Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


## Supporting information

# A Single Pot Organocatalytic Diastereoselective Synthesis of Fluorescent Ring Fused 2-Pyridone Decalines via Domino Knoevenagel/Michael/Hydro-lactamisation Sequence

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**General Information**

A flame dried glass apparatus was used to carry out all the reactions under close atmosphere using A.R. grade solvents as purchased. All the chemicals procured from authentic dealers such as Sigma Aldrich, Alfa Aser, and Thomas Baker etc. Aluminum coated with silica gel 60 $F_{254}$ TLC plates purchased from Merck for TLC chromatography. Products were separated and purified over flash chromatography using 35% ethyl acetate in hexane as a mobile phase packed with 220-400 mesh silica. Products were characterized by using $^{1}$H-NMR and $^{13}$C NMR using $D_6$-DMSO (Reference, 0.01% TMS) as a solvent on 400 MHz Bruker instrument and 500 MHz/600 MHz JEOL instruments. FT-IR has been done on the PerkinElmer frontier instrument in ATR (PIKE make) mode at room temperature. Fluorescent emission spectra were recorded on a HORIBA QM-400 instrument, equipped with a continuous Xenon arc lamp, samples were excited at 300-350 nm. The single-crystal structure was determined using a BRUKER SMART APEX (CCD) diffractometer. HRMS were done on the Agilent 6545 LC/Q-TOF.

**General procedure for the domino synthesis of 2-pyridones**

L-Proline (20 mol%) and PhCOOH (20 mol%) were added to the solution of aldehydes (1 mmol), cyclohexanone (2 mmol) and cyanoacetamides (1.1 mmol) in 25 mL R. B. flask containing 5 mL DMSO solvent. The reaction mixture was then stirred for 6-24 h, and after completion of the reaction monitored by TLC (45% EA in hexane), sat. aq. $NaHCO_3$ (5 mL) was added to quench the reaction. After that reaction mixture was extracted with ethyl acetate and washed subsequently with sat. aq. $NaHCO_3$, $H_2O$, and brine. Finally, the organic layer was dried using anhydrous $Na_2SO_4$, and the crude product was loaded over flash silica (220-400 mesh) to separate the compounds using column chromatography. Isolated yields were calculated after compound separations.

**Fluorescent spectroscopy study of 5k, 5i and 5m compounds**

For the proof of fluorescent nature of the synthesised compounds, studied the fluorescent spectroscopy of the **5k, 5i** and **5m**. All the compounds were excited at λ 300-350 nm emitted the $\lambda_{max}$ in visible region (**Figure SI1**) and thus also studied the aggregation-induced fluorescent of **5l**.

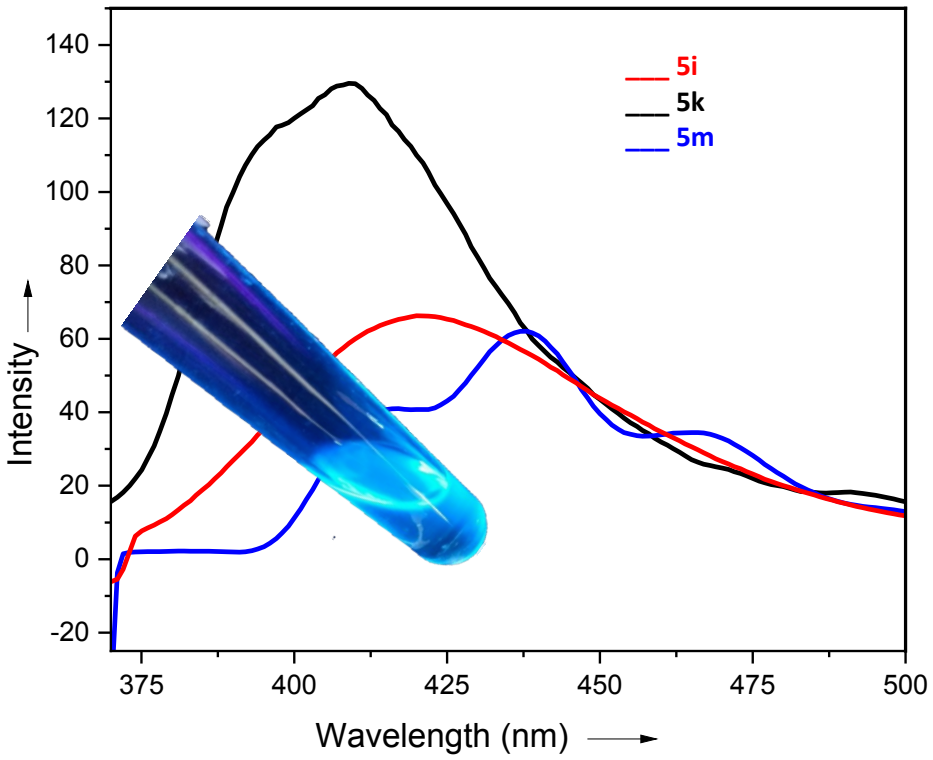



**Figure SI1.** Fluorescent spectroscopic study of **5k**, **5i** and **5m** fused 2-pyridones.

**COSY-GPSW NMR spectroscopy study**

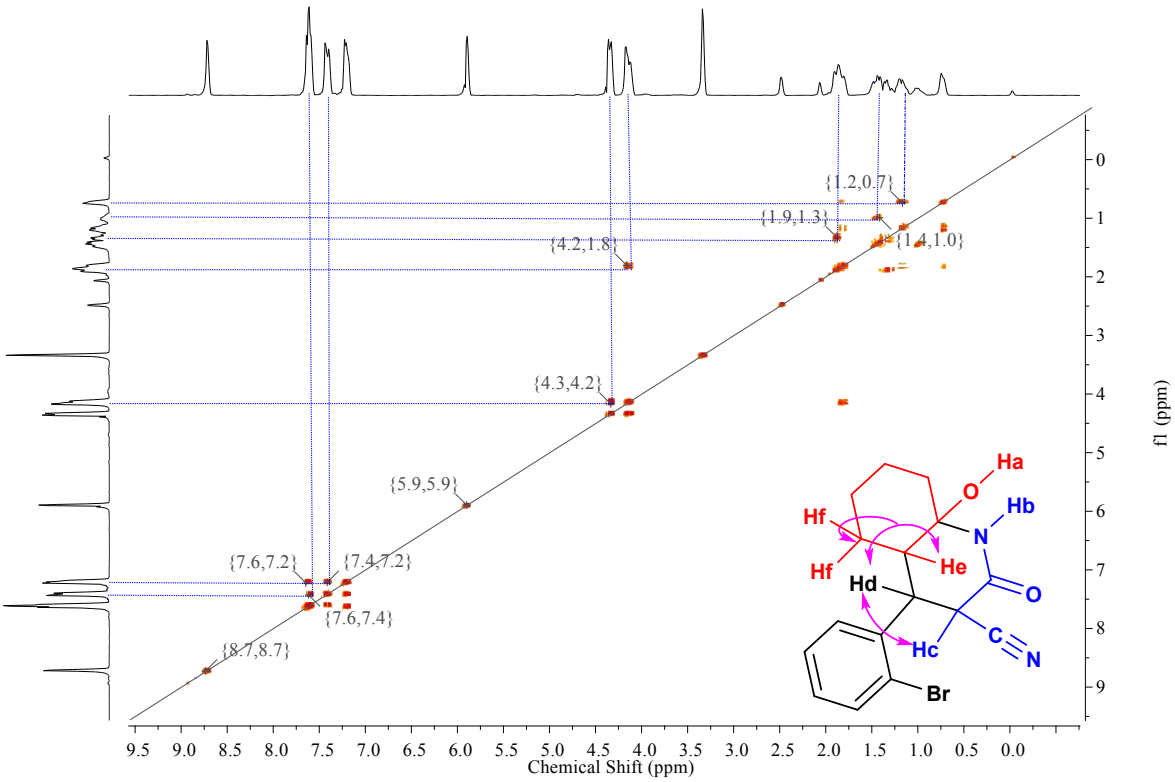



**Figure SI2 .** Study of interaction of protons in compound **5k** using COSY-GPSW NMR spectroscopy

**FT-IR spectroscopy study of 5a**

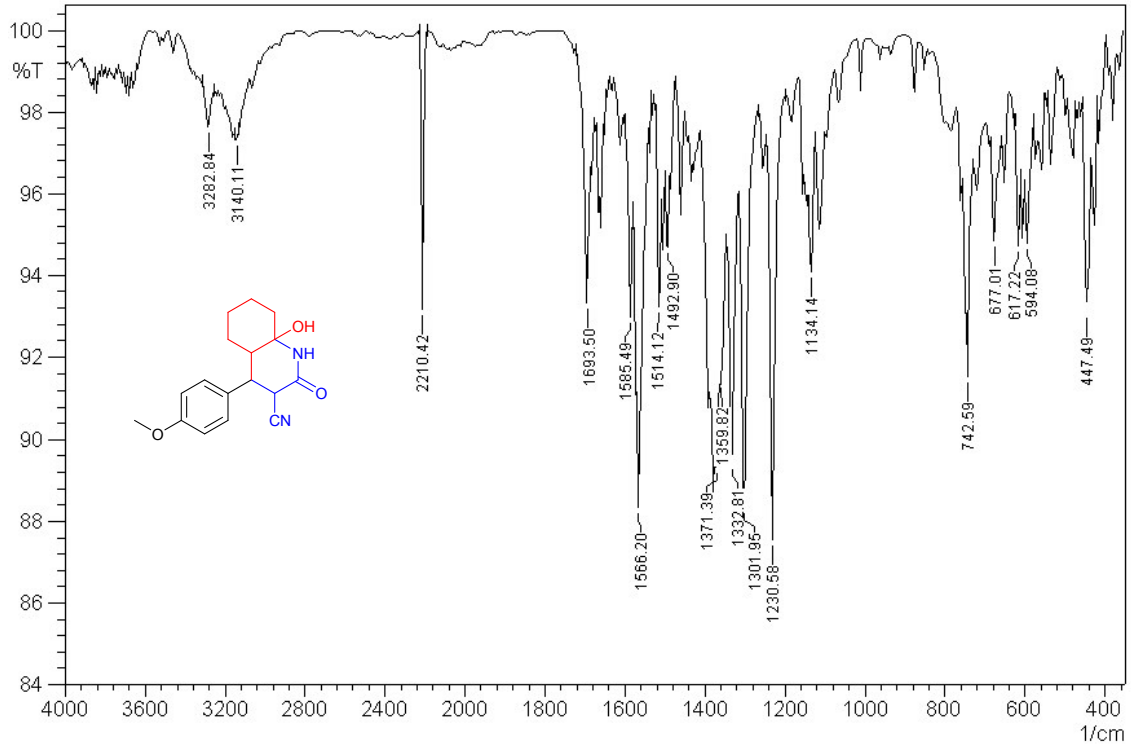
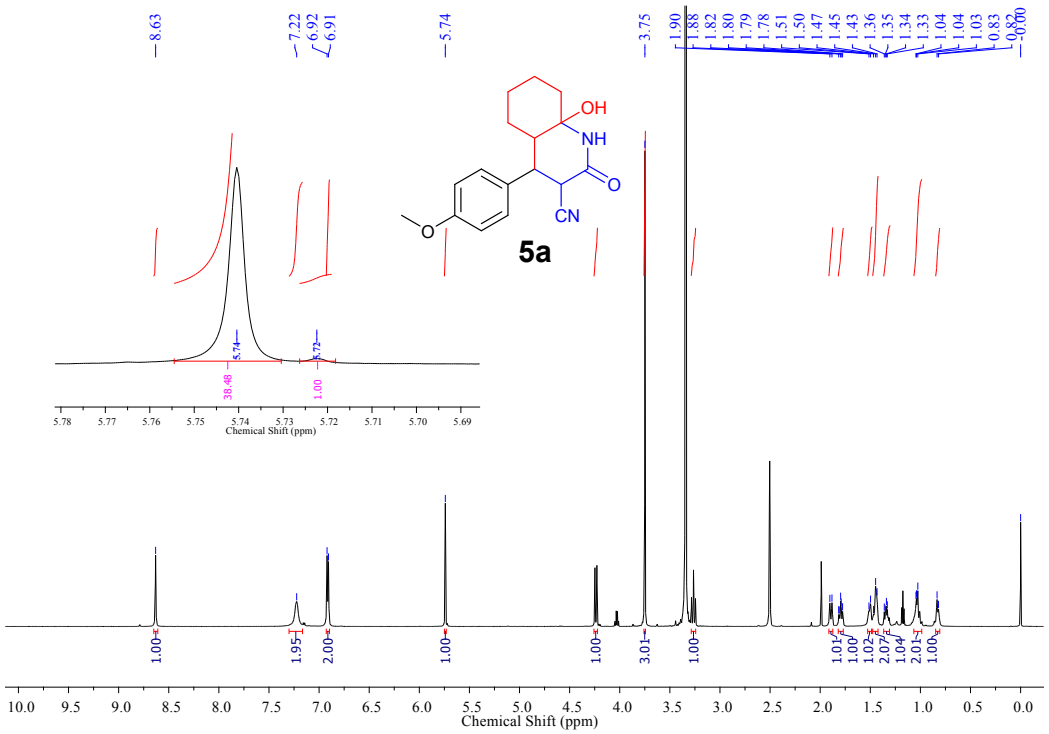



**Figure SI3.** Study of interaction of protons in compound **5k** using COSY-GPSW NMR spectroscopy

**Determination of diastereoselectivity of compound 5a and crude 5d**



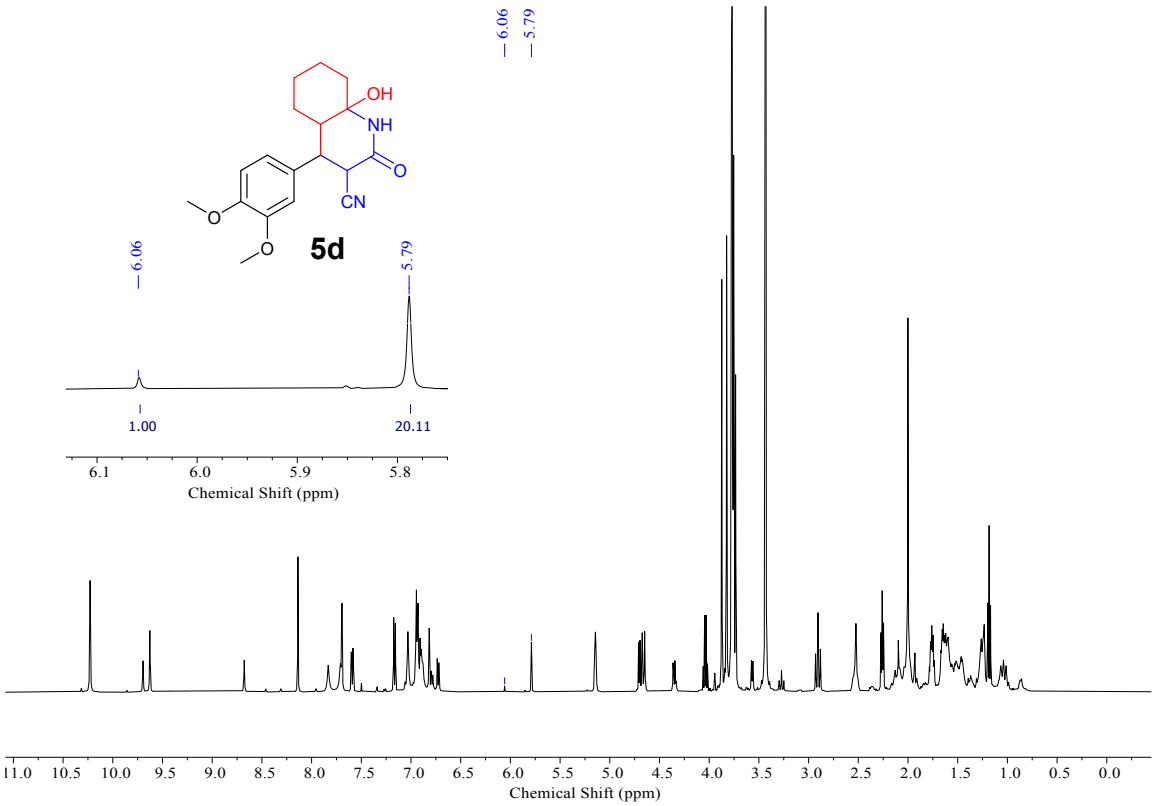
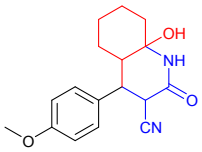


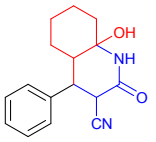

**Figure SI4.** Diastereoselectivity determination using $^{1}$H NMR study of **5a and crude 5d**

**Characterization data of synthesized compounds**




**8a-hydroxy-4-(4-methoxyphenyl)-2-oxodecahydroquinoline-3-carbonitrile *(Compound 5a)***

**Off white Solid (91%), MP: 145-147 ˚C, $^{1}$H NMR** (600 MHz, DMSO-D6) δ 8.63 (s, 1H), 7.22 (d, 2H), 6.91 (d, 2H*J* = 8.5), 5.74 (s, 1H), 4.24 (d, 1H, *J* = 11.8 Hz), 3.75 (s, 3H), 3.26 (t, 1H,*J* = 11.8 Hz), 1.89 (d, 1H *J* =12.5), 1.82 – 1.77 (m, 1H), 1.51 (d, 1H *J* = 9.5), 1.45 (t, 2H *J* = 10.4), 1.34 (dd, 1H *J* = 12.2, 5.8), 1.07 – 0.99 (m, 2H), 0.83 (d, 1H *J* =8.8)ppm.**$^{13}$C NMR** (101 MHz, DMSO-D6) δ 163.76, 158.31, 131.04, 118.05, 114.03, 80.13, 54.94, 45.64, 42.74, 37.14, 24.76, 21.06 ppm.**FT-IR** (ATR) 1/λ 3282.84 (N-H), 3140.11 (N-H), 2210.42 (C≡N), 1693.50 (NH-C=O), 1566.20 (Ar-C-H),1514.12 (Ar-C-H), 1492.90 (Ar-C=C), 1371.39 1332.8, 1359.82, 1301.95, 1230.59, 1134.14 (C-O-C), 742.59, 877.01, 594.09 $cm^{-1}$. **HRMS** (ESI, Q-TOF) m/z: $[M+Na]^{+}$ Calculated for $(C_{17}H_{20}N_2O_3+Na)^{+}$ 323.1372, found 323.1372.




