Electronic Supplementary Information

Oxidative electrochemical aryl C-C coupling of spiropyrans

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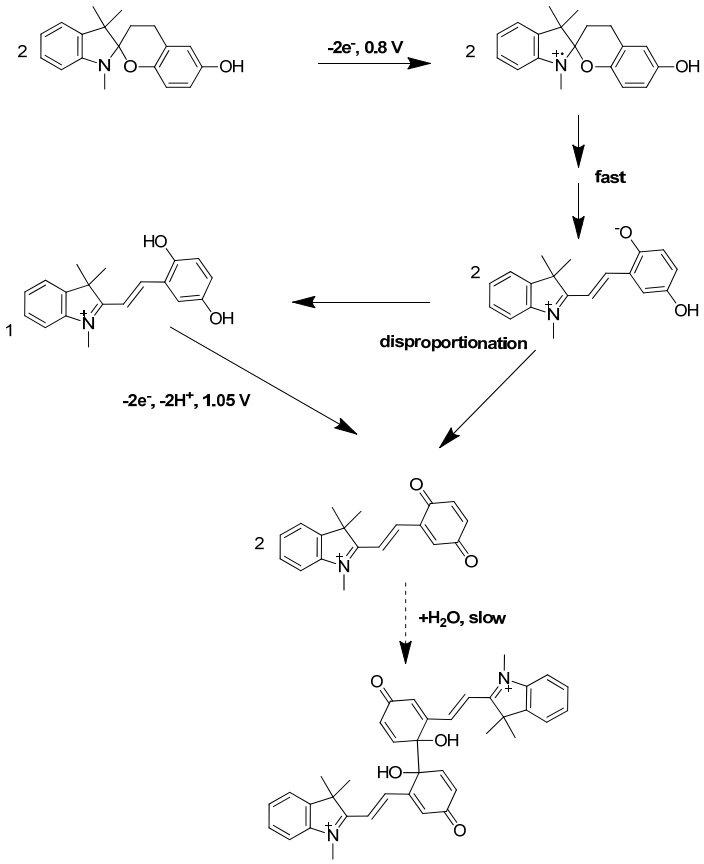
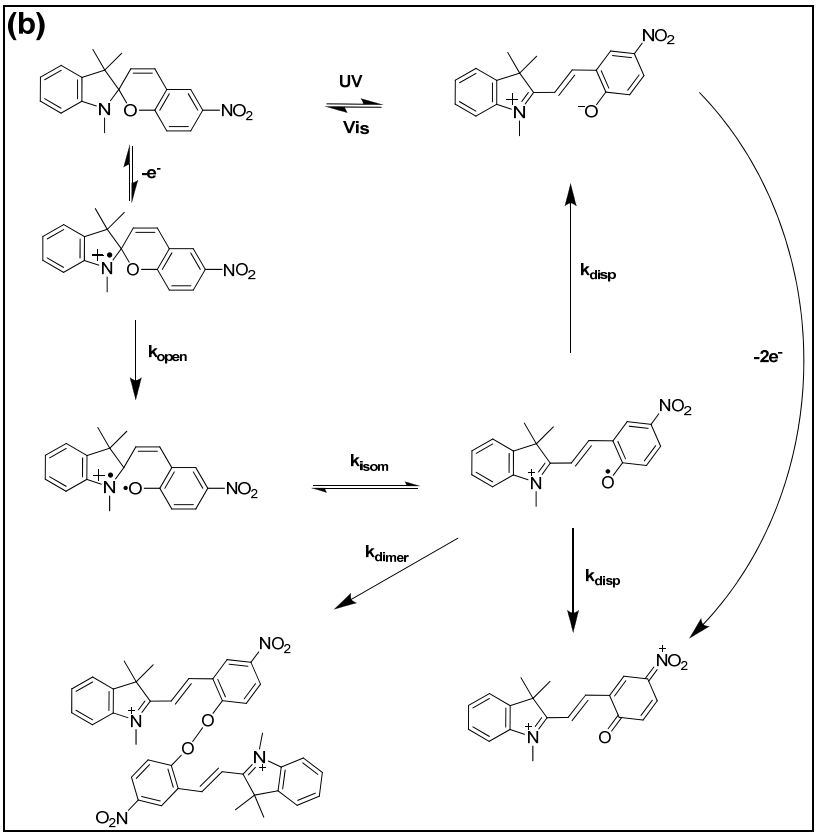
Mechanisms and products of oxidation postulated in the literature:

(a)




(b)
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Vis
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kopen
kdisp
-2e-
kisom
kdimer
kdisp
NO2

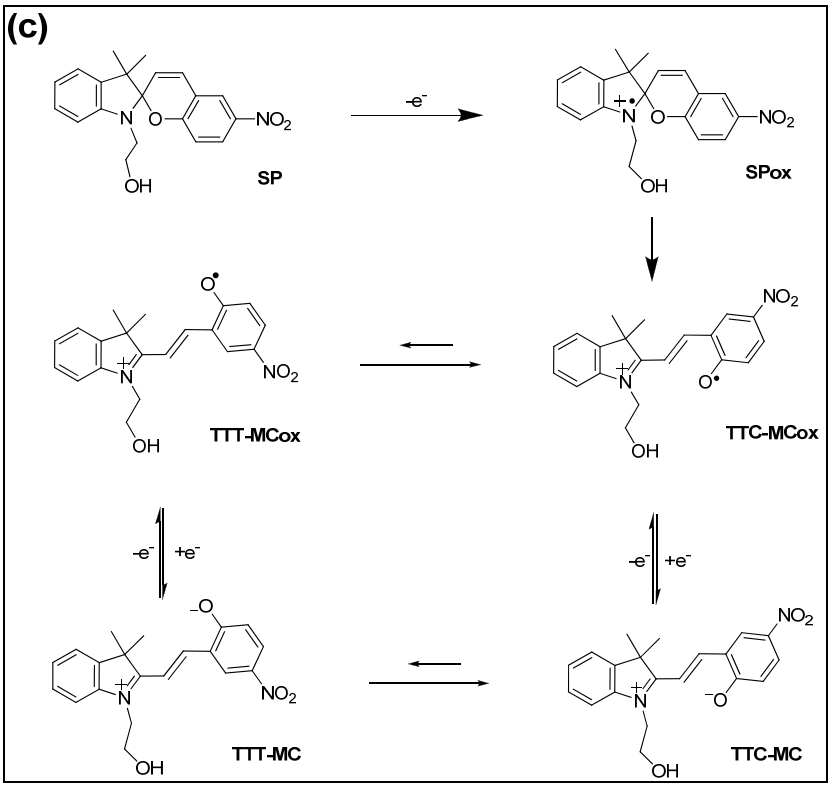


Fig. S1 Mechanisms and products of oxidation in solution proposed by Preigh *et al*. (a),[1] Doménech *et al*. (b),[2] and Wagner *et al*. (c).[3]

Experimental procedures.

Cyclic voltammetry.

Ambient conditions cyclic voltammetry was carried out on a Model 760C Electrochemical Workstation (CH Instruments). A three-electrode arrangement with a SCE reference electrode, Pt wire auxiliary electrode and glassy carbon working electrode was used. The electrolyte was a freshly prepared 0.1 M solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$, Sigma Aldrich Co, electrochemical grade) in dichloromethane. All potentials are reported ± 10 mV with respect to the Saturated Calomel Electrode (SCE).

Cyclic voltammetry was measured in a controlled atmosphere, i.e. glove box, with O_2 and H_2O content of less than 2 ppm. 1,2-Dichloroethane with 0.1 M $TBAPF_6$ was used as supporting electrolyte.

Vibrational and electronic absorption spectroscopy.

UV/vis absorption spectra were obtained using a Analytik Jena Specord S600 diode array spectrophotometer. UV/vis spectroelectrochemistry was measured in the same spectrometer using electrochemical thin layer OTTLE cell with Pt working electrode, Pt counter electrode and Ag wire quasi reference electrode.

Raman spectra were recorded at 785 nm using a Perkin Elmer Raman Station 400F by 20 s accumulations at 70 mW. Analysis of the Raman spectra involved manual multipoint baseline correction and subtraction of the solvent bands.

Infrared spectra were recorded on a Perkin Elmer FT-IR Spectrometer "Spectrum 400" using a UATR attachment and liquid N_2 cooled MCT (Mercury Cadmium Telluride) detector.

Bulk electrolysis of compound 1.

