

The influence of a 1,1-diarylvinyl moiety on the photochromism of naphthopyrans†

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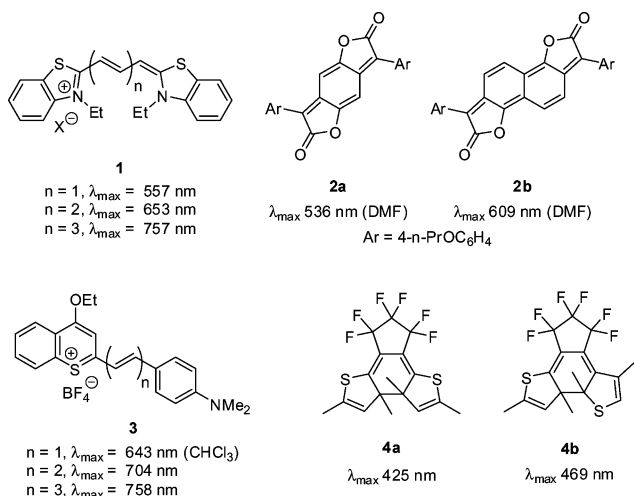
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1,1,3-Triarylprop-2-en-1-yn-3-ols, efficiently obtained in two steps from 1,1,3-triarylprop-2-yn-1-ols by a Meyer-Schuster rearrangement and subsequent addition of lithium trimethylsilylacetylide, react with either a 1- or 2-naphthol to afford photochromic 1,1-diarylvinyl substituted naphtho[1,2-*b*]- or naphtho[2,1-*b*]-pyrans respectively. Irradiation of solutions of these naphthopyrans results in reversible electrocyclic ring-opening to afford photomerocyanines which possess an extended conjugated system and show a bathochromically-shifted λ_{max} relative to the non-vinyl substituted analogues.

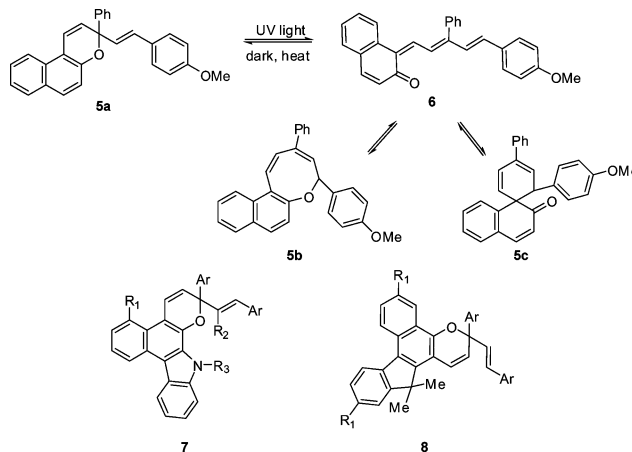
Introduction

A common approach employed to shift the wavelength of the maximum absorption band (λ_{max}) of a dye to longer wavelength, a bathochromic shift, has been through the introduction of additional conjugating groups, *e.g.* vinyl, phenyl, styryl, between the donor and acceptor units of the dye molecule.¹ This approach is perhaps best known for cyanine dyes *e.g.* **1**, where each additional vinyl group introduced between the donor and acceptor termini induces a shift in λ_{max} of *ca.* 100 nm and is termed the vinylene shift.² Bathochromic shifts of varying magnitude in λ_{max} have been noted for the extension of the conjugating pathway of other dye classes including benzodifuranones *e.g.* **2a**, **2b**,³ thiopyrylium salts *e.g.* **3**⁴ and photochromic dithienylethenes⁵ **4a**, **4b** (Scheme 1) and triarylmethines.⁶



Scheme 1

A similar bathochromic shift should operate for photochromic naphthopyrans wherein one or more vinyl units are incorporated between the aryl donor groups and the sp^3 hybridised C-atom of the pyran ring, *e.g.* **5a**. Electrocyclic ring-opening of **5a** initiated by UV irradiation would result in the trienone **6** rather than a typical dienone tautomer expected from a simple di-aryl substituted naphthopyran (Scheme 2).⁷ Interestingly, trienone **6** may either undergo an 8π -electrocyclisation to afford the naphthoxocine **5b** or a 6π -electrocyclisation to the spirocycle **5c**; these alternative modes of cyclisation offer a hitherto unknown aspect of the normal pyran electrocyclic ring-opening. Unsurprisingly, examination of the patent literature reveals that the incorporation of a monosubstituted vinyl unit has been previously reported for the 3*H*-naphtho[2,1-*b*]pyran *e.g.* **5a**,⁸ and then extended in claims to include the indole-fused naphthopyran **7**⁹ and most recently for an indenonaphthopyran **8**,¹⁰ however only in the former account was the influence of the monoarylvinyl unit on the photochromic properties described.

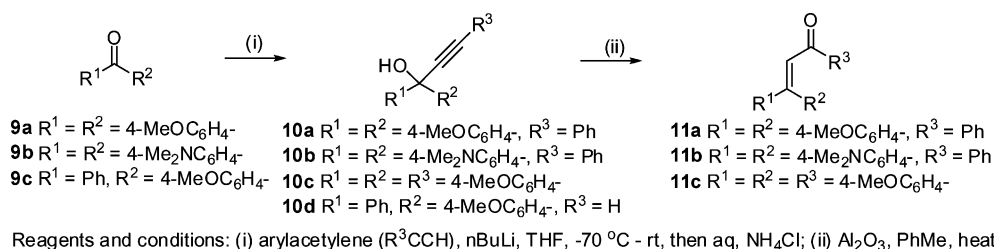


Scheme 2

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We have previously examined a range of colour-structure effects on the photochromic response of various naphthopyran isomers.¹¹ Of relevance to this current study was the observation that electron rich 1,1-diarylprop-2-yn-1-ols and 1,1,3-triarylprop-2-yn-1-ols undergo a facile Meyer-Schuster¹² or Rupe rearrangement¹³ to 3,3-diarylprop-2-enals and 1,3,3-triarylprop-2-enones respectively under the typical reaction conditions employed to access



Scheme 3

naphthopyrans (Scheme 3).¹⁴ It was thought that the latter unsaturated ketones might serve as precursors for new 1,1,3-triarylprop-4-en-1-yn-3-ols which in turn would afford novel 3-(1,1-diarylvinyl)-3-aryl substituted 3*H*-naphtho[2,1-*b*]pyrans upon reaction with a 2-naphthol, thus allowing exploration of the influence of a diarylvinyl group on the photochromic properties of the naphthopyran system. Precursors that allow for the incorporation of the 1,1-diarylvinyl unit in the naphthopyran cannot readily be constructed using the previously reported chalcone-based derived strategy⁸ because of the difficulty of the condensation between electron rich benzophenones and acetophenones which would lead to 1,3,3-triarylprop-2-enones.¹⁵

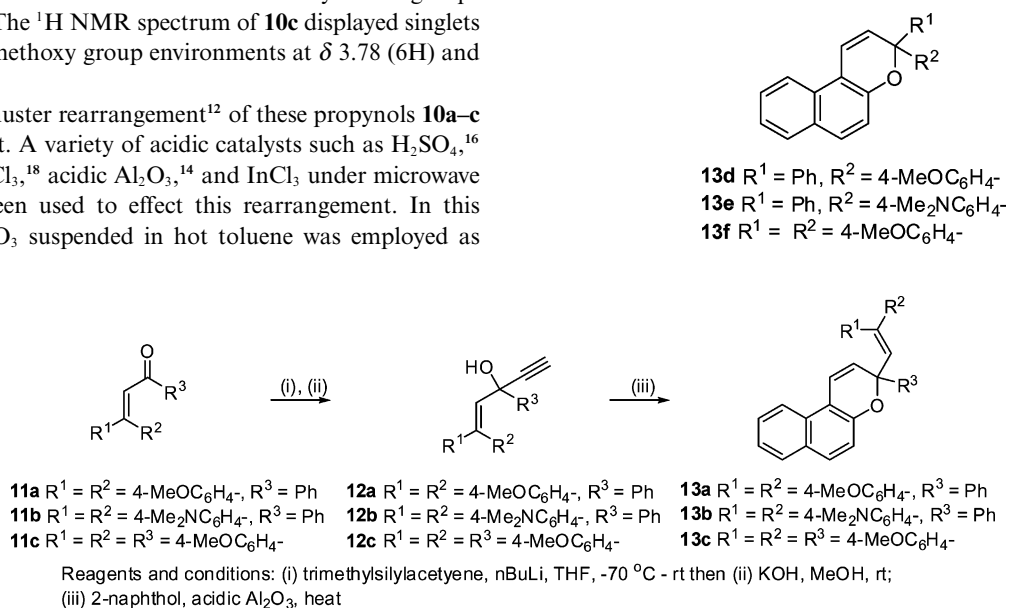
Discussion

Three 1,1,3-triarylprop-2-yn-1-ols **10a–c** were expediently obtained (81–99%) by addition of a benzophenone **9** to a lithium arylacetylide, obtained by deprotonation of the arylacetylene with *n*-butyllithium in THF at *ca.* -70°C , followed by careful neutralisation of the basic solution and extraction. Notably a slightly longer reaction time was required for the addition of phenylacetylide to 4,4'-dimethylaminobenzophenone to afford 1,1-bis(4-dimethylaminophenyl)-3-phenylprop-2-yn-1-ol **10b**. The ^1H NMR spectra of **10a–c** each displayed a slightly broadened singlet for the OH group at *ca.* δ 2.8. The equivalent methoxy groups of **10a** resonated at δ 3.77 and the dimethylamino groups of **10b** at δ 2.93. The ^1H NMR spectrum of **10c** displayed singlets for the different methoxy group environments at δ 3.78 (6H) and δ 3.79 (3H).

