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Supporting information

Systematic variation of thiophene substituents in photochromic spiropyrans

Dushanthi S. Dissanayake, Gregory T. McCandless, Mihaela C. Stefan, and Michael C. Biewer*

Department of Chemistry and Biochemistry, University of Texas at Dallas, 800 West Campbell Road, Richardson, Tx-75080; E-mail: biewerm@utdallas.edu

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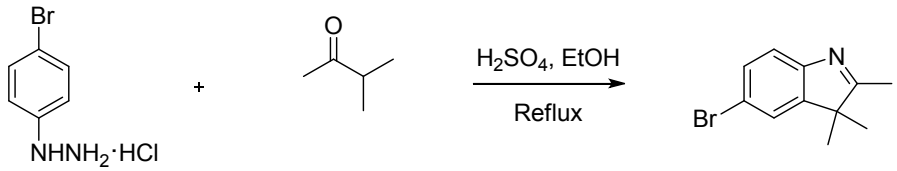
Synthesis of 5-bromo-2,3,3-trimethyl-3*H*-indole[1]



Scheme S1: Synthesis of 5-bromo-2,3,3-trimethyl-3*H*-indole

Synthesis of 5-bromo-2,3,3-trimethyl-3H-indole (1)– A solution of 4-bromophenyl hydrazine (1.0 g, 4.5 mmol), isopropylmethylketone (0.81 g, 9.3 mmol), ethanol (100 mL), and concentrated H_2SO_4 (0.44 g, 4.5 mmol) in a 250 mL round bottomed flask equipped with a reflux condenser was heated under reflux for 12 h. After cooling down to room temperature, the mixture was quenched in 10 % $NaHCO_3$, extracted with ether, washed with deionized water, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to obtain the crude product as a reddish oil (1.0 g, 96 %) which was used in the next step without further purifications. ^{1}H-NMR ($CDCl_3$, 500 MHz; 7.42(m, 3H), 2.27(s, 3H), 1.30(s, 6H). ^{13}C-NMR ($CDCl_3$, 500 MHz; 188.57, 152.47, 147.76, 130.70, 124.88, 121.24, 118.94, 54.14, 30.33, 22.94, 15.41).

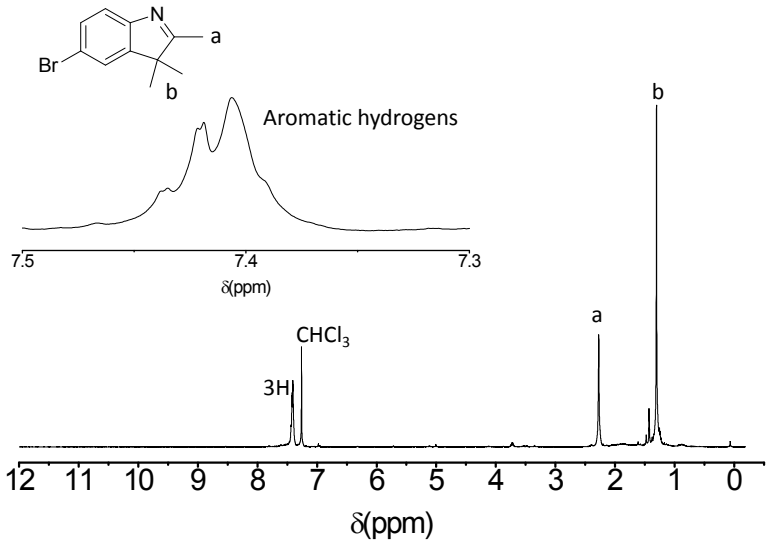


Figure S1: ^{1}H-NMR spectrum of 5-bromo-2,3,3-trimethyl-3*H*-indole

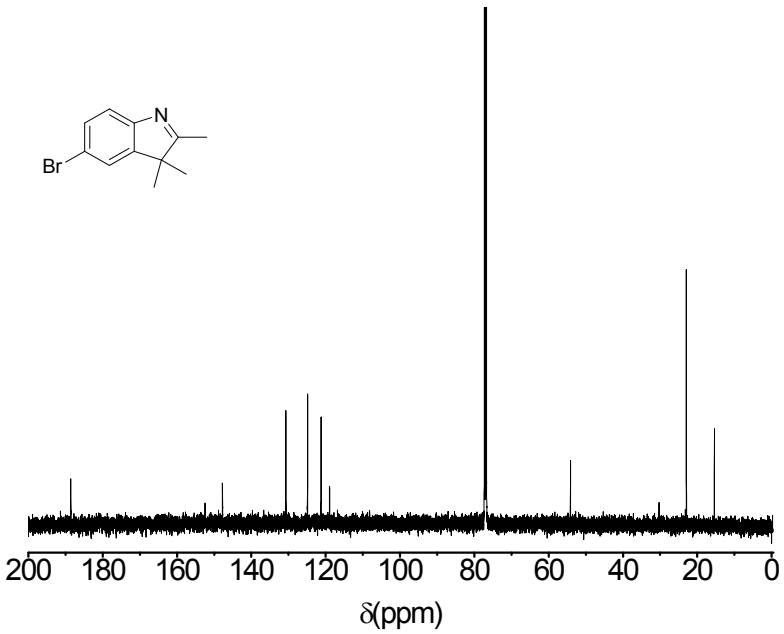


Figure S2: ^{13}C-NMR spectrum of 5-bromo-2,3,3-trimethyl-3*H*-indole

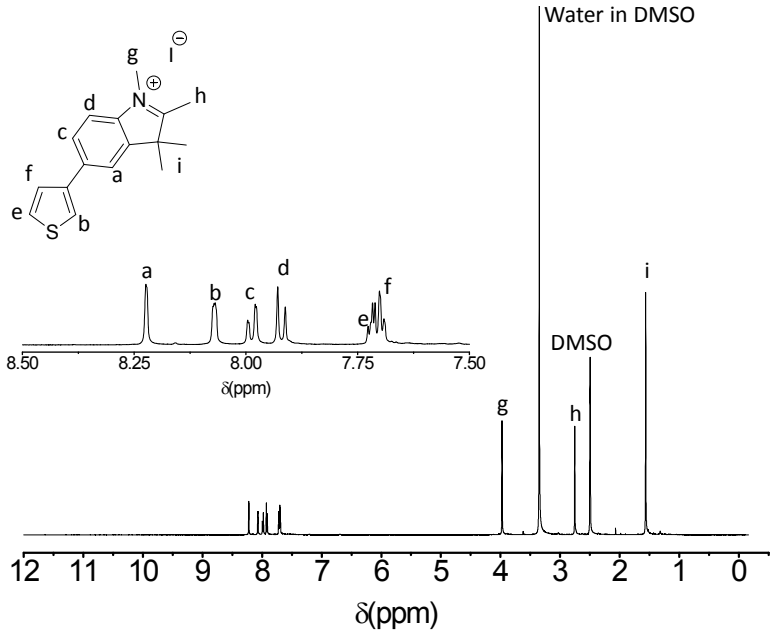


Figure S3: ^{1}H-NMR spectrum of 1,2,3,3-tetramethyl-5-(thiophene-3-yl)-3*H*-indol-1-ium iodide

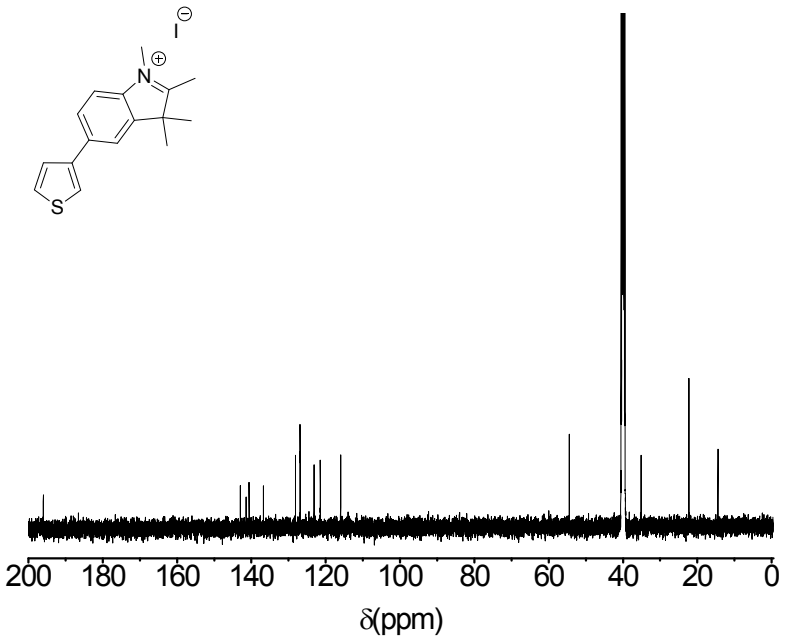


Figure S4: ^{13}C-NMR spectrum of 1,2,3,3-tetramethyl-5-(thiophene-3-yl)-3*H*-indol-1-ium iodide

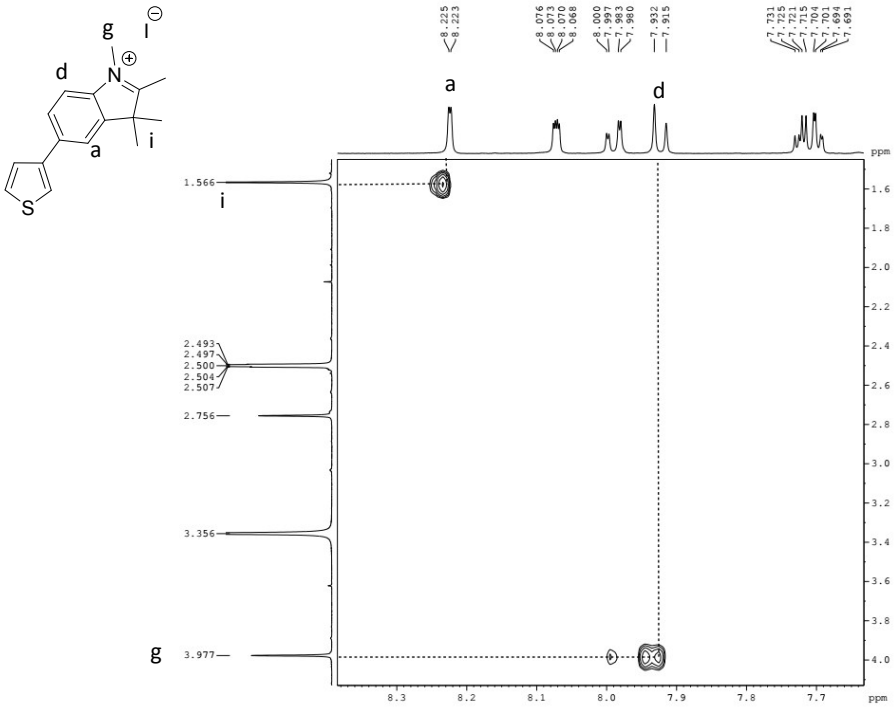


Figure S5: Expanded ^{1}H-^{1}H NOESY spectrum of 1,2,3,3-tetramethyl-5-(thiophene-3-yl)-3*H*-indol-1-ium iodide