A solution of 10 mg (0.03 mmol) of **1** in 60 mL of acetonitrile (0.1 M $NaClO_4$) was placed in an 3-electrode undivided electrolysis cell (porous carbon working electrode, graphite rod counter electrode and SCE reference electrode). Six cycles of anodic electrolysis at 1.2 V and consecutive cathodic electrolysis at 0.2 V were conducted with stirring until >80 % conversion to was achieved (determined by cyclic voltammetry). The solution was filtered and the electrode washed with 50 ml of acetonitrile followed by 50 mL of dichloromethane. The combined filtrate and washings were re-filtered and solvent removed *in vacuo*. The solid obtained was dissolved in the minimum of acetonitrile and diluted with 100 mL of dichloromethane to precipitate excess $NaClO_4$, filtered and solvent removed *in vacuo*.

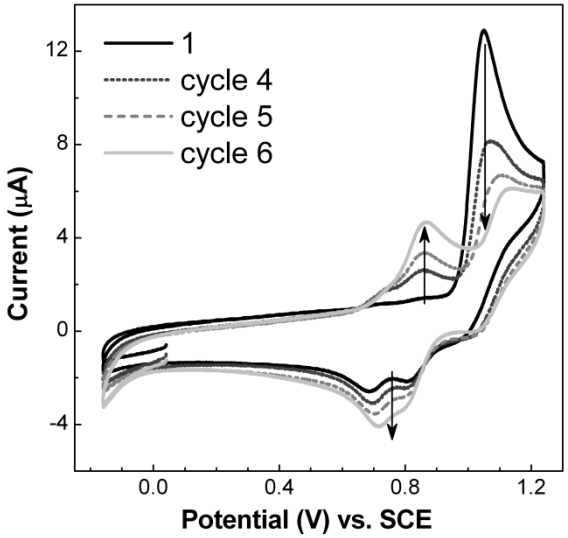


Fig. S2 Cyclic voltammetry of **1** initially and after few (4-6) cycles of electrolysis measured at glassy carbon electrode vs. SCE in the electrolysis cell in acetonitrile (0.1 M $NaClO_4$). Scan rate 0.1 V s^{-1}.

Synthesis and characterization.

General Information.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 399.93 MHz spectrometer. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, bs = broad singlet, m = multiplet), coupling constant (Hz) and integration. Mass spectra were obtained using a ThermoScientific LTQ Orbitrap XL. DCM was distilled over calcium hydride before use. All chemicals are commercially available and were purchased from Aldrich and Acros, and were used without further purifications. 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol (**4**) was synthesised following a literature procedure.[4]

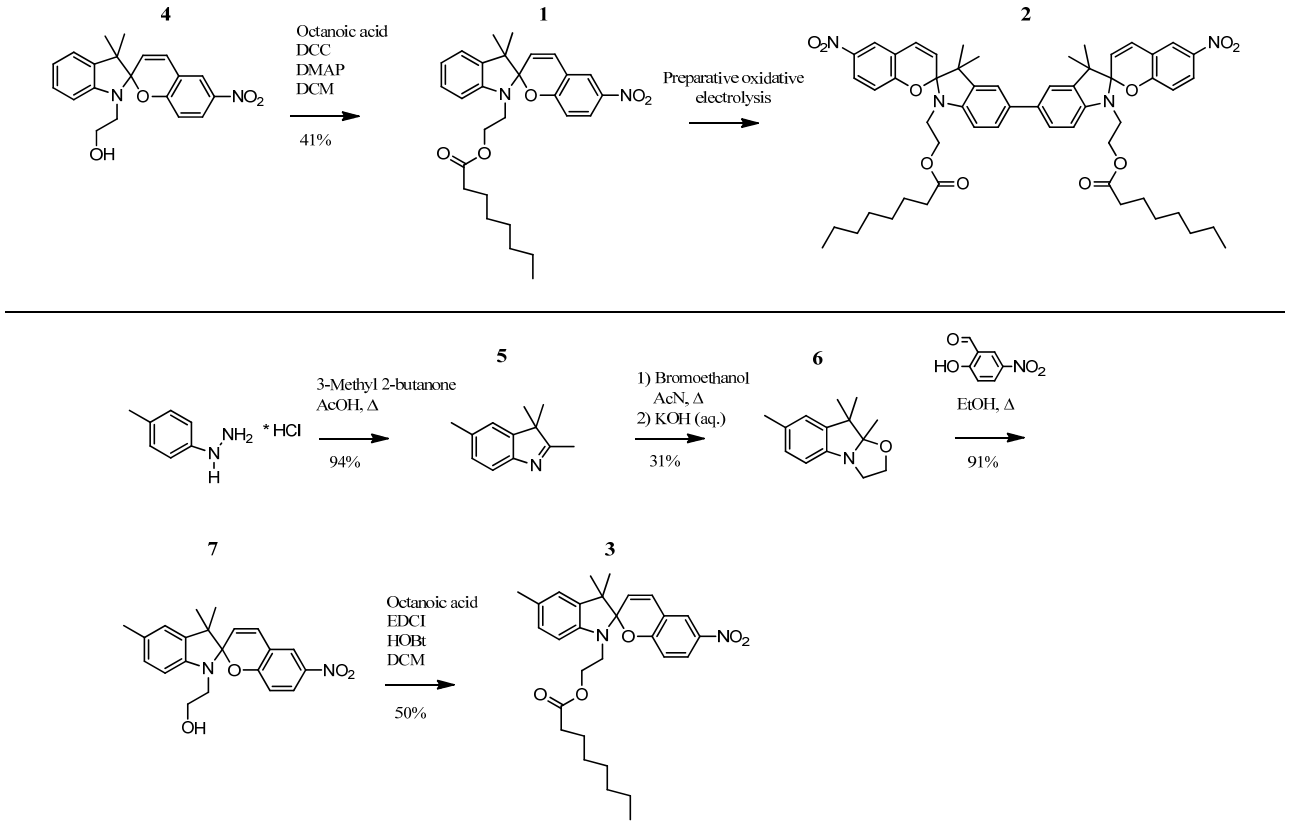


Fig. S3 Synthesis of compounds **1-7**

2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl octanoate (1)
Octanoic acid (0.19 g, 1.3 mmol), 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol (**4**) (0.38 g, 1.08 mmol) and DMAP (0.015 g, 0.12 mmol) were dissolved in 75 mL DCM at 0 ºC under argon atmosphere. A solution of *N,N'*-Dicyclohexylcarbodiimide (0.27 g 1.3 mmol) in 75 mL DCM was added over a 1 h period. The mixture was stirred and allowed to reach room temperature overnight. DCM was removed *in vacuo*. Purification of the crude product by column chromatography over silica gel, using pentane and an increasing gradient of DCM as eluent yielded the product as a yellow solid. (0.21 g, 41%). ^{1}H-NMR ($CDCl_3$): δ 0.86 (m, *J = 6.8 Hz,* 3H), 1.14 (s, 3H), 1.17-1.30 (br, 8H), 1.27 (s, 3H), 1.53 (m, 2H), 2.22 (t, *J = 6.8 Hz,* 2H), 3.38 (m, 1H), 3.45 (m, 1H), 4.16 (m, 1H), 4.22 (m, 1H), 5.87 (d, *J = 10.3 Hz,* 1H), 6.66 (d, *J = 8.4 Hz,* 1H), 6.72 (d, *J = 7.8 Hz,* 1H), 6.87 (m, 2H), 7.06 (d, *J = 7.3 Hz,* 1H), 7.19 (t, 1H), 7.98 (s, 1H), 8.00 (d, *J = 7.3 Hz,* 1H). ^{13}C NMR ($CDCl_3$): δ 14.2, 20.0, 22.7, 25.0, 26.0, 29.0, 29.2, 31.8, 34.3, 42.6, 53.0, 62.4, 106.6, 106.9, 115.7, 118.6, 120.1, 121.95, 121.97, 122.9, 126.1, 128.0, 128.4, 135.8, 141.2, 146.8, 159.6, 173.8. ESI-MS *m/z* 479.25413 $[M+H]^+$ Calcd for $C_{28}H_{35}N_2O_5$: 479.25405 mp: 93.8-96.2°C Anal. Calcd for $C_{40}H_{43}N_3O_6S_2$: C, 70.27; H, 7.16; N, 5.85. Found: C, 70.17; H, 7.18; N, 5.88.

