Synthesis of stereochemically-biassed spiropyrans by microwave-promoted, one-pot alkylation-condensation

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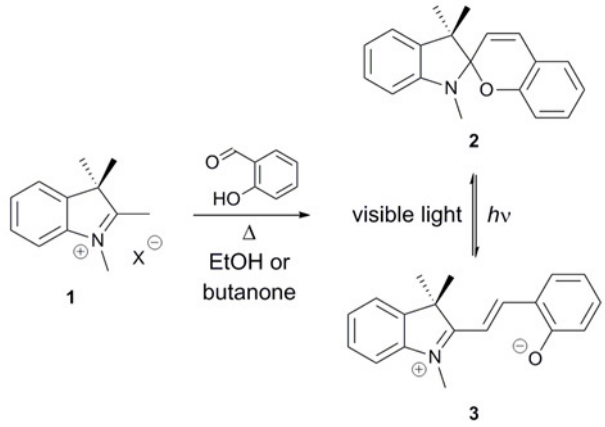
Abstract
A microwave-assisted, two-step, one-pot synthesis of spiropyrans has been developed. This process was used to synthesise a range of sterically-congested spiropyrans from readily available precursors, employing environmentally benign solvents. The unusual substituent pattern possessed by these structures has been shown to influence the stereoselectivity of spiropyran ring-closure.

Introduction
Spiropyrans (e.g. **2**, Scheme 1) are a class of spiro-fused indolochromene that exist in photo-controlled equilibrium with their corresponding merocyanine isomer (e.g. **3**).[1] The profound structural, electronic and optical differences between these isomers, and the controllable nature of this equilibrium, have lead to their widespread use in switching and sensing applications.[2-5]



Scheme 1 – General synthesis and isomerisation of spiropyrans

Spiropyran synthesis is commonly achieved by condensation of a 2-methylindolium salt (e.g. **1**) (or the corresponding exo-methylene enamine) with a salicylaldehyde, either in refluxing alcohol or ketone solvents with or without an amine base (Scheme 1).[2] Many indolium salts and salicylaldehydes are commercially available and can be readily modified; hence, in general, spiropyrans bearing well-defined substituent patterns are accessible. It is striking, however, that the vast majority of spiropyrans contain *gem*-dimethyl substituents in their 3-position, and there are few examples that possess two *different* substituents in this position (see Figure 1).[6-11] As such, this remains an under-explored area of spiropyran research. Given that the 3-position is one of only two tetrahedral carbon atoms in the core spiropyran structure – and the only one present in the merocyanine form – the incorporation of inequivalent 3-position substituents impacts upon spiropyran stereochemistry, enabling facial control of pyran ring-closure,[9,10] and presents an opportunity to influence merocyanine complexation of chiral ligands.

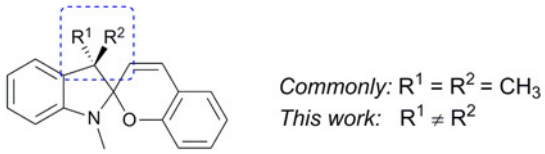
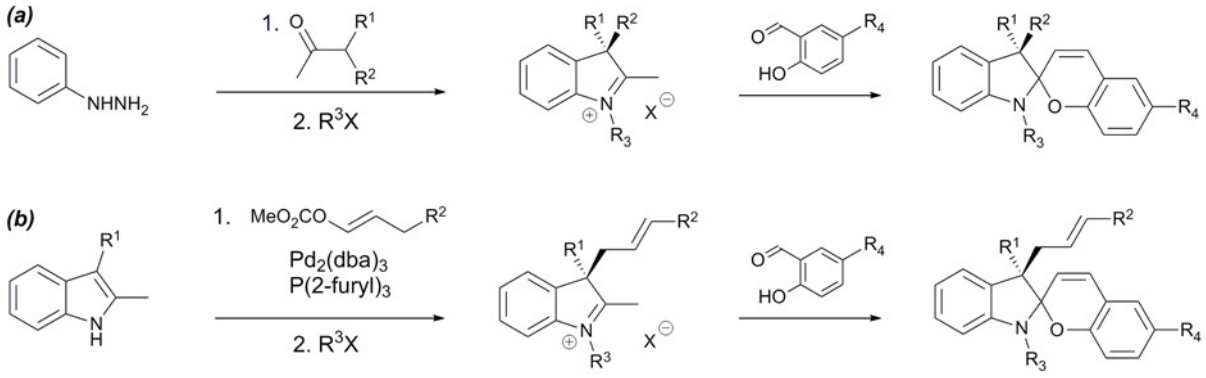


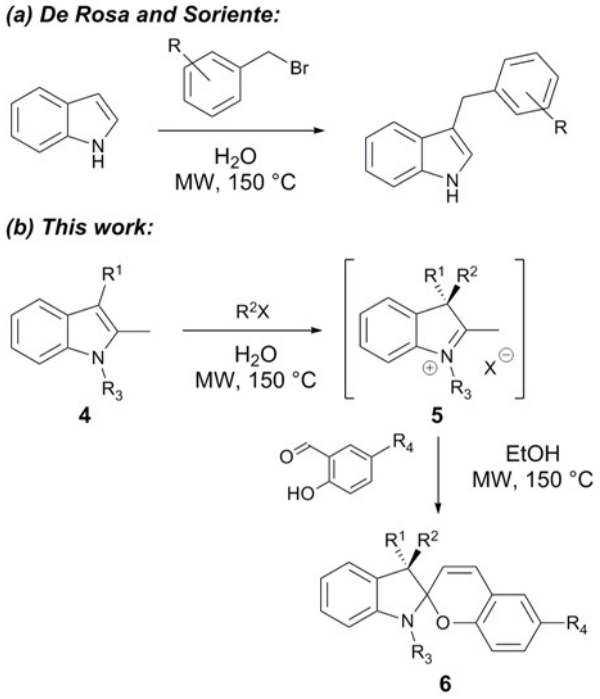
Figure 1 – Typical spiropyran 3-position substituents

The synthetic methods that have been employed to control substitution at the spiropyran 3-position include defining these substituents in the ketone substrate of Fischer indolenine synthesis (Scheme 2a)[7] or by use of 3-substituted indoles as π-nucleophiles in substitution reactions (Scheme 2b), either through direct methylation[8-10] or by palladium-catalysed allylic substitution.[11] Each of these approaches is effective in specific cases but lack generality and synthetic convenience; consequently, we sought general methodology with which to rapidly transform inexpensive and convenient precursors into a range of differentially substituted spiropyrans.



Scheme 2 – Syntheses of spiropyrans bearing inequivalent *C*-3 substituents: *(a) via* Fischer indolenine synthesis; *(b) via* alkylation.

Recently, De Rosa has shown that indoles lacking *C*-2 or *C*-3 substituents undergo 3-selective Friedel–Crafts alkylation in a notable catalyst-free, microwave-promoted S_N1 process conducted in water (Scheme 3a).[12] We envisaged that this methodology could be extended to encompass indolium salt synthesis, *i.e.* that 2-methyl-3-alkyl indoles (e.g. **4**) would behave as viable substrates for this 3-selective alkylation to give 3,3-disubstituted indolium salts (**5**), which in turn would give access to spiropyrans (**6**) *via* condensation with salicylaldehydes (Scheme 3b). Such indolium salt/salicylaldehyde condensations can be accelerated by microwave irradiation;[13] consequently, we surmised that our approach to differentially substituted spiropyrans might be achieved as a two-step, one-pot procedure, utilising microwave irradiation in each step. This methodology is potentially efficient and convenient: microwave-promoted reactions are typically rapid and energy efficient;[14] environmentally benign solvents are employed; and both indole and electrophile substrates are readily accessible. The research presented herein describes the development and optimisation of this process, and exploration of its scope and limitations through application to a range of substrates.



Scheme 3 – Microwave assisted indole alkylation: *(a)* Prior research by De Rosa and Soriente; *(b)* As applied to spiropyran synthesis, explored in this research.

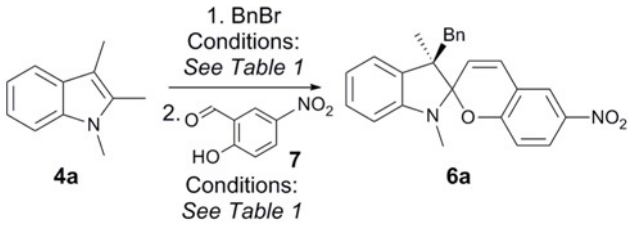
Results and Discussion

Our initial studies sought to establish the viability of the proposed synthetic strategy. Treatment of 1,2,3-trimethylindole (**4a**) with benzyl bromide (2 eq.) in water, using De Rosa and Soriente's conditions (microwave heating, sealed tube, 200 W, 150 °C, 8 minutes), gave crude indolium salt **5a**. The instability of indolium salts is well-documented;[15] consequently, **5a** was reacted directly with 5-nitrosalicylaldehyde (**7**) (1.2 eq.) in refluxing ethanol for 18 hours. Gratifyingly, this produced 3-benzyl-3-methylspiropyran **6a** in 65% yield over 2 steps (Table 1; entry 1). For comparison, the corresponding alkylation process employing standard thermal conditions (open reflux apparatus, 100 °C) failed to reach 25% conversion after 24 hours (entry 2). With this positive result in hand, we successfully repeated this 2-step process, this time using microwave irradiation for both steps (sealed tube, 200 W, 150 °C, 8 minutes for both steps; alkylation in water, condensation in ethanol) and this enabled us to synthesise **6a** with a total heating time under 20 minutes and in 77% yield (entry 3). We then performed further studies to optimise the balance between stoichiometry, heating duration and yield, initially focussing upon the alkylation step. An increased heating period had little impact upon yield in the presence of 2 eq. benzyl bromide (compare entries 3 and 4); however, if fewer molar equivalents were used, increased heating duration became relevant (compare entries 5 and 6) and it was possible to maintain the yield of **6a** using 1.5 eq. benzyl bromide allied to a longer reaction time (compare entries 3 and 6). As such, conditions could be chosen to meet the priorities of a given reaction, either in terms of energy efficiency or atom economy. These results were achieved by employing two consecutive 8 minute heating periods with the temperature held at 150 °C, separated by intermediate cooling to 60 °C. An alternative

protocol, employing a hold time at 150 °C for 16 minutes, was less effective (entry 7) and we speculate that this reflects the reduced microwave energy input in this latter case. Alkylation yield decreased dramatically if 1 equivalent of benzyl bromide was used (entry 8), regardless of heating protocol. With respect to the second step, spiropyran yield was unaffected by increased salicylaldehyde concentration (entry 9) whilst relative amounts lower than 1.2 eq. proved unsatisfactory (entry 10). Attempts to perform both steps in the same solvent, to obviate the requirement of swapping water for ethanol, were ineffective (entries 11 and 12), as was a tandem (as opposed to telescoped) process.

