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Synthesis and photochromic behaviour of novel 2*H*-chromenes derived from fluorenone

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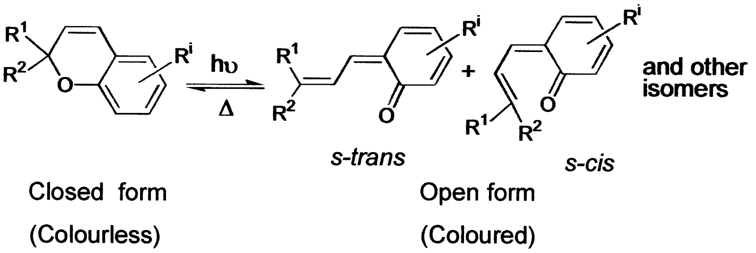
Abstract—The synthesis of 2*H*-chromenes based on a fluorenone nucleus is described. Whereas 2,2-diphenyl-2*H*-pyranofluorenones **4–7** and dicyanomethylidene-2*H*-pyranofluorenes **8–10** do not exhibit photochromism, 2,2-diphenyl-2*H*-pyranofluorenols exhibit photochromic behaviour. The spectrokinetic properties of these compounds in solution are reported. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Since the discovery of the photochromic behaviour of the 2*H*-chromenes (2*H*-1-benzopyrans),[1] much research has been devoted to this important class of oxygenated heterocyclic compounds.[2] These interesting molecules undergo a photo-induced change of colour in solution or in polymer matrices when exposed to UV radiation or direct sunlight exposure, returning to the initial state when the illumination ceases, normally via a thermal pathway. The photochromic behaviour is based on a photoinduced reversible opening of the pyran cycle that converts the colourless form (usually named the 'closed form'), with non-interacting π systems, in a set of isomers with the pyran ring opened (the 'open form') leading to distinct absorption spectra due to an extensively conjugated π system (Scheme 1).[3]

There are many practical and promising applications for this phenomenon, based not only on the reversible colour change, but also on the reversible variation of physico-chemical parameters on account of structural changes.[4] Industrial applications in the field of variable optical transmission materials (photochromic ophthalmic lenses and glasses) have met with significant commercial success.[5] The synthesis of 2*H*-chromenes is frequently achieved by incorporation of a chromenic entity in a molecule with the desired ring structure and/or substituent pattern.[6,7] The nature of substituents is important to improve photochromic properties.[8–10]

In this work, we describe the synthesis and characterisation of novel 2*H*-chromenes containing a fluorenone nucleus. The compounds, although not photochromic in solution at room temperature, constitute excellent precursors for new photochromic molecules through simple modification of the carbonyl group.



Scheme 1.

Keywords: fluorenones; photochromism; 2*H*-chromenes; heterocycles; spectrokinetics.

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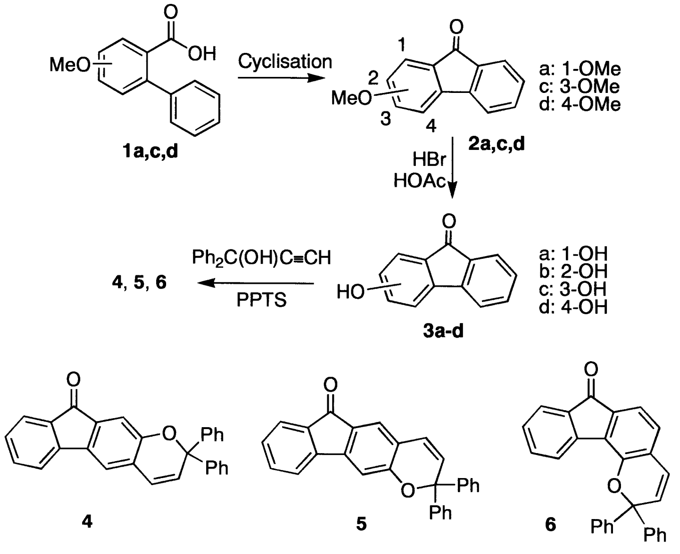


Scheme 2.

