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Supporting information

Synthesis and Solid-State Fluorescence of Aryl Substituted 2-Halogenocinchomeronic Dinitriles

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1. General experimental methods

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). The IR spectra were recorded on an FSM-1202 spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra of were measured in DMSO-d_6 on Bruker DRX-500 (operating frequencies 500MHz for ^{1}H) and Bruker AVANCE III HD (operating frequencies 400 MHz for ^{1}H and 101 MHz for ^{13}C NMR) spectrometers using TMS as an internal reference. The elemental compositions were determined on a CHN analyzer vario Micro cube. The mass spectra (EI, 70 eV) were obtained on a Finnigan MAT INCOS-50 spectrometer. Melting points were determined on a device OptiMelt MPA-100. Fluorescence spectra were recorded at room temperature on a Fluorat-02-Panorama spectrofluorimeter using accessory «Frog» for fluorometric measurements of powders out of a device compartment. Samples for measurements were preliminary crushed in a mortar by a pestle. Crystals of compounds **2j** suitable for X-ray analysis were grown at room temperature from a mixture of acetonitrile**.** The X-ray data was collected by using STOE diffractometer Pilatus100K detector, focusing mirror collimation Cu Kα (1.54186 Å) radiation, rotation method mode. STOE X-AREA software was used for cells refinement and data reduction. Data collection and image processing was performed with X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method). The structures were solved and refined with SHELX program.[1] The non-hydrogen atoms were refined by using the anisotropic full matrix least-square procedure. Molecular geometry calculations were performed with the SHELX program, and the molecular graphics were prepared by using DIAMOND software.[2]

Starting 4-oxoalkane-1,1,2,2-tetracarbonitriles **1** were prepared according to the known procedure.[3]

General procedure for the synthesis of 2-halogenopyridine-3,4-dicarbonitriles 2a-n. To 20 ml of dry propan-2-ol 1.96 g of acetyl chloride (0.025 mol) was carefully added dropwise. The mixture was cooled and then 0.005 mol of appropriate 4-oxoalkane-1,1,2,2-tetracarbonitrile **1** was added. The mixture stirred for 30 min at room temperature and then additionally for 3-4 h at heating (50-60 °C). Then the mixture allowed to cool and precipitated solid was filtered. An additional amount of product could be isolated by evaporation to 1/3 part of reaction mixture and further filtration. The filtrate also could be carefully diluted with water; the precipitated solid could be combined with previously isolated parts after crystallization from propan-2-ol.

General procedure for the synthesis of compounds 2o, 2p. To 0.005 mol of corresponding 2-chloropyridine **2d** or **2g** 3 ml of concentrated nitric acid was added. The mixture was refluxed for 5 min, then cooled and diluted with water. Precipitated solid was filtered and washed with water.

Procedures for the synthesis of compound 2q. To the solution of 1.31 g (0.005 mol) of 3-methyl-4-oxo-4-phenylbutane-1,1,2,2-tetracarbonitrile **1h** in 15 ml of propan-2-ol 1 ml of concentrated hydrobromic acid was added. The reaction mixture was stirred for 1 h at room temperature and additionally for 1 h at 60 °C. Then mixture was cooled, precipitated solid was filtered, an additional amount of product could be isolated by dilution of filtrate with water and filtration.

Procedures for the synthesis of compound 2r. To 1.31 g (0.005 mol) of 3-methyl-4-oxo-4-phenylbutane-1,1,2,2-tetracarbonitrile **1h** 3 ml of concentrated hydroiodic acid was added. The reaction mixture was stirred for 10 min at room temperature and additionally for 2 h at 50 °C. Then mixture was cooled and precipitated solid was filtered.

2. Spectral data

2-Chloro-6-phenylpyridine-3,4-dicarbonitrile (2a). M.p. 113.6 °C. IR ν_{max}/cm^{-1} 2232 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 7.59-7.65 (3H, m, Ar), 8.21-8.24 (2H, m, Ar), 8.89 (1H, s, Py) ppm; *m*/*z* (EI) 239 (M$^+$ [^{35}Cl], 100), 241 (M$^+$ [^{37}Cl], 32); elemental analysis found (%): C, 65.35; H, 2.99; N, 17.78, calculated for $C_{13}H_6ClN_3$ C, 65.15; H, 2.52; N, 17.53.

2-Chloro-6-(4-nitrophenyl)pyridine-3,4-dicarbonitrile (2b). M.p. 165.5 °C. IR ν_{max}/cm^{-1} 2232 (C≡N); ^{1}H NMR (400.17 MHz, DMSO-d_6, TMS) δ_H 8.40 (2H, d, ^3J 7.0 Hz, Ar), 8.45 (2H, d, ^3J 7.0 Hz, Ar), 9.05 (1H, s, Py) ppm; ^{13}C NMR (100.63 MHz, DMSO-d_6, TMS) δ_C 161.04, 152.01, 149.24, 144.80, 129.04, 127.15, 124.34, 123.30, 113.78, 113.09, 111.04 ppm; *m*/*z* (EI) 284 (M$^+$ [^{35}Cl], 100), 286 (M+ [^{37}Cl], 34); elemental analysis found (%): C, 54.93; H, 1.79; N, 19.64, calculated for $C_{13}H_5ClN_4O_2$ C, 54.85; H, 1.77; N, 19.68.

2-Chloro-6-(*p*-tolyl)pyridine-3,4-dicarbonitrile (2c). M.p. 175.5 °C. IR ν_{max}/cm^{-1} 2232 (C≡N); ^{1}H NMR (400.17 MHz, DMSO-d_6, TMS) δ_H 2.40 (3H, s, CH_3) 7.41 (2H, d, ^3J 8.5 Hz, Ar), 8.11 (2H, d, ^3J 8.5 Hz, Ar), 8.84 (1H, s, Py) ppm; ^{13}C NMR (100.63 MHz, DMSO-d_6, TMS) δ_C 160.24, 151.73, 142.86, 131.45, 130.02, 127.74, 126.62, 121.94, 113.98, 113.44, 108.79, 21.04 ppm; *m*/*z* (EI) 253 (M$^+$ [^{35}Cl], 100), 255 (M$^+$ [^{37}Cl], 34); elemental analysis found (%): C, 66.22; H, 3.19; N, 16.59, calculated for $C_{14}H_8ClN_3$ C, 66.28; H, 3.18; N, 16.56.

2-Chloro-6-(4-methoxyphenyl)pyridine-3,4-dicarbonitrile (2d). M.p. 212.2 °C (decomp.). IR ν_{max}/cm^{-1} 2228 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS)

δ_H 3.87 (3H, s, OCH_3), 7.14 (2H, d, ^3J 9.0 Hz, C_6H_4), 8.21 (2H, d, ^3J 9.0 Hz, C_6H_4), 8.79 (1H, s, Py) ppm; *m*/*z* (EI) 269 (M^+ [^{35}Cl], 100), 271 (M^+ [^{37}Cl], 32); elemental analysis found (%): C, 62.75; H, 2.79; N, 14.89, calculated for $C_{14}H_8ClN_3O$ C, 62.35; H, 2.99; N, 15.58.

2-Chloro-6-(2,5-dimethoxyphenyl)pyridine-3,4-dicarbonitrile (2e). M.p. 181.1 °C. IR ν_{max}/cm^{-1} 2232 (C≡N); ^{1}H NMR (400.17 MHz, DMSO-d_6, TMS) δ_H 3.77 (3H, s OCH_3), 3.88 (3H, s, OCH_3), 7.18-7.21 (2H, m Ar), 7.38 (1H, dd, ^4J 2.6 Hz, ^3J 8.5 Hz, Ar), 8.63 (1H, s, Py) ppm; ^{13}C NMR (100.63 MHz, DMSO-d_6, TMS) δ_C 158.86, 153.24, 152.13, 151.28, 126.06, 125.80, 123.67, 119.09, 115.12, 114.07, 113.92, 113.36, 108.99, 56.31, 55.61 ppm; *m*/*z* (EI) 299 (M^+ [^{35}Cl], 100), 301 (M^+ [^{37}Cl], 34); elemental analysis found (%): C, 60.16; H, 3.33; N, 13.98, calculated for $C_{15}H_{10}ClN_3O_2$ C, 60.11; H, 3.36; N, 14.02.

2-Chloro-6-(3,4-dimethoxyphenyl)pyridine-3,4-dicarbonitrile (2f). M.p. 244.3 °C. IR ν_{max}/cm^{-1} 2221 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 3.87 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 7.17 (1H, d, ^3J 8.7 Hz, Ar), 7.74 (1H, d, ^4J 2.2 Hz, Ar), 7.89 (1H, dd, ^4J 2.2 Hz, ^3J 8.6 Hz, Ar), 8.86 (1H, s, Py) ppm; *m*/*z* (EI) 299 (M^+ [^{35}Cl], 100), 301 (M^+ [^{37}Cl], 34); elemental analysis found (%): C, 59.75; H, 3.45; N, 13.42, calculated for $C_{15}H_{10}ClN_3O_2$ C, 60.11; H, 3.36; N, 14.02.

2-Chloro-6-(furan-2-yl)pyridine-3,4-dicarbonitrile (2g). M.p. 143.5 °C. IR ν_{max}/cm^{-1} 2232 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 6.84 (1H, dd, ^3J 1.7 Hz, ^3J 3.6 Hz, Fu), 7.60 (1H, d, ^3J 3.5 Hz, Fu), 8.12 (1H, d, ^3J 1.5 Hz, Fu), 8.52 (1H, s, Py) ppm; *m*/*z* (EI) 229 (M^+ [^{35}Cl], 100), 231 (M^+ [^{37}Cl], 34); elemental analysis found (%): C, 57.59; H, 1.78; N, 18.34, calculated for $C_{11}H_4ClN_3O$ C, 57.54; H, 1.76; N, 18.30.

2-Chloro-5-methyl-6-phenylpyridine-3,4-dicarbonitrile (2h). M.p. 128.3 °C. IR ν_{max}/cm^{-1} 2233 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 2.55 (3H, s, CH_3), 7.56-7.59 (3H, m, Ph), 7.62-7.65 (2H, m, Ph) ppm; *m*/*z* (EI) 253 (M^+ [^{35}Cl], 48), 255 (M^+ [^{37}Cl], 16); elemental analysis found (%): C, 66.36; H, 3.19; N, 16.52, calculated for $C_{14}H_8ClN_3$ C, 66.28; H, 3.18; N, 16.56.

2-Chloro-5-methyl-6-(p-tolyl)pyridine-3,4-dicarbonitrile (2i). M.p. 175.2 °C. IR ν_{max}/cm^{-1} 2233 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 2.40 (3H, s, CH_3), 2.50 (3H, s, CH_3), 7.38 (2H, d, ^3J 8.0 Hz, Ar), 7.55 (2H, d, ^3J 8.0 Hz, Ar) ppm; *m*/*z* (EI) 267 (M^+ [^{35}Cl], 48), 269 (M^+ [^{37}Cl], 16); elemental analysis found (%): C, 67.37; H, 3.79; N, 15.67, calculated for $C_{15}H_{10}ClN_3$ C, 67.30; H, 3.77; N, 15.70.

2-Chloro-6-(4-methoxyphenyl)-5-methylpyridine-3,4-dicarbonitrile (2j). M.p. 161.4 °C. IR ν_{max}/cm^{-1} 2228 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 2.59 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 7.11 d (2H, d, ^3J 8.8 Hz, C_6H_4,), 7.65 d (2H, d, ^3J 8.8 Hz, C_6H_4,) ; *m*/*z* (EI) 283 (M^+ [^{35}Cl], 100), 285 (M^+ [^{37}Cl], 33);

elemental analysis found (%): C, 63.78; H, 3.55; N, 14.81, calculated for $C_{15}H_{10}ClN_3O$ C, 63.50; H, 3.75; N, 15.01.