Overall, we regard conditions that minimise reagent waste without compromising yield as optimal (*i.e.* those represented by entry 6) and in this way, we were able to access **6a** in excellent yield (77% overall, 88% per step) and operational simplicity.

Table 1 – Optimisation of two-step, one-pot microwave-assisted spiropyran synthesis



Entry	Alkylation		Condensation		Yield[b] / %
	BnBr / Eq.	Conditions[a]	**7** / Eq.	Conditions[a]	
1	2	Method A	1.2	Method E	65
2	2	Method B	-	-	-
3	2	Method A	1.2	Method F	77
4	2	Method C	1.2	Method F	78
5	1.5	Method A	1.2	Method F	66
6	1.5	Method C	1.2	Method F	77
7	1.5	Method D	1.2	Method F	69
8	1	Method C	1.2	Method F	45
9	1.5	Method C	1.5	Method F	77
10	1.5	Method C	1	Method F	70
11	2	Method A	1.2	Method A	-
12	2	Method F	1.2	Method F	-

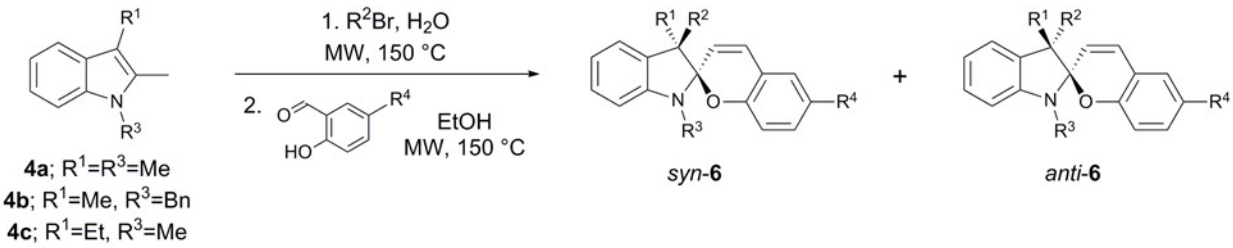
a: All reaction stoichiometry based upon **4a** (0.622 mmol, 1 eq.); maximum microwave power = 200 W: Method A – microwave irradiation, sealed tube, 8 minutes at 150 °C, water (1 mL); Method B – oil bath, open reflux apparatus, 24 h at 100 °C, water (1 mL); Method C – microwave irradiation, sealed tube, 2 × 8 mins at 150 °C, water (1 mL); Method D – microwave irradiation, sealed tube, 16 mins at 150 °C, water (1 mL); Method E – oil bath, open reflux apparatus, 18 h at 78 °C, ethanol (3 mL); Method F – microwave irradiation, sealed tube, 8 mins at 150 °C, ethanol (3 mL). *b*: Isolated yield.

With optimised conditions in hand, we explored the scope of this reaction sequence with respect to alternative substituent patterns (Table 2). In general, classical S_N electrophiles were well tolerated (e.g. benzylic-, allylic- and propargylic bromides; entries 1 – 7), although *t*butyl bromide was not a viable substrate for this reaction (entry 12). Given that this process involves quaternisation of *C*-3 and formation of spiropyran structures with a pair of contiguous quaternary carbon atoms, we assume that incorporation of a *t*butyl group is unfeasible in this sterically demanding environment. Several S_N2 electrophiles were viable substrates: a modest yield of spiropyran **6i** was produced via reaction with iodomethane (entry 9); whilst a good yield of **6h** was produced using an α-bromocarbonyl reagent (entry 8). Less reactive primary and secondary alkyl halides were ineffective substrates under these conditions (entries 10 and 11). Reaction of benzylic electrophiles remained effective with more hindered indole nucleophile **4b** (entries 13 and 14, R^1 = Et) and the consequent formation of sterically congested **6n**, in particular, provides a pleasing result. Alternative substituents were tolerated both on the indole nitrogen (**6o**; entry

15: a removable protecting group) and on the chromene ring (**6p** and **6q**; entries 16 and 17).

As with many nucleophilic substitutions, the balance between S_N1 and S_N2 pathways in this alkylation process is not clear-cut.[16] The inefficient nature of the reaction with methyl and *n*-hexyl halides would suggest that S_N1 is the predominant mechanism (as previously stated, we assume that *t*-butyl bromide was unreactive on steric grounds). Although water – as a polar, protic solvent – favours nucleophilic substitution *via* S_N1 over S_N2, when heated to near-critical temperature (150 – 300 °C) the polarity of water drops considerably (25 °C: $\varepsilon = 78.5$; 250 °C: $\varepsilon = 27.1$; *cf.* acetonitrile: $\varepsilon = 36.6$)[17] and, in this state, it can be regarded as a pseudo-organic solvent suitable for S_N2 reactions.[18,19] Given that we are operating at the lower end of the near-critical temperature range, this, perhaps, explains the grudging tolerance of this reaction for more reactive S_N2 substrates whilst providing greater acceleration for reactions of substrates capable of S_N1.

Table 2 – Application of optimised methodology in spiropyran synthesis over a range of indole, alkyl bromide and salicylaldehyde substrates



Entry[a]	R^1	R^2	R^3	R^4	Product	Yield[b]	*Syn:anti*[c]
1	Me	Bn	Me	NO_2	**6a**	77%	25 : 75
2	Me	2-$NO_2C_6H_4CH_2$	Me	NO_2	**6b**	80%	15 : 85
3	Me	4-$NO_2C_6H_4CH_2$	Me	NO_2	**6c**	86%	22 : 78
4	Me	2-$BrC_6H_4CH_2$	Me	NO_2	**6d**	75%	14 : 86
5	Me	4-$BrC_6H_4CH_2$	Me	NO_2	**6e**	83%	23 : 77
6	Me	Allyl	Me	NO_2	**6f**	73%	44 : 56
7	Me	Propargyl	Me	NO_2	**6g**	80%	48 : 52
8	Me	$PhCOCH_2$	Me	NO_2	**6h**	77%	67 : 33
9	Me	Me[d]	Me	NO_2	**6i**	30%	-
10	Me	*n*-hexyl	Me	NO_2	**6j**	-	-
11	Me	*i*-Pr	Me	NO_2	**6k**	-	-
12	Me	*t*-butyl	Me	NO_2	**6l**	-	-
13	Et	Bn	Me	NO_2	**6m**	76%	33 : 67
14	Et	2-$BrC_6H_4CH_2$	Me	NO_2	**6n**	66%	17 : 83
15	Me	Bn	Bn	NO_2	**6o**	74%	22 : 78
16	Me	Bn	Me	Br	**6p**	83%	27 : 73
17	Me	Bn	Me	CO_2Me	**6q**	70%	26 : 74

a. General conditions: *Alkylation* – **4** (1 eq.), R^2Br (1.5 eq.), water (1 mL/0.6 mmol **4**); microwave irradiation (maximum power = 200 W), sealed tube, 2 × 8 mins at 150 °C. *Condensation* – salicylaldehyde (1.2 eq.), ethanol (3 mL/0.6 mmol **4**); microwave irradiation (maximum power = 200 W), sealed tube, 8 mins at 150 °C. *b*. Isolated yield. *c*. Determined by NOESY analysis. *d*. Iodomethane used.

With the exclusion of **6i**, each spiropyran product exists in solution as a dynamic diastereomeric mixture, reflecting the equilibrium between *spiro* and *mero* forms and the facial selectivity of phenoxide attack upon the merocyanine iminium ion during ring closure. Facial selectivity is influenced by the stereoelectronic environment imposed by the adjacent chiral centre (*C*-3) and this is reflected in the diastereomeric ratios observed in **6a-h** and **6m-q** (Table 2). Assignment of *syn*- and *anti*-configurations was achieved through identification of through-space interactions between alkene protons (chromene 3-position) and either protons on R^1 or R^2 (indole 3-position) by NOESY analysis (Figure 2). Diastereomeric ratios could then be estimated on the basis of ^{1}H NMR integral values. In general, a preference is shown for structures that minimise steric interaction between the larger group on *C*-3 and the chromene oxygen atom (i.e. *anti*-**6a**), and this is consistent with prior studies.[9,10] Ketone **6h**, however, provides an exception to this pattern, in which the major *syn*-isomer minimises interaction between carbonyl and alkene. Higher *dr*s result from

structures possessing the greatest difference in size between *C*-3 substituents and *C*-3 benzylic groups bearing an *ortho* substituent showed the greatest influence upon diastereoselection (e.g. **6b** and **6d**).

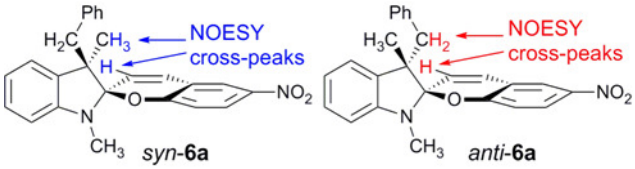


Figure 2 – Determination of spiropyran relative stereochemistry by NOESY analysis

Conclusion

In summary, we have developed a convenient two-step, one-pot protocol which enables rapid access to spiropyran structures displaying a largely neglected pattern of substitution, from readily available precursors, in environmentally benign solvents. Of crucial importance is that this methodology can be used to incorporate a range of functional groups into the spiropyran nucleus that provide convenient handles for further functionalisation, *e.g.* through Pd(0) cross coupling (**6e**), metathesis (**6f**), click chemistry (**6g**) or carbonyl chemistry (**6h**). We intend to explore fully the scope of this new methodology with respect to substrate tolerance and diastereomeric bias in pyran ring closure, and to apply such novel spiropyrans in sensing and switching applications.

