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Photochromic Fused-Naphthopyrans without Residual Color

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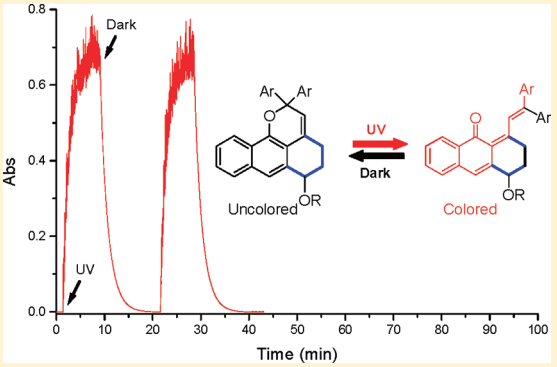
Supporting Information

ABSTRACT: A series of new photochromic fused-naphthopyrans with an alkyl bridge between the pyran ring and the naphthalenic core was synthesized in several steps from 4-(bromomethyl)benzocoumarin. The presence of the alkyl bridge in these new fused-naphthopyrans prevents the formation of one long-lived photoisomer and therefore has a dramatic effect on their photochromic properties: UV irradiation of common naphthopyrans gives rise to two isomeric colored photoisomers, one of which fades very slowly and is responsible for a persistent residual color. UV excitation of these new uncolored fused-naphthopyrans leads to the formation of only one colored photoisomer that fades completely to the uncolored state in few seconds/minutes following a monoexponential decay law, thus avoiding the problem of the residual coloration typically observed with naphthopyrans.



INTRODUCTION

Naphthopyrans are well-known for their photochromic properties. UV irradiation of these uncolored molecules leads to the formation of highly conjugated colored species that, in the absence of light, return thermally, with variable speed, to the closed form.[1] The phenomen occurs in solution or when the molecules are dispersed in polymeric matrices, although the kinetics of the process is highly affected by the nature of the host matrix.[2−8] The relative ease of chemical synthesis, the versatility of the photochromic activity, the thermal stability, and the notable fatigue resistance made these compounds the most commercially important class of photochromic molecules used for the production of photochromic plastic ophthalmic lenses that show a rapid and reversible color change at room temperature when exposed to the sunlight.[9−12]

Under near-UV light irradiation, naphthopyrans undergo an electrocyclic pyran-ring-opening with the formation of two colored photoisomers with a strong absorption in the visible part of the spectrum. UV and NMR studies revealed that the two photoisomers have similar absorption characteristics but different stabilities. The cleavage of the C(sp^3)-O bond of the closed form leads initially to the *transoid-cis* (TC) photoisomer, which is thermally unstable and rapidly returns to the uncolored state, or through light promoted C═C isomerization is converted to the more stable *transoid-trans* (TT) isomer that returns slowly to the uncolored form through the TC isomer (Scheme 1).[13−15]

Diarylnaphthopyrans are very sensitive to structural modifications. A great number of substitutions and/or annelations have been studied in order to increase the ability to produce intense colored forms (colorability), to tailor chromatic properties, or to change the fading rates of these systems.[16−25] The synthesis of naphthopyrans with large optical density and fast return to the uncolored closed form, at ambient temperature, is a key requirement for their industrial application. Although hundreds of naphthopyrans have been prepared in the last two decades, a problem still persists with these molecules: since the two colored photoisomers have different thermal stabilities, they exhibit different fading rates; most of the coloration fades rapidly, typically in few seconds/minutes (TC decay), but 10−20% of the coloration fades very slowly (several minutes/hours) because of the formation of the more stable TT isomer.[26−31] Therefore, although the coloration of the photochromic ophthalmic lenses under sunshine is quite fast (less than one minute), their complete discoloration, once the user returns indoors, is very slow.[32,33] A biexponential color decay is observed, and only after a long time, all the photoisomers are converted back to the closed uncolored form (Scheme 2, black line).

One way to avoid the formation of the TT isomer and overcome the problem of the residual color is to prevent the C═C isomerization of the short-lived TC isomer to the more stable TT isomer. This can be done by incorporating an alkyl bridge between the pyran double bond and the naphthalenic ring (Scheme 3).[34,35] The opening of the pyran ring in such fused-naphthopyrans should lead to only one colored photoisomer (TC), since the isomerization of the C═C bond (leading to TT isomer) is precluded. This photoisomer ought to exhibit a fast monoexponential color decay to the initial uncolored form (Scheme 2, line in red), thus avoiding the persistency of the residual color of the long-lived colored TT

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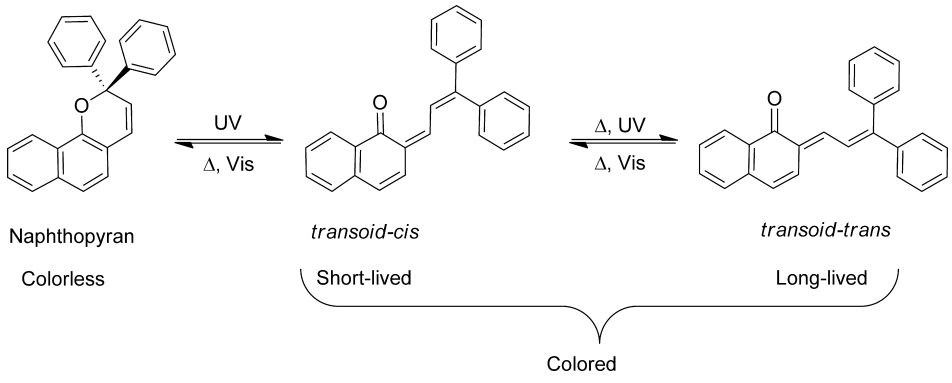
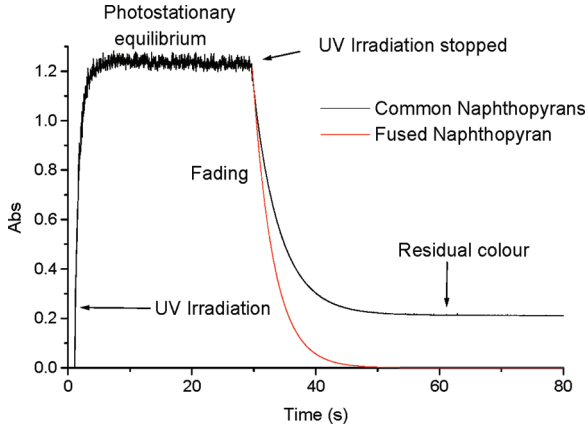
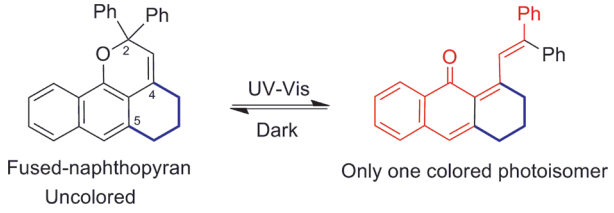
Scheme 1. Photochromic Equilibrium for 2,2-Diphenyl-2*H*-naphtho[1,2-*b*]pyrans



Scheme 2. Color Forming and Color Bleaching for Common Naphthopyrans (in Black) and a Hypothetical Fused-Naphthopyran (in Red) Measured at λ_{max}



Scheme 3. Photochromic Equilibrium for a Fused-Naphtho[1,2-*b*]pyran



isomer. In this paper, we describe the synthesis and photochromic properties of three new fused-naphthopyrans with such an innovative structure (Scheme 3).

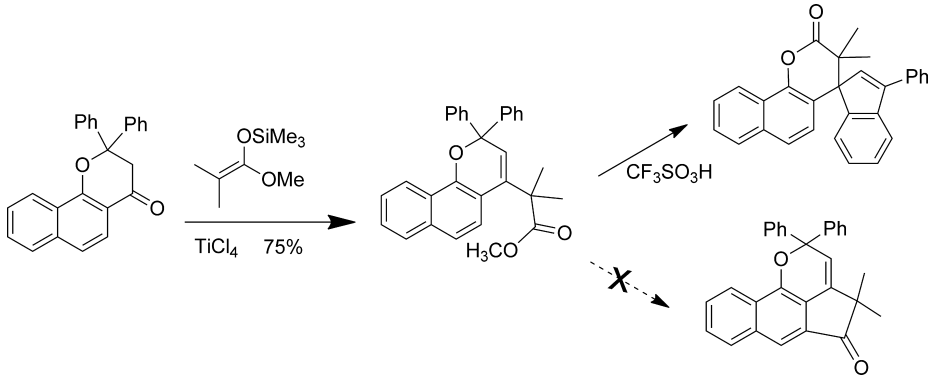
RESULTS AND DISCUSSION

Synthesis of Fused-Naphthopyrans 11−13. For the synthesis of the proposed fused-naphthopyran with a fused ring between carbons 4 and 5, we first explored the synthesis of a naphthopyran bearing an ester chain at carbon 4 that could form a five-membered cycle by an intramolecular ring closure leading to the desired fused-naphthopyran. Although this precursor was easily prepared from 2,2-diphenylnaphtho[1,2-*b*]pyran-4-one, we were unable to perform the intramolecular cyclization reaction under classic Friedel−Crafts conditions (conversion to the acyl chloride followed by Lewis acid treatment) or by the direct action of strong acids. Treatment of this 4-substituted naphthopyran with triflic acid at room temperature gave an unexpected cyclic lactone formed by an initial acid-promoted opening of the pyran ring followed by C−C bond rotation, intramolecular electrophilic aromatic substitution, and acid catalyzed lactone formation (Scheme 4).[36]

Because of the high reactivity of the pyran ring under acidic conditions and since naphthopyrans can also be prepared from coumarins, although usually in low yields,[37,38] we decided to prepare the target fused-naphthopyrans using a different synthetic approach: first the synthesis of a 4-substituted coumarin, then building the fused ring, and in the final step, formation of the pyran ring.

