

Electronic Supplementary Information for

A novel three-position molecular switch based on the transformations of cyano-substituted pyrrol-2-one derivative

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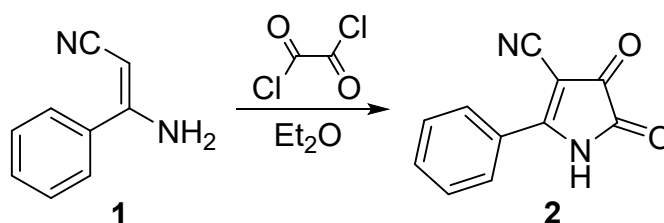
1. Experimental

1.1 General remarks

The progress of reactions and the purity of products were monitored by TLC on Sorbfil plates (spots were visualized under UV light, by treatment with iodine vapor, or by heating). The infrared (IR) spectra were recorded on an FSM-2201 spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra were measured in DMSO-*d*₆ or CDCl₃ on Varian 400 and Bruker DRX-500 spectrometer using tetramethylsilane or residual solvent peak as an internal reference. Elemental analyses were performed using a FlashEA 1112 CHN analyzer. The mass spectra were obtained on a gas chromatograph mass spectrometer Shimadzu GCMS-QP2020 using direct probe inlet. The UV-Vis spectra of solutions (5×10^{-5} M) were recorded on an Agilent Cary 60 UV-Vis Spectrophotometer. Melting points were determined on an OptiMelt MPA100 device.

1.2 Synthetic procedures and spectral data

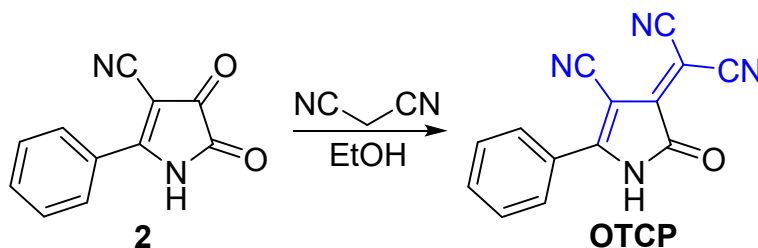
Synthesis of 4,5-dioxo-2-phenyl-4,5-dihydro-1H-pyrrole-3-carbonitrile 2.



A solution of oxalyl chloride (0.762 g, 6 mmol) in dry diethyl ether (3 mL) was slowly added (for 15-20 min) to a cooled ($-5 \dots -8^\circ\text{C}$) solution of enamine **1** (0.865 g, 6 mmol) in dry diethyl ether (10 mL) under argon atmosphere. The rate of (COCl)₂ addition was controlled so that the temperature of the mixture did not exceed 0°C . Then the reaction mass was stirred at $0 \dots -2^\circ\text{C}$ for 1-1.5 hours. After completion of the reaction (TLC controlled) the temperature of the mixture was raised to room temperature, then 1,4-dioxane (4 mL) was added, and the mixture was heated at 50°C in an open flask. After the solvents had been removed, the residue (about 5 mL) was cooled to $2 \dots 5^\circ\text{C}$, and the formed precipitate was filtered. The crude product was crystallized from acetic acid, washed with cold propan-2-ol, and dried in a vacuum

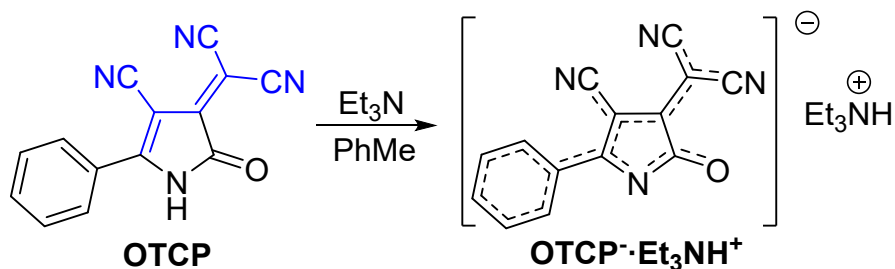
drying cabinet (1 mm Hg) over CaCl₂ at room temperature to constant weight. Yield 71%. Orange crystals, Mp 204–205°C (dec.). ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.75 (2H, t, *J* = 7.9 Hz, C₆H₅), 7.85 (1H, t, *J* = 7.4 Hz, C₆H₅), 8.09 (2H, d, *J* = 7.4 Hz, C₆H₅), 12.24 (1H, s, NH). ¹³C NMR (126 MHz, DMSO-*d*₆): δ 81.89, 113.85, 126.40, 128.62 (2C), 129.72 (2C), 135.80, 159.38, 173.95, 179.07. MS, (EI, 70 eV): *m/z* (%) 198 [M]⁺ (24), 104 [M-94] (100). IR (mineral oil, cm⁻¹): 3216 (NH), 2218 (C≡N), 1757, 1720 (C=O), 1587 (C=C). Anal. Calcd for C₁₁H₆N₂O₂: C, 66.67; H, 3.05; N, 14.14. Found: C, 66.51; H, 3.12; N, 14.25.

Synthesis of 2-(4-cyano-2-oxo-5-phenyl-1,2-dihydro-3H-pyrrol-3-ylidene)malononitrile OTCP.