Experimental

General Considerations

Solvents and reagents were used as commercially supplied. The fraction of light petroleum ether boiling in the range 40 to 60 °C is referred to as "petrol". Water refers to deionised water. Analytical thin layer chromatography was carried out using Merck Kieselgel 60 F254, coated on aluminium plates, with visualisation of spots where necessary by quenching of UV(254 nm) fluorescence. Silica gel with particle size 40–63 mm was used for flash chromatography.

Microwave reactions were performed in a CEM Discover microwave in 10 mL, thick-walled microwave tubes, sealed with septum caps. All microwave reactions were magnetically stirred and conducted with simultaneous compressed air cooling to maximise microwave radiation input.

Infrared spectra were recorded as thin films using attenuated total reflectance with a Nicolet iS5 FTIR spectrometer. Mass spectra were recorded on a QToF 6520 mass spectrometer (Agilent Technologies, Palo Alto, USA). ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively, using a Bruker Avance III HD400 spectrometer. Chemical shifts are quoted in ppm relative to tetramethylsilane, the residual solvent peak being used for referencing purposes. Coupling constants are quoted to the nearest 0.1 Hz with peak multiplicities for single resonances being labelled as: s, singlet; d, doublet; t, triplet; q, quartet; m, unresolved multiplet. NMR assignments of spiropyrans and merocyanines are labelled as depicted in Figure 3, using **6a** as an example.

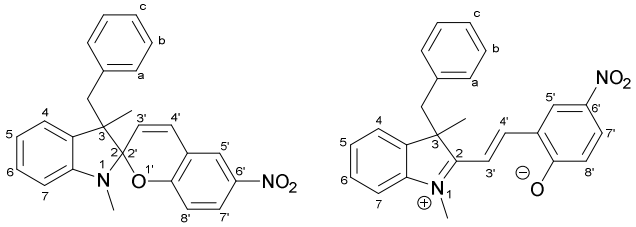


Figure 3 – Atom labelling in **6a** for NMR assignment: (*left*) spiropyran; (*right*) merocyanine

The majority of compounds documented in this publication exist in solution as equilibrating mixtures of spiropyran diastereoisomers which interconvert *via* their merocyanine form. The merocyanines themselves can exist as zwitterionic (denoted "MC"), protonated ("MCH") or quinoidal ("MCQ") forms. Although interpretation of NMR spectra from such multicomponent mixtures is challenging due to overlapping resonances and broadened signals from charged species, and full analysis is often impossible, we have sought to assign nuclei as far as we can within reasonable doubt and merocyanine:*syn*:*anti* ratios are quoted for each ^{1}H NMR spectrum. All spectra were obtained in deuterochloroform which favours the spiropyran form; hence we have assigned all resonances from both spiropyran diastereoisomers. Resonances attributable to merocyanine nuclei have only been noted where not overlapped. 2D NOESY experiments were used – and proved invaluable – for assignment of ^{1}H NMR spectra and for determination of relative configurations.

Synthesis of indole precursors

1,2,3-Trimethylindole[20] 4a

Anhydrous DMF (20 mL) was added slowly to sodium hydride (661 mg of a 60% dispersion in mineral oil, 16.5 mmol) under N_2 with stirring. To the resulting suspension were added slowly 2,3-dimethylindole (2 g, 13.8 mmol) then iodomethane (946 µL, 15.2 mmol). After stirring under N_2 for 22 h, the reaction was quenched with water (20 mL) and extracted with toluene (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography, eluting with 2:98 then 5:95 ethyl acetate:petrol, to give 1,2,3-trimethylindole **4a** (2.032 g, 92%) as a pale yellow oil, spectroscopically identical to that previously reported.[20]

1-Benzyl-2,3-dimethylindole[21] 4b

Using the same general method, 2,3-dimethylindole (200 mg, 1.38 mmol), sodium hydride (66 mg of a 60% dispersion in mineral oil, 1.65 mmol) and benzyl bromide (181 µL, 1.52 mmol) in DMF (3 mL) gave 1-benzyl-2,3-dimethylindole **4b** (230 mg, 71%) as a pale yellow oil, spectroscopically identical to that previously reported.[21]

3-Ethyl-1,2-dimethylindole[22] 4c

A stirred solution of 1-methyl-1-phenylhydrazine (481 µl, 4.09 mmol) and 2-pentanone (871 µL, 8.18 mmol) in glacial acetic acid (4 mL) was heated to 100 °C for 22 hours. The reaction was cooled to room temperature then concentrated under reduced pressure. The resulting crude product was purified by flash chromatography, eluting with 2:98 then 3:97 ethyl acetate:petrol, to give 3-ethyl-1,2-dimethylindole **4c** (481 mg, 68%) as a pale yellow oil, spectroscopically identical to that previously reported.[22]

Synthesis of Spiropyrans

Example procedure for microwave-assisted spiropyran synthesis

***Anti*-(2*R**,3*S**)- and *syn*-(2*R**,3*R**)-3-benzyl-1,3-dimethyl-6′-nitrospiro[chromene-2,2'-indoline] 6a**

A microwave reactor tube equipped with a magnetic follower was charged with a mixture of 1,2,3-trimethylindole (99 mg, 0.622 mmol), benzyl bromide (111 µL, 0.933 mmol) and water (1 mL) and sealed with a septum cap. The reaction mixture was stirred and heated to 150 °C under microwave irradiation (maximum power = 200 W), held at 150 °C for 8 minutes, allowed to cool to 60 °C, then reheated to 150 °C and held at 150 °C for 8 minutes. After cooling to room temperature, the resulting red solution was concentrated under reduced pressure and dissolved in ethanol (3 mL). To this solution was added 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) and the microwave tube was sealed with a septum cap. The reaction mixture was stirred and heated to 150 °C under microwave irradiation (maximum power = 200 W) and held at 150 °C for 8 minutes, then cooled to room temperature and concentrated *in vacuo*. The resulting crude product was purified by flash chromatography, eluting with ethyl acetate, then 10% methanol in ethyl acetate, then 50% methanol in ethyl acetate. The product thus produced was dissolved in dichloromethane and filtered through paper (to remove silica) to give the *spiropyran* **6a** (191 mg, 77%) as an amorphous purple film, R_f 0.3 (5:95 methanol:ethyl acetate); ν_{max} = 3028, 2927, 1709, 1609, 1517, 1481, 1335, 1272, 1220, 1088, 951, 920, 806 and 747 cm^{-1}; δH(400 MHz; $CDCl_3$; 5:24:71 MC:*syn*:*anti*) 8.50 - 8.20 (2 H, m, MC 5'-, 7'-H), 8.01 (1 H, dd, *J* 9.0, 2.7, 7'-H *syn*), 7.98 - 7.93 (2 H, m, 5'-H *anti*; 5'-H *syn*), 7.91 (1 H, dd, *J* 8.7, 2.7, 7'-H *anti*), 7.48 - 7.42 (5 H, m, MC), 7.19 - 6.98 (11 H, m, 6-, b-, c-H *anti*; 4-, 6-, b-, c-H *syn*), 6.94 - 6.92 (2 H, m, a-H *syn*), 6.92 (1 H, d, *J* 10.4, 4'-H *anti*), 6.85 (1 H, d, *J* 9.0, 8'-H *syn*), 6.80 (1 H, t, *J* 7.5, 5-H *syn*), 6.69 (1 H, d, *J* 8.7, 8'-H *anti*), 6.64 - 6.56 (4 H, m, 5-, a-H *anti*; 4'-H *syn*), 6.55 (1 H, d, *J* 7.5, 7-H *anti*), 6.48 (1 H, d, *J* 7.5, 7-H *syn*), 6.10 (1 H, d, *J* 7.5, 4-H *anti*), 5.96 (1 H, d, *J* 10.4, 3'-H *anti*), 5.57 (1 H, d, *J* 10.3, 3'-H *syn*), 3.82 - 3.70 (4 H, m, MC NMe, C*H*H), 3.50 (1 H, br s, MC C*H*H), 3.17 (1 H, d, *J* 13.6,C*H*H *syn*), 3.08 (1 H, d, *J* 13.6,C*H*H *syn*), 2.73 (3 H, s, NMe *anti*), 2.72 (1 H, d, *J* 12.2, C*H*H *anti*), 2.62 (1 H, d, *J* 12.2, C*H*H *anti*), 2.52 (3 H, s, NMe *syn*), 1.30 (3 H, s, MC CMe), 1.20 (3 H, s, CMe *syn*) and 1.18 (3 H, s, CMe *anti*); δC(100 MHz; $CDCl_3$); *anti* diastereoisomer: 160.0, 148.2, 141.0, 136.7, 131.6, 130.9, 128.8, 128.0, 127.6, 127.3, 126.4, 126.0, 125.0, 122.8, 121.8, 118.6, 115.6, 107.7, 107.1 (2-C), 57.3 (3-C), 41.5 (CH_2), 29.3 (NMe) and 16.6 (3-Me); *syn* diastereoisomer: 159.1, 147.0, 141.1, 137.4, 135.7, 132.0, 127.0, 126.4, 125.8, 122.8, 122.7, 122.3, 120.9, 119.8, 119.2, 118.8, 115.7, 107.3, 104.6 (2-C), 54.4 (3-C), 39.3 (CH_2), 28.1 (NMe) and 23.8 (3-Me); HRMS-ES (*m/z*): Found: 399.1703 (MH^+, $C_{25}H_{23}O_3N_2$ requires: 399.1708).

