Design and synthesis of benzylpyrazolyl coumarin derivatives via four-component reaction in water: Investigation on the weak interactions accumulating the crystal structure of a signified compound

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Electronic Supplementary Information (ESI):

Experimental procedure:

1. Materials and methods:

Melting points were determined on a Köfler Block apparatus. Infrared spectra were recorded in KBr pallets in reflection mode on a Perkin Elmer RX-1 FTIR spectrophotometer. ^{1}H NMR Spectra were recorded on a Bruker AV 3000 supercon (300 MHz) spectrometer using the deuterated solvent as an internal deuterium lock. Chemical shift data are given in units δ relative to residual protic solvent where δ (chloroform) =7.26 ppm. and δ (dimethyl sulphoxide) = 3.23 ppm.The multiplicity of a signal is indicated as: br-broad, s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet etc. Coupling constant (*J*) are quoted in Hz and recorded to the nearest 0.1 Hz.^{13}C NMR Spectra were recorded on a Bruker AV 3000 supercon (75 MHz) spectrometer with Broad band proton decoupling using the deuterated solvent as an internal deuterium lock. Chemical

shift data are given in units δ relative to residual protic solvent where δ(chloroform)=77 ppm. δ(dimethyl sulphoxide)=39 ppm.

2. General procedure for the synthesis for benzylpyrazolyl coumarin:

To a mixture of 10 mol% glacial acetic acid and 5 ml water, hydrazine 1 (1 mmol), ethyl acetoacetate 2 (1 mmol), aromatic aldehyde 3 (1 mmol) and 4-hydroxycoumarin 4 were added and heated to reflux. The resulting clear solution, that gradually became turbid, was stirred for the stipulated time mentioned in table 2. After completion of the reaction (indicated by TLC), the free flowing solid was filtered and washed with water(10 ml) to afford product as pale yellow solids. The product thus obtained was recrystallized from ethanol to get pure compounds as white or pale yellow crystals. The isolated compounds were well characterized by IR, 1H NMR, 13C NMR, HRMS, elemental analysis and X-ray crystallographic study.

3. Single crystal X-ray data for compound 5d:

Single crystal suitable for X-ray diffraction of (5d) was grown from ethanol. The crystals were carefully chosen using a stereo zoom microscope supported by a rotatable polarizing stage. The data was collected at room temperature on Bruker-APEX II SMART CCD diffractometer with graphite monochromated Mo-Kα radiation (0.71073 Å). The crystal structure was solved by direct methods using SHELXS-971a and the data was refined by full matrix least-squares refinement on F2 with anisotropic displacement parameters for non-H atoms, using SHELXL-971b.

Crystal data of 5d: Molecular formula = $C_{27}H_{22}N_2O_4$, Formula weight = 438.16, Crystal system = Monoclinic, space group = P21/n, a = 17.188(5)Å, b = b=14.671(5)Å, c = 17.440(5)Å, V = 4390(2)Å^3, T = 293 K, Z = 4, Z'=2, Dx = 1.327 g cm^{-3}, Mu (Mo-Kα) = 0.090mm^{-1}, 6847

reflections measured, R_1_obs = 0.1290, Goodness of fit = 1.076. Crystallographic data (excluding structure factors) for 5d have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 886519.

References:

1.(a) APEX-II, SAINT-Plus, and TWINABS; Bruker-Nonius AXS, Inc.: Madison, WI, 2004(b) Sheldrick, G. M. SAINT, version 6.02 and SADABS, version 2.03; Bruker AXS, Inc.:Madison, I, 2002.

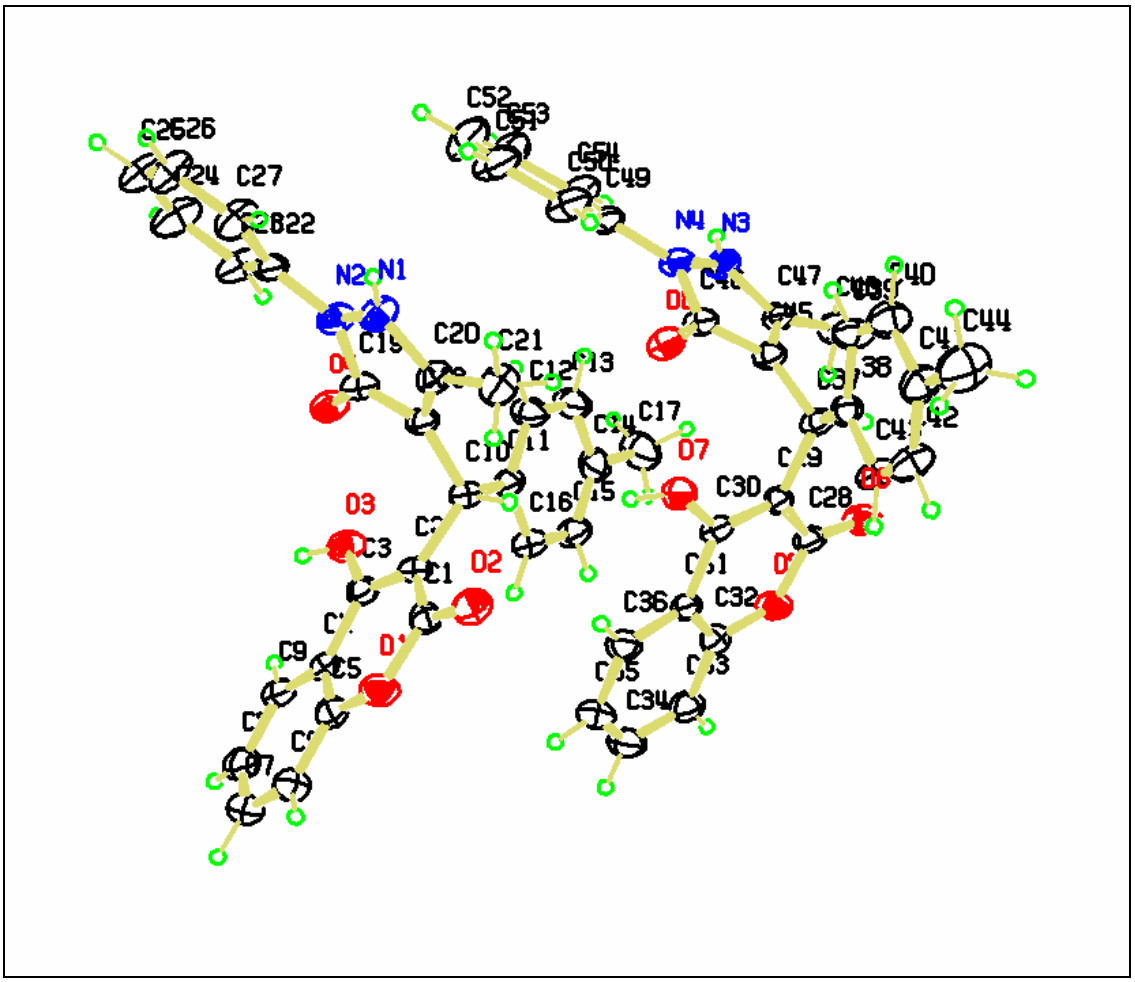
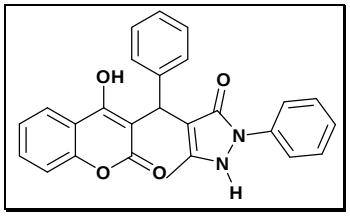


Figure 2: ORTEP diagram of Single crystal of compound 5d: CCDC No. CCDC 886519.

4. Spectral data of all the compounds:

5a. 1,2-dihydro-4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(phenyl)methyl)-5-methyl-2-phenylpyrazol-3-one



Yield: (0.394 g, 93%);

Characteristic: White crystalline solid

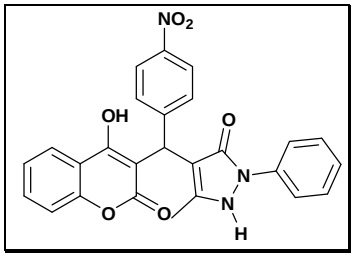
Mp: 232-234 ^{0}C (from EtOH);

IR (KBr): 3080, 1654, 1610, 1563, 1490, 1184, 1034, 751 cm^{-1};

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.36 (s, 3H), 5.71 (s, 1H), 7.06-7.21 (m, 8H), 7.33-7.44 (m, 2H), 7.60-7.62 (m, 2H), 7.74-7.76 (d, *J*=7.8 Hz, 2H), 12.25(bs, 1H) ;

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.3, 33.6, 106.0, 106.6, 115.4, 118.1, 120.4, 123.1, 125.6, 126.1, 126.5, 127.7, 128.2, 128.3, 128.6, 131.1, 135.4, 139.0, 146.7, 151.9, 162.5, 163.6, 164.6; HRMS Calcd for $C_{26}H_{20}N_2O_4$ ($[M+H]^+$) 424.1423 found : 424.1425; Anal. Calcd for $C_{26}H_{20}N_2O_4$: C 73.57, H 4.75 and N 6.60%. Found: C 73.55, H 4.72 and N 6.62%.

5b. 1,2-dihydro-4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(4-nitrophenyl)methyl)-5-methyl-2-phenylpyrazol-3-one



Yield: (0.431 g, 92%)

Characteristic: Pale yellow crystalline solid

Mp: 248-250 ^{0}C (from EtOH);

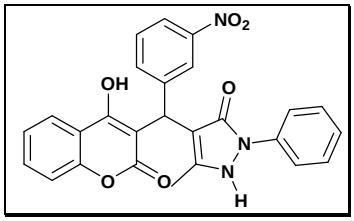
IR (KBr): 3073, 1649, 1608, 1560, 1525, 1178, 1039, 748 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.65 (s, 3H), 6.12 (s, 1H), 7.46-7.78 (m, 9H), 7.94-8.97 (m, 5H);

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 13.4, 35.2, 103.1, 115.8, 118.1, 120.5, 120.9, 121.1, 121.9, 123.6, 124.6, 126.7, 126.5, 127.7, 128.6, 131.1, 131.2, 132.3, 135.8, 138.7, 142.7, 147.8, 151.8, 164.5, 165.9, 166.2;

HRMS Calcd for $C_{26}H_{19}N_3O_6$ ($[M+H]^+$) 469.1274 found : 469.1271; Anal. Calcd for $C_{26}H_{19}N_3O_6$: C 66.52, H 4.08and N 8.95%. Found: C 66.55, H 4.11 and N 8.94%.

5c. 1,2-dihydro-4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(3-nitrophenyl)methyl)-5-methyl-2-phenylpyrazol-3-one



Yield: (0.441 g, 94%)

Characteristic: Pale yellow crystalline solid

Mp: 241-243 ^{0}C (from EtOH);

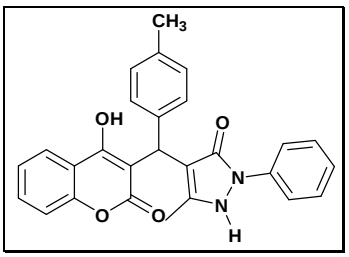
IR (KBr): 3074, 1649, 1609, 1560, 1525, 1179, 1103, 749 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.38 (s, 3H), 5.79 (s, 1H), 7.10-7.21 (m, 3H), 7.32-7.44 (m, 4H), 7.54-7.59 (m, 3H), 7.74-7.76 (d, *J*=7.8 Hz, 2H), 7.92-7.98(m, 2H) ;

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.8, 34.2, 105.5, 106.5, 115.9, 118.4, 121.2, 121.3, 122.1, 123.7, 124.4, 126.9, 129.2, 131.8, 133.7, 135.3, 142.1, 147.1, 148.36, 152.5, 162.6, 164.6, 165.1;

HRMS Calcd for $C_{26}H_{19}N_3O_6$ ($[M+H]^+$) 469.1274 found : 469.1270; Anal. Calcd for $C_{26}H_{19}N_3O_6$: C 66.52, H 4.08and N 8.95%. Found: C 66.53, H 4.10 and N 8.96%.

5d. 1,2-dihydro-4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(p-tolyl)methyl)-5-methyl-2-phenylpyrazol-3-one



Yield: (0.403 g, 92%)

Characteristic: White crystalline solid

Mp: 222-224 ^{0}C (from EtOH);

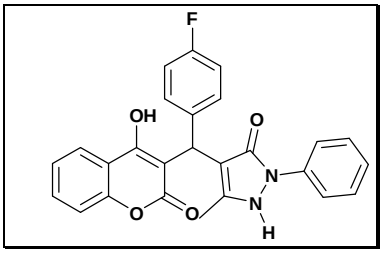
IR (KBr): 3081, 1649, 1610, 1494, 1184, 1031, 752 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.18 (s, 3H), 2.34 (s, 3H), 5.68 (s, 1H), 6.92-7.19 (m, 7H), 7.31-7.41 (m, 4H), 7.58-7.61 (d, *J*=7.8 Hz, 2H), 7.75-7.78 (m, 1H) ;

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.8, 20.9, 33.8, 106.9, 107.3, 115.8, 118.6, 120.9, 123.5, 124.3, 126.9, 128.9, 129.1, 131.4, 135.4, 135.7, 136.3, 147.3, 152.4, 163.2, 164.1, 165.3;

HRMS Calcd for $C_{27}H_{22}N_2O_4$ ($[M+H]^+$) 438.1580 found : 438.1582; Anal. Calcd for $C_{27}H_{22}N_2O_4$: C 73.96, H 5.06 and N 6.39%. Found: C 73.99, H 5.07 and N 6.42%.

