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Full Paper

Synthesis of 5'-Functionalized Indolinospiropyrans with Vinylene Unit as Linker

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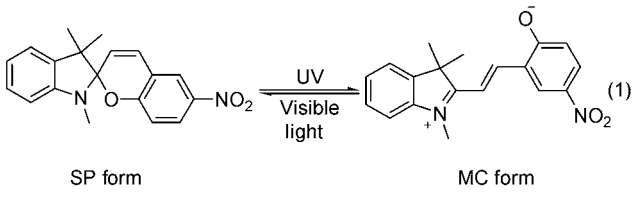
A protocol for the synthesis of a new family of spiropyran derivatives is described. A 5-formylated indoline intermediate (**5**) was achieved for the first time, which was the key intermediate for constructing the spiropyran derivatives with vinylene linker. Five 5'-functionalized indolinospiropyrans (**11**—**15**) were obtained by utilizing vinylene unit as a linkage between the photochromic spiropyran fragment and the ferrocene or triphenylamine donor.

Keywords synthesis, photochromic material, spiropyran compound

Introduction

The ability of photochromic organic compounds to reversibly alter their colors upon absorption of electromagnetic radiations has been attracting intense investigations, resulting in the synthesis of varieties of structural motifs.[1,2] The potential applications for these molecules are numerous including information storage, imaging devices, smart windows, ophthalmic lenses, solar protection lenses, filters and decorative objects.[2] Photochromic materials have also been utilized for photoswitching.[3] Spiropyran derivatives (particularly indolinospiropyrans) belong to a class of organic photochromic compounds that have been intensively studied.[4] A spiropyran converts from the colorless form (SP form) to the colored merocyanine form (MC form) upon irradiation with UV light, but reverts to the SP form when left in the dark or upon irradiation with visible light (Eq. 1). The open MC form has a larger dipole moment than the closed SP form. As a result, the MC form is normally unstable and converts to the SP form automatically. Apparently, the instability of the MC form would significantly limit the applications of spiropyans as advanced materials.



The stability of the MC form strongly depends on the electronic effects of the substituent(s) at the indolium or phenyl sector of indolinospiropyrans. The most effective molecular modification is to introduce a donor group into the 5'-position of the indolinospiropyran core.[5] But until now there have been few reports on the successful synthesis of 5'-donor-substituted indolinospiropyrans.[6,7] Furthermore, the 5'-substituents were linked to the indoline moiety unexceptionally by the triple bond[6] or single bond[5b,7] as shown in Figures 1a and 1b. Generally, the use of the carbon-carbon double bond as linkage between a donor group and a spiropyran core (Figure 1c) should be more favorable for the conjugation effects by which the ability of the donor group to stabilize the MC form would be substantially enhanced. Such spiropyran derivatives, however, have not yet been reported due likely to difficulties in synthesis. This challenge triggered off our interest in performing a synthetic strategy for access to these new spiropyran derivatives. Herein, we want to present our findings in this study.

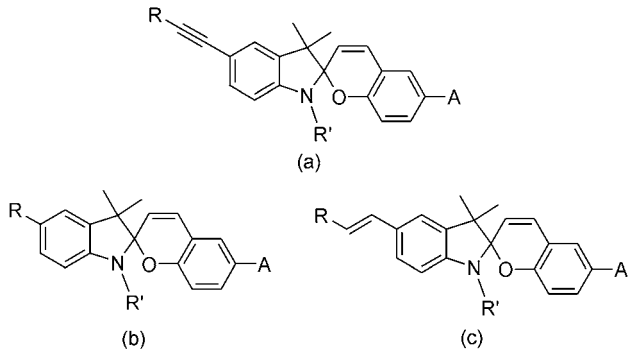


Figure 1 Schematics of reported 5'-fuctionalized spiropyrans (a) and (b), and proposed target molecules (c).

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Results and discussion

The most common photochromic spiropyran scaffold is generally prepared by condensation of the Fischer's base (indoline) with the substituted salicylaldehyde. To construct a carbon-carbon double bond through the Wittig reaction, accessibility to the key intermediates, 5-formylated indoline/spiropyran derivatives as shown in Figure 2, is essential for our synthetic strategy. However, this is not actually an easy task. Direct electrophilic substitution reactions at the 5-position of an indoline or indolinospiropyran proved to fail. For instance, formylation of indolines and spiropyrans by the Vilsmeier reaction led to the undesired outcomes as shown in Figure 3.[8] Thus, the derivatizations of indolines or spiropyrans at the 5- or 5'-position were realized only by the functionality transformation of the existing 5- or 5'-functionalizd ones.[6,9] It needs to be pointed out that we also attempted to adopt a stepwise synthetic route to the target compounds starting from the donor molecule, but found it unfeasible after some experimentation.

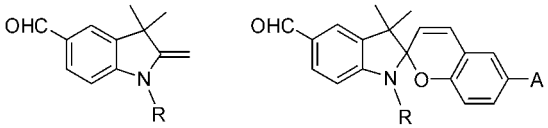


Figure 2 Key intermediates required in this study.

