Synthesis and Spectrokinetic Studies of a New Family of Photochromic 2*H*-Chromenes (= 2*H*-1-Benzopyrans): Dimethyl 6-Aryl-2,2-dimethyl-2*H*-chromene-7,8-dicarboxylates

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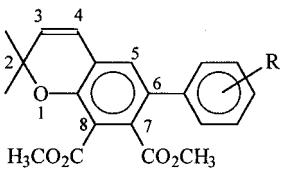
A series of dimethyl 6-aryl-2,2-dimethyl-2*H*-chromene-7,8-dicarboxylates were synthesized, and the photochromic properties of this new family of dimethyl-2*H*-chromenes were studied under continuous irradiation. The presence of the methoxycarbonyl groups was shown to stabilize the colored forms. This stabilization depended on the solvent, and in two cases the formation of long-lived opened forms was observed. Under irradiation with a mercury lamp, this family of 2*H*-chromenes showed a strong resistance to photodegradation.

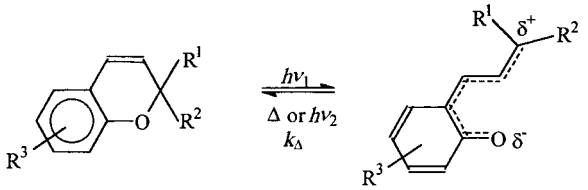
1. Introduction. – Organic photochromic compounds have been extensively studied during the last twenty years because of their potential applications for industrial purposes [1–4]. Among these compounds, the 2*H*-chromene (= 2*H*-1-benzopyran) series was particularly investigated, as it is used in the optical industry (variable-transmission glasses) [5]. The influence of different substituents has been studied to establish structure-reactivity relationships [6][7]. It has been shown that the presence of electron-withdrawing groups at the aromatic ring enhances the photochromic properties (increase of the A_{eq} value, *vide infra*). This is particularly the case with nitro groups. However, in this last case, the 2*H*-chromenes are very sensitive to photodegradation. It was also noted that the photochromic properties are increased (higher A_{eq} value, faster fading rate) when the benzene ring of the benzopyran is replaced by a benzo-condensed framework, such as a naphthalene or a phenanthrene ring. However, the synthesis and the photochromic behavior of 2*H*-chromenes bearing electron-withdrawing groups, such as methoxycarbonyl groups, and substituted with a freely rotating aromatic nucleus were not reported.

We describe here the synthesis and the spectrokinetic properties of a series of chromenes of type **1** bearing phenyl groups with different substituents and two methoxycarbonyl groups at positions 7 and 8.



2. Results. – The photochromic phenomenon of chromenes can be described by an equilibrium, induced by UV irradiation, between, at least, two species (*Scheme 1*). Usually, the opened form is colored while the closed one is colorless.

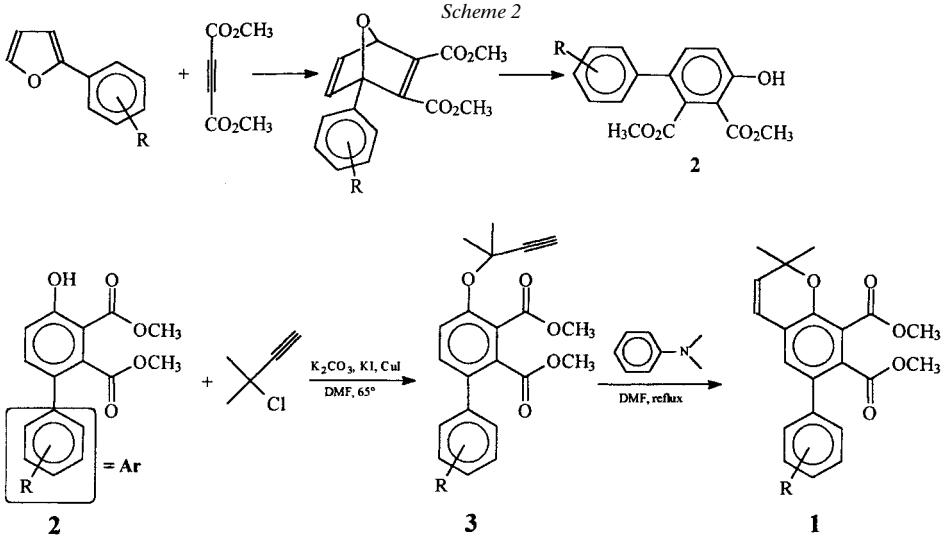
Scheme 1



Closed form Opened form

The various chromenes used in this work were synthesized starting from the corresponding phenol derivatives **2** which were obtained by a previously described method [8] (*Scheme 2*). The chromenes **1** were then prepared *via* **3** by a two-step procedure described by *Mann* and co-workers [9] (*Table 1*).

