Supporting Information

The unprecedented synthesis of novel spiro-1,2,4-triazolidinones

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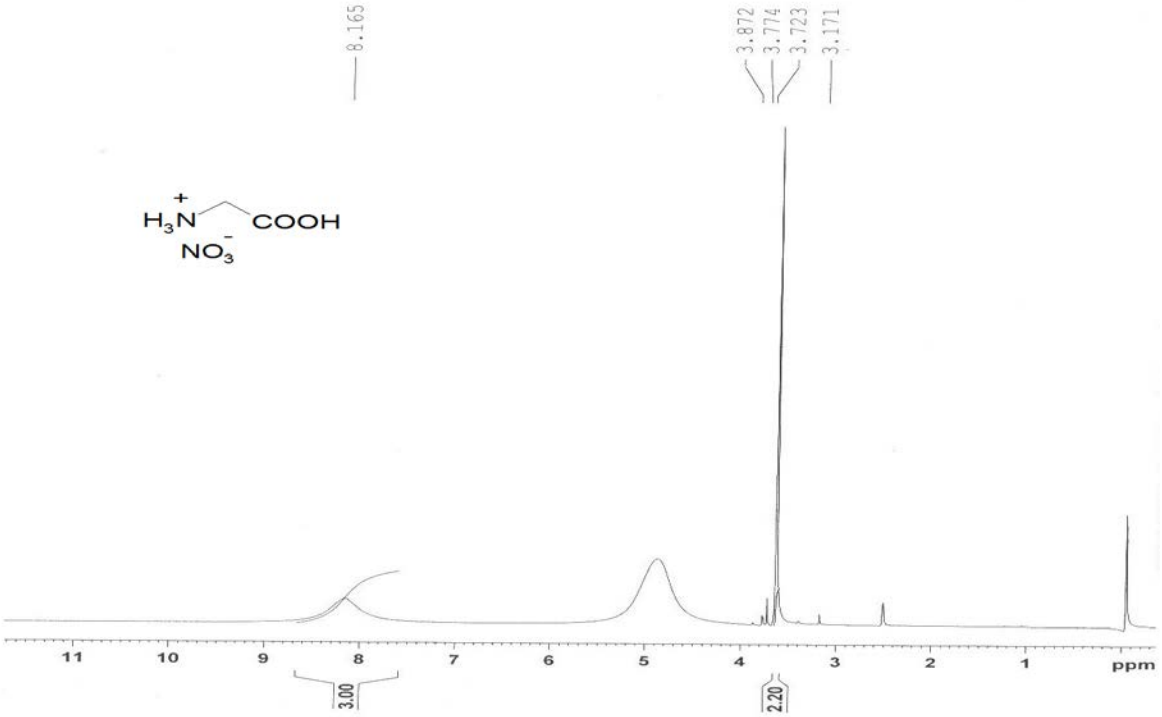
A. General:

IR spectra were recorded on a Perkin–Elmer FT-IR 783 spectrophotometer. NMR spectra were recorded on a BrukerAC-300 MHz spectrometer in DMSO-d_6 using tetramethylsilane as internal standard. Mass spectra were recorded on a Shimadzu QP2010 GCMS. Ionic liquids Gly-NO_3^- Gly-PF_6^- and Gly-Cl^- were prepared following the literature procedure[19].

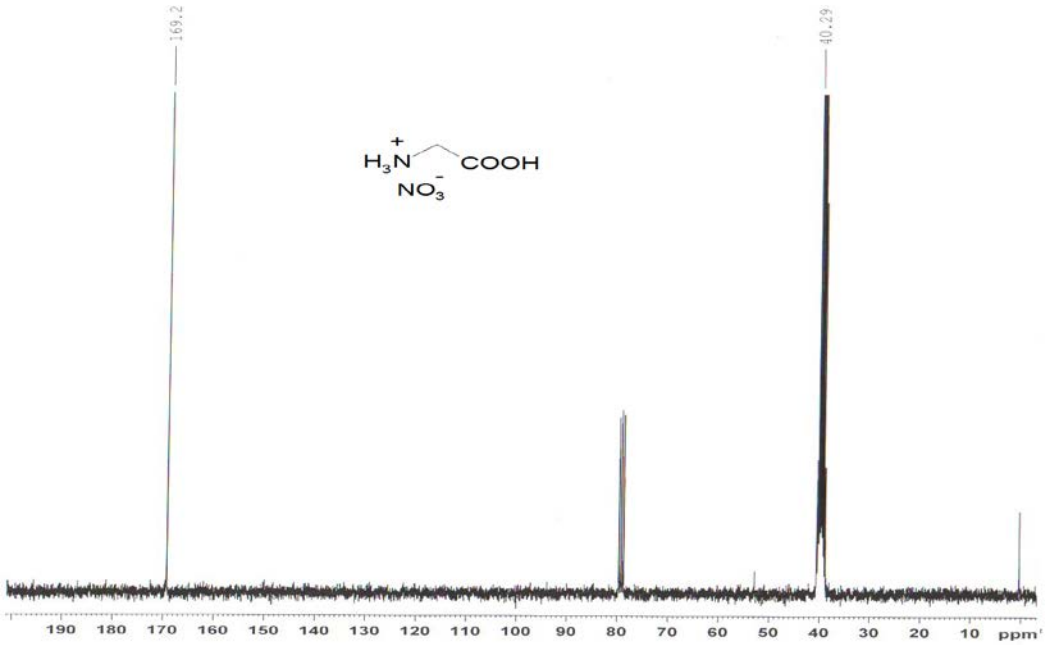
B. Typical procedure:

In a 50 mL round-bottom flask, to a mixture of isatin (1 mmol) and semicarbazide or thio semicarbazide (1.2 mmol) in water (5 mL), glycine nitrate (50 mol %) was added. The reaction mixture was stirred at 80 ^{0}C for the time specified in Table 2. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered to yield corresponding product. These products were characterized by usual spectral techniques. (*i.e.* IR, ^{1}H; ^{13}C NMR and MS).

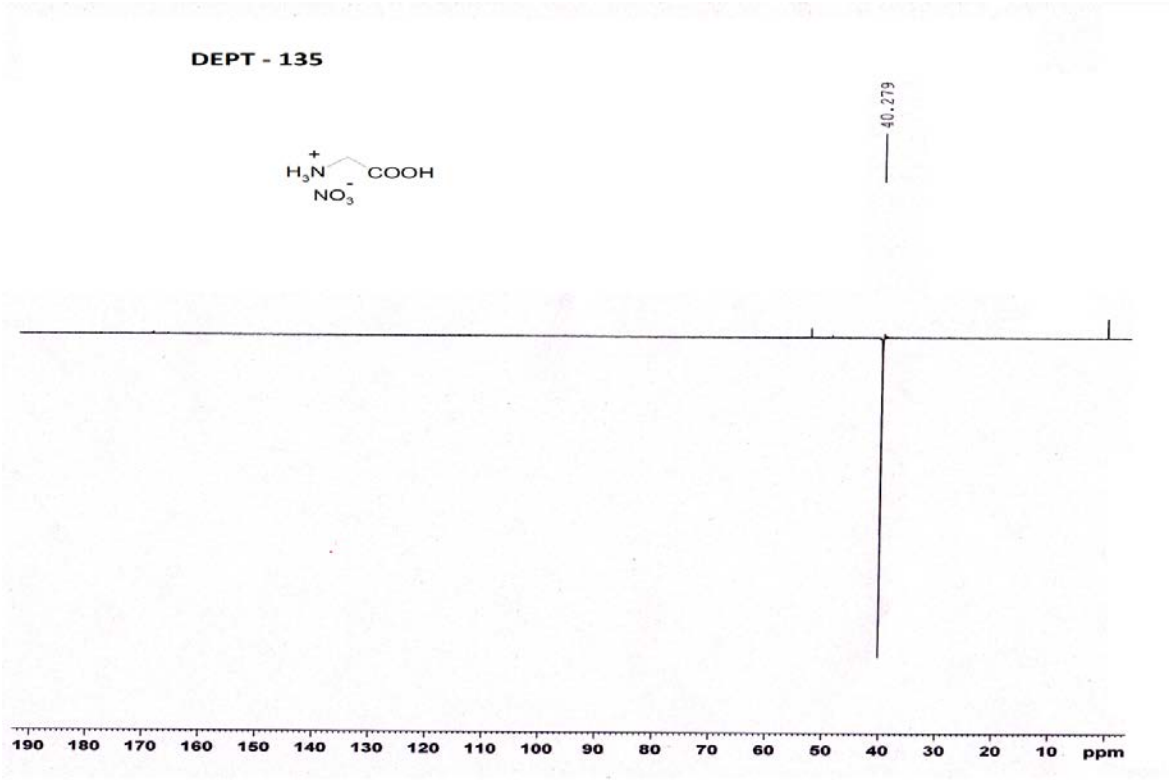
Spectral data of Gly-NO_3^- ionic liquid: ^{1}H-NMR (300 MHz, DMSO-d_6): δ 8.16 (s, 3H, -NH_3), 3.72 (s, 2H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 169.20, 40.29.



^{1}H-NMR of Gly-NO_3^- ionic liquid



^{13}C-NMR of Gly-NO_3^- ionic liquid



DEPT- 135 of Gly-NO_3^- ionic liquid

Spectral data of synthesized compounds:

Entry a, Table 2a: Yellow solid; M.P. 255-257 ^{0}C; IR (KBr): 3625, 3402, 3344, 3169, 1721, 1695, 1606, 1452, 1353, 1199, 1164, 1111, 952 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d$_6$) : δ 10.74 (s, 1H, -NH, D$_2$O exchangeable), 10.19 (s,1H, -NH, D$_2$O exchangeable), 8.04-8.07 (d, 1H, *J*=15 Hz), 7.31-7.36 (t, 1H, *J* = 15 Hz), 7.00-7.05 (t, 1H, *J*=15 Hz), 6.87-6.93 (s, 1H, s, 2-NH, D$_2$O exchangeable). ^{13}C-NMR (75 MHz, DMSO-d$_6$): Due to insufficient solubility we are unable to scan its ^{13}C NMR; MS (EI): 204.18 (m/z).

Entry b, Table2a: Yellow solid; M.P. 265-267 ^{0}C (dec); IR (KBr) : 3469, 3200, 3180, 1718, 1694, 1591, 1476, 1195, 1114, 867 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d$_6$) : δ 10.85 (s, 1H, -NH, D$_2$O exchangeable), 10.48 (s, 1H, -NH, D$_2$O exchangeable), 8.37 (s, 1H), 7.50 (s, 1H), 6.85 (s, 3H); ^{13}C-NMR (75 MHz, DMSO-d$_6$): δ 165, 156.34, 142.37, 134.18, 131.98, 127.86, 117.73, 113.88, 112.60; MS (EI): 283.08 (m/z), 285 (M+2).

Entry c, Table 2a: Yellow solid; M.P. 289-290 ^{0}C (dec); IR (KBr) : 3200, 1718, 1693, 1592, 1476, 1441, 1398, 1300, 1200, 1114, 966 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d$_6$) : δ 10.85 (s, 1H, -NH, D$_2$O exchangeable), 10.46 (s,1H, -NH, D$_2$O exchangeable), 8.25-8.26 (d, 1H, *J* = 3Hz), 7.362-7.396 (dd, 1H, *J* = 8.4, 8.1Hz), 6.87-6.94 (s, 1H, s, 2-NH, D$_2$O exchangeable); ^{13}C NMR (75 MHz, DMSO-d$_6$): δ 165.15, 156.31, 141.99, 132.09, 131.35, 126.21, 125.24, 117.25, 112.11; MS (EI): 238.63 (m/z).

Entry d, Table 2a: Yellow solid; M.P. 277-278 ^{0}C; IR (KBr) : 3484, 3463, 3415, 3394, 3343, 3164, 1710, 1679, 1587, 1193, 1095, 825 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d$_6$) : δ 10.78 (s, 1H, -NH, D$_2$O exchangeable), 10.45 (s, 1H, -NH, D$_2$O exchangeable), 8.46 (s, 1H), 7.656-7.679 (dd, 1H, *J* = 6, 6Hz), 6.72-7.05 (m, 1H, s, 2-NH, D$_2$O exchangeable); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 164.14, 155.88, 142.34, 141.51, 132.67, 117.71, 112.56, 84.41; MS (EI): 330.08 (m/z).

Entry e, Table 2a: Pale yellow solid; M.P.> 300 ^{0}C; IR (KBr): 3504, 3384, 3156, 3117, 1717, 1583, 1479, 1347, 1309, 1200, 1146, 1103, 960 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d$_6$) : δ 11.28 (s, 1H, -NH, D$_2$O exchangeable), 10.96 (s,1H, -NH, D$_2$O exchangeable), 9.04 (s, 1H), 8.116-8.183 (dd, 1H, *J* = 11.4, 18Hz), 6.90-7.00 (s, 1H, s, 2-NH, D$_2$O exchangeable)^{13}C (75 MHz,

DMSO-d_6): δ 165.94, 156.67, 148.62, 142.64, 130.69, 127.69, 121.16, 115.87, 110.63; MS (EI): 249.18 (m/z).

Entry f, Table 2a: Yellow solid; M.P. 291-293 ^{0}C; IR (KBr) : 3175, 1689, 1585, 1483, 1400, 1330, 1225, 1167, 1077, 916 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6) : δ 10.64 (s, 1H, -NH, D_2O exchangeable), 10.07 (s,1H, -NH, D_2O exchangeable), 7.78 (s, 1H), 6.92- 6.97 (s, 1H, s, 2-NH, D_2O exchangeable), 2.24 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 165.91, 156.58, 139.51, 134.07, 133.80, 131.00, 123.58, 119.72, 115.86, 20.84, 16.45; MS (EI): 232.23 (m/z).

Entry g, Table 2a: Yellow solid; M.P. 267-269 ^{0}C; IR (KBr) : 3498, 3451, 3322, 3270, 1687, 1573, 1475, 1336, 1191, 1091, 973 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6) : δ 10.54 (s, 2H, -NH, D_2O exchangeable), 8.38 (s,2H, -NH, D_2O exchangeable), 7.53-7.55 (d, 2H, *J* = 6Hz), 6.99-7.12 (s, 2H, s, 4-NH, D_2O exchangeable), 3.78 (s, 4H), 1.92 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 163.88, 156.42, 142.41, 133.98, 130.80, 127.66, 117.17, 114.67, 111.47, 33.77, 25.55; MS (EI): 606.22 (m/z).

Entry h, Table 2b: Yellow solid. M.P. 250-252 ^{0}C; IR (KBr) : 3268, 3170, 1673, 1595, 1500, 1465, 1349, 1302, 1256, 1150, 1063 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6) : δ 12.47 (s, 1H, -NH, D_2O exchangeable), 11.21(s, 1H, -NH, D_2O exchangeable), 9.04 (s. 1H, -NH, D_2O exchangeable) 8.69 (s, 1H, -NH, D_2O exchangeable) 7.64-7.66(d, 1H, *J* = 6 Hz), 7.32-7.37(td, 1H, *J* = 1.2, 7.8Hz), 7.06-7.11(t, 1H, *J* = 15Hz), 6.91-6.94(d, 1H, *J* =9Hz): ^{13}C NMR (75 MHz, DMSO-d_6) : δ 179.15, 163.09, 142.80, 132.51, 131.73, 122.84, 121.42, 120.43, 111.50; MS (EI): 220.25 (m/z).

