

Synthesis of substituted 5-hydroxypyrazolo[1,5-*a*]quinoxalin-4-ones

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General

IR spectra were measured on a Perkin-Elmer RX-1 spectrometer in the range of 700–4000 cm^{-1} using suspensions of substances in Vaseline oil. Mass spectra were obtained using a FINNIGAN MAT INCOS 50 mass spectrometer; the ionization energy was 70 eV. Mass spectra were recorded on a Shimadzu 2020 LCMS HPLC / MS spectrometer equipped with a Synergi 2.5 μm Hydro-RP 100A HPLC Mercury Cartridge 20 x 2.0 mm chromatographic column, using acetonitrile/water as the eluent (variable composition in accordance with a gradient elution program), and a PDA photo-detector (200-800 nm) operating in negative electrospray ionization mode.

NMR spectra were recorded on a Bruker DRX-400 and DRX-300 instrument at 30 °C for solutions in DMSO- d_6 . Signals of residual protons of the solvent in ^1H NMR spectra (δ_{H} 2.50) or the signal of DMSO- d_6 in ^{13}C spectra (δ_{C} 39.5) were used as references for chemical shift measurements.

Elemental analysis was carried out on a Perkin Elmer 2400 instrument.

General Procedure for 3-arylpyrazole-5-carboxylates 3a-g

Pyrazole **1a-c** (0.012 mol), the corresponding chloronitrobenzene **2a-c** (0.012 mol) and powdered K₂CO₃ (0.50 mg, 0.036 mol) were successively mixed in DMF (3 ml). The reaction mixture was stirred at 50-80 °C for 3-6 h (TLC monitoring). After that, the mixture was cooled and water (5 ml) was added with stirring. The precipitate that formed was filtered off and recrystallized from ethanol.

Ethyl 1-(2-nitro-4-(trifluoromethyl)phenyl)-3-phenyl-1H-pyrazole-5-carboxylate 3a

Yield 410 mg 73 %, yellow powder, mp 122-123 °C. IR (v/cm⁻¹): 1715 (C=O), 1629 (Ar), 1545 (NO₂), 1323 (NO₂), 1244, 1124 (C-O), 1139 (C-F). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.20 (t, 3 H, Me, *J* 7.3 Hz), 4.22 (q, 2 H, CH₂, *J* 7.3 Hz), 7.41 (t, 1 H, H-4', *J* 7.4 Hz), 7.46 (t, 2 H, H-3', H-5', *J* 7.4 Hz), 7.76 (s, 1 H, H-4), 7.91 (d, 2 H, H-2', H-6', *J* 7.4 Hz), 8.13 (d, 1 H, H-6'', *J* 8.3 Hz), 8.42 (d, 1 H, H-5'', *J* 8.3, 1.8 Hz), 8.81 (d, 1 H, H-3'', *J* 1.8 Hz). ¹³C NMR (75 MHz, DMSO-*d*₆) δ: 13.68, 61.51, 109.93, 122.40 (q ³J_{C-F} 3.5 Hz), 125.58 (2 C), 127.58 (q ¹J_{C-F} 274 Hz), 128.89 (2 C) 128.93, 129.69 (q²J_{C-F} 33 Hz), 130.63 (q ³J_{C-F} = 3.5), 130.92, 131.64, 135.58, 136.15(br.s.), 145.22, 152.40, 158.02. MS, m/z (%): 405 [M]⁺ (26), 331 (51), 296 (31), 144 (20), 129 (71), 102 (53), 77 (100). Found (%):C, 56.13; H, 3.46; N, 10.33. Calc. for C₁₉H₁₄F₃N₃O₄ C, 56.30; H, 3.48; N, 10.37.

Ethyl 1-(4-cyano-2-nitrophenyl)-3-phenyl-1H-pyrazole-5-carboxylate 3b

Yield 360 mg 68 %, yellow powder, mp 126-127 °C. IR (v/cm⁻¹): 2237 (CN), 1720 (C=O), 1616, (Ar), 1537 (NO₂), 1354 (NO₂), 1228, 1078 (C-O). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.20 (t, 3 H, Me, *J* 7.1 Hz), 4.22 (q, 2 H, CH₂, *J* 7.1 Hz), 7.41 (t, 1 H, H-4', *J* 7.5 Hz), 7.46 (t, 2 H, H-3', 5', *J* 7.5 Hz), 7.76 (s, 1 H, H-4), 7.91 (d, 2 H, H-2', 6', *J* 7.5 Hz), 8.13 (d, 1 H, H-6'', *J* 8.3 Hz), 8.42 (dd, 1 H, H-5'', *J* 8.3/1.7 Hz), 8.81 (d, 1 H, H-3'', *J* 1.7 Hz). ¹³C NMR (75 MHz DMSO-*d*₆) δ: 13.80, 61.65, 110.19, 113.18, 116.47, 125.68 (2 C), 127.67, 128.97, 129.06 (2 C), 129.23, 130.93, 131.42, 135.65, 136.41, 145.06, 152.62, 158.07. MS, m/z (%): 362 [M]⁺ (57), 288 (100), 129 (65), 102 (46), 77 (75). Found (%):C, 62.72; H, 3.86; N, 15.4. Calc. for C₁₉H₁₄N₄O₄ C, 62.98; H, 3.89; N, 15.46.

Ethyl 1-(2,4-dinitrophenyl)-3-phenyl-1H-pyrazole-5-carboxylate 3c

Yield 381 mg 76 %, yellow powder, mp 144-146 °C. IR (v/cm⁻¹): 1716 (C=O), 1608 (Ar), 1531 (NO₂), 1344 (NO₂), 1240, 1105 (C-O). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.22 (t, 3 H, Me, *J* 7.1 Hz), 4.23 (q, 2 H, CH₂, *J* 7.1 Hz), 7.41 (t, 1 H, H-4', *J* 7.4 Hz), 7.47 (t, 2 H, H-3', H-5', *J* 7.4 Hz), 7.79 (s, 1 H, H-4), 7.92 (d, 2 H, H-2', H-6', *J* 7.4 Hz), 8.20 (d, 1 H, H-6'', *J* 8.8 Hz), 8.71 (dd, 1 H, H-5'', *J* 8.8/2.5 Hz), 8.93 (d, 1 H, H-3'', *J* 2.5 Hz). ¹³C NMR (75 MHz, DMSO-*d*₆) δ: 13.74, 61.63, 110.26, 120.56, 125.62 (2 C), 128.22, 128.90 (2 C), 129.02, 130.79, 131.68, 135.64, 137.40, 144.72, 147.18, 152.68, 158.02. MS, m/z (%): 382 [M]⁺ (82), 308 (100), 262 (29), 129 (42), 102 (24), 77 (26). Found (%):C, 56.24; H, 3.67; N, 14.61. Calc. for C₁₈H₁₄N₄O₆ C, 56.55; H, 3.69; N, 14.65.

Ethyl 3-(4-chlorophenyl)-1-(4-(trifluoromethyl)-2-nitrophenyl)-1H-pyrazole-5-carboxylate 3d

Yield 394 mg 75 %, yellow powder, mp 181-182 °C. IR (v/cm⁻¹): 1719 (C=O), 1629 (Ar), 1547, 1325 (NO₂), 1240, 1080 (C-O), 1123 (C-F). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.18 (t, 3 H, Me,

J 7.1 Hz), 4.22 (q, 2 H, CH₂, *J* 7.1 Hz), 7.53 (d, 2 H, H-3',5', *J* 8.8 Hz), 7.80 (s, 1 H, H-4), 7.94 (d, 2 H, H-2',6', *J* 8.8 Hz), 8.16 (d, 1 H, H-6'', *J* 8.3 Hz), 8.34 (d.d, 1 H, H-5'', *J* 8.3/2.2 Hz), 8.61 (d, 1H, H-3'' *J* 2.2).¹³C NMR (75 MHz, DMSO-*d*₆) δ 13.66, 61.55, 110.08, 122.46 (q ³*J*_{C-F} 3.5 Hz), 124.41 (q ¹*J*_{C-F} 274 Hz), 127.34 (2 C), 128.95 (2 C), 129.49 (q²*J*_{C-F} 33 Hz), 129.83, 130.69 (q ³*J*_{C-F} 3.5 Hz), 131.65, 133.54, 135.74, 136.06 (br.s.) 145.16, 151.30, 157.93. LCMS–ESI:m/z 440 [M+H]⁺. Found (%):C, 51.70; H, 2.96; N, 9.51.Calc. for C₁₉H₁₃ClF₃N₃O₄ C, 51.89; H, 2.98; N, 9.55.

Ethyl-3-(4-chlorophenyl)-1-(4-cyano-2-nitrophenyl)-1H-pyrazole-5-carboxylate 3e

Yield 394 mg 75 %, yellow powder, mp 185-188 °C. IR (v/cm⁻¹): 2239 (CN), 1701 (C=O), 1616, 1539 (Ar), 1225, 1043 (C-O).¹H NMR (400 MHz, DMSO-*d*₆) δ:1.20 (t, 3 H, Me, *J* 7.3 Hz), 4.22 (q, 2 H, CH₂, *J* 7.3 Hz), 7.52 (d, 2 H, H -3',5', *J* 8.8 Hz), 7.80 (s, 1 H, H-4), 7.92 (d, 2 H, H -2',6', *J* 8.80 Hz), 8.13 (d, 1 H, H-6'', *J* 8.3 Hz), 8.42 (dd, 1 H, H-5'', *J* 8.3, 1.7 Hz), 8.82 (d, 1 H, H-3'', *J* 1.7 Hz).¹³C NMR (75 MHz, DMSO-*d*₆) δ:13.80, 61.70, 110.34, 113.29, 116.45, 127.45 (2C), 129.04 (2 C), 129.26, 129.85, 131.44, 133.67, 135.82, 136.32, 137.68, 145.01, 151.52, 157.99. MS, m/z (%): 398 [M]⁺ (19), 396 [M] (53), 324 [M-COOEt]⁺ (37), 322 [M-COOEt]⁺ (100), 163 (17). Found (%):C, 57.29; H, 3.28; N, 14.07.Calc. for C₁₉H₁₃ClN₄O₄ C, 57.51; H, 3.30; Cl, 8.94; N, 14.12.

Ethyl 3-(4-chlorophenyl)-1-(2,4-dinitrophenyl)-1H-pyrazole-5-carboxylate 3f

Yield 349 mg 70 %, yellow powder, mp 169-171 °C. IR (v/cm⁻¹): 1717 (C=O), 1609, (Ar), 1531 (NO₂), 1344 (NO₂), 1240, 1105 (C-O).¹H NMR (400 MHz, DMSO-*d*₆) δ: 1.21 (t, 3 H, Me, *J* 7.1 Hz), 4.23 (q, 2 H, CH₂, *J* 7.1 Hz), 7.53 (d, 2 H, H-3',5', *J* 8.8 Hz), 7.83 (s, 1 H, H-4), 7.95 (d, 2 H, H-2',6', *J* 8.8 Hz), 8.21 (d, 1 H, H-6'' *J* 8.8 Hz), 8.71 (dd, 1 H, H-5'' *J* 8.80/2.4 Hz), 8.93 (d, 1 H, H-3'' *J* 2.4 Hz).¹³C NMR (75 MHz, DMSO-*d*₆) δ:13.82, 61.76, 110.49, 120.66, 127.47 (2 C), 128.36, 129.05(2 C), 129.79, 131.80, 133.73, 135.88, 137.38, 144.77, 147.34, 151.67, 158.03. MS, m/z (%): 418 [M]⁺ (36), 416 [M]⁺ (100), 344 [M-COOEt]⁺ (34), 342 [M-COOEt]⁺ (96), 296 (31), 205 (12), 190 (11), 176 (15), 163 (58), 136 (29), 111 (26), 75 (57). Found (%):C, 51.71; H, 3.11; N, 13.40.Calc. for C₁₈H₁₃ClN₄O₆ C, 51.87; H, 3.14; N, 13.44.

Ethyl 1-(4-cyano-2-nitrophenyl)-3-(4-methylphenyl)-1H-pyrazole-5-carboxylate 3g

Yield 387 mg 79 %) yellow powder, mp 158-161 °C. IR (v/cm⁻¹): 1717 (C=O), 1609, (Ar), 1531 (NO₂), 1344 (NO₂), 1240, 1105 (C-O).¹H NMR (400 MHz DMSO-*d*₆) δ:1.20 (t, 3 H, Me, *J* 7.1 Hz), 2.34 (s, 3 H, 4'-Me), 4.22 (q, 2 H, CH₂, *J* 7.1 Hz), 7.27 (d, 2 H, H-3',5', *J* 8.0 Hz), 7.70 (s, 1 H, H-4), 7.79 (d, 2 H, H-2',6' *J* 8.0 Hz), 8.11 (d, 1 H, H-6'', *J* 8.3 Hz), 8.40 (d.d, 1 H, H-5'', *J* 8.3/1.0 Hz), 8.80 (d, 1 H, H-3'', *J* 1.0 Hz).¹³C NMR (75 MHz, DMSO-*d*₆) δ:13.81, 20.91, 61.61, 110.03, 113.09, 116.48, 125.62 (2 C), 128.18, 129.21, 129.52 (2 C), 131.41, 135.54, 136.44, 137.57, 138.57, 145.05, 152.68, 158.09. LCMS–ESI:m/z 377 [M+H]⁺. Found (%): C, 63.53; H, 4.25; N, 14.82. Calc. for C₂₀H₁₆N₄O₄ C, 63.82; H, 4.28; N, 14.89.

General procedure for 5-hydroxypyrazolo[1,5-*a*]quinoxalin-4-ones **4a-g**

Compound **3a-g** (0.01 mol) was added to a solution of SnCl₂ (3.5 mmol) (for **3c,f** -7.0 mmol) in conc. HCl (2 ml) and EtOH (2 ml), and the mixture was stirred at 50 °C for 3–4 h. The precipitate formed upon cooling of the solution was filtered and recrystallized from EtOH.

*5-Hydroxy-2-phenyl-7-(trifluoromethyl)pyrazolo[1,5-*a*]quinoxalin-4(5H)-one* **4a**

Yield 229 mg 66 %, white powder, mp 284-285 °C (with decomposition). IR (v/cm⁻¹): 3200 (OH), 1659 (C=O), 1614, 1595 (Ar), 1130. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 7.45 (t, 1 H, H-4', *J* 7.6 Hz), 7.52 (t, 2 H, H-3',5', *J* 7.6 Hz), 7.78 (dd, 1 H, H-8, *J* 8.3/1.5 Hz), 7.85 (s, 1 H, H-4), 7.93 (br.s, 1 H, H-6), 8.11 (d, Hz, 2 H, H-2',6', *J* 7.6 Hz), 8.44 (d, 1 H, H-9, *J* 8.3 Hz), 11.91 (s, 1 H, OH). ¹³C NMR (75 MHz, DMSO-*d*₆) δ: 104.82, 110.71 (q, ³*J*=3.9), 116.05, 120.53 (q, ³*J*=3.9), 122.00 (q, ¹*J*=273.0), 125.54, 126.07 (2 C), 126.67 (q²*J*_{C-F} 33 Hz), 128.91 (2 C), 129.16, 129.61, 131.17, 134.64, 150.57, 153.47. MS, m/z (%): 345 [M]⁺ (84), 328 [M-17]⁺ (52), 300 (42), 183 (17), 170 (15), 103 (13), 77 (100). Found (%): C, 58.98; H, 2.90; N, 12.13. Calc. for C₁₇H₁₀F₃N₃O₂ C, 59.14; H, 2.92; N, 12.17.

