorbance measured at the maximum wavelength decays monoexponentially over all the spectra (Figure 3), and similar lifetimes of the coloured open form (125 μs) were obtained when the decays were collected at both maxima (400 and 540 nm). This is indicative of the formation of a single, short-lived, coloured, TC isomer that fades in less than 0.3 ms to the initial uncoloured state (Scheme 8). The lifetimes of this coloured photoisomer seem to be independent of the solvent polarity as very similar lifetimes (100–125 μs) were found in polar (MeCN) and nonpolar (MCH) solvents (Table 1).

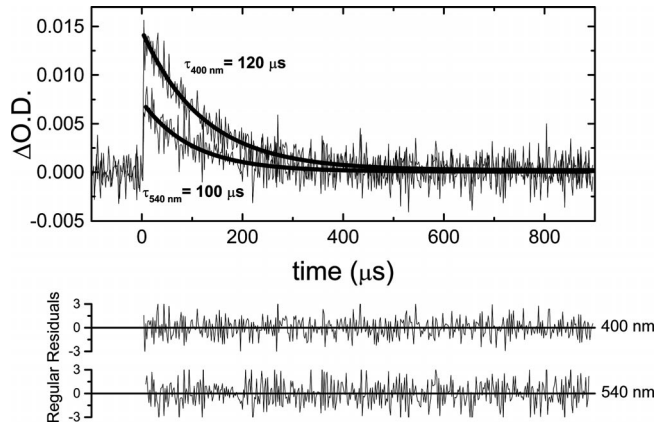
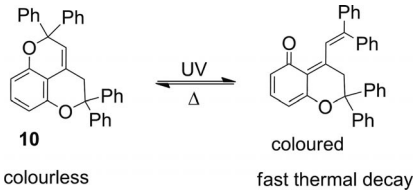


Figure 3. Decay traces for the open form of **10** in MeCN collected at 400 and 540 nm. Also shown are the monoexponential fittings to the decays and the corresponding residuals distribution.



Scheme 8. Photochromic equilibrium for **10**.

This behaviour contrasts with the biexponential decay observed with the common double-bond-unsubstituted 2*H*-chromenes that lead to some remaining colouration. Therefore, one can establish that the presence of the dihydropyran bridge in **10** prevents the formation of the undesirable, long-lived TT isomer, and thus the coloured species fades more quickly and without the persistence of residual colouration.

Conclusions

A new 2*H*-chromene that presents a dehydropyran ring between the pyran double bond and the benzene ring was prepared in five steps from 2′,6′-dihydroxyacetophenone (**1**). Laser irradiation at 266 nm of this symmetrical fused benzopyran led to the formation of a single short-lived coloured species that faded in less than 0.3 ms to the initial closed form according to a monoexponential process. As this structural modification of the benzopyran core prevents the formation of the long-lived TT isomer, the undesirable residual colouration, usually present in these photochromic molecules, was successfully avoided.

Experimental Section

General Methods: The reactions were monitored by TLC with aluminium plates precoated with Merck silica gel 60 F254 (0.25 mm). Column chromatography (CC) was performed on silica gel 60 (70–230 mesh). The new compounds were determined to be > 95% pure by ^{1}H NMR spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded at 298 K in $CDCl_3$ by using a Bruker ARX400 spectrometer (at 400.13 and 100.62 MHz) or in [D_8]toluene by using a Bruker 500 spectrometer (at 500 and 125 MHz). UV/Vis spectra were recorded with a CARY 50 Varian spectrophotometer. IR spectra were obtained with a Perkin–Elmer FTIR 1600 spectrometer by using KBr disks (w: weak; m: medium; s: strong).

Flash Photolysis: The absorption spectra (and decays) of the coloured open form of **10** were obtained by irradiating acetonitrile or MCH solutions of the sample with the fourth harmonic (266 nm) of an Nd:YAG laser (Spectra Physics) and collected at 280–650 nm with a laser flash photolysis apparatus (Applied Photophysics). The detection system is at right angles to the excitation beam, and a pulsed 150 W Xe lamp was used to analyse the absorption of the open form. The signal was fed into a Tektronix TDS 3052B digital analyser and transferred to an IBM RISC computer where the decays were analysed with the appropriate software (Applied Photophysics). For further details, see ref.[30]