The key step of this synthesis was the preparation of 4-(bromomethyl)benzocoumarin **2** (Scheme 5). Since the allylic

Scheme 4. Unexpected Rearrangement of a 4-Substituted Naphthopyran in Triflic Acid



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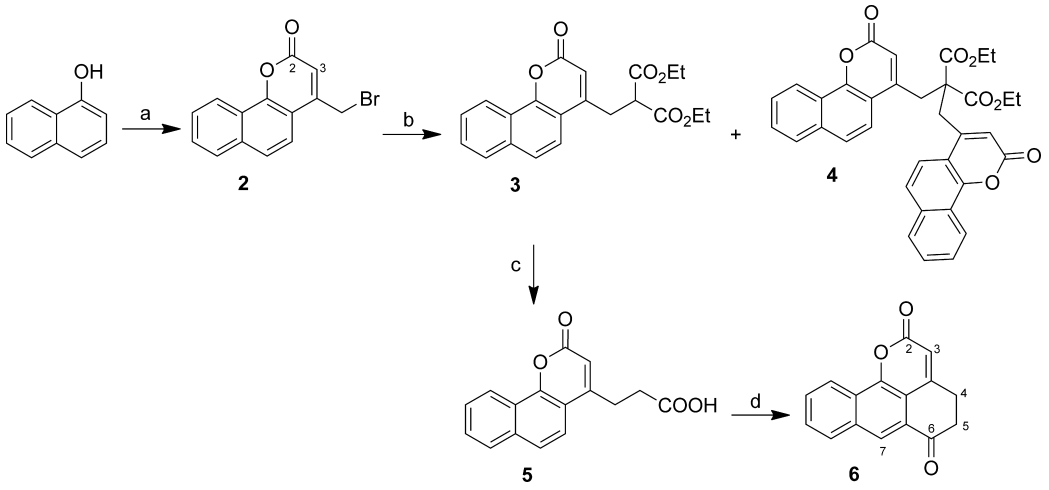
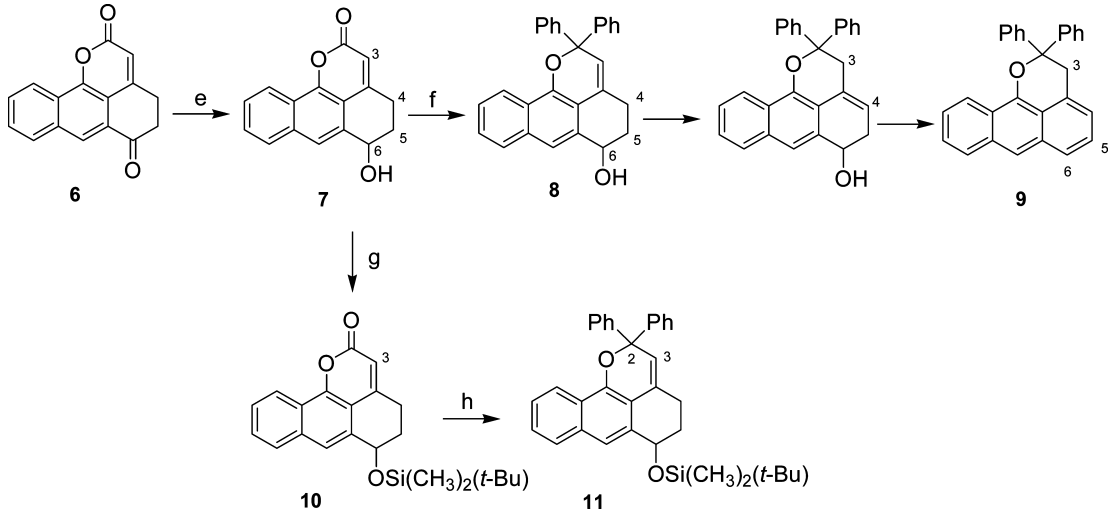
Scheme 5. Synthesis of Fused Coumarin 6[a]



[a](a) $BrCH_2COCH_2COOEt$ **1**, H_2SO_4, 56%; (b) diethyl malonate, NaH, DMSO, 39%; (c) (1) EtOH, NaOH, (2) DMSO, reflux, 97%; (d) $SOCl_2$, $AlCl_3$, 29%.

Scheme 6. Synthesis of Fused-Naphthopyran 11[a]



[a](e) $NaBH_4$/EtOH, 68%; (f) PhMgBr/Et_2O, H_3O^+, 40%; (g) *t*-$BuMe_2SiCl$/Imidazole/DMF, 79%; (h) PhMgBr/Et_2O, H_3O^+, 18%.

bromination of the known 4-methylbenzocoumarin[39] using NBS or LDA/Br_2 did not afford the desired brominated benzocoumarin, we chose to prepare the ethyl γ-bromoacetoacetate **1** by direct bromination of ethyl acetoacetate,[40] and then perform the reaction with 1-naphthol in sulfuric acid, which gave directly the desired 4-(bromomethyl)-benzocoumarin **2** in medium yield (56%) (Scheme 5).[41] The formation of the coumarin ring was confirmed by ^{1}H NMR spectroscopy, which displayed two key singlets at δ 6.56 (1H) and δ 4.54 ppm (2H) assigned to the ethylenic H-3 proton and CH_2Br and by the signals at δ 160.3 and δ 27.2 ppm in the ^{13}C NMR spectrum assigned to the carbonyl and CH_2Br carbons, respectively.

To build the alkyl bridge we performed the reaction of **2** with diethyl malonic ester in basic medium, which afforded the diester **3** along with a minor amount of product **4** formed by dialkylation of the malonic ester.[42] Basic hydrolysis and decarboxylation of the diester **3** under thermal conditions gave the monoacid **5** in good yield, which was then converted to the corresponding acyl chloride. Finally, the intramolecular Friedel–Crafts reaction in the presence of $AlCl_3$ gave the fused benzocoumarin **6** isolated in 29% yield after elution from silica. The formation of the fused ketone **6** was confirmed by ^{1}H NMR spectroscopy, which displayed a key singlet signal at δ 8.40 ppm due to the benzenic proton H-7 and a signal at δ 195.7 ppm in the ^{13}C NMR spectrum assigned to the ketone carbonyl carbon (C-6) (Scheme 5).

The reduction of ketone **6** with $NaBH_4$ gave the alcohol **7** that was then treated with PhMgBr and hydrolyzed in diluted HCl (aq) to afford the fused-naphthopyran **8** (Scheme 6). ^{1}H NMR analysis (see the Supporting Information) showed that this compound is not stable in $CDCl_3$ solution and is slowly (for two days) converted to the aromatized anthracene derivative **9** by migration of the double bond followed by dehydration. In particular, the progressive disappearance of the signals at δ 2.95 (m) and δ 2.60 (m) ppm assigned to protons H-4 was observed with the concomitant appearance of a singlet at δ 3.4 ppm that can be attributed to H-3 after the double bond migration, and later with the appearance of the signals at δ 4.00 (s), 7.71 (d), 7.4 (t), and 7.15 (d) ppm assigned to

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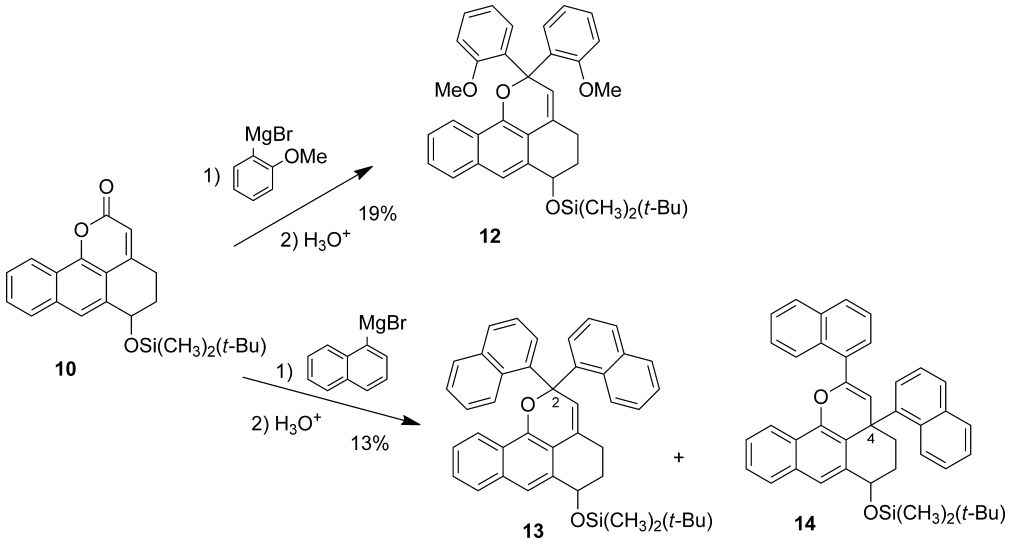
Scheme 7. Synthesis of Fused-Naphthopyrans 12 and 13



protons H-3, H-6, H-5, and H-4, respectively, of the anthracene derivative **9** (Scheme 6).

