JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2007; **20:** 872–877
Published online 27 July 2007 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/poc.1218

5-Nitrogenated-naphthopyrans: toward photoinduced hydrogen-bonded complexes

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Received 4 January 2007; revised 8 March 2007; accepted 16 April 2007

ABSTRACT: A series of 3,3-diphenyl-3H-naphtho[2,1-b]pyrans substituted on 5-position by various nitrogenated functional groups has been synthesized. The photochromic reaction between the pyranic closed form and their open forms has been studied using NMR and UV–Vis spectroscopies. The ability of the photoinduced carbonyl group to promote the formation of hydrogen-bonded complexes has been compared within the series. Copyright © 2007 John Wiley & Sons, Ltd.
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KEYWORDS: photochromism; H-Bond; NMR; supramolecular chemistry

INTRODUCTION

Naphthopyrans constitute a class of photochromic compounds which have been mainly studied for applications as pigments in the ophthalmic industry for over 20 years.[1] UV-irradiation leads to the C_{sp3}—O bond cleavage producing colored isomers, namely photomero-forms. This phenomenon is more often thermally reversible, although it can also be photochemically induced, giving rise to applications in supramolecular chemistry. This electrocyclization process is unique in terms of the accompaning large changes in the structural and electronic characteristics. Consequently, different spirobenzopyran or related naphthopyran derivatives containing ion responsive molecules such as crown ether,[2] amid group,[3] or calixarenes[4] have been synthesized and studied to determine the influence of the irradiation upon the complexation. Photochromic molecules as bistable compounds are suitable for mimicking biological signal transduction processes, and therefore, by combining molecular recognition with photochromic chemistry, conceptually new photoresponsive systems will be created. With that in mind, we aim to prepare and fully characterize suitable 5-amino substituted naphthopyrans that could develop some H-bond network upon irradiation. Electron donor or withdrawal substituents located on the C-5 position significantly affect the well-documented photochromic properties of 3,3-diphenylnaphtho[2,1-b]pyrans[1] and this position is also a geometrical prerequisite for promoting host–guest interaction involving the photoinduced carbonyl group. Furthermore compounds incorporating a carbonyl group like ester or ketone have been recently reported to lead to the formation of simple and efficient photoswitchable system based on an enhanced proportion of stable TT-isomer[5] which remains unusual within 3,3-diphenylnaphtho[2,1-b]pyrans and 2,2-diphenylnaphtho[1,2-b]pyrans.[6] On another hand, ureido derivatives have also been shown to preferentially promote supramolecular recognition event through H-bonding under UV irradiation.[7] A better understanding of these peculiar and promising effects is expected through a structure-property relationship. The comparison of the spectrokinetic properties of the target molecules will also determine the more appropriate structural prerequisite.

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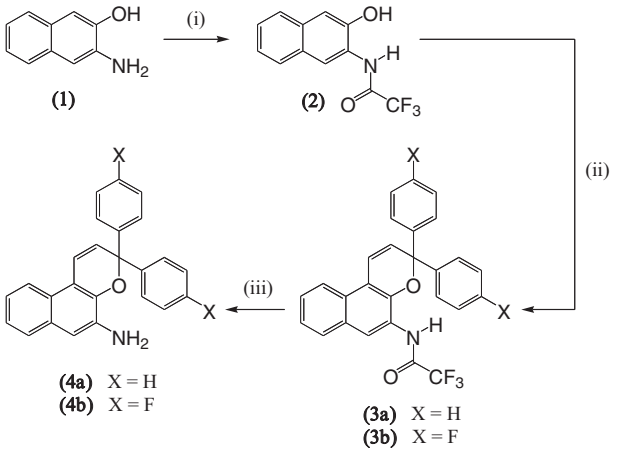
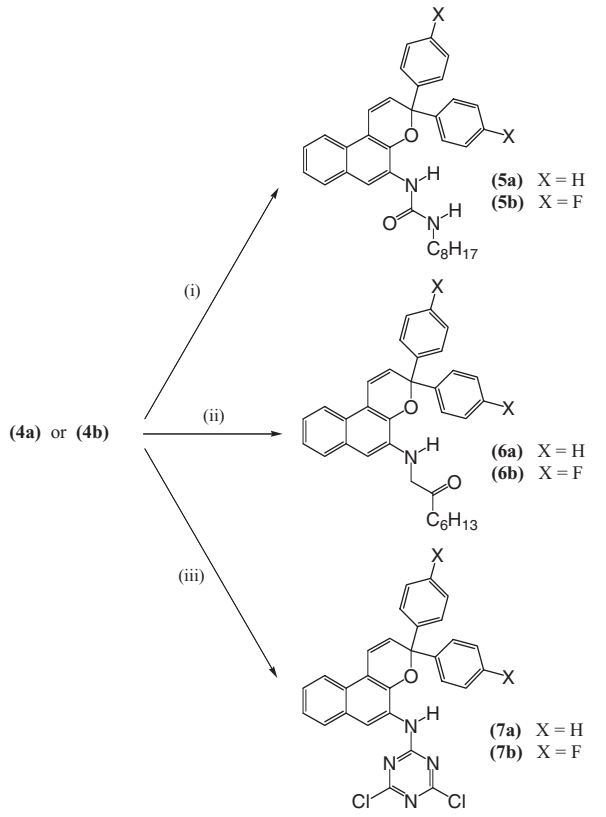
RESULTS AND DISCUSSION

