Electronic Supplementary Information for

First example of unusual reversible nucleophilic addition to 2-(5-aryl-2-oxo-3*H*-pyrrol-3-ylidene)malononitriles – a new tool for the creation of thermosensitive molecular switches

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Contents

1. Experimental

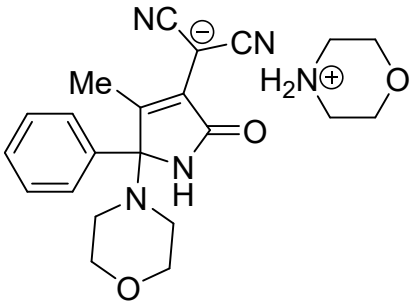
1.1 General remarks

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 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 on Varian 400 spectrometer using 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 equipped with a Peltier 1x1 Cell Holder Accessory. The diffuse reflectance (DR) spectra of solid samples were obtained using Remote Diffuse Reflectance Accessory (DRA) for Agilent Cary 60 UV-Vis Spectrophotometer and converted into equivalent absorption spectra by means of Kubelka-Munk function. Thermogravimetric analysis (TGA) was performed on a simultaneous thermogravimetry/differential thermal analyzer Shimadzu DTG-60. Melting points were determined on an OptiMelt MPA100 device.

1.2 Synthetic procedures and spectral data

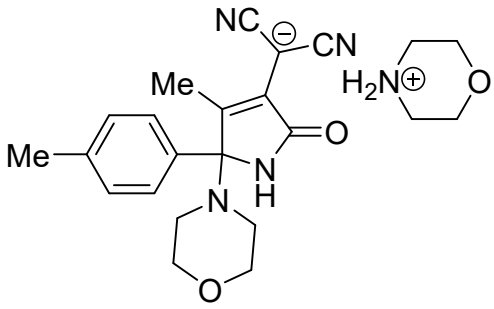
General synthesis procedure of morpholin-4-ium dicyano(5-morpholino-2-oxo-2,5-dihydro-1H-pyrrol-3-yl)methanides **2a-e**. An appropriate starting pyrrole **1** (1 mmol) was suspended in a mixture of dry toluene (4 mL) and dry ethyl acetate (0.2 mL) at room temperature. Then morpholine (0.34 g, 4 mmol) was added at stirring. The reaction mixture was further stirred for 0.5-1 h until the complete disappearance of traces of colored starting compound **1** and homogenization of the resulting suspension of product **2**. The reaction mixture was cooled down to 5-10 °C, and then the precipitated solid was filtered and washed by dry toluene (2-3 mL). The obtained product was dried in a desiccator with $CaCl_2$ at room temperature to the constant weight. Compounds **2** should be stored in a sealed vessel at or below room temperature, which ensures their stability for a long period (minimum 2-3 months).

Morpholin-4-ium dicyano(4-methyl-5-morpholino-2-oxo-5-phenyl-2,5-dihydro-1H-pyrrol-3-yl)methanide **2a**. 0.352 g of product **2a** from 0.235 g of starting material **1a**



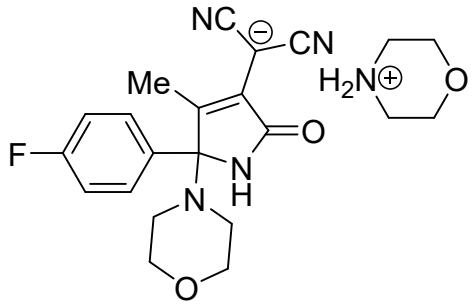
was isolated. Yield 86%. Mp 104–105ºC (dec.) (PhMe). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.57 (3H, s, CH_3), 2.23-2.33 (4H, m, $N(CH_2)_2$), 3.09 (4H, pseudo-t, J = 4.9 Hz, $N(CH_2)_2$), 3.55-3.63 (4H, m, $O(CH_2)_2$), 3.74 (4H, pseudo-t, J = 4.9 Hz, $O(CH_2)_2$), 7.20-7.25 (1H, m, C_6H_5), 7.31 (2H, t, J = 7.6 Hz, C_6H_5), 7.38 (2H, d, J = 7.8 Hz, C_6H_5), 8.51 (1H, s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 9.75, 19.70, 43.14, 46.59, 63.56, 66.54, 83.30, 126.09, 126.24, 126.86, 127.03, 128.17, 128.51, 140.88, 172.34. MS, (EI, 70 eV): *m/z* (%) 322 $[M-87]^+$ (24.1), 235 $[M-174]^+$ (30.0), 105 $[M-304]^+$ (85.0), 86 $[M-323]^+$ (96.0), 56 $[M-353]^+$ (100). IR (mineral oil, cm^{-1}): 3243 (NH), 2174, 2117 (CN), 1673, 1625 (C=O, C=C). Anal. Calcd for $C_{22}H_{27}N_5O_3$: C, 64.53; H, 6.65; N, 17.10. Found: C, 64.77; H, 6.51; N, 17.19.

Morpholin-4-ium dicyano(4-methyl-5-morpholino-2-oxo-5-(p-tolyl)-2,5-dihydro-1H-pyrrol-3-yl)methanide **2b**. 0.376 g of product **2b** from 0.249 g of starting material



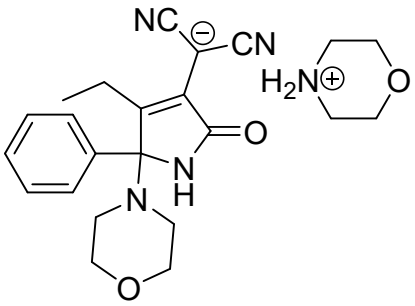
1b was isolated. Yield 89%. Mp 131–132ºC (dec.) (PhMe). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.56 (3H, s, CH_3), 2.21-2.32 (7H, m, $N(CH_2)_2$, CH_3), 3.09 (4H, pseudo-t, J = 5.0 Hz, $N(CH_2)_2$), 3.54-3.63 (4H, m, $O(CH_2)_2$), 3.74 (4H, pseudo-t, J = 4.9 Hz, $O(CH_2)_2$), 7.11 (2H, d, J = 7.9 Hz, C_6H_4), 7.25 (2H, d, J = 7.9 Hz, C_6H_4), 8.47 (1H, s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 9.79, 19.56, 20.55, 43.16, 46.58, 63.58, 66.55, 83.18, 125.88, 126.20, 127.12, 128.77, 128.90, 135.95, 137.84, 172.36. MS, (EI, 70 eV): *m/z* (%) 249 $[M-174]^+$ (64.1), 234 $[M-189]^+$ (30.9), 87 $[M-336]^+$ (77.5), 57 $[M-366]^+$ (100). IR (mineral oil, cm^{-1}): 3286 (NH), 2181, 2135 (CN), 1680, 1609 (C=O, C=C). Anal. Calcd for $C_{23}H_{29}N_5O_3$: C, 65.23; H, 6.90; N, 16.54. Found: C, 65.48; H, 7.02; N, 16.44.