Entry i Table 2b: Yellow solid. M.P. 268-270 ^{0}C; IR (KBr): 3423, 3327, 3167, 1696, 1607, 1491, 1462, 1310, 1204, 1143 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 12.28 (s, 1H, -NH, D_2O exchangeable), 11.29 (s, 1H, -NH, D_2O exchangeable), 9.11 (s, 1H, -NH, D_2O exchangeable), 8.82 (s, 1H, -NH, D_2O exchangeable), 7.87 (s, 1H), 7.48-7.51 (d, 1H, *J* = 9Hz) 6.86-6.89 (d,1H, *J* = 9Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ 179.23, 162.70, 141.81, 133.65, 131.10, 123.92, 122.78, 114.62, 113.41; MS (EI): 299.14 (m/z), 301 (M+2).

Entry j, Table 2b: Yellow solid; M.P. 280-282 ^{0}C ; IR (KBr): 3427, 3321, 3221, 3163, 1697, 1608, 1573, 1491, 1467, 1203, 1142, 854, 812 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 12.30 (s, 1H, -NH, D_2O exchangeable), 11.29 (s, 1H, -NH, D_2O exchangeable), 9.11(s, 1H, -NH, D_2O exchangeable), 8.81 (s, 1H, -NH, D_2O exchangeable), 7.74-7.75 (d, 1H, *J* =3Hz), 7.36-7.39 (dd, 1H, *J* = 8.4, 8.4Hz), 6.92-6.94 (d, 1H, *J* = 6Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ 179.24, 162.86, 141.44, 131.26, 130.90, 126.98, 122.38, 121.11, 112.98; MS (EI): 254.69 (m/z).

Entry k, Table 2b: Yellow solid; M.P. 266-268 ^{0}C; IR (KBr): 3446, 3316, 3160, 3139, 3116, 1687, 1571, 1465, 1434, 1280, 1201, 1133, 1078, 887, 846, 821, 763 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 12.29 (s, 1H, -NH, D_2O exchangeable), 11.28 (s, 1H, -NH, D_2O exchangeable), 9.08 (s, 1H, -NH, D_2O exchangeable), 8.82 (s, 1H, -NH, D_2O exchangeable), 8.031-8.036 (d,1H, *J* = 1.5Hz), 7.64-7.67 (dd,1H, *J* = 8.4, 8.1Hz), 6.76-6.78 (d,1H, *J* = 6Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ 179.51, 162.34, 142.07, 139.17, 130.74, 129.52, 122.62, 113.44, 85.03; MS (EI): 346.14 (m/z).

Entry l, Table 2b: Yellow solid; M.P. >300 ^{0}C; IR (KBr): 3376, 3278, 3195, 3068, 1697, 1610, 1516, 1459, 1337, 1298, 1135, 1091, 1048, 917 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 12.20 (s, 1H, -NH, D_2O exchangeable), 11.78 (s, 1H, -NH, D_2O exchangeable), 9.18 (s, 1H, -NH, D_2O exchangeable), 9.02 (s, 1H, -NH, D_2O exchangeable), 8.57-8.58 (d, 1H, *J* = 3Hz), 8.224-8.261 (dd,1H, *J* = 8.7, 8.7 Hz), 7.07-7.10 (d,1H, *J* = 9Hz), ^{13}C NMR (75 MHz, DMSO-d_6): δ 179.25, 163.38, 147.82, 143.20, 130.45, 127.35, 121.45, 116.89, 111.61; MS (EI): 265.24 (m/z).

Entry m, Table 2b: Brown solid; M.P. 279-280 ^{0}C; IR (KBr): 3504, 3376, 3252, 3167, 1678, 1616, 1577, 1481, 1304, 1252, 1206, 1135, 1098, 1042, 851 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 12.49 (s, 1H, -NH, D_2O exchangeable), 11.15 (s, 1H, -NH, D_2O exchangeable), 8.99 (s, 1H, -NH, D_2O exchangeable), 8.63 (s, 1H, -NH, D_2O exchangeable), 7.32 (s,1H), 6.98 (s,1H), 2.25 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 179.21, 163.54, 139.17, 133.43, 132.95, 131.65, 120.47, 120.00, 119.14, 20.99, 16.23; MS (EI): 248.30 (m/z).

Entry n, Table 2b: Yellow solid; M.P. 270 ^{0}C; IR (KBr): 3429, 3247, 3150, 1677, 1607, 1493, 1450, 1418, 1372, 1341, 1268, 1218, 1100, 1042, 893 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 9.07 (s, 1H, -NH, D_2O exchangeable), 8.72 (s, 1H, -NH, D_2O exchangeable), 7.67-7.69 (d, 1H, *J*

= 6Hz), 7.41-7.46 (t, 1H, *J* =15 Hz), 7.12-7.17 (t, 2H, *J* = 15Hz), 3.20 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 183.92, 166.01, 148.82, 136.46, 136.40, 128.18, 125.82, 124.42, 115.04, 30.91; 234.27 (m/z).

Entry o, Table 2b: Brown solid, M.P. 269-271 ^{0}C; IR (KBr): 3482, 3465, 3401, 3245, 3151, 1697, 1598, 1467, 1434, 1348, 1263, 1149, 1116, 1072, 902, 802 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6) δ 12.16 (s, 2H, -NH, D_2O exchangeable), 9.06 (s, 2H, -NH, D_2O exchangeable), 8.72 (s, 2H, -NH, D_2O exchangeable), 7.862-7.868 (s, 2H, *J* = 1.8Hz), 7.452-7.486 (dd, 2H, *J* = 8.4, 8.4Hz), 7.08-7.10 (d, 2H, *J* = 6Hz), 3.81-3.85 (t, 4H, *J* = 12Hz), 2.01-2.06 (t, 2H, *J* = 15 Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ 179.25, 160.73, 141.76, 133.29, 129.77, 123.72, 121.98, 115.45, 112.24, 37.69, 25.21; MS (EI): 638.35 (m/z).

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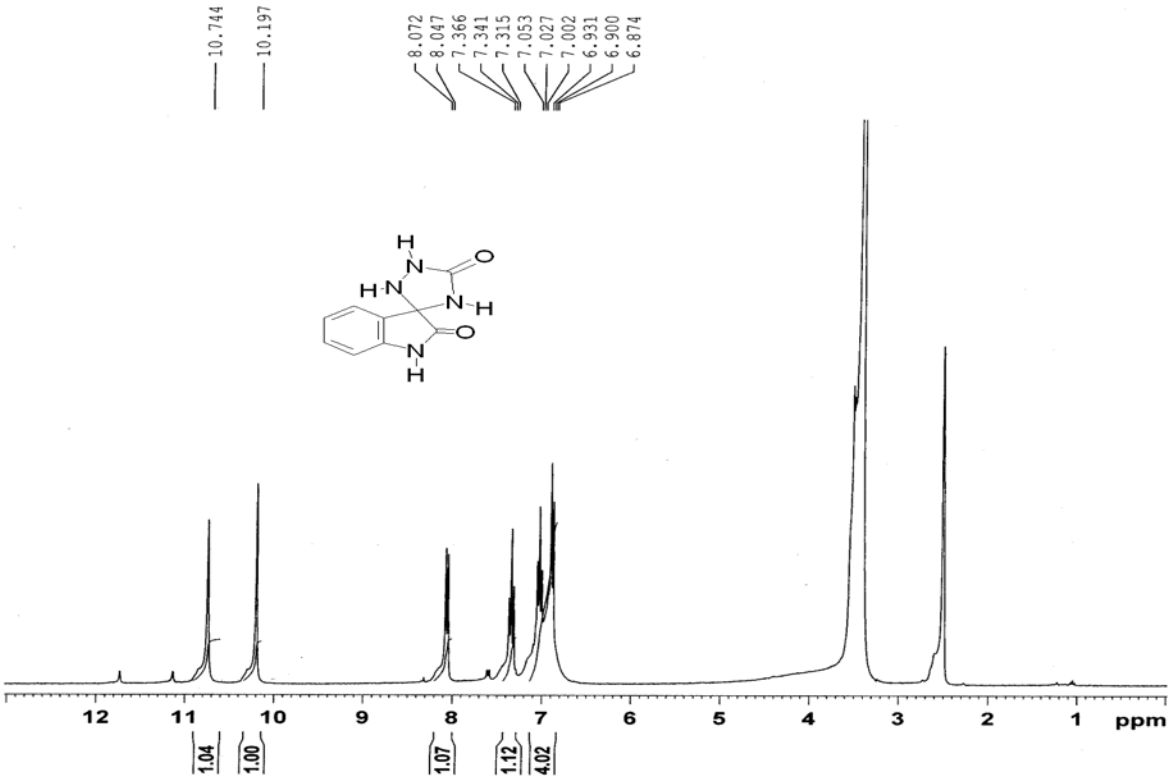

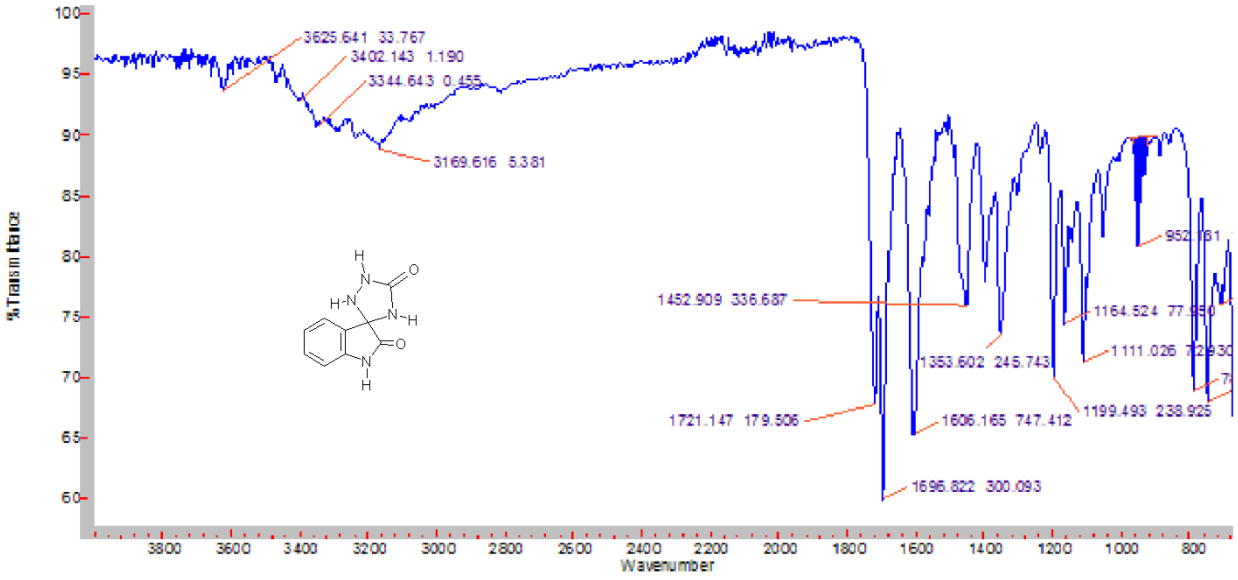

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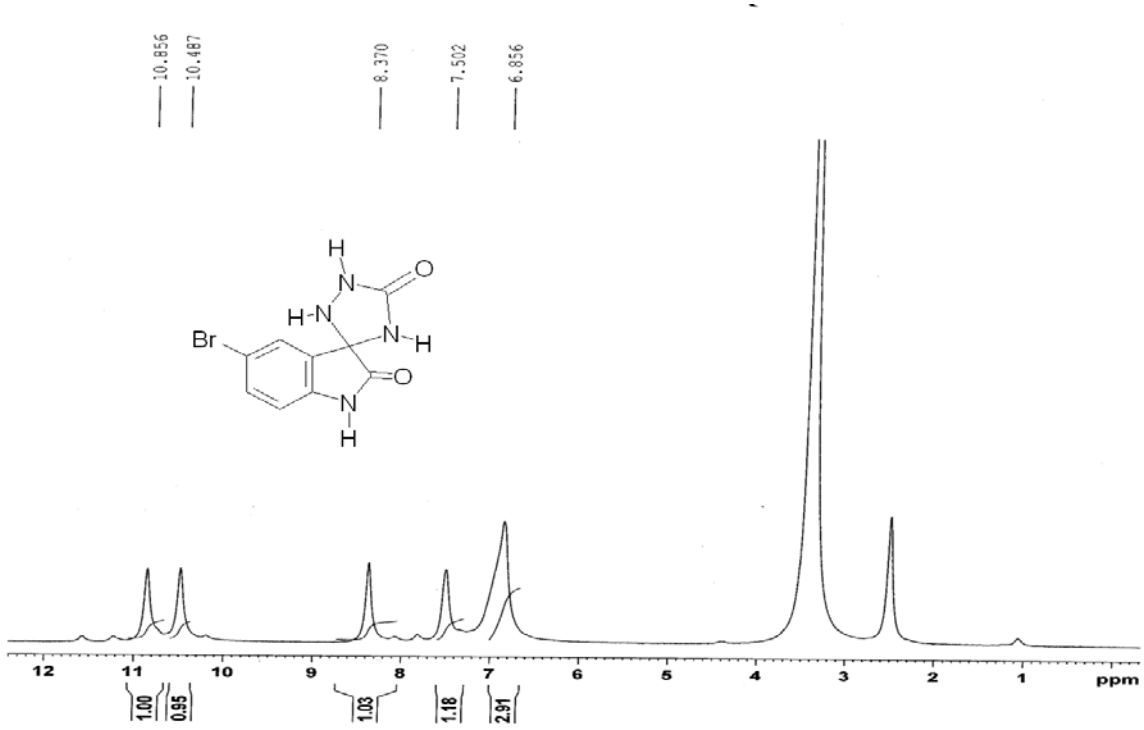

