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Synthesis and Reactivity of Formyl-Substituted Photochromic 3,3-Diphenyl-[3*H*]-naphtho[2,1-b]pyrans

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Abstract: Synthetic accesses to formylated photochromic 3,3-diphenyl-[3*H*]-naphthopyrans (or 2*H*-benzochromenes) are developed through classical cyclization between appropriate hydroxynaphthaldehydes and 1,1-diphenylpropyne-1-ol and also *via* substituent transformations on the naphthopyran skeleton including bromine/lithium exchange and the oxidation of an hydroxymethyl group. Examples of formyl group reactivity (Wittig and Knoevenagel reactions, imine formation) from these compounds are given, showing their interest in the subsequent preparation of supramolecular systems involving a photoreactive entity.

[3*H*]-naphtho[2,1-b]pyrans are an important class of oxygenated heterocyclic compounds to which research has been devoted in connection with their photochromic properties[1,2] and their biological activities.[3] This last decade, structural modifications on diarylnaphthopyrans[4-7] and preparation of various heteroannellated 2*H*-chromenes[8-10] have provided many publications and patents.

Despite the interest of the substitution of the naphthopyran ring with electron-withdrawing group to exhibit interesting photochromic properties as demonstrated in the spirooxazine series,[11] no examples of 3,3-diphenylnaphthopyrans containing such a substitution are known.

In this work, the synthesis and the reactivity of formyl-substituted naphthopyrans are presented. This substituent has been chosen not only for its electronic effect, but also because of its synthetic potential. Indeed, functionalized chromenes could be coupled with various molecules to build supramolecular systems containing a photochromic entity. The interest on the latter, particularly in spirooxazines series, has been recently proved through the design of photomodulable materials.[12-14] To check the validity of our approach and particularly to investigate the possible reactivity of the formyl group without destruction of the photochromic entity, Knoevenagel and Wittig reactions and the condensation with amine have been carried out with the new formylated naphthopyrans.

Results and discussion

The general synthesis of 3,3-diphenylnaphthopyrans can be approached by cyclization reaction between a substituted 2-naphthol and the 1,1-diphenylpropyn-1-ol **1**, in presence of a catalytic amount of *p*-toluene sulphonic acid (pTSA) (route A).[5] The preparation of formyl substituted naphthopyrans *via* this method requires convenient hydroxynaphthaldehydes. Acting along the same line, a novel approach (route B) has been

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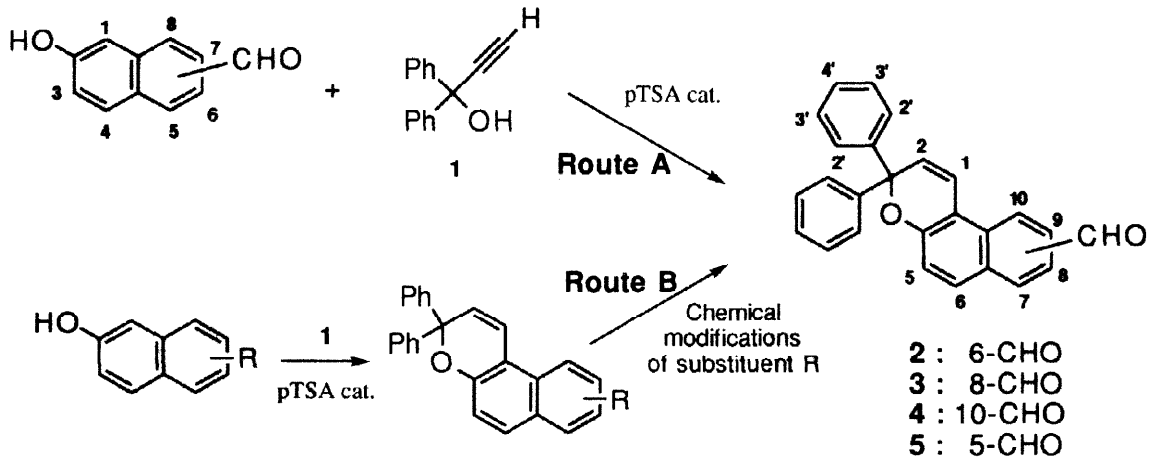
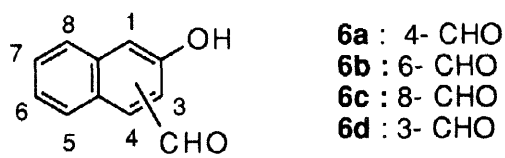
developed, involving chemical modifications of a substituent in a preformed naphthopyran. Formyl-substituted compounds **2-5** have been synthesized using these two complementary approaches as summarized in scheme 1.