Morpholin-4-ium dicyano(5-(4-fluorophenyl)-4-methyl-5-morpholino-2-oxo-2,5-dihydro-1H-pyrrol-3-yl)methanide **2c**. 0.359 g of product **2c** from 0.253 g of starting material **1c** was isolated. Yield 84%. Mp 132–133ºC (dec.) (PhMe). ^{1}H NMR (400

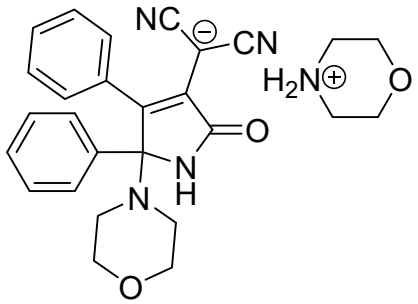


MHz, DMSO-d_6): δ 1.56 (3H, s, CH_3), 2.25-2.30 (4H, m, $N(CH_2)_2$), 3.09 (4H, pseudo-t, J = 5.0 Hz, $N(CH_2)_2$), 3.54-3.61 (4H, m, $O(CH_2)_2$), 3.74 (4H, pseudo-t, J = 5.0 Hz, $O(CH_2)_2$), 7.12-7.16 (2H, m, C_6H_4), 7.36-7.41 (2H, m, C_6H_4), 8.54 (1H, s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 9.65, 19.78, 43.10, 46.55, 63.53, 66.50, 82.92, 114.87 ($^2J_{CF}$ = 21.0 Hz), 126.20, 126.91, 128.07, 128.22 ($^3J_{CF}$ = 7.8 Hz), 136.99, 161.19 ($^1J_{CF}$ = 242.8 Hz), 172.20. MS, (EI, 70 eV): *m/z* (%) 340 $[M-87]^+$ (4.6), 253 $[M-174]^+$ (100). IR (mineral oil, cm^{-1}): 3274 (NH), 2180, 2134 (CN), 1684, 1609 (C=O, C=C). Anal. Calcd for $C_{22}H_{26}FN_5O_3$: C, 61.81; H, 6.13; N, 16.38. Found: C, 62.02; H, 6.22; N, 16.14.

Morpholin-4-ium dicyano(4-ethyl-5-morpholino-2-oxo-5-phenyl-2,5-dihydro-1H-pyrrol-3-yl)methanide **2d**. 0.334 g of product **2d** from 0.249 g of starting material **1d**



was isolated. Yield 79%. Mp 134–135ºC (dec.) (PhMe). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.34 (3H, t, J = 7.3 Hz, $C\underline{H}_3CH_2$), 1.90-2.00 (1H, m, $CH_3C\underline{H}_2$), 2.17-2.36 (5H, m, $N(CH_2)_2$, $CH_3C\underline{H}_2$), 3.07 (4H, pseudo-t, J = 4.9 Hz, $N(CH_2)_2$), 3.53-3.65 (4H, m, $O(CH_2)_2$), 3.73 (4H, pseudo-t, J = 4.9 Hz, $O(CH_2)_2$), 7.20-7.24 (1H, m, C_6H_5), 7.30 (2H, t, J = 7.5 Hz, C_6H_5), 7.41-7.43 (2H, m, C_6H_5), 8.39 (1H, s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.73, 16.79, 20.02, 43.22, 46.93, 63.68, 66.50, 83.30, 125.47, 126.48, 126.74, 126.84, 128.09, 133.58, 140.97, 172.56. MS, (EI, 70 eV): *m/z* (%) 335 $[M-87]^+$ (0.4), 249 $[M-174]^+$ (48.5), 234 $[M-189]^+$ (100). IR (mineral oil, cm^{-1}): 3221 (NH), 2174, 2117 (CN), 1670, 1621 (C=O, C=C). Anal. Calcd for $C_{23}H_{29}N_5O_3$: C, 65.23; H, 6.90; N, 16.54. Found: C, 65.48; H, 7.03; N, 16.67.



Morpholin-4-ium dicyano(5-morpholino-2-oxo-4,5-diphenyl-2,5-dihydro-1H-pyrrol-3-yl)methanide **2e**. 0.344 g of product **2e** from 0.297 g of starting material **1e** was isolated. Yield 73%. Mp 126–127ºC (dec.) (PhMe).^{1}H NMR (400 MHz, DMSO-d_6): δ 2.40-2.58 (4H, m, $N(CH_2)_2$), 2.96 (4H, pseudo-t, J = 4.9 Hz, $N(CH_2)_2$), 3.58-3.77 (8H, m, $2[O(CH_2)_2]$), 6.92-7.29 (10H, m, $2C_6H_5$), 8.77 (1H, s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.34, 43.95, 47.16, 64.63, 66.43, 84.18, 125.52, 126.59, 126.69, 127.48, 127.75, 128.40, 128.89, 129.11, 134.02, 140.41, 171.87. MS, (EI, 70 eV): *m/z* (%) 384 $[M-87]^+$ (25.0), 297 $[M-174]^+$ (100), 87 $[M-384]^+$ (50.1), 57 $[M-414]^+$ (51.8). IR (mineral oil, cm^{-1}): 3206 (NH), 2175, 2124 (CN), 1688, 1609 (C=O, C=C). Anal. Calcd for $C_{27}H_{29}N_5O_3$: C, 68.77; H, 6.20; N, 14.85. Found: C, 69.03; H, 6.33; N, 14.99.