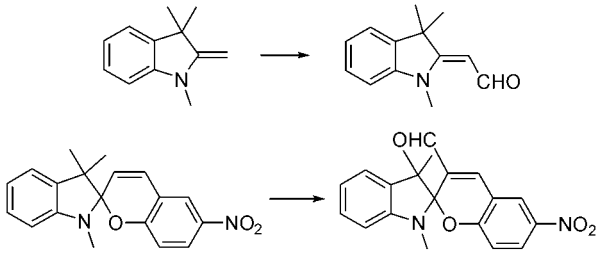
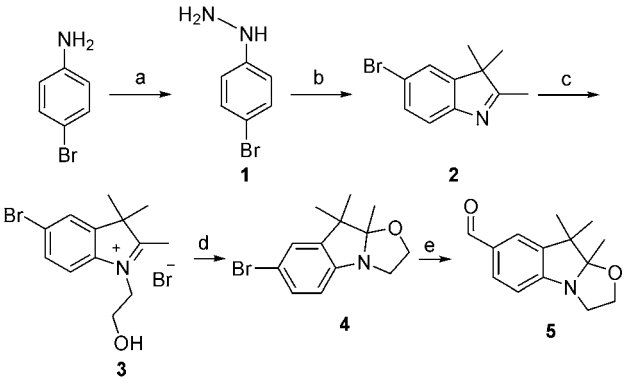


Figure 3 Direct formylation of the indoline or spiropyran.

Since the direct 5-formylation of indolines (or spiropyrans) seemed difficult and even unfeasible, we began to explore an alternative route to the desired aldehyde intermediate. A 5-formylated indoline derivative **5** was prepared in five steps according to Scheme 1. First, 4-bromophenylhydrazine (**1**), from the starting material 4-bromoaniline, was reacted with 3-methylbutan-2-one to give 80% yield of 5-bromo-2,3,3-trimethyl-3*H*-indole (**2**). Then the reaction of compound **2** with 2-bromoethanol afforded 1-(2-hydroxyethyl)-5-bromo-2,3,3-trimethyl-3*H*-indolium bromide (**3**), which was treated with KOH to produce 7-bromo-9,9,9*a*-trimethyl-s,3,9,9*a*-tetrahydro-oxazolo(3,2-*a*)indole (**4**). Finally compound **4** was subjected to a halogen-lithium exchange and subsequent treatment with DMF, affording the desired oxazoloindole aldehyde **5** in a good yield of 76%. The molecular structure of **5** was confirmed by ^{1}H and ^{13}C NMR spectrometry. In the proton NMR spectrum, for example, one sharp singlet appears at δ 9.80 representative of the proton on the CHO group; three singlet peaks (3 protons each peak) are located at δ 1.18, 1.36 and 1.42, respectively, being assigned to the three CH_3 groups.

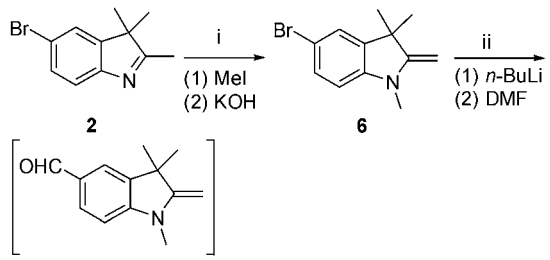
Scheme 1 Synthesis of oxazoloindole aldehyde **5**



Reaction conditions: (a) i. $NaNO_2$/HCl; ii. $SnCl_2$/HCl. (b) 3-methylbutan-2-one, H_2SO_4, reflux. (c) CH_3CN, 2-bromoethanol, reflux. (d) KOH, room temperature. (e) i. BuLi, −78 ℃; ii. DMF, −78 ℃ to room temperature.