Scheme 2



a) For Ar, see *Table 1*

Table 1. *Formation of Propargylic Ether Derivatives* **3** *and 2,2-Dimethyl-2*H*-chromenedicarboxylates* **1**

Ar	Product	[%]	Product	[%]	Ar	Product	[%]	Product	[%]
Ph	**3a**	31	**1a**	49	4-MeO–C_6H_4	**3g**	58	**1g**	50
1-Naphthyl	**b**	91	**b**	59	4-Br–C_6H_4	**h**	88	**h**	47
2-Ph–C_6H_4	**c**	53	**c**	61	4-MeCO–C_6H_4	**i**	82	**i**	35
4-Ph–C_6H_4	**d**	38	**d**	70	4-Cl–C_6H_4	**j**	0	**j**	–
2-PhO–C_6H_4	**e**	73	**e**	63	4-NO_2–C_6H_4	**k**	0	**k**	–
4-PhO–C_6H_4	**f**	86	**f**	51					

The spectrokinetic studies were performed with a modified [10] *Beckman* UV spectrophotometer. The photochromic chromene **1** in toluene, MeCN, or EtOH was irradiated at 23° for 1.5 h under UV light with a Xe lamp (400 W). The irradiation was then stopped and the ring-closure process (*Scheme 1*) monitored by recording the decrease of the absorbance of the opened forms. The results are reported in *Table 2*.

Table 2. *Spectrokinetic Properties of the 2,2-Dimethyl-2*H*-chromenedicarboxylates* **1**

Ar	MeCN			EtOH			Toluene		
	λ_{max}[a]) [nm]	k_Δ[b]) [s^{-1}]	A_{eq}[c])	λ_{max}[a]) [nm]	k_Δ[b]) [s^{-1}]	A_{eq}[c])	λ_{max}[a]) [nm]	k_Δ[b]) [s^{-1}]	A_{eq}[c])
1a Ph	411	$5\cdot10^{-4}$, $2\cdot10^{-4}$	0.10	411	$2\cdot10^{-4}$	0.09	420	$8\cdot10^{-4}$, 10^{-4}	0.09
b 1-Naphthyl	405	$4\cdot10^{-4}$, $3\cdot10^{-4}$	0.05	410	$4\cdot10^{-4}$, $2\cdot10^{-4}$	0.03	418	$3\cdot10^{-4}$, 10^{-4}	0.15
c 2-Ph–C_6H_4	415	$4\cdot10^{-4}$, 10^{-4}	0.10	421	$5\cdot10^{-4}$, 10^{-4}	0.08	419	$32\cdot10^{-4}$, $3\cdot10^{-4}$	0.09
d 4-Ph–C_6H_4	406	$4\cdot10^{-4}$, $2\cdot10^{-4}$	0.09	406	$9\cdot10^{-4}$, $2\cdot10^{-4}$, $7\cdot10^{-4}$	0.11	416	$3\cdot10^{-4}$, $2\cdot10^{-4}$	0.20
e 2-PhO–C_6H_4	412	$4\cdot10^{-4}$, $2\cdot10^{-4}$	0.07	436	$4\cdot10^{-4}$	0.05	437	$1\cdot10^{-4}$	0.08
f 4-PhO–C_6H_4	418	$12\cdot10^{-4}$, $2\cdot10^{-4}$	0.11	415	$7\cdot10^{-4}$, $2\cdot10^{-4}$	0.0451	422	$5\cdot10^{-4}$, 10^{-4}	0.11
g 4-MeO–C_6H_4	409	0	0.11	410	$6\cdot10^{-4}$, 10^{-4}	0.08	420	$4\cdot10^{-4}$, 10^{-3}, $4\cdot10^{-4}$	0.17
h 4-Br–C_6H_4	455	$2\cdot10^{-4}$	0.03	438	$5\cdot10^{-4}$, $2\cdot10^{-4}$, $8\cdot10^{-4}$	0.06	432	$5\cdot10^{-4}$, $2\cdot10^{-4}$	0.03
i 4-MeCO–C_6H_4	437	$9\cdot10^{-4}$, 10^{-4}	0.08	410	0	0.20	437	$2\cdot10^{-4}$	0.04

[a]) λ_{max} of the 'opened form'. [b]) Kinetic constant(s) of the ring closure. [c]) Absorbance at the photostationary state.

3. Discussion. – 3.1. *Synthesis.* As can be seen from *Table 1*, the yields of the propargylic ether derivatives **3** are modest to good, except for the 4-chlorophenyl- and the 4-nitrophenyl-substituted derivatives **3j** and **3k**. In these two cases, the poorer reactivity of the phenolic precursors **2j** and **2k** can be explained by the inductive and resonance effects of these substituents decreasing the nucleophilicity of the phenol moiety. The yield for the subsequent cyclization step leading to the chromenes **1** is low when an electron-attracting group is located at the 4-position (see **1i** in *Table 1*).

3.2. *Influence on the λ_{max} of the Opened Form of* **1**. When toluene is replaced by the more polar MeCN as solvent in the irradiation of **1**, a hypsochromic effect is observed on the λ_{max} value of the opened form (see *Scheme 1*) when the substituent is an electron-donating group (see **1a**–**g**), while no effect is observed for an electron-withdrawing group (see **1i**). Such a negative solvatochromic effect is indicative of the existence of zwitterionic rather than quinone-like opened forms [11].

When toluene or MeCN are replaced by EtOH, the result is not so clear cut, and positive and negative solvatochromic effects are observed, depending on the nature of the substituent. In fact, in most cases, a hypsochromic effect is observed between the

nonpolar toluene and EtOH, while no effect or a bathochromic effect is observed between the aprotic polar MeCN and the protic polar EtOH. This indicates that H-bonding can also participate in the stabilization of opened forms. In a nonpolar solvent (toluene), in which solvatation effects are not important, the A_{eq} value is higher with electron-donating than with electron-withdrawing groups.

