European Journal of Organic Chemistry

Supporting Information

Triptycene End-Capped Indigo Derivatives – Turning Insoluble Pigments to Soluble Dyes

Bahiru P. Benke, Leif Hertwig, Xuan Yang, Frank Rominger, Michael Mastalerz*

Table of Contents

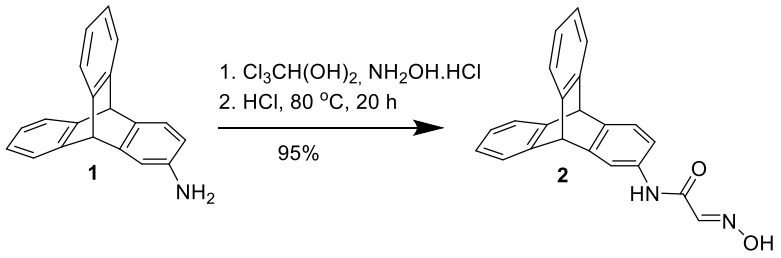
General Methods:

All reagents for synthesis were purchased from commercial suppliers and used without further purification. All air-sensitive reactions were performed using oven-dried glassware under an inert atmosphere of argon. Syringe or cannula was used to transfer air-sensitive solvents, reagents and solutions. Analytical thin layer chromatography (TLC) was performed on MERCK precoated silica gel 60 F_{254} TLC plates. All the compounds were visualized using UV light.

For flash column chromatography silica gel 60 (40–63 μm/230–400 mesh ASTM) or basic alumina (Type IV) was used. NMR spectra were recorded on a Bruker Avance III 300 (300 MHz) or Bruker Avance DRX 300 (300 MHz) or Bruker Avance III 400 (400 MHz) or Bruker Avance III 500 (500 MHz) or Bruker Avance III 600 (600 MHz) spectrometer. The NMR spectra were referenced using residual solvent peak as the standard. Chemical shift values are denoted in parts per million (δ), coupling constants (J) are reported in Hertz (Hz), and spin multiplicities are reported as singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), and multiplet (m). For HRMS measurement, Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer solariX (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7.0 T superconducting magnet and interfaced to an Apollo II Dual ESI/MALDI source was used. MALDI-TOF MS spectra were collected from a Bruker Daltonik Reflex III, on a Bruker ApexQe or on a Bruker AutoFlex Speed TOF with DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as a matrix. Elemental analysis was performed in Microanalytical Laboratory of the University of Heidelberg using an Elementar Vario EL machine. Melting points were measured using a Büchi Melting Point B-545 instrument. Crystal structure analysis was performed on a STOE Stadivari diffractometer with a copper source (Cu Kα λ= 1.54178 Å) All crystallographic information files (CCDC No. 2022650 (**4**) and CCDC No. 2023711 (**5**)) have been deposited in the Cambridge Crystallographic Data Centre and can be downloaded free of charge via www.ccdc.camac.uk/data_request/cif.

2-aminotriptycene (**1**)[S1] and parent bay annulated indigo (**7**)[S2] were prepared according to the literature procedures.

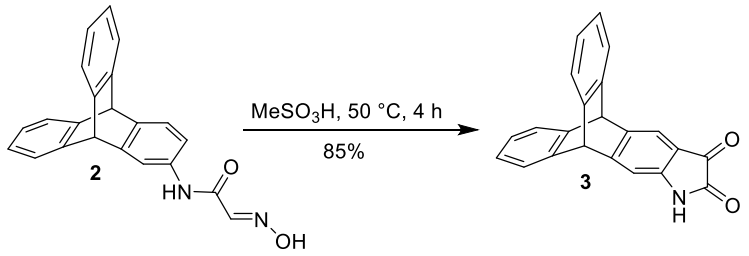
Synthesis of compound 2:



A solution of chloral hydrate (1.79 g, 10.8 mmol, 2.7 eq.) and anhydrous sodium sulphate (9.2 g, 64.8 mmol, 16 eq.) in water (48 mL) was added to a preheated (50 ºC) suspension of 2-aminotriptycene **1** (1.08 g, 3.6 mmol) in water (144 mL). Concentrated hydrochloric acid (1.6 mL) was added and the resulting suspension stirred for 5 minutes before addition of a solution of hydroxylamine hydrochloride (2.26 g, 64.8 mmol, 16 eq.) in water (48 mL). The suspension was stirred for 20 h at 80 ºC. After cooling the reaction mixture down to room temperature, the product was extracted with dichloromethane (4 x 50 mL) and the organic layers combined, dried over sodium sulphate and solvent was removed under reduced pressure. The crude product was suspended in n-pentane (20 mL) and ultrasonicated for 5 minutes before the beige colored powder was collected by filtration, giving **2** in 95% yield (1.30 g, 0.38 mmol).

$\boldsymbol{R}_f$ (DCM/EE, 20:1): 0.21; **Mp:** 243-244 ºC (decomposed); ^{1}**H NMR** (400MHz, DMSO-*d*6, 295 K): δ = 12.11 (s, 1H, OH), 10.06 (s, 1H, N*H*), 7.86 (d, *J* = 1.8 Hz, 1H, Ar*H*), 7.62 (s, 1H, NC*H*), 7.46-7.41 (m, 4H, Ar*H*), 7.37 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.21 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H, Ar*H*), 7.01-6.97 (m, 4H, Ar*H*), 5.62 (s, 1H, C*H*), 5.59 (s, 1H, C*H*).; ^{13}**C NMR** (101MHz, DMSO-*d*6, 295K): δ = 160.0, 145.8, 145.3, 145.1, 144.0, 140.9, 135.3, 125.0, 124.9. 123.6, 123.69, 123.66, 116.1, 116.0, 52.7, 52.0; **IR** (neat, ATR): $\tilde{\nu}$ (cm^{-1}) = 3344 (w), 3138 (br), 3007 (m), 2958 (m), 2859 (m), 2755 (w), 51 1652 (m), 1598 (m), 1537 (s), 1457 (s), 1420 (m), 1337 (w), 1284 (m), 1250 (m), 1156 (w), 1030 (s), 997 (m), 945 (w), 819 (w), 718 (w), 744 (s), 665 (w), 655 (w), 614 (m). **HRMS** (ESI-MS): *m/z* [M-H]$^-$ calcd. for $C_{22}H_{15}N_2O_2$: 339.1139, found: 339.1138: **Elemental Analysis:** calcd. for $C_{22}H_{16}N_2O_2 \cdot H_2O$: C 73.73, H 5.06, N 7.82; found C 73.75, H 5.01, N 7.66;

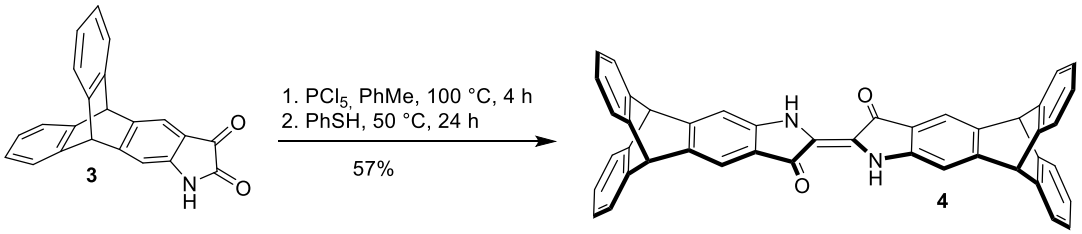
Synthesis of compound 3:



Isonitrosoacetanilide **2** (1.36 g, 4.0 mmol) was added to preheated (50 ºC) methane sulfonic acid (100 mL). After the addition was complete, the reaction temperature was increased to 80 ºC and n the resulting deep red solution stirred for 3.5 h. The reaction mixture was cooled down to room temperature and poured into a water/ice mixture (800 mL) and the orange suspension stirred at ambient temperature for 30 minutes. The aqueous suspension was extracted with DCM (5 x 75 mL) and the combined organic layers were dried over sodium sulphate and solvent removed under reduced pressure. The product was purified by flash column chromatography (SiO_2, DCM) followed by drying in a Kugelrohr (2.7 x 10^{-1} mbar, 10 h) to give pure isatin **3** as a red, crystalline solid in 95% yield (1.2 g, 0.37 mmol).

$\boldsymbol{R}_f$ (DCM/EE, 20:1): 0.21; **Mp**: 205-208ºC; ^{1}**H NMR** (400MHz, $CDCl_3$, 295K): δ = 8.07 (s, 1H, N*H*), 7.50 (s, 1H, Ar*H*), 7.41-7-37 (m, 4H, Ar*H*), 7.07-7.04 (m, 4H, Ar*H*), 6.97 (s, 1H, Ar*H*), 5.44 (s, 1H, C*H*), 5.42 (s, 1H, C*H*).;^{13}**C NMR** (101MHz, $CDCl_3$, 295K): δ = 182.4, 160.0, 157.4, 148.9, 144,3, 142.7, 141.5, 126.0, 125.8, 124.1, 123.8, 120.1, 114.5, 109.2, 54.9, 53.2; **IR** (neat, ATR): $\tilde{\nu}$ (cm^{-1}) = 3174 (br), 3062 (br), 2957 (m), 2849 (w), 2809 (s), 2359 (w), 2336 (w), 1727 (s), 1618 (s) 1603 (s), 1481 (m), 1454 (s), 1308 (m), 1290 (m), 1190 (m), 1171 (m), 1153 (m), 1105 (m), 1071 (s), 1022 (s, br), 952 (s), 915 (w) 859 (w), 869 (w), 802 (w), 741 (s), 626 (m), 561 (m).; **UV-VIS** (CH_2Cl_2): λ (log ε) = 317 nm (3.78), 264 nm (4.29), 252 nm (4.47); **HRMS (ESI-MS):** *m/z* $[M+Na]^+$ calcd. for $C_{22}H_{13}NO_2Na$: 346.0841, found: 346.0838; *m/z* $[M+K]^+$ calcd. for $C_{22}H_{13}NO_2K$: 362.0581, found: 362.0578; *m/z* $[2M+Na]^+$ calcd. for $(C_{22}H_{13}NO_2)_2Na$: 669.1791 found: 669.1791. **Elemental Analysis:** Calcd. for $C_{22}H_{13}NO_2 \cdot 0.9\ H_2O$: C 77.82, H 4.39, N 4.12; found C 77.76, H 4.45, N 3.98

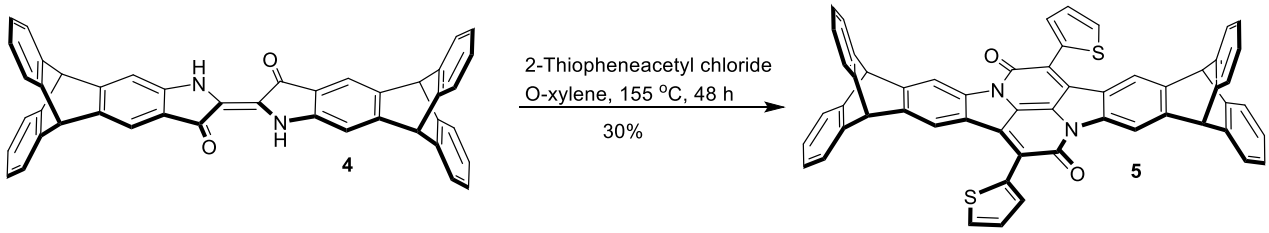
Synthesis of compound 4:



To a mixture of isatin **3** (500 mg, 1.547 mmol) and PCl_5 (338 mg, 1.623 mmol, 1.05 eq.), anhydrous toluene (15 mL) was added and the reaction mixture stirred under argon atmosphere for 5 hours at 100 ºC. The reaction mixture was cooled down to 50 ºC and then a solution of thiophenol (374 mg, (347 µL), 3.401, mmol, 2.2 eq) in toluene (5 mL) was added and stirred 24 h at 50 ºC. After cooling down to room temperature, the reaction mixture was diluted with DCM to a total volume of 250 mL, washed with aq. K_2CO_3 (0.25 M) solution (3 x 30 mL) and dried over sodium sulphate. Solvents were removed under reduced pressure and crude product was purified by column chromatography (Type IV basic alumina, DCM/pentane = 4:6), giving 270 mg (57%) of compound **4** as a deep blue solid.