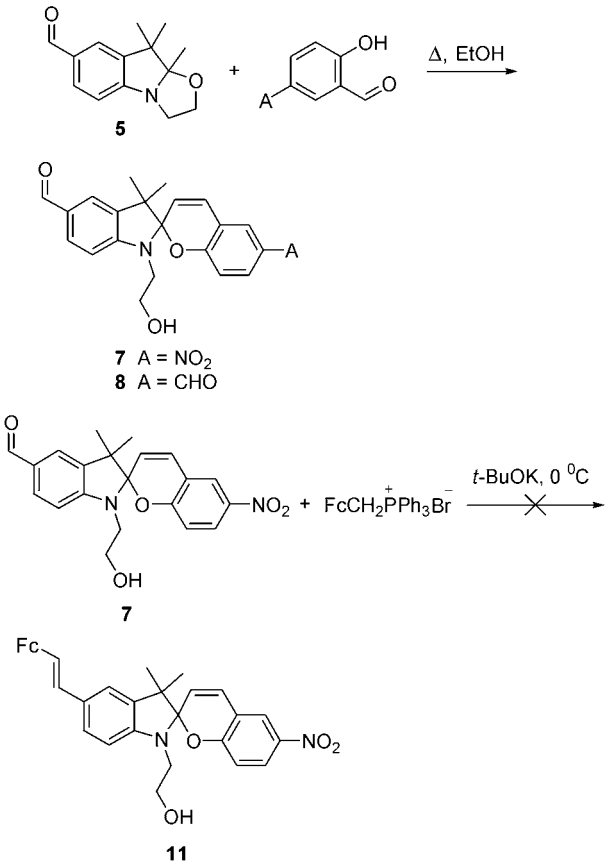
It must be mentioned that we initially attempted to prepare an indoline-5-aldehyde following a simpler mode as shown in Scheme 2. *N*-Methylation of **2** (the step i) proceeded smoothly to give **6**. But the crude products in the step ii were found to be complicated and the desired indoline-5-aldehyde could not be separated out. Presumably, it might be because: (1) compound **6** with 2-methylene group could form an "enamine" structure which would react with the resulting aldehyde such that the pure indoline aldehyde could not be obtained; and (2) the presence of 2-methylene group in compound **6** would make its lithiated species form multiple nucleophilic centers so that the formylation might occur simultaneously at the different positions.

Scheme 2 A failed route to the target indoline-5-aldehyde



With the key intermediate **5** in hand, we began to construct the target spiropyrans according to Scheme 3. Intermediate spiropyrans **7** and **8** were first prepared by the condensation of oxazoloindole aldehyde **5** with substituted salicylaldehydes. Unfortunately, an unidentifiable reaction occurred and the desired product **11** failed to be obtained when **7** was treated with the corresponding Wittig reagent.

Scheme 3 A failed route to the target spiropyrans



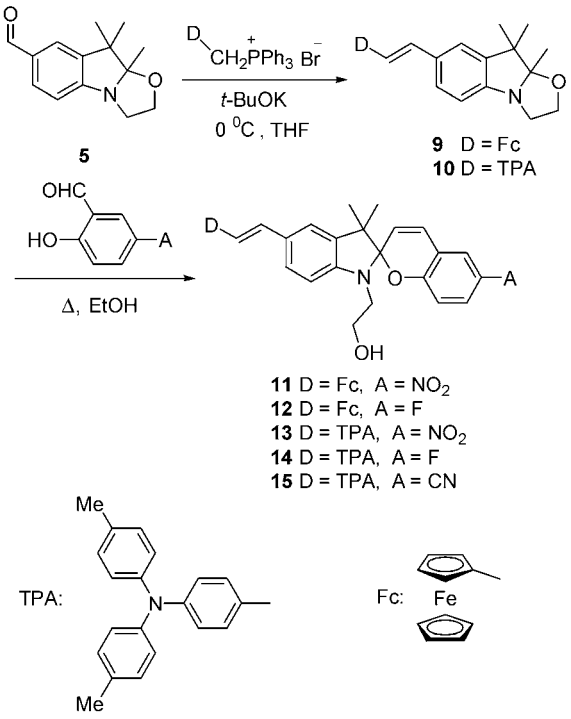
We believed that instability of the spiropyran structure in intermediate **7** under the Wittig reaction conditions may be responsible for this unsuccessful reaction. Therefore, we selected another synthetic route to the target products. As indicated in Scheme 4, the indoline aldehyde **5** was reacted first with the Wittig reagents to give the indoline derivative **9** in 48% yield and **10** in 76% yield, respectively. Compound **9** or **10** existed originally in a mixture of *E*- and *Z*-form isomers and then was transformed to the pure *E*-form isomer by heatment in toluene with catalytic amounts of molecular iodine. Finally the target spiropyran derivatives **11**—**15** were obtained successfully by refluxing a mixture of **9** or **10** and the substituted salicylaldehydes in ethanol with acceptable to good yields.

A demonstration of photochromism for two new spiropyran molecules (**11** and **13**) in acetonitrile solution is shown in the absorption spectra (Figure 4). Their absorption spectra exhibit marked red-shifts compared to the corresponding parent spiropyran molecule because there are larger π-conjugation systems in these 5'-functionalized spiropyran molecules. The bleaching of spiropyran **13** and **11** following irradiation is shown in Figure 5. The absorption spectra of **13** and **11** are characterized by the maxima 588 and 585 nm.

