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Electronic Supplementary Information for

The first example of "turn-off" red fluorescence photoswitching for the representatives of nitrile-rich negative photochromes

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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 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 on Bruker DRX-500 spectrometer using tetramethylsilane 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-QP2010S. The UV spectra were recorded on an Agilent Cary 60 UV-Vis Spectrophotometer (10^{-5} M). To study the photochromic behavior of compounds, the solutions were irradiated with non-filtered visible light by LED XM-LT6 CREE (spectral range of 400-700 nm, a luminous power density equal to 205 mW/cm^2). Melting points were determined on an OptiMelt MPA100 device.

1.2 Synthetic procedures and spectral data

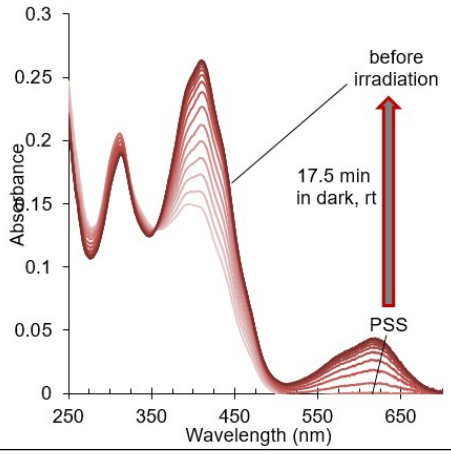
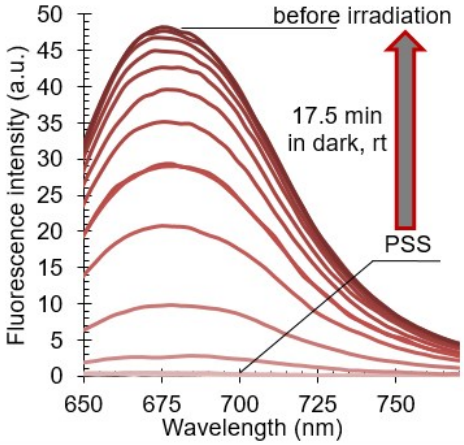
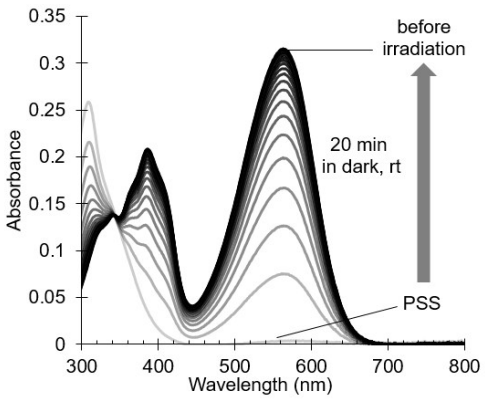
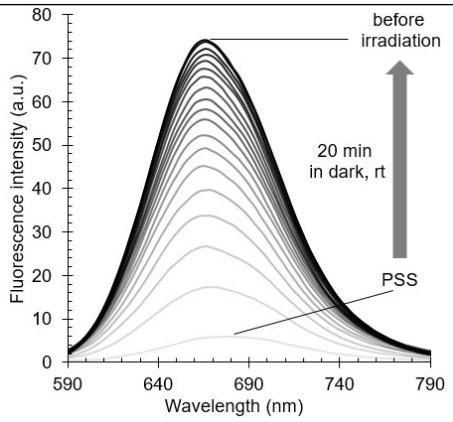
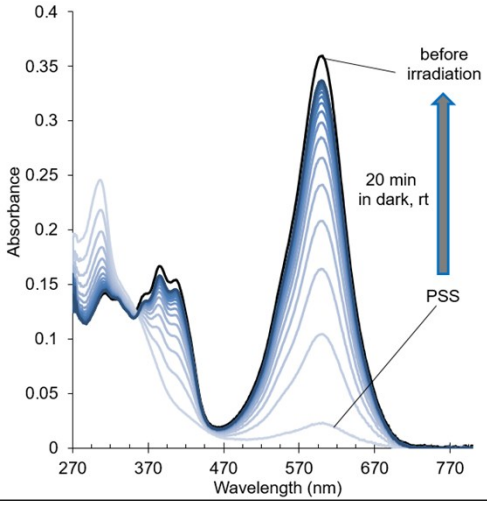
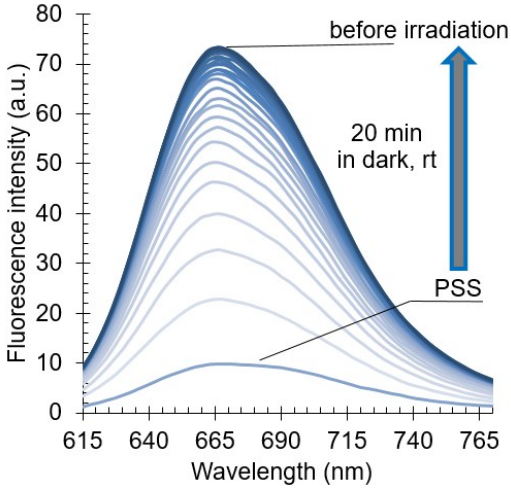
General synthesis procedure of nitro-substituted (E)-2-(3-cyano-4-(2-hydroxystyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitriles **1a-c.** To a suspension of 0.199 g (1 mmol) of TCF acceptor in 2-3 mL of 96% ethanol an appropriate nitrosubstituted 2-hydroxybenzaldehyde and 0.077 g (1 mmol) of dry ammonium acetate were added in an argon atmosphere. The resulting mixture was stirred at 35-40 °C for 2-4 h (TCL controlled). Then 0.5 mL of 5% aqueous HCl was added and the stirring was continued for additional 2 h at room temperature. The resulting mixture was then cooled to 5-10 °C, the precipitated solid was filtered off and washed by 1 mL of water:ethanol (1:1) and 1 mL of cold ethanol (0-5 °C). Dried in a vacuum desiccator over $CaCl_2$ to constant weight.

