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Synthesis and Photochromism of Novel Pyridyl Substituted Naphthopyrans

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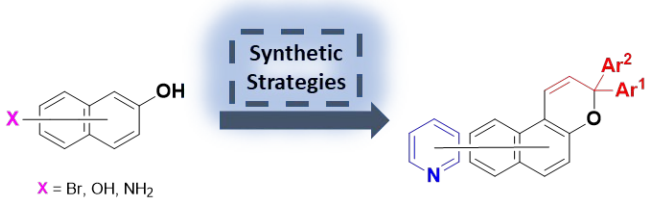


Abstract – Multi-target synthetic strategies to access novel photochromic 3*H*-naphtho[2,1-*b*]pyrans decorated with pyridyl units are described. The new pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans display good photochromic properties with the reversible generation of photomerocyanines which exhibit mainly orange/red hues. Photochromic parameters including photocolourability and persistence of colour vary tremendously on structural modification of the naphthopyran core.

Keywords: Naphthopyrans, Benzochromenes, Heterocycles, Synthesis, Photochromism

Introduction

Photochromism is succinctly defined as the light-induced reversible transformation of a chemical entity into one or more isomeric species that possess different absorption spectra.[1] Photochromism occurs in both organic and inorganic compounds, as well in biological

systems.[2] Major organic photochromic families include diarylethenes,[3] naphthopyrans (benzochromenes),[4] spiropyrans,[5] spirooxines,[6] benzopyrans (chromenes),[7] azobenzenes,[8] stilbenes,[9] anils,[10] viologens,[11] fulgides,[12] and flavyliums.[13] The coloured transient species resulting from a photochromic reaction can possess different physicochemical properties, such as, luminescence, electron conductivity, refractive index, dielectric constant, oxidation/reduction potential and geometry in addition to the expected colour change.[14] As a result, photochromic molecules have been widely employed as switches to modulate various physical properties e.g. conductance, shape, viscosity, fluorescence, in addition to their inherent colour switching.[15] Photochromes have been applied in many fields such as optical information storage media, ophthalmic lenses, chemical sensors and intelligent stimuli-responsive materials.[15,16,17] Naphthopyrans although possessing interesting biological activities,[18] are essentially known for their photochromic properties as they are one the most commercially important classes of photochromic molecules.[19] In this regard, naphthopyrans have been applied to commercially available ophthalmic photochromic sun and contact lenses.[20] Other commercial applications of naphthopyrans include fuel and security markers,[21] UV light intensity indicators,[22] solar cell sensitizer dyes[23] and hair dyes.[24] The commercial success of naphthopyrans can be attributed to the fact that functional groups can be readily introduced in a cost-effective way allowing a wide range of hues that span across the visible spectrum from yellows to blues.[19] Of the three isomeric *geminal* diaryl substituted naphthopyrans, the linear isomer 2*H*-naphtho[2,3-*b*]pyran displays no significant photochromic response at ambient temperature (Figure 1).[25] On the other hand, 2*H*-naphtho[1,2-*b*]pyran and 3*H*-naphtho[2,1-*b*]pyran have received much attention since they display good photochromic properties in both solution and polymers under ambient conditions.[26]

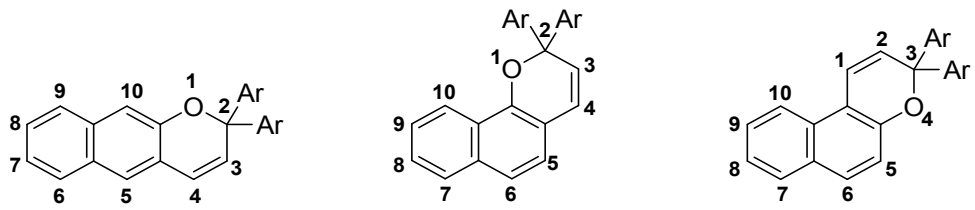


Figure 1. Isomeric geminal diaryl substituted naphthopyrans

Naphthopyrans are the stable colourless ground state heterocycles that undergo a photoinduced electrocyclic ring-opening to the corresponding open-forms, the photomerocyanines, which due to the extended delocalized π-system absorb at a longer wavelength, typically in the visible region (Figure 2).[27,28]

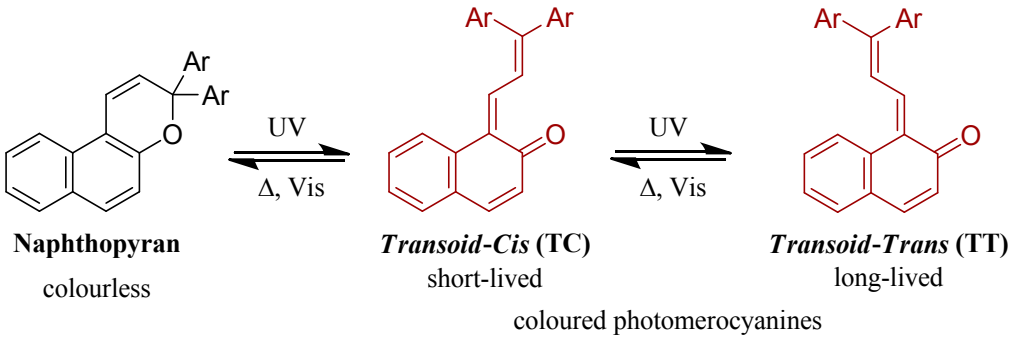
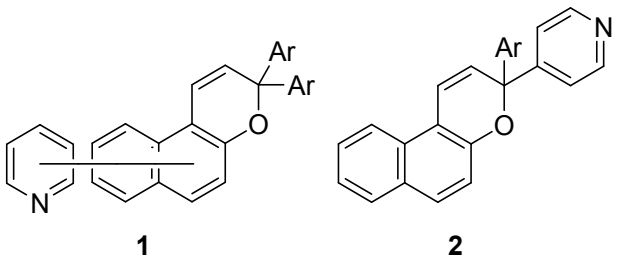


Figure 2. Photoisomerization of 3*H*-naphtho[2,1-*b*]pyran

In recent years, there has been a significant interest in developing transition metal containing photochromic complexes that can perform multi-responsive tasks.[29] The major organic photochromic families have been employed to modulate the physical and chemical properties of transition metal complexes,[30] however naphthopyrans have yet to receive attention as photoresponsive ligands. In this work, we devise and implement multi-target synthetic strategies to obtain novel naphthopyrans decorated with pyridyl units, and to characterize their photochromic response. It was envisioned that the foregoing pyridyl substituted naphthopyrans

1 and **2** could be employed as 'dynamic' ligands in transition metal complexes for a variety of applications (Figure 3).



1 **2**

Figure 3. Target pyridyl substituted naphthopyrans

When conceiving strategies for the preparation of the pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans different factors were considered e.g. the starting material availability and price, the predicted overall yield, and the number of steps for a given pathway. A straightforward strategy (**Strategy A**) involved performing Suzuki cross-coupling reactions, after 'chromenization',[31] between the pyridylboronic acids **3** and either the halo- or pseudo halo- substituted naphthopyrans **4** (Figure 4). Furthermore, the naphthopyran precursors **4** would be prepared by a variant of the established acid-catalysed condensation between the appropriate 1,1-diarylprop-2-yn-1-ols **5** and the 2-naphthols **6**.[32] The foregoing strategy was employed to the forward synthesis of the 10-, 9-, 8-, 7- and 5-pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans. Incorporation of either basic or electron-withdrawing groups at C-3 of the 3*H*-naphtho[2,1-*b*]pyrans by acid-catalysed condensation between 2-naphthol and the corresponding prop-2-yn-1-ol has been previously accomplished only in very poor yields.[33] Inspired by the work of Putala *et al.*,[34] it was envisioned that a Heck cross-coupling reaction could be employed to prepare the 3-pyridyl-3*H*-naphtho[2,1-*b*]pyrans **7** from commercially available and easily attainable 1-halo-2-naphthols **8** (**Strategy B**). Furthermore, it was envisioned an additional strategy (**Strategy C**) that involved effecting a late-stage 'chromenization' by the acid-catalysed cyclization of the alkene **9**, the latter prepared by the Heck cross-coupling reaction

between the appropriate prop-2-en-1-ol **10** and the 1-halo-4-pyridyl-2-naphthol **11**. This route would require the synthesis of the Heck coupling partner **11** by the regioselective halogenation of pyridyl-2-naphthol **12**, the latter prepared by an early-stage Suzuki cross-coupling reaction. The foregoing strategy was employed to the forward synthesis of the 6-pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans.

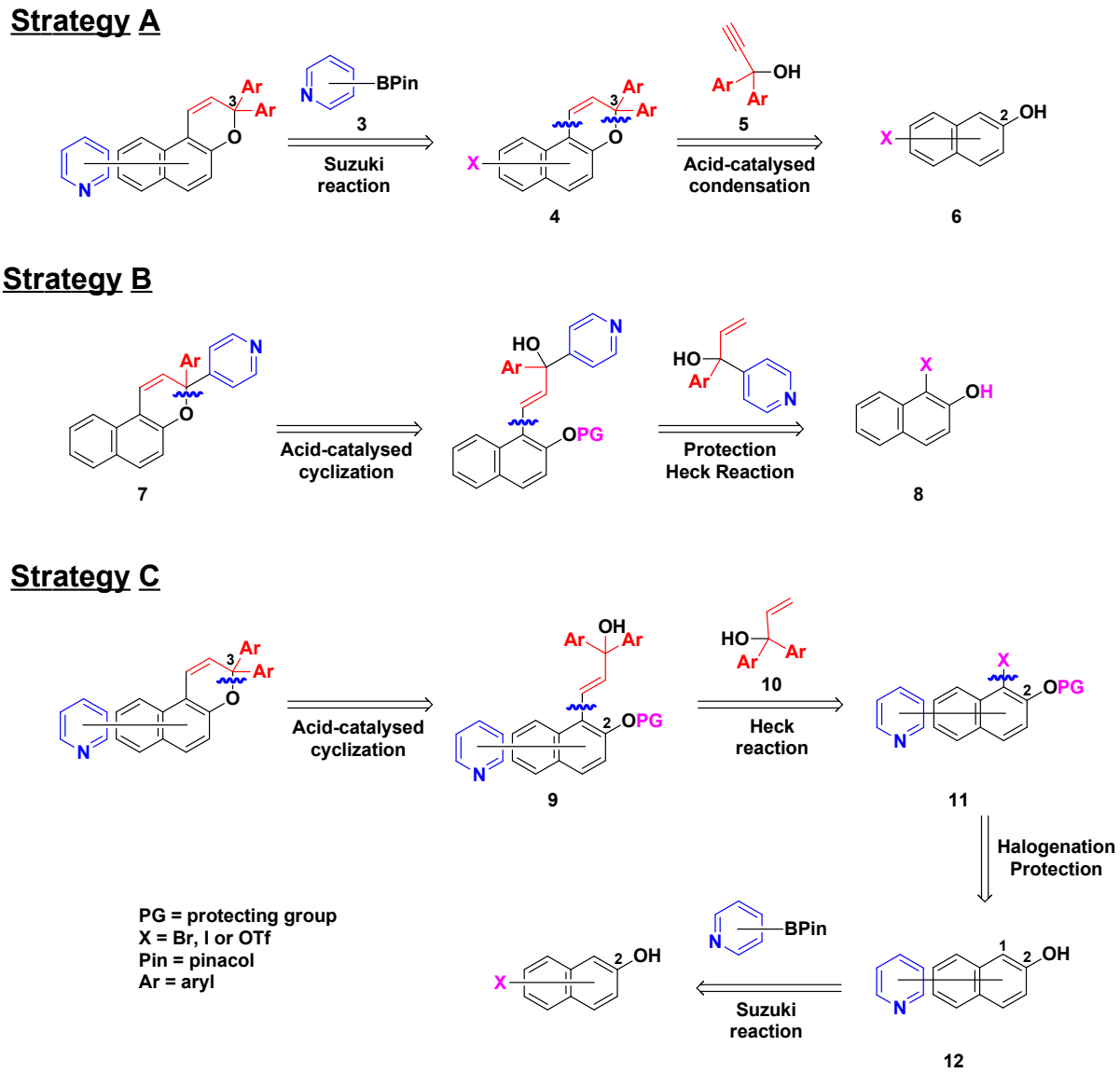


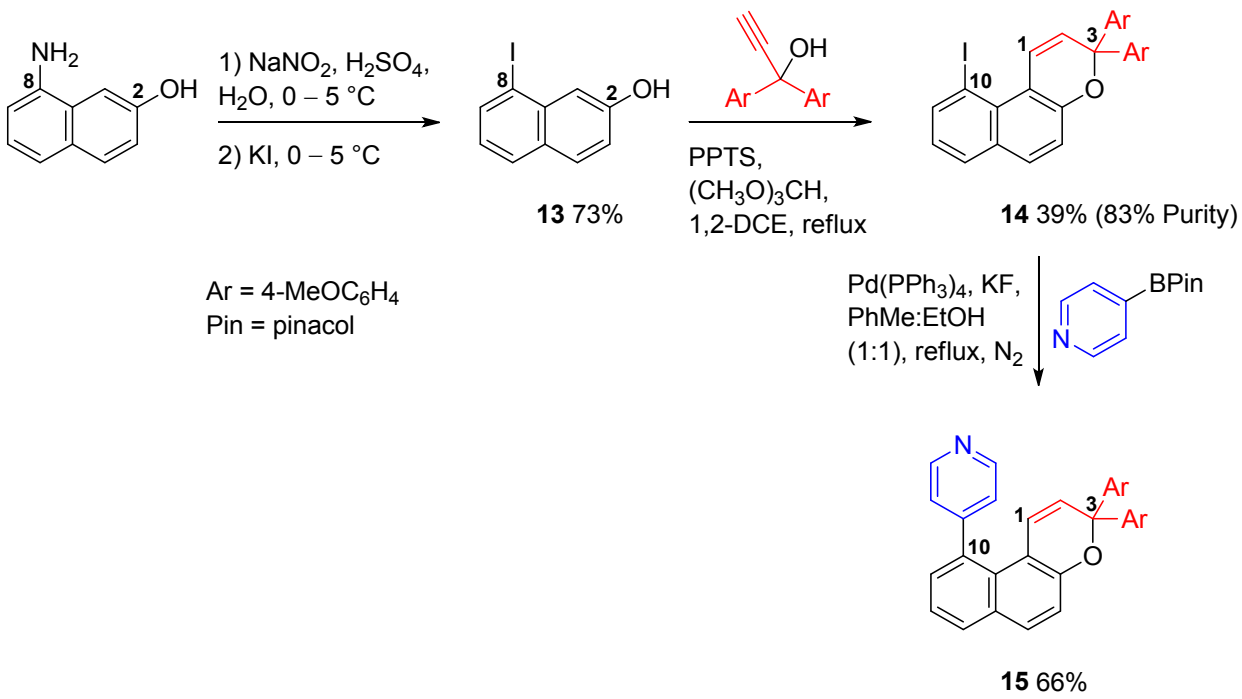
Figure 4. Retrosynthesis of the pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans

There was no interest in synthesizing naphthopyrans with pyridyl substituents at C-1 and C-2 of the naphthopyran scaffold in the present work as it was predicted that the resulting photochromes would show poor colorability under UV irradiation at room-temperature.[35]

Results and Discussion

Synthesis of 10-pyridyl-3*H*-naphtho[2,1-*b*]pyrans (Strategy A)

To prepare the 10-pyridyl-3*H*-naphtho[2,1-*b*]pyrans, it was first necessary to synthesize an 8-halo-2-naphthol, as 8-iodo-2-naphthol was not commercially available and 8-bromo-2-naphthol was expensive. Thus, 8-iodo-2-naphthol **13** was obtained in good yield (73%) from the commercially available and comparatively cheaper 8-amino-2-naphthol by a Sandmeyer-type reaction (Scheme 1).[36] To access the 10-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **15**, the precursor 10-iodo-3*H*-naphtho[2,1-*b*]pyran **14** was first prepared by the acid-catalysed condensation between 8-iodo-2-naphthol **13** and the readily available 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol, following a modification of a procedure from Carreira and co-worker.[32] The poor yield (39%) was attributed to decomposition of the iodonaphthopyran during the column chromatography separation. Even though it was isolated with only approximately 83% purity, due its proclivity to decomposition, it was used directly in the next step without further purification. The Suzuki cross-coupling reaction between **14** and 4-pyridineboronic acid pinacol ester afforded the 10-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **15** in good yield (66%) after 5 days of reflux.[37] By ^{1}H NMR spectroscopy it was determined that 1-H, that usually resonates as a doublet at *ca.* 7.3 ppm,[38] appeared upfield at 6.01 ppm as it was shielded by the induced anisotropic field from the pyridyl substituent at C-10.



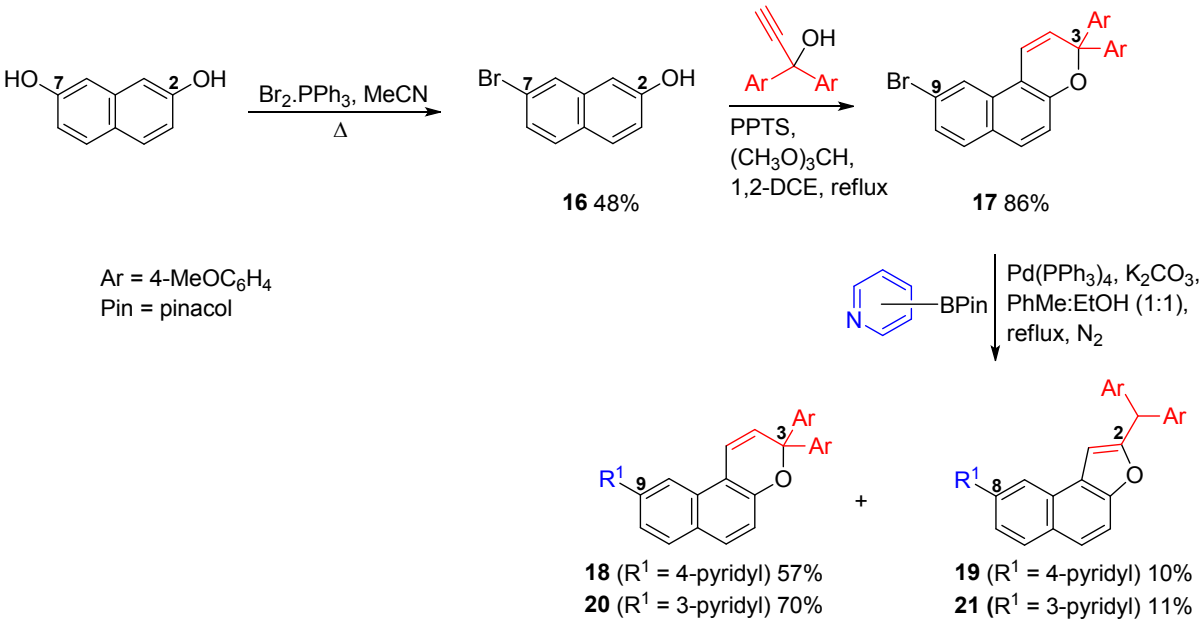
Scheme 1. Synthesis of 10-pyridyl-3*H*-naphtho[2,1-*b*]pyran 15

Overall, 10-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **15** was synthesized from 8-amino-2-naphthol in a three step linear route in 19% yield.

Synthesis of 9-pyridyl-3*H*-naphtho[2,1-*b*]pyrans (Strategy A)

The commercially available and relatively inexpensive 2,7-dihydroxynaphthalene was chosen as starting material for the synthesis of the 9-pyridyl-3*H*-naphtho[2,1-*b*]pyrans. In a first route (Route A), the transformation of 2,7-dihydroxynaphthalene into 7-bromo-2-naphthol **16** was accomplished by reacting the former with a triphenyldibromophosphorane intermediate, formed *in situ* by mixing Br_2 and triphenylphosphine in acetonitrile, followed by heating, affording the desired product **16** in 48% yield (Scheme 2).[39] The acid-catalysed condensation between **16** and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol led to the isolation of the 9-bromo-3*H*-naphtho[2,1-*b*]pyran **17** in very good yield (86%). Suzuki cross-coupling reactions between either 4- or 3- pyridineboronic acid pinacol esters and **17** afforded the corresponding 9-pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans **18** and **20** in fair to good yields (57 – 70%).[40] Besides the desired targets, minor amounts of the naphthofurans **19** and **21** (10 – 11%) were isolated as by-

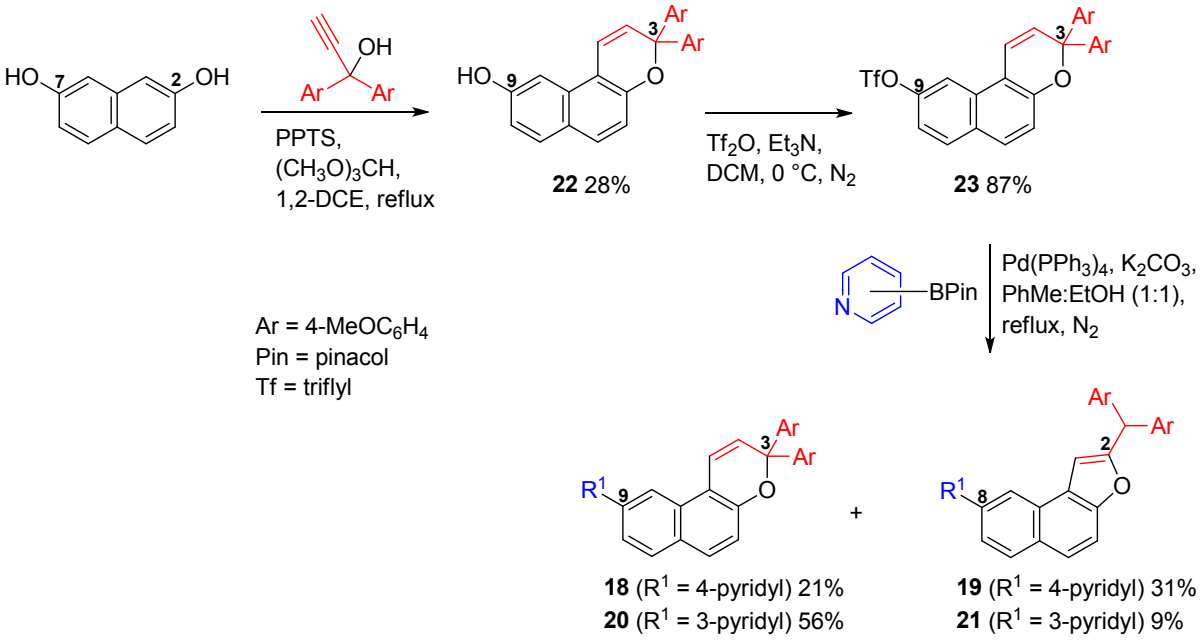
products of the Suzuki reactions, being the result of the ring-contraction of the 9-pyridyl-3*H*-naphtho[2,1-*b*]pyrans.[37] The slightly fluorescent non-photochromic naphthofurans are structural isomers of the corresponding 9-pyridyl-3*H*-naphtho[2,1-*b*]pyrans, and their formation, during the Suzuki cross-coupling reactions, made it extremely complicated to purify each of the 9-pyridyl-3*H*-naphtho[2,1-*b*]pyrans and the corresponding naphthofurans by flash column chromatography as a consequence of their similar R_F values on a variety of TLC plates and solvent systems.



Scheme 2. Synthesis of 9-pyridyl-3*H*-naphtho[2,1-*b*]pyrans 18 and 20 (Route A)

In an alternative route (Route B), the acid-catalysed condensation between 2,7-dihydroxynaphthalene and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol afforded the target 9-hydroxy-3*H*-naphtho[2,1-*b*]pyran **22** in poor yield (28%) which was a result of the poor regioselectivity of the reaction, in conformity with literature observations (Scheme 3).[41] Treatment of **22** with triflic anhydride in the presence of triethylamine generated the 9-triflyloxy-3*H*-naphtho[2,1-*b*]pyran **23** in very good yield (87%).[42] Suzuki cross-coupling reactions between either 4- or 3- pyridineboronic acid pinacol esters and **23** rendered the corresponding 9-pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans **18** and **20** in poor to fair yields

(21 – 56%). Besides the desired targets, the corresponding naphthofurans **19** and **21** were again isolated from the Suzuki reactions (9 – 31%).



