

Reactions of chromone-3-carboxamides with 2-cyanothioacetamides

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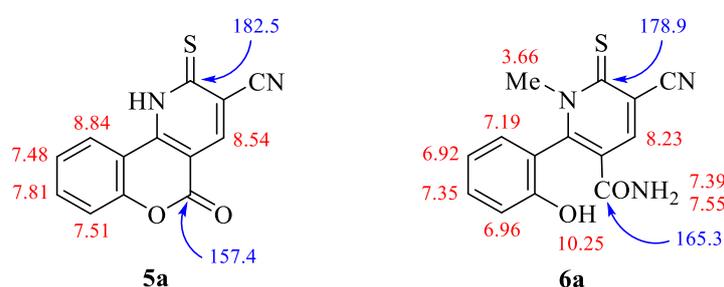


Figure S1 Selected ¹³C and ¹H NMR chemical shifts (δ, ppm) of compounds **5a** and **6a** in DMSO-*d*₆.

Characteristics of compounds **5b,c** and **6b,c**

9-Methyl-5-oxo-2-thioxo-1,5-dihydro-2H-chromeno[4,3-b]pyridine-3-carbonitrile (**5b**). Yield 67%, yellow powder, mp 284–285 °C (decomp.). ¹H NMR (500 MHz, DMSO-*d*₆) δ: 2.41 (s, 3H, Me), 7.39 (d, 1H, H-7, *J* 8.4 Hz), 7.62 (dd, 1H, H-8, *J* 8.4, 1.5 Hz), 8.51 (s, 1H, H-4), 8.72 (s, 1H, H-10) (labile proton was not detected). ¹³C NMR spectrum was not obtained due to low solubility. IR (ν/cm⁻¹): 2237 (CN), 1710 (C=O), 1581 (Ar). Found (%): C, 61.71; H, 2.83; N, 10.49. Calc. for C₁₄H₈N₂O₂S·0.25H₂O (%): C, 61.64; H, 3.14; N, 10.27.