**8a-hydroxy-2-oxo-4-phenyldecahydroquinoline-3-carbonitrile *(Compound 5b)***

**White Solid (89%), MP:170-172 ˚C, $^{1}$H NMR**(500 MHz, DMSO-D6) δ 8.67 (s, 1H), 7.51 – 7.17 (m, 5H), 5.79 (s, 1H), 4.31 (d, 1H, *J* = 11.8), 3.32 (t, 1H, *J* = 8.3), 1.96 – 1.77 (m, 2H), 1.58 – 1.28 (m, 4H), 1.04 (m, 2H), 0.80 (s, 1H) ppm. **$^{13}$C NMR**(126 MHz, DMSO-D6) δ 166.92, 142.77, 132.06, 130.68, 121.38, 83.39, 48.98, 47.02, 45.88, 40.68, 28.18, 24.46 ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{16}H_{18}N_2O_2+H)^+$ 271.1447, found 271.1451

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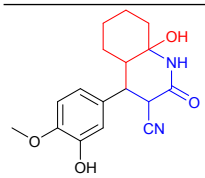


**8a-hydroxy-4-(3-hydroxy-4-methoxyphenyl)-2-oxodecahydroquinoline-3-carbonitrile *(Compound 5c)***

**Off white solid (92%), MP:135-137 ˚C, $^{1}$H NMR** (400 MHz, DMSO-D6) δ 8.95 (s, 1H), 8.63 (s, 1H), 6.88 (d, 1H, *J* = 7.6), 6.70 (s, 2H), 5.76 (s, 1H), 5.72 (s, 1H), 4.18 (d, 1H *J* = 11.8), 3.76 (s, 3H), 3.15 (t, 1H, *J* = 11.6), 1.96 – 1.84 (m, 1H), 1.73 (d, 1H *J* = 10.3), 1.41 (m, 4H), 1.03 (m, 2H), 0.88 (s, 1H) ppm. **$^{13}$C NMR** (101 MHz, DMSO-D6) δ 163.69, 146.72, 131.84, 118.16, 80.01, 55.47, 54.88, 45.78, 42.96, 42.74, 37.33, 24.95, 24.70, 21.14ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$Calculated for $(C_{17}H_{20}N_2O_4+H)$+ 317.1496, found 317.1490

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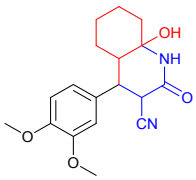


**4-(3,4-dimethoxyphenyl)-8a-hydroxy-2-oxodecahydroquinoline-3-carbonitrile *(Compound 5d)***

**White solid (87%), MP:143-145 ˚C, $^{1}$H NMR** (500 MHz, DMSO-D6) δ 8.65 (s, 1H), 6.85 (d, 3H), 5.75 (s, 1H), 4.32 (d, 1H *J* = 11.3), 3.75 (d, 6H *J* = 3.7), 3.24 (t, 1H, *J* = 11.4), 2.53 (d, 1H *J* = 12.4), 2.02 – 1.74 (m, 2H), 1.48 (d, 2H *J* = 27.9), 1.38 – 1.20 (m, 2H), 0.95 (m, 3H) ppm. **$^{13}$C NMR**(126 MHz, DMSO-D6) δ 167.12, 151.25, 135.14, 121.55, 83.37, 58.81, 49.18, 46.75, 45.94, 40.74, 28.21, 24.51 ppm. **HRMS (ESI, Q-TOF)** m/z: $[M+H]^+$ Calculated for $(C_{18}H_{22}N_2O_4+H)^+$ 331.1652, found 331.1645

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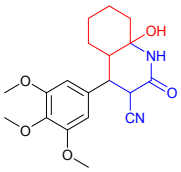


**8a-hydroxy-2-oxo-4-(3,4,5-trimethoxyphenyl)decahydroquinoline-3-carbonitrile *(Compound 5f)***

**White solid (78%), MP:143-144 ˚C, $^{1}$H NMR** (500 MHz, DMSO-D6) δ 8.67 (s, 1H), 6.62 (s, 2H), 4.39 (d, 1H *J* = 11.8), 3.78 (d, 6H *J* = 9.2), 3.65 ( s, 3H), 3.25 (t, 1H, *J* = 11.7), 1.90 (d, 1H *J* = 12.6), 1.79 (dd, 1H *J* = 11.4, 8.4), 1.50 (m, 3H), 1.35 (m, 1H), 1.08 (m, 2H), 0.85 (m, 1H) ppm. **$^{13}$C NMR** (126 MHz, DMSO-D6) δ 167.06, 156.39, 139.67, 138.60, 121.56, 108.64, 83.33, 63.25, 59.25, 49.21, 47.45, 45.60, 40.71, 28.30, 28.08, 24.49ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{19}H_{25}N_2O_5+H)^+$ 361.1758, found 361.1749

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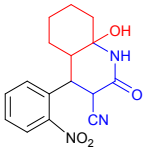


**8a-hydroxy-4-(2-nitrophenyl)-2-oxodecahydroquinoline-3-carbonitrile (*Compound 5g)***

**White solid (90%), MP:150-153 ˚C, $^{1}$H NMR** (600 MHz,DMSO-D6 ) δ 8.75 (s, 1H), 7.80 (d, 3H *J* = 60.2), 7.58 (d, 1H *J* = 32.2), 5.88 (s, 1H), 4.46 (d, 1H *J* = 9.8), 3.93 (s, 1H), 1.92 (s, 2H), 1.48 (d, 4H *J* = 30.6), 1.12 (d, 2H *J* = 70.2), 0.76 (s, 1H) ppm. **$^{13}$C NMR** (151 MHz,DMSO-D6) 163.48, 151.85, 133.69, 133.10, 129.18, 124.10, 117.88, 80.42, 46.59, 42.62, 37.75, 37.57, 25.33, 24.84, 21.51 ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{16}H_{17}N_3O_4+H)^+$ 316.1292, found 316.1285

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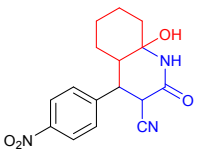


**8a-hydroxy-4-(4-nitrophenyl)-2-oxodecahydroquinoline-3-carbonitrile (*Compound 5h)***

**White solid (82%), MP:160-163 ˚C, $^{1}$H NMR** (400MHz, DMSO-D6) δ 8.79 (s, 1H), 8.24 (d, *J* = 8.2 Hz, 2H), 7.65 (br. s., 2H), 5.91 (s, 1H), 4.46 (s, 1H), 4.49 (s, 1H), 3.61 - 3.47 (m, 1H), 2.05 - 1.84 (m, 2H), 1.54 - 1.43 (m, 4H), 1.15 - 0.94 (m, 2H), 0.86 - 0.67 (m, 1H)ppm. **$^{13}$C NMR** (151 MHz, ) 163.56, 147.75, 147.45, 124.41, 118.15, 80.54, 45.86, 44.13, 42.44, 37.76, 25.28, 21.52, 0.62 ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{16}H_{17}N_3O_4+H)^+$ 316.1292, found 316.1287

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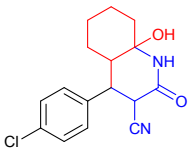


**4-(4-chlorophenyl)-8a-hydroxy-2-oxodecahydroquinoline-3-carbonitrile (*Compound 5i)***

**White Solid (91%), MP: 230-232 ˚C, $^{1}$H NMR** (400 MHz, DMSO-D6) δ 8.71 (s, 1H), 7.40 (t, 4H *J*= 16.3), 5.85 (s, 1H), 4.32 (d, 1H *J* =11.9), 3.34 (t, 1H *J* =11.8), 1.86 (dd, 2H *J* =23.2, 11.7), 1.47 (d, 3H *J* =21.7), 1.39 – 1.29 (m, 1H), 1.05 (dd, 2H *J* =17.9, 9.5), 0.79 (s, 1H)ppm.**$^{13}$C NMR** (101 MHz, DMSO-D6) δ 163.44, 138.15, 131.99, 128.72, 117.80, 80.09, 45.30, 43.02, 42.32, 37.05, 24.65, 20.98 ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{16}H_{17}ClN_2O_2+H)^+$ 305.1051, found 305.1045

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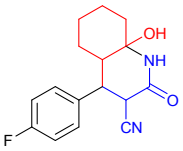


**4-(4-fluorophenyl)-8a-hydroxy-2-oxodecahydroquinoline-3-carbonitrile *(Compound 5j)***

**White Solid (85%), MP: 208-210 ˚C, $^{1}$H NMR** (400 MHz, DMSO-D6) δ 8.70 (s, 1H), 7.23 (dd, 4H *J* = 41.7, 33.1), 5.83 (s, 1H), 4.31 (d, 1H *J* = 11.8), 3.32 (d, 1H *J* = 11.8), 1.86 (dd, 2H *J* = 27.2, 11.6), 1.55 – 1.31 (m, 4H), 1.03 (t, 2H *J* = 9.0), 0.79 (s, 1H) ppm. **$^{13}$C NMR** (101 MHz, DMSO-D6) δ 163.54, 162.52, 160.10, 135.33, 117.86, 115.59, 115.38, 80.10, 45.45, 42.87, 42.57, 37.08, 24.66, 21.00 ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{16}H_{17}FN_2O_2+H)^+$ 289.1347, found 305.1342

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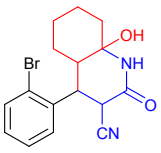


**4-(2-bromophenyl)-8a-hydroxy-2-oxodecahydroquinoline-3-carbonitrile*(Compound 5k)***

**Off white solid (93%), MP: 150-152 ˚C, $^{1}$H NMR** (400 MHz, DMSO-D6) δ 8.74 (br. s.,1H), 7.63 (t, 2H *J* = 8.3 Hz,), 7.43 (t, 1H *J* = 7.3 Hz,), 7.30 - 7.11 (m, 1H), 5.92 (s, 1H), 4.37 (d, 1H *J* = 11.9 Hz,), 4.17 (t, 1H *J* = 11.7 Hz,), 1.91 (d, 1H *J* = 12.3 Hz,), 1.87 - 1.80 (m, 1H), 1.53 - 1.42 (m, 3H), 1.36 (dd, 1H *J* = 4.2, 11.7 Hz,), 1.27 - 1.09 (m, 1H), 1.03 (br. s., 1H), 0.76 (d, 1H *J* = 11.9 Hz) ppm. **$^{13}$C NMR** (101MHz, DMSO-D6) δ 163.4, 138.7, 132.7, 129.1, 128.5, 128.5, 125.4, 117.6, 80.0, 46.5,

41.9, 41.3, 37.1, 24.8, 23.9, 21.0ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{16}H_{17}BrN_2O_2+H)^+$ 349.0546, found 349.0537

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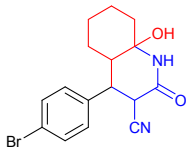


**4-(4-bromophenyl)-8a-hydroxy-2-oxodecahydroquinoline-3-carbonitrile *(Compound 5l)***

**Off white solid (90%), MP: 218-220 ˚C, $^1$H NMR** (500 MHz, DMSO-$D_6$) δ 8.71 (s, 1H), 7.56 (d, 2H *J* = 8.3), 7.30 (d, 2H *J* = 8.9), 5.82 (s, 1H), 4.35 – 4.32 (d, 1H *J* = 3.7), 3.08 (s, 1H), 1.91 – 1.85 (m, 2H), 1.50 – 1.35 (m, 4H), 1.05 (s, 2H), 0.79 (s, 1H) ppm. **$^{13}$C NMR** (101 MHz, DMSO-D6) δ 163.34, 138.76, 131.62, 120.49, 117.85, 79.99, 45.35, 43.14, 42.27, 37.20, 24.74, 21.02 ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{16}H_{17}BrN_2O_2+H)^+$ 349.0546, found 349.0540

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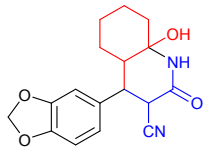


**4-(benzo[d][1,3]dioxol-5-yl)-8a-hydroxy-2-oxodecahydroquinoline-3-carbonitrile (*Compound 5m*)**

**White solid (93%), MP: 159-160 ˚C,$^1$H NMR** (400 MHz, DMSO-D6) δ 8.67 (s, 5H), 6.98 (br. s., 5H), 6.91 - 6.82 (m, 6H), 6.79 - 6.65 (m, 5H), 6.01 (dd, 11H *J* = 1.0, 4.0 Hz,), 5.77 (s, 6H), 4.23 (s, 3H), 4.26 (s, 3H), 3.24 (t, 6H *J* = 11.8 Hz,), 1.87 (s, 3H), 1.90 (s, 3H), 1.84 - 1.72 (m, 6H), 1.56 - 1.47 (m, 6H), 1.44 (br. s., 10H), 1.40 - 1.27 (m, 6H), 1.12 - 0.96 (m, 11H), 0.93 - 0.80 (m, 6H) ppm.**$^{13}$C NMR** (101MHz, DMSO-D6) δ 163.6, 146.3, 133.2, 118.0, 101.0, 80.0, 45.7, 43.4, 42.6, 37.3, 24.9, 24.7, 21.1 ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{17}H_{18}N_2O_4+H)^+$ 315.1339, found 315.1356

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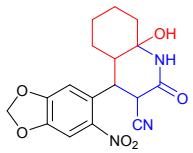


**8a-hydroxy-4-(6-nitrobenzo[d][1,3]dioxol-5-yl)-2-oxodecahydroquinoline-3-carbonitrile *(Compound 5n)***

**Off white solid (87%), MP: 157-158 ˚C, $^1$H NMR**(600 MHz, DMSO-D6) δ 8.71 (s, 1H), 7.49 (s, 1H), 7.39 (s, 1H), 6.23 (d, 2H *J* = 14.1), 5.88 (s, 1H), 4.36 (d, 1H *J* = 11.9), 4.04 (t, 1H *J* = 11.6), 1.93 – 1.85 (m, 2H), 1.53 (d, 1H *J* = 12.1), 1.45 (s, 2H), 1.35 (dd, 1H *J* = 19.1, 10.8), 1.16 – 1.06 (m, 2H),

0.86 (d, 1H *J* = 11.7)ppm. **$^{13}$C NMR** (151 MHz, DMSO-D6) δ 163.57, 151.95, 147.25, 145.69, 129.30, 117.87, 107.27, 104.96, 103.85, 80.42, 46.41, 42.52, 37.65, 25.30, 24.73, 21.51, 0.61ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{17}H_{17}N_3O_6+H)^+$ 360.1196, found missmatched

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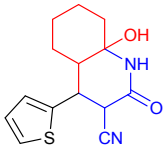


**8a-hydroxy-2-oxo-4-(thiophen-2-yl)decahydroquinoline-3-carbonitrile *(Compound 5o)***

**Brownish white solid (81%), MP: 138-140 ˚C,$^1$H NMR**(600 MHz, DMSO-D6 ) δ 8.71 (s, 1H), 7.44 (s, 1H), 7.06 (d, 2H *J* = 32.3), 5.81 (s, 1H), 4.31 (d, 1H *J* = 11.2), 3.62 (t, 1H *J* = 11.1), 1.83 (dd, 2H *J* = 70.3, 10.7), 1.45 (t, 4H *J* = 67.3), 1.04 (dd, 3H *J* = 56.9, 7.2) ppm. **$^{13}$C NMR** (151 MHz, DMSO-D6) δ 163.59, 142.97, 127.86, 126.32, 125.44, 118.35, 80.43, 47.67, 44.26, 39.51, 37.76, 25.39, 21.61 ppm. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{14}H_{16}N_2O_2S+H)^+$ 277.1005, found 277.1001

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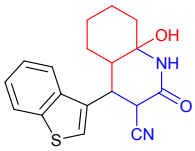


**4-(benzo[b]thiophen-3-yl)-8a-hydroxy-2-oxodecahydroquinoline-3-carbonitrile *(compound 5p)***

**White solid (89%), MP: 148-150 ˚C,$^1$H NMR** (500 MHz, DMSO-D6) δ 8.79 (s, 1H), 8.02 (d, 1H), 7.83 (dd, 2H *J* = 22.9, 15.1), 7.43 (dd, 2H *J* = 18.1, 7.2), 5.93 (s, 1H,), 4.62 (d,1H *J* = 11.8), 4.06 (t, 1H *J* = 11.5), 1.98 – 1.80 (m, 2H), 1.40 (d, 4H), 1.12 (m 2H), 0.76 (d, 1H). **$^{13}$C NMR** (126 MHz, DMSO-D6) δ 166.90, 142.76, 138.80, 127.99, 127.63, 126.48, 124.75, 121.53, 83.51, 51.53, 45.54, 40.69, 38.52, 28.27, 28.00, 24.48, 18.51. **HRMS** (ESI, Q-TOF) m/z: $[M+H]^+$ Calculated for $(C_{18}H_{18}N_2O_2S+H)^+$ 327.1162, found 327.1153

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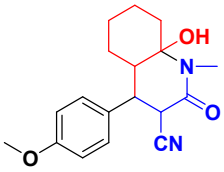


**8a-hydroxy-4-(4-methoxyphenyl)-1-methyl-2-oxodecahydroquinoline-3-carbonitrile *(Compound 5q)***

**White solid (41%), MP: 110-115˚C, $^{1}$H NMR** (600 MHz, DMSO-$D_6$) 7.25 (d, 2H *J* = 8.3), 6.92 (d, 2H *J* = 8.9), 6.02 (s, 1H), 4.37 (d, 1H *J* = 12.2), 3.75 (S, 3H), 3.25 (d, 1H *J* = 23.9), 2.92 (s, 3H), 1.52 (d, 2H *J* = 19.0), 1.25 (d, 2H *J* = 13.9), 1.17 (m, 2H), 1.07 – 1.01 (m, 2H), 0.89 – 0.86 (m, 1H) ppm. **$^{13}$C NMR** (151 MHz, DMSO-$D_6$) δ 163.44, 158.95, 131.69, 129.45, 118.68, 114.45, 93.27, 84.90, 55.53, 47.01, 43.79, 42.43, 36.14, 31.24, 27.08, 25.97, 25.00, 22.20 ppm.

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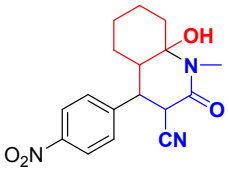


**8a-hydroxy-1-methyl-4-(4-nitrophenyl)-2-oxodecahydroquinoline-3-carbonitrile *(Compound 5r)***

**White solid (56%), MP: 125-127˚C, $^{1}$H NMR** (600 MHz, DMSO-$D_6$) 8.26 (d, 2H *J* = 8.0), 7.65 (s, 2H), 6.15 (s, 1H), 4.59 (d, 1H *J* = 12.2), 3.58 – 3.51 (t, 1H), 2.95 (s, 3H), 2.70 (s, 2H), 2.24 (m, 1H *J* = 12.2), 2.18 (t, 2H *J* = 7.9), 2.12 – 2.06 (m, 2H), 1.91 (m, 2H *J* = 14.3, 7.6) ppm. **$^{13}$C NMR** (151 MHz, DMSO-D6) δ 162.81, 147.66, 147.50, 124.50, 118.18, 84.83, 49.01, 46.47, 43.20, 42.96, 36.07, 30.64, 29.53, 27.16, 26.00, 24.85, 22.06, 17.75 ppm.

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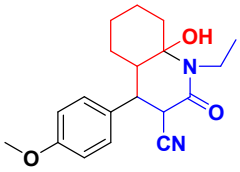


**1-ethyl-8a-hydroxy-4-(4-methoxyphenyl)-2-oxodecahydroquinoline-3-carbonitrile *(Compound 5s)***

**White solid (65%), MP: 142-143˚C, $^{1}$H NMR** (600 MHz, DMSO-$D_6$) 7.28 – 7.16 (d, 2H J = 8.0), 6.92 (d, 2H *J* = 8.1), 5.92 (s, 1H), 4.40 – 4.38 (d, 1H *J* = 12.2), 3.75 (s, 3H), 3.62-3.58 (dd, 1H), 2.19 (d, 1H *J* = 12.6), 1.93 – 1.88 (m, 1H), 1.52 (m, 4H), 1.40 – 1.37 (m, 1H), 1.24 (s, 1H), 1.12 – 1.09 (m, 3H), 1.05 (d, 2H *J* = 8.6), 0.87 (m, 1H *J* = 8.9) ppm. **$^{13}$C NMR** (151 MHz, DMSO-D6) δ 162.54, 158.28, 131.06, 118.03, 84.86, 54.88, 48.01, 46.64, 45.77, 43.15, 41.64, 35.84, 30.60, 25.34, 24.39, 21.60, 14.75 ppm.

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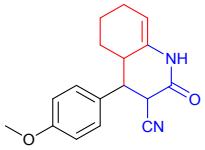


***4-(4-methoxyphenyl)-2-oxo-1,2,3,4,4a,5,6,7-octahydroquinoline-3-carbonitrile (Compound 13a)***

**White crystalline solid (90%), MP: 123-126˚C, $^{1}$H NMR** (600 MHz, DMSO-D6) δ 10.20 (s, 1H), 7.29 (d, 2H *J* = 7.7), 6.94 (d, 2H *J* = 8.0), 5.12 (d, 1H, *J* = 1.7), 4.59 (d, 1H *J* = 12.0), 3.76 (s, 3H),

2.93 (t, 1H *J* = 12.0), 2.05 – 1.94 (m, 2H), 1.63 (d, 1H *J* = 12.2), 1.28 – 1.18 (m, 2H), 1.01 (dd, 1H *J* = 18.3, 7.3) ppm. **$^{13}$C NMR** (151 MHz, DMSO-D6) δ 162.05, 159.07, 135.47, 131.54, 117.74, 114.60, 104.93, 55.55, 46.49, 42.65, 38.26, 27.48, 23.76, 21.85 ppm.

