

Expeditious synthesis of functionalized tricyclic 4-spiro pyrano[2,3-c]pyrazoles in aqueous medium using dodecylbenzenesulphonic acid as a Brønsted acid-surfactant-combined catalyst

Prasun Mukherjee, Sanjay Paul, Asish R. Das*

§Department of Chemistry, University of Calcutta, Kolkata-700009, India.

*Corresponding author. Tel.: +913323501014, +919433120265; fax: +913323519754;

E-mail address: ardchem@caluniv.ac.in, ardas66@rediffmail.com (A R Das)

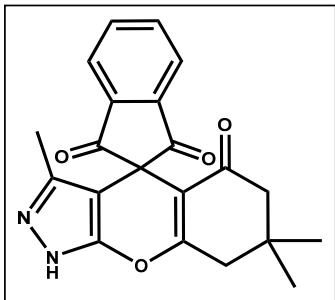
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Materials and Method

^1H -NMR and ^{13}C -NMR spectral analysis were carried out on Bruker-Advance Digital 300 MHz and 75 MHz instruments where 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. High Resolution Mass Spectra were obtained using a QTOFMICRO YA263 mass spectrometer. Suitable single crystals of compound 6a, 6f, 6i, 7h and 8c were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator. All the reactions were monitored by thin layer chromatography carried out on Merck aluminum-blocked silica gel plates coated with silica gel G under UV light and also by exposure to iodine vapour for detection. Melting points were recorded on a Köfler Block apparatus and are uncorrected. Synthetic grade chemicals from Sigma-Aldrich, Spectrochem and E-Merck were used for carrying out the organic reactions. For column chromatography Spectrochem 100-200 mesh silica gel was used. All the organic solvents, used in the reaction, were distilled and dried over Na_2SO_4 .

6a. 3,7,7-trimethyl-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,2'-indene]-1',3',5(6H)-trione



Yield: 96%

Characteristics: pale yellow solid

Mp: >300°C

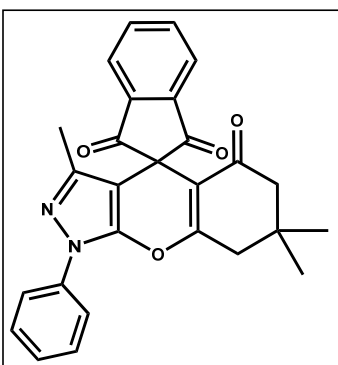
IR (KBr) : 3225, 1750, 1720, 1615, 1594, 1492, 1370, 1342, 1262, 1238, 1223, 1063, 775, 764, 657, 554 cm^{-1} ;

δ_{H} (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 0.96 (s, 6H), 1.30 (s, 3H), 2.11 (s, 2H), 2.62 (s, 2H), 7.91-7.96 (m, 4H), 12.32 (s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 10.4, 27.6, 32.8, 41.3, 49.6, 53.4, 94.8, 110.7, 123.5, 135.3, 136.9, 141.5, 155.6, 170.0, 197.0, 199.0;

Anal. Calcd for C $_{21}$ H $_{18}$ N $_2$ O $_4$: C 69.60, H 5.01, and N 7.73% Found: C 69.62, H 5.03, and N 7.72%.

6b. 3,7,7-trimethyl-1-phenyl-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,2'-indene]-1',3',5(6H)-trione



Yield: 87%

Characteristics: off white solid

Mp: 220-222°C

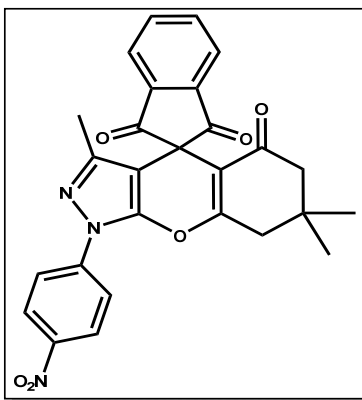
IR (KBr) : 2960, 1748, 1718, 1652, 1600, 1521, 1360, 1325, 1265, 1210, 1040, 764, 662, 550 cm^{-1} ;

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): δ 1.17(s, 6H), 1.57(s, 3H), 2.29(s, 2H), 2.71(s, 2H), 7.30-7.48(m, 3H), 7.64-7.67(d, $J=8.1$, 2H), 7.91-7.94(m, 2H), 8.06-8.09(m, 2H);

δ_{C} (75 MHz; CDCl_3 ; Me_4Si): δ 13.3, 27.7, 32.4, 41.4, 49.7, 121.0, 123.0, 126.6, 128.8, 135.4, 137.1, 141.5, 144.0, 167.4, 196.3, 198.6;

Anal. Calcd for $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_4$: C 73.96, H 5.06 and N 6.39%. Found: C 73.98, H 5.08 and N 6.40%.

6c. 3,7,7-trimethyl-1-(4-nitrophenyl)-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,2'-indene]-1',3',5(6H)-trione



Yield: 82%

Characteristics: yellow solid

Mp: 262-264°C

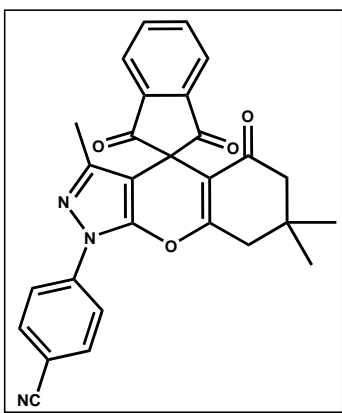
IR (KBr) : 2962, 1716, 1652, 1598, 1520, 1347, 1337, 1324, 1262, 1115, 1054, 858. 772, 666,548 cm^{-1} ;

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): δ 1.16 (s, 6H), 1.55 (s, 3H), 2.27 (s, 2H), 2.73 (s, 2H), 7.89-7.92 (m, 4H), 8.03-8.06 (m, 2H), 8.28-8.31(d, $J=8.3$, 2H);

δ_C (75 MHz; $CDCl_3$; Me_4Si): δ 13.3, 27.6, 32.4, 41.3, 49.6, 53.2, 97.1, 112.0, 119.6, 119.7, 123.0, 124.6, 135.5, 141.4, 142.0, 145.0, 145.9, 146.0, 161.2, 167.0, 196.1, 198.1;

Anal. Calcd for $C_{27}H_{21}N_3O_6$: C 67.08, H 4.38 and N 8.69%. Found: C 67.06, H 4.40 and N 8.67%.

6d. 4-(3,7,7-trimethyl-1',3',5-trioxo-1',3',5,6,7,8-hexahydro-1H-spiro[chromeno[2,3-c]pyrazole-4,2'-inden]-1-yl)benzotrile



Yield: 86%

Characteristics: pale yellow solid

Mp: 214-216°C

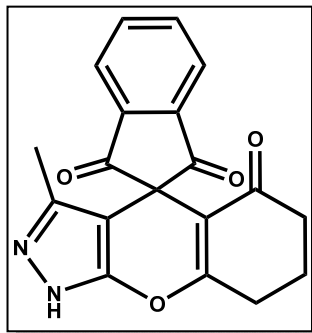
IR (KBr) : 2959, 2227, 1746, 1717, 1652, 1605, 1523, 1359, 1322, 1261, 1201, 1037, 764, 664, 545 cm^{-1} ;

δ_H (300 MHz; $DMSO-d_6$; Me_4Si): δ 1.07 (s, 6H), 1.43 (s, 3H), 2.27 (s, 2H), 2.87 (s, 2H), 7.96-7.97 (d, $J=2.7$, 4H), 8.08 (s, 4H);

δ_C (75 MHz; $DMSO-d_6$; Me_4Si): δ 13.7, 14.5, 21.2, 27.6, 33.0, 49.6, 53.6, 60.2, 97.0, 109.5, 111.6, 118.8, 120.9, 123.7, 134.3, 137.2, 140.6, 141.5, 145.5, 146.2, 168.7, 197.3, 198.6;

Anal. Calcd for $C_{28}H_{21}N_3O_4$: C 72.56, H 4.57 and N 9.07%. Found: C 72.54, H 4.58 and N 9.05%.

6e. 3-methyl-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,2'-indene]-1',3',5(6H)-trione



Yield: 95%

Characteristics: pale yellow solid

Mp: >300°C

IR (KBr) : 3254, 1716, 1608, 1588, 1491, 1375, 1356, 1335, 1326, 1264, 1237, 1220, 1202, 776, 756, 655, 537 cm^{-1} ;

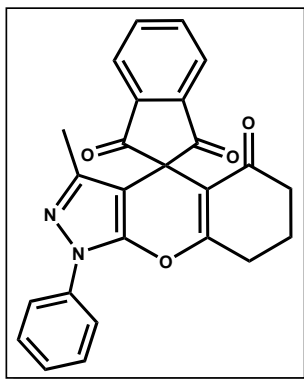
δ_{H} (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.39 (s, 6H), 1.96-2.00 (t, $J=5.9$, 2H), 2.29-2.33 (t, $J=6.0$, 2H), 2.80-2.84 (t, $J=5.55$, 2H), 8.03-8.04 (d, $J=2.4$, 4H), 12.44 (s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 10.5, 20.6, 28.1, 36.1, 53.5, 94.8, 111.8, 123.6, 135.3, 137.0, 141.5, 155.5, 172.0, 197.2, 199.1;

HRMS (ESI-TOF) m/z Calculated for $[\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_4+\text{H}]^+$: 335.1026, found: 335.1028.

Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_4$: C 68.26, H 4.22 and N 8.38%. Found: C 68.28, H 4.20 and N 8.36%.

6f. 3-methyl-1-phenyl-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,2'-indene]-1',3',5(6H)-trione



Yield: 88%

Characteristics: off white solid

Mp: 252-254°C

IR (KBr) : 2961, 1746, 1719, 1654, 1598, 1522, 1360, 1325, 1265, 1210, 1040, 764, 662, 552 cm^{-1} ;

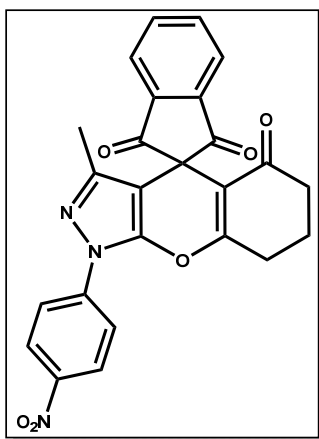
δ_{H} (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.33 (s, 6H), 1.91-1.95 (t, $J=6.2$, 2H), 2.26-2.30 (t, $J=6.45$, 2H), 2.82-2.86 (t, $J=5.9$, 2H), 7.31-7.33 (d, $J=7.5$, 1H), 7.43-7.48 (t, $J=7.8$, 2H), 7.63-7.65 (d, $J=7.8$, 2H), 8.00 (s, 4H);

δ_{C} (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 13.4, 20.3, 27.4, 35.8, 79.4, 95.9, 121.2, 123.4, 127.4, 129.8, 136.9, 137.1, 141.3, 143.8, 145.3, 170.4, 197.1, 198.6;

HRMS (ESI-TOF) m/z Calculated for $[\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}_4+\text{H}]^+$: 411.1339, found: 411.1337.

Anal. Calcd for $\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}_4$: C 73.16, H 4.42 and N 6.83%. Found: C 73.18, H 4.44 and N 6.82%.

6g. 3-methyl-1-(4-nitrophenyl)-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,2'-indene]-1',3',5(6H)-trione



Yield: 83%

Characteristics: yellow solid

Mp: >300°C

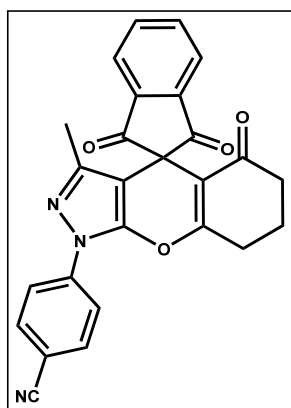
IR (KBr) : 1746, 1712, 1669, 1651, 1594, 1525, 1514, 1480, 1359, 1344, 1335, 1312, 1263, 1184, 1173, 1095, 1053, 864, 834, 762, 661 cm^{-1} ;

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): δ 1.55 (s, 3H), 2.14-2.18 (m, 2H), 2.39-2.44 (t, $J=6.60$, 2H), 2.84-2.88 (t, $J=6.30$, 2H), 7.89-7.93 (m, 4H), 8.03-8.06 (m, 2H), 8.29-8.32 (d, $J=7.2$, 2H);

δ_{C} (75 MHz; CDCl_3 ; Me_4Si): δ 13.3, 19.8, 27.7, 35.6, 113.1, 119.7, 123.0, 124.6, 135.6, 141.3, 141.9, 145.0, 145.9, 168.6, 196.0, 198.1;

Anal. Calcd for $\text{C}_{25}\text{H}_{17}\text{N}_3\text{O}_6$: C 65.93, H 3.67 and N 9.23%. Found: C 65.91, H 3.66 and N 9.21%.

6h. 4-(3-methyl-1',3',5-trioxo-1',3',5,6,7,8-hexahydro-1H-spiro[chromeno[2,3-c]pyrazole-4,2'-inden]-1-yl)benzotrile



Yield: 87%

Characteristics: off white solid

Mp: 250-252°C

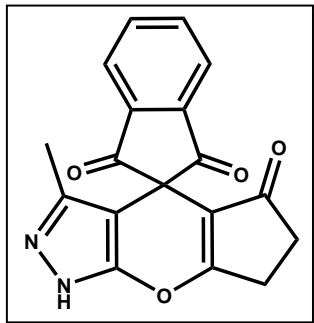
IR (KBr) : 2952, 2233, 1712, 1669, 1651, 1603, 1518, 1350, 1322, 1261, 1201, 1037, 764, 664, 545 cm^{-1} ;

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): δ 1.56 (s, 3H), 2.14-2.21(m, 2H), 2.41-2.45 (t, $J=6.60$, 2H), 2.85-2.89 (t, $J=6.15$, 2H), 7.72-7.87 (m, 4H), 7.90-7.96 (m, 2H), 8.04-8.09 (m, 2H);

δ_{C} (75 MHz; CDCl_3 ; Me_4Si): δ 13.8, 20.3, 28.1, 36.1, 53.8, 97.2, 109.9, 113.5, 118.3, 120.5, 123.4, 133.4, 136.0, 140.9, 141.8, 146.0, 146.2, 169.1, 196.5, 198.6;

Anal. Calcd for $\text{C}_{26}\text{H}_{17}\text{N}_3\text{O}_4$: C 71.72, H 3.94 and N 9.65%. Found: C 71.73, H 3.95 and N 9.64%.

6i. 3-methyl-6,7-dihydro-1H,5H-spiro[cyclopenta[5,6]pyrano[2,3-c]pyrazole-4,2'-indene]-1',3',5-trione



Yield: 94%

Characteristics: white solid

Mp: >300°C

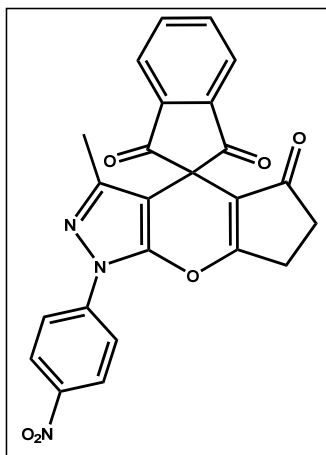
IR (KBr) : 3316, 2947, 1750, 1722, 1705, 1696, 1635, 1486, 1440, 1351, 1315, 1266, 1229, 1035, 773, 765, 660, 560 cm^{-1} ;

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): δ 1.60 (s, 3H), 2.44-2.46 (m, 2H), 2.86-2.89 (m, 2H), 7.86-7.89 (m, 2H), 7.99-8.02 (m, 2H);

δ_{C} (75 MHz; DMSO-d_6 ; Me_4Si): δ 4.6, 20.5, 27.4, 46.1, 73.5, 89.1, 108.9, 118.1, 130.2, 131.9, 136.0, 152.0, 177.8, 192.7, 195.7;

Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_4$: C 67.50, H 3.78 and N 8.75%. Found: C 67.52, H 3.76 and N 8.74%.

6j. 3-methyl-1-(4-nitrophenyl)-6,7-dihydro-1H,5H-spiro[cyclopenta[5,6]pyrano[2,3-c]pyrazole-4,2'-indene]-1',3',5-trione



Yield: 78%

Characteristics: yellow solid

Mp: >300°C

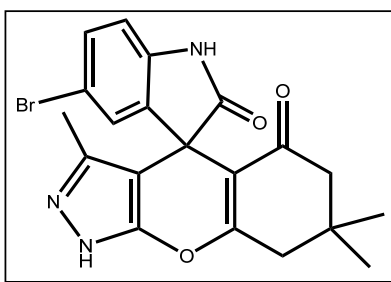
IR (KBr) : 1746, 1712, 1669, 1651, 1594, 1525, 1514, 1480, 1359, 1344, 1335, 1312, 1263, 1184, 1173, 1095, 1053, 864, 834, 762, 661, 561 cm^{-1} ;

δ_{H} (300 MHz; CDCl_3 ; Me_4Si): δ 1.41(s, 3H), 2.33-2.38 (m, 2H), 2.80-2.82 (m, 2H), 7.73-7.88 (m, 6H), 8.09-8.12 (d, $J=9$, 2H);

δ_{C} (75 MHz; CDCl_3 ; Me_4Si): δ 13.1, 25.62, 33.4, 120.1, 123.0, 123.3, 124.7, 136.4, 141.5, 141.8, 145.2, 146.1, 180.3, 197.0, 199.6;

Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{N}_3\text{O}_6$: C 65.31, H 3.43 and N 9.52%. Found: C 65.32, H 3.42 and N 9.51%.

7a. 5'-bromo-3,7,7-trimethyl-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,3'-indoline]-2',5(6H)-dione



Yield: 93%

Characteristics: white solid

Mp: >300°C

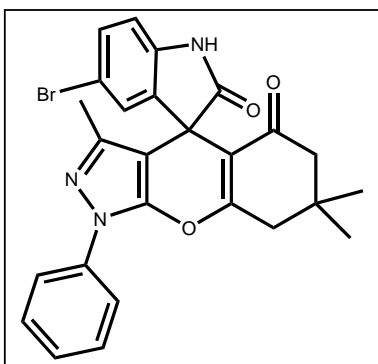
IR (KBr) : 3316,3240, 2918, 1722, 1650, 1610, 1600, 1520, 1473, 1346, 1209, 1175, 1115, 1030, 821, 772, 710, 685, 520 cm^{-1} ;

δ_{H} (300 MHz; DMSO- d_6 ; Me_4Si): δ 1.07 (s, 6H), 1.66 (s, 3H), 2.21-2.26 (d, $J=16.20$ Hz, 2H), 2.63-2.78 (dd, $J_1=26.55$ Hz, $J_2=17.25$ Hz, 2H), 6.83-6.86 (d, $J=8.1$, 1H), 6.99-7.00 (d, $J=1.8$, 1H), 7.32-7.35 (d, $J=8.10$, 1H), 10.67 (s, 1H), 12.37 (s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me_4Si): δ 9.3, 27.5, 27.8, 32.2, 46.7, 50.6, 97.2, 110.7, 111.3, 113.6, 125.8, 130.8, 135.4, 137.6, 141.6, 155.2, 168.1, 177.8, 196.0;

Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{BrN}_3\text{O}_3$: C 56.09, H 4.24 and N 9.81%. Found: C 56.11, H 4.22 and N 9.79%.

7b. 5'-bromo-3,7,7-trimethyl-1-phenyl-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,3'-indoline]-2',5(6H)-dione



Yield: 86%

Characteristics: off white solid

Mp: 272-274°C

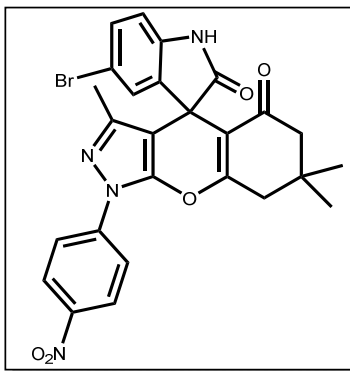
IR (KBr) : 3230, 2920, 1719, 1648, 1610, 1600, 1520, 1473, 1346, 1209, 1178, 1117, 1030, 821, 772, 713, 686, 522 cm^{-1} ;

δ_{H} (300 MHz; DMSO- d_6 ; Me_4Si): δ 1.03 (s, 6H), 1.61 (s, 3H), 2.20 (s, 2H), 2.74 (s, 2H), 6.81-6.83 (d, $J=8.40$, 1H), 7.19 (s, 1H), 7.31-7.34 (m, 2H), 7.47-7.52 (t, $J=7.57$, 2H), 7.70-7.73 (d, $J=7.95$, 2H), 10.74 (s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me_4Si): δ 12.0, 27.4, 27.7, 32.4, 47.2, 50.6, 98.2, 111.4, 111.6, 113.7, 120.8, 126.5, 126.9, 129.7, 131.2, 136.8, 137.5, 141.7, 144.5, 145.1, 166.7, 177.5, 196.1;

Anal. Calcd for $C_{26}H_{22}BrN_3O_3$: C 61.91, H 4.40 and N 8.33%. Found: C 61.93, H 4.42 and N 8.36%.

