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Synthesis and photochromic properties of symmetrical aryl ether linked bi- and tri-naphthopyrans

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Abstract

A range of aryl ether linked benzophenones (**8**) has been conveniently obtained by nucleophilic displacement of fluoride from 4-fluorobenzophenone with a dihydroxy-benzene or -naphthalene. The linked benzophenones were efficiently transformed in two steps to symmetrically linked naphthopyrans (**10d**–**k**). The photochromic response of these novel systems under steady state irradiation is characterised by a two stage fading process and their colourability is only marginally improved over the related monomeric analogues (**10a**–**c**).

Keywords: S_NAr; Aryloxybenzophenones; Linked naphthopyrans; Photochromism

1. Introduction

The synthesis, properties and applications of photochromic naphthopyrans have been the subject of recent reviews [1,2]. The isomeric naphthopyrans **1** and **2**, or fused carbocyclic analogues, are almost exclusively employed for imparting a photochromic response into a host object and significant research effort has been directed to their design and synthesis for application in ophthalmic photochromic sun lenses [3]. The naphthopyrans **1** and **2** display photochromism by means of a photo-induced reversible electrocyclic opening of the pyran ring to produce a coloured valence isomer (Scheme 1).

One active area of development of photochromic naphthopyrans has been the union of two photochromic naphthopyran systems through one of the aryl units located on the sp^3 hybridised C atom of the pyran ring. Examples include the symmetrically substituted fluorine containing naphthopyran **3** [4], the bithienyl compound **4** [5], and the alkyl and ether bridged series **5** [6]. More recently, a detailed study of the thermal dependence of the photochromic properties of phenylene linked naphthopyrans, e.g. **6** [7], has been reported and the synthesis and ambient temperature spectrokinetic properties of the unsymmetrical linked systems, e.g. **7**, have been described [8]. We were interested in obtaining some high molecular weight symmetrical ether linked naphthopyrans that should provide for intense yellow/orange colour generation upon irradiation and be less prone to leaching from polymeric substrates as a consequence of their topology.

2. Discussion

The key starting components in the efficient synthesis of naphthopyrans are naphthols and substituted benzophenones [1,2]. The benzophenones are readily converted into prop-2-yn-1-ols, which undergo an *in situ* Claisen rearrangement upon acid catalysed etherification with a naphthol to give the naphthopyran [9]. 4-Fluorobenzophenones readily undergo nucleophilic aromatic substitution reactions with a variety of nucleophiles [10]. One reaction of particular interest was the

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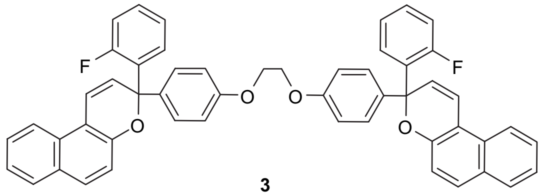

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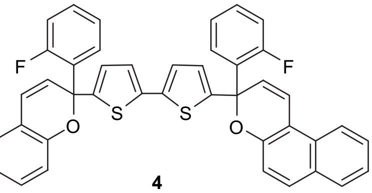

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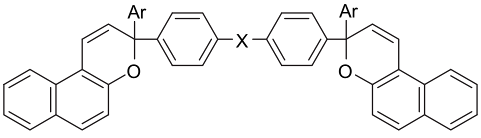
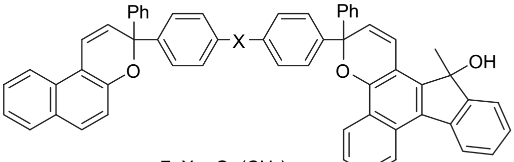
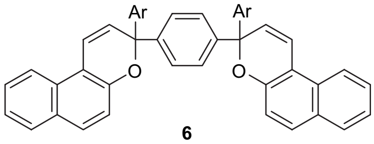


5, X = $(CH_2)_2$, $(CH_2)_6$, CH_2OCH_2



7, X = O, $(CH_2)_2$



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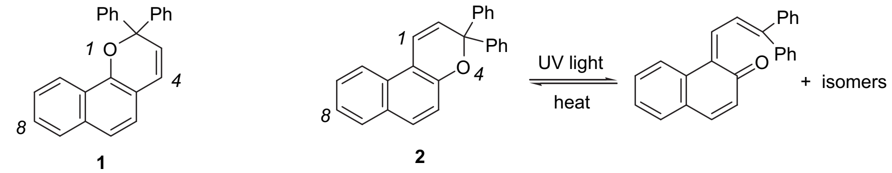
preparation of aromatic poly(ether ketones) that relies upon the nucleophilic displacement of fluoride from aromatic ketones, such as 4,4′-difluorobenzophenone and related compounds, with dihydroxy-benzenes [11] or naphthalenes [12]. As a preliminary survey of this chemistry, 4-fluorobenzophenone and phenol were heated overnight in DMSO containing 1 equiv of K_2CO_3 to afford, after routine aqueous work-up and recrystallisation, 4-phenoxybenzophenone **8a** in 79% yield. Benzophenones **8b**, **c** were similarly obtained in 90 and 92% yield, respectively, from 1- and 2-naphthol (Scheme 2). Using an identical procedure but employing 2 equiv of 4-fluorobenzophenone and K_2CO_3 with a dihydroxynaphthalene gave the linked benzophenones **8d**–**i** in good yield (47–85%). The use of DMSO as solvent for these S_NAr reactions would appear to be superior to *N*,*N*-dimethylacetamide (DMAc)/PhMe mixtures as indicated by the simplified work-up and improved yield noted for the formation of **8d** 79% using DMSO compared with 44% using DMAc/PhMe [12]. Replacing the dihydroxynaphthalene with 2,2′-dihydroxy-1,1′-biphenyl gave the biphenyl linked ketone **8j** in 46% yield. The ^1H NMR spectra of the new linked benzophenones are complex though the protons on the benzophenone unit *ortho* to the *O* atom resonate upfield (*ca.* δ 7.1) of those protons that are adjacent to the carbonyl group (*ca.* δ 7.8).

It is interesting to note that these new linked benzophenones may have wider application as alternative type II photoinitiators [13] for ink and surface coating formulations where the use of benzophenone, although cheap, is increasingly threatened by its toxicological, processing and efficiency problems.

With the range of benzophenones **8** to hand their conversion to the propynols **9** proved straightforward upon reaction with lithium trimethylsilylacetylide (LiTMSA) in THF with subsequent methanolic KOH promoted desilylation (Scheme 3); yields for this exceptionally clean two-step one-pot sequence are typically high [4,14]. The terminal acetylene protons resonate at *ca.* δ 2.9 and the hydroxyl protons at *ca.* δ 3.2 in their ^1H NMR spectra.

Heating a solution of an alkynol **9** with 2-naphthol in toluene containing suspended acidic alumina for *ca.* 2 h gave the linked naphthopyrans **10a**–**j** in 31–77% yield (Scheme 4) after removal of the alumina, evaporation of the toluene and flash chromatography. The formation of the naphthopyrans was confirmed by ^1H NMR spectroscopy, which indicated that 2-H resonated at *ca.* δ 6.25 with a coupling constant of ~10 Hz [2]. The formation of diastereoisomers was apparent from the ^1H NMR spectra of naphthopyrans **10g**, **i** and **j**, each of which displayed distinct doublets ($J = 10$ Hz) for 2-H.