R_f (DCM/PE, 3:2): 0.35; **Mp:** > 350 ºC; ^{1}**H NMR** (600 MHz, $CDCl_3$, 300K): δ = 8.66 (s, 1H, N*H*), 7.60 (s, 1H, Ar*H*), 7.40-7.37 (m, 8H, Ar*H*), 7.04-7.01 (m, 10H, Ar*H*), 5.41 (s, 2H, C*H*), 5.39 (s, 2H, C*H*). ^{13}**C NMR** (125 MHz, $CDCl_3$, 300K): 188.1, 154.5, 151.6, 144.9, 143.5, 138.3, 126.0, 125.7, 124.0, 123.7, 122.1, 118.7, 116.8, 108.5, 54.9, 53.4; **IR** (neat, ATR): $\tilde{\nu}$ (cm^{-1}) = 3355 (br, w), 3066 (w), 3045 (w), 3020 (w), 2958 (w), 1618 (s), 1575 (w), 1481 (s), 1444 (m), 1398 (w), 1344 (w), 1278 (w), 1253 (w), 11990 (w), 1161 (m), 1151 (m), 1105 (s), 1091 (s), 1029 (w), 1024 (w), 891 (w), 831 (w), 764 (w), 736 (s), 700 (w), 642 (w), 624 (m).; **UV-VIS** ($CHCl_3$): λ (log ε) = 299 nm (4.04), 372 nm (3.75), 612 nm (3.64). **MALDI-TOF** (DCTB): *m/z* $[M]^+$ calcd. for $C_{44}H_{26}N_2O_2$: 614.1994, found: 614.990. **Elemental Analysis:** Calcd. for $C_{44}H_{26}N_2O_2 \cdot 1.5\ CH_2Cl_2$: C 73.64, H 3.94, N 3.77; found C 73.38, H 4.28, N 3.60;

Synthesis of compound 5:



To a refluxing solution of compound **4** (100 mg, 0.163 mmol, 1 eq.) in anhydrous O-xylene (10 mL) a solution of 2-thiopheneacetyl chloride (104.6 mg, 0.652 mmol, 4 eq.) in O-xylene (4 mL) was added dropwise over a period of ten minutes following which reaction mixture was stirred under argon atmosphere for 48 hours at 155 ºC. Afterwards, reaction mixture was cooled down to room temperature and passed through the basic alumina column (Type IV, pentane/DCM 1:0 to 7:3). Pink coloured fraction was collected in round bottom flask and solvents were removed under reduced pressure. The solid was dissolved in small amount of DCM (~ 1 mL) and precipitated with the addition of pentane (~10 mL). The precipitate was separated by centrifugation technique. The precipitation was repeated thrice afforded 40 mg of compound **5** as a purple solid in 30% yield.

Mp: >350 ºC; ^{1}**H NMR** (600 MHz, CD_2Cl_2): δ = 8.59 (s, 1H, Ar*H*), 8.08 (s, 1H, Ar*H*), 7.75 (dd, *J* = 5.4 Hz, *J* = 1.2 Hz, 2H), 7.71 (dd, *J* = 5.4 Hz, *J* = 1.2 Hz, 2H), 7.45-7.39 (m, 8H, Ar*H*), 7.36 (dd, *J* = 5.4 Hz, *J* = 5.4 Hz, 2H), 7.04-7.02 (m, 8H, Ar*H*), 5.61 (s, 2H, C*H*), 5.39 (s, 2H, C*H*). ^{13}**C NMR** (125 MHz, CD_2Cl_2): 158.9, 151.0, 145.0, 144.6, 144.2, 142.7, 135.5, 130.9, 130.3, 130.2, 126.9, 126.0, 124.3, 124.2, 124.1, 122.92, 122.86, 120.2, 114.0, 54.8; ^{13}**C DEPT NMR** (125 MHz, CD_2Cl_2): 130.3, 130.2, 126.8, 126.0, 124.3, 124.1, 120.2, 114.0, 54.8, 54.2, 54.0, 53.8; **IR** (1, ATR): $\tilde{\nu}$ (cm^{-1}) = 3120 (w), 3064 (w), 3020 (w), 2958 (w), 1620 (m), 1560 (w), 1471 (w), 1458 (w), 1438 (w), 1413 (s), 1379 (w), 1292 (w), 1257 (w), 1193 (w), 1141 (w), 1097 (w), 1037 (w) 937 (w), 893 (w), 858 (w), 835 (w), 823 (w), 802 (w), 784 (w), 740 (m), 700 (w), 653 (w), 624 (w); **UV-VIS** (CH_2Cl_2): λ (log ε) = 301 nm (4.91), 378 nm (4.13), 552 nm (4.48), 585 nm (4.59). **Elemental Analysis:** Calcd. for $C_{56}H_{30}N_2O_2S_2 \cdot 2.5\ H_2O$: C 77.13, H 4.05, N 3.21; found C 77.17, H 4.01, N 2.86; **MALDI-TOF** (DCTB): *m/z* $[M+H]^+$ calcd. for $C_{56}H_{31}N_2O_2S_2$: 827.1827, found: 827.1817.

Spectra:

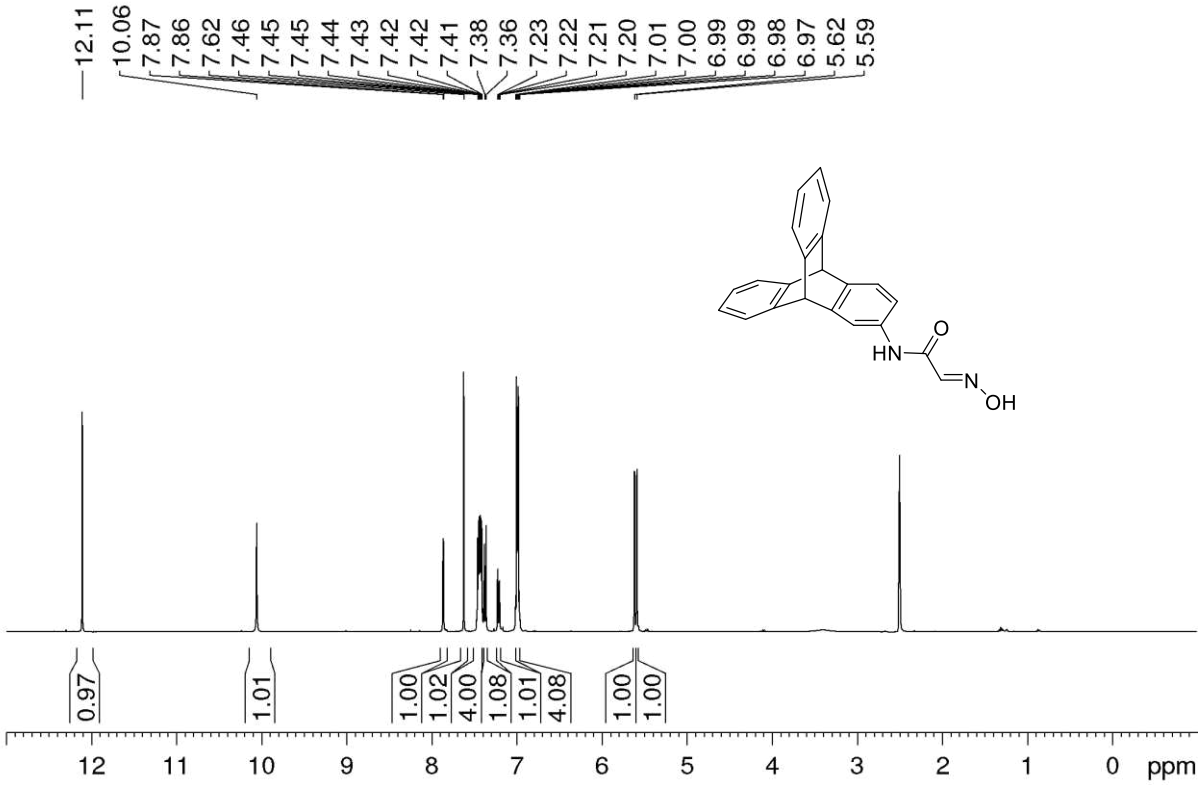


Figure S1. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **2**.

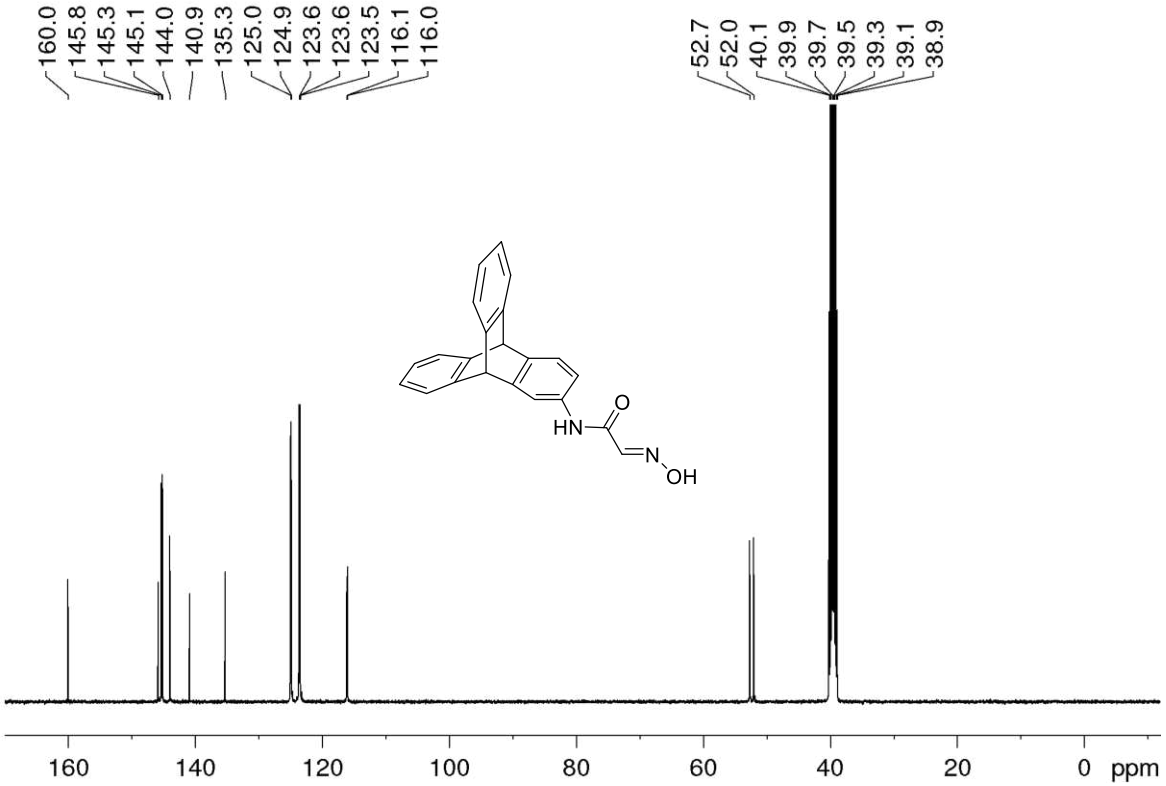


Figure S2. ^{13}C NMR (400 MHz, DMSO-d_6) spectrum of compound **2**.

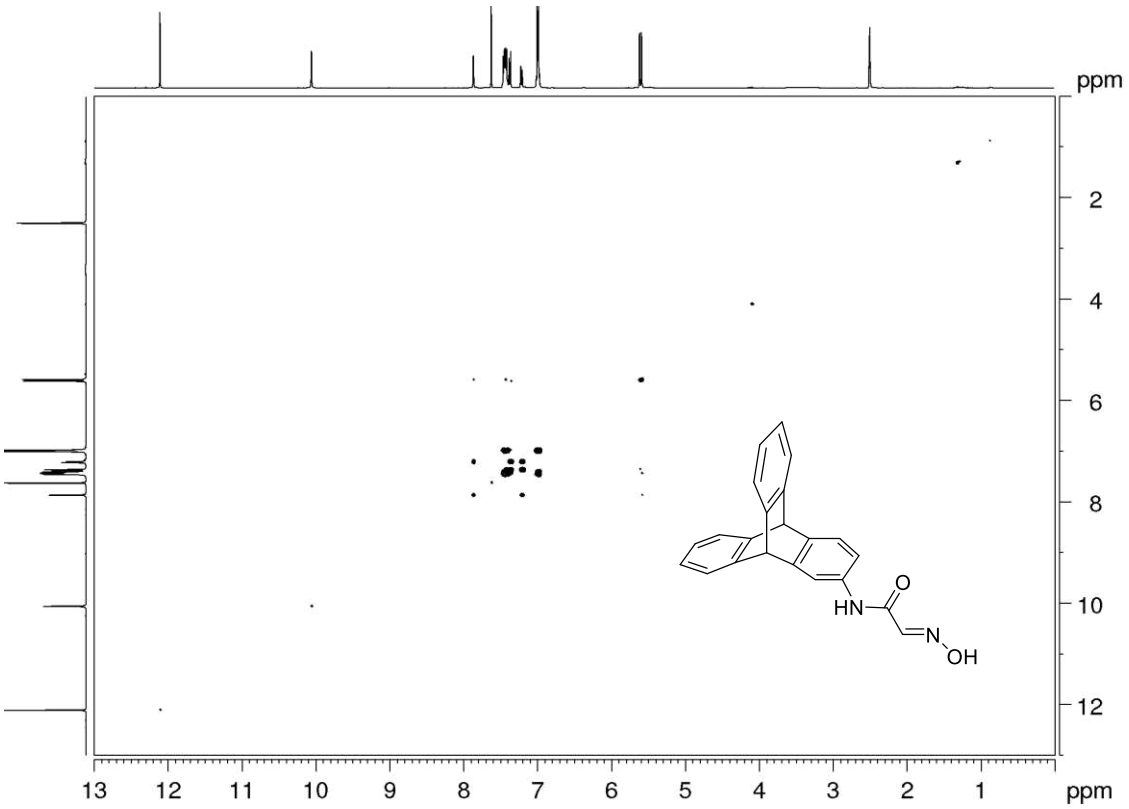


Figure S3. ^{1}H-^{1}H COSY NMR spectrum (400 MHz, DMSO-d_6) of compound **2**.

