

Tungstic acid functionalized polycalix[4]resorcinarene as a cavity-containing hyper-branched supramolecular and recoverable acidic catalyst in the 4H-pyran synthesis

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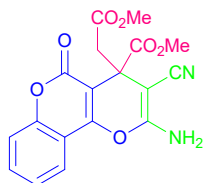
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Spectral data of the synthesized 4H-pyran derivatives:

Methyl 2-amino-3-cyano-4-(2-methoxy-2-oxoethyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-4-carboxylate (4a):



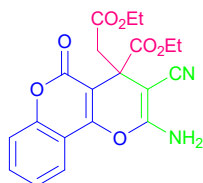
White crystalline solid

Mp: 205-207 °C

IR (KBr): 1365, 1677, 1739, 2202, 3205, 3451 cm⁻¹

¹H NMR (300 MHz, DMSO-*d*₆): δ = 3.01 (1H, d, *J* = 15.4 Hz), 3.21 (1H, d, *J* = 15.4 Hz), 3.49 (3H, s), 3.68 (3H, s), 7.78 (2H, s), 7.81 (2H, m), 7.84 (1H, d, *J* = 1.7 Hz), 7.88 (1H, dd, *J*₁ = 6.8 Hz, *J*₂ = 1.4 Hz) ppm; ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 38.0, 44.0, 52.1, 53.6, 55.7, 102.3, 112.6, 117.3, 117.4, 123.0, 125.7, 134.2, 152.4, 154.6, 159.4, 159.9, 170.3, 171.2 ppm.

Ethyl 2-amino-3-cyano-4-(2-ethoxy-2-oxoethyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-4-carboxylate (4b):



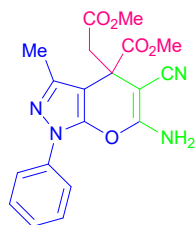
White crystalline solid

Mp: 207-209 °C

IR (KBr): 1362, 1670, 1727, 2194, 3324, 3444 cm⁻¹

¹H NMR (300 MHz, DMSO-*d*₆): δ = 0.94 (3H, t, *J* = 7.0 Hz), 1.12 (3H, t, *J* = 7.0 Hz), 2.97 (1H, d, *J* = 15.5 Hz), 3.17 (1H, d, *J* = 15.5 Hz), 3.89 (2H, q, *J* = 7.0 Hz), 4.11-4.22 (2H, m), 7.79 (2H, s), 7.81 (2H, t, *J* = 7.9 Hz), 7.84 (1H, d, *J* = 7.9 Hz), 7.88 (1H, dd, *J*₁ = 6.7 Hz, *J*₂ = 1.3 Hz) ppm; ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 14.2, 14.3, 38.8, 44.2, 55.9, 60.4, 62.32, 102.5, 112.6, 117.3, 117.3, 122.9, 125.7, 134.2, 152.4, 154.4, 159.3, 159.8, 169.8, 170.5 ppm.

Methyl 6-amino-5-cyano-4-(2-methoxy-2-oxoethyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-4-carboxylate (4c):



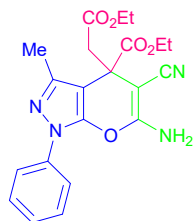
White crystalline solid

Mp: 198-201 °C

IR (KBr): 1392, 1646, 1735, 2194, 3336, 3436 cm⁻¹

^1H NMR (300 MHz, DMSO- d_6): δ = 2.16 (3H, s), 2.98 (1H, d, J = 15.6 Hz), 3.12 (1H, d, J = 15.6 Hz), 3.49 (3H, s), 3.72 (3H, s), 7.33 (1H, t, J = 7.3 Hz), 7.49 (2H, s), 7.50 (2H, t, J = 7.4 Hz), 7.78 (2H, d, J = 7.7 Hz) ppm; ^{13}C NMR (75 MHz, DMSO- d_6): δ = 13.7, 39.1, 44.4, 51.9, 53.6, 57.0, 96.0, 118.7, 120.4, 127.0, 129.9, 137.6, 144.6, 145.2, 160.9, 169.8, 172.0 ppm.

Ethyl 6-amino-5-cyano-4-(2-ethoxy-2-oxoethyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-4-carboxylate (4d):



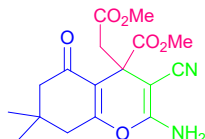
White crystalline solid

Mp: 113-115 °C

IR (KBr): 1234, 1392, 1645, 1731, 2194, 3340, 3448 cm^{-1}

^1H NMR (300 MHz, DMSO- d_6): δ = .94 (3H, t, J = 7.0 Hz), 1.18 (3H, t, J = 7.0 Hz), 2.18 (3H, s), 2.92 (1H, d, J = 14.9 Hz), 3.08 (1H, d, J = 14.9 Hz), 3.87-3.97 (2H, m), 4.16 (2H, q, J = 7.0 Hz), 7.33 (1H, t, J = 7.4 Hz), 7.49 (2H, t, J = 7.9 Hz), 7.50 (2H, s), 7.75 (2H, d, J = 7.9 Hz) ppm; ^{13}C NMR (75 MHz, DMSO- d_6): δ = 13.8, 14.1, 14.5, 44.7, 57.4, 60.3, 62.4, 96.0, 118.7, 120.4, 126.9, 129.9, 137.6, 144.5, 145.4, 160.9, 169.3, 171.4 ppm.

Methyl 2-amino-3-cyano-4-(2-methoxy-2-oxoethyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-4-carboxylate (4e):



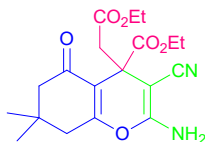
White crystalline solid

Mp: 180-183 °C

IR (KBr): 1353, 1662, 1735, 2183, 2962, 3324, 3413 cm^{-1}

^1H NMR (300 MHz, DMSO- d_6): δ = 1.04 (3H, s), 1.06 (3H, s), 2.18 (2H, d, J = 3.6 Hz), 2.40-2.55 (2H, m), 2.81 (1H, d, J = 15.2 Hz), 2.97 (1H, d, J = 15.2 Hz), 3.53 (3H, s), 3.58 (3H, s), 7.31 (2H, s) ppm; ^{13}C NMR (75 MHz, DMSO- d_6): δ = 27.4, 28.0, 32.3, 38.8, 43.1, 50.4, 51.8, 53.0, 56.2, 111.1, 117.9, 159.8, 163.9, 170.6, 172.1, 196.7 ppm.