7c. 5'-bromo-3,7,7-trimethyl-1-(4-nitrophenyl)-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,3'-indoline]-2',5(6H)-dione



Yield: 80%

Characteristics: pale yellow solid

Mp: >300°C

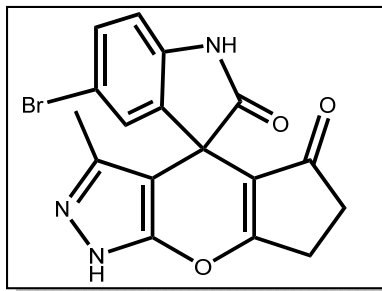
IR (KBr) : 3388, 2955, 1725, 1671, 1651, 1618, 1597, 1517, 1340, 1305, 1216, 1181, 1104, 840, 750, 471 cm^{-1} ;

δ_H (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.00 (s, 6H), 1.60 (s, 3H), 2.18 (s, 2H), 2.76 (s, 2H), 6.77-6.80 (d, $J=8.40$, 1H), 7.20 (s, 1H), 7.28-7.31 (d, $J=8.40$, 1H), 10.76 (s, 1H);

δ_C (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 11.9, 27.2, 27.5, 32.2, 46.8, 50.3, 99.3, 111.2, 111.5, 113.6, 120.1, 125.4, 126.5, 131.2, 136.2, 141.5, 142.2, 144.8, 145.8, 146.4, 166.3, 177.1, 195.9;

Anal. Calcd for $C_{26}H_{21}BrN_4O_5$: C 56.84, H 3.85 and N 10.20%. Found: C 56.86, H 3.88 and N 10.22%.

7d. 5'-bromo-3-methyl-6,7-dihydro-1H,5H-spiro[cyclopenta[5,6]pyrano[2,3-c]pyrazole-4,3'-indoline]-2',5-dione



Yield: 94%

Characteristics: white solid

Mp: >300°C

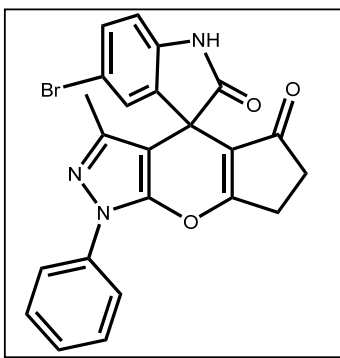
IR (KBr) : 3380,3225, 2930, 1712, 1652, 1614, 1596, 1522, 1473, 1346, 1209, 1178, 1120, 1040, 816, 772, 716, 686, 522 cm^{-1} ;

δ_{H} (300 MHz; DMSO- d_6 ; Me_4Si): δ 1.60 (s, 6H), 2.38-2.39 (d, $J=3.6$, 2H), 2.84-2.86 (m, 2H), 6.83-6.86 (d, $J=8.1$, 1H), 7.04 (s, 1H), 7.31-7.35 (d, $J=8.25$, 1H), 10.90 (s, 1H), 12.63 (s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me_4Si): δ 14.1, 19.2, 30.5, 38.3, 64.9, 116.5, 118.7, 120.0, 131.8, 136.3, 140.1, 140.9, 146.5, 181.4, 186.8, 205.7;

Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{BrN}_3\text{O}_3$: C 52.87, H 3.13 and N 10.88%. Found: C 52.89, H 3.15 and N 10.90%.

7e. 5'-bromo-3-methyl-1-phenyl-6,7-dihydro-1H,5H-spiro[cyclopenta[5,6]pyrano[2,3-c]pyrazole-4,3'-indoline]-2',5-dione



Yield: 84%

Characteristics: off white solid

Mp: 298-300°C

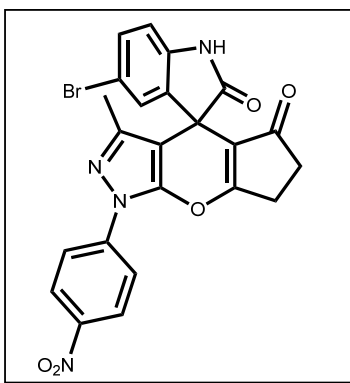
IR (KBr) : 3219, 2926, 1709, 1652, 1614, 1596, 1522, 1473, 1346, 1209, 1178, 1117, 1038, 821, 772, 713, 686, 522 cm^{-1} ;

δ_{H} (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.61(s, 3H), 2.47-2.49 (d, $J=5.40$, 2H), 2.92-2.94 (d, $J=5.7$, 2H), 6.85-6.87 (d, $J=8.10$, 1H), 7.28-7.29 (d, $J=1.8$, 1H), 7.36-7.40 (m, 2H), 7.50-7.55 (t, $J=7.95$, 2H), 7.71-7.73 (d, $J=7.80$, 2H), 10.93 (s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 12.3, 25.5, 34.4, 46.1, 98.8, 111.9, 114.3, 116.7, 121.4, 121.5, 127.5, 127.8, 130.0, 132.1, 134.8, 137.5, 141.8, 145.1, 147.5, 176.4, 180.6, 200.8;

Anal. Calcd for C $_{23}$ H $_{16}$ BrN $_3$ O $_3$: C 59.76, H 3.49 and N 9.09%. Found: C 59.78, H 3.52 and N 9.12%.

7f. 5'-bromo-3-methyl-1-(4-nitrophenyl)-6,7-dihydro-1H,5H-spiro[cyclopenta[5,6]pyrano[2,3-c]pyrazole-4,3'-indoline]-2',5-dione



Yield: 78%

Characteristics: pale yellow solid

Mp: >300°C

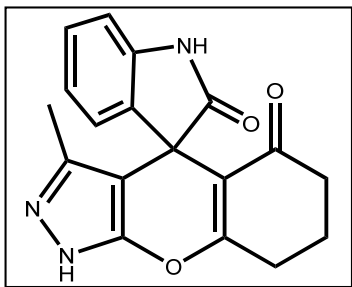
IR (KBr) : 3375, 2960, 1725, 1671, 1654, 1616, 1595, 1517, 1340, 1305, 1216, 1186, 1104, 840, 750, 471 cm^{-1} ;

δ_{H} (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.57 (s, 3H), 2.45 (s, 2H), 2.90-2.92 (d, $J=5.4$, 2H), 6.79-6.81 (d, $J=8.1$, 1H), 7.25-7.26 (d, $J=1.8$, 1H), 7.31-7.35 (d, $J=8.3$, 1H), 7.96-7.99 (d, $J=9.3$, 2H), 8.31-8.34 (d, $J=9.3$ Hz, 2H), 10.89 (s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 12.3, 25.5, 31.1, 34.5, 100.0, 112.0, 114.4, 120.9, 125.8, 127.9, 132.2, 134.4, 141.8, 142.4, 145.5, 147.1, 148.3, 176.1, 180.3, 200.7;

Anal. Calcd for C₂₃H₁₅BrN₄O₅: C 54.46, H 2.98 and N 11.04%. Found: C 54.48, H 3.00 and N 11.06%.

7g. 3-methyl-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,3'-indoline]-2',5(6H)-dione



Yield: 94%

Characteristics: white solid

Mp: >300°C

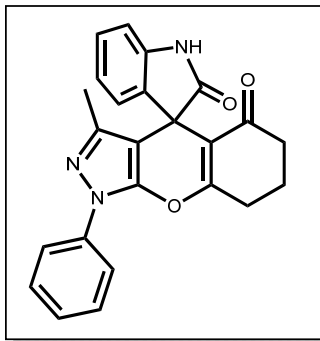
IR (KBr) : 3330,3235, 2918, 1722, 1650, 1615, 1605, 1520, 1473, 1346, 1209, 1175, 1115, 1030, 819, 770, 708 cm⁻¹;

δ_H (300 MHz; DMSO-d₆; Me₄Si): δ 1.56-1.59 (d, $J=9$, 3H), 1.92-1.98 (m, 2H), 2.22-2.24 (d, $J=5.70$ Hz, 2H), 2.71-2.78 (m, 2H), 6.78-6.84 (m, 3H), 7.06-7.14 (m, 1H), 10.46-10.49 (d, $J=8.70$ Hz, 1H), 12.22-12.25 (d, $J=8.7$ Hz, 1H);

δ_C (75 MHz; DMSO-d₆; Me₄Si): δ 9.4, 20.6, 28.5, 37.2, 46.8, 98.0, 109.3, 112.5, 122.1, 123.3, 128.1, 135.4, 135.5, 142.4, 155.3, 169.7, 178.5, 196.1;

Anal. Calcd for C₁₈H₁₅N₃O₃: C 67.28, H 4.71 and N 13.08%. Found: C 67.30, H 4.73 and N 13.10%.

7h. 3-methyl-1-phenyl-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,3'-indoline]-2',5(6H)-dione



Yield: 88%

Characteristics: off white solid

Mp: 296-298°C

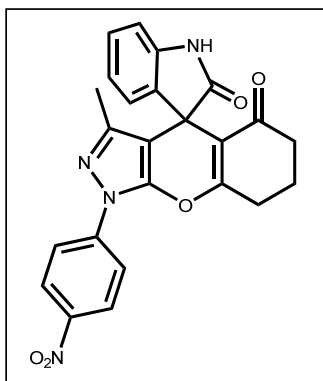
IR (KBr) : 3195, 1716, 1672, 1645, 1617, 1597, 1518, 1471, 1354, 1333, 1304, 1181, 1126, 754, 690, 620 cm^{-1} ;

δ_{H} (300 MHz; DMSO- d_6 ; Me_4Si): δ 1.67 (s, 3H), 2.02-2.06 (t, $J=5.85$ Hz, 2H), 2.34-2.37 (t, $J=3.30$ Hz, 2H), 2.92-2.93 (d, $J=2.40$ Hz, 2H), 6.91-6.95 (t, $J=5.40$ Hz, 2H), 7.01-7.03 (d, $J=6.90$ Hz, 1H), 7.21-7.26 (t, $J=7.65$ Hz, 1H), 7.39-7.44 (t, $J=7.20$ Hz, 1H), 7.56-7.61 (t, $J=7.80$ Hz, 2H), 7.78-7.81 (d, $J=8.10$ Hz, 2H), 10.70 (s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me_4Si): δ 11.8, 20.1, 27.6, 36.8, 47.0, 98.7, 109.1, 113.0, 120.5, 121.8, 123.4, 126.7, 128.2, 129.5, 134.4, 137.3, 142.1, 144.5, 144.6, 167.9, 177.8, 195.8;

Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_3$: C 72.53, H 4.82 and N 10.57%. Found: C 72.56, H 4.84 and N 10.60%.

7i. 3-methyl-1-(4-nitrophenyl)-7,8-dihydro-1H-spiro[chromeno[2,3-c]pyrazole-4,3'-indoline]-2',5(6H)-dione



Yield: 82%

Characteristics: pale yellow solid

Mp: >300 °C

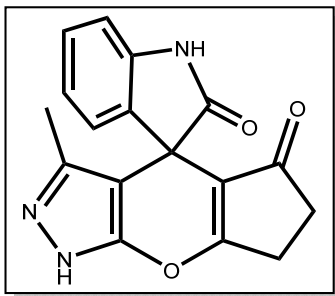
IR (KBr) : 3200, 2955, 1725, 1672, 1651, 1597, 1517, 1484, 1471, 1340, 1306, 1216, 1181, 1104, 840, 750, 471 cm^{-1} ;

δ_{H} (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.63(s, 3H), 1.98-2.02 (t, $J=6.15\text{Hz}$, 2H), 2.32 (s, 2H), 2.92 (s, 2), 6.87-6.89 (d, $J=6.15\text{Hz}$, 2H), 6.98-7.01 (d, $J=7.50\text{ Hz}$, 1H), 7.18 (s, 1H), 8.02-8.05 (d, $J=9.00\text{Hz}$, 2H), 8.36-8.39 (d, $J=9.00\text{ Hz}$, 2H), 10.68 (s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 11.8, 20.1, 27.6, 36.8, 46.8, 100.0, 109.2, 113.0, 119.9, 121.9, 123.6, 125.4, 128.4, 134.0, 142.1, 144.8, 145.5, 146.6, 167.8, 177.5, 195.8;

Anal. Calcd for C $_{24}$ H $_{18}$ N $_4$ O $_5$: C 65.15, H 4.10 and N 12.66%. Found: C 65.17, H 4.12 and N 12.68%.

7j. 3-methyl-6,7-dihydro-1H,5H-spiro[cyclopenta[5,6]pyrano[2,3-c]pyrazole-4,3'-indoline]-2',5-dione



Yield: 92%

Characteristics: white solid

Mp: >300°C

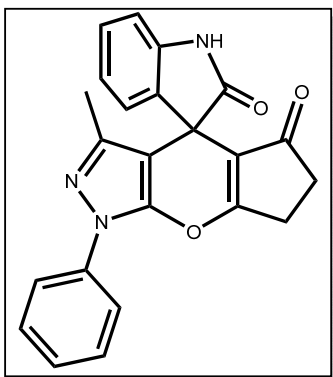
IR (KBr) : 3346,3228, 2935, 1722, 1650, 1612, 1590, 1520, 1473, 1346, 1209, 1165, 1115, 1030, 822, 765, 701 cm^{-1} ;

δ_{H} (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.51 (s, 3H), 2.33 (s, 2H), 2.82 (s, 2H), 6.79-6.83 (m, 3H), 7.08-7.13 (m, 1H), 10.58 (s, 1H), 12.33 (s, 1H);

δ_C (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 9.4, 25.7, 33.7, 45.6, 97.9, 109.7, 116.0, 122.5, 124.3, 128.8, 133.1, 136.2, 142.4, 157.5, 177.1, 181.7, 200.9;

Anal. Calcd for C $_{17}$ H $_{13}$ N $_3$ O $_3$: C 66.44, H 4.26 and N 13.67%. Found: C 66.46, H 4.28 and N 13.69%.

7k. 3-methyl-1-phenyl-6,7-dihydro-1H,5H-spiro[cyclopenta[5,6]pyrano[2,3-c]pyrazole-4,3'-indoline]-2',5-dione



Yield: 86%

Characteristics: off white solid

Mp: >300°C

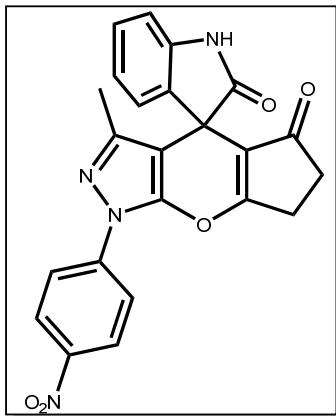
IR (KBr) : 3138, 3070, 1715, 1650, 1617, 1599, 1520, 1470, 1349, 1307, 1220, 1208, 932, 764, 680 cm^{-1} ;

δ_H (300 MHz; CDCl $_3$; Me $_4$ Si): δ 1.69 (s, 3H), 2.51-2.56(m, 2H), 2.89-2.90 (d, $J=5.40\text{Hz}$, 2H), 6.85-6.94 (dd, $J_1=19.35\text{Hz}$, $J_2=7.95\text{Hz}$, 3H), 7.18-7.19 (d, $J=3.00\text{Hz}$, 1H), 7.27-7.29 (d, $J=7.50\text{Hz}$, 1H), 7.39-7.44 (t, $J=7.80\text{Hz}$, 2H), 7.63-7.66 (d, $J=7.80\text{Hz}$, 2H), 8.02 (s, 1H);

δ_C (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 11.8, 25.0, 34.0, 45.6, 98.9, 109.5, 116.9, 120.9, 122.2, 124.4, 127.0, 128.8, 129.6, 132.1, 137.2, 142.1, 144.9, 146.9, 176.3, 179.8, 200.3;

Anal. Calcd for C $_{23}$ H $_{17}$ N $_3$ O $_3$: C 72.05, H 4.47 and N 10.96%. Found: C 72.07, H 4.49 and N 10.98%.

7l. 3-methyl-1-(4-nitrophenyl)-6,7-dihydro-1H,5H-spiro[cyclopenta[5,6]pyrano[2,3-c]pyrazole-4,3'-indoline]-2',5-dione



Yield: 79%

Characteristics: pale yellow solid

Mp: >300°C

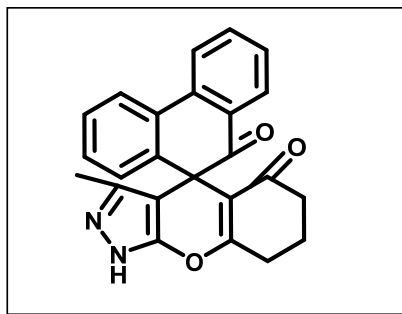
IR (KBr) : 3212, 2960, 1716, 1665, 1649, 1600, 1515, 1475, 1479, 1335, 1311, 1210, 1179, 1109, 840, 750, 470 cm^{-1} ;

δ_{H} (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.59(s, 3H), 2.48-2.51(t, $J=4.50\text{Hz}$, 2H), 2.97-2.99(d, $J=5.70\text{Hz}$, 2H), 6.88-6.92(t, $J=7.05\text{Hz}$, 2H), 7.02-7.04(d, $J=6.90\text{Hz}$, 1H), 7.18-7.7.23(t, $J=7.65\text{Hz}$, 1H), 8.03-8.06(d, $J=9.00\text{Hz}$, 2H), 8.37-8.40(d, $J=9.30\text{Hz}$, 2H), 10.81(s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 12.2, 25.4, 34.5, 45.9, 100.7, 110.0, 117.4, 120.8, 122.6, 124.9, 125.8, 129.4, 132.1, 142.5, 145.4, 147.2, 148.1, 176.5, 180.0, 200.6;

Anal. Calcd for $\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_5$: C 64.48, H 3.76 and N 13.08%. Found: C 64.50, H 3.78 and N 13.10%.

8a. 3-methyl-7,8-dihydro-1H,10'H-spiro[chromeno[2,3-c]pyrazole-4,9'-phenanthrene]-5,10'(6H)-dione



Yield: 78%

Characteristics: off white solid

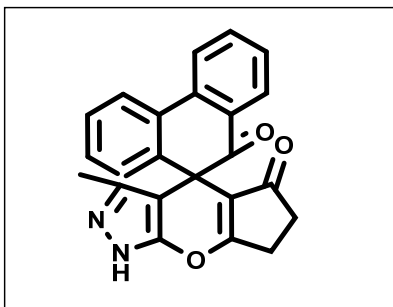
Mp: >300°C

δ_{H} (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.29 (s, 3H), 2.00-2.04 (m, 2H), 2.23-2.27 (m, 2H), 2.89-2.90 (d, $J=3.90$ Hz, 2H), 7.09-7.12 (d, $J=7.50$ Hz, 1H), 7.26-7.36 (m, 2H), 7.53-7.58 (t, $J=7.50$ Hz, 1H), 7.83-7.88 (m, 1H), 7.99-8.01 (d, $J=7.50$ Hz, 1H), 8.25-8.27 (d, $J=7.50$ Hz, 1H), 8.39-8.42 (d, $J=8.10$ Hz, 1H), 12.19 (s, 1H);

δ_{C} (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 9.9, 20.6, 28.1, 37.0, 48.8, 100.9, 117.9, 123.4, 124.1, 127.3, 127.6, 128.6, 128.9, 129.1, 129.8, 135.3, 135.3, 137.6, 143.9, 154.3, 168.9, 195.9, 196.3;

Anal. Calcd for C $_{24}$ H $_{18}$ N $_2$ O $_3$: C 75.38, H 4.74 and N 7.40%. Found: C 75.41, H 4.78 and N 7.42%.

