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SYNTHESIS OF GREEN COLORED PHOTOCHROMIC 6′-ARYLAMINO SPIRO [2H]NAPHTH[1,2-b]OXAZINES

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The published route to a series of 6′-arylamino substituted photochromic spirooxazines has been investigated with improvements made to perform the synthesis in satisfactory yield. The route has been exemplified with several novel derivatives prepared (including hydroxyl functionalised). Additionally, a one-pot procedure for the conversion of suitably functionalized 1,2-naphthoquinones into the photochromic compounds is reported.

Keywords: Photochromic; photochromism; spirooxazine

INTRODUCTION

Spirooxazines are an important class of photochromic dye which on irradiation with ultraviolet light undergo a reversible colour change (Scheme 1) from the colourless spirocyclic form, **1** to the coloured merocyanine form, **2**.[1,2] Amongst the spirooxazines in commercial use the 6′-arylamino compounds exemplified by commercially available material **3** (Fig. 1), Reversacol aqua green,[3] are of interest due to their green coloration upon exposure to UV light. These compounds were first disclosed by Rickwood et al.,[4] however, the regiochemistry of the spirooxazine substituents was incorrectly assigned and the correct structures were later published by Clarke and coworkers.[3] The focus of our research involves the attachment of polymers to photochromic dyes in order to control their switching speed in polymer matrices.[5–14] Thus, the preparation of hydroxyl functionalised photochromic dyes is a key requirement. However, during the course of this work we encountered difficulty in reproducing the published syntheses of the 6′-arylamino spirooxazines. This prompted a study of the synthesis of these green spirooxazines, both with and without hydroxyl functionalisation, the results of which are presented herein.

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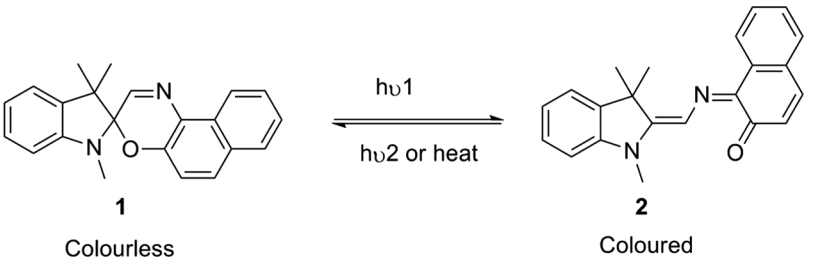


Scheme 1. Photochromic isomerisation of a spirooxazine.

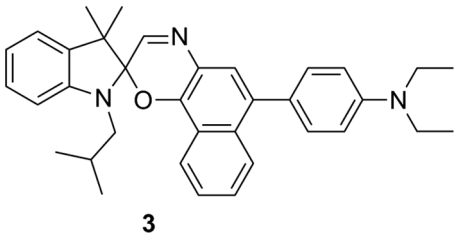
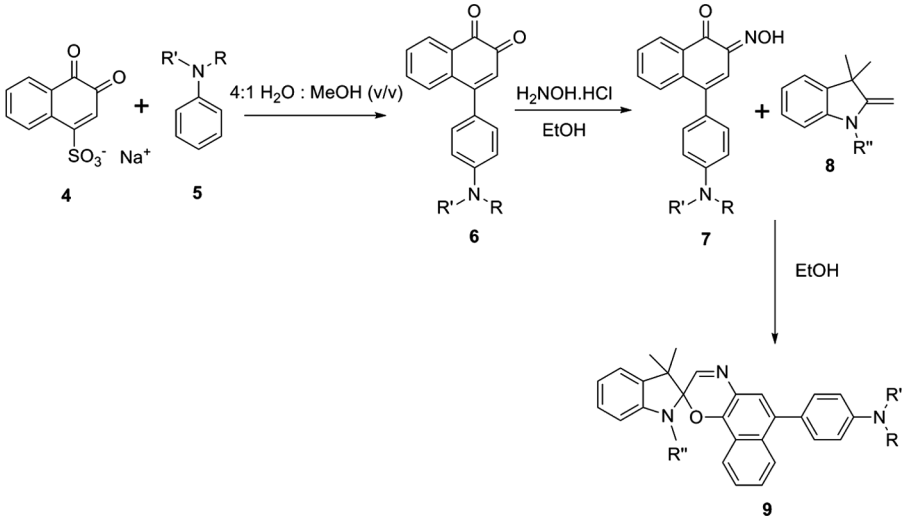


Figure 1. Reversacol aqua green.