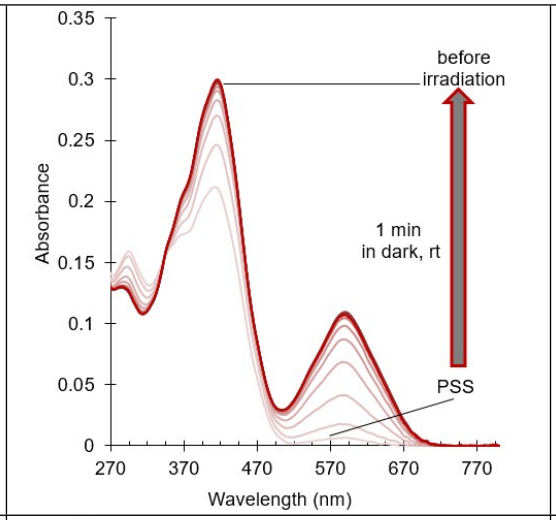
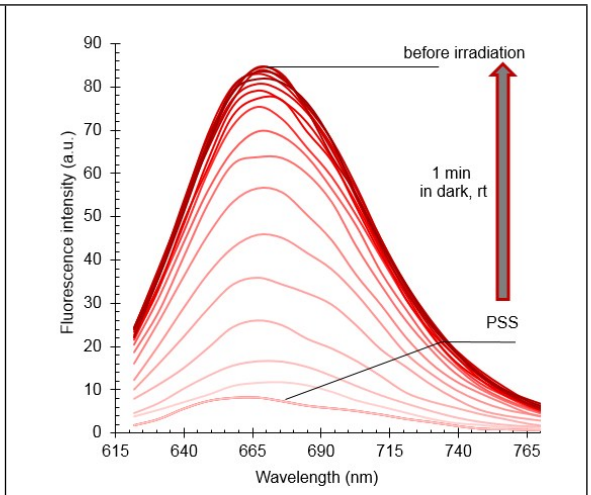
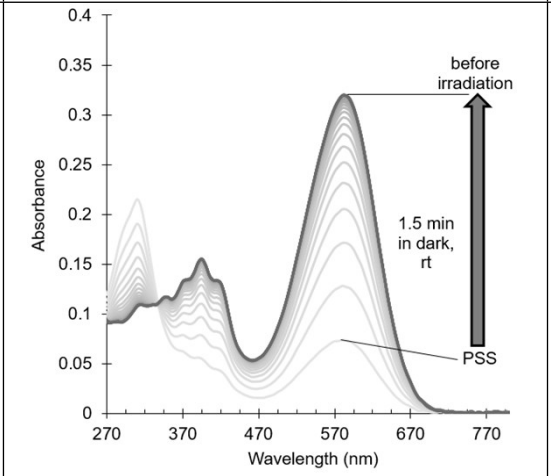
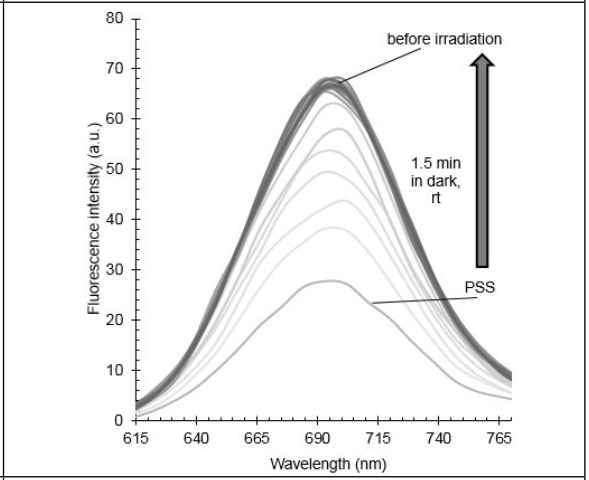
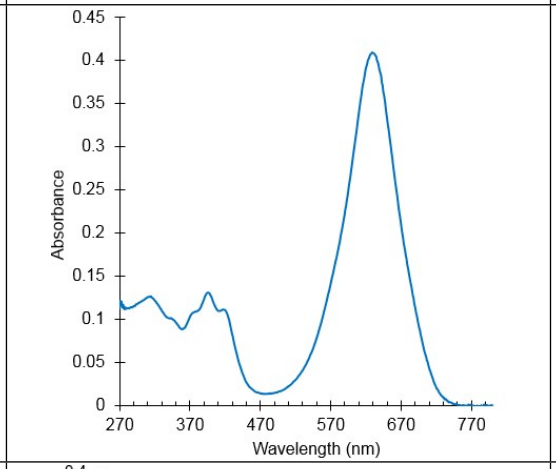
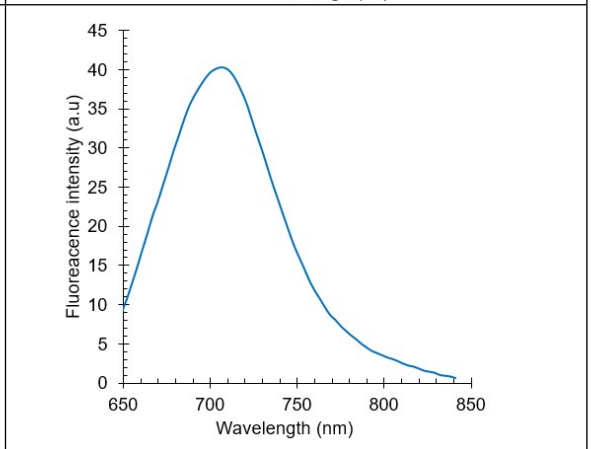