2-Chloro-5-ethyl-6-phenylpyridine-3,4-dicarbonitrile (2k). M.p. 154.0 °C. IR ν_{max}/cm^{-1} 2233 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 1.12 (3H, t, ^3J 7.5 Hz, CH_3), 2.86 (2H, q, ^3J 7.4 Hz, CH_2), 7.54-7.59 (5H, m, Ph) ppm; *m*/*z* (EI) 267 (M^+ [^{35}Cl], 48), 269 (M^+ [^{37}Cl], 16); elemental analysis found (%): C, 67.23; H, 3.74; N, 15.66, calculated for $C_{15}H_{10}ClN_3$ C, 67.30; H, 3.77; N, 15.70.

2-Chloro-5-(4-methoxyphenyl)-6-methylpyridine-3,4-dicarbonitrile (2l). M.p. 198.8 °C. IR ν_{max}/cm^{-1} 2233 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 2.45 (3H, s, CH_3), 3.85 (3H, s, OCH_3), 7.14 (2H, d, ^3J 8.8 Hz, Ar), 7.43 (2H, d, ^3J 8.8 Hz, Ar) ppm; *m*/*z* (EI) 283 (M^+ [^{35}Cl], 48), 285 (M^+ [^{37}Cl], 16); elemental analysis found (%): C, 63.56; H, 3.52; N, 14.77, calculated for $C_{15}H_{10}ClN_3O$ C, 63.50; H, 3.55; N, 14.81.

2-Chloro-5,6-diphenylpyridine-3,4-dicarbonitrile (2m). M.p. 214.9 °C. IR ν_{max}/cm^{-1} 2223 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 7.26-7.39 (8H, m, Ph), 7.44-7.48 m (2H, m, Ph); *m*/*z* (EI) 315 (M^+ [^{35}Cl], 32), 317 (M^+ [^{37}Cl], 10); elemental analysis found (%): C, 72.19; H, 3.25; N, 13.39, calculated for $C_{19}H_{10}ClN_3$ C, 72.27; H, 3.19; N, 13.31.

2-Chloro-5,6-dihydrobenzo[h]quinoline-3,4-dicarbonitrile (2n). M.p. 208.0 °C. IR ν_{max}/cm^{-1} 2233 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 3.04 (2H, t, ^3J 7.9 Hz, CH_2), 3.17 (2H, t, ^3J 7.9 Hz, CH_2), 7.43 (1H, d, ^3J 7.5 Hz, Ar), 7.46 (1H, t, ^3J 7.6 Hz, Ar), 7.55 (1H, dt, ^4J 1.3 Hz, ^3J 7.5 Hz, Ar), 8.15 (1H, dd, ^4J 1.1 Hz, ^3J 7.7 Hz, Ar) ppm; *m*/*z* (EI) 265 (M^+ [^{35}Cl], 48), 267 (M^+ [^{37}Cl], 16); elemental analysis found (%): C, 67.77; H, 3.01; N, 15.79, calculated for $C_{15}H_8ClN_3$ C, 67.81; H, 3.04; N, 15.82.

2-Chloro-6-(4-methoxy-3-nitrophenyl)pyridine-3,4-dicarbonitrile (2o). M.p. 189-190 °C. IR ν_{max}/cm^{-1} 2233 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 4.05 (3H, s, OCH_3), 7.60 (1H, d, ^3J 9.0 Hz, Ar), 8.51 (1H, dd, ^4J 2.4 Hz, ^3J 8.9 Hz, Ar), 8.73 (1H, d, 4J 2.3 Hz, Ar), 8.95 (1H, s, Py) ppm; *m*/*z* (EI) 314 (M^+ [^{35}Cl], 16), 316 (M^+ [^{37}Cl], 5); elemental analysis found (%): C, 53.48; H, 2.21; N, 17.76, calculated for $C_{14}H_7ClN_4O_3$ C, 53.44; H, 2.24; N, 17.80.

2-Chloro-6-(5-nitrofuran-2-yl)pyridine-3,4-dicarbonitrile (2p). IR ν_{max}/cm^{-1} 2233 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 8.23 (1H, d, ^3J 4.5 Hz, Fu), 8.30 (1H, d, ^3J 4.5 Hz, Fu), 9.02 (1H, s, Py) ppm; *m*/*z* (EI) 274 (M^+ [^{35}Cl], 36), 276 (M^+ [^{37}Cl], 13); elemental analysis found (%): C, 48.02; H, 1.11; N, 20.37, calculated for $C_{11}H_3ClN_4O$ C, 48.11; H, 1.10; N, 20.40.

2-Bromo-5-methyl-6-phenylpyridine-3,4-dicarbonitrile (2q). M.p. 147.6 °C. IR ν_{max}/cm^{-1} 2234 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 2.52 (3H, s, CH_3), 7.56-7.59 (3H, m, Ph), 7.61-7.64 (2H, m, Ph) ppm; *m*/*z* (EI) 297 (M^+ [^{79}Br],

26), 299 (M^+ [^{81}Br], 25); elemental analysis found (%): C, 56.43; H, 2.71; N, 14.05, calculated for $C_{14}H_8BrN_3$ C, 56.40; H, 2.70; N, 14.09.

2-Iodo-5-methyl-6-phenylpyridine-3,4-dicarbonitrile (2r). M.p. 173.8 °C. IR ν_{max}/cm^{-1} 2234 (C≡N); ^{1}H NMR (500.13 MHz, DMSO-d_6, TMS) δ_H 2.52 (3H, s, CH_3), 7.56-7.59 (3H, m, Ph), 7.61-7.64 (2H, m, Ph) ppm; *m*/*z* (EI) 345 (M^+, 41); elemental analysis found (%): C, 48.67; H, 2.35; N, 12.14, calculated for $C_{14}H_8IN_3$, C 48.72; H, 2.34; N, 12.17.

3. NMR spectra

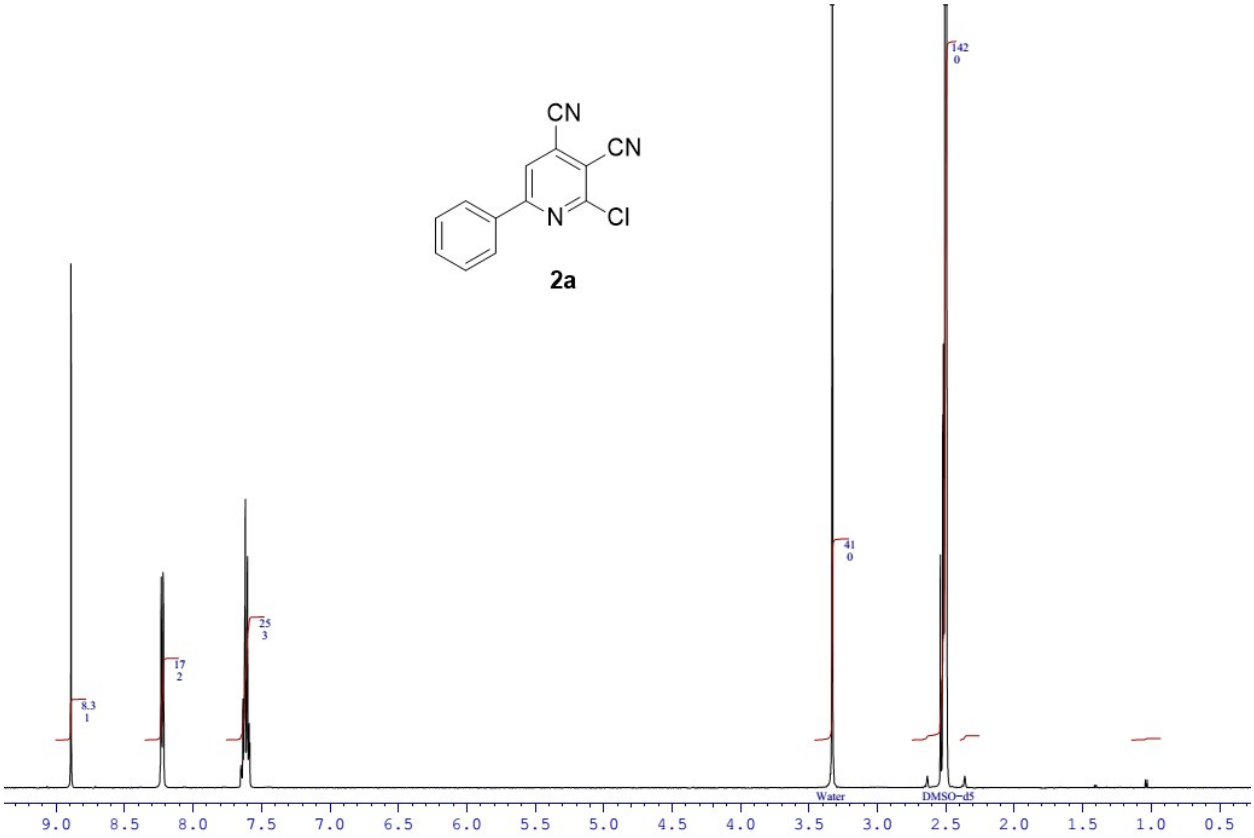

Fig. 1. ^{1}H NMR-spectrum of **2a** (500.13 MHz, DMSO−d_6)

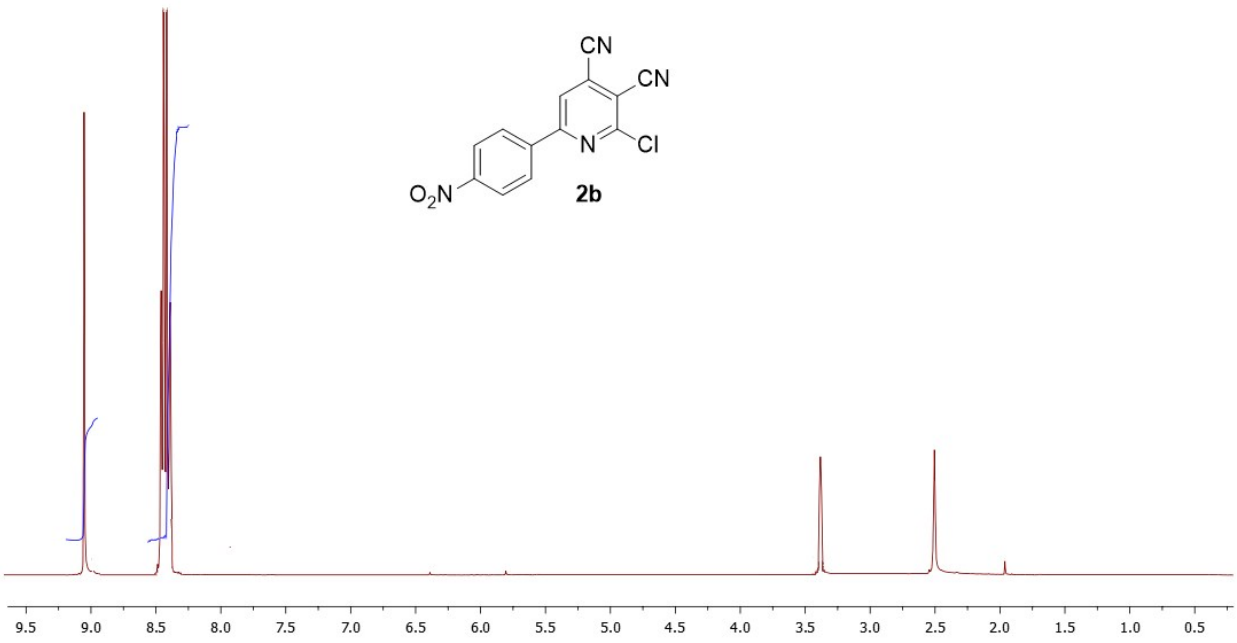

Fig. 2. ^{1}H NMR-spectrum of **2b** (400.17 MHz, DMSO−d_6)