2. Diffuse reflectance spectra

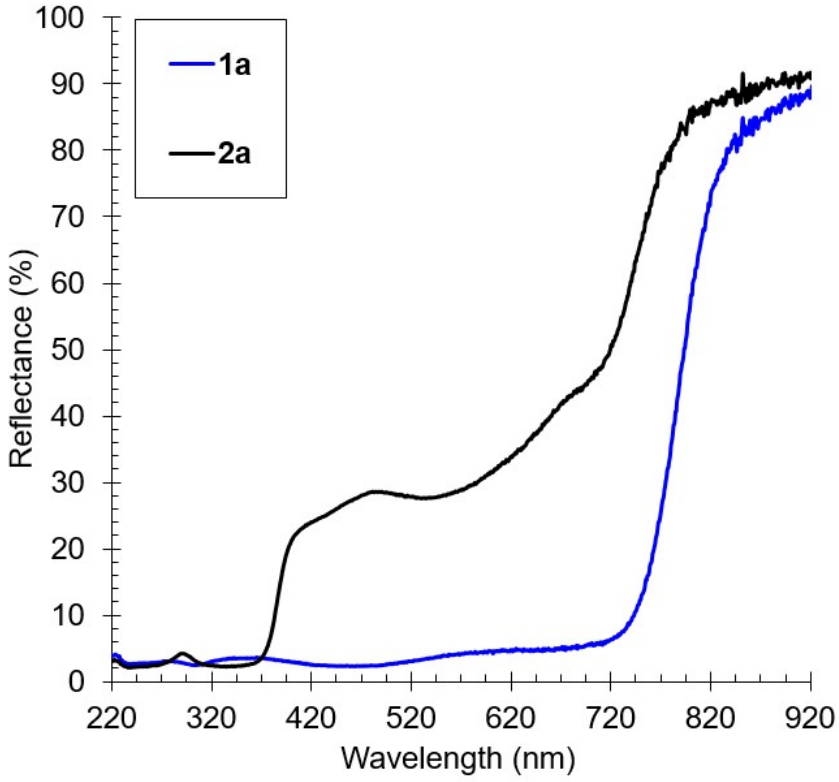


Fig. 1. DR spectra of individual powders of compounds **1a** and **2a**

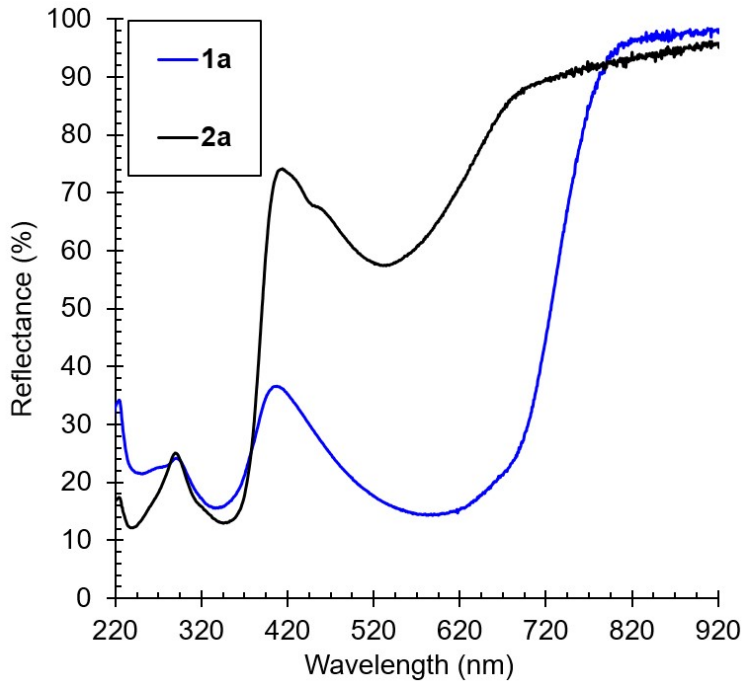


Fig. 2. DR spectra of samples of compounds **1a** and **2a** (1% w/w) prepared in a mixture with KBr (99% w/w)

3. The ratio of compounds 1 and 2 in solution depending on temperature*

Temperature, °C	Mole content of **1a**, %	Mole content of **2a**, %
0	9	91
5	14	86
10	22	78
15	32	68
20	42	58
25	53	47
30	62	38
35	70	30
40	76	24

*A mixture of compound **1a** (5×10^{-5} M) with morpholine (100 equiv.) in propan-2-ol

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

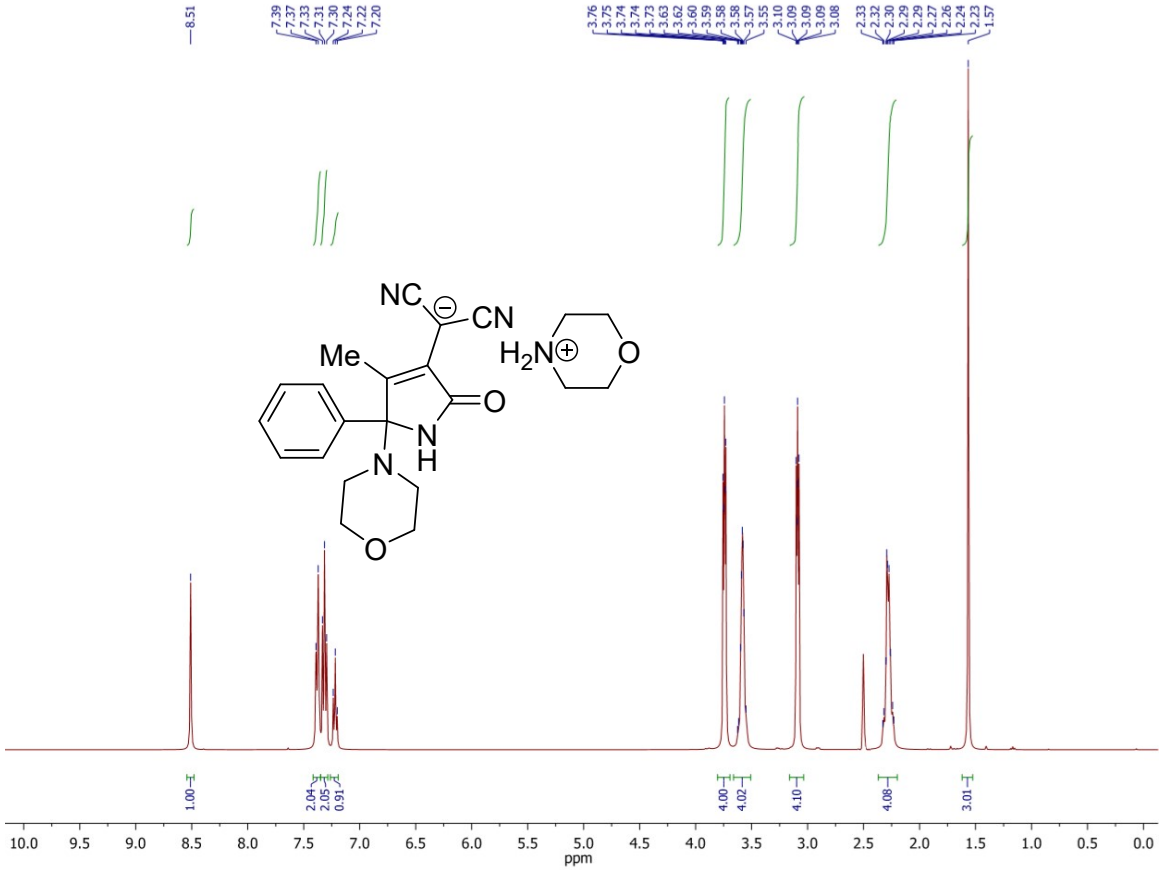


Fig. 3. ^{1}H-NMR-spectrum of compound **2a** (400 MHz, DMSO−d6)

