

# Electronic Supplementary Information file

**“On water” highly atom economical and rapid synthesis of a novel class of 3-hydroxy-2-oxindole scaffolds under catalyst-free and column chromatography-free protocol at room temperature**

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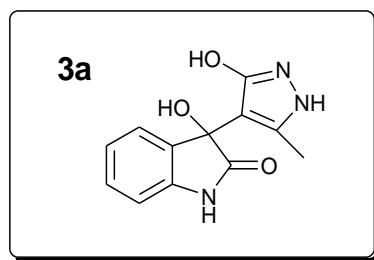
## General Information

All materials used in this study were obtained from commercial supplier and used without further purification as received. All reactions were carried out in an open atmosphere of air. All  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in DMSO  $d_6$  on Avance 300 MHz/Inova 500 MHz spectrometers. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to either residual TMS ( $^1\text{H}$ :  $\delta$  0.00 ppm,  $^{13}\text{C}$ :  $\delta$  00.00 ppm) or DMSO  $d_6$  ( $^1\text{H}$ :  $\delta$  2.50 ppm,  $^{13}\text{C}$ :  $\delta$  39.43 ppm) as an internal reference. The number of protons (n) for a given resonance is indicated by nH. Coupling constants ( $J$ ) are reported in Hertz (Hz). Peak multiplicity is indicated as follows: s—singlet, d—doublet, t—triplet, q—quartet, br—broad, m—multiplet, dd—doublet of doublet and br s —broad singlet. Melting points were measured on a BUCHI melting point machine. IR spectra were recorded on Thermo Nicolet FT/IR-5700 spectrometer. Mass spectra were recorded using Waters mass spectrometers. High resolution mass spectrums (HRMS) were recorded using Applied Bio-Sciences HRMS spectrometer at national center for mass spectroscopy-IICT.

### **General procedure for the rapid and atom economical synthesis of 3-(2-pyrazolin-5-one derivatives) substituted, 3-hydroxy-2-oxindole frameworks under catalyst-free and column chromatography free condition using tap water.**

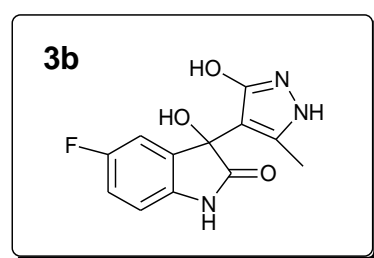
Mixture of isatin **1(a-l)** (1.0 mmol) and 2-pyrazolin-5-one derivatives **2(a-c)** (1 mmol) was stirred in 5 ml tap water at room temperature for stipulated time (10 min). The progress of reaction was monitored by the visualisation of the change of colour of reaction mixture from red (at the begning of the reaction) to white (at the end of the reaction). The progress of reaction was also confirmed by the TLC. The obtained thick white precipitate was filtered and dried to afford the desired product **3(a-p)** in very good yield and purity. All products **3(a-p)** were characterized by NMR, Mass and IR spectroscopic techniques. (*Note that the signal for -OH and -NH proton of pyrazol ring of the products remains undetectable in  $^1\text{H}$  NMR spectrum which might be due to the rapid exchange ability of such protons* ).

## Characterization Data of Synthesized Compounds (3a-3p, Table 2):



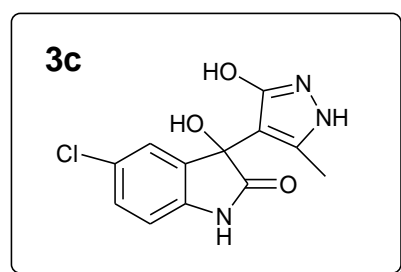
### 3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)indolin-2-one (3a, Table 2)

Yield: 99 %; Time 10 min; Pale yellow solid; mp 226-228 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.19 (s, 1H), 7.24-7.03 (m, 2H), 6.90 (t,  $J=7.3$  Hz, 1H), 6.78 (d,  $J=7.7$  Hz, 1H), 6.29 (br s, 1H), 2.07 (s, 3H), ppm;  $^{13}\text{C}$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 178.16, 158.66, 141.65, 137.41, 133.08, 128.75, 124.57, 121.40, 109.37, 100.41, 73.84, 11.23 ppm; IR (KBr):  $\nu=3377, 3184, 3152, 1692, 1612, 1470, 1386, 1193, 788, 753, 664, 596$   $\text{cm}^{-1}$ ; MS (ESI):  $m/z=268$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}_3\text{Na}$   $[\text{M}+\text{Na}]^+=268.06926$ , found 268.06873.



### 5-fluoro-3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)indolin-2-one (3b, Table 2)

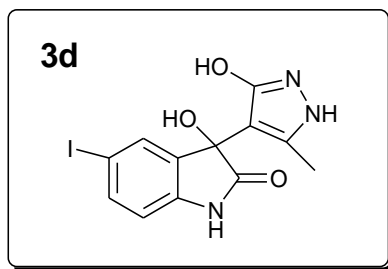
Yield: 99 %; Time 10 min; White solid, mp 194-196 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.21 (s, 1H), 7.06-6.87 (m, 2H), 7.78-6.74 (m, 1H), 6.32 (br s, 1H), 2.18 (s, 3H), ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO  $d_6$ )  $\delta$ : 178.40, 159.13, 158.67, 157.24, 138.45, 137.96, 135.21, 135.14, 115.21, 115.03, 112.28, 112.18, 110.20, 110.14, 100.33, 74.23, 11.70 ppm; IR (KBr):  $\nu=3370, 3145, 2765, 1694, 1625, 1487, 1381, 1322, 1270, 1194, 1150, 1048, 821, 658, 610$   $\text{cm}^{-1}$ ; MS (ESI):  $m/z=264$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{11}\text{O}_3\text{N}_3\text{F}$   $[\text{M}+\text{H}]^+=264.07790$ , found 264.07764.



### 5-chloro-3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)indolin-2-one (3c, Table 2)

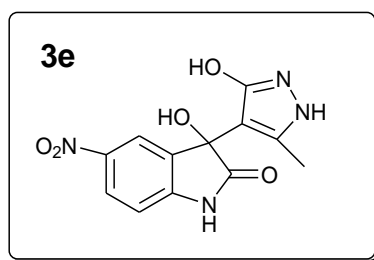
Yield: 99 %; Time 10 min; White solid; mp 196-198 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.22 (s, 1H), 7.23-6.98 (m, 2H), 6.75 (d,  $J=7.9$  Hz, 1H), 6.50 (br, 1H), 2.00 (s, 3H), ppm;  $^{13}\text{C}$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 177.96, 158.67, 140.49, 138.10, 135.13, 128.44, 125.71, 124.54, 110.87, 99.90, 79.92,

11.43 ppm; IR (KBr):  $\nu=3479, 3087, 2822, 2725, 1696, 1586, 1445, 1321, 1183, 819, 781 \text{ cm}^{-1}$ ; MS (ESI):  $m/z=302 [M+Na]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $C_{12}H_{10}O_3N_3ClNa [M+Na]^+=302.03029$ , found 302.02921



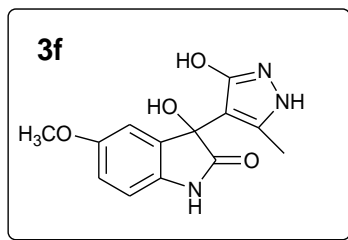
**3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-5-iodoindolin-2-one (3d, Table 2)**

Yield: 99 %; Time 10 min; White solid; mp 218-220 °C;  $^1H$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.27 (s, 1H), 7.55-7.38 (m, 2H), 6.66 (d,  $J=8.4$  Hz, 1H), 6.59 (br s, 1H), 2.00 (s, 3H) ppm;  $^{13}C$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 177.37, 158.62, 141.32, 137.63, 136.96, 135.61132.61, 111.79, 99.68, 83.60, 73.62, 11.15 ppm; IR (KBr):  $\nu=3023, 2957, 2771, 1718, 1617, 1467, 1435, 1233, 1178 \text{ cm}^{-1}$ ; MS (ESI):  $m/z=372 [M+H]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $C_{12}H_{11}O_3N_3I [M+H]^+=371.98396$ , found 371.98291.



**3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-5-nitroindolin-2-one (3e, Table 2)**

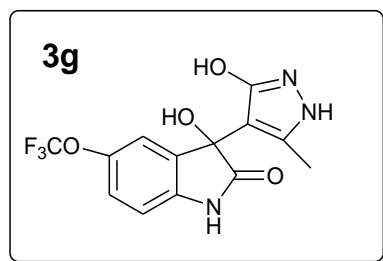
Yield: 99%, Time 10 h; White solid; mp 193-195 °C.  $^1H$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$  10.84 (s, 1H), 8.13 (dd,  $J=8.4, 1.1$  Hz, 1H), 8.03 (d,  $J=1.1$  Hz, 1H), 6.98 (dd,  $J=8.4$ , Hz, 1H), 6.62 (br s, 1H), 2.20 (s, 3H) ppm;  $^{13}C$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 178.75, 159.19, 148.12, 142.53, 139.22, 133.86, 125.99, 120.24, 109.85, 99.33, 73.68, 11.50 ppm; IR (KBr):  $\nu=3528, 3050, 1714, 1586, 1527, 1415, 1345, 1302, 1256, 1183, 1107, 903, 836, 783, 740, 603 \text{ cm}^{-1}$ ; MS (ESI):  $m/z=291 [M+H]^+$ . HRMS (ESI):  $m/z$  calcd. for  $C_{12}H_{11}O_5N_4 [M+H]^+=291.07240$ , found 291.07138.



**3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-5-methoxyindolin-2-one (3f, Table 2)**

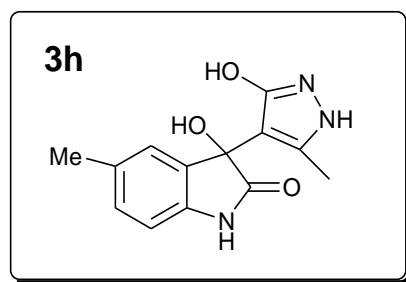
Yield: 99 %; Time 10 min; White solid; mp 193-195 °C;  $^1H$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.04 (s, 1H), 6.86-6.68 (m, 3H), 6.28 (br s, 1H), 3.66 (s, 3H), 2.06 (s, 3H) ppm;  $^{13}C$  NMR (75 MHz, DMSO  $d_6$ )

$\delta$ : 178.31, 158.89, 154.96, 137.84, 135.03, 134.48, 113.64, 111.54, 109.99, 100.62, 74.40, 55.52, 11.49 ppm; IR (KBr):  $\nu$ =3415, 3361, 3201, 2929, 2835, 2563, 1711, 1607, 1533, 1494, 1365, 1290, 1210, 1159, 1029, 815, 640  $\text{cm}^{-1}$ ; MS (ESI):  $m/z$ =298  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{13}\text{O}_4\text{N}_3\text{Na}$   $[\text{M}+\text{Na}]^+$ = 298.07983, found 298.07907.



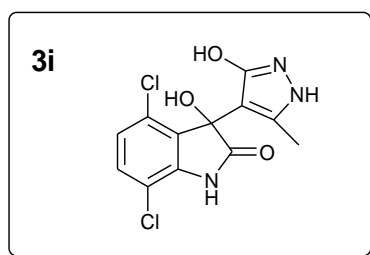
**3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-5-(trifluoromethoxy)indolin-2-one (3g, Table 2)**

Yield: 99 %; Time 10 min; White solid; mp 193-195 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.43 (s, 1H), 7.22-6.99 (m, 2H), 6.83 (d,  $J$ =9.1 Hz, 1H), 6.42 (br s, 1H), 2.1 (s, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 178.34, 158.89, 143.33, 140.79, 138.21, 134.77, 130.97, 121.87, 118.12, 110.32, 99.79, 74.02, 11.39 ppm; IR (KBr):  $\nu$ =3372, 3201, 2569, 1727, 1600, 1533, 1487, 1275, 1186  $\text{cm}^{-1}$ ; MS (ESI):  $m/z$ =330  $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{11}\text{O}_4\text{N}_3\text{F}_3$   $[\text{M}+\text{H}]^+$ = 330.06962, found 330.06888.



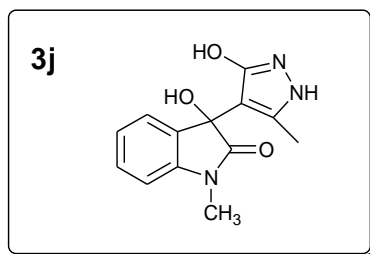
**3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-5-methylindolin-2-one (3h, Table 2)**

Yield: 94 %; Time 10 min; Grey-white solid; mp 197-198 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.10 (s, 1H), 7.08-6.83 (m, 2H), 6.67 (d,  $J$ =8.7 Hz, 1H), 6.22 (br s, 1H), 2.21 (s, 3H), 2.09 (s, 3H) ppm; IR (KBr):  $\nu$ =3414, 3345, 3197, 2923, 2563, 1713, 1629, 1532, 1492, 1366, 1149, 816  $\text{cm}^{-1}$ ; MS (ESI):  $m/z$ =260  $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{14}\text{O}_3\text{N}_3$   $[\text{M}+\text{H}]^+$ = 260.10352, found 260.10278.



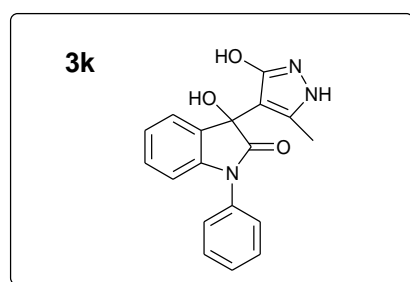
**4,7-dichloro-3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)indolin-2-one (3i, Table 2)**

Yield: 98 %; Time 10 min; White solid; mp 138-140 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.61 (br s, 1H), 7.76 (s, 1H), 7.08 (d,  $J=8.4$  Hz, 1H), 6.78 (d,  $J=8.4$  Hz, 1H), 2.07 (s, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 177.39, 161.16, 141.32, 139.55, 130.29, 129.77, 129.09, 123.11, 112.56, 97.39, 75.19, 11.53 ppm; IR (KBr):  $\nu=3156, 1731, 1613, 1466, 1163, 795$   $\text{cm}^{-1}$ ; MS (ESI):  $m/z=314$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{12}\text{H}_{10}\text{O}_3\text{N}_3\text{Cl}_2$   $[\text{M}+\text{H}]^+=314.00937$ , found 314.00882.



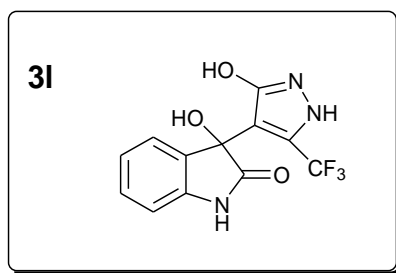
**3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-1-methylindolin-2-one (3j, Table 2)**

Yield: 99 %; Time 10 min; White solid; mp 141-143 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 7.37-7.18 (m, 2H), 7.00 (t,  $J=7.7$  Hz, 1H), 6.90 (d,  $J=7.7$  Hz, 1H), 6.59 (br s, 1H), 3.15 (s, 3H), 1.99 (s, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 176.81, 159.13, 143.20, 138.25, 132.42, 129.31, 124.36, 122.57, 108.47, 100.48, 73.94, 26.12, 11.41 ppm; IR (KBr):  $\nu=3256, 2523, 1706, 1612, 1515, 1470, 1377, 1089, 1040, 921, 785, 749, 688$   $\text{cm}^{-1}$ ; MS (ESI):  $m/z=260$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{14}\text{O}_3\text{N}_3$   $[\text{M}+\text{H}]^+=260.10352$ , found 260.10278.



