Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Magnetically retrievable nano crystalline $CuFe_2O_4$ catalyzed multi-component reaction: A facile and efficient synthesis of functionalized dihydropyrano[2,3-c]pyrazol, pyrano[3,2-c]coumarin and 4H-chromene derivatives in aqueous media

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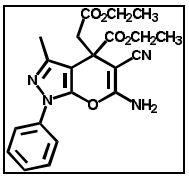
Spectral data of the synthesized compounds:

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



Characteristic: White crystalline solid

Mp: 112-114 ^{0}C

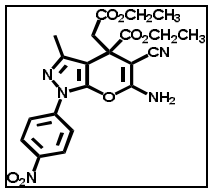
IR (KBr): 1238, 1395, 1646, 1730, 2192, 3341 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (3H, t, J=7.2 Hz), 1.23 (3H, t, J=7.2 Hz), 2.22 (3H, s), 3.03 (1H, d, J=15.6 Hz), 3.13 (1H, d, J=15.6 Hz), 3.93 (2H, q, J=7.2 Hz), 4.14-4.21 (2H, m), 4.76 (2H, s), 7.23 (1H, t, J=7.5 Hz), 7.36 (2H, t, J=7.8 Hz), 7.52 (2H, d, J=7.8 Hz)

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 13.9, 14.1, 40.3, 44.7, 60.5, 62.2, 62.6, 95.5, 117.8, 121.5, 127.0, 129.1, 129.2, 129.3, 137.2, 143.9, 145.7, 159.7, 169.3, 170.8

Anal. Calcd for $C_{21}H_{22}N_4O_5$: C 61.45, H 5.40, N 13.65%. Found: C 61.48, H 5.38, N 13.66%.

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



Characteristic: White crystalline solid

Mp: 190-192 ^{0}C

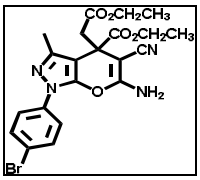
IR (KBr): 1340, 1517, 1661, 1713, 2200, 3373 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (3H, t, J= 7.2 Hz), 1.24 (3H, t, J=7.2 Hz), 2.23 (3H, s), 3.06 (1H, d, J= 15.6 Hz), 3.13 (1H, d, J= 15.6 Hz), 3.96 (2H, q, J=7.2 Hz), 4.17-4.22 (2H, m), 5.02(2H, s), 7.79 (2H, dd, J_1= 7.2 Hz, J_2=1.8 Hz), 8.21 (2H, dd, J_1= 7.2 Hz, J_2=1.8 Hz)

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.0, 14.1, 39.9, 44.5, 60.7, 62.3, 62.8, 97.2, 117.4, 120.1, 125.0, 129.0, 142.3, 144.6, 145.3, 147.6, 159.4, 169.2, 170.5

Anal. Calcd for $C_{21}H_{21}N_5O_7$: C 55.38, H 4.65, N 15.38%. Found: C 55.36, H 4.68, N 15.37%.

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



Characteristic: White crystalline solid

Mp: 194-196 ^{0}C

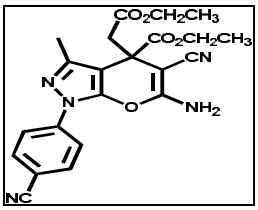
IR (KBr): 1395, 1522, 1660, 1714, 1737, 2199, 3322 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (3H, t, J= 7.2 Hz), 1.28 (3H, t, J= 7.2 Hz), 2.25 (3H, s), 3.08 (1H, d, J=15.6 Hz), 3.16 (1H, d, J=15.6 Hz), 3.98 (2H, q, J=7.2 Hz), 4.19-4.27 (2H, m), 4.88 (2H, s), 7.46-7.54 (4H, m)

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.3, 13.5, 13.6, 39.7, 44.2, 61.1, 61.9, 62.2, 95.5, 117.2, 119.9, 122.0, 122.1, 122.2, 131.9, 135.9, 143.5, 145.6, 159.1, 168.7, 170.2

Anal. Calcd for $C_{21}H_{21}BrN_4O_5$: C 51.55, H 4.33, N 11.45%. Found: C 51.52, H 4.36, N 11.47%.

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



Characteristic: White crystalline solid

Mp: 210-212 ^{0}C

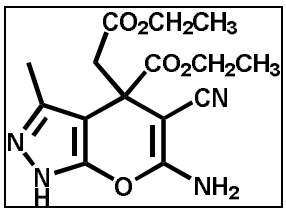
IR (KBr): 1393, 1661, 1715, 2201, 3317 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 1.06 (3H, t, J=7.2 Hz), 1.25 (3H, t, J=7.2 Hz), 2.24 (3H, s), 3.07 (1H, d, J= 15.0 Hz), 3.13 (1H, d, J= 15.0 Hz), 3.96 (2H, q, J= 7.2 Hz), 4.17-4.25 (2H, m), 4.93 (2H, s), 7.66 (2H, d, J= 8.4 Hz), 7.77 (2H, d, J= 8.7 Hz)

^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 18.5, 18.7, 18.9, 49.3, 65.0, 66.5, 67.0, 101.6, 113.7, 117.9, 123.0, 124.7, 129.3, 138.0, 145.8, 149.8, 151.8, 165.3, 173.8, 175.7

Anal. Calcd for $C_{22}H_{21}N_5O_5$: C 60.68, H 4.86, N 16.08%. Found: C 60.65, H 4.89, N 16.06%.

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



Characteristic: White crystalline solid

Mp: 178-180 ^{0}C

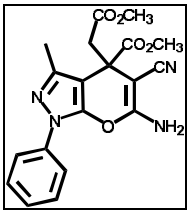
IR (KBr): 1413, 1610, 1666, 1707, 1733, 2194, 3177, 3345 cm^{-1}

^1H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 0.94 (3H, t, J= 7.2 Hz), 1.11 (3H, t, J=7.2 Hz), 2.09 (3H, s), 2.84 (1H, d, J=14.4 Hz), 2.94 (1H, d, J=14.4 Hz), 3.81 (2H, q, J=7.2 Hz), 3.99-4.08 (2H, m), 6.27 (2H, s)

^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 15.7, 18.7, 18.9, 48.9, 62.5, 64.8, 66.6, 99.2, 124.3, 141.3, 159.8, 166.8, 173.9, 176.4

Anal. Calcd for $C_{15}H_{18}N_4O_5$: C 53.89, H 5.43, N 16.76%. Found: C 53.86, H 5.46, N 16.74%.

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



Characteristic: White crystalline solid

Mp: 198-200 ^0C

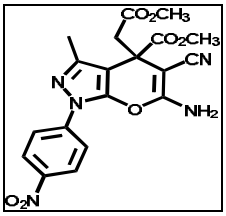
IR (KBr): 1395, 1645, 1737, 2193, 3339 cm^{-1}

^1H NMR (300 MHz, $CDCl_3$): δ 2.20 (3H, s), 3.07 (1H, d, J= 15.9 Hz), 3.16 (1H, d, J= 15.9 Hz), 3.50 (3H, s), 3.73 (3H, s), 4.84 (2H, s), 7.24 (1H, t, J= 7.5 Hz), 7.37 (2H, t, J= 7.8 Hz), 7.53 (2H, d, J= 8.1 Hz)

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 39.9, 44.6, 51.7, 53.3, 62.2, 95.4, 117.8, 121.5, 127.0, 129.2, 130.0, 137.2, 144.0, 145.5, 159.9, 169.7, 171.4

Anal. Calcd for $C_{19}H_{18}N_4O_5$: C 59.68, H 4.74, N 14.65%. Found: C 59.70, H 4.73, N 14.67%.

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



Characteristic: White crystalline solid

Mp: 160-162 ^0C

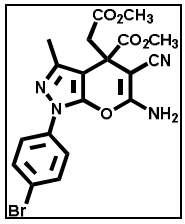
IR (KBr): 1335, 1512, 1597, 1626, 2196 cm^{-1}

^1H NMR (300 MHz, DMSO-d_6): δ 2.08 (3H, s), 2.90 (1H, d, J= 15.6 Hz), 3.04 (1H, d, J= 15.6 Hz), 3.37 (3H, s), 3.61 (3H, s), 7.52 (2H, s), 7.95-8.00 (2H, m), 8.18-8.23 (2H, m)

^{13}C NMR (75 MHz, DMSO-d_6): δ 13.8, 44.4, 52.0, 53.7, 57.1, 97.4, 118.4, 120.0, 125.6, 142.4, 145.1, 145.4, 147.4, 160.8, 169.8, 171.8

Anal. Calcd for $C_{19}H_{17}N_5O_7$: C 53.40, H 4.01, N 16.39%. Found: C 53.43, H 3.98, N 16.37%.

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



Characteristic: White crystalline solid

Mp: 198-200 ^{0}C

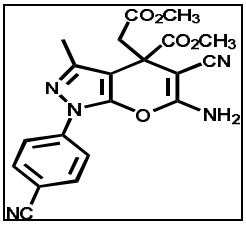
IR (KBr): 1393, 1523, 1660, 1720, 1738, 2196, 3329 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 2.19 (3H, s), 3.07 (1H, d, J= 15.9 Hz), 3.14 (1H, d, J= 15.9 Hz), 3.50 (3H, s), 3.72 (3H, s), 4.91 (2H, s), 7.42-7.50 (4H, m)

^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 12.5, 43.3, 50.4, 52.0, 57.1, 94.8, 117.4, 118.2, 120.9, 122.0, 131.0, 135.6, 143.3, 144.5, 159.7, 168.4, 170.5

Anal. Calcd for $C_{19}H_{17}BrN_4O_5$: C 49.47, H 3.71, N 12.15%. Found: C 49.44, H 3.72, N 12.19%.

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



Characteristic: White crystalline solid

Mp: 184-186 ^{0}C

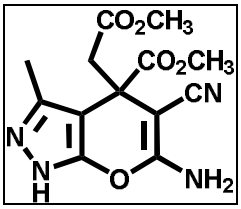
IR (KBr): 1238, 1392, 1524, 1663, 1719, 1742, 2200, 2224, 3392 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 2.07 (3H, s), 2.90 (1H, d, J= 15.6 Hz), 3.03 (1H, d, J=15.6 Hz), 3.37 (3H, s), 3.61 (3H, s), 7.52 (2H, s), 7.81-7.94 (4H, m)

^{13}C NMR (75 MHz, DMSO-d_6): δ 14.5, 34.3, 44.4, 51.9, 53.7, 57.1, 97.2, 108.9, 118.4, 118.9, 119.8, 120.0, 134.2, 145.2, 146.9, 147.0, 160.8, 169.8, 170.0, 171.8

Anal. Calcd for $C_{20}H_{17}N_5O_5$: C 58.97, H 4.21, N 17.19%. Found: C 58.95, H 4.24, N 17.22%.

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



Characteristic: White crystalline solid

Mp: 170-172 ^{0}C

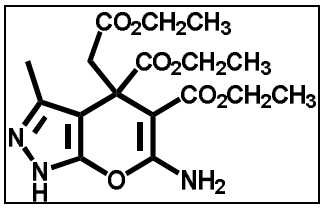
IR (KBr): 1409, 1594, 1731, 2197, 3169 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 2.10 (3H, s), 2.89 (1H, d, J= 15.3 Hz), 3.04 (1H, d, J= 15.3 Hz), 3.42 (3H, s), 3.63 (3H, s), 7.05 (2H, s), 12.23 (1H, s)

^{13}C NMR (75 MHz, DMSO-d_6): δ 14.5, 44.0, 51.8, 53.4, 56.3, 60.2, 94.7, 119.6, 136.4, 155.1, 162.3, 169.8, 172.6

Anal. Calcd for $C_{13}H_{14}N_4O_5$: C 50.98, H 4.61, N 18.29%. Found: C 50.99, H 4.63, N 18.26%.

Diethyl 6-amino-4-(2-ethoxy-2-oxoethyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-4,5-dicarboxylate (5k):



Characteristic: White crystalline solid

Mp: 156-158 ^{0}C

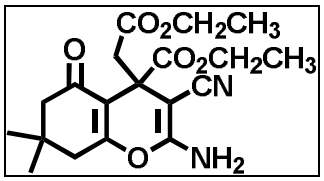
IR (KBr): 1054, 1247, 1700, 1724, 3273 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.82 (3H, t, J= 7.2 Hz), 0.96 (3H, t, J= 7.2 Hz), 1.01 (3H, t, J= 7.2 Hz), 1.96 (3H, s), 2.85 (1H, d, J= 15.6 Hz), 2.99 (1H, d, J= 15.6 Hz), 3.66 (2H, q, J=7.2 Hz), 3.85-3.93 (4H, m), 7.75 (2H, s), 12.00 (1H, s)

^{13}C NMR (75 MHz, DMSO-d_6): δ 10.4, 14.3, 14.4, 14.6, 42.0, 43.8, 59.3, 59.7, 61.2, 75.8, 96.8, 135.6, 154.9, 162.6, 168.5, 170.5, 173.3

Anal. Calcd for $C_{17}H_{23}N_3O_7$: C 53.54, H 6.08, N 11.02%. Found: C 53.55, H 6.05, N 11.04%.

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



Characteristic: White crystalline solid

Mp: 230-232 ^{0}C

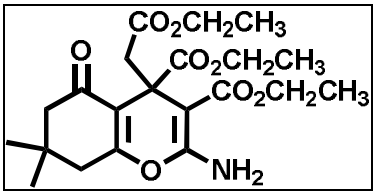
IR (KBr): 1220, 1360, 1650, 1682, 1735, 2199, 2970, 3182 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33-1.51 (12H, m), 2.53 (2H, s), 2.64 (1H, d, J= 17.7 Hz), 2.72 (1H, d, J= 17.7 Hz), 3.34 (1H, d, J= 16.2 Hz), 3.47 (1H, d, J= 16.5 Hz), 4.24-4.51 (4H, m), 5.13 (2H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 14.2, 27.9, 28.0, 32.2, 38.3, 40.7, 42.9, 50.8, 60.3, 60.8, 62.1, 112.0, 116.8, 158.9, 163.0, 170.7, 171.1, 196.3

Anal. Calcd for $C_{19}H_{24}N_2O_6$: C 60.63, H 6.43, N 7.44%. Found: C 60.65, H 6.40, N 7.46%.

Diethyl 2-amino-4-(2-ethoxy-2-oxoethyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4-dicarboxylate (7b):



Characteristic: White crystalline solid

Mp: 240-242 ^{0}C

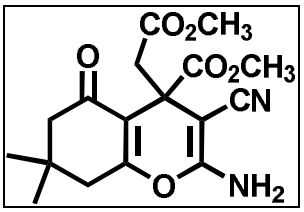
IR (KBr): 1351, 1685, 1735, 2968, 3310, 3421 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09-1.29 (15H, m), 2.26 (2H, s), 2.41 (2H, s), 3.08 (1H, d, J= 15.6 Hz), 3.29 (1H, d, J=15.6 Hz), 3.94-4.22 (6H, m), 6.47 (2H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 14.2, 27.6, 28.5, 31.9, 38.9, 41.0, 43.5, 51.3, 59.9, 60.0, 61.2, 114.3, 159.1, 162.9, 168.4, 171.7, 173.4, 196.4

Anal. Calcd for $C_{21}H_{29}NO_8$: C 59.56, H 6.90, N 3.31%. Found: C 59.58, H 6.91, N 3.33%.

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



Characteristic: White crystalline solid

Mp: 180-182 ^{0}C

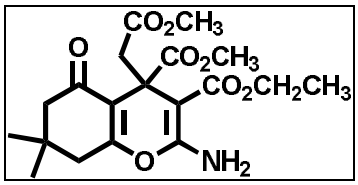
IR (KBr): 1355, 1663, 1727, 2181, 2968, 3415 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.92 (3H, s), 0.93 (3H, s), 2.12 (2H, d, J= 3.3 Hz), 2.33-2.39 (2H, m), 2.71 (1H, d, J= 15.0 Hz), 2.87 (1H, d, J= 15.0 Hz), 3.41 (3H, s), 3.46 (3H, s), 7.17 (2H, s)

^{13}C NMR (75 MHz, DMSO-d_6): δ 27.1, 27.9, 31.9, 42.8, 50.1, 51.5, 52.6, 55.9, 110.7, 117.5, 159.5, 163.6, 170.2, 171.7, 196.3

Anal. Calcd for $C_{17}H_{20}N_2O_6$: C 58.61, H 5.79, N 8.04%. Found: C 58.64, H 5.77, N 8.07%.

3-ethyl 4-methyl 2-amino-4-(2-methoxy-2-oxoethyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4-dicarboxylate (7d):



Characteristic: White crystalline solid

Mp: 138-140 ^{0}C

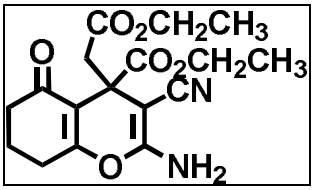
IR (KBr): 1352, 1688, 1743, 3314, 3424 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (6H, s), 1.26 (3H, t, J= 6.9 Hz), 2.27 (2H, s), 2.43 (2H, s), 3.12 (1H, d, J= 15.9 Hz), 3.27 (1H, d, J= 15.9 Hz), 3.55 (3H, s), 3.69 (3H, s), 4.16 (2H, q, J= 6.9 Hz), 6.49 (2H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 27.3, 28.7, 31.8, 38.5, 41.0, 43.4, 51.2, 51.3, 52.3, 59.9, 114.1, 159.1, 163.1, 168.3, 172.1, 174.2, 196.5

Anal. Calcd for $C_{19}H_{25}NO_8$: C 57.71, H 6.37, N 3.54%. Found: C 57.74, H 6.35, N 3.55%.

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



Characteristic: White crystalline solid

Mp: 118-120 ^{0}C

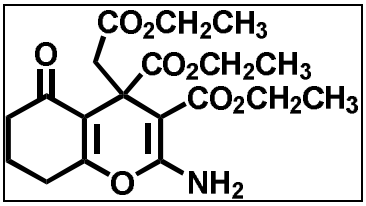
IR (KBr): 1211, 1680, 1735, 2196, 2967, 3202, 3362 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (3H, t, J= 7.2 Hz), 1.24 (3H, t, J= 7.2 Hz), 1.99-2.06 (2H, m), 2.38-2.44 (2H, m), 2.56 (2H, t, J= 6.0 Hz), 3.05 (1H, d, J= 16.2 Hz), 3.18 (1H, d, J= 16.2 Hz), 3.97-4.23 (4H, m), 4.86 (2H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 14.2, 20.0, 27.1, 36.9, 38.6, 43.1, 60.3, 60.9, 62.1, 113.1, 116.8, 158.7, 164.5, 170.6, 171.2, 196.2

Anal. Calcd for $C_{17}H_{20}N_2O_6$: C 58.61, H 5.79, N 8.04%. Found: C 58.64, H 5.77, N 8.06%.

Diethyl 2-amino-4-(2-ethoxy-2-oxoethyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4-dicarboxylate (7f):



Characteristic: White crystalline solid

Mp: 128-130 ^{0}C

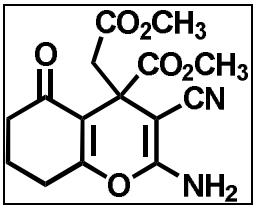
IR (KBr): 1191, 1654, 1688, 1740, 2983, 3379 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.04 (3H, t, J= 7.1 Hz), 1.11-1.17 (6H, m), 1.90 (2H, q, J=6.0 Hz), 2.28 (2H, dd, J_1= 12.9 Hz, J_2= 6.0 Hz), 2.42 (2H, t, J= 6.0 Hz), 2.93 (1H, d, J= 15.3 Hz), 3.12 (1H, d, J= 15.3 Hz), 3.81-4.10 (6H, m), 6.35 (2H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.1, 19.9, 27.4, 37.4, 39.1, 43.6, 59.8, 59.9, 61.1, 115.3, 158.8, 164.3, 168.3, 171.6, 173.7, 196.4

Anal. Calcd for $C_{19}H_{25}NO_8$: C 57.71, H 6.37, N 3.54%. Found: C 57.74, H 6.34, N 3.56%.

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



Characteristic: White crystalline solid

Mp: 136-138 ^{0}C

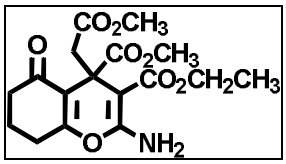
IR (KBr): 1207, 1356, 1667, 1722, 2193, 2954, 3212, 3379 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00-2.08 (2H, m), 2.40-2.45 (2H, m), 2.58 (2H, t, J= 6.3 Hz), 3.08 (1H, d, J= 16.8 Hz), 3.22 (1H, d, J= 16.5 Hz), 3.60 (3H, s), 3.73 (3H, s), 4.78 (2H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 19.9, 27.0, 36.8, 38.1, 43.0, 51.4, 53.1, 112.9, 116.6, 158.7, 164.6, 171.0, 171.6, 196.2

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C 56.25, H 5.04, N 8.75%. Found: C 56.28, H 5.03, N 8.77%.

3-ethyl 4-methyl 2-amino-4-(2-methoxy-2-oxoethyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4-dicarboxylate (7h):



Characteristic: White crystalline solid

Mp: 128-130 ^{0}C

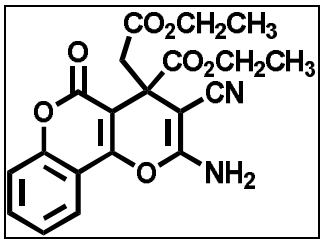
IR (KBr): 1351, 1650, 1686, 1741, 3314, 3427 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16 (3H, t, J= 7.2 Hz), 1.91-1.96 (2H, m), 2.30-2.35 (2H, m), 2.46-2.50 (2H, m), 3.00 (1H, d, J= 15.9 Hz), 3.15 (1H, d, J= 15.9 Hz), 3.47 (3H, s), 3.62 (3H, s), 4.07 (2H, d, J= 7.2 Hz), 6.42 (2H, s)

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 20.0, 27.4, 37.4, 38.7, 43.6, 51.3, 52.3, 59.9, 115.1, 159.1, 164.7, 168.3, 172.0, 174.4, 196.5

Anal. Calcd for $C_{17}H_{21}NO_8$: C 55.58, H 5.76, N 3.81%. Found: C 55.55, H 5.79, N 3.79%.

Ethyl 2-amino-3-cyano-4-(2-ethoxy-2-oxoethyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-4-carboxylate (7i):



Characteristic: White crystalline solid

Mp: 206-208 ^{0}C

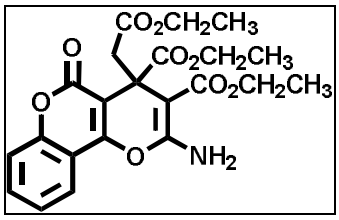
IR (KBr): 1365, 1675, 1726, 2200, 3330, 3407 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 0.95 (3H, t, J= 7.2 Hz), 1.11 (3H, t, J=7.2 Hz), 3.04 (1H, d, J= 16.5 Hz), 3.22 (1H, d, J= 16.5 Hz), 3.84 (2H, q, J= 7.2 Hz), 4.02-4.12 (2H, m), 6.73 (2H, s), 7.26 (2H, t, J= 7.8 Hz), 7.47-7.55 (1H, m), 7.78 (1H, d, J= 7.8 Hz)

^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 18.8, 42.9, 48.7, 62.1, 65.0, 67.0, 107.4, 117.6, 121.4, 122.0, 127.8, 129.4, 137.8, 157.3, 159.4, 164.1, 164.8, 174.7, 175.2

Anal. Calcd for $C_{20}H_{18}N_2O_7$: C 60.30, H 4.55, N 7.03%. Found: C 60.32, H 4.53, N 7.06%.

Diethyl 2-amino-4-(2-ethoxy-2-oxoethyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3,4-dicarboxylate (7j):



Characteristic: White crystalline solid

Mp: 210-212 ^{0}C

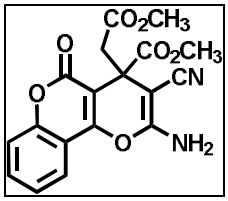
IR (KBr): 1097, 1366, 1694, 1731, 3417 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06 (3H, t, J= 7.2 Hz), 1.24-1.31 (6H, m), 3.35 (1H, d, J= 16.2 Hz), 3.41 (1H, d, J= 16.2 Hz), 3.94 (2H, q, J= 7.2 Hz), 4.11-4.28 (4H, m), 6.75 (2H, s), 7.29-7.33 (2H, m), 7.54-7.59 (1H, m), 7.79-7.81 (1H, m)

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.0, 14.1, 38.4, 44.4, 60.1, 60.2, 61.8, 112.9, 116.7, 122.7, 124.3, 132.7, 152.7, 154.5, 158.7, 159.9, 168.1, 171.3, 172.6

Anal. Calcd for $C_{22}H_{23}NO_9$: C 59.32, H 5.20, N 3.14%. Found: C 59.35, H 5.18, N 3.12%.

Methyl 2-amino-3-cyano-4-(2-methoxy-2-oxoethyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-4-carboxylate (7k):



Characteristic: White crystalline solid

Mp: 206-208 ^{0}C

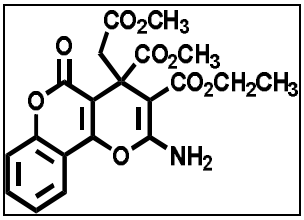
IR (KBr): 1367, 1680, 1738, 2203, 3207 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 3.03 (1H, d, J= 16.5 Hz), 3.14 (1H, d, J= 16.5 Hz), 3.41 (3H, s), 3.59 (3H, s), 7.13 (2H, s), 7.26-7.32 (2H, m), 7.52-7.58 (1H, m), 7.82 (1H, dd, J_1= 7.9 Hz, J_2= 1.2 Hz)

^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 36.3, 42.5, 50.2, 51.8, 55.0, 100.9, 111.5, 115.3, 115.9, 121.8, 123.5, 131.9, 151.2, 153.4, 158.1, 158.7, 168.9, 169.6

Anal. Calcd for $C_{18}H_{14}N_2O_7$: C 58.38, H 3.81, N 7.56%. Found: C 58.36, H 3.84, N 7.53%.

3-ethyl 4-methyl 2-amino-4-(2-methoxy-2-oxoethyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3,4-dicarboxylate (7l):



Characteristic: White crystalline solid

Mp: 212-214 ^{0}C

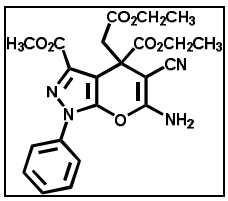
IR (KBr): 1097, 1365, 1693, 1735, 3310, 3429 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (3H, t, J= 6.9 Hz), 3.41 (2H, s), 3.51 (3H, s), 3.75 (3H, s), 4.16-4.25 (2H, m), 6.76 (2H, s), 7.31-7.36 (2H, m), 7.56-7.62 (1H, m), 7.86 (1H, dd, J_1= 8.1 Hz, J_2= 1.2 Hz)

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 37.4, 43.8, 51.0, 52.4, 59.9, 104.6, 112.5, 116.3, 122.3, 124.0, 132.4, 152.3, 158.5, 159.5, 167.6, 171.3, 172.7

Anal. Calcd for $C_{20}H_{19}NO_9$: C 57.55, H 4.59, N 3.36%. Found: C 57.57, H 4.56, N 3.39%.

4-ethyl 3-methyl 6-amino-5-cyano-4-(2-ethoxy-2-oxoethyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9a):



Characteristic: White crystalline solid

Mp: 158-160 ^{0}C

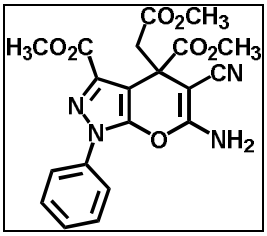
IR (KBr): 1230, 1392, 1654, 1724, 2195, 3334 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.89 (3H, t, J= 7.2 Hz), 1.07 (3H, t, J= 7.2 Hz), 3.01 (1H, d, J= 15.0 Hz), 3.15 (1H, d, J= 15.0 Hz), 3.77-3.83 (5H, m), 4.08 (2H, q, J= 7.2 Hz), 7.45 (1H, d, J= 7.5 Hz), 7.54 (4H, t, J= 7.5 Hz), 7.76 (2H, d, J= 7.8 Hz)

^{13}C NMR (75 MHz, DMSO-d_6): δ 14.1, 14.4, 44.6, 52.4, 57.1, 60.2, 62.0, 100.6, 117.9, 121.8, 121.9, 128.7, 130.2, 136.9, 138.3, 145.5, 160.7, 161.8, 169.8, 170.6

Anal. Calcd for $C_{22}H_{22}N_4O_7$: C 58.15, H 4.88, N 12.33%. Found: C 58.18, H 4.86, N 12.35%.

Dimethyl 6-amino-5-cyano-4-(2-methoxy-2-oxoethyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9b):



Characteristic: White crystalline solid

Mp: 170-172 ^{0}C

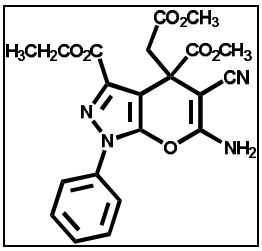
IR (KBr): 1238, 1402, 1660, 1728, 2202, 3324, 3401 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.06 (1H, d, J= 16.2 Hz), 3.17 (1H, d, J= 16.2 Hz), 3.39 (3H, s), 3.59 (3H, s), 3.77 (3H, s), 7.46 (1H, d, J= 7.2 Hz), 7.52-7.59 (4H, m), 7.77 (2H, d, J= 7.8 Hz)

^{13}C NMR (75 MHz, DMSO-d_6): δ 44.4, 51.8, 52.5, 53.3, 56.8, 100.6, 117.6, 122.0, 128.8, 130.2, 136.9, 138.2, 145.6, 160.9, 161.9, 170.3, 171.2

Anal. Calcd for $C_{20}H_{18}N_4O_7$: C 56.34, H 4.26, N 13.14%. Found: C 56.36, H 4.23, N 13.15%.

3-ethyl 4-methyl 6-amino-5-cyano-4-(2-methoxy-2-oxoethyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9c):



Characteristic: White crystalline solid

Mp: 210-212 ^{0}C

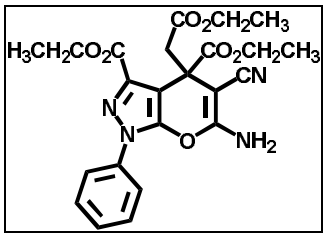
IR (KBr): 1402, 1662, 1728, 2202, 3398 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.23 (3H, t, J= 7.2 Hz), 3.07 (1H, d, J=15.9 Hz), 3.18 (1H, d, J=15.9 Hz), 3.39 (3H, s), 3.59 (3H, s), 4.23 (2H, q, J= 7.2 Hz), 7.46 (1H, d, J= 7.2 Hz), 7.55 (4H, t, J= 7.8 Hz), 7.76 (2H, d, J=7.5 Hz)

^{13}C NMR (75 MHz, DMSO-d_6): δ 14.4, 31.1, 44.4, 51.8, 53.3, 56.8, 61.6, 100.4, 117.9, 122.0, 128.8, 130.2, 136.9, 138.4, 145.6, 160.9, 161.3, 170.3, 171.2

Anal. Calcd for $C_{21}H_{20}N_4O_7$: C 57.27, H 4.58, N 12.72%. Found: C 57.24, H 4.59, N 12.70%

Diethyl 6-amino-5-cyano-4-(2-ethoxy-2-oxoethyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9d):



Characteristic: White crystalline solid

Mp: 136-138 ^{0}C

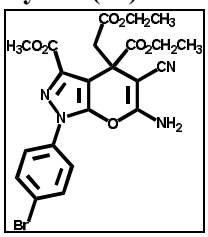
IR (KBr): 1402, 1660, 1732, 2200, 3324, 3399 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (3H, t, J= 7.2 Hz), 1.26 (3H, t, J= 7.2 Hz), 1.38 (3H, t, J= 7.2 Hz), 3.30 (1H, d, J= 16.5 Hz), 3.44 (1H, d, J= 16.5 Hz), 3.91-3.98 (2H, m), 4.19-4.27 (2H, m), 4.35-4.42 (2H, m), 5.12 (2H, s), 7.39-7.50 (3H, m), 7.68 (2H, d, J= 8.1 Hz)

^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 14.1, 14.2, 39.6, 44.5, 60.3, 61.6, 61.8, 62.3, 100.4, 117.1, 122.6, 128.4, 129.3, 136.7, 138.7, 145.1, 159.8, 161.5, 170.2, 170.3

Anal. Calcd for $C_{23}H_{24}N_4O_7$: C 58.97, H 5.16, N 11.96%. Found: C 58.95, H 5.18, N 11.98%.

