Electronic Supplementary Information for

Tuning the photochromic properties of chromophores containing a nitrile-rich acceptor: a novel branch in the investigation of negative photochromes

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Contents

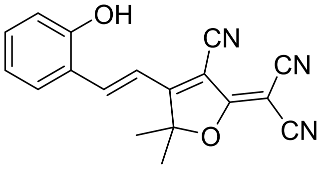
1. Experimental

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 a FSM-1202 spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra were measured in DMSO-d_6 on Bruker DRX-500 and AV600 spectrometers using tetramethylsilane as an internal reference. Elemental analyses were performed using a Perkin–Elmer 2400 CHN elemental 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. Melting points were determined on an OptiMelt MPA100 device. 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).

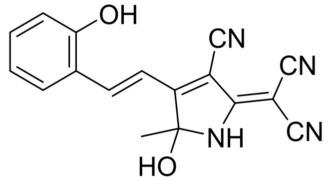
1.2 Synthetic procedures and spectral data

*Synthesis of (E)-2-(3-cyano-4-(2-hydroxystyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile **1a***



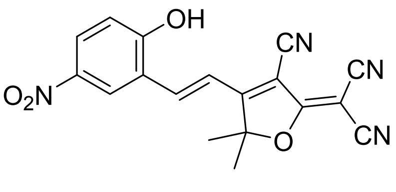
To a suspension of 0.199 g (1 mmol) of **TCF** acceptor in 2 mL of 96% ethanol 1.05 mmol of 2-hydroxybenzaldehyde and 0.077 g (1 mmol) of dry ammonium acetate were added. The resulting mixture was stirred at 40-50°C for 10 min, then for 2 h at room temperature (TLC controlled). After the reaction completion, the mixture was cooled to 0-5 ºC then precipitated product was filtered, washed with cold ethanol and dried in a vacuum desiccator over $CaCl_2$ to constant weight. Mp 294–295 ºC (dec.). ^1H NMR (500.13 MHz, DMSO-d$_6$): δ 1.78 (6H, s, 2CH_3), 6.91-6.98 (2H, m, C_6H_4), 7.37 (1H, t, J = 7.7 Hz, C_6H_4), 7.42 (1H, d, J = 16.5, Hz, CH=), 7.84 (1H, d, J = 7.7 Hz, C_6H_4), 8.18 (1H, d, J = 16.5 Hz, CH=), 10.83 (1H, s, OH). ^{13}C NMR (125.67 MHz, DMSO-d$_6$): δ 25.09, 53.71, 97.37, 99.00, 111.15, 111.88, 112.73, 115.00, 116.50, 119.71, 121.22, 130.47, 133.97, 143.91, 158.35, 176.18, 177.22. MS, (EI, 70 eV): *m/z* (%) 303 [M]$^+$ (64), 288 [M-Me]$^+$ (24), 218 (100). IR (mineral oil, cm^{-1}): 3255 (OH, NH), 2232 (CN). 1575 (C=C). Anal. Calcd for $C_{18}H_{13}N_3O_2$: C, 71.28; H, 4.32; N, 13.85. Found: C, 71.16; H, 4.39; N, 13.74.

(E)-2-(3-cyano-5-hydroxy-4-(2-hydroxystyryl)-5-methyl-1H-pyrrol-2(5H)-ylidene)malononitrile **1b**



To a suspension of 0.2 g (1 mmol) of 2-(3-cyano-5-hydroxy-4,5-dimethyl-1*H*-pyrrol-2(5*H*)-ylidene)malononitrile **HTCP** in 2 mL of 96% ethanol 1.05 mmol of 2-hydroxybenzaldehyde and 0.077 g (1 mmol) of dry ammonium acetate were added. The resulting mixture was strirred at room temperature for 4 h (TLC controlled). After the reaction completion, the mixture was cooled to 0-5 ºC then precipitated product was filtered, washed with cold ethanol and dried in a vacuum desiccator over $CaCl_2$ to constant weight. Mp 172–173 ºC (dec.). ^1H NMR (500.13 MHz, DMSO-d_6): δ 1.68 (3H, s, CH_3), 6.90 (1H, t, *J* = 7.6 Hz, C_6H_4), 6.95 (1H, d, *J* = 8.2 Hz, C_6H_4), 7.16 (1H, s, OH pyrrol), 7.29-7.34 (1H, m, C_6H_4), 7.67-7.69 (1H, m, C_6H_4), 8.10 (1H, d, *J* = 16.4 Hz, CH=), 10.51 (1H, s, OH), 10.61 (1H, s, OH). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 27.05, 45.25, 94.71, 100.07, 113.09, 115.29, 116.49, 117.10, 117.65, 121.05, 120.71, 130.57, 134.31, 143.27, 158.99, 161.56, 172.63. MS, (EI, 70 eV): *m/z* (%) 304 $[M]^+$ (5), 286 $[M-H_2O]^+$ (78). IR (mineral oil, cm^{-1}): 3335-3200 (OH, NH), 2226 (CN). 1597 (C=C). Anal. Calcd for $C_{17}H_{12}N_4O_2$: C, 67.10; H, 3.97; N, 18.41. Found: C, 66.98; H, 4.08; N, 18.29.

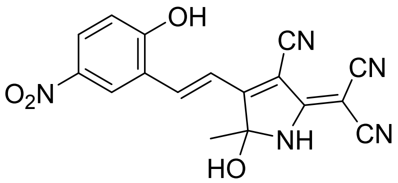
(E)-2-(3-cyano-4-(2-hydroxy-5-nitrostyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile **1c**



To a suspension of 0.199 g (1 mmol) of **TCF** acceptor in 2 mL of 96% ethanol 1.05 mmol of 2-hydroxy-5-nitrobenzaldehyde and 0.077 g (1 mmol) of dry ammonium acetate were added. The resulting mixture was stirred at room temperature for 4 h. Then to the obtained mixture 0.5 ml of 5% aqueous HCl was added, and stirring continued for additional 2 h. After the reaction completion (TLC controlled), the mixture was cooled to 5-10 ºC then precipitated product was filtered, washed with cold ethanol and dried in a vacuum desiccator over $CaCl_2$ to constant weight. Mp 283–284 ºC (dec.). ^1H NMR (500.13 MHz, DMSO-d_6): δ 1.81 (6H, s, $2CH_3$), 7.11 (1H, d, *J* = 9.1 Hz, C_6H_3), 7.70 (1H, d, *J* = 16.6 Hz, CH=), 8.10 (1H, d, *J* = 16.6

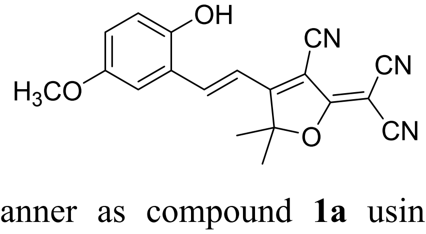
Hz, CH=), 8.22 (1H, dd, $J = 9.1, 2.9$ Hz, C_6H_3), 8.84 (1H, d, $J = 2.9$ Hz, C_6H_3), 12.43 (1H, br. s, OH). ^{13}C NMR (125.67 MHz, DMSO-d$_6$): δ 25.06, 54.65, 99.52, 99.74, 110.98, 111.82, 112.66, 117.16, 118.09, 121.58, 127.54, 128.27, 140.11, 141.83, 163.65, 175.79, 177.08. MS, (EI, 70 eV): *m/z* (%) 348 $[M]^+$ (33), 333 $[M\text{-}Me]^+$ (10), 263 (34),. IR (mineral oil, cm^{-1}): 3435 (OH, NH), 2235 (CN). 1572 (C=C). Anal. Calcd for $C_{18}H_{12}N_4O_4$: C, 62.07; H, 3.47; N, 16.09. Found: C, 61.96; H, 3.56; N, 15.95.

(E)-2-(3-cyano-5-hydroxy-4-(2-hydroxy-5-nitrostyryl)-5-methyl-1H-pyrrol-2(5H)-ylidene)malononitrile **1d**



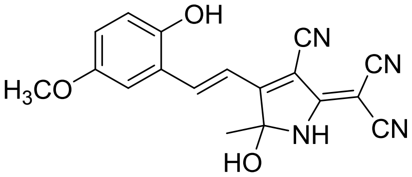
Prepared in a similar manner as compound **1c** using 0.2 g (1 mmol) of **HTCP** acceptor. Mp 219–220 ºC (dec.). ^1H NMR (500.13 MHz, DMSO-d$_6$): δ 1.71 (3H, s, CH_3), 7.12 (1H, d, $J = 9.1$ Hz, C_6H_3), 7.19 (1H, s, OH pyrrol), 7.51 (1H, d, $J = 16.5$ Hz, CH=), 8.04 (1H, d, $J = 16.5$ Hz, CH=), 8.19 (1H, dd, $J = 9.1, 2.8$ Hz, C_6H_3), 8.62 (1H, d, $J = 2.8$ Hz, C_6H_3), 12.21 (1H, br. s, OH). ^{13}C NMR (125.67 MHz, DMSO-d$_6$): δ 25.92, 45.02, 94.05, 101.25, 112.02, 114.28, 115.52, 117.29, 119.01, 122.31, 125.96, 127.99, 139.78, 140.49, 160.48, 163.37, 171.00. MS, (EI, 70 eV): *m/z* (%) 349 $[M]^+$ (3), 333 (12), 331 $[M\text{-}H_2O]^+$ (25). IR (mineral oil, cm^{-1}): 3495-3150 (OH, NH), 2235 (CN). 1572 (C=C). Anal. Calcd for $C_{17}H_{11}N_5O_4$: C, 58.45; H, 3.17; N, 20.05. Found: C, 58.36; H, 3.26; N, 19.91.