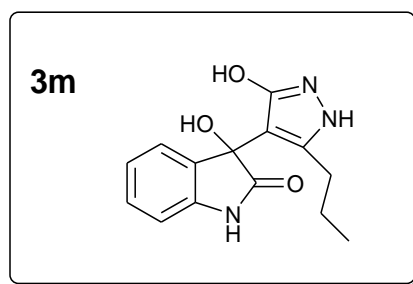
**3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-1-phenylindolin-2-one (3k, Table 2)**

Yield: 99 %; Time 10 min; White solid; mp 174-176 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 7.98-6.95 (m, 9H), 6.67 (br s, 1H), 2.06 (s, 3H) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO  $d_6$ )  $\delta$ : 175.88, 158.42, 142.68, 137.67, 134.44, 132.32, 129.19, 128.57, 127.52, 126.30, 124.47, 122.59, 108.53, 100.68, 73.72, 11.27 ppm; IR (KBr):  $\nu=3472, 3299, 3062, 2561, 1712, 1614, 1529, 1465, 1376, 1188, 760, 698$   $\text{cm}^{-1}$ ; MS (ESI):  $m/z=322$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{N}_3$   $[\text{M}+\text{H}]^+=322.11862$ , found 322.11807.



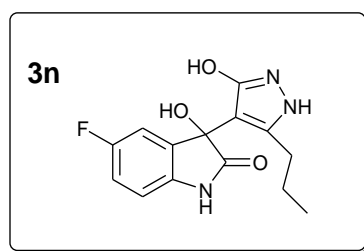
**3-(5-(trifluoromethyl)-3-hydroxy-1H-pyrazol-4-yl)-3-hydroxyindolin-2-one (3l, Table 2)**

Yield: 92 %; Time 10 min; Pale yellow solid; mp 181-183 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 11.16 (br s, 1H), 10.73 (br s, 1H), 7.8 (d,  $J=7.4$  Hz, 1H), 7.36 (t,  $J=7.4$  Hz, 1H), 7.04 (t,  $J=7.4$  Hz, 1H), 6.92 (d,  $J=7.4$  Hz, 1H), ppm;  $^{13}\text{C}$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 164.39, 163.46, 160.52, 142.39, 137.62, 131.14, 123.63, 122.68, 120.81, 120.41, 119.36, 113.50, 109.54, 90.20, 75.10 ppm; IR (KBr):  $\nu=3404, 3304, 3198, 1709, 1684, 1615, 1513, 1461, 1351, 1180, 1124, 786$   $\text{cm}^{-1}$ ; MS (ESI):  $m/z=300$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{12}\text{H}_9\text{O}_3\text{N}_3\text{F}_3$   $[\text{M}+\text{H}]^+=300.05905$ , found 300.05842.



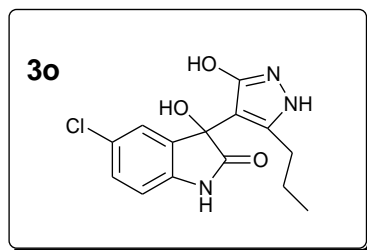
**3-hydroxy-3-(3-hydroxy-5-propyl-1H-pyrazol-4-yl)indolin-2-one (3m, Table 2)**

Yield: 99 %; Time 10 min; White solid; mp 184-186 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.21 (s, 1H), 7.23-7.06 (m, 2H), 6.90 (d,  $J=7.2$  Hz, 1H), 6.78 (d,  $J=7.5$  Hz, 1H), 6.32 (br s, 1H), 2.47-2.28 (m, 2H), 1.59-1.38 (m, 2H), 0.78 (t,  $J=7.2$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 178.18, 158.63, 141.79, 141.62, 133.09, 128.84, 124.51, 121.41, 109.34, 99.67, 74.04, 27.25, 22.44, 13.77 ppm; IR (KBr):  $\nu=3371, 3215, 2962, 2560, 1737, 1698, 1625, 1598, 1530, 1471, 1378, 1183, 1182, 1105, 754$   $\text{cm}^{-1}$ ; MS (ESI):  $m/z=274$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{16}\text{O}_3\text{N}_3$   $[\text{M}+\text{Na}]^+=274.11862$ , found 274.11867.



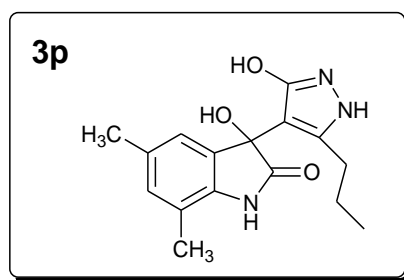
**5-fluoro-3-hydroxy-3-(3-hydroxy-5-propyl-1H-pyrazol-4-yl)indolin-2-one (3n, Table 2)**

: 99 %; Time 10 min; White solid; mp 170-172 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.23 (s, 1H), 7.04-6.97 (m, 1H), 6.92-6.89 (m, 1H), 6.79-6.75 (m, 1H), 6.36 (br s, 1H), 2.63-2.52 (m, 1H), 2.48-2.20 (m, 1H), 1.60-1.47 (m, 2H), 0.82 (t,  $J=7.2$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 178.12, 159.46, 158.35, 156.32, 142.05, 137.93, 135.05, 134.96, 115.07, 114.76, 112.08, 111.76, 110.13, 110.03, 99.34, 74.24, 27.36, 22.54, 13.79 ppm; IR (KBr):  $\nu=3371, 3214, 2963, 2875, 2558, 1739, 1696, 1596, 1529, 1489, 1311, 1187, 1147, 815, 701, 596$   $\text{cm}^{-1}$ ; MS (ESI):  $m/z=292$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{15}\text{O}_3\text{N}_3\text{F}$   $[\text{M}+\text{H}]^+=292.10920$ , found 292.10912.



### 5-chloro-3-hydroxy-3-(3-hydroxy-5-propyl-1H-pyrazol-4-yl)indolin-2-one (3o, Table 2)

Yield: 98 %; Time 10 min; White solid; mp 182-184 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.33 (s, 1H), 7.21 (dd,  $J=8.3, 2.1$  Hz, 1H), 7.04 (d,  $J=2.1$  Hz, 1H), 6.79 (d,  $J=8.1$  Hz, 1H), 6.34 (br s, 1H), 2.73-2.52 (m, 2H), 1.65-1.46 (m, 2H), 0.84 (t,  $J=7.3$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 177.79, 158.21, 142.15, 140.70, 135.45, 128.46, 125.23, 124.34, 110.80, 99.33, 74.00, 27.42, 22.63, 13.79 ppm; IR (KBr):  $\nu=3376, 3203, 2963, 2873, 2558, 1740, 1692, 1596, 1529, 1480, 1178, 822$   $\text{cm}^{-1}$ ; MS (ESI):  $m/z=308$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{15}\text{O}_3\text{N}_3\text{Cl}$   $[\text{M}+\text{H}]^+=308.07965$ , found 308.07976.



### 3-hydroxy-3-(3-hydroxy-5-propyl-1H-pyrazol-4-yl)-5,7-dimethylindolin-2-one (3p, Table 2)

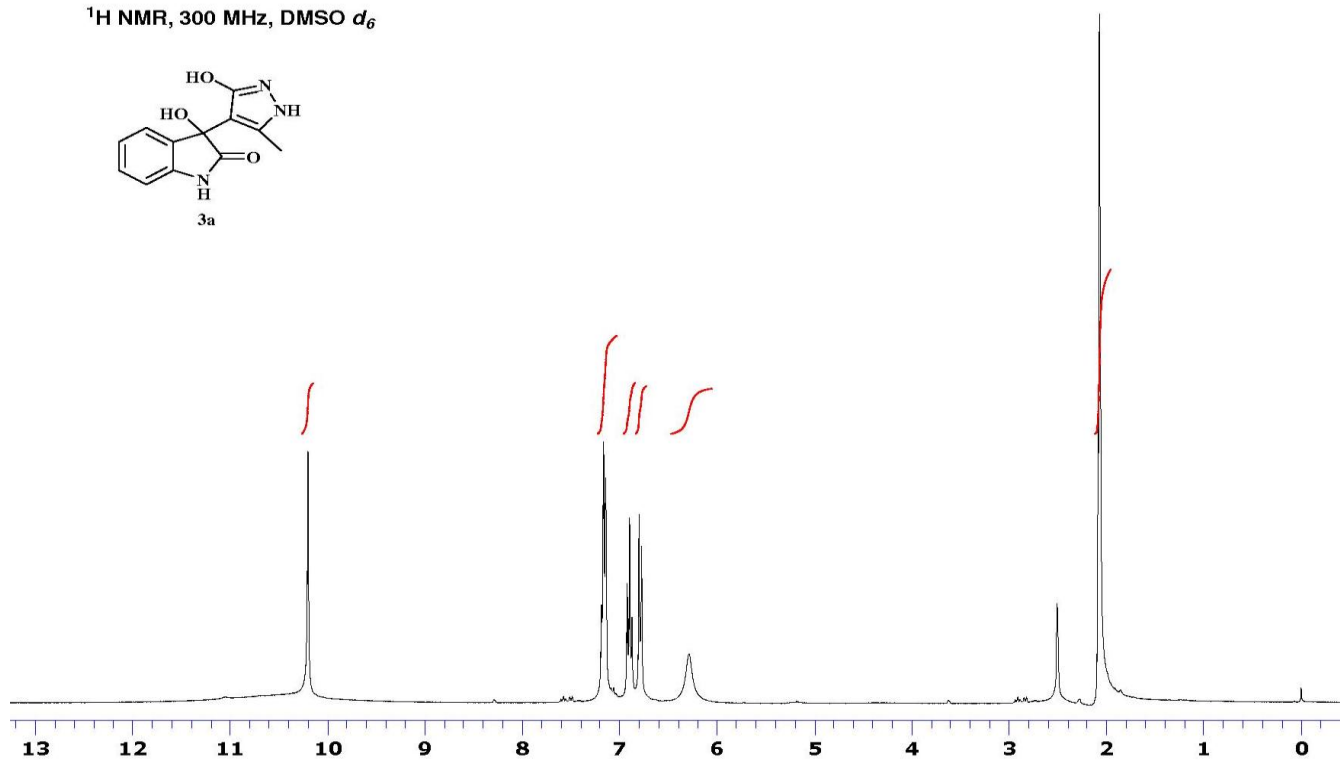
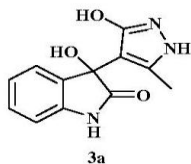
Yield: 91 %; Time 10 min; Grey-white solid; mp 160-162 °C;  $^1\text{H}$  NMR (300 MHz, DMSO  $d_6$ )  $\delta$ : 10.18 (s, 1H), 6.82 (s, 1H), 6.76 (s, 1H), 6.29 (br s, 1H), 2.43-2.22 (m, 2H), 2.17 (s, 3H), 2.15 (s, 3H), 1.67-1.32 (m, 2H), 0.77 (t,  $J=7.2$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (75 MHz, DMSO  $d_6$ )  $\delta$ : 178.63, 158.78, 141.42, 137.79, 132.73, 130.44, 130.09, 122.51, 118.22, 99.82, 74.40, 27.18, 22.44, 20.49, 16.16, 13.75 ppm; IR (KBr):  $\nu=3212, 2977, 2806, 1713, 1596, 1469, 1428, 1315, 1210, 1144, 741$   $\text{cm}^{-1}$ ; MS (ESI):  $m/z=302$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{20}\text{O}_3\text{N}_3$   $[\text{M}+\text{H}]^+=302.14992$ , found 302.15002.



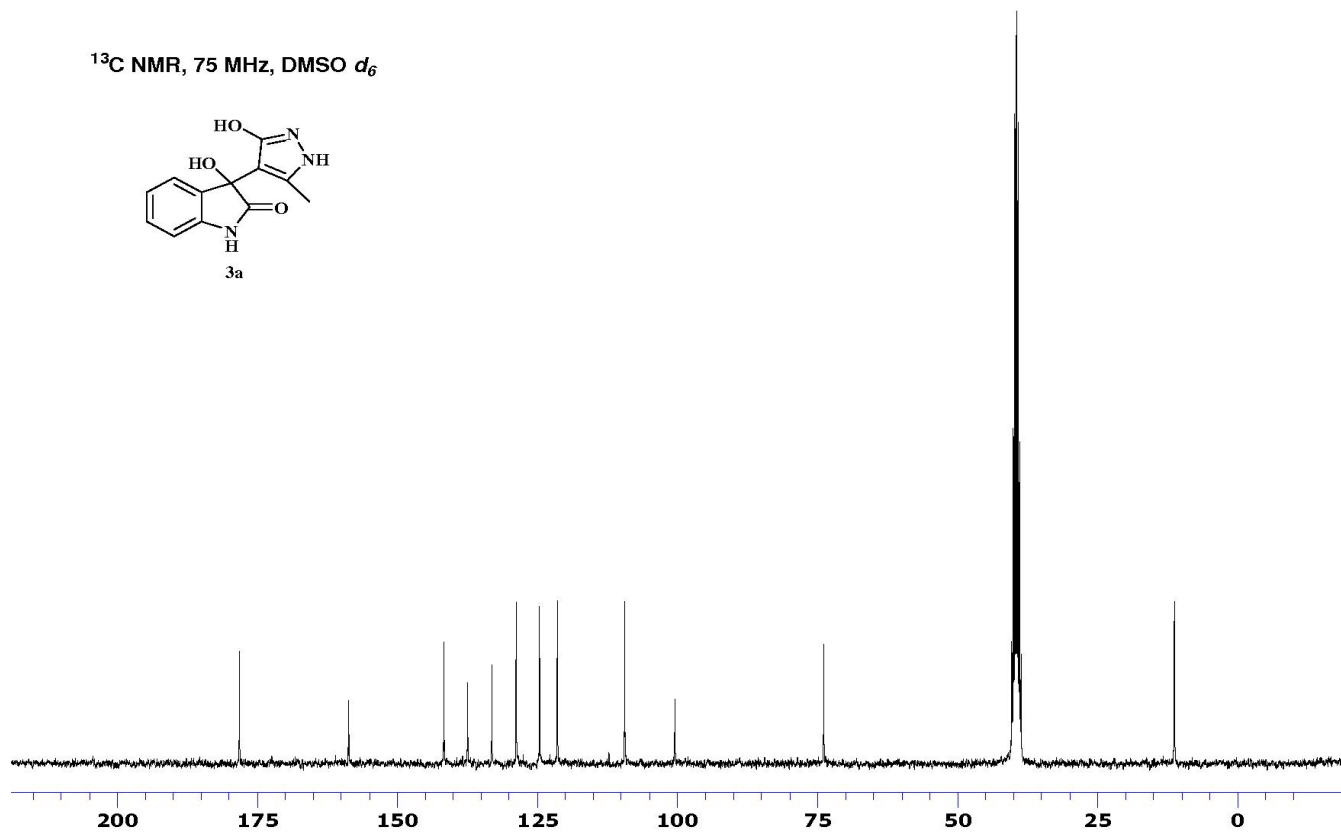
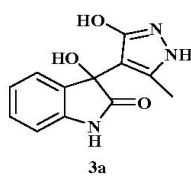
### $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

