Photochromic Properties of New Benzoindene-Fused 2*H*-Chromenes

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The synthesis and the photochromic properties of new photochromic 6,7- and 7,8-benzoindene annellated benzopyrans are described. When compared to parent indeno-fused 2*H*-chromenes (2*H*-[1]benzopyrans), compounds **10** and **12** exhibit a significant bathochromic shift of maximum-absorption wavelength, an increase in the colorability, and similar fading rates.

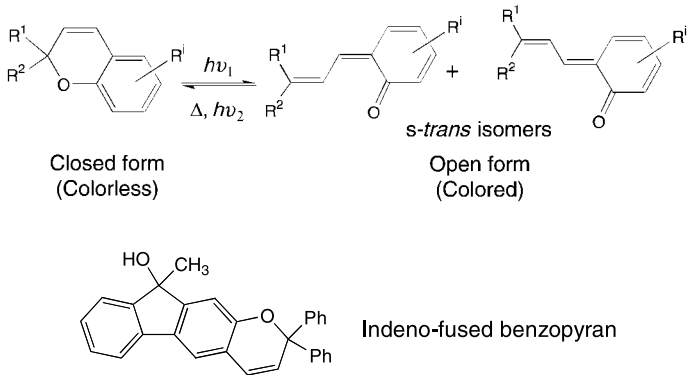
1. Introduction. – The great commercial success of photochromic plastic ophthalmic lenses in the last decade attracted the attention to the search for new organic molecules that exhibit photochromic behavior in polymeric matrices at room temperature [1]. These systems have the ability to undergo a reversible transformation between two states with different absorption spectra induced, at least in one direction, by electromagnetic radiation. If the photo-activated state absorbs in the visible region of the spectrum, a noticeable reversible change of color occurs as a consequence of the transformation. This makes these systems particularly useful for the production of variable-transmission optical materials, namely eyewear that darken under sunlight.

Benzo- and naphthopyrans are two classes of photochromic compounds that have been extensively studied in the last years [2]. Although most of them generate colors from yellow to red, recently, the introduction of some substituents allowed attainment of colors ranging from yellow to blue [3]. Thus, with a mixture of naphthopyrans it is possible to cover almost the whole visible spectrum. However, it is necessary that all compounds have similar discoloration rates in order to obtain a homogeneous behavior in the return to the original uncolored state. These photochromic compounds must also have a high colorability in order to obtain significant absorption at minimal concentration.

Benzo- and naphthopyrans undergo a photoinduced ring-opening process to give a set of stereoisomers with an extended conjugated π system (*Scheme 1*).

Recent studies have shown that the introduction of heterocycles, such as thiophene, as substituents [4][5] or the annellation with aromatic or heteroaromatic rings [6–8] have a great influence on the photochromic properties (discoloration rate, colorability, maximum absorption wavelength, fatigue resistance). We have recently observed that indeno-fused benzopyrans exhibit important properties, namely extended absorption in the visible spectra with two bands (around 430 and 500–570 nm) and interesting discoloration rates (0.12–0.91 s^{-1}) [8].

Scheme 1

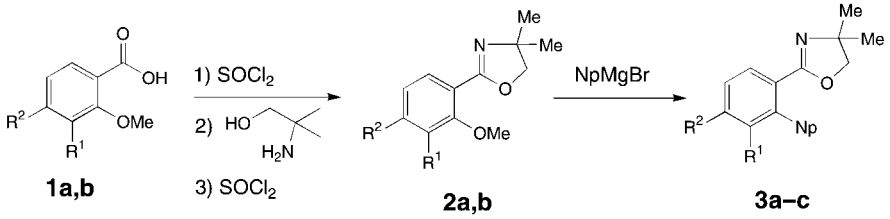


In this paper, we describe the synthesis of new benzoindeno-annellated benzopyrans. The extended conjugation of these compounds should improve their photochromic properties.

2. Results and Discussion. – 2.1. *Synthesis.* A widely used method for the synthesis of benzopyrans involves the acid-catalyzed reaction of phenols with propargylic alcohols [9][10]. The yields of this one-pot reaction are usually low, but the availability of the starting materials and the simplicity of the procedure rendered this reaction a suitable method for the synthesis of a large number of benzo- and naphthopyrans [2].

Besides the low yields that are often obtained, the main difficulty of this method is the synthesis of the phenolic precursors. The synthesis of some 'simple' phenols requires often several steps [9]. We carried out the synthesis of hydroxybenzofluorenones **5a**–**5d** in five steps from dimethoxybenzoic acids **1a**,**b**. To introduce the naphthyl group, the acids **1a**,**b** were transformed into the corresponding dihydrooxazoles **2a**,**b**, which are very reactive toward organometallic reagents and allow the nucleophilic aromatic substitution of the 2-MeO group by aryl groups [11]. The reaction of dihydrooxazoles with *Grignard* reagents derived from 1-bromo- and 2-bromonaphthalene gave the naphthyl-oxazoles **3c** and **3a**,**b**, respectively (*Scheme 2*).