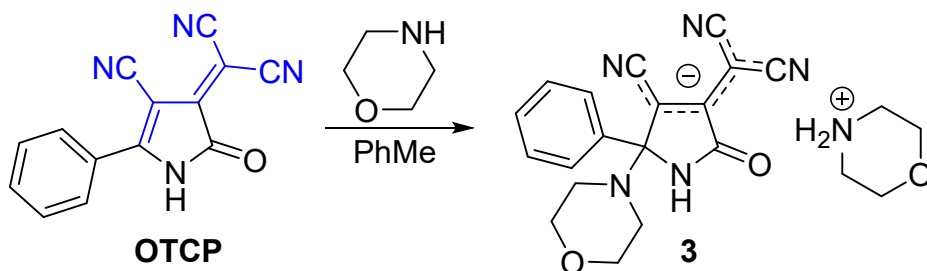
Malononitrile (0.073 g, 1.1 mmol) was added to a suspension of compound **2** (0.198 g, 1 mmol) in ethanol (4 mL). The reaction mixture was stirred for 2 h at room temperature, starting material was dissolving followed by precipitation of solid **OTCP**. After the reaction completion (TLC controlled) the mixture was cooled to 5°C, product was filtered by vacuum filtration and washed with cooled propan-2-ol. The crude product was crystallized from acetic acid, filtered, washed with cold propan-2-ol, and dried in a vacuum drying cabinet (1 mm Hg) over calcium chloride to constant weight. Yield 79%. Dark red crystals, Mp 273–274°C (dec.). ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.74 (2H, t, *J* = 7.9 Hz, C₆H₅), 7.85 (1H, t, *J* = 7.5 Hz, C₆H₅), 8.08 (2H, d, *J* = 7.5 Hz, C₆H₅), 12.78 (1H, s, NH). ¹³C NMR (126 MHz, DMSO-*d*₆): δ 76.47, 81.47, 111.40, 112.09, 112.62, 125.54, 129.33 (2C), 129.82 (2C), 135.85, 148.55, 164.42, 167.84. MS, (EI, 70 eV): *m/z* (%) 246 [M]⁺ (100), 104 [M-142]⁺ (74). 77 [M-169]⁺ (94). IR (mineral oil, cm⁻¹): 3292 (NH), 2227, 2214 (C≡N), 1746 (C=O), 1569 (C=C). Anal. Calcd for C₁₄H₆N₄O: C, 68.29; H, 2.46; N, 22.75. Found: C, 68.10; H, 2.52; N, 22.64.

Synthesis of triethylammonium 4-cyano-3-(dicyanomethylene)-2-oxo-5-phenyl-2,3-dihydropyrrol-1-ide **OTCP**⁻·**Et₃N**⁺.



Dry triethylamine (0.182 g, 1.8 mmol) was added to a solution of **OTCP** (0.148 g, 0.6 mmol) in dry toluene (4 mL). The resulting mixture was stirred at room temperature for 4 h and then kept at 0°C for 30 min. The precipitated solid was filtered by vacuum filtration, washed by three portions of cooled to 0°C toluene (3×0.5 mL). Then product was dried in a desiccator over CaCl₂ for 48 h to constant weight. Yield 87%. Dark solid, Mp 158–159°C (dec.). ¹H NMR (400 MHz, CDCl₃): δ 1.27 (9H, t, *J* = 7.3 Hz, 3CH₃), 3.17 (6H, q, *J* = 7.3 Hz, 3CH₂), 7.50 (2H, t, *J* = 7.6 Hz, C₆H₅), 7.59 (1H, t, *J* = 7.5 Hz, C₆H₅), 8.09 (2H, d, *J* = 7.6 Hz, C₆H₅), 9.35 (1H, br. s, NH⁺). ¹³C NMR (100 MHz, CDCl₃): δ 8.88 (3C), 46.45 (3C), 66.87, 79.69, 113.64, 114.98, 116.03, 129.01 (2C), 129.26 (2C), 132.31, 133.88, 153.87, 179.27, 186.52. MS, (EI, 70 eV): *m/z* (%) 246 [M-101]⁺ (100), 104 [M-243]⁺ (45), 86 [M-261]⁺ (94). IR (mineral oil, cm⁻¹): 2497, 2337 (NH⁺), 2217, 2196 (CN), 1689 (C=C), 1564 (C=C). Anal. Calcd for C₂₀H₂₁N₅O: C, 69.14; H, 6.09; N, 20.16. Found: C, 69.33; H, 6.02; N, 20.30.

Synthesis of morpholin-4-ium dicyano(4-cyano-5-morpholino-2-oxo-5-phenyl-2,5-dihydro-1H-pyrrol-3-yl)methanide **3**.



Dry morpholine (0.348 g, 2 mmol) was added to a solution of **OTCP** (0.123 g, 0.5 mmol) in dry toluene (4 mL). The resulting mixture was stirred at room temperature for about 30 min to the complete disappearing of the colored starting material (**OTCP**). The

precipitated solid was filtered by vacuum filtration, washed by three portions of cooled to 0°C toluene (3×0.5 mL). Then product was dried in a desiccator over CaCl₂ for 48 h to constant weight. Yield 79 %. Pale beige solid, Mp 76–77°C (dec.). ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.21-2.30 (2H, m, NCH₂), 2.42-2.50 (2H, m, NCH₂), 3.09 (4H, pseudo-t, *J* = 4.9 Hz, N(CH₂)₂), 3.53-3.62 (4H, m, O(CH₂)₂), 3.74 (4H, pseudo-t, *J* = 4.9 Hz, O(CH₂)₂), 7.25-7.33 (1H, m, C₆H₅), 7.37 (2H, t, *J* = 7.5 Hz, C₆H₅), 7.48 (2H, d, *J* = 7.6 Hz, C₆H₅), 9.36 (1H, s, NH). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 34.48, 43.01 (2C), 46.45 (2C), 63.42 (2C), 66.37 (2C), 81.99, 91.49, 116.37, 120.28 (2C), 125.64 (2C), 127.61, 128.46 (2C), 140.59, 142.21, 168.26. MS, (EI, 70 eV): *m/z* (%) 332 [M-88]⁺ (100), 264 [M-156]⁺ (46), 104 [M-316]⁺ (83). IR (mineral oil, cm⁻¹): 3307 (NH), 2511 (NH₂⁺), 2205, 2179, 2163 (CN), 1711 (C=O), 1573 (C=C). Anal. Calcd for C₂₂H₂₄N₆O₃: C, 62.84; H, 5.75; N, 19.99. Found: C, 62.67; H, 5.82; N, 19.87.