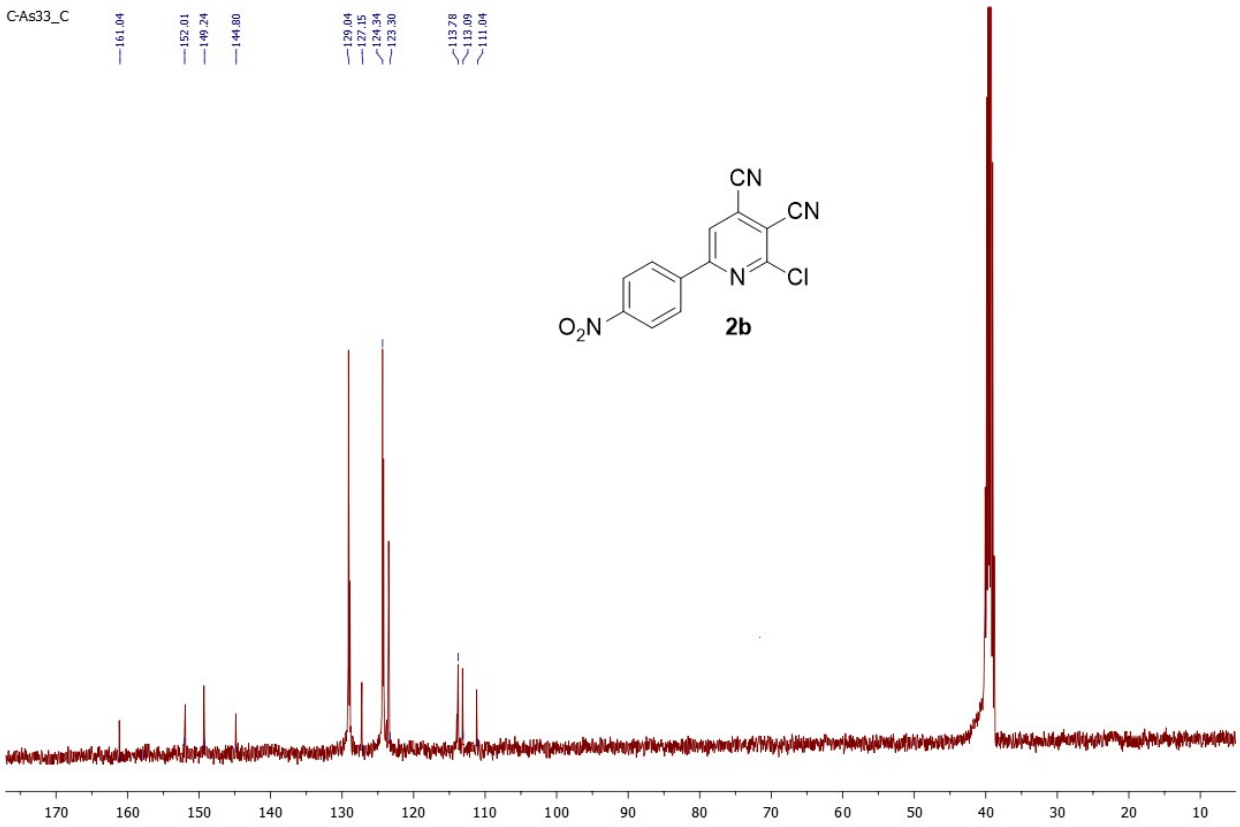

Fig. 3. ^{13}C NMR-spectrum of **2b** (100.63 MHz, DMSO−d_6)

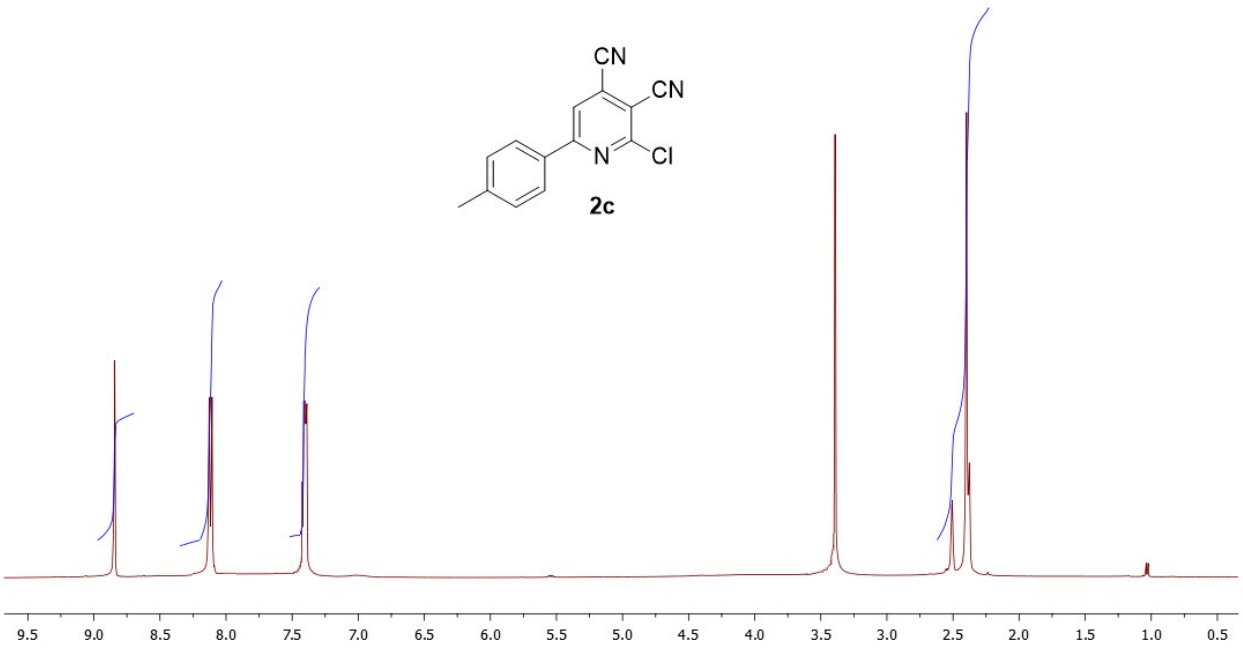

Fig. 4. ^{1}H NMR-spectrum of **2c** (400.17 MHz, DMSO−d_6)

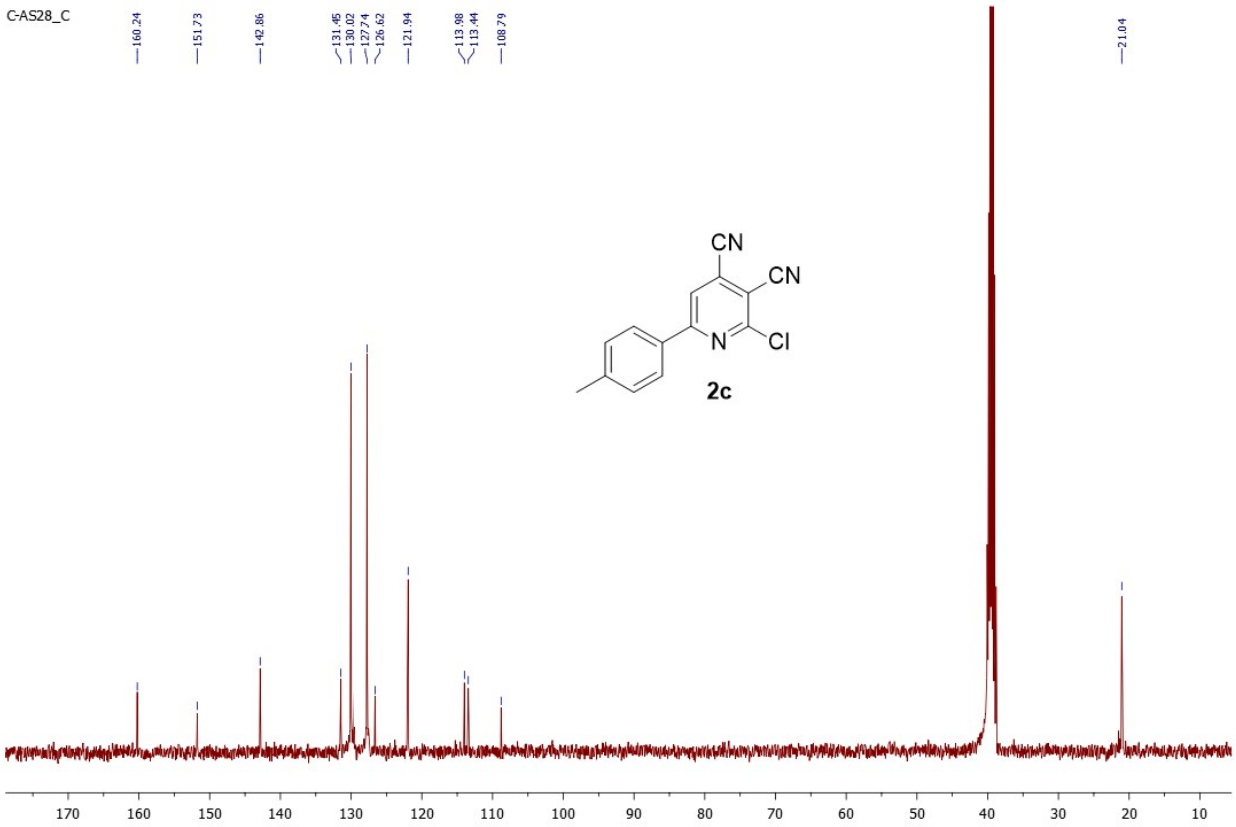

Fig. 5. ^{13}C NMR-spectrum of **2c** (100.63 MHz, DMSO−d_6)