The synthesis of target molecules with various donor and acceptor hydrogen-bond sites requires the preparation of a common key molecule: 5-amino-3,3-diphenyl-[3H]naphtho[2,1-b]pyran **(4a)** (Scheme 1). This compound was synthesized in three steps from the commercially available 3-amino-2-naphthol **(1)**. The first step consists of the protection of the amino function in presence of trifluoroacetic anhydride[8] to afford **(2)**. This reduces the basic character of the nitrogen atom of naphthol **(2)** and allows its chromenization using acid



Scheme 1. *Reagents and conditions*: (i) $(CF_3CO)_2O$, THF, 65°C; (ii) 1,1-diphenylprop-2-yn-1-ol or 1,1-(4,4′- difluorophenyl)prop-2-yn-1-ol, *p*-toluenesulfonic acid (cat), toluene, reflux; (iii) K_2CO_3, MeOH, H_2O, reflux

catalysis[9] with 1,1-diphenylprop-2-yn-1-ol.[10] The protective group is then removed by treatment with K_2CO_3 in refluxing methanol/water mixture[11] to afford **(4a)**. A similar synthetic pathway is used to prepare the difluorinated corresponding compound **(4b)**. This latter product was obtained in lower yield in comparison with **(4a)** due to the purification process.



Scheme 2. *Reagents and conditions*: (i) *n*-octylisocyanate, CH_2Cl_2, 25 °C; (ii) 1-bromooctan-2-one, THF, 25 °C; (iii) cyanuric acid, *N,N*-diisopropylethylamine, THF, 25 °C

The target molecules are obtained in one step from **(4a)** or **(4b)** intermediates (Scheme 2). The reaction with the *n*-octyl-isocyanate leads to the formation of urea derivatives[12] **(5a)** and **(5b)**. Reaction with 1-bromooctan-2-one[13] affords respectively **(6a)** and **(6b)** according to SN_2 substitution. Compounds **(7a)** and **(7b)** are obtained by reacting respectively 5-aminochromenes **(4a)** or **(4b)** with cyanuric acid[14] and diisopropylamine as base at room temperature, these conditions allow the control of the monosubstitution of the triazine unit. All the described compounds **5a–7b** with two hydrogen-bonding groups gave satisfactory elemental analysis and spectroscopic data.

The photochromic behavior of target molecules and key amino intermediates has been determined under continuous irradiation at room temperature using toluene as solvent (see Experimental section for details). Three main spectrokinetic parameters: (1) absorption maxima of the colored form (λ_{max} OF), (2) thermal bleaching rate (k_Δ), and (3) absorbance at the photostationnary state (A_{pss}) measured upon continuous irradiation have been quantified for all non-fluorinated compounds and are collected in Table 1. Previous studies have shown that the fluorine atoms located on the phenyl groups do not affect the spectrokinetic data inducing very tiny changes.[15] The presence of nitrogenated group directly linked on the 5-position of the 3,3-diphenyl-[3H]naphtho[2,1-b]pyran does not suppress the photochromic behavior. Indeed A_{pss} values indicate a good response to irradiation even if slightly lowered with respect to parent molecule ($A_{pss} = 1.12$).[15] Comparison with unsubstitued parent chromene also reveals a bathochromic effect on the maximum absorption for the colored open forms, this one shifting from 425 to 439–455 nm. More interestingly, the photogenerated forms are more stable even at room temperature as indicated by a significant decrease of thermal bleaching constant rates. Some of us have previously demonstrated that NMR spectroscopy is a powerful technique to investigate the photochromic behavior of chromenes.[16] ^{19}F NMR is especially suitable to distinguish between the various open form isomers and to follow all the kinetic pathways. The evolution of ^1H and ^{19}F NMR spectra corresponding to the five naphthopyrans difluorinated on the 4-position of phenyl groups **3b–7b** has been monitored at 243K in toluene