When the phenyl substituent of the parent chromene **1a** is substituted by another phenyl group, the effect on the λ_{max} value depends on the position of the latter substituent. Thus, in the case of the ([1,1′-biphenyl]-4-yl)-substituted compound **1d**, λ_{max} is smaller than in the case of the parent **1a** or the ([1,1′-biphenyl]-2-yl)-substituted compound **1c**. This reflects the coplanarity of the two aromatic rings of the biphenyl moiety in the case of **1d**, and thus that the two rings are conjugated. This effect on λ_{max} is not observed when non-conjugated substituents are introduced at the 2- or 4-position of the phenyl substituent of the parent **1a** (see **1e** and **1f**). The highest λ_{max} value is observed when a Br-atom is located at the 4-position (see **1h**). Compound **1i** shows a high λ_{max} value in aprotic solvents.

3.3 *Influence on the Kinetic Constants of the Ring Closure* (see *Scheme 1*). In most cases, we observed two kinetic constants, and in one case three constants (**1d**). This means that at least two opened species are involved in the ring-closure process. The only difference between these forms lies in the relative configuration of the conjugated system (*cis-cis-cis*, *cis-trans-trans*, *cis-trans-cis*, *trans-trans-trans*, *trans-trans-cis*, *etc.*) [12].

As in the case of nitro groups, the presence of the two carboxylate functions on the chromene structure decreases significantly the bleaching kinetic constants. Indeed, the chromene analog of **1a**, without the two ester groups does not exhibit any photochromic properties: its fading rate is so fast that the opened form cannot be detected under our experimental conditions. The decrease of the kinetic constants is due to the stabilization of the opened forms by the strong electron-withdrawing effect of the ester groups and also by an extended conjugation. Furthermore, k_{Δ} for **1g** in MeCN and **1i** in EtOH cannot be measured. In solution, the opened forms of these substrates are very stable and are still colored one month after the end of irradiation. If in the case of **1i** a strong stabilization can be envisioned because of the polarity and the chelating properties of EtOH, this is not the case for **1g**; the behavior of the latter can not be explained for the moment.

Table 2 shows that, at equilibrium (between the closed and the opened forms), the absorbances A_{eq} are not very important for the compounds studied, the highest one being 0.2 for **1d** in toluene and **1i** in EtOH. Usually, in the 2*H*-chromene series, these A_{eq} values are between 0.2 and 0.7 under the conditions we use.

In the case of **1d**, the equilibrium between the opened and the closed forms depends on the nature of the irradiation source. With a Xe lamp, an A_{eq} of 0.2 is observed at the equilibrium state, while on irradiation with a Hg lamp (500 W), A_{eq} reaches a value of 0.9. In fact, chromene **1d** exhibits in the UV spectrum a λ_{max} at a slightly lower value (334 nm) than the value usually observed for 2,2-dimethyl-2*H*-chromenes (*ca.* 345 nm) [13]. Thus, because of its emission spectrum, the Hg lamp is much more appropriate to induce the opening of chromene **1d**.

It must be noted that this type of irradiation with a Hg lamp is used to study the photodegradation processes of photochromic compounds. Usually under these conditions, degradation is observed already after 10 min of irradiation [14]. In the

case of the chromene **1d**, we did not observe any degradation after 1.5 h of irradiation. Thus, **1d** is particularly stable towards photodegradation.

Conclusion. – The synthesis of a new family of 2,2-dimethyl-2*H*-chromenes **1** that are substituted with an aryl and two ester groups is described. Depending on the nature of the aryl substituent, the yields are modest to good. As compared with the unsubstituted parent 2*H*-chromenes, the introduction of the aryl substituent does not lead to important modifications of the photochromic properties. However, the introduction of the methoxycarbonyl groups reduces the thermal bleaching constant, thus inducing photochromic behavior or enabling the observation of permanently colored forms. Moreover, the presence of these two functions has an effect on the photochromic properties similar to the one of a nitro group, but leads to much more stable compounds upon UV irradiation. It is shown that the influence of the irradiation source is very important: a stronger absorbance is observed with a Hg lamp than with a Xe lamp in the case of **1d**.

Experimental Part

General. TLC. *Merck* F_{254} silica gel. Column chromatography *Merck* silica gel *60* or *60 H* (for flash chromatography (FC)). M.p.: *Electrothermal-IA-9100* apparatus; in capillary tubes. LR Spectra: *Perkin-Elmer-297* spectrometer; $CHCl_3$ soln.; $\tilde{\nu}_{max}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-AC-250* spectrometer; at 250 and 62.2 MHz, resp., in $CDCl_3$ soln.; chemical shifts δ in ppm, coupling constants J in Hz.

Propargylic-Ether Formation: General Procedure. To a mixture of the polysubstituted arylphenol (2 mmol), K_2CO_3 (4 mmol), KI (3.4 mmol), and CuI (0.04 mmol) in dry DMF (8 ml) under Ar, 3-chloro-3-methylbut-1-yne [15] (4 mmol) is added. The mixture is stirred at 65° until no further conversion is observed by TLC. After cooling, H_2O (15–20 ml) is added and the mixture extracted with CH_2Cl_2 (3×20 ml). The combined CH_2Cl_2 extract is washed successively with 2N NaOH (2×15–20 ml), 2N HCl (2×15–20 ml), and H_2O to neutrality, dried ($MgSO_4$) and evaporated. The product is purified by FC (hexane/Et_2O).