RESULTS AND DISCUSSION

The published synthesis of the 6′-arylamino spirooxazines begins with the reaction of a suitably substituted aniline with Folin's reagent (1,2-naphthoquinone-4-sulfonate, **4**) to yield the corresponding 4-substituted naphthoquinone, **6**. This is then converted to the oxime, **7**, which on reaction with a methyleneindoline, **8** gives the spirooxazine product, **9** (Scheme 2).[3]



Scheme 2. Synthesis of 6′-arylamino spirooxazines, **9**.

Arylation of Folin's Reagent

The arylation of Folin's reagent, **4**, with anilines to give 4-arylamino naphthoquinones, **6**, is a process that has been reported to proceed in the presence of stoichiometric nickel[15] and more recently in the absence of metals.[4] The published procedure reports the dropwise addition of a methanolic solution of *N,N*-diethylaniline to an equimolar solution of Folin's reagent in 4:1 water:methanol. After stirring for 24 hours at room temperature the product was obtained by filtration, washing with water and air drying in 42% yield.[3] In our hands, however, attempts to repeat this process gave a precipitate containing significant amounts of water and 35% of the starting aniline by mass. After chromatography a 30% yield of the arylated naphthoquinone was obtained (Table 1, Entry 1a). In order to remove the need for chromatography the mixture of Folin's reagent and N,N-diethylaniline was heated to 60 °C for 18 hours before removal of the methanol *in vacuo* and cooling in an ice bath. Filtration of the precipitate and oven drying gave the pure product in 48% yield (Table 1, Entry 1b). These conditions were also used to arylate Folin's reagent with two further anilines (Table 1, Entries 2 and 3).

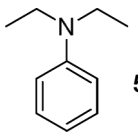
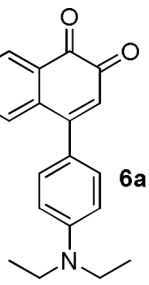
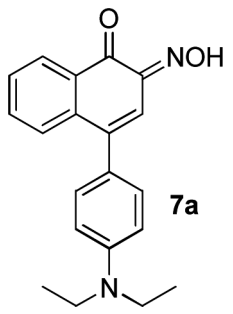
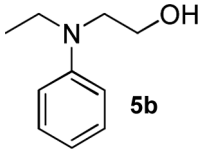
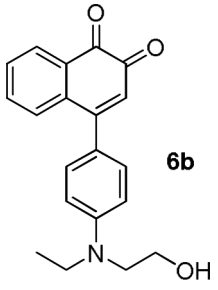
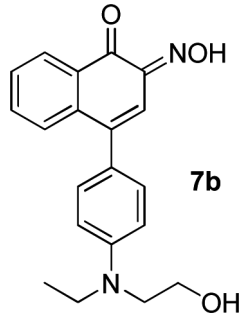
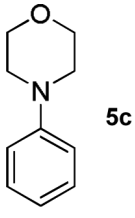
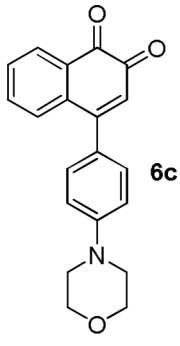
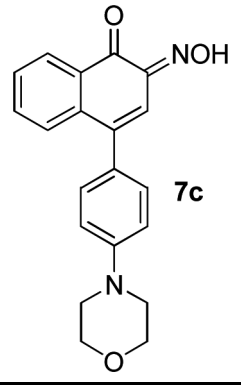
Oxime Formation

The published procedure for the conversion of naphthoquinone, **6a** into oxime, **7a** calls for the addition of 4 molar equivalents of hydroxylamine hydrochloride to an anhydrous ethanolic solution of the naphthoquinone. The mixture is then refluxed until the reaction is complete by thin layer chromatography, cooled, diluted with water and the oxime collected in 75% yield by filtration and water washing.[3] Unfortunately, attempts to repeat this procedure failed, with refluxing the solution even for a short time (1 h) leading to the isolation of an impure product containing predominantly bis oxime material, **10** (Fig. 2), which failed to react to give any photochromic product in the next stage. If the reaction was performed at room temperature a small amount of the correct product, **7a** (10%) could be obtained by filtration. It is proposed that the low yield was a result of the product being retained in the mother liquor. Attempts to improve the isolated yield of the product by filtration of the reaction mixture without the addition of water, and washing the precipitate with ether lead to the isolation of hydrochloride salt, **11** (Fig. 2) as the main product, albeit in increased yield (70%). The salt was unreactive in the following stage of the synthesis. The desired oxime could be isolated in essentially quantitative yield by stirring a mixture of the starting naphthoquinone and 2 molar equivalents of hydroxylamine hydrochloride in ethanol at room temperature for 1 hour, followed by evaporation, partitioning between water and ethyl acetate and basification of the aqueous phase (Table 1, Entry 1b). Two further novel oximes were also prepared in this manner (Table 1, Entries 2–3).

