Electronic Supplementary Information for

First representatives of functionalized D-π-A chromophores containing tunable hydroxytricyanopyrrole (HTCP) acceptor and *N*,*N*-disubstituted aminophenyl donor

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Contents

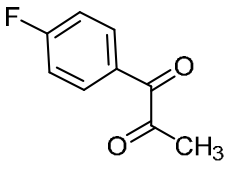
1. Experimental

1.1 General remarks

The progress of reactions and the purity of the products were monitored by TLC on Sorbfil plates (spots were visualized under UV light, by treatment with iodine vapor, or by heating). Melting points were determined on the device OptiMelt MPA100. The IR spectra were recorded on an FSM-1202 spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra were measured in DMSO-d_6 on a Bruker DRX-500 spectrometer using tetramethylsilane as an internal reference. The elemental compositions were determined on a CHN-analyzer Perkin Elmer-2400. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS-50 spectrometer. The UV spectra were recorded on an Agilent Cary 60 UV-Vis Spectrophotometer. Studies of cyclic voltammetry were carried out using a Keithley 2450-EC Graphical Potentiostat and a voltammetric three-electrode VC-2 cell (working electrode – platinum, reference electrode – silver chloride, auxiliary electrode – platinum). The voltammograms were recorded in acetonitrile using tetrabutylammonium hexafluorophosphate (TBAPF, 0.1 M) as electrolyte, the potential sweep rate was 50 mV/s. Ferrocene (Fc^+/Fc) solution was used for calibration. The energy of the highest occupied molecular orbital (HOMO) was calculated using the oxidation potential by the equation HOMO = -e(E_{ox}^{onset} + 4.4). Band gap (Eg) was refined using electronic spectra of TCPy solutions in acetonitrile according to the equation $E_g = 1242/\lambda_{abs}^{onset}$. The energy of the lowest unoccupied molecular orbital (LUMO) was found from the values of HOMO and E_g as LUMO = HOMO + E_g.

1.2 Synthetic procedures and spectral data

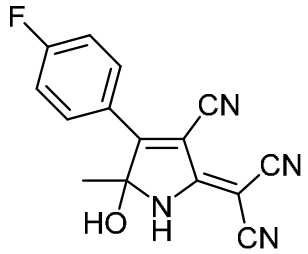
Synthesis of 1-(4-fluorophenyl)propane-1,2-dione.



To 0.25 mol of 1-(4-fluorophenyl)propan-1-one in a 500 ml three-necked flask equipped with stirrer, reflux condenser and thermometer 0.25 mol of SeO_2 in 180 ml of dioxane and 20 ml of water were added by drops (the temperature should not exceed 20 °C). The reaction mixture was heated at reflux for 6 h with stirring, then filtered 2 times through a folded paper filter (without vacuum) and washed with dioxane (3 times 10 ml). The solvent was distilled off in vacuo. The residue

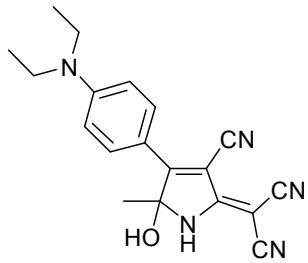
was purified by flash column chromatography (ethyl acetate / hexane = 1 / 4 (v) as eluent) to give the desired 1,2-diketone as yellow oil, yield 68%.

Synthesis of 2-(3-cyano-4-(4-fluorophenyl)-5-hydroxy-5-methyl-1,5-dihydro-2H-pyrrol-2-ylidene)malononitrile **4-F-C_6H_4-HTCP**.



To the solution of 1.32 g (10 mmol) malononitrile dimer (DMN) and 2.49 g (15 mmol) of 1-(4-fluorophenyl)propane-1,2-dione in 6 mL of ethanol / water = 80% / 20% (v) 0.154 g (2 mmol) of dry ammonium acetate were added. The reaction mixture was stirred at 0°C for 72 h. After the reaction was completed (TLC) precipitated crude product filtered, washed with cooled propan-2-ol, purified by recrystallization from *i*-PrOH, dried in a vacuum desiccator over $CaCl_2$. Yellow solid; mp 158-159 °C (dec.); yield 71%; IR (mineral oil, *v*, cm^{-1}): 3328, 3251 (OH, NH), 2212, 2201 (C≡N). ^1H NMR (500.13 MHz, DMSO-d_6) δ: 10.78 (s, 1H, NH), 8.14-8.10 (m, 2H, *o*-Ph), 7.53-7.48 (m, 2H, *m*-Ph), 7.37 (s, 1H, OH), 1.49 (s, 3H, CH_3). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 170.16, 164.37 ($^1J_{CF}$ = 253.2 Hz), 160.17, 131.51 ($^3J_{CF}$ = 9.3 Hz), 124.90 ($^4J_{CF}$ = 3.1 Hz), 116.50 ($^2J_{CF}$ = 22.1 Hz), 114.96, 113.53, 112.39, 101.51, 94.47, 45.28, 24.14. MS, (EI, 70 eV): *m/z* (%) 280 $[M]^+$ (8), 264 $[M-16]^+$ (89). Anal. Calcd. for $C_{15}H_9FN_4O$: C, 64.28; H, 3.24; N, 19.99. Found: C, 64.62; H, 3.40; N, 19.74.

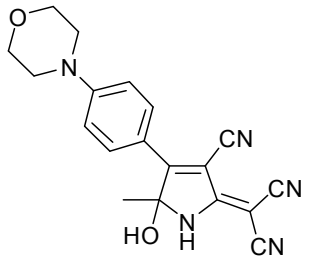
Synthesis of 2-(3-Cyano-4-(4-(diethylamino)phenyl)-5-hydroxy-5-methyl-1,5-dihydro-2H-pyrrol-2-ylidene)malononitrile ***3a***.



To the solution of 0.28 g (1 mmol) **3** (**4-F-C_6H_4-HTCP**) in 2 mL of pyridine 3 mmol of corresponding secondary amine was added. The reaction mixture was stirred at room temperature for 24-48 h. After the reaction was completed (TLC) the mixture was diluted with water, precipitated crude product was filtered off, washed with water, dried in a vacuum desiccator over $CaCl_2$, purified by silica gel flash chromatography (ethyl acetate / hexane = 4 / 1 (v) as eluent). Red solid; mp 175-

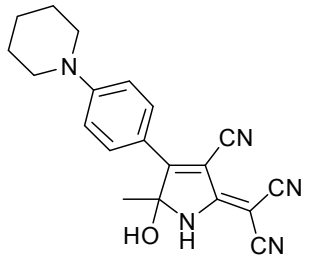
177 °C (dec.); yield 52%; IR (mineral oil, *v*, cm^{-1}): 3339, 3189 (OH, NH), 2216, 2206 (C≡N). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 10.25 (s, 1H, NH), 8.15 (d, 2H, *J* = 9.4 Hz, *o*-Ph), 7.20 (s, 1H, OH), 6.88 (d, 2H, *J* = 9.4 Hz, *m*-Ph), 3.50 (q, 4H, *J* = 7.1 Hz, $2CH_2$), 1.59 (s, 3H, CH_3), 1.15 (t, 6H, *J* = 7.0 Hz, $2CH_3$). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 169.96, 161.57, 151.50, 132.10, 116.10, 114.86, 114.58, 114.23, 111.38, 93.79, 90.14, 44.18, 42.41, 26.52, 12.50. MS, (EI, 70 eV): *m/z* (%) 333 $[M]^+$ (17), 317 $[M-16]^+$ (46). Anal. Calcd. for $C_{19}H_{19}N_5O$: C, 68.45; H, 5.74; N, 21.01. Found: C, 68.94; H, 5.97; N, 21.40.

Synthesis of 2-(3-cyano-5-hydroxy-5-methyl-4-(4-morpholinophenyl)-1,5-dihydro-2H-pyrrol-2-ylidene)malononitrile **3b.**



Prepared in a similar manner as compound **3a**. Red solid; mp 176-178 °C (dec.); yield 68%; IR (mineral oil, *v*, cm^{-1}): 3319, 3246 (OH, NH), 2218, 2209 (C≡N). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 10.41 (s, 1H, NH), 8.14 (d, 2H, *J* = 9.3 Hz, *o*-Ph), 7.25 (s, 1H, OH), 7.13 (d, 2H, *J* = 9.3 Hz, *m*-Ph), 3.75-3.72 (m, 4H, $2CH_2$ morpholine), 3.45-3.42 (m, 4H, $2CH_2$ morpholine), 1.56 (s, 3H, CH_3). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 170.23, 161.21, 153.79, 131.44, 116.73, 115.80, 114.28, 114.24, 113.20, 94.03, 93.31, 65.80, 46.28, 43.32, 25.98. MS, (EI, 70 eV): *m/z* (%) 347 $[M]^+$ (5), 331 $[M-16]^+$ (89). Anal. Calcd. for $C_{19}H_{17}N_5O_2$: C, 65.69; H, 4.93; N, 20.16. Found: C, 65.91; H, 5.08; N, 20.01.

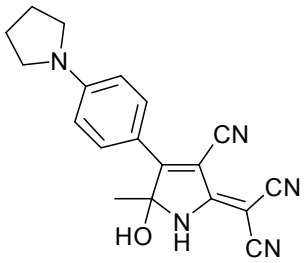
Synthesis of 2-(3-cyano-5-hydroxy-5-methyl-4-(4-(piperidin-1-yl)phenyl)-1,5-dihydro-2H-pyrrol-2-ylidene)malononitrile **3c.**



Prepared in a similar manner as compound **3a**. Red solid; mp 170-172 °C (dec.); yield 84%; IR (mineral oil, *v*, cm^{-1}): 3308, 3251 (OH, NH), 2216, 2196 (C≡N). ^{1}H NMR (500.13

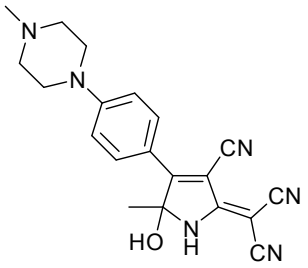
MHz, DMSO-d_6) δ: 10.31 (s, 1H, NH), 8.14 (d, 2H, J = 9.4 Hz, *o*-Ph), 7.21 (s, 1H, OH), 7.09 (d, 2H, J = 9.4 Hz, *m*-Ph), 3.54-3.51 (m, 4H, $2CH_2$ piperidine), 1.62-1.66 (m, 6H, $3CH_2$ piperidine), 1.58 (s, 3H, CH_3). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 169.81, 161.30, 153.29, 131.75, 115.83, 115.16, 114.46, 114.31, 112.82, 93.76, 91.38, 47.28, 42.70, 26.17, 25.00, 23.90. MS, (EI, 70 eV): *m/z* (%) 345 $[M]^+$ (5), 329 $[M\text{-}16]^+$ (100). Anal. Calcd. for $C_{20}H_{19}N_5O$: C, 69.55; H, 5.54; N, 20.28. Found: C, 69.86; H, 5.31; N, 20.43.