2. Results and discussion

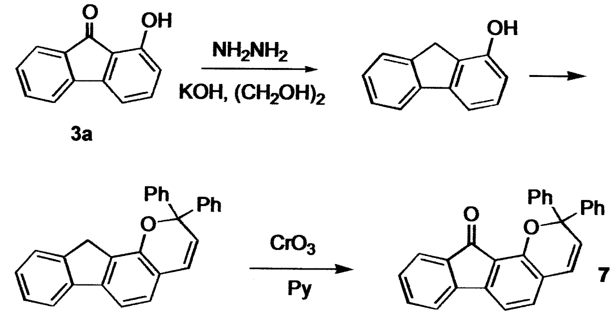
2.1. Synthesis

Naphthopyrans can be prepared, in reasonable yield, by cyclisation of naphthols with 1,1-diphenylprop-2-yn-1-ol in the presence of a catalytic amount of pyridinium *p*-toluenesulphonate (PPTS).[7,11] Using this strategy, the preparation of 2*H*-chromenes containing a fluorenone nucleus requires the availability of hydroxyfluorenones. Hydroxyfluorenones **3a**,**c**,**d** were synthesised in several reaction steps as shown in Scheme 2 (2-hydroxyfluorenone **3b** is commercially available). 2-Phenylbenzoic acids **1a**,**c**,**d** were prepared from commercial compounds using known procedures.[12–15] Cyclisation of acids **1a**,**c**,**d** to methoxyfluorenones **2a**,**c**,**d** was achieved using different methods as shown in Table 1. Treatment of compounds **2a**,**c**,**d** with HBr/HOAc gave hydroxyfluorenones **3a**,**c**,**d** (quantitative).

Table 1. Synthesis of methoxyfluorenones **2a**,**c**,**d**

2-Phenylbenzoic acid		Cyclisation method	Product	Yield (%)
1a	6-OMe	H_2SO_4	**2a**	85
1c	4-OMe	PPA	**2c**	73
1d	3-OMe	$SOCl_2/AlCl_3$	**2d**	45

Condensation of 1,1-diphenylprop-2-yn-1-ol with hydroxyfluorenones **3b–d** in $CHCl_3$ under PPTS catalysis gave 2*H*-pyranofluorenones **4–6**, respectively in fair yields. The chromenization reaction of hydroxyfluorenones **3b**,**c** was completely regioselective giving only the linear isomer. Under these conditions no reaction was observed with 1-hydroxyfluorenone **3a** due to the intramolecular hydrogen bond.[7] Thus, it was decided to reduce fluorenone **1a** to 1-hydroxyfluorene, which was converted to the corresponding 2*H*-chromene and oxidised to pyranofluorenone **7** (Scheme 3).



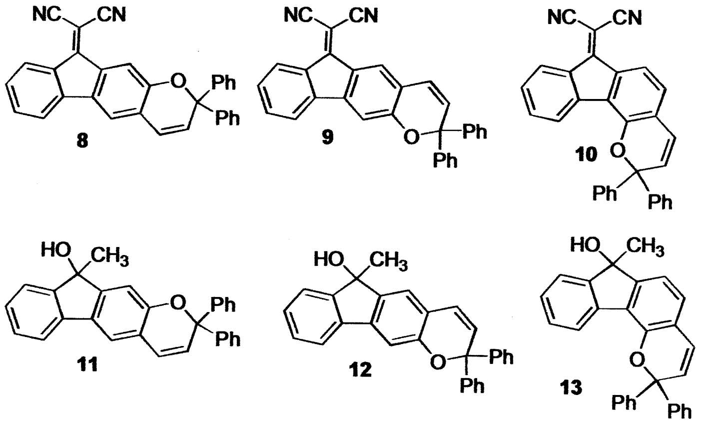
Scheme 3.

2*H*-Pyranofluorenones **4–6** are very versatile compounds, since the carbonyl group can be further functionalised to new classes of chromenes. Thus, heating an ethanolic solution of 2*H*-pyranofluorenones **4–6** and malononitrile (piperidine as catalyst) gave dicyanomethylidene-2*H*-pyranofluorenes **8–10** in modest yields (Scheme 4). Under these conditions, no reaction was observed with chromene **7**, probably due to the steric hindrance of the 2,2-diphenylpyrano ring. Treatment of 2*H*-pyranofluorenones **4–6** with methyl magnesium iodide gave, after hydrolysis, 2*H*-pyranofluorenols **11–13** in excellent yields.

2.2. Photochromic properties

The photochromic characteristics were determined using flash irradiation coupled to a rapid UV–Vis spectrometer (Table 2).[16] 2,2-Diphenyl-2*H*-pyranofluorenones **4–7** and dicyanomethylidene-2*H*-pyranofluorenes **8–10** did not exhibit photochromic activity.

For compounds **4–7**, this observation can be explained by the absence of significant activation in the wavelength domain of the light used for the irradiation (Fig. 1) (above 295 nm with the filter used in the experiments); photochromic compounds **11–13** exhibit absorption maxima around 340 nm which allows a efficient light absorption.