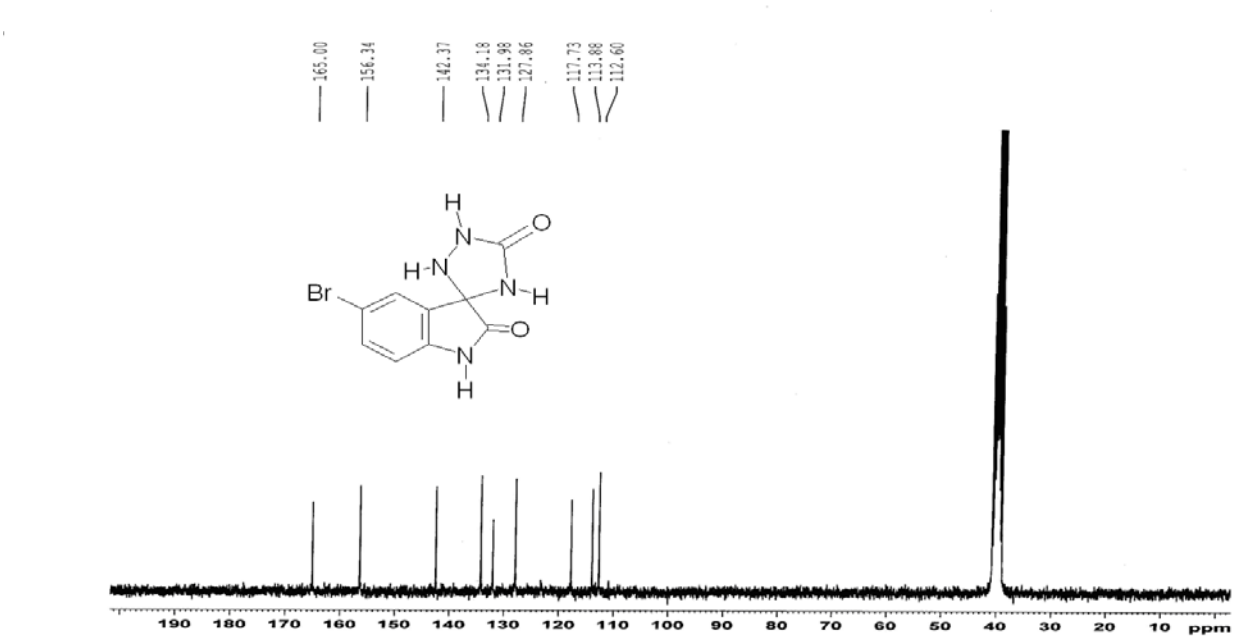

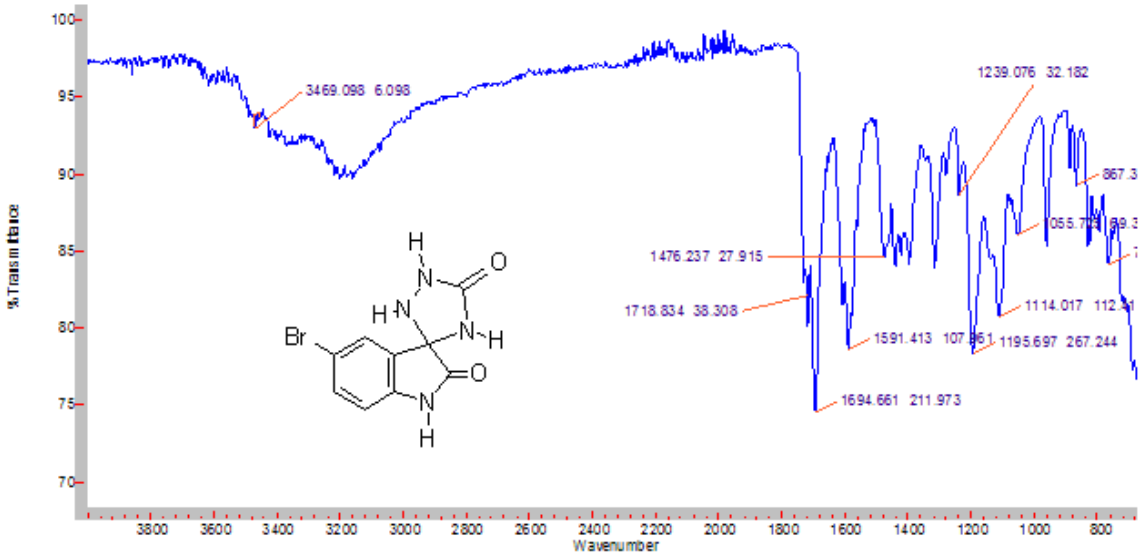

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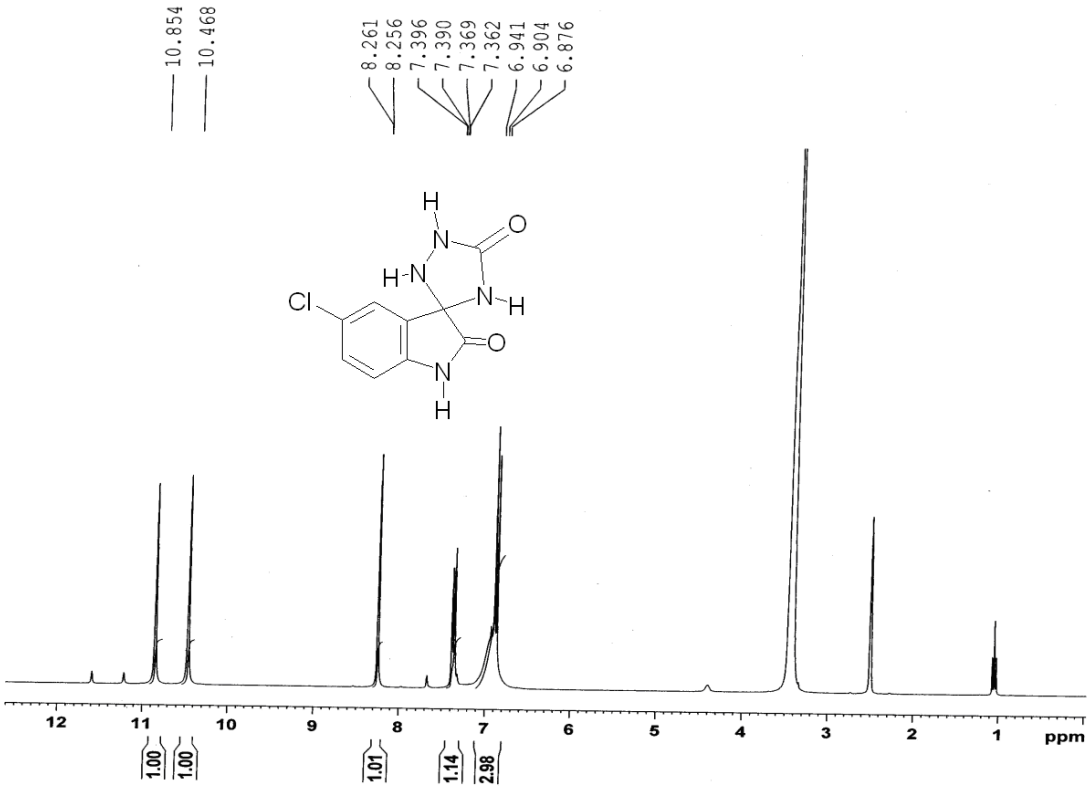

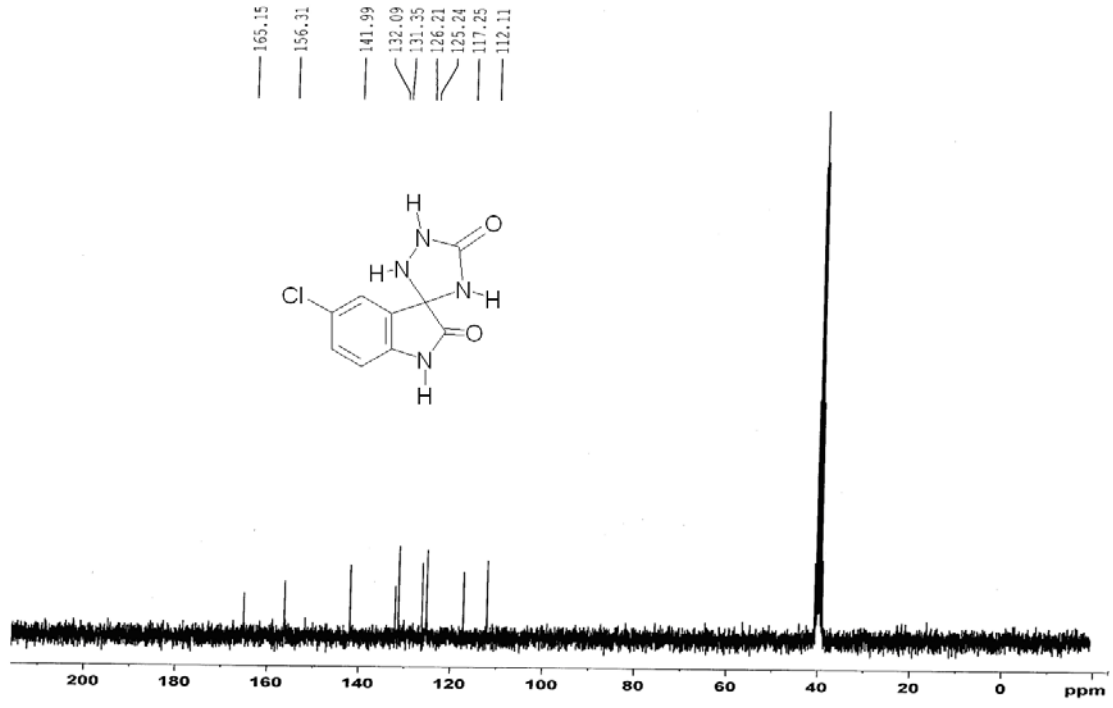

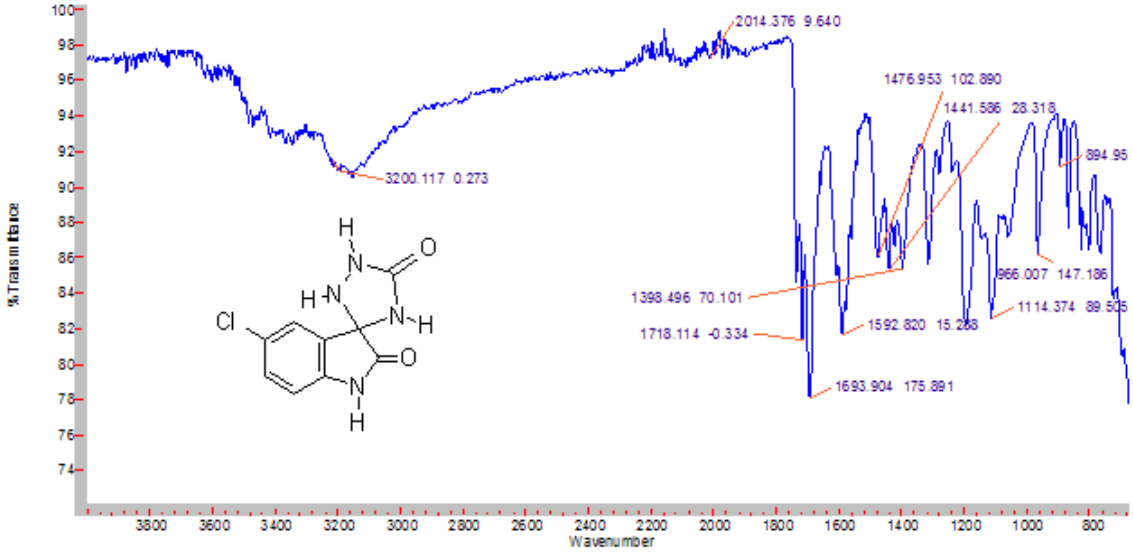

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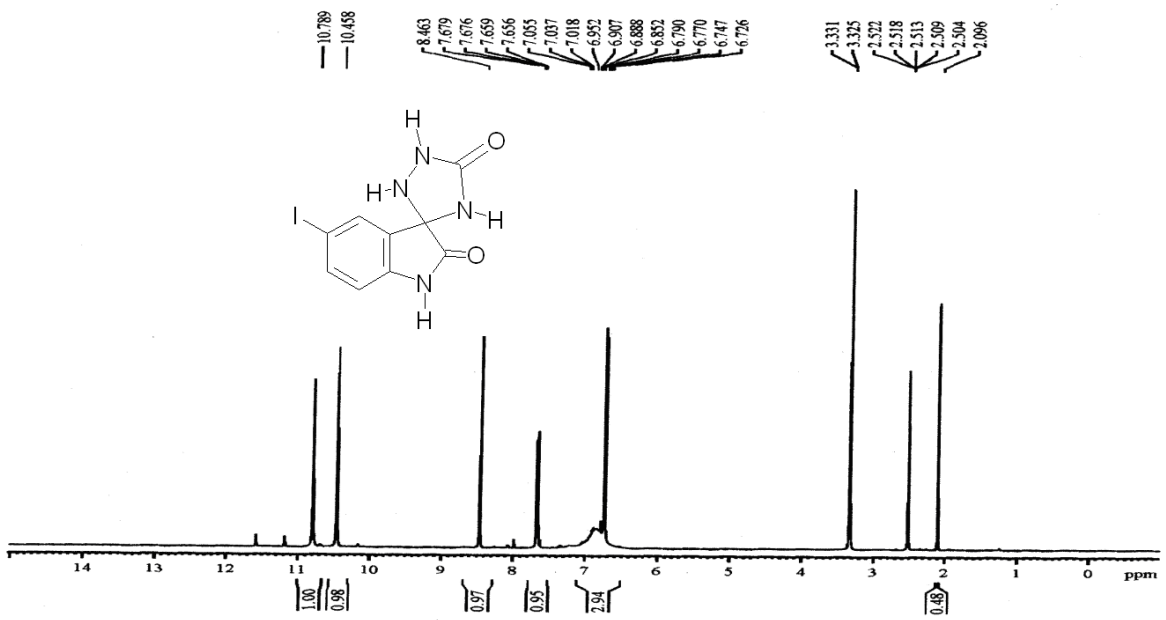

