Schulz-Senft, M., Gates, P. J., Sönnichsen, F. D., & Staubitz, A. C. (2017). Diversely halogenated spiropyrans: Useful synthetic building blocks for a versatile class of molecular switches. *Dyes and Pigments*, 136, 292-301. <https://doi.org/10.1016/j.dyepig.2016.08.039>

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[10.1016/j.dyepig.2016.08.039](https://doi.org/10.1016/j.dyepig.2016.08.039)

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Supplementary Material

for

Diversely Halogenated Spiropyrans - Useful Synthetic Building Blocks for a Versatile Class of Molecular Switches

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Abbreviations

The use of abbreviations follows the conventions from the ACS Style guide.[1] In addition, the following abbreviations are used.

Abbreviation	Long form
at (NMR)	Apparent triplet
ATR	Attenuated total reflection (IR)
CI	Chemical ionization
COSY	Correlation spectroscopy
DCM	Dichloromethane
dd (NMR)	Doublet of doublets
DMSO	Dimethyl sulfoxide
EI	Electron ionization
ESI	Electrospray ionization
FT	Fourier transform
HMBC	Heteronuclear multiple bond correlation
HPLC	High performance liquid chromatography
HSQC	Heteronuclear single quantum coherence
NOESY	Nuclear Overhauser enhancement spectroscopy
PSS	Photostationary state
THF	Tetrahydrofuran
TOF	Time-of-flight mass detector
v/v	Volume concentration (volume/volume)

Analytical Equipment and Equipment for Syntheses

NMR spectra were either recorded on a Bruker DRX 500 (^1H NMR: 500 MHz) or on a Bruker Advance 600 (^1H NMR: 600 MHz) FT-NMR spectrometer. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced against the solvent residual proton signals (^1H) or the solvent itself (^{13}C). ^{19}F NMR spectra were referenced internally against CCl_3F . The exact assignment of the peaks was performed by two-dimensional NMR spectroscopy such as ^1H COSY, ^1H NOESY, $^1\text{H}/^{13}\text{C}$ HSQC or $^1\text{H}/^{13}\text{C}$ HMBC if possible.

^1H NMR spectra for the determination of the ratio between spiropyran and merocyanine form were recorded on a Bruker Advance 600 MHz FT-NMR spectrometer. Due to the low concentration of the samples (ca. 50 $\mu\text{mol/L}$), excitation sculpting was used to suppress residual solvent lines and 1024 scans were recorded. Mass spectrometric measurements were performed in the positive ion mode using a JEOL-Accu TOF 4GGCV EI mass spectrometer, a Bruker Daltonics micrOTOF II ESI mass spectrometer or a VG Analytical Autospec apparatus for CI. Electron ionization (EI) and Chemical ionization (CI) were performed using an ionization potential of 70 eV. In the case of CI ionization, methane was used as the reagent gas.

IR spectra were measured using a Perkin Elmer Paragon 1000 FT-IR spectrometer equipped with an A531-G Golden-Gate-ATR-unit.

UV spectra were recorded at 25 °C using a Perkin Elmer Lambda 14 UV spectrometer. Quartz cuvettes with a light path length of 10 mm from Hellma Analytics were used.

Melting points were measured on an electrothermal IA6304 capillary melting point apparatus and are uncorrected.

The irradiation experiments were carried out using LED light sources with an optical power of 1050 mW (Nichia NC4U033A; 365 nm) and 350 mW (Luxeon LXML-PX02; 565 nm).

Reagents

If not noted otherwise, all reagents were used as received.

Reagent	Supplier	Purity/concentration	Notes
2-Bromophenol	ABCR	98%	
2-Iodophenol	Sigma-Aldrich	98%	
3-Methyl-2-butanone	ABCR	98%	
4-Bromophenyl hydrazine hydrochloride	Sigma-Aldrich	99%	
4-Iodophenyl hydrazine	Maybridge	95%	
4-Methoxyphenyl hydrazine hydrochloride	TCI	>98%	
Hydrobromic acid	Sigma-Aldrich	48%	Reagent grade
Hydrochloric acid	Grüssing	37%	
Iodomethane	Sigma-Aldrich	99%	Contains copper as stabilizer
Magnesium chloride	Acros	99.9%	Anhydrous
Magnesium sulfate	Grüssing	99%	
Nitric acid	Merck	100% (fuming)	
o-Vanillin	AlfaAesar	99%	
Paraformaldehyde	ABCR	97%	
Piperidine	Acros	>99.5%	
Potassium hydroxide	Grüssing	85%	
Pyridine	Acros	99.5%	Extra dry, over molecular sieve
Silica gel 60	Merck		15-40 µm
Sodium chloride	Grüssing	99.5%	
Sodium hydroxide	Grüssing	98%	
Sodium sulfate	Grüssing	98%	
Trichlorofluoromethane	Sigma-Aldrich	>99%	
Triethylamine	Acros	99.5%	Predried over KOH, distilled from CaH ₂
Trifluoromethanesulfonic anhydride	ABCR	>99%	

Solvents

All solvents which were purchased in technical grade were purified by evaporation prior to use. Solvents of purities higher than 99% were not purified further. Some solvents were degassed by three freeze-pump-thaw cycles, backfilled with nitrogen and stored over molecular sieve 3 Å.

The following solvents were dried in a solvent purification system PS-MD-5 by Innovative Technology: dichloromethane, diethyl ether, tetrahydrofuran.

Solvent	Supplier	Purity	Drying procedure	Degassed
Acetic acid	Grüssing	99.5%	Distilled from copper(II) sulfate	No
Acetone	Walter-CMP	Technical grade	none	No
Acetonitrile	Sigma-Aldrich	>99.9%, HPLC grade	none	No
Acetonitrile- d_3	Deutero	99.8% D	none	No
Chloroform- d	Euriso-top	99.8% D	none	No
Dichloromethane	VWR	HPLC grade	PS-MD-5	Yes
Dichloromethane- d_2	Deutero	99.6% D	none	No
Diethyl ether	VWR	HPLC grade	PS-MD-5	Yes
Dimethyl sulfoxide- d_6	Euriso-top	99.8% D	none	No
Ethanol	VWR	Technical grade, denaturated with petroleum oil	Distilled from calcium oxide	No
Ethyl acetate	Walter-CMP	Technical grade	none	No
<i>n</i> -Heptane	AlfaAesar	>99%	none	No
<i>n</i> -Hexane	Sigma-Aldrich	>99.9%, HPLC grade	none	No
Tetrahydrofuran	VWR	HPLC grade	PS-MD-5	Yes
Toluene	VWR	Technical grade	none	No

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Experimental Procedures

5-Bromo-2,3,3-trimethyl-3*H*-indole[2] (8a)

A solution of *p*-bromophenylhydrazine hydrochloride (1.50 g, 6.72 mmol), 3-methyl-2-butanone (1.16 g, 13.4 mmol) in dry glacial AcOH (120 mL) was heated to 130 °C under a nitrogen atmosphere for 6 h. The reaction mixture was allowed to cool to ambient temperature and subsequently the solvent was removed under reduced pressure. After dissolving the residue in Et₂O (150 mL) and addition of water (100 mL), the aqueous layer was extracted with *n*-hexane (2 × 100 mL) and Et₂O (1 × 150 mL). The organic phases were combined and washed with KOH (10%, 3 × 100 mL) and water (3 × 100 mL). Removal of the solvent and drying in vacuo gave the product as dark brown oil (1.34 g, 5.65 mmol, 84%, Lit.[2] 97%).^a

¹H NMR (500 MHz, CDCl₃): δ = 7.42 – 7.36 (m, 3H, *H*-4, *H*-6, *H*-7), 2.25 (s, 3H, *H*-8), 1.28 (s, 6H, *H*-9, *H*-10) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 188.6 (C-2), 152.8 (C-5), 147.9 (C-7a), 130.8 (C-4), 125.0 (C-6), 121.4 (C-7), 119.0 (C-3a), 54.3 (C-3), 23.1 (C-9, C-10), 15.5 (C-8) ppm.

IR (ATR): $\tilde{\nu}$ = 2964 (m), 2927 (w), 1574 (s), 1462 (m), 1446 (s), 1428 (s), 1416 (m), 1376 (m), 1315 (w), 1245 (m), 1199 (m), 1083 (w), 1051 (w), 937 (w), 866 (m), 821 (vs), 707 (w), 677 (m), 634 (w), 537 (m) cm⁻¹.

HRMS (EI-TOF): *m/z* (%): [M]⁺ calcd for [C₁₁H₁₂⁷⁹BrN]⁺ 237.0153; found 237.0145 (98); calcd for [C₁₁H₁₂⁸¹BrN]⁺ 239.0133; found 239.01411 (100); 231.99 (80) [M-CH₃]⁺; 170.97 (83) [M-C(CH₃)₂C(CH₃)]⁺.

5-Bromo-1,2,3,3-tetramethyl-3*H*-indolium iodide (3a)

5-Bromo-2,3,3-trimethyl-3*H*-indole (1.34 g 5.65 mmol) was dissolved in iodomethane (15.0 mL, 240 mmol) and heated to 45 °C for 9 h. After allowing the reaction mixture to cool to ambient temperature, the dispersion was diluted with Et₂O (1 × 15 mL), filtered and rinsed with Et₂O (1 × 15 mL) to yield 5-bromo-1,2,3,3-tetramethyl-3*H*-indolium iodide as light purple solid (1.87 g, 4.92 mmol, 87%).

^a The ¹H NMR data are in agreement with reference[2]. Further data were not provided in this reference.

Melting point: $T = 245\text{ }^{\circ}\text{C}$.

^1H NMR (500 MHz, $\text{DMSO}-d_6$): $\delta = 8.16$ (s, 1H, $H-4$), 7.88-7.84 (m, 2H, $H-6$, $H-7$), 3.95 (s, 3H, $H-8$), 2.75 (s, 3H, $H-9$), 1.53 (s, 6H, $H-10$, $H-11$) ppm.

^{13}C NMR (126 MHz, $\text{DMSO}-d_6$): $\delta = 196.6$ (C-2), 143.9 (C-3a), 141.4 (C-7a), 131.7 (C-7), 126.7 (C-4), 122.6 (C-5), 117.1 (C-6), 54.2 (C-3), 34.8 (C-8), 21.5 (C-10, C-11), 15.5 (C-9) ppm.

IR (ATR): $\tilde{\nu} = 3042$ (w), 2966 (m), 2926 (w), 2869 (w), 1628 (m), 1606 (m), 1583 (m), 1469 (s), 1450 (s), 1406 (s), 1365 (m), 1336 (m), 1319 (m), 1254 (m), 1234 (m), 1134 (s), 1079 (s), 992 (m), 935 (s), 879 (m), 824 (vs), 795 (s), 747 (m), 556 (s) cm^{-1} .

HRMS (ESI-TOF): m/z (%): $[\text{M}-\text{I}]^+$ calcd for $[\text{C}_{12}\text{H}_{15}^{79}\text{BrN}]^+$ 252.0382; found 252.0382 (100); calcd for $[\text{C}_{12}\text{H}_{15}^{81}\text{BrN}]^+$ 254.0367; found 254.0362 (99).

5-Iodo-2,3,3-trimethyl-3*H*-indole (8b)

4-Iodophenylhydrazine (1.30 g, 5.55 mmol), 3-methyl-2-butanone (956 mg, 11.1 mmol) and dry glacial AcOH (30 mL) were heated to $130\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere for 3 h. After allowing the reaction mixture to cool to ambient temperature, the solvent was removed in vacuo and the residue was dissolved in Et_2O (150 mL) and water (100 mL) was added. After phase separation, the aqueous phase was extracted with *n*-hexane (2 x 100 mL) and Et_2O (1 x 100 mL). The combined organic phases were then washed with aqueous KOH solution (10%, 3 x 100 mL) and water (3 x 100 mL). After drying over MgSO_4 , the solvent was removed and the remaining product was dried *in vacuo* to give a dark brown oil (1.35 g, 4.73 mmol, 85%).^a

^1H NMR (500 MHz, CDCl_3): $\delta = 7.62$ (dd, $^3J = 8.1\text{ Hz}$, $^4J = 1.7\text{ Hz}$, 1H, $H-6$), 7.59 (d, $^4J = 1.7\text{ Hz}$, 1H, $H-4$), 7.29 (d, $^3J = 8.1\text{ Hz}$, 1H, $H-7$), 2.27 (s, 3H, $H-8$), 1.29 (s, 6H, $H-9$, $H-10$) ppm.