Table 1. Spectrokinetic data obtained for non-fluorinated naphthopyrans[a]

Compounds	λ_{max} CF (nm)	λ_{max} OF (nm)	A_{eq}	$^{298}k_\Delta$ (s^{-1})
3a	329	455	0.58	0.017
4a	336	439	0.86	0.007
5a	337	438	0.64	0.015
6a	335	425	0.77	0.021
7a	333	454	0.84	0.028

[a] 5×10^{-5} M solutions in toluene.

DOI: 10.1002/poc

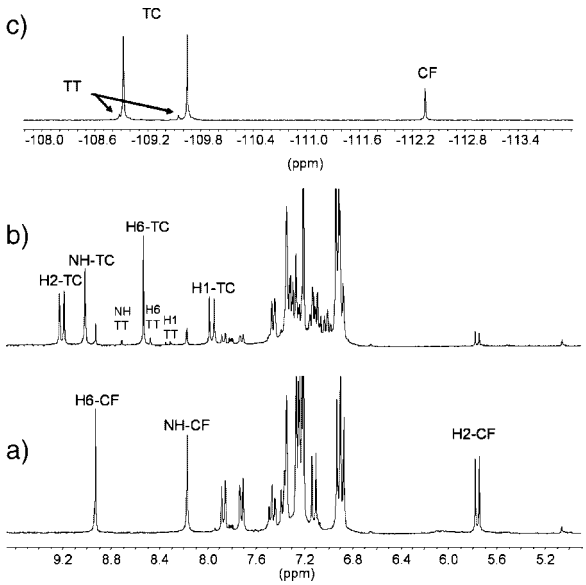


Figure 1. ^{1}H NMR spectra (a) before and (b) after irradiation of **7b** at 243 K, (c) ^{19}F NMR spectrum after irradiation