Conclusion

We have demonstrated an intriguing protocol for the

Scheme 4 Synthesis of the target spiropyran derivatives



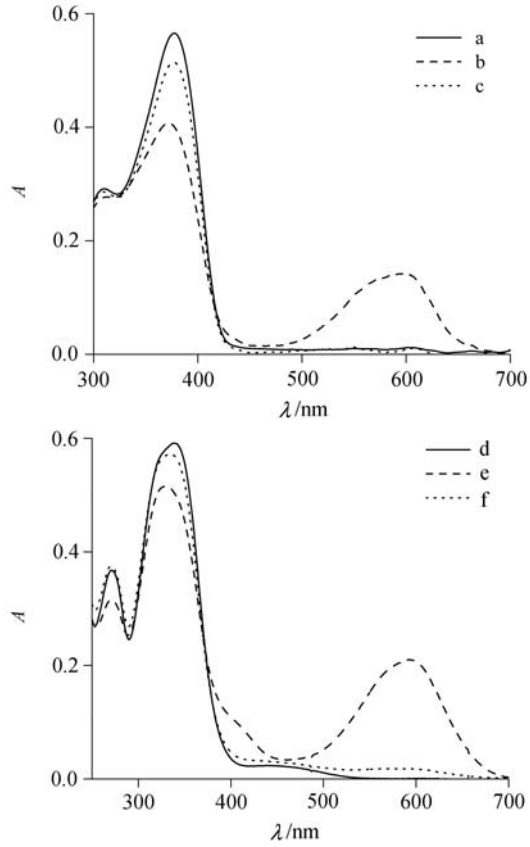


Figure 4 Sequential spectral changes of **13** (curves a—c) and **11** (curves d—f) in MeCN solution: initial state (curve a or d); after irradiation for 4 min with 254 nm light (curve b or e); and after irradiation with visible light (curve c or f).

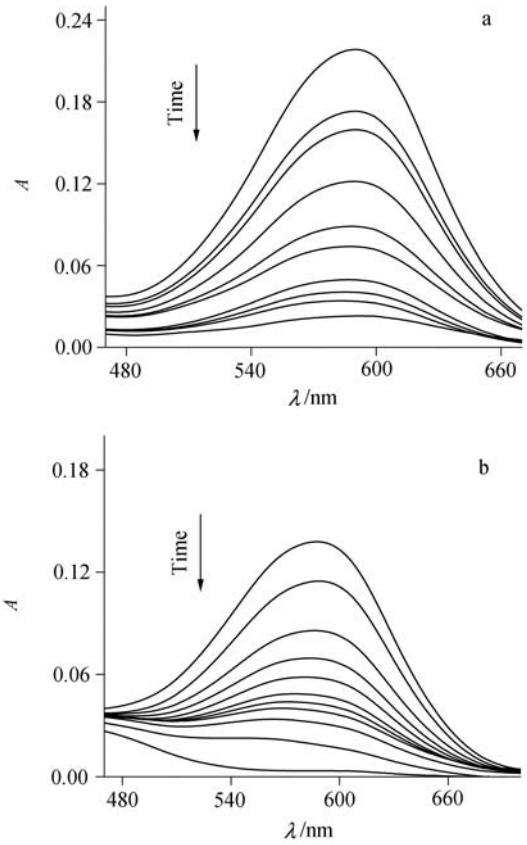


Figure 5 Solution of spiropyrans were irradiated with ultraviolet light and then monitored by absorption under visible light per 30 s over 5 min. The absorption spectra were shown in a (for spiropyran **13**) and b (for spiropyran **11**).

synthesis of 5'-funtionalized spiropyran derivatives with vinylene unit as linkage between the photochromic spiropyran core and the donor substituent. Additionally, an approach to the 5-formylation of indolines was developed. To our knowledge, this is the first example of 5-formylated indoline derivatives. The 5-formylindoline was a key intermediate for constructing our target spiropyran derivatives and will be a very useful and versatile precursor for the synthesis of a wide diversity of spiropyran-based functional materials. These new photochromic materials could possess valuable and interesting performances in applications. Study on their potential applications is under progress and results will be reported as they become available.

Experimental

General considerations THF was distilled from sodium/benzophenone. 4-Bromoaniline, 2-bromoethanol, potassium *tert*-butoxide, *n*-butyllithium, ferrocenylaldehyde, salicylaldehyde, 5-fluorosalicylaldehyde, 4-hydroxybenzonitrile, 4-hydroxybenzaldehyde were available commercially and used without further purification. All other solvents and reagents were used as received. 5-Formylsalicylaldehyde,[10] 5-cyanosalicylaldehyde,[11] (ferrocenylmethyl)triphenylphosphonium bromide,[11] and {4-[di(*p*-tolyl)amino]benzyl}triphenylphosphonium bromide[12] were synthesized according to the literature procedures. Chromatographic separations were carried out on silica gel (200—300 mesh) or aluminum oxide (neutral, 200—300 mesh). The intermediate compounds were confirmed by ^{1}H and/or ^{13}C NMR, and MS. Five target spiropyran derivatives were characterized by ^{1}H and ^{13}C NMR, and HRMS.