Although this aromatization was only observed when compound **8** was dissolved in $CDCl_3$, we decided to protect the secondary hydroxyl function of compound **7** in the form of a silyl ether to improve its chemical stability. The TBDMS ether **10** was easily formed in DMF, and it is stable under the acid conditions needed to prepare the final diaryl naphthopyrans. Finally, the protected naphthopyran-2-one **10** was treated with $PhMgBr/Et_2O$ and hydrolyzed in HCl (5%) overnight to afford the stable fused-naphthopyran **11** in low yield (18%). The NMR spectra of this compound showed an upfield shift of proton H-3 from δ 6.29 ppm to δ 5.87 ppm and a signal for C-2 at δ 83.2 ppm, characteristic of the pyran ring.[1]

In 2006, Heron et al. showed that the kinetics of the ring closure reaction could be slowed down, placing substituents, such as methoxy, chlorine, fluorine, or methyl in the *ortho* position of the phenyl rings.[43] This structural change increased 4−20 times the lifetime of colored open form, and it has been attributed to a steric effect in which the *ortho* substituent hinders the thermal ring closure of the photogenerated colored species, and therefore an appreciable concentration of these colored species is obtained, which is manifest by an intensification of the developed color. More recently, Guo and Chen showed that the substitution of the phenyl groups by two 1-naphthyl groups also increases significantly the lifetime of the open colored species leading to high steady-state optical density at room temperature.[44] Taking into account these results, we prepared the diaryl naphthopyrans **12** and **13** with 2-methoxyphenyl and 1-naphthyl substituents at C-2, by reaction of naphthopyran-2-one **10** with the Grignard reagents derived from 1-bromoanisole and 1-bromonaphthalene, followed by acid treatment (Scheme 7). The reaction afforded the expected compounds, but their isolation was complicated because of their low polarity and the presence of side products. After column chromatography and two preparative thin layer chromatographies, compounds **12** and **13** were isolated in 13−19% yield. ^{1}H NMR analysis of compound **13** showed that it was contaminated with the pyran **14** (the ratio of **13**/**14** is 40/60) formed by 1,2- and 1,4-addition of the Grignard reagent to the coumarin ring, followed by hemicetal formation and dehydration.[37,38] The separation of these two isomers was found to be too difficult because of their low and equal polarity in different mixtures of eluants. Their structural characterization was possible by 2D NMR spectroscopy (see the Supporting Information). At room temperature, the ^{1}H NMR signals of **13** are broad because of the exchange between different conformations. To increase the resolution, NMR spectra were recorded at high temperature (T = 343 K). Compound **13** is characterized by the sp^3 C-2 in the pyran ring at δ 85.8 ppm, whereas the aliphatic quaternary carbon, C-4, in compound **14** with a naphthyl substituent is much less deshielded at δ 42.2 ppm. The two naphthyl substituents for naphthopyran **13** are symmetrical with the same chemical shift for the equivalent protons in each group. On the contrary, the two naphthyl groups of **14** are magnetically unequivalent, as they are attached to two different carbons, thus resulting in a set of different signals for the protons of each naphthyl group.

Photochromic Behavior of Fused-Naphthopyrans 11−13. In toluene solution (1.0×10^{-4} M), fused-naphthopyrans **11**−**13** are nearly colorless with a very strong absorption in the UV region between 320 and 370 nm. Continuous UV−vis light irradiation (150 W ozone free Xe lamp) at 20 °C leads to the development of orange solutions with maximal absorption between 450 and 455 nm (Figure 1, Table 1).

When the UV irradiation was turned off, the absorbance at the maximum wavelength of absorption decreased, following a monoexponential kinetic decay law, and after several seconds, the absorbance reached exactly the initial value (Figure 2). This monoexponential decay contrasts with the usual behavior of naphthopyrans and is indicative of the formation of only one colored species.[24]

The fading rate constants and therefore the lifetime of the colored species are very dependent on the nature of the aryl substituents at the sp^3 carbon atom. While naphthopyran **11** with two phenyl groups gave rise to rather unstable colored opened forms with an half-life time of 0.30 s, naphthopyrans **12** and **13**, which have two sterically hindered groups at C-2, generated more stable colored species with a much higher lifetime. The lifetime of the colored forms of naphthopyran **13** bearing two naphth-1-yl groups ($t_{1/2}$ = 32 s) is 100 times higher than for the parent 2,2-diphenyl-naphthopyran **11**, while for naphthopyran **12**, with two *o*-methoxyphenyl groups, the lifetime ($t_{1/2}$ = 66 s) is 220 times higher.

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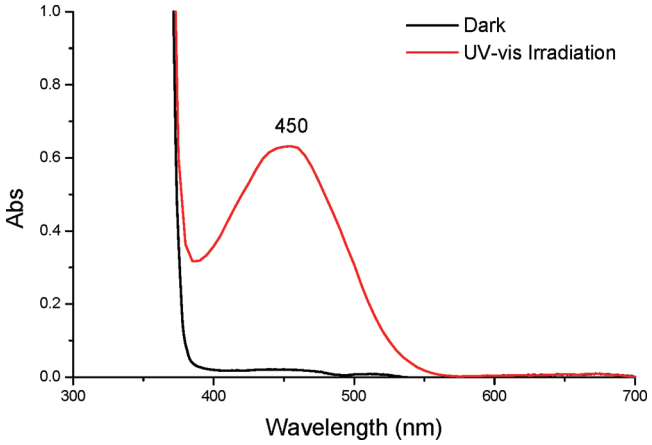

Figure 1. UV−vis absorption spectra of fused-naphthopyran **12** before and after UV irradiation.

Under continuous UV irradiation, the absorbance at the photostationary state is inversely related to the kinetic rate of the discoloration process, and therefore the slower photochromic systems give rise to more colored solutions. Hence, UV irradiation of slow fading naphthopyrans **12** and **13** originates highly colored orange solutions, while for the fast fading fused-naphthopyran **11**, the color variation (A = 0.01) is too small and not easily perceivable by the eye at room temperature.

The remarkable reproducibility of the UV−vis irradiation/dark cycles can be seen in the fact that after each coloration/fading sequence, the absorbance returns to the same initial value, and no residual color is formed. The modulation of the fading kinetic obtained by changing the nature of the sp^3 aryl substituents allows us to go from very fast interconversion between the uncolored and colored forms (naphthopyran **11** that, as a result, exhibits at room temperature a very small color change) to considerably slow switching systems (naphthopyran **12**). The fused-naphthopyran **13** shows an intermediate behavior: the UV−vis irradiation for 4 min gave an orange solution (A = 0.36) that faded completely in 4 min without any residual color (Figure 2).

It is also noteworthy that the coloration/fading process for these naphthopyrans is reproducible, and after several cycles, the same maximal absorbance is attained, which is indicative that these compounds are resistant to photodegradation even when exposed for several minutes to UV−vis light (40 W) (Figure 2).