Spirooxazine Formation

The formation of photochromic spirooxazines by the condensation of nitrosonaphthols (or their oxime tautomers) with methyleneindoline compounds is a well known process.[1] The synthesis of Reversacol aqua green, **3** requires the reaction

Table 1. Arylation of Folin's reagent and subsequent oxime formation

Entry	Aniline	Product	Yield (%)[a]	Oxime	Yield (%)[a]
1a	 **5a**	 **6a**	30[b]	 **7a**	>95
1b			48[c]		
2	 **5b**	 **6b**	54[c]	 **7b**	>95
3	 **5c**	 **6c**	45[c]	 **7c**	90

[a]Isolated yield.
[b]Reaction performed at room temperature for 24 h followed by chromatographic purification.
[c]Reaction performed at 60 °C for 18 h followed by precipitation.

between oxime, **7a** and 1-isobutyl-3,3-dimethyl-2-methyleneindoline, **8a** which is synthesized as outlined in Scheme 3. The formation of intermediate indolenium iodide **13** is reported to occur in 85% yield after heating a *n*-butanol solution of starting indolenine **12** with isobutyl iodide in an autoclave at 125–130 °C.[16] In our hands, this procedure gave material contaminated with approximately 20% of a related indolenium iodide (thought to be a butyl impurity arising from reaction with the

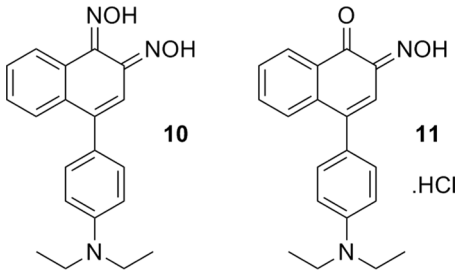
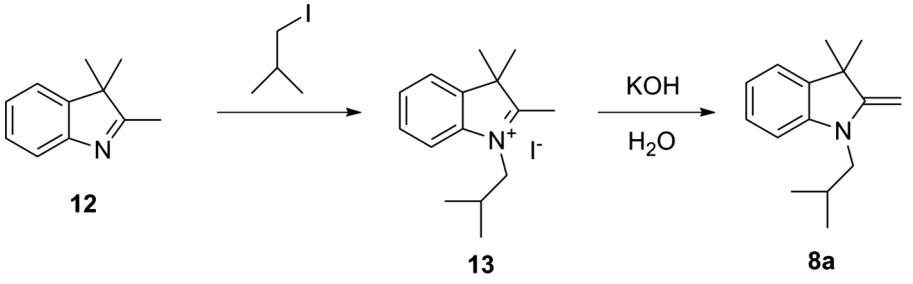


Figure 2. Impurities formed during the synthesis of oxime **7**.

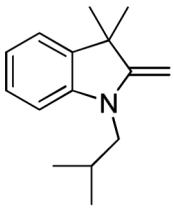
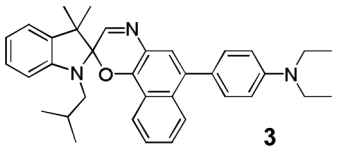
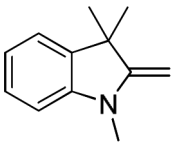
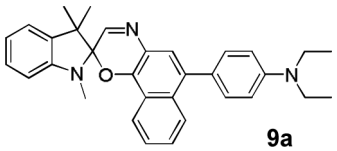
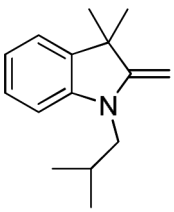
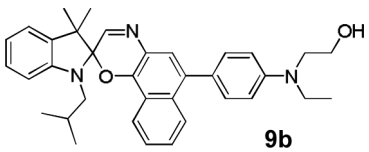
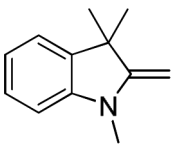
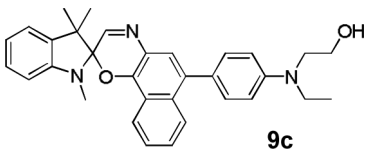
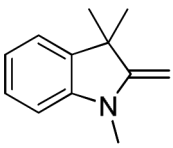
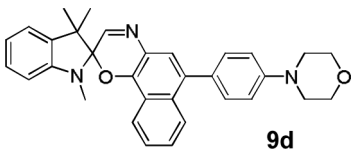
solvent). As this impurity is very closely related to the desired product and reacts in an identical fashion we were not successful in removing this impurity from either the salt, **13** or indeed any of the following synthetic steps in the synthesis of **3**, making this route unsuitable for the synthesis of pure spirooxazines. The use of solvent free conditions or 1,4-dioxane as solvent, however, gave material free from the related impurity, albeit in lower yield. This was then converted with base to pure methyleneindoline, **8a** in 30% (1,4-dioxane) or 18% (solvent free) overall yield.