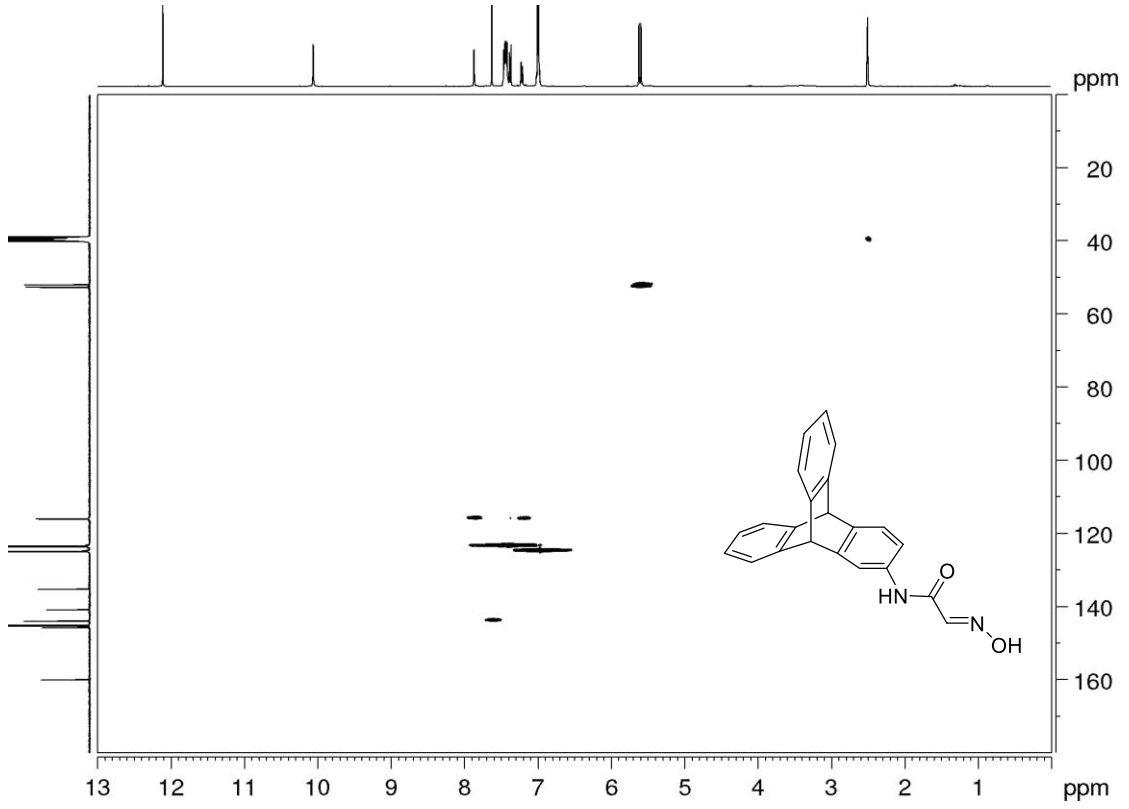


Figure S4. ^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d_6) spectrum of compound **2**.

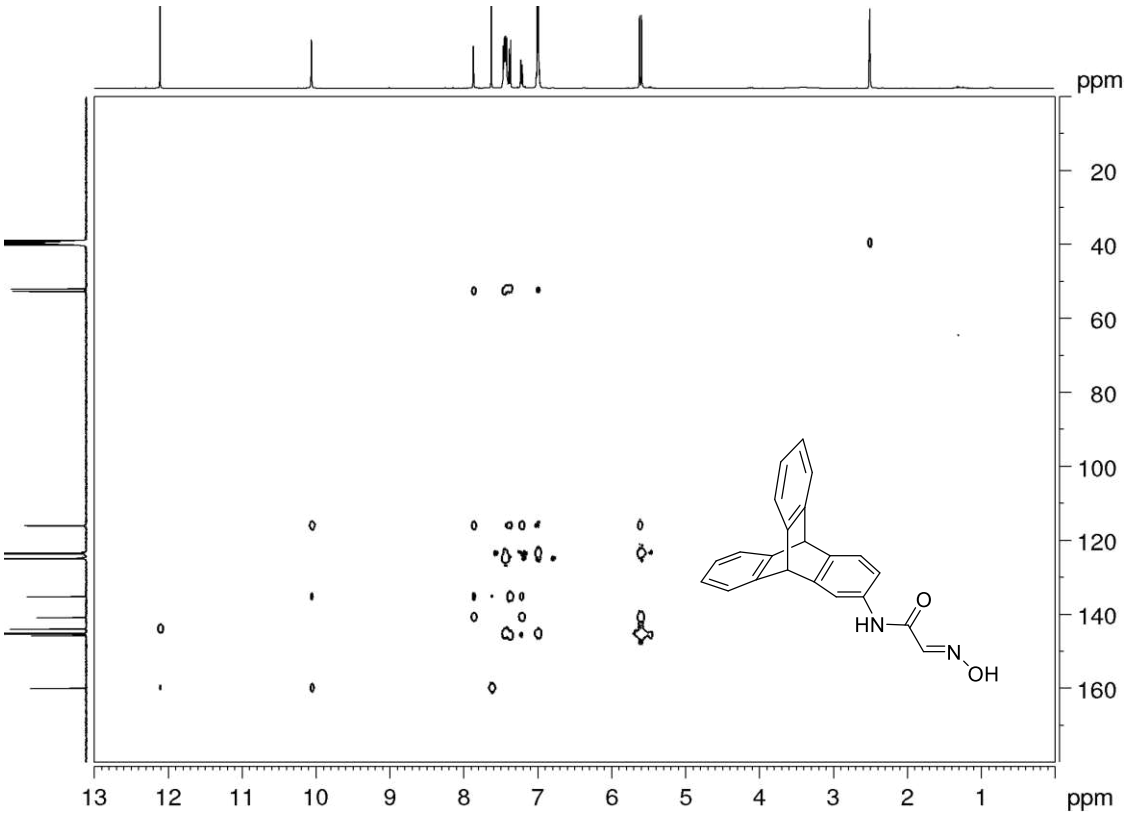


Figure S5. ^{1}H-^{13}C HMBC NMR (400 MHz, DMSO-d_6) spectrum of compound **2**.

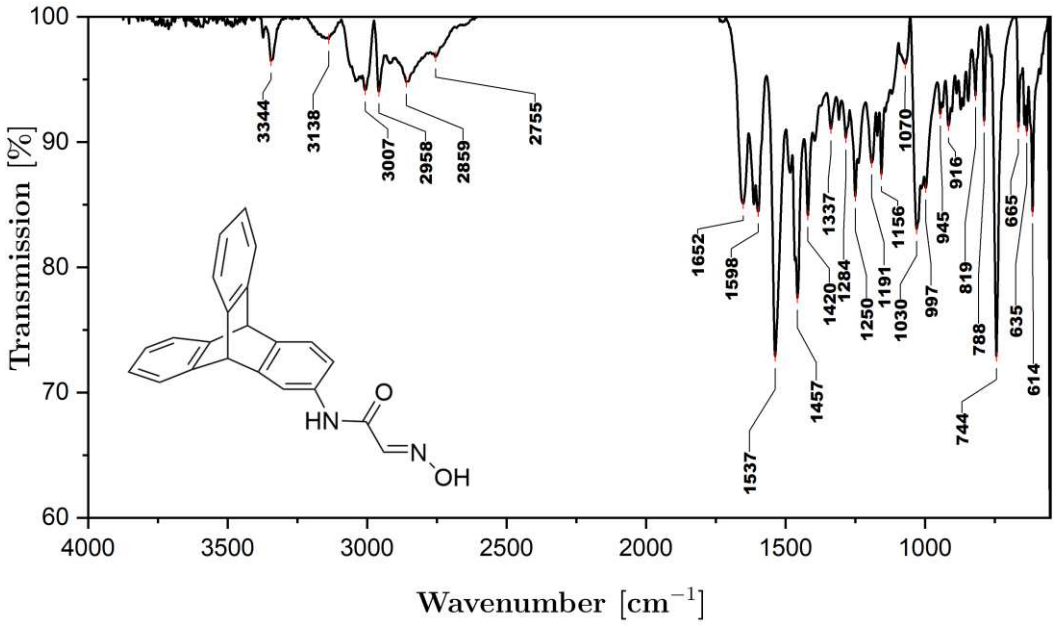


Figure S6. FT-IR (ATR) spectrum of compound **2**.

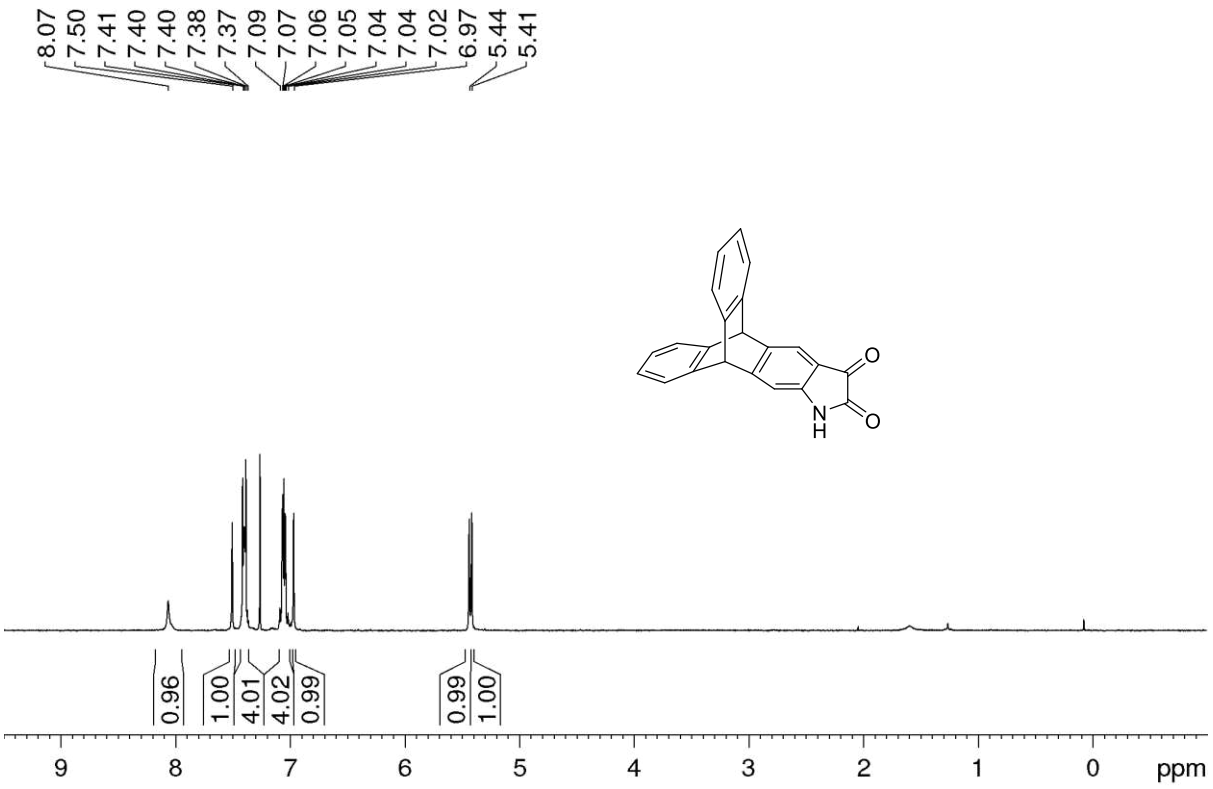


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**.

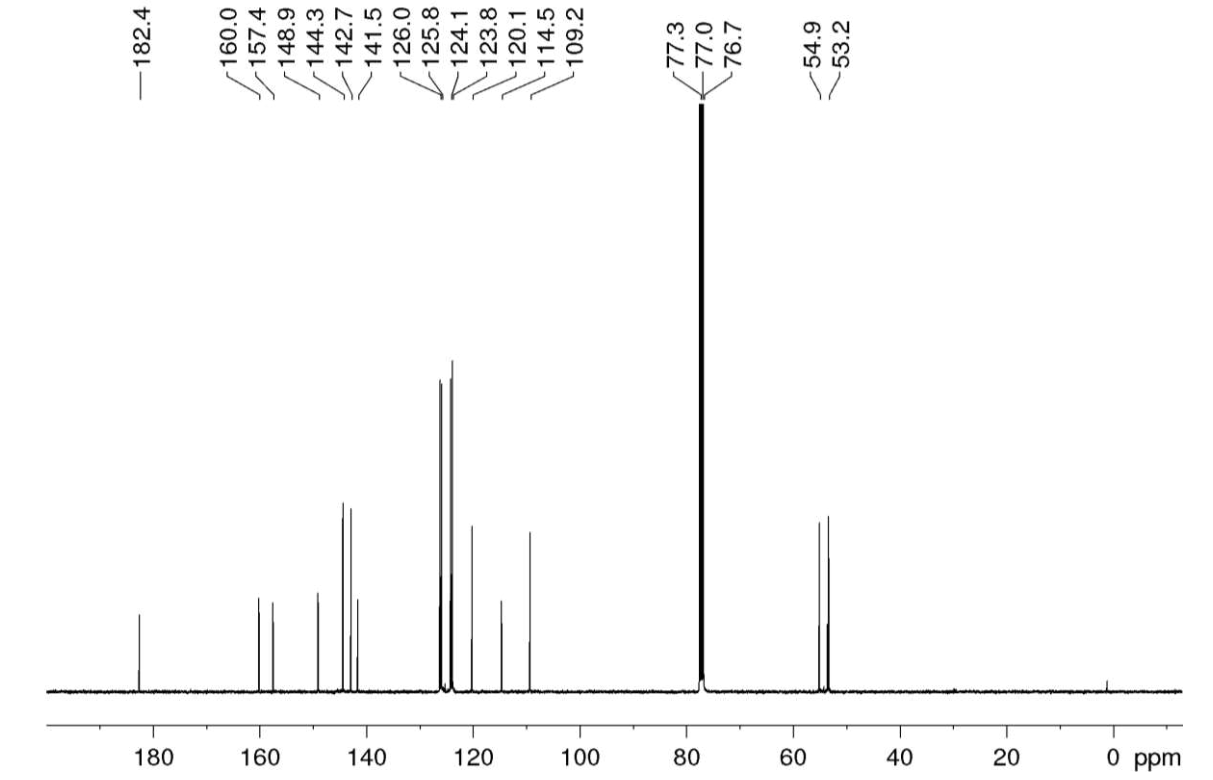


Figure S8. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of compound **3**.