***Anti*-(2*R**,3*S**)- and *syn*-(2*R**,3*R**)-1,3-dimethyl-6′-nitro-3-(2-nitrobenzyl)spiro[chromene-2,2'-indoline] 6b**

Using the same general method, 1,2,3-trimethylindole (99 mg, 0.622 mmol), 2-nitrobenzyl bromide (202 mg, 0.933 mmol) and 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) gave *spiropyran* **6b** (221 mg, 80%) as a purple amorphous film, R_f 0.1 (5:95 methanol:ethyl acetate); ν_{max} = 2970, 1708, 1606, 1520, 1334, 1269, 1087, 950, 807 and 747 cm^{-1}; δH(400 MHz; $CDCl_3$; 8:14:78 MC:*syn*:*anti*) 8.40 (1 H, br s, MC 5'-H), 8.10 (1 H, br d, *J* 15.3, MC 4'-H), 8.03 (1 H, dd, *J*9.0, 2.7, 7'-H *syn*), 7.96 (1 H, d, *J* 2.7, 5'-H *syn*), 7.96 (1 H, d, *J* 2.7, 5'-H *anti*), 7.92 (1 H, dd, *J* 8.9, 2.7, 7'-H *anti*), 7.70 (1 H, dd, *J* 7.0, 1.9, a-H *anti*), 7.67 (1 H, d, *J* 8.0, a-H *syn*), 7.52 - 7.44 (4 H, m, MC), 7.37 - 7.28 (3 H, m, b-, c-H *anti*; b-H *syn*), 7.24 (1 H, t, *J* 8.0, c-H *syn*), 7.16 (1

H, dt, *J* 7.5, 1.0, 6-H *anti*), 7.16 - 7.14 (1 H, m, 6-H *syn*), 6.97 (1 H, d, *J* 10.4, 4'-H *anti*), 7.12 (1 H, d, *J* 7.5, 4-H *syn*), 6.89 (1 H, d, *J* 9.0, 8'-H *syn*), 6.78 (1 H, t, *J* 7.5, 5-H *syn*), 6.75 - 6.70 (2 H, m, d-H *anti*; 4'-H *syn*), 6.67 (1 H, d, *J* 8.9, 8'-H *anti*), 6.67 (1 H, m, d-H *syn*), 6.57 (1 H, t, *J* 7.5, 5-H *anti*), 6.56 (1 H, d, *J* 7.5, 7-H *anti*), 6.41 (1 H, d, *J* 7.5, 7-H *syn*), 5.99 (1 H, d, *J* 10.4, 3'-H *anti*), 5.95 (1 H, d, *J* 7.5, 4-H *anti*), 5.58 (1 H, d, *J* 10.3, 3'-H *syn*), 4.08 (3 H, br s, MC NMe), 3.90 (1 H, d, *J* 14.2, C*H*H *syn*), 3.77 (1 H, br d, *J* 13.0, MC C*H*H), 3.42 (1 H, d, *J* 14.2, C*H*H *syn*), 3.31 (1 H, d, *J* 12.5, C*H*H *anti*), 3.21 (1 H, d, *J* 12.5, C*H*H *anti*), 2.72 (3 H, s, NMe *anti*), 2.50 (3 H, s, NMe *syn*), 1.18 (3 H, s, CMe *syn*), 1.14 (3 H, s, MC CMe) and 1.03 (3 H, s, CMe *anti*); δC(100 MHz; $CDCl_3$); *anti* diastereoisomer: 159.7, 151.0, 148.4, 141.1, 134.9, 131.8, 131.5, 131.1, 129.3, 128.6, 127.8, 126.0, 124.5, 123.8, 122.8, 121.3, 119.1, 118.8, 115.6, 107.5, 107.4 (2-C), 57.6 (3-C), 36.0 (CH_2), 29.3 (NMe) and 16.3 (3-Me); *syn* diastereoisomer: 158.7, 151.2, 146.6, 141.5, 134.3, 134.0, 132.3, 131.6, 128.4, 127.6, 127.2, 125.9, 124.6, 122.7, 122.3, 120.8, 119.9, 119.2, 115.9, 107.4, 104.4 (2-C), 55.0 (3-C), 33.8 (CH_2), 28.2 (NMe) and 22.2 (3-Me); HRMS-ES (*m/z*): Found: 444.1562 (MH^+, $C_{25}H_{22}O_5N_3$ requires: 444.1559).

Anti-(2*R,3*S**)- and _syn_-(2*R**,3*R**)-1,3-dimethyl-6′-nitro-3-(4-nitrobenzyl)spiro[chromene-2,2'-indoline] 6c**

Using the same general method, 1,2,3-trimethylindole (99 mg, 0.622 mmol), 4-nitrobenzyl bromide (202 mg, 0.933 mmol) and 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) gave *spiropyran* **6c** (237 mg, 86%) as a purple amorphous film, R_f 0.2 (5:95 methanol:ethyl acetate) ν_{max} = 2929, 1708, 1604, 1515, 1480, 1335, 1269, 1220, 1176, 1086, 949, 806 and 747 cm^{-1}; δH(400 MHz; $CDCl_3$; 5:21:74 MC:*syn*:*anti*) 8.60 (1 H, br d, *J* 16.1, MC 4'-H), 8.56 (1 H, br s, MC 5'-H), 8.50 (1 H, d, *J* 2.7, MCQ 5'-H), 8.33 (1 H, dd, *J* 9.0, 2.7, MCQ 7'-H), 8.03 (1 H, dd, *J* 9.0, 2.7, 7'-H *syn*), 7.98 - 7.92 (4 H, m, 5'-, 7'-, b-H *anti*; 5'-H *syn*), 7.88 (2 H, d, *J* 8.7, b-H *syn*), 7.82 (2 H, br d, *J* 8.5, MC b-H), 7.60 - 7.52 (4 H, m, MC), 7.38 (1 H, br d, *J* 7.9, MC), 7.33 (1 H, br d, *J* 8.6, MC), 7.19 (1 H, t, *J* 7.5, 6-H *syn*), 7.18 (1 H, t, *J* 7.5, 6-H *anti*), 7.10 (2 H, d, *J* 8.7, a-H *syn*), 6.96 (1 H, d, *J* 10.4, 4-H *anti*), 6.95 (1 H, d, *J* 7.5, 4-H *syn*), 6.87 (1 H, d, *J* 9.0, 8'-H *syn*), 6.81 (1 H, t, *J* 7.5,5-H *syn*), 6.75 (2 H, d, *J* 8.7, a-H *anti*), 6.69 (1 H, d, *J* 8.7, 8'-H *anti*), 6.65 (1 H, d, *J* 10.3, 4'-H *syn*), 6.62 (1 H, t, *J* 7.5, 5-H *anti*), 6.53 (1 H, d, *J* 7.5, 7-H *anti*), 6.48 (1 H, d, *J* 7.5, 7-H *syn*), 6.09 (1 H, d, *J* 7.5, 4-H *anti*), 5.93 (1 H, d, *J* 10.43'-H *anti*), 5.57 (1 H, d, *J* 10.3, 3'-H *syn*), 3.72 (2 H, br s, MC CH_2), 3.30 (1 H, d, *J* 13.5, C*H*H *syn*), 3.18 (1 H, d, *J* 13.5, C*H*H *syn*), 2.83 (1 H, d, *J* 12.0, C*H*H *anti*), 2.76 (1 H, d, *J* 12.0, C*H*H *anti*), 2.73 (3 H, s, NMe *anti*), 2.58 (3 H, s, NMe *syn*), 1.22 (3 H, s, CMe *syn*), 1.18 (3 H, s, MC CMe) and 1.15 (3 H, s, CMe *anti*); δC(100 MHz; $CDCl_3$); *anti* diastereoisomer: 159.7, 148.3, 146.8, 144.9, 141.2, 132.2, 129.4, 128.6, 126.1, 124.5, 122.8, 122.7, 122.5, 121.1, 118.9, 118.7, 115.7, 107.6, 107.3 (2-C), 57.1 (3-C), 41.4 (CH_2), 29.3 (NMe) and 16.5 (3-Me); *syn* diastereoisomer: 158.6, 146.7, 145.6, 141.5, 134.5, 131.6, 131.1, 128.5, 127.3, 126.0, 122.7, 122.5, 120.6, 119.9, 119.1, 115.7, 107.5, 104.2 (2-C), 54.2 (3-C), 39.4 (CH_2), 28.1 (NMe) and 23.5 (3-Me) (one peak missing); HRMS-ES (*m/z*): Found: 444.1562 (MH^+, $C_{25}H_{22}O_5N_3$ requires: 444.1559).

Anti-(2*R,3*S**)- and _syn_-(2*R**,3*R**)-3-(2-bromobenzyl)-1,3-dimethyl-6′-nitrospiro[chromene-2,2'-indoline] 6d**

Using the same general method, 1,2,3-trimethylindole (99 mg, 0.622 mmol), 2-bromobenzyl bromide (233 mg, 0.933 mmol) and 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) gave *spiropyran* **6d** (223 mg, 75%) as a purple amorphous film, R_f 0.2