(E)-2-(3-cyano-4-(2-hydroxy-5-methoxystyryl)-5,5-dimethylfuran-2(5H)-ylidene)malononitrile **1e**



Prepared in a similar manner as compound **1a** using 1.05 mmol of 2-hydroxy-5-methoxybenzaldehyde. Mp 258–259 ºC (dec.). ^1H NMR (500.13 MHz, DMSO-d_6): δ 1.77 (6H, s, $2CH_3$), 3.76 (3H, s, OCH_3), 6.98 (1H, d, $J = 8.9$ Hz, C_6H_3), 7.01 (1H, dd, $J = 8.9, 3.1$ Hz, C_6H_3), 7.39 (1H, d, $J = 3.1$ Hz, C_6H_3), 7.43 (1H, d, $J = 16.4$ Hz, CH=), 8.18 (1H, d, $J = 16.4$ Hz, CH=), 10.42 (1H, s, OH). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 25.20, 53.74, 55.74, 97.24, 99.16, 111.34, 112.04, 112.91, 113.08, 115.26, 117.57, 121.40, 121.67, 143.96, 152.45, 153.04, 176.28, 177.41. MS, (EI, 70 eV): *m/z* (%)333 [M]$^+$ (72), 318 [M-Me]$^+$ (18), 248 (100). IR (mineral oil, cm^{-1}): 3290 (OH), 2222 (CN). 1607 (C=C). Anal. Calcd for $C_{19}H_{15}N_3O_3$: C, 68.46; H, 4.54; N, 12.61. Found: C, 68.30; H, 4.64; N, 12.77.

(E)-2-(3-cyano-5-hydroxy-4-(2-hydroxy-5-methoxystyryl)-5-methyl-1H-pyrrol-2(5H)-ylidene)malononitrile **1f**



Prepared in a similar manner as compound **1b** using 1.05 mmol of 2-hydroxy-5-methoxybenzaldehyde. Mp 156–157 ºC (dec.). ^{1}H NMR (500.13 MHz, DMSO-d_6): δ 1.68 (3H, s, CH$_3$), 3.75 (3H, s, OCH$_3$), 6.88 (1H, d, J = 8.9 Hz, C_6H_3), 6.96 (1H, dd, J = 8.9, 3.0 Hz, C_6H_3), 7.15 (1H, s, OH pyrrol), 7.20 (1H, d, J = 3.0 Hz, C_6H_3), 7.33 (1H, d, J = 16.4 Hz, CH=), 8.09 (1H, d, J = 16.4 Hz, CH=), 10.18 (1H, s, OH), 10.50 (1H, s, NH). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 25.87, 44.14, 55.69, 93.59, 98.83, 111.96, 112.08, 114.12, 115.35, 116.21, 117.49, 120.52, 121.73, 142.04, 152.29, 152.50, 160.47, 171.44. MS, (EI, 70 eV): *m/z* (%) 334 [M]$^+$ (2), 318 (71), 316 [M-H$_2$O]$^+$ (35). IR (mineral oil, cm^{-1}): 3340-3205 (OH, NH), 2226 (CN). 1586 (C=C). Anal. Calcd for $C_{18}H_{14}N_4O_3$: C, 64.66; H, 4.22; N, 16.76. Found: C, 64.48; H, 4.35; N, 16.58.

2. Absorption spectra

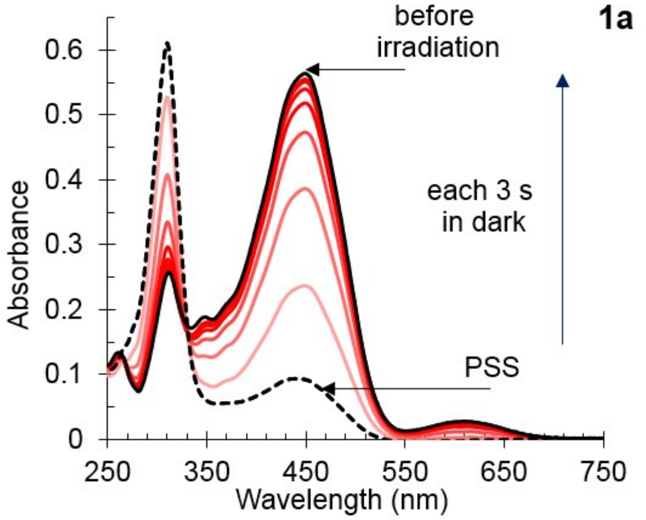


Fig. 1. Absorption spectra of the compound **1a** in EtOH (C=2.5×10^{-5} M) before and after irradiation

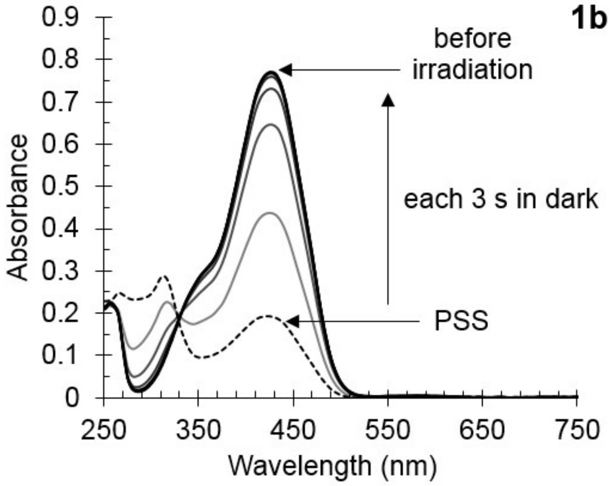


Fig. 2. Absorption spectra of the compound **1b** in EtOH (C=2.5×10^{-5} M) before and after irradiation

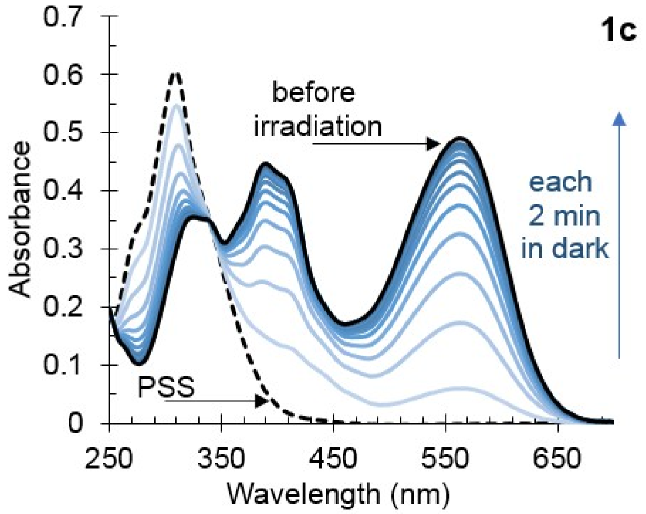


Fig. 3. Absorption spectra of the compound **1c** in EtOH (C=2.5×10^{-5} M) before and after irradiation

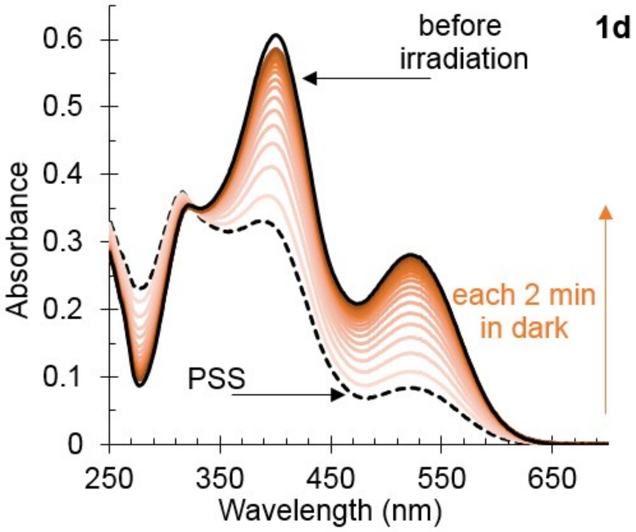


Fig. 4. Absorption spectra of the compound **1d** in EtOH (C=2.5×10^{-5} M) before and after irradiation

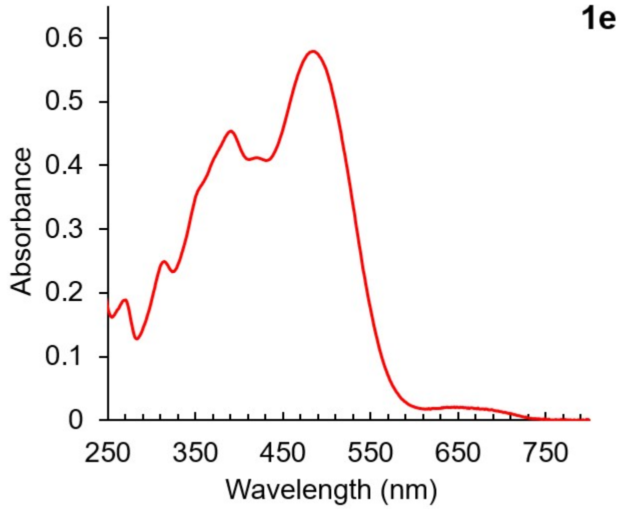


Fig. 5. Absorption spectrum of the compound **1e** in EtOH (C=2.5×10^{-5} M)

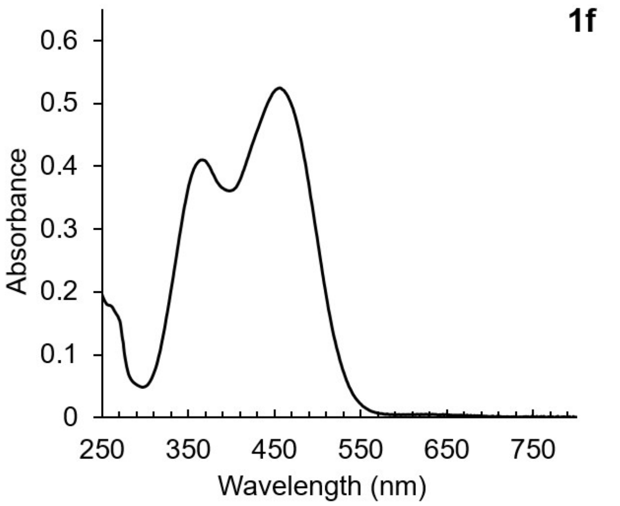


Fig. 6. Absorption spectrum of the compound **1f** in EtOH (C=2.5×10^{-5} M)

