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The effect of a sulphur bridge on the photochromic properties of indeno-fused naphthopyrans

Paulo J. Coelho,* Maria A. Salvador, M. Manuel Oliveira and Luis M. Carvalho

Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, Quinta dos Prados, 5001-911 Vila Real, Portugal

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Abstract—The synthesis of four new 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyrans with a fused indeno group at the *f* face and a sulphur junction between the 2,2-phenyl groups is described. The photochromic properties in solution of these novel compounds were investigated under continuous irradiation. Compared to known indeno-fused naphthopyrans, these new compounds showed a significant bathochromic shift in the spectra of the open forms, faster ring closure kinetics and an expected decrease in the colourabilities.

1. Introduction

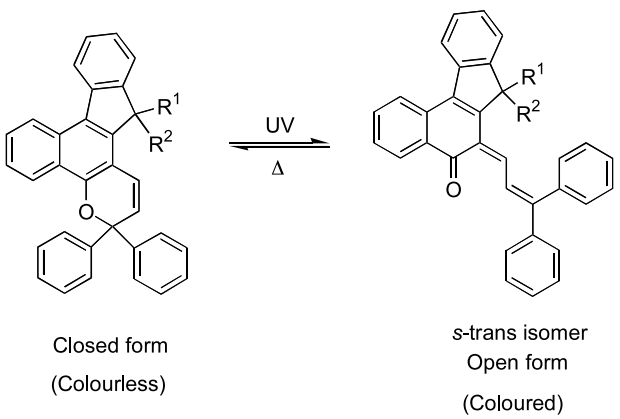
Naphthopyrans are one of the most studied classes of photochromic compounds due to their use in plastic lenses. When exposed to sunlight, in solution or in polymer matrices, these molecules exhibit colours from orange to blue/gray. [1] When the irradiation ceases the solution returns to its original colourless state, normally via a thermal electrocyclic ring closure. The change in the visible absorption spectrum of these compounds is due to the photoinduced reversible opening of the pyran ring leading to the formation of an 'open form' with an extensively conjugated π system (Scheme 1). The photochromic properties of naphthopyrans are strongly dependent on structural features. [1–3] The fusion of an indeno group to the 5,6 positions (*f* face) of 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyrans is a well known strategy to improve the photochromic properties because it effectively extends the π-system conjugation and introduces important nonbonding interactions in the open forms, without affecting the process that leads to the coloured forms. [1] The net result are readily obtained coloured forms with an observable bathochromic shift in the visible spectra and interesting bleaching kinetics due to the increased instability of the open forms. These indeno-fused naphthopyrans exhibit a wide range of colours, a high molar absortivity in the near-UV and interesting discolouration kinetics (Scheme 1). [4–8]

The set of isomers that constitute the open form of the 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyrans, obtained upon UV irradiation, are not completely planar, due to the steric hindrance between the two phenyl groups. In recent studies it was showed that in some naphthopyrans the linkage of the two phenyl sp^3-substituents through a sulphur bridge results in the increase of the maximum wavelength of absorption and in a very significant increase of the discolouration rate. [9] In order to study this effect on indeno-fused naphthopyrans we decided to prepare some new indeno-fused spiro[thioxanthene-naphthopyrans]. In this paper, we report the synthesis and photochromic behaviour of these novel compounds.

2. Results and discussion

2.1. Synthesis

Naphthopyrans are usually prepared in fair to good yield by reaction of phenols with propynols. This reaction is quite general and a large variety of substituted or fused naphthols



Scheme 1.

Keywords: Photochromism; Naphthopyrans; Spectrokinetics; Heterocycles; Spiro[thioxanthene-naphthopyrans].
* Corresponding author. Tel.: +351-259-350284; fax: +351-259-350480; e-mail address: pcoelho@utad.pt

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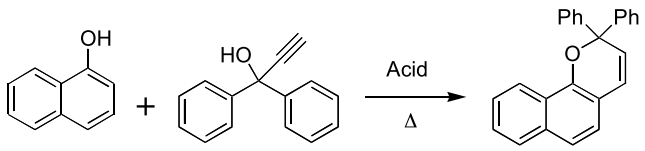
can be used. Several different aromatic propynols have also been used (Scheme 2). [10]

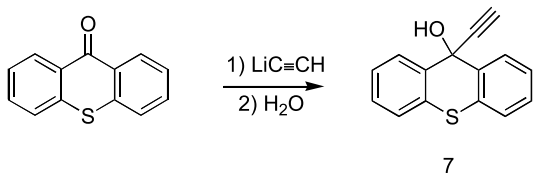


Scheme 2.