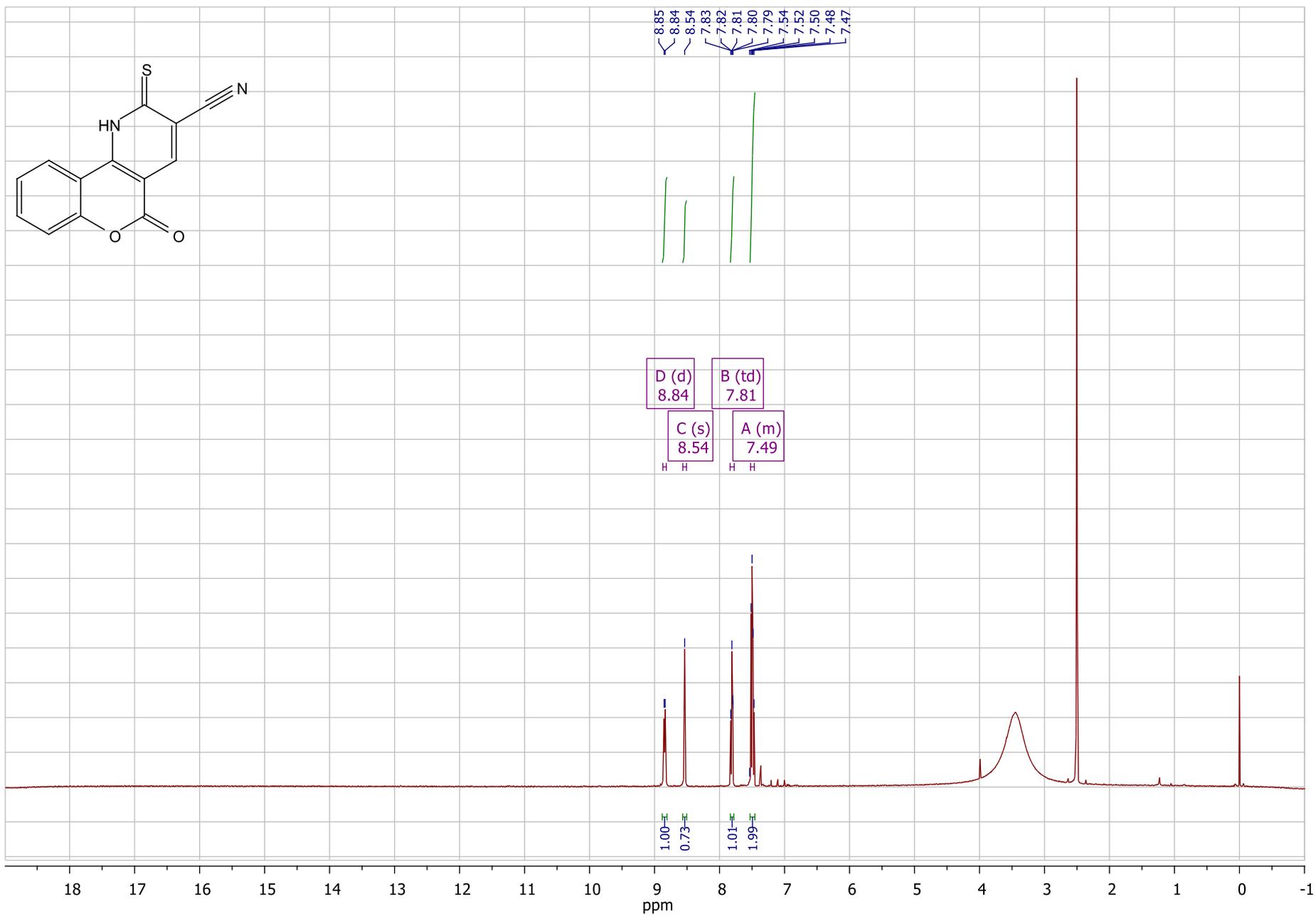
9-Chloro-5-oxo-2-thioxo-1,5-dihydro-2H-chromeno[4,3-b]pyridine-3-carbonitrile (**5c**). Yield 71%, orange powder, mp 282–283 °C (decomp.). ¹H NMR (400 MHz, DMSO-*d*₆) δ: 7.54 (d, 1H, H-7, *J* 8.9 Hz), 7.83 (dd, 1H, H-8, *J* 8.9, 2.4 Hz), 8.50 (s, 1H, H-4), 8.96 (s, 1H, H-10) (labile proton was not detected). ¹³C NMR (126 MHz, DMSO) δ: 107.4, 113.6, 116.0, 117.3, 119.6, 124.7, 129.2, 134.5, 141.6, 147.3, 151.9, 157.4 (C=O), 183.2 (C=S). IR (ν/cm⁻¹): 2239 (CN), 1716 (C=O), 1579 (Ar). Found (%): C, 54.03; H, 1.78; N, 9.69. Calc. for C₁₃H₅ClN₂O₂S (%): C, 54.08; H, 1.75; N, 9.70.