5e. 4-((4-fluorophenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-1,2-dihydro-5-methyl-2-phenylpyrazol-3-one



Yield: (0.411 g, 93%)

Characteristic: White crystalline solid

Mp: 240-242 ^{0}C (from EtOH);

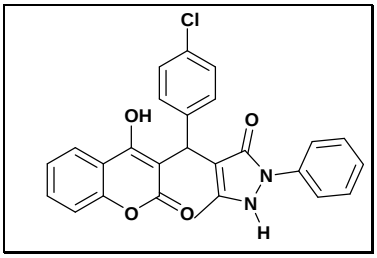
IR (KBr): 3081, 1656, 1607, 1566, 1499, 1187, 1040, 754 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.36 (s, 3H), 5.70 (s, 1H), 6.80-6.86 (m, 2H), 7.09-7.19 (m, 5H), 7.31-7.42 (m, 3H), 7.57-7.60 (d, *J*=8.1Hz, 2H), 7.76-7.79 (m, 1H), 12.03 (bs, 1H) ;

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.8, 33.6, 106.6, 107.2, 114.7, 115.0, 115.9, 118.6, 120.9, 123.6, 124.4, 126.6, 128.6, 128.7, 129.1, 131.5, 135.1, 135.6, 147.2, 152.4, 159.6, 162.9, 164.3, 165.3;

HRMS Calcd for $C_{26}H_{19}FN_2O_4$ ($[M+H]^+$) 442.1329 found : 442.1332; Anal. Calcd for $C_{26}H_{19}FN_2O_4$: C 70.58, H 4.33and N 6.33%. Found: C 70.61, H 4.35 and N 6.36%.

5f. 4-((4-chlorophenyl)(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)-1,2-dihydro-5-methyl-2-phenylpyrazol-3-one



Yield: (0.426 g, 93%)

Characteristic: White crystalline solid

Mp: 227-229 ^{0}C (from EtOH);

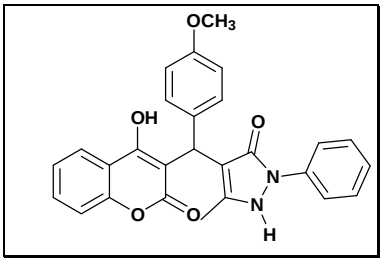
IR (KBr): 3081, 1655, 1609, 1566, 1490, 1184, 1099, 755 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.35(s, 3H), 5.66 (s, 1H), 7.12-7.25 (m, 8H), 7.34-7.49 (m, 3H), 7.58-7.89 (m, 3H) ;

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.3, 33.2, 105.4, 106.4, 115.5, 118.0, 120.5, 121.0, 123.3,123.7, 126.3, 127.7, 128.2, 128.4, 128.7, 130.9, 131.3, 135.1, 138.1, 146.6, 151.9, 162.2, 163.6, 164.3;

HRMS Calcd for $C_{26}H_{19}ClN_2O_4$ ($[M+H]^+$) 458.1033 found : 458.1036; Anal. Calcd for $C_{26}H_{19}ClN_2O_4$: C 68.05, H 4.17and N 6.10%. Found: C 68.07, H 4.20 and N 6.13%.

5g. 1,2-dihydro-4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(4-methoxyphenyl)methyl)-5-methyl-2-phenylpyrazol-3-one



Yield: (0.408 g, 90%)

Characteristic: White crystalline solid

Mp: 205-207 ^{0}C (from EtOH);

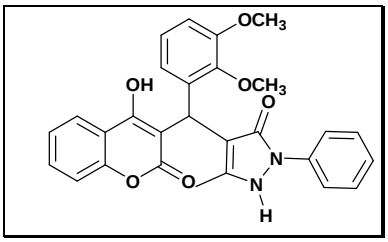
IR (KBr): 3081, 1654, 1610, 1556, 1500, 1179, 1037, 754 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.34(s, 3H), 3.63(s, 3H), 5.64 (s, 1H), 6.65-6.68(d, *J*=8.7Hz, 2H), 7.03-7.19 (m, 5H), 7.31-7.41 (m, 3H), 7.57-7.59 (d, *J*=8.1Hz, 2H), 7.73-7.75(d, *J*=7.8Hz, 1H);

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 9.6, 32.3, 54.0, 105.7, 106.2, 112.5, 114.7, 117.5, 119.7, 122.4,123.1, 125.4, 126.9, 128.0, 130.2, 130.4, 134.6, 146.0, 151.3, 156.8, 162.9, 164.1;

HRMS Calcd for $C_{27}H_{22}N_2O_4$ ($[M+H]^+$) 454.1529 found : 454.1527; Anal. Calcd for $C_{27}H_{22}N_2O_4$: C 71.35, H 4.88and N 6.16%. Found: C 71.38, H 4.91 and N 6.18%.

5h. 1,2-dihydro-4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(2,3-dimethoxyphenyl)methyl)-5-methyl-2-phenylpyrazol-3-one



Yield: (0.430 g, 89%)

Characteristic: Pale yellow crystalline solid

Mp: 223-225 ^{0}C (from EtOH);

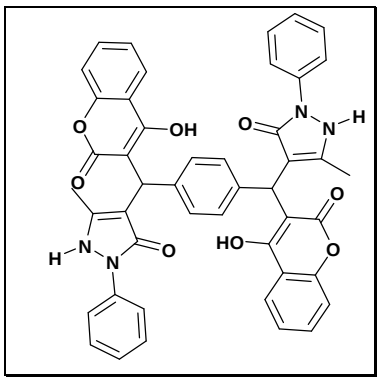
IR (KBr): 2934, 1666, 1613, 1477, 1277, 1181, 1071, 753 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.35(s, 3H), 3.53(s, 3H), 3.69(s, 3H), 5.82 (s, 1H), 6.73-7.02(m, 3H), 7.14-7.38 (m, 6H), 7.61 (bs, 2H), 7.74-7.76(d, *J*=7.8Hz, 2H);

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.8, 11.8, 30.5, 55.7, 59.8, 106.1, 108.1, 111.3, 115.8, 118.8, 121.0, 121.1, 123.1, 123.6, 124.2, 124.3, 126.6, 128.0, 129.2, 131.4, 134.3, 135.7, 146.1, 146.8, 147.0, 152.2, 152.7, 163.0, 163.5;

HRMS Calcd for $C_{28}H_{24}N_2O_6$ ($[M+H]^+$) 484.1634 found : 484.1637; Anal. Calcd for $C_{28}H_{24}N_2O_6$: C 69.41, H 4.99and N 5.78%. Found: C 69.44, H 5.03and N 5.80%.

5i. Benzyl bis-(pyrazolyl coumarin)



Yield: (0.678g, 88%)

Characteristic: White crystalline solid

Mp: >300 ^{0}C (from EtOH);

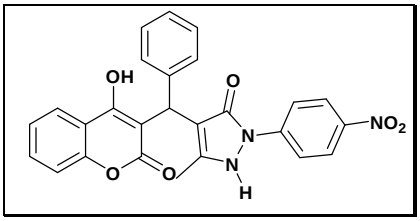
IR (KBr): 3081, 1656, 1607, 1556, 1490, 1184, 1056, 754 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.35(s, 6H), 4.91(bs, 2H), 5.69 (s, 2H), 7.01-7.19(m, 10H), 7.33-7.45 (m, 7H), 7.58 (bs, 3H), 7.72-7.86(m, 2H);

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.8, 11.3, 33.8, 106.9, 115.9, 116.2, 118.6, 120.9, 122.0, 123.7, 124.3, 124.3, 126.6, 127.0, 127.2, 129.2, 131.7, 135.7, 147.3, 152.4, 162.9, 163.9, 164.9;

HRMS Calcd for $C_{46}H_{34}N_4O_8$ ($[M+H]^+$) 770.2377 found : 770.2379; Anal. Calcd for $C_{46}H_{34}N_4O_8$: C 71.68, H 4.45 and N 7.27%. Found: C 71.65, H 4.43and N 7.30%.

5j. 1,2-dihydro-4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(phenyl)methyl)-5-methyl-2-(4-nitrophenyl)pyrazol-3-one



Yield: (0.403 g, 86%)

Characteristic: Pale yellow crystalline solid Mp: >300 ^{0}C (from EtOH);

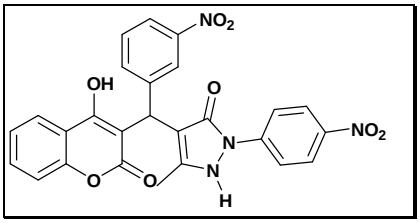
IR (KBr): 3082, 1656, 1611, 1535, 1489, 1187, 1043, 754 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.80(s, 3H), 6.07 (s, 1H), 7.12-7.20(m, 7H), 7.32-7.46(m, 3H), 7.60-7.91(m, 3H);

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.4, 11.3, 33.0, 106.3, 106.9, 111.3, 114.3, 115.5, 117.4, 118.3, 120.8,123.2, 123.4, 125.4, 126.3, 128.5, 128.9, 131.8, 135.3, 145.7, 146.8, 151.1, 162.6, 163.1, 164.9;

HRMS Calcd for $C_{26}H_{19}N_3O_6$ ($[M+H]^+$) 469.1274 found : 469.1270; Anal. Calcd for $C_{26}H_{19}N_3O_6$: C 66.52, H 4.08 and N 8.95%. Found: C 66.55, H 4.11 and N 8.91%.

5k. 1,2-dihydro-4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(3-nitrophenyl)methyl)-5-methyl-2-(4-nitrophenyl)pyrazol-3-one



Yield: (0.426 g, 83%)

Characteristic: Pale yellow crystalline solid

Mp: >300 ^{0}C (from EtOH);

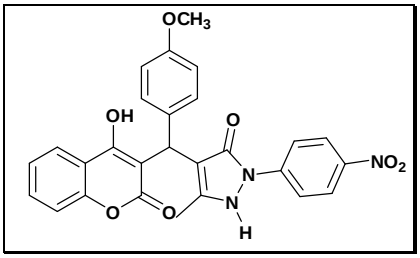
IR (KBr): 3080, 1651, 1609, 1555, 1469, 1188, 1041, 754cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.36(s, 3H), 5.59 (s, 1H), 6.96-7.03(m, 4H), 7.12-7.20(m, 2H), 7.25-7.30(m, 2H), 7.41-7.47(m, 2H), 7.84-7.87(m, 2H);

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.2, 11.3, 32.5, 55.5, 106.1, 106.5, 111.5, 114.6, 115.1, 117.5, 118.3, 120.2,120.7, 123.5, 123.8, 125.6, 126.1, 128.5, 128.8, 131.1, 131.8, 135.3, 145.2, 146.8, 151.9, 162.5, 163.2, 164.5;

HRMS Calcd for $C_{26}H_{18}N_4O_8$ ($[M+H]^+$) 514.1125 found : 514.1122; Anal. Calcd for $C_{26}H_{18}N_4O_8$: C 60.70, H 3.53 and N 10.89%. Found: C 60.72, H 3.57 and N 10.91%.

5l. 1,2-dihydro-4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(4-methoxyphenyl)methyl)-5-methyl-2-(4-nitrophenyl)pyrazol-3-one



Yield: (0.400 g, 80%)

Characteristic: Pale yellow crystalline solid

Mp:.>300 ^{0}C (from EtOH);

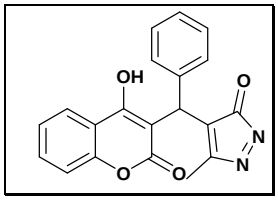
IR (KBr): 3082, 1652, 1605, 1560, 1499, 1187, 1044, 756cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.72(s, 3H), 4.14(s, 3H), 5.21 (s, 1H), 7.00-7.15(m, 3H), 7.59-8.12 (m, 9H);

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.3, 11.3, 32.5, 55.5, 106.4, 106.9, 111.3, 114.3, 115.5, 117.4, 118.3, 119.7, 120.4,123.2, 123.8, 125.6, 126.1, 128.5, 128.7, 131.1, 135.3, 145.7, 146.8, 151.9, 162.6, 163.6, 164.7;

HRMS Calcd for $C_{27}H_{21}N_3O_7$ ($[M+H]^+$) 499.1380 found : 499.1382; Anal. Calcd for $C_{27}H_{21}N_3O_7$: C 64.93, H 4.24 and N 8.41%. Found: C 64.96, H 4.27 and N 8.45%.

5m. 4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(phenyl)methyl)-5-methyl-3H-pyrazol-3-one



Yield: (0.315 g, 91%)

Characteristic: White crystalline solid

Mp: 231-233 ^{0}C (from EtOH);

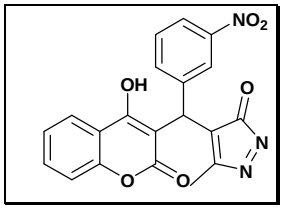
IR (KBr): 2743, 1616, 1538, 1275 1185, 1037, 750 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.23(s, 3H), 5.63 (s, 1H), 7.01-7.16(m, 6H), 7.32-7.48 (m, 2H), 7.75-7.78(d, *J*=8.1Hz, 1H);

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.6, 33.8, 105.3, 106.7, 115.8, 119.7, 123.3, 124.4, 125.8, 127.1, 128.0, 131.2, 140.7, 144.7, 152.6, 163.3, 165.8;

HRMS Calcd for $C_{20}H_{14}N_2O_4$ ($[M+H]^+$) 346.0954 found : 346.0957; Anal. Calcd for $C_{20}H_{14}N_2O_4$: C 69.36, H 4.07 and N 8.09%. Found: C 69.40, H 4.10and N 8.13%.