8b. 3-methyl-6,7-dihydro-1H,5H,10'H-spiro[cyclopenta[5,6]pyrano[2,3-c]pyrazole-4,9'-phenanthrene]-5,10'-dione



Yield: 75%

Characteristics: off white solid

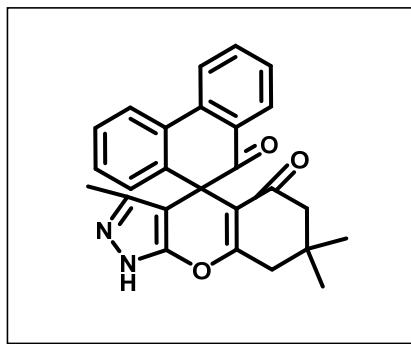
Mp: >300°C

δ_{H} (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.28-1.29 (d, $J=3.90$ Hz, 1H), 2.36-2.41 (m, 2H), 2.92-2.97 (m, 2H), 7.04-8.36 (m, 8H), 12.32 (s, 1H);

δ_C (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 9.5, 25.5, 33.7, 46.6, 47.5, 100.8, 119.6, 122.0, 123.2, 123.4, 123.8, 124.0, 126.9, 127.6, 127.7, 127.8, 128.3, 128.5, 128.8, 128.9, 129.2, 129.6, 129.7, 129.9, 135.2, 135.6, 135.8, 137.5, 137.6, 139.4, 140.6, 178.6, 181.0, 196.0, 200.2;

Anal. Calcd for C $_{23}$ H $_{16}$ N $_2$ O $_3$: C 74.99, H 4.38 and N 7.60%. Found: C 75.02, H 4.42 and N 7.67%.

8c. 3,7,7-trimethyl-7,8-dihydro-1H,10'H-spiro[chromeno[2,3-c]pyrazole-4,9'-phenanthrene]-5,10'(6H)-dione



Yield: 76%

Characteristics: off white solid

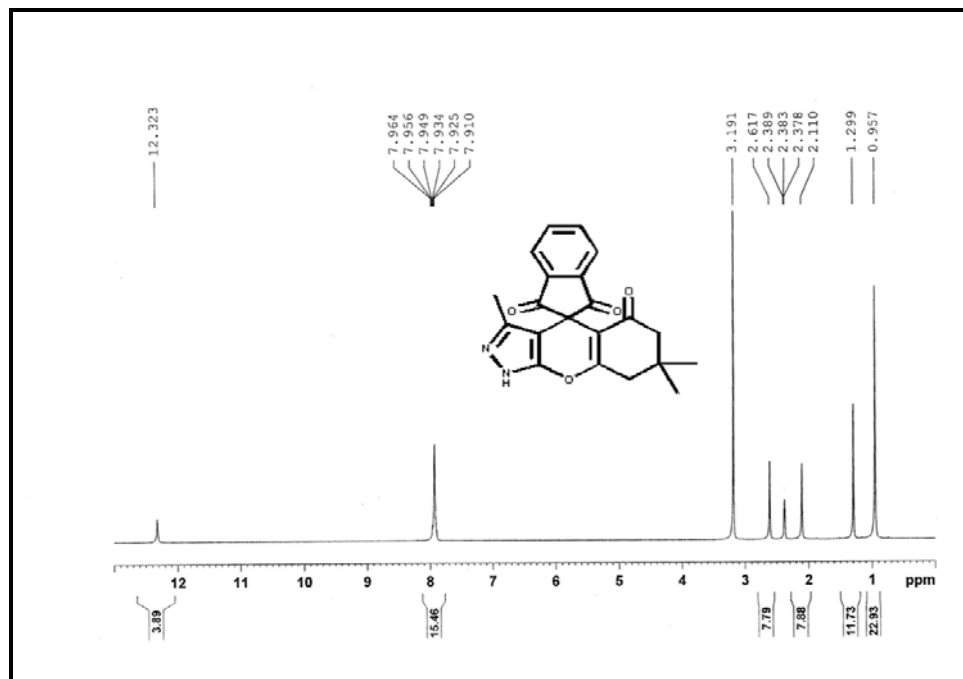
Mp: >300°C

δ_H (300 MHz; DMSO- d_6 ; Me $_4$ Si): δ 1.08-1.16 (m, 6H), 1.27 (s, 1H), 2.11-2.20 (m, 2H), 2.67-2.90 (dd, $J_1=52.5$ Hz, $J_2=17.4$ Hz, 2H), 7.04-7.06 (d, $J=7.2$ Hz, 1H), 7.26-7.34 (m, 2H), 7.51-7.56 (m, 1H), 7.81-7.85 (t, $J=7.2$ Hz, 1H), 7.96-7.99 (d, $J=7.5$ Hz, 1H), 8.23-8.25 (d, $J=7.2$ Hz, 1H), 8.37-8.39 (d, $J=7.8$ Hz, 1H), 12.20 (s, 1H);

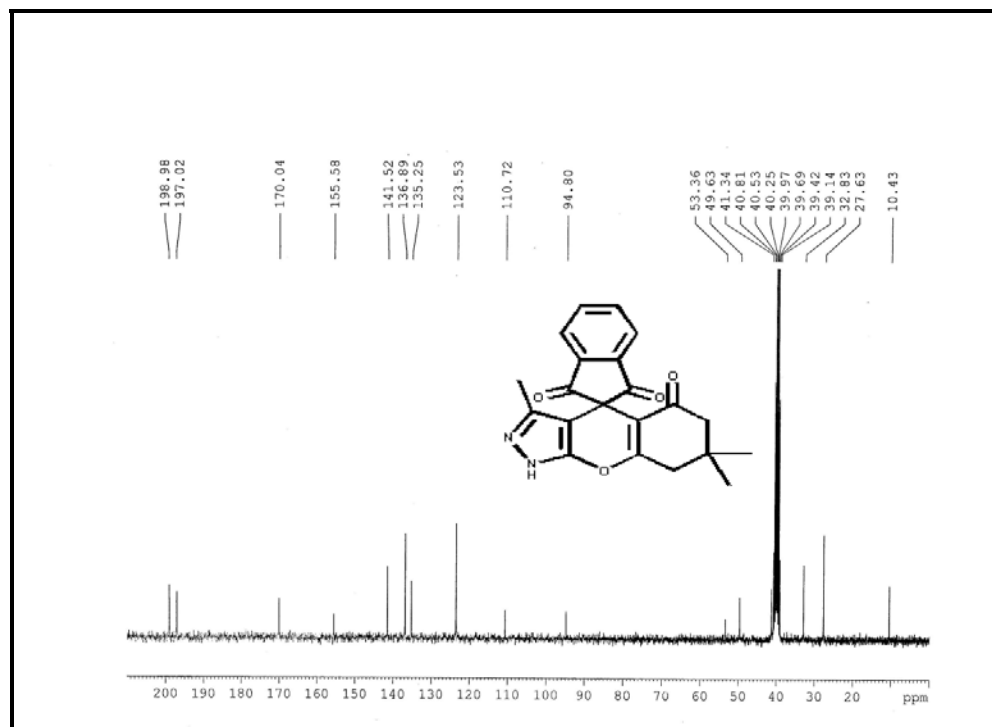
δ_C (75 MHz; DMSO- d_6 ; Me $_4$ Si): δ 9.5, 27.2, 28.1, 32.6, 48.4, 50.3, 100.5, 116.3, 123.1, 123.8, 127.0, 127.4, 128.4, 128.6, 129.4, 135.0, 135.1, 137.3, 143.4, 154.2, 166.8, 195.6, 196.1;

Anal. Calcd for C $_{26}$ H $_{22}$ N $_2$ O $_3$: C 76.08, H 5.40 and N 6.82%. Found: C 76.12, H 5.45 and N 6.86%.

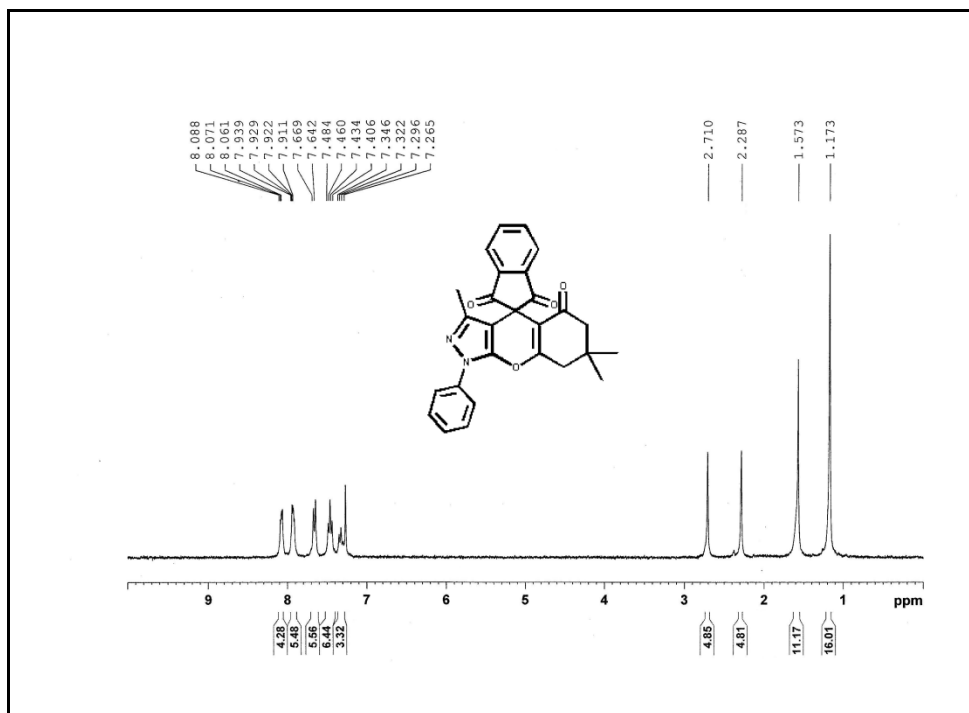
Spectra (^1H NMR and ^{13}C NMR):