Scheme 2

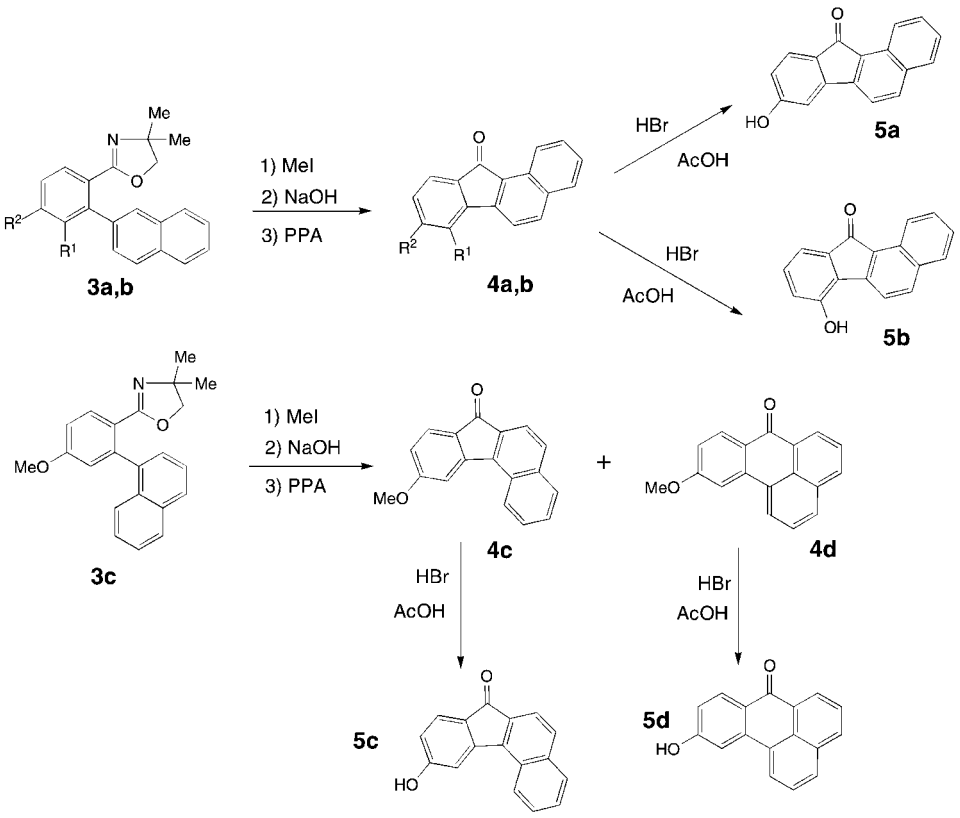


a R^1=H, R^2= MeO, **b** R^1=MeO, R^2= H, **c** R^1 = H, R^2 = MeO (Np = naphthyl)

The removal of the dihydrooxazole activating group is usually carried out under acidic conditions [11], but, with dihydrooxazoles **3a**–**3c**, only degradation products

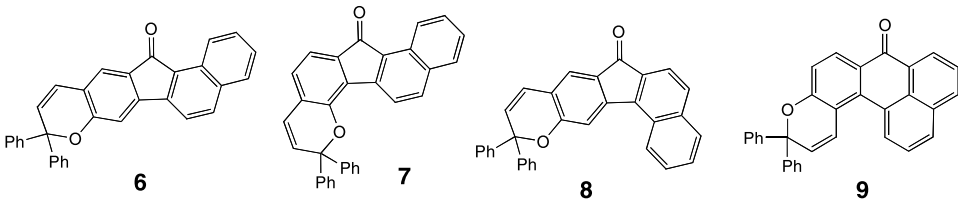
were obtained. The removal of the dihydrooxazole group was finally achieved by treating **3a**–**3c** with an excess of MeI, followed by the basic hydrolysis of the oxazolinium salt to yield the corresponding benzoic acids. Treatment with polyphosphoric acid (PPA) afforded ketones **4a**–**4d** (*Scheme 3*).

Scheme 3



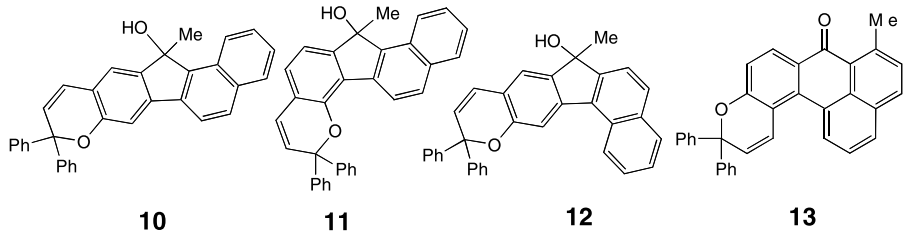
While the PPA cyclization of dihydrooxazoles **3a**,**b** gave only one product, the cyclization of the dihydrooxazole **3c** gave a mixture of methoxy-benzofluorenone **4c** and methoxy-benzo-anthracenone **4d**. The intramolecular *Friedel–Crafts* cyclization of dihydrooxazole **3c** ($SOCl_2/AlCl_3$) at $-10°$ was more selective, giving only the methoxy-benzanthrenone **4d**. Finally, treatment of **4a**–**4d** with HBr/AcOH converted the methoxy ketones to the corresponding phenols in acceptable yield (37–74%).

The condensation of phenols **5a**–**5d** with 1,1-diphenylprop-2-yn-1-ol under pyridinium toluene-4-sulfonate (PPTS) catalysis gave 2*H*-chromenes (=2*H*-[1]benzopyrans) **6**–**9**, respectively, in moderate yields. The reaction of hydroxybenzofluorenones **5a**,**c** gave only the linear isomers **6** and **8**, respectively. These compounds were not photochromic at room temperature.



As observed with the corresponding pyranofluorenones, the photochromic behavior of compounds **6**–**8** is strongly dependent on the presence of an sp^3-C-atom between the 2,2-diphenyl-2*H*-chromene and the naphthalene moieties [9].

Converting the C=O group to an alcohol allowed the production of products that exhibited photochromism at room temperature. Treatment of **6**–**8** with an ethereal solution of MeMgI gave, after hydrolysis, pyranofluorenols **10**–**12**, respectively, that exhibit photochromic behavior in toluene solutions at room temperature. For pyranobenzo-anthracenone **9**, this reaction gave only degradation products. The reaction of MeLi with **9** proceeded *via* 1,4 addition, followed by aromatization, and provided 2*H*-chromene **13**. No 1,2-addition to the C=O group was detected.