Scheme 1

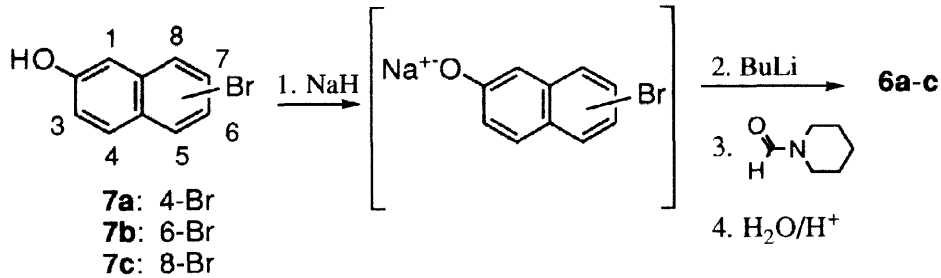
The synthesis of naphthopyrans **2-5** by route A, needs the preliminary preparation of hydroxynaphthaldehydes **6a-d** (scheme 2). Unfortunately, the direct formylation of 2-naphthols does not lead to substitution in the desired positions.[15] The bromine/lithium exchange on bromonaphthols, followed by the reaction with electrophiles (dimethylformamide or N-formylpiperidine) is a good way to prepare these



Scheme 2

compounds. This approach has been developed, but only with compounds bearing protected hydroxy group.[16] To simplify the synthesis, avoiding protection/deprotection steps, *in-situ* protection *via* the sodium salt of the naphthol has been used, a technique recently developed in the quinolinic series.[17]

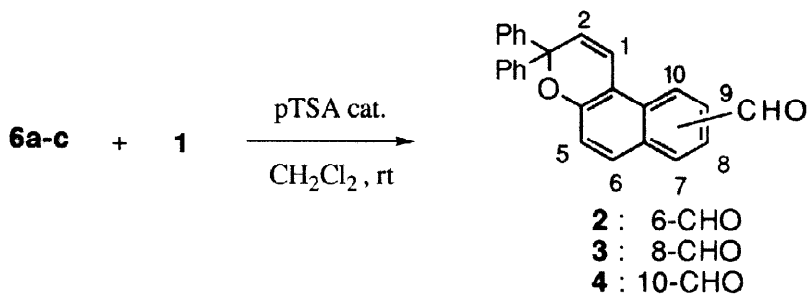
The hydroxynaphthaldehydes (**6a-6c**) were obtained (41% to 67% yields), starting from 4-bromo-2-naphthol (**7a**),[18] 8-bromo-2-naphthol[19] (**7c**) or commercially available 6-bromo-2-naphthol (**7b**), using the N-formylpiperidine as electrophilic agent (scheme 3).



Scheme 3

The preparation of 3-hydroxy-2-naphthaldehyde (**6d**) using this strategy was forsaken, due to the difficulty in obtaining the precursor 3-bromo-2-naphthol; this compound was obtained by a described method.[20]

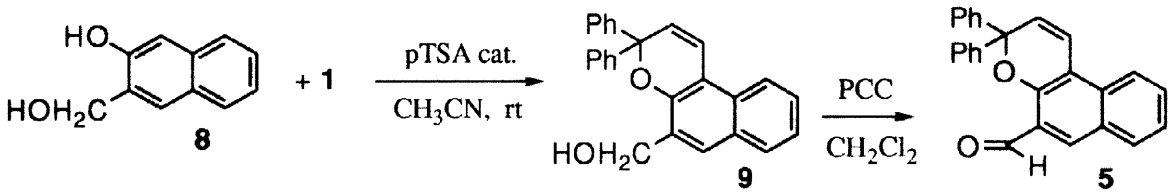
Classical cyclization, using acidic catalysis (pTSA), between hydroxynaphthaldehydes **6a-6c** and propargylic alcohol **1**, afforded corresponding formylated naphthopyrans **2** to **4** (scheme 4). For **6d** this reaction was not satisfying due probably to the weak stability of this compound in acidic medium, and the synthesis of the corresponding 3,3-diphenyl-5-formyl-[3*H*]naphtho[2,1-b]pyran (**5**) was achieved by the route B.



Scheme 4

This approach consists in the preliminary preparation of **9**, followed by the oxidation of the hydroxymethyl group linked to the 5-position into a formyl group (scheme 5). Compound **9** was obtained through the cyclization reaction of 3-hydroxymethyl-2-naphthol **8**[21] with 1,1-diphenylpropyne-1-ol **1**.

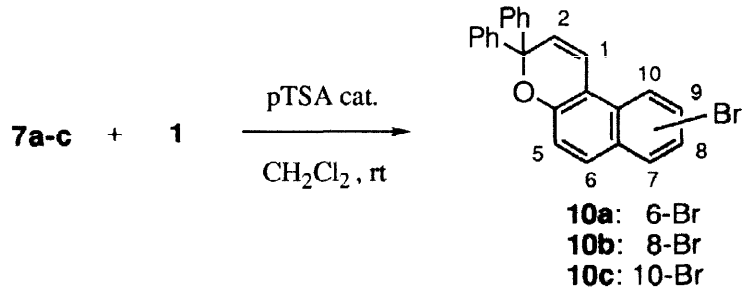
The solubility of **8** in dichloromethane, benzene or toluene (usual solvents for this reaction) being low, acetonitrile has been used despite the moderated yield of the transformation. The 5-formylnaphthopyran **5** was obtained from **9** (83 % yield), using pyridinium chlorochromate (PCC) as oxidizing agent, at room temperature in methylenechloride (scheme 5).