The Meyer-Schuster rearrangement¹² of these propynols **10a–c** was explored next. A variety of acidic catalysts such as H_2SO_4 ,¹⁶ acetic acid,¹⁷ AuCl_3 ,¹⁸ acidic Al_2O_3 ,¹⁴ and InCl_3 under microwave heating¹⁹ have been used to effect this rearrangement. In this work, acidic Al_2O_3 suspended in hot toluene was employed as

the acid catalyst–solvent system of choice because of the ease of catalyst removal from the reaction mixture by simple filtration. Thus treatment of propynol **10a** gave 1,1-bis(4-methoxyphenyl)-3-phenylprop-2-enone **11a** in 70% yield as dark yellow micro-crystals after elution from silica (20% EtOAc–hexane) (Scheme 3). In a similar manner, propynols **10b** and **10c** yielded **11b** (65%) and **11c** (89%) respectively. The ^1H NMR spectra of **11a–c** displayed a singlet at *ca.* δ 7.0 which confirms the rearrangement and is assigned to the alkene proton. ^{13}C NMR spectroscopy also supported the rearrangement by the presence of a low field signal at δ 192 for the $\text{C}=\text{O}$ group. This two step protocol from commercially available benzophenones is more efficient and convenient than the benzotriazole-mediated process reported for **11a**.²⁰

The unsaturated ketones **11a–c** were smoothly and efficiently converted into the respective 1,1,3-triarylprop-4-en-1-yn-3-ols **12a–c** in excellent yield (86–98%) by the addition of lithium trimethylsilylacetylide with subsequent *in situ* hydroxide-promoted desilylation (Scheme 4). The ^1H NMR spectrum of **12a** derived from **11a** displayed a singlet for the terminal alkyne proton at δ 2.70 and a broadened singlet for hydroxyl proton at δ 2.71. The alkene proton resonated at δ 6.33 shifted upfield relative to that in the ketone precursor **11a**. Similar chemical shifts were recorded for the corresponding protons of the new pent-4-en-1-yn-3-ols **12b** and **12c**.

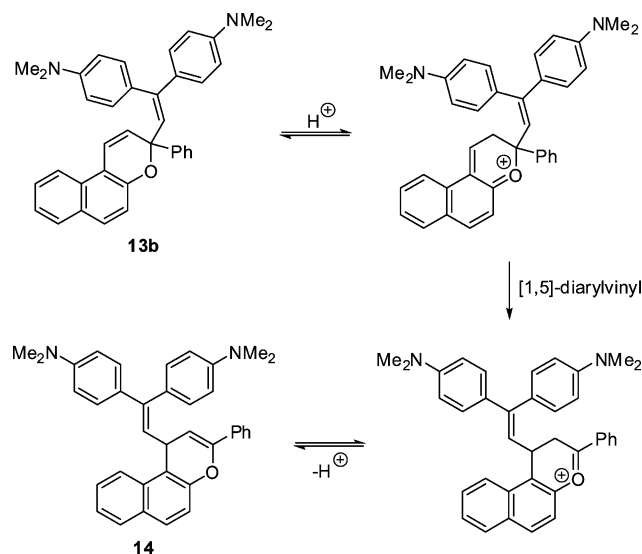


Scheme 4

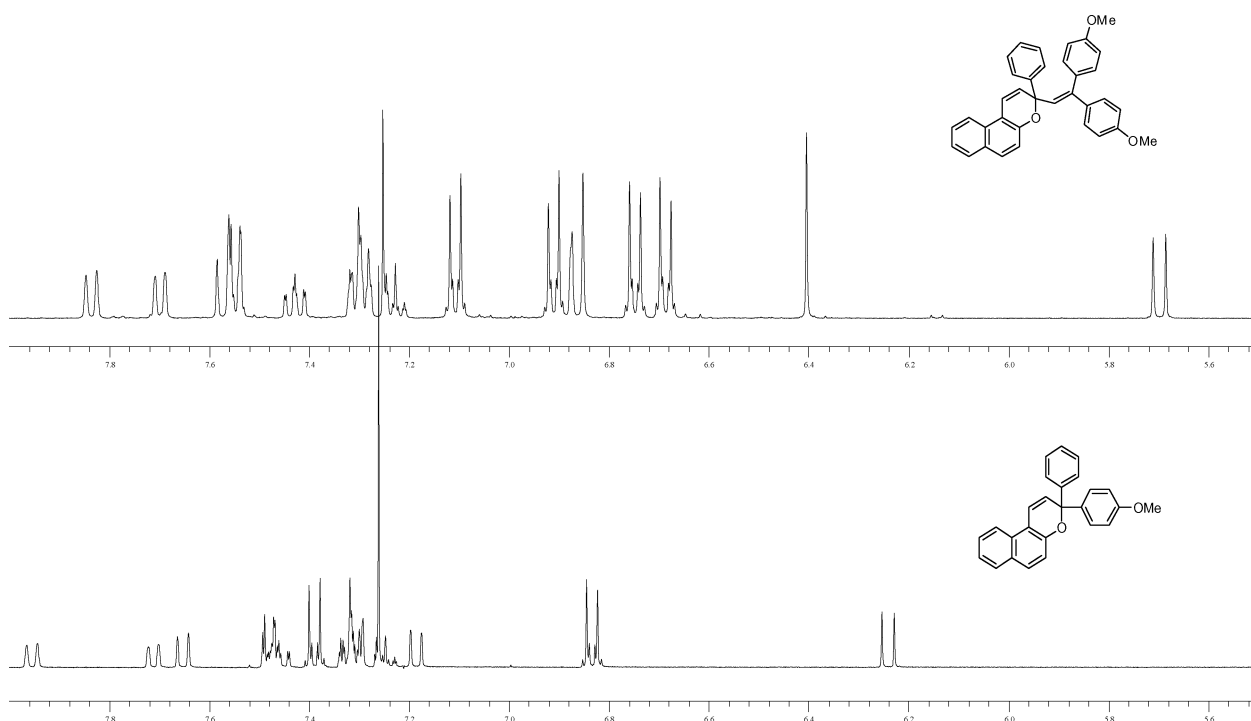
A toluene solution of each of the crude foregoing vinylalkynols **12a–c** was heated directly with 2-naphthol in the presence of acidic alumina according to the established protocol.¹⁴ Naphthopyrans **13a** and **13c** were isolated after flash chromatography in 28% and 52% yield from **12a** and **12c** respectively (Scheme 4). The ¹H NMR spectrum of **13a** was remarkable in that the key pyran ring signal, 2-H, resonated at δ 5.69 shifted upfield by *ca.* 0.5 ppm relative to the usual narrow range for this signal at δ 6.2.²¹ This chemical shift is more akin to that of the corresponding proton (3-H) in simple 2,2-dialkyl substituted 2H-[1]benzopyrans which appears at *ca.* δ 5.4–5.6.²² The chemical shift of 1-H, δ 7.23, and the coupling constant $J_{1,2} = 9.9$ Hz are in accordance with those routinely reported for other naphthopyrans.²¹ It is likely that 2-H is shielded by one of the nearby aryl rings on the vinyl moiety. The vinyl proton appeared as a sharp singlet at δ 6.40 and the non-equivalent methoxy groups resonated at δ 3.75 and δ 3.76. The ¹H NMR spectrum of **13a** is displayed together with that of **13d** (expected signal for 2-H at δ 6.23 with a coupling constant of 9.9 Hz) to allow a comparison of the pyran ring and aromatic signals (Fig. 1). The ¹H NMR spectrum of **13c** also indicated an upfield shift for 2-H which appeared at δ 5.66 and with 1-H appearing at δ 6.88 for which $J_{1,2} = 9.9$ Hz. The vinyl proton appeared as a sharp singlet at δ 6.42 and the non-equivalent methoxy groups resonated at δ 3.75, δ 3.76 and δ 3.77. The signal for 3-C of the pyran ring of **13a, c** appeared in the expected region at δ 81.0 in the ¹³C NMR spectrum.²¹