2. Solvatochromic characteristics of OTCP

Solvent	λ_{\max} , nm	$\epsilon_{\max} \cdot 10^4$, M ⁻¹ ·cm ⁻¹	Solvent	λ_{\max} , nm	$\epsilon_{\max} \cdot 10^4$, M ⁻¹ ·cm ⁻¹
1,4-Dioxane	316	1.2	DMSO	328	0.9
	489	1.0		517	0.5
CH ₂ Cl ₂	322	2.0	DMA	336	1.3
	490	1.9		513	0.6
EtOAc	317	1.6	DMF	349	1.5
	493	1.3		612	0.8
MeCN	320	1.6	Pyridine	325	1.3
	495	1.2		614	0.8

3. Data on the OTCP/morpholine mixtures

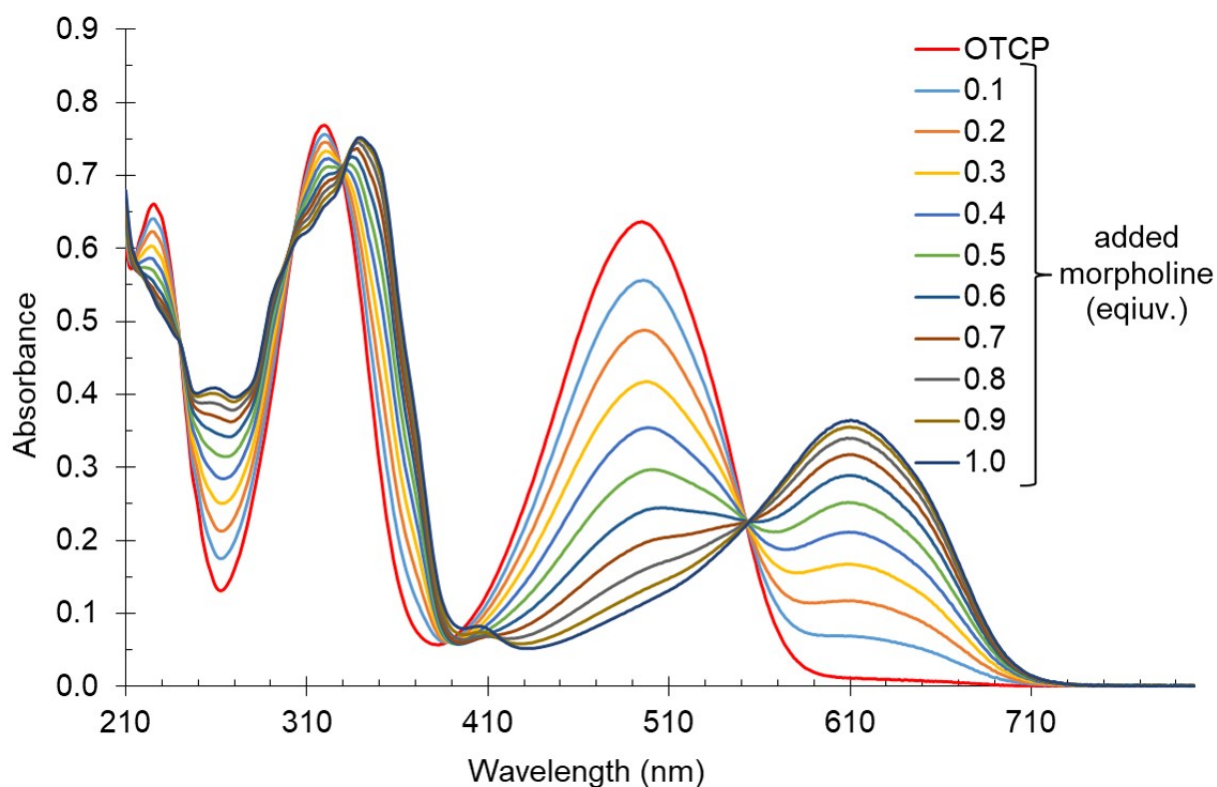


Figure S1. UV-Vis spectra of **OTCP** in MeCN ($C=5 \cdot 10^{-5}$ M) upon sequential addition of morpholine (0.1-1.0 equiv.) at 25°C

Table S1. The ratio of forms **3** and **G** in MeCN solution of **OTCP** (5×10^{-5} M) with morpholine (10 equiv.) depending on temperature

Temperature, °C	Mole content of G , %	Mole content of 3 , %
0	5	95
5	8	92
10	12	88
15	18	82
20	26	74
25	36	64
30	47	53
35	58	42
40	67	33
45	75	25
50	81	19