4-ethyl 3-methyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(2-ethoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9e):



Characteristic: White crystalline solid

Mp: 162-164 ^{0}C

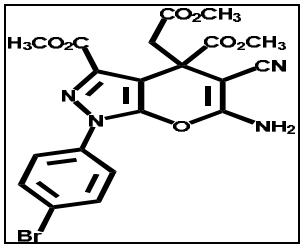
IR (KBr): 1277, 1570, 1733, 2202, 3401 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.84 (3H, t, J= 7.2 Hz), 1.02 (3H, t, J= 7.2 Hz), 2.96 (1H, d, J= 15.3 Hz), 3.10 (1H, d, J= 15.3 Hz), 3.73-3.78 (5H, m), 4.03 (2H, q, J= 7.2 Hz), 7.55 (2H, s), 7.69 (4H, dd, J_1= 14.1 Hz, J_2= 9.3 Hz)

^{13}C NMR (75 MHz, DMSO-d_6): δ 14.1, 14.4, 44.5, 52.4, 52.5, 56.9, 60.3, 62.0, 100.8, 117.8, 121.3, 123.5, 127.9, 131.8, 133.1, 136.1, 138.6, 145.6, 159.4, 160.7, 169.8, 170.5

Anal. Calcd for $C_{22}H_{21}BrN_4O_7$: C 49.54, H 3.97, 10.51%. Found: C 49.58, H 3.95, 10.49%.

Dimethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(2-methoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9f):



Characteristic: White crystalline solid

Mp: 220-222 ^{0}C

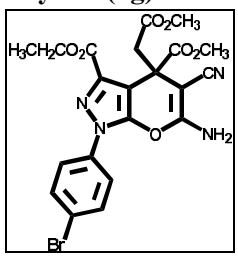
IR (KBr): 1233, 1404, 1661, 1736, 2201, 3394 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.02 (1H, d, J= 15.9 Hz), 3.12 (1H, d, J= 16.2 Hz), 3.34 (3H, s), 3.55 (3H, s), 3.73 (3H, s), 7.57 (2H, s), 7.70 (4H, dd, J_1= 13.5 Hz, J_2= 9.0 Hz)

^{13}C NMR (75 MHz, DMSO-d_6): δ 43.9, 51.4, 52.1, 52.9, 56.3, 100.3, 117.4, 121.0, 123.3, 132.6, 135.7, 138.0, 145.2, 160.4, 161.3, 169.9, 170.7

Anal. Calcd for $C_{20}H_{17}BrN_4O_7$: C 47.54, H 3.39, 11.09%. Found: C 47.58, H 3.36, 11.11%.

3-ethyl 4-methyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(2-methoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9g):



Characteristic: White crystalline solid

Mp: 216-218 ^{0}C

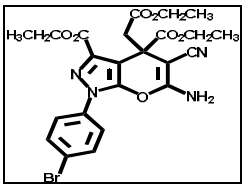
IR (KBr): 1154, 1403, 1660, 1734, 2200, 3403 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.89 (3H, t, J= 7.2 Hz), 3.02 (1H, d, J= 16.2 Hz), 3.13 (1H, d, J= 16.2 Hz), 3.34 (3H, s), 3.54 (3H, s), 4.11 (2H, q, J= 7.2 Hz), 7.56 (2H, s), 7.66-7.73 (4H, m)

^{13}C NMR (75 MHz, DMSO-d_6): δ 14.4, 30.1, 44.4, 51.8, 53.3, 56.8, 61.7, 100.5, 117.8, 121.4, 123.8, 133.1, 136.1, 138.8, 145.6, 160.8, 161.2, 170.3, 171.4

Anal. Calcd for $C_{21}H_{19}BrN_4O_7$: C 48.57, H 3.69, 10.79%. Found: C 48.53, H 3.72, 10.81%.

Diethyl 6-amino-1-(4-bromophenyl)-5-cyano-4-(2-ethoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9h):



Characteristic: White crystalline solid

Mp: 176-178 ^{0}C

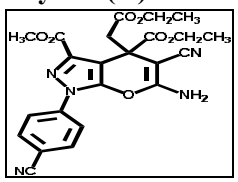
IR (KBr): 1392, 1655, 1742, 2201, 3400 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.84 (3H, t, J= 7.2 Hz), 1.03 (3H, t, J= 7.2 Hz), 1.19 (3H, t, J= 7.2 Hz), 2.97 (1H, d, J= 15.0 Hz), 3.12 (1H, d, J= 15.0 Hz), 3.77 (2H, q, J= 7.2 Hz), 3.96-4.23 (4H, m), 7.55 (2H, s), 7.66-7.73 (4H, m)

^{13}C NMR (75 MHz, DMSO-d_6): δ 14.1, 14.4, 14.5, 44.6, 57.1, 60.2, 61.6, 61.9, 100.6, 117.8, 121.4, 123.6, 129.9, 133.1, 136.1, 139.0, 145.5, 160.6, 161.2, 169.8, 170.5

Anal. Calcd for $C_{23}H_{23}BrN_4O_7$: C 50.47, H 4.24, 10.24%. Found: C 50.44, H 4.28, 10.26%.

4-ethyl 3-methyl 6-amino-5-cyano-1-(4-cyanophenyl)-4-(2-ethoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9i):



Characteristic: White crystalline solid

Mp: 180-182 ^{0}C

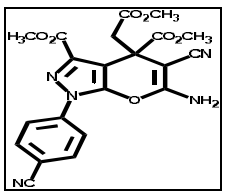
IR (KBr): 1392, 1519, 1665, 1725, 2202, 2231, 3206, 3321, 3384 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.92 (3H, t, J= 7.2 Hz), 1.10 (3H, t, J= 7.2 Hz), 3.03 (1H, d, J= 15.0 Hz), 3.18 (1H, d, J= 15.0 Hz), 3.82-3.86 (5H, m), 4.11 (2H, q, J= 7.2 Hz), 7.71 (2H, s), 8.06 (4H, dd, J_1= 15.9 Hz, J_2= 6.0 Hz)

^{13}C NMR (75 MHz, DMSO-d_6): δ 14.1, 14.4, 44.4, 52.6, 56.9, 60.3, 62.1, 101.2, 110.9, 117.4, 118.5, 121.6, 134.5, 139.4, 140.2, 146.0, 160.6, 161.6, 169.8, 170.4

Anal. Calcd for $C_{23}H_{21}N_5O_7$: C 57.62, H 4.41, 14.61%. Found: C 57.65, H 4.39, 14.63%.

Dimethyl 6-amino-5-cyano-1-(4-cyanophenyl)-4-(2-methoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9j):



Characteristic: White crystalline solid

Mp: 208-210 ^{0}C

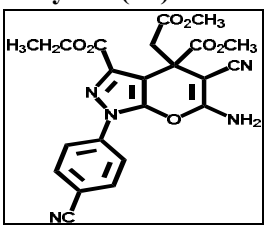
IR (KBr): 1236, 1391, 1661, 1741, 2200, 2231 3208, 3323, 3383 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.02 (1H, d, J= 16.2 Hz), 3.12 (1H, d, J= 16.2 Hz), 3.35 (3H, s), 3.55 (3H, s), 3.74 (3H, s), 7.65 (2H, s), 7.99 (4H, dd, J_1= 15.3 Hz, J_2= 8.7 Hz)

^{13}C NMR (75 MHz, DMSO-d_6): δ 44.3, 51.9, 52.7, 53.4, 56.7, 101.2, 110.9, 117.8, 118.6, 121.7, 134.5, 139.3, 140.3, 146.2, 160.7, 161.6, 170.3, 171.1

Anal. Calcd for $C_{21}H_{17}N_5O_7$: C 55.88, H 3.80, 15.52%. Found: C 55.91, H 3.78, 15.55%.

3-ethyl 4-methyl 6-amino-5-cyano-1-(4-cyanophenyl)-4-(2-methoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9k):



Characteristic: White crystalline solid

Mp: 200-202 ^{0}C

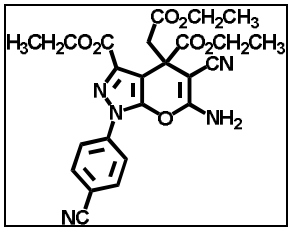
IR (KBr): 1389, 1662, 1738, 2200, 2230, 3211, 3324, 3393 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.27 (3H, t, J= 6.9 Hz), 3.10 (1H, d, J= 16.2 Hz), 3.21 (1H, d, J= 16.2 Hz), 3.42 (3H, s), 3.62 (3H, s), 4.30 (2H, q, J= 6.9 Hz), 7.72 (2H, s), 8.06 (4H, dd, J_1= 13.2 Hz), J_2= 9.0 Hz)

^{13}C NMR (75 MHz, DMSO-d_6): δ 14.4, 44.3, 51.9, 53.3, 56.7, 61.8, 100.9, 110.9, 117.8, 118.6, 121.8, 134.5, 139.6, 140.2, 146.1, 160.7, 161.1, 170.3, 171.0

Anal. Calcd for $C_{22}H_{19}N_5O_7$: C 56.77, H 4.11, 15.05%. Found: C 56.79, H 4.08, 15.08%.

Diethyl 6-amino-5-cyano-1-(4-cyanophenyl)-4-(2-ethoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9l):



Characteristic: White crystalline solid

Mp: 204-206 ^{0}C

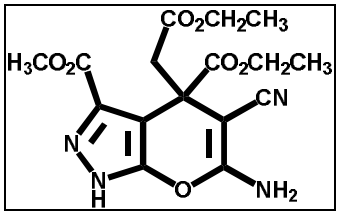
IR (KBr): 1392, 1655, 1720, 1743, 2202, 2231, 3385 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.92 (3H, t, J= 7.2 Hz), 1.10 (3H, t, J= 7.2 Hz), 1.27 (3H, t, J= 7.2 Hz), 3.06 (1H, d, J= 15.3 Hz), 3.20 (1H, d, J= 15.3 Hz), 3.85 (2H, q, J= 6.9 Hz), 4.04-4.16 (2H, m), 4.28-4.32 (2H, m), 7.70 (2H, s), 8.06 (4H, dd, J_1= 15.9 Hz, J_2= 9.0 Hz)

^{13}C NMR (75 MHz, DMSO-d_6): δ 14.1, 14.3, 14.4, 44.5, 57.0, 60.3, 61.8, 62.1, 101.0, 110.9, 117.7, 118.6, 121.6, 134.5, 139.7, 140.3, 146.0, 160.6, 161.1, 169.8, 170.4

Anal. Calcd for $C_{24}H_{23}N_5O_7$: C 58.41, H 4.70, N 14.19%. Found: C 58.43, H 4.73, N 14.16%.

4-ethyl 3-methyl 6-amino-5-cyano-4-(2-ethoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9m):



Characteristic: White crystalline solid

Mp: 178- 180 ^{0}C

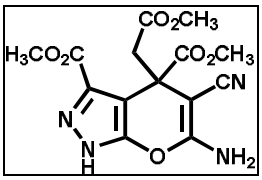
IR (KBr): 1224, 1399, 1637, 1706, 2198 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 0.93 (3H, t, J= 7.1 Hz), 1.05 (3H, t, J= 7.1 Hz), 3.02 (1H, d, J= 15.3 Hz), 3.08 (1H, d, J= 16.2 Hz), 3.73-3.80 (5H, m), 3.94- 4.07 (2H, m), 6.59 (2H, s)

^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 13.7, 13.8, 43.6, 51.9, 56.2, 59.6, 59.7, 61.4, 101.8, 118.3, 128.6, 155.4, 158.4, 161.7, 169.3, 170.5

Anal. Calcd for $C_{16}H_{18}N_4O_7$: C 50.79, H 4.80, N 14.81%. Found: C 50.82, H 4.77, N 14.83%.

Dimethyl 6-amino-5-cyano-4-(2-methoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9n):



Characteristic: White crystalline solid

Mp: 220-222 ^{0}C

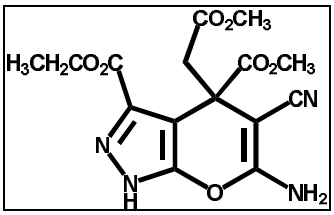
IR (KBr): 1259, 1327, 1400, 1654, 1724, 2203, 3214, 3313, 3380 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.02 (1H, d, J= 15.9 Hz), 3.12 (1H, d, J= 15.9 Hz), 3.36 (3H, s), 3.55 (3H, s), 3.77 (3H, s), 7.26 (2H, s), 13.80 (1H, s)

^{13}C NMR (75 MHz, DMSO-d_6): δ 43.8, 51.7, 52.7, 53.2, 55.8, 102.2, 118.6, 128.9, 155.8, 158.8, 162.1, 170.1, 171.6

Anal. Calcd for $C_{14}H_{14}N_4O_7$: C 48.00, H 4.03, N 15.99%. Found: C 48.03, H 4.00, N 16.02%.

3-ethyl 4-methyl 6-amino-5-cyano-4-(2-methoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9o):



Characteristic: White crystalline solid

Mp: 250-252 ^{0}C

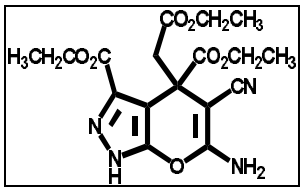
IR (KBr): 1233, 1401, 1648, 1718, 2201, 3218, 3318, 3411 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d$_6$): δ 1.74 (3H, t, J= 7.2 Hz), 2.99 (1H, d, J= 15.9 Hz), 3.09 (1H, d, J= 15.9 Hz), 3.32 (3H, s), 3.51 (3H, s), 4.19 (2H, q, J= 7.2 Hz), 7.21 (2H, s), 13.73 (1H, s)

^{13}C NMR (75 MHz, DMSO-d$_6$): δ 14.1, 43.7, 51.5, 53.1, 55.6, 61.8, 101.6, 118.5, 129.1, 155.6, 158.3. 161.9, 170.0, 171.4

Anal. Calcd for $C_{15}H_{16}N_4O_7$: C 49.45, H 4.43, N 15.38%. Found: C 49.48, H 4.45, N 15.35%.

Diethyl 6-amino-5-cyano-4-(2-ethoxy-2-oxoethyl)-1,4-dihydropyrano[2,3-c]pyrazole-3,4-dicarboxylate (9p):



Characteristic: White crystalline solid

Mp: 202-204 ^{0}C

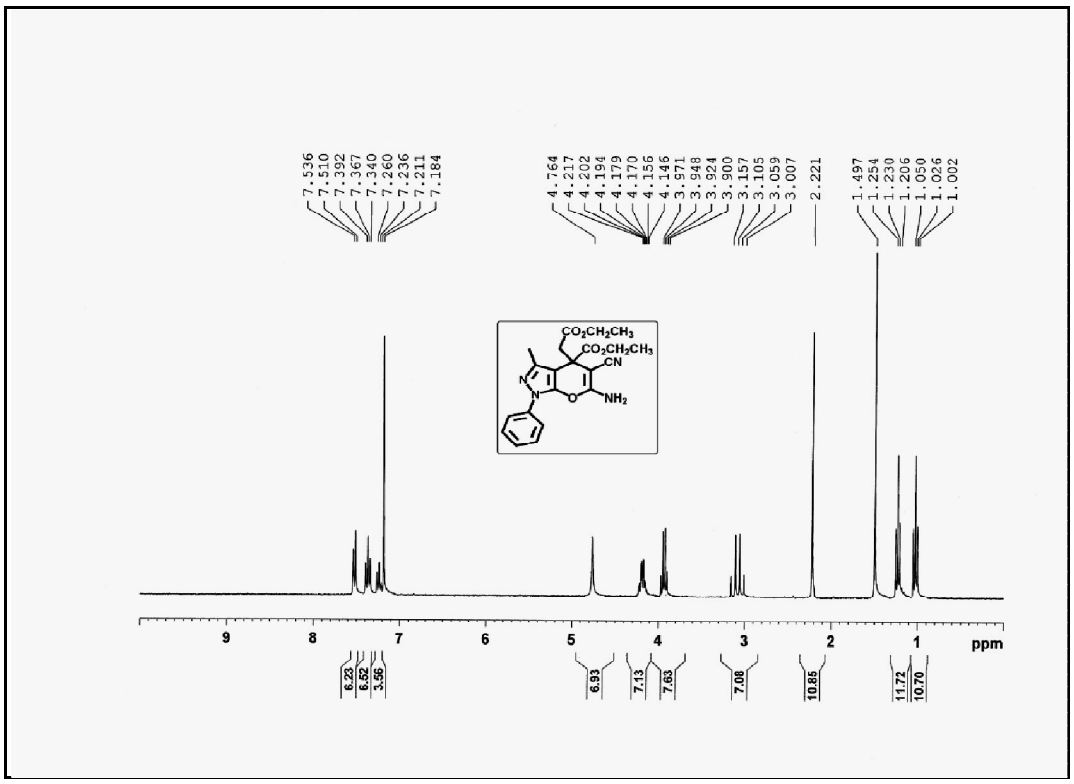
IR (KBr): 1399, 1637, 1718, 1748, 2202, 3214, 3318, 3426 cm^{-1}

^{1}H NMR (300 MHz, DMSO-d$_6$): δ 0.86 (3H, t, J= 7.2 Hz), 1.00 (3H, t, J= 7.2 Hz), 1.17 (3H, t, J= 7.2 Hz), 2.94 (1H, d, J= 15.0 Hz), 3.06 (1H, d, J= 15.0 Hz), 3.75 (2H, q, J= 7.2 Hz), 3.97-4.02 (2H, m), 4.20 (2H, t, J= 7.2 Hz), 7.19 (2H, s), 13.73 (1H, s)

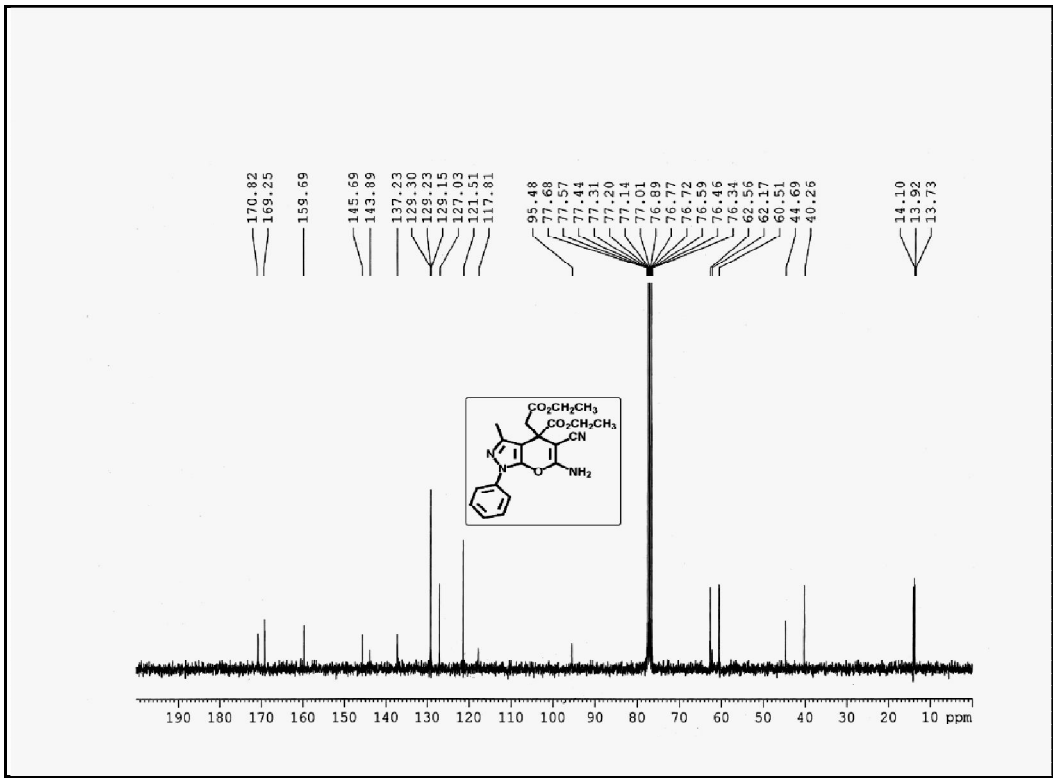
^{13}C NMR (75 MHz, DMSO-d$_6$): δ 14.1, 14.3, 14.4, 44.0, 56.1, 60.1, 61.8, 61.9, 101.8, 118.6, 129.4, 155.7, 158.5, 161.9, 169.7, 170.9

Anal. Calcd for $C_{17}H_{20}N_4O_7$: C 52.04, H 5.14, N 14.28%. Found: C 52.06, H 5.11, N 14.30.

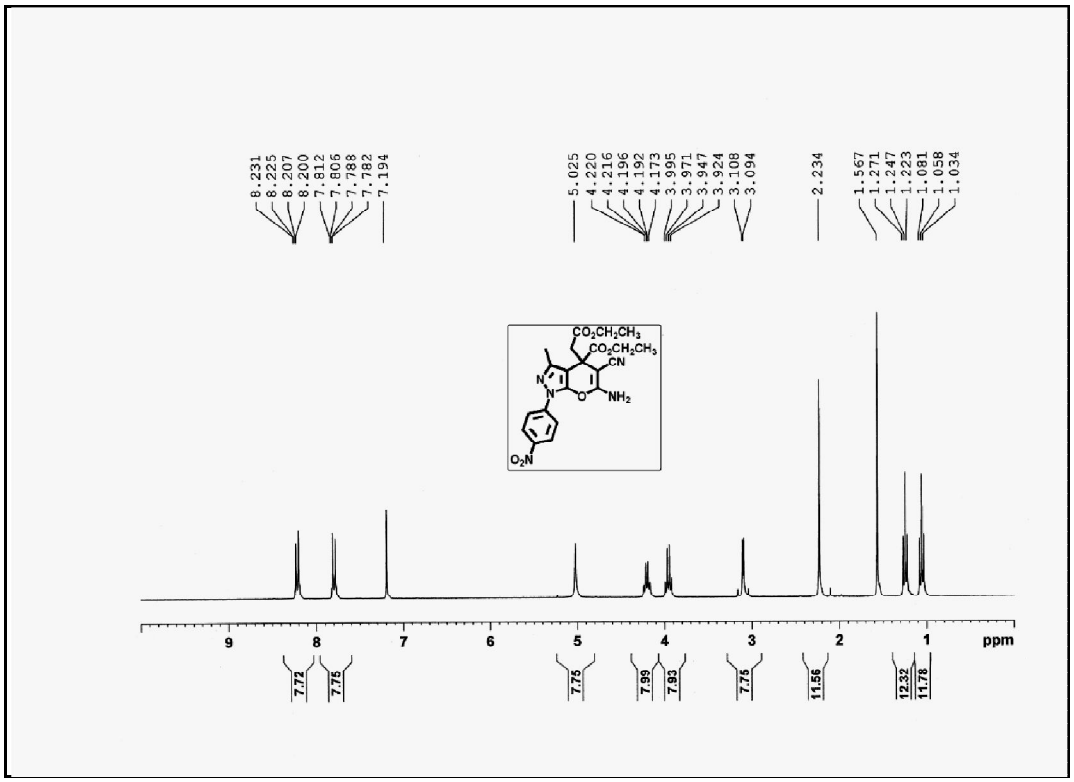
^{1}H and ^{13}C NMR spectra of the synthesized compounds:



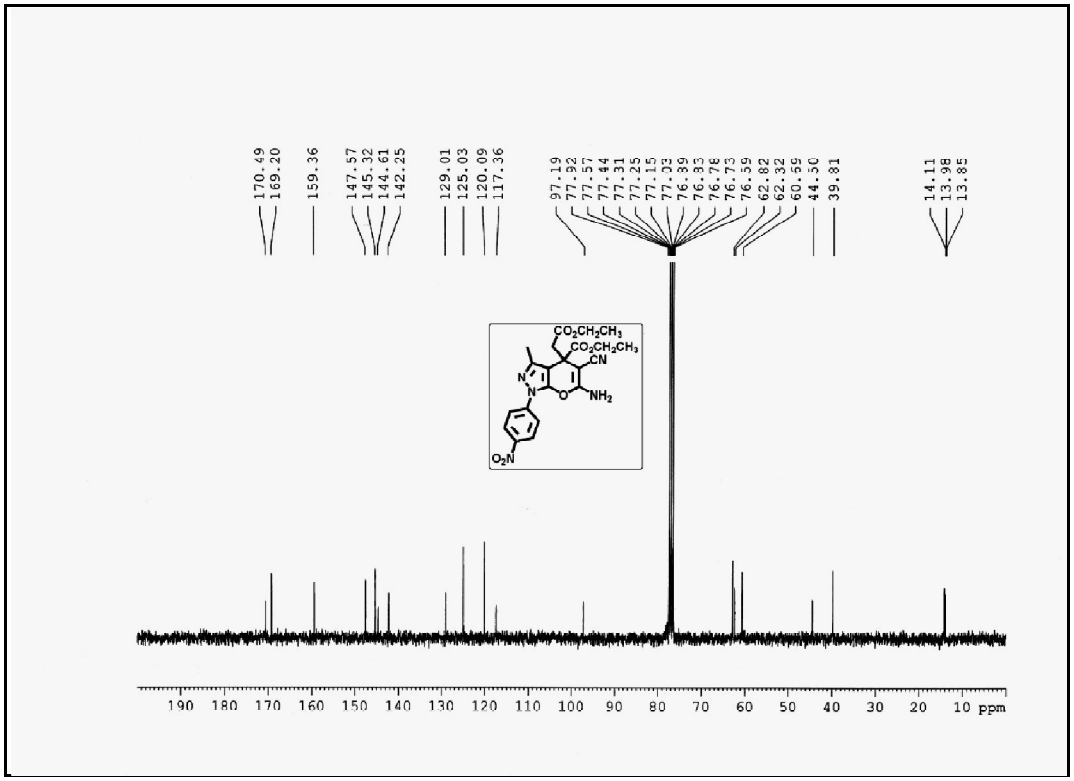
^{1}H NMR spectrum of the product 5a



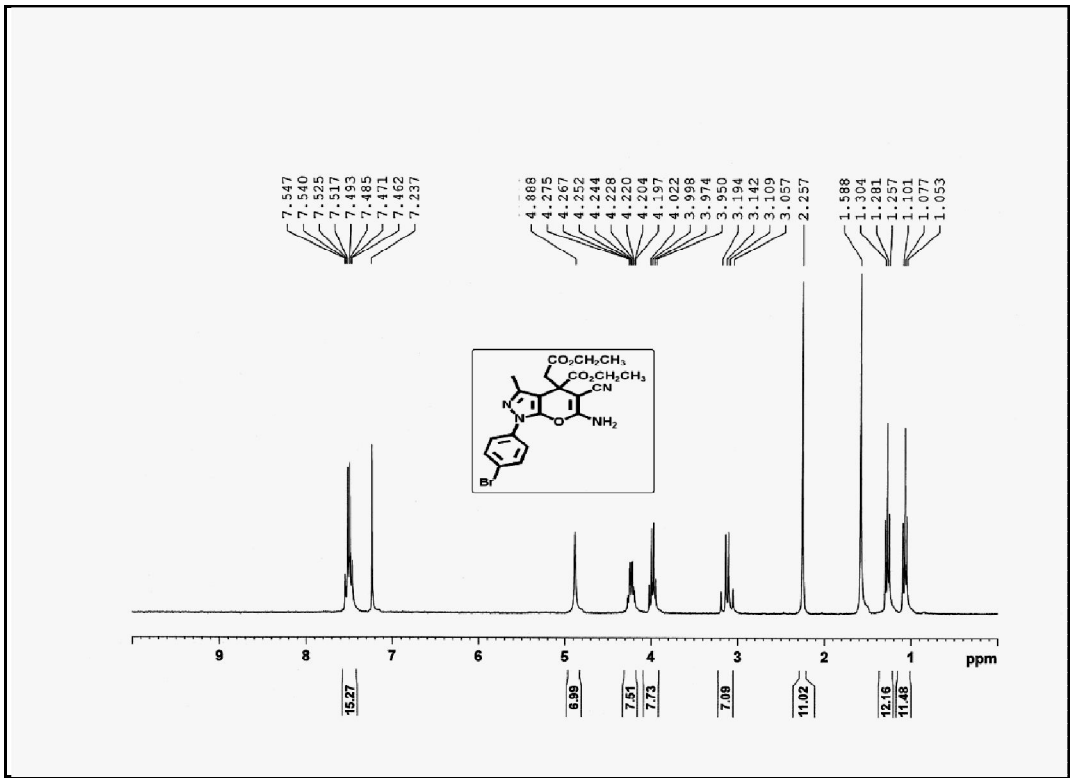
^{13}C NMR spectrum of the product 5a



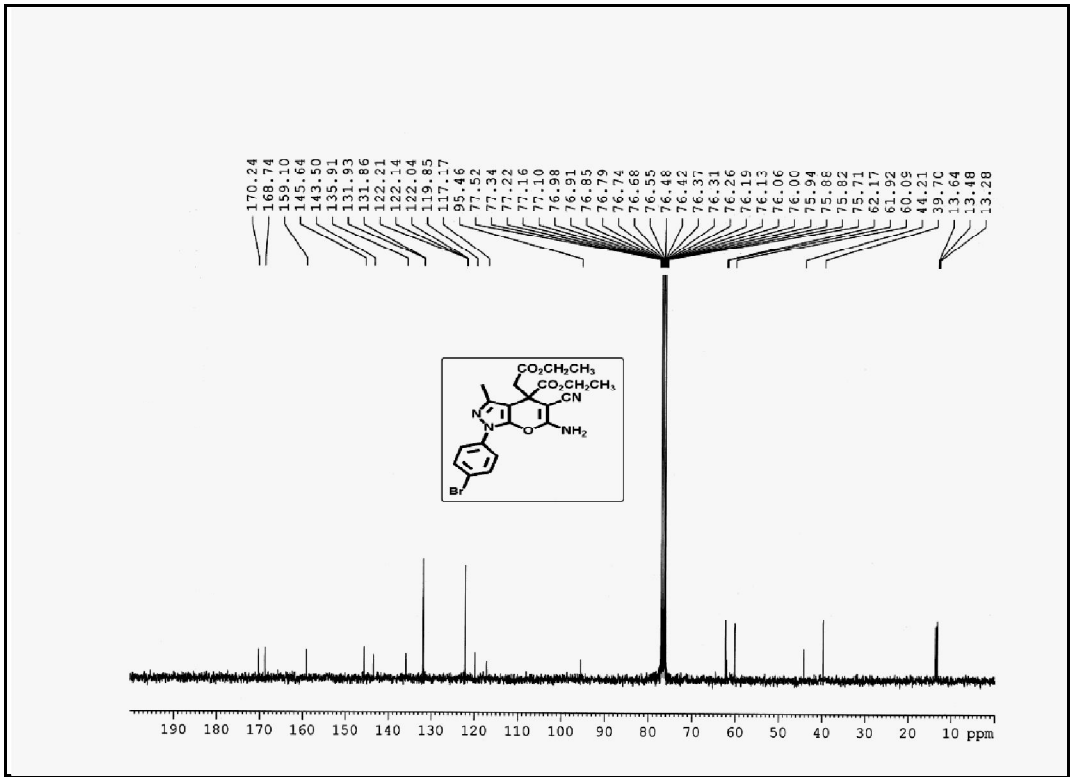
^{1}H NMR spectrum of the product 5b



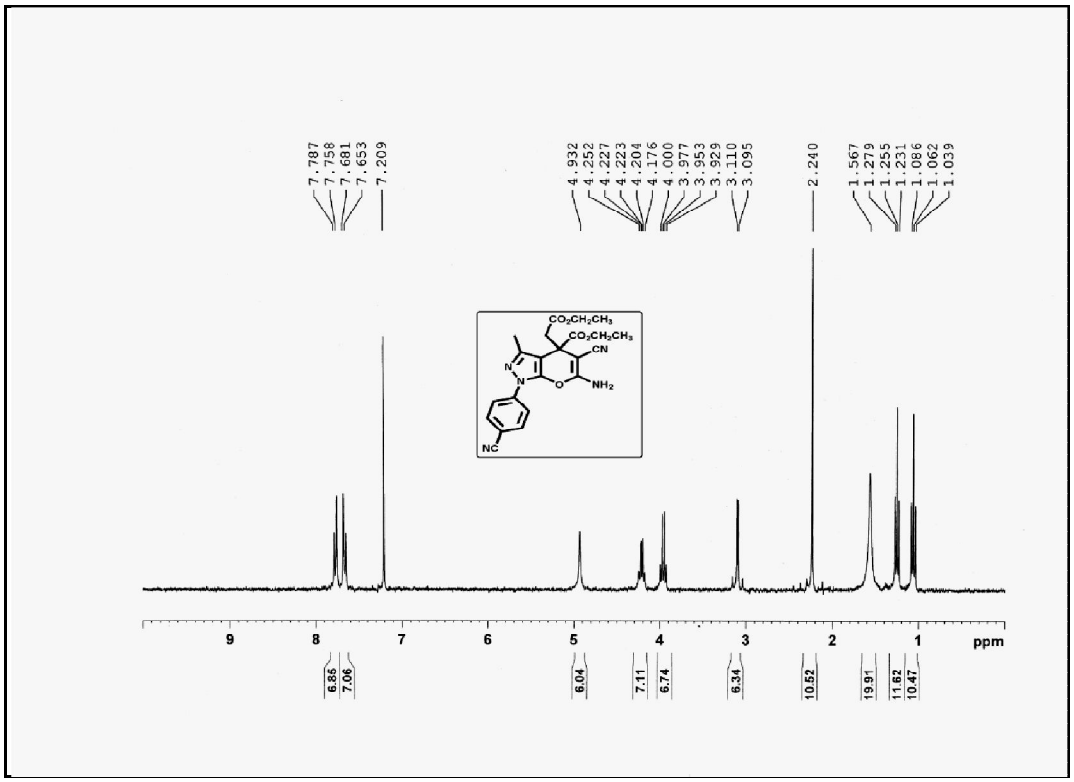
^{13}C NMR spectrum of the product 5b



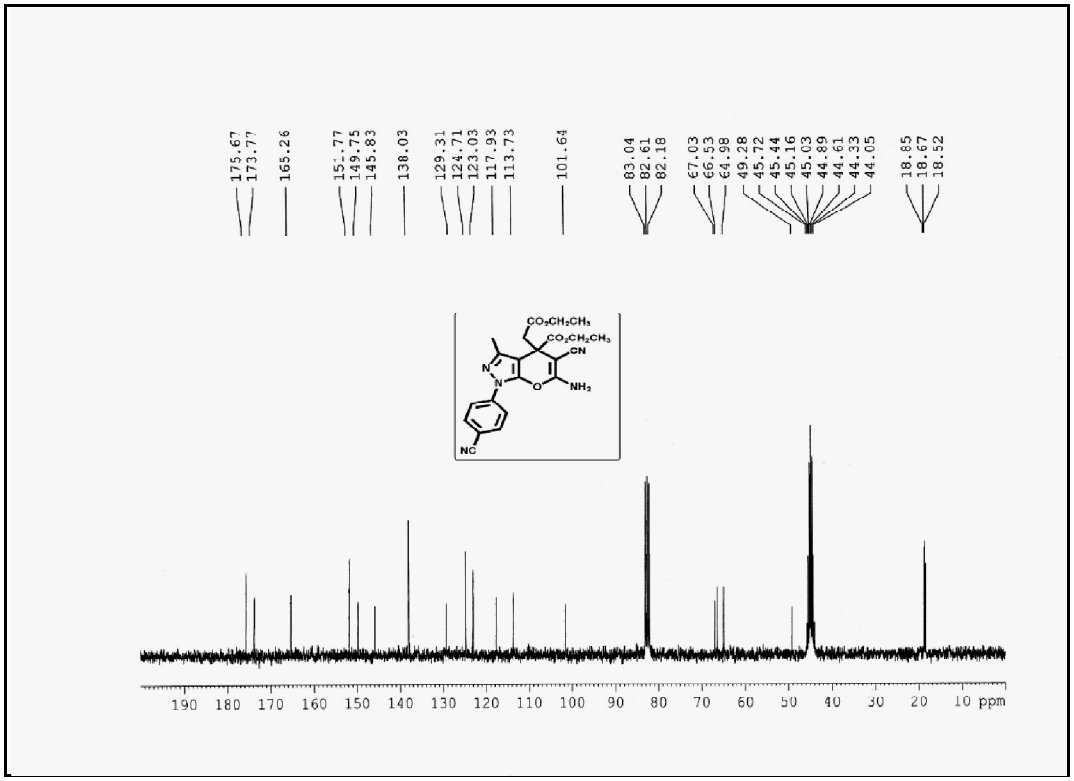
^{1}H NMR spectrum of the product 5c



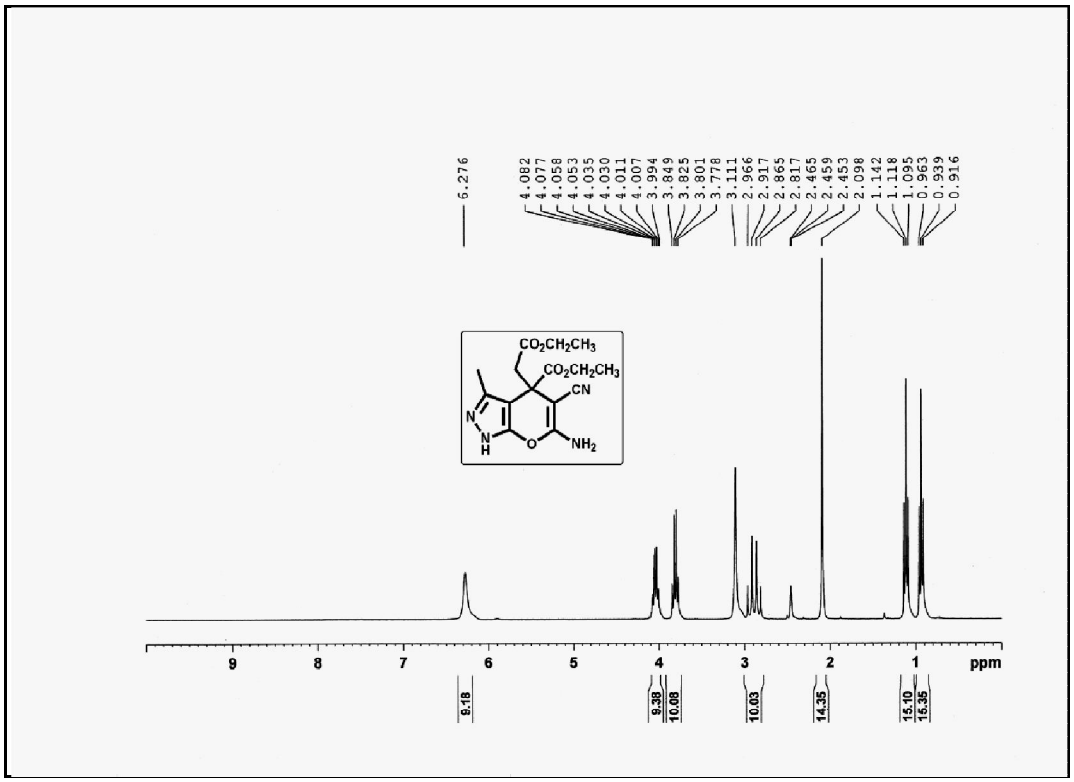
^{13}C NMR spectrum of the product 5c



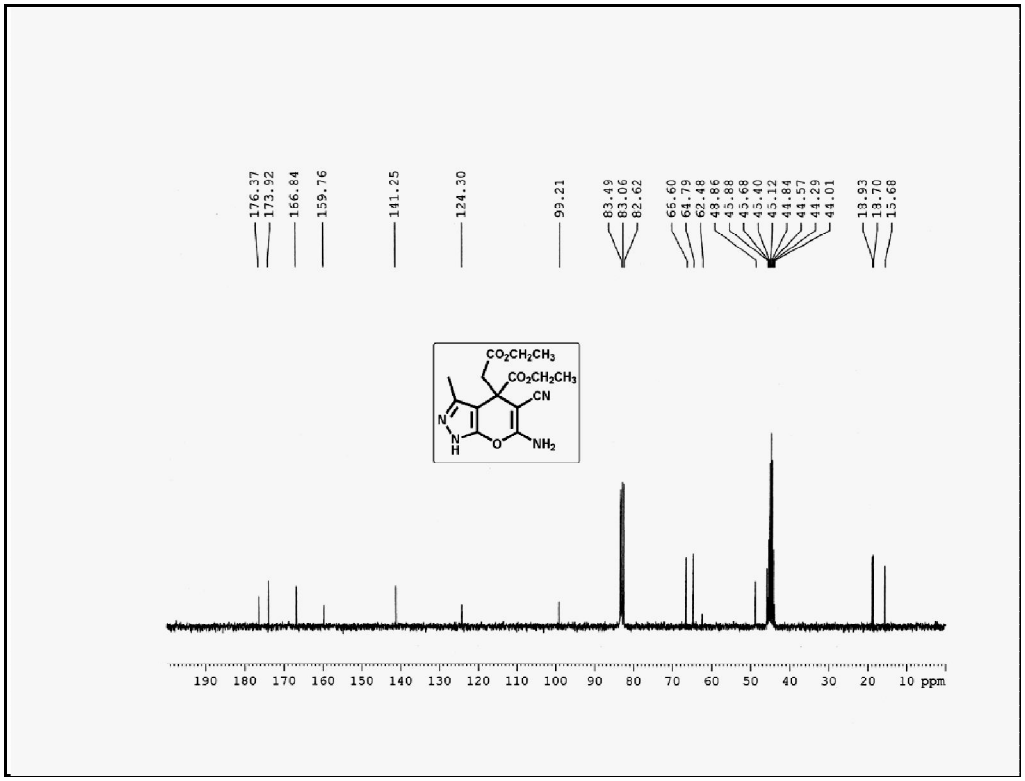
^{1}H NMR spectrum of the product 5d



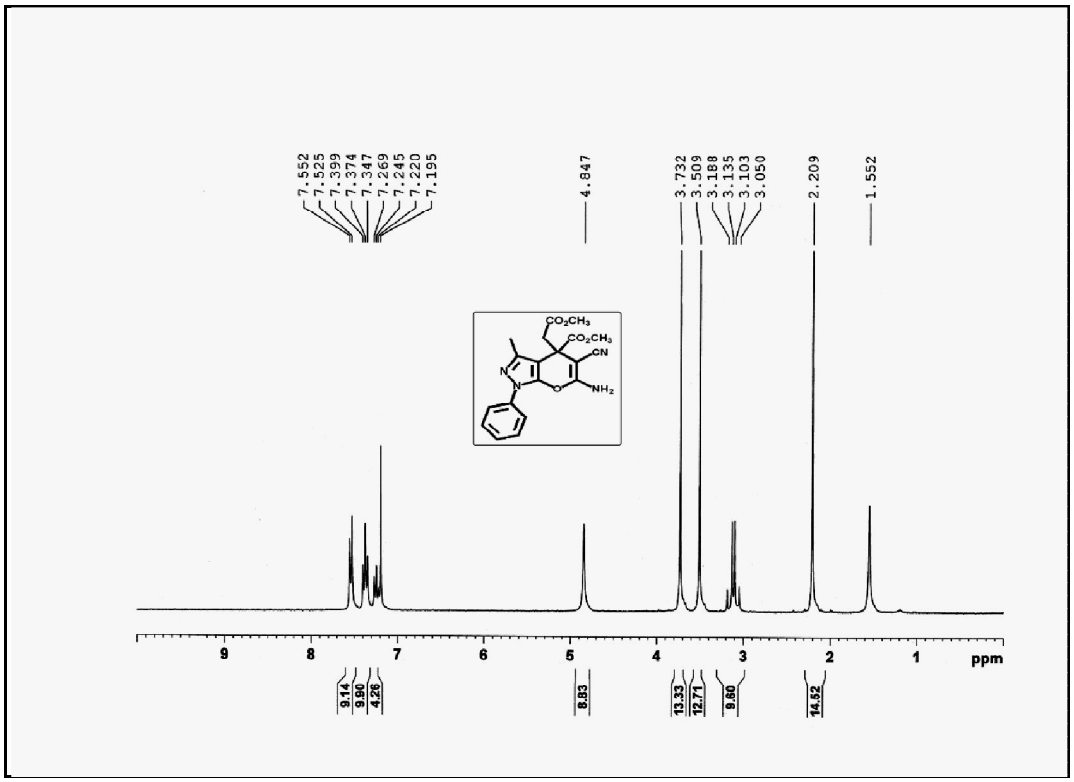
^{13}C NMR spectrum of the product 5d



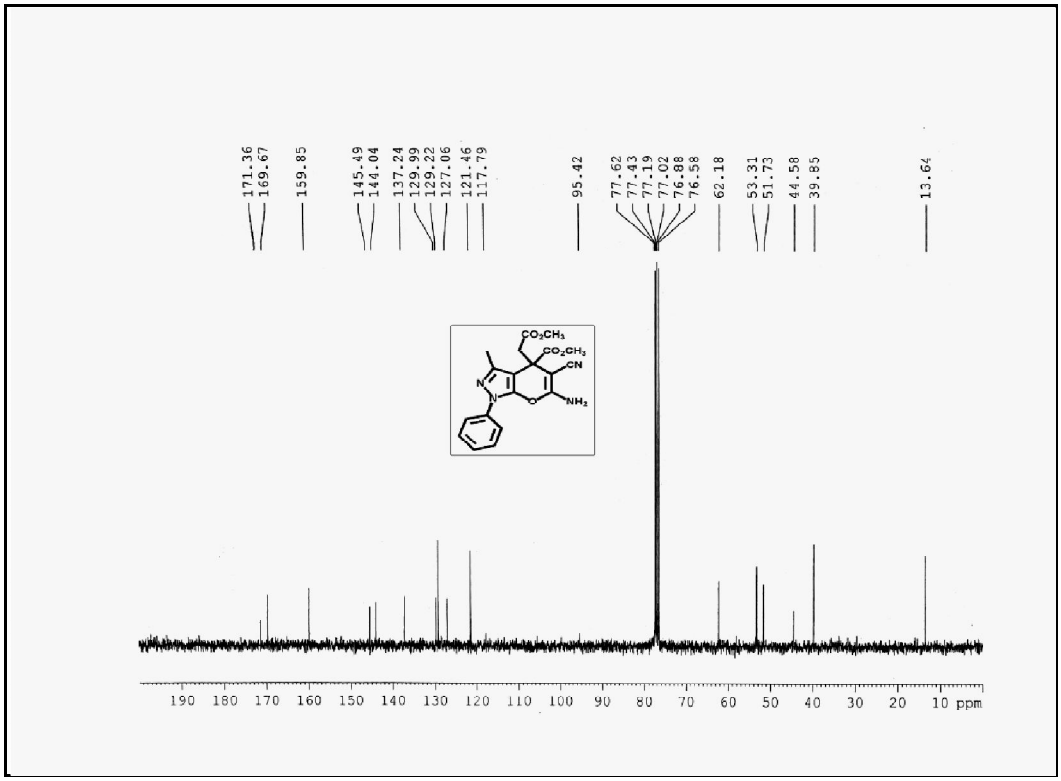
^{1}H NMR spectrum of the product 5e



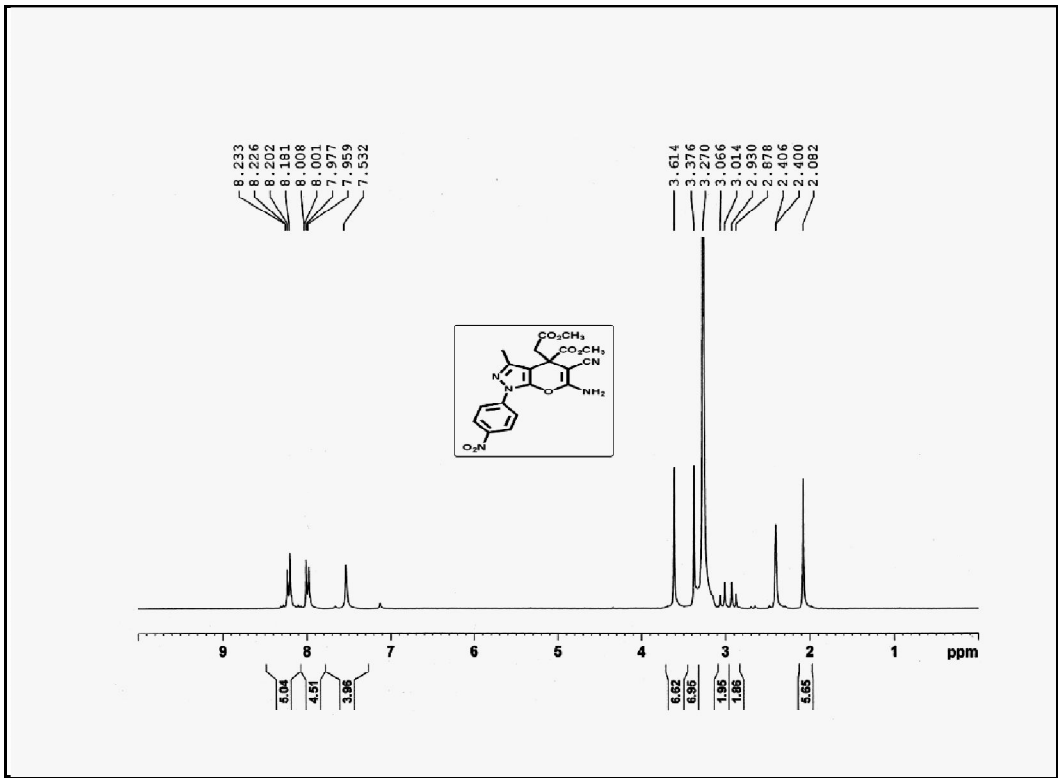
^{13}C NMR spectrum of the product 5e



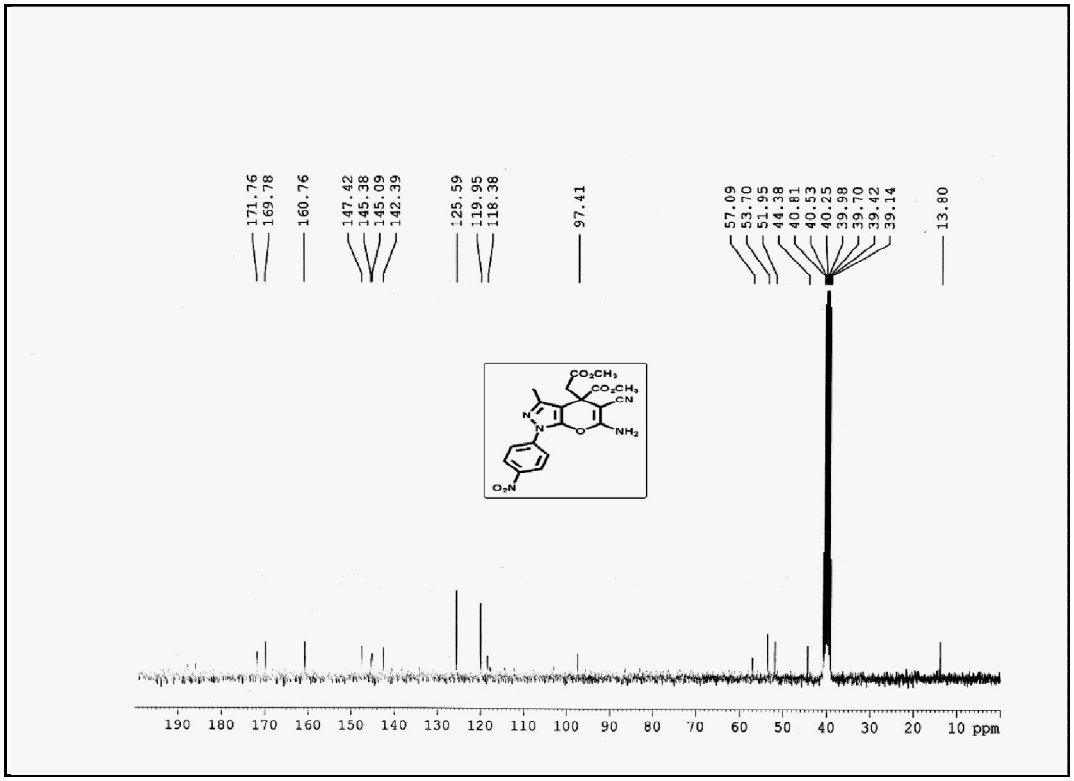
^{1}H NMR spectrum of the product 5f



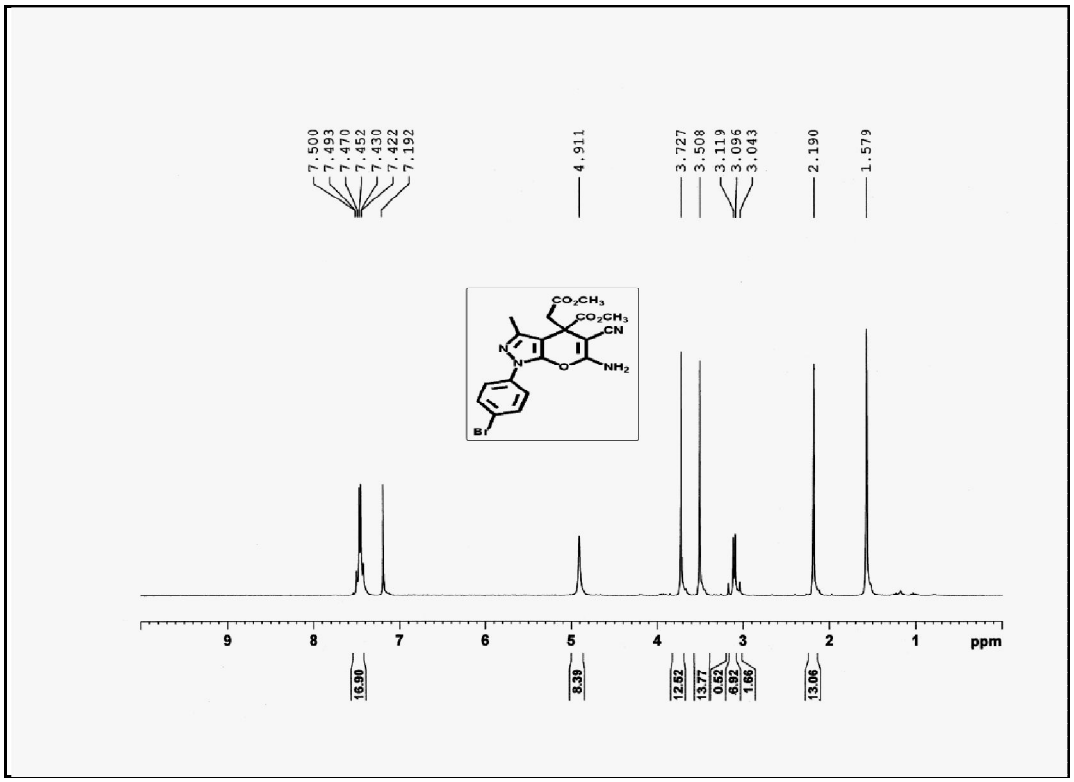
^{13}C NMR spectrum of the product 5f



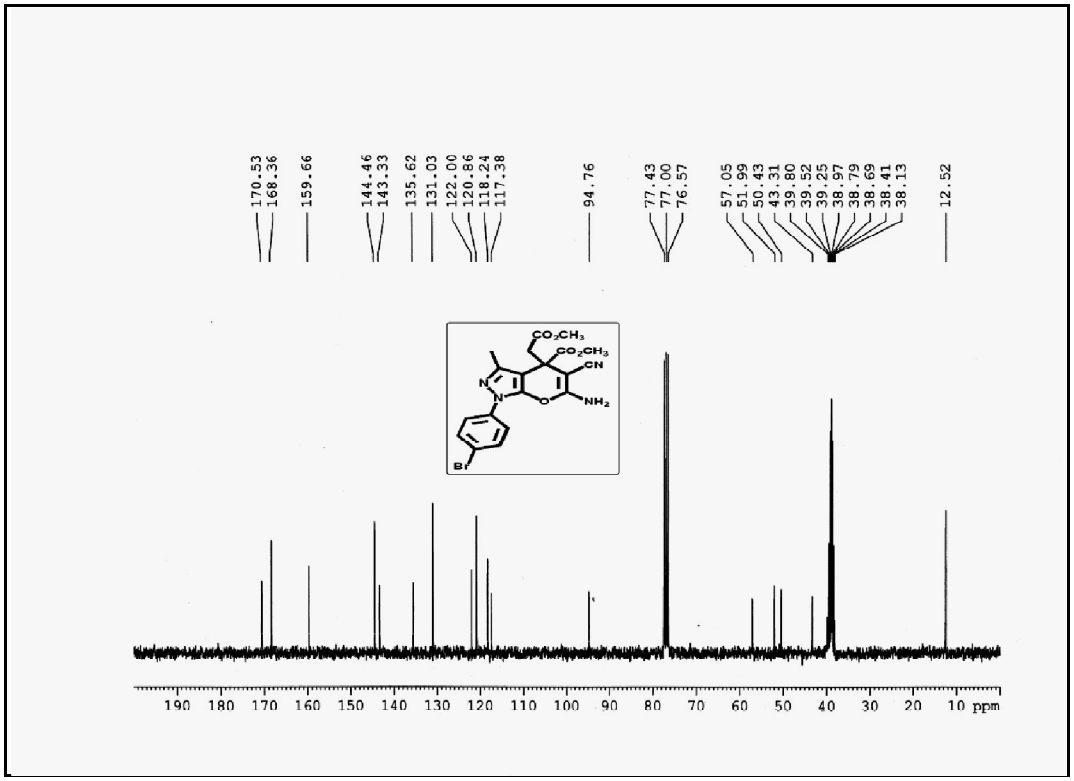
^{1}H NMR spectrum of the product 5g



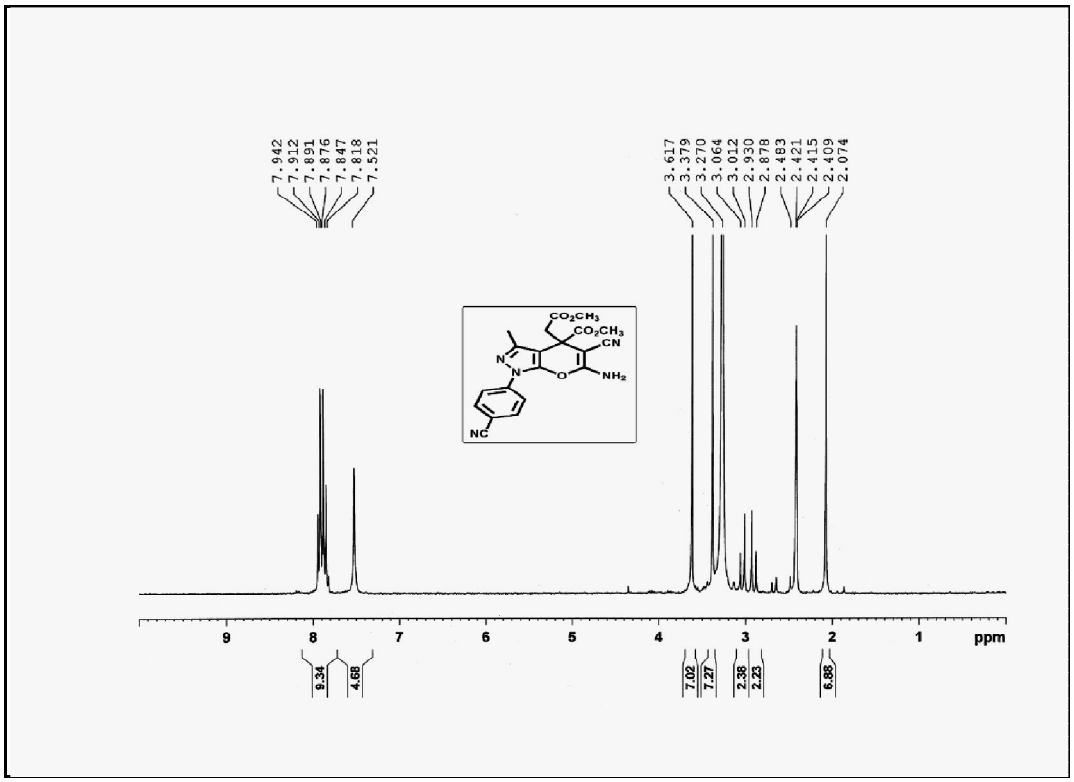
^{13}C NMR spectrum of the product 5g



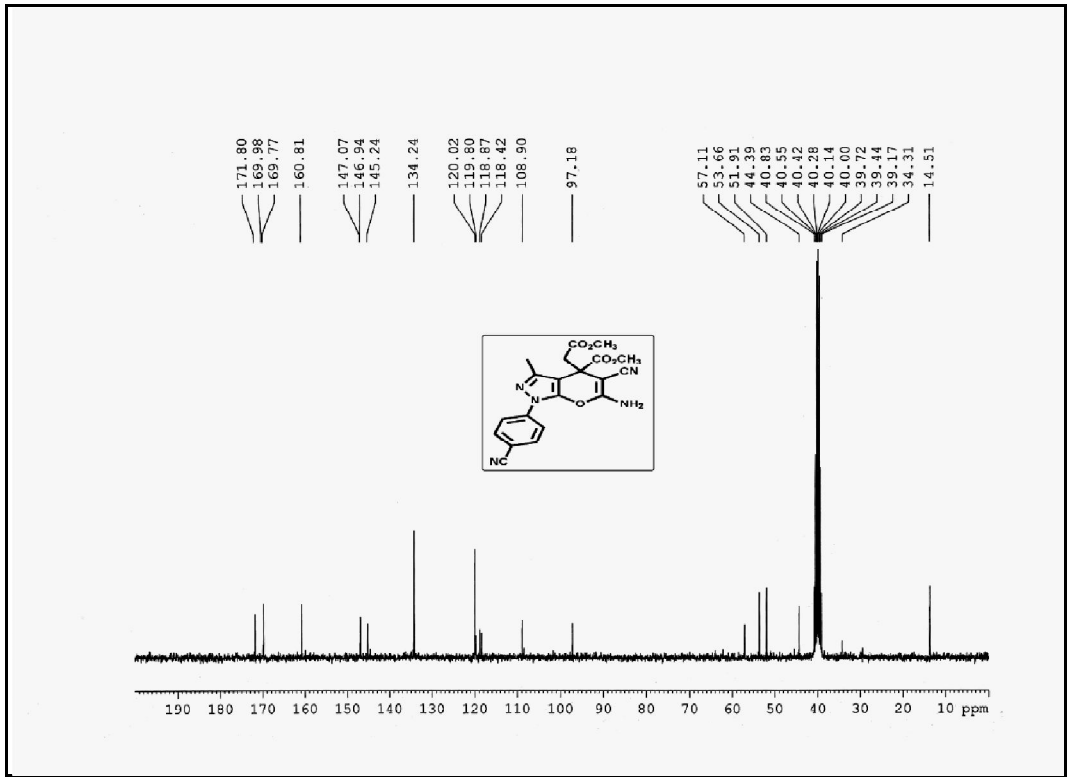