#### 3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)indolin-2-one (3a, Table 2)

$^1\text{H}$  NMR, 300 MHz,  $\text{DMSO } d_6$

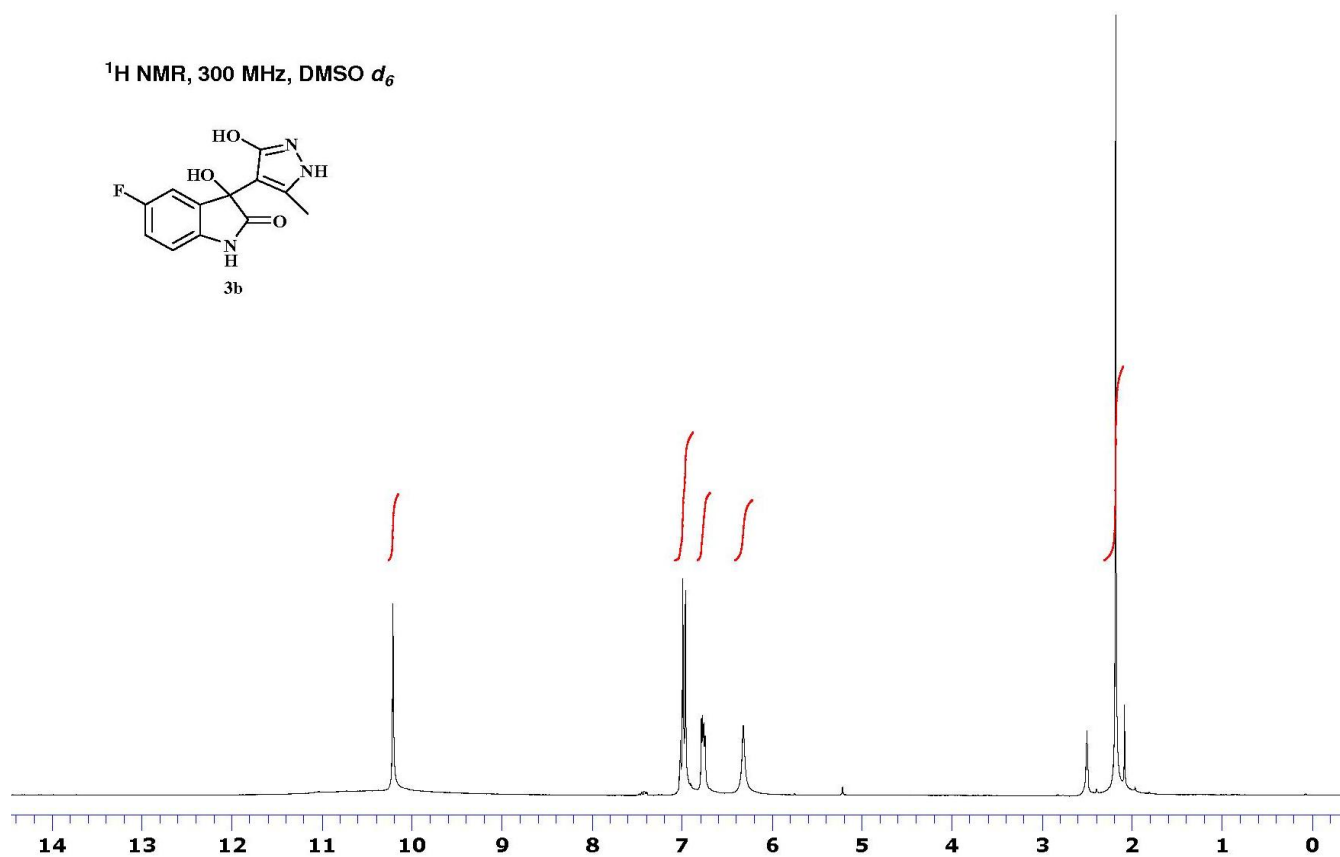
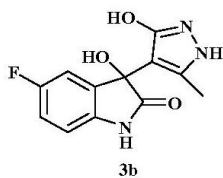


$^{13}\text{C}$  NMR, 75 MHz,  $\text{DMSO } d_6$

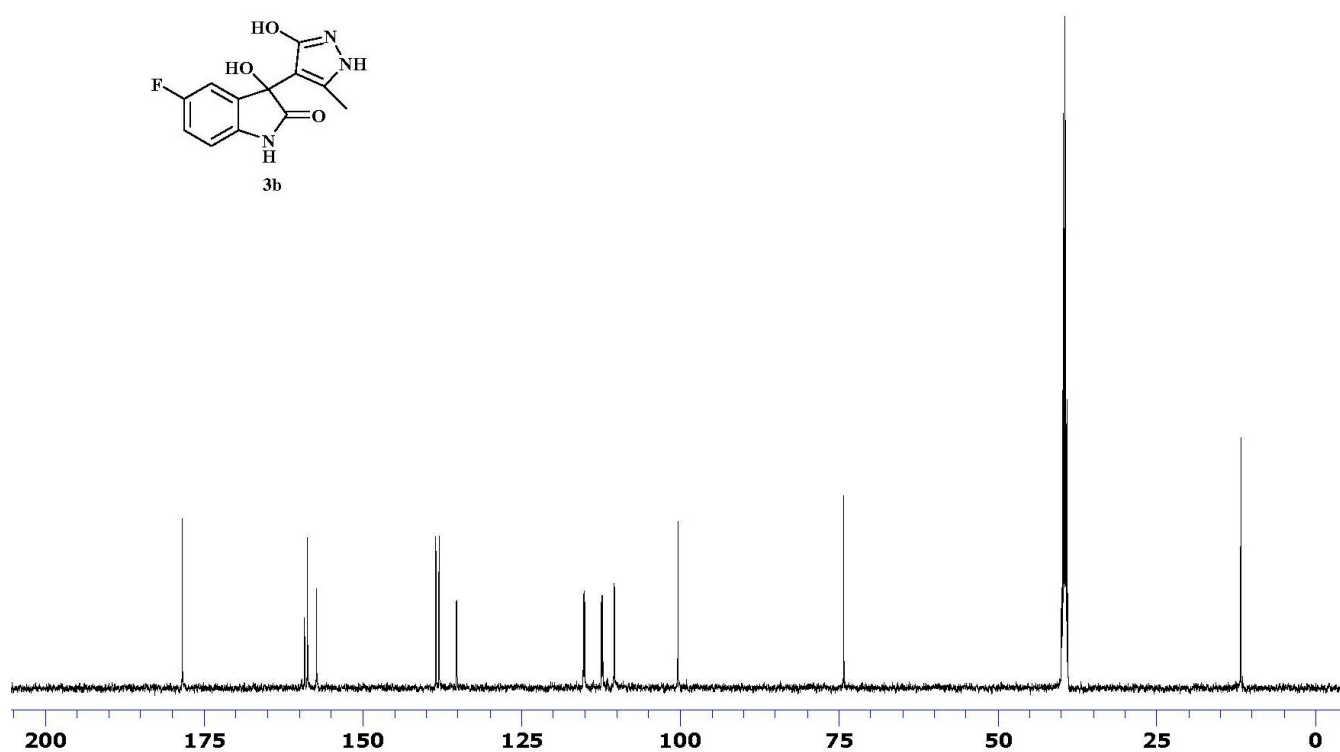
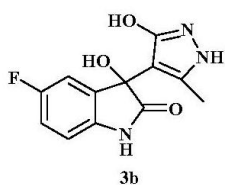


### 5-fluoro-3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)indolin-2-one (3b, Table 2)

$^1\text{H NMR}$ , 300 MHz,  $\text{DMSO } d_6$

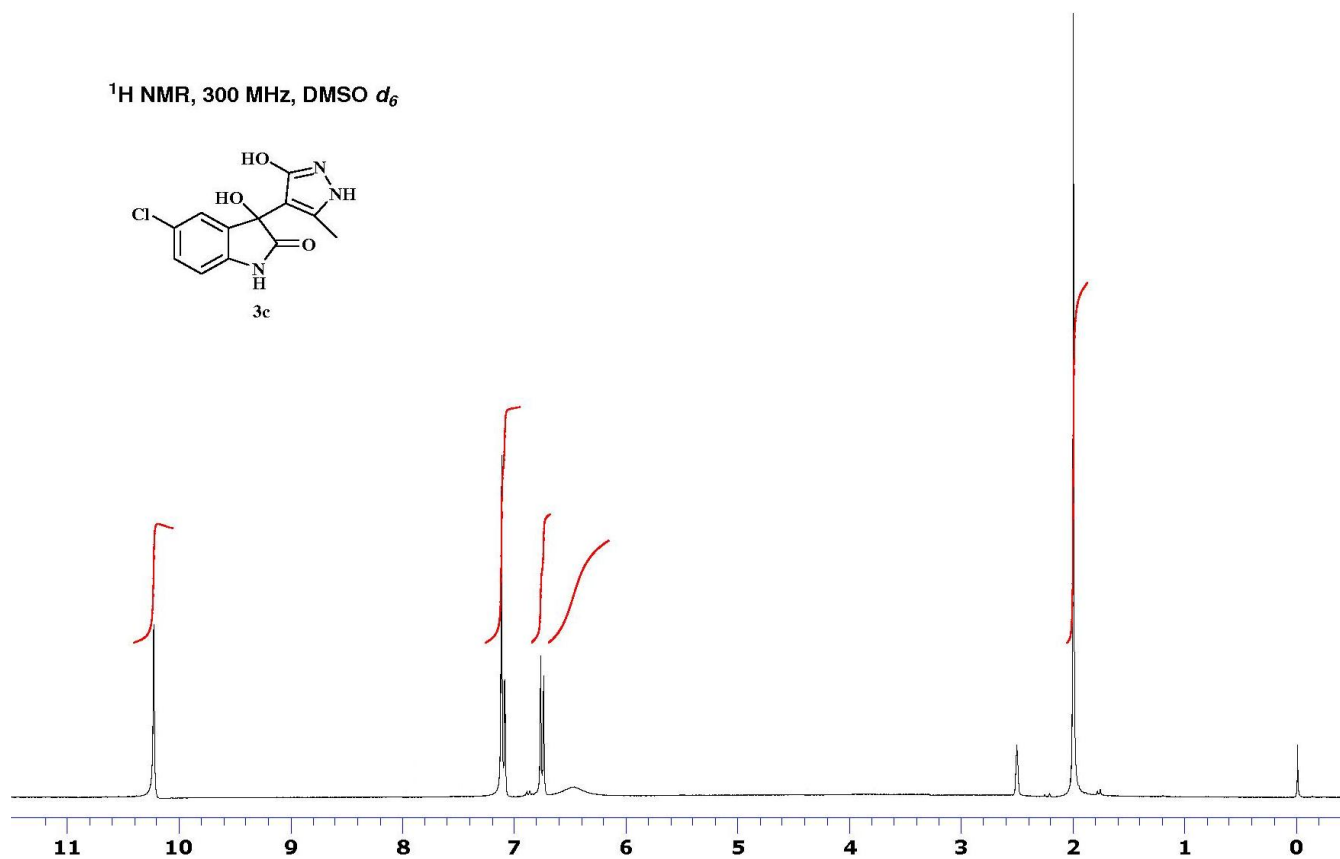
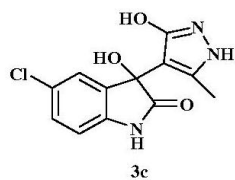


$^{13}\text{C NMR}$ , 125 MHz,  $\text{DMSO } d_6$

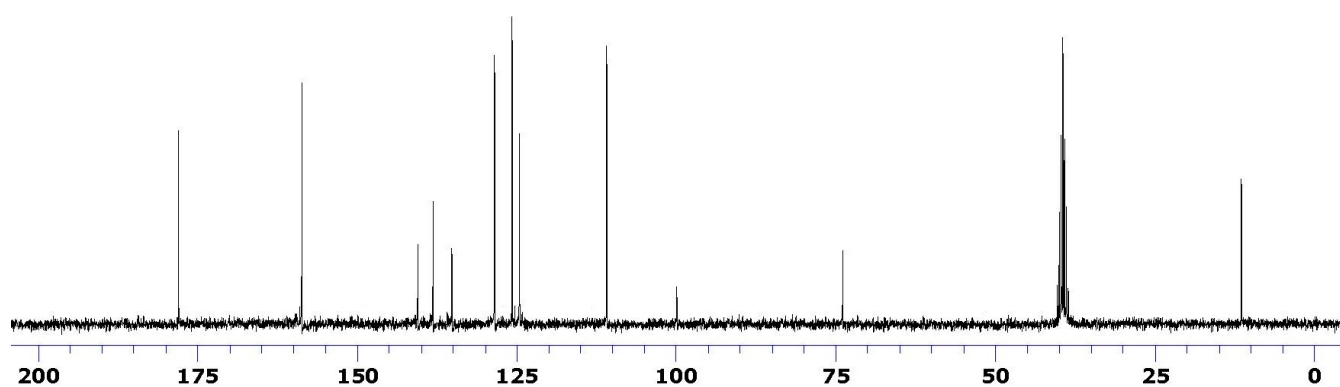
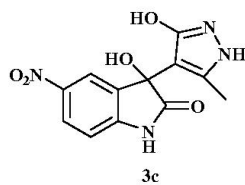


### 5-chloro-3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)indolin-2-one (3c, Table 2)

$^1\text{H NMR}$ , 300 MHz,  $\text{DMSO } d_6$

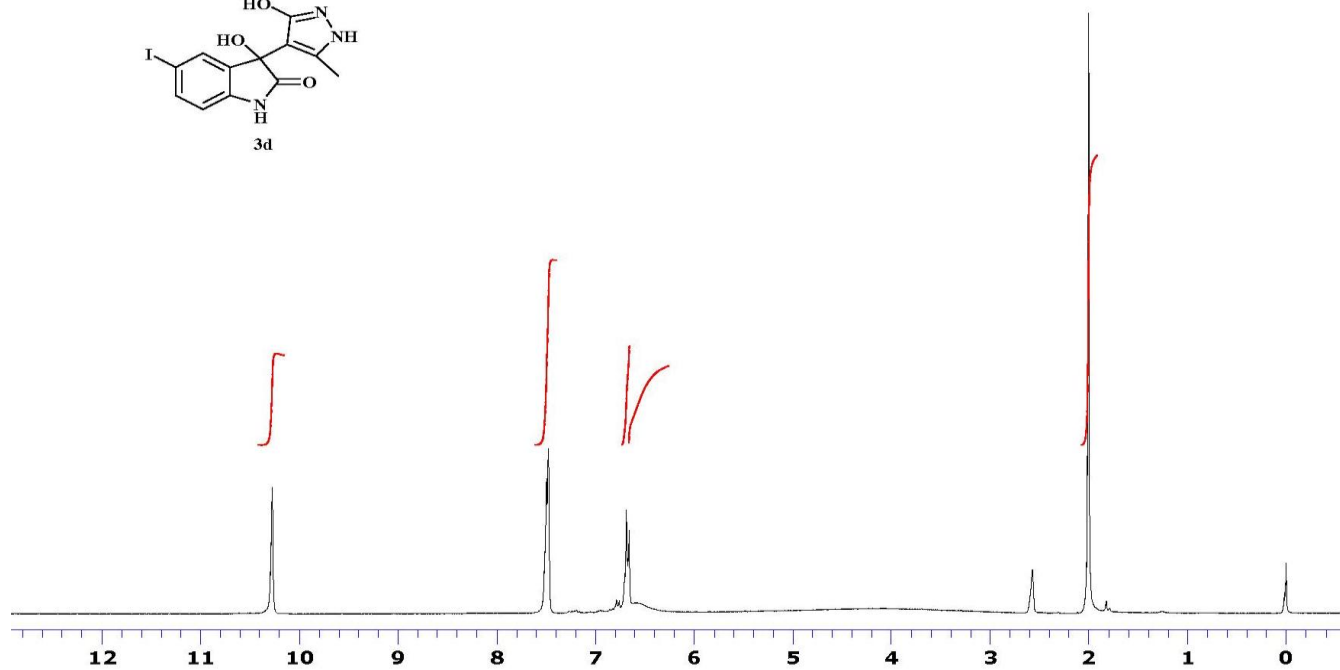
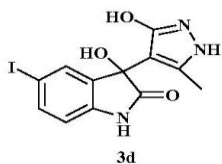