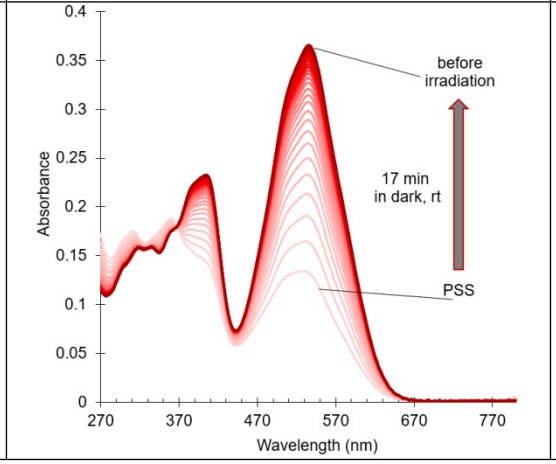
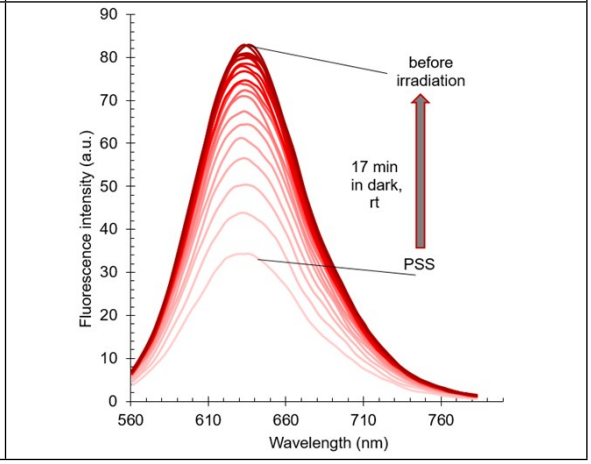
(E)-2-(3-Cyano-4-(2-hydroxy-5-nitrostyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile **1a**. The physical and spectral data are consistent with the literature [1].