3. Kinetic curves for the reverse thermal transformation

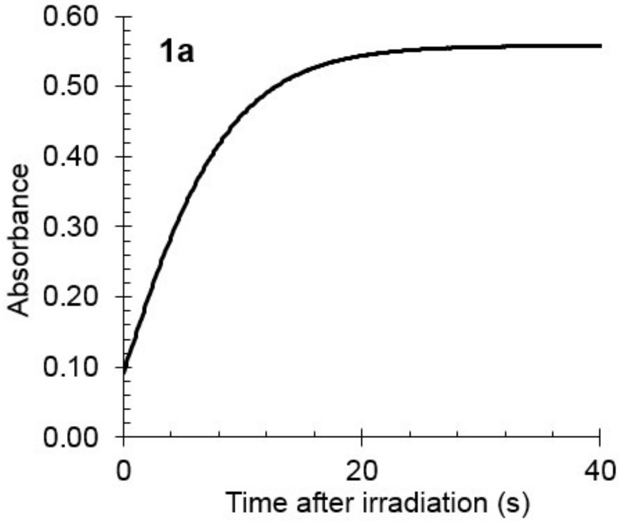


Fig. 7.1. Kinetics of the reverse thermal transformation for the compound **1a** (at 450 nm)

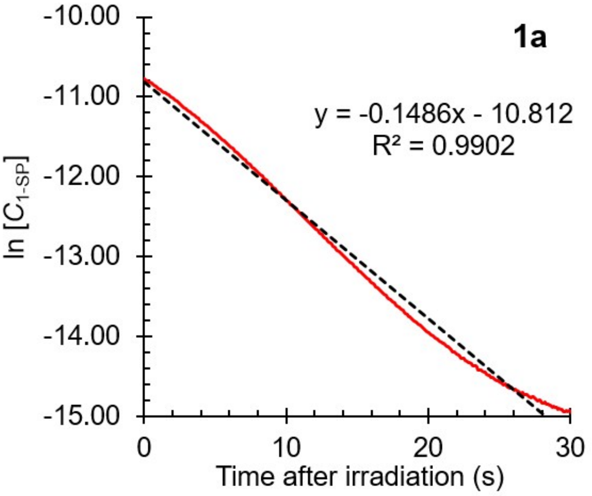


Fig. 7.2. Fitted kinetics of the reverse thermal transformation for the compound **1a** (at 450 nm)

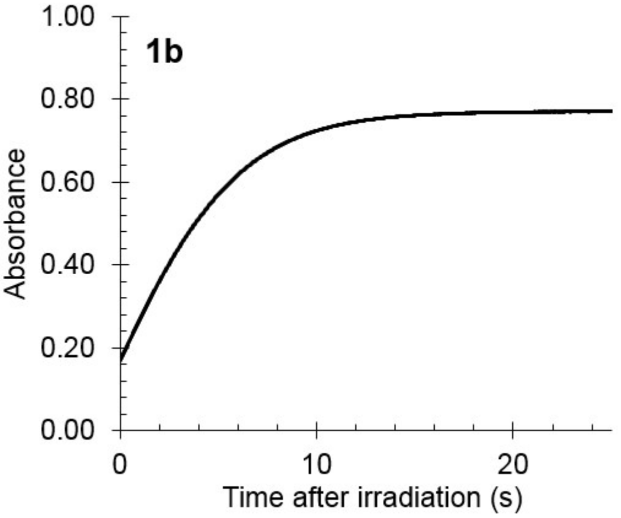


Fig. 8.1. Kinetics of the reverse thermal transformation for the compound **1b** (at 425 nm)

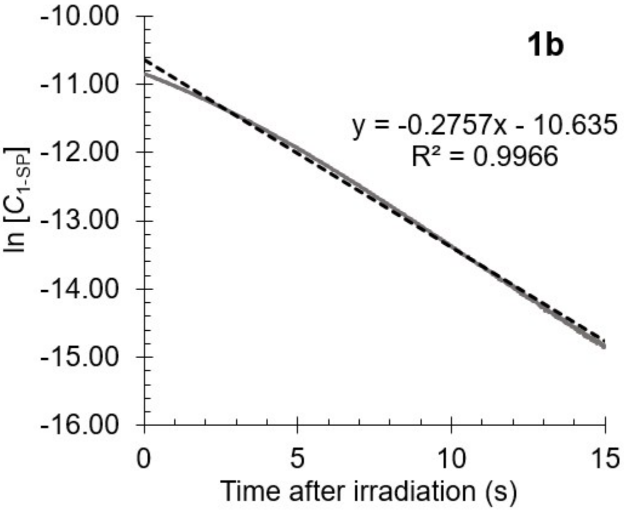


Fig. 8.2. Fitted kinetics of the reverse thermal transformation for the compound **1b** (at 425 nm)

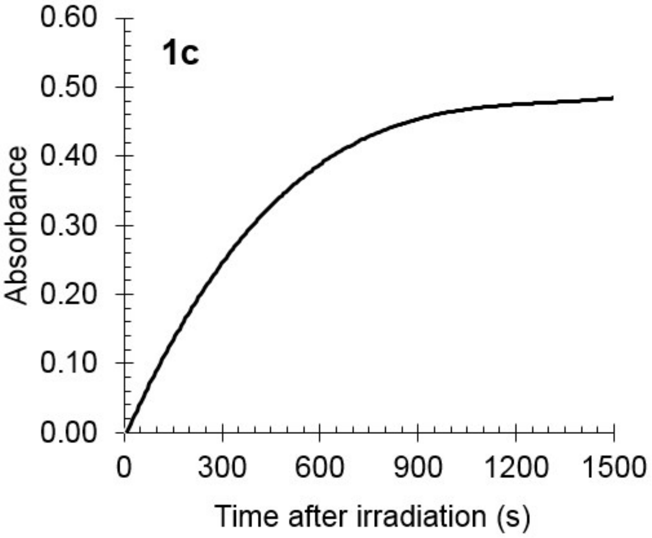


Fig. 9.1. Kinetics of the reverse thermal transformation for the compound **1c** (at 564 nm)

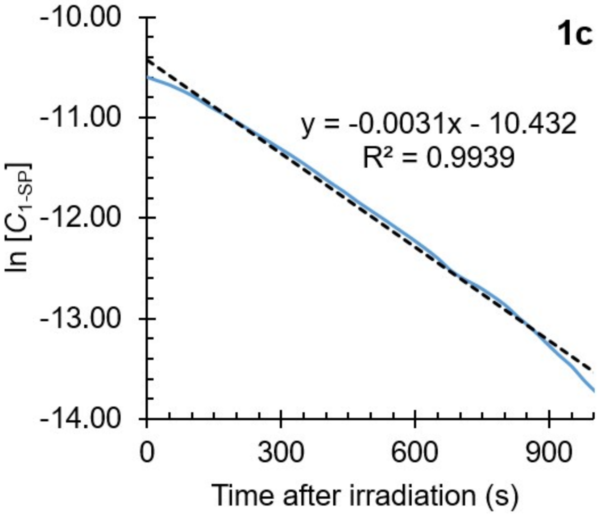


Fig. 9.2. Fitted kinetics of the reverse thermal transformation for the compound **1c** (at 564 nm)

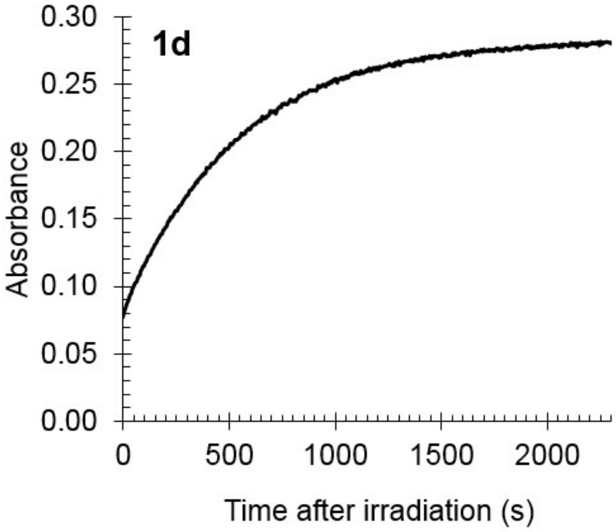


Fig. 10.1 Kinetics of the reverse thermal transformation for the compound **1d** (at 520 nm)

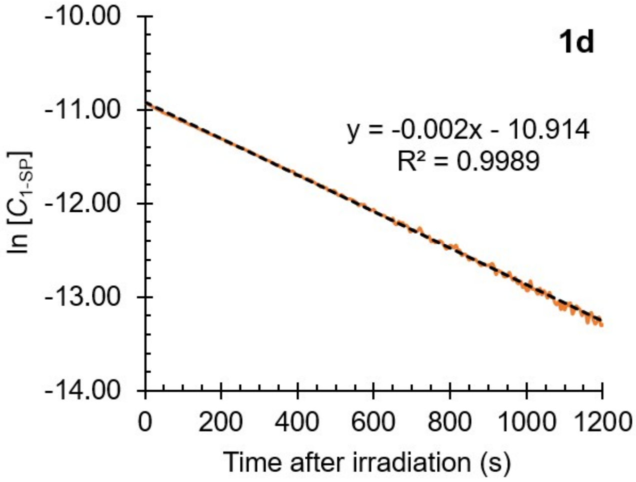


Fig. 10.2. Fitted kinetics of the reverse thermal transformation for the compound **1d** (at 520 nm)

