Supplementary information of *New Journal of Chemistry*

Spiropyran-Based Photoswitchable Dimethylaminopyridine

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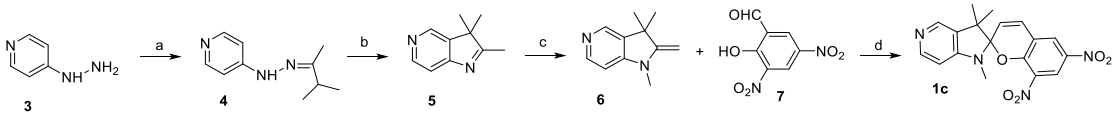
1. Generals

Reagents and solvents were purchased from commercial sources and used without further purification. Diethyl ether was freshly distilled from Na/benzophenone under a nitrogen atmosphere before utilization. The products were purified by column chromatography on silica gel (200-300 mesh). NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer. Chemical shifts for ^{1}H NMR were expressed in parts per million (ppm) relative to $CHCl_3$ (δ 7.26 ppm) or CH_2Cl_2 (δ 5.32 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. High-resolution mass spectra were recorded with an Orbitrap Fusion Lumos Tribrid mass spectrometer. UV-vis spectra were obtained from a Shimadzu UV-2660 spectrophotometer.

2. Synthesis

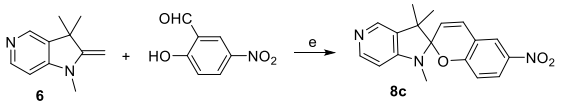


Scheme S1: Synthesis of **1c**. a: 3-methylbutan-2-one, water, r.t., 4 h, 100 %. b: (i) diethylene glycol, 270 °C, 12 h; (ii) ethylene glycol, 210 °C, overnight, 45 %; c: n-BuLi, dimethyl sulfate, Et_2O, r.t., 10 h., d: ethanol/acetonitrile (1/1, v/v), 85 °C, overnight, 27 % (two steps).
Compounds **3**[1], **4**[2], **5**[2], **7**[3] and **ZnP** [4] were prepared according to the literature methods.

Synthesis of **6**: To a solution of compound 5 (100 mg, 0.63 mmol) in dry diethyl ether (7 mL) was added n-BuLi (0.58 mL, 1.6 mol/L) dropwise via a syringe at 20 °C under a nitrogen atmosphere. The mixture was stirred for 1 h and then Me_2SO_4 (65 μL, 0.66 mmol) was added. The solution was stirred overnight at room temperature and then quenched with aqueous NaOH solution (1N). The mixture was extracted with DCM (50 mL × 2). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuum to give the crude product **6**. The crude ^{1}H-NMR data was consistent with the desired structure of **6**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 5.5 Hz, 1H), 8.12 (s, 1H), 6.46 (d, J = 5.4 Hz, 1H), 4.01 (q, J = 2.3 Hz, 2H), 3.05 (s, 3H), 1.37 (s, 6H). Note: compound **6** was not stable on silica gel. Therefore, it was used in the next step without further purification.

Synthesis of **1c:** Compound **6** (obtained in the previous step, 0.63 mmol, theoretical) and **7** (146 mg, 0.68 mmol) were dissolved in a mixture of CH_3CN (4 mL) and ethanol (4 mL). The solution was stirred overnight at 85 °C under a nitrogen atmosphere. After cooling to room temperature, the solvents were evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent, DCM: methanol = 25: 1, v/v) to afford **1c** as a light yellow solid. The product was further purified by recrystallization from DCM/n-hexane to give pure **1c** (58 mg, 27 %, two steps). Melting point of **1c** was not available, and the powder of **1c** turns black after being heated up to ~70 °C, due to some unidentified transformation. Purity: > 98 % (HPLC); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.65 (d, J = 2.7 Hz, 1H), 8.35 (d, J = 6.0 Hz, 1H), 8.25 (d, J = 2.7 Hz, 1H), 8.17 (s, 1H), 7.13 (d, J = 10.5 Hz, 1H), 6.66 (d, J = 5.9 Hz, 1H), 6.02 (d, J = 10.5 Hz, 1H), 2.91 (s, 3H), 1.43 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 154.22, 152.53, 149.40, 141.59, 140.08, 136.73, 131.86, 128.84, 126.15, 122.41, 122.22, 121.97, 108.50, 103.18, 52.25, 28.64, 26.04, 19.75; HRMS (ESI): calcd. for $C_{18}H_{17}O_5N_4$ $[M+H]^+$: 369.1194, found: 369.1194.

A mono-nitro substituted switch **8c** was prepared. It was used as a control to study the effect of nitro-group on the binding strength of the embedded DMAP.



Scheme S2: Synthesis of compound **8c**. e: ethanol/acetonitrile (1/1, v/v), 85 °C, overnight, 24 %.

Synthesis of **8c**: Following the procedure of compound **1c**, a mixture of 5-nitrosalicylaldehyde (150 mg, 0.90 mmol) and compound **6** (106 mg, 0.61 mmol, theoretical) was heated at 85 °C under nitrogen atmosphere overnight. The crude product was purified by silica gel column chromatography (eluent, DCM: methanol = 50: 1, v/v) to afford a light yellow solid. The product was further purified by recrystallization from DCM/n-hexane to give pure **8c** (47 mg, 24 %, two steps). Purity: > 98 % (HPLC); Mp: 45.7 – 46.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, J = 5.4 Hz, 1H), 8.16 (s, 1H), 8.08 – 8.00 (m, 2H), 6.97 (d, J = 10.4 Hz, 1H), 6.79 (d, J = 8.7 Hz, 1H), 6.48 (d, J = 5.4 Hz, 1H), 5.82 (d, J = 10.3 Hz, 1H), 2.79 (s, 3H), 1.34 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.14, 153.94, 150.05, 142.35, 141.52, 131.78, 129.00, 126.22, 122.95, 120.67, 118.52, 115.65, 105.59, 102.74, 51.56, 28.41, 25.90, 19.97. HRMS (ESI): calcd. for $C_{18}H_{18}O_3N_3$ $[M+H]^+$: 324.1342, found: 324.1339.

3. Reversible Switching

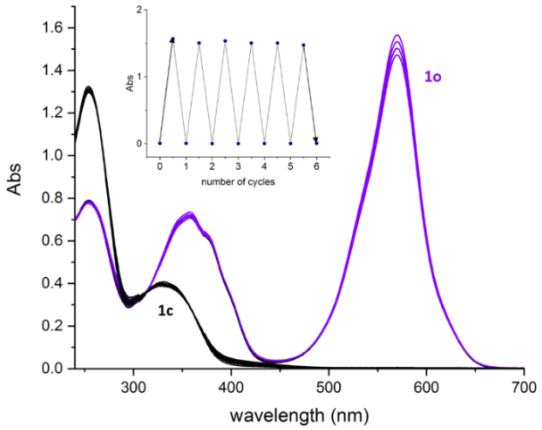


Figure S1: Absorption spectral changes of **1c** (50 μM) in DCM, after alternative irradiation at 330 and 570 nm.

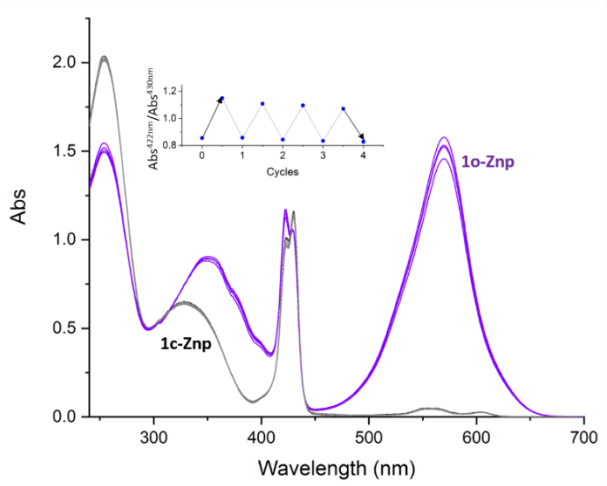


Figure S2: Reversible coordination of the **1-ZnP** complex, initiated by irradiation at 330 or 570 nm, [**1**] = 75 μM, [**ZnP**] = 2.5 μM. A loss of fidelity after repetitive irradiation (inset) might be caused by the decomposition of **ZnP** under irradiation.