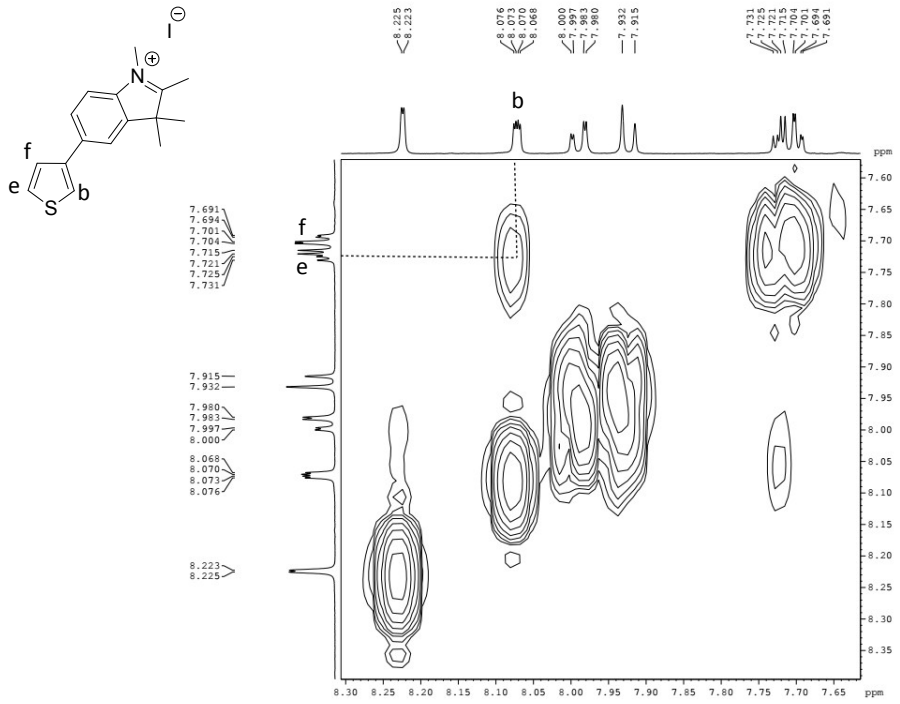


Figure S6: Expanded ^{1}H-^{1}H COSY spectrum of 1,2,3,3-tetramethyl-5-(thiophene-3-yl)-3*H*-indol-1-ium iodide

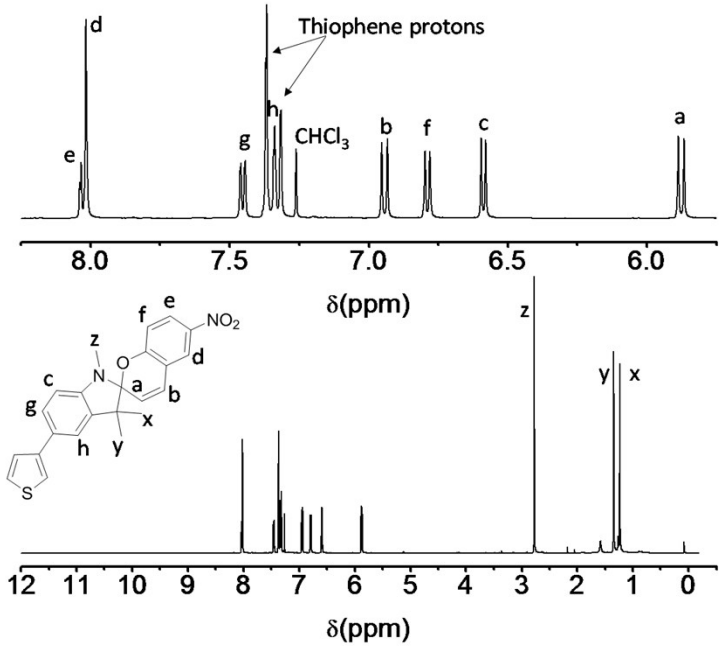


Figure S7: ^{1}H-NMR spectrum of 1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline]; peak assignment is based on 2D-NMR analysis.

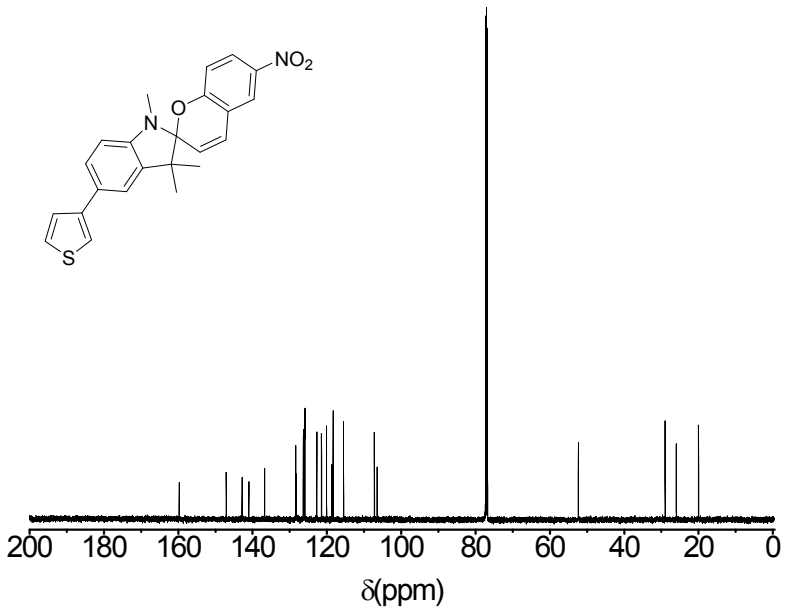


Figure S8: ^{13}C-NMR spectrum of 1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline]

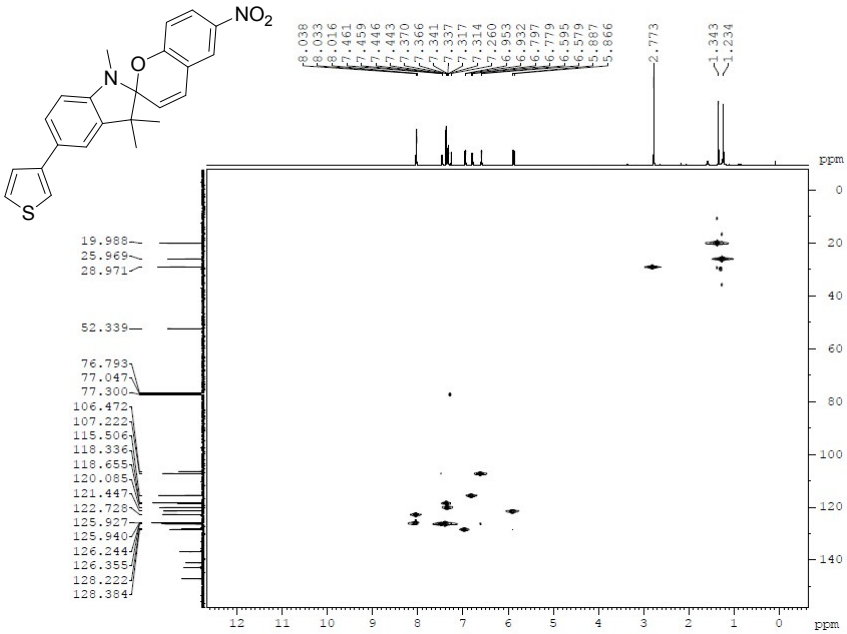


Figure S9: 2D-HSQC spectrum of 1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline]

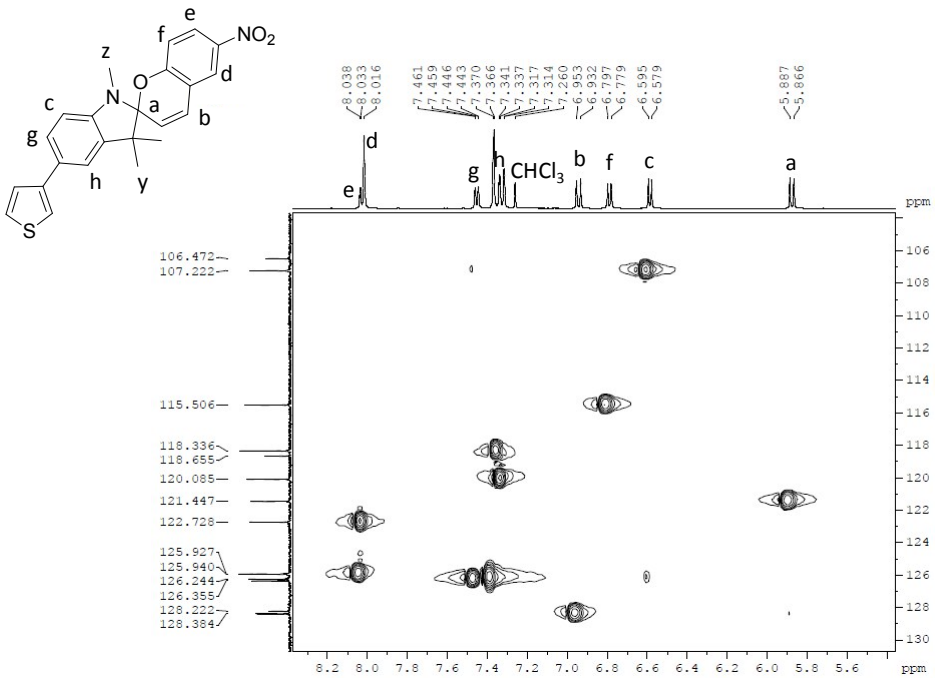


Figure S10: Expanded 2D-HSQC spectrum of 1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline]

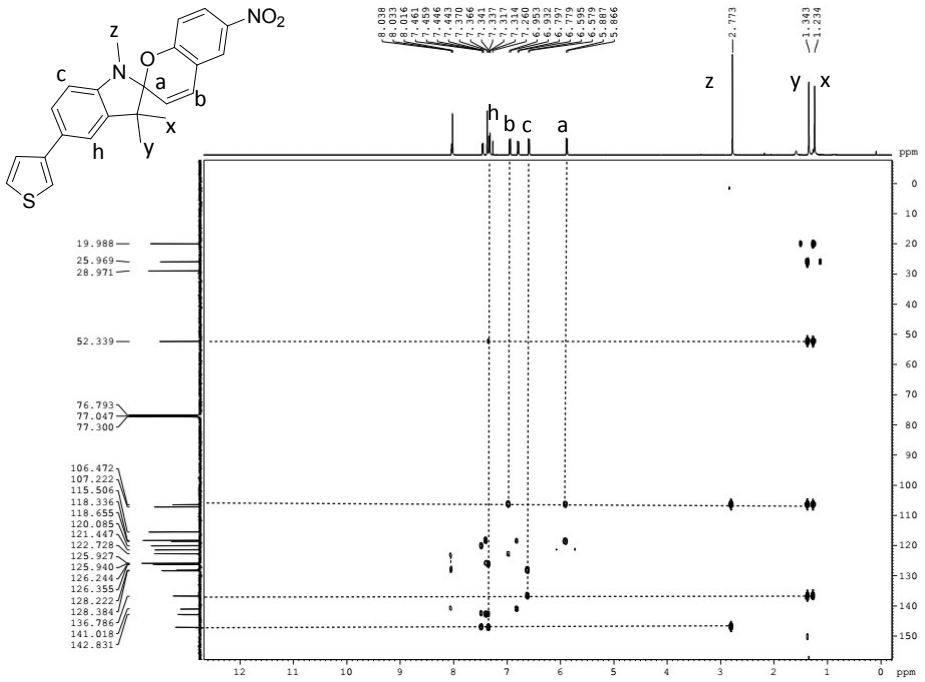


Figure S11: 2D-HMBC spectrum of 1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline]

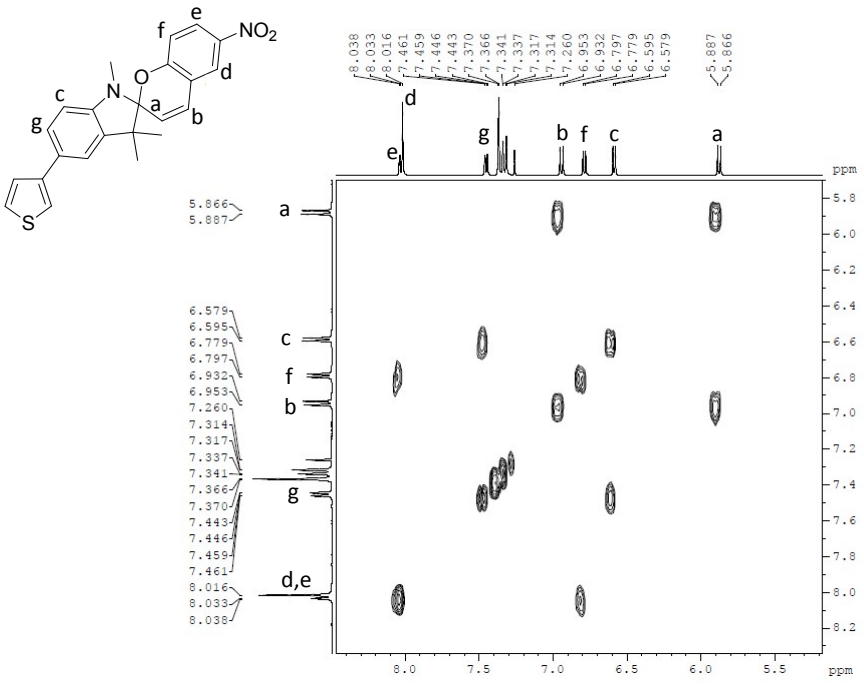


Figure S12: Expanded ^{1}H-^{1}H COSY spectrum of 1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline]