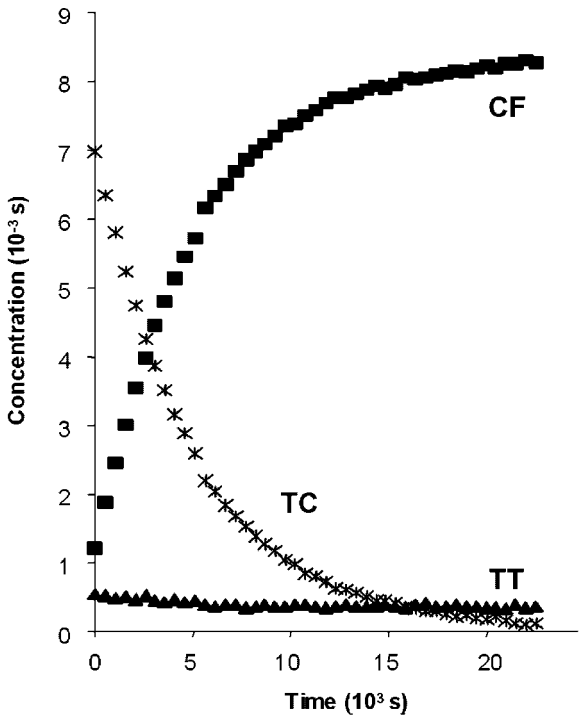


Figure 2. Time evolution concentrations of **7b** at 243 K after irradiation

solution. Those corresponding to compound **7b** are depicted in Fig. 1. Comparison of ^{1}H NMR spectra before and just after irradiation indicates the decrease of signals belonging to the initial closed form (**7b**) and the appearance of new resonances with different peak-intensities. These observations are more evident in the ^{19}F NMR spectrum, where two pairs of signals are detected after irradiation characterizing the presence of both expected transoid photomerocyanines, TC and TT. The more concentrated photomerocyanine is identified as TC isomer due to the more deshielded doublet signal at 9.2 ppm, characterizing proton H-2 with a coupling constant of 12.4 Hz.[14] The thermal relaxation of irradiated solutions has been followed by recording NMR spectra at regular time-intervals for several hours after the irradiation was stopped. The measurement of peak-intensities makes it possible to plot time evolution of their concentrations (Fig. 2). The major concentrated isomer TC follows a mono-exponential decay while the second isomer, TT, presents no significant thermal evolution at 243 K. Similar behaviors have been observed for each of the five investigated molecules, and the calculated rate constants of bleaching, $^{243}k_{\Delta}$ TC → CF are reported in Table 2. In contrast, ^{19}F NMR chemical shift changes and broadening of one signal in TC isomer are restricted to compound **(5b)** which possesses a urea group inducing a self-association process as previously reported.[7] Replacement of this group by amino-β-carbonylated **(6b)** or aminotriazine units **(7b)** totally suppress self-assembling. This has been also observed for intermediates **(3b,4b)**. This opens new prospect in designing 2H-chromenes that could act as receptor through multiple hydrogen-bond complementarity which will be revealed only for the colored forms. These selected side arms could promote an ADA system (Fig. 3). The aminotriazine unit which has extensively used in supramolecular chemistry[17] appears particularly attractive as a second substitution is easily achieved so numerous structural variations are reachable including systems with quadruple hydrogen-bond. Preparation of such compounds and characterization of selective association under irradiation are under progress.

CONCLUSION

We have demonstrated that simple 5-aminosusbtituted 3,3-diphenyl-naphtho[2,1-b]pyrans are excellent photochromic compounds. Conveniently substituted 5-nitrogenated naphthopyrans appear to be promising building blocks for supramolecular purpose through the use of their photoinduced carbonyl group as hydrogen-bonding acceptor group as self-assembly through hydrogen-bond of their corresponding open forms is restricted to ureido derivatives. This approach constitutes a new route toward nanosized architecture which could be reversibly influenced upon irradiation.

EXPERIMENTAL

Photochromic measurements (UV–Vis) were performed in toluene solution (5×10^{-5} M) of spectrometric grade (Aldrich) at 20 °C. The analysis cell (optical pathlength 1 cm) was placed in a thermostated copper block with magnetic stirring inside the sample chamber of a

DOI: 10.1002/poc

Table 2. Rate constants of bleaching and ratio obtained after 10 min of UV irradiation determined by NMR spectroscopy

Compounds	$^{243}k_{\Delta}$ (s^{-1})	TC/TT/CF
4b	3.22×10^{-5}	74/21/5
5b	3.46×10^{-5}	79/13/8
6b	1.16×10^{-5}	73/13/14
7b	18.0×10^{-5}	80/6/14

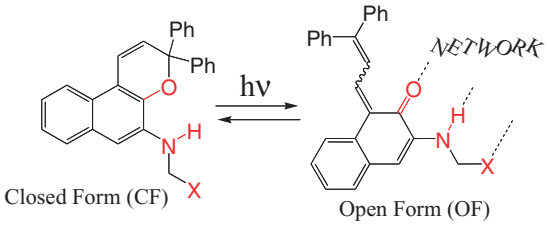


Figure 3. Photochromic process. This figure is available in colour online at www.interscience.wiley.com/journal/poc

Beckman-DU-7500-diode-array spectrometer. An Oriel 150 W high pressure Xe lamp was used for irradiation.

For NMR investigations, samples (2×10^{-3} M in toluene-d_8) were irradiated directly in the NMR tube (5 mm), thermoregulated, using a 1000 W Xe–Hg HP filtered short-arc lamp (Oriel) equipped with filter for UV irradiation (Schott 011FG09, $259<\lambda<388$ nm). After irradiation, the sample was transferred into the thermoregulated probe of a Bruker Avance-DPX or AC-300P NMR spectrometer (^{1}H, 300 MHz, ^{19}F, 282 MHz).