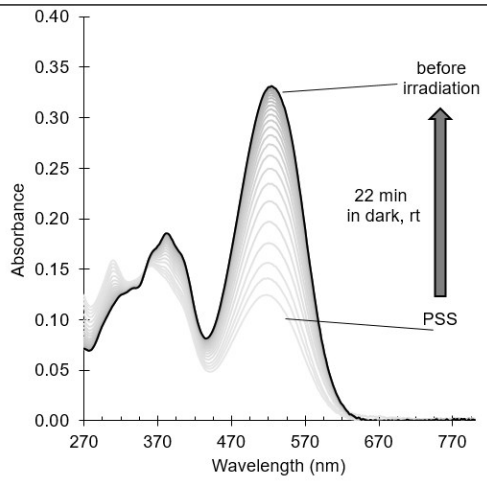
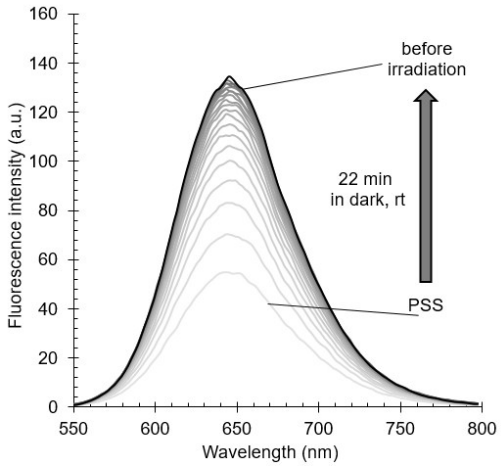
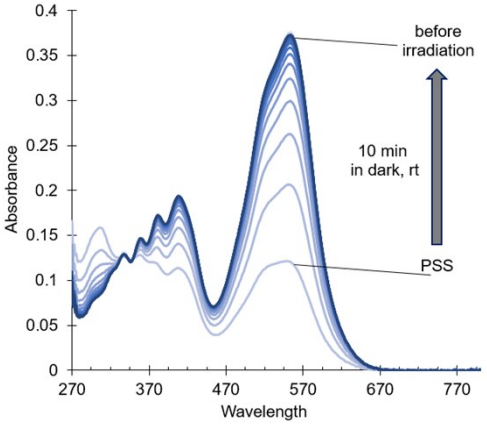
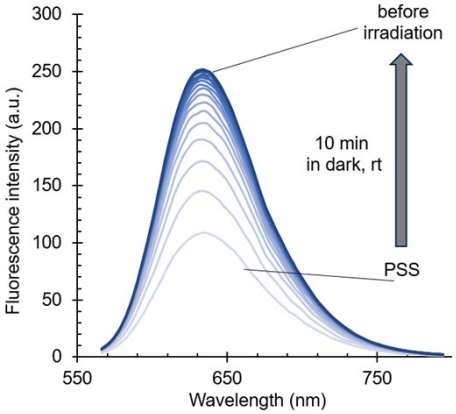
(E)-2-(3-Cyano-4-(2-hydroxy-3-nitrostyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile **1b**. Mp 267–268 ºC (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 1.78 (6H, s, 2CH_3), 7.18 (1H, t, *J* = 8.0 Hz, C_6H_3), 7.42 (1H, d, *J* = 16.6 Hz, CH=), 8.14 (1H, dd, *J* = 1.4, 8.3 Hz, C_6H_3), 8.24 (1H, d, *J* = 16.6 Hz, CH=), 8.34 (1H, dd, *J* = 1.4, 7.8 Hz, C_6H_3), 11.00-11.50 (1H, br. s, OH). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 24.73, 54.78, 99.32, 99.42, 110.95, 111.65, 112.51, 117.37, 119.93, 125.77, 128.33, 135.50, 137.07, 139.79, 151.60, 174.90, 177.14. MS, (EI, 70 eV): *m/z* (%) 348 $[M]^+$ (26), 333 $[M\text{-}Me]^+$ (12). IR (mineral oil, cm^{-1}): 3240 (OH), 2234, 2216 (CN), 1585 (C=C). Anal. Calcd for $C_{18}H_{12}N_4O_4$: C, 62.07; H, 3.47; N, 16.09. Found: C, 61.93; H, 3.57; N, 15.92.