5n. 4-((4-hydroxy-2-oxo-2H-chromen-3-yl) (3-nitrophenyl) methyl)-5-methyl-3H-pyrazol-3-one



Yield: (0.352 g, 90%)

Characteristic: Pale yellow crystalline solid

Mp: 207-209 ^{0}C (from EtOH);

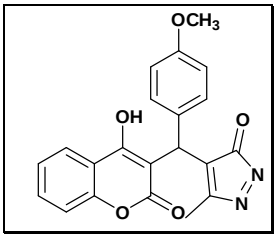
IR (KBr): 3083, 1613, 1527, 1347, 1186, 1038, 758cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.26(s, 3H), 5.66 (s, 1H), 7.07-7.91(m, 8H);

δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.5, 33.8, 104.4, 105.8, 115.9, 119.9, 121.0, 121.9, 123.35, 124.5, 129.1, 131.4, 133.8, 143.7, 144.5, 148.2, 152.7, 165.5, 167.2;

HRMS Calcd for $C_{20}H_{13}N_3O_6$ ($[M+H]^+$) 391.0804 found : 391.0807; Anal. Calcd for $C_{20}H_{13}N_3O_6$: C 61.38, H 3.35 and N 10.74%. Found: C 61.40, H 3.38 and N 10.77%.

5o. 4-((4-hydroxy-2-oxo-2H-chromen-3-yl) (4-methoxyphenyl) methyl)-5-methyl-3H-pyrazol-3-one



Yield: (0.338g, 90%)

Characteristic: White crystalline solid

Mp: 202-204^{0}C (from EtOH);

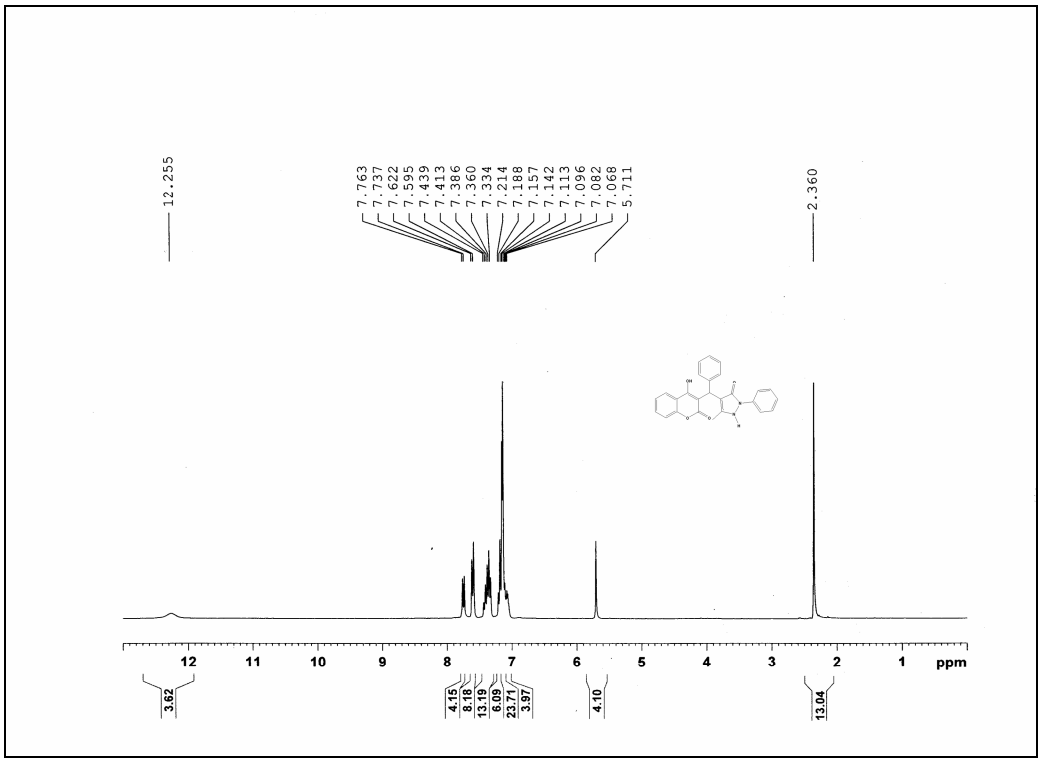
IR (KBr): 3171, 1613, 1509, 1247, 1179, 1033, 756 cm^{-1}

δ_H (300 MHz; DMSO-d_6; Me_4Si): δ 2.22(s, 3H), 3.62(s, 3H), 5.56 (s, 1H), 6.64(d, *J*=8.4Hz, 2H), 6.97-7.18(m, 4H), 7.37(t, *J*=7.3Hz, 1H) 7.73-7.75(d, *J*=7.5Hz, 1H);

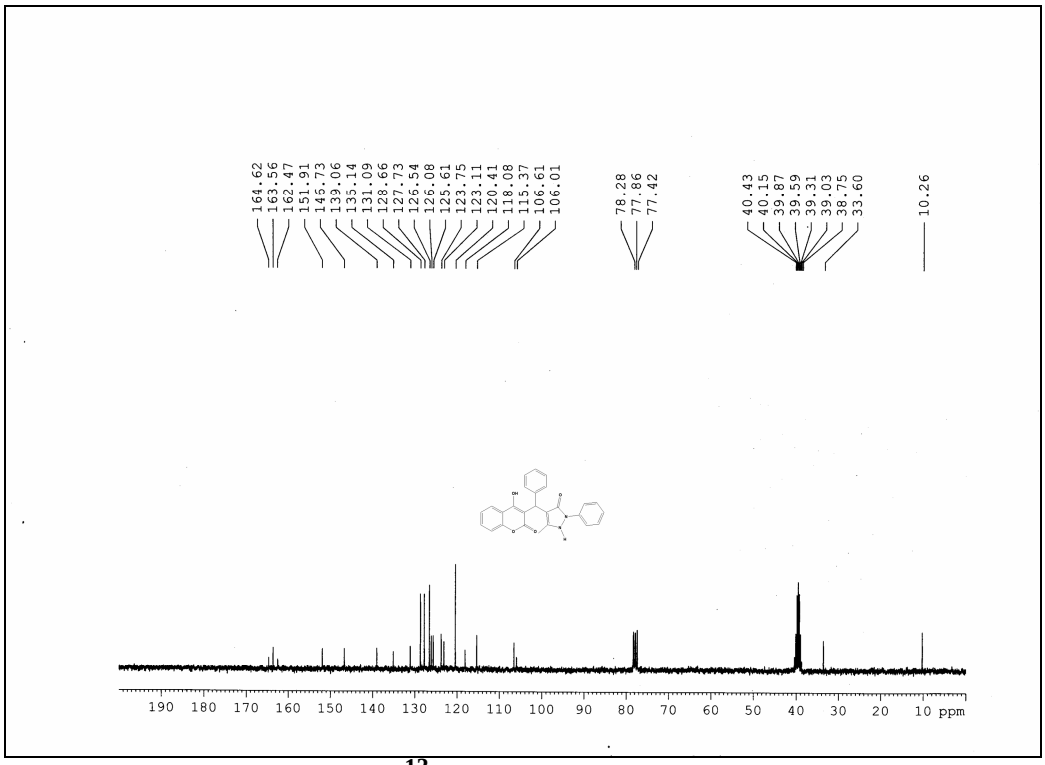
δ_C (75 MHz, DMSO-d_6; Me_4Si)): δ 10.0, 32.6, 54.7, 105.1, 106.1, 113.0, 115.3, 119.6, 122.8, 123.9, 127.6, 127.9, 130.7, 132.5, 143.8, 152.1, 157.2, 162.5, 165.0, 166.0;

HRMS Calcd for $C_{21}H_{16}N_2O_5$ ($[M+H]^+$) 376.1059 found : 376.1057; Anal. Calcd for $C_{21}H_{16}N_2O_5$: C 67.02, H 4.28 and N 7.44%. Found: C 67.04, H 4.31 and N 7.41%.

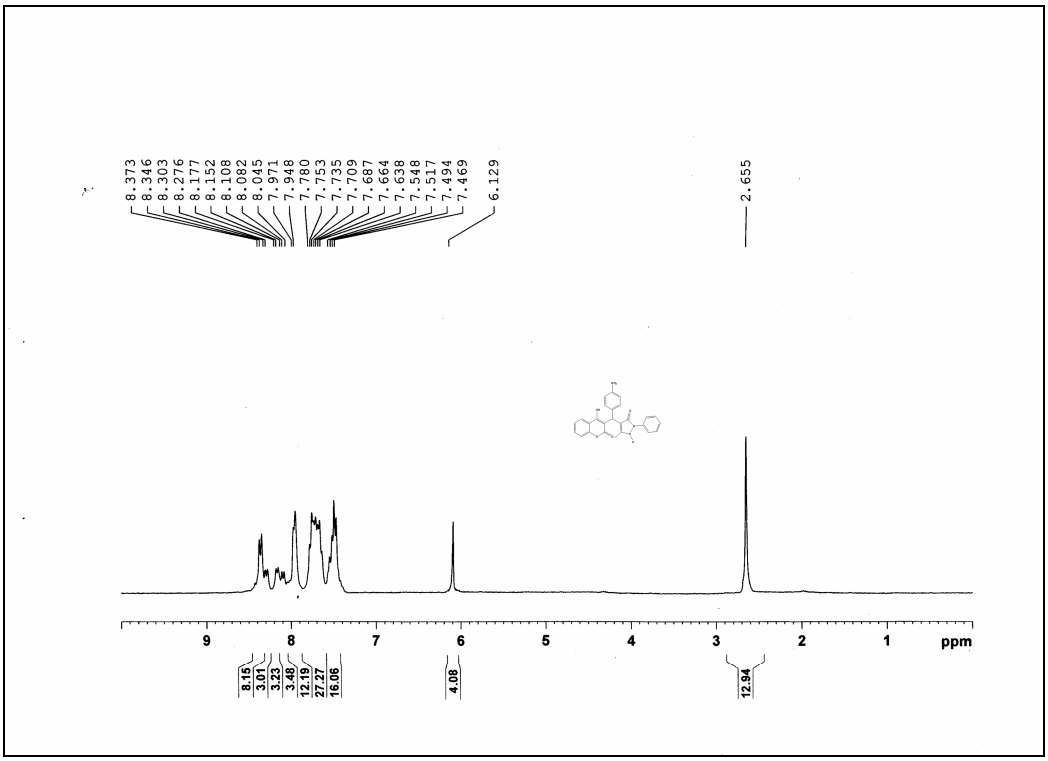
5. Spectra (^{1}H NMR and ^{13}C NMR):