Synthesis of 2-(3-cyano-5-hydroxy-5-methyl-4-(4-(pyrrolidin-1-yl)phenyl)-1,5-dihydro-2H-pyrrol-2-ylidene)malononitrile **3d.**



Prepared in a similar manner as compound **3a**. Red solid; mp 173-175 °C (dec.); yield 57%; IR (mineral oil, v, cm^{-1}): 3306, 3248 (OH, NH), 2209, 2201 (C≡N). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 10.25 (s, 1H, NH), 8.17 (d, 2H, J = 9.2 Hz, *o*-Ph), 7.21 (s, 1H, OH), 6.75 (d, 2H, J = 9.2 Hz, *m*-Ph), 3.44-3.39 (m, 4H, $2CH_2$ pyrrolidine), 2.01-1.97 (m, 4H, $2CH_2$), 1.58 (s, 3H, CH_3). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 170.20, 161.55, 151.04, 131.83, 116.09, 114.86, 114.56, 114.50, 112.13, 93.81, 90.26, 47.60, 42.46, 26.50, 24.90. MS, (EI, 70 eV): *m/z* (%) 331 $[M]^+$ (11), 315 $[M\text{-}16]^+$ (91). Anal. Calcd. for $C_{19}H_{179}N_5O$: C, 68.87; H, 5.17; N, 21.13. Found: C, 69.19; H, 5.29; N, 21.01.

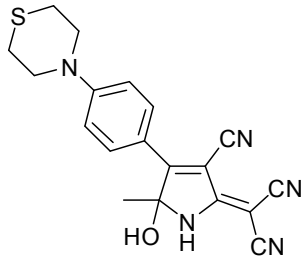
Synthesis of 2-(3-cyano-5-hydroxy-5-methyl-4-(4-(4-methylpiperazin-1-yl)phenyl)-1,5-dihydro-2H-pyrrol-2-ylidene)malononitrile **3e.**



Prepared in a similar manner as compound **3a**. Brown solid; mp 168-170 °C (dec.); yield 66%; IR (mineral oil, v, cm^{-1}): 3368, 3245 (OH, NH), 2215, 2206 (C≡N). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 10.38 (br s, 1H, NH), 8.13 (d, 2H, J = 9.3 Hz, *o*-Ph), 7.24 (s, 1H, OH),

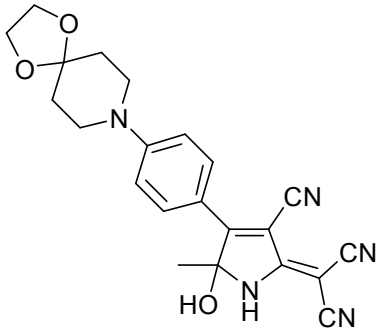
7.12 (d, 2H, J = 9.3 Hz, *m*-Ph), 3.50-3.46 (m, 4H, $2CH_2$ piperazine), 2.47-2.44 (m, 4H, $2CH_2$ piperazine), 2.24 (s, 3H, N-CH_3), 1.57 (s, 3H, CH_3). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 170.16, 161.28, 153.53, 131.57, 123.95, 116.27, 115.85, 114.33, 113.29, 94.00, 92.80, 54.13, 45.92, 45.51, 43.18, 26.08. MS, (EI, 70 eV): *m/z* (%) 360 $[M]^+$ (2), 344 $[M-16]^+$ (23). Anal. Calcd. for $C_{20}H_{20}N_6O$: C, 66.65; H, 5.59; N, 23.32. Found: C, 66.93; H, 5.76; N, 23.02.

Synthesis of 2-(3-cyano-5-hydroxy-5-methyl-4-(4-thiomorpholinophenyl)-1,5-dihydro-2H-pyrrol-2-ylidene)malononitrile **3f.**



Prepared in a similar manner as compound **3a**. Red solid; mp 165-167 °C (dec.); yield 78%; IR (mineral oil, v, cm^{-1}): 3305, 3271 (OH, NH), 2220, 2209 (C≡N). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 10.37 (s, 1H, NH), 8.15 (d, 2H, J = 8.9 Hz, *o*-Ph), 7.23 (s, 1H, OH), 7.11 (d, 2H, J = 9.0 Hz, *m*-Ph), 3.92-3.89 (m, 4H, $2CH_2$ thiomorpholine), 2.67-2.65 (m, 4H, $2CH_2$ thiomorpholine), 1.58 (s, 3H, CH_3). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 169.94, 161.25, 252.22, 131.78, 115.81, 115.75, 114.36, 114.29, 113.33, 93.90, 92.38, 49.29, 43.02, 26.09, 25.19. MS, (EI, 70 eV): *m/z* (%) 363 $[M]^+$ (4), 347 $[M-16]^+$ (60). Anal. Calcd. for $C_{19}H_{17}N_5OS$: C, 62.79; H, 4.71; N, 19.27. Found: C, 63.16; H, 4.87; N, 18.97.

Synthesis of 2-(4-(4-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)phenyl)-3-cyano-5-hydroxy-5-methyl-1,5-dihydro-2H-pyrrol-2-ylidene)malononitrile **3g.**



Prepared in a similar manner as compound **3a**. Light-Brown solid; mp 177-178 °C (dec.); yield 59%; IR (mineral oil, v, cm^{-1}): 3312, 3260 (OH, NH), 2221, 2208 (C≡N). ^{1}H NMR (500.13 MHz, DMSO-d_6) δ: 10.36 (s, 1H, NH), 8.14 (d, 2H, J = 9.3 Hz, *o*-Ph), 7.23 (s, 1H,

OH), 7.14 (d, 2H, J = 9.4 Hz, *m*-Ph), 3.93 (s, 4H, OCH_2CH_2O), 3.63-3.59 (m, 4H, $2CH_2$ piperidine), 1.71-1.69 (m, 4H, $2CH_2$ piperidine), 1.58 (s, 3H, CH_3). ^{13}C NMR (125.67 MHz, DMSO-d_6): δ 170.03, 161.32, 152.88, 131.77, 115.90, 115.88, 114.42, 114.36, 113.31, 106.33, 93.96, 92.36, 63.91, 44.74, 43.06, 34.13, 26.16. MS, (EI, 70 eV): *m/z* (%) 403 $[M]^+$ (4), 387 $[M-16]^+$ (75). Anal. Calcd. for $C_{22}H_{21}N_5O_3$: C, 65.50; H, 5.25; N, 17.36. Found: C, 65.90; H, 5.47; N, 17.11.

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

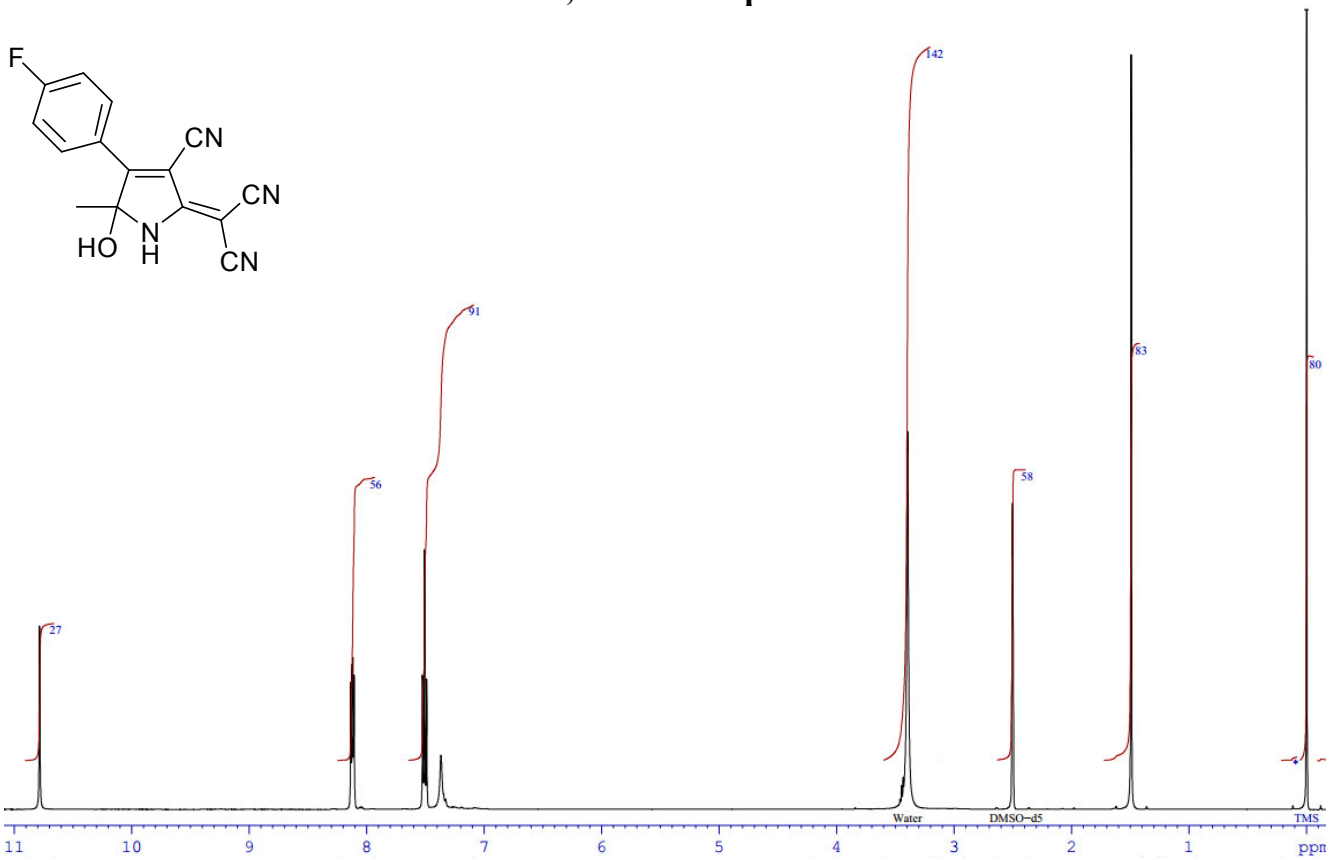


Fig. 1. ^{1}H-NMR-spectrum of **F-Ph-HTCP** (500.13 MHz, DMSO−d6, 298K)