4. Fatigue resistance of the photo-thermal transformations

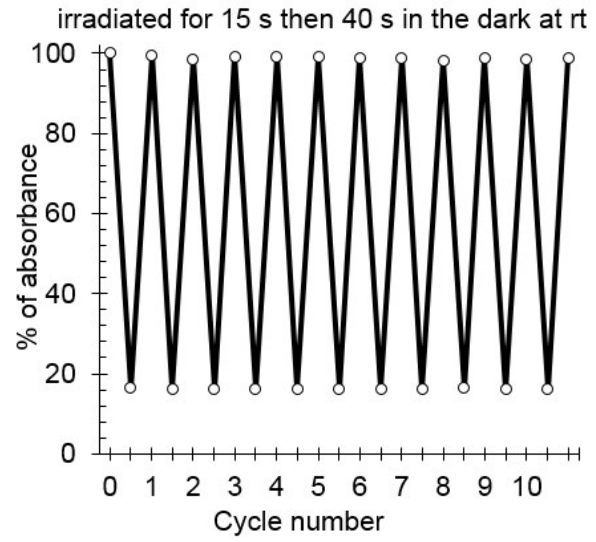


Fig. 11. Cyclicity of the photo-transformations of compound **1a** in EtOH (at 450 nm)

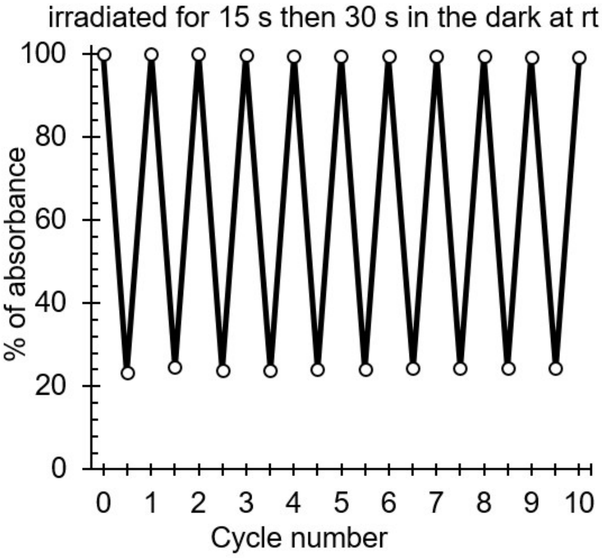


Fig. 12. Cyclicity of the photo-transformations of compound **1b** in EtOH (at 420 nm)

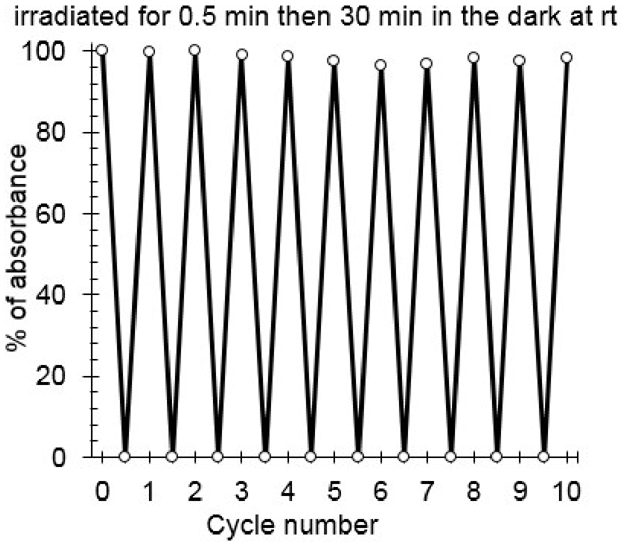


Fig. 13. Cyclicity of the photo-transformations of compound **1c** in EtOH (at 564 nm)

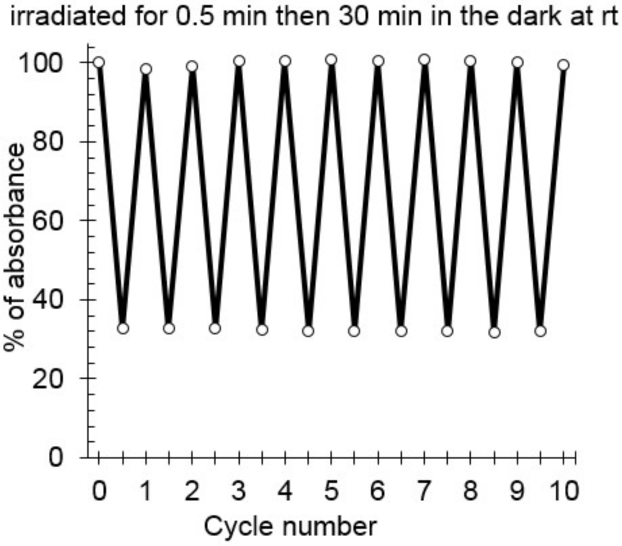


Fig. 14. Cyclicity of the photo-transformations of compound **1d** in EtOH (at 520 nm)

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

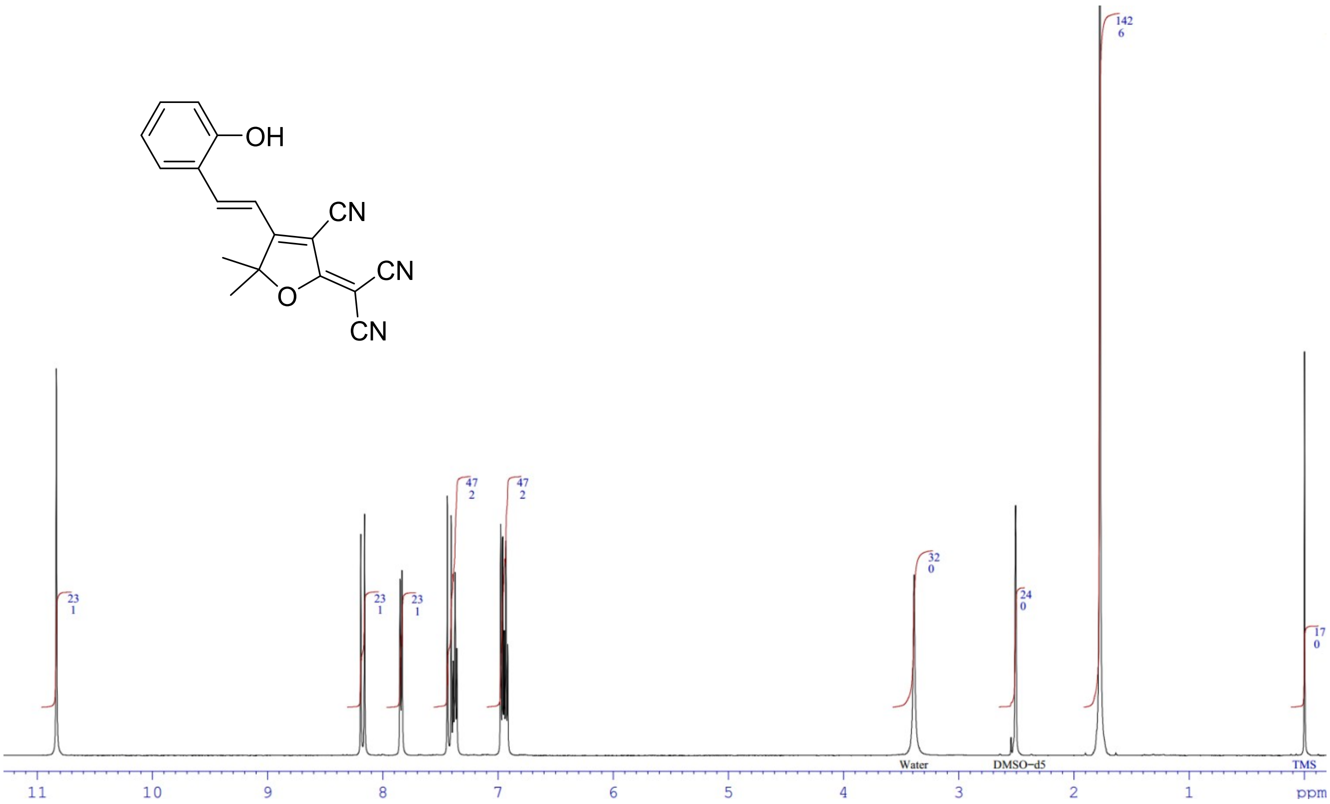


Fig. 15. ^{1}H-NMR-spectrum of **1a** (500.13 MHz, DMSO−d_6, 293K)

