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On the photochromic activity of some diphenyl-3*H*-naphtho[2,1-*b*]pyran derivatives: Synthesis, NMR characterisation and spectrokinetic studies

Angelo Alberti [a], Yannick Teral [b], Gabriel Roubaud [b], Robert Faure [b], Mylène Campredon [b],*

[a] *CNR-ISOF, Area della Ricerca di Bologna, Via P. Gobetti 101, I-40129 Bologna, Italy*
[b] *UMR-CNRS 6263, Aix-Marseille Université, campus de St Jérôme, Service 512, F-13397 Marseille, Cedex 20, France*

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ABSTRACT

The synthesis, NMR and mass spectrometric characterisation of a several novel compounds of the naphthopyran family containing either halogen or phosphonate substituents are reported. All of the compounds exhibited photochromic properties in solution and their thermal bleaching after exposure to polychromatic light was monitored using UV–vis spectrophotometry. The bleaching of the merocyanines from these compounds involved two first-order processes, the first of these being more relevant than the second. The effects of substituents upon bleaching kinetics are discussed.

1. Introduction

The photochromic properties of 3*H*-naphthopyrans were first described in 1966 by Becker and Michl [1]. It was then shown that these properties originate from a reversible light induced opening of the pyran ring. The open forms are known as photo-merocyanines, may exist as different geometrical isomers, and are usually yellow or red in solution, their actual colour strongly depending on the substitution [2]. These compounds have been exploited in a wide range of applications that spans from the manufacturing of functional eyewear items to optical recording. While several aspects of the chemistry of organic photochromic compounds have been recently reviewed [3], we now report on the synthesis and photochromic properties of some new diphenyl-3*H*-naphthopyran derivatives.

2. Results and discussion

3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran (**1**), 3-phenyl-3-(2-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran (**2**), 3-phenyl-3-(3-trifluoromethylphenyl)-3*H*-naphtho[2,1-*b*]pyran (**3**), 3-phenyl-3-(4-trifluoromethylphenyl)-3*H*-naphtho[2,1-*b*]pyran (**4**), 3-phenyl-3-(4-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran (**5**), 3-phenyl-3-(4-bromophenyl)-3*H*-naphtho[2,1-*b*]pyran (**6**), 3,3-di(4-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran (**7**), 3,3-di(4-fluorophenyl)-8-bromo-3*H*-naphtho[2,1-*b*]pyran (**8**), 3,3-di(4-chlorophenyl)-8-bromo-3*H*-naphtho[2,1-*b*]pyran (**9**), 3,3-di(4-bromophenyl)-8-bromo-3*H*-naphtho[2,1-*b*]pyran (**10**), 3-phenyl-3-[4′-(diethoxyphosphoryl)phenyl]-3*H*-naphtho[2,1-*b*]pyran (**11**), 3,3-di(4-fluorophenyl)-8-diethoxyphosphoryl-3*H*-naphtho[2,1-*b*]pyran (**12**) were synthesised via the most convenient route [4], namely the condensation of a propargyl alcohol and a substituted naphthol in dichloromethane in the presence of TsOH (*para*-toluensulphonic acid). Compounds (**11**) and (**12**) were also obtained by the palladium-catalysed coupling of diethylphosphite with the respective bromonaphthopyrans **6** and **8** [5]. The overall synthetic routes to compounds (**1**–**12**) are outlined in Scheme 1a and b.

It is well documented that the photochromic activity of 3,3-disubstituted naphthopyrans is due to the light induced reversible opening of the pyran ring via cleavage of the sp^3 carbon–oxygen bond (see Fig. 1b) [3]. Accordingly, colourless toluene solutions of compounds **1**–**12** assumed a yellow colour upon UV irradiation, their UV–vis spectra changing drastically with the appearance of an absorption band in the visible region due to the open forms of **1**–**12**, the so called merocyanines, that are present in two main isomeric forms *trans*, *trans* and *trans*, *cis* (TT and TC). The λ_{max} observed for the different compounds under irradiation are collected in Table 1.

Some considerations can be made based on an examination of the measured values. It would thus appear that the presence of a fluorine atom in the *ortho* position of an aromatic ring induces

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* Corresponding author. Tel.: +334 91288900; fax: +334 42980870.
E-mail address: Mylene.Campredon@univmed.fr (M. Campredon).

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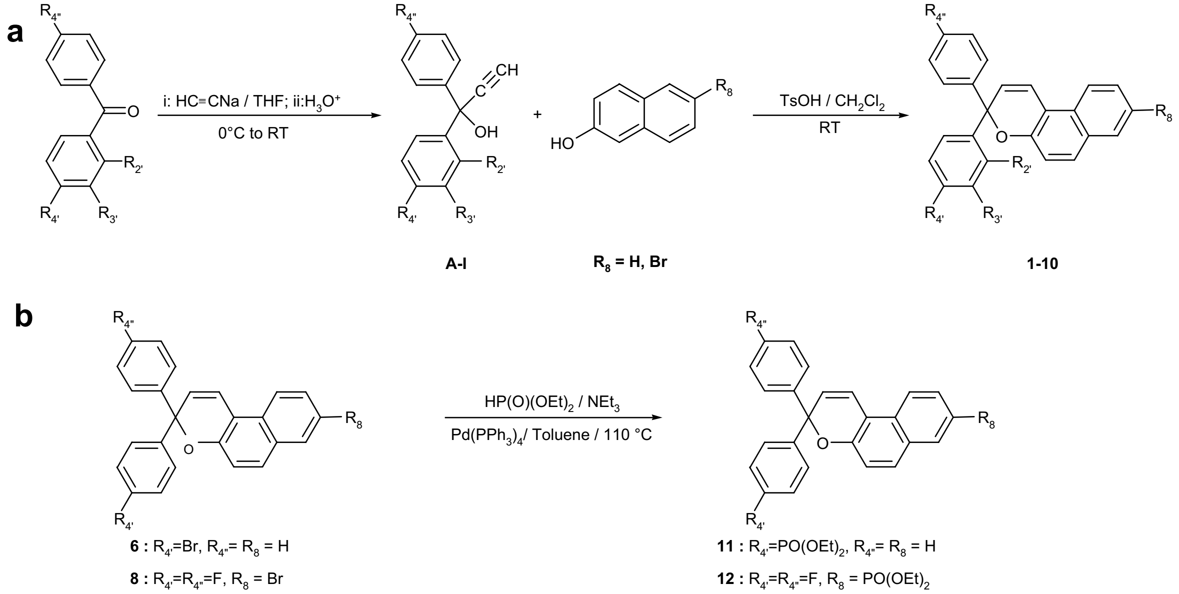


Scheme 1. Synthetic route to compounds **1**–**12**.

a blue shift of ca. 11 nm, whereas a *para*-fluorine atom only causes a modest 1 nm decrease of the absorption maximum wavelength. We tentatively attribute these different effects to the occurrence of hydrogen bonding between the *ortho* fluorine atom and a vinylic hydrogen (see **2** TC in Fig. 2). Such an interaction would disfavour the hydrogen bond between the same vinylic hydrogen and the carbonyl oxygen. The net effect of this diminished H bonding would be to facilitate deplanarisation of the chromophore by rotation about the C–C single bond of the dienone (merocyanine) system (see **1** TC in Fig. 2). Any reduction in the efficiency of conjugation would be concomitant with a decrease in the λ_{max} value. It should however be noted that the hypsochromic shift of the long wavelength band exhibited by the merocyanine from a similar 3-(2-fluorophenyl) naphtho[2,1-*b*]pyran with respect to the unsubstituted parent compound has been attributed to twisting of the substituted aromatic ring [6]. Fluorine hydrogen bonding is not available in the *para* derivative **5** for which only electronic (mesomeric and inductive) effects, if any, are possible. The introduction of an additional *para*-fluorine atom in the second ring has also no effect.