For the synthesis of indeno-fused spiro[thioxantene-naphthopyrans] we needed indeno-fused naphthols and the propynol derived from thioxanthone. Indeno-fused naphthol **6** was prepared in five steps from commercially available 1,4-dihydroxy-2-naphthoic acid **1**. This acid was converted into the 1,4-dimethoxy-2-naphthoic acid **2** by methylation followed by basic hydrolysis. In order to introduce a phenyl group in position 1 the acid **2** was converted into the 4,5-dihydrooxazole **3**. The activating effect of the 4,5-dihydrooxazole ring allows the nucleophilic substitution of the methoxy group by an alkyl/aryl group through reaction with Grignard reagents at room temperature. [11] The 4,5-dihydrooxazole **4** was then hydrolysed to the corresponding acid and treated for 5 min with concentrated sulphuric acid affording methoxybenzofluorenone **5**. Finally, heating a solution of methoxybenzofluorenone in HBr/HOAc gave the naphthol **6** in good yield (Scheme 3).

Diaryl propynols are usually prepared through reaction of diarylketones with lithium or sodium acetylide (Scheme 4). The reaction is incomplete and gives a diol as secondary product. Due to the presence of this by-product and a significant amount of the unreacted ketone, column chromatography purification is usually necessary. [12]

The reaction of thioxanthone with lithium acetylide gave the expected products but the purification of the propynol **7** proved to be very difficult since an extended decomposition is observed upon silica or alumina column chromatography. However, an almost pure sample of this alcohol was obtained through silica gel flash chromatography. Although limited to small amounts the use of this technique allowed the preparation of several grams of alcohol **7** in approximately 67% overall yield (Scheme 5).

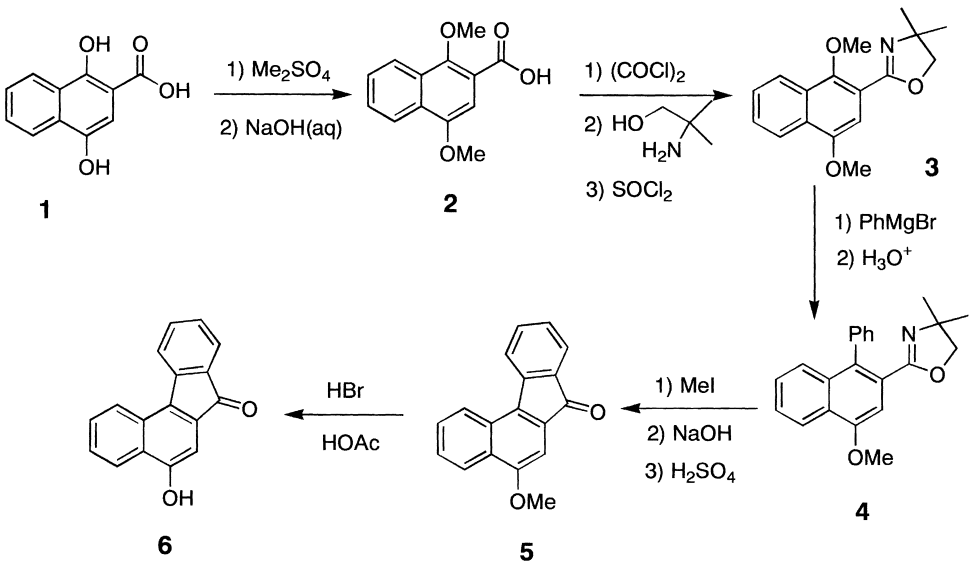


Scheme 5.

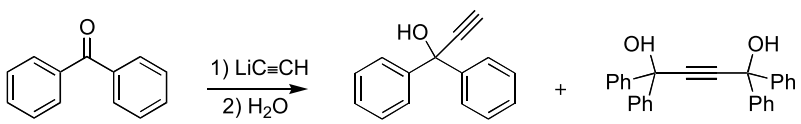
Heating a chloroform solution of naphthol **6** with propynol **7** in the presence of a catalytic amount of PPTS gave spiro[thioxanthene-naphthopyran] **8** in 62% yield. This compound is not photochromic (Scheme 6). [13] Treatment of **8** with the Grignard reagents derived from methyliodide, *tert*-butylcloride, bromobenzene and 2-bromothiophene gave, after hydrolysis, the photochromic spiro[thioxanthene-naphthopyran] **9a–d** in low to good yield (24–84%).