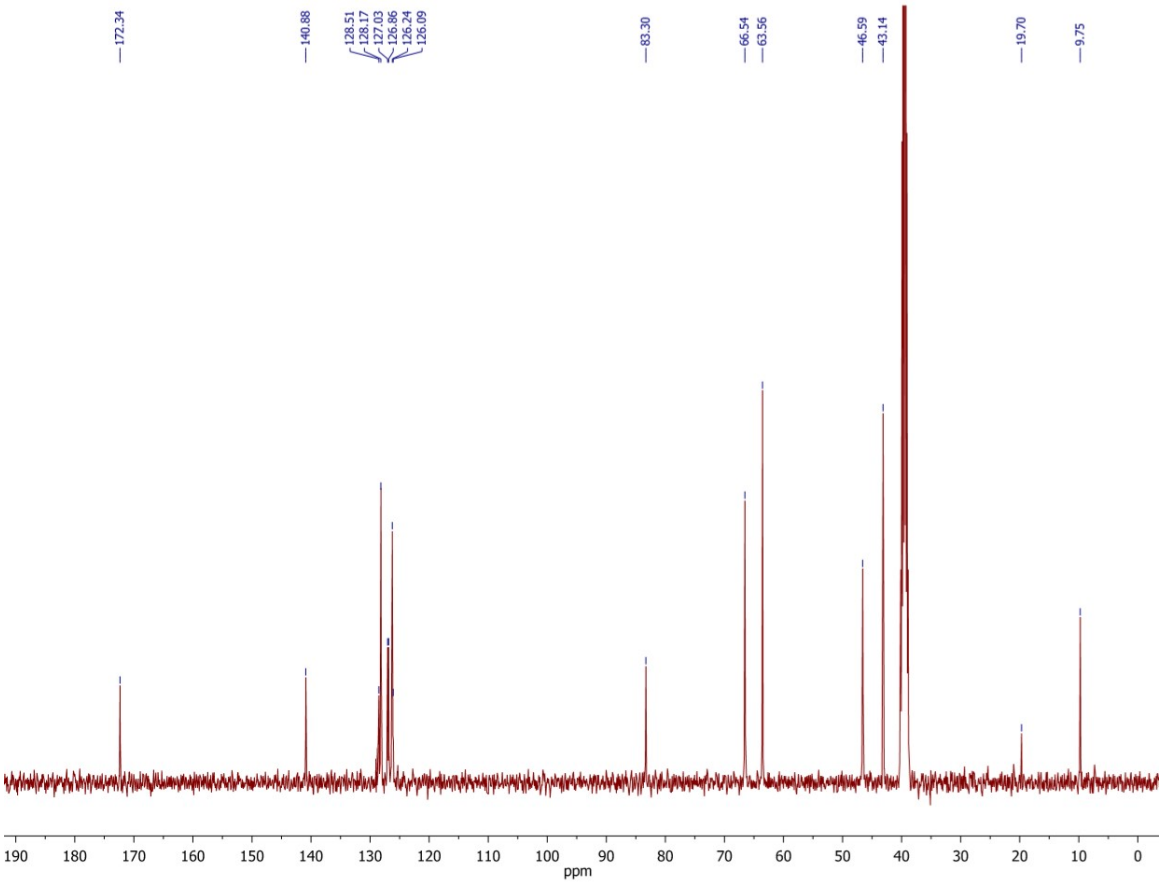


Fig. 4. ^{13}C-NMR-spectrum of compound **2a** (100 MHz, DMSO−d6)

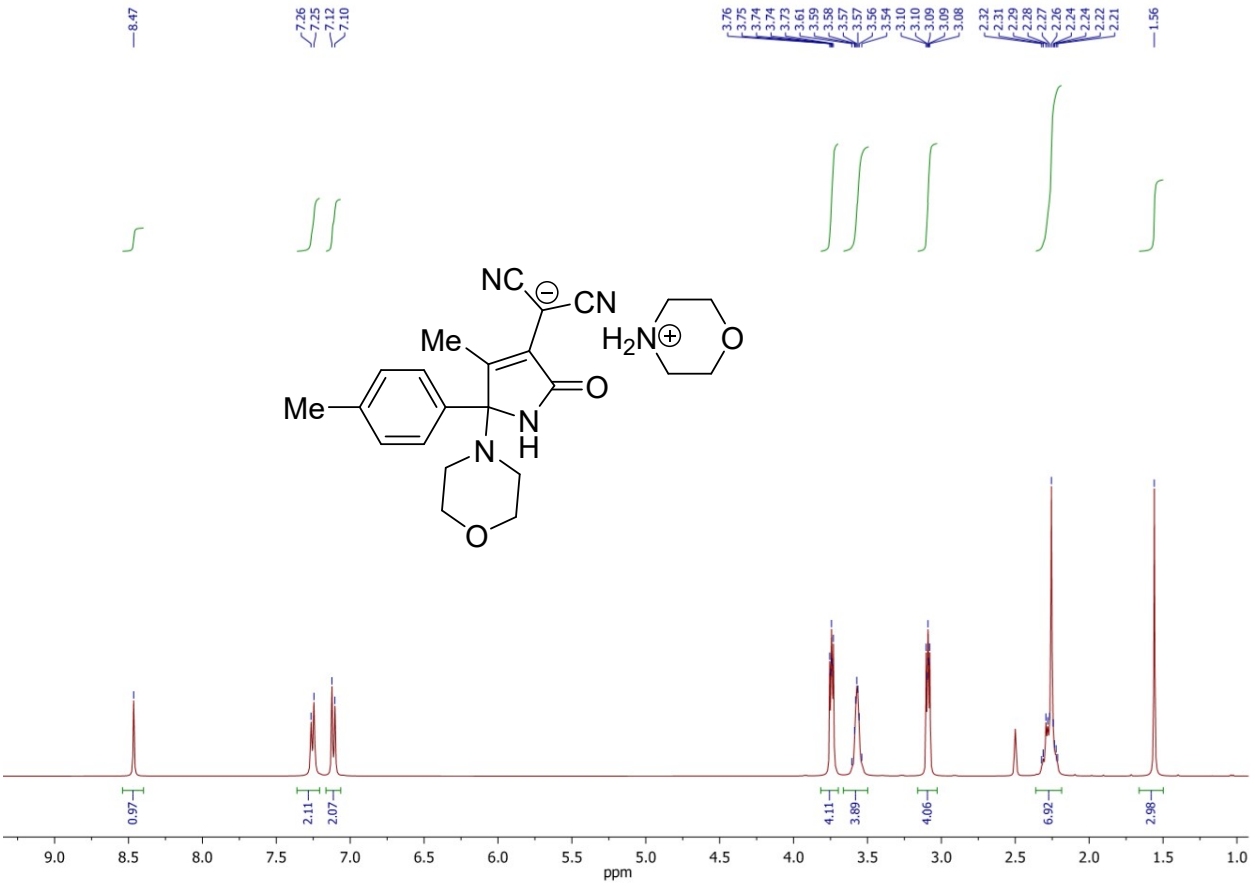


Fig. 5. ^{1}H-NMR-spectrum of compound **2b** (400 MHz, DMSO−d6)

