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Synthesis and characterization of symmetric and non-symmetric *bis*-spiropyranylethyne

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Abstract

Symmetric *bis*-spiropyrans have been synthesized by the reaction of 5-[2-(3-formyl-4-hydroxyphenyl)ethynyl]-2-hydroxybenzaldehyde, which had previously been prepared by a palladium-catalyzed reaction of 2-hydroxy-5-iodobenzaldehyde and 5-ethynyl-2-hydroxybenzaldehyde, with 2 equiv. of Fischer's bases. Non-symmetric *bis*-spiropyrans were synthesized by palladium-catalyzed reaction of 6-iodospiropyrans with 6-ethynylspiropyrans, which had been prepared by reaction of 2-hydroxy-5-iodobenzaldehyde with 1 equiv. of Fischer's base, and the reaction of 5-ethynyl-2-hydroxybenzaldehyde with 1 equiv. of Fischer's base respectively. The *bis*-spiropyrans obtained were characterized by ^{1}H NMR, IR spectroscopy, UV and GC-MS. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photochromic dyes; Symmetric *bis*-spiropyran; Non-symmetric *bis*-spiropyran; Palladium-catalyzed reactions

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1. Introduction

In recent years, photochromic and thermochromic benzospiropyrans have been receiving considerable attention, due to their potential application in many new technologies, such as data recording and storage, optical switching, displays, and non-linear optics [1,2].

Since the stability of the spiropyran, the absorption associated with the merocyanine chromophore of the ring-opened form produced by exposure to light and other physical properties are strongly dependent on the substituent, it was of interest to investigate the influence of structural changes of the parent spiropyran, especially for a ferroelectric liquid crystal optical switch, based on the principle of photo-resolution [3]. In this respect, relevant structural modifications of spiropyrans have been investigated [4,5].

In this paper, we report on the synthesis and the characterization of some symmetric and non-symmetric spiropyrans, in which two spiropyrans are linked by an ethynyl group. We have previously synthesized and reported on the *bis*-spiropyran in which two spiropyrans were connected directly through C-6 [6]. The key step for the synthesis of these *bis*-spiropyrans is the palladium-catalyzed reaction, for which reaction conditions in the

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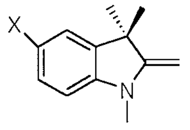
6-iodospiropyran system have been recently reported by us [7]. The symmetric *bis*-spiropyrans **5a**–**5c** were synthesized by the reaction of 5-[2-(3-formyl-4-hydroxyphenyl)ethynyl]-2-hydroxybenzaldehyde (**3**) with 2 equiv. of Fischer's bases **4a**–**4c** in refluxing ethanol and THF respectively (Scheme 1). The non-symmetric *bis*-spiropyrans **8a**–**8c** were prepared by the palladium-catalyzed reaction of 6-iodospiropyrans **6a**, and **6b** with 6-ethynylspiropyrans **7a** and **7b** in the presence of palladium (II) chloride, triethylamine, copper (I) iodide in a solution of acetonitrile and THF.

2. Result and discussion

2.1. Synthesis

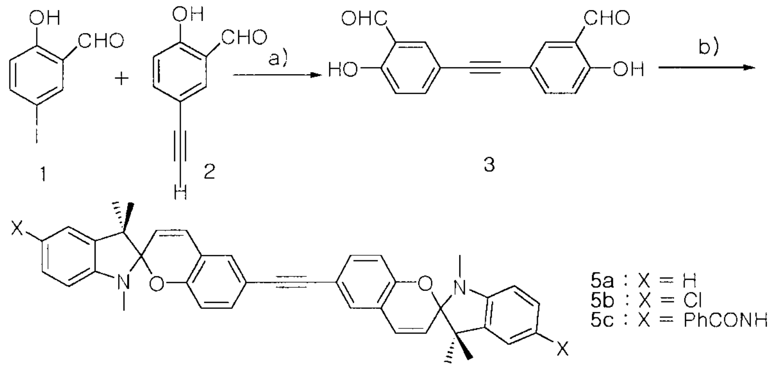
The symmetric *bis*-spiropyrans **5a**–**5c** were prepared by refluxing the 5-[2-(3-formyl-4-hydroxyphenyl)-ethynyl]-2-hydroxybenzaldehyde **3** with Fischer's bases **4a**–**4c**. The 5-[2-(3-formyl-4-hydroxyphenyl)-ethynyl]-2-hydroxybenzaldehyde was prepared by reaction of 2-hydroxy-5-iodobenzaldehyde with 5-ethynyl-2-hydroxybenzaldehyde using Palladium (0), which was generated in situ. The reagent and reaction conditions for this reaction were the aryl iodide, palladium (II) chloride, CuI, triethylamine (excess) in refluxing acetonitrile and THF, by dropwise addition of the ethyne compound in acetonitrile (generally over 20 min). By such dropwise addition, the formation of the by-product (dimer), which was formed during reaction with terminal ethyne, could be avoided. Because the solubility of *bis*-spiropyran **5c** was not good, this compound was separated by adding THF to the concentrate and filtering. The other *bis*-spiropyrans **5a**, and **5b** was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane 1:50).