4. Thermal 1o-to-1c transformation

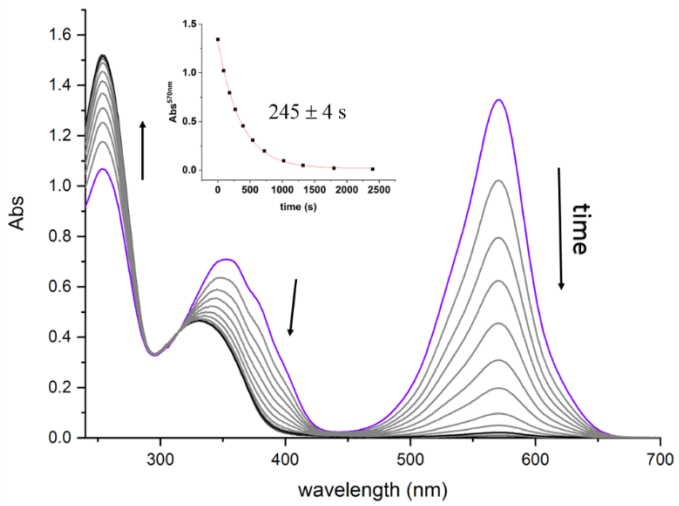


Figure S3: Absorption spectral change following the thermal **1o**-to-**1c** transformation at 20 °C in DCM ([**1**] = 60 μM). Inset: absorption decay curve monitored at 570 nm. The half-life time $\tau^{1/2}$ at 20 °C was determined to be 245 s.

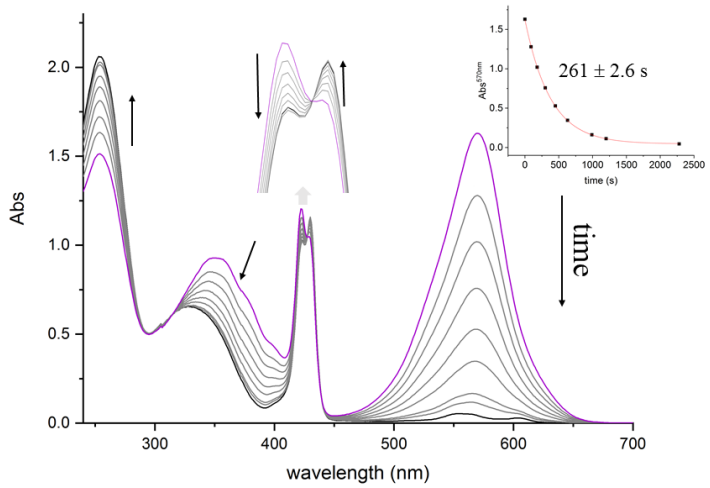


Figure S4: Absorption spectral change following the thermal **1o**-to-**1c** transformation at 20 °C in DCM ([**1**] = 75 μM) in the presence of **ZnP** (2.5 μM). Inset: enlarged absorption at the Soret band and the decay curve monitored at 570 nm. The half-life time $\tau^{1/2}$ was determined to be 261 s.

5. Molar absorption coefficient of 1o

The molar coefficient of **1o** was determined by a combination of the ^{1}H-NMR and UV-vis absorption measurements at 263 K. Note: at 263 K, **1o** was stable without significant **1o**-to-**1c** transformation, see Figure S5.

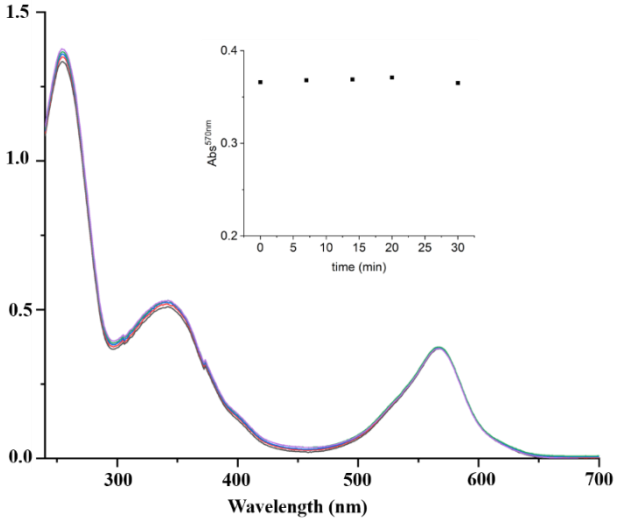


Figure S5: UV-vis absorption measurement for the mixture of **1o** and **1c** within a period of 30 min. Inset: Absorption monitored at 570 nm. The result indicated a good thermal stability of **1o** at 263 K.

Determine the mole ratio of **1o** to **1c** by ^{1}H-NMR data:

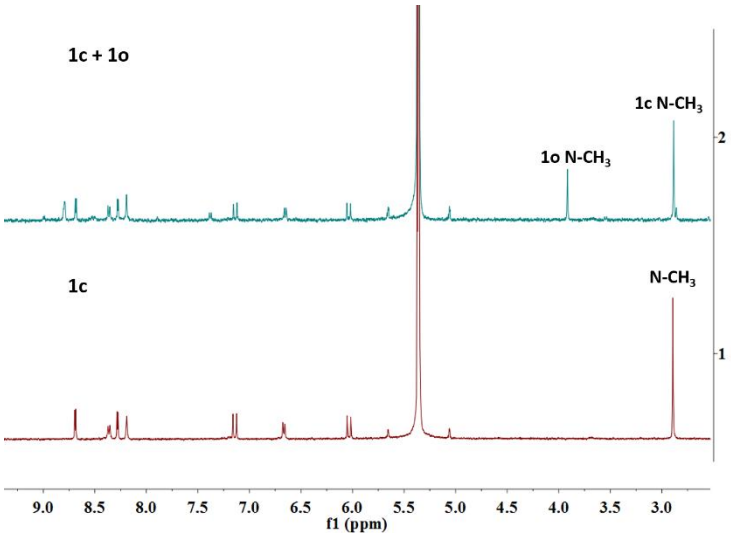


Figure S6: ^{1}H-NMR spectrum (CD_2Cl_2, 263 K) of **1c** (0.9 mM) before (bottom) and after (top) irradiation at 330 nm for 10 min. After irradiation, both **1c** and **1o** are present. Their mole ratio was determined to be ca. 71:29 (**1c**/**1o**).

Determine the molar absorption coefficient of **1o**:

The ^{1}H-NMR sample mentioned above was transferred into a 1mm quartz cell to measure the UV-Vis absorption spectrum, see Figure S7.

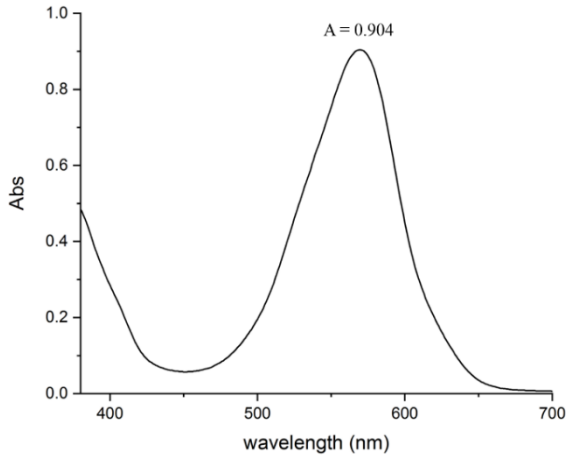


Figure S7: UV-vis absorption spectrum of a mixed solution of **1o** (0.9 mM × 29%) and **1c** (0.9 mM × 71%). Note: mole ratio of **1o** to **1c** in the mixture was determined by ^{1}H-NMR measurement, see Figure S6.

The molar absorption coefficient of **1o** at 570 nm was calculated to be 3.5×10^{4} L•mol^{-1}•cm^{-1}. **1c** has no absorption > 500 nm.

6. Mole ratio of 1c/1o in the photostationary state

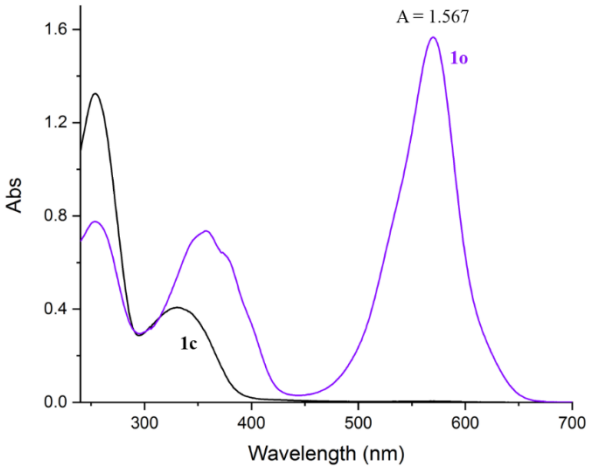


Figure S8: Absorption spectrum of a mixture of **1c** and **1o** in DCM at the photostationary state (violet), generated by irradiation at 330 nm at 20 °C ([**1**] = 50 µM, 1cm cell).

With the known molar absorption coefficient of **1o** (3.5×10^{4} L•mol^{-1}•cm^{-1}), [**1o**] was calculated to be 45 µM, and the mole ratio of **1c**/**1o** at PSS was determined to be ca. 10:90.