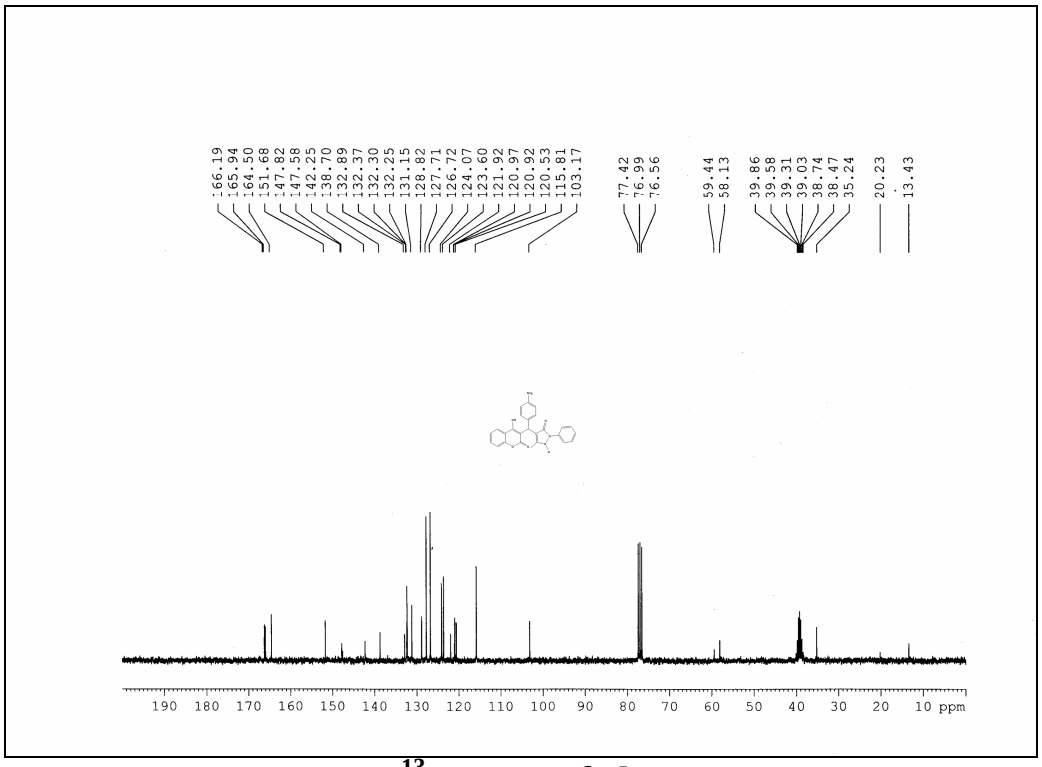
^{1}H NMR of 5a



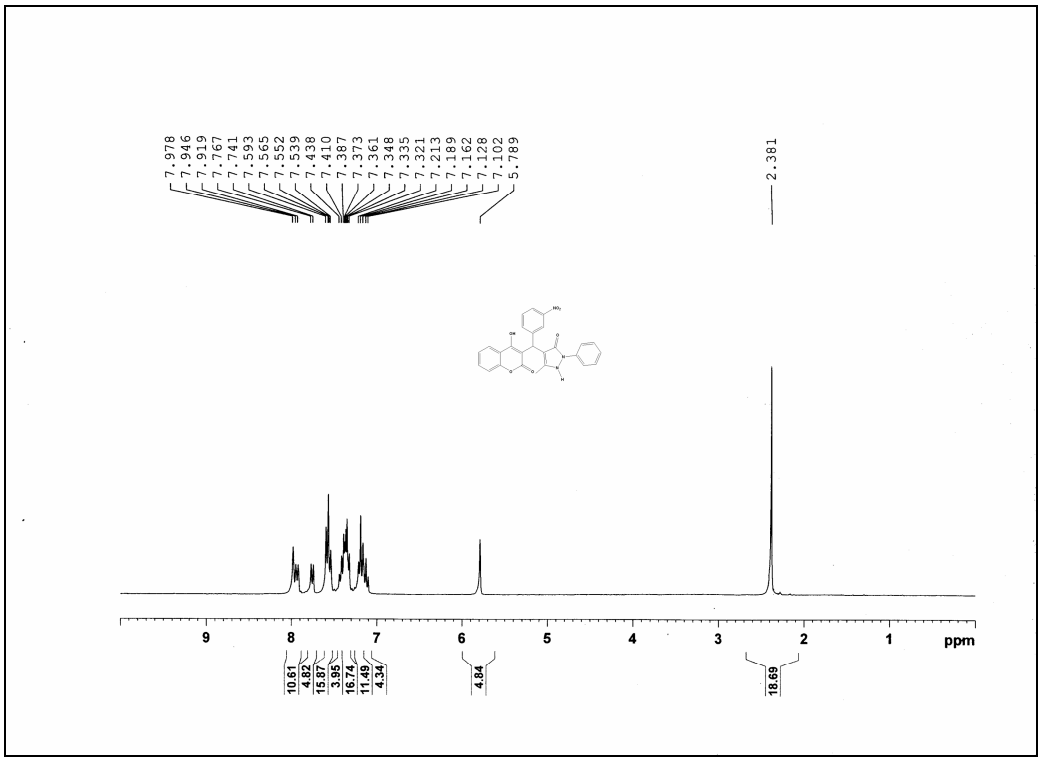
^{13}C NMR of 5a



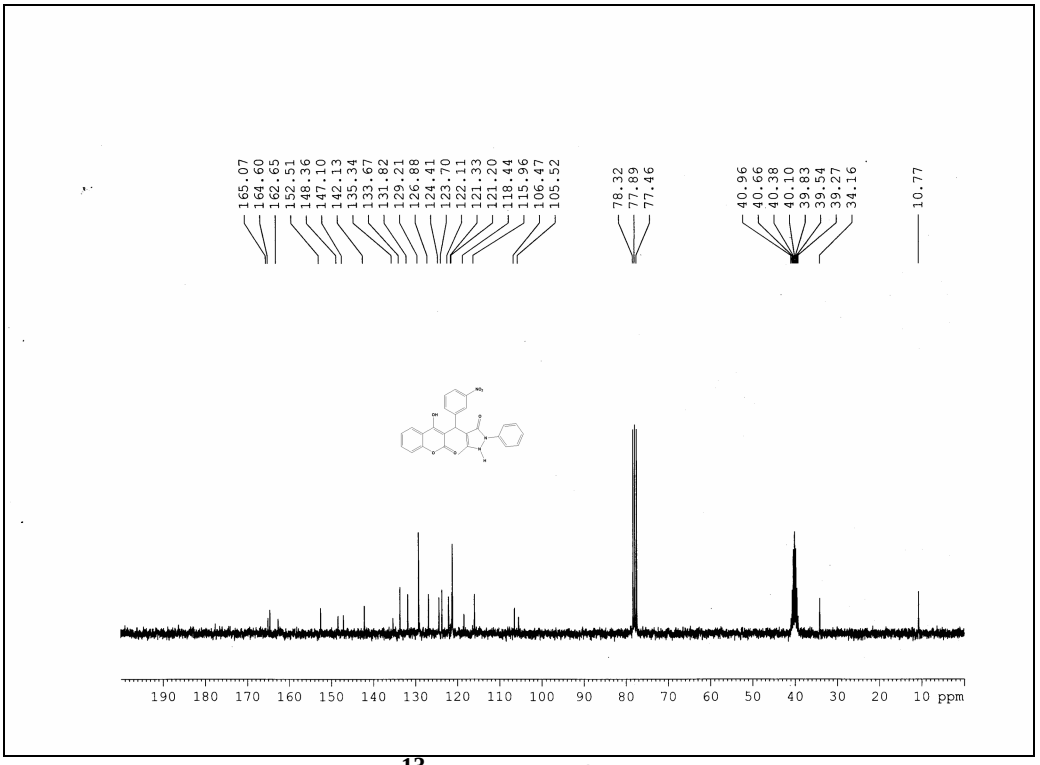
^{1}H NMR of 5b



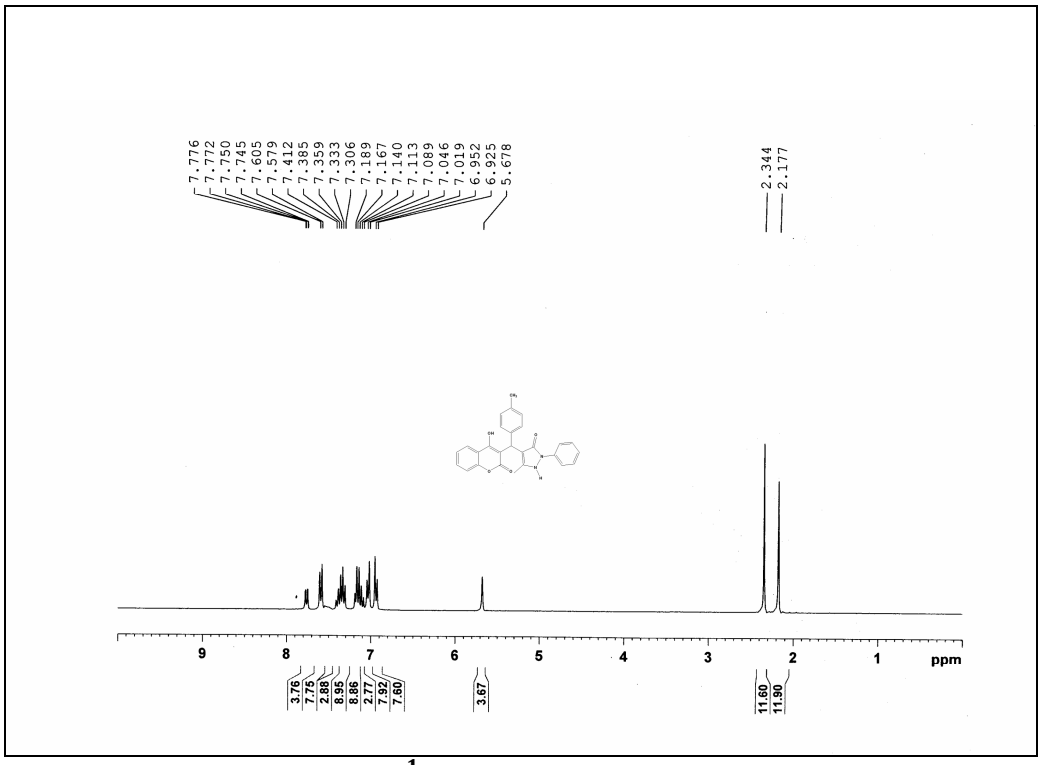
^{13}C NMR of 5b



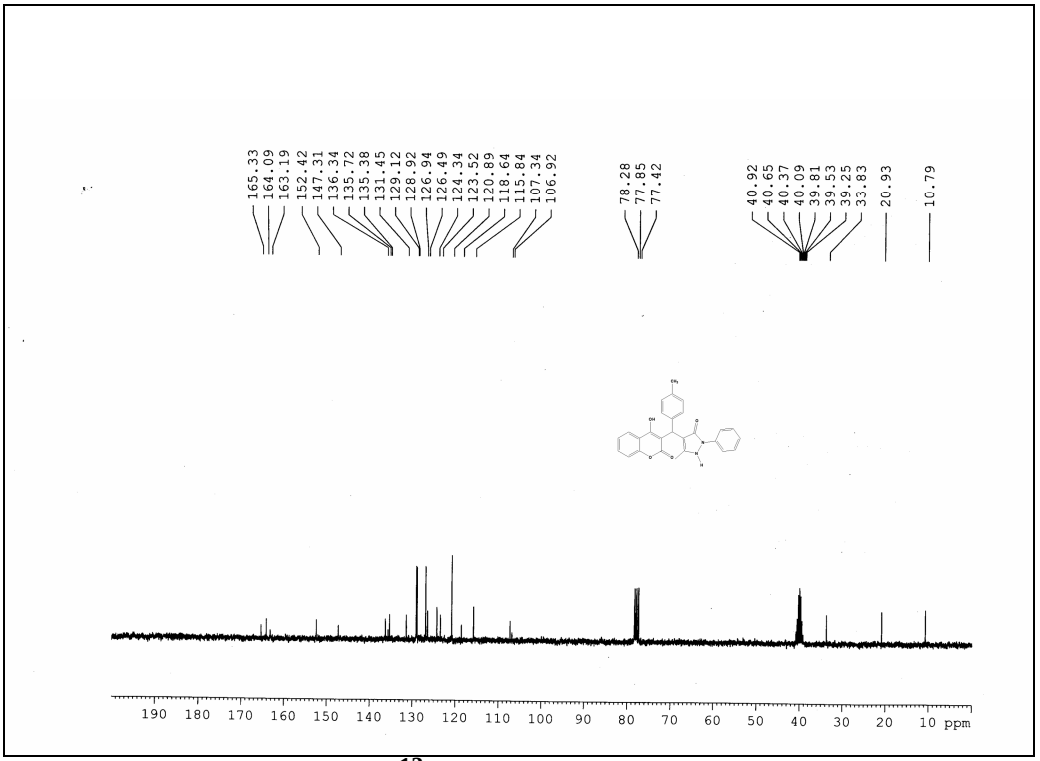
^{1}H NMR of 5c



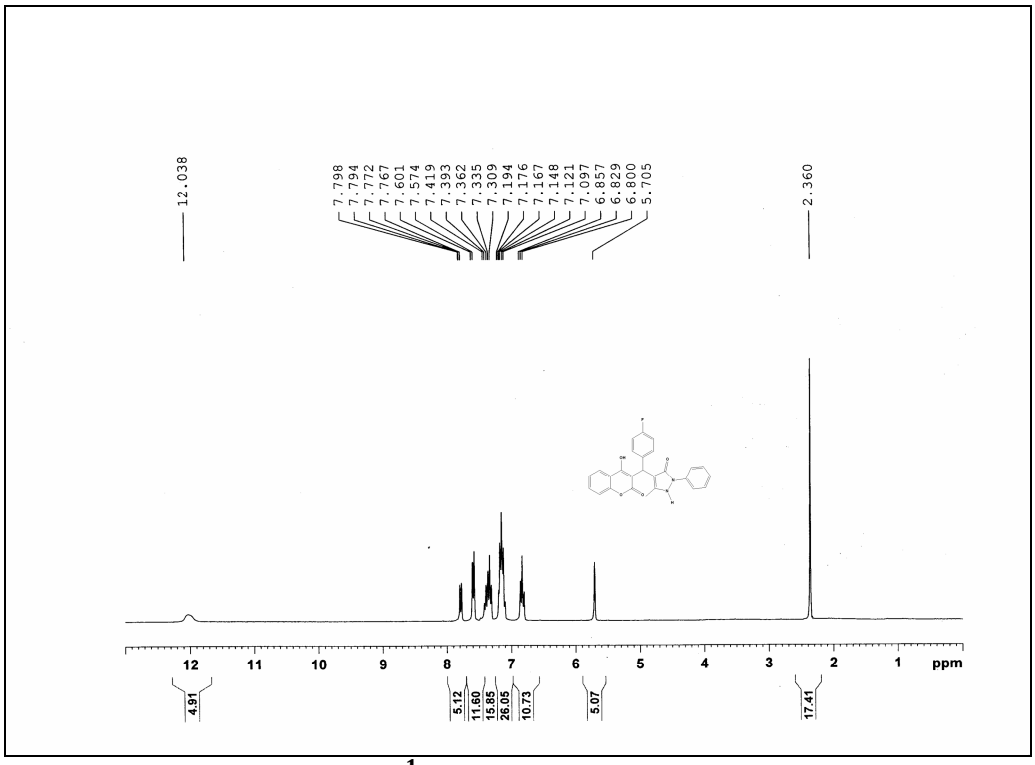