^{1}H NMR spectrum of the product 5h



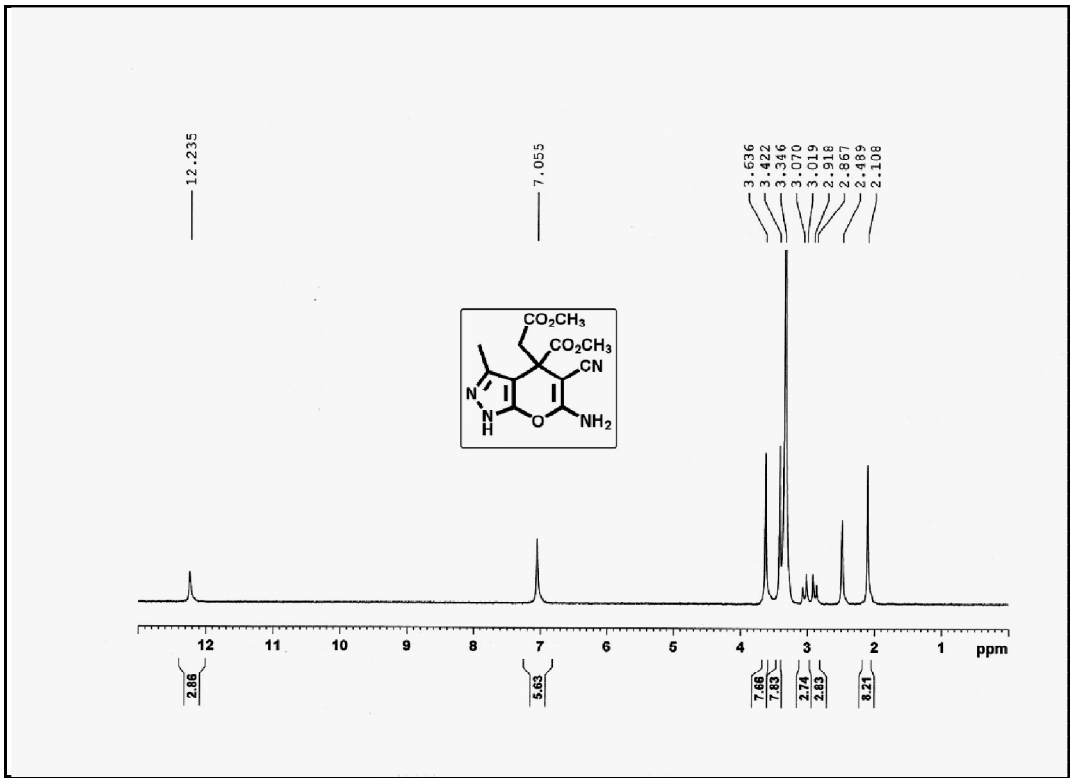
^{13}C NMR spectrum of the product 5h



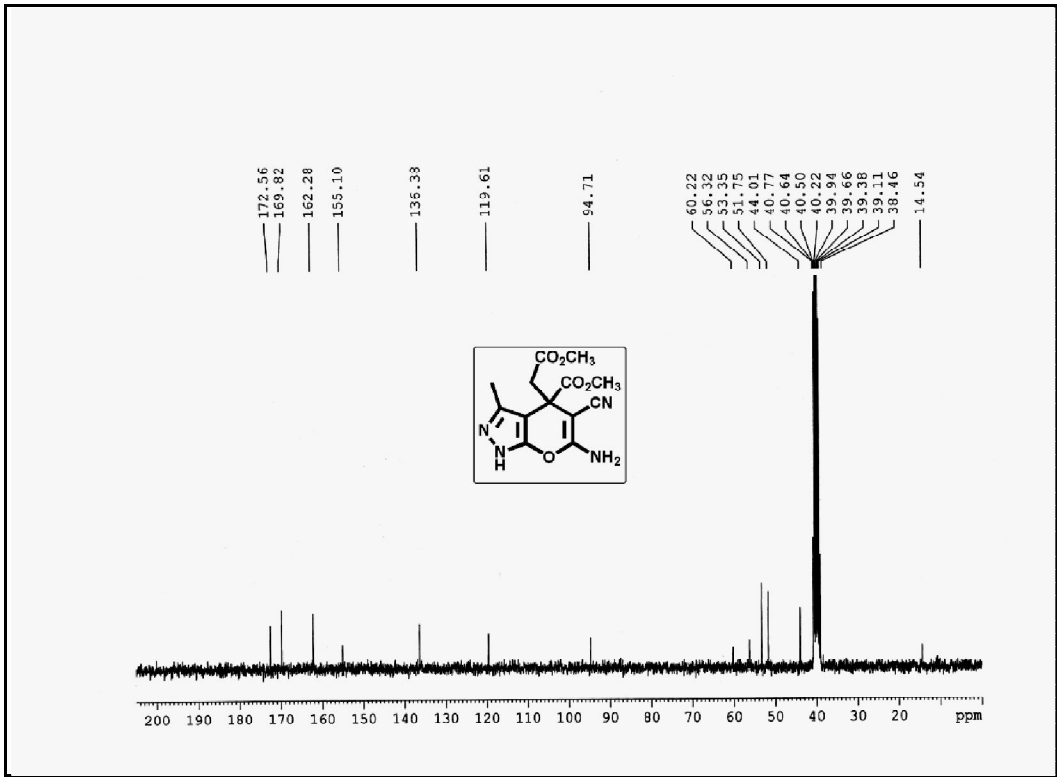
^{1}H NMR spectrum of the product 5i



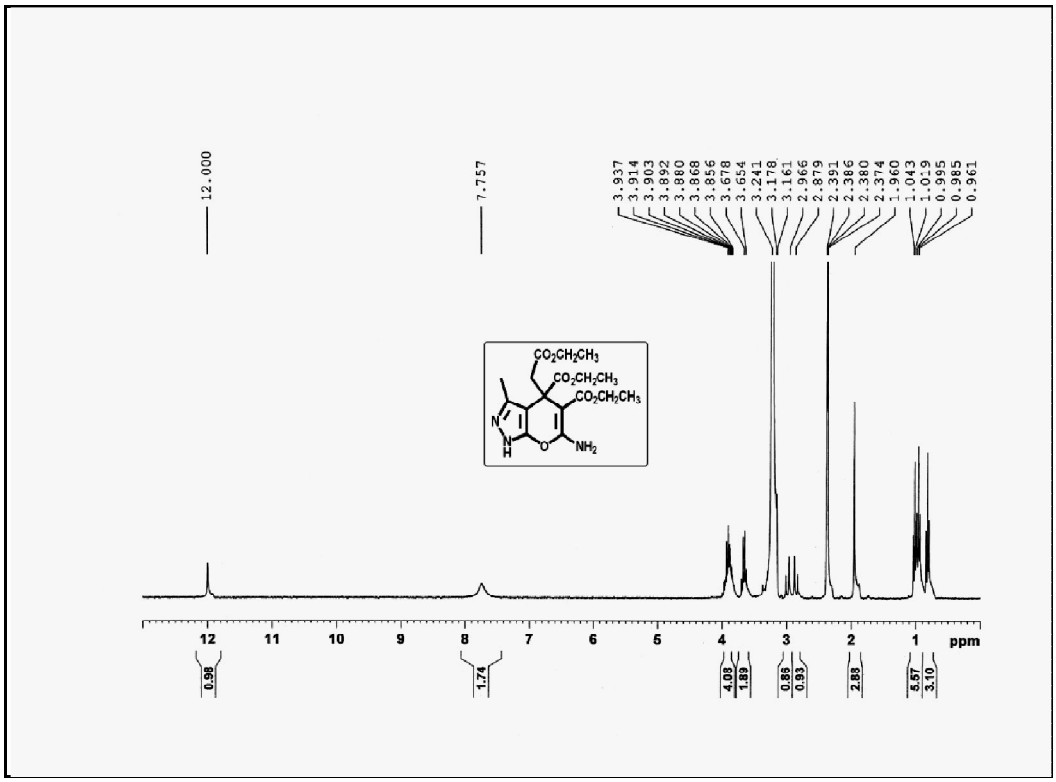
^{13}C NMR spectrum of the product 5i



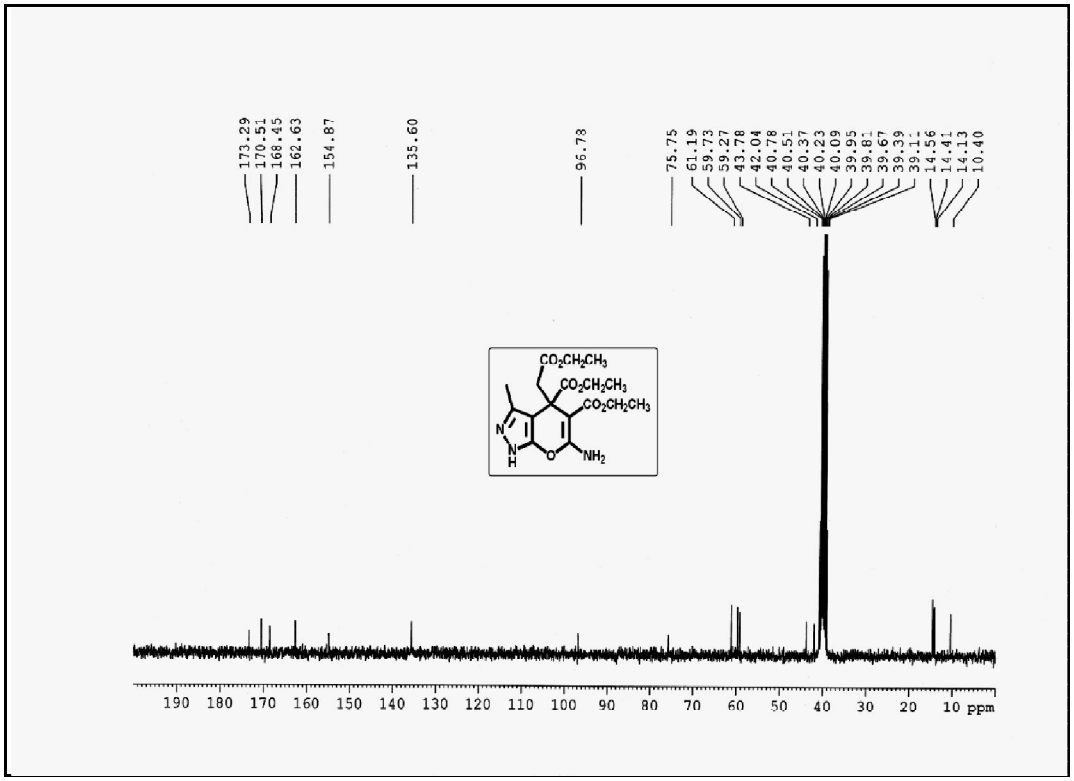
^{1}H NMR spectrum of the product 5j



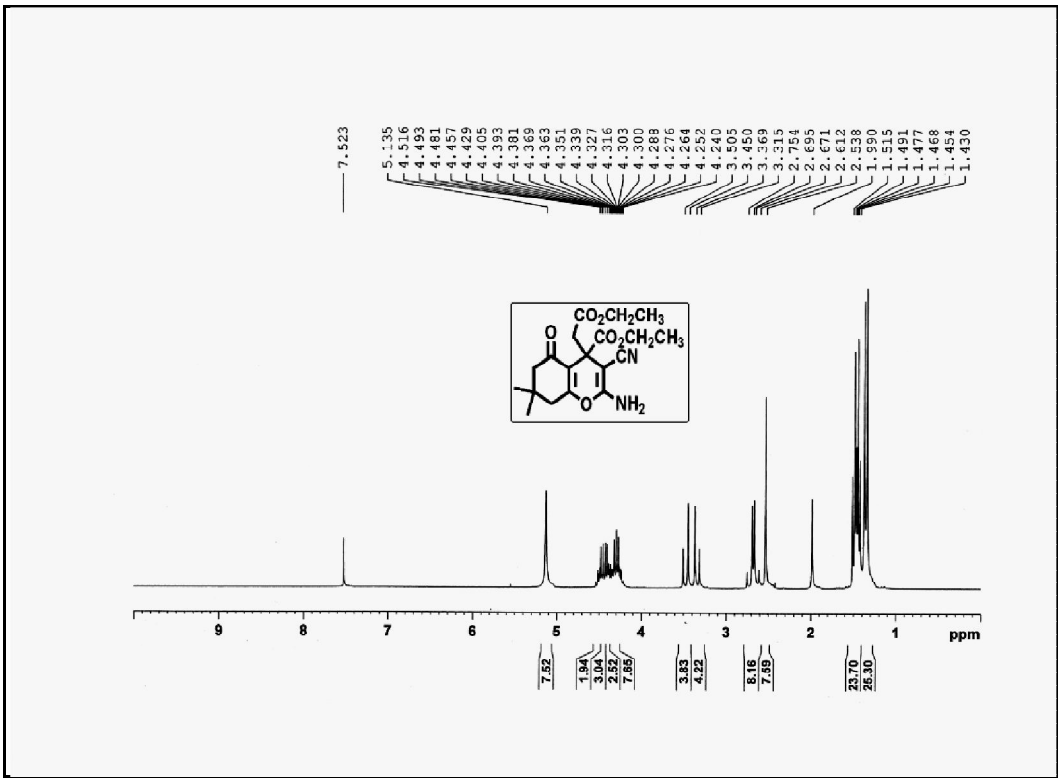
^{13}C NMR spectrum of the product 5j



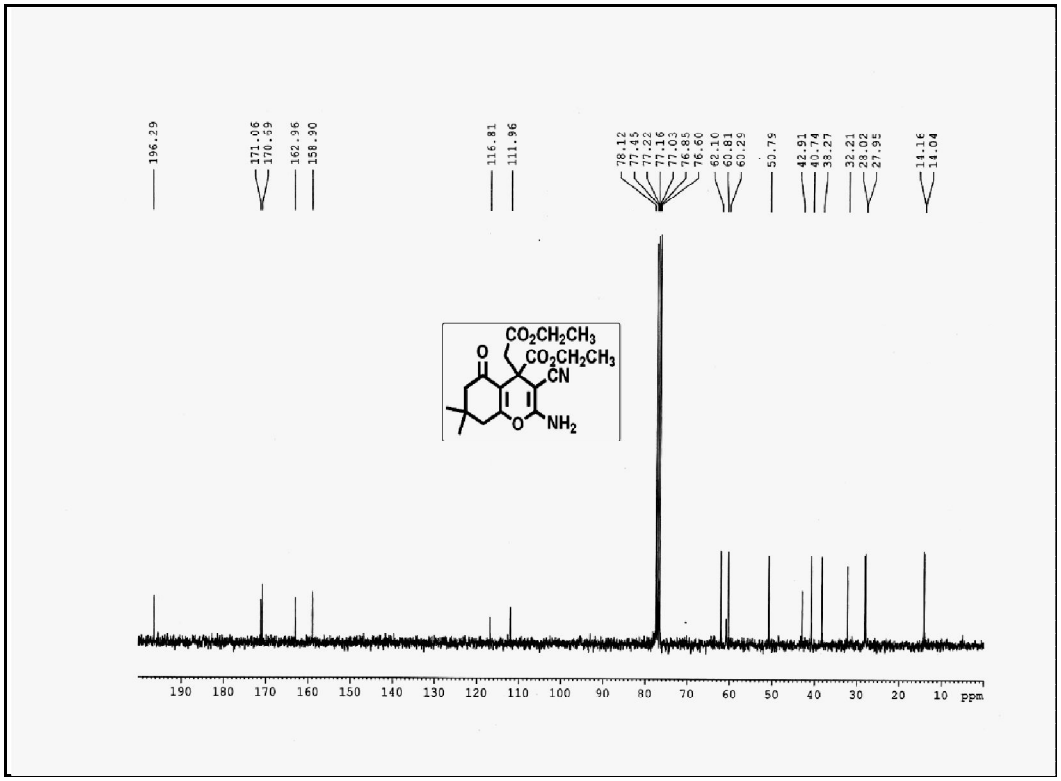
^{1}H NMR spectrum of the product 5k



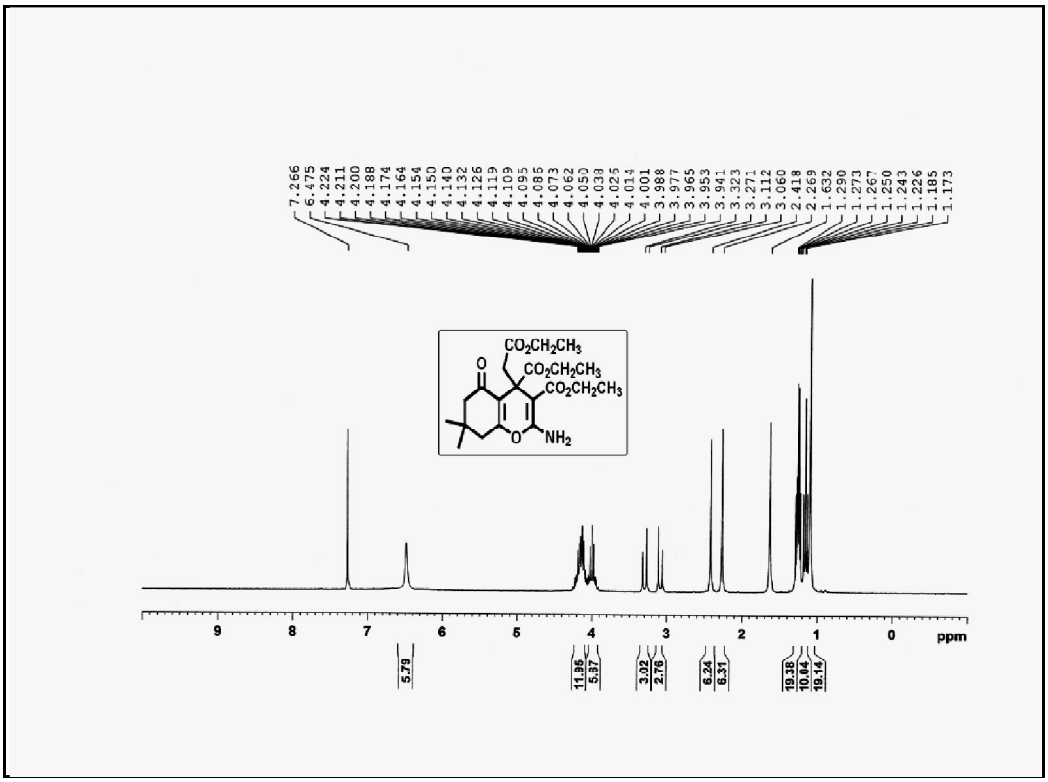
^{13}C NMR spectrum of the product 5k



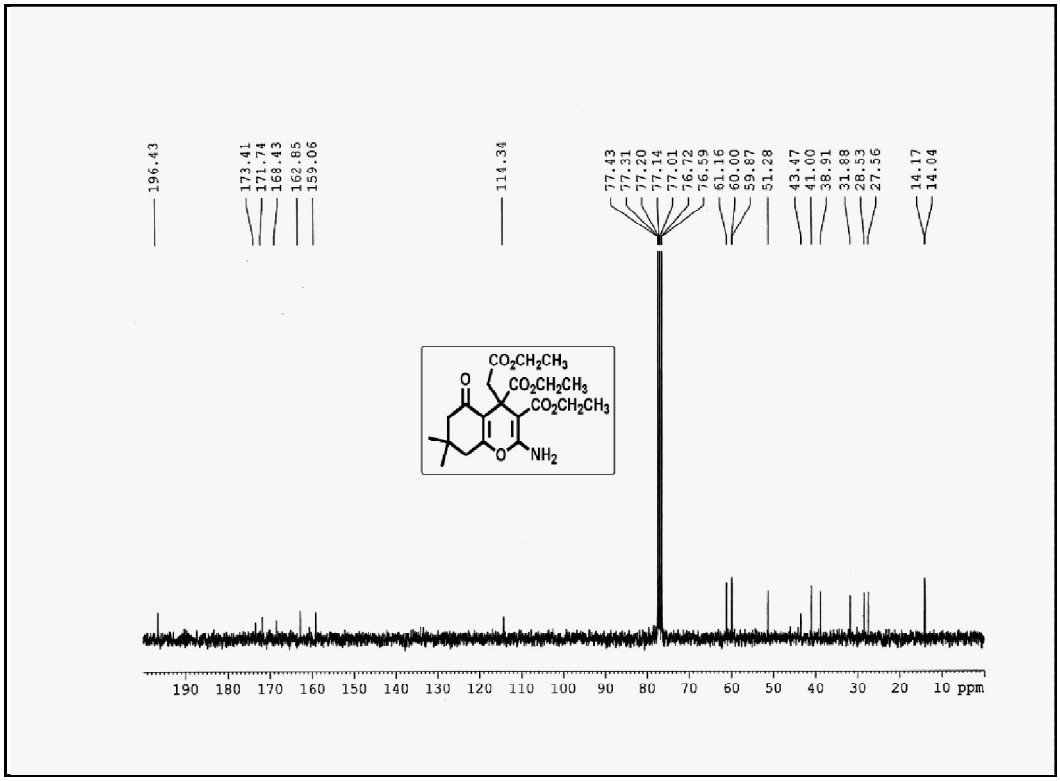
^{1}H NMR spectrum of the product 7a



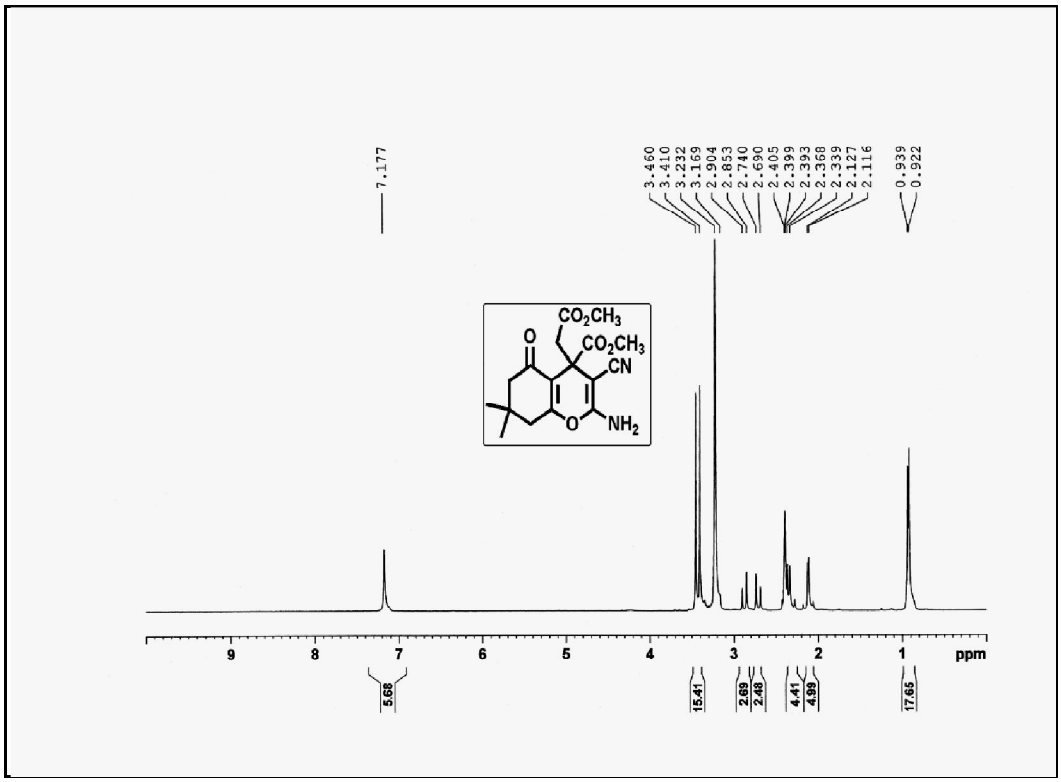
^{13}C NMR spectrum of the product 7a



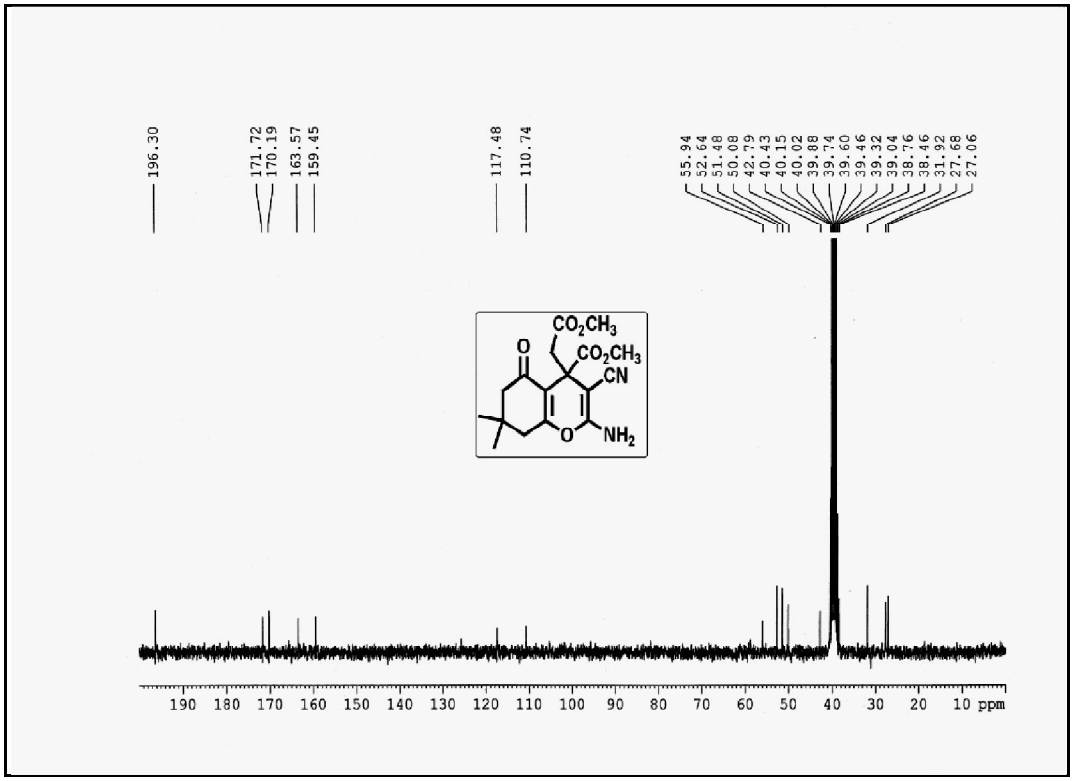
^{1}H NMR spectrum of the product 7b



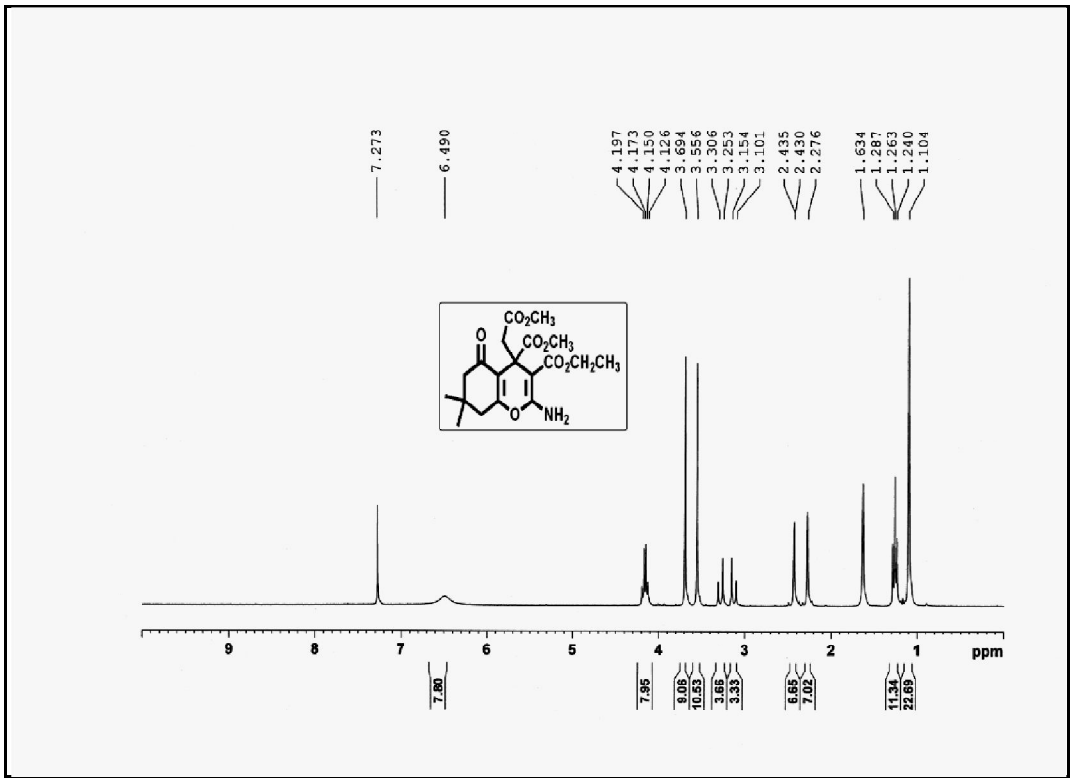
^{13}C NMR spectrum of the product 7b



^{1}H NMR spectrum of the product 7c



^{13}C NMR spectrum of the product 7c



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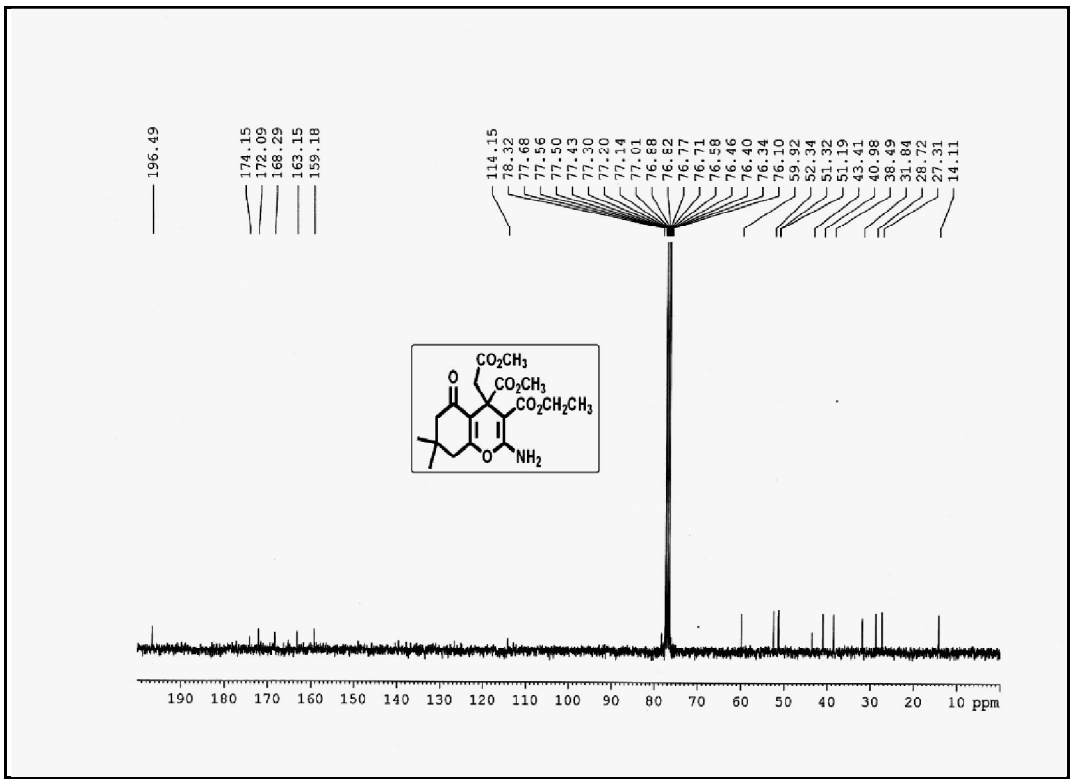
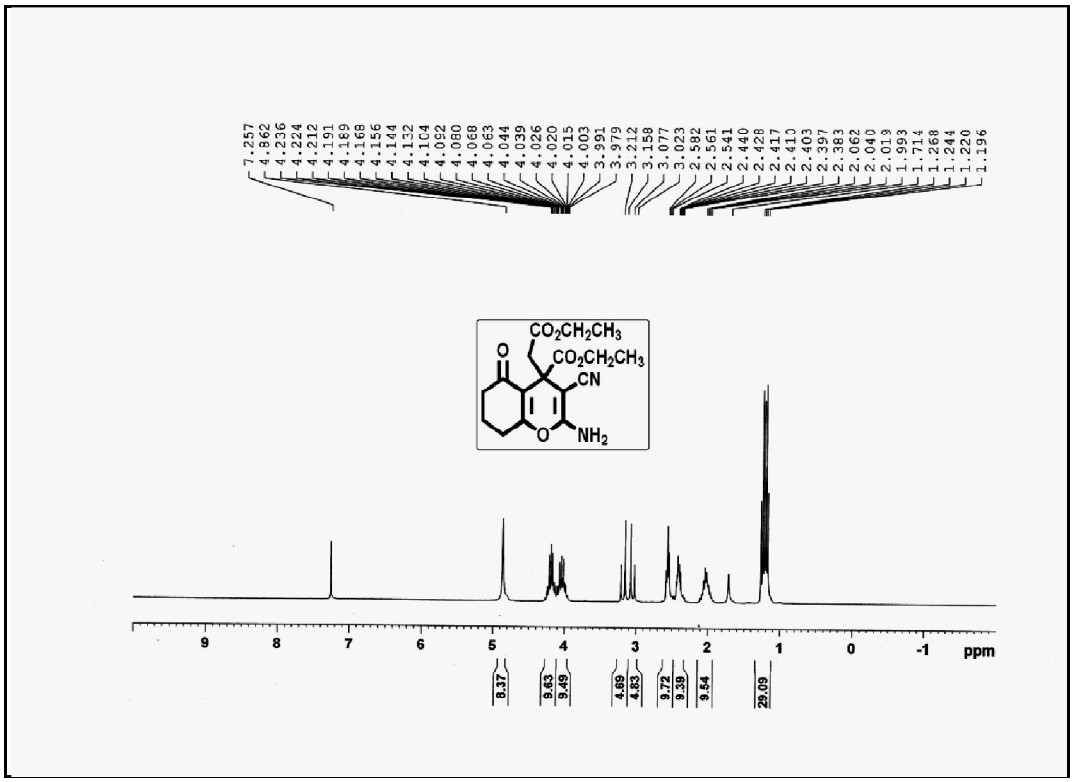