Scheme 5

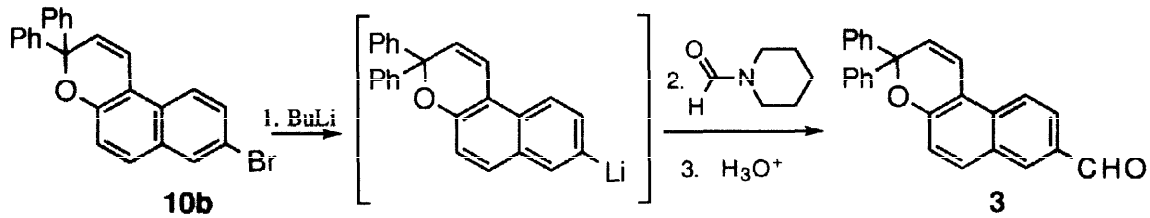
To investigate the potential of this strategy involving a chemical modification of a preformed photochromic compound, the preparation of formylated naphthopyrans **2** to **4** from the corresponding bromo-derivatives was studied.

Indeed, bromine/lithium exchanges followed by formylation were recently carried out in the 2*H*-benzopyran series.[22-24] The bromonaphthopyrans **10a-10c** were prepared through the classical condensation of 4-bromo-2-naphthol **7a**,[18] 6-bromo-2-naphthol **7b** and 8-bromo-2-naphthol **7c**[19] with the propargylic alcohol **1** (scheme 6).



Scheme 6

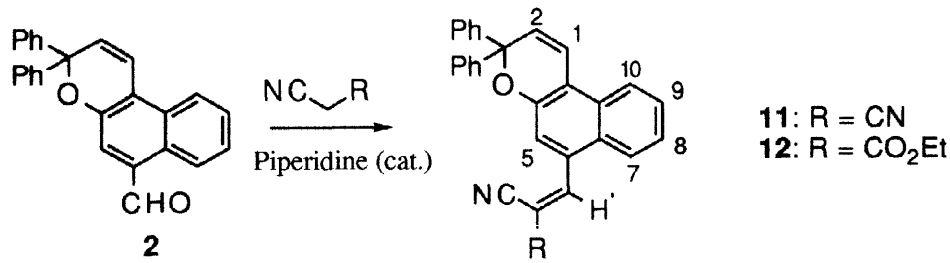
Lithiation of compounds **10a-c** and addition of *N*-formylpiperidine was then investigated. The 8-bromo-naphthopyran **10b** led to the expected photochromic compound **3** (scheme 7).



Scheme 7

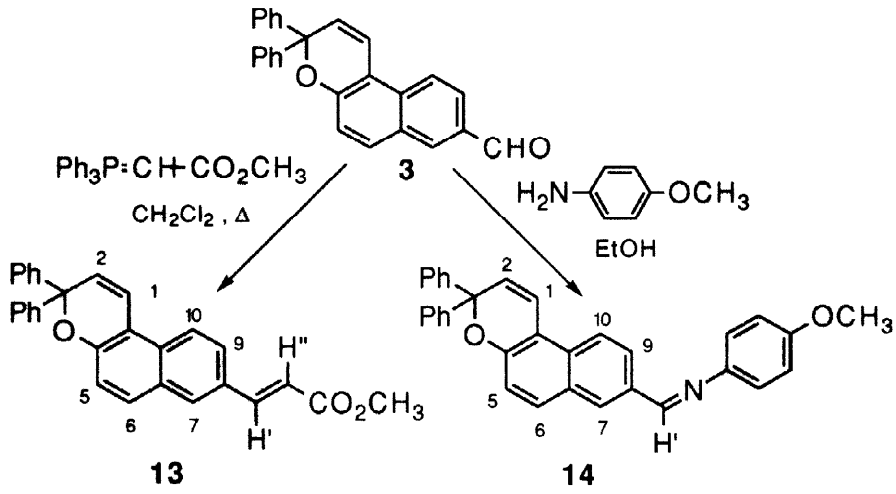
The overyields of preparation of **3**, from 6-bromo-2-naphthol, were 76% and 46% with method A and method B respectively. Unfortunately this last method failed in the preparation of formylnaphthopyrans **2** and **4**, confirming that, as previously described in the 2*H*-benzopyran series,[23] the position of the halogen atom is the decisive factor for the success of this reaction, side processes (especially ring opening) being always possible.

Naphthopyrans **2-5** bearing a reactive formyl group constitute interesting precursors in the aim of the preparation of bistable or photomodulable supramolecular systems. In order to highlight the chemical reactivity of these functionalized photochromic compounds, three kinds of reactions were performed. For instance applying the Knoëvenagel reaction[25] to the 6-formylnaphthopyran (**2**) led to compounds **11** and **12** using respectively malononitrile and ethyl cyanoacetate as reagent (scheme 8).