Structural Elucidation of the Colored Open Form by NMR. Recently, NMR has emerged as a very powerful technique for the study of the mechanism of the photochromic phenomenon.[45] NMR analysis of irradiated solutions gives information about the structure and number of species formed under irradiation, their evolution in time, and the individual fading rates.[46] To investigate the structure of the products

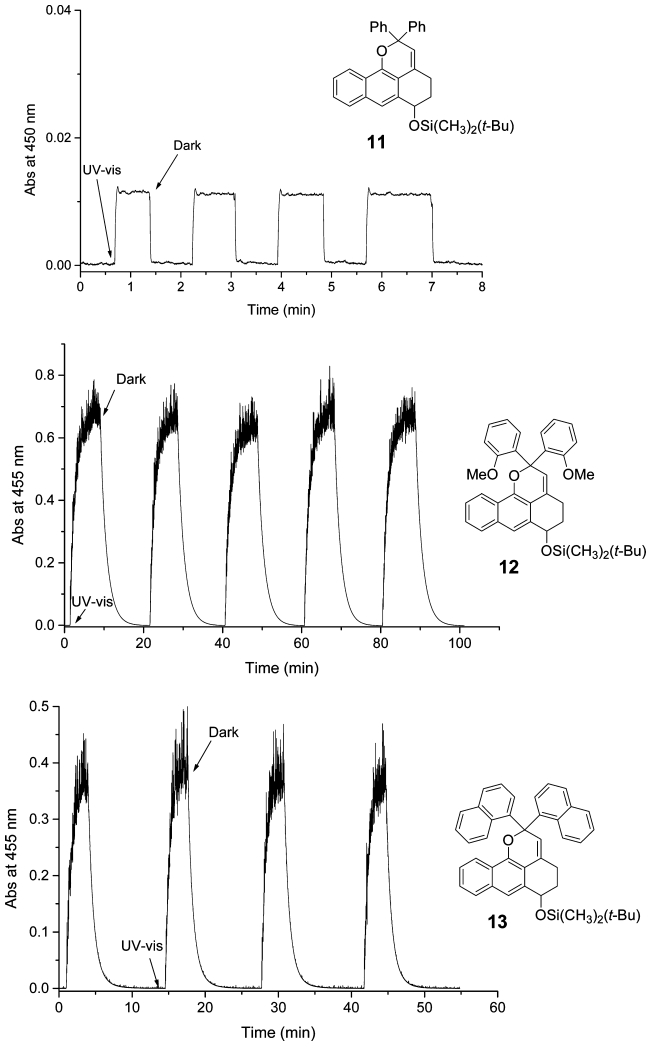

Figure 2. UV−vis irradiation/dark cycles for fused-naphthopyrans **11**−**13**.

formed upon UV irradiation of fused-naphthopyrans **11**−**12**, NMR studies were carried out before and after UV irradiation. Since the lifetimes of the colored species of these compounds are low at rt, fresh samples of naphthopyrans **11** and **12** in toluene-d_8 were directly irradiated in the NMR tube (5 mm) at low temperature (−60 °C) using a 1000 W Xe−Hg short-arc lamp. After irradiation, the sample was rapidly transferred into the thermoregulated probe of a 500 MHz NMR spectrometer. The ^{1}H NMR spectra were recorded at regular time intervals to monitor the changes in peak-intensities and thus obtain information about the formation of photoproducts and the evolution of their concentration in time.

UV irradiation of fused-naphthopyrans **11**−**12** leads to the formation of a set of new signals that are typical of an opened

Table 1. Maximal Wavelengths of the Colored Forms (λ_{max}, nm), Colorability (Maximum Absorbance at λ_{max} Attained at the Photostationary State), Fading Rate Constants (K, min^{-1}), and Half-Life (s) for Fused-Naphthopyrans 11−13 in Toluene Solutions (1.0 × 10^{-4} M at 20 °C) under UV−vis Continuous Irradiation

naphthopyran	Ar	$\lambda_{max\ (open\ form)}$	ΔAbs	K (min^{-1})	$t_{1/2}$ (s)
11	Ph	450	0.01	127	0.30
12	2-methoxyphenyl	455	0.65	0.63	66
13	1-naphthyl	455	0.36	1.39	32

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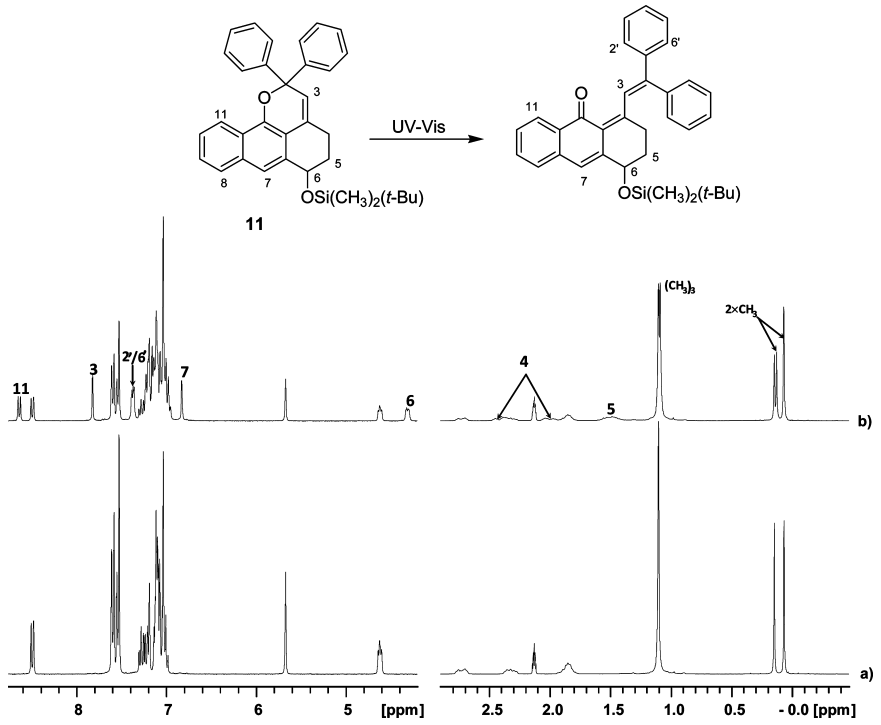

Figure 3. ^{1}H NMR spectrum of fused-naphthopyran **11** before (a) and after (b) UV irradiation at −60 °C.

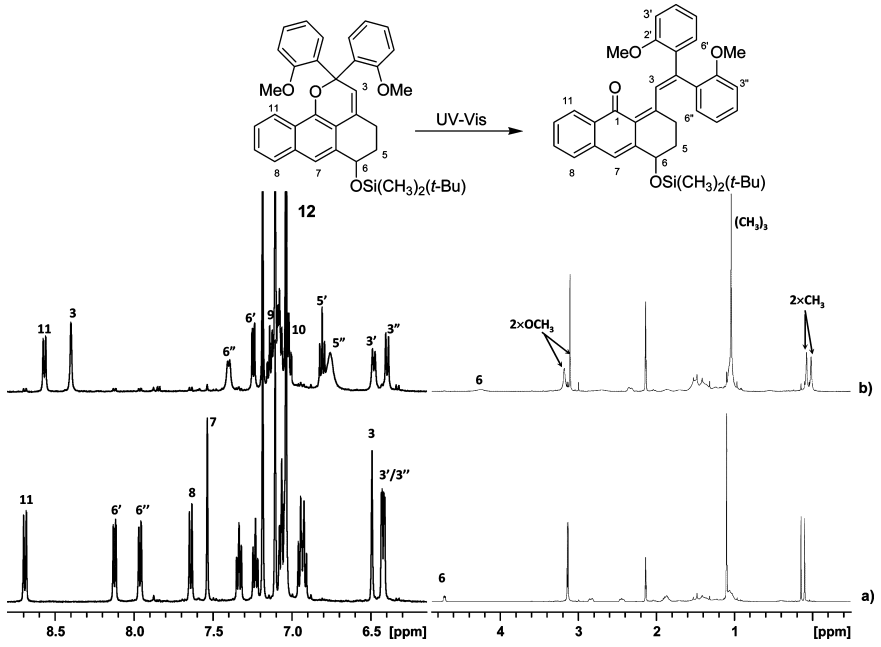

Figure 4. ^{1}H NMR spectrum of fused-naphthopyran **12** (a) before and (b) after UV irradiation at −60 °C.

pyran ring conjugated photoisomer. In particular, a high deshielding singlet at δ 7.90 ppm for **11** and δ 8.40 ppm for **12**, characteristic of proton H-3, was observed, which is indicative of a *trans*−*cis* configuration (TC) for these colored opened species (Figures 3 and 4). The fast bleaching at −60 °C of the opened form of naphthopyran **11** did not allow us to record 2D experiments. Therefore, to establish the structure of the opened form, a ROESY-1D experiment was performed that confirmed a strong correlation between protons H-3 and H-2′/6′ and between H-7/H-6 and H-8 (Figure 5).

The colored species of naphthopyran **12** is more stable at −60 °C. 2D HMBC experiment (see the Supporting Information) evidenced a carbonyl group at δ 184.7 ppm (C-1), characteristic of an open form and correlated with H-11. The high deshielding of the H-3 signal at δ 8.40 ppm, correlated with C-1′/1″, confirms the TC configuration of this opened colored species.