^{13}C NMR spectrum of the product 7d



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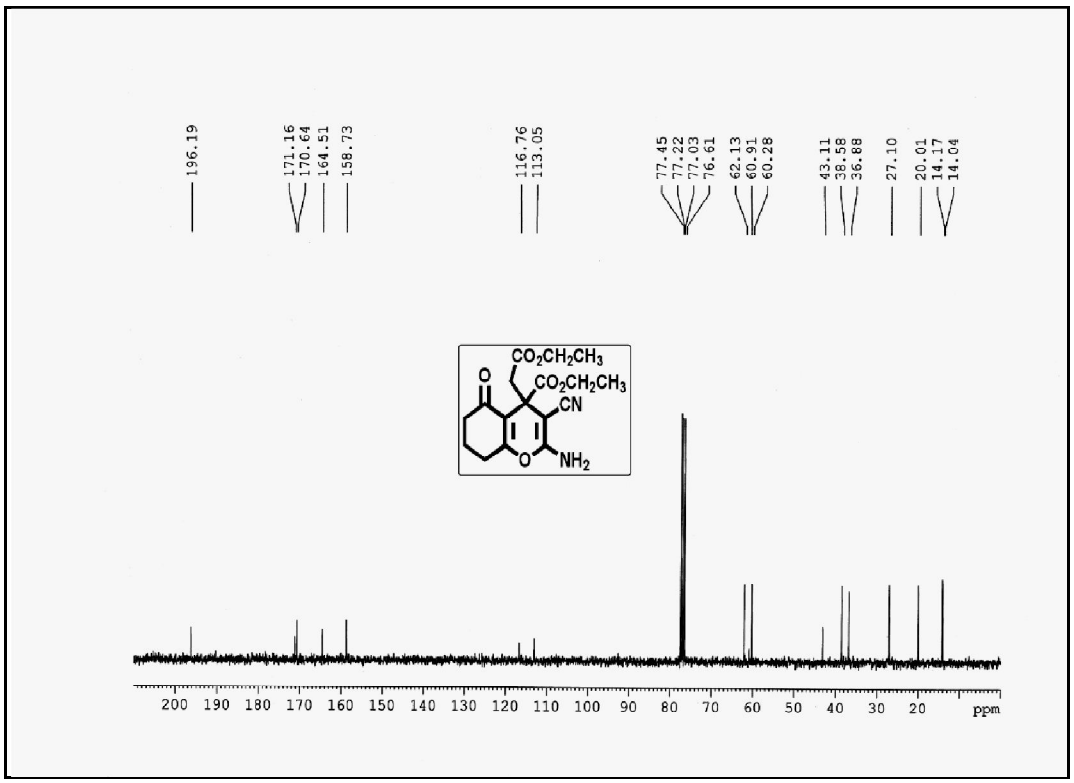

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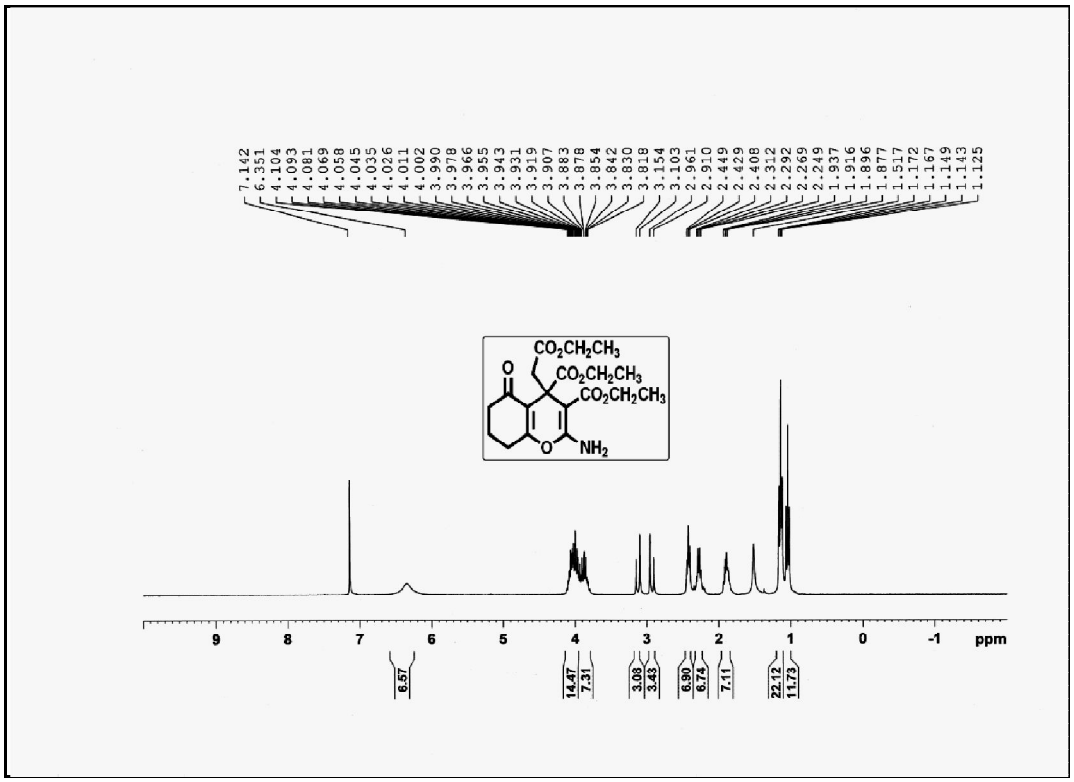
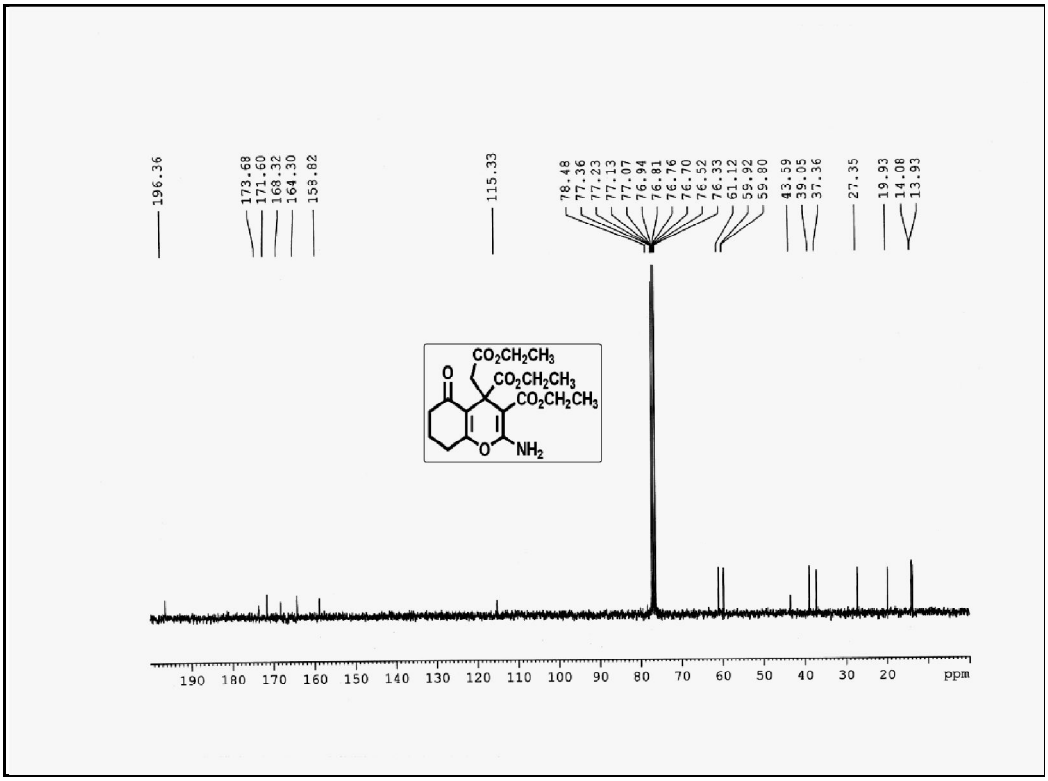


^{1}H NMR spectrum of the product 7f



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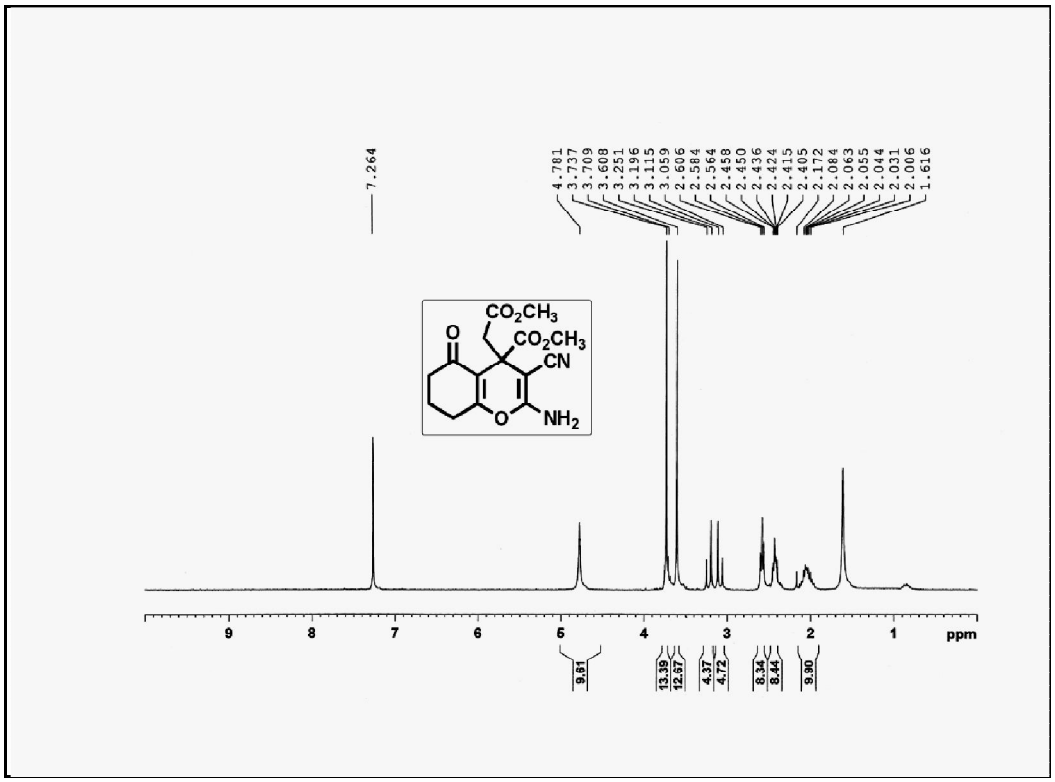

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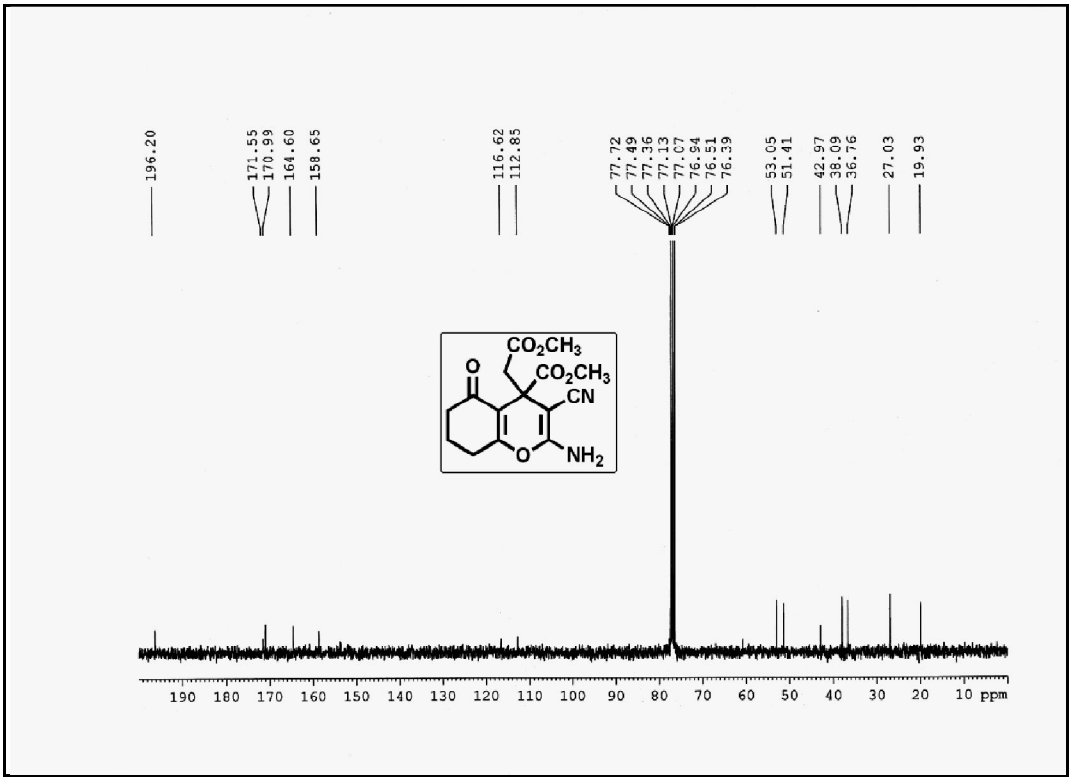
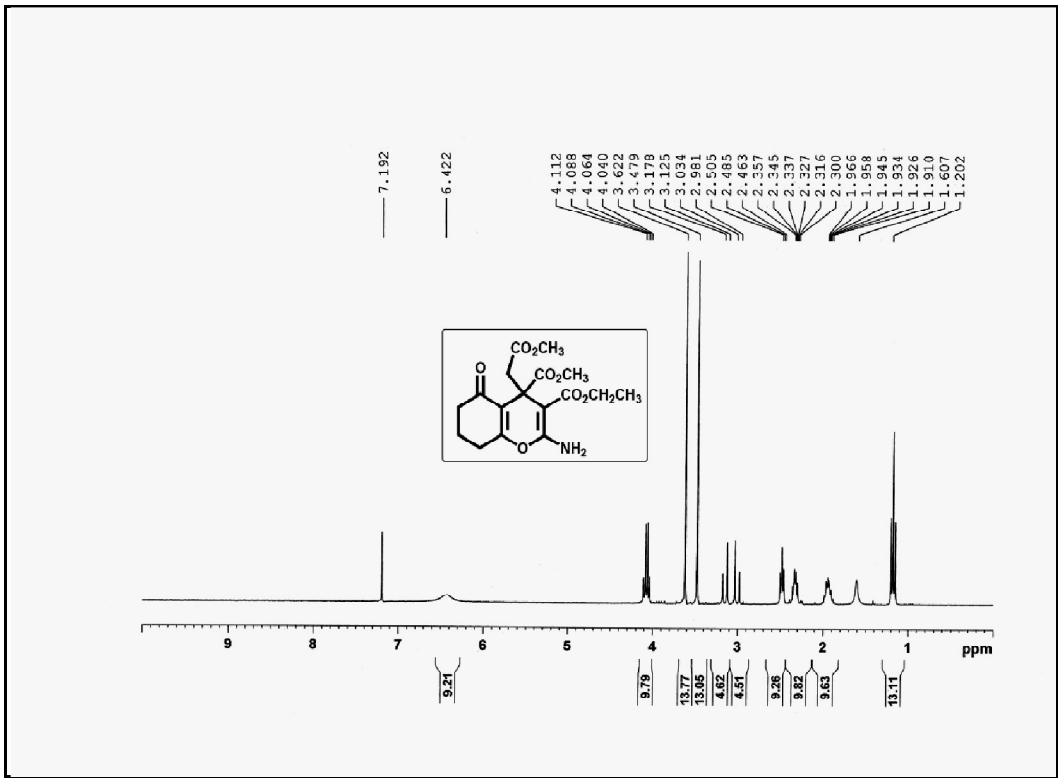
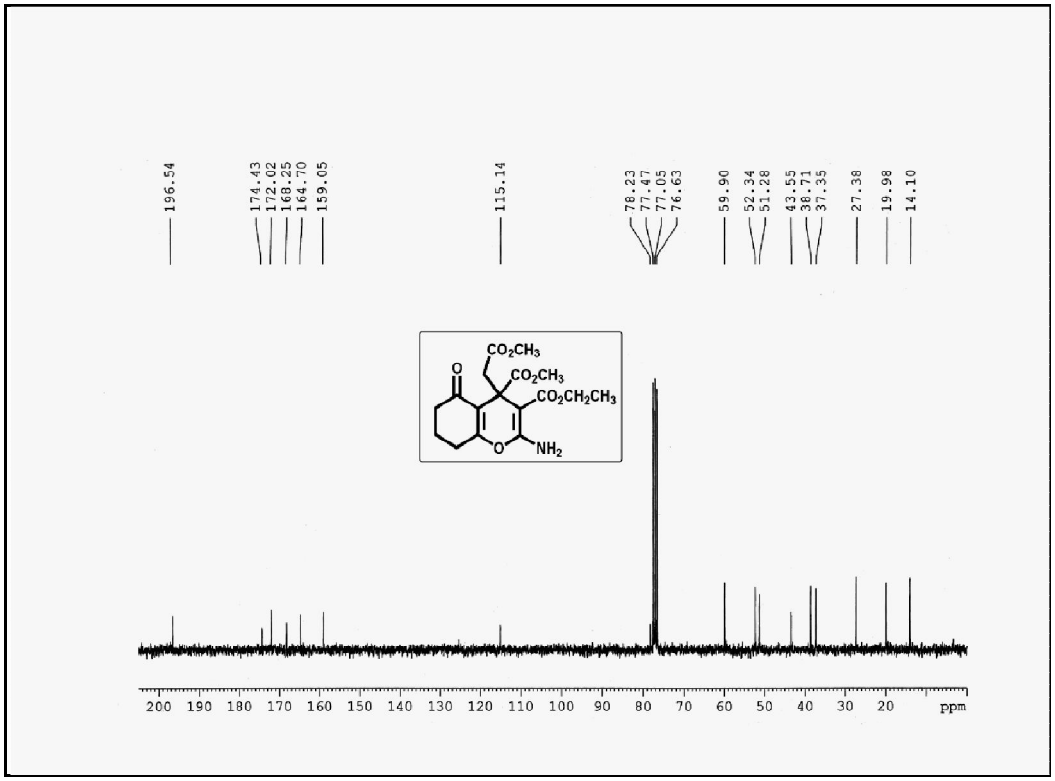


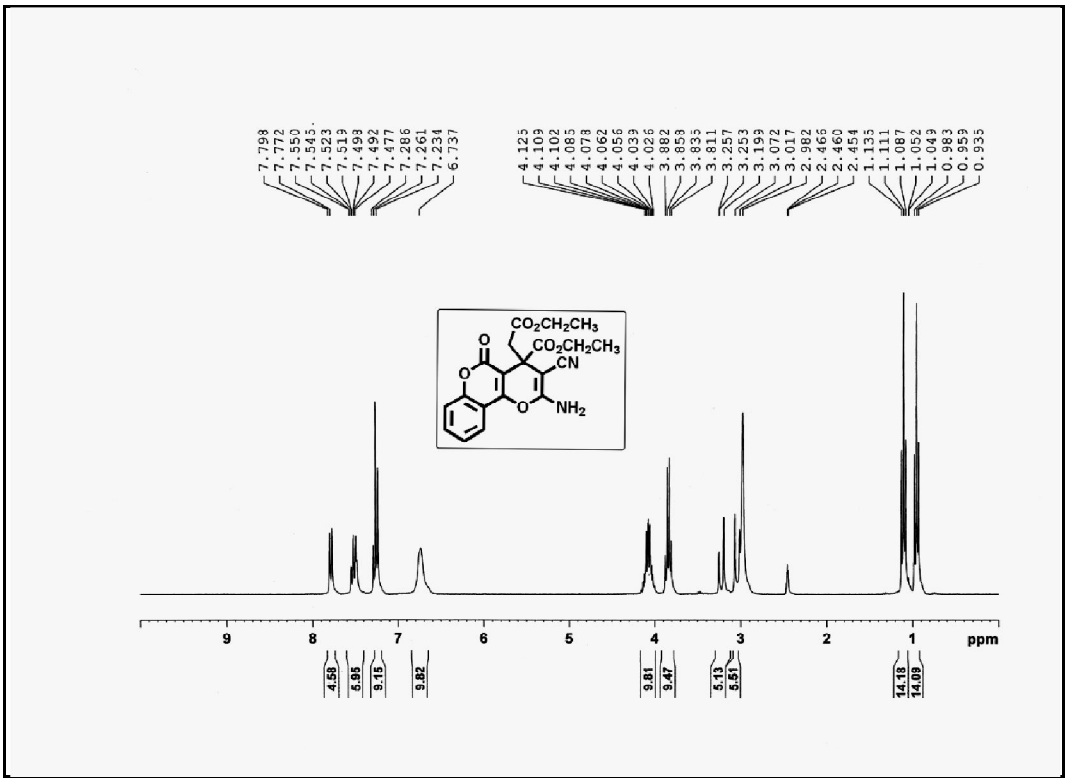
^{13}C NMR spectrum of the product 7g



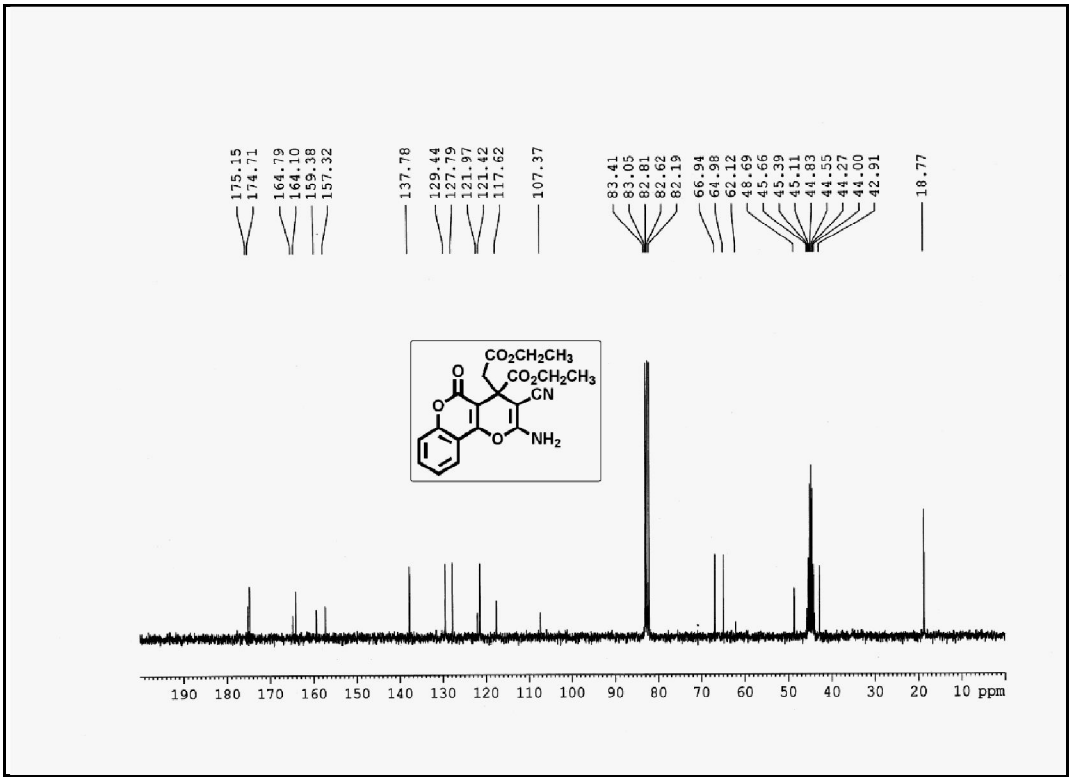
^{1}H NMR spectrum of the product 7h



^{13}C NMR spectrum of the product 7h



^{1}H NMR spectrum of the product 7i



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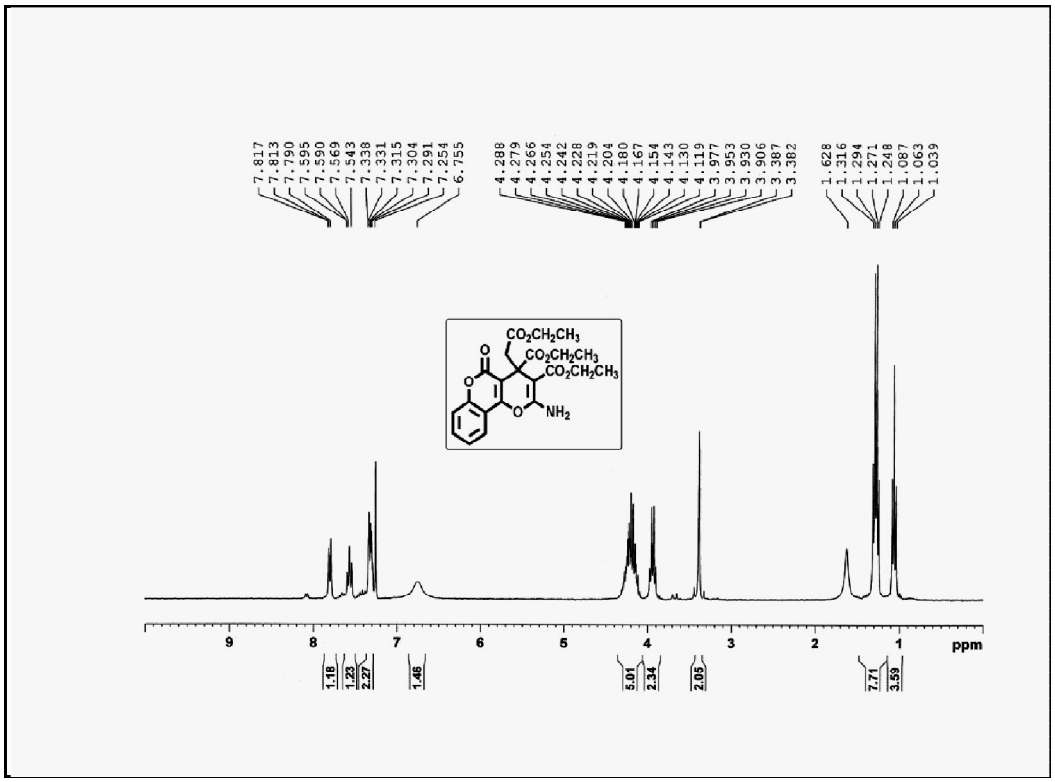

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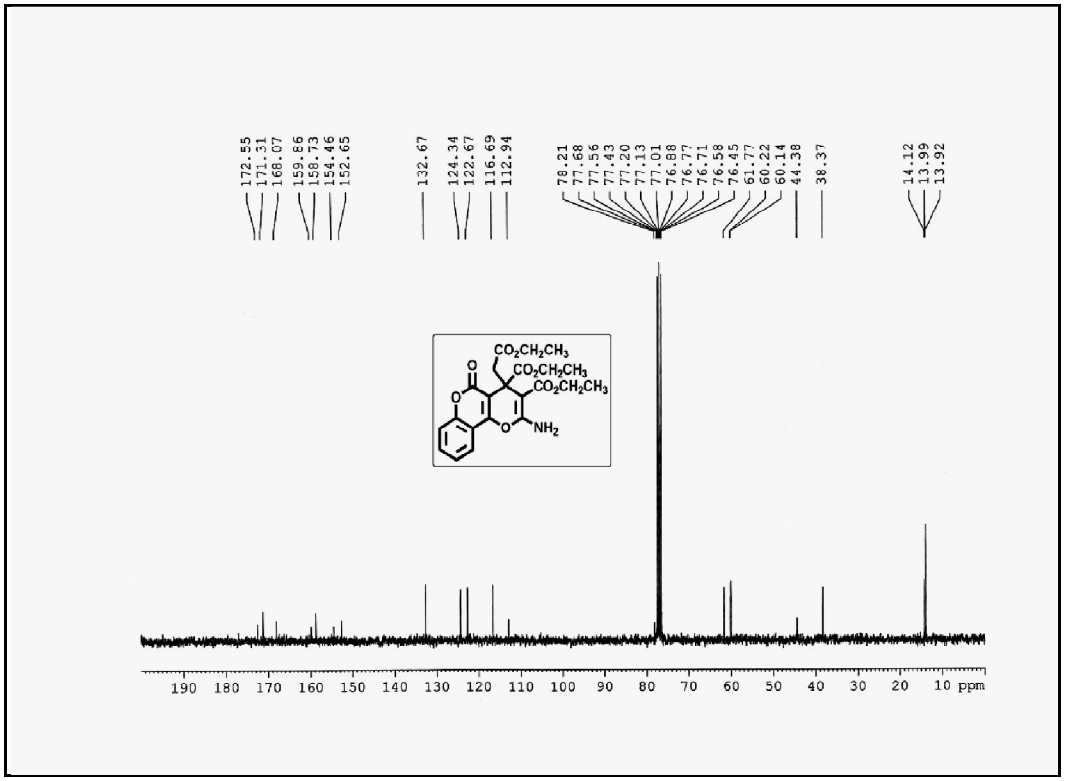