4. NMR ^1H , ^{13}C spectra

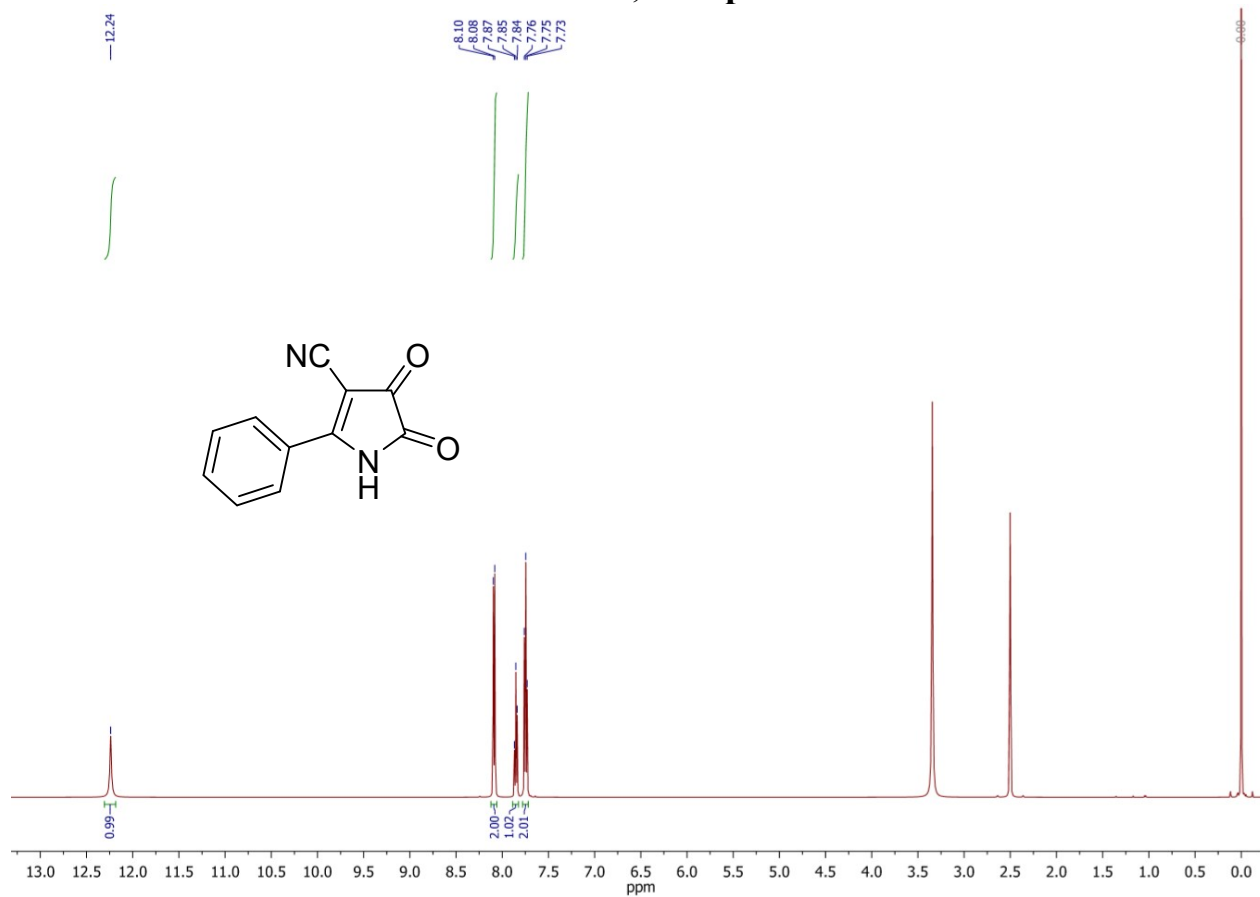


Fig. S2. ^1H -NMR-spectrum of compound **2** (500 MHz, $\text{DMSO-}d_6$)

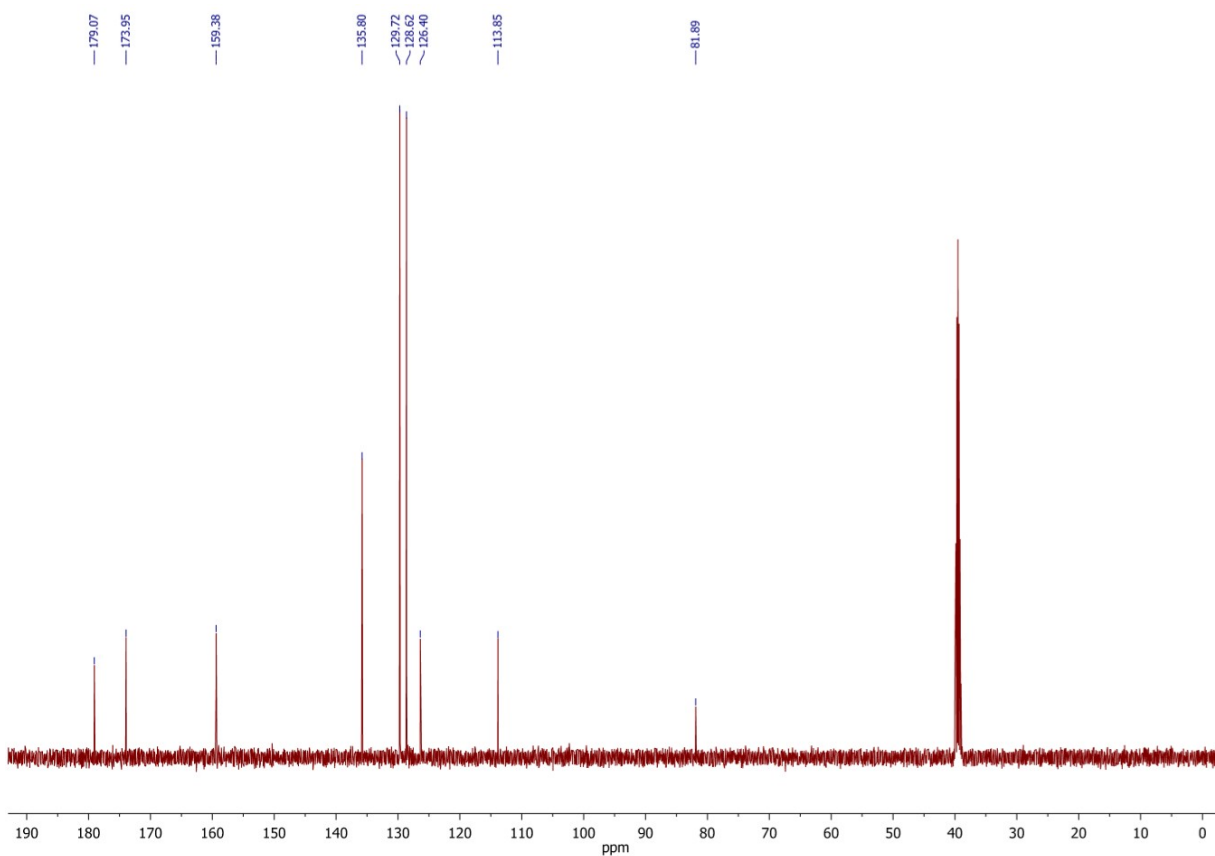


Fig. S3. ^{13}C -NMR-spectrum of compound **2** (126 MHz, $\text{DMSO-}d_6$)