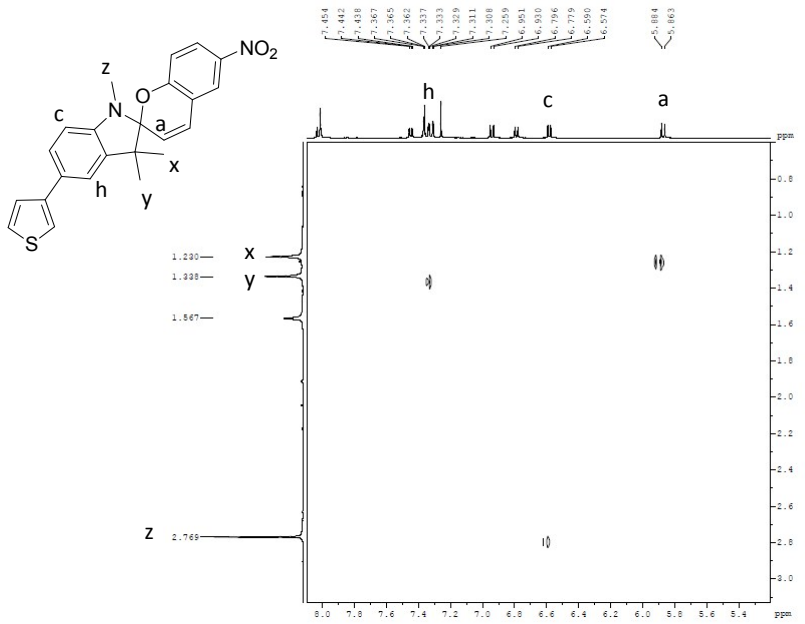


Figure S13: Expanded ^{1}H-^{1}H NOESY spectrum of 1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline]

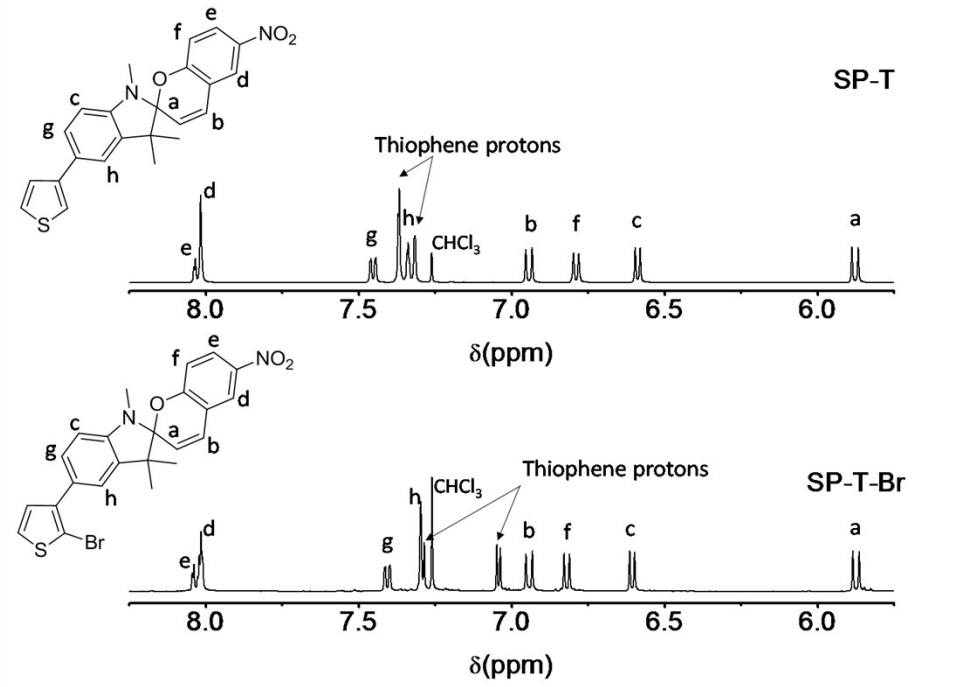


Figure S14: [1]H-NMR spectrum of 5'-(2-bromothiophen-3-yl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] in comparison with 1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline] in downfield region

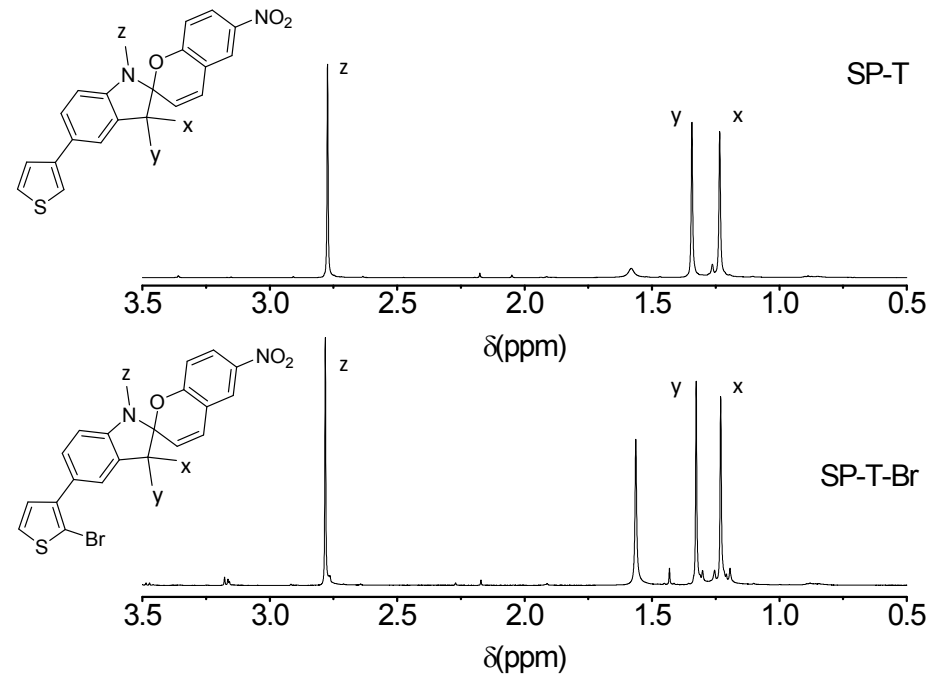


Figure S15: [1]H-NMR spectrum of 5'-(2-bromothiophen-3-yl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] in comparison with 1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline] in upfield region

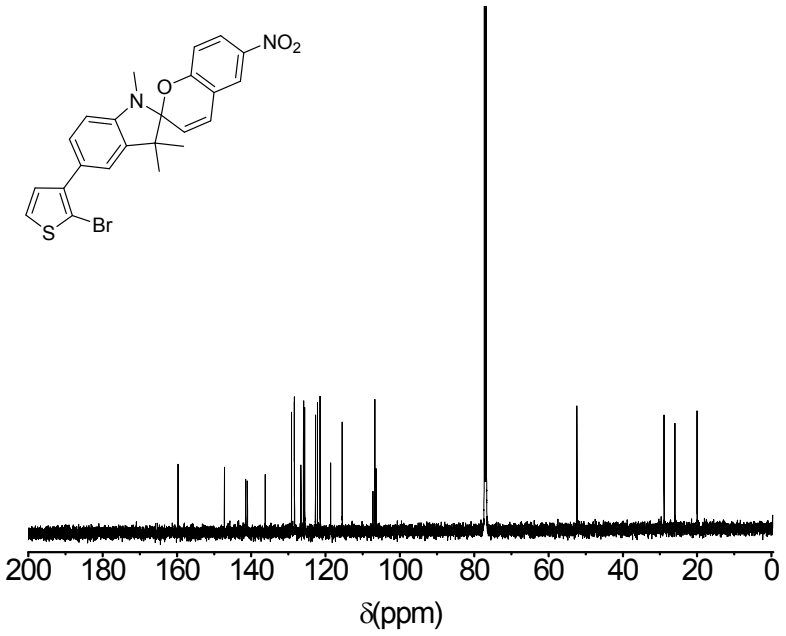


Figure S16: ^{13}C-NMR spectrum of 5'-(2-bromothiophen-3-yl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]

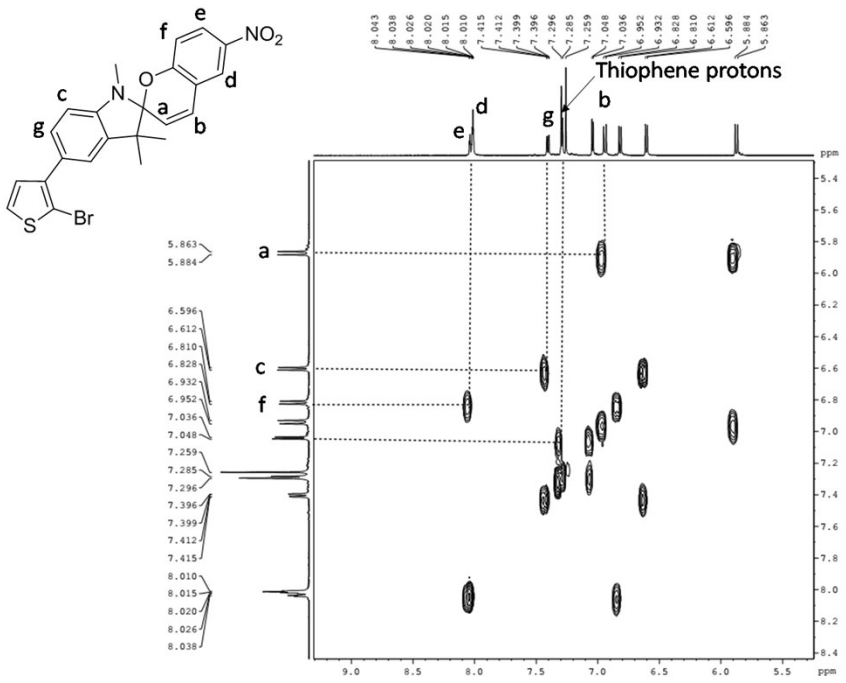


Figure S17: Expanded ^{1}H-^{1}H COSY spectrum of 5'-(2-bromothiophen-3-yl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]

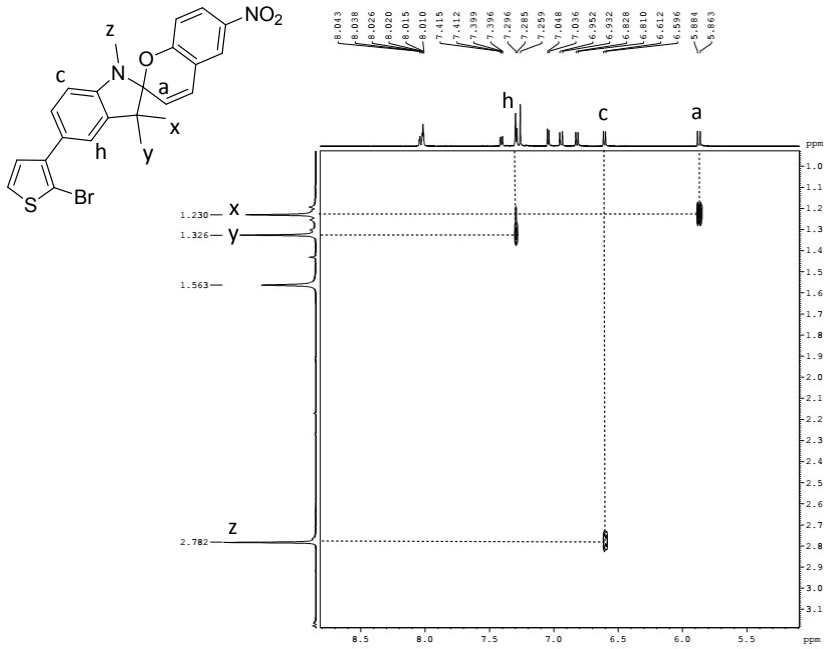


Figure S18: Expanded ^{1}H-^{1}H NOESY spectrum of 5'-(2-bromothiophen-3-yl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]