7. Complexation with metalloporphyrin

Zn-porphyrin and pyridine derivative associate in a 1:1 stoichiometry.[4,5] The UV-Vis absorption and fluorescence titration curves were analyzed by fitting with the following equation:

y = y0 + ((ylim-y0)/2)*(1+ x/cl + 1/(Ks*cl) ((1+ x/cl + 1/(Ks*cl))^2 - 4* x/cl)^0.5)

where y is the absorption at 422 nm (or the fluorescence at 600 nm), y0 is the absorption at 422 nm (or fluorescence of free **ZnP** at 600 nm), ylim is the absorption of the complex at 422 nm (or the fluorescence of the complex at 600 nm), x is the concentration of the ligand (pyridine, DMAP, **1c** or **8c**), Ks is the binding constant, and cl is the concentration of **ZnP**.

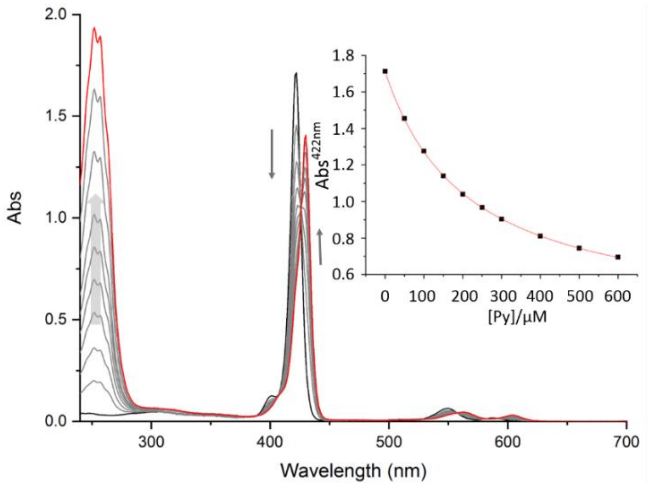


Figure S9: Complexation of pyridine to **ZnP** (2.5 μM) followed by UV-vis absorption spectra. Inset: the titration curve used for the determination of *K* (0.47 × 10^4 M^{-1}). Absorption around 250 nm results from the increased concentration of pyridine.

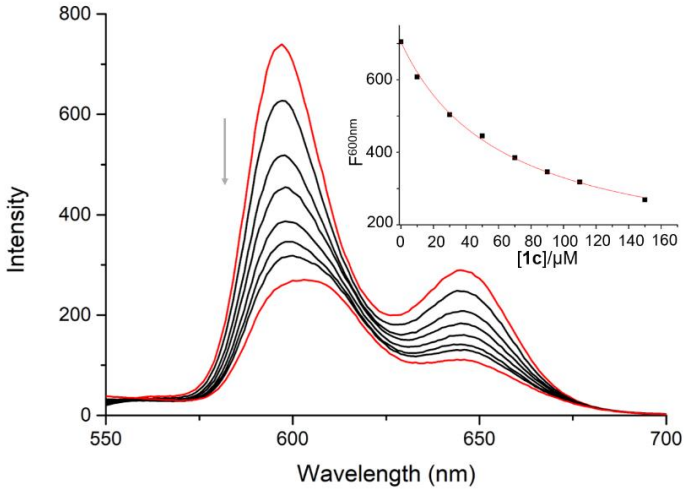


Figure S10: Complexation of **1c** to **ZnP** (0.5 μM, λ_{ex} = 426 nm) followed by fluorescence spectra. Inset: nonlinear fitting of the titration data gives a binding constant of 1.6 × 10^4 M^{-1}.

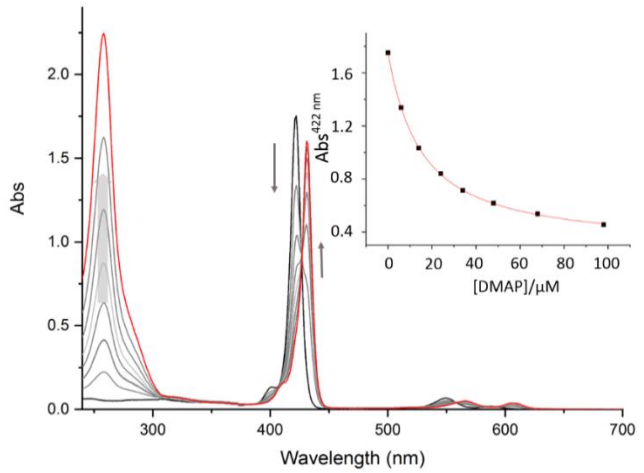


Figure S11: Complexation of DMAP to **ZnP** (2.5 μM) followed by UV-vis absorption spectra. Inset: the titration curve used for the determination of *K* (7.3×10^4 M^{-1}). Absorption around 250 nm results from the increased concentration of DMAP.

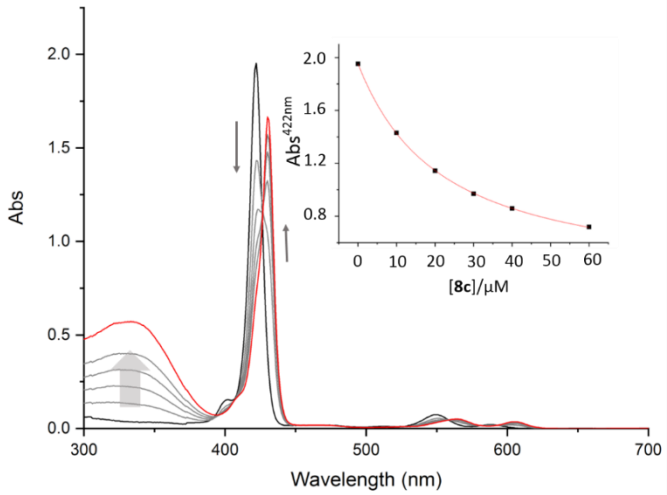


Figure S12: Complexation of **8c** to **ZnP** (2.5 μM) followed by UV-vis absorption spectra. Inset: the titration curve used for the determination of *K* (5.0×10^4 M^{-1}). Absorption around 330 nm results from the increased concentration of **8c**. Note: binding constant of **8c**-**ZnP** complex was much larger compared with that of **1c**-**ZnP** (1.8×10^4 M^{-1}), a result indicating that the electron-withdrawing nitro-group weakens the complexation.

In the presence of **3o**, the Soret band of **ZnP** do not change, see below, indicating that the phenolate moiety of the SP switch in the open state do not interact with **ZnP**.

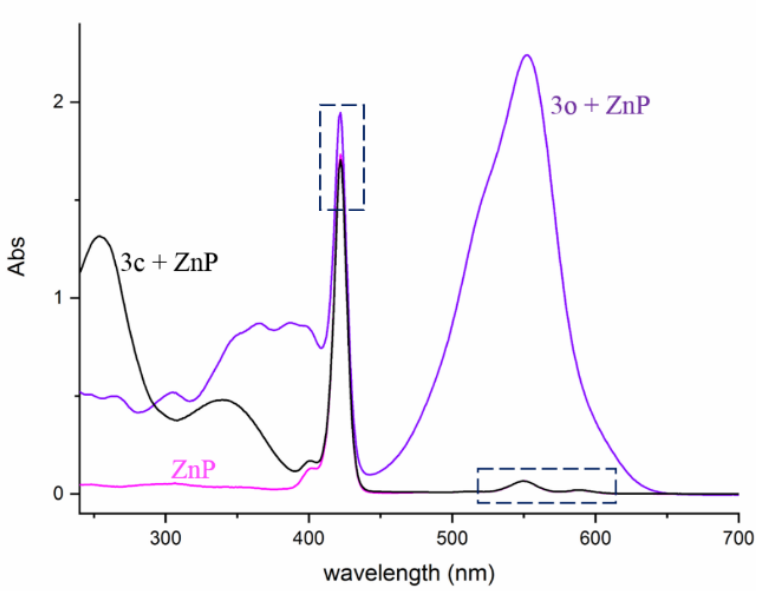


Figure S13: Absorption spectra of **ZnP** (2.5 μM, pink line) in the presence of **3o** (50 μM, violet line) or **3c** (50 μM, black line), no shift of Soret band (422 nm) and Q-band (520-630 nm) was observed.

Complexation of 1o to ZnP

The association constant *K* of the **1o-ZnP** complex was obtained by quantitative analysis of the spectral data (Figure 5 in the text).

