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SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF METHOXY SUBSTITUTED 2,2-DIARYL-2*H*-NAPHTHO[1,2-*b*]PYRANS

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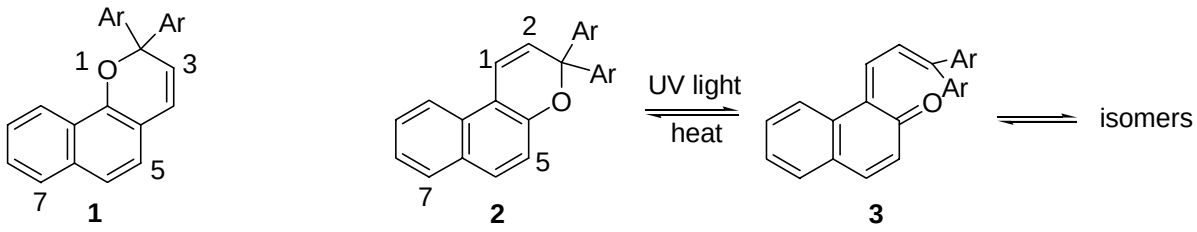
Abstract - A series of methoxy-substituted 2,2-di(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyrans has been synthesised from 3-alkoxycarbonyl-1-naphthols and 1,1-di(4-methoxyphenyl)prop-2-yn-1-ol. The influence of the methoxy group on the wavelength of maximum absorption and the stability of the ring-opened naphthopyrans is discussed.

INTRODUCTION

The synthesis of organic photochromic dyes and their application has been the subject of several reviews.[1] Naphthopyrans in particular are used to impart photochromism to host objects such as optical and fashion sunglasses.[2] The isomeric naphthopyrans (**1**) and (**2**) display photochromism by means of a photo-induced reversible electrocyclic ring opening of the pyran ring to produce the valence isomer (**3**) (Scheme 1). It has been established by time resolved spectroscopy studies[3] and by ^{19}F NMR spectroscopy[4] that this isomer undergoes conversion into rotamers and other geometrical isomers. More recently 2D NMR spectral studies have revealed that an allenylnaphthol intermediate may also be involved in the photoisomerisation processes.[5]



1 **2** **3**

Scheme 1

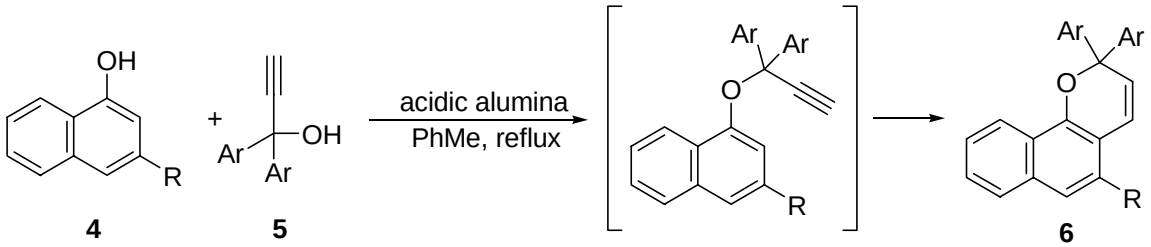
Of these two naphthopyran isomers, the [1,2-*b*] system (**1**) appears to be the more widely used in ophthalmic applications and ever increasingly complex analogues with additional fused carbocyclic[6] or heterocyclic rings[7]

have been developed to meet the stringent demands in performance made upon these dynamic molecules. Two factors probably account for the greater use of the 2*H*-naphtho[1,2-*b*]pyran system (**1**) over the 3*H*-naphtho[2,1-*b*]pyran isomer (**2**): the photogenerated color of **1** is shifted to the red relative to identically substituted **2** and secondly good control over the rate of fade of the photogenerated color of **1** is possible by the introduction of judiciously placed substituents.[8] Various research groups have described the synthesis of 5-alkoxycarbonyl-substituted 2*H*-naphtho[1,2-*b*]naphthopyrans[9] and Van Gemert and co-workers, have demonstrated that a 5-methoxycarbonyl substituent in a 2*H*-naphtho[1,2-*b*]naphthopyran promotes more rapid fade of the photogenerated isomers compared with the corresponding 5-methyl substituted compound.[10] Surprisingly, there is relatively little information documented for substituent effects on the photochromism of the 2*H*-naphtho[1,2-*b*]pyran system in contrast to that pertaining to the 3*H*-naphtho[2,1-*b*]pyrans.[11] We now describe our results concerning the synthesis of some methoxy-substituted 5-alkoxycarbonyl-2*H*-naphtho[1,2-*b*]pyrans and discuss the influence of the methoxy group on the color and stability of the photogenerated valence isomers.[12]

DISCUSSION

Symmetrically diaryl substituted naphthopyrans have been synthesised by the addition of aryl Grignard reagents to naphthopyranones (benzocoumarins), although this reaction often gives multiple products, arising in part from both 1,2- and 1,4- addition to the carbonyl function. Furthermore, the initially formed tertiary alcohols undergo a variety of reactions besides the dehydrative cyclisation to the pyran and yields of the naphthopyrans are consequently low.[13] Quenching the dianion derived from 2-bromo-1-naphthol and n-butyllithium with β-phenylcinnamaldehyde affords allylic alcohols, which undergo a dehydrative cyclisation to the naphthopyran.[14] A more efficient variation of this protocol has been developed that relies upon the reaction of titanium(IV) naphtholates with β-arylcinnamaldehydes to access the naphthopyrans.[15]

The approach to naphthopyrans that offers greatest versatility is based upon a strategy first reported by Iwae and Ide in 1962.[16] In the current one-pot version of this strategy, a naphthol is heated with a propargyl alcohol (**5**) in toluene under acid catalysis (Scheme 2). The initial generation of a naphthyl propargyl ether is followed by a Claisen rearrangement. A 1,5-sigmatropic hydrogen shift and a subsequent electrocylisation complete the sequence.[17]