Likewise that of a *para*-fluorine, the presence of a *para*-bromine atom on a phenyl ring is irrelevant. On the other hand, it seems that the electron-withdrawing trifluoromethyl group induces a blue shift similar to that of the *ortho* fluorine atom, independently from its position in the aromatic ring. Quite surprisingly, in compound **11** the presence of a *para* diethoxyphosphoryl group, that exerts an electron-withdrawing effect similar to that of a trifluoromethyl group, does not result in a significant change of the λ_{max} value. Substitution in position 8 of the naphthalene moiety appears to be more effective and sensitive to the nature of the substituent. Thus, the diethoxyphosphoryl group in **12** produces a 10 nm blue shift whereas the bromine atom in **8** induces a 23 nm red shift of the absorption band. On the other hand, the presence of two chlorine or bromine atoms in the 4′ and 4″ *para* positions of the aromatic rings more than counterbalance the effect of the bromine atom in position 8, resulting in a blue shift of 5 and 7 nm for **9** and **10**, respectively.

As previously noted the photochromic properties of all the compounds investigated reflect the equilibrium shown in Fig. 1b. Under continuous irradiation a photostationary state is reached that represents the stabilization of the equilibrium between the closed and opened forms. The thermal kinetic constants of ring closure can be determined by monitoring the decrease in optical density at the appropriate λ_{max} for each individual compound (See

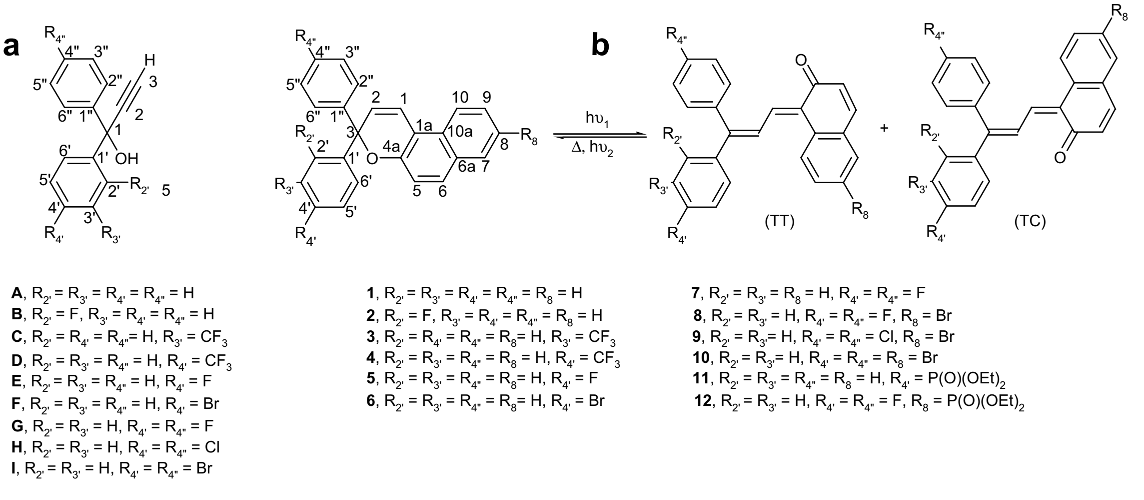


Fig. 1. (**a**) Numbering system for propargyl alcohols (**A**-**I**); (**b**) Photochromic equilibrium and numbering system for 3*H*-naphtho[2,1-*b*]pyran compounds (**1**–**12**).

Table 1

Spectroscopic data for compounds **1**–**12** measured in toluene at 293 K.

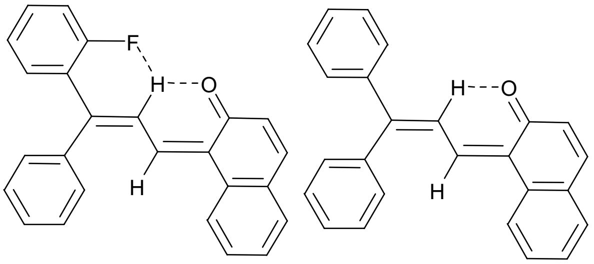
Compound	λ_{max} (nm)
1	432
2	421
3	420
4	421
5	431
6	432
7	430
8	455
9	427
10	425
11	433
12	422

Fig. 3). We found that the thermal bleaching curves for derivatives **1**–**7** could be fitted using the bi-exponential equation.

$$A_0(t) = a_1 e^{-k_1 t} + a_2 e^{-k_2 t} + \text{offset}$$

where k_1 is the first thermal bleaching rate constant, a_1 the amplitude of the first kinetic, k_2 the second thermal bleaching rate constant, a_2 the amplitude of the second kinetic, while A_0 and offset are the photostationary and residual optical densities, respectively. In all cases the first bleaching process, that has been previously attributed to ring closure of the TC isomer [7], proved much faster than the second, i.e. ring closure of the TT isomer, by at least an order of magnitude and accounted for most of the optical density.

The ring-closure rate constants are expected to be sensitive to the presence of substituents on the aromatic rings as well as to their nature. In particular, electron-donating substituents in the *para* position of a 3-phenyl ring should stabilize the open form bearing a partial positive charge on C3, possibly decreasing the bleaching rate, while electron-withdrawing substituents in the same position should exert an opposite, destabilizing effect leading to faster ring-closure rates. Indeed, in a pioneering work on the photodegradation of spiropyrans such a trend has been found to hold for a variety of compounds bearing electron-donating or electron-withdrawing substituents on either the indoline or the chromene moiety [8]. Actually, the k_1 values measured for compounds **1**–**7** do not show a univocal trend and seem to contradict expectations. Thus, the k_1 values for compounds **3** and **4** are both smaller than that measured for the unsubstituted derivative **1**, despite the presence of the CF_3 group that exerts a negative (i.e. electron-withdrawing) field effect. Also halogen has a negative field effect but at the same time they may exert a positive resonance effect, their overall action being a balance of the effects. The data in Table 2 indicate that the presence of a 4-bromine atom in **6** causes a decrease of the k_1 value intermediate to those observed for **3** and **4** with respect to **1**, while that of a 4-fluorine atom in **5** leads to a sharp increase of the bleaching rate constant, despite the fact that both substituents have a positive Hammett σ constant. The opposite effect promoted by the two halogens is substantiated by the k_1 value measured for the difluoro derivative **7** that is again larger than that found for **1**. Although the opposite effects exerted by a *para*-bromine and *para*-fluorine atom may be considered in line with the σ_p^+ values (positive for the former halogen and negative for the latter) the use of which might be preferable due to the presence of the partial positive charge on C3 [9], the extent of the increase of k_1 found for **5** remains unaccounted for.