^{13}C NMR of 5c



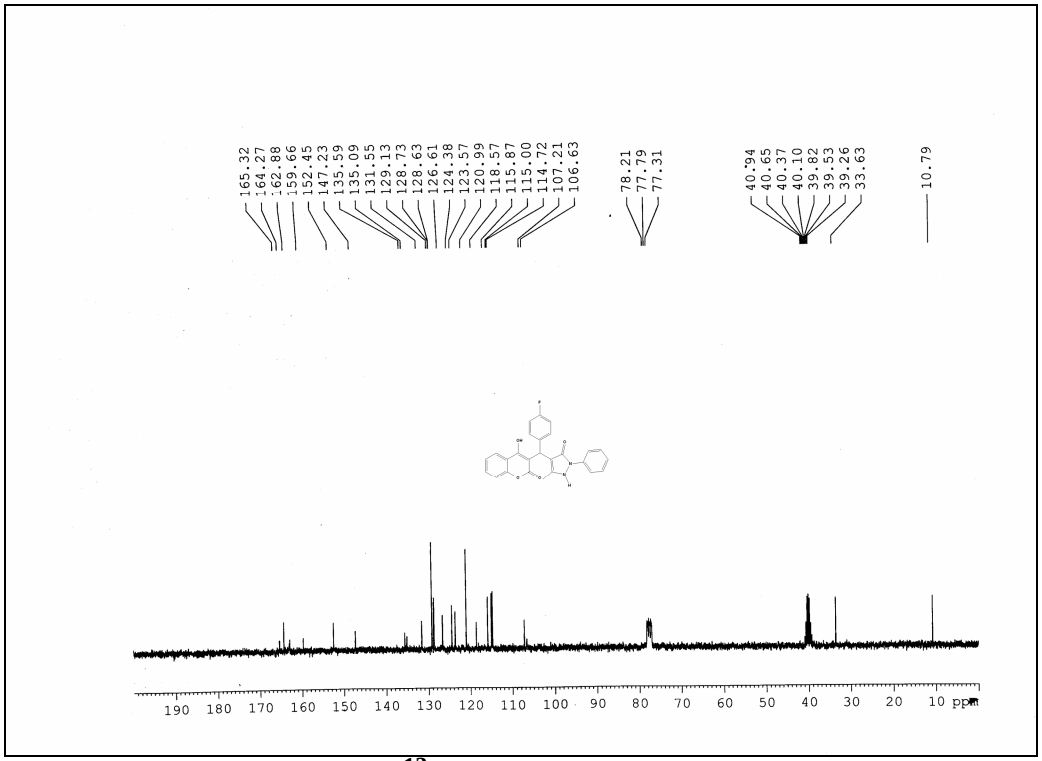
^{1}H NMR of 5d



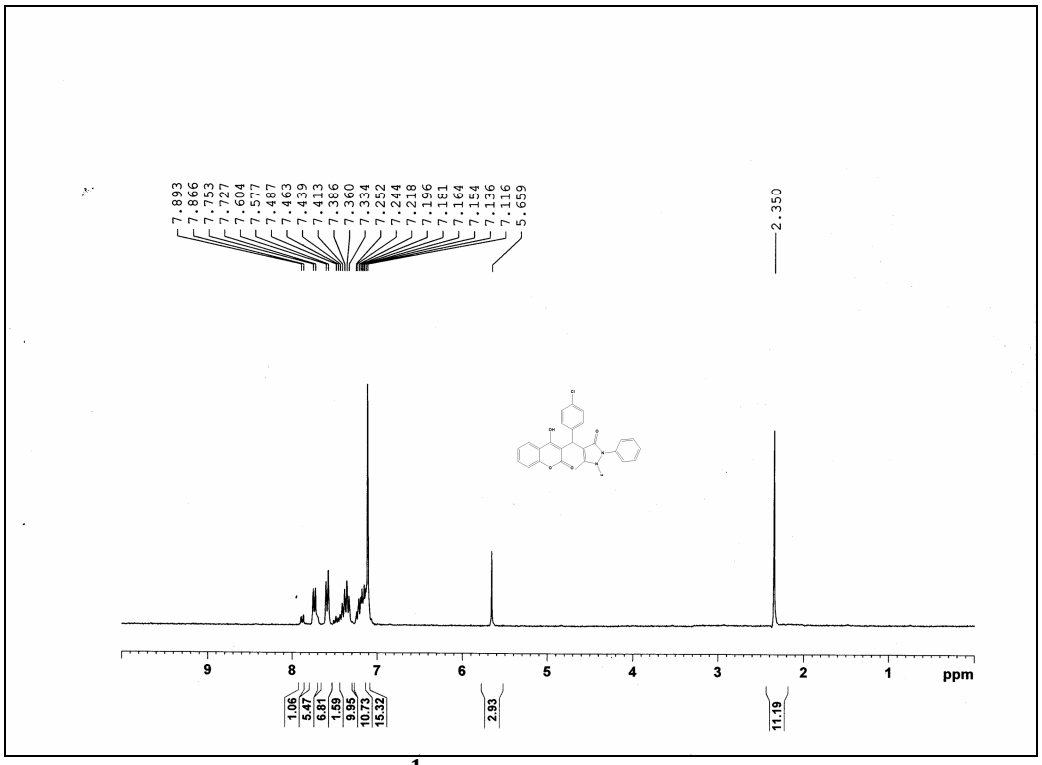
^{13}C NMR of 5d



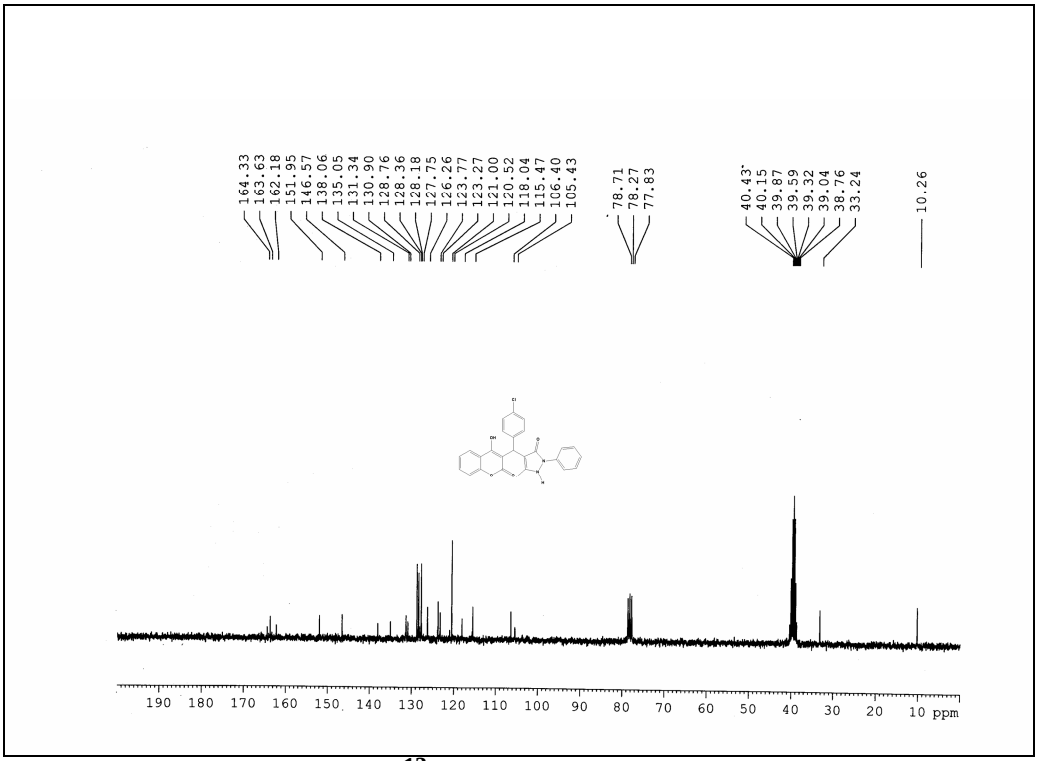
^{1}H NMR of 5e



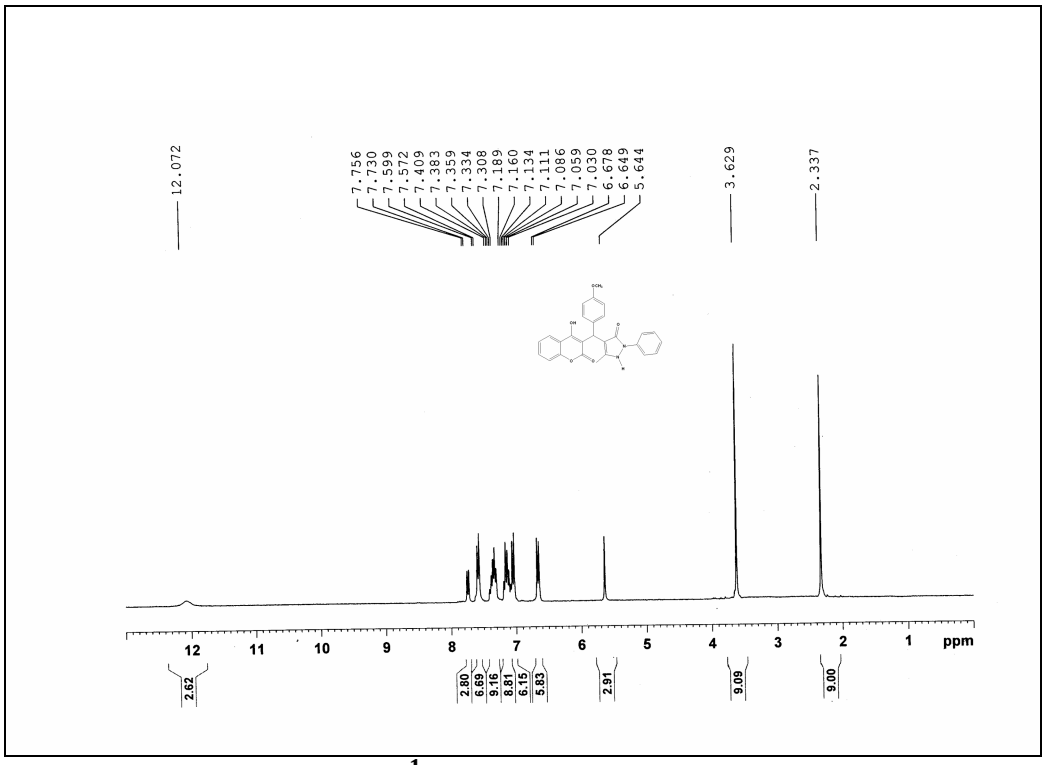
^{13}C NMR of 5e



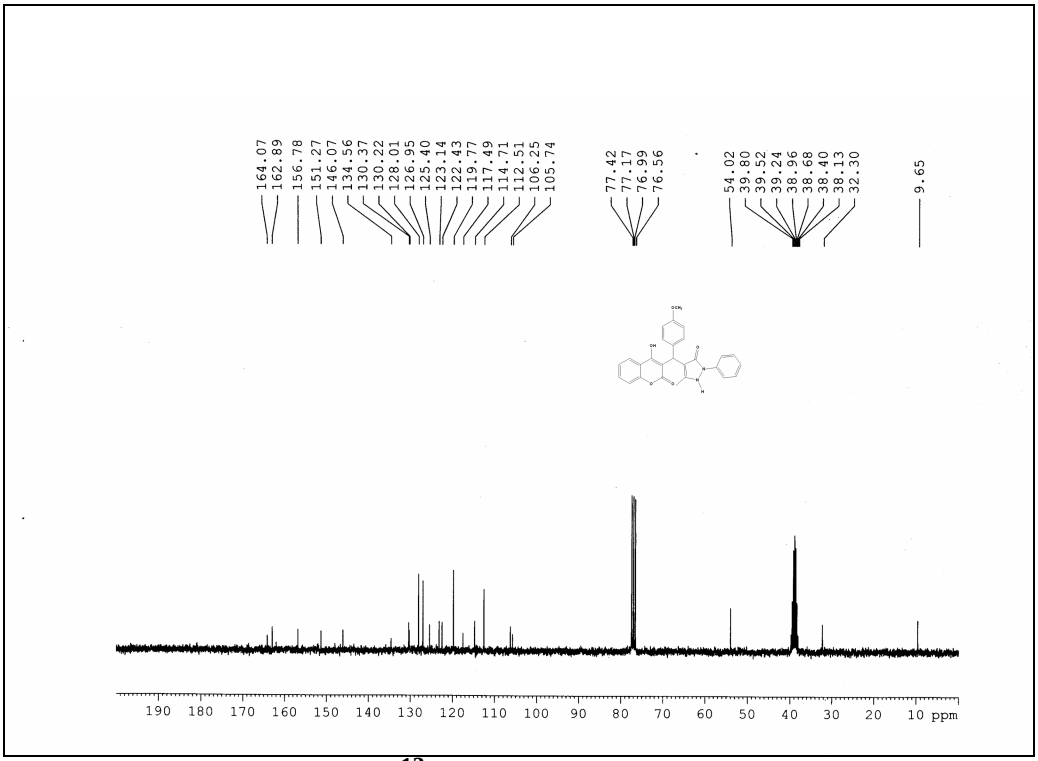
^{1}H NMR of 5f