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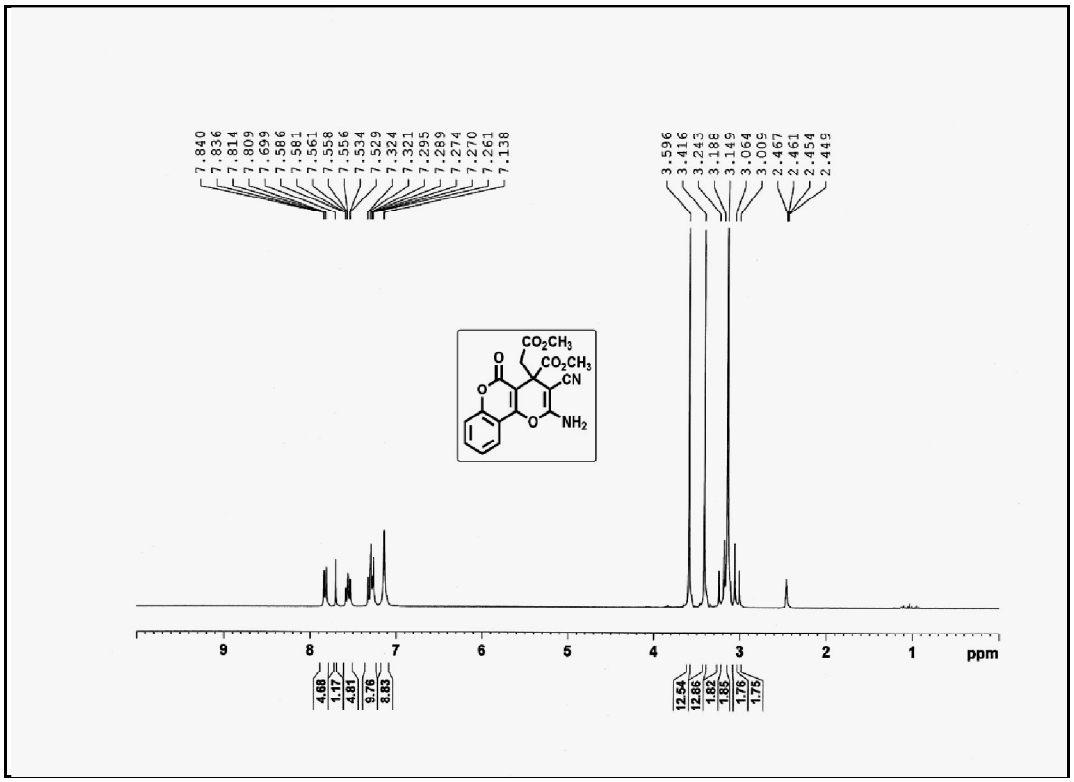

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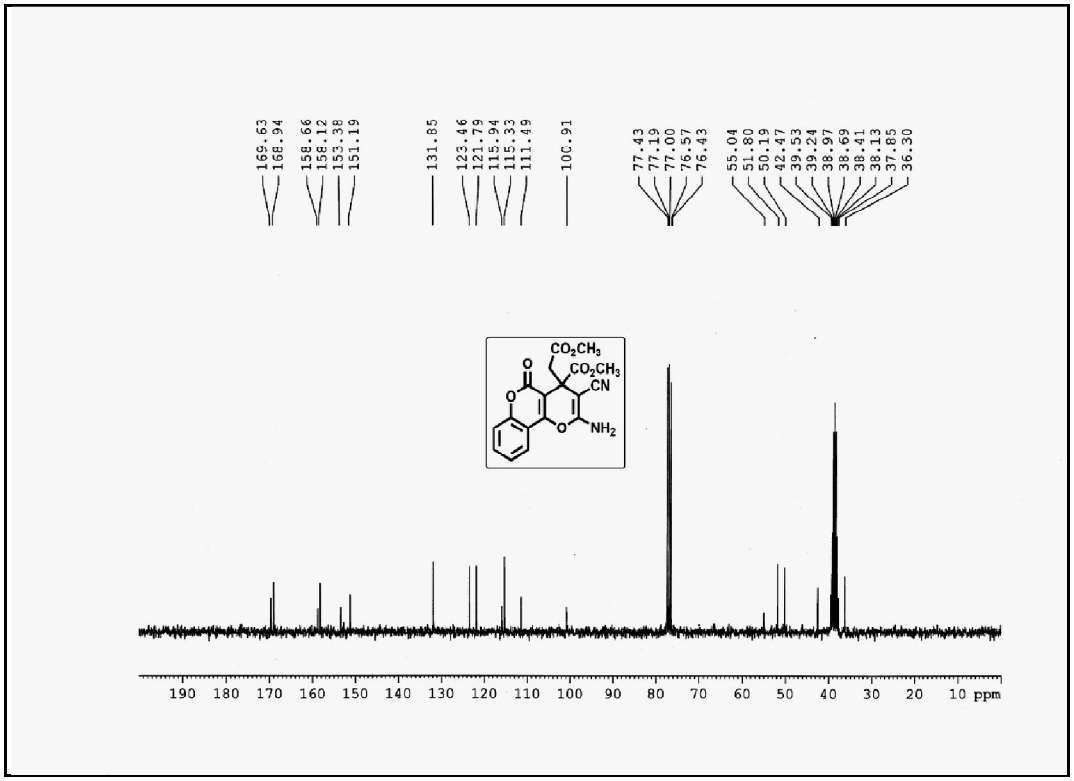

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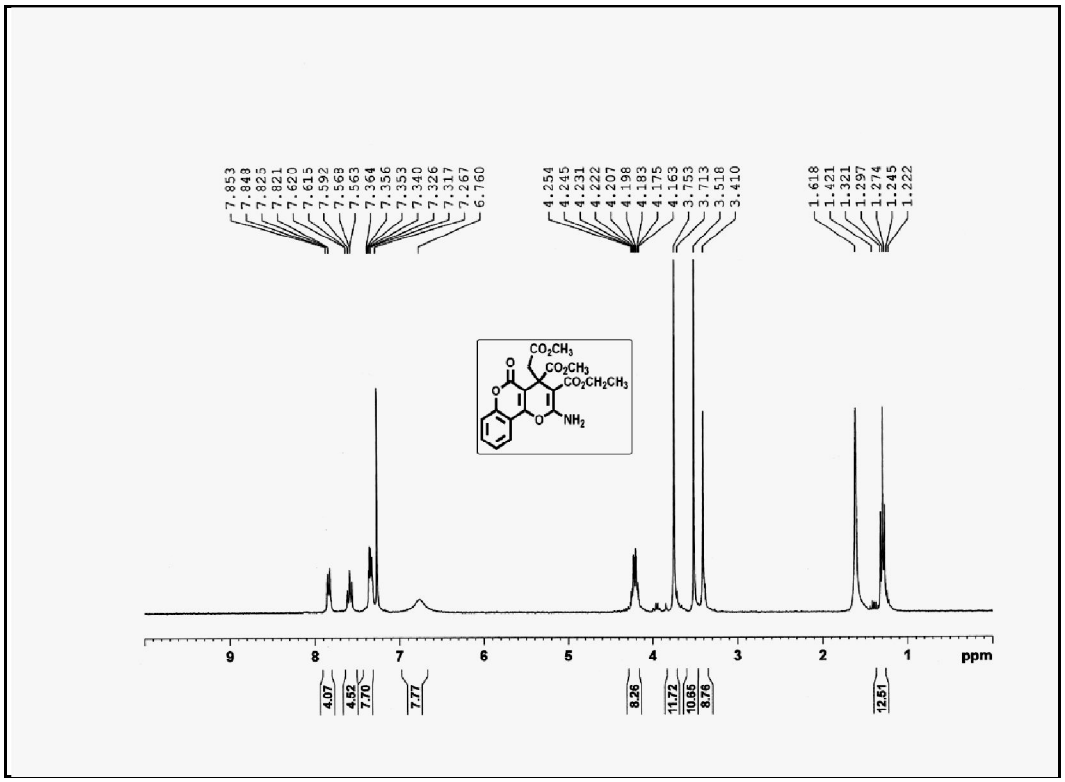
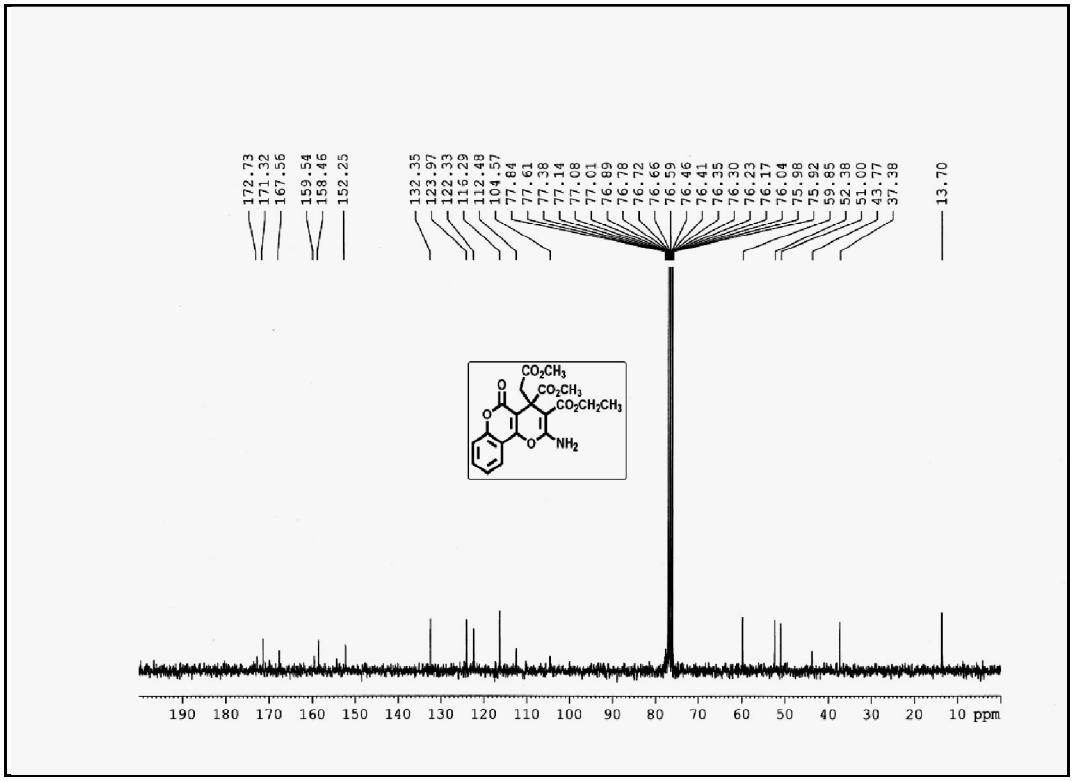


^{1}H NMR spectrum of the product 7l



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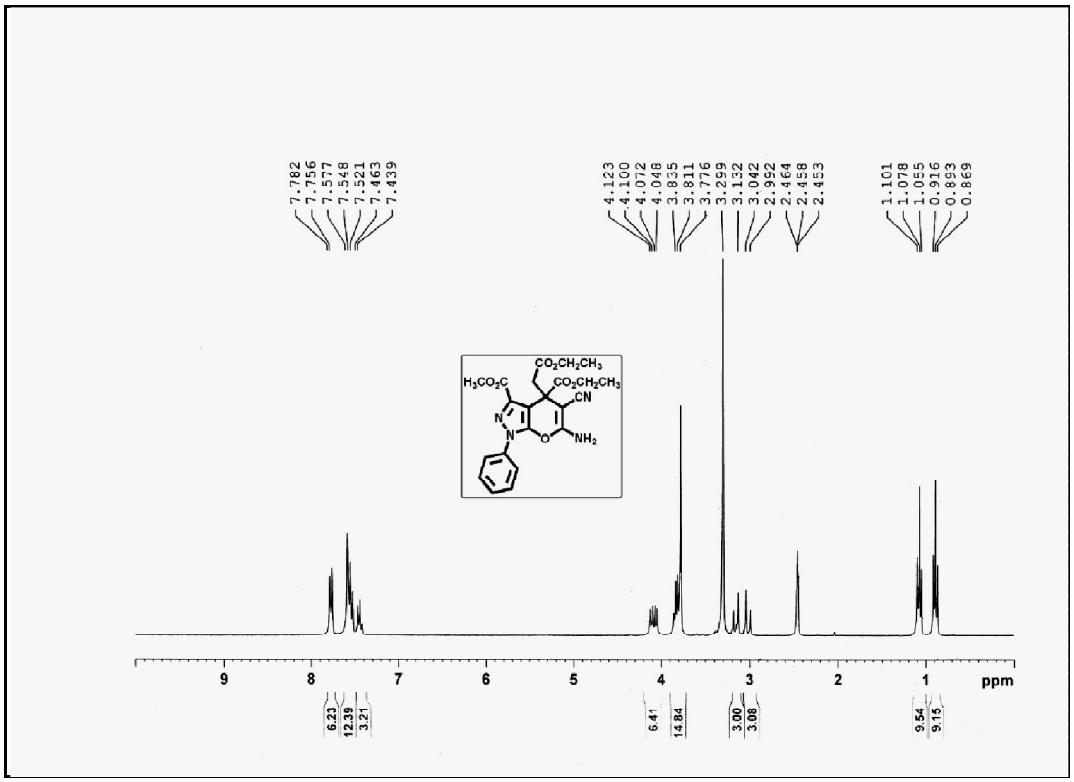
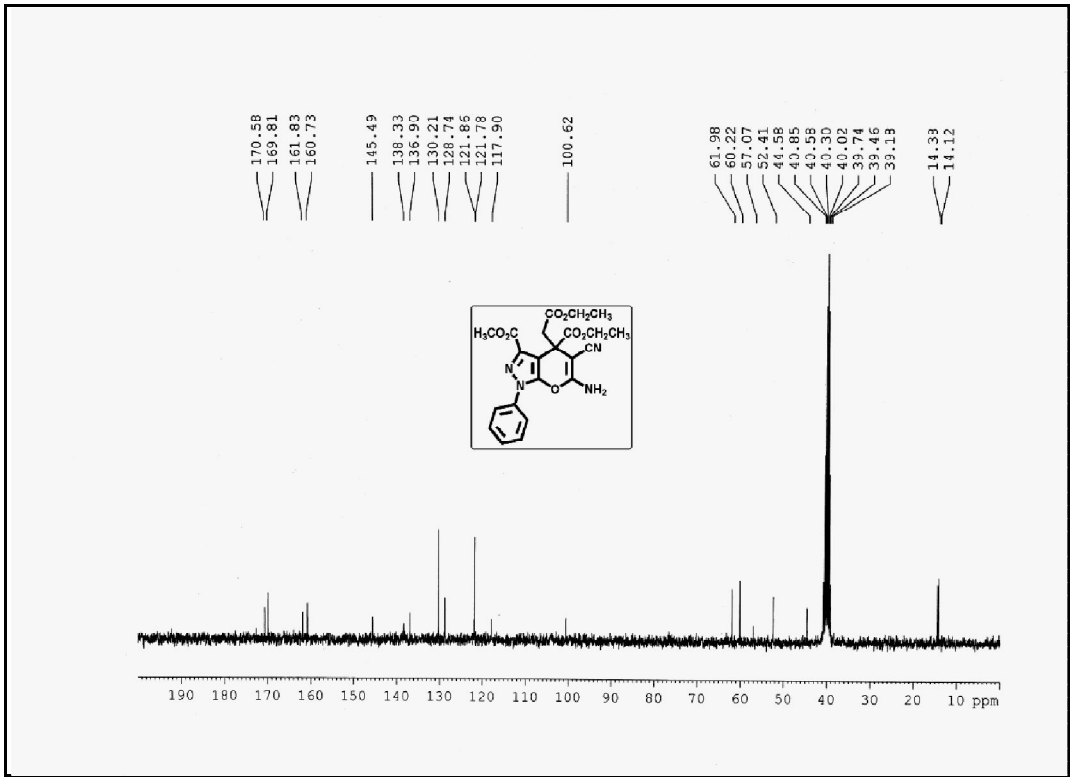
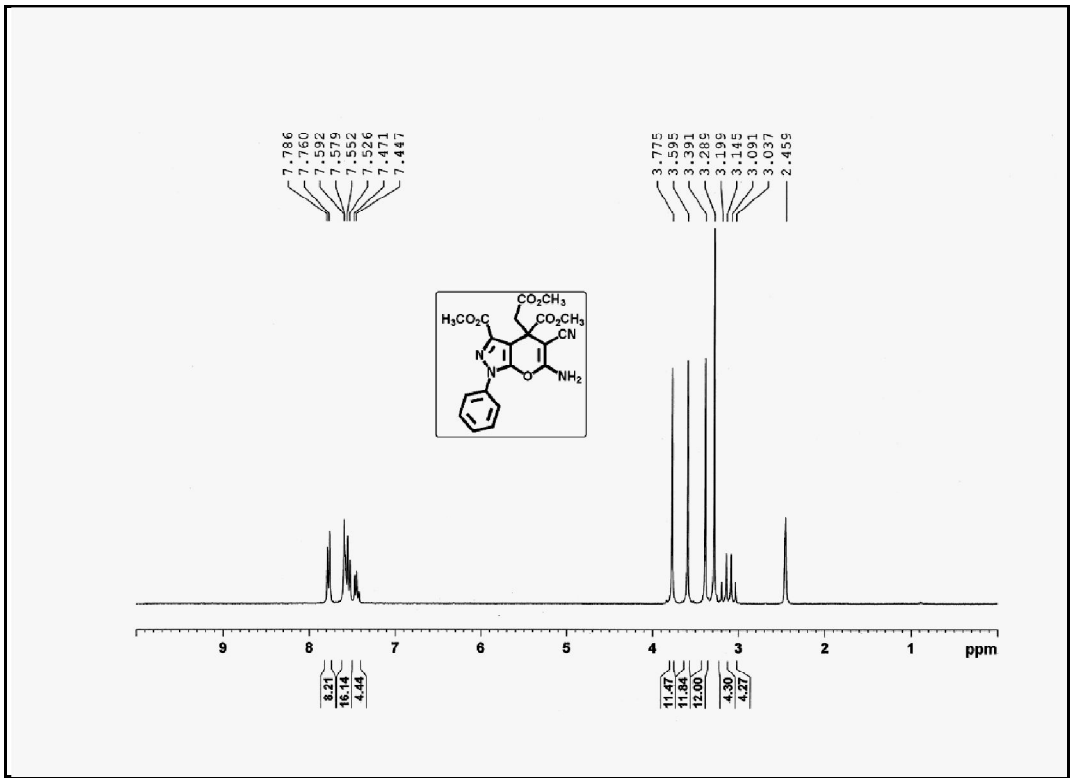