The condensation between **7a** and **8a** is reported to proceed in 66% yield when an equimolar solution of the reagents in anhydrous ethanol is heated to reflux until complete by TLC. The mixture is then cooled, reduced in volume and the product collected by filtration and washing with a little cold ethanol.[3] Unfortunately we were unable to obtain pure material on repetition of this method, as in our experience the reaction never proceeded to completion by TLC and prolonged heating for greater than 24 h seemed to result in product decomposition. After heating for 22 h a small amount of highly impure aqua green, **3** could be isolated by precipitation in the fashion described although this readily dissolved on washing with ethanol. Evaporation of the filtrates and purification by column chromatography gave 33% of the desired product (Table 2, Entry 1a). This could be increased to 58% by performing the reaction at 100 °C in a sealed tube for 3 h (Table 2, Entry 1b). Improvements in yield for reactions in a sealed tube were also observed when methyleneindoline, **8a** was replaced with 1,3,3-trimethyl-2-methyleneindoline, **8b** (Table 2, Entries 2a vs. 2b). Interestingly, the presence of a free hydroxyl group in the aniline portion of the starting materials gave an increased yield of the final spirooxazine (Table 2, Entries 3 and 4). However, the electronically similar morpholino



Scheme 3. Synthesis of 1-isobutyl-3,3-dimethyl-2-methyleneindoline, **8a**.

Table 2. Synthesis of spirooxazines

Entry	Oxime	Indoline	Product	Yield (%)[a]
1a	**7a**	 **8a**	 **3**	33[b]
1b				58[c]
2a	**7a**	 **8b**	 **9a**	52[b]
2b				68[c]
3	**7b**	 **8a**	 **9b**	84[c]
4a	**7b**	 **8b**	 **9c**	82[c]
4b				73[d]
5	**7c**	 **8b**	 **9d**	40[c]

[a]Isolated yield.
[b]Reaction performed at reflux for 22 h followed by chromatographic purification.
[c]Reaction performed at 100 °C in a sealed tube for 3 h followed by chromatographic purification.
[d]Reaction performed at 100 °C in a sealed tube for 3 h followed by precipitation.

functionalised spirooxazine, **9d** was only obtained in a relatively poor 40% yield (Table 2, Entry 5).

One-Pot Oxime/Spirooxazine Formation

In an effort to speed the discovery and synthesis of new spirooxazine dyes a one-pot oxime/spirooxazine formation process was developed using naphthoquinone, **6a** and methyleneindoline, **8b** as substrates to give spirooxazine, **9a** (Table 3). In agreement with observations made during the oxime formation,

Table 3. One-pot oxime/spirooxazine formation

Entry	Solvent	Additive	Conditions	Yield (%)[a]
1	EtOH	None	70 °C, 4 h	13[b]
2	EtOH	Et_3N (1eq.)	70 °C, 3 h	18[b]
3	EtOH	K_2CO_3 (1 eq.)	70 °C, 3 h	45[b]
4	EtOH	K_2CO_3 (1 eq.)	80 °C, 4 h	46[c]
5	EtOH	NaOAc (1 eq.)	80 °C, 5 h	24[b]
6	EtOH	NaOAc (2 eq.)	80 °C, 5 h	49[b]
7	IPA	K_2CO_3 (1 eq.)	80 °C, 3 h	15[b]
8	CH_3CN	K_2CO_3 (1 eq.)	70 °C, 4 h	<10[d]
9	Toluene	K_2CO_3 (1 eq.)	70 °C, 4 h	<10[d]
10	EtOH	K_2CO_3 (1 eq.)	100 °C, 3 h	34[e]
11	EtOH	K_2CO_3 (1 eq.)	100 °C, 3 h	25[f]

[a]Isolated yield.
[b]**6a** (1 eq.) and $NH_3OH.Cl$ (1.1 eq.) were stirred at RT for 1 h. **8b** (1.3 eq.) and additive added, then the mixture was heated as indicated.
[c]**6a** (1 eq.), **8a** (1.3 eq.), $NH_3OH.Cl$ (1.1 eq.) and additive were stirred at RT for 1 h, then the mixture was heated as indicated.
[d]**6a** (1 eq.), $NH_3OH.Cl$ (1.1 eq.) and additive were stirred at RT for 1 h. **8b** (1.3 eq.) added, then the mixture was heated as indicated.
[e]As [b]but **6b** used as starting material to yield **9c**.
[f]As [b]but **6c** used as starting material to yield **9d**.