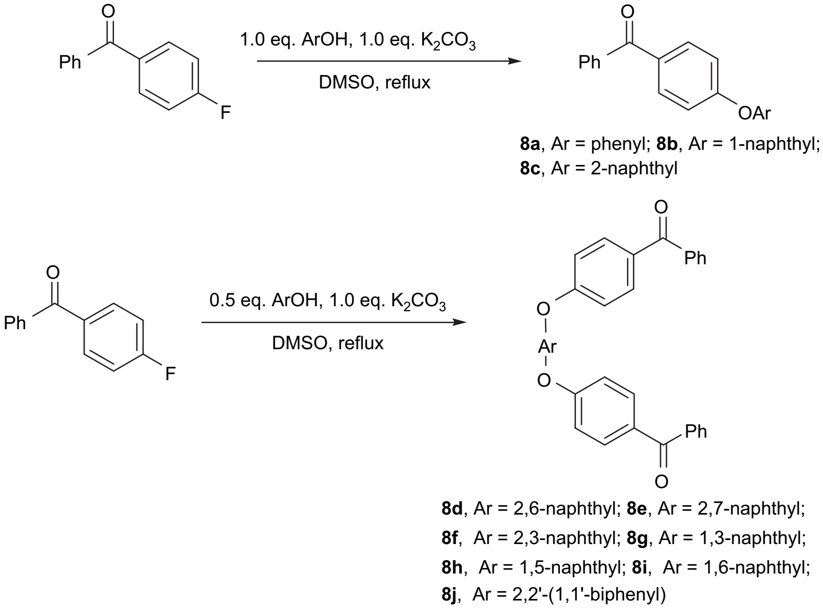
The successful synthesis of the linked naphthopyrans **10** using this relatively efficient three step sequence prompted an investigation of a system containing three linked naphthopyran units. Thus heating phloroglucinol in DMSO containing



1
2*H*-naphtho[1,2-*b*]pyran

2
3*H*-naphtho[2,1-*b*]pyran

Scheme 1.

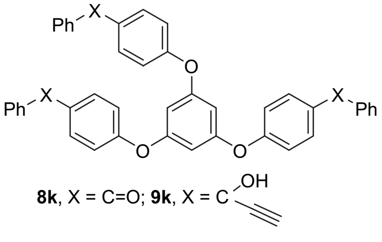


8a, Ar = phenyl; **8b**, Ar = 1-naphthyl;
8c, Ar = 2-naphthyl

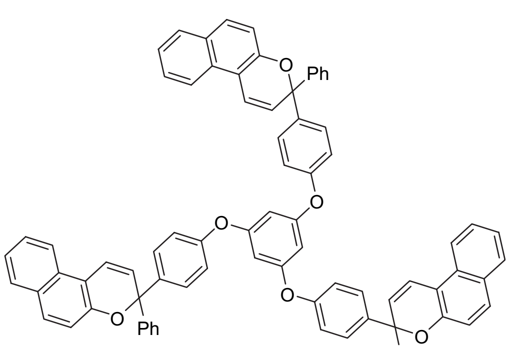
8d, Ar = 2,6-naphthyl; **8e**, Ar = 2,7-naphthyl;
8f, Ar = 2,3-naphthyl; **8g**, Ar = 1,3-naphthyl;
8h, Ar = 1,5-naphthyl; **8i**, Ar = 1,6-naphthyl;
8j, Ar = 2,2'-(1,1'-biphenyl)

Scheme 2.

excess 4-fluorobenzophenone and K_2CO_3 gave, after column chromatography, tri-1,3,5-(4-benzoylphenoxy)benzene **8k** in 38% yield. The ^{1}H NMR spectrum of this symmetrical compound was relatively simple with the central core aromatic protons appearing as a singlet at δ 6.62. Conversion to the alkynol **9k** was accomplished in moderate yield (47%) using excess LiTMSA though the alkynol remained as a sticky gum. Direct reaction of this gum with 2-naphthol (3 equiv) gave a complex product from which the pure tris-naphthopyran **10k** was isolated by column chromatography in 17% yield. The ^{1}H NMR spectrum of this compound displayed the expected doublet accounting for three protons at δ 6.21 ($J = 9.9$ Hz) for 2-H and a singlet at δ 6.35 for the three central ring protons.

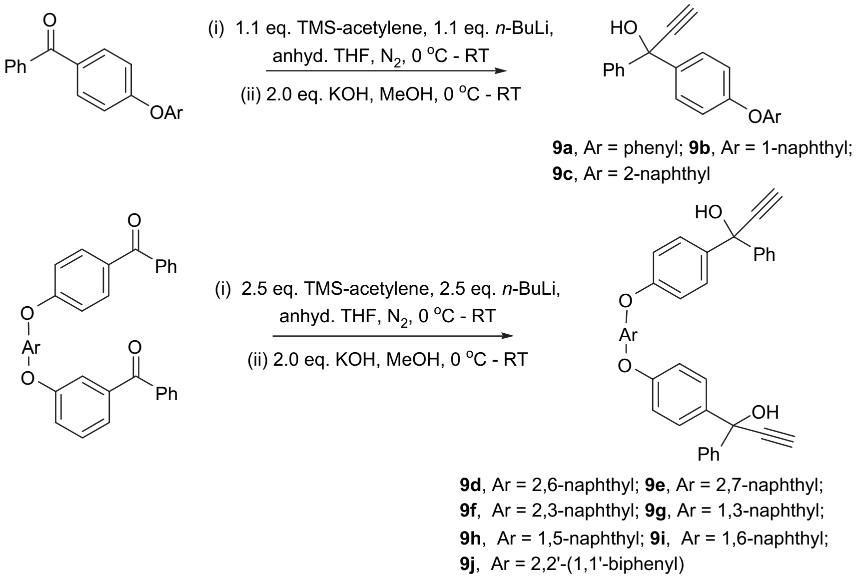


8k, X = C=O; **9k**, X = C



10k

The photochromic properties of these new naphthopyrans **10a–k** (Table 1) merit some comments. Continuous irradiation of a toluene solution (*ca.* 1×10^{-4} M) of the naphthopyran with ultraviolet light resulted in the development of a yellow/orange colour (λ_{max} 436–452 nm) (Fig. 1 for **10d**) that faded relatively rapidly ($K_{\Delta 1} \sim 9 \times 10^{-2}\ s^{-1}$) upon cessation of irradiation though noticeably a residual colour (*ca.* 20% of the original absorbance) persists even after 1 h (Fig. 2 for **10d**). The initial rapid fading of the photogenerated colour coupled with a second more gradual fade ($k_{\Delta 2} < \sim 2 \times 10^{-4}\ s^{-1}$) has been documented for photochromic naphthopyrans with the latter attributed to the persistence of a relatively stable *trans trans* ring-opened isomer [15]. Upon comparison of the photochromic properties of the simple naphthopyrans **10a–c** with that of the reference compound **2** it is apparent that **10** have λ_{max} shifted bathochromically and generate a less intense colour under steady state irradiation which is less persistent. This longer wavelength absorption and more rapid fade is typical for 3*H*-naphtho[2,1-*b*]pyrans that possess an electron rich aryl substituent at C-3 [1,2]. The linked naphthopyrans **10d–j** afforded only a marginally more intense colour under steady state conditions with λ_{max} and rates of fade comparable to those of **10a–c**. The tris substituted compound **10k** gave a more intense colour under steady state irradiation that indicates that more than one pyran unit is opened. This is corroborated by the increase in the



9a, Ar = phenyl; **9b**, Ar = 1-naphthyl;
9c, Ar = 2-naphthyl

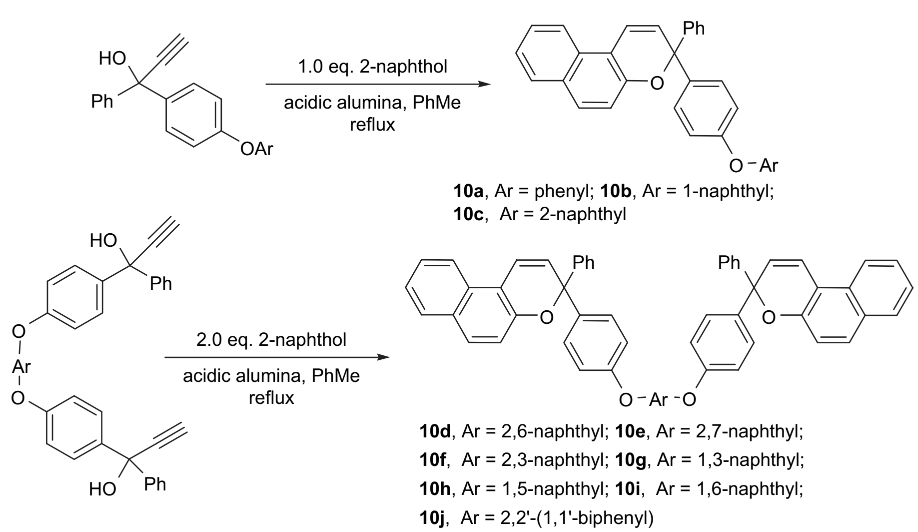
9d, Ar = 2,6-naphthyl; **9e**, Ar = 2,7-naphthyl;
9f, Ar = 2,3-naphthyl; **9g**, Ar = 1,3-naphthyl;
9h, Ar = 1,5-naphthyl; **9i**, Ar = 1,6-naphthyl;
9j, Ar = 2,2'-(1,1'-biphenyl)

Scheme 3.

residual colour observed for the tri-naphthopyran **10k** (0.08 a.u.) compared to the mono naphthopyrans **10a–c** (0.04 a.u.). It should be noted that an equilibrium absorbance value for a molecule containing more than one naphthopyran unit, cannot be anticipated, due to chemical deviations from Beer's law, which are more pronounced for faster responding systems [8].