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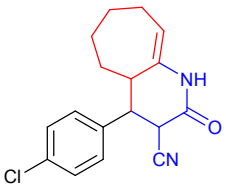


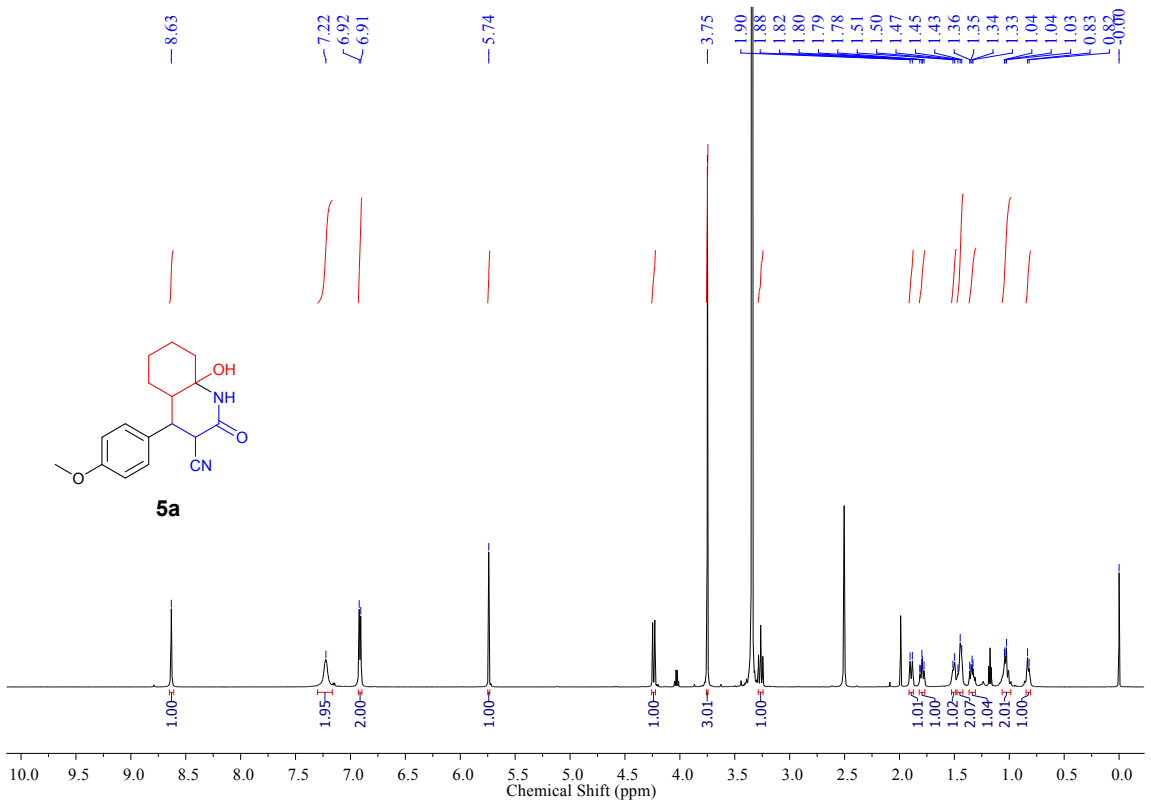

**4-(4-chlorophenyl)-2-oxo-2,3,4,4a,5,6,7,8-octahydro-1H-cyclohepta[b]pyridine-3-carbonitrile**

***(Compound 15i)***

**White solid (92%), MP: 121-124°C, $^{1}$H NMR** (600 MHz, DMSO-$D_6$) 9.65 (s, 1H), 7.44 (d, 2H *J* = 8.2), 7.25 (d, 2H *J* = 8.2), 4.75 (d, 1H *J* = 7.6), 4.13 – 3.95 (m, 1H), 3.75 (d, 1H *J* = 7.5), 3.36 (m, 1 H), 2.31 – 2.28 (m, 1H), 2.19 – 2.14 (m, 1H), 1.99 – 1.93 (m, 1H), 1.67 (m, 1H), 1.60 – 1.54 (m, 2H), 1.44 – 1.43 (m, 2H), 1.09 – 1.04 (m, 1H) ppm. **$^{13}$C NMR** (151 MHz, DMSO-$D_6$) δ 162.04, 137.23, 135.85, 133.06, 130.63, 130.55, 129.31, 129.22, 116.92, 115.81, 46.63, 41.21, 31.90, 31.67, 31.55, 31.34, 27.17, 25.69 ppm.

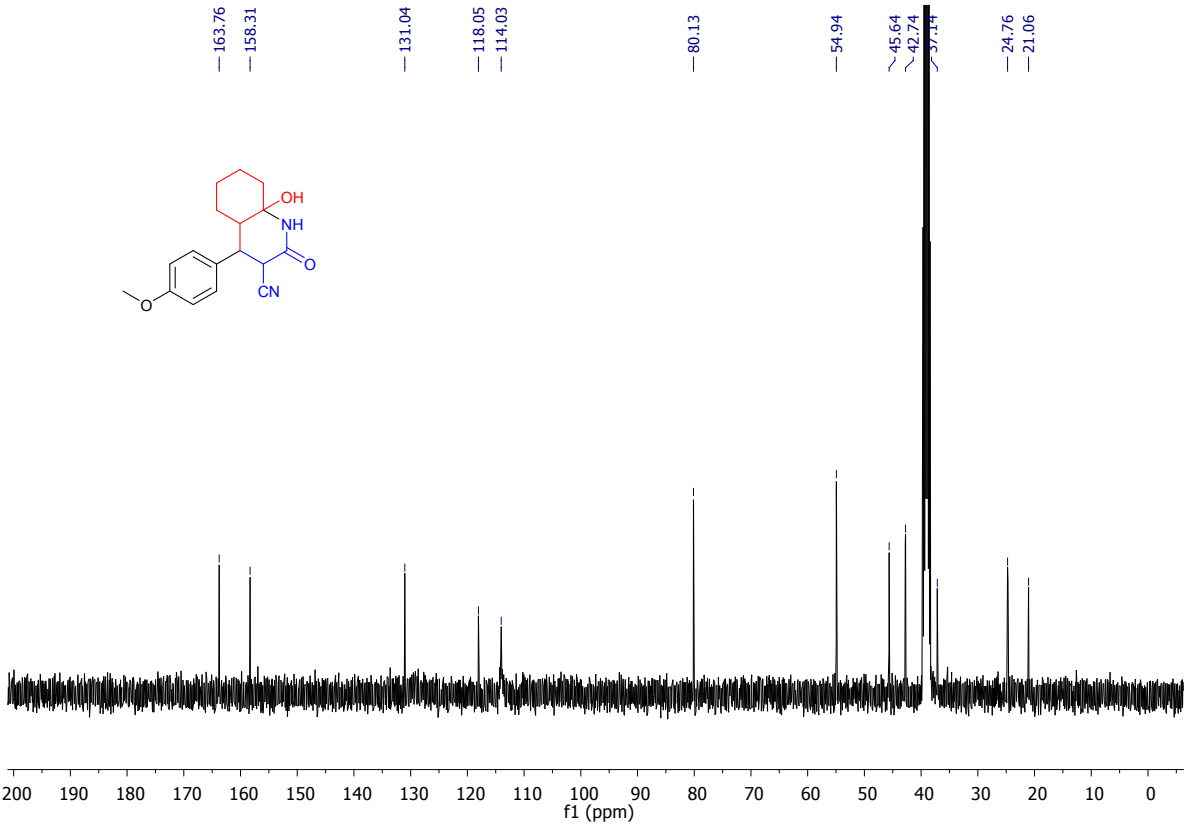
## $^{1}$H and $^{13}$C NMR spectra of the compounds

### $^{1}$H NMR

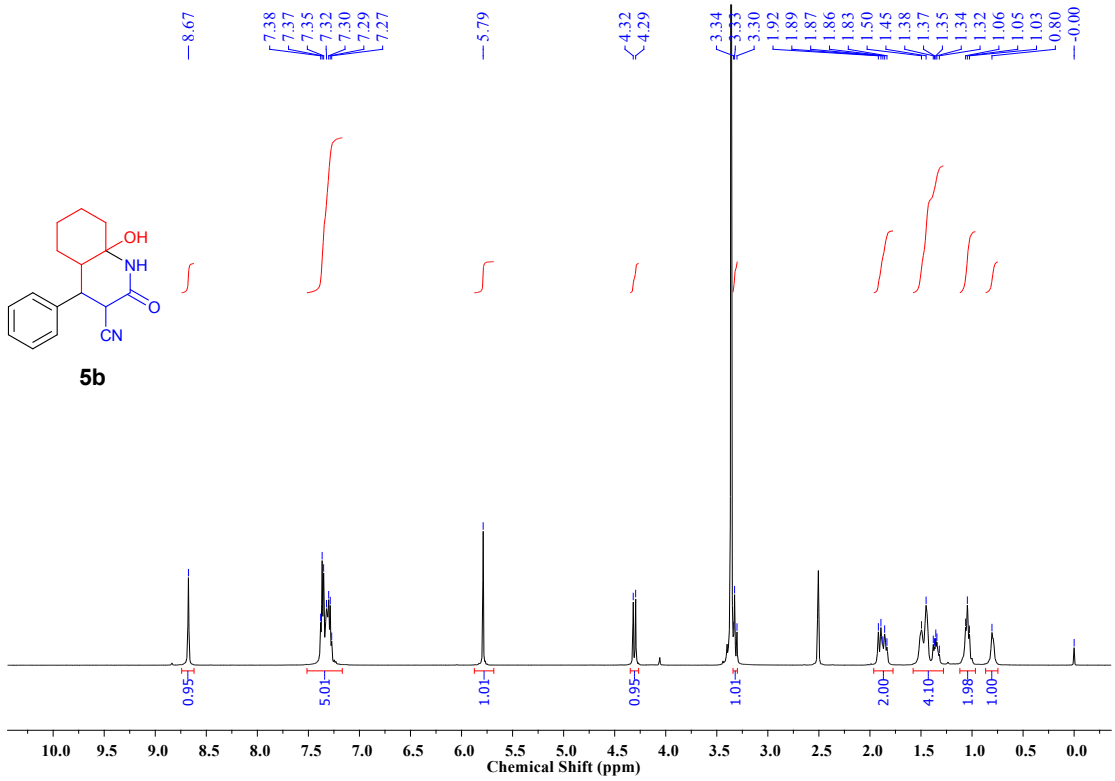



**5a**

### $^{13}$C NMR

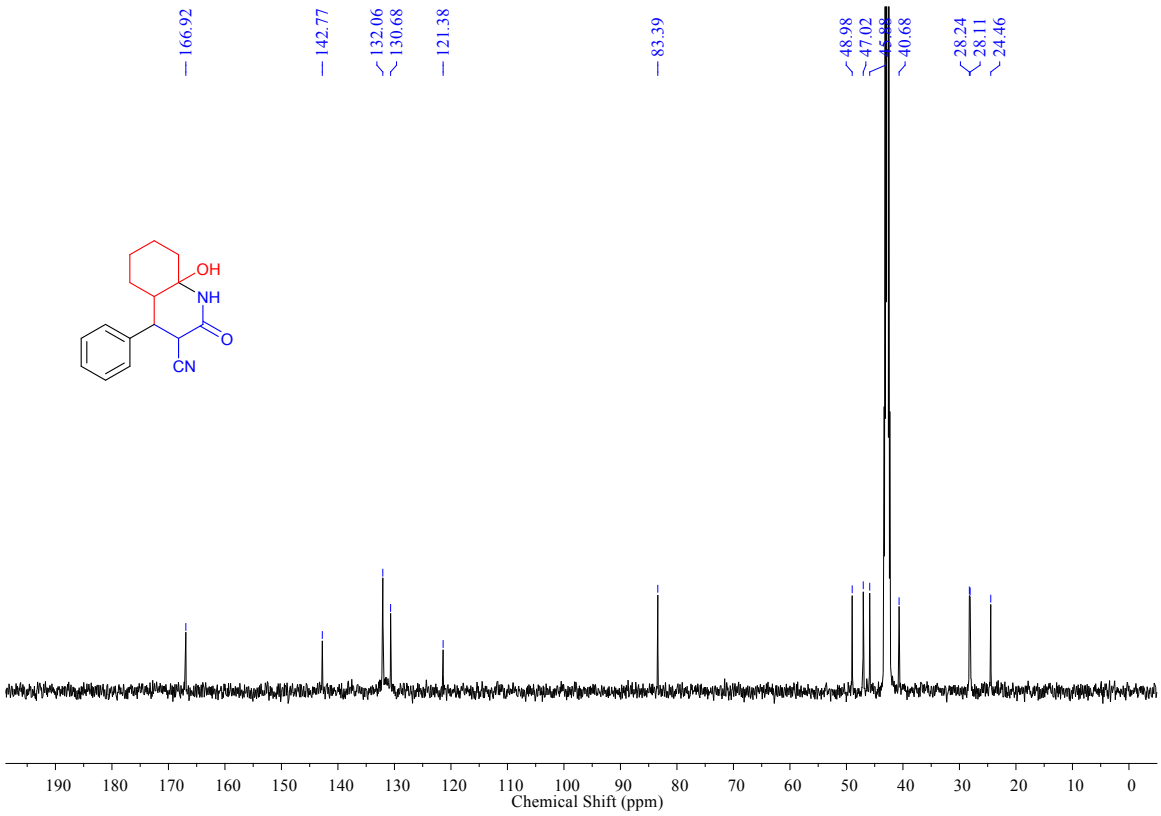


**$^{1}$H NMR**




**5b**

**$^{13}$C NMR**



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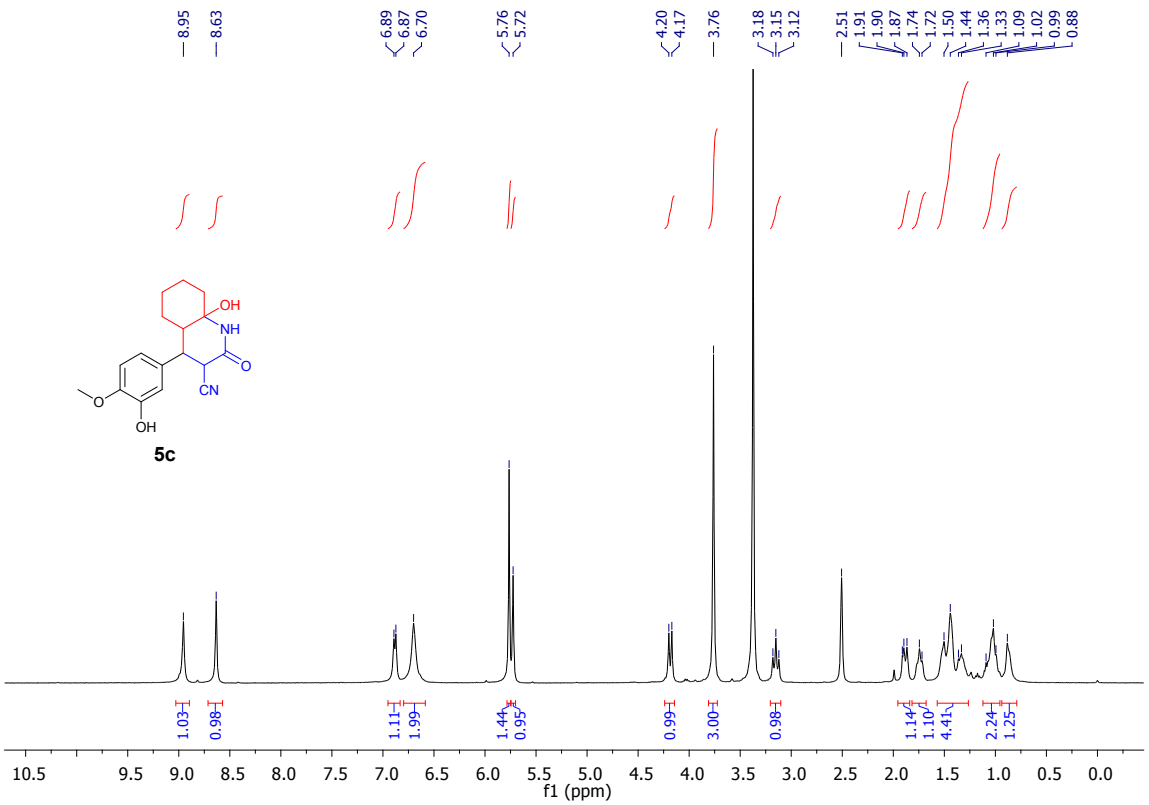
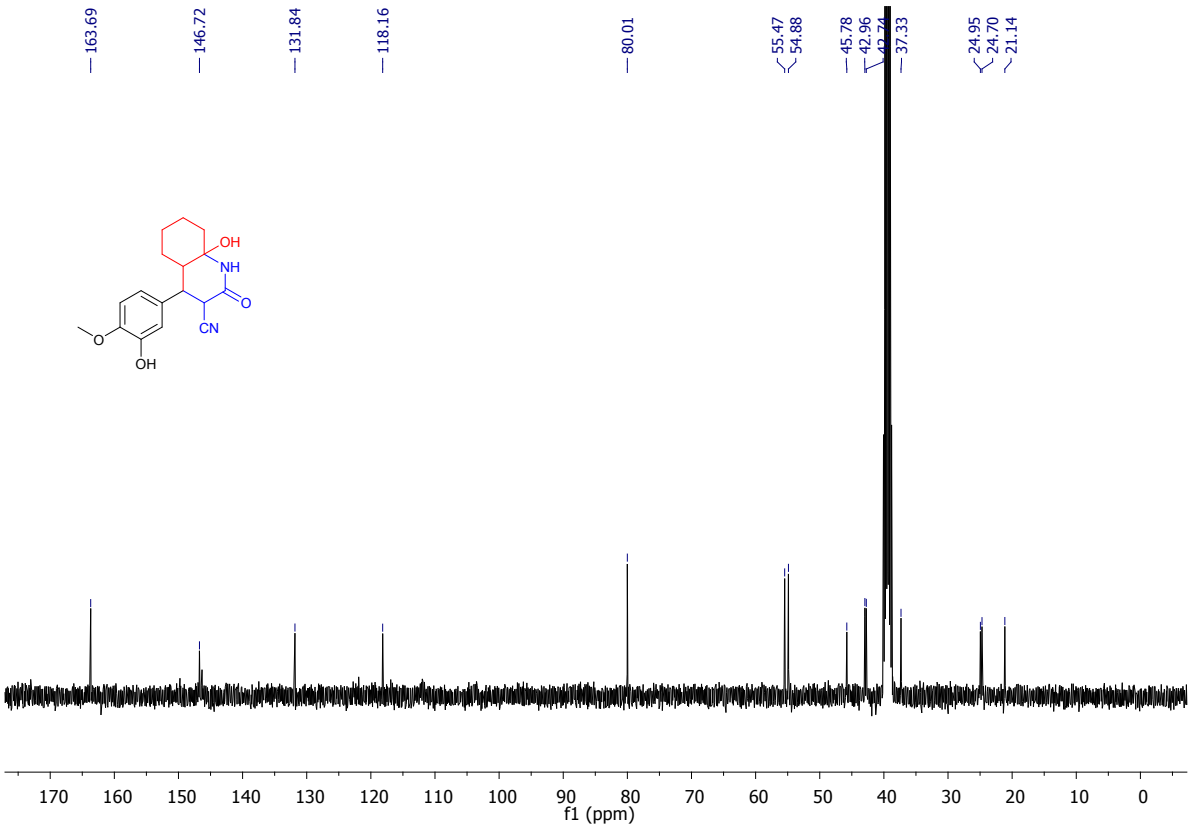



**5c**

**$^{13}$C NMR**



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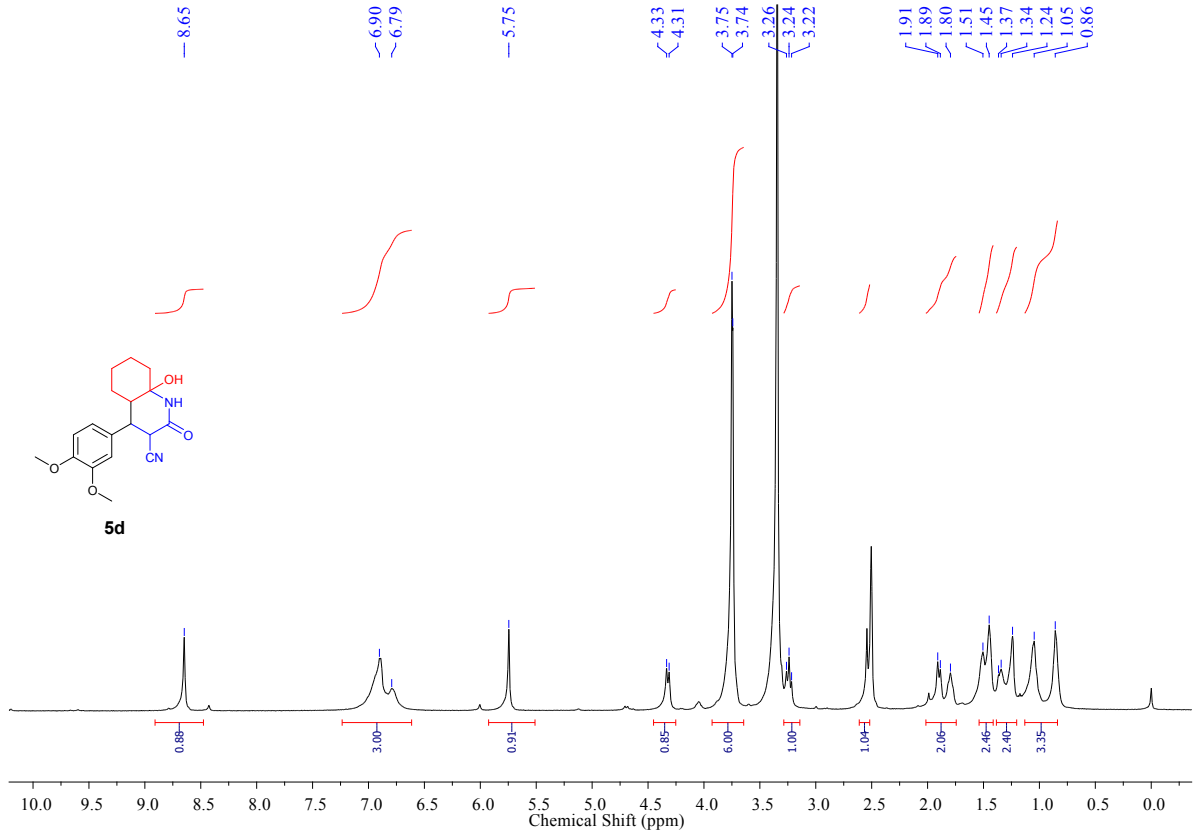