Scheme 8

Two other examples concerned the reaction of 8-formylnaphthopyran (**3**) with the carbomethoxy-methylenetriphenyl phosphorane and with *p*-methoxyaniline (scheme 9).



Scheme 9

Both the Wittig product **13** (isolated as the E isomer, evidenced by ^1H NMR) and the imine **14** were obtained in good yields (76% and 75% respectively).

In summary, formylated naphthopyrans have been synthesized using two different synthetic approaches. One of them, involving chemical modifications on a preformed naphthopyran opens new perspectives to prepare compounds of this family which are difficult to obtain through convergent synthesis from substituted naphthols. Finally the reactivity of the introduced formyl groups towards different nucleophiles, opens up the elaboration of supramolecular photomodulable systems.

EXPERIMENTAL

Materials and methods

Solvents (SDS Company, France) were used without further purification other than drying over molecular sieves.

^1H and ^{13}C NMR spectra were recorded on a Bruker BM 250 spectrometer (250 MHz and 62.5 MHz respectively for ^1H and ^{13}C) using tetramethylsilane as internal standard. Chemical shifts are given in ppm and coupling constants in Hz.

Melting points (°C), measured in capillary tubes on a Buchi 510 apparatus, are uncorrected.

Column chromatography was performed on silica gel Merck 60 (70-230 mesh) and flash chromatography on silica gel Merck 60H (5-50 mesh).

Elemental analysis was performed by the Microanalytical Centre of the University of Aix-Marseille III.

The identification of previously reported compounds was made by ^1H NMR and melting points comparison with literature data.

Starting materials

Compounds **1** (Interchim), **7b** (Aldrich) were commercially available.

Compounds **6d**[20],**7a**,[18] **7c**,[19], **8**[21] were prepared according to previously described methods.

General method for the synthesis of hydroxynaphthaldehydes 6a-6c, from bromonaphthols 7a-7c.

A solution of 3.00 g (12.4 mmol) of bromonaphthol in 100 ml of anhydrous Et_2O was added dropwise to a stirred solution of 0.64 g (16 mmol) of sodium hydride (60% in mineral oil) in 100 ml of anhydrous Et_2O (argon atmosphere, ambient temperature). After 2h stirring, 13 ml (21 mmol) of butyllithium (1.6 M in hexane) was added dropwise. 1h later, 2.38 g (21 mmol) of N-formylpiperidine was added and after 2h of additional stirring the mixture was acidified with an ice cooled solution (2N) of hydrochloric acid, then extracted with Et_2O (3x150 ml). The combined extracts were washed with a solution of $NaHCO_3$ (10 % in water), dried ($MgSO_4$) and evaporated. The crude product is purified by column chromatography on silica gel.

3-Hydroxy-1-naphthaldehyde (**6a**): 61% yield, purification by column chromatography, eluent CH_2Cl_2/Et_2O (90/10). Crystallization gave pale yellow cristals, Mp. 139 (from ethanol). NMR ^1H ($DMSOd_6$): 7.40-7.56 (3H, m, 2-H, 6-H, 7-H); 7.71 (1H, d, J = 2.5, 4-H); 7.82 (1H, dd, J = 7.6 and 2.3, 5-H); 8.94 (1H, dd, J = 7.6 and 2.3, 8-H); 10.21 (1H, s broad, OH), 10.34 (1H, s, CHO). NMR ^{13}C (Acetone d_6): 116.9 (d); 125.0 (d); 126.3 (s); 126.4 (d); 127.6 (d); 127.8 (d); 128.5 (d); 133.7 (s); 136.5 (s) ; 155.2 (s); 193.6 (d). Anal. calc. for $C_{11}H_8O_2$: C 76.73, H 4.68; found C 76.67, H 4.66.

6-Hydroxy-2-naphthaldehyde (**6b**): 67% yield, purification by column chromatography, eluent pentane/Et_2O (50/50). Crystallization gave white cristals, Mp. 180 (from ethanol). NMR ^1H (Acetone d_6): 7.28-7.38 (2H, m, 5-H, 7-H); 7.80-7.90 (2H, m, 3-H, 4-H); 8.05 (1H, d, J = 8.7, 8-H); 8.42 (1H, s, 1-H); 9.25 (1H, s broad, OH); 10.10 (1H, s, CHO). NMR ^{13}C (Acetone d_6): 110.3 (d); 120. 3 (d); 123.6 (d); 127.9 (d); 128.9 (s); 132.4 (d); 133.0 (s); 135.3 (d); 139.3 (s); 159.1 (s); 192.2 (d). Anal. calc. for $C_{11}H_8O_2$: C 76.73, H 4.68; found C 76.80, H 4.69.

7-Hydroxy-1-naphthaldehyde (**6c**): 41% yield, purification by column chromatography, eluent CH_2Cl_2. Crystallization gave white needles, Mp. 230 (from ethanol). NMR ^1H (Acetone d_6): 7.26 (1H, dd, J = 8.9 and 2.5, 6-H); 7.51 (1H, dd, J = 7.2, 3-H); 7.93 (1H, d, J = 8.9, 5-H); 8.06 (1H, dd, J = 7.1 and 1.6, 4-H); 8.13 (1H, d, J = 8.1, 2-H); 8.70 (1H, d, J = 2.5, 8-H); 9.07 (1H, s broad, OH); 10.31 (1H, s, CHO). NMR ^{13}C (DMSO d_6): 106.1 (d); 119.0 (d); 121.7 (d); 127.9 (s); 129.1 (s); 130.3 (d); 131.4 (s); 135.1 (d); 138.1 (s); 158.4 (d); 194.2 (d). Anal. calc. for $C_{11}H_8O_2$: C 76.73, H 4.68; found C 76.65, H 4.65.

General method for the synthesis of naphthopyrans 2 to 4 (Route A) and 10a to 10c .

A solution of 10 mmol of the hydroxynaphthalene, 10 mmol of 1,1-diphenylpropyn-1-ol **1** and a catalytic amount of *p*-toluenesulfonic acid, in 40 ml of methylenechloride was stirred at ambient temperature overnight. The solution was washed with a solution of $NaHCO_3$ (5% in water), and then with water. The organic layer was dried ($MgSO_4$), filtered and evaporated to give an oil.

3,3-Diphenyl-6-formyl-[3H]-naphtho[2,1-b]pyran (**2**): 46% yield, purification by flash chromatography, eluent pentane/CH_2Cl_2 (70/30). Crystallization gave white cristals, Mp. 145 (from heptane). NMR ^1H ($CDCl_3$): 6.47 (1H, d, J = 10.0, 2-H); 7.24-7.39 (6H, m, 3'-H, 4'-H); 7.37 (1H, d, J = 10.1, 1-H); 7.47 (4H, dd, J= 8.2 and 1.5, 2'-H); 7.46-7.60 (2H, m, 8-H, 9-H); 7.71 (1H, s, 5-H); 8.04 (1H, dd, J = 8.7 and 1.8, 7-H); 9.11 (1H, dd, J = 7.0 and 1.8, 10-H); 10.30 (1H, s, CHO). NMR ^{13}C ($CDCl_3$): 83.0 (s); 119.3 (d); 120.5 (s); 121.9 (d); 125.4 (d); 126.7 (d); 127.1 (d); 127.7 (d); 127.8 (d); 128.0 (d); 128.4 (d); 130.4 (s); 131.9 (d); 132.3 (s); 144.3 (s); 149.7 (s); 192.4 (d). Anal. calc. for $C_{26}H_{18}O_2$: C 86.17, H 5.01; found C 86.07, H 5.00.

3,3-Diphenyl-8-formyl-[3H]-naphtho[2,1-b]pyran (**3**): 76% yield, purification by column chromatography, eluent pentane/Et_2O (85/15). Crystallization gave white needles. Mp. 134 (from heptane). NMR ^1H ($CDCl_3$) : 6.32 (1H, d, J = 9.9, 2-H); 7.24-7.36 (8H, m, 1-H, 3'-H, 4'-H, 5-H); 7.46 (4H, dd, J = 8.0 and 1.6, 2'-H); 7.79 (1H, d, J = 9.1, 6-H); 7.91 (1H, dd, J = 8.6 and 1.5, 9-H); 8.01 (1H, d, J = 8.6, 10-H); 8.16 (1H, d, J = 1.5, 7-H); 10.05 (1H, s, CHO). NMR ^{13}C ($CDCl_3$): 83.2 (s); 114.4 (s); 119.0 (d); 119.6 (d); 122.4 (d); 123.8 (d); 127.1 (d); 127.9 (d); 128.3 (d); 128.4 (s); 128.5 (d); 131.7 (d); 132.3 (s); 133.1 (s); 135.1 (d); 144.5 (s); 153.4 (s); 192.0 (d). Anal. calc. for $C_{26}H_{18}O_2$: C 86.17, H 5.01; found C 86.04, H 5.05.

3,3-Diphenyl-10-formyl-[3H]-naphtho[2,1-b]pyran (**4**): 36% yield, purification by column chromatography, eluent CH_2Cl_2. Crystallization gave pale yellow cristals, Mp. 132 (from heptane). NMR ^1H ($CDCl_3$): 6.09 (1H, d, J = 9.6, 2-H); 6.96 (1H, d, J = 9.6, 1-H); 7.25-7.35 (7H, m, 3'-H, 4'-H, 5-H); 7.40 (1H, dd, J = 7.7 and 7.6, 8-H); 7.49-7.55 (4H, m, 2'-H); 7.77 (1H, d, J = 8.9, 6-H); 7.91 (1H, d, J = 8.1, 7-H); 7.99 (1H, dd, J = 7.3 and 7.3, 9-H); 10.54 (1H, s, CHO). NMR ^{13}C ($CDCl_3$): 83.2 (s); 114.9 (s); 119.5 (d); 123.4 (d); 125.0 (d); 125.4 (d); 127.3 (d); 128.0 (d); 128.4 (d); 130.0 (s); 130.5 (s); 130.9 (d); 131.8 (d); 132.9 (s); 134.9 (d); 144.3 (s); 153.7 (s); 192.4 (s). Anal. calc. for $C_{26}H_{18}O_2$: C 86.17, H 5.01; found C 85.96, H 5.12.