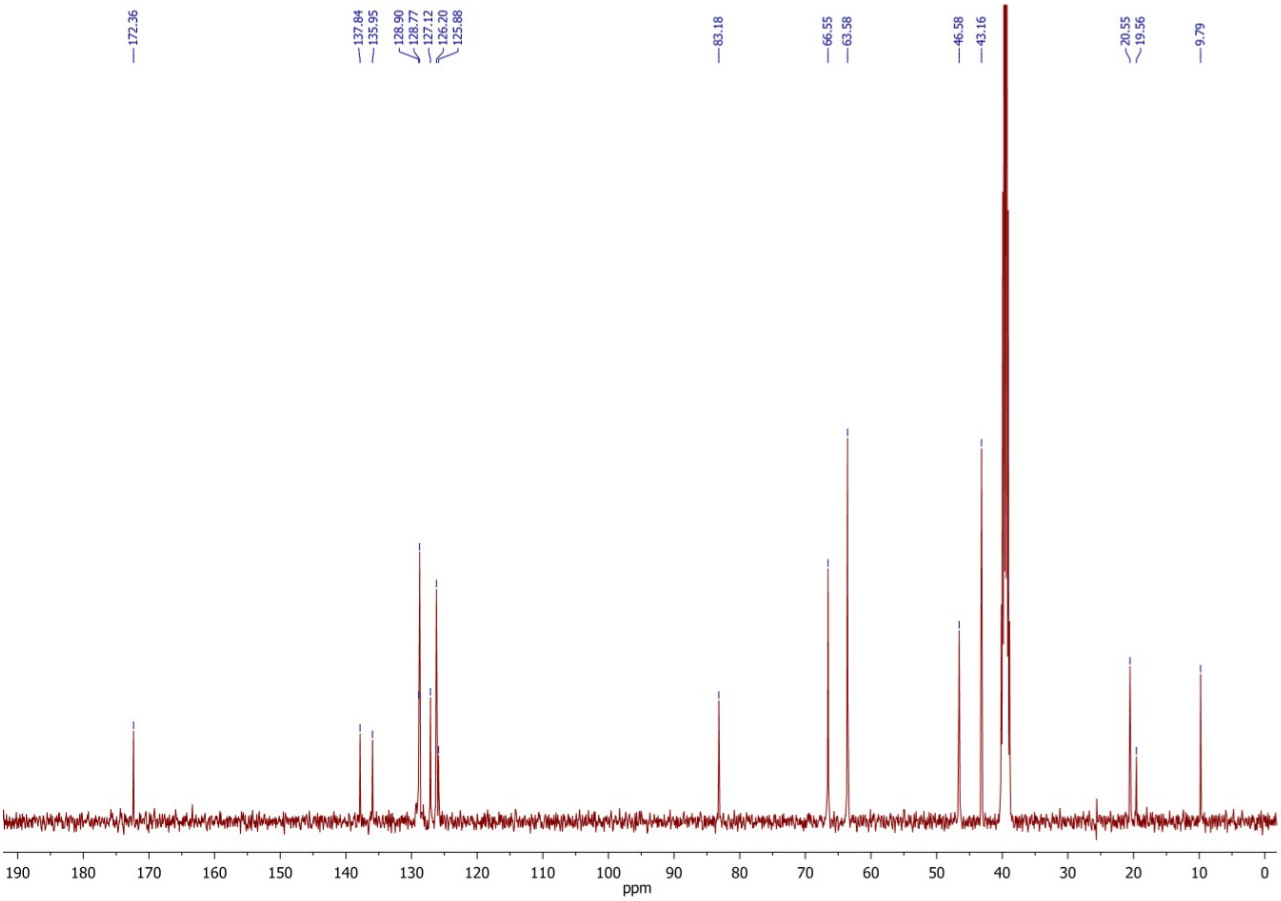


Fig. 6. ^{13}C-NMR-spectrum of compound **2b** (100 MHz, DMSO−d6)

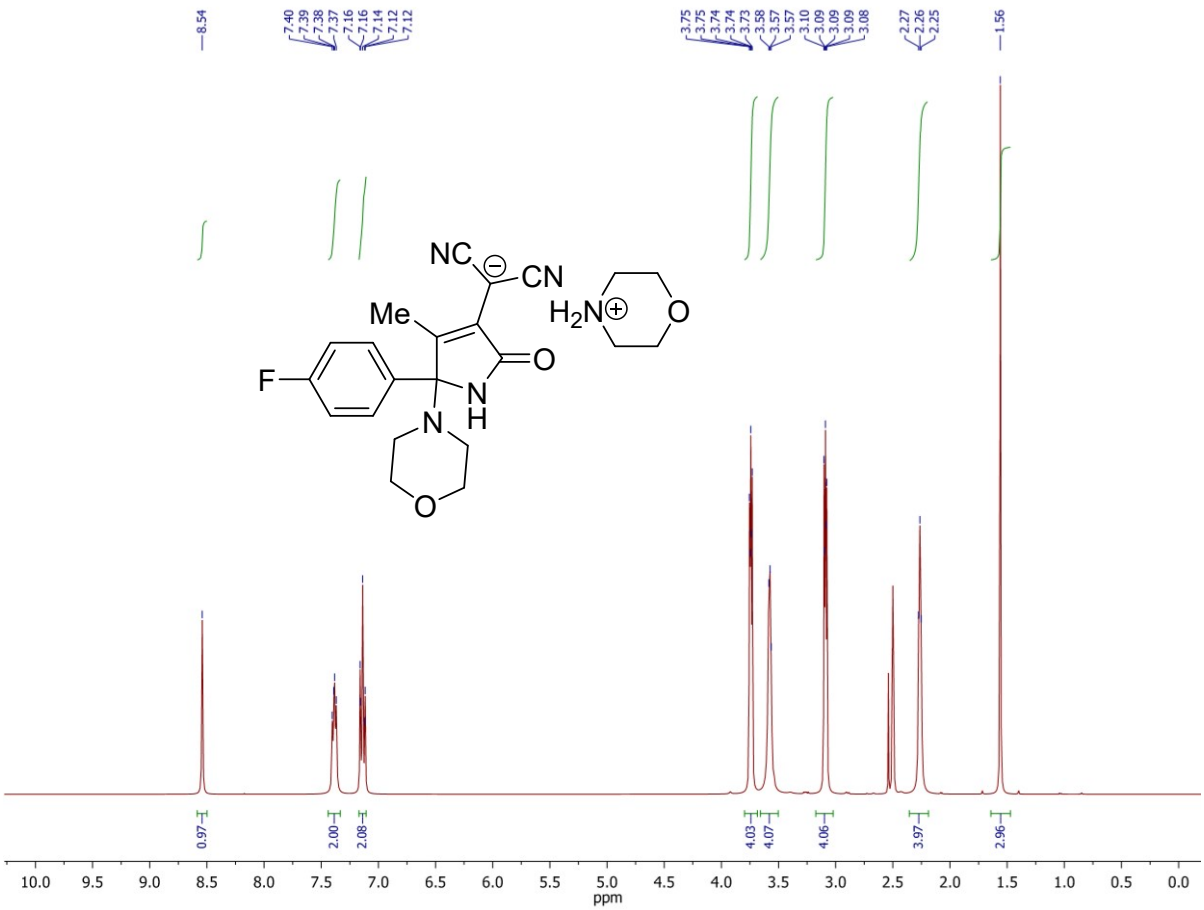


Fig. 7. ^{1}H-NMR-spectrum of compound **2c** (400 MHz, DMSO−d6)