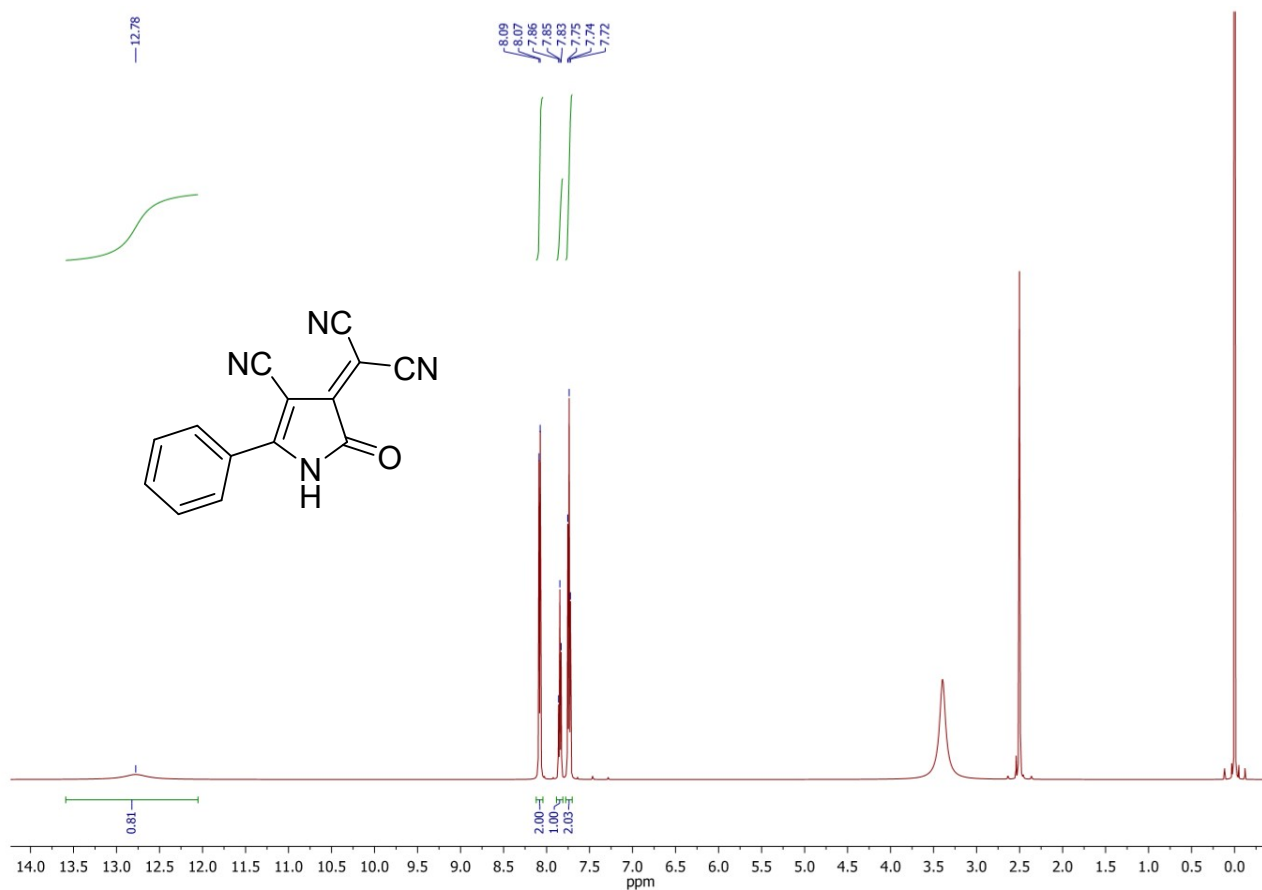


Fig. S4. ¹H-NMR-spectrum of compound **OTCP** (500 MHz, DMSO-*d*₆)