2.2. Photochromic properties

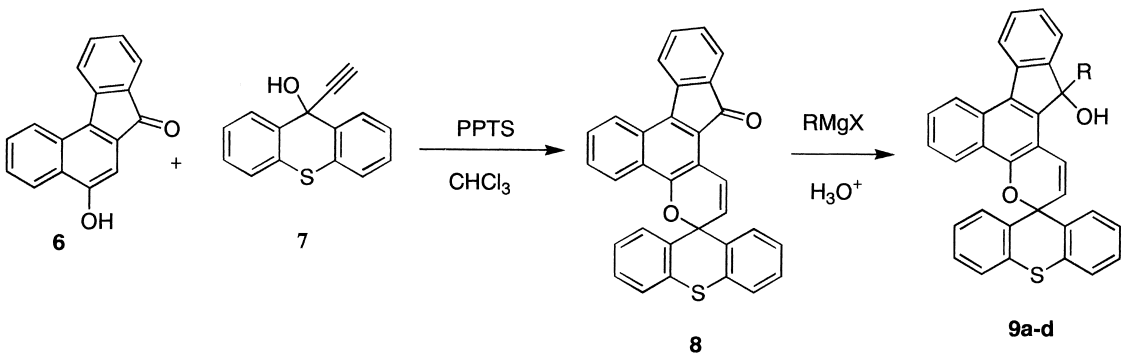
The photochromic behaviour of compounds **9a–d** was studied in toluene solutions under continuous near-UV irradiation. Three spectrokinetic parameters namely, the maximum wavelength of absorption of the open form



Scheme 3.

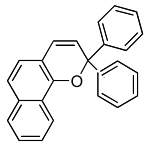
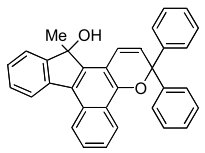
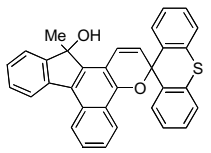
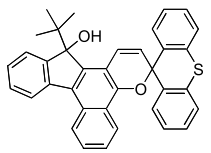
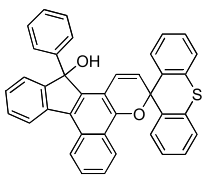
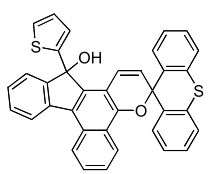


Scheme 4.



Scheme 6.

Table 1. Spectrokinetic properties under continuous irradiation: maxima wavelengths of the coloured form (λ_{max}), colourability (A_{eq} is the absorbance after photostationary equilibrium at λ_{max}), thermal bleaching rate (k_{Δ}) of compounds **9a**–**d**, and two reference compounds in toluene solutions: **10** (2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran), **11** (13-hydroxy-13-methyl-3,3-diphenyl-indeno[2,1-*f*]naphtho[1,2-*b*]pyran)

Compound		λ_{max} (nm)	A_{eq}	k_{Δ} (s^{-1})
10		469	0.72	0.0006 (98) 0.0003 (2)
11		530	1.2	0.004 (98) 0.0001 (2)
9a		552	0.66	0.047 (90) <0.0001 (10)
9b		557	0.27	0.047 (90) <0.0001 (10)
9c		558	0.49	0.10 (91) 0.0001 (9)
9d		556	0.44	0.11 (83) <0.0001 (17)

(λ_{max}), the thermal bleaching rate, (k_{Δ}) and the colourability or absorbance of the solution after reaching photostationary equilibrium (A_{eq}) were evaluated. The data are summarised in Table 1. For comparison purposes the same parameters were obtained, under identical experimental conditions, for two known naphthopyrans: the compound without any substituents 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran **10** and the known indeno-fused naphthopyran without the sulphur bridge, 3,3-diphenyl-13-hydroxy-13-methyl-indeno[2,1-*f*]naphtho[1,2-*b*]pyran **11**.

All of the new naphthopyrans, **9a**–**d**, exhibited photochromic behaviour at room temperature in toluene solutions. Compared to the reference naphthopyran **10** the absorption wavelength in the visible range obtained after irradiation, λ_{max}, show, as expected, substantial bathochromic shifts for all the new indeno-fused derivatives. From the data presented in Table 1, it can be observed that the extension of the π-conjugation is due to not only the indeno moiety but results also from the presence of the sulphur bridge: similarly substituted indeno-fused naphthopyrans (**9a** and **11**) exhibit significantly different λ_{max} (+22 nm) confirming that the introduction of a sulphur bridge linking the 2,2-diphenyl groups is an efficient way to increase the participation of each phenyl nucleus in the π-conjugation of the open forms. [9]

On the other hand, all of the new compounds exhibit absorption localised at ca. 555 nm indicating that the nature of the substituents at the indeno sp^3-carbon atom have only a minor influence in the conjugation of the open forms.