Dimethyl 4-[(1,1-Dimethylprop-2-ynyl)oxy][1,1′-biphenyl]-2,3-dicarboxylate (**3a**): IR ($CHCl_3$): 1719, 1739 (C=O); 2386 (C≡C); 3300 (≡CH). ^{1}H-NMR: 1.59 (*s*, 6 H); 2.58 (*s*, 1 H); 3.51 (*s*, 3 H); 3.81 (*s*, 3 H); 7.17–7.76 (*m*, 7 H). ^{13}C-NMR: 29.69 (*q*); 29.69 (*q*); 52.53 (*q*); 52.69 (*q*); 72.94 (*s*); 73.91 (*d*); 86.13 (*s*); 122.03 (*d*); 122.13 (*s*); 126.96 (*s*); 127.71 (*d*); 127.71 (*d*); 128.55 (*d*); 128.55 (*d*); 132.30 (*d*); 132.47 (*d*); 135.59 (*s*); 140.15 (*s*); 152.96 (*s*); 167.33 (*s*); 168.50 (*s*). Anal. calc. for $C_{21}H_{20}O_5$ (352.38): C 71.51, H 5.67; found: C 71.39, H 5.94.

Dimethyl 3-[(1,1-Dimethylprop-2-ynyl)oxy]-6-(naphthalen-1-yl)benzene-1,2-dicarboxylate (**3b**): IR ($CHCl_3$): 1725, 1735 (C=O); 2395 (C≡C); 3300 (C≡CH). ^{1}H-NMR: 1.56 (*s*, 3 H); 1.58 (*s*, 3 H); 2.55 (*s*, 1 H); 3.09 (*s*, 3 H); 3.73 (*s*, 3 H); 7.09–7.32 (*m*, 6 H); 7.44 (*d*, $J = 8.0$, 1 H); 7.65 (*d*, $J = 8.6$, 1 H); 7.73 (*d*, $J = 8.0$, 1 H). ^{13}C-NMR: 29.50 (*q*); 29.79 (*q*); 52.19 (*q*); 52.61 (*q*); 73.79 (*s*); 75.02 (*d*); 86.00 (*s*); 121.79 (*d*); 122.09 (*s*); 125.26 (*d*); 125.90 (*d*); 126.36 (*d*); 126.92 (*d*); 127.20 (*s*); 128.16 (*d*); 128.38 (*d*); 132.16 (*s*); 133.11 (*s*); 133.51 (*d*); 133.58 (*d*); 134.08 (*s*); 137.86 (*s*); 153.19 (*s*); 167.37 (*s*); 167.57 (*s*). Anal. calc. for $C_{25}H_{22}O_5$ (402.44): C 74.54, H 5.47; found: C 74.73, H 5.50.

Dimethyl 4-[(1,1-Dimethylprop-2-ynyl)oxy][1,1′:2′,1″-terphenyl]-2,3-dicarboxylate (**3c**): IR ($CHCl_3$): 1725, 1738 (C=O); 2326 (C≡C); 3300 (C≡CH). ^{1}H-NMR: 1.52 (*s*, 6 H); 2.47 (*s*, 1 H); 3.45 (*s*, 3 H); 3.77 (*s*, 3 H); 6.83 (*d*, $J = 8.6$, 1 H); 7.12–7.35 (*m*, 9 H); 7.44 (*d*, $J = 8.6$, 1 H). ^{13}C-NMR: 29.30 (*q*); 29.86 (*q*); 52.47 (*q*); 52.62 (*q*); 73.95 (*s*); 74.56 (*d*); 86.17 (*s*); 121.98 (*d*); 125.51 (*s*); 126.92 (*d*); 127.26 (*d*); 128.20 (*d*); 128.20 (*d*); 128.75 (*d*); 129.94 (*d*); 129.94 (*d*); 130.19 (*d*); 130.47 (*d*); 132.58 (*s*); 133.83 (*d*); 135.85 (*s*); 138.63 (*s*); 140.84 (*s*); 141.04 (*s*); 152.50 (*s*); 167.41 (*s*); 167.93 (*s*). Anal. calc. for $C_{27}H_{24}O_5$ (428.48): C 75.61, H 5.60; found: C 75.76, H 5.64.

Dimethyl 4-[(1,1-Dimethylprop-2-ynyl)oxy][1,1′:4′,1″-terphenyl]-2,3-dicarboxylate (**3d**): IR ($CHCl_3$): 1728, 1733 (C=O); 2350 (C≡C); 3300 (C≡CH). ^{1}H-NMR: 1.61 (*s*, 6 H); 2.57 (*s*, 1 H); 3.53 (*s*, 3 H); 3.81 (*s*, 3 H); 7.24–7.40 (*m*, 6 H); 7.54 (*d*, $J = 8.2$, 2 H); 7.55 (*d*, $J = 7.9$, 2 H); 7.74 (*d*, $J = 8.7$, 1 H). ^{13}C-NMR: 29.59 (*q*); 29.59 (*q*); 52.49 (*q*); 52.57 (*q*); 73.83 (*s*); 74.65 (*d*); 86.02 (*s*); 121.95 (*d*); 126.93 (*s*); 127.14 (*d*); 127.14 (*d*); 127.20 (*d*); 127.20 (*d*); 127.58 (*s*); 128.87 (*d*); 128.87 (*d*); 128.98 (*d*); 128.98 (*d*); 132.16 (*s*); 132.35 (*d*); 135.02 (*s*); 138.99 (*s*); 140.35 (*d*); 140.68 (*s*); 152.92 (*s*); 166.92 (*s*); 168.41 (*s*). Anal. calc. for $C_{27}H_{24}O_5$ (428.48): C 75.61, H 5.60; found: C 75.81, H 5.77.