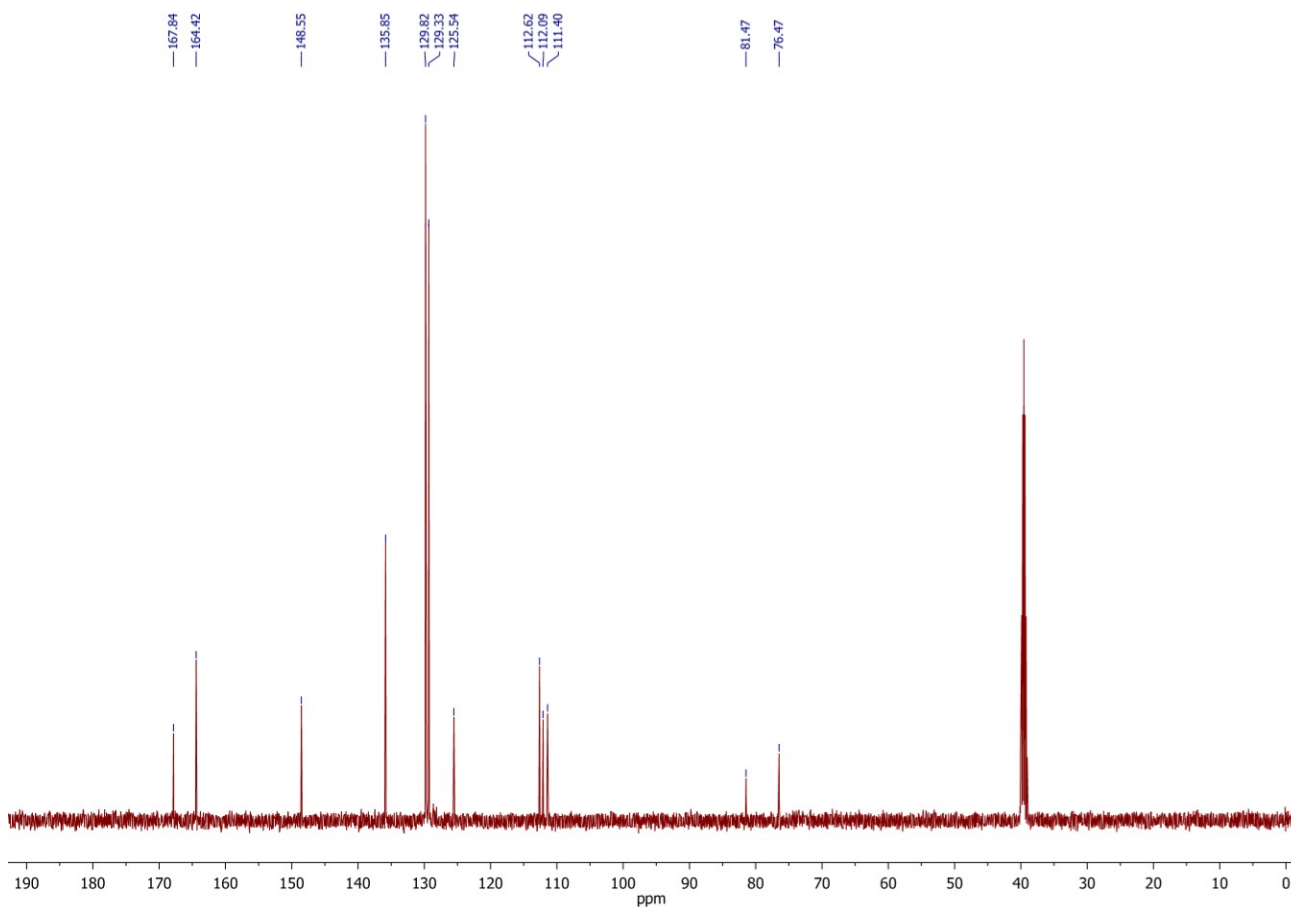
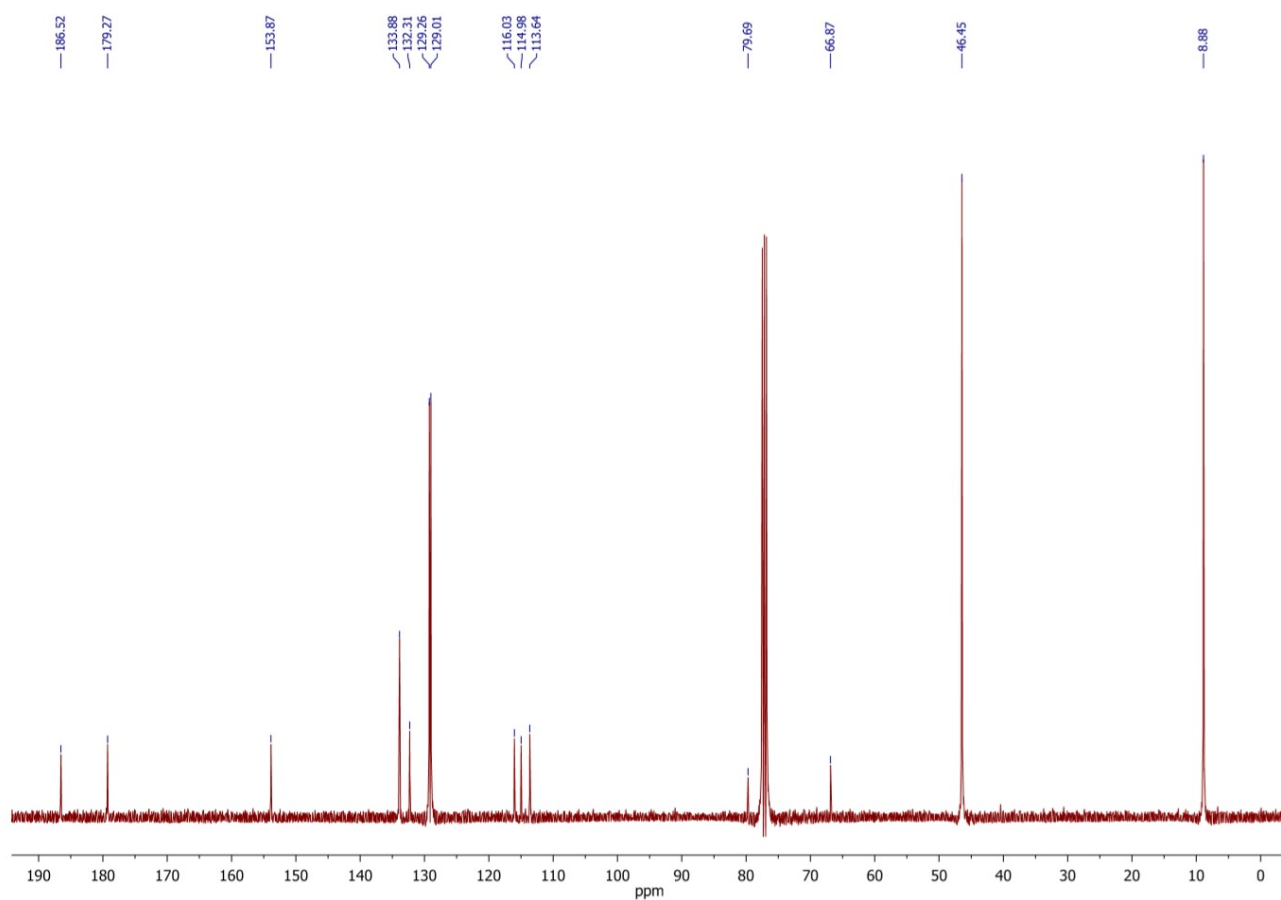