*5-Hydroxy-4-oxo-2-phenyl-4,5-dihydropyrazolo[1,5-*a*]quinoxaline-7-carbonitrile* **4b**

Yield 196 mg 65 %, white powder, mp 275-277 °C. IR (v/cm⁻¹): 3140 (OH), 2230 (CN), 1668 (C=O), 1612 (Ar). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 7.45 (t, 1 H, H-4', *J* 7.5 Hz), 7.52 (t, 2 H, H-3',5', *J* 7.5 Hz), 7.85 (s, 1H, H-4), 7.86 (dd, 1 H, H-8, *J* 8.5/1.7 Hz), 8.09 (br.s, 1H, H-6), 8.10 (d, 2 H, H-2',6', *J* 7.5 Hz), 8.38 (d, 1 H, H-9, *J* 8.5 Hz), 11.89 (s, 1 H, OH). ¹³C NMR (75 MHz, DMSO-*d*₆) δ: 106.11, 108.97, 116.04, 117.66, 118.20, 125.90, 126.14 (2C), 127.68, 128.96, 129.30(2C), 129.74, 131.08, 134.76, 150.49, 153.77. MS, m/z (%): 302 [M]⁺ (100), 285 (47), 257 (39), 77 (59). Found (%): C, 67.28; H, 3.29; N, 18.45. Calc. for C₁₇H₁₀N₄O₂ C, 67.55; H, 3.33; N, 18.53.

*7-Amino-5-hydroxy-2-phenylpyrazolo[1,5-*a*]quinoxalin-4(5H)-one* **4c**

Yield 178 mg 61 %, white powder, mp 273-275 °C. IR (v/cm⁻¹): 2605 (OH+NH), 1647 (C=O), 1606 (Ar). ¹H NMR (500 MHz, DMSO-*d*₆) δ: 6.88 (d.d, 1 H, H-8, *J* 8.8/1.0 Hz), 7.18 (d, 1 H, H-6, *J* 1.0 Hz) 7.38 (t, 1 H, H-4', *J* 7.8 Hz), 7.47 - 7.50 (t, 2 H, H-3',5', *J* 7.8 Hz), 7.63 (s, 1 H, H-3), 8.03 (d, 2 H, H-2',6', *J* 7.8 Hz), 8.07 (d, 1 H, *J* 8.8 Hz), (NH₂+ OH -in exchange). ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 103.88, 106.00, 116.22, 116.70, 120.31, 125.96 (2 C), 128.91, 128.93 (2 C), 130.17, 131.55, 133.61, 135.28, 150.80, 152.46. MS, m/z (%): 293 [M]⁺ (18), 292 [M]⁺ (100), 276 (29), 275 [M-17]⁺ (57), 247 (58), 172 (26), 117 (24), 105 (25), 90 (20), 77 (89). LCMS-ESI: m/z 291 [M-H]⁻. Found (%): C, 65.61; H, 4.11; N, 19.12. Calc. for C₁₆H₁₂N₄O₂ C, 65.75; H, 4.14; N, 19.17.

2-(4-Chlorophenyl)-5-hydroxy-7-(trifluoromethyl)pyrazolo[1,5-a]quinoxalin-4(5H)-one **4d**

Yield 225 mg (59%), white powder, mp 292-294 °C. IR (ν/cm^{-1}): 3161 (OH), 1653 (C=O), 1623, 1606 (Ar), 1128 (C-F). ^1H NMR (400 MHz, DMSO- d_6) δ : 7.54 (d, 2 H, H-3',5', J 8.5 Hz), 7.75 (d,d, 1 H, H-8, J 8.8/1.1 Hz), 7.83 (s, 1 H, H-3), 7.89 (d, 1 H, H-6, J 1.1 Hz), 8.08 (d, 2 H, H-2',6', J 8.5 Hz), 8.38 (d, 1 H, H-9, J 8.8 Hz), 11.92 (s, 1 H, OH). ^{13}C NMR (75 MHz, DMSO- d_6) δ : 104.98, 110.74 (q $^3J_{\text{C-F}}$ 3.5 Hz), 116.10, 120.55, 121.98 (q $^3J_{\text{C-F}}$ 3.5 Hz), 125.46, 126.79 (q $^2J_{\text{C-F}}$ 33 Hz), 127.77 (2 C), 128.97 (2 C), 129.67 (q $^1J_{\text{C-F}}$ 274 Hz), 130.07, 133.79, 134.77, 150.53, 152.26. MS, m/z (%): 381 [M] $^+$ (31), 379 [M] $^+$ (100), 364 [M-17] $^+$ (22), 362 [M-17] $^+$ (39), 334 (35), 138 (21), 111 (57), 75 (63). Found (%) C, 53.61; H, 2.37; N, 11.04. Calc. for $\text{C}_{17}\text{H}_9\text{ClF}_3\text{N}_3\text{O}_2$, C, 53.77; H, 2.39; N, 11.07.

2-(4-Chlorophenyl)-5-hydroxy-4-oxo-4,5-dihydropyrazolo[1,5-a] quinoxaline-7-carbonitrile **4e**

Yield 185 mg (55%), white powder, mp 298-300 °C (with decomposition). IR (ν/cm^{-1}): 3078 (OH), 2230 (CN), 1668 (C=O), 1612, 1601(Ar), 1130. ^1H NMR (400 MHz, DMSO- d_6) δ : 7.55 (d, 2 H, H-3',5', J 8.5 Hz), 7.83 (d,d, 1 H, H-8, J 8.5/1.2 Hz), 8.84 (s, 1 H, H-3), 8.06(d, 1H, H-6, J 1.2 Hz), 8.08 (d, 2 H, H-2',6', J 8.5 Hz), 8.33 (d, 1 H, H-9, J 8.5 Hz), 11.90 (br. s., 1 H). ^{13}C NMR (75 MHz (DMSO- d_6) δ : 105.20, 109.09, 116.05, 117.69, 118.15, 125.77, 127.64, 127.80 (2 C), 128.99 (2 C), 129.77, 129.96, 133.90, 134.85, 150.40, 152.56. MS, m/z (%): 338 [M] $^+$ (36), 336 [M] $^+$ (100), 319 [M-17] $^+$ (45), 291 (40), 127 (15), 115 (21), 111 (36), 75 (30). Found (%): C, 60.41; H, 2.66; N, 16.59. Calc. for $\text{C}_{17}\text{H}_9\text{ClN}_4\text{O}_2$ C, 60.64; H, 2.69; N, 16.64.

7-Amino-2-(4-chlorophenyl)-5-hydroxypyrazolo[1,5-a]quinoxalin-4(5H)-one **4f**

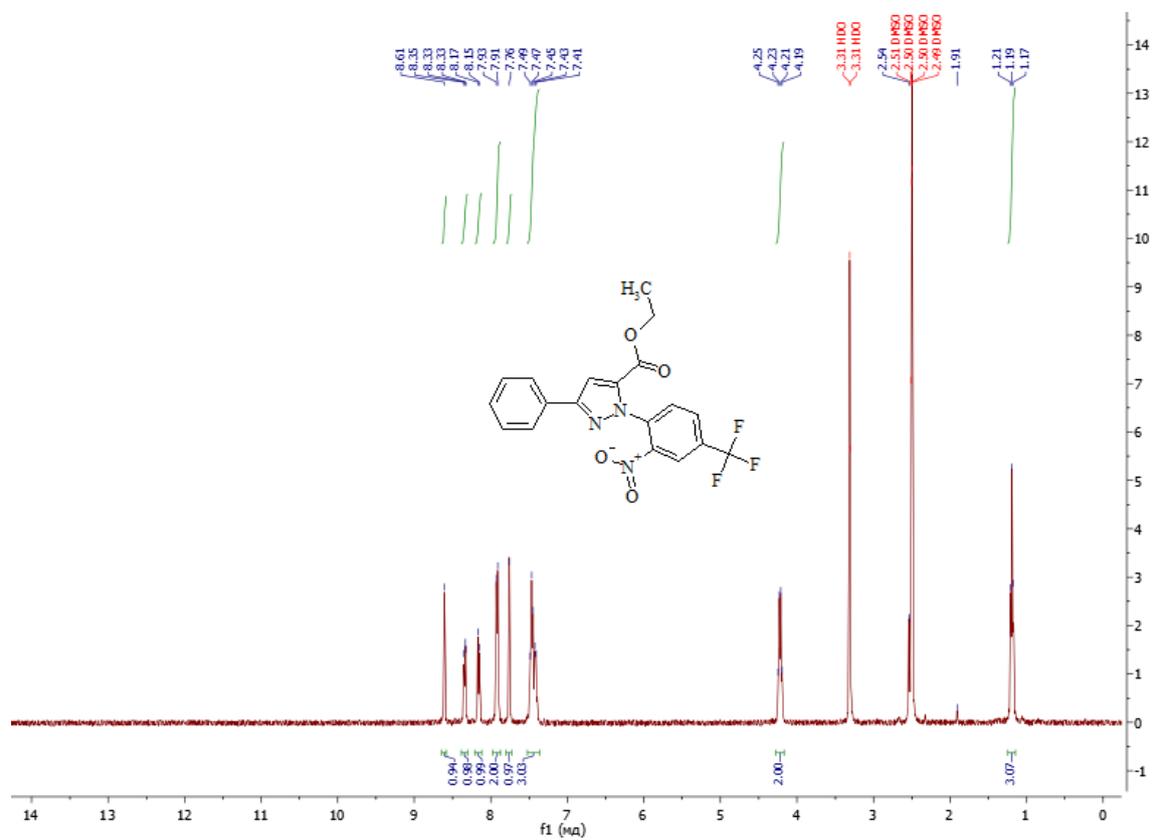
Yield 218 mg (67%), yellow powder, mp 289-290 °C. IR (ν/cm^{-1}): 2679, 2558 (NH+OH), 1663, 1653 (C=O), 1614, 1595(Ar), ^1H NMR (400 MHz, DMSO- d_6) δ : 7.14 (dd, 1H, H-8, J 8.8/2.3 Hz), 7.46 (br.s., 1H, H-6, J 2.3 Hz), 7.55 (d, 2H, H-3',5', J 8.8 Hz), 7.75 (s, 1H, H-3), 8.08 (d, 2H, H-2'6', J 8.8Hz), 8.19 (d, J 8.8 Hz, 1H, 9-H), (NH $_2$ + OH -in exchange). ^{13}C NMR (75 MHz, DMSO- d_6) δ : 103.89 (C-3), 104.21 (C-4), 115.50 (C-8), 116.23 (C-9), 119.00 (9a), 127.65 (C-3',5'), 129.00 (C-2',6'), 130.33 (C-5a), 130.61 (C-3a), 133.41 (1'), 133.50 (C-4'), 138.00 (C-7), 150.76 (C-2), 151.06 (C-4). MS, m/z (%): 328 [M] $^+$ (36), 326 (100), 311 [M-17] $^+$ (21), 309 [M-17] $^+$ (45), 283 (17), 281 (38), 283 (17), 183 (24), 172 (23), 170 (22), 117 (34), 111 (65), 105 (38), 75 (42). Found (%): C, 58.59; H, 3.36; N, 17.09. Calc. for $\text{C}_{16}\text{H}_{11}\text{ClN}_4\text{O}_2$ C, 58.82; H, 3.39; N, 17.15.

5-Hydroxy-2-(4-methylphenyl)-4-oxo-4,5-dihydropyrazolo[1,5-a]quinoxaline-7-carbonitrile **4g**

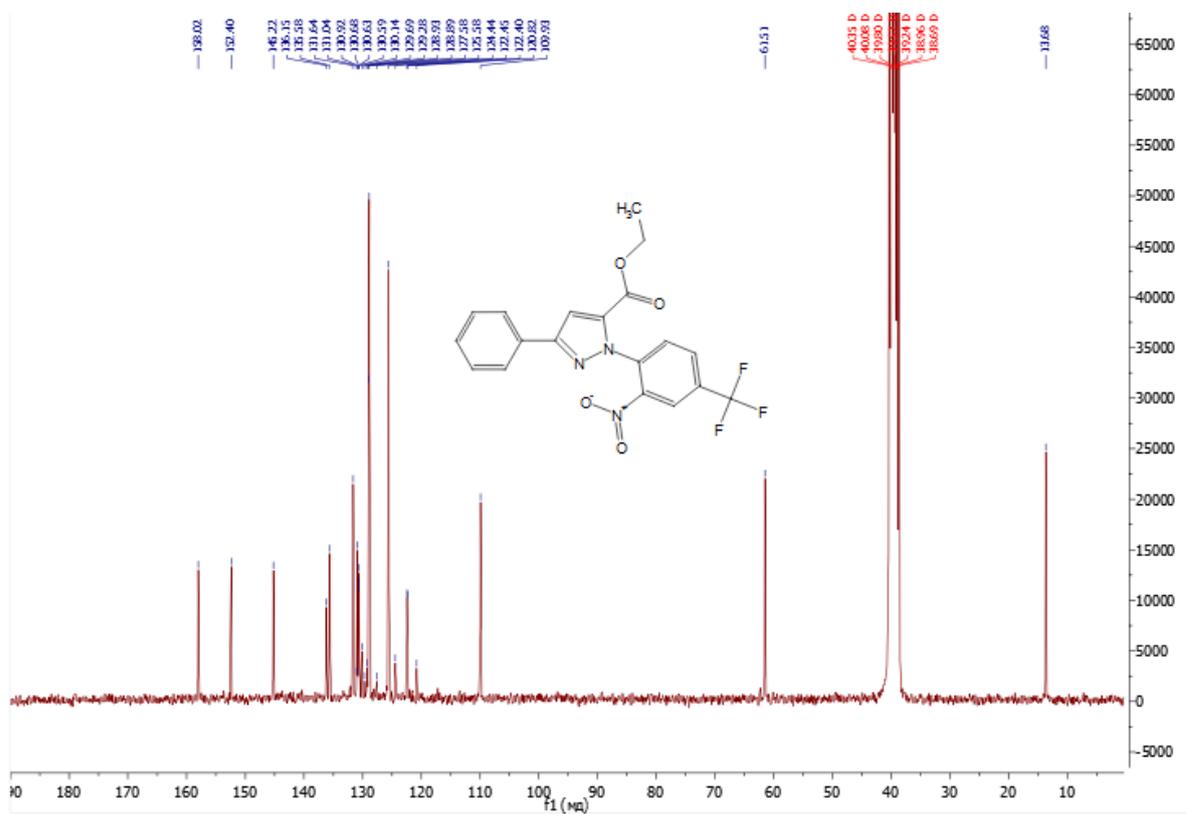
Yield 178 mg (56%), white powder, mp 330-333 °C (decomp.). IR (ν/cm^{-1}): 3140 (OH), 2228 (CN), 1668 (C=O), 1612 (Ar). ^1H NMR (400 MHz, DMSO- d_6) δ : 2.36 (s, 3 H, Me), 7.30 (d, 2 H, H-3',5', J 8.0 Hz), 7.77 (s, 1 H, H-3), 7.83 (br.d, 1 H, H-8, J 8.3 Hz), 7.96 (d, 2 H, H-2',6', J 8.0 Hz), 8.06 (br.s, 1 H, H-6), 8.34 (d, 1 H, H-9, J 8.3 Hz), 11.87 (br. s., 1 H, OH). ^{13}C NMR (126

MHz DMSO-*d*₆) δ : 20.84, 104.71, 108.75, 115.90, 117.52, 118.13, 125.93 (2 C), 126.17, 127.57, 128.18, 129.40 (2 C), 129.53, 134.53, 138.79, 150.37, 153.75. MS, *m/z* (%): 316 [M]⁺ (12), 315 (52), 300 (77), 285 (66), 256 (26), 225 (18), 155 (16), 128 (25), 116 (26), 115 (24), 91 (44). LCMS–ESI:*m/z* 315 [M–H][–]. Found (%): C, 68.07; H, 3.78; N, 17.65. Calc. for C₁₈H₁₂N₄O₂ C, 68.35; H, 3.82; N, 17.71.