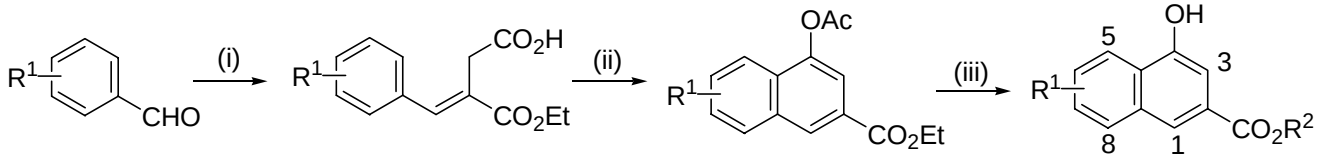


4 **5** **6**

Scheme 2

The key reagents for our preparation of **6**, R ≠ H are a 3-substituted 1-naphthol (**4**) and a 1,1-diarylprop-2-yn-1-ol (**5**). We have previously reported an efficient synthesis of a range of **5**,[18] and we now illustrate a versatile and reproducible route to 3-substituted 1-naphthols. This strategy for 3-substituted 1-naphthols relies upon the cyclisation of arylidenesuccinic acids which in turn are readily available from the Stobbe condensation of a benzaldehyde with a dialkyl succinate.[19,]

Thus, heating a solution of 4-methoxybenzaldehyde with diethyl succinate in anhydrous ethanol containing 2 equivalents of sodium ethoxide gave the half ester (**7**, R^1 = 4-MeO), in excellent yield. Anhydrous ethanol was critical to the success of this reaction, reagent grade solvent failed to afford appreciable amounts of the half ester (**7**). The direct cyclisation of **7** was achieved by refluxing it in acetic anhydride containing one equivalent of sodium acetate (Scheme 3).[20] This cyclisation reaction proceeds *via* the formation of a mixed anhydride and subsequent removal of an acidic α-hydrogen atom to generate a ketene intermediate. Intramolecular acylation of the aromatic ring by the ketene moiety and *O*-acetylation complete the sequence to afford **8b**. Removal of the acetyl group, either by base hydrolysis and subsequent re-esterification or, in a single step with alcoholic K_2CO_3, gave the naphthol (**9b)** (Scheme 3).



7 **8a - e** **9a - e**

9a: R^1 = H, R^2 = Et;
9b: R^1 = 6-MeO, R^2 = Et;
9c: R^1 = 8-MeO, R^2 = Et;
9d: R^1 = 5-MeO, R^2 = Me;
9e: R^1 = 7-MeO, R^2 = Me;

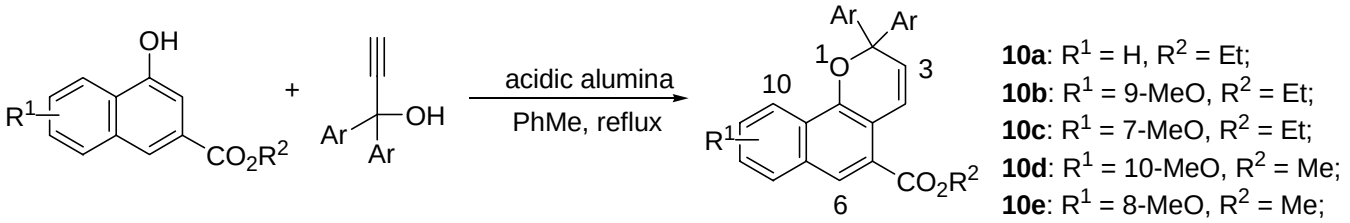
Reagents: (i) diethyl succinate, anhyd. EtOH, NaOEt, reflux 4 h;
(ii) anhyd. NaOAc, Ac_2O, reflux 3 h; (iii) either K_2CO_3, MeOH, rt, ~ 2 h
or NaOH, aq. EtOH, rt, 15 h then cat. c.H_2SO_4, MeOH, reflux 17 h.

Scheme 3

In like manner, benzaldehyde and 2-methoxybenzaldehyde gave naphthols (**9a**) and (**9c**) respectively. 3-Methoxybenzaldehyde gave an unequal mixture of two isomeric naphthols (**9d**) and (**9e**) that result from the non-regiospecific cyclisation of the half ester. Such behaviour is not uncommon for cyclisation reactions of *m*-disubstituted aromatic compounds. For instance, 3-(3-substituted phenoxy)propanoic acids yield mixtures of the 5- and 7- substituted benzopyran-4-ones on acid catalysed dehydrative cyclisation.[21] The 7-methoxy isomer (**9e**) is favored here, since steric interactions between the ketene moiety and the methoxy group are minimised in the cyclisation step.

The naphthopyrans (**10a** – **e**) and (**12**) were obtained in 40 – 76% yield on heating the propynol (**5**) with the appropriate naphthol (**9**) in toluene in the presence of acidic alumina (Scheme 4). Naphthopyran formation was confirmed by the appearance of a pair of doublets at *ca*. 6.1 and 7.6 ppm with a coupling constant of about 10 Hz in the ^{1}H NMR spectra, corresponding to 3-H and 4-H, respectively. These data compare favorably with published chemical shifts for the corresponding protons in other benzo- and naphtho- pyrans.[11, 17, 22] It is of

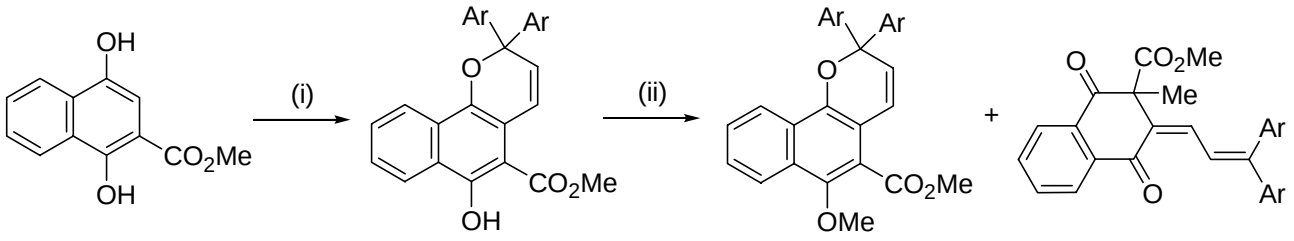
interest to note that 1-arylprop-2-yn-1-ols undergo a cycloaddition reaction with electron rich phenols in the presence of thiolate-bridged diruthenium complexes to give 4*H*-[1]benzopyrans.[23] The use of 1,3-diphenylprop-2-yn-1-ol under similar transition metal catalysed conditions with 2-naphthol results in a low yield of 1,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran.[24]



9a - e **5**: Ar = 4-$MeOC_6H_4$ **10a - e**

Scheme 4

The synthesis of the 6-methoxynaphthopyran involved initial esterification of 1,4-dihydroxynaphthalene-2-carboxylic acid using $NaHCO_3$ and MeI in anhydrous DMF according to the literature procedure to afford **11**.[25] Reaction with **5** gave the known 6-hydroxynaphthopyran (12)[26] in 69% yield over two steps (Scheme 5).