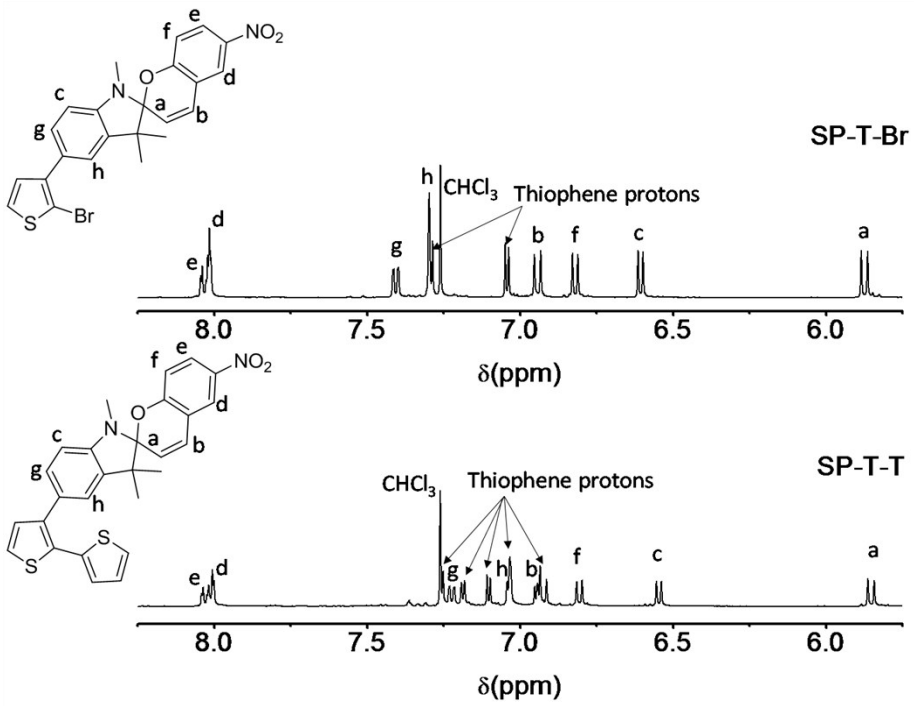


Figure S19: ^{1}H-NMR spectrum of 5′-([2,2′-bithiophene]-3-yl)-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline] in comparison with 5'-(2-bromothiophen-3-yl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] in the downfield region

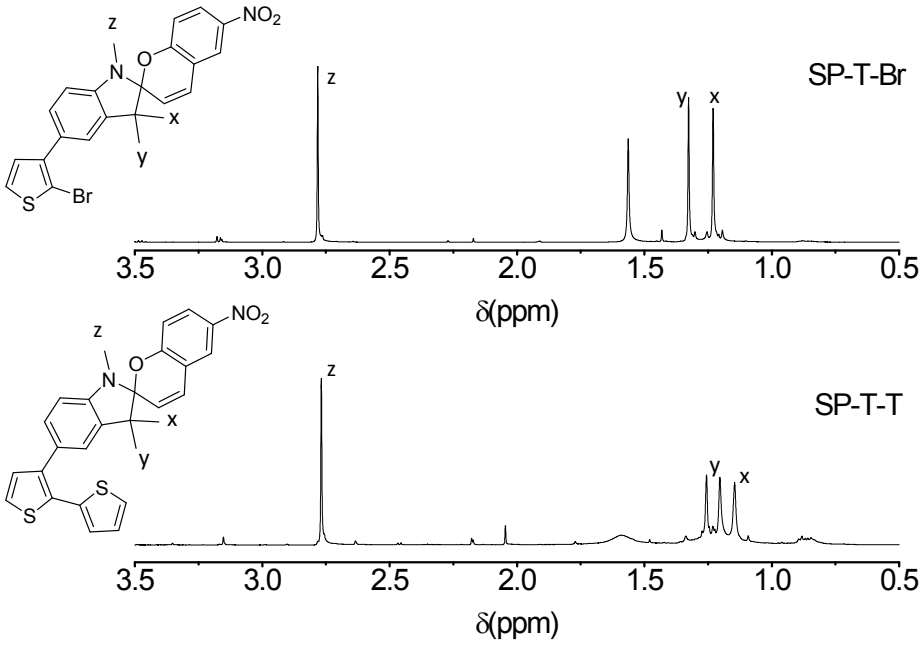


Figure S20: ^{1}H-NMR spectrum of 5′-([2,2′-bithiophene]-3-yl)-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline] in comparison with 5'-(2-bromothiophen-3-yl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] in the upfield region

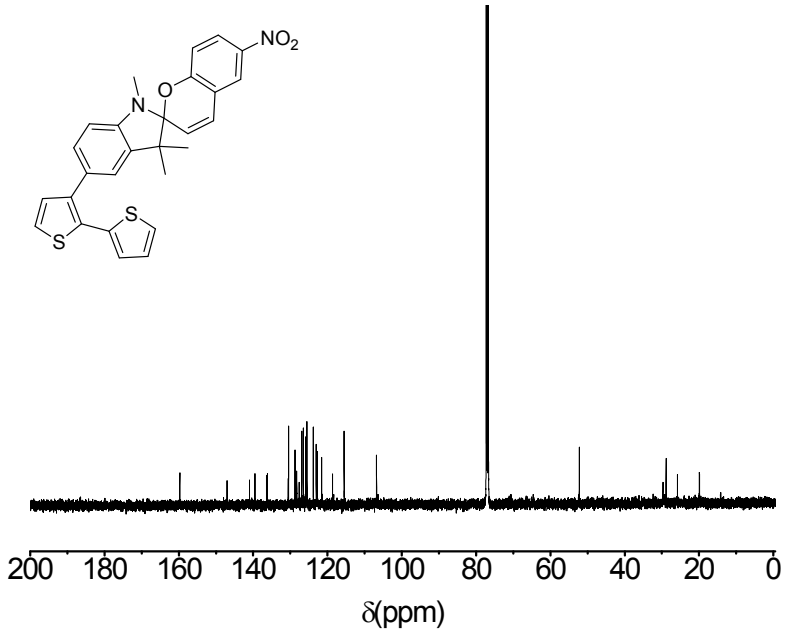


Figure S21: ^{13}C-NMR spectrum of 5′-([2,2′-bithiophene]-3-yl)-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline]

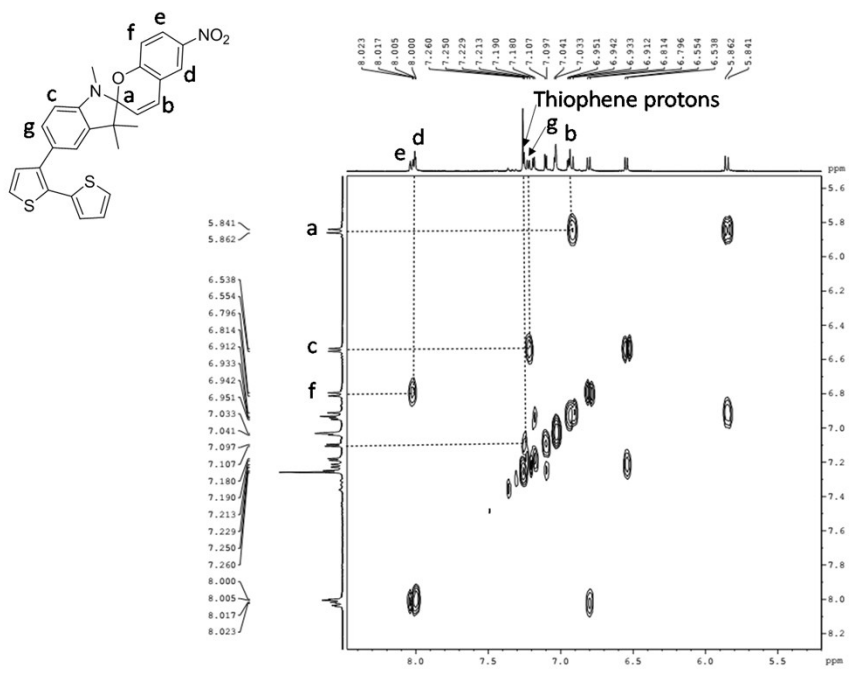


Figure S22: Expanded ^{1}H-^{1}H COSY spectrum of 5′-([2,2′-bithiophene]-3-yl)-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline]

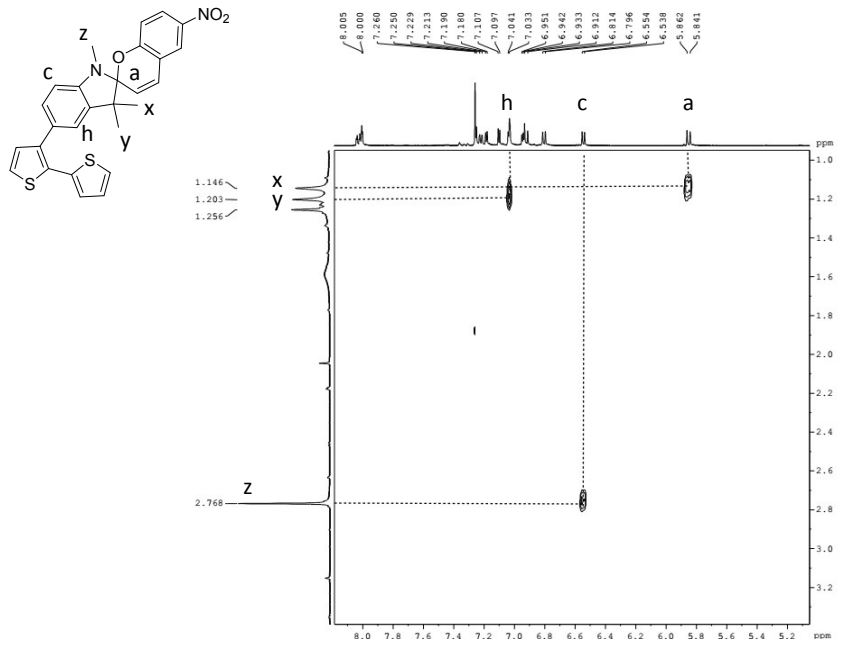


Figure S23: Expanded ^{1}H-^{1}H NOESY spectrum of 5′-([2,2′-bithiophene]-3-yl)-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline]

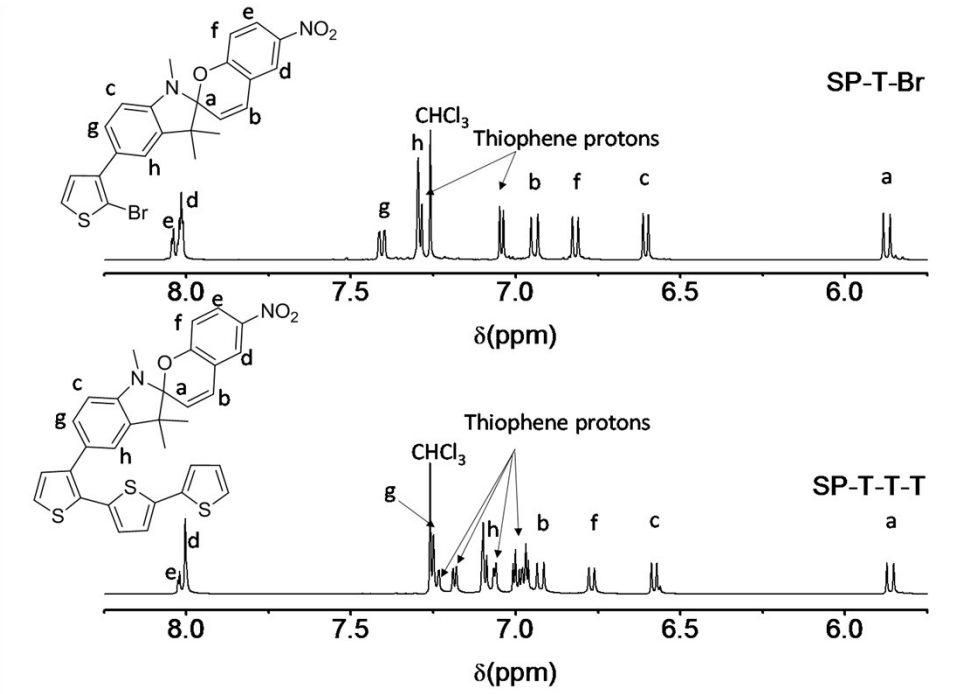


Figure S24: [1]H-NMR spectrum of 5′-([2,2′:5′,2″-terthiophene]-3-yl)-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline] in comparison with 5'-(2-bromothiophen-3-yl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] in the downfield region