(E)-2-(3-Cyano-4-(2-hydroxy-3,5-dinitrostyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile **1c**. Mp 259–260 ºC (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 1.80 (6H, s, 2CH_3), 7.87 (1H, d, *J* = 15.9 Hz, CH=), 8.23 (1H, d, *J* = 15.9 Hz, CH=), 8.54 (1H, d, *J* = 3.2, Hz, C_6H_3), 8.66 (1H, d, *J* = 3.2, Hz, C_6H_3), ^{13}C NMR (125.67 MHz, DMSO-d_6): δ25.54, 53.45, 97.77, 99.06, 111.11, 112.14, 112.96, 116.03, 124.44, 126.80, 130.78, 132.85, 139.52, 144.97, 165.92, 176.98, 177.13. MS, (EI, 70 eV): *m/z* (%) 393 $[M]^+$ (35), 378 $[M\text{-}Me]^+$ (19), 346 (5). IR (mineral oil, cm^{-1}): 2235, 2218 (CN), 1581 (C=C). Anal. Calcd for $C_{18}H_{11}N_5O_6$: C, 54.97; H, 2.82; N, 17.81. Found: C, 54.82; H, 2.91; N, 17.64.

2. Absorption and Emission spectra

Comp.	Solvent	UV-Vis spectra	Emission spectra
1a	THF		
	EtOH		
	DMF		

1b	THF		
	EtOH		
	DMF		
	THF		

	EtOH	 Absorbance Wavelength (nm) before irradiation 22 min in dark, rt PSS	 Fluorescence intensity (a.u.) Wavelength (nm) before irradiation 22 min in dark, rt PSS
	DMF	 Absorbance Wavelength before irradiation 10 min in dark, rt PSS	 Fluorescence intensity (a.u.) Wavelength (nm) before irradiation 10 min in dark, rt PSS

