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Synthesis of SO_3H-bearing carbonaceous solid catalyst, PEG-SAC: Application for the easy access of a diversified library of pyran derivatives

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Materials and Methods

^{1}H-NMR and ^{13}C-NMR spectral analysis were carried out on Bruker-Advance Digital 300 MHz and 75 MHz instruments; tetramethylsilane (TMS) was used as internal standard. Infrared spectra were recorded in KBr pallets in reflection mode on a Perkin Elmer RX-1 FTIR spectrophotometer. Sonication was performed by UIP 1000 hd (20KHz, 1000W). Mesoporous structure of the catalyst high-resolution transmission electron microscope (HRTEM; JEOL 2010). X-ray powder diffraction study was carried out on a Philips PW-1830 X-Ray diffractometer at a voltage of 35 kV and current 25mA. Melting points were recorded on a Köfler Block apparatus. Merck aluminum-blocked silica gel plates coated with silica gel G were used for analytical TLC and monitored under UV light and also by exposure to iodine vapor. Synthetic grade chemicals from Sigma-Aldrich, Spectrochem and E-Merck were used for the preparation of the catalyst and for carrying out the organic reactions. All the solvents used in the reaction were distilled and dried properly.

Element	Peak area	Area Sigma	k factor	Abs Corrn.	Weight %	Atomic %
C K	1913	82	1.504	1.000	85.18	95.22
O K	178	24	1.309	1.000	8.89	6.84
S K	77	25	1.047	1.000	5.93	2.28
Totals					100.00	

Table S1: Elemental analysis of the PEG-SAC catalyst

3-Amino-5-oxo-1-phenyl-1,5-dihydro-pyrano[2,3-c]chromene-2-carbonitrile (2a) : Characteristic: Yellow crystalline solid; mp: 248 ^{0}C; IR (KBr): 3438, 3285, 3175, 2191, 1736, 1658, 1599, 1409, 1274, 1163, 1114 cm^{-1};^{1}H NMR (300 MHz; DMSO-d_6): δ 5.06 (s,1H,CH), 7.21-7.65 (m, 11H, Ar, NH_2); ^{13}C NMR (75 MHz, DMSO-d_6)): δ 37.6, 57.1, 116.5, 117.0, 117.8, 119.6, 124.8, 125.2, 126.5, 127.5, 129.1, 130.3, 134.3, 143.1, 150.3, 154.1, 159.0; HRMS Calcd for $C_{19}H_{12}N_2O_3$ ($[M+H]^+$) 317.0927 found : 317.0922

3-Amino-1-(4-nitro-phenyl)-5-oxo-1,5-dihydro-pyrano[2,3-c]chromene-2-carbonitrile (2b): Characteristic: Yellow crystalline solid; mp: 256 ^{0}C; IR (KBr): 3403, 2372, 2156, 1746, 1619, 1516, 1411, 1343, 1161, 1020 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.33(s,1H,CH), 7.16-7.45 (m,6H,Ar,NH_2) , 7.67(d, J=7.8 Hz, 2H) , 8.14 (d, J=7.8 Hz, 2H, Ar); ^{13}C NMR (75 MHz, DMSO-d_6): δ 37.1, 55.8, 116.5, 116.9, 118.7, 121.3, 124.2, 125.0, 128.9, 129.0, 129.6, 129.8, 133.6, 139.8, 151.5, 155.0, 159.0; HR-MS Calcd for $C_{19}H_{11}N_3O_5$ ($[M+H]^+$) 362.0778 found : 362.0774

3-Amino-1-(4-methoxy-phenyl)-5-oxo-1,5-dihydro-pyrano[2,3-c]chromene-2-carbonitrile (2c): Characteristic: Yellow crystalline solid; mp: 234 ^{0}C; IR (KBr):3428, 3290, 3179, 2374, 2198, 2101, 1727, 1655, 1602, 1509, 1456, 1407, 1259, 1166, 1117, 1027,750, 630, 544 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.62 (s, 3H, OCH_3), 4.97 (s, 1H, CH), 6.78-7.49 (m, 10H, Ar, NH_2) ; ^{13}C NMR (75 MHz, DMSO-

d_6): δ 36.9, 55.1, 57.4, 114.4, 116.4, 117.0, 119.7, 124.7, 125.2, 126.8, 128.7, 130.3, 134.0, 135.3, 150.3, 154.1, 158.5, 158.9; HR-MS Calcd for $C_{20}H_{14}N_2O_4$ ($[M+H]^+$) : 347.1033 found : 347.1017

3-Amino-1-(4-bromo-phenyl)-5-oxo-1,5-dihydro-pyrano[2,3-c]chromene-2-carbonitrile (2d): Characteristic: Yellow crystalline solid; mp: 210 ^{0}C; IR (KBr):3429, 3292, 3177, 2921, 2864, 2193, 1727, 1653, 1599, 1406, 1297, 1167, 1114, 1009,830, 751 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.11(s, 1H, CH), 7.17-7.49 (m, 10H, Ar, NH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 36.9, 56.58, 116.5, 116.9, 119.5, 120.7, 124.8, 125.1, 125.8, 129.8, 130.4, 131.4, 131.9, 134.5, 142.6, 150.3, 154.1, 159.0; HR-MS Calcd for $C_{19}H_{11}BrN_2O_3$ ($[M+H]^+$) : 395.0032 found : 395.0035

3-Amino-5-oxo-1-p-tolyl-1,5-dihydro-pyrano[2,3-c]chromene-2-carbonitrile (2e): Characteristic: Yellow crystalline solid; mp: 231 ^{0}C; IR (KBr):3430, 3296, 3173, 2198, 1727, 1659, 1597, 1406, 1295, 1165, 1116, 753 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ2.14 (s, 3H, CH_3), 4.96 ((s, 1H, CH), 7.01-7.44(m, 10H, Ar, NH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 20.7, 37.3, 57.3, 116.4, 117.0, 119.6, 124.7, 125.2, 126.7, 127.4, 129.6, 130.3, 134.1, 136.7, 140.2, 150.3, 154.1, 158.9; HR-MS Calcd for $C_{20}H_{14}N_2O_3$ ($[M+H]^+$) : 331.1083 found : 331.1082

3-Amino-1-naphthalen-2-yl-5-oxo-1,5-dihydro-pyrano[2,3-c]chromene-2-carbonitrile (2f): Characteristic: Yellow crystalline solid; mp: 276 ^{0}C; IR (KBr): 3427, 2924, 2852, 2195, 1731, 1657, 1602, 1454, 1407, 1302, 1173, 1121 cm^{-1} ; ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.26(s, 1H, CH), 7.23-7.48 (m, 9H, Ar, NH_2), 7.85 (d, J=8.4Hz, 3H, Ar), 7.94 (s, 1H, Ar) ; ^{13}C NMR (75 MHz, DMSO-d_6): δ37.9, 57.0, 116.5, 117.1, 117.8, 119.7, 124.8, 125.2, 125.6, 126.1, 126.2, 126.3, 126.6, 127.7, 127.9, 129.0, 130.4, 132.3, 133.1, 134.4, 140.5, 150.3, 154.2, 159.0 ; HR-MS Calcd for $C_{23}H_{14}N_2O_3$ ($[M+H]^+$) : 367.1083 found : 367.1087

3-Amino-1-(4-fluoro-phenyl)-5-oxo-1,5-dihydro-pyrano[2,3-c]chromene-2-carbonitrile (2g): Characteristic: Yellow crystalline solid; mp: 203 ^{0}C; IR (KBr):3442, 3283, 3174, 1739, 1661, 1660, 1505, 1453, 1410, 1226, 1163, 1114, 1058, 997, 843, 750cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.12(s, 1H,

CH), 7.07-7.46 (m, 10H, Ar, NH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 36.8, 56.9, 115.7, 115.9, 116.5, 116.9, 117.8, 119.6, 124.8, 125.2, 126.1, 129.6, 129.7, 130.4, 134.4, 139.4, 150.3, 154.1 ; HR-MS Calcd for $C_{19}H_{11}FN_2O_3$ ($[M+H]^+$) : 335.0833 found : 335.0830

3-Amino-1-(4-cyano-phenyl)-5-oxo-1,5-dihydro-pyrano[2,3-c]chromene-2-carbonitrile (2h): Characteristic: Yellow crystalline solid; mp: 242 ^{0}C; IR (KBr):3323, 3198, 2234, 2192, 1741, 1665, 1602, 1411, 1160, 1117, 762 cm^{-1} ; ^1H NMR (300 MHz, DMSO-d_6): δ 5.25 (s, 1H, CH), 7.16-7.78 (m, 10H, Ar, NH_2); ^{13}C NMR (75 MHz, DMSO-d_6): δ 37.4, 56.0, 110.4, 116.5, 116.9, 118.6, 119.3, 124.8, 125.0, 128.7, 130.4, 133.0, 134.8, 148.3, 150.3, 154.0, 159.2; HR-MS Calcd for $C_{20}H_{11}N_3O_3$ ($[M+H]^+$) : 342.0879 found : 342.0890

3-Amino-5-oxo-1-thiophen-1,5-dihydro-pyrano[2,3-c]chromene-2-carbonitrile (2i): Characteristic: Yellow crystalline solid; mp: 205 ^{0}C; IR (KBr): 3448, 3278, 2252, 1702, 1600, 1374, 1187, 1077, 971cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 5.13(s, 1H, CH), 7.19-7.84 (m, 8H, Ar, NH_2), 8.15 (s, 1H, Ar); ^{13}C NMR (75 MHz, DMSO-d_6): δ 37.6, 56.9, 116.3, 116.5, 117.8, 118.7, 120.1, 125.0, 129.1, 132.7, 142.5, 142.8, 153.2, 159.25, 164.0; HR-MS Calcd for $C_{17}H_{10}N_2O_3S$ ($[M+H]^+$) : 323.0509 found : 323.0502

Bis[pyrano[2,3-c]chromene-2-carbonitrile] (2j): Characteristic: Yellow crystalline solid; mp: 272 ^{0}C; IR (KBr):3341, 3206, 2193, 1720, 1659, 1606, 1459, 1406, 1168, 1119 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 5.14 (s, 2H, CH), 7.34-7.47 (m, 6H, Ar, NH_2), 7.60-7.66 (m, 4H), 7.83-7.89 (m, 4H, Ar), 8.15-8.18(m, 2H, Ar); ^{13}C NMR (75 MHz, DMSO-d_6): δ 37.4, 56.0, 110.4, 116.5, 116.9, 118.6, 119.3, 124.8, 125.0, 128.7, 130.4, 133.0, 134.8, 148.3, 150.3, 154.0, 159.2; HR-MS Calcd for $C_{32}H_{18}N_4O_6$ ($[M+H]^+$) : 342.0879 found : 342.0890

2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (3a): Characteristic: white crystalline solid; mp: 232 ^{o}C; IR (KBr): 3393, 3323, 2166, 1662 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 0.86-1.05 (6H, m), 2.03-2.16 (2H, m), 2.35 (2H, s), 4.24 (1H, s), 5.40 (2H, s), 7.04-7.18 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 27.1, 28.3, 31.6, 35.2, 50.2, 113.4,

126.4, 127.0, 127.9, 161.2, 195.3; Anal. Calcd for $C_{18}H_{18}N_2O_2$: C 73.45, H 6.16, N 9.52 %. Found: C 73.47, H 6.13, N 9.54 %; HRMS of [$C_{18}H_{18}N_2O_2 + H^+$]: Calcd: 295.1447 found: 295.1449

2-Amino-7,7-dimethyl-4-(4-nitro-phenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

(3b): Characteristic: yellow crystalline solid; mp: 176 ^oC; IR (KBr): 3389, 3319, 2191, 1682 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 0.84-1.05 (6H, m), 1.89-2.16 (4H, m), 4.33 (1H, s), 6.18(2H, s), 7.29 (2H, d, *J*= 4.2 Hz), 8.02 (2H, d, *J*= 4.2 Hz) ; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 13.7, 20.5, 27.1, 28.4, 31.7, 35.5, 50.0, 58.3, 59.7, 112.2, 118.7, 123.2, 128.2, 146.3, 151.1, 158.3, 162.3, 195.4; Anal. Calcd for $C_{18}H_{17}N_3O_4$: C 63.71, H 5.05, N 12.38 %. Found: C 63.73, H 5.08, N 12.34 %; HRMS of [$C_{18}H_{17}N_3O_4 + H^+$]: Calcd: 340.1298 found: 340.1301

2-Amino-7,7-dimethyl-4-(4-methoxy-phenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

(3c): Characteristic: white crystalline solid; mp: 200 ^oC; IR (KBr): 3371, 3192, 2191, 1654 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 0.73 (3H, s), 0.81 (3H, s), 1.84-1.97 (2H, m), 2.17 (2H, s), 3.46 (3H, s), 5.55 (2H, s), 6.50 (2H, d, *J*=8.7 Hz), 6.85 (2H, d, *J*=8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 26.8, 28.1, 31.3, 34.2, 49.9, 54.4, 60.2, 113.1, 118.9, 127.8, 135.6, 157.6, 160.9, 195.2; Anal. Calcd for $C_{19}H_{20}N_2O_3$: C 70.35, H 6.21, N 8.64 %. Found: C 70.37, H 6.19, N 8.66 %; HRMS of [$C_{19}H_{20}N_2O_3 + H^+$]: Calcd: 325.1553 found: 325.1557

2-Amino-7,7-dimethyl-4-(4-methyl-phenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile

(3d): Characteristic: white crystalline solid; mp: 212 ^oC; IR (KBr): 3390, 3320, 2192, 1653 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 0.89 (3H, s), 0.97 (3H, s), 1.89-2.12 (4H, m), 2.33 (3H, s), 4.13 (1H, s), 5.81 (2H, s), 6.91-6.97 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 14.2, 21.0, 27.6, 28.9, 32.1, 35.4, 50.7, 60.2, 113.9, 119.7, 127.4, 129.1, 136.2, 141.2, 158.5, 161.9, 195.9; Anal. Calcd for $C_{19}H_{20}N_2O_2$: C 74.00, H 6.54, N 9.08 %. Found: C 74.01, H 6.57, N 9.06 %; HRMS of [$C_{19}H_{20}N_2O_2 + H^+$]: Calcd: 309.1604 found: 309.1607

2-Amino-4-(4-dimethylamino-phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (3e): Characteristic: orange crystalline solid; mp: 214 ^{o}C; IR (KBr): 3398, 3326, 2187, 1662 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 0.99 (3H, s), 1.07 (3H, s), 2.07-2.23 (2H, m), 2.44 (2H, s), 2.88 (6H, s), 4.15 (1H, s), 6.22 (2H, s), 6.61 (2H, d, *J*=8.4 Hz), 7.01 (2H, d, *J*=8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 26.1, 30.7, 49.3, 59.0, 111.3, 112.6, 118.7, 126.8, 157.1, 160.3, 194.5; Anal. Calcd for $C_{20}H_{23}N_3O_2$: C 71.19, H 6.87, N 12.45 %. Found: C 71.21, H 6.90, N 12.43 %; HRMS of [$C_{20}H_{23}N_3O_2$ + H^+]: Calcd: 338.1869 found: 338.1872

2-Amino-4-furan-2-yl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (3f): Characteristic: white crystalline solid; mp: 224 ^{o}C; IR (KBr): 3395, 3327, 2195, 1665 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06 (3H, s), 1.12 (3H, s), 2.28 (2H, s), 2.44 (2H, s), 4.57 (1H, s), 4.62 (2H, s), 6.18 (1H, d, *J*=3.0 Hz), 6.27 (1H, dd, *J*=3.0 & 1.8 Hz), 7.26 (1H, d, *J*=1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.4, 28.9, 29.0, 32.2, 40.7, 50.6, 106.2, 110.5, 141.7, 154.2, 158.3, 162.4, 195.6; Anal. Calcd for $C_{16}H_{16}N_2O_3$: C 67.59, H 5.67, N 9.85 %. Found: C 67.61, H 5.64, N 9.84 %; HRMS of [$C_{16}H_{16}N_2O_3$ + H^+]: Calcd: 285.1240 found: 285.1237

2-Amino-7,7-dimethyl-5-oxo-4-pyridin-4-yl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (3g): Characteristic: white crystalline solid; mp: 192 ^{o}C; IR (KBr): 3392, 3042, 2184, 1673 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 0.91 (3H, s), 0.99 (3H, s), 2.03-2.17 (2H, m), 2.37 (2H, s), 4.21 (1H, s), 6.16 (2H, s), 7.06-7.08 (2H, m), 8.36, 8.38 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 27.5, 28.8, 32.1, 35.5, 50.5, 58.5, 112.5, 119.3, 122.9, 149.7, 152.8, 158.9, 162.9, 195.8; Anal. Calcd for $C_{17}H_{17}N_3O_2$: C 69.14, H 5.80, N 14.23 %. Found: C 69.16, H 5.82, N 14.26 %. HRMS of [$C_{17}H_{17}N_3O_2$ + H^+]: Calcd: 296.1400 found: 296.1398

3-amino-1-phenyl-1H-benzo[f]chromene-2-carbonitrile (4a):

White solid: mp 209 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.09 (1H, s), 6.30 (2H, br s), 7.02-7.29 (7H, m), 7.61-7.78 (3H, m); ^{13}C NMR (75 MHz, DMSO-d_6) δ 58.7, 115.0, 116.5, 120.2, 123.1, 124.4, 126.3, 126.6, 128.3, 129.0, 130.7, 144.9, 146.8, 159.4; Anal. Calcd for $C_{20}H_{14}N_2O$: C, 80.52; H, 4.73; N, 9.39 % Found: C, 80.58; H, 4.75; N, 9.32 %

3-amino-1-(4-methoxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (4b):

White solid: mp 224 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.61 (3H, s), 5.10 (1H, s), 6.30 (2H, s), 6.72 (2H, d, J=8.4 Hz), 7.09 (2H, d, J=8.4 Hz) 7.31-7.41 (3H, m), 7.55-7.60 (2H, m), 7.78 (1H, d, J=7.8 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ 55.0, 58.1, 102.0, 111.1, 113.1, 113.4, 116.9, 117.8, 122.8, 124.0, 128.7, 131.9, 138.2, 141.9, 149.4, 152.1, 157.7, 160.4. Anal. Calcd for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53 %. Found: C, 76.85; H, 4.93; N, 8.57 %

3-amino-1-(4-nitrophenyl)-1H-benzo[f]chromene-2-carbonitrile (4c):

White solid: mp 229 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.25 (1H, s), 6.22(2H, s), 7.16-7.88 (10H, m); ^{13}C NMR (75 MHz, DMSO-d_6) δ 58.3, 113.9, 117.0, 120.2, 121.8, 121.9, 123.2, 125.2, 127.5, 128.7, 130.0, 130.3, 131.3, 133.5, 147.3, 148.5, 160.0; Anal. Calcd for $C_{20}H_{13}N_3O_3$: C, 69.96; H, 3.82; N, 12.24 %. Found: C, 69.90; H, 3.81; N, 12.29 %

2-Amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]-chromene-3-carbonitrile (**5a**): White solid: mp 264−265 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90−7.93 (d, J = 7.8 Hz, 1 H), 7.69−7.72 (t, J = 6.9 Hz, 1 H), 7.42−7.52 (m, 3 H), 7.25−7.33 (m, 5 H), 4.46 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.5, 157.9, 153.4, 152.1, 143.3, 132.9, 128.5, 127.6, 127.1, 124.6, 122.4, 119.2, 116.5, 112.9, 104.0, 57.9, 36.9; IR (neat) 3350, 3320, 2921, 2852, 2195, 1700, 1669, 1603, 1373, 1044, 759 cm^{-1}; HRMS (ESI) $C_{19}H_{12}N_2O_3$ $[M + H]^+$ calcd 317.0921, found 317.0926

2-Amino-4-(4-chlorophenyl)-5-oxo-4,5-dihydropyrano-[3,2-c]chromene-3-carbonitrile (5b): White solid: mp 233−234°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90−7.93 (d, J = 7.5 Hz, 1 H), 7.70−7.75 (t, J = 7.5 Hz, 1 H), 7.45−7.53 (m, 3 H), 7.30−7.39 (dd, J = 8.4 Hz, 19.5 Hz, 4 H), 4.50 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.0, 158.4, 154.0, 152.6, 142.8, 133.5, 132.2, 130.1, 128.9, 125.1, 123.0, 119.5, 117.0, 113.4, 103.9, 58.0, 36.8; IR (neat) 3404, 2924, 2255, 2184, 2128, 1704, 1668, 1378, 1026, 1001, 763 cm^{-1}; HRMS (ESI) $C_{19}H_{11}ClN_2O_3$ $[M + NH_4]^+$ calcd 368.0796, found 368.0804.

2-Amino-4-(4-methoxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile (5c): White solid: mp 233−234 °C**;** ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90−7.93 (d, J= 7.8 Hz, 1 H), 7.69−7.74 (t, J = 7.5 Hz, 1 H), 7.44−7.52 (m, 3 H), 7.23−7.28 (t, J = 8.4 Hz, 1 H), 6.85 (s, 1 H), 6.82 (s, 2 H), 4.45 (s, 1H), 3.74 (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.5, 159.2, 157.9, 153.4, 152.1, 144.8, 132.9, 129.6, 124.6, 122.4, 119.7, 119.1, 116.5, 113.8, 112.9, 111.9, 103.8, 57.8, 54.9, 36.8; IR (neat) 3364, 3313, 3177, 2920, 2850, 2189, 1710, 1668, 1371, 1051, 766 cm^{-1}; HRMS (ESI) $C_{20}H_{14}N_2O_4$ $[M + H]^+$ calcd 347.1026, found 347.1031.

2-Amino-4-(4-fluorophenyl)-5-oxo-4,5-dihydropyrano-[3,2-c]chromene-3-carbonitrile (5d): White solid: mp 243−244 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90−7.93 (d, J = 7.8 Hz, 1 H), 7.69−7.74 (t, J = 7.2 Hz, 1 H), 7.44−7.52 (m, 3 H), 7.32−7.36 (dd, J = 5.4 Hz, 8.4 Hz, 2 H), 7.12−7.18 (t, J = 9.0 Hz, 2 H), 4.50 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.8, 159.5 (d, J = 6.8 Hz), 157.8, 153.3, 152.1, 139.4, 132.9, 129.6 (d, J = 8.3 Hz), 124.6, 122.4, 119.1, 116.5, 115.1 (d, J = 21.8 Hz), 112.9, 103.7, 57.7, 36.2; IR (neat) 3378, 2922, 2852, 2254, 2191, 1714, 1673, 1376, 1025, 1000, 761 cm^{-1}; HRMS (ESI) $C_{19}H_{11}FN_2O_3$ $[M + H]^+$ calcd 335.0826, found 335.0834.