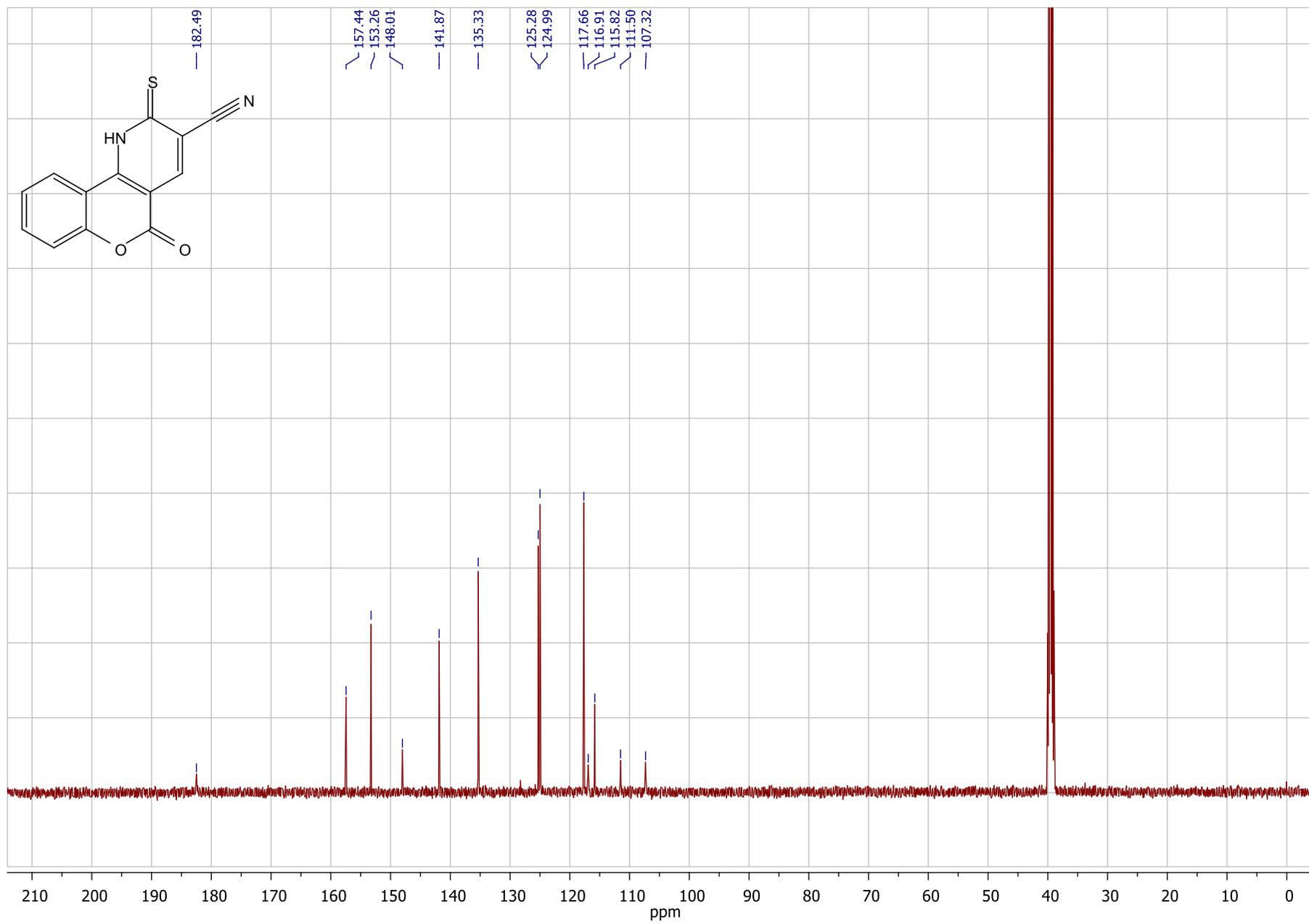
5-Cyano-2-(2-hydroxy-5-methylphenyl)-1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxamide (**6b**). Yield 73%, orange powder, mp 263–265 °C. ¹H NMR (500 MHz, DMSO-*d*₆) δ: 2.21 (s, 3H, Me), 3.66 (s, 3H, NMe), 6.85 (d, 1H, H-3', *J* 8.4 Hz), 6.99 (d, 1H, H-6', *J* 1.8 Hz), 7.16 (dd, 1H, H-4', *J* 8.4, 1.8 Hz), 7.39 (br. s, 1H, NHH), 7.50 (br. s, 1H, NHH), 8.22 (s, 1H, H-4), 10.00 (s, 1H, OH). ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 20.0 (Me), 42.2 (NMe), 115.7, 116.1, 116.8, 119.7, 124.1, 127.7, 129.3, 132.4, 140.5, 152.2, 153.5, 165.3 (C=O), 178.9 (C=S). IR (ν/cm⁻¹): 3400–3150 (OH and NH₂), 2233 (CN), 1664 (C=O), 1589 (Ar). Found (%): C, 60.08; H, 4.31; N, 14.07. Calc. for C₁₅H₁₃N₃O₂S (%): C, 60.19; H, 4.38; N, 14.04.