(4-Bromophenyl)hydrazine (**1**) A suspension of 4-bromoaniline (5.0 g, 29 mmol) in concentrated hydrochloric acid (50 mL, *w* 36%—37%) was diazotized at 0 ℃ with a solution of sodium nitrite (2.7 g, 39 mmol) in water (25 mL). Then the reaction mixture was reduced at 0 ℃ with $SnCl_2$•$2H_2O$ (17 g, 75 mmol) in concentrated hydrochloric acid (17 mL, *w* 36%—37%) and continuously stirred at room temperature for 1 h. The precipitate produced was collected by filtration and treated with aqueous NaOH (*w*=5%). After extraction with dichloromethane (DCM), the organic solvent was evaporated under vacuum to give the product **1** as a pale-yellow solid (4.46 g, yield 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.56 (s, 2H), 5.18 (s, 1H), 6.72 (d, J=7.95 Hz, 2H), 7.32 (d, J=7.95 Hz, 2H).

5-Bromo-2,3,3-trimethyl-3*H*-indole (**2**) A solution of **1** (1.28 g, 6.8 mmol) and 3-methylbutan-2-one (0.7 mL, 6.5 mmol) in ethanol (7 mL) was refluxed for 3 h. Then a solution of concentrated sulfuric acid (0.7 mL, *w*=98%) in ethanol (7 mL) was added dropwise, and the reaction mixture was refluxed for another 3 h. After cooling to room temperature, water (50 mL) was added and the product extracted with DCM. The organic solvent was evaporated and the residue was purified by column chromatography on silica gel to give the product **2** as a yellow oil (1.31 g, yield 80%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.30 (s, 6H), 2.27 (s, 3H), 7.35—7.49 (m, 3H).

5-Bromo-1-(2-hydroxyethyl)-2,3,3-trimethyl-3*H*-indolium bromide (**3**) A solution of **2** (2.76 g, 11.6 mmol) and 2-bromoethanol (2.6 g, 21 mmol) in acetonitrile (20 mL) was refluxed for 3 d under N_2 atmosphere. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue suspended in diethyl ether to be solidified. The crude product **3** of 3.8 g was collected by suction filtration and used directly in the next step without future purification.

7-Bromo-9,9,9*a*-trimethyl-s,3,9,9*a*-tetrahydro-oxazolo[3,2-*a*]indole (**4**) To a solution of KOH (3.8 g) in H_2O (50 mL) was added 3.8 g of the crude **3**, the mixture stirred at ambient temperature for 10 min, then was extracted with Et_2O and the organic phase was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to give the product **4** as a yellow oil (2.15 g, yield 72%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 1.09 (s, 3H), 1.27 (s, 3H), 1.32 (s, 3H), 3.37—3.58 (m, 2H), 3.64—3.81 (m, 2H), 6.79 (d, J=8.2 Hz, 1H), 7.23 (d, J=8.3 Hz, 1H), 7.26 (d, J=1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ:

17.4, 20.6, 27.9, 47.1, 50.0, 63.0, 109.1, 113.5, 113.8, 125.7, 130.2, 142.4, 149.8.

7-Formyl-9,9,9*a*-trimethyl-s,3,9,9*a*-tetrahydro-oxazolo[3,2-*a*]indole (**5**) To a solution of **4** (2.15 g, 7.6 mmol) in THF (30 mL) was at −78 ℃ added *n*-BuLi (7.5 mL, 1.6 mol•L^{-1} in hexane) and the mixture stirred for 45 min. After addition of anhydrous DMF (1.5 mL), the reaction mixture was stirred at −78 ℃ for 1 h and at room temperature for 3 h. Water (50 mL) was added, followed by extraction with DCM. The organic phase was separated and concentrated. The resulting pink residue was purified by alumina oxide column chromatography to afford the product **5** (1.31 g, yield 76%). ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 1.18 (s, 3H), 1.36 (s, 3H), 1.42 (s, 3H), 3.50—3.69 (m, 2H), 3.70—3.80 (m, 1H), 3.83—3.92 (m, 1H), 6.79 (d, J=8.1 Hz, 1H), 7.60 (d, J=1.2 Hz, 1H), 7.64 (dd, J_1=8.1 Hz, J_2=1.5 Hz, 1H), 9.80 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 16.6, 20.2, 27.3, 45.9, 48.7, 62.5, 108.3, 111.0, 123.0, 130.7, 132.1, 140.6, 156.5, 190.4; MS (EI) *m*/*z*: 231 [M^+].

5-Bromo-1,3,3-trimethyl-2-methylideneindoline (**6**) A solution of **2** (1.1 g, 4.6 mmol) and CH_3I (1.6 g, 11.5 mmol) in $CHCl_3$ (10 mL) was stirred at ambient temperature for 3 d under N_2 atmosphere. The solvent was evaporated under reduced pressure and the residue suspended in diethyl ether and solidified. After filtration, the cake was added to a solution of KOH (3.0 g) in H_2O (30 mL), followed by stirring for 10 min. Then the mixture was extracted with Et_2O and the organic phase was concentrated under reduced pressure. The crude product **6** was got as colorless oil (0.87 g), which turned pink quickly. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.32 (s, 6H), 3.00 (s, 3H), 3.85 (s, 2H), 6.39 (d, J=8.3 Hz, 1H), 7.14 (d, J=1.9 Hz, 1H), 7.21 (dd, J_1=8.3 Hz, J_2=2.0 Hz, 1H).