reaction in the absence of a base or buffer proceeded in poor yield (Table 3, Entry 1). This could, however, be improved to approximately 50% by the addition of either K_2CO_3 (Table 3, Entry 3) or NaOAc (Table 3, Entry 6). While this is somewhat lower than the 68% obtained when the reactions are performed in a stepwise fashion, the reaction sequence as a whole can be performed in a much more efficient manner. Reaction in a number of alternative solvents failed to increase the yield observed and indeed resulted in a large drop in the isolated yield of the final product (Table 3, Entries 7–9). The one-pot scheme was also performed successfully in the synthesis of two further spirooxazines (Table 3, Entries 10–11).

CONCLUSION

In conclusion, the published synthesis of spirooxazine photochromic dye, **3** and related compounds was investigated and improvements necessary to perform the synthesis in a satisfactory yield were made. A one-pot oxime/spirooxazine formation was also developed that allows the removal of a synthetic step from the process and may be of use in the discovery of novel dyes. Synthesis of hydroxyl functionalised green spirooxazines was achieved in very high yields and a report on the effect of polymer conjugation to these dyes will be published elsewhere.

EXPERIMENTAL

All starting materials were purchased from Sigma-Aldrich and used without further purification with the exception of hydroxylamine hydrochloride which was

recrystallised from aqueous 75% ethanol[17] and 1,3,3-trimethyl-2-methyleneindoline which was distilled under reduced pressure. Melting points were obtained using a Gallenkamp capillary melting point apparatus and are uncorrected. NMR data were collected on Bruker Av200 (200 MHz) or Bruker Av400 (400 MHz) spectrometers. Unless otherwise specified $CDCl_3$ was used as the solvent. Positive ion EI mass spectra were run on a ThermoQuest MAT95XL mass spectrometer using an ionization energy of 70 eV.

4-(4-(Diethylamino)phenyl)naphthalene-1,2-dione (6a): General Procedure for the Arylation of Folin's Reagent

A suspension of 1,2-napthoquinone-4-sulfonic acid sodium salt, **4** (8.00 g, 30.7 mmol) in a 9:1 mixture of water:MeOH (180 mL) was treated in one portion with *N,N*-diethylaniline (4.59 g, 30.7 mmol) and stirred at 60 °C for 18 h. The mixture was then cooled, the MeOH removed *in vacuo* and the resulting suspension filtered. The precipitate was then washed with water and oven dried at 50 °C to give the title product as a dark purple solid (4.50 g, 48%). ^{1}H NMR data were identical to those reported in the literature.[18]

4-(4-(Ethyl(2-hydroxyethyl)amino)phenyl)naphthalene-1,2-dione (6b). Was obtained as a dark purple solid (6.80 g, 54%). Mp 161–163 °C (dec). ^{1}H NMR (400 MHz); δ8.20 (dd, 1H, $J = 1.3$ and 7.5 Hz), 7.61–7.50 (m, 3H), 7.40 (d, $J = 8.8$ Hz, 2H), 6.84 (d, 2H, $J = 8.8$ Hz), 6.43 (s, 1H), 3.89 (q, $J = 3.9$ Hz, 2H), 3.60–3.50 (m, 4H), 1.63 (t, $J = 5.7$ Hz, 1H) and 1.25 (t, $J = 7.1$ Hz, 3H). MS (EI); $m/z = 321$ [M^+].

4-(4-Morpholinophenyl)naphthalene-1,2-dione (6c). Was obtained as a red solid (0.26 g, 45%). Mp 170–172 °C. ^{1}H NMR (200 MHz); δ8.20 (dd, 1H, $J = 1.6$ and 7.1 Hz), 7.63–7.38 (m, 5H), 6.99 (d, 2H, $J = 8.7$ Hz), 6.43 (s, 1H), 3.90 (t, $J = 4.9$ Hz, 4H) and 3.29 (t, $J = 4.9$ Hz, 4H). MS (EI); $m/z = 319$ [M^+].