The non-symmetric *bis*-spiropyrans **8a**–**8c** were synthesized by the palladium-catalyzed reaction of 6-ethynylspiropyrans **7a**, and **7b** with 6-iodospiropyrans **6a** and **6b** using in situ generated palladium



4a : X = H
4b : X = Cl
4c : X = PhCONH

Fischer's bases



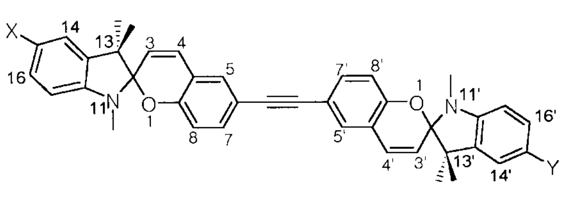
5a : X = H
5b : X = Cl
5c : X = PhCONH

a) $PdCl_2$, PPh_3, CuI, Et_3N in refluxing acetonitrile
b) Fisher base (4a–4c) in refluxing ethanol and THF

Scheme 1.

(0). To avoid the formation of the dimer of 6-ethynylspiropyrans **7a** and **7b**, we used a mixed solvent system (acetonitrile and THF), and added the 6-ethynylspiropyrans **7a** and **7b** dropwise over 20 min. The 6-iodospiropyrans **6a** and **6b** were synthesized by reaction of 2-hydroxy-5-iodobenzaldehyde **1** with the Fischer's bases **4a** and **4c** respectively in refluxing ethanol, and the 6-ethynylspiropyrans **7a** and **7b** were synthesized by reaction of 5-ethynyl-2-hydroxybenzaldehyde **2** with the Fischer's bases **4a** and **4b** in refluxing ethanol.

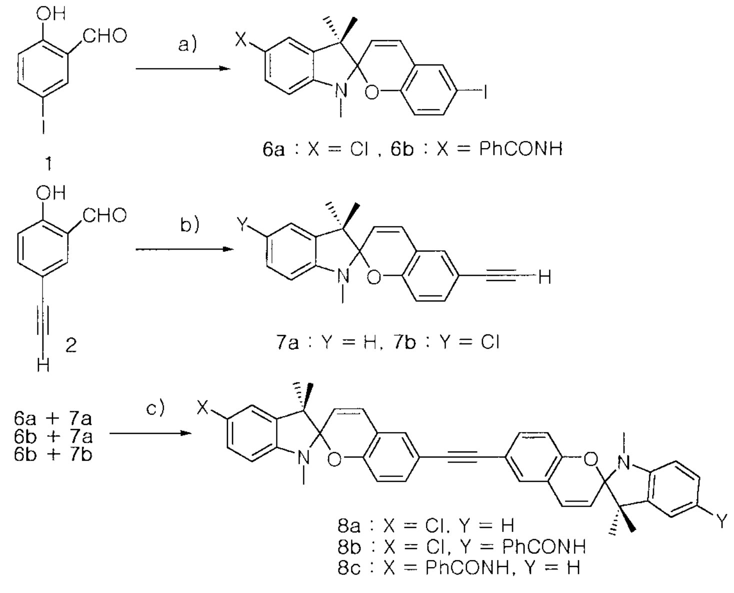
2.2. *Characterization of* bis-*spiropyran*



Ring numbering of bis−spiropyrans

The intermediates for the synthesis of *bis*-spiropyran were characterized by ^{1}H NMR and IR (Table 1); other data (m.p., yield and reaction time) are also shown in Table 1.