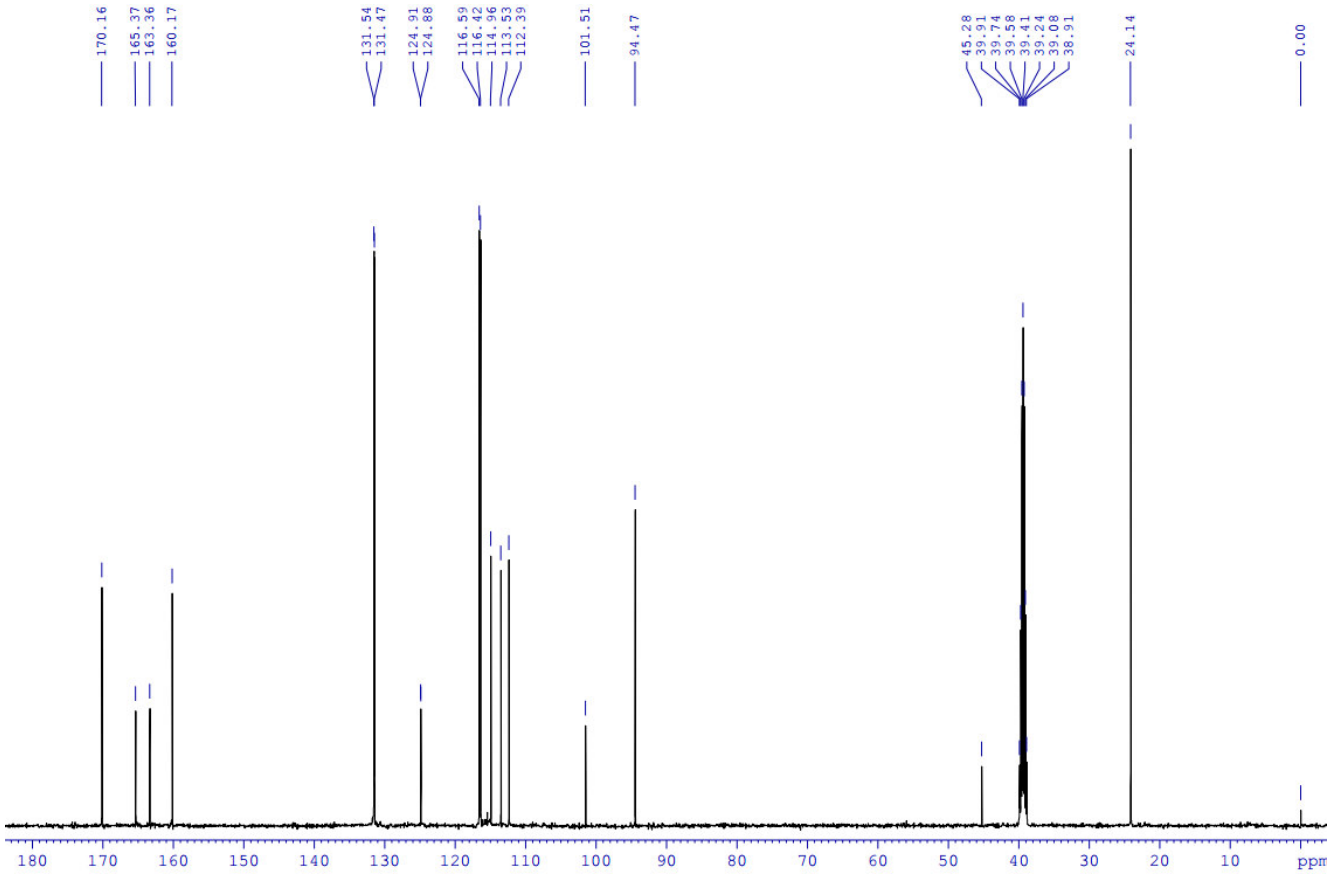


Fig. 2. ^{13}C-NMR-spectrum of **F-Ph-HTCP** (125.76 MHz, DMSO−d6, 299K)

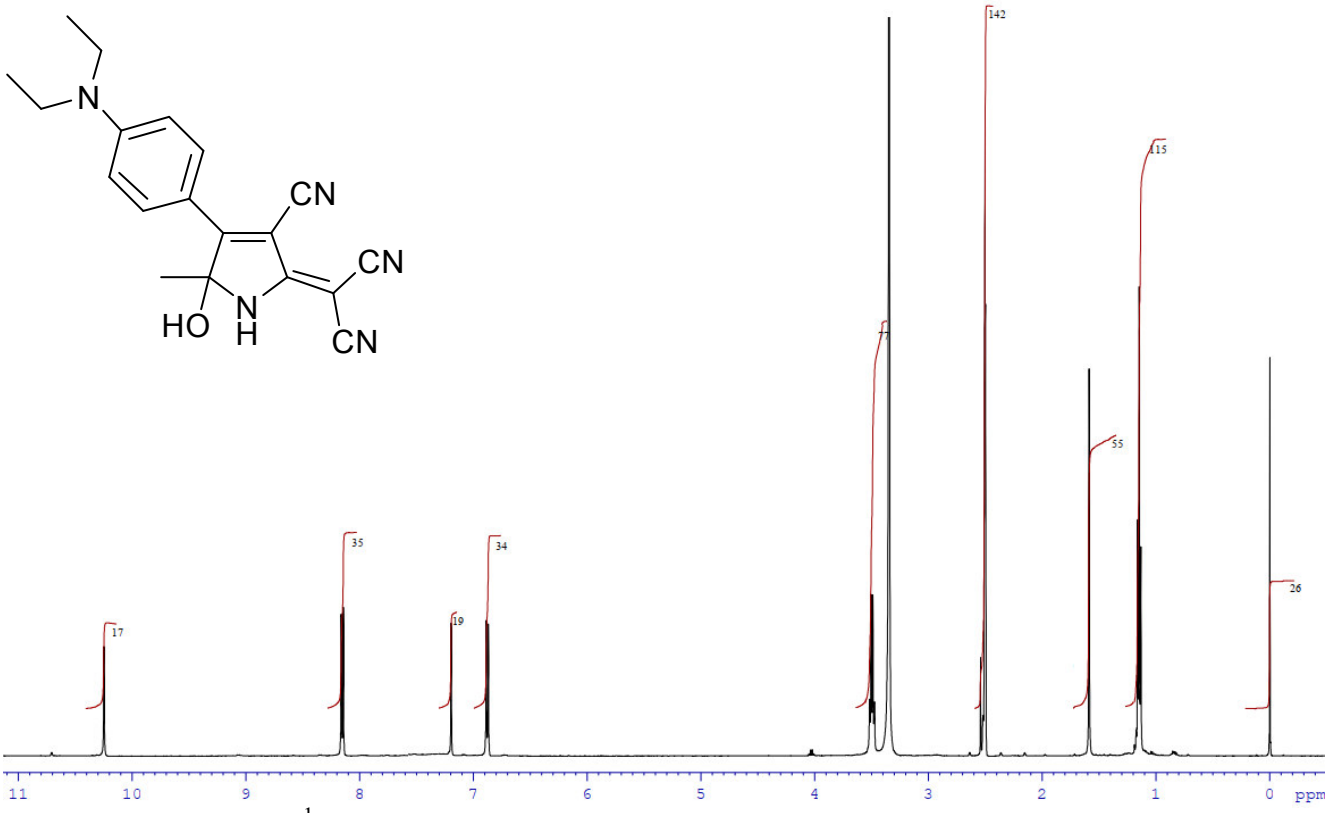


Fig. 1. ^{1}H-NMR-spectrum of **3a** (500.13 MHz, DMSO−d6, 299K)

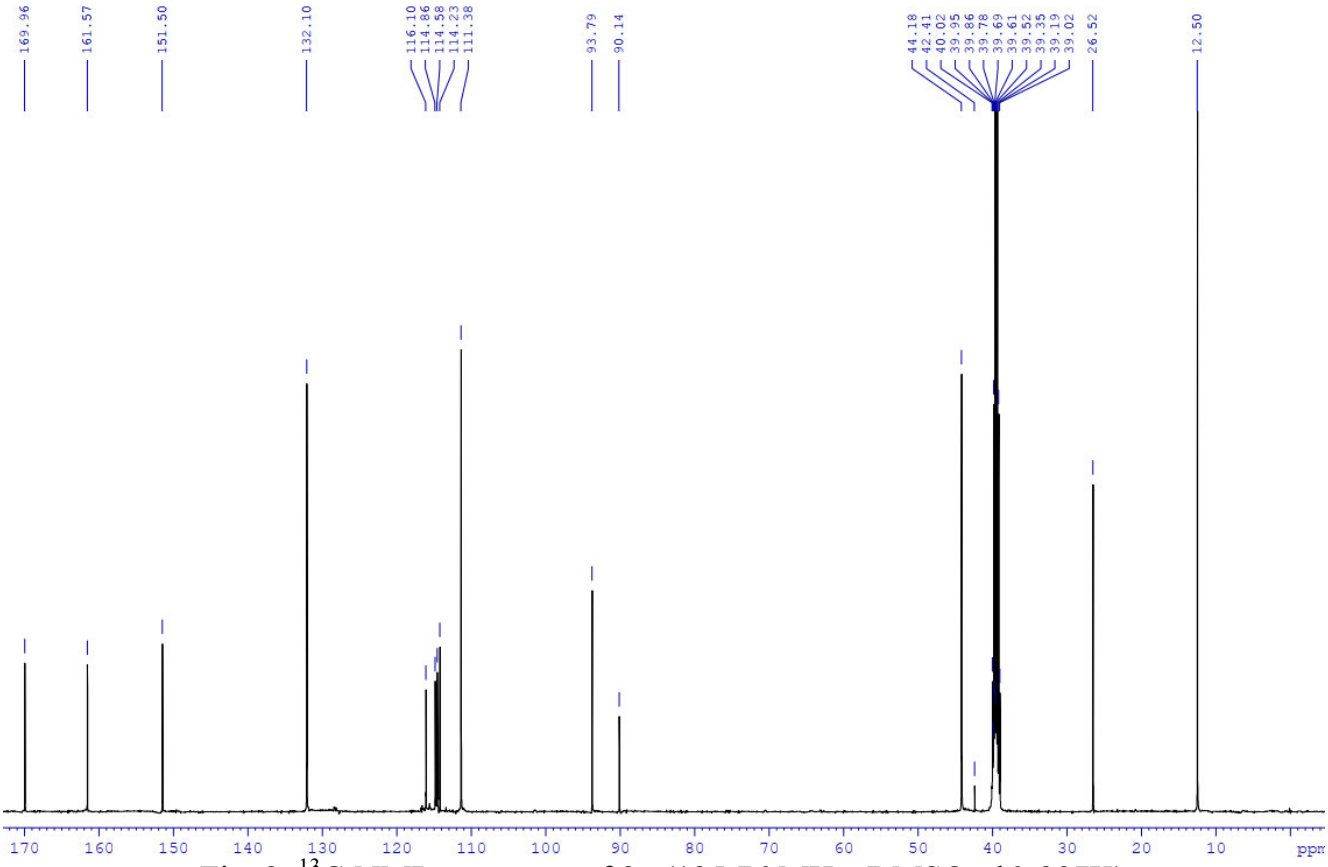


Fig. 2. ^{13}C-NMR-spectrum of **3a** (125.76 MHz, DMSO−d6, 297K)