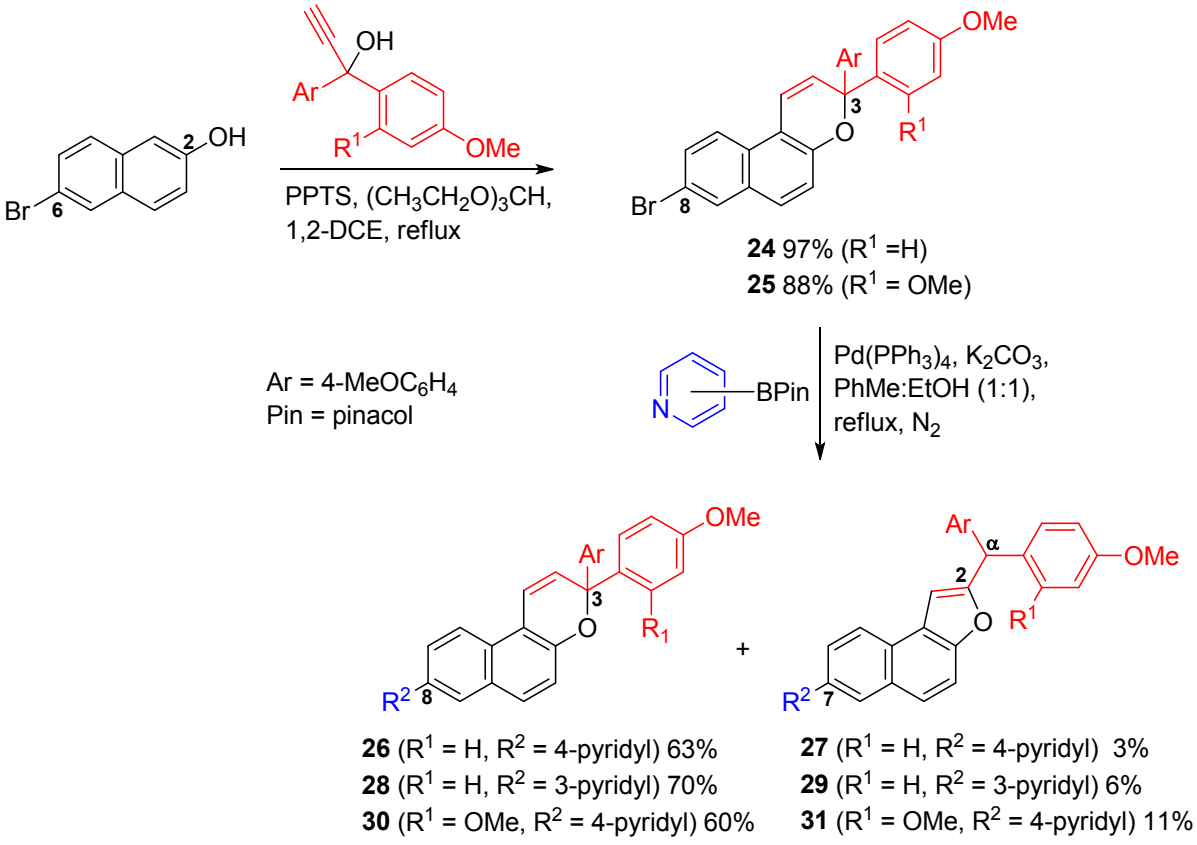
Scheme 3. Synthesis of 9-pyridyl-3*H*-naphtho[2,1-*b*]pyrans 18 and 20 (Route B)

In summary, Route A afforded the 9-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **18** and 9-(3-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **20** in a three step linear route in 24% and 29% yield, respectively. On the other hand, Route B afforded the 9-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **18** and 9-(3-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **20** in a three step linear route in 5% and 14% yield, respectively. As a result, Route A provided the desired targets with a higher overall yield in the same number of steps when compared to Route B. Interestingly, 9-triflyloxy-3*H*-naphtho[2,1-*b*]pyran **23** has proven to be a less effective coupling partner than 9-bromo-3*H*-naphtho[2,1-*b*]pyran **17**, since the yield of the Suzuki cross-coupling reaction involving the former (21 – 56%) was lower than the latter (57 – 70%).

Synthesis of 8-pyridyl-3*H*-naphtho[2,1-*b*]pyrans (Strategy A)

The synthesis of the 8-pyridyl-3*H*-naphtho[2,1-*b*]pyrans was accomplished by starting from the inexpensive and commercially available 6-bromo-2-naphthol. The acid-catalysed

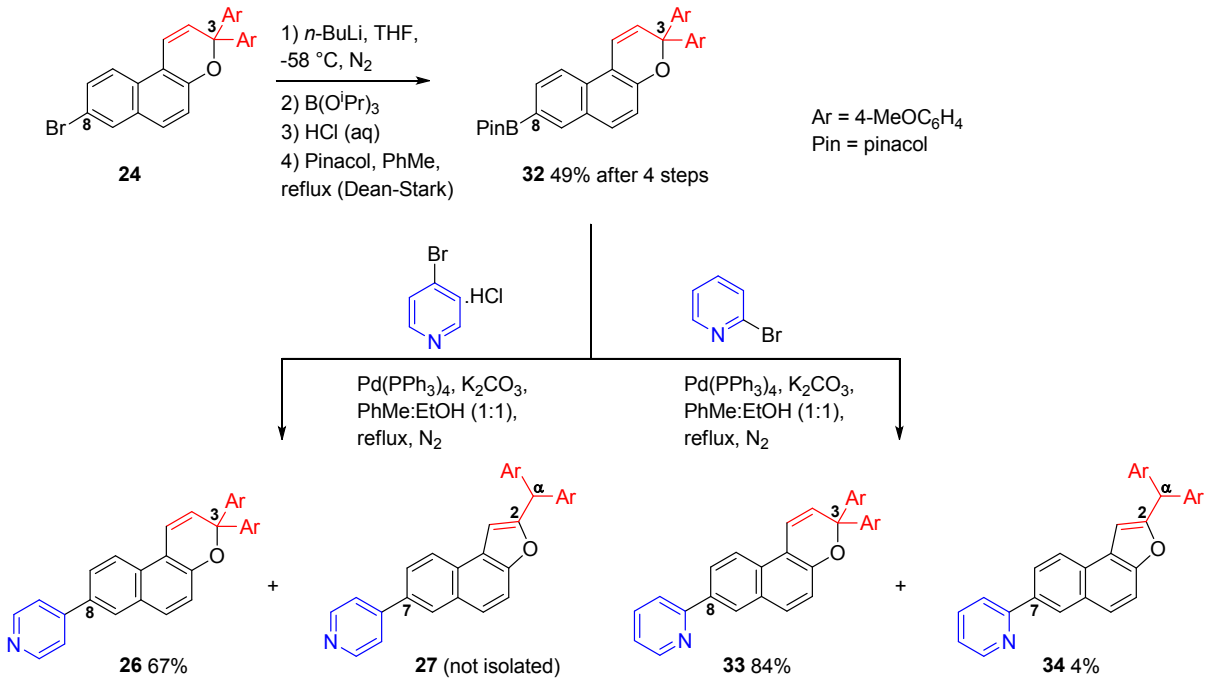
condensation between 6-bromo-2-naphthol and either 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol or 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol afforded the 8-bromo-3*H*-naphtho[2,1-*b*]pyrans **24** and **25** in very good yields (88 – 97%) (Scheme 4). Suzuki cross-coupling reactions between either 4- or 3- pyridineboronic acid pinacol esters and the 8-bromo-3*H*-naphtho[2,1-*b*]pyrans **24** and **25** led to the corresponding 8-pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans **26**, **28** and **30** in fair to good yields (60 – 70%). Besides the desired targets, the corresponding naphthofurans **27**, **29** and **31** were again isolated (3 – 11%), after extensive flash column chromatography separations, being the result of the ring-contraction of the 8-pyridyl-3*H*-naphtho[2,1-*b*]pyrans. In summary, 8-pyridyl-3*H*-naphtho[2,1-*b*]pyrans **26**, **28** and **30** were prepared in a two step linear route from 6-bromo-2-naphthol in 53 – 68% yield.



Scheme 4. Synthesis of 8-pyridyl-3*H*-naphtho[2,1-*b*]pyrans 26, 28 and 30

The frailty of pyridine-2-boronic acids under Suzuki cross-coupling conditions is known.[43] Given this fact, it was envisioned that the 8-(2-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **33** could be

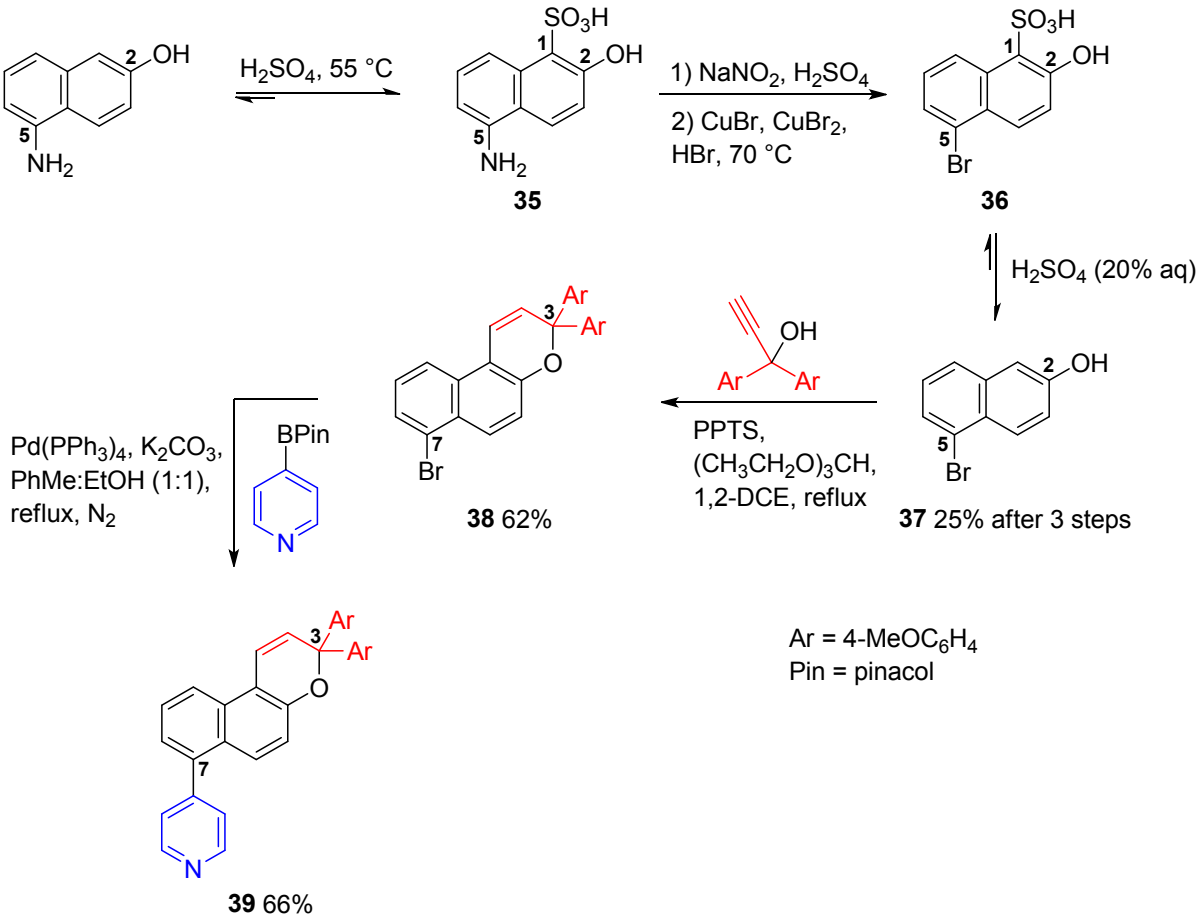
prepared by the Suzuki cross-coupling reaction between the inverted coupling partners 8-boronyl-3*H*-naphtho[2,1-*b*]pyran **32** – prepared from the borylation of 8-bromo-3*H*-naphtho[2,1-*b*]pyran **24** – and the stable 2-bromopyridine. The boronic acid was first prepared from 8-bromo-3*H*-naphtho[2,1-*b*]pyran **24** by a two-step metalation protocol,[44] and then esterified with pinacol affording the 8-boronyl-3*H*-naphtho[2,1-*b*]pyran **32** in 49% yield after four steps (Scheme 5). Hence, **32** was successfully coupled to 4-bromopyridine, liberated from its hydrochloride salt by the addition of excess base, under Suzuki-Miyaura conditions, affording the 8-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **26** in 67% yield. The corresponding naphthofuran **27** was formed during the reaction but it was not isolated in this instance. In a similar fashion, Suzuki cross-coupling reaction between **32** and 2-bromopyridine rendered the 8-(2-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **33** in very good yield (84%). Once again, the corresponding naphthofuran **34** was isolated as a by-product (4%). In summary, 8-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **26** was prepared from 6-bromo-2-naphthol in a five step linear route, via a two-step metalation protocol, in 32% yield and similarly 8-(2-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **33** was prepared from 6-bromo-2-naphthol in a five step linear route in 40% yield.



Scheme 5. Synthesis of 8-pyridyl-3*H*-naphtho[2,1-*b*]pyrans 26 and 33

Synthesis of 7-pyridyl-3*H*-naphtho[2,1-*b*]pyrans (Strategy A)

For the synthesis of the 7-pyridyl-3*H*-naphtho[2,1-*b*]pyrans it was first necessary to prepare 5-bromo-2-naphthol **37** as it was not commercially available. The latter was derivatized from the readily accessible 5-amino-2-naphthol by a Sandmeyer reaction. Thus, 5-bromo-2-naphthol **37** was prepared in three steps from 5-amino-2-naphthol in 25% overall yield following a literature procedure described by Abelt *et al*. (Scheme 6).[45] First, the sulfonation of 5-amino-2-naphthol, by treatment with H_2SO_4, generated 1-sulfonyl-5-amino-2-naphthol **35**. The sulfonyl group at C-1 was intended to favour the Sandmeyer reaction and block this activated position from potential complications arising from azo-coupling. The Sandmeyer reaction of **35** generated 1-sulfonyl-5-bromo-2-naphthol **36**, which was immediately hydrolysed to 5-bromo-2-naphthol **37** by treatment with aq. H_2SO_4. The acid-catalysed condensation between **37** and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol afforded the 7-bromo-3*H*-naphtho[2,1-*b*]pyran **38** in 62% yield. Hence, the Suzuki cross-coupling reaction between **38** and 4-pyridineboronic acid pinacol ester afforded the 7-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **39** in fair yield (66%). Similar to previous Suzuki cross-coupling reactions, the naphthofuran derived from the ring-contraction of **39** was formed as a by-product of the reaction, but could not be isolated in a pure state.

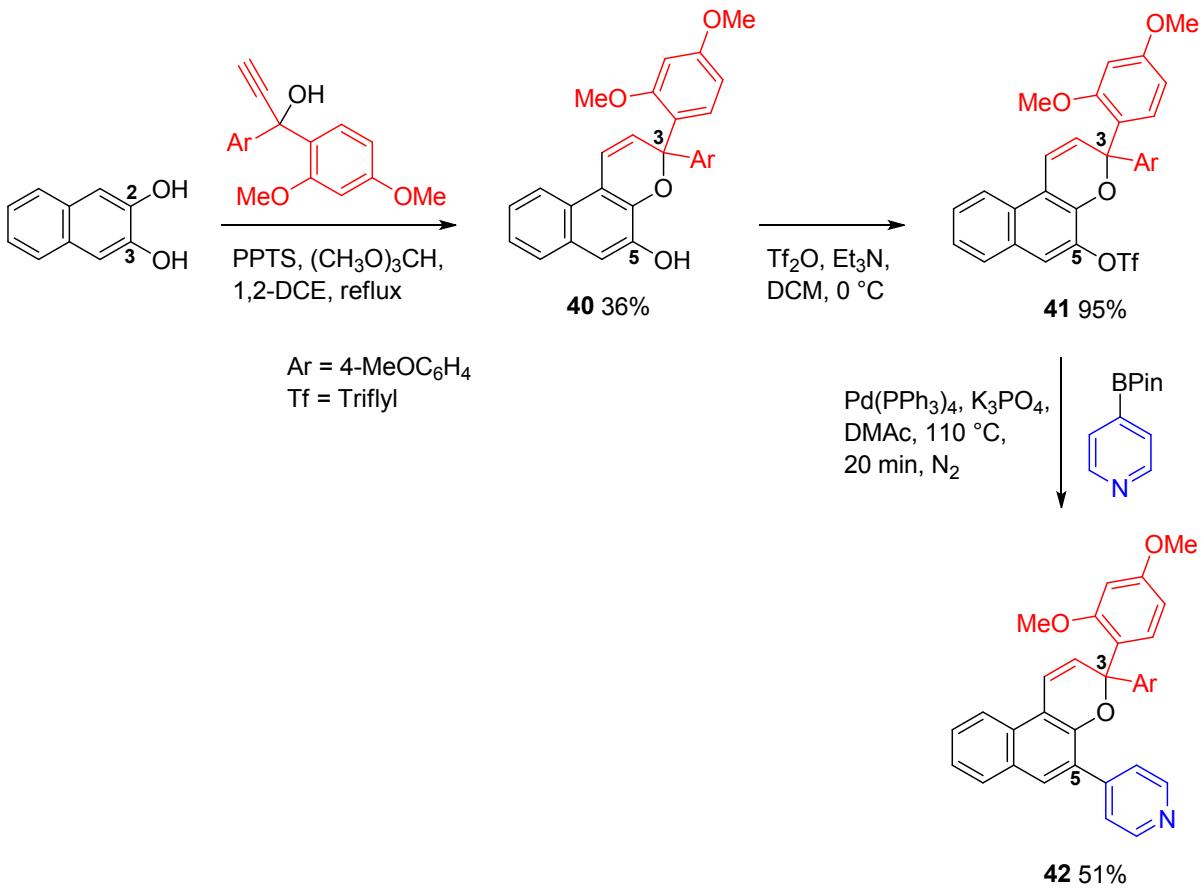


Scheme 6. Synthesis of 7-pyridyl-3*H*-naphtho[2,1-*b*]pyran 39

In summary, 7-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **39** was prepared from 5-amino-2-naphthol in a five step linear route in 10% yield.

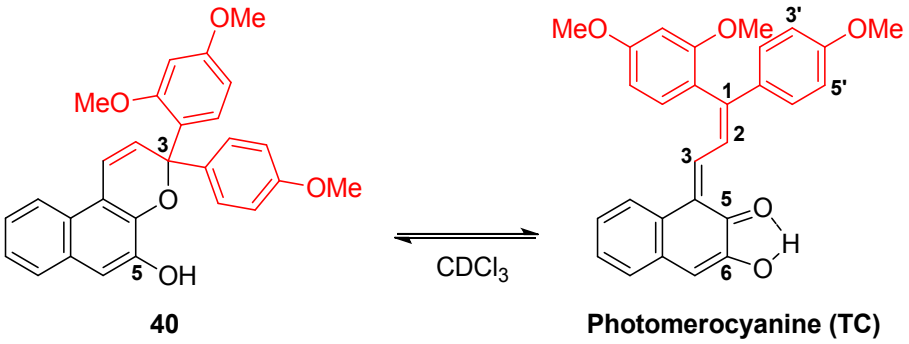
Synthesis of 5-pyridyl-3*H*-naphtho[2,1-*b*]pyrans (Strategy A)

The widely available and relatively inexpensive 2,3-dihydroxynaphthalene was used as the starting material for the synthesis of the 5-pyridyl-3*H*-naphtho[2,1-*b*]pyrans. The acid-catalysed condensation between 2,3-dihydroxynaphthalene and 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol afforded the 5-hydroxy-3*H*-naphtho[2,1-*b*]pyran **40** in 36% yield (Scheme 7). Similar to the 'chromenization' of 2,7-dihydroxynaphthalene, the poor yield was attributed to the poor regioselectivity of the reaction.



Scheme 7. Synthesis of 5-pyridyl-3*H*-naphtho[2,1-*b*]pyran 42

Moreover, 5-hydroxy-3*H*-naphtho[2,1-*b*]pyran **40** forms a naphthopyran : photomerocyanine (85 : 15) equilibrium mixture in $CDCl_3$, due to the particular stabilizing hydrogen-bond formation in the photomerocyanine (Scheme 8). This hypothesis is supported by the ^{1}H NMR spectrum of the mixture that clearly shows a doublet at 8.95 ppm (J = 12 Hz) corresponding to the resonance of 2-H of the *transoid-cis* (TC), a doublet at 6.87 ppm (J = 8.9 Hz) corresponding to the resonance of 3′, 5′-H protons (anisyl) and three singlets at 3.65, 3.85 and 3.93 ppm corresponding to the resonance of the methoxy hydrogens (TC) (Figure S41). The doublet (J = 12 Hz) corresponding to the resonance of 3-H (TC) is underneath a multiplet at 7.85 ppm, and it is identified by COSY NMR as it correlates with 2-H (TC) (Figures S43 and S44). The chemical shifts and coupling constants of the signals shown in Figure S41 are identical to the signals from ^{1}H NMR spectra of analogous photomerocyanines reported in the literature.[46]



40 **Photomerocyanine (TC)**

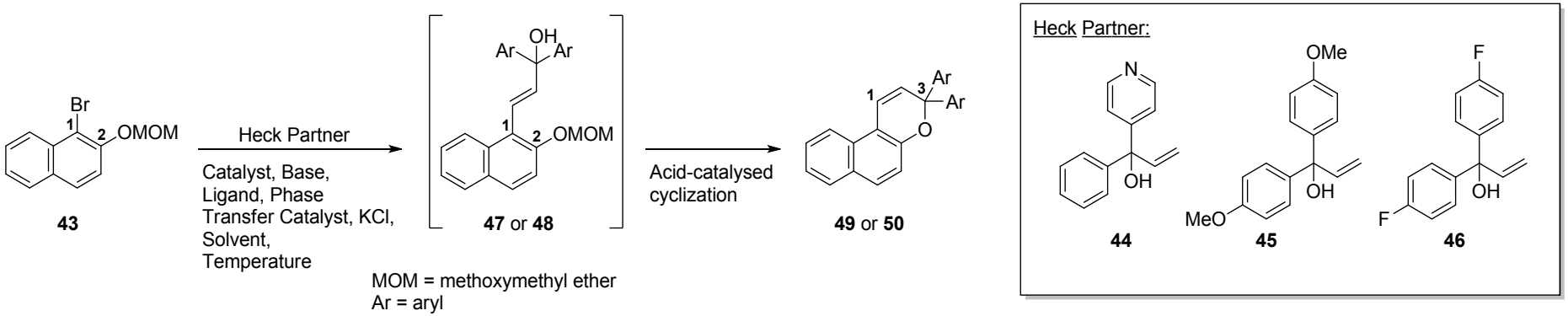
Scheme 8. Equilibration of 5-hydroxy-3*H*-naphtho[2,1-*b*]pyran 40 in $CDCl_3$ solution

Triflation of 5-hydroxy-3*H*-naphtho[2,1-*b*]pyran **40** afforded the 5-triflyloxy-3*H*-naphtho[2,1-*b*]pyran **41** in excellent yield (95%) – the photomerocyanine was no longer discernible in the ^{1}H NMR spectrum in $CDCl_3$ as no hydrogen bond could be established. Suzuki cross-coupling reaction between **41** and 4-pyridineboronic acid pinacol ester rendered the desired 5-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **42** in fair yield (51%). Overall, 5-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **42** was prepared from 2,3-dihydroxynaphthalene in a three step linear route in 17% yield.

Synthesis of 3-pyridyl-3*H*-naphtho[2,1-*b*]pyrans (Strategy B)

For the synthesis of the 3-pyridyl-3*H*-naphtho[2,1-*b*]pyrans, the commercially available 1-bromo-2-naphthol was used as starting material. In order to facilitate the key Heck cross-coupling reaction, the hydroxyl group of 1-bromo-2-naphthol was first protected as a methoxymethyl ether by reaction with chloromethyl methyl ether to afford **43** in excellent yield (99%).[47] A successful Heck reaction between **43** and prop-2-en-1-ol **44**, derived from the addition of vinylmagnesium chloride to 4-benzoylpyridine, resulted in the formation of **47** in moderate yield (41%), when employing $Pd(OAc)_2$ (8 mol%), K_2CO_3 (1.5 equiv), TBAB (1.5 equiv), KCl (1 equiv) in DMF at 100 °C (Scheme 9; Entry 1, Table 1).[48] In order to understand the scope of the reaction, the same phosphine-free conditions were applied to the Heck reaction between **43** and the more electron-rich prop-2-en-1-ol **45**. However, these conditions proved

to be less effective as the Heck product **48** was isolated in very poor yield (9%) (Scheme 9; Entry 2, Table 1). When employing $Pd(OAc)_2$ (5 mol%), *N*-methyldicyclohexylamine [Cy_2NMe] (1.5 equiv), PPh_3 (10 mol%), TBAC (11 mol%) in DMAc at 80 °C, the Heck adduct **48** was again isolated in very poor yield (8%) (Scheme 9; Entry 3, Table 1). It was rationalized that by mixing $Pd(dba)_2$ (2 mol%) with tri-*tert*-butylphosphonium tetrafluoroborate [TTBP·HBF_4] (4 mol%), the very active bis(tri-*tert*-butylphosphine)palladium(0) (Pd(*t*-$Bu_3P)_2$) would be formed *in situ*. The *t*-Bu_3P is a strong electron-rich phosphine ligand that stabilise proficiently the palladium(II) salt obtained from the oxidative addition step.[49] On the other hand, the bulkiness of the *t*-Bu_3P favours the reductive elimination step. Thus, when using $Pd(dba)_2$ (2 mol%), TTBP·HBF_4 (4 mol%), Cy_2NMe (1.5 equiv), TBAC (10 mol%) in DMAc at 80 °C, the 3*H*-naphtho[2,1-b]pyran **49** was isolated directly in a much improved yield (50%) (Scheme 9; Entry 4, Table 1).[50] It was possible that either the strong acid HBF_4 or the conjugated acid of Cy_2NMe formed during the reaction promoted the unmasking of the naphthol unit with concomitant acid-catalysed cyclization of the Heck product **48** to the corresponding 3*H*-naphtho[2,1-b]pyran **49**. However, the same non-optimized conditions did not prove to be as successful when employed to the more electron-deficient prop-2-en-1-ol **46**, as the 3*H*-naphtho[2,1-b]pyran **50** was isolated in only 25% yield (Scheme 9; Entry 5, Table 1).