2,3,3,5-tetramethyl-3H-indole (5)
Compound **6** was synthesised using an adapted literature procedure.[5] *p*-Tolylhydrazine*HCl (4.0 g, 25.2 mmol) and 3-methyl-2-butanone (5.6 g, 57.0 mmol) were dissolved in 40 mL acetic acid and the mixture heated at reflux for 3 h. The cooled mixture was diluted with 100 mL water and

brought to neutral pH with NaOH (aq). The aqueous layer was extracted with DCM (3x 50 mL) and the combined organic layers were dried on Na_2SO_4. DCM was removed *in vacuo* and the residue was purified by column chromatography over silica gel, using toluene/ethyl acetate 10:1 as eluent, giving the product as a red liquid in 94% yield. (4.1 g, 23.6 mmol). ^{1}H-NMR ($CDCl_3$): δ 1.29 (s, 3H), 2.27 (s, 3H), 2.39 (s, 3H), 7.08 (s, 1H), 7.10 (d, *J = 7.7 Hz,* 1H), 7.42 (d, *J = 7.7 Hz,* 1H). ^{13}C NMR ($CDCl_3$): δ 187.3, 145.8, 135.1, 128.3, 122.3, 119.5, 53.5, 23.3, 21.6, 15.4. ESI-MS *m/z* 174.1277 $[M+H]^+$ Calcd for $C_{12}H_{16}N$: 174.1277

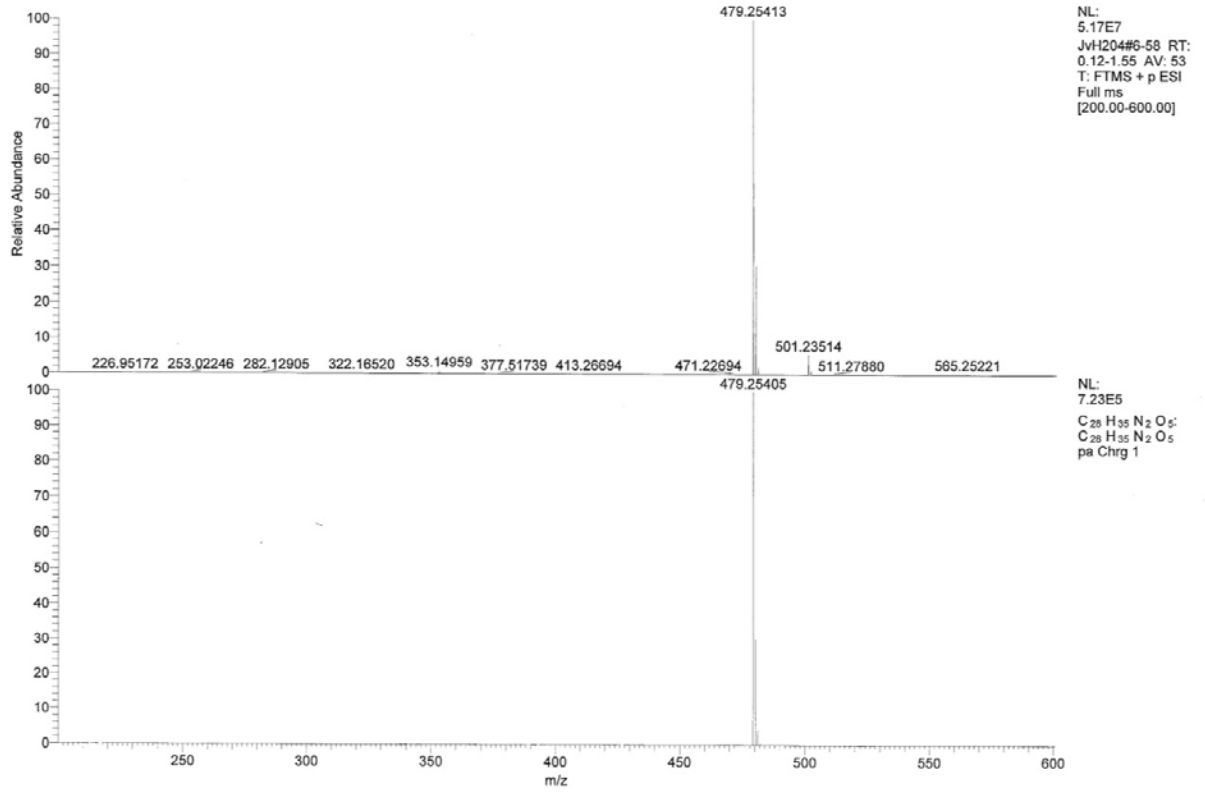
7,9,9,9a-tetramethyl-2,3,9,9a-tetrahydrooxazolo[3,2-a]indole (6)
Compound **6** (4.1 g, 23.6 mmol) and bromoethanol (3.25 g, 26.0 mmol) were dissolved in 40 mL acetonitrile and the mixture heated at reflux for 3 h. The solvent was removed *in vacuo* and 40 mL pentane was added to the residue. After 5 min sonication the product was cooled to -10 °C and the pentane was removed by decantation. The resulting red viscous liquid was added to 100 mL KOH aq. (1 M) and stirred for 1 h. The aqueous layer was extracted with diethyl ether (3x 30 mL) and the combined organic layers were dried on $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by column chromatography over silica gel, using pet. ether 40-60/diethyl ether 5:1 as eluent, giving the product as an orange solid in 31% yield. (1.6 g, 7.4 mmol). ^{1}H-NMR ($CDCl_3$): δ 6.93 (d, *J* = 7.9 *Hz*, 1H), 6.89 (s, 1H), 6.66 (d, *J* = 7.9 *Hz*, 1H), 3.91-3.42 (m, 4H), 2.30 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H), 1.17 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 148.3, 140.2, 131.2, 128.1, 123.3, 111.9, 109.4, 63.1, 50.4, 47.1, 28.2, 21.1, 20.9, 17.7. ESI-MS *m/z* 218.1539 $[M+H]^+$ Calcd for $C_{14}H_{20}NO$: 218.1539

2-(3',3',5'-trimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol (7)
Compound **7** (1.5 g, 6.9 mmol) and 2-hydroxy-5-nitrobenzaldehyde (1.33 g, 8.0 mmol) were dissolved in 40 mL ethanol and refluxed for 3 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography over silica gel, using diethyl ether/ethanol 10:1 as eluent, giving the product as a purple solid in 91% yield. (2.3 g, 6.3 mmol). ^{1}H-NMR ($CDCl_3$): δ 8.02 (d, *J* = 2.7 *Hz*, 1H), 7.98 (s, 1H), 6.99 (d, *J* = 7.9 *Hz*, 1H), 6.92 (s, 1H), 6.90 (d, *J* = 10.8 *Hz*, 1H), 6.75 (d, *J* = 8.5 *Hz*, 1H), 6.57 (d, *J* = 7.9 *Hz*, 1H), 5.88 (d, *J* = 10.4 *Hz*, 1H), 3.88-3.64 (m, 2H), 3.55-3.21 (m, 2H), 2.33 (s, 3H), 2.25-1.90 (bs, 1H), 1.28 (s, 3H), 1.19 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 159.5, 145.0, 141.2, 136.1, 129.5, 128.3, 128.2, 126.0, 122.9, 122.1, 118.7, 115.6, 107.1, 106.8, 77.6, 77.2, 76.7, 61.0, 52.9, 46.4, 26.1, 21.0, 20.1. ESI-MS *m/z* 367.1651 $[M+H]^+$ Calcd for $C_{21}H_{23}N_2O_4$: 367.1652.