Ethyl 2-amino-3-cyano-4-(2-ethoxy-2-oxoethyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-4-carboxylate (4f):



White crystalline solid

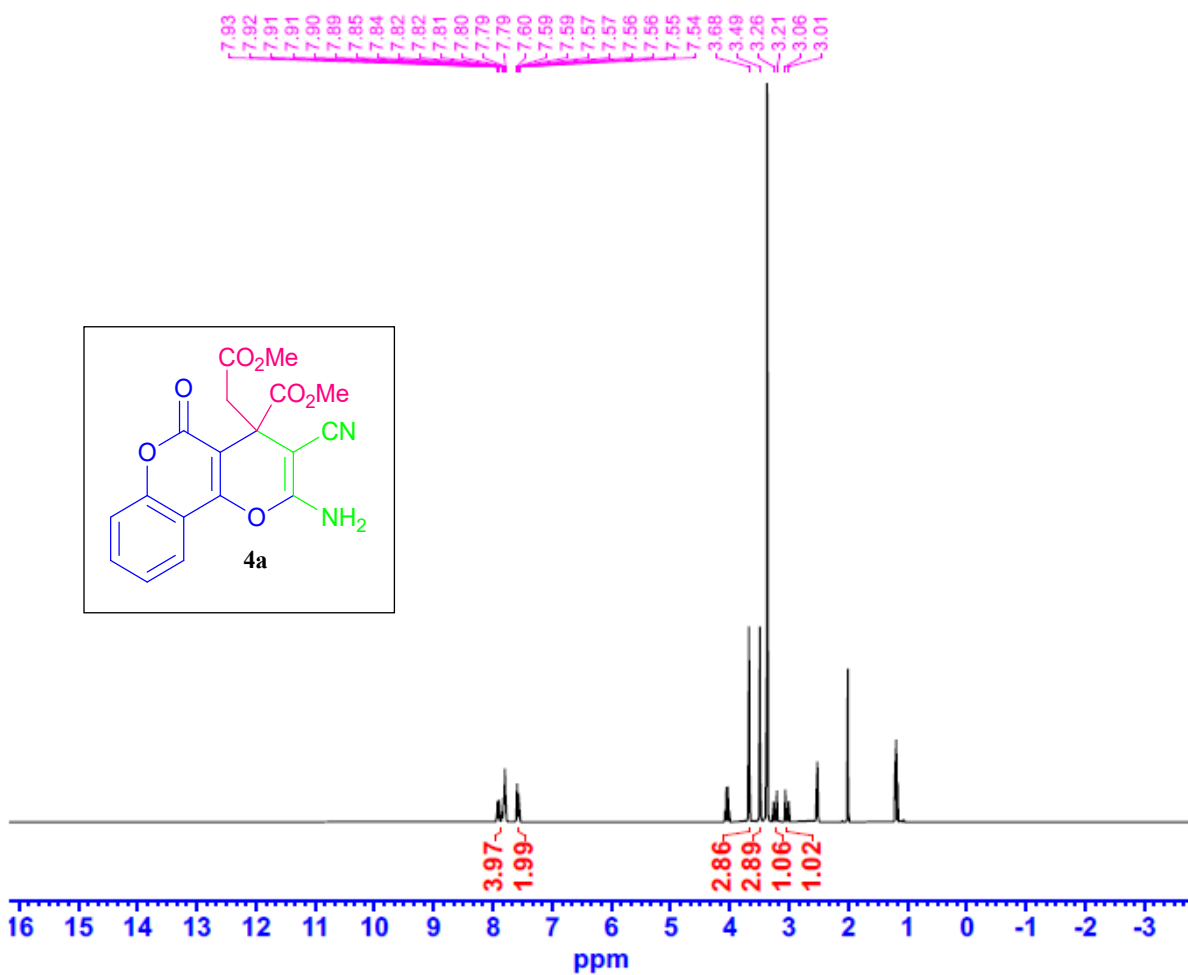
Mp: 230-233 °C

IR (KBr): 1222, 1361, 1650, 1681, 1735, 2198, 2969, 3181, 3363 cm^{-1}

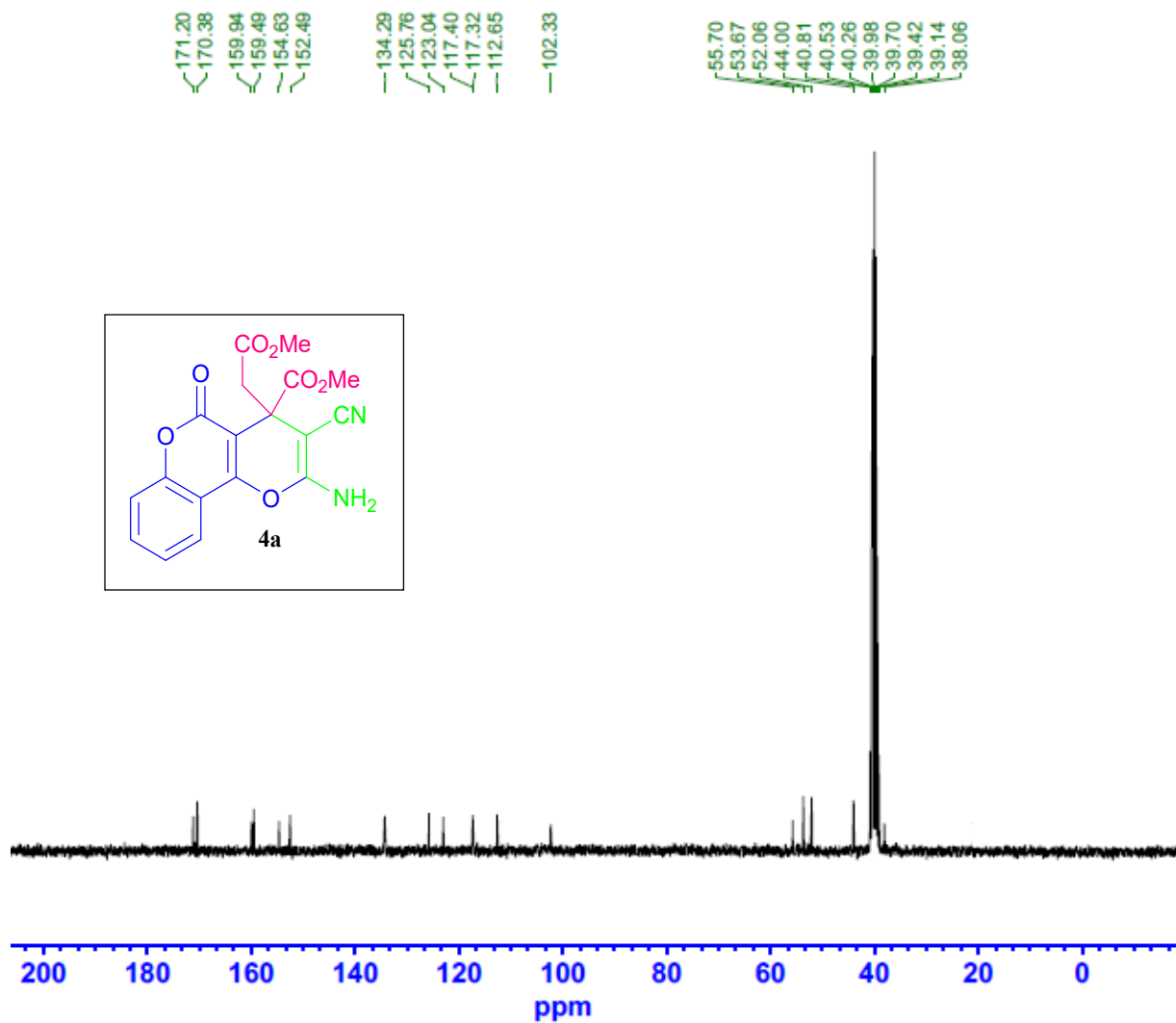
^1H NMR (300 MHz, DMSO- d_6): δ = 1.06 (3H, s), 1.07 (3H, s), 1.09 (6H, q, J = 7.1 Hz), 2.24 (2H, s), 2.46 (2H, s), 2.80 (1H, d, J = 14.9 Hz), 2.93 (1H, d, J = 14.9 Hz), 3.91-4.15 (4H, m), 7.29 (2H, s) ppm; ^{13}C NMR