Dimethyl 4-[(1,1-Dimethylprop-2-ynyl)oxy]-2′-phenoxy[1,1′-diphenyl]-2,3-dicarboxylate (**3e**): IR ($CHCl_3$): 1724, 1735 (C=O); 2333 (C≡C); 3300 (≡CH). ^{1}H-NMR: 1.47 (*s*, 6 H); 2.49 (*s*, 1 H); 3.43 (*s*, 3 H); 3.69 (*s*, 3 H); 6.71–6.84 (*m*, 4 H); 6.97–7.18 (*m*, 6 H); 7.62 (*d*, *J* = 8.6, 1 H). ^{13}C-NMR: 28.48 (*q*); 30.50 (*q*); 51.12 (*q*); 53.36 (*q*); 72.78 (*s*); 73.60 (*d*); 86.35 (*s*); 117.21 (*d*); 117.21 (*d*); 119.81 (*d*); 122.52 (*d*); 123.12 (*d*); 124.35 (*d*); 125.02 (*d*); 127.57 (*s*); 128.37 (*d*); 128.37 (*d*); 130.85 (*d*); 131.72 (*d*); 131.90 (*s*); 131.97 (*s*); 134.40 (*s*); 152.75 (*s*); 153.76 (*s*); 157.19 (*s*); 167.37 (*s*); 167.41 (*s*). Anal. calc. for $C_{27}H_{24}O_6$ (444.48): C 72.89, H 5.40; found: C 73.13, H 5.38.

Dimethyl 4-[(1,1-Dimethylprop-2-ynyl)oxy]-4′-phenoxy[1,1′-biphenyl]-2,3-dicarboxylate (**3f**): IR ($CHCl_3$): 1720, 1735 (C=O); 2325 (C≡); 3300 (≡CH). ^{1}H-NMR: 1.37 (*s*, 6 H); 2.55 (*s*, 1 H); 3.51 (*s*, 3 H); 3.76 (*s*, 3 H); 6.87–7.03 (*m*, 5 H); 7.12–7.26 (*m*, 5 H); 7.69 (*d*, *J* = 8.6, 1 H). ^{13}C-NMR: 29.27 (*q*); 29.27 (*q*); 51.35 (*q*); 53.68 (*q*); 72.57 (*s*); 73.80 (*d*); 86.07 (*s*); 117.30 (*d*); 118.13 (*d*); 118.13 (*d*); 119.84 (*s*); 120.70 (*d*); 120.70 (*d*); 125.06 (*d*); 126.93 (*s*); 128.68 (*s*); 131.15 (*d*); 131.15 (*d*); 132.25 (*d*); 132.25 (*d*); 134.82 (*s*); 134.88 (*d*); 152.85 (*s*); 157.07 (*s*); 157.19 (*s*); 167.22 (*s*); 168.45 (*s*). Anal. calc. for $C_{27}H_{24}O_6$ (444.48): C 72.89, H 5.40; found: C 73.11, H 5.46.

Dimethyl 4-[(1,1-Dimethylprop-2-ynyl)oxy]-4′-methoxy[1,1′-biphenyl]-2,3-dicarboxylate (**3g**): IR ($CHCl_3$): 1722, 1736 (C=O); 2321 (C≡C); 3300 (≡CH). ^{1}H-NMR: 1.58 (*s*, 6 H); 2.57 (*s*, 1 H); 3.52 (*s*, 3 H); 3.73 (*s*, 3 H); 3.78 (*s*, 3 H); 6.83 (*d*, *J* = 8.7, 2 H); 7.14 (*d*, *J* = 8.7, 2 H); 7.26 (*d*, *J* = 8.6, 1 H); 7.69 (*d*, *J* = 8.6, 1 H). ^{13}C-NMR: 29.32 (*q*); 29.32 (*q*); 52.23 (*q*); 52.30 (*q*); 55.16 (*q*); 73.55 (*s*); 74.39 (*d*); 85.83 (*s*); 113.69 (*d*); 113.69 (*d*); 121.77 (*d*); 126.52 (*s*); 129.32 (*d*); 129.32 (*d*); 131.90 (*s*); 132.10 (*d*); 132.15 (*s*); 134.87 (*s*); 152.32 (*s*); 159.01 (*s*); 167.00 (*s*); 168.33 (*s*). Anal. calc. for $C_{22}H_{22}O_6$ (382.41): C 69.03, H 5.75; found: C 69.15, H 5.82.

Dimethyl 4′-Bromo-4-[(1,1-dimethylprop-2-ynyl)oxy][1,1′-biphenyl]-2,3-dicarboxylate (**3h**): IR ($CHCl_3$): 1725, 1735 (C=O); 2392 (C≡C); 3300 (≡CH). ^{1}H-NMR: 1.60 (*s*, 6 H); 2.58 (*s*, 1 H); 3.53 (*s*, 3 H); 3.81 (*s*, 3 H); 7.10 (*d*, *J* = 8.4, 2 H); 7.30 (*d*, *J* = 8.7, 1 H); 7.44 (*d*, *J* = 8.4, 2 H); 7.73 (*d*, *J* = 8.7, 1 H). ^{13}C-NMR: 29.34 (*q*); 29.34 (*q*); 52.35 (*q*); 52.41 (*q*); 73.63 (*s*); 74.55 (*d*); 85.65 (*s*); 121.69 (*d*); 121.73 (*s*); 126.77 (*s*); 129.89 (*d*); 129.79 (*d*); 131.38 (*d*); 131.38 (*d*); 131.77 (*s*); 131.96 (*d*); 133.92 (*s*); 138.77 (*s*); 152.92 (*s*); 166.84 (*s*); 167.85 (*s*). Anal. calc. for $C_{21}H_{19}BrO_5$ (431.88): C 58.43, H 4.40; found: C 58.28, H 4.66.