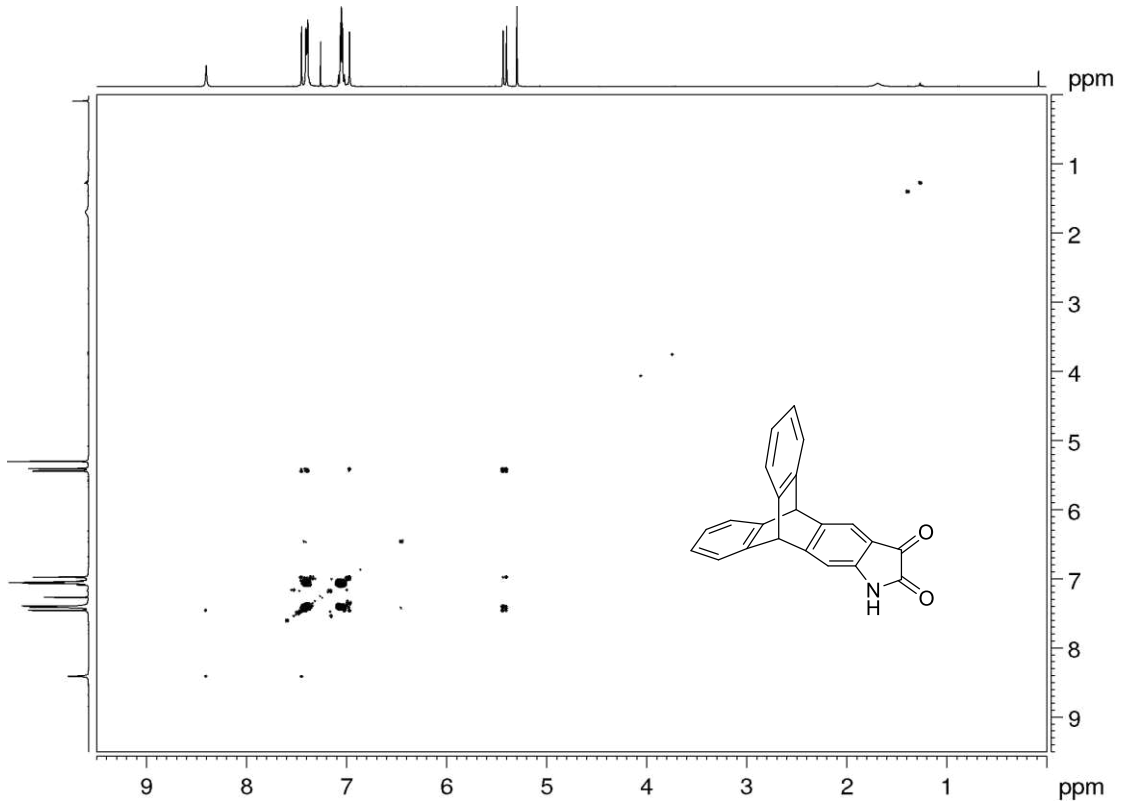


Figure S9. ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$) of compound **3**.

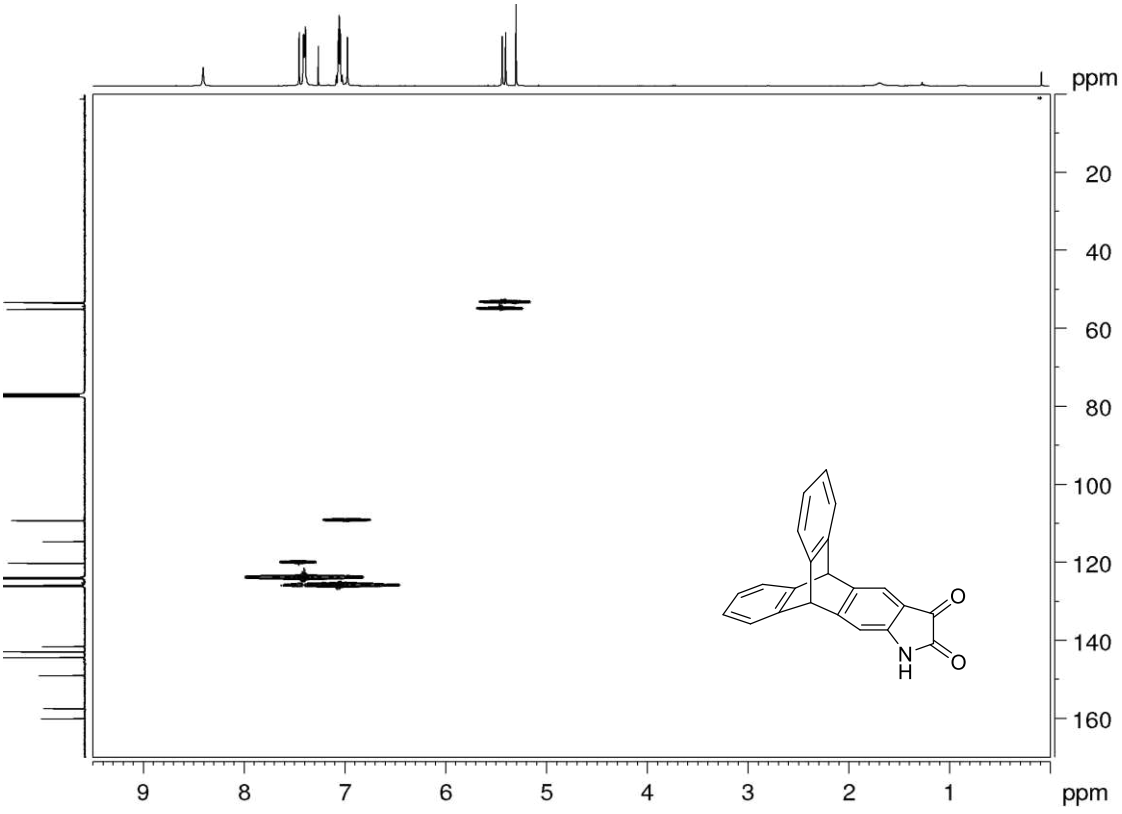


Figure S10. ^{1}H-^{13}C HSQC NMR (400 MHz, $CDCl_3$) spectrum of compound **3**.

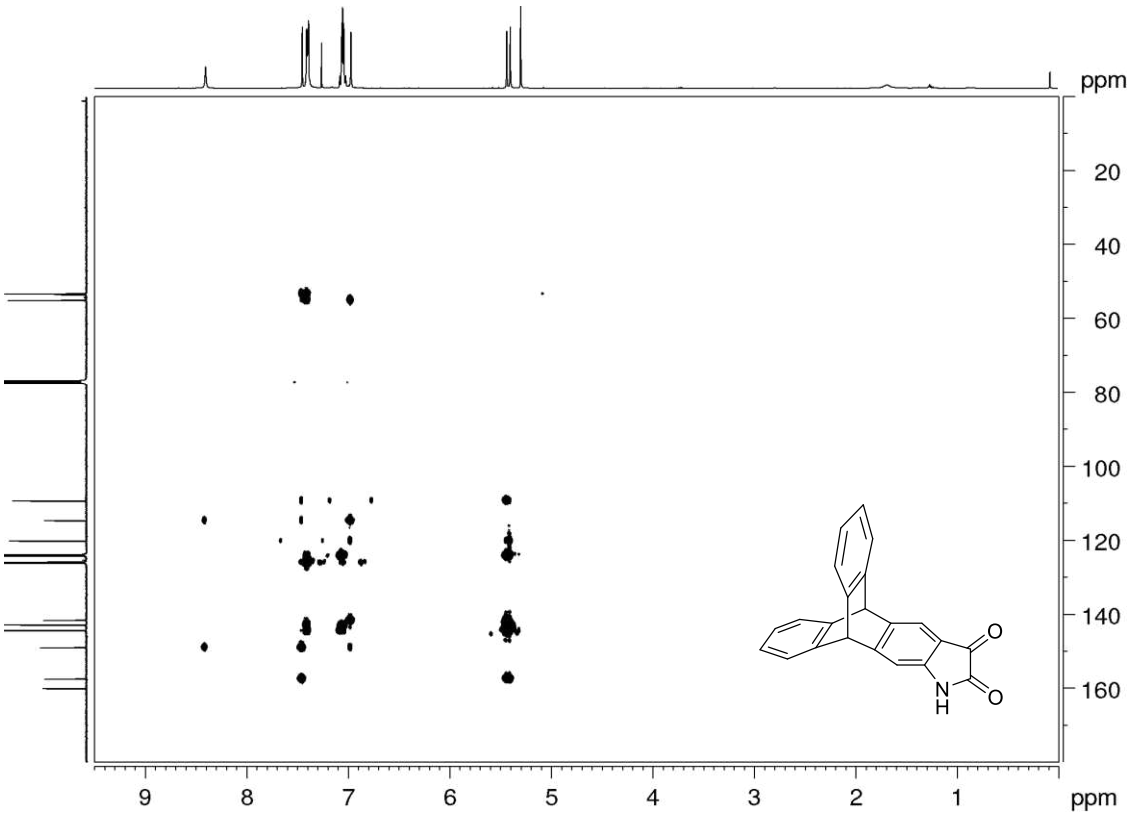


Figure S11. ^{1}H-^{13}C HMBC NMR (400 MHz, $CDCl_3$) spectrum of compound **3**.

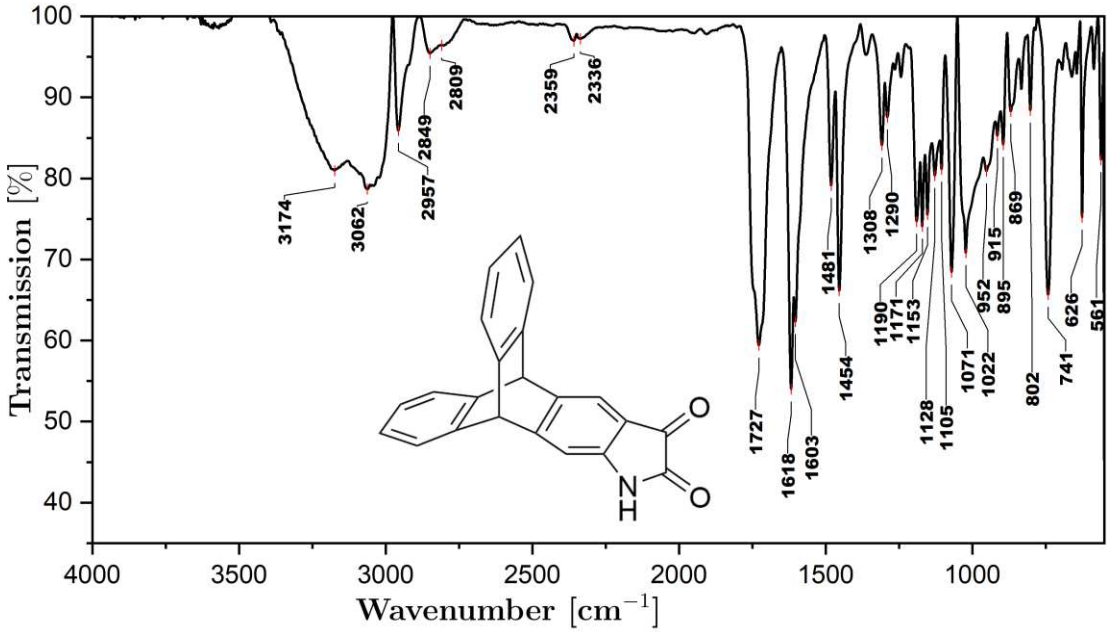


Figure S12. FT-IR (ATR) spectrum of compound **3**.