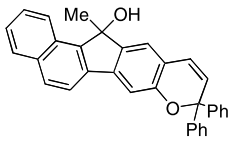
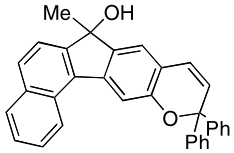
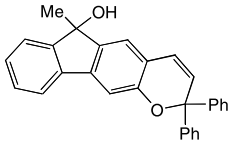
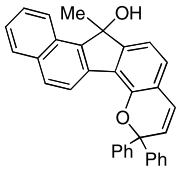
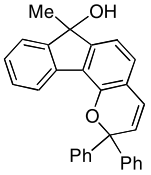
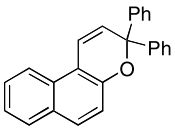


2.2. *Photochromic Properties.* The photochromic characteristics of the new compounds **10**–**12** were quantified by the flash-irradiation technique coupled to a rapid spectrophotometer (for details, *c.f. Exper. Part*). The photochromic behavior of the compounds described can be evaluated through the data listed in the *Table*, where the corresponding pyranofluorenols (Ref 1, Ref 2) and a naphthopyran (Ref 3) were also included for comparison.

All compounds exhibit two absorption bands, the first one between 444 and 463 nm and the second one in the region of 538–620 nm. The colorability is higher at the first band and, for compounds **10** and **12**, it reaches a high value (2.7 and 4.0). All compounds exhibit two phases of fading kinetics, which are probably due to different isomers present in the mixture obtained after irradiation. The second kinetic constant, although less important (2–20%), is 5–50 times lower than the first. As a consequence, after irradiation, rapid decay of the coloration was observed, followed by slow decay, which is probably responsible for the persistence of a residual color during several minutes after irradiation. This may be also due to colored photodegradation products.

When compared to the parent indeno-fused 2*H*-chromenes (Ref 1) compounds **10** and **12** exhibit a significant bathochromic shift of maximum-absorption wavelength (18–27 nm for the first band and 33–39 nm for the second), as expected. The

Table. *Spectrokinetic Properties: Maxima Wavelengths of the Colored Form* (λ_1, λ_2), *Colorability* (A_{01}, A_{02} are the absorbances just after the flash at λ_1 and λ_2, resp.), *and Thermal Bleaching Rate* (k_Δ) *of* 2H-*Chromenes* **10**–**12**, *and Three Reference Compounds in Toluene Solutions* (2.5×10^{-5} M at 25°); Ref 1 = *6-hydroxy-6-methyl-2,2-diphenyl-2*H-*pyrano[5,6-*b*]fluorene,* Ref 2 = *7-hydroxy-7-methyl-2,2-diphenyl-2*H-*pyrano[5,6-*c*]fluorene*, Ref 3 = *3,3-diphenyl-3*H-*naphtho[2,1-*b*]pyran*.

Compound	Structure	Annellation	λ_1 [nm]	A_{01}	λ_2 [nm]	A_{02}	k_Δ (amplitude) [s^{-1}] ([%])
10		6,7	457	4.0	538	0.99	0.091 (80) 0.017 (20)
12		6,7	463	2.7	544	0.68	0.11 (75) 0.022 (25)
Ref 1		6,7	439	1.4	505	0.63	0.120 (82) 0.011 (18)
11		7,8	444	0.94	620	0.24	0.88 (98) 0.014 (2)
Ref 2		7,8	432	0.57	573	0.15	0.91 (92) 0.110 (8)
Ref 3		5,6	432	0.84	–	–	0.090

colorability of both compounds is also higher in particular at the first absorption band. The fading rates are very similar with a slight increase of the lowest constant.

The same behavior is observed for compound **11**. The annellation of a benzene ring to the indene moiety of the molecule led to an increase of the maximum wavelength of absorption (from 432 and 573 nm in Ref 3 to 444 and 620 nm for **11**) and the

colorability (from 0.57 at 432 nm for Ref 2 to 0.94 at 444 nm). The first rate constant of compounds **11** and Ref 2 are very similar, while the second constant is lower for compound **11**.

3. Conclusions. – Three new benzoindeno-fused 2*H*-chromenes were prepared. These photochromic compounds exhibit improved colorabilities and important bathochromic shifts when compared to the corresponding indeno-fused 2*H*-chromenes. The annellation of an additional benzene ring has little effect on the fading rate. Compounds **10** and **12** exhibit high colorabilities, two bands of absorption, and k_Δ values that are well-suited for practical applications. Compound **11**, although exhibiting a maximum of absorption located at higher wavelength (620 nm), has a rather low colorability, and its discoloration rate is too high.

Experimental Part

1. *General*. Column chromatography (CC): silica gel *60* (70–230 mesh). M.p.: uncorrected. FT-IR spectra: *Perkin-Elmer FTIR 1600*; in cm^{-1} (KBr disc). ^{1}H-NMR Spectra: in $CDCl_3$ (if not stated otherwise) on a *Varian Unity Plus* (300 MHz); δ in ppm relative 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).

2. *Spectrokinetic Measurements*. For the determination at 25° of λ_1 and λ_2, A_{01} and A_{02}, and k_Δ, 50 μM of **10**–**12** in toluene were used. The flash-photolysis apparatus was coupled to a *Warner and Swasey* rapid spectrophotometer, to allow recording of absorption spectra of the colored forms in the visible 400–700 nm range (acquisition time: 1 ms, repetitiveness: 1.25 ms). Flashes (duration: 50 μs) were generated by two Xe tubes with a quartz envelope. The energy of the flashes was 60 J for the whole polychromatic emission spectrum. Thermostated (25°) 100-mm cells were used. The light from the analysis lamp (50 W, quartz-iodide) was filtered with 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, and the decrease in absorbance with time was monitored. The rate constants were calculated with a biexponential model.