2-Amino-4-(2-chlorophenyl)-5-oxo-4,5-dihydropyrano-[3,2-c]chromene-3-carbonitrile (5e): White solid: mp 227−228 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.91−7.93 (d, J = 7.8 Hz, 1 H), 7.70−7.75 (t, J = 7.5 Hz, 1 H), 7.45−7.52 (m, 3 H), 7.26−7.37 (m, 4 H), 4.53 (s, 1 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.0, 158.4, 154.2, 152.6, 146.2, 133.5, 133.4, 130.8, 128.0, 127.6, 127.0, 125.1, 123.0, 119.5, 117.0,

113.4, 103.6, 57.8, 37.1; IR (neat) 3350, 3185, 2923, 2854, 2196, 1725, 1672, 1603, 1371, 1025, 756 cm^{-1}; HRMS (ESI) $C_{19}H_{11}ClN_2O_3$ $[M + NH_4]^+$ calcd 368.0796, found 368.0802.

2-Amino-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6a): White solid: mp 211−212 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 7.25−7.30 (t, J = 7.5 Hz, 2 H), 7.14−7.17 (m, 3 H), 6.99 (s, 2 H), 4.19 (s, 1 H), 2.58−2.61 (m, 2 H), 2.20−2.31 (m, 2 H), 1.84−1.99 (m, 2 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 196.3, 164.9, 158.9, 145.2, 128.8, 127.6, 127.0, 120.2, 114.2, 58.7, 36.8, 35.9, 26.9, 20.3; IR (neat) 3326, 3208, 2923, 2855, 2187, 1678, 1645, 1601, 1361, 994, 692 cm^{-1}; HRMS (ESI) $C_{16}H_{14}N_2O_2$ $[M + H]^+$ calcd 267.1128, found 267.1131.

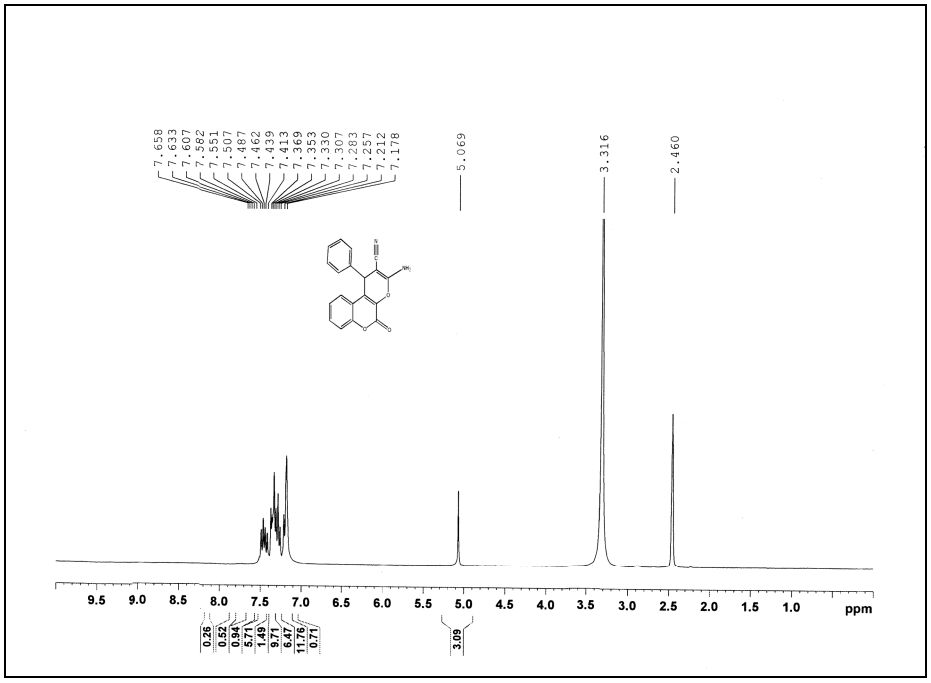
2-Amino-4-(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6b): White solid: mp 206−207 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 7.05−7.08 (dd, J = 1.8 Hz, 6.6 Hz, 2H), 6.95 (s, 1 H), 6.82−6.85 (dd, J = 2.1 Hz, 6.9 Hz, 2 H), 4.13 (s, 1H), 3.71 (s, 3 H), 2.60−2.62 (m, 2 H), 2.24−2.30 (m, 2 H), 1.86−1.99 (m, 2 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 196.3, 164.6, 158.8, 158.4, 137.4, 128.6, 120.3, 114.5, 114.1, 58.9, 55.5, 36.8, 35.0, 26.9, 20.3; IR (neat) 3330, 3212, 3187, 2928, 2193, 1682, 1654, 1367, 1260, 1170, 535 cm^{-1}; HRMS (ESI) $C_{17}H_{16}N_2O_3$ $[M + H]^+$ calcd 297.1234, found 297.1232.

2-Amino-4-(4-fluorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6c): White solid: mp 209−210 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 7.18−7.22 (m, 2 H), 7.07−7.13 (m, 2H), 7.04 (s, 2 H), 4.21 (s, 1 H), 2.61−2.63 (m, 2 H), 2.27−2.28 (m, 2 H), 1.90−1.99 (m, 2 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ196.4, 165.0, 163.0, 159.7, 158.9, 141.4, 129.5 (d, J = 8.3 Hz), 120.1, 115.4 (d, J = 21.0 Hz), 114.1, 58.5, 36.7, 35.2, 26.9, 20.2; IR (neat) 3414, 3335, 3218, 2928, 2193, 1683, 1654, 1367, 1209, 1002, 533 cm−1; HRMS (ESI) $C_{16}H_{13}FN_2O_2$ $[M + H]^+$ calcd 285.1034, found 285.1043.

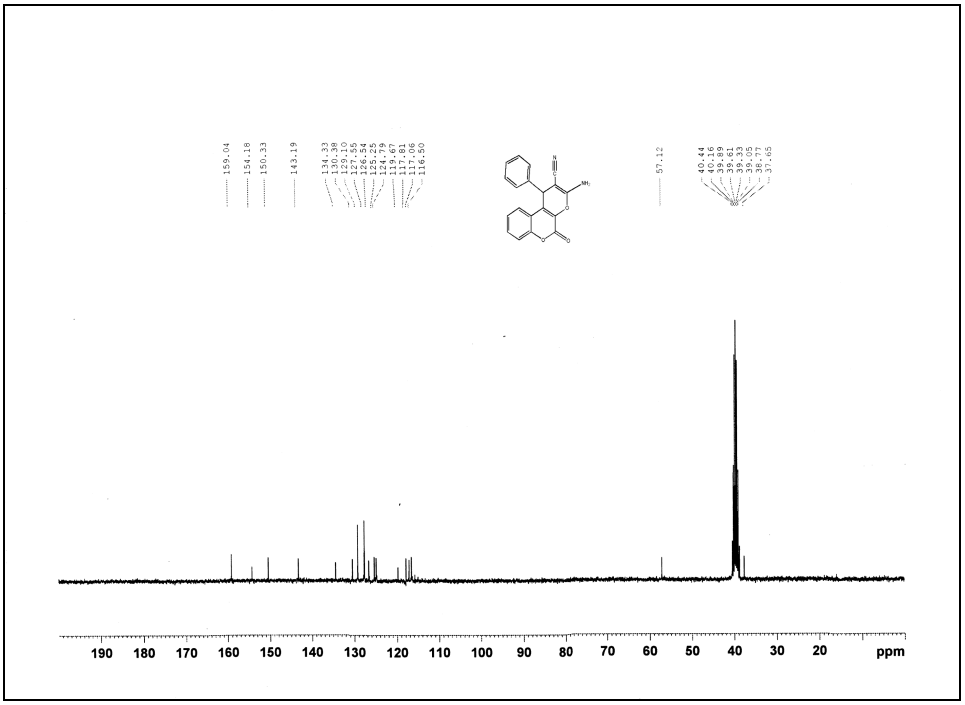
2-Amino-4-(4-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (6d): White solid: mp 239−240 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 7.26−7.54 (dd, J = 1.8 Hz, 6.6 Hz, 2 H), 7.17−7.20 (dd, J = 1.8 Hz, 6.6 Hz, 2 H), 7.05 (s, 1 H), 4.20 (s, 1 H), 2.59−2.63 (m, 2 H), 2.21−2.31 (m, 2 H), 1.85−1.99 (m, 2 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 196.3, 165.1, 158.9, 144.2, 131.5, 129.5, 128.7,

120.0, 113.8, 58.1, 36.7, 35.4, 26.9, 20.2; IR (neat) 3413, 3334, 3215, 2918, 2194, 1682, 1653, 1365, 1131, 1005, 507 cm^{-1}; HRMS (ESI) $C_{16}H_{13}ClN_2O_2$ $[M + H]^+$ calcd 301.0738, found 301.0743.

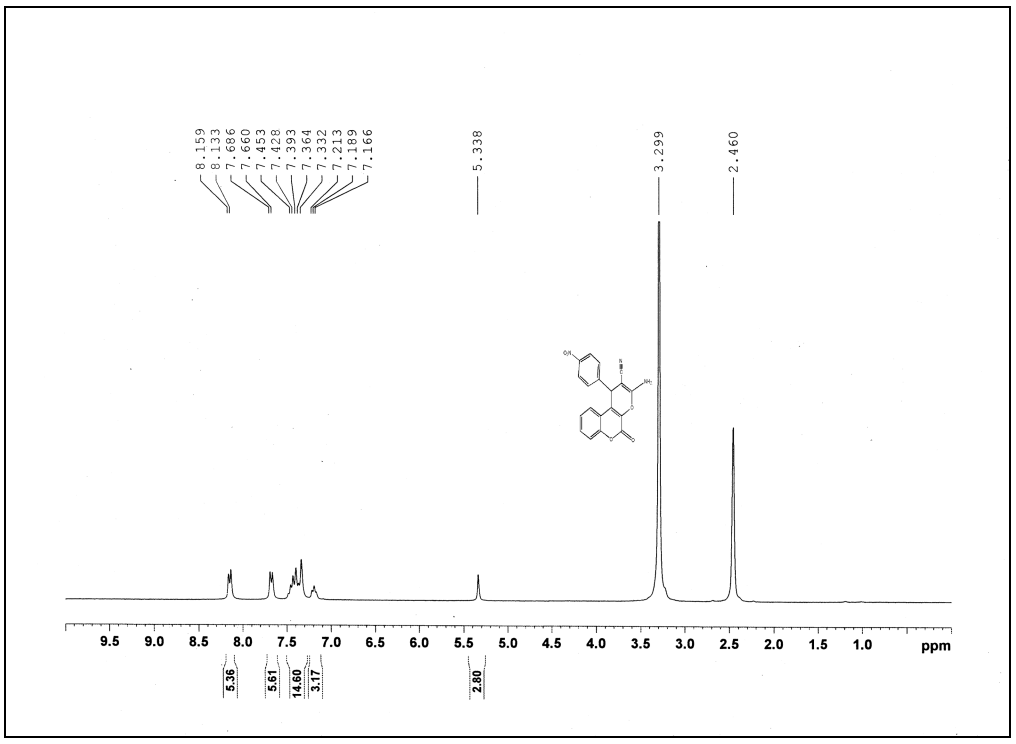
^{1}HNMR, ^{13}CNMR Spectra of the Compounds



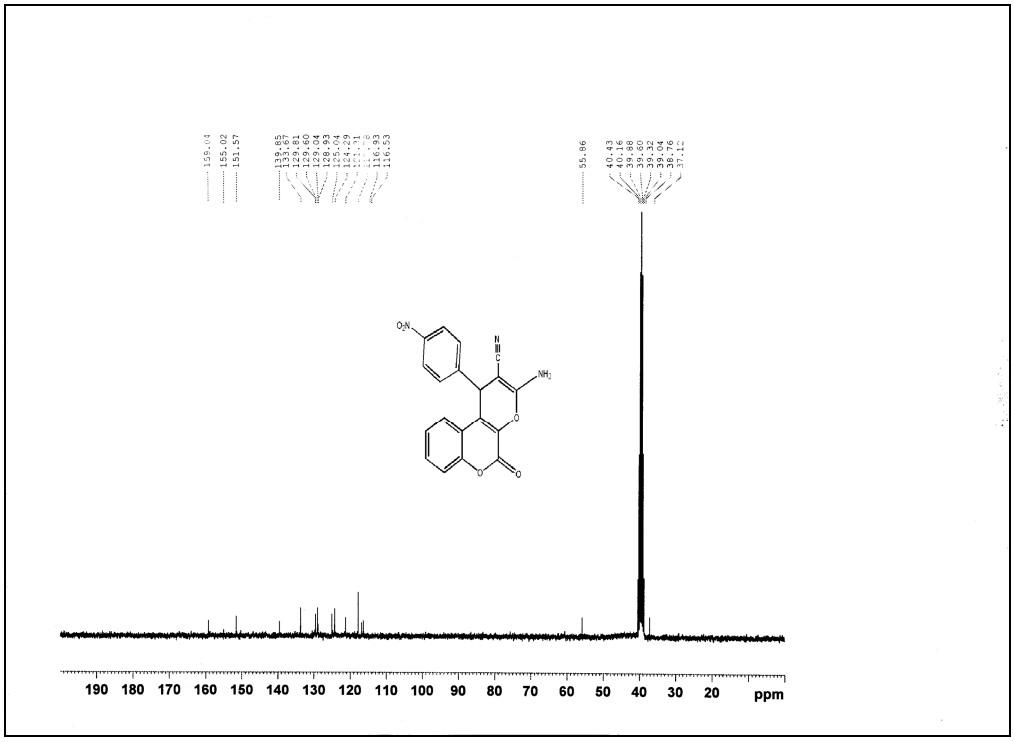
^{1}H NMR spectrum of the product **2a**



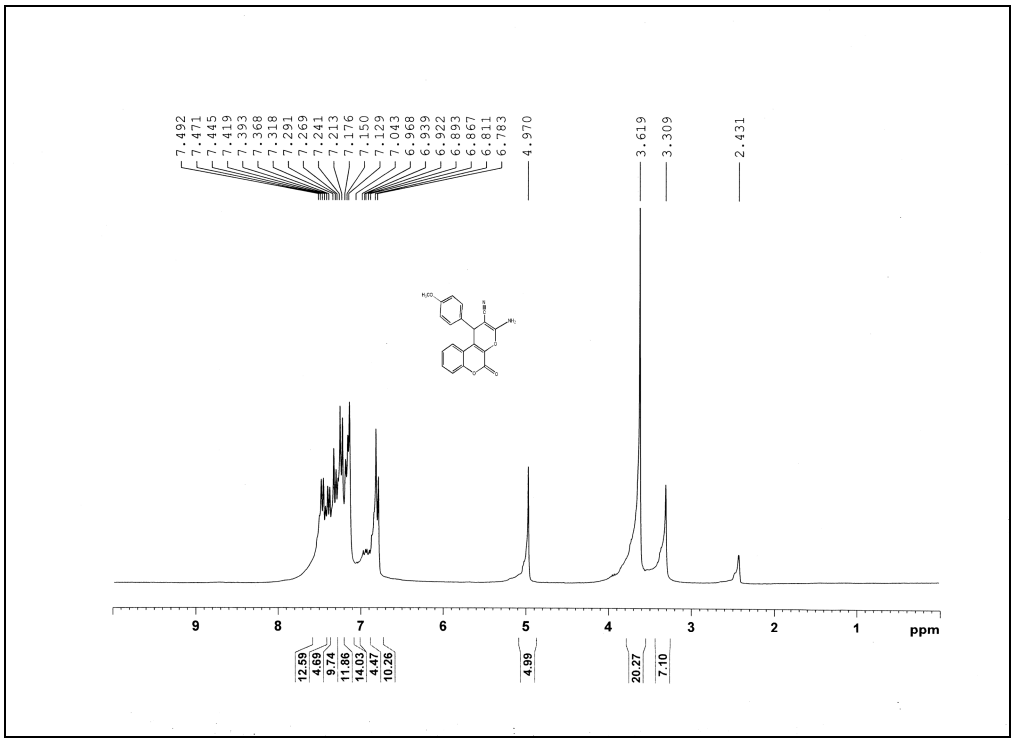
^{13}C NMR spectrum of the product **2a**



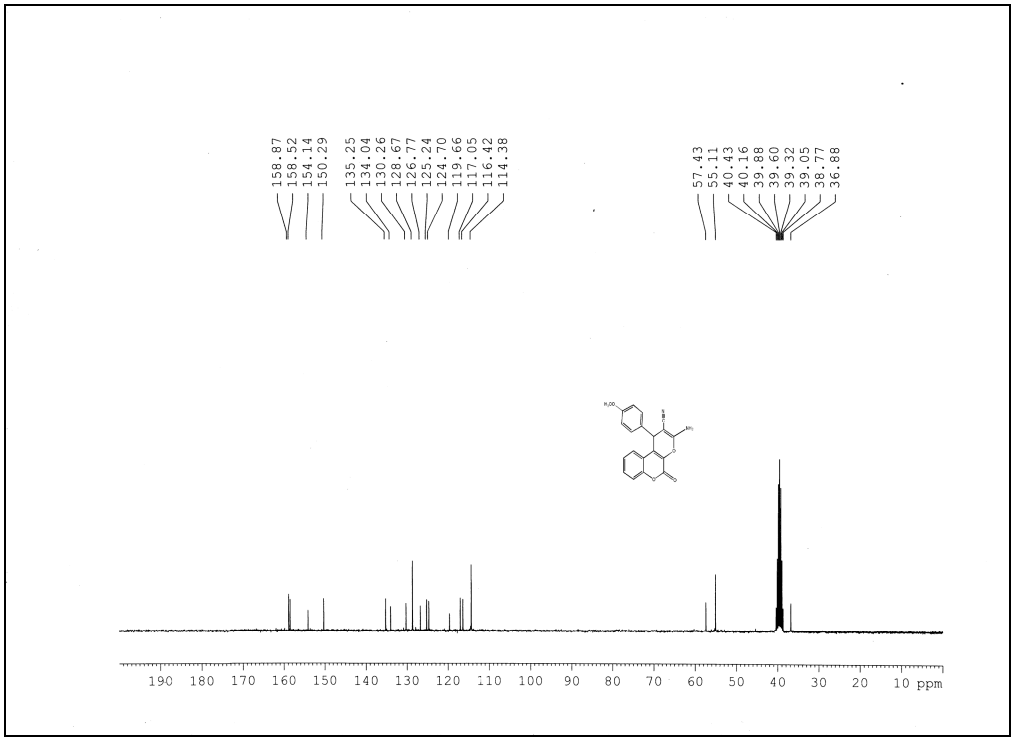
^{1}H NMR spectrum of the product **2b**



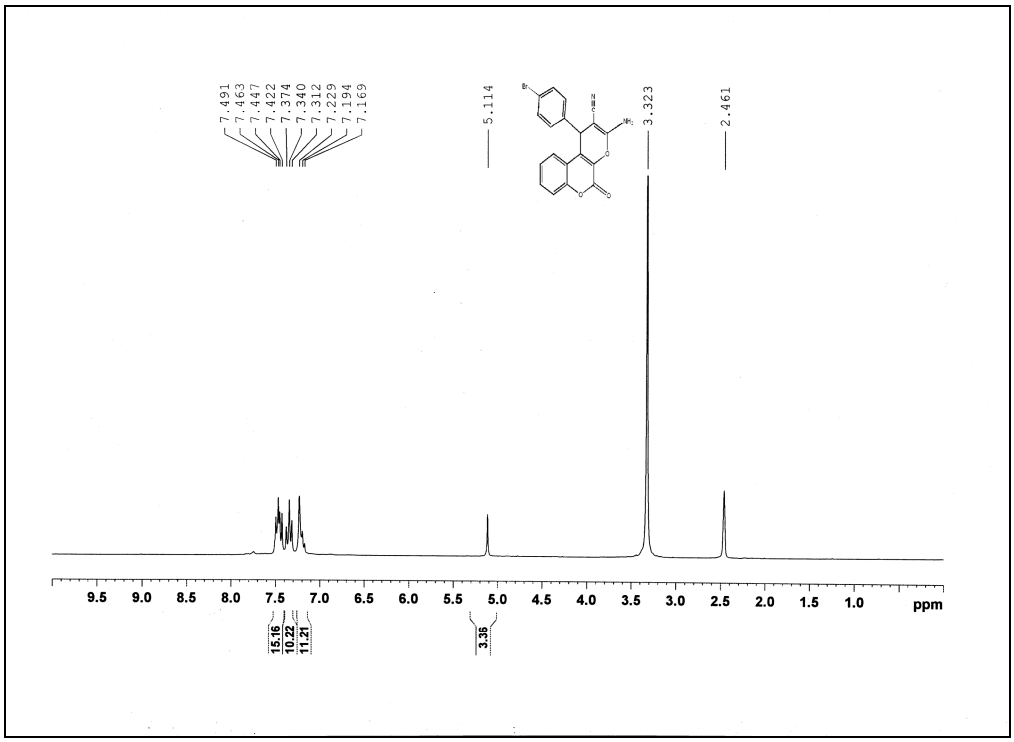
^{13}C NMR spectrum of the product **2b**



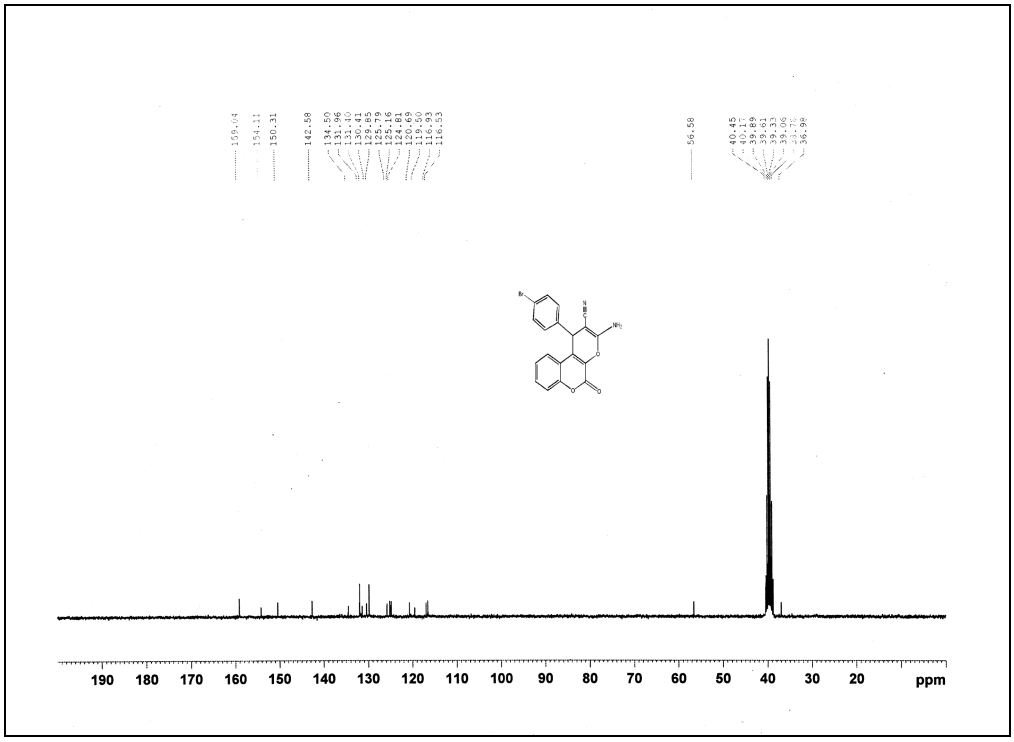
^{1}H NMR spectrum of the product **2c**