$^{13}\text{C NMR}$ , 75 MHz,  $\text{DMSO } d_6$

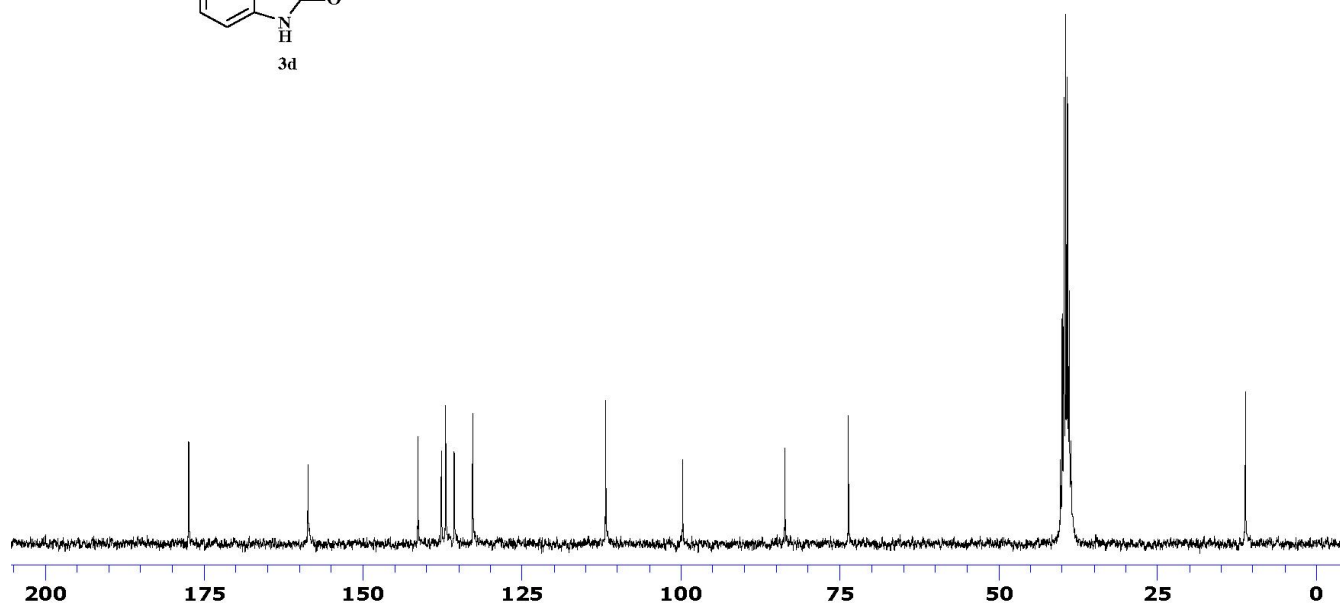
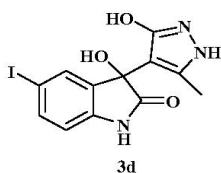


### 3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-5-iodoindolin-2-one (3d, Table 2)

$^1\text{H NMR}$ , 300 MHz,  $\text{DMSO } d_6$

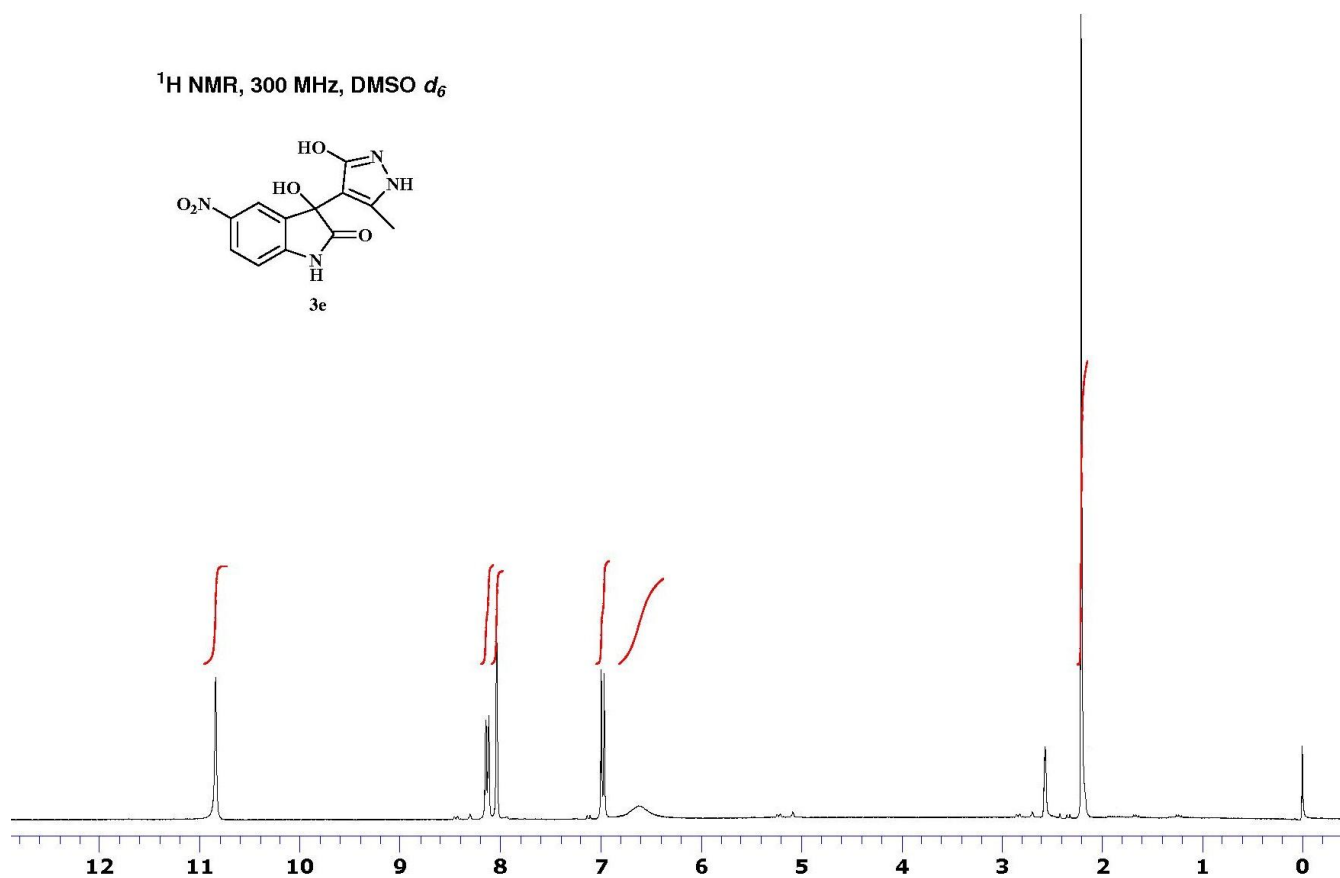
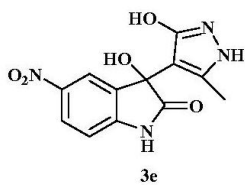


$^{13}\text{C NMR}$ , 75 MHz,  $\text{DMSO } d_6$

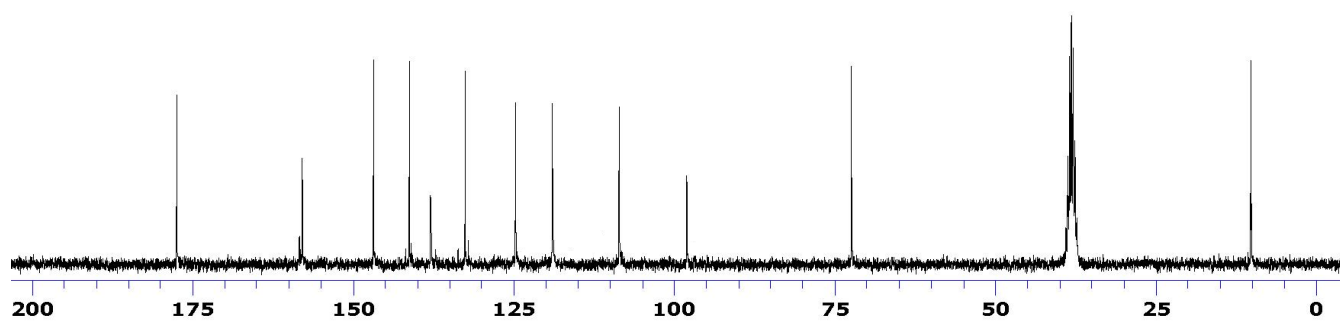
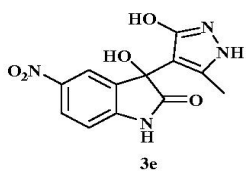


### 3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-5-nitroindolin-2-one (3e, Table 2)

$^1\text{H NMR}$ , 300 MHz,  $\text{DMSO } d_6$

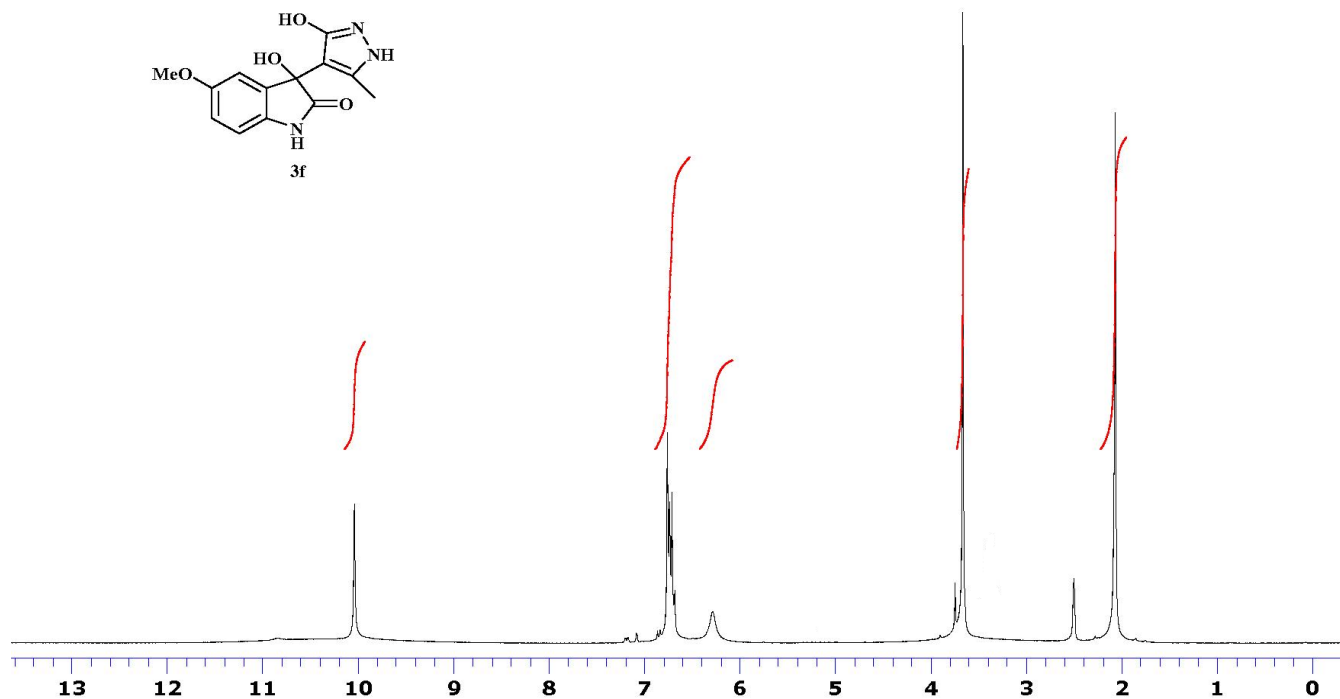
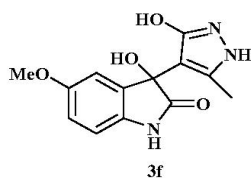


$^{13}\text{C NMR}$ , 75 MHz,  $\text{DMSO } d_6$

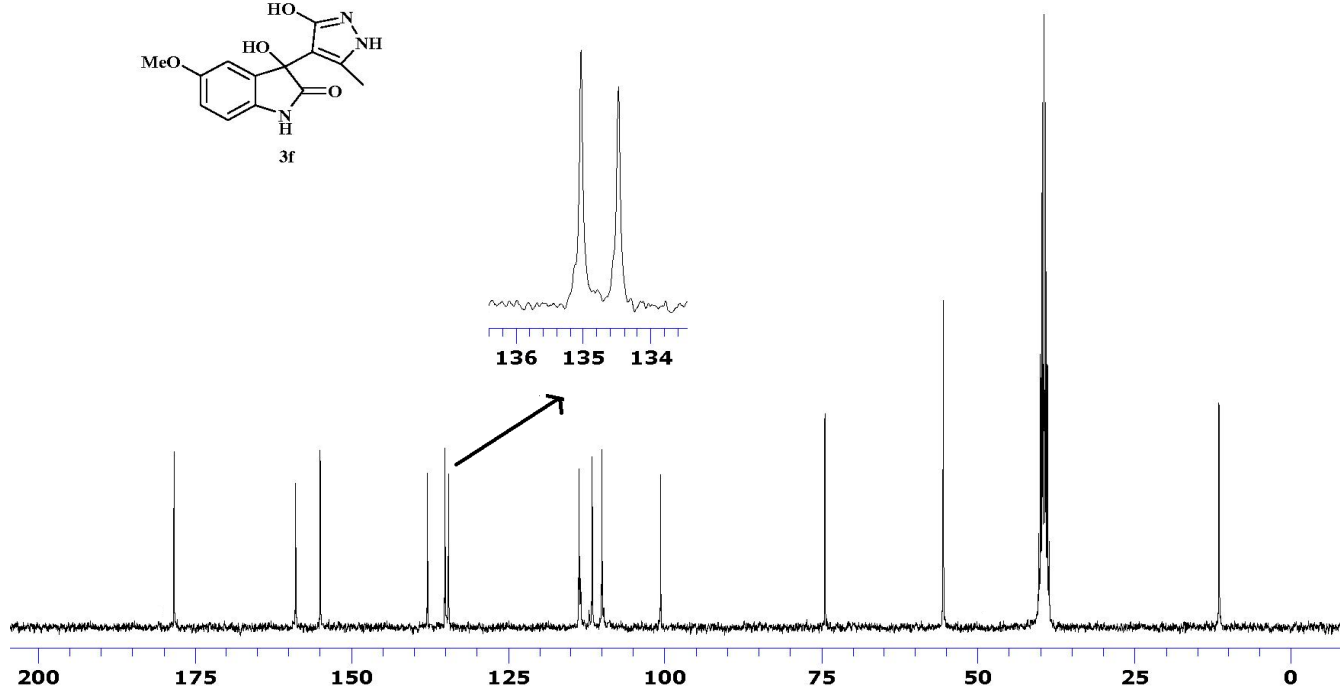
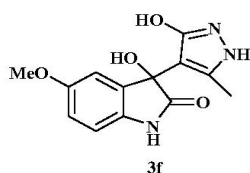