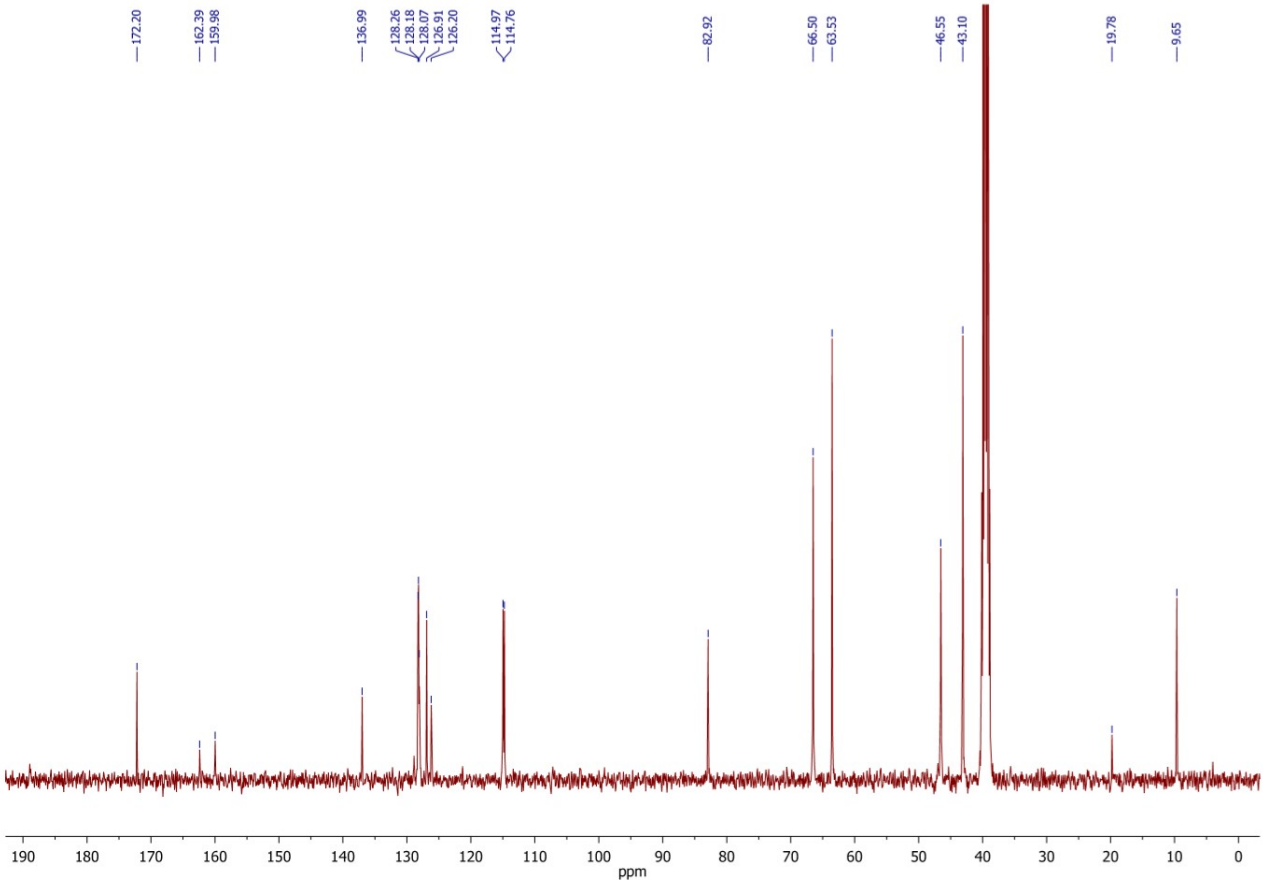


Fig. 8. ^{13}C-NMR-spectrum of compound **2c** (100 MHz, DMSO−d6)

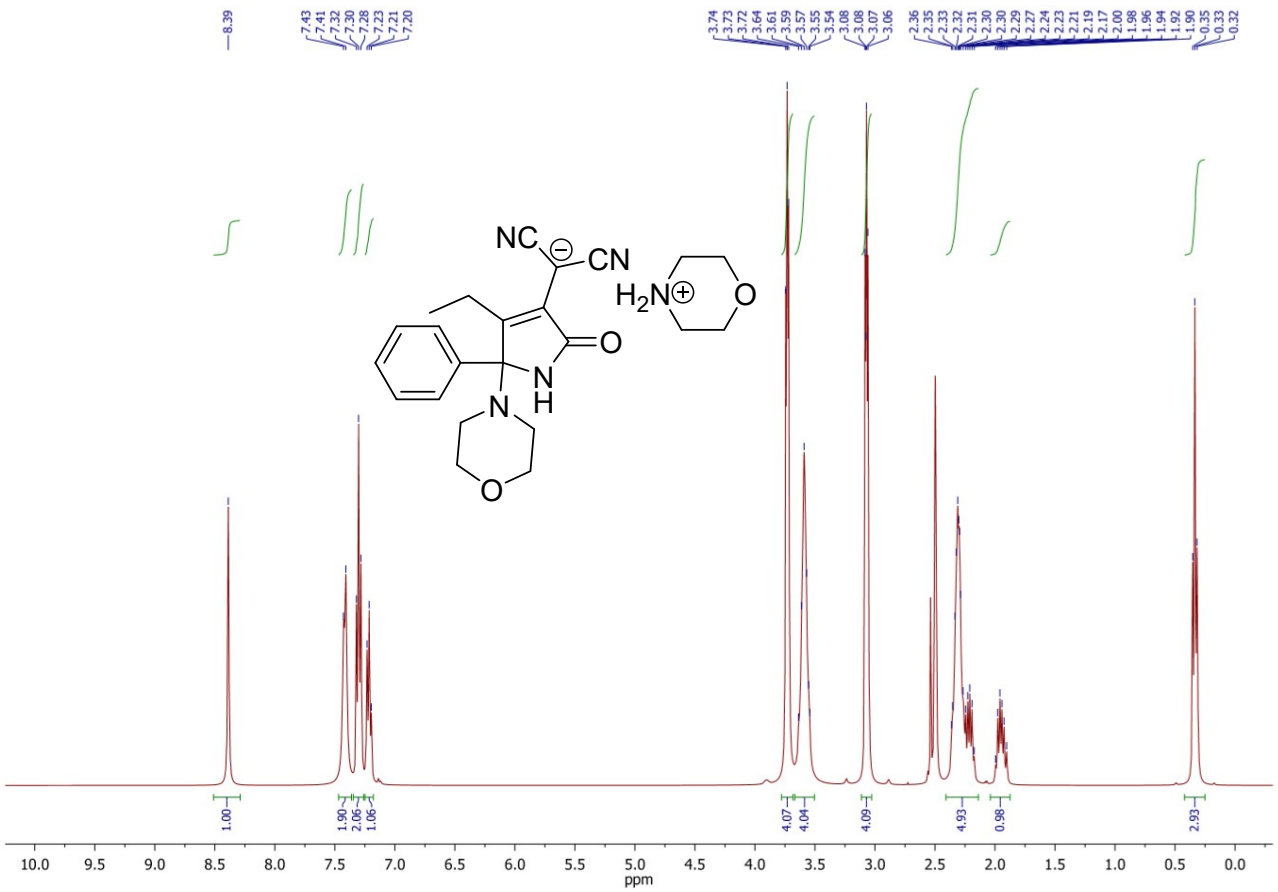


Fig. 9. [1]H-NMR-spectrum of compound **2d** (400 MHz, DMSO−d6)