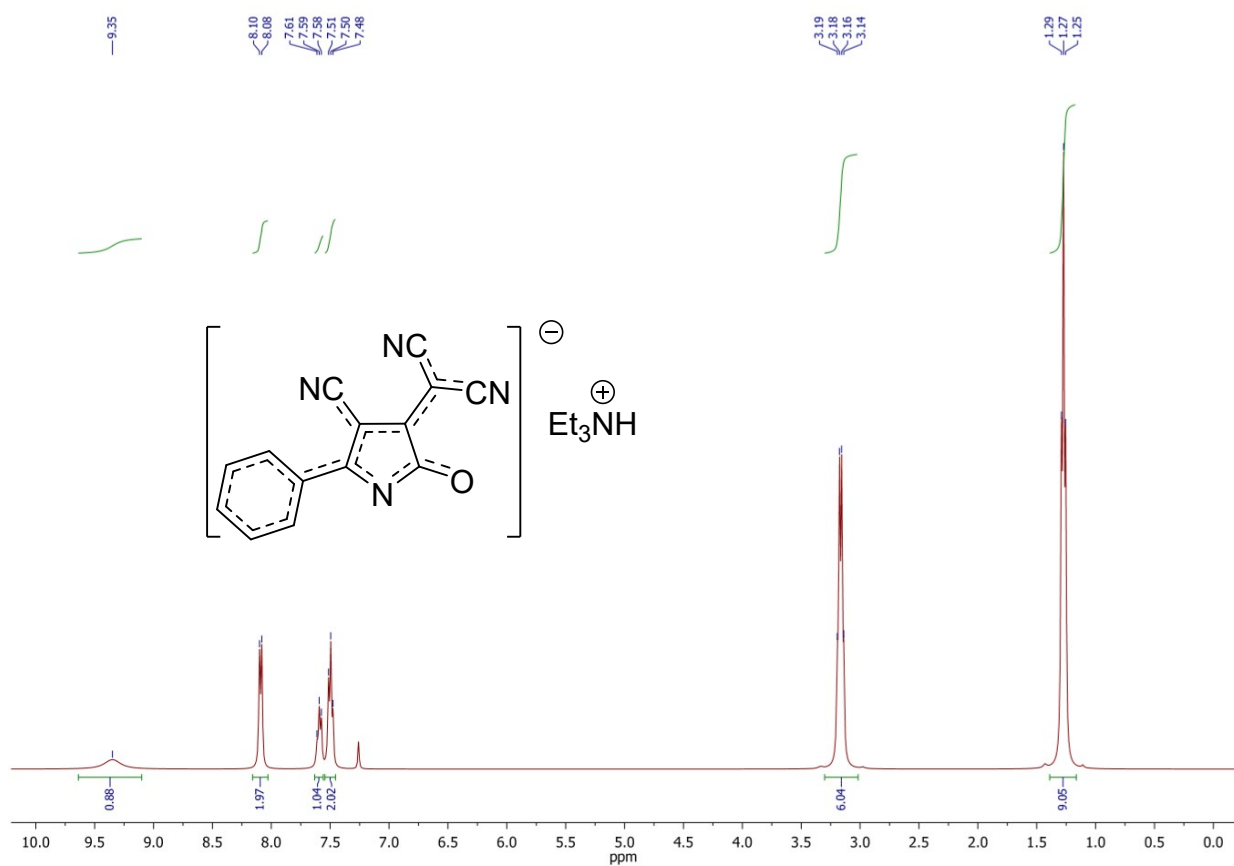