With regard to the ring closure kinetics, the new described compounds exhibit two phases kinetics with similar amplitudes. It is apparent that the open forms of the compounds with the sulphur bridge are thermally less stable than the reference compounds (rate of ring closure 10–20 times faster than **11**). The same was already observed with spiro[thioxanthene-naphthopyrans] [9] and is probably due to some strain in the planar open forms promoted by the sulphur bridge. The first rate constant, 0.047–0.11 s^{-1}, is higher than that observed for the reference compounds with an amplitude a little lower, around 90%. The second rate constant is very slow, as for the reference compounds, and is responsible for the persistence of a residual colour even after several minutes after the removal of the source of the

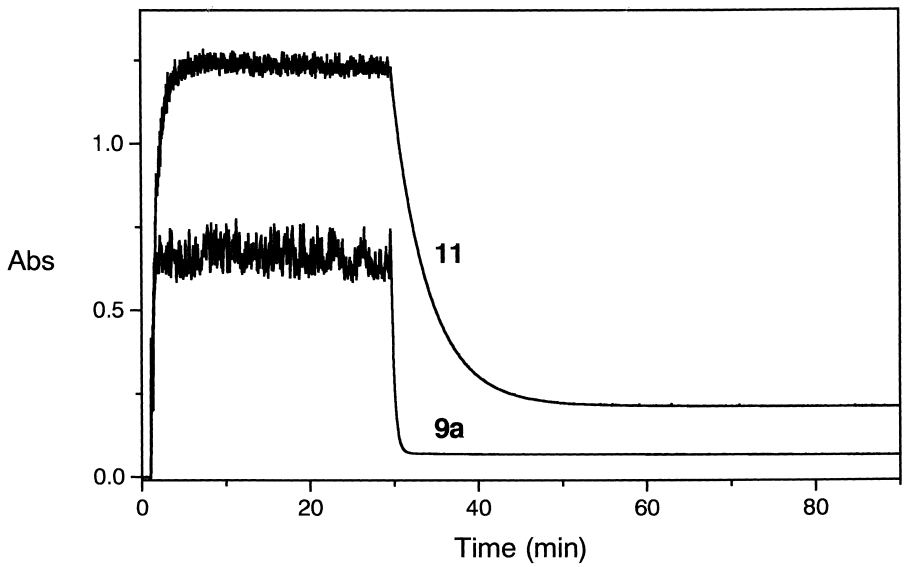


Figure 1. Variation of the absorbance at λ_{max} of **11** and **9a** (toluene solution, 1×10^{-4} M) under continuous UV irradiation (150 W Xe lamp, 30 min) and then when the irradiation is stopped (20 °C).

activating light. However, as can be shown in Figure 1, the spiro[thioxantene-naphthopyran] **9a** is much faster (almost 6 times) than **11**: naphthopyran **9a** reaches one half the highest absorbance attained in 39 s; **11** takes 246 s to reach one half of its maximum absorbance. The residual colour of **9a** is also significantly lower (0.07 after 30 min in the dark) than for **11** (0.21 in the same time). The observed kinetics make the novel compounds more acceptable compounds for application in variable optical transmission materials.

The presence of an aromatic group at the indeno sp^3-carbon atom (compounds **9c** and **9d**) contributes to the instability of the coloured forms leading to two-fold increase in the first kinetic rate constant. This does not seem to be a steric effect as compounds **9a** and **9b** differ markedly in the size of the substituent group and exhibit similar rates of ring closure.

The colourabilities of all the new described compounds are variable and lower than the observed for the reference compounds. This can be related to the faster thermal fading rates. Under continuous irradiation at low concentration, the colourability is proportional to both the quantum yield of photocolouration and the molar absortivity of the coloured form, but inversely proportional to the fading-rate constant. Faster bleaching kinetics are normally accompanied by lower colourabilities due to the lower concentration of coloured products at the photostationary state (Fig. 1).

3. Conclusion

Four new photochromic indeno-fused naphthopyrans were synthesised in good yield. Spiro[thioxanthene-naphthopyrans] **9a**–**d** showed a general significant bathochromic shift in the spectra of the open forms, higher ring closure rates and an expected decrease in the colourabilities when compared to a similar known indeno-fused naphthopyran (**11**). Although all compounds showed a residual colour even after several minutes in the dark, the absorbance is considerably lower than that observed for the reference compound without the sulphur bridge (**11**). The linkage of the two C-sp^3 phenyl groups in diphenyl indeno-fused naphthopyrans through a sulphur bridge increases the participation of each phenyl nucleus in the π-conjugation of the open forms and constitutes an effective way to extend the chromophore and to accelerate the ring closure kinetics. The nature of the substituents at the C-sp^3 of the indeno group seems to have little effect on the π-conjugation of the open forms. Bulky substituents at this atom do not have a marked effect on the thermal stability of the open forms but aromatic substituents promote some instability. These indeno-fused spiro[thioxanthene-naphthopyrans] would appear to be promising compounds for application in ophthalmic photochromic lenses.