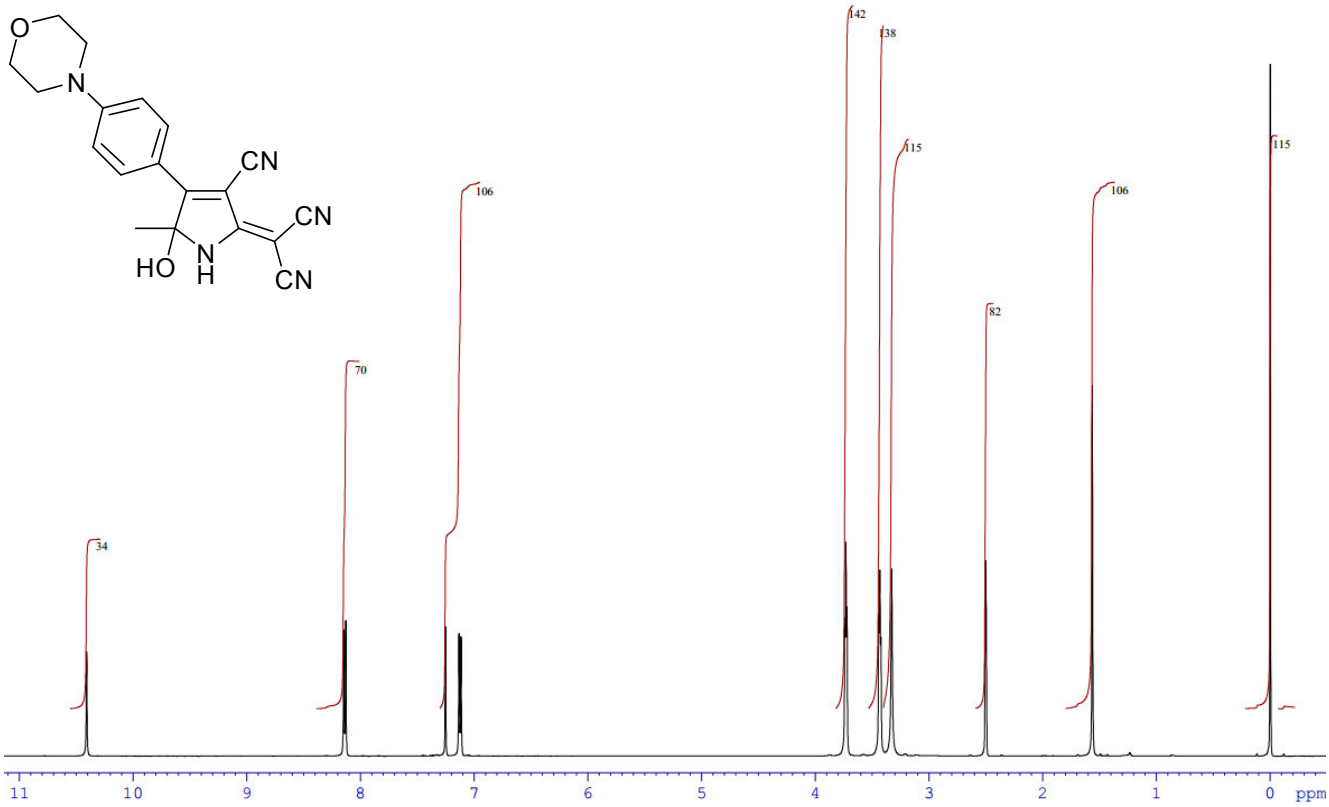


Fig. 3. ^{1}H-NMR-spectrum of **3b** (500.13 MHz, DMSO−d6, 298K)

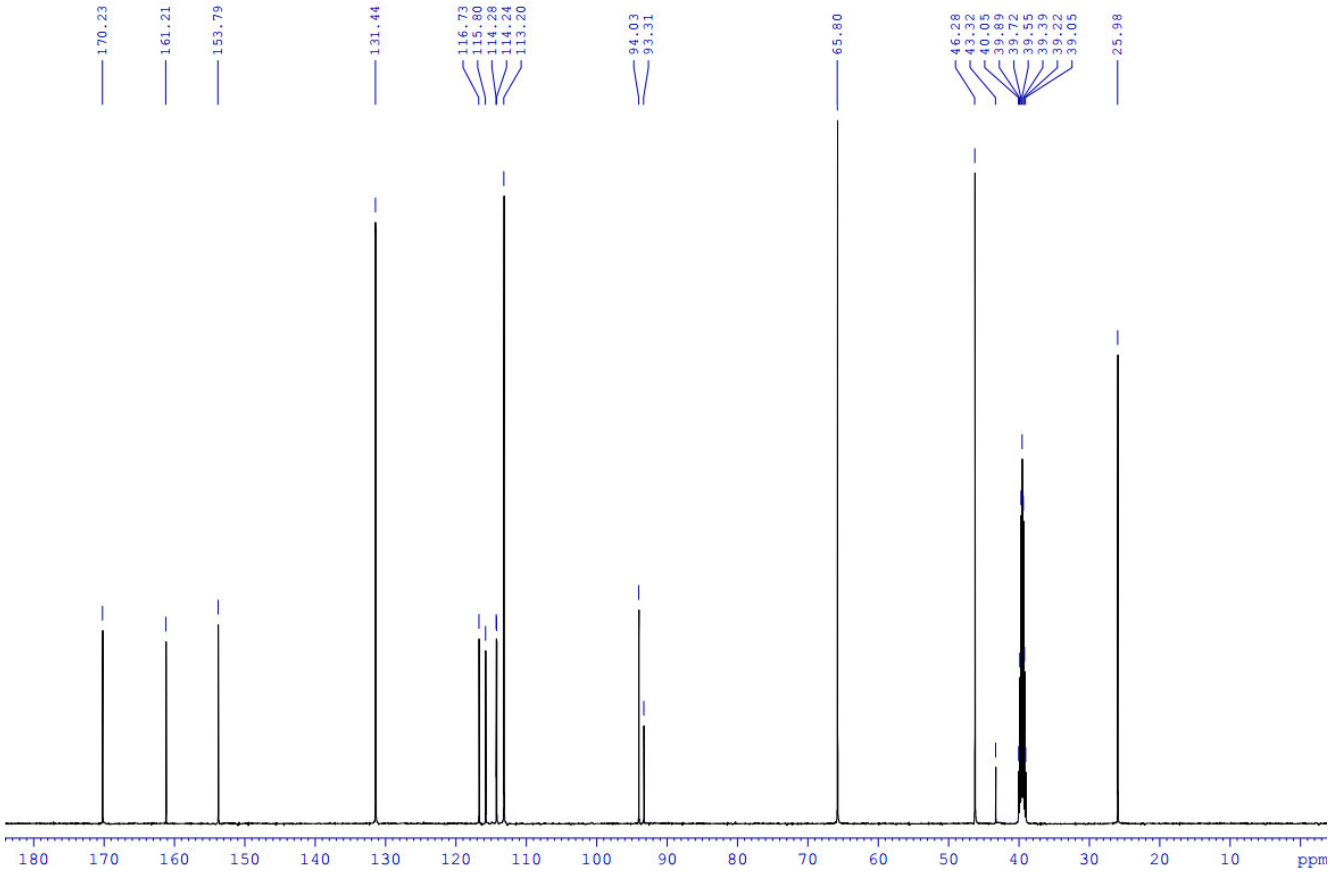


Fig. 4. ^{13}C-NMR-spectrum of **3b** (125.76 MHz, DMSO−d6, 299K)

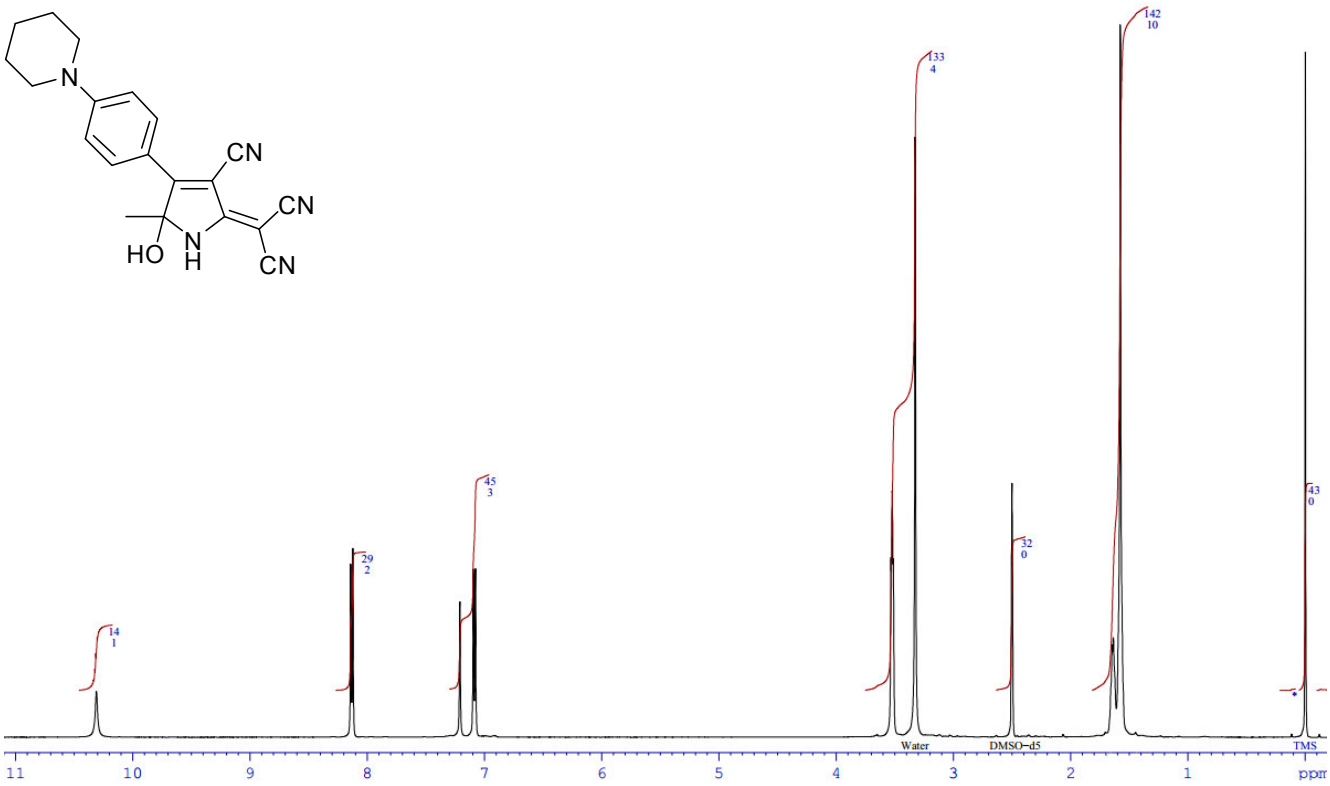


Fig. 5. ^{1}H-NMR-spectrum of **3c** (500.13 MHz, DMSO−d6, 298K)