(5:95 methanol:ethyl acetate); ν_{max} = 2930, 1710, 1608, 1519, 1471, 1337, 1273, 1088, 951, 807 and 749 cm^{-1}; δH(400 MHz; $CDCl_3$; 5:17:11:67 MCQ:MC:*syn*:*anti*) 8.49 (1 H, d, *J* 2.7, MCQ 5'-H), 8.33 (1 H, dd, *J* 9.2, 2.7, MCQ 7'-H), 8.25 (1 H, d, *J* 2.6, MC 5'-H), 8.05 (1 H, d, *J* 16.3, MC 4'-H), 8.00 - 7.91 (4 H, m, 5'-, 7'-H *anti*; 5'-, 7'-H *syn*), 7.84 (1 H, d, *J* 16.3, MC 3'-H), 7.75 (1 H, d, *J* 9.2, MC), 7.55 - 7.42 (5 H, m, MC), 7.39 (1 H, dd, *J* 7.8, 1.4, a-H *anti*), 7.30 (1 H, d, *J* 8.0, a-H *syn*), 7.16 (1 H, dd, *J* 7.5, 1.1, 6-H *anti*), 7.16 - 7.14 (1 H, m, 6-H *syn*), 7.07 - 6.97 (4 H, m, b-, c-H *anti*; b-, c-H *syn*), 6.96 (1 H, d, *J* 10.4, 4'-H *anti*), 6.83 (1 H, d, *J* 7.5, 8'-H *syn*), 6.82 - 6.76 (2 H, m, 4'-, 5-H *syn*), 6.69 (1 H, d, *J* 8.9, 8'-H *anti*), 6.69 - 6.67 (1 H, m, 4-H *syn*), 6.62 (1 H, dd, *J* 7.5, 0.7, 5-H *anti*), 6.57 (1 H, dd, *J* 7.5, 1.8, d-H *anti*), 6.57 - 6.54 (1 H, m, d-H *syn*), 6.52 (1 H, d, *J* 7.5, 7-H *anti*), 6.47 (1 H, d, *J* 7.5, 7-H *syn*), 6.13 (1 H, d, *J* 7.5, 4-H *anti*), 5.99 (1 H, d, *J* 10.4, 3'-H *anti*), 4.10 (3 H, s, MC NMe), 3.58 (1 H, d, *J* 14.2, C*H*H *syn*), 3.55 (1 H, d, *J* 14.0, MC C*H*H), 3.43 (1 H, d, *J* 14.0, MC C*H*H), 3.26 (1 H, d, *J* 14.2, C*H*H *syn*), 2.99 (1 H, d, *J* 12.4, C*H*H *anti*), 2.86 (1 H, d, *J* 12.4, C*H*H *anti*), 2.76 (3 H, s, NMe *anti*), 2.58 (3 H, s, NMe *syn*), 1.21 (3 H, s, CMe *syn*), 1.20 (3 H, s, MC CMe) and 1.18 (3 H, s, CMe *anti*); δC(100 MHz; $CDCl_3$); *anti* diastereoisomer: 160.0, 148.7, 141.0, 136.5, 133.6, 132.7, 131.9, 129.0, 128.3, 128.2, 127.2, 126.2, 126.0, 124.6, 122.8, 121.7, 119.0, 118.8, 115.6, 107.6, 107.3 (2-C), 57.8 (3-C), 39.4 (CH_2), 29.3 (NMe) and 16.9 (3-Me); *syn* diastereoisomer: 159.0, 146.8, 141.4, 137.5, 134.9, 133.0, 132.8, 132.5, 128.9, 128.0, 127.3, 126.9, 126.7, 126.1, 125.9, 121.5, 119.7, 119.2, 116.0, 107.2, 104.8 (2-C), 55.0 (3-C), 37.5 (CH_2), 28.3 (NMe) and 22.8 (3-Me); HRMS-ES (*m/z*): Found: 477.0809 (MH^+, $C_{25}H_{22}O_3N_2Br$ requires: 477.0814).

Anti-(2_R_*,3_S_*)- and _syn_-(2_R_*,3_R_*)-3-(4-bromobenzyl)-1,3-dimethyl-6′-nitrospiro[chromene-2,2'-indoline] 6e

Using the same general method, 1,2,3-trimethylindole (99 mg, 0.622 mmol), 4-bromobenzyl bromide (233 mg, 0.933 mmol) and 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) gave *spiropyran* **6e** (246 mg, 83%) as a purple amorphous film, R_f 0.2 (5:95 methanol:ethyl acetate); ν_{max} = 2926, 1709, 1610, 1517, 1481, 1333, 1270, 1071, 949, 804 and 746 cm^{-1}; δH(400 MHz; $CDCl_3$; 7:22:71 MC:*syn*:*anti*) 8.51 (1 H, br d, *J* 2.1, MC 5'-H), 8.45 (1 H, br d, *J* 16.2, MC 4'-H), 8.02 (1 H, dd, *J* 9.0, 2.7, 7'-H *syn*), 7.97 - 7.91 (3 H, m, 5'-, 7'-H *anti*; 5'-H *syn*), 7.82 (1 H, br d, *J* 16.2, MC 3'-H), 7.78 (1 H, br d, *J* 9.3, MC), 7.54 - 7.48 (2 H, m, MC), 7.40 - 7.34 (2 H, m, MC), 7.22 (2 H, d, *J* 8.3, b-H *anti*), 7.20 - 7.12 (4 H, m, 6-H *anti*; 6-, b-H *syn*), 7.08 (2 H, d, *J* 8.3, MC a-H), 6.98 (1 H, d, *J* 7.5, 4-H *syn*), 6.93 (1 H, d, *J* 10.4, 4'-H *anti*), 6.86 - 6.78 (4 H, m, a-, 8'-, 5-*syn*), 6.68 (1 H, d, *J* 8.4, 8'-H *anti*), 6.64 (1 H, d, *J* 10.3, 4'-H *syn*), 6.62 (1 H, t, *J* 7.5, 5-H *anti*), 6.54 (1 H, d, *J* 7.5, 7-H *anti*), 6.42 (1 H, d, *J* 7.5, 7-H *syn*), 6.14 (1 H, d, *J* 7.5, 4-H *anti*), 5.92 (1 H, d, *J* 10.4, 3'-H *anti*), 5.57 (1 H, d, *J* 10.3, 3'-H *syn*), 3.92 (3 H, br s, MC NMe), 3.50 (2 H, br s, MC C*H*H), 3.14 (1 H, d, *J* 13.6, C*H*H *syn*), 3.04 (1 H, d, *J* 13.6, C*H*H *syn*), 2.73 (3 H, s, NMe *anti*), 2.66 (1 H, d, *J* 12.2, C*H*H *anti*), 2.58 (1 H, d, *J* 12.2, C*H*H *anti*), 2.52 (3 H, s, NMe *syn*), 1.19 (3 H, s, CMe *anti*) and 1.11 (3 H, s, CMe *syn*); δC(100 MHz; $CDCl_3$); *anti* diastereoisomer: 159.9, 148.2, 141.0, 135.8, 133.2, 132.5, 130.7, 130.4, 129.0, 128.2, 126.1, 124.9, 122.8, 121.6, 120.6, 118.7, 115.6, 107.5, 107.3 (2-C), 57.1 (3-C), 40.9 (CH_2), 29.3 (NMe) and 16.5 (3-Me); *syn* diastereoisomer: 158.9, 146.9, 141.3, 136.4, 135.2, 131.6, 131.5, 128.2, 127.2, 125.9, 122.7, 122.2, 120.8, 120.5, 119.8, 119.2, 115.7, 107.4, 104.4 (2-C), 54.1 (3-C), 38.7 (CH_2), 28.1 (NMe) and 23.6 (3-Me); HRMS-ES (*m/z*): Found: 477.0810 (MH^+, $C_{25}H_{22}O_3N_2Br$ requires: 477.0814).

***Anti*-(2*R**,3*S**)- and *syn*-(2*R**,3*R**)-3-allyl-1,3-dimethyl-6′-nitrospiro[chromene-2,2'-indoline] 6f**

Using the same general method, 1,2,3-trimethylindole (99 mg, 0.622 mmol), allyl bromide (81 μL, 0.933 mmol) and 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) gave *spiropyran* **6f** (159 mg, 73%) as a purple amorphous film, R_f 0.3 (5:95 methanol:ethyl acetate); ν_{max} = 2973, 1707, 1582, 1518, 1485, 1335, 1281, 1087, 948, 834 and 748 cm^{-1}; δH(400 MHz; CDCl3; 3:5:43:49 MCQ:MC:*syn*:*anti*) 8.39 (1 H, br s, MC 5'-H), 8.31 (1 H, br d, *J* 15.0, MC 4'-H), 8.15 (1 H, d, *J* 2.7, MCQ 5'-H), 8.07 (1 H, dd, *J* 7.5, 2.7, MCQ 7'-H), 7.96 (1 H, dd, *J* 8.9, 2.7, 7'-H *anti*), 7.95 - 7.90 (3 H, m, 5'-H *anti*; 5'-, 7'-H *syn*), 7.90 - 7.80 (4 H, m, MC / MCQ), 7.74 (1 H, dd, *J* 8.9, 2.7, MC 7'-H), 7.55 - 7.40 (6 H, m, MC / MCQ), 7.36 - 7.30 (1 H, m, MC), 7.15 (1 H, dt, *J* 7.5, 1.2, 6-H *anti*), 7.13 (1 H, dt, *J* 7.5, 1.2, 6-H *syn*), 7.07 (1 H, dd, *J* 7.5, 0.7, 4-H *syn*), 7.04 - 6.96 (4 H, m, MC / MCQ), 6.94 (1 H, dd, *J* 7.5, 0.8, 4-H *anti*), 6.85 (1 H, d, *J* 10.4, 4'-H *anti*), 6.82 (1 H, dt, *J* 7.5, 0.9, 5-H *syn*), 6.81 (1 H, d, *J* 10.3, 4'-H *syn*), 6.74 (1 H, br d, *J* 7.0, MC), 6.72 (1 H, d, *J* 8.8, 8'-H *anti*), 6.68 (1 H, d, *J* 8.4, 8'-H *syn*), 6.64 - 6.53 (3 H, m, MC / MCQ), 6.51 (1 H, d, *J* 7.5, 7-H *anti*), 6.47 (1 H, d, *J* 7.5, 7-H *syn*), 6.32 (1 H, d, *J* 16.4, MC b-H), 6.23 (1 H, d, *J* 16.3, MCQ b-H), 5.84 (1 H, d, *J* 10.4, 3'-H *anti*), 5.79 (1 H, d, *J* 10.3, 3'-H *syn*), 5.68 (1 H, ddt, *J* 17.0, 10.0, 7.5, a-H *syn*), 5.50 (1 H, ddt, *J* 17.0, 10.0, 7.5, a-H *anti*), 4.96 (1 H, dd, *J* 10.0, 1.2, c-H *anti*), 4.88 (1 H, dd, *J* 17.0, 1.2, b-H *anti*), 4.84 (1 H, dd, *J* 17.0, 1.5, b-H *syn*), 4.79 (1 H, dd, *J* 10.0, 1.5, c-H *syn*), 3.97 (3 H, s, MC NMe), 2.68 (3 H, s, NMe *anti*), 2.61 (1 H, dd, *J* 14.0, 7.5, C*H*H *syn*), 2.58 (3 H, s, NMe *syn*), 2.49 (1 H, dd, *J* 14.0, 7.5, C*H*H *syn*), 2.22 (1 H, dd, *J* 13.7, 7.5, C*H*H *anti*), 2.16 (1 H, dd, *J* 13.7, 7.5, C*H*H *anti*), 1.22 (3 H, s, MC CMe), 1.18 (3 H, s, CMe *syn*), 1.17 (3 H, s, CMe *anti*) and 1.12 (3 H, s, MCQ CMe); δC(100 MHz; $CDCl_3$); both diastereoisomers: 159.9, 159.3, 148.3, 147.3, 140.9, 135.8, 134.1, 133.9, 133.1, 128.5, 128.0, 128.0, 127.5, 125.9, 125.8, 123.4, 122.8, 122.7, 121.9, 121.7, 121.7, 121.6, 119.8, 119.3, 118.7, 118.5, 118.2, 117.9, 115.5, 115.5, 107.2, 107.1, 106.9 (2-C), 105.0 (2-C), 55.8 (3-C), 53.7 (3-C), 41.1 (CH_2), 39.0 (CH_2), 29.0 (NMe), 28.1 (NMe), 23.3 (3-Me) and 17.6 (3-Me); HRMS-ES (*m/z*): Found: 349.1548 (MH^+, $C_{21}H_{21}O_3N_2$ requires: 349.1552).