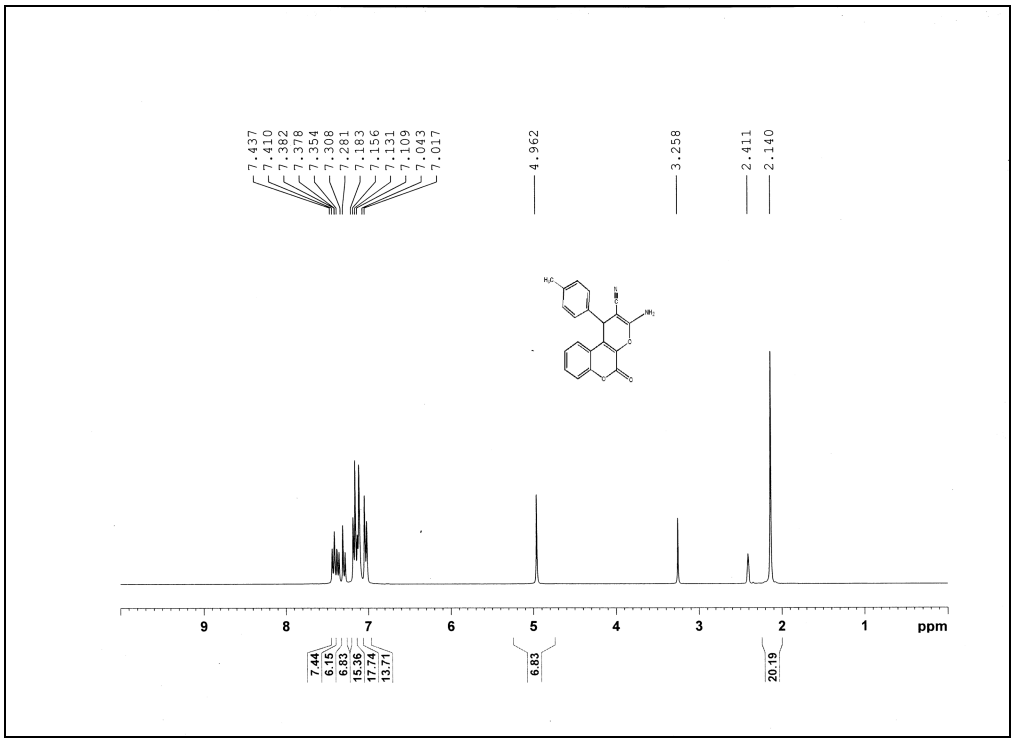
^{13}C NMR spectrum of the product 2**c**



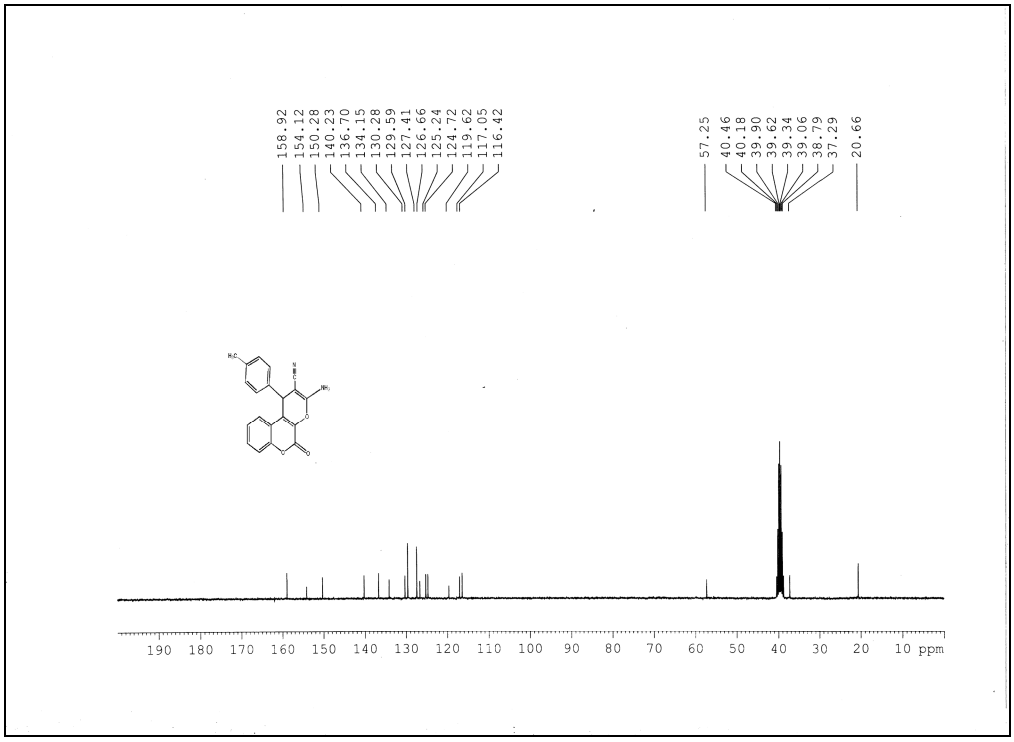
^{1}H NMR spectrum of the product **2d**



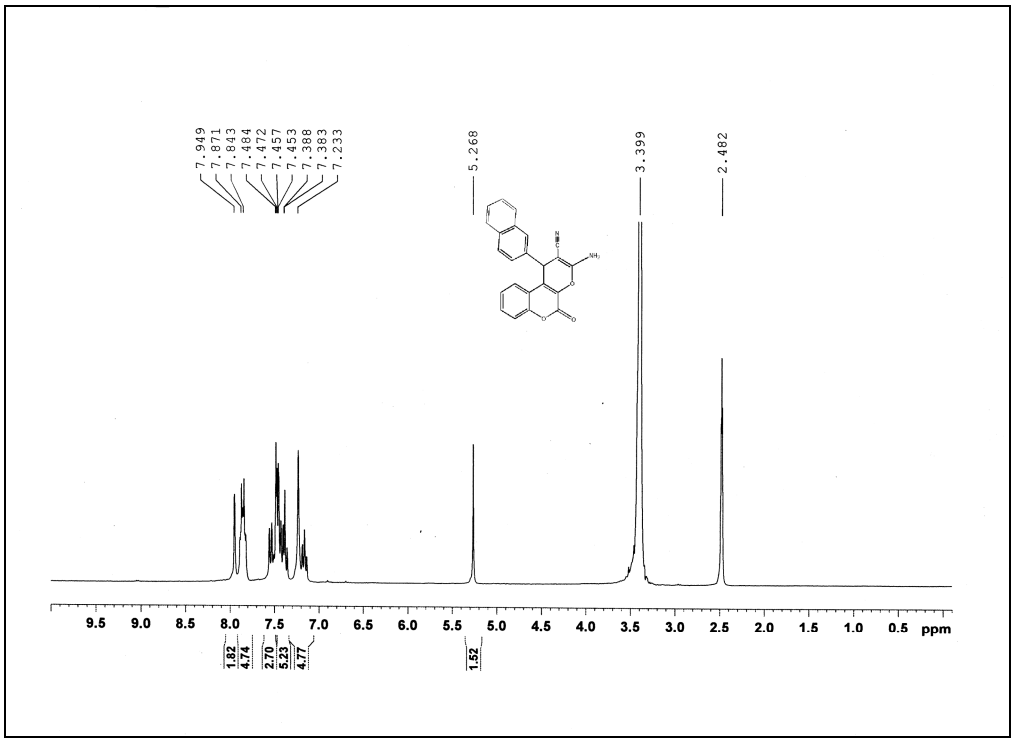
^{13}C NMR spectrum of the product **2d**



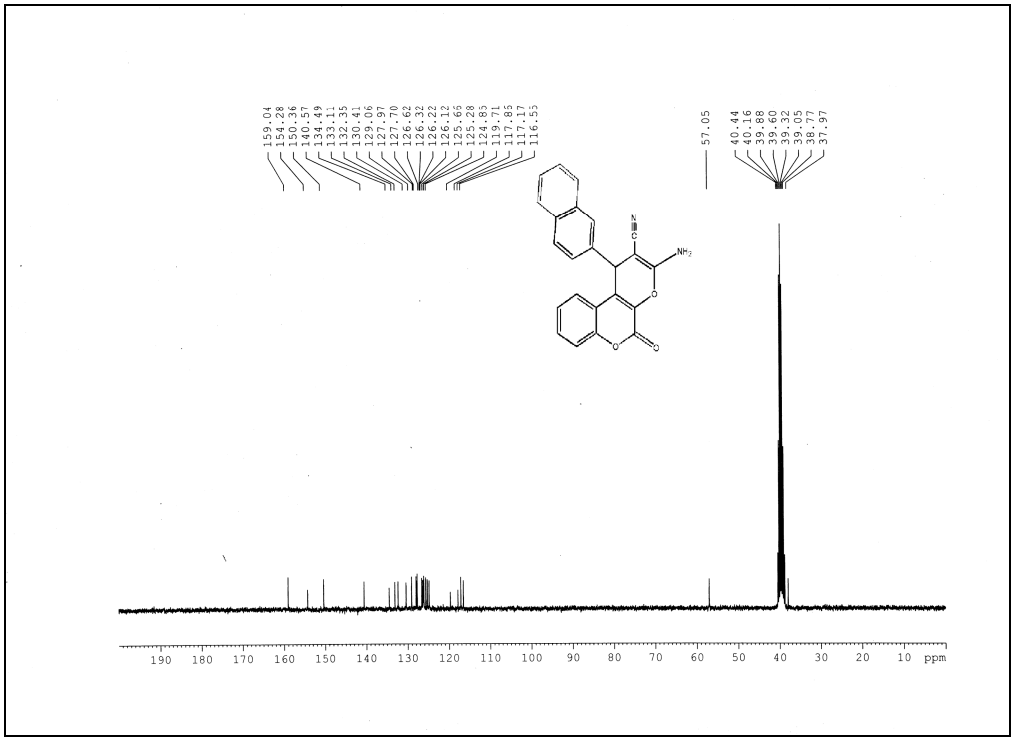
^{1}H NMR spectrum of the product **2e**



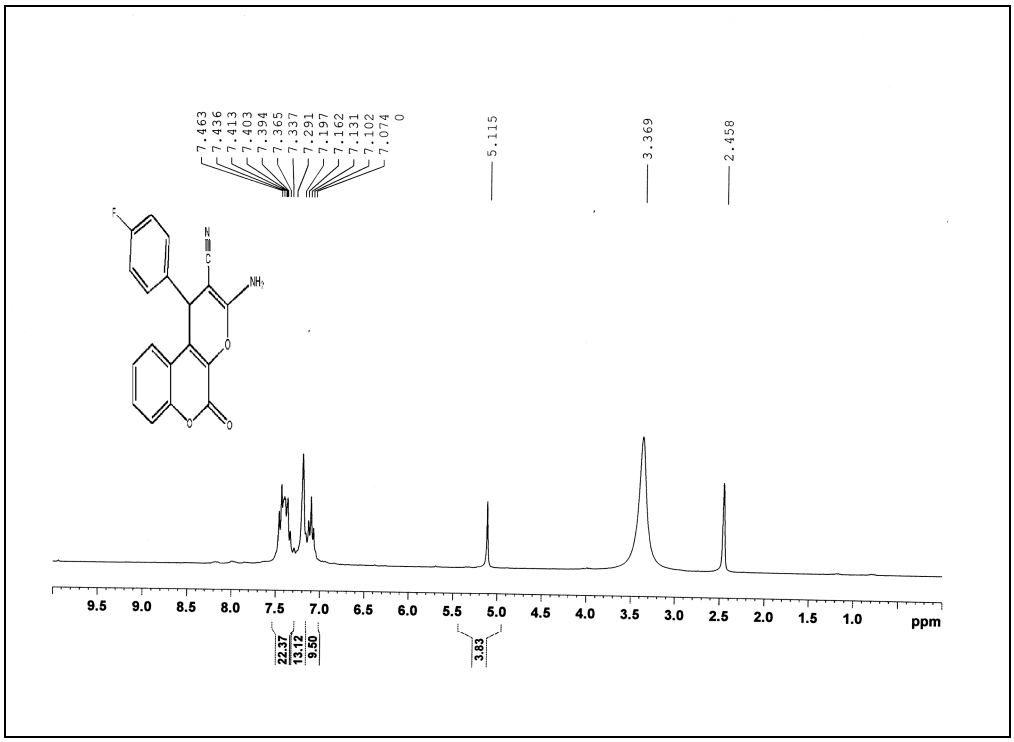
^{13}C NMR spectrum of the product **2e**



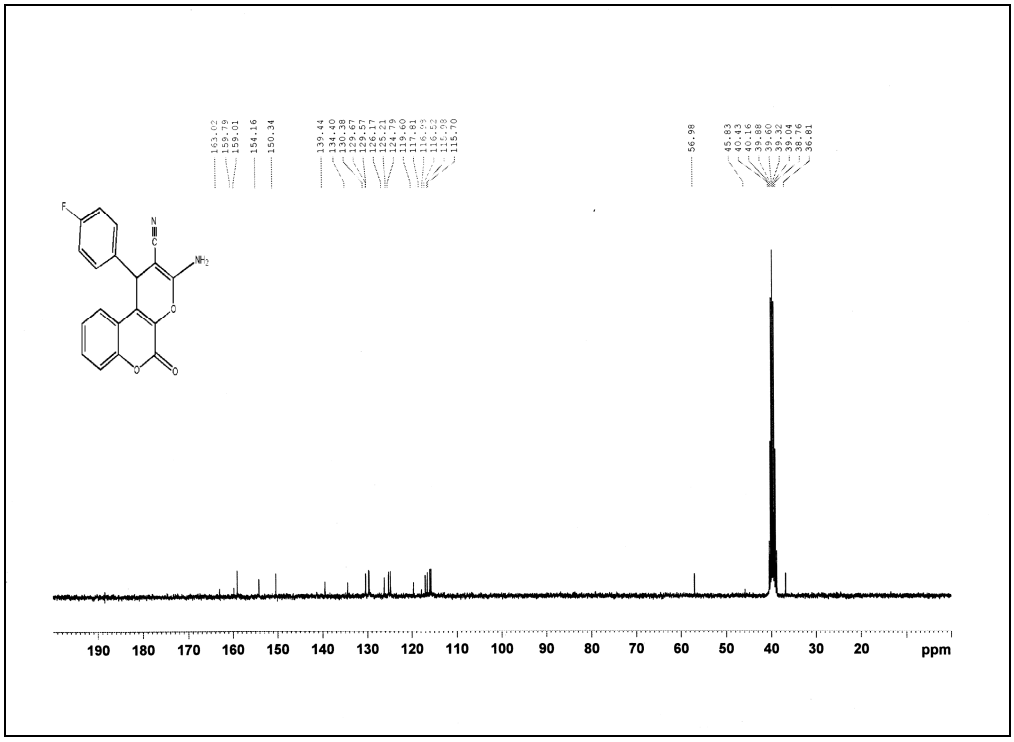
^{1}H NMR spectrum of the product **2f**



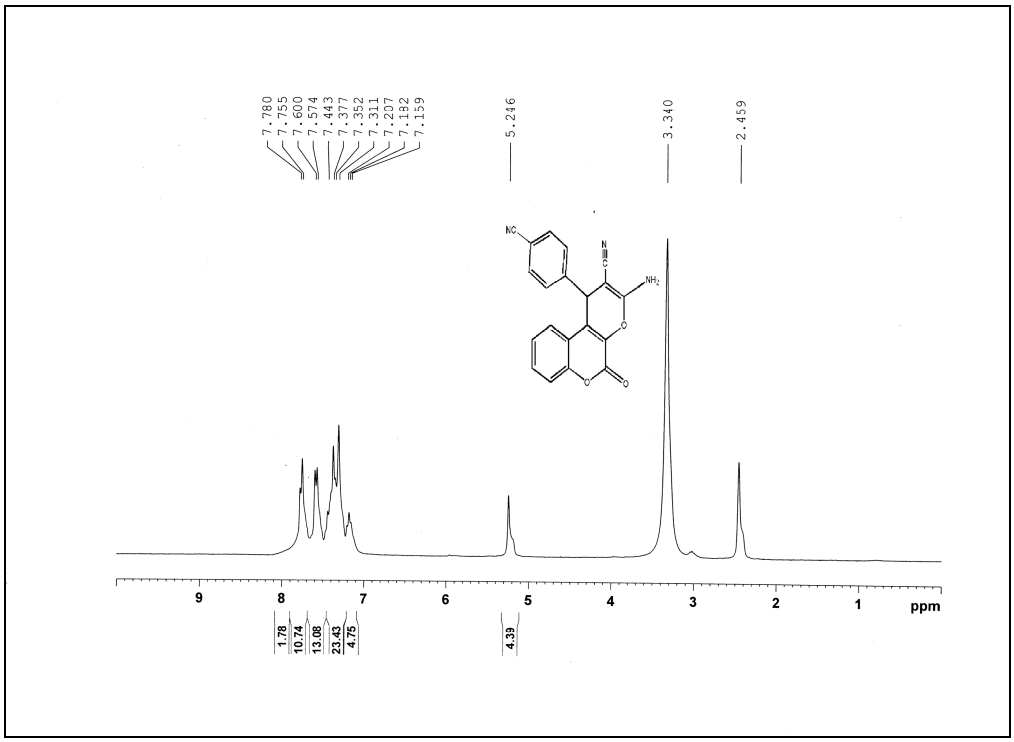
^{13}C NMR spectrum of the product **2f**



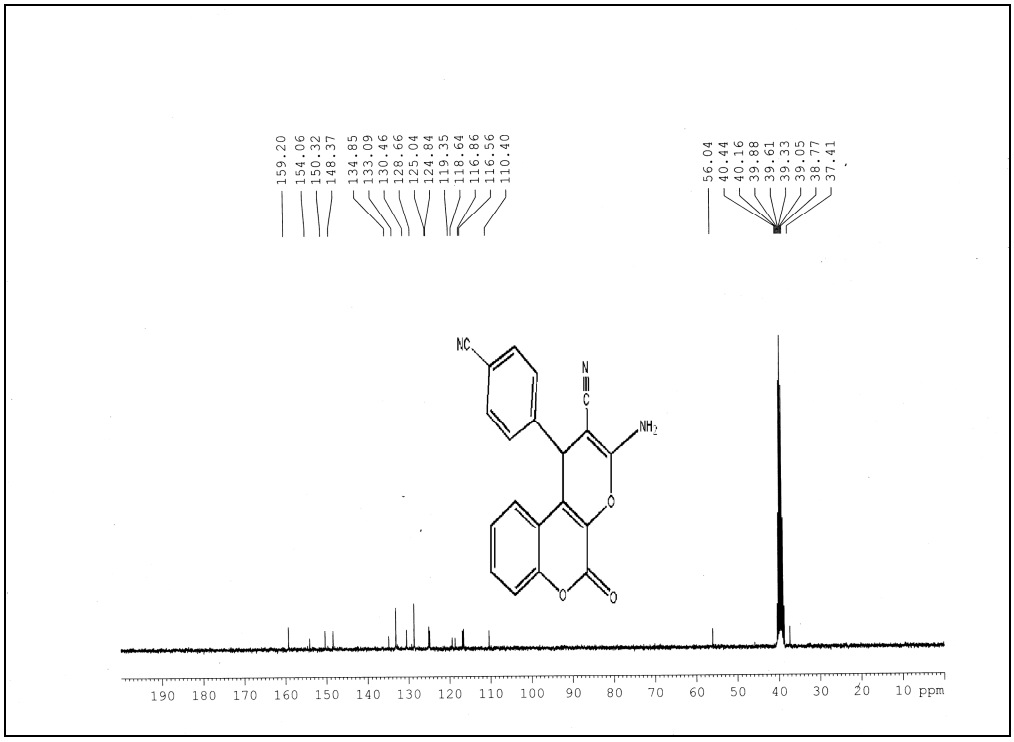
^{1}H NMR spectrum of the product **2g**



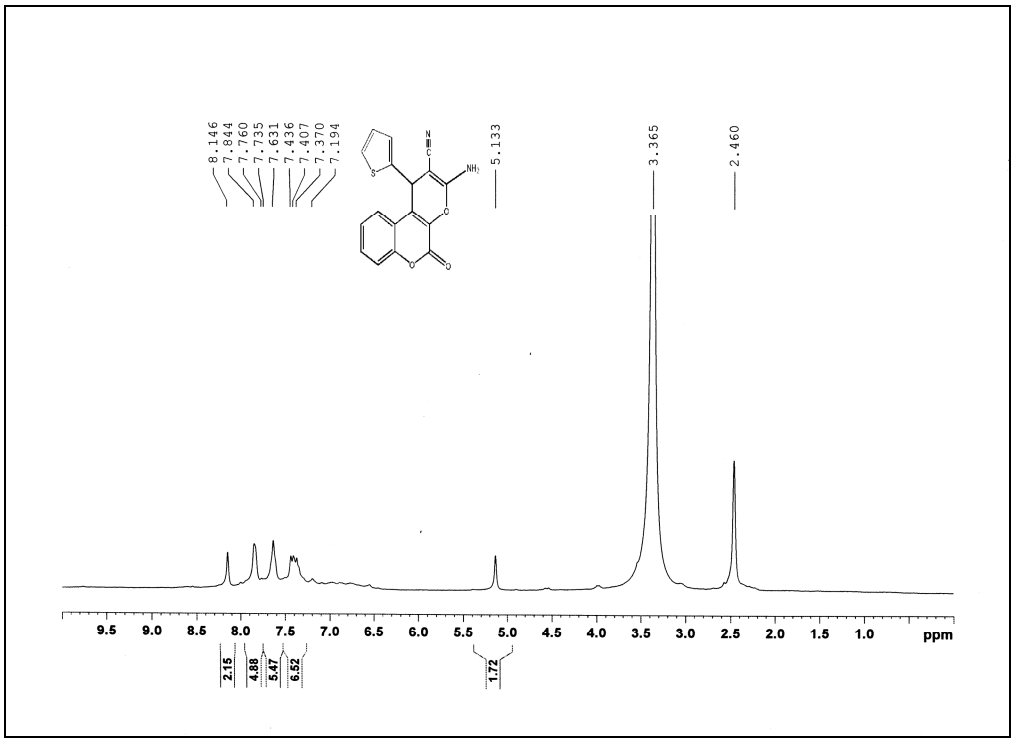
^{13}C NMR spectrum of the product **2g**