Scheme 4.

Table 2. Spectrokinetic properties: wavelengths of the absorption maxima of the coloured forms (λ_1, λ_2), colourability (A_{01}, A_{02} are the absorbances just after the flash at λ_1 and λ_2, respectively) and thermal bleaching rate (k_Δ) of 2*H*-chromenes **11–13** and two reference compounds in toluene (2.5×10^{-5} M) at 25°C: $\mathrm{Ref_1}$=3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran, $\mathrm{Ref_2}$=2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran[16]

Compound	Annellation	λ_1(nm)	A_{01}	λ_2(nm)	A_{02}	k_Δ (amplitude) ($\mathrm{s^{-1}}$) (%)
11	6,7	427	0.52	524	0.55	0.160 (91) and 0.025 (9)
12	6,7	439	1.4	505	0.63	0.120 (82) and 0.011 (18)
13	7,8	432	0.57	573	0.15	0.910 (92) and 0.110 (8)
$\mathrm{Ref_1}$	5,6	432	0.84	–	–	0.090
$\mathrm{Ref_2}$	7,8	403	1.08	481	1.62	0.002

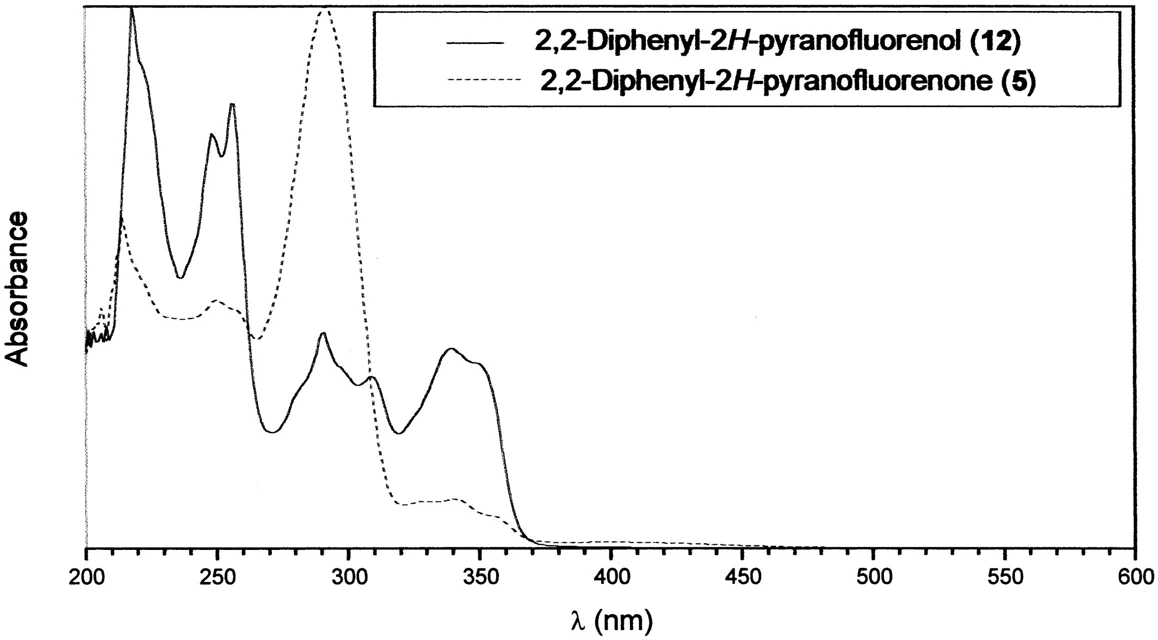


Figure 1.

Moreover, it appears that 2*H*-pyranofluorenones **4–7** fluoresce from the excited state, which usually leads to cleavage of the C–O bond. Compounds **8–10** are already deeply coloured before the flash and observation of photochromism is not straightforward. As compounds **11–13** exhibit indeed photochromic behaviour, substitution of a sp^3 carbon atom for a carbonyl in the five-membered ring fused to the benzopyran moiety is clearly a determining factor.[9]

Interestingly, the 2*H*-1-benzopyran moiety in compounds **11** and **12** is fused at the 6,7-positions, whereas compound

13 is fused at positions 7,8. 6,7-Annellation is in 2*H*-1-benzopyrans less frequently encountered than 7,8-annellation.[2] The open forms exhibit absorption bands around 430 nm and between 500 and 600 nm (analogous to five-membered heterocyclic 2*H*-chromenes),[17] which opens interesting avenues regarding applications in variable optical transmission materials. Nevertheless, the photocolouration efficiency, a function of the quantum yield of photocolouration and the molar absorptivity of the coloured species, is low.

