Observations on the Synthesis of Photochromic Naphthopyrans

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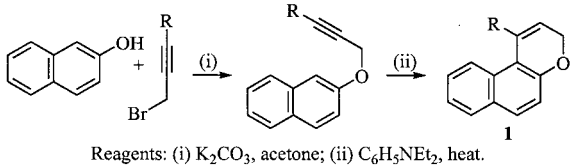
1-Naphthol reacts with 1,1-diarylprop-2-yn-1-ols **5a**,**b**, under alumina catalysis, by two pathways to give the photochromic naphtho[1,2-*b*]pyrans **6a**,**b**, together with the propenylidenenaphthalenones **7a**,**b**, representatives of a new class of merocyanine dyes. With 2-methyl-1-naphthol, formation of the photochrome is suppressed; the only products are merocyanines **7c**,**d**. The cyclocondensation of 2-naphthol with **5a**,**b** proceeds much more efficiently, to give the naphtho[2,1-*b*]pyrans **14a**,**b**. Pyran formation is not suppressed from either 1-bromo- or 1-(4-methoxyphenyl)-2-naphthol; reaction with **5a**,**b** merely results in expulsion of the C-1 substituent. An alternative pathway supervenes in the reaction of 1-methyl-2-naphthol with **5a** to give the benz[*e*]indanone **17**, the constitution of which was determined by X-ray crystallography. Reaction of the 1,3,3-triarylpropynols **19a**,**b** with 1-naphthol affords the naphthopyrans **20** together with merocyanines **21**, whilst the isomeric pyrans **23** are efficiently produced from 2-naphthol. The configuration of merocyanines **7a** and **21a** was unequivocally established by X-ray crystallography.

Introduction

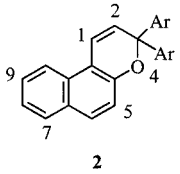
Claisen first described the rearrangement of allyl phenyl ethers to *o*- or *p*-allylphenols in 1912.[1] Since this report the Claisen rearrangement has been widely employed in synthesis and has featured in many review articles.[2] Our interest in this rearrangement relates to the preparation of photochromic naphthopyrans, which are obtained by the Claisen rearrangement of a naphthyl propargyl ether formed in situ from the acid-catalysed etherification of a naphthol with a prop-2-yn-1-ol.[3] The first application of a Claisen rearrangement to the synthesis of the naphthopyran system **1** was reported by Iwae and Ide in 1962 (Scheme 1).[4]



Scheme 1

Photochromic diarylnaphthopyrans can be accessed in a single step using a substantially modified version of this protocol. Thus, heating 1,1-diarylprop-2-yn-1-ols with a naphthol in toluene containing an acidic catalyst, required to promote the initial naphthyl propargyl ether formation, affords the naphthopyrans directly in good yield.[5] This chemistry has recently been adapted for the solid-state synthesis of naphthopyrans.[6] From our earlier studies on the formation of photochromic diaryl-substituted 3*H*-naphtho[2,1-*b*]pyrans **2** and the isomeric 2*H*-naphtho[1,2-*b*]pyrans **3** it was apparent that the former were frequently obtained in superior yield and with less extensive by-product formation than the isomeric 2*H*-naphtho[1,2-*b*]pyrans.[7]

We now report our results and observations on the synthesis of some naphthopyrans from the acid-catalysed reaction between a prop-2-yn-1-ol and a naphthol.



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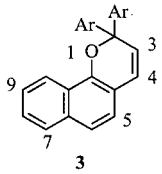

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Results and Discussion

Heating 1-naphthol **4a** with a 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (**5a**), which was conveniently prepared by the addition of lithium trimethylsilylacetylide (LTSA) to a

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substituted benzophenone with subsequent removal of the trimethylsilyl group,[8] in toluene containing acidic aluminium oxide for 1.5 h gave a deep-red multi-component gum after workup. Elution of this gum from silica gave the expected naphthopyran **6a** as pale pink microcrystals in 37% yield (Scheme 2). A more polar, intense red fraction was also isolated. The ^{1}H NMR spectrum of this red compound was complex due to a number of overlapping signals in the aromatic region. However, it was apparent this compound did not contain a pyran ring, since the signals of the AB system of the pyran unit which appear at δ = 6.11 and 6.69 ppm with 9.8 Hz coupling for 3-H and 4-H, respectively, in **6a**, were absent. The pyran ring protons of the 2*H*-naphtho[1,2-*b*]pyrans typically resonate at δ = 6.1 and 6.8 ppm with $J \approx 10$ Hz.[9] Additionally, the methoxy groups of the red product are nonequivalent giving rise to signals at δ = 3.86 and 3.92 ppm unlike the methoxy groups of **6a** which are equivalent and resonate at δ = 3.76 ppm. The ^{1}H NMR spectrum of the red product also displays the following well-resolved signals in the aromatic region: a doublet of doublets (J = 10.2, 1.5 Hz) at δ = 6.62 ppm, a doublet (J = 10.2 Hz) at δ = 8.11 ppm and a doublet of doublets (J = 7.9, 1.6 Hz) at δ = 8.27 ppm. The ^{13}C NMR spectrum displays a low-field signal at δ = 184.9 ppm which is indicative of a carbonyl function.[10] The presence of the C=O group was corroborated by infrared spectroscopy which gave a C=O stretching band at 1630 cm^{-1} suggestive of an α,β-unsaturated C=O group.[11] High resolution electron impact mass spectrometry gave a molecular mass of 395.1642 for $[M + H]^+$ ($C_{27}H_{22}O_3$) identical to that required for the naphthopyran **6a**, but did not give a fragmentation pattern in keeping with the presence of a pyran unit. 2*H*[1]-Benzopyrans and naphthopyrans readily fragment by loss of one of the *geminal* substituents to give a pyrylium-type radical cation which then suffers multiple fragmentation.[12] However, the chemical ionisation mass spectrum gave very similar fragmentation patterns, with both the naphthopyran **6a** and the unknown compound showing loss of a 4-methoxyphenyl group. The UV/Vis spectrum of this unknown exhibits λ_{max} (EtOH) = 462 nm with ε_m = 4.0 × 10^4 mol^{-1}·dm^3·cm^{-1}.

Clearly the spectroscopic data accrued for this unknown are incongruous with both a pyran ring containing structure such as **6a** and with compound **8**. The formation of **8** may be rationalised by a *para*-Claisen rearrangement of the intermediate ether, which requires the presence of both an exchangeable and an acetylenic signal in its ^{1}H NMR spectrum. The absolute structure of the red product was unequivocally established by X-ray crystallography (Figure 1) as the enone **7a**.[13] The observed *s-trans* geometry is in agreement with the minimisation of steric interactions between the diarylprop-2-enyl function and the naphthalenone moiety. It is noteworthy that one of the aryl groups is significantly twisted out of the main plane of the molecule to alleviate the steric interactions between the *ortho*-protons in a planar array. This contrasts with the triphenylmethine dye unit where all three of the aryl rings are twisted out of the plane to minimise steric interactions between the *ortho*-protons.[14]

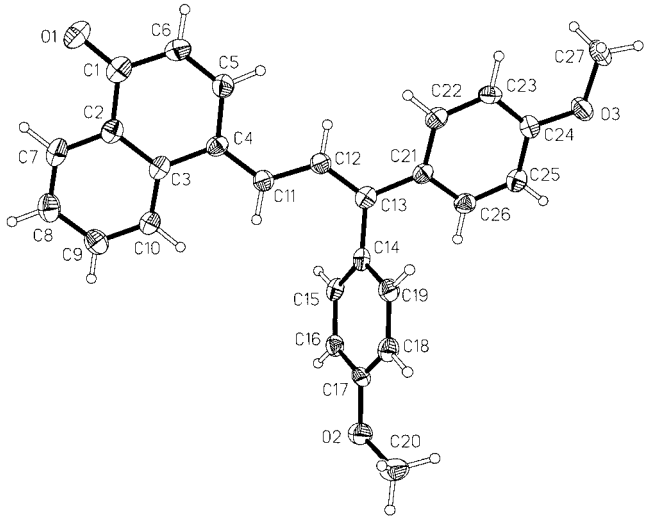
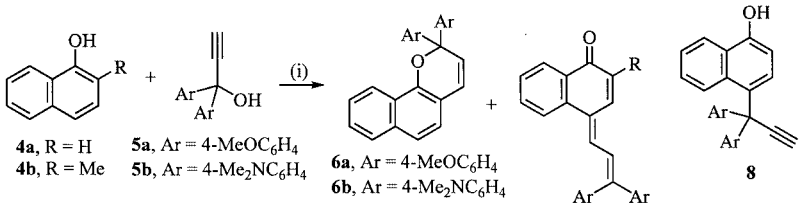


Figure 1. X-ray crystallographic structure of enone **7a**

Similar results were obtained when 1-naphthol was treated with prop-2-yn-1-ol **5b**. The naphthopyran **6b** was obtained after chromatography as pale blue microcrystals in 43% yield together with an intense red dye **7b** [λ_{max} (EtOH) = 556 nm with ε_m = 3.8 × 10^4 mol^{-1}dm^{3}cm^{-1}]. The bathochromic shift in λ_{max} of 94 nm compared with dye **7a** is in agreement with the increasing strength of the donor groups (NMe_2 vs. OMe). The signals in the aromatic