TC 2 TC 1

Fig. 2. Some possible hydrogen-bonds in the *trans*, *cis* merocyanines from **1** to **2**.

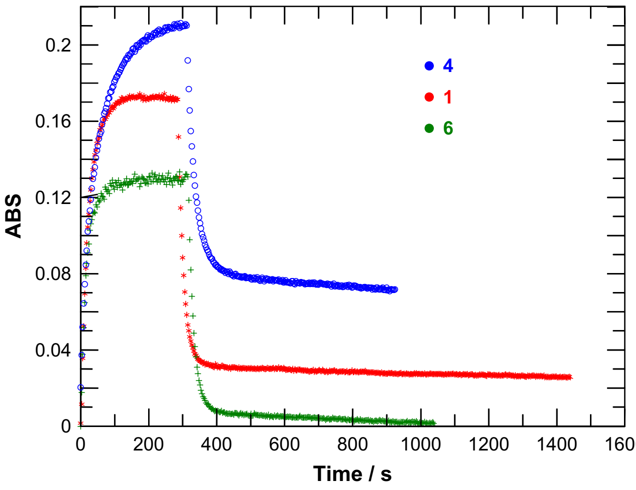


Fig. 3. Kinetic profiles of the irradiation of compounds **1**, **4** and **6**.

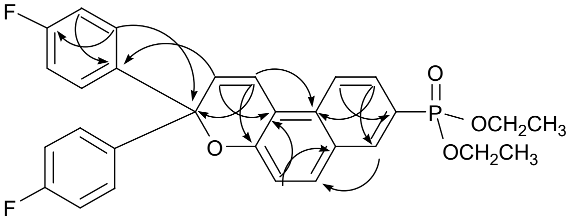
Table 2

Photostationary optical densities, bleaching rate constants for compounds **1**–**7** as measured at 293 K in toluene solutions.

Compound	A_0	$10^3 \times k_1$ (s^{-1})	a_1 (%)	$10^3 \times k_2$ (s^{-1})
1	0.17	62.0	81	0.2
2	0.22	47.8	70	0.3
3	0.15	54.1	80	0.3
4	0.21	38.8	69	0.2
5	0.14	176.2	85	0.4
6	0.13	49.3	88	0.2
7	0.16	75.1	85	0.2

The low k_1 value exhibited by compound **2** cannot be compared with those of **1** and **3**–**7**. Indeed, as already mentioned, in this derivative the position of the fluorine atom is such that it may interact with a vinylic hydrogen (see structure **2** TC in Fig. 2). As a result of hydrogen bonding, the merocyanine from **2** is likely to assume geometrical conformations that may be unfavourable for the ring closure.

Complete assignment of ^1H and ^{13}C resonances was performed by concerted application of homonuclear (*gs*-COSY), proton-detected (C, H) one-bond (*gs*-HMQC) and long-range (*gs*-HMBC) heteronuclear two-dimensional chemical shift correlation experiments. All the CH_n groups were unambiguously characterised from the analysis of long-range correlation responses over two and three bonds (^2J and ^3J couplings) using the *gs*-HMBC sequence. By way of illustration some significant HMBC correlations observed for compound **12** are shown in Scheme 2 (Arrows link a proton to a carbon.).



Scheme 2. Significant HMBC correlations observed for compound **12**.

3. Conclusions

Several novel photochromic naphthopyrans containing halogen, trifluoromethyl or phosphorus substituents were prepared. Halogen substitution on either the phenyl or the naphthopyran moieties of a number of photochromic compounds affects the visible spectra of the corresponding merocyanines as well as their decolouration rate constants. While the observed λ_{max} shifts can be reasonably accounted for, the bleaching rate constant variations are not in line with what was expected on the basis of a normal substituent effect. The introduction of a phosphorus or a fluoro atom as a molecular probe would be of interest for further study of the mechanistic aspects of the photochemical process.

4. Experimental

4.1. Materials

Compounds **1**–**12** were synthesised according to Scheme 1. All reagents were obtained from Aldrich and were used as supplied. Reaction solvents were pre-dried and distilled immediately prior to use: dichloromethane was distilled from phosphorous pentoxide and tetrahydrofuran (THF) was pre-dried over potassium hydroxide and distilled from sodium/benzophenone. Flash column chromatography was carried out using Merck 60 silica gel (0.063–0.200 nm), solvents were used as supplied.

The compounds were characterised by NMR, UV–vis and MS spectra.

4.2. Instrumentation

NMR spectra were recorded in $CDCl_3$ solutions at 300 K using a Bruker Avance DRX 500 spectrometer equipped with a Bruker CryoPlatform and 5 mm cryo TXI probe; the temperature of the probe and preamplifier was 30 K. Chemical shifts were referenced to $CDCl_3$: $\delta_H = 7.25$ ppm, $\delta_C = 77.1$ ppm [10]. For two-dimensional experiments Bruker microprograms using gradient selection (*gs*) were applied. The *gs*-COSY spectra [11] were obtained with an F_2 spectral width of 10 ppm in 2 K data points for 256 t_1 increments and sine-bell windows in both dimensions. The *gs*-HMQC spectra [12] resulted from 256 × 1024 data matrix size with 2–16 scans per t_1 depending on the sample concentration, an inter-pulse delay of 3.2 ms and a 5:3:4 gradient combination. The *gs*-HMBC spectra [13] were measured using a pulse sequence optimised on ^3J aromatic couplings (inter-pulse delay for the evolution of long-range couplings: 50 ms), and the same gradient ratio as described for the HMQC experiments. In this way, direct responses (^1J couplings) were not completely removed.

The visible absorption spectra of photomerocyanines were recorded for 10^{-4} M photochromic solutions in spectroscopic grade toluene in 10 mm quartz cells using a Beckman DU 7500 diode array spectrometer [14]. Samples were irradiated with a Xe lamp at 293 K and 400 W m^2.

The photochromic compounds were dissolved in toluene (sample concentration: 10^{-4} M). Irradiation was derived from an ozone-free Oriel xenon 150 W lamp equipped with diaphragm and water filter, which removed most of the infrared radiation. Polychromatic light intensity was determined by an Oriel quantum photoradiometer. The quartz analysis cell was enclosed in a thermostated copper block placed inside the sample chamber of the spectrophotometer. The temperature was controlled with a Bioblock Scientific thermocouple. The cell had an optical path length of 1 cm. The aerated solutions were stirred continuously using a mechanical stirrer. Spectra of photostationary mixtures were measured and the decay of the open form was followed at the maximum absorption wavelength, at $T = 293$ K, flux = 220 W m^2.