As observed for a majority of chromenes dual kinetics of thermal bleaching with variable amplitudes are observed (probably due to different isomers). The slow fading rate is normally attributed to the most stable s-*trans*-isomer. The values of k_Δ reveal that the stability, in solution and at room temperature, of the open coloured forms of compounds **11–13**, are well suited for practical applications.

3. Conclusion

Three new classes of 2*H*-chromenes, based on a fluorenone nucleus, were synthesised. Although 2*H*-pyranofluorenones **4–7** and dicyanomethylidene-2*H*-pyranofluorenes **8–10** were not photochromic under the experimental conditions used in the measurements, 2*H*-pyranofluorenes **11–13** exhibit very interesting spectrokinetic properties. In particular, the rate of thermal bleaching and the absorption maxima of the open forms are interesting for applications in the field of variable optical transmission materials. The presence of a sp^3 carbon bridge between the 2,2-diphenyl-2*H*-chromene moiety and the phenyl nucleus seems essential for photochromism in solution at room temperature.

4. Experimental

4.1. Spectrokinetic measurements

For the determination of λ_1 and λ_2, A_{01} and A_{02}, and k_Δ, 5.10^{-5} mol dm^{-3} toluene solutions were used. The flash photolysis apparatus was monitored by a Warner and Swasey rapid spectrometer, allowing to record visible absorption spectra of the coloured forms in the 400–700 nm range (acquisition time 1 ms, repetitivity 1.25 ms).[18,19] Flashes (duration 50 μs) were generated by two xenon tubes with a quartz envelope. The energy of the flashes was 60 J for the full polychromatic emission spectrum. Thermostated (25°C) 100 mm cells were used. The light from the analysis lamp (50 W, quartz–iodide) was filtered using a Schott GG400 high-pass filter. In a preliminary experiment, 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 of the absorbance with time was monitored. The rate constants were calculated using a bi-exponential model.

4.2. Apparatus

^{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. Chemical shifts are given in ppm. NMR assignments were based on irradiation experiments. IR spectra were recorded on a Perkin–Elmer FTIR 1600 spectrometer (wavenumbers in cm^{-1}). Elemental analyses were carried out using a LECO 932 CHNS analyser. Mass spectra were measured on a AutoSpecE spectrometer. HRMS determinations were carried out on the molecular ion, using samples that were purified by TLC. Melting points are uncorrected. Column chromatography was performed on Silica 60 (70–230 mesh).

4.2.1. 1-Methoxyfluorenone (2a). A mixture of 6-methoxy-2-phenylbenzoic acid **1a** (1.73 g, 7.95 mmol) and H$_2$SO$_4$ (10 ml) was stirred for 8 h at rt. The red-coloured solution was poured into 200 ml of water and extracted with ethyl acetate (3×50 ml). The organic phase was dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. Crude 1-methoxyfluorenone was purified by column chromatography (hexane/ethyl acetate, 80:20). Yield: 85%. Mp 133–139°C (lit. 141.5–142.5°C[20]). ^{1}H NMR: 4.00 (s, 3H, OCH$_3$), 6.85 (d, *J*=8.4 Hz, 1H), 7.15 (d, *J*=7.5 Hz, 1H), 7.30 (ddd, *J*=7.2, 7.2, 1.5 Hz, 1H, H-7), 7.45 (d, *J*=7.8 Hz, 1H, H-5), 7.50 (m, 2H, H-6 and H-3), 7.66 (d, *J*=7.2 Hz, 1H, H-8).

4.2.2. 3-Methoxyfluorenone (2c). A mixture of 4-methoxy-2-phenylbenzoic acid **1c** (0.900 g, 4.13 mmol) and polyphosphoric acid (20 g) was stirred for 1 day at 60°C. The dark-coloured solution was poured into 200 ml water and extracted with diethyl ether (3×50 ml). The organic phase was dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. Crude 3-methoxyfluorenone was purified by column chromatography (hexane/ethyl acetate, 80:20). Yield: 73%. Mp 101–104.5°C (lit. 99°C[20]). ^{1}H NMR: 3.93 (s, 3H, OCH$_3$), 6.75 (dd, *J*=8.1, 2.4 Hz, 1H, H-2), 7.04 (d, *J*=2.1 Hz, 1H, H-4), 7.31 (m,1H, H-7), 7.49 (m, 2H, H-5 and H-6), 7.63 (d, *J*=8.4 Hz, 1H, H-1), 7.64 (d, *J*=7.5 Hz, 1H, H-8).