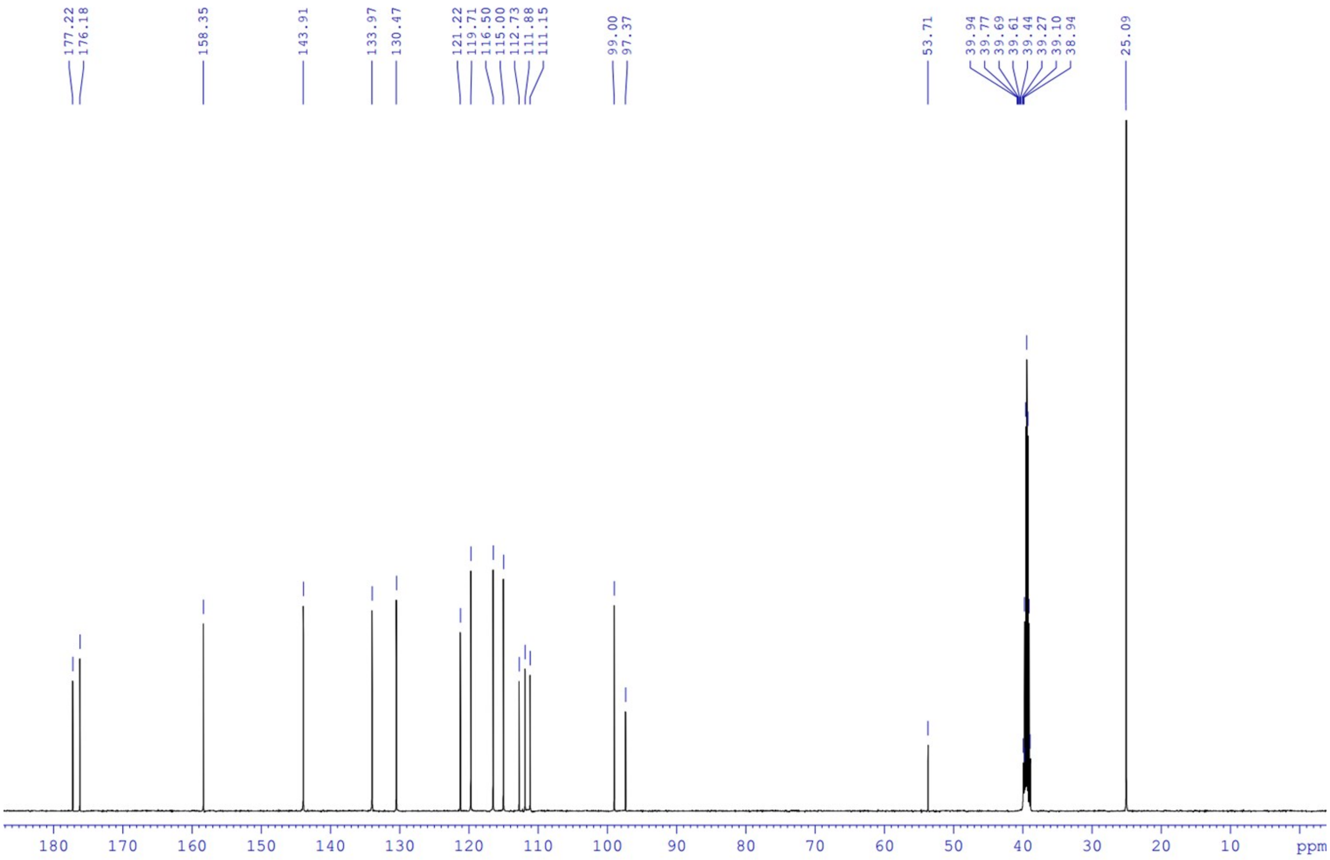


Fig. 16. ^{13}C-NMR-spectrum of **1a** (125.76 MHz, DMSO−d_6, 296K)

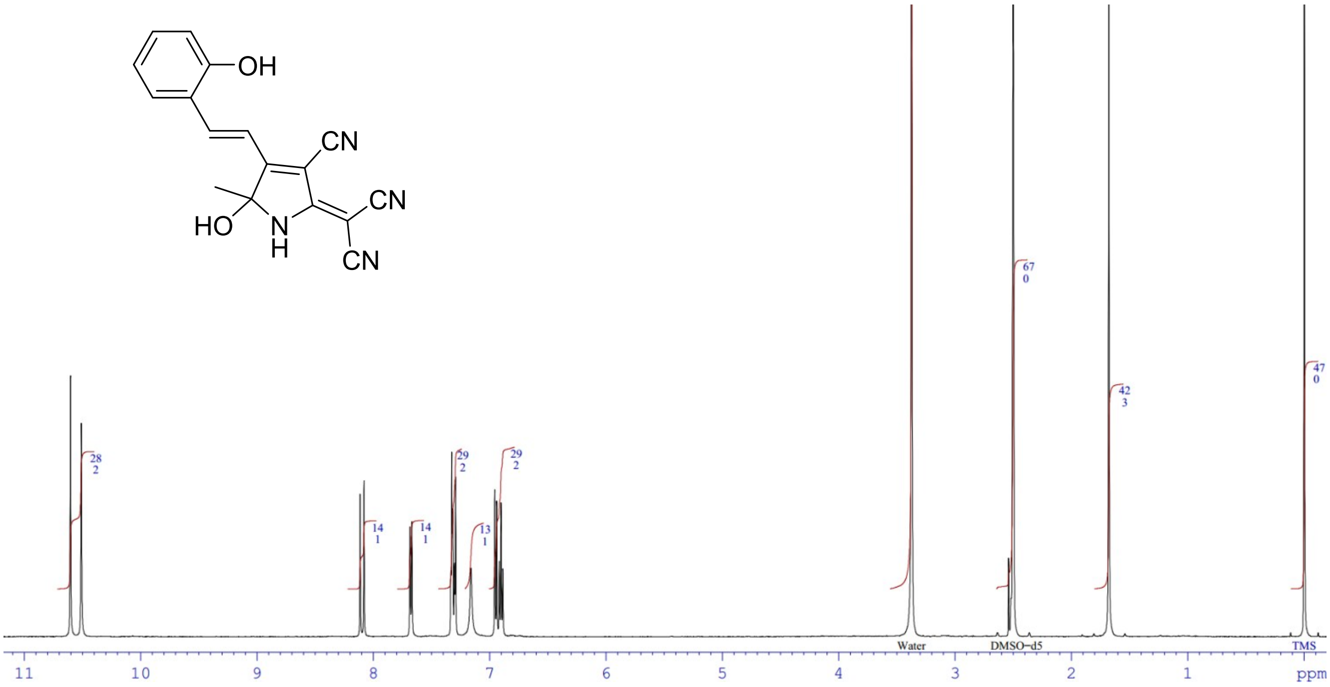


Fig. 17. ^{1}H-NMR-spectrum of **1b** (500.13 MHz, DMSO−d_6, 293K)

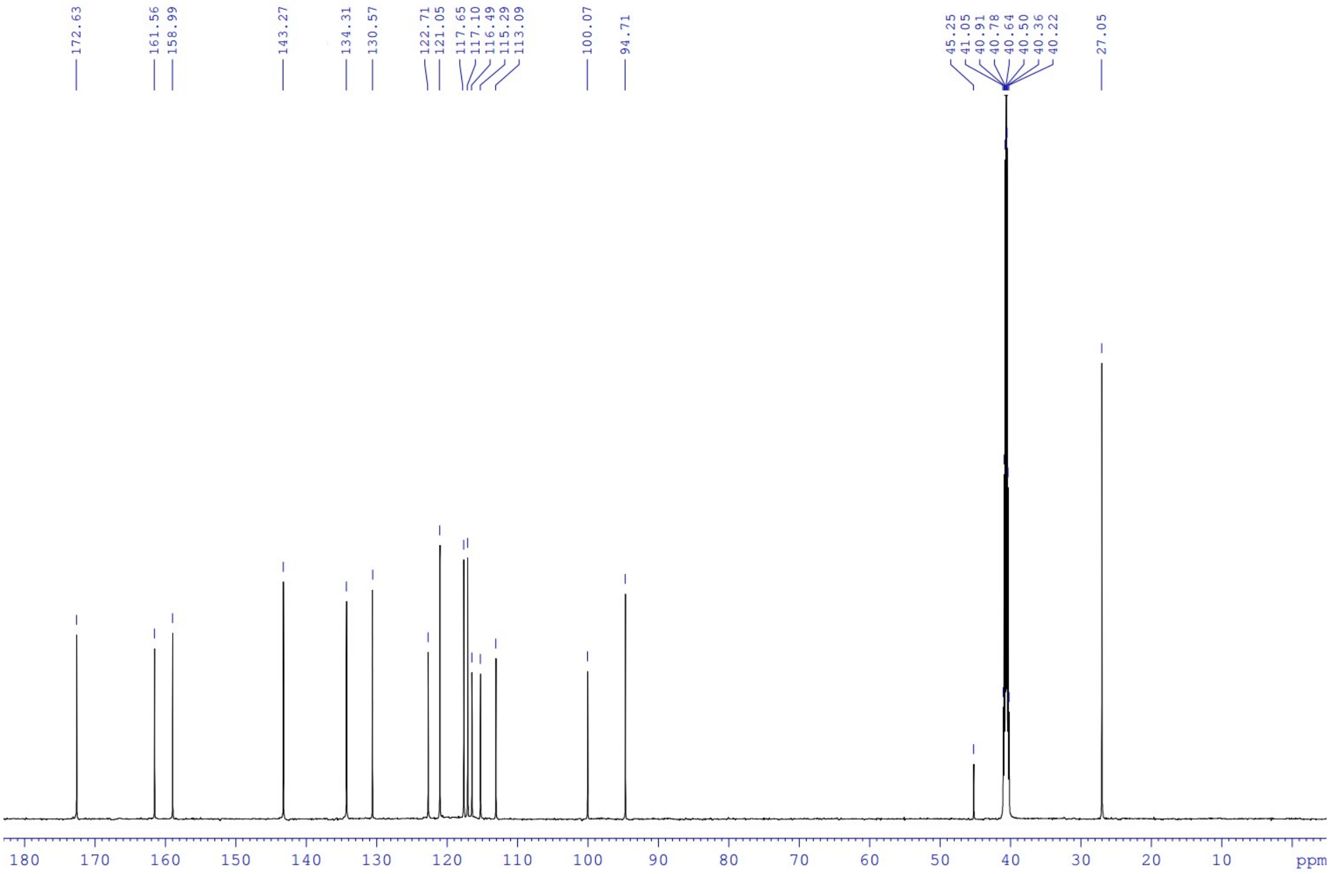


Fig. 18. ^{13}C-NMR-spectrum of **1b** (150.90 MHz, DMSO−d_6, 296K)