Mass spectrometric analysis was performed with a Hewlett Packard 5987 mass spectrometer operating in electron impact (70 eV), using direct insertion probe interface. For analysis direct probe temperature was programmed from 323 to 473 K at 30 K min^{-1} and the ion source was held at 473 K.

Melting points were measured using an Electrothermal 9100 apparatus.

4.3. Synthetic procedures for the preparation of propargyl alcohol

Propargyl alcohols **A**-**I** were prepared as outlined in Scheme 1. A solution of the appropriate ketone (11.0 mmol) in THF (100 mL) was added dropwise to a solution of sodium acetylide (solution in xylene, 30 mL, 10 eq. – note: corrosive and flammable) in freshly distilled THF (250 mL) at 263 K. On completion of addition, the mixture was allowed to warm to room temperature. The reaction mixture was poured into ice/water and the two phases separated. The organic phase was washed with saturated aqueous ammonium chloride solution (100 mL). The aqueous phase was further extracted with ether (3 × 100 mL) and the combined organic extracts were dried (Na_2SO_4), filtered and concentrated under vacuum. The xylenes were removed by azeotropic distillation of a methanol/xylene mixture. Chromatography (silica/0–5% ethyl ether in pentane) afforded the alcohol **A** as a white powder (80% yield), while alcohols **B**-**I** were obtained in good yields (70–95%) as yellow oils.

4.3.1. 1,1-Diphenyl-prop-2-propyn-1-ol, **A** [15]

From benzophenone as a white solid (80%), m.p. 78.1–79.2 °C.

4.3.2. 1-(2′-Fluorophenyl)-1-phenyl-2-propyn-1-ol, **B** [16]

From 2-fluorobenzophenone as a pale yellow oil (70%), ^{1}H NMR (500.13 MHz, $CDCl_3$), δ 2.85 (1H, s, *H*-3), 3.02 (1H, s, O–H), 7.02 (1H, m, *H*-3′), 7.13 (1H, m, *H*-5′), 7.30 (5H, m, *H*-2″, *H*-3″, *H*-4″, *H*-5″ and *H*-6″), 7.58 (1H, m, *H*-4′), 7.75 (1H, m, *H*-6′), ^{13}C NMR (125,8 MHz, $CDCl_3$) δ 72.4 (1C, s, C-1), 75.8 (1C, s, C-3), 85.1 (1C, s, C-2), 116.7 (1C, d, $^2J_{C3'-F} = 21.6$, C-3′), 123.9 (1C, d, $^4J_{C4'-F} = 3.6$, C-5′), 126.2 (2C, s, C-2″ and 6″), 127.8 (1C, d, $^4J_{C6'-F} = 2.6$, C-6′), 128.7 (1C, s, C-4″), 128.8 (2C, s, C-3″ and 5″), 130.4 (1C, d, $^3J_{C4'-F} = 8.4$, C-4′), 130.8 (1C, d, $^2J_{C1'-F} = 1.4$, C-1′),143.1 (1C, s, C-1″),160.1 (1C, d, $^1J_{C-F} = 249.4$, C-2′).

4.3.3. 1-(3′-Trifluoromethylphenyl)-1-phenyl-2-propyn-1-ol, **C**

From 4-trifluoromethylbenzophenone as a yellow oil (90%), ^{1}H NMR (250 MHz, $CDCl_3$), δ 2.70 (1H, s, H *H*-3), 2.85 (1H, s, O–H), 6.80–7.80 (9H, m, H *H*-2′, *H*-4′, *H*-5′, *H*-6′, *H*-2″, *H*-3″, *H*-4″, *H*-5″ and *H*-6″), ^{13}C NMR (62,9 MHz, $CDCl_3$) δ 74.1 (1C, s, C-1), 76.5 (1C, s, C-3), 85.9 (1C, s, C-2), 122.8 (1C, s, C-2′), 124.9 (1C, s, C-4′), 126.2 (2C, s, C-2″ and 6″), 128.5 (1C, s, C-6′), 128.8 (2C, s, C-3″ and 5″), 129.0 (1C, s, C-4″), 129.8 (1C, C-5′), 143.9 (1C, s, C-1″), 145.7 (1C, s, C-1′).

4.3.4. 1-(4′-Trifluoromethylphenyl)-1-phenyl-2-propyn-1-ol, **D**

From 4-trifluoromethylbenzophenone as a yellow oil (95%), ^{1}H NMR (250 MHz, $CDCl_3$), δ 2.86 (1H, s, *H*-3), 3.03 (1H, s, O–H), 7.10–7.31 (3*H*, m), 7.32–7.37 (3*H*, m), 7.42 (1H, t,), 7.62 (1H, d), 7.97 (1H, d). ^{13}C NMR (62,9 MHz, $CDCl_3$) δ 74.3 (1C, s, C-1), 76.6 (1C, s, C-3), 85.6 (1C, s, C-2), 126.2 (2C, s, C-2″ and 6″), 127.2–128.4 m, 131.5 (1C, s, C-4″), 141.4 (1C, s, C-1″), 144.1 (1C, s, C-1′).

4.3.5. 1-(4′-Fluorophenyl)-1-phenyl-2-propyn-1-ol, **E** [17]

From 4-fluorobenzophenone as a yellow oil (80%).

4.3.6. 1-(4′-Bromophenyl)-1-phenyl-2-propyn-1-ol, **F**

From 4-bromobenzophenone as a yellow oil (77%), ^{1}H NMR (250 MHz, $CDCl_3$), δ 2.90 (1H, s, *H*-3), 7.29–7.61 (10H, m). ^{13}C NMR (62,9 MHz, $CDCl_3$) δ_C: 74.0 (1C, s, C-1), 76.1 (1C, s, C-3), 86.5 (1C, s, C-2), 112.1 (1C, s, C-4′), 126.0 (2C, s, C-2″ and 6″), 127.9 (2C, s, C-3″ and 5″), 128.3 (1C, s, C-4″), 128.6 (2C, s, C-2′ and 6′), 131.5 (2C, s, C-3′ and 5′), 143.7 (1C, s, C-1′), 144.1 (1C, s, C-1″).

4.3.7. 1,1-Di(4′-fluorophenyl)-2-propyn-1-ol, ***G*** *[17]*

From 4,4′-difluorobenzophenone as a yellow oil (75%).

4.3.8. 1,1-Di(4′-chlorophenyl)-2-propyn-1-ol, ***H***

From 4,4′-dichlorobenzophenone as a yellow oil (92%), ^{1}H NMR (500.13 MHz, $CDCl_3$), δ 2.90 (1H, s, *H*-3), 2.94 (1H, s, OH) 7.30 (4H, dt, $^{3}J_{\mathrm{H-H}} = 8.7$ Hz, *H*-3′, *H*-3″, *H*-5′ and *H*-5″), 7.51 (4H, dt, $^{3}J_{\mathrm{H-H}} = 8.5$, *H*-2′, *H*-2″, *H*-6′ and *H*-6″). ^{13}C NMR (125,8 MHz, $CDCl_3$) δ 73.5 (1C, s, C-1), 76.4 (1C, s, C-3), 83.5 (1C, s, C-2), 127.5 (4C, s, C-3′, C-3″, C-5′ and C-5″), 128.7 (4C, s, C-2′, C-2″, C-6′ and C-6″), 134.1 (2C, s, C-4′ and C-4″), 162.4 (2C, s, C-1′ and C-1″).