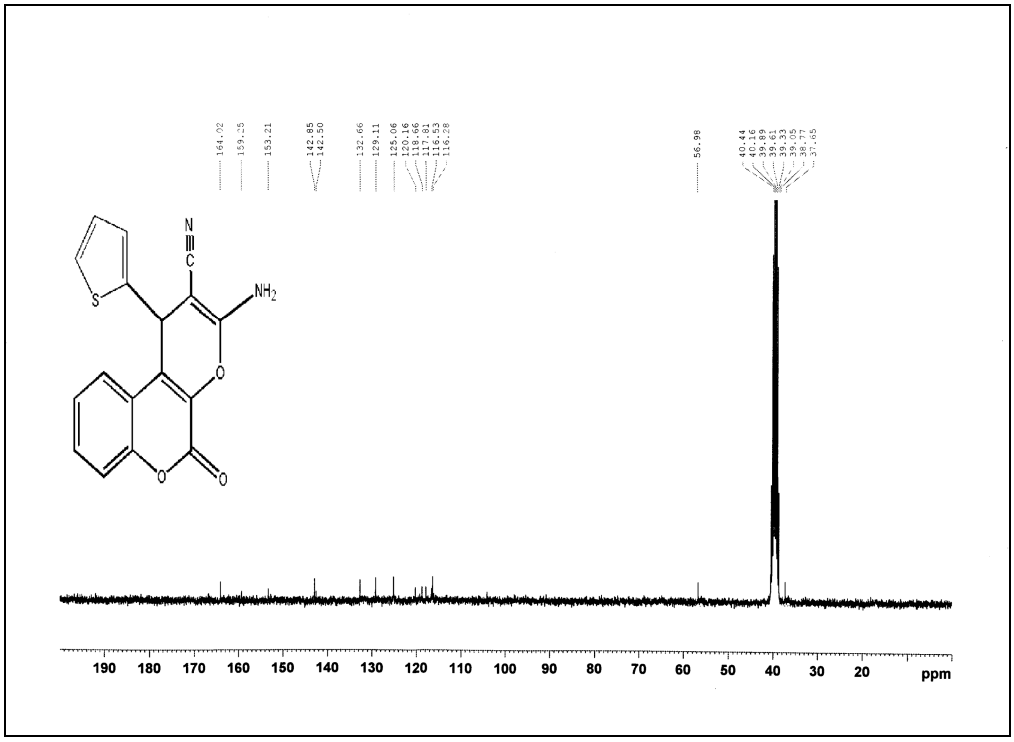
^{1}H NMR spectrum of the product **2h**



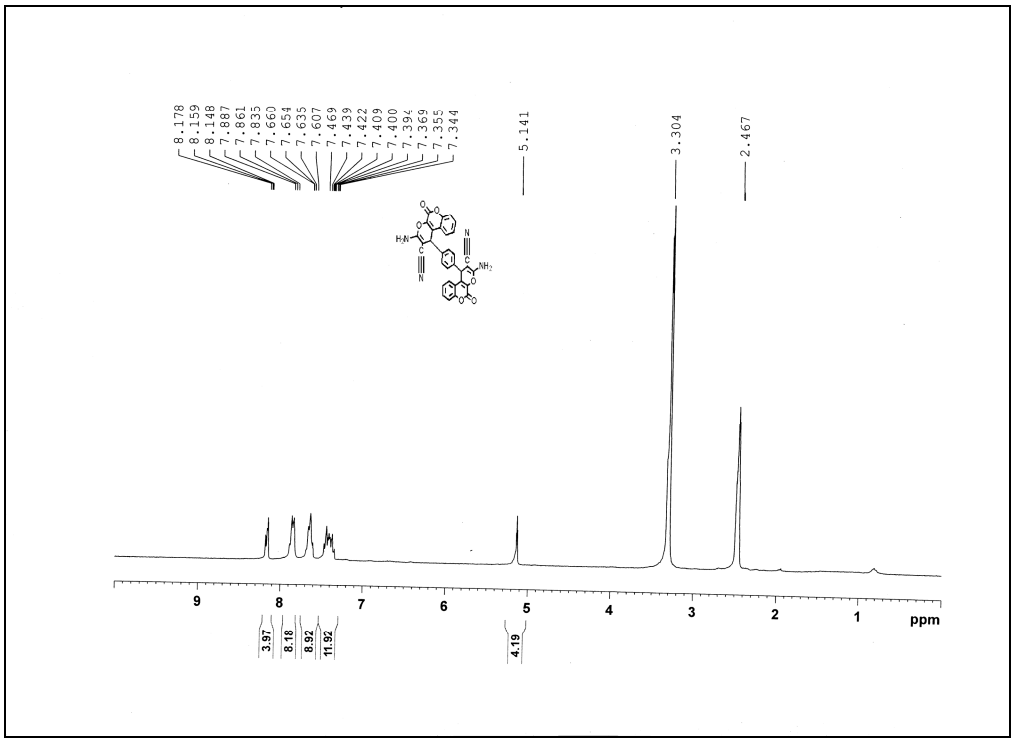
^{13}C NMR spectrum of the product **2h**



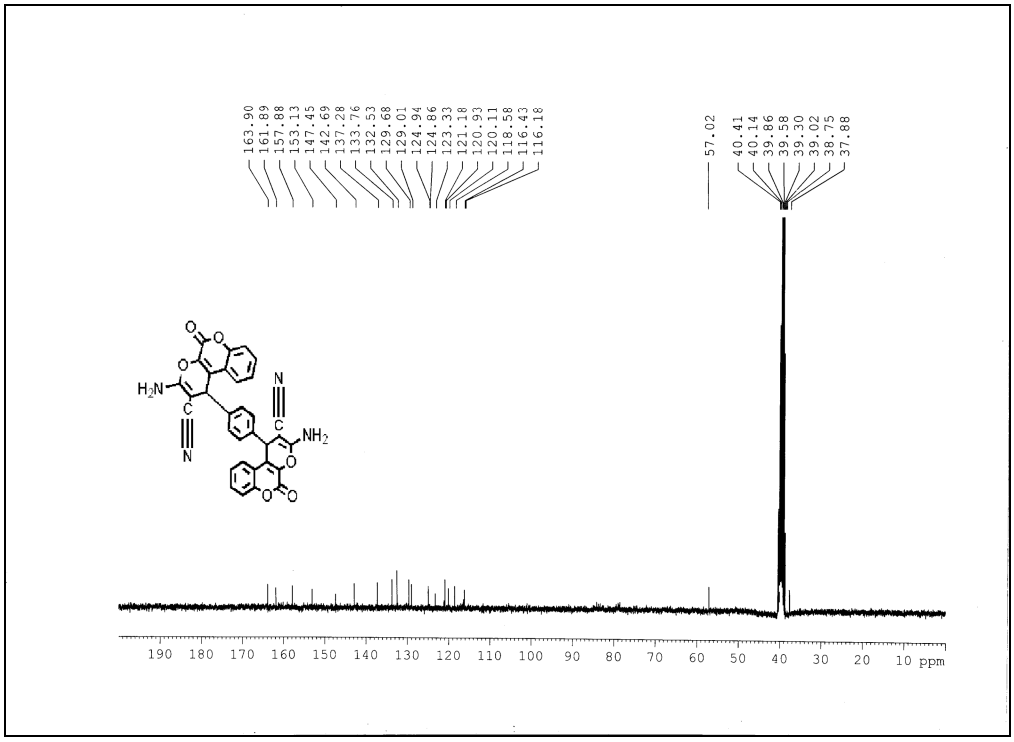
^{1}H NMR spectrum of the product **2i**



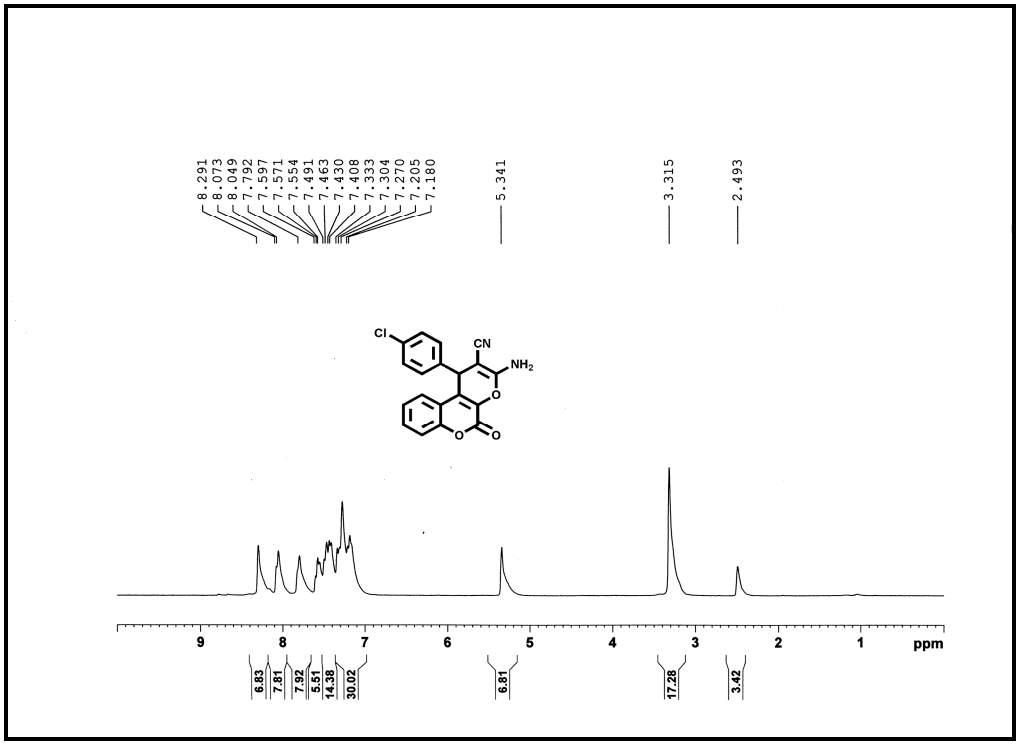
^{13}C NMR spectrum of the product **2i**



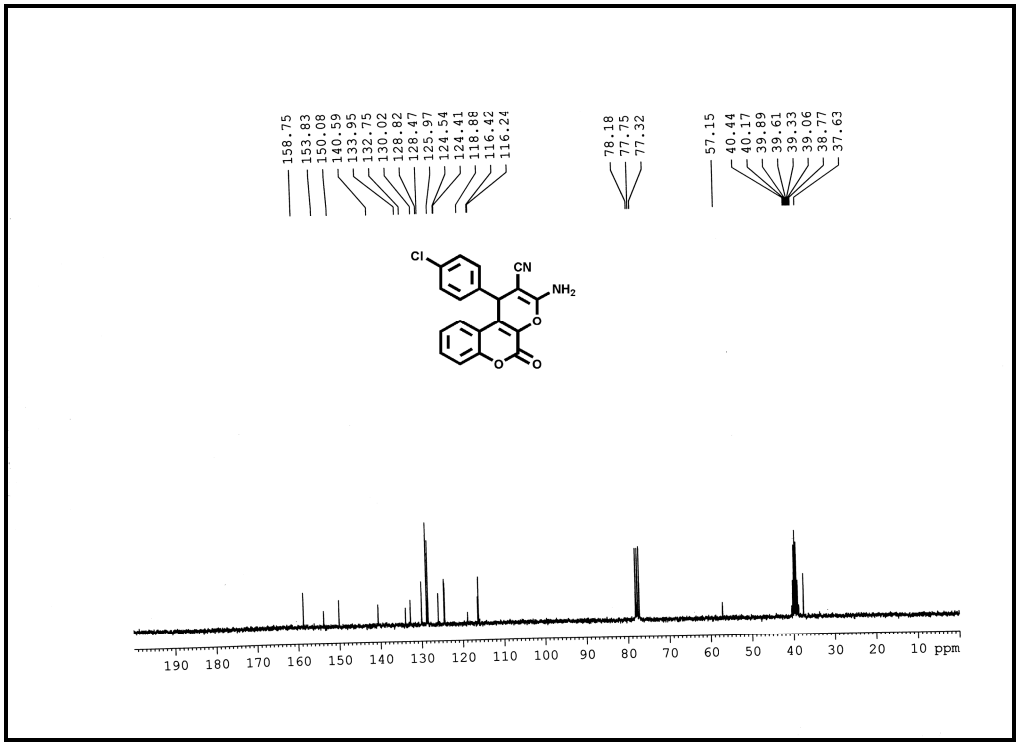
^{1}H NMR spectrum of the product **2j**



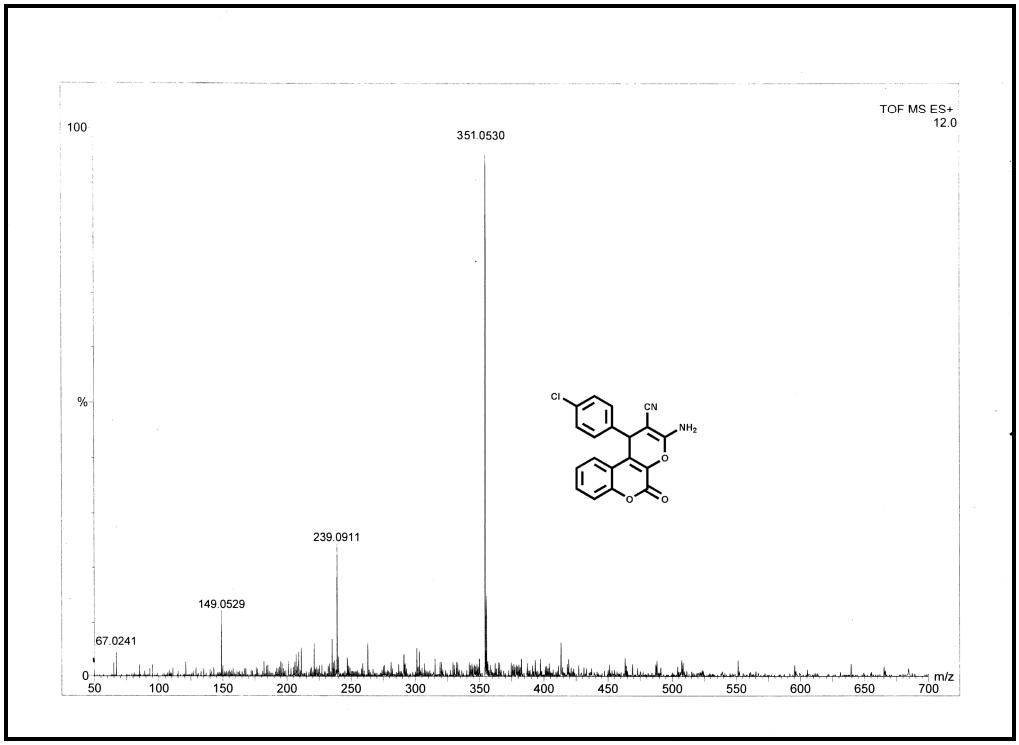
^{13}C NMR spectrum of the product 2**j**



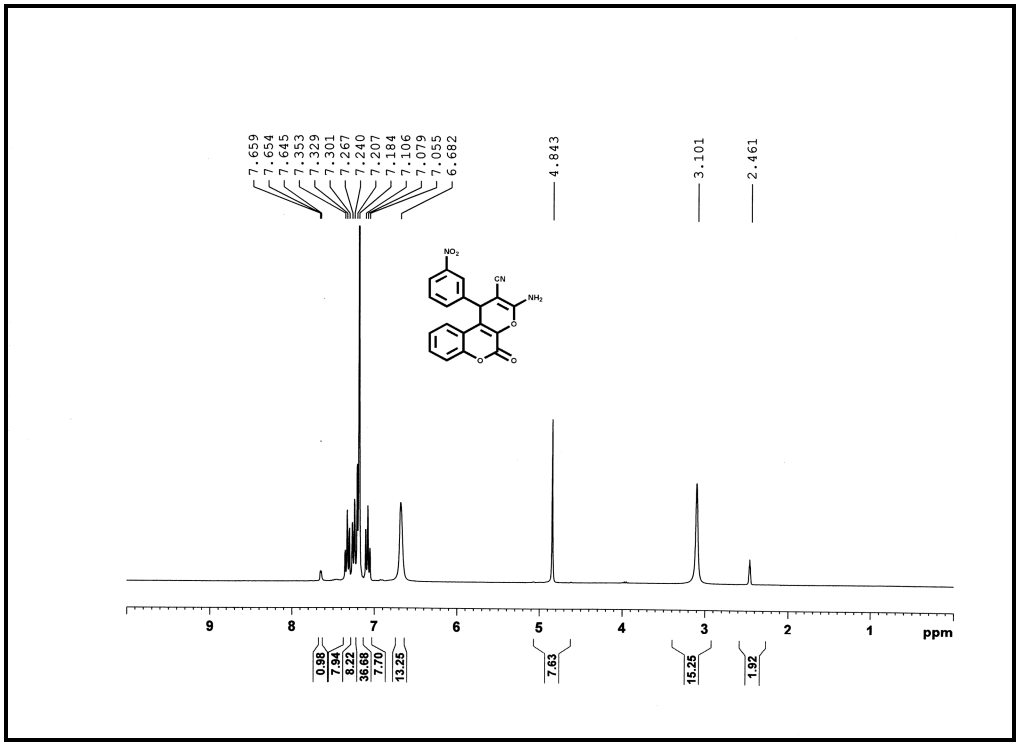
^{1}H NMR spectrum of the product **2k**



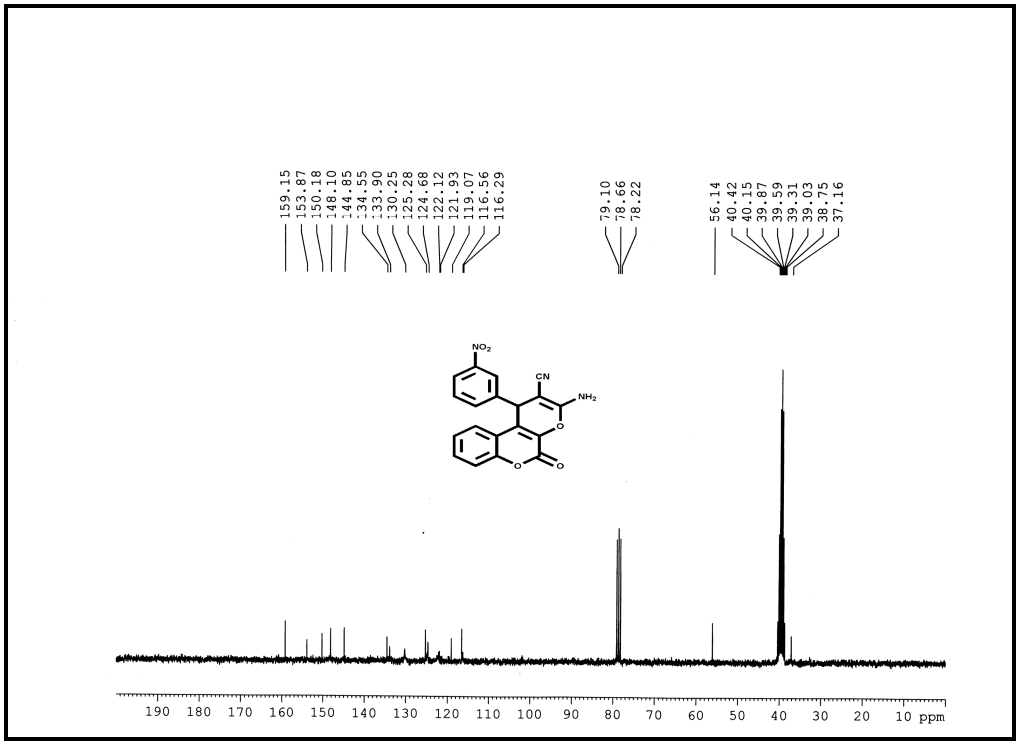
^{13}C NMR spectrum of the product 2**k**



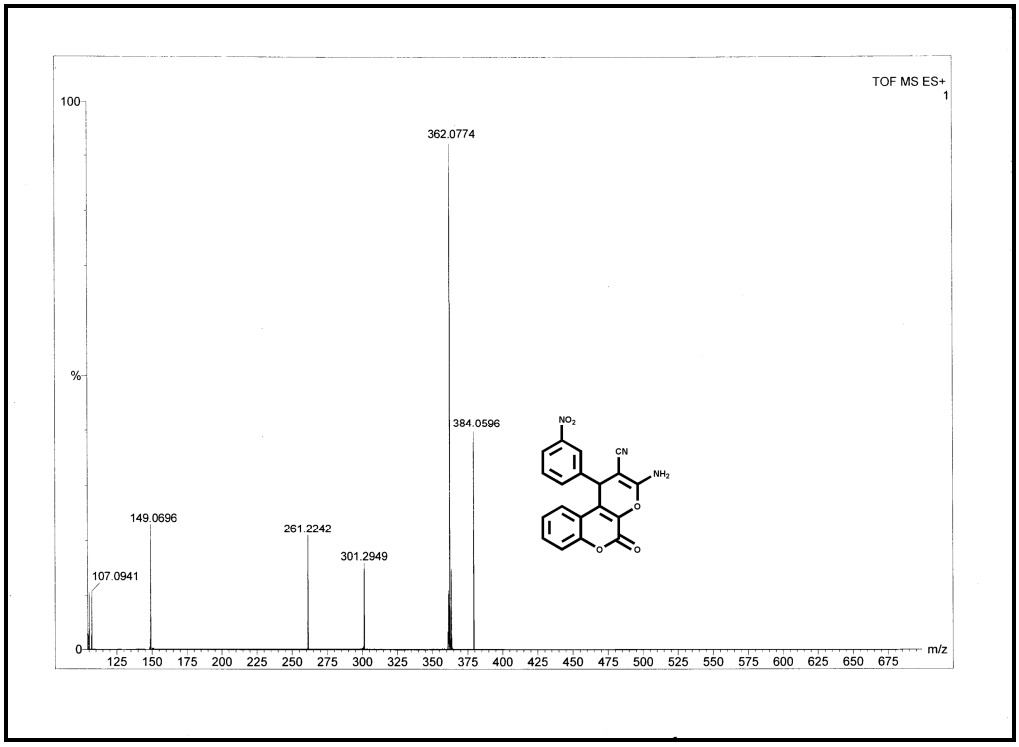
HRMS spectrum of the product 2**k**



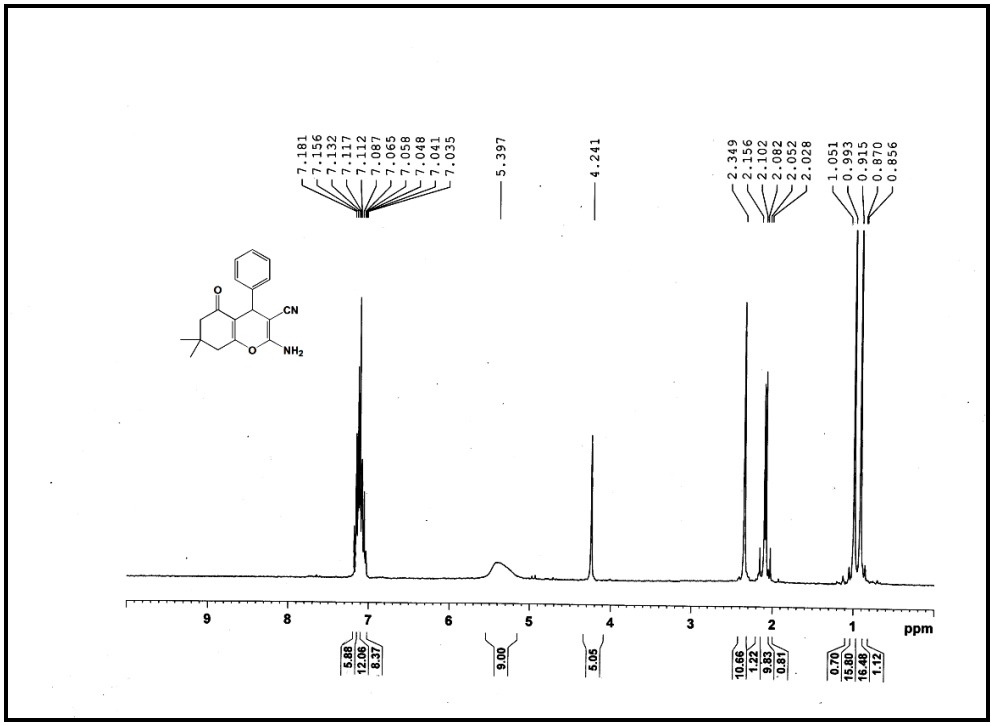
^{1}H NMR spectrum of the product **2l**