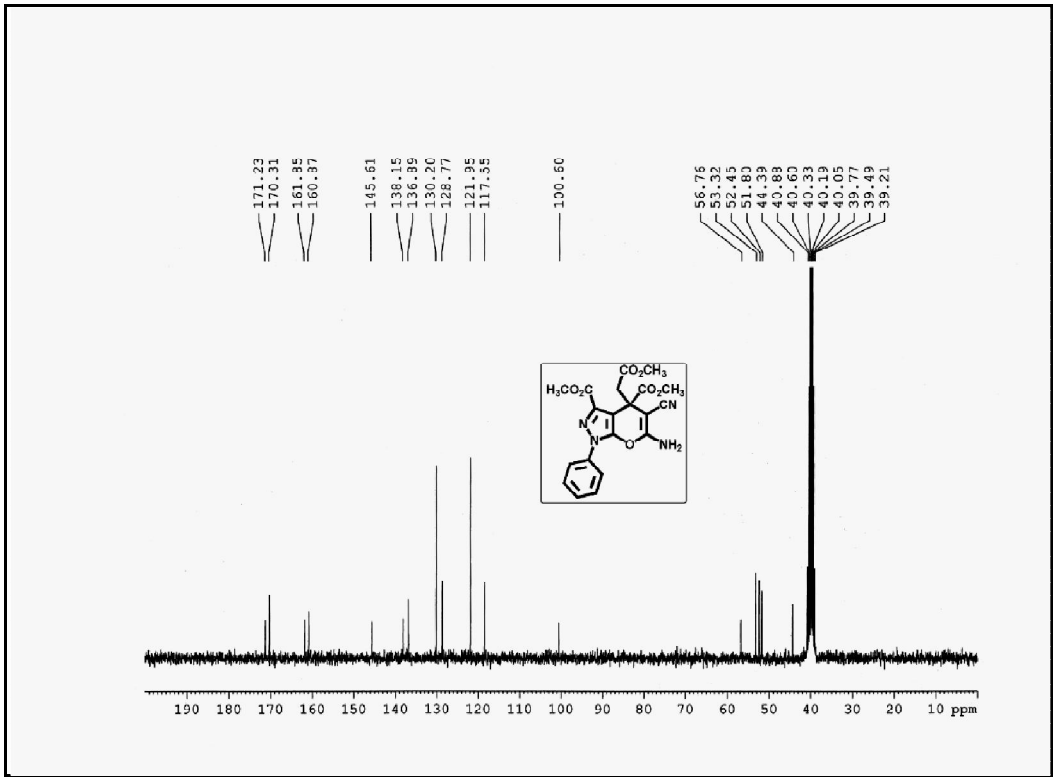
^{1}H NMR spectrum of the product 9a



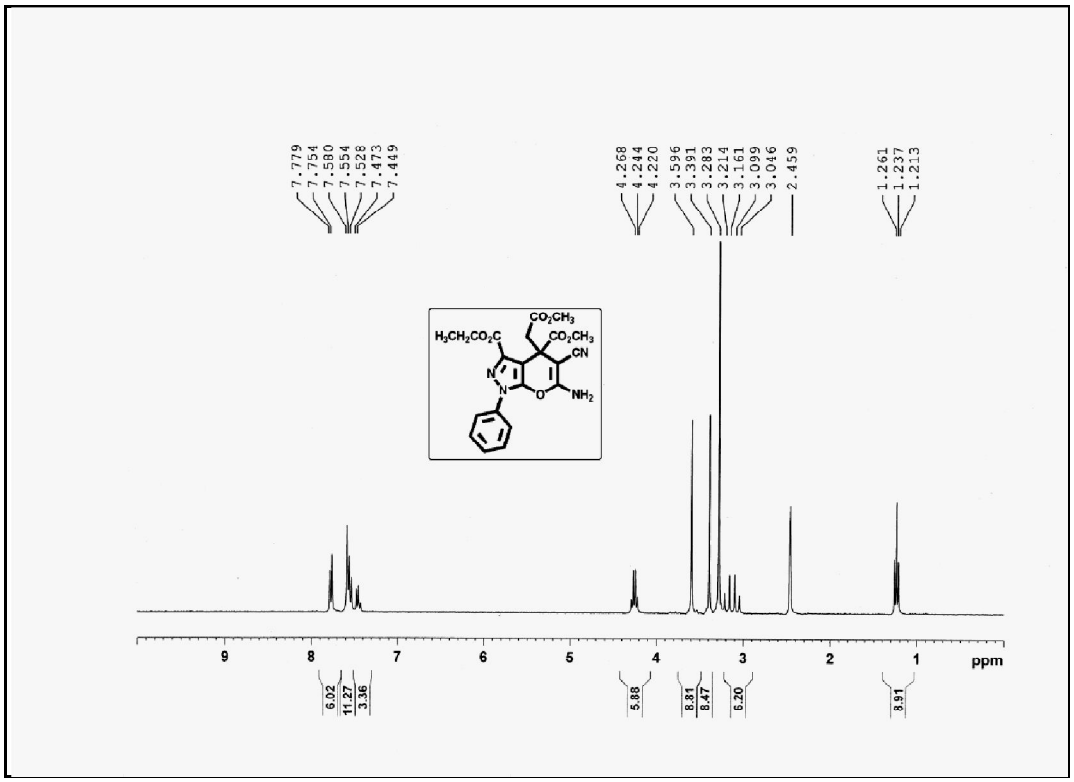
^{13}C NMR spectrum of the product 9a



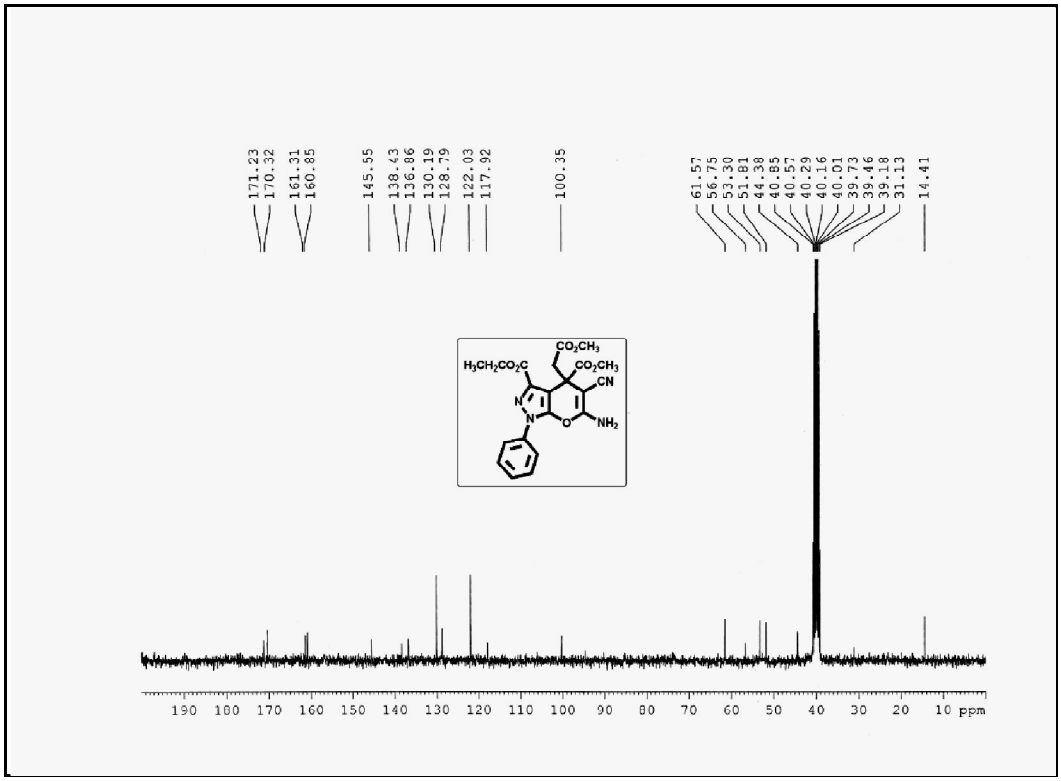
^{1}H NMR spectrum of the product 9b



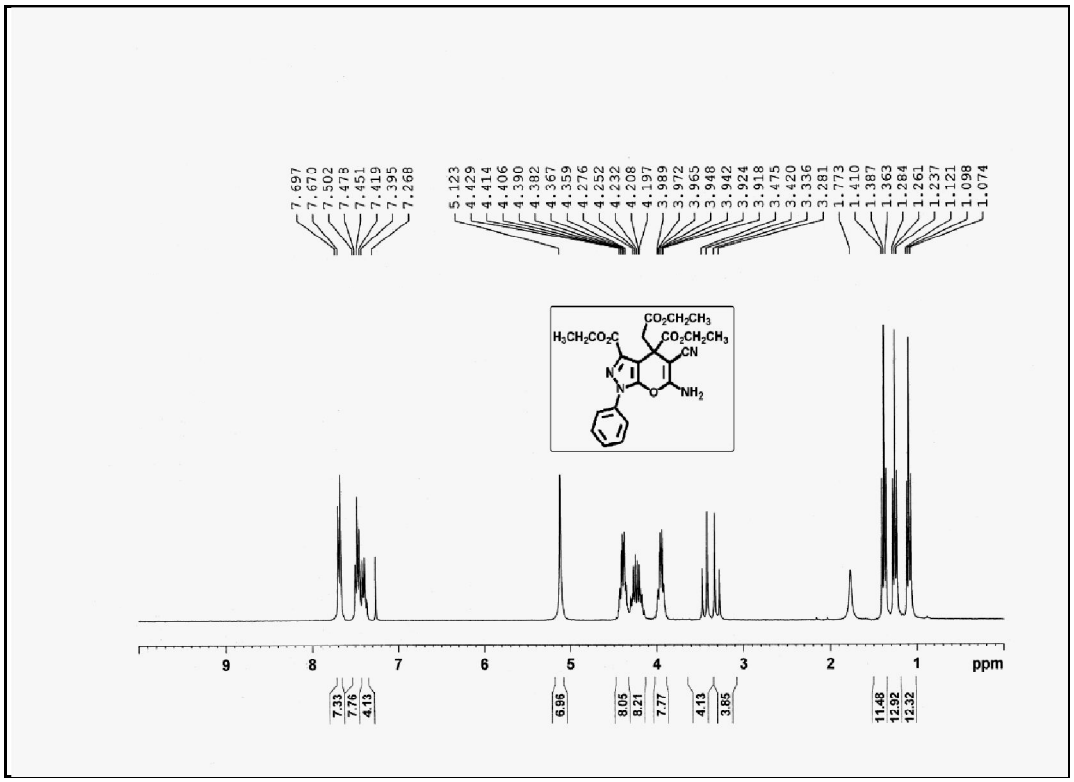
^{13}C NMR spectrum of the product 9b



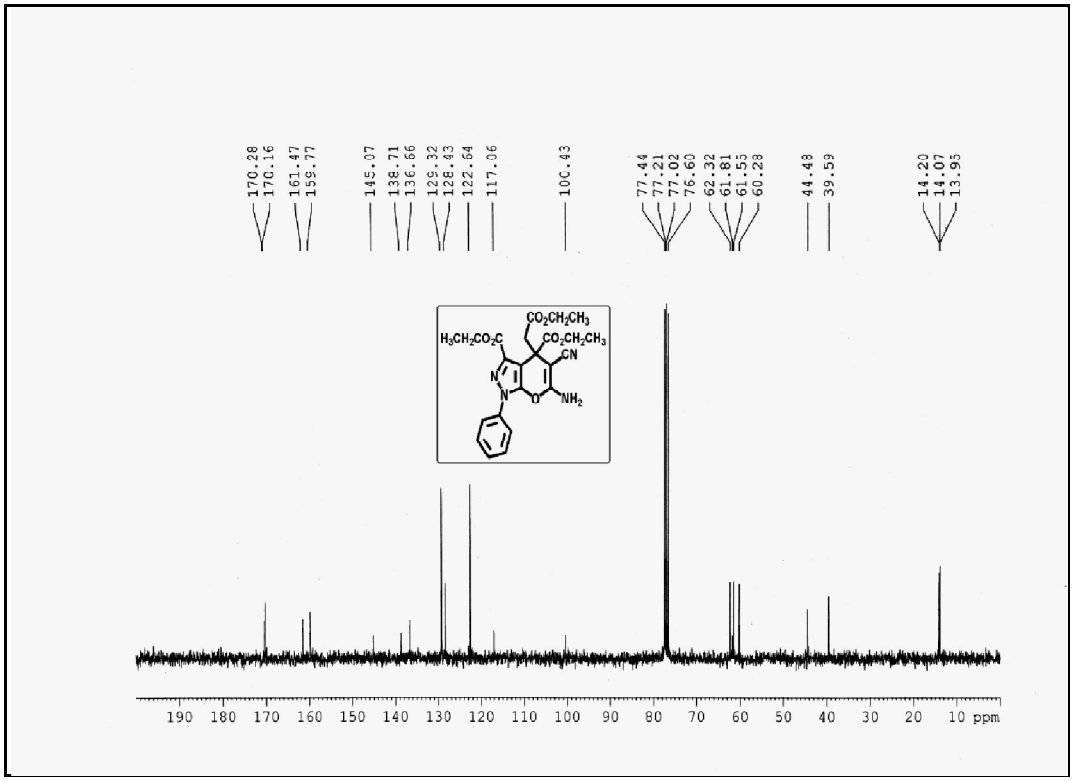
^{1}H NMR spectrum of the product 9c



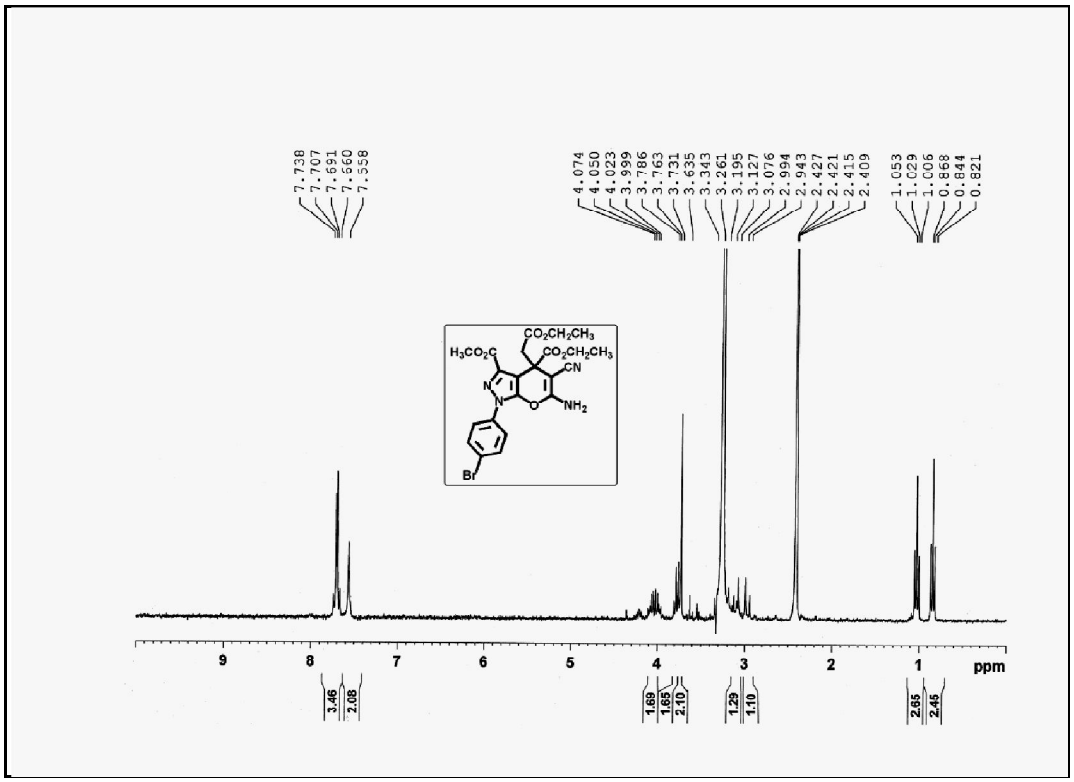
^{13}C NMR spectrum of the product 9c



^{1}H NMR spectrum of the product 9d



^{13}C NMR spectrum of the product 9d



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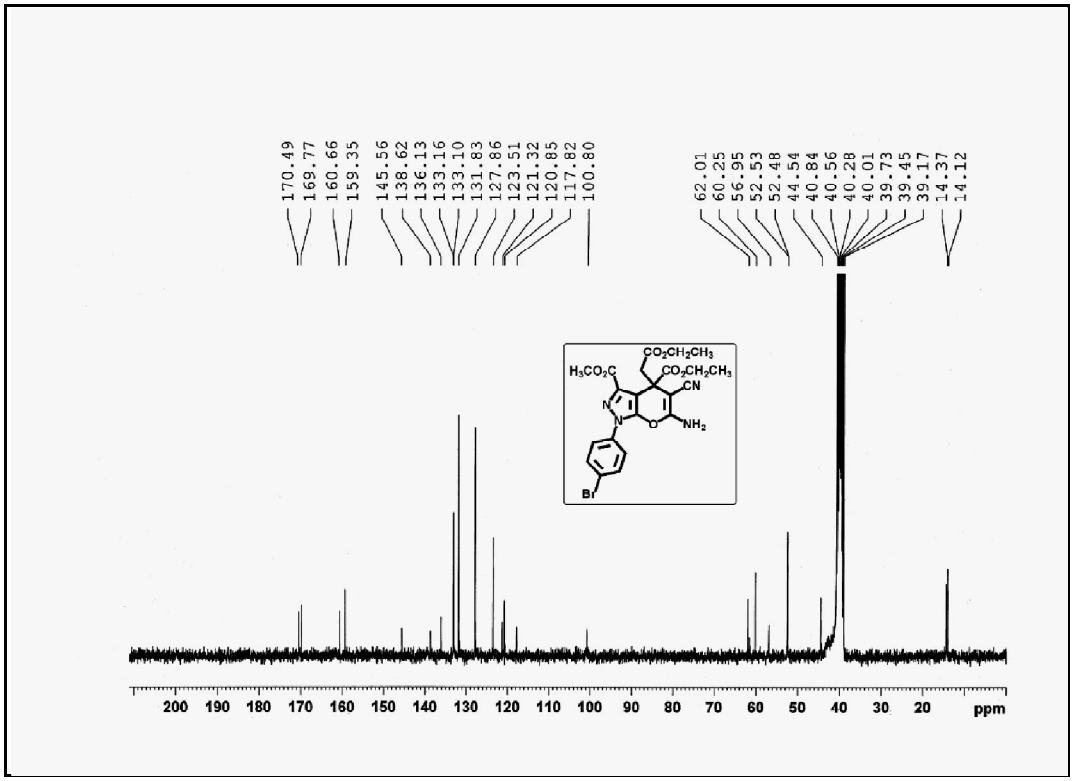

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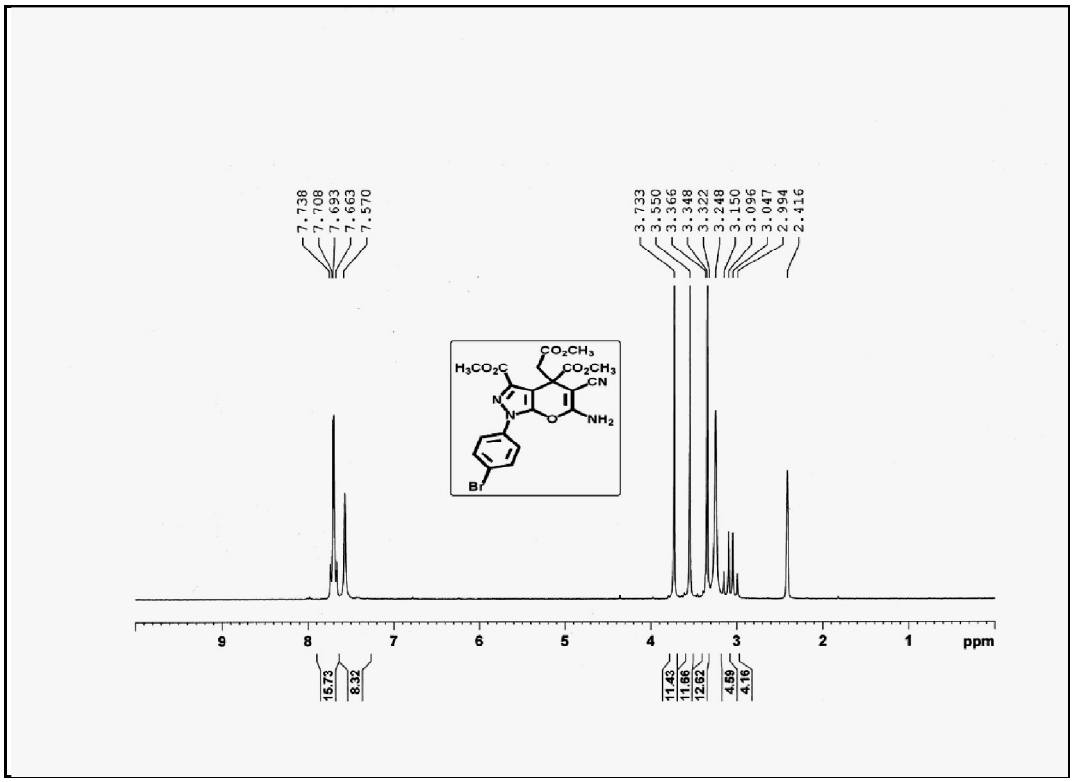
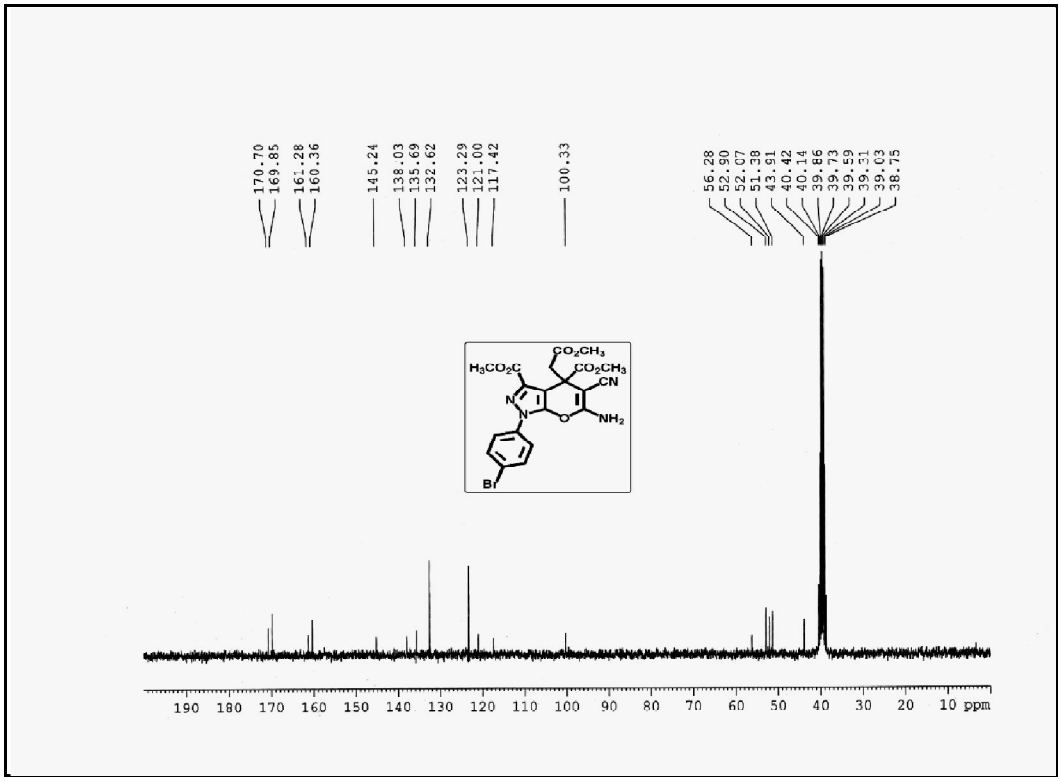


^{1}H NMR spectrum of the product 9f



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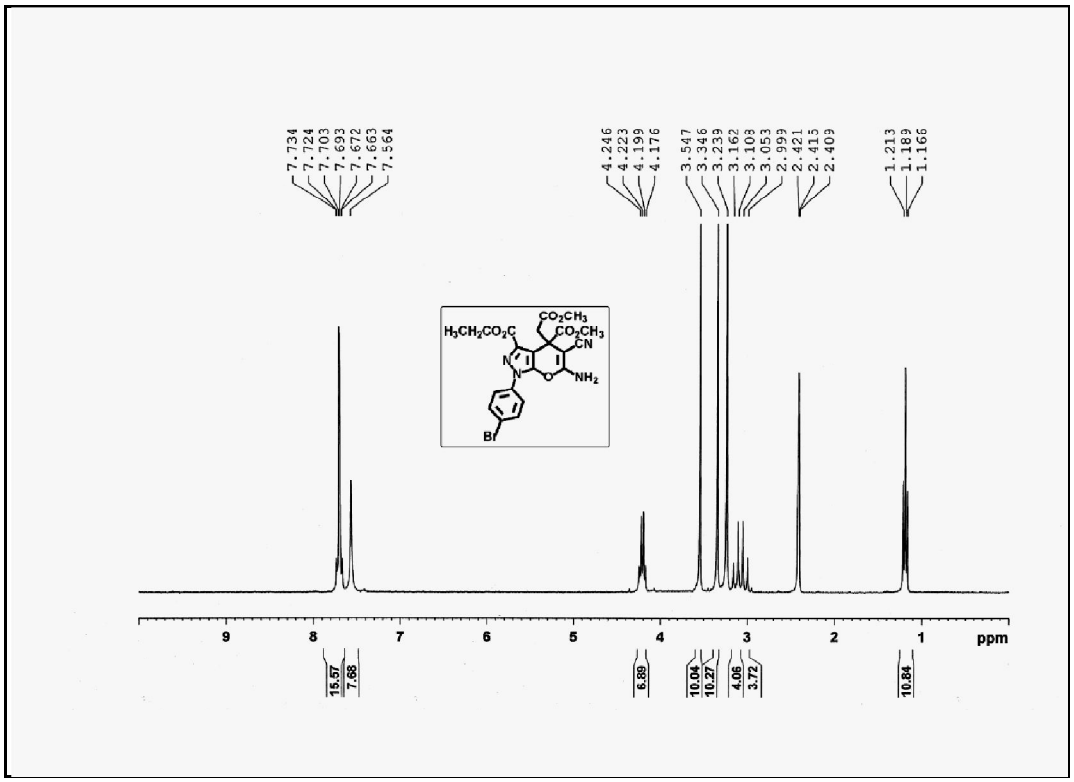

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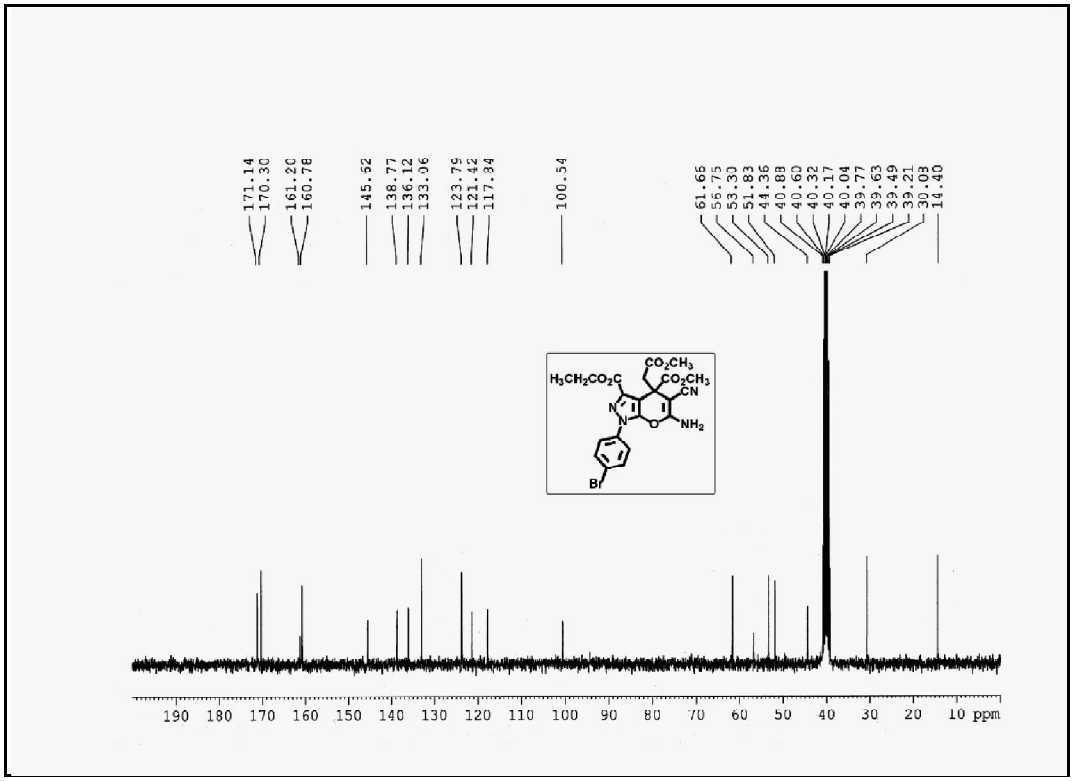
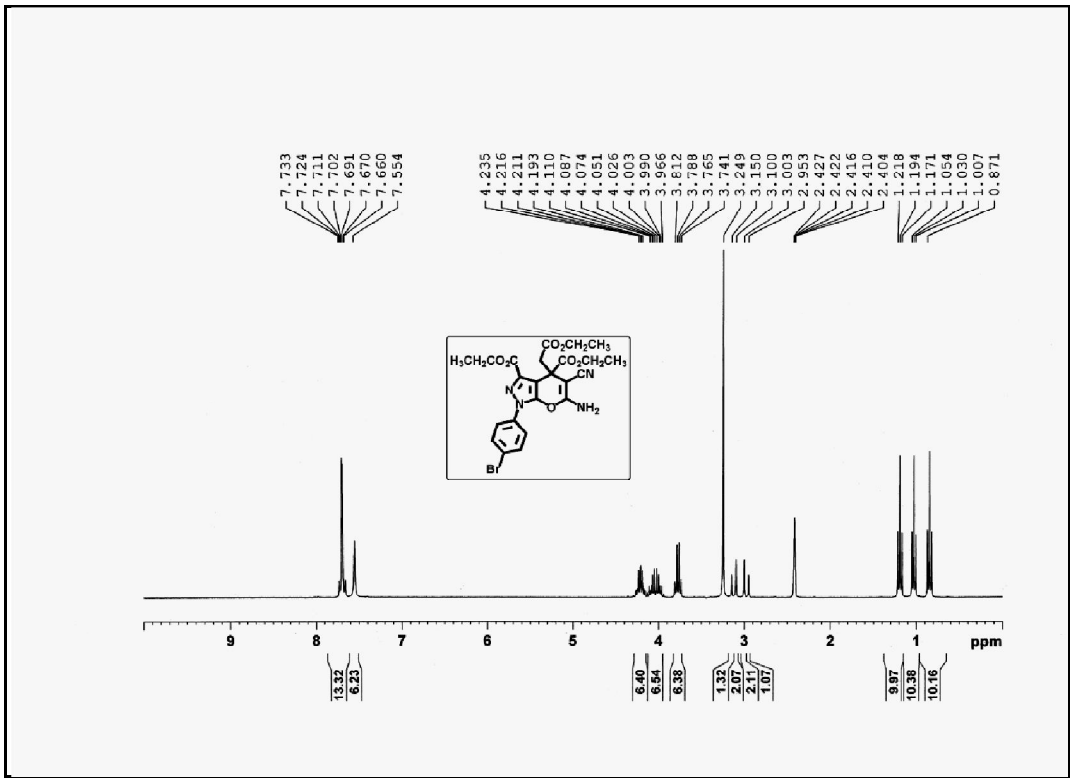


^{13}C NMR spectrum of the product 9g



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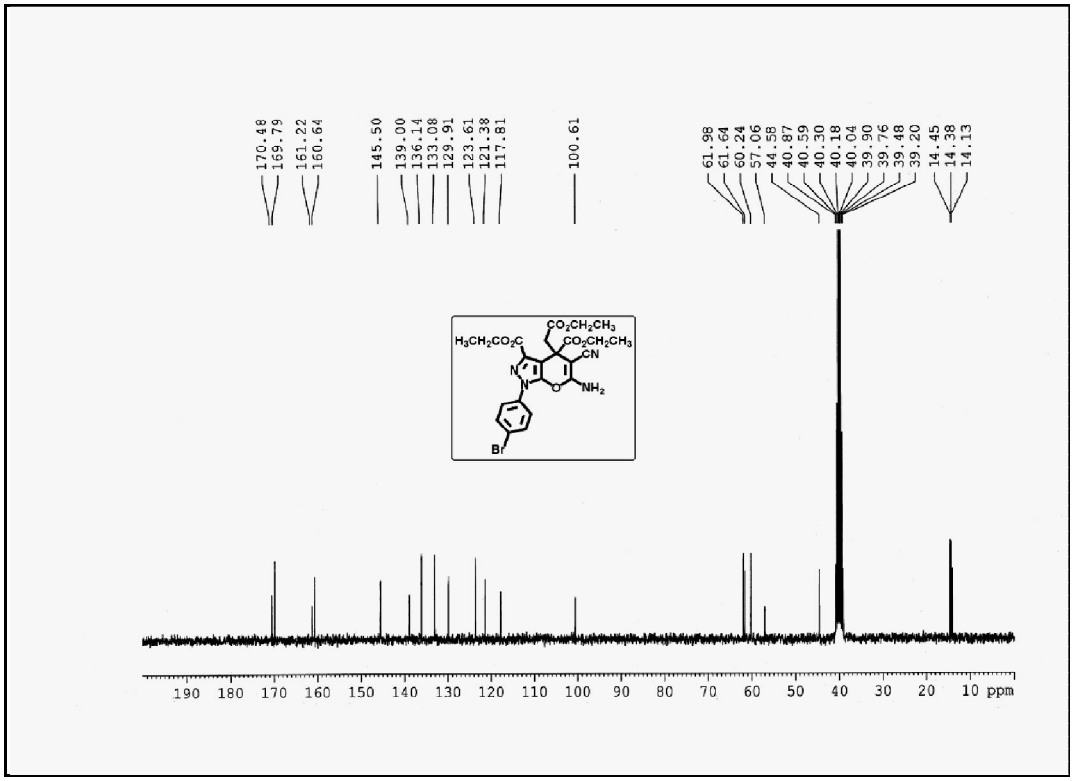
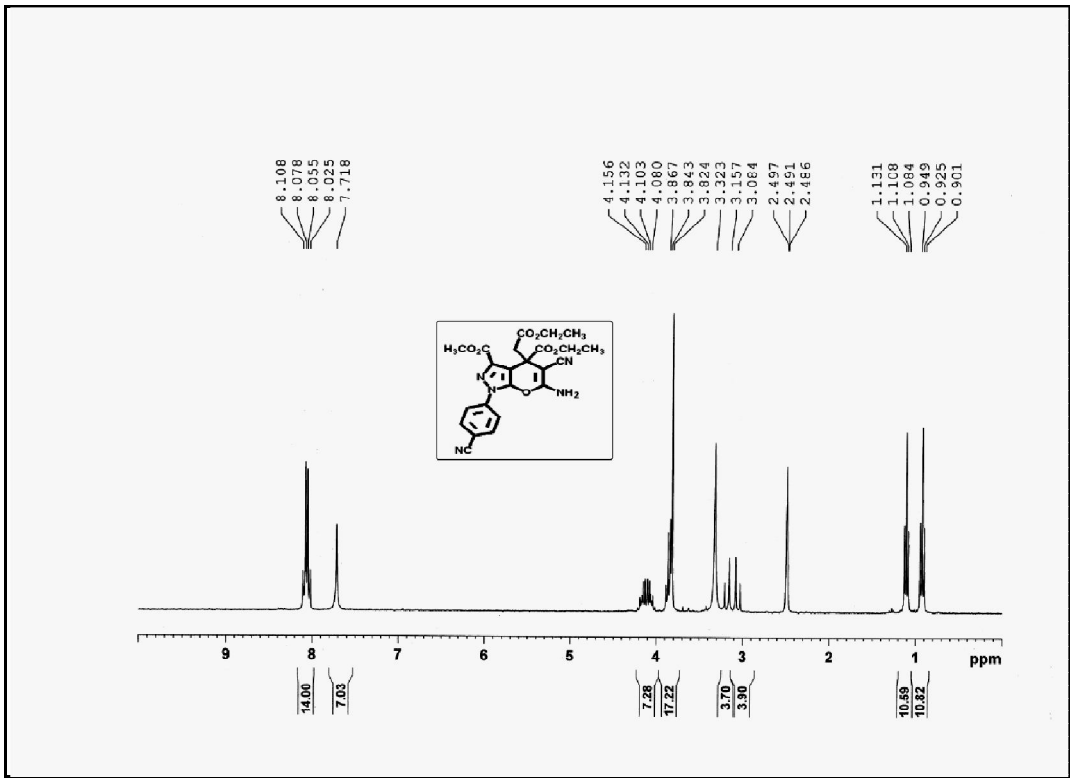
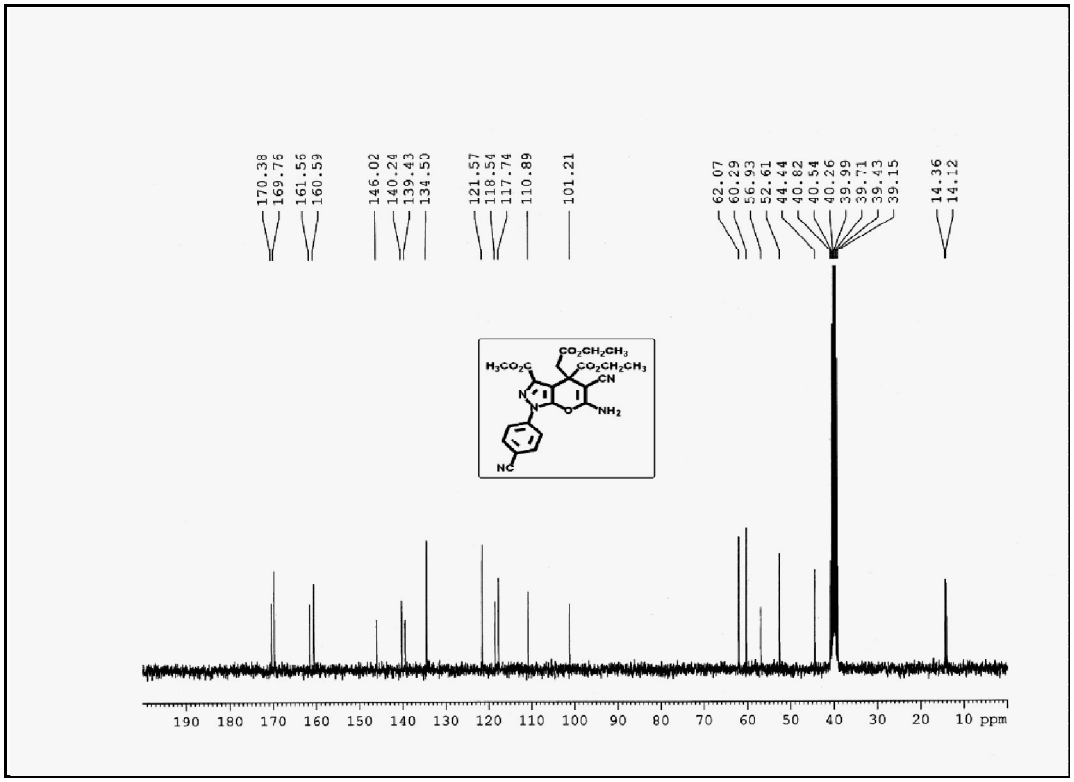


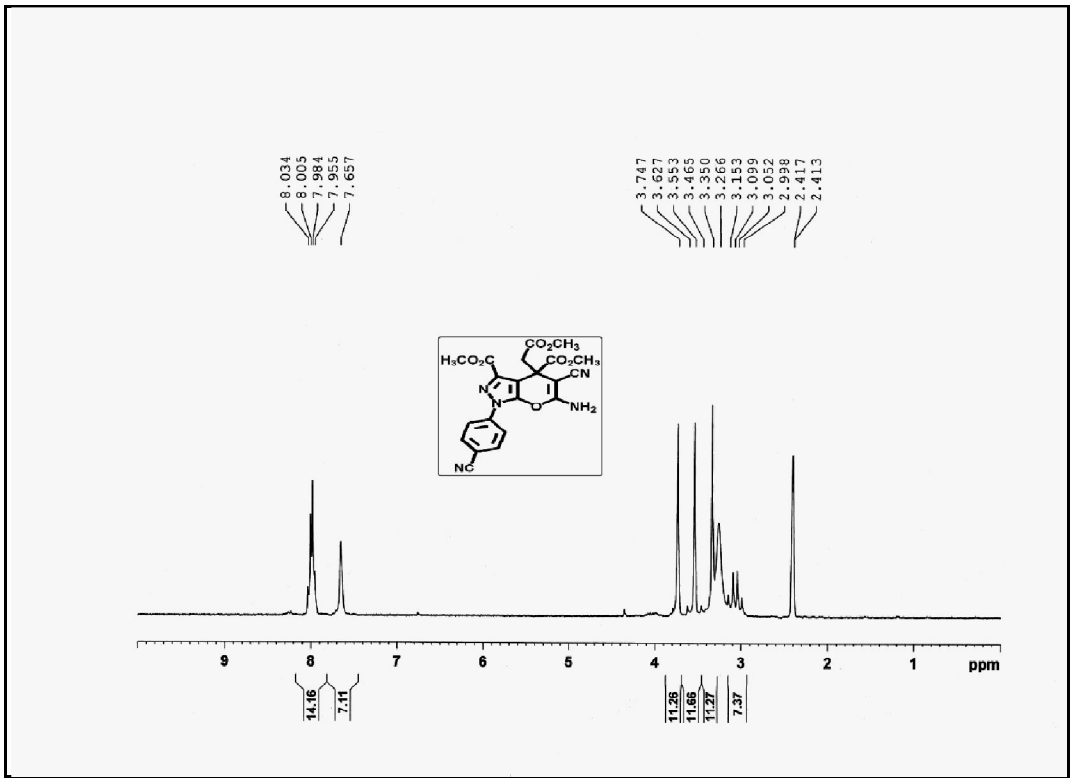
^{13}C NMR spectrum of the product 9h



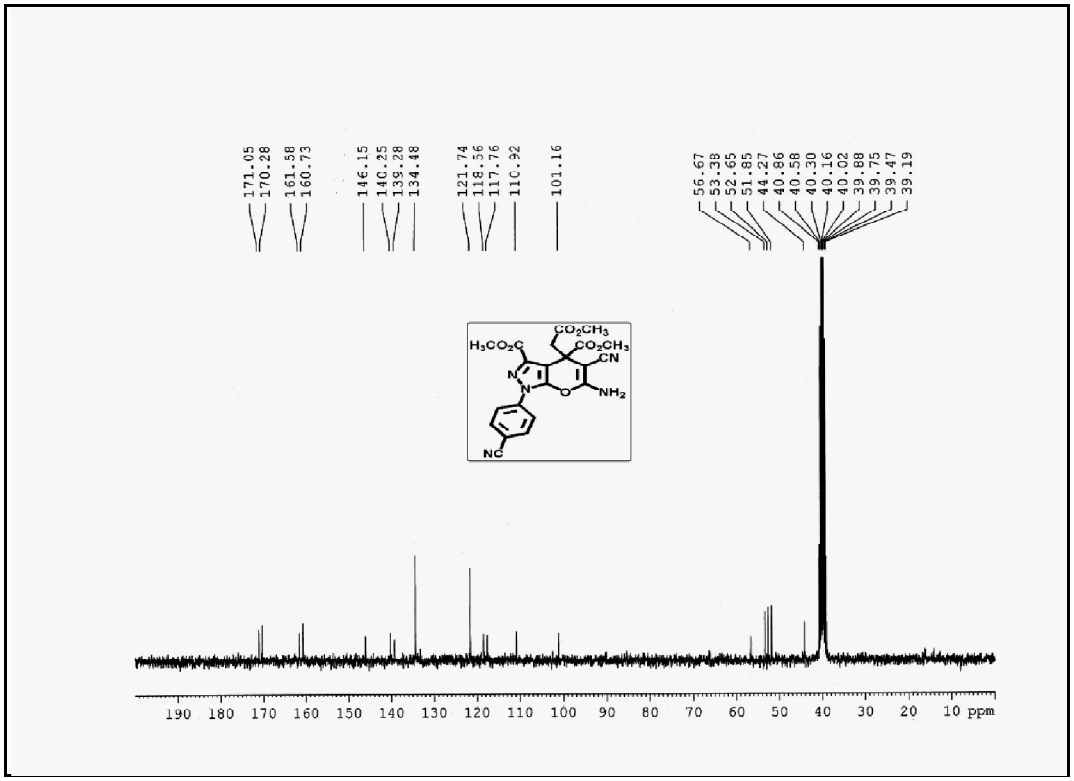
^{1}H NMR spectrum of the product 9i



^{13}C NMR spectrum of the product 9i



^{1}H NMR spectrum of the product 9j



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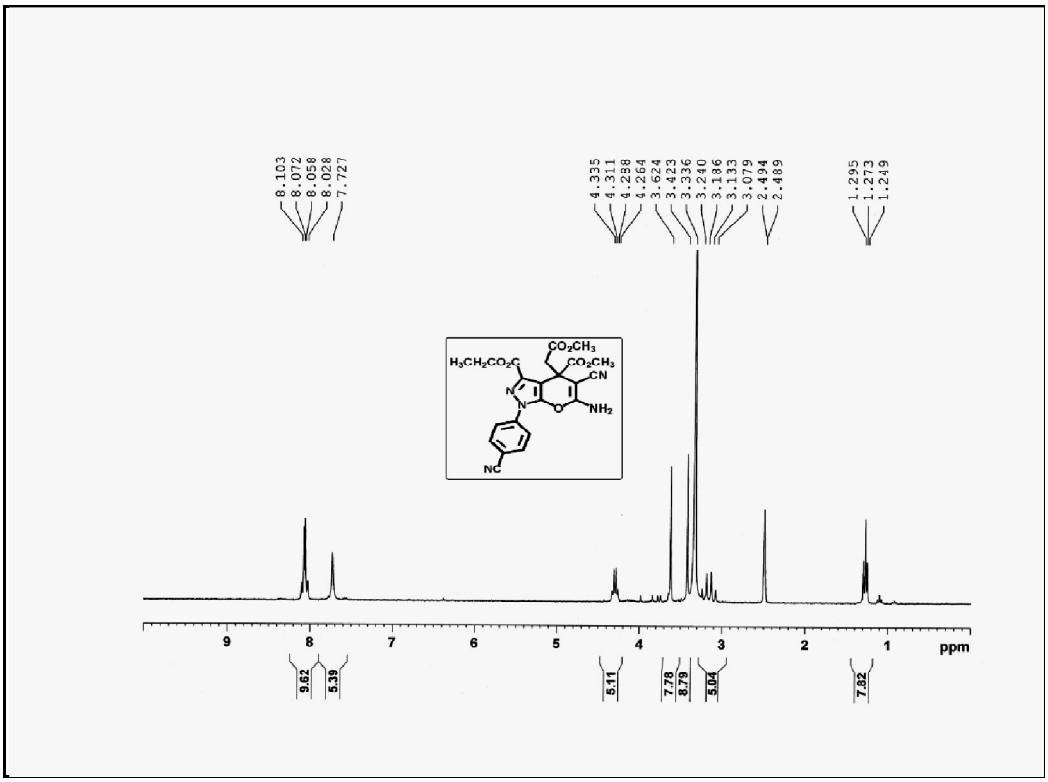