4.3.9. 1,1-Di(4′-bromophenyl)-2-propyn-1-ol, ***I***

From 4,4′-dibromobenzophenone as a yellow oil (81%), ^{1}H NMR (500.13 MHz, $CDCl_3$), δ 2.82 (1H, s, *H*-3), 2.90 (1H, s, OH) 7.45 (8H, m, H-2′, H-2″, H-3′, H-3″, H-5′, H-5″, H-6′ and H-6″). ^{13}C NMR (125,8 MHz, $CDCl_3$) δ 73.6 (1C, s, C-1), 76.4 (1C, s, C-3), 83.4 (1C, s, C-2), 122.4 (2C, s, C-4′, C-4″), 127.8 (4C, s, C-3′, C-3″, C-5′, C-5″), 131.6 (4C, s, C-2′, C-2″, C-6′, C-6″), 143.1 (2C, s, C-1′, C-1″).

4.4. Synthetic procedures for the preparation of naphthopyrans

3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyrans from **1** to **10** were prepared as outlined in Scheme 1a. The propargyl alcohol (7 mmol) was dissolved in DCM (20 mL) at 298 K and then a catalytic amount of TsOH was added. After 10 min a solution of substituted 2-naphthol (10 mmol) in DCM (20 mL) was added dropwise. After 2 h, the solvent was evaporated and the organic residue was purified by flash chromatography on silica with pentane-diethyl ether as eluant (with a gradient from 0 to 5% Et_2O). After evaporation of the eluate and pentane recrystallisation, the pure naphthopyran was obtained as a "white-yellow" powder.

*4.4.1. Synthesis of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (**1**) [18]*

From **A** and 2-naphthol as white powder (62%) after elution from silica with a gradient from 0 to 5% Et_2O in pentane and recrystallisation from pentane, m.p. 158–159 °C.

*4.4.2. Synthesis of 3-phenyl-3-(2-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran (**2**) [17]*

From **B** and 2-naphthol as white powder (51%) after elution from silica with a gradient from 0 to 5% Et_2O in pentane and recrystallisation from pentane, m.p. 131–132 °C.

*4.4.3. Synthesis of 3-phenyl-3-(3-trifluoromethylphenyl)-3*H*-naphtho[2,1-*b*]pyran (**3**) [16]*

From **C** and 2-naphthol as white powder (43%) after elution from silica with a gradient from 0 to 5% Et_2O in pentane and recrystallisation from pentane, m.p. 119–120 °C.

Compound **3**, ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.53 (1H, d, $^{3}J_{\mathrm{H1-H2}} = 10.1$, *H*-2), 7.30–7.41 (5H, m, H-5, H-6′, H-3″, H-4″, H-5″), 7.42 (1H, ddd, $^{3}J_{\mathrm{H8-H7}} = {}^{3}J_{\mathrm{H8-H9}} = 7.0$, $^{3}J_{\mathrm{H8-H10}} = 1.2$, *H*-8), 7.52 (1H, d, $^{3}J_{\mathrm{H1-H2}} = 10.1$, *H*-1), 7.54–7.60 (3H, m, H-5′, H-2″, H-6″), 7.79–7.88 (3H, m, *H*-6, *H*-7, *H*-4′), 7.64 (1H, dd, $^{3}J_{\mathrm{H9-H10}} = 8.6$, $^{3}J_{\mathrm{H9-H8}} = 7.0$, *H*-9), 7.93 (1H, *H*-2′), 8.07 (1H, dd, $^{3}J_{\mathrm{H10-H9}} = 8.6$, $^{3}J_{\mathrm{H10-H8}} = 1.2$, *H*-10). ^{13}C NMR (75,5 MHz, $CDCl_3$): δ 81.5 (1C, s, *C*-3), 112.8 (1C, q, $^{3}J_{\mathrm{C2'-F3}} = 4.0$, *C*-2′), 114.0 (1C, s, *C*-1a), 117.9 (1C, s, *C*-5), 120.3 (1C, s, *C*-1), 121.3 (1C, s, *C*-1), 124.0 (1C, s, *C*-8), 124.1 (1C, q, $^{1}J_{\mathrm{C-F3}} = 272.0$, CF_3), 124.2 (1C, q, $^{3}J_{\mathrm{C-F3}} = 4.0$, *C*-4′), 126.4 (1C, s, *C*-9), 126.9 (2C, s, *C*-2″, *C*-6″), 127.5 (1C, s, *C*-2), 127.8 (1C, s, *C*-4″), 128.2 (2C, s, *C*-3″, *C*-5″), 128.3 (1C, s, *C*-7), 128.5 (1C, q, $^{2}J_{\mathrm{C3'-F3}} = 21.8$, *C*-3′), 129.1 (1C, s, *C*-6′), 129.3 (1C, q, *C*-10a), 129.4 (1C, s, *C*-6a), 130.0 (1C, s, *C*-6), 130.5 (1C, q, $^{4}J_{\mathrm{C5'-F3}} = 2.0$, *C*-5′), 143.9 (1C, s, *C*-1″), 146.1 (1C, s, *C*-1′), 149.9 (1C, s, *C*-4a).

MS (70 eV) *m*/*z* (%): 402(76) M^+, 383(8), 325(93), 257 (100).

*4.4.4. Synthesis of 3-phenyl-3-(4-trifluoromethylphenyl)-3*H*-naphtho[2,1-*b*]pyran (**4**)*

From **D** and 2-naphthol as white powder (38%) after elution from silica with a gradient from 0 to 5% Et_2O in pentane and recrystallisation from pentane, m.p. 133–134 °C.