4.2.3. 4-Methoxyfluorenone (2d). A solution of 3-methoxy-2-phenylbenzoic acid **1d** (0.400 g, 1.75 mmol) and SOCl$_2$ (2.0 ml) was heated under reflux for 2 h. After removal of the SOCl$_2$ excess by evaporation under reduced pressure, the residue was diluted with benzene (10 ml) and AlCl$_3$ (0.300 g, 2.25 mmol) was added. The suspension was stirred at rt for 10 min and then quenched with NH$_4$Cl (aq), and extracted with EtOAc. The organic phase was dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. Crude 4-methoxyfluorenone was purified by column chromatography (hexane/ethyl acetate, 80:20). Yield: 52%. Mp 102.5–105.5°C. ^{1}H NMR: 4.57 (s, 3H, OCH$_3$), 7.06 (dd, *J*=7.8, 1.8 Hz, 1H, H-3), 7.20–7.32 (m, 3H, H-6, H-1 and H-2), 7.46 (dd, *J*=7.5, 7.2, 1.2 Hz, 1H, H-7), 7.64 (d, *J*=7.2 Hz, 1H, H-5), 7.84 (d, *J*=7.2 Hz, 1H, H-8).

4.3. Synthesis of hydroxyfluorenones (3). General procedure

A mixture of methoxyfluorenones **2a**,**c**,**d** (1.0 mmol), acetic acid (1.4 ml), and HBr 47% (2.5 ml) was heated under reflux for 8 h. After cooling, the reaction mixture was poured into 100 ml of water and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude hydroxyfluorenones were purified by column chromatography (hexane/ethyl acetate, 75:25–50:50).

4.3.1. 1-Hydroxyfluorenone (3a). Yield: 95%. Mp 108–109.5°C (lit. 115°C[20]). ^1H NMR: 6.78 (d, *J*=8.4 Hz, 1H), 7.05 (d, *J*=7.2 Hz, 1H), 7.31 (ddd, *J*=7.2, 8.4, 2.1 Hz, 1H, H-7), 7.38 (dd, *J*=7.2, 8.4 Hz, 1H, H-3), 7.51 (m, 2H, H-5 and H-6), 7.65 (d, *J*=7.5 Hz, 1H, H-8), 8.42 (s, 1H, OH).

4.3.2. 3-Hydroxyfluorenone (3c). Yield: 95%. Mp 215–220°C(lit. 225°C[20]). ^1H NMR: 6.69 (dd, *J*=7.8, 2.1 Hz, 1H, H-2), 7.00 (d, *J*=2.1 Hz, 1H, H-4), 7.31 (m,1H, H-7), 7.47 (m, 2H, H-5 and H-6), 7.59 (d, *J*=8.1 Hz, 1H, H-8), 7.64 (d, *J*=7.5 Hz, 1H, H-1), 8.50 (s, 1H, OH).

4.3.3. 4-Hydroxyfluorenone (3d). Yield: 95%. Mp 250–253°C (lit. 249°C[20]). ^1H NMR: 7.10 (d, *J*=7.2 Hz, 1H, H-8), 7.13 (dd, *J*=7.8, 1.5 Hz, 1H, H-1), 7.17 (dd, *J*=7.2, 1.5 Hz, 1H, H-3), 7.24 (dd, *J*=7.5, 7.5 Hz, 1H, H-2), 7.32 (ddd, *J*=7.2, 7.2, 0.9 Hz, 1H, H-6), 7.56 (dd, *J*=7.2, 1.2 Hz, 1H, H-5), 7.60 (m, 1H, H-7), 9.45 (s, 1H, OH).

4.4. Preparation of pyranofluorenones (4–6). General procedure

To a mixture of hydroxyfluorenone **3a**,**c**,**d** (1.00 mmol), 1,1-diphenylprop-2-yn-1-ol (312 mg, 1.50 mmol) and PPTS (50 mg) were added 50 ml of dry chloroform. The suspension was refluxed for 3 days under an argon atmosphere and then treated with 5% NaOH (150 ml). The aqueous phase was extracted with chloroform (3×30 ml). The organic phase was dried over anhydrous Na_2SO_4. Solvent evaporation gave a yellow oil, which was purified by column chromatography (hexane/ethyl acetate 96:4). Recrystallization from pentane/CH_2Cl_2 gave a crystalline material.