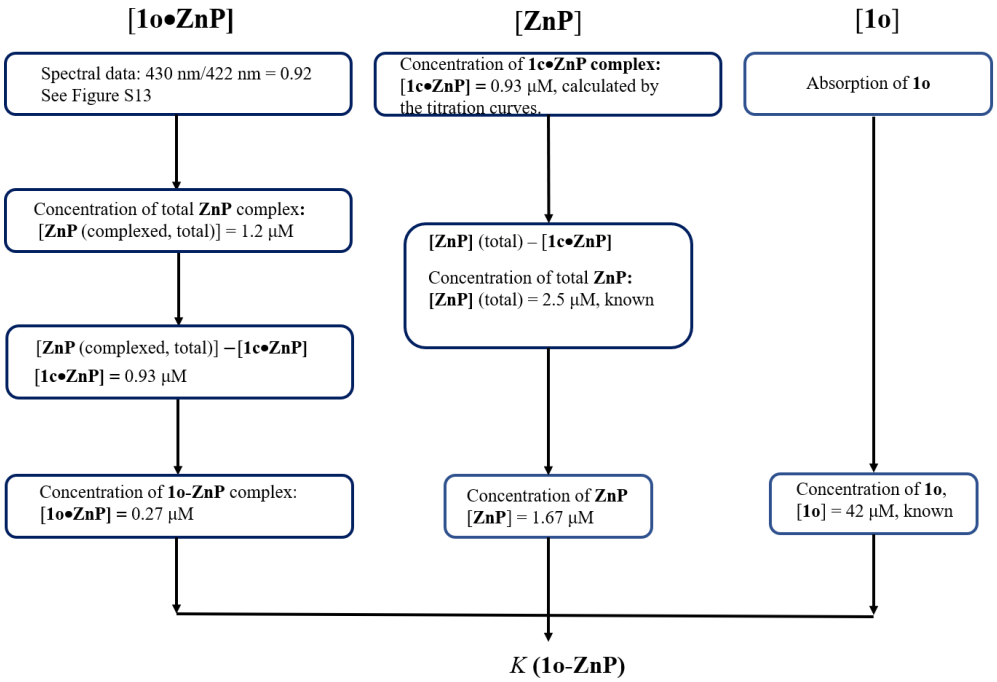
For determining *K*, we make the following approximation: delta epsilon for ZnP complex is identical for **1o** and **1c**.

$K = [\mathbf{1o{\bullet}ZnP}]/(([\mathbf{1o}]-[\mathbf{1o{\bullet}ZnP}])\times([\mathbf{ZnP}]-[\mathbf{1o{\bullet}ZnP}]))$

Where [**1o•ZnP**] is the concentration of **1o-ZnP** complex, [**1o**] is the concentration of **1o,** [**ZnP**] is the concentration of free **ZnP**.

Concentrations of **1o, ZnP,** and **1o•ZnP** complex were calculated based on Scheme S3:

Scheme S3:



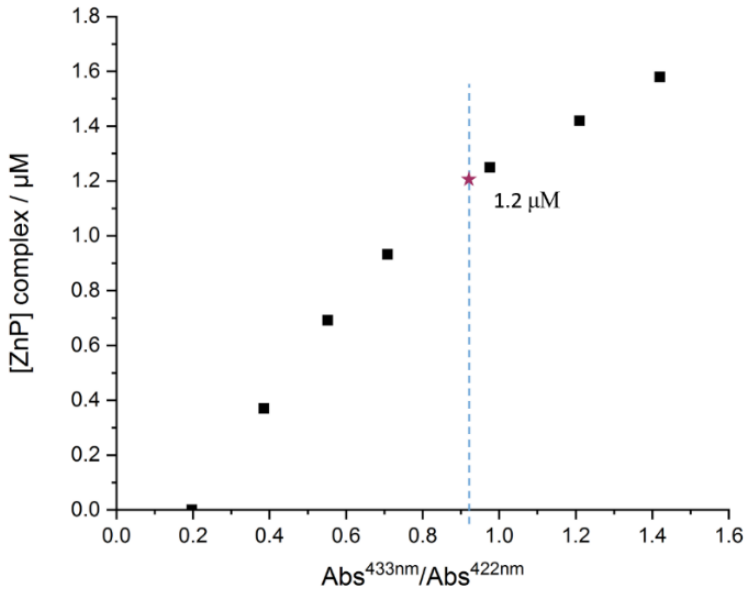


Figure S14: Theoretical concentration of the **ZnP** complex as a function of Abs^{433nm}/Abs^{422nm}. When $Abs^{433nm}/Abs^{422nm} = 0.92$, concentration of the **ZnP** complex was determined to be 1.2 μM.

8. DFT calculations

The Gaussian 16 suite of program[6] was employed for all the calculations. The geometry was optimized at CAM-B3LYP/6-311+ G (d, p) level of theory.[7] The charge distribution was studied by using natural bond orbital (NBO) analysis at the same level of theory based on the optimized structure.[8,9] Spartan software, MM force field, was used to build the initial molecular models.

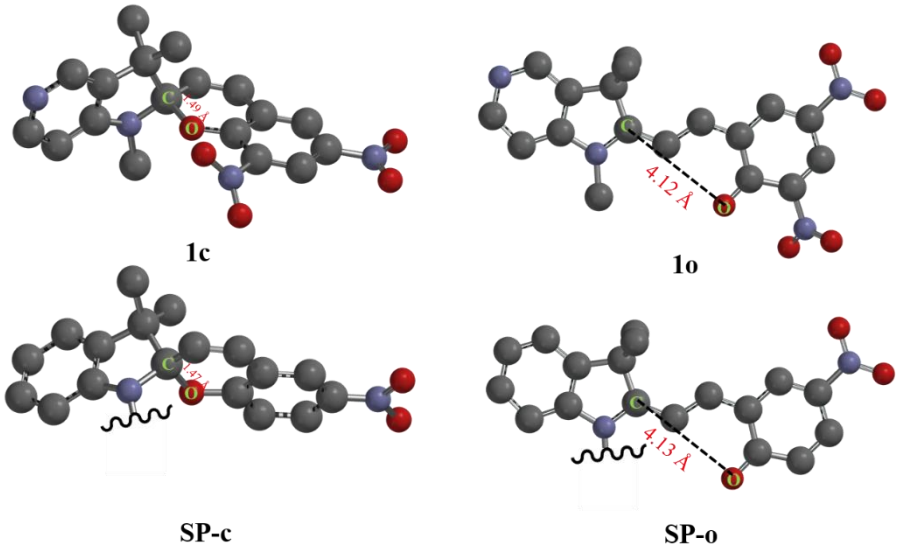


Figure S15: Optimized **1c** and **1o**, which are comparable to the calculated structures of spiropyran compounds (**SP-c**, **SP-o**) known in literature.[7]

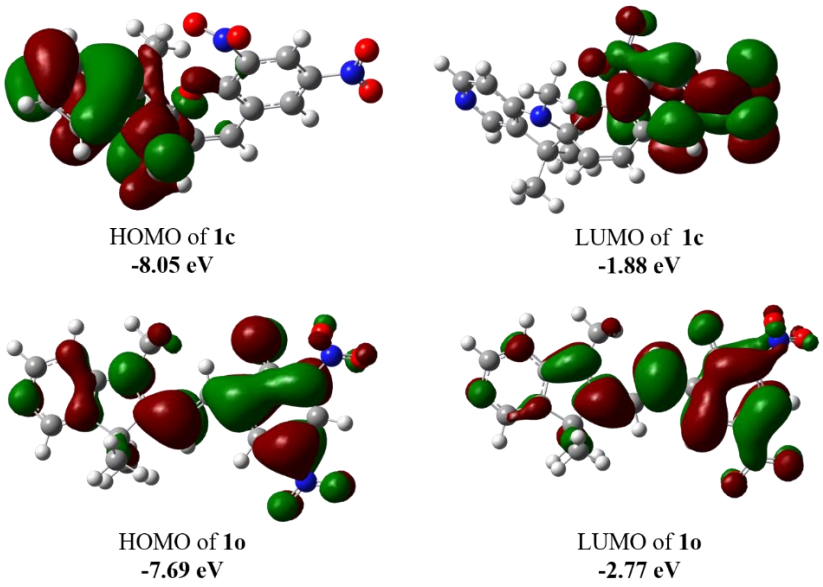


Figure S16: Frontier molecular orbitals of **1c** and **1o** calculated at the CAM-B3LYP/6-311+ G (d, p) level of theory.

Table S1: Cartesian coordinates and energies of compound **1c**.

Electronic energies (E) = -1290.21309296 Hartree

H	-4.18914	0.6507	-2.34883
C	-4.14005	0.6355	-1.264
C	-4.09324	0.68498	1.47898
C	-3.16776	-0.07588	-0.60298
N	-5.07215	1.35266	-0.62182
C	-5.03351	1.36308	0.70422
C	-3.14731	-0.05041	0.78888
H	-5.79764	1.95709	1.19653
H	-4.11517	0.75372	2.55829
C	-2.06695	-0.99014	-1.09576
C	-2.67212	-2.36344	-1.43132
H	-3.39216	-2.24538	-2.24208
H	-3.20109	-2.79231	-0.57814
H	-1.90489	-3.06672	-1.76293
C	-1.29262	-0.45719	-2.29815
H	-1.94421	-0.44635	-3.17399
H	-0.4454	-1.10773	-2.53365
H	-0.9285	0.55435	-2.12844
N	-2.10619	-0.83503	1.27255
C	-1.63717	-0.7013	2.63696
H	-1.21912	0.29169	2.8348
H	-0.87159	-1.45183	2.83145
H	-2.4634	-0.88068	3.32526
C	-1.1789	-1.08107	0.20243
C	-0.42349	-2.36086	0.37833
H	-1.03195	-3.24145	0.53303
C	0.90214	-2.44146	0.34664
H	1.40033	-3.39618	0.46921
O	-0.25919	0.07631	0.18296
C	1.72651	-1.25602	0.16797
C	3.20482	1.10935	-0.06107
C	3.10856	-1.29787	0.114
C	1.05923	-0.02138	0.08705
C	1.82554	1.14324	-0.03502
C	3.82947	-0.12033	-0.00058
H	3.77804	2.02265	-0.13338
N	1.17974	2.45747	-0.15024
O	1.68479	3.37242	0.47037
O	0.21334	2.54929	-0.87642
N	5.29452	-0.17832	-0.04949

O	5.89666	0.87156	-0.15308
O	5.81425	-1.27605	0.01668
H	3.63684	-2.24017	0.17242

Table S2: Cartesian coordinates and energies of compound **1o**.