Synthesis of 2,3-Dihydro-5-methoxy-2,2-diphenylchromen-4-one (3): A suspension of 2′-hydroxy-6′-methoxyacetophenone (**2**) (893 mg, 5.38 mmol), benzophenone (3.00 g, 16.5 mmol) and sodium *tert*-butoxide (2.60 g, 27.1 mmol) in toluene (30 mL) was heated under reflux for 1 h. During heating, the suspension became progressively orange. After cooling to room temperature, the solution was quenched with water (100 mL), extracted with ethyl acetate (3 × 50 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to leave a brown oil. H_2SO_4 (10 mL) was added, and the solution was stirred at 0 °C for 30 min. The black solution was quenched with ice (100 g) and extracted with ethyl acetate (3 × 50 mL). The organic phases were dried (Na_2SO_4) and concentrated under reduced pressure to leave a brown oil, which was purified by CC (0–30% EtOAc/petroleum ether) to give **3** as white crystals (1.137 g, 64%). M.p. 138–140 °C IR: $\tilde{\nu}$ = 3030 (w, C–H), 2985, 2941, 2830, 1691 (s, C=O), 1602, 1572, 1468 (s), 1334, 1244 (s, C–O), 1208, 1088 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.40 (m, 4 H), 7.37 (t, J = 8.5 Hz, 1 H), 7.33–7.20 (m, 6 H), 6.74 (d, J = 8.3 Hz, 1 H), 6.42 (d, J = 8.3 Hz, 1 H), 3.82 (s, OCH_3), 3.47 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.8, 161.4, 160.4, 142.7, 136.0, 128.4, 127.7, 126.1, 111.6, 110.7, 103.9, 85.1, 56.0, 49.7 ppm. EI-MS (TOF): *m*/*z* (%) = 330 (6.2) $[M]^+$, 253 (100) $[M - C_6H_5]^+$, 178 (41), 165 (29), 150 (83), 122 (39), 107 (62). HRMS: calcd. for $C_{22}H_{18}O_3$ $[M]^+$ 330.1256; found 330.1257.

Reformatsky Reaction of 3 with Ethyl Bromoacetate: A solution of **3** (300 mg, 0.91 mmol) and ethyl bromoacetate (600 μL, 5.4 mmol) in diethyl ether/benzene (1:4, 10 mL) was slowly added to a mixture of zinc (2.0 g, 31 mmol) and iodine (three small crystals) over 1 h and heated with stirring under reflux. After the addition was complete, the solution was maintained under reflux for 30 min and then quenched with water (100 mL). The aqueous phase was extracted with EtOAc (3 × 50 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. CH_3COOH (5 mL) was added to the residue, and the solution heated under reflux for 30 min. After cooling to room temperature, water (75 mL) was added, and the solution was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with water, dried (Na_2SO_4), and the solvent was evaporated under reduced pressure to leave a brown oil, which was purified by silica gel CC (0–12% EtOAc/petroleum ether) to give **4** (53 mg, 17%), **5** (100 mg, 33%) and **6** (15 mg, 5%).

Ethyl 2-[(*E*)-2,3-Dihydro-5-methoxy-2,2-diphenylchromen-4-ylidene]acetate (4): M.p. 164–166 °C. IR: $\tilde{\nu}$ = 3060 (w, C–H), 2979, 2933, 1728 (s, C=O), 1646, 1565 (m), 1476, 1460 (m), 1371, 1327, 1282 (s), 1237 (s, C–O), 1200 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.2 Hz, 4 H), 7.25 (m, 7 H), 7.03 (t, J = 1.3 Hz, 1 H), 6.80 (dd, J = 1.1, 8.3 Hz, 1 H), 6.46 (dd, J = 1.0, 8.4 Hz, 1 H), 4.27 (q, J = 7.0 Hz, 2 H), 4.18 (d, J = 1.3 Hz, 2 H), 3.84 (s, 3 H), 1.36 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 159.3, 156.7, 144.1, 143.8, 131.0, 128.3, 127.3, 126.1, 117.1, 111.1, 111.0, 103.3, 82.3, 59.9, 55.6, 35.8, 14.5 ppm. EI-MS (TOF): *m*/*z* (%) = 400 (2.8) $[M]^+$, 355 (7.5) $[M - OEt]^+$, 327 (72) $[M - COOEt]^+$, 326 (100), 276 (16), 167 (35). HRMS: calcd. for $C_{26}H_{24}O_4$ $[M]^+$ 400.1675; found 400.1673.

Ethyl 2-(5-Methoxy-2,2-diphenyl-2*H*-chromen-4-yl)acetate (5): M.p. 163–164 °C. IR: $\tilde{\nu}$ = 3041 (w, C–H), 2997, 2971, 2833, 1730 (s, C=O), 1651, 1599 (m), 1566, 1481 (m), 1462, 1409, 1364, 1272 (s), 1233 (s, C–O), 1201 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, J = 8.5 Hz, 4 H), 7.36–7.21 (m, 6 H), 7.06 (t, J = 8.3 Hz, 1 H), 6.62 (dd, J = 1.0, 8.1 Hz, 1 H), 6.39 (dd, J = 1.0, 8.3 Hz, 1 H), 5.89 (t, J = 1.0 Hz, 1 H), 4.22 (q, J = 7.0 Hz, 2 H), 3.72 (s, 3 H), 3.57 (d, J = 0.9 Hz, 2 H), 1.31 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.8, 156.3, 154.0, 144.6, 129.8, 129.5, 128.0, 127.4, 127.2, 127.1, 112.0, 110.6, 104.4, 82.0, 60.5, 55.0, 41.6, 14.4 ppm. EI-MS (TOF): *m*/*z* (%) = 400 (9.5) $[M]^+$, 371 (4) $[M - Et]^+$, 354 (8.2), 327 $[M - COOEt]^+$, 323 (42) $[M - C_6H_5]^+$, 313 (100) $[M - CH_2COOEt]^+$, 235 (12), 165 (10). HRMS: calcd. for $C_{26}H_{24}O_4$ $[M]^+$ 400.1675; found 400.1671.