During thermal evolution at −20 °C, the signals of the opened species decreased following a monoexponential kinetic decay law ($t_{1/2}$= 32 min), and the signals of the closed forms increased (see the Supporting Information). The results

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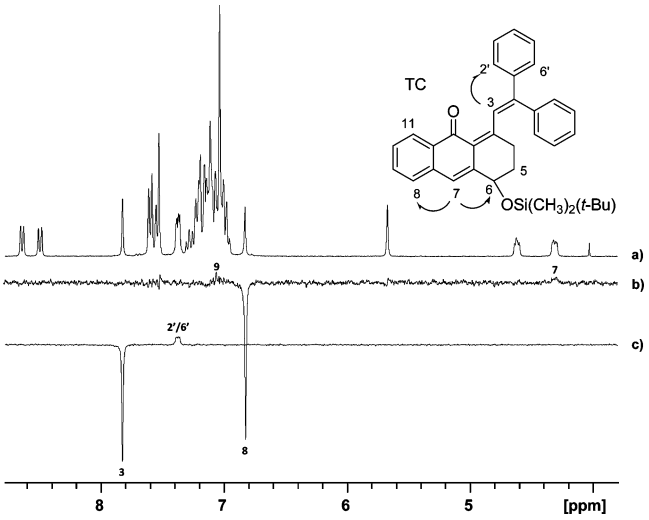
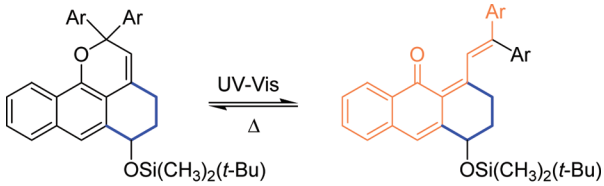


Figure 5. ROESY-1D spectrum of fused-naphthopyran **11**: (a) ^{1}H NMR spectrum, (b) 1D NOESY spectrum with an irradiation of H-7, and (c) 1D NOESY spectrum with an irradiation of H-3.

obtained by NMR are in agreement with those obtained by UV−vis spectroscopy and confirm that UV irradiation of these fused-naphthopyrans leads to the opening of the pyran ring with formation of a single colored TC opened species. The fact that under UV−vis light these fused-naphthopyrans do not generate the TT-photoisomer allows the system to return thermally and completely to the initial uncolored form in few minutes, thus avoiding the usual residual color due to this unwanted photoisomer (Scheme 8).

Scheme 8. Photochromic Equilibrium for Fused-Naphthopyrans 11−13



11-13

The irradiation experiments on the mixture of compounds **13**/**14** at 228 K are less clear because of the superposed signals of the initial compounds. However, it can be concluded that compound **13** leads to two TC conformers (characterized by aliphatic signals $C(CH_3)_3$ at 0.97 and 1.06 ppm, H-6 signal at 4.08 and 4.18 ppm, and aromatic signals H-3 at 7.88 and 7.94 ppm and H-11 at 8.79 and 8.90 ppm) that thermally return to the initial form, while compound **14** is irreversibly converted into two unidentified photoproducts that stay present in the sample after the return to room temperature.

CONCLUSION

A set of new fused-naphthopyrans with an alkyl bridge between the pyran ring and the naphthalenic core was synthesized in seven steps from 1-naphthol using a synthetic approach involving benzocoumarins. UV light irradiation of these compounds in solution originates one colored compound that fades completely to the uncolored state in few seconds/minutes. A significant steric effect of the aromatic substituents on the sp^3 carbon atom was observed, which led to an increase of the lifetime of the colored form, and therefore, a colored solution with an high optical density was obtained. The structure of the photoisomer was proven by NMR to have a *trans*−*cis* configuration. Unlike common naphthopyrans, which under UV light originates two isomeric photomerocyanines (TC and TT) with different stabilities and consequently different fading kinetics, this type of fused-naphthopyrans produces only one colored compound, and thus, when the light source is removed, the color fades monoexponentially and completely to the uncolored state without the formation of a residual coloration.

EXPERIMENTAL SECTION

Spectrokinetic Studies under Continuous Irradiation. UV−visible irradiation experiments were made using a UV−vis spectrometer coupled to a 150 W ozone free Xenon lamp. The light from the UV lamp was filtered using a water filter and then carried to the spectrophotometer holder at the right angle to the monitoring beam using an optical fiber system. 40 W m^{-2} light flux was used (measured with a Photometer with UV-A probe). A temperature controlled (20 °C) stirred 10 mm quartz cell (3.5 mL of sample solution) was used. In a preliminary experiment, the UV−vis absorption spectra of the closed and open forms and the λ_{max} of the open form were determined. In a second experiment, the absorbance at photostationary equilibrium, A_{eq}, was measured at λ_{max} and then the decrease in the absorbance vs time was monitored. The sample solutions were not deaerated.

NMR Studies. The ^{1}H and ^{13}C NMR spectra (at 400.13 and 100.62 MHz) were recorded at 298 K in $CDCl_3$, DMSO, or acetone-d_6. Chemical shifts (δ) are reported in ppm. For NMR investigations of the colored species, samples of the naphthopyrans in toluene-d_8 were irradiated directly in the NMR tube (5 mm) and thermoregulated using a 1000 W Xe−Hg HP filtered short-arc lamp equipped with a filter for UV irradiation ($259 < \lambda < 388$ nm). After irradiation had been stopped, the samples were transferred to the thermoregulated probe, QNP or TXI, of an 500 NMR spectrometer (ν_0 (^{1}H) = 500 MHz, ν_0 (^{13}C) = 125 MHz.

Ethyl 4-Bromo-3-oxobutanoate (1). To a solution of ethyl acetoacetate (30 g; 0.23 mol) in dry Et_2O (50 mL) at 0 °C was added bromine (12 mL; 0.23 mol) dropwise over 45 min with vigorous stirring. After the mixture was stirred at room temperature for 24 h, ice was added (100 g), and the organic phase washed with a sodium hydrogenocarbonate solution (5%) saturated with sodium chloride (200 mL) and again washed with a saturated sodium of chloride solution (200 mL). The organic phase was dried (Na_2SO_4) for 2 h, and the solvent was removed under reduced pressure to give an orange oil (31.9 g; 65%) stabilized immediately by the addition of barium carbonate (50 mg; 0.26 mmol). The orange oil contained small amounts of a highly lachrymatory oil, probably the ethyl α-bromoacetoacetate.

4-(Bromomethyl)-2*H*-naphtho[1,2-*b*]pyran-2-one (2). A solution of 1-naphthol (2.00 g, 13.8 mmol) and ethyl 4-bromoacetoacetate **1** (1.9 mL, 13.8 mmol) was cooled to 0 °C, and then H_2SO_4 (10 mL) was slowly added over 30 min under constant stirring, during which the solution became darker in color. After stirring for an additional 2 h at 0 °C, the reaction mixture was treated with ice (100 g), and then $NaHCO_3$ (sat, 100 mL) was carefully added with stirring for 0.5 h (gas evolution) and stirred for an additional 2 h. The solution was extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic phase was dried (Na_2SO_4). The solvent was removed under reduced pressure, yielding a red oil that was dissolved in ethanol (50 mL) at room temperature and precipitated overnight. Filtration and washing with cold ethanol gave the benzocoumarin **2** as a yellow solid (2.240 g; 56% yield): mp 155−166 °C; IR (KBr, cm^{-1}) 3028, 2987, 1711, 1634, 1598, 1475, 1375, 1121; ^{1}H NMR (400 MHz, $CDCl_3$) 8.50 (dd, J = 2.5, 6.5 Hz, 1H), 7.86 (dd, J = 2.5, 6.4 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.68−7.60 (m, 3H), 6.56 (s, 1H), 4.54 (s, 2H); ^{13}C NMR (100

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MHz, $CDCl_3$) 160.3, 151.4, 150.8, 134.9, 129.0, 127.7, 127.3, 124.4, 123.2, 122.6, 119.8, 115.2, 112.6, 27.2; EI-MS (TOF) *m*/*z* (%) 290 (4.3, $[M + 2]^+$), 288 (4.35, M^+), 210 (76), 182 (100), 181 (86), 153 (25), 152 (48). HRMS calculated for $C_{14}H_9BrO_2$: 287.9786. Found: 287.9783.

Alkylation of Diethyl Malonate with 2. Diethyl malonate (550 μL, 3.60 mmol) was added to a suspension of NaH (60% dispersion in mineral oil, 266 mg, 6.65 mmol) in DMSO (6.0 mL). After the foaming subsided and the suspension cleared to a solution, 4-(bromomethyl)benzocoumarin **2** (1.00 g, 3.47 mmol) was added all at once. After 5 min of stirring, the solution was quenched with HCl (5%, 50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic phases were dried (Na_2SO_4), and the solvent was evaporated under reduced pressure, leaving a yellow oil that was dissolved in ethanol (50 mL). The solid formed after standing overnight at room temperature was filtered and washed with cold ethanol to give the diester **3** as slightly yellow crystals. Recrystallization from CH_2Cl_2/Et_2O gave diester **3** as white crystals. The filtered ethanol solution and the recrystallization mother liquid were gathered and evaporated, leaving a yellow solid that was purified by column chromatography on silica (20% EtOAc/5% CH_2Cl_2/petroleum ether), affording an extra amount of diester **3** and the pure **4**.