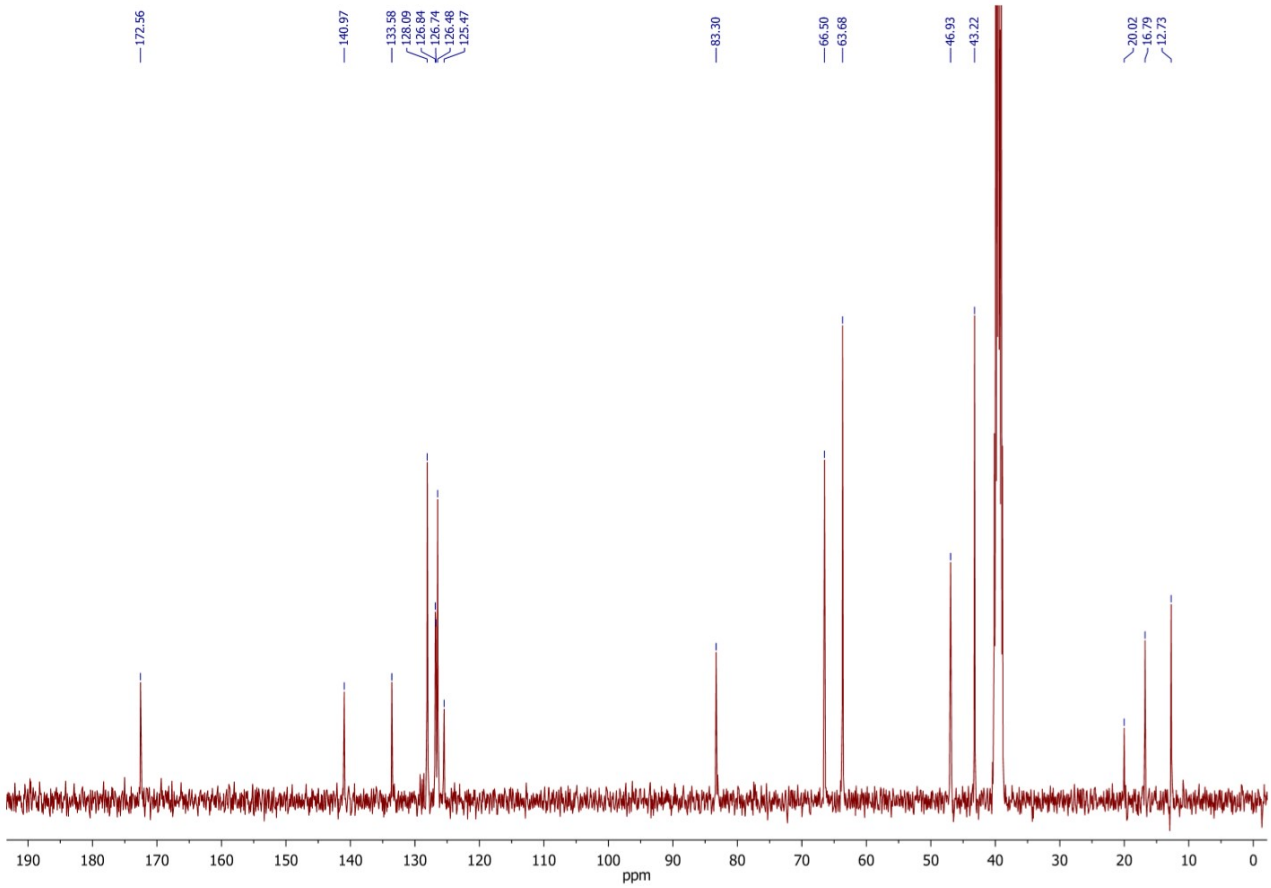


Fig. 10. [13]C-NMR-spectrum of compound **2d** (100 MHz, DMSO−d6)

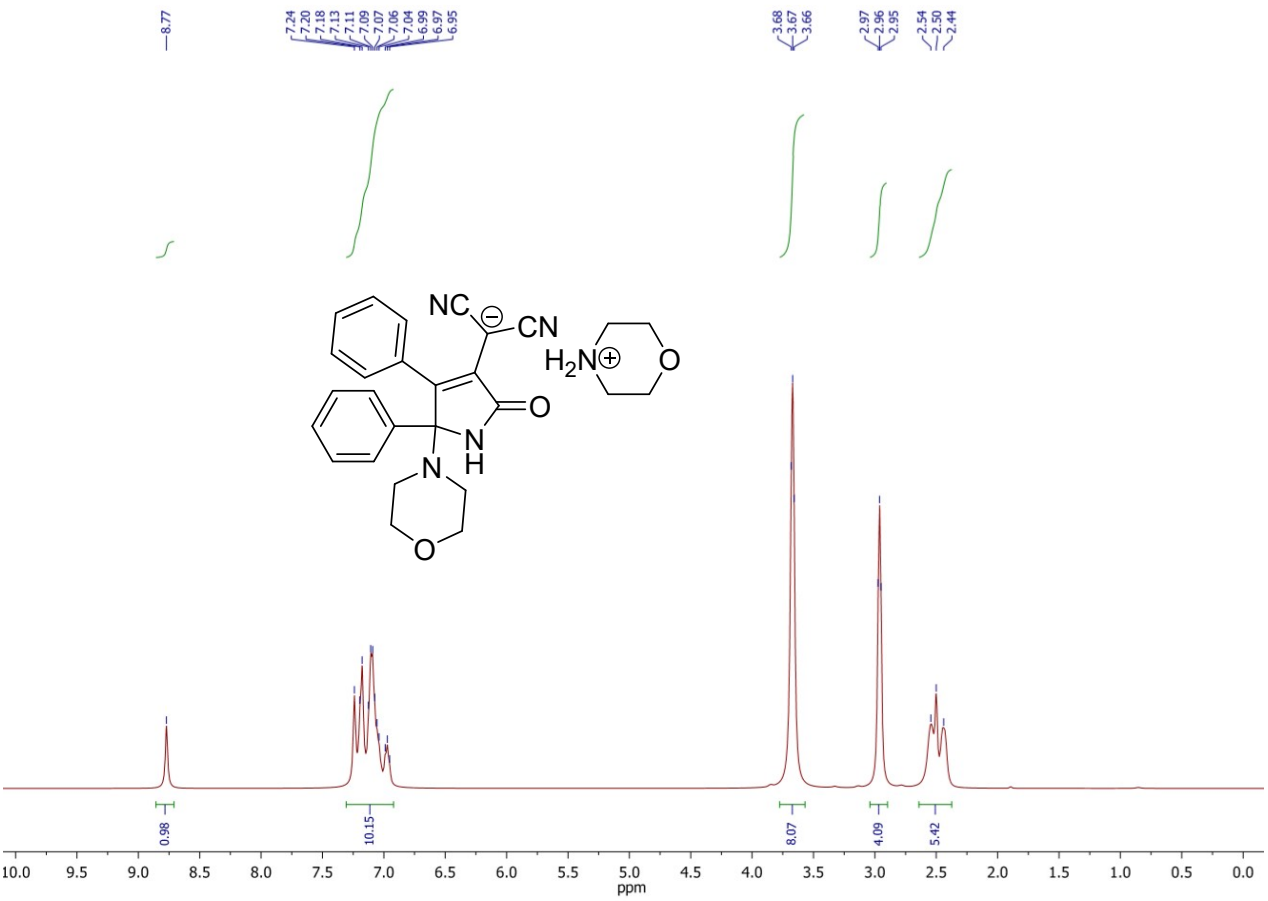


Fig. 11. ^{1}H-NMR-spectrum of compound **2e** (400 MHz, DMSO−d6)