4-(2,2-Diphenylvinyl)-2*H*-chromen-2-one (6): M.p. 122–128 °C. IR: $\tilde{\nu}$ = 3023 (w, C–H), 2933, 2837, 1728 (s, C=O), 1602 (s, C=C), 1468 (m), 1438, 1363, 1312, 1252 (m, C–O), 1185 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (t, J = 8.4 Hz, 1 H), 7.42–7.35 (m, 5 H), 7.30–7.24 (m, 4 H), 7.14 (m, 2 H), 6.97 (dd, J = 1.0, 8.4 Hz, 1 H), 6.79 (dd, J = 1.0, 8.4 Hz, 1 H), 5.84 (d, J = 1.4 Hz, 1 H), 3.87 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7, 157.9, 155.3, 151.8, 144.0, 142.2, 138.9, 131.9, 130.3, 128.5, 128.3, 128.1, 127.9, 126.8, 115.4, 110.4, 110.1, 106.3, 56.4 ppm. EI-MS (TOF): *m*/*z* (%) = 354 (100) $[M]^+$, 337 (94), 323 (42) $[M - OMe]^+$, 277 (48), 265 (30), 165 (62).

Synthesis of 5-Hydroxy-4-(2,2-diphenylvinyl)-2*H*-chromen-2-one (7): To a solution of **4** (53 mg, 0.13 mmol) in dry CH_2Cl_2 (5 mL) at 0 °C was added dropwise BBr_3 (200 μL, 1 M in CH_2Cl_2) under constant stirring. After the addition was complete, the solution was maintained at room temperature for 22 h. Cold water (75 mL) was added and the solution extracted with ethyl acetate (2 × 75 mL). The combined organic phases were dried (Na_2SO_4), and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and crystallised after addition of petroleum ether to give orange crystals, which were collected by filtration and washed with petroleum ether (10 mg, 23%). M.p. 143 °C (dec.). IR: $\tilde{\nu}$ = 3432 (m, O–H), 2904, 1674 (s, C=O), 1604 (s, C=C), 1498, 1453 (m), 1379, 1252, 1200, 1074 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.33 (m, 6 H), 7.32–7.26 (m, 3 H), 7.23 (d, J = 1.4 Hz, 1 H), 7.15 (m, 2 H), 6.92 (dd, J = 1.0, 8.4 Hz, 1 H), 6.73 (dd, J = 1.0, 8.2 Hz, 1 H), 6.27 (s, 1 H), 5.85 (d, J = 1.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 155.0, 154.3, 151.0, 148.2, 141.3, 138.0, 132.1, 130.1, 128.9, 128.6, 128.5, 128.4, 128.3, 123.9, 115.1, 111.7, 109.7, 108.9 ppm. EI-MS (TOF): *m*/*z* (%) = 340 (100) $[M]^+$, 323 (92) $[M - OH]^+$, 312 (57), 263 (44) $[M - C_6H_5]^+$, 235 (33), 178 (32). HRMS: calcd. for $C_{23}H_{16}O_3$ $[M]^+$ 340.1099; found 340.1086.

Synthesis of 2,3-Dihydro-5-hydroxy-2,2-diphenylchromen-4-one (8): To a suspension of **3** (0.928 g, 2.81 mmol) in dry diethyl ether (10 mL) at 0 °C was added dropwise BBr_3 (11 mL, 1 M in CH_2Cl_2) under constant stirring. After the addition was complete, the solution was maintained at 0 °C for 30 min, quenched with ice (75 g) and extracted with ethyl acetate (2 × 75 mL). The organic phases were dried (Na_2SO_4), and the solvent was removed under reduced pressure give to **8** as slightly yellow crystals, which were collected by filtration, washed with ethyl ether and air-dried (0.870 g, 98%). M.p. 176–177 °C. IR: $\tilde{\nu}$ = 3224 (w, O–H), 3023 (w, C–H), 2979, 1639 (s, C=O), 1565, 1498, 1460 (s), 1363, 1230 (s, C–O), 1208, 1155 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 11.48 (OH), 7.42–7.37 (m, 4 H), 7.35–7.28 (m, 5 H), 7.28–7.23 (m, 2 H), 6.58 (d, J = 8.2 Hz, 1 H), 6.41 (d, J = 8.3 Hz, 1 H), 3.51 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.1, 161.7, 159.6, 142.4, 138.3, 128.6, 128.0, 126.2, 109.4, 108.6, 108.2, 85.5, 47.8 ppm. EI-MS (TOF): *m*/*z* (%) = 316 (10) $[M]^+$, 239 (100) $[M - C_6H_5]^+$, 178 (19), 165 (19), 136 (17), 108 (16). HRMS: calcd. for $C_{21}H_{16}O_3$ $[M]^+$ 316.1099; found 316.1093.