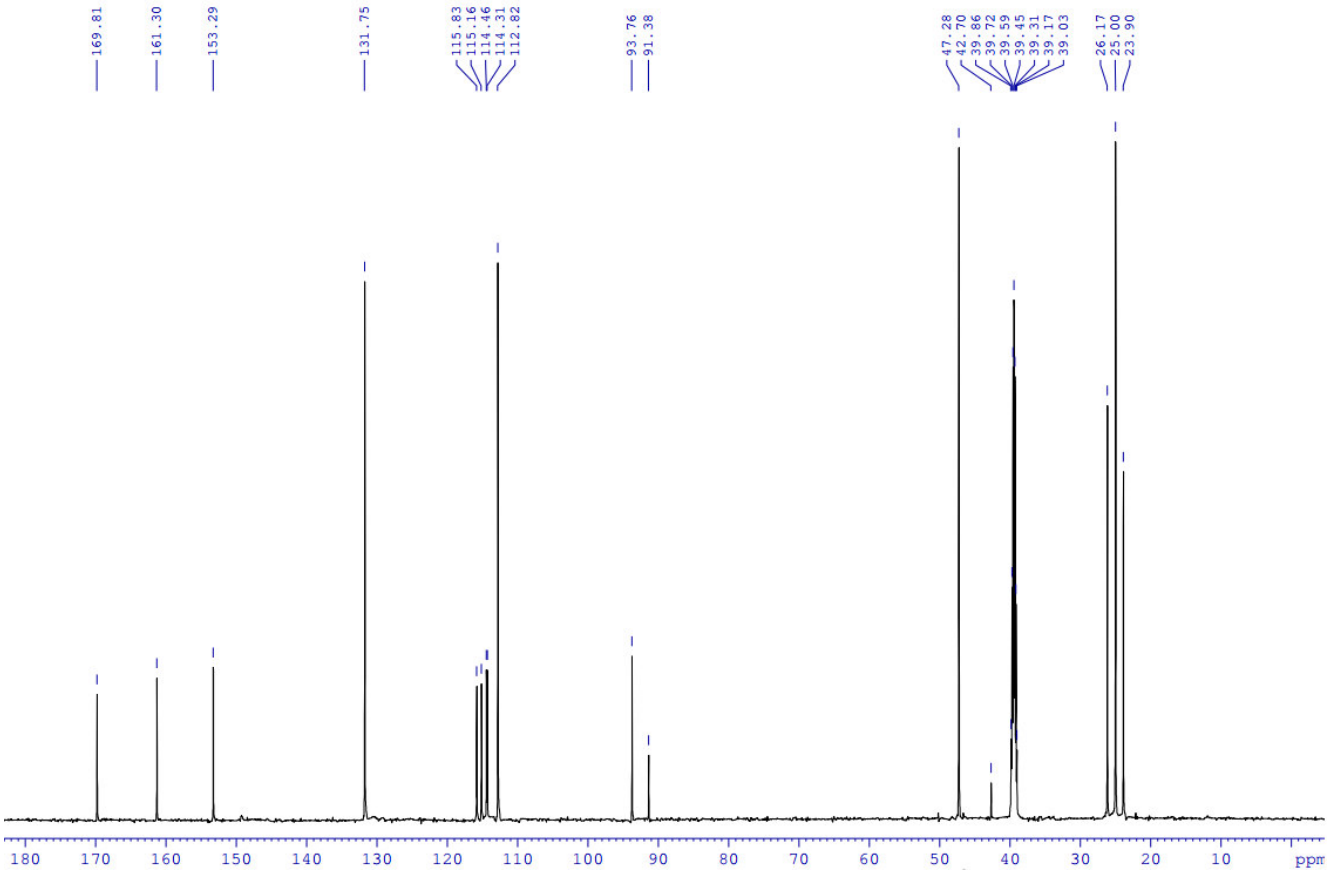


Fig. 6. ^{13}C-NMR-spectrum of **3c** (125.76 MHz, DMSO−d6, 298K)

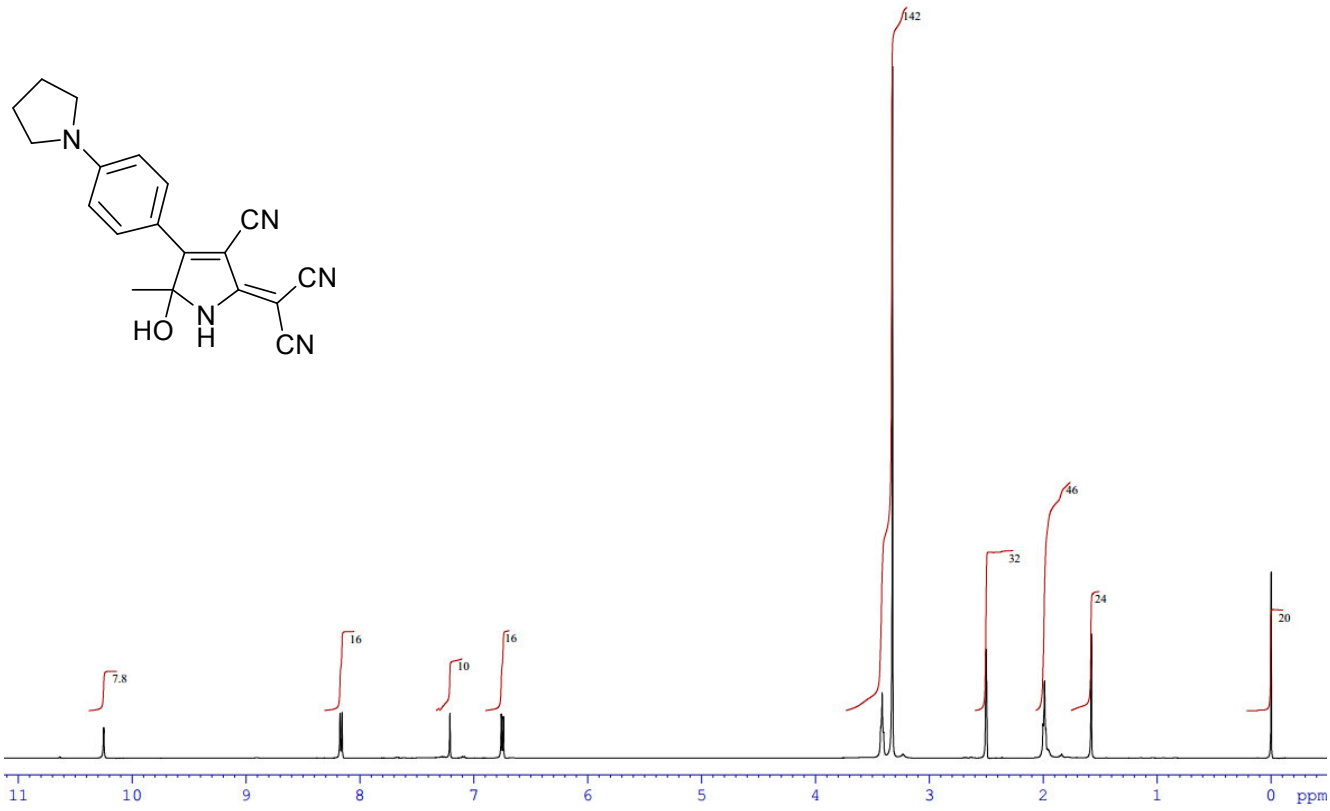


Fig. 7. ^{1}H-NMR-spectrum of **3d** (500.13 MHz, DMSO−d6, 300K)

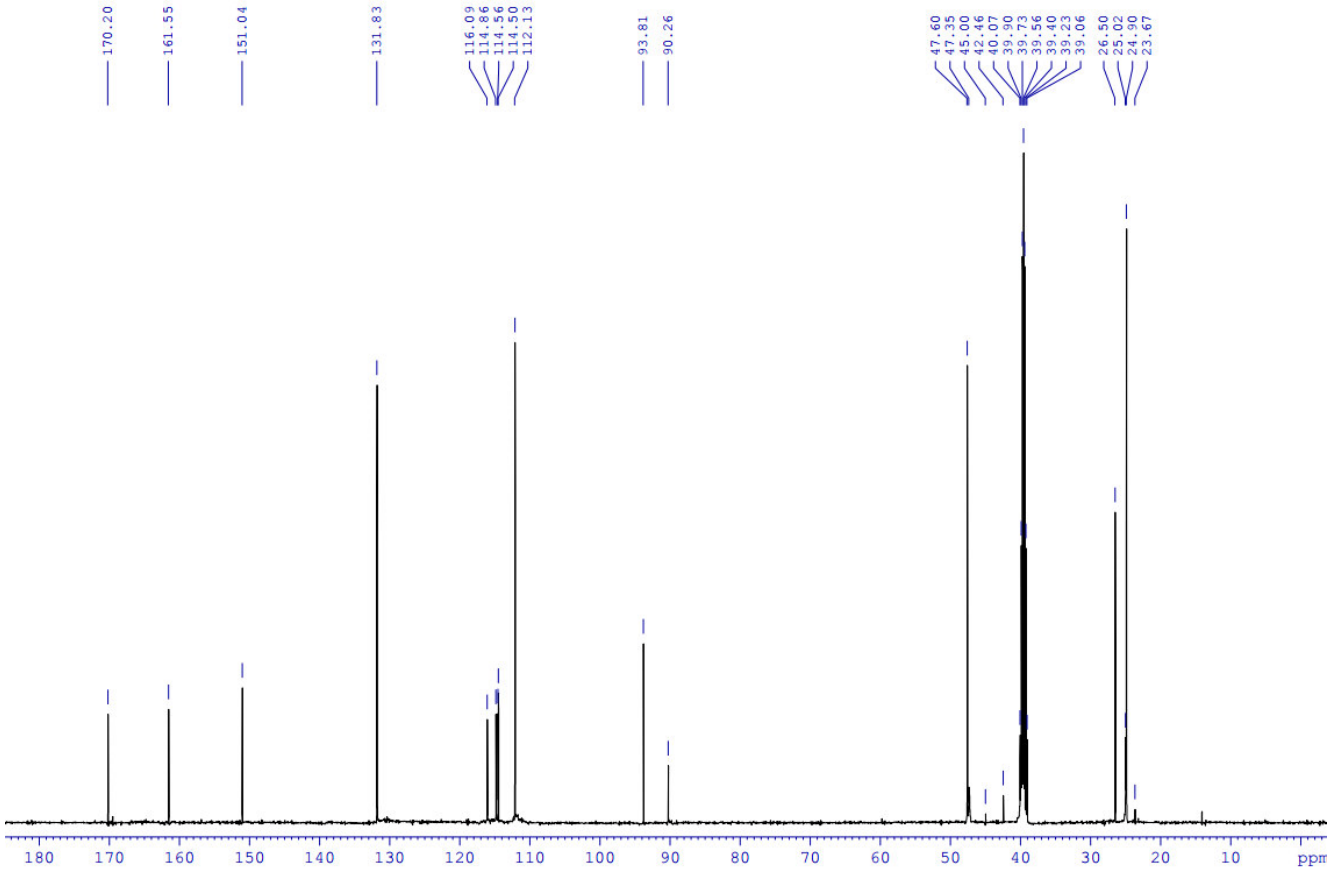


Fig. 8. ^{13}C-NMR-spectrum of **3d** (125.76 MHz, DMSO−d6, 299K)