4.4.1. 2,2-Diphenyl-2*H*-pyrano[6,5-*b*]fluorenone (4). Yield: 31%. Mp 146.5–148°C. IR: 3060, 1714, 1604, 1448, 1430, 1380, 1243, 752, 701. ^1H NMR: 6.35 (d, *J*=9.9 Hz, 1H, H-3), 6.68 (d, *J*=9.9 Hz, 1H, H-4), 7.15 (s, 1H, H-11), 7.19 (ddd, *J*=7.5, 7.5, 1.2 Hz, 1H, H-8), 7.24 (s, 1H, H-5), 7.25–7.46 (m, 12H), 7.58 (d, *J*=7.2 Hz, 1H, H-9). ^{13}C NMR: 83.1 (C-2), 113.4, 118.4, 119.4, 123.2, 124.1, 126.2, 126.9, 127.8, 128.0, 128.2, 131.6, 134.4, 134.7, 135.3, 137.6, 144.1, 144.4, 153.9, 192.2 (C═O). MS: *m*/*z* (%) 386 (65, M^+), 309 (100) 252 (20). $C_{28}H_{18}O_2$: calcd C 87.05, H 4.66; found C 86.66, H 4.76.

4.4.2. 2,2-Diphenyl-2*H*-pyrano[5,6-*b*]fluorenone (5). Yield: 32%. Mp 250–254.5°C. IR: 3083, 1706, 1614, 1446, 1184, 1108, 765, 698. ^1H NMR: 6.19 (d, *J*=9.6 Hz, 1H, H-3), 6.64 (d, *J*=9.6 Hz, 1H, H-4), 7.07 (s, 1H, H-10), 7.25–7.46 (m, 14H), 7.60 (d, *J*=7.8 Hz, 1H, H-6). ^{13}C NMR: 84.0 (C-2), 109.3, 120.2, 120.7, 122.8, 123.1, 123.8, 125.9, 126.9, 127.8, 128.25, 128.27, 129.2, 134.2, 135.1, 143.4, 144.2, 146.7, 158.0, 192.4 (C═O). MS: *m*/*z* (%) 386 (85, M^+), 309 (100), 252 (22), 191 (10), 165 (12). Exact mass for $C_{28}H_{18}O_2$: 386.130680; found 386.130644.

4.4.3. 2,2-Diphenyl-2*H*-pyrano[5,6-*c*]fluorenone (6). Yield: 25%. Mp 199–200.5°C. ^1H NMR: 6.36 (d, *J*=10 Hz, 1H, H-3), 6.69 (d, *J*=10 Hz, 1H, H-4), 6.95 (d, *J*=7.5 Hz, 1H), 7.23 (d, *J*=7.5 Hz, 1H), 7.23–7.40 (m, 9H), 7.44–7.52 (m, 4H), 7.93 (d, *J*=7.2 Hz, 1H, H-8). MS: *m*/*z* (%) 386 (10, M^+), 358 (100), 329 (15), 281 (20), 252 (18). Exact mass for $C_{28}H_{18}O_2$: 386.130680; found 386.129576.

4.4.4. 2,2-Diphenyl-2*H*-pyrano[6,5-*a*]fluorenone (7). A mixture of 1-hydroxyfluorenone **3a** (654 mg, 3.33 mmol), KOH (0.984 g, 17.6 mmol), hydrazine (1.0 ml) and ethane-1,2-diol (5.0 ml) was stirred for 30 min at 110°C, then 2.5 h at 160°C and 2.5 h at 200°C. The mixture was treated with a saturated solution of NH_4Cl and extracted with diethyl ether. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed by evaporation. A solution of the crude 1-hydroxyfluorene, 1,1-diphenyl-prop-2-yn-1-ol (1.041 g, 5.00 mmol) and PPTS (50 mg) in 50 ml of dry chloroform was refluxed for 3 days under an argon atmosphere. The suspension was then treated with 5% NaOH (150 ml) and the aqueous phase was extracted with chloroform (3×30 ml). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. Pyridine (4.0 ml) and CrO_3 (1.0 g) were added to the crude pyranofluorene and the suspension was stirred overnight. The mixture was then treated with HCl (10%) and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed by evaporation leaving a yellow oil, which was purified by column chromatography (hexane/ethyl acetate 98:2). Recrystallization from pentane/CH_2Cl_2 gave pure **7**. Yield: 12.4%. Mp 204.5–206.8°C. ^1H NMR: 6.44 (d, *J*=10.2 Hz, 1H, H-3), 6.68 (d, *J*=10.2 Hz, 1H, H-4), 7.04 (d, *J*=7.2 Hz, 1H, H-5), 7.12 (d, *J*=7.2 Hz, 1H, H-6), 7.25–7.40 (m, 9H), 7.48 (m, 2H, H-7 and H-8), 7.56–7.64 (m, 4H), 7.63 (d, *J*=7.2 Hz, 1H, H-10). ^{13}C NMR: 83.2 (C-2), 113.2, 119.8, 120.1, 122.8, 123.7, 123.8, 126.5, 127.6, 128.3, 129.0, 129.5, 132.6, 133.9, 134.9, 143.4, 144.6, 145.5, 151.6, 191.1 (C═O). MS: *m*/*z* (%) 386 (55, M^+), 309 (100) 252 (10). Exact mass for $C_{28}H_{18}O_2$: 386.130680; found 386.131033.