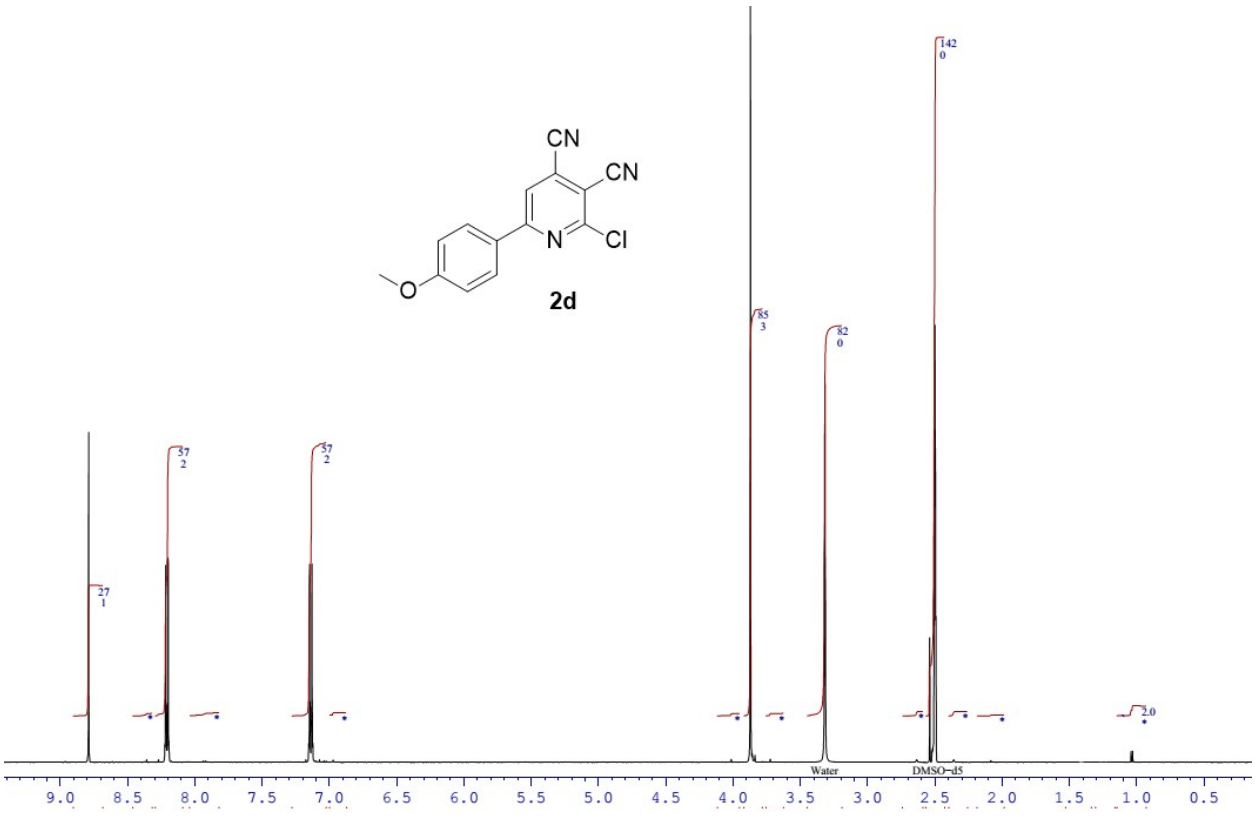

Fig. 6. ^{1}H NMR-spectrum of **2d** (500.13 MHz, DMSO−d_6)

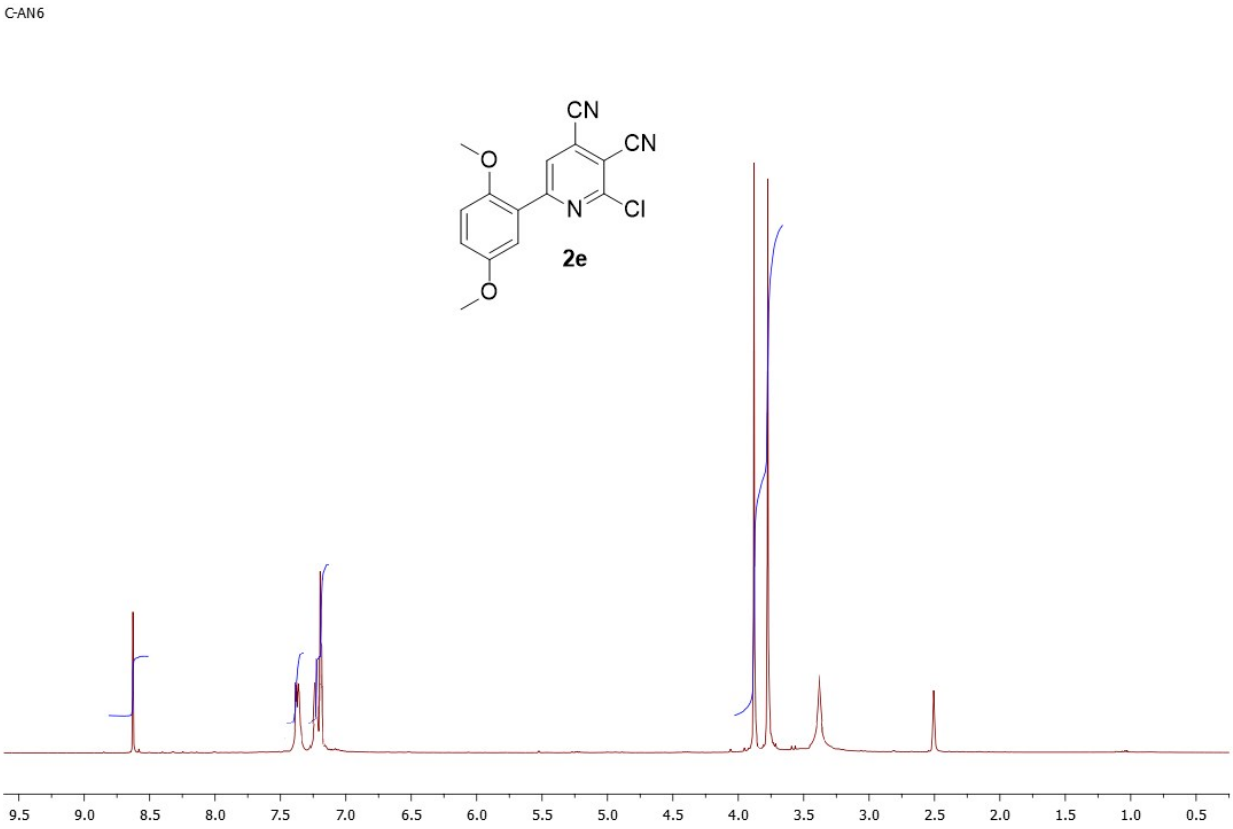

Fig. 7. ^{1}H NMR-spectrum of **2e** (400.17 MHz, DMSO−d_6)

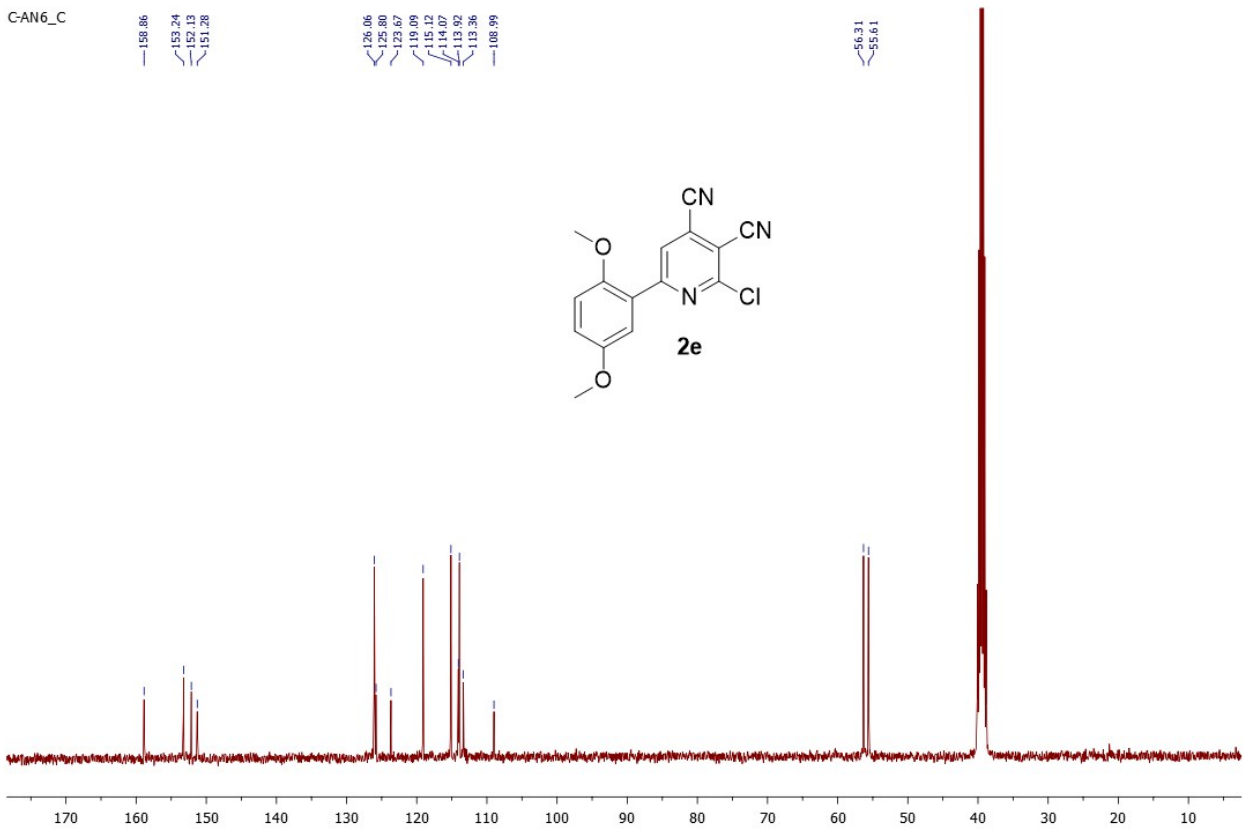

Fig. 8. ^{13}C NMR-spectrum of **2e** (100.63 MHz, DMSO−d_6)

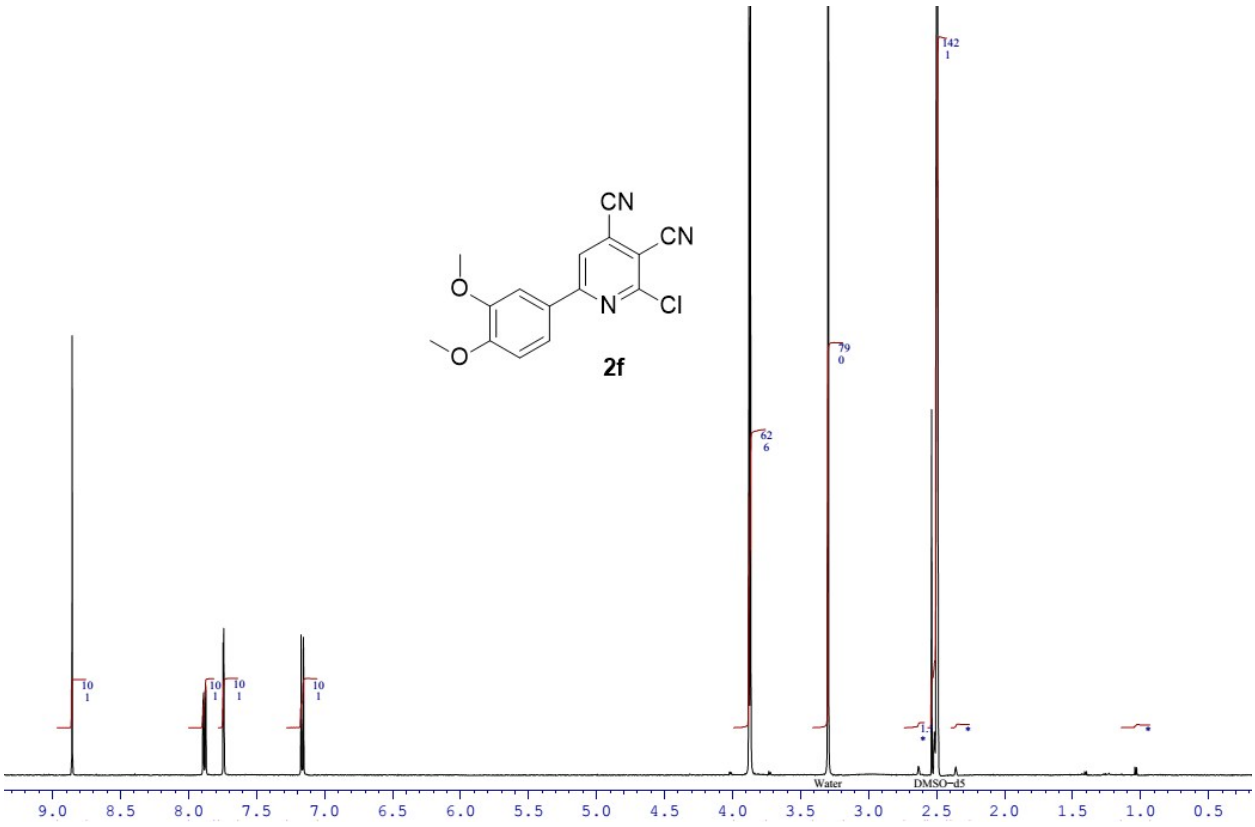

Fig. 9. ^{1}H NMR-spectrum of **2f** (500.13 MHz, DMSO−d_6)