The final *bis*-spiropyran was characterized by ^{1}H NMR, IR, UV and GC-MS, and relevant data are shown in Tables 2 and 3. The two ethenylic protons (3, 3′ and 4, 4′) of symmetric *bis*-spiropyrans **5a**–**5c** have the same chemical shift [$\delta = 5.72$ (**5a**), 5.69 (**5b**), 5.72 (**5c**) for protons at C-3 and C-3′ respectively] and [$\delta = 6.83$ (**5a**), 6.84 (**5b** and **5c**) for protons at C-4 and C-4′ respectively] (Table 3). The coupling constants of these spiropyrans are $J = 10.2$ Hz (**5a**), 10.4 Hz (**5b** and **5c**) respectively. These data indicate that protons at C-3 and C-3′ (C-4 and C-4′) are in the same magnetic environment in all symmetric *bis*-spiropyrans. The NH proton of *bis*-spiropyran **5c** appears at 7.72 ppm as a singlet. The carbonyl band of the benzamido group of **5c** appears in 1651 cm^{-1} in the IR (Table 2). The $\lambda_{\max}$ values of symmetric *bis*-spiropyrans are 303 nm (**5a**), 305 nm (**5b**) and 310



a) Fisher base (4a and 4c) in refluxing ethanol b) Fischer's base (4a and 4b) in refluxing ethanol c) $PdCl_2$, Ph_3P, CuI Et_3N in refluxing acetonitrile and THF

Scheme 2.

nm (**5c**) respectively. The substituents (Cl and benzamido) did not seem to affect the $\lambda_{\max}$ of UV very much. The symmetric *bis*-spiropyrans **5a**–**5c** did not show CC stretching absorption band, but the CC triple bond of 6-ethynylspiropyrans **7a** and **7b** appeared at 2152 cm^{-1} as a weak band.

The two ethenylic protons of the non-symmetric *bis*-spiropyrans **8a** and **8b** showed different chemical shifts [$\delta = 5.69$ (**8a**), 5.71 (**8b**) for proton at C-3, and $\delta = 5.72$ (**8a**) and 5.68 (**8b**) for proton at C-3′ respectively] as expected, and the coupling constant, *J*, was 10.4 Hz for **8a**, 10.2 Hz for **8b**, which implies that the substituent at the C-15 and C-15′ positions electronically influence the chemical shift of the ethenylic protons. The ethenylic protons (3, 3′) of **8c** have the same chemical shift ($\delta = 5.72$) and coupling constant ($J = 10.2$ Hz), which indicates their same chemical environment.

Table 1
Yield and characterization data of intermediates

SP	Reaction time	Yield	m.p. (°C)	IR (KBr pellet) cm^{-1}	^1H NMR (200 Hz) δ
3	2 h	98%	160	2874 (m), 2101 (w), 1657 (s), 1488 (s)	(DMSO-d_6) 7.00 (d, $J = 8.6$ Hz, aromatic 1H), 7.64 (d, $J = 8.6$ Hz, aromatic 1H), 7.76 (s, aromatic 1H), 10.24 (s, 1H, CHO), 11.11 (s, 1H, OH)
6a	18 h	89%	69.1	2963 (m), 1646 (m), 1605 (s), 1475 (s)	($CDCl_3$) 1.16 (s, 3H), 1.29 (s, 3H), 2.72, (s, 3H), 2.96 (s, 1H), 5.72 (d, $J = 10.4$ Hz, 1H), 6.53 (d, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 9.0$ Hz, 1H), 6.81 (d, $J = 10.4$ Hz, 1H), 6.84 (t, $J = 7.0$ Hz, 1H), 7.08 (d, $J = 7.0$ Hz, 1H), 7.14–7.26 (m, 3H)
6b	47 h	65%	216.2	2964 (m), 1644 (s), 1493 (s)	($CDCl_3$) 1.78 (s, 3H), 1.29 (s, 3H), 2.70 (s, 3H), 5.70 (d, $J = 10.4$ Hz, 1H), 6.48 (d, $J = 9.2$ Hz, 1 H), 6.49 (d, $J = 8.4$ Hz, 1H), 6.77 (d, $J = 10.4$ Hz, 1H), 7.25–7.51 (m, 7H), 7.72 (s, 1H), 7.84–7.88 (m, 2H)
7a	16 h	96%	90.1	2969 (m), 2868 (m), 2153 (w), 1607 (s), 1486 (s)	($CDCl_3$) 1.63 (s, 3H), 1.29 (s, 3H), 2.72 (s, 3H), 2.96 (s, 1H), 5.72 (d, $J = 10.4$ Hz, 1H), 6.53 (d, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 9.0$ Hz, 1H), 6.81 (d, $J = 10.4$ Hz, 1H), 6.84 (t, $J = 7.0$ Hz, 1H), 7.08 (d, $J = 7.0$ Hz, 1H), 7.14–7.26 (m, 3H)
7b	22 h	95%	94.4	2961 (m), 2151 (w), 1605 (s), 1484 (s)	($CDCl_3$) 1.45 (s, 3H), 1.25 (s, 3H), 2.68 (s, 3H), 2.96 (s, 1H), 5.68 (d, $J = 10.2$ Hz, 1H), 6.41 (d, $J = 8.0$ Hz, 1H), 6.64 (d, $J = 8.2$ Hz, 1H) 6.81 (d, $J = 10.2$ Hz, 1H) 7.00 (d, $J = 1.8$ Hz, 1H), 7.11 (dd, $J = 8.0$ Hz and 1.8 Hz, 1H), 7.20–7.25 (m, 2H)