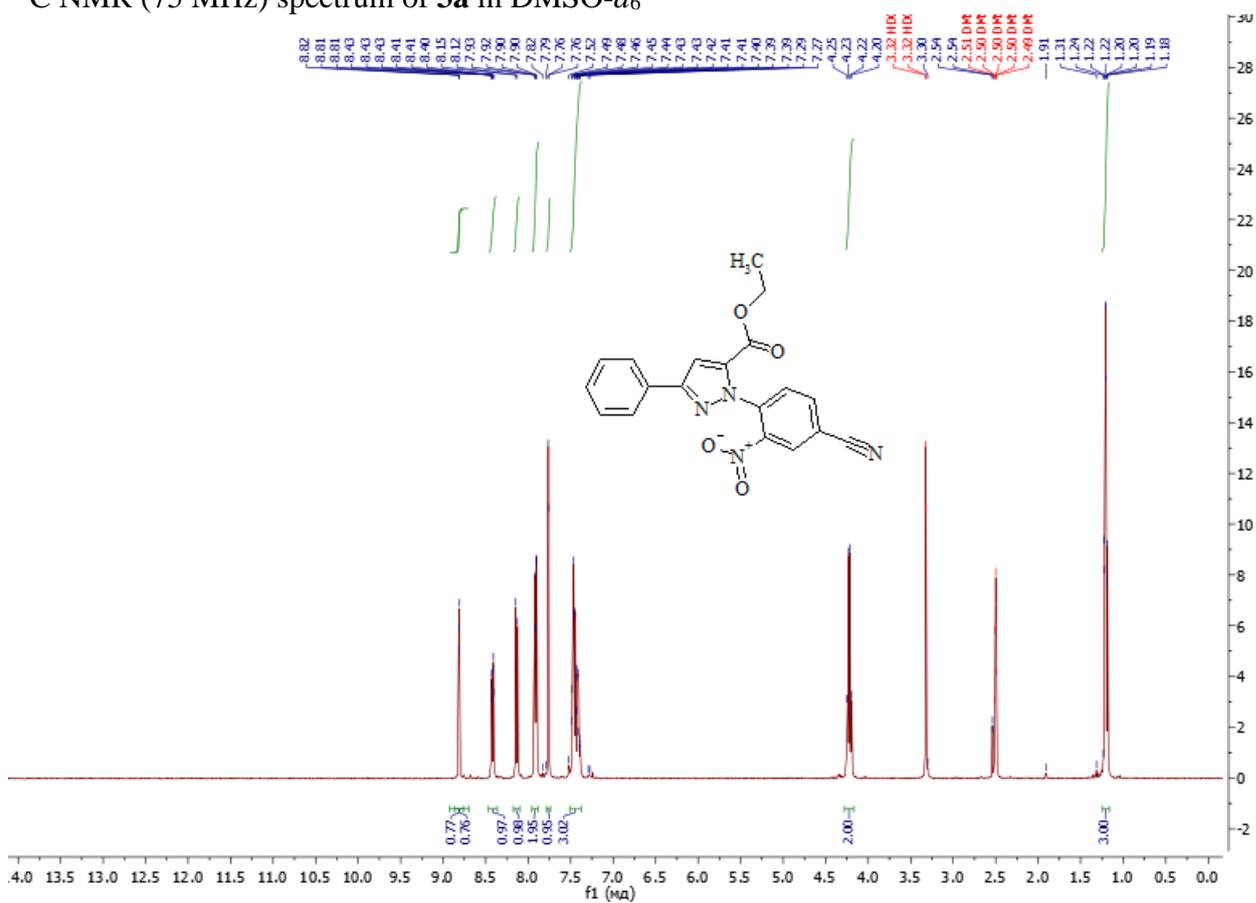
NMR spectra of 3-arylpyrazole-5-carboxylates **3a-g**



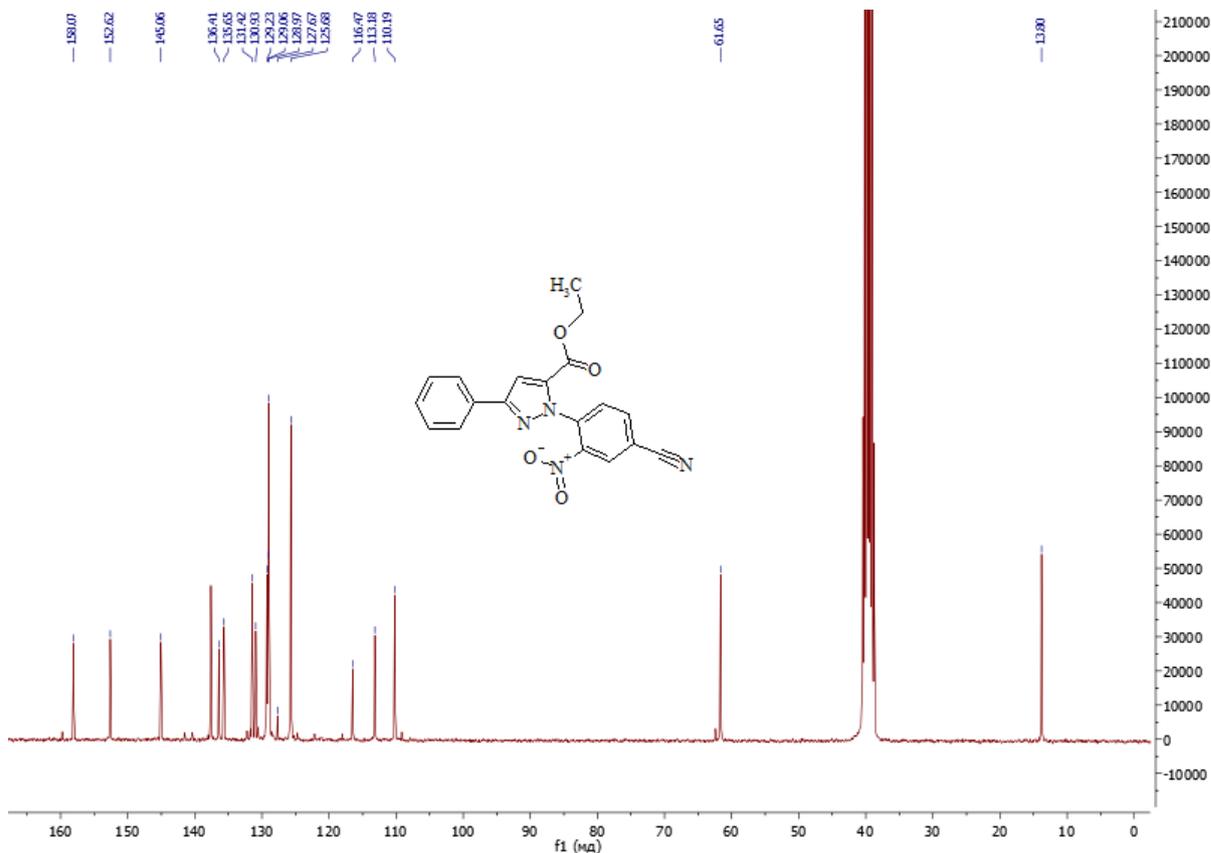
¹H NMR (400 MHz) spectrum of **3a** in DMSO-*d*₆



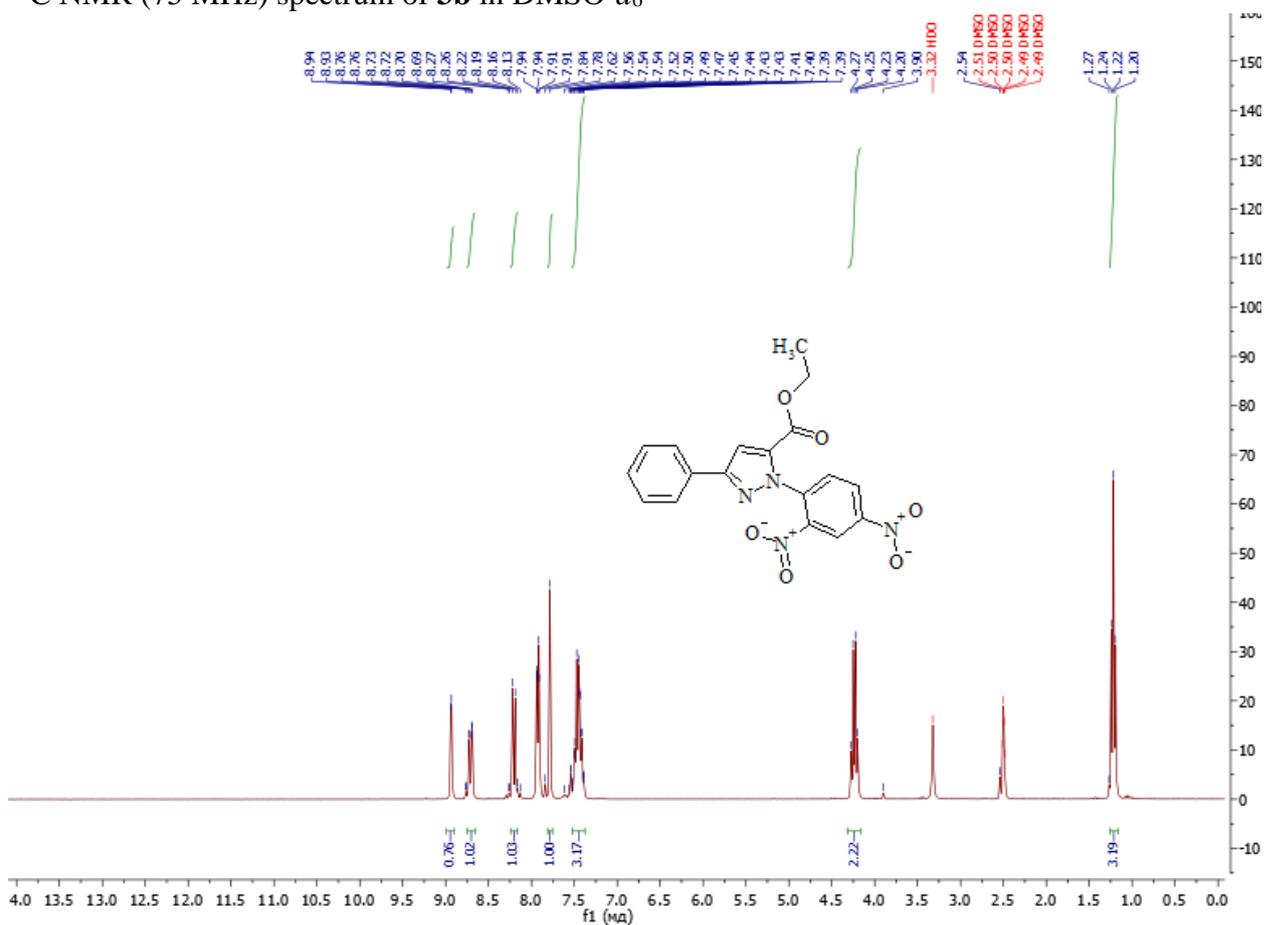
¹³C NMR (75 MHz) spectrum of **3a** in DMSO-*d*₆



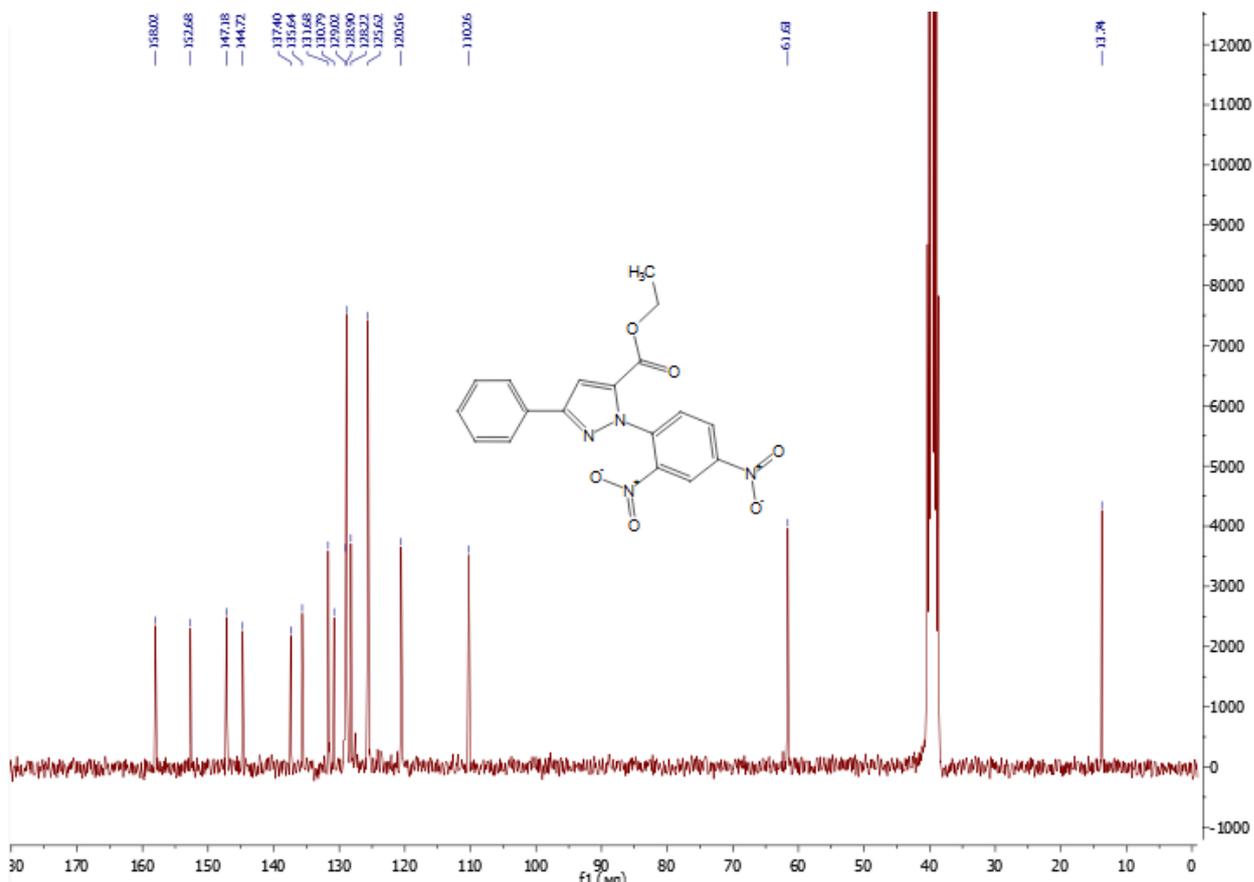
¹H NMR (400 MHz) spectrum of **3b** in DMSO-*d*₆