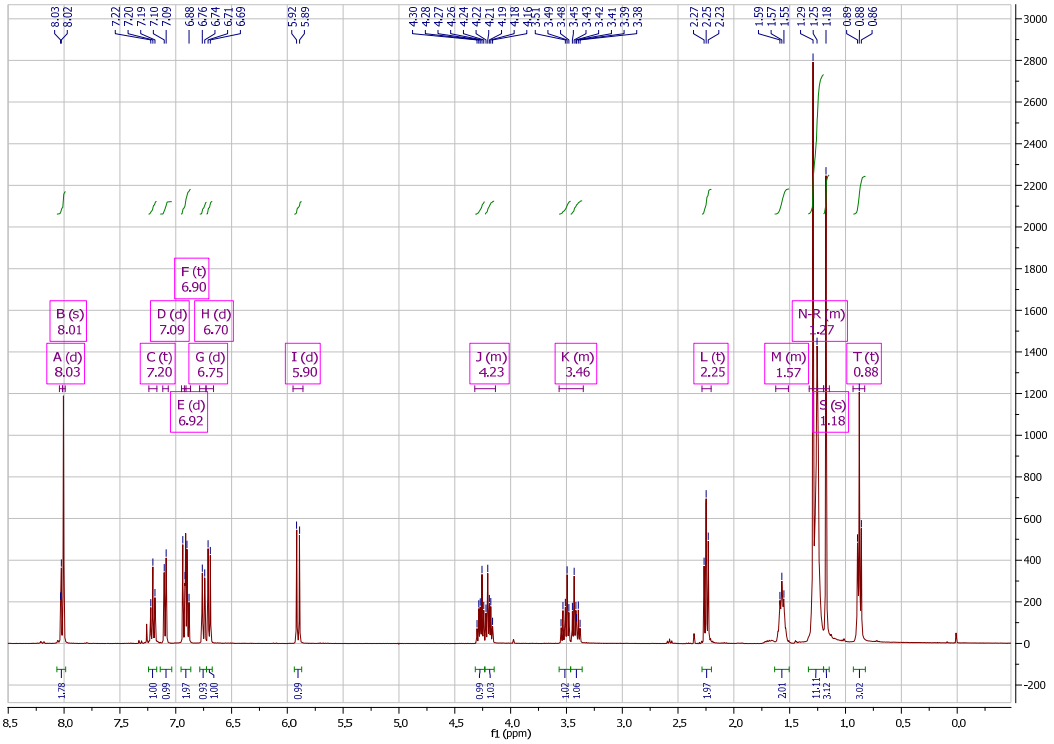
2-(3',3',5'-trimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl octanoate (3)
Compound **8** (1.06 g, 2.89 mmol), HOBt (0.41 g, 3.0 mmol), EDCI (0.58 g, 3.0 mmol) and octanoic acid (0.43 g, 3.0 mmol) were dissolved in 40 mL dichloromethane and stirred overnight at rt. The solution was washed with 3x10 mL 1M $NaHCO_3$ (aq.), 3 x 10 mL water and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was purified by column chromatography over silica gel, using toluene/pentane 3:1 as eluent, giving the product as a yellow solid in 50% yield. (0.71 g, 1.44 mmol). ^{1}H-NMR ($CDCl_3$): δ 8.03 (d, *J* = 2.7 *Hz*, 1H), 8.00 (s, 1H), 7.00 (d, *J* = 7.9 *Hz*, 1H), 6.92 (s, 1H), 6.90 (d, *J* = 8.0 *Hz*, 1H), 6.75 (d, *J* = 8.5 *Hz*, 1H), 6.59 (d, *J* = 7.9 *Hz*, 1H), 5.89 (d, *J* = 10.4 *Hz*, 1H), 4.37-4.06 (m, 2H), 3.62-3.22 (m, 2H), 2.33 (s, 3H), 2.24 (t, *J* = 7.5 *Hz*, 2H), 1.68-1.45 (m, 2H), 1.37-1.21 (m, 8H), 1.27 (s, 3H), 1.16 (s, 3H), 0.87 (t, *J* = 6.7, 3H). ^{13}C NMR ($CDCl_3$): δ 173.7, 159.6, 144.7, 141.2, 135.9, 129.3, 128.3, 128.2, 126.0, 122.8, 122.8, 122.0, 118.6, 115.6, 106.9, 106.7, 62.4, 53.0, 42.7, 34.3, 31.7, 29.2,

29.0, 26.0, 25.0, 22.7, 21.1, 20.0, 14.1. ESI-MS *m/z* 493.2698 $[M+H]^+$ Calcd for $C_{29}H_{37}N_2O_5$: 493.2697 mp:98.9-99.2°C Anal. Calcd for $C_{40}H_{43}N_3O_6S_2$: C, 70.71; H, 7.37; N, 5.69. Found: C, 70.75; H, 7.38; N, 5.68.

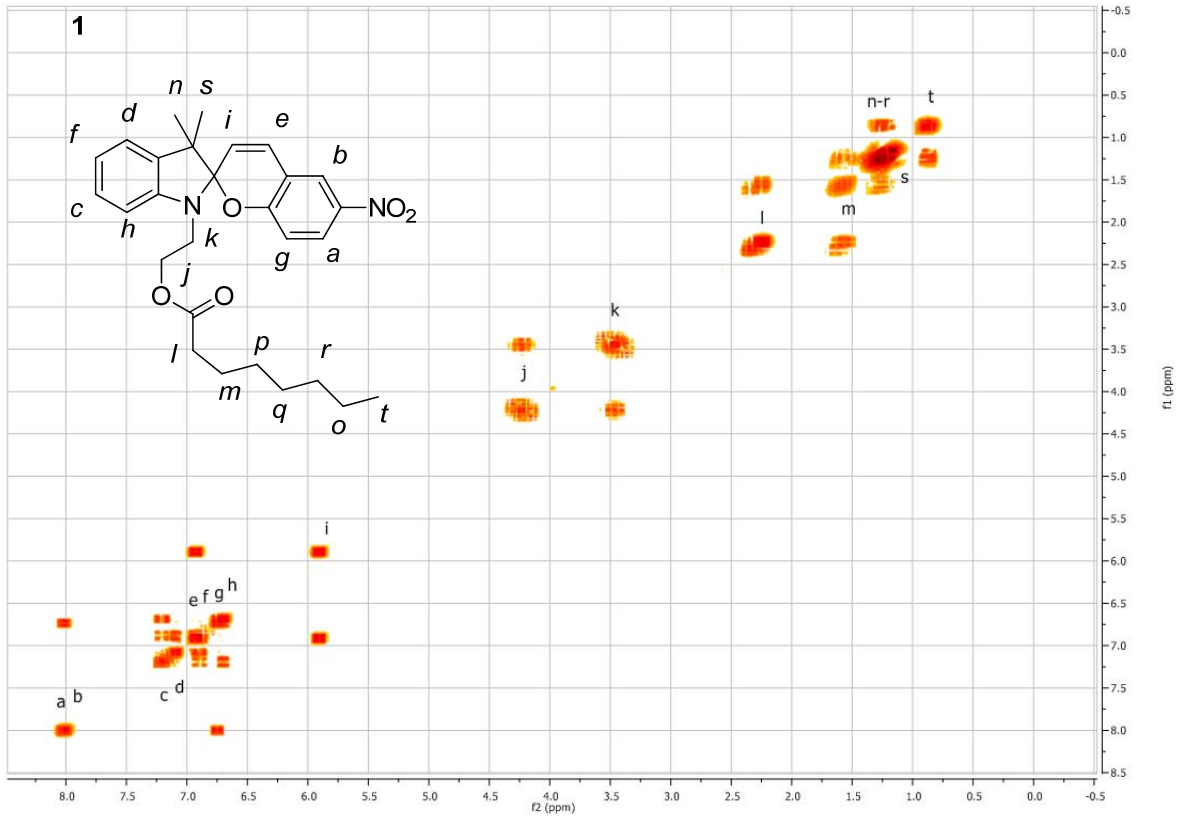
ESI-Mass spectrogram of **1**:



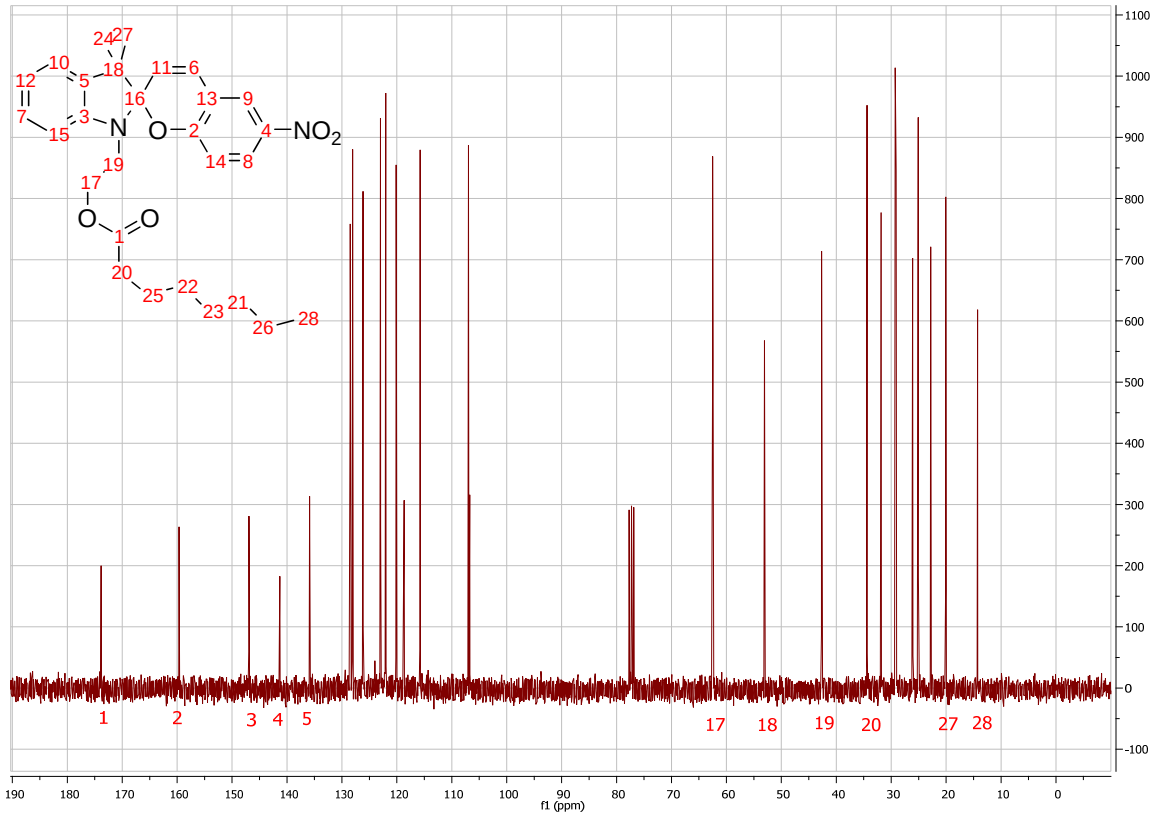
^{1}H NMR spectrum of **1** in $CDCl_3$:

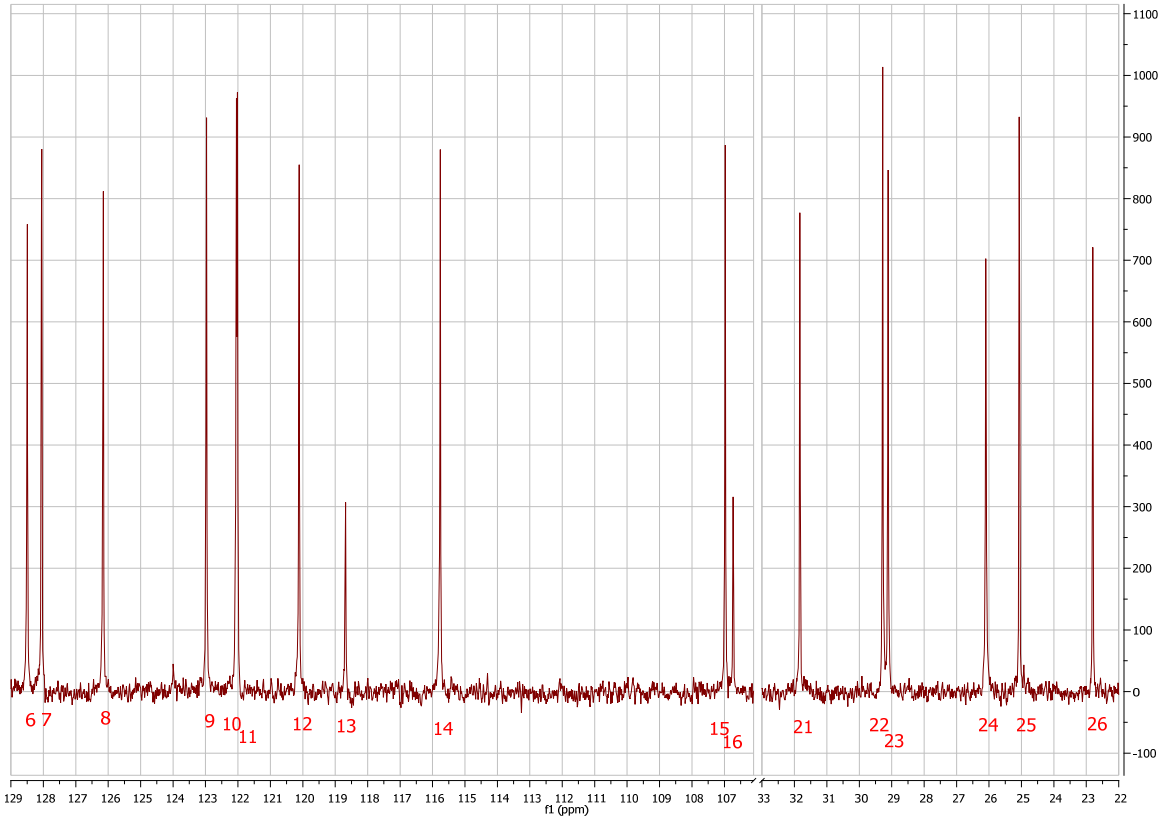


^{1}H COSY-NMR spectrum of **1** in $CDCl_3$:



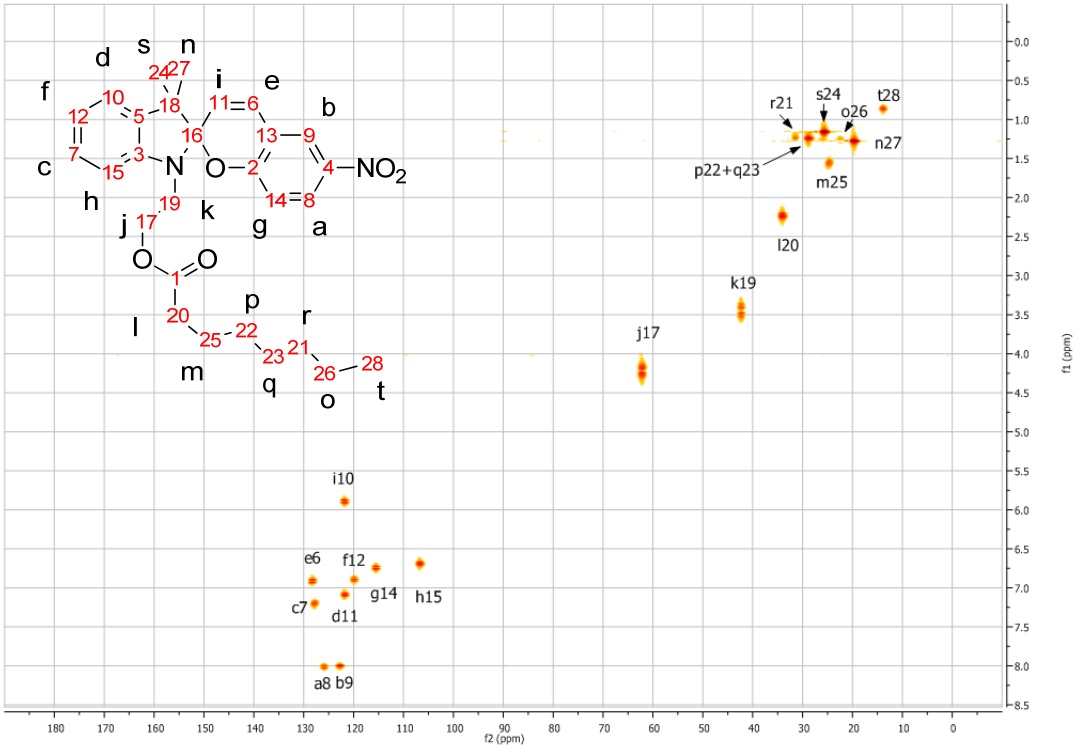
^{13}C NMR spectrum of **1** in $CDCl_3$:



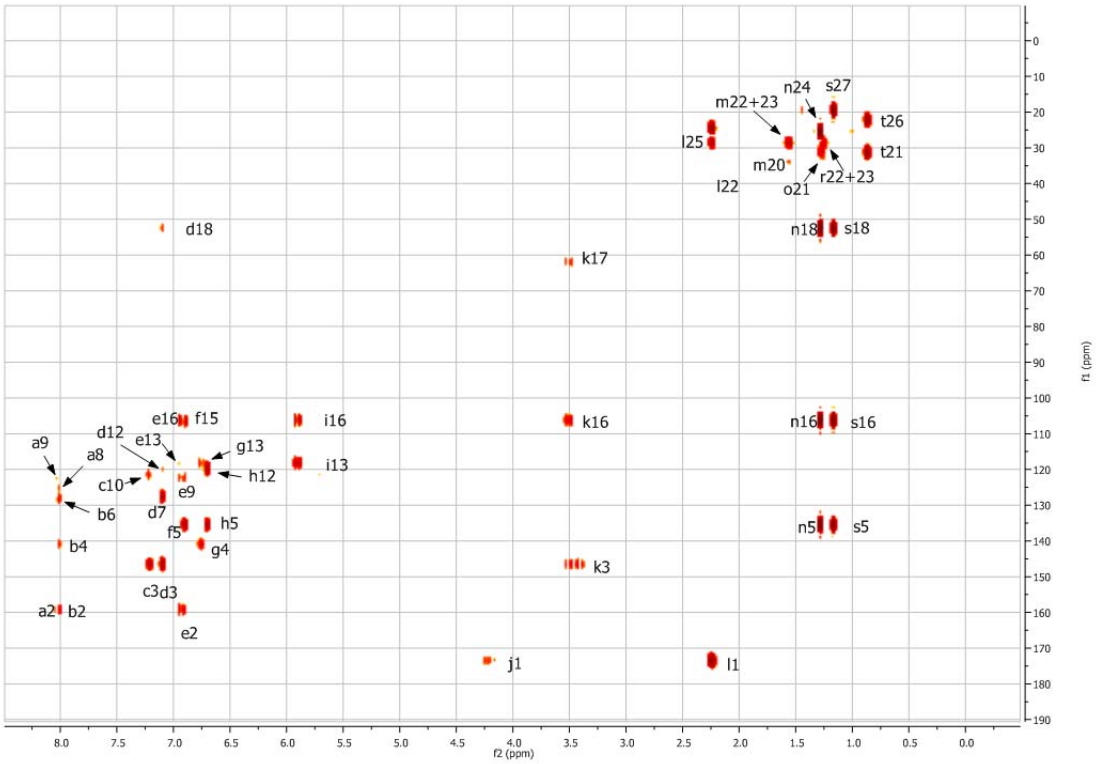


Additional HSQC and HMBC experiments were performed to correctly assign all the signals in the proton spectra:

HSQC of **1** in $CDCl_3$:

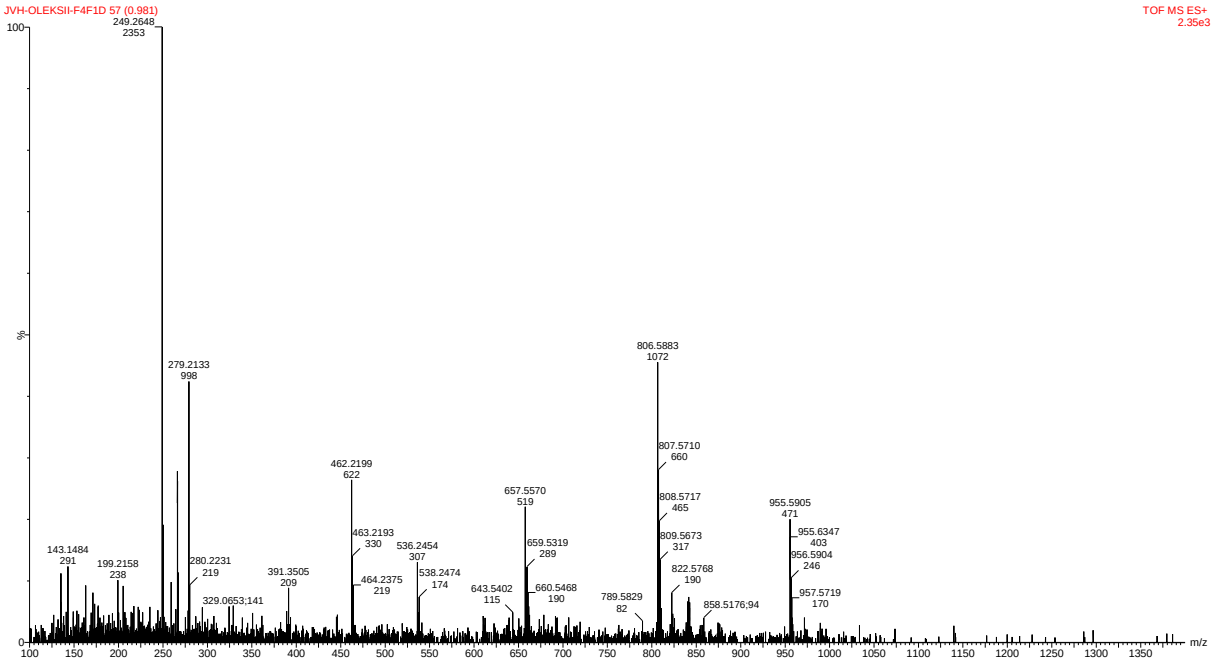


HMBC spectrum of **1**:

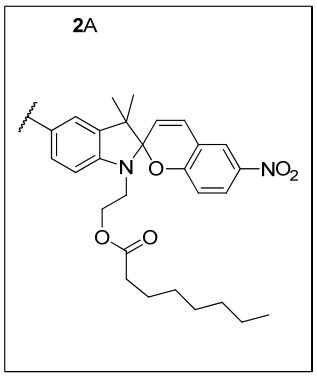


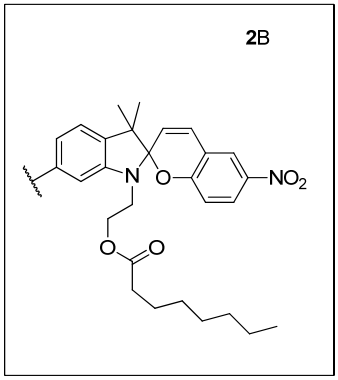
Product obtained after preparative oxidative electrolysis:
Purification by column chromatography over SiO_2 (pentane+20% diethyl ether) yielded two distinct fractions,
1 (starting material) (Rf=0.5) and **2** (Rf =0.1) in a ratio 5:4

The mass of **2** (positive mode) is 955.5905 [2M-1], which suggests dimerization.



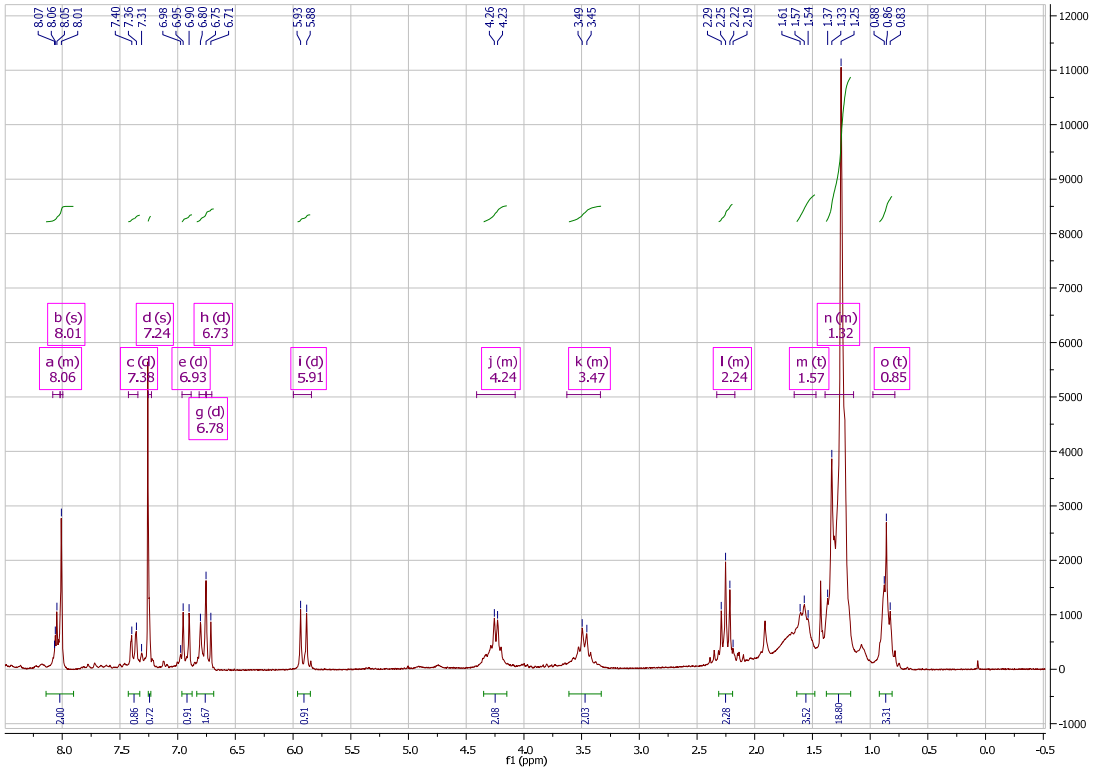
2 has a similar ^{1}H-NMR compared to **1** but lacks one signal in the aromatic region, indicating symmetric dimerization through a phenyl-phenyl bond. ^{1}H and ^{1}H COSY NMR show two doublets and a singlet in the indoline aromatic ring, allowing two different structures (**2**A and **2**B).