11 **12** **13** **14**

Reagents: (i) 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol (**5**), acidic alumina, PhMe, reflux 1.5 h;
(ii) K_2CO_3, MeI, anhyd. Me_2CO, 7 h

Scheme 5

Methylation of **12** using standard alkylation conditions (2 eq. MeI, 5 eq. K_2CO_3, anhydrous acetone) gave a disappointing yield (33%) of naphthopyran (**13**),[26] which was separated from the major yellow product by elution from silica (Scheme 5). It is noteworthy that the methylation reaction mixture was intensely colored, which was indicative of the formation of an extended conjugated system resulting from opening of the pyran ring during the reaction. The ^{1}H NMR spectrum of this yellow compound was not in accord with a naphthopyran structure. The coupling constant, 11.7 Hz, of the alkenic signal which appeared as a doublet at δ 6.68, within the chemical shift range for H-3 of a naphthopyran, is not compatible with the normal value of 10 Hz for the *cis* disposed protons at the 3- and 4- positions of a naphthopyran ring[11, 17, 22] but would instead suggest that the alkenic protons are *trans* disposed.[18] Furthermore, the spectrum lacks a methoxy signal but shows a methyl signal at δ 1.58. The structure of this yellow product was established as the naphthalene-1,4-dione (**14**) by X-Ray crystallography (Figure 1).[27]

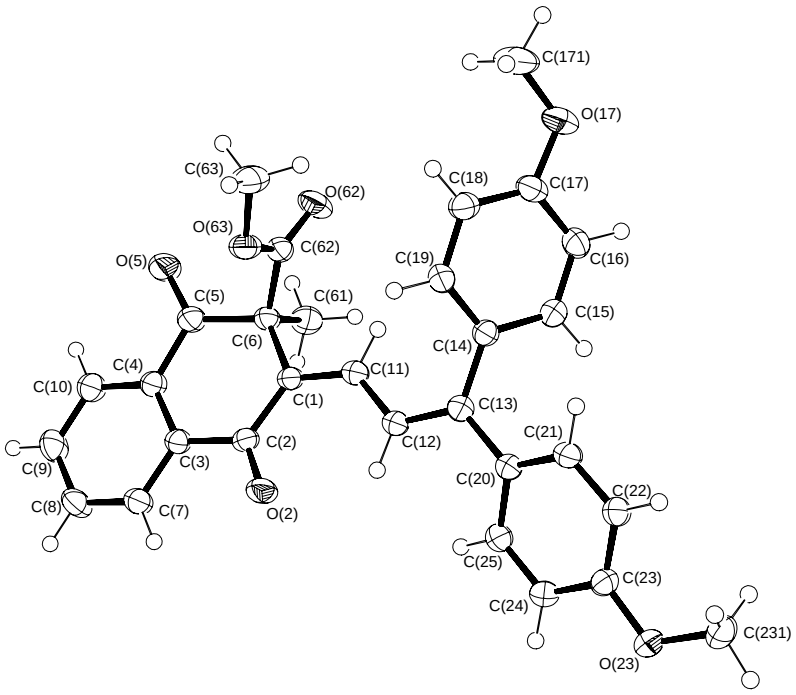
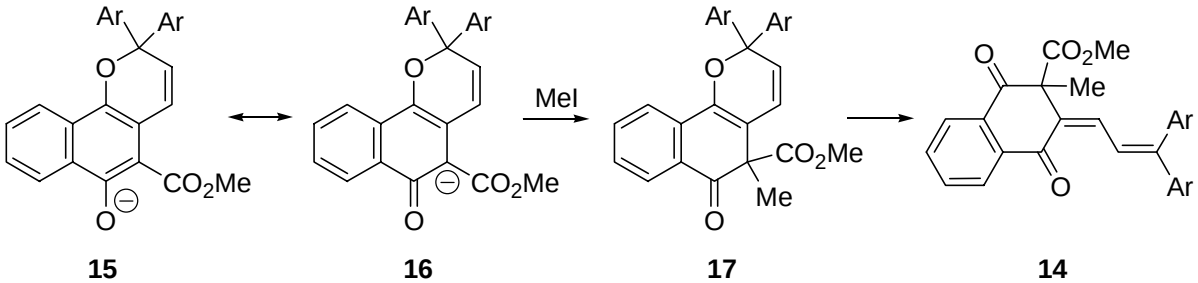


Figure 1. X-Ray crystallographic structure of one enantiomer of **14**

The formation of **14** may be rationalised by considering the stability of the oxyanion that results from deprotonation of the 6-hydroxynaphthopyran (**12**). The phenoxide (**15**) can be efficiently resonance stabilised by delocalisation of the negative charge onto 5-C, (**16**), which can be considered as the central carbon of a β-keto ester (Scheme 6). Once the carbanion (**16**) is intercepted (*C*-methylation) to give **17** the aromaticity of the central ring is permanently lost and the conjugated ring-opened system (**14**) is preferred. We have previously observed that disruption of the aromatic character of the naphthalene ring directly fused to the pyran unit favours the extended conjugation of the ring-opened system.[18]



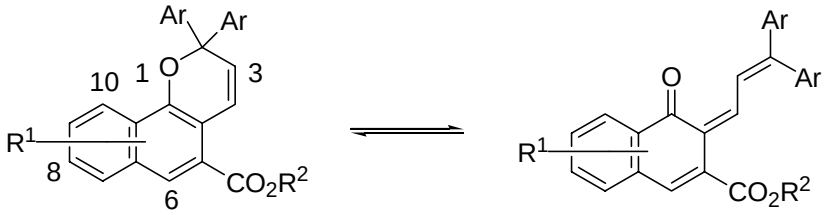
Scheme 6

On irradiation with UV light, solutions of the naphthopyrans in toluene became orange – red, consistent with their conversion into ring-opened species (**18**). The spectral characteristics of the *ca*. 10^{-5} mol dm^{-3} solutions of the naphthopyrans (**10a** – **e**, **13**) in spectroscopic grade toluene after irradiation with UV light (365 nm) to constant intensity at 20 ^{o}C are collated in Table 1.

The intensity of the absorption (ε_{max}) is of limited significance and is not reported since evidence acquired from flash photolysis studies indicate that only a small, but here unknown, proportion of the molecules undergo valence isomerisation.[28] Nevertheless, by irradiation to constant intensity, it is considered that a steady state

was reached in which the number of molecules undergoing ring opening is balanced by those reconverting to the pyran. The half-life, $t^{½}$, is the time taken for the intensity of the absorbance to fade to a half of its original value. Since the fade data are obtained under standard conditions, even though the values are not absolute, they are comparative and hence provide a measure of the influence of the substituents on the photochromic properties.