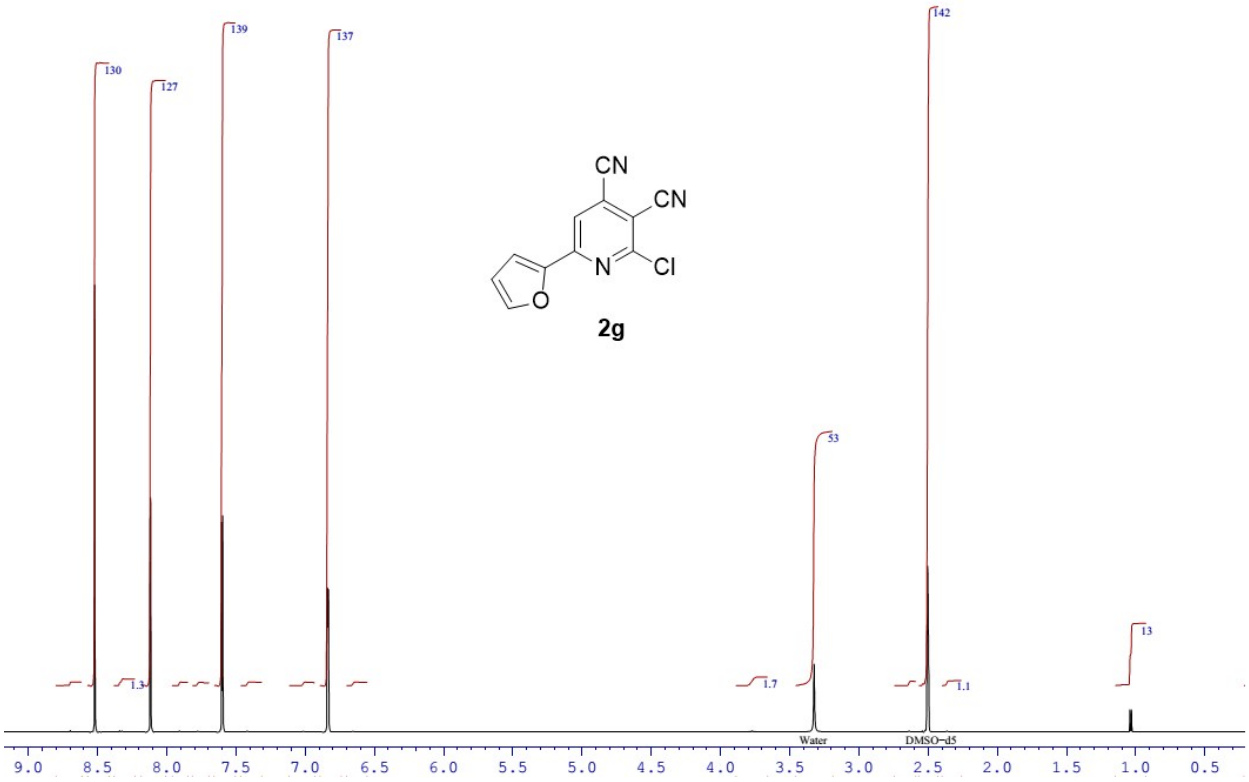

Fig. 10. ^{1}H NMR-spectrum of **2g** (500.13 MHz, DMSO−d_6)

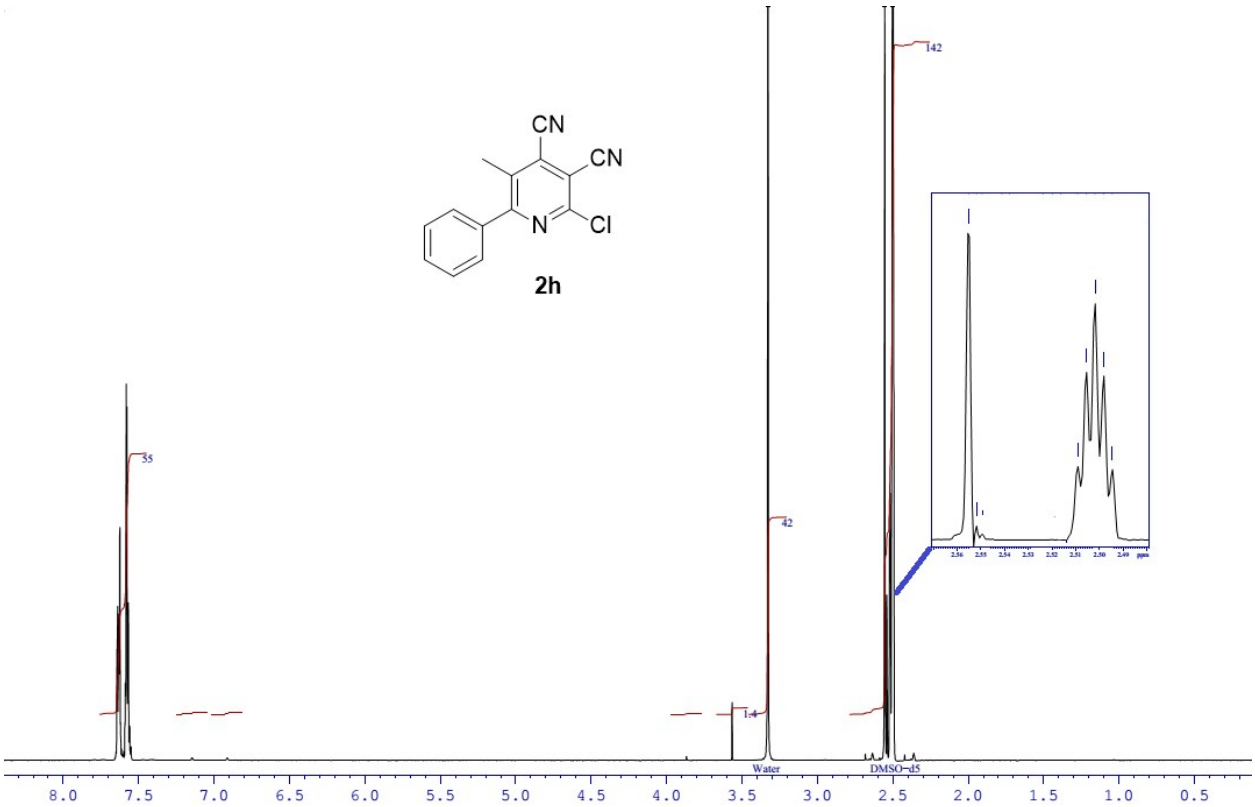

Fig. 11. ^{1}H NMR-spectrum of **2h** (500.13 MHz, DMSO−d_6)

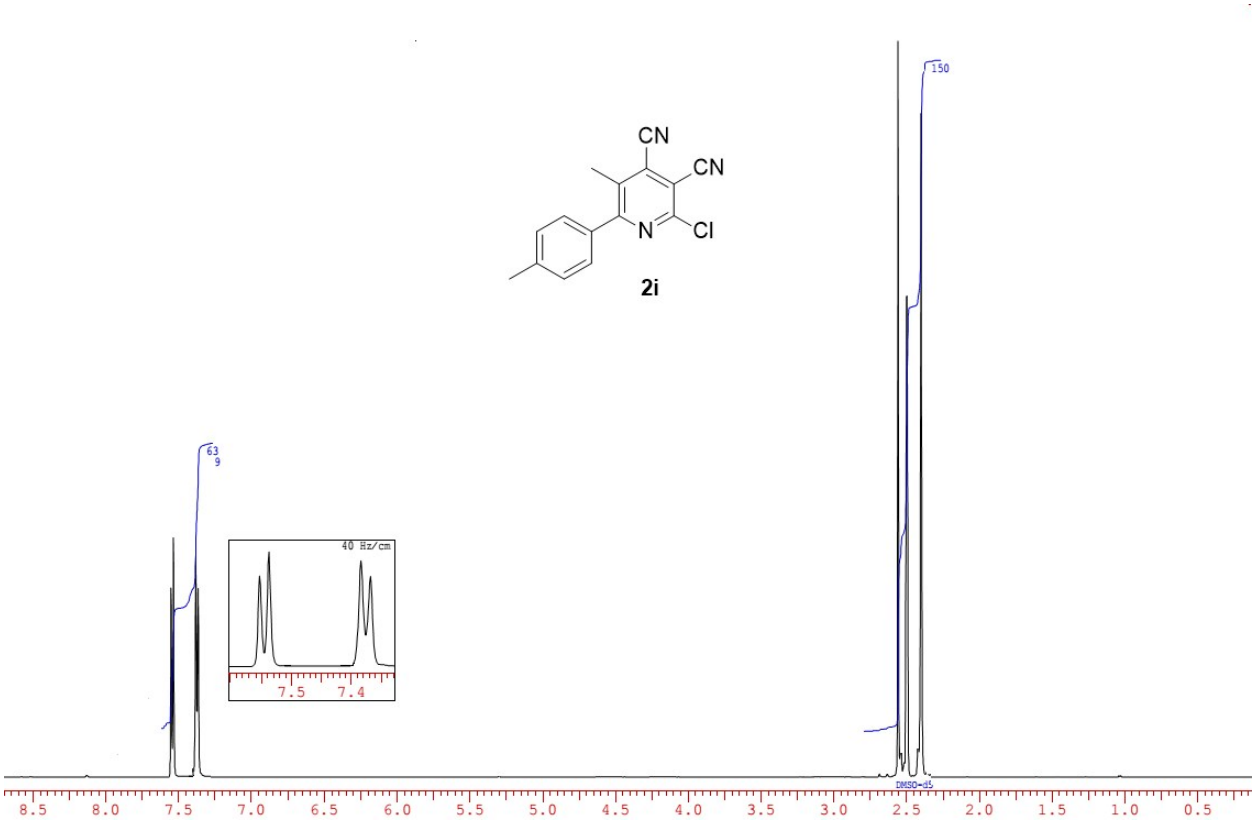

Fig. 12. ^{1}H NMR-spectrum of **2i** (500.13 MHz, DMSO−d_6)