Electronic energies (E) = -1290.19667147 Hartree

H	-5.51551	-2.43982	0.06271
C	-5.4845	-1.35472	0.03521
C	-5.52814	1.39294	-0.03397
C	-4.28962	-0.66895	0.01261
N	-6.66579	-0.73109	0.02468
C	-6.67105	0.59679	-0.00884
C	-4.32393	0.71671	-0.02212
H	-7.64836	1.06826	-0.01649
H	-5.61077	2.4705	-0.06104
C	-2.85217	-1.14038	0.01852
C	-2.55103	-1.92098	1.31031
H	-3.19339	-2.80179	1.35973
H	-2.74554	-1.31069	2.19331
H	-1.51545	-2.25677	1.34959
C	-2.56181	-1.9884	-1.23243
H	-3.20395	-2.87077	-1.22953
H	-1.52635	-2.32554	-1.26274
H	-2.76424	-1.42585	-2.14485
C	-2.10706	0.19821	-0.01996
C	-0.7502	0.46721	-0.03697
H	-0.42474	1.49545	-0.07401
C	0.2536	-0.49438	-0.01233
H	-0.03358	-1.53948	0.01948
O	1.54248	2.10701	-0.16081
C	1.63354	-0.27136	-0.0186
C	4.45169	0.00272	-0.00976
C	2.48064	-1.40288	0.00611
C	2.21281	1.08737	-0.05478
C	3.67745	1.10745	0.00241
C	3.83562	-1.273	0.00004
H	5.53063	0.07972	-0.01846
N	4.35132	2.40723	0.05808
O	5.30785	2.57536	-0.67794
O	3.93077	3.21683	0.85507
N	4.67285	-2.46223	0.01709
O	5.88023	-2.30254	0.02444

O	4.12111	-3.55024	0.02266
H	2.05476	-2.39837	0.0257
N	-3.01034	1.20533	-0.0402
C	-2.65734	2.6153	-0.07908
H	-2.08496	2.83976	-0.98014
H	-2.05913	2.88185	0.7932
H	-3.56616	3.20962	-0.07961

9. HPLC analysis

The purities of compound **1c** and **8c** were carried out by using high performance liquid chromatography (HPLC) equipped with an OD column at 25 °C (UV detector: 254 nm).

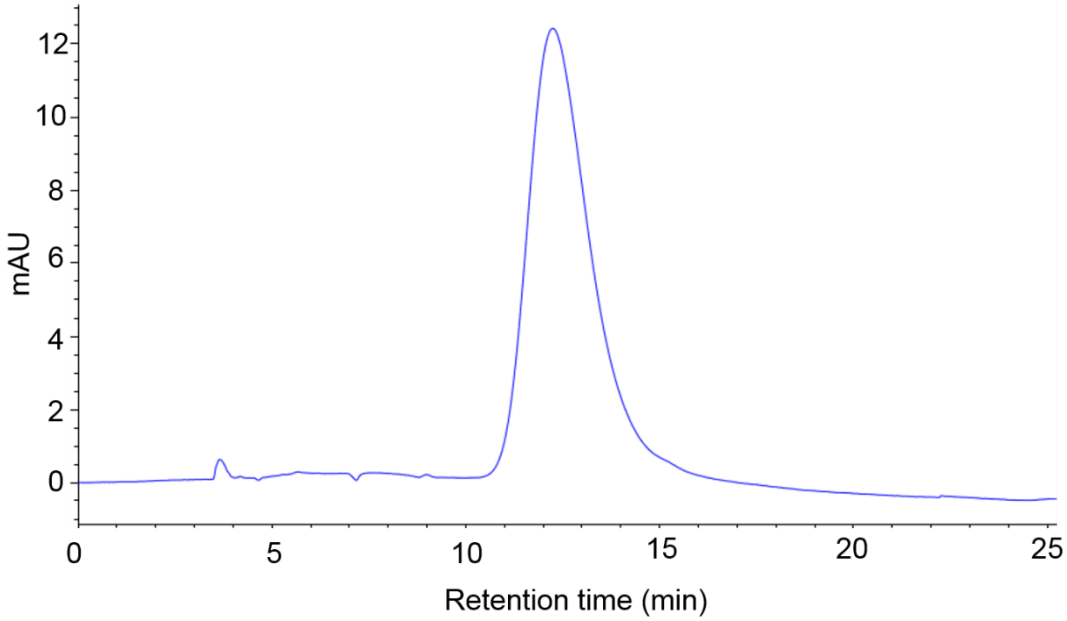


Figure S17: HPLC chromatogram of **1c** (eluent: isopropanol/hexane, 25/75, v/v, 0.8 mL/min)

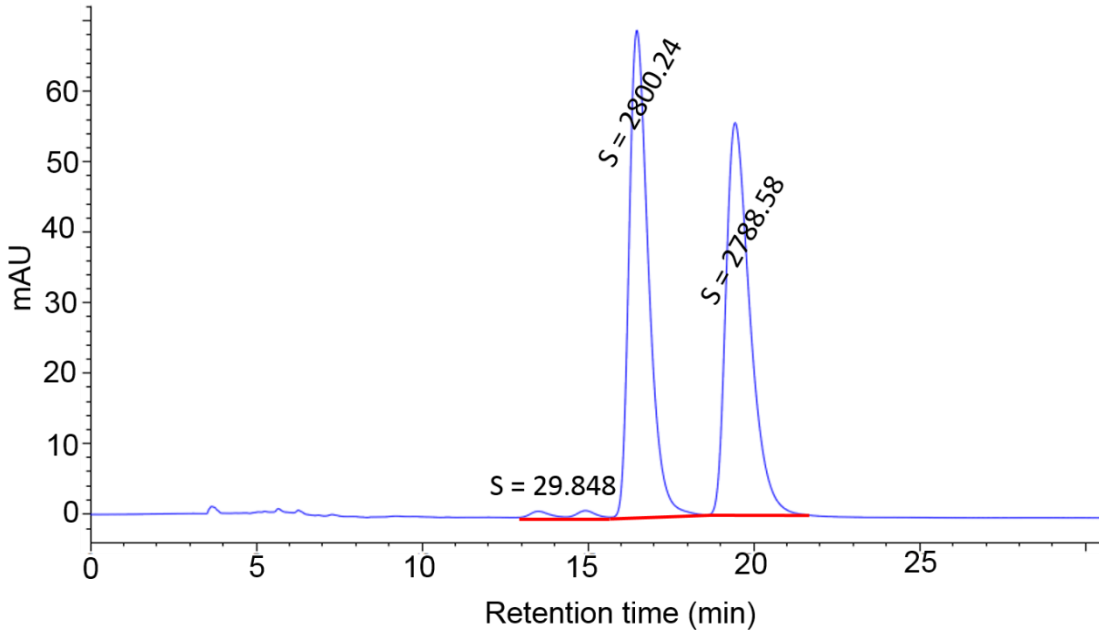
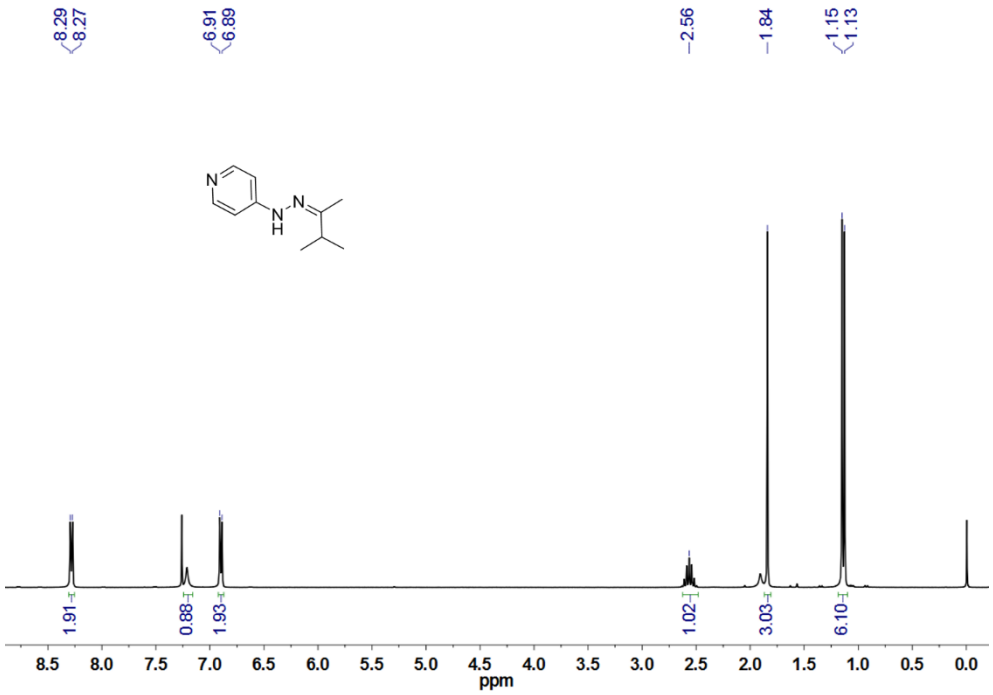