4a, R = H
4b, R = Me

5a, Ar = 4-$MeOC_6H_4$
5b, Ar = 4-$Me_2NC_6H_4$

6a, Ar = 4-$MeOC_6H_4$
6b, Ar = 4-$Me_2NC_6H_4$

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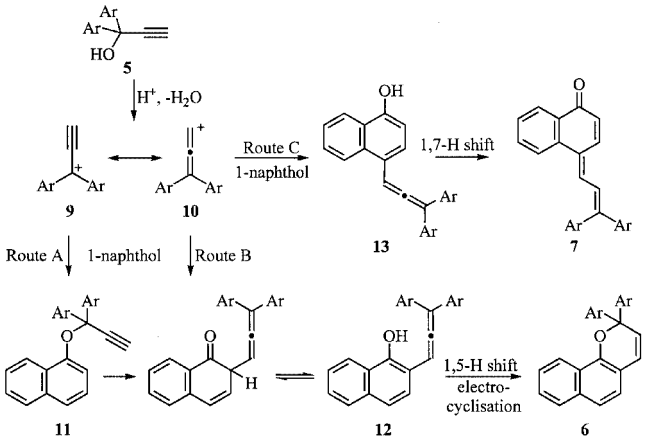
7a, Ar = 4-$MeOC_6H_4$, R = H
7b, Ar = 4-$Me_2NC_6H_4$, R = H
7c, Ar = 4-$MeOC_6H_4$, R = Me
7d, Ar = 4-$Me_2NC_6H_4$, R = Me

Reagents: (i) PhMe, acidic aluminium oxide, heat

Scheme 2

region of the ^{1}H NMR spectrum of **7b** are well resolved and could be unequivocally assigned from a ^{1}H-^{1}H COSY experiment. The *cis* relationship between 2-H (δ = 6.60 ppm) and 3-H (δ = 8.16 ppm) of **7b** was confirmed by the 10 Hz coupling constant. As in example **7a**, the signal for 2-H shows long range coupling (ca. 1.4 Hz) to 1′-H. The *s-trans* arrangement of the propenylidene function was confirmed by the coupling between 1′-H and 2′-H of 11.9 Hz.[8]

The formation of the naphthopyrans **6** and dyes **7** is outlined in the mechanism depicted in Scheme 3. Protonation and loss of water from the propynol **5** generates the carbocation **9**. The currently accepted mechanism for the formation of the naphthopyran follows route A, which commences with interception of **9** by 1-naphthol to afford the propargyl naphthyl ether **11**. A Claisen rearrangement and subsequent enolisation afford the allenylnaphthol **12**. The naphthopyran **6** results from a 1,5-H shift and an electrocyclisation. Alternatively, **9** may be intercepted by either the 2- or 4-position of 1-naphthol (route B and route C, respectively) in a Meyer−Schuster[15] or Rupe-like[16] rearrangement. The overall process is suggestive of participation of an allenyl cation **10**. In the former route the common allenylnaphthol intermediate **12** is obtained, which ultimately affords **6**. However, in the latter an alternative allenylnaphthol, **13**, is obtained, which undergoes a 1,7-H shift to afford the dye **7**. The loss of aromaticity in one ring of the allenylnaphthol **13** is presumably balanced by the stabilisation gained on generation of the extended conjugated system in **7**.



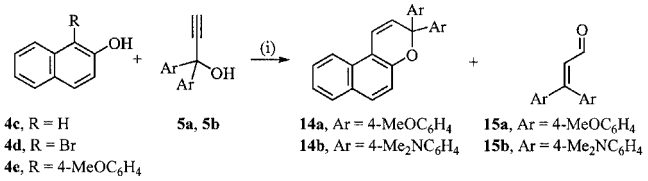
Scheme 3

Claisen rearrangements are markedly dependent upon the reaction solvent[17] and are particularly facile in trifluoroacetic acid.[18] However, it has been suggested that when Claisen rearrangements are performed with an added Lewis acid catalyst, the mechanism may no longer be cyclic and instead follows the typical Friedel−Crafts-type process.[19] It may well be the case that under the present reaction conditions both electrophilic aromatic substitution (of 1-naphthol by the alkyne-substituted carbocation **9**) and a Claisen cyclic mechanism are in operation. We have previously suggested the involvement of alkynyl and allenyl cations such as **9** and **10**, derived from 1,1-diarylprop-2-yn-1-ols, in electrophilic addition reactions to dimedone to afford merocyanine dyes,[8] and allenyl cations derived from 1,1-disubstituted *O*-(trimethylsilyl)prop-2-yn-1-ols upon reaction with trimethylsilyl trifluoromethanesulfonate have recently been implicated in novel C−C bond-forming reactions.[20] Olah and co-workers have investigated the structure and reactivity of alkynyl-allenyl cations and have concluded that such cations may be considered as alkyne-substituted carbocations.[21] The reactivity of such cations has recently been reviewed and their ambident reactivity is markedly dependent upon their substitution pattern.[22]

It was of interest to attempt to improve the formation of the novel dye system **7**. Clearly, blocking the 2-position of 1-naphthol, the normal terminus of the Claisen rearrangement, with a methyl group should prevent the formation of the pyran ring (routes A and B) and favour route C. Thus, heating 2-methyl-1-naphthol (**4b**), obtained by the reductive cleavage of 1-acetoxy-2-methylnaphthalene[23] with $LiAlH_4$ in THF, with prop-2-yn-1-ol (**5a**) gave the new enone **7c** in an improved but still low yield (19%) together with some unchanged starting material. The ^{1}H NMR spectrum of this compound displays a singlet at δ = 2.2 ppm assigned to the methyl group and a singlet at δ = 8.0 ppm assigned to 3-H. 1′-H appears as a doublet at δ = 7.60 ppm with J = 12.0 Hz, indicative of the *s-trans* arrangement; the signal for 2′-H is superimposed on the aromatic signals. The corresponding dye from **4b** and prop-2-yn-1-ol **5b** was obtained in 27% yield. The greater yield of both the dyes and naphthopyrans derived from propynol **5b** would infer that the formation of the cations (**9** and **10**) is favoured when the aryl rings contain efficient electron-releasing groups.

We next investigated the Claisen rearrangement of naphthyl propargyl ethers derived from 2-naphthols and diarylprop-2-yn-1-ols. The reaction of 2-naphthol (**4c**) with propynol **5a** under the standard conditions gave the photochromic naphthopyran **14a** in 82% yield together with a small amount of the unsaturated aldehyde **15a** after elution from silica and recrystallisation (Scheme 4). Repeating the reaction with propynol **5b** gave the expected naphthopyran **14b** (85%) and the aldehyde **15b** (4%). The ^{1}H NMR spectra of these 3*H*-naphtho[2,1-*b*]pyrans **14** are similar, with 2-H resonating at δ ≈ 6.2 ppm, upfield of the signal for 1-H, which appears at about δ = 7.3 ppm and with $J_{1,2}$ = 10 Hz.[9] The formation of the aldehydes **15** can be rationalised by interception of the alkyne-substituted carbocation **9** (Schemes 3 and 4) with water and subsequent tautomerisation (a Meyer−Schuster rearrangement[15]). It is noteworthy that higher yields of the naphthopyrans were observed when 2-naphthol was employed and also that a greater amount of the α,β-unsaturated aldehyde was obtained when a more electron-rich propynol (**5b**) was used.

We explored the reaction between 1-bromo-2-naphthol (**4d**) and **5a** in which the terminus of the Claisen rearrangement is blocked with a bromine atom. The major product isolated from the reaction mixture was the naphthopyran **14a** in a yield of 19%; a considerable amount of intractable

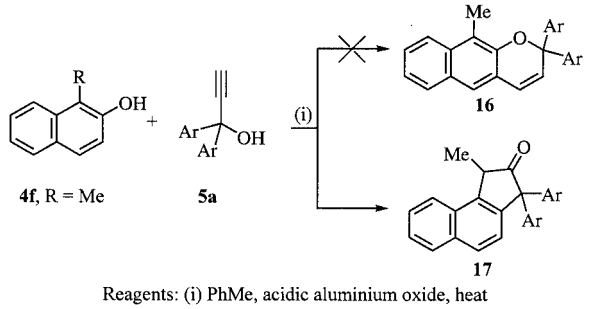


Scheme 4

polar material remained irreversibly bound to the chromatography silica. The elimination of the bromine atom as Br^+ from 1-bromo-2-naphthol during the acid-catalysed formation of fluorans has been reported.[24]

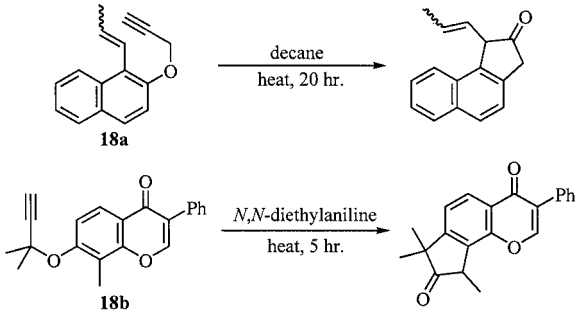
1-(4-Methoxyphenyl)-2-naphthol (**4e**) was conveniently obtained in 56% yield by the Suzuki coupling[25] of **4d** with (4-methoxyphenyl)boronic acid. Heating **4e** with propynol **5a** followed by elution of the complex reaction mixture from silica also gave naphthopyran **14a** in low yield (8%); no pure components, other than some recovered **4e** and **5a**, were isolated. It is likely that the 4-methoxyphenyl function has been lost as the resonance-stabilised carbocation, $[4\text{-}MeOC_6H_4]^+$, which would have been intercepted by any nucleophilic species in the reaction mixture. However, examination of the crude reaction mixture by GC-MS for components that contained the $MeOC_6H_4$ fragment was inconclusive.