3. *Synthesis. General Procedure for the Synthesis of* **2a** and **2b.** A mixture of dimethoxybenzoic acid (0.182 g, 1.0 mmol) in $SOCl_2$ (10 ml) was stirred at r.t., for 24 h. The excess $SOCl_2$ was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (10 ml). This soln. was added dropwise to a soln. of 2-amino-2-methylpropan-1-ol (0.178 g, 2.0 mmol) in CH_2Cl_2 (10 ml) kept between −10 and 0°. After stirring for 20 h at r.t. the suspension was filtered, and the filtrate was evaporated to give the amide as a yellow oil. The latter was treated dropwise with $SOCl_2$ (10 ml) and stirred at r.t. for 7 h. The soln. was then poured into dry Et_2O (100 ml), and the dihydrooxazole hydrochloride precipitated. The salt was filtered and treated with aq. 20% NaOH (50 ml). The alkaline soln. was extracted with Et_2O, dried (Na_2SO_4) and concentrated *in vacuo* to give the dihydrooxazole as a yellow oil.

4,5-Dihydro-2-(2′,4′-dimethoxyphenyl)-4,4-dimethyloxazole (**2a**). Yield 85%. FT-IR: 1641, 1608, 1274. ^{1}H-NMR: 1.36 (*s*, 2 Me); 3.81 (*s*, MeO); 3.85 (*s*, MeO); 4.04 (*s*, H–C(5)); 6.46–6.49 (*m*, H–C(3′), H–C(5′)); 7.71 (*d*, *J* = 9.0, H–C(6′)). MS: 235 (90, M^+), 220 (100), 192 (56), 165 (88), 149 (59), 135 (31), 121 (28), 106 (11), 92 (9), 77 (12).

4,5-Dihydro-2-(2′,3′-dimethoxyphenyl)-4,4-dimethyloxazole (**2b**). Yield 84%. FT-IR: 1646, 1577, 1261. ^{1}H-NMR: 1.39 (*s*, 2 Me); 3.86 (*s*, MeO); 3.87 (*s*, MeO); 4.11 (*s*, H–C(5)); 7.00 (*dd*, *J* = 8.0, 2.0, H–C(4′) or H–C(6′)); 7.05 (*t*, *J* = 8.0, H–C(5′)); 7.30 (*dd*, *J* = 8.0, 2.0, H–C(4′) or H–C(6′)). MS: 235 (100, M^+), 220 (48), 206 (44), 192 (31), 178 (28), 163 (96), 149 (72), 135 (43), 121 (42), 106 (19), 92 (19), 77 (26).

General Procedure for the Synthesis of **3a**–**3c**: A soln. of naphthylmagnesium bromide (prepared from bromonaphthalene (0.621 g, 3.0 mmol) and Mg (0.144 g, 6.0 mmol) in 20 ml of dry THF) was slowly added to a soln. of **2** (0.235 g, 1.0 mmol) in THF (15 ml). After stirring at r.t. for 24 h, the soln. was quenched in aq. sat. NH_4Cl, extracted with Et_2O (3 × 40 ml), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by CC (0–30% AcOEt/light petroleum).

4,5-Dihydro-2-[4′-methoxy-2′-(naphthalen-2″-yl)phenyl]-4,4-dimethyloxazole (**3a**). Yield 90%. FT-IR: 3054, 1648, 1604. ^{1}H-NMR: 1.29 (*s*, 2 Me); 3.71 (*s*, H–C(5)); 3.88 (*s*, MeO); 6.94 (*dd*, *J* = 8.7, 3.0, H–C(5′));

7.00 (*d*, *J* = 2.7, H–C(3′)); 7.49–7.52 (*m*, 2 H); 7.54 (*d*, *J* = 1.8, H–C(1″)); 7.76 (*d*, *J* = 9.0, H–C(6′)); 7.84–7.89 (*m* , 4 H).

4,5-Dihydro-2-[3′-methoxy-2′-(naphthalen-2″-yl)phenyl]-4,4-dimethyloxazole (**3b**). Yield 89%. FT-IR: 3052, 1658, 1577. ^{1}H-NMR: 1.15 (*s*, 2 Me); 3.58 (*s*, H–C(5)); 3.78 (*s*, MeO); 7.09 (*dd*, *J* = 7.5, 1.5, H–C(4′) or H–C(6′)); 7.34 (*dd*, *J* = 8.1, 2.1, H–C(4′) or H–C(6′)); 7.39 (*t*, *J* = 7.8, H–C(5′)); 7.46–7.49 (*m*, 2 H); 7.52 (*dd*, *J* = 8.5, 1.5, H–C(5″) or H–C(8″)); 7.80–7.88 (*m*, 4 H).

4,5-Dihydro-2-[4′-methoxy-2′-(naphthalen-1″-yl)phenyl]-4,4-dimethyloxazole (**3c**). Yield 90%. FT-IR: 3045, 1644, 1602. ^{1}H-NMR: ((D$_6$)DMSO): 0.69 (*s*, Me); 0.86 (*s*, Me); 3.17, 3.20, 3.44, 3.47 (*AB*, *J* = 8.0, H–C(5)); 3.83 (*s*, MeO); 6.92 (*d*, *J* = 3.0, H–C(3′)); 7.09 (*dd*, *J* = 8.7, 3.0, H–C(5′)); 7.32–7.54 (*m*, 5 H); 7.75 (*d*, *J* = 8.7, H–C(6′)); 7.87–7.95 (*m*, H–C(8″), H–C(4″)).