4-(4-(Diethylamino)phenyl)-2-(hydroxyimino)naphthalen-1(2h)-one (7a): General Procedure for Oxime Formation

A suspension of 4-(4-(diethylamino)phenyl)naphthalene-1,2-dione **6a** (3.00 g, 9.84 mmol) in absolute ethanol (75 mL) was treated in one portion with hydroxylamine hydrochloride (1.37 g, 19.67 mmol) and stirred at room temperature for 1 h. The mixture was then evaporated *in vacuo* and the residue suspended in H_2O (100 mL). The aqueous phase was then basified to pH10 with ammonium hydroxide solution and extracted into EtOAc (x4). The combined organic phases were then dried (Na_2SO_4) and evaporated *in vacuo* to afford the title compound as a dark red solid (3.15 g, >95%). Mp 165–168 °C (dec.) (lit. 176–178 °C).[3] ^{1}H NMR (200 MHz, d6 DMSO); δ8.12 (dd, 1H, $J = 1.3$ and 7.6 Hz), 7.70–7.45 (m, 3H), 7.25 (d, $J = 8.7$ Hz, 2H), 6.91 (s, 1H), 6.74 (d, $J = 8.7$ Hz, 2H), 3.36 (q, $J = 6.9$ Hz, 4H) and 1.10 (t, $J = 6.9$ Hz, 6H). MS (EI); $m/z = 320$ [M^+].

4-(4-(Ethyl(2-hydroxyethyl)amino)phenyl)-2-(hydroxyimino)naphthalen-1(2h)-one (7b). Was obtained as a dark red solid (9.10 g, >95%). Mp 180–181 °C.

^{1}H NMR (200 MHz, d6 DMSO); δ8.12 (dd, 1H, $J = 1.2$ and 7.6 Hz), 7.71–7.40 (m, 3H), 7.25 (d, $J = 8.5$ Hz, 2H), 6.90 (s, 1H), 6.76 (d, 2H, $J = 8.6$ Hz), 3.60–3.30 (m, 6H) and 1.10 (t, $J = 6.8$ Hz, 3H). MS (EI); m/z = 336 [M^+].

2-(Hydroxyimino)-4-(4-morpholinophenyl)naphthalen-1(2H)-one (7c). Was obtained as a red solid (0.11 g, 90%). Mp 104–107 °C (dec.). ^{1}H NMR (200 MHz, d6 DMSO); δ8.13 (dd, 1H, $J = 1.3$ and 7.8 Hz), 7.70–7.30 (m, 5H), 7.05 (d, $J = 8.7$ Hz, 2H), 6.92 (s, 1H), 3.75 (t, $J = 4.6$ Hz, 4H) and 3.18 (t, $J = 4.7$ Hz, 4H). MS (EI); m/z = 334 [M^+].

1-Isobutyl-3,3-dimethyl-2-methyleneindoline (8a). A mixture of 2,3,3-trimethylindolenine (3.15 g, 19.78 mmol) and 1-iodo-2-methylpropane (3.44 mL, 29.70 mmol) in 1,4-dioxane were heated in a sealed tube at 115 °C for 72 h. The mixture was then cooled, poured into Et_2O (150 mL) and the liquors decanted. The residue was then washed with three further Et_2O portions and dried *in vacuo*. The residual hygroscopic purple glass was suspended in H_2O (100 mL), treated with KOH (1.12 g, 19.83 mmol) and stirred rapidly at room temperature for 30 min after which time the mixture was extracted with Et_2O (x3), dried with Na_2SO_4 and evaporated to a brown oil which was purified by column chromatography eluting with 0–10% v/v EtOAc/petroleum ether 40–60 to afford the title product as an orange oil (1.28 g, 30%) which was stored in a freezer until used. ^{1}H NMR (200 MHz); δ 7.14–7.06 (m, 2H), 6.74 (t, $J = 7.7$ Hz, 1H), 6.54 (d, $J = 7.6$ Hz, 1H), 3.85 (dd, $J = 1.8$ and 8.7 Hz, 2H), 3.29 (d, $J = 7.5$ Hz, 2H), 2.21 (septet, $J = 6.9$ Hz, 1H), 1.34 (s, 6H) and 0.95 (d, $J = 6.7$ Hz, 6H).

2-(Ethyl(4-(1,3,3-trimethylspiro[indoline-2,2′-naphtho[1,2-b][1,4]oxazine]-6′yl)phenyl)amino)ethanol (9c): General Procedure for Spirooxazine Formation

A suspension of 4-(4-(ethyl(2-hydroxyethyl)amino)phenyl)-2-(hydroxyimino) naphthalen-1(2H)-one, **7b** (4.00 g, 11.89 mmol) in anhydrous ethanol (100 mL) was treated with 1,3,3-trimethyl-2-methyleneindoline, **8b** (2.68 g, 15.46 mmol) in one portion and heated to 100 °C in a sealed tube for 3 h. The mixture was then cooled to room temperature and left to stand overnight. The resulting suspension was evaporated *in vacuo* to approx. 25 mL total volume, MeOH added (25 mL) and the mixture stored in the freezer for 3 hrs. After this time the product was collected by filtration and washed with a little MeOH to afford the title compound as pale green fibres (4.15 g, 73%). Mp 174–175 °C. ^{1}H NMR (200 MHz); δ 8.10–7.88 (m, 2H), 7.72 (s, 1H), 7.49 (s, 1H), 7.42–7.19 (m, 5H), 7.12 (d, $J = 6.9$ Hz, 1H), 6.96–6.83 (m, 3H), 6.60 (d, $J = 7.7$ Hz, 1H), 3.87 (q, $J = 4.8$ Hz, 2H), 3.60–3.20 (m, 4H), 2.78 (s, 3H), 1.83 (t, $J = 5.7$ Hz, 1H), 1.39 (d, $J = 3.7$ Hz, 6H) and 1.25 (t, $J = 7.0$ Hz, 3H). MS (EI); m/z = 491 [M^+].