The reaction between 1-methyl-2-naphthol (**4f**) and propynol **5a** was next investigated (Scheme 5) since the likelihood of elimination of CH_3^+ is remote. A single pure major component was obtained by flash chromatography. The ^1H NMR spectrum is particularly simple and displays a doublet at $\delta = 1.54$ ppm ($J = 7.5$ Hz) coupled with a quadruplet at $\delta = 4.07$ ppm. A singlet at $\delta = 3.75$ ppm and another at $\delta = 3.78$ ppm, each accounting for a methoxy group, are also present. The 14 aromatic protons appear in the range $\delta = 6.7-7.9$ ppm. Infrared spectroscopy ($\tilde{\nu}_{max} = 1746$ cm^{-1}) and ^{13}C NMR spectroscopy ($\delta_{C=O} = 218.8$ ppm) confirm the presence of a C=O group in the molecule. Electron impact mass spectrometry gave $[M^+]$ at $m/z = 408.1719$ corresponding to a molecular formula of $C_{28}H_{24}O_3$. Whilst this molecular formula would accommodate a linear naphthopyran of structure **16** the remaining spectroscopic data would suggest an alternative structure.



Scheme 5

Examination of the literature revealed that substituted cyclopentanones have been observed from the Claisen rearrangement of propargylic ethers **18a**[26] and **18b**[27] in which the favoured terminus of the rearrangement is blocked. A multi-step sequence has been proposed to account for this remarkable annelation reaction.[26]



With this information to hand we proposed the substituted indanone **17** as the crystalline product from **4f** and **5a**. The structure of **17**[28] was confirmed by X-ray crystallography (Figure 2).

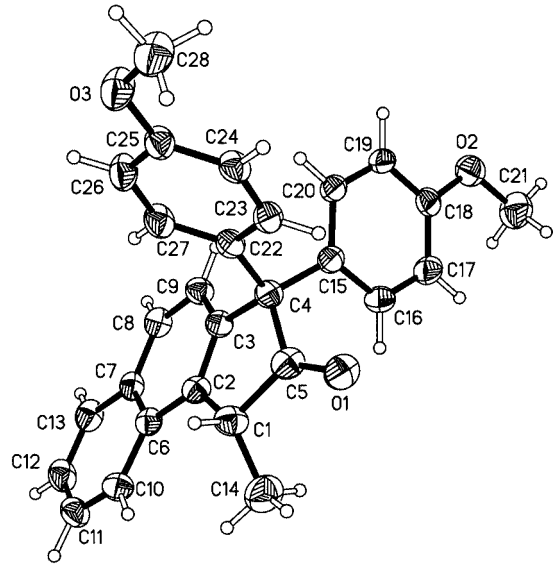


Figure 2. X-ray crystallographic structure of benzindanone **17**

The involvement of a diarylpropargyl naphthyl ether **11** (Scheme 3) in the mechanism proposed for the formation of the naphthopyrans is widely accepted.[3] However, to the best of our knowledge the isolation of such diaryl-substituted ethers has never been reported, whereas simple naphthyl propargyl ethers have been obtained.[4] The Mitsunobu coupling reaction offers an efficient route for the coupling of phenols with alcohols to form alkyl aryl ethers using the ylide generated in situ from Ph_3P and diethyl azodicarboxylate (DEAD).[29] The mild conditions typically used to effect this transformation (room temp. and ether solvents) were thought to be ideal for the preparation of ethers **11**. Thus, stirring a solution of propynol **5b** with 2-naphthol in anhydrous THF containing Ph_3P and DEAD according to

the general procedure[30] gave a complex mixture (TLC) which, remarkably, contained a photochromic component. Aqueous workup and elution of the crude mixture from silica gave some recovered 2-naphthol and alkynol **5b** together with the naphthopyran **14b** in low yield (16%). None of the desired propargyl ether was obtained. The use of a weak acid catalyst has recently been advocated to improve the yield of the Mitsunobu reaction.[31] When the procedure was repeated with the addition of 0.2 equiv. of 4-nitrophenol the naphthopyran **14b** was obtained in an improved yield (27%). The formation of the naphthopyran under these mild conditions is quite remarkable and would account for the fact that ethers such as **11** have not been observed, since under the standard conditions employed for the synthesis of naphthopyrans (PhMe, heat, H^+ cat.), they readily rearrange. Investigation of the modified coupling procedure with 1-naphthol and **5b** gave a complex intensely coloured product from which the naphthopyran **6b** (11%) and the dye **7b** in 3% yield were isolated.

There are relatively few examples of the synthesis of triaryl-substituted naphthopyrans from naphthols and triaryl-substituted propynols.[32] Triaryl-substituted propynols **19a**, **b** were conveniently obtained by the addition of a lithium arylacetylide to 4,4′-dimethoxybenzophenone. Propynol **19a** was obtained as a viscous gum (93%) that gradually solidifies on standing. Repeating the procedure with lithium (4-methoxyphenyl)acetylide afforded **19b** (92%) also as a viscous gum, but which does not solidify on standing. In an attempt to encourage crystallisation a small quantity of this propynol was eluted from flash chromatography silica. The ^{1}H NMR spectrum of the resulting compound indicated that some **19b** had rearranged to afford the α,β-unsaturated ketone **24**, the methoxy groups of which are non-equivalent and give rise to signals at δ = 3.73, 3.76 and 3.78 ppm, whereas in propynol **19b** the methoxy groups of the *geminal* aryl rings are equivalent and give rise to a signal at δ = 3.80 ppm, with the remaining methoxy group resonating at δ = 3.83 ppm. The most striking difference between the ^{1}H NMR spectra of **24** and **19b** is the presence of a singlet at δ = 6.96 ppm, assigned to the alkenic proton of **24**. Complete rearrangement of propynol **19b** to **24** was effected on heating **19b** in toluene containing acidic alumina for 2 h (Scheme 6). Heating **19a** with 1-naphthol under the standard conditions gave two pure fractions after elution from silica. The least-polar fraction was identified as the naphthopyran **20a** (32%) with 3-H resonating at δ = 6.11 ppm as a singlet. The more polar, major fraction, was intensely coloured [λ_{max} (EtOH) = 471 nm, $\varepsilon_{max} = 2.6 \times 10^4$ mol^{-1}dm^{3}cm^{-1}] and was presumed to be the dye **21a** rather than the isomer **22a** in which there is significant crowding between the *peri*-proton (5-H) of the naphthalene unit and the proximate aryl group at C-1′. The geometry of the dye **21a**[33] was determined by X-ray crystallography (Figure 3). It is significant that in this triaryl-substituted merocyanine dye all three of the aryl rings are twisted out of the main plane of the molecule to alleviate steric interactions. It is noteworthy that the dye **21a** is the major component (36%) obtained from the reaction, a feature that implies that a Friedel−Crafts-type process predominates.

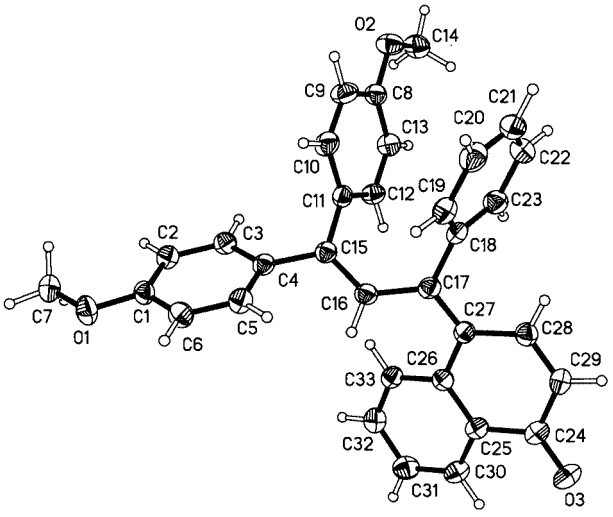
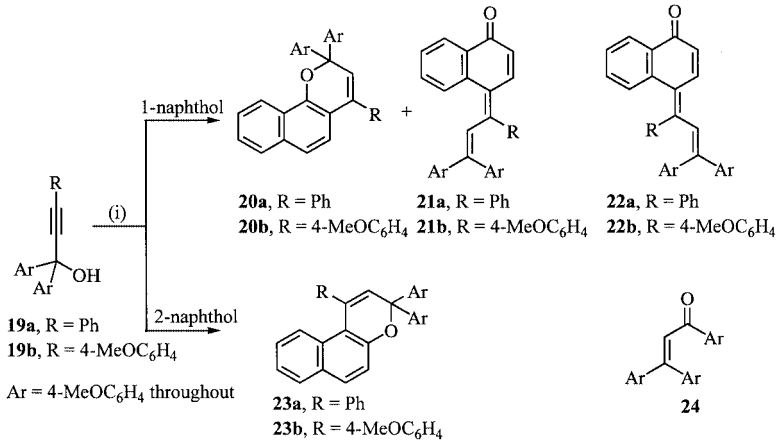