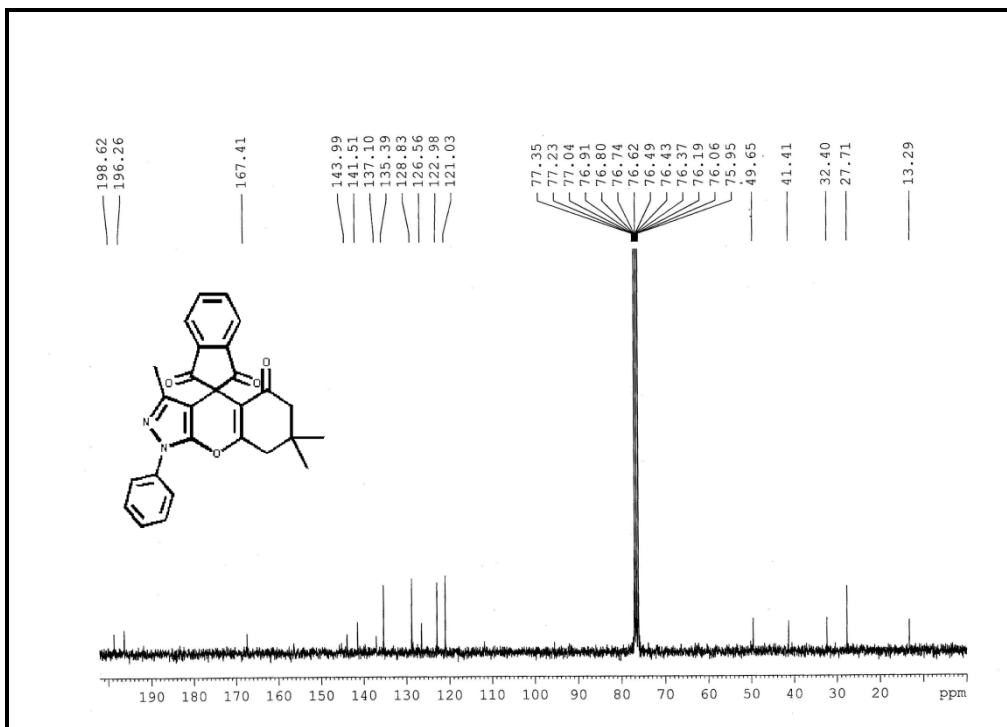
^1H NMR of 6a



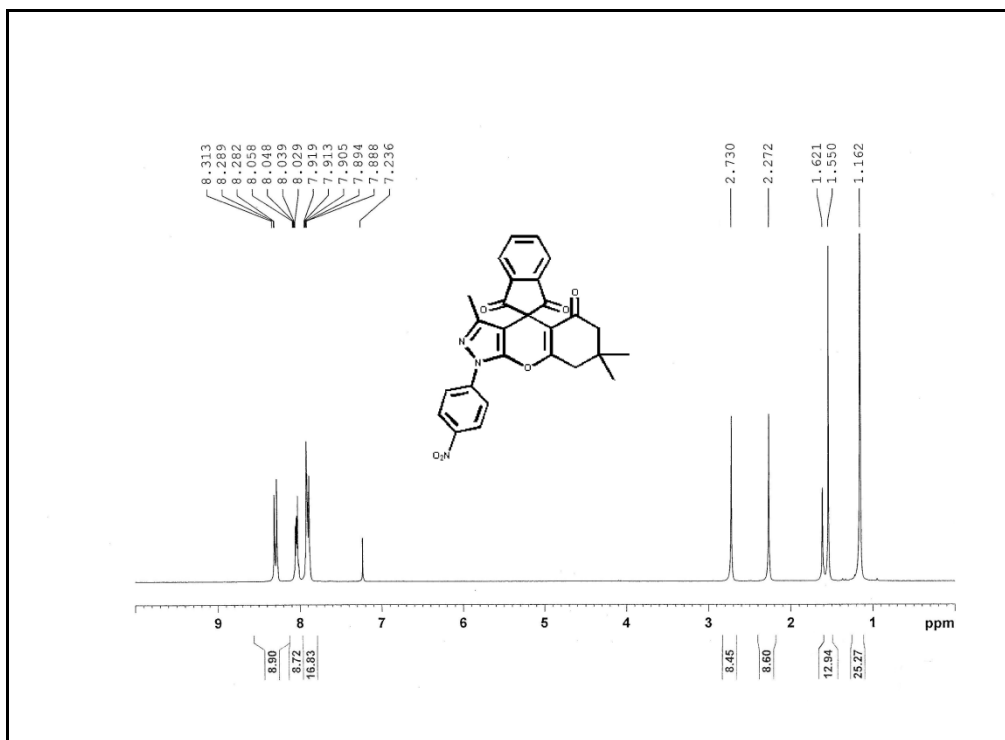
^{13}C NMR of 6a



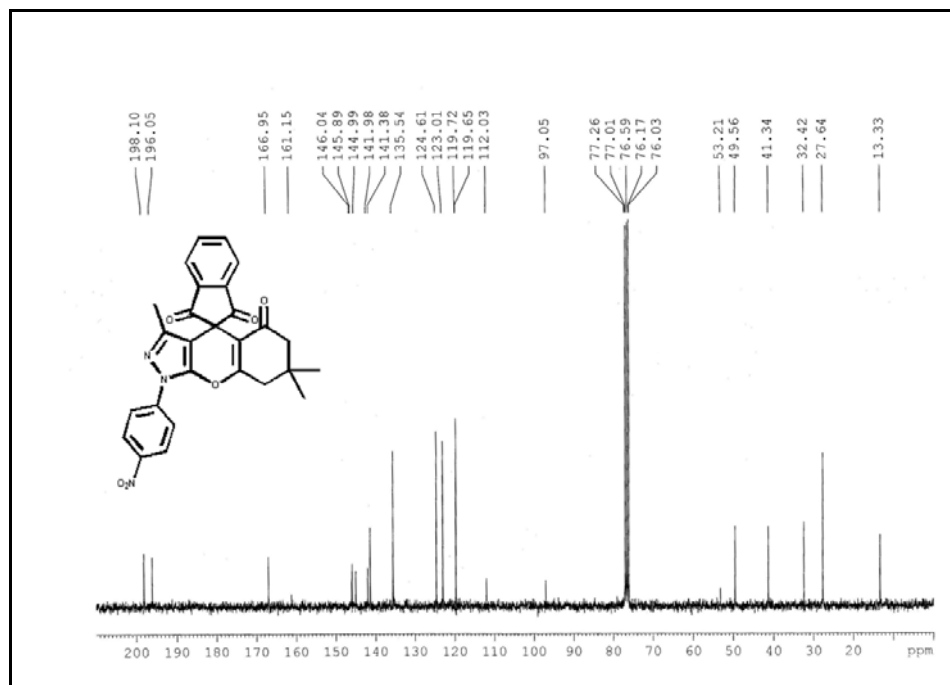
¹H NMR of 6b



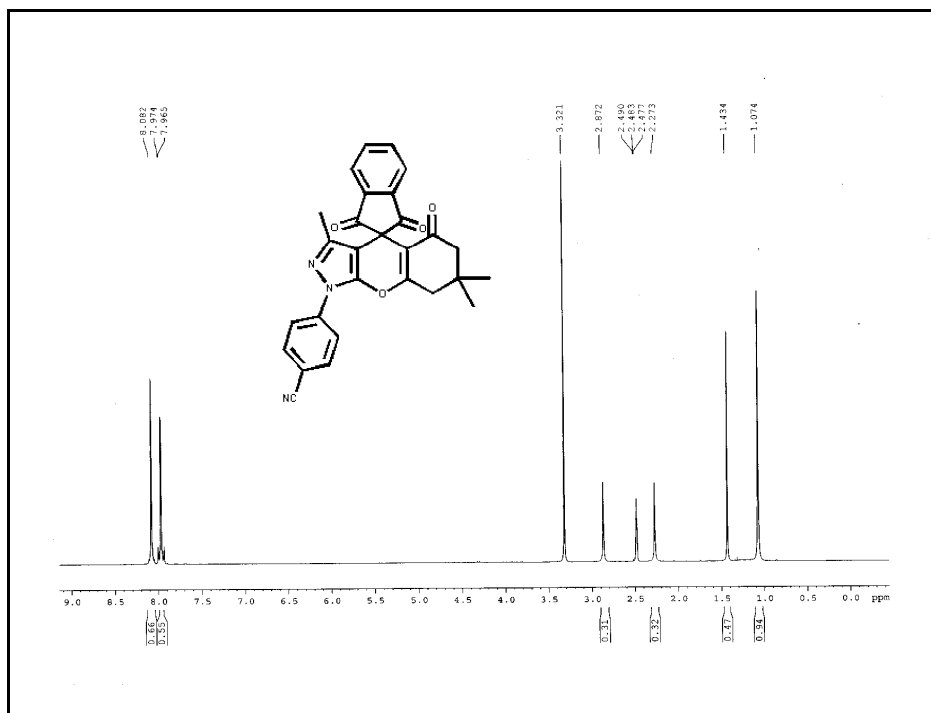
¹³C NMR of 6b



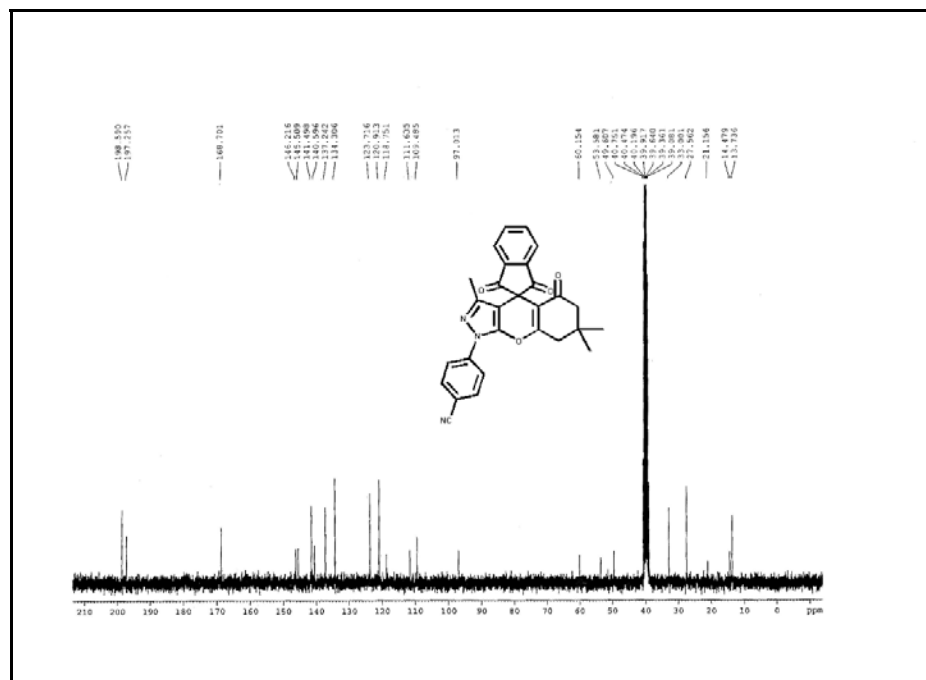
¹H NMR of 6c



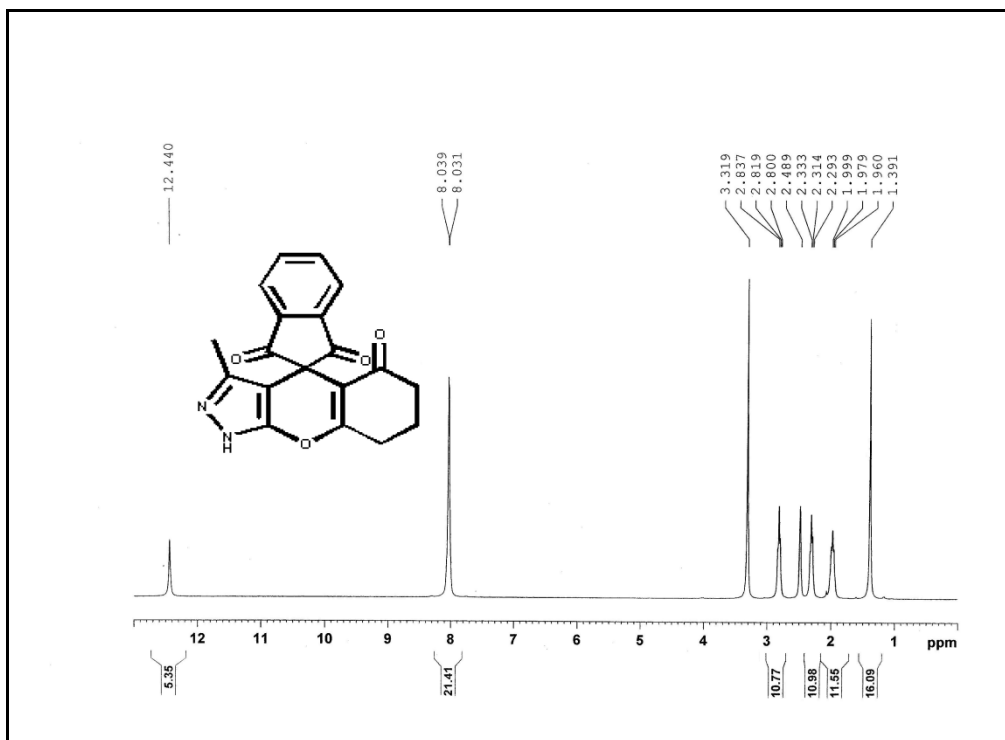
¹³C NMR of 6c



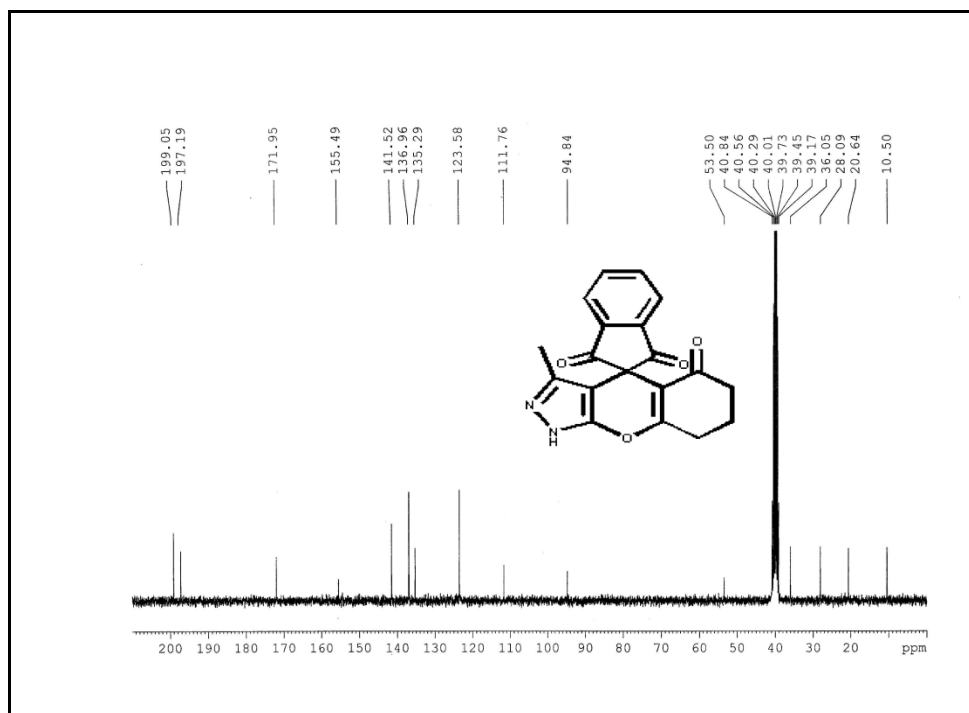
¹H NMR of 6d



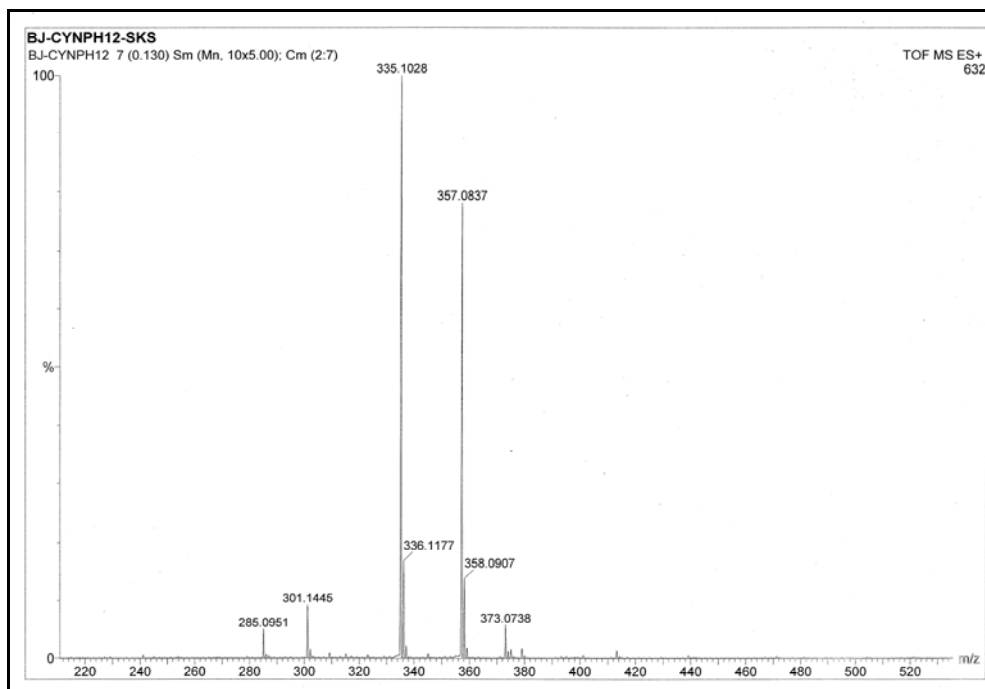
¹³C NMR of 6d



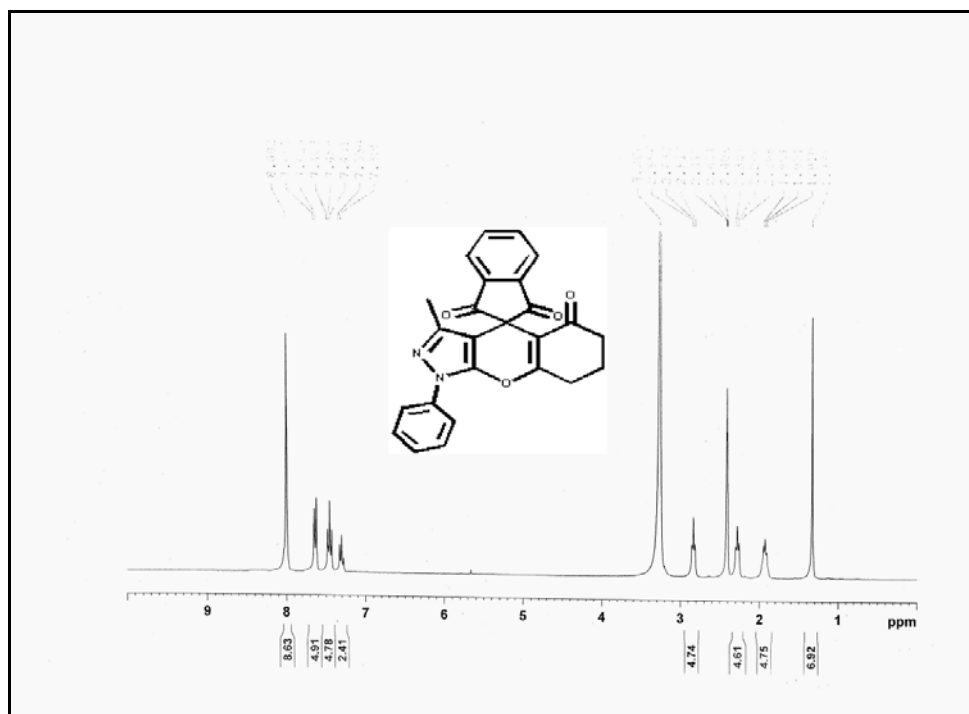
¹H NMR of 6e



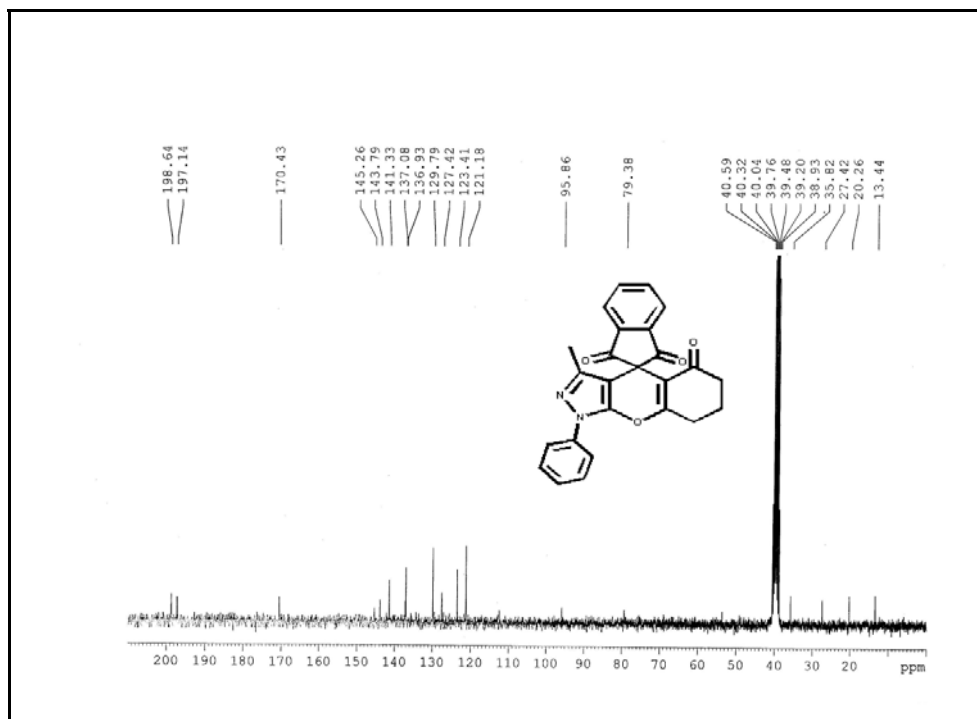
¹³C NMR of 6e



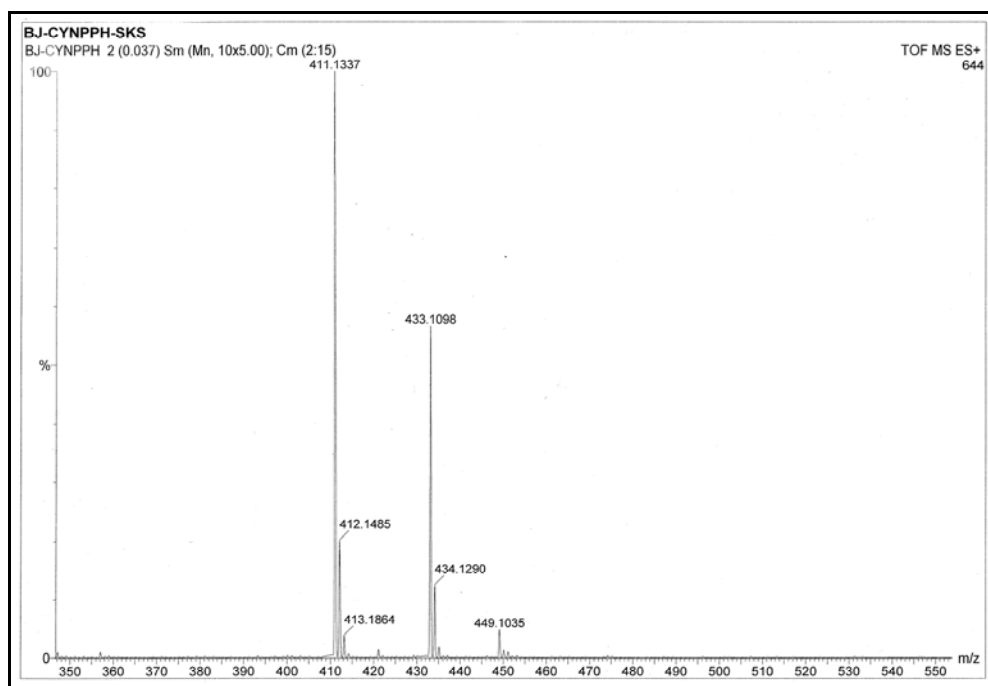