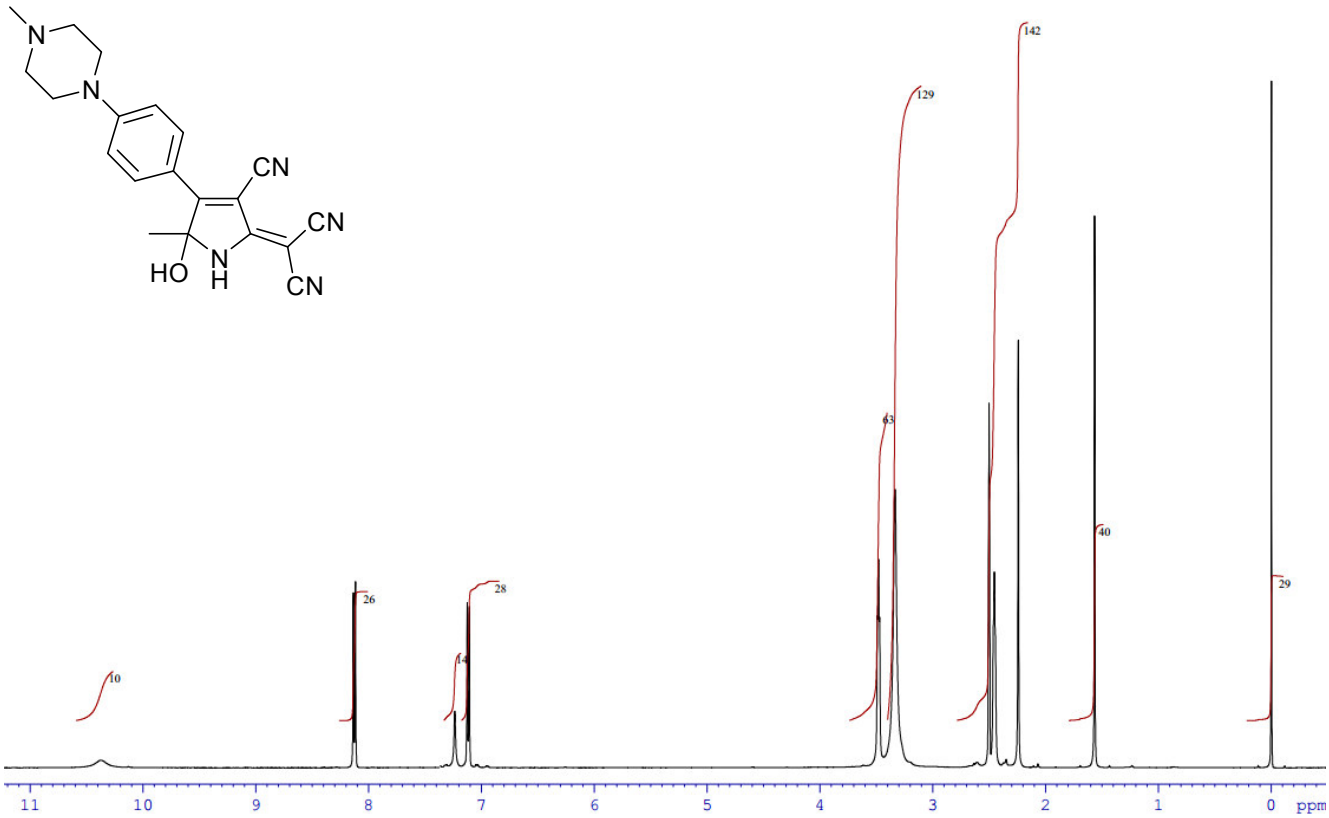


Fig. 9. ^{1}H-NMR-spectrum of **3e** (500.13 MHz, DMSO−d6, 300K)

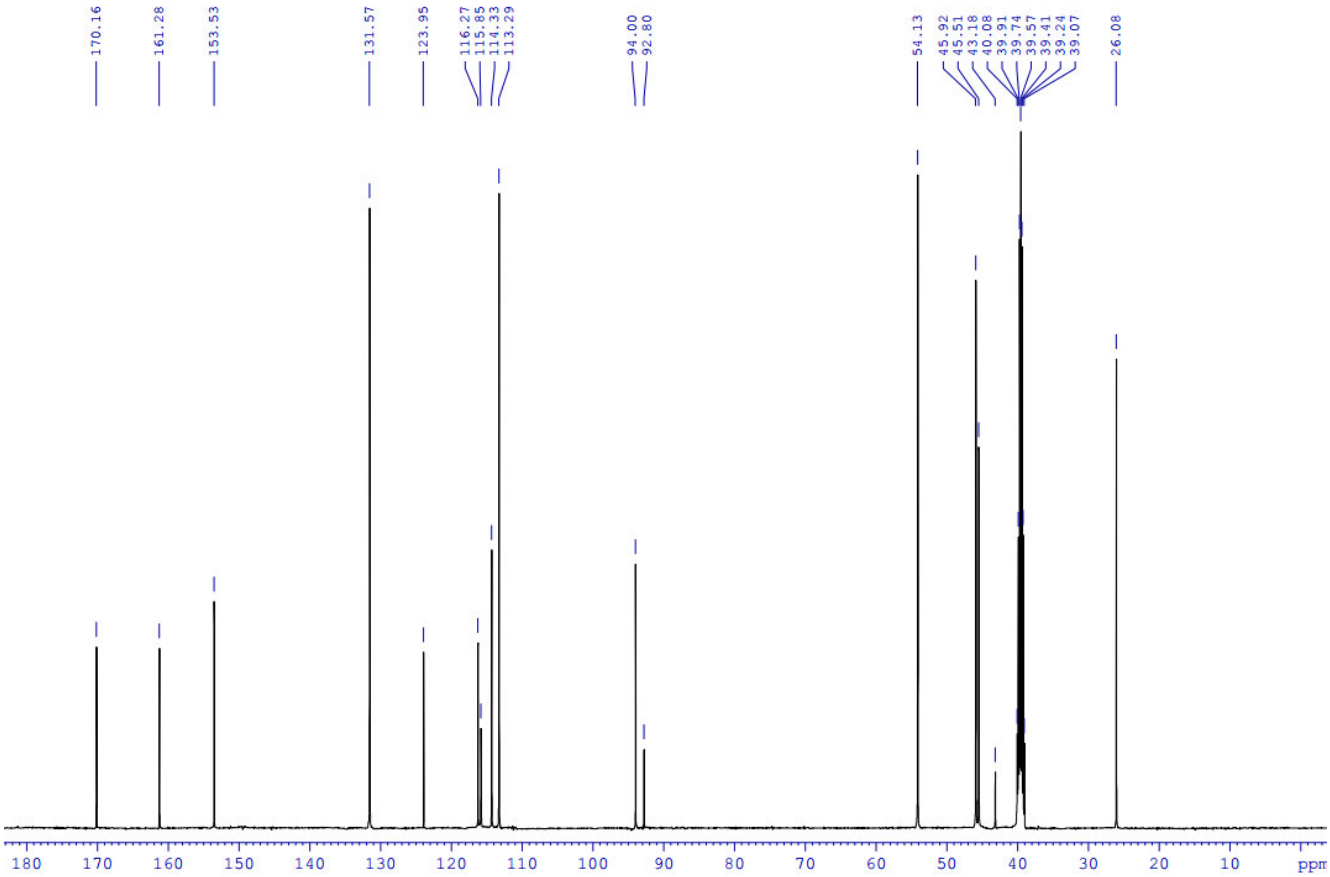


Fig. 10. ^{13}C-NMR-spectrum of **3e** (125.76 MHz, DMSO−d6, 299K)

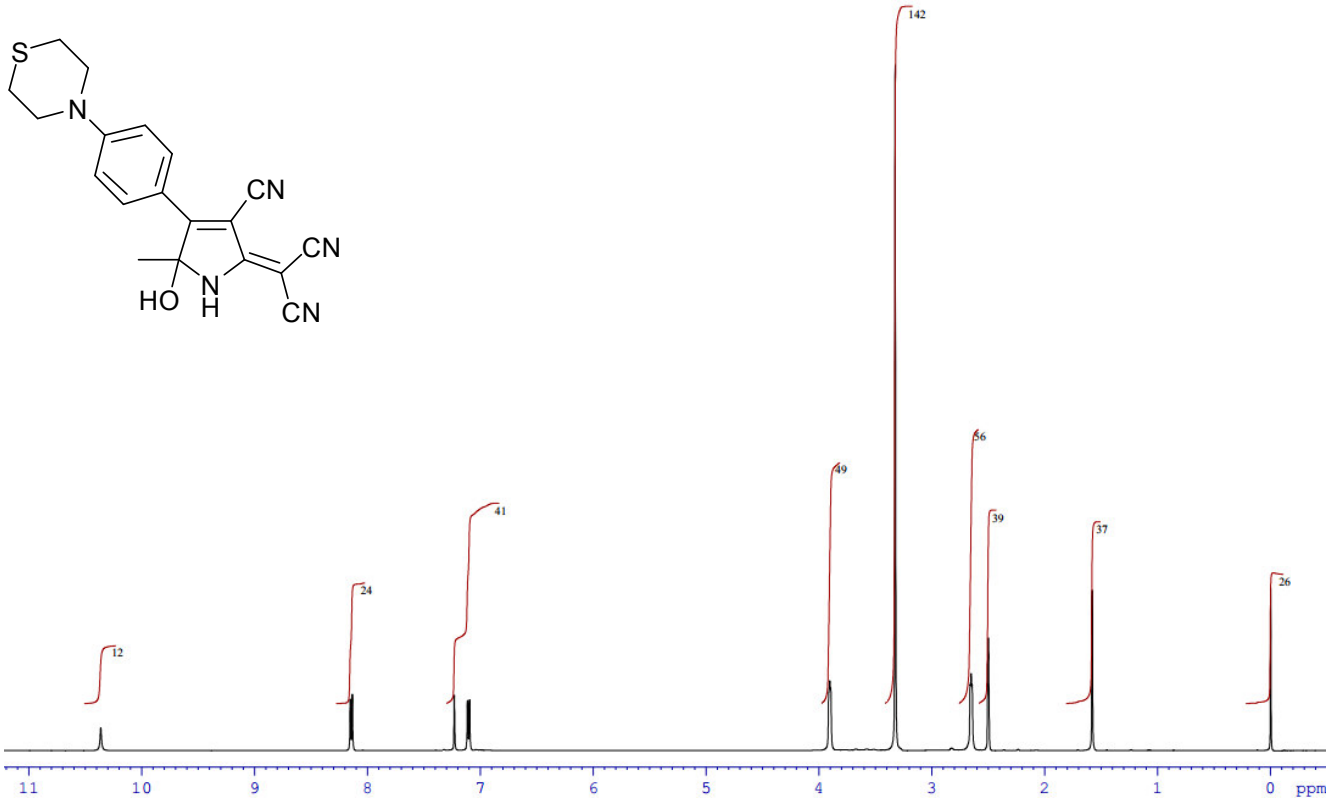


Fig. 11. ^{1}H-NMR-spectrum of **3f** (500.13 MHz, DMSO−d6, 300K)