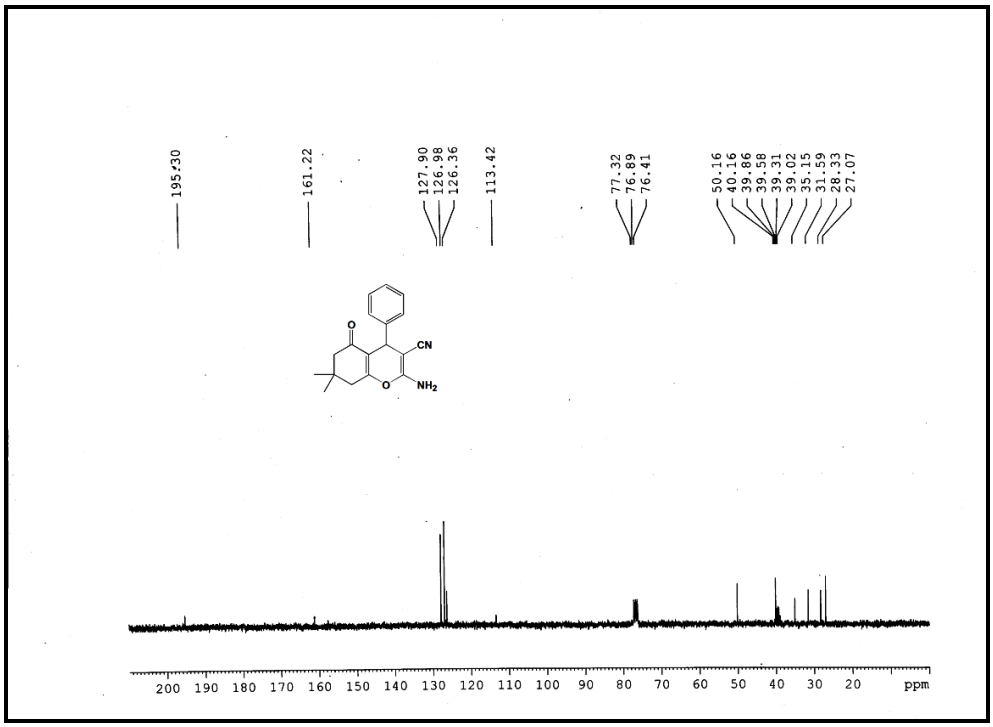
^{13}C NMR spectrum of the product 2**l**