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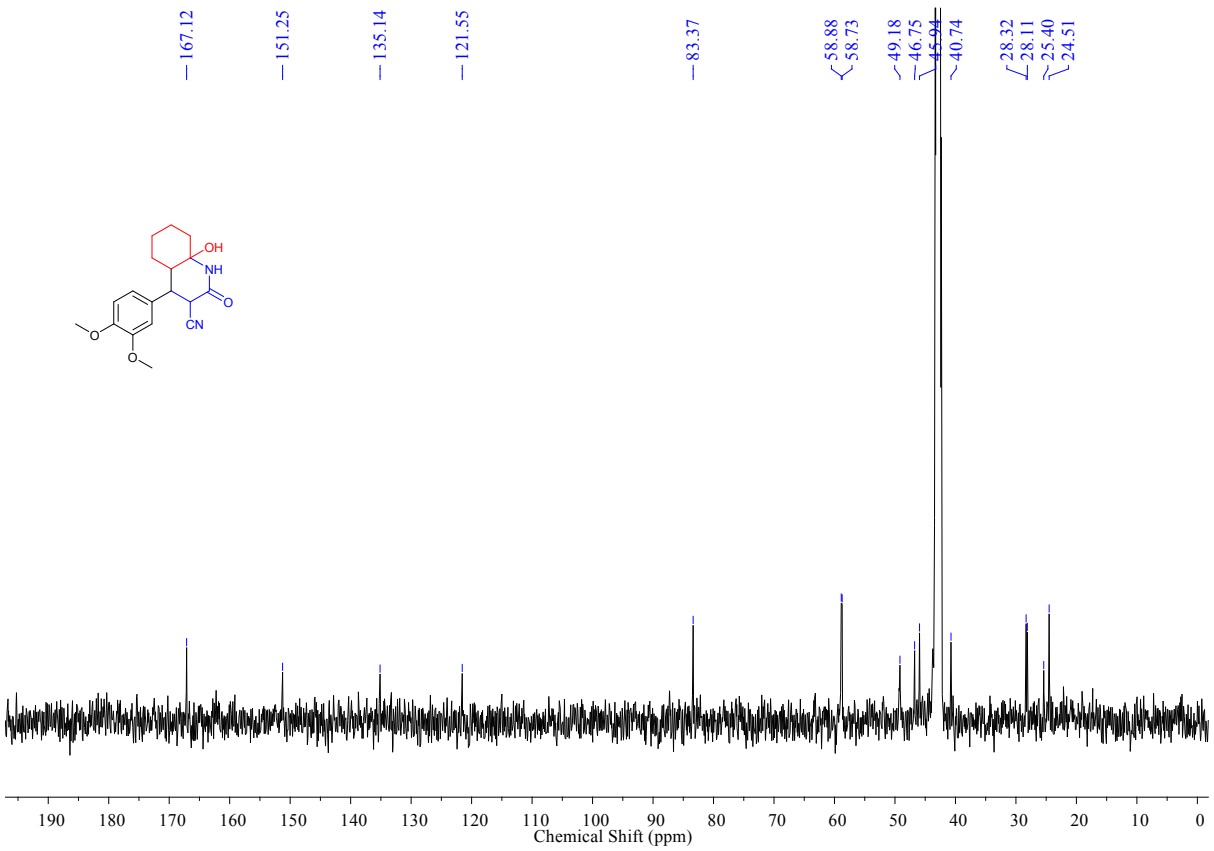
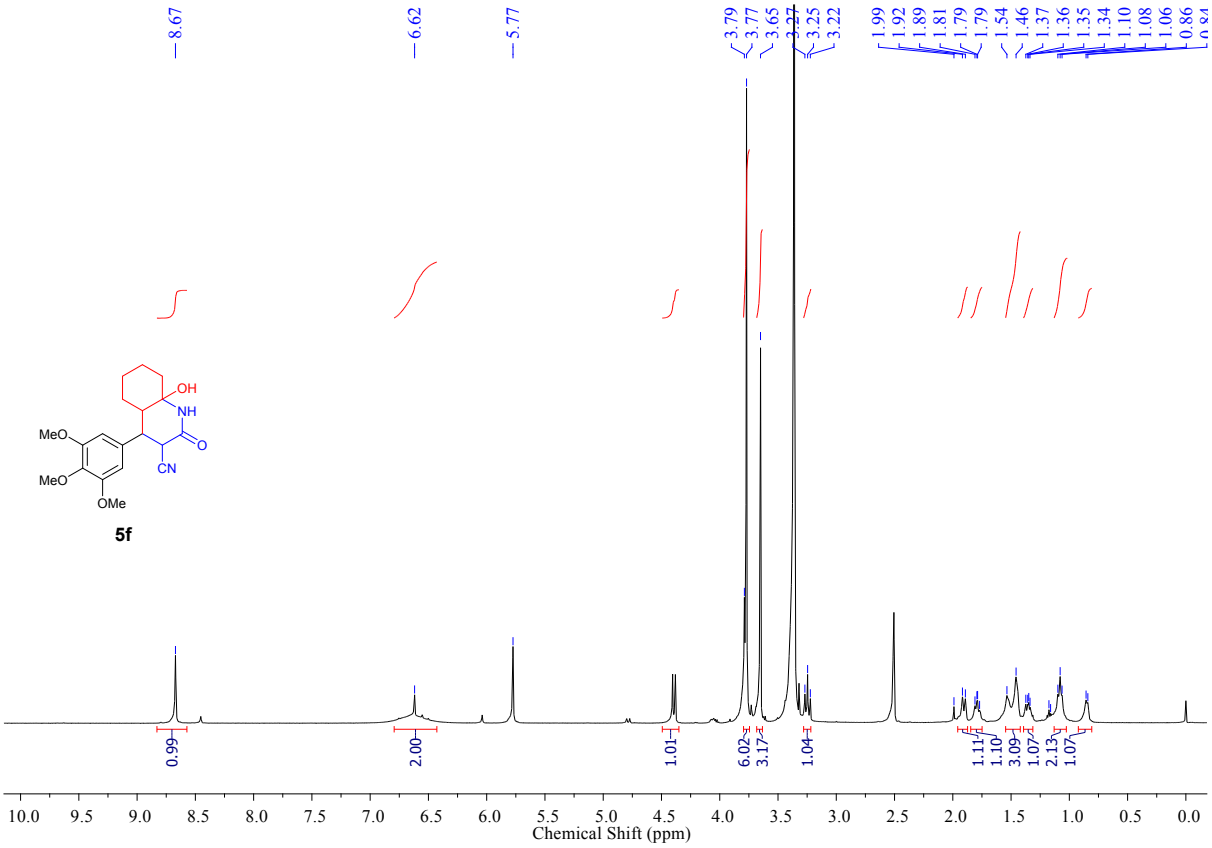
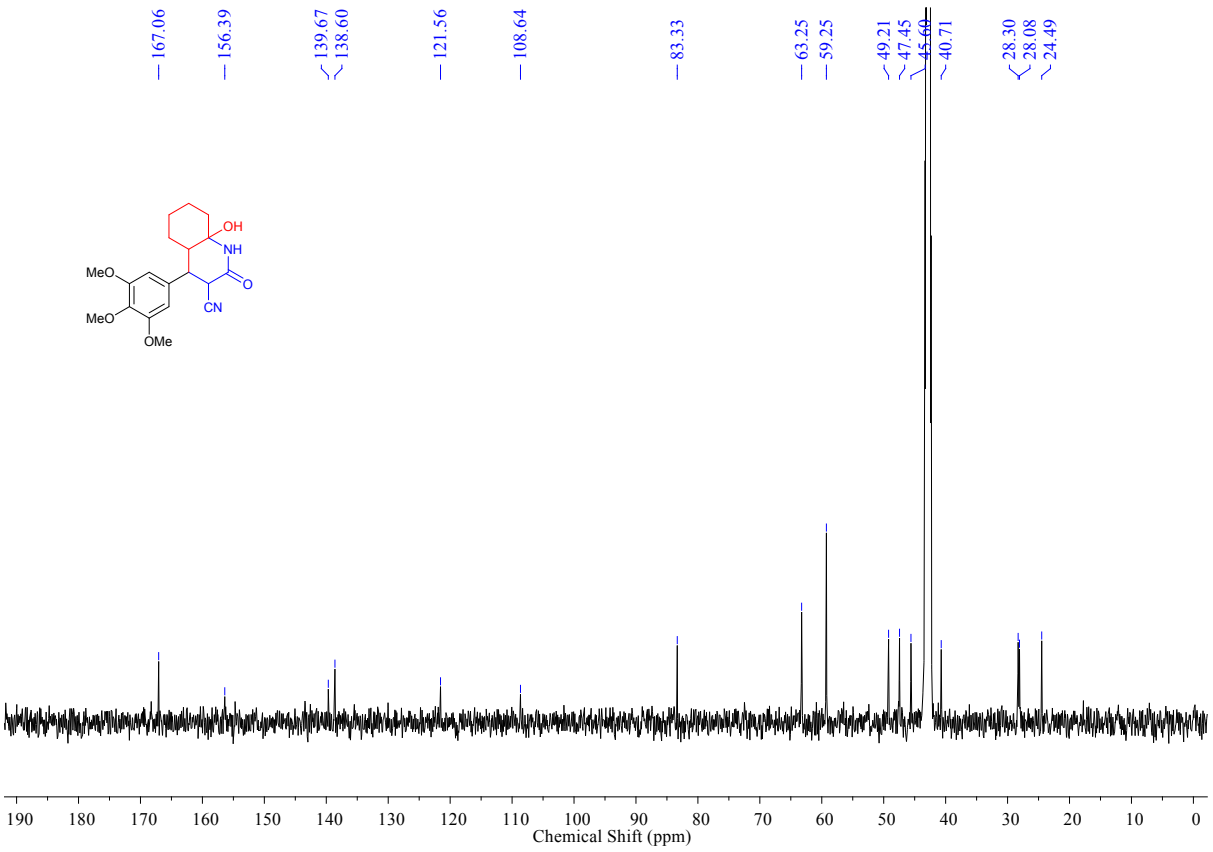


**$^{1}$H NMR**




**5f**

**$^{13}$C NMR**



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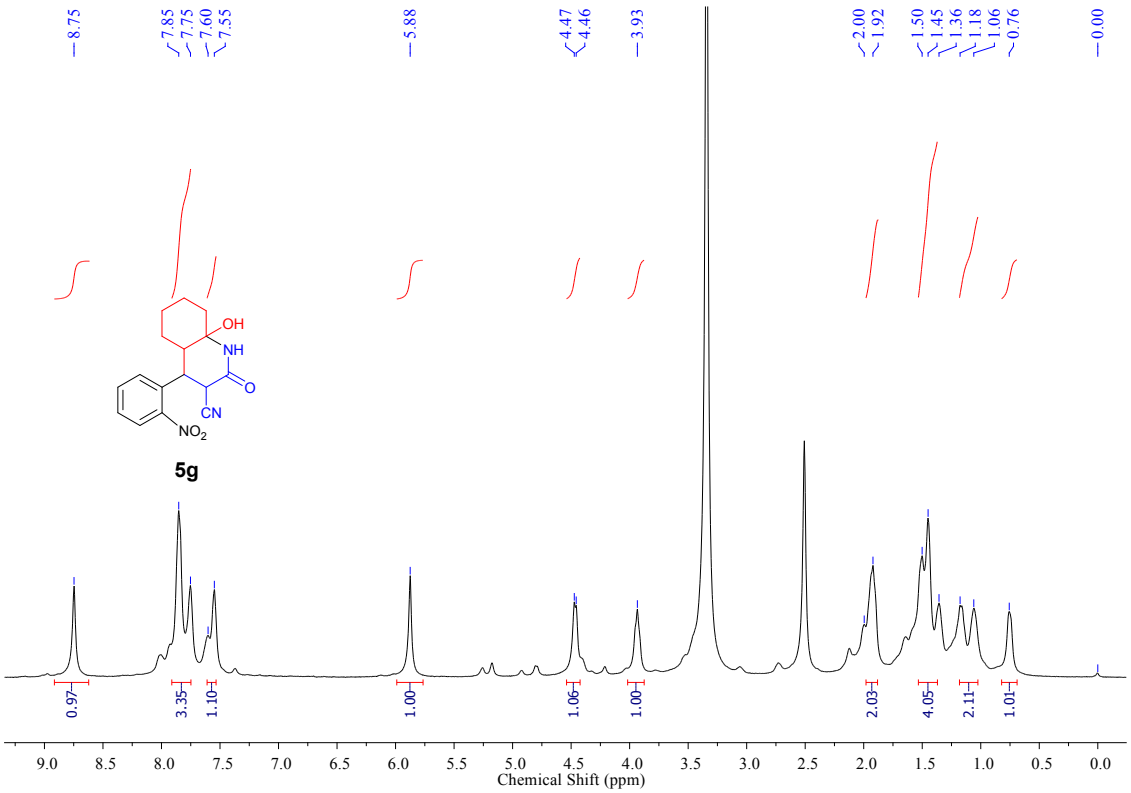
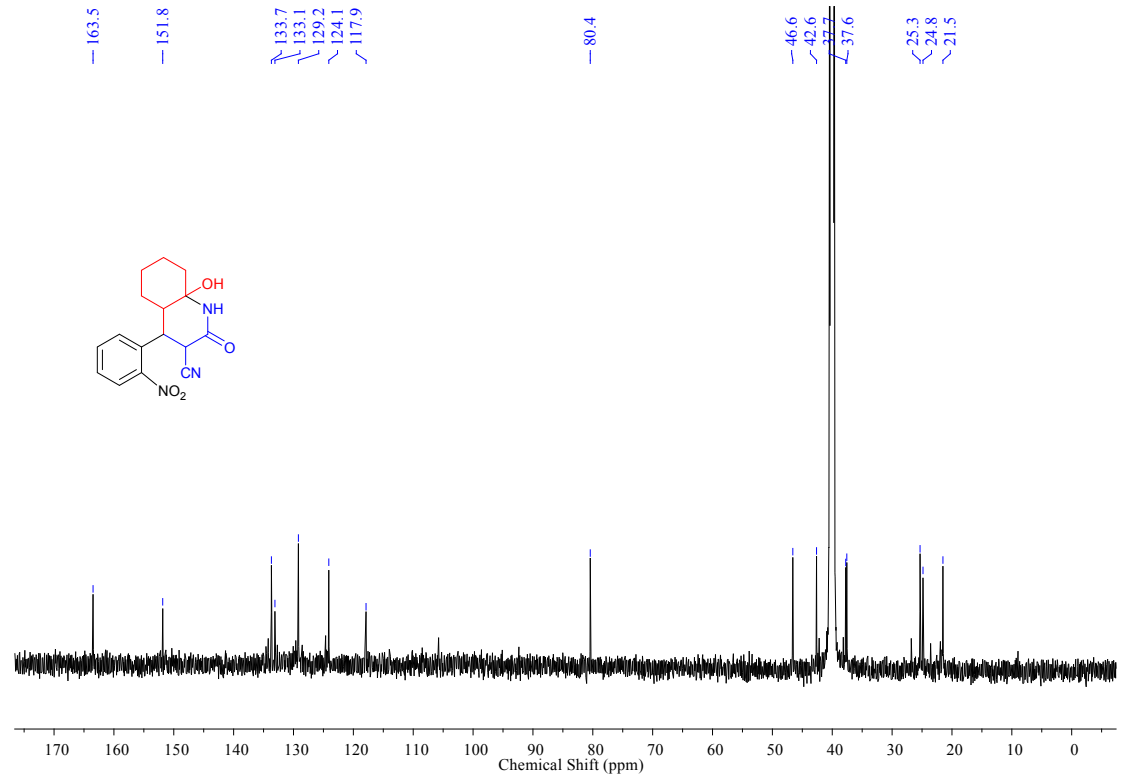



**5g**

## $^{13}$C NMR



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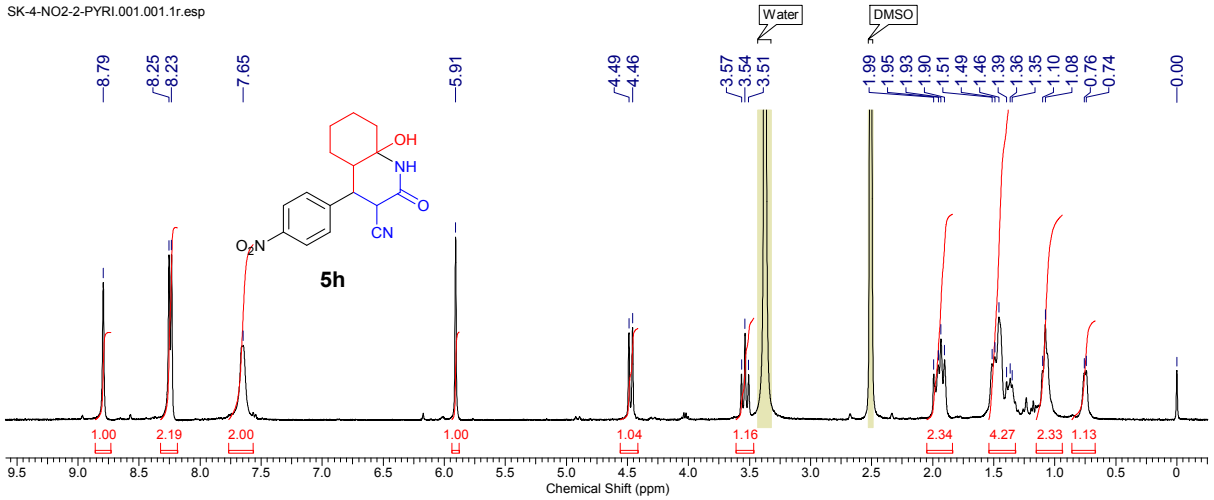


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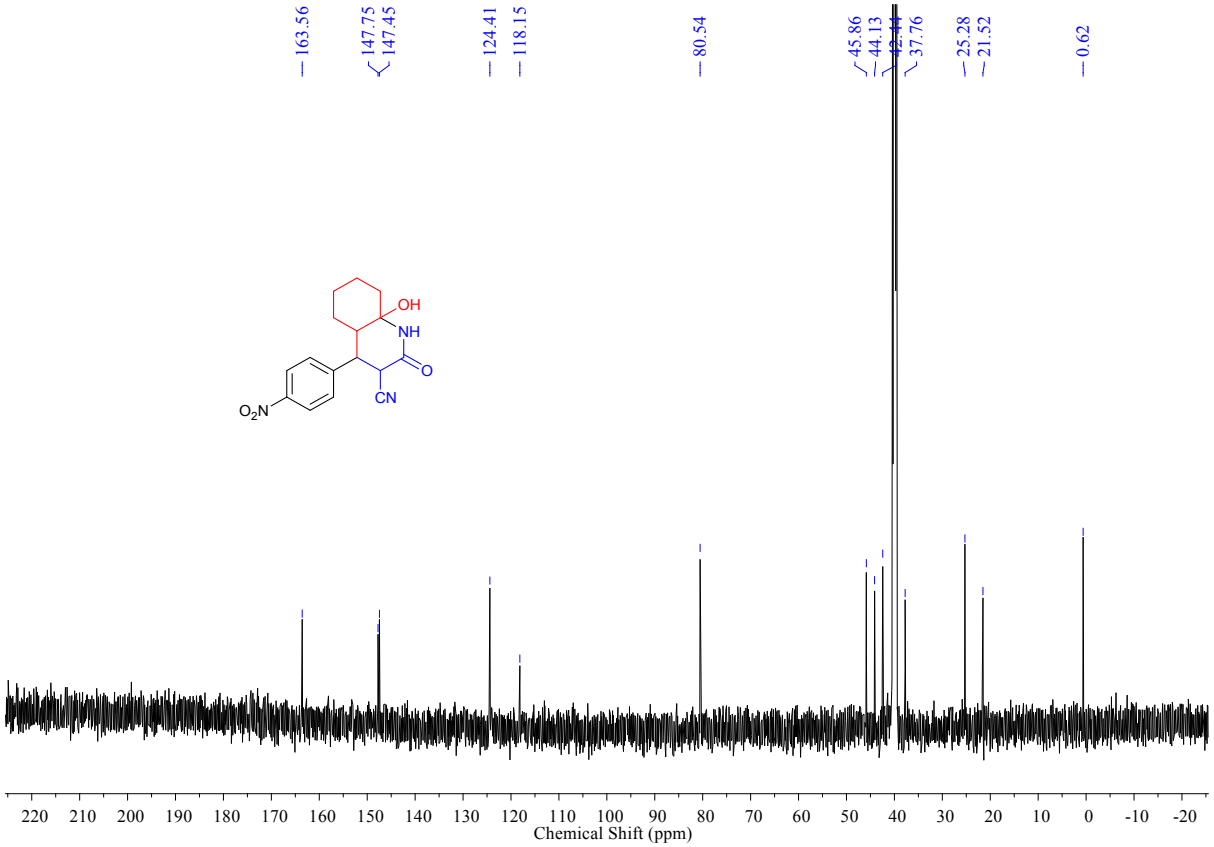