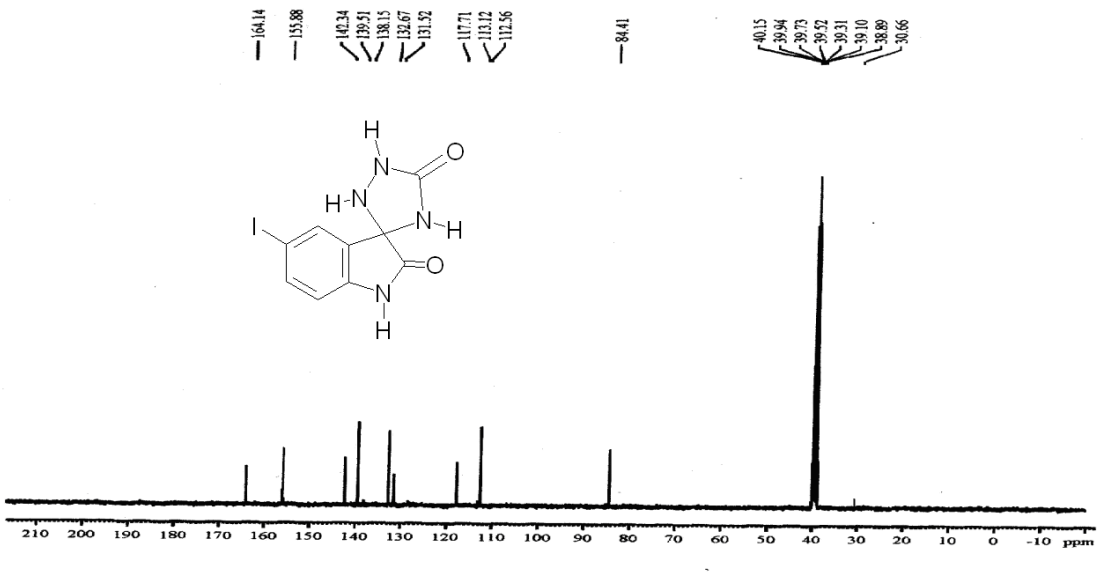

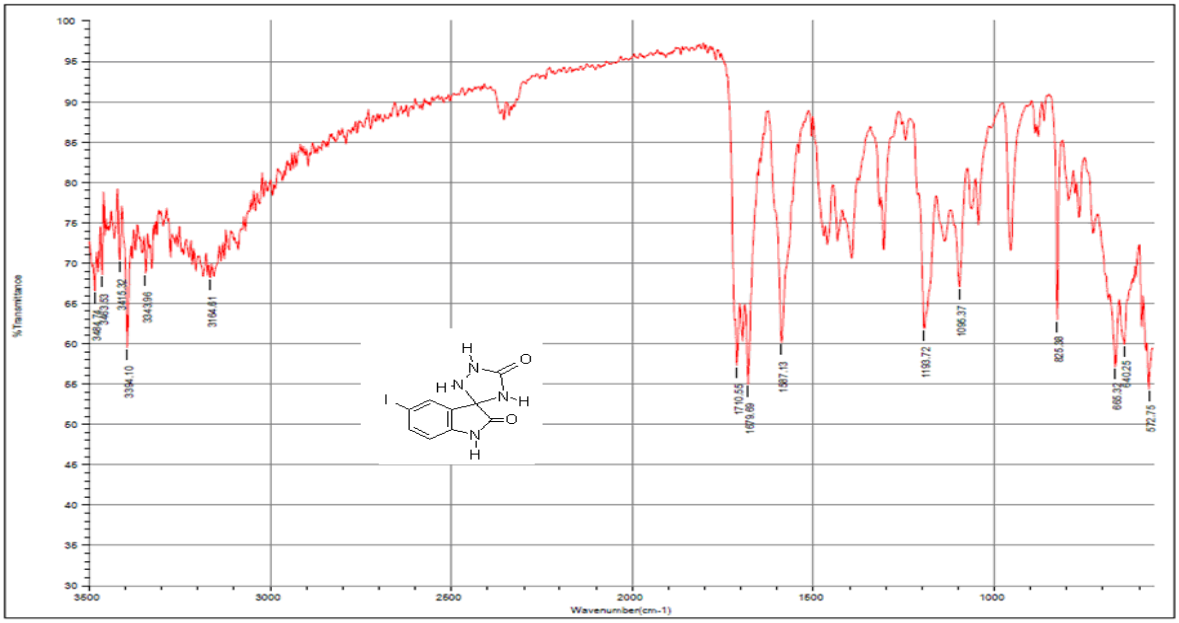

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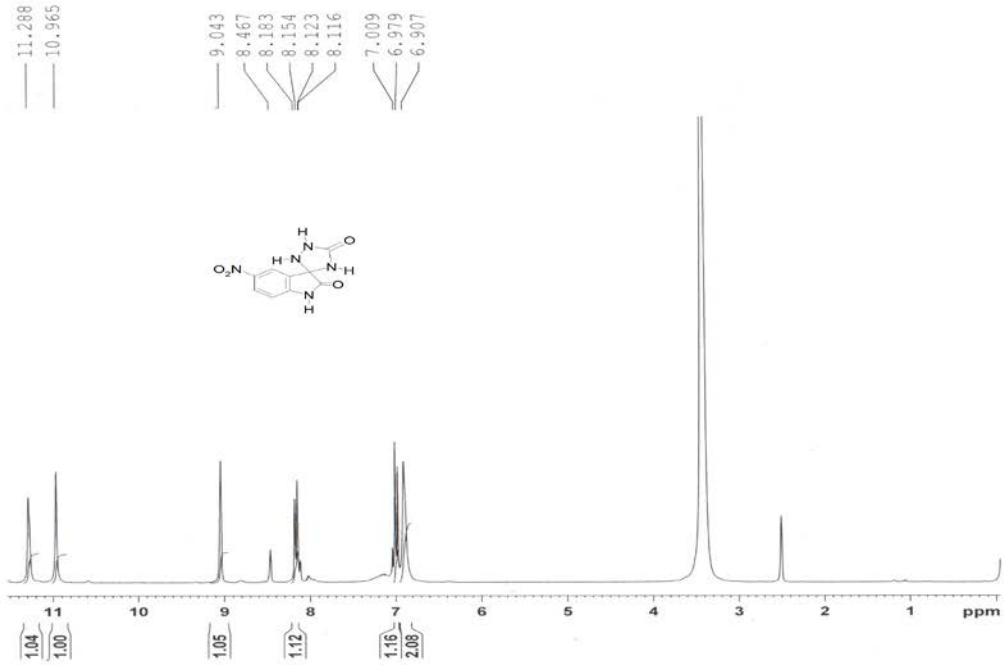

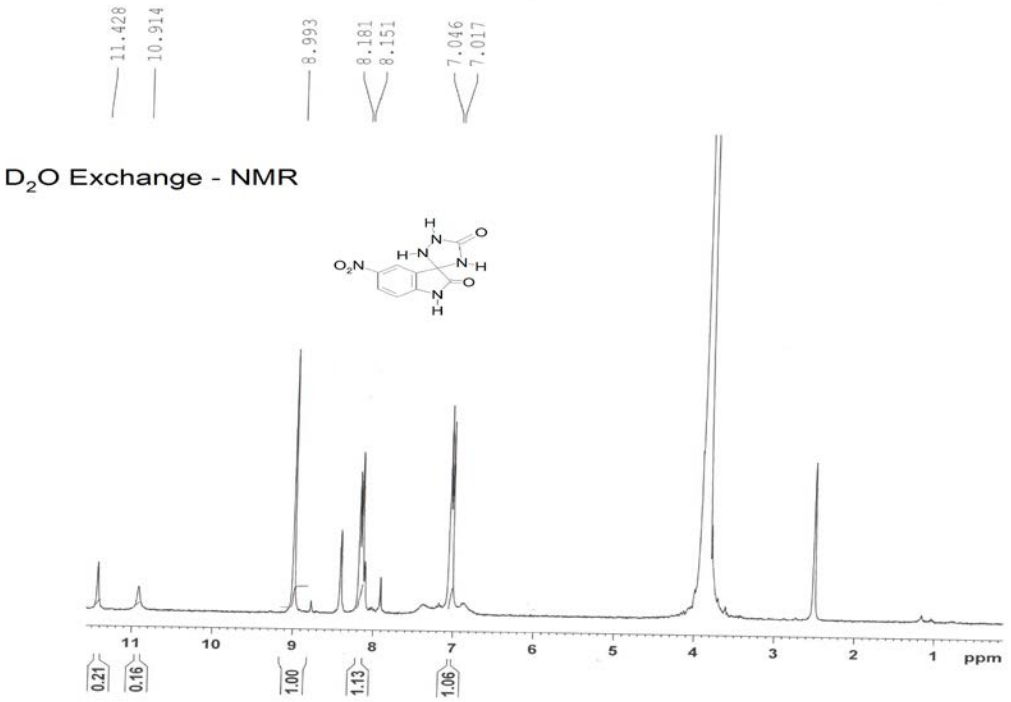

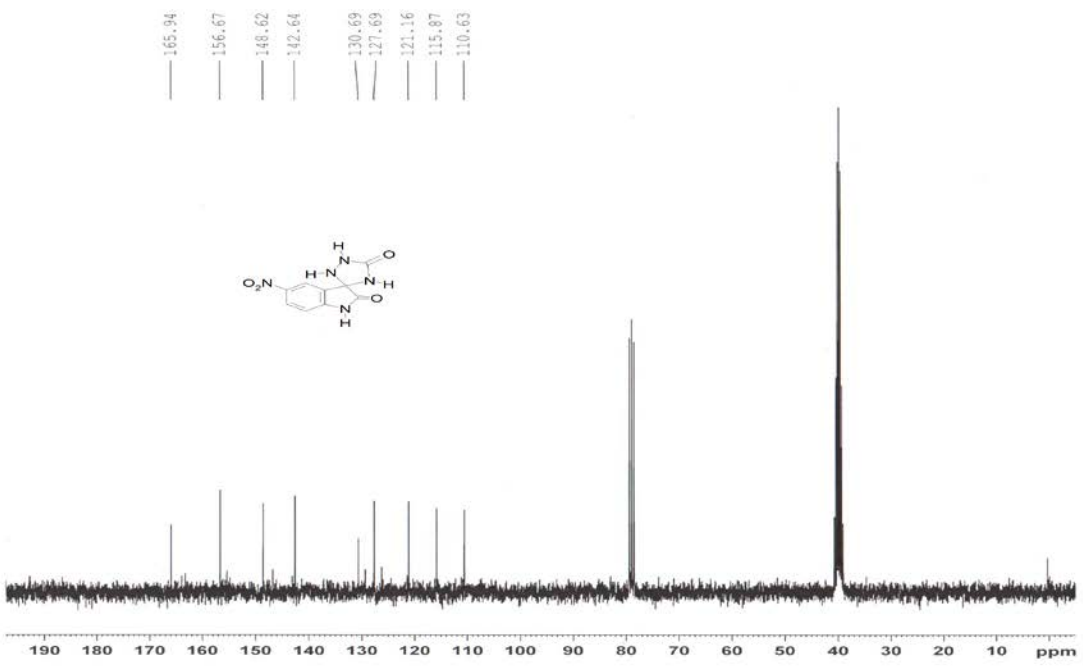

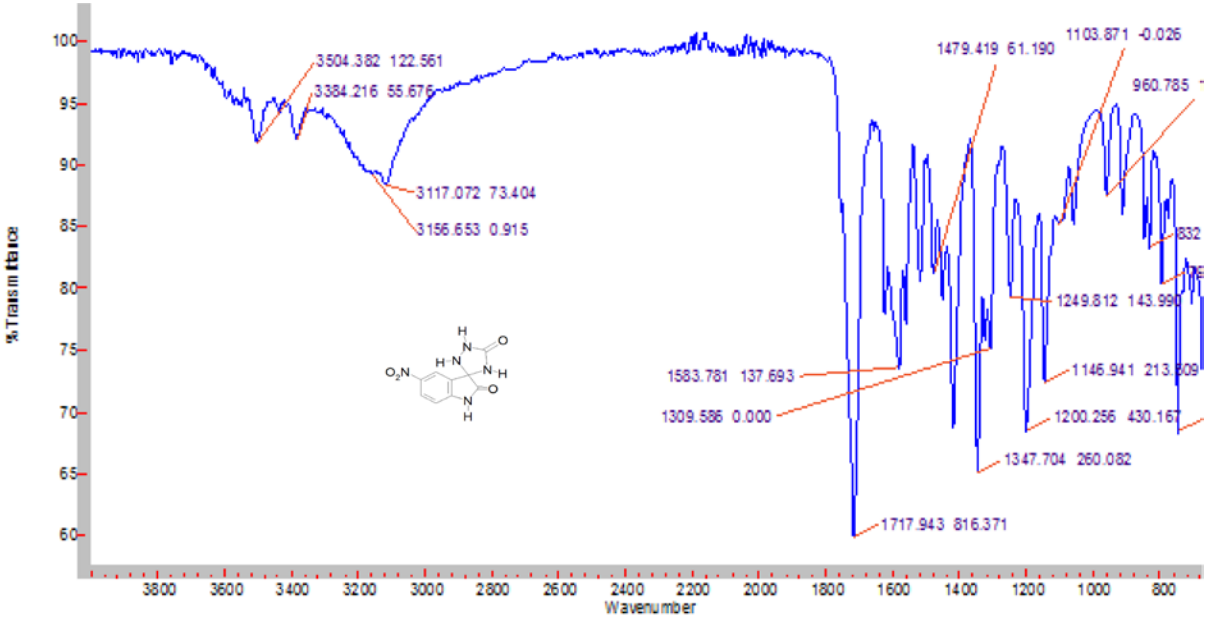

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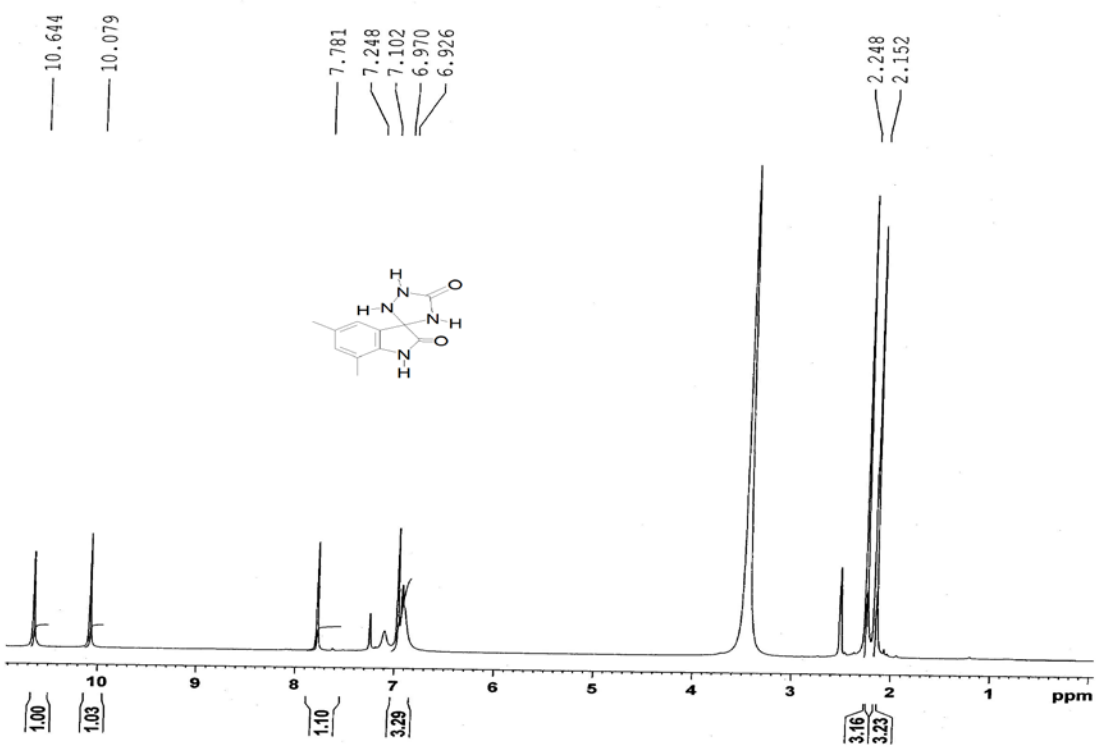