***Anti*-(2*R**,3*S**)- and *syn*-(2*R**,3*R**)-1,3-dimethyl-6′-nitro-3-(prop-2-yn-1-yl)spiro[chromene-2,2'-indoline] 6g**

Using the same general method, 1,2,3-trimethylindole (99 mg, 0.622 mmol), propargyl bromide (100 μL of an 80% w/w solution in toluene, 0.933 mmol) and 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) gave *spiropyran* **6g** (172 mg, 80%) as a purple amorphous film, R_f 0.3 (5:95 methanol:ethyl acetate); ν_{max} = 3284, 2927, 1709, 1608, 1517, 1482, 1334, 1272, 1086, 950, 808 and 747 cm^{-1}; δH(400 MHz; $CDCl_3$; 48:52 *syn*:*anti*) 7.97 - 7.91 (4 H, m, 5'-, 7'-H *anti*; 5'-, 7'-H *syn*), 7.23 (1 H, d, *J* 7.4, 4-H *syn*), 7.18 (1 H, d, *J* 7.5, 4-H *anti*), 7.14 (2 H, t, *J* 7.6, 6-H *anti*; 6-H *syn*), 6.87 (1 H, d, *J* 10.4, 4'-H *syn*), 6.85 (1 H, d, *J* 10.4, 4'-H *anti*), 6.84 (1 H, t, *J* 7.6, 5-H *anti*), 6.83 (1 H, t, *J* 7.6, 5-H *syn*), 6.72 (1 H, d, *J* 8.5, 8'-H *anti*), 6.7 (1 H, d, *J* 8.5, 8'-H *syn*), 6.51 (1 H, d, *J* 7.6, 7-H *syn*), 6.48 (1 H, d, *J* 7.6, 7-H *anti*), 5.82 (1 H, d, *J* 10.4, 3'-H *syn*), 5.78 (1 H, d, *J* 10.4, 3'-H *anti*), 2.68 (3 H, s, NMe *anti*), 2.66 (1 H, dd, *J* 16.0, 2.7, C*H*H *syn*), 2.60 (3 H, s, NMe *syn*), 2.58 (1 H, dd, *J* 16.0, 2.7, C*H*H *syn*), 2.40 (1 H, dd, *J* 16.0, 2.7, C*H*H *anti*), 2.26 (1 H, dd, *J* 16.0, 2.7, C*H*H *anti*), 1.94 (1 H, t, *J* 2.7, C≡CH *syn*), 1.78 (1 H, t, *J* 2.7, C≡CH *syn*), 1.34 (3 H, s, CMe *syn*) and 1.33 (3 H, s, CMe *anti*); δC(100 MHz; $CDCl_3$); both diastereoisomers: 159.6, 159.2, 148.0, 147.2, 141.1, 141.1, 134.2, 132.6, 128.9, 128.5, 128.4, 127.9, 126.0, 125.8, 123.5, 122.8, 122.7, 122.1, 121.3, 121.1, 119.8, 119.6, 118.7, 118.6, 115.6, 115.4, 107.2,

107.1, 106.0 (2-C), 104.8 (2-C), 80.6 (*C*≡C), 80.6 (*C*≡C), 71.4 (C≡*C*), 70.7 (C≡*C*), 54.7 (3-C), 53.0 (3-C), 28.9 (NMe), 28.3 (NMe), 27.4 (CH_2), 24.4 (CH_2), 23.0 (3-Me) and 17.3 (3-Me); HRMS-ES (*m/z*): Found: 347.1393 (MH^+, $C_{21}H_{19}O_3N_2$ requires: 347.1395).

2-(*Anti*-(2*R,3*S**) and *syn*-(2*R**,3*R**)-1,3-dimethyl-6'-nitrospiro[chromene-2,2'-indolin]-3-yl)-1-phenylethan-1-one 6h**

Using the same general method, 1,2,3-trimethylindole (99 mg, 0.622 mmol), 2-bromoacetophenone (186 mg, 0.933 mmol) and 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) gave *spiropyran* **6h** (205 mg, 77%) as a purple amorphous film, R_f 0.4 (5:95 methanol:ethyl acetate); ν_{max} = 2929, 1709, 1682, 1606, 1519, 1486, 1448, 1338, 1289, 1221, 1089, 955, 912 and 748 cm^{-1}; δH(400 MHz; $CDCl_3$; 15:34:34:17 MCQ:MC:*syn*:*anti*) 8.60 (1 H, br s, MC 5'-H), 8.49 (1 H, d, *J* 2.7, MCQ 5'-H), 8.36 (1 H, br d, *J* 16.0, MC 4'-H), 8.31 (1 H, dd, *J* 9.2, 2.7, MCQ 7'-H), 7.97 - 7.92 (2 H, m, 5'-, 7'-H *anti*), 7.86 (1 H, d, *J* 2.7, 5'-H *syn*), 7.83 - 7.74 (4 H, m, MC), 7.70 (1 H, dd, *J* 9.0, 2.7, 7'-H *syn*), 7.61 (2 H, dd, *J* 8.5, 1.2, a-H *syn*), 7.60 - 7.50 (4 H, m, MC), 7.43 (2 H, dd, *J* 8.4, 2.1, a-H *anti*), 7.42 - 7.38 (2 H, m, MC), 7.35 - 7.12 (8 H, m, 4-, 6-, b-, c-H *syn*; b-, c-H *anti*), 7.25 (1 H, br t, *J* 7.2, MC), 7.06 (1 H, d, *J* 9.0, 8'-H *anti*), 7.04 (1 H, dt, *J* 7.6, 1.0, 6-H *anti*), 6.92 (1 H, d, *J* 10.4, 4'-H *anti*), 6.91 (1 H, d, *J* 7.5, 4-H *anti*), 6.85 (1 H, dt, *J* 7.5, 0.6, 5-H *syn*), 6.83 (1 H, d, *J* 10.3, 4'-H *syn*), 6.62 (1 H, t, *J* 7.5, MCQ), 6.56 (1 H, t, *J* 7.4, 5-H *anti*), 6.45 (2 H, d, *J* 7.6, 7-H *syn*; 7-H *anti*), 6.41 (1 H, d, *J* 9.0, 8'-H *syn*), 5.96 (1 H, d, *J* 10.3, 3'-H *syn*), 5.90 (1 H, d, *J* 10.4, 3'-H *anti*), 4.60 (1 H, br s, MC C*H*H), 4.19 (3 H, br s, MC NMe), 4.17 (1 H, br s, MC C*H*H), 3.71 (1 H, d, *J* 16.6, C*H*H *syn*), 3.35 (1 H, d, *J* 13.8, C*H*H *anti*), 3.24 (1 H, d, *J* 16.6, C*H*H *syn*), 2.77 (1 H, d, *J* 13.8, C*H*H *anti*), 2.72 (3 H, s, NMe *anti*), 2.58 (3 H, s, MCQ NMe), 2.54 (3 H, s, NMe *syn*), 1.50 (3 H, s, MC CMe), 1.43 (3 H, s, CMe *anti*) and 1.18 (3 H, s, CMe *syn*); δC(100 MHz; $CDCl_3$); *syn* diastereoisomer: 198.3 (C=O), 158.4, 146.4, 141.0, 137.5, 135.4, 132.8, 128.4, 128.3, 128.2, 128.0, 127.7, 125.1, 122.5, 122.2, 121.8, 119.8, 115.2, 107.4, 107.1 (2-C), 53.8 (3-C), 41.7 (CH_2), 27.9 (NMe) and 23.8 (3-Me); *anti* diastereoisomer: 198.7 (C=O), 159.8, 148.1, 140.1, 138.0, 134.6, 132.7, 128.5, 126.1, 126.0, 124.4, 122.8, 121.1, 119.6, 119.0, 118.9, 118.7, 115.6, 107.1, 103.9 (2-C), 55.6 (3-C), 42.5 (CH_2), 29.3 (NMe) and 17.2 (3-Me); merocyanine / quinoidal merocyanine: 195.4 (C=O), 195.3 (C=O), 183.6 (2-C MC), 166.2, 165.3, 147.8, 142.3, 141.6, 134.3, 132.3, 131.6, 129.9, 129.7, 129.6, 129.5, 129.3, 129.2, 129.1, 128.9, 127.8, 125.9, 125.5, 124.6, 122.3, 120.8, 119.5, 114.6, 113.9, 61.9 (NMe MC), 53.4 (3-C), 50.9 (3-C), 34.9 (NMe MCQ), 31.8 (CH_2), 26.6 (CH_2), 25.9 (3-Me) and 19.9 (3-Me). 12 peaks missing; HRMS-ES (*m/z*): Found: 427.1659 (MH^+, $C_{26}H_{23}O_4N_2$ requires: 427.1658).