General Procedure for the Synthesis of **4a**–**4d**. A soln. of **3a**–**3c** (1.0 g) in 6 ml of MeI was stirred at r.t. overnight, and the excess MeI was removed *in vacuo*. To the crude MeI salt MeOH (12 ml) and NaOH 20% (12 ml) were added, and the mixture was heated to reflux for 12 h. The soln. was extracted with Et$_2$O, and the org. layer was discarded. The aq. layer was acidified with HCl (aq), extracted with Et$_2$O, dried (Na$_2$SO$_4$), and concentrated to give the corresponding acids. Without further purification, the benzoic acids were added to polyphosphoric acid (20 g; prepared by mixing P$_2$O$_5$ (13 g) with H$_3$PO$_4$ (7 g)), and the suspension was stirred at 60–70° for 8–24 h. The resulting dark-colored soln. was poured into 200 ml of H$_2$O and extracted with Et$_2$O (3 × 50 ml). The org. layer was dried (Na$_2$SO$_4$), and the solvent was evaporated under reduced pressure. The crude ketone was purified by CC (0–30% AcOEt/light petroleum).

*8-Methoxybenzo[*a*]fluoren-11-one* (**4a**). Yield 64% M.p. 148–150°. FT-IR: 1697, 1612, 1218. ^{1}H-NMR: 3.93 (*s*, MeO); 6.71 (*dd*, *J* = 8.1, 2.0, H–C(9)); 7.04 (*d*, *J* = 2.0, H–C(7)); 7.46 (*td*, *J* = 8.0, 1.2, H–C(3)); 7.56–7.64 (*m*, H–C(2), H–C(10), and H–C(5) or H–C(6)); 7.79 (*d*, *J* = 8.4, H–C(4)); 8.0 (*d*, *J* = 8.4, H–C(5) or H–C(6)); 8.99 (*dd*, *J* = 8.4, 0.9, H–C(1)). MS: 260 (100, *M*$^+$), 217 (14), 189 (25).

*7-Methoxybenzo[*a*]fluoren-11-one* (**4b**). Yield 94%. M.p. 121–123°. FT-IR: 1698, 1579, 1272. ^{1}H-NMR: 4.01 (*s*, MeO); 7.03 (*dd*, *J* = 6.6, 2.7, H–C(8)) or H–C(10)); 7.21–7.26 (*m*, 2 H); 7.41 (*td*, *J* = 6.6, 1.2, H–C(2) or H–C(3)); 7.57 (*td*, *J* = 6.6, 1.2, H–C(2) or H–C(3)); 7.77 (*d*, *J* = 8.7, H–C(4)); 7.95 (*d*, *J* = 8.4, H–C(5) or H–C(6)); 8.03 (*d*, *J* = 8.1, H–C(5) or H–C(6)); 8.95 (*dd*, *J* = 8.4, 0.6, H–C(1)). MS: 260 (100, *M*$^+$), 245 (30), 231 (15), 217 (24), 202 (13), 189 (52), 163 (19), 95 (13), 82 (4).

*10-Methoxybenzo[*c*]fluoren-7-one* (**4c**). Yield 12%. M.p. 148–150°. FT-IR: 1726, 1597, 1290. ^{1}H-NMR: 4.0 (*s*, MeO); 6.75 (*dd*, *J* = 8.0, 2.0, H–C(9)); 7.59–7.69 (*m*, 4 H); 7.75, 7.77, 7.82, 7.85 (AB, *J* = 8.1, H–C(5), H–C(6)); 7.89 (*dd*, *J* = 7.8, 1.8, H–C(1) or H–C(4)); 8.47 (*d*, *J* = 8.4, H–C(1) or H–C(4)). MS: 260 (8, *M*$^+$), 167 (51), 149 (100), 113 (22), 83 (8), 70 (33).

*10-Methoxybenzo[*d,e*]anthracen-7-one* (**4d**). Yield 34%. M.p. 158–160°. FT-IR: 3054, 1705, 1609. ^{1}H-NMR: 4.0 (*s*, MeO); 7.12 (*dd*, *J* = 9.0, 2.4, H–C(9)); 7.68–7.82 (*m*, 3 H); 8.04 (*d*, *J* = 8.4, H–C(3)); 8.22 (*dd*, *J* = 8.4. 1.2, H–C(4)); 8.44 (*d*, *J* = 6.9, H–C(1)); 8.51 (*d*, *J* = 9.0, H–C(8)); 8.77 (*dd*, *J* = 7.2, 1.2, H–C(6)). MS: 260 (5, *M*$^+$), 167 (6), 149 (22), 118 (6), 83 (10), 71 (6), 57 (9).

General Procedure for the Synthesis of **5a**–**5d**. A mixture of **4a**–**4d** (0.260 g, 1.0 mmol), AcOH (2.5 ml), and HBr 47% (5 ml) was heated under reflux for 6–20 h. After cooling, the mixture was poured into 100 ml of H$_2$O and extracted with Et$_2$O (3 × 50 ml). The org. layer was dried (Na$_2$SO$_4$), and the solvent was evaporated under reduced pressure. The crude ketone was purified by CC (0–50% AcOEt/light petroleum).