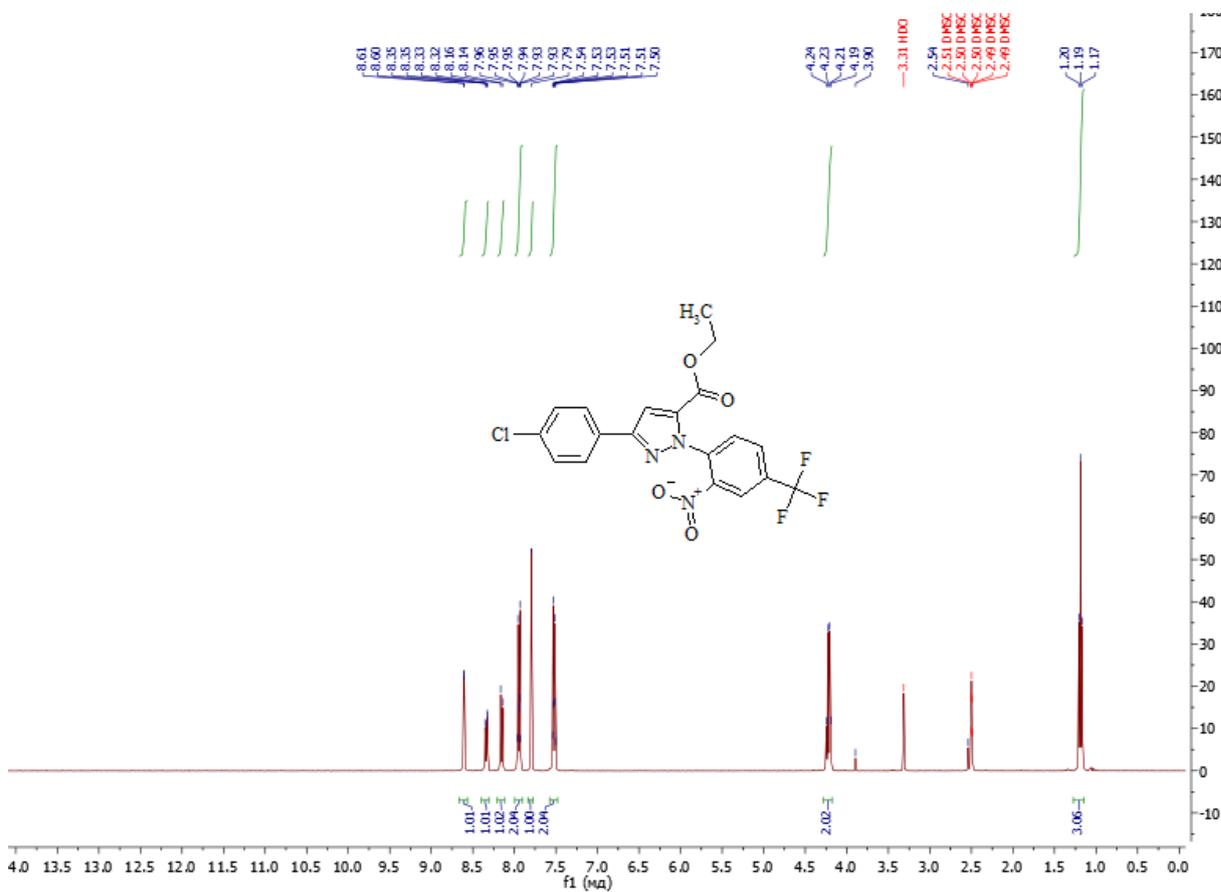
¹³C NMR (75 MHz) spectrum of **3b** in DMSO-*d*₆



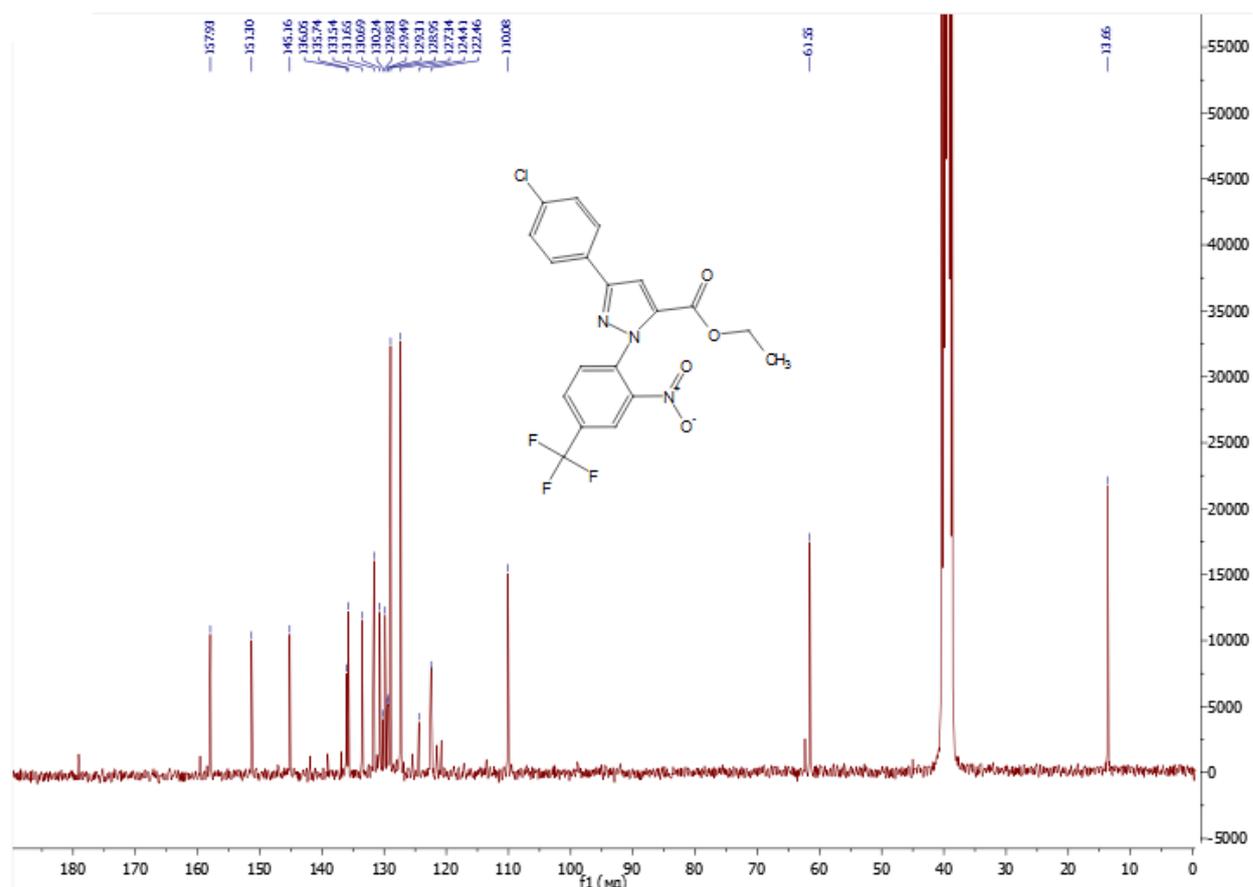
¹H NMR (400 MHz) spectrum of **3c** in DMSO-*d*₆



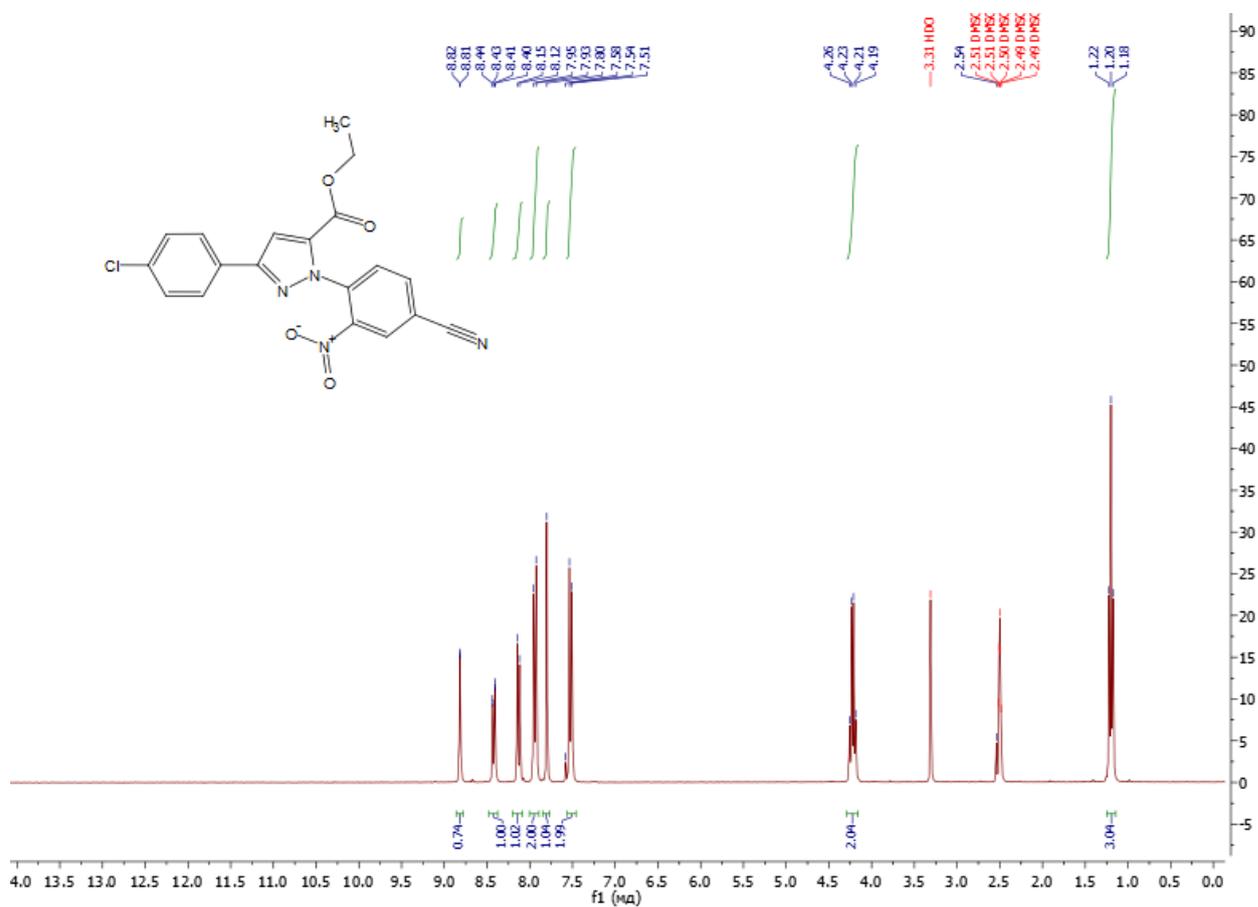
¹³C NMR (75 MHz) spectrum of **3c** in DMSO-*d*₆



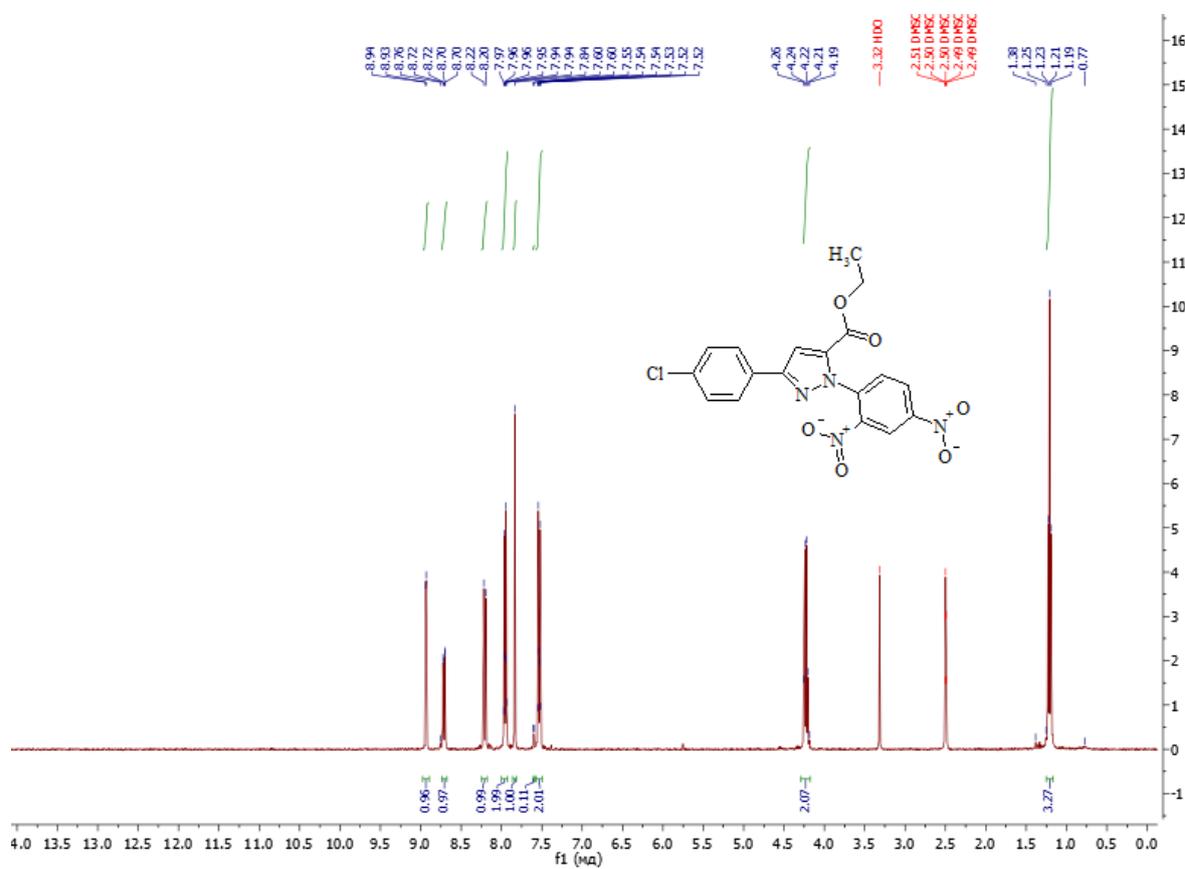
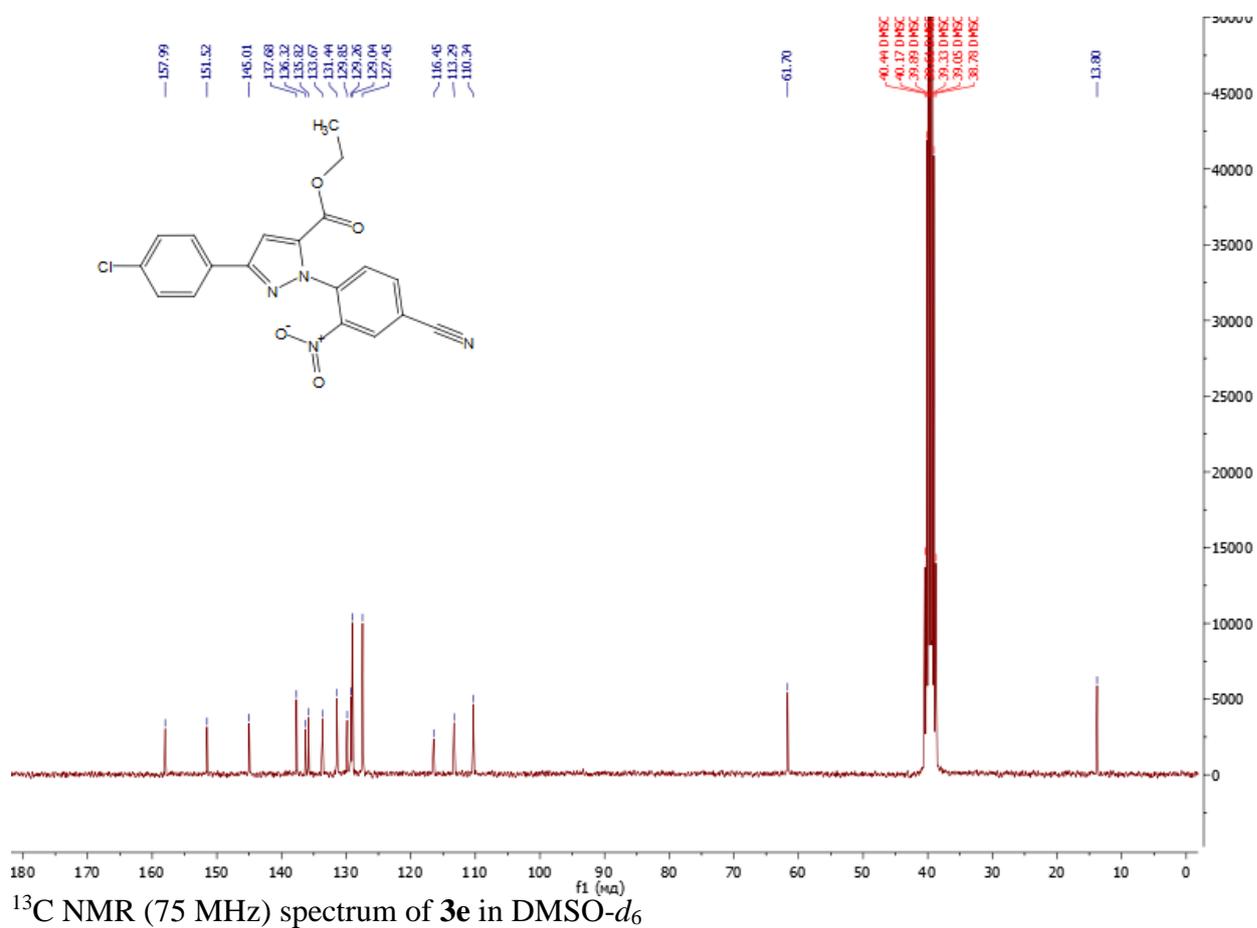
¹H NMR (400 MHz) spectrum of **3d** in DMSO-*d*₆

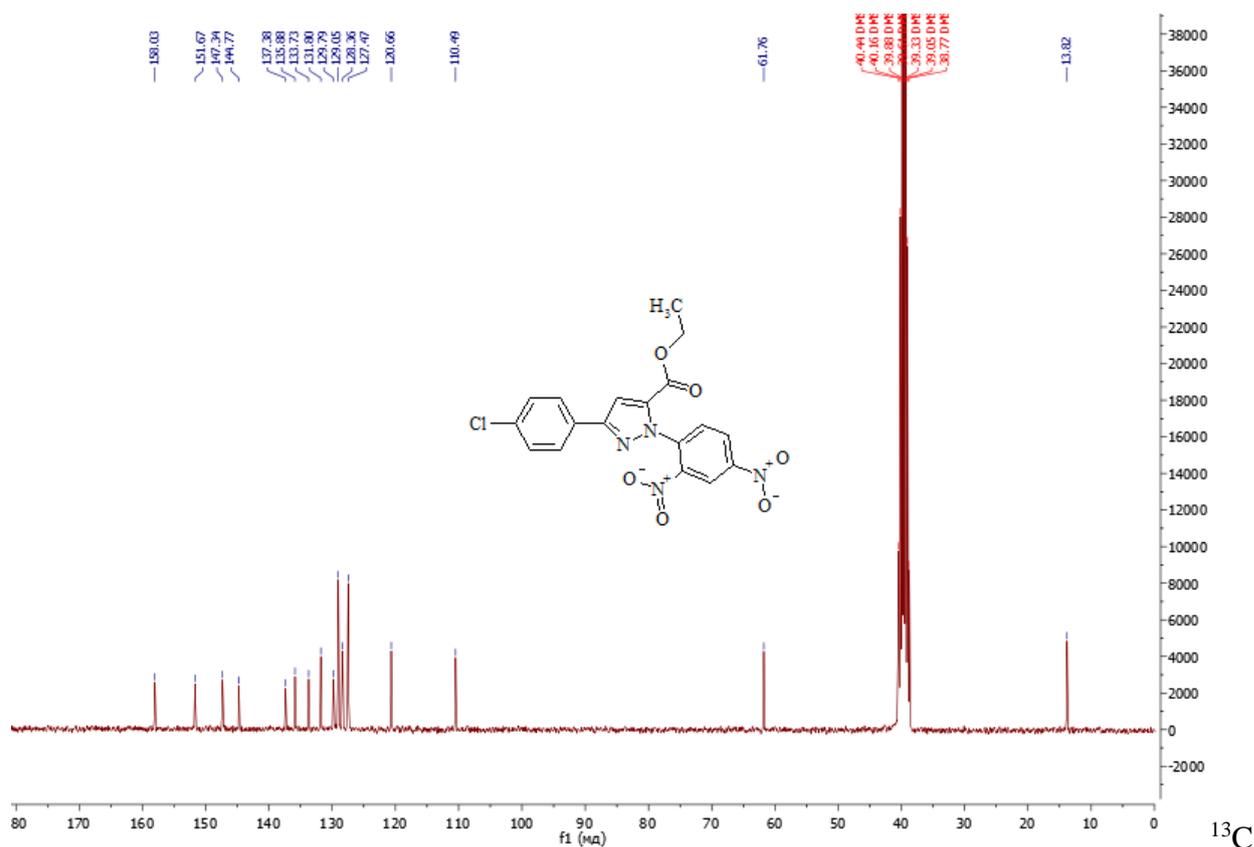


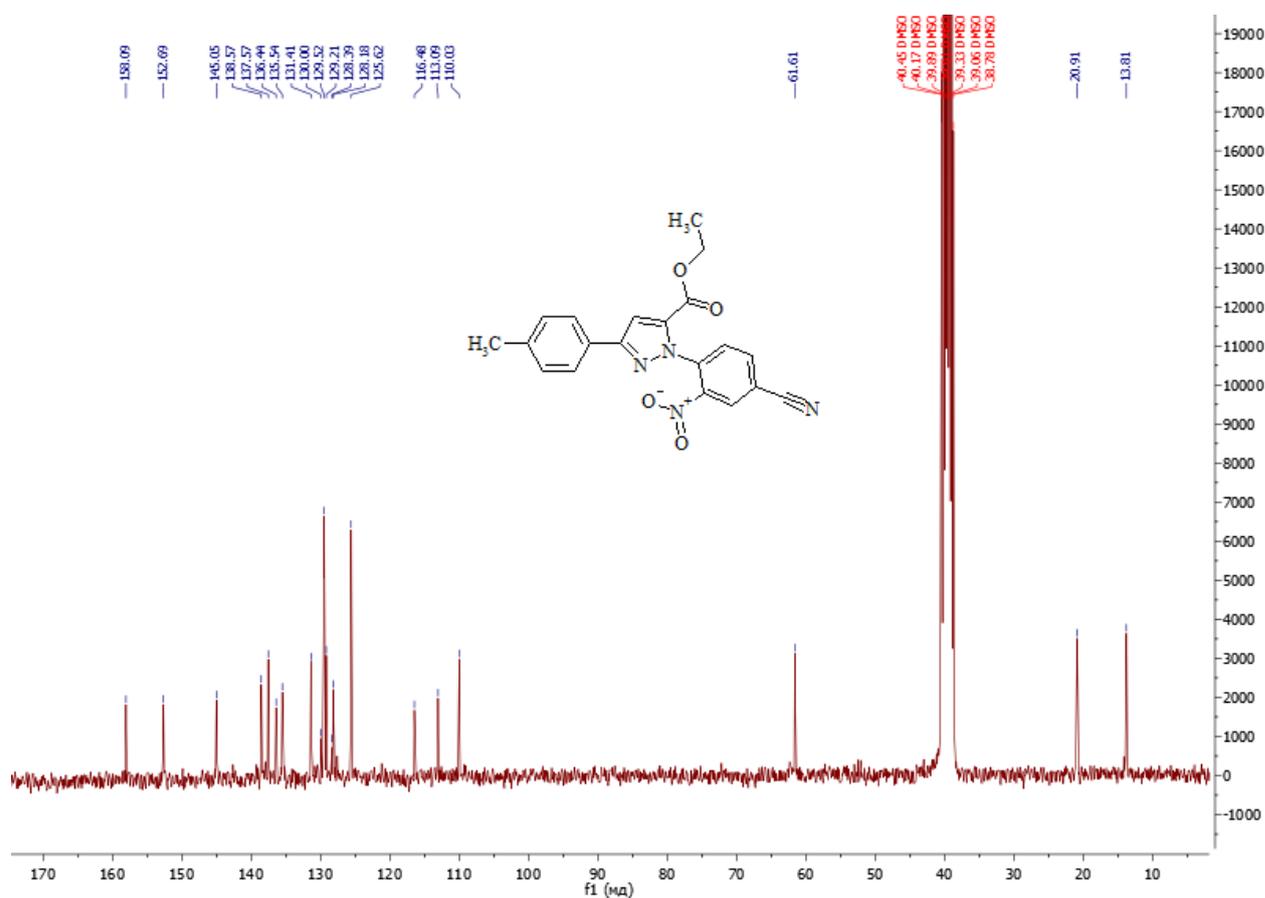
¹³C NMR (75 MHz) spectrum of **3d** in DMSO-*d*₆



¹H NMR (400 MHz) spectrum of **3e** in DMSO-*d*₆

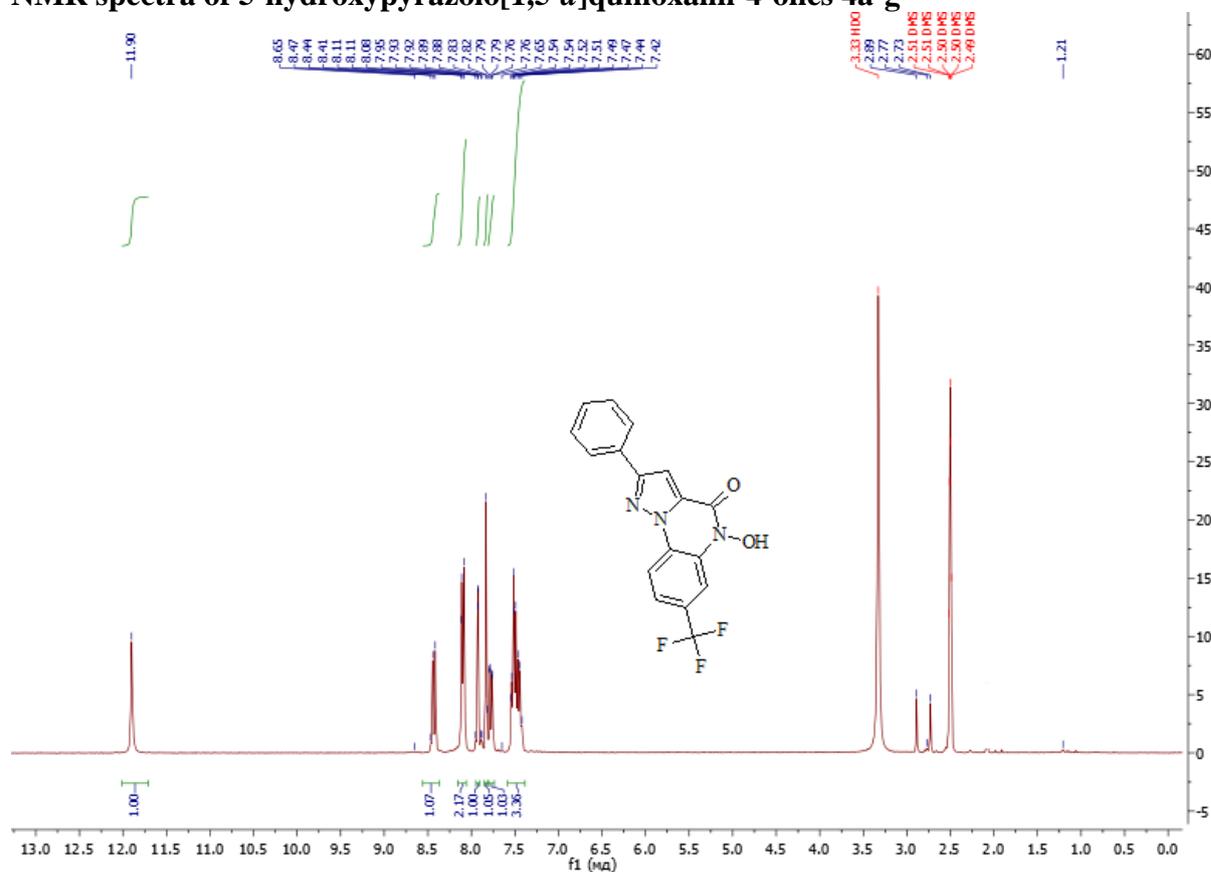




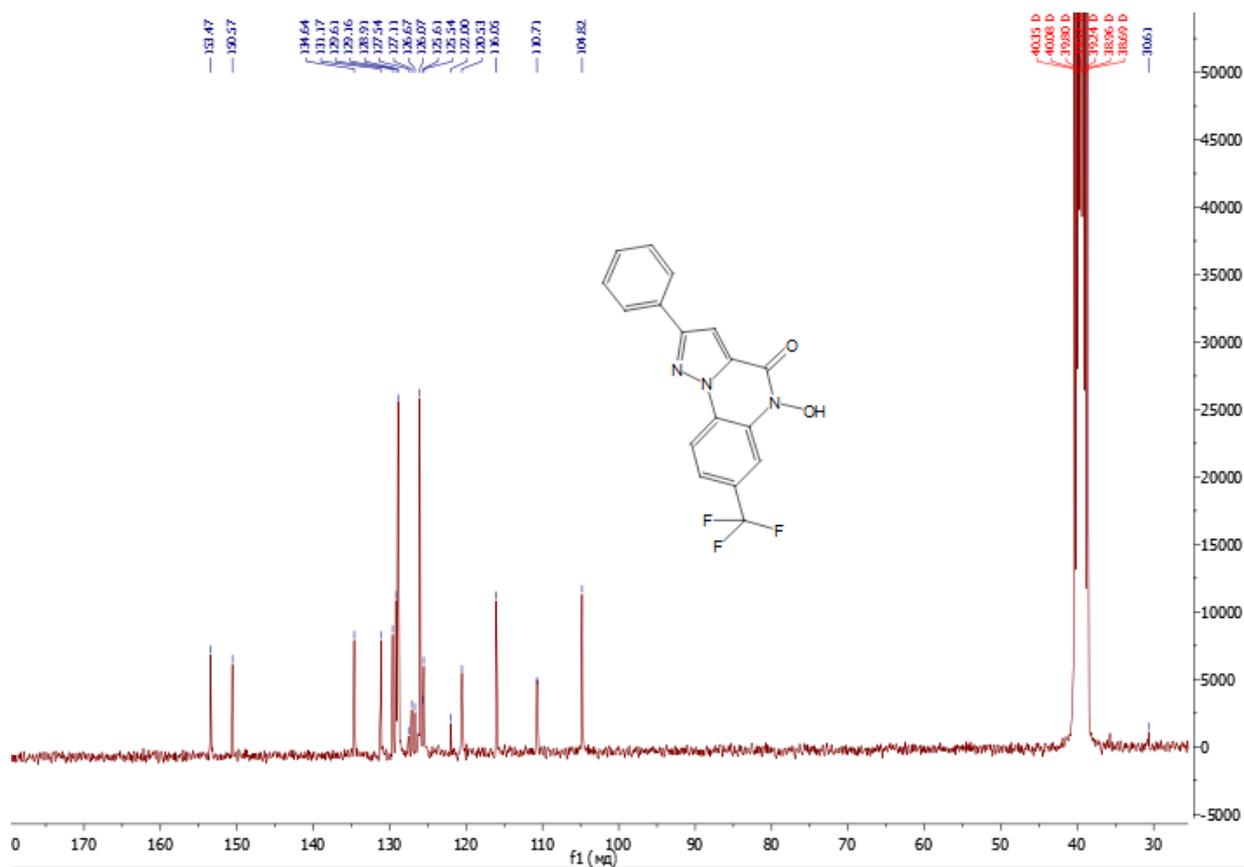


¹³C NMR (75 MHz) spectrum of **3g** in DMSO-*d*₆

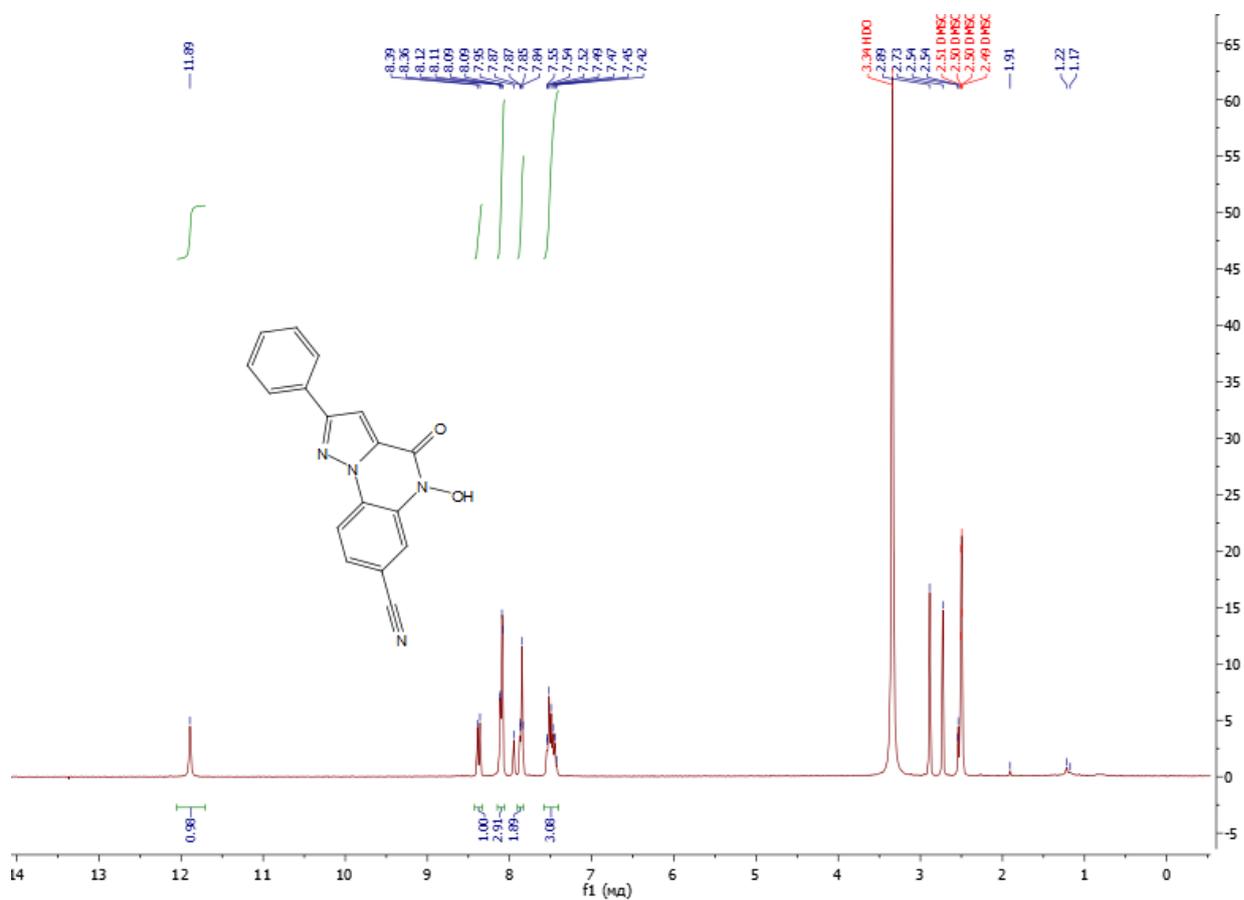
NMR spectra of 5-hydroxypyrazolo[1,5-*a*]quinoxalin-4-ones **4a-g**



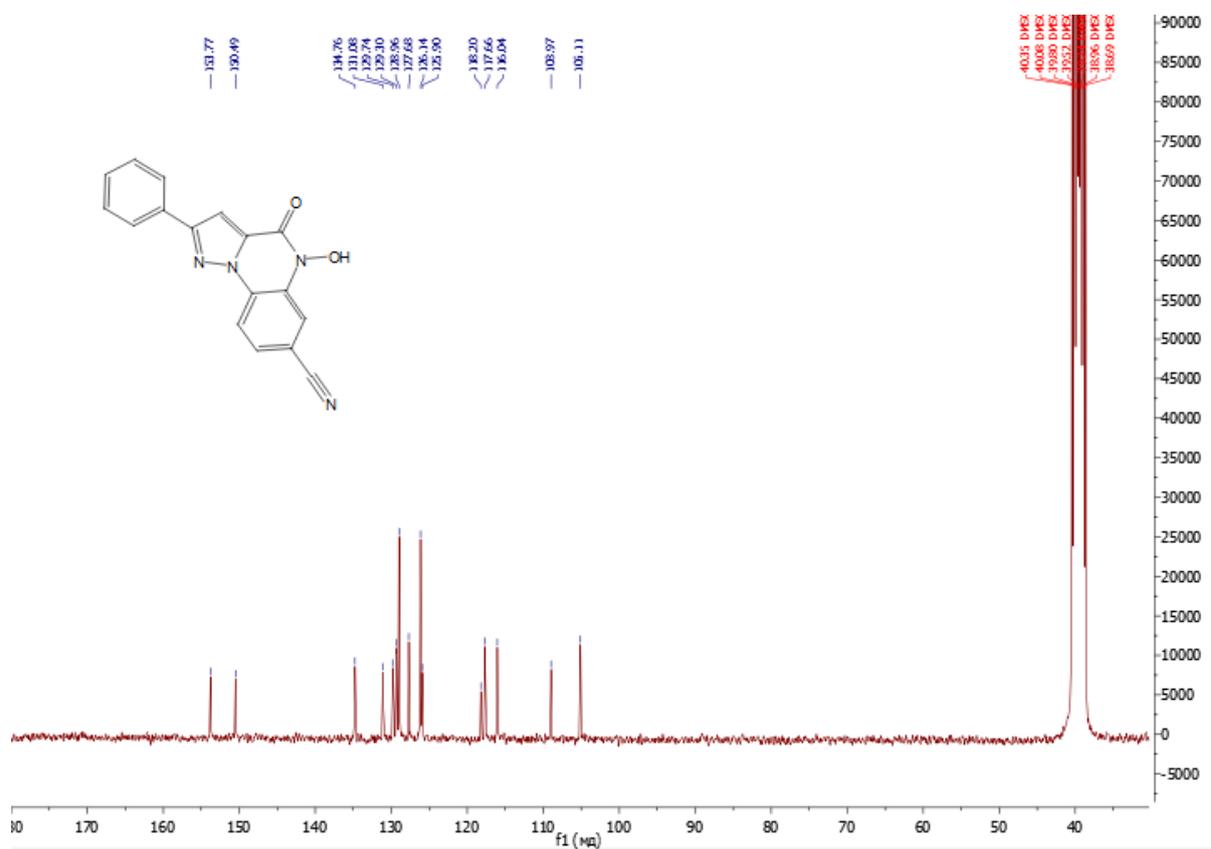
¹H NMR (400 MHz) spectrum of **4a** in DMSO-*d*₆



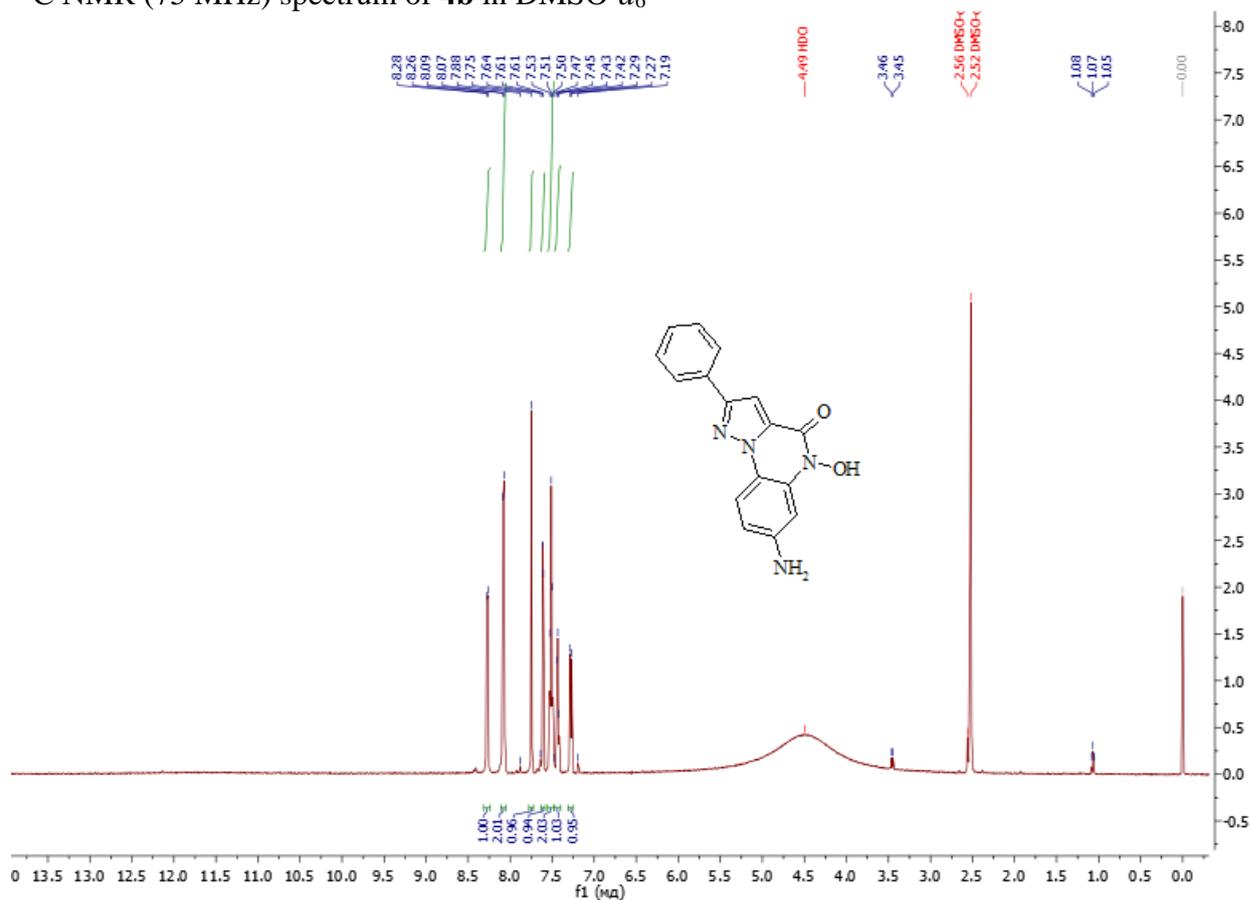
¹³C NMR (75 MHz) spectrum of **4a** in DMSO-*d*₆



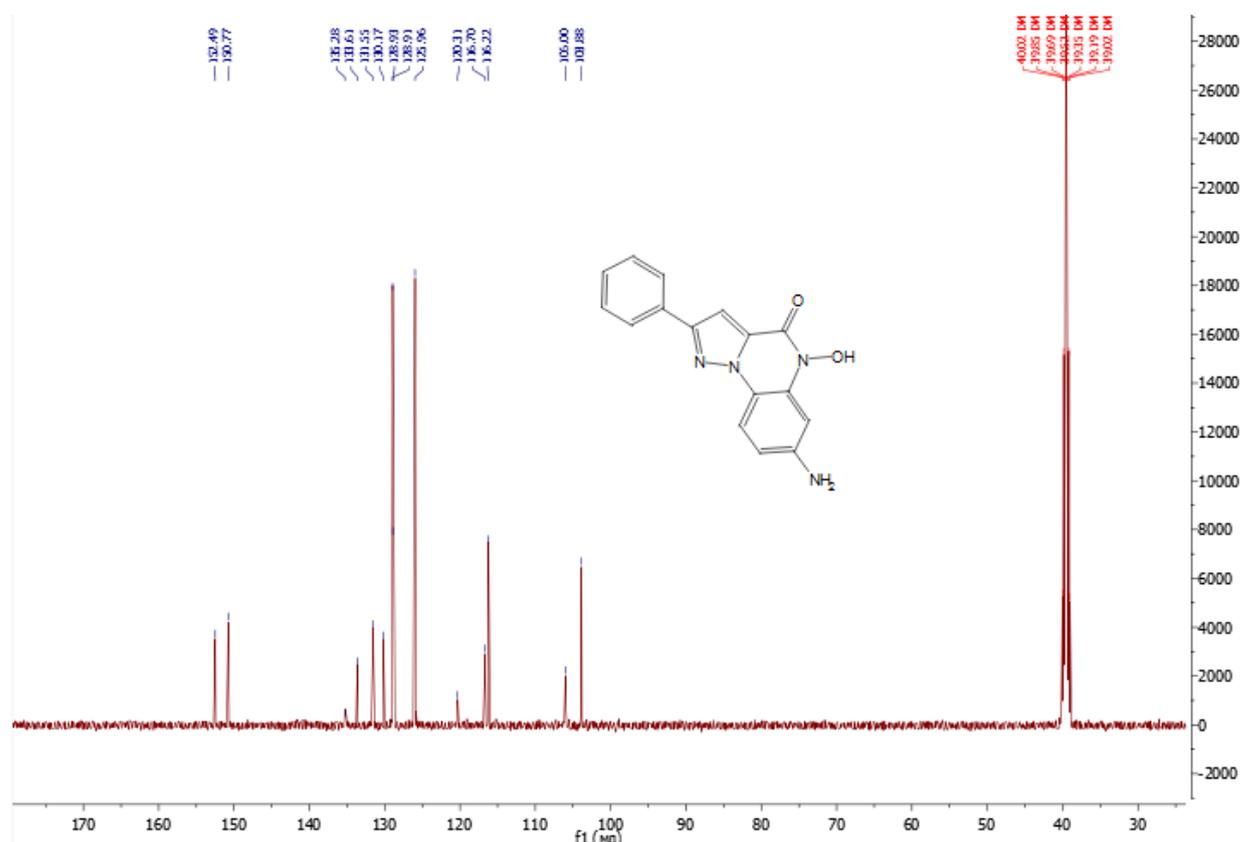
¹H NMR (400 MHz) spectrum of **4b** in DMSO-*d*₆



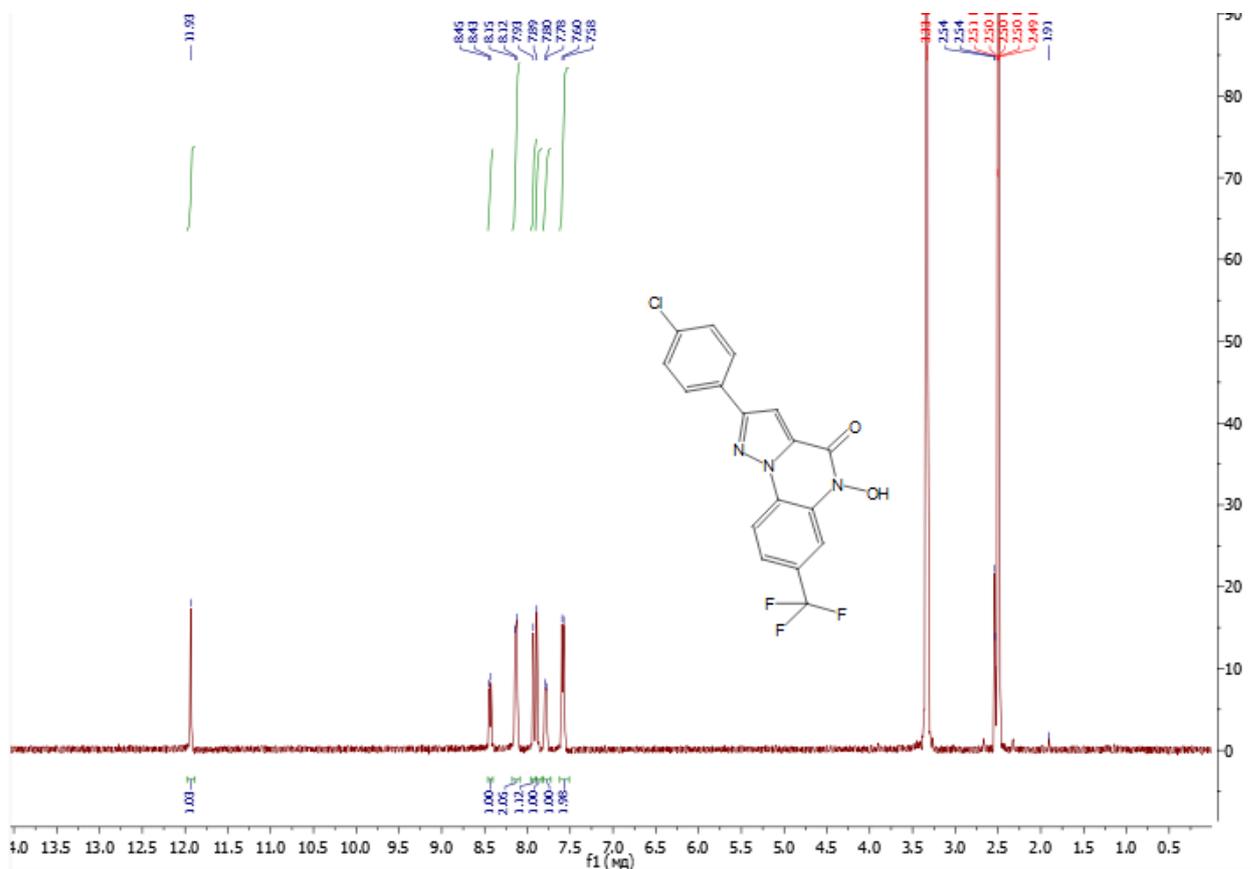
^{13}C NMR (75 MHz) spectrum of **4b** in $\text{DMSO-}d_6$



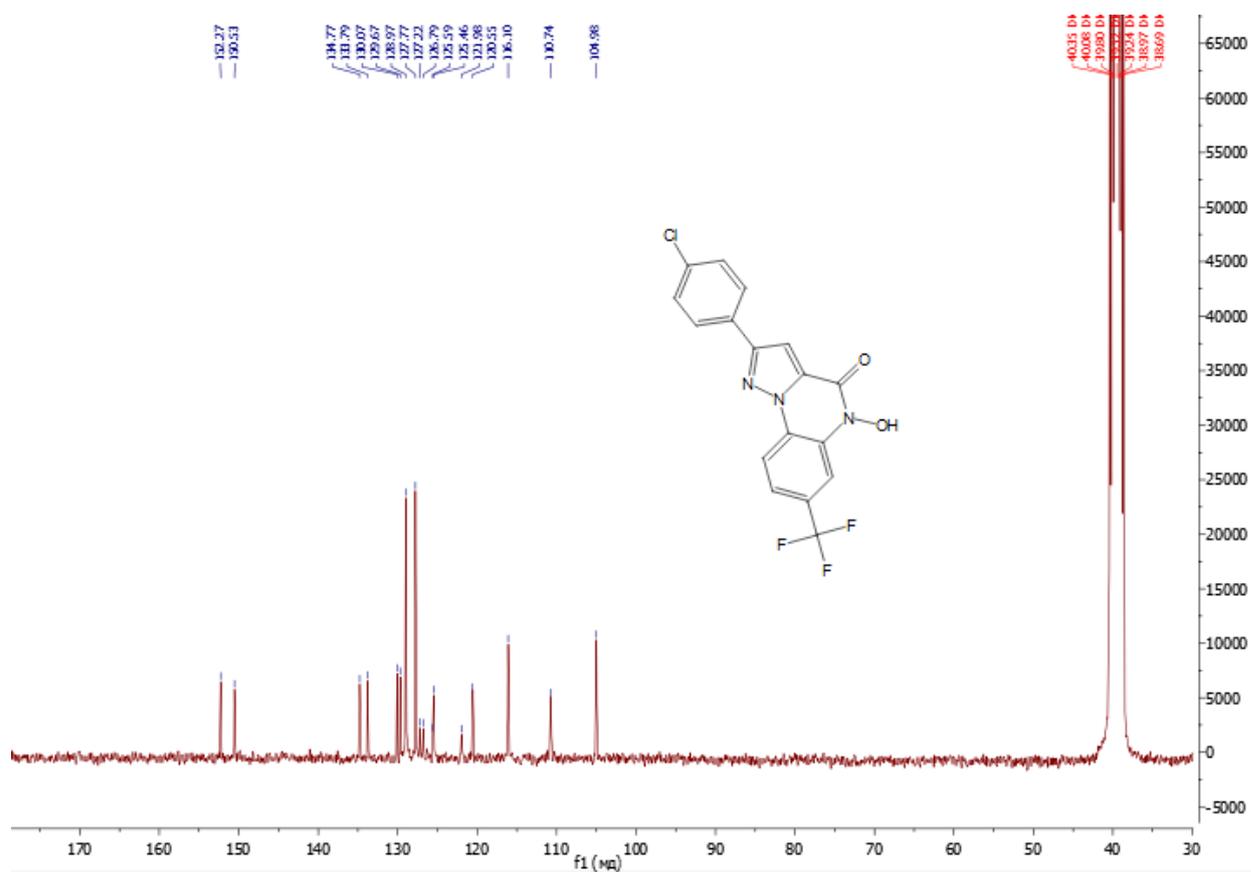
^1H NMR (400 MHz) spectrum of **4c** in $\text{DMSO-}d_6$



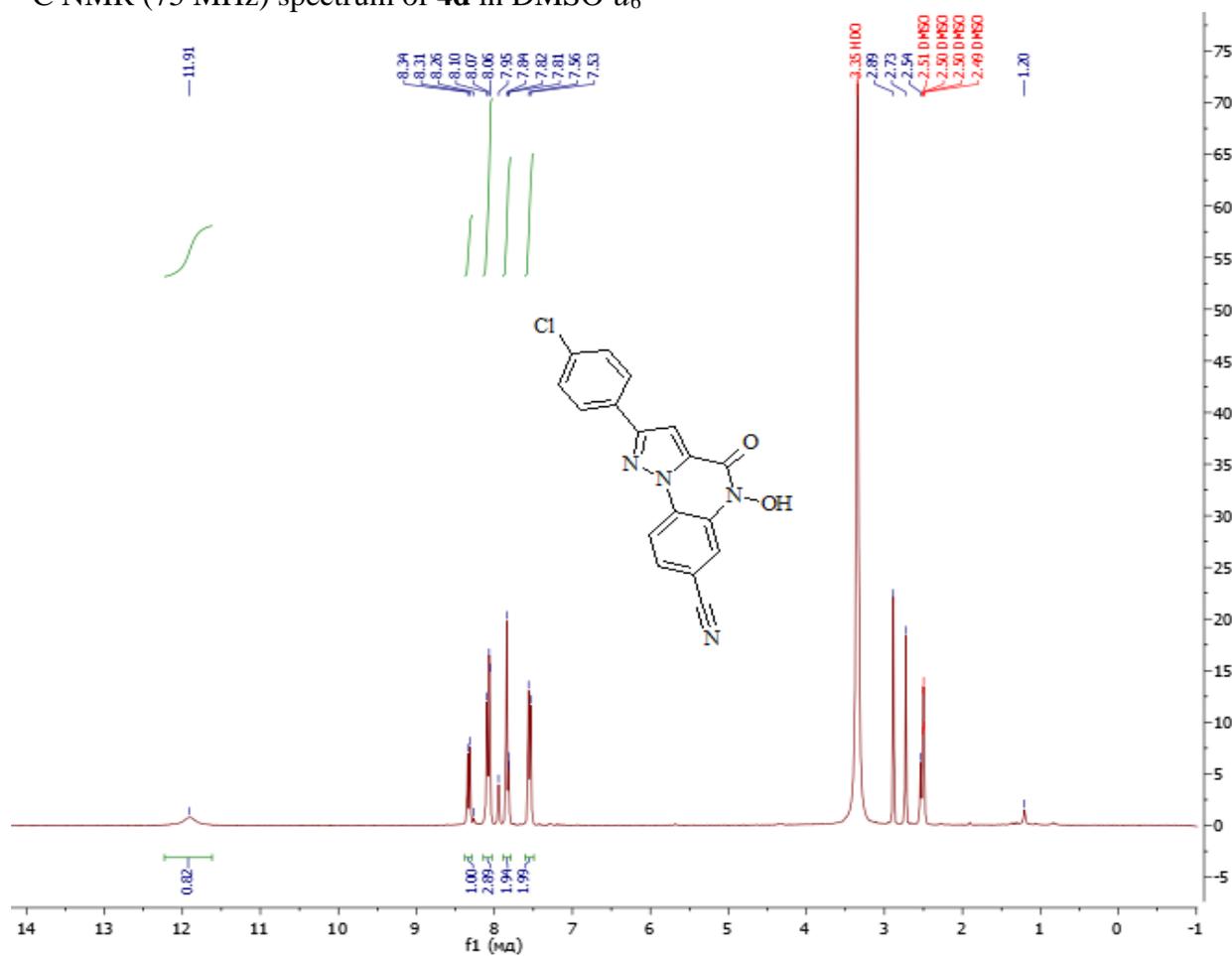
¹³C NMR (75 MHz) spectrum of **4c** in DMSO-*d*₆



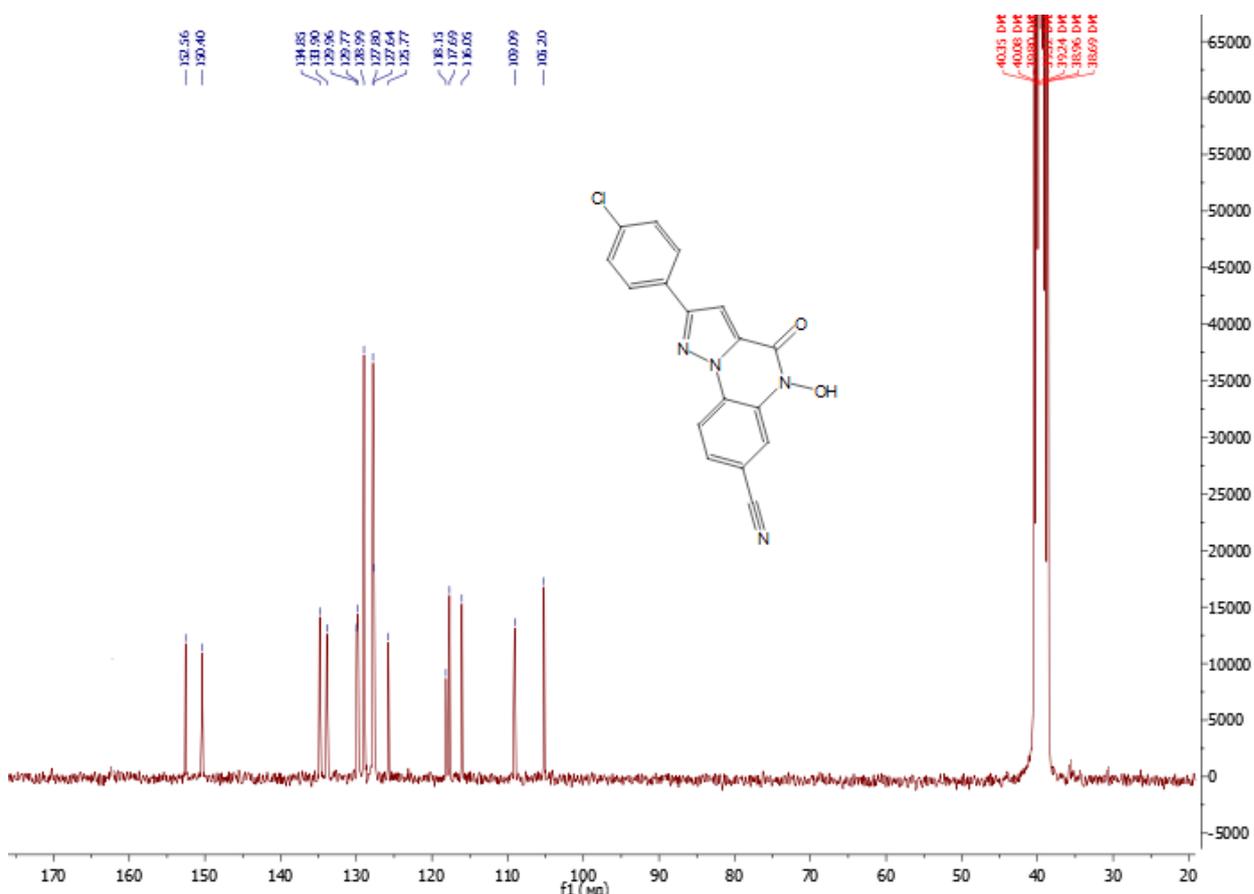
¹H NMR (400 MHz) spectrum of **4d** in DMSO-*d*₆



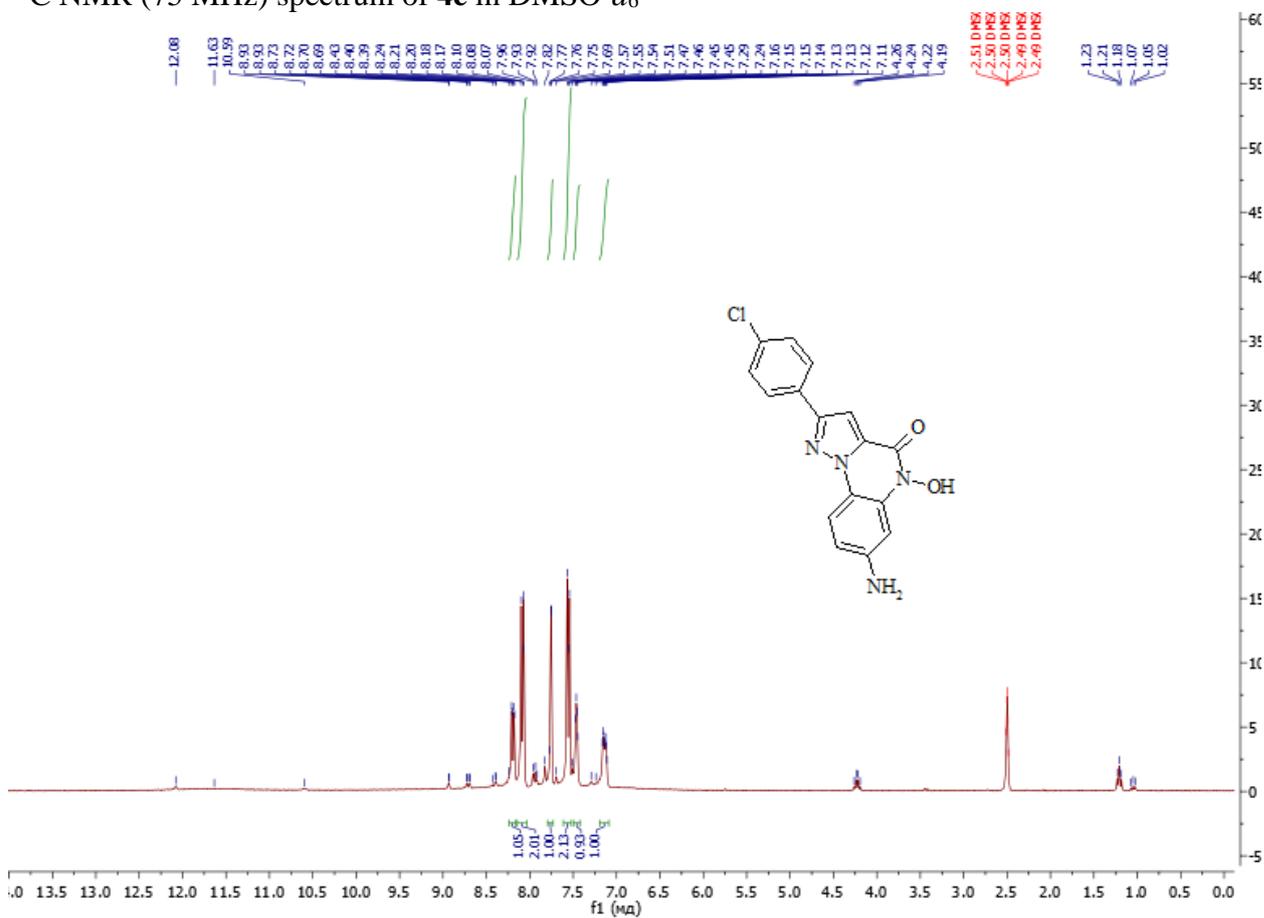
¹³C NMR (75 MHz) spectrum of **4d** in DMSO-*d*₆