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

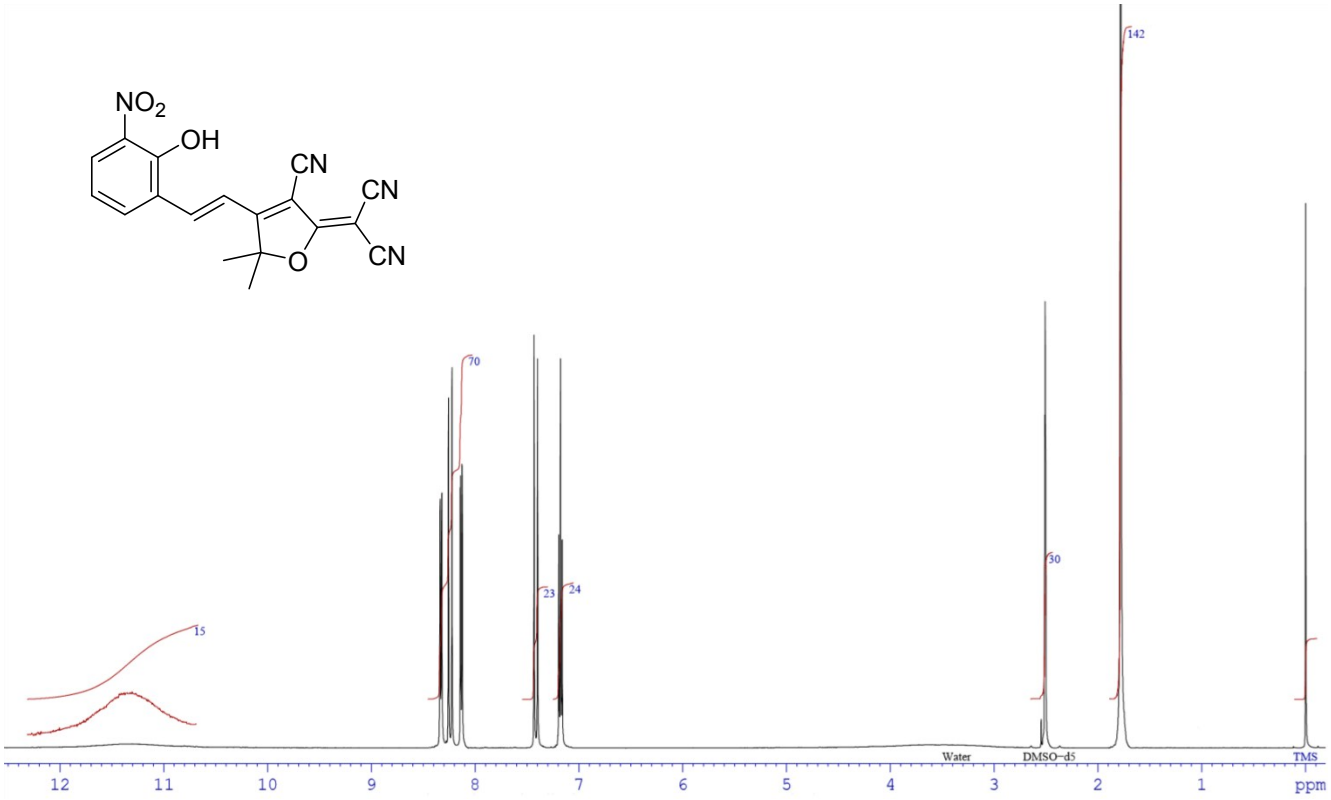


Fig. 1. ^{1}H-NMR-spectrum of **1b** (500 MHz, DMSO−d_6, 293K)