Compound **4**, ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 6.26 (1H, d, $^{3}J_{\mathrm{H1-H2}} = 10.0$, *H*-2), 7.16 (1H, d, $^{3}J_{\mathrm{H5-H6}} = 8.8$, *H*-5), 7.28 (1H, dd, $^{3}J_{\mathrm{H3''-H4''}} = 7.2$, $^{3}J_{\mathrm{H4''-H2''}} = 1.3$, *H*-4″), 7.33 (1H, dd, $^{3}J_{\mathrm{H7-H8}} = 8.1$, $^{3}J_{\mathrm{H8-H9}} = 7.1$, *H*-8), 7.36 (1H, d, $^{3}J_{\mathrm{H1-H2}} = 10.0$, *H*-1), 7.36 (2H, dd, $^{3}J_{\mathrm{H2''-H3''}} = 8.4$, $^{3}J_{\mathrm{H3''-H4''}} = 7.2$, *H*-3″), 7.48 (2H, dd, $^{3}J_{\mathrm{H2''-H3''}} = 8.4$, $^{3}J_{\mathrm{H2''-H4''}} = 1.3$, *H*-2″), 7.50 (1H, ddd, $^{3}J_{\mathrm{H8-H9}} = 7.1$, $^{3}J_{\mathrm{H9-H10}} = 8.5$, $^{3}J_{\mathrm{H7-H9}} = 1.1$, *H*-9), 7.57 (2H, d, $^{3}J_{\mathrm{H3'-H2'}} = 8.5$, *H*-3′), 7.65 (2H, d, $^{3}J_{\mathrm{H2'-H3'}} = 8.5$, *H*-2′), 7.70 (1H, d, $^{3}J_{\mathrm{H5-H6}} = 8.8$, *H*-6), 7.74 (1H, dd, $^{3}J_{\mathrm{H7-H8}} = 8.1$, $^{3}J_{\mathrm{H7-H9}} = 1.1$, *H*-7), 7.98 (1H, d, $^{3}J_{\mathrm{H9-H10}} = 8.5$, *H*-10). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 82.5 (1C, s, *C*-3), 114.4 (1C, s, *C*-1a), 118.5 (1C, s, *C*-5), 120.7 (1C, s, *C*-1), 121.7 (1C, s, *C*-10), 124.2 (1C, s, *C*-8), 124.5 (1C, q, $^{3}J_{\mathrm{C-F3}} = 272.6$, CF_3), 125.5 (2C, q, $^{3}J_{\mathrm{C-F3}} = 3.7$, *C*-3′ and *C*-5′), 127.3 (1C, s, *C*-2), 127.2 (1C, s, *C*-9), 127.3 (2C, s, *C*-2″ and *C*-6″), 127.7 (2C, s, *C*-2′ and *C*-6′), 128.3 (1C, s, *C*-4″), 128.7 (2C, s, *C*-3″ and *C*-5″), 128.9 (1C, s, *C*-7), 129.9 (1C, s, *C*-6a), 130.1 (1C, q, $^{2}J_{\mathrm{C4'-F3}} = 32.7$, *C*-4′), 130.2 (1C, s, *C*-10a), 130.6 (1C, s, *C*-6), 144.5 (1C, s, *C*-1″), 149.2 (1C, s, *C*-1′), 150.7 (1C, s, *C*-4a).

MS (70 eV) *m*/*z* (%): 402(76) M^+, 383(8), 325(93), 257 (100).

*4.4.5. Synthesis of 3-phenyl-3-(4-fluorophenyl)- 3*H*-naphtho[2,1-*b*]pyran (**5**)*

From **E** and 2-naphthol as white powder (60%) after elution from silica with a gradient from 0 to 5% Et_2O in pentane and recrystallisation from pentane, m.p. 118–120 °C. [17].

*4.4.6. Synthesis of 3-phenyl-3-(4-bromophenyl)-3*H*-naphtho[2,1-*b*]pyran (**6**)*

From **F** and 2-naphthol as white powder (62%) after elution from silica with a gradient from 0 to 5% Et_2O in pentane and recrystallisation from pentane, m.p. 183–184 °C.

Compound **6**, ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 6.35 (1H, d, $^{3}J_{\mathrm{H1-H2}} = 9.8$, *H*-2), 7.29 (1H, d, $^{3}J_{\mathrm{H5-H6}} = 8.0$, *H*-5), 7.40–7.65 (12H, m), 7.75 (1H, d, $^{3}J_{\mathrm{H6-H5}} = 8.0$, *H*-6), 7.85 (1H, d, $^{3}J_{\mathrm{H7-H8}} = 7.1$, *H*-7), 8.2 (1H, d, $^{3}J_{\mathrm{H9-H10}} = 8.5$, *H*-10). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 82.3 (1C, s, *C*-3), 114.2 (1C, s, *C*-1a), 118.4 (1C, s, *C*-5), 120.2 (1C, s, *C*-4′), 121.5 (1C, s, *C*-1), 121.9 (1C, s, *C*-10), 127.0 (2C, s, *C*-2″ and *C*-6″), 127.1 (1C, s, *C*-4″), 127.4 (1C, s, *C*-2), 127.9 (1C, s, *C*-9), 128.5 (2C, s, *C*-3″ and *C*-5″), 128.8 (1C, s, *C*-7), 129.0 (1C, s, *C*-8), 129.1 (1C, s, *C*-2′), 129.6 (1C, s, *C*-6a), 129.9 (1C, s, *C*-10a), 130.3 (1C, s, *C*-6), 131.4 (2C, s, *C*-3′ and *C*-5′), 144.1 (1C, s, *C*-1′), 144.6 (1C, s, *C*-1″), 150.5 (1C, s, *C*-4a).

MS (70 eV) *m*/*z* (%): 414; 412 (72) M^+, 337; 335 (10), 325(91), 257 (100).

*4.4.7. Synthesis of 3,3-di(4-fluorophenyl)-3*H*-naphtho[2,1-*b*]pyran (**7**) [18,19]*

From **G** and 2-naphthol as white powder (53%) after elution from silica with a gradient from 0 to 5% Et_2O in pentane and recrystallisation from pentane, m.p. 124–125 °C.

MS (70 eV) *m*/*z* (%): 370 (37), 275 (100), 244 (13), 227 (15), 201 (17).

*4.4.8. Synthesis of 3,3-di(4-fluorophenyl)-8-bromo-3*H*-naphtho[2,1-*b*]pyran (**8**)*

From **G** and 6-bromo-2-naphthol as white powder (68%) after elution from silica with a gradient from 0 to 5% Et_2O in pentane and recrystallisation from pentane, m.p. 170–171 °C.

Compound **8**, ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 6.05 (1H, d, $^{3}J_{\mathrm{H1-H2}} = 10.2$, *H*-2), 6.75 (4H, Dd, $^{3}J_{\mathrm{H2'-H3'}} = 9.3$, $^{3}J_{\mathrm{H3'-F}} = 8.8$, *H*-3′), 6.96 (1H, d, $^{3}J_{\mathrm{H5-H6}} = 8.0$, *H*-5), 7.10 (1H, d, $^{3}J_{\mathrm{H1-H2}} = 10.2$, *H*-1), 7.20 (4H, m, *H*-2′), 7.35 (1H, d, $^{3}J_{\mathrm{H9-H10}} = 8.9$, *H*-9), 7.40 (1H, d, $^{3}J_{\mathrm{H6-H5}} = 8.0$, H-6), 7.60 (1H, d, $^{3}J_{\mathrm{H9-H10}} = 8.9$, *H*-10), 7.61 (1H, s, *H*-7). ^{13}C NMR

(125.8 MHz, $CDCl_3$): δ 82.2 (1C, s, *C*-3), 114.4 (1C, s, *C*-8), 115.4 (4C, d, $^{2}J_{C3'-F} = 21.6$, *C*-3′), 117.8 (1C, s, *C*-1a), 119.5 (1C, s, *C*-5), 119.8 (1C, s, *C*-8), 123.4 (1C, s, *C*-10), 128.5 (1C, s, *C*-9), 129.0 (1C, s, *C*-6a), 129.1 (4C, d, $^{3}J_{C2'-F} = 8.4$, *C*-2′), 119.5 (1C, s, *C*-5), 129.2 (1C, s, *C*-2), 130.3 (1C, s, *C*-7), 130.7 (1C, s, *C*-6), 130.8 (1C, s, *C*-10a), 140.5 (2C, d, $^{4}J_{C4'-F} = 3.1$, *C*-1′ and *C*-1″), 150.7 (1C, s, *C*-4a), 162.5 (2C, d, $^{1}J_{C4'-F} = 247.2$, *C*-4′ and *C*-4″).