HRMS of 6e



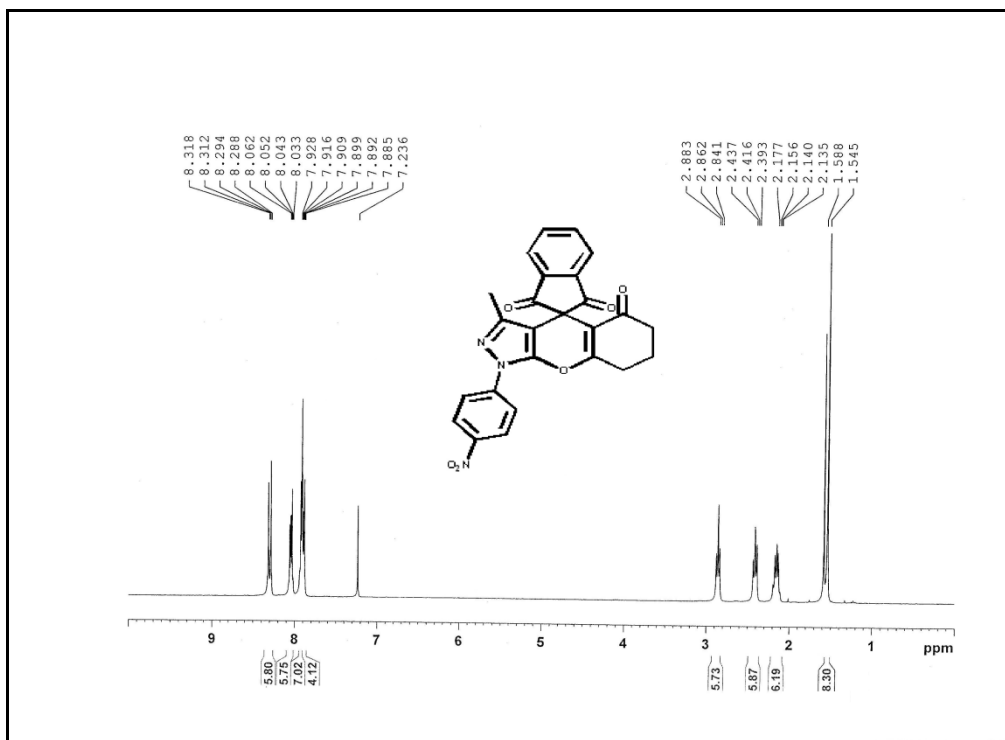
¹H NMR of 6f



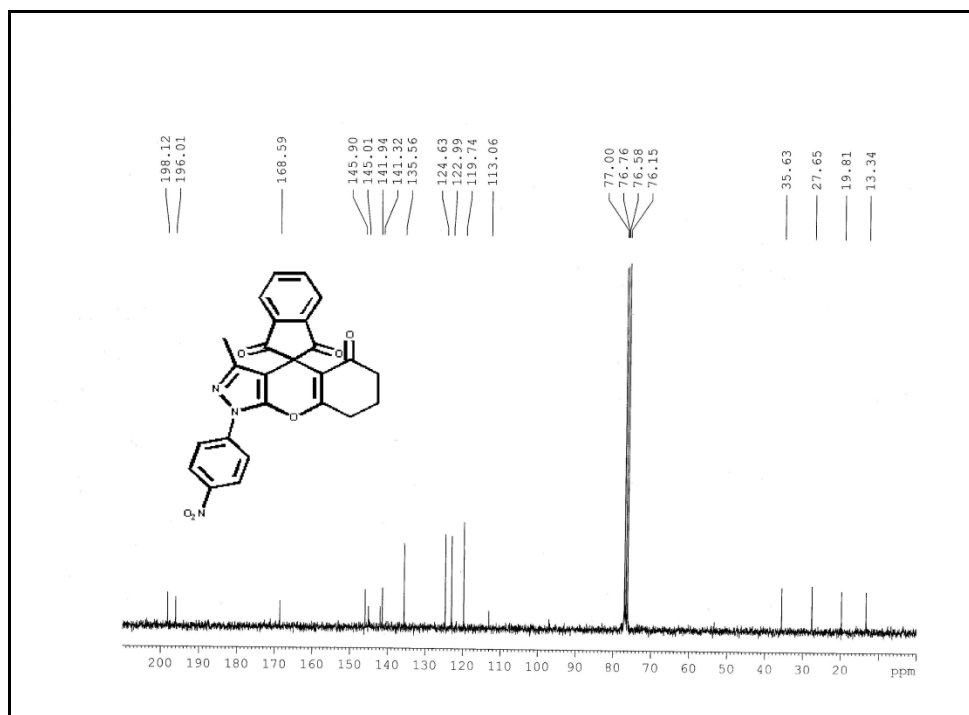
¹³C NMR of 6f



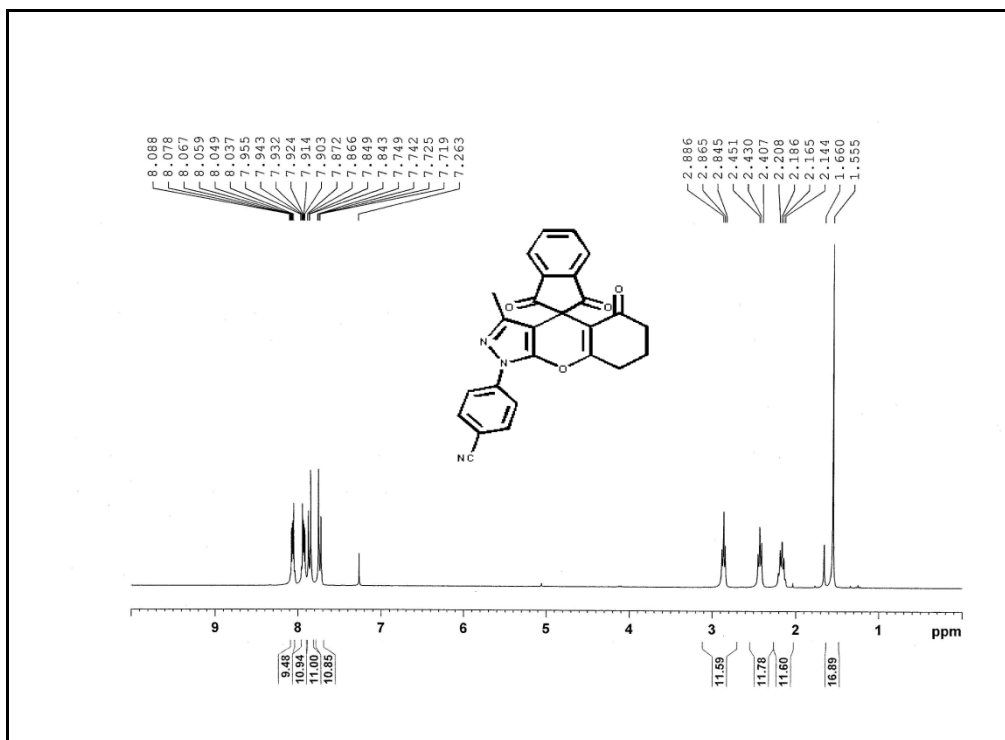
HRMS of 6f



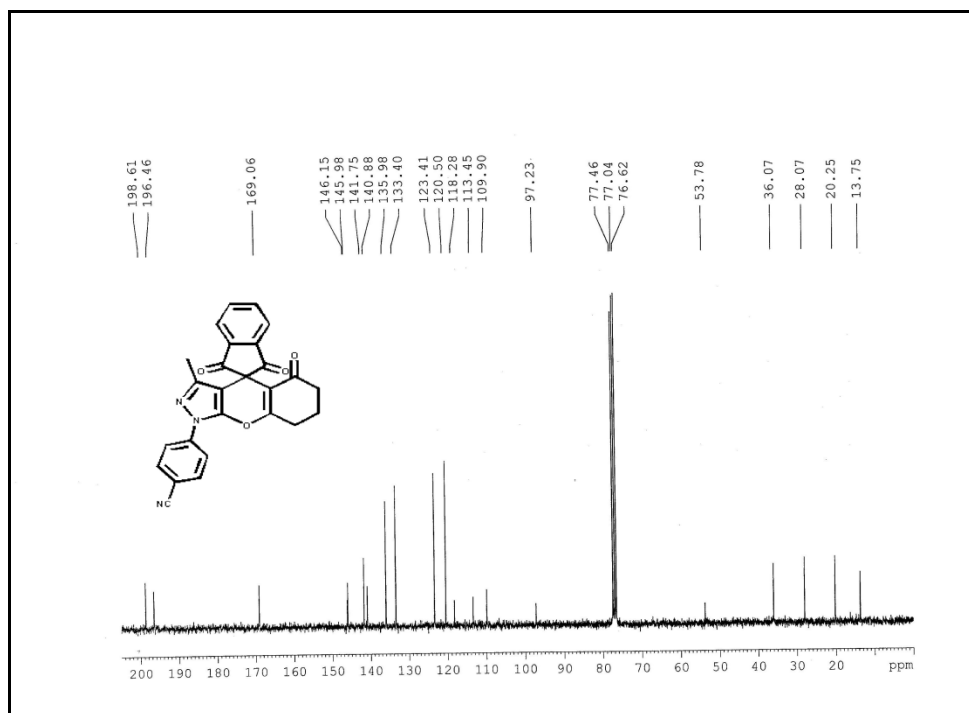
¹H NMR of 6g



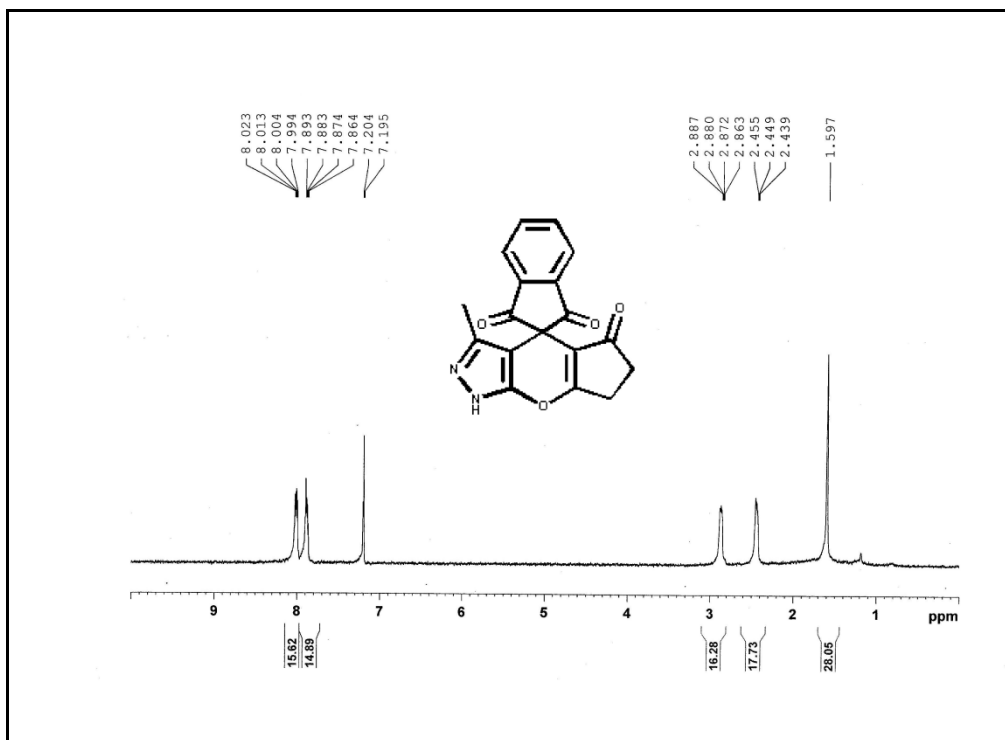
¹³C NMR of 6g



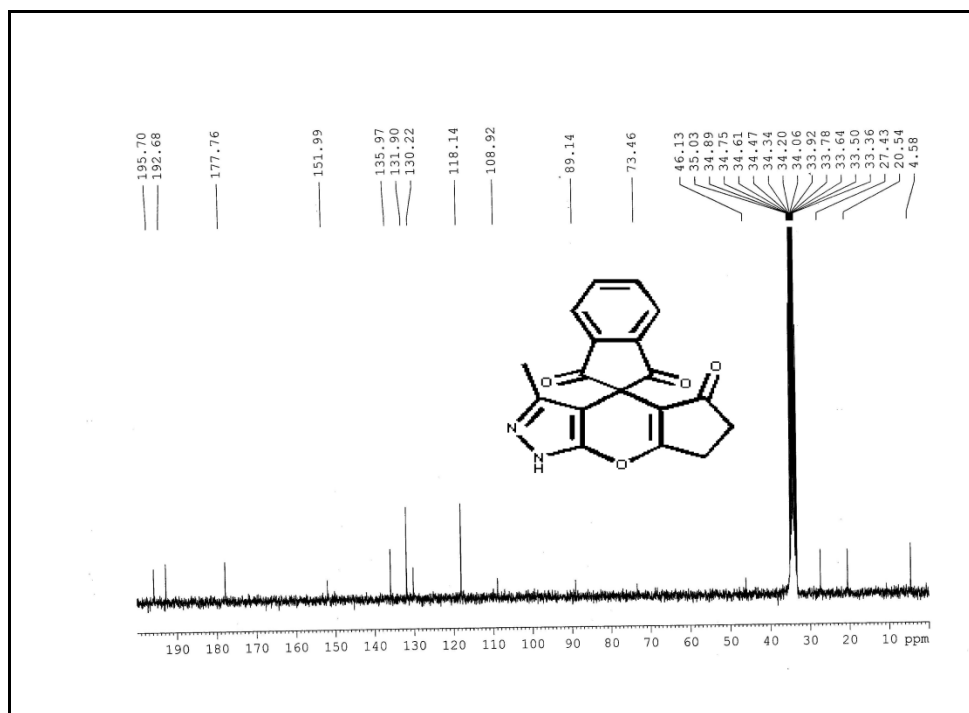
¹H NMR of 6h



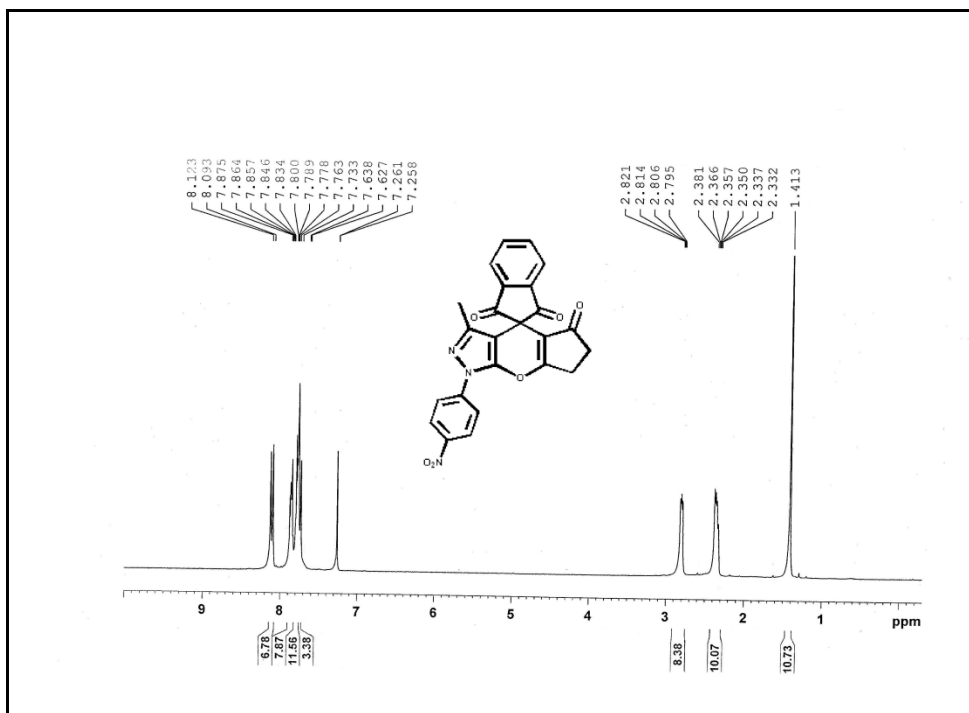
¹³C NMR of 6h



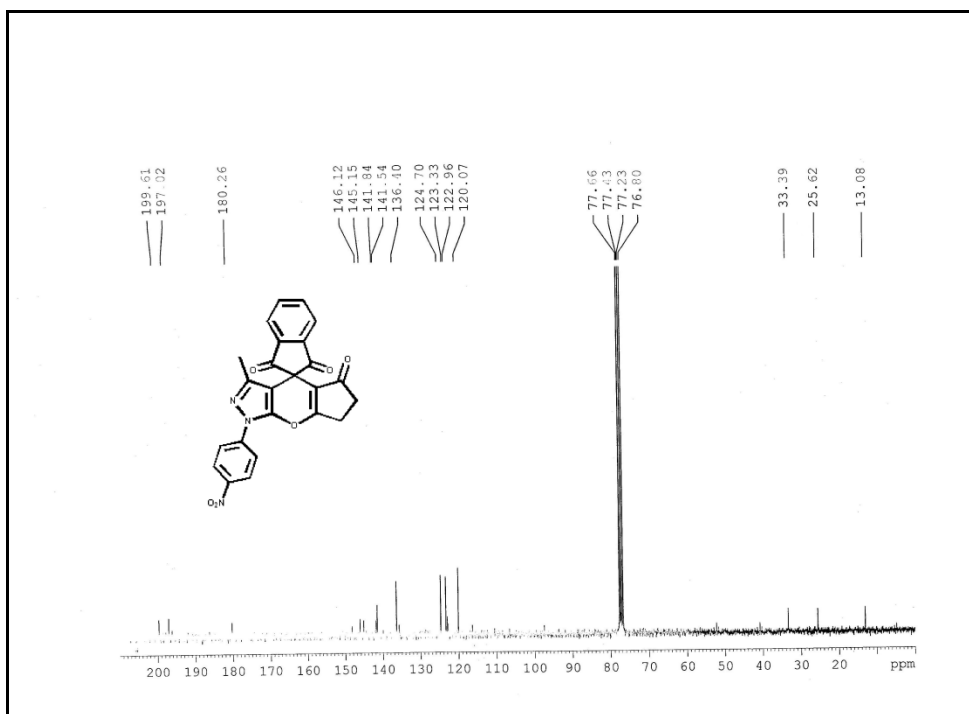
¹H NMR of 6i



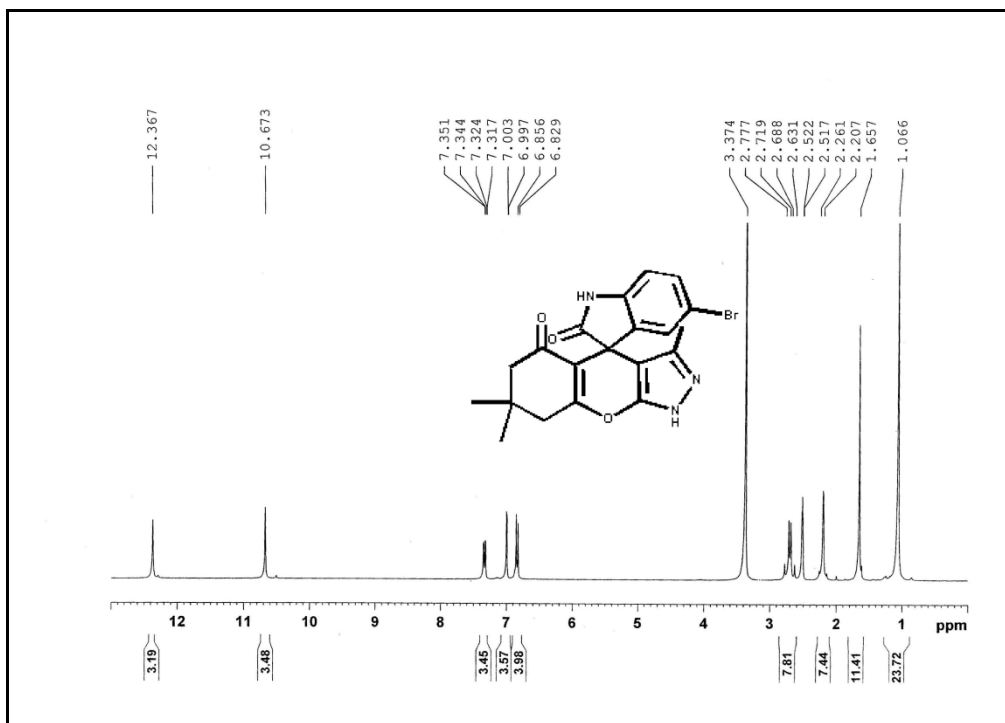
¹³C NMR of 6i



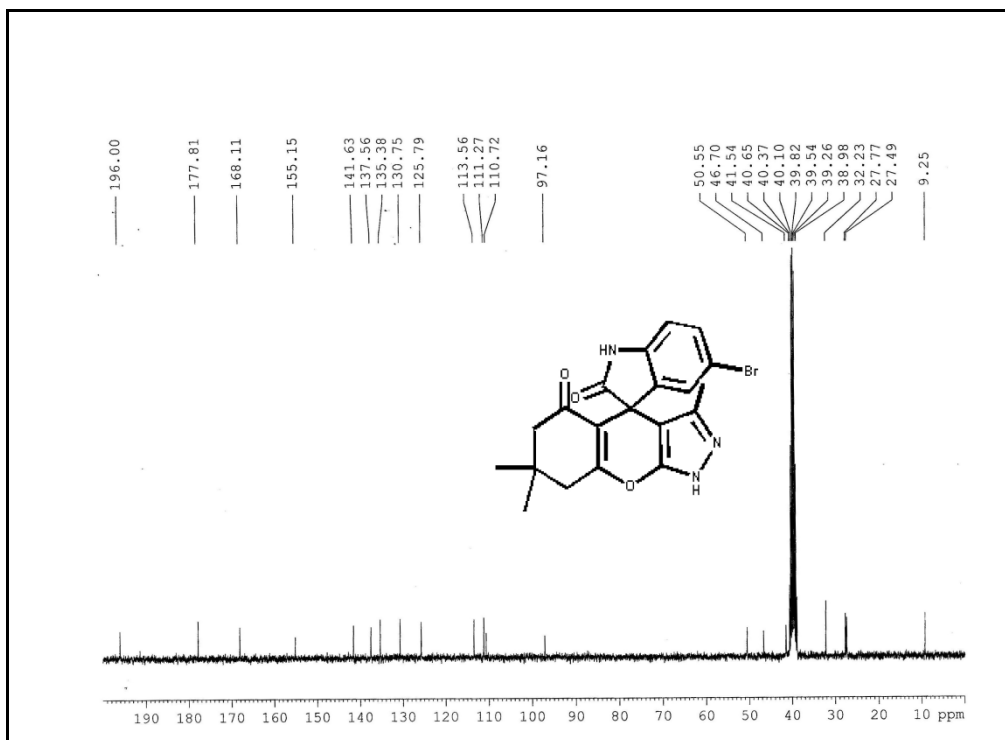
¹H NMR of 6j



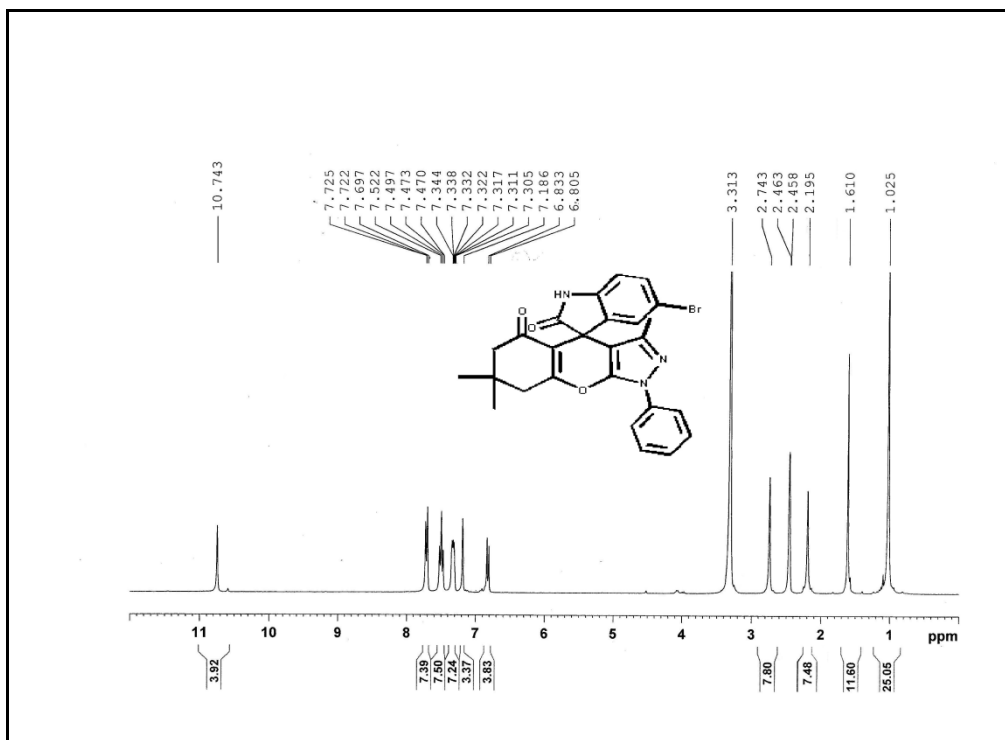