*8-Hydroxybenzo[*a*]fluoren-11-one* (**5a**). Yield 57%. M.p. 235–237°. FT-IR 3442, 3054, 1707, 1612. ^{1}H-NMR: 6.64 (*dd*, *J* = 7.8, 2.1, H–C(9)); 7.00 (*d*, *J* = 2.1, H–C(7)); 7.45–7.63 (*m*, 4 H); 7.80 (*d*, *J* = 7.8, H–C(4)); 7.99 (*d*, *J* = 8.4, H–C(5) or H–C(6)); 8.98 (*d*, *J* = 8.7, H–C-(1)). MS: 246 (100, *M*$^+$), 218 (5), 189 (33), 163 (5), 123 (3), 109 (7), 95 (85).

*7-Hydroxybenzo[*a*]fluoren-11-one* (**5b**). Yield 74%. M.p. 268–270°. FT-IR: 3286, 3059, 1651. ^{1}H-NMR: 6.93–7.12 (*m*, 3 H); 7.35 (*td*, *J* = 8.1, 0.9, H–C(2) or H–C(3)); 7.51 (*td*, *J* = 8.1, 1.2, H–C(2) or H–C(3)); 7.73 (*d*, *J* = 8.1, H–C(4)); 7.89, 7.92, 8.04, 8.07 (AB, *J* = 8.4, H–C(5), H–C(6)); 8.89 (*d*, *J* = 8.7, H–C(1)); 9.38 (*s*, OH). MS: 246 (100, *M*$^+$), 218 (20), 189 (49), 163 (14), 153 (4), 123 (6), 109 (4), 95 (10).

*10-Hydroxybenzo[*c*]fluoren-7-one* (**5c**). Yield 42%. M.p. 198–199°. ^{1}H-NMR: ((D$_6$)DMSO): 6.70 (*dd*, *J* = 7.9, 2.0, H–C(9)); 7.50 (*d*, *J* = 8.4, H–C(10)); 7.63–7.74 (*m*, H–C(2), H–C(3), H–C(5), H–C(11)); 7.95 (*d*, *J* = 8.1, H–C(1) or H–C(4)); 8.04 (*dd*, *J* = 7.8. 1.8, H–C(1) or H–C(4)); 8.51 (*d*, *J* = 8.4, H–C(6)). MS: 246 (100, *M*$^+$), 218 (10), 189 (34), 163 (10), 149 (19), 123 (4), 109 (8), 95 (8), 71 (4), 57 (5).

*10-Hydroxybenzo[*d,e*]anthracen-7-one* (**5d**). Yield 37%. M.p. 282–283°. FT-IR: 3284, 3059, 1644. ^{1}H-NMR: 7.04 (*dd*, *J* = 9.0, 2.7, H–C(9)); 7.78 (*t*, *J* = 7.8, H–C(5)); 7.83–7.88 (*m*, H–C(2), H–C(11)); 8.18–8.24 (*m*, H–C(4), H–C(8)); 8.40 (*dd*, *J* = 8.1, 1.2, H–C(3)); 8.56–8.59 (*m*, H–C(1), H–C(6)). MS: 246 (100, *M*$^+$), 218 (18), 189 (35), 163 (5), 149 (5), 109 (9), 95 (7).

*General Procedure for the Synthesis of 2*H-*Chromenes* **6**–**9**. To a mixture of **5a**–**5d** (0.246 g, 1.00 mmol), 1,1-diphenylprop-2-yn-1-ol (0.416 g, 2.0 mmol) and PPTS (10 mg) were added 50 ml of dry $CHCl_3$. The suspension was refluxed for 2 d under Ar. Solvent evaporation gave a red oil, which was purified by CC (4% AcOEt/hexane). Recrystallization from hexane/CH_2Cl_2 gave a crystalline material.

*9,9-Diphenyl-9*H,*13*H-*benzo[7,8]fluoreno[3,2-*b*]pyran-13-one* (**6**). Yield 51%. M.p. 232–233°. FT-IR: 3046, 1681, 1224. ^{1}H-NMR: 6.16 (*d*, *J* = 9.6, H–C(10)); 6.64 (*d*, *J* = 9.9, H–C(11); 7.07 (*s*, H–C(7) or H–C(12)); 7.30–7.46 (*m*, 12 H); 7.54–7.58 (*m*, 2 H); 7.77 (*d*, *J* = 8.4, H–C(4)); 7.90 (*d*, *J* = 8.1, H–C(5) or H–C(6)); 8.94 (*dd*, *J* = 7.5, 0.9, H–C(1)). DEPT: 84.10 (C_q); 109.60 (CH); 118.13 (CH); 120.55 (C_q); 122.93 (CH); 123.05 (CH); 124.42 (CH); 126.10 (CH); 126.54 (CH); 127.10 (CH); 127.99 (CH); 128.44 (CH); 128.60 (CH); 129.35 (CH); 130.09 (C_q); 134.62 (C_q); 135.52 (CH); 144.44 (C_q); 144.91 (C_q); 146.23 (C_q); 158.23 (C_q); 194.26 (CO). The signals of two C-atoms are probably buried under other signals. MS: 436 (100, M^+), 359 (96), 302 (12), 218 (8), 191 (7), 165 (9), 93 (4), 77 (5).