Table 2
Yield and characterization data of *bis*-spiropyrans

SP	**5a**	**5b**	**5c**	**8a**	**8b**	**8c**
Reaction time (h)	22	12	13	2	2	2
Yield (%)	35	72.5	21.5	91.2	95.9	97.4
Colour	Pale pink	Pink	Pale violet	Ivory	Ivory	Ivory
m.p.(°C)	148–149	143–144	97	102	155	153
GCMS(*m*/*z*)	576	644	814	611	730	695
UV ($\lambda_{\max}$, nm)	303	305	310	305	308	310
IR (KBr pallet) cm^{-1}	2963 (m), 1606 (s), 1489 (s)	2964 (m), 1605 (s), 1485 (s)	2961 (m), 1651 (m), 1608 (s), 1493 (s)	2962 (m), 1608 (s), 1467 (s)	2962 (m), 1651 (m), 1608 (s), 1492 (s)	2973 (m), 1650 (m), 1606 (s), 1492 (s)

Table 3
^{1}H NMR data of *bis*-spiropyrans

bis-SP	^{1}H NMR ($CDCl_3$, 200 MHz) δ
5a	1.17 (s, 6H), 1.30 (s, 6H), 2.73 (s, 6H), 5.72 (d, J = 10.2 Hz, 2H), 6.53 (d, J = 7.6 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 10.2 Hz, 2H), 6.86 (t, J = 6.8 Hz, 2H), 7.08 (d, J = 6.8 Hz, 2H), 7.15–7.26 (m, 6H)
5b	1.16 (s, 6H), 1.27 (s, 6H), 2.70 (s, 6H), 5.69 (d, J = 10.4 Hz, 2H), 6.43 (d, J = 8.2 Hz, 2H), 6.67 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 10.4 Hz, 2H), 7.01 (d, J = 2.2 Hz, 2H), 7.12 (dd, J = 8.2 Hz, and 2.2 Hz, 2H), 7.22–7.26 (m, 4H)
5c	1.20 (s, 6H), 1.31 (s, 6H), 2.72 (s, 6H), 5.72 (d, J = 10.4 Hz, 2H), 6.51 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 10.4 Hz, 2H), 7.21–7.55 (m, 14H), 7.72 (s, 2H), 7.85–7.80 (m, 4H)
8a	1.17 (s, 6H), 1.29 (s, 3H), 1.30 (s, 3H), 2.70 (s, 3H), 2.73 (s, 3H), 5.69 (d, J = 10.4 Hz, 1H), 5.72 (d, J = 10.2 Hz, 1H), 6.43 (d, J = 8.2 Hz, 1H), 6.54 (d, J = 7.8 Hz, 1H), 6.67 (d, J = 8.2 Hz, 2H), 6.82–6.89 (m, 3H), 7.02 (d, J = 1.8 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 7.12 (dd, J = 8,2 and 1.8 Hz, 1H), 7.19–7.26 (m, 5H)
8b	1.15 (s, 3H), 1. 19 (s, 3H), 1.26 (s, 3H), 1.30 (s, 3H), 2.69 (s, 3H), 2.71 (s, 3H), 5.68 (d, J = 10.2 Hz, 1H), 5.71 (d, J = 10.2 Hz, 1H), 6.41 (d, J = 8.4 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 2H), 6.83 (d, J 10.2 Hz, 2H), 7.00 (d, J = 2.2 Hz, 1H), 7.11 (dd, J = 8.4 and 2.2 Hz, 1H), 7.20–7.51 (m, 9H), 7.70 (s, 1H), 7.84–7.95 (m, 2H)
8c	1.17 (s, 3H), 1.20 (s, 3H), 1.30 (s, 3H), 1.31 (s, 3H), 2.73 (s, 6H), 5.72 (d, J = 10.2 Hz, 2H), 6.51 (d, J = 8.4 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 6.68 (d, J = 8.8 Hz, 2H), 6.84 (d, 10.2 Hz, 2H), 6.86 (t, J = 7.8 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 7.15–7.52 (m, 10H), 7.72 (s, 1H), 7.86–7.89 (m, 2H)