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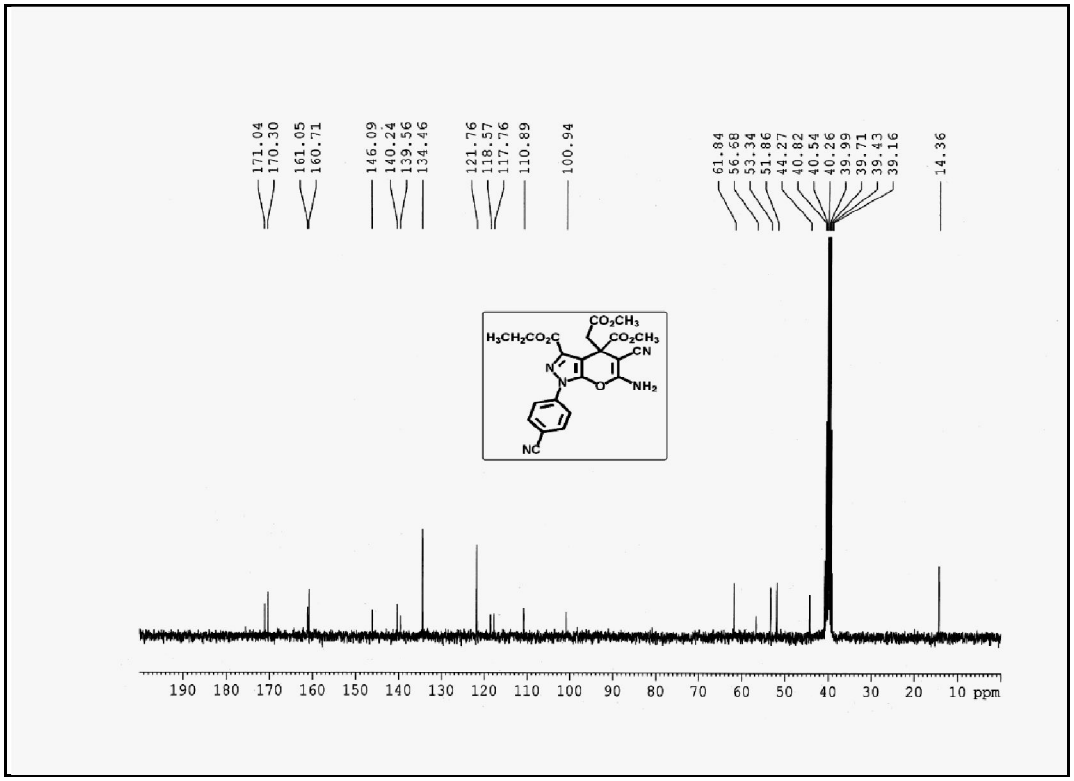

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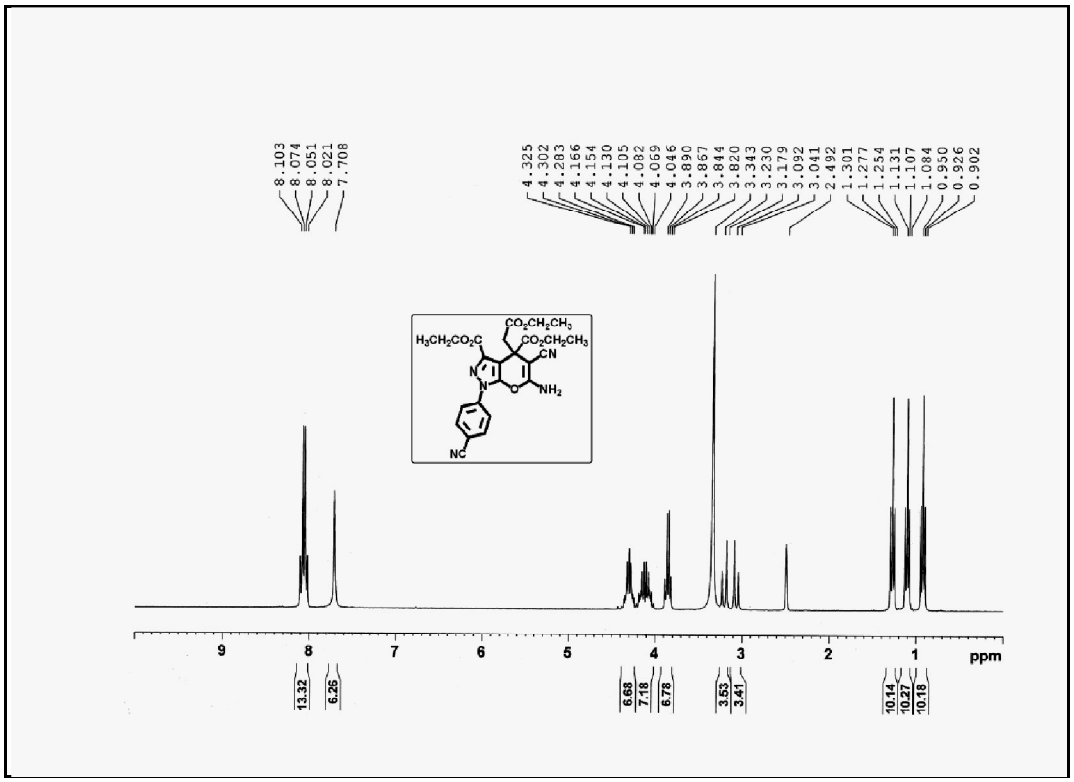
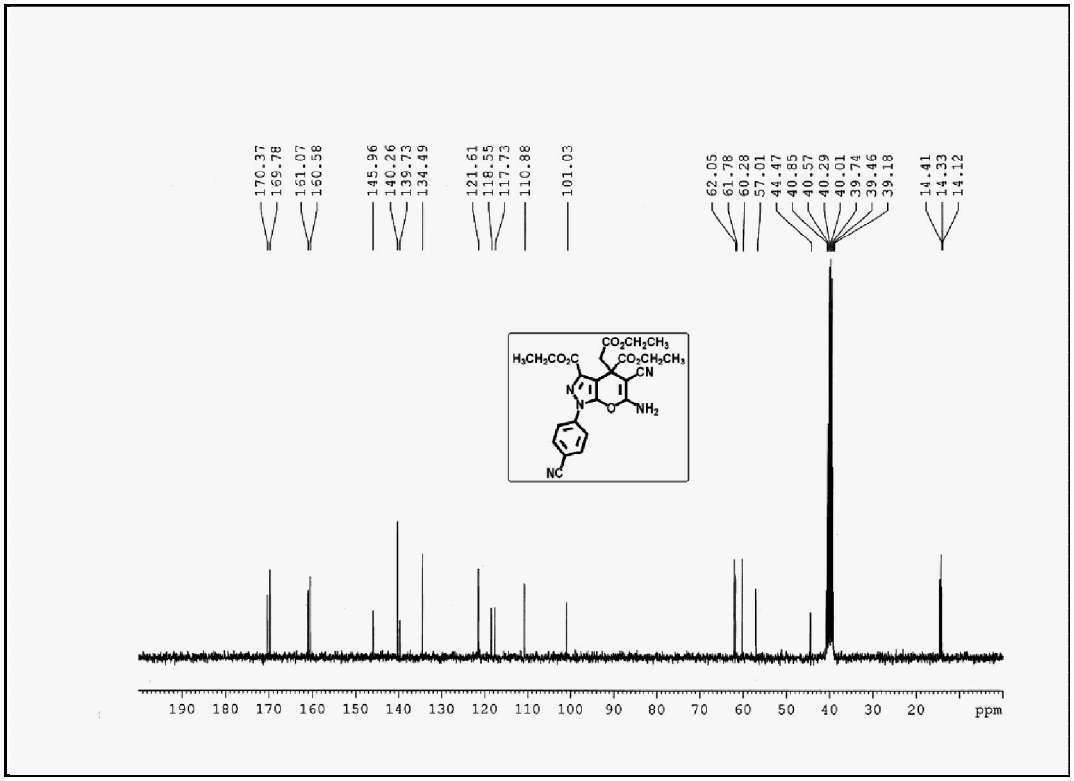
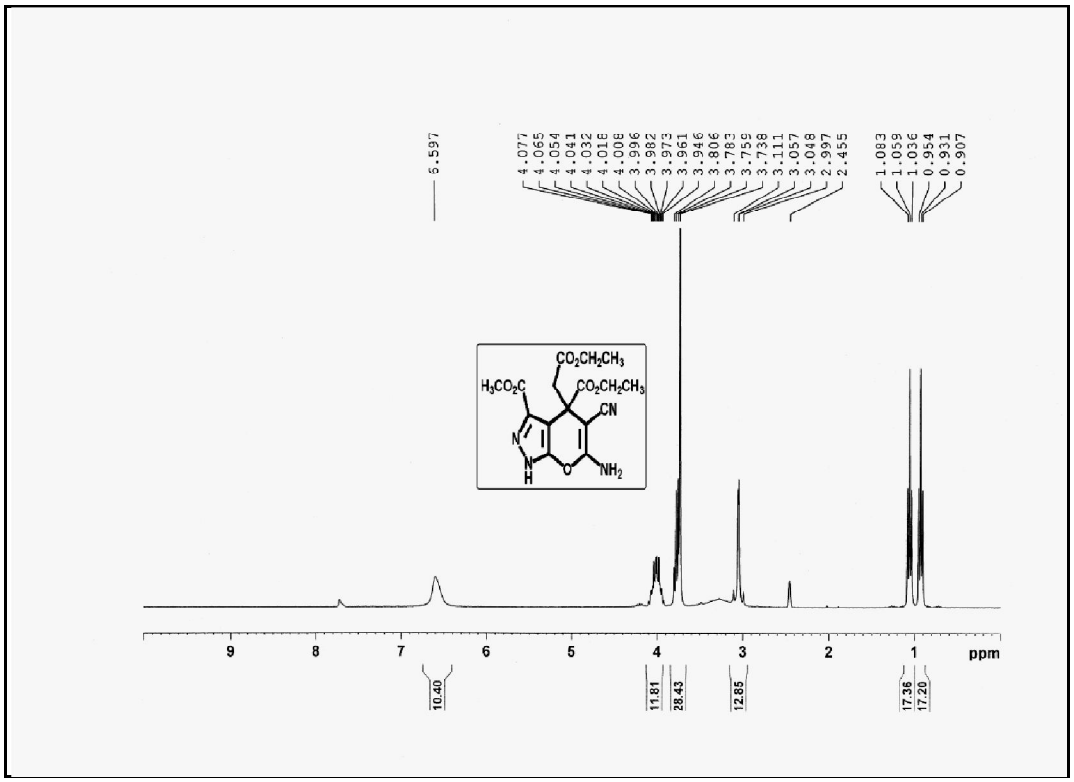


^{1}H NMR spectrum of the product 9l



^{13}C NMR spectrum of the product 9l



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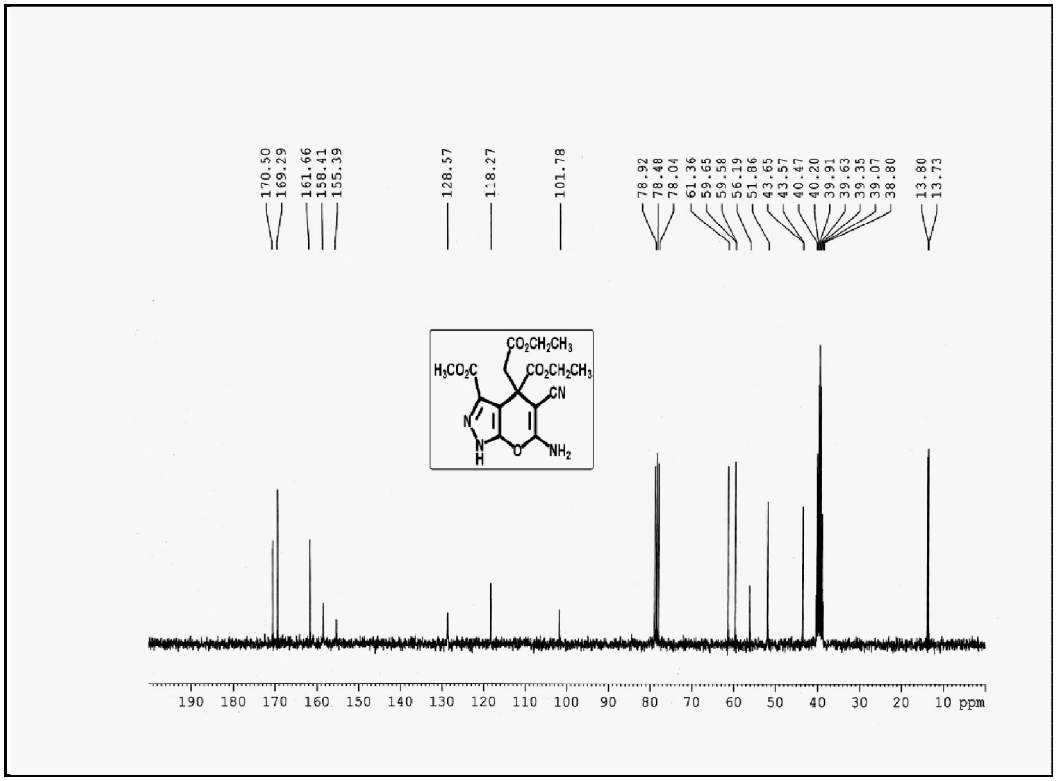
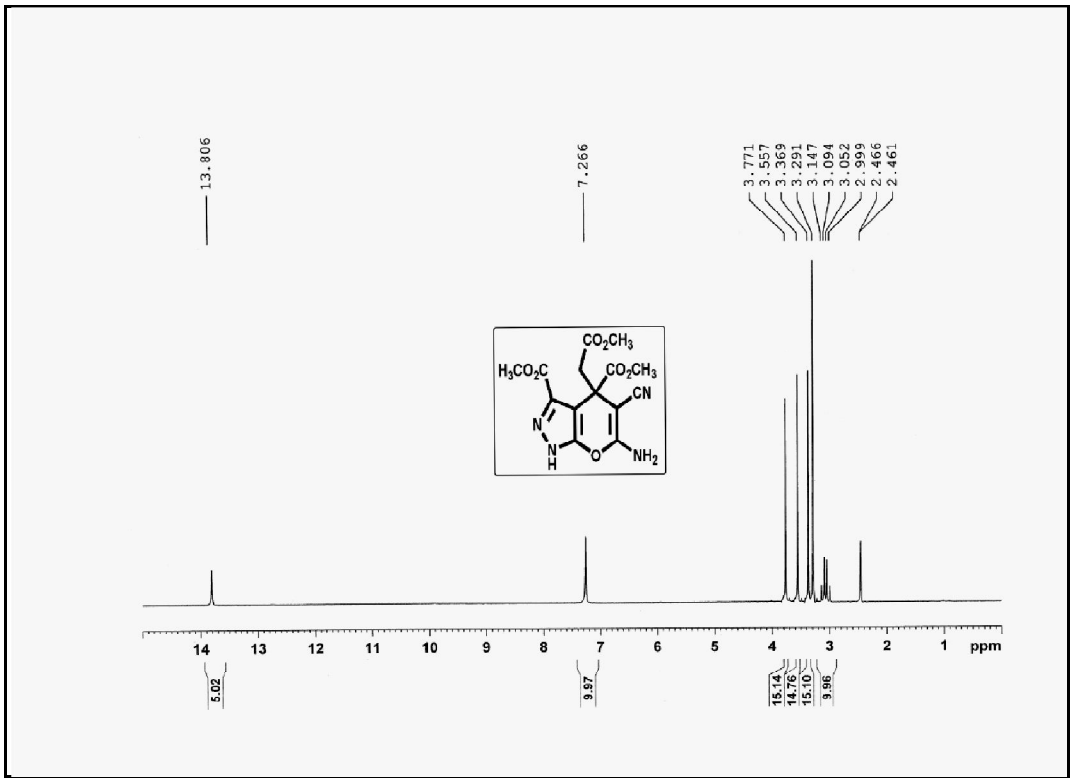
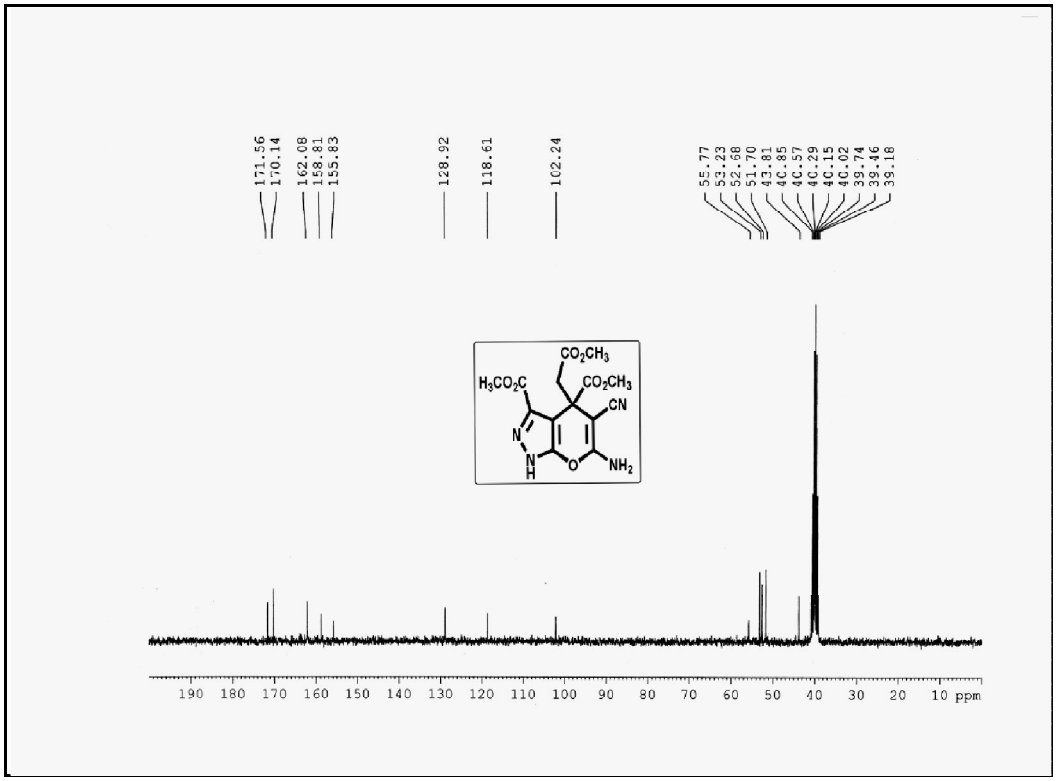


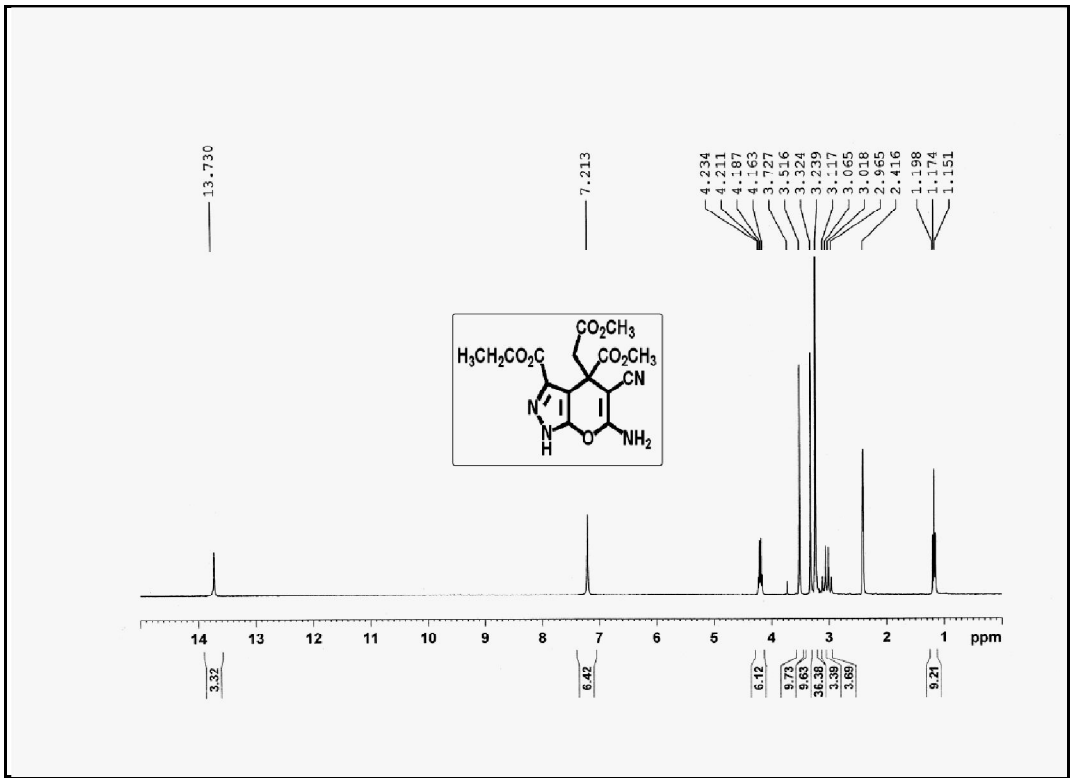
^{13}C NMR spectrum of the product 9m



^{1}H NMR spectrum of the product 9n



^{13}C NMR spectrum of the product 9n



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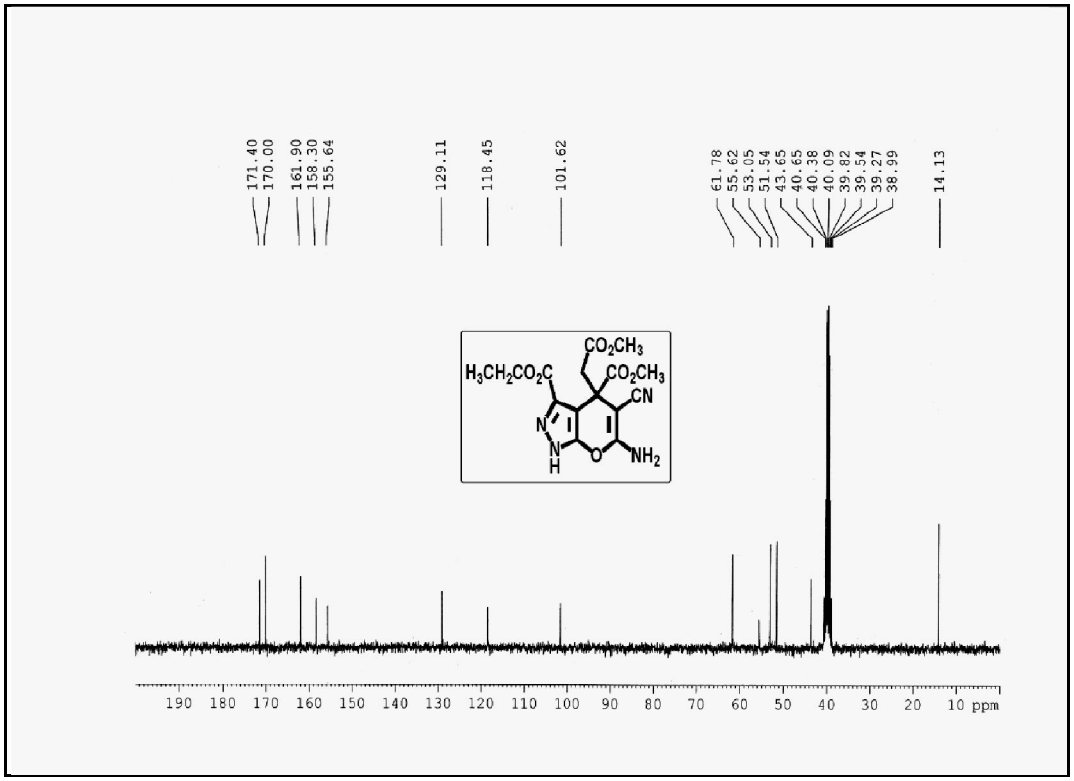
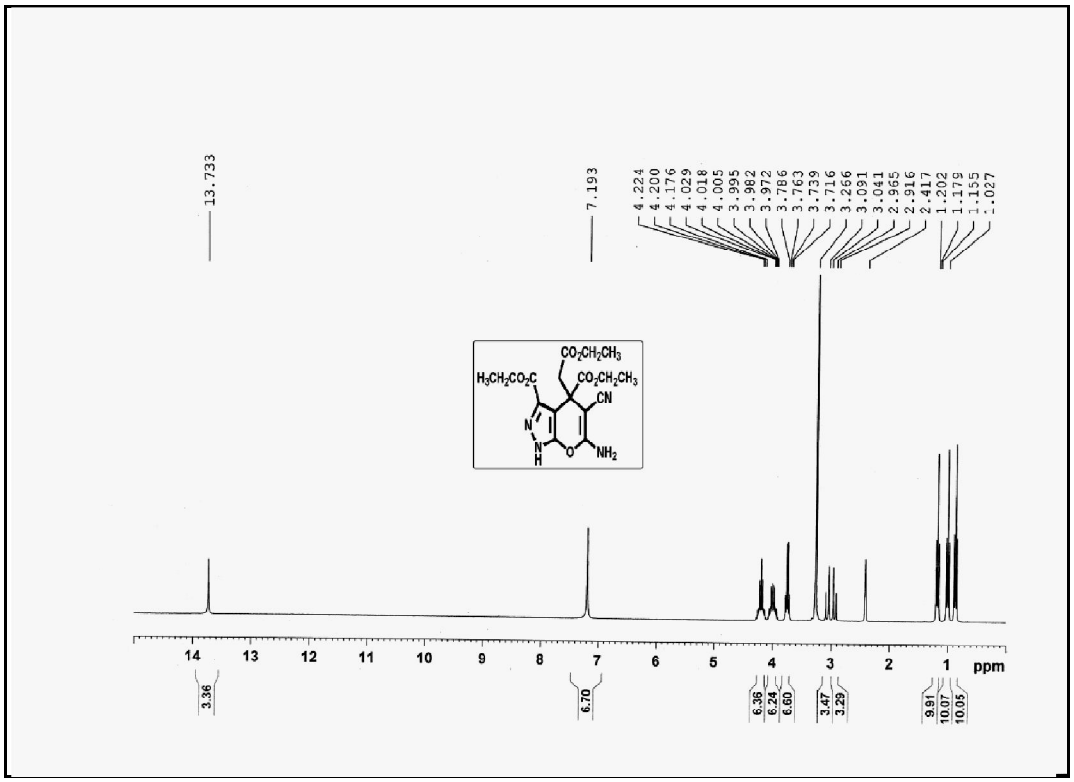
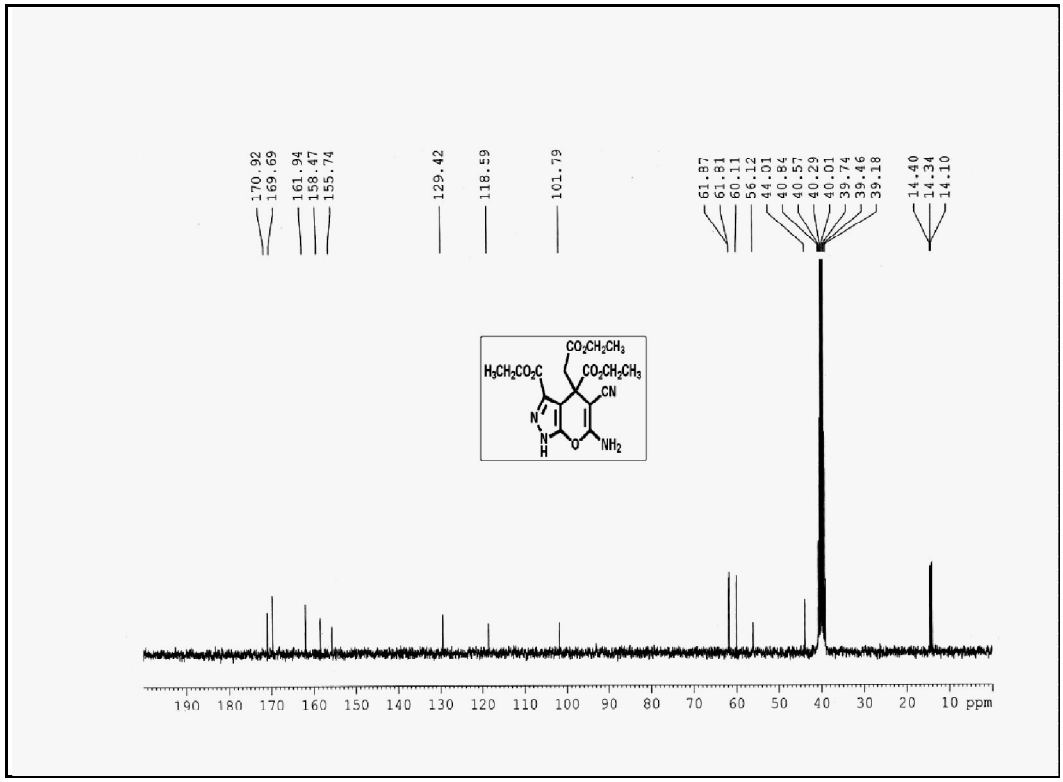


^{13}C NMR spectrum of the product 9o



^{1}H NMR spectrum of the product 9p



^{13}C NMR spectrum of the product 9p