Figure 3. X-ray crystallographic structure of **21a**



Reagents: (i) PhMe, acidic aluminium oxide, heat

Scheme 6

A similar result was noted when tris(4-methoxyphenyl)prop-2-yn-1-ol (**19b**) was treated with 1-naphthol, with the naphthopyran **20b** isolated in 25% yield. 3-H in this compound resonates slightly upfield of that for **20a** at δ = 6.07 ppm. The dye **21b**, isolated in 42% yield, has λ_{max} slightly bathochromically shifted [λ_{max} (EtOH) = 479 nm, $\Delta\lambda$ = 8 nm] compared with **21a**. In the ^{1}H NMR spectra of dyes **21** the coupling constant for the *cis*-disposed protons, 2-H and 3-H, is about 10.2 Hz, and 8-H resonates furthest downfield at δ = 8.44 ppm due to the proximity of these protons to the *peri*-carbonyl function.

Heating 2-naphthol with propynols **19a** and **19b** gave the 3*H*-naphtho[2,1-*b*]pyrans **23a**,**b** in 76 and 97% yield, respectively. In the ^{1}H NMR spectra of these naphthopyrans 2-H resonates at δ ≈ 6.1 ppm. The furthest downfield signal in the ^{1}H NMR spectra of **23a**,**b** appears at δ ≈ 7.7 ppm, shifted upfield from the corresponding signal in naphthopyran **14a** (δ = 7.93 ppm) and is assigned to 10-H. It would appear that 10-H lies in the shielding zone of the 1-aryl ring, suggesting that the disposition of this ring must approach perpendicularity with respect to the major plane of the molecule.[34] None of the rearranged product **24** was isolated from either of these reaction mixtures.

The photochromic properties of the simple naphthopyrans **6** and **14** derived from the 1,1-diarylprop-2-yn-1-ols **5** are well documented.[3] The novel isomeric triaryl-substituted naphthopyrans **20** and **23** derived from the 1,1,3-triarylprop-2-yn-1-ols **19** failed to display any photochromic response in toluene solution at room temperature. It was thought that the thermal reversion of the ring-opened forms to the pyran ring would be rapid at room temperature as a consequence of the steric pressures exerted in the crowded isomeric ring-opened forms, which are minimised in the pyran tautomers. This results in a photostationary state with an undetectably low level of the ring-opened isomers. Re-examination of the toluene solutions after cooling to −30 °C also failed to give a detectable photochromic response (Scheme 7).

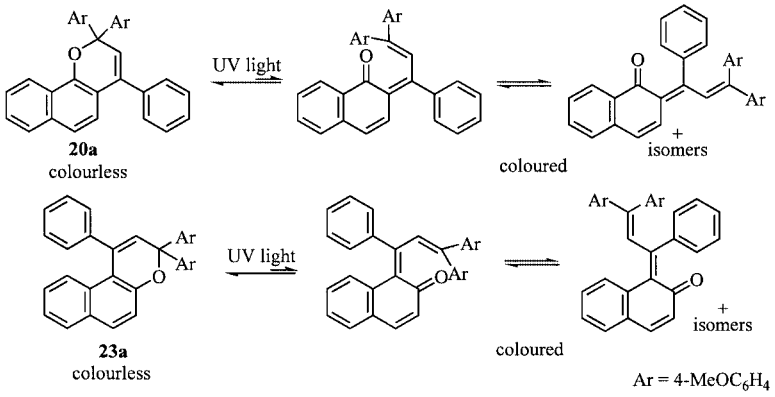
Conclusion

The reaction of 1,1-diaryl- and 1,1,3-triarylprop-2-yn-1-ols with 1-naphthol proceeds to afford 2*H*-naphtho[1,2-*b*]pyrans in moderate yield together with a novel merocyanine dye system. Naphthopyran formation is suppressed when 2-methyl-1-naphthol is treated with a prop-2-yn-1-ol. The formation of these merocyanines is rationalised by nucleophilic interception of an alkyne-substituted carbocation **9** by the 4-position of 1-naphthol and a subsequent 1,7-H shift. A similar process initiated by interception of the alkyne-substituted cation by C-2 of 1-naphthol may operate to afford an allenylnaphthol which leads to the naphthopyran, a mechanism that may occur in tandem with the widely accepted mechanism for the formation of naphthopyrans involving a Claisen rearrangement.

The 3*H*-naphtho[2,1-*b*]pyrans are obtained more efficiently than their [1,2-*b*]-isomers, from the corresponding reaction of a prop-2-yn-1-ol with a 2-naphthol. Only a small amount of an α,β-unsaturated aldehyde accompanied the formation of the 3*H*-naphtho[2,1-*b*]pyrans. When the 1-position of 2-naphthol is substituted with a Br atom or a 4-methoxyphenyl group, the naphthopyran is obtained in reduced yield through expulsion of the 1-substituent. However, when 1-methyl-2-naphthol is employed a complex rearrangement ensues to afford a benz[*e*]indanone.

Experimental Section

General: Flash chromatography was performed using chromatography silica (40−63 micron particle size distribution) supplied by Fluorochem Ltd. according to the published procedure.[35] Melting points were recorded in capillaries and are uncorrected. Infrared spectra were recorded with a Perkin−Elmer 882 infrared spectrophotometer in KBr discs unless otherwise specified. NMR spectra were recorded in $CDCl_3$, unless stated otherwise, using a Bruker Avance 400 MHz instrument; coupling constants are quoted in Hz. Visible spectra were recorded in either spectroscopic grade ethanol



Scheme 7

or toluene in 1-cm quartz cells using a Perkin−Elmer λ5 spectrophotometer.

Crystal Structure Determination: Details of the crystal data and a summary of data collection parameters for compounds **7a**, **17a** and **21a** are given below.[13,28,33] Intensity data were recorded at 150 K, using a Nonius-Kappa CCD area-detector diffractometer mounted at the window of a rotating anode FR591 generator with a molybdenum anode (λ = 0.71073 Å); φ- and ω-scans were carried out to fill the Ewald sphere. An empirical absorption correction was applied using SORTAV. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares refinements.[36]

Preparation of Intermediates

2-Methyl-1-naphthol (4b): A solution of 1-acetoxy-2-methylnaphthalene (25 mmol) in anhydrous THF (15 mL) was added over 30 min to a suspension of $LiAlH_4$ (50 mmol) in anhydrous THF (50 mL). The resulting suspension was refluxed for 1 h. EtOAc (5 mL) was cautiously added to the cooled (5 °C) reaction mixture followed by water (100 mL). The resulting mixture was acidified (HCl, 2 M aq.) and extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with water (100 mL), dried (anhyd. Na_2SO_4) and the solvents evaporated to yield **4b** as an off-white solid which gradually darkened on standing in air (2.77 g, 70%), m.p. 58−60 °C (ref.[37] 61.5−62 °C). ^{1}H NMR: δ = 2.41 (s, 3 H, 2-Me), 5.10 (br. s, 1 H, OH), 7.23 (m, 1 H, 4-H), 7.44 (m, 3 H, Ar-H), 7.76 (d, J = 7.8 Hz, 1 H, 5-H), 8.10 (d, J = 7.8 Hz, 1 H, 8-H) ppm.

1-(4-Methoxyphenyl)-2-naphthol (4e): 1-Bromo-2-naphthol (9.0 mmol) was added to a suspension of $Pd(PPh_3)_4$ (0.3 mmol) in 1,2-dimethoxyethane (40 mL) and the mixture stirred for 10 min. To this mixture was added (4-methoxyphenyl)boronic acid (13.5 mmol) in ethanol (5 mL) followed by aqueous sodium carbonate (2 M, 9 mL). The resulting solution was refluxed until no starting material remained (ca. 4 h). The solution was cooled to room temperature, poured into water (500 mL), and then acidified to pH ≈ 4 by addition of hydrochloric acid before extraction with ethyl acetate (4 × 50 mL). The organic extracts were dried (anhyd. Na_2SO_4) and the solvent was removed to give a brown tar. Elution from silica with 30% ethyl acetate/hexane afforded **4e** as fine white microcrystals (1.26 g, 56%), m.p. 101−103 °C (ref.[39] 98.5−100.5 °C). ^{1}H NMR: δ = 3.91 (s, 3 H, OMe), 5.17 (s, 1 H, OH), 7.12 (m, 2 H, Ar-H), 7.32 (m, 5 H, Ar-H), 7.78 (m, 3 H, Ar-H) ppm. HRMS: $[M + H]^+$ 250.0991, $C_{17}H_{14}O_2$ requires $[M + H]^+$ 250.0994.