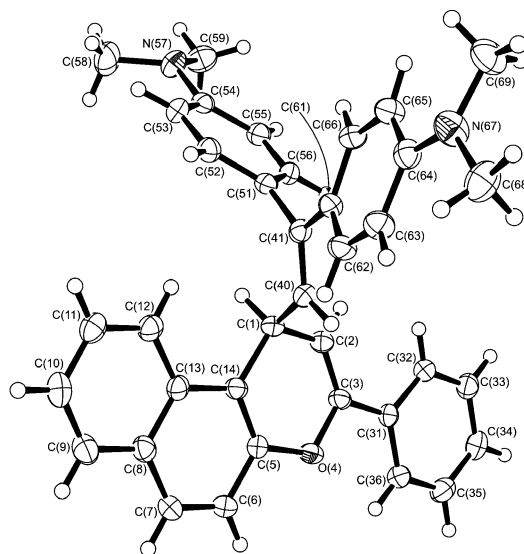
However, a similar reaction of the vinylalkynol **12b** with 2-naphthol gave a complex mixture from which a new compound **14** was isolated in 22% yield after extensive chromatography. The ¹H NMR spectrum of **14** showed 1-H as double doublet at δ 4.85 coupled to 2-H (δ 5.70, $J_{1,2} = 5.1$ Hz) and to the vinyl proton which appeared as a doublet at δ 5.89 ($J = 9.7$ Hz), respectively. Interestingly the NMe₂ groups were non-equivalent

and afforded signals at *ca.* δ 2.9. The ¹³C NMR spectrum of **14** provided a signal at δ 33.2 assigned to the methine carbon atom (1-C). The absence of a signal at $\sim \delta$ 81, present in all known 3,3-diaryl substituted naphtho[2,1-*b*]pyrans, suggested that the product lacked a quaternary 3-C atom. A crystallographic analysis confirmed the structure as **14** (Fig. 2)²³ The formation of this product in which the diarylvinyl unit and the phenyl substituent are now 1,3-disposed may be rationalised by protonation at 2-C assisted by the pyran ring oxygen atom. A subsequent sigmatropic [1,5]-diarylvinyl shift affords a new oxonium ion; the elimination of a proton from which affords the product **14** (Scheme 5). Migrations of vinyl groups though relatively scarce have been



Scheme 5

Fig. 1 ¹H NMR spectra of vinyl substituted naphthopyran **13a** and diaryl naphthopyran **13d**.



documented²⁴ as have acid initiated sigmatropic shifts, for example the rearrangement of 1-allyl-1-methyl-1*H*(2)-naphthalenone to 4-allyl-1-methyl-2-naphthol proceeds by a [3,4]-sigmatropic shift induced by a catalytic amount of H₂SO₄.²⁵ Investigations on the formation of this unexpected product from this study on photochromic naphthopyrans is ongoing.

The reaction of vinylalkynol **12b** was repeated but using a weaker acidic catalyst, Sasol Pural MG-30 (magnesium aluminium hydroxy carbonate, 30% Mg content on silica), which resulted in the formation of the expected vinyl substituted naphthopyran **13b** in 25% yield. The ^1H NMR spectrum of **13b** displayed the key pyran signal for 2-H at δ 5.69 and for 1-H at δ 6.95 with a coupling constant of 10.0 Hz. The vinyl proton resonated at δ 6.33 as a singlet and the non-equivalent NMe₂ groups appeared at *ca.* δ 2.9. The ^{13}C NMR spectrum of **13b** displayed a signal for a quaternary C atom at δ 81.4, confirming the *geminal* disubstitution at 3-C.²¹

The photochromic response of the new naphthopyrans **13** were examined and compared with structurally close analogues to enable the influence of the diarylvinyl unit to be quantified. To enable a close comparison to be made, the naphthopyran **13d** was synthesised from 2-naphthol and 1-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol **10d**, which was obtained from 4-methoxybenzophenone and lithium trimethylacetylide in the usual manner. Conversion to **13d** was achieved in excellent yield using a combination of pyridinium *p*-toluenesulfonate (PPTS) and trimethyl orthoformate in 1,2-dichloroethane.²⁶

A toluene solution of **13a** (*ca.* 1×10^{-5} mol dm⁻³) displayed an intense red colour under UV irradiation with an absorption maxima of 502 nm. The half-life ($t_{1/2}$, the time taken for the developed colour under steady state conditions to fade to half of the original intensity) was 9 s. By comparison, naphthopyran **13d** appears orange in solution (λ_{max} 465 nm) and has a similar fade rate with $t_{1/2}$ of 8 s.^{21,27} The difference between λ_{max} for these two analogues, *i.e.* the vinylenic shift, was 37 nm and constitutes a useful bathochromic shift for a relatively simple structural modification (Fig. 3).

Compound **13b** displayed an unusual broad absorption spectrum which was manifest as a purple-grey shade with an absorption maximum centred at 566 nm (PhMe) upon irradiation together with a half-life ($t_{1/2}$) 6 s (Fig. 4). The non-vinyl analogue of this compound, 3-(4-dimethylaminophenyl)-3-phenyl-3*H*-naphtho[2,1-*b*]pyran **13e** has a reported absorption maximum at 533 nm with half-life of 5.4 s in toluene solution.^{27,28} Once again there is no appreciable change in the stability of the ring-opened species but a significant shift to longer wavelength with a $\Delta\lambda_{\text{max}}$ of 33 nm is noted, a value comparable to that observed for the di(4-methoxyphenyl)vinyl compound **13a**.

Irradiation of a solution of **13c** resulted in the development of a red colour with an absorption maximum at 506 nm (PhMe) with a half-life ($t_{1/2}$) of 3.2 s (Fig. 5). The non-vinyl analogue, 3,3-bis-(4-methoxyphenyl)-3H-naphtho[2,1-b]pyran **13f** has an absorption maximum of 478 nm and a comparably short half-life with $t_{1/2}$ of 2.4 s.²⁷ Once again this simple structural modification has shown merit with a bathochromic shift of 28 nm. Irradiation (365 nm) of a CDCl₃ solution of **13c** resulted in the development of the expected red colour which gradually faded upon cessation of irradiation. Re-examination of the ¹H NMR spectrum of the recycled material gave no indication of the presence of alternative cyclisation products akin to **5b** and **5c**. Additionally TLC examination of this solution in a series of solvent systems failed to indicate the presence of a new component.

Noting this bathochromic vinylenic shift for the series of naphthopyrans derived from 2-naphthol it was decided to explore this effect on the isomeric 2*H*-naphtho[1,2-*b*]pyrans derived from a 1-naphthol. Thus heating 1,1-bis-(4-methoxyphenyl)-3-phenylpent-1-en-4-yn-3-ol **12a** with ethyl 4-hydroxynaphthalene-2-carboxylate **15**²⁹ in toluene containing acidic alumina under reflux gave ethyl 2-[2,2-bis-(4-methoxyphenyl)vinyl]-2-phenyl-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate **16a** in 19% yield (Scheme 5). The ¹H NMR spectrum of **16a** displayed a doublet (*J* = 10 Hz) for 3-*H* at δ 5.80 again shifted upfield relative to that for the non-vinyl analogues where 3-*H* resonates at *ca.* δ 6.2.²⁷ The alkene proton

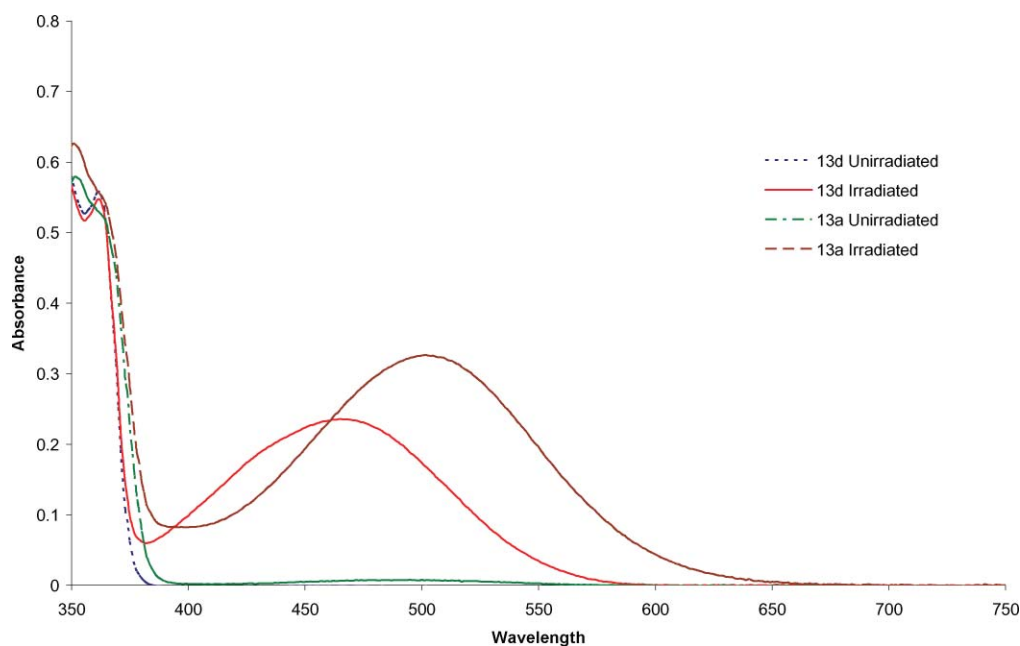


Fig. 3 UV-visible spectra of naphthopyrans **13a** and **13d**.

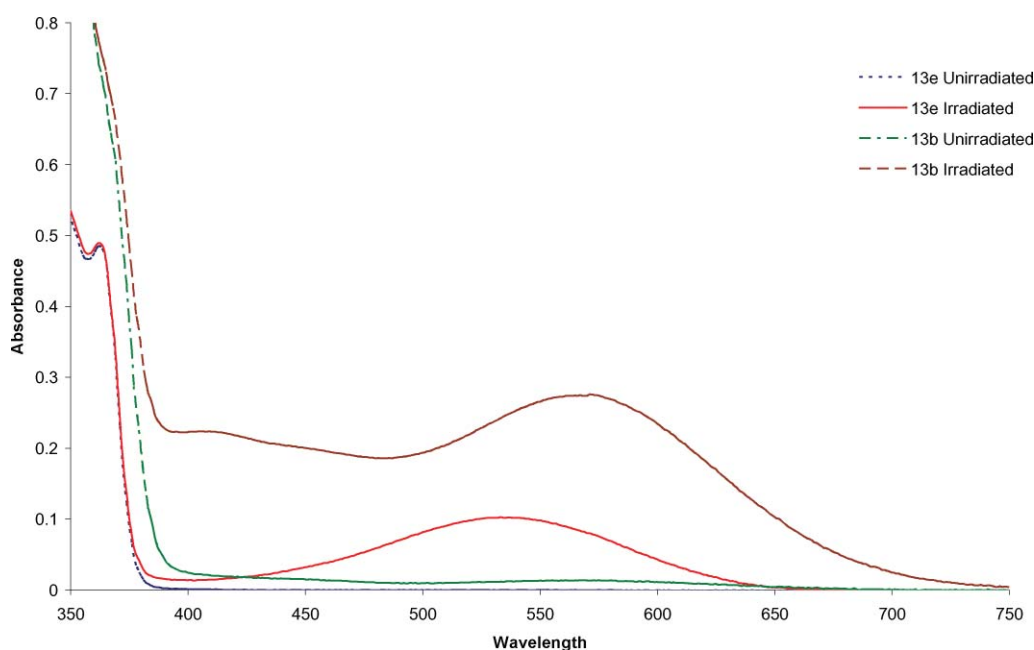


Fig. 4 UV-visible spectra of naphthopyrans **13b** and **13e**.

appears as a sharp singlet at δ 6.01. Ethyl 2-(4-methoxyphenyl)-2-phenyl-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate **16b** was prepared for comparative purposes in 75% yield using the PPTS/(MeO)₃CH protocol with naphthol **15** and propynol **10d** (Scheme 6). The ¹H NMR spectrum of **16b** exhibited doublets for the pyran ring protons, 3-H at δ 6.20 and 4-H at δ 7.64 (J = 9.4 Hz).²¹

A toluene solution of naphthopyran **16a** displayed a dark cherry red shade upon UV-irradiation, with an absorption maximum at 516 nm and $t_{1/2}$ of 17 s. Its non-vinyl analogue, **16b**, has an absorption maximum of 483 nm and a half-life of 7 s. The difference between the absorption maximum values ($\Delta\lambda_{\text{max}}$) gave a

vinylene shift of 33 nm (Fig. 6) confirming that the effect translates to the isomeric 2*H*-naphtho[1,2-*b*]pyran isomers; interestingly a longer half-life was noted for the vinyl compound.

Conclusions

The incorporation of a 1,1-diaryl-substituted vinyl unit into the classical naphthopyran structure enables longer wavelength absorption bands to be generated through the additional conjugation consequent upon ring-opening to the merocyanine. This vinylenic

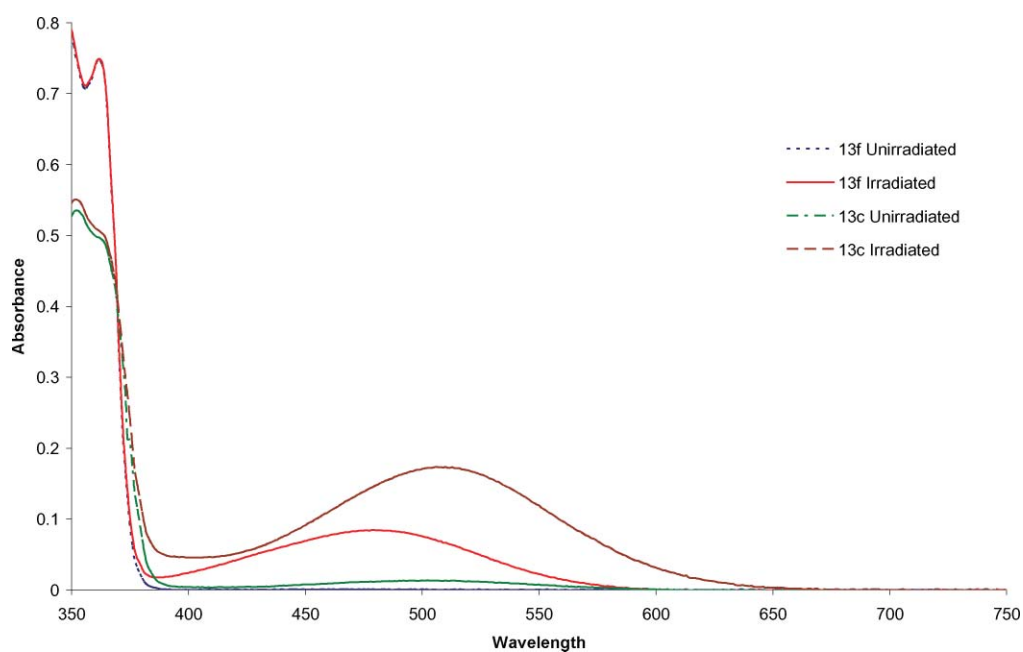


Fig. 5 UV-visible spectra of naphthopyrans **13c** and **13f**.

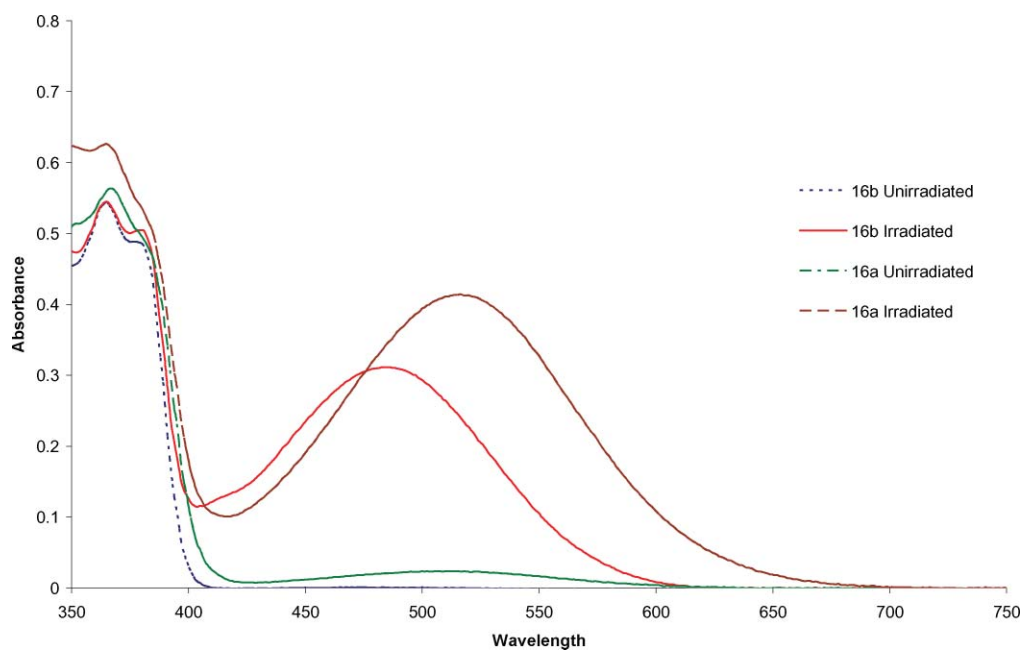
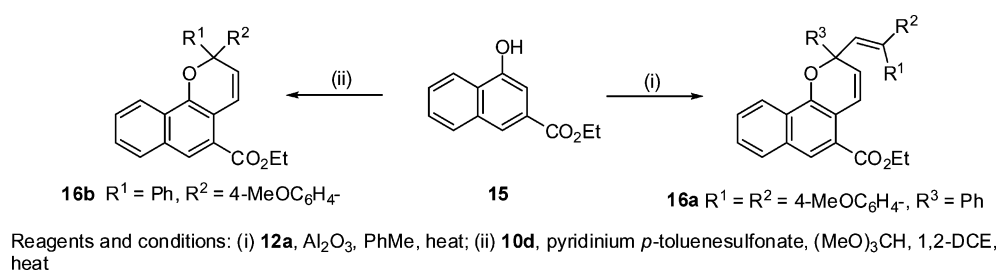


Fig. 6 UV-visible spectra of naphthopyrans **16a** and **16b**.



Scheme 6

shift of *ca.* 25–40 nm is observed for both the [2,1-*b*] and [1,2-*b*] naphthopyrans.

Experimental

Unless otherwise stated, reagents were used as supplied. NMR spectra were recorded on a Bruker Avance 400 MHz spectrophotometer (^1H NMR 400 MHz, ^{13}C NMR 100 MHz) for sample solutions in CDCl_3 with tetramethylsilane as an internal reference. The crystal structure determination was carried out at 150 K on a Bruker-Nonius Apex X8 diffractometer equipped with an Apex II CCD detector and using graphite monochromated Mo-K α radiation from a FR591 rotating anode generator. The structure was solved by direct methods and refined using SHELXL-97. FT-IR spectra were recorded on either a Perkin Elmer Spectrum One spectrophotometer system equipped with a golden gate ATR attachment (neat sample) or in KBr discs. UV-visible spectra were recorded in quartz cuvettes (10 mm pathlength) for spectroscopic grade toluene solutions of the naphthopyrans (*ca.* 1×10^{-5} mol dm^{-3}) using a Cary 50 Probe spectrophotometer with activating irradiation provided by a TLC inspection lamp (Spectroline E Series 365 nm, 8 W). Half-life determinations were obtained using the Cary 50 Probe spectrophotometer kinetic analysis software; samples were irradiated at a lamp wavelength of 365 nm for 5 min with thorough mixing immediately prior to kinetic data collection. All compounds were homogeneous by TLC using a range of eluent systems of differing polarity. Mass spectra were recorded at the National EPSRC Mass Spectrometry Service Centre, Swansea. Sasol Pural MG-30 (magnesium aluminium hydroxy carbonate, 30% Mg content on silica) was supplied by James Robinson Ltd.

Preparation of 1,1-bis(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol 10a and related 1,1,3-triarylprop-2-yn-1-ols 10b and c

n-BuLi (1.6 M in hexanes, 17.3 mmol, 10.8 mL) was added slowly to a cold (-70°C) stirred solution of the phenylacetylene (1.7 g, 17.3 mmol) in anhydrous THF (70 mL) under nitrogen. Upon completion of the addition the cold solution was stirred for 30 min. 4,4'-Dimethoxybenzophenone (4.0 g, 16.5 mmol) was added in a single portion and the mixture stirred until no benzophenone remained by TLC (~ 2 h). The mixture was poured into water (250 mL) containing saturated aq. NH_4Cl solution (40 mL), the organic layer was separated and the aqueous layer extracted with EtOAc (3×50 mL). The organic extracts were combined and washed with water (2×100 mL) and dried over anhyd. Na_2SO_4 . Removal of the solvent afforded the 1,1-bis(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol 10a (5.62 g) 99% yield as yellow coloured solid, m.p. $94-96^\circ\text{C}$ [lit m.p. $92-94^\circ\text{C}$,¹⁴]; ν_{max} 1245, 1605, 2189, 3445 cm^{-1} ; δ_{H} 2.88 (1H, bs, OH), 3.78 (6H, s, $(\text{OMe})_2$), 6.85 (4H, m, Ar-H), 7.31 (3H, m, Ar-H), 7.50 (2H, m, Ar-H), 7.55 (4H, m, Ar-H).

The following propynols were obtained in this way:

i) 1,1-Bis(4-dimethylaminophenyl)-3-phenylprop-2-yn-1-ol 10b.

From 4,4'-dimethylaminobenzophenone (5.39 g) 98% yield as a pale greenish-blue solid, m.p. $161-163^\circ\text{C}$ [lit m.p. $163-164^\circ\text{C}$,³⁰]; δ_{H} 2.68 (1H, bs, OH), 2.93 (12H, s, $(\text{NMe}_2)_2$), 6.69 (4H, m, Ar-H), 7.31 (3H, m, Ar-H), 7.52 (6H, m, Ar-H).

ii) 1,1,3-Tris(4-methoxyphenyl)prop-2-yn-1-ol 10c. From 4,4'-dimethoxybenzophenone and 4-methoxyphenylacetylene (6.04 g) 81% yield as a viscous pale yellow oil; ν_{max} 1242, 2195, 3675 cm^{-1} ; δ_{H} 2.89 (1H, bs, OH), 3.79 (6H, s, $(\text{OMe})_2$), 3.81 (3H, s, OMe), 6.84 (6H, m, Ar-H), 7.41 (2H, m, Ar-H), 7.55 (4H, m, Ar-H). Spectroscopic data were identical to those reported previously.^{14,31}

General method for acid-catalysed rearrangement of 1,1,3-triarylprop-2-yn-1-ols 10

A stirred solution of 1,1-bis(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol 10a (5.6 g, 16.5 mmol) in toluene (100 mL) was warmed to 50°C . Acidic alumina (3.0 g) was added and the mixture was refluxed until none of the prop-2-yn-1-ol remained by TLC (~ 1.5 h). The cooled mixture was filtered and the alumina was washed with hot toluene (2×50 mL). Removal of the toluene from the combined washings and elution from silica (20% EtOAc in hexane) gave 1,1-bis(4-methoxyphenyl)-3-phenylprop-2-enone 11a (3.97 g) 70% yield as deep yellow micro-crystals, m.p. $94-95^\circ\text{C}$; ν_{max} 509, 550, 703, 763, 786, 821, 959, 1032, 1185, 1242, 1424, 1507, 1553, 1578, 1596, 1650, 2839, 2933, 3010, 3064 cm^{-1} ; δ_{H} 3.78 (3H, s, OMe), 3.85 (3H, s, OMe), 6.80 (2H, m, Ar-H), 6.88 (2H, m, Ar-H), 7.00 (1H, s, alkene-H), 7.12 (2H, m, Ar-H), 7.36 (4H, m, Ar-H), 7.46 (1H, m, Ar-H), 7.89 (2H, m, Ar-H); δ_{C} 55.19, 55.40, 113.40, 113.75, 121.40, 128.30, 128.65, 130.32, 131.43, 131.46, 132.39, 134.24, 138.74, 155.13, 159.81, 160.76, 192.55; Found $[\text{M}+\text{H}]^+ = 345.1485$. $\text{C}_{23}\text{H}_{20}\text{O}_3$ requires $[\text{M}+\text{H}]^+ = 345.1489$. Spectroscopic data were identical with that reported previously.²⁰

The following compounds were obtained in this manner:

i) 1,1-Bis(4-dimethylaminophenyl)-3-phenylprop-2-enone 11b.

From 1,1-bis(4-dimethylaminophenyl)-3-phenylprop-2-yn-1-ol 10b (3.82 g) 65% yield after elution from silica (40% EtOAc in hexane) as orange micro-crystals, m.p. $143-145^\circ\text{C}$ [lit. m.p. $148-149^\circ\text{C}$,³²]; ν_{max} 507, 545, 644, 673, 749, 823, 842, 947, 1017, 1066, 1149, 1188, 1351, 1445, 1516, 1571, 1604, 1650, 1897, 2803, 2892 cm^{-1} ; δ_{H} 2.96 (6H, s, $(\text{NMe}_2)_2$), 3.02 (6H, s, $(\text{NMe}_2)_2$), 6.60 (2H, m, Ar-H), 6.66 (2H, m, Ar-H), 6.92 (1H, m, alkene-H), 7.11 (2H, m, Ar-H), 7.33 (4H, m, Ar-H), 7.44 (1H, m, Ar-H), 7.91 (2H, m, Ar-H); δ_{C} 40.27, 105.92, 111.18, 111.42, 117.86, 126.86, 128.10, 128.51, 129.79, 130.61, 131.72, 131.84, 139.83, 150.65, 151.29, 157.89, 191.95; Found $[\text{M}+\text{H}]^+ = 371.2118$. $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}$ requires $[\text{M}+\text{H}]^+ = 371.2117$.

ii) 1,1,3-Tris(4-methoxyphenyl)prop-2-enone 11c. From 1,1,3-tris(4-methoxyphenyl)prop-2-yn-1-ol 10c (5.33 g) 89% yield as a glassy oil after elution from silica (5% EtOAc in toluene), ν_{max} 417, 512, 609, 757, 827, 958, 1020, 1111, 1151, 1165, 1214, 1223, 1352, 1419, 1459, 1505, 1595, 1650, 1734, 2837, 2934, 3001 cm^{-1} ; δ_{H} 3.79 (3H, s, OMe), 3.84 (6H, s, $(\text{OMe})_2$), 6.84 (4H, m, Ar-H), 6.96 (1H, m, alkene-H), 7.11 (2H, m, Ar-H), 7.32 (2H, m, Ar-H), 7.91 (2H, m, Ar-H); δ_{C} 55.16, 55.38, 55.43, 113.39, 113.51, 113.70, 121.71, 130.19, 130.98, 131.35, 131.59, 131.61, 134.42, 153.88, 159.67, 160.57, 163.05, 191.25. Spectroscopic data were identical with that reported previously.¹⁴

General method for the preparation of 1,1,3-triarylpent-4-en-1-yn-3-ols 12

n-Butyllithium (1.6 M in hexanes, 9.5 mL, 15.2 mmol) was added slowly *via* syringe to a cold (-70°C), stirred solution

of trimethylsilylacetylene (2.15 mL, 15.2 mmol) in anhydrous tetrahydrofuran (70 mL) under a nitrogen atmosphere. On completion of the addition (*ca.* 15 min) the cold solution was allowed to stir for 1 h. 1,1-Bis(4-methoxyphenyl)-3-phenylprop-2-enone **11a** (3.5 g, 10.1 mmol) was added in a single portion and the mixture stirred at room temperature until TLC examination of the reaction mixture indicated that none of this ketone remained (*ca.* 2 h). The reaction mixture was re-cooled to 0 °C and a solution of methanolic potassium hydroxide [(from potassium hydroxide (1.1 g, 20 mmol) in methanol (10 mL)] was added in a single portion. The cooling bath was then removed and the mixture warmed to room temperature. After *ca.* 20 min TLC examination indicated that desilylation was complete. The mixture was poured into water (300 mL) and carefully neutralised to pH ~ 7 using glacial acetic acid. The organic layer was separated and the aqueous layer extracted with ethyl acetate (3 × 70 mL). The combined organic phases were washed with water (3 × 50 mL) and dried (anhyd. Na₂SO₄). Removal of the solvent gave the crude 1,1-bis(4-methoxyphenyl)-3-phenylpent-4-en-1-yn-3-ol **12a** (3.66 g) 98% yield as a pale yellow viscous oil; ν_{\max} 825, 1019, 1167, 1240, 1507, 1593, 1650, 2834, 2935 cm⁻¹; δ_{H} 2.66 (1H, s, alkyne-H), 2.71 (1H, bs, OH), 3.76 (3H, s, OMe), 3.82 (3H, s, OMe), 6.33 (1H, s, alkene-H), 6.81 (4H, m, Ar-H), 7.10 (4H, m, Ar-H), 7.25–7.38 (4H, m, Ar-H), 7.60 (2H, m, Ar-H).

Other compounds prepared using this protocol:

i) 1,1-Bis-(4-dimethylaminophenyl)-3-phenylpent-4-en-1-yn-3-ol 12b. From 1,1-bis(4-dimethylaminophenyl)-3-phenylprop-2-enone **11b** as a straw coloured viscous oil (2.29 g) 86% yield; ν_{\max} 828, 1024, 1165, 1237, 1514, 1591, 1653, 2839, 2936 cm⁻¹; δ_{H} 2.69 (1H, s, alkyne-H), 2.92 (6H, s, (NMe₂)₂), 2.97 (6H, s, (NMe₂)₂), 3.04 (1H, bs, OH), 6.23 (1H, s, alkene-H), 6.59 (2H, m, Ar-H), 6.67 (2H, m, Ar-H), 7.09 (2H, m, Ar-H), 7.13 (2H, m, Ar-H), 7.28 (1H, m, Ar-H), 7.32 (2H, m, Ar-H), 7.66 (2H, m, Ar-H).

ii) 1,1,3-Tris-(4-methoxyphenyl)pent-4-en-1-yn-3-ol 12c. From 1,3,3-tris(4-methoxyphenyl)prop-2-en-one **11c** as a viscous yellow oil (5.74 g) 96% yield; ν_{\max} 826, 1021, 1164, 1233, 1504, 1595, 1649, 2836, 2933 cm⁻¹; δ_{H} 2.63 (1H, s, alkyne-H), 2.64 (1H, bs, OH), 3.78 (3H, s, OMe), 3.810 (3H, s, OMe), 3.816 (3H, s, OMe), 6.33 (1H, s, alkene-H), 6.76–6.86 (6H, m, Ar-H), 7.08 (2H, m, Ar-H), 7.13 (2H, m, Ar-H), 7.52 (2H, m, Ar-H).

Preparation of 1-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol 10d

n-Butyllithium (1.6 M in hexanes, 31.8 mL, 50.5 mmol) was added slowly *via* syringe to a cold (–78 °C), stirred solution of trimethylsilylacetylene (7.20 mL, 50.8 mmol) in anhydrous tetrahydrofuran (120 mL) under a nitrogen atmosphere. On completion of the addition the cold solution was allowed to stir for 1 h. 4-Methoxybenzophenone (9.0 g, 42.4 mmol) was added in a single portion and the mixture stirred at room temperature until TLC examination of the reaction mixture indicated that none of the benzophenone remained (*ca.* 2 h). The reaction mixture was re-cooled to 0 °C and a solution of methanolic potassium hydroxide [(from potassium hydroxide (4.7 g, 84.8 mmol) in methanol (50 mL)] was added in a single portion. The cooling bath was then removed and the mixture warmed to room temperature, after *ca.* 20 min TLC examination indicated that desilylation was complete. The mixture was neutralised to pH ~ 7 using glacial

acetic acid and then poured into water (700 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (3 × 100 mL). The organic phases were combined, washed with water (3 × 100 mL) and dried (anhyd. Na₂SO₄). Removal of the solvent gave the title compound **10d** as a viscous pale yellow oil (9.99 g) 99% yield which gradually solidified upon standing, m.p. 41–43 °C [lit m.p. 43 °C³³]; ν_{\max} 700, 1030, 1174, 1247, 1448, 1585, 1607, 3281, 3422 cm⁻¹; δ_{H} 2.84 (1H, s, alkyne-H), 2.98 (1H, bs, OH), 3.75 (3H, s, OMe), 6.83 (2H, m, Ar-H), 7.27–7.31 (3H, m, Ar-H), 7.49 (2H, m, Ar-H), 7.58 (2H, m, Ar-H).

Synthesis of 1-(2,2-bis(4-dimethylaminophenyl)vinyl)-3-phenyl-1H-naphtho[2,1-*b*]pyran 14

A stirred solution of 2-naphthol (1.09 g, 7.5 mmol) and the crude 1,1-bis(4-dimethylaminophenyl)-3-phenylpent-4-en-1-yn-3-ol **12b** (3.0 g, 7.5 mmol) in toluene (80 mL) was warmed to 50 °C. Acidic alumina (2.5 g) was added and the mixture was heated under reflux until TLC examination indicated that none of the pent-1-en-4-yn-3-ol remained (*ca.* 1 h). The mixture was cooled to ~50 °C, filtered and the alumina was washed with hot toluene (3 × 20 mL). Removal of the toluene from the combined washings and filtrate gave a viscous brown oil that was eluted from silica (25% EtOAc in hexane). Recrystallisation from acetone and MeOH gave 1-(2,2-bis(4-dimethylaminophenyl)vinyl)-3-phenyl-1H-naphtho[2,1-*b*]pyran **14** (0.86 g) 22% yield as pale green micro-crystals, m.p. 221–223 °C; ν_{\max} 417, 564, 690, 746, 765, 809, 813, 944, 1017, 1097, 1166, 1188, 1221, 1325, 1353, 1516, 1597, 1608, 1665, 2796, 2883 cm⁻¹; δ_{H} 2.87 (6H, s, (NMe₂)₂), 3.05 (6H, s, (NMe₂)₂), 4.86 (1H, dd, *J* = 9.7 Hz, 5.1 Hz, 1-H), 5.69 (1H, d, *J* = 5.1 Hz, 2-H), 5.89 (1H, d, *J* = 9.7 Hz, alkene-H), 6.53 (2H, m, Ar-H), 6.89 (2H, m, Ar-H), 7.03 (2H, m, Ar-H), 7.28–7.43 (8H, m, Ar-H), 7.61 (1H, m, Ar-H), 7.72 (1H, d, *J* = 8.8 Hz, 7-H), 7.77 (3H, m, Ar-H); δ_{C} 33.25, 40.61, 100.53, 112.03, 112.35, 115.74, 117.99, 123.97, 124.16, 124.66, 126.09, 128.05, 128.29, 128.37, 130.66, 130.73, 132.26, 134.32, 139.11, 147.82, 148.44, 149.77; Found [M+H]⁺ = 523.2744. C₃₇H₃₄N₂O requires [M+H]⁺ = 523.2747.

Preparation of 3-[2,2-bis(4-methoxyphenyl)vinyl]-3-phenyl-3H-naphtho[2,1-*b*]pyran 13a and related diarylvinyl substituted naphthopyrans 13c and 16a

A stirred solution of 2-naphthol (0.39 g, 2.7 mmol) and 1,1-bis(4-methoxyphenyl)-3-phenylpent-4-en-1-yn-3-ol **12a** (1.0 g, 2.7 mmol) in toluene (40 mL) was warmed to 50 °C. Acidic alumina (1.5 g) was added and the mixture was heated under reflux until TLC examination indicated that none of the pent-1-en-4-yn-3-ol remained (*ca.* 1 h). The mixture was cooled to ~50 °C, filtered and the alumina was washed with hot toluene (2 × 20 mL). Removal of the toluene from the combined washings and filtrate gave a viscous brown oil that was eluted from silica (30% EtOAc in hexane); recrystallisation from acetone/MeOH gave 3-[2,2-bis(4-methoxyphenyl)vinyl]-3-phenyl-3H-naphtho[2,1-*b*]pyran **13a** (0.37 g) 28% yield as colourless micro-crystals, m.p. 101–103 °C; λ_{\max} 502 nm (PhMe); ν_{\max} 526, 545, 585, 678, 700, 730, 804, 963, 1018, 1032, 1088, 1173, 1249, 1298, 1461, 1507, 1603, 1626, 2837, 2959, 3008 cm⁻¹; δ_{H} 3.756 (3H, s, OMe), 3.760 (3H, s, OMe), 5.69 (1H, d, *J* = 9.9 Hz, 2-H), 6.40 (1H, s, alkene-H), 6.69 (2H, m,

Ar-H), 6.74 (2H, m, Ar-H), 6.86 (2H, d, J = 8.8 Hz, 5-H, Ar-H), 6.90 (2H, m, Ar-H), 7.11 (2H, m, Ar-H), 7.23 (1H, d, J = 9.9 Hz, 1-H), 7.30 (3H, m, Ar-H), 7.42 (1H, m, Ar-H), 7.53–7.58 (3H, m, Ar-H), 7.69 (1H, d, J = 8.0 Hz, 7-H), 7.83 (1H, d, J = 8.4 Hz, 10-H); δ_c 55.19, 55.26, 81.09, 112.77, 113.33, 113.95, 117.87, 118.28, 121.27, 123.34, 126.25, 126.33, 127.02, 127.36, 128.17, 128.42, 128.77, 129.17, 129.18, 129.70, 130.50, 131.40, 132.13, 135.73, 143.23, 145.85, 150.52, 158.68, 159.20; Found $[M]^+$ = 496.2028. $C_{35}H_{28}O_3$ requires $[M]^+$ = 496.2033.

The following naphthopyrans were obtained using a similar method:

i) 3-[2,2-Bis-(4-methoxyphenyl)vinyl]-3-(4-methoxyphenyl)-3H-naphtho[2,1-*b*]pyran 13c. From 2-naphthol and 1,1,3-tris-(4-methoxyphenyl)pent-4-en-1-yn-3-ol **12c** after elution from silica (30% DCM in hexane) and recrystallisation from acetone/MeOH gave the title compound (1.02 g) 52% yield as pale purple coloured micro-crystals, m.p. 125–127 °C; ν_{max} 426, 549, 584, 719, 752, 804, 837, 961, 1018, 1029, 1081, 1173, 1252, 1298, 1452, 1506, 1603, 1629, 2836, 2954, 3064 cm^{-1} ; λ_{max} 506 nm (PhMe); δ_H 3.75 (3H, s, OMe), 3.76 (3H, s, OMe), 3.77 (3H, s, OMe), 5.66 (1H, d, J = 9.9 Hz, 2-H), 6.42 (1H, s, alkene-H), 6.69 (2H, m, Ar-H), 6.74 (2H, m, Ar-H), 6.82 (3H, d, J = 8.8 Hz, 5-H, Ar-H), 6.88 (3H, m, 1-H, Ar-H), 7.11 (2H, m, Ar-H), 7.29 (1H, m, Ar-H), 7.41 (1H, m, Ar-H), 7.44 (2H, m, Ar-H), 7.55 (1H, d, J = 8.8 Hz, 6-H), 7.69 (1H, d, J = 8.0 Hz, 7-H), 7.84 (1H, d, J = 8.4 Hz, 10-H); δ_c 55.20, 55.26, 80.96, 112.80, 113.33, 113.48, 114.01, 117.93, 118.33, 121.26, 123.306, 126.311, 126.99, 127.78, 128.42, 128.75, 129.12, 129.16, 129.70, 130.79, 131.38, 132.19, 135.82, 137.96, 142.74, 150.49, 158.65, 158.83, 159.17; Found $[M+H]^+$ = 527.2213. $C_{36}H_{30}O_4$ requires $[M+H]^+$ = 527.2217.

ii) Ethyl 2-[2,2-bis-(4-methoxyphenyl)vinyl]-2-phenyl-2H-naphtho[1,2-*b*]pyran-5-carboxylate 16a. From ethyl-4-hydroxynaphthalene-2-carboxylate **15** and 1,1-bis-(4-methoxyphenyl)-3-phenylpent-4-en-1-yn-3-ol **12a** after elution from silica (50% DCM in hexane) and recrystallisation from acetone/MeOH, as pale yellow micro-crystals (0.40 g) 19% yield, m.p. 191–193 °C; ν_{max} 515, 541, 585, 617, 698, 760, 829, 837, 965, 995, 1026, 1104, 1175, 1195, 1290, 1364, 1450, 1506, 1572, 1604, 1711, 2836, 2953 cm^{-1} ; λ_{max} 516 nm (PhMe); δ_H 1.42 (3H, t, 7.1 Hz, CH_2CH_3), 3.73 (3H, s, OMe), 3.77 (3H, s, OMe), 4.38 (2H, q, J = 7.1 Hz, CH_2CH_3), 5.80 (1H, d, J = 10.0 Hz, 3-H), 6.49 (1H, s, alkene-H), 6.65 (2H, m, Ar-H), 6.75 (2H, m, Ar-H), 6.90 (2H, m, Ar-H), 7.12 (2H, m, Ar-H), 7.20 (1H, m, Ar-H), 7.23–7.28 (3H, m, 4-H, Ar-H), 7.44 (2H, m, 8-H, 9-H), 7.51 (2H, m, Ar-H), 7.75 (1H, m, 7-H), 7.92 (1H, m, 10-H), 8.00 (1H, bs, 6-H); δ_c 14.37, 55.15, 55.28, 60.98, 81.04, 112.96, 113.37, 114.62, 120.80, 122.34, 124.15, 124.72, 126.09, 126.52, 126.78, 127.35, 128.17, 128.55, 128.70, 131.10, 131.21, 132.08, 132.40, 135.77, 142.91, 145.67, 148.57, 158.62, 159.23, 167.08; Found $[M]^+$ = 568.2244. $C_{38}H_{32}O_5$ requires $[M]^+$ = 568.2246.