### 3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-5-methoxyindolin-2-one (3f, Table 2)

$^1\text{H}$  NMR, 300 MHz,  $\text{DMSO } d_6$

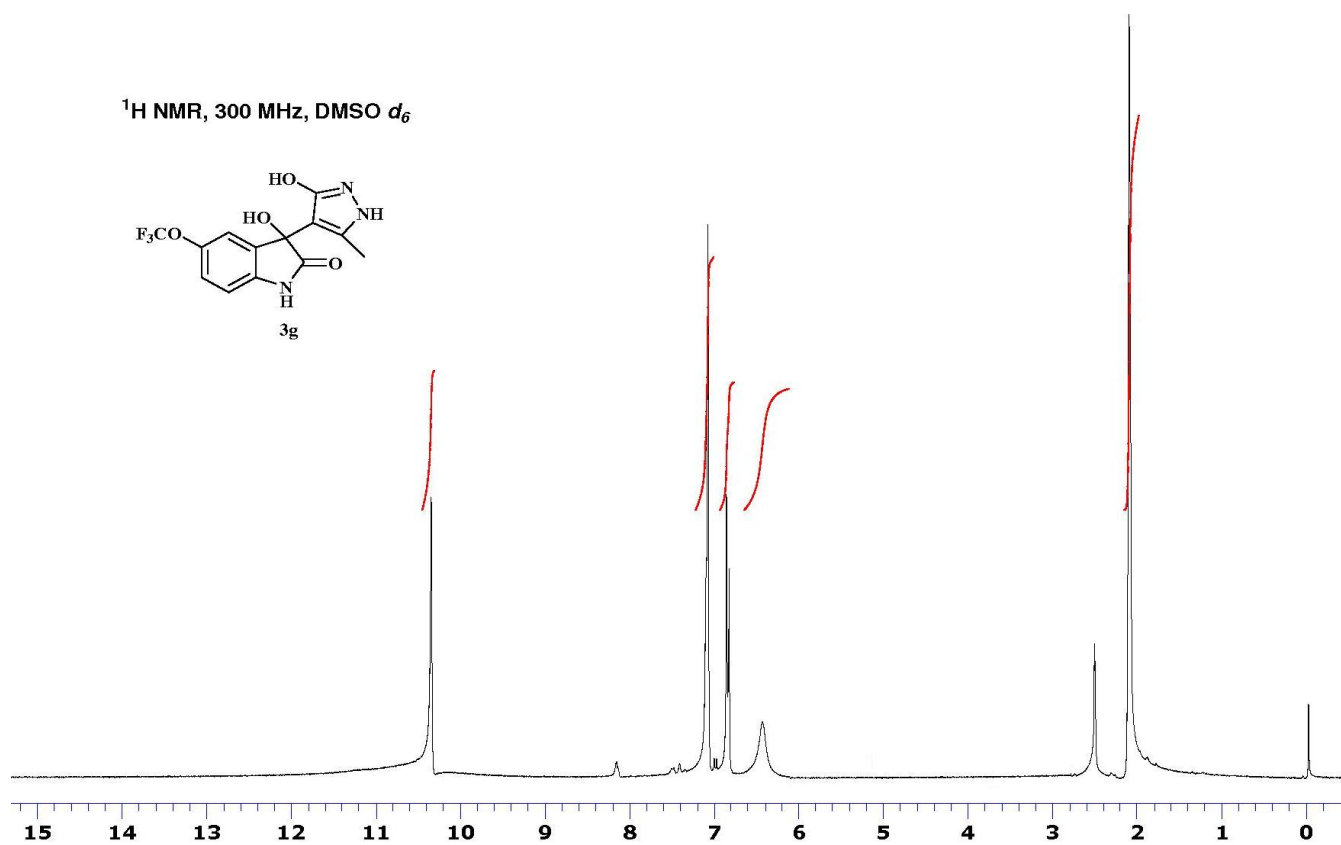
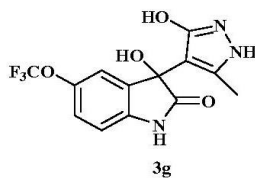


$^{13}\text{C}$  NMR, 75 MHz,  $\text{DMSO } d_6$

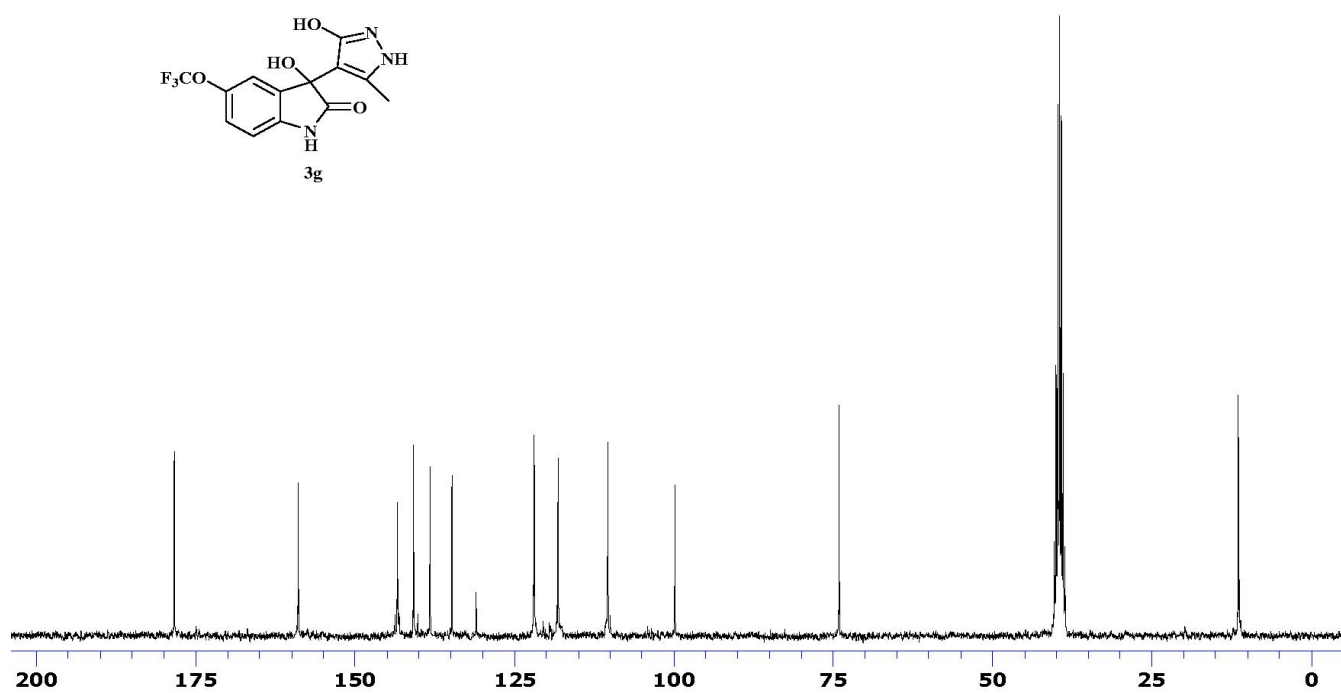
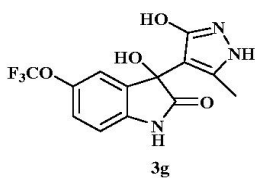


**3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-5-(trifluoromethoxy)indolin-2-one (3g, Table 2)**

<sup>1</sup>H NMR, 300 MHz, DMSO *d*<sub>6</sub>

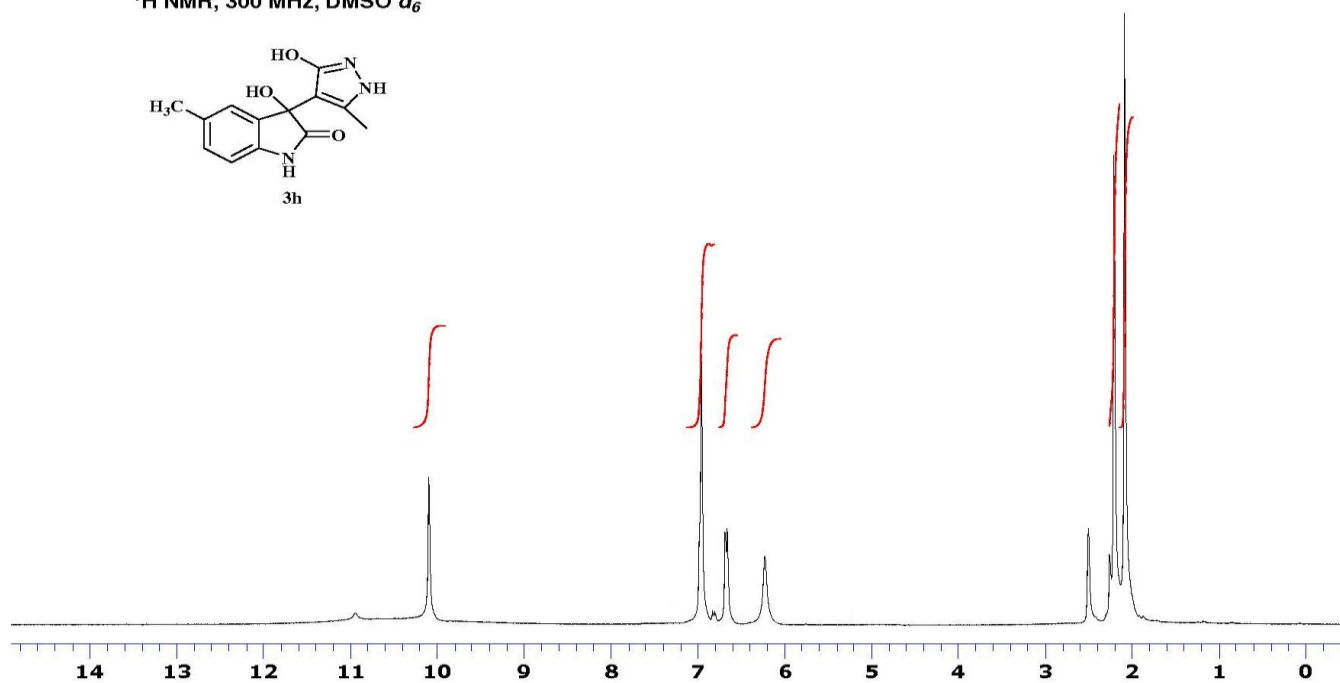
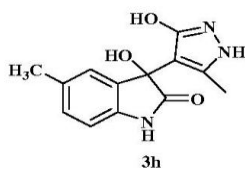


<sup>13</sup>C NMR, 75 MHz, DMSO *d*<sub>6</sub>

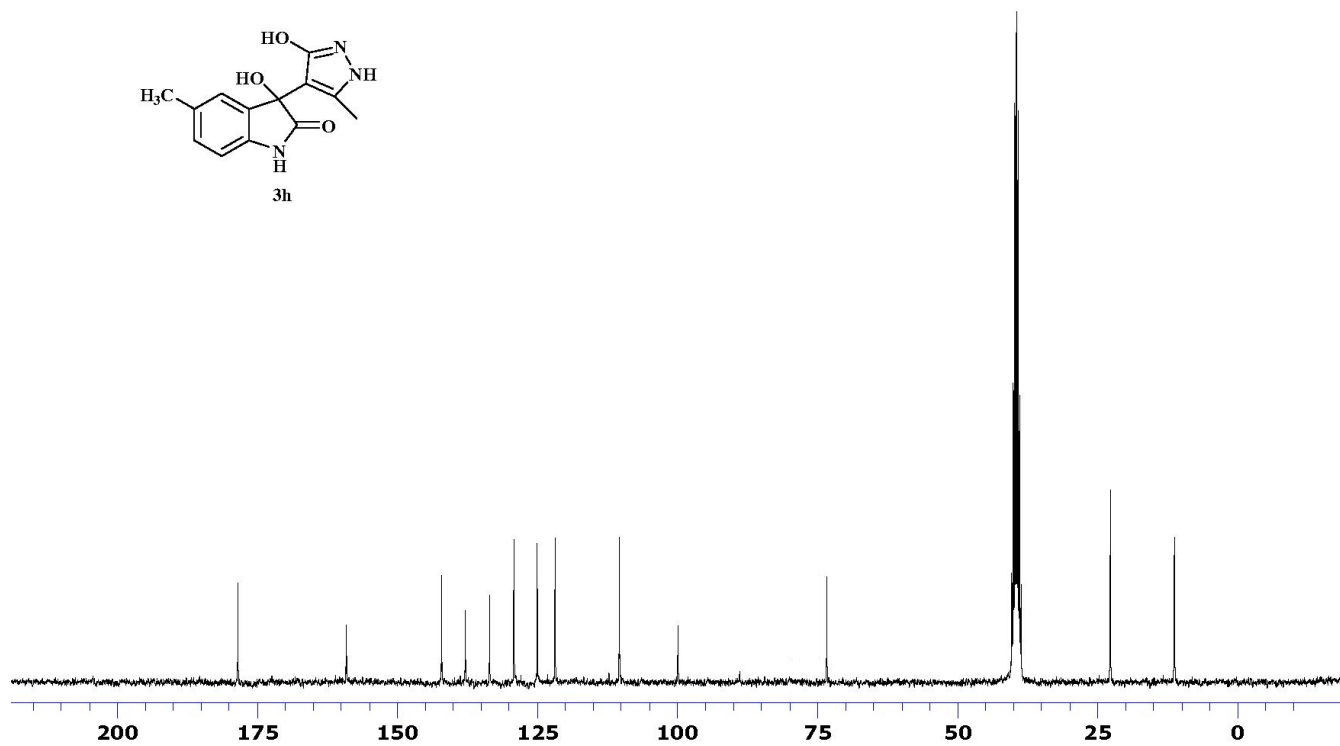
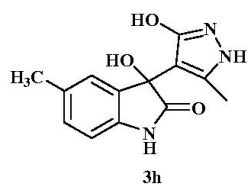


### Ethyl 3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-5-methylindolin-2-one (3h, Table 2)

<sup>1</sup>H NMR, 300 MHz, DMSO *d*<sub>6</sub>



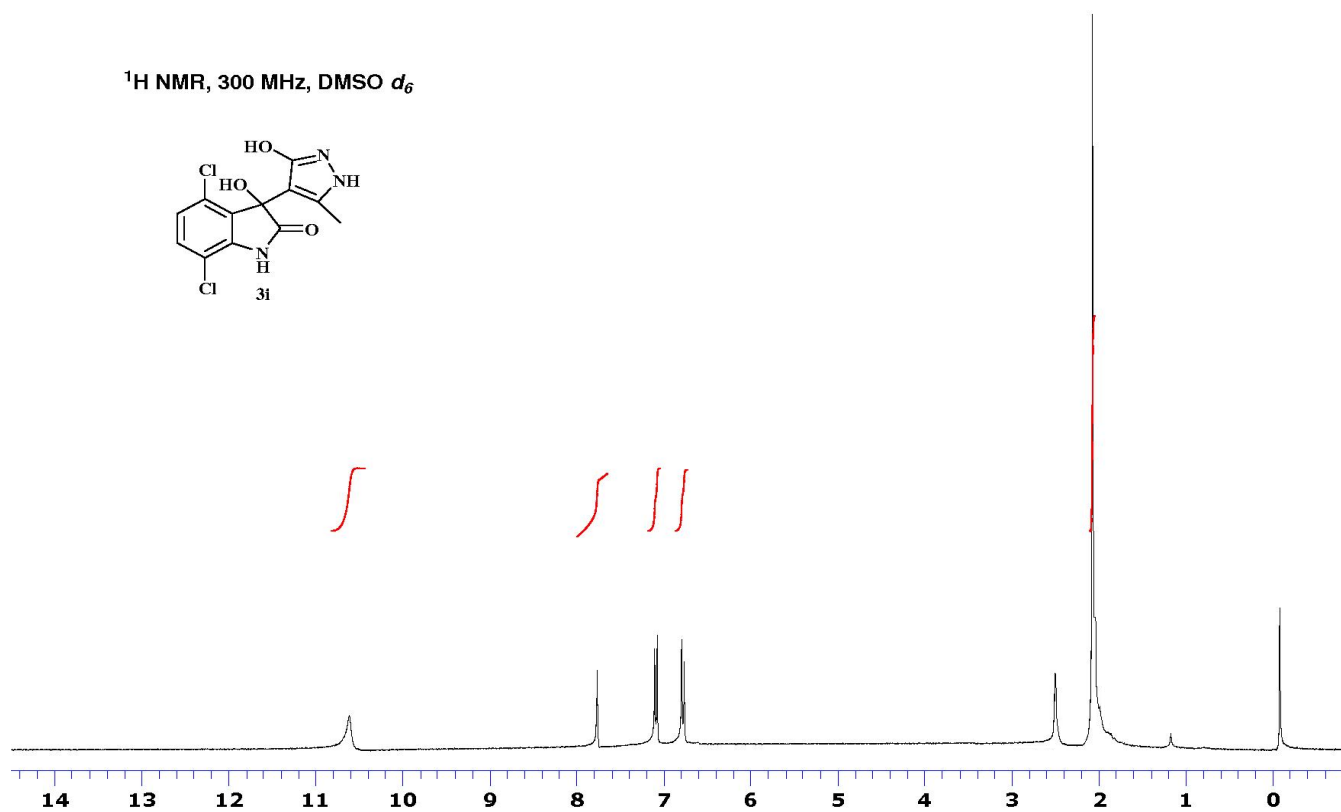
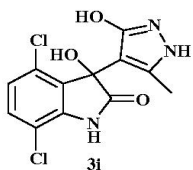
<sup>13</sup>C NMR, 75 MHz, DMSO *d*<sub>6</sub>