(75 MHz, DMSO- d_6): $\delta = 14.3, 14.4, 27.7, 27.8, 32.4, 39.4, 43.2, 50.5, 56.4, 60.3, 61.5, 111.3, 117.8, 159.7, 163.6, 170.1, 171.4, 196.6$ ppm.

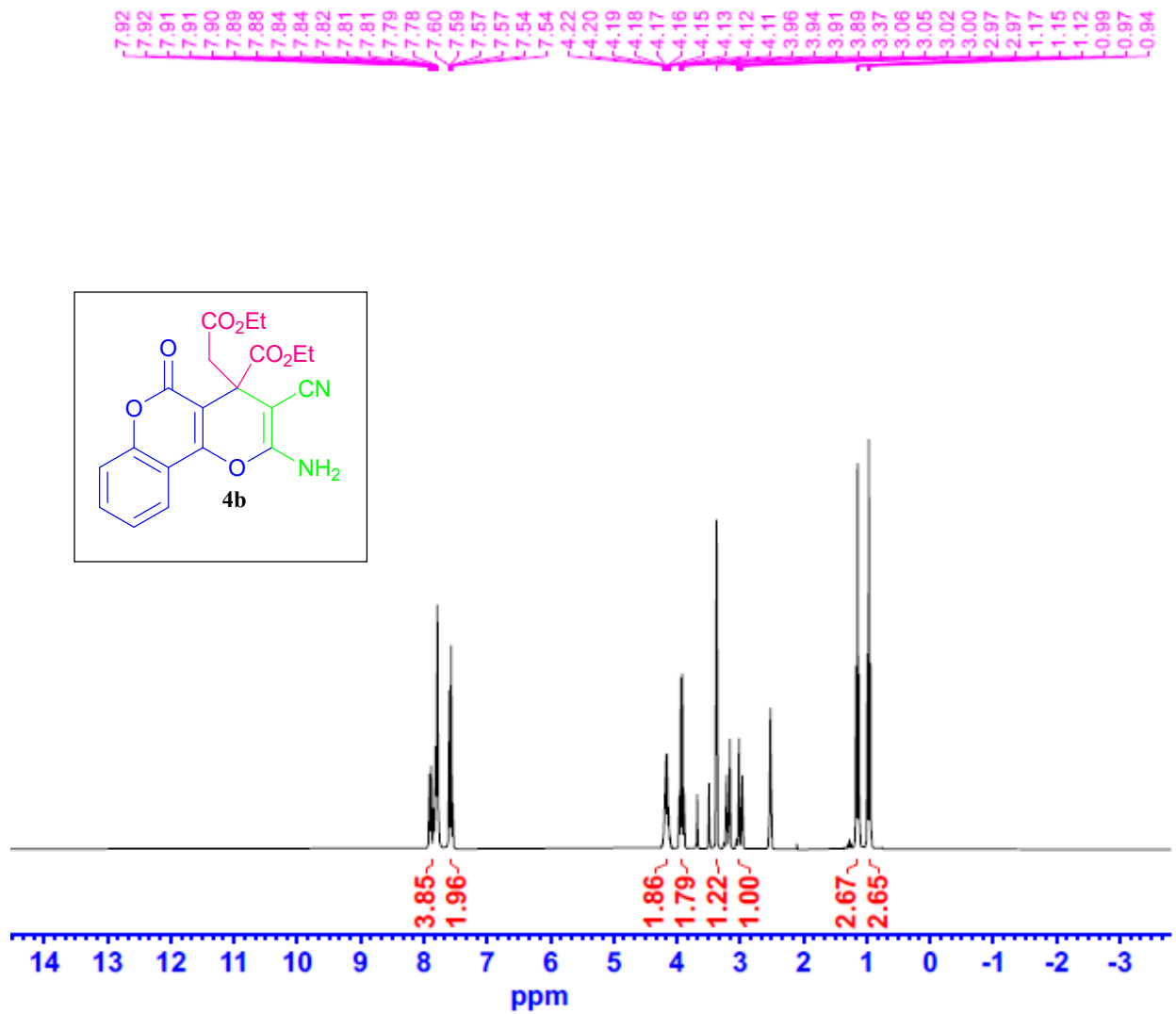
^1H NMR and ^{13}C NMR spectra of synthesized 4H-pyran derivatives:



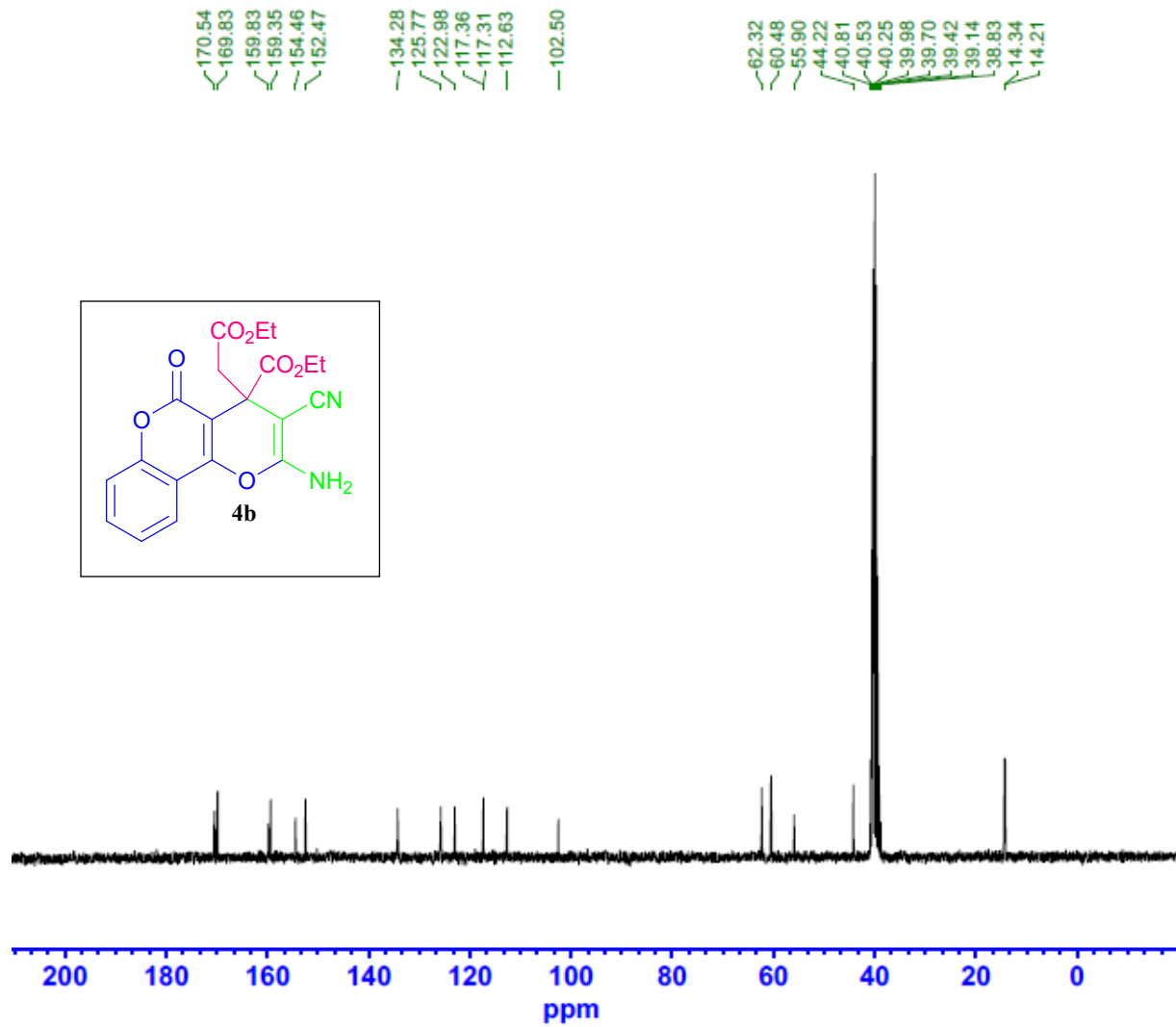
^1H NMR spectrum of compound 4a



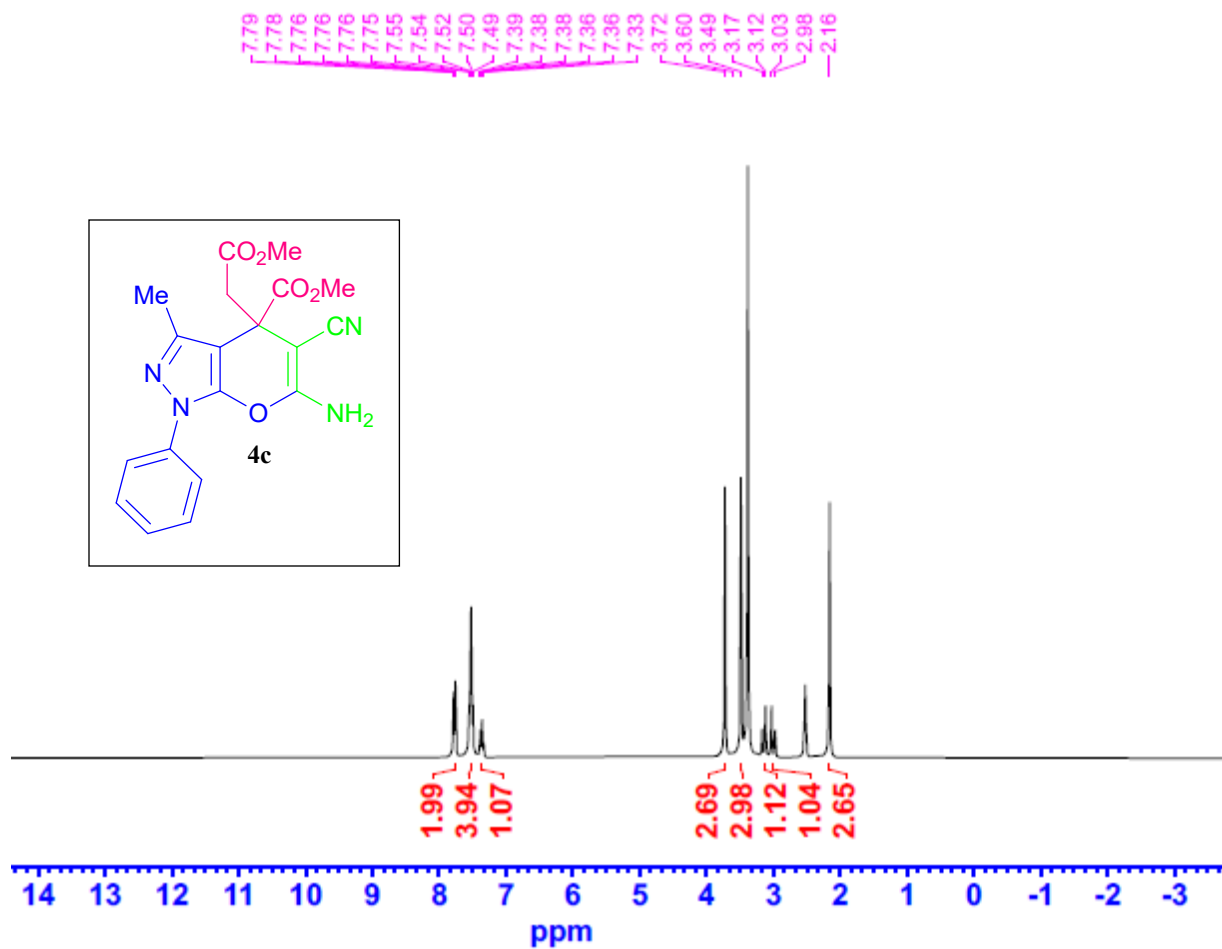
¹³C NMR spectrum of compound 4a