Dimethyl 4′-Acetyl-4-[(1,1-dimethylprop-2-ynyl)oxy][1,1′-biphenyl]-2,3-dicarboxylate (**3i**): IR ($CHCl_3$): 1705 (C=O, ketone); 1723, 1734 (C=O, esters); 2351 (C≡C); 3300 (≡CH). ^{1}H-NMR: 1.60 (*s*, 6 H); 2.55 (*s*, 3 H); 2.60 (*s*, 1 H); 3.51 (*s*, 3 H); 3.80 (*s*, 3 H); 7.29 (*d*, *J* = 8.6, 1 H); 7.31 (*d*, *J* = 8.4, 2 H); 7.76 (*d*, *J* = 8.6, 1 H); 7.90 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR: 26.66 (*q*); 29.41 (*q*); 29.41 (*q*); 52.44 (*q*); 52.50 (*q*); 73.74 (*s*); 74.76 (*d*); 85.64 (*s*); 121.70 (*d*); 127.00 (*s*); 128.40 (*d*); 128.40 (*d*); 128.57 (*d*); 128.57 (*d*); 131.81 (*s*); 132.00 (*d*); 134.08 (*s*); 136.00 (*s*); 144.80 (*s*); 153.26 (*s*); 166.88 (*s*); 167.79 (*s*); 197.68 (*s*). Anal. calc. for $C_{23}H_{22}O_6$ (394.42): C 69.98, H 5.58; found: C 70.13, H 5.39.

*Dimethyl 2,2-Dimethyl-2*H*-chromene-7,8-dicarboxylate* (= *Dimethyl 2,2-Dimethyl-2*H*-1-benzopyran-7,8-dicarboxylate) Formation: General Procedure.* To a soln. of the dicarboxylate **3** (1 mmol) in dry DMF (5 ml), *N*,*N*-dimethylaniline (0.05 ml) is added. The mixture is stirred under Ar at 140–145° overnight. After cooling, the mixture is poured into H_2O (10–15 ml) and extracted with CH_2Cl_2 (3 × 10–15 ml). The combined extract is washed successively with 2N NaOH (2 × 5 ml), 2N HCl (2 × 5 ml), and H_2O to neutrality, dried ($MgSO_4$), and evaporated. The product is purified by FC (hexane/Et_2O).

*Dimethyl 2,2-Dimethyl-6-phenyl-2*H*-chromene-7,8-dicarboxylate* (**1a**): IR ($CHCl_3$): 1725, 1735 (C=O). ^{1}H-NMR: 1.40 (*s*, 6 H); 3.49 (*s*, 3 H); 3.82 (*s*, 3 H); 5.71 (*d*, *J* = 9.9, 1 H); 6.27 (*d*, *J* = 9.9, 1 H); 6.97 (*s*, 1 H); 7.18–7.33 (*m*, 5 H). ^{13}C-NMR: 27.84 (*q*); 27.84 (*q*); 52.09 (*q*); 52.33 (*q*); 121.13 (*d*); 122.07 (*s*); 123.60 (*d*); 127.21 (*d*); 127.84 (*s*); 128.14 (*s*); 128.16 (*d*); 128.16 (*d*); 129.33 (*d*); 129.33 (*d*); 131.01 (*s*); 133.61 (*d*); 133.66 (*s*); 139.85 (*s*); 149.92 (*s*); 166.61 (*s*); 168.10 (*s*). Anal. calc. for $C_{21}H_{20}O_5$ (352.38): C 71.51, H 5.67; found: C 71.86, H 5.82.

*Dimethyl 2,2-Dimethyl-6-(naphthalen-1-yl)-2*H*-chromene-7,8-dicarboxylate* (**1b**): M.p. 171°. IR ($CHCl_3$): 1725, 1735 (C=O). ^{1}H-NMR: 1.42 (*s*, 3 H); 1.44 (*s*, 3 H); 3.16 (*s*, 3 H); 3.81 (*s*, 3 H); 5.69 (*d*, *J* = 9.9, 1 H); 6.22 (*d*, *J* = 9.9, 1 H); 6.95 (*s*, 1 H); 7.16–7.39 (*m*, 4 H); 7.54 (*d*, *J* = 8.2, 1 H); 7.71–7.79 (*m*, 2 H). ^{13}C-NMR: 27.94 (*q*); 28.03 (*q*); 51.92 (*q*); 52.44 (*q*); 77.58 (*s*); 121.14 (*d*); 121.90 (*s*); 123.73 (*s*); 125.04 (*d*); 125.74 (*d*); 125.80 (*d*); 126.05 (*d*); 126.63 (*d*); 127.80 (*d*); 128.12 (*d*); 130.39 (*d*); 131.77 (*s*); 132.06 (*s*); 132.37 (*s*); 133.36 (*s*); 133.88 (*d*); 137.80 (*s*); 150.09 (*s*); 166.87 (*s*); 167.30 (*s*). Anal. calc. for $C_{25}H_{22}O_5$ (402.44): C 74.54, H 5.47; found: C 74.54, H 5.68.

*Dimethyl 6-([1,1′-Biphenyl]-2-yl)-2,2-dimethyl-2*H*-chromene-7,8-dicarboxylate* (**1c**): IR ($CHCl_3$): 1725 and 1738 (C=O). ^{1}H-NMR: 1.32 (*s*, 6 H); 3.44 (*s*, 3 H); 3.78 (*s*, 3 H); 5.59 (*d*, *J* = 9.8, 1 H); 5.99 (*d*, *J* = 9.8, 1 H); 6.53 (*s*, 1 H); 7.12–7.34 (*m*, 9 H). ^{13}C-NMR: 27.78 (*q*); 27.97 (*q*); 52.26 (*q*); 52.50 (*q*); 77.54 (*s*); 121.39 (*d*); 123.52 (*s*); 126.84 (*d*); 127.14 (*d*); 127.97 (*d*); 128.13 (*d*); 128.87 (*d*); 129.81 (*d*); 129.81 (*d*); 130.23 (*d*); 130.23 (*d*); 130.34 (*d*); 131.16 (*d*); 131.57 (*s*); 133.66 (*s*); 133.98 (*s*); 138.63 (*s*); 140.75 (*s*); 141.03 (*s*); 149.63 (*s*); 166.97 (*s*); 167.78 (*s*). Anal. calc. for $C_{27}H_{24}O_5$ (428.48): C 75.61, H 5.60; found: C 75.72, H 5.60.

*Dimethyl 6-([1,1′-Biphenyl]-4-yl)-2,2-dimethyl-2*H*-chromene-7,8-dicarboxylate* (**1d**). M.p. 180°. IR ($CHCl_3$): 1728, 1733 (C=O). ^{1}H-NMR: 1.41 (*s*, 6 H); 3.53 (*s*, 3 H); 3.83 (*s*, 3 H); 5.72 (*d*, *J* = 9.9, 1 H); 6.28 (*d*, *J* = 9.9, 1 H); 7.01 (*s*, 1 H); 7.27 – 7.41 (*m*, 5 H); 7.52 – 7.57 (*m*, 4 H). ^{13}C-NMR: 28.29 (*q*); 29.57 (*q*); 52.58 (*q*); 52.75 (*q*); 77.50 (*s*); 121.56 (*d*); 124.08 (*s*); 127.27 (*d*); 127.27 (*d*); 127.39 (*d*); 127.39 (*d*); 127.73 (*d*); 127.81 (*s*); 129.05 (*d*); 129.05 (*d*); 129.15 (*d*); 129.15 (*d*); 129.75 (*d*); 133.12 (*s*); 133.63 (*s*); 134.06 (*d*); 139.37 (*s*); 140.42 (*s*); 140.97 (*s*); 150.44 (*s*); 167.01 (*s*); 168.55 (*s*). Anal. calc. for $C_{27}H_{24}O_5$ (428.48): C 75.61, H 5.60; found: C 75.64, H 5.76.

*Dimethyl 2,2-Dimethyl-6-(2-phenoxyphenyl)-2*H*-chromene-7,8-dicarboxylate* (**1e**): M.p. 111°. IR ($CHCl_3$): 1724, 1735 (C=O). ^{1}H-NMR: 1.33 (*s*, 6 H); 3.44 (*s*, 3 H); 3.78 (*s*, 3 H); 5.59 (*d*, *J* = 9.8, 1 H); 5.95 (*d*, *J* = 9.8, 1 H); 6.53 (*s*, 1 H); 6.99 – 7.35 (*m*, 9 H). ^{13}C-NMR: 27.62 (*q*); 27.82 (*q*); 52.12 (*q*); 52.36 (*q*); 77.38 (*s*); 121.24 (*d*); 121.72 (*s*); 123.38 (*s*); 126.69 (*d*); 126.99 (*d*); 127.82 (*d*); 127.98 (*d*); 127.98 (*d*); 129.66 (*d*); 129.66 (*d*); 103.07 (*d*); 130.19 (*d*); 130.66 (*d*); 131.41 (*s*); 133.51 (*d*); 133.84 (*s*); 138.47 (*s*); 140.58 (*s*); 140.87 (*s*); 149.48 (*s*); 166.83 (*s*); 167.64 (*s*). Anal. calc. for $C_{27}H_{24}O_6$ (444.48): C 72.89, H 5.40; found: C 72.91, H 5.53.

*Dimethyl 2,2-Dimethyl-6-(4-phenoxyphenyl)-2*H*-chromene-7,8-dicarboxylate* (**1f**): IR ($CHCl_3$): 1720, 1735 (C=O). ^{1}H-NMR: 1.37 (*s*, 6 H); 3.51 (*s*, 3 H); 3.79 (*s*, 3 H); 5.67 (*d*, *J* = 9.9, 1 H); 6.22 (*d*, *J* = 9.9, 1 H); 6.87 – 7.27 (*m*, 10 H). ^{13}C-NMR: 27.98 (*q*); 27.98 (*q*); 52.27 (*q*); 52.46 (*q*); 77.70 (*s*); 118.47 (*d*); 118.47 (*d*); 119.19 (*d*); 119.19 (*d*); 121.25 (*d*); 121.58 (*s*); 123.56 (*d*); 123.79 (*s*); 129.48 (*d*); 129.73 (*d*); 129.73 (*d*); 129.88 (*d*); 129.88 (*d*); 131.20 (*s*); 133.08 (*s*); 133.80 (*d*); 134.98 (*s*); 150.04 (*s*); 156.87 (*s*); 157.06 (*s*); 166.71 (*s*); 168.25 (*s*). Anal. calc. for $C_{27}H_{24}O_6$ (444.48): C 72.89, H 5.40; found: C 72.98, H 5.45.