1,3,3-Trimethyl-6′-nitrospiro[chromene-2,2'-indoline][23] 6i

Using the same general method, 1,2,3-trimethylindole (99 mg, 0.622 mmol), iodomethane (58 μL, 0.933 mmol) and 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) gave spiropyran **6i** (60 mg, 30%) as a purple amorphous film, spectroscopically identical to that previously reported.[23]

***Anti*-(2*R**,3*S**)- and *syn*-(2*R**,3*R**)-3-benzyl-3-ethyl-1-methyl-6′-nitrospiro[chromene-2,2'-indoline] 6m**

Using the same general method, 3-ethyl-1,2-dimethylindole (108 mg, 0.622 mmol), benzyl bromide (111 μL, 0.933 mmol) and 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) gave *spiropyran* **6m** (194 mg, 76%) as a purple amorphous film, R_f 0.4 (5:95

methanol:ethyl acetate); ν_{max} = 2966, 1707, 1602, 1521, 1495, 1472, 1339, 1289, 1088, 948 and 749 cm^{-1}; δH(400 MHz; $CDCl_3$; 47:18:35 MC:*syn*:*anti*) 8.67 (1 H, br s, MC 5'-H), 8.55 (1 H, br d, *J* 15.9, MC 4'-H), 8.09 - 7.92 (3 H, m, 5'-,7'-H *anti*; 7'-*syn*), 7.85 (1 H, d, *J* 2.0, 5'-H *syn*), 7.58 - 7.42 (4 H, m, MC), 7.35 (1 H, br d, *J* 7.5, MC), 7.16 - 6.81 (10 H, m, 6-, b-, c-H *anti*; 6-, a-, b-, c-H *syn*), 6.68 (1 H, d, *J* 8.9, 8'-H *anti*), 6.62 (2 H, d, *J* 6.9, a-H *anti*), 6.54 (1 H, t, *J* 7.5, 5-H *anti*), 6.52 - 6.42 (5 H, m, 4'-, 7-H *anti*; 4-, 4'-, 5-H *syn*), 6.09 (1 H, d, *J* 10.4, 3'-H *anti*), 6.00 (1 H, d, *J* 7.5, 4-H *anti*), 5.54 (1 H, d, *J* 10.3, 3'-H *syn*), 3.78 (3 H, br s, MC NMe), 3.55 (1 H, br d, *J* 14.5, MC ArC*H*H), 3.50 (1 H, br d, *J* 14.5, MC ArC*H*H), 3.19 (1 H, d, *J* 14.0, ArC*H*H *syn*), 3.11 (1 H, d, *J* 14.0, ArC*H*H *syn*), 3.08 (1 H, d, *J* 13.4, ArC*H*H *anti*), 2.58 (3 H, s, NMe *anti*), 2.50 (1 H, d, *J* 13.4, ArC*H*H *anti*), 2.42 (3 H, s, NMe *syn*), 1.81 - 1.70 (3 H, m, CH_2Me *anti*; C*H*HMe *syn*), 1.52 (1 H, dq, *J* 13.8, 7.3, C*H*HMe *syn*), 0.88 (3 H, t, *J* 7.4, CMe *anti*), 0.85 (3 H, t, *J* 7.3, CMe *syn*) and 0.42 (3 H, t, *J* 6.9, MC CMe); δC(100 MHz; $CDCl_3$); *anti* diastereoisomer: 159.4, 147.4, 142.9, 136.7, 133.2, 131.4, 129.1, 128.2, 127.4, 126.4, 125.9, 124.9, 123.6, 122.9, 122.2, 118.6, 115.5, 107.1, 105.7 (2-C), 58.6 (3-C), 37.0 ($ArCH_2$), 29.3 (NMe), 28.1 (CH_2CH_3) and 8.9 (CH_2CH_3); *syn* diastereoisomer: 159.1, 150.9, 140.9, 138.9, 137.5, 132.7, 128.0, 127.8, 127.5, 126.7, 126.3, 125.7, 122.6, 121.0, 120.6, 118.4, 115.6, 107.3, 104.7 (2-C), 53.8 (3-C), 35.5 ($ArCH_2$), 31.8 (NMe), 27.9 (CH_2CH_3) and 8.6 (CH_2CH_3); merocyanine: 180.6 (2-C), 169.9, 150.9, 141.3, 131.5, 130.5, 130.0, 129.8, 129.4, 129.2, 128.8, 128.8, 128.7, 128.1, 120.2, 119.4, 119.2, 114.1, 113.1, 64.1 (NMe), 47.2 (3-C), 33.5 ($ArCH_2$), 22.7 (CH_2CH_3) and 8.8 (CH_2CH_3); HRMS-ES (*m/z*): Found: 413.1861 (MH^+, $C_{26}H_{25}O_3N_2$ requires: 413.1865).

Anti-(2*R,3*S**)- and _syn_-(2*R**,3*R**)-3-(2-bromobenzyl)-3-ethyl-1-methyl-6′-nitrospiro[chromene-2,2'-indoline] 6n**

Using the same general method, 3-ethyl-1,2-dimethylindole (108 mg, 0.622 mmol), 2-bromobenzyl bromide (233 mg, 0.933 mmol) and 5-nitrosalicylaldehyde (125 mg, 0.746 mmol) gave *spiropyran* **6n** (191 mg, 66%) as a purple amorphous film, R_f 0.5 (5:95 methanol:ethyl acetate); ν_{max} = 2967, 1708, 1602, 1519, 1470, 1337, 1288, 1088, 948 and 749 cm^{-1}; δH(400 MHz; $CDCl_3$; 65:6:29 MC:*syn*:*anti*) 8.49 (1 H, br s, MC 5'-H), 8.21 (1 H, br d, *J* 15.6, MC 4'-H), 8.01 - 7.85 (2 H, m, 5'-, 7'-H *anti*), 7.60 - 7.40 (4 H, m, MC), 7.35 (1 H, br t, *J* 6.9, MC), 7.29 (1 H, d, *J* 7.9, a-H *anti*), 7.10 (1 H, t, *J* 7.5, 6-H *anti*), 7.01 (2 H, br d, *J* 6.9, MC), 7.00 - 6.92 (3 H, m, b-, c-, d-H *anti*), 6.90 (1 H, d, *J* 10.4, 4'-H *anti*), 6.71 (1 H, d, *J* 8.9, 8'-H *anti*), 6.55 (1 H, t, *J* 7.5, 5-H *anti*), 6.44 (1 H, d, *J* 7.5, 7-H *anti*), 6.08 (1 H, d, *J* 10.4, 3'-H *anti*), 5.91 (1 H, d, *J* 7.5, 4-H *anti*), 5.75 (1 H, d, *J* 10.3, 3'-H *syn*), 4.13 (3 H, br s, MC NCH3), 3.62 (1 H, br d, *J* 13.7, MC ArC*H*H), 3.52 (1 H, br d, *J* 13.7, MC ArC*H*H), 3.05 (2 H, br s, ArC*H*H *anti*), 2.73 - 2.38 (2 H, m, MC C*H*HMe), 2.60 (3 H, s, NMe *anti*), 2.56 (3 H, s, NMe *syn*), 1.91 (1 H, dq, *J* 14.8, 7.4, C*H*HMe *anti*), 1.85 (1 H, dq, *J* 14.8, 7.4, C*H*HMe *anti*), 1.80 - 1.72 (2 H, m, C*H*HMe *syn*), 0.89 (3 H, t, *J* 7.4, CMe *anti*), 0.62 (3 H, t, *J* 7.3, CMe *syn*) and 0.36 (3 H, br s, MC CMe); δC(100 MHz; $CDCl_3$); *anti* diastereoisomer: 159.4, 148.3, 140.9, 136.6, 132.5, 132.4, 129.7, 128.2, 128.0, 127.5, 126.4, 126.3, 123.9, 122.9, 121.9, 119.2, 118.4, 115.5, 107.2, 105.5 (2-C), 58.4 (3-C), 35.3 ($ArCH_2$), 29.3 (NMe), 28.2 (CH_2CH_3) and 8.9 (CH_2CH_3); *syn* diastereoisomer: 158.8, 147.8, 141.2, 137.7, 132.9, 131.6, 127.2, 127.0, 126.7, 126.6, 125.7, 124.8, 123.7, 122.6, 121.2, 115.9, 106.8, 104.5 (2-C), 53.8 (3-C), 34.8 ($ArCH_2$), 31.8 (NMe), 28.2 (CH_2CH_3) and 8.6 (CH_2CH_3)(3 peaks missing); merocyanine: 180.9 (2-C), 168.1, 150.2, 142.7, 139.3, 138.4, 133.2, 132.1, 132.0, 131.6, 130.0, 129.6, 129.3, 127.8, 126.0, 124.2, 120.9, 119.4, 119.3, 114.4, 113.6, 63.0 (NMe), 44.6 (3-C), 32.8

($ArCH_2$), 22.9 (CH_2CH_3) and 8.6 (CH_2CH_3); HRMS-ES (*m/z*): Found: 491.0968 (MH^+, $C_{26}H_{24}O_3N_2Br$ requires: 491.0970).

Anti-(2*R,3*S**)- and _syn_-(2*R**,3*R**)-1,3-dibenzyl-3-methyl-6′-nitrospiro[chromene-2,2'-indoline] 6o**

Using the same general method, 1-benzyl-2,3-dimethylindole (136 mg, 0.578 mmol), benzyl bromide (103 μL, 0.867 mmol) and 5-nitrosalicylaldehyde (116 mg, 0.694 mmol) gave *spiropyran* **6o** (203 mg, 74%) as a purple amorphous film, R_f 0.6 (5:95 methanol:ethyl acetate); ν_{max} = 3028, 2926, 1710, 1605, 1517, 1479, 1334, 1271, 1088, 948, 807 and 747 cm^{-1}; δH(400 MHz; $CDCl_3$; 22:78 *syn*:*anti*) 8.01 (1 H, dd, *J* 9.0, 2.4, 7'-H *syn*), 7.95 - 7.90 (2 H, m, 5'-, 7'-H *anti*), 7.86 (1 H, d, *J* 2.4, 5'-H *syn*), 7.25 - 7.06 (12 H, m, a'-, b'-, c'-, b-H *anti*; b'-, c'-, b-H *syn*), 7.05 - 6.94 (5 H, m, 6-H *anti*; a-, 4-, 6-H *syn*), 6.86 (1 H, d, *J* 10.4, 4'-H *anti*), 6.80 (1 H, d, *J* 9.0, 8'-H *syn*), 6.78 (1 H, t, *J* 7.5, 5-H *syn*), 6.70 (1 H, d, *J* 8.6, 8'-H *anti*), 6.68 - 6.60 (3 H, m, 5-, a-H *anti*), 6.53 (1 H, d, *J* 10.3, 4'-H *syn*), 6.30 (1 H, d, *J* 7.8, 7-H *anti*), 6.29 (1 H, d, *J* 7.1, 4-H *anti*), 6.24 (1 H, d, *J* 7.8, 7-H *syn*), 6.01 (1 H, d, *J* 10.4, 3'-H *anti*), 5.68 (1 H, d, *J* 10.3, 3'-H *syn*), 4.48 (1 H, d, *J* 16.5, NC*H*H *anti*), 4.22 (1 H, d, *J* 16.2, NC*H*H *syn*), 4.17 (1 H, d, *J* 16.5,NC*H*H *anti*), 3.99 (1 H, d, *J* 16.2, NC*H*H *syn*), 3.18 (1 H, d, *J* 13.5, 3-C*H*H *syn*), 3.16 (1 H, d, *J* 13.5, 3-C*H*H *syn*), 2.81 (1 H, d, *J* 12.6, 3-C*H*H *anti*), 2.79 (1 H, d, *J* 12.6, 3-C*H*H *anti*), 1.34 (3 H, s, Me *syn*) and 1.20 (3 H, s, Me *anti*); δC(100 MHz; $CDCl_3$); *anti* diastereoisomer: 159.8, 147.9, 141.1, 138.6, 136.7, 131.4, 131.0, 128.9, 128.7, 128.0, 127.4, 127.1, 126.5, 126.4, 126.3, 126.1, 124.7, 122.8, 121.9, 119.0, 115.7, 108.0, 107.9 (2-C), 57.8 (3-C), 48.1 (NCH_2), 42.4 (3-CH_2) and 17.3 (3-Me); *syn* diastereoisomer: 158.9, 146.4, 141.2, 138.4, 137.4, 135.6, 132.2, 128.8, 128.5, 128.3, 127.6, 127.4, 126.6, 125.8, 122.7, 122.4, 121.1, 119.9, 119.0, 118.7, 115.9, 108.2, 105.0 (2-C), 54.9 (3-C), 46.9 (NCH_2), 39.4 (3-CH_2) and 24.2 (3-Me); HRMS-ES (*m/z*): Found: 475.2010 (MH^+, $C_{31}H_{27}O_3N_2$ requires: 475.2021).