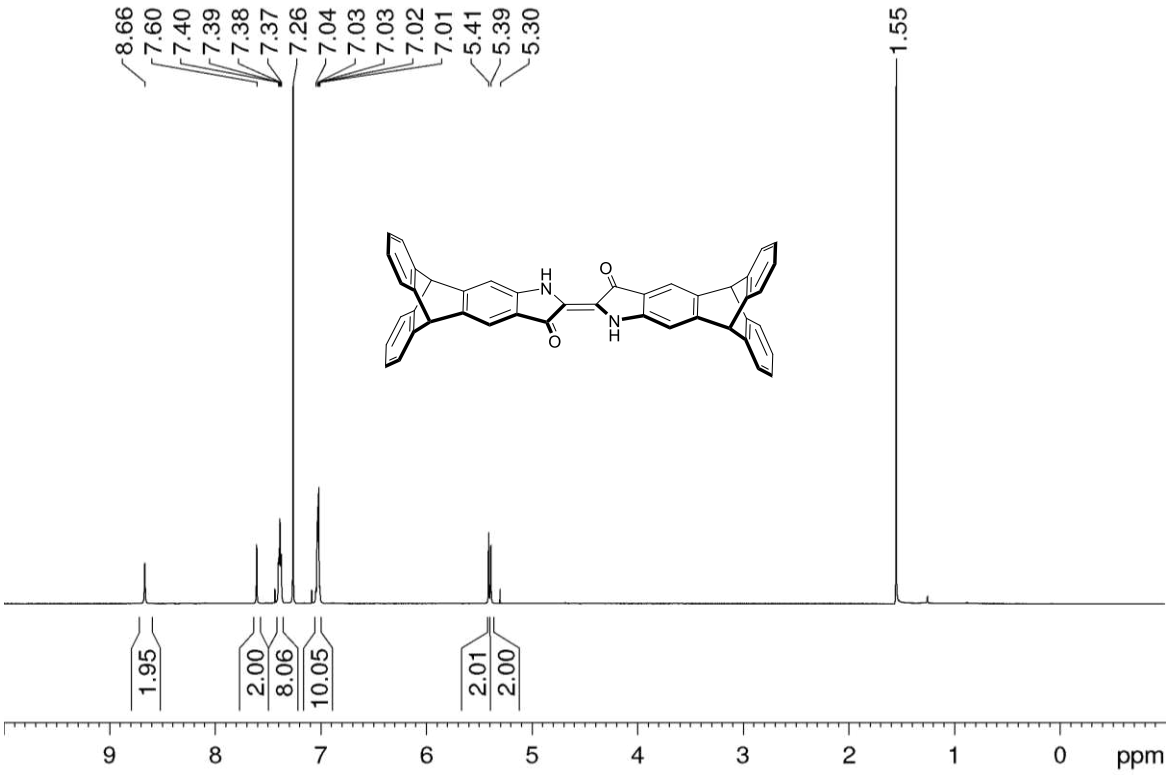


Figure S13. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound **4**.

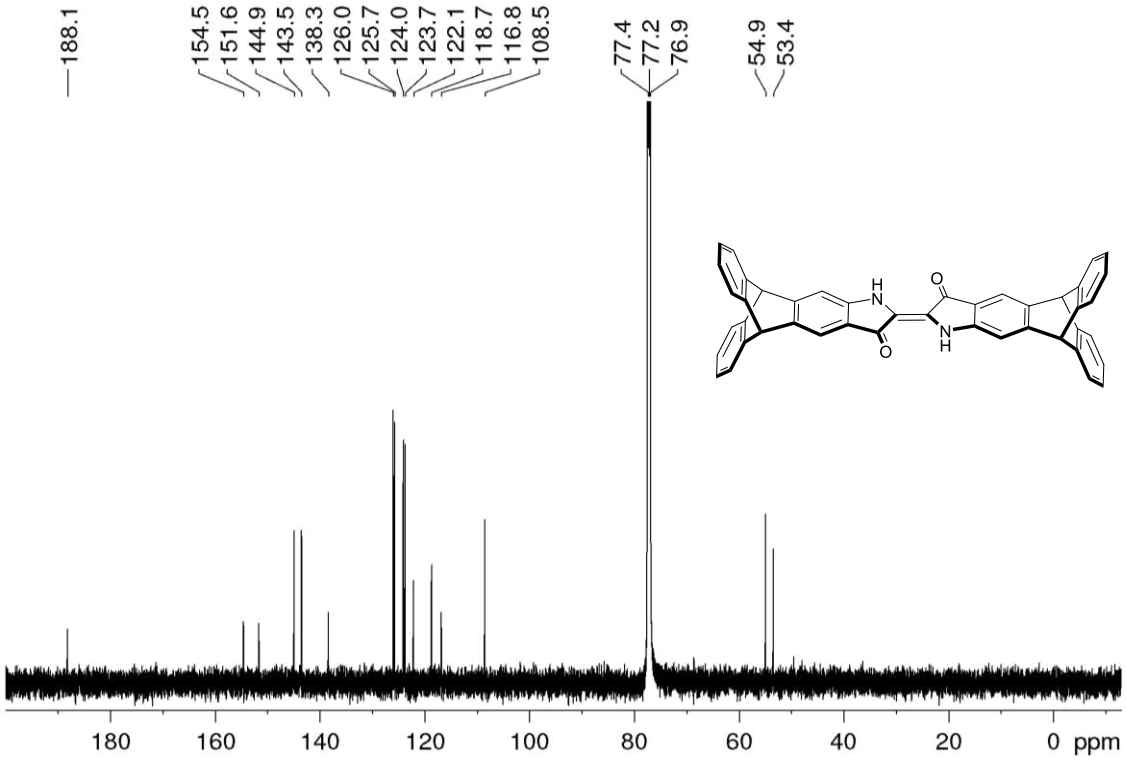


Figure S14. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of compound **4**.

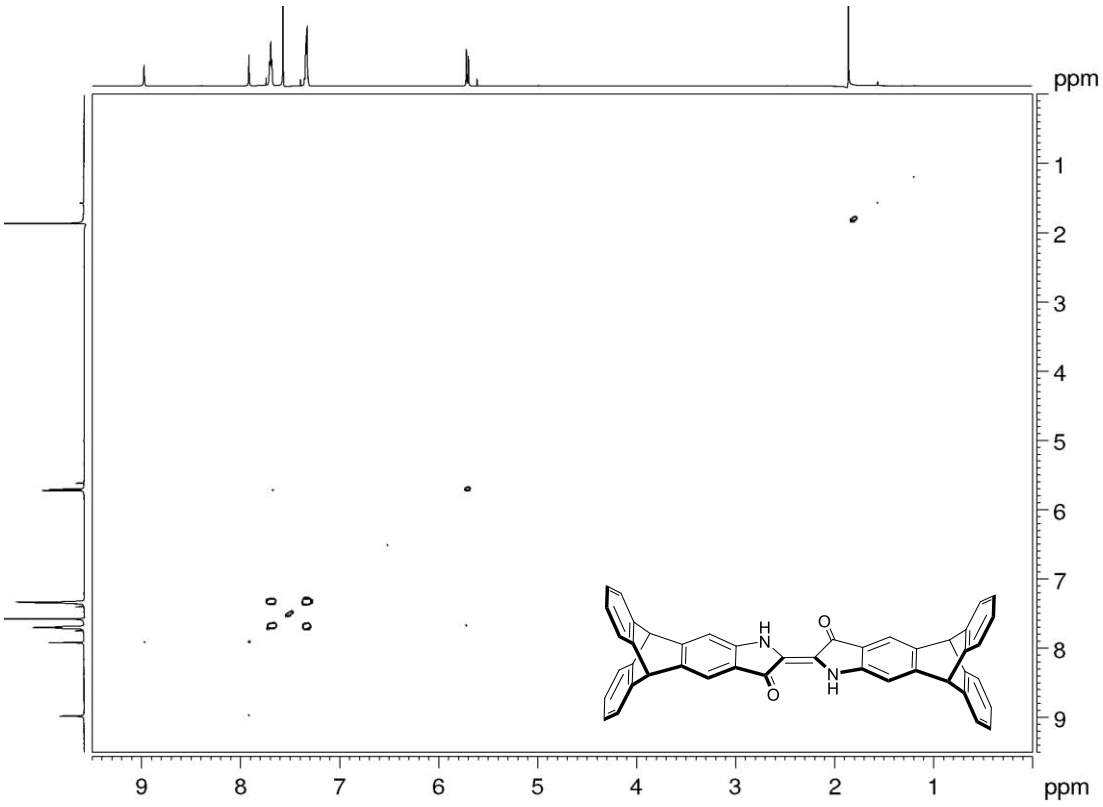


Figure S15. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, $CDCl_3$) of compound **4**.

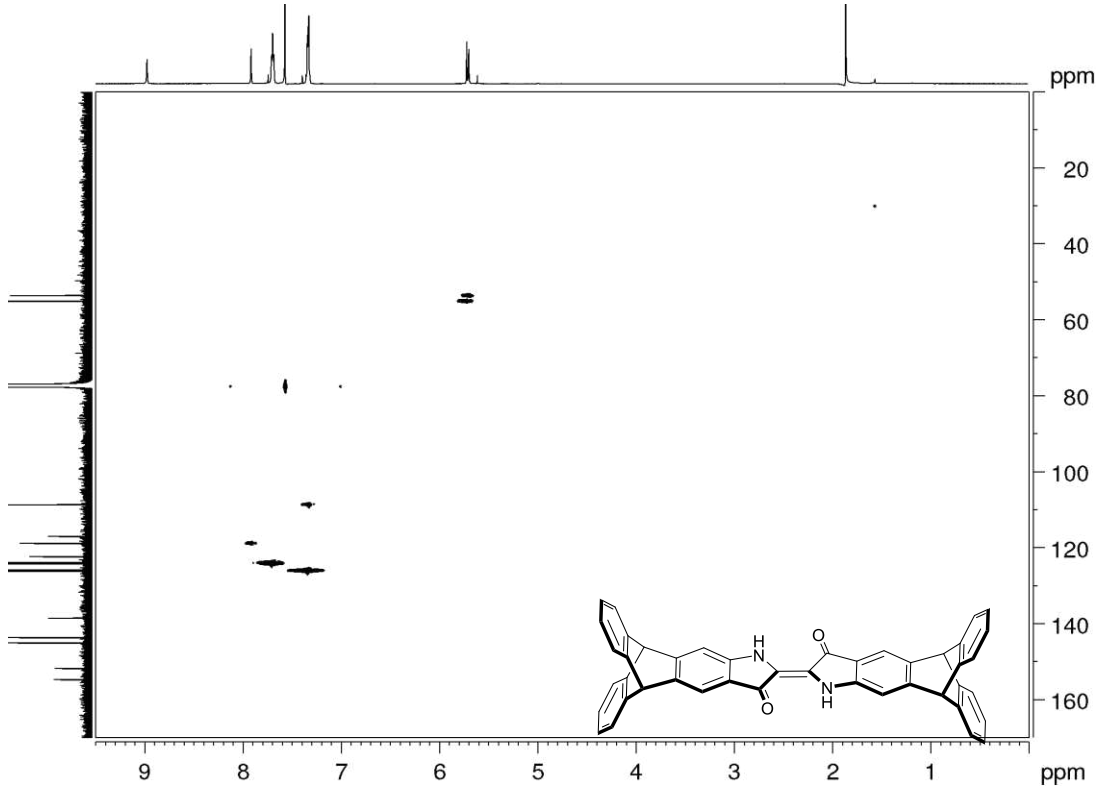


Figure S16. ^{1}H-^{13}C HSQC NMR (600 MHz, $CDCl_3$) spectrum of compound **4**.

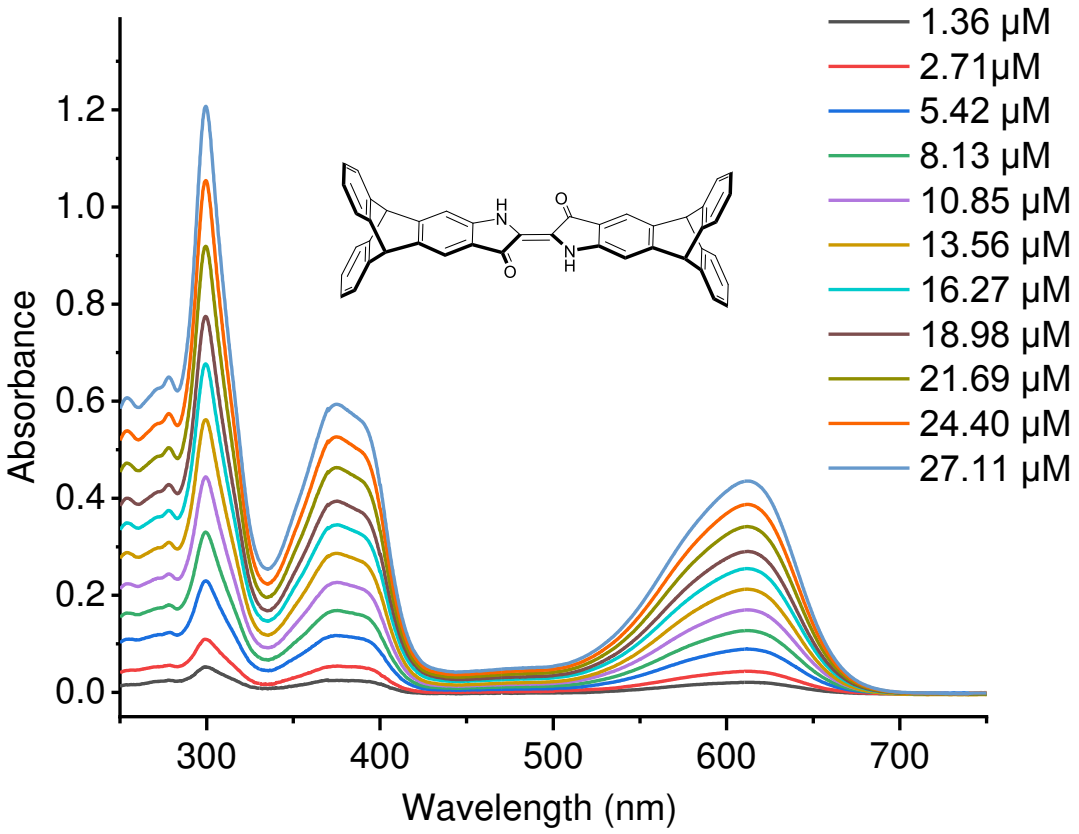


Figure S17. UV/vis spectrum ($CHCl_3$) of compound **4** at different concentrations.