^{13}C NMR (126 MHz, CDCl_3): $\delta = 188.6$ (C-2), 153.2 (C-5), 148.2 (C-7a), 136.9 (C-6), 130.8 (C-4), 121.9 (C-7), 90.2 (C-3a), 54.2 (C-3), 23.1 (C-9, C-10), 15.5 (C-8) ppm.

IR (ATR): $\tilde{\nu} = 2962$ (m), 2924 (m), 2867 (w), 1690 (w), 1604 (w), 1579 (s), 1460 (s), 1445 (s), 1258 (s), 1200 (s), 878 (m), 861 (m), 820 (vs), 805 (vs) cm^{-1} .

HRMS (ESI-TOF): m/z (%): $[\text{M}+\text{H}]^+$ calcd for $[\text{C}_{11}\text{H}_{12}\text{IN}+\text{H}]^+$ 286.0087; found 286.0091 (100).

^a This compound has been prepared previously by different routes in yields of 79%[3], 81%[4], 96%[5] and 94%[6], respectively. ^1H NMR data agree with reported values of references[4,6], but not with references[3,5]. ^{13}C NMR data are in agreement with the reported values of references[3,5] references[4,6] did not provide ^{13}C NMR data. HRMS and IR data were not reported by these references.

5-Iodo-1,2,3,3-tetramethyl-3*H*-indolium iodide (**3b**)

5-Iodo-2,3,3-trimethyl-3*H*-indole (1.35 g, 4.73 mmol) was dissolved in iodomethane (15.0 mL, 240 mmol) and heated to 45 °C for 15 h. After allowing the reaction mixture to cool to ambient temperature and filtration and washing with Et₂O (2 mL), the product was obtained as light brown solid (1.75 g, 4.09 mmol, 86%).^a

Melting point: *T* = 255 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ = 8.28 (d, ⁴*J* = 1.5 Hz, 1H, *H*-4), 7.99 (dd, ³*J* = 8.4 Hz, ⁴*J* = 1.5 Hz, 1H, *H*-6), 7.72 (d, ³*J* = 8.4 Hz, 1H, *H*-7), 3.94 (s, 3H, *H*-8), 2.74 (s, 3H, *H*-9), 1.52 (s, 6H, *H*-10, *H*-11) ppm.

¹³C NMR (126 MHz, DMSO-*d*₆): δ = 196.1 (C-2), 143.8 (C-3a), 141.9 (C-7a), 137.4 (C-6), 132.2 (C-4), 117.1 (C-7), 96.0 (C-5), 54.0 (C-3), 34.8 (C-8), 21.5 (C-10, C-11), 14.2 (C-9) ppm.

IR (ATR): $\tilde{\nu}$ = 3057 (w), 2969 (w), 2926 (w), 1628 (m), 1605 (m), 1583 (m), 1463 (s), 1442 (m), 1411 (s), 1398 (s), 1317 (m), 1256 (m), 1134 (s), 984 (m), 937 (m), 862 (m), 817 (vs), 789 (s), 760 (m), 745 (m), 613 (m), 556 (s), 449 (m) cm⁻¹.

HRMS (ESI-TOF): *m/z* (%): [M-I]⁺ calcd for [C₁₂H₁₅N]⁺ 300.0244; found 300.0244 (100).

5-Methoxy-2,3,3-trimethyl-3*H*-indole[8] (**8c**)

(4-Methoxy)-phenyl hydrazine hydrochloride (**26**) (10.0 g, 57.3 mmol) and 3-methyl-2-butanone (**7**) (4.93 g, 57.3 mmol) were dissolved in abs. EtOH (260 mL) and heated to reflux under a N₂ atmosphere for 5 h. Then the solution was allowed to cool to 24 °C and was filtered through silica gel (eluent: EtOAc). The product **27** was obtained as reddish-brown viscous oil (8.44 g, 44.6 mmol, 78 %, Lit.[8] 76 %)^b

^a This compound has been prepared previously by different routes in yields of 70%[7] and 74%[5]. ¹H NMR data do agree with reported values of references[5,7]. ¹³C NMR data are in agreement with the reported values of reference[5]. Reference[7] did not provide ¹³C NMR data. HRMS and IR data were not reported by these references.

^b ¹H NMR, ¹³C NMR, HRMS and mp data are in agreement with reference[8]. IR data were not reported.

¹H NMR (500 MHz, CDCl₃): δ = 7.42 (d, ³J = 8.3 Hz, 1H, H-7), 6.84 – 6.80 (m, 2H, H-4, H-6), 3.82 (s, 3H, H-11), 2.24 (s, 3H, H-8), 1.28 (s, 6H, H-9, H-10) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 185.9 (C-2), 158.1 (C-5), 147.5 (C-7a), 147.4 (C-3a), 120.2 (C-7), 112.2 (C-4), 108.3 (C-6), 55.8 (C-11), 53.9 (C-3), 23.4 (C-9, C-10), 15.4 (C-8) ppm.

IR (ATR): $\tilde{\nu}$ = 3248 (w, b), 2961 (m), 2928 (m), 2864 (s), 2833 (s), 1713 (w), 1613 (m), 1580 (m), 1462 (vs), 1431 (s), 1380 (m), 1287 (s), 1212 (s), 1199 (s), 1178 (s), 1144 (m), 1068 (s), 1028 (s), 866 (m), 817 (s), 749 (m), 697 (w), 617 (m), 587 (m) cm⁻¹.

HRMS (EI-TOF): *m/z* (%): [M]⁺ calcd for [C₁₂H₁₅NO]⁺ 189.1154; found 189.1154 (100); 174.10 (100) [M-CH₃]⁺.

5-Hydroxy-2,3,3-trimethyl-3*H*-indole[9] (8d)

5-Methoxy-2,3,3-trimethyl-3*H*-indole (3.00 g, 15.9 mmol) was dissolved in hydrobromic acid (48%, 53.0 mL, 477 mmol). After heating at 140 °C for 2 h, the solution was allowed to cool, and diluted with water (200 mL). Solid NaOH was added until the mixture reached pH = 8. The aqueous solution was extracted with DCM (4 x 100 mL). The combined organic layers were washed with brine (300 mL), dried over Na₂SO₄, filtered, and the solvent was removed *in vacuo* to yield **8** as a brown solid (2.46 g, 13.4 mmol, 79%, Lit.[9] 97%).^a

Melting point: *T* = 175 °C.

¹H NMR (600 MHz, CDCl₃): δ = 7.32 (d, ³J = 8.3 Hz, 1 H, H-7), 6.85 (d, ⁴J = 2.3 Hz, 1H, H-4), 6.78 (dd, ³J = 8.3 Hz, ⁴J = 2.3 Hz, 1H, H-6), 2.26 (s, 3H, H-8), 1.28 (s, 6H, H-9, H-10) ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 186.0 (C-2), 155.7 (C-5), 147.4 (C-7a), 145.2 (C-3a), 120.0 (C-7), 114.3 (C-6), 109.9 (C-4), 53.8 (C-3), 23.3 (C-9, C-10), 15.1 (C-8) ppm.

IR (ATR): $\tilde{\nu}$ = 3248 (w, b), 2961 (m), 2928 (m), 2864 (s), 2833 (s), 1713 (w), 1613 (m), 1580 (m), 1462 (vs), 1431 (s), 1380 (m), 1287 (s), 1212 (s), 1199 (s), 1178 (s), 1144 (m), 1068 (s), 1028 (s), 866 (m), 817 (s), 749 (m), 697 (w), 617 (m), 587 (m) cm⁻¹.

HRMS (EI-TOF): *m/z* (%): [M]⁺ calcd. for C₁₁H₁₃NO⁺ 175.0997; found 175.0995 (95); 160.0 (100) [M-CH₃]⁺.

^a This compound has also been prepared via a different route in a yield of 91%[8]. ¹H NMR, ¹³C NMR, HRMS and mp data are in agreement with reference[8]. IR data were not reported. In reference[9], no analytical data were reported.

5-Hydroxy-1,2,3,3-tetramethyl-3*H*-indolium iodide[8] (3c)

5-Hydroxy-2,3,3-trimethyl-3*H*-indole (2.37 g, 13.5 mmol) was dissolved in iodomethane (25.0 mL, 400 mmol) in a nitrogen atmosphere and heated at 50 °C for 17 h. After allowing the reaction mixture to cool to ambient temperature, the dispersion was diluted with Et₂O (10 mL) and filtered. After drying in vacuo, 5-hydroxy-1,2,3,3-tetramethyl-3*H*-indolinium iodide was obtained as a brown solid (4.02 g, 12.7 mmol, 94%, Lit.[8] 64%) without further purification.^a

Melting point: *T* = 242 °C.

¹H NMR (500 MHz, DMSO-*d*₆): δ = 10.24 (s, 1H, *OH*), 7.68 (d, ³*J* = 8.7 Hz, 1H, *H*-7), 7.12 (d, ⁴*J* = 2.3 Hz, 1H, *H*-4), 6.94 (dd, ³*J* = 8.7 Hz, ⁴*J* = 2.3 Hz, 1H, *H*-6), 3.90 (s, 3H, *H*-8), 2.67 (s, 3H, *H*-9), 1.47 (s, 6H, *H*-10, *H*-11) ppm.

¹³C NMR (126 MHz, DMSO-*d*₆): δ = 191.9 (C-2), 159.0 (C-5), 143.7 (C-3a), 134.1 (C-7a), 116.1 (C-7), 115.0 (C-6), 110.3 (C-4), 53.4 (C-3), 34.5 (C-8), 21.9 (C-10, C-11), 13.6 (C-9) ppm.

IR (ATR): $\tilde{\nu}$ = 3178 (m, b), 3023 (w), 2973 (w), 1619 (m), 1597 (m), 1495 (m), 1471 (m), 1356 (m), 1296 (s), 1194 (s), 1055 (w), 947 (w), 993 (w), 899 (m), 800 (s), 648 (s), 551 (m) cm⁻¹.

HRMS (ESI-TOF): *m/z* (%): [*M*-I]⁺ calcd. for [C₁₂H₁₆NO]⁺ 190.1226; found 190.1233 (100).

3-Bromo-2-hydroxybenzaldehyde (5a)

Anhydrous MgCl₂ (1.90 g, 20.0 mmol) and 2-bromophenol (1.73 g, 10.0 mmol) were dissolved in dry THF (50 mL), before dry TEA (2.8 mL, 2.02 g, 20.0 mmol) and paraformaldehyde (1.20 g, 40.0 mmol) were added. The reaction mixture was heated to 90 °C for 6 h. During this period, the color of the solution changed from white to yellow. After cooling to 22 °C, Et₂O (50 mL) was added and the organic phase was washed with hydrochloric acid (2 N, 2 x 50 mL) and water (2 x 50 mL). After phase

^a ¹H NMR, ¹³C NMR, HRMS and mp data are in agreement with reference[8]. IR data were not reported.

separation and drying over MgSO_4 , the solvent was removed *in vacuo* and the crude product was dissolved in DCM/*n*-heptane (1/1, v/v 30 mL) and crystallized after removal of DCM at $-25\text{ }^\circ\text{C}$. Drying *in vacuo* gave the 3-bromo-2-hydroxybenzaldehyde as colorless crystalline needles (1.48 g, 7.35 mmol, 73%).