1-Methyl-2-naphthol (4f): A stirred solution of 2-methoxy-1-naphthaldehyde (54 mmol), hydrazine hydrate (100 mmol) in diethylene glycol (60 mL) was heated at 100 °C for 5 min and then cooled to room temperature. KOH (54 mmol) was added and the mixture refluxed for 1.5 h. The cooled mixture was poured into water (400 mL) and extracted with toluene (5 × 50 mL). The combined extracts were washed with HCl (3 × 50 mL, 2 M aq.), water (2 × 50 mL) and dried (anhyd. Na_2SO_4). Removal of the toluene gave crude 2-methoxy-1-methylnaphthalene, which was refluxed for 30 min with pyridine hydrochloride (265 mmol). The cooled mixture was diluted with water (200 mL) and extracted with CH_2Cl_2 (5 × 50 mL). Removal of the dried (anhyd. Na_2SO_4) solvent gave **4f** as a pale brown solid (6.74 g, 79%), m.p. 105−107 °C (ref.[38] 110−111 °C). ^{1}H NMR: δ = 2.52 (s, 3 H, 1-Me), 4.56 (br. s, 1 H, OH), 7.07 (d, J = 8.8 Hz, 1 H, Ar-H), 7.32 (m, 1 H, Ar-H), 7.47 (m, 1 H, Ar-H), 7.58 (d, J = 8.8 Hz, 1 H, Ar-H), 7.73 (dd, J = 8.5, 1.4 Hz, 1 H, Ar-H), 7.88 (dd, 1 H, J, 8.7, 1.4, Ar-H) ppm.

Preparation of 1,1-Diarylprop-2-yn-1-ols: *n*-Butyllithium (2.5 M in hexanes) (33 mmol) was added slowly with a syringe to a cold (−10 °C), stirred solution of (trimethylsilyl)acetylene (33 mmol) in anhydrous tetrahydrofuran (100 mL) under nitrogen. On completion of the addition (ca. 5 min) the cold solution was stirred for 1 h. The benzophenone (30 mmol) slurried in anhydrous tetrahydrofuran (50 mL) was then added in a single portion and the mixture stirred until no benzophenone remained by TLC (ca. 3 h.). The reaction mixture was then recooled to 0 °C and a solution of methanolic potassium hydroxide was added [from potassium hydroxide (40 mmol) in methanol (30 mL)] in a single portion. The cooling bath was then removed and the mixture warmed to room temperature, after ca. 15 min TLC indicated that deprotection was complete. The mixture was acidified to pH ≈ 7 using glacial acetic acid and then poured into water (400 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (3 × 75 mL), the organic phases were combined, washed with water (2 × 100 mL) and dried (anhyd. Na_2SO_4). Removal of the solvent gave the prop-2-yn-1-ol, which was sufficiently pure for subsequent use. Analytically pure compounds were obtained by recrystallisation from hexane and ethyl acetate. The following alkynols were obtained in this way.

1,1-Bis(4-methoxyphenyl)prop-2-yn-1-ol (5a): From 4,4′-dimethoxybenzophenone. Isolated as an off-white powder (7.56 g, 94%) after recrystallisation from ethyl acetate and hexane, m.p. 90.0−92.0 °C (ref.[40] 89.0−91.5 °C). IR (KBr): $\tilde{\nu}_{max}$ = 3472, 3245, 1608 cm^{-1}. ^{1}H NMR: δ = 2.76 (s, 1 H, alkynic-H), 2.86 (s, 1 H, OH), 3.79 (s, 6 H, OMe), 6.85 (m, 4 H, Ar-H), 7.49 (m, 4 H, Ar-H) ppm.

1,1-Bis(4-dimethylaminophenyl)prop-2-yn-1-ol (5b): From 4,4′-bis(dimethylamino)benzophenone. Isolated as an off-white powder (7.59 g, 86%) after recrystallisation from ethyl acetate and hexane, m.p. 158.0−160.0 °C (ref.[41] 154−155 °C). IR (Nujol): $\tilde{\nu}_{max}$ = 3351, 3252, 2110, 1611 cm^{-1}. ^{1}H NMR: δ = 2.75 (s, 1 H, alkynic-H), 2.97 (br. s, 1 H, OH), 3.23 [s, 12 H, $(NMe_2)_2$], 6.88 (m, 4 H, Ar-H), 7.64 (m, 4 H, Ar-H) ppm.

Preparation of 1,1,3-Triarylprop-2-yn-1-ols: *n*-Butyllithium (2.5 M in hexanes) (33 mmol) was added slowly with a syringe to a cold (−10 °C), stirred solution of the arylacetylene (33 mmol) in anhydrous tetrahydrofuran (100 mL) under nitrogen. On completion of the addition (ca. 5 min) the cold solution was stirred for 1 h. The benzophenone (30 mmol) slurried in anhydrous tetrahydrofuran (50 mL) was then added in a single portion and the mixture stirred until no benzophenone remained by TLC (ca. 2 h.). The mixture was poured into water (300 mL) containing ammonium chloride solution (50 mL aq. sat.). The organic layer was separated and the aqueous layer extracted with ethyl acetate (3 × 75 mL), the organic phases were combined, washed with water (2 × 100 mL) and dried (anhyd. Na_2SO_4). Removal of the solvent gave the triarylprop-2-yn-1-ol, which was sufficiently pure for subsequent use. Analytically pure material was obtained by recrystallisation from hexane and ethyl acetate. The following alkynols were obtained in this way.

1,1-Bis(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol (19a): From 4,4′-dimethoxybenzophenone and phenylacetylene. Isolated as a viscous oil (9.60 g, 93%) which gradually solidified on standing m.p. 92−94 °C (ref.[42] 96 °C). IR (KBr): $\tilde{\nu}_{max}$ = 3442, 1606, 1243 cm^{-1}. ^{1}H NMR: δ = 2.79 (s, 1 H, OH), 3.79 (s, 6 H, OMe), 6.86 (m, 4 H, Ar-H), 7.31 (m, 3 H, Ar-H), 7.50 (m, 6 H, Ar-H) ppm. HRMS: $[M^+]$ 344.1409, $C_{23}H_{20}O_3$ requires $[M^+]$ 344.1412(5).

1,1,3-Tris(4-methoxyphenyl)prop-2-yn-1-ol (19b): From 4,4′-dimethoxybenzophenone and 4-methoxyphenylacetylene. Isolated as

a viscous oil (10.32 g, 92%). IR (KBr): $\tilde{\nu}_{max}$ = 3677, 1242 cm^{-1}. ^1H NMR: δ = 2.88 (br. s, 1 H, OH), 3.80 (s, 6 H, OMe), 3.83 (s, 3 H, OMe), 6.85 (m, 6 H, Ar-H), 7.41 (m, 2 H, Ar-H), 7.55 (m, 4 H, Ar-H) ppm. HRMS: $[M + H]^+$ 375.1594, $C_{24}H_{22}O_4$ requires $[M + H]^+$ 375.1596. $C_{24}H_{22}O_4$ (374.22): calcd. C 77.0, H 5.93; found C 76.6, H 5.8.

General Method for the Acid-Catalysed Reaction of Naphthols with Prop-2-yn-1-ols: A stirred solution of the naphthol (3.2 mmol) and the prop-2-yn-1-ol (3.2 mmol) in toluene (40 mL) was warmed to 50 °C. Acidic alumina (2.5 g) was added and the mixture was refluxed until none of the prop-2-yn-1-ol remained by TLC (ca. 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 filtrate gave a deep red gum that was eluted from silica to afford the pure products. The following compounds were obtained using this protocol.

1: From 1-naphthol and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol after elution from silica with 40% EtOAc/hexane. **Fraction 1:** 2,2-Bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran (**6a**) as salmon-pink microcrystals from EtOAc/hexane (467 mg, 37%), m.p. 137−138 °C (ref.[44] 143−145 °C). IR (KBr): $\tilde{\nu}_{max}$ = 1607, 1252, 1176 cm^{-1}. ^1H NMR: δ = 3.76 (s, 6 H, OMe), 6.11 (d, *J* = 9.8 Hz, 1 H, 3-H), 6.69 (d, *J* = 9.8 Hz, 1 H, 4-H), 6.83 (m, 4 H, Ar-H), 7.14 (d, *J* = 8.2 Hz, 1 H, Ar-H), 7.31 (d, *J* = 8.1 Hz, 1 H, Ar-H), 7.42 (m, 6 H, Ar-H), 7.70 (dd, *J* = 7.5, 1.8 Hz, 1 H, Ar-H), 8.30 (dd, *J* = 7.6, 1.5 Hz, 1 H, Ar-H) ppm. **Fraction 2:** 4-[(*E*)-3′,3′-Bis(4-methoxyphenyl)prop-2-enylidene]-4*H*-naphthalen-1-one (**7a**) as maroon needles from EtOAc/hexane (12.6 mg, 1%), m.p. 148−150 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1630 cm^{-1}. UV (EtOH): λ_{max} (ε_m) = 462 nm (4.0×10^4 $mol^{-1}dm^3cm^{-1}$). ^1H NMR: δ = 3.86 (s, 3 H, OMe), 3.92 (s, 3 H, OMe), 6.62 (dd, *J* = 10.2, 1.5 Hz, 1 H, 2-H), 6.91 (m, 2 H, Ar-H), 7.02 (m, 2 H, Ar-H), 7.27 (m, 2 H, Ar-H), 7.36 (m, 2 H, Ar-H), 7.45 (m, 2 H, Ar-H, alkenic-H), 7.53 (m, 1 H, Ar-H), 7.68 (m, 2 H, Ar-H, alkenic-H), 8.11 (d, *J* = 10.2 Hz, 1 H, 3-H), 8.27 (dd, *J* = 7.9, 1.6 Hz, 1 H, 8-H), δ_C = 55.4, 113.8, 113.9, 120.6, 121.9, 126.6, 126.7, 127.3, 127.6, 130.2, 131.2, 131.6, 132.6, 134.6, 135.6, 136.0, 136.1, 152.2, 160.2, 160.7, 185.0 ppm. HRMS: $[M + H]^+$ 395.1642, $C_{27}H_{22}O_3$ requires $[M + H]^+$ 395.1647. $C_{27}H_{22}O_3$ (394.22): calcd. C 82.2, H 5.6; found C 81.9, H 5.4.