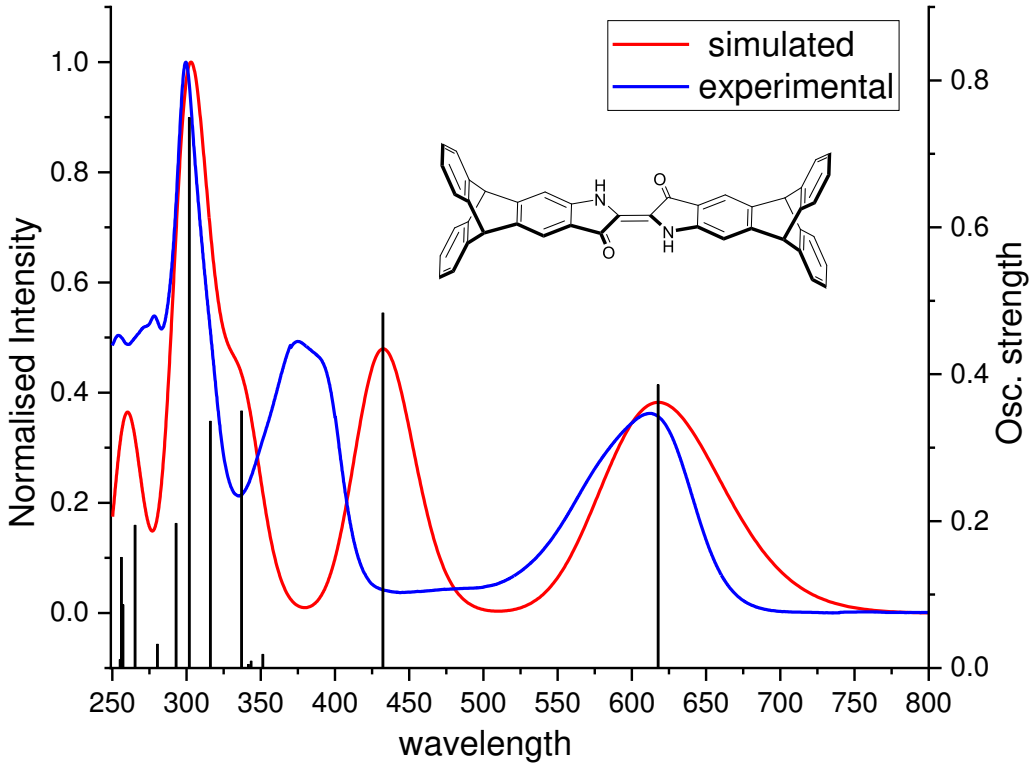


Figure S18. Overlapped simulated and experimental UV-Vis spectra (solvent: chloroform) of end capped indigo **4**.

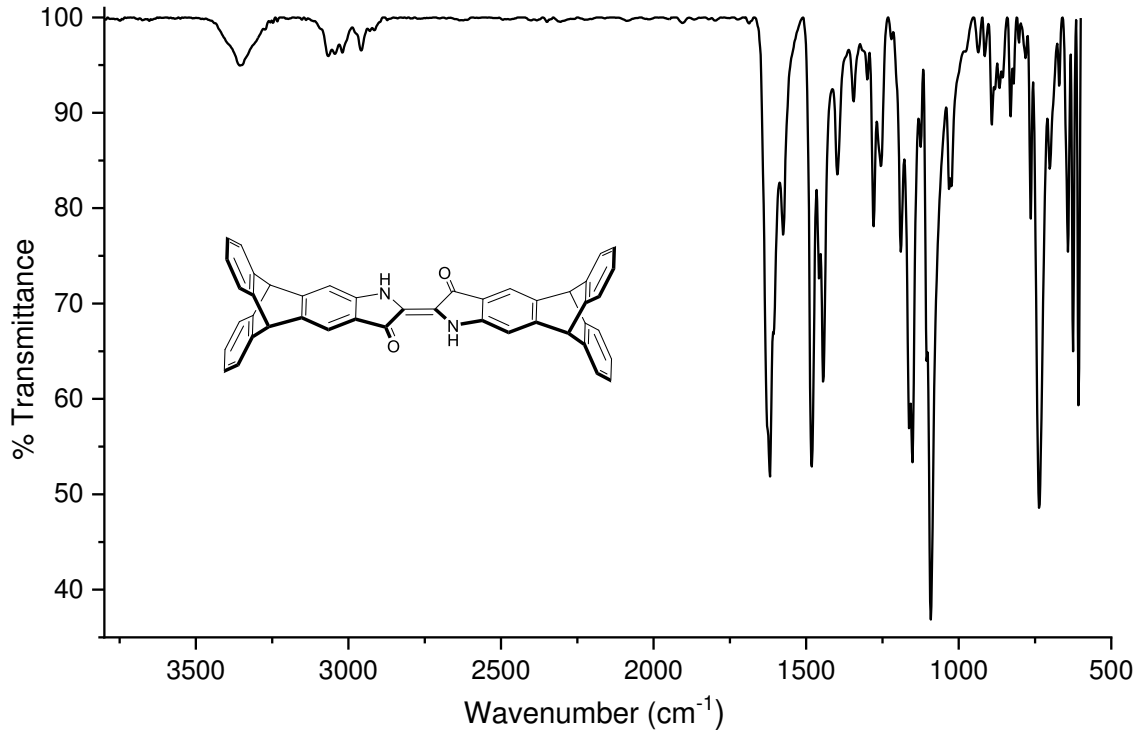


Figure S19. FT-IR (ATR) spectrum of compound **4**.

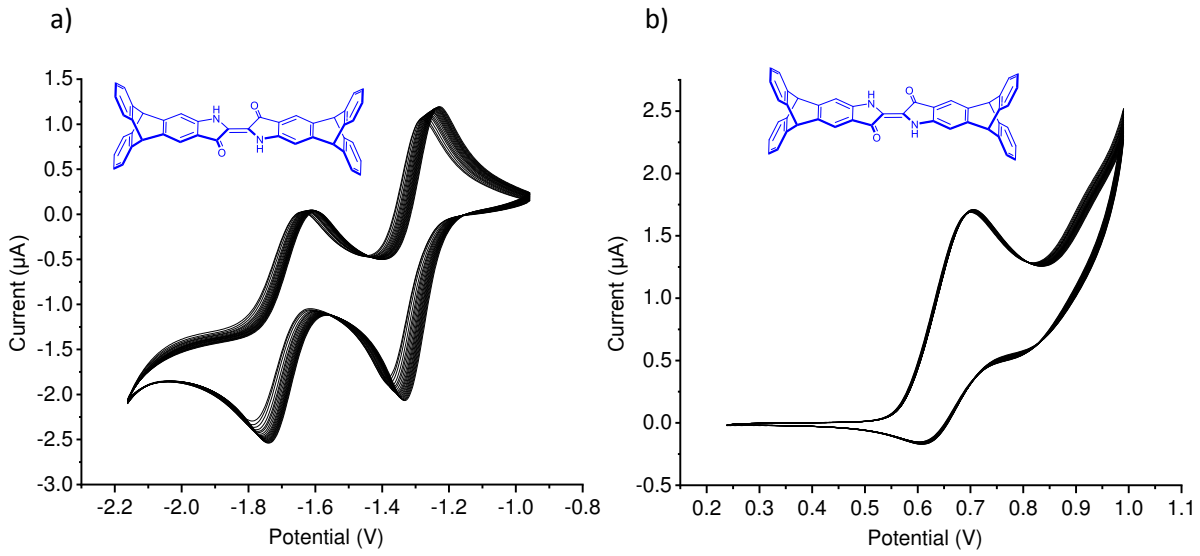


Figure S20. a) and b) cyclic voltammograms of **4** (20 cycles). (DCM, nBu_4NPF_6 (0.10M) measured at room temperature with a Pt electrode and Fc/Fc^+ as internal reference (scanning speed: 100 mV/s).

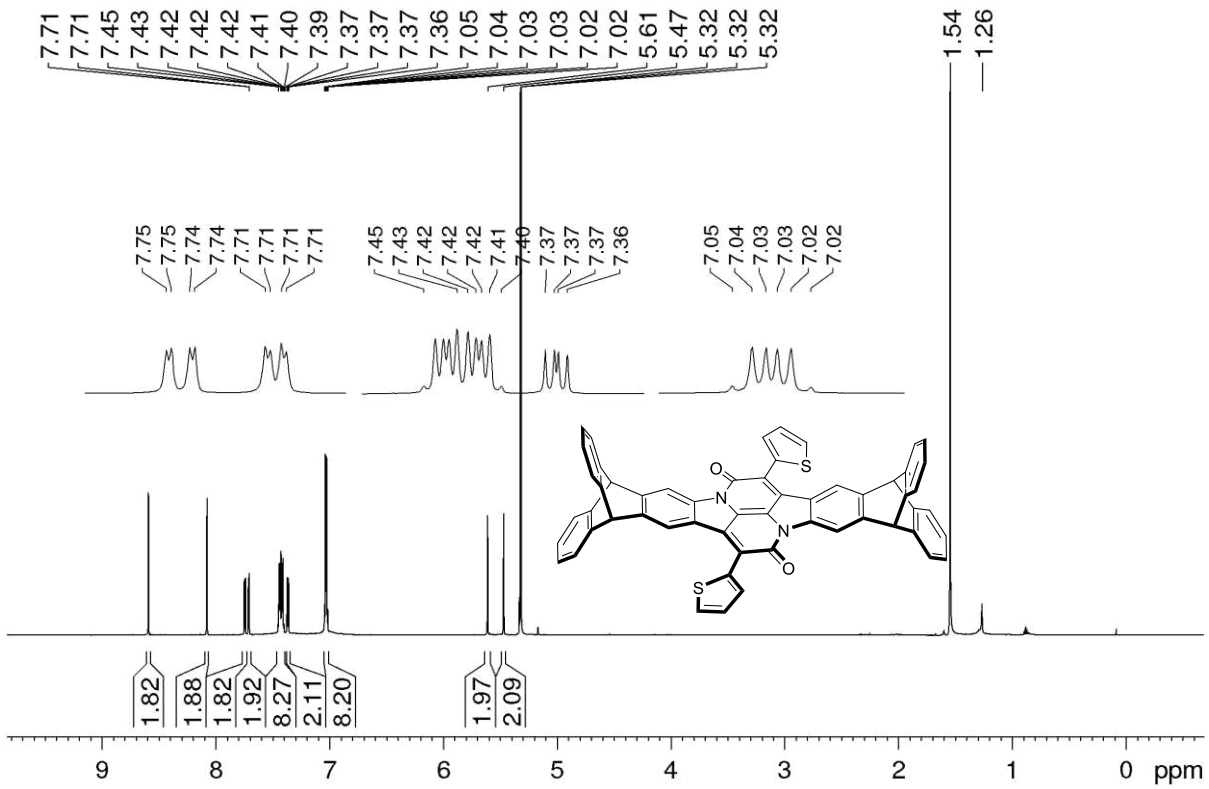


Figure S21. ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of compound **5**.

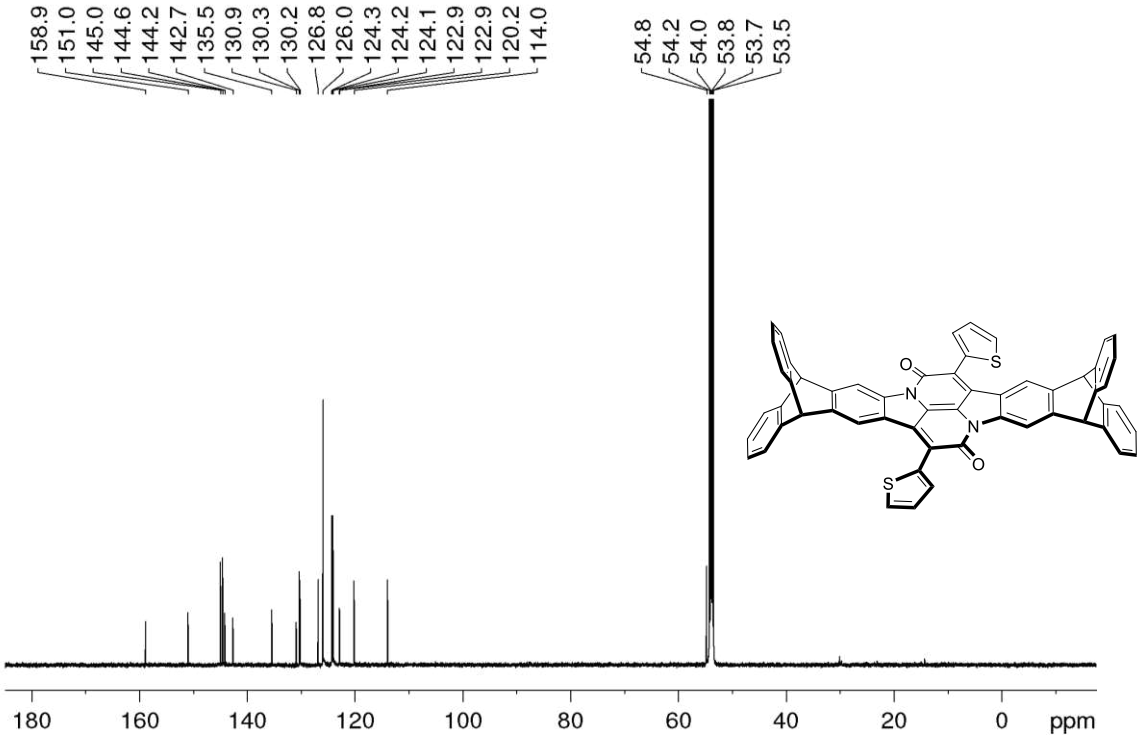


Figure S22. ^{13}C NMR (125 MHz, CD_2Cl_2) spectrum of compound **5**.