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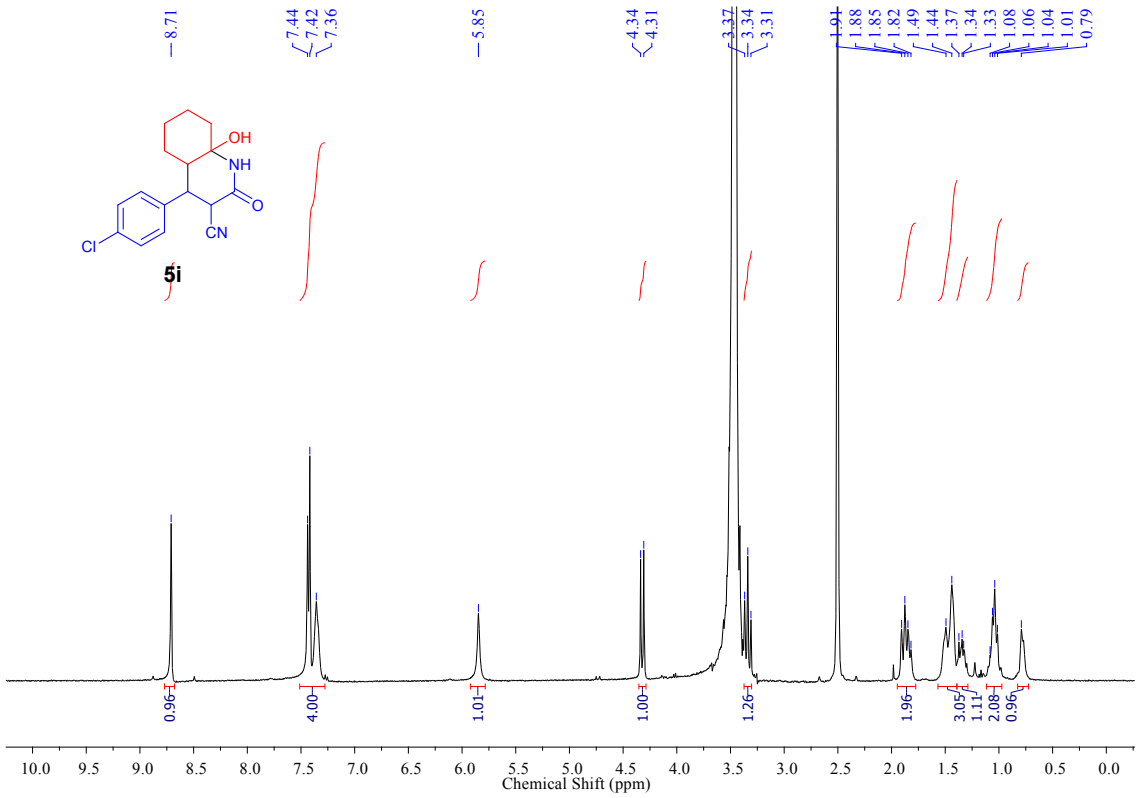


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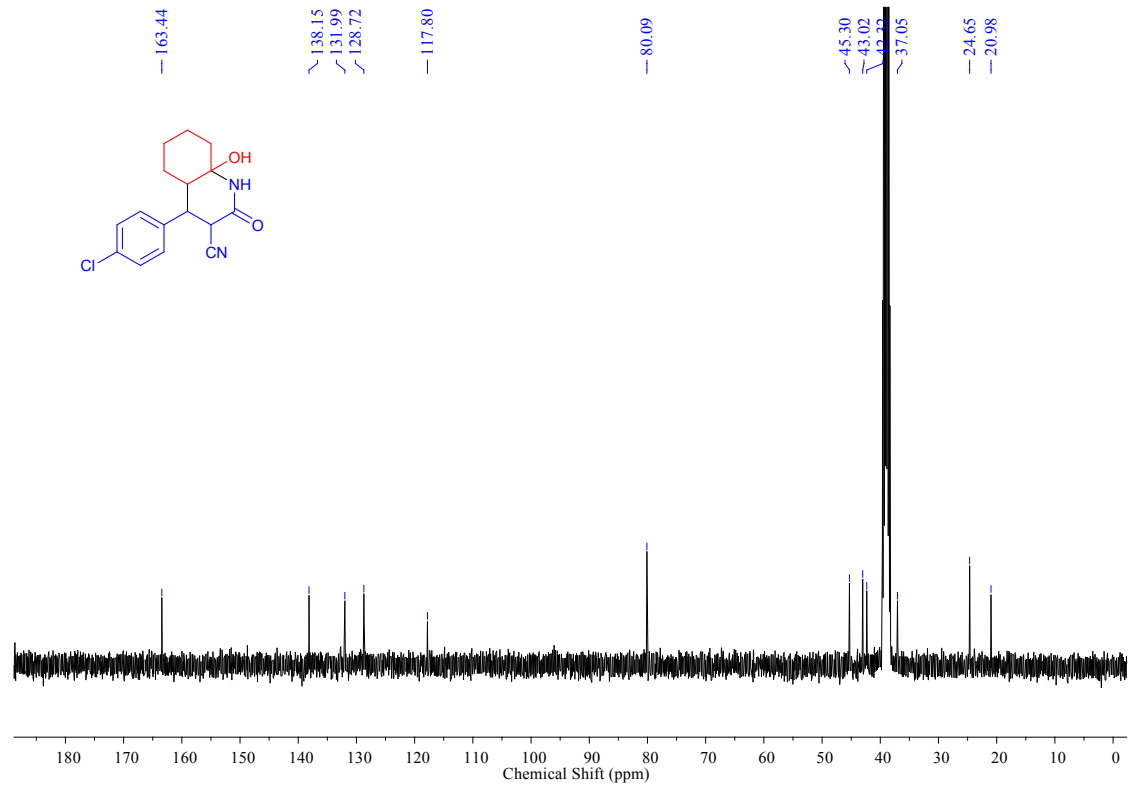
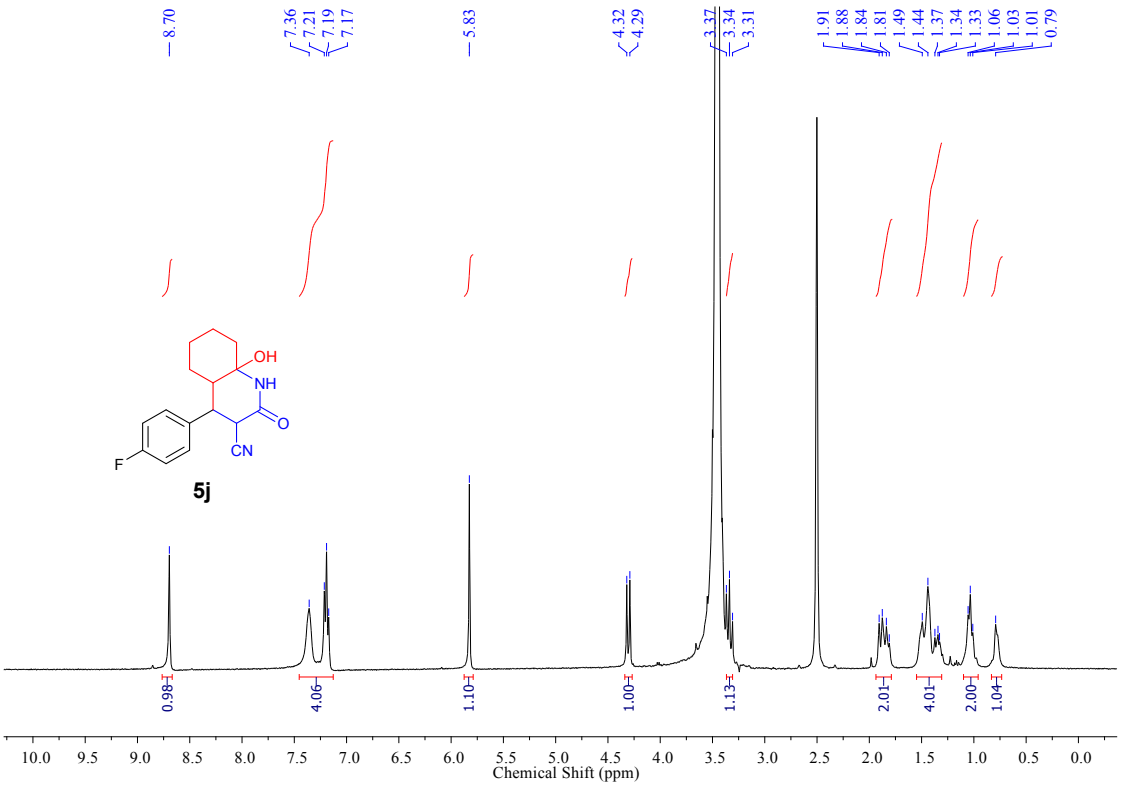


**$^{1}$H NMR**

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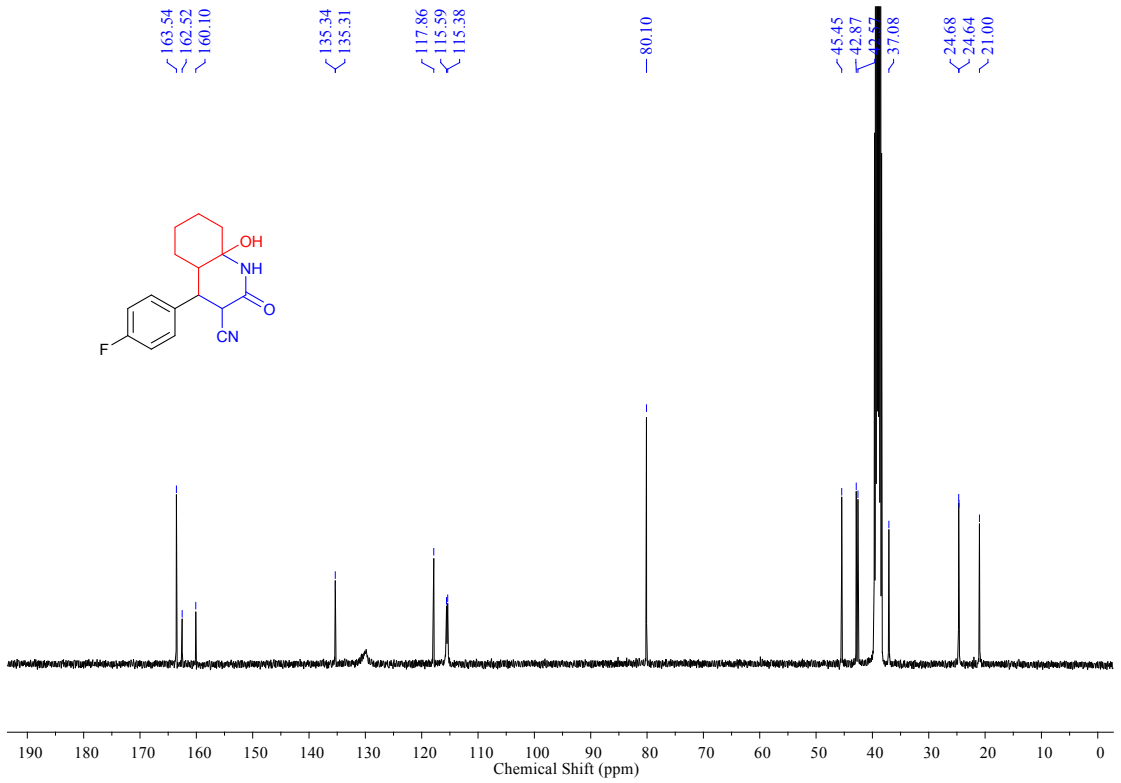

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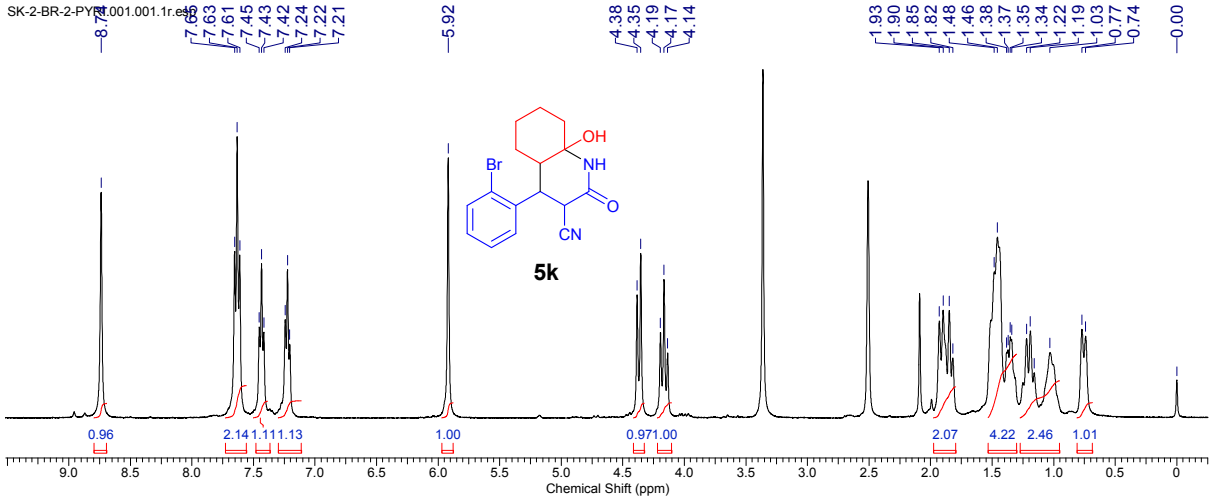


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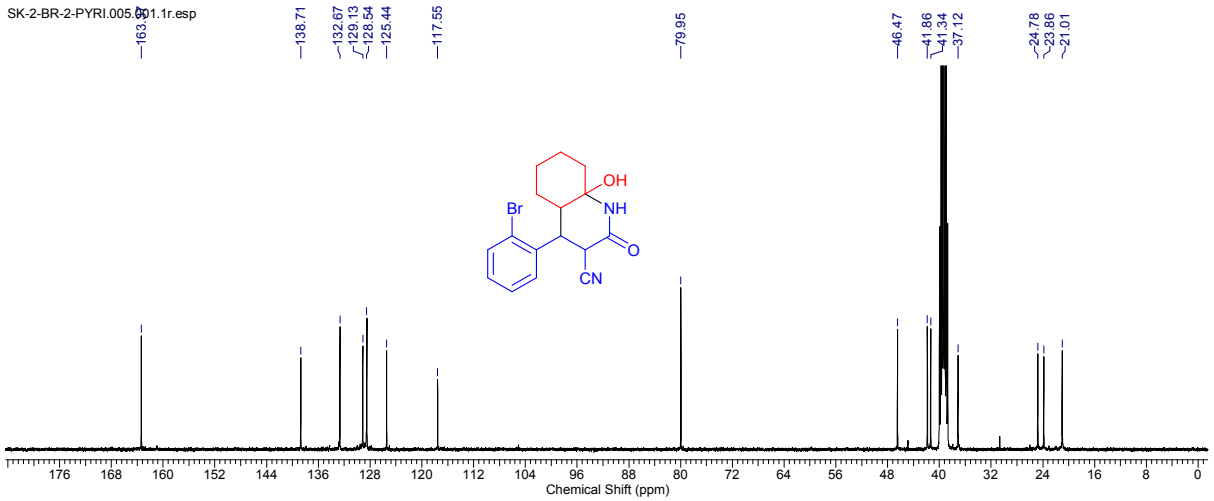

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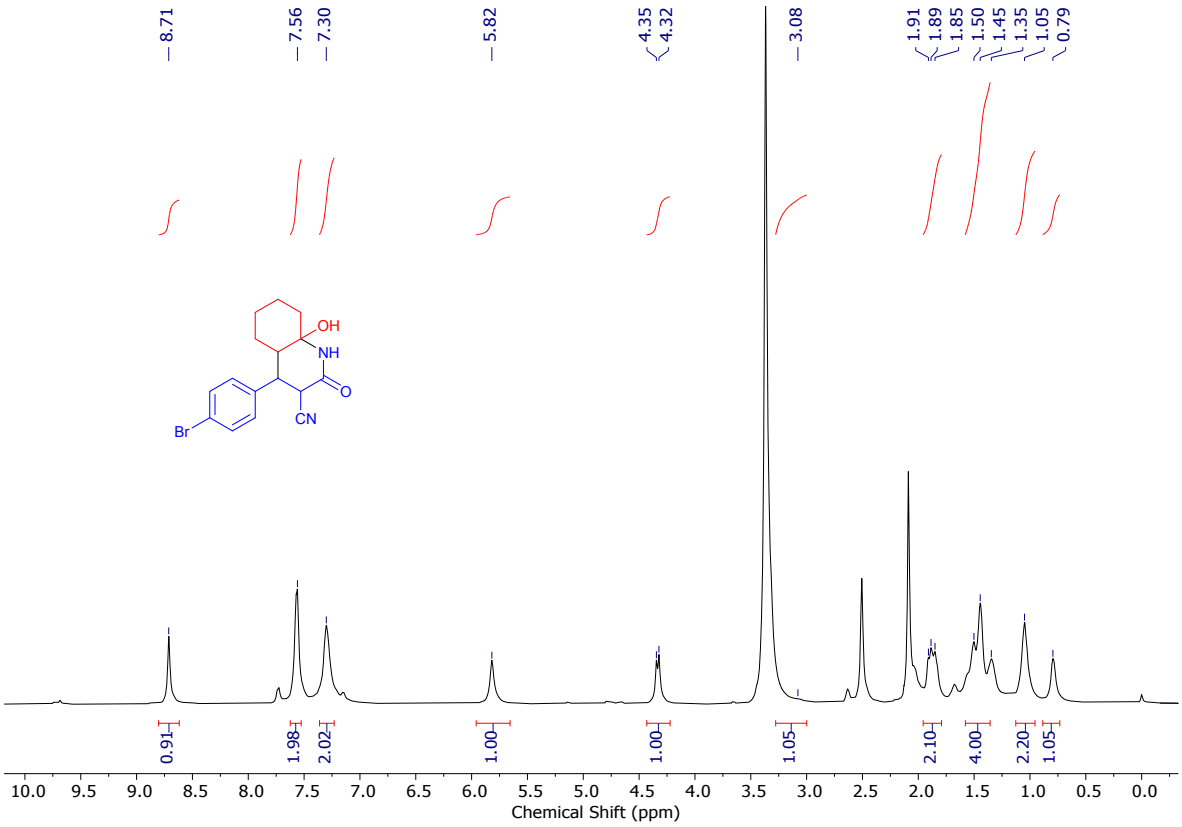