4. Experimental

4.1. Spectrokinetic studies under continuous irradiation

For measurements of λ_{max}, A_{eq} and k_{Δ} under continuous irradiation, 1×10^{-4} M toluene solutions were used. Irradiation experiments were made using a CARY 50 Varian spectrometer coupled to a 150 W Ozone free Xenon lamp (6255 Oriel Instruments). The light from the UV lamp was filtered using a water filter (61945 Oriel Instruments) and then carried to the spectrophotometer holder at the right angle to the monitoring beam using a fiber-optic system (77654 Oriel Instruments). A light flux of 40 W m^{-2}, measured with a Goldilux Photometer with a UV-A probe was used. A thermostated (20 °C) 10 mm quartz cell, containing the sample solution (3.5 ml), equipped with magnetic stirring was used. In a preliminary experiment, the visible absorption spectrum of the closed form 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 with the time was monitored. The rate constants were calculated using a multi exponential model.

4.2. General remarks

^{1}H spectra were recorded in $CDCl_3$ on a Varian Unity Plus at 300 MHz. ^{13}C spectra were recorded in $CDCl_3$ on a Varian Unity Plus at 75.4 MHz. IR spectra were recorded on a Perkin–Elmer FTIR 1600 spectrometer, wave numbers in cm^{-1}. Mass spectra were measured on an AutoSpecE spectrometer. Melting points are uncorrected. Column chromatography was performed on silica gel 60 (70–230 mesh). All new compounds were determined to be >95% pure by ^{1}H NMR spectroscopy. Compounds **10** and **11** were prepared from 1-naphthol and 5-hydroxy-7*H*-benzo[*c*] fluoren-7-one, respectively, using standard procedures.[1,4] The melting points of photochromic naphthopyrans **9a–d** were not measured because thermochromism was observed at high temperatures.

4.2.1. 1,4-Dimethoxynaphthoic acid 2. A mixture of 1,4-dihydroxynaphthoic acid (10.0 g, 0.0490 mol), K_2CO_3 (61 g, 0.44 mol), dimethyl sulphate (14 ml, 0.15 mol) and acetone (100 ml) was heated for 2 days at reflux under argon atmosphere. After return to room temperature the mixture was filtered and the filtrate evaporated to give the crude 1,4-dimethoxynaphthoic methyl ester. 100 ml of aqueous NaOH (20%) was added to the crude ester and the solution heated under reflux for 3 h. After return to room temperature the aqueous solution was extracted with CH_2Cl_2 and the organic phase discarded. The aqueous phase was acidified with HCl (10%) and extracted with Et_2O (3×100 ml). The combined organic layers were dried (Na_2SO_4) and concentrated to give pure 1,4-dimethoxynaphthoic acid **2** (10.80 g, 0.0466 mmol) as a light brown solid. Yield: 95%. Mp 68.3–69.2 (lit. [14] 57–59). IR: 3200–2400 broad band, 1675, 1367, 1110; ^{1}H NMR: 11.5 (s, 1H, COOH), 8.32 (m, 1H), 8.11 (m, 1H), 7.66 (m, 2H), 7.39 (s, 1H), 4.13 (s, 2H, OCH_3), 4.06 (s, 2H, OCH_3). Exact mass for $C_{13}H_{12}O_4$: 232.0736. Found 232.0735.

4.2.2. 2-(1′,4′-Dimethoxynaphth-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 3. A mixture of 1,4-dimethoxynaphthoic acid (1.00 g, 4.31 mmol), CH_2Cl_2 (60 ml) and oxalyl chloride (0.60 ml, 5.6 mmol) was stirred at room temperature for 24 h. The solvent and the oxalyl chloride excess were removed by rotary evaporation. 1,2-Dichloroethane (15 ml) was added followed by additional rotary evaporation in order to remove any residual oxalyl chloride. The crude acyl chloride was then dissolved in 1,2-dichloroethane (30 ml) and treated successively with triethylamine (0.80 ml, 5.76 mmol) and 2-amino-2-methyl-1-propanol (574 mg, 6.44 mmol) at 0 °C and stirred overnight at room temperature. Aq. sat. NH_4Cl (15 ml) and water (15 ml) was added and then the entire mixture was transferred to a separatory funnel and extracted with Et_2O (3×100 ml). The combined organic layers were dried (Na_2SO_4) and concentrated to give the crude hydroxy amide which was redissolved in CH_2Cl_2 (120 ml) and benzene (20 ml) and placed at 0 °C. Thionyl chloride (2.0 ml, 27.5 mmol) was added and the mixture stirred 4 h at room temperature. After solvent evaporation, ether (260 ml), aq. sat. $NaHCO_3$ (24 ml), water (24 ml) and NaOH (2 N, 24 ml) were added. The mixture was stirred 30 min and then the organic layer removed and the aqueous layer re-extracted with ether (2×100 ml). The combined organic layers were dried, concentrated and the product purified by column chromatography (0–20% ethyl acetate/light petroleum) to give pure 4,5-dihydrooxazole **3** (1.027 g, 3.60 mmol) as a yellow oil. [15] Yield: 84%. IR: 2961, 1650, 1370, 1261, 1106; ^{1}H NMR: 8.21 (m, 2H), 7.56 (m, 2H), 7.14 (s, 1H), 4.19 (s, 2H, CH_2O), 4.03 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 1.45 (s, 6H, 2×CH_3). MS: *m*/*z* (%): 285 (45), 232 (48), 215 (100), 149 (75), 58 (90). Exact mass for $C_{17}H_{19}O_3N$: 285.1365. Found 285.1354.