3-[2,2-Bis-(4-dimethylaminophenyl)vinyl]-3-phenyl-3H-naphtho[2,1-*b*]pyran 13b

This was obtained using the foregoing method for the preparation of **13a**, **c**, and **16a** but using Sasol Pural MG-30 (magnesium aluminium hydroxy carbonate, 30% Mg content on silica) 1.5 g as the catalyst in place of acidic alumina. The title compound from

2-naphthol and 1,1-bis-(4-dimethylaminophenyl)-3-phenylpent-4-en-1-yn-3-ol **12b** after elution from silica (30% EtOAc in hexane) and recrystallisation from acetone/MeOH (0.41 g) 25% yield as very pale green coloured micro-crystals, m.p. 170–172 °C; ν_{max} 513, 692, 748, 811, 902, 945, 1017, 1081, 1126, 1191, 1208, 1350, 1445, 1516, 1601, 2796 cm^{-1} ; λ_{max} 566 nm (PhMe); δ_H 2.90 (6H, s, $(NMe_2)_2$), 2.91 (6H, s, $(NMe_2)_2$), 5.69 (1H, d, J = 10.0 Hz, 2-H), 6.33 (1H, s, alkene-H), 6.51 (2H, m, Ar-H), 6.56 (2H, m, Ar-H), 6.81 (1H, d, J = 10.0 Hz, 1-H), 6.88 (2H, m, Ar-H), 6.95 (1H, d, J = 8.7 Hz, 5-H), 7.09 (2H, m, Ar-H), 7.21 (1H, m, Ar-H), 7.27–7.31 (3H, m, Ar-H), 7.41 (1H, app. t, J = 7.3 Hz, 9-H), 7.57 (3H, m, Ar-H, 6-H), 7.69 (1H, d, J = 8.0 Hz, 7-H), 7.82 (1H, d, J = 8.4 Hz, 10-H); δ_c 39.63, 40.49, 40.61, 81.42, 111.36, 111.77, 114.32, 117.41, 118.47, 121.35, 123.18, 126.15, 126.37, 127.17, 127.58, 128.05, 128.26, 128.38, 128.58, 128.89, 129.16, 129.76, 131.27, 131.75, 144.29, 146.39, 149.59, 150.00, 150.78; Found $[M+H]^+$ = 523.2739. $C_{37}H_{34}N_2O_3$ requires $[M+H]^+$ = 523.2744.

General method for preparation of naphthopyrans 13d and 16b using pyridinium *p*-toluenesulfonate catalysis

A stirred solution of 2-naphthol (2.0 g, 13.8 mmol), the 1-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol **10d** (3.6 g, 15.2 mmol), trimethyl orthoformate (2.9 g, 27.7 mmol) with catalytic amount of PPTS in 1,2-dichloroethane (70 mL) was heated under reflux until TLC examination indicated that none of the prop-2-yn-1-ol remained (*ca.* 1 h). The mixture was cooled to –50 °C and washed with water (2 × 50 mL). Removal of the combined solvent gave the crude compound which was eluted from silica (70% DCM in hexane), followed by recrystallisation from acetone/MeOH to afford 3-(4-methoxyphenyl)-3-phenyl-3H-naphtho[2,1-*b*]pyran **13d** as colourless micro-crystals (4.67 g) 93% yield, m.p. 146–149 °C [lit. m.p. 154–157 °C,³⁴]; λ_{max} 465 nm (PhMe); ν_{max} 422, 571, 766, 934, 1080, 1217, 1302, 1448, 1509, 1581, 1609, 1630, 2959, 3064 cm^{-1} ; δ_H 3.76 (3H, s, OMe), 6.23 (1H, d, J = 9.9 Hz, 2-H), 6.82 (2H, m, Ar-H), 7.18 (1H, d, J = 8.8 Hz, 5-H), 7.24 (1H, m, Ar-H), 7.32 (4H, m, Ar-H, 1-H), 7.38 (2H, m, Ar-H), 7.46 (3H, m, Ar-H), 7.65 (1H, d, J = 8.8 Hz, 6-H), 7.71 (1H, d, J = 8.0 Hz, 7-H), 7.95 (1H, d, J = 8.4 Hz, 10-H); δ_c 55.22, 82.33, 113.37, 113.94, 118.35, 119.35, 121.30, 123.54, 126.57, 126.86, 127.40, 127.86, 128.05, 128.49, 129.27, 129.76, 136.91, 145.07, 150.52, 158.90.

The following pyran was also obtained using this method:

i) Ethyl 2-(4-methoxyphenyl)-2-phenyl-2H-naphtho[1,2-*b*]pyran-5-carboxylate 16b. From ethyl 4-hydroxynaphthalene-2-carboxylate **15** and 1-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ol **10d** after elution from silica (50% DCM in hexane) and recrystallisation from acetone/MeOH, as colourless micro-crystals (0.39 g) 75% yield m.p. 102–103 °C; ν_{max} 414, 538, 566, 591, 677, 697, 748, 770, 803, 839, 961, 997, 1012, 1041, 1056, 1181, 1200, 1244, 1291, 1363, 1377, 1448, 1510, 1583, 1609, 1708, 2903, 2978 cm^{-1} ; λ_{max} 483 nm (PhMe); δ_H 1.41 (3H, t, J = 6.8 Hz, CH_2CH_3), 3.71 (3H, s, OMe), 4.39 (2H, q, J = 6.8 Hz, CH_2CH_3), 6.20 (1H, d, J = 9.9 Hz, 3-H), 6.81 (2H, m, Ar-H), 7.23 (1H, m, Ar-H), 7.30 (2H, m, Ar-H), 7.42 (2H, m, Ar-H), 7.46–7.51 (3H, m, Ar-H), 7.56 (1H, app. t, J = 7.5 Hz, Ar-H), 7.65 (1H, d, J = 9.9 Hz, 4-H), 7.78 (1H, d, J = 8.0 Hz, 7-H), 8.06 (1H, s, 6-H), 8.35 (1H, d, J = 8.5 Hz, 10-H); δ_c 14.81, 55.60, 61.45, 82.76, 113.91, 115.40, 122.56, 122.65, 125.02, 125.20, 126.78, 127.43, 127.83, 128.22, 128.34, 128.55, 128.82, 129.25, 133.13, 137.29, 145.56,

149.00, 159.43, 167.45; Found $[M+H]^+ = 437.1750$. $C_{29}H_{24}O_4$ requires $[M+H]^+ = 437.1747$.

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- 23 Crystallographic data for compound **14** (CCDC 777577): Formula = $C_{37}H_{34}N_2O$; Formula weight = 522.66; Size = $0.19 \times 0.11 \times 0.05$ mm; Crystal morphology = colourless fragment; $T = 150$ K, Wavelength = 0.71073 \AA [Mo-K α]; Crystal system = orthorhombic; Space group = $P2_12_12_1$; Unit cell dimensions, $a = 10.9909(10) \text{ \AA}$, $\alpha = 90^\circ$, $b = 13.0053(11) \text{ \AA}$, $\beta = 90^\circ$, $c = 20.0553(18) \text{ \AA}$, $\gamma = 90^\circ$; Volume = $2866.7(4) \text{ \AA}^3$; $Z = 4$; Density (calculated) = 1.211 Mg m^{-3} ; Absorption coefficient 0.072 mm^{-1} ; $F(000) = 1112$; Data collection range = $2.57 \leq \theta \leq 27.94^\circ$; Index ranges = $-13 \leq h \leq 14$, $-14 \leq k \leq 17$, $-25 \leq l \leq 26$; Reflections collected = 27053; Independent reflections = 3842 [$R(\text{int}) = 0.0786$]; Observed reflections = 2744 [$I > 2\sigma(I)$]; Absorption correction = multi-scan; Max. and min. transmission = 0.9964 and 0.8278; Refinement method = Full; Data/restraints/parameters = 3114/0/365; Goodness of fit = 1.063; Final R indices [$I > 2\sigma(I)$] $R_1 = 0.0431$, $wR_2 = 0.0957$; R indices (all data): $R_1 = 0.0669$, $wR_2 = 0.1087$; Largest diff. peak and hole = 0.190 and $-0.182 \text{ e \AA}^{-3}$.
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