Table 1. Photochromic Properties of Naphthopyrans



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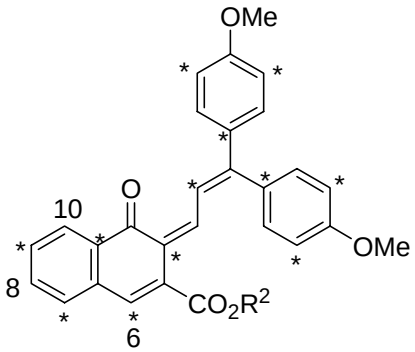
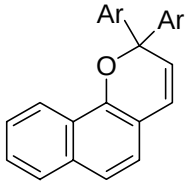
	R^1	R^2	λ_{max} (nm)	$t^{½}$ (sec)
10a	H	Et	493	3
10b	9-MeO	Et	505	3
10c	7-MeO	Et	508	3
10d	10-MeO	Me	485	21
10e	8-MeO	Me	480	11
13	6-MeO	Me	502	73

It is clear from the data presented in Table 1 that introduction of a methoxy group can cause either a bathochromic or hypsochromic shift in λ_{max} relative to that observed for **10a** according to its location. These shifts in wavelength can be rationalised by treating the ring-opened colored form as an odd alternant hydrocarbon and applying Dewar's rules[29] to the indexed system (**18a**) in which positions 6, 7 and 9 are starred (*) or 'active'.



18a



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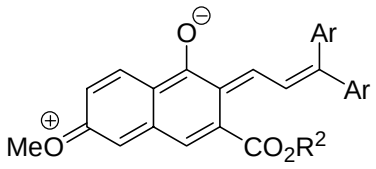
Dewar's rules postulate that decreasing the electronegativity of the atoms at the starred sites induces a bathochromic shift in λ_{max} of the dye. This feature is clearly demonstrated by the data in Table 1, where compounds (**10b**, **c** and **13**) substituted with an electron-releasing methoxy group at positions 9, 7 and 6, respectively have λ_{max} greater than that for **10a**. Conversely, **10d** and **10e** absorb *ca*. 10 nm lower than **10a**, in keeping with the prediction that electron-releasing groups at unstarred sites induce a hypsochromic shift.

The rate of fade, expressed as $t^{½}$ values, also exhibits some interesting trends. Although the 5-ester substituent has only a marginal influence on the wavelength of maximum absorption, it does exert a significant steric effect as is apparent from a comparison of photochromic properties of **10a** with those of the unsubstituted compound (**19**). The former has λ_{max} at 493 nm with $t^{½}$ of 3 seconds and the latter has λ_{max} at 495 nm with $t^{½}$ of several hours.[11]

The 9- and 7- methoxy compounds (**10b** and **c**) have $t^{½}$ essentially identical to that for the unsubstituted compound (**10a**), suggesting that the open forms of the three compounds are stabilised to a similar degree. However, the 6-, 8- and 10-methoxy substituted isomers (**13**, **10e** and **d**) have a longer half-life (Table 1). An additional resonance form **20** can be drawn for **10e** involving localisation of the negative charge on the carbonyl oxygen of the ring-opened form. A similar situation pertains for **10d**, as a result from a contribution from **21**. A further effect arising from these resonance forms is a reduction in the electron accepting capability of the carbonyl group in the colored ring-opened form, reflected in the hypsochromic shifts shown by these compounds. The presence of additional zwitterionic resonance forms has been previously suggested to account for the hyperchromicity of some photochromic 6-amino and 6-methoxy substituted 3*H*-naphtho[2,1-*b*]pyrans.[11]



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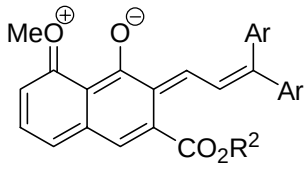

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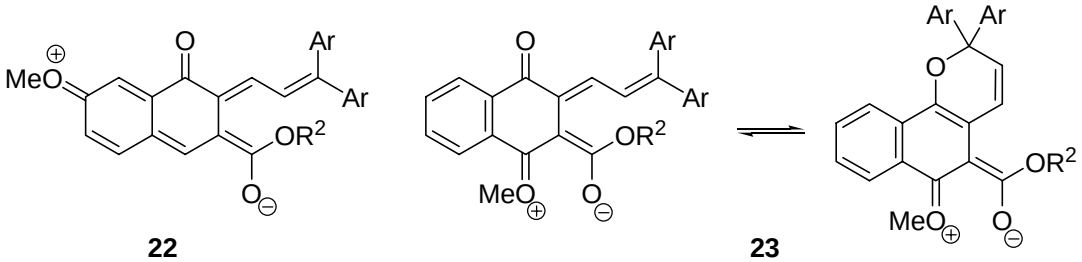
A different situation obtains for the 7- and 9- methoxy substituted isomers. The methoxy groups are in conjugation with the 5-ester function *e.g*. **22** and no effective additional resonance forms can be produced to stabilise the ring-opened form. This lack of additional stabilisation of the ring-opened form results in the 7- and 9- methoxy derivatives having similar $t^{½}$ values to the parent compound (**10a**). The 6-methoxy compound is at odds with this trend since a resonance form (**23**) can be drawn which is comparable with **22**. However, in **23** the ring adjacent to the pyran unit has lost some of its π-electron character, *c.f*. **22**. We have previously observed that the ring-opened valence isomers are preferred when the π-electron character (aromaticity) of this ring is diminished.[18]



22 **23**

CONCLUSION

An efficient and versatile three step synthesis of 3-substituted 1-naphthols has been developed. The 2*H*-naphtho[1,2-*b*]pyrans derived from these naphthols by reaction with a prop-2-yn-1-ol possess useful photochromic properties. Introduction of a methoxy group at the 8- and 10- positions results in increased half-lives for the ring-opened valence isomers, the absorption maxima of which are hypsochromically shifted compared with the parent compound and the 7- and 9- methoxy substituted analogues.

EXPERIMENTAL

Flash chromatography was performed using chromatography silica (40 – 63 micron particle size distribution) supplied by Fluorochem Ltd. Melting points were recorded in capillaries and are uncorrected. IR spectra were recorded on 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. VIS spectra were recorded in spectroscopic grade toluene in 1 cm quartz cells using a Specord S 100 diode array spectrophotometer with kinetic data analysis software.