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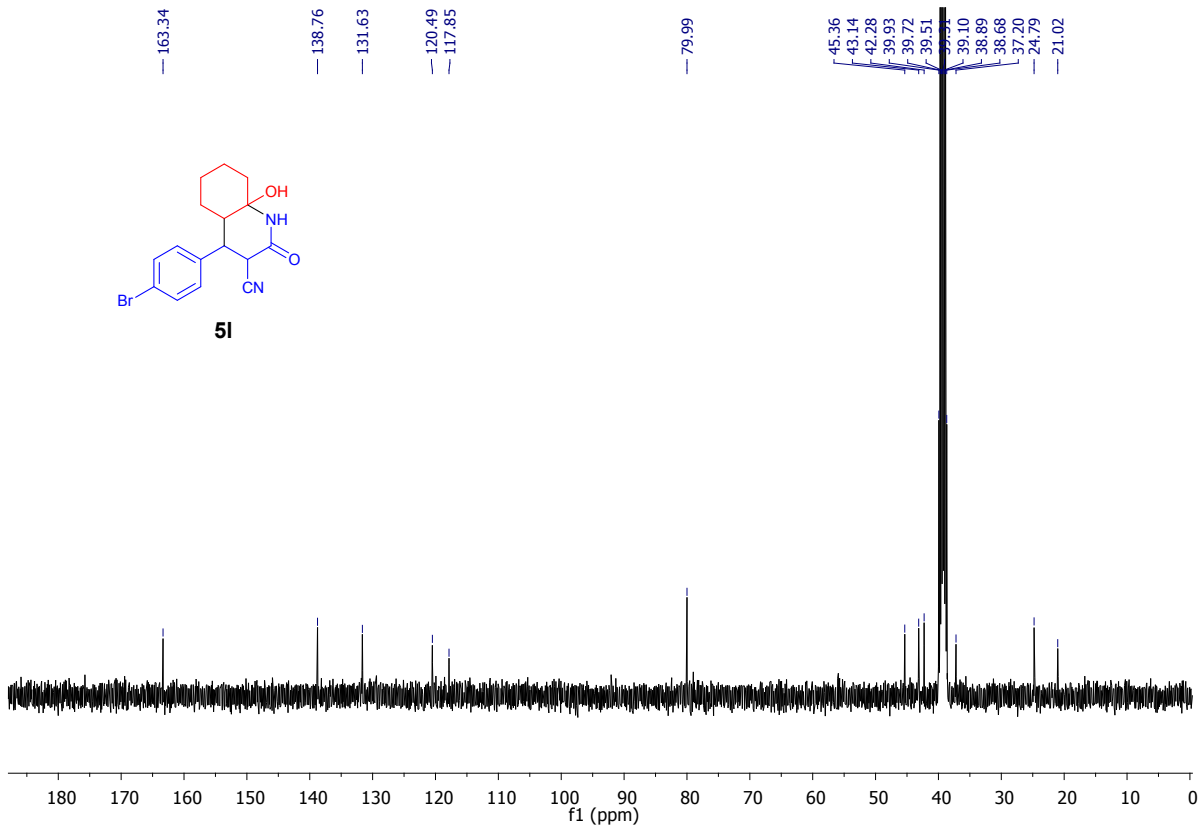
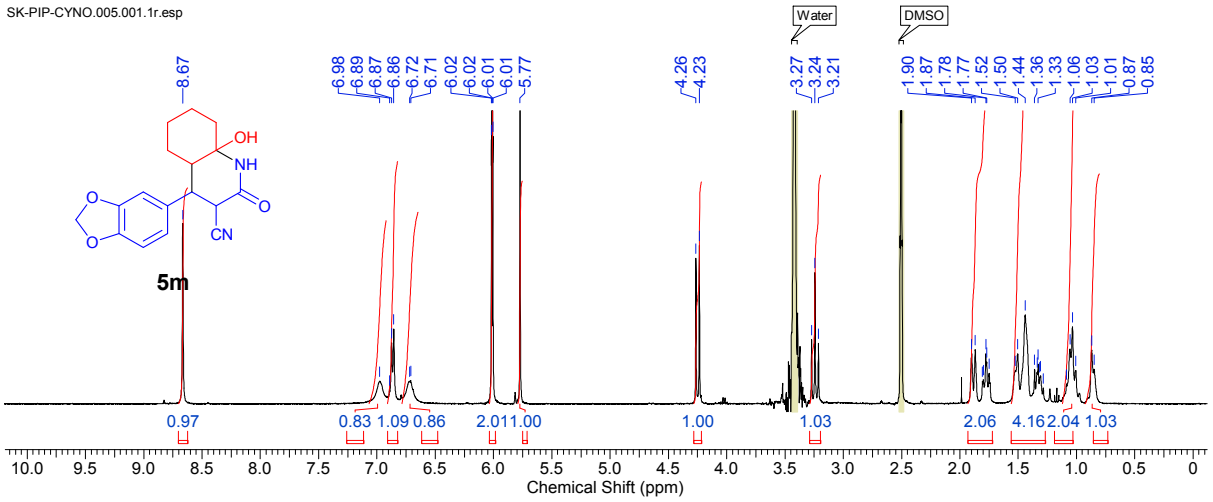


## $^{1}$H NMR

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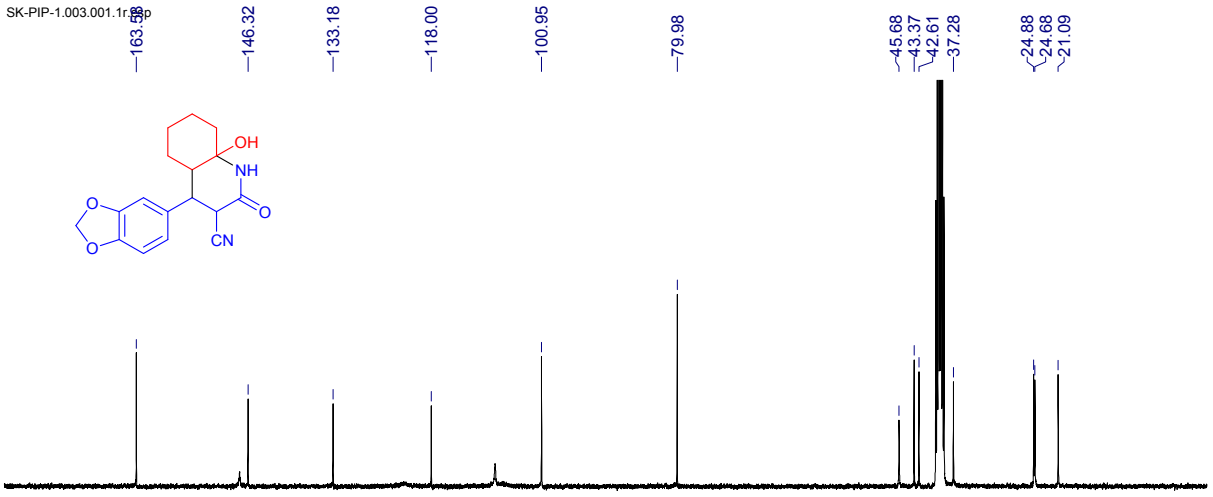

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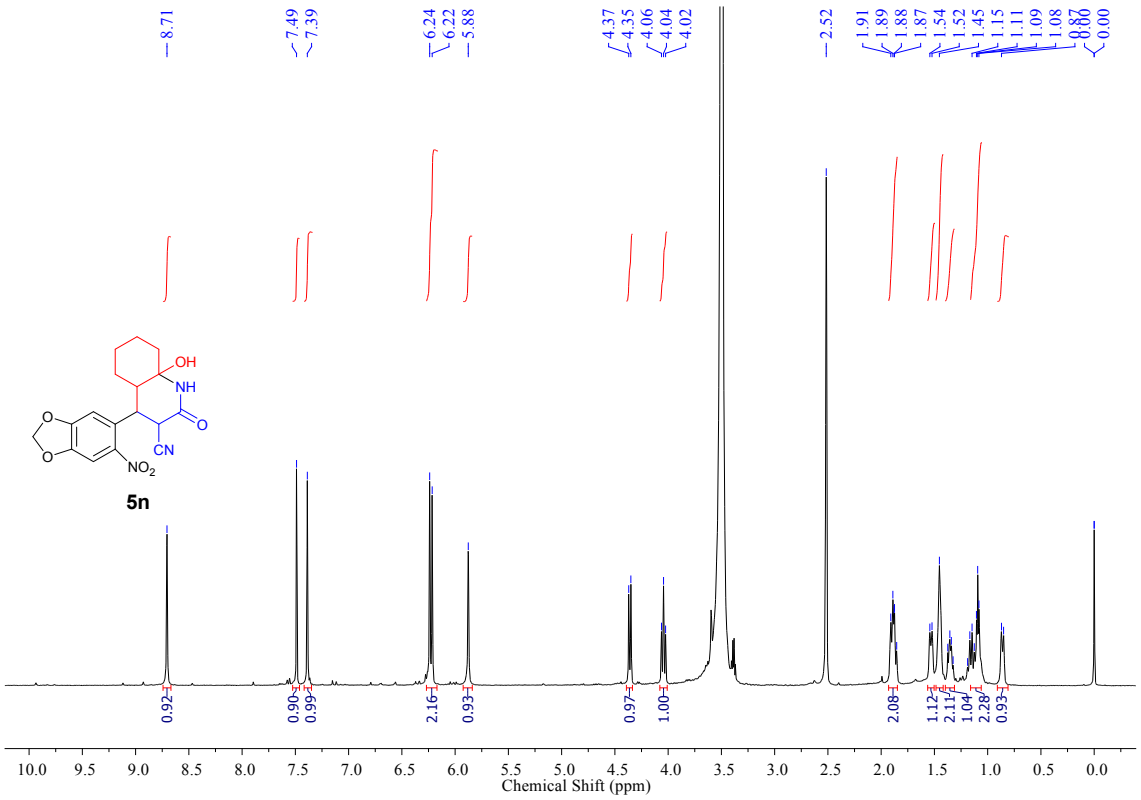


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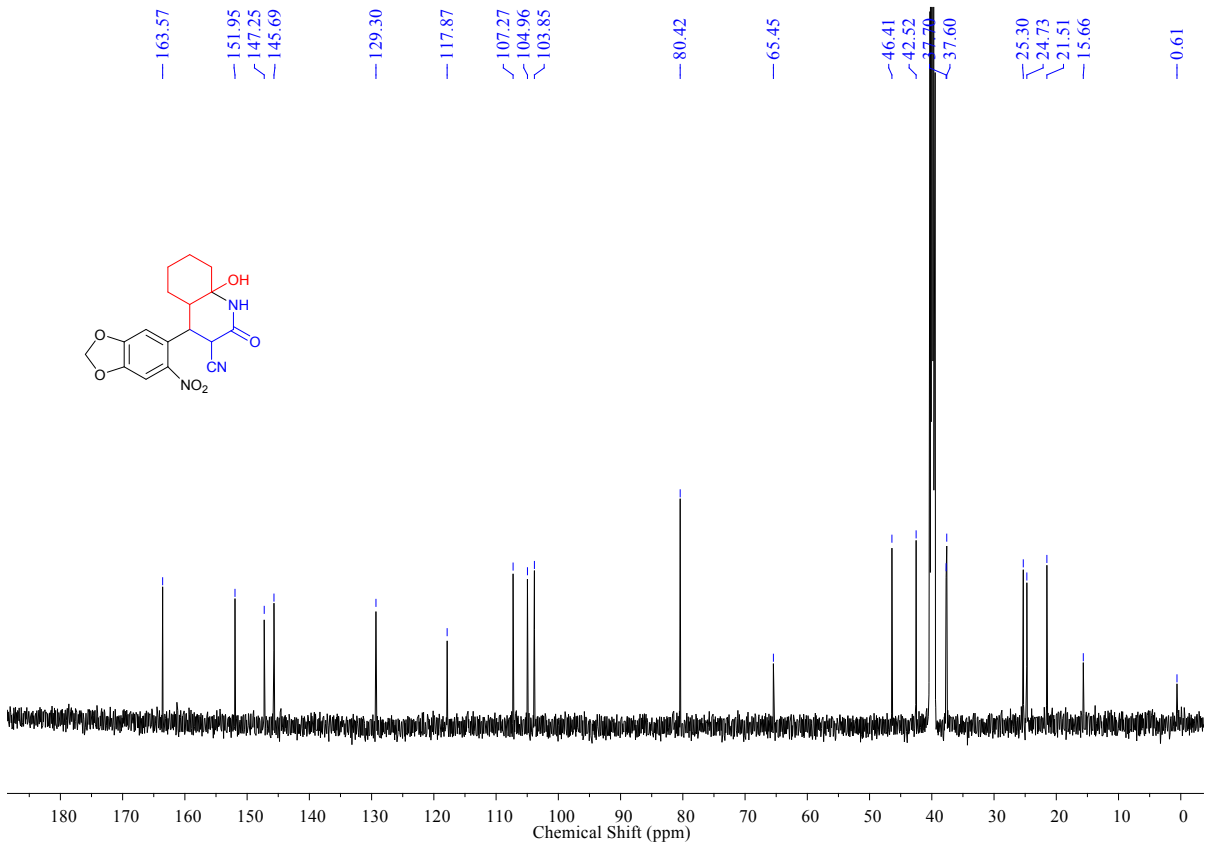
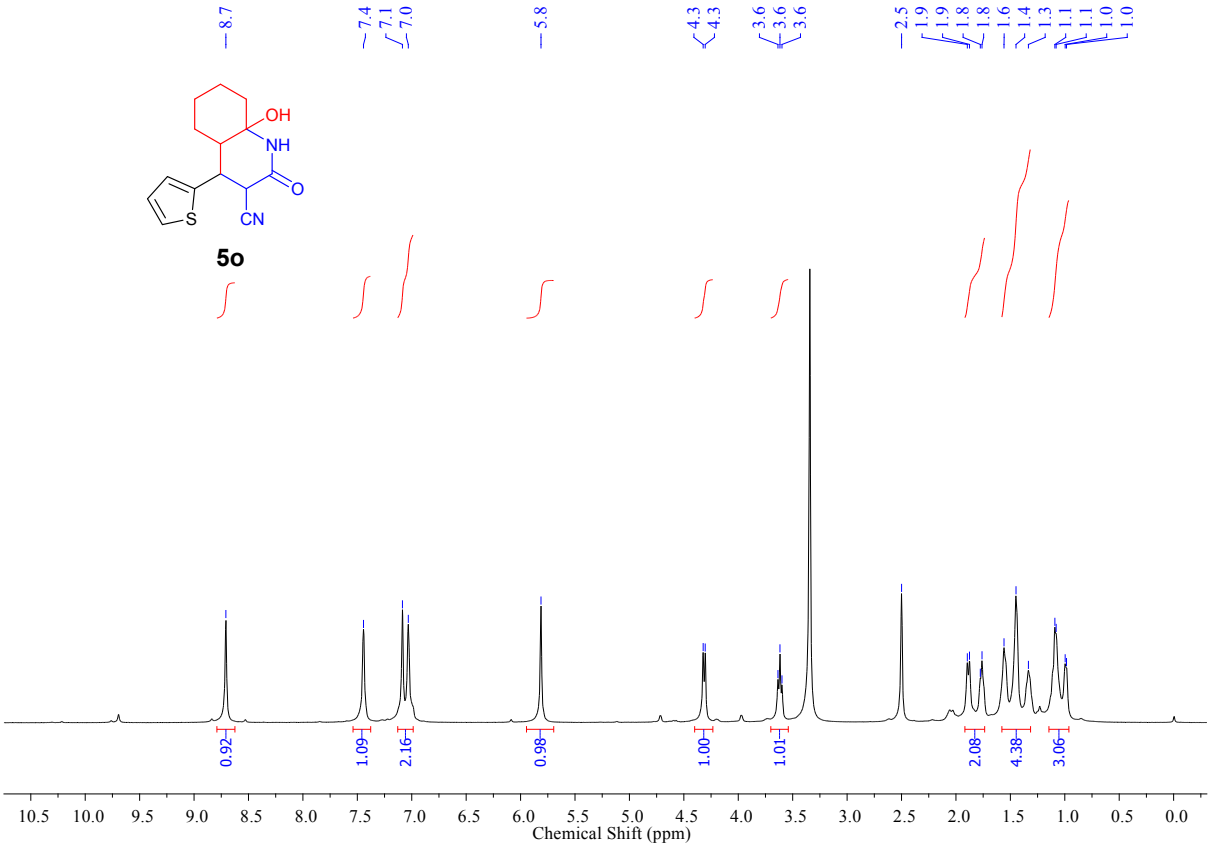


**$^{1}$H NMR**

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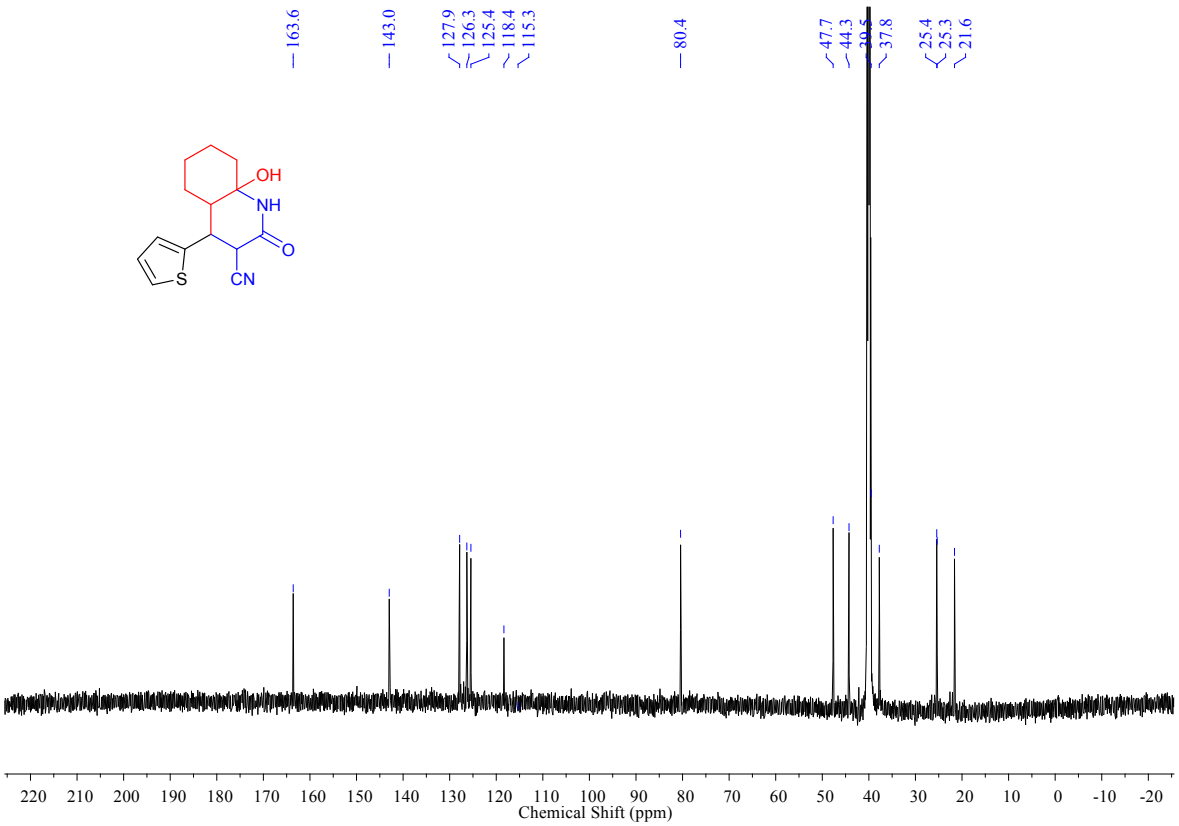
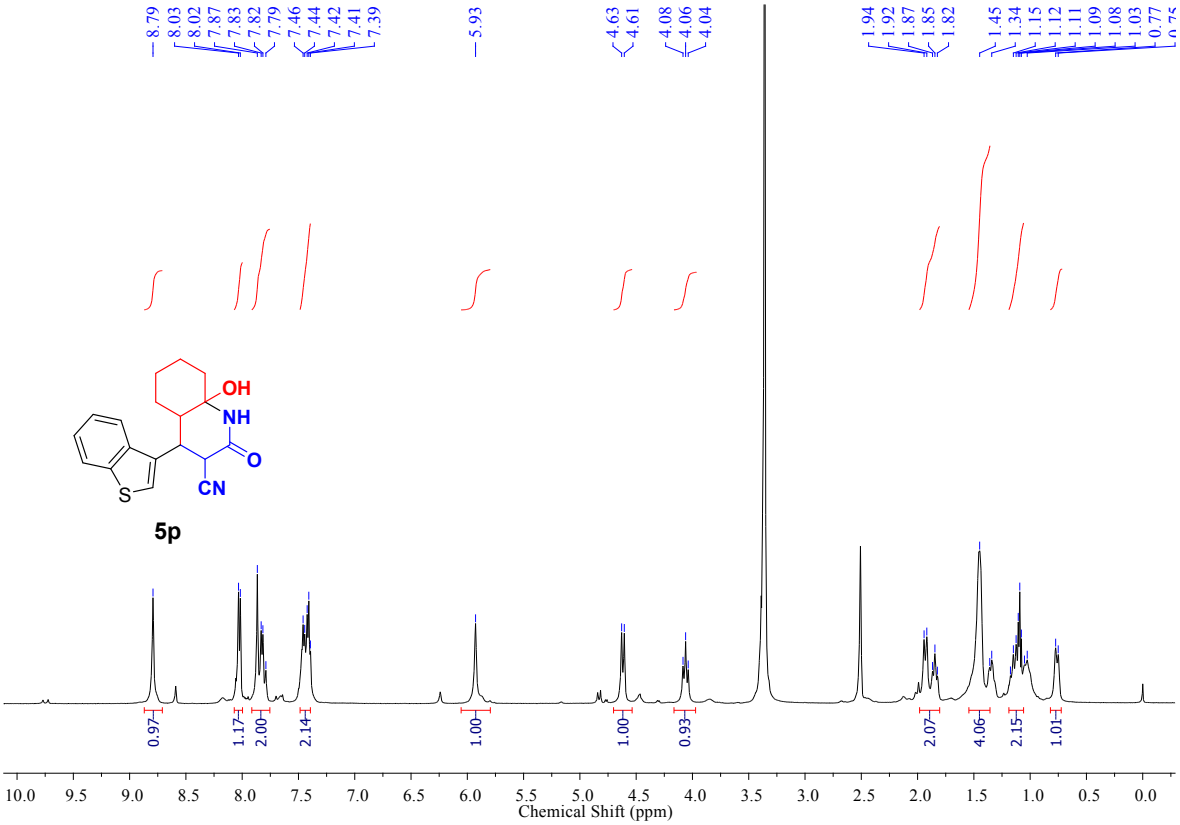
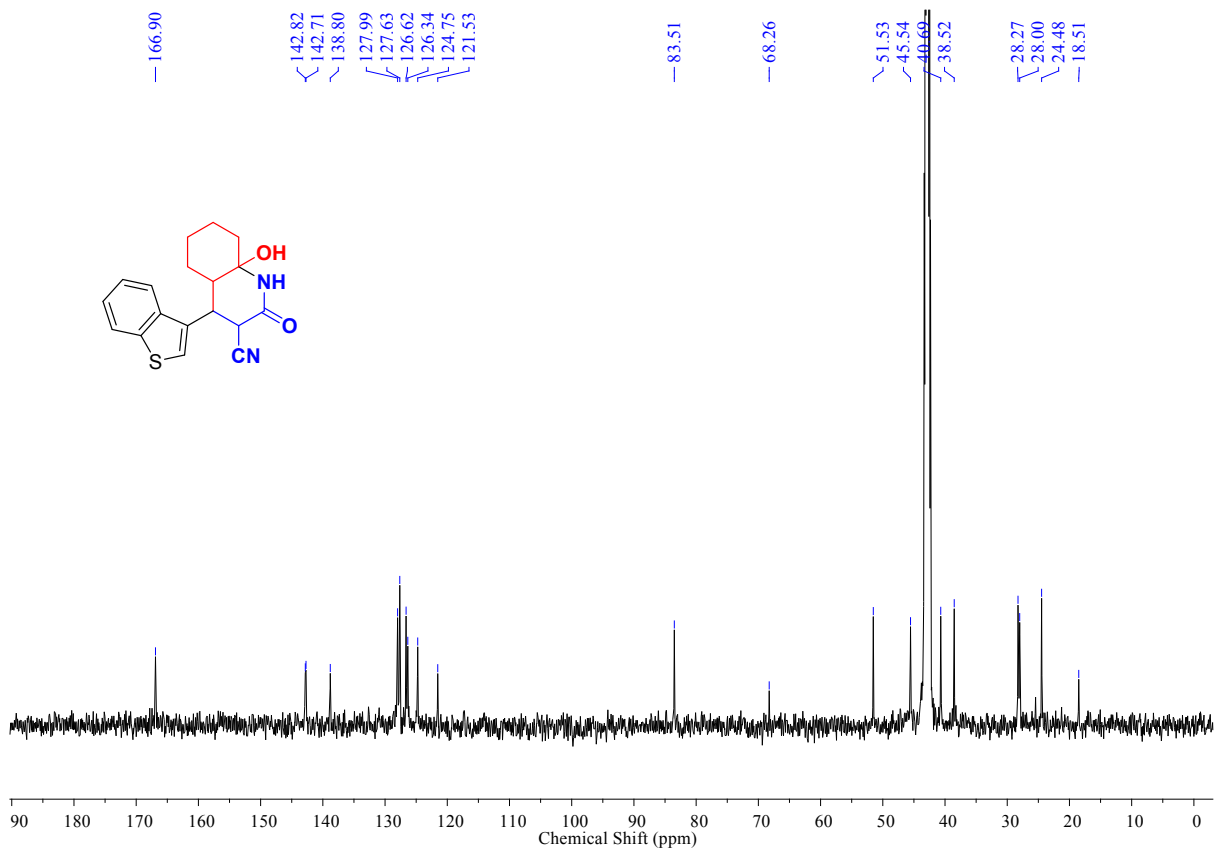