¹³C NMR of 6j



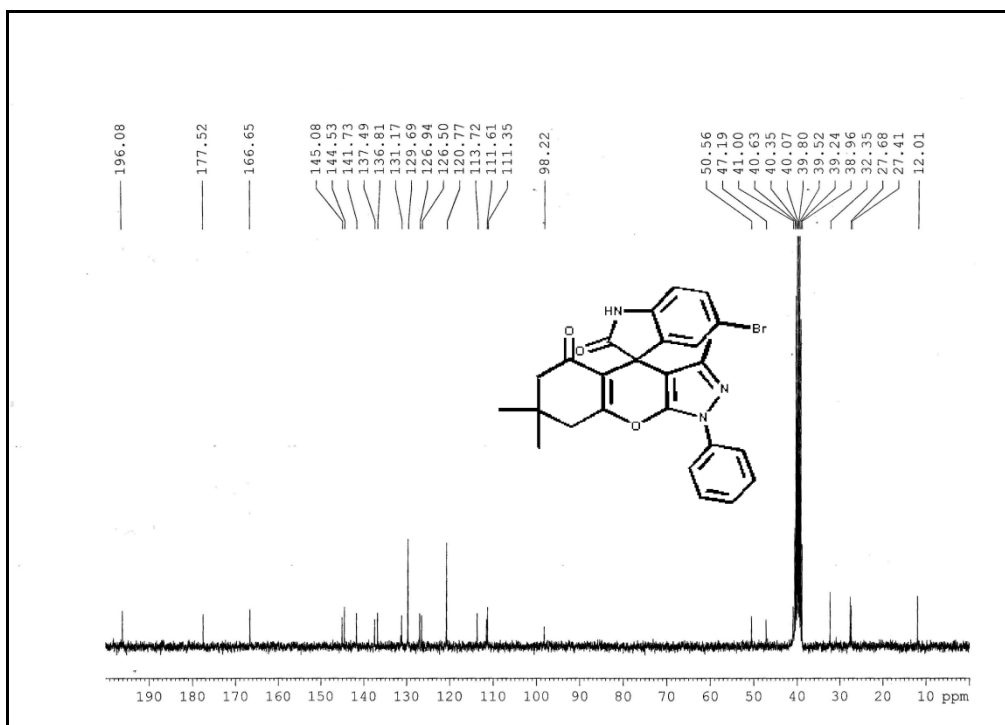
¹H NMR of 7a



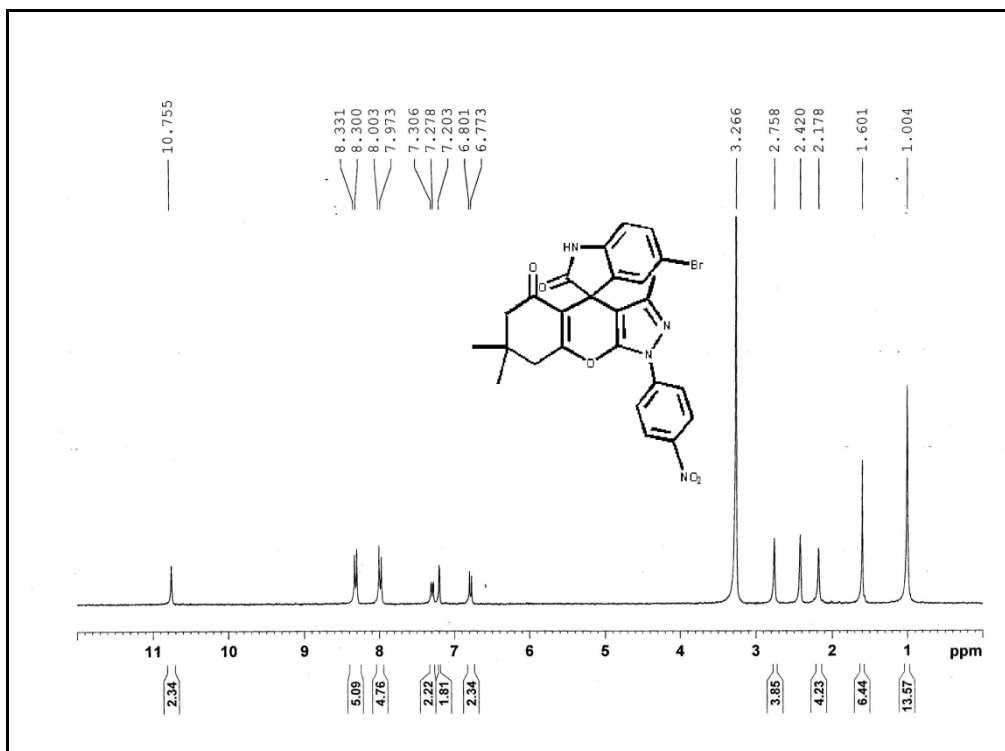
¹³C NMR of 7a



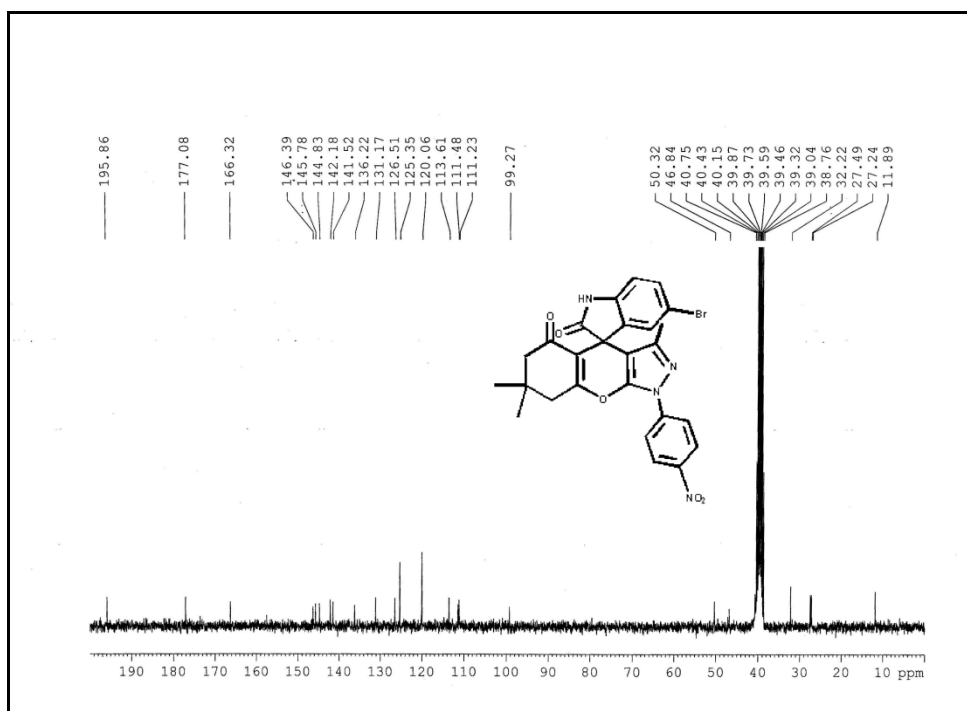
¹H NMR of 7b



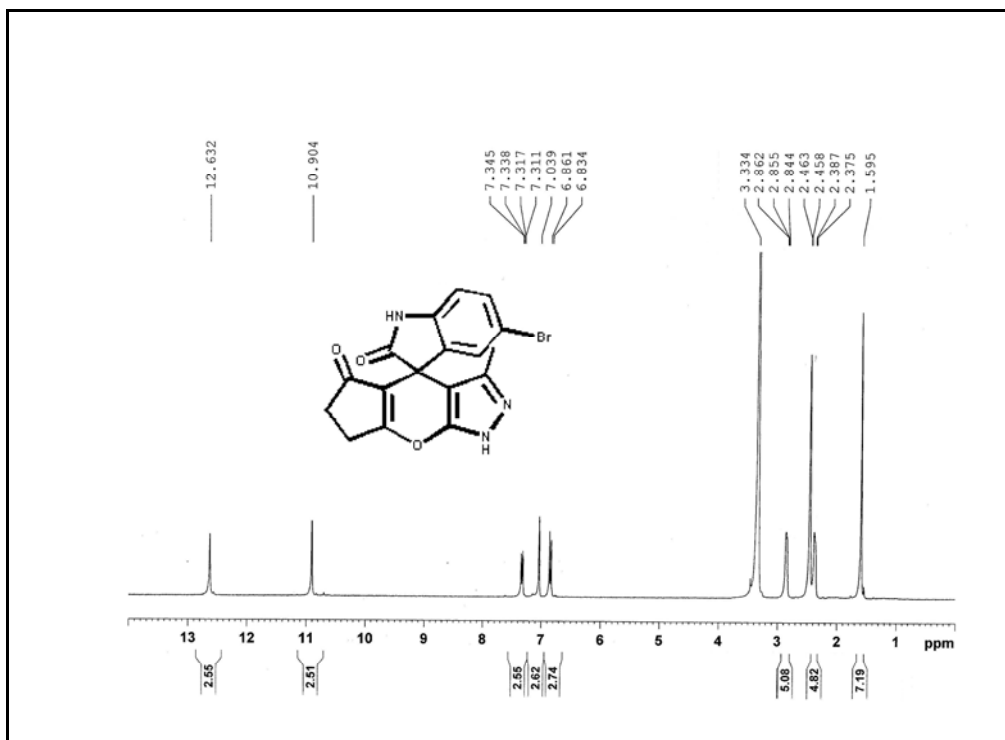
¹³C NMR of 7b



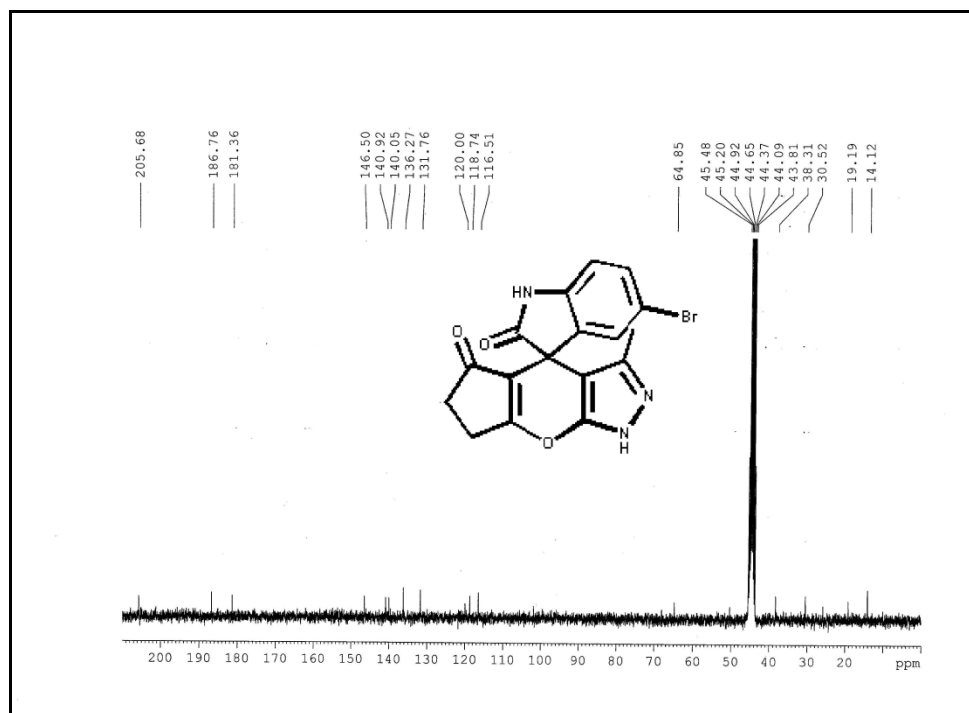
¹H NMR of 7c



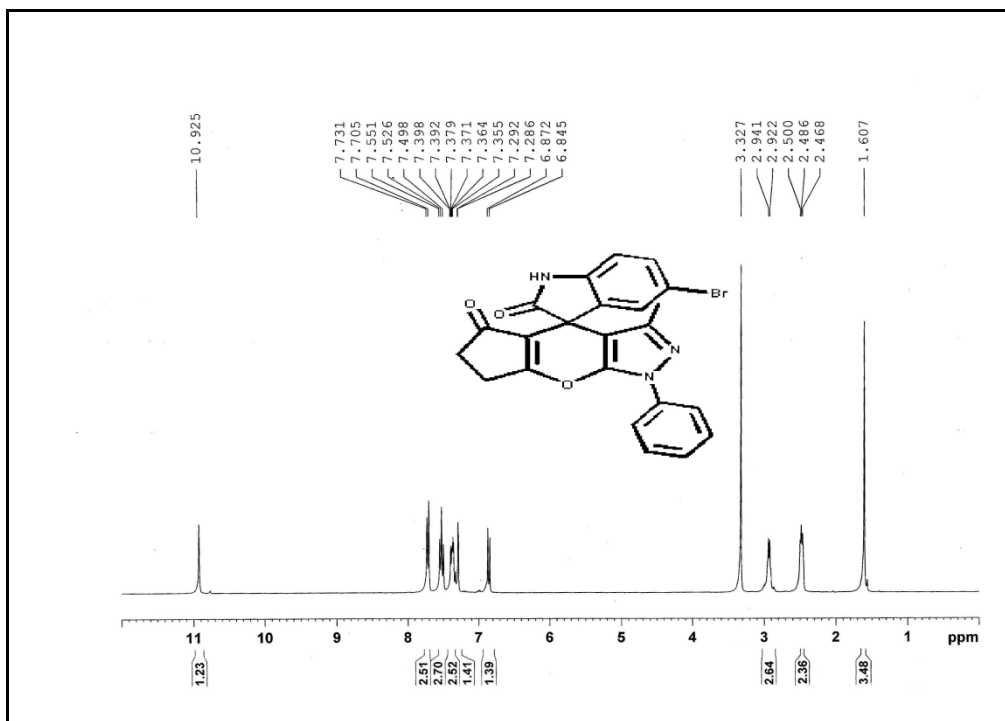
¹³C NMR of 7c



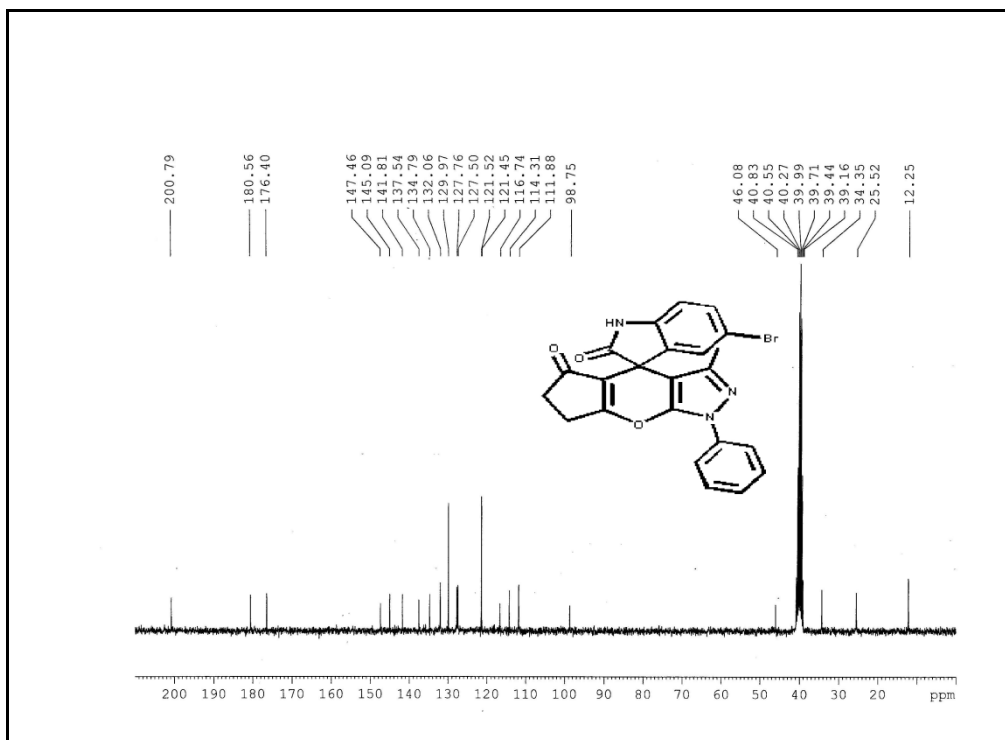
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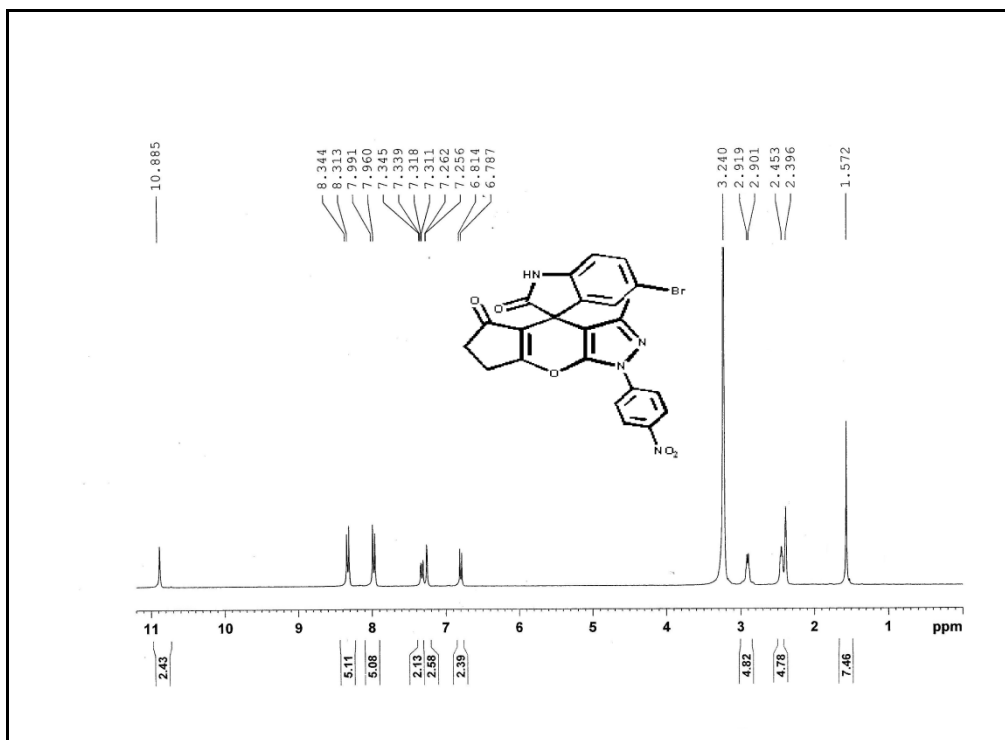
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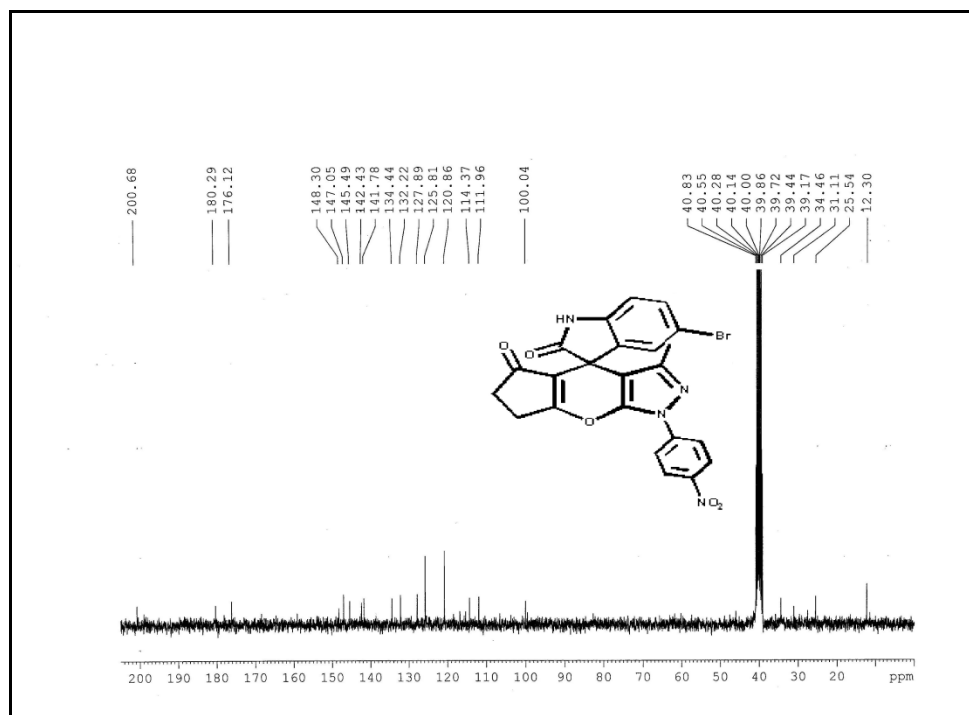
¹H NMR of 7e