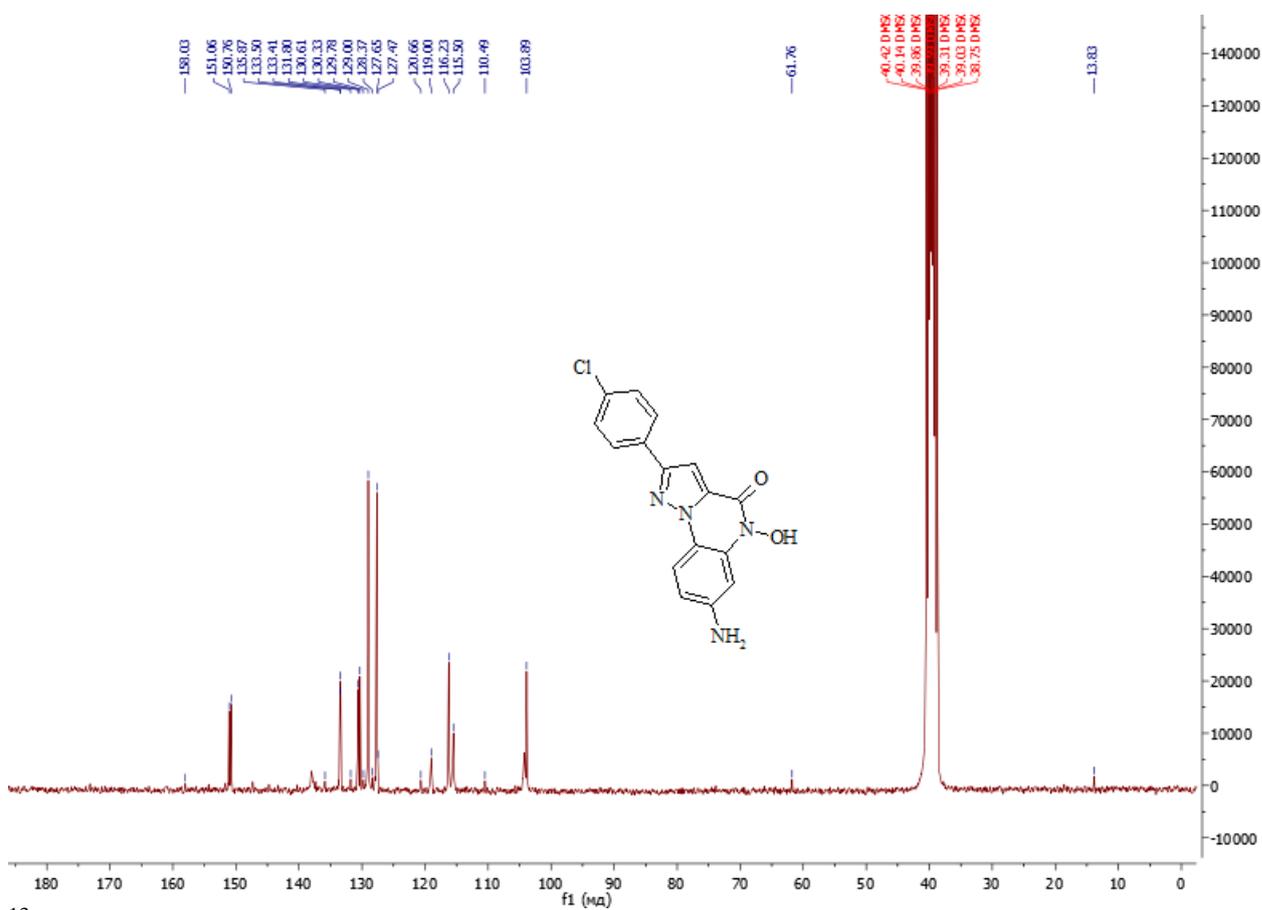
¹H NMR (400 MHz) spectrum of **4e** in DMSO-*d*₆



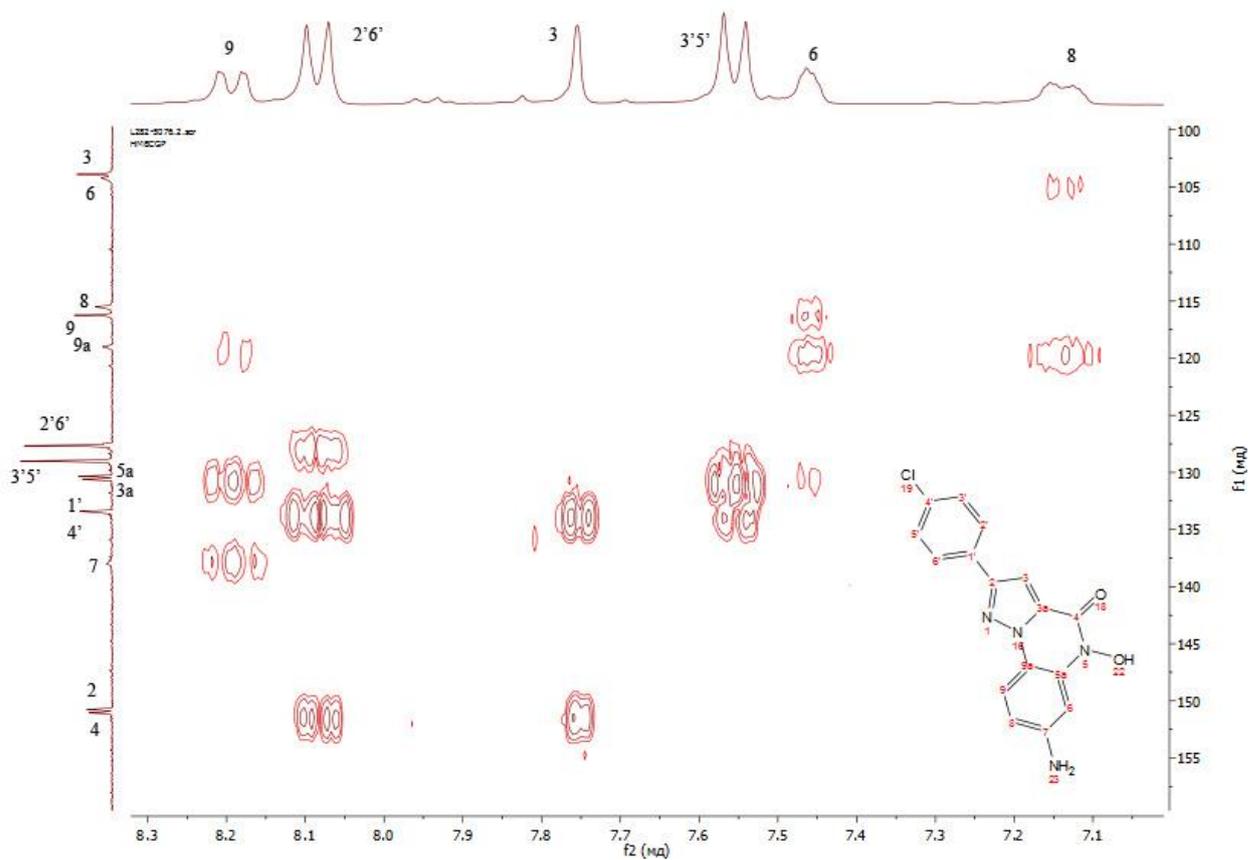
^{13}C NMR (75 MHz) spectrum of **4e** in $\text{DMSO-}d_6$



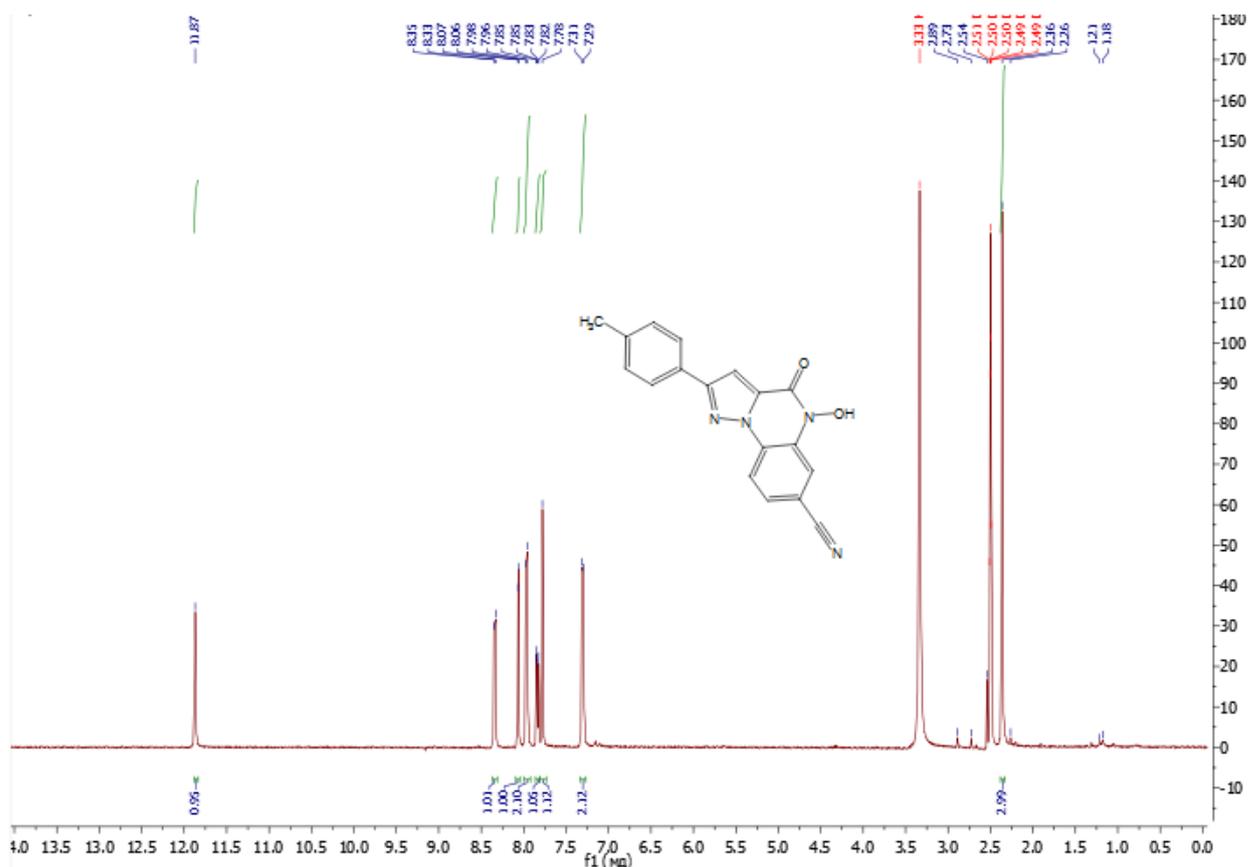
^1H NMR (400 MHz) spectrum of **4f** in $\text{DMSO-}d_6$



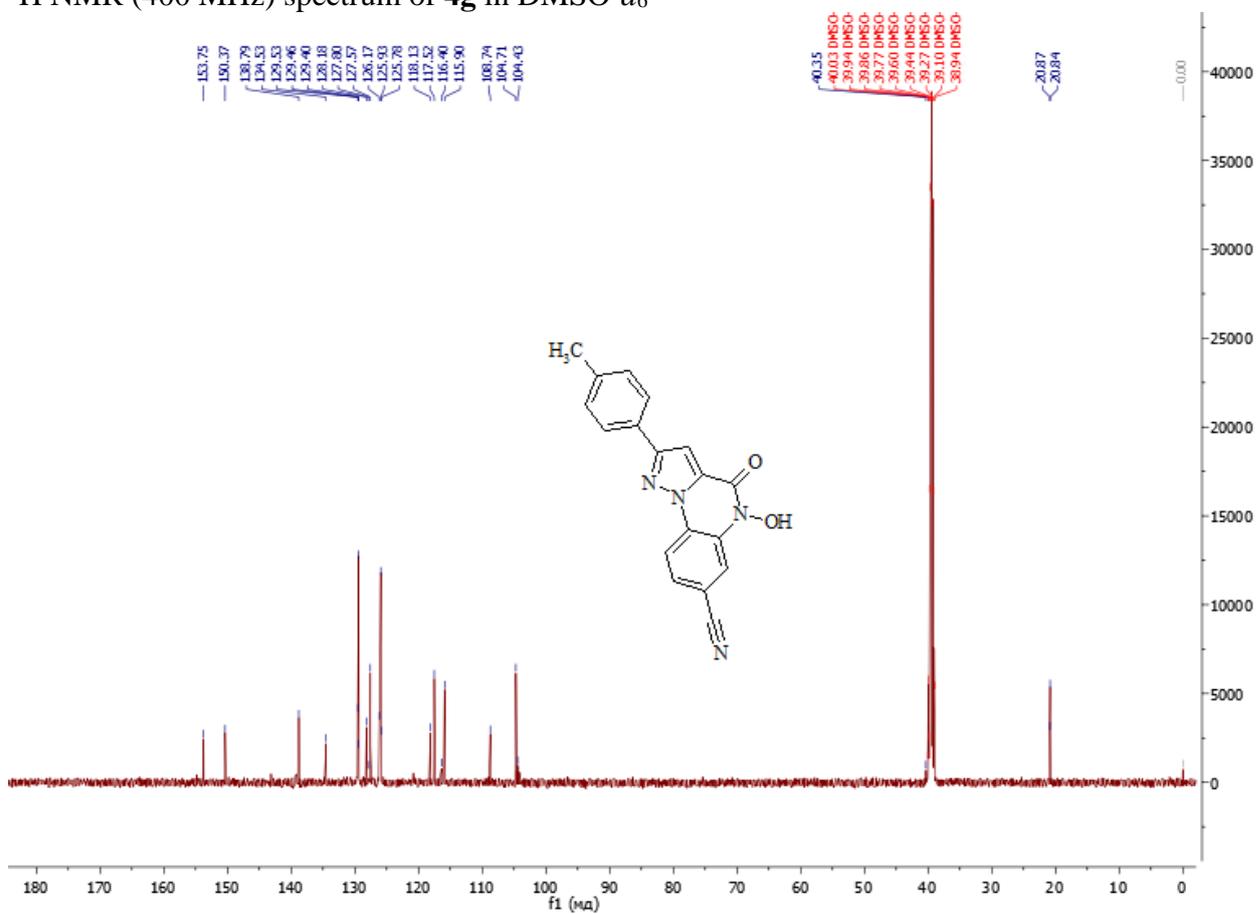
¹³C NMR (75 MHz) spectrum of **4f** in DMSO-*d*₆



HMBC- spectrum of **4f** in DMSO-*d*₆



¹H NMR (400 MHz) spectrum of **4g** in DMSO-*d*₆



¹³C NMR (75 MHz) spectrum of **4g** in DMSO-*d*₆