5'-Formyl-3',3'-dimethyl-1'-(2-hydroxyethyl)-6-nitrospiro[2*H*-1-benzopyran-2,2'-indoline] (**7**) A solution of 5 (0.1 g, 0.44 mmol) and 5-nitrosalicyl-aldehyde (1.3 equiv.) in ethanol (5 mL) was refluxed for 3 h. After purification by silica-gel column chromatography, the product **7** was obtained as a red oil (0.06 g, yield 40%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.17 (s, 3H), 1.29 (s, 3H), 3.30—3.63 (m, 2H), 3.63—3.90 (m, 2H), 5.88 (d, J=10.3 Hz, 1H), 6.72 (d, J=7.9 Hz, 1H), 6.74 (d, J=8.2 Hz, 1H), 6.93 (d, J=10.3 Hz, 1H), 7.59 (s, 1H), 7.64 (d, J=8.1 Hz, 1H), 7.90—8.10 (m, 2H), 9.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 19.9, 25.8, 45.7, 52.3, 60.7, 106.2, 106.3, 115.6, 118.3, 121.0, 122.1, 122.9, 126.1, 128.6, 129.4, 134.2, 136.9, 141.4, 152.6, 158.6, 190.6; MS (EI) *m*/*z*: 380 [M^+].

5'-Formyl-3',3'-dimethyl-1'-(2-hydroxyethyl)-6-formylspiro[2*H*-1-benzopyran-2,2'-indoline] (**8**) A solution of **5** (0.8 g, 3.5 mmol) and 5-formylsalicylaldehyde (1.3 equiv.) in ethanol (30 mL) was refluxed for 3 h. After purification by silica-gel column chromatography, the product **8** was obtained as a yellow oil (0.8 g, yield 75%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.17 (s, 3H), 1.30 (s, 3H), 3.32—3.49 (m, 1H), 3.49—3.66 (m, 1H), 3.68—3.90 (m, 2H), 5.81 (d, J=10.3 Hz, 1H), 6.72 (d, J=8.1 Hz, 1H), 6.78 (d, J=8.3 Hz, 1H), 6.93 (d, J=10.3 Hz, 1H), 7.51—7.75 (m, 4H), 9.73 (s, 1H), 9.79 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 19.9, 25.9, 45.7, 52.1, 60.8, 105.7, 106.2, 115.7, 118.6, 120.0, 122.1, 128.6, 129.2, 129.3, 130.1, 132.8, 134.2, 137.1, 152.7, 158.6, 190.5, 190.6; MS (EI) *m*/*z*: 363 [M^+].

***trans*-7-(2-Ferrocenylvinyl)-9,9,9*a*-trimethyl-s,3,-9,9*a*-tetrahydro-oxazolo[3,2-*a*]indole** (**9**) To a slurry of (ferrocenylmethyl)triphenylphosphonium bromide (2.1 g, 3.9 mmol) in THF (50 mL) was added potassium *tert*-butoxide (0.5 g, 4.5 mmol) at 0 ℃ under N_2 atmosphere, and the reaction mixture stirred at 0 ℃ for 30 min. Then a solution of **5** (0.6 g, 2.6 mmol) in THF (10 mL) was added slowly, and the resulting mixture stirred at 0 ℃ for 30 min and at room temperature for additional 2 h, then poured into ice water and extracted with diethyl ether. The ether layer was washed with brine and dried with $MgSO_4$. A mixture of the *cis* and *trans* products was obtained by a short silica-gel column chromatography. Isomerization to the *trans* product was performed with I_2 in refluxed toluene. The pure *trans* product was obtained as a red solid (0.48 g, yield 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21 (s, 3H), 1.39 (s, 3H), 1.46 (s, 3H), 3.51—3.61 (m, 2H), 3.67—3.77 (m, 1H), 3.80—3.90 (m, 1H), 4.12 (s, 5H), 4.24 (s, 2H), 4.43 (s, 2H), 6.62—6.73 (m, 3H), 7.16 (s, 1H), 7.20 (d, J=8.0 Hz, 1H); MS (EI) *m*/*z*: 413 [M^+].

***trans*-7-{2-[*p*-(Di(*p*-tolyl)amino)phenyl]vinyl}-9,9,9*a*-trimethyl-*s*,3,9,9*a*-tetrahydro-oxazolo[3,2-*a*]indole** (**10**) The product **10** (0.38 g, yield 76%) was obtained in a manner similar to that of product **9** from **5** (0.23 g, 1.0 mmol) and {4-[di(*p*-tolyl)amino]benzyl}triphenylphosphonium bromide (0.94 g, 1.3 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.23 (s, 3H), 1.41 (s, 3H), 1.48 (s, 3H), 3.52—3.68 (m, 2H), 3.68—3.82 (m, 1H), 3.83—3.98 (m, 1H), 6.75 (d, J = 7.9 Hz, 1H), 6.88—7.15 (m, 12H), 7.20—7.42 (m, 4H).