2: From 1-naphthol and 1,1-bis(4-dimethylaminophenyl)prop-2-yn-1-ol after elution from silica 20% EtOAc/hexane. **Fraction 1:** 2,2-Bis(4-dimethylaminophenyl)-2*H*-naphtho[1,2-*b*]pyran (**6b**), as pale blue microcrystals from EtOAc/hexane (578 mg, 43%), m.p. 203−205 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1608, 1359, 1226, 1166 cm^{-1}. UV (PhMe): λ_{max} = 567, 447 nm. ^1H NMR (CD_3CO_2D): δ = 3.12 (s, 12 H, NMe_2), 6.36 (d, *J* = 9.8 Hz, 1 H, 3-H), 6.87 (d, *J* = 9.8 Hz, 1 H, 4-H), 7.23 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.41 (m, 5 H, Ar-H), 7.51 (m, 2 H, Ar-H), 7.66 (m, 4 H, Ar-H), 7.77 (d, *J* = 7.9 Hz, 1 H, Ar-H), 8.37 (d, *J* = 8.2 Hz, 1 H, 10-H) ppm. HRMS: $[M^+]$ 420.2209, $C_{29}H_{28}N_2O$ requires $[M^+]$ 420.2202. $C_{29}H_{28}N_2O$ (420.30): calcd. C 82.8, H 6.7, N 6.7; found C 82.6, H 6.4, N 6.5. **Fraction 2:** 4-[(*E*)-3′,3′-Bis(4-dimethylaminophenyl)prop-2-enylidene]-4*H*-naphthalen-1-one (**7b**) as lustrous maroon crystals from EtOAc/hexane (134 mg, 10%), m.p. 137−138 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1626 cm^{-1}. UV (EtOH): λ_{max} (ε_{max}) = 556 nm (3.8×10^4 $mol^{-1}dm^3cm^{-1}$). ^1H NMR: δ = 3.03 (s, 6 H, NMe_2), 3.09 (s, 6 H, NMe_2), 6.60 (dd, *J* = 10.0, 1.3 Hz, 1 H, 2-H), 6.68 (m, 2 H, Ar-H), 6.78 (m, 2 H, Ar-H), 7.24 (m, 2 H, Ar-H), 7.37 (m, 3 H, Ar-H, 2′-H), 7.41 (m, 1 H, 7-H), 7.49 (m, 1 H, 6-H), 7.75 (d, *J* = 8.1 Hz, 1 H, 5-H), 7.85 (d, *J* = 11.9 Hz, 1 H, 1′-H), 8.16 (d, *J* = 10.0 Hz, 1 H, 3-H), 8.29 (dd, *J* = 7.9, 1.2 Hz, 1 H, 8-H) ppm. HRMS: $[M^+]$ 420.2201, $C_{29}H_{28}N_2O$ requires $[M^+]$ 420.2202. $C_{29}H_{28}N_2O$ (420.30): calcd. C 82.8, H 6.7, N 6.7; found C 82.6, H 6.6, N 6.4.

3: From 2-methyl-1-naphthol and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol after elution from silica with 20% EtOAc/hexane. **Fraction 1:** 4-[(*E*)-3′,3′-Bis(4-methoxyphenyl)-2-methylprop-2-enylidene]-4*H*-naphthalen-1-one (**7c**) as orange needles from EtOAc/hexane (248 mg, 19%), m.p. 198−200 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1626 cm^{-1}. UV (EtOH): λ_{max} (ε_m) = 458 nm (4.4×10^4 $mol^{-1}dm^3cm^{-1}$). ^1H NMR: δ = 2.24 (s, 3 H, 2-Me), 3.85 (s, 3 H, OMe), 3.92 (s, 3 H, OMe), 6.90 (m, 2 H, Ar-H), 7.00 (m, 2 H, Ar-H), 7.26 (m, 3 H, Ar-H, 2′-H), 7.43 (m, 4 H, Ar-H), 7.60 (d, *J* = 12.0 Hz, 1 H, 1′-H), 7.66 (d, *J* = 7.9 Hz, 1 H, Ar-H), 7.97 (s, 1 H, 3-H), 8.29 (dd, *J* = 7.8, 1.3 Hz, 1 H, 8-H). HRMS: $[M + H]^+$ 409.1809, $C_{28}H_{24}O_3$ requires $[M + H]^+$ 409.1803. $C_{28}H_{24}O_3$ (408.24): calcd. C 82.3, H 5.9; found C 82.1, H 5.7.

4: From 2-methyl-1-naphthol and 1,1-bis(4-dimethylaminophenyl)-prop-2-yn-1-ol after elution from silica 20% EtOAc/hexane. **Fraction 1:** 4-[(*E*)-3′,3′-Bis(4-dimethylaminophenyl)-2-methylprop-2-enylidene]-4*H*-naphthalen-1-one (**7d**) as deep red crystals from EtOAc/hexane (375 mg, 27%), m.p. 235−236 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1650 cm^{-1}. UV (EtOH): λ_{max} (ε_{max}) = 542 nm (4.6×10^4 $mol^{-1}dm^3cm^{-1}$). ^1H NMR: δ = 2.24 (s, 3 H, 2-Me), 3.04 (s, 6 H, NMe_2), 3.08 (s, 6 H, NMe_2), 6.70 (m, 2 H, Ar-H), 6.78 (m, 2 H, Ar-H), 7.25 (m, 2 H, Ar-H), 7.37 (m, 3 H, Ar-H, 2′-H), 7.47 (m, 2 H, 6-H, 7-H), 7.73 (d, *J* = 7.5 Hz, 1 H, Ar-H), 7.76 (d, *J* = 12.0 Hz, 1 H, 1′-H), 8.02 (s, 1 H, 3-H), 8.31 (dd, *J* = 7.8, 1.4 Hz, 1 H, 8-H) ppm. HRMS: $[M + H]^+$ 435.2433, $C_{30}H_{30}N_2O$ requires $[M + H]^+$ 435.2463. $C_{30}H_{30}N_2O$ (434.32): calcd. C 82.9, H 7.0, N 6.4; found C 82.7, H 6.6, N 6.2.

5: From 2-naphthol and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol after elution from silica with 30% EtOAc/hexane. **Fraction 1:** 3,3-Bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (**14a**) as colourless crystals from EtOAc/hexane (1.03 g, 82%), m.p. 173−174.5 °C (ref.[45] 175−176 °C). IR (KBr): $\tilde{\nu}_{max}$ = 16808, 1250, 1176 cm^{-1}. UV (PhMe): λ_{max} = 475 nm. ^1H NMR: δ = 3.75 (s, 6 H, OMe), 6.19 (d, *J* = 10.0 Hz, 1 H, 2-H), 6.82 (m, 4 H, Ar-H), 7.15 (d, *J* = 8.8 Hz, 1 H, 5-H), 7.27 (d, *J* = 10.0 Hz, 1 H, 1-H), 7.29 (m, 1 H, Ar-H), 7.38 (m, 4 H, Ar-H), 7.43 (m, 1 H, Ar-H), 7.62 (d, *J* = 8.8 Hz, 1 H, 6-H), 7.69 (d, *J* = 7.8 Hz, 1 H, Ar-H), 7.93 (d, *J* = 8.6 Hz, 1 H, 10-H) ppm. **Fraction 2:** 3,3-Bis(4-methoxyphenyl)prop-2-enal (**15a**) as orange-red crystals from EtOAc/hexane (8.6 mg, 1%), m.p. 58−60 °C (ref.[46] 56−57 °C). IR (KBr): $\tilde{\nu}_{max}$ = 1659, 1609 cm^{-1}. ^1H NMR: δ = 3.84 (s, 3 H, OMe), 3.88 (s, 3 H, OMe), 6.49 (d, *J* = 8.1 Hz, 1 H, 2-H), 6.89 (m, 2 H, Ar-H), 6.96 (m, 2 H, Ar-H), 7.24 (m, 2 H, Ar-H), 7.32 (m, 2 H, Ar-H), 9.48 (d, *J* = 8.1 Hz, 1 H, 1-H) ppm.