MS (70 eV) *m*/*z* (%): 302(61) M^+, 283(4), 225(100).

4.4.9. *Synthesis of 3,3-di(4-chlorophenyl)-8-bromo-3*H-*naphtho[2,1-*b*]-pyran (**9**)*

From **H** and 6-bromo-2-naphthol as white powder (11%) after elution from silica with a gradient from 0 to 5% Et_2O in pentane and recrystallisation from pentane, m.p. 150–151 °C.

Compound **9**, ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 6.17 (1H, d, $^{3}J_{H2-H1} = 10.2$, *H*-2), 7.16 (1H, d, $^{3}J_{H5-H6} = 8.8$, *H*-5), 7.26 (1H, d, $^{3}J_{H1-H2} = 10.2$, *H*-1), 7.28 (4H, m, *H*-2′, *H*-2″, *H*-6′ and *H*-6″), 7.37 (4H, m, *H*-3′, *H*-3″, *H*-5′ and *H*-5″), 7.53 (1H, Dd, $^{3}J_{H9-H10} = 8.9$, $^{3}J_{H9-H7} = 2.0$, *H*-9), 7.57 (1H, d, $^{3}J_{H6-H5} = 8.8$, H-6), 7.80 (1H, d, $^{3}J_{H10-H9} = 8.9$, *H*-10), 7.86 (1H, d, $^{4}J_{H7-H9} = 2.0$, *H*-7). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 81.9 (1C, *C*-3), 114.2 (1C, *C*-1a), 117.1 (1C, *C*-8), 119.3 (1C, s, *C*-5), 119.9 (1C, *C*-1), 123.2 (1C, *C*-10), 127.3 (1C, *C*-2), 128.3 (1C, *C*-6a), 128.4 (4C, *C*-3′, *C*-5′, *C*-3″ and *C*-5″), 128.5 (4C, *C*-2′, *C*-6′, *C*-2″ and *C*-6″), 129.3 (1C, *C*-9), 130.1 (1C, *C*-7), 130.5 (1C, *C*-6), 130.7 (1C, *C*-10a), 133.9 (2C, *C*-4′ and *C*-4″), 142.7 (1C, *C*-4a), 150.4 (2C, *C*-1′ and *C*-1″).

4.4.10. *Synthesis of 3,3-di(4-bromophenyl)-8-bromo-3*H-*naphtho[2,1-*b*]pyran (**10**)*

From **I** and 6-bromo-2-naphthol as white powder (10%) after elution from silica with a gradient from 0 to 5% Et_2O in pentane and recrystallisation from pentane, m.p. 152–153.5 °C.

Compound **10**, ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 6.27 (1H, d, $^{3}J_{H2-H1} = 9.9$, *H*-2), 7.22 (1H, d, $^{3}J_{H5-H6} = 8.8$, *H*-5), 7.32 (1H, d, $^{3}J_{H1-H2} = 9.9$, *H*-1), 7.39 (4H, m, *H*-2′, *H*-2″, *H*-6′ and *H*-6″), 7.51 (1H, d, $^{3}J_{H9-H10} = 8.9$, *H*-9) 7.55 (1H, d, $^{3}J_{H6-H5} = 8.8$, *H*-6), 7.65 (4H, m, *H*-3′, *H*-3″, *H*-5′ and *H*-5″), 7.8 (1H, d, $^{3}J_{H10-H9} = 8.9$, *H*-10), 7.85 (1H, s, *H*-7). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 82.5 (1C, s, *C*-3), 114.2 (1C, s, *C*-1a), 117.4 (1C, s, *C*-8), 119.2 (1C, s, *C*-5), 119.5 (1C, s, *C*-1), 120.2 (2C, s, *C*-4′ and *C*-4″), 123.2 (1C, s, *C*-10), 127.1 (4C, s, *C*-3′, *C*-5′, *C*-3″ and *C*-5″), 127.7 (1C, s, *C*-2), 128.4 (1C, s, *C*-6a), 128.9 (1C, s, *C*-9), 129.9 (1C, s, *C*-7), 130.4 (1C, s, *C*-6), 130.6 (1C, s, *C*-10a), 131.5 (4C, s, *C*-2′ *C*-6′, *C*-2″ and *C*-6″), 144.1 (2C, s, *C*-1′ and *C*-1″), 150.8 (1C, s, *C*-4a).

4.5. *Synthetic procedures for the phosphorylation of naphthopyrans **6** and **8***

Compounds **11** and **12** were prepared as outlined in Scheme 1, respectively, from **6** to **8**.

A solution of tetrakis(triphenylphosphine)palladium(0) (0.18 mmol–0.2 g) and *o*-diethyl phosphite (0.5 mL) in 0.5 mL of triethylamine was gently added under an atmosphere of nitrogen to the bromo compound (0.9 g) in anhydrous toluene at room temperature. The mixture was then heated at reflux for 2 h. The reaction mixture was subsequently hydrolysed and filtered. The aqueous phase was further extracted with diethyl ether. The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated under vacuum. The product was purified by chromatography DCM/Et_2O (75/25) to afford, after evaporation of the eluent and pentane recrystallisation, compounds (**11**–**12**) as white powders.

4.5.1. *Synthesis of 3-phenyl-3-[4′-(diethoxyphosphoryl)phenyl]-3*H-*naphtho[2,1-*b*]pyran (**11**) [20]*

From 3-phenyl-3-(4-bromophenyl)-3*H*-naphtho[2,1-*b*]pyran (**6**) as a white powder (25%) after elution from silica with DCM/Et_2O (75/25) and recrystallisation from pentane, m.p. 102–103 °C.