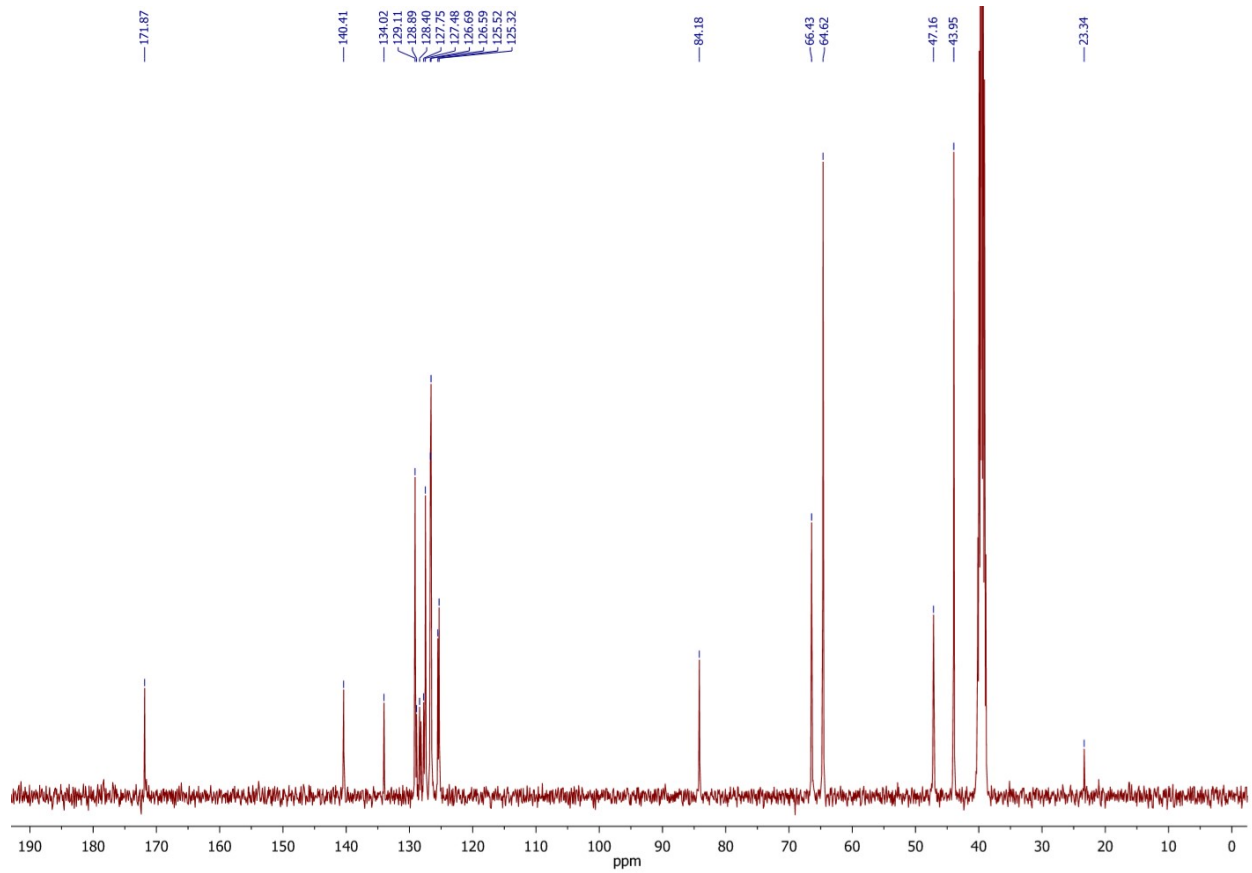


Fig. 12. ^{13}C-NMR-spectrum of compound **2e** (100 MHz, DMSO−d6)

5. Thermochromic behaviour of the 1a/morpholine mixture

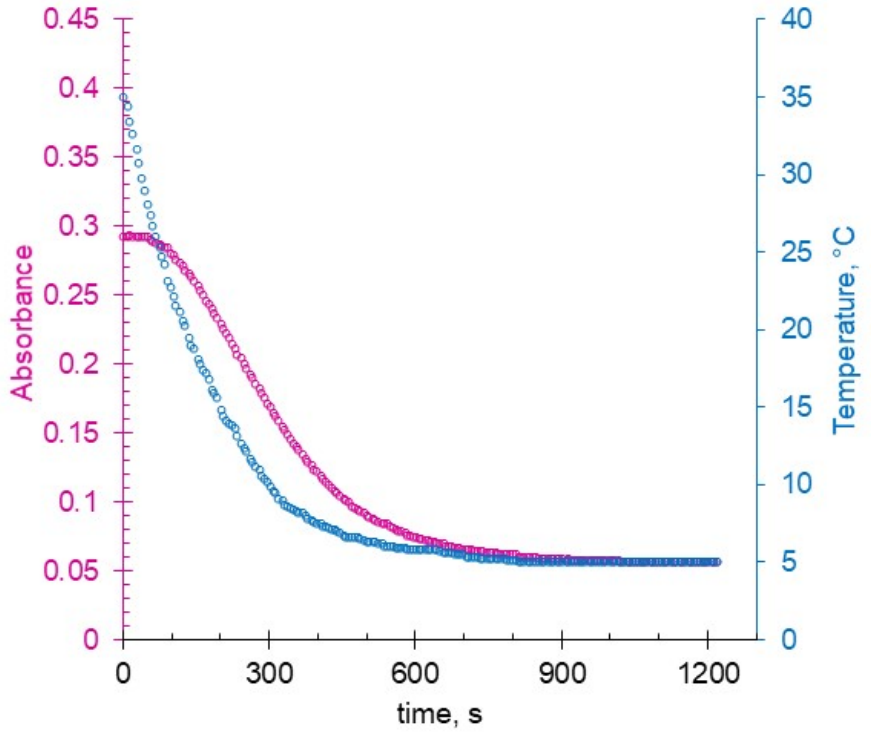


Fig. 13. Plots of absorbance (magenta) and temperature (blue) changes vs. time registered at cooling (from 35 °C to 5 °C) of the mixture containing compound **1a** and morpholine (100 eq.)

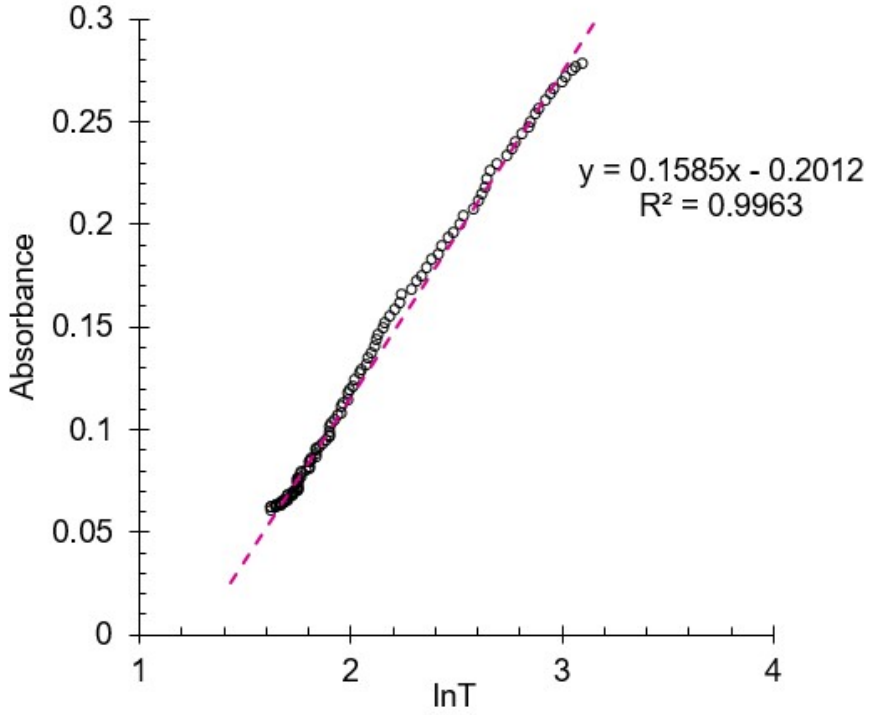


Fig. 14. Plot of absorbance changes vs. natural logarithm of temperature (T) for the mixture containing compound **1a** and morpholine (100 eq.)