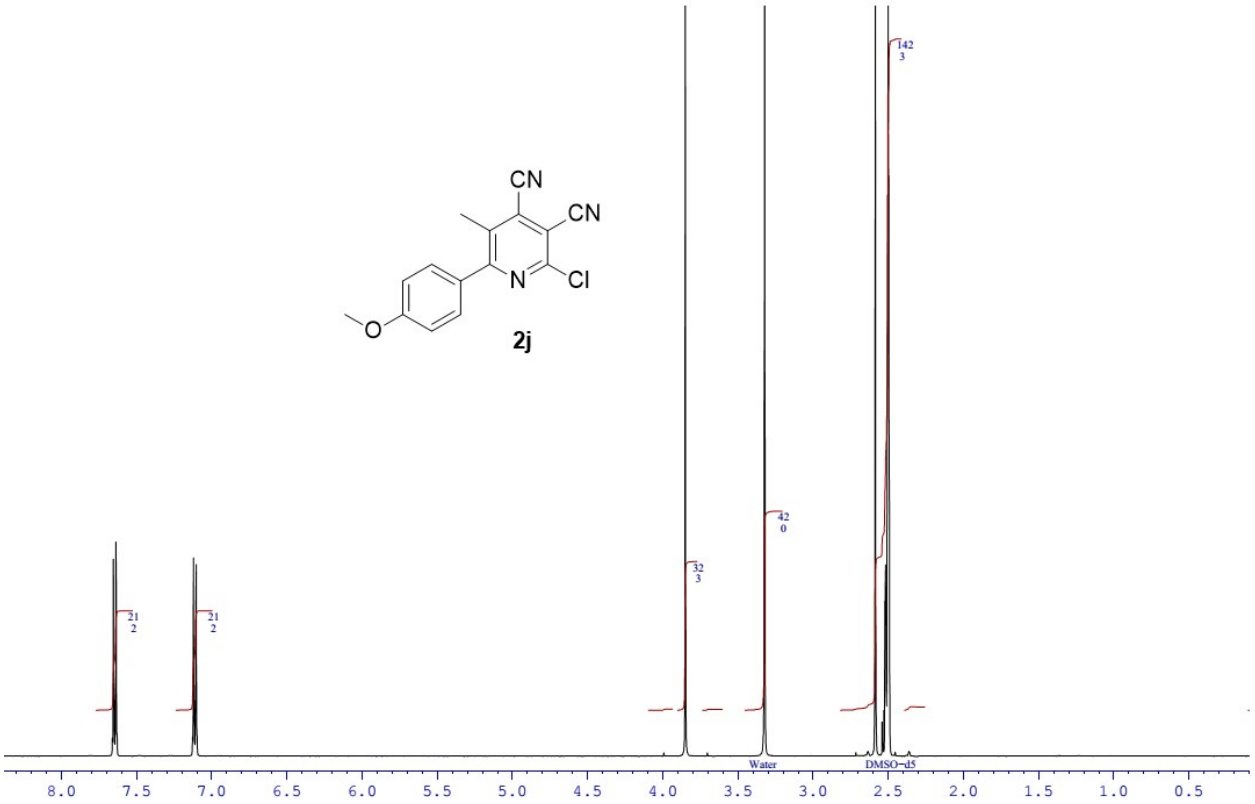

Fig. 13. ^{1}H NMR-spectrum of **2j** (500.13 MHz, DMSO−d_6)

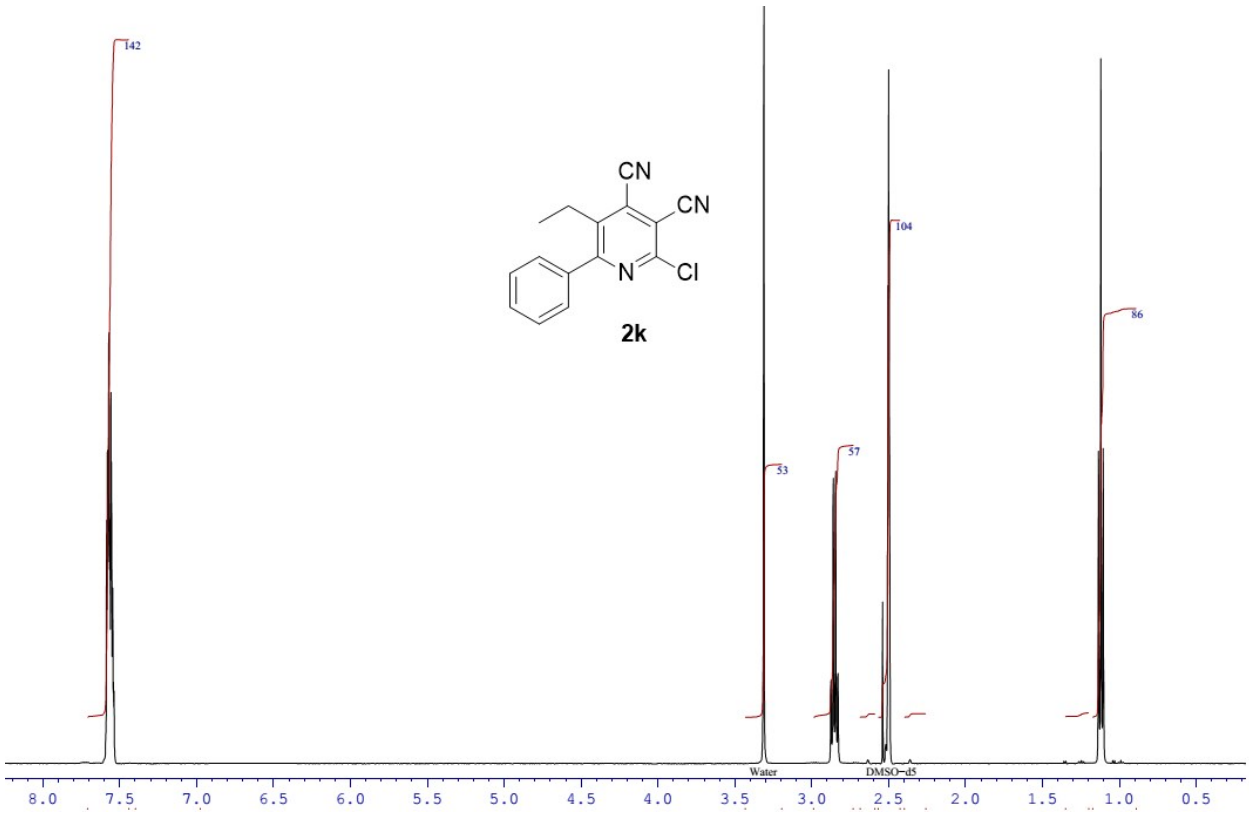

Fig. 14. ^{1}H NMR-spectrum of **2k** (500.13 MHz, DMSO−d_6)

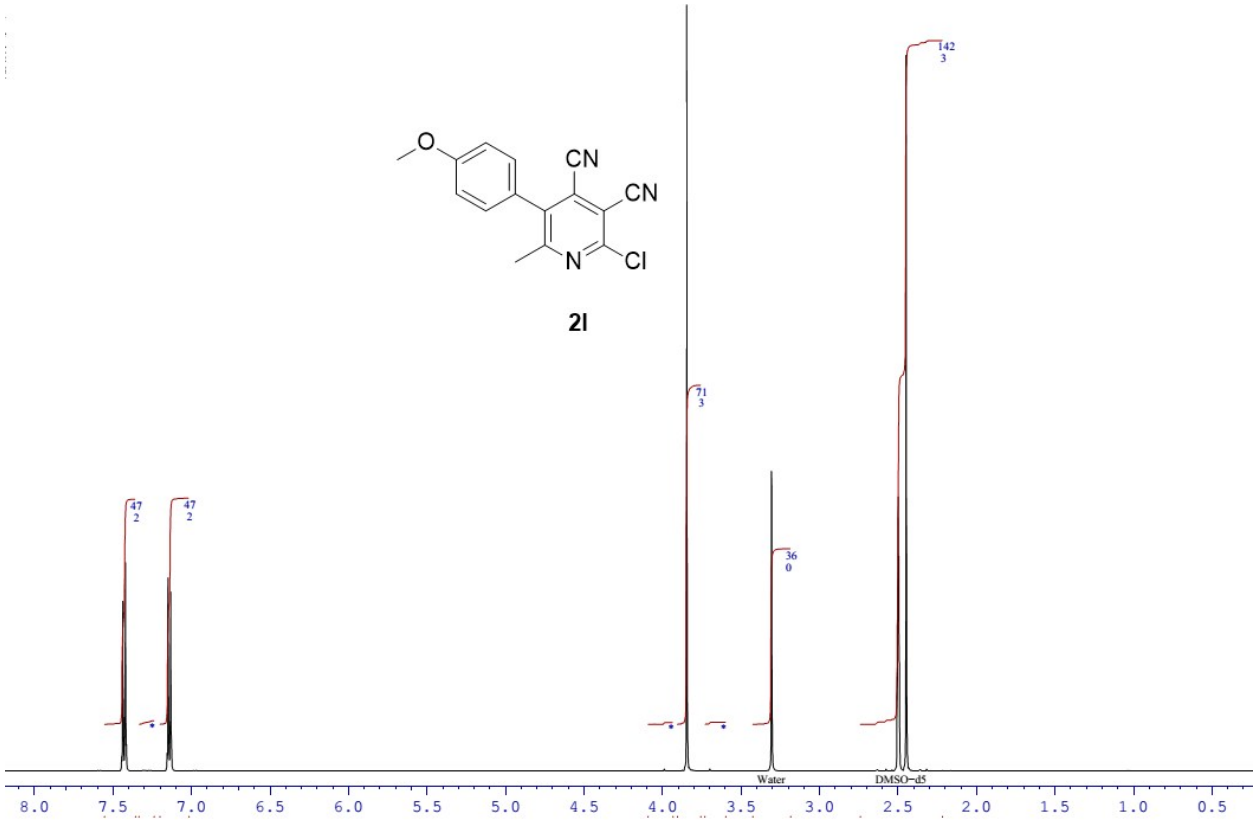

Fig. 15. ^{1}H NMR-spectrum of **2l** (500.13 MHz, DMSO−d_6)

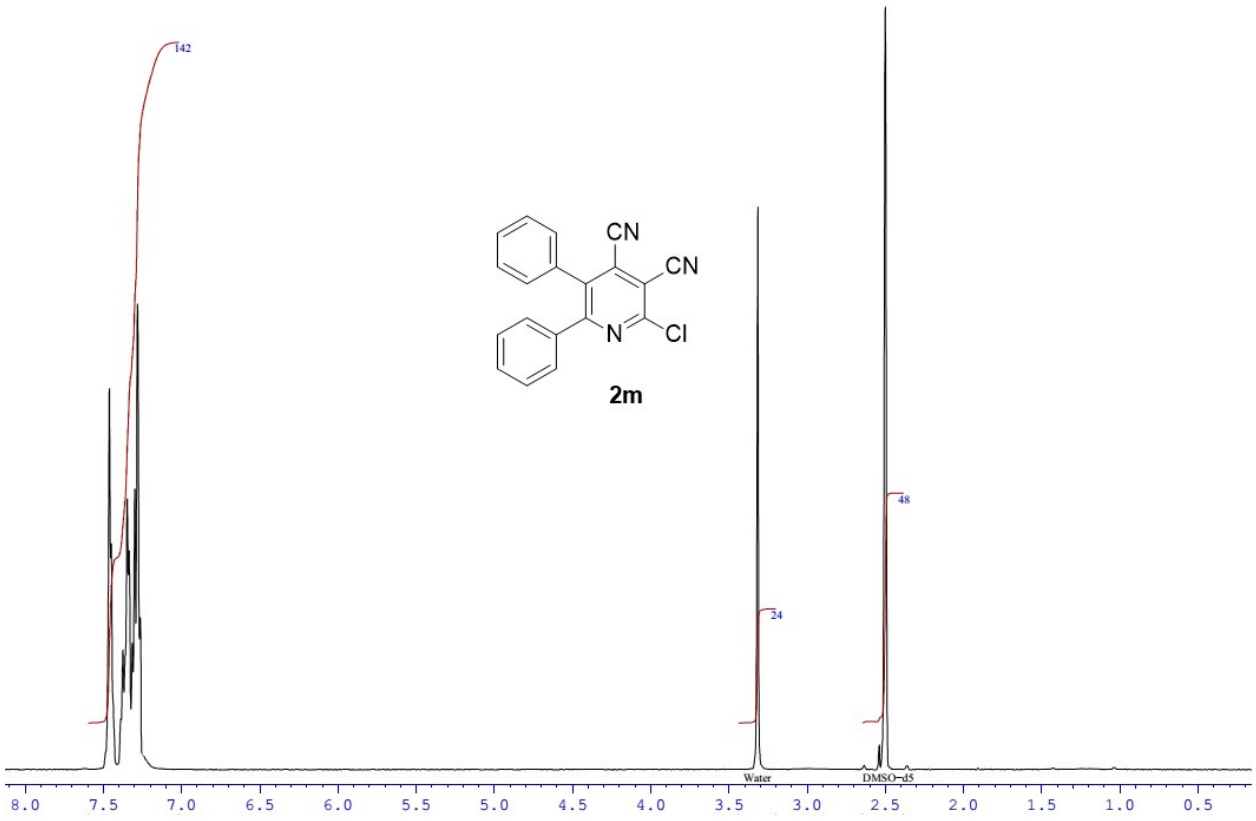

Fig. 16. ^{1}H NMR-spectrum of **2m** (500.13 MHz, DMSO−d_6)

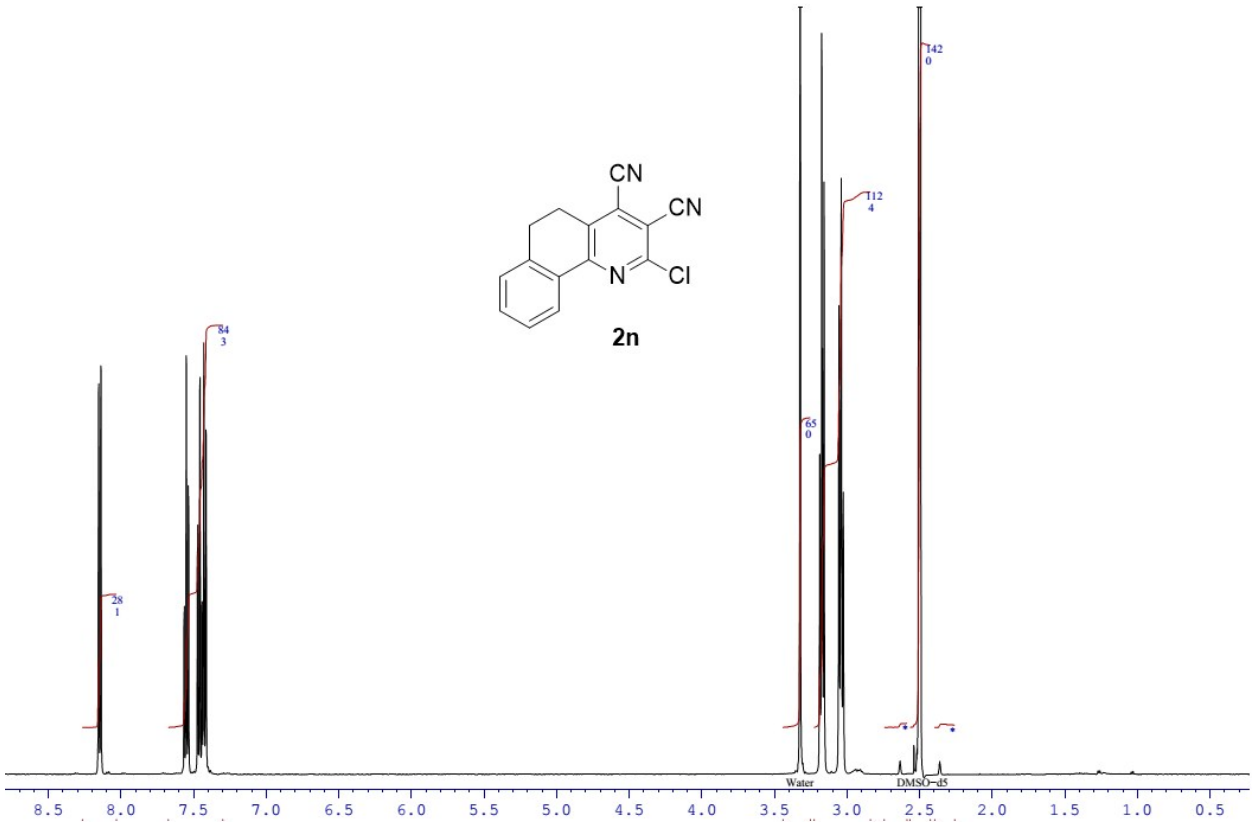

Fig. 17. ^{1}H NMR-spectrum of **2n** (500.13 MHz, DMSO−d_6)

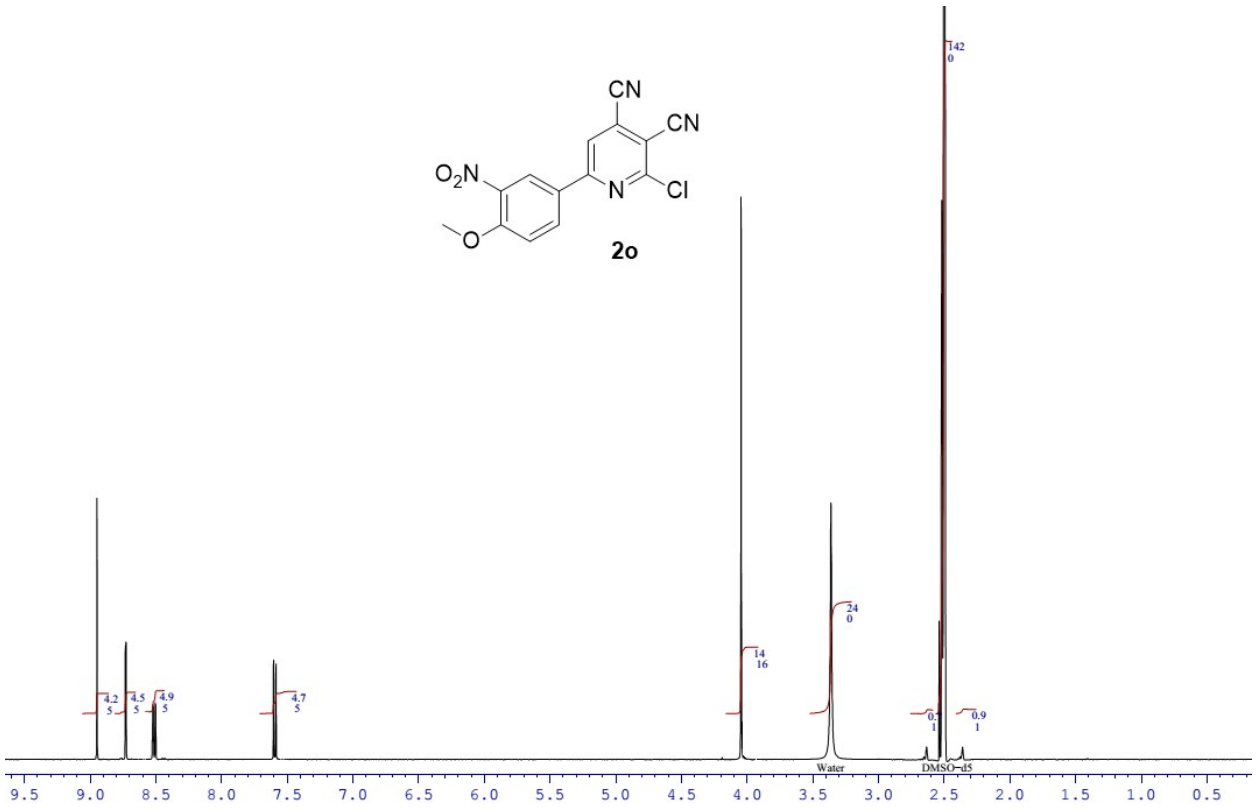

Fig. 18. ^{1}H NMR-spectrum of **2o** (500.13 MHz, DMSO−d_6)

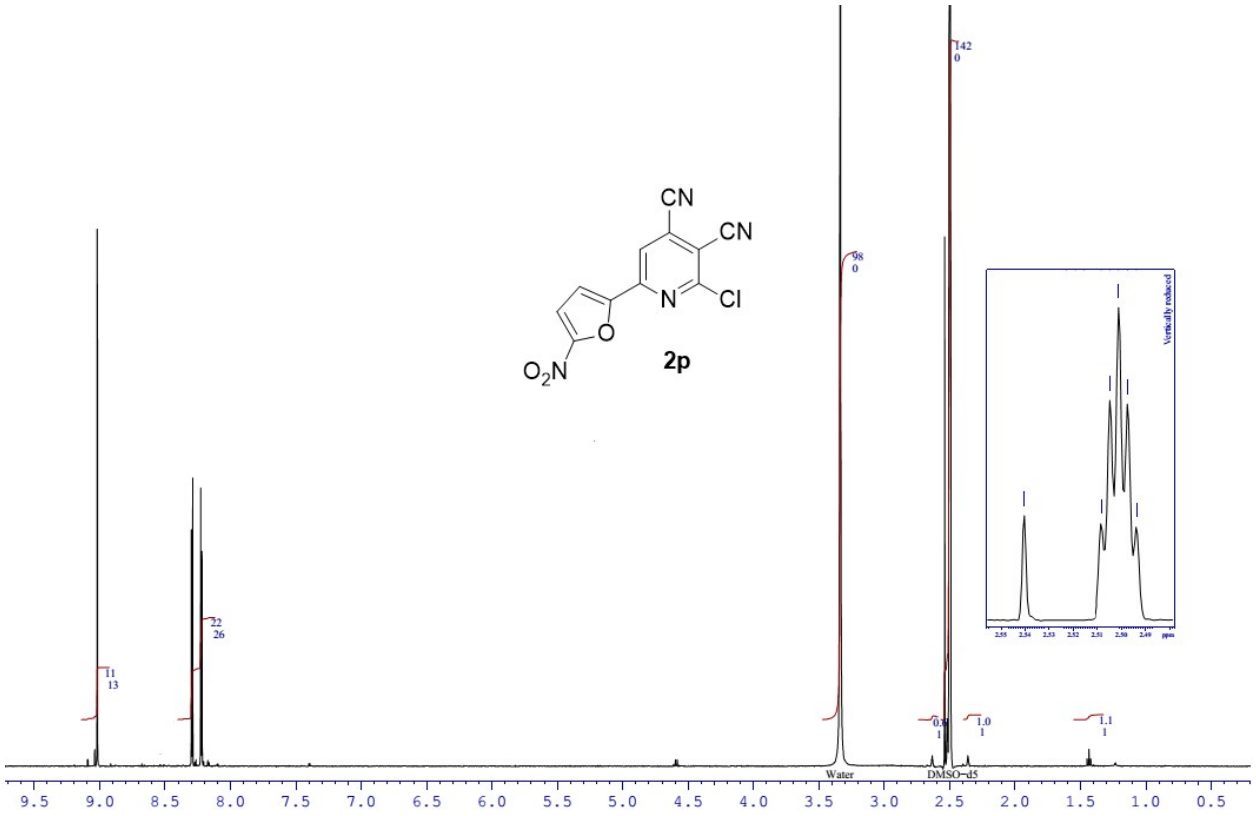

Fig. 19. ^{1}H NMR-spectrum of **2p** (500.13 MHz, DMSO−d_6)