6-Bromo-3,3-diphenyl-[3H]-naphtho[2,1-b]pyran (**10a**): 67% yield, purification by flash chromatography, eluent pentane. Crystallization gave white cristals, Mp. 167 (from ethanol). NMR ^1H ($CDCl_3$): 6.28 (1H, d, J = 10.0, 2-H); 7.23-7.36 (7H, m, 1-H, 3'-H, 4'-H); 7.38-7.53 (2H, m, 8-H, 9-H); 7.46 (4H, dd, J = 8.2 and 1.5, 2'-H); 7.56 (1H, s, 5-H); 7.95 (1H, d , J = 8.1, 7-H); 8.12 (1H, d , J = 7.5, 10-H). NMR ^{13}C ($CDCl_3$) : 82.9 (s); 114.0 (s); 119.1 (d); 121.6 (d); 122.3 (d); 123.4 (s); 124.8 (d); 126.9 (d); 127.3 (d); 127.6 (d); 127.8 (s); 128.1 (d); 130.4 (s); 144.4 (s); 150.1 (s). Anal. calc. for $C_{25}H_{17}BrO$: C 72.65, H 4.15; found C 72.48, H 4.18.

8-Bromo-3,3-diphenyl-[3H]-naphtho[2,1-b]pyran (**10b**): 90% yield, purification by column chromatography, eluent CH_2Cl_2. Crystallization gave white cristals, Mp. 148 (from heptane). NMR ^1H ($CDCl_3$): 6.32 (1H, d, J = 10.0, 2-H); 7.18-7.35 (8H, m, 1-H, 3'-H, 4'-H, 5-H); 7.44-7.56 (6H, m, 2'-H, 6-H, 9-H); 7.80 (1H, d, J = 8.9, 10-H); 7.84 (1H, d, J = 1.9, 7-H). NMR ^{13}C ($CDCl_3$): 82.7 (s); 114.1 (s); 117.3 (s); 119.1 (d); 119.4 (d); 123.1 (d); 126.9 (d); 127.6 (d); 128.1 (d); 128.2 (d); 128.8 (d); 129.7 (d); 130.3 (d); 130.5 (s); 144.6 (s); 150.7 (s). Anal. calc. for : $C_{25}H_{17}BrO$: C 72.65, H 4.15; found C 72.50, H 4.10.

10-Bromo-3,3-diphenyl-[3H]-naphtho[2,1-b]pyran (**10c**): 88% yield, purification by column chromatography, eluent CH_2Cl_2. Crystallization gave white cristals, Mp. 123 (from heptane). NMR ^1H ($CDCl_3$): 6.05 (1H, d, J = 9.9, 2-H); 7.08 (1H, dd, J = 7.8 and 7.8, 8-H); 7.20-7.35 (7H, m, 3'-H, 4'-H, 5-H); 7.48-7.55 (4H, m, 2'-H); 7.62 (1H, d, J = 8.8, 6-H); 7.63 (1H, d, J = 8.8, 7-H); 7.73 (1H, d, J =7.5, 9-H); 8.17 (1H, d, J = 9.8, 1-H). NMR ^{13}C ($CDCl_3$): 81.9 (s); 116.2 (s); 118.5 (s); 119.6 (d); 123.5 (d); 124.2 (d); 124.6 (d); 127.5 (d); 127.8 (d); 128.3 (d); 129.5 (s); 130.0 (d); 131.2 (d); 132.06 (s); 133.9 (d); 144.7 (s); 153.0 (s). Anal. calc. for $C_{25}H_{17}BrO$: C 72.65, H 4.15; found C 72.73, H 4.29.

Synthesis of naphthopyrans 3 and 5 (route B)

3,3-Diphenyl-8-formyl-[3H]-naphtho[2,1-b]pyran (**3**): 1 ml of a solution (2.5 M in hexane) of n-butyllithium was added to a stirred solution of **10b**, 1.03 g (2.5 mmol), in 80 ml of anhydrous Et_2O, at 0°C, under argon atmosphere. The resulting mixture was stirred for 1h, whereupon N-formylpiperidine 0.28 g (2.5

mmol) was added. After stirring for an additional 1h, the mixture was acidified with a solution (2N) of hydrochloric acid and extracted several times with Et_2O. The combined extracts were washed with a solution of $NaHCO_3$ (10 % in water), dried with $MgSO_4$ and evaporated. Purification method, physical and NMR characteristics are the same as described above. Yield 46%.