Diethyl 2-((2-Oxo-2*H*-naphtho[1,2-*b*]pyran-4-yl)methyl)-malonate (3). Spectral data (498 mg, 39% yield): mp 109.6−112.2 °C; IR (KBr, cm^{-1}) 3040, 2987, 1722, 1328, 1269, 1222, 1145; ^1H NMR (400 MHz, $CDCl_3$) 8.50 (m, 1H), 7.84 (m, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.63−7.57 (m, 3H), 6.33 (s, 1H), 4.22 (m, 4H), 3.78 (t, *J* = 7.5 Hz, 1H), 3.45 (d, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 168.0, 160.3, 152.8, 150.9, 134.7, 128.8, 127.6, 127.2, 124.4, 123.2, 122.6, 119.5, 114.2, 113.8, 62.1, 50.4, 30.7, 14.0; EI-MS (TOF) *m*/*z* (%) 368 (100, M^+), 323 (9, $[M - OCH_2CH_3]^+$), 295 (24, $[M - CO_2CH_2CH_3]^+$), 267 (17), 249 (64), 222 (29), 221 (79), 194 (39), 181 (30), 165 (75). HRMS calculated for $C_{21}H_{20}O_6$: 368.1260. Found: 368.1263.

Diethyl 2,2-bis((2-Oxo-2*H*-naphtho[1,2-*b*]pyran-4-yl)-methyl)malonate (4). Spectral data (200 mg, 10%): mp 199.9−202.1 °C; IR (KBr, cm^{-1}) 3076, 2976, 1710, 1475, 1374, 1245, 1198; ^1H NMR (400 MHz, $CDCl_3$) 8.53 (m, 2H), 7.80 (m, 2H), 7.70−7.60 (m, 6H), 7.53 (t, *J* = 8.9 Hz, 2H), 6.47 (s, 2H), 4.04 (m, 4H), 3.64 (s, 4H), 1.05 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 169.4, 160.1, 151.3, 150.8, 134.7, 129.0, 127.6, 127.4, 124.3, 123.2, 122.6, 119.6, 115.9, 114.6, 62.6, 50.5, 34.3, 13.6; EI-MS (TOF) *m*/*z* (%) 576 (45, M^+), 548 (12), 368 (60), 275 (50), 221 (85), 210 (97), 182 (100), 165 (77). HRMS calculated for $C_{35}H_{28}O_8$: 576.1784. Found: 576.1769.

3-(2-Oxo-2*H*-naphtho[1,2-*b*]pyran-4-yl)propanoic Acid (5). A mixture of diester **3** (540 mg, 1.47 mmol) and NaOH (640 mg, 16 mmol) in pure EtOH (20 mL) was heated under reflux for 2 h. After returning to room temperature, the solvent was removed under reduced pressure, and a solution of HCl (5%, 50 mL) was added and stirred for 20 min. The solid thus formed was filtered to afford the corresponding diacid as a yellow solid. This compound was dissolved in DMSO (5 mL) and heated at reflux for 10 min, during which some CO_2 evolution occurs. After the mixture returned to room temperature, water (25 mL) was added, and the solid thus formed was filtered, washed with water, and dried under a high vacuum to afford the monoacid **5** as a white powder (382 mg, 97%): mp 187−191 °C; IR (KBr, cm^{-1}) 2940 (large), 1716, 1610, 1369, 1263, 1169; ^1H NMR (400 MHz, DMSO) 12.4 (s, 1H, OH), 8.39 (m, 1H), 8.06 (m, 1H), 7.90−7.85 (m, 2H), 7.73−7.70 (m, 2H), 6.45 (s, 1H), 3.16 (t, *J* = 7.0 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) 173.2, 169.7, 159.6, 156.1, 149.8, 134.3, 128.8, 127.9, 127.4, 124.1, 121.6, 120.7, 114.2, 112.8, 31.7, 26.5; EI-MS (TOF) *m*/*z* (%) 268 (90, M^+), 240 (31), 223 (9, $[M - COOH]^+$), 222 (11), 195 (100, $[M - CH_2CH_2COOH]^+$), 181 (38), 165 (30), 152 (47), 139 (22). HRMS calculated for $C_{16}H_{12}O_4$: 268.0736. Found: 268.0733.

4*H*-5,6-Dihydroanthraceno[9,1-*bc*]pyran-2,6-dione (6). A solution of the carboxylic acid **5** (1.986 g; 7.41 mmol) in $SOCl_2$ (1 mL) was heated at reflux for 1 h, and after cooling to room temperature, the $SOCl_2$ excess was removed under reduced pressure. To the residue were added dry CH_2Cl_2 (5 mL) and $AlCl_3$ (0.990 g, 7.41 mmol) at room temperature with constant stirring. After 1 h, another equivalent of $AlCl_3$ was added, and the solution was kept at room temperature for 1 h. The solution was then quenched with water (30 mL) and extracted with EtOAc (3 × 20 mL). The combined organic phases were dried (Na_2SO_4), and the solvent was evaporated under reduced pressure, leaving a solid residue that was purified by column chromatography on silica (0−40% EtOAc/petroleum ether) to give the fused anthracenopyran-2,6-dione **6** as an orange solid (538 mg; 29%): mp 203−207 °C; IR (KBr, cm^{-1}) 3046, 2948, 1733, 1687, 1587, 1299; ^1H NMR (400 MHz, $CDCl_3$) 8.58 (d, *J* = 8.0 Hz, 1H), 8.40 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.79 (t, *J* = 7.1 Hz, 1H), 7.73 (t, *J* = 6.9 Hz, 1H), 6.48 (t, *J* = 1.5 Hz, 1H), 3.30 (td, *J* = 7.3 Hz, *J* = 1.5 Hz, 2H), 2.99 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR(100 MHz, $CDCl_3$) 195.7, 160.2, 151.7, 150.5, 133.9, 130.2, 129.7, 129.5, 126.3, 125.4, 123.9, 122.7, 113.9, 112.6, 37.1, 28.0; EI-MS (TOF) *m*/*z* (%) 250 (100, M^+), 248 (51), 222 (71, $[M - CO]^+$), 220 (71), 194 (69), 165 (71), 164 (57), 163 (53). HRMS calculated for $C_{16}H_{10}O_3$: 250.0630. Found: 250.0638.

4*H*-5,6-Dihydroanthraceno[9,1-*bc*]pyran-6-ol-2-one (7). $NaBH_4$ (44 mg; 1.28 mmol) was added to a solution of anthracenopyran-2,6-dione **6** (321 mg; 1.28 mmol) in pure ethanol (5 mL) at room temperature with constant stirring. After standing for 1 h, the ethanol was removed under reduced pressure, and HCl (5%, 50 mL) was added. The solution was extracted with EtOAc (2 × 50 mL), and the organic phases were combined and dried (Na_2SO_4). The solvent was removed under reduced pressure to give alcohol **7** as slightly yellow crystals (220 mg; 68%): mp 179.2−181.6 °C; IR (KBr, cm^{-1}) 3358, 3046, 2928, 1710, 1463, 1198; ^1H NMR (400 MHz, acetone-d_6) 8.6 (d, *J* = 7.4 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.90 (s, 1H), 7.71−7.65 (m, 2H), 6.32 (s, 1H), 5.10 (m, 1H, OH), 4.70 (d, *J* = 5.2 Hz, 1H), 3.20 (m, 1H), 2.95 (m, 1H), 2.25 (m, 1H), 2.05 (m, 1H); ^{13}C NMR (100 MHz, acetone-d_6) 161.5, 156.6, 152.4, 138.7, 136.7, 130.5, 129.9, 128.6, 124.1, 123.7, 122.9, 114.0, 112.9, 69.1, 32.9, 27.9; EI-MS (TOF) *m*/*z* (%) 252 (42, M^+), 234 (54, $[M - H_2O]^+$), 206 (100), 178 (50), 177 (32), 176 (44), 165 (15), 152(17), 151 (19). HRMS calculated for $C_{16}H_{12}O_3$: 252.0786. Found: 252.0796.

2,2-Diphenyl-2*H*-anthraceno[9,1-*bc*]pyran (9). A solution of PhMgBr (prepared from bromobenzene (0.50 g, 3.2 mmol) and magnesium (1.0 g)) in dry Et_2O (10 mL) was slowly added to a stirred solution of dihydroanthracenopyran-6-ol-2-one **7** (184 mg, 0.73 mmol) in dry Et_2O (5 mL). After 15 min at room temperature, the solvent was removed under reduced pressure, and then HCl (5%, 20 mL) was added, and the solution was stirred overnight. The solution was then extracted with EtOAc (3 × 25 mL), and the combined organic layers were dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by chromatography column on silica (25% EtOAc/petroleum ether) to give **8** as a white solid (114 mg, 40%): ^1H NMR (400 MHz, $CDCl_3$) 8.45 (d, 1H), 7.75 (d, 1H), 7.6−7.5 (m), 7.5−7.4 (m), 7.5−7.2 (m), 7.64 (s, 1H), 5.95 (s, 1H), 4.95 (m, 1H), 2.95 (m, 1H), 2.60 (m, 1H), 2.20−2.0 (m, 2H); EI-MS (TOF) *m*/*z* (%) 390 (8, M^+), 372 (92, $[M - H_2O]^+$), 313 (45), 295 (100), 265 (75), 252 (32), 205 (86), 165 (22). HRMS calculated for $C_{28}H_{22}O_2$: 390.1620. Found: 390.1631. In $CDCl_3$ solution, this compound is not stable and in two days is converted by dehydration and double bond migration to the anthracenopyran **9**: ^1H NMR (100 MHz, $CDCl_3$) 8.45 (dd, *J* = 1.5, 6.7 Hz, 1H), 7.91 (d, *J* = 8 Hz, 1H), 7.90 (s, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.59−7.55 (m, 4H), 7.52−7.44 (m, 2H), 7.33−7.30 (t, *J* = 6.6 Hz, 1H), 7.25−7.10 (m, 7H), 4.00 (s, 2H); EI-MS (TOF) *m*/*z* (%) 372 (71, M^+), 281 (18), 265 (13), 205 (100), 177 (24), 176 (19), 167 (16). EI-HRMS calculated for $C_{28}H_{20}O$: 372.1514. Found: 372.1518.