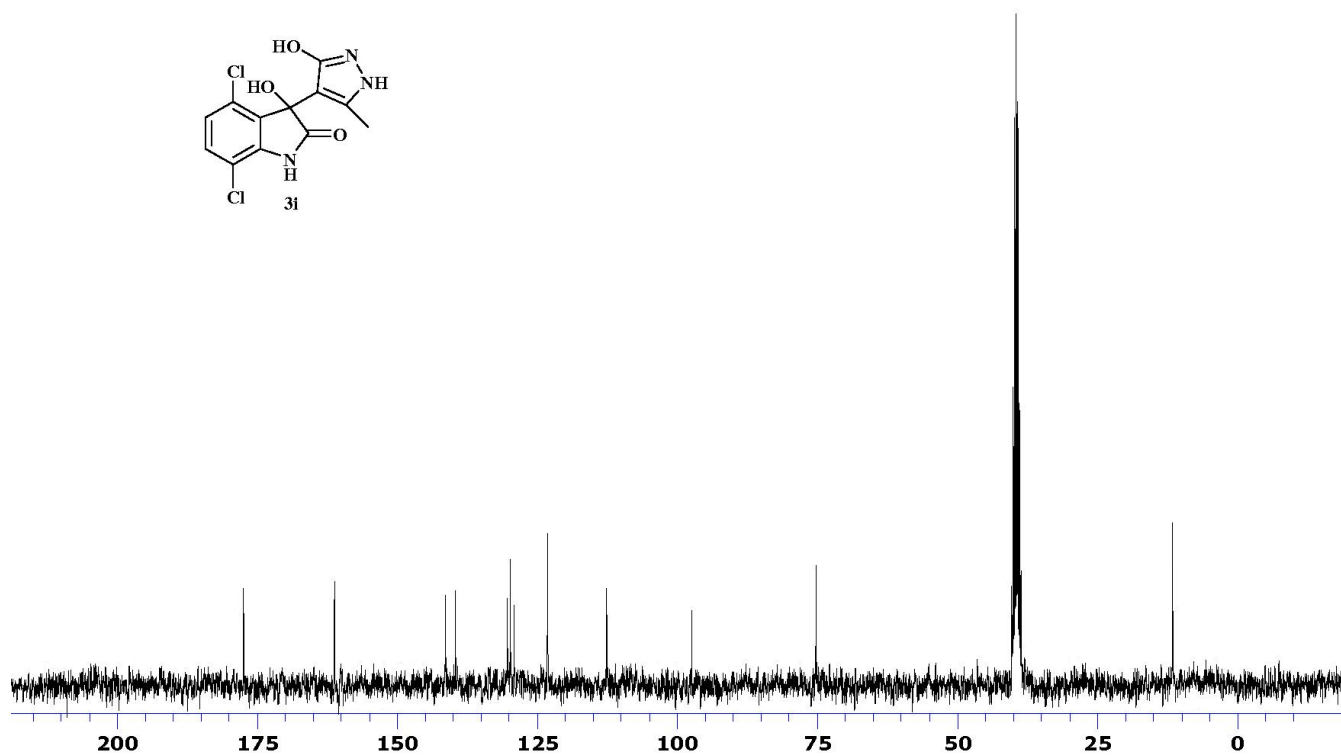
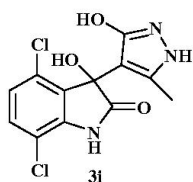


### 4,7-dichloro-3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)indolin-2-one (3i, Table 2)

$^1\text{H}$  NMR, 300 MHz,  $\text{DMSO } d_6$

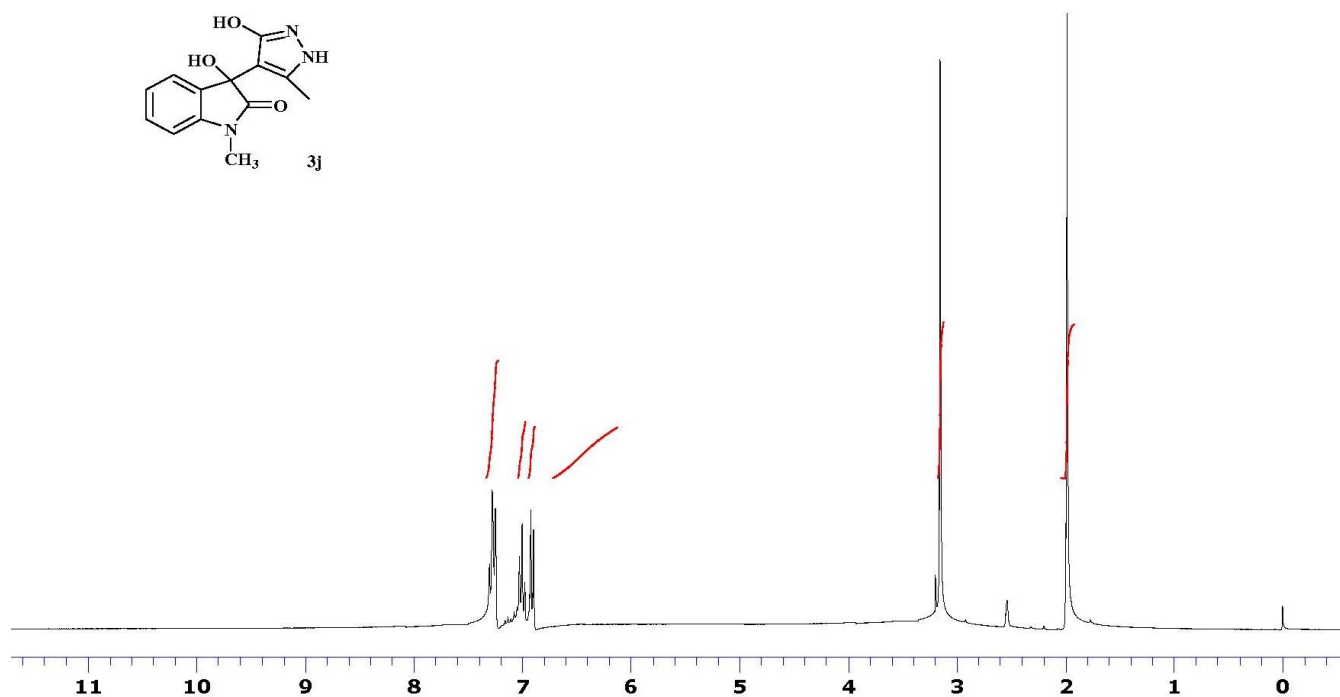
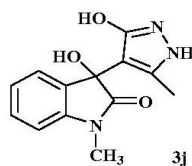


$^{13}\text{C}$  NMR, 75 MHz,  $\text{DMSO } d_6$

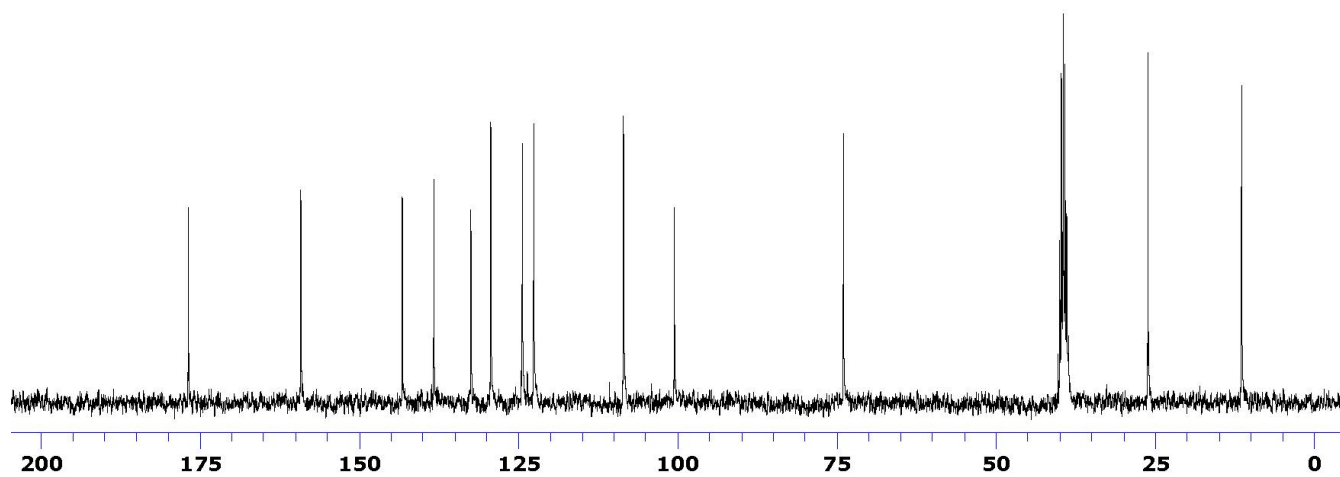
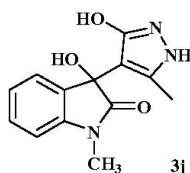


### 3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-1-methylindolin-2-one (3j, Table 2)

$^1\text{H}$  NMR, 300 MHz,  $\text{DMSO } d_6$

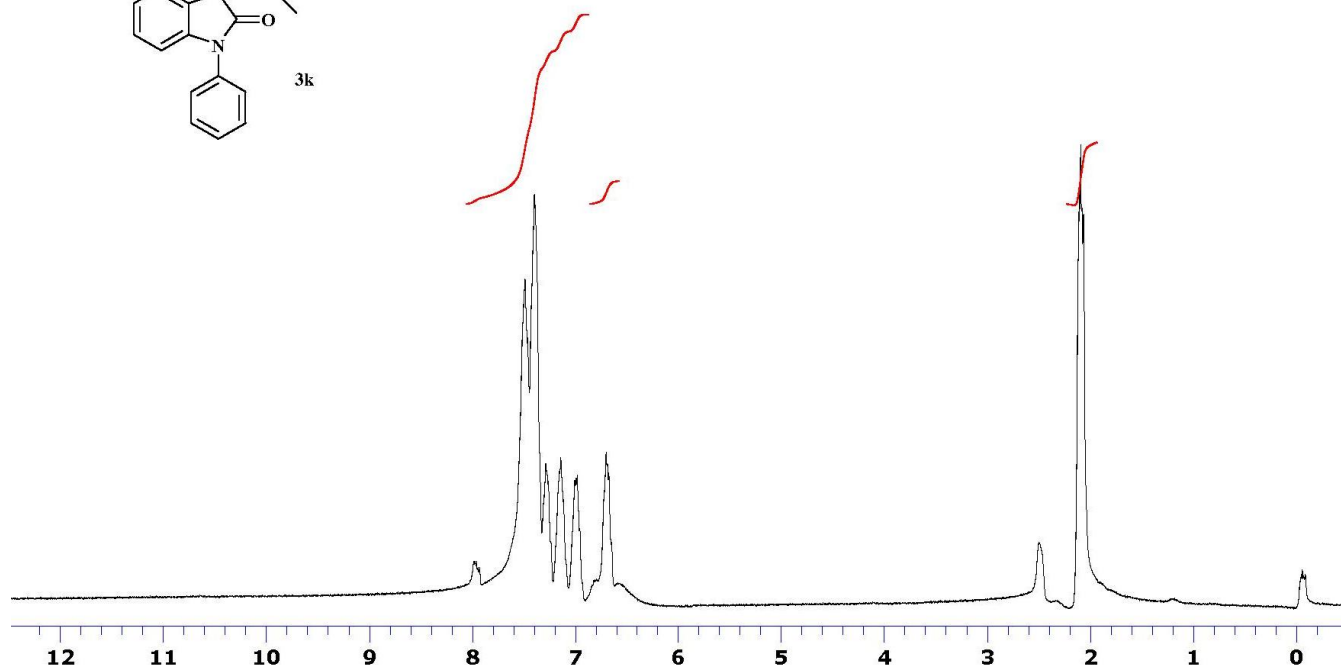
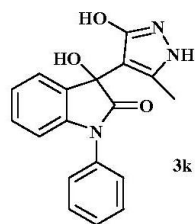


$^{13}\text{C}$  NMR, 75 MHz,  $\text{DMSO } d_6$

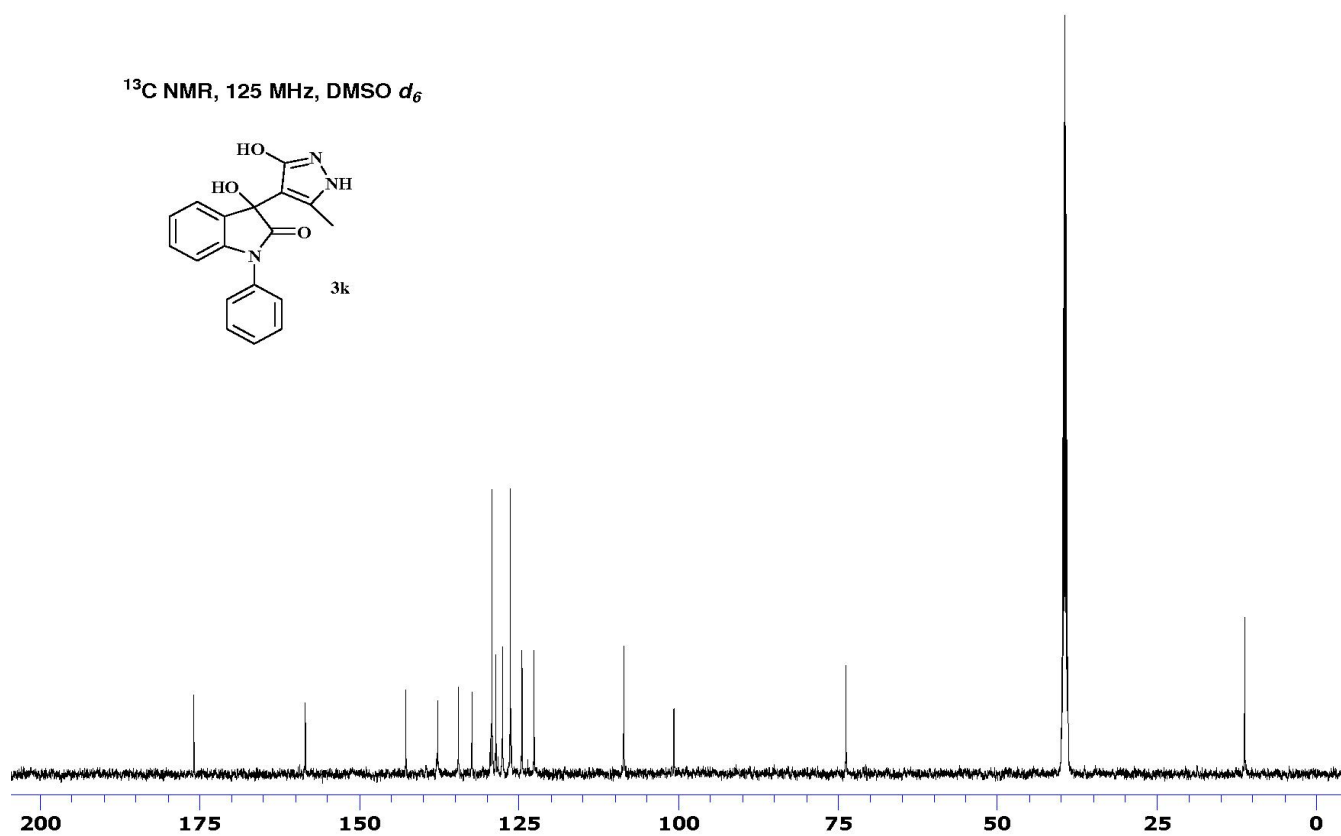
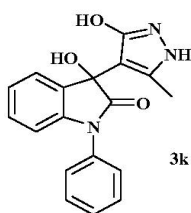