Fig. S5. ¹³C-NMR-spectrum of compound **OTCP** (126 MHz, DMSO-*d*₆)



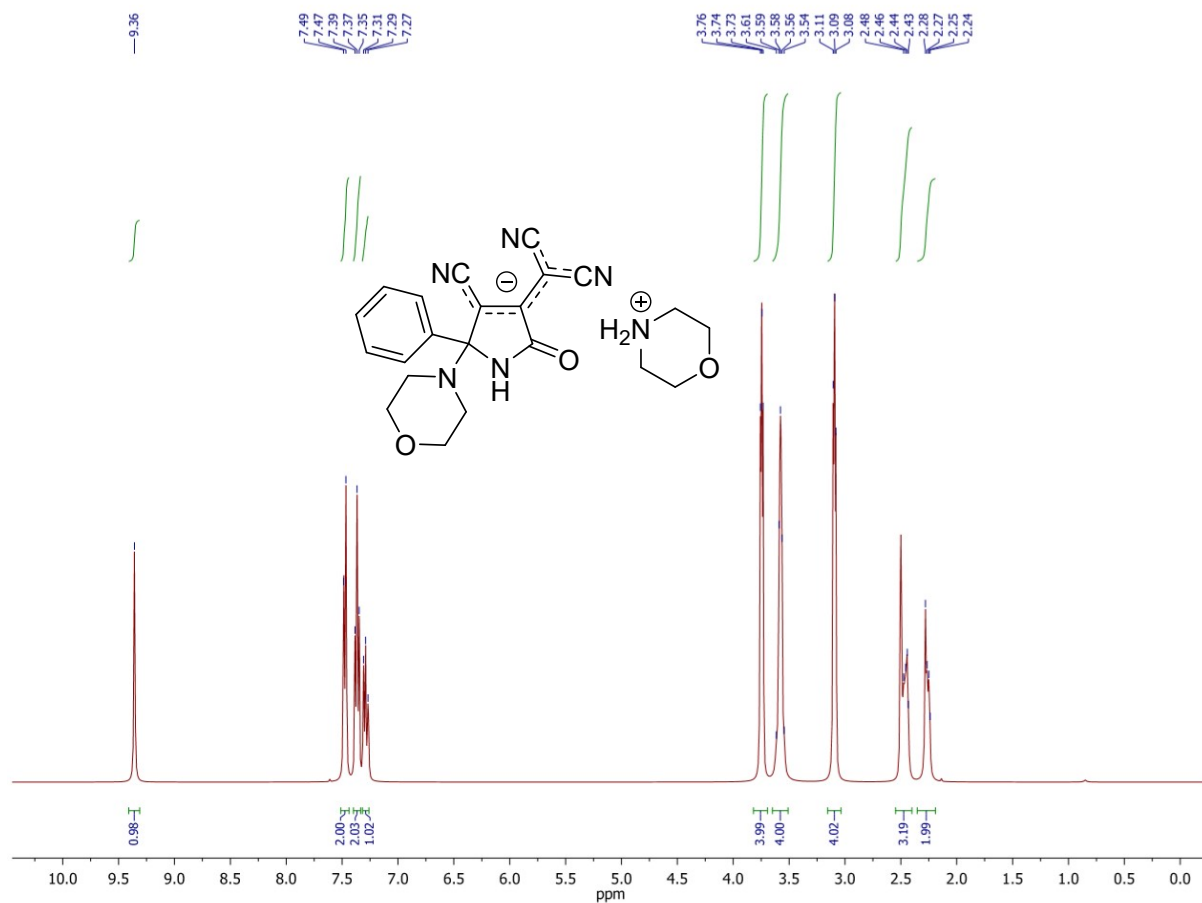


Fig. S8. ^1H -NMR-spectrum of compound **3** (400 MHz, $\text{DMSO}-d_6$)

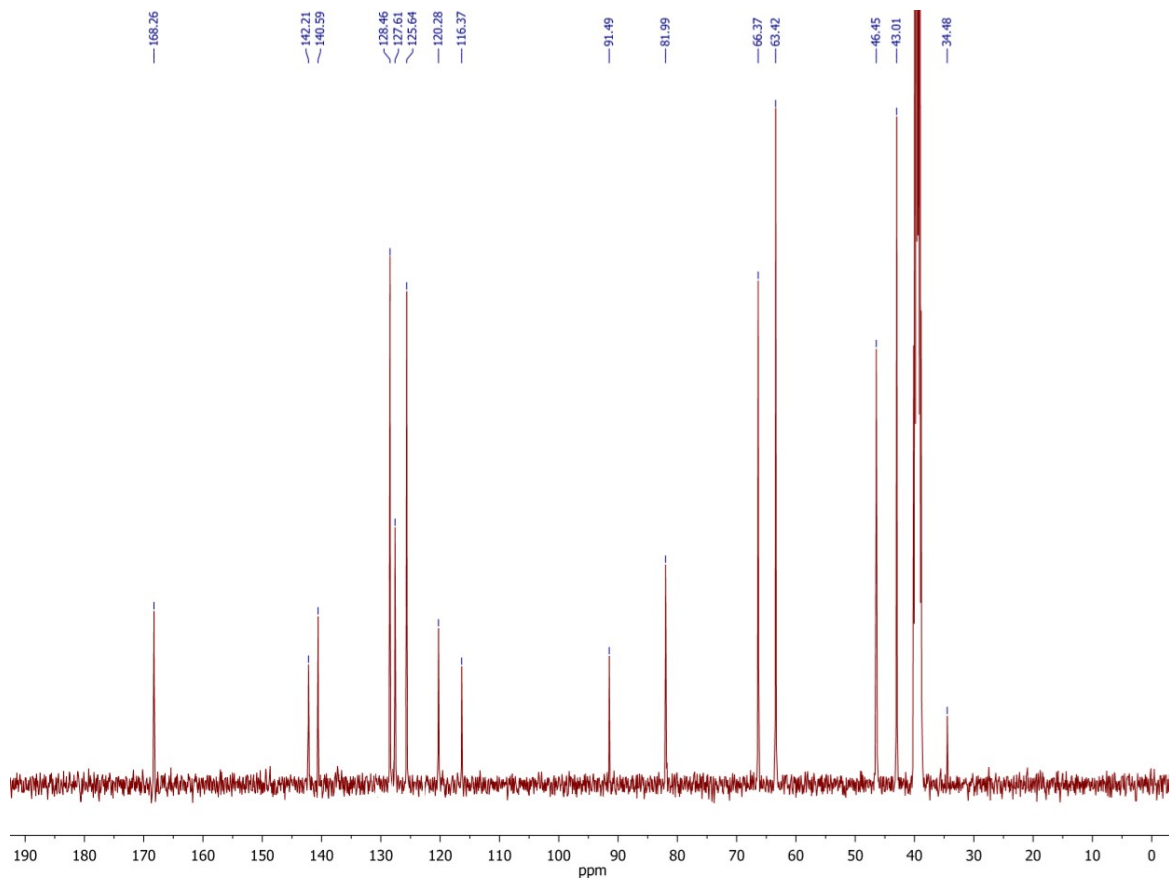


Fig. S9. ^{13}C -NMR-spectrum of compound **3** (100 MHz, $\text{DMSO}-d_6$)