The ethenylic protons of **8a** appear in the multiples region (6.82–6.89 ppm), with the C-15′ proton. The other ethenylic protons (4, 4′) of the non-symmetric *bis*-spiropyrans **8b** and **8c** appear at $\delta =$ 6.83 (J = 10.2 Hz), 6.84 (J = 10.2 Hz) ppm respectively. The λ_{max} of the non-symmetric *bis*-spiropyrans **8a**–**8c** were at 305, 308 and 310 nm respectively. The absorption band of the ethynyl group of the non-symmetric *bis*-spiropyrans was not apparent in the IR spectra, which means that the substituents at C-15 and C-15′ in **8a**–**8c** do not influence the appearance of the triple bond in the IR spectra. The UV and IR data of the *bis*-spiropyrans are shown in Table 2.

Bis-spiropyrans **5a**, **5b**, **8a** and **8b** formed colored merocyanine (MC) form with UV light radiation, which have a very short life time. Colored merocyanine forms did not seem to be formed with UV light radiation in *bis*-spiropyrans **5c** and **8c**. Further detailed studies of the *bis*-spiropyrans **5a**–**5c** and **8a**–**8c** will be reported later.

3. Experimental

Melting points were determined using an Electrothermal IA 900 apparatus and are uncorrected. IR spectra were taken with an Analet Instrument FT–IR (MAP-60) spectrometer using KBr pellets, and UV-Visible absorption spectra were recorded on a Varian Cary 1E UV-Visible spectrometer. The ^{1}H NMR Spectra were recorded on a Bruker Ac 200. EI mass spectra were recorded on a Shimadzu GCMS-QP1000 spectrophotometer.

Synthesis of 5-[2-(3-formyl-4-hydroxyphenyl)-ethynyl]-2-hydroxybenzaldehyde 3

To a solution of 2-hydroxy-5-iodobenzaldehyde (100 mg, 0.40 mmol) in 5 ml of acetonitrile was added triethylamine (0.39 ml), $PdCl_2$ (3.57 mg, 0.02 mmol), triphenylphosphine (10.6 mg, 0.04 mmol) and CuI (1.9 mg, 0.01 mmol). The solution was heated to reflux. To the solution was added dropwise a solution of 5-ethynyl-2-hydroxybenzaldehyde (58.9 mg, 0.40 mmol) in 2 ml of acetonitrile. The reaction was monitored by tlc, on Merck precoated TLC plates (silica gel 60 PF_{254}, 0.25 mm) using a mixture of methylene chloride and hexane (1:1). The solution was then heated to reflux for 4 h. Silica gel (230–400 mesh) was added to the reaction mixture, the solution concentrated, and then run through a short pad of silica gel, using initially 30% methylene chloride in hexane, followed by 50% methylene chloride in hexane, and finally concentrated to give a yellow solid. Relevant characterization data are shown in Table 1.

3.1. General synthetic procedure for symmetric bis-*spiropyrans*

11,13,13-trimethyl-6-[2-(11′,13′,13′-trimethylspiro-[2*H*-chromene-2′,12′-indoline]-6′-yl)]ethynyl]spiro-[2*H*-chromene-2,12-indoline] 5a,15-Chloro-6-[2-(15′-chloro-11′,13′,13′-trimethylspiro[2*H*-chromene-2′,12′-indoline]-6′-yl)ethynyl]-11,13,13-trimethylspiro[2*H*-chromene-2,12-indoline] 5b, *N*-(11,13,13-trimethyl-6-{2-[11′,13′,13′-trimethyl-15′-(benzamido)spiro[2*H*-chromene-2′,12′-indoline]-6′-yl]ethynyl}spiro[2*H*-chromene-2,12-indoline]-15-yl)benzamide 5c.

To a solution of 5-[2-(3-formyl-4-hydroxyphenyl) ethynyl]-2-hydroxybenzaldehyde **3** (100 mg, 0.38 mmol) in anhydrous ethanol (10 ml) and THF (5 ml) was added the appropriate Fischer's base derivative **4a**, **4b** and **4c** (1.13 mmol). The solution was refluxed, and the reaction liquor was then concentrated under reduced pressure. The reaction was monitored by tlc (ethyl acetate: hexane = 1:10).

5a and **5b**: The concentrate was chromatographed on silica gel using a mixture of ethyl acetate and hexane (1:50); Concentration of the eluate gave the symmetric *bis*-spiropyrans.

5c: THF was added to the undissolved solid; residual solid was filtered and dried to give the product. Relevant characterization data are shown in Table 1.

3.2. General synthetic procedure of other spiropyrans

15-Chloro-6-iodo-11,13,13-trimethylspiro[2H-chromene-2,12-indoline] 6a, *N*-(6-*iodo*-11,13,13-trimethylspiro[2*H*-chromene-2,12-indoline]-15-yl)-benzamide 6b, 6-Ethynyl-11,13,13-trimethylspiro-[2*H*-chromene-2,12-indoline] 7a, 15-chloro-6-ethynyl-11,13,13-trimethylspiro[2*H*-chromene-2,12-indoline] 7b.

A solution of 100 mg (0.4 mmol of the 2-hydroxy-5-iodobenzaldehyde **1** and 0.68 mmol of the 5-ethynyl-2-hydroxybenzaldehyde **2**), and the corresponding Fischer's bases (1 equiv.) (**4a**, **4b** and **4c**) in ethanol was refluxed. The reaction was monitored by tlc (ethyl acetate: hexane = 1:10). The reaction was then concentrated to give a syrup; appropriate products were isolated as follows:

6a, **7a** and **7b**: The concentrate was chromatographed on silica gel using a mixture of ethyl acetate and hexane (1:100) as eluant, and concentrated to give solid products, viz: **6a** and **7a** ivory, and **7b** pink.

6b: ethyl acetate was added to the concentrate; undissolved solid was filtered and dried to give a pale ivory solid.

3.3. General synthetic procedure of non-symmetric bis-*spiropyrans*

15-Chloro-11,13,13-trimethyl-6-[2-(11′,13′,13′-trimethylspiro[2*H*-chromene-2′,12′-indoline]-6′-yl)ethynyl]spiro[2*H*-chromene-2,12-indoline] 8a, *N*-{16-[2(15-Chloro-11,13,13-trimethylspiro[2*H*-chromene-2,12-indoline]-6-yl)ethynyl]-11′,13′,13′-trimethylspiro-[2*H*-chromene-2′,12′-indoline]-15′-yl)benzamide 8b, *N*-{11,13,13-trimethyl-6-[2-(11′,13′,13′-trimethyl-spiro[2*H*-chromene-2′,12′-indoline]-6′-yl)ethynyl]-spiro[2*H*-chromene-2,12-indoline]-15-yl}benzamide 8c.

To a solution of 6-iodospiropyrans (0.23 mmol **6a** and **6b**), palladium chloride (2 mg, 0.01 mmol), triphenylphosphine (6 mg, 0.02 mmol), triethylamine (0.22 ml), copper iodide (1.1 mg, 0.006 mmol) in a hot mixture of THF (2 ml) and acetonitrile (6 ml) was added the 6-ethynylspiropyran **7a** or **7b** (1 equiv.) in acetonitrile dropwise over 20 min under a nitrogen atmosphere. The resulting solution was refluxed for 2 h and concentrated to give a syrup. The syrup was chromatographed on silica gel using a mixture of ethyl acetate and hexane (**8a** 1:50) (**8b** and **8c**: 1:5), and the eluant concentrated to give the required products.

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