### 3-hydroxy-3-(3-hydroxy-5-methyl-1H-pyrazol-4-yl)-1-phenylindolin-2-one (3k, Table 2)

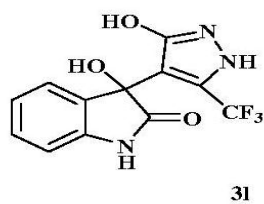
$^1\text{H}$  NMR, 300 MHz,  $\text{DMSO } d_6$



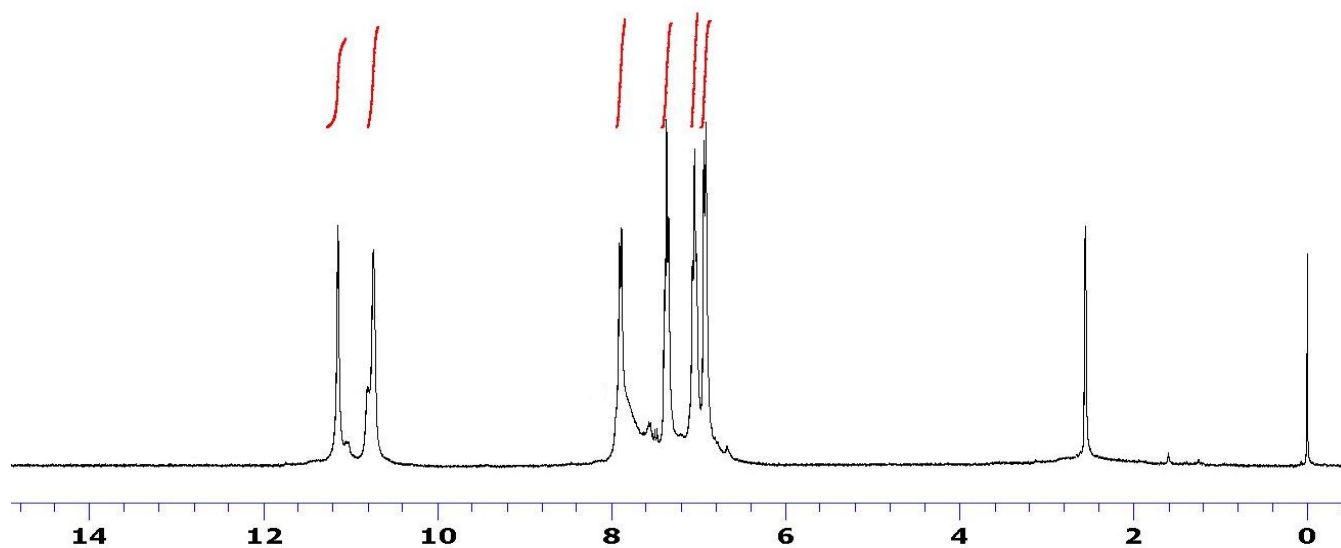
$^{13}\text{C}$  NMR, 125 MHz,  $\text{DMSO } d_6$



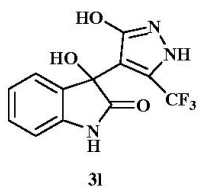
### 3-(5-(trifluoromethyl)-3-hydroxy-1H-pyrazol-4-yl)-3-hydroxyindolin-2-one (31, Table 2)



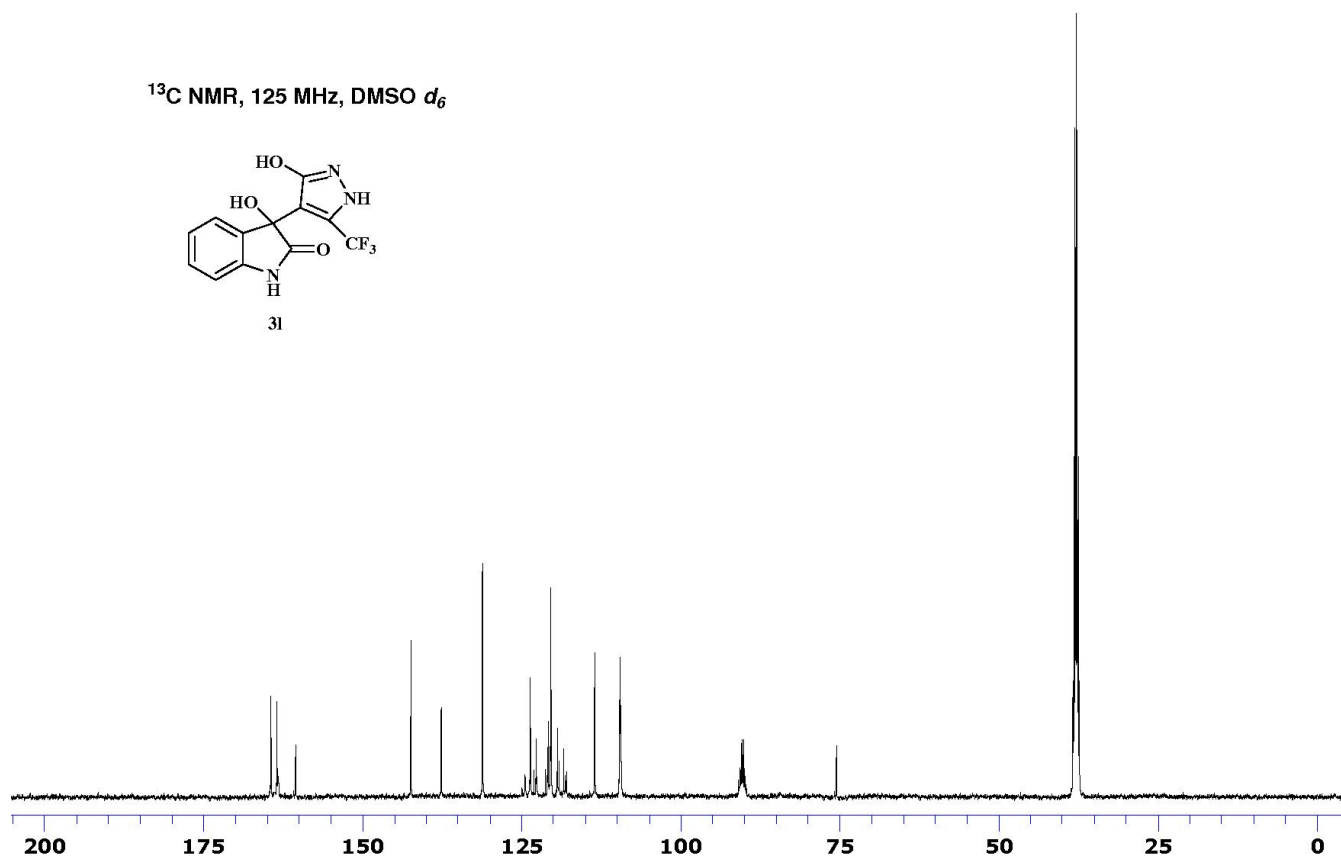
31



<sup>13</sup>C NMR, 125 MHz, DMSO *d*<sub>6</sub>

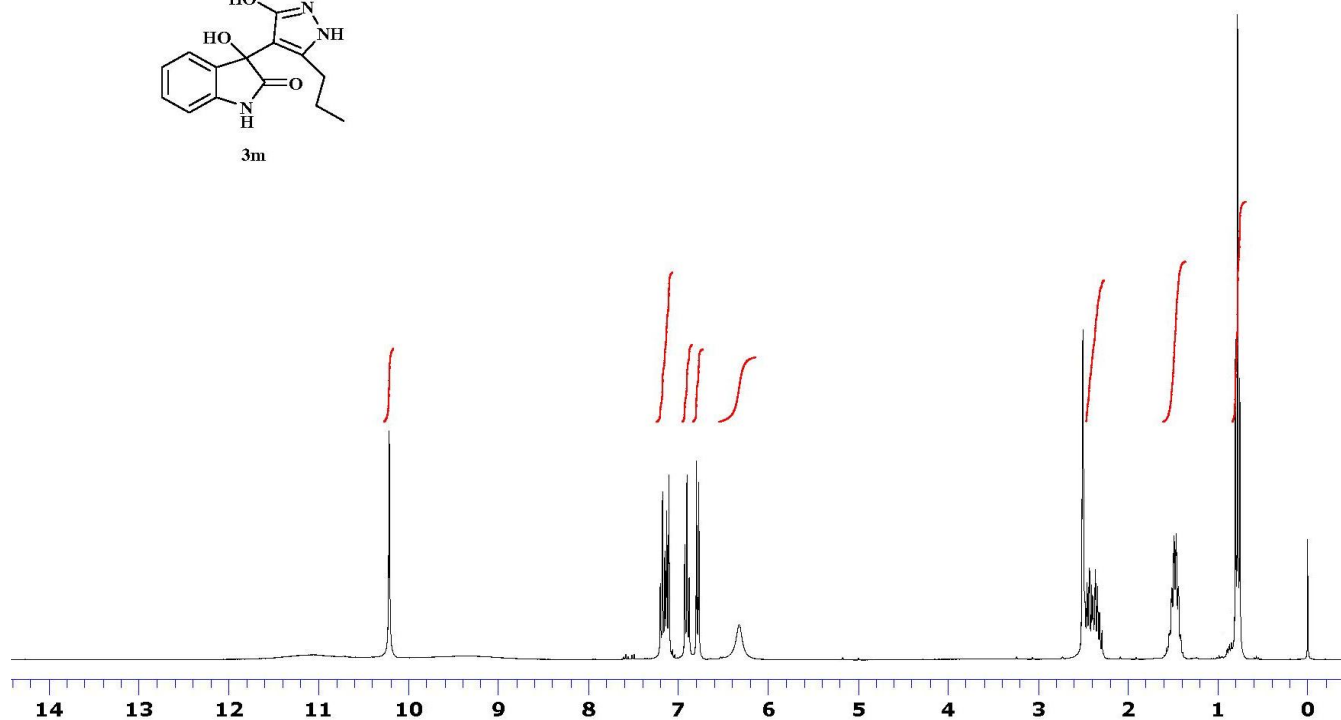
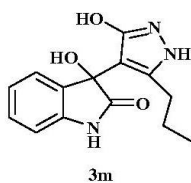


31

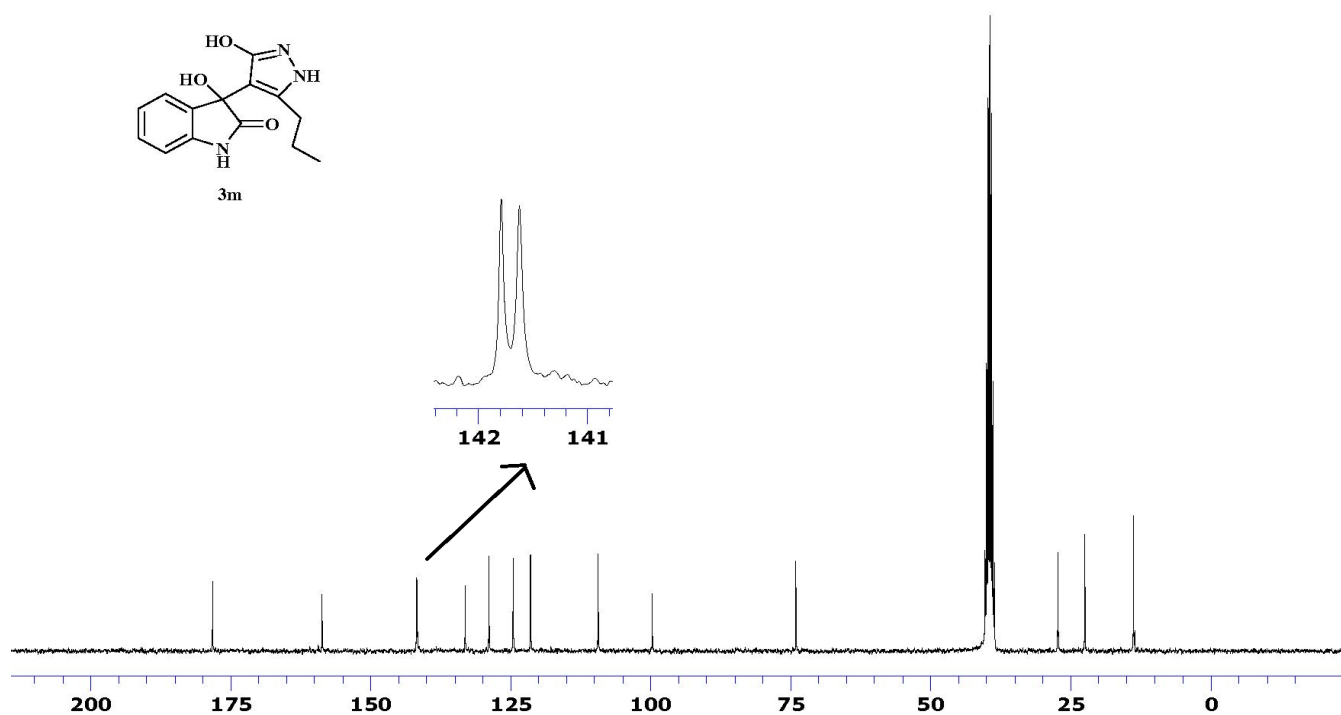
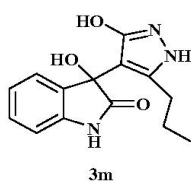


### 3-hydroxy-3-(3-hydroxy-5-propyl-1H-pyrazol-4-yl)indolin-2-one (3m, Table 2)

$^1\text{H}$  NMR, 300 MHz,  $\text{DMSO } d_6$

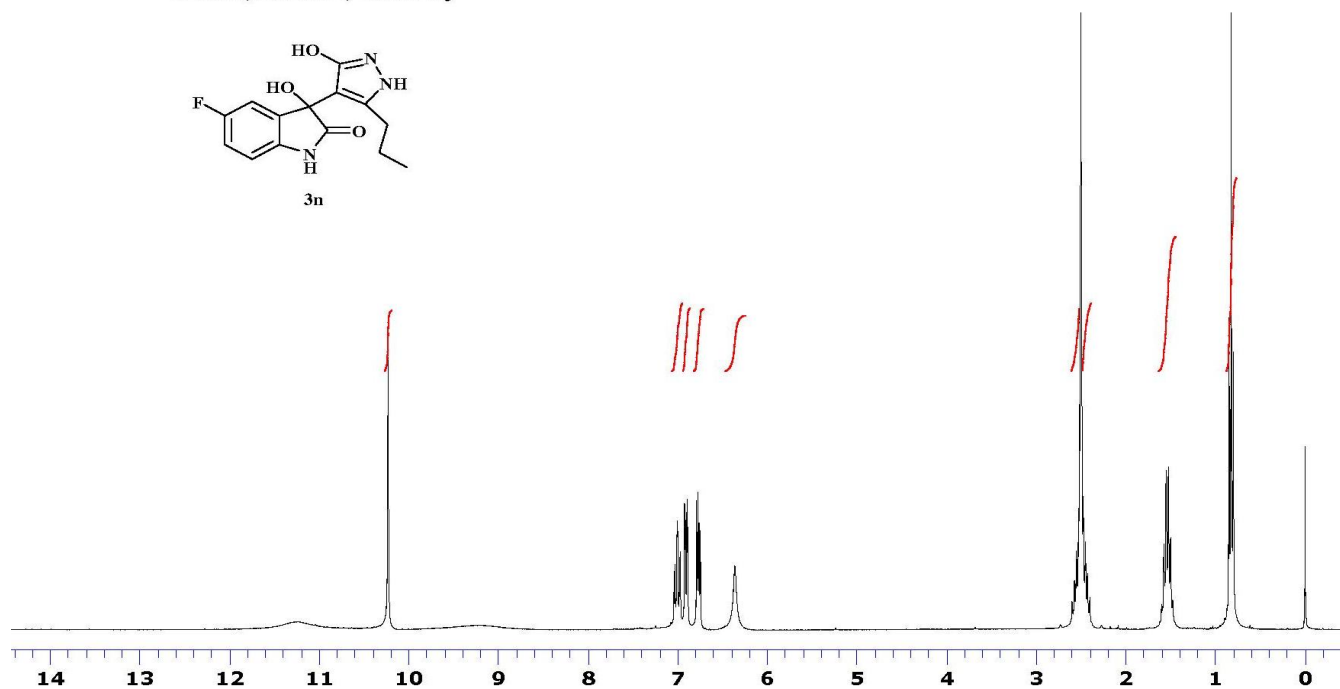
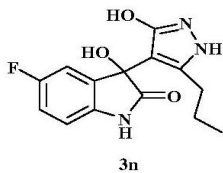