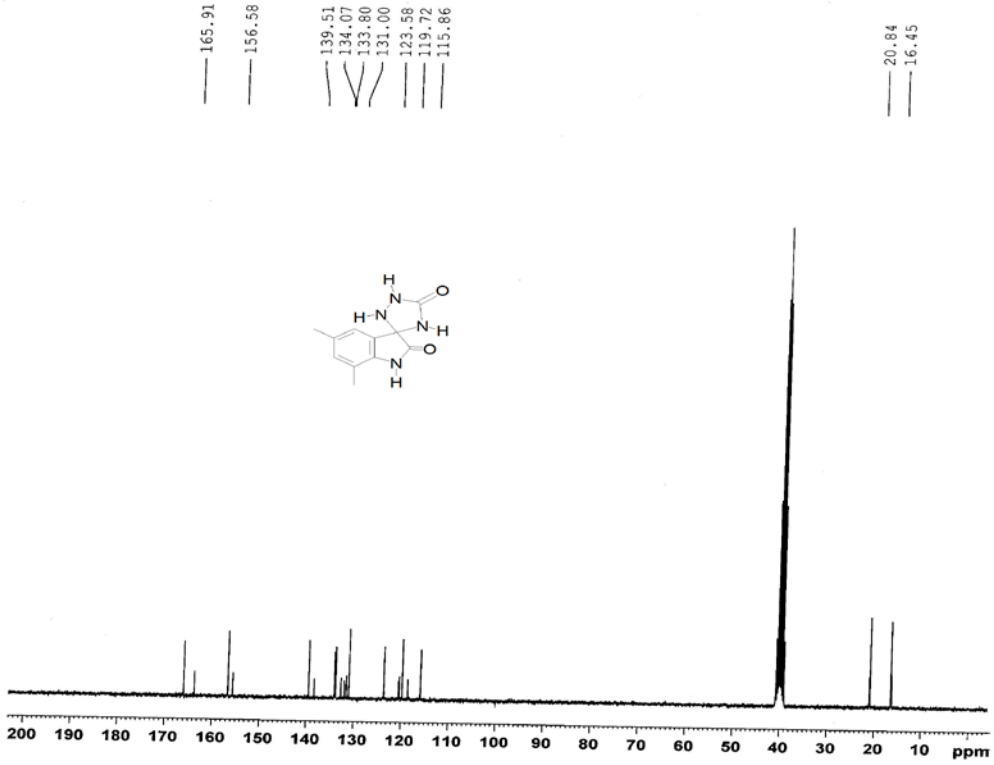

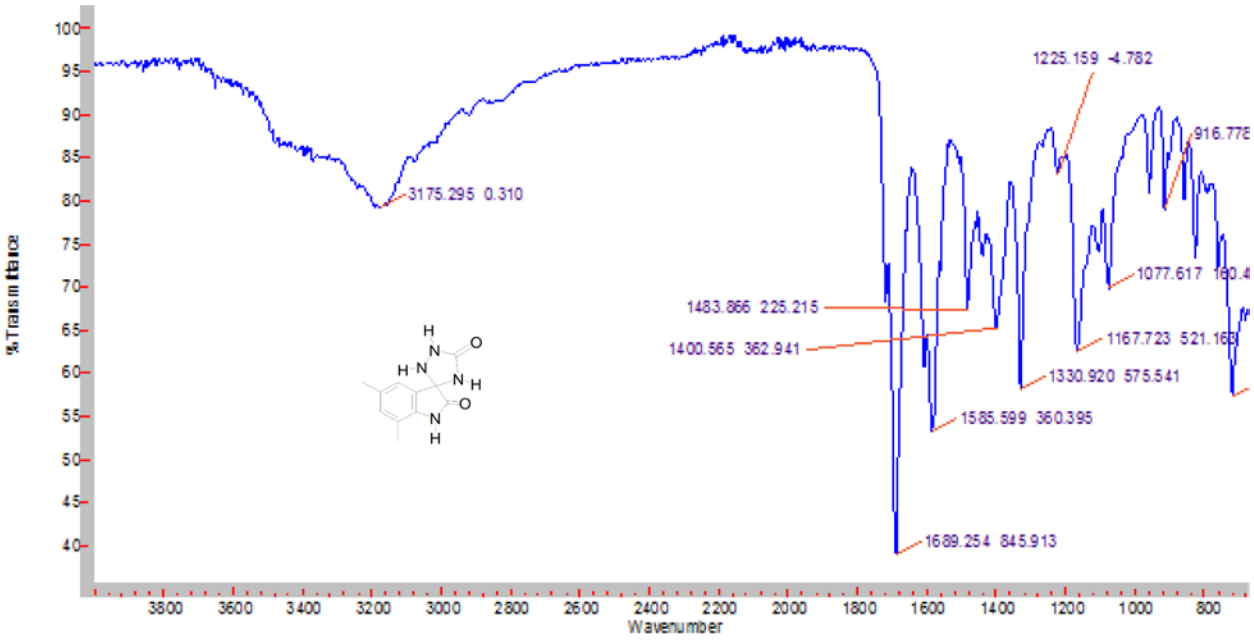

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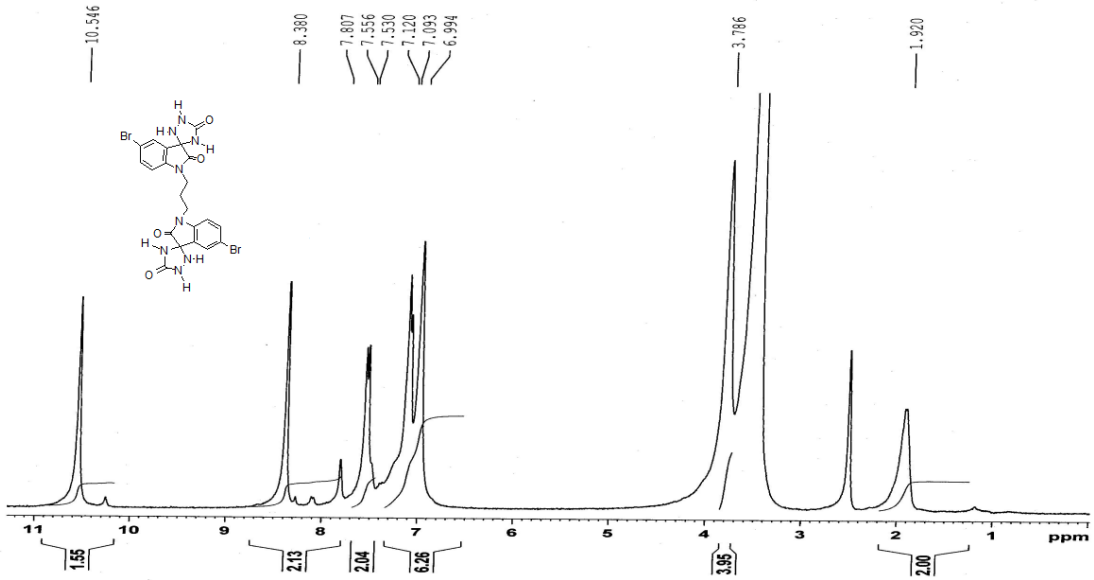

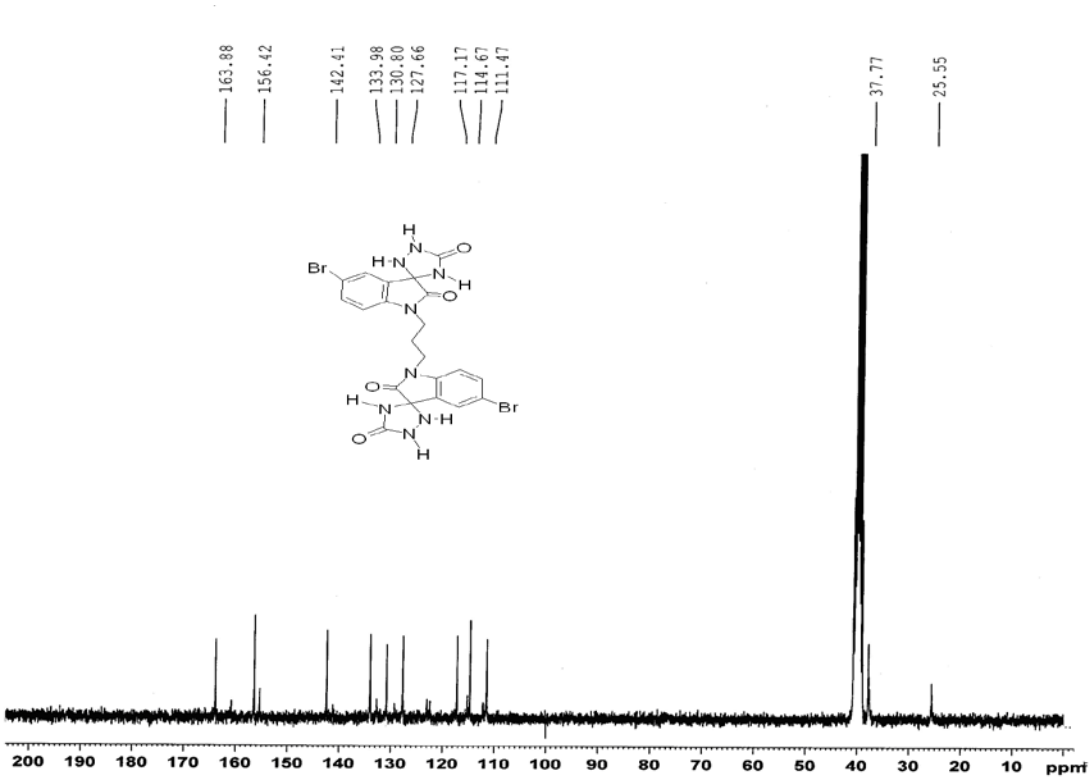

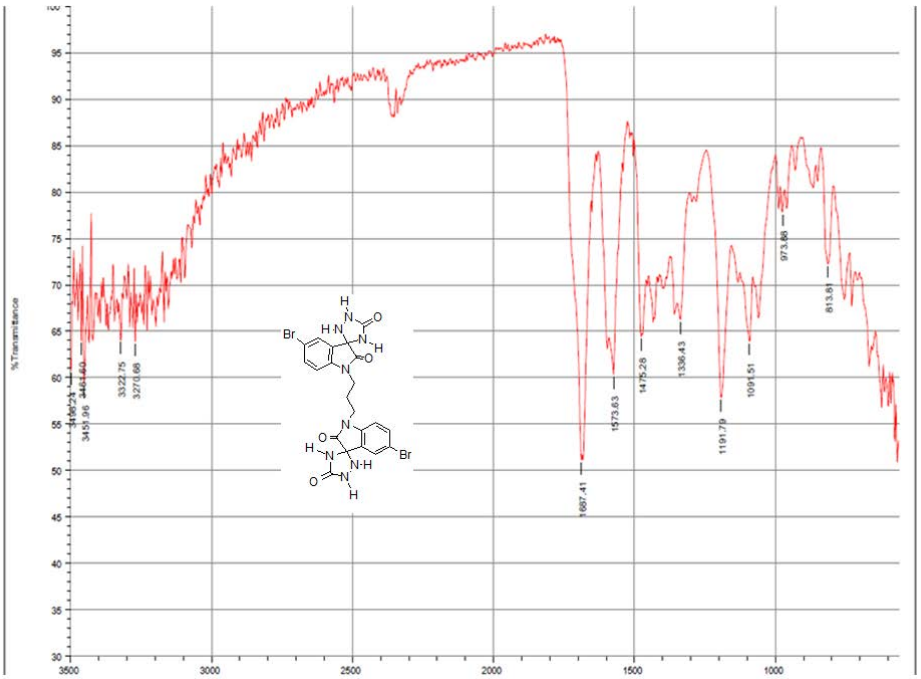

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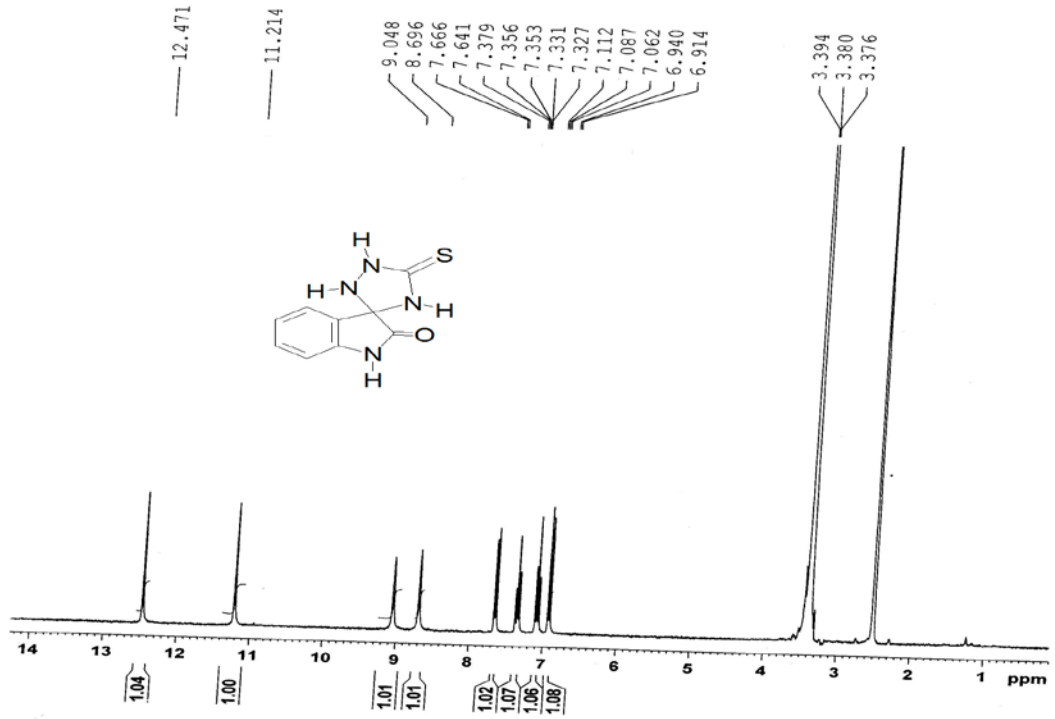
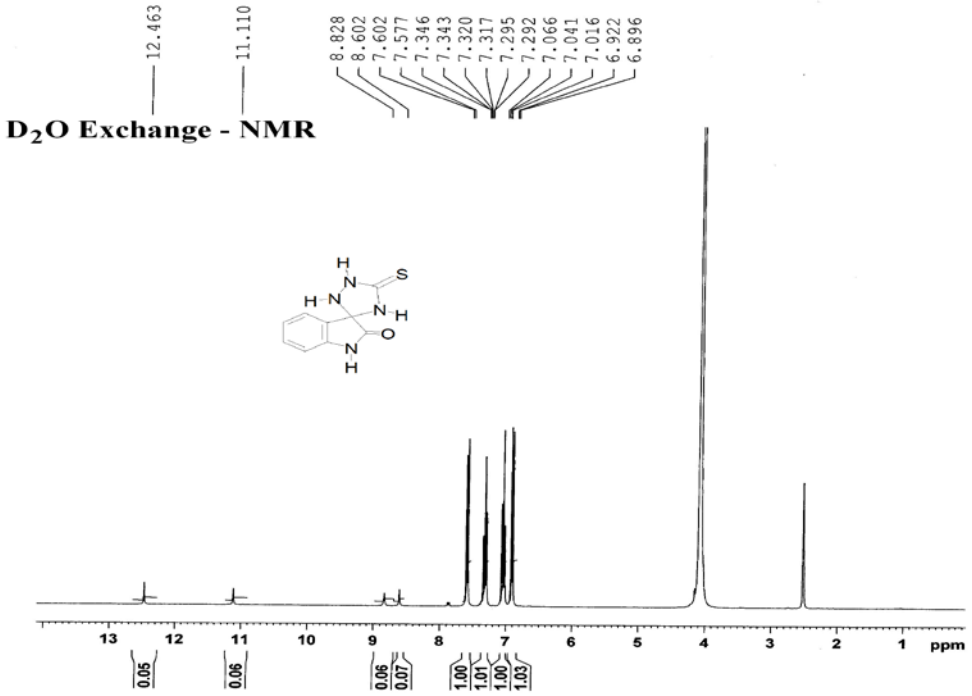
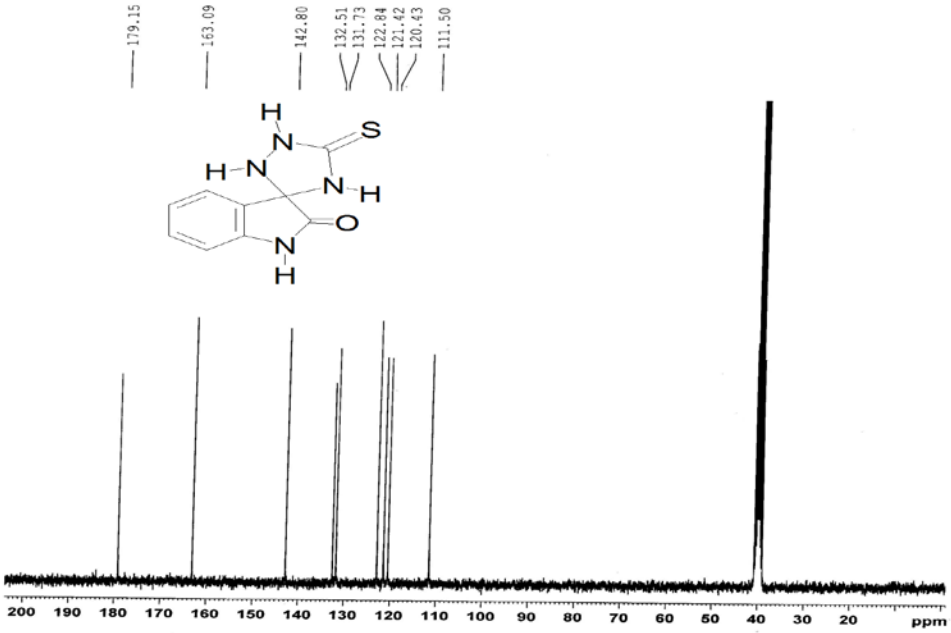
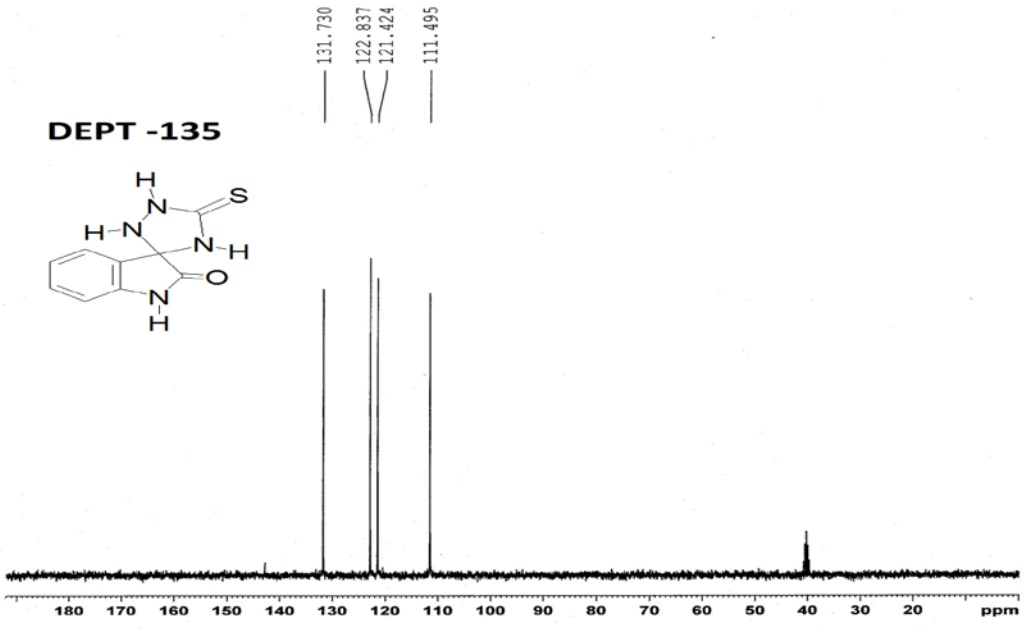
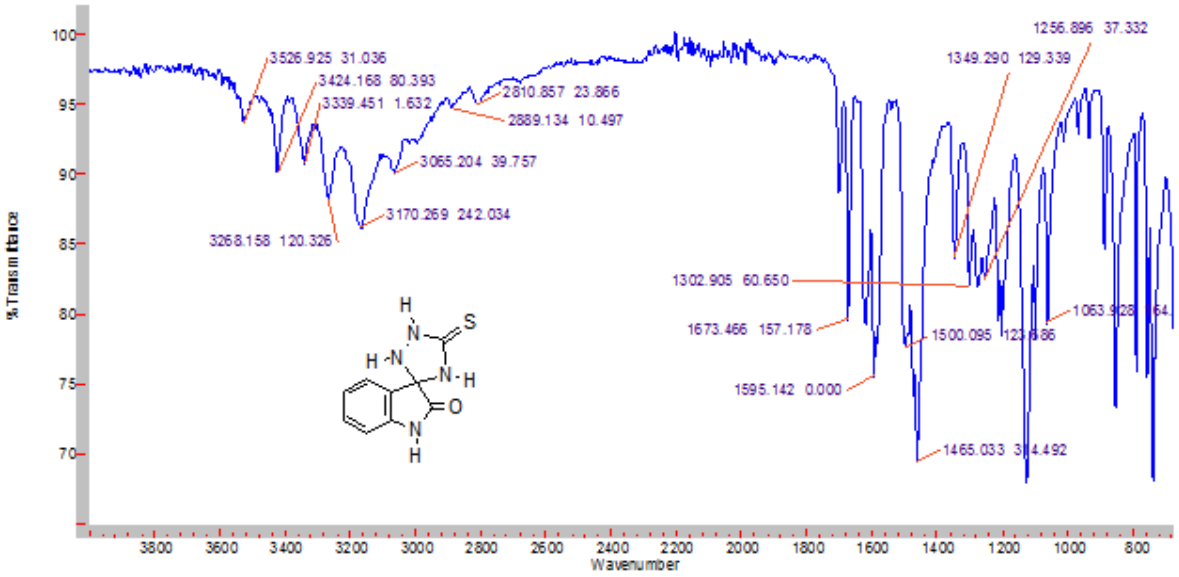