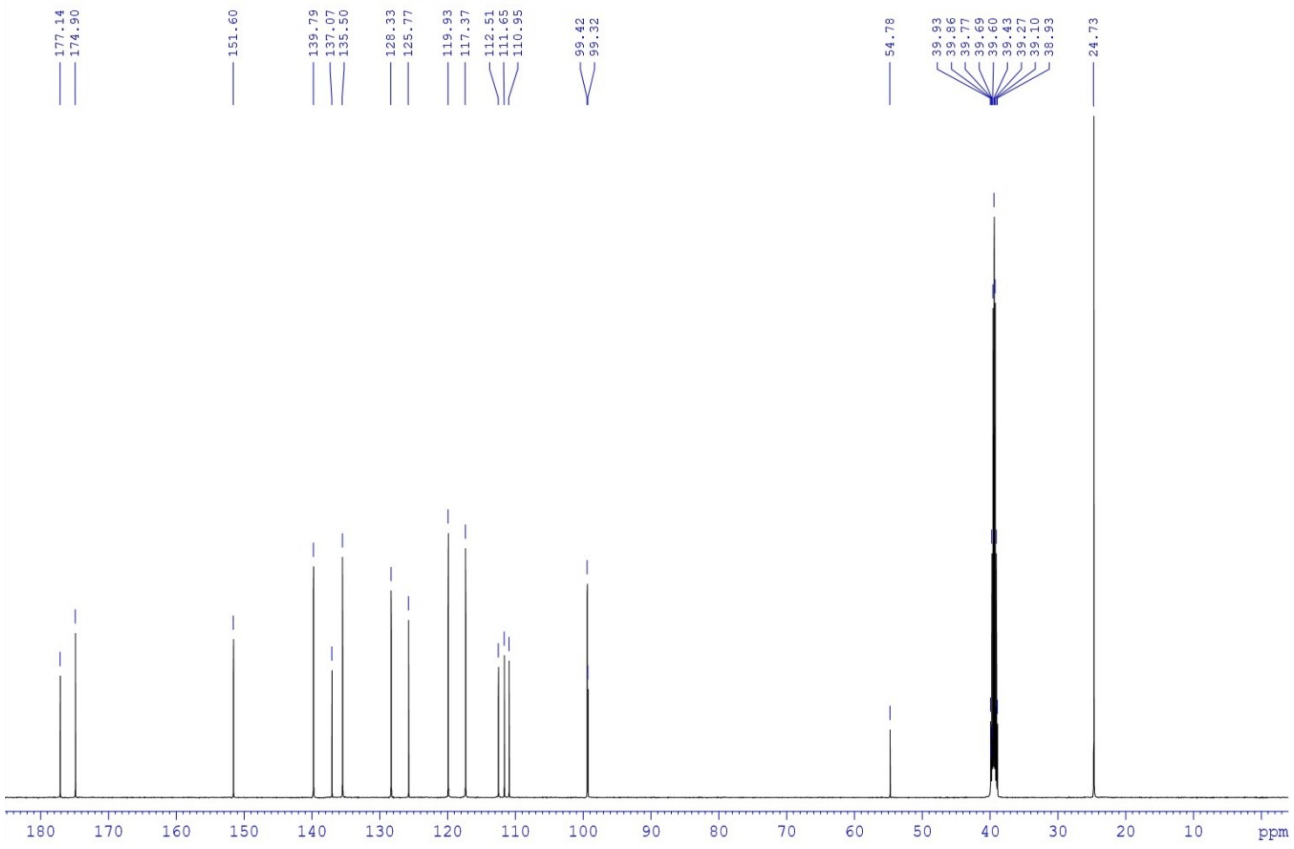


Fig. 2. ^{13}C-NMR-spectrum of **1b** (126 MHz, DMSO−d_6, 296K)

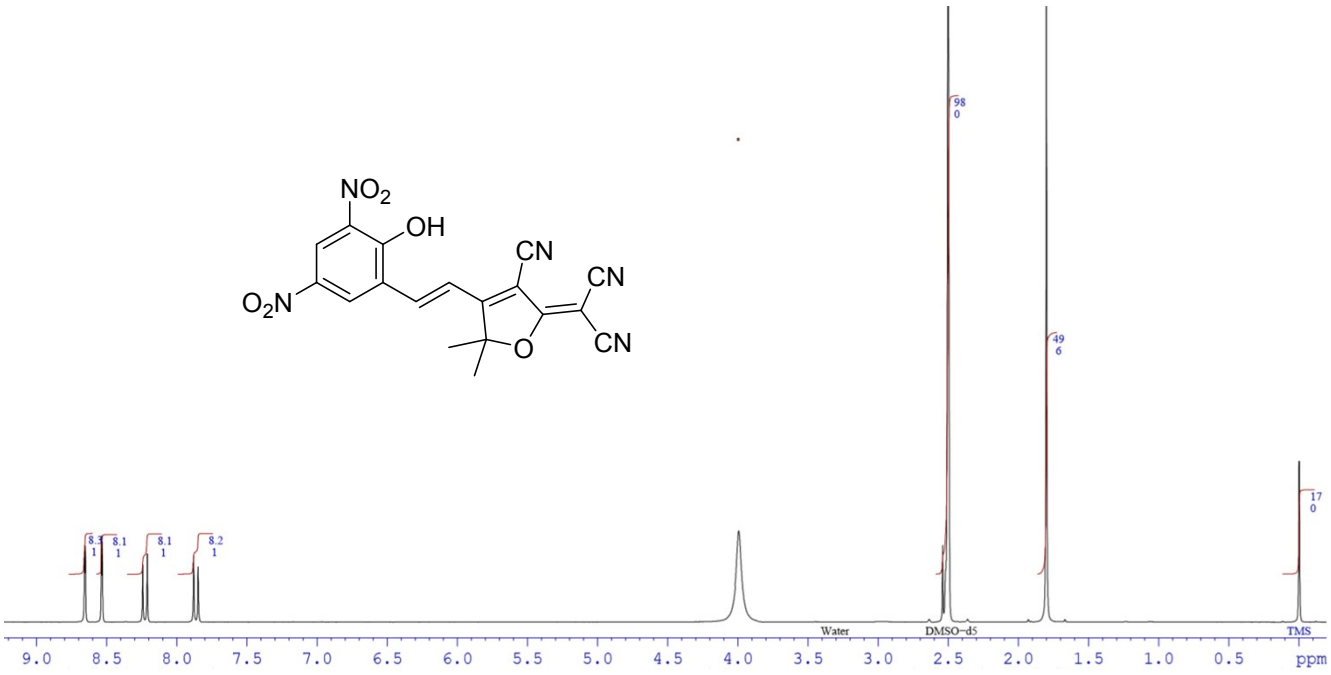


Fig. 3. ^{1}H-NMR-spectrum of **1c** (500 MHz, DMSO−d_6, 300K)