Preparation of alkyl 4-acetoxynaphthalene-2-carboxylates (8)

A solution of the aromatic aldehyde (150 mmol) and diethyl succinate (27.9 g, 160 mmol) in anhydrous ethanol (50 mL) was added drop wise over 45 min to a stirred, warm (~ 50°C) solution of sodium ethoxide (20.4 g, 300 mmol) in anhydrous ethanol (300 mL). The color of the reaction mixture changed from colorless through yellow to orange during the addition. The mixture was then refluxed for 4 h before being cooled to rt, reduced to ~ 1/5 of the original volume whereupon the resultant orange/brown solution diluted with water (800 mL), acidified (conc. HCl) and extracted with ethyl acetate (5 x 100 mL). The combined organic extracts were then washed with water (2 x 100 mL), dried (anhyd. $MgSO_4$) and evaporated to give the crude product as an orange oil. This crude half ester was mixed with anhydrous sodium acetate (12.3 g, 150 mmol) in acetic anhydride (100 mL, 1.06 mol) and refluxed for 3 h. The resulting brown solution was then cooled to ~ 40°C and diluted with water (1500 mL) and stirred for 1.5 h. The brown tar was extracted with ethyl acetate (4 x 100 mL) and the combined organic extracts were washed with water (100 mL), saturated aqueous $NaHCO_3$ solution (3 x 100 mL) and then water (200 mL). The extracts were dried (anhydrous $MgSO_4$) and evaporated to give a brown oil. Elution from silica (30% ethyl acetate/hexane) gave the following 4-acetoxynaphthalene derivatives.

1. Ethyl 4-acetoxynaphthalene-2-carboxylate (**8a**), 87 %, from benzaldehyde and diethyl succinate as pale brown micro-crystals from EtOAc / hexane, mp 75 – 77 °C, ν_{max}/cm^{-1} (KBr) 1714, 1768, δ_H 1.44 (3H, t, *J* 7.1, $CH_2C\underline{H}_3$), 2.48 (3H, s, Ac), 4.43 (2H, q, *J* 7.1, $C\underline{H}_2CH_3$), 7.60 (2H, m, Ar-H), 7.83 (1H, d, *J* 1.5, 3-H), 7.88 (1H, dd, *J* 7.8, 1.6, Ar-H), 7.99 (1H, dd, *J* 8.2, 1.6, 5-H), 8.52 (1H, s, 1-H). Found: $[M+NH_4]^+$ 276.1236. $C_{15}H_{14}O_4$ requires $[M+NH_4]^+$ 276.1236. Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.7; H, 5.5. Found: C, 70.2; H, 5.6.

2. Ethyl 4-acetoxy-6-methoxynaphthalene-2-carboxylate (**8b**), 51%, from 4-methoxybenzaldehyde and diethyl succinate as tan colored micro-crystals from EtOAc / hexane, mp 92 – 95 °C, ν_{max}/cm^{-1} (KBr) 1708, 1769, δ_H 1.42 (3H, t, *J* 7.3, $CH_2C\underline{H}_3$), 2.48 (3H, s, Ac), 3.94 (3H, s, OMe), 4.41 (2H, q, *J*, 7.3, $C\underline{H}_2CH_3$), 7.10 (1H, d, *J* 1.5, 5-H), 7.21 (1H, dd, *J* 9.0, 1.5, 7-H), 7.81 (1H, d, *J* 1.5, 3-H), 7.83 (1H, d, *J* 9.0, 8-H), 8.44 (1H, s, 1-H). Found: MH^+ 289.1074. $C_{16}H_{16}O_5$ requires MH^+ 289.1076. Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.6; H, 5.6. Found: C, 66.6; H, 5.7.

3. Ethyl 4-acetoxy-8-methoxynaphthalene-2-carboxylate (**8c**), 60%, from 2-methoxybenzaldehyde and diethyl succinate as a yellow micro-crystals from EtOAc / hexane, mp 97 – 101 °C, ν_{max}/cm^{-1} (KBr) 1708, 1769, δ_H 1.43 (3H, t, *J* 7.0, $CH_2C\underline{H}_3$), 2.46 (3H, s, Ac), 4.02 (3H, s, OMe), 4.42 (2H, q, *J* 7.0, $C\underline{H}_2CH_3$), 6.89 (1H, d, *J* 7.4, 1.1, 7-H), 7.42 (1H, m, Ar-H), 7.52 (1H, m, Ar-H), 7.84 (1H, d, *J* 0.8, 3-H), 8.91 (1H, d, *J* 0.8, 1-H). Found: MH^+ 289.1076. $C_{16}H_{16}O_5$ requires MH^+ 289.1076. Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.6; H, 5.6. Found: C, 66.7; H, 5.8.

4. Elution of the crude product resulting from 3-methoxybenzaldehyde and diethyl succinate from silica (50% ethyl acetate/hexane) gave two fractions. Fraction 1. Ethyl 4-acetoxy-7-methoxynaphthalene-2-carboxylate (**8e**) from EtOAc/hexane as pale yellow micro-crystals, 56%, mp 43 – 45°C, ν_{max}/cm^{-1} 1718, 1767, δ_H 1.42 (3H, t, *J* 7.1, $CH_2C\underline{H}_3$), 2.45 (3H, s, Ac), 3.92 (3H, s, OMe), 4.42 (2H, q, *J* 7.1, $C\underline{H}_2CH_3$), 7.17 (1H, dd, *J* 8.8, 1.5, 6-H), 7.24 (1H, d, *J* 0.7, 3-H), 7.68 (1H, d, *J* 1.5, 8-H), 7.77 (1H, d, *J*, 8.8, 5-H), 8.40 (1H, s, 1-H). Found: $[M+NH_4]^+$ 306.1340. $C_{16}H_{16}O_5$ requires $[M+NH_4]^+$ 306.1341. Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.6; H, 5.6. Found: C, 66.2; H, 5.6. Fraction 2. Ethyl 4-acetoxy-5-methoxynaphthalene-2-carboxylate (**8d**) from EtOAc/hexane as pale yellow micro-crystals, 17%, mp 45 – 47°C, ν_{max}/cm^{-1} 1716, 1767, δ_H 1.43 (3H, t, *J* 7.1, $CH_2C\underline{H}_3$), 2.39 (3H, s, Ac), 3.95 (3H, s, OMe), 4.43 (2H, q, *J* 7.1, $C\underline{H}_2CH_3$), 6.95 (1H, d, *J* 7.7, 6-H), 7.45 (1H, m, 7-H), 7.47 (1H, dd, *J*, 8.0, 1.3, 8-H), 7.65 (1H, d, *J* 1.6, 3-H), 8.44 (1H, d, *J* 1.6, 1-H). Found: $[M+NH_4]^+$ 306.1336. $C_{16}H_{16}O_5$ requires $[M+NH_4]^+$ 306.1341. Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.6; H, 5.6. Found: C, 66.6; H, 5.5.

Preparation of substituted 1-naphthols (K_2CO_3 route)

Finely ground potassium carbonate (19.9 g, 144 mmol) was added to a suspension of the ethyl 4-acetoxynapthalene-2-carboxylate (115 mmol) in methanol (100 mL) and the resulting mixture stirred at rt until no starting material remained by TLC (*ca*. 1.5 h). The mixture was then diluted with excess water (~800 mL), acidified to pH ~6 (2 M aq., HCl). After stirring for 30 min, the solid was collected by vacuum filtration, washed with water (150 mL) and air-dried. Recrystallisation from ethyl acetate/hexane gave the title compounds.

1. Ethyl 4-hydroxynaphthalene-2-carboxylate (**9a**), 49%, as a pale brown solid, mp 147 – 148 °C [lit.,[30] mp 144 – 146 ºC], ν_{max}/cm^{-1} (KBr) 1687, δ_H 1.45 (3H, t, *J* 7.0, $CH_2C\underline{H}_3$), 4.45 (2H, q, *J* 7.0, $C\underline{H}_2CH_3$), 6.79 (1H, s, OH), 7.55 (2H, m, Ar-H), 7.63 (1H, d, *J* 1.5, 3-H), 7.89 (1H, dd, *J* 8.1, 1.8, 8-H), 8.19 (1H, d, *J* 1.5, 1-H), 8.26 (1H, d, *J* 7.8, 5-H). Found: $[M+NH_4]^+$ 234.1133. $C_{13}H_{12}O_3$ requires $[M+NH_4]^+$ 234.1130.

2. Ethyl 4-hydroxy-6-methoxynaphthalene-2-carboxylate (**9b**), 75%, as colorless micro-crystals from ethyl 4-acetoxy-6-methoxynaphthalene-2-carboxylate, mp 153 – 155 °C, ν_{max}/cm^{-1} (KBr) 1683, δ_H 1.44 (3H, t, *J* 7.0, $CH_2C\underline{H}_3$), 3.97 (3H, s, OMe), 4.43 (2H, q, *J* 7.0, $C\underline{H}_2CH_3$), 6.27 (1H, s, OH), 7.20 (1H, dd, *J* 8.8, 1.5, 7-H), 7.51 (1H, d, *J*, 1.5, 5-H), 7.55 (1H, s, 3-H), 7.81 (1H, d, *J* 8.8, 8-H), 8.15 (1H, s, 1-H). Found: MH^+ 247.0968. $C_{14}H_{14}O_4$ requires MH^+ 247.0970. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.3; H, 5.7. Found: C, 68.4; H, 5.5.

3. Ethyl 4-hydroxy-8-methoxynaphthalene-2-carboxylate (**9c**), 53%, as a brown micro-crystals from ethyl 4-acetoxy-8-methoxynaphthalene-2-carboxylate, mp 179 – 182 °C, ν_{max}/cm^{-1} (KBr) 1685, δ_H 1.44 (3H, t, *J* 7.0, $CH_2C\underline{H}_3$), 4.42 (3H, s, OMe), 4.43 (2H, q, *J* 7.0, $C\underline{H}_2CH_3$), 4.80 (1H, s, OH), 6.91 (1H, m, 7-H), 7.46 (1H, s, 3-H), 7.52 (1H, m, 6-H), 7.79 (1H, dd, *J* 8.5, 1.4, 5-H), 8.59 (1H, s, 1-H). Found: MH^+ 247.0975. $C_{14}H_{14}O_4$ requires MH^+ 247.0970. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.3; H, 5.7. Found: C, 68.0; H, 5.8.

Preparation of methyl 5-methoxy- and 7-methoxy- 4-hydroxynaphthalene-2-carboxylates (hydrolysis – esterification route)

A solution of the isomeric mixture of ethyl 5-methoxy- and 7-methoxy- 4-hydroxynaphthalene-2-carboxylates (51 mmol) in aqueous ethanol (EtOH:H_2O; 4:1, 100 mL) and sodium hydroxide (10.3 g, 258 mmol) was stirred at rt for 15 h. The resulting mixture was quenched with water (200 mL), carefully neutralised with (4 M, HCl) to pH 6 and extracted with CH_2Cl_2 (5 x 75 mL). The combined organic extracts were washed with water (2 x 100 mL), dried (anhyd. Na_2SO_4) and evaporated to afford the crude carboxylic acids as a pale brown solid. A solution of the foregoing acids in methanol (170 mL) containing conc. H_2SO_4 (1 mL) was refluxed for 17 h. The cooled solution was quenched with water (400 mL) and extracted with ethyl acetate (4 x 50 mL). The

organic extracts were washed with aq. saturated sodium bicarbonate solution (2 x 50 mL), water (2 x 100 mL) and dried (anhyd. Na_2SO_4). Removal of the solvent gave a brown solid which was eluted from silica with 10 % EtOAc / toluene to afford two fractions. Fraction 1. Methyl 4-hydroxy-5-methoxynaphthalene-2-carboxylate (**9d**), 36%, as an off-white solid mp 103 – 106 °C, ν_{max}/cm^{-1} (KBr) 1715, δ_H 3.96 (3H, s, OMe), 4.08 (3H, s, OMe), 6.89 (1H, dd, *J* 8.0, 0.6, 6-H), 7.38 (1H, m, Ar-H), 7.44 (1H, d, *J* 1.3, 3-H), 7.52 (1H, m, Ar-H), 8.05 (1H, d, *J* 1.2, 1-H), 9.36 (1H, s, OH). Found: MH^+ 233.0813. $C_{13}H_{12}O_4$ requires MH^+ 233.0813. Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.2; H, 5.2. Found: C, 66.9; H, 5.0. Fraction 2. Methyl 4-hydroxy-7-methoxynaphthalene-2-carboxylate (**9e**), 46%, as a cream solid mp 171 – 173 °C, ν_{max}/cm^{-1} (KBr) 1689, δ_H 3.93 (3H, s, OMe), 3.97 (3H, s, OMe), 5.92 (1H, s, OH), 7.20 (1H, d, *J* 1.4, 8-H), 7.22 (1H, dd, *J* 8.3, 1.4, 6-H), 7.34 (1H, d, *J* 0.5, 3-H), 8.10 (1H, s, 1-H), 8.14 (1H, d, *J* 8.3, 5-H). Found: MH^+ 232.0813. $C_{13}H_{12}O_4$ requires MH^+ 233.0813. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.2; H, 5.2. Found: C, 67.0; H, 5.1.

General method for the preparation of substituted naphthopyrans

Aluminium oxide (activated, acidic, Brockmann, standard grade) (4.0 g) was added in a single portion to a warm (*ca*. 40 °C), stirred solution of the alkyl 4-hydroxynaphthalene-2-carboxylate (9.3 mmol) and 1,1-bis-(4-methoxyphenyl)prop-2-yn-1-ol (2.74 g, 10.2 mmol) in toluene (100 mL). The resulting suspension was refluxed until no starting materials remained (TLC) (*ca*. 1.5 h). The solution was cooled (~ 50 °C) and filtered and the spent alumina catalyst was washed with hot toluene (2 x 50 mL). Evaporation of the toluene from the combined washings and filtrate afforded the crude product that was purified by either elution from silica gel or recrystallisation.

1. Ethyl 2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate (**10a**), 51% as cream micro-crystals from ethyl 4-hydroxynaphthalene-2-carboxylate after elution from silica (20% ethyl acetate/hexane) and recrystallsation from EtOAc / hexane, mp 93 – 95 °C, ν_{max}/cm^{-1} (KBr) 1709, δ_H 1.44 (3H, t, *J* 7.25, $CH_2C\underline{H}_3$), 3.76 (6H, s, OMe), 4.41 (2H, q, *J* 7.25, $C\underline{H}_2CH_3$), 6.16 (1H, d, *J* 10.0, 3-H), 6.82 (4H, m, Ar-H), 7.42 (4H, m, Ar-H), 7.50 (2H, m, 8-H, 9-H), 7.63 (1H, d, *J* 10.0, 4-H), 7.79 (1H, d, *J* 7.5, 7-H), 8.06 (1H, s, 6-H), 8.33 (1H, d, *J* 7.5, 10-H). Found: MH^+ 467.1856. $C_{30}H_{26}O_5$ requires MH^+ 467.1858. Anal. Calcd for $C_{30}H_{26}O_5$: C, 77.2; H, 5.6. Found: C, 77.3; H, 5.7.

2. Ethyl 9-methoxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate (**10b**), 53%, from ethyl 4-hydroxy-6-methoxynaphthalene-2-carboxylate as colorless micro-crystals after elution from silica (40% ethyl acetate/hexane) and recrystallsation from EtOAc / hexane, mp 146 – 148 °C, ν_{max}/cm^{-1} (KBr) 1708, δ_H 1.42 (3H, t, *J* 7.1, $CH_2C\underline{H}_3$), 3.76 (6H, s, OMe), 3.94 (3H, s, 9-OMe), 4.38 (2H, q, *J* 7.1, $C\underline{H}_2CH_3$), 6.15 (1H, d, *J* 10.0, 3-H), 6.81 (4H, m, Ar-H), 7.14 (1H, dd, *J* 8.9, 2.6, 8-H), 7.41 (4H, Ar-H), 7.56 (1H, d, *J* 2.6, 10-H), 7.68

(2H, d, *J* 8.9, 7-H and d, *J* 10.0, 4-H), 8.02 (1H, s, 6-H). Found: MH^+ 497.1969. $C_{31}H_{28}O_6$ requires MH^+ 497.1964. Anal. Calcd for $C_{31}H_{28}O_6$: C, 75.0; H, 5.7. Found: C, 75.0; H, 5.7.

3. Ethyl 7-methoxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate (**10c**), 57%, from ethyl 4-hydroxy-8-methoxynaphthalene-2-carboxylate as a tan colored solid after elution from silica (10% ethyl acetate/toluene) and recrystallsation from EtOAc / hexane, mp 109 – 112°C, ν_{max}/cm^{-1} (KBr) 1711, δ_H 1.43 (3H, t, *J* 7.2, $CH_2C\underline{H}_3$), 3.75 (6H, s, OMe), 3.98 (3H, s, 7-OMe), 4.40 (2H, q, *J* 7.2, $C\underline{H}_2CH_3$), 6.18 (1H, d, *J* 10.0, 3-H), 6.82 (4H, m, Ar-H), 7.45 (6H, m, Ar-H, 8-H, 9-H), 7.65 (1H, d, *J* 10.0, 4-H), 7.90 (1H, d, *J* 8.9, 10-H), 8.45 (1H, s, 6-H). Found: MH^+ 497.1965. $C_{31}H_{28}O_6$ requires MH^+ 497.1964. Anal. Calcd for $C_{31}H_{28}O_6$: C, 75.0; H, 5.7. Found: C, 74.6; H, 5.9.

4. Methyl 10-methoxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate (**10d**), 40%, from methyl 4-hydroxy-5-methoxynaphthalene-2-carboxylate as pale brown micro-crystals after elution from silica (70% ethyl acetate/hexane) and recrystallsation from EtOAc / hexane, mp 122 – 128°C, ν_{max}/cm^{-1} (KBr) 1718, δ_H 3.74 (6H, s, OMe), 3.92 (3H, s, OMe), 4.02 (3H, s, OMe), 6.24 (1H, d, *J* 10.0, 3-H), 6.79 (4H, m, Ar-H), 6.89 (1H, m, 9-H), 7.34 (2H, m, 7-H, 8-H), 7.52 (5H, m, Ar-H, 4-H), 7.94 (1H, s, 6-H). Found: MH^+ 483.1806. $C_{30}H_{26}O_6$ requires MH^+ 483.1807. Anal. Calcd for $C_{30}H_{26}O_6$: C, 74.6; H, 5.4. Found: C, 74.8; H, 5.5.

5. Methyl 8-methoxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate (**10e**), 55%, from methyl 4-hydroxy-7-methoxynaphthalene-2-carboxylate as a tan solid after elution from silica (30% ethyl acetate/hexane) and recrystallsation from EtOAc / hexane, mp 170 – 173°C, ν_{max}/cm^{-1} (KBr) 1714, δ_H 3.76 (6H, s, OMe), 3.90 (3H, s, OMe), 3.93 (3H, s, OMe), 6.12 (1H, d, *J* 10.0, 3-H), 6.81 (4H, m, Ar-H), 7.07 (1H, d, *J* 2.4, 7-H), 7.19 (1H, dd, *J* 9.2, 2.4, 9-H), 7.39 (4H, m, Ar-H), 7.58 (1H, d, *J* 10.0, 4-H), 7.95 (1H, s, 6-H), 8.24 (1H, d, *J* 9.2, 10-H). Found: MH^+ 483.1818. $C_{30}H_{26}O_6$ requires MH^+ 483.1807. Anal. Calcd for $C_{30}H_{26}O_6$: C, 74.6; H, 5.4. Found: C, 74.6; H, 5.6.

6 Methyl 6-hydroxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate (**12**), 76%, as cream micro-crystals from methyl 1,4-dihydroxynaphthalene-2-carboxylate after elution from silica (20% ethyl acetate/hexane) and recrystallsation from EtOAc / hexane, mp 175.5 – 178 °C [lit.,[26] mp 160 ºC], ν_{max}/cm^{-1} (KBr) 1646, 3435, δ_H 3.75 (6H, s, OMe), 4.01 (3H, s, CO_2Me), 6.11 (1H, d, *J* 10.0, 3-H), 6.81 (4H, m, Ar-H), 7.40 (5H, m, Ar-H and d, *J* 10.0, 4-H), 7.50 (1H, m, Ar-H), 7.63 (1H, m, Ar-H), 8.32 (2H, m, 7-H, 10-H), 12.20 (1H, s, OH). Found: MH^+ 469.1651. $C_{29}H_{24}O_6$ requires MH^+ 469.1662.

Methylation of Methyl 6-hydroxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate

A suspension of the naphthopyran (**12**) (3.2 mmol) in anhydrous acetone (70 mL) containing anhydrous K_2CO_3 (2.2 g, 16 mmol) was refluxed for 30 min. The solution was cooled slightly and iodomethane (0.91 g, 6.4 mmol) was added dropwise over 5 min *via* syringe. The resulting mixture was refluxed for 7 h. Removal of the cooled solvent gave a paste that was diluted with water (200 mL) and extracted with EtOAc (4 x 50 mL). Removal of the dried (anhyd. Na_2SO_4) solvent gave a pale brown gum that was eluted from silica (20% EtOAc / hexane) to give two pure fractions. Fraction 1. Methyl 6-methoxy-2,2-bis(4-methoxyphenyl)-2*H*-naphtho[1,2-*b*]pyran-5-carboxylate (**13**), 33%, as pale pink micro-crystals from EtOAc / hexane mp 186.5 – 189 °C [lit.,[26] mp 175 – 177 ºC], ν_{max}/cm^{-1} (KBr) 1738, δ_H 3.77 (6H, s, OMe), 3.94 (3H, s, 6-OMe), 3.99 (3H, s, CO_2Me), 6.13 (1H, d, *J* 10.0, 3-H), 6.70 (1H, d, *J* 10.0, 4-H), 6.83 (4H, m, Ar-H), 7.38 (4H, m, Ar-H), 7.51 (2H, m, 8-H, 9-H), 8.01 (1H, ddd, *J* 8.2, 2.1, 0.9, Ar-H), 8.31 (1H, ddd, *J* 8.3, 2.1, 0.9, Ar-H). Found: MH^+ 483.1803. $C_{30}H_{26}O_6$ requires MH^+ 483.1807. Anal. Calcd for $C_{30}H_{26}O_6$: C, 74.6; H, 5.4. Found: C, 74.5; H, 5.5. Fraction 2. Methyl 3-[3',3'-bis(4-methoxyphenyl)prop-2-en-(*Z*)-ylidene]-2-methyl-1,4-dioxo-1,2,3,4-tetrahydro-naphthalene-2-carboxylate (**14**), 40%, as deep orange prisms from EtOAc / hexane mp 166 – 168 °C, ν_{max}/cm^{-1} (KBr) 1745, 1688, 1603, δ_H 1.58 (3H, s, 2-Me), 3.56 (3H, OMe), 3.80 (3H, s, OMe), 3.85 (3H, s, OMe), 6.68 (1H, d, *J* 11.7, 2'-H), 6.82 (2H, m, Ar-H), 6.92 (2H, m, Ar-H), 7.12 (2H, m, Ar-H), 7.29 (2H, m, Ar-H), 7.68 (1H, m, Ar-H), 7.77 (1H, m, Ar-H), 8.00 (2H, d, *J* 11.7, 1'-H and dd, *J* 7.7, 1.3, 8-H), 8.22 (1H, dd, *J* 7.8, 1.3, 5-H); δ_C 20.79, 53.08, 55.28, 55.31, 62.88, 100.52, 113.52, 113.66, 113.93, 122.15, 127.08, 127.28, 130.16, 130.83, 131.37, 132.15, 132.43, 133.31, 133.59, 134.31, 134.60, 136.35, 139.24, 153.59, 159.86, 160.37, 171.32, 185.61, 193.34. Found: MH^+ 483.1812. $C_{30}H_{26}O_6$ requires MH^+ 483.1807. Anal. Calcd for $C_{30}H_{26}O_6$: C, 74.6; H, 5.4. Found: C, 74.2; H, 5.6.

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27. Crystal structure data for compound (**14**): Formula, $C_{30}H_{26}O_6$; formula weight, 482.51; crystal size, 0.42 x 0.29 x 0.07 mm; crystal morphology, orange/red prism; temperature 150(2) K; wavelength 0.71073 Å [Mo-K_α]; crystal system, monoclinic; space group, $P2_1/a$; unit cell dimensions, a = 8.02050(10) Å, α = 90°, b = 32.1901(4) Å, β = 94.4902(7)°; c = 9.41080(10) Å, γ = 90°; volume 2422.23(5) Å^3; Z 4; density (calculated), 1.323 Mg/m^3; absorption coefficient, 0.092 mm^{-1}; F(000), 1016; data collection range, 2.62 ≤ θ ≤ 26°; index ranges, -9 ≤ h ≤9, -39 ≤ k ≤ 39, -11 ≤ l ≤ 11; reflections collected, 33637; independent reflections, 4748 [R(int) = 0.0615]; observed reflections, 4167 [I >2σ(I)]; absorption correction, multi-scan; max. and min. transmission, 0.9936 and 0.9624, refinement method, full; data / restraints / parameters, 4748 / 0 / 330; goodness of fit, 1.06; final R indices [I >2σ(I)], R_1 = 0.0422, wR_2 = 0.1088; R indices (all data), R_1 = 0.0487, wR_2 = 0.1136; extinction parameter, 0.010(2); largest diff. peak and hole, 0.365 and

0.219e.Å^{-3}. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number no. CCDC 213811.

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