**$^{1}$H NMR**




5p

**$^{13}$C NMR**



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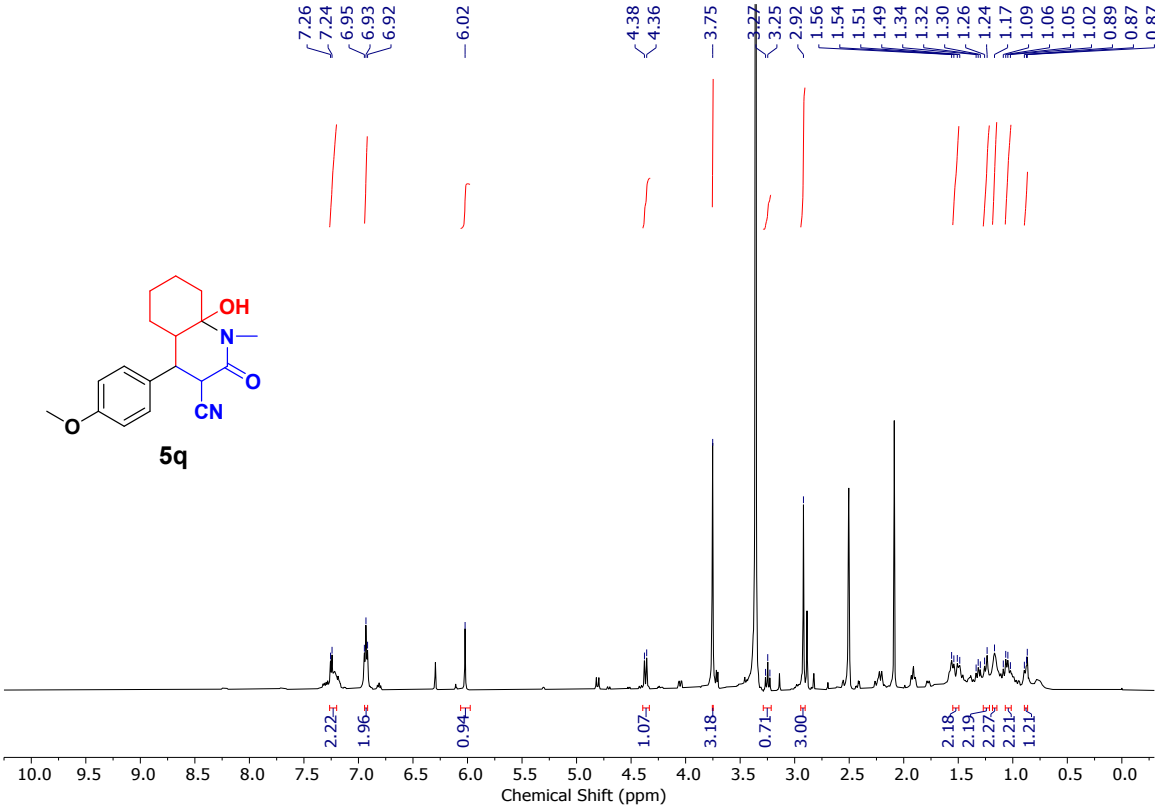


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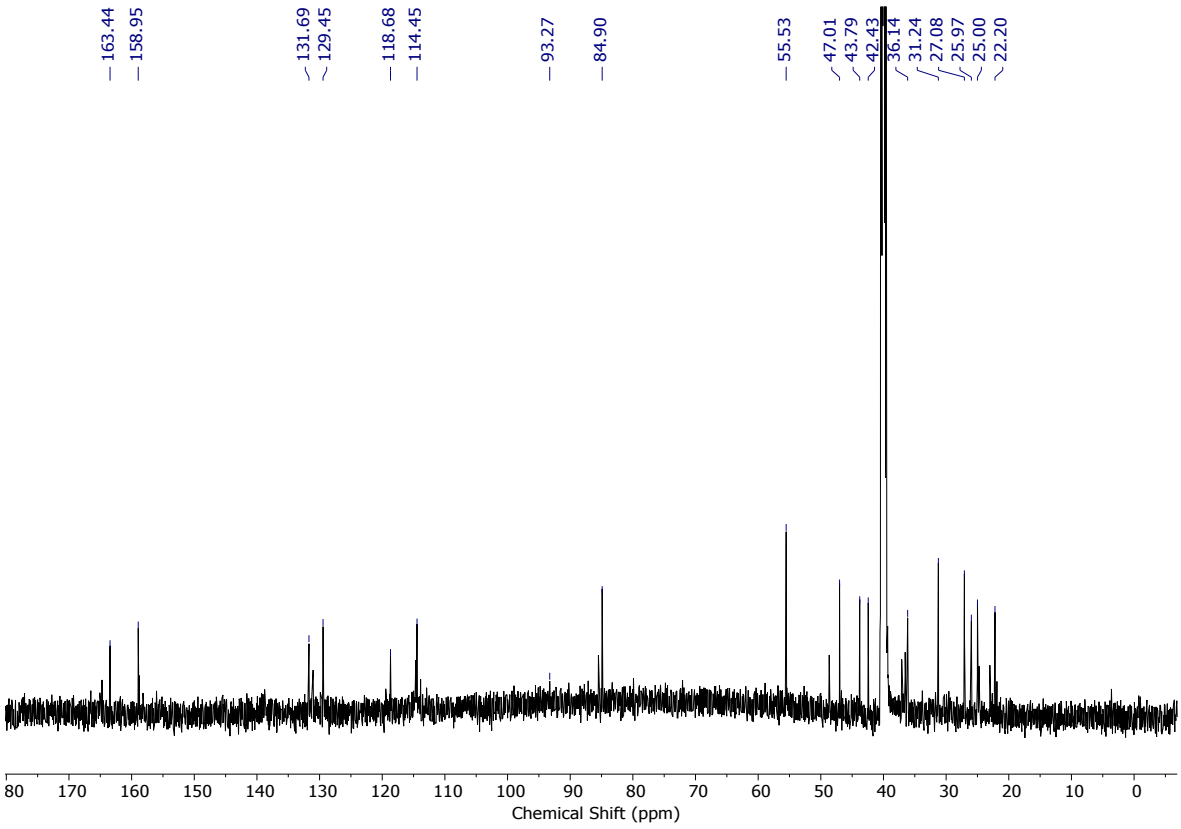
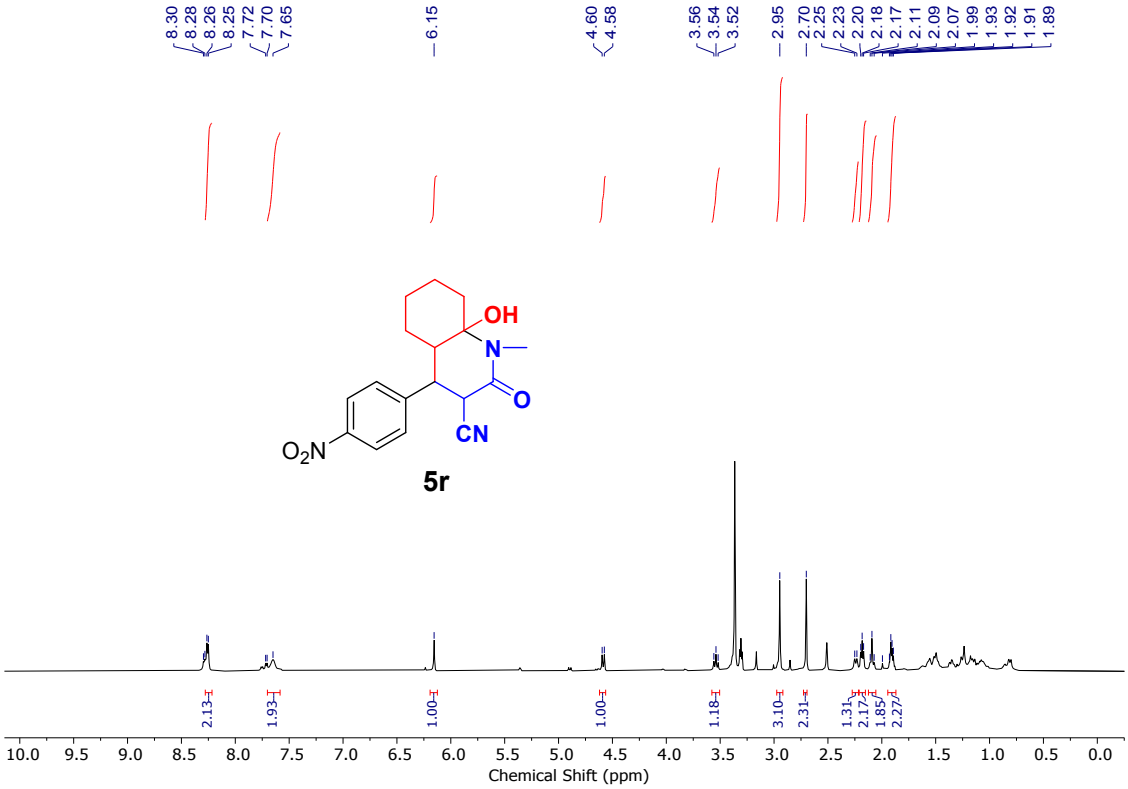
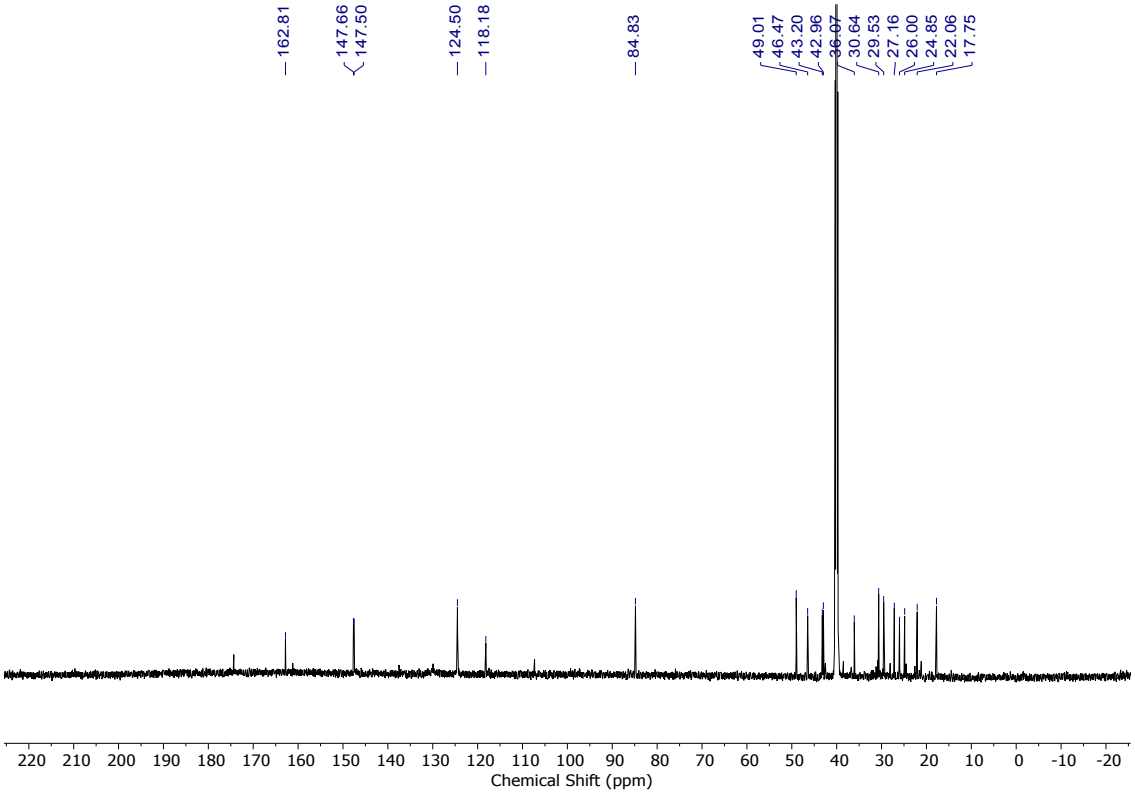