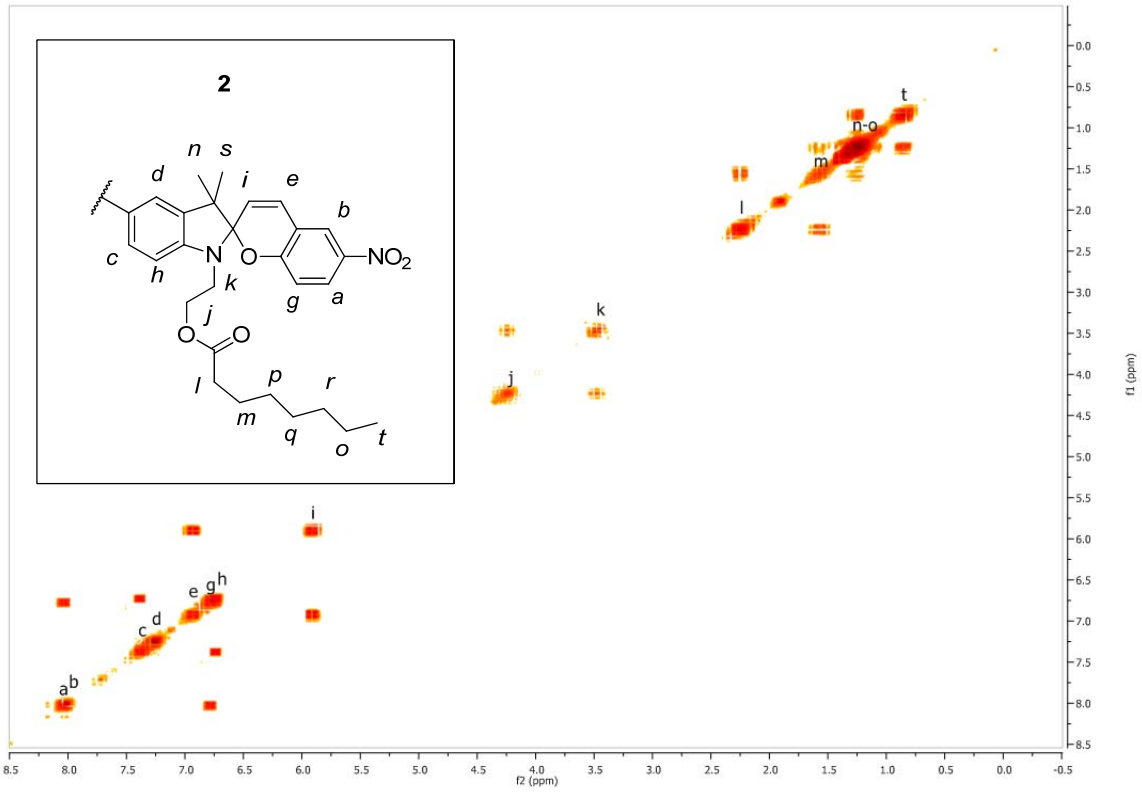


Comparison of the new ^{1}H NMR spectra with the original shows that signal f has disappeared, both in the ^{1}H NMR spectrum, and in the interaction with signal d in the COSY spectrum. Signals c,d and h have remained at their correct position with respect to their *meta*- and *ortho*-orientation with respect to the nitrogen. Therefore structure **2**A can be assigned as the correct one, which is the expected position for oxidative coupling.

^{1}H NMR spectrum of **2** in $CDCl_3$:



^{1}H COSY NMR spectrum of **2** in $CDCl_3$:



FTIR and Raman Spectroscopy

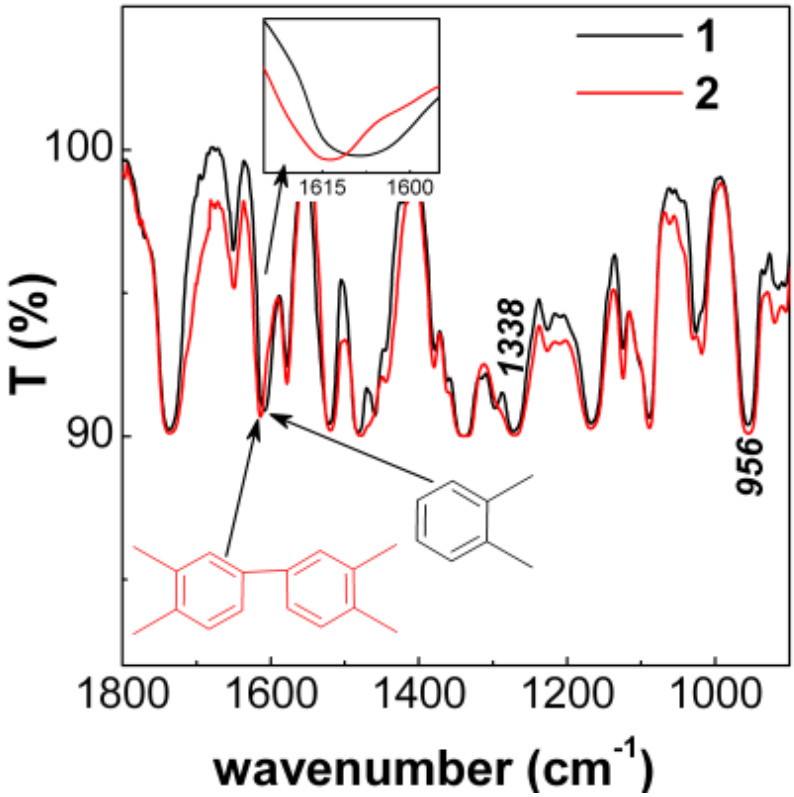


Fig S4 ATR FTIR spectra of **1** (black line) and **2** (red line). The small shift in the aromatic C=C stretching band as an inset.

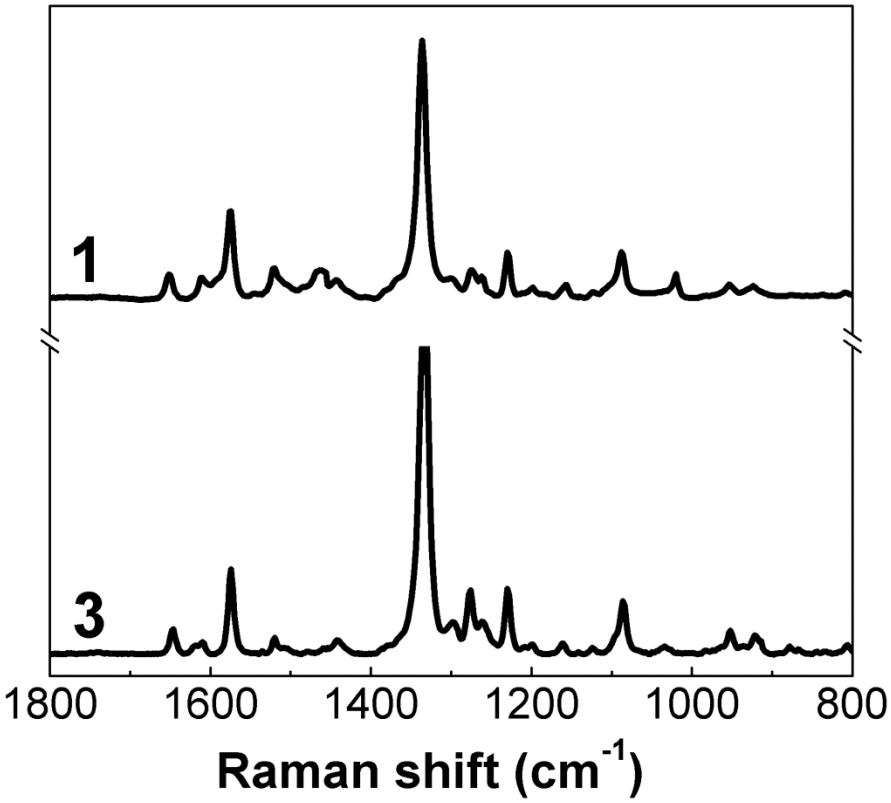


Fig. S5 Solid state Raman spectra of **1** and **3**, recorded at λ_{exc} 785 nm.

UV/Vis absorption Spectroelectrochemistry of 3

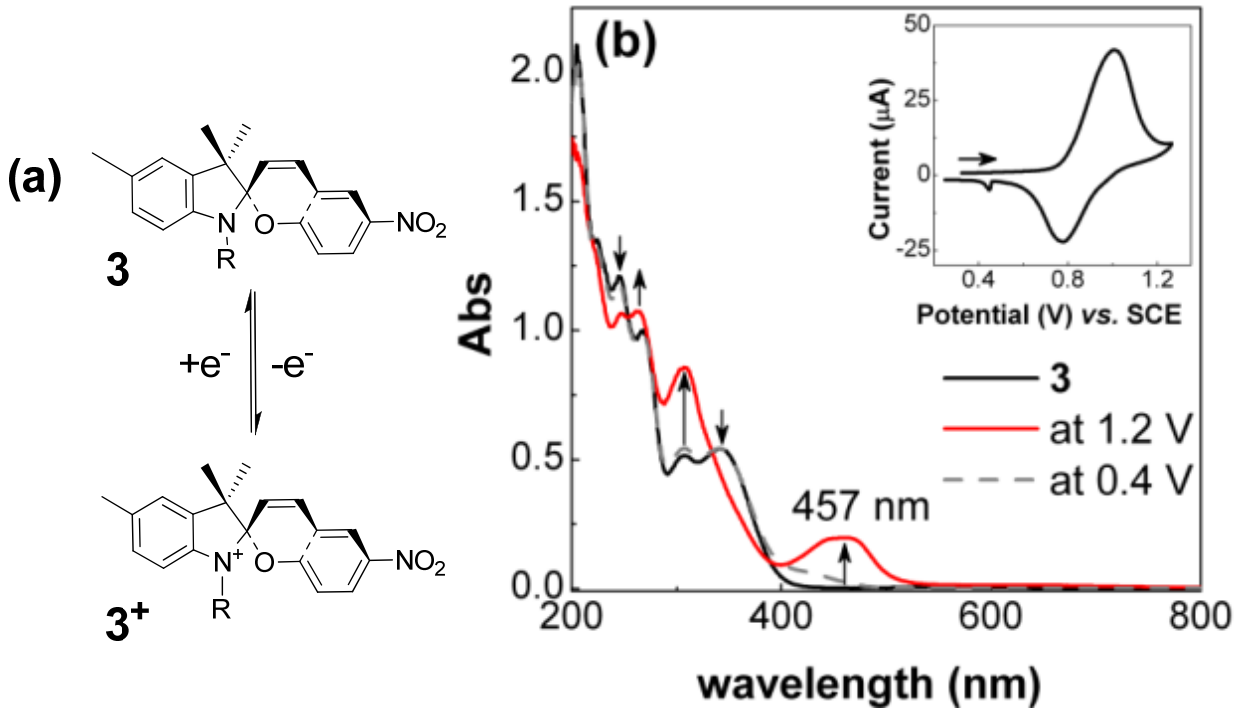
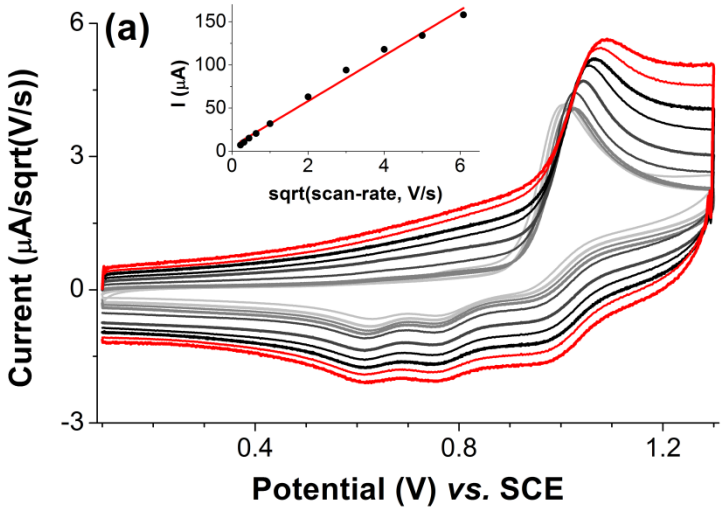


Fig. S6 (a) Reversible oxidation of methyl-nitro-spiropyran **3**. R = -C_2H_4-OC(=O)-C_7H_{15}. (b) UV/vis absorption spectra of **3** recorded upon oxidation in acetonitrile (0.1 M $TBAPF_6$) at a scan rate 0.05 V s^{-1}. Upon reduction **3** is recovered. Partial photochemical conversion to the MC form occurs during spectra acquisition, manifested in the absorption at *ca.* 430 nm.

Scan rate dependent and concentration dependent cyclic voltammetry of 1



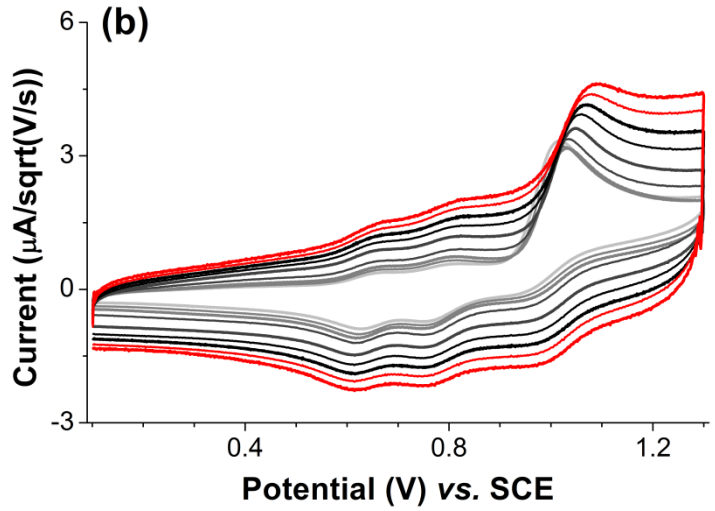


Fig. S7 Scan-rate dependent cyclic voltammetry of **1** measured in CH_3CN (0.1 M $TBAPF_6$) at GCE at 0.05 V s^{-1} – 36 V s^{-1}. First (a) and the second (b) cycles of CV show linear dependence of initial oxidation current at *ca.* 1 V on sqrt of scan-rate, plotted in the inset.

The cyclic voltammetry of **1** obeys the sqrt dependence on scan rate of a diffusion controlled process and when normalized. The shift in the $E_{p,a}$ is consistant with an irrerversible oxidation and at high scan rates some reversibility in the oxidation of the spiropyran is observed.

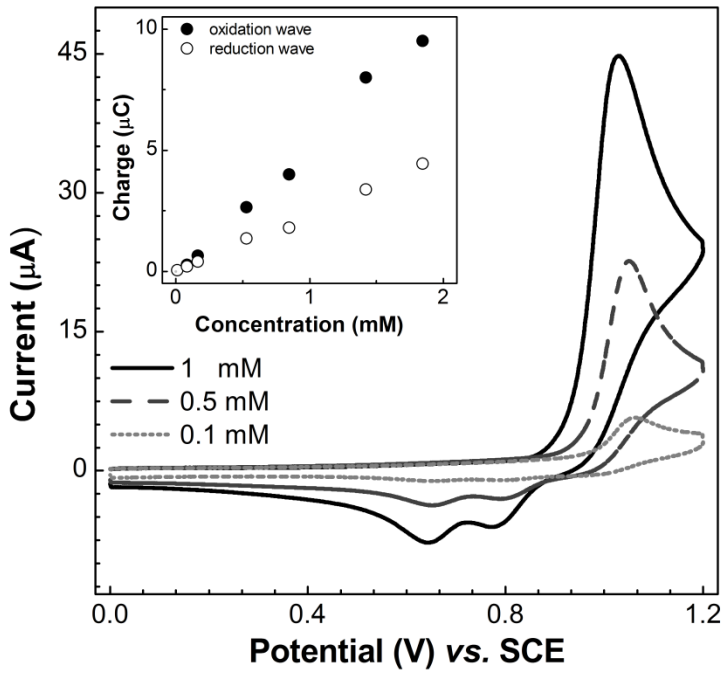


Fig. S8 Concentration dependent cyclic voltammetry of **1** measured in CH_3CN (0.1 M $TBAPF_6$) at GCE at 0.2 V s^{-1}. The charge transferred during the oxidation at 1 V is roughly twice that transferred in the two reduction steps, which is consistent with an initial one-electron oxidation of two spiropyrans (-2e^-), dimerization and deprotonation to yield a neutral dimer and immediate

reoxidation of the dimer at the same potential (-2e$^-$) and final two step reduction (+e$^-$ and +e$^-$), thus -4e$^-$/+2e$^-$.

1 M. J. Preigh, M. T. Stauffer, F.-T. Lin and S. G. Weber, *Faraday Trans.*, 1996, **92**, 3991.
2 A. Doménech, H. García, I. Casades and M. Esplá, *J. Phys. Chem. B*, 2004, **108**, 20064.
3 K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G. G. Wallace and D. L. Officer, *J. Am. Chem. Soc.*, 2011, **133**, 5453.
4 S. J. Lee, S. H. Jung, S.-H. Lee, W. S. Han and J. H. Jung, *J. Nanosci. Nanotech.*, 2009, **9**, 5990.
5 S. Sajjadifar, H. Vahedi, A. Massoudi and O. Louie, *Molecules*, 2010, **15**, 2491.