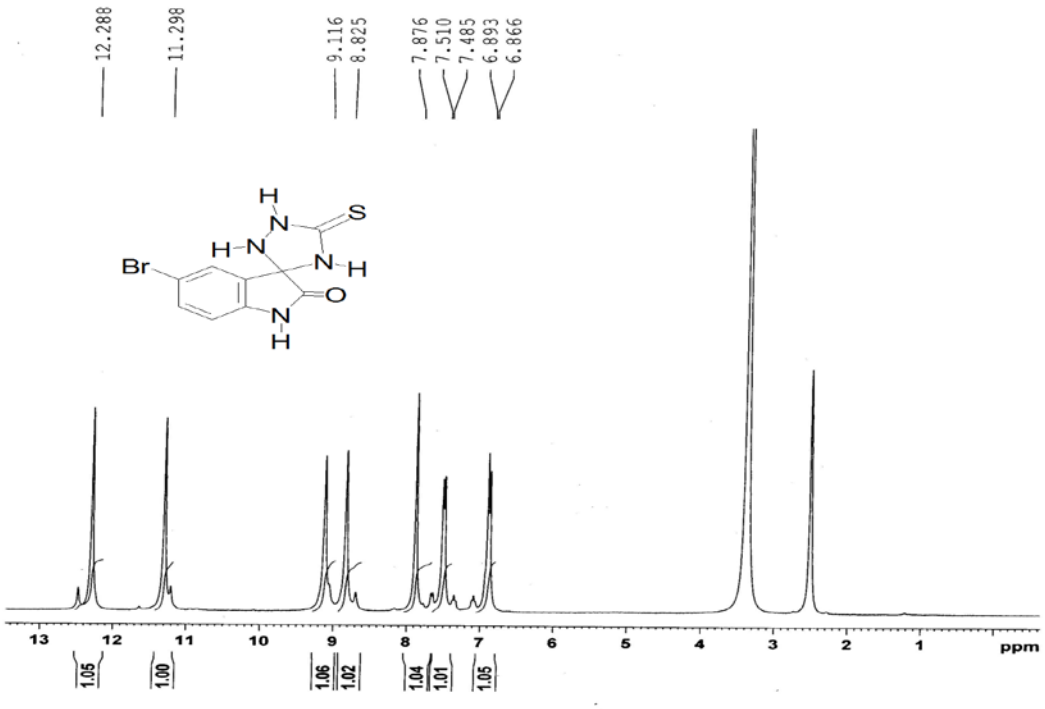


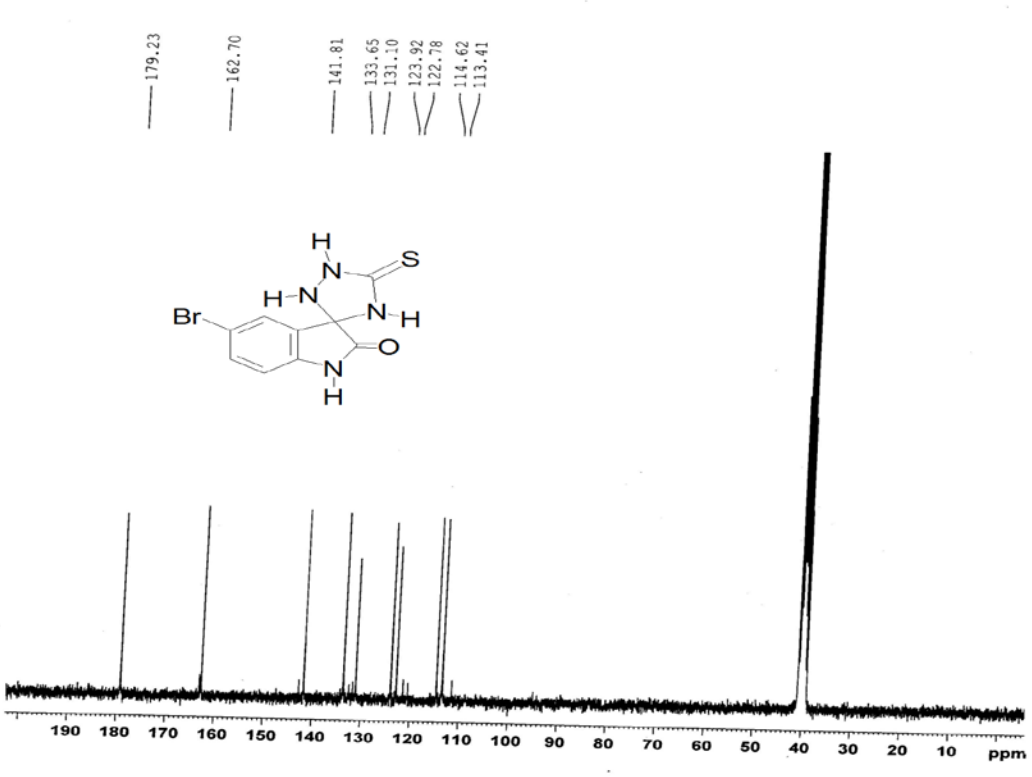


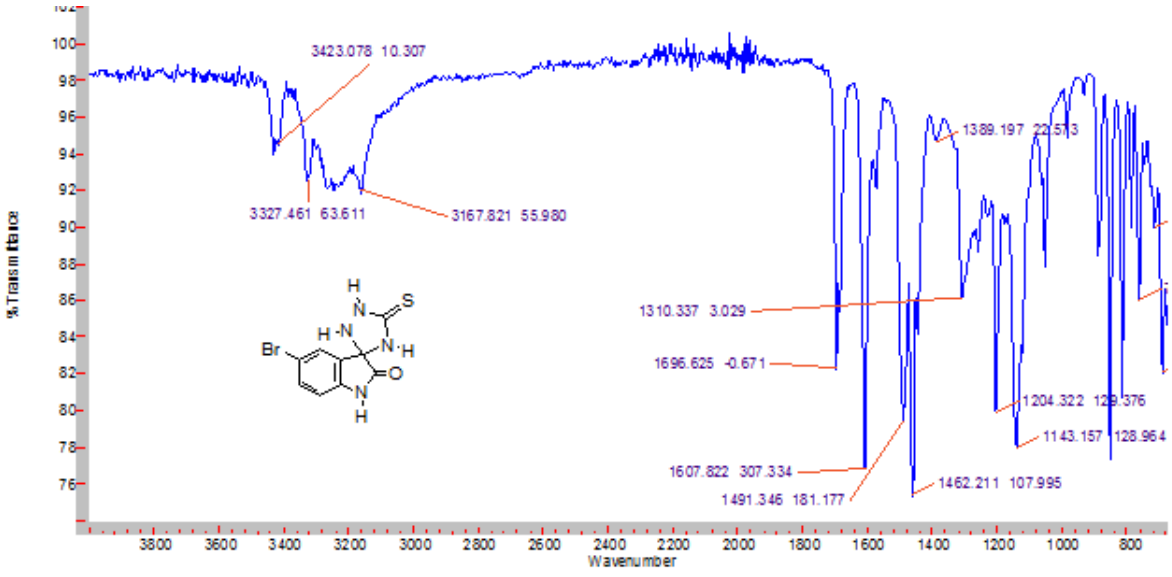




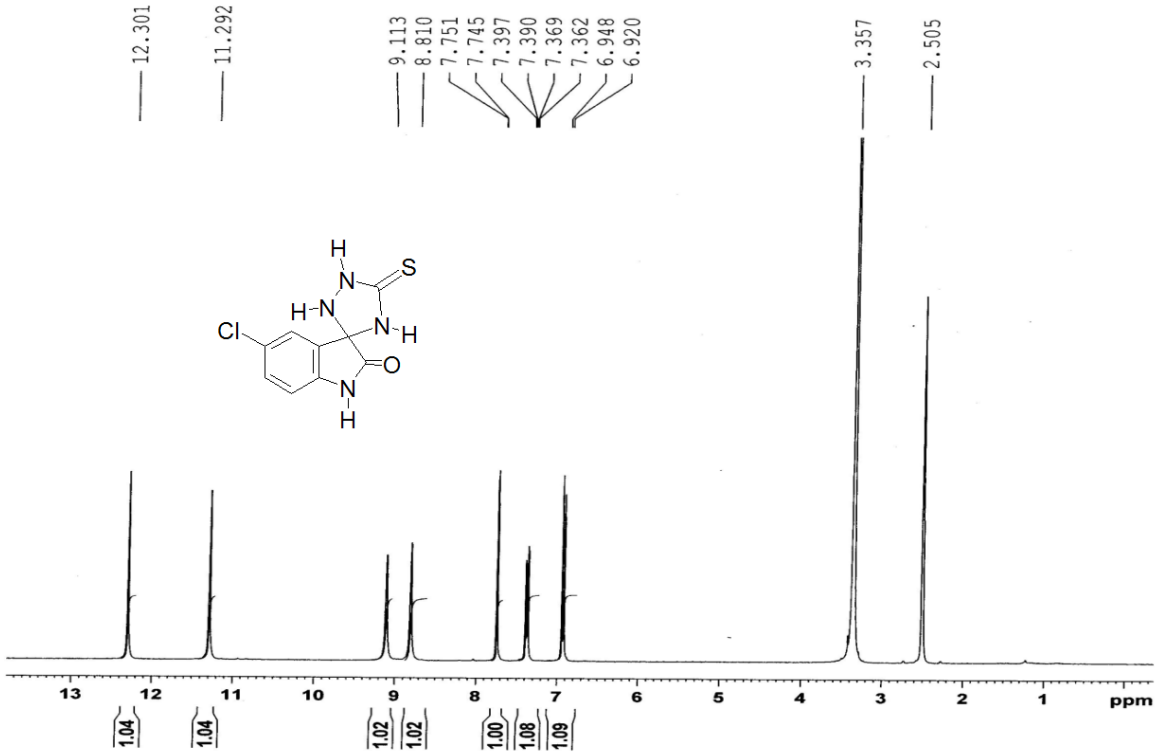
Entry i, Table 2a:

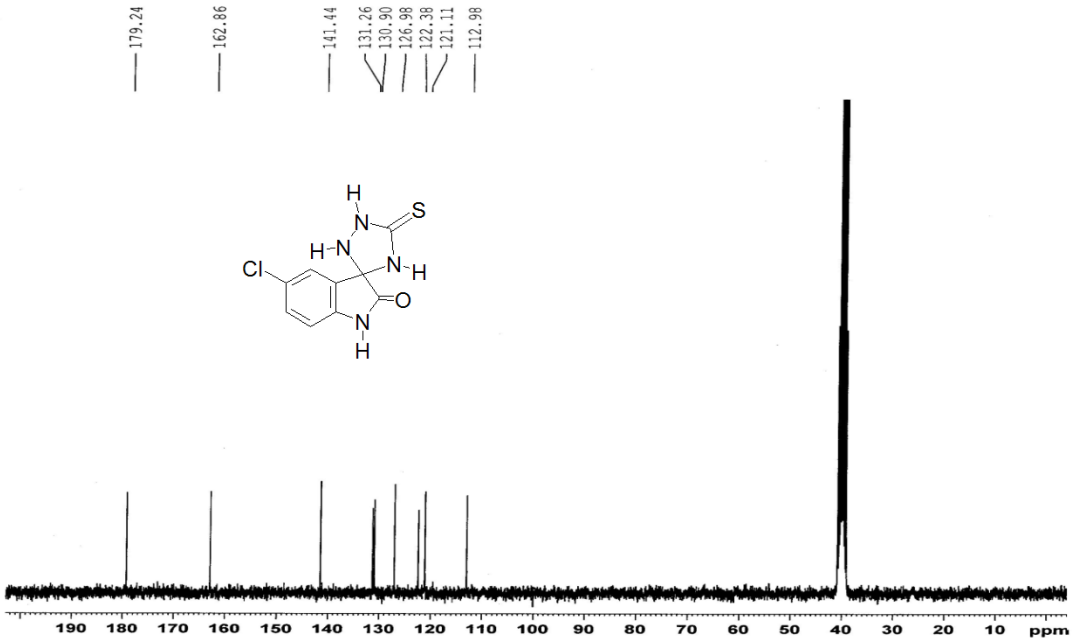


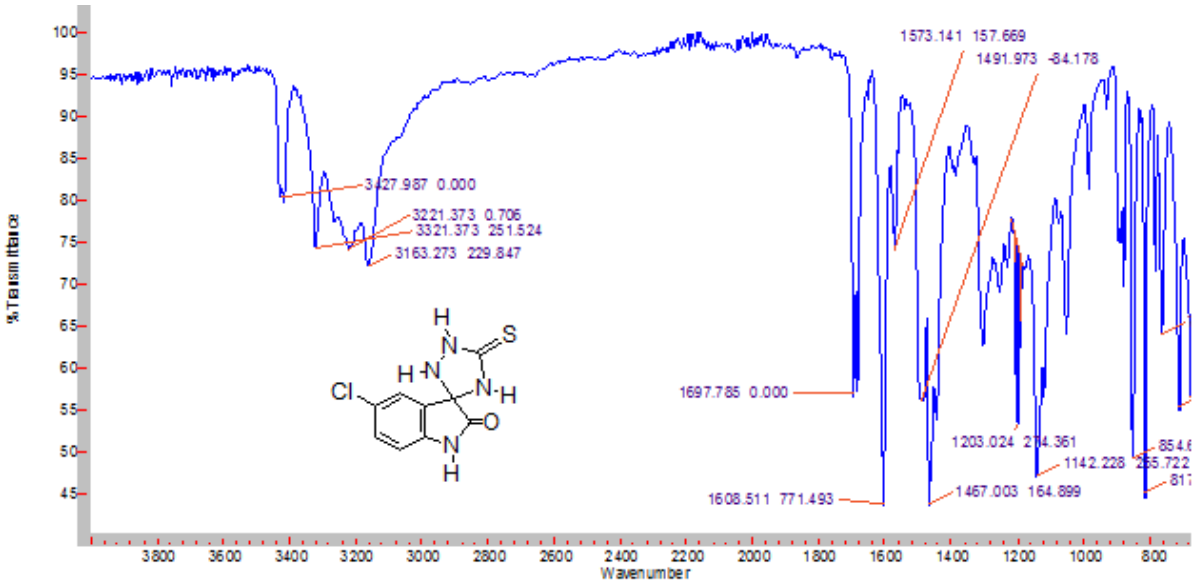




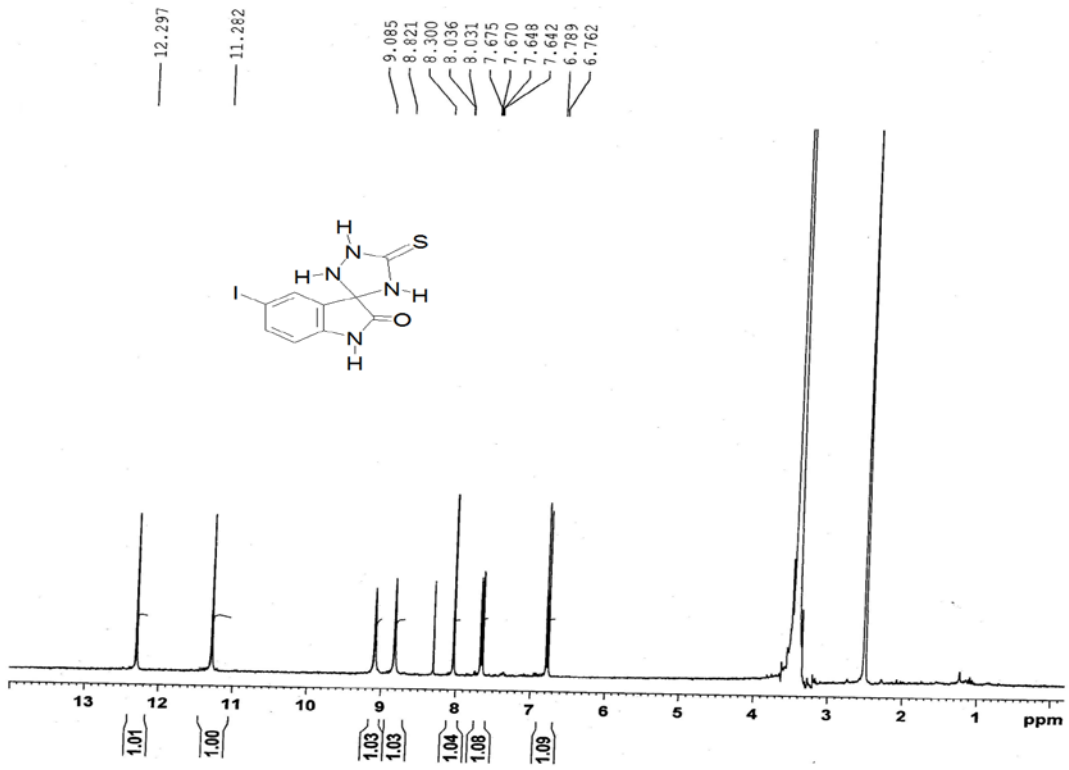
Entry j, Table 2b:

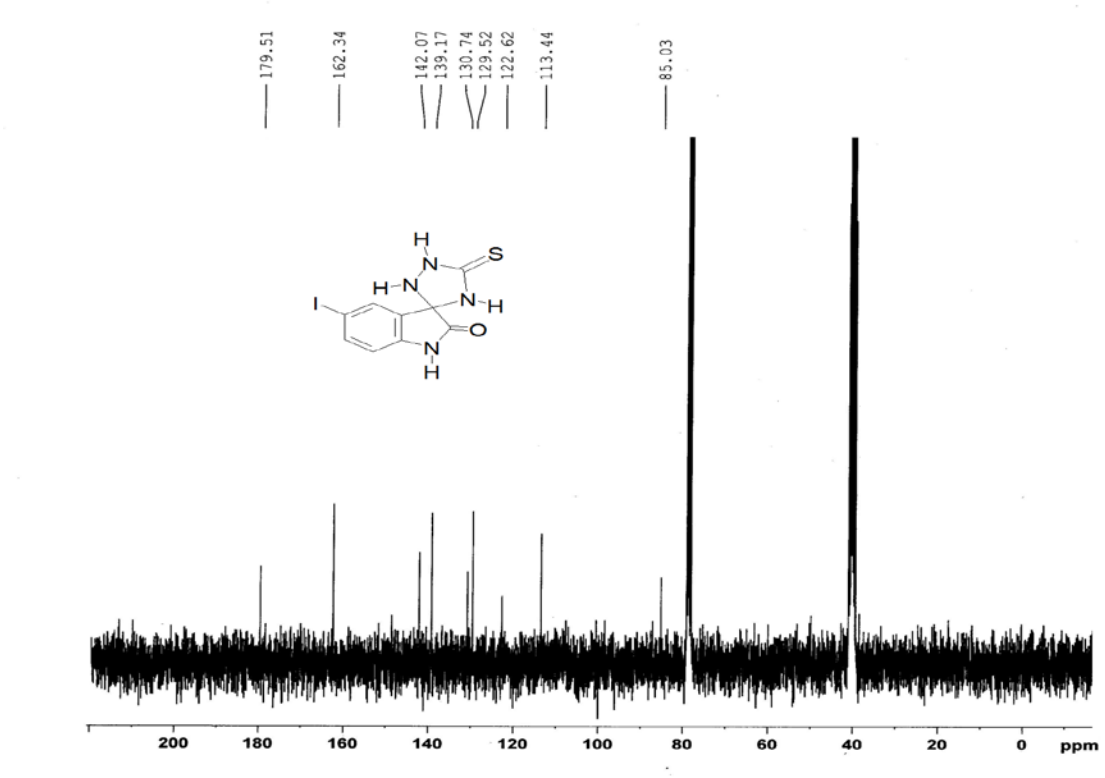


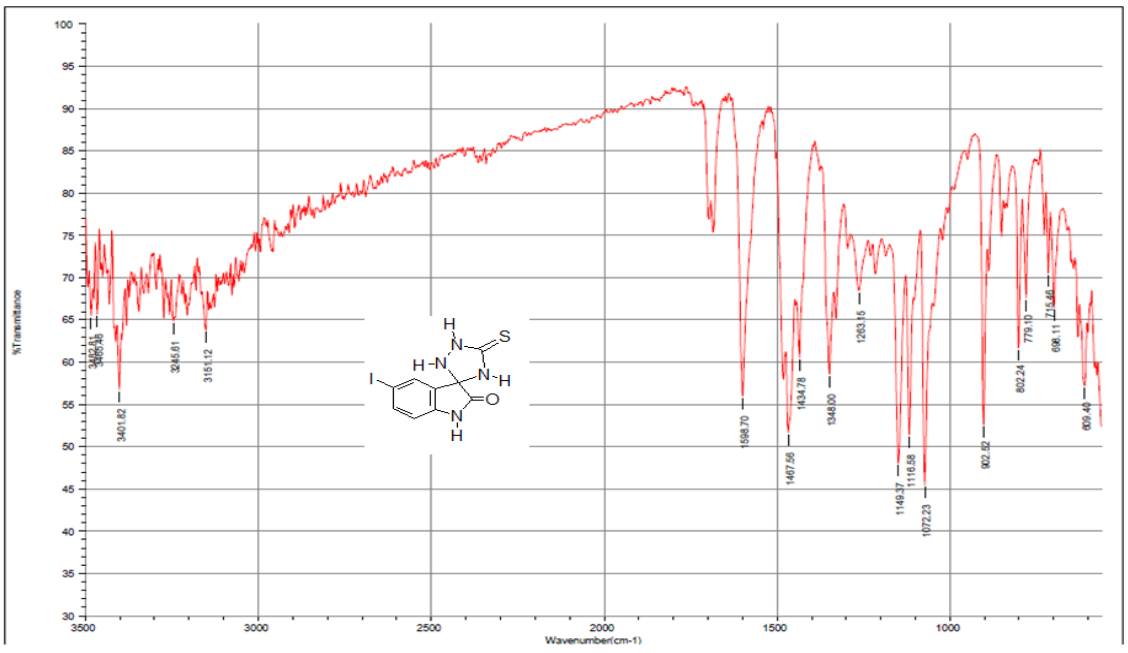




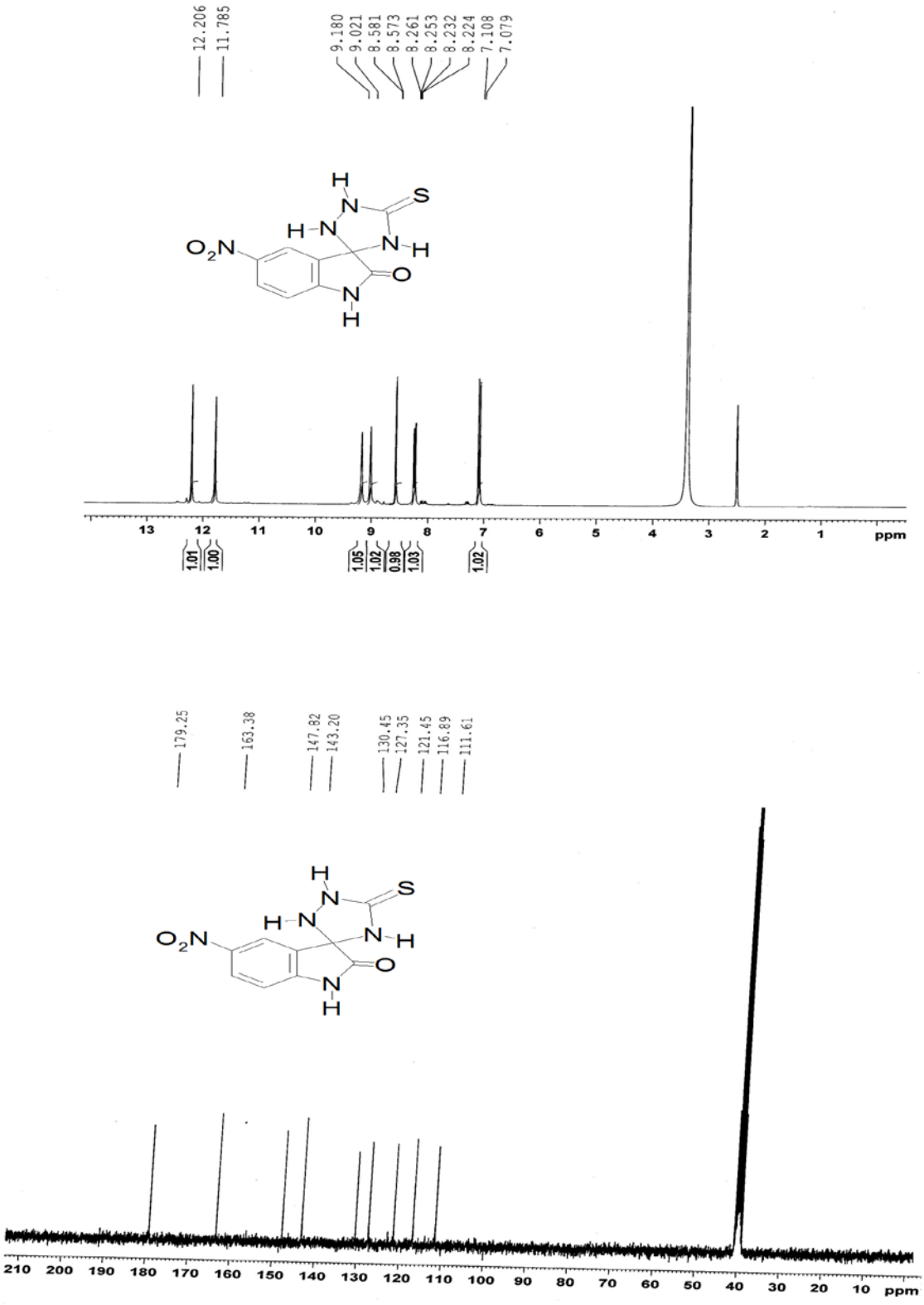
Entry k, Table 2b:

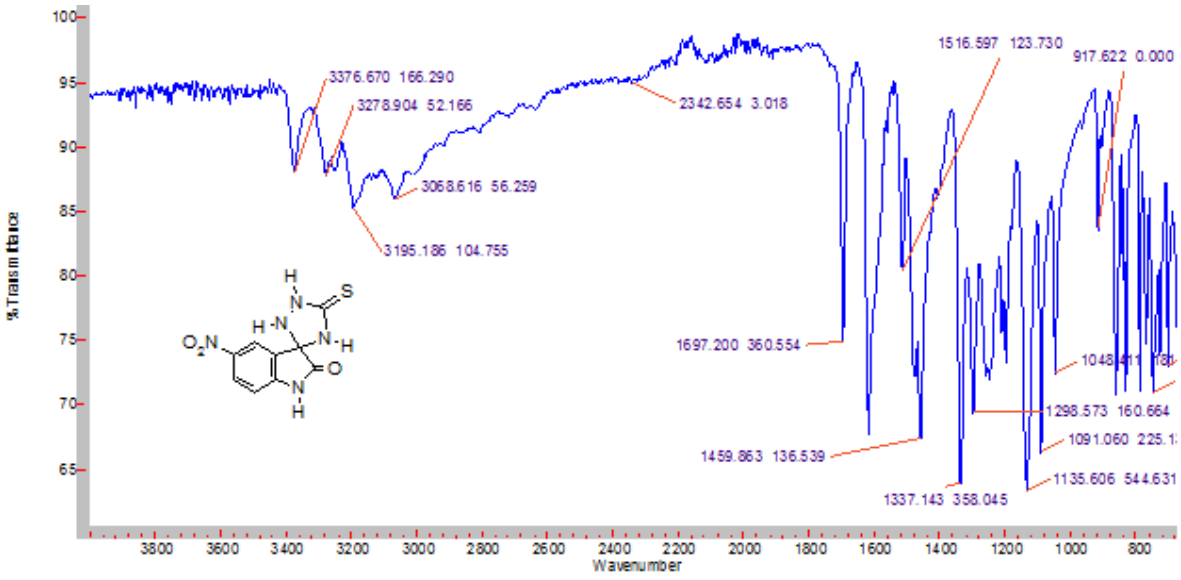



179.51
162.34
142.07
139.17
130.74
129.52
122.62
113.44
85.03
200
180
160
140
120
100
80
60
40
20
0
ppm