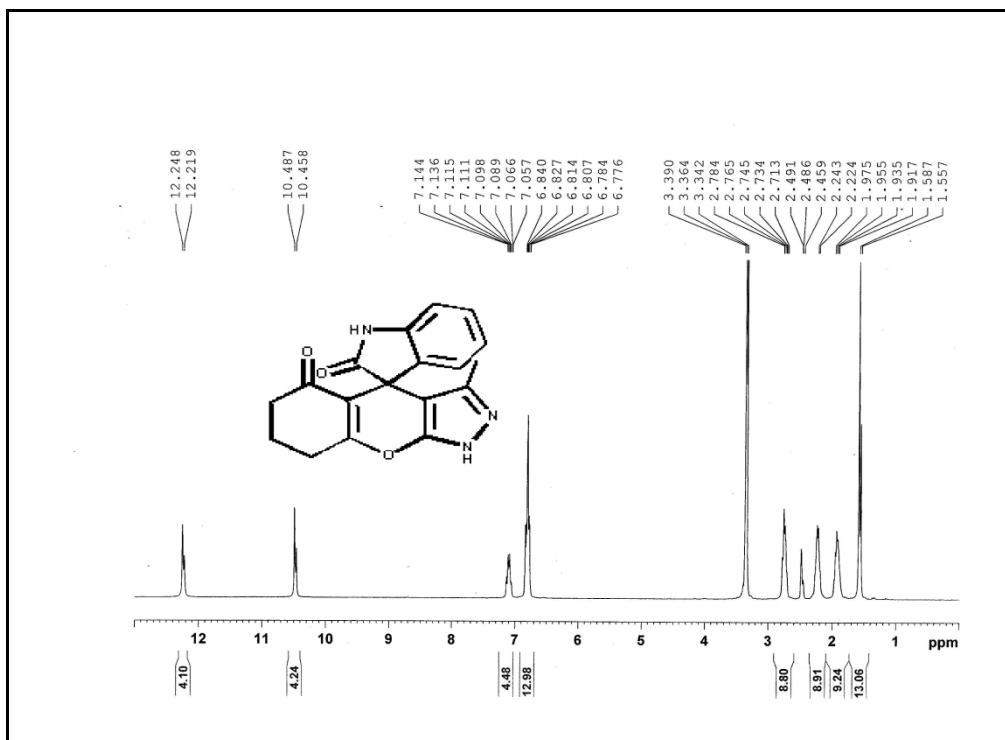
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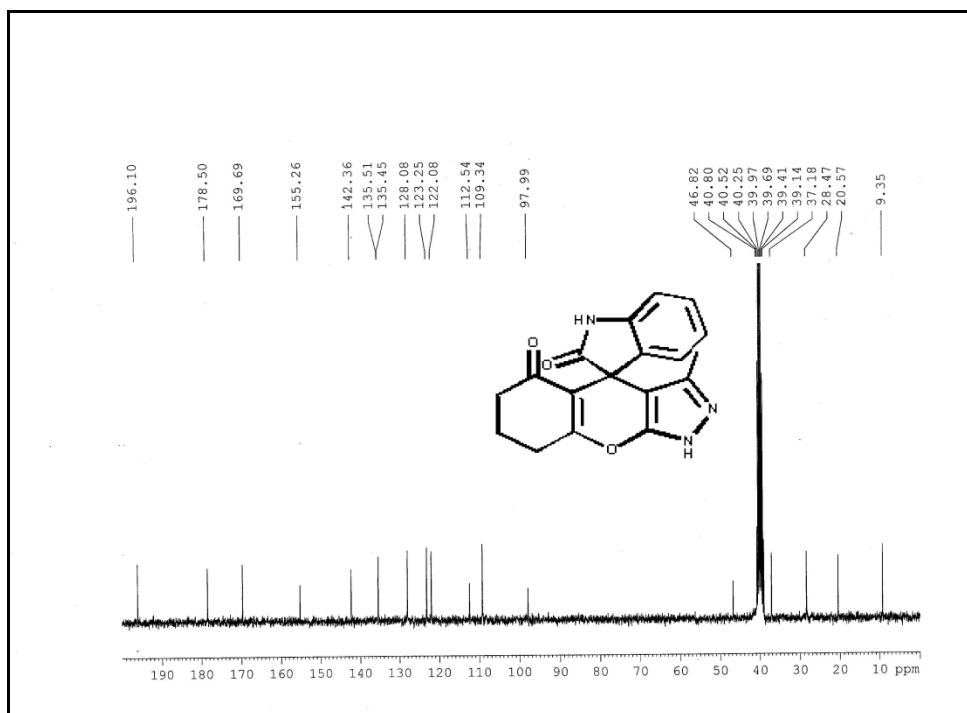
¹H NMR of 7f



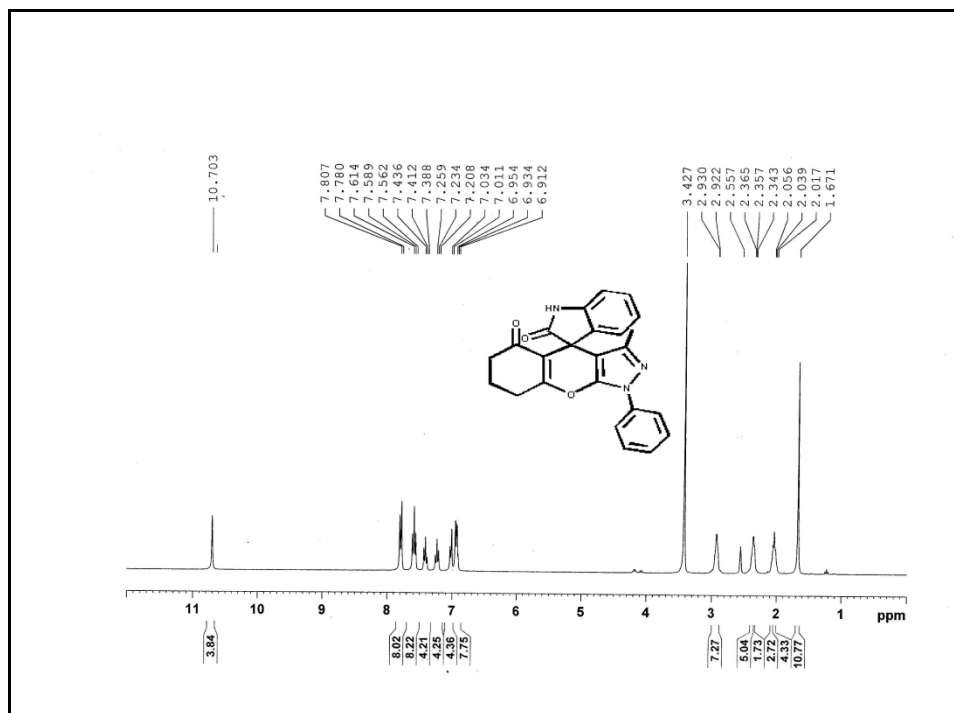
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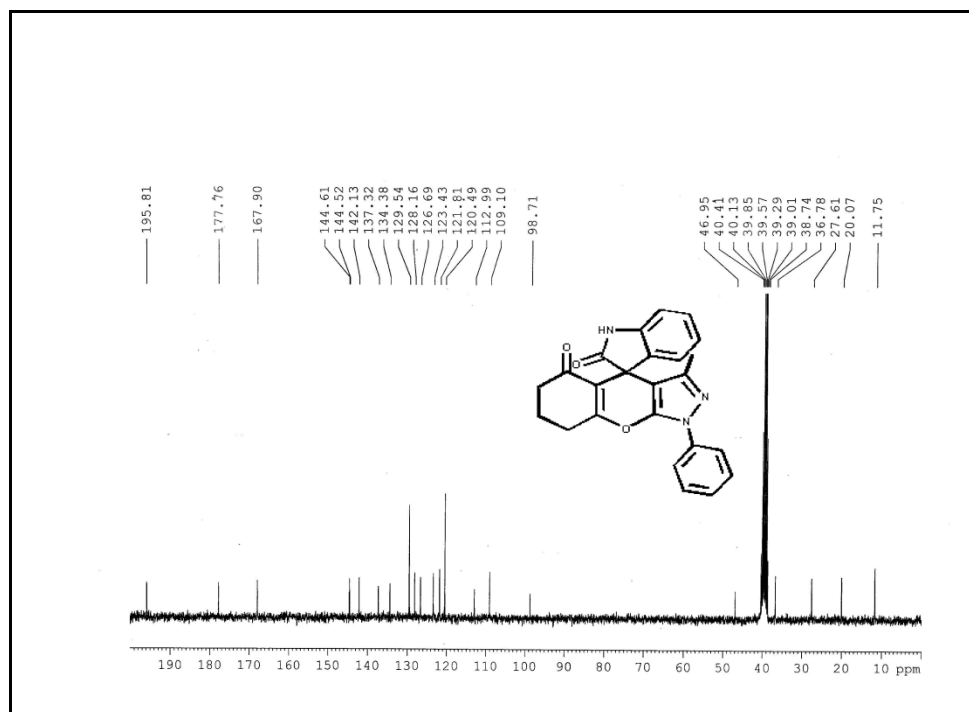
¹H NMR of 7g



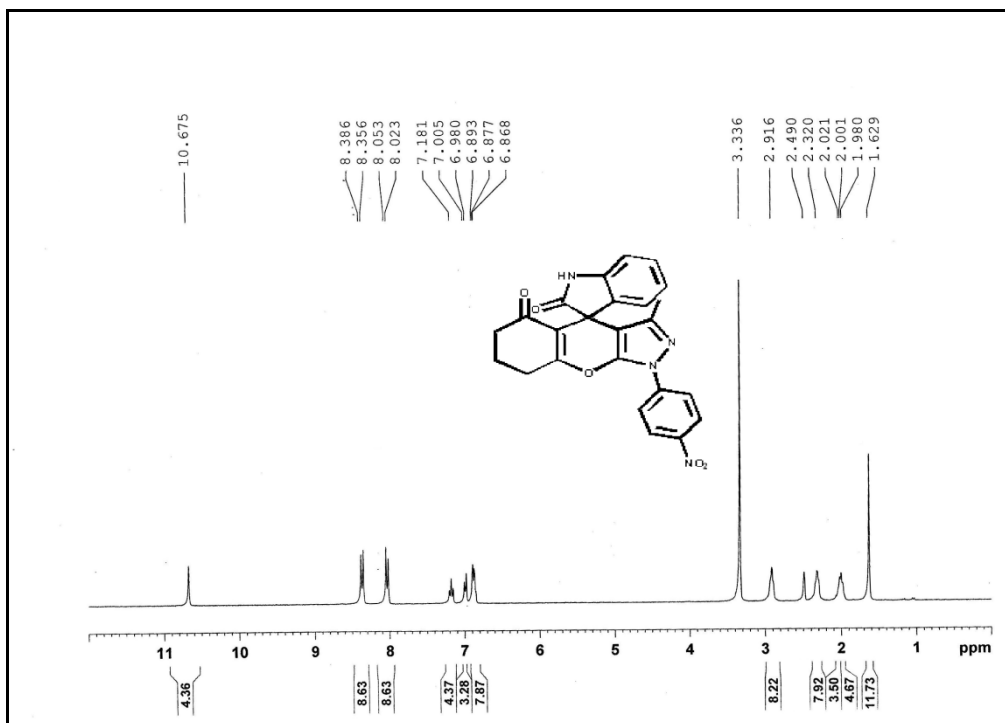
¹³C NMR of 7g



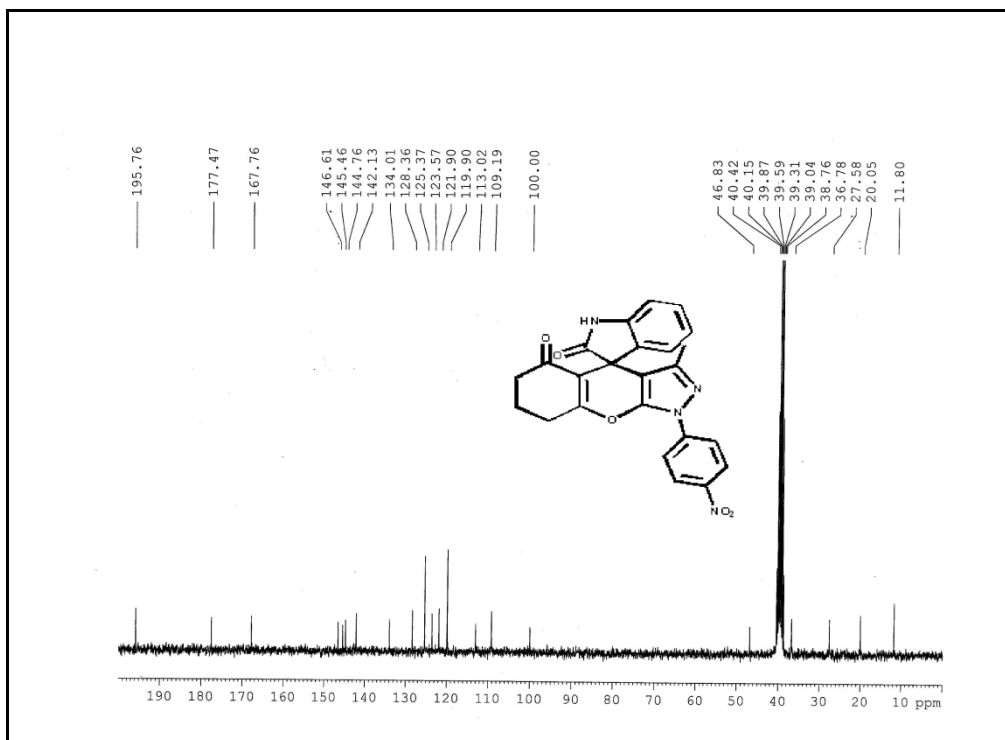
¹H NMR of 7h



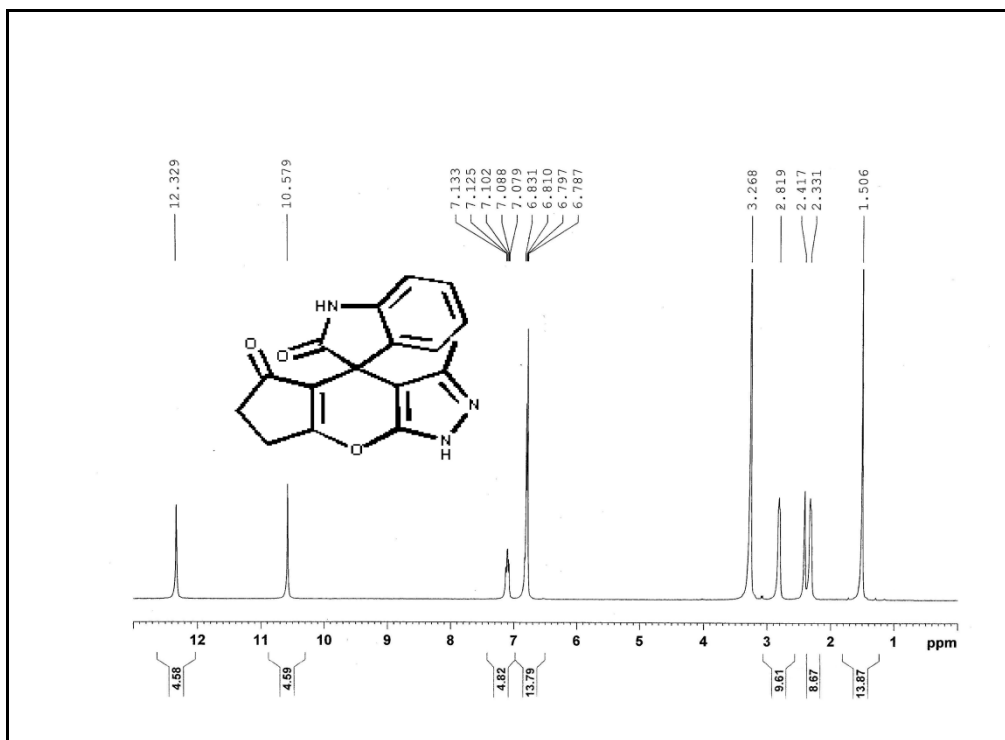
¹³C NMR of 7h



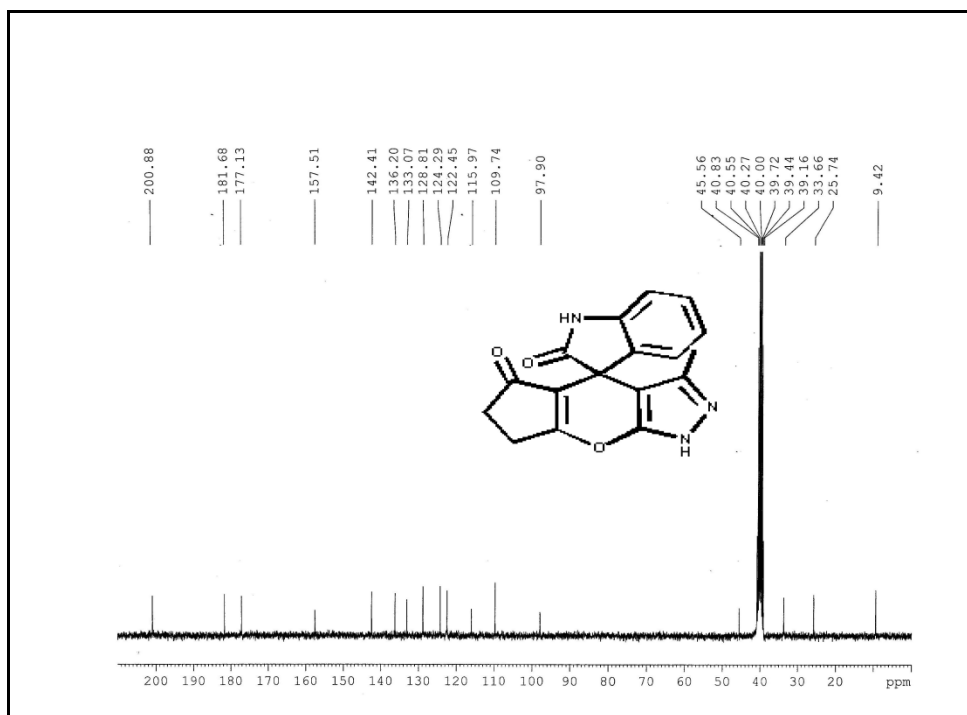
¹H NMR of 7i



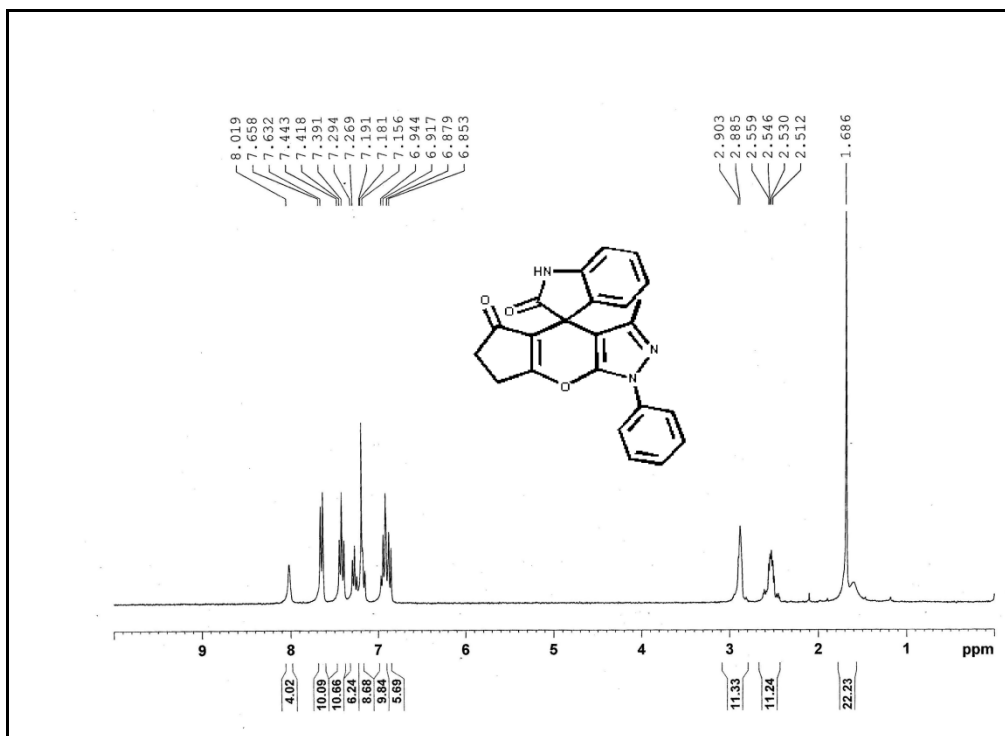
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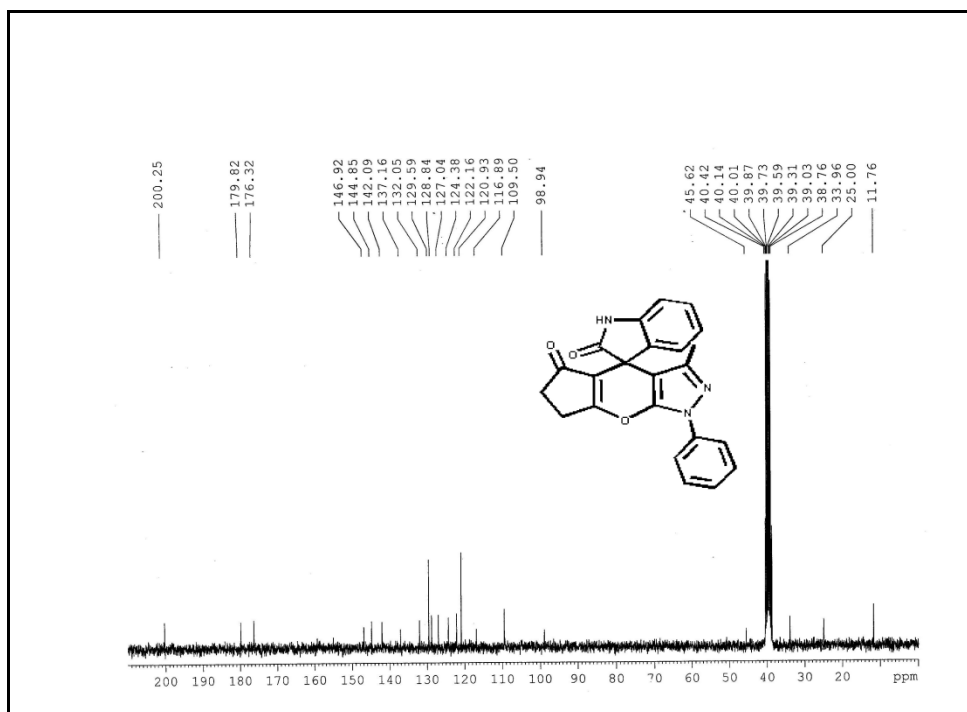
¹H NMR of 7j