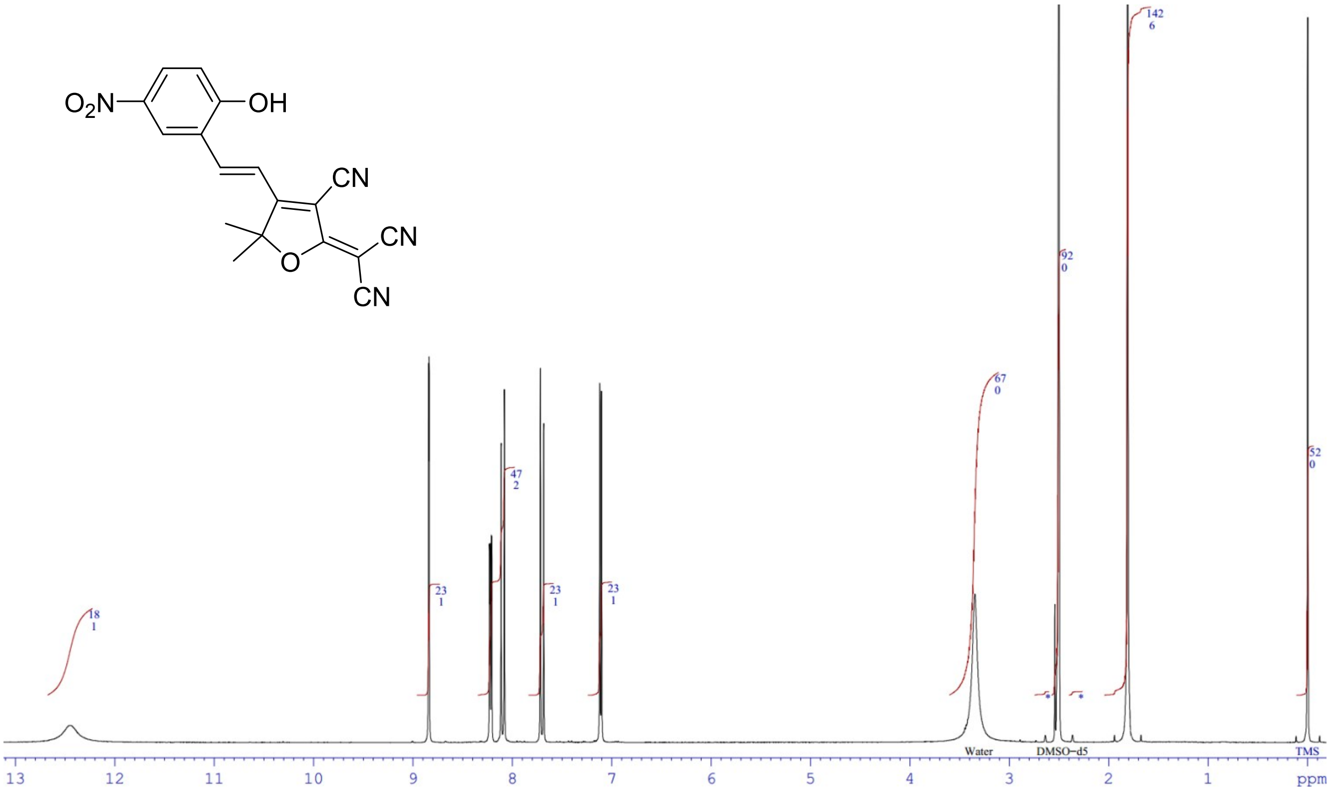


Fig. 19. ^{1}H-NMR-spectrum of **1c** (500.13 MHz, DMSO−d_6, 300K)

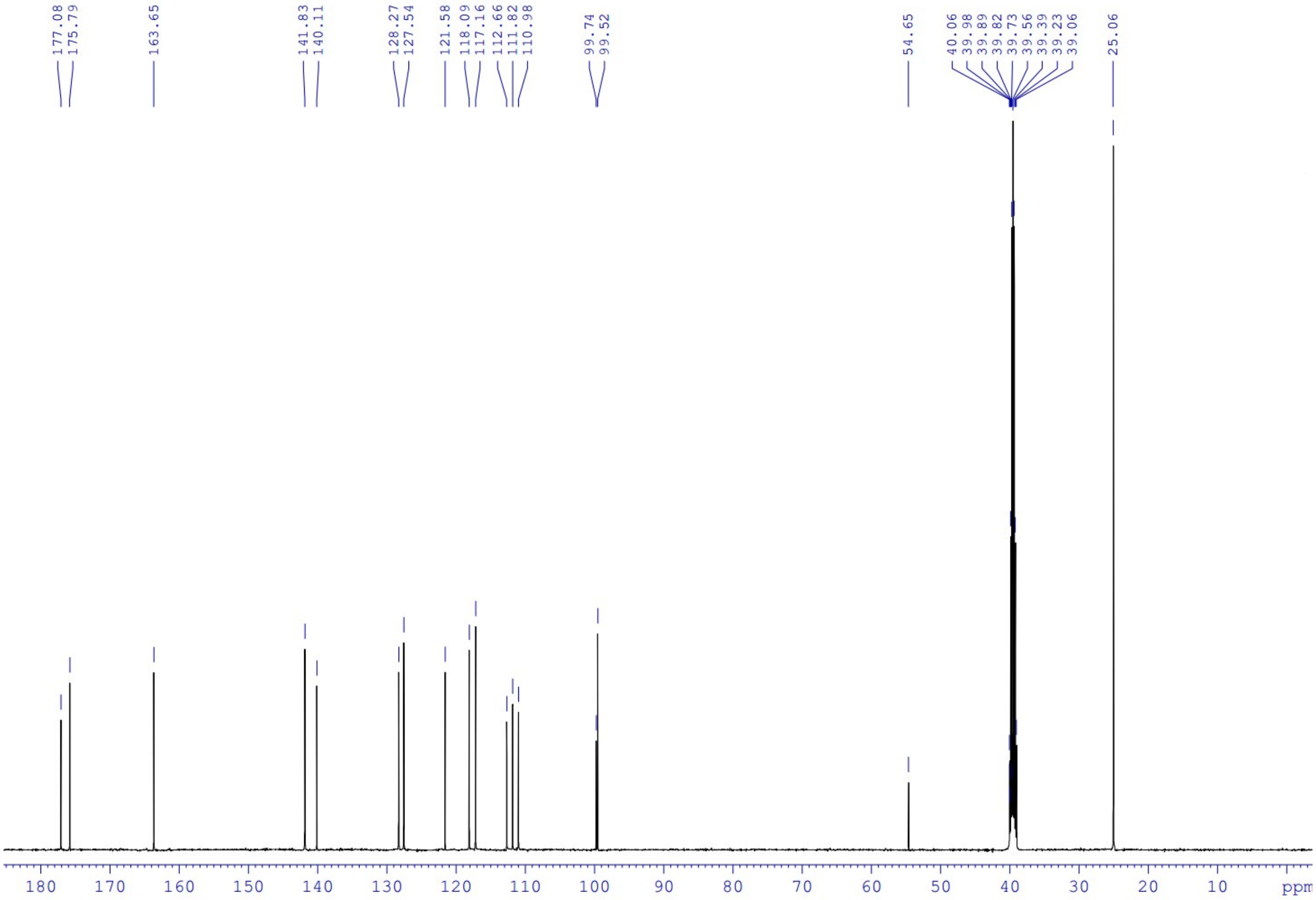


Fig. 20. ^{13}C-NMR-spectrum of **1c** (125.76 MHz, DMSO−d_6, 299K)

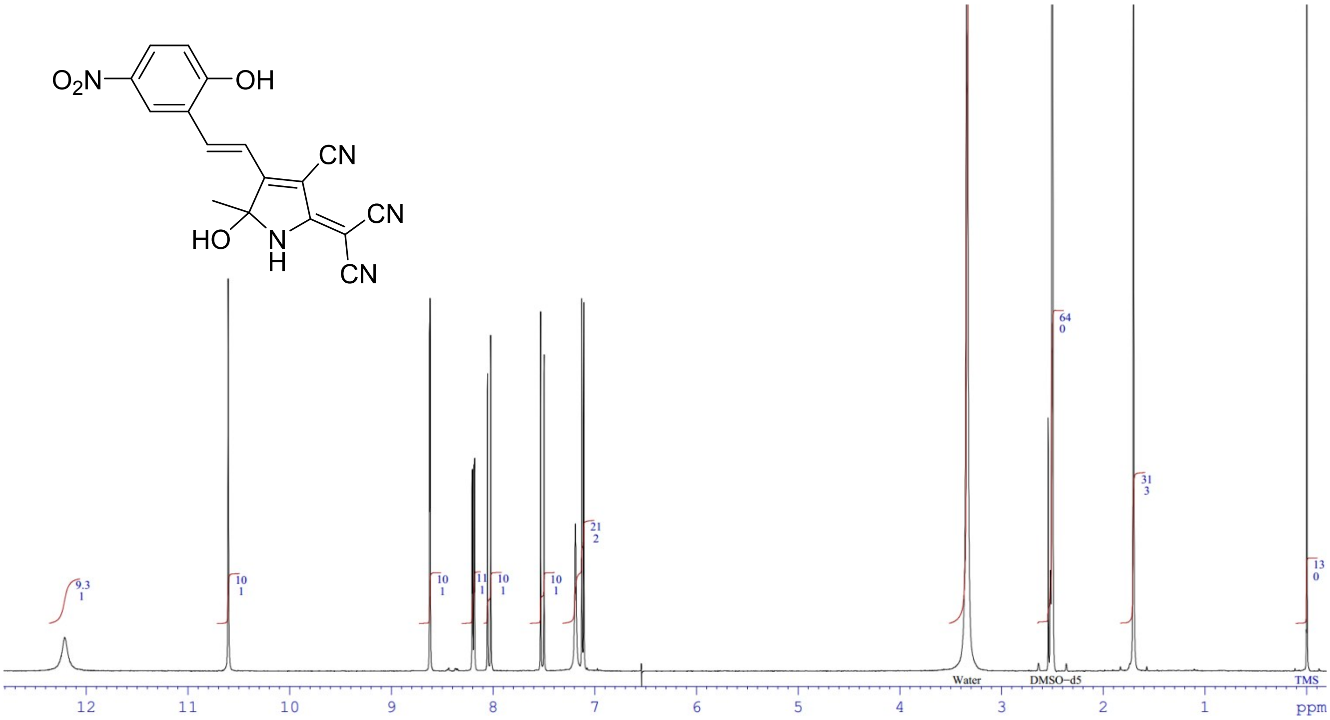


Fig. 21. ^{1}H-NMR-spectrum of **1d** (500.13 MHz, DMSO−d_6, 298K)