6: From 1-bromo-2-naphthol and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol after elution from silica with 30% EtOAc/hexane. **Fraction 1:** 3,3-Bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (**14a**) as colourless crystals from EtOAc/hexane (240 mg, 19%), m.p. 173−174 °C (ref.[45] 175−176 °C). Spectroscopically identical in all aspects to the sample prepared previously.

7: From 1-(4-methoxyphenyl)-2-naphthol and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol after elution from silica with 5% EtOAc/PhMe. **Fraction 1:** 3,3-Bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (**14a**) as colourless crystals from EtOAc/hexane (101 mg, 8%), m.p. 173−175 °C (ref.[45] 175−176 °C). Spectroscopically identical in all aspects to the sample prepared previously.

8: From 2-naphthol and 1,1-bis(4-dimethylaminophenyl)prop-2-yn-1-ol after elution from silica with 20% EtOAc/hexane. **Fraction 1:**

3,3-Bis(4-dimethylaminophenyl)-3*H*-naphtho[2,1-*b*]pyran (**14b**) as pale green microcrystals from EtOAc/hexane (1.14 g, 85%), m.p. 221.0−222.0 °C (ref.[47] 223 °C). UV (PhMe): λ_{max} = 558, 446 nm. IR (KBr): $\tilde{\nu}_{max}$ = 1613, 1358, 1234, 1167 cm^{-1}. ^1H NMR: δ = 2.96 [s, 12 H, $(NMe_2)_2$], 6.26 (d, *J* = 10.0 Hz, 1 H, 2-H), 6.75 (m, 4 H, Ar-H), 7.21 (d, *J* = 8.8 Hz, 1 H, 5-H), 7.38 (m, 7 H, Ar-H, 1-H), 7.67 (d, *J* = 8.8 Hz, 1 H, 6-H), 7.74 (m, 1 H, Ar-H), 7.99 (m, 1 H, Ar-H) ppm HRMS: $[M^+]$ 420.2209, $C_{29}H_{28}N_2O$ requires $[M^+]$ 420.2201(6). $C_{29}H_{28}N_2O$ (420.30): calcd. C 82.7, H 6.7, N 6.7; found C 82.8, H 6.7, N 6.8. **Fraction 2:** 3,3-Bis(4-dimethylaminophenyl)prop-2-enal (**15b**) as yellow-green plates from EtOAc/hexane (37.7 mg, 4%), m.p. 170−172 °C (ref.[48] 171−172 °C). IR (Nujol): $\tilde{\nu}_{max}$ = 2895, 2747, 1649, 1607 cm^{-1}. ^1H NMR: δ = 3.02 (s, 6 H, NMe_2), 3.04 (s, 6 H, NMe_2), 6.41 (d, *J* = 8.0 Hz, 1 H, 2-H), 6.50 (m, 2 H, Ar-H), 6.72 (m, 2 H, Ar-H), 7.20 (m, 2 H, Ar-H), 7.30 (m, 2 H, Ar-H), 9.46 (d, *J* = 8.0 Hz, 1 H, 1-H) ppm.

9: From 1-methyl-2-naphthol and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol after elution from silica with 30% EtOAc/hexane. **Fraction 1:** 3,3-Bis(4-methoxyphenyl)-1-methylbenz[*e*]indan-2-one (**17**) as colourless plates after recrystallisation from EtOAc/hexane (850 mg, 65%), m.p. 135−137 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1746 cm^{-1}. ^1H NMR: δ = 1.54 (d, *J* = 7.5 Hz, 3 H, 1-Me), 3.75 (s, 3 H, OMe), 3.78 (s, 3 H, OMe), 4.07 (q, *J* = 7.5 Hz, 1 H, 1-H), 6.79 (m, 4 H, Ar-H), 6.95 (m, 2 H, Ar-H), 7.15 (m, 2 H, Ar-H), 7.23 (d, *J* = 8.7 Hz, 1 H, 4-H), 7.55 (m, 2 H, 7-H, 8-H), 7.81 (d, *J* = 8.7 Hz, 1 H, 5-H), 7.91 (m, 2 H, 6-H, 9-H) ppm. ^{13}C NMR: δ = 18.4 (Me), 46.6 (C-1), 55.2 (OMe), 67.5 (C-3), 113.6, 113.7, 124.3, 124.4, 126.0, 126.7, 128.6, 129.2, 129.6, 130.0, 130.2, 133.3, 134.4, 135.6, 137.2, 141.5, 147.1, 158.4, 158.6, 218.8 ppm. HRMS: $[M^+]$ 408.1719, $C_{28}H_{24}O_3$ requires $[M^+]$ 408.1719. $C_{28}H_{24}O_3$ (408.44): calcd. C 82.4, H 5.9; found C 82.3, H 6.0.

10: From 1-naphthol and 1,1-bis(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol after elution from silica with 20% EtOAc/hexane. **Fraction 1:** 2,2-Bis(4-methoxyphenyl)-4-phenyl-2*H*-naphtho[1,2-*b*]pyran (**20a**) as colourless microcrystals from EtOAc/hexane (428 mg, 32%), m.p. 103−105 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1252 cm^{-1}. ^1H NMR: δ = 3.75 (s, 6 H, OMe), 6.11 (s, 1 H, 3-H), 6.82 (m, 4 H, Ar-H), 7.17 (d, *J* = 8.3 Hz, 1 H, Ar-H), 7.44 (m, 12 H, Ar-H), 7.68 (dd, *J* = 8.5, 2.1 Hz, 1 H, Ar-H), 8.41 (dd, *J* = 8.3, 2.2 Hz, 1 H) ppm. HRMS: $[M + H]^+$ 471.1951, $C_{33}H_{26}O_3$ requires $[M + H]^+$ 471.1960. $C_{33}H_{26}O_3$ (470.26): calcd. C 84.2, H 5.6; found C 84.0, H 5.7. **Fraction 2:** 4-[(*E*)-3′,3′-Bis(4-methoxyphenyl)-1′-phenylprop-2-enylidene]-4*H*-naphthalen-1-one (**21a**) as maroon needles from EtOAc/hexane (542 mg, 36%), m.p. 201.0−202.5 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1635, 1249 cm^{-1}. UV (EtOH): λ_{max} (ε_{max}) = 470 nm (2.6 × 10^4 $mol^{-1}dm^3cm^{-1}$). ^1H NMR: δ = 3.73 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 6.34 (d, *J* = 10.3 Hz, 1 H, 2-H), 6.53 (m, 2 H, Ar-H), 6.81 (m, 2 H, Ar-H), 6.87 (m, 2 H, Ar-H), 7.07 (m, 5 H, Ar-H), 7.31 (m, 4 H, Ar-H, 2′-H), 7.52 (m, 2 H, 6-H, 7-H), 8.33 (d, *J* = 7.3 Hz, 1 H, Ar-H), 8.44 (d, *J* = 7.8 Hz, 1 H, 8-H) ppm. HRMS: $[M + H]^+$ 471.1957, $C_{33}H_{26}O_3$ requires $[M + H]^+$ 471.1960. $C_{33}H_{26}O_3$ (470.26): calcd. C 84.2, H 5.6; found C 84.2, H 5.4.

11: From 1-naphthol and 1,1,3-tris(4-methoxyphenyl)prop-2-yn-1-ol after elution from silica with 5% EtOAc/toluene. **Fraction 1:** 2,2,4-Tris(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran (**20b**) as colourless microcrystals from EtOAc/hexane (400 mg, 25%), m.p. 118−120 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1617, 1249 cm^{-1}. ^1H NMR: δ = 3.75 (s, 6 H, OMe), 3.86 (s, 3 H, OMe), 6.07 (s, 1 H, 3-H), 6.81 (m, 4 H, Ar-H), 6.96 (m, 2 H, Ar-H), 7.18 (d, *J* = 8.5 Hz, 1 H, Ar-H), 7.28 (d, *J* = 8.5 Hz, 1 H, Ar-H), 7.42 (m, 8 H, Ar-H), 7.70 (dd, *J* = 7.5, 1.1 Hz, 1 H, Ar-H), 8.39 (dd, *J* = 7.6, 0.9 Hz, 1 H, Ar-H) ppm. HRMS: $[M + H]^+$ 501.2061, $C_{34}H_{28}O_4$ requires $[M + H]^+$ 501.2066. $C_{34}H_{28}O_4$ (500.28): calcd. C 81.6, H 5.6; found C 81.4, H 5.8. **Fraction 2:** 4-[(*E*)-1′,3′,3′-Tris(4-methoxyphenyl)prop-2-enylidene]-4*H*-naphthalen-1-one (**21b**) as maroon needles from EtOAc/hexane (672 mg, 42%), m.p. 155.5−158.0 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1625, 1250 cm^{-1}. UV (EtOH): λ_{max} (ε_m) = 479 nm (5.4 × 10^4 $mol^{-1}dm^3cm^{-1}$). ^1H NMR: δ = 3.73 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 6.35 (d, *J* = 10.2 Hz, 1 H, 2-H), 6.54 (m, 2 H, Ar-H), 6.60 (m, 2 H, Ar-H), 6.84 (m, 2 H, Ar-H), 6.88 (m, 2 H, Ar-H), 7.03 (m, 2 H, Ar-H), 7.31 (m, 3 H, Ar-H, 2′-H), 7.44 (d, *J* = 10.2 Hz, 1 H, 3-H), 7.52 (m, 2 H, 6-H, 7-H), 8.33 (dd, *J* = 7.7, 1.5 Hz, 1 H, 5-H), 8.44 (d, *J* = 7.9 Hz, 1 H, 8-H) ppm. HRMS: $[M + H]^+$ 501.2065, $C_{34}H_{28}O_4$ requires $[M + H]^+$ 501.2066. $C_{34}H_{28}O_4$ (500.28): calcd. C 81.6, H 5.6; found C 81.4, H 5.4.