$^{13}\text{C}$  NMR, 125 MHz,  $\text{DMSO } d_6$

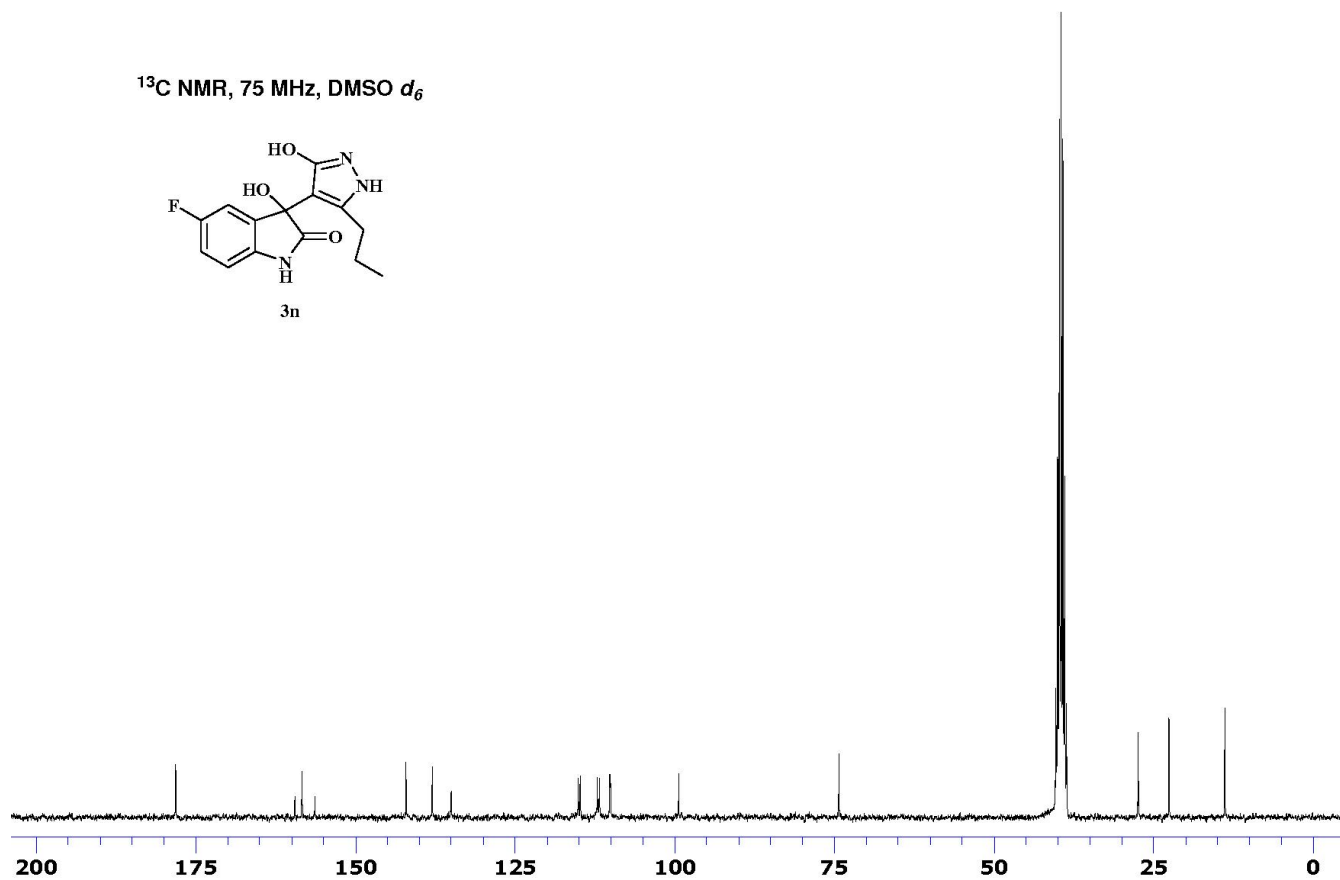
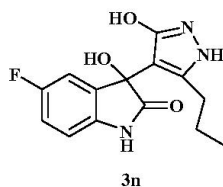


### 5-fluoro-3-hydroxy-3-(3-hydroxy-5-propyl-1H-pyrazol-4-yl)indolin-2-one (3n, Table 2)

$^1\text{H}$  NMR, 300 MHz,  $\text{DMSO } d_6$

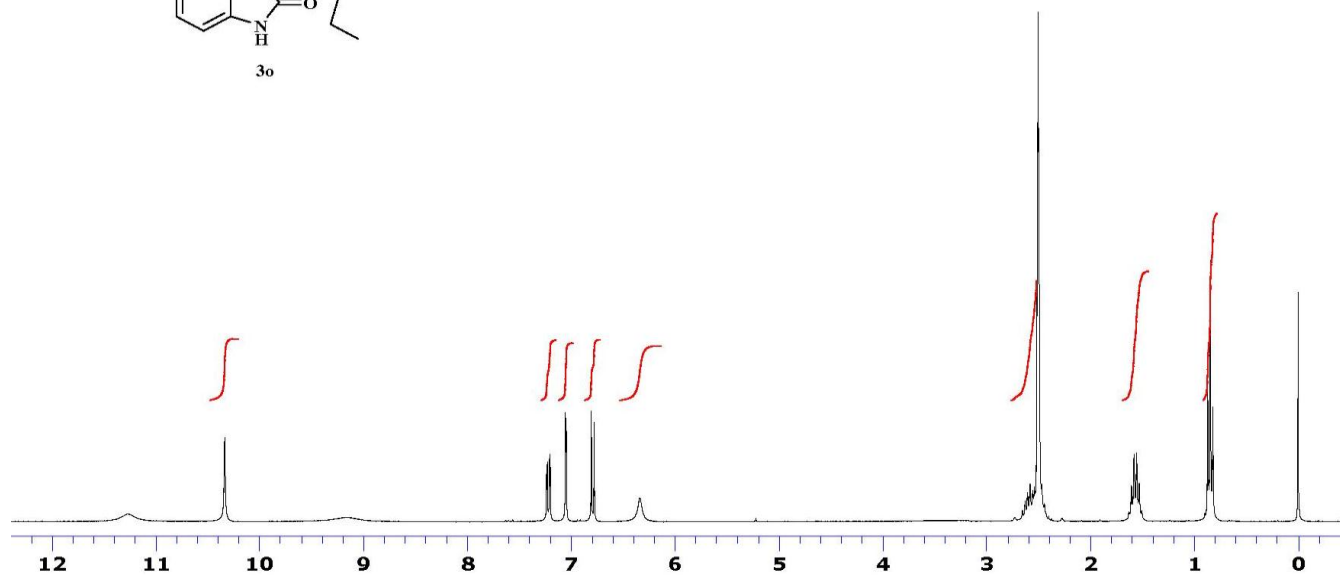
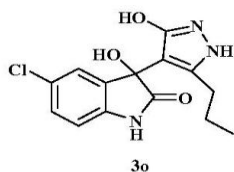


$^{13}\text{C}$  NMR, 75 MHz,  $\text{DMSO } d_6$

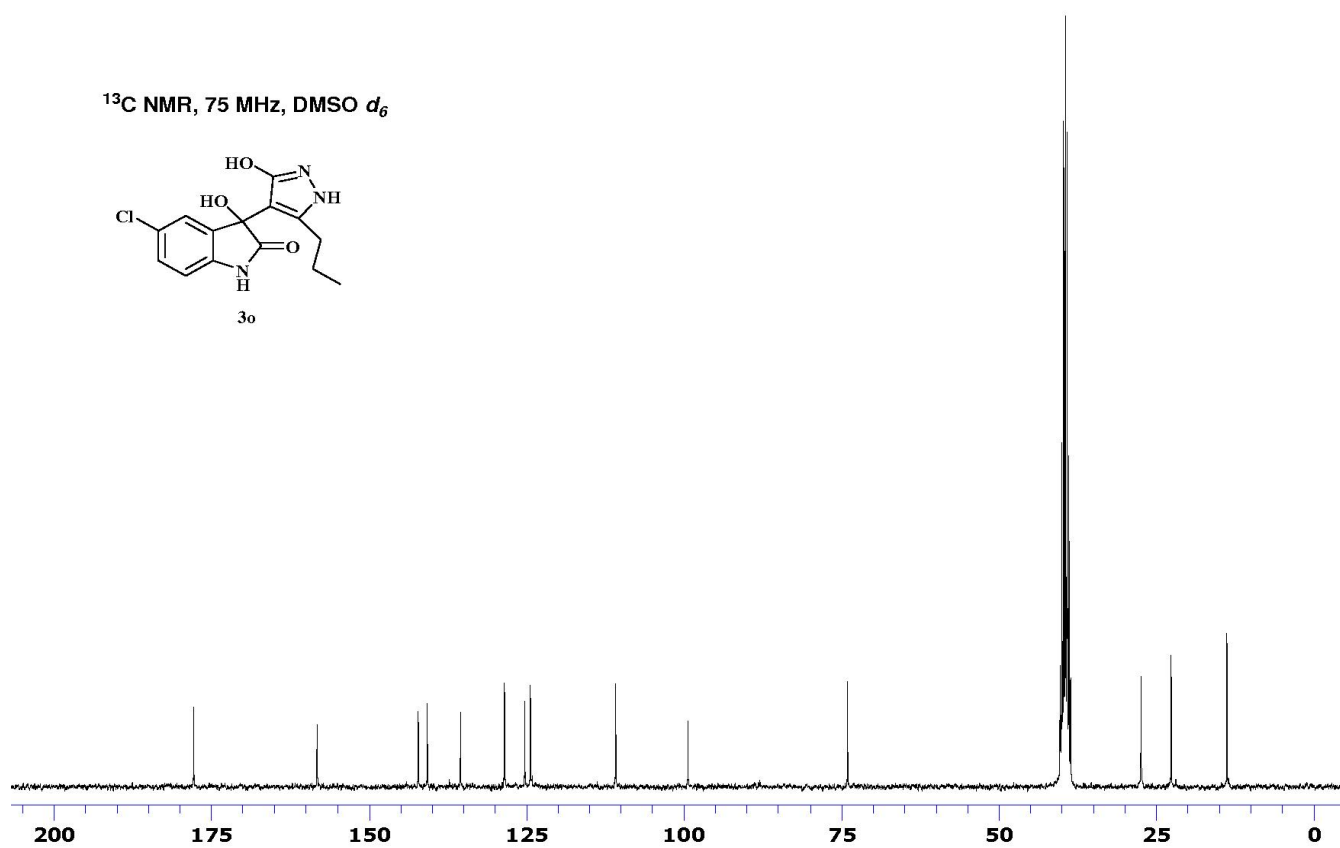
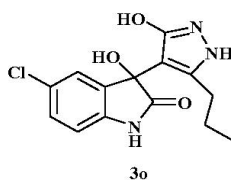


### 5-chloro-3-hydroxy-3-(3-hydroxy-5-propyl-1H-pyrazol-4-yl)indolin-2-one (30, Table 2)

$^1\text{H NMR}$ , 300 MHz,  $\text{DMSO } d_6$

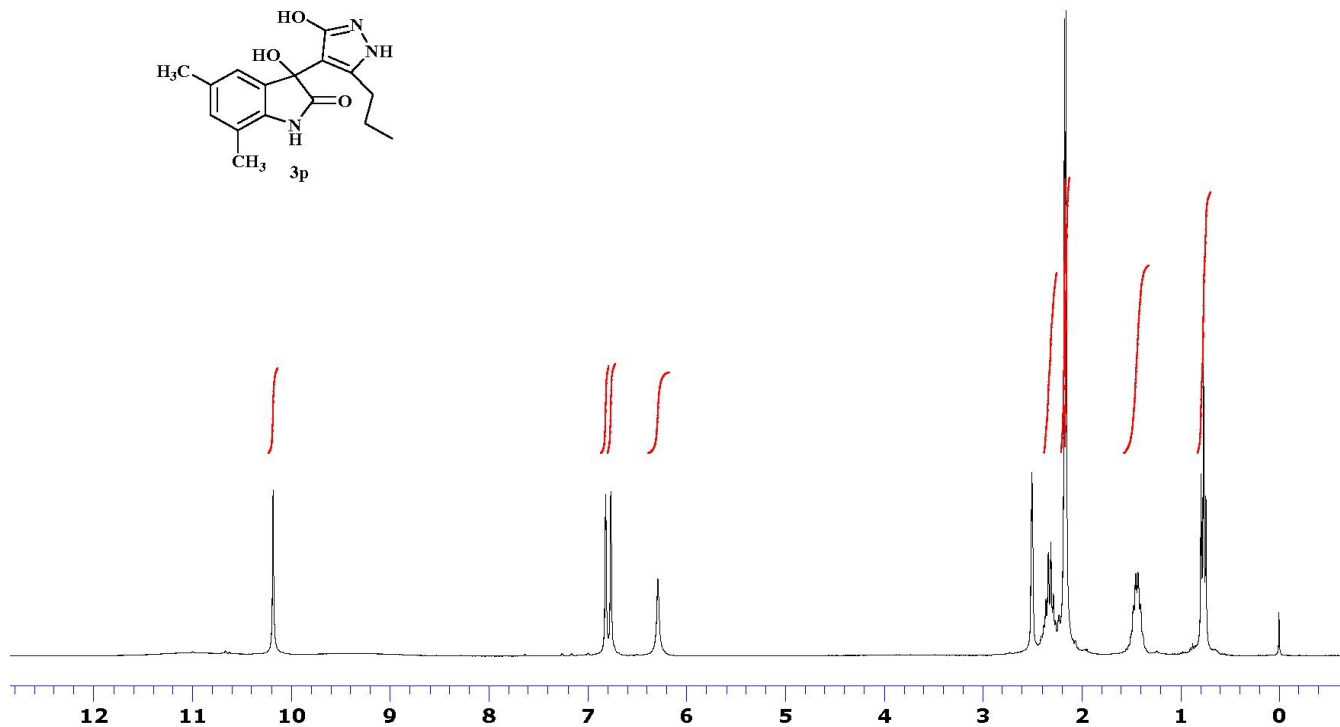
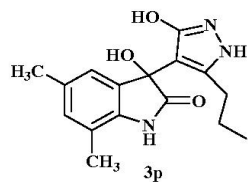


$^{13}\text{C NMR}$ , 75 MHz,  $\text{DMSO } d_6$



### 3-hydroxy-3-(3-hydroxy-5-propyl-1H-pyrazol-4-yl)-5,7-dimethylindolin-2-one (3p, Table 2)

$^1\text{H NMR}$ , 300 MHz,  $\text{DMSO } d_6$



$^{13}\text{C NMR}$ , 75 MHz,  $\text{DMSO } d_6$