*2,2-Diphenyl-2*H,*7*H-*benzo[7,8]fluoreno[4,3-*b*]pyran-7-one* (**7**). Yield 28%. M.p. 233–234°. FT-IR: 1693, 1581, 1230. ^{1}H-NMR: 6.37 (*d*, *J* = 9.9, H–C(9)); 6.69 (*d*, *J* = 9.9, H–C(10)); 6.92, 6.94, 7.18, 7.20 (AB, *J* = 7.2, H–C(11), H–C(12)); 7.31–7.60 (*m*, 12 H); 7.78 (*d*, *J* = 8.1, H–C(4)); 7.97, 7.99, 8.13, 8.15 (*AB*, *J* = 8.4, H–C(5), H–C(6)); 8.96 (*dd*, *J* = 8.7, 1.2, H–C(1)). DEPT: 83.79 (C_q); 117.53 (CH); 121.99 (CH); 123.37 (CH.); 124.33 (CH); 126.28 (CH); 127.04 (CH); 127.59 (CH); 127.91 (C_q); 128.02 (CH); 128.53 (CH); 128.79 (C_q); 129.33 (CH); 130.19 (C_q); 131.03 (CH); 131.6 (CH.); 132.56 (C_q); 133.86 (C_q); 136.07 (CH); 136.43 (C_q); 144.49 (C_q.); 145.34 (C_q); 147.85 (C_q); 194.3 (CO). MS: 436 (100, M^+), 359 (45), 302 (7), 218 (5), 165 (5).

*11,11-Diphenyl-7*H,*11*H-*benzo[5,6]fluoreno[3,2-*b*]pyran-7-one* (**8**). Yield 54%. Mp. 210–211°. FT-IR: 1682, 1594, 1260. ^{1}H-NMR: 6.20 (*d*, *J* = 9.6, H–C(10)); 6.66 (*d*, *J* = 9.9, H–C(9)); 7.31–7.41 (*m*, 8 H); 7.46–7.49 (*m*, 3 H); 7.59–7.62 (*m*, 3 H); 7.70, 7.73, 7.76, 7.79 (AB, *J* = 8.4, H–C(5), H–C(6)); 7.79 (*dd*, *J* = 7.8, 1.8, H–C(1) or H–C(4)); 8.45 (*dd*, *J* = 7.8, 1.5, H–C(1) or H–C(4)). DEPT: 82.36 (C_q); 117.36 (CH); 118.47 (C_q); 125.08 (CH); 125.88 (C_q); 126.03 (CH); 126.49 (CH); 126.60 (C_q); 127.11 (CH); 127.82 (CH); 127.90 (CH); 128.30 (CH); 129.56 (CH); 129.97 (CH); 130.14 (CH); 130.68 (CH); 132.60 (C_q); 134.74 (CH); 135.74 (C_q); 144.15 (C_q); 144.52 (C_q); 158.10 (C_q); 182.88 (CO). The signal of one C-atom is probably buried under other signal. MS: 436 (100, M^+), 359 (97), 302 (8), 246 (10), 225 (6), 218 (8), 191 (6), 165 (7), 106 (16), 91 (7), 57 (9).

*3,3-Diphenyl-3*H,*7*H-*benzo[8,9]anthraceno[2,1-*b*]pyran-7-one* (**9**). Yield 57%. FT-IR: 3058, 1700, 1650. ^{1}H-NMR: 6.33 (*d*, *J* = 9.6, H–C(12)); 7.23–7.40 (*m*, 7 H); 7.55–7.65 (*m*, 5 H); 7.69 (*t*, *J* = 8.0, H–C(2)); 7.75 (*t*, *J* = 8.0, H–C(5)); 8.00 (*d*, *J* = 8.1, H–C(1) or H–C(3)); 8.20 (*m*, H–C(4), H–C(1) or H–C(3)); 8.43 (*d*, *J* = 8.4, H–C(8)); 8.68 (*dd*, *J* = 7.5, 1.2, H–C(6)). DEPT: 84.25 (C_q); 113.07 (CH); 116.68 (CH); 119.76 (C_q); 122.78 (CH); 124.67 (CH); 127.11 (CH); 127.76 (CH); 128.03 (CH); 128.12 (CH.); 128.19 (CH); 128.46 (CH); 128.65 (CH); 129.66 (CH); 130.15 (CH); 132.96 (C_q); 137.79 (C_q); 141.50 (C_q); 144.38 (C_q); 146.99 (C_q); 158.03 (C_q); 193.12 (CO). The signals of two C-atoms are probably buried under other signals. MS: 436 (100, M^+), 359 (83), 329 (7), 300 (6), 254 (6), 218 (4), 179 (7), 165 (17), 106 (3), 77 (74).

*General Procedure for the Synthesis of 2*H-*Chromenes* **10**–**12.** A soln. of MeMgI in Et_2O (2.0 ml, 2.0 mmol) was slowly added to a soln. of **6**–**9** (0.436 g, 1.0 mmol) in Et_2O (10 ml) under Ar. After stirring for 1–2 h, the soln. was treated with a sat. soln. of NH_4Cl, extracted with Et_2O (3 × 20 ml), and the org. layer was dried (Na_2SO_4). Solvent evaporation gave an orange oil, which was purified by CC (0–30% ethyl AcOEt/hexane).

*18-Methyl-9,9-diphenyl-9*H,*13*H-*benzo[7,8]fluoreno[3,2-*b*]pyran-13-ol* (**10**). Yield 57%. M.p. 180–182°. FT-IR: 3534, 1614. ^{1}H-NMR: 1.89 (*s*, CH_3), 6.22 (*d*, *J* = 9.6, H–C(10)); 6.73 (*d*, *J* = 9.6, H–C(11)); 7.28–7.39 (*m*, 8 H); 7.48–7.51 (*m*, 5 H); 7.57 (*td*, *J* = 8.4, 1.5, H–C(2) or H–C(3)); 7.69 (*d*, *J* = 8.1, H–C(4) or H–C(1)); 7.85–7.92 (*m*, 2 H); 8.44 (*d*, *J* = 8.1, H–C(4) or H–C(1)). DEPT: 26.7 (CH_3); 81.2 (C_q); 83.1 (C_q); 108.4 (C_q); 118.5 (CH); 121.0 (CH); 123.9 (CH); 124.6 (CH); 125.6 (CH); 126.7 (CH); 127.1 (CH); 127.2 (CH); 127.7 (CH); 128.3 (CH); 129.3 (CH); 129.4 (C_q); 130.0 (CH); 134.1 (C_q); 135.8 (C_q); 140.5 (C_q); 144.4 (C_q); 144.6 (C_q); 145.0 (C_q); 145.1 (C_q), 153.7 (C_q). MS: 452 (100, M^+), 437 (33), 375 (87), 359 (31), 331 (7), 302 (7), 226 (6), 191 (17), 180 (13), 167 (8), 149 (12), 83 (7), 57 (11). HR-MS: 452.179482 ($C_{33}H_{24}O_2$; calc. 452.177630).