Melting point: $T = 53\text{ }^\circ\text{C}$.

^1H NMR (500 MHz, CDCl_3): $\delta = 11.61$ (d, $^5J = 0.5\text{ Hz}$, 1H, OH), 9.87 (s, 1H, H-7), 7.79 (ddd, $^3J = 7.9\text{ Hz}$, $^4J = 1.6\text{ Hz}$, $^5J = 0.5\text{ Hz}$, 1H, H-4), 7.55 (dd, $^3J = 7.7\text{ Hz}$, $^4J = 1.6\text{ Hz}$, 1H, H-6), 6.95 (at, $^3J = 7.8\text{ Hz}$, 1H, H-5) ppm.

^{13}C NMR (126 MHz, CDCl_3): $\delta = 196.2$ (C-7), 158.3 (C-2), 140.2 (C-4), 133.1 (C-6), 121.5 (C-3), 120.9 (C-5), 111.4 (C-1) ppm.

IR (ATR): $\tilde{\nu} = 3071$ (w), 3022 (w), 2856 (m), 2755 (w), 1644 (vs), 1610 (s), 1568 (m), 1473 (m), 1436 (vs), 1383 (vs), 1339 (m), 1309 (m), 1291 (vs), 1268 (s), 1216 (vs), 1171 (vs), 1127 (vs), 1072 (s), 900 (s), 818 (s), 778 (s), 772 (vs), 666 (vs), 591 (vs), 546 (m) cm^{-1}

HRMS (EI-TOF): m/z (%): $[\text{M}]^+$ calcd for $[\text{C}_7\text{H}_5^{79}\text{BrO}_2]^+$ 199.9473; found 199.9467 (68); calcd for $[\text{C}_7\text{H}_5^{81}\text{BrO}_2]^+$ 201.9453; found 201.94472 (67); 118.99 (100) $[\text{M}-\text{Br}]^+$.

3-Bromo-2-hydroxy-5-nitrobenzaldehyde (2a)

3-Bromo-2-hydroxybenzaldehyde (9.00 g, 44.8 mmol) was dissolved in glacial AcOH (225 mL) and cooled to $15\text{ }^\circ\text{C}$. A mixture of glacial AcOH and fuming nitric acid (1/1 v/v, 3.75 mL) was added over the course of 30 min while the internal temperature was kept at $15\text{ }^\circ\text{C}$. Then the reaction mixture was stirred at $15\text{ }^\circ\text{C}$ for another 1 h. Subsequently, the cooling bath was removed and the reaction stirred for 18 h at $35\text{ }^\circ\text{C}$. After diluting the solution with water (200 mL), the formed yellow precipitate was filtered and washed with AcOH (20 mL). Subsequent crystallization from DCM/*n*-hexane (100 mL/100 mL) gave the product as yellow solid (6.47 g, 26.3 mmol, 59%).

Melting point: $T = 144\text{ }^\circ\text{C}$.

^1H NMR (500 MHz, CDCl_3): $\delta = 12.23$ (s, 1H, OH), 9.98 (s, 1H, H-7), 8.69 (d, $^4J = 2.6\text{ Hz}$, 1H, H-4), 8.54 (d, $^4J = 2.6\text{ Hz}$, 1H, H-6) ppm.

^{13}C NMR (126 MHz, CDCl_3): $\delta = 195.1$ (C-7), 163.1 (C-2), 140.8 (C-5), 134.6 (C-4), 128.4 (C-2), 119.6 (C-1), 112.5 (C-3) ppm.

IR (ATR): $\tilde{\nu} = 3300$ (w), 3087 (m), 3073 (m), 2884 (w), 1657 (s), 1613 (s), 1537 (s), 1426 (s), 1339 (s), 1283 (s), 1210 (s), 1162 (s), 1096 (s), 947 (s), 918 (s), 902 (s), 759 (s), 742 (vs), 714 (vs), 694 (vs), 488 (m), 478 (m) cm^{-1} .

HRMS (EI-TOF): m/z (%): $[\text{M}]^+$ calcd for $[\text{C}_7\text{H}_4^{79}\text{BrNO}_4]^+$ 244.9324; found 244.9316 (100); calcd for $[\text{C}_7\text{H}_4^{81}\text{BrNO}_4]^+$ 246.9303; found 246.9296 (98); 216.94 (13) $[\text{M}-\text{CO}]^+$.

2-Hydroxy-3-iodobenzaldehyde[10] (5b)

To a stirred solution of 2-iodophenol (15.0 g, 68.2 mmol) in dry THF (340 mL), anhydrous MgCl_2 (12.9 g, 136 mmol), dry TEA (18.9 mL, 136 mmol) and paraformaldehyde (8.20 g, 273 mmol) were added under an atmosphere of dry nitrogen. The reaction mixture was heated to reflux for 12 h. The color of the reaction mixture changed from colorless via yellow to a reddish ochre. After cooling to 20 °C, Et_2O (200 mL) was added. After phase separation, the organic phase was washed with hydrochloric acid (2 N, 3 x 150 mL), water (1 x 150 mL) and brine (1 x 150 mL). The hydrochloric washings were combined and extracted with Et_2O (1 x 200 mL). The organic phases were combined and after drying over MgSO_4 , the solvent was removed *in vacuo*. The residue was taken up with EtOAc (40 mL), crystallized at -20 °C and filtered. The filtrate was concentrated *in vacuo* and recrystallized another time from EtOAc (10 mL). The product was obtained as yellow crystals (8.20 g, 33.1 mmol, 49%, Lit.[10] 84%).^a

Melting point: $T = 72\text{ °C}$.

^1H NMR (500 MHz, CDCl_3): $\delta = 11.82$ (s, 1H, OH), 9.77 (s, 1H, H-7), 8.00 – 7.98 (m, 1H, H-4), 7.58 (dd, $^3J = 7.7\text{ Hz}$, $^4J = 1.6\text{ Hz}$, 1H, H-6), 6.84 (at, $^3J = 7.7\text{ Hz}$, 1H, H-5) ppm.

^{13}C NMR (126 MHz, CDCl_3): $\delta = 196.1$ (C-7), 160.6 (C-2), 146.3 (C-4), 134.1 (C-6), 121.8 (C-3), 120.7 (C-5), 85.6 (C-1) ppm.

IR (ATR): $\tilde{\nu} = 3061$ (w, b), 3022 (w), 2853 (m), 1639 (vs), 1603 (s), 1469 (m), 1431 (s), 1382 (s), 1296 (s), 1282 (s), 1264 (s), 1213 (s), 1170 (s), 1117 (vs), 892 (s), 730 (vs), 662 (vs), 585 (vs) cm^{-1} .

HRMS (EI-TOF): m/z (%): $[\text{M}]^+$ calcd for $[\text{C}_7\text{H}_5\text{IO}_2]^+$ 247.9334; found 247.9337 (100); 126.90 (15) $[\text{I}]^+$; 92.03 (25) $[\text{M-I-CHO}]^+$.

Hydroxy-3-iodo-5-nitrobenzaldehyde (2b)

^a ^1H NMR, ^{13}C NMR, IR and mp data are in agreement with reference[10]. HRMS data were not reported.

2-Hydroxy-3-iodobenzaldehyde (8.20 g, 33.1 mmol) was dissolved in glacial AcOH (160 mL) and cooled to 15 °C. A mixture of glacial AcOH and fuming nitric acid (1/1 v/v; 5.52 mL) was added over the course of 30 min while the internal temperature was kept at 15 °C and then the reaction mixture was stirred at 15 °C for another 1 h. The solution turned dark red. Subsequently, the cooling bath was removed and the reaction stirred at 40 °C for 14 h. After diluting with water (160 mL), the solution was filtered. The filtrate was diluted with more water (160 mL) and filtered again. The combined precipitates were washed with Et₂O (30 mL), giving a yellow powder which was dried *in vacuo* to obtain the product (3.80 g, 13.0 mmol, 39%).

Melting point: $T = 150\text{ }^{\circ}\text{C}$.

¹H NMR (500 MHz, DMSO-*d*₆): $\delta = 10.09$ (s, 1H, *H*-7), 8.77 (d, $^4J = 2.7$ Hz, 1H, *H*-6), 8.67 (d, $^4J = 2.7$ Hz, 1H, *H*-4) ppm.

¹³C NMR (126 MHz, DMSO-*d*₆): $\delta = 194.5$ (C-7), 164.7 (C-5), 140.9 (C-4), 139.5 (C-2), 128.5 (C-6), 120.9 (C-1), 89.1 (C-3) ppm.

IR (ATR): $\tilde{\nu} = 3086$ (m), 3071 (m), 2874 (w), 1653 (s), 1646 (s), 1608 (s), 1527 (s), 1422 (s), 1341 (s), 1333 (vs), 1299 (s), 1282 (vs), 1270 (s), 1210 (s), 1155 (s), 1104 (s), 744 (vs), 713 (vs), 682 (vs), 486 (s) cm⁻¹.

HRMS (CI-TOF, methane): m/z (%): $[M+H]^+$ calcd for $[C_7H_4INO_4+H]^+$ 293.9263; found 293.9267 (100); 308.0 (35) $[M+CH_4]^+$.

2-Hydroxy-3-methoxy-5-nitrobenzaldehyde[9] (5c)

o-Vanillin (30.0 g, 197 mmol) was dissolved in glacial AcOH (138 mL) and water (7 mL) and cooled to 15 °C. A mixture of glacial AcOH and fuming nitric acid (2/1 v/v; 30 mL) was added over the course of 45 min at a temperature of 15 °C. The reaction mixture was stirred at 15 °C for another 90 min. Subsequently, the solution was diluted with water (300 mL).

The yellow precipitate which formed was filtered and washed with water (20 mL). After washing the precipitate with Et₂O (30 mL), it was dried *in vacuo* to obtain the product as a yellow powder (21.6 g, 110 mmol, 56%, Lit.[9] 50%).^a

Melting point: $T = 131\text{ }^{\circ}\text{C}$.

¹H NMR (500 MHz, DMSO-*d*₆): $\delta = 10.32$ (s, 1H, *H*-7), 8.09 (d, $^4J = 2.7$ Hz, 1H, *H*-6), 7.92 (d, $^4J = 2.7$ Hz, 1H, *H*-4), 3.99 (s, 3H, *H*-8) ppm.

^a ¹H NMR, ¹³C NMR, HRMS spectroscopic and mp data are in agreement with reference[9]. IR data were not reported.

^{13}C NMR (126 MHz, $\text{DMSO}-d_6$): δ = 189.3 (C-7), 156.4 (C-5), 149.1 (C-3), 139.4 (C-2), 121.6 (C-1), 115.7 (C-6), 110.3 (C-4), 56.8 (C-8) ppm.

IR (ATR): $\tilde{\nu}$ = 3168 (w, b), 3093 (m), 1667 (s), 1520 (s), 1480 (s), 1447 (s), 1393 (s), 1340 (vs), 1267 (vs), 1199 (s), 1092 (vs), 953 (vs), 885 (s), 765 (s), 722 (vs), 581 (s) cm^{-1} .

HRMS (EI-TOF): m/z (%): $[\text{M}]^+$ calcd for $[\text{C}_8\text{H}_7\text{NO}_5]^+$ 197.0324; found 197.0328 (100); 151.02 (42) $[\text{M}-\text{NO}_2]^+$.

2,3-Dihydroxy-5-nitrobenzaldehyde[9] (2c)

2-Hydroxy-3-methoxy-5-nitrobenzaldehyde (13.8 g, 70.0 mmol) was dissolved in hydrobromic acid (48%, 233 mL) and heated at 140 °C for 5 h. Subsequently, the solution was diluted with water (500 mL), cooled to 0 °C and filtered. The precipitate was washed with water (100 mL) and was dried *in vacuo* to yield 2,3-dihydroxy-5-nitrobenzaldehyde as brown powder without further purification (12.1 g, 66.3 mmol, 95%, Lit:[9] 86%).^a

Melting point: T = 191 °C.

^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ = 11.10 (s, OH), 10.30 (s, 1H, H-7), 7.98 (d, 4J = 2.8 Hz, 1H, H-6), 7.78 (d, 4J = 2.8 Hz, 1H, H-4) ppm.

^{13}C NMR (126 MHz, $\text{DMSO}-d_6$): δ = 189.8 (C-7), 155.9 (C-2), 147.2 (C-3), 139.3 (C-5), 121.8 (C-1), 114.6 (C-6), 113.2 (C-4) ppm.

IR (ATR): $\tilde{\nu}$ = 3259 (m, b), 3088 (m), 1663 (s), 1518 (s), 1456 (s), 1341 (vs), 1262 (vs), 1181 (vs), 950 (s), 903 (s), 754 (vs), 742 (vs), 595 (vs), 563 (vs), 542 (vs) cm^{-1} .

HRMS (EI-TOF): m/z (%): $[\text{M}]^+$ calcd for $[\text{C}_7\text{H}_5\text{NO}_5]^+$ 183.0168; found 183.0172 (100); 168.98 (25) $[\text{M}-\text{O}]^+$.

5'8-Dibromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9a)

^a ^1H NMR, ^{13}C NMR, HRMS and mp data are in agreement with reference[9]. IR data were not reported.

5-Bromo-1,2,3,3-tetramethyl-3*H*-indolium iodide (1.00 g, 2.63 mmol), 3-bromo-2-hydroxybenzaldehyde (647 mg, 2.63 mmol) and dry piperidine (0.520 mL, 5.26 mmol) were dissolved in EtOH (45 mL) and heated to reflux under a nitrogen atmosphere for 5 h. After cooling down to -25 °C, the product had crystallized. The crude product was dissolved in a mixture of DCM (25 mL) and *n*-heptane (25 mL) and crystallized by removal of DCM under reduced pressure. The product was obtained as dark blue solid (979 mg, 2.04 mmol, 78%).

Melting point: $T = 252\text{ }^{\circ}\text{C}$.

^1H NMR (500 MHz, CD_2Cl_2 , 300 K): $\delta = 8.28$ (d, $^4J = 2.6$ Hz, 1 H, H-5), 7.98 (d, $^4J = 2.6$ Hz, 1 H, H-7), 7.30 (dd, $^3J = 8.2$ Hz, $^4J = 1.9$ Hz, 1 H, H-6'), 7.19 (d, $^4J = 1.9$ Hz, 1 H, H-4'), 6.95 (d, $^3J = 10.3$ Hz, 1 H, H-4), 6.47 (d, $^3J = 8.2$ Hz, 1 H, H-7'), 5.89 (d, $^3J = 10.3$ Hz, 1 H, H-3), 2.71 (s, 3 H, H-12'), 1.28 (s, 3 H, H-13'), 1.19 (s, 3H, H-14') ppm.

^{13}C NMR (126 MHz, CD_2Cl_2 , 300 K): $\delta = 156.4$ (C-8a), 147.3 (C-7'a), 141.6 (C-6), 139.1 (C-3'a), 130.9 (C-6'), 129.2 (C-7), 129.0 (C-4), 125.4 (C-4'), 122.4 (C-3), 122.1 (C-5), 120.2 (C-4a), 112.0 (C-5'), 109.8 (C-8), 109.2 (C-7'), 108.5 (C-2), 53.0 (C-3'), 29.2 (C-12'), 26.0 (C-14'), 20.1 (C-13') ppm.

IR (ATR): $\tilde{\nu} = 3101$ (w), 3072 (w), 2984 (w), 2936 (w), 1597 (s), 1507 (vs), 1440 (s), 1397 (s), 1286 (s), 1254 (s), 1201 (vs), 1165 (vs), 1117 (vs), 1078 (vs), 1040 (vs), 959 (vs), 886 (s), 871 (s), 852 (s), 822 (s), 801 (s), 772 (s), 745 (s), 729 (s), 696 (vs) cm^{-1} .

HRMS (EI-TOF): m/z (%): $[\text{M}]^+$ calcd for $[\text{C}_{19}\text{H}_{16}\text{N}_2^{79}\text{Br}_2\text{O}_3]^+$ 477.9528; found 477.9515 (38); calcd for $[\text{C}_{19}\text{H}_{16}\text{N}_2^{79}\text{Br}^{81}\text{BrO}_3]^+$ 479.9507; found 479.9497 (75); calcd for $[\text{C}_{19}\text{H}_{16}\text{N}_2^{81}\text{Br}_2\text{O}_3]^+$ 481.9687; found 481.9500 (38); 237.00 (100) $[\text{M}-(\text{PhBrONO}_2\text{C}_2\text{H})]^+$.

5'-Bromo-8-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9b)

5-Bromo-1,2,3,3-tetramethyl-3*H*-indolium iodide (3.80 g, 10.0 mmol), 3-iodo-2-hydroxybenzaldehyde (2.93 g, 10.0 mmol) and dry piperidine (1.17 g, 20.0 mmol) were dissolved in EtOH (170 mL) and heated to reflux under a nitrogen atmosphere for 4.5 h. After cooling to -20 °C, the product had crystallized and was filtered to be obtained as dark blue solid (2.66 g, 5.04 mmol, 50%).^a

Melting point: $T = 187\text{ }^{\circ}\text{C}$

^a The color suggests that the compound was obtained in the merocyanine form, but in CDCl_3 , which was used for NMR spectroscopy, the spiropyran was detected.

¹H NMR (600 MHz, CDCl₃, 300 K): δ = 8.48 (d, ⁴*J* = 2.6 Hz, 1 H, H-5), 7.99 (d, ⁴*J* = 2.6 Hz, 1 H, H-7), 7.29 (dd, ³*J* = 8.2 Hz, ⁴*J* = 2.0 Hz, 1 H, H-6'), 7.18 (d, ⁴*J* = 2.0 Hz, 1 H, H-4'), 6.87 (d, ³*J* = 10.3 Hz, 1 H, H-4), 6.44 (d, ³*J* = 8.2 Hz, 1 H, H-7'), 5.84 (d, ³*J* = 10.3 Hz, 1 H, H-3), 2.67 (s, 3 H, H-12'), 1.28 (s, 3 H, H-13'), 1.20 (s, 3H, H-14') ppm.

¹³C NMR (151 MHz, CDCl₃, 300 K): δ = 158.0 (C-6), 146.8 (C-5'), 141.7 (C-8a), 138.5 (C-7'a), 134.8 (C-5), 130.6 (C-6'), 128.7 (C-4), 125.0 (C-4'), 122.5 (C-7), 121.8 (C-3), 118.5 (C-8), 112.0 (C-3'a), 108.9 (C-7'), 108.4 (C-2), 82.7 (C-4a), 52.4 (C-3'), 29.1 (C-12'), 25.8 (C-14'), 20.2 (C-13') ppm.

IR (ATR): $\tilde{\nu}$ = 3071 (w), 2996 (w), 2960 (m), 2927 (w), 1653 (w), 1599 (m), 1511 (s), 1479 (s), 1431 (s), 1333 (vs), 1275 (s), 1261 (s), 1225 (m), 1186 (m), 1110 (m), 1092 (s), 1071 (m), 1016 (s), 963 (s), 913 (m), 897 (m), 846 (s), 809 (s), 779 (m), 752 (s), 741 (s), 722 (s), 710 (s), 655 (s), 579 (m), 503 (m) cm⁻¹

HRMS (ESI-TOF): *m/z* (%): [M+H]⁺ calcd for [C₁₉H₁₆N₂⁷⁹BrIO₃+H]⁺ 526.9462; found 526.9473 (98); calcd for [C₁₉H₁₆N₂⁸¹BrIO₃+H]⁺ 528.9447; found 528.9452 (100).

5'-Bromo-8-hydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9c)

5-Bromo-1,2,3,3-tetramethyl-3*H*-indolium iodide (3.80 g, 10.0 mmol), 2,3-dihydroxy-5-nitrobenzaldehyde (1.83 g, 10.0 mmol) and dry piperidine (1.17 g, 20.0 mmol) were dissolved in dry EtOH (170 mL) under a nitrogen atmosphere and heated to reflux for 4.5 h. After cooling to -20 °C, the product had crystallized and was filtered to be obtained as dark blue solid (3.68 g, 8.82 mmol, 88%).^a

Melting point: *T* = 275 °C.

¹H NMR (500 MHz, DMSO-*d*₆, 300 K): δ = 10.18 (s, 1 H, OH), 7.73 (d, ⁴*J* = 2.7 Hz, 1 H, H-5), 7.56 (d, ⁴*J* = 2.7 Hz, 1 H, H-7), 7.30-7.27 (m, 2 H, H-4', H-7'), 7.15 (d, ³*J* = 10.3 Hz, 1 H, H-4), 6.59 (dd, ³*J* = 7.4 Hz, ⁴*J* = 2.5 Hz, 1 H, H-6'), 5.93 (d, ³*J* = 10.3 Hz, 1 H, H-3), 2.67 (s, 3H, H-12'), 1.21 (s, 3H, H-13'), 1.11 (s, 3H, H-14') ppm.

¹³C NMR (126 MHz, DMSO-*d*₆, 300 K): δ = 147.7 (C-6), 146.8 (C-7'a), 144.7 (C-8), 139.9 (C-4a), 138.8 (C-3'a), 130.0 (C-6'), 128.6 (C-4), 124.7 (C-7'), 120.8 (C-3), 118.8 (C-8a), 113.6 (C-5), 110.9 (C-7), 110.2 (C-5'), 108.8 (C-4'), 105.4 (C-2), 51.9 (C-3'), 28.4 (C-12'), 25.4 (C-13'), 19.2 (C-14') ppm.

^a The color suggests that the compound was obtained in the merocyanine form, but in DMSO, which was used for NMR spectroscopy, the spiropyran was detected.

IR (ATR): $\tilde{\nu}$ = 3214 (m, b), 3082 (w), 2976 (w), 1615 (w), 1590 (m), 1568 (m), 1510 (s), 1432 (s), 1400 (s), 1287 (s), 1190 (vs), 1171 (vs), 877 (vs), 789 (vs), 746 (vs), 539 (vs), 459 (vs) cm^{-1} .

HRMS (EI-TOF): m/z (%): $[M]^+$ calcd for $[\text{C}_{19}\text{H}_{17}\text{N}_2^{79}\text{BrO}_4]^+$ 416.0372; found 416.0365 (51); calcd for $[\text{C}_{19}\text{H}_{17}\text{N}_2^{81}\text{BrO}_4]^+$ 418.0351; found 418.0345 (50); 237.00/239.00 (100/98) $[\text{M}-(\text{PhO}_2\text{HNO}_2\text{C}_2\text{H}_2)]^+$.

5'-Bromo-8-trifluoromethylsulfonyl-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9j)

Trifluoromethanesulfonic anhydride (2.85 g, 10.0 mmol) was added to a solution of 5'-bromo-8-hydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (3.50 g, 8.39 mmol) and anhydrous pyridine (2.6 mL) in anhydrous DCM (33 mL) over the course of 10 min at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 1.5 h, the cooling bath was removed and the reaction mixture stirred at 24 °C for 1 h before heating it to 40 °C for 2 h. The reaction mixture was purified by filtration through silica gel (eluent: EtOAc) and after removal of the solvent *in vac.*, the residue was dissolved in toluene (20 mL) and dried *in vacuo* again to remove remaining pyridine as azeotropic mixture to give the product as dark blue solid (3.42 g, 6.22 mmol, 74%).^{ab}

Melting point: $T = 195$ °C.

^1H NMR (500 MHz, CDCl_3 , 300 K): δ = 8.06 (d, $^4J = 2.6$ Hz, 1H, H-5), 7.99 (d, $^4J = 2.6$ Hz, 1H, H-7), 7.29 (dd, $^3J = 8.2$ Hz, $^4J = 2.0$ Hz, 1H, H-6'), 7.17 (d, $J = 2.0$ Hz, 1H, H-4'), 7.01 (d, $J = 10.5$ Hz, 1H, H-4), 6.43 (d, $^3J = 8.2$ Hz, 1H, H-7'), 5.98 (d, $^3J = 10.5$ Hz, 1H, H-3), 2.72 (s, 3H, H-12'), 1.31 (s, 3H, H-13'), 1.22 (s, 3H, H-14') ppm.

^{13}C NMR (126 MHz, CDCl_3 , 300 K): δ = 151.7 (C-6), 146.3 (C-7'a), 140.0 (C-8), 137.9 (C-3'a), 135.3 (C-4a), 130.7 (C-6'), 128.2 (C-4), 124.9 (C-4'), 122.5 (C-3),

^a The color suggested that the compound was obtained in the merocyanine form, but in CDCl_3 , which was used for NMR spectroscopy, a mixture of spiropyran:merocyanine was detected in a ratio of 1:0.14 (in the plotted spectrum, 5 peaks of the merocyanine species which do not overlay with spiropyran peaks were integrated).

^b The carbon atom of the trifluoromethanesulfonic ester (C-9) was not detectable via ^{13}C NMR spectroscopy, due to the large coupling constant of approx. 400 Hz, the quadruplet peaks are expected to be distributed over a range of 13 ppm and be lower in their intensity.

122.0 (C-5), 120.8 (C-8a), 119.0 (C-7), 112.2 (C-5'), 109.0 (C-2), 108.9 (C-7'), 52.6 (C-3'), 28.7 (C-12'), 26.0 (C-14'), 19.7 (C-13') ppm.

¹⁹F NMR (471 MHz, CDCl₃, 300 K): δ = -73.8 ppm.^a

IR (ATR): $\tilde{\nu}$ = 3098 (w), 2969 (w), 2938 (w), 2871 (w), 1604 (w), 1517 (m), 1475 (m), 1416 (m), 1336 (s), 1281 (s), 1215 (vs), 1132 (s), 1039 (s), 809 (vs), 729 (vs), 574 (s), 495 (s) cm⁻¹.

HRMS (EI-TOF): m/z (%): [M]⁺ calcd for [C₂₀H₁₆N₂⁷⁹BrF₃O₆S]⁺ 547.9865 found 547.9857 (40); calcd for [C₂₀H₁₆N₂⁸¹BrF₃O₆S]⁺ 549.9844; found 549.9839 (42); 417.02 (100) [M-(SO₂CF₃)]⁺.

5'-Iodo-8-bromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9d)

5-Iodo-1,2,3,3-tetramethyl-3*H*-indolium iodide (1.12 g, 2.63 mmol), 3-bromo-2-hydroxybenzaldehyde (647 mg, 2.63 mmol) and dry piperidine (0.520 mL, 5.26 mmol) were dissolved in EtOH (45 mL) and heated to reflux under a nitrogen atmosphere for 5 h. After cooling down to -20 °C, the product had crystallized and was filtered to be obtained as dark brown solid (1.09 g, 2.07 mmol, 79%).

Melting point: T = 228 °C.

¹H NMR (500 MHz, CD₃Cl, 300 K): δ = 8.28 (d, ⁴ J = 2.5 Hz, 1H, H-5), 7.95 (d, ⁴ J = 2.5 Hz, 1H, H-7), 7.47 (dd, ³ J = 8.1 Hz, ⁴ J = 1.4 Hz, 1H, H-6'), 7.32 (d, ⁴ J = 1.4 Hz, 1H, H-4'), 6.91 (d, ³ J = 10.3 Hz, 1H, H-4), 6.35 (d, ³ J = 8.1 Hz, 1H, H-7'), 5.86 (d, ³ J = 10.3 Hz, 1H, H-3), 2.71 (s, H-12'), 1.27 (s, 3H, H-13'), 1.19 (s, 3H, H-14') ppm.

¹³C NMR (126 MHz, CD₃Cl, 300 K): δ = 155.9 (C-8a), 147.4 (C-7a'), 141.1 (C-6), 138.8 (C-3a'), 136.7 (C-6'), 130.6 (C-4'), 129.0 (C-7), 128.4 (C-4), 122.0 (C-3), 121.6 (C-5), 119.4 (C-4a), 109.6 (C-8), 109.6 (C-7'), 107.7 (C-2), 81.3 (C-5'), 52.4 (C-3'), 29.0 (C-12'), 25.9 (C-14'), 20.1 (C-13') ppm.

IR (ATR): $\tilde{\nu}$ = 3081 (w), 3066 (w), 2965 (w), 2925 (w), 1661 (w), 1591 (s), 1513 (s), 1442 (m), 1399 (m), 1265 (vs), 1201 (vs), 1171 (s), 1115 (s), 1078 (s), 962 (s), 810 (s), 790 (s), 774 (s), 747 (s), 727 (s), 697 (s), 662 (s) cm⁻¹.

HRMS (EI-TOF): m/z (%): [M]⁺ calcd for [C₁₉H₁₆N₂⁷⁹Br¹²⁷I¹²⁷O₃]⁺ 525.9389; found 525.9411 (61); calcd for [C₁₉H₁₆N₂⁸¹Br¹²⁷I¹²⁷O₃]⁺ 527.9369; found 527.9394 (60); 285.00 (100) [M-(PhI^{NO}₂C₂H)]⁺.

^a The ¹⁹F NMR spectrum of this compound was obtained without adding an internal standard.

5',8-Diiodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9e)

5-Iodo-1,2,3,3-tetramethyl-3*H*-indolium iodide (3.42 g, 8.00 mmol), 3-iodo-2-hydroxybenzaldehyde (2.33 g, 8.00 mmol) and dry piperidine (1.60 mL, 16.0 mmol) were dissolved in dry EtOH (150 mL) and heated to reflux under a nitrogen atmosphere for 3 h. After cooling down to -30 °C, the product had crystallized. The crude product was dissolved in a mixture of acetone (25 mL) and *n*-heptane (25 mL) and crystallized by removal of acetone under reduced pressure. The product was obtained as dark violet solid (3.08 g, 5.36 mmol, 67 %).

Melting point: *T* = 231 °C.

¹H NMR (500 MHz, CD₃Cl, 300 K): δ = 8.48 (d, 4J = 2.6 Hz, 1H, H-5), 7.99 (d, 4J = 2.6 Hz, 1H, H-7), 7.48 (dd, 3J = 8.1 Hz, 4J = 1.8 Hz, 1H, H-6'), 7.34 (d, 4J = 1.8 Hz, 1H, H-4'), 6.87 (d, 3J = 10.3 Hz, 1H, H-4), 6.36 (d, 3J = 8.1 Hz, 1H, H-7'), 5.84 (d, 3J = 10.3 Hz, 1H, H-3), 2.67 (s, 3H, H-12'), 1.27 (s, 3H, H-13'), 1.20 (s, 3H, H-14') ppm.

¹³C NMR (126 MHz, CD₃Cl, 300 K): δ = 157.9 (C-8a), 147.2 (C-7'a), 141.4 (C-6)^a, 138.7 (C-3'a), 136.5 (C-6'), 134.7 (C-7), 130.4 (C-4'), 128.5 (C-4), 122.4 (C-5), 121.6 (C-3), 118.3 (C-2), 109.5 (C-7'), 108.0 (C-4a), 82.6 (C-8), 81.2 (C-5'), 52.1 (C-3'), 28.9 (C-12'), 25.6 (C-14'), 20.1 (C-13') ppm.

IR (ATR): $\tilde{\nu}$ = 3083 (w), 3054 (w), 2983 (w), 2958 (w), 1583 (s), 1515 (s), 1497 (s), 1477 (m), 1444 (m), 1390 (m), 1282 (vs), 1265 (vs), 1203 (vs), 1173 (vs), 1081 (vs), 948 (vs), 810 (s), 726 (s), 681 (s), 489 (s) cm⁻¹.

HRMS (EI-TOF): *m/z* (%): [*M*]⁺ calcd for [C₁₉H₁₆N₂¹²⁷I₂O₃]⁺ 573.9250; found 573.9241 (80); 283.99 (100) iu⁺.

5'-Iodo-8-hydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9f)

Iodoindoliniumiodide (1.12 g, 2.63 mmol), 2,3-dihydroxybenzaldehyde (482 mg, 2.63 mmol, 1 eq) and dry piperidine (0.520 mL, 5.26 mmol) were dissolved in dry EtOH (25 mL) and heated to reflux under a nitrogen atmosphere for 4.5 h, followed

^a The ¹³C NMR spectroscopic signal of the atom 4a was only observed and assigned by a ¹H/¹³C HMBC experiment. The signal's intensity in the ¹H decoupled ¹³C NMR is too low for an assignment.

by stirring at 20 °C for 16 h. After crystallization at -30 °C, the product was obtained as dark purple solid (1.09 g, 2.33 mmol, 89%).

Melting point: $T = 240\text{ }^{\circ}\text{C}$.

^1H NMR (500 MHz, $\text{DMSO}-d_6$, 300 K): $\delta = 7.72$ (d, $^4J = 2.7$ Hz, 1H, H-5), 7.56 (d, $^4J = 2.7$ Hz, 1H, H-7), 7.44 (dd, $^3J = 8.1$ Hz, $^4J = 1.7$ Hz, 1H, H-6'), 7.41 (d, $^4J = 1.7$ Hz, 1H, H-4'), 7.14 (d, $^3J = 10.4$ Hz, 1H, H-4), 6.49 (d, $^3J = 8.1$ Hz, 1H, H-7'), 5.92 (d, $^3J = 10.4$ Hz, 1H, H-3), 2.66 (s, 3H, H-12'), 1.19 (s, 3H, H-13'), 1.10 (s, 3H, H-14') ppm.

^{13}C NMR (126 MHz $\text{DMSO}-d_6$, 300 K): $\delta = 147.8$ (C-6), 147.4 (C-7'a), 144.7 (C-8a), 139.9 (C-8a), 139.1 (C-3'a), 135.9 (C-6'), 130.0 (C-4'), 128.6 (C-4), 120.8 (C-3), 118.8 (C-8a), 113.6 (C-5), 110.9 (C-7), 109.6 (C-7'), 105.3 (C-2), 80.6 (C-5'), 51.8 (C-3'), 28.3 (C-12'), 25.2 (C-14'), 19.2 (C-13') ppm.

IR (ATR): $\tilde{\nu} = 3219$ (w, b), 3082 (w), 2973 (w), 2932 (w), 1615 (m), 1588 (m), 1568 (m), 1509 (s), 1431 (s), 1399 (s), 1283 (s), 1211 (s), 1189 (vs), 1168 (vs), 1113 (vs), 1048 (vs), 957 (vs), 876 (vs), 789 (vs), 745 (s), 663 (s), 536 (s), 458 (s) cm^{-1} .

HRMS (EI-TOF): m/z (%): $[\text{M}]^+$ calcd for $[\text{C}_{19}\text{H}_{17}\text{N}_2^{127}\text{IO}_4]^+$ 464.0233; found 464.0217 (80); 285.00 (100) $[\text{M}-(\text{PhO}_2\text{HNO}_2\text{C}_2\text{H})]^+$.

5'-Iodo-8-trifluoromethylsulfonyl-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9k)

Trifluoromethanesulfonic anhydride (367 mg, 0.22 μL , 1.30 mmol) was added to a solution of 8-hydroxy-5'-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (464 mg, 1.00 mmol) and anhydrous pyridine (396 mg, 400 μL , 5.00 mmol) in anhydrous DCM (10 mL) over the course of 10 min at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 1.5 h, the cooling bath was removed and the reaction mixture stirred at 20 °C for 1 h before heating it to reflux for 2 h. The reaction mixture was purified by filtration through silica gel (eluent: EtOAc) and after removal of the solvent *in vacuo*, the residue was dissolved in toluene (20 mL) and dried *in vacuo* again to remove remaining pyridine as azeotropic mixture. The crude product was dissolved in a mixture of DCM (20 mL) and *n*-

heptane (20 mL) and crystallized by removal of DCM under reduced pressure. The product was obtained as orange solid (335 mg, 561 μ mol, 56%).^a

Melting point: $T = 205\text{ }^{\circ}\text{C}$.

¹H NMR (500 MHz, CD₃Cl, 300 K): $\delta = 8.05$ (d, $^4J = 2.6$ Hz, 1H, H-7), 7.99 (d, $^4J = 2.6$ Hz, 1H, H-5), 7.48 (dd, $^3J = 8.2$ Hz, $^4J = 1.7$ Hz, 1H, H-6'), 7.33 (d, $^4J = 1.7$ Hz, 1H, H-4'), 7.01 (d, $^3J = 10.5$ Hz, 1H, H-4), 6.35 (d, $^3J = 8.2$ Hz, 1H, H-7'), 5.97 (d, $^3J = 10.5$ Hz, 1H, H-3), 2.72 (s, 3H, H-12'), 1.30 (s, 3H, H-13'), 1.21 (s, 3H, H-14') ppm.

¹³C NMR (126 MHz, CD₃Cl, 300 K): $\delta = 151.7$ (C-8a), 146.9 (C-7'a), 140.0 (C-6), 138.3 (C-3'a), 136.7 (C-6'), 135.3 (C-8), 130.4 (C-4'), 128.1 (C-4), 122.5 (C-3), 122.0 (C-5), 120.8 (C-4a), 119.0 (C-7), 109.6 (C-7'), 108.8 (C-2), 81.5 (C-5'), 52.5 (C-3'), 28.7 (C-12'), 26.0 (C-14'), 19.7 (C-13') ppm.

IR (ATR): $\tilde{\nu} = 3097$ (w), 2976 (w), 2936 (w), 2872 (w), 1601 (m), 1515 (s), 1515 (s), 1422 (s), 1336 (s), 1280 (s), 1233 (s), 1213 (vs), 1181 (s), 1133 (s), 1081 (s), 1039 (s), 952 (s), 899 (s), 881 (s), 815 (s), 806 (vs), 743 (s), 728 (vs), 593 (s), 572 (s), 497 (s) cm⁻¹.

HRMS (EI-TOF): m/z (%): [M]⁺ calcd for [C₂₀H₁₆N₂¹²⁷IF₃O₆S]⁺ 595.9726; found 595.9721 (60); 463.00 (100) [M-(SO₂CF₃)]⁺.

5'-Hydroxy-8-bromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9g)

5-Hydroxy-1,2,3,3-tetramethyl-3*H*-indolium iodide (834 mg, 2.63 mmol), 3-bromo-2-hydroxybenzaldehyde (647 mg, 2.63 mmol) and dry piperidine (0.52 mL, 5.26 mmol) were dissolved in dry EtOH (45 mL) and heated to reflux under a nitrogen atmosphere for 3 h. After cooling down to $-30\text{ }^{\circ}\text{C}$, the product had crystallized and was filtered to be obtained as dark brown solid (990 mg, 2.37 mmol, 90%). ¹H NOESY NMR experiments confirmed the species present in solution (DMSO-*d*₆, HCl) as merocyanine form in the *trans* conformation; likely in its protonated form.

Melting point: $T = 268\text{ }^{\circ}\text{C}$.

¹H NMR (500 MHz, DMSO-*d*₆, 300 K): $\delta = 8.82$ (d, $^4J = 2.7$ Hz, 1H, H-5), 8.41-8.35 (m, 2H, H-4, H-7), 7.67 (d, $^3J = 8.8$ Hz, 1H, H-7'), 7.62 (d, $^3J = 16.4$ Hz, 1H, H-3), 7.13 (d, $^4J = 2.3$ Hz, 1H, H-4'), 7.02 (dd, $^3J = 8.8$ Hz, $^4J = 2.3$ Hz, 1H, H-6'), 4.06 (s, 3H, H-12'), 1.62 (s, 6H, H-13', H-14') ppm.

^a The carbon atom of the trifluoromethanesulfonic ester (C-9) was not detectable via ¹³C NMR spectroscopy. Due to the large coupling constant of approx. 400 Hz, the quadruplet peaks are expected to be distributed over a range of 13 ppm and be decreased in their intensity.

^{13}C NMR (126 MHz DMSO- d_6 , 300 K): δ = 179.0 (C-2'), 161.0 (C-5'), 160.4 (C-9), 147.0 (C-3a'), 143.8 (C-4), 141.5 (C-6), 134.5 (C-7a'), 131.4 (C-7), 125.5 (C-4a), 124.6 (C-5), 117.7 (C-7'), 117.0 (C-3), 116.7 (C-6'), 114.8 (C-8), 110.7 (C-4'), 52.8 (C-3'), 36.0 (C-12'), 26.1 (C-13', C-14') ppm.

IR (ATR): $\tilde{\nu}$ = 3166 (w,b), 3048 (w), 2989 (w), 2971 (w), 2929 (w), 1617 (m), 1584 (s), 1516 (s), 1429 (s), 1401 (s), 1358 (s), 1306 (s), 1277 (vs), 1226 (vs), 1206 (vs), 1172 (s), 1122 (s), 1071 (s), 1039 (s), 970 (s), 894 (s), 849 (s), 810 (s), 747 (vs), 701 (vs), 638 (s), 461 (s) cm^{-1} .

HRMS (EI-TOF): m/z (%): $[\text{M}]^+$ calcd for $[\text{C}_{19}\text{H}_{17}\text{N}_2^{79}\text{BrO}_4]^+$ 416.0372; found 416.0359 (31); calcd for $[\text{C}_{19}\text{H}_{17}\text{N}_2^{81}\text{BrO}_4]^+$ 418.0351; found 418.0342 (30); 175.09 (100) $[\text{M}-(\text{PhOBrNO}_2\text{C}_2\text{H})]^+$.

5'-Hydroxy-8-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9h)

5-Hydroxy-1,2,3,3-tetramethyl-3*H*-indolium iodide (834 mg, 2.63 mmol), 3-iodo-2-hydroxybenzaldehyde (771 mg, 2.63 mmol) and dry piperidine (0.520 mL, 5.26 mmol) were dissolved in dry EtOH (45 mL) and heated to reflux under a nitrogen atmosphere for 3 h. After cooling down to $-20\text{ }^{\circ}\text{C}$, the product had crystallized and was filtered to be obtained as dark solid (1.08 g, 2.32 mmol, 88%).

Melting point: $T = 259\text{ }^{\circ}\text{C}$.

^1H NMR (500 MHz, DMSO- d_6 , 300 K): δ = 8.68 (d, $^4J = 3.0\text{ Hz}$, 1H, H-5), 8.45 (d, $^4J = 3.0\text{ Hz}$, 1H, H-7), 8.36 (d, $^3J = 15.5\text{ Hz}$, 1H, H-4), 8.24 (d, $^3J = 15.5\text{ Hz}$, 1H, H-3), 7.57 (d, $^3J = 8.7\text{ Hz}$, 1H, H-7'), 7.11 (d, $^4J = 2.2\text{ Hz}$, 1H, H-4'), 6.92 (dd, $^3J = 8.7\text{ Hz}$, $^4J = 2.2\text{ Hz}$, 1H, H-6'), 3.88 (s, 3H, H-12'), 1.70 (s, 6H, H-13', H-14') ppm.

^{13}C NMR (126 MHz DMSO- d_6 , 300 K): δ = 179.3 (C-2'), 174.8 (C-8a), 158.3 (C-5'), 151.7 (C-4), 145.1 (C-3a'), 135.6 (C-5), 134.1 (C-7a'), 132.7 (C-7), 131.8 (C-6), 118.5 (C-4a), 115.2 (C-6'), 115.0 (C-7'), 109.8 (C-4'), 109.0 (C-3), 99.8 (C-8), 50.9 (C-3'), 33.3 (C-12'), 26.2 (C-13', 14') ppm.

IR (ATR): $\tilde{\nu}$ = 3112 (m, b), 2974 (w), 1595 (m), 1573 (w), 1507 (s), 1475 (m), 1455 (m), 1397 (m), 1368 (s), 1283 (vs), 1254 (vs), 1202 (vs), 1084 (vs), 956 (s), 833 (s), 771 (m), 743 (s), 685 (vs), 648 (s), 552 (m) cm^{-1} .

HRMS (EI-TOF): m/z (%): $[\text{M}]^+$ calcd for $[\text{C}_{19}\text{H}_{17}\text{N}_2^{127}\text{IO}_4]^+$ 464.0233; found 464.0217 (62); 175.10 (100) $[\text{M}-(\text{PhOINO}_2\text{C}_2\text{H})]^+$.

5',8-Dihydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline][11] and its corresponding merocyanine form (9i)

5-Hydroxy-1,2,3,3-tetramethyl-3*H*-indolium iodide (1.79 g, 5.64 mmol) and 2,3-dihydroxy-5-nitrobenzaldehyde (735 mg, 4.04 mmol) were dissolved in EtOH (55 mL) and piperidine (790 μ L, 8.0 mmol) under a nitrogen atmosphere. The reaction mixture was heated to 80 $^{\circ}$ C for 3 h and cooled down to -20 $^{\circ}$ C subsequently. After filtration and washing with EtOH (30 mL, -20 $^{\circ}$ C), the wet filter cake was dried *in vacuo* to yield 5',8-dihydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] as dark green solid (1.41 g, 3.97 mmol, 98%, Lit.[11] 99%). ^1H NOESY NMR experiments confirmed the species present in solution (DMSO- d_6 , HCl) as merocyanine form in the *trans* conformation; likely in its protonated form.

mp: > 300 $^{\circ}$ C

^1H NMR (500 MHz, DMSO- d_6 , 300 K): δ = 8.51 (d, 4J = 2.7 Hz, 1 H, H-7), 8.31 (d, 3J = 16.5 Hz, 1 H, H-4), 7.96 (d, 4J = 2.7 Hz, 1 H, H-5), 7.74 (d, 3J = 16.6 Hz, 1 H, H-3), 7.72 (d, 3J = 8.7 Hz, 1 H, H-7'), 7.22 (d, 4J = 2.7 Hz, 1 H, H-4'), 7.07 (dd, 3J = 8.7 Hz, 4J = 2.7 Hz, 1 H, H-6'), 4.09 (s, 3H, H-12'), 1.70 (s, 6H, H-13', H-14') ppm.

^{13}C NMR (126 MHz, DMSO- d_6 , 300 K): δ = 178.5 (C-4a), 160.1 (C-5'), 153.3 (C-6), 146.6 (C-3a'), 146.0 (C-8), 143.9 (C-4), 139.9 (C-8a), 133.9 (C-7a'), 121.2 (C-2'), 116.7 (C-7, C-7'), 115.9 (C-6'), 114.8 (C-3), 112.1 (C-5), 110.0 (C-4'), 51.9 (C-3'), 34.8 (C-12'), 25.9 (C-13', C-14') ppm.

IR (ATR): $\tilde{\nu}$ = 3203 (w, b), 2981 (w), 1596 (m), 1513 (m), 1454 (m), 1411 (m), 1359 (m), 1273 (s), 1244 (m), 1215 (s), 1180 (s), 1061 (s), 961 (s), 899 (m), 863 (s), 800 (s), 788 (m), 764 (m), 739 (s), 544 (s) cm^{-1} .

HRMS (EI-TOF): m/z (%): $[\text{M}]^+$ calcd for $[\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_5+\text{H}]^+$ 354.1216; found 354.1214 (40); 175.09 (100) $[\text{M}-(\text{PhO}_2\text{HNO}_2\text{C}_2\text{H}_2)]^+$.

5'-Trifluoromethylsulfonyl-8-bromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9l)

Trifluoromethanesulfonic anhydride (500 mg, 1.77 mmol) was added to a solution of 5'-bromo-8-hydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (417 mg, 1.00 mmol) and anhydrous pyridine (0.4 mL, 396 mg, 5 mmol) in anhydrous DCM (10 mL) over the course of 6 min at 0 °C. The reaction mixture was stirred at 0 °C for 1.5 h, before the cooling bath was removed and the reaction mixture stirred at 24 °C for 1 h followed by heating it to 40 °C for 2 h. After the reaction cooled down, the mixture was diluted with DCM (10 mL) and the remaining anhydride was deactivated by addition of water (20 mL). The phases were separated, the aqueous phase was extracted with DCM (2 x 10 mL) and the solvent was removed *in vacuo*. The remaining solid was dissolved in EtOAc (20 mL), which was then washed with hydrochloric acid (1 mol/L, 2 x 20 mL) and water (20 mL). After drying over MgSO₄ and removal of solvent, the crude product was dissolved in chloroform (20 mL) and the solution was filtered. Removal of the solvent gave the product as dark purple solid (239 mg, 435 μmol, 43%).

Melting point: $T = 87\text{ }^{\circ}\text{C}$.

¹H NMR (500 MHz, CDCl₃, 300 K): $\delta = 8.29$ (d, $^4J = 2.6$ Hz, 1H, H-7), 7.97 (d, $^4J = 2.6$ Hz, 1H, H-5), 7.09 (dd, $^3J = 8.5$ Hz, $^4J = 2.5$ Hz, 1H, H-6'), 6.97 (d, $^4J = 2.5$ Hz, 1H, H-4'), 6.94 (d, $^3J = 10.3$ Hz, 1H, H-4), 6.53 (d, $^3J = 8.5$ Hz, 1H, H-7'), 5.88 (d, $^3J = 10.3$ Hz, 1H, H-3), 2.74 (s, 3H, H-12'), 1.30 (s, 3H, H-13'), 1.22 (s, 3H, H-14') ppm.

¹³C NMR (126 MHz, CDCl₃, 300 K): $\delta = 155.8$ (C-8a), 147.2 (C-7'a), 143.2 (C-5'), 141.3 (C-4a), 138.2 (C-3'a), 129.1 (C-7), 128.7 (C-4), 121.7 (C-3), 121.6 (C-5), 120.9 (C-6'), 115.5 (H-4'), 109.6 (C-8), 108.0 (C-2), 107.5 (C-7'), 52.5 (C-3'), 29.1 (C-12'), 25.6 (C-14'), 19.9 (C-13') ppm.^a

¹⁹F NMR (471 MHz, CDCl₃, 300 K): $\delta = -78.6$ ppm.^b

IR (ATR): $\tilde{\nu} = 3091$ (w), 2966 (w), 2926 (w), 2852 (w), 1599 (w), 1520 (m), 1486 (m), 1419 (s), 1336 (s), 1269 (m), 1243 (s), 1205 (vs), 1139 (vs), 1091 (s), 1019 (m), 966 (m), 923 (m), 900 (s), 858 (m), 832 (s), 810 (s), 743 (s), 712 (s), 615 (s) cm⁻¹.

HRMS (EI-TOF): m/z (%): $[M]^+$ calcd for $[\text{C}_{20}\text{H}_{16}^{79}\text{BrF}_3\text{N}_2\text{O}_6\text{S}]^+$ 547.9865; found 547.9856 (20); calcd for $[\text{C}_{20}\text{H}_{16}^{81}\text{BrF}_3\text{N}_2\text{O}_6\text{S}]^+$ 549.9844; found 549.9846 (21); 415.03/417.03 (100) $[M-(\text{CF}_3\text{SO}_2)]^+$.

^a The carbon atom of the trifluoromethanesulfonic ester (C-9) was not detectable via ¹³C NMR spectroscopy, due to the large coupling constant of approx. 400 Hz, the quadruplet peaks are expected to be distributed over a range of 13 ppm and be lower in their intensity.

^b The ¹⁹F NMR spectrum of this compound was obtained without adding an internal standard.

5'-Trifluoromethylsulfonyl-8-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9m)

Trifluoromethanesulfonic anhydride (635 mg, 1.3 mmol) was added to a solution of 5'-hydroxy-8-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (464 mg, 1.00 mmol) in anhydrous DCM (10 mL) over the course of 2 min at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, the cooling bath was removed and the reaction mixture stirred at 20 °C for 1 h before heating it to reflux for 2 h. The reaction mixture was purified by filtration through silica gel (Macherey-Nagel, eluent: EtOAc) and after removal of the solvent *in vacuo*, the residue was dissolved in toluene (20 mL) and dried *in vacuo* again to remove remaining pyridine as azeotropic mixture. The crude product was purified by column chromatography (silica gel, MeOH/EtOAc 5/95 v/v) to obtain a dark purple solid (259 mg, 434 μmol, 43%).

TLC (MeOH/EtOAc, 5/95): R_f = 0.15

Melting point: $T = 85$ °C.

^1H NMR (600 MHz, CD_2Cl_2 , 300 K):

Signals assigned to the *spiropyran* (closed) form: δ = 8.29 (d, 4J = 2.6 Hz, 1H, H-5), 7.99 (d, 4J = 2.6 Hz, 1H, H-7), 7.11 (dd, 3J = 8.5 Hz, 4J = 2.5 Hz, 1H, H-6'), 7.00 (d, 4J = 2.5 Hz, 1H, H-4'), 6.97 (d, $^3J_{\text{Z}}$ = 10.3 Hz, 1H, H-4), 6.57 (d, 3J = 8.5 Hz, 1H, H-7'), 5.90 (d, $^3J_{\text{Z}}$ = 10.3 Hz, 1H, H-3), 2.76 (s, 3H, H-12'), 1.30 (s, 3H, H-13'), 1.21 (s, 3H, H-14') ppm.

Signals assigned to the *merocyanine* (open) form: δ = 9.12 (d, 4J = 2.6 Hz, 1H, H-5), 8.75 (4J = 2.6 Hz, 1H, H-7), 8.28 (d, $^3J_{\text{E}}$ = 16.3 Hz, 1H, H-4), 7.86 (d, 3J = 8.8 Hz, 1H, H-7'), 7.83 (d, $^3J_{\text{E}}$ = 16.3 Hz, 1H, H-3), 7.62 (dd, 3J = 8.8 Hz, 4J = 2.3 Hz, 1H, H-6'), 7.58 (d, 4J = 2.3 Hz, 1H, H-4'), 4.37 (s, 3H, H-12'), 1.88 (s, 6H, H-13', H-14') ppm.

^{13}C NMR (151 MHz, CD_2Cl_2 , 300 K):^a

Signals assigned to the *spiropyran* (closed) form: δ = 147.9 (C-8a), 147.5 (C-3'a), 143.4 (C-5'), 141.7 (C-6), 138.8 (C-7'a), 129.3 (C-5), 129.2 (C-4), 123.2 (C-8), 122.1 (C-7, C-3), 121.2 (C-6'), 120.1 (C-4a), 115.9 (C-4'), 108.6 (C-2) 107.7 (C-7'), 52.9 (C-3'), 30.3 (C-12'), 25.8 (C-14'), 20.0 (C-13') ppm.

Signals assigned to the *merocyanine* (open) form: δ = 184.7 (C-2'), 151.5 (C-5'), 148.1 (C-6), 146.9 (C-8a), 146.5 (C-3'a), 143.6 (C-4), 141.2 (C-7'a), 133.3 (C-7),

^a The carbon atom of the trifluoromethanesulfonic ester (C-9) was not detectable via ^{13}C NMR spectroscopy, due to the large coupling constant of approx. 400 Hz, the quadruplet peaks are expected to be distributed over a range of 13 ppm and be lower in their intensity.

124.7 (C-5), 124.1 (C-6'), 120.6 (C-3), 119.4 (C-8), 118.4 (C-7'), 117.4 (C-4'), 109.8 (C-4a), 54.7 (C-3'), 37.0 (C-12'), 25.9 (C-13', C-14') ppm.

IR (ATR): $\tilde{\nu}$ = 3085 (w), 2973 (w), 1604 (m), 1538 (w), 1420 (s), 1342 (m), 1257 (vs), 1231 (vs), 1170 (vs), 1137 (vs), 1035 (vs), 905 (s), 870 (s), 832 (s), 765 (s), 743 (s), 632 (vs), 616 (vs), 600 (vs), 512 (vs) cm^{-1}

HRMS (EI-TOF): m/z (%): $[M]^+$ calcd for $[\text{C}_{20}\text{H}_{16}\text{F}_3^{127}\text{IN}_2\text{O}_6\text{S}]^+$ 595.97258; found 595.97047 (16); 463.07 (100) $[\text{M}-(\text{CF}_3\text{SO}_2)]^+$.

Bis-5',8-(trifluoromethylsulfonyl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9n)

Trifluoromethanesulfonic anhydride (1.69 g, 1.01 mL, 6.00 mmol) was added to a solution of 5',8-dihydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (886 mg, 2.50 mmol) and anhydrous pyridine (791 mg, 0.81 mL, 10.0 mmol) in anhydrous DCM (10 mL) over the course of 10 min at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 1.5 h, the cooling bath was removed and the reaction mixture stirred at 20 °C for 1 h before heating it to 50 °C for 2 h. The reaction mixture was filtered through silica gel (silica gel, eluent: EtOAc) and after removal of the solvent *in vac.*, the residue was dissolved in toluene (20 mL) and dried *in vac.* again to remove remaining pyridine as azeotropic mixture. The crude product was purified by column chromatography (silica gel, eluent: TEA/DCM 5% *v/v*). After removal of the solvent *in vacuo*, the product was obtained as purple solid (1.37 g, 2.22 mmol, 89%).

TLC (silica gel, UV, TEA/DCM 5% *v/v*): R_f = 1.0 – 0.5

Melting point: T = 96 °C

^1H NMR (500 MHz, CDCl_3 , 300 K): δ = 8.07 (d, 4J = 2.5 Hz, 1 H, H-5), 8.00 (d, 4J = 2.5 Hz, 1 H, H-7), 7.10 (dd, 4J = 2.5 Hz, 3J = 8.5 Hz, 1 H, H-6'), 7.05 (d, 3J = 10.5 Hz, 1 H, H-4), 6.99 (d, 4J = 2.5 Hz, 1 H, H-4'), 6.53 (d, 3J = 8.5 Hz, 1 H, H-7'), 6.01 (d, 3J = 10.5 Hz, 1 H, H-3), 2.75 (s, 3H, H-12'), 1.34 (s, 3H, H-13'), 1.25 (s, 3H, H-14') ppm.

^{13}C NMR (126 MHz, CDCl_3 , 300 K): δ = 151.5 (C-6), 146.8 (C-7'a), 143.5 (C-5'), 140.2 (C-8), 137.8 (C-3'a), 135.1 (C-4a), 128.5 (C-4), 122.1 (C-7), 121.9 (C-3), 120.9

(C-6'), 120.7 (C-8a), 119.6 (C-9), 119.1 (C-5), 117.5 (C-15'), 115.4 (C-4'), 108.9 (C-2), 107.7 (C-7'), 52.4 (C-3'), 28.8 (C-12'), 25.9 (C-13'), 19.5 (C-14') ppm.^a

¹⁹F NMR (471 MHz, CDCl₃, 300 K): δ = -72.7, -74.0 ppm.

IR (ATR): $\tilde{\nu}$ = 3104 (w), 2966 (w), 1647 (w), 1615 (m), 1588 (w), 1531 (m), 1476 (m), 1416 (s), 1345(s), 1301 (m), 1223 (vs), 1209 (vs), 1136 (vs), 1103 (s), 1082 (s), 1047 (m), 1017 (m), 1001 (m), 955 (m), 942 (m), 905 (vs), 876 (s), 837 (s), 815 (vs), 772 (m), 730 (s), 657 (m), 620 (s), 595 (s), 587 (s), 503 (s) cm⁻¹.

HRMS (ESI-TOF): *m/z* (%): [M+H]⁺ calcd for [C₂₁H₁₆N₂F₆O₉S₂+H]⁺ 619.0274; found 619.0278 (75); 641.01 (100) [M+Na]⁺.

^a The carbon atom of the trifluoromethanesulfonic ester (C-9) was not detectable via ¹³C NMR spectroscopy, due to the large coupling constant of approx. 400 Hz, the quadruplet peaks are expected to be distributed over a range of 13 ppm and be lower in their intensity.

UV/vis Measurements and Determination of Attenuation Coefficients by ^1H NMR Spectroscopy

Sample Preparation

Of each new spiropyran, a stock solution was prepared in acetonitrile (HPLC-grade, 100 mL, circa 0.1 mmol/L). A defined volume (1 – 5 mL) was taken out of this solution and diluted to give a final volume of 10 mL to obtain the desired various sample concentrations (circa 10 – 50 $\mu\text{mol/L}$).

For the determination of the ratio between the spiropyran and merocyanine species in a dark environment by ^1H NMR spectroscopy, 500 μL of the most concentrated solution (circa 50 $\mu\text{mol/L}$) and 50 μL of deuterated acetonitrile were combined.

Table i: Preparation of stock solutions.

<i>Compound</i>	<i>Mol. Weight (g/mol)</i>	<i>Targeted conc. stock solution (mol/L)</i>	<i>Targeted weight (mg)</i>	<i>Actual sample weight (mg)</i>	<i>Volume stock solution (mL)</i>	<i>Conc. stock solution (mol/L)</i>
9a	480.16	1.00E-04	4.80	4.86	100	1.01E-04
9b	527.16	1.00E-04	5.27	5.65	100	1.07E-04
9c	417.26	1.00E-04	4.17	2.98	100	7.14E-05
9j	549.32	1.00E-04	5.49	5.91	100	1.08E-04
9d	527.16	1.00E-04	5.27	5.45	100	1.03E-04
9e	574.16	1.00E-04	5.74	4.35	100	7.58E-05
9f	464.26	1.00E-04	4.64	2.76	100	5.94E-05
9k	596.32	1.00E-04	5.96	6.91	100	1.16E-04
9g	417.26	1.00E-04	4.17	5.86	100	1.40E-04
9h	464.26	1.00E-04	4.64	3.76	100	8.10E-05
9l	549.32	1.00E-04	5.49	5.34	100	9.72E-05
9m	596.32	1.00E-04	5.96	6.86	100	1.15E-04
9n	618.47	1.00E-04	6.18	6.25	100	1.01E-04

Summarized Results

For all new spiropyrans, 5 different dilutions were investigated by UV/vis spectroscopy under the following conditions: **(a)** after illumination with green light (565 nm), until a photostationary state was reached, in which mostly spiropyran form was present; **(b)** after irradiation with UV light (365 nm), until a photostationary state was reached, in which the merocyanine forms are enriched; **(c)** after keeping the sample solutions dark for at least 24 hours, the measurement was carried out under red light (i.e. no absorption possible); **(d)** time dependent measurements after

PSS³⁶⁵; typically, 120 scans were taken with a time interval of less than 2 min,^a **(e)** time dependent measurements after PSS⁵⁶⁵, typically, 120 scans were taken with a time interval of 6 min.^b

The graphs **(a-c)** contain a plot of the measured intensities at the absorption maxima and a linear fit; the results are summarized in table ii. Plots of time dependent measurements **(d, e)** contain a plot of the measured absorption at the maximum which corresponds to the merocyanine state and an exponential fit. These results are summarized in table iii.

For the determination of the ratio between merocyanine and spiropyran, ¹H NMR spectra of the most concentrated samples from **(c)** were recorded and plotted in **(f)**. The signals used to determine the ratio are marked with green (merocyanine) and orange (spiropyran) boxes. Table iv shows the obtained results.

^a The intervals were: 2 min for **9a**, 1 min for **9b,d,e,m**, 15 s for **9c,f,l**.

^b For **9b** and **9e**, 2 min and 1 min were used, respectively.

Table ii: Absorption maxima and calculated attenuation coefficients from a linear fit (using a fixed intercept at 0;0) including errors.

Name	Wavelength of abs. max. (nm)		Attenuation ($L(\text{mol cm})^{-1}$)					
	SP form	MC form	PSS (565 nm)		PSS (365 nm)		Equilibrium in dark conditions	
			Slope (linear fit)	Std. error	Slope (linear fit)	Std. error	Slope (linear fit)	Std. error
9a	315	556	9168	50	30591	381	1858	37
9b	306	559	7709	129	11500	98	1082	15
9c	355	568	8765	37	27520	221	2424	26
9j	308	536	8699	74	6885	183	21876	335
9d	308	559	8826	69	19770	103	1576	10
9e	314	561	5534	36	8320	82	828	24
9f	355	570	7849	67	24215	511	2209	20
9k	311	538	8881	72	5274	52	23936	224
9g	320	547	9948	107	1747	13	31621	330
9h	320	549	7583	160	1972	51	15851	658
9l	331	561	7364	40	23266	277	336	1.5
9m	335	557	4948	166	6292	210	289	13
9n	304	537	6483	49	11532	97	6879	33

Table iii: The half-life times $t_{1/2}$ refer to samples, which, after illumination, were allowed to isomerize in the dark. The absorption maximum of merocyanine was plotted in dependence on time, before an exponential fit ($y = y_0 + A_1 e^{-x/t_1}$) was applied.

Name	Decay after PSS (365 nm)			Decay after PSS (565 nm)		
	t_1 (min)	Std. error	$t_{1/2}$ (hh:mm:ss)	t_1 (min)	Std. error	$t_{1/2}$ (hh:mm:ss)
	Exp. fit	Exp. fit		Exp. fit	Exp. fit	
9a	22.15155	0.00964	00:15:21	33.3562 2		00:23:07
9b	16.54166	0.0599	00:11:28	32.1321 5	0.09491	00:22:16
9c	1.3287	0.00237	00:00:55	n.n. ^b		
9j	n.n. ^a			365.409 87	1.33004	04:13:17
9d	20.75646	0.01001	00:14:23	36.2259 8	0.29487	00:25:07
9e	19.24909	0.19885	00:13:21	12.7739 9	0.02188	00:08:51
9f	1.73289	0.00153	00:01:12	n.n. ^b		
9k	n.n. ^a			300.356 14	1.07554	03:28:11
9g	n.n. ^a			411.942 73	1.57521	04:45:32
9h	n.n. ^a			392.056 5	0.55513	04:31:45
9l	3.87585	0.01548	00:02:41	n.n. ^b		
9m			00:00:00	n.n. ^b		
9n	81.52332	0.27588	00:56:30	175.046 44	0.66688	02:01:20

^a A decay measurement was not performed, because the concentration of merocyanine was lower at the PSS₃₆₅ compared to dark conditions. This is because the merocyanine form also absorbs at this wavelength, leading to the formation of the spiropyran form, an effect that is not present in the dark equilibrium.

^b A decay measurement was not performed, because the concentration of merocyanine at the PSS₅₆₅ was the same compared to dark conditions.

Table iviv: Determination of the absolute attenuation coefficient ϵ_{MC} of merocyanine form by combined UV/vis and 1H NMR spectral analysis and calculation of the ratio between merocyanine and spiropyran forms in the photostationary state after irradiation with 365 nm for 30 sec.

Compound	Equilibrium in dark conditions						Photostationary state (365 nm)			
	Attenuation (L(mol cm) ⁻¹)		Ratio [MC]:[SP]		ϵ^{MC} (L(mol cm) ⁻¹)		Attenuation (L(mol cm) ⁻¹)		Calculated Ratio [MC]:[SP]	
	Slope (linear fit)	Std. error	Integration of 1H NMR	Integration error	Calculated $\epsilon_{dark}/Int.$	Error	Slope (linear fit)	Std. error	[MC]	[SP]
9a	1858	37	08:92	0.02	24447	6434	30591	381	125	-25
9b	1082	15	12:88	0.01	9328	804	11500	98	123	-23
9c	2424	26	07:93	0.00	34629	0	27520	221	79	21
9j	21876	335	59:41	0.01	37078	628	6885	183	19	81
9d	1576	10	07:93	0.01	22514	3216	19770	103	88	12
9e	828	24	04:96	0.01	20700	5175	8320	82	40	60
9f	2209	20	06:94	0.00	36817	0	24215	511	66	34
9k	23936	224	52:48	0.00	46031	0	5274	52	11	89
9g	31621	330	58:42	0.00	54519	0	1747	13	03	97
9h	15851	658	56:44	0.00	28305	0	1972	51	07	93
9l	336	1.5	02:98	0.00	16800	0	24402	268	138	-38
9m	289	556	48:52	0.00	556	0	6292	210	348	-248
9n	6879	33	27:73	0.02	25478	1887	11532	97	45	55

UV/vis Spectra and Corresponding ^1H NMR Spectra

5'8-Dibromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9a)

5'-Bromo-8-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9b)

5'-Bromo-8-hydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9c)

5'-Bromo-8-trifluoromethylsulfonyl-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9)

5'-Iodo-8-bromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9d)

5',8-Diiodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9e)

5'-Iodo-8-hydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9f)

5'-Iodo-8-trifluoromethylsulfonyl-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9k)

5'-Hydroxy-8-bromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9g)

5'-Hydroxy-8-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9h)

5'-Trifluoromethylsulfonyl-8-bromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9l)

5'-Trifluoromethylsulfonyl-8-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9m)

Bis-5',8-(trifluoromethylsulfonyl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9n)

^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra

5-Bromo-2,3,3-trimethyl-3H-indole (8a)

5-Bromo-1,2,3,3-tetramethyl-3H-indolium iodide (3a)

5-Iodo-2,3,3-trimethyl-3H-indole (8b)

5-Iodo-1,2,3,3-tetramethyl-3H-indolium iodide (3b)

5-Methoxy-2,3,3-trimethyl-3H-indole (8c)

5-Hydroxy-2,3,3-trimethyl-3H-indole (8d)

5-Hydroxy-1,2,3,3-tetramethyl-3*H*-indolium iodide (3c)

3-Bromo-2-hydroxybenzaldehyde (5a)

3-Bromo-2-hydroxy-5-nitrobenzaldehyde (2a)

2-Hydroxy-3-iodobenzaldehyde (5b)

2-Hydroxy-3-iodo-5-nitrobenzaldehyde (2b)

2-Hydroxy-3-methoxy-5-nitrobenzaldehyde (5c)

2,3-Dihydroxy-5-nitrobenzaldehyde (2c)

5'8-Dibromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9a)

5'-Bromo-8-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9b)

5'-Bromo-8-hydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9c)

5'-Bromo-8-trifluoromethylsulfonyl-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9)

5'-Iodo-8-bromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9d)

5',8-Diiodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9e)

5'-Iodo-8-hydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9f)

5'-Iodo-8-trifluoromethylsulfonyl-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9k)

5'-Hydroxy-8-bromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9g)

5'-Hydroxy-8-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9h)

5',8-Dihydroxy-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline][11] (9i)

5'-Trifluoromethylsulfonyl-8-bromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9l)

5'-Trifluoromethylsulfonyl-8-iodo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9m)

Bis-5',8-(trifluoromethylsulfonyl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (9n)