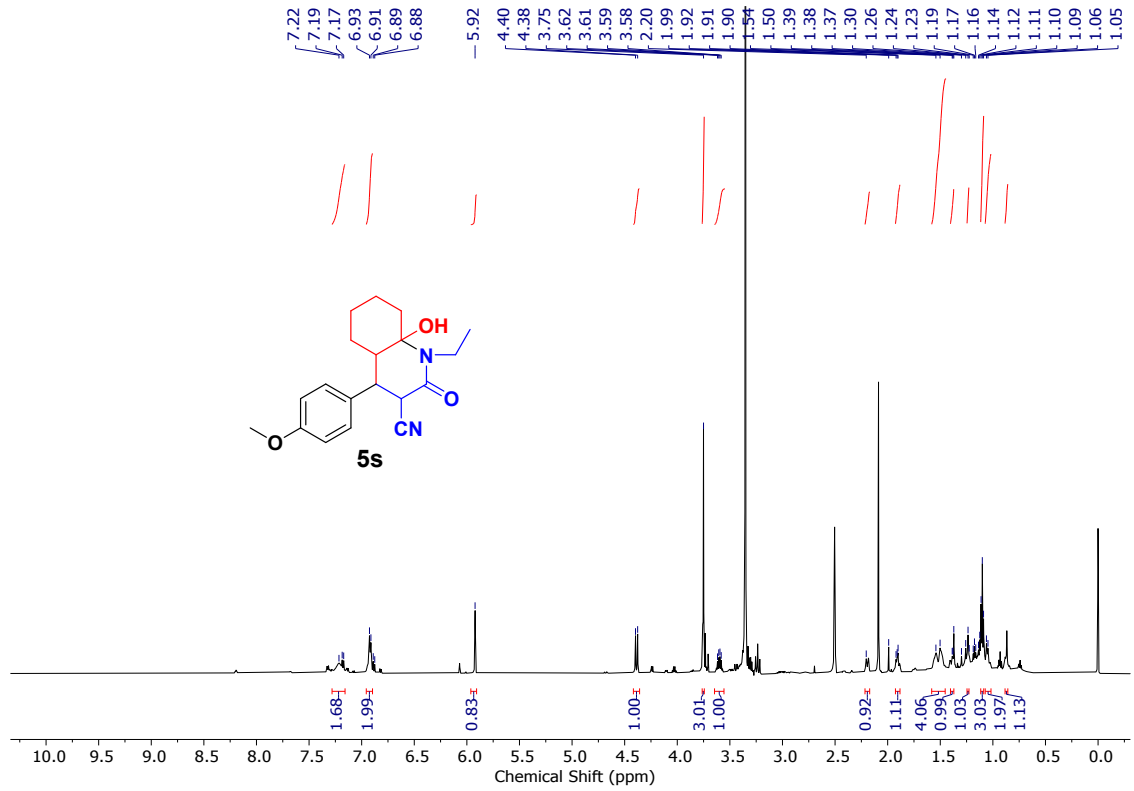
**$^{1}$H NMR**



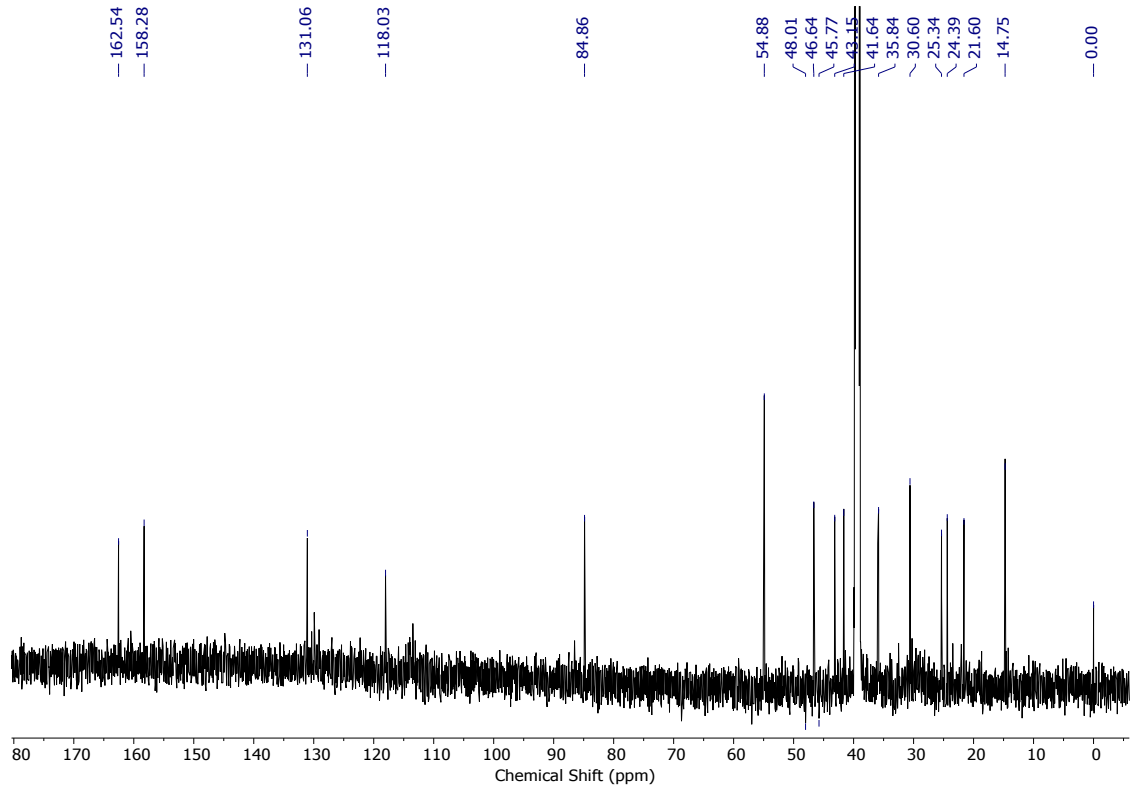

**$^{13}$C NMR**



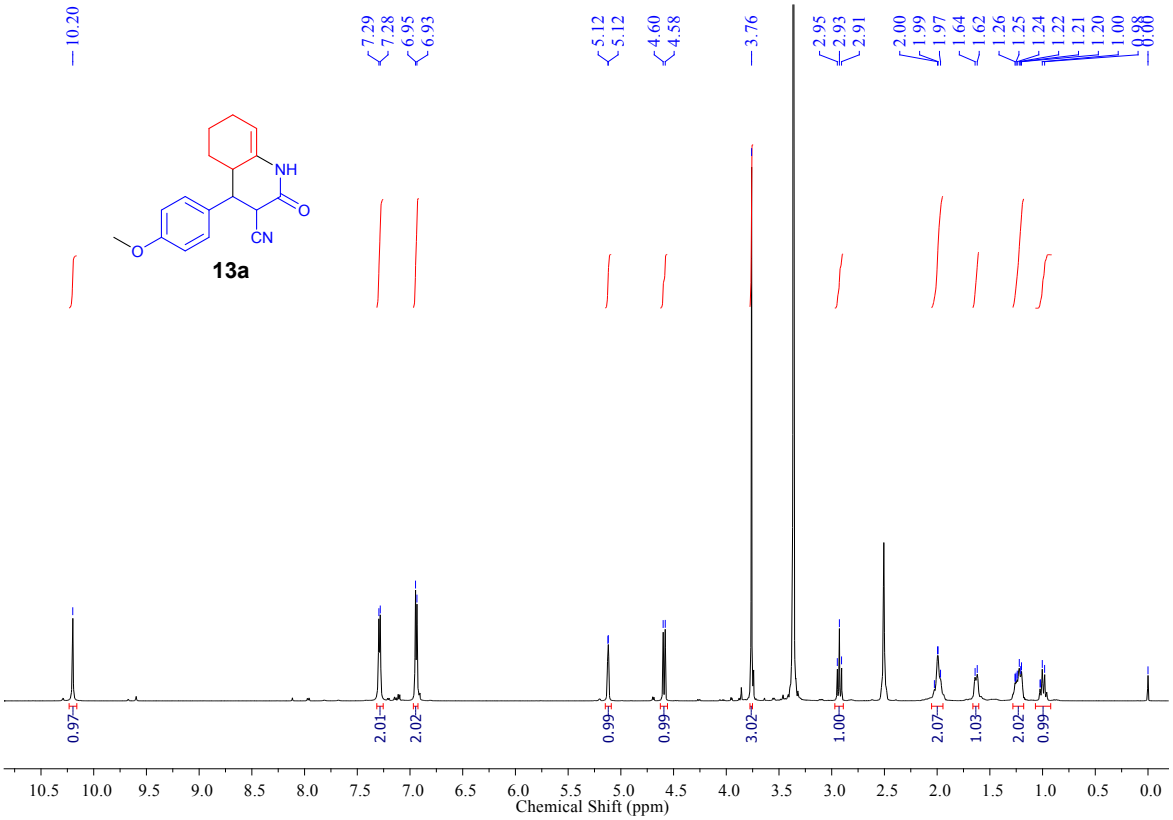
**$^{1}$H NMR**



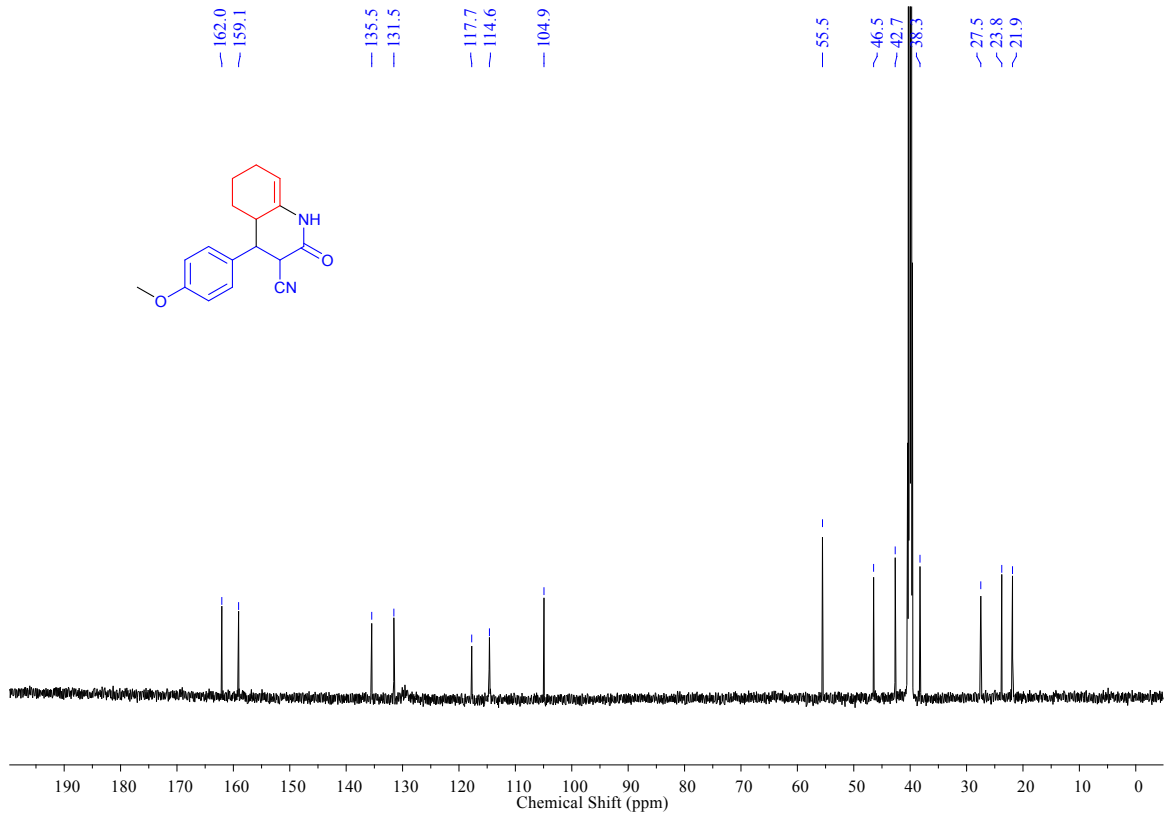

**$^{13}$C NMR**



**$^{1}$H NMR**

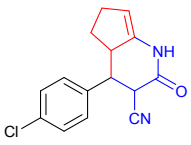



**$^{13}$C NMR**

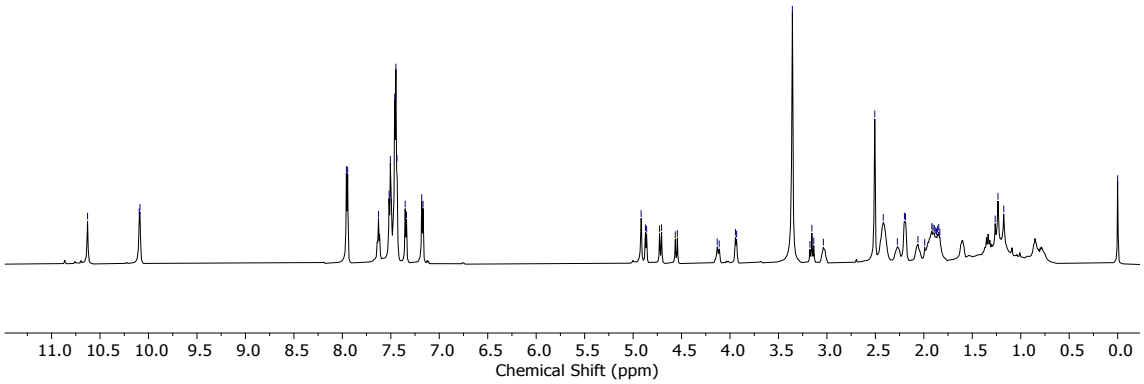



**$^{1}$H NMR**

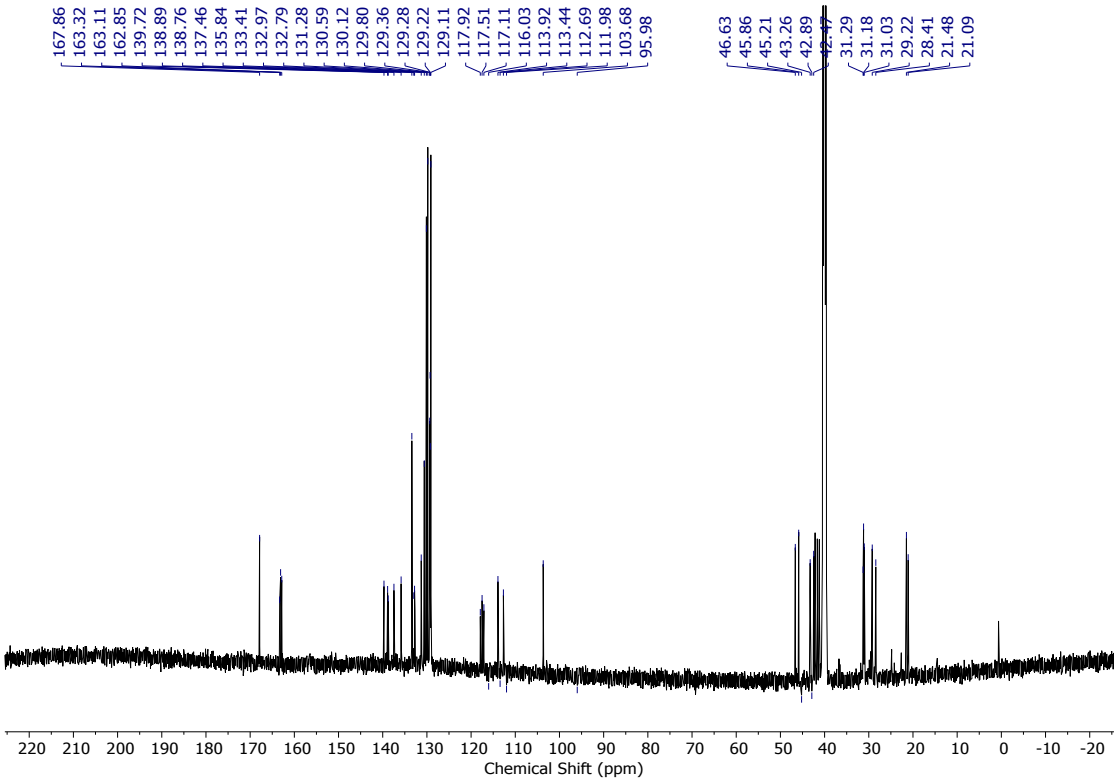

10.63
10.10
10.09
7.96
7.95
7.63
7.52
7.51
7.49
7.46
7.45
7.44
7.35
7.34
7.18
7.17
4.92
4.87
4.86
4.73
4.71
4.56
4.54
4.13
4.11
3.94
3.93
3.36
3.18
3.16
3.14
3.04
2.51
2.42
2.27
2.20
2.19
2.06
1.99
1.92
1.91
1.89
1.88
1.87
1.86
1.85
1.84
1.26
1.23
1.18
-0.00


NH
O
CN
Cl

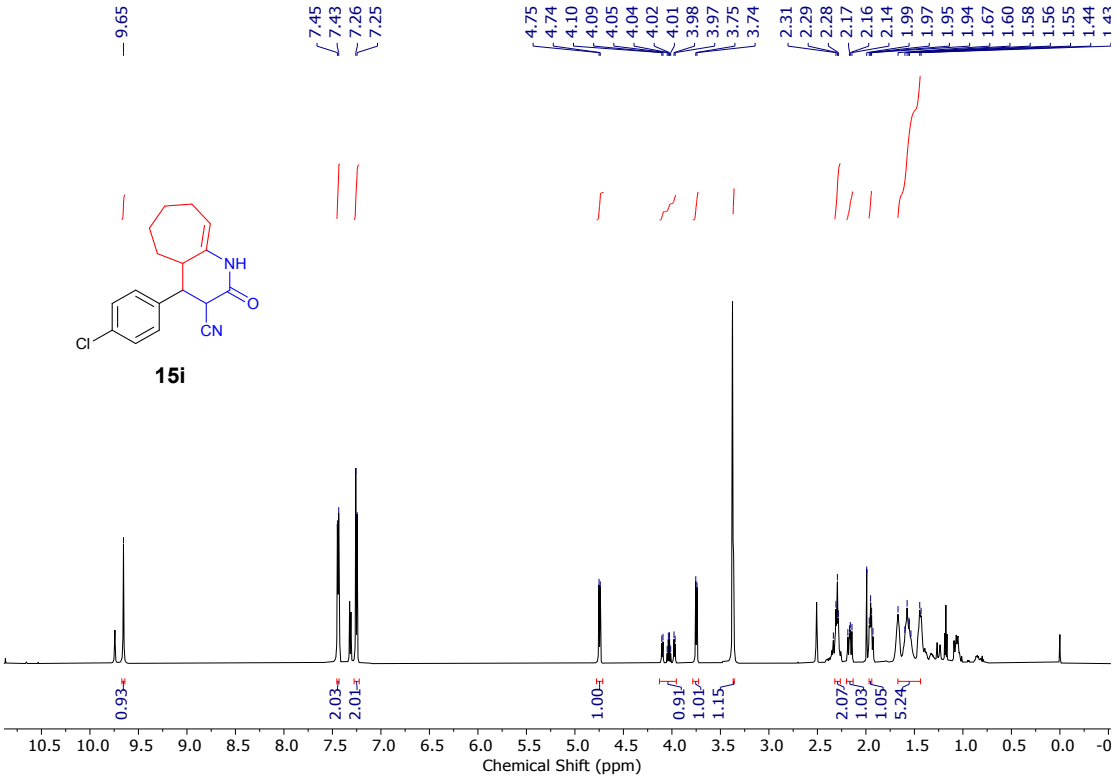
**14i**


11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

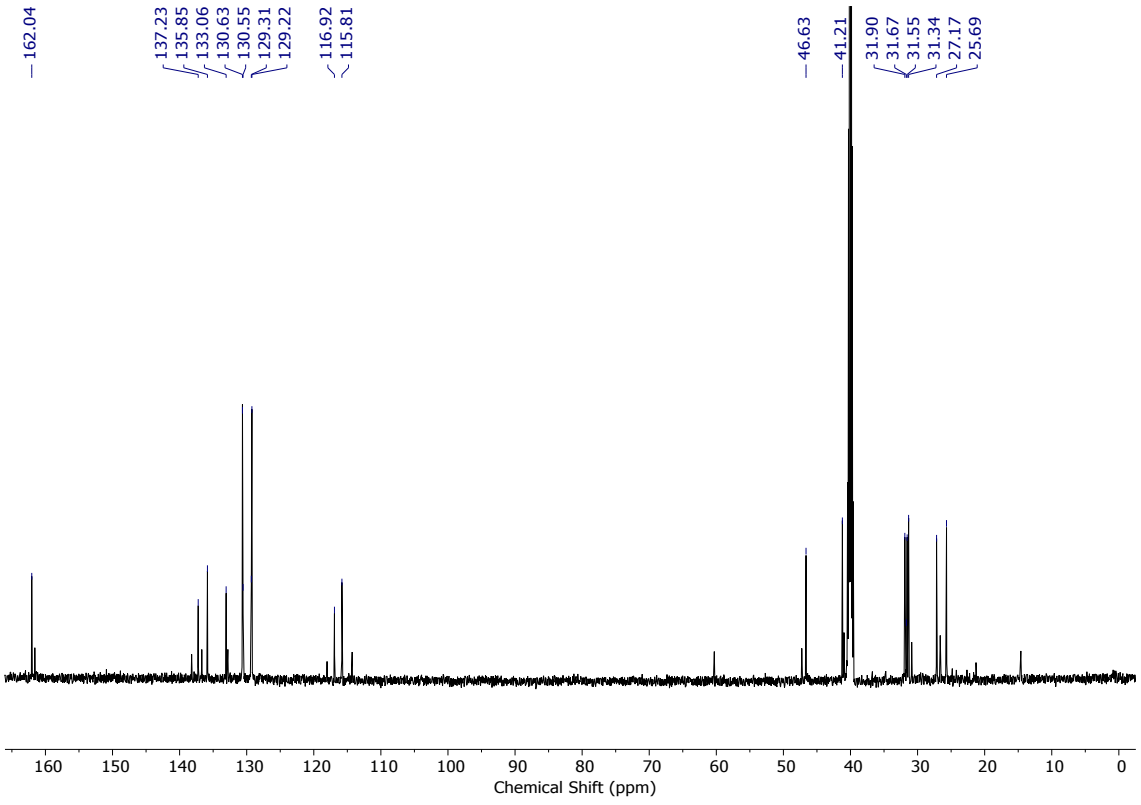
**$^{13}$C NMR**


167.86
163.32
163.11
162.85
139.72
138.89
138.76
137.46
135.84
133.41
132.97
132.79
131.28
130.59
130.12
129.80
129.36
129.28
129.22
129.11
117.92
117.51
117.11
116.03
113.92
113.44
112.69
111.98
103.68
95.98
46.63
45.86
45.21
43.26
42.89
31.29
31.18
31.03
29.22
28.41
21.48
21.09
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
Chemical Shift (ppm)

**$^{1}$H NMR**




**$^{13}$C NMR**



**Single crystal XRD data of the 13a**

Crystals were not grown by compounds **5** even after various tries while due to the high crystalline nature, we studied the structural confirmation of **13a** (Dehydrated **5a**) formed after prolonged reaction time. CCDC number is ***CCDC 2070982***and also CIF file is attached separately.

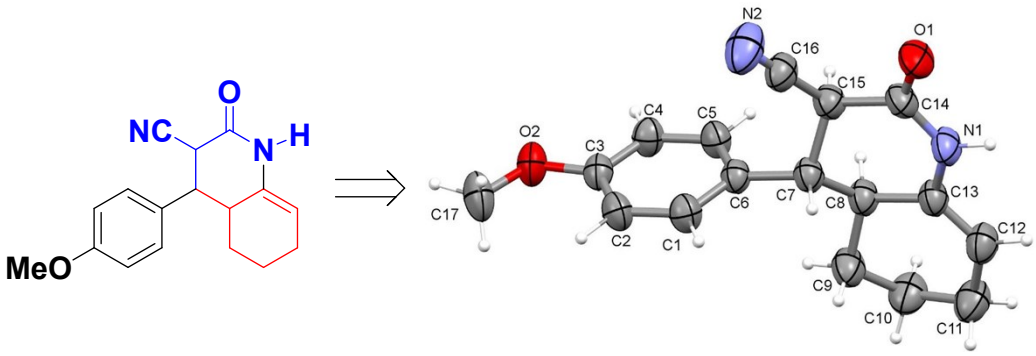



**Figure SI.** ORETP diagram of the compound **13a** with atom numbering scheme (45% probability factor for the thermal ellipsoids), *CCDC Number: 2070982*

**Datablockof compound 13a by single crystal study**

Bond precision C-C = 0.0031 A

Wavelength = 0.71073

Cell a = 12.8817(7) b=7.5056(4) c=16.1720(8)

alpha = 90 beta = 111.587(2) gamma = 90

Temperature = 300 K

| Data | Calculated | Reported |
|---|---|---|
| Volume | 1453.92(13) | 1453.92(13) |
| Space group | P 21/c | P1 21/c1 |
| Hall group | -P2ybc | -P2ybc |
| Moiety formula | $C_{17}H_{18}N_2O_2$ | - |
| Sum formula | $C_{17}H_{18}N_2O_2$ | $C_{17}H_{18}N_2O_2$ |
| Mr | 282.33 | 282.33 |
| Dx,g cm-3 | 1.290 | 1.290 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.086 | 0.086 |
| F000 | 600.0 | 600.0 |
| F000’ | 600.25 | - |

| | | |
|---|---|---|
| h,k,lmax | 19,11,24 | 19,11,24 |
| Nref | 5564 | 5542 |
| Tmin,Tmax | 0.984,0.993 | 0.957,0.993 |
| Tmin’ | 0.957 | - |

Correction method= # Reported T Limits: Tmin=0.957 Tmax=0.993

AbsCorr = MULTI SCAN

Data completeness= 0.996

Theta(max)= 33.200

R(reflections)= 0.0655( 2493)

wR2(reflections)= 0.2294( 5542)

S = 1.028

Npar= 223