6-*t*-Butyldimethylsilyloxy-4*H*-5,6-dihydroanthraceno[9,1-*bc*]pyran-2-one (10). A solution of the alcohol **7** (981 mg; 2.71 mmol), *t*-butyldimethylsilyl chloride (490 mg; 3.25 mmol), and imidazole (662 mg, 9.72 mmol) in dimethylformamide (10 mL) was stirred at room temperature. After 24 h, another 1.2 equiv of *t*-butyldimethylsilyl chloride was added, and the solution was kept at room temperature for 2 days with stirring. After the reaction was confirmed complete by TLC, NH_4Cl (22%, 50 mL) was added, and

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the solution was extracted with EtOAc (2 × 30 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under a vacuum to afford the crude silyl ether, which was purified by chromatography on silica gel (0−6% EtOAc/petroleum ether) to give the silyl ether **10** as slightly yellow crystals (790 mg; 79%): mp 149.8−151.1 °C; IR (KBr, cm^{-1}) 3070, 2952, 2858, 1716, 1463, 1245; ^1H NMR (400 MHz, $CDCl_3$) 8.51 (d, J = 7.3 Hz, 1H), 7.83 (d, J = 7.3 Hz, 1H), 7.64 (s, 1H), 7.63−7.55 (m, 2H), 6.29 (s, 1H), 5.05 (m, 1H), 3.18 (m, 1H), 2.83 (m, 1H), 2.20−2.0 (m, 2H), 0.935 (s, 9H), 0.21 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 161.0, 154.3, 150.8, 135.4, 134.6, 128.7, 127.8, 126.7, 122.5 (two signals), 121.2, 112.1, 111.3, 68.8, 31.5, 26.2, 25.8, 18.2, −4.4, −4.5; EI-MS (TOF) m/z (%) 366 (3, M^+), 309 (100, $[M - C_4H_9]^+$), 235 (53, $[M - OSiMe_2(t\text{-}Bu)]^+$), 207 (25), 206 (21), 205 (21), 165 (7), 75(82). EI-HRMS calculated for $C_{22}H_{26}O_3Si$: 366.1651. Found: 366.1650.

General Procedure for the Reaction of Dihydroanthracenopyran-2-one 10 with Grignard Reagents. A solution of the Grignard reagent (5 equiv) in dry Et_2O (10 mL) was slowly added to a stirred solution of dihydroanthracenopyran-2-one **10** (270 mg; 0.73 mmol) in dry Et_2O (5 mL). After 15 min at room temperature, the Et_2O was removed under reduced pressure, and then HCl (5%, 20 mL) was added, and the solution was stirred overnight. The solution was then extracted with EtOAc (3 × 25 mL), and the combined organic layers were dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by chromatography column on silica (petroleum ether) followed by preparative TLC (5% EtOAc/petroleum ether).

6-*t*-Butyldimethylsilyloxy-2,2-diphenyl-2*H*,4*H*-5,6-dihydroanthraceno[9,1-*bc*]pyran (11). Prepared from dihydroanthracenopyran-2-one **10** (270 mg; 0.73 mmol) and PhMgBr (from bromobenzene (0.50 g, 3.2 mmol) and magnesium (1.0 g)) and obtained as a white solid (92 mg; 18%): ^1H NMR (400 MHz, $CDCl_3$) 8.30 (m, 1H), 7.83 (m, 1H), 7.50−7.42 (m, 4H), 7.40−7.36 (m, 2H), 7.35 (s, 1H), 7.31−7.17 (m, 5H), 5.87 (s, 1H), 4.93 (m, 1H), 2.87 (m, 1H), 2.60 (m, 1H), 2.05 (m, 1H), 1.90 (m, 1H), 0.935 (s, 9H), 0.16 (s, 3H), 0.10 (s, 3H) or ^1H NMR (400 MHz, toluene-d_8) 8.44 (dd, J = 8.2 Hz, J = 1.5 Hz, 1H), 7.6−7.55 (m, 5H), 7.42 (s, 1H), 7.27 (ddd, J = 8.2 Hz, J = 6.9 Hz, J = 1.4 Hz, 1H), 7.21 (ddd, J = 8.2 Hz, J = 6.9 Hz, J = 1.4 Hz, 1H), 7.17−7.07 (m, 4H), 7.07−6.97 (m, 2H), 5.76 (t, J = 1.6 Hz, 1H), 4.77 (dd, J = 6.6 Hz, J = 4.4 Hz, 1H), 2.81 (m, 1H), 2.38 (m, 1H), 1.87 (m, 2H), 1.02 (s, 9H), 0.14 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, toluene-d_8) 147.3, 145.8, 135.9, 134.2, 129.9, 127.8, 127.5, 127.3, 127.0, 126.2, 125.0, 124.2, 122.0, 120.9, 117.9, 113.3, 83.2, 69.5, 32.1, 25.6, 24.9, 18.0, −4.8, −5.0; EI-MS (TOF) m/z (%) 504 (10, M^+), 447 (6, $[M - C_4H_9]^+$), 427 (14, $[M - C_6H_5]^+$), 372 (26), 295 (100), 281 (10), 265 (16), 252 (10), 205(26), 75 (33). EI-HRMS calculated for $C_{34}H_{36}O_2Si$: 504.2485. Found: 504.2493.

6-*t*-Butyldimethylsilyloxy-2,2-(2′-methoxyphenyl)-2*H*,4*H*-5,6-dihydroanthraceno[9,1-*bc*]pyran (12). Prepared from dihydroanthracenopyran-2-one **10** (270 mg; 0.73 mmol) and *o*-$CH_3OPhMgBr$ (from 2-bromoanisole (0.60 g, 3.2 mmol) and magnesium (1.0 g)) and obtained as a white solid (53 mg; 13%): IR (KBr, cm^{-1}) 3070, 2940, 1469, 1239, 1080; ^1H NMR (400 MHz, $CDCl_3$) 8.28 (m, 1H), 7.68−7.64 (m, 2H), 7.60 (dd, J = 1.7, 7.7 Hz, 1H), 7.38−7.33 (m, 2H), 7.31 (s, 1H), 7.20−7.13 (m, 2H), 6.93−6.82 (m, 2H), 7.80 (t, J = 7.2 Hz, 2H) 1H), 6.08 (s, 1H), 4.92 (m, 1H), 3.49 (s, 6H), 2.85 (m, 1H), 2.58 (m, 1H), 2.04 (m, 1H), 1.90 (m, 1H), 0.95 (s, 9H), 0.16 (s, 3H), 0.11 (s, 3H) or ^1H NMR (400 MHz, toluene-d_8) 8.60 (d, J = 8.2 Hz, 1H), 8.01 (dd, J = 7.9 Hz, J = 1.7 Hz, 1H), 7.89 (dd, J = 7.9 Hz, J = 1.7 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.28 (td, J = 7.9 Hz, J = 1.4 Hz, 1H), 7.21 (td, J = 8.0 Hz, J = 1.4 Hz, 1H), 6.55 (dd, J = 8.0 Hz, J = 0.9 Hz, 1H), 6.52 (dd, J = 8.0 Hz, J = 0.9 Hz, 1H), 6.36 (t, J = 1.6 Hz, 1H), 4.81 (dd, J = 6.5 Hz, J = 4.8 Hz, 1H), 3.19 (s, 3H), 3.17 (s, 3H), 2.87 (m, 1H), 2.44 (m, 1H), 1.90 (m, 2H), 1.03 (s, 9H), 0.15 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, toluene-d_8) 156.4, 147.8, 136.1, 133.8, 133.4, 128.8, 128.6, 128.3, 127.9, 127.4, 125.7, 124.8, 124.4, 122.6, 120.1, 119.9, 117.4, 113.1, 112.3, 81.6, 69.7, 32.2, 25.6, 25.1, 17.7, −4.7, −4.9; EI-MS (TOF) m/z (%) 564 (17, M^+), 507 (4, $[M - C_4H_9]^+$), 457 (6, $[M - C_6H_4OCH_3]^+$), 432 (72), 401 (11), 325 (100), 311 (32), 227 (29), 205 (15), 165 (13), 121 (65). EI-HRMS calculated for $C_{36}H_{40}O_4Si$: 564.2696. Found: 564.2701.