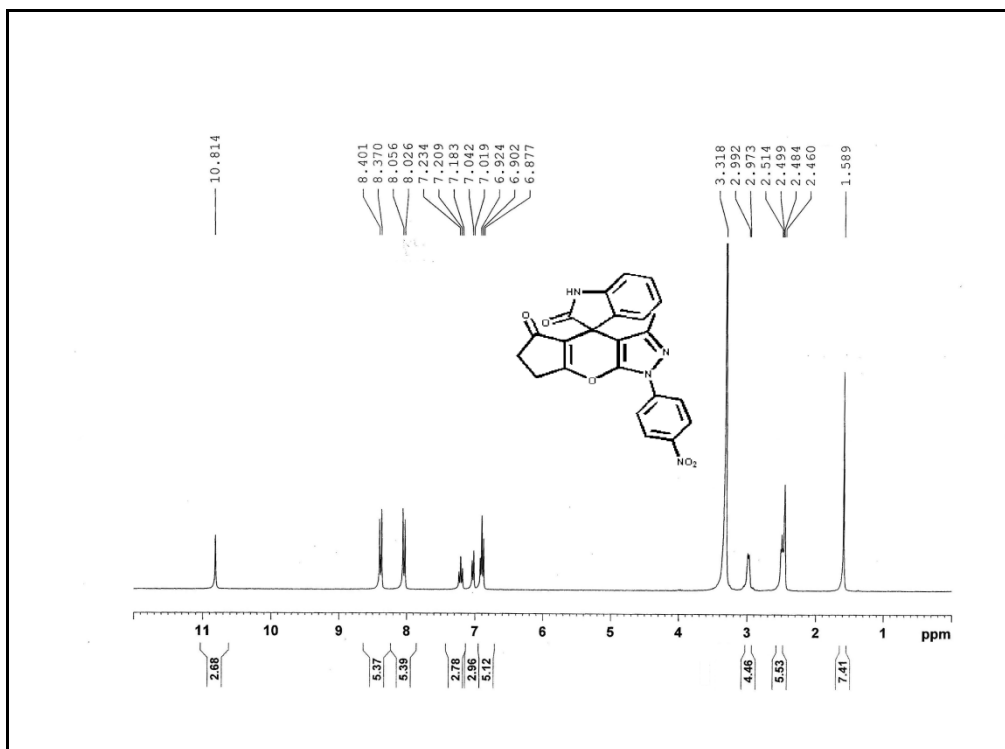
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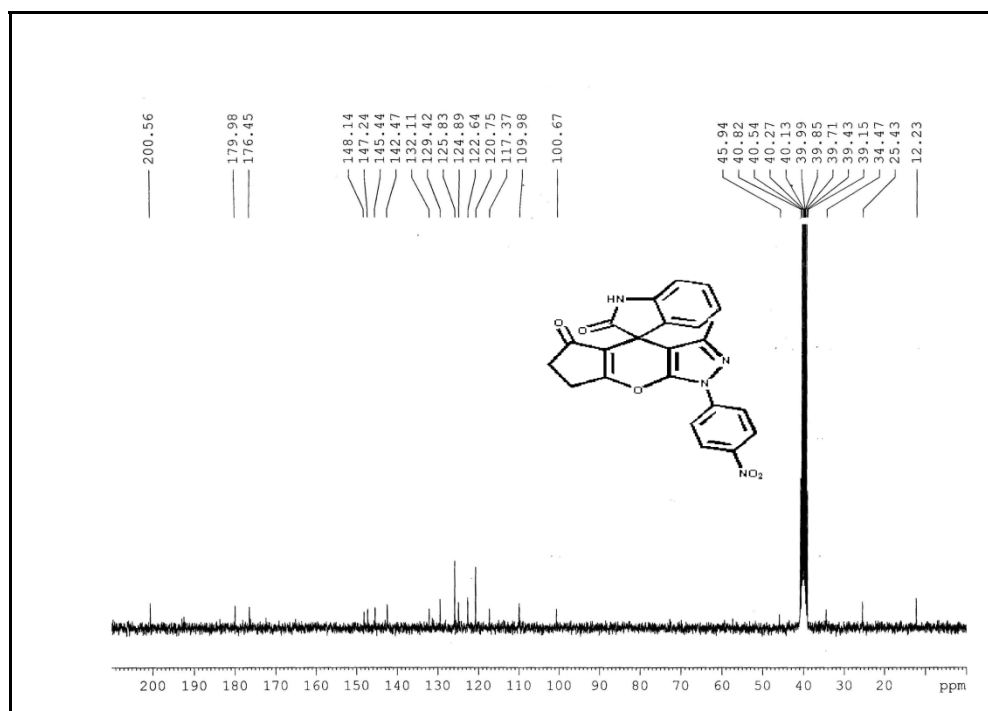
¹H NMR of 7k



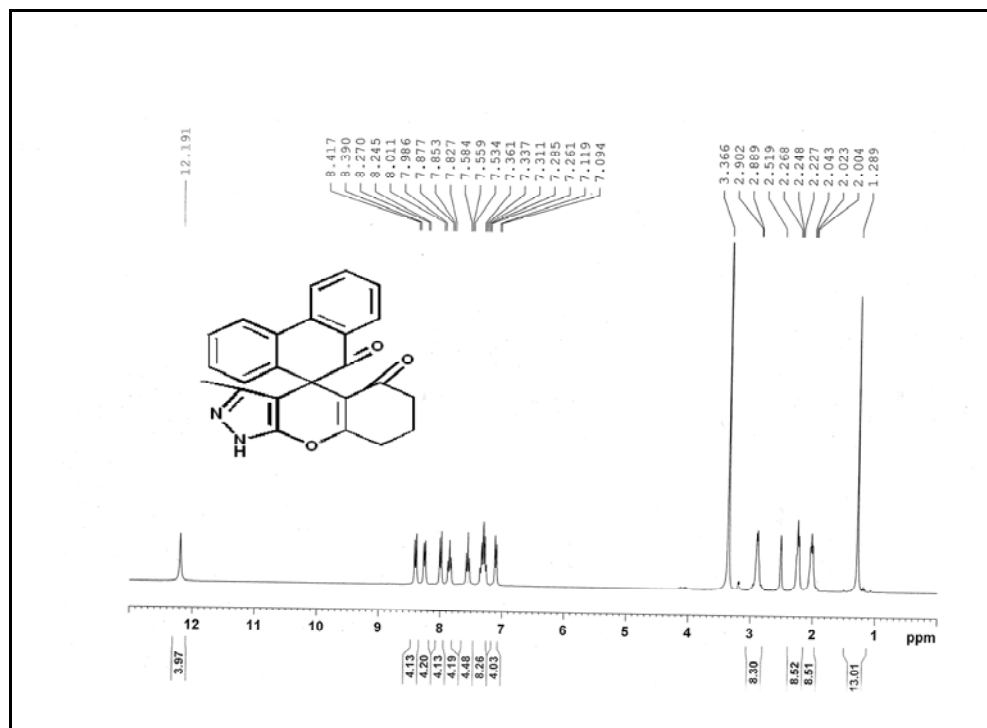
¹³C NMR of 7k



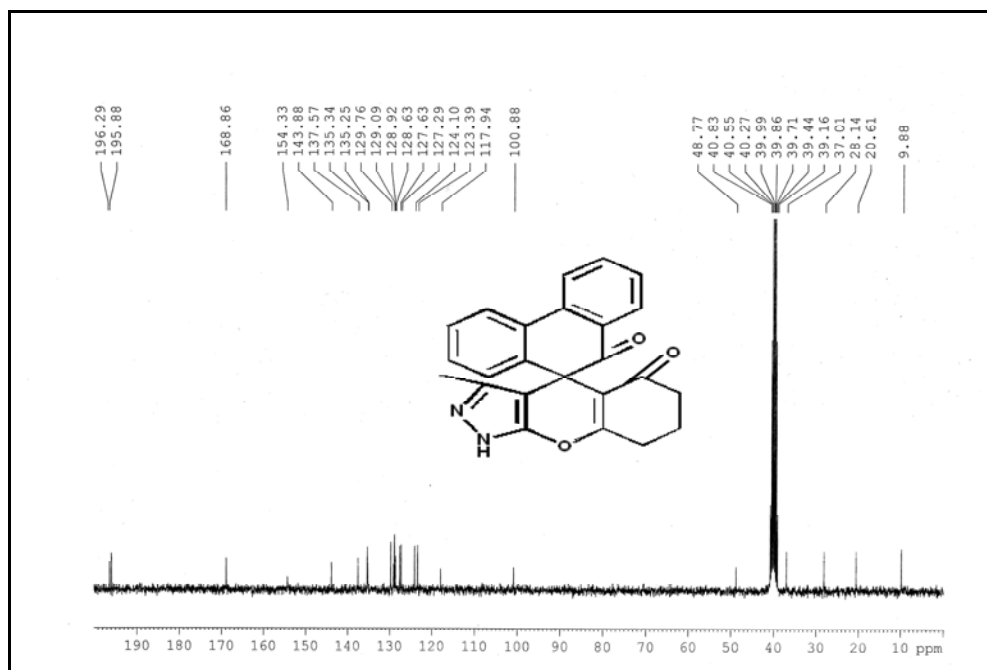
¹H NMR of 71



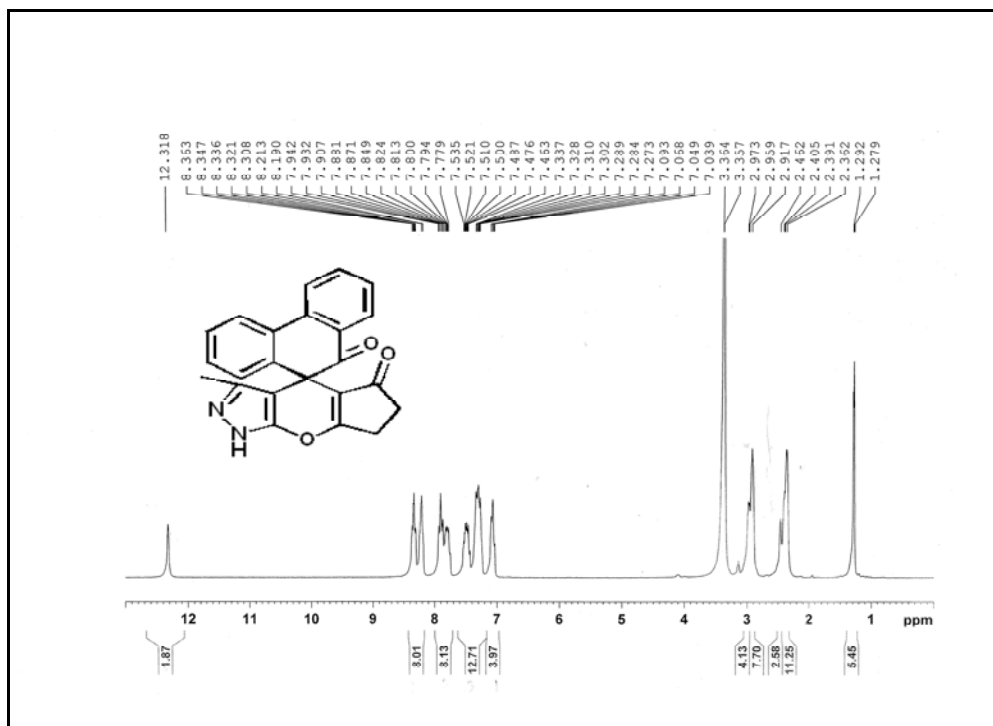
¹³C NMR of 71



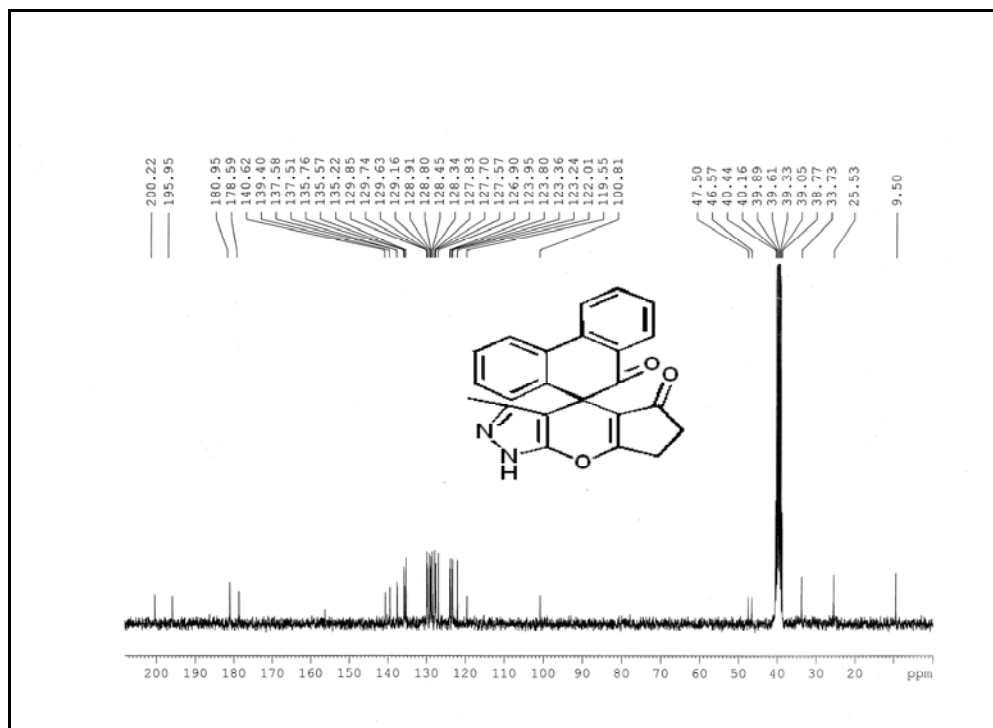
¹H NMR of 8a



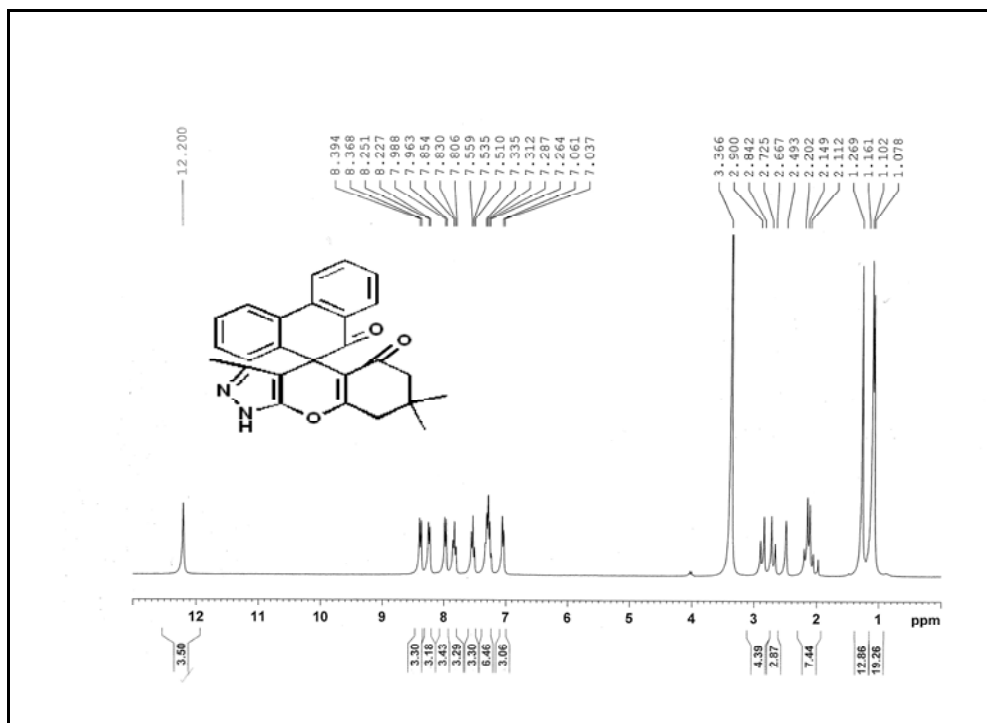
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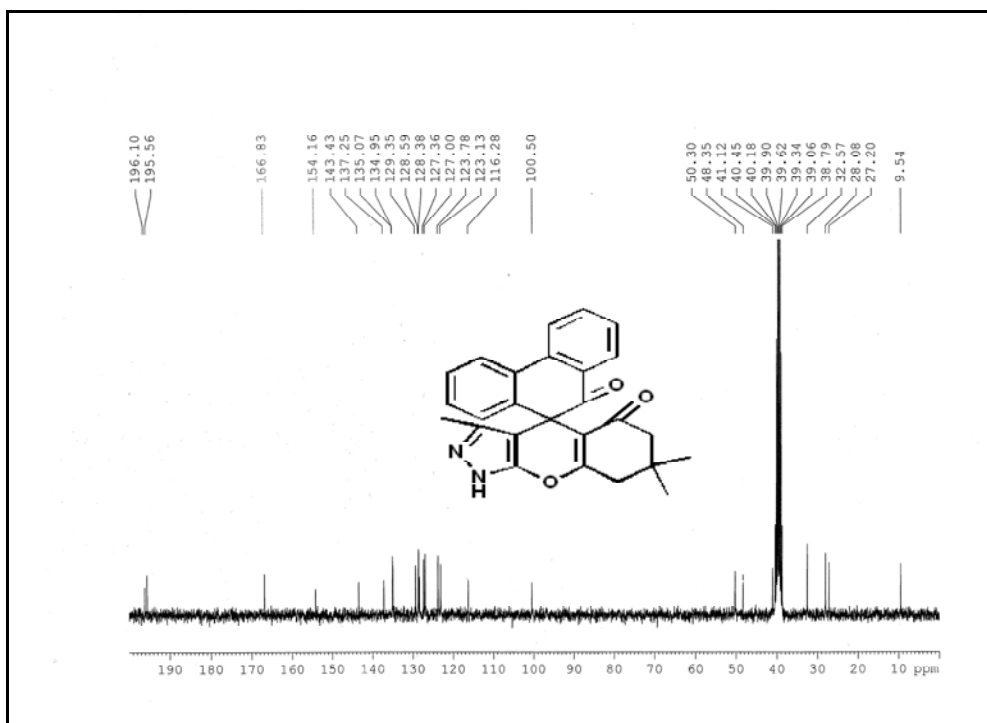
¹H NMR of 8b



¹³C NMR of 8b



$^1\text{H NMR}$ of 8c



$^{13}\text{C NMR}$ of 8c