N,N-diethyl-4-(1-isobutyl-3,3-dimethylspiro[indoline-2,2′-naphtho[1,2-b][1,4]oxazine]-6′-yl)aniline (3). Was obtained as a green solid (0.17 g, 58%) after purification by column chromatography eluting with 0–5% v/v EtOAc/petroleum ether 40–60. Mp 161–163 °C (lit. 166.5–168.5 °C).[3] ^{1}H NMR (200 MHz); δ8.06–7.94 (m, 2H), 7.72 (s, 1H), 7.47 (s, 1H), 7.42–7.17 (m, 5H), 7.09 (dd, $J = 1.1$ and

6.9 Hz, 1H), 6.93–6.77 (m, 3H), 6.61 (d, $J = 7.7$ Hz, 1H), 3.44 (q, $J = 7.1$ Hz, 4H), 3.10–2.86 (m, 2H), 2.19–1.97 (m, 1H), 1.39 (d, $J = 2.1$ Hz, 6H), 1.24 (t, $J = 7.1$ Hz, 6H) and 0.95 (dd, $J = 6.6$ and 10.5 Hz, 6H). MS (EI); m/z = 517 [M^+].

N,N-Diethyl-4-(1,3,3-trimethylspiro[indoline-2,2′-naphtho[1,2-b][1,4] oxazine]-6′-yl)aniline (9a). Was obtained as a light green foam (0.10 g, 68%) after purification by column chromatography eluting with 0–3% v/v EtOAc/petroleum ether 40–60. Mp 128–131 °C. ^{1}H NMR (200 MHz); 8.07–7.94 (m, 2H), 7.72 (s, 1H), 7.49 (s, 1H), 7.42–7.18 (m, 5H), 7.11 (d, $J = 7.2$ Hz, 1H), 6.95–6.77 (m, 3H), 6.60 (d, $J = 7.8$ Hz, 1H), 3.44 (q, $J = 7.1$ Hz, 4H), 2.80 (s, 3H), 1.39 (d, $J = 3.5$ Hz, 6H) and 1.24 (t, $J = 7.0$ Hz, 6H). δ MS (EI); m/z = 475 [M^+].

2-(Ethyl(4-(1-isobutyl-3,3-dimethylspiro[indoline-2,2′-naphtho[1,2-b][1,4] oxazine]-6′-yl)phenyl)amino)ethanol (9b). Was obtained as a light green foam (1.60 g, 84%) after purification by column chromatography eluting with 10–50% v/v EtOAc / petroleum ether 40–60. Mp 180–183 °C (dec.). ^{1}H NMR (200 MHz); 8.06–7.89 (m, 2H), 7.73 (s, 1H), 7.46 (s, 1H), 7.39–7.29 (m, 4H), 7.19 (dd, $J = 1.2$ and 7.6 Hz, 1H), 7.10 (d, $J = 6.4$ Hz, 1H), 6.91–6.81 (m, 3H), 6.62 (d, $J = 7.8$ Hz, 1H), 3.89 (q, $J = 5.8$ Hz, 2H), 3.58–3.45 (m, 4H), 3.10–2.80 (m, 2H), 2.19–2.00 (m, 1H), 1.39 (d, $J = 2.1$ Hz, 6H), 1.24 (t, $J = 7.0$ Hz, 3H) and 0.95 (dd, $J = 6.6$ and 10.6 Hz, 6H). δ MS (EI); m/z = 533 [M^+].

1,3,3-Trimethyl-6′-(4-morpholinophenyl)spiro[indoline-2,2′-naphtho[1,2-b][1,4]oxazine] (9d). Was obtained as a pale brown foam (0.05 g, 40%) after purification by column chromatography eluting with 0–25% v/v EtOAc/petroleum ether 40–60. Mp 200–204 °C. ^{1}H NMR (200 MHz); 8.08–8.03 (m, 1H), 7.89–7.85 (m, 1H), 7.72 (s, 1H), 7.48 (s, 1H), 7.44–7.31 (m, 4H), 7.25–6.84 (m, 5H), 6.60 (d, $J = 7.7$ Hz, 1H), 3.91 (t, $J = 4.8$ Hz, 4H), 3.26 (t, $J = 4.8$ Hz, 4H), 2.80 (s, 3H) and 1.39 (d, $J = 3.3$ Hz, 6H). δ MS (EI); m/z = 489 [M^+].