5'-*trans*-(2-Ferrocenylvinyl)-3',3'-dimethyl-1'-(2-hydroxyethyl)-6-nitrospiro[2*H*-1-benzopyran-2,2'-indoline] (**11**) A mixture of **9** (0.15 g, 0.36 mmol) and 5-nitrosalicylaldehyde (0.08 g, 0.48 mmol) in ethanol (10 mL) was refluxed for 3 h. The solvent was evaporated under reduced pressure and the crude product was separated by alumina column chromatography to give the product **11** as a red solid (0.14 g, yield 63%). ^{1}H NMR (acetone-d_6, 400 MHz) δ: 1.22 (s, 3H), 1.32 (s, 3H), 3.27—3.36 (m, 1H), 3.36—3.45 (m, 1H), 3.59—3.70 (m, 1H), 3.70—3.83 (m, 2H), 4.11 (s, 5H), 4.24 (t, J=1.8 Hz, 2H), 4.48 (d, J=1.8 Hz, 2H), 6.10 (d, J=10.4 Hz, 1H), 6.66 (d, J=8.0 Hz, 1H), 6.78 (d, J=16.2 Hz, 1H), 6.79 (d, J=16.3 Hz, 1H), 6.86 (d, J=9.0 Hz, 1H), 7.18 (d, J=10.4 Hz, 1H), 7.24 (dd, J_1=8.0 Hz, J_2=1.7 Hz, 1H), 7.34 (d, J=1.5 Hz, 1H), 8.05 (dd, J_1=9.0 Hz, J_2=2.8 Hz, 1H), 8.08 (d, J=2.7 Hz, 1H); ^{13}C NMR (acetone-d_6, 75 MHz) δ: 18.8, 24.9, 45.6, 52.0, 59.5, 65.8, 65.9, 67.9, 68.4, 84.1, 106.2, 106.5, 114.9, 118.4, 118.6, 121.7, 122.1, 122.2, 125.0, 125.7, 126.2, 127.5, 129.6, 136.1, 140.6, 146.2, 159.0; HRMS (EI-

TOF) calcd for $C_{32}H_{30}FeN_2O_4$ 562.1555, found 562.1559.

5'-*trans*-(2-Ferrocenylvinyl)-3',3'-dimethyl-1'-(2-hydroxyethyl)-6-fluorospiro[2*H*-1-benzopyran-2,2'-indoline] (**12**) A mixture of **9** (0.23 g, 0.56 mmol) and 5-fluorosalicylaldehyde (1.3 equiv.) in ethanol (15 mL) was refluxed for 3 h. The solvent was evaporated under reduced pressure. The resulting residue was separated by silica-gel column chromatography and the red band was collected to yield the product **12** as a brown solid (0.23 g, yield 76%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.18 (s, 3H), 1.30 (s, 3H), 3.19—3.29 (m, 1H), 3.37—3.48 (m, 1H), 3.60—3.78 (m, 3H), 4.11 (s, 5H), 4.23 (t, J=1.7 Hz, 2H), 4.48 (d, J=1.7 Hz, 2H), 5.94 (d, J=10.3 Hz, 1H), 6.61 (d, J=8.0 Hz, 1H), 6.66 (dd, J_1=8.8 Hz, J_2=4.6 Hz, 1H), 6.74 (d, J=16.3 Hz, 1H), 6.79 (d, J=16.3 Hz, 1H), 6.88 (dt, J_1=8.7 Hz, J_2=3.1 Hz, 1H), 6.93—7.01 (m, 2H), 7.20 (dd, J_1=8.0 Hz, J_2=1.6 Hz, 1H), 7.31 (d, J=1.4 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 19.8, 25.7, 45.7, 51.9, 59.2, 66.1, 66.2, 68.8, 84.3, 104.3, 106.2, 115.6, 118.7, 119.3, 119.4, 121.3, 122.0, 126.0, 128.2, 128.7, 136.5, 146.5, 149.4, 154.4, 157.5; HRMS (EI-TOF) calcd for $C_{32}H_{30}FeFNO_2$ 535.1610, found 535.1614. Anal. calcd for $C_{32}H_{30}FeF$- NO_2: C 71.78, H 5.65, N 2.62; found C 71.56, H 5.88, N 2.70.