3,3-Diphenyl-5-hydroxymethyl-[3H]-naphtho-[2,1-b]-pyrane (**9**): A solution of 2.0 g (11.5 mmol) of 3-hydroxymethyl-2-naphthol **8**, 2.3 g (11.5 mmol) of 1,1-diphenyl-2-propyn-1-ol **1** and a catalytic amount of *p*-toluenesulfonic acid, in 200 ml of CH_3CN were stirred 12h, at ambient temperature. After evaporation of the solvent, the residue was purified by column chromatography (eluent CH_2Cl_2) to give 1.5 g (36%) of **9** as white cristals. Mp. 128 (from heptane). NMR ^1H ($CDCl_3$): 2.19 (1H, s, OH); 4.88 (2H, s, CH_2); 6.18 (1H, d, J = 9.9, 2-H); 7.23-7.34 (8H, m, 1-H, 3'-H, 4'-H, 8-H); 7.42-7.47 (5H, m, 2'-H, 9-H); 7.65 (1H, s, 6-H); 7.69 (1H, d, J = 8.1, 7-H); 7.94 (1H, d, J = 8.4, 10-H). NMR ^{13}C ($CDCl_3$): 61.7 (t) ; 83.1 (s); 113.9 (s); 119.7 (d); 121.3 (d); 124.0 (d); 126.6 (d); 127.0 (d); 127.3 (d); 127.7 (d); 127.8 (d); 128.4 (d); 128.6 (d); 129.0 (s); 129.4 (s); 129.5 (s); 144.7 (s); 148.5 (s). Anal. calc. for $C_{26}H_{20}O_2$: C 85.69, H 5.53; found C 85.67, H 5.54.

3,3-Diphenyl-5-formyl-[3H]-naphtho[2,1-b]pyran (**5**): A suspension of 4.3 g (20 mmol) of PCC in 200 ml of dry CH_2Cl_2 was added dropwise to a stirred solution of 3.6 g (10 mmol) of **9** in 200 ml of dry CH_2Cl_2. The mixture was stirred for an 1h at room temperature. Then 200 ml of ether was added and the mixture filtered on celite. After evaporation of the solvent, the residue was purified by column chromatography (eluent pentane/Et_2O : 80/20), to give 3.0 g (83%) of **5** as yellow cristals. Mp. 130 (from heptane). NMR ^1H ($CDCl_3$): 6.32 (1H, d, J = 10.0, 2-H); 7.22-7.38 (8H, m, 1-H, 3'-H, 4'-H, 8-H); 7.49 (4H, dd, J = 8.4 and 1.6, 2'-H); 7.55 (1H, ddd, J = 7.6, 7.6 and 1.2, 9-H); 7.82 (1H, d, J = 8.1, 7-H); 7.95 (1H, d, J = 8.5, 10-H); 8.25 (1H, s, 6-H); 10.74 (1H, s, CHO). NMR ^{13}C ($CDCl_3$) : 83.5 (s); 115.6 (s); 119.5 (d); 121.7 (d); 124.7 (s); 124.9 (d); 127.1 (d); 128.0 (d); 128.4 (s); 128.5 (d); 128.8 (d); 129.6 (d); 130.5 (d); 131.0 (d); 132.8 (s); 144.4 (s); 150.9 (s); 189.9 (d). Anal. calc. for $C_{26}H_{18}O_2$: C 86.17, H 5.01 ; found C 86.07, H 5.06.

Reactivity of formylated naphthopyrans

6-(2,2-Dicyanoethen-1-yl)-3,3-diphenyl-[3H]-naphtho[2,1-b]pyran (**11**): 0.36g (1 mmol) of **2** and 0.07g (1 mmol) of malononitrile, in 10ml of EtOH, were heated 5 min to 60°C. Then catalytic amount of piperidine was added. After stirring 1h at 60°C, the reaction mixture was cooled to room temperature and filtered. Washed with cold EtOH the precipitate gave 0.29g (71%) of **11** as yellow-orange cristals. Mp. 250 (from EtOH). NMR ^1H ($CDCl_3$) : 6.53 (1H, d, J = 10.0, 2-H); 7.25-7.37 (7H, m, 1-H, 3'-H, 4'-H); 7.47 (4H, d broad, J = 6.7, 2'-H); 7.48 (1H, m, 8-H); 7.58 (1H, dd, J = 7.3, 9-H); 7.79 (1H, d, J = 8.3, 7-H); 8.01 (1H, s, 5-H); 8.05 (1H, d , J = 8.3, 10-H) ; 8.46 (1H, s, H'). NMR ^{13}C ($CDCl_3$) : 82.9 (s); 84.7 (s); 112.7 (s); 113.9 (s); 119.1 (d); 119.4 (d); 120.4 (d); 120.9 (s); 122.8 (d); 122.9 (d); 126.3 (d); 127.1 (d); 127.4 (s); 127.9 (d); 128.0 (d); 128.3 (s); 128.4 (d); 129.9 (s); 132.9 (d); 143.9 (s); 149.6 (s); 156.3 (d). Anal. calc. for $C_{29}H_{18}N_2O$: C 84.86, H 4.42, N 6.82 ; found C 84.71, H 4.37, N 6.71.