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REFERENCES

1. Lokshin, V.; Samat, A.; Metelitsa, A. V. Spirooxazines: Synthesis, structure, spectral and photochromic properties. *Russ. Chem. Rev.* **2002**, *71*, 893–916.
2. Bouas-Laurent, H.; Durr, H. Organic photochromism. *Pure Appl. Chem.* **2001**, *73*, 639–665.
3. Clarke, D. A.; Heron, B. M.; Gabbutt, C. D.; Hepworth, J. D.; Partington, S. M.; Corns, S. N. Photochromic compounds. U.S. Patent 6,303,673, Oct. 16, 2001.
4. Rickwood, M.; Marsden, S. D.; Askew, V. E. Photochromic spiroxazine compounds. U.S. Patent 5,446,150, Apr. 29, 1995.
5. Ercole, F.; Davis, T. P.; Evans, R. A. Comprehensive modulation of naphthopyran photochromism in a rigid host matrix by applying polymer conjugation. *Macromolecules* **2009**, *42*, 1500–1511.

6. Malic, N.; Campbell, J. A.; Evans, R. A. Superior photochromic performance of napthopyrans in a rigid host matrix using polymer conjugation: Fast, dark and tuneable. *Macromolecules* **2008**, *41*, 1206–1214.
7. Such, G. K.; Evans, R. A.; Davis, T. P. The use of block copolymers to systematically modify photochromic behaviour. *Macromolecules* **2006**, *39*, 9562–9570.
8. Malic, N.; Evans, R. A. Synthesis of carboxylic acid and ester mid-functionalized polymers using RAFT polymerization and ATRP. *Aust. J. Chem.* **2006**, *59*, 763–771.
9. Such, G. K.; Evans, R. A.; Davis, T. P. Rapid photochromic switching in a rigid polymer matrix using living radical polymerisation (ATRP). *Macromolecules* **2006**, *39*, 1391–1396.
10. Evans, R. A.; Such, G. K. Research trends in photochromism: Control of photochromism in rigid polymer matrices and other advances. *Aust. J. Chem.* **2005**, *58*, 825–830.
11. Evans, R. A.; Hanley, T. L.; Skidmore, M. A.; Davis, T. P.; Such, G. K.; Yee, L. H.; Ball, G. E.; Lewis, D. A. The generic enhancement of photochromic dye switching speeds in rigid polymer matrices. *Nat. Mater.* **2005**, *4*, 294–253.
12. Such, G. K.; Evans, R. A.; Davis, T. P. Tailoring photochromic performance of polymer-dye conjugates using living radical polymerization (ATRP). *Liq. Cryst. Mol. Cryst.* **2005**, *430*, 273–279.
13. Such, G.; Evans, R. A.; Davis, T. P. Control of photochromism through local environment effects using living radical polymerisation. *Macromolecules* **2004**, *37*, 9664–9666.
14. Such, G.; Evans, R. A.; Yee, L. H.; Davis, T. P. Factors influencing photochromism of spiro—compounds with polymeric matrices. *J. Macromol. Sci. Part C Polymer Reviews* **2003**, *C43*, 547.
15. Yoshida, K.; Koujiri, T.; Oga, N.; Ishiguro, M.; Kubo, Y. The effect of metal chelate complexation on the reactivity and absorption spectra of 1,2-naphthoquinones: The synthesis of new types of near i.r. absorbing dyes. *J. Chem. Soc., Chem. Commun.* **1989**, 708–710.
16. Arsenov, V. D.; Gorelik, A. M.; Strokach, Y. P.; Barachevsky, B. A.; Alfimov, M. V. 1-N-alkyl-5′-[(N'-(un)substituted)amido]spiroindolino naphthoxazines, their preparation, compositions and (co)polymer matrices containing them. European Patent 1044978, Oct. 18, 2000.
17. Armarego, W. L. F.; Perrin, D. D. *Purifcation of Laboratory Chemicals*; Butterworth Heinemann: Oxford, 1997.
18. Ooyama, Y.; Nagano, S.; Okamura, M.; Yoshida, K. Solid-State Fluorescence changes of 2-(4-cyanophenyl)-5-[4-(diethylamino)-phenyl]-3*H*-imidazo[4,5-*a*]naphthalene upon inclusion of organic solvent molecules. *Eur. J. Org. Chem.* **2008**, 5899–5906.