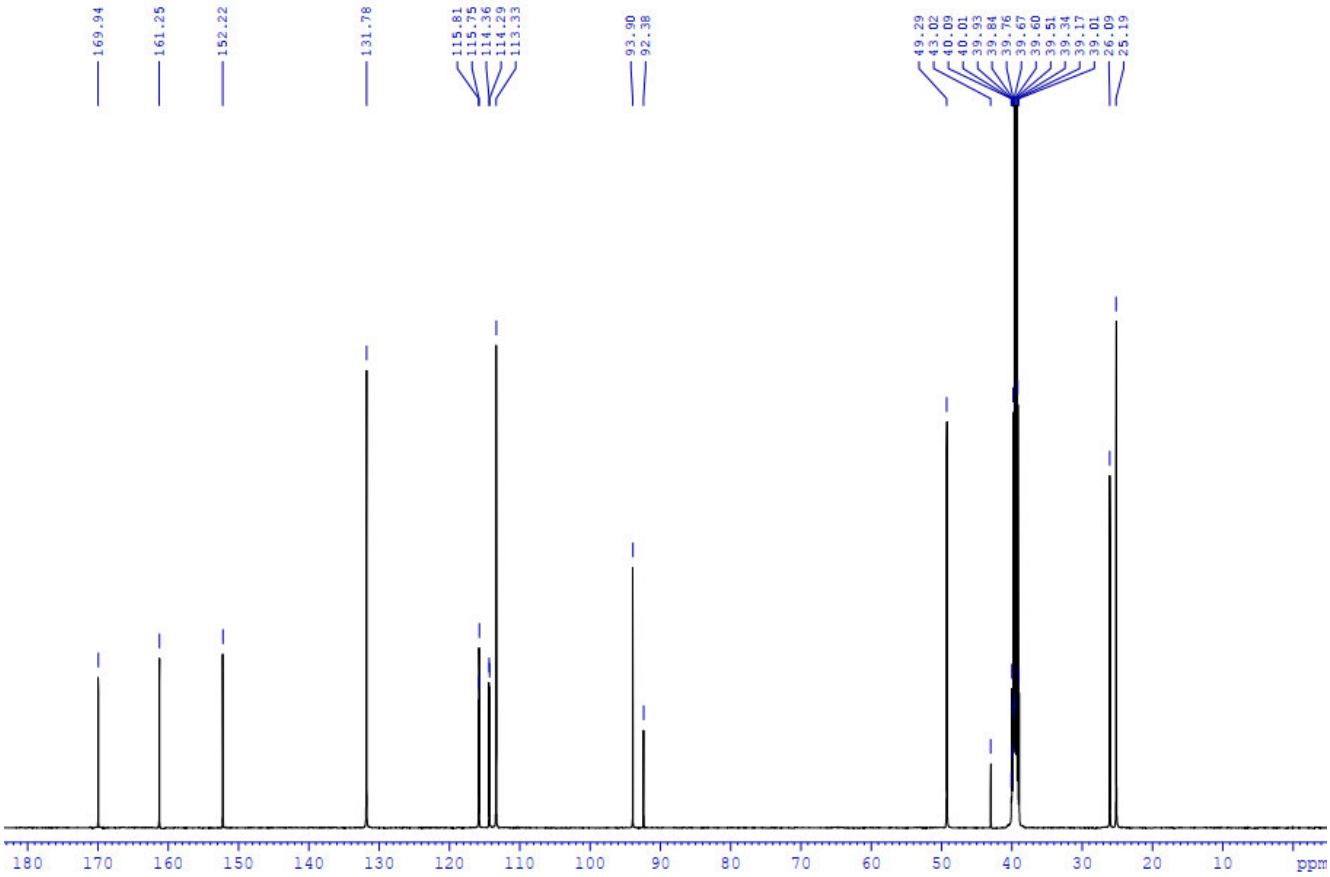


Fig. 12. ^{13}C-NMR-spectrum of **3f** (125.76 MHz, DMSO−d6, 297K)

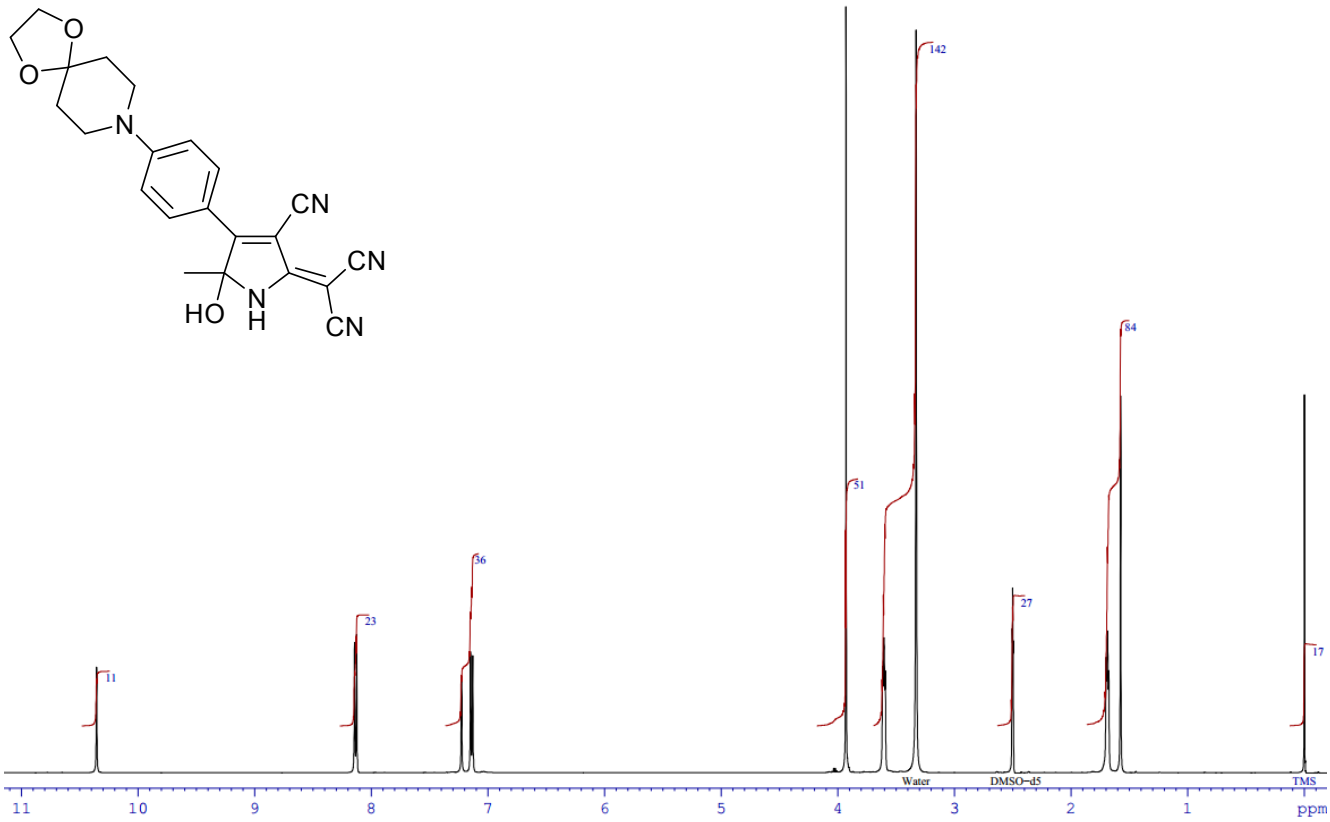


Fig. 13. ^{1}H-NMR-spectrum of **3g** (500.13 MHz, DMSO−d6, 300K)

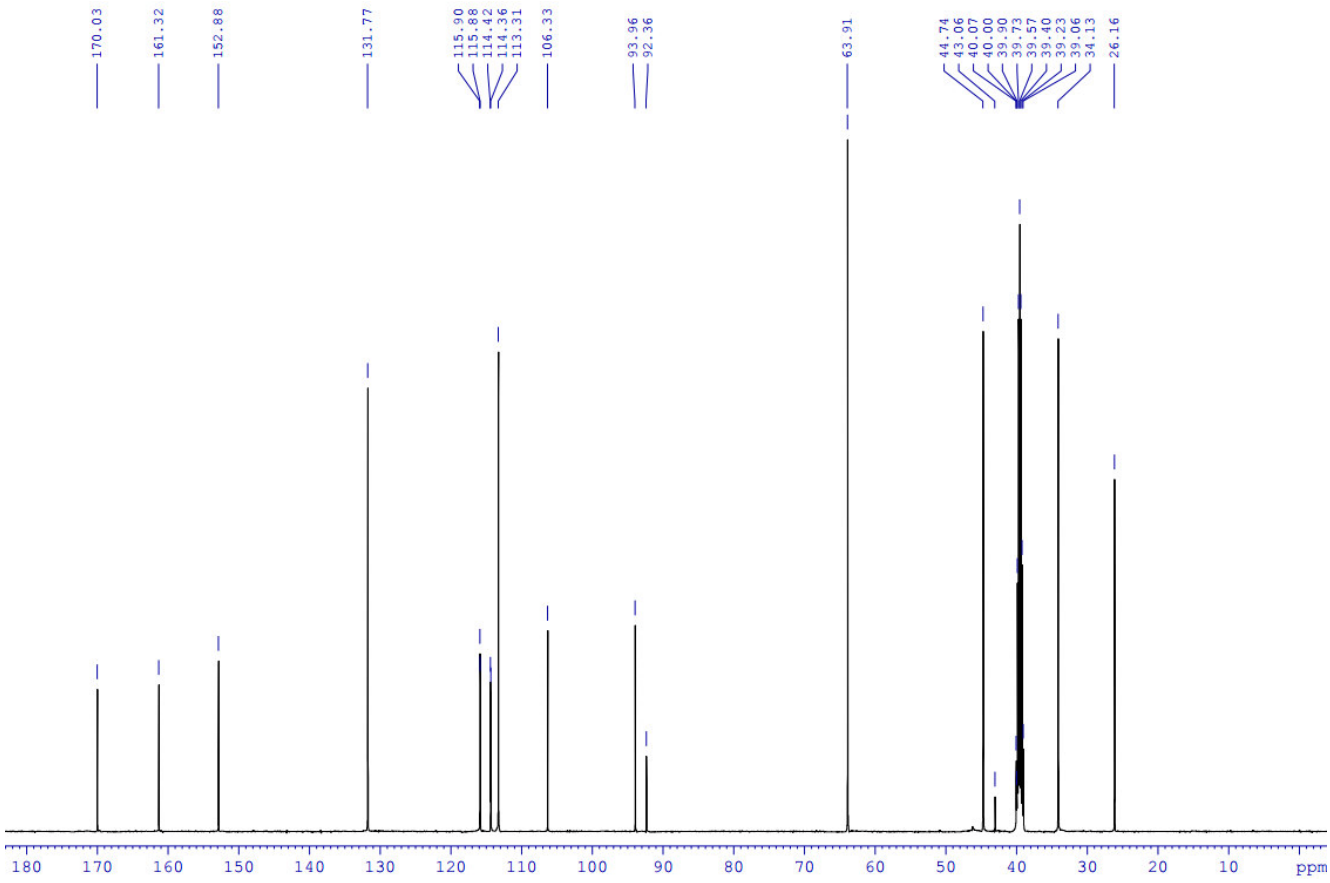


Fig. 14. ^{13}C-NMR-spectrum of **3g** (125.76 MHz, DMSO−d6, 299K)