4.2.3. 2-(1′-Phenyl-4′-methoxynaphth-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 4. A solution of phenylmagnesium bromide (prepared from bromobenzene (2.84 g, 18.1 mmol) and magnesium (0.435 g, 18.1 mmol) in 20 ml of dry ethyl ether) was slowly added to a solution of 4,5-dihydrooxazole **3** (1.00 g, 3.02 mmol) in ethyl ether (15 ml). After stirring at room temperature for 24 h, the solution was quenched in aq. sat. NH_4Cl, extracted with Et_2O (3×40 ml), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by CC (0–30% ethyl acetate/light petroleum) to give pure 4,5-dihydrooxazole **4** (0.740 g, 2.24 mmol) as a yellow oil. Yield: 75%. IR: 2969, 2877, 1658, 1592, 1457, 1145; ^{1}H NMR: 8.33 (d, *J*=8.4 Hz, 1H), 7.62 (d, *J*=8.0 Hz, 1H), 7.52 (dt, *J*=8.4 Hz, 1.5, 1H), 7.48–7.30 (m, 6H), 7.11 (s, 1H), 4.10 (s, 3H, OCH_3), 3.72 (s, OCH_2, 2H), 1.23 (s, 6H, 2×CH_3). MS: *m*/*z* (%): 331 (55), 330 (100), 316 (25), 245 (24), 189 (24), 77 (14). Exact mass for $C_{22}H_{21}O_2N$: 331.1572. Found 331.1568.

4.2.4. 5-Methoxy-7*H*-benzo[*c*]fluoren-7-one 5. A solution of 4,5-dihydrooxazole **4** (0.690 g, 2.08 mmol) in MeI (10 ml) was stirred at room temperature overnight and the excess of MeI removed under reduced pressure. To the crude methyl iodide salt, were added methanol (12 ml) and NaOH 20% (12 ml) and the mixture heated to reflux for 12 h. The solution was extracted with Et_2O and the organic layer discarded. The aqueous layer was acidified with HCl (aq.), extracted with Et_2O, dried (Na_2SO_4) and concentrated to give the 4-methoxy-1-phenylnaphthoic acid. Without further purification, H_2SO_4 (5 ml) was added. After stirring for 5 min at room temperature the resulting dark coloured solution was poured into ice (50 g) and then extracted with Et_2O (3×50 ml). The organic layer was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure to give pure ketone **5** (0.340 g, 1.31 mmol) as a red solid. Yield: 63%. Mp 142.0–143.3 (lit. [16] 155–156). IR: 2930, 1718, 1270, 1122; ^{1}H NMR: 8.43 (d, *J*=7.8 Hz, 1H), 8.34 (d, *J*=8.1 Hz, 1H), 7.91 (d, *J*=7.8 Hz, 1H), 7.70–7.55 (m, 3H), 7.48 (dt, *J*=1.2 Hz, 7.5, 1H), 7.22 (dt, *J*=1.0 Hz, 7.5, 1H), 7.13 (s, 1H), 4.08 (s, 3H, OCH_3). MS: *m*/*z* (%): 260 (55), 245 (37), 217 (22), 189 (20), 167 (45), 149 (100). Exact mass for $C_{18}H_{12}O_2$: 260.0837. Found 260.0827.

4.2.5. 5-Hydroxy-7*H*-benzo[*c*]fluoren-7-one 6. A mixture of ketone **5** (0.340 g, 1.31 mmol), acetic acid (2.5 ml) and HBr 47% (5 ml) was heated under reflux for 5 h. After cooling the reaction mixture was poured into 100 ml of water and extracted with ethyl ether (3×50 ml). The combined organic layers were extracted 3 times with NaOH (5%, 20 ml) and the organic phase discarded. The aqueous phase was acidified with HCl 10%, and extracted with ether (3×50 ml). The combined organic layers were dried (Na_2SO_4) and the solvent evaporated under reduced

pressure giving the pure hydroxybenzofluorenone **6** (0.212 g, 0.86 mmol) as a red solid. Yield: 66%. Mp 252.2–253.3 (lit.[16] above 235). IR: 3397, 1714, 1579, 1351; ^{1}H NMR (acetone-d_6): 9.78 (s, 1H, OH), 8.60 (d, *J*=8.5 Hz, 1H), 8.36 (d, *J*=8.4 Hz, 1H), 8.11 (d, *J*=7.8 Hz, 1H), 7.72 (t, *J*=7.5 Hz, 1H), 7.64 (t, *J*=7.5 Hz, 1H), 7.57 (m, 2H), 7.28 (t, *J*=7.5 Hz, 1H), 7.16 (s, 1H). MS: *m*/*z* (%): 246 (100), 217 (6), 189 (40), 149 (7), 95 (14). Exact mass for $C_{17}H_{10}O_2$: 246.0681. Found 246.0680.