Flash column chromatography was performed on silica gel (Merck 40–63 μm). Melting point was determined by a melting point apparatus from Electrothermal Eng. Ltd and was uncorrected. ^{1}H and ^{13}C NMR spectra were determined on a Bruker AC 250 NMR spectrometer with $CDCl_3$ or DMSO-d_6 as solvent and TMS as internal standard ($\delta = 0$ ppm). ^{19}F NMR spectra were obtained on a Bruker (DPX 300 or AC 300) NMR spectrometer with toluene-d_8 as solvent. Mass spectra were recorded on a VG AutoSpec apparatus using electronic impact at 70 eV. Microanalyses were carried out in the microanalytical Laboratory at the CNRS, Vernaison.

Preparation of compounds

1,3,3-trifluoro-N-2-(3′hydroxynaphthyl)ethanamide (2). A mixture of 3-amino-2-naphtol (1 g, 6.28 mmol) and trifluoroacetic anhydride (1.35 g, 6.66 mmol) is dissolved in THF (40 mL) and stirred for 1 h at 65 °C. The solvent removed, the crude product was washed with water and dried. Recrystallization in ethanol affords title compound **2**. Yield 870 mg (54%); mp 243 °C; δ_H (250 MHz, DMSO-d_6): 7.3 (1H, s, H-1), 7.35 (1H, t, *J* 7.6 Hz, H-6), 7.48 (1H, t, *J* 7.6 Hz, H-7), 7.72 (1H, d, *J* 7.6 Hz, H-8), 7.85 (1H, t, *J* 7.6 Hz, H-5), 8.13 (1H, s, H-4), 10.5–10.72 (2H, br, NH and OH); δ_C (62.5 MHz, DMSO-d_6): 150.7, 140.9, 134.1, 128.8, 128.3, 127.6, 127.0, 125.7, 125.2, 124.8, 119.5, 110.9.

5-trifluoroacetamido-3,3-diphenylnaphto[2,1-b]pyrane (3a). A mixture of 1,1,1-*N*-2(3′-hydroxynaphtyl) ethanamide (**2**) (820 mg, 3.21 mmol), 1,1-diphenylpropyn-1-ol (672 mg, 3.24 mmol), and APTS (80 mg, 0.42 mmol) is dissolved in toluene (40 mL) and refluxed for 10 h. The solvent removed, the crude product was purified by flash column chromatography using CH_2Cl_2/petroleum ether (1:1) as eluent [comme éluant un mélange éther de pétrole/CH_2Cl_2 (1:1)]. The solid is then washed with pentane to afford **3** as a white solid. Yield 830 mg (58%); mp 207–208 °C; δ_H (250 MHz, DMSO-d_6): 6.27 (1H, d, *J* 10 Hz, H-2), 7.31–7.55 (13H, H-8,9,1,2′,3′,4′), 7.78 (1H, d, *J* 8.6 Hz, H-7), 7.94 (1H, d, *J* 8.6 Hz, H-10), 8.69 (1H, s, H-6), 8.87 (1H, s, NH); δ_C (62.5 MHz, DMSO-d_6): 129.2, 128.9, 128.6, 128.5, 127.2, 127.0, 125.4, 121.5, 119.6, 118.8; MS (FAB) *m/z* 446 (MH^+), 368 (M-C_6H_5).

5-trifluoroacetamido-3,3-di-(4′-fluorophenyl)naphto[2,1-b]pyrane (3b). A mixture of 1,1,1-*N*-2(3′-hydroxynaphtyl)ethanamide (**2**) (350 mg, 1.37 mmol), 1,1-di-4′fluorophenylpropyn-1-ol (325 mg, 1.37 mmol), and APTS (60 mg, 0.315 mmol) is dissolved in toluene (20 mL) and refluxed for 14 h. The solvent removed, the crude product was purified by flash column chromatography using CH_2Cl_2/hexane (1:3) as eluent. Yield 315 mg (48%); mp 203 °C; δ_H (250 MHz, DMSO-d_6): 6.27 (1H, d, *J* 10 Hz, H-2), 7.31–7.55 (13H, H-8,9,1,2′,3′,4′), 7.78 (1H, d, *J* 8.6 Hz, H-7), 7.94 (1H, d, *J* 8.6 Hz, H-10), 8.69 (1H, s, H-6), 8.87 (1H, s, NH); δ_C (62.5 MHz, DMSO-d_6): 164.6, 160.7, 145.8, 141.7, 129.9, 129.6, 129.4, 129.3, 128.7, 127.8, 126.1, 124.8, 123.1, 121.1, 116.6, 116.4, 116.2, 82.8; δ_F (toluene-d_8): -112.9; MS (FAB) *m/z* 482 (MH^+), 385 (M-C_6H_4F).