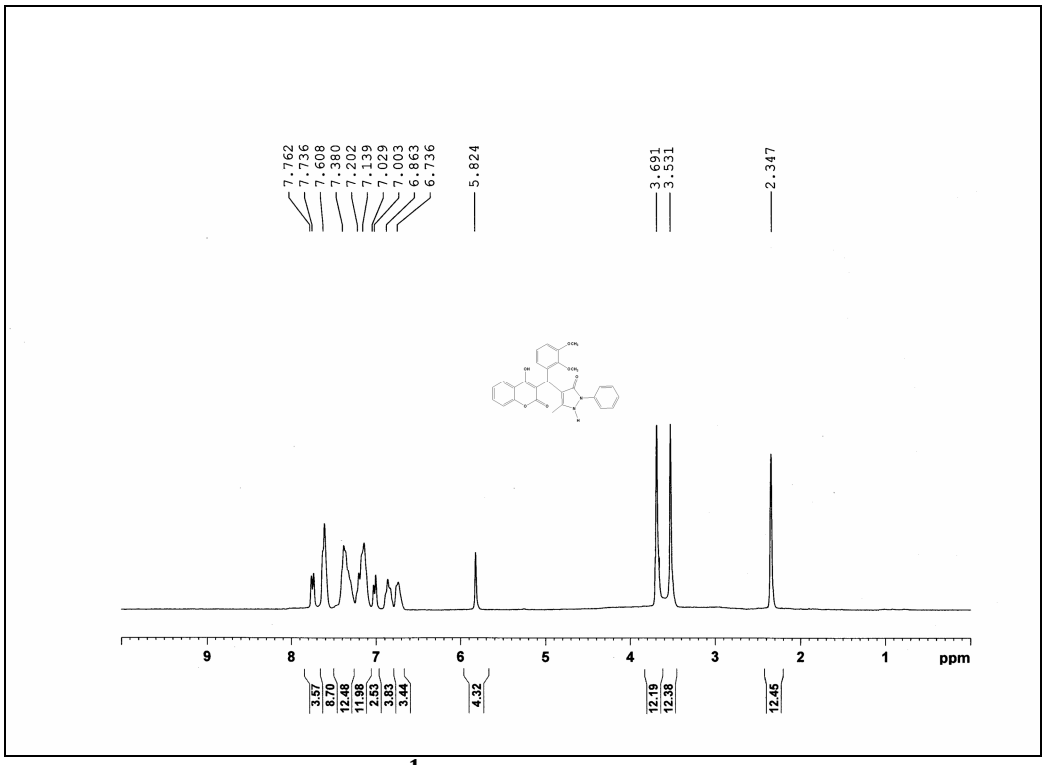
^{13}C NMR of 5f



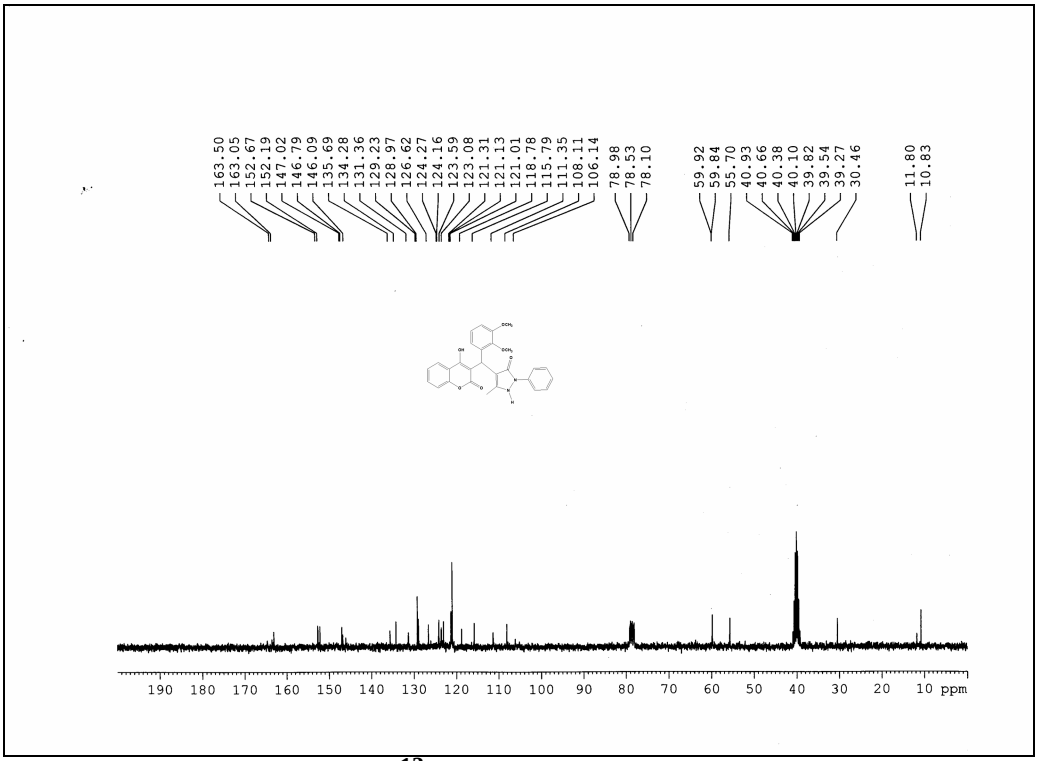
^{1}H NMR of 5g



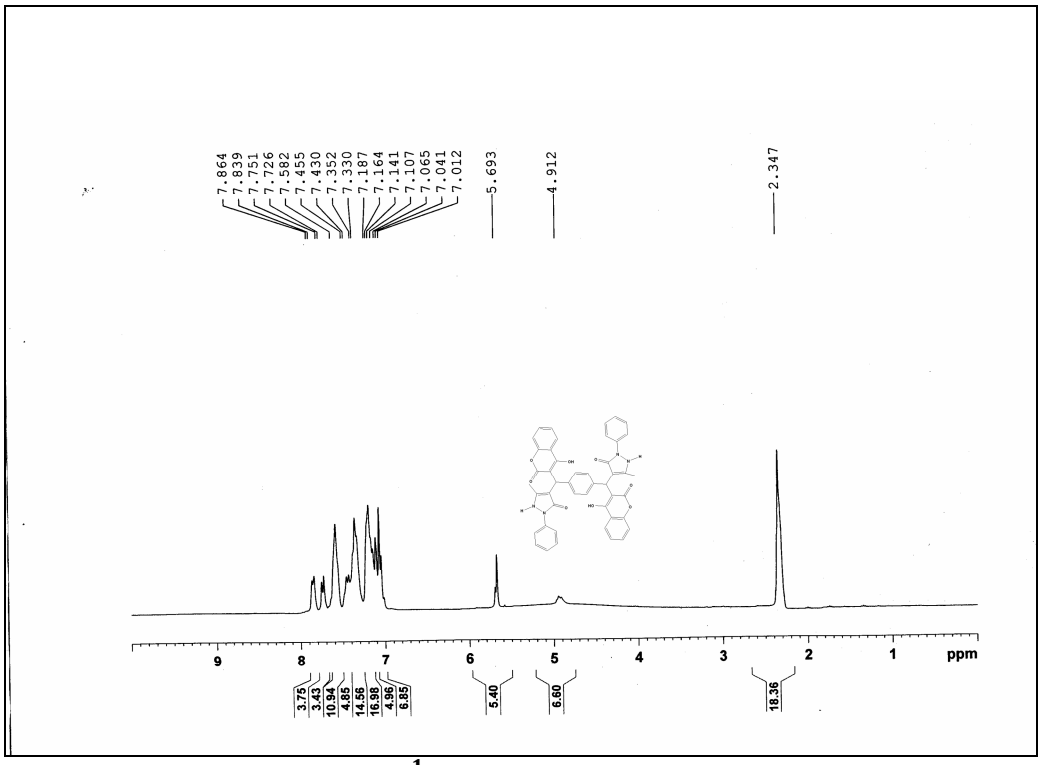
^{13}C NMR of 5g



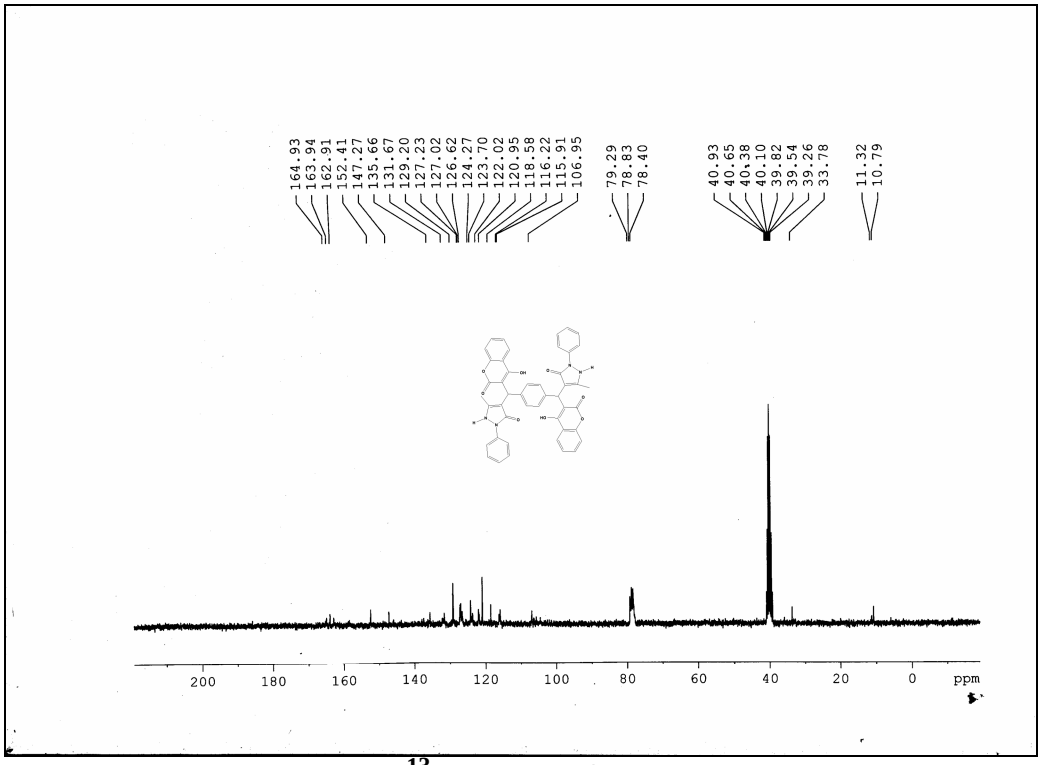
^{1}H NMR of 5h



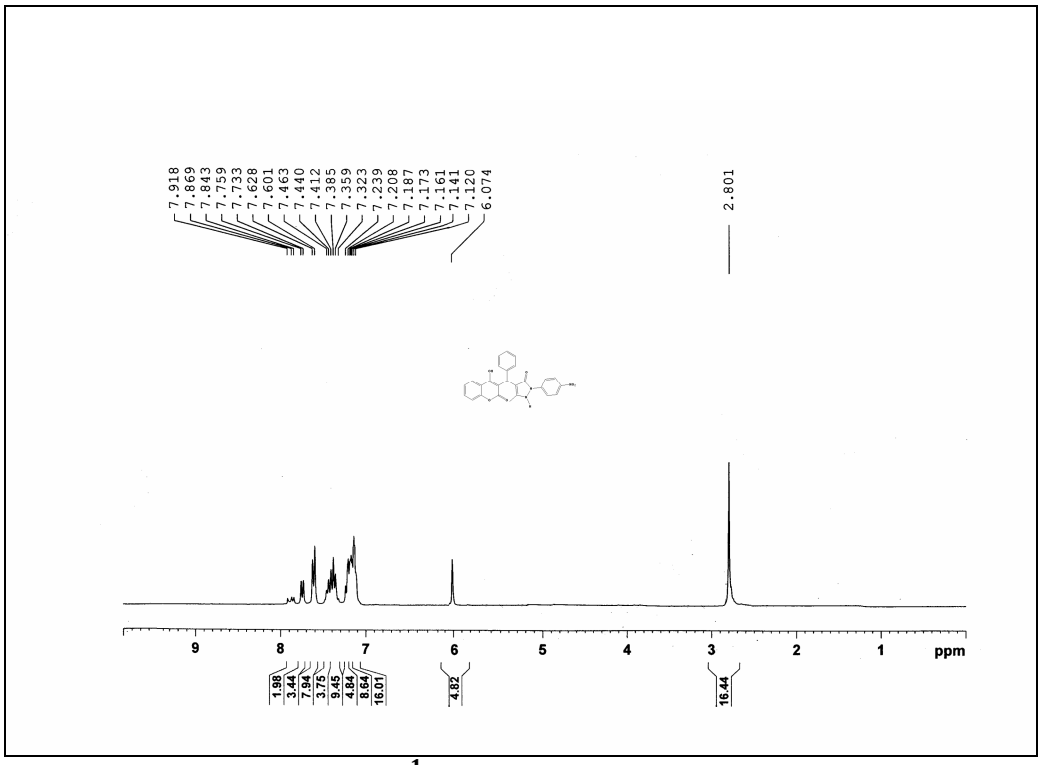
^{13}C NMR of 5h



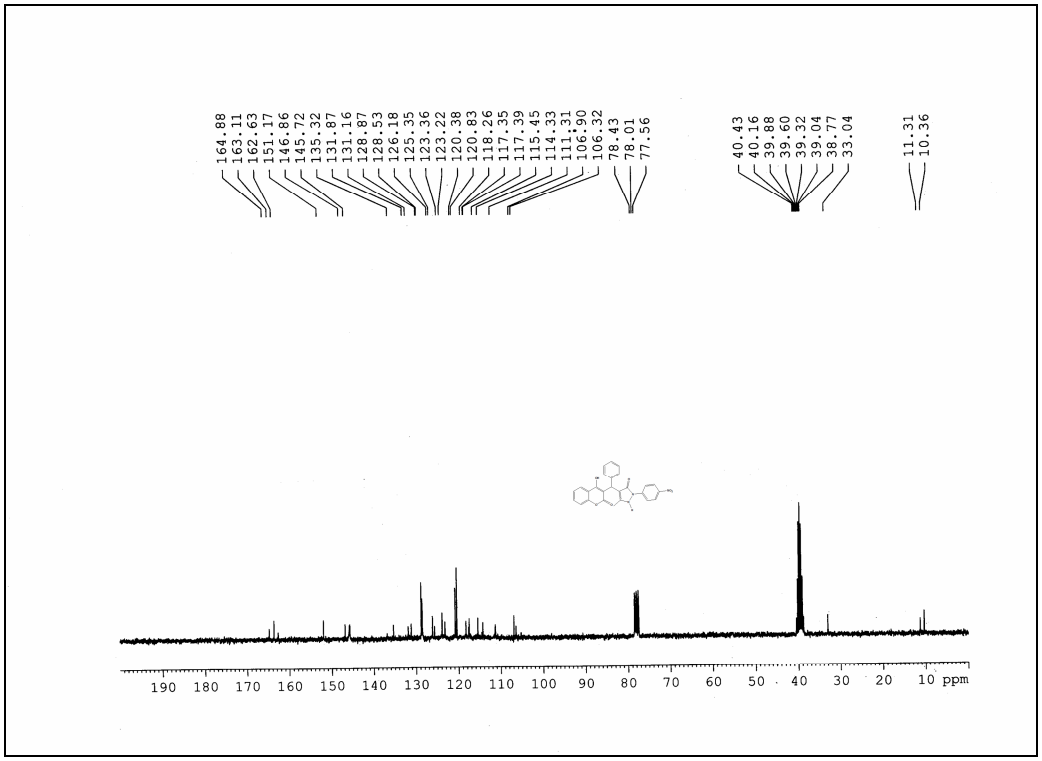