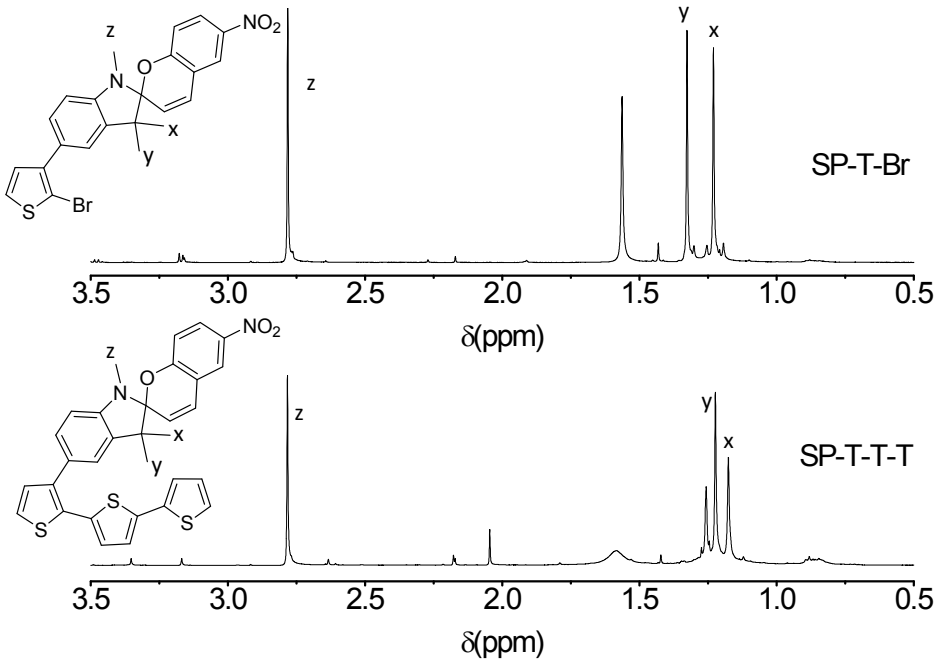


Figure S25: [1]H-NMR spectrum of 5′-([2,2′:5′,2″-terthiophene]-3-yl)-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline] in comparison with 5'-(2-bromothiophen-3-yl)-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] in the upfield region

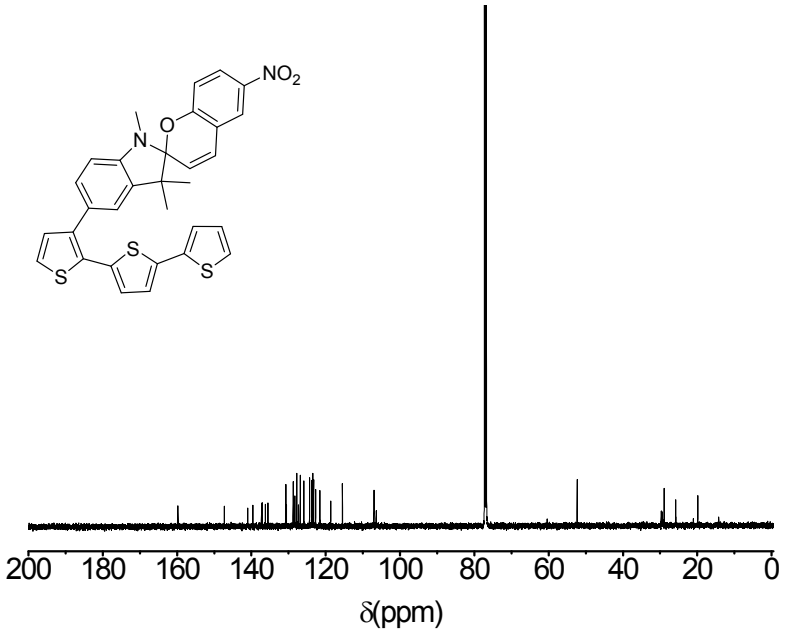


Figure S26: ^{13}C-NMR spectrum of 5′-([2,2′:5′,2″-terthiophene]-3-yl)-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline]

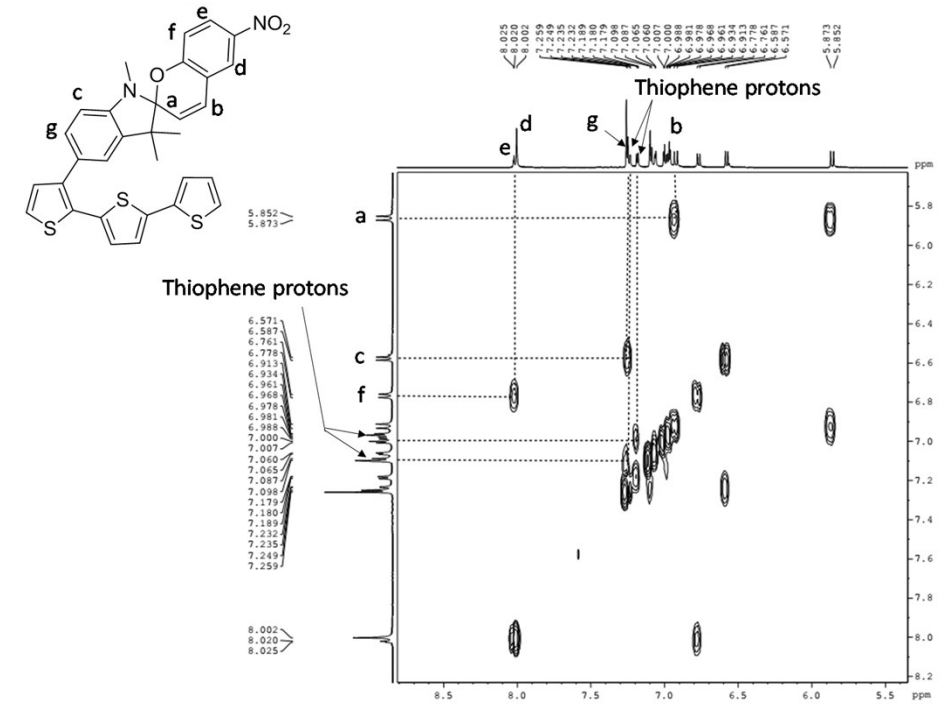


Figure S27: Expanded ^{1}H-^{1}H COSY spectrum of 5′-([2,2′:5′,2″-terthiophene]-3-yl)-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline]

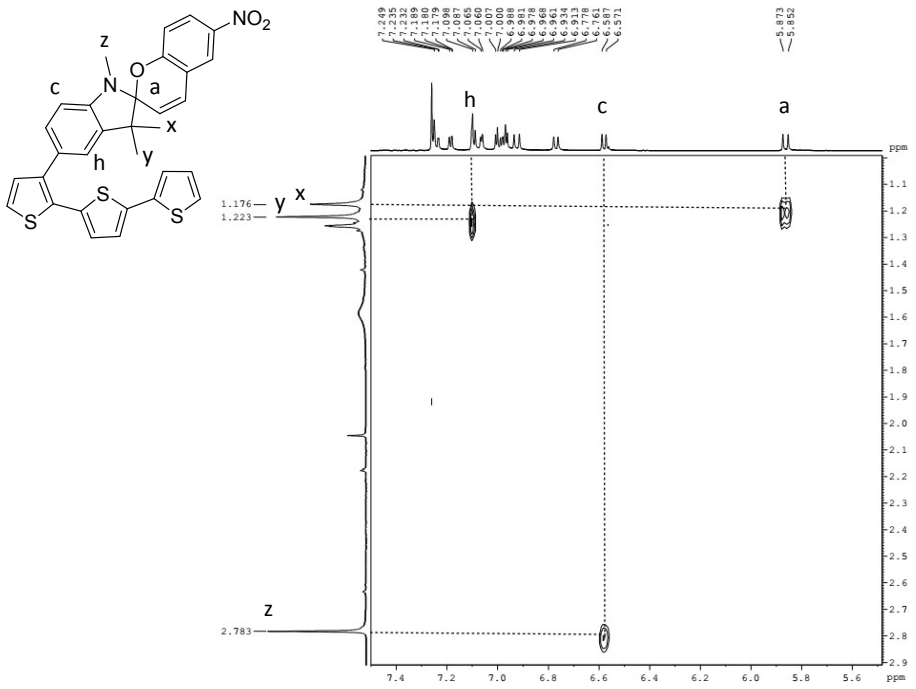


Figure S28: Expanded ^{1}H-^{1}H NOESY spectrum of 5′-([2,2′:5′,2″-terthiophene]-3-yl)-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline]

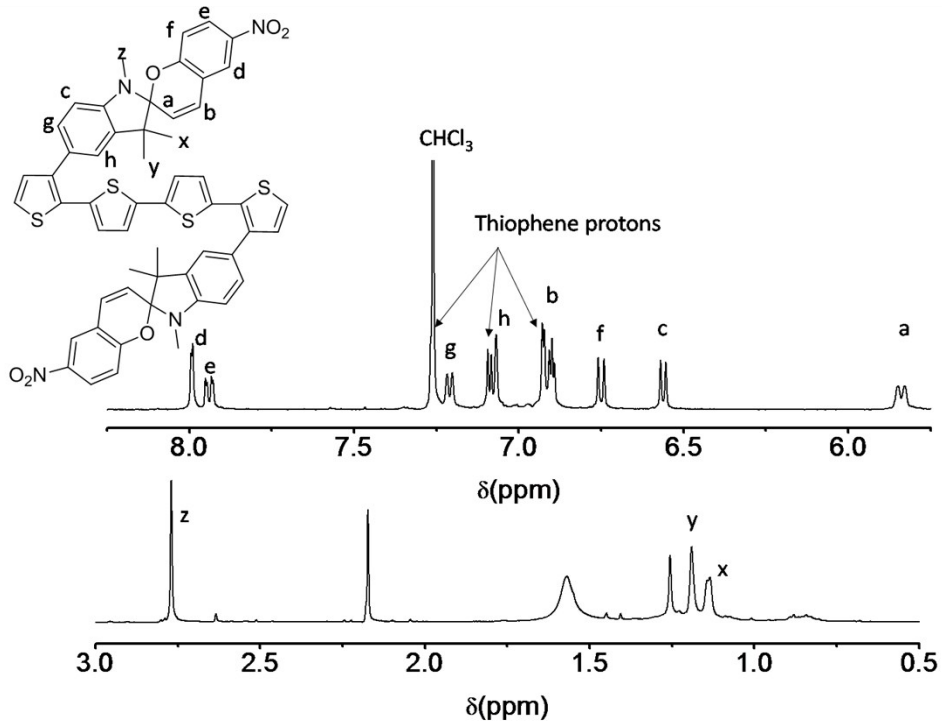


Figure S29: ^{1}H-NMR spectrum of 3,3'''-bis(1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)-2,2':5',2'':5'',2'''-quaterthiophene