5-amino-3,3-diphenylnaphto[2,1-b]pyrane (4a). A mixture of 5-trifluoroacetamido-3,3-diphenylnaphto[2,1-b]pyrane (**3a**) (307 mg, 0.69 mmol) and potassium carbonate (600 mg, 4.34 mmol) is dissolved in a mixture of methanol (25 mL) and water (1.6 mL). The reaction mixture is then refluxed for 2 h. The solvent removed, the crude product was purified by flash column chromatography using CH_2Cl_2/petroleum ether (1:1) as eluent. The solid is then washed with pentane to afford **3** as a white solid. Yield 830 mg (58%); mp 187 °C; δ_H (250 MHz, DMSO-d_6): 5.50 (2H, s, NH_2), 6.57 (1H, d, *J* 9.9 Hz, H-2), 6.85 (1H, s, H-6), 7.03–7.34 (8H, m, H-8,9,3′,4′), 7.37 (1H, d, *J* 8.5 Hz, H-1), 7.41 (1H, d, *J* 7.6 Hz, H-7), 7.56 (4H, m, H-2′), 7.82 (1H, d, *J* 7.8 Hz, H-10); δ_C (62.5 MHz, DMSO-d_6): 138.8, 131.4, 129.2, 128.7, 127.4, 125.2, 123.2, 122.5, 121.3, 109.4; MS (FAB) *m/z* 350 (MH^+), 272 (M-C_6H_5).

DOI: 10.1002/poc

5-amino-3,3-di-4′fluorophenylnaphto[2,1-b]pyrane (4b). A mixture of **3b** (300 mg, 0.62 mmol) and potassium carbonate (520 mg, 3.76 mmol) is dissolved in a mixture of methanol (25 mL) and water (1.6 mL). The reaction mixture is then refluxed for 2 h. The solvent removed, the crude product was purified by flash column chromatography using CH_2Cl_2/petroleum ether (1:3) as eluent. The solid is then washed with pentane to afford **3** as a white solid. Yield 195 mg (81%); mp 74 °C; δ_H (250 MHz, DMSO-d_6): 5.50 (2H, s, NH_2), 6.58 (1H, d, *J* 10 Hz, H-2), 6.89 (1H, s, H-6), 7.08–7.24 (6H, m, H-8,9,2′), 7.38–7.49 (2H, m, H-1,7), 7.63 (4H, m, H-3′), 7.86 (1H, d, *J* 8.2 Hz, H-10); δ_C (62.5 MHz, DMSO-d_6): 164.6, 160.7, 142.2, 138.8, 131.5, 129.6, 128.9, 126.7, 125.3, 123.7, 123.2, 122.6, 121.6, 116.4, 115.9, 115.1, 109.4, 82.2; δ_F (toluene-d_8): -113.3; MS (FAB) *m/z* 386 (MH^+), 289 (M-C_6H_4F).

1-(3,3-diphenyl-[3H]naphtho[2,1-b]pyran)-3-octylurea (5a). To *n*-octylisocyanate (0.270 g, 1.74 mmol) in CH_2Cl_2 (3 mL) was added dropwise a solution of **4a** (0.150 g, 0.43 mmol) in CH_2Cl_2 (8 mL). The mixture was stirred at room temperature for 72 h. The solvent removed, the crude product was purified by flash column chromatography using CH_2Cl_2/petroleum ether (1:2) as eluent. Yield 0.120 g (56%); mp 181–182 °C; δ_H (250 MHz, DMSO-d_6): 0.85 (3H, t, *J* 6 Hz, CH_3), 1.38 (12H, m, C—CH_2—C), 3.10 (2H, q, *J* 5.9 Hz, N—CH_2), 6.50 (1H, d, *J* 9.9 Hz, H-2), 7.19–7.42 (8H, m, H-8,9,3′,4′), 7.47 (1H, d, *J* 10.1 Hz, H-1), 7.54 (4H, m, H-2′), 7.62 (1H, d, *J* 8.2 Hz, H-7), 7.97 (1H, d, *J* 8 Hz, H-10), 8.06 (1H, s, NH), 8.52 (1H, s, NH); δ_C (62.5 MHz, DMSO-d_6): 156.4, 145.6, 141.4, 130.4, 130.3, 130, 129.4, 128.9, 128.7, 127.9, 125.7, 125.5, 122.6, 120.8, 116.1, 115.1, 84.1, 32.6, 31, 30.1, 30, 27.8, 23.4, 15.3; MS (FAB) *m/z* 505 (MH^+), 427 (M-C_6H_5); Anal calc for $C_{34}H_{36}N_2O_2$: C, 80.92; H, 7.19; found: C, 81.02, H, 7.21.