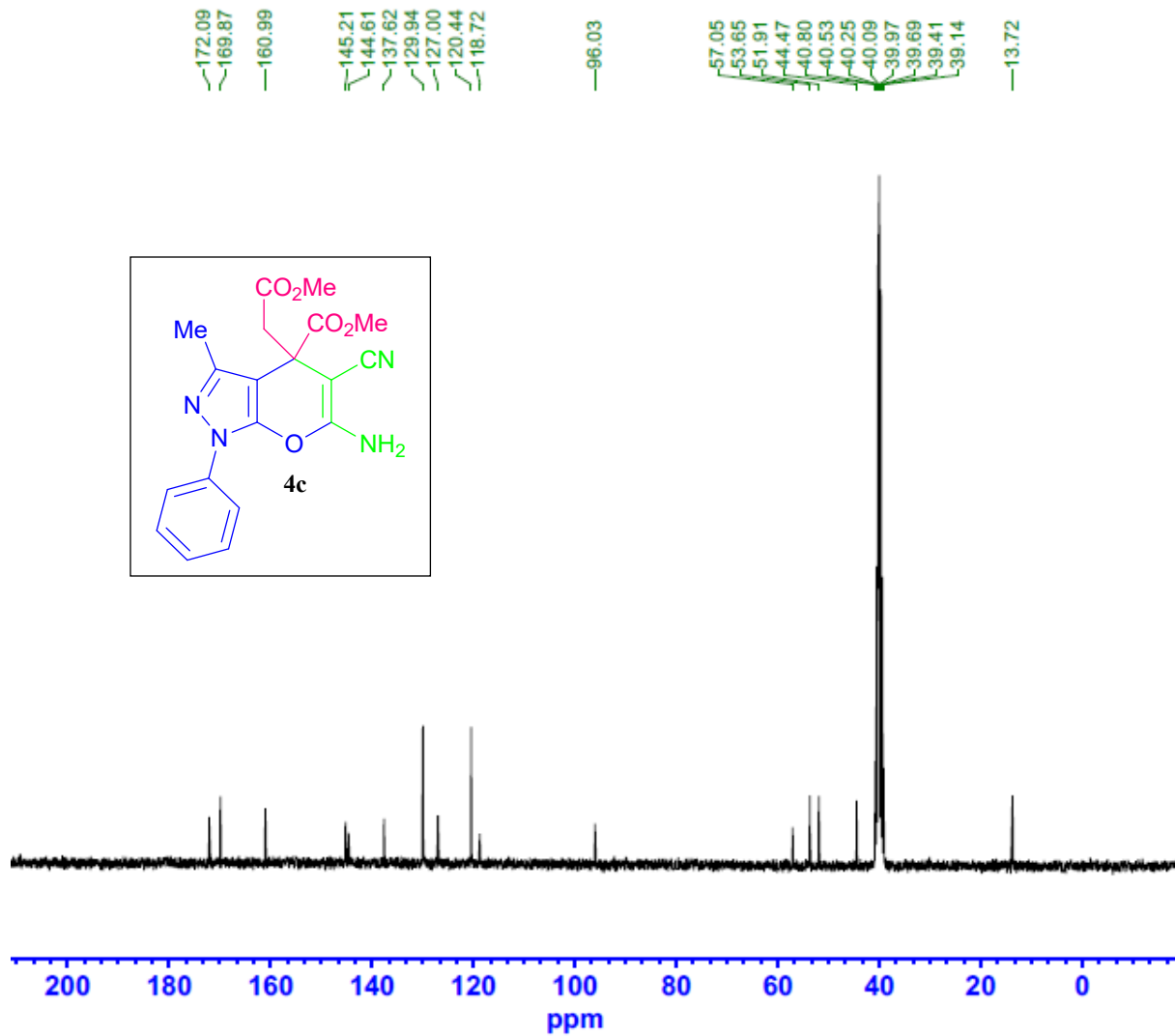
¹H NMR spectrum of compound 4b



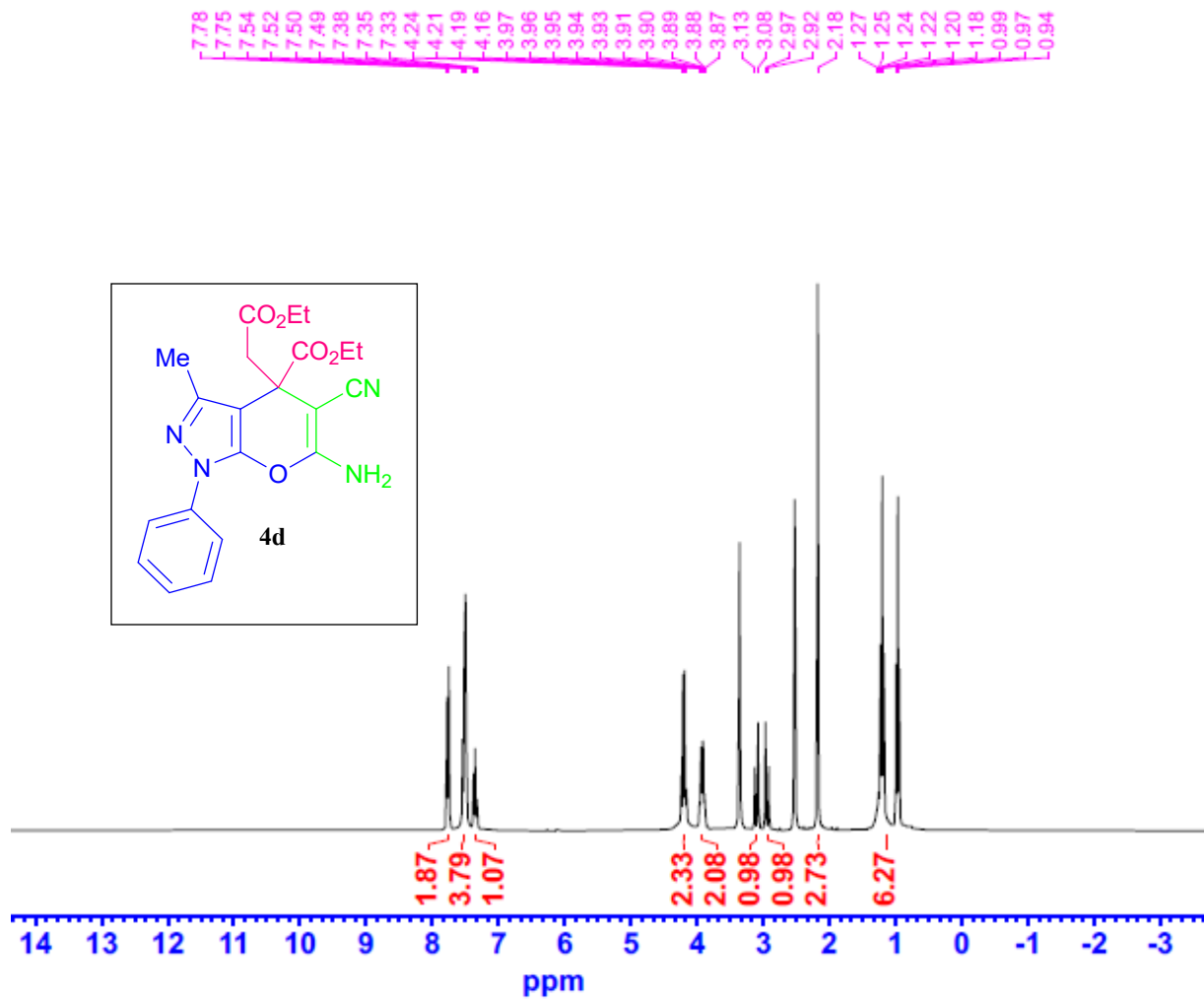
¹³C NMR spectrum of compound 4b