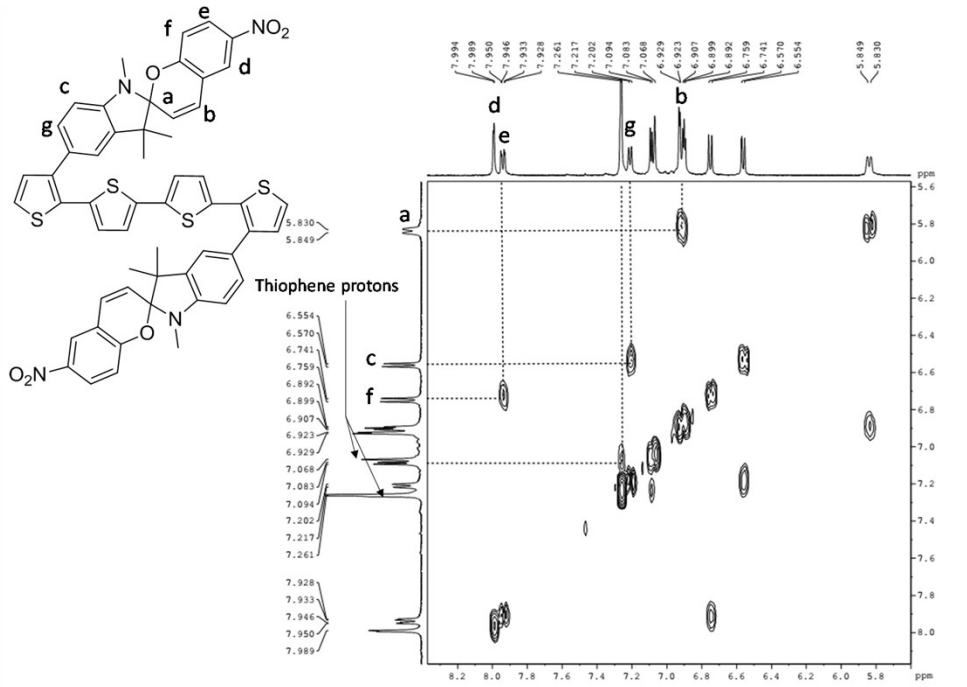


Figure S30: Expanded ^{1}H-^{1}H COSY spectrum of 3,3'''-bis(1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)-2,2':5',2'':5'',2'''-quaterthiophene

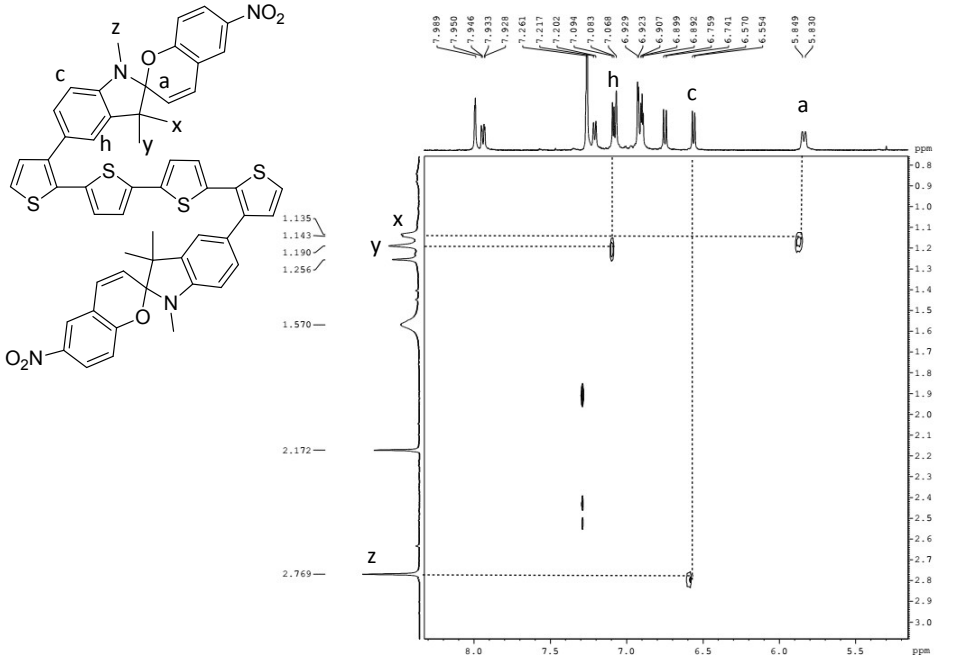
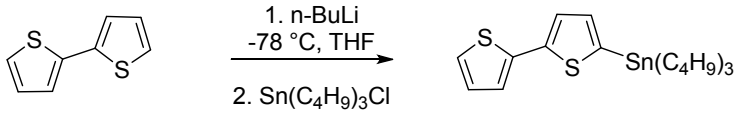


Figure S31: Expanded ^{1}H-^{1}H NOESY spectrum of 3,3'''-bis(1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indolin]-5'-yl)-2,2':5',2'':5'',2'''-quaterthiophene

Synthesis of [2,2′-bithiophene]-5-yltributylstannane



Scheme S2: Synthesis of [2,2′-bithiophene]-5-yltributylstannane

Synthesis of [2,2'-bithiophene]-5-yltributylstannane

A solution of 2,2′-bithiophene (0.50 g, 3.0 mmol) in freshly distilled THF in a 100 mL three-necked round bottomed flask equipped with a reflux condenser was cooled down to -78 °C under nitrogen prior to the addition of n-butyllithium (1.2 mL, 3.0 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 1 h under nitrogen. The solution was warmed to ~ -40 °C, upon which tributyltin chloride (1.0 mL, 6.3 mmol) was added and then the mixture was stirred at room temperature overnight. The reaction mixture was quenched with deionized water and extracted with ethyl acetate(100 mL × 3). Combined organic layer was washed with deionized water and brine (100 mL × 3), dried over $MgSO_4$ and evaporated under reduced pressure. The crude compound was dissolved in hexane and filtered. The filtrate was evaporated under reduced pressure to obtained [2,2′-bithiophene]-5-yltributylstannane as a yellow oil (868 mg, 1.9 mmol, 64 %). ^{1}H-NMR ($CDCl_3$, 500 MHz; 7.29 (d, 1H), 7.18 (m, 2H), 7.06 (d, 1H), 7.00 (t, 1H), 1.58 (m, 6H), 1.36 (m, 6H), 1.12 (m, 6H), 0.91 (m, 9H)). ^{13}C-NMR ($CDCl_3$, 500 MHz; 142.77, 137.72, 136.65, 136.08, 127.74, 124.99, 123.97, 123.46, 28.97, 27.28, 13.69, 10.90).

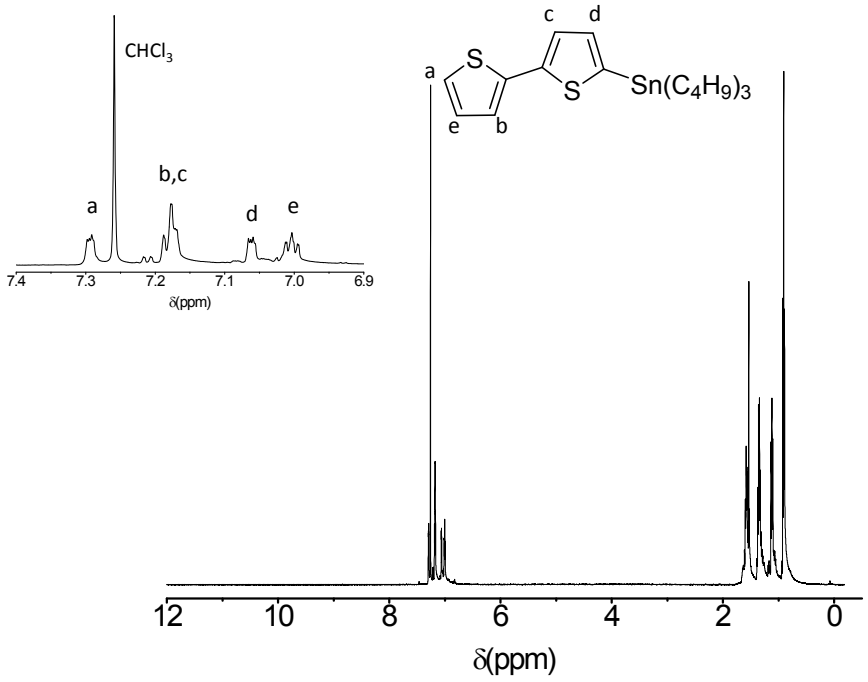


Figure S32: ^{1}H-NMR spectrum of [2,2′-bithiophene]-5-yltributylstannane

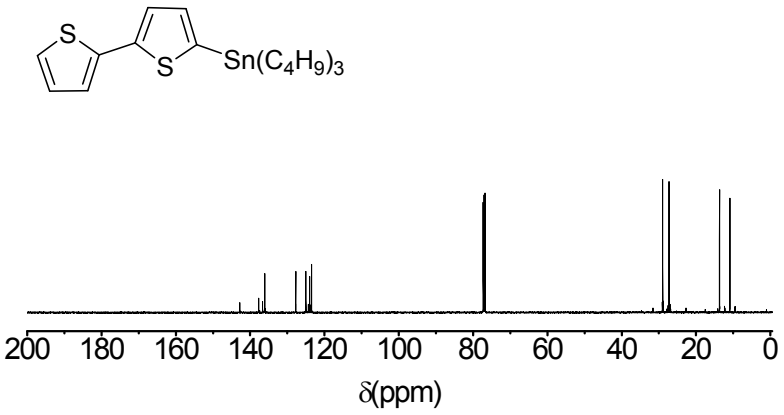
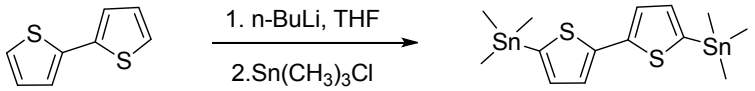


Figure S33: ^{13}C-NMR spectrum of [2,2′-bithiophene]-5-yltributylstannane

Synthesis of 5,5′-bis(trimethylstannyl)-2,2′-bithiophene2[2]



Scheme S3: Synthesis of 5,5′-bis(trimethylstannyl)-2,2′-bithiophene

Synthesis of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene

A solution of 2,2′-bithiophene (0.50 g, 3.0 mmol) in freshly distilled THF in a 100 mL three-necked round bottomed flask equipped with a reflux condenser was cooled down to -78 °C under nitrogen prior to the addition of n-butyllithium (2.5 mL, 6.3 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 1 h under nitrogen. The solution was warmed to 0 °C, upon which trimethyltin chloride (6.3 mL, 6.3 mmol) was added and then the mixture was stirred at room temperature overnight. The reaction mixture was quenched with deionized water and extracted with ethyl acetate. Combined organic layer was washed with deionized water and brine, dried over $MgSO_4$ and evaporated under reduced pressure. The crude compound was purified by recrystallization using ethanol to obtain the pure compound as light blue color crystals. (478 mg, 0.97 mmol, 32 %, MP = 95-97 ˚C). ^{1}H-NMR ($CDCl_3$, 500 MHz; 7.28 (d, 2H), 7.09(d, 2H), 0.38(s, 18 H). ^{13}C-NMR ($CDCl_3$, 500 MHz; 143.04, 137.07, 135.86, - 8.22).