*7-Methyl-(2,2)-diphenyl-2*H,*7*H-*benzo[7,8]fluoreno[4,3-*b*]pyran-7-ol* (**11**). Yield 97%. M.p. 191–192°. FT-IR: 3430, 1615, 1230. ^{1}H-NMR: 1.87 (*s*, Me_3); 6.23 (*d*, *J* = 9.6, H–C(9)); 6.72 (*d*, *J* = 9.9, H–C(10)); 7.01 (*d*, *J* = 7.5, 1 H); 7.14 (*d*, *J* = .5, 1 H); 7.22–7.59 (*m*, 12 H); 7.88–7.93 (*m*, 2 H); 8.36 (*d*, *J* = 8.4, 1 H); 8.46 (*d*, *J* = 8.4, 1 H). DEPT: 29.81 (Me); 81.65 (C_q); 83.45 (C_q); 115.53 (CH); 121.92 (C_q); 122.21 (CH); 123.67 (CH); 124.46 (CH); 125.35 (CH); 126.38 (CH); 126.50 (CH); 127.10 (CH); 127.72 (CH); 128.41 (CH); 128.72 (CH); 129.14 (CH); 129.34 (C_q); 130.05 (CH); 133.53 (C_q); 135.11 (C_q); 143.31 (C_q); 145.09 (C_q); 145.26 (C_q); 148.07 (C_q); 153.92 (C_q). MS: 452 (100, M^+), 437 (86), 375 (42), 360 (24), 331 (10), 302 (9), 259 (4), 219 (21), 191 (23), 165 (12), 91 (5). HR-MS: 452.177304. ($C_{33}H_{24}O_2$; calc. 452.177630).

*7-Methyl-11,11-diphenyl-7*H,*11*H-*benzo[5,6]fluoreno[3,2*-b*]pyran-7-ol* (**12**). Yield 93%. FT-IR: 3442, 1610. ^{1}H-NMR: 1.78 (*s*, Me); 6.22 (*d*, *J* = 9.9, H–C(10)); 6.71 (*d*, *J* = 9.9, H–C(9)); 7.26–7.39 (*m*, 7 H); 7.48–7.52 (*m*, 2 H); 7.59–7.64 (*m*, 4 H); 7.68, 7.71, 7.84, 7.87 (*AB*, *J* = 8.4, H–C(5), H–C(6)); 7.80 (*s*, H–C(8) or H–C(3)); 7.92 (*d*, *J* = 8.4, H–C(1) or H–C(4)); 8.61 (*d*, *J* = 8.1, H–C(1) or H–C(4)). DEPT: 29.46 (Me); 77.68 (C_q); 83.10 (C_q); 111.78 (CH); 119.76 (C_q); 120.99 (CH); 123.65 (CH); 124.09 (CH); 125.71 (CH); 126.94 (CH); 127.18 (CH); 127.64 (CH); 128.27 (CH); 128.62 (CH); 128.87 (CH); 129.34 (CH); 130.95 (CH); 134.61 (C_q); 141.14 (C_q); 144.09 (C_q); 144.81 (C_q); 145.02 (C_q); 149.75 (C_q); 153.40 (C_q); 167.82 (C_q). MS: 452 (100, M^+). 380 (8), 338 (7), 330 (100), 322 (4), 316 (20), 301 (7), 295 (10), 281 (74), 264 (19), 254 (33), 245 (25), 238 (21), 222 (50). HR-MS: 452.176941 ($C_{33}H_{24}O_2$; calc. 452.177630).

*8-Methyl-3,3-diphenyl-3*H,*7*H-*benzo[8,9]anthraceno[2,1*-b*]pyran-7-one* (**13**). A soln. of MeLi in hexane (10.0 ml, 10.0 mmol) was slowly added to a soln. of **9** (0.109 g, 0.25 mmol) in Et_2O (10 ml) under Ar at 0°. After stirring for 24 h at r.t., the soln. was treated with NH_4Cl, extracted with Et_2O (3 × 20 ml), and the org. layer was dried (Na_2SO_4). Solvent evaporation gave an orange oil, which was purified by CC (0–30% AcOEt/hexane) to provide **13** (0.090 g, 20%). FT-IR: 3060, 1695, 1650. ^{1}H-NMR: 3.05 (*s*, Me); 6.30 (*d*, *J* = 9.6, H–C(12)); 7.23–7.39 (*m*, 11 H); 7.54–7.57 (*m*, 2 H); 7.59–7.68 (*m*, H–C(2), H–C(5)); 7.98 (*dd*, *J* = 8.4, 1.2, H–C(1) or H–C(3)); 8.07 (*d*, *J* = 8.1, H–C(4)); 8,16 (*d*, *J* = 7.5, 0.9, H–C(1) or H–C(3)); 8.40 (*d*, *J* = 8.7, H–C(8) or H–C(9)). MS: 450 (100, M^+), 435 (65), 373 (68), 279 (7), 186 (8), 167 (11), 149 (22), 105 (4), 83 (5), 71 (8), 57 (13).

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