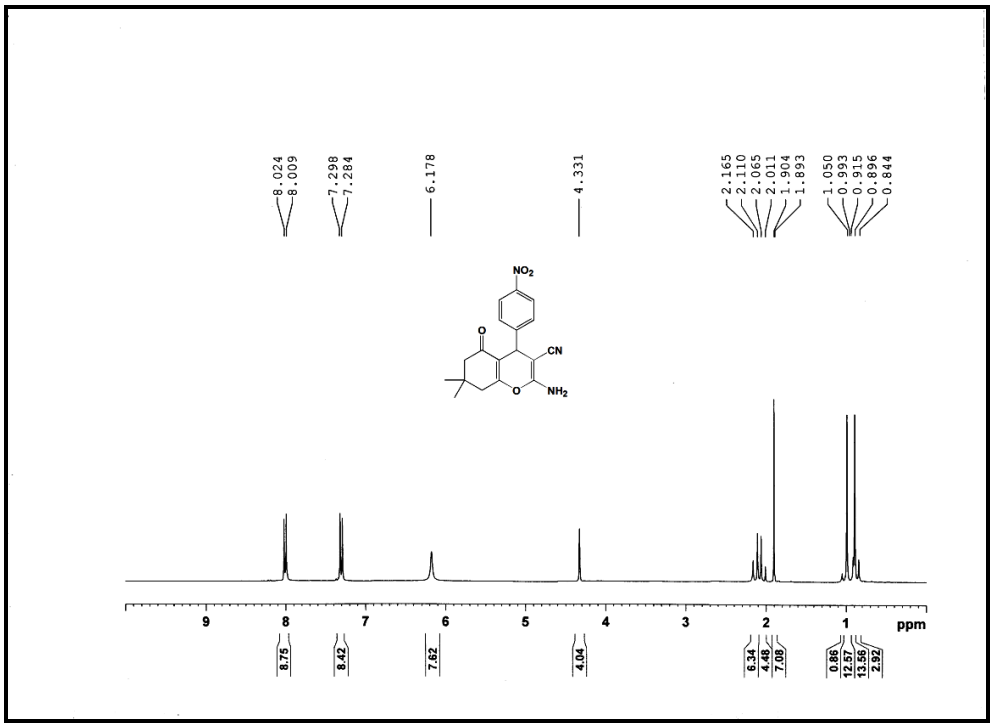
HRMS spectrum of the product 2**l**



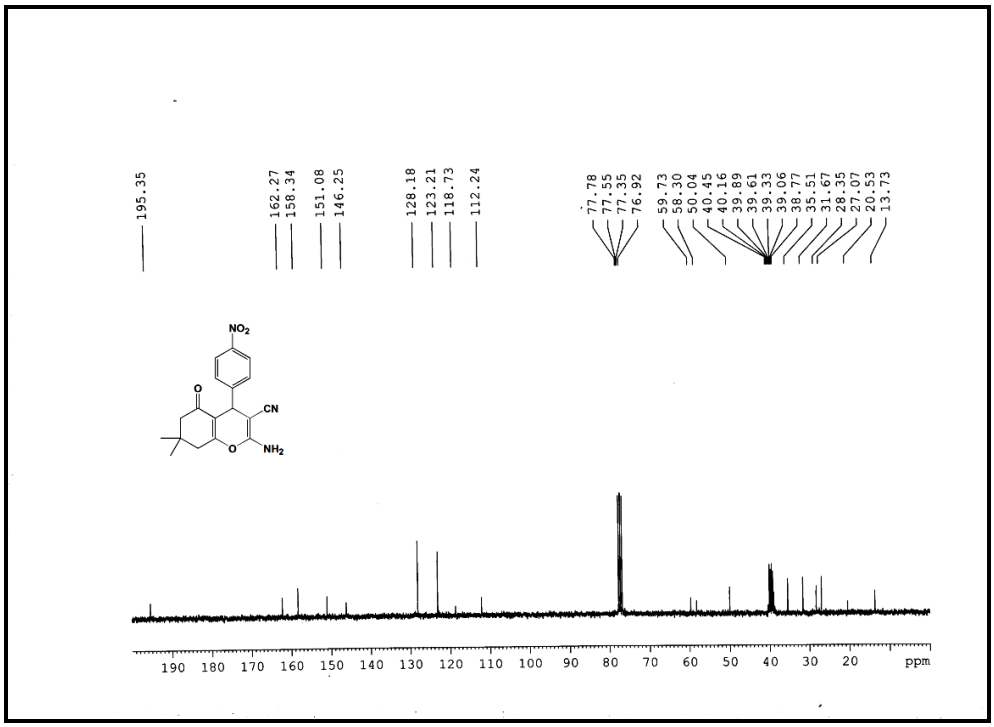
^{1}H NMR spectra of compound **3a**



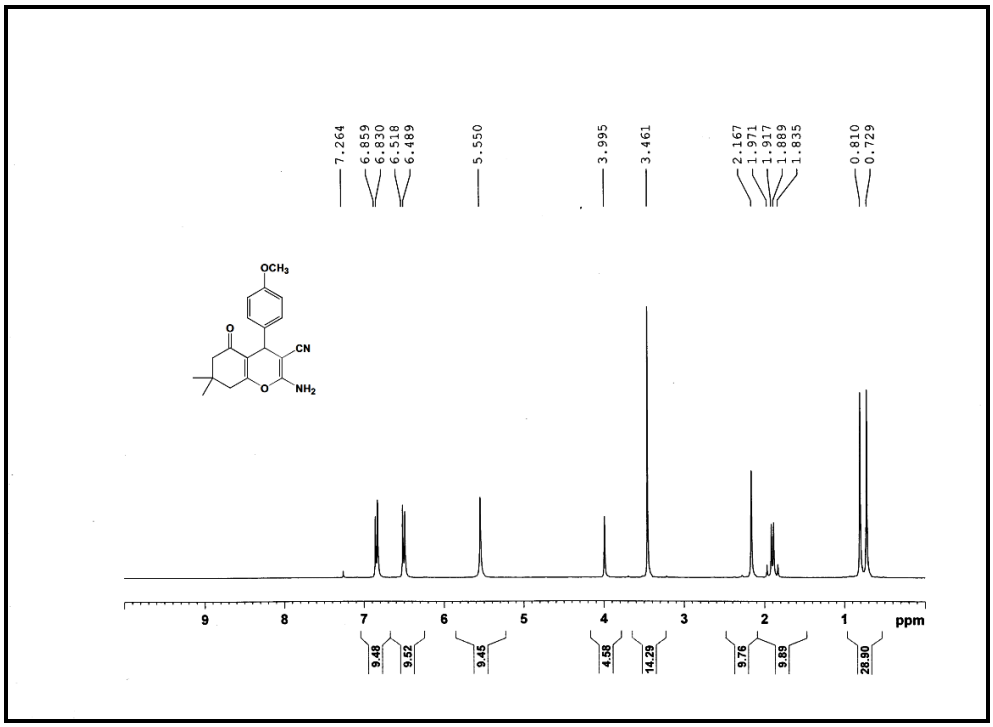
^{13}C NMR spectra of compound 3a



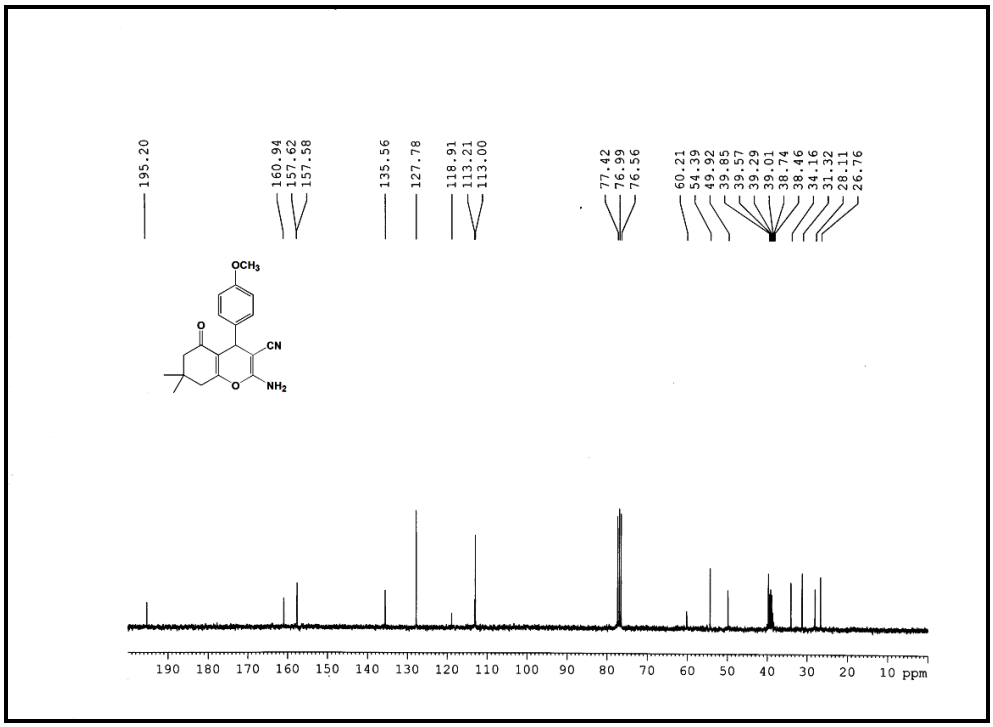
^{1}H NMR spectra of compound 3b



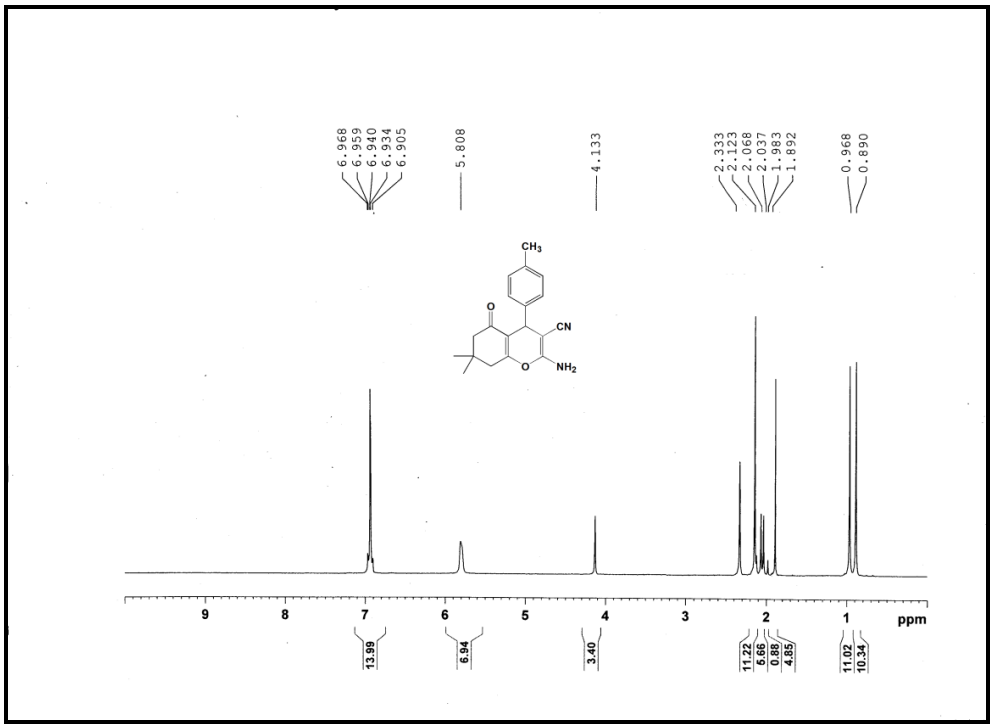
^{13}C NMR spectra of compound 3b



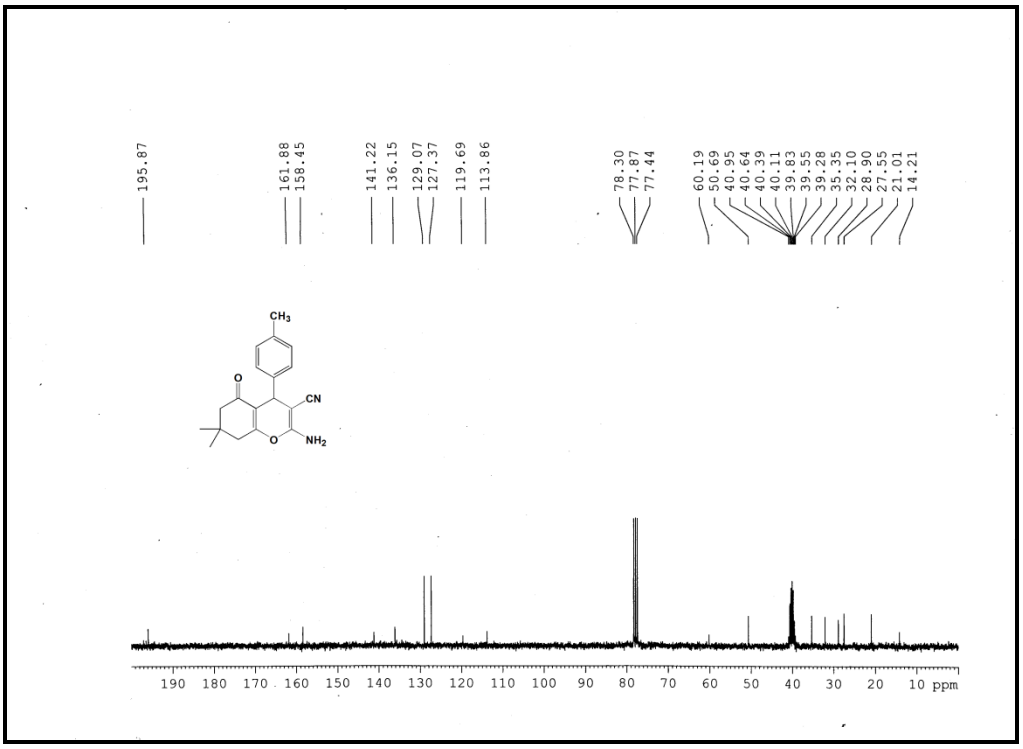
^{1}H NMR spectra of compound 3c



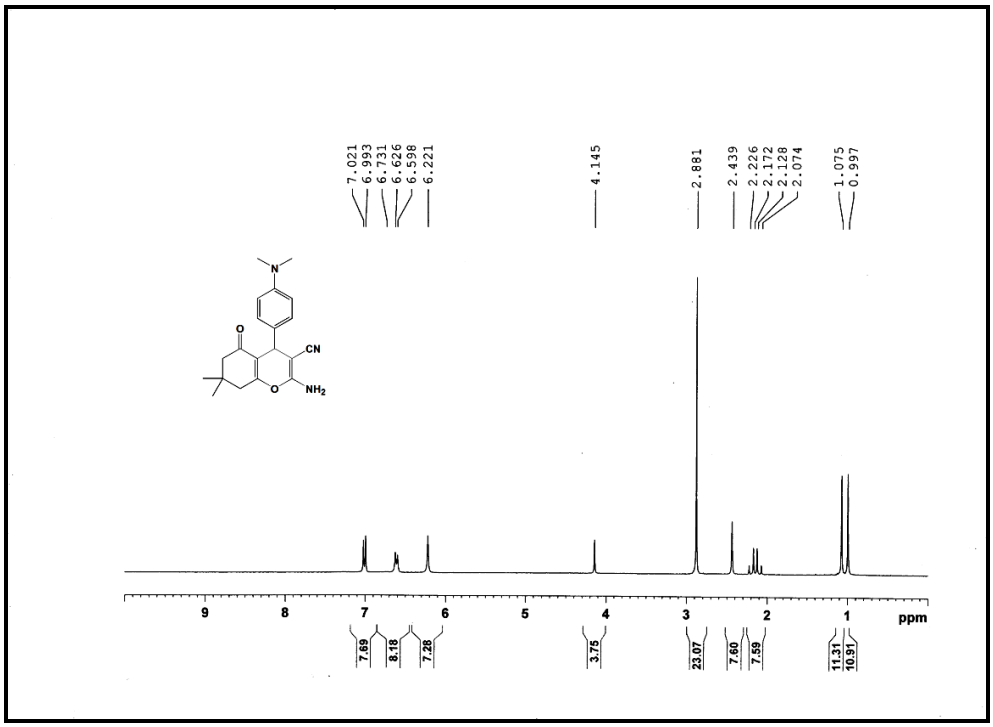
^{13}C NMR spectra of compound 3c



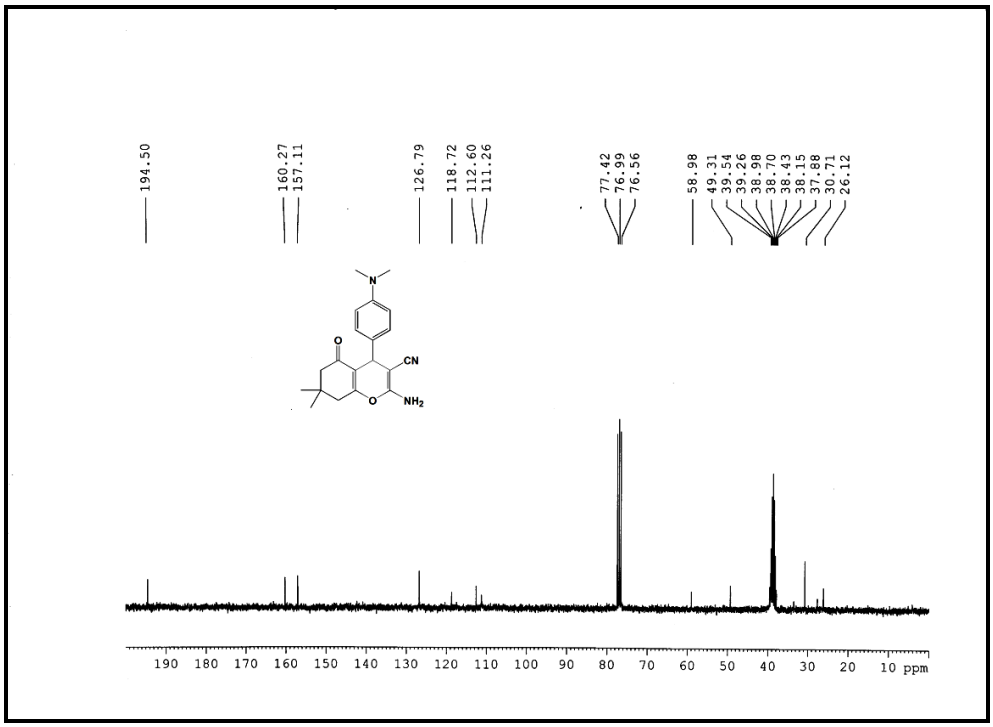
^{1}H NMR spectra of compound 3d



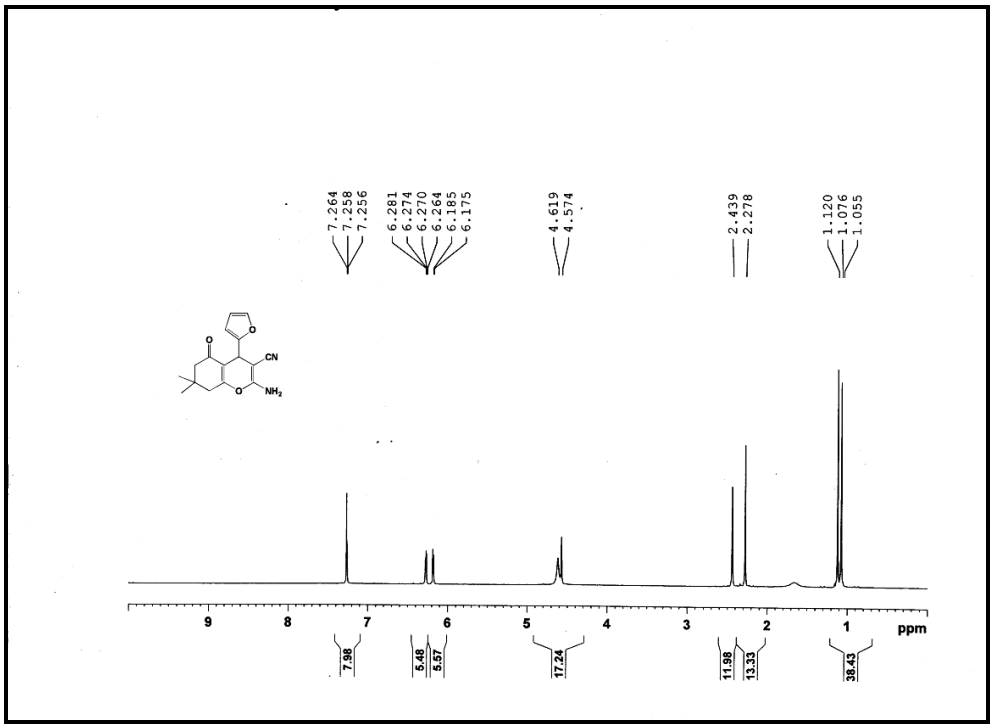
^{13}C NMR spectra of compound 3d



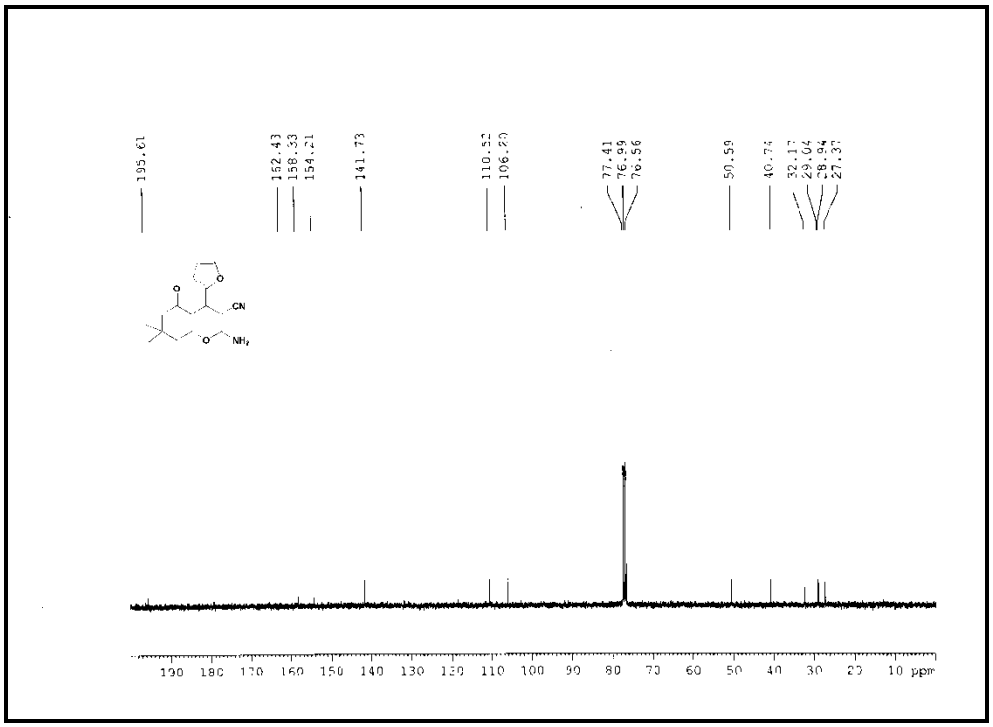
^{1}H NMR spectra of compound 3e



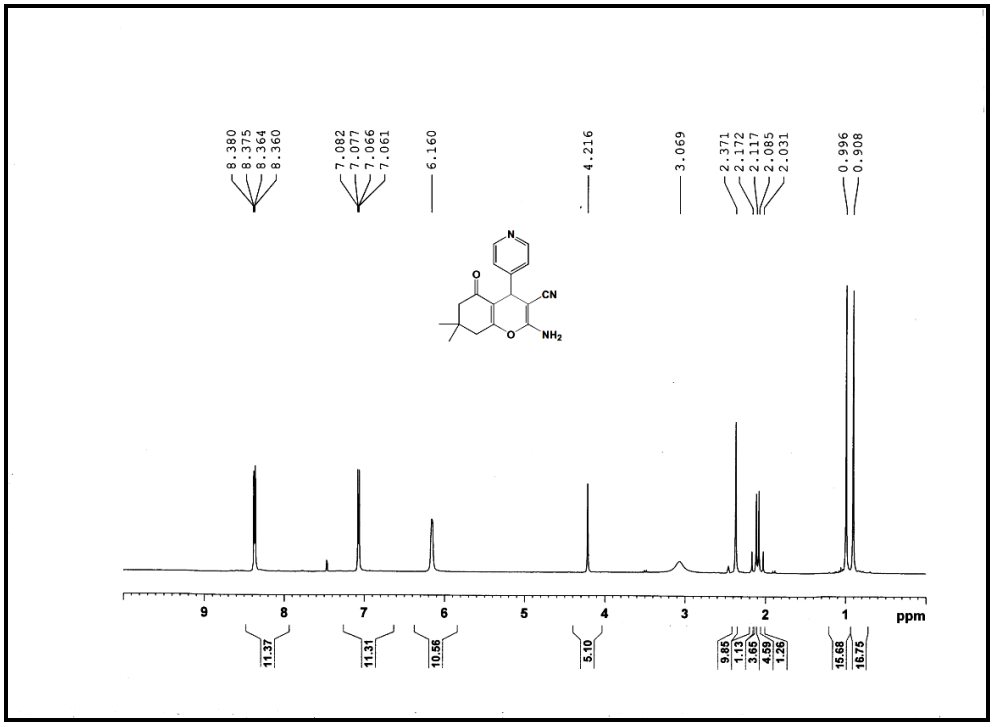
^{13}C NMR spectra of compound 3e



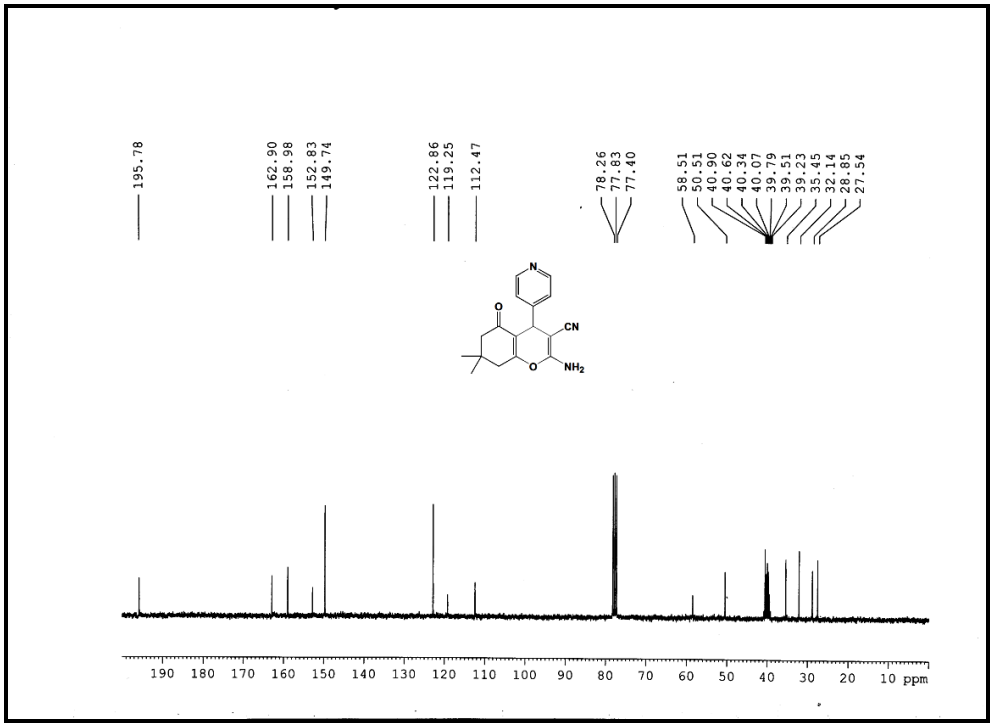
^{1}H NMR spectra of compound 3f



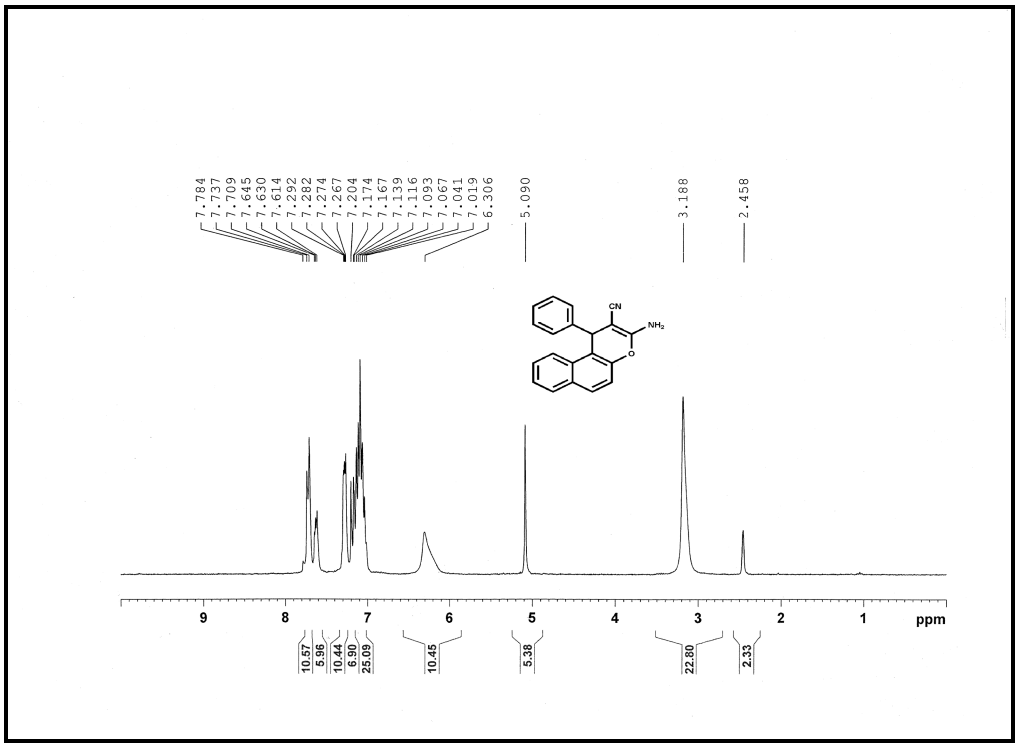