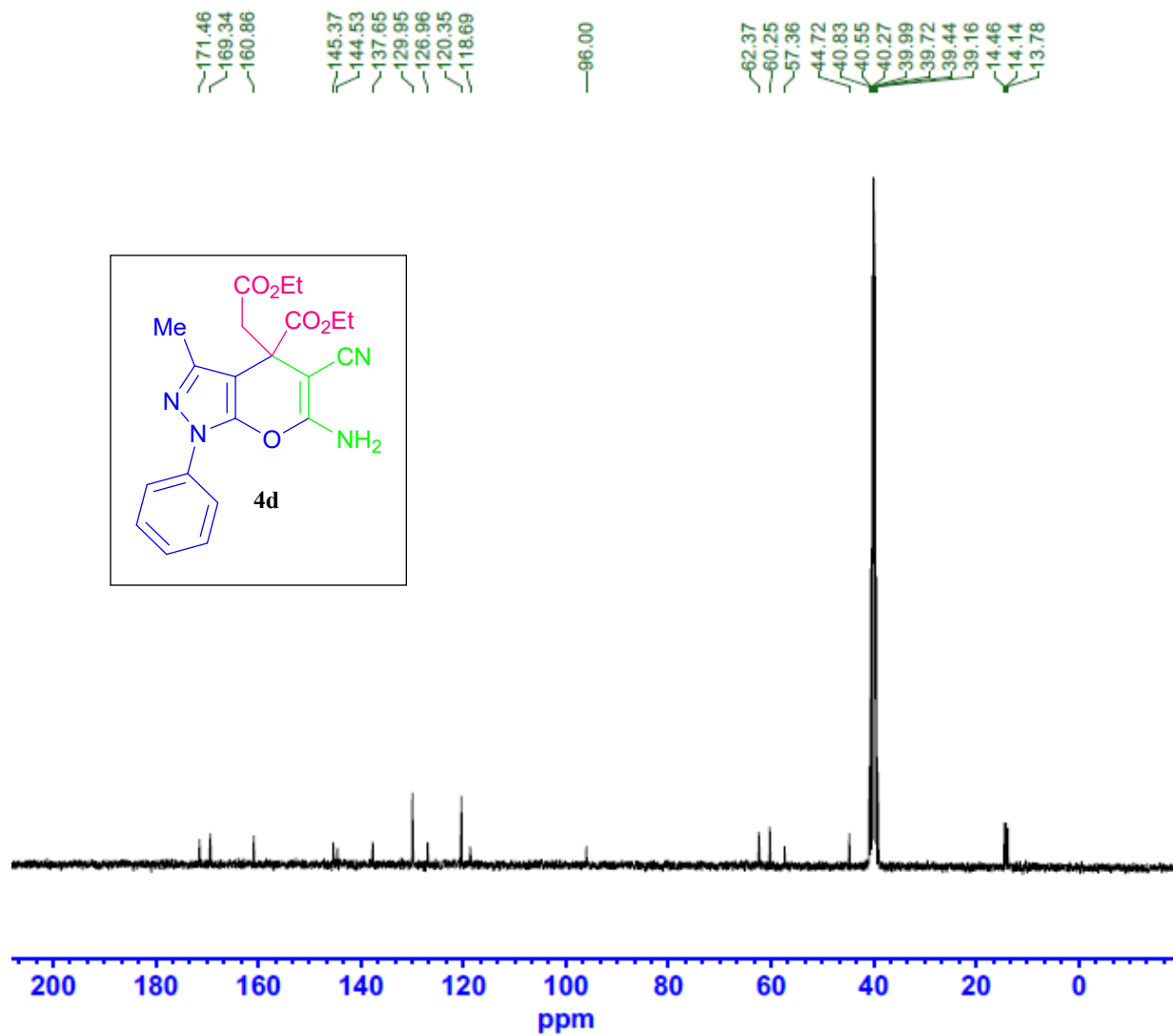
¹H NMR spectrum of compound 4c



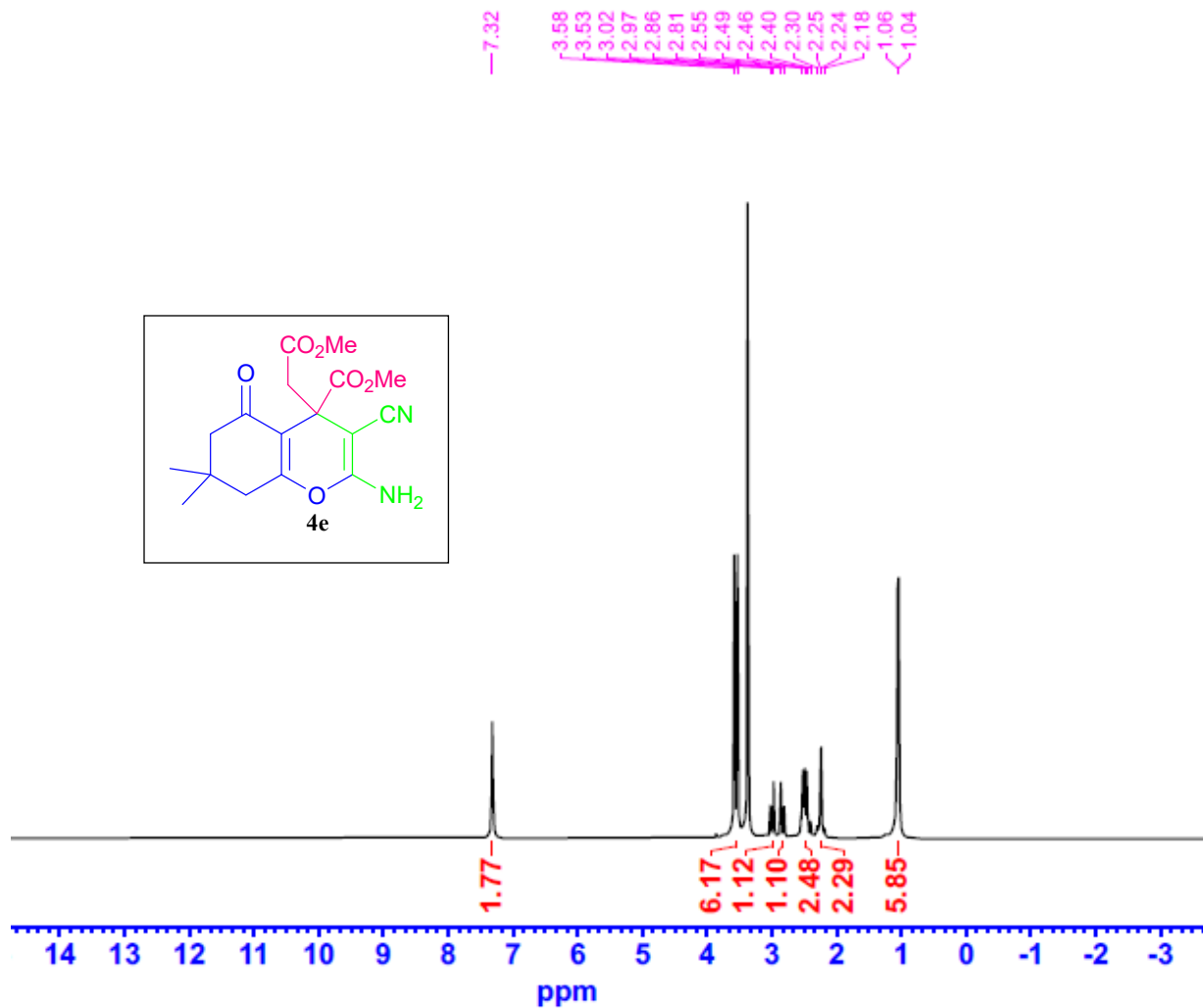
¹³C NMR spectrum of compound 4c