1-(3,3-(4,4′-difluorophenyl)-[3H]naphtho[2,1-b]pyran)-3-octylurea (5b). Starting with **4b** (0.180 g, 0.467 mmol), the same procedure as for **5a** was applied with *n*-octylisocyanate (0.270 g, 1.74 mmol). Yield 0.106 g (42%); mp 185 °C; δ_H (250 MHz, DMSO-d_6): 0.85 (3H, t, *J* 6.2 Hz, CH_3), 1.1–1.58 (12H, m, C—CH_2—C), 3.12 (2H, q, *J* 5.9 Hz, N—CH_2), 6.47 (1H, d, *J* 10 Hz, H-2), 7.15–7.38 (7H, m, H-6,8,9, 2′), 7.47 (1H, d, *J* 9.8 Hz, H-1), 7.52–7.62 (4H, m, H-3′), 7.63 (1H, d, *J* 8.1 Hz, H-7), 7.98 (1H, d, *J* 8.3 Hz, H-10), 8.07 (1H, s, NH), 8.53 (1H, s, NH); δ_F (toluene-d_8): -112.75; MS (FAB) *m/z* 541 (MH^+), 444 (M-C_6H_4F). Anal calc for $C_{34}H_{34}F_2N_2O_2$: C, 75.53; H, 6.34; found: C, 75.41, H, 6.23.

1-(3,3-diphenyl-[3H]naphtho[2,1-b]pyran-5-amino)-octan-2-one (6a). A solution of **4a** (0.170 g, 0.487 mmol) and 1-bromooctan-2-one (0.360 g, 1.74 mmol) in THF (10 mL) was stirred at room temperature for 24 h. The solvent removed, the crude product was purified by flash column chromatography using CH_2Cl_2/petroleum ether (1:2) as eluent. Yield 0.100 g (43%); mp 146–147 °C; δ_H (250 MHz, $CDCl_3$): 0.88 (3H, t, *J* 6.2 Hz, CH_3), 1.31 (6H, m, C—CH_2—C), 1.66 (2H, qu, *J* 7.0 Hz, CO—C—CH_2), 2.54 (2H, t, *J* 7.1 Hz, CO—CH_2), 4.09 (2H, d, *J* 6.3 Hz, N—CH_2—CO), 5.58 (1H, t, *J* 6.5 Hz, NH), 6.27 (1H, d, *J* 10 Hz, H-2), 6.62 (1H, s, H-6), 7.15–7.40 (10H, m, H-1,7,8,9, 3′,4′), 7.47 (4H, m, H-2′), 7.84 (1H, d, *J* 8.3 Hz, H-10); δ_C (62.5 MHz, $CDCl_3$): 155.1, 148.2, 145.1, 136.2, 129.3, 128.8, 128.1, 127.9, 127.2, 126.3, 124, 121.9, 120.1, 119.6, 105.4, 53.2, 41, 32.1, 28.8, 24.1, 23; MS (FAB) *m/z* 476 (MH^+), 398 (M-C_6H_5), 362 (ArNHCH$_2$); Anal calc for $C_{33}H_{33}NO_2$: C, 83.33; H, 6.99; found: C, 83.48, H, 7.04.