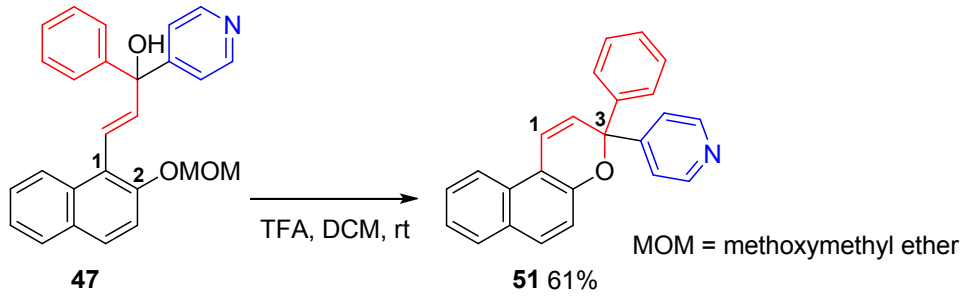
Scheme 9. Heck reactions between 1-bromo-2-naphthol 43 and either prop-2-en-1-ols 44, 45 or 46 under different conditions

Table 1. Summary of Heck reactions between 1-bromo-2-naphthol 43 and either prop-2-en-1-ols 44, 45 or 46 under different conditions

Entry	Heck Partner	Catalyst	Base	Ligand	Phase Transfer Catalyst	KCl	Solvent	Temp.	Yield (%)
1	**44** (1.1 equiv)	$Pd(OAc)_2$ (8 mol%)	K_2CO_3 (1.5 equiv)	N/A	TBAB (1.5 equiv)	1 equiv	DMF	100 °C	**47** (41%)
2	**45** (1.2 equiv)	$Pd(OAc)_2$ (9 mol%)	K_2CO_3 (1.5 equiv)	N/A	TBAB (1.5 equiv)	1.1 equiv	DMAc	100 °C	**48** (9%)
3	**45** (1.2 equiv)	$Pd(OAc)_2$ (5 mol%)	Cy_2NMe (1.5 equiv)	PPh_3 (10 mol%)	TBAC (11 mol%)	N/A	DMAc	80 °C	**48** (8%)
4	**45** (1.4 equiv)	$Pd(dba)_2$ (2 mol%)	Cy_2NMe (1.5 equiv)	TTBP·HBF_4 (4 mol%)	TBAC (10 mol%)	N/A	DMAc	80 °C	**49** (50%)
5	**46** (1.3 equiv)	$Pd(dba)_2$ (2 mol%)	Cy_2NMe (1.5 equiv)	TTBP·HBF_4 (4 mol%)	TBAC (10 mol%)	N/A	DMAc	80 °C	**50** (25%)

Temp. = Temperature

Hence, unmasking of the naphthol function of **47** was attended by the concomitant cyclisation to the 3-pyridyl-3*H*-naphtho[2,1-*b*]pyran **51** in fair yield (61%) upon treatment with TFA at room temperature (Scheme 10).



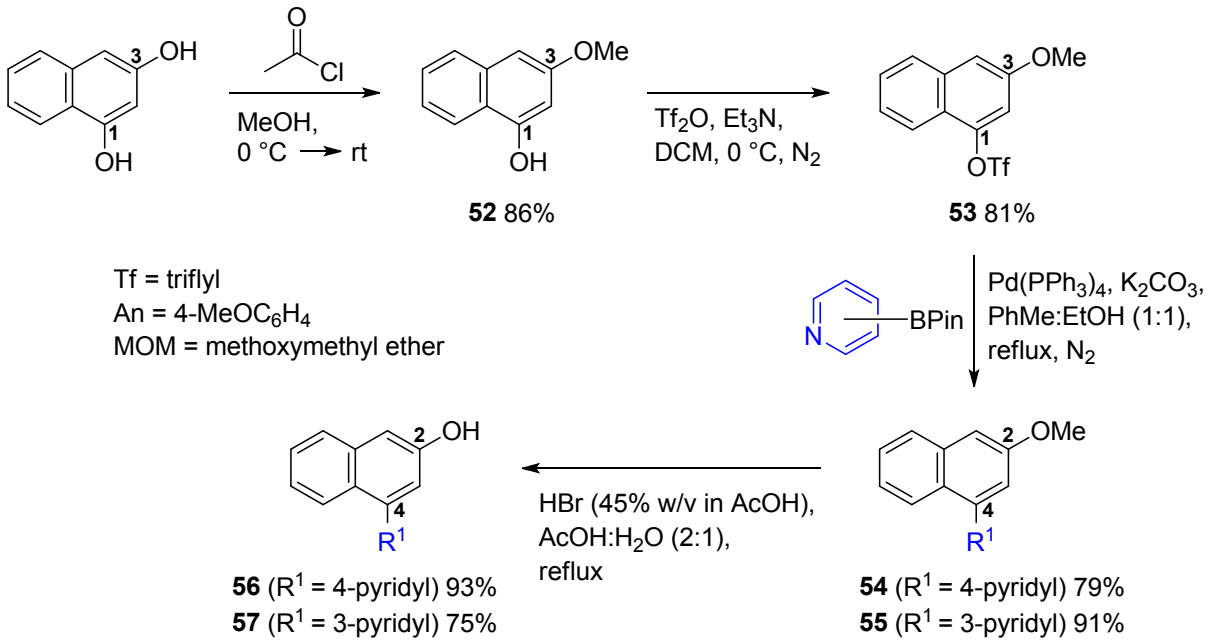
47 **51** 61%

Scheme 10. Synthesis of 5-pyridyl-3*H*-naphtho[2,1-*b*]pyran 51

In summary, 3-pyridyl-3*H*-naphtho[2,1-*b*]pyran **51** was prepared from 1-bromo-2-naphthol in a three step linear route in 25% yield.

Synthesis of 6-pyridyl-3*H*-naphtho[2,1-*b*]pyrans (Strategy C)

The commercially available 1,3-dihydroxynaphthalene was chosen as starting material for the synthesis of the 6-pyridyl-3*H*-naphtho[2,1-*b*]pyrans. First, 3-methoxy-1-naphthol **52** was synthesized in 86% yield by the regioselective *O*-methylation of 1,3-dihydroxynaphthalene by treatment with dry methanolic HCl generated *in situ* from the reaction between acetyl chloride and methanol (Scheme 11).[51] Triflation of **52** by reaction with triflic anhydride and triethylamine in dichloromethane afforded the desired 3-methoxy-1-triflyloxynaphthalene **53** in very good yield (81%). Subsequently, **53** was successfully coupled to 4-pyridine- and 3-pyridine- boronic acid pinacol ester rendering the corresponding 2-methoxy-4-pyridylnaphthalenes **54** and **55** in good to excellent yield (79 – 91%). The latter were demethylated by hydrobromic acid (45% w/v) in acetic acid:H_2O at reflux giving the corresponding 4-pyridyl-2-naphthols **56** and **57** in good to excellent yield (75 – 93%).

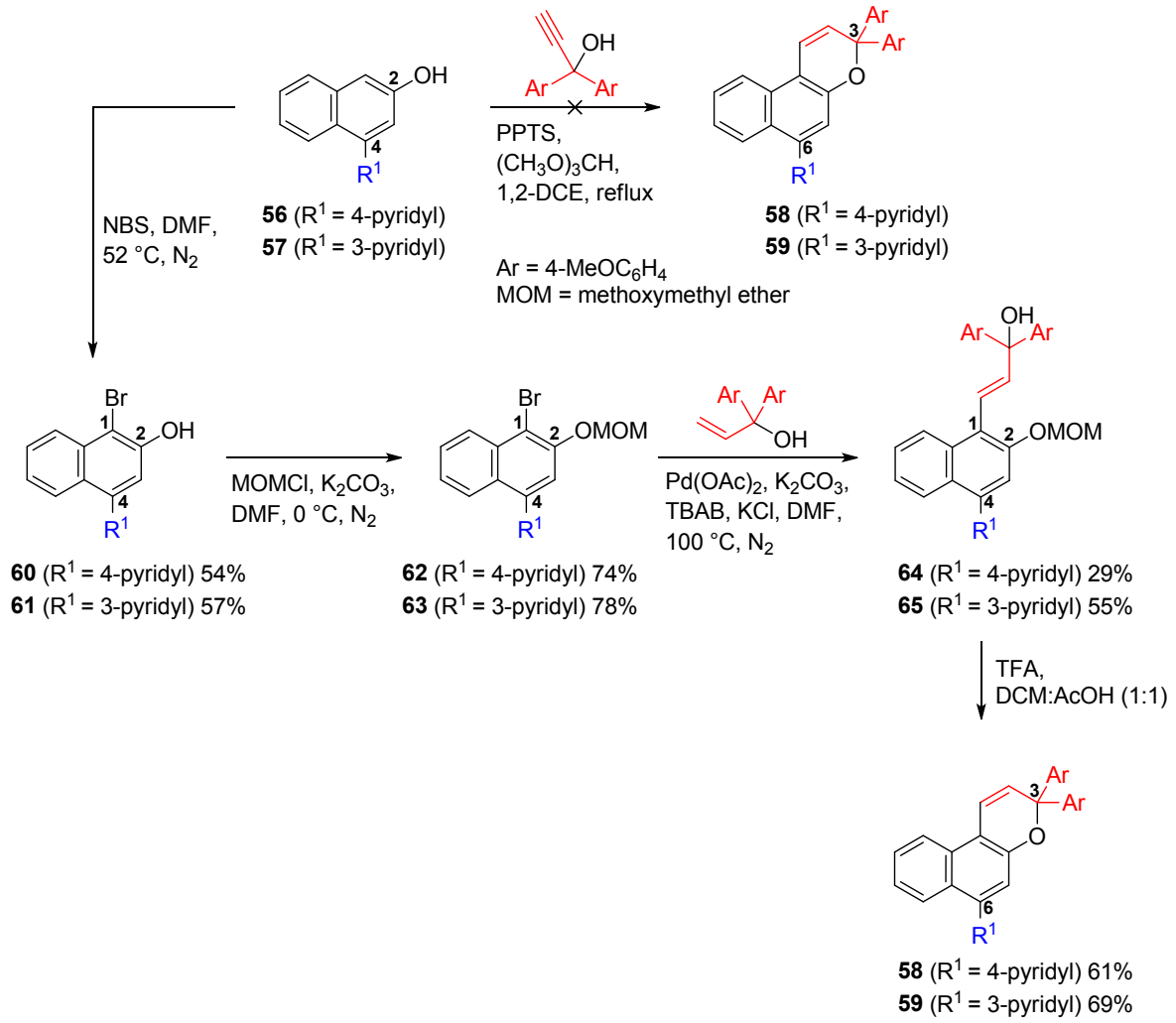


Scheme 11. Synthesis of 4-pyridyl-2-naphthols 56 and 57

Attempts to perform the direct acid-catalysed condensation between pyridyl-2-naphthols **56** and **57** and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol systematically failed to provide the desired products (Scheme 12). It was rationalized that the pyridinium-2-naphthol *p*-toluenesulfonate salts, formed *in situ* under the reaction conditions, were too deactivated to undergo acid-catalysed condensations. Alternatively, the Heck partners **62** and **63** were prepared from the regioselective bromination of **56** and **57** with NBS in fair yields (54 – 57%), followed by protection of the hydroxyl groups of the naphthols **60** and **61** as methoxymethyl ethers by treatment with MOMCl in good yields (74 – 78%). Even though a previous Heck reaction between **43** and prop-2-en-1-ol **45** led to an unsatisfactory outcome (Scheme 9; Entry 2, Table 1), for comparison, the same conditions were applied to the Heck reactions between **62** and **63** and 1,1-bis(4-methoxyphenyl)prop-2-en-1-ol. Surprisingly, TLC analysis indicated that the cross-coupling reactions were virtually finished after two days of reaction as there were just minor amounts of the starting materials in the crude mixture. Thus, flash column chromatography purification rendered the Heck products **64** and **65** in 29% and 55% yield,

respectively. In a final step, the acid-catalysed unmasking of the hydroxyl group of **64** and **65** with concomitant cyclization afforded the corresponding 6-pyridyl-3*H*-naphtho[2,1-*b*]pyrans **58** and **59** in fair yield (61 – 69%).

In summary, 6-pyridyl-3*H*-naphtho[2,1-*b*]pyrans **58** and **59** were prepared from 1,3-dihydroxynaphthalene in a eight step linear route in 4% and 8% yield, respectively.



Scheme 12. Synthesis of 6-pyridyl-3*H*-naphtho[2,1-*b*]pyrans 58 and 59 from 4-pyridyl-2-naphthols 56 and 57

Photochromic Properties

Whilst there are reports of naphthopyrans bearing electron-withdrawing groups,[52] there is a paucity of data concerning their influence on their photochromic properties.[53] In contrast, much

has been reported concerning the photochromic response of the 3*H*-naphtho[2,1-*b*]pyran isomer decorated around the periphery of the naphthalene unit with electron-donating methoxy substituents.[54] For electron-donating methoxy and dialkylamino groups, influential naphthalene ring positions have been identified.[54] The presence of a methoxy group at C-8 induces a bathochromic shift in the wavelength of maximum absorption (λ_{max}) of the derived photomerocyanine accompanied with augmented absorption at the photostationary state (PSS),[55] and the presence of either a dialkylamino[56] or a methoxy group[57] at C-6 exhibits a similar hyperchromism but with a hypsochromic shift in the λ_{max}. The hyperchromic effect of various electron-donating substituents has, in some instances, been associated with increased populations of the photomerocyanine isomers at the PSS as a consequence of an increase in the half-life ($t_{½}$) / decrease of the thermal bleaching rate constant (k_{Δ}).[58] However, hyperchromism has been observed for 2-naphthol derived keto-hydrazone dyes purely as a consequence of the location of a dialkylamino substituent at C-4.[59] It is well established that the UV irradiation of a naphthopyran generates two major photomerocyanines, the TC and TT isomers in varying proportions.[60] Whilst only minor differences in the λ_{max} and in the molar attenuation coefficients (ε) have been observed for the isomeric photomerocyanines derived from 3*H*-naphtho[1,2-*b*]pyrans,[60] the differential fade rates of these isomeric photomerocyanines from either angular naphthopyran isomer, in particular the very slow fading of the TT isomer, has been noted and much interesting exploration of the design of naphthopyrans has been undertaken to obviate the formation of this persistent photomerocyanine.[61] With the foregoing features considered the photochromic response of the new series of pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans was explored (Figure 5). Their photochromic behaviour was studied in aerated toluene solutions under continuous UV irradiation (300-Watt xenon arc lamp source set at 150 W coupled with an UG11 filter, λ_{exc} 325 nm) at 23 °C. The following standard photochromic parameters[62] were analysed: 1) wavelength of maximum absorption (λ_{max}) of the

derived photomerocyanines; 2) persistence of colour in the dark which was measured by recording the thermal bleaching rates constants (k_Δ), and 3) photocolourability which is the induced optical density (ΔA) of the coloured species at its λ_{max} achieved after irradiation (10 min) to a constant value – photostationary state (PSS). Thus, variations in concentration were considered in the photocolourability by calculation of the parameter ΔA_{Conc} which is defined as the colour generated at the PSS after continuous UV irradiation of 1 mole of a given naphthopyran in solution. 4) Fatigue resistance was evaluated for selected examples. Additionally, electronic emission spectra of the pyridyl substituted naphthopyrans were also recorded.

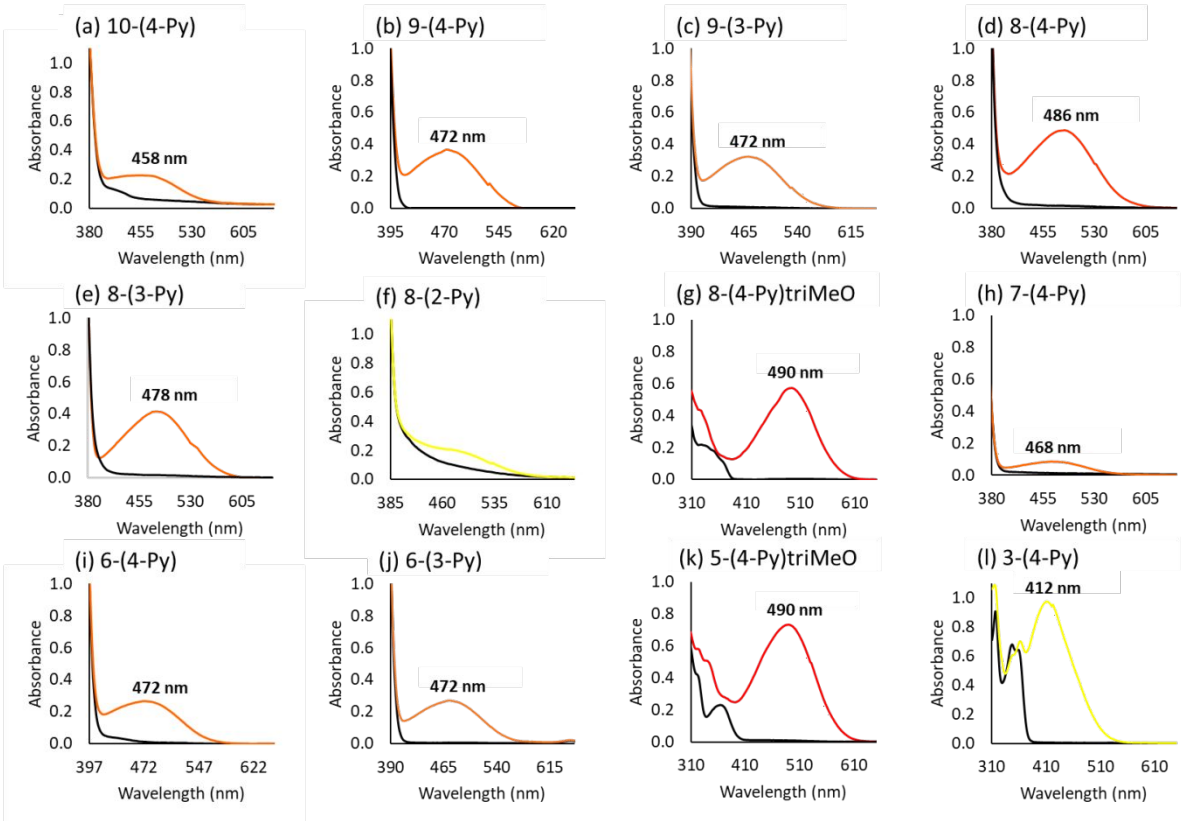


Figure 5. UV-Vis absorption spectra of the pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans in aerated toluene in the closed form (black) and in the PSS (coloured) after continuous (10 min) UV irradiation (λ_{irr} 325 nm) by employing an Oriel 300-Watt xenon arc lamp source (set at 150 W): (a) 15 (1.1 mM); (b) 18 (1.7 mM); (c) 20 (1.7 mM); (d) 26 (1.7 mM);

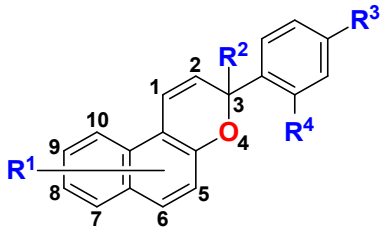
(e) 28 (1.8 mM); (f) 33 (5.2 mM); (g) 30 (0.040 mM); (h) 39 (0.69 mM); (i) 58 (4.0 mM in toluene:dichloromethane (1:1)); (j) 59 (1.7 mM); (k) 42 (0.065 mM); (l) 51 (0.15 mM)

The majority of the pyridyl substituted naphthopyrans produced orange/red hues (λ_{max} 458 – 490 nm) in toluene solution under UV irradiation (Table 2), one exception being the 3-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **51** (λ_{max} 412 nm; ΔA_{Conc} 6.5 × 10^3 M^{-1}; Entry 12, Table 2) that produced an intense pale yellow hue. The introduction of the 4-pyridyl group at C-3 on the naphthopyran core induced a large hypsochromic shift in accordance to reported examples of naphthopyrans with electron-withdrawing groups at this position.[63] From the series, the 3-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **51** was the only example that showed photodecomposition after two fatigue cycles when irradiated for 10 min (Figure S177). The 10-pyridyl-3*H*-naphtho[2,1-*b*]pyran **15** (λ_{max} 458 nm; ΔA_{Conc} 2.1 × 10^2 M^{-1}; Entry 1, Table 2) produced a more predominantly orange hue than most of the other naphthalene ring substituted isomers, corresponding to a hypsochromic shift of 17 nm when compared to the simple 3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (λ_{max} 475 nm; Entry 13, Table 2). It was rationalized that the blue shift was a result of the steric clash between the bulky 4-pyridyl group at C-10 and the hydrogens of the diene unit, which led to a more twisted conformation and consequently to less efficient conjugation. The introduction of pyridyl substituents at C-6, C-7 and C-9 (Entries 2, 3, 8, 9, 10, Table 2) had a small effect on the λ_{max}, in accord with previous observations on the substitution of methoxy groups at these positions.[54] Thus, there was a poor electronic conjugation of the pyridyl groups at these positions with the photo-generated π–systems irrespective of the orientation of the pyridyl moiety. The weak colour (ΔA_{Conc} 1.3 × 10^2 M^{-1} – 2.2 × 10^2 M^{-1}) generated for these isomers (λ_{max} 468 – 472 nm) was slightly hypsochromic shifted when compared to the simple 3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (λ_{max} 475 nm; Entry 13, Table 2), most likely as a result of the small negative inductive effect of the pyridyl unit.

Table 2. Summary of the spectrokinetic properties of the target pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans and respective PSS obtained after continuous (10 min) UV irradiation (λ_{irr} 325 nm, 150 W) in toluene solution

Entry	NP	Conc / mM	R^1	R^2	R^3	R^4	λ_{max} / nm	ΔA	ΔA_{Conc} / M^{-1}	k_Δ / s^{-1} (Amplitude %)	λ_{em} / nm (λ_{exc} / nm)
1	**15**	1.1	10-(4-Py)	4-$MeOC_6H_4$	OMe	H	458	0.227	2.1×10^2	$> 10^{-1}$ $< 10^{-6}$	Not recorded
2	**18**	1.7	9-(4-Py)	4-$MeOC_6H_4$	OMe	H	472	0.366	2.2×10^2	6.5×10^{-1} (4) 3.2×10^{-4} (96)	407 (370)
3	**20**	1.7	9-(3-Py)	4-$MeOC_6H_4$	OMe	H	472	0.322	1.9×10^2	6.9×10^{-1} (3) 3.2×10^{-4} (97)	391 (360)
4	**26**	1.7	8-(4-Py)	4-$MeOC_6H_4$	OMe	H	486	0.487	2.9×10^2	5.3×10^{-1} (3) 1.8×10^{-5} (97)	450 (367)
5	**28**	1.8	8-(3-Py)	4-$MeOC_6H_4$	OMe	H	478	0.415	2.3×10^2	6.0×10^{-1} (4) 2.3×10^{-5} (96)	387 (353)
6	**33**	5.2	8-(2-Py)	4-$MeOC_6H_4$	OMe	H	N/A	N/A	N/A	N/A	Not recorded
7	**30**	0.040	8-(4-Py)	4-$MeOC_6H_4$	OMe	OMe	490	0.553	1.4×10^4	3.1×10^{-1} (17) 2.7×10^{-3} (83)	402 (337)
8	**39**	0.69	7-(4-Py)	4-$MeOC_6H_4$	OMe	H	468	0.087	1.3×10^2	9.1×10^{-1} (1) 1.3×10^{-5} (99)	411 (352)
9	**58**	4.0†	6-(4-Py)	4-$MeOC_6H_4$	OMe	H	472†	0.267†	67†	7.3×10^{-1}† 2.4×10^{-4} (100)†	405 (360)
10	**59**	1.7	6-(3-Py)	4-$MeOC_6H_4$	OMe	H	472	0.268	1.6×10^2	7.3×10^{-1} 3.4×10^{-5} (100)	419 (360)
11	**42**	0.065	5-(4-Py)	4-$MeOC_6H_4$	OMe	OMe	490	0.735	1.1×10^4	4.2×10^{-1} (21) 2.2×10^{-3} (79)	413 (364)
12	**51**	0.15	H	4-Py	H	H	412	0.975	6.5×10^3	4.1×10^{-1} (39) 4.2×10^{-5} (61)	375 (346)
13[26a]	**N/A**	N/A	H	4-$MeOC_6H_4$	OMe	H	475	N/A	N/A	N/A	N/A
14[64]	**N/A**	N/A	H	4-$MeOC_6H_4$	OMe	OMe	476	N/A	N/A	N/A	N/A

Table S1 includes all 14 structures and can be found in the ESI. †toluene:dichloromethane (1:1). NP = naphthopyran. Conc = concentration of the naphthopyran in solution prior to UV irradiation (mM). λ_{max} = maximum wavelength of absorption at the photostationary state. ΔA = induced optical density at λ_{max}. ΔA_{Conc} = colour generated at the photostationary state after continuous UV irradiation of 1 mole of a given naphthopyran in solution, calculated as ΔA / Conc. k_Δ = thermal bleaching rate constant. Amplitude (%).[63a] λ_{em} = maximum wavelength of emission of the naphthopyrans in aerated toluene. λ_{exc} = excitation wavelength, corresponding to the maximum wavelength of absorbance of the naphthopyran.