5'-*trans*-{2-[*p*-(Di(*p*-tolyl)amino)phenyl]vinyl}-3',3'-dimethyl-1'-(2-hydroxyethyl)-6-nitrospiro[2*H*-1-benzopyran-2,2'-indoline] (**13**) A mixture of **10** (0.38 g, 0.76 mmol) and 5-nitrosalicylaldehyde (1.3 equiv.) in ethanol (25 mL) was refluxed for 3 h. After purification by column chromatography on alumina, the product **13** was obtained as a dark-green solid (0.26 g, yield 54%); ^{1}H NMR (acetone-d_6, 400 MHz) δ: 1.16 (s, 3H), 1.26 (s, 3H), 2.23 (s, 6H), 3.19—3.29 (m, 1H), 3.30—3.41 (m, 1H), 3.52—3.64 (m, 1H), 3.65—3.75 (m, 1H), 3.75—3.80 (m, 1H), 6.04 (d, J=10.4 Hz, 1H), 6.63 (d, J=8.1 Hz, 1H), 6.80 (d, J=8.9 Hz, 1H), 6.82—6.93 (m, 6H), 6.95—7.09 (m, 6H), 7.12 (d, J=10.3 Hz, 1H), 7.24 (d, J=8.0 Hz, 1H), 7.30—7.40 (m, 3H), 7.99 (d, J=9.0 Hz, 1H), 8.08 (d, J=2.7 Hz, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ: 19.3, 19.9, 25.4, 46.1, 52.6, 60.0, 106.7, 106.9, 115.4, 119.1, 119.2, 122.2, 122.5, 122.6, 124.3, 124.5, 125.6, 126.8, 127.0, 127.3, 128.0, 129.7, 129.9, 131.9, 132.5, 136.7, 141.2, 145.3, 147.1, 159.5; HRMS (EI-TOF) calcd for $C_{42}H_{39}N_3O_4$ 649.2941, found 649.2946.

5'-*trans*-{2-[*p*-(Di(*p*-tolyl)amino)phenyl]vinyl}-3',3'-dimethyl-1'-(2-hydroxyethyl)-6-fluorospiro[2*H*-1-benzopyran-2,2'-indoline] (**14**) A mixture of **10** (0.15 g, 0.3 mmol) and 5-fluorosalicylaldehyde (1.3 equiv.) in ethanol (10 mL) was refluxed for 3 h. After purification by column chromatography on alumina, the product **14** was obtained as a green solid (0.13 g, yield 68%). ^{1}H NMR (acetone-d_6, 400 MHz) δ: 1.12 (s, 3H), 1.24 (s, 3H), 2.22 (s, 6H), 3.12—3.23 (m, 1H), 3.29—3.41 (m, 1H), 3.50—3.71 (m, 3H), 5.87 (d, J=10.2 Hz, 1H), 6.50—6.62 (m, 2H), 6.72—6.92 (m, 10H), 6.92—7.08 (m, 6H), 7.22 (d, J=8.0 Hz, 1H), 7.29—7.40 (m, 3H); ^{13}C NMR (acetone-d_6, 75 MHz) δ: 19.5, 20.0, 25.8, 46.2, 52.2, 60.2, 105.0, 106.5, 112.6, 115.6 115.9, 119.2, 119.8, 119.9, 121.7, 122.6, 124.0, 124.4, 124.5, 126.8, 127.0, 127.6, 128.4, 129.3, 129.9, 130.0, 132.1, 132.5, 137.1, 145.4, 147.1, 147.5, 150.4, 158.3; HRMS (EI-TOF) calcd for $C_{42}H_{39}FN_2O_2$, 622.2996, found 622.3000.

5'-*trans*-{2-[*p*-(Di(*p*-tolyl)amino)phenyl]vinyl}-3',3'-dimethyl-1'-(2-hydroxyethyl)-6-cyanospiro[2*H*-1-benzopyran-2,2'-indoline] (**15**) A mixture of 10 (50 mg, 0.1 mmol) and 5-cyanosalicylaldehyde (1.3 equiv.) in ethanol (5 mL) was refluxed for 3 h. After purification by column chromatography on alumina, the product 15 was obtained as a dark-green solid (30 mg, yield 46%). ^{1}H NMR (acetone-d_6, 400 MHz) δ: 1.20 (s, 3H), 1.28 (s, 3H), 2.29 (s, 6H), 3.23—3.32 (m, 1H), 3.32—3.45 (m, 1H), 3.59—3.68 (m, 1H), 3.68—3.85 (m, 2H), 6.03 (d, J=10.3 Hz, 1H), 6.67 (d, J=8.0 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 6.88—7.02 (m, 6H), 7.02—7.15 (m, 7H), 7.30 (d, J = 8.2 Hz, 1H), 7.35—7.43 (m, 3H), 7.51 (d, J=8.5 Hz, 1H), 7.60 (s, 1H); ^{13}C NMR (acetone-d_6, 75 MHz) δ: 19.3, 19.9, 25.3, 46.1, 52.4, 60.0, 103.4, 106.3, 106.6, 116.0, 118.6, 119.2, 119.9, 121.9, 122.5, 124.2, 124.5, 126.8, 127.0, 127.3, 127.8, 129.6, 129.9, 130.9, 131.9, 132.5, 133.8, 136.7, 145.3, 147.1, 147.2, 157.6; HRMS (EI-TOF) *m*/*z*: [M^+] calcd for $C_{43}H_{39}$- N_3O_2, 629.3042, found 629.3048.

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