*Dimethyl 2,2-Dimethyl-6-(4-methoxyphenyl)-2*H*-chromene-7,8-dicarboxylate* (**1g**): IR ($CHCl_3$): 1722, 1736 (C=O). ^{1}H-NMR: 1.37 (*s*, 6 H); 3.51 (*s*, 3 H); 3.72 (*s*, 3 H); 3.79 (*s*, 3 H); 5.67 (*d*, *J* = 9.9, 1 H); 6.23 (*d*, *J* = 9.9, 1 H); 6.80 (*d*, *J* = 8.6, 2 H); 6.92 (*s*, 1 H); 7.11 (*d*, *J* = 8.6, 2 H). ^{13}C-NMR: 28.10 (*q*); 28.10 (*q*); 52.45 (*q*); 52.62 (*q*); 55.46 (*q*); 77.73 (*s*); 113.94 (*d*); 113.94 (*d*); 121.48 (*d*); 121.58 (*s*); 123.90 (*s*); 129.59 (*d*); 129.71 (*d*); 131.31 (*s*); 132.56 (*s*); 133.52 (*s*); 133.88 (*d*); 149.99 (*s*); 159.21 (*s*); 166.94 (*s*); 168.61 (*s*). Anal. calc. for $C_{22}H_{22}O_6$ (431.41): C 69.03, H 5.75; found: C 69.15, H 5.67.

*Dimethyl 6-(4-Bromophenyl)-2,2-dimethyl-2*H*-chromene-7,8-dicarboxylate* (**1h**): M.p. 141°. IR ($CHCl_3$): 1725, 1735 (C=O). ^{1}H-NMR: 1.4 (*s*, 6 H); 3.52 (*s*, 3 H); 3.81 (*s*, 3 H); 5.72 (*d*, *J* = 9.9, 1 H); 6.25 (*d*, *J* = 9.9, 1 H); 6.90 (*s*, 1 H); 7.07 (*d*, *J* = 8.4, 2 H); 7.42 (*d*, *J* = 8.4, 2 H). ^{13}C-NMR: 27.95 (*q*); 27.95 (*q*); 52.36 (*q*); 52.51 (*q*); 77.74 (*s*); 121.06 (*d*); 121.63 (*s*); 122.42 (*s*); 123.88 (*s*); 129.21 (*d*); 129.67 (*s*); 129.97 (*d*); 129.97 (*d*); 131.40 (*d*); 131.40 (*d*); 132.48 (*s*); 133.94 (*d*); 139.01 (*s*); 150.29 (*s*); 166.57 (*s*); 167.91 (*s*). Anal. calc. for $C_{21}H_{19}BrO_5$ (431.88): C 58.43, H 4.40; found: C 58.49, H 4.46.

*Dimethyl 6-(4-Acetylphenyl)-2,2-dimethyl-2*H*-chromene-7,8-dicarboxylate* (**1i**): M.p. 116°. IR ($CHCl_3$): 1705 (C=O, ketone); 1723, 1734 (C=O, esters). ^{1}H-NMR: 1.41 (*s*, 6 H); 2.55 (*s*, 3 H); 3.51 (*s*, 3 H); 3.83 (*s*, 3 H); 5.73 (*d*, *J* = 9.8, 1 H); 6.27 (*d*, *J* = 9.8, 1 H); 6.95 (*s*, 1 H); 7.30 (*d*, *J* = 8.2, 2 H); 7.89 (*d*, *J* = 8.2, 2 H). ^{13}C-NMR: 26.88 (*q*); 28.19 (*q*); 28.19 (*q*); 52.57 (*q*); 52.73 (*q*); 78.06 (*s*); 121.23 (*d*); 122.15 (*s*); 124.16 (*s*); 128.58 (*d*); 128.58 (*d*); 128.78 (*d*); 128.78 (*d*); 129.33 (*d*); 130.86 (*s*); 132.88 (*s*); 134.24 (*d*); 136.15 (*s*); 145.24 (*s*); 150.75 (*s*); 167.95 (*s*); 168.00 (*s*); 197.95 (*s*). Anal. calc. for $C_{23}H_{22}O_6$ (394.42): C 69.98, H 5.58; found: C 70.04, H 5.62.

Spectrokinetics Studies. For the spectrokinetic studies, a *Beckman* UV spectrophotometer modified as previously described [10] is used. A $5 \cdot 10^{-4}$M soln. of the photochromic compound in toluene, MeCN, or EtOH is irradiated for *ca.* 1.5 h under UV light at 23° with a Xe lamp at a flux of 400 W/m^2. The irradiation is then stopped and the ring-closure process monitored by recording the decrease of the absorbance *A* of the opened forms. A Hg lamp (500 W) is also used. The data are analyzed with *Grafit*® software, which divides the experimental curve into mono-, bi-, or tri-exponential graphs and calculates the corresponding kinetic constants.

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