Synthesis of 5,6-Dihydro-6,6-diphenylpyrano[2,3,4-*de*]chromen-2-one (9): A mixture of zinc (2.0 g, 31 mmol) and iodine (three small crystals) in diethyl ether/benzene (1:4, 4 mL) was stirred and heated

under reflux. A solution of **8** (1.00 g, 3.16 mmol) and ethyl bromoacetate (1.60 mL, 14.5 mmol) in diethyl ether/benzene (1:4, 4 mL) was slowly added over 1 h. After the addition was complete, the suspension was maintained under reflux for 2 h and then poured into water (100 mL). The aqueous phase was extracted with ethyl acetate (3 × 50 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. CH_3COOH (5 mL) was added to the residue, and the solution was heated under reflux for 30 min. After cooling to room temperature, water (75 mL) was added, and the solution extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water, dried (Na_2SO_4), and the solvent was evaporated under reduced pressure to leave a brown oil, which was purified by silica gel CC (0–10% EtOAc/petroleum ether) to give **9** as slightly yellow crystals (0.296 g, 28%). M.p. 169–172 °C. IR: $\tilde{\nu}$ = 3062 (w, C–H), 3023, 2971, 1730 (s, C=O), 1632, 1606 (m), 1462 (m), 1442, 1285, 1253, 1207, 1168, 1102 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.20 (m, 11 H), 6.91 (d, J = 8.2 Hz, 1 H), 6.79 (d, J = 8.3 Hz, 1 H), 6.20 (s, 1 H), 3.62 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 153.4, 153.2, 147.7, 142.5, 132.9, 128.5, 128.0, 126.4, 112.2, 109.9, 108.8, 107.4, 83.4, 39.0 ppm. EI-MS (TOF): *m*/*z* (%) = 340 (100) $[M]^+$, 323 (95), 312 (52), 263 (41), 235 (27), 178 (35), 165 (31). HRMS: calcd. for $C_{23}H_{16}O_3$ $[M]^+$ 340.1099; found 340.1087.

Synthesis of 5,6-Dihydro-2,2,5,5-tetraphenylpyrano[2,3,4-*de*]-chromen-2-one 10: A solution of **9** (100 mg, 0.29 mmol) in dry diethyl ether (4 mL) was treated with PhMgBr (8 mL, 1 M in Et_2O) and heated at reflux for 20 min. After removal of the solvent under reduced pressure, the residue was hydrolysed with HCl (5%, 20 mL) and stirred for 3 d. The solution was extracted with ethyl acetate (3 × 50 mL) and dried with anhydrous Na_2SO_4. Removal of the solvent under reduced pressure left a brown oil, which was purified by silica gel CC (0–4% EtOAc/petroleum ether) to give **10** as white crystals (65 mg, 47%). M.p. 182–183 °C. IR: $\tilde{\nu}$ = 3060 (w, C–H), 3030 (w, C–H), 2963, 2904, 1662 (m, C=C), 1609 (m), 1572 (m), 1490 (m), 1460, 1438, 1363, 1267 (m, C–O), 1208, 1074 cm^{-1}. ^1H NMR (500 MHz, [D$_8$]toluene): δ = 7.48–7.44 (m, 4 H), 7.35–7.22 (m, 6 H), 7.20–7.10 (m, 10 H), 7.01 (t, J = 8.2 Hz, 1 H), 6.59 (d, J = 8.2 Hz, 1 H), 6.37 (d, J = 8.0 Hz, 1 H), 5.66 (s, 1 H), 3.35 (s, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_8$]toluene): δ = 152.3, 152.0, 144.6, 143.5, 130.3, 128.4, 128.0, 127.5, 127.2, 127.1, 126.6, 125.0, 121.5, 109.3, 108.4, 108.2, 83.4, 83.1, 38.2 ppm. EI-MS (TOF): *m*/*z* (%) = 478 (31) $[M]^+$, 401 (100), 323 (17), 311 (20), 298 (15), 165 (31). HRMS: calcd. for $C_{35}H_{26}O_2$ $[M]^+$ 478.1933; found 478,1934.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra for all new compounds.

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