12: From 2-naphthol and 1,1-bis(4-methoxyphenyl)-3-phenylprop-2-yn-1-ol after recrystallisation from EtOAc/hexane. 3,3-Bis(4-methoxyphenyl)-1-phenyl-3*H*-naphtho[2,1-*b*]pyran (**23a**) as colourless microcrystals (1.14 g, 76%), m.p. 195−197 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1609, 1251 cm^{-1}. ^1H NMR: δ = 3.74 (s, 6 H, OMe), 6.13 (s, 1 H, 2-H), 6.84 (m, 4 H, Ar-H), 7.06 (m, 2 H, Ar-H), 7.30 (m, 7 H, Ar-H), 7.41 (m, 4 H, Ar-H), 7.67 (m, 2 H, Ar-H) ppm. HRMS: $[M^+]$ 470.1876, $C_{33}H_{26}O_3$ requires $[M^+]$ 470.1882. $C_{33}H_{26}O_3$ (470.26): calcd. C 84.2, H 5.6; found C 84.3, H 5.6.

13: From 2-naphthol and 1,1,3-tris(4-methoxyphenyl)prop-2-yn-1-ol after elution from silica with 20% EtOAc/hexane. **Fraction 1:** 1,3,3-Tris(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (**23b**) as colourless microcrystals after recrystallisation from EtOAc/hexane (1.55 g, 97%), m.p. 111−113 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1608, 1250 cm^{-1}. ^1H NMR: δ = 3.76 (s, 6 H, OMe), 3.86 (s, 3 H, OMe), 6.11 (s, 1 H, 2-H), 6.81 (m, 4 H, Ar-H), 6.89 (m, 2 H, Ar-H), 7.02 (m, 1 H, Ar-H), 7.18 (m, 1 H, Ar-H), 7.29 (m, 4 H, Ar-H), 7.44 (m, 4 H, Ar-H), 7.68 (m, 2 H, Ar-H) ppm. HRMS: $[M + H]^+$ 501.2061, $C_{34}H_{28}O_4$ requires $[M + H]^+$ 501.2066. $C_{34}H_{28}O_4$ (500.28): calcd. C 81.6, H 5.6; found C 81.5, H 5.6.

Acid-Catalysed Rearrangement of 1,1,3-Tris(4-methoxyphenyl)prop-2-yn-1-ol: A stirred solution of 1,1,3-tris(4-methoxyphenyl)prop-2-yn-1-ol (1.34 mmol) in toluene (20 mL) was warmed to 50 °C. Acidic alumina (0.8 g) was added and the mixture was refluxed until none of the prop-2-yn-1-ol remained by TLC (ca. 2 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 filtrate gave 1,3,3-tris(4-methoxyphenyl)prop-2-enone (**24**) as a viscous oil[43] (446 mg, 89%). IR (KBr): $\tilde{\nu}_{max}$ = 1651, 1595, 1244, 1165 cm^{-1}. ^1H NMR: δ = 3.73 (s, 3 H, OMe), 3.76 (s, 3 H, OMe), 3.78 (s, 3 H, OMe), 6.76 (m, 2 H, Ar-H), 6.82 (m, 4 H, Ar-H), 6.96 (s, 1 H, 2-H), 7.11 (m, 2 H, Ar-H), 7.31 (m, 2 H, Ar-H), 7.90 (m, 2 H, Ar-H) ppm.

Mitsonubu Coupling Procedure: Diethyl azodicarboxylate (6.9 mmol) was added to a stirred solution of 2-naphthol (3.5 mmol), 1,1-bis(4-dimethylaminophenyl)prop-2-yn-1-ol (**5b**) (3.5 mmol) and triphenylphosphane (6.9 mmol) in tetrahydrofuran (25 mL) at room temperature. The resultant brown solution was stirred until no further reaction was observed by TLC (ca. 5 h). The mixture was then poured into water (200 mL) and extracted with ethyl acetate (4 × 50 mL). These extracts were then washed with brine (2 × 50 mL), water (100 mL) and dried (anhyd. Na_2SO_4). Removal of the solvent gave a dark blue tar which, upon elution from silica (5% ethyl acetate/toluene), afforded 3,3-bis(4-dimethylaminophenyl)-3*H*-naphtho[2,1-*b*]pyran as pale green microcrystals **14b** (235 mg, 16%), m.p. 223−225 °C, (ref.[47] 223 °C) identical in all aspects to the previously prepared material.

Modified Mitsonubu Coupling Procedure: Diethyl azodicarboxylate (6.9 mmol) was added to a stirred solution of 2-naphthol (3.5 mmol), 1,1-bis(4-dimethylaminophenyl)prop-2-yn-1-ol (**5b**) (3.5 mmol), triphenylphosphane (6.9 mmol) and 4-nitrophenol (0.7 mmol) in tetrahydrofuran (35 mL) at room temperature. The resultant brown solution was stirred until no further reaction was observed by TLC (ca. 3.5 h). The mixture was then poured into water (200 mL) and extracted with ethyl acetate (4 × 50 mL). These extracts were then washed with brine (2 × 50 mL), water (100 mL) and dried (anhyd. Na_2SO_4). Removal of the solvent gave a dark blue tar which, upon elution from silica (5% ethyl acetate/toluene), afforded 3,3-bis(4-dimethylaminophenyl)-3*H*-naphtho[2,1-*b*]pyran (**14b**) as pale green microcrystals (397 mg, 27%), m.p. 222−224 °C, (ref.[47] 223 °C) identical in all aspects to the previously prepared material. The following compounds were obtained by this protocol.

1: From 1-naphthol and 1,1-bis(4-dimethylaminophenyl)prop-2-yn-1-ol after elution from silica with 10% ethyl acetate/toluene. **Fraction 1:** 2,2-Bis(4-dimethylaminophenyl)-2*H*-naphtho[1,2-*b*]pyran (**6b**) as pale blue microcrystals (162 mg, 11%), m.p. 203−205 °C. This material was identical in all aspects to that obtained previously. **Fraction 2:** 4-[(*E*)-3′,3′-Bis(4-dimethylaminophenyl)prop-2-enylidene]-4*H*-naphthalen-1-one (**7b**) as maroon crystals (44 mg, 3%), m.p. 137−138 °C. This material was identical in all aspects to that obtained previously.

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[13] Crystallographic data for compound **7a**: Empirical formula $C_{27}H_{22}O_3$, M = 394.45, monoclinic, space group $P2_1/n$, a = 16.8022(5) Å, b = 6.0430(2) Å, c = 20.1317(8) Å, β = 104.182(1)°, V = 1981.8(1) Å^3, Z = 4; $D_{calcd.}$ = 1.322 Mg/m^3; μ (Mo-K_α) = 0.085 mm^{-1}. Red needle, crystal size 0.40 × 0.02 × 0.02 mm. θ range for data collection 3.1−25.1°, 11938 reflections of which 3461 are independent (R_{int} = 0.096). Refinement with 3461 data for 294 parameters, GOF = 0.891, final R indices for data with [$F^2 > 2\sigma(F^2)$] $R1$ = 0.052, $wR2$ = 0.081; R indices for all data $R1$ = 0.1411, $wR2$ = 0.0968. CCDC-195498 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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[33] Crystalloghraphic data for compound **21a**: Empirical formula $C_{33}H_{26}O_3$, M = 470.54, monoclinic; space group $P2_1/c$, unit cell dimensions a = 7.93070(10) Å, b = 11.8436(2) Å, c = 26.0902(5) Å, β = 98.4873(6)°, V = 2423.76(7) Å^3, Z = 4, $D_{calcd.}$ = 1.289 Mg/m^3, μ (Mo-K_α) = 0.081 mm^{-1}. Red prism, red, crystal size 0.20 × 0.15 × 0.05 mm. θ range for data collection 2.9−26.0°; 18150 collected reflections of which 4750 are independent (R_{int} = 0.0849). Structure refinement with 4750 data for 352 parameters, GOF = 0.991, final R indices for data with [$F^2 > 2\sigma(F^2)$] $R1$ = 0.042, $wR2$ = 0.089; R indices for all data $R1$ = 0.058, $wR2$ = 0.094. CCDC-195500 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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