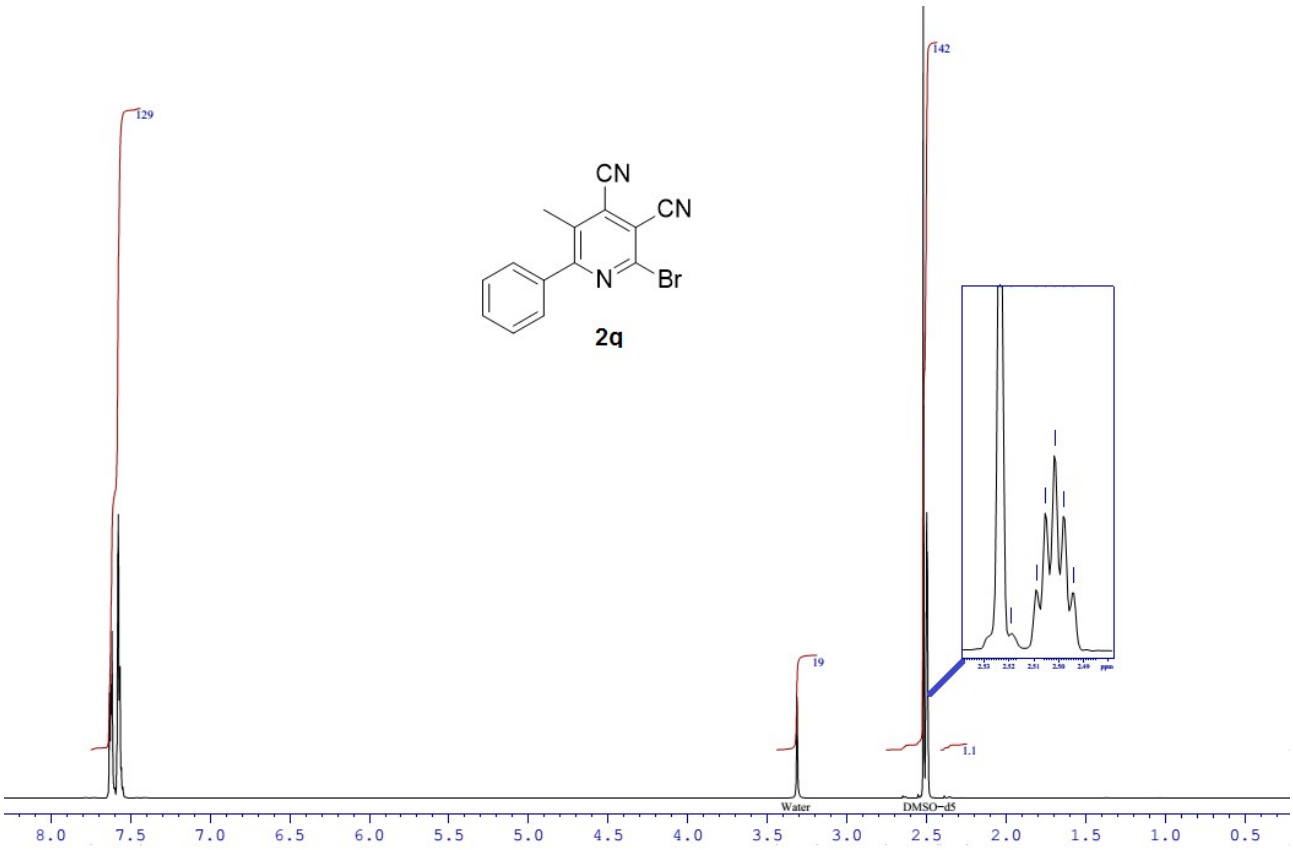

Fig. 20. ^{1}H NMR-spectrum of **2q** (500.13 MHz, DMSO−d_6)

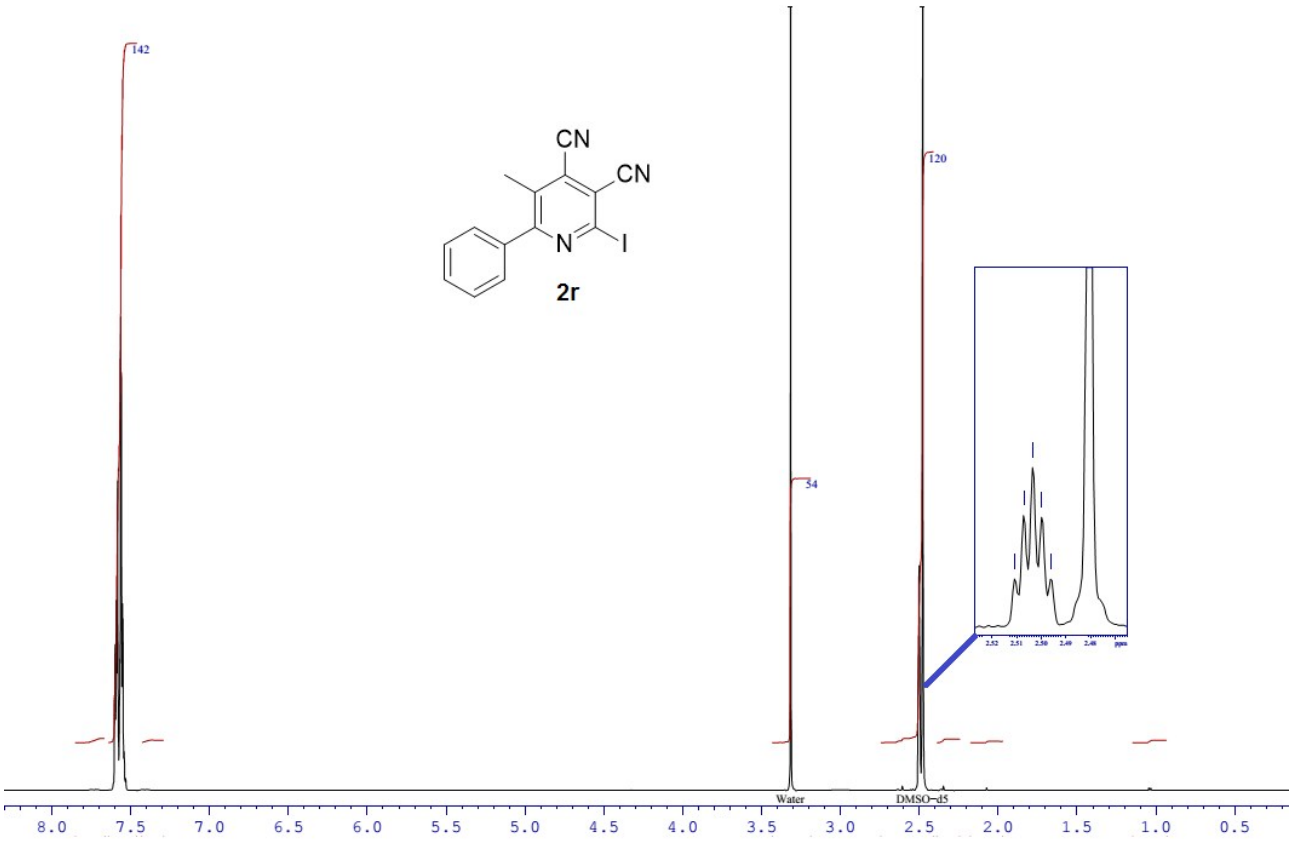

Fig. 21. ^{1}H NMR-spectrum of **2r** (500.13 MHz, DMSO−d_6)

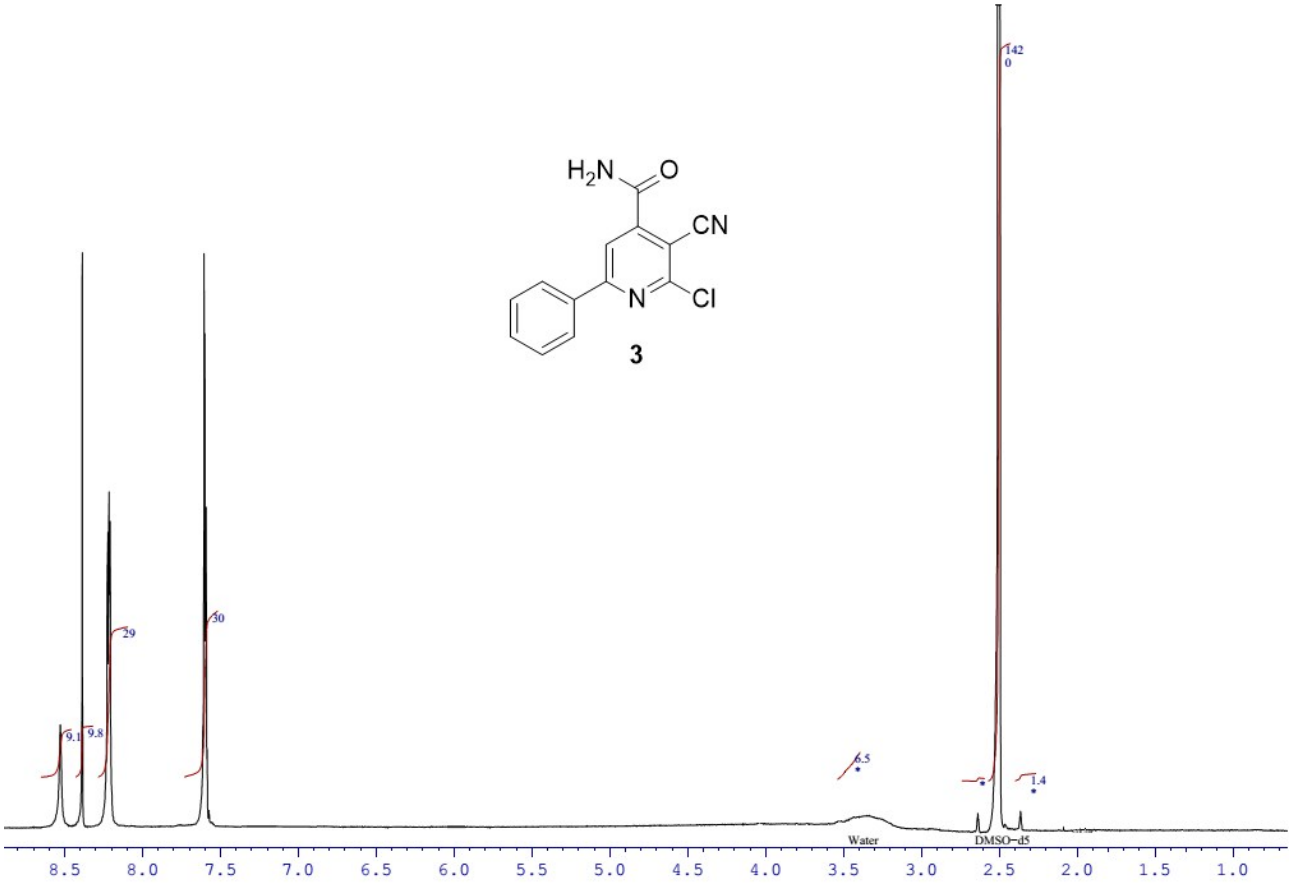

Fig. 21. 1H NMR-spectrum of **3** (500.13 MHz, DMSO−d_6)

4. References

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