6-(2-Carboethoxy-2-cyanoethen-1-yl)-3,3-diphenyl-[3H]-naphtho[2,1-b]pyran (**12**): As described for **11**, (0.36 g (1 mmol)) of **2** and ethylcyanoacetate (0.12 g (1 mmol)) gave 0.27 g (59 %) of **12** as bright yellow needles. Mp. 138 (from heptane). NMR ^1H ($CDCl_3$) : 1.43 (3H, t, J = 7.1, CH_3); 4.43 (2H, q, J = 7.1, CH_2); 6.48 (1H, d, J = 10.0, 2-H); 7.25-7.36 (7H, m, 1-H, 3'-H, 4'-H); 7.41-7.57 (6H, m, 8-H, 9-H, 2'-H); 7.94 (1H, d , 2'-H); 8.03 (1H, d , J = 8.3, 10-H); 8.09 (1H, s, 5-H); 8.99 (1H, s, H'). NMR ^{13}C

($CDCl_3$) : 14.2 (q); 62.8 (t); 82.8 (s); 105.6 (s); 115.2 (d); 119.1 (d); 119.4 (s); 120.2 (d); 122.4 (d) ; 123.4 (d); 125.4 (d); 127.0 (d); 127.4 (d); 127.8 (d); 128.0 (s); 128.2 (d); 129.3 (s); 129.9 (s); 131.7(d); 144.1 (s) ; 149.7 (s) ; 151.6 (d) ; 162.43 (s). Anal. calc. for $C_{31}H_{23}NO_3$: C 81.38, H 5.07, N 3.06 ; found C 81.33 , H 5.01, N 2.97.

8-(2-Carbomethoxyethen-1-yl)-3,3-diphenyl-[3H]-naphtho[2,1-b]pyran (**13**): A solution of 0.13 g (0.36 mmol) of **3** and 0.12 g (0.36 mmol) of carbomethoxymethylenetriphenyl phosphorane in 10 ml of CH_2Cl_2 were refluxed 18h. After evaporation of the solvent, the residue was purified by column chromatography (eluent CH_2Cl_2) to give 0.115 g (76%) of the E-isomer **13** as pale yellow needles. Mp. 176 (from heptane). NMR ^1H ($CDCl_3$) : 3.80 (3H, s, CH_3) ; 6.27 (1H, d, J = 10.0, 2-H); 6.47 (1H, d, J = 16.0, H"); 7.18-7.34 (8H, m, 1-H, 5-H, 3'-H, 4'-H); 7.47 (4H, d, J = 7.0, 2'-H); 7.61 (2H, m, 6-H, 9-H); 7.74 (1H, s, 7-H); 7.77 (1H, d, J = 16.0, H') 8.86 (1H, d broad, J = 8.9, 10-H). NMR ^{13}C ($CDCl_3$) : 51.8 (q), 83.0 (s), 114.3 (s), 117.1 (d), 119.2 (d), 119.3 (d), 122.3 (d), 124.4 (d), 127.1 (d), 127.8 (d), 128.3 (d), 129.2 (s), 129.8 (s), 130.6 (d), 130.7 (d), 130.8 (s), 144.7 (s), 144.9 (d), 151.9 (s), 167.7 (d). Anal. calc. for $C_{29}H_{22}O_3$: C 83.23, H 5.30 ; found C 83.17, H 5.38.

8-(4-Methoxyphenyliminomethyl)-3,3-diphenyl-[3H]-naphtho[2,1-b]pyrane (**14**): 0.36g (1 mmol) of **3** and 0.12 g (1 mmol) of *p*-methoxyaniline were refluxed in 10ml of EtOH 15 min. Then the reaction mixture was cooled to room temperature and filtered. The collected white precipitate, washed with cold EtOH, gave 0.34 g (75 %) of **14** as white needles. Mp. 228 (from EtOH/$CHCl_3$ (1:1)). NMR ^1H (Acetone d_6): 3.83 (3H, s, CH_3); 6,29 (1H, d, J = 9.9, 2-H); 6.94 (2H, d, J = 8.9, $2H_{arom.}$); 7.21-7.36 (10H, m, 1-H, 5-H, 3'-H, 4'-H, $2H_{arom.}$); 7.48 (4H, dd, J = 8.4 and 1.6) ; 7.73 (1H, d, J = 8.8, 10-H); 8.00 (1H, d, J = 8.8, 6-H); 8.04 (1H, s, 7-H); 8.12 (1H, d, J = 8.8, 9-H); 8.55 (1H, s, H'). Anal. calc. for $C_{32}H_{25}NO_2$: C 84.37, H 5.53, N 3.07 ; found C 84.28, H 5.50, N 3.16.

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