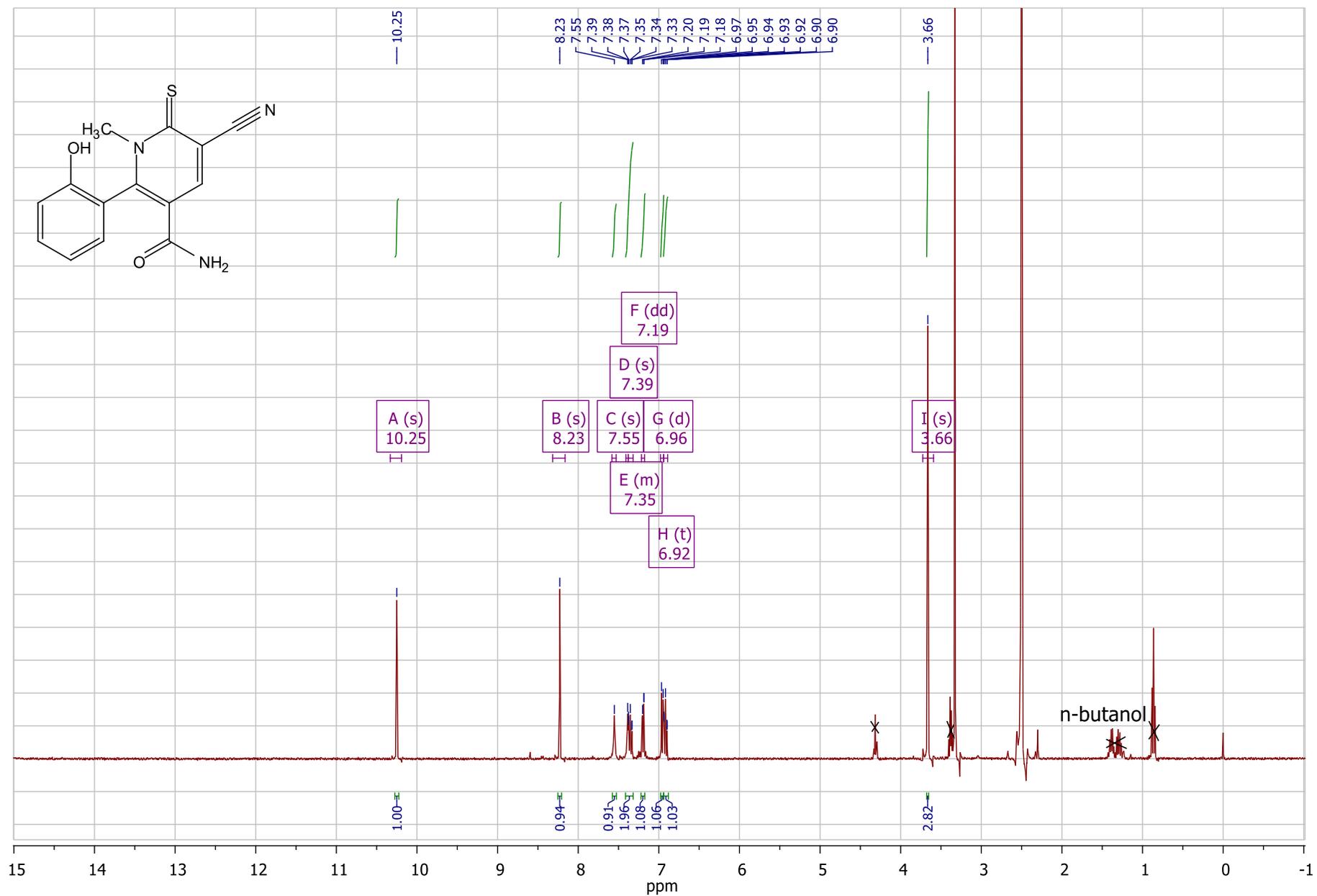
2-(5-Chloro-2-hydroxyphenyl)-5-cyano-1-methyl-6-thioxo-1,6-dihydropyridine-3-carboxamide (**6c**). Yield 72%, yellow powder, mp 274–275 °C (ethanol). ¹H NMR (500 MHz, DMSO-*d*₆) δ: 3.67 (s, 3H, Me), 6.96 (d, 1H, H-3', *J* 8.8 Hz), 7.30 (d, 1H, H-6', *J* 2.7 Hz), 7.39 (dd, 1H, H-4', *J* 8.8, 2.7 Hz), 7.43 (br. s, 1H, NHH), 7.68 (br. s, 1H, NHH), 8.24 (s, 1H, H-4), 10.52 (s, 1H, OH). ¹³C NMR (126 MHz, DMSO-*d*₆) δ: 42.1 (Me), 116.5, 116.6, 117.3, 121.5, 122.4, 123.9, 128.9, 131.4, 140.4, 151.9, 153.5, 165.1 (C=O), 179.0 (C=S). IR (ν/cm⁻¹): 3500–3000 (OH and NH₂), 2227 (CN), 1676 (C=O), 1594 (Ar). Found (%): C, 52.23; H, 4.41; N, 11.31. Calc. for C₁₄H₁₀ClN₃O₂S·EtOH (%): C, 52.53; H, 4.41; N, 11.49.

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Compound **5a**, ^1H NMR (500 MHz, DMSO- d_6)



Compound **5a**, ^{13}C NMR (126 MHz, DMSO- d_6)

Compound **6a**, ^1H NMR (400 MHz, DMSO- d_6)

Compound **6a**, ^{13}C NMR (126 MHz, DMSO- d_6)