4.2.6. Spiro[13-oxoindeno[2,1-*f*]naphtho[1,2-*b*]pyran-3,9′-thioxanthene] 8. A suspension of thioxanthone (2.00 g, 9.43 mmol), and lithium acetylide ethylene diamine complex (3.00 g, 29.4 mmol) in dry THF (250 ml) was stirred under an argon atmosphere for 24 h. The suspension was treated with water (200 ml) and the aqueous phase extracted with ethyl ether (3×100 ml). The organic phase was dried over anhydrous Na_2SO_4 and the solvent evaporated leaving the crude 9-hydroxy-9-ethynyl-9*H*-thioxanthene. The crude product was further divided into four fractions each one was submitted to flash column chromatography (10% ethyl acetate/hexane) (not more than 30 min) affording almost pure 9-hydroxy-9-ethynyl-9*H*-thioxanthene **7** (1.5 g, 67% yield); [17] ^{1}H NMR: 8.15 (dd, *J*=7.8 Hz, 2.1, 2H), 7.52 (dd, *J*=7.2 Hz, 2.1, 2H), 7.37 (ddd, *J*=7.5 Hz, 7.5, 1.8, 2H), 7.33 (ddd, *J*=7.5 Hz, 7.5, 1.8, 2H), 2.94 (s, 2H).

A solution of 9-hydroxy-9-ethynyl-9*H*-thioxanthene **7** (0.800 mg, 3.36 mmol), 5-hydroxy-7*H*-benzo[*c*]fluoren-7-one **6** (0.174 g, 0.707 mmol) *p*-toluenosulphonic acid (50 mg) and $CHCl_3$ (60 ml) was refluxed for 4 h under an argon atmosphere. Solvent evaporation gave a brown oil which was purified by silica gel column chromatography (3% ethyl acetate/hexane). Recrystallisation from $CHCl_3$/pentane gave a crystalline red compound (0.240 g, 0.515 mmol). Yield: 73%. Mp 234–235 °C. IR: 3052, 2921, 1698, 1641, 1270, 1068; ^{1}H NMR: 8.46 (dd, *J*=7.8 Hz, 1.2, 1H), 8.38 (dd, *J*=7.8 Hz, 1.2, 1H), 7.95 (d, *J*=7.5 Hz, 1H), 7.81 (d, *J*=10.2 Hz, 1H), 7.76–7.68 (m, 2H), 7.68–7.46 (m, 6H), 7.36–7.20 (m, 5H), 6.37 (d, *J*=10.2 Hz, 1H). ^{13}C NMR 195.70; 148.95; 144.83; 137.52; 135.48; 134.56; 134.45; 129.90; 129.61; 128.16; 128.06; 127.80; 127.64; 127.09; 126.92 (two carbons overlapped); 126.50; 126.10; 124.80; 124.24; 123.76; 123.53; 122.36; 117.63; 111.56; 80.53. MS: *m*/*z* (%): 466 (100), 449 (20), 330 (26), 233 (45), 221 (90), 210 (35).

4.3. Procedure for the reaction of naphthopyran 8 with Grignard reagents

A solution of the Grignard reagent prepared in ethyl ether (2.0 ml, 2.0 mmol) was added to a solution of the naphthopyran **8** (0.100 mg, 0.215 mmol) dissolved in THF (10 ml) at 0 °C. After stirring at room temperature for 4 h, the solution was quenched in aq. sat. NH_4Cl, extracted with Et_2O (3×40 ml) and the combined organic layers dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by CC (3% ethyl acetate/light petroleum) to give the pure naphthopyrans **9a**–**d**.

4.3.1. 13-Hydroxy-13-methyl-spiro[indeno[2,1-*f*]naphtho[1,2-*b*]pyran-3,9′-thioxanthene] 9a. Light yellow solid. Yield: 44%. IR: 3386, 3058, 2950, 1457, 1268, 1112. UV/Vis (closed form): 372 (ε 7800), 392 (ε 4700); ^{1}H NMR: 8.64 (dd, *J*=8.4 Hz, 1H), 8.48 (dd, *J*=8.4 Hz, 1.0, 1H), 8.15 (d, *J*=7.8 Hz, 1H), 7.80–7.72 (m, 2H), 7.67 (dt, *J*=8.4 Hz, 1.5, 1H), 7.60 (dd, *J*=7.5 Hz, 1.0, 1H), 7.57–7.50 (m, 2H), 7.44 (dt, *J*=7.8 Hz, 1.2, 1H), 7.40–7.20 (m, 7H), 6.30 (d, *J*=10.2 Hz, 1H), 1.80 (s, CH_3, 3H). ^{13}C NMR: 151.14, 148.59, 143.96, 139.47, 138.44, 138.32, 130.86, 130.13, 129.69, 129.46, 128.97, 127.64, 127.62, 127.54, 126.99, 126.92, 126.87, 126.44, 126.31, 126.26, 126.18, 125.72, 124.58, 124.08, 123.20, 122.44, 122.12, 122.02, 118.35, 110.88, 80.78, 80.21, 26.59. MS: *m*/*z* (%): 482 (50), 464 (33), 449 (100), 221 (35), 197 (46). Exact mass for $C_{33}H_{22}O_2S$: 482.1341. Found 482.1349.