3. Experimental

Melting points were determined in capillary tubes and are uncorrected. For measurements of λ_{max}, A_{eq} and k_{Δ} under continuous UV–vis irradiation, 1×10^{-4} M toluene solutions were used. Irradiation experiments were conducted using a CARY 50 Varian spectrophotometer coupled to a 150 W ozone-free Xenon lamp (6255 Oriel Instruments). The light from the UV–vis lamp was filtered using a water filter (61945 Oriel Instruments) and then carried to the spectrophotometer holder perpendicular to the monitoring beam using a fibre-optic system (77654 Oriel Instruments). A 40 W m^{-2} light flux, measured with a Goldilux Photometer with a UV-A probe, was used. A thermostated (20 °C) 10 mm quartz cell, containing the sample solution (3.5 ml), equipped with magnetic stirring was used. Three spectrokinetic parameters, normally quoted when describing the properties of photochromic compounds, were evaluated—maximum wavelength of absorption of the open form (λ_{max}), thermal bleaching rates (k_{Δ}) and colourability (A_{eq})—and estimated by the absorbance of the solution after reaching a photostationary equilibrium under the experimental conditions. The bleaching kinetics were studied in the dark, under thermal conditions. ^1H NMR spectra were recorded on a Bruker Avance 400 MHz instrument for solutions in $CDCl_3$ containing 0.03%



10a, Ar = phenyl; **10b**, Ar = 1-naphthyl;
10c, Ar = 2-naphthyl

10d, Ar = 2,6-naphthyl; **10e**, Ar = 2,7-naphthyl;
10f, Ar = 2,3-naphthyl; **10g**, Ar = 1,3-naphthyl;
10h, Ar = 1,5-naphthyl; **10i**, Ar = 1,6-naphthyl;
10j, Ar = 2,2'-(1,1'-biphenyl)

Scheme 4.

Table 1
Spectrokinetic properties under constant irradiation: maximum wavelength of coloured form (λ_{max}); colourability (A_{eq}) is the steady state absorbance at λ_{max} just after cessation of irradiation; thermal bleaching rate ($k_{\Delta 1}$, $k_{\Delta 2}$)

No	λ_{max} (nm)	$k_{\Delta 1}$ (s^{-1})	$k_{\Delta 2}$ (s^{-1})	A_{eq}
2	426	6.1×10^{-2}	2.3×10^{-6}	0.30
10a	436	9.6×10^{-2}	3.0×10^{-5}	0.20
10b	446	9.9×10^{-2}	2.0×10^{-5}	0.20
10c	446	9.4×10^{-2}	3.0×10^{-5}	0.18
10d	441	9.1×10^{-2}	6.0×10^{-5}	0.26
10e	446	9.0×10^{-2}	6.0×10^{-5}	0.23
10f	446	9.5×10^{-2}	1.6×10^{-4}	0.22
10g	441	8.7×10^{-2}	7.0×10^{-5}	0.26
10h	441	9.0×10^{-2}	5.0×10^{-5}	0.23
10i	441	9.3×10^{-2}	1.1×10^{-4}	0.20
10j	452	8.4×10^{-2}	1.0×10^{-5}	0.21
10k	441	8.0×10^{-2}	2.0×10^{-5}	0.37

tetramethylsilane (TMS); *J* values are given in Hertz. Infrared spectra were recorded using a Perkin Elmer Spectrum One with a golden gate ATR. A high-resolution mass spectrometry service was provided by the EPSRC (University of Wales, Swansea).

3.1. Preparation of 4-(naphthoxy)- and 4-phenoxy-benzophenones

A mixture of 4-fluorobenzophenone (18.7 mmol), a phenol or naphthol (18.7 mmol), potassium carbonate (18.7 mmol) and DMSO (50 mL) was heated under reflux until no further change in the composition of the reaction mixture was evident by TLC. The reaction mixture was cooled to room temperature and poured into brine (600 mL). The aqueous solution was extracted with chloroform (3 × 100 mL) and the combined organic extracts were washed with brine (3 × 50 mL), water (3 × 50 mL), dried (anhyd. Na_2SO_4) and evaporated. Purification was effected by recrystallisation from ethyl acetate and hexane with charcoal treatment to afford the following benzophenones:

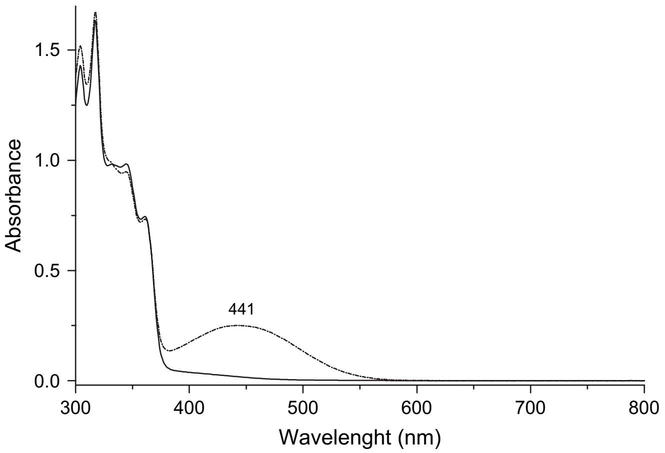


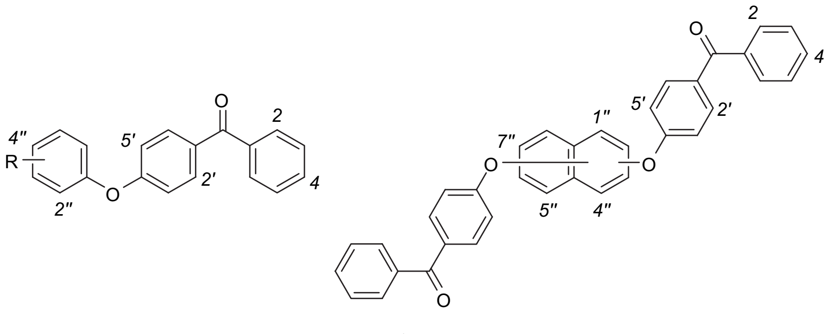
Fig. 1. UV–vis absorption spectra of naphthopyran **10d** before (——) and after (- - - -) UV irradiation.

*3.1.2. (4-[Naphthalen-1-yloxy]phenyl)phenylmethanone **(8b)***

This is prepared from 1-naphthol and 4-fluorobenzophenone as pale brown microcrystals from EtOAc/hexane (90%), m.p. 64–66 °C, ν_{max} 1650, 1598, 1259, 693 cm^{-1}, δ_H 7.09 (2H, m, 3′,5′-H), 7.28 (1H, dd, *J* 8.9, 2.4, 2″-H), 7.48 (5H, m, Ar-H), 7.58 (1H, m, Ar-H), 7.78 (3H, m, Ar-H), 7.85 (3H, m, Ar-H), 7.99 (1H, d, *J* 8.9, 8″-H). Found: $[M+H]^+$ 325.1222; $C_{23}H_{16}O_2$ requires $[M+H]^+$ 325.1223.

*3.1.3. (4-[Naphthalen-2-yloxy]phenyl)phenylmethanone **(8c)***

This is prepared from 2-naphthol and 4-fluorobenzophenone as off-white microcrystals from EtOAc/hexane (92%), m.p. 85–87 °C, ν_{max} 1645, 1596, 1284, 1234, 770 cm^{-1}, δ_H 7.03 (2H, m, 3′,5′-H), 7.14 (1H, d, *J* 8.5, 2.4, 3″-H), 7.47 (5H, m, Ar-H), 7.58 (1H, m, 4-H), 7.78 (3H, m, Ar-H), 7.83 (3H, m, Ar-H), 7.89 (1H, d, *J* 8.2, Ar-H). Found: $[M+H]^+$ 325.1218; $C_{23}H_{16}O_2$ requires $[M+H]^+$ 325.1223.



Numbering system employed for ^{1}H NMR assignments

*3.1.1. (4-Phenoxyphenyl)phenylmethanone **(8a)***

This is prepared from 4-fluorobenzophenone and phenol (79%) after recrystallisation from EtOAc/hexane, as off-white crystals, m.p. 64–66 °C (lit. m.p. 69–70 °C) [16].

3.2. Preparation of linked benzophenones

A mixture of the 4-fluorobenzophenone (37.4 mmol), a dihydroxy compound (18.7 mmol), potassium carbonate

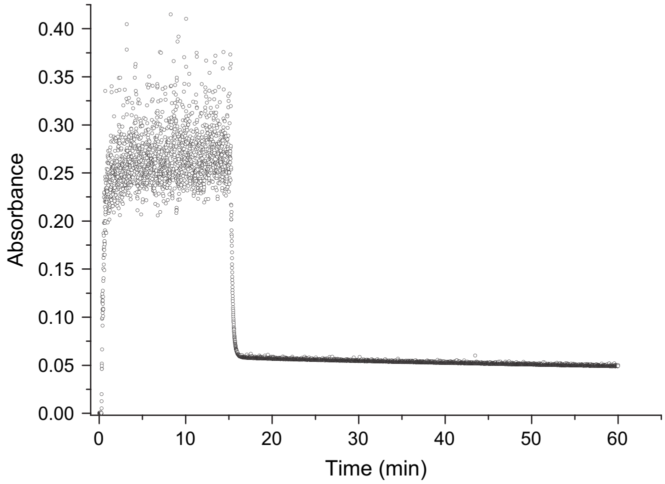


Fig. 2. Kinetics of thermal relaxation of **10d** recorded at λ_{max}.

(37.4 mmol) and DMSO (50 mL) was heated under reflux until no further change in the composition of the reaction mixture was evident by TLC (*ca.* 6 h). The reaction mixture was cooled to room temperature and poured into brine (750 mL). The aqueous mixture was extracted with chloroform (3 × 100 mL) and the combined organic extracts were washed with brine (3 × 50 mL), water (3 × 50 mL), dried (anhyd. Na_2SO_4) and evaporated. Purification was effected by either recrystallisation from ethyl acetate and hexane with charcoal treatment or by elution from silica to afford the following benzophenones.

3.2.1. {4-[6-(4-Benzoylphenoxy)naphthalen-2-yloxy]-phenyl}phenylmethanone ***(8d)***

This is prepared from 2,6-dihydroxynaphthalene and 4-fluorobenzophenone as pale brown microcrystals from ethyl acetate/hexane and charcoal (79%), m.p. 201–203 °C (lit. m.p. 209 °C) [12].

3.2.2. {4-[7-(4-Benzoylphenoxy)naphthalen-2-yloxy]-phenyl}phenylmethanone ***(8e)***

This is prepared from 2,7-dihydroxynaphthalene and 4-fluorobenzophenone as off-white microcrystals from EtOAc/hexane and charcoal (74%), m.p. 149–151 °C, ν_{max} 1650, 1598, 1259, 693 cm^{-1}, δ_H 7.11 (4H, m, 3′,5′-H), 7.26 (2H, dd, *J* 8.8, 2.4, 3″,6″-H), 7.37 (2H, d, *J* 2.4, 1″,8″-H), 7.49 (4H, m, 3,5-H), 7.59 (2H, m, 4-H), 7.79 (4H, m, 2,6-H), 7.85 (4H, m, 2′,6′-H), 7.90 (2H, d, *J* 8.8, 4″,5″-H). Found: M^+ 520.1664; $C_{36}H_{24}O_4$ requires M^+ 520.1669.

3.2.3. {4-[3-(4-Benzoylphenoxy)naphthalen-2-yloxy]-phenyl}phenylmethanone ***(8f)***

This is prepared from 2,3-dihydroxynaphthalene and 4-fluorobenzophenone as pale brown microcrystals from EtOAc/hexane and charcoal (52%), m.p. 154–156 °C, ν_{max} 1648, 1599, 1266 cm^{-1}, δ_H 6.98 (4H, m, 3′,5′-H), 7.48 (6H, m, Ar-H), 7.57 (2H, m, 4-H), 7.63 (2H, s, 1″,4″-H), 7.75 (4H, m, Ar-H), 7.78 (6H, m, 2,6-H, 2′,6′-H, 5″,8″-H). Found: $[M+H]^+$ 521.1750; $C_{36}H_{24}O_4$ requires $[M+H]^+$ 521.1747.

3.2.4. {4-[3-(4-Benzoylphenoxy)naphthalen-1-yloxy]-phenyl}phenylmethanone ***(8g)***

This is prepared from 1,3-dihydroxynaphthalene and 4-fluorobenzophenone as an orange glassy solid after column chromatography 5% EtOAc/PhMe (47%), ν_{max} 1651, 1590, 1574, 1217, 694 cm^{-1}, δ_H 6.93 (1H, d, *J* 2.3, 2″-H), 7.13 (6H, m, 3′,5′-H, Ar-H), 7.24 (2H, m, 4-H), 7.31 (1H, d, *J* 2.2, 4″-H), 7.50 (7H, m, Ar-H), 7.78 (2H, m, Ar-H), 7.84 (4H, m, 2′,6′-H), 8.11 (1H, d, *J* 8.4, 8″-H). Found: C, 82.9; H, 4.6; $C_{36}H_{24}O_4$ requires C, 83.1; H, 4.6%.

3.2.5. {4-[5-(4-Benzoylphenoxy)naphthalen-1-yloxy]-phenyl}phenylmethanone ***(8h)***

This is prepared from 1,5-dihydroxynaphthalene and 4-fluorobenzophenone as yellow microcrystals from EtOAc/hexane and charcoal (85%), m.p. 168–170 °C, ν_{max} 1650, 1594, 1250, 693 cm^{-1}, δ_H 7.09 (4H, m, 3′,5′-H), 7.19 (2H, dd, *J* 8.3, 2.1, 2″,6″-H), 7.48 (6H, m, 3,4,5-H), 7.58 (2H, m, 7.5, 3″,7″-H), 7.79 (4H, m, 2,6-H), 7.85 (4H, m, 2′,6′-H), 7.98 (2H, d, *J* 8.6, 4″,8″-H). Found: M^+ 520.1662; $C_{36}H_{24}O_4$ requires M^+ 520.1669.

3.2.6. {4-[6-(4-Benzoylphenoxy)naphthalen-1-yloxy]-phenyl}phenylmethanone ***(8i)***

This is prepared from 1,6-dihydroxynaphthalene and 4-fluorobenzophenone as a pale brown glassy oil (77%), ν_{max} 1651, 1591, 1574, 1223, 695 cm^{-1}, δ_H 7.10 (5H, m, 3′,5′-H, 5″-H), 7.29 (1H, dd, *J* 8.9, 2.4, 2″-H), 7.48 (6H, m, Ar-H), 7.59 (3H, m, Ar-H), 7.79 (4H, m, 2,6-H), 7.85 (4H, m, 2′,6′-H), 8.13 (1H, d, *J* 9.0, 8″-H). Found: C, 82.7; H, 4.4; $C_{36}H_{24}O_4$ requires C, 83.1; H, 4.6%.

3.2.7. 2,2′-Bis(4-benzoylphenoxy)-1,1′-biphenyl ***(8j)***

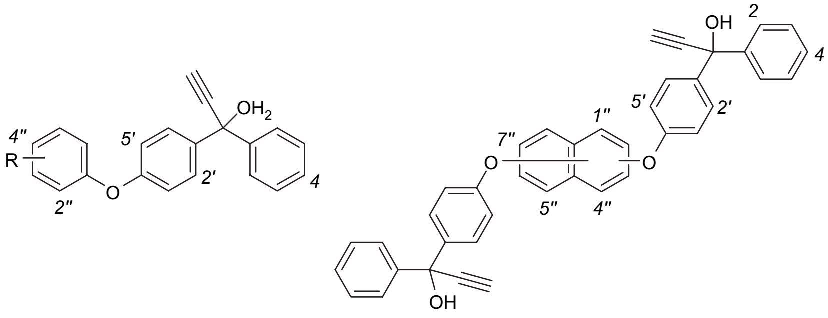
This is prepared from 2,2′-dihydroxy-1,1′-biphenyl and 4-fluorobenzophenone as pale brown microcrystals EtOAc/hexane (46%), m.p. 146–150 °C, ν_{max} 1651, 1595, 1228, 698 cm^{-1}, δ_H 6.87 (4H, m, 3′,5′-H), 7.03 (2H, dd, *J* 8.0, 1.2, 3″-H), 7.21 (2H, m, 5″-H), 7.34 (2H, m, Ar-H), 7.43 (6H, m, Ar-H), 7.54 (2H, m, 4-H), 7.69 (8H, m, 2,6-H, 2′,6′-H). Found: C, 83.2; H, 4.5; $C_{38}H_{26}O_4$ requires C, 83.5; H, 4.8%.

3.2.8. 1,3,5-Tris(4-benzoylphenoxy)benzene ***(8k)***

This is prepared from phloroglucinol and 3 equiv of 4-fluorobenzophenone as colourless crystals after column chromatography 20% EtOAc/hexane (38%), m.p. 92–94 °C, ν_{max} 1641, 1587, 1261, 694 cm^{-1}, δ_H 6.62 (3H, s, 2″,4″,6″-H), 7.12 (6H, m, 3′,5′-H), 7.49 (6H, m, 3,5-H), 7.57 (3H, m, 4-H), 7.77 (6H, m, 2,6-H), 7.85 (6H, m, 2′,6′-H). Found: $[M+H]^+$ 667.2120; $C_{46}H_{30}O_4$ requires $[M+H]^+$ 667.2115.

3.3. General method for the preparation of simple prop-2-yn-1-ols

n-Butyllithium (2.5 M in hexanes) (33 mmol) was added slowly *via* syringe to a cold (−10 °C), stirred solution of trimethylsilylacetylene (33 mmol) in anhydrous tetrahydrofuran (100 mL) under a nitrogen atmosphere. On completion of the addition (*ca.* 5 min) the cold solution was allowed to stir for 1 h. The finely powdered benzophenone (30 mmol) was added in a single portion and the mixture stirred until TLC examination of the reaction mixture indicated that no benzophenone remained (*ca.* 3 h). The reaction mixture was then re-cooled to 0 °C and a solution of methanolic potassium hydroxide (from potassium hydroxide (60 mmol) in methanol (30 mL)) was added in a single portion. The cooling bath was removed and the mixture was warmed to RT; after *ca.* 15 min TLC indicated that removal of the trimethylsilyl group was complete. The mixture was acidified to pH ~ 7 using glacial acetic acid and then poured into water (500 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (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 that was sufficiently pure for subsequent use. The following alkynols were obtained in this way:



Numbering system employed for ^{1}H NMR assignments

3.3.1. 1-(4-Phenoxyphenyl)-1-phenylprop-2-yn-1-ol *(9a)*

This is prepared from (4-phenoxyphenyl)phenylmethanone **8a** as an orange viscous oil, which decomposed on attempted vacuum distillation (89%), ν_{max} 3419, 3285, 1586, 1487, 1230, 751 cm^{-1}, δ_H 2.81 (1H, s, alkyne-H), 2.94 (1H, s, OH), 6.95 (2H, m, 3′,5′-H), 7.00 (2H, m, 2″,6″-H), 7.12 (1H, m, Ar-H), 7.30 (5H, m, Ar-H), 7.58 (2H, m, Ar-H), 7.63 (2H, m, Ar-H). A repeat batch of crude material was used directly for the preparation of **10a**.

3.3.2. 1-(4-(Naphthalen-1-yloxy)phenyl)-1-phenylprop-2-yn-1-ol *(9b)*

This is prepared from (4-[naphthalen-1-yloxy]phenyl)phenylmethanone **8b** as an orange glassy oil (85%), ν_{max} 3474, 3284, 1591, 1499, 1233 cm^{-1}, δ_H 2.72 (1H, s, alkyne-H), 2.78 (1H, bs, OH), 6.83 (3H, m, 3′,5′-H, 1″-H), 7.13 (1H, m, 4-H), 7.21 (3H, m, Ar-H), 7.33 (2H, m, Ar-H), 7.41 (2H, m, Ar-H), 7.47 (3H, m, Ar-H), 7.71 (1H, d, *J* 8.4, 5″-H), 7.99 (1H, d, *J* 8.6, 8″-H). Found: C, 85.9; H, 5.4; $C_{25}H_{18}O_2$ requires C, 85.7; H, 5.1%.

3.3.3. 1-(4-(Naphthalen-2-yloxy)phenyl)-1-phenylprop-2-yn-1-ol *(9c)*

This is prepared from (4-[naphthalen-2-yloxy]phenyl)phenylmethanone **8c** as a pale brown glassy oil (87%), ν_{max} 3480, 3291, 1595, 1499, 1246, 1222 cm^{-1}, δ_H 2.72 (1H, s, alkyne-H), 2.78 (1H, bs, OH), 6.83 (3H, m, 3′,5′-H, 1″-H), 7.12 (3H, m, Ar-H), 7.34 (4H, m, Ar-H), 7.41 (2H, m, Ar-H), 7.48 (2H, m, Ar-H), 7.72 (1H, d, *J* 8.0, 8″-H†), 8.00 (1H, d, *J* 8.2, 5″-H†). Found: C, 85.6; H, 5.1; $C_{25}H_{18}O_2$ requires C, 85.7; H, 5.1%. [†indicates assignments may be reversed.]

3.4. General method for the preparation of linked prop-2-yn-1-ols

n-Butyllithium (1.6 M in hexanes) (29.7 mmol) was added slowly *via* syringe to a cold (−10 °C), stirred solution of trimethylsilylacetylene (29.7 mmol) in anhydrous tetrahydrofuran (THF) (100 mL) under nitrogen atmosphere. On completion of the addition (*ca.* 5 min) the cold solution was allowed to stir for 1 h. The benzophenone (11.9 mmol) was then added in a single portion and the mixture stirred until TLC examination of the reaction mixture indicated that none of the linked benzophenone remained (*ca.* 3 h). The reaction mixture was then re-cooled to 0 °C and a solution of methanolic potassium hydroxide was added (from potassium hydroxide (29.7 mmol) in methanol (20 mL)) in a single portion. The cooling bath was then removed and the mixture warmed to room temperature; after *ca.* 15 min, TLC examination indicated that removal of the trimethylsilyl group was complete. The mixture was acidified to pH ~ 7 using glacial acetic acid and then poured into water (500 mL). The organic layer was separated and the aqueous layer extracted with EtOAc (3 × 100 mL); the organic phases were combined, washed with water (3 × 50 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 samples were obtained by recrystallisation from hexane and EtOAc. The following alkynols were obtained in this way.

3.4.1. 1-(4-{6-[4-(1-Hydroxy-1-phenylprop-2-yn-1-yl)-phenoxy]naphthalene-2-yloxy}phenyl)-1-phenylprop-2-yn-1-ol *(9d)*

This is prepared from {4-[6-(4-benzoylphenoxy)naphthalen-2-yloxy]phenyl}phenylmethanone **8d** as pale brown microcrystals (52%), m.p. 150–152 °C, ν_{max} 3492, 3284, 1596, 1501, 1232, 1166 cm^{-1}, δ_H 2.27 (2H, br s, OH), 2.88 (2H, s, alkyne-H), 6.97 (4H, m, 3′,5′-H), 7.21 (2H, dd, *J* 8.8, 2.1, 3″,7″-H), 7.26 (2H, m, 4-H), 7.33 (6H, m, Ar-H), 7.59 (4H, m, 2′,6′-H), 7.65 (4H, m, Ar-H), 7.67 (2H, d, *J* 8.8, 4″,8″-H). Found: M^+ 572.1965; $C_{40}H_{28}O_4$ requires M^+ 572.1982.

*3.4.2. 1-(4-{7-[4-(1-Hydroxy-1-phenylprop-2-yn-1-yl)-phenoxy]naphthalene-2-yloxy}phenyl)-1-phenylprop-2-yn-1-ol **(9e)***

This is prepared from {4-[7-(4-benzoylphenoxy)naphthalen-2-yloxy]phenyl}phenylmethanone **8e** as pale brown microcrystals (95%), m.p. 90–92 °C, ν_{max} 3459, 3282, 1601, 1500, 1246, 1222 cm^{-1}, δ_H 2.74 (1H, s, alkyne-H), 2.76 (1H, s, alkyne-H), 2.80 (2H, br s, OH), 6.85 (4H, m, 3′,5′-H), 7.00 (4H, m, Ar-H), 7.14 (2H, m, 4-H), 7.20 (4H, m, Ar-H), 7.42 (4H, m, 3,5-H), 7.48 (4H, m, Ar-H), 7.63 (2H, m, Ar-H). Found: $[M + NH_4]^+$ 590.2329; $C_{40}H_{28}O_4$ requires $[M + NH_4]^+$ 590.2326.

*3.4.3. 1-(4-{3-[4-(1-Hydroxy-1-phenylprop-2-yn-1-yl)-phenoxy]naphthalene-2-yloxy}phenyl)-1-phenylprop-2-yn-1-ol **(9f)***

This is prepared from {4-[3-(4-benzoylphenoxy)naphthalen-2-yloxy]phenyl}phenylmethanone **8f** as a viscous orange gum (91%), ν_{max} 3467, 3290, 1604, 1498, 1466, 1255, 1210, 1167 cm^{-1}, δ_H 2.72 (2H, s, alkyne-H), 2.98 (2H, br s, OH), 6.75 (4H, m, 3′,5′-H), 7.13 (2H, m, 4-H), 7.19 (4H, m, Ar-H), 7.25 (2H, dd, *J* 8.2, 1.9, Ar-H), 7.28 (2H, s, 1″,4″-H), 7.37 (4H, m, 2′,6′-H), 7.45 (4H, m, Ar-H), 7.52 (2H, dd, *J* 8.2, 1.8, 5″,8″-H). Found: C, 83.5; H, 4.7; $C_{40}H_{28}O_4$ requires C, 83.9; H, 4.9%.

*3.4.4. 1-(4-{3-[4-(1-Hydroxy-1-phenylprop-2-yn-1-yl)-phenoxy]naphthalene-1-yloxy}phenyl)-1-phenylprop-2-yn-1-ol **(9g)***

This is prepared from {4-[3-(4-benzoylphenoxy)naphthalen-1-yloxy]phenyl}phenylmethanone **8g** as a pale brown gum (92%), ν_{max} 3481, 3279, 1597, 1496, 1214 cm^{-1}, δ_H 2.85 (1H, s, alkyne-H), 2.86 (1H, s, alkyne-H), 3.16 (2H, br s, OH), 6.71 (1H, d, *J* 2.2, 2″-H), 6.99 (5H, m, 3′,5′-H, 4″-H), 7.29 (6H, m, Ar-H), 7.38 (1H, m, Ar-H), 7.45 (1H, m, Ar-H), 7.58 (8H, m, Ar-H), 7.65 (1H, d, *J* 8.2, Ar-H), 8.12 (1H, d, *J* 8.3, 8″-H). This material was used directly in the preparation of the naphthopyran **10g**.

*3.4.5. 1-(4-{5-[4-(1-Hydroxy-1-phenylprop-2-yn-1-yl)-phenoxy]naphthalene-1-yloxy}phenyl)-1-phenylprop-2-yn-1-ol **(9h)***

This is prepared from {4-[5-(4-benzoylphenoxy)naphthalen-1-yloxy]phenyl}phenylmethanone **8h** as tan microcrystals (91%), m.p. 179–181 °C, ν_{max} 3482, 3289, 1599, 1497, 1403, 1249, 1219 cm^{-1}, δ_H 2.84 (2H, br s, OH), 2.88 (2H, s, alkyne-H), 7.00 (6H, m, 3′,5′-H, 2″-H, 6″-H), 7.29 (2H, m, Ar-H), 7.36 (6H, m, Ar-H), 7.57 (4H, m, Ar-H), 7.63 (4H, m, Ar-H), 7.93 (2H, d, *J* 8.6, 4″,8″-H). Found: M^+ 572.1971; $C_{40}H_{28}O_4$ requires M^+ 572.1982.

*3.4.6. 1-(4-{6-[4-(1-Hydroxy-1-phenylprop-2-yn-1-yl)-phenoxy]naphthalene-1-yloxy}phenyl)-1-phenylprop-2-yn-1-ol **(9i)***

This is prepared from {4-[6-(4-benzoylphenoxy)naphthalen-1-yloxy]phenyl}phenylmethanone **8i** as a pale brown gum (73%) as a mixture of diastereisomers, ν_{max} 3465, 3279, 1601, 1499, 1221 cm^{-1}, δ_H (all distinct signals) 2.87 (1H, s, alkyne-H), 2.88 (1H, s, alkyne-H), 3.19 (2H, br s, OH), 6.84 (1H, dd, *J* 7.6, 1.5 2″-H), 6.99 (4H, m, 3′,5′-H), 7.10 (2H, m, 4-H), 7.20 (1H, d, *J* 9.1, 2.4, 7″-H), 7.31 (7H, m, Ar-H), 7.43 (1H, d, *J* 8.3, 4″-H), 7.59 (7H, m, Ar-H), 8.04 (1H, d, *J* 9.0, 8″-H), 8.12 (1H, d, *J* 9.1, 8″-H). Found: M^+ 572.1976; $C_{40}H_{28}O_4$ requires M^+ 572.1982.

*3.4.7. 2,2′-Bis(1,1-(4-phenoxy)phenylprop-2-yn-1-ol)-1,1′-biphenyl **(9j)***

This is prepared from 2,2′-bis(4-benzoylphenoxy)-1,1′-biphenyl **8j** as a pale yellow viscous oil (75%) as a mixture of diastereoisomers, ν_{max} 3420, 3278, 1601, 1472, 1225, 756, 697 cm^{-1}, δ_H (all distinct signals) 2.85 (1H, s, alkyne-H), 2.99 (1H, s, alkyne-H), 3.01 (2H, br s, OH), 6.72 (4H, m, 3′,5′-H), 6.90 (2H, dd, *J* 8.4, 0.8, 3″-H), 7.12 (2H, m, 5″-H), 7.26 (6H, m, Ar-H), 7.33 (4H, m, Ar-H), 7.39 (4H, m, Ar-H), 7.56 (4H, m, Ar-H). Found: M^+, 598.2139; $C_{42}H_{30}O_4$ requires M^+, 598.2139.

*3.4.8. 1,3,5-Tris[4-(1-hydroxy-1-phenylprop-2-yn-1-yl)-phenoxy]benzene **(9k)***

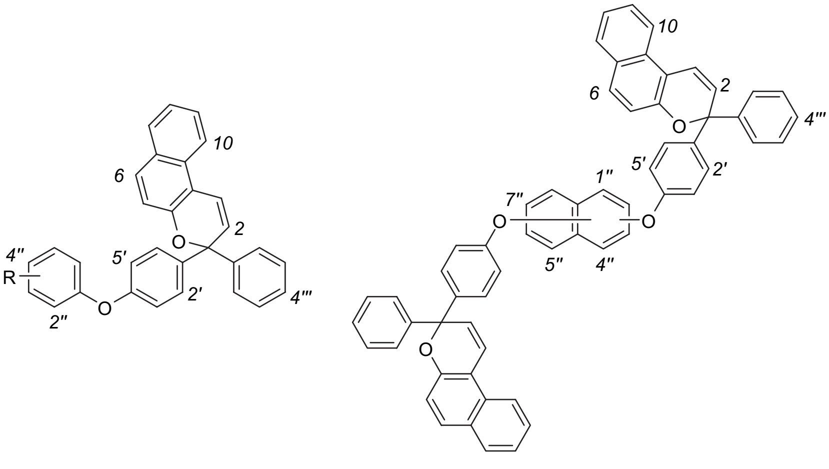
This is prepared from 1,3,5-tris(4-benzoylphenoxy)benzene **8k** and 3.5 equiv of LiTMSA as a brown gum (47%), δ_H 2.82 (3H, s, alkyne-H), 2.87 (3H, br s, OH), 6.33 (3H, s, 2″,4″,6″-H), 6.95 (6H, m, 3′,5′-H), 7.30 (9H, m, Ar-H), 7.52 (6H, m, Ar-H), 7.60 (6H, m, Ar-H). This material was used directly in the preparation of the naphthopyran **10k**.

3.5. General method for the preparation of simple 3H-naphtho[2,1-b]pyrans

A stirred solution of 2-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 heated under reflux until TLC indicated that none of the prop-2-yn-1-ol remained (*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 (40% ethyl acetate/hexane) to afford the naphthopyran. The following naphthopyrans were obtained using this protocol:

*3.5.1. 3-(4-Phenoxyphenyl)-3-phenyl-3H-naphtho[2,1-b]-pyran **(10a)***

This is prepared from 1-(4-phenoxyphenyl)-1-phenylprop-2-yn-1-ol **9a** as an orange glassy oil after elution from silica with 2% EtOAc/PhMe, (33%), ν_{max} 1601, 1501, 1242 cm^{-1}, δ_H 6.25 (1H, d, *J* 10.0, 2-H), 6.91 (2H, m, 3′,5′-H), 6.99 (2H, m, 2‴,6‴-H), 7.11 (1H, m, Ar-H), 7.19 (1H, d, *J* 8.8, 5-H), 7.32 (7H, m, Ar-H), 7.42 (2H, m, Ar-H), 7.46 (3H, m, Ar-H), 7.66 (1H, d, *J* 8.8, 6-H), 7.72 (1H, d, *J* 8.0, Ar-H),



Numbering system employed for ^{1}H NMR assignments

7.96 (1H, d, *J* 8.3, 10-H). Found: $M+H^+$, 427.1689; $C_{31}H_{22}O_2$ requires $M+H^+$, 427.1693.

3.5.2. 3-(4-(Naphthalen-1-yloxy)phenyl)-3-phenyl-3H-naphtho[2,1-b]pyran *(10b)*

This is prepared from 1-(4-(naphthalen-1-yloxy)phenyl)-1-phenylprop-2-yn-1-ol **9b** as orange microcrystals (65%), m.p. 142–144 °C, ν_{max} 1596, 1501, 1250, 1230 cm^{-1}, δ_H 6.25 (1H, d, *J* 9.9, 2-H), 6.95 (2H, m, 3′,5′-H), 7.32 (13H, m, Ar-H), 7.50 (2H, m, Ar-H), 7.65 (3H, m, Ar-H), 7.78 (2H, d, *J* 8.8, Ar-H), 7.94 (1H, d, *J* 8.4, 10-H). Found: C, 88.0; H, 5.1; $C_{35}H_{24}O_2$ requires C, 88.2; H, 5.0%.

3.5.3. 3-(4-(Naphthalen-2-yloxy)phenyl)-3-phenyl-3H-naphtho[2,1-b]pyran *(10c)*

This is prepared from 1-(4-(naphthalen-2-yloxy)phenyl)-1-phenylprop-2-yn-1-ol **9c** as cream microcrystals (68%), m.p. 131–133 °C, ν_{max} 1596, 1501, 1238 cm^{-1}, δ_H 6.24 (1H, d, *J* 9.9, 2-H), 6.97 (3H, m, 3′,5′-H), 7.20 (1H, d, *J* 8.8, 5-H), 7.25 (1H, m, Ar-H), 7.31 (5H, m, Ar-H), 7.45 (7H, m, Ar-H), 7.60 (1H, d, *J* 8.3, Ar-H), 7.65 (1H, d, *J* 8.8, Ar-H), 7.71 (1H, d, *J* 8.2, Ar-H), 7.84 (1H, d, *J* 8.7, Ar-H), 7.94 (1H, d, *J* 8.5, Ar-H), 8.14 (1H, d, *J* 8.2, 10-H). Found: C, 88.1; H, 5.0; $C_{35}H_{24}O_2$ requires C, 88.2; H, 5.0%.

3.6. General method for the preparation of linked 3H-naphtho[2,1-b]pyrans

A stirred solution of 2-naphthol (3.70 mmol) and the linked prop-2-yn-1-ol (1.85 mmol) in toluene (50 mL) was warmed to 50 °C. Acidic alumina (2.5 g) was added and the mixture was heated under reflux until TLC examination showed that none of the prop-2-yn-1-ol remained (*ca.* 2 h). The mixture was cooled to ~50 °C, filtered and the alumina was washed with hot toluene (2 × 20 mL). Removal of the toluene from the combined washings and filtrate gave a gum that was eluted from silica (40% ethyl acetate/hexane) to afford the naphthopyran. The following naphthopyrans were obtained using this protocol.

3.6.1. 2,6-Bis[4-(3-phenyl-3H-naphtho[2,1-b]pyran-3-yl)-phenoxy]naphthalene *(10d)*

This is prepared from 1-(4-{6-[4-(1-hydroxy-1-phenylprop-2-yn-1-yl)phenoxy]naphthalene-2-yloxy}phenyl)-1-phenylprop-2-yn-1-ol **9d** as orange microcrystals (77%), m.p. 117–119 °C, ν_{max} 1595, 1500, 1233 cm^{-1}, δ_H 6.24 (2H, d, *J* 9.9, 2-H), 6.96 (4H, m, 3′,5′-H), 7.21 (10H, m, Ar-H), 7.31 (8H, m, Ar-H), 7.43 (6H, m, Ar-H), 7.50 (4H, m, Ar-H), 7.64 (2H, m, Ar-H), 7.70 (2H, m, Ar-H), 7.94 (2H, m, 10-H). Found: C, 86.9; H, 4.7; $C_{60}H_{40}O_4$ requires C, 87.3; H, 4.9%.

3.6.2. 2,7-Bis[4-(3-phenyl-3H-naphtho[2,1-b]pyran-3-yl)-phenoxy]naphthalene *(10e)*

This is prepared from 1-(4-{7-[4-(1-hydroxy-1-phenylprop-2-yn-1-yl)phenoxy]naphthalene-2-yloxy}phenyl)-1-phenylprop-2-yn-1-ol **9e** as orange microcrystals (64%), m.p. 90–95 °C, ν_{max} 1632, 1601, 1499, 1244, 1224 cm^{-1}, δ_H 6.26 (2H, d, *J* 9.9, 2-H), 6.96 (4H, m, 3′,5′-H), 7.16 (8H, m, Ar-H), 7.28 (2H, m, Ar-H), 7.32 (8H, m, Ar-H), 7.47 (8H, m, Ar-H), 7.66 (2H, d, *J* 8.4, Ar-H), 7.72 (2H, d, *J* 8.2, Ar-H), 7.75 (2H, d, *J* 8.5, Ar-H), 7.96 (2H, d, *J* 8.4, 10-H). Found: $[M+H]^+$ 825.2979; C, 86.9; H, 4.9; $C_{60}H_{40}O_4$ requires $[M+H]^+$ 825.2999; C, 87.3; H, 4.9%.

3.6.3. 2,3-Bis[4-(3-phenyl-3H-naphtho[2,1-b]pyran-3-yl)-phenoxy]naphthalene *(10f)*

This is prepared from 1-(4-{3-[4-(1-hydroxy-1-phenylprop-2-yn-1-yl)phenoxy]naphthalene-2-yloxy}phenyl)-1-phenylprop-2-yn-1-ol **9f** as pale orange microcrystals (74%), m.p. 86–88 °C, ν_{max} 1632, 1591, 1500, 1467, 1260, 1216 cm^{-1}, δ_H 6.20 (2H, d, *J* 9.9, 2-H), 6.80 (4H, m, 3′,5′-H), 7.17 (4H, m, Ar-H), 7.26 (4H, m, Ar-H), 7.33 (12H, m, Ar-H), 7.46 (6H, m, Ar-H), 7.65 (4H, m, Ar-H), 7.71 (2H, m, Ar-H), 7.95 (2H, d, *J* 8.3, 10-H). Found: C, 87.3; H, 4.8; $C_{60}H_{40}O_4$ requires C, 87.3; H, 4.9%.

*3.6.4. 1,3-Bis[4-(3-phenyl-3H-naphtho[2,1-b]pyran-3-yl)-phenoxy]naphthalene **(10g)***

This is prepared from 1-(4-{3-[4-(1-hydroxy-1-phenylprop-2-yn-1-yl)phenoxy]naphthalene-1-yloxy}phenyl)-1-phenyl-prop-2-yn-1-ol **9g** as orange microcrystals (51%) as a mixture of diastereoisomers, m.p. 79–82 °C, ν_{max} 1629, 1598, 1495, 1215, 696 cm^{-1}, δ_H (all distinct signals) 6.19 (1H, d, *J* 9.9, 2-H), 6.20 (1H, d, *J* 9.9, 2-H), 6.74 (1H, d, *J* 2.2, 2″-H), 6.95 (4H, m, 3′,5′-H), 7.02 (2H, m, Ar-H), 7.15 (4H, m, Ar-H), 7.25 (6H, m, Ar-H), 7.41 (6H, m, Ar-H), 7.48 (4H, m, Ar-H), 7.60 (4H, m, Ar-H), 7.69 (4H, m, Ar-H), 7.90 (2H, d, *J* 8.5, 10-H), 8.10 (1H, d, *J* 8.2, 8″-H). Found: C, 87.1; H, 4.95; $C_{60}H_{40}O_4$ requires C, 87.3; H, 4.9%.

*3.6.5. 1,5-Bis[4-(3-phenyl-3H-naphtho[2,1-b]pyran-3-yl)-phenoxy]naphthalene **(10h)***

This is prepared from 1-(4-{5-[4-(1-hydroxy-1-phenylprop-2-yn-1-yl)phenoxy]naphthalene-1-yloxy}phenyl)-1-phenyl-prop-2-yn-1-ol **9h** as a glassy orange solid (56%), m.p. 88–93 °C, ν_{max} 1632, 1596, 1498, 1400, 1250, 1222 cm^{-1}, δ_H 6.25 (2H, d, *J* 10.0, 2-H), 6.97 (4H, m, 3′,5′-H), 7.19 (2H, d, *J* 8.9, 5-H), 7.24 (2H, m, Ar-H), 7.32 (8H, m, Ar-H), 7.43 (10H, m, Ar-H), 7.49 (4H, m, Ar-H), 7.65 (2H, d, *J* 8.9, Ar-H), 7.71 (2H, d, *J* 8.4, Ar-H), 7.90 (2H, d, *J* 8.5, 4″,8″-H), 7.95 (2H, d, *J* 8.4, 10-H). Found: C, 87.0, H, 4.8; $C_{60}H_{40}O_4$ requires C, 87.3; H, 4.9%.

*3.6.6. 1,6-Bis[4-(3-phenyl-3H-naphtho[2,1-b]pyran-3-yl)-phenoxy]naphthalene **(10i)***

This is prepared from 1-(4-{6-[4-(1-hydroxy-1-phenylprop-2-yn-1-yl)phenoxy]naphthalene-1-yloxy}phenyl)-1-phenyl-prop-2-yn-1-ol **9i** as orange microcrystals (54%) as a mixture of diastereoisomers, m.p. 64–67 °C (decomp.), ν_{max} 1499, 1222, 742, 696 cm^{-1}, δ_H 6.24 (1H, d, *J* 9.9, 2-H), 6.25 (1H, d, *J* 9.9, 2-H), 6.83 (1H, dd, *J* 8.2, 1.9, 2″-H), 6.97 (4H, m, 3′,5′-H), 7.08 (2H, m, Ar-H), 7.22 (3H, m, Ar-H), 7.31 (10H, m, Ar-H), 7.45 (8H, m, Ar-H), 7.64 (2H, m, Ar-H), 7.71 (2H, m, Ar-H), 7.78 (2H, m, Ar-H), 7.84 (1H, m, Ar-H), 7.94 (2H, m, 10-H), 8.11 (1H, d, *J* 9.1, 8″-H). Found: C, 87.0; H, 4.7; $C_{60}H_{40}O_4$ requires C, 87.3; H, 4.9%.

*3.6.7. 2,2′-Bis[4-(3-phenyl-3H-naphtho[2,1-b]pyran-3-yl)-phenoxy]1,1′-biphenyl **(10j)***

This is prepared from 1-(4-{2′-[4-(1-hydroxy-1-phenyl-prop-2-yn-1-yl)phenoxy]biphenyl-2-yloxy}phenyl)-1-phenyl-prop-2-yn-1-ol **9j** after elution from silica with 2% ethyl acetate in toluene, as pale yellow microcrystals as a mixture of diastereoisomers (31%), m.p. 85–95 °C, ν_{max} 1593, 1497, 1229 cm^{-1}, δ_H (all distinct signals) 6.15 (2H, d, *J* 9.9, 2-H), 6.18 (2H, d, *J* 9.9, 2-H), 6.71 (4H, m, 3′,5′-H), 6.83 (2H, d, *J* 8.4, 5-H), 7.05 (4H, m, H), 7.15 (4H, m, Ar-H), 7.22 (4H, m, Ar-H), 7.31 (10H, m, Ar-H), 7.44 (6H, m, Ar-H), 7.62 (2H, d, *J* 8.3, Ar-H), 7.69 (2H, d, *J* 8.0, Ar-H), 7.92 (2H, d, *J* 8.4, 10-H). Found: C, 87.5; H, 4.9; $C_{62}H_{42}O_4$ requires C, 87.5; H, 4.9%.

*3.6.8. Tris-1,3,5-[4-(3-phenyl-3H-naphtho[2,1-b]pyran-3-yl)phenoxy]benzene **(10k)***

This is prepared from 1,3,5-tris[4-(1-hydroxy-1-phenyl-prop-2-yn-1-yl)phenoxy]benzene **9k** and 3 equiv of 2-naphthol after elution from silica with 10% EtOAc/PhMe, as pale yellow microcrystals (17%), m.p. 154–156 °C, ν_{max} 1589, 1492, 1231 cm^{-1}, δ_H 6.21 (3H, d, *J* 9.9, 2-H), 6.35 (3H, s, 2″,4″,6″-H), 6.91 (6H, m, 3′,5′-H), 7.18 (3H, d, *J* 8.8, 5-H), 7.32 (15H, m, Ar-H, 1-H), 7.40 (6H, m, 2′,6′-H), 7.47 (9H, m, Ar-H), 7.64 (3H, d, *J*, 8.8, 6-H), 7.71 (3H, d, *J* 8.2, 7-H), 7.94 (3H, d, *J* 8.3, 10-H). Found: C, 86.6; H, 4.9; $C_{81}H_{54}O_6$ requires C, 86.6; H, 4.8%, this sample also gave an excellent correlation between the theoretical isotope pattern for the molecular ion (M^+ 1122.4) and that determined by MALDI spectrometry.

4. Conclusion

The nucleophilic displacement of fluoride from 4-fluorobenzophenone with di- and tri-hydroxy-benzenes and -naphthalenes in DMSO provides an efficient route to linked benzophenone scaffolds. Their subsequent treatment with LTMSA afforded the linked alkynols, which in turn gave the symmetrical photochromic linked bis- and tris-naphthopyrans (**10d–k**) in moderate yields on heating with 2-naphthol under heterogeneous acid catalysis. Comparison of the photochromic properties of **10d–k** with those of the simple naphthopyran analogues **10a–c** indicated that only marginally more intense colourability was observed, which is suggestive of only partial dual pyran ring-opening under the applied experimental conditions.

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