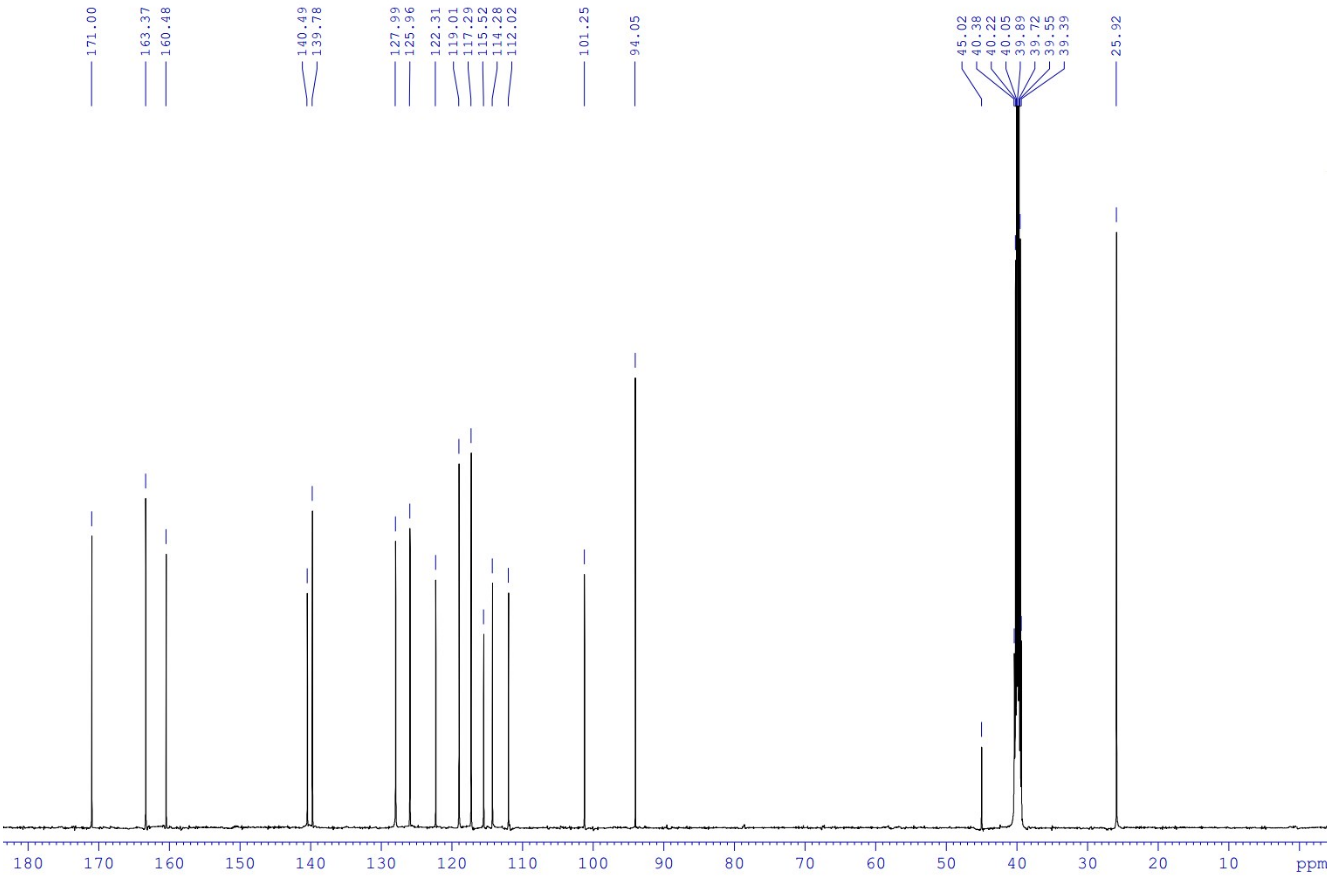


Fig. 22. ^{13}C-NMR-spectrum of **1d** (125.76 MHz, DMSO−d_6, 296K)

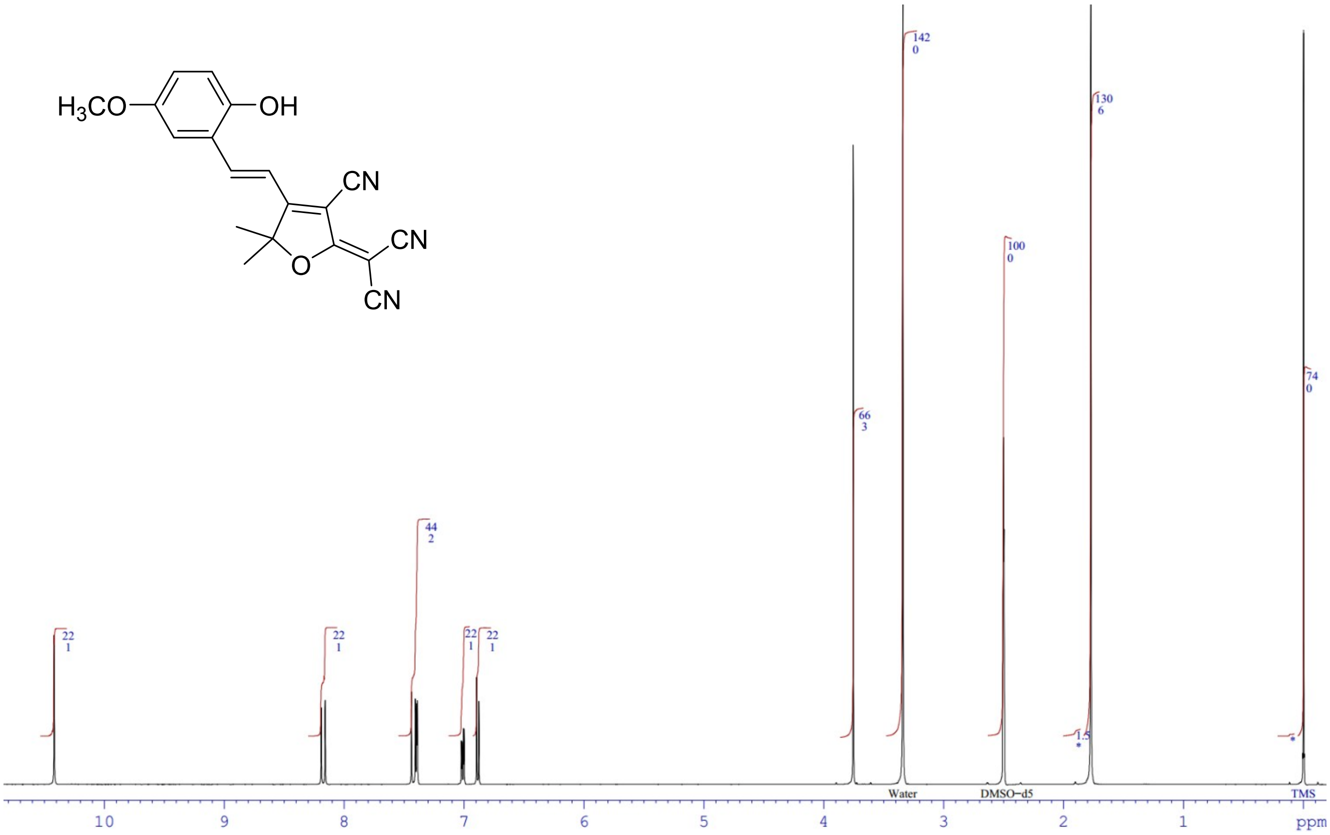


Fig. 23. ^{1}H-NMR-spectrum of **1e** (500.13 MHz, DMSO−d_6, 293K)