6-*t*-Butyldimethylsilyloxy-2,2-(naphth-1-yl)-2*H*,4*H*-5,6-dihydroanthraceno[9,1-*bc*]pyran (13). Prepared from dihydroanthracenopyran-2-one **10** (270 mg; 0.73 mmol) and 1-NpMgBr (from 1-bromonaphthalene (0.66 g, 3.2 mmol) and magnesium (1.0 g)) and obtained as a white solid (91 mg; 19%) (mixture of isomeric dihydroanthracenopyran **13** and **14**): IR (KBr, cm^{-1}) 3052, 2940, 2858, 1374, 1251, 1074; for NMR details see the Supporting Information; EI-MS (TOF) m/z (%) 604 (6, M^+), 547 (2, $[M - C_4H_9]^+$), 472 (100), 345 (58), 344 (62), 343 (47), 315 (25). EI-HRMS calculated for $C_{42}H_{40}O_2Si$: 604.2798. Found: 604.2792.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra (^1H and ^{13}C) for all new compounds, 2D NMR data for the new fused-napthopyrans **11**−**13**, NMR data for irradiated solutions of compounds **11** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hepworth, J. D.; Heron, B. M. *Functional Dyes*; Sung-Hoon, K., Ed.; Elsevier: Amsterdam, 2006.
(2) Malic, N.; Campbell, J. A.; Ali, A. S.; Francis, C. L.; Evans, R. A. *J. Polym. Sci., Polym. Chem.* **2011**, *49*, 476.
(3) Xie, B. J.; Wang, G.; Zhao, X. C. *J. Appl. Polym. Sci.* **2011**, *122*, 3377.
(4) Pardo, R.; Zayat, M.; Levy, D. *Chem. Soc. Rev.* **2011**, *40*, 672.
(5) Coelho, P. J.; Carvalho, L. M.; Goncalves, L.; Silva, C. J. R.; Campos, A. M.; Gomes, M. J. *J. Sol-Gel Sci. Technol.* **2010**, *56*, 203.
(6) Pardo, R.; Zayat, M.; Levy, D. *J. Photochem. Photobiol., A.* **2008**, *198*, 232.
(7) Favaro, G.; Ortica, F.; Romani, A.; Smimmo, P. *J. Photochem. Photobiol., A.* **2008**, *196*, 190.
(8) Sriprom, W.; Neel, M.; Gabbutt, C. D.; Heron, B. M.; Perrier, S. *J. Mater. Chem.* **2007**, *17*, 1885.
(9) Tomasulo, M. US Patent 0108781A1 (2011).
(10) Aiken, S.; Cano J.-P.; Gabbutt C. D.; Heron, B. M.; Kosa, T.; Su L.; Sukhomlinova, L.; Taheri, B. US Patent 0202033A1 (2010)
(11) Kim, B.-K.; Deng, J.; Xiao, W.; Van gemert, B.; Chopra, A.; Molock, F.; Mahadevan, S. US Patent 0072206A1 (2009).
(12) Breyne, O.; Chan Y.-P.; Jean, P. US Patent 6506538B1 (2003).
(13) Delbaere, S.; Micheau, J. C.; Teral, Y.; Bochu, C.; Campredon, M.; Vermeersch, G. *Photochem. Photobiol.* **2001**, *74*, 694.
(14) Coelho, P. J.; Salvador, M. A.; Heron, B. M.; Carvalho, L. M. *Tetrahedron* **2005**, *61*, 11730.
(15) Delbaere, S.; Luccioni-Houze, B.; Bochu, C.; Teral, Y.; Campredon, M.; Vermeersch, G. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1153.

(16) Guo, K. P.; Chen, Y. *J. Phys. Org. Chem.* **2010**, *23*, 207.
(17) Delbaere, S.; Vermeersch, G.; Frigoli, M.; Mehl, G. H. *Org. Lett.* **2010**, *12*, 4090.
(18) Gabbutt, C. D.; Heron, B. M.; Kilner, C.; Kolla, S. B. *Org. Biomol. Chem.* **2010**, *8*, 4874.
(19) Coelho, P. J.; Carvalho, L. M.; Vermeersch, G.; Delbaere, S. *Tetrahedron* **2009**, *65*, 5369.
(20) Alberti, A.; Teral, Y.; Roubaud, G.; Faure, R.; Campredon, M. *Dyes Pigm.* **2009**, *81*, 85.
(21) Gabbutt, C. D.; Heron, B. M.; Kolla, S. B.; McGivern, M. *Eur. J. Org. Chem.* **2008**, 2031.
(22) Kumar, S.; Hernandez, D.; Hoa, B.; Lee, Y.; Yang, J. S.; McCurdy, A. *Org. Lett.* **2008**, *10*, 3761.
(23) Gabbutt, C. D.; Heron, B. M.; Instone, A. C.; Horton, P. N.; Hursthouse, M. B. *Tetrahedron* **2005**, *61*, 463.
(24) Coelho, P. J.; Salvador, M. A.; Oliveira, M. M.; Carvalho, L. M. *J. Photochem. Photobiol., A.* **2005**, *172*, 300.
(25) Coelho, P. J.; Salvador, M. A.; Oliveira, M. M.; Carvalho, L. M. *Tetrahedron* **2004**, *60*, 2593.
(26) Ercole, F.; Malic, N.; Harrisson, S.; Davis, T. P.; Evans, R. A. *Macromolecules* **2010**, *43*, 249.
(27) Berthet, J.; Coelho, P. J.; Carvalho, L. M.; Vermeersch, G.; Delbaere, S. *J. Photochem. Photobiol., A.* **2009**, *208*, 180.
(28) Moorthy, J. N.; Koner, A. L.; Samanta, S.; Roy, A.; Nau, W. M. *Chem.—Eur. J.* **2009**, *15*, 4289.
(29) Ercole, F.; Davis, T. P.; Evans, R. A. *Macromolecules* **2009**, *42*, 1500.
(30) Oliveira, M. M.; Salvador, M. A.; Delbaere, S.; Berthet, J.; Vermeersch, G.; Micheau, J. C.; Coelho, P. J.; Carvalho, L. M. *J. Photochem. Photobiol., A.* **2008**, *198*, 242.
(31) Sallenave, X.; Delbaere, S.; Vermeersch, G.; Saleh, A.; Pozzo, J. L. *Tetrahedron Lett.* **2005**, *46*, 3257.
(32) Nabais, C.; Heron, B. M.; de Sousa, H. C.; Gil, M. H.; Sobral, A. *J. Biomater. Sci., Polym. Ed.* **2011**, *22*, 139.
(33) Corns, S. N.; Partington, S. M.; Towns, A. D. *Color. Technol.* **2009**, *125*, 249.
(34) Sousa, C. M.; Pina, J.; de Melo, J. S.; Berthet, J.; Delbaere, S.; Coelho, P. J. *Org. Lett.* **2011**, *13*, 4040.
(35) Sousa, C. M.; Pina, J.; de Melo, J. S.; Berthet, J.; Delbaere, S.; Coelho, P. *Eur. J. Org. Chem.* **2012**, 1768−1773.
(36) Sousa, C. M.; Coelho, P. J.; Vermeersch, G.; Berthet, J.; Delbaere, S. *J. Photochem. Photobiol., A.* **2010**, *216*, 73.
(37) Tickle, R. W.; Tickle, W.; Melton, T.; Elvidge, J. A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 569.
(38) Cotterill, W. D.; Iqbal, M.; Livingstone, R. *J. Chem. Res., Synop.* **1998**, 2.
(39) Valizadeh, H.; Shockravi, A. *Tetrahedron Lett.* **2005**, *46*, 3501.
(40) Burger, A.; Ullyot, G. E. *J. Org. Chem.* **1947**, *12*, 342.
(41) Basanagouda, M.; Shivashankar, K.; Kulkarni, M. V.; Rasal, V. P.; Patel, H.; Mutha, S. S.; Mohite, A. A. *Eur. J. Med. Chem.* **2010**, *45*, 1151.
(42) Celebuski J. E.; US patent 5,247,099 (1993).
(43) Gabbutt, C. D.; Heron, B. M.; Instone, A. C. *Tetrahedron* **2006**, *62*, 737.
(44) Guo, K. P.; Chen, Y. *J. Mater. Chem.* **2010**, *20*, 4193.
(45) Delbaere, S.; Vermeersch, G. *J. Photochem. Photobiol., C* **2008**, *9*, 61.
(46) Delbaere, S.; Vermeersch, G.; Micheau, J. C. *J. Photochem. Photobiol., C* **2011**, *12*, 74.