The introduction of a 4-pyridyl substituent at C-8 (**26**) (λ_{max} 486 nm; ΔA_{Conc} 2.9×10^2 M^{-1}; Entry 4, Table 2) induced a bathochromic shift (11 nm) when compared to the 3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (λ_{max} 475 nm; Entry 13, Table 2). It is pertinent to note that the introduction of an electron-donating methoxy group at C-8 results in a more substantial red shift in the λ_{max}.[54] A larger bathochromic shift (15 nm) was observed for the trimethoxy substituted 8-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **30** (λ_{max} 490 nm; ΔA_{Conc} 2.1×10^4 M^{-1}; Entry 7, Table 2) and 5-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **42** (λ_{max} 490 nm; ΔA_{Conc} 1.1×10^4 M^{-1}; Entry 11, Table 2) when compared to the simple trimethoxy substituted 3*H*-

naphtho[2,1-*b*]pyran (λ_{max} 476 nm; Entry 14, Table 2). For the 8-substituted 3*H*-naphtho[2,1-*b*]pyrans **26** (Entry 4, Table 2), **30** (Entry 7, Table 2) and 5-substituted 3*H*-naphtho[2,1-*b*]pyran **42** (Entry 11, Table 2), the red shift of the λ_{max} was presumably a consequence of the balance between the more extended conjugated π system of the corresponding photomerocyanines and the electron-withdrawing nature of the pyridyl ring. The augmentation of the λ_{max} by 25 nm through extension of the merocyanine chromophore by introduction of an acetoxy group at C-5 has been noted by Van Gemert.[65] Similarly, the introduction of the electron-withdrawing *N*-phenylamido group at C-5 has also been reported to induce a substantial bathochromic shift in the λ_{max} by 60 nm accompanied by faster bleaching kinetics.[66] By changing the orientation of the pyridyl at C-8 in **28** (λ_{max} 478 nm; ΔA_{Conc} 2.3 × 10^2 M^{-1}; Entry 5, Table 2) the electronic conjugation was disturbed which resulted in a negligible shift when compared to 3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (λ_{max} 475 nm; Entry 13, Table 2). This contrasts with data reported for the photomerocyanines derived from 3,3,8-triphenyl-3*H*-naphtho[2,1-*b*]pyran where similar conjugation of the merocyanine upon introduction of the 8-phenyl substituent affords a red shift of 30 nm.[67] Distinct from the 8-(4-pyridyl)- (**26**) **(**Entry 4, Table 2) and 8-(3-pyridyl)- (**28**) (Entry 5, Table 2) isomers, the insertion of a 2-pyridyl substituent at C-8, to afford **33** (Entry 6, Table 2), resulted in a weak yellow background hue accompanied by very poor photochromic response.

The location of the pyridyl unit on the naphthopyran core has an influence on the persistence of the photogenerated colour. It is well established that the absorption spectrum of the irradiated naphthopyran results from an equilibrium mixture of photomerocyanine isomers at the PSS, and that the TC isomer fades relatively quickly while the TT isomer can fade over many hours, leading to the impression of the generation of a permanent dye. Such differential fading has led to the report of thermal bleaching rate constants (k_Δ) for the initial rapidly fading TC isomer traditionally in the order of 10^{-1} – 10^{-3} s^{-1} and then a second k_Δ for the slower fading TT isomer

generally in the order of 10^{-4} – 10^{-6} s^{-1}.[63a,68] In this work it should be noted that the 3*H*-naphtho[2,1-*b*]pyrans displayed such dual fading characteristics with the majority of the examples exhibiting a first k_Δ in the order of 10^{-1} s^{-1} and the second k_Δ in the order of 10^{-5} s^{-1}, irrespectively of the position and orientation of the pyridyl group (Table 2). A few exceptions, solely characterized by changes in the second k_Δ, include naphthopyrans **18** (Entry 2, Table 2) and **20** (Entry 3, Table 2) in which the pyridyl at C-9 led to a one order of magnitude smaller second k_Δ (10^{-4} s^{-1}). A more pronounced effect was recorded for naphthopyran **15** (Entry 1, Table 2) in which the pyridyl at C-10 led to the generation of a particularly thermally stable photochrome as no fading of colour was detected after 30 min of standing in the dark (Figure S165). The combined effect of the introduction of a pyridyl substituent in the naphthopyran scaffold and an *ortho* methoxy in one of the anisyl substituents at C-3 for naphthopyrans **30** (Entry 7, Table 2; also Figure 6) and **42** (Entry 11, Table 2) led to a second k_Δ in the order of 10^{-3} s^{-1}.

The UV-Vis absorption spectra of the pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans revealed absorption bands centred at 337 – 370 nm assigned to $\pi \rightarrow \pi^*$ electronic transitions (Figures S166 – S176).[69] Besides triggering the photochromic reaction, excitation at these transitions resulted in the evolution of structured and high energy emission bands centred at 375 – 450 nm attributed to $\pi \rightarrow \pi^*$ fluorescence (Figure S179). Considering the electron-withdrawing nature of the pyridyl substituent, the fluorescence behaviour of the naphthopyrans may be justified by a potential charge-transfer (CT) character of the $\pi \rightarrow \pi^*$ transition. Curiously, for the selected examples **30** and **42**, the photochromic reaction appears to disrupt the CT character of the bathochromic shifted $\pi \rightarrow \pi^*$ transition as no emission was recorded at the PSS (Figure S180).

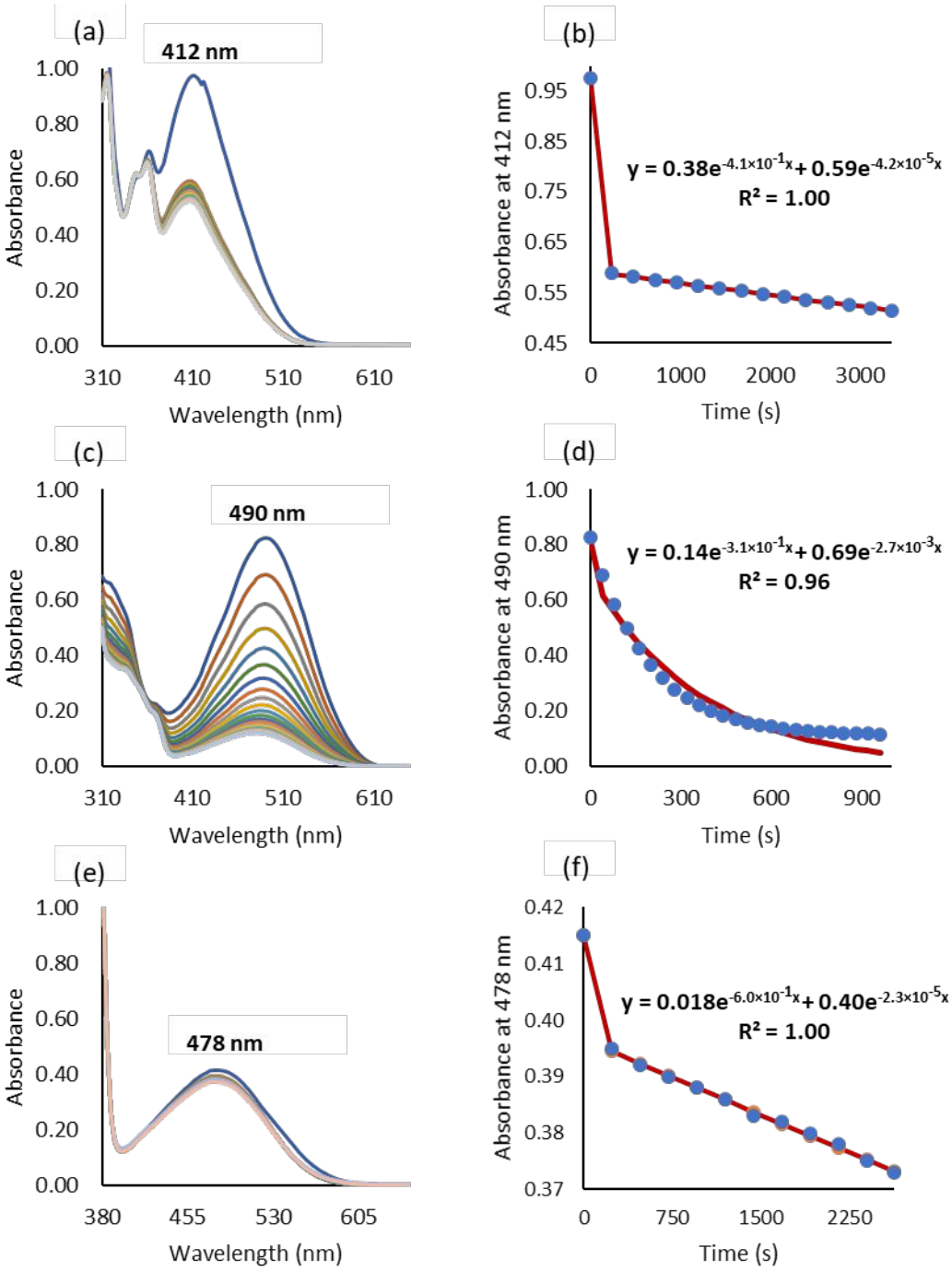


Figure 6. Thermal bleaching of the PSS in aerated toluene after continuous (10 min) UV irradiation (λ_{irr} 325 nm) by employing an Oriel 300-Watt xenon arc lamp source (set at 150 W): (a) UV-Vis absorption spectra of the bleaching in the dark of the PSS of 51 (0.15 mM) with a 240 seconds scan interval; (b) Bi-exponential fit of absorbance of 51 at 412 nm = f (t); (c) UV-Vis absorption spectra of the bleaching in the dark of the PSS of 30

(0.040 mM) with a 40 seconds scan interval; (d) Bi-exponential fit of absorbance of 30 at 490 nm = f(t); (e) UV-Vis absorption spectra of the bleaching in the dark of the PSS of 28 (1.8 mM) with a 240 seconds scan interval; (f) Bi-exponential fit of absorbance of 28 at 478 nm = f (t)

The ideal combination of photochromic properties for variable optical transmission devices is the rapid intense colour generation from a colourless inactivated state with a reasonably rapid rate of fade (seconds) of the coloured form at room temperature. It is also important that the photochromes exhibit good fatigue resistance; the photochromic cycles must be repeatable many times without loss of performance. From the series, the two examples that better combine strong photocolourability and relatively fast bleaching kinetics are the trimethoxy substituted 8-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **30** (λ_{max} 490 nm; ΔA_{Conc} 2.1 × 10^4 M^{-1}; $t_{½}$ 190 s; Entry 7, Table 2) and 5-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran **42** (λ_{max} 490 nm; ΔA_{Conc} 1.1 × 10^4 M^{-1}; $t_{½}$ 210 s; Entry 11, Table 2). Considering their potential interest to the community, the fatigue resistance of naphthopyrans **30** and **42** was evaluated. The fatigue resistance plots showed that the photochromes possess good photostability (ΔAbs = 0.02) after continuous irradiation for 130 min with a strong light source (Figure 7). Furthermore, the bleaching of colour, besides occurring thermally, was assisted by irradiation with visible light, revealing the mixed P- and T-type photochromic character of the pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans.

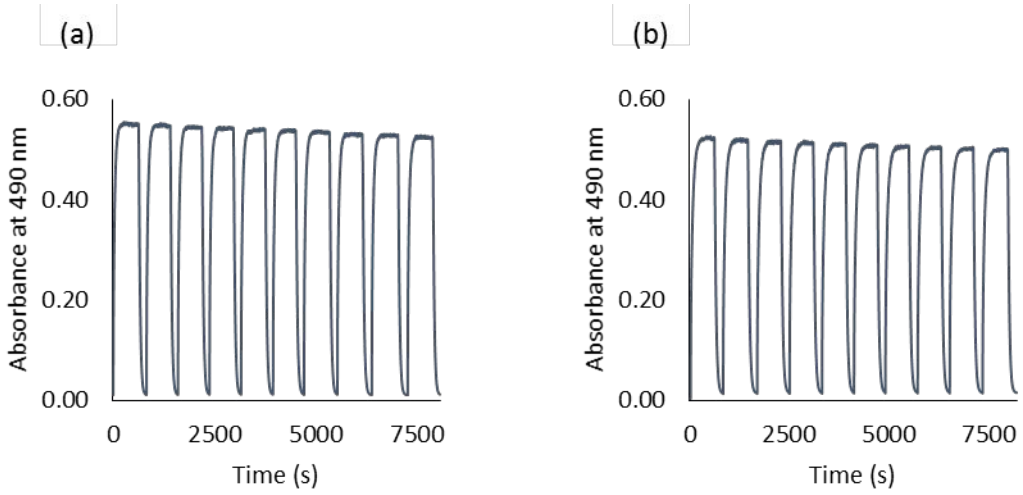


Figure 7. Fatigue resistance plots – PSS reached after continuous (10 min) UV irradiation (λ_{irr} 325 nm) by employing an Oriel 300-Watt xenon arc lamp source (set in 150 W) and bleaching effected by continuous irradiation (3 min) with visible light (λ_{irr} > 420 nm) by employing an Oriel 300-Watt xenon arc lamp source (set in 150 W): (a) 30 (0.040 mM in aerated toluene); (b) 42 (0.040 mM in aerated toluene)

Conclusions

A series of twelve novel pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans were synthesized by following different strategic ideas: a) a Suzuki reaction after 'chromenization' was employed to the synthesis of the 10-, 9-, 8-, 7- and 5-pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans (**Strategy A**); b) a Heck reaction was used to prepare a 3-pyridyl substituted 3*H*-naphtho[2,1-*b*]pyran (**Strategy B**); (c) a Suzuki reaction prior to 'chromenization' effected by a late stage Heck reaction was employed to prepare the 6-pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans (**Strategy C**).

The majority of the target pyridyl substituted 3*H*-naphtho[2,1-*b*]pyrans exhibited fully reversible positive photochromism, generating predominantly orange/red hues (λ_{max} 458 – 490 nm) in toluene solution under UV irradiation, with the colour reverting back to the original colourless state either thermally or with assistance of visible light. Photocolourability was

accessed as being generally weak but could be substantially increased by the inclusion of an *ortho* methoxy substituent at one the anisyl groups at C-3 of the pyridyl substituted naphthopyrans. The thermal bleaching kinetics of the photochromes varied with structural modification, including the position of the pyridyl ring which was particularly evident for positions C-9 and C-10 of the naphthopyran scaffold, and with the introduction of an *ortho* methoxy substituent at one the anisyl groups at C-3. Electronic emission spectra of the naphthopyrans revealed high energy and structured emission bands attributed to $\pi \rightarrow \pi^*$ fluorescence that was quenched upon the generation of the photostationary states. Selected examples that combined both strong photocolourability and relatively fast bleaching kinetics showed good fatigue resistance of their photochromic properties over ten irradiation cycles.

Experimental Section

Unless otherwise stated, reagents were purchased from major chemical catalogue companies and were used as supplied. For reactions requiring heating, DrySyn® aluminium heating blocks in conjunction with electrical stirrer hotplates were used as the heat source. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a Bruker Avance DPX400 in either $CDCl_3$ or acetone-d_6 or DMSO-d_6 unless stated otherwise. Chemical shifts (δ) are provided in parts per million (ppm) using either the residual solvent peak or TMS as the internal reference. 2D NMR experiments (COSY, HSQC, HMBC and NOESY) were performed to unequivocally sign the protons of the molecules. Coupling constants (*J*) are provided in Hz. FT-IR spectra were recorded on a Nicolet 380 FT-IR spectrophotometer equipped with a diamond ATR attachment (neat sample). Flash column chromatography was performed on chromatography silica gel (either Sigma-Aldrich, 40-63 μm particle size distribution or Fluorochem Silica gel 40-63 μm particle size distribution, unless stated otherwise). All final compounds were homogeneous by TLC using a range of eluent systems of differing polarity (either Merck TLC aluminium sheets silica gel 60 F254 (cat. No 105554)

or Fluorochem (cat. No. LC0927)). Melting points were determined in capillary tubes, using a Stuart SMP10 melting point apparatus, and are uncorrected. Accurate mass measurements were obtained from the Innovative Physical Organic Solutions (IPOS) centre at the University of Huddersfield. UV-visible spectra were recorded for either toluene or toluene:dichloromethane (1:1) solutions of the samples (10 mm path length quartz cuvette, PTFE capped, concentration in the range 10^{-3} – 10^{-5} mol.dm^{-3}). A bespoke Shimadzu UV-3600 Plus UV-Vis-NIR spectrophotometer was used and equipped with a single cell Peltier temperature controlled (23 °C) magnetically stirred fluorescence cell holder attachment. The spectrophotometer sample chamber door was modified to accept activating irradiation delivered from the light source by liquid light guides (Newport 77557, Newport 77569). Irradiation was provided by a xenon ozone free arc lamp (Newport 6255) powered by an Oriel 300-Watt xenon arc lamp source (Newport 66906) (set in Power Mode 150 W). When mentioned irradiation was also provided by a Weltool M2-OL 365 nm UV Flashlight (2 W). An in-line distilled water liquid filter (Newport 6177), multiple filter holder (Newport 62020), UG11 filter (Newport FSO-UG11), fibre optic coupler (Newport 77799) completed the irradiation equipment. Activation of the colourless closed forms of the photochromic compounds to a photostationary state was achieved by using UV irradiation using the Newport filter (UG11). Bleaching of the coloured (opened forms) when required was effected by irradiation with visible light using the Newport filter (GG420, Cut-On 420 nm). In a first experiment, spectra (310 – 650 nm) were recorded prior to (ground state) and immediately after cessation of activating irradiation to a photostationary state (10 min irradiation). In a second experiment, the decrease of the absorbance at the photostationary state in the dark was recorded over time by either running 20 – 240 s interval full scans (in Spectrum Mode). The thermal bleaching rate constants, k_{Δ}, were calculated by fitting the absorbance curve obtained in the dark to a bi-exponential model.

1,1-Bis(4-methoxyphenyl)prop-2-yn-1-ol (**A**) was prepared according to an established procedure, and both physical and spectroscopic properties were in excellent agreement with those previously reported in the literature for their preparation.[35b] 2,4,4-Trimethoxybenzophenone was prepared by the Friedel-Crafts acylation of 1,3-dimethoxybenzene with 4-methoxybenzoic acid in warm polyphosphoric acid.[70]

Synthesis of 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (C)

Experimental procedure for the synthesis of (2,4-dimethoxyphenyl)(4-methoxyphenyl)methanone (B): *p*-anisic acid (31.99 g, 0.2103 mmol), 1,3-dimethoxybenzene (26.0 g, 0.200 mmol) and polyphosphoric acid (214 mL) were stirred and heated to 90 °C for 17 h. After this time, further 1,3-dimethoxybenzene (13.0 mL, 0.100 mmol) was added and the reaction mixture stirred at 90 °C for 5 h. The mixture was then poured into ice water. The product was extracted into DCM. The combined organic extracts were washed with 2M NaOH (2 × 250 mL), the organic layer dried with anhydrous sodium sulfate and evaporated to dryness giving a red oil. The desired product was obtained by crystallization from Et_2O at -20 °C, followed by recrystallization from hot EtOH, giving the corresponding product as a cream crystalline solid (32.76 g, 57%). m.p. = 70–71 °C; ν_{max} (neat) 1633, 1592, 1249, 1212, 1170, 1102, 1020, 954, 835, 770, 601 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.69 (3H, s, OMe), 3.82–3.83 (6H, m, OMe), 6.51–6.53 (2H, m, 3, 5-H), 6.88 (2H, d, J = 8.7 Hz, 3′, 5′-H), 7.32 (1H, d, J = 8.2 Hz, 6-H), 7.77 (2H, d, J = 8.7 Hz, 2′, 6′-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.4, 55.46, 55.55, 98.8, 104.6, 113.3, 121.9, 131.4, 131.5, 132.1, 159.1, 162.9, 163.2, 194.3 ppm; HRMS (ESI) found $[M+H]^+$ = 273.11209 $C_{16}H_{16}O_4$ requires $[M+H]^+$ = 273.11214.

Experimental procedure for the synthesis of 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (C): *n*-BuLi (54.0 mL, 2.5 M in hexanes, 135 mmol) was

added dropwise via a syringe to a cold (-5 °C) stirred solution of TMS acetylene (19.0 mL, 137 mmol) in anhydrous THF (500 mL) under N_2. The solution was stirred for 30 min at -5 °C. Afterwards, (2,4-dimethoxyphenyl)(4-methoxyphenyl)methanone (32.01 g, 117.6 mmol) was added in a single portion and the cooling bath was removed and the mixture stirred at room temperature for 4 h. The solution was re-cooled to 0 °C and a solution of powdered KOH (85%, 15.5 g) in MeOH (80 mL) was added in a single portion, after which the cooling bath was removed and the mixture stirred for 30 min. Upon completion, the mixture was diluted with water (100 mL) and the layers separated. The aqueous layer was extracted with EtOAc (3 × 150 mL) and the combined organic layers washed with water (2 × 150 mL), dried with anhydrous sodium sulfate and evaporated to dryness, leading to the corresponding product as a yellow oil (35.23 g, quant.), which solidified upon standing. m.p. = 80–83 °C; ν_{max} (neat) 3269, 1607, 1582, 1502, 1299, 1250, 1208, 1168, 1127, 1027, 830, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.81 (1H, s, 3-H), 3.80 (3H, s, OMe), 3.82 (3H, s, OMe), 3.83 (3H, s, OMe), 4.79 (1H, s, OH), 6.46 (1H, dd, J = 8.6, 2.0 Hz, 5′-H), 6.53 (1H, d, J = 2.0 Hz, 3′-H), 6.89 (2H, d, J = 8.7 Hz, 3″, 5″-H), 7.23 (1H, d, J = 8.6 Hz, 6′-H), 7.49 (2H, d, J = 8.7 Hz, 2″, 6″-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 55.4, 55.8, 73.6, 74.4, 86.2 100.1, 104.0, 113.3, 125.1, 127.6, 129.1, 136.4, 157.8, 159.0, 160.8 ppm; HRMS (ESI) found $[M+Na]^+$ = 321.1084 $C_{18}H_{18}O_4$ requires $[M+Na]^+$ = 321.1097.

Synthesis of 10-pyridyl-3*H*-naphtho[2,1-*b*]pyrans

Synthesis of 8-iodo-2-naphthol 13: a stirred mixture of 8-amino-2-naphthol (10.00 g, 62.82 mmol) in water (200 mL) was cooled to 0–5 °C and then a solution of H_2SO_4 (95–98%, 11 mL) in water (20 mL) was added at such a rate that the internal temperature never exceeded 5 ºC. To the resulting mixture was added a solution of $NaNO_2$ (4.34 g, 62.9 mmol) dissolved in water (200 mL) over a period of 30 min at 0–5 °C. The resulting reaction mixture was stirred at 0–5 °C for further 30 min. A solution of KI (10.43 g, 62.83 mmol) dissolved in water (125 mL) was

added to the reaction mixture over a period of 30 min at 0–5 °C and stirred for 3 h. After completion, the reaction mixture was allowed to reach room temperature, diluted with water (200 mL) and extracted with EtOAc (3 × 500 mL). The combined organic layers were washed with brine (2 × 500 mL). The organic layer was dried with anhydrous sodium sulfate and evaporated to dryness under reduced pressure, giving the corresponding product as a black powder (12.37 g, 73%) that was used in the next step without further purification. m.p. = 103–106 °C [lit. m.p. = 109 °C[71]]; ν_{max} (neat) 3254 (br), 1621, 1590, 1504, 1440, 1371, 1335, 1222, 1168, 1122, 970, 898, 819, 648 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 5.19 (1H, s, OH), 7.04 (1H, t, *J* = 7.7 Hz, 6-H), 7.13 (1H, dd, *J* = 8.8, 2.3 Hz, 3-H), 7.44 (1H, d, *J* = 2.3 Hz, 1-H), 7.70 (1H, d, *J* = 8.8 Hz, 4-H), 7.76 (1H, d, *J* = 7.7 Hz, 5-H), 8.03 (1H, d, *J* = 7.7 Hz, 7-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 97.3, 114.2, 118.5, 124.7, 128.8, 129.4, 130.9, 135.8, 138.0, 155.1 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_8IO^+$ 270.9614; Found 270.9616.

Synthesis of 10-iodo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran 14: 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (1.04 g, 3.88 mmol) and 8-iodo-2-naphthol (1.00 g, 3.70 mmol) in the presence of PPTS (0.05 g, 0.2 mmol) and trimethyl orthoformate (0.80 mL, 7.3 mmol) in 1,2-DCE (21.0 mL) were refluxed for 5 h under N_2. Solvent was removed under reduced pressure, the residue dissolved in EtOAc (100 mL), washed with water (3 × 100 mL), dried with anhydrous sodium sulfate and evaporated to dryness. Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: EtOAc (20%) in hexanes, fraction 2] led to the corresponding product as a brown powder (0.90 g, 39%) – approximately 83% pure by ^1H NMR analysis – and it was used in the next step without further purification. m.p. = 50–53 °C; ν_{max} (neat) 2922, 2852, 1606, 1506, 1460, 1246, 1171, 1031, 995, 821, 708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.76 (6H, s, OMe), 5.97 (1H, d, *J* = 9.7 Hz, 2-H), 6.82–6.85 (4H, m, 3′, 3″, 5′, 5″-H), 6.92 (1H, t, *J* = 7.7 Hz, 8-H), 7.21 (1H, d, *J* = 8.8 Hz, 5-H), 7.42–7.45 (4H, m, 2′, 2″, 6′, 6″-H), 7.55 (1H, d, *J* = 8.8 Hz, 6-H), 7.65–7.67 (1H, m, 7-H), 8.08–8.13 (2H, m, 1, 9-H)

ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.2, 81.6, 89.7, 113.3, 116.9, 119.2, 122.6, 124.4, 124.6, 128.6, 129.5, 130.9, 131.0, 131.8, 136.5, 141.5, 152.7, 158.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}IO_3^+$ 521.0608; Found 521.0610.

Synthesis of 3,3-bis(4-methoxyphenyl)-10-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 15: a mixture of 10-iodo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (83%) (200.3 mg, 0.3195 mmol), 4-pyridineboronic acid pinacol ester (98.3 mg, 0.479 mmol), KF (27.8 mg, 0.478 mmol) and $Pd(PPh_3)_4$ (18.6 mg, 0.0161 mmol) in PhMe (5.0 mL) and EtOH (5.0 mL) was heated at reflux under N_2 for 5 days. After this time, the mixture was evaporated to dryness. Afterwards, the residue was dissolved in DCM (50 mL), washed with water (3 × 50 mL), the organic layer dried with anhydrous sodium sulfate and the solvent removed under reduced pressure. Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: EtOAc (50%) in hexanes, fraction 4] led to the corresponding product as a light-yellow powder (99.8 mg, 66%). m.p. = 59–63 °C; ν_{max} (neat) 1607, 1593, 1507, 1452, 1245, 1172, 1032, 998, 819, 732 cm^{-1}; Photomerocyanine λ_{max} = 458 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 5.64 (1H, d, *J* = 9.7 Hz, 2-H), 6.01 (1H, d, *J* = 9.7 Hz, 1-H), 6.84 (4H, app. d, *J* = 8.8 Hz, 3′, 5′, 3″, 5″-H), 7.17 (2H, app. d, *J* = 5.8 Hz, 2‴, 6‴-H), 7.25–7.37 (7H, m, Ar-H), 7.73–7.76 (2H, m, Ar-H), 8.67 (2H, app. d, *J* = 5.8 Hz, 3‴, 5‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 81.6, 113.2, 115.3, 119.0, 123.2, 123.9, 124.4, 125.0, 128.4, 129.5, 130.0, 130.5, 130.9, 135.3, 136.7, 149.6, 151.7, 152.9, 159.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1906.

Synthesis of 9-pyridyl-3*H*-naphtho[2,1-*b*]pyrans

Synthesis of 7-bromo-2-naphthol 16: bromine (3.4 mL, 66 mmol) was added slowly over 30 min to a cold (0 ºC) vigorously stirred suspension of triphenylphosphine (17.01 g, 64.85 mmol) in MeCN (3.0 mL). The mixture was warmed to room temperature and 2,7-

dihydroxynaphthalene (10.39 g, 64.87 mmol) was added in one portion. Afterwards, the reaction was heated to 85 ºC for 2 h. The resulting brown tar was heated, slowly, to 250 ºC for 6 h. Upon cooling, the mixture was purified by flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: EtOAc/hexane (3:7)], with subsequent recrystallization from EtOAc/hexane, affording the corresponding product as a brown powder (7.01 g, 48%). m.p. = 129–131 °C [lit. m.p. = 132–133 °C[72]]; ν_{max} (neat) 3626, 3046 (br), 1649, 1573, 1500, 1435, 1351, 1206, 1062, 919, 855, 827, 736, 596 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.35 (1H, s, OH), 7.06 (1H, app. s, 1-H), 7.11 (1H, dd, J = 8.8, 2.1 Hz, 3-H), 7.39 (1H, d, J = 8.7 Hz, 6-H), 7.63 (1H, d, J = 8.7 Hz, 5-H), 7.71 (1H, d, J = 8.8 Hz, 4-H), 7.84 (1H, s, 8-H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 108.7, 118.2, 120.8, 127.0, 127.3, 128.3, 129.4, 129.9, 135.8, 154.1 ppm; HRMS (APCI) m/z: $[M-H]^-$ Calcd for $C_{10}H_6{}^{79}BrO$ 220.9608; Found 220.9604.

Synthesis of 9-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran 17: 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (5.69 g, 21.2 mmol) and 7-bromo-2-naphthol (4.50 g, 20.2 mmol) in the presence of PPTS (0.25 g, 1.0 mmol) and trimethyl orthoformate (4.5 mL, 41 mmol) in 1,2-DCE (41 mL) was refluxed for 3 h under N_2 atmosphere. Solvent was removed under reduced pressure and the residue taken in DCM (150 mL), washed with water (3 × 300 mL) and the organic layer dried with anhydrous sodium sulfate. The residue was crystallized from DCM/hexane giving the title compound as a brick red crystalline solid (8.24 g, 86%). m.p. = 124–127 °C; ν_{max} (neat) 1606, 1581, 1505, 1441, 1301, 1249, 1172, 1031, 1017, 822, 721, 589 cm^{-1}; Photomerocyanine λ_{max} = 456 nm (PhMe); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 6.21 (1H, d, J = 9.9 Hz, 2-H), 6.84 (4H, app. d, J = 8.8 Hz, 3′, 5′, 3″, 5″-H), 7.15–7.20 (2H, m, 1, 5-H), 7.35–7.38 (5H, m, 8, 2′, 6′, 2″, 6″-H), 7.56 (1H, d, J = 8.7 Hz, 7-H), 7.60 (1H, J = 8.8 Hz, 6-H), 8.09 (1H, s, 10-H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.4, 113.3, 113.4, 118.75, 118.84, 121.1, 123.9, 126.8, 127.7, 128.4, 128.6, 129.6, 130.1,

131.0, 136.9, 151.3, 159.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}{}^{79}BrO_3{}^+$ 473.0747; Found 473.0746.

Synthesis of 9-hydroxy-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran 22: 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (5.04 g, 18.8 mmol) and 2,7-dihydroxynaphthalene (3.01 g, 18.8 mmol) in the presence of PPTS (0.24 g, 0.96 mmol) and trimethyl orthoformate (4.2 mL, 38 mmol) in 1,2-DCE (38.0 mL) was refluxed for 3 h under N_2 atmosphere. Solvent was removed under reduced pressure and the residue purified by flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: DCM], to give the corresponding product as a brown powder (2.16 g, 28%). m.p. = 154–156 °C; ν_{max} (neat) 3390, 1622, 1505, 1452, 1243, 1172, 1082, 1008, 830, 723, 566 cm^{-1}; Photomerocyanine λ_{max} = 444 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 4.88 (1H, s, OH), 6.17 (1H, d, *J* = 9.9 Hz, 2-H), 6.83 (4H, app. d, *J* = 8.8 Hz, 3′, 5, 3″, 5″-H), 6.90 (1H, dd, *J* = 8.8, 2.4 Hz, 8-H), 7.01 (1H, d, *J* = 8.8 Hz, 5-H), 7.14 (1H, d, *J* = 9.9 Hz, 1-H), 7.24–7.26 (1H, m, 10-H), 7.37 (4H, app. d, *J* = 8.8 Hz, 2′, 6′, 2″, 6″-H), 7.56 (1H, d, *J* = 8.8 Hz, 6-H), 7.61 (1H, d, *J* = 8.8 Hz, 7-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.2, 104.0, 112.8, 113.4, 115.0, 116.0, 119.2, 124.8, 127.6, 128.3, 129.7, 130.5, 131.3, 137.3, 151.3, 154.3, 158.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}O_4{}^+$ 411.1591; Found 411.1591.

Synthesis of 3,3-bis(4-methoxyphenyl)-9-triflyloxy-3*H*-naphtho[2,1-*b*]pyran 23: triflic anhydride (0.64 mL, 3.9 mmol) was added dropwise to a solution of 9-hydroxy-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (1.56 g, 3.80 mmol) and Et_3N (1.2 mL) in DCM (11.5 mL) at 0º C. After 1 h the resulting solution was washed with HCl (1 M) (50 mL), a saturated $NaHCO_3$ solution (50 mL), dried with anhydrous sodium sulfate and evaporated to dryness. Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: EtOAc/hexane (3:7), fraction 1] led to the title compound as a canary yellow powder (1.80 g, 87%). m.p. = 90–93 °C; ν_{max} (neat) 1609, 1509, 1401, 1215, 1173, 1122, 1033, 866, 831, 640,

584 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.78 (6H, s, OMe), 6.25 (1H, d, J = 10.0 Hz, 2-H), 6.85 (4H, app. d, J = 8.8 Hz, 3′, 5′, 3″, 5″-H), 7.15 (1H, d, J = 10.0 Hz, 1-H), 7.19 (1H, dd, J = 8.9, 2.4 Hz, 8-H), 7.23 (1H, d, J = 8.9 Hz, 5-H), 7.36 (4H, app. d, J = 8.8 Hz, 2′, 6′, 2″, 6″-H), 7.67 (1H, d, J = 8.9 Hz, 6-H), 7.77–7.80 (2H, m, 7, 10-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.7, 113.3, 113.5, 114.2, 116.9, 117.2, 119.1 (1C, q, J = 318.8 Hz, CF_3) 119.8, 128.2, 128.3, 128.9, 129.6, 130.3, 131.1, 136.8, 148.1, 151.9, 159.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F -72.8 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{22}F_3O_6S^+$ 543.1084; Found 543.1072.

Synthesis of 3,3-bis(4-methoxyphenyl)-9-pyridyl-3*H*-naphtho[2,1-*b*]pyran

Method A – A mixture of 9-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (3.17 mmol), the appropriate pyridineboronic acid pinacol ester (4.8 mmol), K_2CO_3 (4.8 mmol) and $Pd(PPh_3)_4$ (0.16 mmol) in PhMe (37 mL) and EtOH (37 mL) was heated at reflux under N_2 for 16–19 h. After this time, the mixture was cooled and water added (150 mL). Afterwards, the residue was extracted with DCM (3 × 200 mL), washed with water (3 × 200 mL), the organic layer dried with anhydrous sodium sulfate and the solvent removed under reduced pressure to afford the target compounds after purification.

Method B – A mixture of 3,3-bis(4-methoxyphenyl)-9-triflyloxy-3*H*-naphtho[2,1-*b*]pyran (0.3692 mmol), the appropriate pyridineboronic acid pinacol ester (0.5520 mmol), K_2CO_3 (0.559 mmol) and $Pd(PPh_3)_4$ (0.0189 mmol) in PhMe (5 mL) and EtOH (5 mL) was heated at reflux under N_2 for 16 h. After this time, the mixture was cooled and added water (50 mL). The residue was extracted with DCM (3 × 50 mL), washed with water (3 × 50 mL), the organic layer dried with anhydrous sodium sulfate and the solvent removed under reduced pressure to afford the target compounds after purification.

Synthesis of 2-(bis(4-methoxyphenyl)methyl)-8-(4-pyridyl)naphtho[2,1-*b*]furan 19: from 9-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (Method A: 1.50 g) and 4-pyridineboronic acid pinacol ester after 16 h of reaction; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 1] provided the title compound as a brown powder (0.15 g, 10%). From 3,3-bis(4-methoxyphenyl)-9-triflyloxy-3*H*-naphtho[2,1-*b*]pyran (Method B: 200.3 mg) and 4-pyridineboronic acid pinacol ester; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O /DCM (9:1), fraction 1] provided the title compound as a brown powder (54.8 mg, 31%). m.p. = 156–160 °C; ν_{max} (neat) 1607, 1508, 1462, 1301, 1244, 1173, 1030, 992, 816, 550 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.82 (6H, s, OMe), 5.62 (1H, s, α- H), 6.77 (1H, s, 1-H), 6.90 (4H, app. d, *J* = 8.7 Hz, 3′, 5′, 3″, 5″-H), 7.18 (4H, app. d, *J* = 8.7 Hz, 2′, 6′, 2″, 6″-H), 7.63–7.66 (3H, m, 4, 2‴, 6‴-H), 7.70–7.74 (2H, m, 5, 7-H), 8.03 (1H, d, *J* = 8.5 Hz, 6-H), 8.28 (1H, d, *J* = 1.7 Hz, 9-H), 8.70 (1H, d, *J* = 6.1 Hz, 3‴, 5‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 49.9, 55.3, 104.4, 113.4, 114.0, 121.9, 122.1, 123.0, 124.0, 124.2, 127.7, 129.7, 129.8, 130.3, 133.5, 135.6, 148.4, 150.3, 152.9, 158.6, 160.7 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1914.

Synthesis of 3,3-bis(4-methoxyphenyl)-9-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 18: from 9-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (Method A: 1.50 g) and 4-pyridineboronic acid pinacol ester after 16 h of reaction; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 2] provided the title compound as a salmon pink powder (0.85 g, 57%). From 3,3-bis(4-methoxyphenyl)-9-triflyloxy-3*H*-naphtho[2,1-*b*]pyran (Method B: 200.3 mg) and 4-pyridineboronic acid pinacol ester; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 2] provided the title compound as a salmon pink powder (36.9 mg, 21%). m.p. = 89–93 °C; ν_{max} (neat) 1597, 1506, 1440, 1302, 1247, 1172, 1088, 1007, 945, 820, 688, 587

cm^{-1}. Photomerocyanine λ_{max} = 472 nm (PhMe); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 6.26 (1H, d, *J* = 10.0 Hz, 2-H), 6.85 (4H, app. d, *J* = 8.9 Hz, 3′, 5′, 3″, 5″-H), 7.22 (1H, d, *J* = 8.8 Hz, 5-H), 7.36 (1H, d, *J* = 10.0 Hz, 1-H), 7.39 (4H, app. d, *J* = 8.9 Hz, 2′, 6′, 2″, 6″-H), 7.57 (1H, dd, *J* = 8.4, 1.7 Hz, 8-H), 7.62 (2H, d, *J* = 6.1 Hz, 2‴, 6‴-H), 7.69 (1H, d, *J* = 8.8 Hz, 6-H), 7.82 (1H, d, *J* = 8.4 Hz, 7-H), 8.19 (1H, s, 10-H), 8.70 (2H, d, *J* = 6.1 Hz, 3‴, 5‴-H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.4, 113.4, 114.5, 118.9, 119.4, 120.1, 122.0, 122.3, 128.4, 128.6, 129.3, 129.50, 129.53, 129.9, 136.2, 137.0, 148.7, 150.3, 151.3, 159.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1907.

Synthesis of 2-(bis(4-methoxyphenyl)methyl)-8-(3-pyridyl)naphtho[2,1-*b*]furan 21: from 9-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (Method A: 1.50 g) and 3-pyridineboronic acid pinacol ester after 19 h of reaction; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 1] provided the title compound as a brown powder (0.17 g, 11%). From 3,3-bis(4-methoxyphenyl)-9-triflyloxy-3*H*-naphtho[2,1-*b*]pyran (Method B: 204.7 mg) and 3-pyridineboronic acid pinacol ester; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 1] provided the title compound as a brown powder (15.7 mg, 9%). m.p. = 126–130 °C; ν_{max} (neat) 1607, 1583, 1507, 1461, 1301, 1244, 1173, 1110, 1030, 994, 804, 710, 554 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.81 (6H, s, OMe), 5.61 (1H, s, α-H), 6.77 (1H, s, 1-H), 6.89 (4H, app. d, *J* = 8.7 Hz, 3′, 5′, 3″, 5″-H), 7.18 (4H, app. d, *J* = 8.7 Hz, 2′, 6′, 2″, 6″-H), 7.40 (1H, dd, *J* = 7.8, 4.8 Hz, 5‴-H), 7.62 (1H, d, *J* = 8.9 Hz, 4-H), 7.67–7.72 (2H, m, 5, 7-H), 8.00–8.04 (2H, m, 6, 6‴-H), 8.20 (1H, d, *J* = 1.6 Hz, 9-H), 8.62 (1H, dd, *J* = 4.8, 1.6 Hz, 4‴-H), 8.98 (1H, d, *J* = 1.8 Hz, 2‴-H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ_C 49.9, 55.3, 104.4, 113.0, 114.0, 121.9, 123.5, 123.6, 123.9, 124.2, 127.8, 129.6, 129.7, 129.8, 133.6, 134.7, 135.4, 136.7, 148.5, 148.7, 152.9, 158.6, 160.5 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1909.

Synthesis of 3,3-bis(4-methoxyphenyl)-9-(3-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 20: from 9-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (Method A: 1.50 g) and 3-pyridineboronic acid pinacol ester after 19 h of reaction; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 2] provided the title compound as a salmon pink powder (1.05 g, 70%). From 3,3-bis(4-methoxyphenyl)-9-triflyloxy-3*H*-naphtho[2,1-*b*]pyran (Method B: 204.7 mg) and 3-pyridineboronic acid pinacol ester; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 2] provided the title compound as a salmon pink powder (99.7 mg, 56%). m.p. = 80–83 °C; ν_{max} (neat) 1604, 1505, 1451, 1440, 1378, 1302, 1246, 1172, 1088, 1030, 1003, 945, 824, 711, 588 cm^{-1}; Photomerocyanine λ_{max} = 472 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 6.25 (1H, d, *J* = 10.0 Hz, 2-H), 6.85 (4H, app. d, *J* = 8.8 Hz, 3′, 5′, 3″, 5″-H), 7.21 (1H, d, *J* = 8.8 Hz, 5-H), 7.35 (1H, d, *J* = 10.0 Hz, 1-H), 7.38–7.42 (5H, m, 2′, 6′, 2″, 6″, 5‴-H), 7.53 (1H, dd, *J* = 8.4, 1.6 Hz, 8-H), 7.69 (1H, d, *J* = 8.8 Hz, 6-H), 7.82 (1H, d, *J* = 8.4 Hz, 7-H), 7.98 (1H, dt, *J* = 7.9, 2.0 Hz, 6‴-H), 8.12 (1H, s, 10-H), 8.63 (1H, dd, *J* = 4.8, 1.8 Hz, 4‴-H), 8.96 (1H, d, *J* = 2.0 Hz, 2‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.3, 113.4, 114.3, 118.96, 119.00, 119.9, 122.8, 123.6, 128.4, 128.5, 128.7, 129.5, 129.5, 130.0, 134.7, 135.9, 137.0, 137.1, 148.56, 148.63, 151.2, 158.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1906.

Synthesis of 8-pyridyl-3*H*-naphtho[2,1-*b*]pyrans

Synthesis of 8-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran 24: 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (9.47 g, 35.3 mmol) and 6-bromo-2-naphthol (7.50 g, 33.6 mmol) in the presence of PPTS (0.43 g, 1.7 mmol) and triethyl orthoformate (11.2 mL, 67.3 mmol) in 1,2-DCE (67.2 mL) was refluxed for 3 h under N_2 atmosphere. Solvent was removed under reduced pressure, the residue taken in DCM (400 mL), washed with water (3 × 300 mL) and the organic layer dried with anhydrous sodium sulfate. Subsequently, after solvent

evaporation, the residue was recrystallized from DCM/hexane (3:2) giving the corresponding product as a beige crystalline solid in excellent yield (15.48 g, 97%). m.p. = 175–177 °C; ν_{max} (neat) 1607, 1578, 1508, 1248, 1175, 1033, 999, 834, 812, 596 cm^{-1}; Photomerocyanine λ_{max} = 474 nm (PhMe); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 6.21 (1H, d, *J* = 10.0 Hz, 2-H), 6.84 (4H, app. d, *J* = 8.9 Hz, 3′, 5′, 3″, 5″-H), 7.17 (1H, d, *J* = 8.9 Hz, 5-H), 7.21 (1H, d, *J* = 10.0 Hz, 1-H), 7.36 (4H, app. d, *J* = 8.9 Hz, 2′, 6′, 2″, 6″-H), 7.50 (1H, dd, *J* = 9.0, 2.0 Hz, 9-H), 7.54 (1H, d, *J* = 8.9 Hz, 6-H), 7.81 (1H, d, *J* = 9.0 Hz, 10-H), 7.85 (1H, d, *J* = 2.0 Hz, 7-H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.4, 113.4, 114.1, 117.2, 118.7, 119.5, 123.2, 128.3, 128.6, 128.7, 129.7, 130.37, 130.44, 137.0, 150.8, 159.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}{}^{79}BrO_3^+$ 473.0747; Found 473.0745.

Synthesis of 2-(3,3-bis(4-methoxyphenyl)-3*H*-benzo[*f*]chromen-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 32: *n*-BuLi (6.5 mL, 2.5 M in hexanes) was added dropwise over 10 min to a solution of 8-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (7.00 g, 14.8 mmol) in anhydrous THF (120 mL) at -58 ºC under N_2 atmosphere. The resulting solution was stirred for 1 h, after which $B(O^iPr)_3$ (4.2 mL, 18 mmol) was added dropwise over 10 min. The resulting solution was stirred for 2 h whilst warming to room temperature. The reaction was stopped by adding water (100 mL) and aq. HCl (2M, 12 mL). The phases were separated, the aqueous layer extracted with EtOAc (3 × 100 mL), the combined organic extracts dried with anhydrous sodium sulfate and then evaporated to dryness under reduced pressure. Afterwards, pinacol (1.90 g, 16.1 mmol) was added in one portion to a mixture of the former residue in PhMe (110 mL) and heated under reflux (Dean-Stark). After 2h, the mixture was allowed to cool to room temperature and the solvent removed under reduced pressure to give the title product after flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: DCM/hexane (1:1), fraction 2] and recrystallization from a mixture of DCM/hexane provided the title compound as a pale white crystalline solid (3.74 g, 49%). m.p. = 240–241 ºC; ν_{max}

(neat) 1607, 1509, 1464, 1369, 1324, 1298, 1246, 1173, 1138, 1078, 1031, 999, 954, 821, 728, 655, 596 cm^{-1}; Photomerocyanine λ_{max} = 474 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 1.38 (12H, s, CH_3), 3.77 (6H, s, OMe), 6.19 (1H, d, *J* = 10.0 Hz, 2-H), 6.84 (4H, app. d, *J* = 8.8 Hz, 3′, 5′, 3″, 5″-H), 7.15 (1H, d, *J* = 8.8 Hz, 5-H), 7.29 (1H, d, *J* = 10.0 Hz, 1-H), 7.38 (4H, app. d, *J* = 8.8 Hz, 2′, 6′, 2″, 6″-H), 7.68 (1H, d, *J* = 8.8 Hz, 6-H), 7.81 (1H, dd, *J* = 8.5, 1.0 Hz, 9-H), 7.92 (1H, d, *J* = 8.5 Hz, 10-H), 8.22 (1H, s, 7-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 24.9, 55.3, 82.4, 83.8, 113.4, 113.8, 118.3, 119.1, 120.5, 127.9, 128.4, 128.7, 130.7, 131.3, 131.5, 136.9, 137.2, 151.6, 158.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{34}BO_5^+$ 520.2530; Found 520.2501.

Synthesis of 3,3-bis(4-methoxyphenyl)-8-pyridyl-3*H*-naphtho[2,1-*b*]pyran

Method A – A mixture of 8-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (3.18 mmol), the appropriate pyridineboronic acid pinacol ester (4.8 mmol), K_2CO_3 (4.8 mmol) and $Pd(PPh_3)_4$ (0.16 mmol) in PhMe (37 mL) and EtOH (37 mL) was heated at reflux under N_2 for 16–19 h. After this time, the residue was cooled and added water (200 mL). The residue was extracted with DCM (3 × 200 mL), washed with water (3 × 200 mL), the organic layer dried with anhydrous sodium sulfate and the solvent removed under reduced pressure to afford the target compounds after purification.

Method B – A mixture of 4-bromopyridine hydrochloride (1.4 mmol), 2-(3,3-bis(4-methoxyphenyl)-3*H*-benzo[*f*]chromen-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.96 mmol), K_2CO_3 (2.2 mmol) and $Pd(PPh_3)_4$ (0.05 mmol) in PhMe (8 mL) and EtOH (8 mL) was heated at reflux under N_2 for 16 h. After this time, the mixture was cooled and added water (50 mL). The residue was extracted with DCM (4 × 50 mL), washed with water (3 × 50 mL), the organic layer dried over anhydrous sodium sulfate and the solvent removed under reduced pressure to afford the target compounds after purification.

Method C – A mixture of 2-bromopyridine (1.4 mmol), 2-(3,3-bis(4-methoxyphenyl)-3*H*-benzo[*f*]chromen-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.96 mmol), K_2CO_3 (1.4 mmol) and $Pd(PPh_3)_4$ (0.05 mmol) in PhMe (8 mL) and EtOH (8 mL) was heated at reflux under N_2 for 16 h. After this time, the mixture was cooled and added water (50 mL). The residue was extracted with DCM (4 × 50 mL), washed with water (3 × 50 mL), the organic layer dried over anhydrous sodium sulfate and the solvent removed under reduced pressure to afford the target compounds after purification.

2-(bis(4-methoxyphenyl)methyl)-7-(4-pyridyl)naphtho[2,1-*b*]furan 27: from 8-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (Method A: 1.50 g) and 4-pyridineboronic acid pinacol ester after 16 h of reaction; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/EtOAc (9:1), fraction 1] provided the title compound as a brown powder (0.05 g, 3%). From 2-(3,3-bis(4-methoxyphenyl)-3*H*-benzo[*f*]chromen-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Method B: 0.50 g); Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 1] provided the title compound as a brown powder (0.05 g, 12%). m.p. = 168–172 °C; ν_{max} (neat) 1594, 1507, 1462, 1301, 1244, 1174, 1031, 994, 805, 727, 586 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.81 (6H, s, OMe), 5.61 (1H, s, α-H), 6.76 (1H, s, 1-H), 6.89 (4H, app. d, *J* = 8.7 Hz, 3′, 5′, 3″, 5″-H), 7.18 (4H, app. d, *J* = 8.7 Hz, 2′, 6′, 2″, 6″-H), 7.64–7.66 (3H, m, 4, 2‴, 6‴-H), 7.75 (1H, d, *J* = 9.0 Hz, 5-H), 7.80 (1H, dd, *J* = 8.5, 1.7 Hz, 8-H), 8.13 (1H, d, *J* = 8.5 Hz, 9-H), 8.21 (1H, d, *J* = 1.7 Hz, 6-H), 8.70 (2H, d, *J* = 5.9 Hz, 3‴, 5‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 49.9, 55.3, 104.4, 113.3, 114.0, 121.8, 123.6, 124.57, 124.63, 124.9, 127.3, 127.7, 129.8, 130.4, 133.5, 133.8, 148.6, 150.1, 153.0, 158.6, 160.6 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1908.

3,3-bis(4-methoxyphenyl)-8-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 26: from 8-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (Method A: 1.50 g) and 4-pyridineboronic

acid pinacol ester after 16 h of reaction; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/EtOAc (9:1), fraction 2] followed by recrystallization from DCM/hexane provided the title compound as a pale white crystalline solid (0.92 g, 63%). From 2-(3,3-bis(4-methoxyphenyl)-3*H*-benzo[*f*]chromen-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Method B: 0.50 g); Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 2] provided the title compound as a pale yellow powder (0.30 g, 67%). m.p. = 180–184 °C; ν_{max} (neat) 1581, 1505, 1462, 1303, 1250, 1173, 1032, 999, 955, 810, 787, 725, 552 cm^{-1}; Photomerocyanine λ_{max} = 482 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.78 (6H, s, OMe), 6.25 (1H, d, *J* = 10.0 Hz, 2-H), 6.85 (4H, app. d, *J* = 8.8 Hz, 3′, 5′, 3″, 5″-H), 7.23 (1H, d, *J* = 8.8 Hz, 5-H), 7.30 (1H, d, *J* = 10.0 Hz, 1-H), 7.39 (4H, app. d, *J* = 8.8 Hz, 2′, 6′, 2″, 6″-H), 7.60 (2H, d, *J* = 5.5 Hz, 2‴, 6‴-H), 7.72–7.75 (2H, m, 6, 9-H), 8.00 (1H, d, *J* = 1.6 Hz, 7-H), 8.06 (1H, d, *J* = 8.8 Hz, 10-H), 8.68 (2H, d, *J* = 5.5 Hz, 3‴, 5‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.5, 113.4, 114.0, 118.9, 119.3, 121.5, 122.5, 125.1, 127.0, 128.4, 128.5, 129.3, 129.9, 130.3, 133.0, 137.0, 148.1, 150.3, 151.4, 159.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1900.

2-(bis(4-methoxyphenyl)methyl)-7-(3-pyridyl)naphtho[2,1-*b*]furan 29: from 8-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (Method A: 1.50 g) and 3-pyridineboronic acid pinacol ester after 16 h of reaction; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 1] provided the title compound as a brown powder (0.09 g, 6%). m.p. = 166–170 °C; ν_{max} (neat) 1606, 1582, 1507, 1462, 1302, 1243, 1173, 1029, 991, 802, 708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.73 (6H, s, OMe), 5.53 (1H, s, α-H), 6.67 (1H, s, 1-H), 6.81 (4H, app. d, *J* = 8.7 Hz, 3′, 5′, 3″, 5″-H), 7.10 (4H, app. d, *J* = 8.7 Hz, 2′, 6′, 2″, 6″-H), 7.32 (1H, dd, *J* = 7.9, 4.4 Hz, 5‴-H), 7.55 (1H, d, *J* = 9.0 Hz, 4-H), 7.64–7.68 (2H, m, 5, 8-H), 7.92 (1H, dt, *J* = 7.9, 1.9 Hz, 6‴-H), 8.02–8.04 (2H, m, 6, 9-H),

8.53 (1H, d, J = 4.4 Hz, 4‴-H), 8.90 (1H, s, 2‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 49.9, 55.3, 104.4, 113.2, 114.0, 123.5, 123.6, 124.5, 124.7, 125.1, 127.0, 129.8, 130.5, 133.6, 133.7, 134.6, 148.3, 148.5, 152.8, 158.6, 160.4 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1921.

3,3-bis(4-methoxyphenyl)-8-(3-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 28: from 8-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (Method A: 1.50 g) and 3-pyridineboronic acid pinacol ester after 16 h of reaction; Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/DCM (9:1), fraction 2] provided the title compound as a pale yellow powder (1.05 g, 70%). m.p. = 174–176 °C; ν_{max} (neat) 1608, 1582, 1505, 1413, 1307, 1248, 1173, 1030, 999, 810, 787, 709, 551 cm^{-1}; Photomerocyanine λ_{max} = 476 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.78 (6H, s, OMe), 6.25 (1H, d, J = 9.9 Hz, 2-H), 6.85 (4H, app. d, J = 8.9 Hz, 3′, 5′, 3″, 5″-H), 7.22 (1H, d, J = 8.8 Hz, 5-H), 7.30 (1H, d, J = 9.9 Hz, 1-H), 7.38–7.40 (5H, m, 2′, 6′, 2″, 5″, 6‴-H), 7.69–7.74 (2H, m, 6, 9-H), 7.92 (1H, d, J = 1.8 Hz, 7-H), 7.96 (1H, dt, J = 7.9, 2.0 Hz, 6‴-H), 8.06 (1H, d, J = 8.8 Hz, 10-H), 8.60 (2H, d, J = 3.9 Hz, 3‴, 5‴-H), 8.94 (1H, s, 2‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.4, 113.4, 114.0, 119.0, 119.2, 122.4, 123.6, 125.6, 126.7, 128.4, 128.5, 129.3, 129.5, 130.1, 132.8, 134.3, 136.4, 137.1, 148.3, 148.4, 151.1, 159.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1911.

2-(bis(4-methoxyphenyl)methyl)-7-(2-pyridyl)naphtho[2,1-*b*]furan 34: from 2-(3,3-bis(4-methoxyphenyl)-3*H*-benzo[*f*]chromen-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Method C: 0.50 g); Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/hexane (3:2), fraction 1] provided the title compound as a brown powder (0.02 g, 4%). m.p. = 149–151°C; ν_{max} (neat) 1608, 1582, 1506, 1462, 1439, 1300, 1240, 1174, 1028, 991, 785, 586 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.81 (6H, s, OMe), 5.61 (1H, s, α-H), 6.75 (1H, s, 1-H), 6.89 (4H, app. d, J = 8.7 Hz, 3′, 5′, 3″, 5″-H), 7.19 (4H, app. d, J = 8.7 Hz, 2′, 6′, 2″,

6″-H), 7.24–7.27 (1H, m, 4‴-H), 7.61 (1H, d, *J* = 8.9 Hz, 4-H), 7.77–7.81 (2H, m, 5, 5‴-H), 7.89 (1H, d, *J* = 8.0 Hz, 6‴-H), 8.11 (1H, d, *J* = 8.6 Hz, 9-H), 8.19 (1H, dd, *J* = 8.6, 1.5 Hz, 8-H), 8.56 (1H, d, *J* =1.5 Hz, 6-H), 8.75 (1H, d, *J* = 4.4 Hz, 3‴-H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 49.9, 55.3, 104.5, 112.9, 114.0, 120.8, 122.0, 123.5, 124.1, 124.7, 125.3, 127.2, 127.8, 129.8, 130.4, 133.6, 135.1, 136.9, 149.7, 153.0, 157.4, 158.5, 160.3 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1906.

3,3-bis(4-methoxyphenyl)-8-(2-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 33: from 2-(3,3-bis(4-methoxyphenyl)-3*H*-benzo[*f*]chromen-8-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Method C: 0.50 g); Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O/hexane (3:2), fraction 2] provided the title compound as a salmon pink powder (0.41 g, 84%). m.p. = 175–178 °C; ν_{max} (neat) 2951, 2833, 1607, 1582, 1506, 1471, 1462, 1304, 1248, 1173, 1088, 1031, 1001, 955, 837, 771, 734, 726, 586 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 6.22 (1H, d, *J* = 10.0 Hz, 2-H), 6.84 (4H, app. d, *J* = 8.8 Hz, 3′, 5′, 3″, 5″-H), 7.18–7.25 (2H, m, 5, 4‴-H), 7.30 (1H, d, *J* = 10.0 Hz, 1-H), 7.39 (4H, app. d, *J* = 8.8 Hz, 2′, 6′, 2″, 6″-H), 7.73–7.77 (2H, m, 6, 5‴-H), 7.82 (1H, d, *J* = 7.9 Hz, 6‴-H), 8.04 (1H, d, *J* = 8.9 Hz, 10-H), 8.12 (1H, dd, *J* = 8.9, 1.5 Hz, 9-H), 8.35 (1H, d, *J* = 1.5 Hz, 7-H), 8.71 (1H, d, *J* = 4.7 Hz, 3‴-H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.4, 113.4, 113.8, 118.9, 119.1, 120.5, 121.9, 125.2, 126.9, 128.2, 128.4, 129.4, 130.1, 130.6, 134.4, 136.8, 137.2, 149.7, 151.2, 157.2, 158.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1907.

Synthesis of 8-bromo-3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran 25: 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (2.81 g, 9.42 mmol) and 6-bromo-2-naphthol (2.00 g, 8.97 mmol) in the presence of PPTS (0.12 g, 0.48 mmol) and trimethyl orthoformate (2.0 mL, 18 mmol) in 1,2-DCE (50 mL) was refluxed for 4 h under N_2. Solvent was removed under reduced pressure and the residue was taken in DCM

(100 mL), washed with water (3 × 200 mL) and the organic layer dried with anhydrous sodium sulfate. Subsequently, the residue was crystallized from a DCM/hexane mixture giving the corresponding product as a brown powder (3.98 g, 88%). m.p. = 121–125 °C; ν_{max} (neat) 1606, 1584, 1505, 1248, 1172, 1028, 1000, 827, 809 cm^{-1}; Photomerocyanine λ_{max} = 486 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.57 (3H, s, OMe), 3.75 (3H, s, OMe), 3.76 (3H, s, OMe), 6.45–6.47 (2H, m, 3′, 5′-H), 6.51 (1H, d, *J* = 10.1 Hz, 2-H), 6.78–6.82 (2H, m, 3″, 5″-H), 7.12 (1H, d, *J* = 10.1 Hz, 1-H), 7.18 (1H, d, *J* = 8.9 Hz, 5-H), 7.31–7.35 (2H, m, 2″, 6″-H), 7.48 (1H, dd, *J* = 9.0, 2.1 Hz, 9-H), 7.52 (1H, d, *J* = 8.9 Hz, 6-H), 7.55–7.58 (1H, m, 6′-H), 7.78 (1H, d, *J* = 9.0 Hz, 10-H), 7.84 (1H, d, *J* = 2.1 Hz, 7-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.2, 55.3, 55.5, 81.9, 100.2, 103.7, 113.2, 114.1, 117.1, 117.7, 119.4, 123.3, 124.7, 128.0, 128.1, 128.30, 128.33, 128.4, 129.6, 130.3, 130.4 136.7, 150.6, 156.8, 158.8, 160.6 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{24}{}^{79}BrO_4{}^+$ 503.0852; Found 503.0849.

Synthesis of 3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-8-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 30: a mixture of 8-bromo-3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (1.00 g, 1.99 mmol), 4-pyridineboronic acid pinacol ester (0.61 g, 3.0 mmol), K_2CO_3 (0.41 g, 3.0 mmol) and $Pd(PPh_3)_4$ (0.11 g, 0.095 mmol) in PhMe (23.0 mL) and EtOH (23.0 mL) was heated at reflux under N_2. After 15 h of reaction, the crude was evaporated to dryness. The residue was dissolved in DCM (100 mL), washed with water (3 × 200 mL), the organic layer dried with anhydrous sodium sulfate and the solvent removed under reduced pressure. Afterwards, the residue was purified two times by flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: Et_2O] to give two pure fractions.

Fraction 1 – **4-(2-((2,4-dimethoxyphenyl)(4-methoxyphenyl)methyl)naphtho[2,1-*b*]furan-7-yl)pyridine 31** as a brown powder (0.11 g, 11%). m.p. = 163–167 °C; ν_{max} (neat) 1583, 1508, 1460, 1437, 1417, 1259, 1242, 1207, 1116, 1039, 995, 803 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)

δ_H 3.69 (3H, s, OMe), 3.72 (6H, s, OMe), 5.90 (1H, s, α-H), 6.37 (1H, app. d, J = 8.4 Hz, 5′-H), 6.44 (1H, d, J = 1.6 Hz, 3′-H), 6.62 (1H, s, 1-H), 6.79 (2H, d, J = 8.4 Hz, 3″, 5″-H), 6.87 (1H, d, J = 8.4 Hz, 2′-H), 7.10 (2H, d, J = 8.4 Hz, 2″, 6″-H), 7.54–7.72 (5H, m, 4, 5, 8, 3″, 5″-H), 8.03 (1H, d, J = 8.5 Hz, 9-H), 8.11 (1H, s, 6-H), 8.61 (2H, d, J = 5.0 Hz, 3‴, 5‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 43.0, 55.3, 55.4, 55.7, 98.8, 104.1, 104.2, 113.3, 113.9, 121.8, 122.5, 123.7, 124.5, 124.6, 124.7, 127.2, 127.6, 129.9, 130.0, 130.3, 133.4, 133.7, 148.5, 150.3, 152.9, 157.8, 158.4, 160.0, 160.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{28}NO_4^+$ 502.2013; Found 502.2013.

Fraction 2 – **3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-8-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 30** after trituration with cold Et_2O gave the corresponding product as an off-white powder (0.59 g, 60%). m.p. = 179–181 °C; ν_{max} (neat) 1606, 1584, 1506, 1465, 1286, 1251, 1206, 1175, 1027, 999, 828, 814 cm^{-1}; Photomerocyanine λ_{max} = 490 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.59 (3H, s, OMe), 3.77–3.78 (6H, m, OMe), 6.46–6.49 (2H, m, 3′, 5′-H), 6.54 (1H, d, J = 10.1 Hz, 2-H), 6.81 (2H, app. d, J = 8.7 Hz, 3″, 5″-H), 7.20–7.25 (2H, m, 1, 5-H), 7.35 (2H, app.d, J = 8.7 Hz, 2″, 6″-H), 7.59–7.60 (3H, m, 2‴, 6‴, 6′-H), 7.71–7.74 (2H, m, 6, 9-H), 7.99 (1H, app. s, 7-H), 8.05 (1H, d, J = 8.8 Hz, 10-H), 8.67 (2H, d, J = 5.8 Hz, 3‴, 5‴-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.2, 55.3, 55.5, 82.0, 100.2, 103.8, 113.2, 113.9, 117.8, 119.2, 121.5, 122.5, 124.8, 124.9, 126.9, 127.99, 128.03, 128.3, 129.3, 129.91, 129.92, 132.8, 136.8, 148.1, 150.3, 151.3, 156.9, 158.9, 160.6 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{28}NO_4^+$ 502.2013; Found 502.2004.

Synthesis of 7-pyridyl-3*H*-naphtho[2,1-*b*]pyrans

Synthesis of 5-bromo-2-naphthol 37: 5-amino-2-naphthol (10.00 g, 62.82 mmol) was ground to a fine powder and heated to 55 ºC under a stream of N_2. Sulfuric acid (95%, 13.0 mL, 232 mmol) was added in one portion and mixed rapidly with the solid. Stirring was continued until

the mixture became too viscous to stir. The heat was removed, the reaction covered and allowed to stand overnight. The solid was suspended in water (300 mL) and collected by filtration, washed with acetone and air-dried. The resulting product (13.00 g, 54.34 mmol), NaOH (2.24 g, 56.0 mmol) and $NaNO_2$ (3.75 g, 54.3 mmol) were dissolved in water (93 mL). This solution was added dropwise to a solution of H_2SO_4 (95–98%, 9.6 mL) in water (20.0 mL) at such a rate that the internal temperature never exceeded 5 ºC. The yellow diazonium sulfate precipitate was collected by filtration and washed several times with ice cold water. The moist* filter cake was transferred to a mixture of CuBr (7.80 g, 54.4 mmol), $CuBr_2$ (12.14 g, 54.35 mmol), HBr (6.0 mL) and water (200 mL). The mixture was warmed to 70 ºC for 1 h and then filtered by gravity. The filtrate was saturated with NaCl (105 g) and the solution stirred overnight. The precipitate was collected by filtration. The black solid was air-dried giving the corresponding 5-bromo-2-hydroxynaphthalene-1-sulfonic acid (7.02 g, 37%). Afterwards, the 5-bromo-2-hydroxynaphthalene-1-sulfonic acid (6.80 g, 22.4 mmol) was mixed with 20% aq. H_2SO_4 (153 mL). The slurry was heated to reflux for 20 min. After the reaction cooled, it was extracted with Et_2O (3 × 200 mL). The ether layers were combined, washed with water (3 × 200 mL), dried with anhydrous sodium sulfate and evaporated to dryness, giving the desired product as a dark brown powder (3.51 g, 70%). m.p. = 108–110 °C [lit. m.p. = 110–111 °C[45]]; ν_{max} (neat) 3200 (br), 1636, 1561, 1501, 1424, 1343, 1300, 1251, 1229, 1152, 1131, 963, 860, 801, 770, 738, 655, 543 cm^{-1}; ^1H NMR (400 MHz, Methanol-d_4) δ_H 4.90 (1H, s, OH), 7.13 (1H, d, J = 2.4 Hz, 1-H), 7.18 (1H, dd, J = 9.1, 2.4 Hz, 3-H), 7.23 (1H, dd, J = 8.2, 7.5 Hz, 7-H), 7.54 (1H, dd, J = 7.5, 0.9 Hz, 6-H), 7.64 (1H, d, J = 8.2 Hz, 8-H), 8.05 (1H, d, J = 9.1 Hz, 4-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, Methanol-d_4) δ_C 110.9, 121.2, 123.8, 128.0, 128.2, 128.4, 128.5, 130.0, 138.2, 157.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_8{}^{79}BrO^+$ 222.9753; Found 222.9757.

*Hazard - Many diazonium salts are explosive/shock-sensitive when dried. The diazonium salt must be kept damp with water at all times.

Synthesis of 7-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran 38: 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (3.78 g, 14.1 mmol) and 5-bromo-2-naphthol (3.00 g, 13.4 mmol) in the presence of PPTS (0.17 g, 0.68 mmol) and trimethyl orthoformate (3.0 mL, 27 mmol) in 1,2-DCE (27 mL) was refluxed for 3 h under N_2 atmosphere. Solvent was removed under reduced pressure, the residue taken in DCM (3 × 200 mL), washed with water (3 × 200 mL) and the organic layer dried with anhydrous sodium sulfate. Subsequently, after solvent evaporation, the residue was crystallized from DCM/hexane giving the corresponding product as a brown crystalline solid (3.94 g, 62%). m.p. = 185–189 °C; ν_{max} (neat) 1606, 1506, 1458, 1248, 1170, 1092, 1032, 1021, 963, 841, 756, 572 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 6.24 (1H, d, J = 10.0 Hz, 2-H), 6.84 (4H, app. d, J = 8.8 Hz, 3′, 5′, 3″, 5″-H), 7.24–7.30 (3H, m, 1, 5, 9-H), 7.37 (4H, app. d, J = 8.8 Hz, 2′, 6′, 2″, 6″-H), 7.60 (1H, d, J = 7.3 Hz, 8-H), 7.93 (1H, d, J = 8.6 Hz, 10-H), 8.08 (1H, d, J = 9.2 Hz, 6-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.4, 113.4, 114.2, 119.0, 119.6, 121.3, 123.6, 126.8, 127.68, 127.71, 128.3, 128.8, 129.0, 131.1, 136.9, 151.2, 159.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}{}^{79}BrO_3^+$ 473.0747; Found 473.0749.

Synthesis of 3,3-bis(4-methoxyphenyl)-7-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 39: a mixture of 7-bromo-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (1.00 g, 2.11 mmol), 4-pyridineboronic acid pinacol ester (0.65 g, 3.2 mmol), K_2CO_3 (0.66 g, 3.2 mmol) and $Pd(PPh_3)_4$ (0.19 g, 0.11 mmol) in PhMe (25 mL) and EtOH (25 mL) was heated at reflux under N_2 for 16 h. After this time, the mixture was cooled and added water (150 mL). Afterwards, the residue was extracted with DCM (3 × 200 mL), washed with water (3 × 200 mL), the organic layer dried with anhydrous sodium sulfate and the solvent removed under reduced pressure. The residue was then recrystallized from a mixture of DCM/hexane leading to the

corresponding product as a grey powder (0.64 g, 66%). m.p. = 229–232 °C; ν_{max} (neat) 1604, 1585, 1509, 1463, 1406, 1298, 1249, 1174, 1082, 1033, 953, 838, 767, 592, 561 cm^{-1}; Photomerocyanine λ_{max} = 470 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.78 (6H, s, OMe), 6.26 (1H, d, *J* = 10.0 Hz, 2-H), 6.84 (4H, app. d, *J* = 8.8 Hz, 3′, 5′, 3″, 5″-H), 7.15 (1H, d, *J* = 9.2 Hz, 5-H), 7.23 (1H, d, *J* = 7.8 Hz, 8-H), 7.33 (1H, d, *J* = 10.0 Hz, 1-H), 7.36–7.39 (6H, m, 2′, 6′, 2″, 6″, 2‴, 6‴-H), 7.52 (1H, t, *J* = 7.8 Hz, 9-H), 7.62 (1H, d, *J* = 9.2 Hz, 6-H), 8.04 (1H, d, *J* = 7.8 Hz, 10-H), 8.70 (2H, d, *J* = 5.7 Hz, 3‴, 5‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.3, 113.4, 114.3, 118.9, 119.1, 122.1, 124.6, 125.0, 126.1, 126.6, 127.1, 128.4, 128.6, 130.3, 137.0, 138.0, 148.9, 149.7, 150.7, 159.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1907.

Synthesis of 5-pyridyl-3*H*-naphtho[2,1-*b*]pyrans

Synthesis of 5-hydroxy-3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran 40: 1-(2,4-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-ol (18.65 g, 62.51 mmol) and 2,3-dihydroxynaphthalene (10.00 g, 62.43 mmol) in the presence of PPTS (0.78 g, 3.1 mmol) and trimethyl orthoformate (14.0 mL, 128 mmol) in 1,2-DCE (126 mL) was refluxed for 3 h under N_2 atmosphere. Solvent was removed under reduced pressure and the residue taken in EtOAc (200 mL), washed with water (2 × 150 mL) and the organic layer dried with anhydrous sodium sulfate. Subsequently, the residue (30 g) was purified in 10 g portions by flash column chromatography [Aldrich silica gel (60 Å 230-400 mesh 40-63 μm), eluent: 20% EtOAc in Petroleum Ether] giving the corresponding product as a red powder (9.91 g, 36%). m.p. = 69–73 °C; ν_{max} (neat) 3365 (br), 2930, 2834, 1606, 1508, 1452, 1247, 1206, 1173, 1028, 999, 831, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.59 (3H, s, OMe), 3.77 (3H, s, OMe), 3.79 (3H, s, OMe), 6.14 (1H, bs, OH), 6.34 (1H, d, *J* = 10.1 Hz, 2-H), 6.43 (1H, dd, *J* = 8.5, 2.3 Hz, 5′-H), 6.46 (1H, d, *J* = 2.3 Hz, 3′-H), 6.84 (2H, d, *J* = 8.8 Hz, 3″, 5″-H, 7.18 (1H, s, 6-H), 7.23 (1H, d, *J* = 10.1 Hz, 1-H), 7.29–7.33 (4H, m, 2″, 6″, 8, 9-H), 7.44 (1H, d, *J* = 8.6 Hz,

6′-H), 7.26 (1H, d, *J* = 8.1 Hz, 7-H), 7.88 (1H, d, *J* = 8.1 Hz, 10-H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.25, 55.34, 55.6, 82.8, 100.5, 103.6, 110.3, 113.3, 114.7, 118.7, 121.2, 123.4, 124.0, 124.2, 124.7, 127.2, 127.9, 128.37, 128.42, 129.8, 136.6, 140.1, 144.7, 157.7, 158.8, 160.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}O_5^+$ 441.1697; Found 441.1656.

Synthesis of 3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-5-triflyloxy-3*H*-naphtho[2,1-*b*]pyran 41: triflic anhydride (1.1 mL, 6.5 mmol) was added dropwise to an aerated solution of 5-hydroxy-3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (2.69 g, 6.11 mmol), Et_3N (1.9 mL, 14 mmol) in DCM at 0 °C. After stirring for 1 h at 0 °C, triflic anhydride (0.4 mL, 2.4 mmol) was added dropwise to force the reaction to completion. After stirring for 30 min at 0 °C, the organic phase was washed with HCl (1M, 50 mL). The phases were separated, the organic phase washed with a saturated solution of $NaHCO_3$ (100 mL), dried with anhydrous sodium sulfate and evaporated to dryness, giving the corresponding product as a red powder (3.32 g, 95%) that was used in the next step without further purification. m.p. = 64–67 °C (darkened at 57 °C); ν_{max} (neat) 1418, 1245, 1204, 1173, 1135, 1103, 1022, 999, 889, 824, 806, 620 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.55 (3H, s, OMe), 3.75 (3H, s, OMe), 3.80 (3H, s, OMe), 6.44 (1H, d, *J* = 2.4 Hz, 3′-H), 6.53–6.57 (2H, m, 2, 5′-H), 6.78 (2H, d, *J* = 8.8 Hz, 3″, 5″-H), 7.24 (1H, d, *J* = 10.2 Hz, 1-H), 7.35–7.41 (3H, m, 2″, 6″, 8-H), 7.50–7.54 (2H, m, 6, 9-H), 7.71 (2H, app. d., *J* = 8.6 Hz, 7, 6′-H), 7.98 (1H, d, *J* = 8.5 Hz, 10-H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.1, 55.3, 55.4, 82.9, 100.2, 103.8, 113.0, 117.4, 117.8, 120.1, 121.6, 124.2, 125.0, 127.5, 127.95, 128.01, 128.2, 128.58, 128.62, 129.2, 135.7, 138.1, 142.3, 156.9, 158.7, 160.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F -73.8 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{24}F_3O_7S^+$ 573.1163; Found 573.1189.

Synthesis of 3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-5-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 42: 3-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)-5-triflyloxy-3*H*-naphtho[2,1-*b*]pyran (500.0 mg, 0.8733 mmol), 4-pyridineboronic acid pinacol ester (196.9

mg, 0.9602 mmol), K_3PO_4 (213.1 mg, 1.004 mmol), $Pd(PPh_3)_4$ (50.5 mg, 0.0437 mmol) were added to a dry 25 mL two-neck round-bottom flask. Once the air was evacuated and the flask flushed with N_2, anhydrous DMAc (7.5 mL) was added. The mixture was degassed for 15 min and then stirred at 110 °C under N_2. After 20 min of reaction, the crude was poured into water (50 mL) and the residue extracted with DCM (4 × 50 mL). The organic phase was washed with water (2 × 100 mL), dried with anhydrous sodium sulfate and evaporated to dryness. The resulting red oil was purified by flash column chromatography [Aldrich silica gel (60 Å 230-400 mesh 40-63 μm), eluent: 50% EtOAc in hexanes] giving the corresponding product as a red powder (225.2 mg, 51%). m.p. = 74–77 °C; ν_{max} (neat) 1605, 1506, 1461, 1246, 1172, 1030, 1000, 824, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.45 (3H, s, OMe), 3.749 (3H, s, OMe), 3.753 (3H, s, OMe), 6.37–6.40 (2H, m, 3′, 5′-H), 6.49 (1H, d, *J* = 10.1 Hz, 2-H), 6.74 (2H, d, *J* = 6.8 Hz, 3″, 5″-H), 7.19–7.26 (2H, m, 2″, 6″-H), 7.31–7.37 (3H, m, 1, 8, 6′-H), 7.49–7.53 (3H, m, 9, 2‴, 6‴-H), 7.68 (1H, s, 7-H), 7.75 (1H, d, *J* = 8.0 Hz, 7-H), 8.01 (1H, d, *J* = 8.5 Hz, 10-H), 8.65 (2H, d, *J* = 6.0 Hz, 3‴, 5‴-H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.1, 55.2, 55.3, 81.9, 100.1, 103.6, 112.9, 115.2, 118.8, 121.4, 124.1, 124.6, 127.1, 127.8, 128.0, 128.2, 128.6, 128.75, 128.84, 129.1, 129.7, 129.9, 136.1, 146.0, 147.4, 149.4, 156.9, 158.6, 160.4 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{28}NO_4^+$ 502.2013; Found 502.1991.

Synthesis of 3-pyridyl-3*H*-naphtho[2,1-*b*]pyrans

Synthesis of 1-phenyl-1-(4-pyridyl)prop-2-en-1-ol 44: vinylmagnesium chloride [1.6 M in THF] (56.0 mL, 89.6 mmol) was added to a mixture of phenyl(pyridin-4-yl)methanone (98%) (8.00 g, 42.8 mmol) under N_2 in anhydrous THF (200 mL) at such a rate that the temperature did not rise above 0 °C. The resulting mixture was stirred for 30 min at this temperature and then allowed to reach room temperature. After stirring for 3 h, the reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (65 mL), after which THF was evaporated under reduced pressure. The aqueous layer was extracted with EtOAc (2 × 200 mL).

The organic phase was reduced to 200 mL, washed with water (3 × 200 mL), dried with anhydrous sodium sulfate and evaporated to dryness. The desired product was obtained by crystallization from an EtOAc/hexane mixture as brown microcrystals (7.76 g, 86%). m.p. = 131–133 °C [lit. m.p. = 135–137 °C[73]]; ν_{max} (neat) 3061 (br), 2795 (br), 1597, 1488, 1446, 1223, 1194, 1004, 919, 764, 694 cm^{-1}; ^1H NMR (400 MHz, Acetone-d_6) δ_H 5.26 (1H, s, OH), 5.29–5.35 (2H, m, 3-H_{cis}, 3-H_{trans}), 6.59 (1H, dd, J = 17.0, 10.6 Hz, 2-H), 7.23–7.27 (1H, m, 4″-H), 7.30–7.34 (2H, m, 3″, 5″-H), 7.36–7.42 (4H, m, 2′, 6′, 2″, 6″-H), 8.47–8.49 (2H, m, 3′, 5′-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, Acetone-d_6) δ_C 77.9, 113.8, 121.6, 126.9, 127.2, 128.0, 143.1, 145.7, 149.4, 155.3 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}NO^+$ 212.1070; Found 212.1077.

Synthesis of 1,1-bis(4-methoxyphenyl)prop-2-en-1-ol 45: vinylmagnesium chloride [1.6 M in THF] (42.0 mL, 67.2 mmol) was added dropwise to a mixture of bis(4-methoxyphenyl)methanone (8.00 g, 33.0 mmol) in anhydrous THF (160 mL) at 0 °C under N_2. The resulting mixture was stirred for 30 min at this temperature and then allowed to reach room temperature. After stirring for 2 h, the reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (50 mL), after which THF was evaporated under reduced pressure. The aqueous layer was extracted with EtOAc (2 × 100 mL). The organic phase was reduced to 100 mL, washed with water (4 × 100 mL), dried with anhydrous sodium sulfate and evaporated to dryness. The resulting crude allyl alcohol was obtained as a pale-yellow oil (8.87 g, 99%) that was used in the next step without further purification. ν_{max} (neat) 3486 (br), 2955, 2835, 1607, 1582, 1506, 1462, 1299, 1242, 1172, 1030, 826 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.24 (s, 1H, OH), 3.79 (6H, s, OMe), 5.25–5.30 (2H, m, 3-H_{cis}, 3-H_{trans}), 6.45 (1H, dd, J = 17.0, 10.6 Hz, 2-H), 6.82–6.87 (4H, m, 3′, 3″, 5′, 5″-H), 7.25–7.30 (4H, m, 2′, 2″, 6′, 6″-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 78.9, 113.4, 128.2, 138.2, 143.9, 158.7 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{18}O_3Na^+$ 293.1148; Found 293.1142.

Synthesis of 1,1-bis(4-fluorophenyl)prop-2-en-1-ol 46: in a dry 250 mL round-bottom flask flushed with nitrogen, vinyl magnesium chloride (1.6 M in THF) (43.2 mL, 67.8 mmol) was added dropwise to a mixture of 4,4′-difluorobenzophenone (5.00 g, 20.6 mmol) in anhydrous THF (100 mL) at 0 °C. The resulting mixture was then stirred for 30 minutes at 0 °C and then allowed to stir at room temperature for 18 hours. The reaction mixture was quenched by the addition of a saturated aqueous solution of ammonium chloride (30 mL), after which it was filtered through a sinter with washings of EtOAc and evaporated to remove THF. The organic layer was washed with water (4 × 100 mL) and extracted with EtOAc (100 mL), dried with anhydrous magnesium sulfate and evaporated to dryness. The resulting crude alcohol was obtained as a pale yellow oil (5.37 g, 95%); ν_{max} (neat) 3449, 3072, 1600, 1504, 1408, 1222, 1157, 1094, 1014, 997, 975, 931, 912, 829, 649, 625, 585, 556 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 2.35 (1H, s, OH), 5.28 (1H, d, J = 17.1 Hz, 3-H_{trans}), 5.33 (1H, d, J = 10.6 Hz, 3-H_{cis}), 6.45 (1H, dd, J = 17.1, 10.6 Hz, 2-H), 7.01 (4H, app. t, J = 10.8, 6.7 Hz, Ar-H), 7.33 (4H, app. dd, J = 5.3, 9.9 Hz, Ar-H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 78.7, 114.5, 114.9, 115.1, 128.6, 128.7, 141.3, 141.4, 143.22, 160.8, 163.2 ppm; HRMS (ESI) m/z: $[M\text{-}H_2O+H]^+$ Calcd for $C_{15}H_{11}F_2^+$ 229.0823; Found 229.0823.

Synthesis of 1-bromo-2-(methoxymethoxy)naphthalene 43: MOMCl (3.3 mL, 43 mmol) was added dropwise to a degassed mixture of 1-bromo-2-naphthol (97%, 5.00 g, 21.7 mmol) and K_2CO_3 (9.30 g, 67.3 mmol) in anhydrous MeCN (500 mL) at -15 °C under N_2. The reaction mixture was left stirring for 30 min, after which it was warmed to room temperature and left stirring overnight. After 17 h, the crude was filtered through celite and evaporated to dryness. The resulting red oil was dissolved in EtOAc (50 mL), washed with water (3 × 50 mL), dried with anhydrous sodium sulfate and evaporated to dryness. The residue was then distilled by bulb-to-bulb distillation (impurity distilled at 80 °C at 2.5 x 10^{-2} torr), giving the corresponding product as a brick red oil (5.72 g, 99%) that was used in the next step without further

purification. ν_{max} (neat) 1624, 1595, 1501, 1464, 1352, 1240, 1148, 1082, 1007, 889, 803, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.57 (3H, s, CH_3), 5.35 (2H, s, CH_2), 7.39–7.43 (2H, m, 3, 6-H), 7.54–7.58 (1H, m, 7-H), 7.76–7.78 (2H, m, 4, 5-H), 8.23 (1H, app. d, J = 8.6 Hz, 8-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 56.6, 95.6, 110.5, 117.0, 124.9, 126.4, 127.7, 128.1, 128.9, 130.5, 133.1, 151.8 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}{}^{81}BrO_2{}^+$ 269.0000; Found 268.9992.

Heck cross-coupling reactions between 1-bromo-2-(methoxymethoxy)naphthalene 43 and different prop-2-en-1-ols under multiple conditions (Table 1):

Entry 1 – A mixture of 1-bromo-2-(methoxymethoxy)naphthalene (250.3 mg, 0.9370 mmol), 1-phenyl-1-(4-pyridyl)prop-2-en-1-ol (217.2 mg, 1.028 mmol), K_2CO_3 (193.9 mg, 1.403 mmol), $Pd(OAc)_2$ (17.0 mg, 0.0757 mmol), TBAB (452.7 mg, 1.404 mmol), KCl (69.9 mg, 0.938 mmol) in DMF (16.0 mL) was heated at 100 °C under N_2 for 24 h. After this time, the crude was poured into water (250 mL) and the pH adjusted to 7. The residue was extracted with DCM (3 × 200 mL) and the organic phase reduced to 100 mL. The latter was washed with brine (100 mL), water (2 × 150 mL), dried with anhydrous sodium sulfate and evaporated to dryness. Purification by flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: 20% EtOAc in PhMe → 40% EtOAc in PhMe, fraction 3], followed by crystallization from hot PhMe, led to the corresponding product **47** as off-white needles (150.9 mg, 41%). m.p. = 202–203 °C; ν_{max} (neat) 1595, 1445, 1231, 1192, 1148, 1068, 1000, 991, 752, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.92 (1H, s, OH), 3.43 (3H, s, CH_3), 5.24 (2H, s, CH_2), 6.87 (1H, d, J = 16.1 Hz, 2-H), 7.07 (1H, d, J = 16.1 Hz, 3-H), 7.33–7.42 (6H, m, Ar-H), 7.48 (2H, app. d, J = 5.9 Hz, 2″, 6″-H), 7.53 (2H, app. d, J = 7.3 Hz, Ar-H), 7.73–7.79 (2H, m, Ar-H), 7.92 (1H, d, J = 8.4 Hz, Ar-H), 8.58 (2H, app. d, J = 5.9 Hz, 3″, 5″-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 56.3, 79.2, 95.3, 116.4, 120.9, 121.8, 123.2, 124.0, 124.1, 126.6, 127.1,

128.0, 128.3, 128.6, 129.1, 129.8, 132.6, 140.2, 145.1, 149.7, 152.0, 154.8 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{24}NO_3^+$ 398.1751; Found 398.1752.

Entry 2 – $Pd(OAc)_2$ (15.9 mg, 0.0708 mmol) was added to a degassed mixture of 1-bromo-2-(methoxymethoxy)naphthalene (199.2 mg, 0.7457 mmol), 1,1-bis(4-methoxyphenyl)prop-2-en-1-ol (245.2 mg, 0.9070 mmol), K_2CO_3 (153.0 mg, 1.107 mmol), TBAB (364.4 mg, 1.130 mmol), KCl (59.7 mg, 0.801 mmol) in anhydrous DMAc [12.0 mL, dried under activated 4Å molecular sieves] and heated at 100 °C under N_2 for 28 h. After this time, brine (50 mL) was added, the residue extracted with EtOAc (3 × 50 mL), washed with brine (50 mL), dried with anhydrous sodium sulfate and evaporated to dryness. The resulting residue was purified by flash column chromatography [Aldrich silica gel (60 Å 230-400 mesh 40-63 μm), eluent: 20% EtOAc in hexanes, fraction 3] giving the corresponding product **48** as yellow oil (31.5 mg, 9%). m.p. = 81–85 °C; ν_{max} (neat) 1606, 1505, 1242, 1172, 1148, 1031, 1014, 996, 929, 811, 746, 580 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.53 (1H, s, OH), 3.43 (3H, s, CH_3), 3.80 (6H, s, OMe), 5.21 (2H, s, CH_2), 6.82–6.89 (5H, m, 2, 3″, 3‴, 5″, 5‴-H), 6.98 (1H, d (AB), J = 16.1 Hz, 1-H), 7.33–7.41 (3H, m, Ar-H), 7.44 (4H, app. d, J = 8.9 Hz, 2″, 2‴, 6″, 6‴-H), 7.71 (1H, d, J = 9.0 Hz, Ar-H), 7.76 (1H, d, J = 7.6 Hz, Ar-H), 7.99 (1H, d, J = 8.5 Hz, Ar-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 56.3, 79.4, 95.4, 113.5, 116.7, 121.4, 121.9, 124.0, 124.3, 126.4, 128.2, 128.4, 128.6, 129.8, 132.8, 138.7, 142.4, 151.9, 158.7 ppm; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{28}O_5Na^+$ 479.1829; Found 479.1833.

Entry 3 – $Pd(OAc)_2$ (8.5 mg, 0.038 mmol) was added to a degassed mixture of 1-bromo-2-(methoxymethoxy)naphthalene (199.4 mg, 0.7465 mmol), 1,1-bis(4-methoxyphenyl)prop-2-en-1-ol (248.3 mg, 0.9185 mmol), anhydrous *N*-methyldicyclohexylamine [(0.24 mL, 1.1 mmol), distilled over calcium hydride], TBAC (23.7 mg, 0.0853 mmol), triphenylphosphine (19.7 mg, 0.0751 mmol) in anhydrous DMAc [1.4 mL, dried under activated 4Å molecular sieves] and heated at 80 °C under N_2 for 25 h. After this time, brine (50 mL) was added to the

crude, the residue extracted with EtOAc (2 × 50 mL), washed with brine (50 mL), dried with anhydrous sodium sulfate and evaporated to dryness. The resulting residue was purified by flash column chromatography [Aldrich silica gel (60 Å 230-400 mesh 40-63 μm), eluent: 20% EtOAc in hexanes, fraction 3] giving the desired product **48** as a yellow oil (25.8 mg, 8%).

Entry 4 – A dry three-neck 50 mL round-bottom flask was loaded with 1,1-bis(4-methoxyphenyl)prop-2-en-1-ol (0.64 g, 2.6 mmol), 1-bromo-2-(methoxymethoxy)naphthalene (0.50 g, 1.9 mmol), bis(dibenzylideneacetone)palladium(0) (0.02 g, 0.04 mmol, 2 mol%), *N*-methyldicyclohexylamine (0.34 mL, 2.7 mmol), tetrabutylammonium chloride (0.05 g, 0.2 mmol, 10 mol%) and tri-*tert*-butylphosphonium tetrafluoroborate (0.02 g, 0.07 mmol, 4 mol%). After the air was evacuated and the flask flushed with N_2, anhydrous dimethylacetamide (2.9 mL) was added. The reaction mixture was degassed and then heated to 80 °C under N_2 for 18 h. After this time, brine (30 mL) was added to quench the reaction. Brine (50 mL) was added to the reaction mixture in a separating funnel, and the aqueous phase extracted with EtOAc (2 × 50 mL), dried with anhydrous magnesium sulfate and evaporated to dryness to give a dark red-brown oil. The oil was recrystallized overnight using diethyl ether and hexane to afford the corresponding product **49** as pure white crystals (0.37 g, 50 %). m.p. = 174–177 °C; ν_{max} (neat) 1508, 1247, 1174, 1029, 1000, 827, 813, 805, 746, 724, 590 cm^{-1}; Photomerocyanine λ_{max} = 474 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 6.20 (1H, d, *J* = 9.9 Hz, 2-H), 6.84 (4H, app. d, *J* = 8.7 Hz, 3′, 3″, 5′, 5″-H), 7.16 (1H, d, *J* = 8.8 Hz, Ar-H), 7.24–7.32 (2H, m, 1-H, Ar-H), 7.38 (4H, app. d, *J* = 8.7 Hz, 2′, 2″, 6′, 6″-H), 7.45 (1H, t, *J* = 7.6 Hz, Ar-H), 7.64 (1H, d, *J* = 8.8 Hz, Ar-H), 7.71 (1H, d, *J* = 8.2 Hz, Ar-H), 7.95 (1H, d, *J* = 8.5 Hz, Ar-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.26, 82.20, 113.39, 113.94, 118.40, 119.18, 121.33, 123.53, 126.58, 128.07, 128.36, 128.51, 129.29, 129.74, 129.81, 137.22, 150.58, 158.88 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}O_3^+$ 395.1642; Found 395.1649.

Entry 5 – A dry three-neck 50 mL round-bottom flask was loaded with 1,1-bis(4-fluorophenyl)prop-2-en-1-ol (0.61 g, 2.5 mmol), 1-bromo-2-(methoxymethoxy)naphthalene (0.50 g, 1.9 mmol), bis(dibenzylideneacetone)palladium(0) (0.02 g, 0.04 mmol, 2 mol%), *N*-methyldicyclohexylamine (0.34 mL, 2.7 mmol), tetrabutylammonium chloride (0.05 g, 0.2 mmol, 10 mol%) and tri-*tert*-butylphosphonium tetrafluoroborate (0.02 g, 0.07 mmol, 4 mol%). After the air was evacuated and the flask flushed with N_2, anhydrous dimethylacetamide (2.9 mL) was added. The reaction mixture was degassed and then heated to 80 °C under N_2 for 24 h. After this time, brine (30 mL) was added to quench the reaction. Brine (50 mL) was added to the reaction mixture in a separating funnel and the aqueous phase extracted with EtOAc (2 × 50 mL), dried with anhydrous magnesium sulfate and evaporated to dryness to give a yellow-brown oil. The crude oil was then purified by flash chromatography (20 % EtOAc in hexanes) to give the pure photochromic product **50** as a white powder (0.17 g, 25 %). mp = 122 – 123 °C (Lit. m.p. = 123 – 124 °C); ν_{max} (neat) 3066, 2924, 1630, 1600, 1586, 1504, 1227, 1200, 1184, 1157, 1105, 1080, 1056, 1003, 951, 829, 806, 751, 729, 722, 687, 661, 563, 548, 530, 513, 500 cm^{-1}; Photomerocyanine λ_{max} = 426 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 6.18 (1H, d, *J* = 9.9 Hz, 2-H), 7.01 (4H, app. t, *J* = 8.7 Hz, Ar-H), 7.18 (1H, d, *J* = 8.8 Hz, Ar-H), 7.34 (1H, d, *J* = 10.0 Hz, 1-H), 7.36 (1H, d, *J* = 7.5 Hz, Ar-H), 7.45 (4H, app. t, *J* = 7.1 Hz, Ar-H), 7.50 (1H, app. d, *J* = 7.0 Hz, Ar-H), 7.68 (1H, d, *J* = 8.8 Hz, Ar-H), 7.74 (1H, d, *J* = 8.1 Hz, Ar-H), 7.97 (1H, d, *J* = 8.5 Hz, Ar-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 81.76, 113.97, 114.95, 115.16, 118.19, 119.99, 121.32, 123.84, 126.83, 127.27, 128.60, 128.79, 128.87, 129.43, 129.75, 130.13, 140.44, 140.47, 150.21, 160.94, 163.39 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{17}F_2O^+$ 371.1236; Found 371.1236.

Synthesis of 3-phenyl-3-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 51: TFA (2.1 mL, 27 mmol) was added dropwise to a mixture of (*E*)-3-(2-(methoxymethoxy)naphthalen-1-yl)-1-phenyl-1-(pyridin-4-yl)prop-2-en-1-ol (0.35 g, 0.88 mmol) in DCM (45 mL). After 2 h, the crude was

washed with a saturated aqueous solution of $NaHCO_3$ (100 mL). The resulting yellow solution was washed with water (2 × 200 mL), dried with anhydrous sodium sulfate and evaporated to dryness. The residue was triturated with Et_2O, filtered and dried under reduced pressure giving the desired product as an off-white powder (0.16 g, 54%). The resulting filtrate was crystallized from Et_2O/acetone as off-white crystalline plates (0.02 g, 7%). m.p. = 147–148 °C; ν_{max} (neat) 1633, 1588, 1246, 1206, 1192, 1015, 812, 754, 733, 702 cm^{-1}; Photomerocyanine λ_{max} = 414 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 6.21 (1H, d, *J* = 9.9 Hz, 2-H), 7.21 (1H, d, *J* = 8.8 Hz, 5-H), 7.25–7.50 (9H, m, Ar-H, 1-H), 7.67–7.73 (2H, m, 6, 7-H), 7.95 (1H, d, *J* = 8.5 Hz, 10-H), 8.56 (2H, app. d, *J* = 6.1 Hz, 3′, 5′-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 81.5, 114.0, 118.1, 120.8, 121.3, 121.6, 124.0, 126.2, 126.9, 127.0, 128.1, 128.4, 128.6, 129.5, 129.8, 130.3, 143.3, 149.8, 150.2, 153.6 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{18}NO^+$ 336.1383; Found 336.1383.

Synthesis of 6-pyridyl-3*H*-naphtho[2,1-*b*]pyrans

Synthesis of 3-methoxy-1-naphthol 52: a solution of methanolic hydrogen chloride was prepared by the dropwise addition of acetyl chloride (18.5 mL) to MeOH (184.0 mL) at 0 °C. Solid 1,3-dihydroxynaphthalene (9.22 g, 57.6 mmol) was added in one portion to the foregoing methanolic HCl solution and the resulting solution stirred for 24 h at room temperature. The mixture was poured into water (300 mL) and extracted with DCM (3 × 100 mL). The extracts were washed with water (3 × 200 mL), the organic layer dried with anhydrous sodium sulfate and the solvent removed under reduced pressure. The resulting mixture was purified by flash column chromatography [Fluorochem silica gel (60 Å, 40-63 μm), eluent: EtOAc/hexane (1:9 → 3:7)] to afford the corresponding product as a pale brown oil that solidified upon standing (8.59 g, 86%). m.p. = 96–98 °C (lit. m.p. = 99–100 °C[51]); ν_{max} (neat) 3383 (br), 1632, 1588, 1408, 1262, 1236, 1137, 1084, 817, 748, 649 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.87 (3H, s, OMe), 5.58 (1H, s, OH), 6.51 (1H, d, *J* = 1.9 Hz, 2-H), 6.76 (1H, d, *J* = 1.9 Hz, 4-H), 7.32

(1H, t, J = 7.6 Hz, 6-H), 7.44 (1H, t, J = 7.5 Hz, 7-H), 7.68 (1H, d, J = 8.2 Hz, 8-H), 8.06 (1H, d, J = 8.3 Hz, 5-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.4, 98.9, 101.5, 120.6, 121.7, 123.0, 126.7 127.1, 135.5, 152.7, 157.8 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}O_2^+$ 175.07536; Found 175.07541.