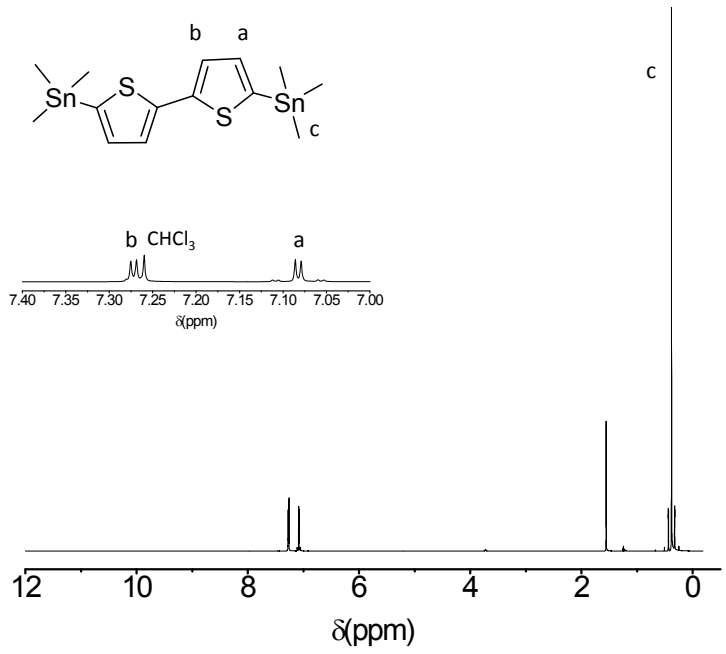


Figure S34: ^{1}H-NMR spectrum of 5,5′-bis(trimethylstannyl)-2,2′-bithiophene

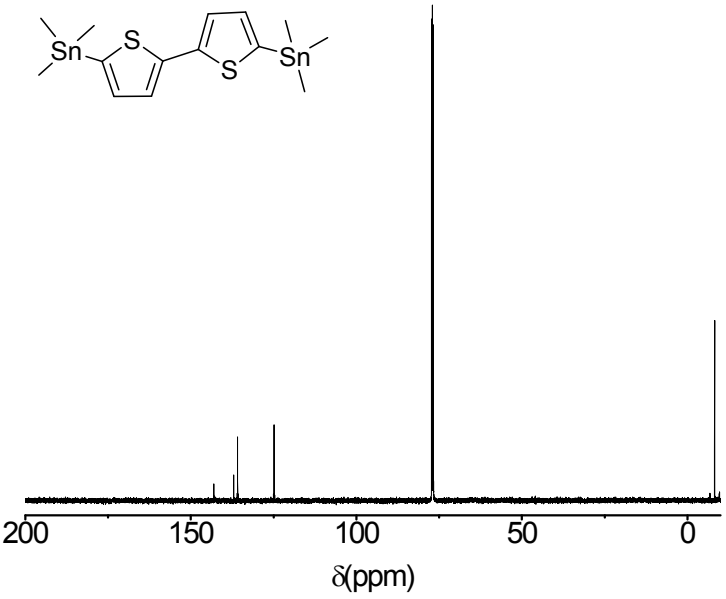
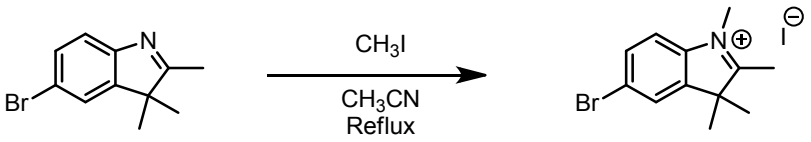


Figure S35: ^{13}C-NMR spectrum of 5,5′-bis(trimethylstannyl)-2,2′-bithiophene

Synthesis of 5-bromo-1,2,3,3-tetramethyl-3*H*-indol-1-ium iodide



Scheme S4: Synthesis of 5-bromo-1,2,3,3-tetramethyl-3*H*-indol-1-ium iodide

Synthesis of 5-bromo-1,2,3,3-tetramethyl-3H-indol-1-ium iodide – 5-bromo-2,3,3-trimethyl-3*H*-indole (200 mg, 0.84 mmol) in anhydrous acetonitrile was kept in a 100 mL three-necked round bottomed flask equipped with a reflux condenser under nitrogen prior to the addition of methyl iodide (251 mg, 1.68 mmol) at room temperature and the reaction mixture was heated under reflux. An aliquot was taken out in 6 h and 12 h intervals, quenched with deionized water, extracted with ether and GC-MS analysis were carried out to monitor the consumption of starting materials. With no starting materials remaining after 12 h, the reaction mixture was allowed to cool to room temperature, the product was filtered off and washed with acetonitrile (108 mg, 0.43 mmol, 51 %). ^{1}H-NMR (DMSO-d_6, 500 MHz; 8.16(s, 6H), 7.88-7.84(m, 2H), 3.94(s, 3H), 2.74(s, 3H), 1.52(s, 6H)). ^{13}C-NMR (DMSO-d_6, 500 MHz; 197.02, 144.34, 141.92, 132.22, 127.18, 123.13, 117.56, 54.66, 35.29, 21.93, 14.63)

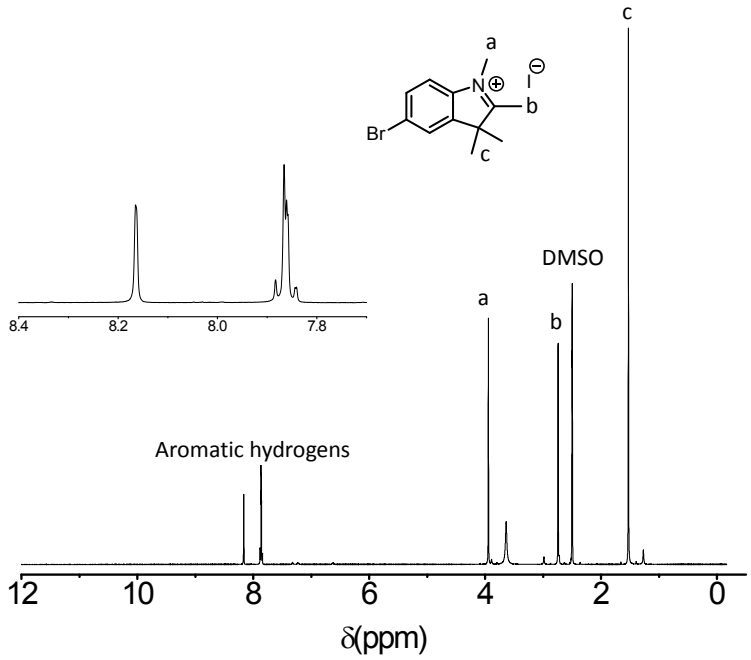


Figure S36: ^{1}H-NMR spectrum of 5-bromo-1,2,3,3-tetramethyl-3*H*-indol-1-ium iodide

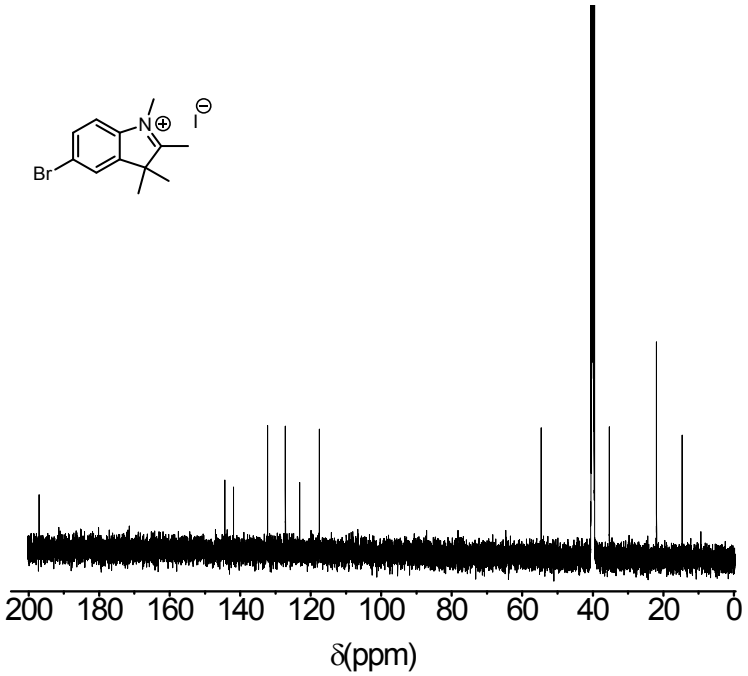
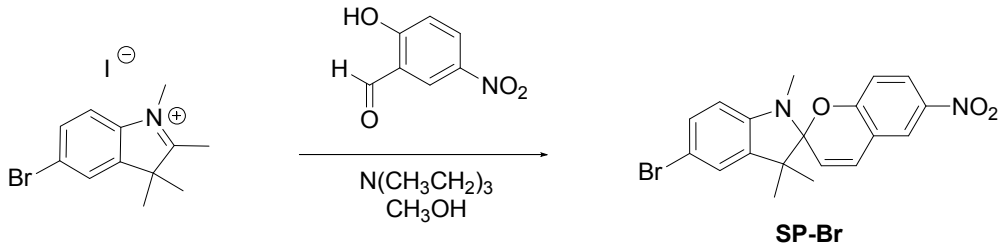


Figure S37: ^{13}C-NMR spectrum of 5-bromo-1,2,3,3-tetramethyl-3*H*-indol-1-ium iodide

Synthesis of 5′-bromo-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline]



Scheme S5: Synthesis of 5′-bromo-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline]

Synthesis of 5'-bromo-1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] 5-Bromo-1,2,3,3 -tetramethyl-3*H*-indol-1-ium iodide (0.50 g, 1.98 mmol) and 2-hydroxy-5-nitrobenzaldehyde (0.33 g, 1.98 mmol) were kept in a 100 mL three-necked round bottomed flask equipped with a reflux condenser under nitrogen for 15 min prior to the addition of methanol (50 mL). To the above stirred solution four drops of triethylamine was added at room temperature and the reaction mixture was allowed to reflux gently for 3 h under N_2, allowed to cool to room temperature, quenched in deionized water and extracted with ethyl acetate (100 mL x 3). The combined organic layer was washed with deionized water (100 mL x 3), dried over magnesium sulfate and the solvent was evaporated under reduced pressure. The crude in chloroform was purified by column chromatography using ethyl acetate:hexane (1:4) as the eluting solvent. The pure compound was obtained as a yellow solid (178 mg, 0.44 mmol, 22 %). ^{1}H-NMR ($CDCl_3$, 500 MHz; 8.02 (m, 2H), 7.28(dd, 2H), 7.16(d, 1H), 6.93(d, 1H), 6.77(d, 1H), 6.42(d, 1H), 5.83(d, 1H), 2.71(s, 3H), 1.27(s, 3H), 1.18(s, 3H)).^{13}C-NMR ($CDCl_3$, 500 MHz; 159.50, 146.83, 141.12, 138.50, 130.48, 128.58, 125.98, 124.90, 122.76, 121.05, 118.54, 115.47, 111.53, 108.60, 106.24, 52.32, 28.93, 25.73, 19.78)

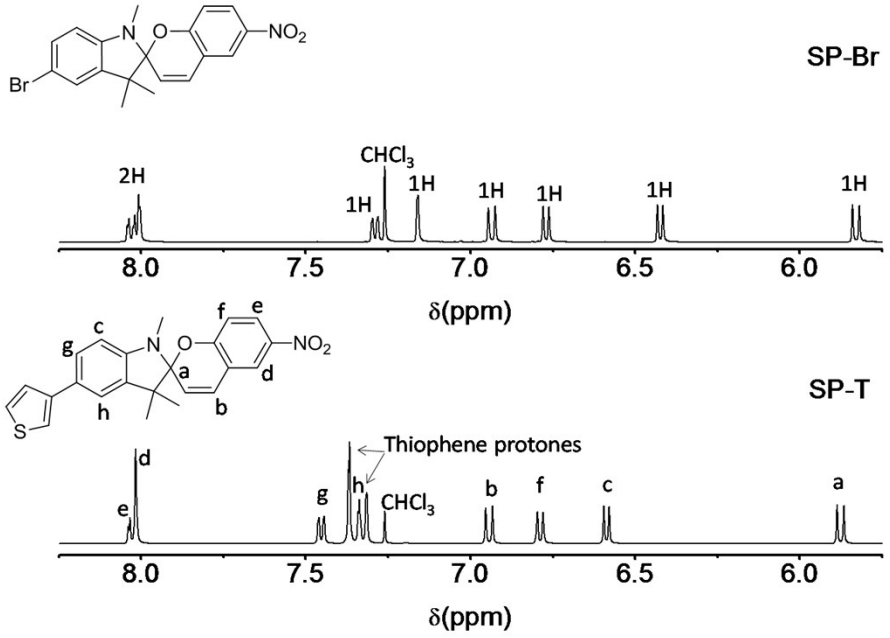


Figure S38: ^{1}H-NMR spectrum of 5′-bromo-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline] in comparison with1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline] in downfield region