Compound **11**, ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 1.29(6H, td, $^{3}J_{Hb-Ha} = 7.1$, $^{4}J_{Hb-P} = 1.9$, CH_3), 4.04 (4H, m, CH_2), 6.24 (1H, d, $^{3}J_{H2-H1} = 10.9$, *H*-2), 7.19 (1H, d, $^{3}J_{H5-H6} = 8.8$, *H*-5), 7.24 (1H, m, *H*-4″) 7.31 (3H, m, $^{3}J_{H5-H6} = 8.8$, *H*-3″, *H*-5″ and *H*-8), 7.33 (1H, d, $^{3}J_{H1-H2} = 10.9$, *H*-1), 7.45 (3H, m, *H*-2″, *H*-6″ and *H*-9), 5.59(2H, dd, $^{3}J_{H2'-H3'} = 8.2$, $^{4}J_{H2'-P} = 3.8$, *H*-2′ and *H*-6′), 7.66 (1H, d, $^{3}J_{H6-H5} = 8.8$, *H*-6), 7.71 (1H, d, $^{3}J_{H7-H8} = 8.8$, *H*-7), 7.74 (2H, dd, $^{3}J_{H3'-P} = 13.0$, $^{3}J_{H3'-H2'} = 8.2$, *H*-3′ and *H*-5′), 7.94 (1H, d, $^{3}J_{H10-H9} = 8.5$, *H*-10), ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 15.9 (2C, d, $^{3}J_{C-P} = 6.4$, CH_3), 62.2 (2C, d, $^{2}J_{C-P} = 5.3$, CH_2), 82.3 (1C, s, *C*-3), 114.1 (1C, s, *C*-1a), 118.3 (1C, s, *C*-5), 120.2 (1C, s, *C*-1), 121.4 (1C, s, *C*-10), 123.9 (1C, s, *C*-8),126.7 (1C, s, *C*-9), 127.0 (1C, d, $^{3}J_{C2'-P} = 14.8$, *C*-2′), 127.1 (3C, s, *C*-2, 2″ and 6″), 127.5 (1C, s, $^{1}J_{C4'-P} = 189.0$, *C*-4′), 127.9 (1C, s, *C*-4″), 128.3 (1C, s, *C*-3″), 128.6 (1C, s, *C*-7), 129.5 (1C, s, *C*-6a), 129.8 (1C, s, *C*-10a), 130.2 (1C, s, *C*-6), 131.7 (2C, d, $^{2}J_{C3'-P} = 10.3$, *C*-3′ and *C*-5′), 144.2 (1C, s, *C*-1″), 149.4 (1C, s, *C*-1′), 150.4 (1C, s, *C*-4a).

4.5.2. *Synthesis of 3,3-di(4-fluorophenyl)-8-diethoxyphosphoryl-3*H-*naphtho[2,1-*b*]pyran (**12**) [18]*

From 3,3-di(4-fluorophenyl)-8-bromo-3*H*-naphtho[2,1-*b*]pyran (**8**) as a white powder (60%) after elution from silica with DCM/Et_2O (75/25) and recrystallisation from pentane, m.p. 166–167 °C.

Compound **12**, ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 1.29(6H, td, $^{3}J_{Hb-Ha} = 7.1$, $^{4}J_{Hb-P} = 1.9$, CH_3), 4.04 (4H, m, CH_2), 6.28 (1H, d, $^{3}J_{H2-H1} = 10.0$, *H*-2), 7.13 (4H, dd, $^{3}J_{H2'-H3'} = 9.3$, $^{3}J_{H3'-F} = 8.8$, *H*-3′, *H*-3″, *H*-5′ and *H*-5″), 7.25 (1H, d, $^{3}J_{H5-H6} = 8.7$, *H*-5), 7.28 (1H, d, $^{3}J_{H1-H2} = 10.0$, *H*-1), 7.59 (4H, m, *H*-2′, *H*-2″, *H*-6′ and *H*-6″), 7.72 (2H, m, *H*-6 and *H*-9), 8.00 (1H, dd, $^{3}J_{H10-H9} = 8.7$, $^{4}J_{H10-P} = 3.8$, *H*-10), 8.26 (1H, dd, $^{3}J_{H7-p} = 15.2$, $J_{H7-H9} = 1.2$, *H*-7). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 16.41 (2C, d, $^{3}J_{P-C} = 6.5$ Hz, CH_3), 62.16 (2C, d, $^{2}J_{P-C} = 5.0$ Hz, CH_2), 83.01 (1C, s, *C*-3), 104.21 (1C, d, $^{2}J_{P-C} = 12$ Hz, *C*-10), 114.05 (1C, s, *C*-1a), 114.6 (4C, d, $^{2}J_{C-F} = 21.6$, *C*-3′, *C*-3″, *C*5′ and *C*-5″), 116.3 (1C, d, $^{1}J_{P-C} = 134.0$ Hz, *C*-8), 119.07 (1C, s, *C*-1), 119.44 (1C, s, *C*-5), 124.3 (1C, s, *C*-6a), 127.09 (1C, s, *C*-2), 128.5 (4C, d, $^{3}J_{C-F} = 6.5$ Hz, *C*-2′, *C*-2″, *C*-6′ and *C*-6″), 129.43 (1C, d, $^{2}J_{P-C} = 10.0$ Hz, *C*-7), 129.49 (1C, s, *C*-6), 131.13 (1C, s, *C*-10a), 140.4 (2C, d, $^{4}J_{C-F} = 2.2$, *C*-1′ and *C*-1″), 149.87 (1C, d, $^{2}J_{P-C} = 10.0$ Hz, *C*-8), 151.25 (1C, s, *C*-4a), 162.0 (2C, d, $^{1}J_{C-F} = 245.0$, *C*-4′ and *C*-4″).

MS (70 eV) *m*/*z* (%): 506(53) M^+, 411(69), 369(38), 337(48), 207(100).

References

[1] Becker RS, Michl J. J Am Chem Soc 1966;88:5931–3.
[2] Van Gemert B, Bergomi M, Knowles D. Mol Cryst Liq Cryst 1994;246:67–73.
[3] Crano JC, Guglielmetti RI, editors. Organic photochromic and thermochromic compounds. New York: Kluver Academic/Plenum Publishers; 1998.
[4] Kumar A, Van Gemert B, Knowles D. PPG Ind., Inc., WOP 95/16215; 1995.
[5] Hirao T, Masunnaga T, Yamada N, Ohshiro Y, Agawa T. Bull Chem Soc Jpn 1982;55:909–13.
[6] Gabbutt CD, Heron BM, Instone AC. Tetrahedron 2006;62:737–45.
[7] Demadrille R, Rabourdin A, Campredon M, Giusti G. J Photochem Photobiol A Chem 2004;168:143–52.
[8] Gautron R. Bull Soc Chim Fr 1968:3190–200.
[9] March J. Advanced organic chemistry. New York: John Wiley & Sons; 1985.
[10] Günther H. La spectroscopie de RMN. Paris: Masson; 1994. p. 60.
[11] Hurd RE. J Magn Reson 1990;87:422–8.
[12] Hurd RE, John BK. J Magn Reson 1991;91:648–53.
[13] Wilker W, Leibfritz D, Kerssebaum R, Bermel W. Magn Reson Chem 1993;31:287–92.
[14] Luccioni-Houzé B, Campredon M, Guglielmetti R, Giusti G. Mol Cryst Liq Cryst 1997;297:161–5.
[15] Arnall-Culliford JC, Teral Y, Sgarabotto P, Campredon M, Giusti G. J Photochem Photobiol A Chem 2003;159:7–16.
[16] Gabbutt CD, Gelbrich T, Hepworth JD, Heron BM, Hursthouse MB, Partington SM. Dyes Pigments 2002;54:79–93.
[17] Cotterill WD, Livingstone R, Walshaw MV. J Chem Soc C 1970:1758–64.
[18] Barberis C, Campredon M, Lokshin V, Giusti G, Faure R. Magn Reson Chem 1995;33:977–8.
[19] Delbaere S, Teral Y, Bochu C, Campredon M, Vermeersch G. Magn Reson Chem 1999;37:159–62.
[20] Teral Y. Thesis, Marseille; 2001.