4.5. Reaction of pyranofluorenones (4–6) with malononitrile. General procedure

A solution of pyranofluorenones **4**–**6** (0.259 mmol), malononitrile (185 mg, 2.8 mmol) and piperidine (2 drops) in ethanol (15 ml) was heated for 30 min under reflux. The reaction mixture was then treated with NH_4Cl, extracted with ethyl acetate, and the organic phase was dried over anhydrous Na_2SO_4. Solvent evaporation gave orange oil, which was purified by column chromatography (hexane/$CHCl_3$, increasing polarity). Recrystallization from methanol/$CHCl_3$ gave a crystalline material.

4.5.1. 10-Dicyanomethylidene-2,2-diphenyl-2*H*-pyrano-[6,5-*b*]fluorene (8). Yield: 60%. Mp 290–291°C. IR: 3056, 2219, 1637, 1560, 1450, 1199, 1130, 730, 700. ^1H NMR: 6.39 (d, *J*=9.9 Hz, 1H, H-3), 6.67 (d, *J*=9.9 Hz, 1H, H-4), 7.15 (s, 1H, H-5), 7.21 (ddd, J=7.5, 7.5, 1.2 Hz, 1H, H-8), 7.28–7.44 (m, 12H), 7.93 (s, 1H, H-11), 8.28 (d, J=8.1 Hz, 1H, H-9). MS: m/z (%) 434 (85, M^+), 357 (100), 191 (10). Exact mass for $C_{31}H_{18}ON_2$: 434.141913; found 434.141948.

4.5.2. 6-Dicyanomethylidene-2,2-diphenyl-2*H*-pyrano-[5,6-*b*]fluorene (9). Yield: 71%. Mp 275–277°C. IR: 3054, 2219, 1562, 1450, 1199, 1130, 730, 698. ^{1}H NMR: 6.23 (d, J=9.9 Hz, 1H), 6.67 (d, J=10 Hz, 1H), 7.09 (s, 1H, H-11), 7.25–7.50 (m, 13H), 8.05 (s, 1H, H-5), 8.32 (d, J=8.4 Hz, 1H, H-7). ^{13}C NMR: 84.5 (C-2), 109.6, 113.7, 113.9, 120.6, 120.8, 122.6, 125.7, 125.9, 126.5, 126.9, 127.0, 128.0, 128.4, 128.7, 129.3, 134.2, 135.2, 141.3, 143.9, 144.9, 158.8, 160.8. MS: m/z (%) 434 (85, M^+), 357 (80), 191 (10), 169 (12), 141 (17), 132 (24), 113 (25), 99 (30), 85 (65), 71 (83), 57 (100). Exact mass for $C_{31}H_{18}ON_2$: 434.141913; found 434.141268.

4.5.3. 7-Dicyanomethylidene-2,2-diphenyl-2*H*-pyrano-[5,6-*c*]fluorene (10). Yield 53%. ^{1}H NMR: 6.41 (d, J=10 Hz, 1H, H-3), 6.71 (d, J=10 Hz, 1H, H-4), 6.95 (d, J=7.5 Hz, 1H, H-5), 7.23–7.50 (m, 12H), 7.96 (d, J=7.5 Hz, 1H, H-6), 8.01 (d, J=6.9 Hz, 1H, H-11), 8.37 (d, J=7.8 Hz, 1H, H-8). ^{13}C NMR: 84.0 (C-2), 113.68, 113.72, 120.8, 122.8, 124.4, 126.6, 126.8, 126.9, 127.6, 128.0, 128.2, 128.5, 132.6, 134.0, 134.9, 135.6, 141.1, 143.9, 148.3, 161.1. MS: m/z (%) 434 (100, M^+), 357 (75). Exact mass for $C_{31}H_{18}ON_2$: 434.141913; found 434.141933.