3. Visualized HOMO (a) and LUMO (b) orbitals of compound 3a-g

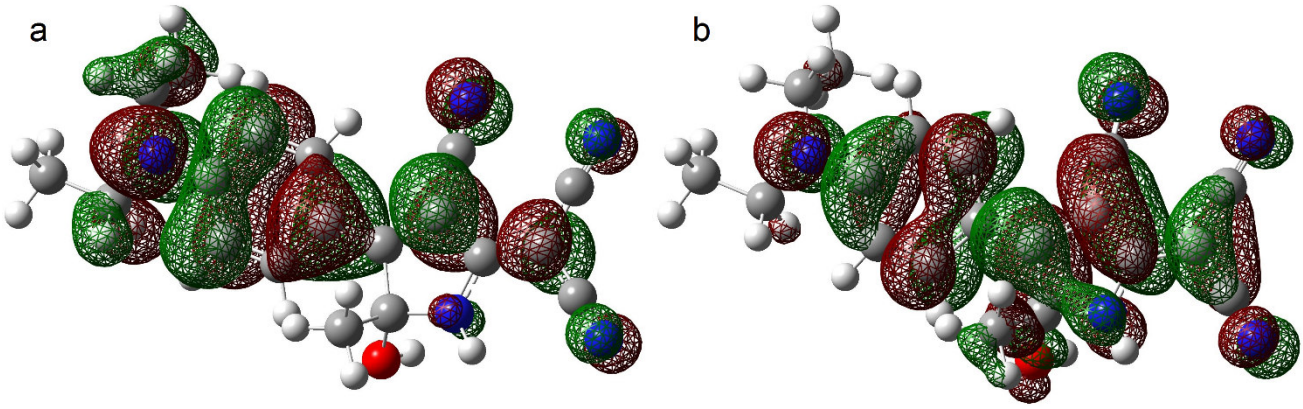


Fig. 15. Visualized HOMO (a) and LUMO (b) orbitals of compound **3a**

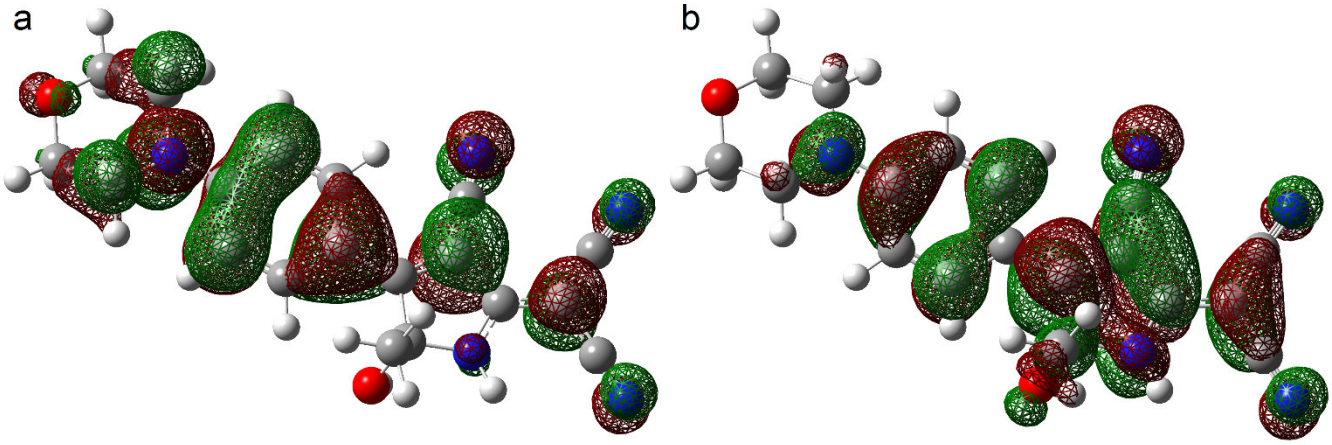


Fig. 16. Visualized HOMO (a) and LUMO (b) orbitals of compound **3b**

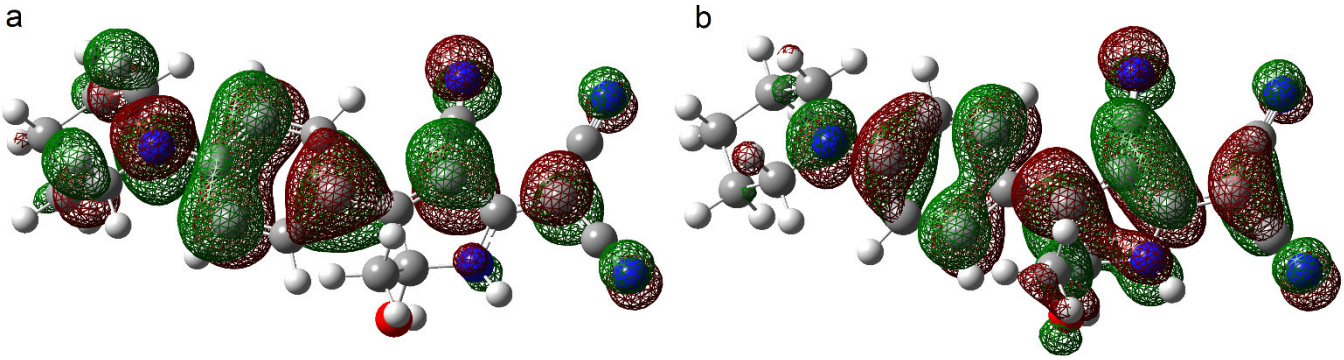


Fig. 17. Visualized HOMO (a) and LUMO (b) orbitals of compound **3c**

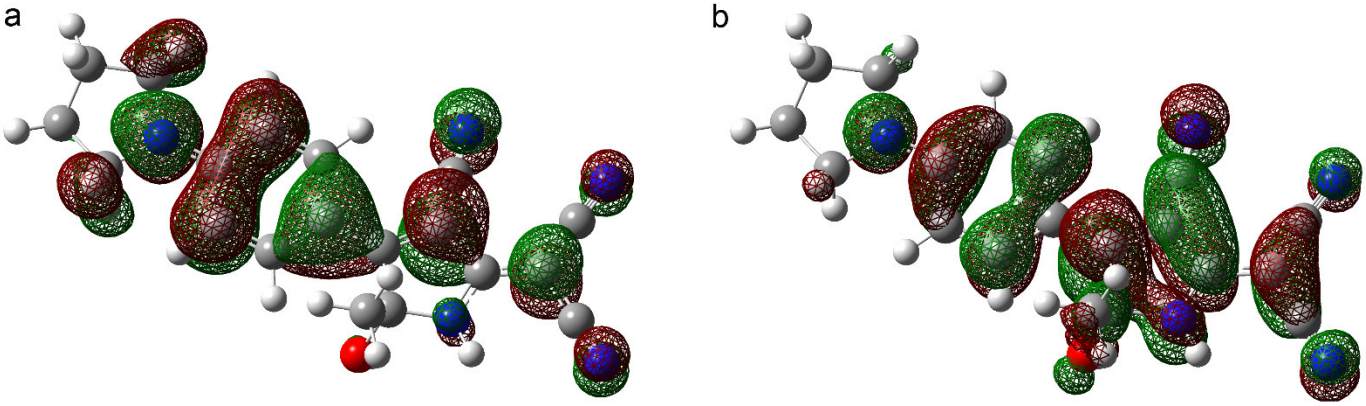


Fig. 18. Visualized HOMO (a) and LUMO (b) orbitals of compound **3d**

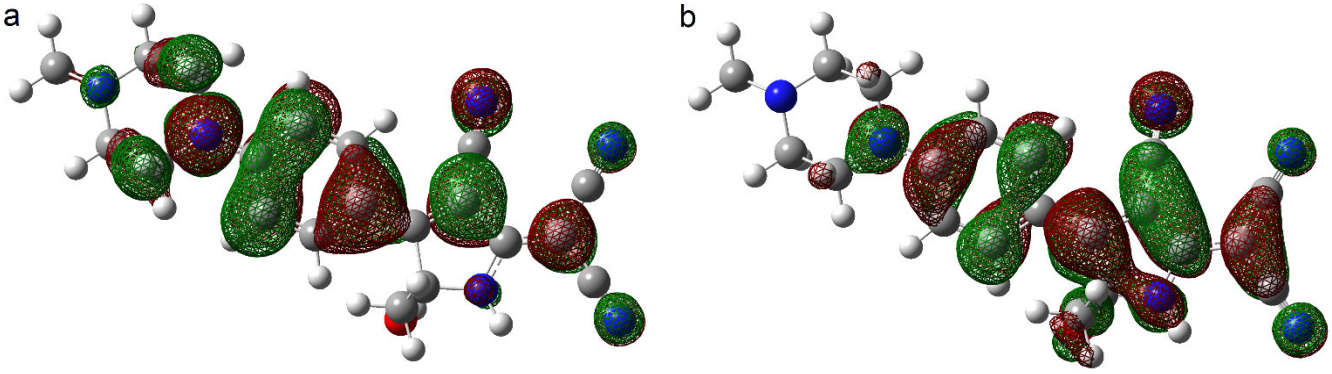


Fig. 19. Visualized HOMO (a) and LUMO (b) orbitals of compound **3e**

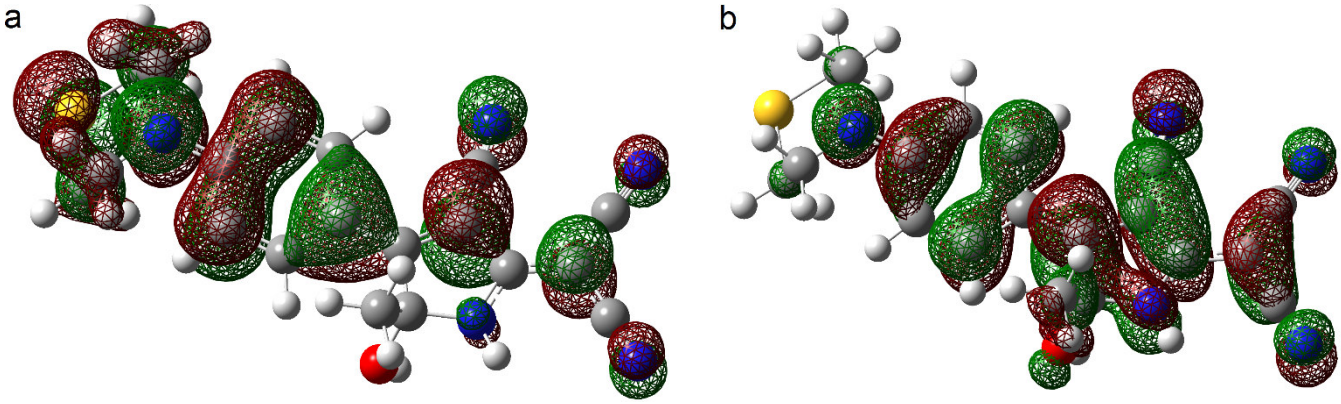


Fig. 20. Visualized HOMO (a) and LUMO (b) orbitals of compound **3f**

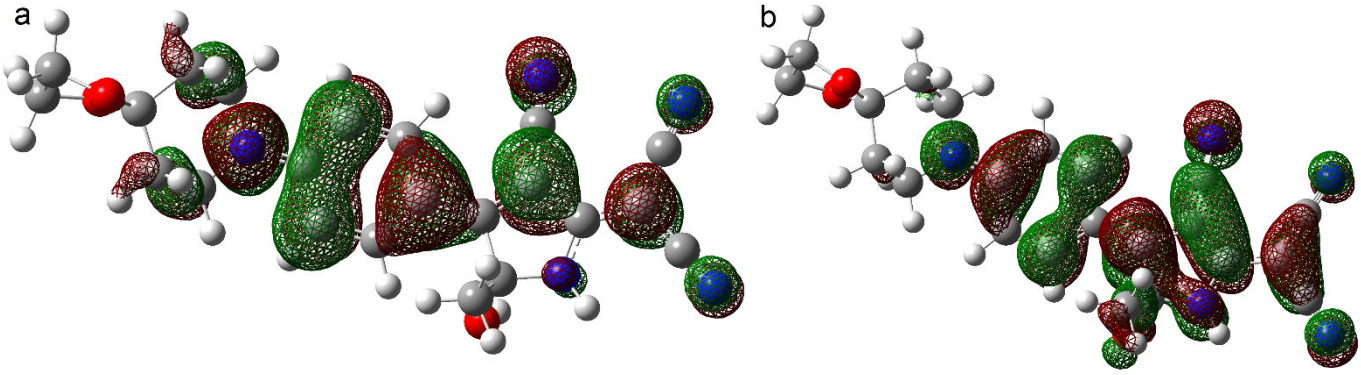


Fig. 21. Visualized HOMO (a) and LUMO (b) orbitals of compound **3g**