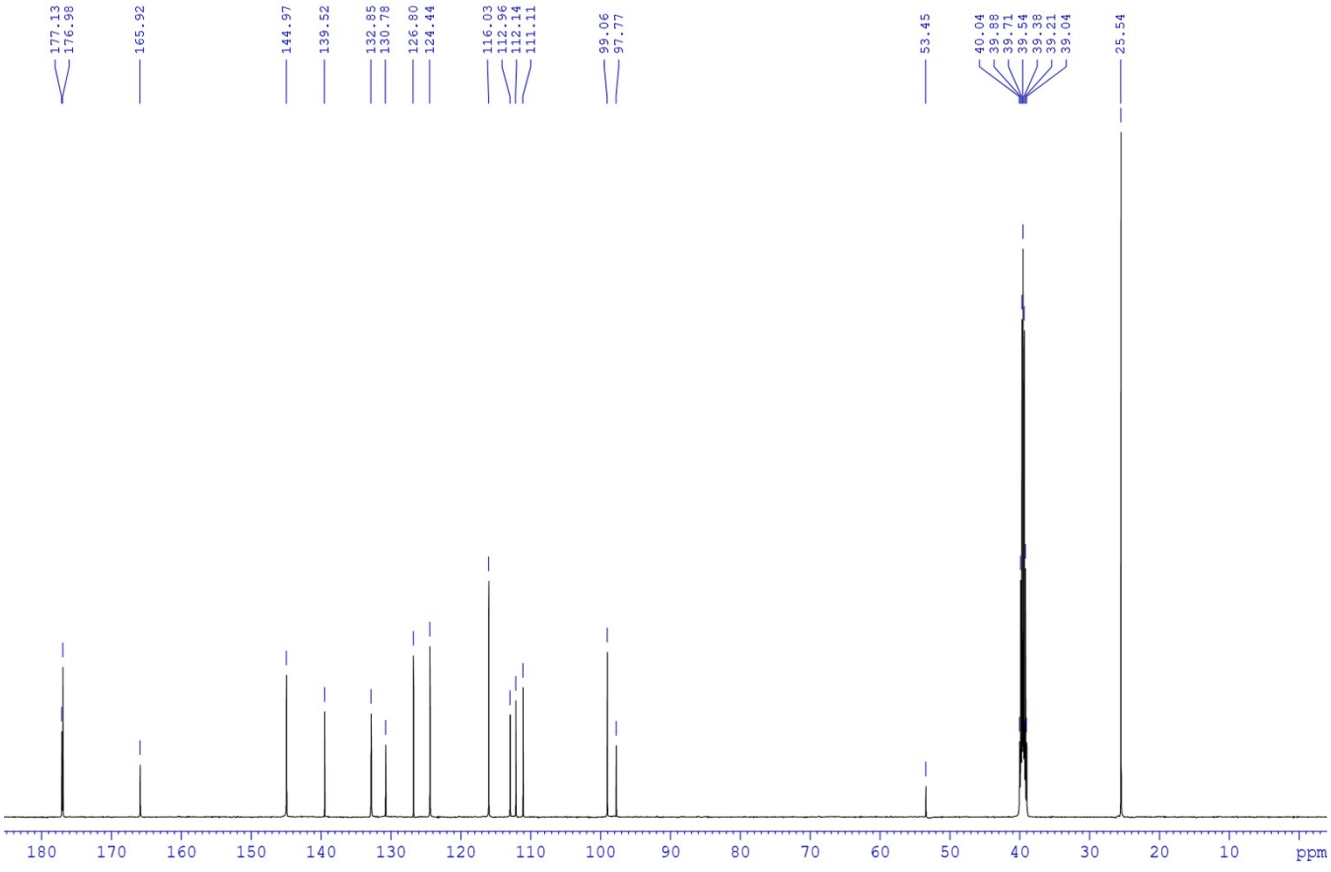


Fig. 4. ^{13}C-NMR-spectrum of **1c** (126 MHz, DMSO−d_6, 300K)