1-(3,3-(4,4′-difluorophenyl)-[3H]naphtho[2,1-b]-pyran-5-a-mino)-octan-2-one (6b). Starting with **4b** (0.150 g, 0.311 mmol), the same procedure as for **6a** was applied with 1-bromooctan-2-one (0.250 g, 1.20 mmol) and stirring for 72 h. Yield 0.060 g (38%); mp 148 °C; δ_H (250 MHz, DMSO-d_6): 0.88 (3H, t, *J* 6.2 Hz, CH_3), 1.42 (6H, m, C—CH_2—C), 1.70 (2H, qu, *J* 7.3 Hz, CO—C—CH_2), 2.60 (2H, t, *J* 7.1 Hz, CO—CH_2), 4.10 (2H, d, *J* 6.3 Hz, N—CH_2—CO), 5.58 (1H, t, *J* 6.5 Hz, NH), 6.27 (1H, d, *J* 10.1 Hz, H-2), 6.65 (1H, s, H-6), 6.93–7.12 (4H, m, H-2′), 7.25–7.36 (3H, m, H-1,8,9), 7.39–7.55 (4H, m, H-3′), 7.58 (1H, d, *J* 8.1 Hz, H-7), 7.88 (1H, d, *J* 8.2 Hz, H-10); δ_F (toluene-d_8): -113.35; MS (FAB) *m/z* 512 (MH^+), 415 (M-C_6H_4F), 398 (ArNHCH$_2$); Anal calc for $C_{33}H_{31}F_2NO_2$: C, 77.42; H, 6.11; found: C, 77.49, H, 6.12.

2,4-dichloro-6-(3,3-diphenyl-[3H]naphtho[2,1-b]-pyran-5-a-mino)-1,3,5-triazine (7a). A solution of cyanuric acid (0.084 g, 0.455 mmol) and THF (5 mL) under nitrogen was stirred at 0 °C. **4a** (0.150 g, 0.430 mmol) in THF (5 mL) was added dropwise and *N*,*N*-diisopropylethylamine (0.056 g, 0.434 mmol) was then added to the solution. The mixture was stirred at 25 °C for 2 h. The solvent evaporated, the crude product was purified by flash column chromatography using CH_2Cl_2/petroleum ether (2:3) as eluent. Yield 0.130 g (61%); mp 250–252 °C; δ_H (250 MHz, DMSO-d_6): 6.62 (1H, d, *J* 10 Hz, H-2), 7.17–7.35 (6H, m, H-3′,4′), 7.36–7.48 (5H, m, H-1,2′), 7.49–7.61 (2H, m, H-8,9), 7.86 (1H, s, H-6), 7.93 (1H, d, *J* 8.5 Hz, H-7), 8.14 (1H, d, *J* 8.5 Hz, H-10), 11.11 (1H, s, NH); MS (LSIMS) *m/z* 498.4 (MH^+); Anal calc for $C_{28}H_{18}Cl_2N_4O$: C, 67.61; H, 3.65; found: C, 67.75, H, 3.59.

2,4-dichloro-6-(3,3-(4,4′-difluorophenyl)-[3H]naphtho[2,1-b]pyran-5-amino)-1,3,5-triazine (7b). Starting with **4b** (0.100 g, 0.260 mmol), the same procedure as for **7a** was applied with cyanuric acid (0.052 g, 0.28 mmol). Yield 0.057 g (42%); mp 182 °C; δ_H

DOI: 10.1002/poc

(250 MHz, DMSO-d_6): 6.62 (1H, d, J 9.8 Hz, H-2), 7.08–7.28 (4H, m, H-2′), 7.38–7.68 (7H, m, H-3′,1,8,9), 7.88 (1H, d, J 8.5 Hz, H-7), 7.97 (1H, s, H-6), 8.19 (1H, d, J 8.4 Hz, H-10), 11.31 (1H, s, NH); δ_F (toluene-d_8): -112.7; MS (LSIMS) m/z 534.4 (MH^+); Anal calc for $C_{28}H_{16}Cl_2F_2N_4O$: C, 63.05; H, 3.02; found: C, 62.97, H, 3.00.

Acknowledgements

The 300 MHz NMR facilities were funded by the Region Nord-Pas-de-Calais, the Ministère de la Jeunesse, de l'Education Nationale et de la Recherche, and FEDER. This collaborative work was realized within the framework CNRS GDR 2466. S. D. and J-L P. acknowledge 'Phenics' (**Ph**otoswitchable Orga**nic** Molecular Systems & Device**s**) GDRI CNRS n 93 for financial support and G. V. is indebted to the French Embassy in Japan, for the financial support, during Japan-French Seminar in Japan.

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DOI: 10.1002/poc