^{1}H NMR of 5i



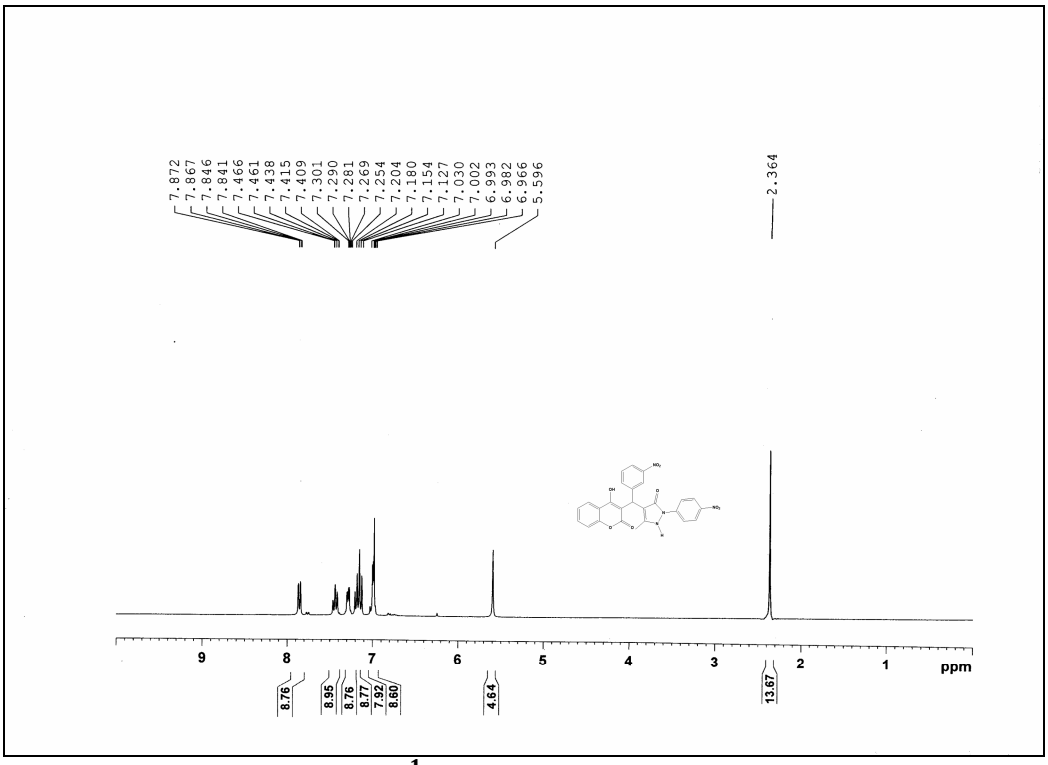
^{13}C NMR of 5i



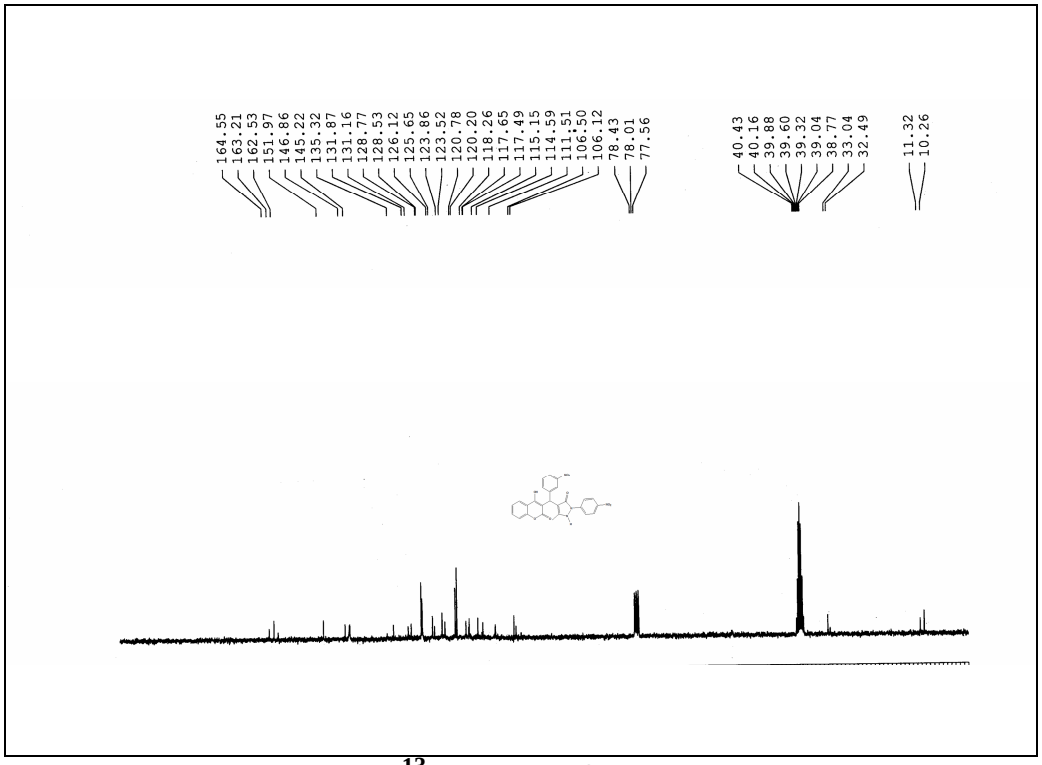
^{1}H NMR of 5j



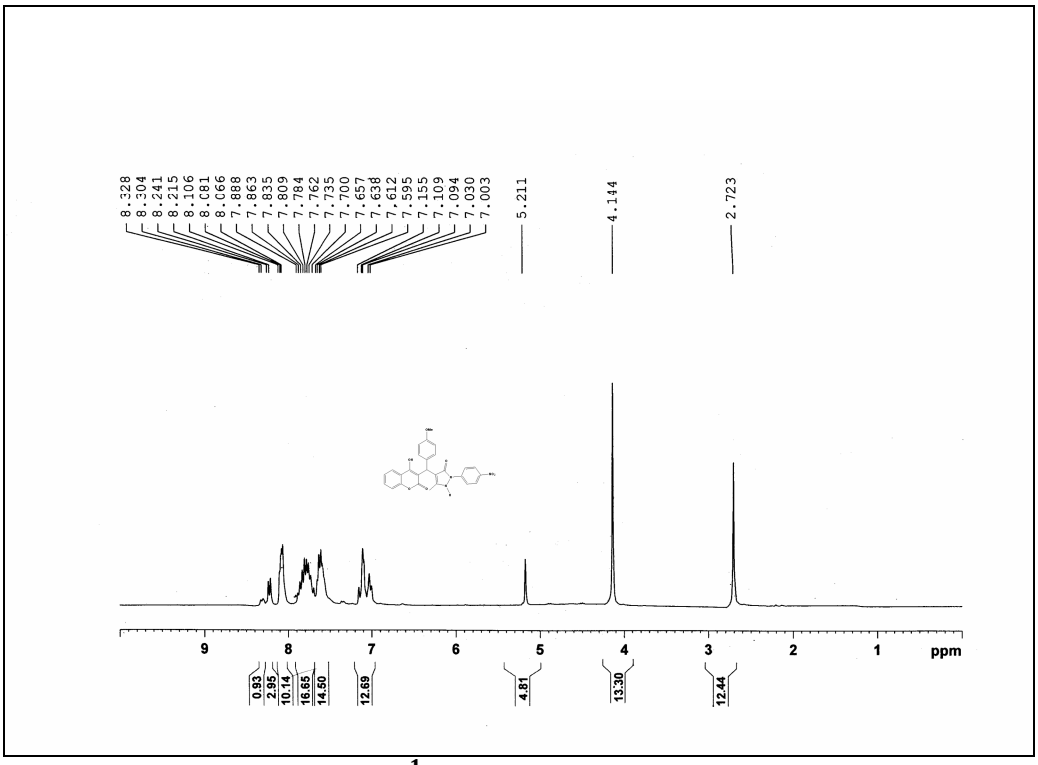
^{13}C NMR of 5j



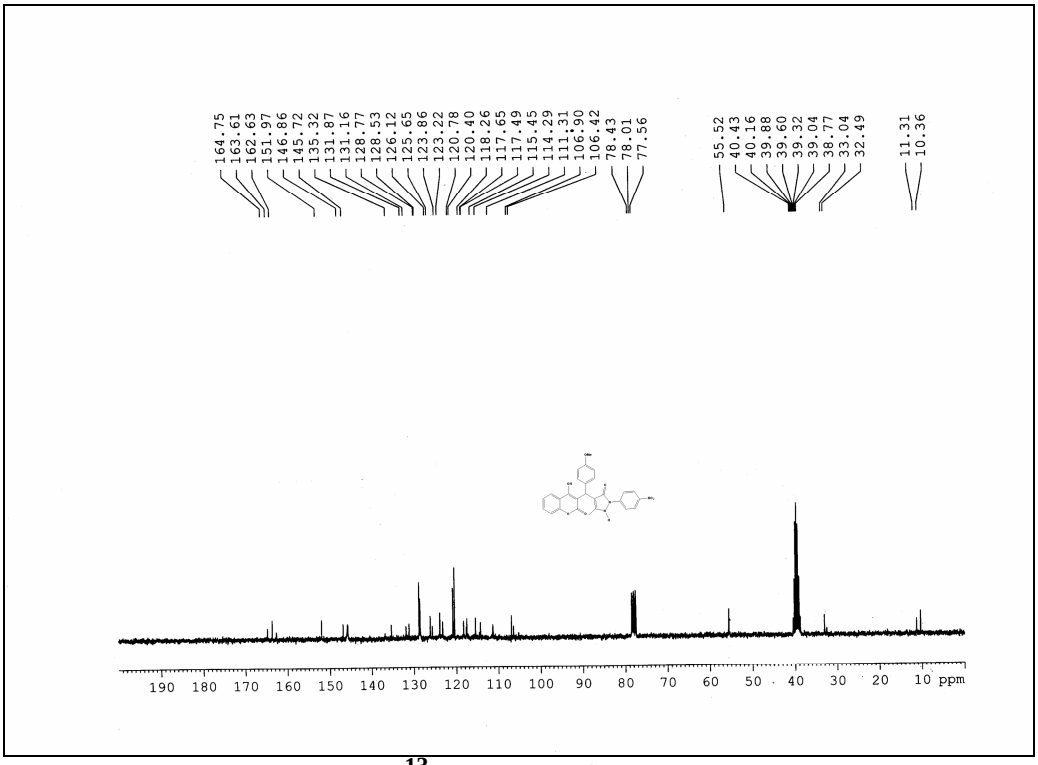
^{1}H NMR of 5k



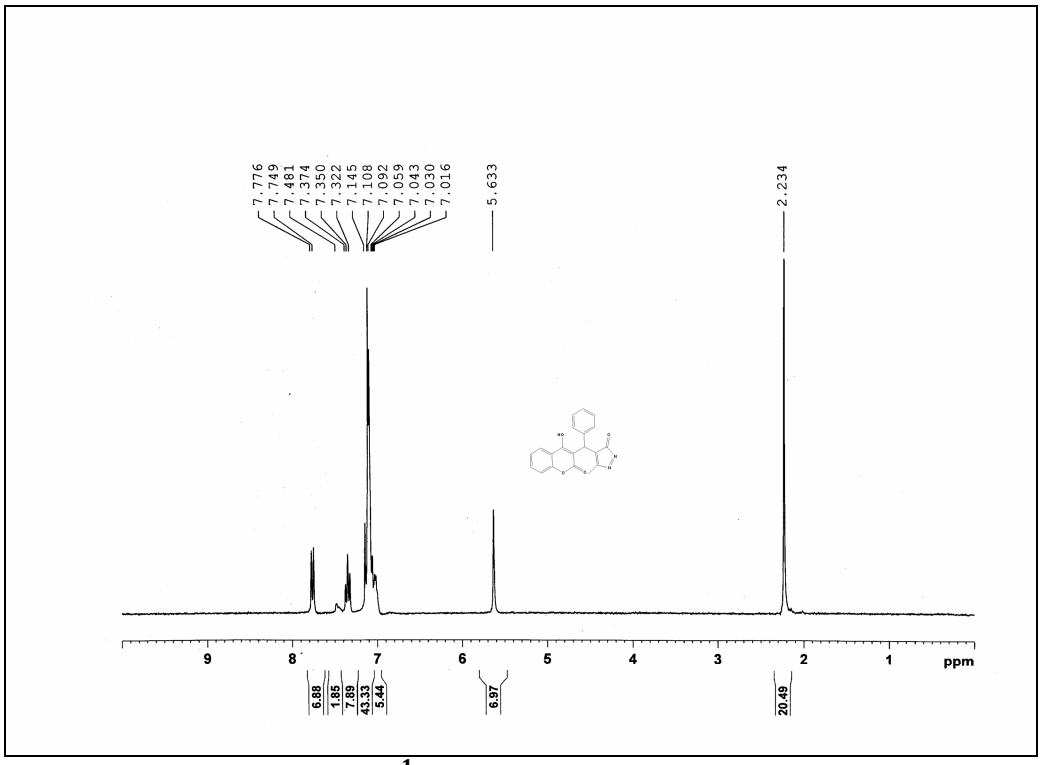
^{13}C NMR of 5k