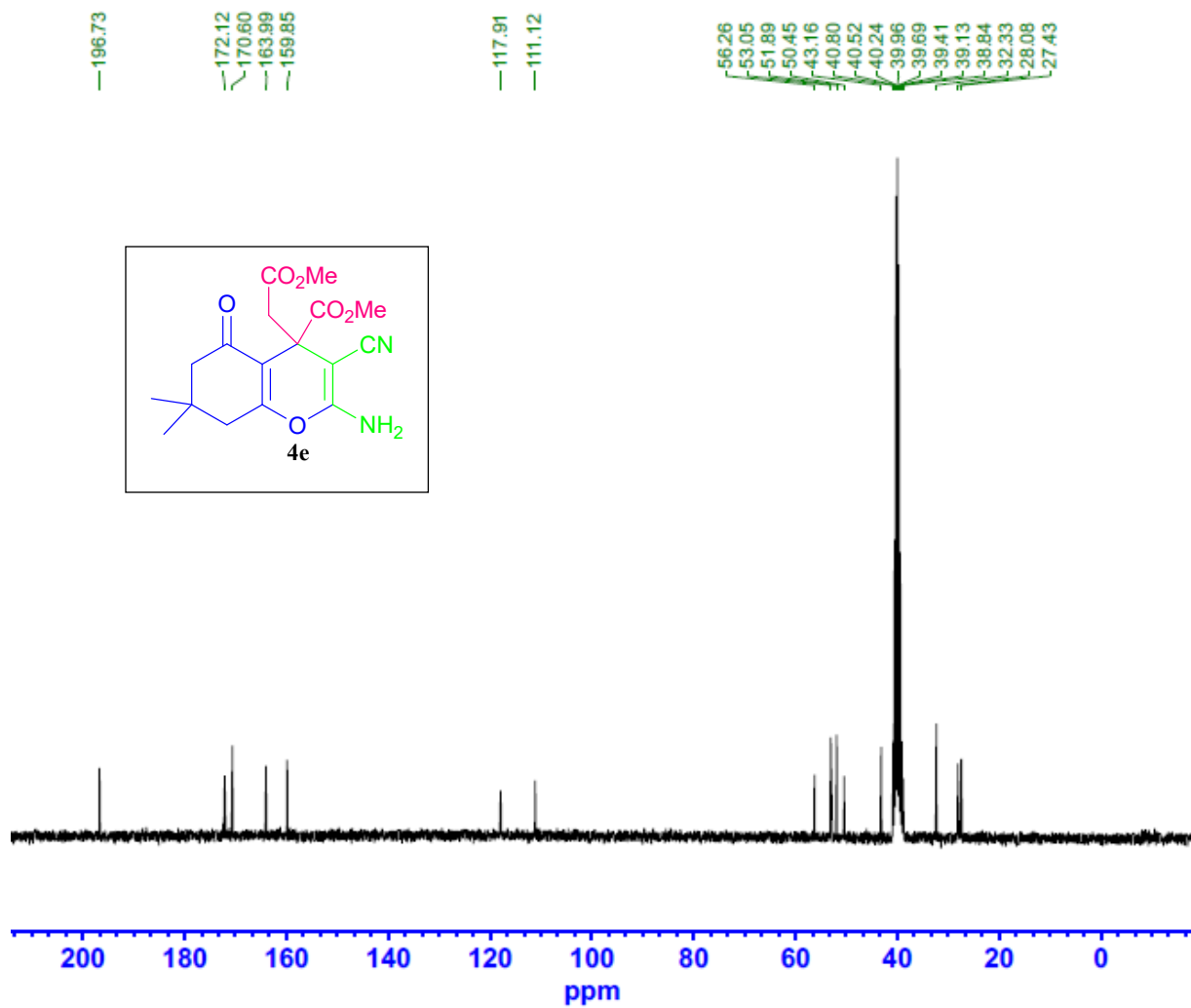
¹H NMR spectrum of compound 4d



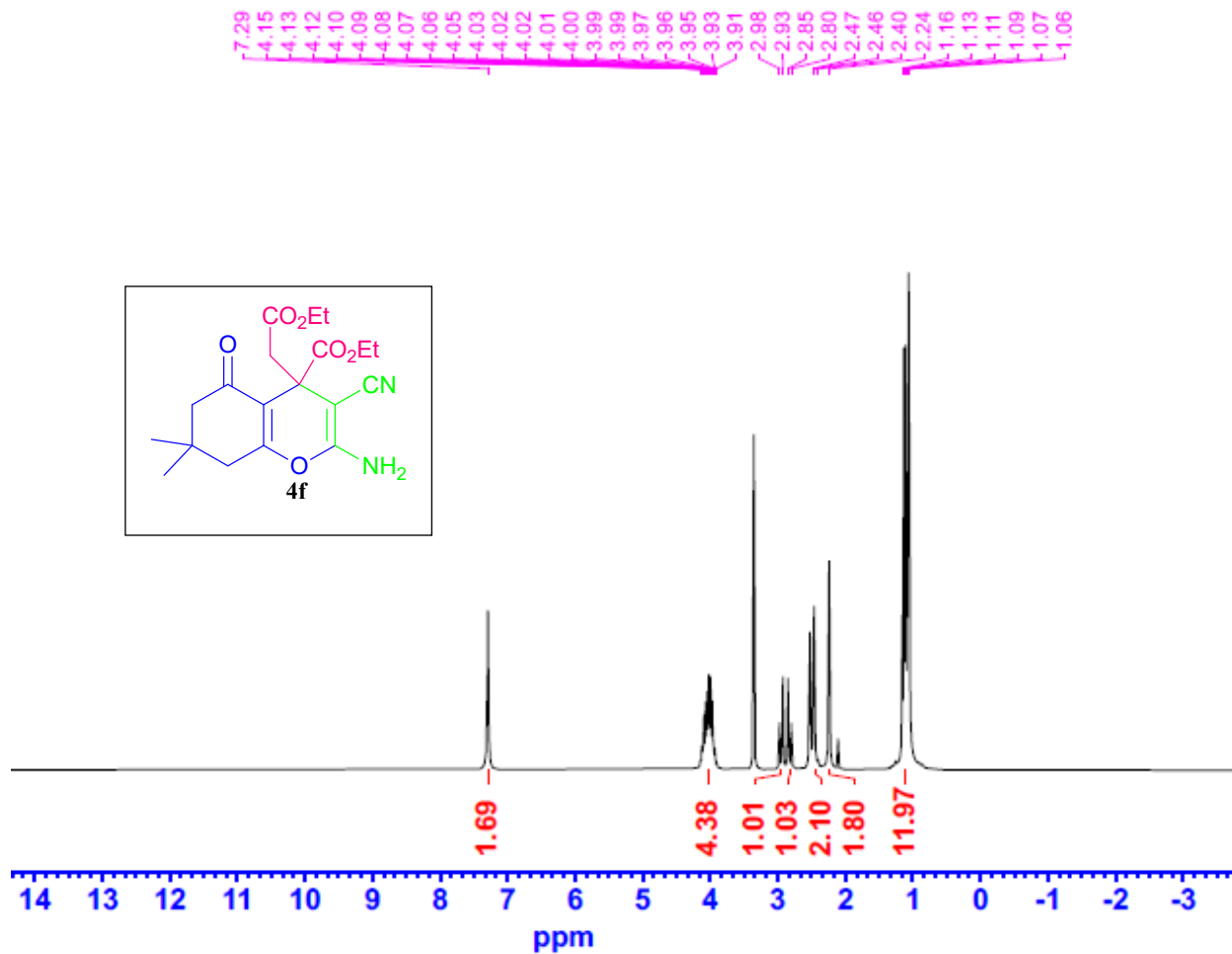
¹³C NMR spectrum of compound 4d



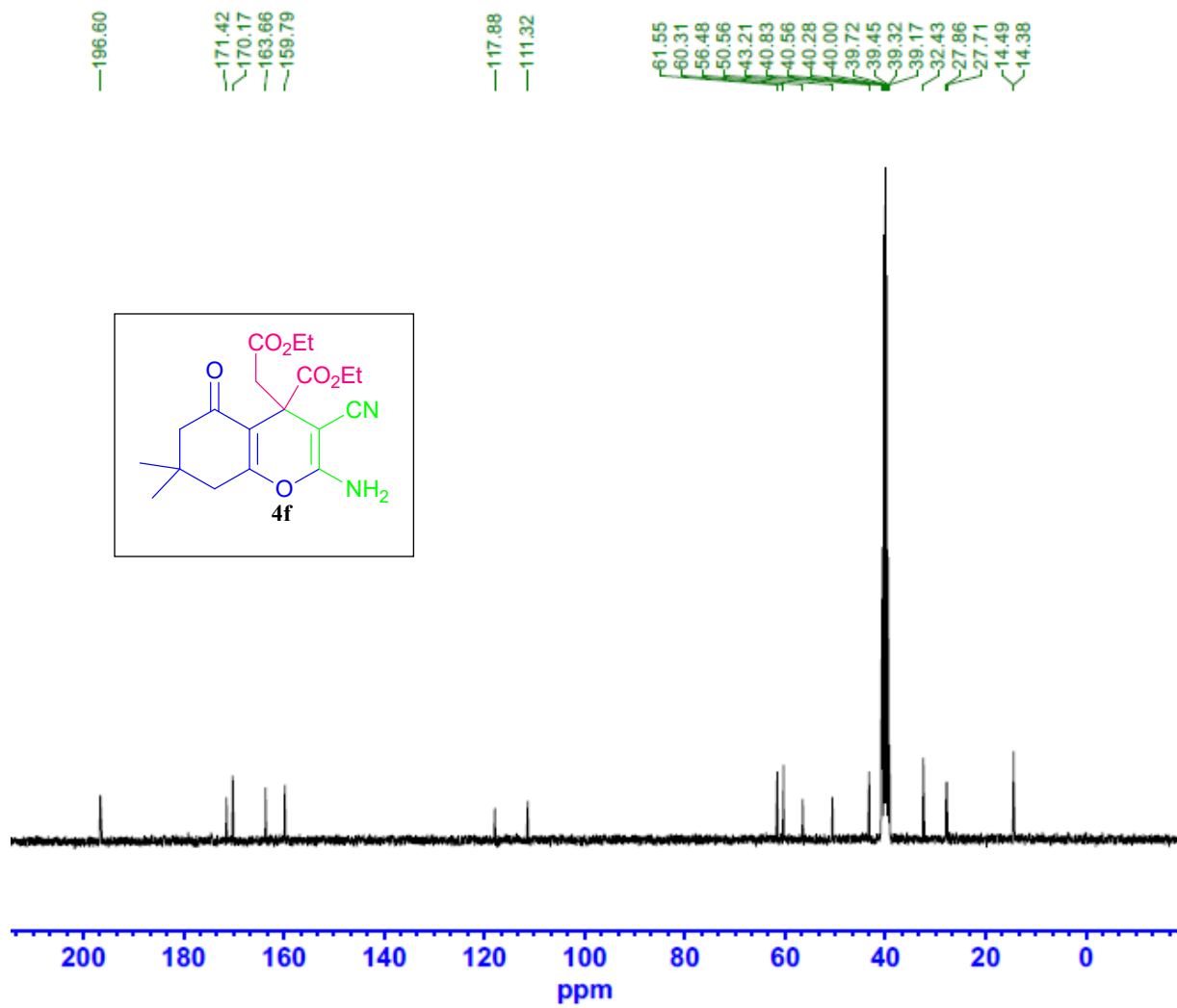
¹H NMR spectrum of compound 4e



^{13}C NMR spectrum of compound 4e



¹H NMR spectrum of compound 4f



¹³C NMR spectrum of compound 4f