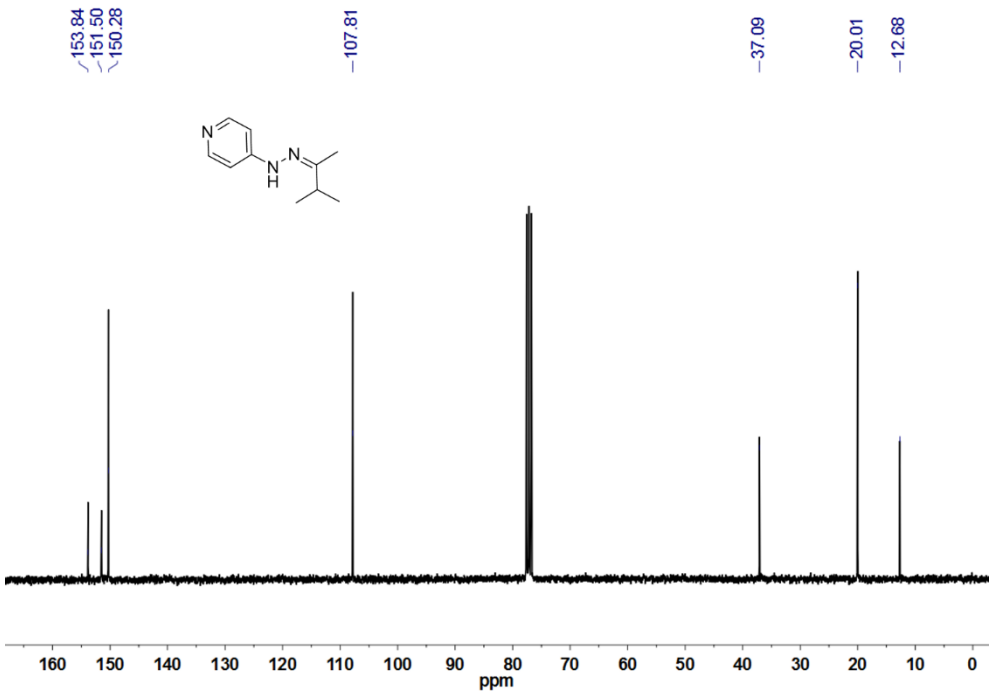
Figure S18: HPLC chromatogram of **8c** (eluent: isopropanol/hexane, 20/80, v/v, 0.8 mL/min). Note, two main peaks were caused by the chirality of spiropyran.

10. NMR and MS spectra

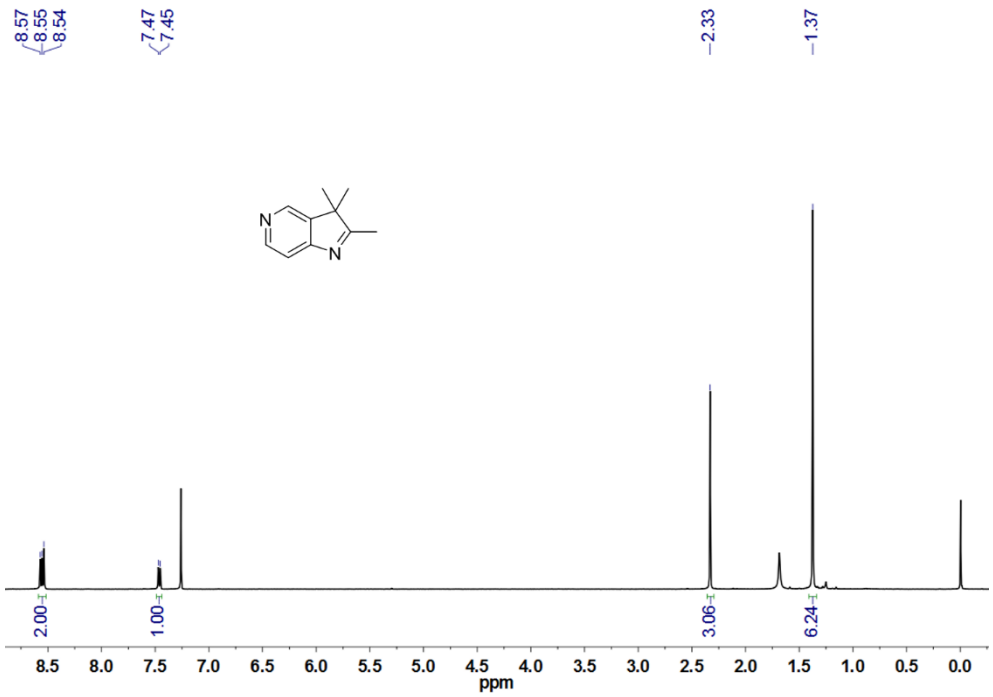
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4** at 298 K.



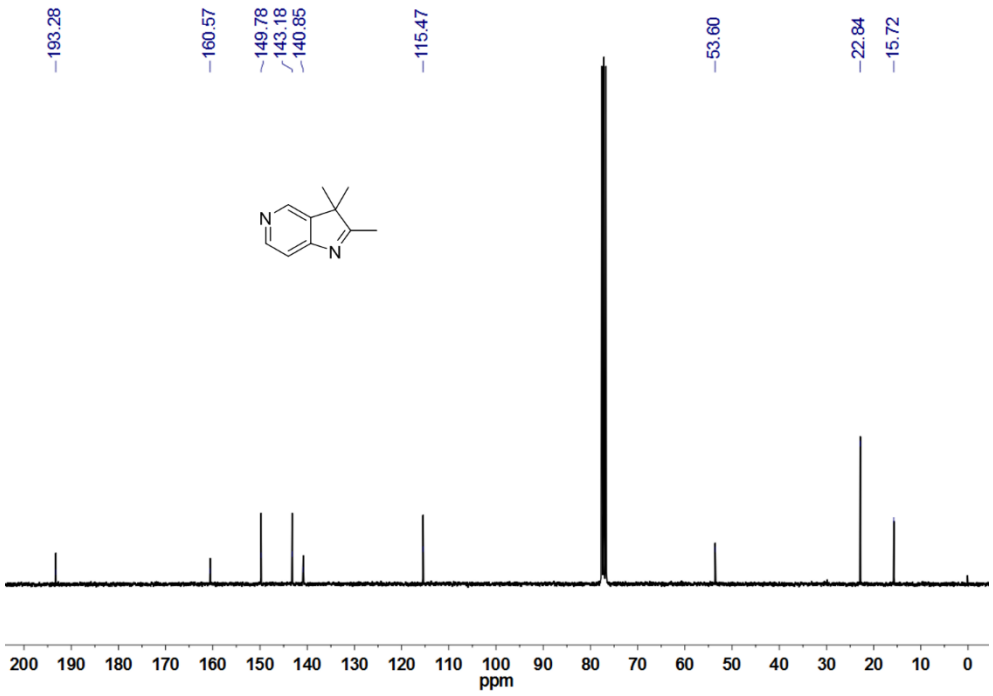
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **4** at 298 K.