^{13}C NMR spectra of compound 3f



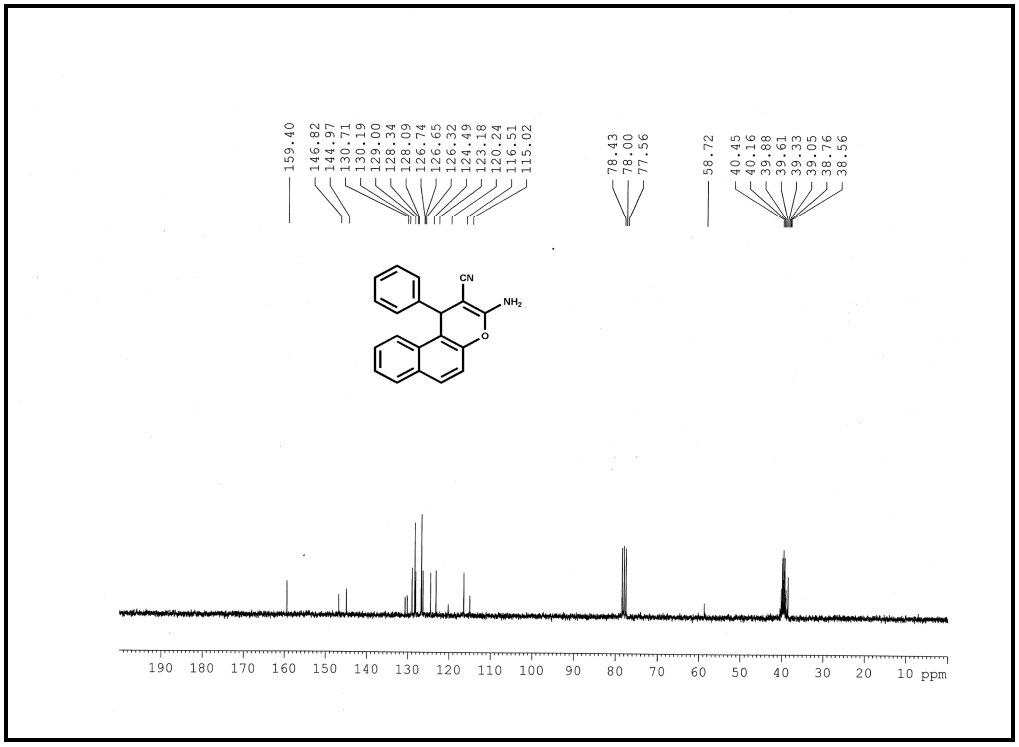
^{1}H NMR spectra of compound 3g



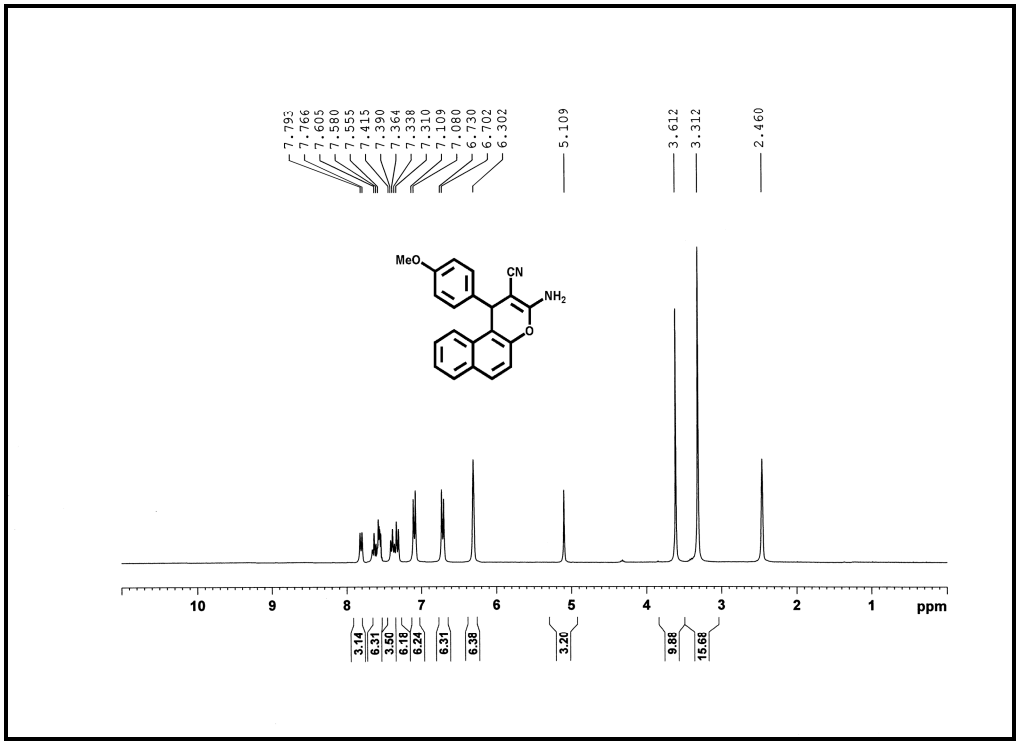
^{13}C NMR spectra of compound 3g



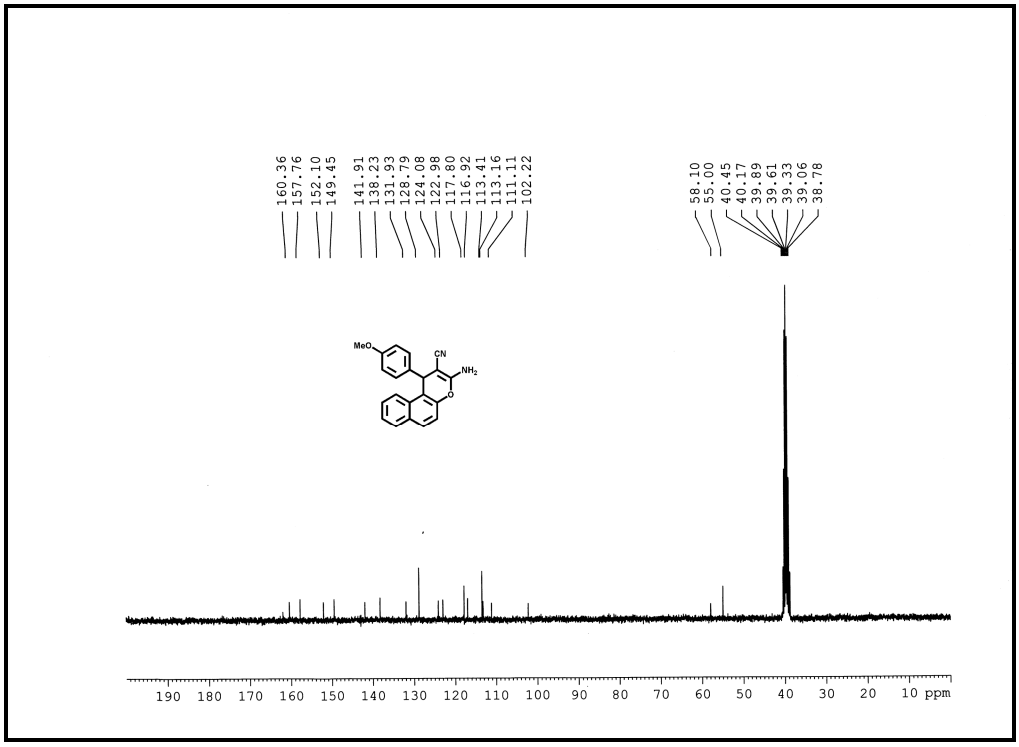
^{1}H NMR spectra of compound 4a



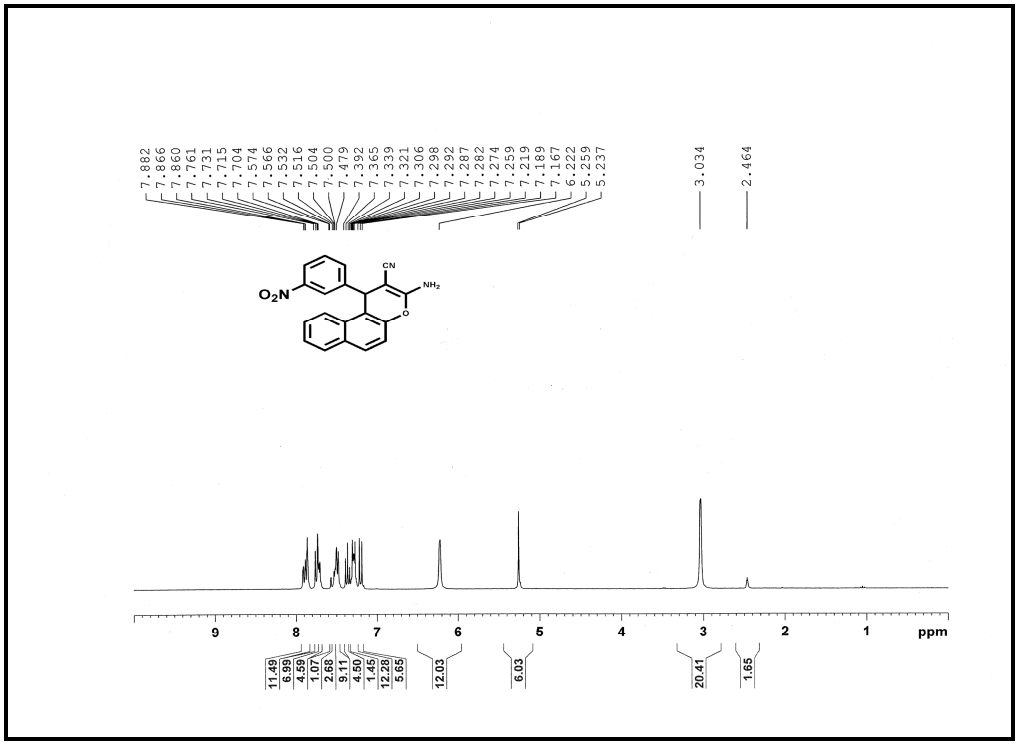
^{13}C NMR spectra of compound 4a



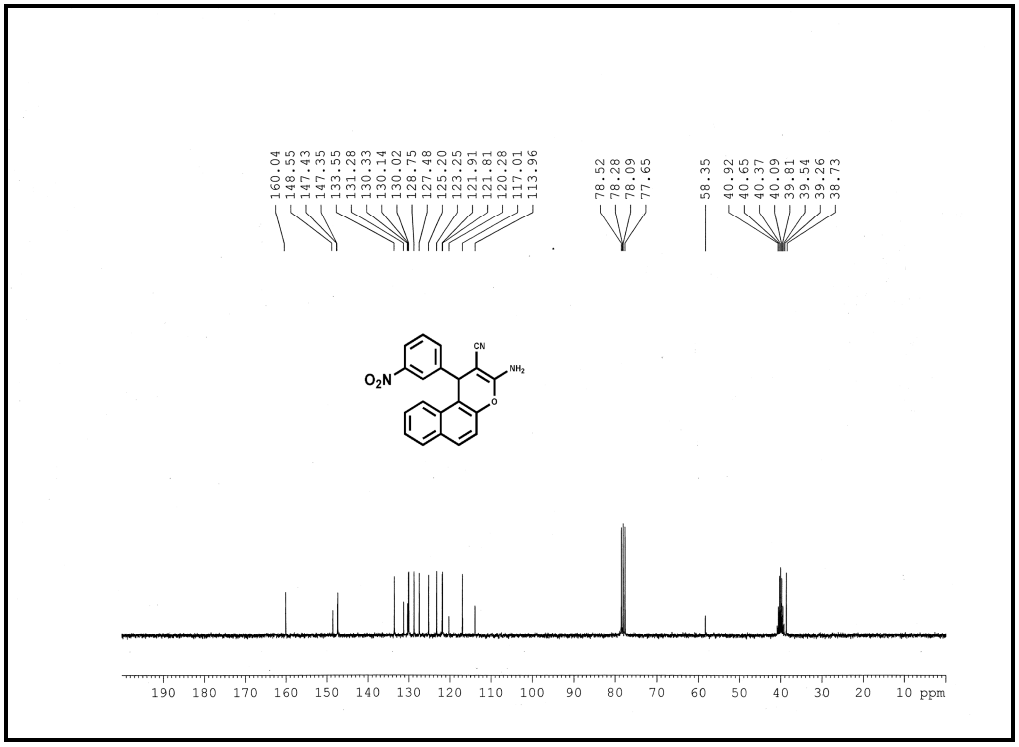
^{1}H NMR spectra of compound 4b



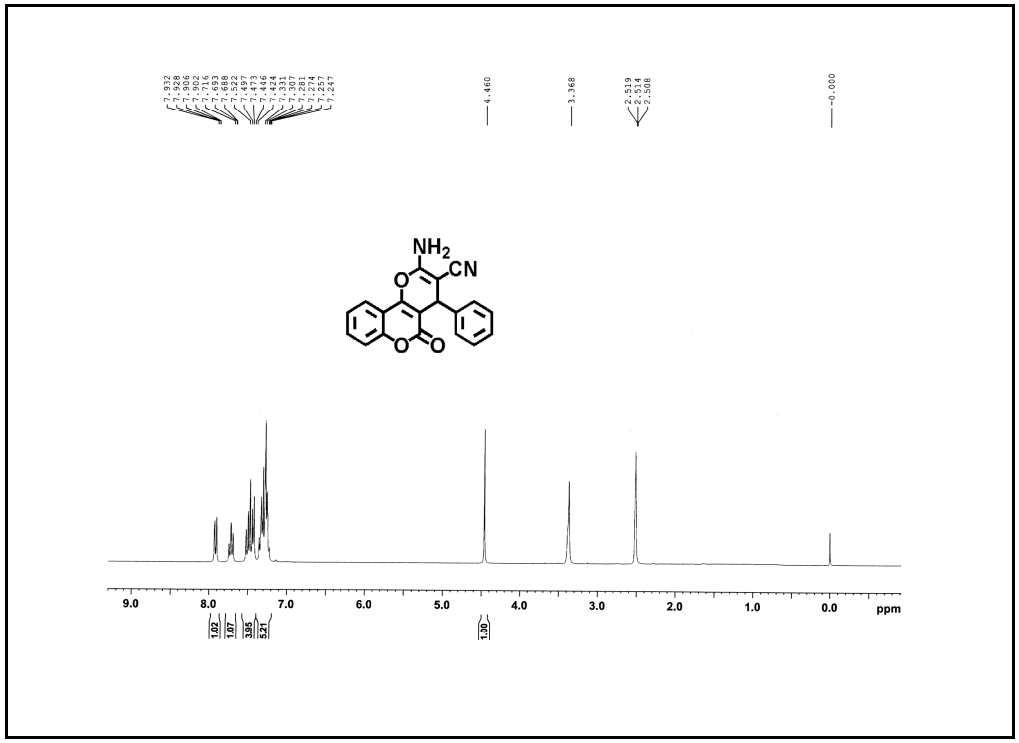
^{13}C NMR spectra of compound 4b



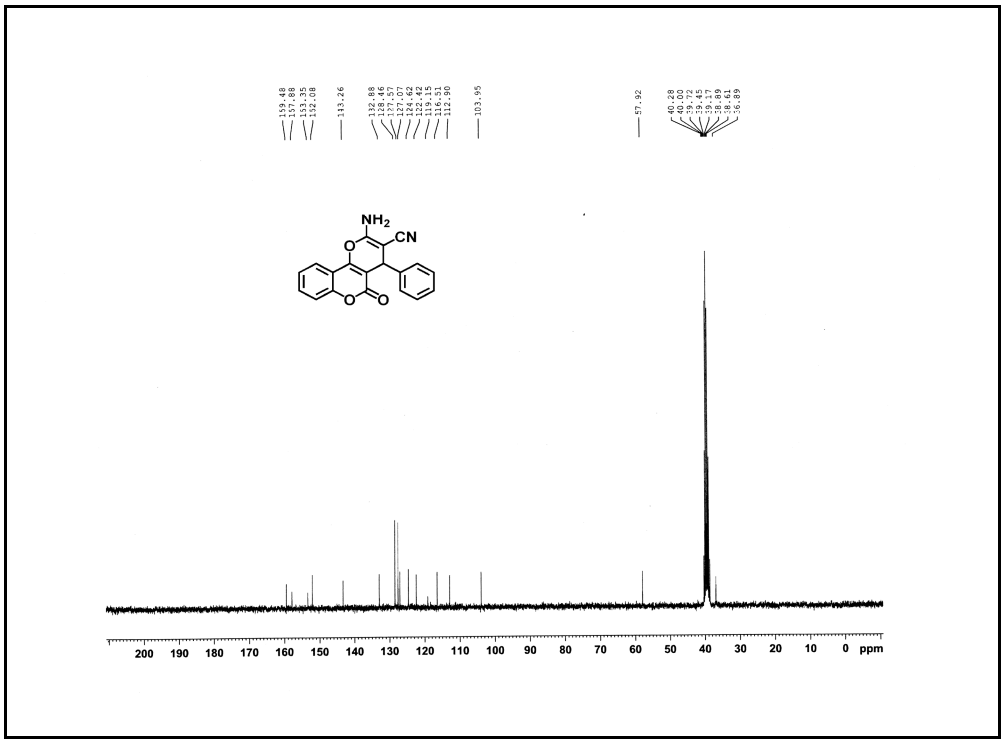
^{1}H NMR spectra of compound 4c



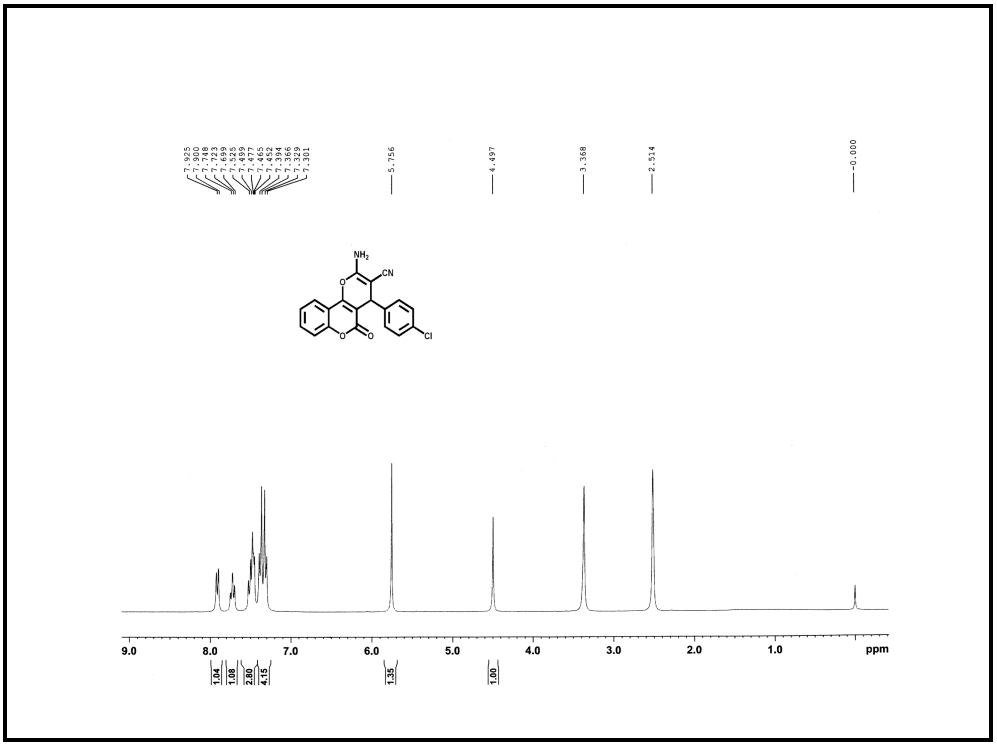
^{13}C NMR spectra of compound 4c



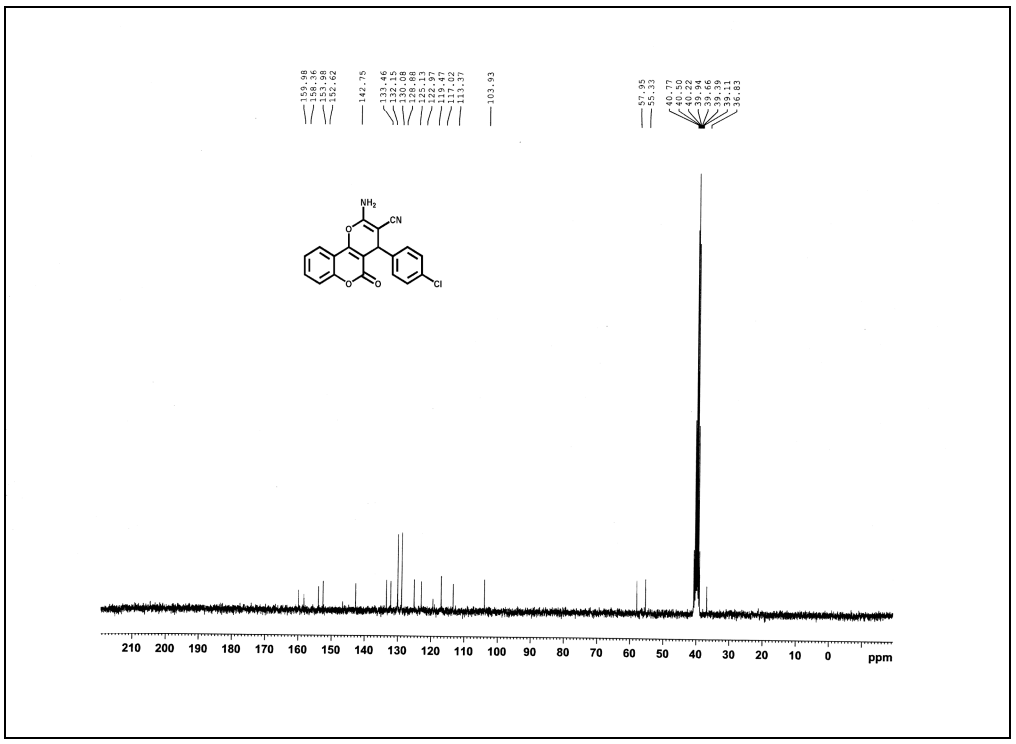
^{1}H NMR spectra of compound 5a



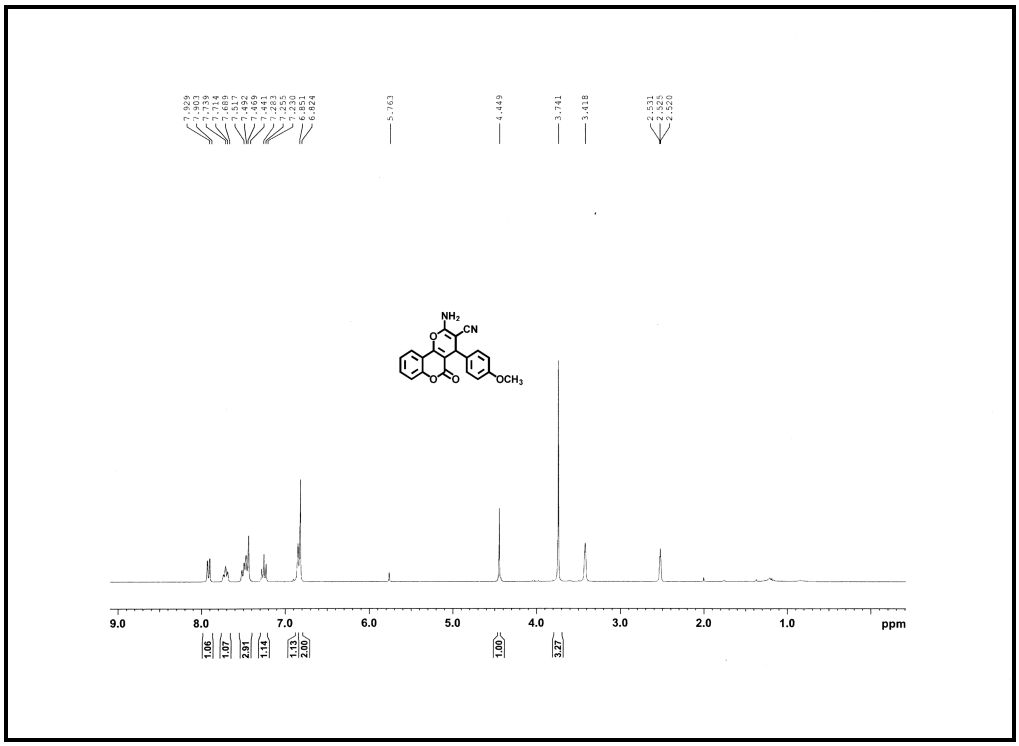
^{13}C NMR spectra of compound 5a



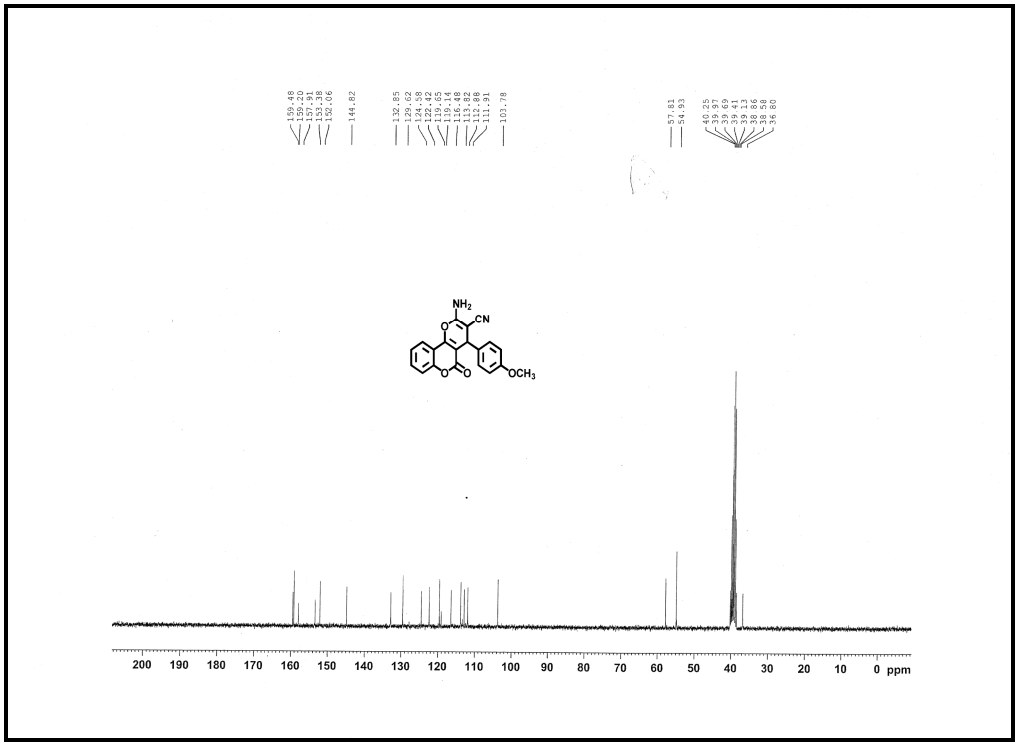
^{1}H NMR spectra of compound **5b**



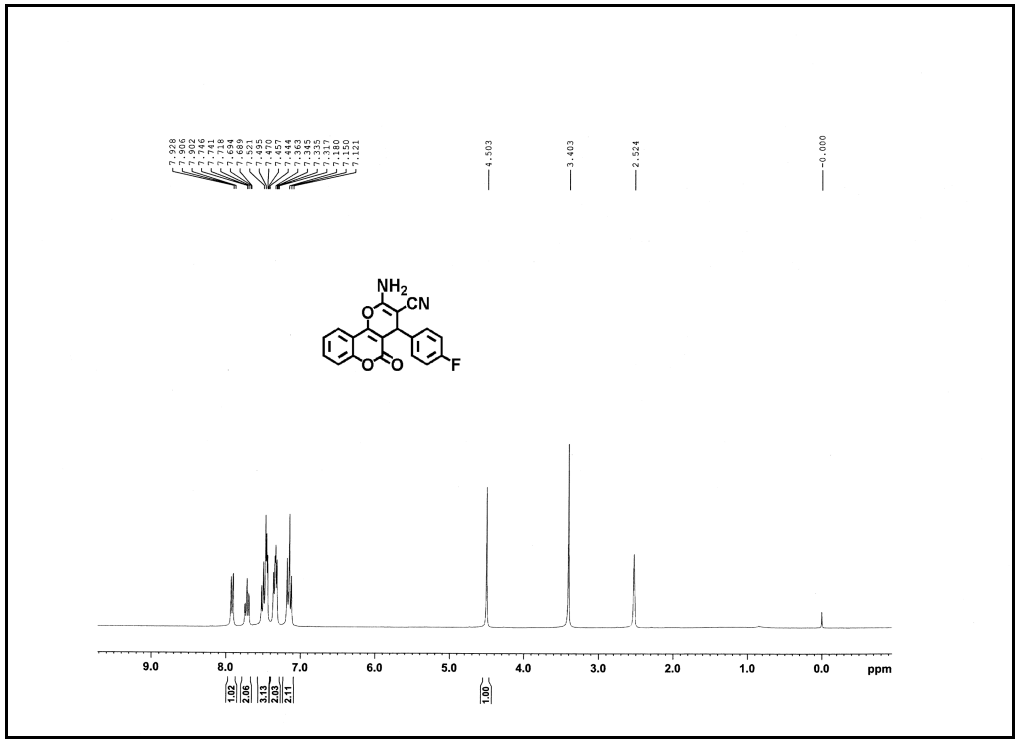
^{13}C NMR spectra of compound **5b**