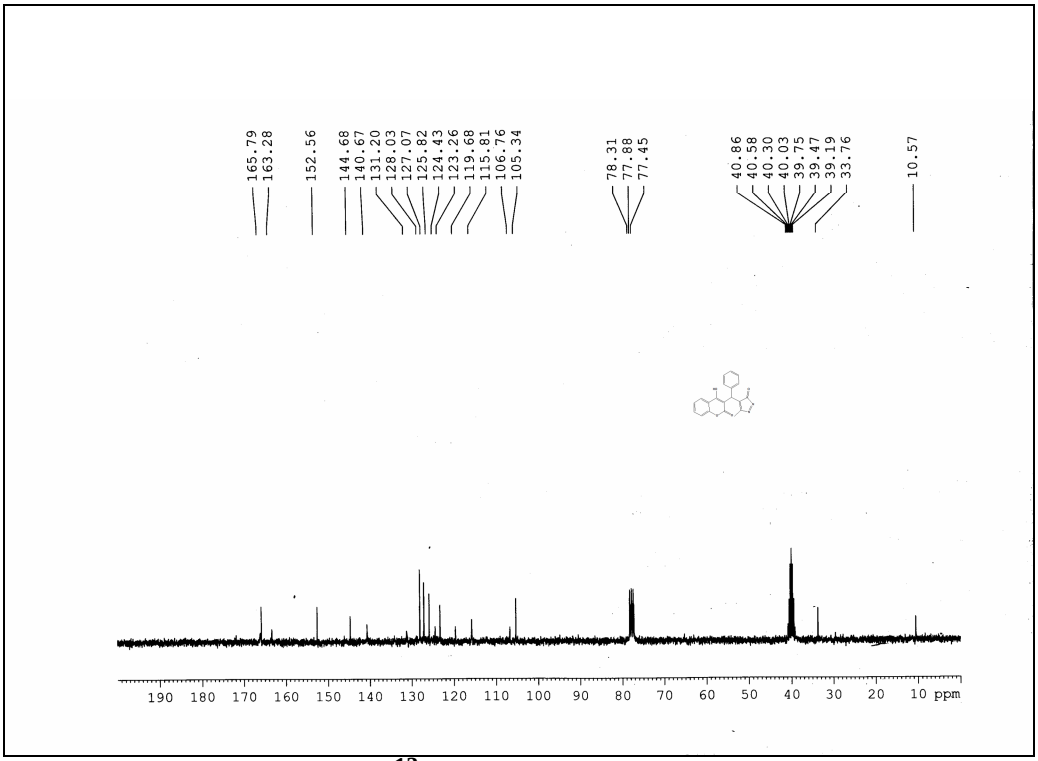
^{1}H NMR of 5l



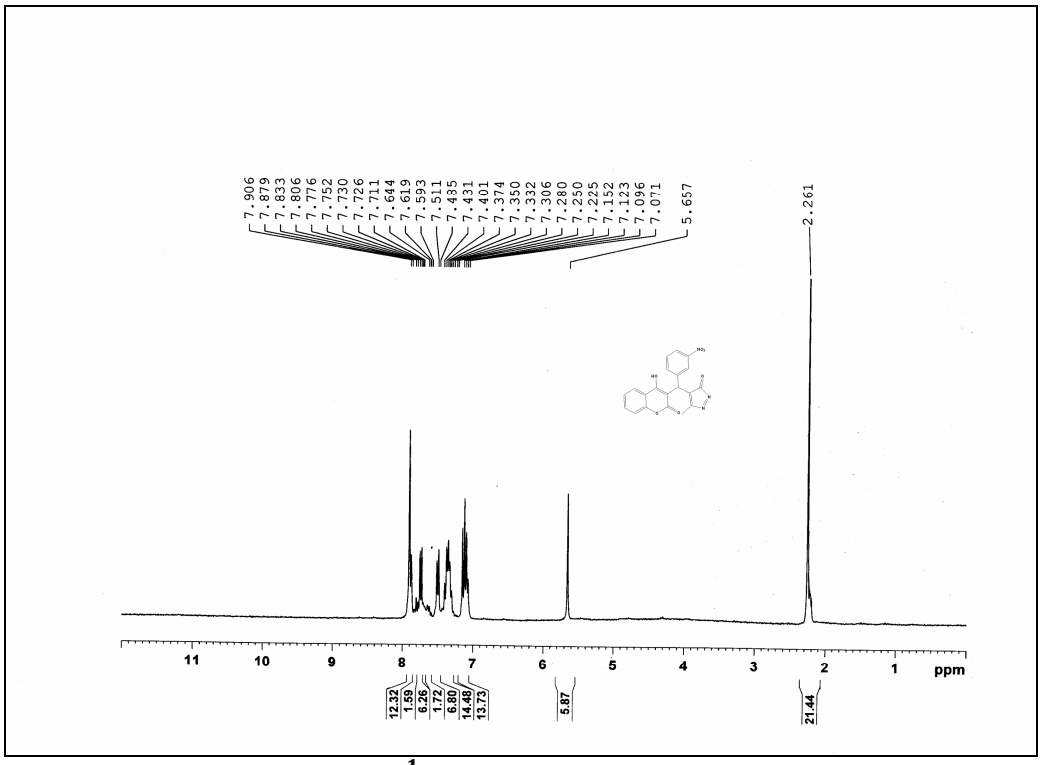
^{13}C NMR of 5l



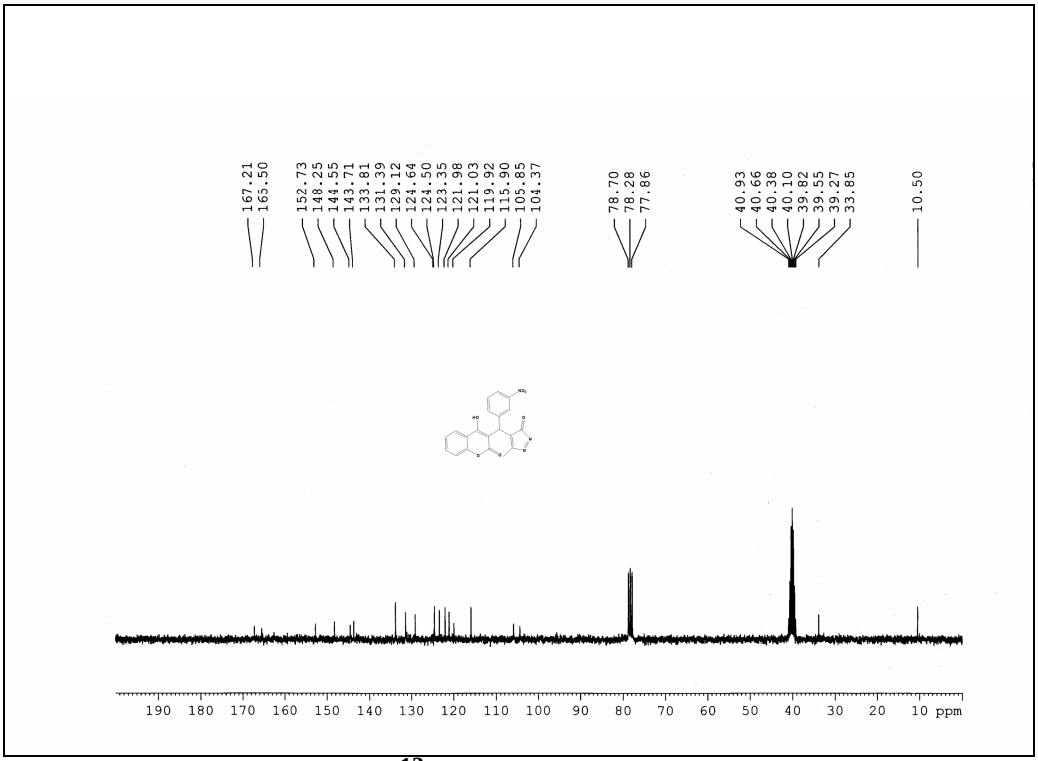
^{1}H NMR of 5m



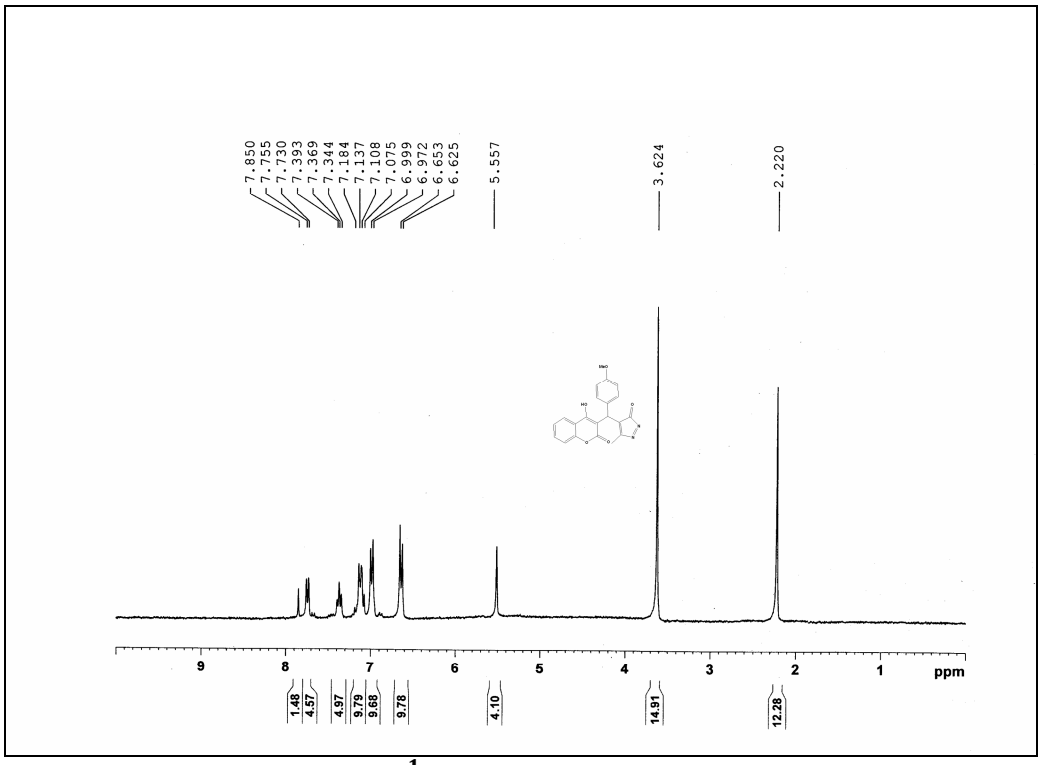
^{13}C NMR of 5m



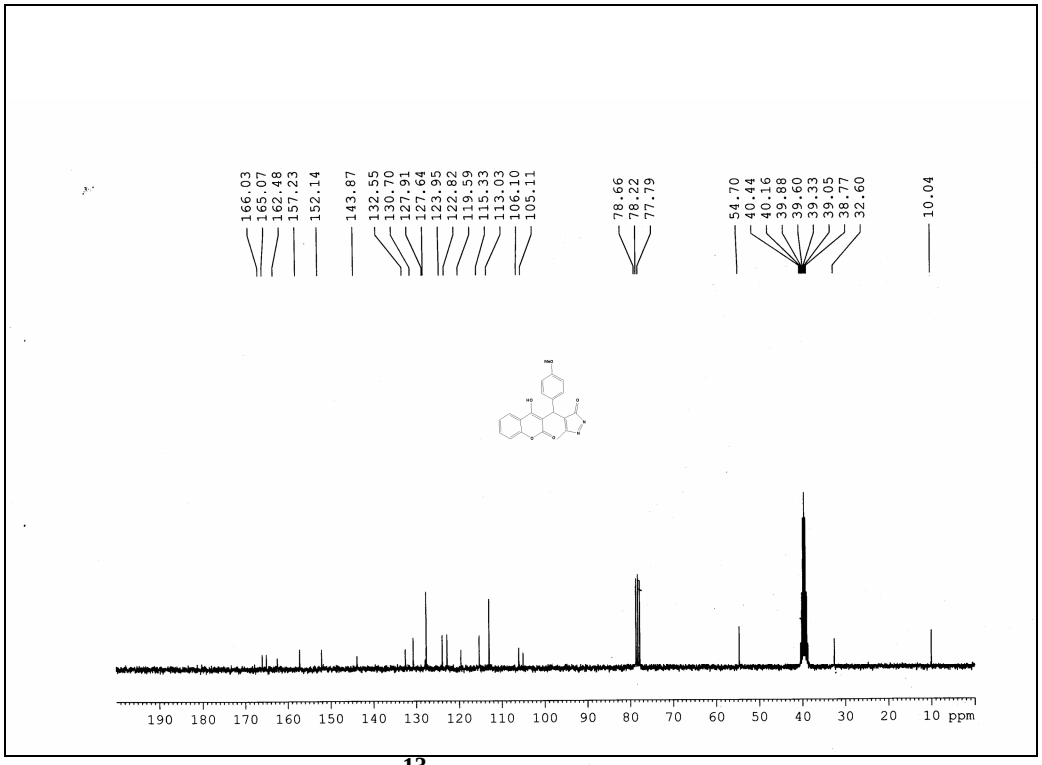
^{1}H NMR of 5n



^{13}C NMR of 5n



^{1}H NMR of 5o



^{13}C NMR of 5o