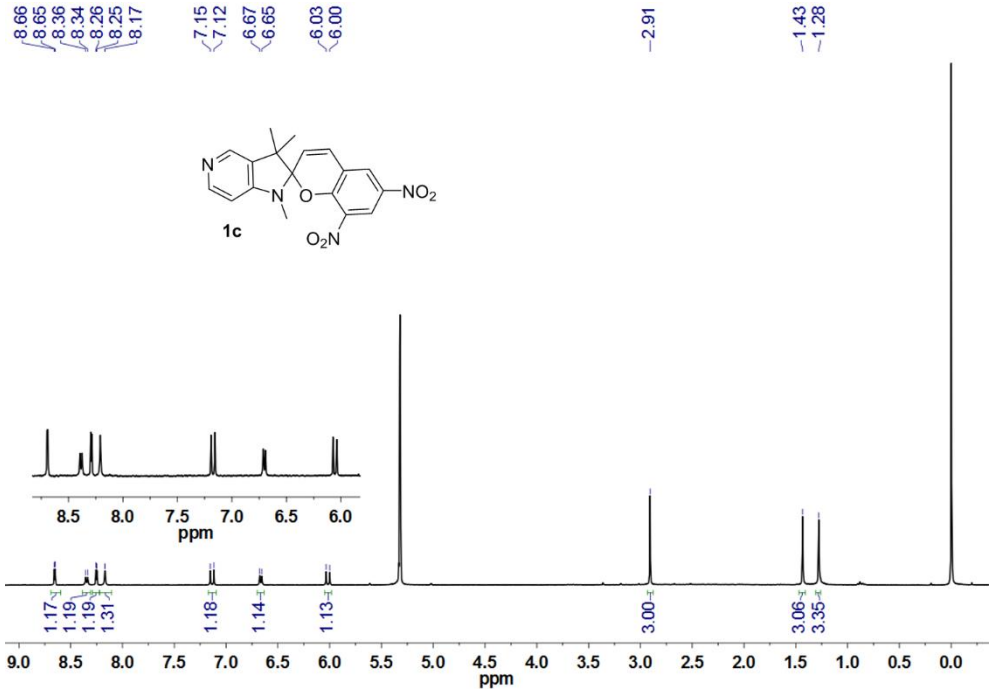
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **5** at 298 K.



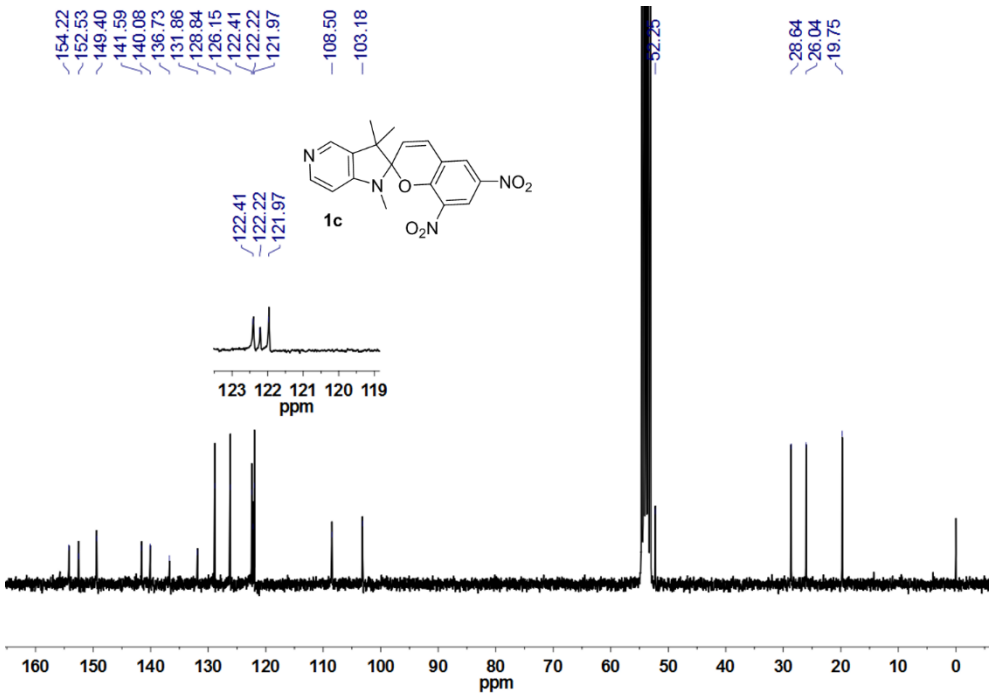
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **5** at 298 K.



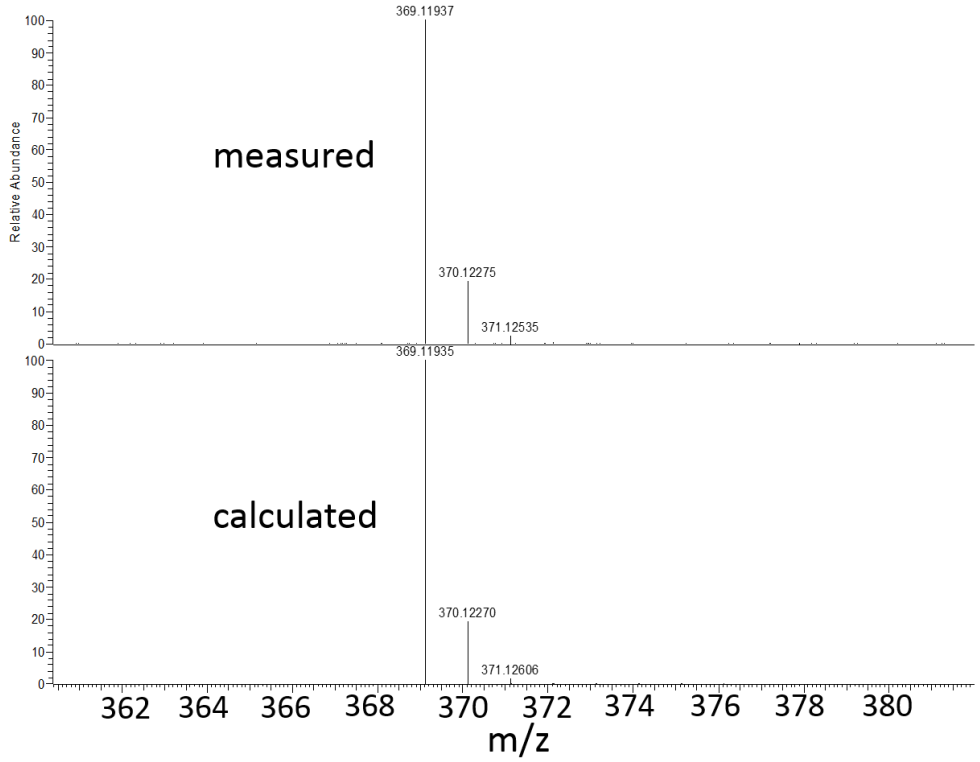
^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of **1c** at 298 K.



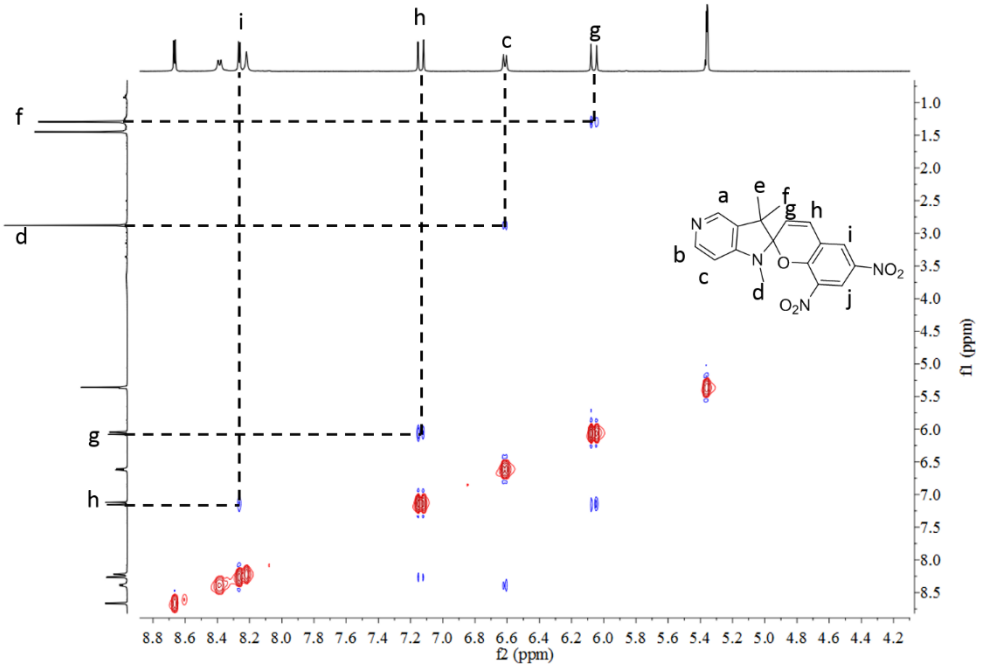
^{13}C NMR spectrum (75 MHz, CD_2Cl_2) of **1c** at 298 K.



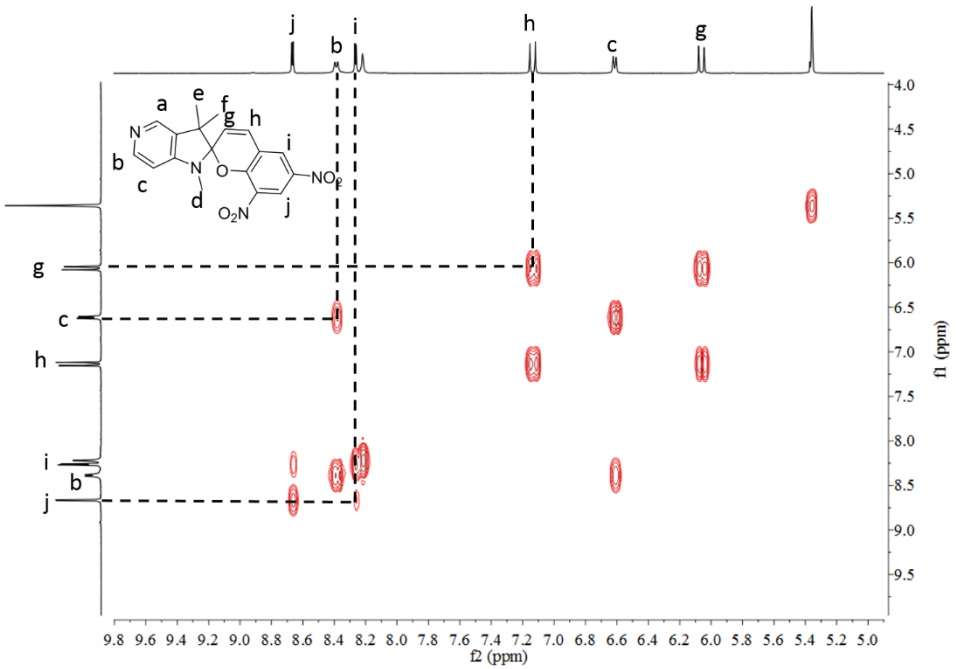
HRMS (ESI) of **1c**, calculated for $C_{18}H_{17}O_5N_4$ $[M+H]^+$: 369.1194, found: 369.1194.



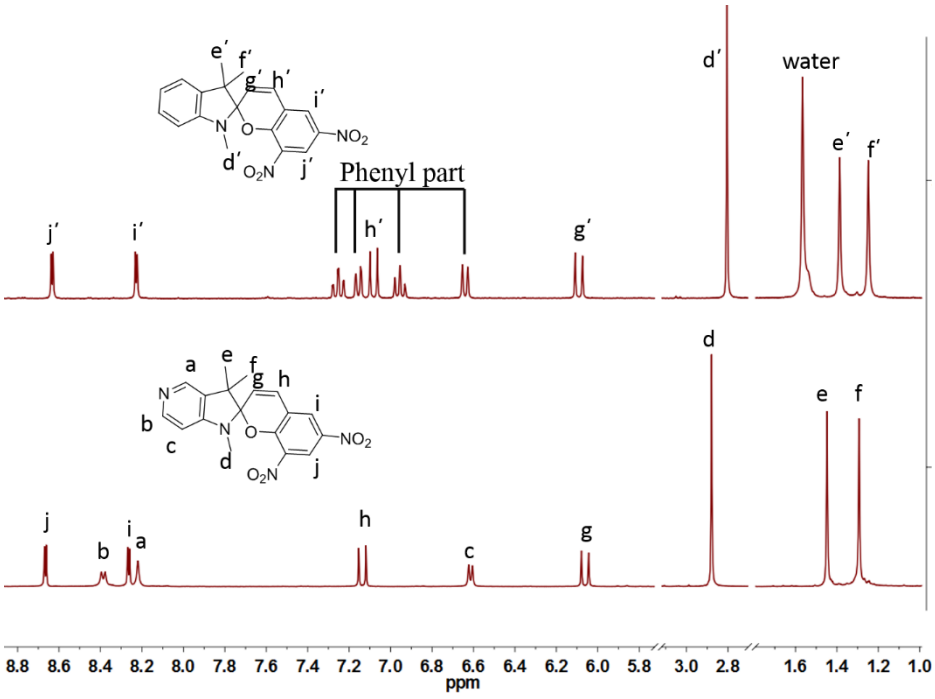
Partial ^{1}H-^{1}H NOESY spectrum (300 MHz, CD_2Cl_2) of **1c** at 298 K.



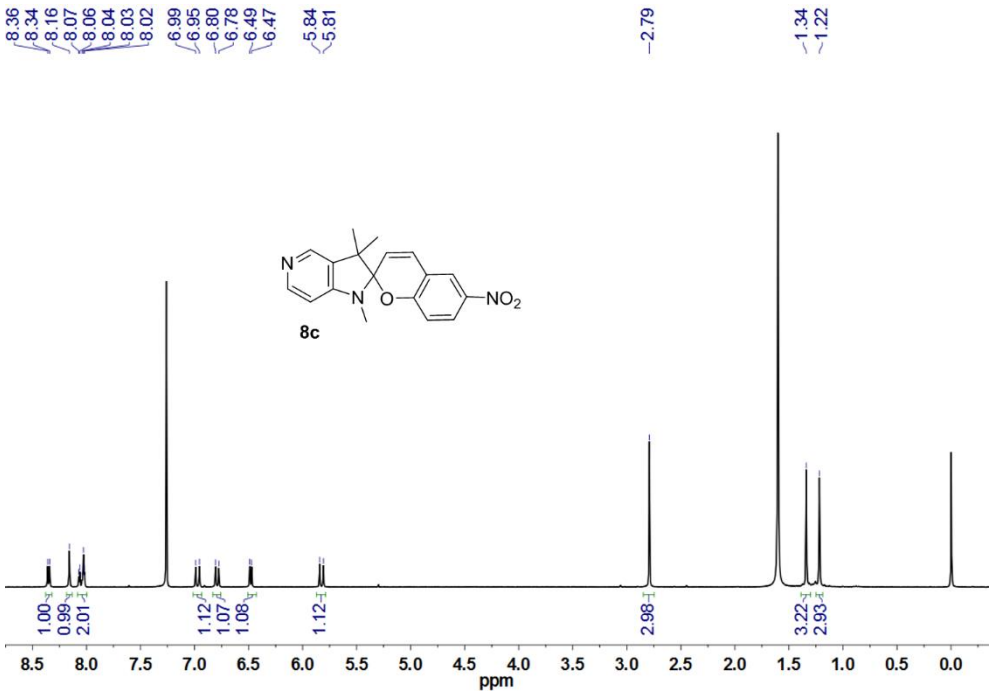
Partial ^{1}H-^{1}H COSY spectrum (300 MHz, CD_2Cl_2) of **1c** at 298 K.



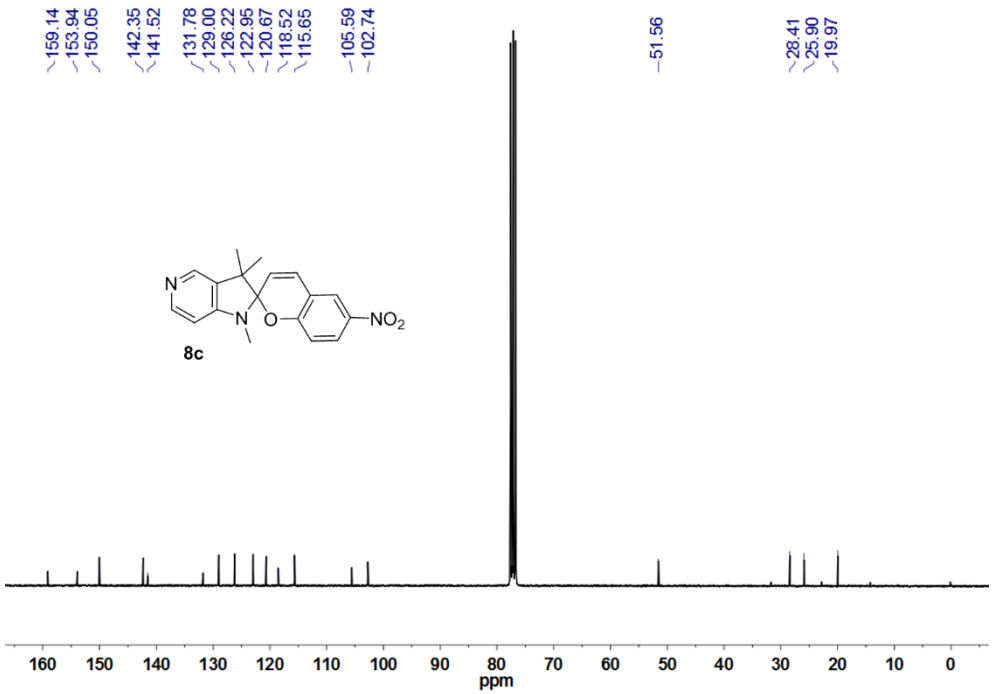
Compared partial ^{1}H NMR spectra (300 MHz, CD_2Cl_2) of **1c** (bottom) and **3c** (up) at 298 K.、



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **8c** at 298 K.



^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **8c** at 298 K.



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