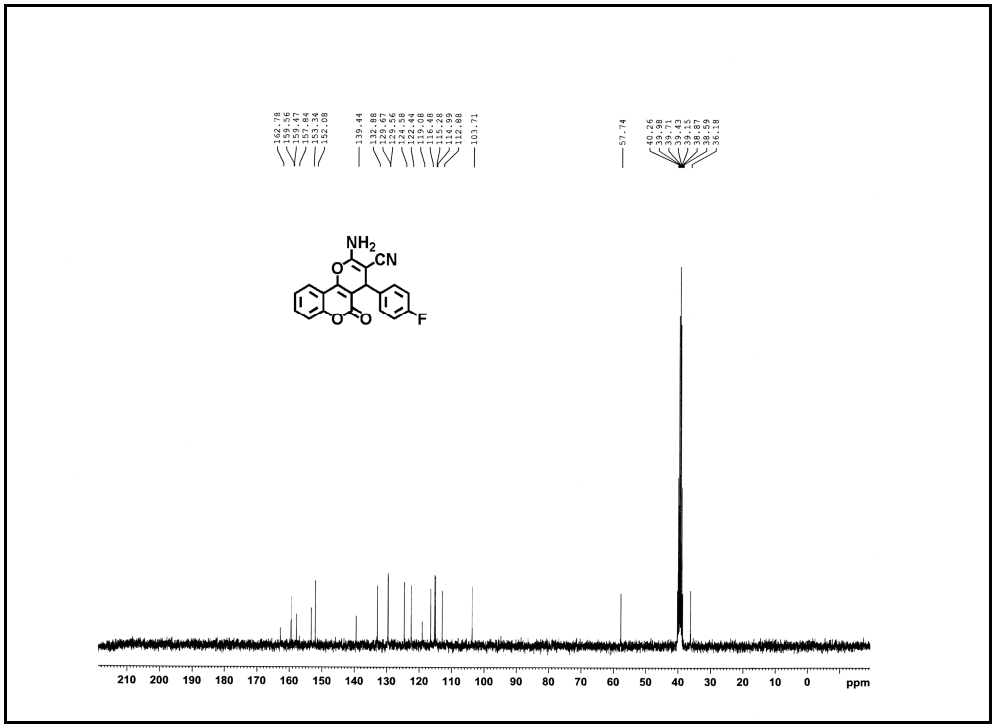
^{1}H NMR spectra of compound 5c



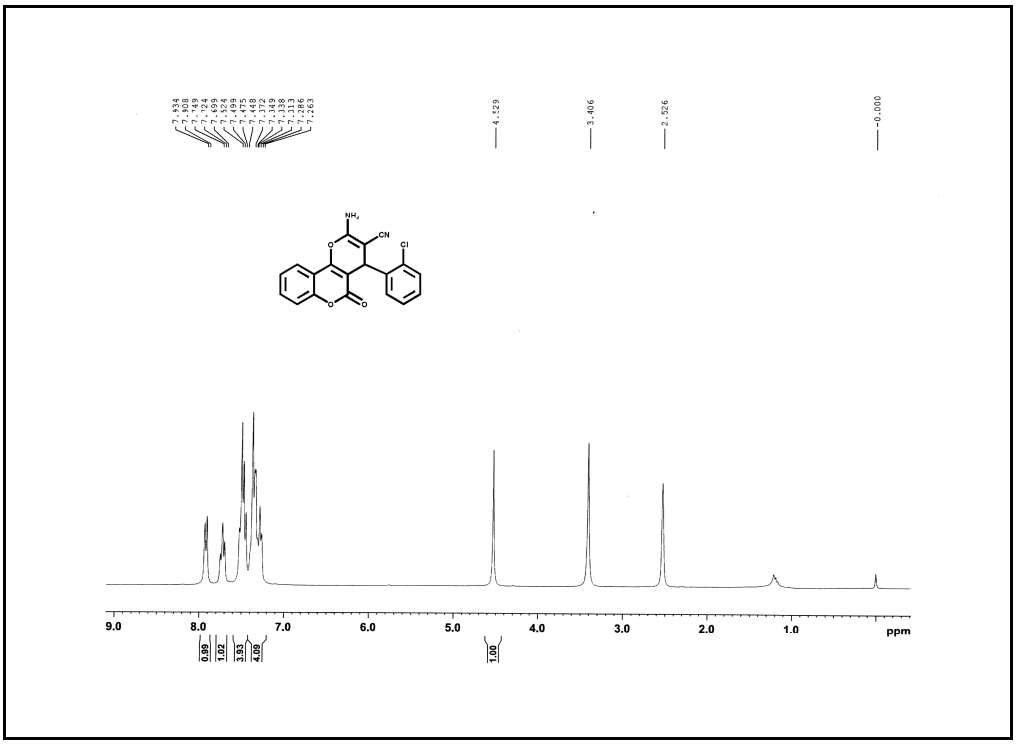
^{13}C NMR spectra of compound 5c



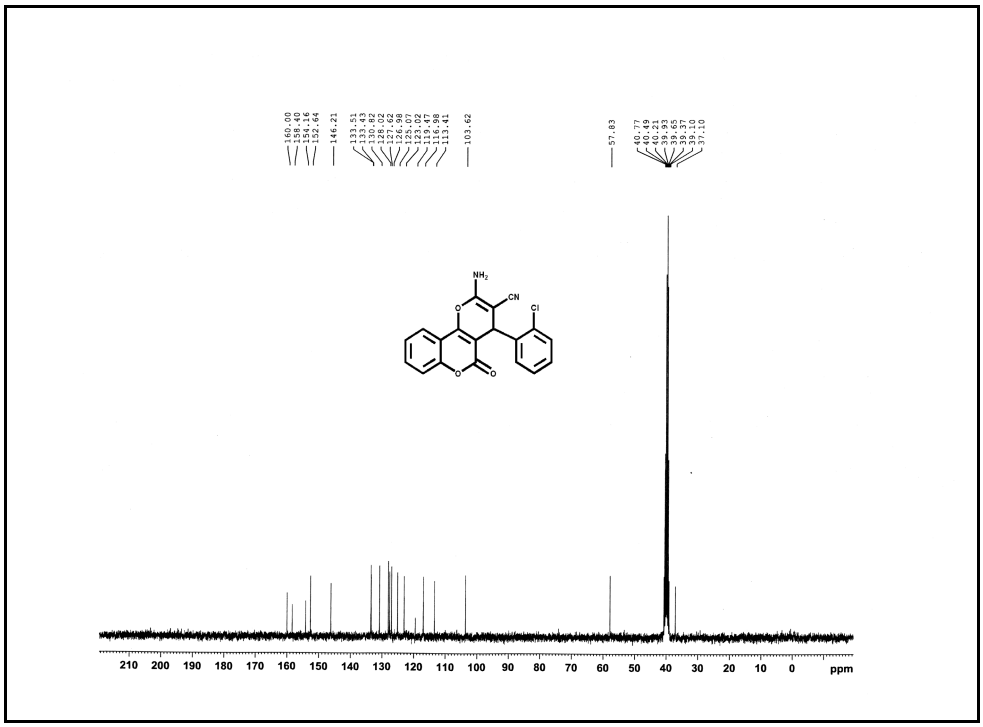
^{1}H NMR spectra of compound 5d



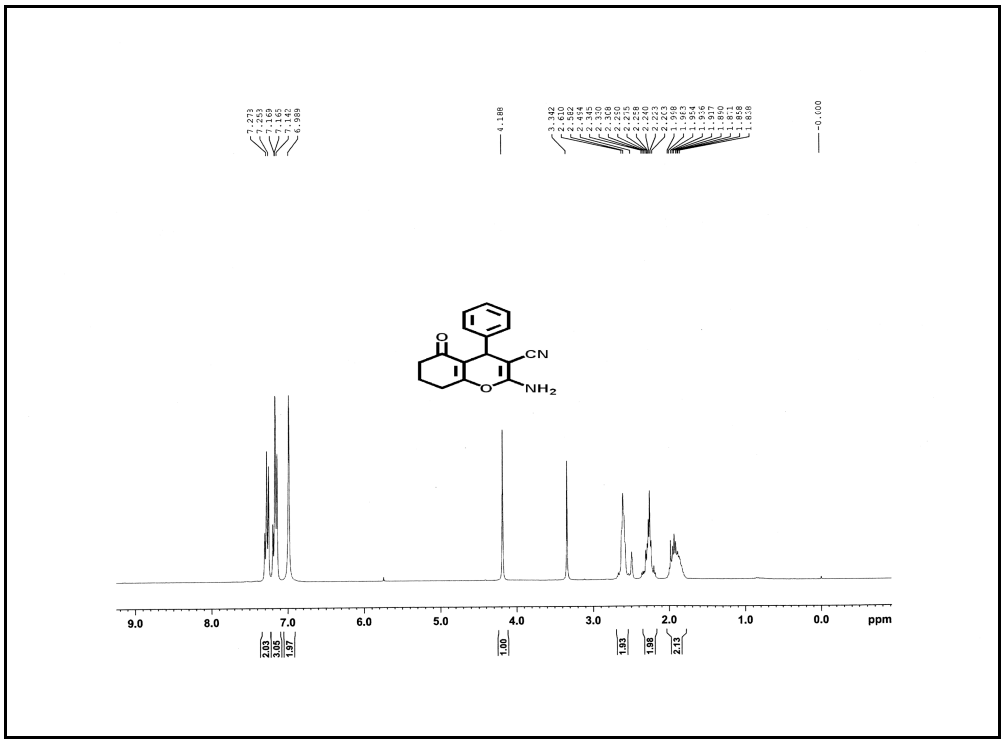
^{13}C NMR spectra of compound 5d



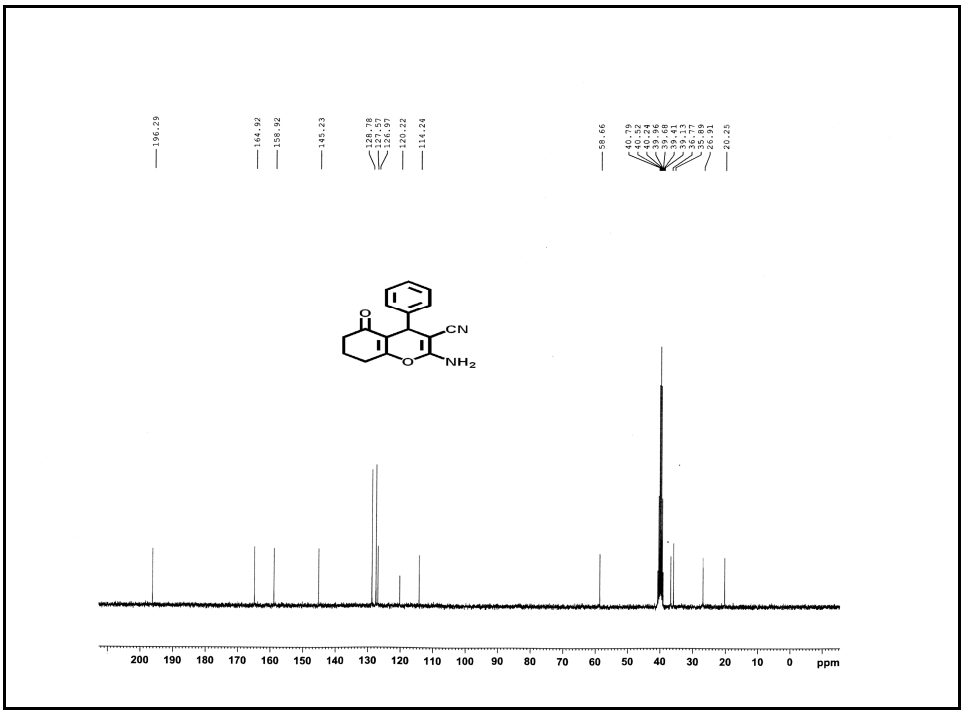
^{1}H NMR spectra of compound 5e



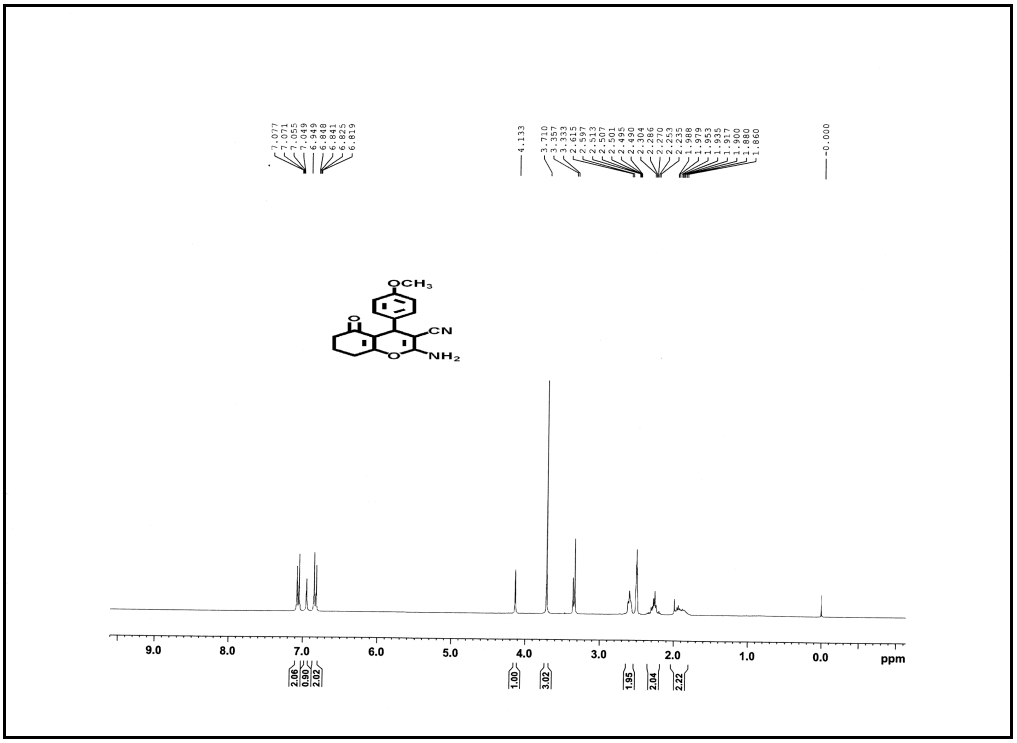
^{13}C NMR spectra of compound 5e



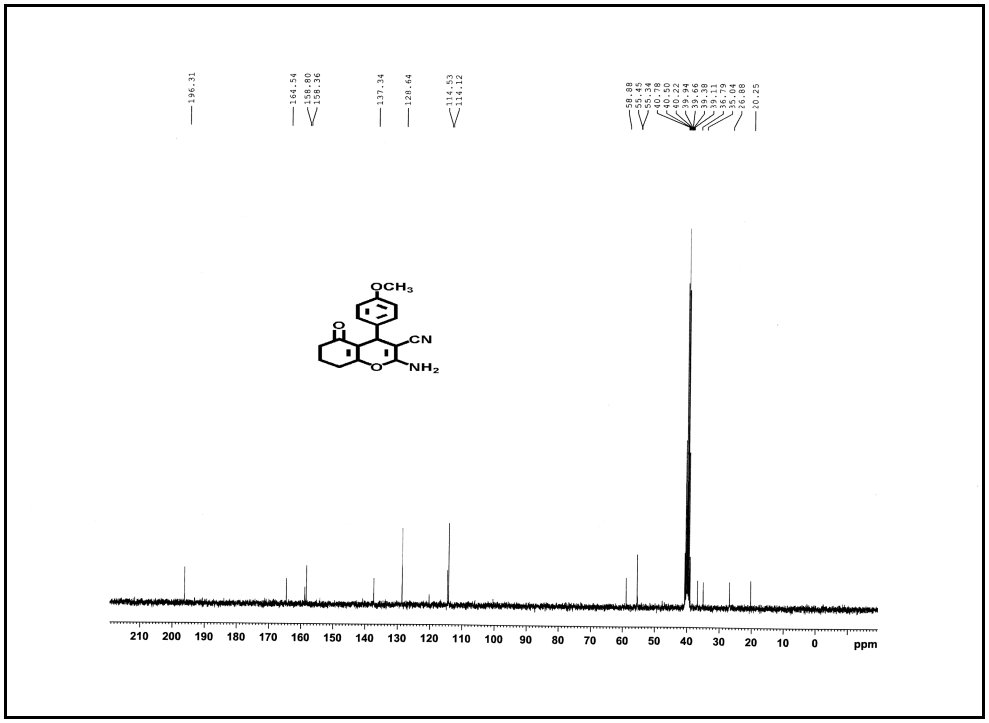
^{1}H NMR spectra of compound 6a



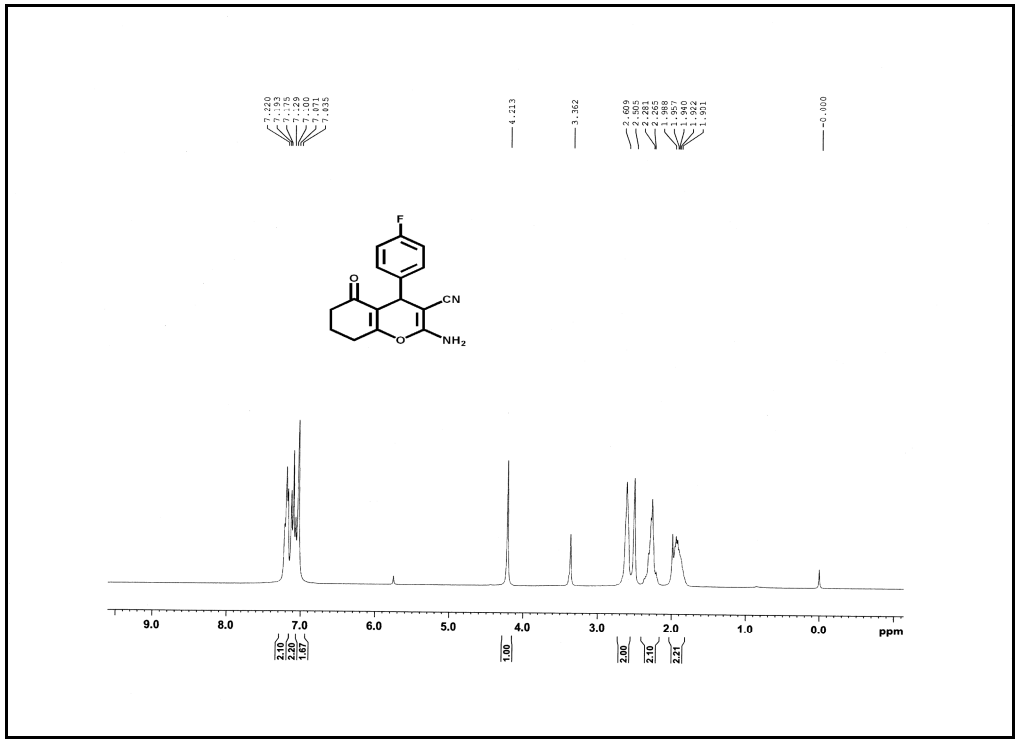
^{13}C NMR spectra of compound 6a



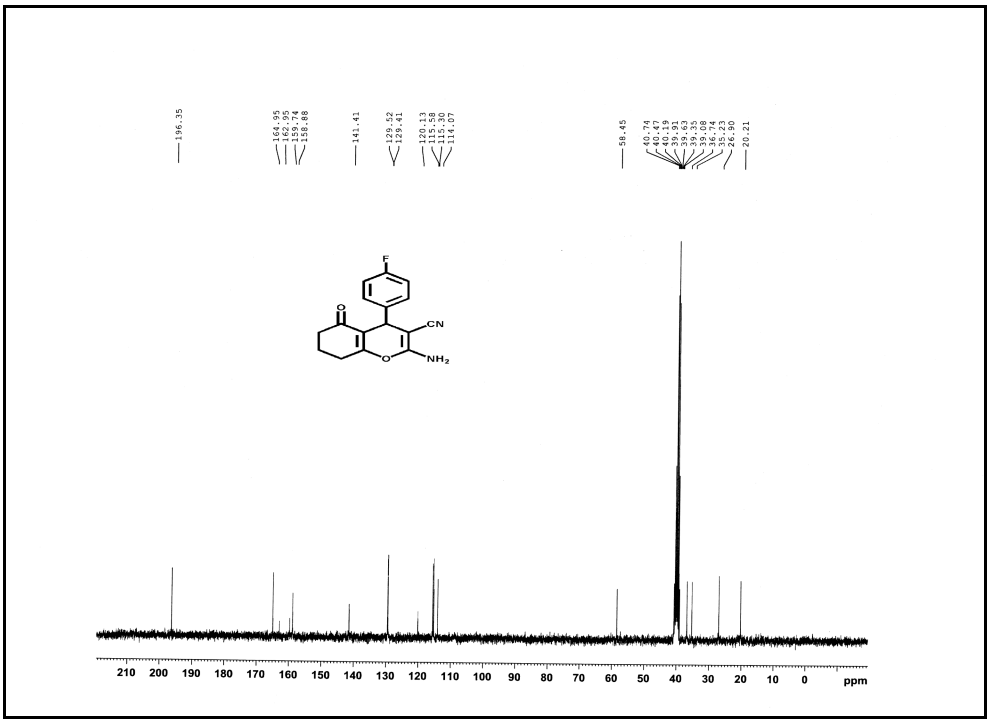
^{1}H NMR spectra of compound 6b



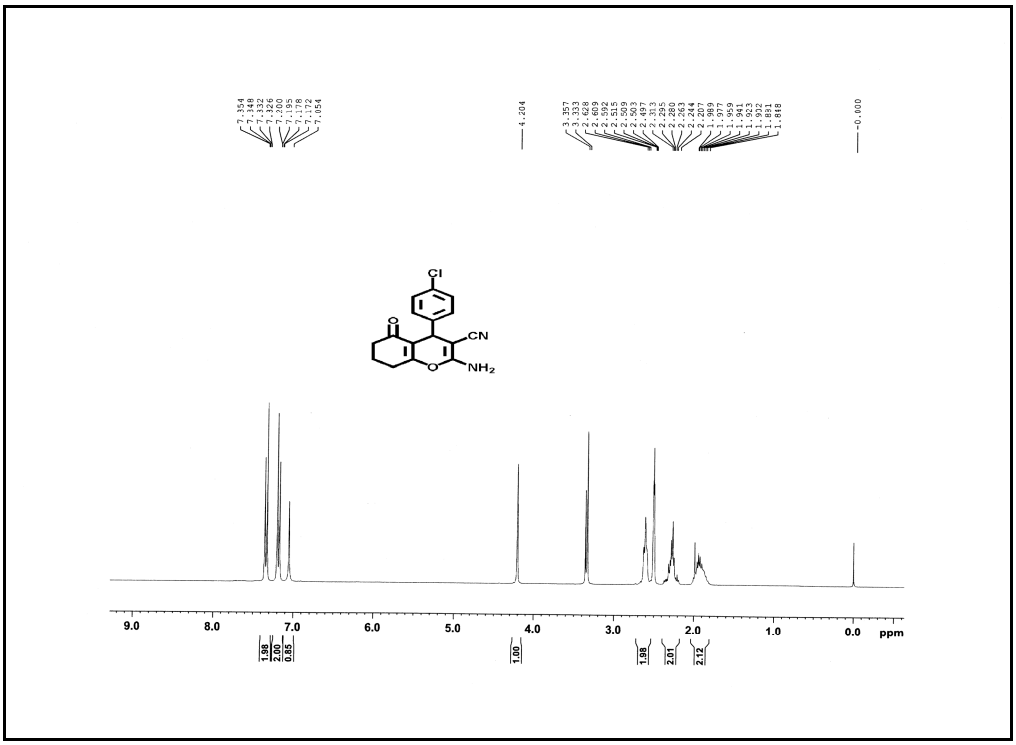
^{13}C NMR spectra of compound 6b



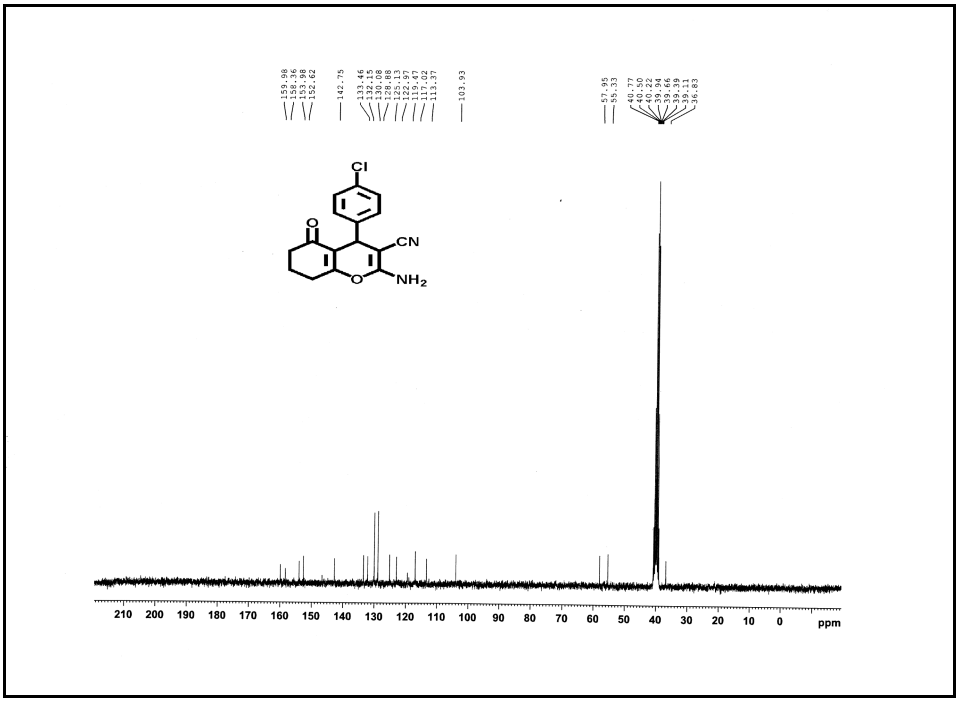
^{1}H NMR spectra of compound 6c



^{13}C NMR spectra of compound 6c



^{1}H NMR spectra of compound 6d



^{13}C NMR spectra of compound 6d