4.6. Reaction of pyranofluorenones (4–6) with CH_3MgI. General procedure

A solution of CH_3MgI in diethyl ether (2.0 ml, 2.0 mmol) was slowly added to a solution of pyranofluorenones **4–6** (0.259 mmol) in Et_2O (10 ml) under an argon atmosphere. After stirring overnight, the solution was treated with NH_4Cl, extracted with ethyl acetate, and the organic phase was dried over anhydrous Na_2SO_4. Solvent evaporation gave an orange oil, which was purified by column chromatography (hexane/ethyl acetate, 96:4).

4.6.1. 10-Hydroxy-10-methyl-2,2-diphenyl-2*H*-pyrano-[6,5-*b*]fluorene (11). Yield 85%. Mp 158–162°C. IR: 3434, 3079, 2964, 1633, 1428, 1367, 1299, 1247, 1091, 1002, 754, 700. ^{1}H NMR: 1.70 (s, 3H, CH_3) 1.90 (s, 1H, OH), 6.40 (d, J=9.9 Hz, 1H, H-3), 6.68 (d, J=9.9 Hz, 1H, H-4), 7.15 (s, 1H, H-5), 7.42–7.53 (m, 7H), 7.20–7.39 (m, 8H). ^{13}C NMR: 26.0 (CH_3), 79.3, 82.8 (C-2), 111.9, 117.9, 119.0, 121.4, 123.0, 123.4, 126.88, 126.93, 127.0, 127.47, 127.53, 128.09, 128.13, 128.78, 128.82, 131.8, 138.5, 144.6, 144.9, 149.4, 151.6, 153.0. MS: m/z (%) 402 (100, M^+), 387 (60), 325 (65), 310 (24), 308 (16), 191 (10), 165 (10). Exact mass for $C_{29}H_{22}O_2$: 402.161980; found 402.161665.

4.6.2. 6-Hydroxy-6-methyl-2,2-diphenyl-2*H*-pyrano[5,6-*b*]fluorene (12). Yield: 90%. Mp 78–80°C. IR: 3409, 3056, 2923, 1617, 1446, 1367, 1299, 1182, 991, 761, 730, 695. ^{1}H NMR: 1.70 (s, 3H, CH_3), 1.90 (s, 1H, OH), 6.20 (d, J=9.9 Hz, 1H, H-3), 6.67 (d, J=9.9 Hz, 1H, H-4), 7.19 (s, 1H) and 7.18 (s, 1H) (H-5 and H-11), 7.24–7.39 (m, 7H), 7.44–7.55 (m, 7H). ^{13}C NMR: 26.0 (CH_3), 79.0, 82.9 (C-2), 108.3, 120.0, 120.7, 121.3, 123.0, 123.7, 126.9, 127.5, 128.1, 128.4, 128.8, 138.3, 140.2, 142.6, 144.7, 144.9, 150.4, 153.5. MS: m/z (%) 402 (87, M^+), 387 (27), 384 (60), 325 (100), 307 (95), 191 (22), 165 (10). Exact mass for $C_{29}H_{22}O_2$: 402.161980; found 402.161322.

4.6.3. 7-Hydroxy-7-methyl-2,2-diphenyl-2*H*-pyrano[5,6-*c*]fluorene (13). Yield 82%. Mp 63–66°C. ^{1}H NMR: 1.71 (s, 3H, CH_3), 1.98 (s, 1H, OH), 6.20 (d, J=9.9 Hz, 1H, H-3), 6.68 (d, J=9.9 Hz, 1H, H-4), 6.99 (d, J=10 Hz, 1H), 7.08 (d, J=7.5 Hz, 1H, H-5), 7.22–7.42 (m, 8H), 7.48–7.60 (m, 5H), 8.10 (d, J=7.5 Hz, 1H). ^{13}C NMR: 26.1 (CH_3), 79.6, 83.3 (C-2), 115.7, 121.6, 122.8, 123.3, 123.8, 125.4, 126.6, 126.9, 127.3, 127.5, 127.6, 128.22, 128.24, 128.5, 129.1, 137.4, 145.0, 145.1, 148.1, 149.4, 152.0. MS: m/z (%) 402 (83, M^+), 387 (100), 384 (80), 325 (75), 307 (88), 191 (15), 165 (14). Exact mass for $C_{29}H_{22}O_2$: 402.161980; found 402.161978.

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