Anti-(2*R,3*S**)- and _syn_-(2*R**,3*R**)-3-benzyl-6′-bromo-1,3-dimethylspiro[chromene-2,2'-indoline] 6p**

Using the same general method, 1,2,3-trimethylindole (99 mg, 0.622 mmol), benzyl bromide (111 μL, 0.933 mmol) and 5-bromosalicylaldehyde (150 mg, 0.746 mmol) gave *spiropyran* **6p** (222 mg, 83%) as a purple amorphous film, R_f 0.4 (5:95 methanol:ethyl acetate); ν_{max} = 3027, 2926, 1711, 1605, 1474, 1361, 957, 815, 752 and 703 cm^{-1}; δH(400 MHz; $CDCl_3$; 5:26:69 MC:*syn*:*anti*) 8.31 (1 H, br d, *J* 15.9, MC 4'-H), 7.70 - 7.54 (3 H, m, MC), 7.48 - 7.40 (4 H, m, MC), 7.18 (1 H, dd, *J* 8.5, 2.4, 7'-H *syn*), 7.15 - 7.01 (9 H, m, 5'-, 7-', 6-, c-H *anti*; 5'-, 6-, b-, c-H *syn*), 6.98 - 6.94 (3 H, m, 4-, a-H *syn*), 6.79 (1 H, d, *J* 10.3, 4'-H *anti*), 6.77 (1 H, t, *J* 7.4, 5-H *syn*), 6.68 (1 H, d, *J* 8.5, 8'-H *syn*), 6.62 (2 H, dd, *J* 7.8, 1.6, a-H *anti*), 6.56 (1 H, t, *J* 7.2, 5-H *anti*), 6.53 - 6.50 (2 H, m, 7-, 8'-H *anti*), 6.48 (1 H, d, *J* 10.2, 4'-H *syn*), 6.42 (1 H, d, *J* 7.8, 7-H *syn*), 6.08 (1 H, d, *J* 7.2, 4-H *anti*), 5.82 (1 H, d, *J* 10.3, 3'-H *anti*), 5.43 (1 H, d, *J* 10.2, 3'-H *syn*), 3.72 (3 H, br s, MC NMe), 3.42 (2 H, s, MC CH_2), 3.20 (1 H, d, *J* 13.5, C*H*H *syn*), 3.05 (1 H, d, *J* 13.5, C*H*H *syn*), 2.72 (3 H, s, NMe *anti*), 2.71 (1 H, d, *J* 12.2, C*H*H *anti*), 2.60 (1 H, d, *J* 12.2, C*H*H *anti*), 2.51 (3 H, s, NMe *syn*), 1.18 (3 H, s, MC CMe), 1.16 (3 H, s, CMe *syn*) and 1.13 (3 H, s, CMe *anti*); δC(100 MHz; $CDCl_3$); *anti* diastereoisomer: 153.7, 148.6, 137.2, 132.4, 131.6, 131.1, 129.1, 129.0, 127.8, 127.5, 127.2, 126.3, 124.9, 120.9, 118.2, 117.0, 111.9, 106.9, 105.9 (2-C), 57.0 (3-C), 41.4 (CH_2), 29.3 (NMe) and 16.7 (3-Me); *syn* diastereoisomer: 152.9, 147.3, 137.8, 135.9, 132.3, 129.1, 128.8, 127.9, 127.1, 126.2, 122.3, 121.2, 120.7, 120.0, 119.2, 117.1, 112.2, 107.1, 102.8 (2-C), 53.9 (3-C), 39.3

(CH_2), 28.2 (NMe) and 23.4 (3-Me); HRMS-ES (*m/z*): Found: 432.0954 (MH^+, $C_{25}H_{23}ONBr$ requires: 432.0963).

Methyl *anti*-(2*R,3*S**)- and *syn*-(2*R**,3*R**)-3-benzyl-1,3-dimethylspiro[chromene-2,2'-indoline]-6′-carboxylate 6q**

Using the same general method, 1,2,3-trimethylindole (99 mg, 0.622 mmol), benzyl bromide (111 μL, 0.933 mmol) and methyl 3-formyl-4-hydroxybenzoate (134 mg, 0.746 mmol) gave *spiropyran* **6q** (179 mg, 70%) as a purple amorphous film, R_f 0.3 (5:95 methanol:ethyl acetate); ν_{max} = 2950, 1711, 1647, 1606, 1483, 1449, 1360, 1286, 1266, 1206, 1171, 953, 767 and 753 cm^{-1}; δH(400 MHz; $CDCl_3$; 21:21:58 MC:*syn*:*anti*) 8.42 (1 H, d, *J* 16.2, MC 4'-H), 8.12 (1 H, d, *J* 1.9, MC 5'-H), 7.81 (1 H, dd, *J* 8.5, 2.1, 7'-H *syn*), 7.75 - 7.71 (2 H, m, 5'-H *syn* and *anti*), 7.70 (1 H, dd, *J* 8.0, 2.1, 7'-H *anti*), 7.66 (1 H, d, *J* 16.2, MC 3'-H), 7.50 - 7.43 (3 H, m, MC), 7.30 (1 H, d, *J* 8.0, MC), 7.18 - 6.92 (10 H, m, *J* 7.9, 6-, b-, c-H *anti*; 6-, a-, b-, c-H *syn*), 6.90 (1 H, d, *J* 10.3, 4'-H *anti*), 6.82 (1 H, d, *J* 8.2, 8'-H *syn*), 6.79 (1 H, t, *J* 7.5, 5-H *syn*), 6.65 (1 H, d, *J* 8.0, 8'-H *anti*), 6.62 (2 H, dd, *J* 8.0, 1.5, a-H *anti*), 6.58 (1 H, t, *J* 7.2, 5-H *anti*), 6.57 (1 H, d, *J* 10.2, 4'-H *syn*), 6.53 (1 H, d, *J* 7.8, 7-H *anti*), 6.46 (1 H, d, *J* 7.5, 4-H *syn*), 6.45 (1 H, d, *J* 7.5, 7-H *syn*), 6.04 (1 H, d, *J* 7.2, 4-H *anti*), 5.84 (1 H, d, *J* 10.3, 3'-H *anti*), 5.47 (1 H, d, *J* 10.2, 3'-H *syn*), 3.82 (3 H, s, OMe *syn*), 3.81 (3 H, s, OMe *anti*), 3.80 (3 H, s, MC OMe), 3.76 (3 H, s, MC NMe), 3.47 (2 H, s, MC CH_2), 3.20 (1 H, d, *J* 13.5, C*H*H *syn*), 3.07 (1 H, d, *J* 13.5, C*H*H *syn*), 2.71 (3 H, s, NMe *anti*), 2.70 (1 H, d, *J* 12.2, C*H*H *anti*), 2.63 (1 H, d, *J* 12.2, C*H*H *anti*), 2.52 (3 H, s, NMe *syn*), 1.19 (3 H, s, CMe *syn*), 1.19 (3 H, s, MC CMe) and 1.12 (3 H, s, CMe *anti*); δC(100 MHz; $CDCl_3$); *anti* diastereoisomer: 166.8 (C=O), 158.6, 148.5, 137.1, 132.4, 131.8, 131.6, 131.0, 129.6, 128.8, 127.9, 127.2, 127.1, 126.3, 125.0, 120.2, 118.3, 115.1, 107.1, 106.6 (2-C), 57.0 (3-C), 51.9 (OMe), 41.5 (CH_2), 29.3 (NMe) and 16.6 (3-Me); *syn* diastereoisomer: 166.8 (C=O), 157.8, 147.2, 140.7, 137.7, 135.9, 129.0, 128.7, 128.2, 128.0, 127.8, 126.2, 122.3, 122.1, 119.4, 118.5, 115.2, 114.2, 107.1, 103.6 (2-C), 58.1 (3-C), 52.2 (OMe), 39.3 (CH_2), 28.1 (NMe) and 23.6 (3-Me); merocyanine: 181.4 (2-C), 166.1 (C=O), 164.5, 151.7, 142.2, 136.5, 133.5, 133.1, 129.8, 129.4, 128.9, 128.5, 123.6, 122.3, 121.9, 120.4, 119.0, 118.5, 112.9, 54.1 (NMe), 52.0 (OMe), 47.7 (3-C), 34.5 (CH_2) and 25.2 (3-Me); HRMS-ES (*m/z*): Found: 412.1910 (MH^+, $C_{27}H_{26}O_3N$ requires: 412.1912).

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