4.3.2. 13-*tert*-Butyl-13-hydroxy-spiro[indeno[2,1-*f*]naphtho[1,2-*b*]pyran-3,9′-thioxanthene] 9b. Light yellow solid. Yield: 28%. IR: 3410, 3050, 2982, 1620. UV/Vis (closed form): 366 (ε 3500); ^{1}H NMR: 8.64 (d, *J*=8.1 Hz, 1H), 8.48 (d, *J*=8.2 Hz, 1H), 8.11 (d, *J*=7.9 Hz, 1H), 7.80–7.78 (m, 1H), 7.73–7.71 (m, 4H), 7.66–7.63 (t, *J*=7.5 Hz, 1H), 7.55–7.50 (m, 3H), 7.40–7.38 (t, *J*=7.5 Hz, 1H), 7.30–7.20 (m, 4H), 6.20 (d, *J*=10.3 Hz, 1H), 0.92 (s, CH_3, 9H). MS: *m*/*z* (%): 524 (20), 467 (42), 450 (10), 271 (17), 221 (40), 210 (45), 197 (57), 149 (100). Exact mass for $C_{36}H_{28}O_2S$: 524.1810. Found 524.1827.

4.3.3. 13-Hydroxy-13-phenyl-spiro[indeno[2,1-*f*]naphtho[1,2-*b*]pyran-3,9′-thioxanthene] 9c. Light blue solid. Yield: 81%. IR: 3457, 3058, 2923, 1457, 1268, 1162. UV/Vis (closed form): 372 (ε 12300), 393 (ε 7400); ^{1}H NMR: 8.67 (d, *J*=8.7 Hz, 1H), 8.43 (d, *J*=8.4 Hz, 1H), 8.15 (d, *J*=7.8 Hz, 1H), 7.74–7.15 (m, 18H), 6.75 (d, *J*=10.2 Hz, 1H), 6.07 (d, *J*=10.2 Hz, 1H). MS: *m*/*z* (%): 544 (1), 526 (1), 444 (4), 347 (5), 287 (28), 273 (15), 213 (100), 184 (31), 77 (31). Exact mass for $C_{38}H_{24}O_2S$: 544.1497. Found 544.1498.

4.3.4. 13-Hydroxy-13-thiophen-2-yl-spiro[indeno[2,1-*f*]naphtho[1,2-*b*]pyran-3,9′-thioxanthene] 9d. Light brown solid. Yield: 84%. IR: 3519, 3062, 2915, 1562, 1455, 1365, 1268, 1110. UV/Vis (closed form): 368 (ε 11000); ^{1}H NMR: 8.64 (d, *J*=8.4 Hz, 1H), 8.45 (d, *J*=8.1 Hz, 1H), 8.13 (d, *J*=7.5 Hz, 1H), 7.76–7.70 (m, 2H), 7.67 (dt, *J*=7.5 Hz, 1.2, 1H), 7.57 (dt, *J*=7.5 Hz, 1.2, 1H) 7.54–7.46 (m, 2H), 7.40 (dt, *J*=7.5 Hz, 1.2, 1H), 7.30–7.20 (m, 6H), 7.19 (dd, *J*=4.5 Hz, 1.0, 1H), 6.93 (d, *J*=10.2 Hz, 1H), 6.83 (dd, *J*=4.5 Hz, 4.8, 1H), 6.68 (dd, *J*=4.5 Hz, 1.0, 1H), 6.15 (d, *J*=10.2 Hz, 1H). ^{13}C NMR: 150.50; 148.83; 147.00; 142.84; 139.32; 137.77; 137.22; 130.10; 129.87; 129.25; 127.70; 127.65; 127.50; 126.88; 126.84; 126.77; 126.69; 126.61; 126.58; 126.02; 125.27; 124.48, 124.18; 123.74; 123.35; 122.30; 122.01; 119.30; 111.58; 82.59; 80.09. MS: *m*/*z* (%): 550 (98), 532 (82), 466 (42), 449 (43), 221 (55), 197 (100). Exact mass for $C_{36}H_{22}O_2S_2$: 550.1061. Found 550.1050.

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