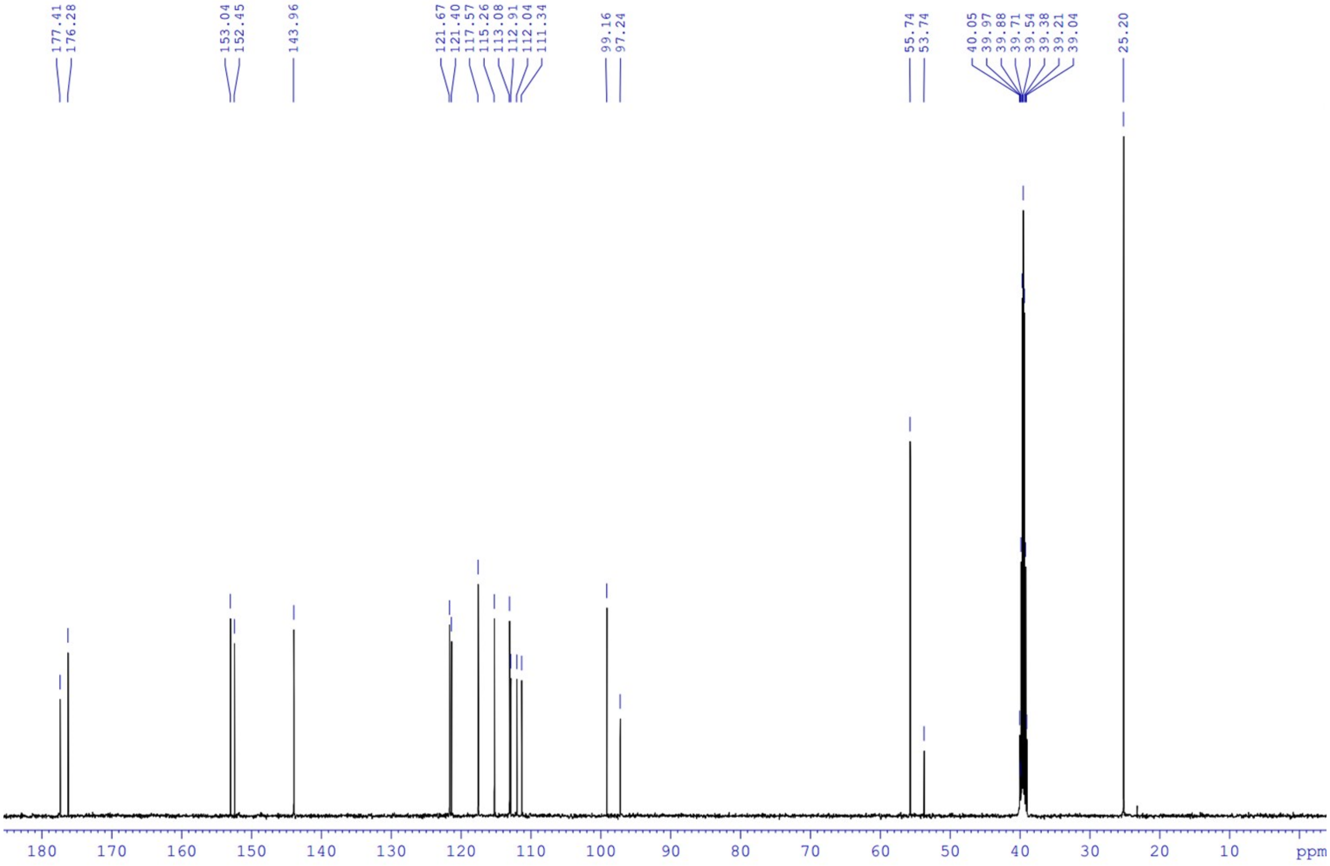


Fig. 24. ^{13}C-NMR-spectrum of **1e** (125.76 MHz, DMSO−d_6, 296K)

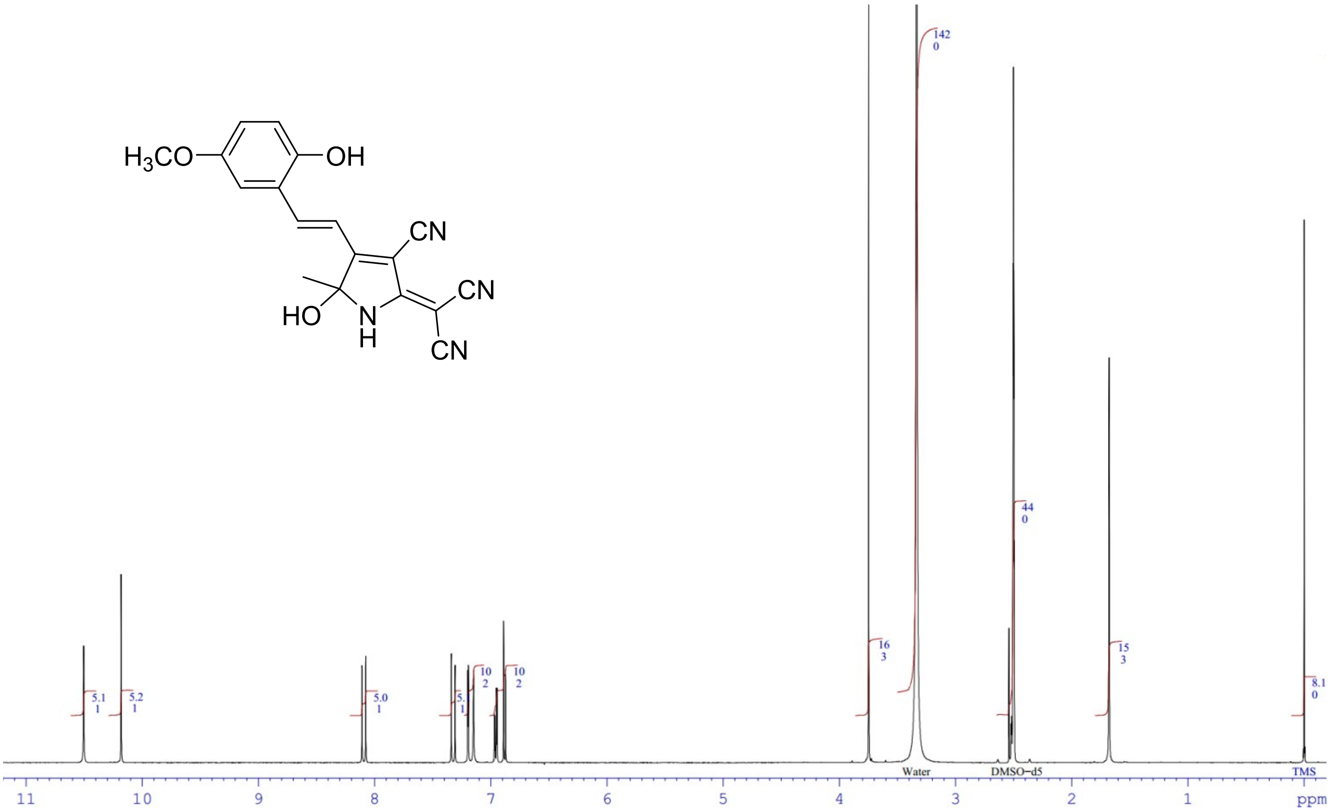


Fig. 25. ^{1}H-NMR-spectrum of **1f** (500.13 MHz, DMSO−d_6, 293K)

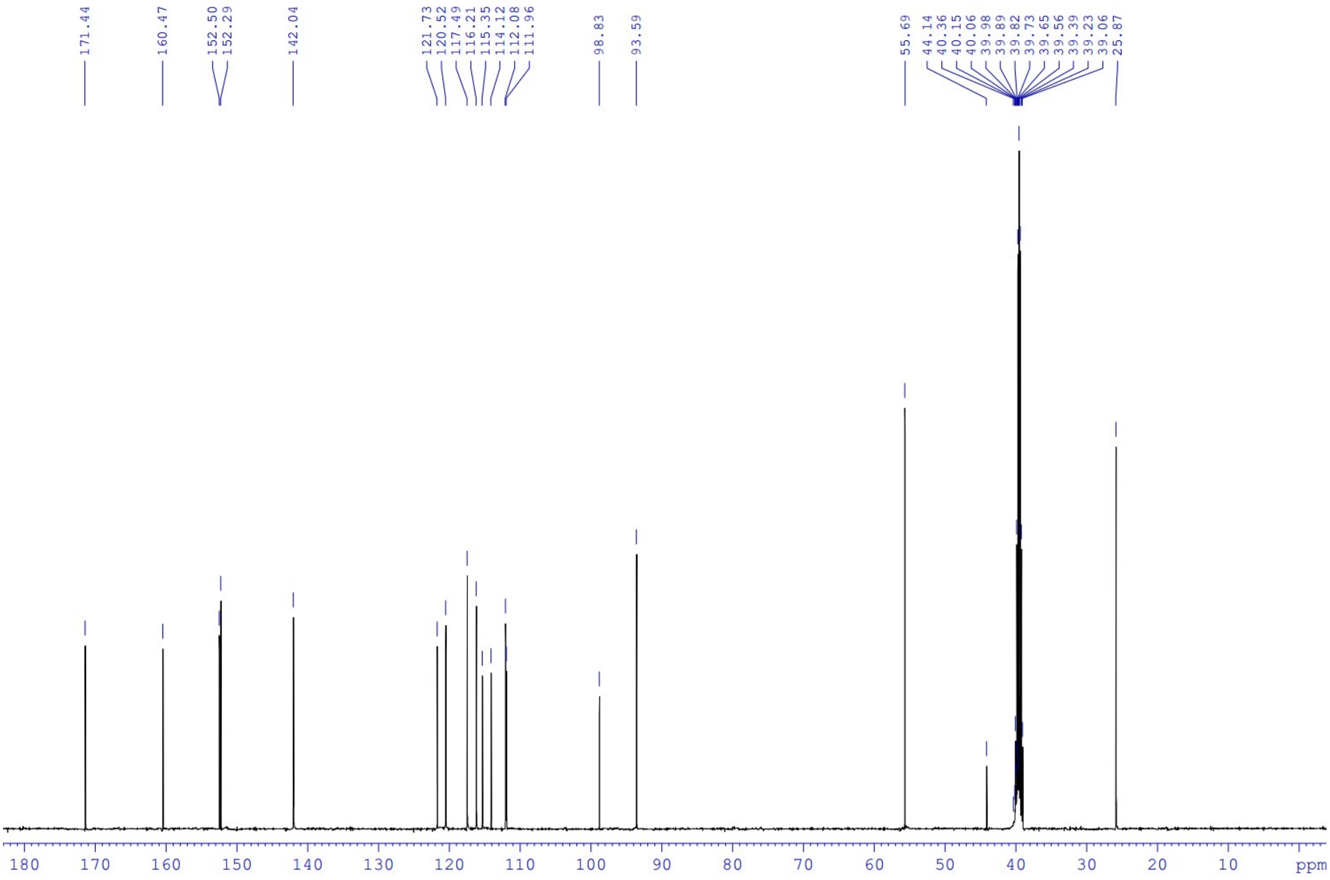


Fig. 26. ^{13}C-NMR-spectrum of **1f** (125.76 MHz, DMSO−d_6, 296K)