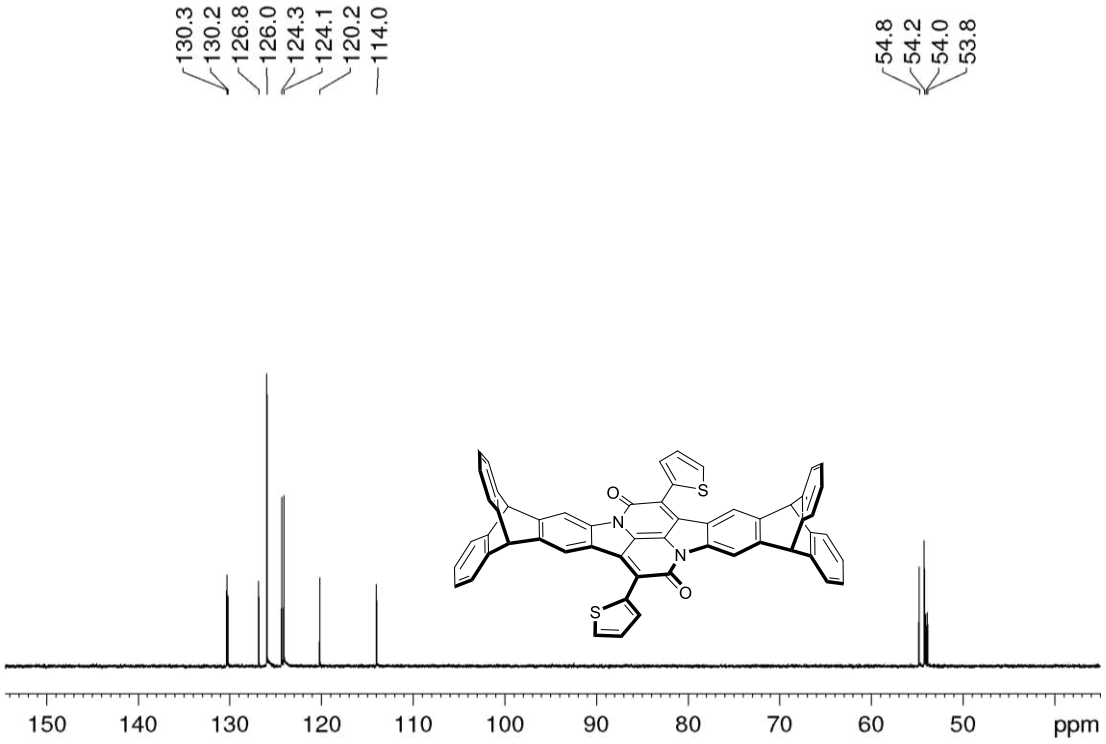


Figure S23. ^{13}C DEPT-135 NMR (125 MHz, CD_2Cl_2) spectrum of compound **5**.

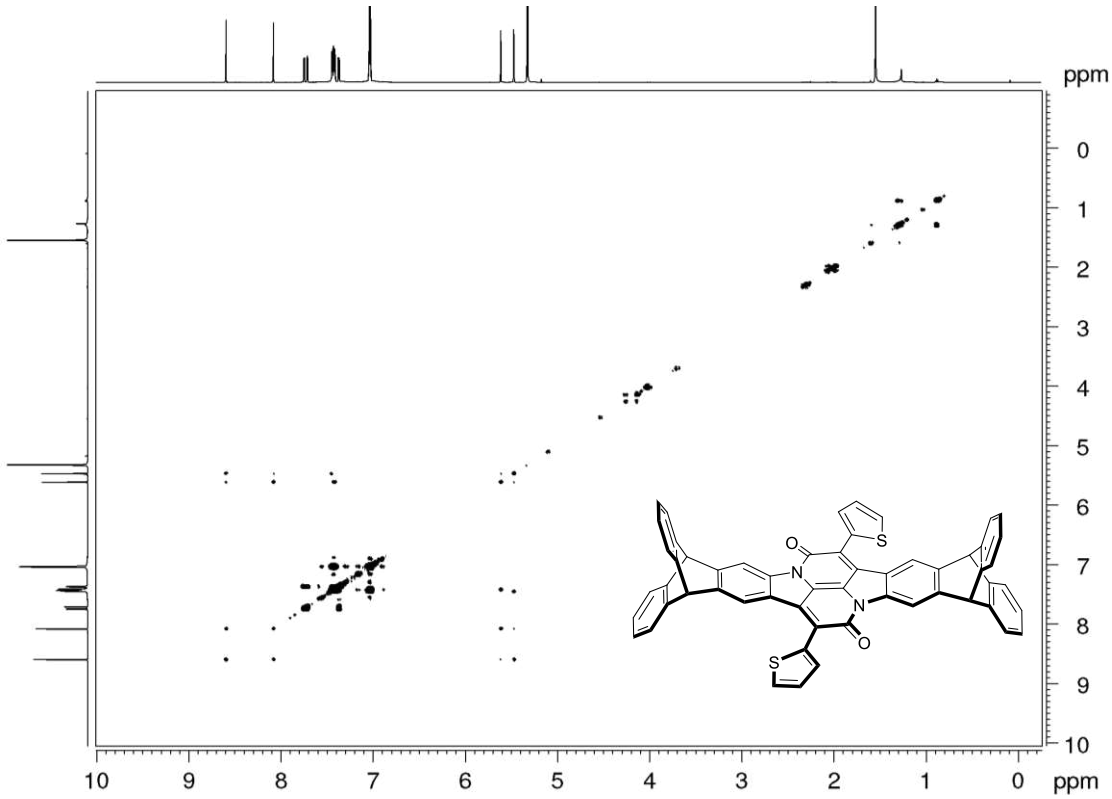


Figure S24. ^{1}H-^{1}H COSY NMR spectrum (600 MHz, CD_2Cl_2) of compound **5**.

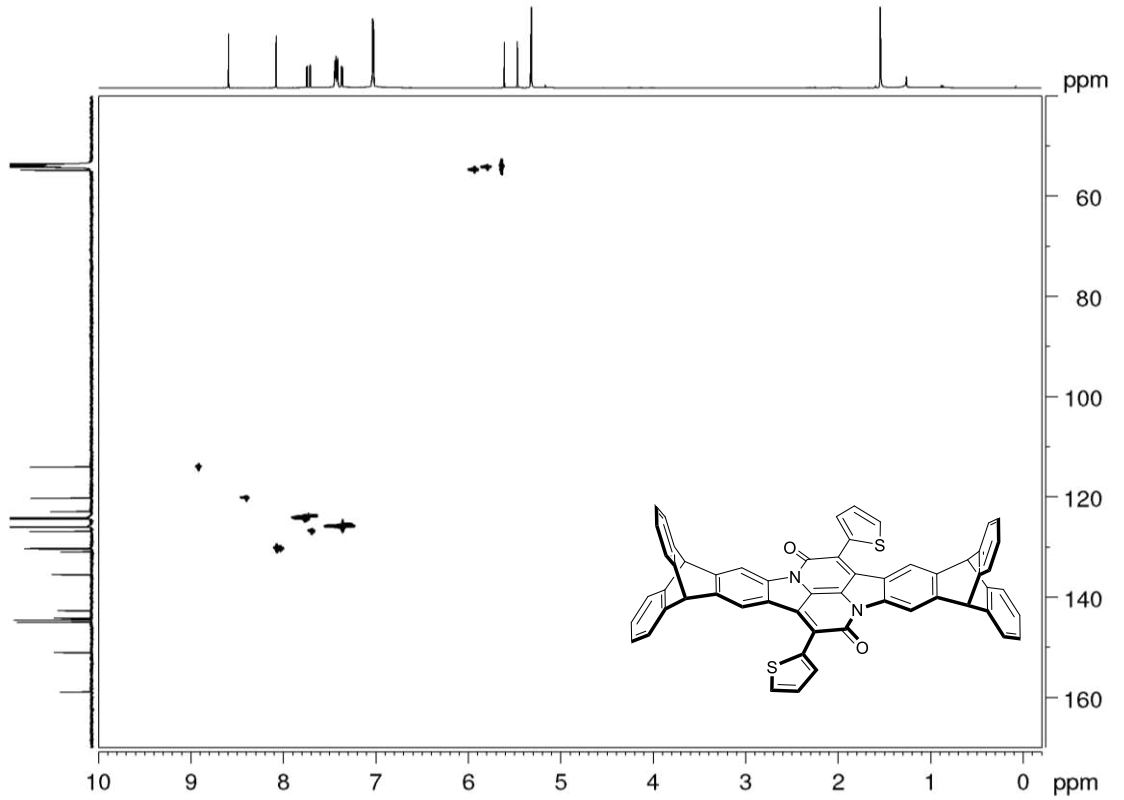


Figure S25. ^{1}H-^{13}C HSQC NMR (600 MHz, CD_2Cl_2) spectrum of compound **5**.

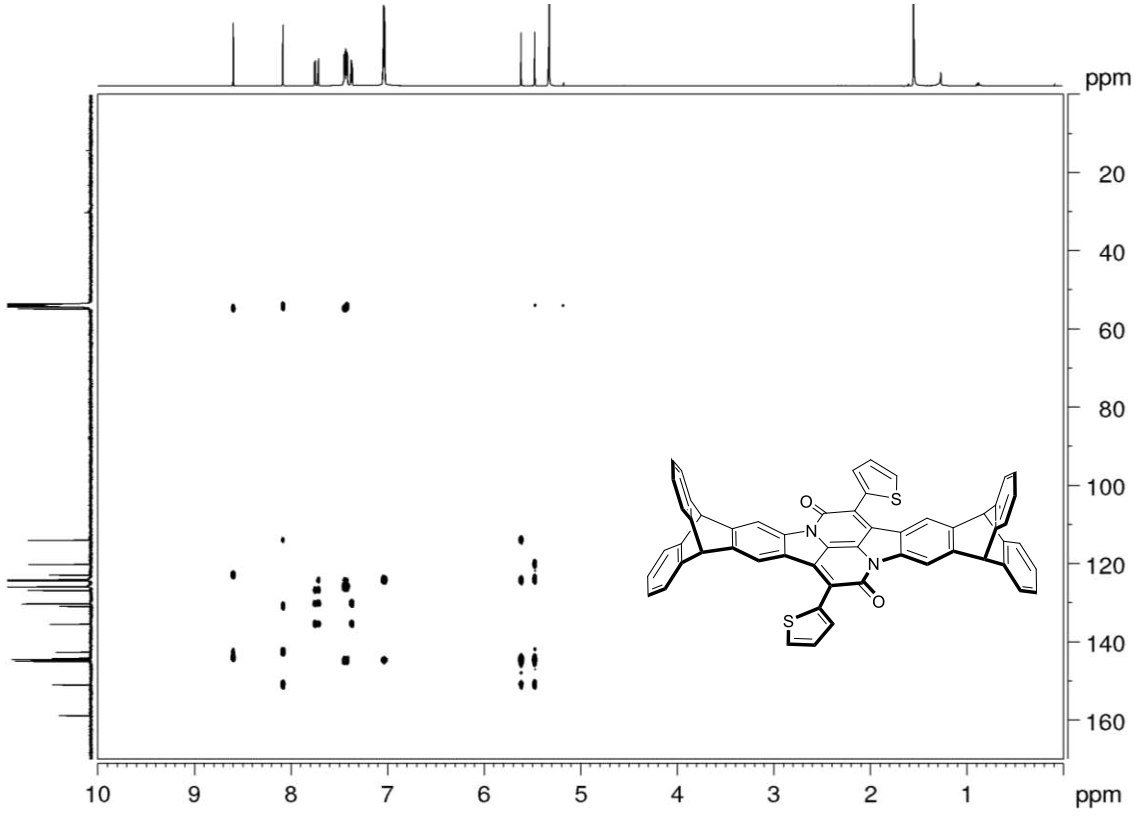


Figure S26. ^{1}H-^{13}C HMBC NMR (600 MHz, CD_2Cl_{23}) spectrum of compound **5**.