Synthesis of 3-methoxy-1-triflyloxynaphthalene 53: triflic anhydride (10.9 mL, 64.9 mmol) was added dropwise to a solution of 3-methoxy-1-naphthol (10.94 g, 62.80 mmol) and Et_3N (22.5 mL, 161 mmol) in DCM (134.0 mL) at 0 ºC under N_2. After 90 min, the resulting solution was washed with HCl (1 M) (50 mL), with a saturated $NaHCO_3$ (100 mL), dried with anhydrous sodium sulfate and the solvent removed under reduced pressure. The residue was purified by flash column chromatography [Fluorochem silica gel (60 Å, 40-63 μm), eluent: EtOAc/hexane (1:9), fraction 1] leading to the corresponding product as a pale-yellow oil (15.55 g, 81%). ν_{max} (neat) 1638, 1605, 1418, 1202, 1129, 1046, 1007, 952, 815, 746, 600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.94 (3H, s, OMe), 7.168–7.174 (2H, m, 2-H and 4-H), 7.46–7.50 (1H, m, 6-H), 7.52–7.56 (1H, m, 7-H), 7.79 (1H, d, J = 8.2 Hz, 8-H), 7.97 (1H, d, J = 8.3 Hz, 5-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.8, 106.4, 111.3, 120.8, 121.9, 122.1 (1C, q, J = 320.8 Hz, CF_3), 125.3, 127.0, 128.0, 135.3, 146.1, 156.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ_F -73.3 ppm; HRMS (APCI) m/z: $[M]^+$ Calcd for $C_{12}H_9F_3O_4S^+$ 306.0174; Found 306.0171.

Synthesis of 2-methoxy-4-(4-pyridyl)naphthalene 54: a mixture of 3-methoxy-1-triflyloxynaphthalene (7.21 g, 23.5 mmol), 4-pyridineboronic acid pinacol ester (7.22 g, 35.2 mmol), K_2CO_3 (4.86 g, 35.2 mmol), $Pd(PPh_3)_4$ (1.36 g, 1.18 mmol) in PhMe (274 mL) and EtOH (274 mL) were mixed at reflux under N_2. After 16 h of reaction, the mixture was evaporated to dryness, the residue extracted with EtOAc (100 mL), washed with water (3 × 100 mL), the organic layer dried with anhydrous sodium sulfate and the solvent removed under reduced pressure. The resulting brown oil was filtered through a plug of silica [Fluorochem silica gel (60 Å, 40-63 μm), EtOAc (25%) in hexanes → EtOAc (100%)] and recrystallized

from hot EtOH, giving the corresponding product as a beige crystalline solid (4.37 g, 79%). m.p. = 128–129 °C; ν_{max} (neat) 1619, 1592, 1543, 1398, 1194, 1166, 1038, 1023, 824, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.95 (3H, s, OMe), 7.09 (1H, d, J = 1.8 Hz, 3-H), 7.20 (1H, app. s, 1-H), 7.31 (1H, t, J = 7.6 Hz, 6-H), 7.41 (2H, app. d, J = 4.2 Hz, 2′, 6′-H), 7.47 (1H, t, J = 7.4 Hz, 7-H), 7.71 (1H, d, J = 8.4 Hz, 5-H), 7.81 (1H, d, J = 8.2 Hz, 8-H), 8.72 (2H, d, J = 4.2 Hz, 3′, 5′-H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.4, 106.6, 119.6, 124.3, 124.9, 125.2, 126.5, 126.7, 127.4, 135.2, 139.0, 148.2, 149.8, 156.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}NO^+$ 236.1070; Found 236.1070.

Synthesis of 2-methoxy-4-(3-pyridyl)naphthalene 55: a mixture of 3-methoxy-1-triflyloxynaphthalene (3.50 g, 11.4 mmol), 3-pyridineboronic acid pinacol ester (3.52 g, 17.2 mmol), K_2CO_3 (2.37 g, 17.1 mmol), $Pd(PPh_3)_4$ (0.66 g, 0.57 mmol) in PhMe (130.0 mL) and EtOH (130.0 mL) were mixed at reflux under N_2. After 16 h of reaction, the mixture was evaporated to dryness, the residue dissolved in EtOAc (100 mL), washed with water (3 × 100 mL), the organic layer dried with anhydrous sodium sulfate and the solvent removed under reduced pressure, resulting in the formation of a brown oil that solidified upon standing. The residue was triturated with Et_2O (10 mL), the solid filtered off, rinsed with cold Et_2O (10 mL), cold MeOH (10 mL) and dried under reduced pressure, giving the corresponding product as an off-white powder (1.07 g, 40%). The filtrate was purified by flash column chromatography [Fluorochem silica gel (60 Å, 40-63 μm), EtOAc (40%) in hexanes, fraction 1] leading to the corresponding product as an off-white powder (1.38 g, 51%). m.p. = 72–74 °C; ν_{max} (neat) 1622, 1603, 1589, 1565, 1398, 1220, 1167, 1042, 1022, 820, 720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.97 (3H, s, OMe), 7.11 (1H, d, J = 2.4 Hz, 3-H), 7.21 (1H, d, J = 2.4 Hz, 1-H), 7.30–7.34 (1H, m, 6-H), 7.42–7.50 (2H, m, 7, 5′-H), 7.70 (1H, d, J = 8.4 Hz, 5-H), 7.80–7.83 (2H, m, 8, 6′-H), 8.69 (1H, dd, J = 4.9, 1.6 Hz, 4′-H), 8.747–8.752 (1H, m, 2′-H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.4, 106.3, 120.1, 123.1, 124.2, 125.3, 126.7, 127.2, 127.4, 135.2,

135.9, 137.2, 138.0, 148.8, 150.5, 156.9 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}NO^+$ 236.1070; Found 236.1070.

Synthesis of 4-(4-pyridyl)-2-naphthol 56: hydrobromic acid (45% w/v solution in AcOH) (51.0 mL) was added slowly to a solution of 2-methoxy-4-(4-pyridyl)naphthalene (4.00 g, 17.0 mmol), AcOH (50.0 mL) and water (25.0 mL), and refluxed for 21 h. The reaction mixture was then cooled, added water (200 mL) and the solution neutralized (pH = 7) with the cautious addition of $NaHCO_3$. As a result, a precipitate was formed, filtered and the solid rinsed with water (2 × 100 mL). Recrystallization from DMF/EtOH provided the corresponding product as an off-white powder (2.93 g, 78%). m.p. = 275–279 °C; ν_{max} (neat) 2580 (br), 1592, 1383, 1208, 1178, 1069, 833, 762, 665, 622, 599 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ_H 7.06 (1H, d, *J* = 2.1 Hz, 3-H), 7.26–7.29 (2H, m, 1, 6-H), 7.45 (1H, t, *J* = 7.4 Hz, 7-H), 7.51 (1H, d, *J* = 5.4 Hz, 2′, 6′-H), 7.62 (1H, d, *J* = 8.4 Hz, 5-H), 7.81 (1H, d, *J* = 8.2 Hz, 8-H), 8.72 (2H, d, *J* = 5.4 Hz, 3′, 5′-H), 9.99 (1H, s, OH) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ_C 110.1, 119.9, 124.0, 125.1, 125.2, 125.4, 126.9, 127.3, 135.7, 138.9, 147.9, 150.2, 155.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}NO^+$ 222.0913; Found 222.0913.

Synthesis of 4-(3-pyridyl)-2-naphthol 57: hydrobromic acid (45% w/v solution in AcOH) (58.0 mL) was added slowly to a solution of 2-methoxy-4-(3-pyridyl)naphthalene (4.50 g, 19.1 mmol), AcOH (58.0 mL) and water (29.0 mL), and refluxed for 21 h. The reaction mixture was then cooled, added water (200 mL) and the solution neutralized (pH = 7) with the cautious addition of $NaHCO_3$. As a result, a precipitate was formed, filtered and rinsed with water (2 × 100 mL). Recrystallization from hot EtOH provided the corresponding product as a grey crystalline solid (3.16 g, 75%). m.p. = 193–195 °C; ν_{max} (neat) 3020 (br), 2741 (br), 2579 (br), 1587, 1348, 1294, 1205, 1190, 866, 822, 714 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ_H 7.056–7.062 (1H, m, 3-H), 7.24–7.28 (2H, m, 1, 6-H), 7.44 (1H, app. t, *J* = 7.5 Hz, 7-H), 7.55–7.57 (2H, m, 5, 5′-H), 7.80 (1H, d, *J* = 8.2 Hz, 8-H), 7.91 (1H, dt, *J* = 7.8, 1.8 Hz, 6′-H), 8.67 (2H,

app. s, 2′, 4′-H), 9.99 (1H, bs, OH); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ_C 109.7, 120.3, 123.9, 124.0, 125.2, 126.1, 126.9, 127.3, 135.7, 135.9, 137.6, 138.0, 149.1, 150.2, 155.1 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}NO^+$ 222.0913; Found 222.0918.

Synthesis of 1-bromo-4-(4-pyridyl)-2-naphthol 60: *N*-bromosuccinimide (2.17 g, 12.2 mmol) was added in a single portion to a solution of 4-(4-pyridyl)-2-naphthol (2.70 g, 12.2 mmol) in DMF (164.0 mL) and stirred for 110 min at 52 °C under N_2. The solvent was reduced to 20 mL and the crude poured into cold water (400 mL). The resulting orange precipitate was filtered off, rinsed with water (100 mL) and dried under reduced pressure. Purification by flash column chromatography [Fluorochem silica gel (60 Å, 40-63 μm), eluent: 4% MeOH in DCM, fraction 3] led to the corresponding product as a yellow powder (1.97 g, 54%). m.p. = 219–222 °C; ν_{max} (neat) 1604, 1541, 1514, 1379, 1224, 1213, 1003, 828, 752, 617 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.23 (1H, s, 3-H), 7.39 (1H, app. t, J = 7.56 Hz, Ar-H), 7.51 (2H, app. d, J = 5.8 Hz, 2′, 6′-H), 7.62–7.66 (2H, m, Ar-H), 8.16 (1H, d, J = 8.6 Hz, 8-H), 8.74 (2H, d, J = 5.8 Hz, 3′, 5′-H), 10.8 (1H, s, OH) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ_C 105.6, 119.4, 124.8, 125.1, 125.9, 126.0, 126.4, 128.6, 133.5, 138.3, 147.2, 150.3, 152.3 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}{}^{79}BrNO^+$ 300.0019; Found 300.0026.

Synthesis of 1-bromo-4-(3-pyridyl)-2-naphthol 61: *N*-bromosuccinimide (2.42 g, 13.6 mmol) was added in a single portion to a solution of 4-(3-pyridyl)-2-naphthol (3.00 g, 13.6 mmol) in DMF (35.0 mL) and stirred for 110 min at 52 °C under N_2. After this time, the crude was poured into cold water (400 mL). The resulting beige precipitate was filtered off, rinsed with water (100 mL) and dried under reduced pressure. Purification by flash column chromatography [Fluorochem silica gel (60 Å, 40-63 μm), eluent: 4% MeOH in DCM, fraction 1] led to the corresponding product as an off-white powder (2.34 g, 57%). m.p. = 227–228 °C; ν_{max} (neat) 2536 (br), 1440, 1385, 1315, 1230, 945, 867, 808, 753, 708, 646 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.23 (1H, s, 3-H), 7.39 (1H, app. t, J = 7.1 Hz, 6-H), 7.57–7.66 (3H,

m, 5, 7, 5′-H), 7.92 (1H, dt, *J* = 7.8, 1.9 Hz, 6′-H), 8.16 (1H, d, *J* = 8.4 Hz, 8-H), 8.67 (1H, d, *J* = 1.8 Hz, 2′-H), 8.71 (1H, dd, *J* = 4.8, 1.6 Hz, 4′-H), 10.8 (1H, bs, OH) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ_C 105.2, 119.9, 124.0, 124.7, 126.0, 126.1, 127.1, 128.5, 133.5, 135.2, 137.4, 137.6, 149.5, 150.1, 152.3 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}{}^{79}BrNO^+$ 300.0019; Found 300.0011.

General experimental procedure for the synthesis of 1-bromo-2-(methoxymethoxy)-4-pyridyl-2-naphthol: MOMCl (5.3 mmol) was added dropwise to a dried 250 mL two-neck round-bottom flask containing a degassed mixture of 1-bromo-4-pyridyl-2-naphthol (5.00 mmol) and K_2CO_3 (10.5 mmol) in anhydrous DMF (81.0 mL) at 0 °C under N_2. The reaction mixture was warmed to room temperature. After 4 h, water (100 mL) was added and the residue extracted with DCM (3 × 100 mL). The organic phase was washed with water (2 × 200 mL), dried with anhydrous sodium sulfate and evaporated to dryness. Flash column chromatography [Aldrich silica gel (60 Å, 40-63 μm), eluent: 4% MeOH in DCM, fraction 1] led to the pure products.

1-Bromo-2-methoxymethoxy-4-(4-pyridyl)naphthalene 62: from 1-bromo-(4-pyridyl)-2-naphthol (1.50 g, 5.00 mmol) giving a brown oil that solidified upon standing (1.34 g, 78%). m.p. = 104–107 °C; ν_{max} (neat) 1159, 1142, 1126, 1099, 886, 736, 703, 649, 627 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.57 (3H, s, CH_3), 5.37 (2H, s, CH_2), 7.36–7.41 (4H, m, 3, 6, 2′, 6′-H), 7.59 (1H, t, *J* = 7.6 Hz, 7-H), 7.72 (1H, d, *J* = 8.4 Hz, 5-H), 8.34 (1H, d, *J* = 8.6 Hz, 8-H), 8.73 (2H, d, *J* = 5.8 Hz, 3′, 5′-H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C 56.6, 95.6, 111.3, 117.8, 124.9, 125.5, 125.6, 127.0, 127.9, 133.3, 138.3, 147.6, 149.9, 151.1 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}{}^{79}BrNO_2^+$ 344.0281; Found 344.0276.

1-Bromo-2-methoxymethoxy-4-(3-pyridyl)naphthalene 63: from 1-bromo-4-(3-pyridyl)-2-naphthol (1.70 g, 5.66 mmol) giving a brown oil (1.44 g, 74%). ν_{max} (neat) 1344, 1228, 1149,

1086, 1042, 1015, 976, 921, 886, 756, 715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.58 (3H, s, CH_3), 5.38 (2H, s, CH_2), 7.38–7.45 (3H, m, 3, 6, 5′-H), 7.60 (1H, t, J = 7.7 Hz, 7-H), 7.70 (1H, d, J = 8.4 Hz, 5-H), 7.80 (1H, dt, J = 7.8, 1.9 Hz, 6′-H), 8.35 (1H, d, J = 8.5 Hz, 8-H), 8.71 (1H, dd, J = 4.8, 1.5 Hz, 4′-H), 8.74 (1H, d, J = 1.8 Hz, 2′-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 56.7, 95.7, 111.0, 118.4, 123.2, 125.4, 125.8, 127.0, 127.9, 128.8, 133.4, 135.5, 137.3, 137.5, 149.1, 150.4, 151.2 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}{}^{79}BrNO_2^+$ 344.0281; Found 344.0285.

General experimental procedure for the synthesis of (*E*)-3-(2-methoxymethoxy-4-pyridylnaphthalen-1-yl)-1,1-bis(4-methoxyphenyl)prop-2-en-1-ol: $Pd(OAc)_2$ (7 mmol%), 1-bromo-2-methoxymethoxy-4-pyridylnaphthalene (1 mmol), 1,1-bis(4-methoxyphenyl)prop-2-en-1-ol (2 mmol), K_2CO_3 (1.5 mmol), TBAB (1.5 mmol), KCl (1 mmol) were degassed in anhydrous DMF (18.5 mL) and heated at 100 °C under N_2. After 2 days of reaction, the crude was diluted with DCM (100 mL), filtered through celite, washed with water (2 × 200 mL), dried with anhydrous sodium sulfate and evaporated to dryness, leading to the desired products after purification.

(*E*)-3-(2-Methoxymethoxy-4-(4-pyridyl)naphthalen-1-yl)-1,1-bis(4-methoxyphenyl)prop-2-en-1-ol 64: from 1-bromo-2-methoxymethoxy-4-(4-pyridyl)naphthalene (0.92 g, 2.7 mmol); Flash column chromatography [Aldrich silica gel (60 Å 230-400 mesh 40-63 µm), eluent: 40% EtOAc in PhMe, fraction 4] led the corresponding product as a yellow oil that solidified upon standing (0.36 g, 29%). m.p. = 158–163 °C; ν_{max} (neat) 1584, 1505, 1240, 1185, 1148, 1074, 1041, 1022, 993, 922, 815, 772, 586 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.73 (1H, bs, OH), 3.45 (3H, s, CH_3), 3.82 (6H, s, OMe), 5.24 (2H, s, CH_2), 6.85–6.92 (5H, m, 2, 3″, 5″, 3‴, 5‴-H), 7.04 (1H, d, J = 16.1 Hz, 3-H), 7.32–7.36 (2H, m, 3′, 6′-H), 7.41–7.47 (7H, m, 7′, 2″, 6″, 2‴, 6‴, 2⁗, 6⁗-H), 7.74 (1H, d, J = 8.3 Hz, 5′-H), 8.08 (d, 1H, d, J = 8.5 Hz, 8′-H), 8.71 (2H, d, J = 5.8 Hz, 3⁗, 5⁗-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 56.4, 79.3, 95.4,

113.5, 117.7, 120.8, 122.8, 124.7, 125.00, 125.05, 125.6, 126.7, 127.2, 128.4, 133.3, 137.9, 138.6, 143.1, 148.4, 149.8, 151.2, 158.8 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{32}NO_5^+$ 534.2275; Found 534.2267.

(*E*)-3-(2-Methoxymethoxy-4-(3-pyridyl)naphthalen-1-yl)-1,1-bis(4-methoxyphenyl)prop-2-en-1-ol 65: from 1-bromo-2-methoxymethoxy-4-(3-pyridyl)naphthalene (1.00 g, 2.91 mmol); Flash column chromatography [Aldrich silica gel (60 Å 230-400 mesh 40-63 μm), eluent: 40% EtOAc in PhMe, fraction 4] giving the corresponding product as a yellow powder (0.87 g, 55%). m.p. = 68–72 °C; ν_{max} (neat) 1606, 1582, 1506, 1244, 1172, 1150, 1001, 919, 828, 757, 714, 580 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ_H 2.80 (1H, bs, OH), 3.44 (3H, s, CH_3), 3.81 (6H, s, OMe), 5.23 (2H, s, CH_2), 6.86–6.91 (5H, m, 2, 3″, 5″, 3‴, 5‴-H), 7.04 (1H, d, *J* = 16.1 Hz, 3-H), 7.30–7.34 (2H, m, 3′, 6′-H), 7.41–7.48 (6H, m, 7′, 2″, 6″, 2‴, 6‴, 5⁗-H), 7.70 (1H, d, *J* = 8.2 Hz, 5′-H), 7.80 (1H, dt, *J* = 1.9, 7.8 Hz, 6⁗-H), 8.08 (1H, d, *J* = 8.5 Hz, 8′-H), 8.66 (1H, dd, *J* = 1.3, 4.8 Hz, 4⁗-H), 8.71 (1H, d, *J* = 1.6 Hz, 2⁗-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 55.4, 79.3, 95.5, 113.5, 118.3, 120.9, 122.4, 123.2, 124.6, 124.9, 125.7, 126.6, 128.0, 128.4, 133.3, 136.2, 136.9, 137.4, 138.6, 143.0, 148.7, 150.5, 151.2, 158.8 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{32}NO_5^+$ 534.2275; Found 534.2261.

General experimental procedure for the synthesis of 3,3-bis(4-methoxyphenyl)-6-pyridyl-3*H*-naphtho[2,1-*b*]pyran: TFA (17 mmol) was added dropwise at 0 °C under N_2 to a mixture of (*E*)-3-(2-methoxymethoxy-4-pyridylnaphthalen-1-yl)-1,1-bis(4-methoxyphenyl)prop-2-en-1-ol (0.56 mmol) in DCM (20.0 mL) and glacial AcOH (20.0 mL). The resulting fading blue solution was warmed to room temperature and stirred for 4 h as it acquired a brown colour. Afterwards, the crude was diluted with DCM (100 mL), poured into water (100 mL), neutralized by the addition of $NaHCO_3$ and the phases separated. The resulting yellow organic phase was washed with water (2 × 100 mL), dried with anhydrous sodium sulfate and evaporated to dryness, leading to the corresponding product after purification.

3,3-Bis(4-methoxyphenyl)-6-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 58: from (*E*)-3-(2-methoxymethoxy-4-(4-pyridyl)naphthalen-1-yl)-1,1-bis(4-methoxyphenyl)prop-2-en-1-ol (0.30 g, 0.56 mmol); Flash column chromatography [Aldrich silica gel (60 Å 230-400 mesh 40-63 μm), eluent: 50% EtOAc in hexanes, fraction 1] led to the corresponding product as a pink powder (0.16 g, 61%). m.p. = 141–143 °C; ν_{max} (neat) 1605, 1507, 1246, 1172, 1032, 1002, 825, 716, 586 cm^{-1}; Photomerocyanine λ_{max} = 472 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 6.25 (1H, d, *J* = 10.0 Hz, 2-H), 6.85 (4H, app. d, *J* = 8.9 Hz, 3′, 5′, 3″, 5″-H), 7.13 (1H, s, 5-H), 7.25–7.34 (2H, m, 1, 8-H), 7.37–7.41 (6H, m, 2′, 6′, 2″, 6″, 2‴, 6‴-H), 7.50 (1H, app. t, *J* = 8.2 Hz, 9-H), 7.71 (1H, d, *J* = 8.3 Hz, 7-H), 8.04 (1H, d, *J* = 8.5 Hz, 10-H), 8.70 (2H, app. d, *J* = 6.0 Hz, 3‴, 5‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.4, 113.5, 114.5, 118.8, 119.3, 121.9, 124.2, 124.9, 125.8, 126.8, 126.9, 128.4, 128.8, 130.3, 137.0, 139.0, 148.2, 149.8, 149.9, 159.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1894.

3,3-Bis(4-methoxyphenyl)-6-(3-pyridyl)-3*H*-naphtho[2,1-*b*]pyran 59: from (*E*)-3-(2-methoxymethoxy-4-(3-pyridyl)naphthalen-1-yl)-1,1-bis(4-methoxyphenyl)prop-2-en-1-ol (99.7 mg, 0.187 mmol); Flash column chromatography [Aldrich silica gel (60 Å 230-400 mesh 40-63 μm), eluent: 50% EtOAc in hexanes, fraction 1] led to the corresponding product as a pink powder (60.4 mg, 69%). m.p. = 147–149 °C; ν_{max} (neat) 1606, 1506, 1246, 1172, 1032, 1002, 824, 716, 587 cm^{-1}; Photomerocyanine λ_{max} = 474 nm (PhMe); ^1H NMR (400 MHz, $CDCl_3$) δ_H 3.77 (6H, s, OMe), 6.25 (1H, d, *J* = 10.0 Hz, 2-H), 6.85 (4H, app. d, *J* = 8.9 Hz, 3′, 5′, 3″, 5″-H), 7.14 (1H, s, 5-H), 7.28 (1H, app. t, *J* = 7.1 Hz, 8-H), 7.33 (1H, d, *J* = 10.0 Hz, 1-H), 7.37–7.41 (5H, m, 2′, 6′, 2″, 6″, 5‴-H), 7.49 (1H, app. t, *J* = 7.1 Hz, 9-H), 7.68 (1H, d, *J* = 8.3 Hz, 7-H), 7.77 (1H, dt, *J* = 2.0, 7.8 Hz, 6‴-H), 8.04 (1H, d, *J* = 8.5 Hz, 10-H), 8.66 (1H, dd, *J* = 1.6, 8.4 Hz, 4‴-H), 8.71 (1H, d, *J* = 1.7 Hz, 2‴-H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C 55.3, 82.4, 113.5, 114.2, 118.9, 119.8, 121.8, 123.1, 124.1, 126.0, 126.8, 127.5,

128.4, 128.6, 130.3, 136.0, 137.1, 137.3, 138.1, 148.7, 149.9, 150.5, 159.0 ppm; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_3^+$ 472.1907; Found 472.1903.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.xxxxxx.

^1H and $^{13}C\{^1H\}$ NMR Spectra, Mass Spectral Data for compounds **B**, **C**, **13**, **14**, **15**, **16**, **17**, **18**, **19**, **20**, **21**, **22**, **23**, **24**, **25**, **26**, **27**, **28**, **29**, **30**, **31**, **32**, **33**, **34**, **37**, **38**, **39**, **40**, **41**, **42**, **43**, **44**, **45**, **46**, **47**, **48**, **49**, **50**, **51**, **52**, **53**, **54**, **55**, **56**, **57**, **58**, **59**, **60**, **61**, **62**, **63**, **64** and **65**. Selected 2D NMR Spectra for compound **40**. Spectrokinetic data (UV-Vis absorption spectra and rate plots) for compounds **15**, **18**, **20**, **26**, **28**, **30**, **33**, **39**, **42**, **51**, **58** and **59** (PDF). Electronic Emission Spectra for compounds **18**, **20**, **26**, **28**, **30**, **39**, **42**, **51**, **58** and **59**.

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Notes

The authors declare no competing financial interest.

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