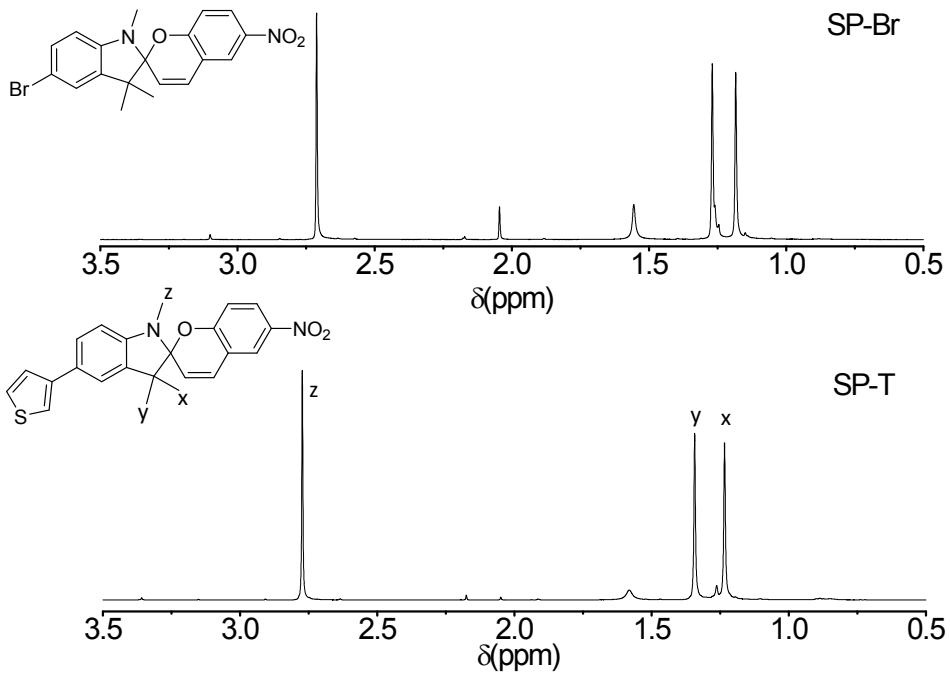


Figure S39: ^{1}H-NMR spectrum of 5′-bromo-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline] in comparison with1′,3′3′-trimethyl-6-nitro-5′-(thiophene-3-yl)spiro[chromene-2,2′-indoline] in upfield region

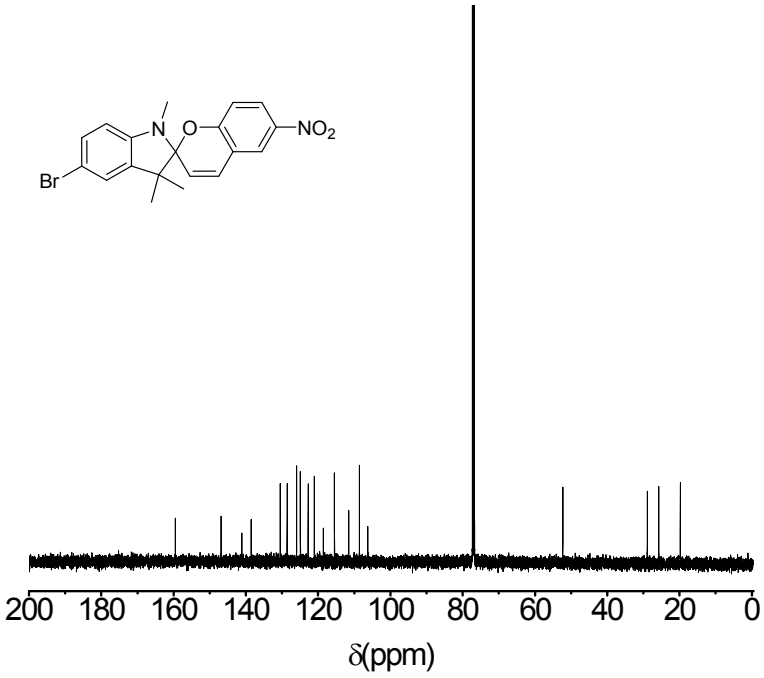


Figure S40: ^{13}C-NMR spectrum of 5′-bromo-1′,3′,3′-trimethyl-6-nitrospiro[chromene-2,2′-indoline]

Table S1. Photodegradation of spiropyran (SP) in methanol[a]

Compound	Absorbance upon first irradiation	Absorbance upon second irradiation	Absorbance upon third irradiation
SP-Br	0.183±0.00765	0.169±0.00760	0.172±0.00508
SP-T	0.142±0.0132	0.148±0.00762	0.145±0.00248
SP-T-Br	0.359±0.0232	0.369±0.0545	0.355±0.0283
SP-T-T	0.0795±0.00522	0.0692±0.00131	0.0712±0.00198
SP-T-T-T	0.110±0.00411	0.100±0.00536	0.106±0.00866
SP-T-T-T-T-SP	0.214±0.00104[b]	0.181±0.0134[b]	0.196±0.0110[b]

[a] Recorded value is an average of three independent runs, absorbance = Abs(t)- Abs(t=0), Abs(t) indicates the maximum absorbance at 540 nm, Abs(t=0) indicates the absorbance at 540 nm before any irradiation begins.
[b]Measured at 545 nm

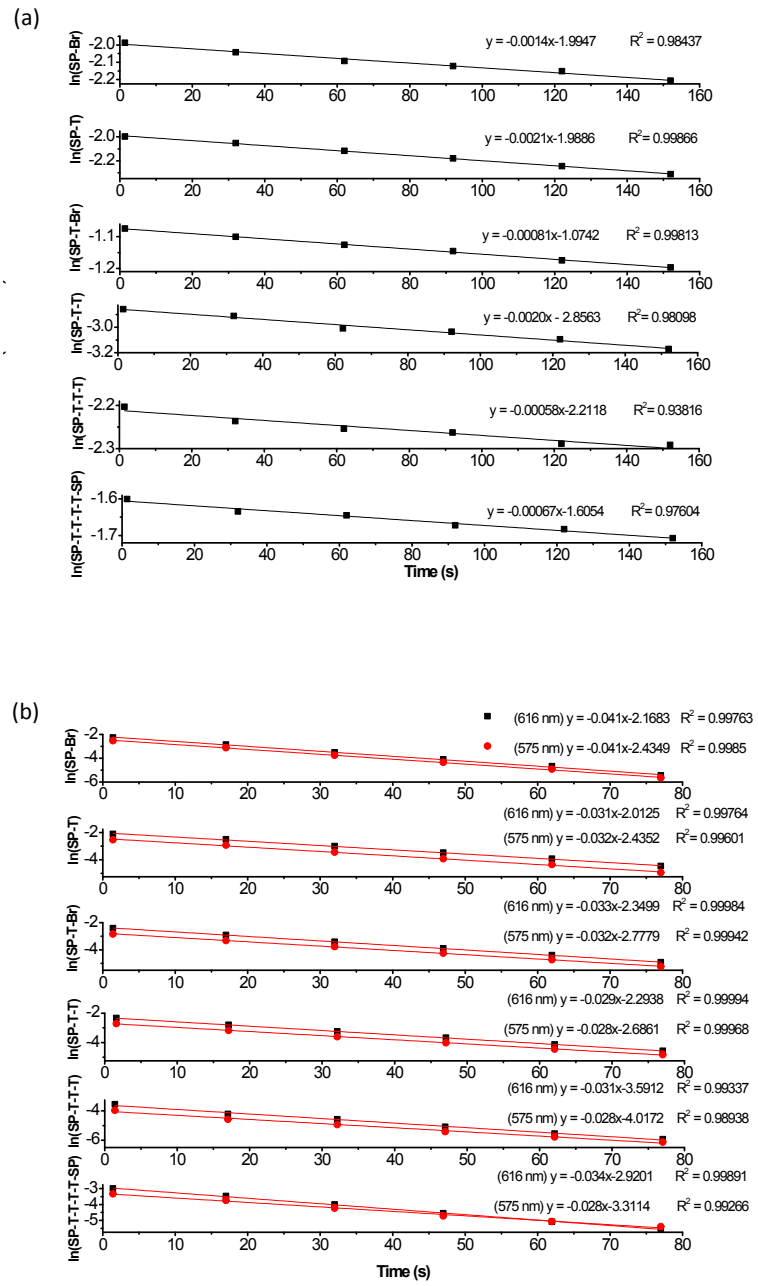
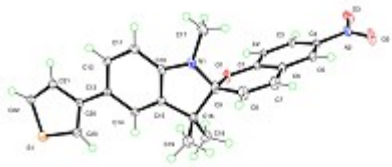


Figure S41: Absorbance decay of photochromic peak in methanol (a), in toluene (b).

structure report

Abstract



Experimental

(scd0687)

Crystal data

$C_{23}H_{28}N_2O_3S$
$M_r = 404.47$
Monoclinic, $P2_1/n$
$a = 10.020$ (2) Å
$b = 11.238$ (3) Å
$c = 17.984$ (5) Å
$\beta = 101.851$ (11)°
$V = 1981.9$ (9) Å^3
$Z = 4$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$\mu = 0.19$ mm^{-1}
$T = 90$ K
0.18 × 0.18 × 0.04 mm

Data collection

Bruker Kappa D8 Quest CMOS diffractometer (with an Oxford Cryosystems cryostream cooler)
Absorption correction: multi-scan *SADABS* (Sheldrick, 2002)
$T_{min} = 0.696$, $T_{max} = 0.746$
40647 measured reflections
6036 independent reflections
4727 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$

Refinement

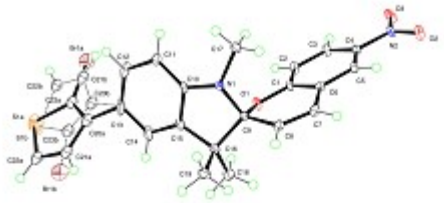
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.125$
$S = 1.04$
6036 reflections
265 parameters
0 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Data collection: Bruker *APEX2*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SHELXTL* Intrinsic Phasing (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2014); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

References

NOT FOUND

Abstract



Experimental

(scd0686_SimplerModel)

Crystal data

$C_{25}H_{19}BrN_2O_3S$
$M_r = 483.37$
Monoclinic, $P2_1/c$
$a = 19.967$ (7) Å
$b = 11.759$ (3) Å
$c = 8.670$ (2) Å
$\beta = 94.660$ (18)°
$V = 2028.8$ (10) Å^3
$Z = 4$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$\mu = 2.16$ mm^{-1}
$T = 90$ K
0.24 × 0.20 × 0.04 mm

Data collection

Bruker Kappa D8 Quest CMOS diffractometer (with an Oxford Cryosystems cryostream cooler)
Absorption correction: multi-scan *SADABS* (Sheldrick, 2002)
$T_{min} = 0.600$, $T_{max} = 0.746$
41789 measured reflections
6241 independent reflections
4775 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.080$
$wR(F^2) = 0.200$
$S = 1.05$
6241 reflections
275 parameters
13 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 1.87$ e Å^{-3}
$\Delta\rho_{min} = -2.51$ e Å^{-3}

Data collection: Bruker *APEX2*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SHELXTL* Intrinsic Phasing (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2014); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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NOT FOUND

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(1) Jin, L.-M.; Li, Y.; Ma, J.; Li, Q. Synthesis of Novel Thermally Reversible Photochromic Axially Chiral Spirooxazines. *Organic Letters* **2010**, *12*, 3552-3555.

(2) Choi, J.; Kim, K.-H.; Yu, H.; Lee, C.; Kang, H.; Song, I.; Kim, Y.; Oh, J. H.; Kim, B. J. Importance of Electron Transport Ability in Naphthalene Diimide-Based Polymer Acceptors for High-Performance, Additive-Free, All-Polymer Solar Cells. *Chemistry of Materials* **2015**, *27*, 5230-5237.