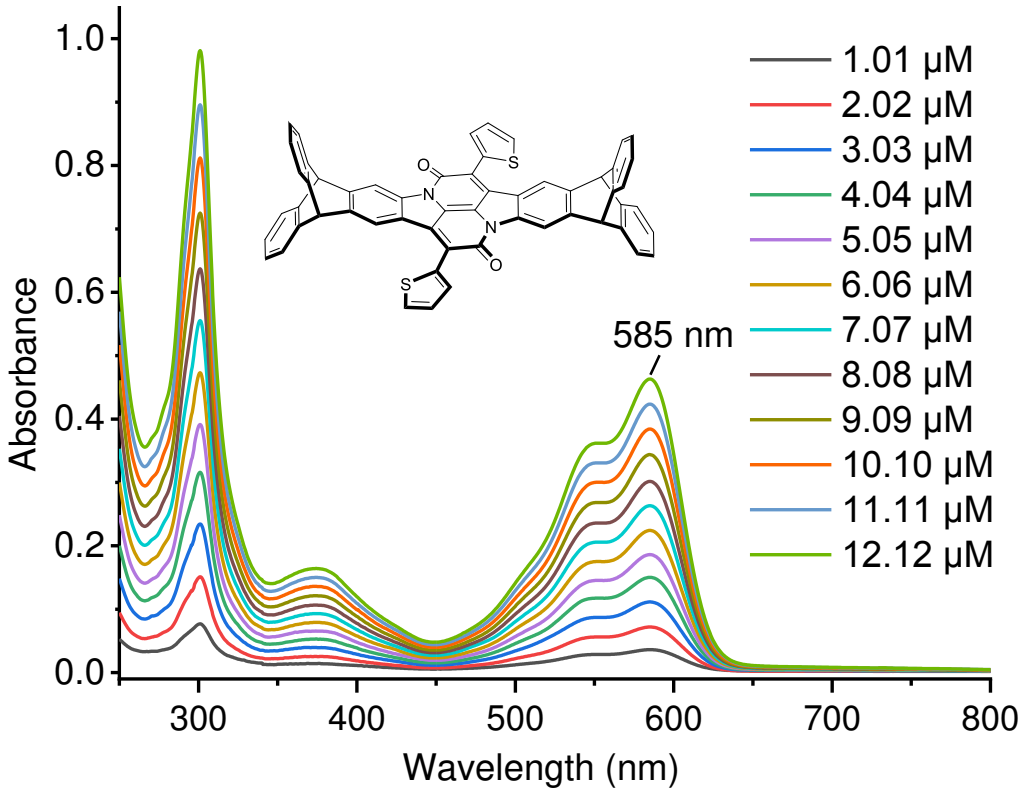


Figure S27. UV/vis spectrum (CH_2Cl_2) of compound **5** at different concentrations.

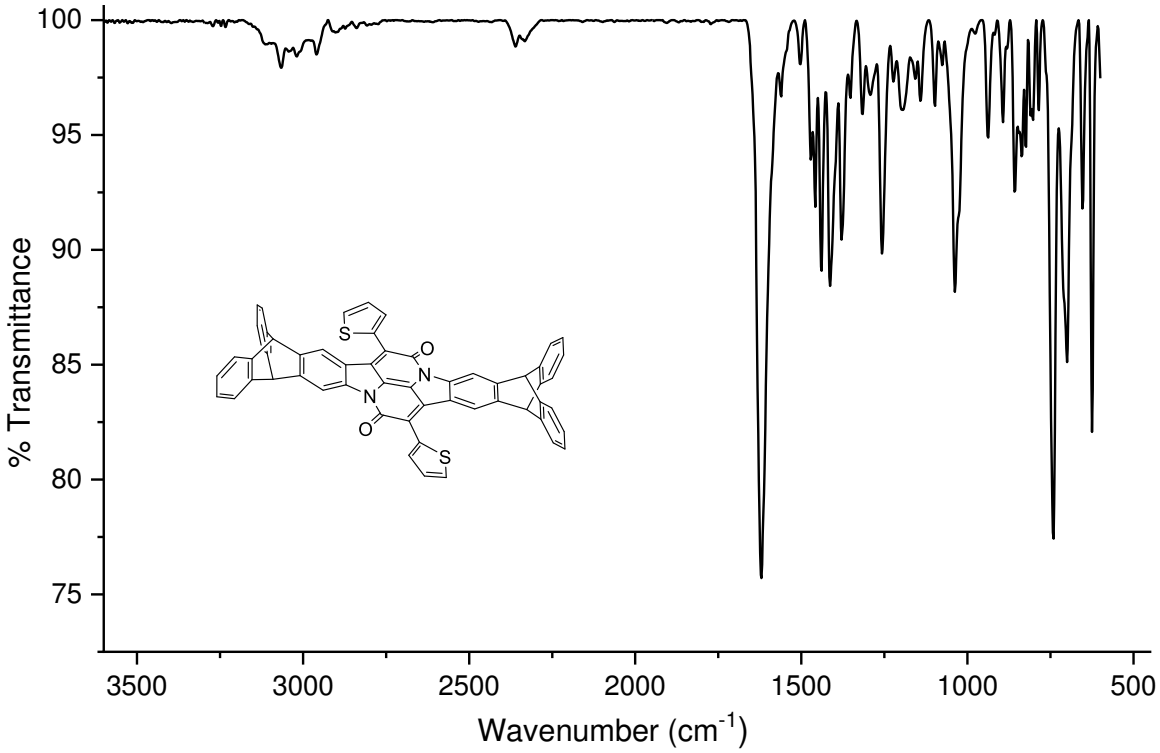


Figure S28. FT-IR (ATR) spectrum of compound **5**.

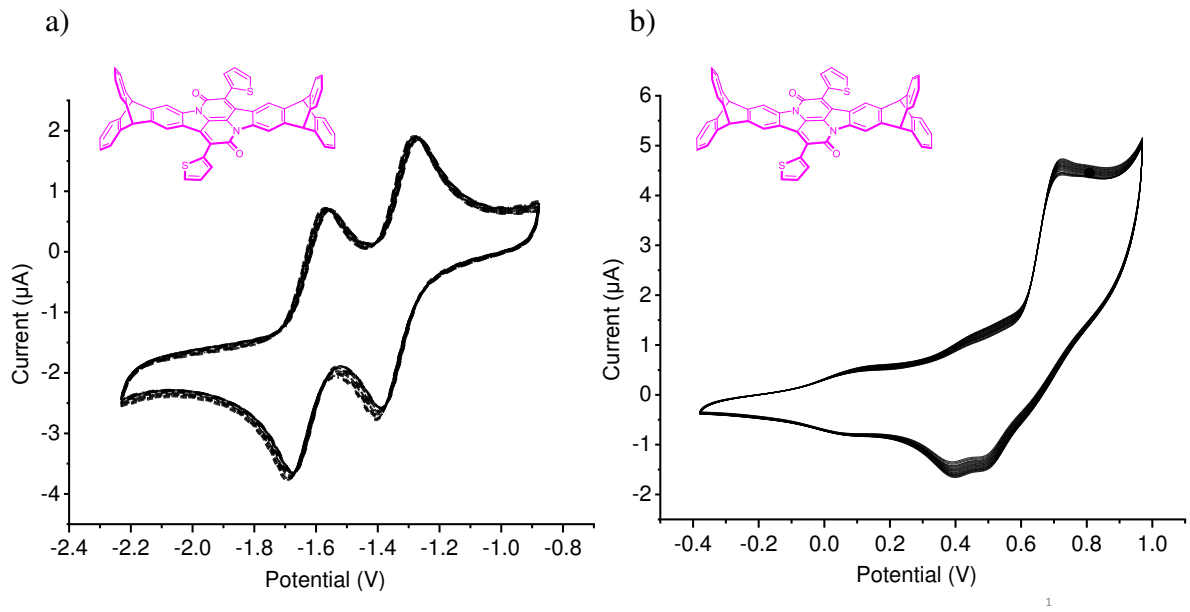


Figure S29. a) and b) cyclic voltammograms of **5** (20 cycles). (DCM, nBu_4NPF_6 (0.10M) measured at room temperature with a Pt electrode and Fc/Fc^+ as internal reference (scanning speed: 100 mV/s).

Table S1. Screened reaction conditions using PPA as a cyclization reagent for isatin **3**

Entry	**PPA (eq.)**	**Time (h)**	**T (^{o}C)**	**Color**
1	106	0.5	70	brown
2	106	2	70	brown
3	106	5	70	brown
4	106	2.5	55	red
5	106	7	55	red

Solubility studies for 4, **5**, **6** and **7** at 25 °C**:** For solubility studies saturated solution of each compound was stirred for 18 hours at RT in the different solvents. Afterwards, the solutions were filtered through the 0.2 μM PTFE membrane filter and solvents were evaporated under reduced pressure. All the compounds were dried under high vacuum for 12 hours and then weight of each sample was measured. (Microbalance was used to measure the weight of all samples.)

Table S2: Crystal data and structure refinement for compound **4**.

Identification code	**4**	
Empirical formula	$C_{47}H_{29}Cl_9N_2O_2$	
Formula weight	972.77	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Z	2	
Unit cell dimensions	a = 11.4556(6) Å	α = 85.222(4)°
	b = 11.5347(5) Å	β = 81.492(4)°
	c = 17.3049(9) Å	γ = 87.129(4)°
Volume	2251.94(19) $Å^3$	
Density (calculated)	1.43 g/cm^3	
Absorption coefficient	5.45 mm^{-1}	
Crystal shape	plank	
Crystal size	0.173 x 0.042 x 0.020 mm^3	
Crystal colour	metallic blue	
Theta range for data collection	3.8 to 57.9°	
Index ranges	-11≤h≤12, −8≤k≤12, −18≤l≤19	
Reflections collected	17845	
Independent reflections	6233 (R(int) = 0.0558)	
Observed reflections	3899 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.97 and 0.50	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6233 / 183 / 567	
Goodness-of-fit on F^2	1.02	
Final R indices (I>2sigma(I))	R1 = 0.084, wR2 = 0.220	
Largest diff. peak and hole	0.50 and -0.82 $eÅ^{-3}$	

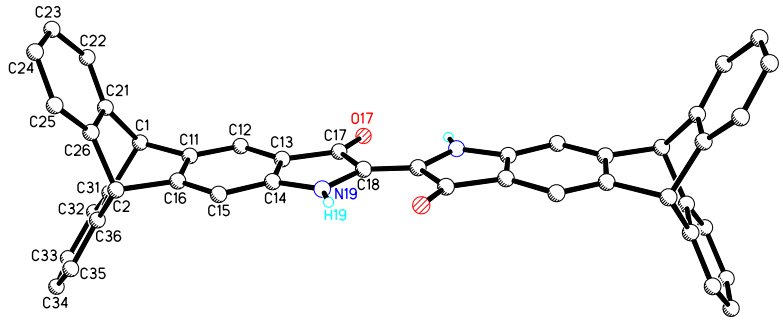


Figure S30. structure of compound **4**.

Table S3: Crystal data and structure refinement for compound **5**.

Identification code	**5**
Empirical formula	$C_{56}H_{30}N_2O_2S_2$
Formula weight	826.94
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Z	2
Unit cell dimensions	a = 11.9534(8) Å α = 90.701(5)°
	b = 11.8453(7) Å β = 96.272(5)°
	c = 15.9243(10) Å γ = 93.946 (5)°
Volume	2235.5 (2) $Å^3$
Density (calculated)	1.23 g/cm^3
Absorption coefficient	1.43 mm^{-1}
Crystal shape	plank
Crystal size	0.096 x 0.053 x 0.035 mm^3
Crystal colour	violet
Theta range for data collection	3.7 to 62.1°
Index ranges	-13≤h≤13, -13≤k≤13, -17≤l≤17
Reflections collected	23032
Independent reflections	6764 (R(int) = 0.0360)
Observed reflections	4159 (I > 2σ(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.37 and 0.71
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	23032 / 896 / 597
Goodness-of-fit on F^2	1.08
Final R indices (I>2sigma(I))	R1 = 0.078, wR2 = 0.208
Largest diff. peak and hole	0.54 and -0.36 $eÅ^{-3}$

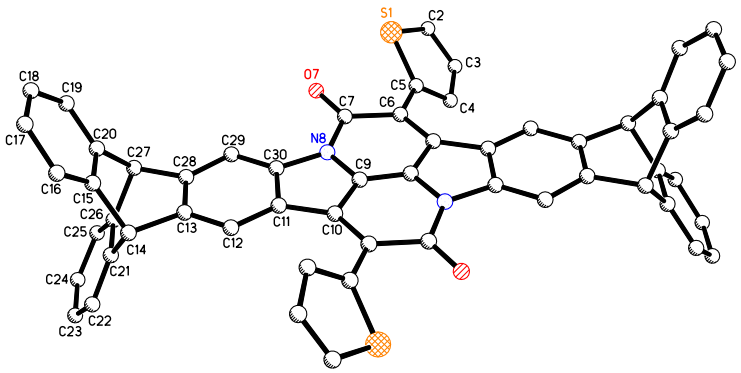


Figure S31. structure of compound **5**.

References:

[S1] W. Huang, M. Einzinger, T. Zhu, H. S. Chae, S. Jeon, S.-G. Ihn, M. Sim, S. Kim, M. Su, G. Teverovskiy, T. Wu, T. Van Voorhis, T. M. Swager, M. A. Baldo, S. L. Buchwald, *Chem. Mater.* **2018**, *30*, 1462–1466.

[S2] B. He, A. B. Pun, D. Zherebetskyy, Y. Liu, F. Liu, L. M. Klivansky, A. M. McGough, B. A. Zhang, K. Lo and T. P. Russell, *J. Am. Chem. Soc.* **2014**, *136*, 15093-15101.