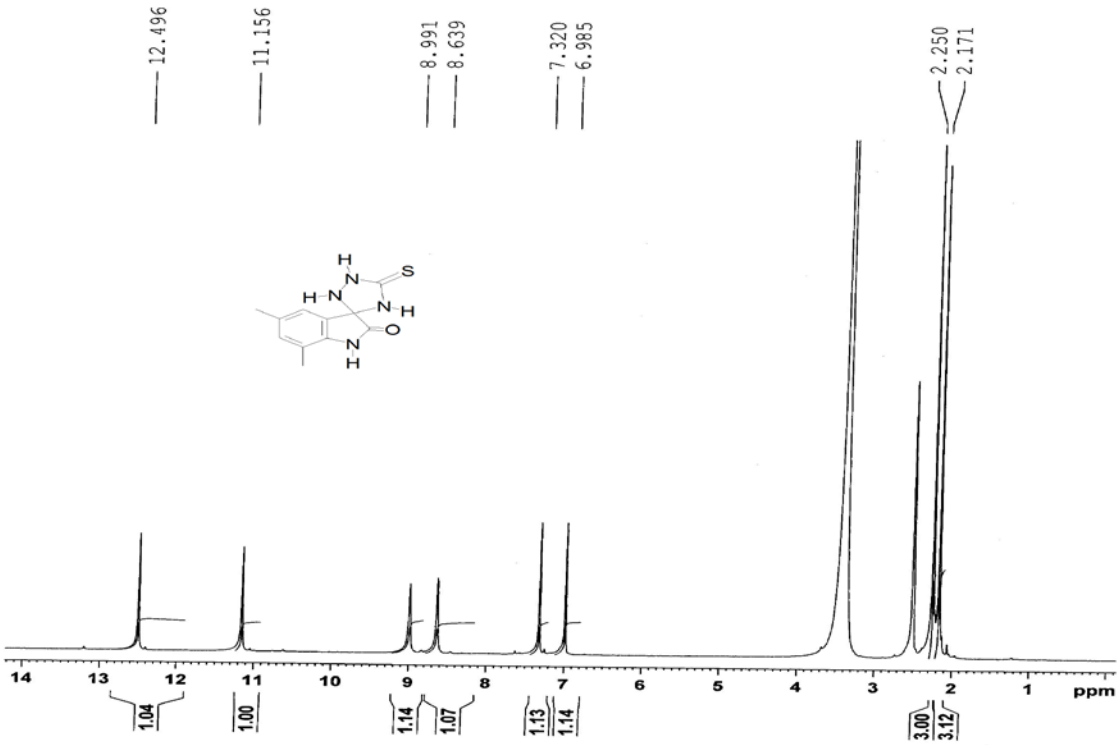

%Transmittance
3401.82
3245.61
3151.12
1598.70
1467.56
1434.78
1348.00
1263.15
1149.37
1116.58
1072.23
802.62
779.10
714.46
698.11
609.49
3500
3000
2500
2000
1500
1000
Wavenumber(cm-1)

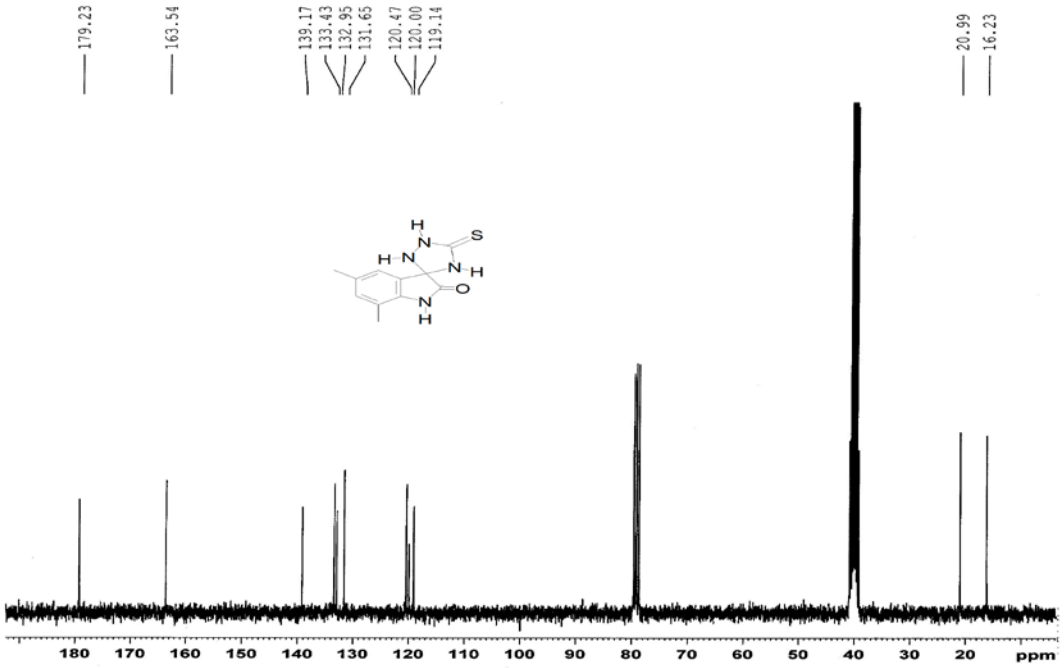
Entry l, Table 2b:

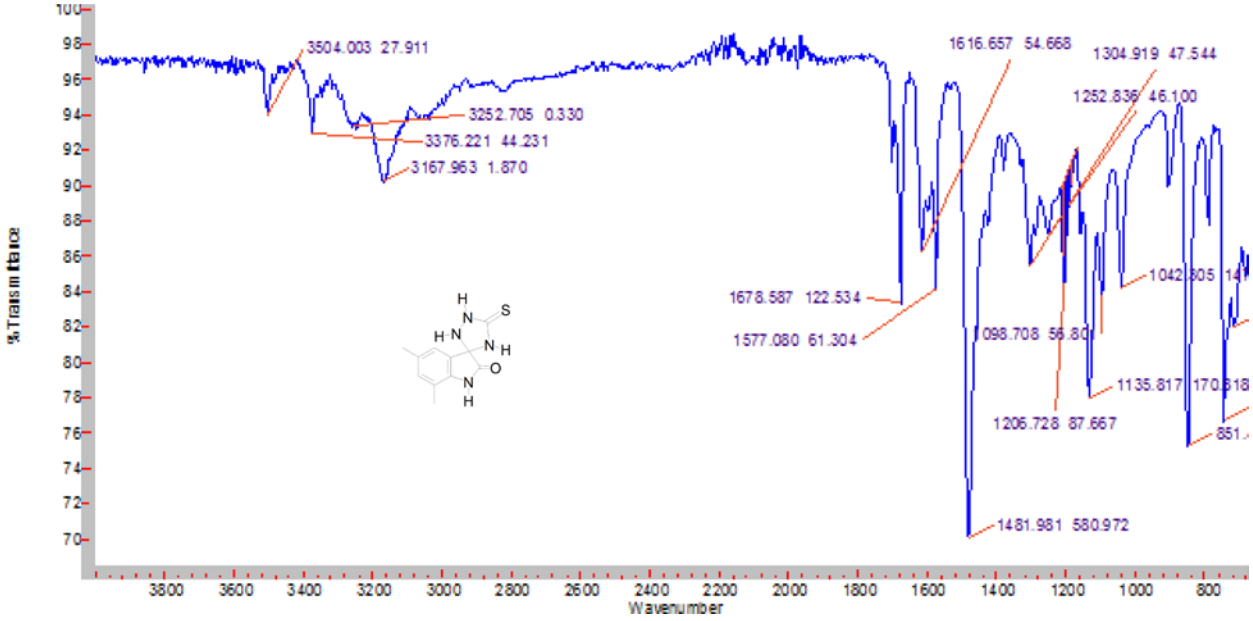




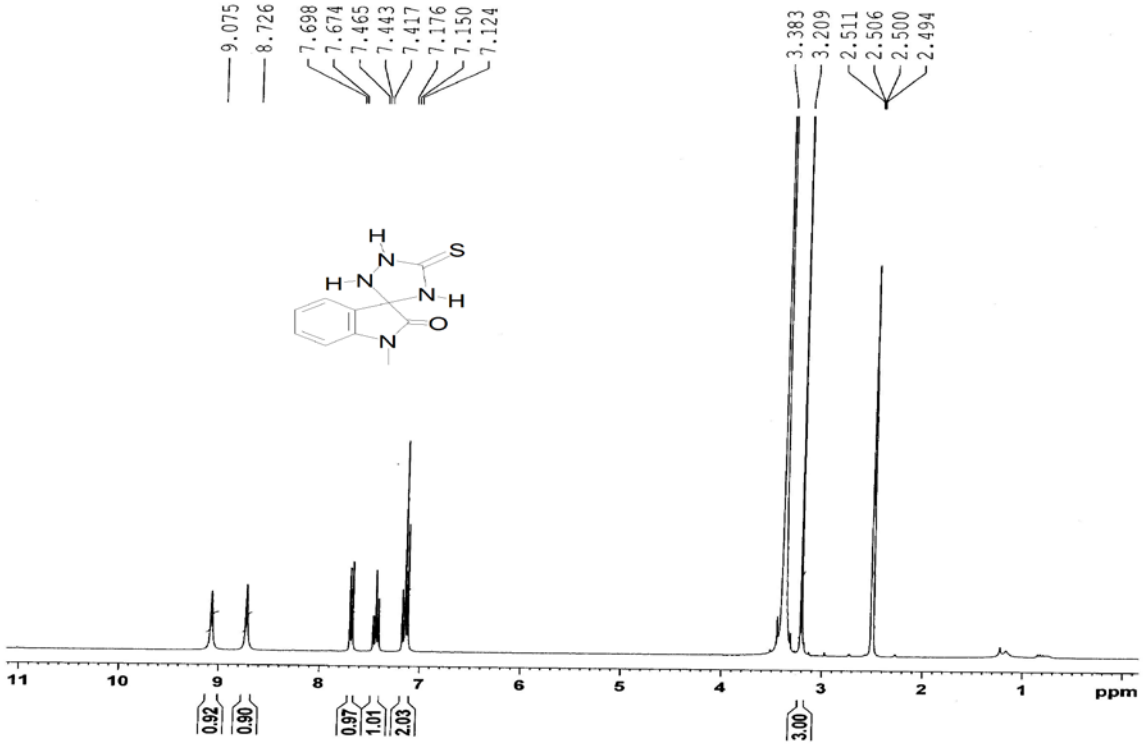
Entry m, Table 2b

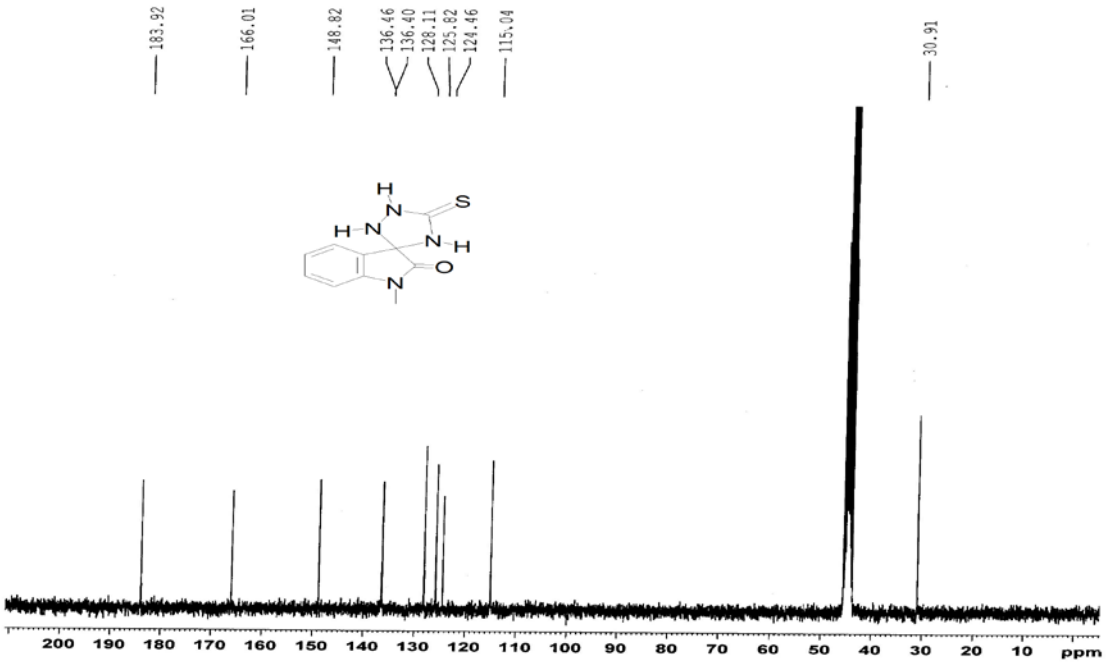


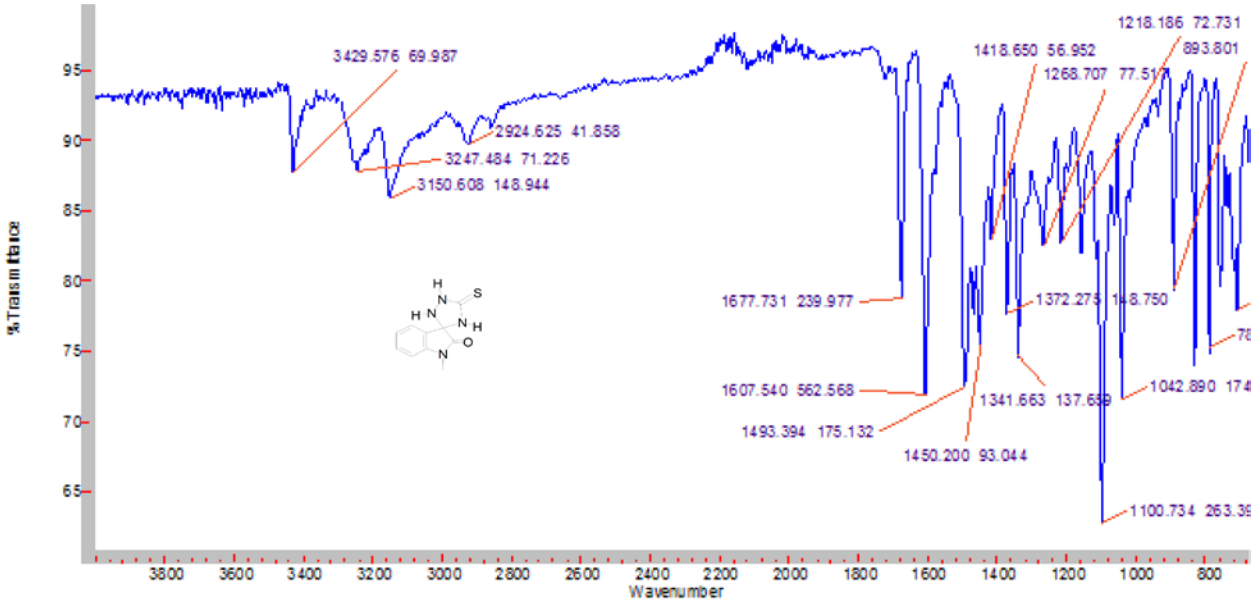




Entry n, Table 2b:







Entry o, Table 2b: