# Ammonium hydroxide as ultimate amino source for synthesis of *N*-unprotected 3-tetrasubstituted aminooxindoles *via* catalyst-free direct amination

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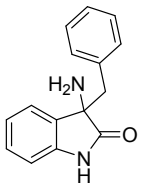
## 1. General information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. $^{1}H$ and $^{13}C$NMR spectra were obtained using a Bruker DPX-400 or DPX-600 spectrometer. $^{1}H$ NMR chemical shifts are reported in ppm ($\delta$) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. $^{13}C$ NMR chemical shifts are reported in ppm ($\delta$) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Melting points were measured on an electrothermal digital melting point apparatus.

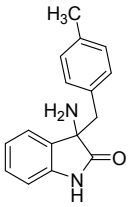
## 2. Typical experimental procedures for synthesis of compounds 2

In a sealed tube equipped with a magnetic stirring bar, to 2.0 mL of $NH_3 \cdot H_2O$ (25%) was added **1** (0.20 mmol). The reaction mixture was stirred at rt for 3 h. After completion of the reaction, as indicated by TLC, purification by flash column chromatography (hexane/EtOAc, 6/1, v/v) was carried out to furnish the corresponding product **2**.

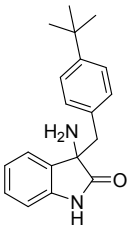
## 3. Characterization data of compounds 2



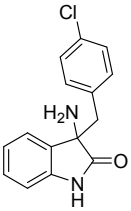

**2a**: Light yellow solid, m.p. 169.8-175.0 °C; yield 85%; $^{1}H$ NMR (DMSO-$d_6$, 400 MHz) $\delta$: 2.20 (br s, 2H), 2.93 (d, $J$ = 13.2 Hz, 1H), 3.03 (d, $J$ = 13.2 Hz, 1H), 6.58 (d, $J$ = 7.6 Hz, 1H), 6.81-6.83 (m, 2H), 6.90-6.94 (m, 1H), 7.04-7.09 (m, 4H), 7.24 (d, $J$ = 7.2 Hz, 1H), 10.00 (br s, 1H); $^{13}C$ NMR (DMSO-$d_6$, 100 MHz) $\delta$: 45.3, 62.9, 109.5, 121.5, 124.5, 126.6, 127.8, 128.6, 130.3, 132.6, 136.2, 142.0, 181.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{15}N_2O$ $[M+H]^+$: 239.1179; Found: 239.1184.



**2b**: Light yellow solid, m.p. 160.0-163.7 °C; yield 87%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 2.16 (s, 3H), 2.26 (br s, 1H), 2.90 (d, $J$ = 12.6 Hz, 1H), 3.00 (d, $J$ = 13.2 Hz, 1H), 6.60 (d, $J$ = 8.4 Hz, 1H), 6.72 (d, $J$ = 8.4 Hz, 2H), 6.85 (d, $J$ = 8.4 Hz, 2H), 6.92-6.95 (m, 1H), 7.08-7.10 (m, 1H), 7.27 (d, $J$ = 7.8 Hz, 1H), 9.98 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 21.0, 45.0, 63.0, 109.6, 121.6, 124.7, 128.5, 128.7, 130.2, 132.8, 133.1, 135.5, 142.2, 181.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{17}N_2O$ $[M+H]^+$: 253.1335; Found: 253.1341.

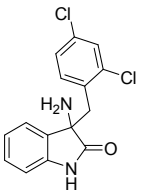


**2c**: Light yellow solid, m.p. 61.8-63.0 °C; yield 91%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 1.18 (s, 9H), 2.19 (br s, 1H), 2.90 (d, $J$ = 13.2 Hz, 1H), 3.01 (d, $J$ = 12.6 Hz, 1H), 6.63 (d, $J$ = 7.8 Hz, 1H), 6.78 (d, $J$ = 8.4 Hz, 2H), 6.93-6.96 (m, 1H), 7.08-7.12 (m, 3H), 7.26 (d, $J$ = 7.8 Hz, 1H), 10.03 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 31.6, 34.5, 44.8, 62.7, 109.6, 121.6, 124.6, 124.7, 128.7, 130.1, 132.9, 133.2, 142.2, 148.8, 181.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{19}H_{23}N_2O$ $[M+H]^+$: 295.1805; Found: 295.1803.

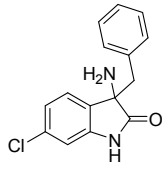


**2d**: Light yellow solid, m.p. 123.5-125.7 °C; yield 85%; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 2.27 (br s, 1H), 2.91 (d, $J$ = 13.2 Hz, 1H), 3.02 (d, $J$ = 13.2 Hz, 1H), 6.01 (d, J = 7.6 Hz, 1H), 6.83 (d, $J$ = 8.4 Hz, 2H), 6.91-6.95 (m, 1H), 7.07-7.12 (m, 3H), 7.23 (d, $J$ = 7.2 Hz, 1H), 10.05 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 44.0, 62.4, 109.2, 121.3, 124.3, 127.4, 128.4, 131.0, 131.7, 131.9, 134.8, 141.6, 180.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{14}ClN_2O$ $[M+H]^+$: 273.0789;

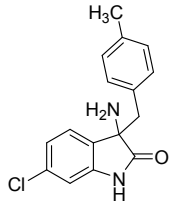
Found: 273.0793.




**2e**: Light yellow solid, m.p. 136.7-139.5 °C; yield 82%; $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 2.24 (br s, 2H), 2.98 (d, $J$ = 13.2 Hz, 1H), 3.18 (d, $J$ = 13.2 Hz, 1H), 6.69 (d, $J$ = 7.2 Hz, 1H), 6.82-6.86 (m, 1H), 6.95 (d, $J$ = 7.2 Hz, 1H), 7.09-7.13 (m, 1H), 7.27 (s, 2H), 7.38 (s, 1H), 10.25 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 61.8, 109.2, 121.1, 124.6, 126.5, 128.2, 128.5, 131.6, 131.8, 132.9, 133.3, 135.0, 141.3, 181.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{13}Cl_2N_2O$ $[M+H]^+$: 307.0399; Found: 307.0403.

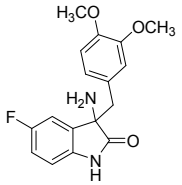



**2f**: Light yellow solid, m.p. 207.6-207.9 °C; yield 80%; $^{1}$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 2.29 (br s, 2H), 2.95 (d, $J$ = 12.6 Hz, 1H), 3.05 (d, $J$ = 12.6 Hz, 1H), 6.60 (s, 1H), 6.85-6.86 (m, 2H), 6.97-6.98 (m, 1H), 7.08-7.09 (m, 3H), 7.25 (d, $J$ = 7.8 Hz, 1H), 10.16 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 45.1, 62.8, 109.6, 121.3, 126.3, 126.8, 128.0, 130.3, 131.7, 132.8, 136.0, 143.6, 181.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{14}ClN_2O$ $[M+H]^+$: 273.0789; Found: 273.0784.

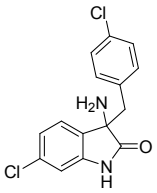



**2g**: Light yellow solid, m.p. 143.6-147.9 °C; yield 83%; $^{1}$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 2.15 (s, 3H), 2.30 (br s, 1H), 2.89 (d, $J$ = 12.8 Hz, 1H), 2.98 (d, $J$ = 12.8 Hz, 1H), 6.59 (s, 1H), 6.70 (d, $J$ = 8.0 Hz, 2H), 6.87 (d, $J$ = 7.6 Hz, 2H), 6.95-6.98 (m, 1H), 7.25 (d, $J$ = 7.6 Hz, 1H), 10.14 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 20.6, 44.2, 62.4, 109.1, 120.8, 125.8, 128.2, 129.7, 131.3, 132.3, 132.4, 135.3, 143.2, 180.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{16}ClN_2O$ $[M+H]^+$:

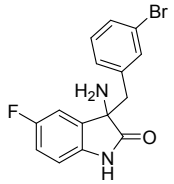
287.0946; Found: 287.0942.




**2h**: Light yellow solid, m.p. 167.0-171.5 °C; yield 81%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 2.90 (d, $J$ = 12.6 Hz, 1H), 3.00 (d, $J$ = 12.6 Hz, 1H), 3.49 (s, 3H), 3.63 (s, 3H), 6.35 (s, 1H), 6.42 (d, $J$ = 7.8 Hz, 1H), 6.57-6.59 (m, 1H), 6.67 (d, $J$ = 8.4 Hz, 1H), 6.92-6.95 (m, 1H), 7.19-7.21 (m, 1H), 10.01 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 45.0, 55.4, 55.7, 63.7, 110.2, 111.3, 112.5 (d, $J_{CF}$ = 25.4 Hz), 113.9, 114.7 (d, $J_{CF}$ = 25.3 Hz), 122.4, 128.2, 135.0, 138.4, 147.7, 148.0, 158.8 (d, $J_{CF}$ = 234.6 Hz), 181.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{17}H_{18}FN_2O_3$ $[M+H]^+$: 317.1296; Found: 317.1296.

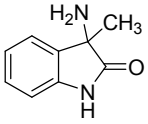



**2i**: Light yellow solid, m.p. 237.6-239.7 °C; yield 80%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 2.34 (br s, 2H), 2.92 (d, $J$ = 12.6 Hz, 1H), 3.04 (d, $J$ = 12.6 Hz, 1H), 6.63 (s, 1H), 6.87 (d, $J$ = 8.4 Hz, 2H), 6.98-6.99 (m, 1H), 7.16-7.23 (m, 3H), 10.19 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 44.1, 62.7, 109.7, 121.4, 126.3, 128.0, 131.4, 131.6, 132.2, 133.0, 135.0, 143.6, 181.2; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{13}Cl_2N_2O$ $[M+H]^+$: 307.0399; Found: 307.0394.

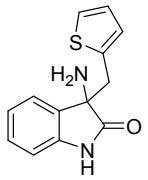



**2j**: White solid, m.p. 188.5-189.7 °C; yield 86%; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 2.33 (br s, 2H), 2.92 (d, $J$ = 12.4 Hz, 1H), 3.05 (d, $J$ = 12.4 Hz, 1H), 6.57-6.60 (m, 1H), 6.84 (d, $J$ = 7.6 Hz, 1H), 6.90-6.95 (m, 1H), 7.02-7.05 (m, 2H), 7.10-7.13 (m, 1H), 7.27 (d, $J$ = 8.0 Hz, 1H), 10.12 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 44.0, 63.0, 109.9 (d, $J_{CF}$ = 3.2 Hz), 112.1(d, $J_{CF}$ = 24.2 Hz), 114.5 (d, $J_{CF}$ = 23.2 Hz), 120.7, 129.0, 129.3, 129.6, 132.6, 133.8, 137.7, 138.4, 157.8 (d, $J_{CF}$

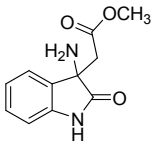
= 236.4 Hz), 180.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{13}BrFN_2O$ $[M+H]^+$: 335.0190; Found: 335.0193.



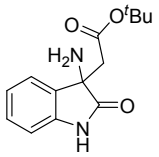
**2k**: Light yellow solid, m.p. 189.7-190.6 °C; yield 83%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 1.27 (s, 3H), 6.83 (d, $J$ = 8.4 Hz, 1H), 6.94-6.96 (m, 1H), 7.15-7.18 (m, 1H), 7.30 (d, $J$ = 7.8 Hz, 1H), 10.23 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 26.2, 58.1, 109.9, 121.9, 123.8, 128.6, 135.4, 141.5, 182.7; HRMS (ESI-TOF) m/z: Calcd. for $C_9H_{11}N_2O$ $[M+H]^+$: 163.0866; Found: 163.0868.



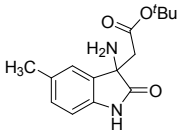
**2l**: Light yellow solid, m.p. 156.9-158.1 °C; yield 81%; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 2.70 (br s, 2H), 3.18 (d, $J$ = 14.0 Hz, 1H), 3.24 (d, $J$ = 14.0 Hz, 1H), 6.51 (d, $J$ = 3.2 Hz, 1H), 6.67 (d, $J$ = 7.6 Hz, 1H), 6.74-6.78 (m, 1H), 6.92-6.96 (m, 1H), 7.12-7.15 (m, 2H), 7.24 (d, $J$ = 7.2 Hz, 1H), 10.12 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 62.1, 109.3, 121.3, 124.2, 124.7, 126.1, 126.7, 128.6, 132.1, 137.5, 142.1, 180.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{13}H_{13}N_2OS$ $[M+H]^+$: 245.0743; Found: 245.0746.



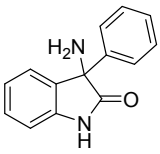
**2m**: Light yellow solid, m.p. 168.5-170.0 °C; yield 77%; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 2.25 (br s, 2H), 2.87-2.95 (m, 2H), 3.45 (s, 3H), 6.85 (d, $J$ = 7.6 Hz, 1H), 6.95-6.99 (m, 1H), 7.20-7.24 (m, 1H), 7.33 (d, $J$ = 7.2 Hz, 1H), 10.32 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 42.7, 51.6, 58.8, 109.8, 121.7, 124.1, 129.0, 132.9, 142.7, 170.2, 180.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{11}H_{13}N_2O_3$ $[M+H]^+$: 221.0921; Found: 221.0917.



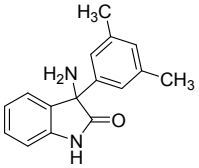
**2n**: Light yellow solid, m.p. 196.5-198.0 °C; yield 86%; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 1.12 (s, 9H), 2.20 (br s, 2H), 2.72 (d, $J$ = 14.4 Hz, 1H), 2.86 (d, $J$ = 14.8 Hz, 1H), 6.86 (d, $J$ = 7.6 Hz, 1H), 6.96-7.00 (m, 1H), 7.21-7.25 (m, 1H), 7.32 (d, $J$ = 7.2 Hz, 1H), 10.31 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 27.6, 44.8, 59.1, 80.3, 109.8, 121.6, 124.2, 128.9, 132.7, 142.9, 168.6, 180.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{14}H_{19}N_2O_3$ $[M+H]^+$: 263.1390; Found: 263.1397.



**2o**: Light yellow solid, m.p. 180.5-181.0 °C; yield 88%; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 1.08 (s, 9H), 2.11 (br s, 2H), 2.24 (s, 3H), 2.63 (d, $J$ = 14.4 Hz, 1H), 2.77 (d, $J$ = 14.4 Hz, 1H), 6.68 (d, $J$ = 7.6 Hz, 1H), 6.97-6.99 (m, 1H), 7.10 (s, 1H), 10.14 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 21.2, 27.6, 44.8, 59.2, 80.2, 109.5, 124.9, 129.0, 130.3, 132.8, 140.4, 168.7, 180.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{21}N_2O_3$ $[M+H]^+$: 277.1547; Found: 277.1541.

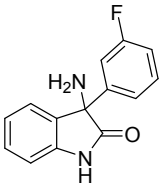


**2p**: Light yellow solid, m.p. 198.3-199.9 °C; yield 84%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 2.65 (br s, 2H), 6.92-6.96 (m, 2H), 7.12 (d, $J$ = 7.8 Hz, 1H), 7.20-7.25 (m, 2H), 7.29-7.31 (m, 2H), 7.37 (d, $J$ = 7.8 Hz, 2H), 10.47 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 64.6, 110.2, 122.3, 125.0, 126.1, 127.6, 128.6, 129.0, 135.6, 142.1, 143.2, 181.3; HRMS (ESI-TOF) m/z: Calcd. for $C_{14}H_{13}N_2O$ $[M+H]^+$: 225.1022; Found: 225.1026.

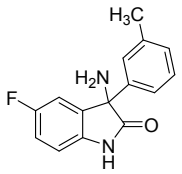


**2q**: White solid, m.p. 239.6-243.7 °C; yield 82%; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 2.21 (s,

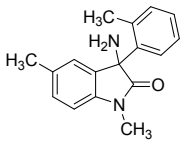
6H), 2.54 (br s, 2H), 6.86-6.94 (m, 5H), 7.09 (d, $J$ = 7.2 Hz, 1H), 7.18-7.21 (m, 1H), 10.40 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 21.5, 64.4, 110.2, 122.3, 123.8, 124.9, 128.9, 129.0, 135.8, 137.5, 142.1, 143.0, 181.4; HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{17}N_2O$ $[M+H]^+$: 253.1335; Found: 253.1337.




**2r**: White solid, m.p. 214.6-219.7 °C; yield 80%; $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$: 2.72 (br s, 2H), 6.93-6.97 (m, 2H), 7.01 (d, $J$ = 7.8 Hz, 1H), 7.06-7.09 (m, 1H), 7.14 (d, $J$ = 7.8 Hz, 1H), 7.22-7.24 (m, 1H), 7.30-7.33 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$: 64.4, 110.4, 113.2 (d, $J_{CF}$ = 22.5 Hz), 114.4 (d, $J_{CF}$ = 21.0 Hz), 122.2, 122.5, 125.0, 129.2, 135.1, 142.1, 146.2, 146.3, 162.6 (d, $J_{CF}$ = 241.5 Hz), 180.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{14}H_{12}FN_2O$ $[M+H]^+$: 243.0928; Found: 243.0921.

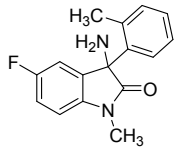



**2s**: White solid, m.p. 63.9-67.6 °C; yield 80%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 2.27 (s, 3H), 2.67 (br s, 2H), 6.89-6.91 (m, 1H), 6.96-6.98 (m, 1H), 7.03-7.12 (m, 3H), 7.18-7.20 (m, 2H), 10.46 (br s, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 21.6, 65.0, 111.0, 112.5 (d, $J_{CF}$ = 24.3 Hz), 115.1 (d, $J_{CF}$ = 23.1 Hz), 123.2, 126.6, 128.4, 128.6, 137.5, 137.6, 137.8, 138.2, 142.6, 158.6 (d, $J_{CF}$ = 235.5 Hz), 181.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{15}H_{14}FN_2O$ $[M+H]^+$: 257.1085; Found: 257.1089.

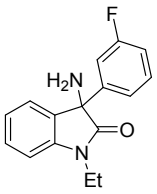



**2t**: White solid, m.p. 72.2-73.9 °C; yield 72%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 1.60 (s, 3H), 2.18 (s, 3H), 3.20 (s, 3H), 6.66 (s, 1H), 6.98-7.02 (m, 2H), 7.13 (d, $J$ = 7.0 Hz, 1H), 7.18-7.20 (m,

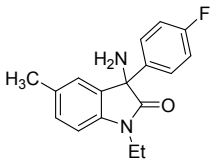
1H), 7.29-7.32 (m, 1H), 8.14 (d, $J$ = 6.5 Hz, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 19.1, 21.0, 26.6, 63.5, 108.8, 124.8, 126.1, 127.4, 127.9, 129.4, 131.5, 132.0, 133.0, 135.2, 140.3, 141.9, 179.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{17}H_{19}N_2O$ $[M+H]^+$: 267.1492; Found: 267.1497.




**2u**: White solid, m.p. 86.5-89.3 °C; yield 71%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 1.60 (s, 3H), 2.68 (br s, 2H), 3.22 (s, 3H), 6.66-6.81 (m, 1H), 7.03 (d, $J$ = 7.2 Hz, 1H), 7.10-7.12 (m, 1H), 7.15-7.23 (m, 2H), 7.30-7.33 (m, 1H), 8.06-8.11 (m, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 19.1, 26.7, 63.7, 109.9 (d, $J_{CF}$ = 3.1 Hz), 111.9 (d, $J_{CF}$ = 24.2 Hz), 112.0, 115.3 (d, $J_{CF}$ = 24.3 Hz), 126.2, 127.5, 128.2, 131.5, 134.8, 134.9, 135.2, 139.6, 140.4, 159.1 (d, $J_{CF}$ = 237.3 Hz), 178.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{16}FN_2O$ $[M+H]^+$: 271.1241; Found: 271.1242.

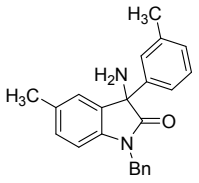



**2v**: White solid, m.p. 56.0-60.1 °C; yield 78%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 1.20-1.22 (m, 3H), 2.76 (br s, 2H), 3.71-3.80 (m, 2H), 6.99 (d, $J$ = 7.8 Hz, 1H), 7.01-7.04 (m, 1H), 7.06-7.10 (m, 1H), 7.13 (d, $J$ = 7.8 Hz, 1H), 7.20 (d, $J$ = 7.8 Hz, 1H), 7.30-7.34 (m, 3H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 13.0, 34.7, 64.0, 109.4, 113.2 (d, $J_{CF}$ = 22.5 Hz), 114.4, 114.6, 122.1, 123.0, 124.8, 129.3, 134.6, 142.5, 146.1, 146.2, 162.7 (d, $J_{CF}$ = 241.5 Hz), 178.6; HRMS (ESI-TOF) m/z: Calcd. for $C_{16}H_{16}FN_2O$ $[M+H]^+$: 271.1241; Found: 271.1247.

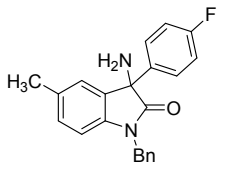



**2w**: Light yellow solid, m.p. 159.7-60.9 °C; yield 77%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 1.22-1.24 (m, 3H), 2.27 (s, 3H), 2.70 (br s, 2H), 3.72-3.81 (m, 2H), 7.04-7.06 (m, 2H), 7.15-7.18 (m, 3H), 7.39-7.41 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 13.0, 21.1, 34.7, 63.8, 109.1, 115.4 (d, $J_{CF}$ = 21.2 Hz), 125.3, 128.1, 128.2, 129.4, 131.9, 135.0, 139.3, 140.0, 161.8 (d, $J_{CF}$ = 241.5 Hz),

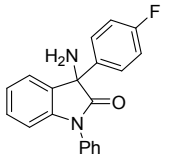
178.9; HRMS (ESI-TOF) m/z: Calcd. for $C_{17}H_{18}FN_2O$ $[M+H]^+$: 285.1398; Found: 285.1403.



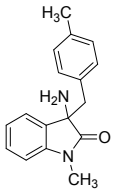

**2x**: White solid, m.p. 46.7-48.2 °C; yield 76%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 2.18 (s, 3H), 2.23 (s, 3H), 2.69 (br, 2H), 4.88 (d, $J$ = 13.0 Hz, 1H), 4.96 (d, $J$ = 13.0 Hz, 1H), 6.85 (d, $J$ = 7.0 Hz, 1H), 6.98-7.01 (m, 2H), 7.05 (d, $J$ = 5.5 Hz, 1H), 7.14-7.20 (m, 3H), 7.26-7.29 (m, 1H), 7.33-7.38 (m, 4H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 21.1, 21.6, 43.2, 64.4, 109.6, 123.2, 125.3, 126.6, 127.8, 127.9, 128.3, 128.6, 129.1, 132.1, 135.1, 137.0, 137.7, 140.1, 143.1, 179.8; HRMS (ESI-TOF) m/z: Calcd. for $C_{23}H_{23}N_2O$ $[M+H]^+$: 343.1805; Found: 343.1805.




**2y**: White solid, m.p. 135.5-137.8 °C; yield 77%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 2.20 (s, 3H), 4.89-4.95 (m, 2H), 6.84 (d, $J$ = 8.4 Hz, 1H), 7.03 (s, 2H), 7.13-7.16 (m, 2H), 7.26-7.29 (m, 1H), 7.33-7.36 (m, 4H), 7.39-7.41 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 21.1, 43.3, 64.0, 109.7, 115.4 (d, $J_{CF}$ = 22.5 Hz), 125.4, 127.6, 127.9, 128.3, 128.4, 129.1, 129.3, 132.3, 134.8, 136.9, 139.2, 140.1, 161.9 (d, $J_{CF}$ = 241.2 Hz), 179.5; HRMS (ESI-TOF) m/z: Calcd. for $C_{22}H_{20}FN_2O$ $[M+H]^+$: 347.1554; Found: 347.1559.

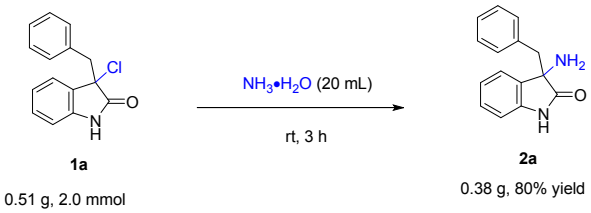



**2z**: White solid, m.p. 115.5-116.7 °C; yield 78%; $^1$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 2.91 (br s, 2H), 6.80 (d, $J$ = 8.4 Hz, 1H), 7.07-7.10 (m, 1H), 7.17-7.20 (m, 2H), 7.25-7.28 (m, 2H), 7.47-7.54 (m, 5H), 7.59-7.62 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 64.1, 109.7, 115.6 (d, $J_{CF}$ = 24.3 Hz), 123.7, 125.2, 127.3, 128.4, 128.6, 129.2, 130.1, 134.6, 134.8, 139.0, 143.3, 161.9 (d, $J_{CF}$ = 243.3 Hz), 179.1; HRMS (ESI-TOF) m/z: Calcd. for $C_{20}H_{16}FN_2O$ $[M+H]^+$: 319.1241; Found: 319.1235.



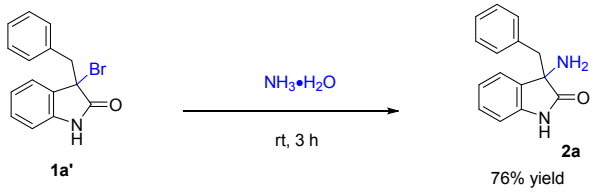
**2za**: White solid, m.p. 93.6-95.7 °C; yield 75%; $^{1}$H NMR (DMSO-$d_6$, 600 MHz) $\delta$: 2.14 (s, 3H), 2.87 (s, 3H), 2.93 (d, $J$ = 12.6 Hz, 1H), 3.00 (d, $J$ = 12.6 Hz, 1H), 6.67 (d, $J$ = 7.8 Hz, 2H), 6.74 (d, $J$ = 7.8 Hz, 1H), 6.83 (d, $J$ = 7.8 Hz, 2H), 6.99-7.02 (m, 1H), 7.16-7.19 (m, 1H), 7.29 (d, $J$ = 7.2 Hz, 1H); $^{13}$C NMR (DMSO-$d_6$, 150 MHz) $\delta$: 21.0, 26.1, 45.1, 62.8, 108.4, 122.3, 124.3, 128.4, 128.8, 130.0, 132.1, 132.9, 135.6, 143.6, 179.7; HRMS (ESI-TOF) m/z: Calcd. for $C_{17}H_{19}N_2O$ $[M+H]^+$: 267.1492; Found: 267.1487.

**4. Gram scale synthesis of the product 2a**



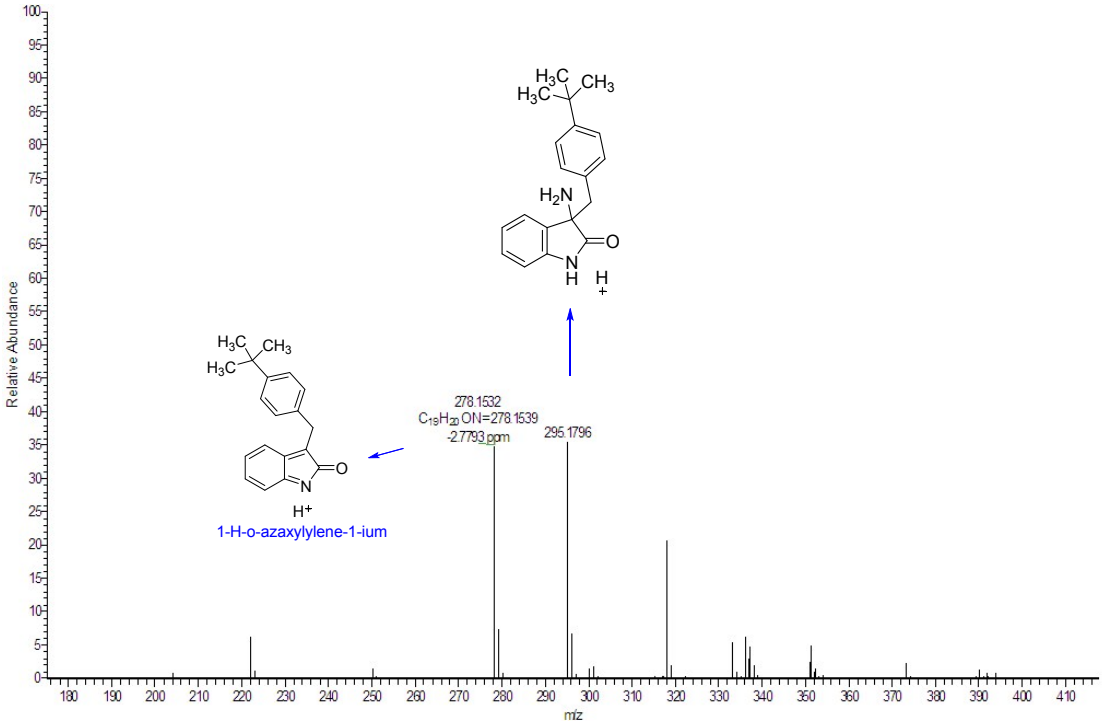

In a sealed tube equipped with a magnetic stirring bar, to 20 mL of $NH_3 \cdot H_2O$ (25%) was added **1a** (0.51 g, 2.0 mmol). The reaction mixture was stirred at rt for 3 h. After completion of the reaction, as indicated by TLC, purification by flash column chromatography (hexane/EtOAc, 6/1, v/v) was carried out to furnish the corresponding product **2a** (0.38 g, 80% yield).

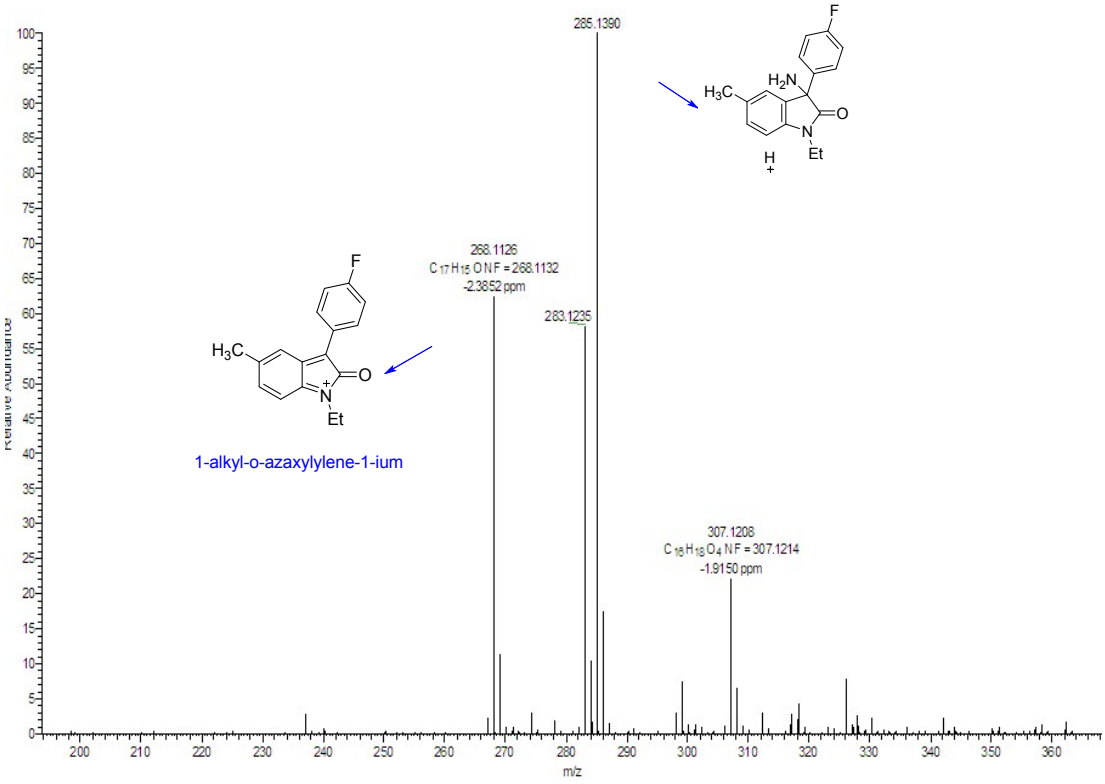
**5. Bromooxindole 1a′ as a test substrate.**



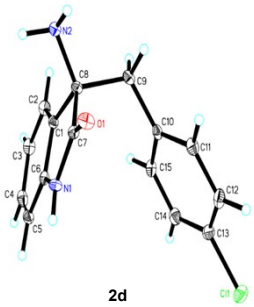

In a sealed tube equipped with a magnetic stirring bar, to 2.0 mL of $NH_3 \cdot H_2O$ (25%) was added **1a′** (0.20 mmol). The reaction mixture was stirred at rt for 3 h. After completion of the reaction, as indicated by TLC, purification by flash column chromatography (hexane/EtOAc, 6/1, v/v) was carried out to furnish the corresponding product **2a** in 76% yield.

**6. Figure S1: new species detected by ESI-MS analysis.**

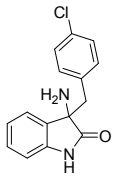



## 7. X-ray crystal data for compounds 2d and 2g




2d



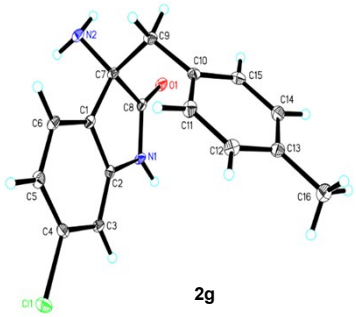

2d

**Table S1 Crystal data and structure refinement for 2d**

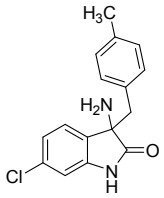
| | |
|---|---|
| Identification code | **2d** |
| Empirical formula | $C_{15}H_{13}ClN_2O$ |
| Formula weight | 272.72 |
| Temperature/K | 100.00(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å, b/Å, c/Å | 11.3479(5), 10.0774(5), 11.9461(6) |
| α/°, β/°, γ/° | 90, 98.694(4), 90. |
| Volume/Å$^3$ | 1350.43(11) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.341 |
| μ/mm$^{-1}$ | 0.276 |
| F(000) | 568.0 |
| Crystal size/mm$^3$ | 0.13 × 0.12 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.314 to 49.982 |
| Index ranges | $-11 \le h \le 13$, $-11 \le k \le 9$, $-13 \le l \le 14$ |
| Reflections collected | 6037 |
| Independent reflections | 2370 [$R_{int}$ = 0.0315, $R_{sigma}$ = 0.0405] |
| Data/restraints/parameters | 2370/0/180 |
| Goodness-of-fit on F$^2$ | 1.070 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0457, $wR_2$ = 0.1136 |
| Final R indexes [all data] | $R_1$ = 0.0561, $wR_2$ = 0.1220 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.90/-0.52 |

**Crystal structure determination of 2d**

**Crystal Data** for $C_{15}H_{13}ClN_2O$ ($M$ =272.72 g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a$ = 11.3479(5) Å, $b$ = 10.0774(5) Å, $c$ = 11.9461(6) Å, $\beta$ = 98.694(4)°, $V$ = 1350.43(11) Å$^3$, $Z$ = 4, $T$ = 100.00(10) K, μ(MoKα) = 0.276 mm$^{-1}$, *Dcalc* = 1.341 g/cm$^3$, 6037 reflections measured ($5.314° \le 2\Theta \le 49.982°$), 2370 unique ($R_{int}$ = 0.0315, $R_{sigma}$ = 0.0405) which were used in all calculations. The final $R_1$ was 0.0457 ($I > 2\sigma(I)$) and $wR_2$ was 0.1220 (all data).




2g




2g

**Table S2 Crystal data and structure refinement for 2g**

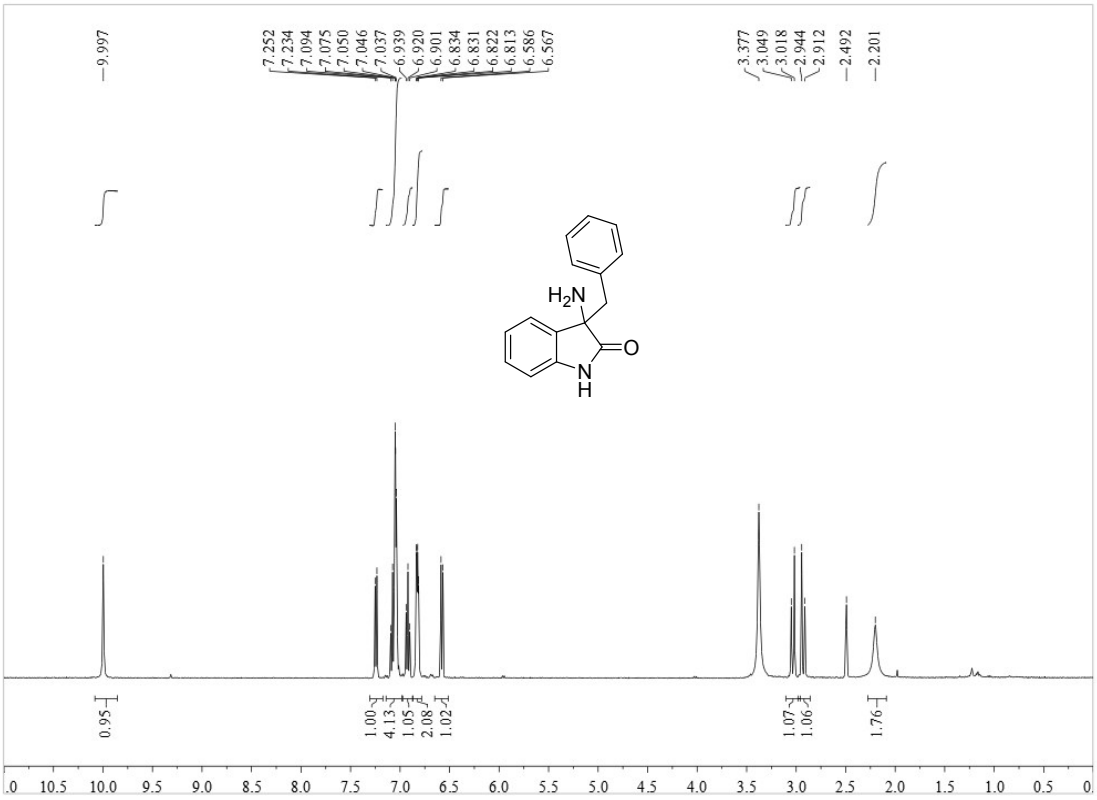
| | |
|---|---|
| Identification code | **2g** |
| Empirical formula | $C_{16}H_{15}ClN_2O$ |
| Formula weight | 286.75 |
| Temperature/K | 100.00(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å, b/Å, c/Å | 12.8233(13), 10.2114(7), 12.0326(13) |
| α/°, β/°, γ/° | 90, 116.906(13), 90. |
| Volume/Å$^3$ | 1405.0(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.356 |
| μ/mm$^{-1}$ | 0.268 |
| F(000) | 600.0 |
| Crystal size/mm$^3$ | 0.14 × 0.12 × 0.11 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.348 to 49.992 |
| Index ranges | -13 ≤ h ≤ 15, -12 ≤ k ≤ 11, -14 ≤ l ≤ 10 |
| Reflections collected | 5918 |
| Independent reflections | 2474 [$R_{int}$ = 0.0324, $R_{sigma}$ = 0.0468] |
| Data/restraints/parameters | 2474/0/190 |
| Goodness-of-fit on F$^2$ | 1.022 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0437, w$R_2$ = 0.0944 |
| Final R indexes [all data] | $R_1$ = 0.0562, w$R_2$ = 0.1027 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.27/-0.32 |

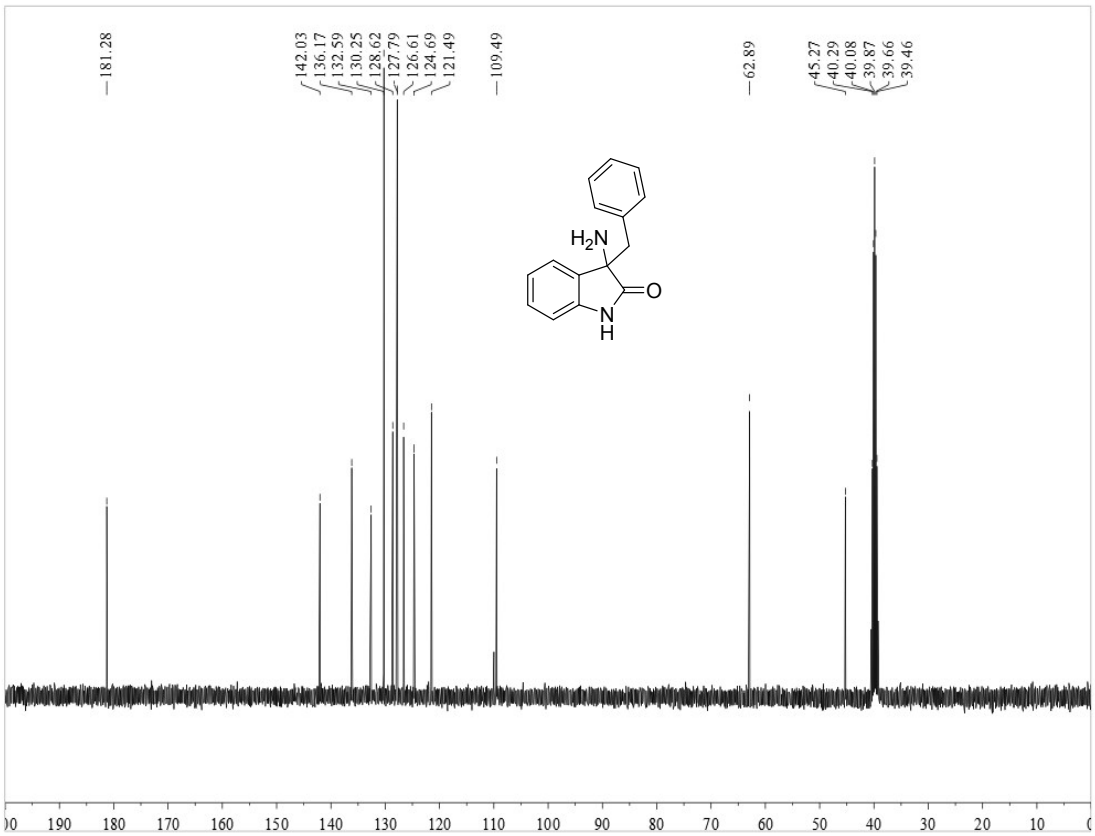
**Crystal structure determination of 2g**

**Crystal Data** for $C_{16}H_{15}ClN_2O$ ($M$ =286.75 g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a$ = 12.8233(13) Å, $b$ = 10.2114(7) Å, $c$ = 12.0326(13) Å, $\beta$ = 116.906(13)°, $V$ = 1405.0(3) Å$^3$, $Z$ = 4, $T$ = 100.00(10) K, μ(MoKα) = 0.268 mm$^{-1}$, $Dcalc$ = 1.356 g/cm$^3$, 5918 reflections measured (5.348° ≤ 2Θ ≤ 49.992°), 2474 unique ($R_{int}$ = 0.0324, $R_{sigma}$ = 0.0468) which were used in all calculations. The final $R_1$ was 0.0437 (I > 2σ(I)) and $wR_2$ was 0.1027 (all data).

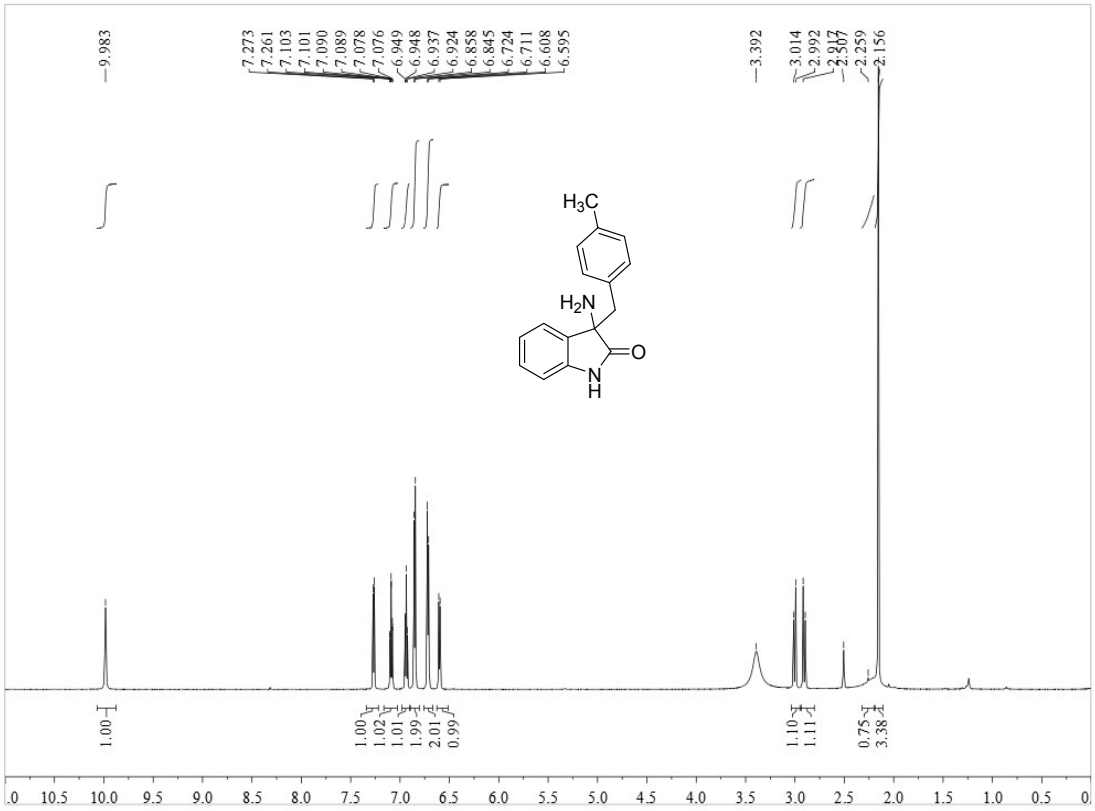
**8. The copies of 1H NMR and 13C NMR spectra for compounds 2**

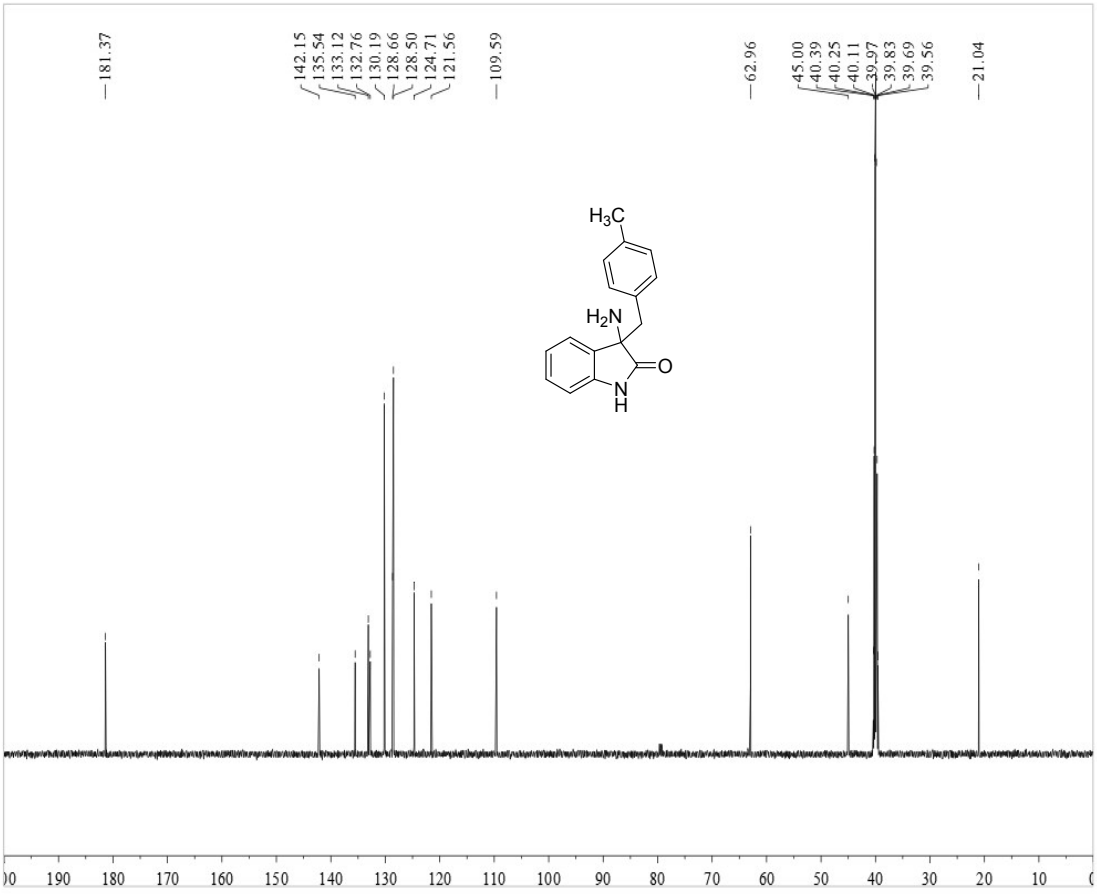
**$^{1}$H and $^{13}$C NMR of 2a**



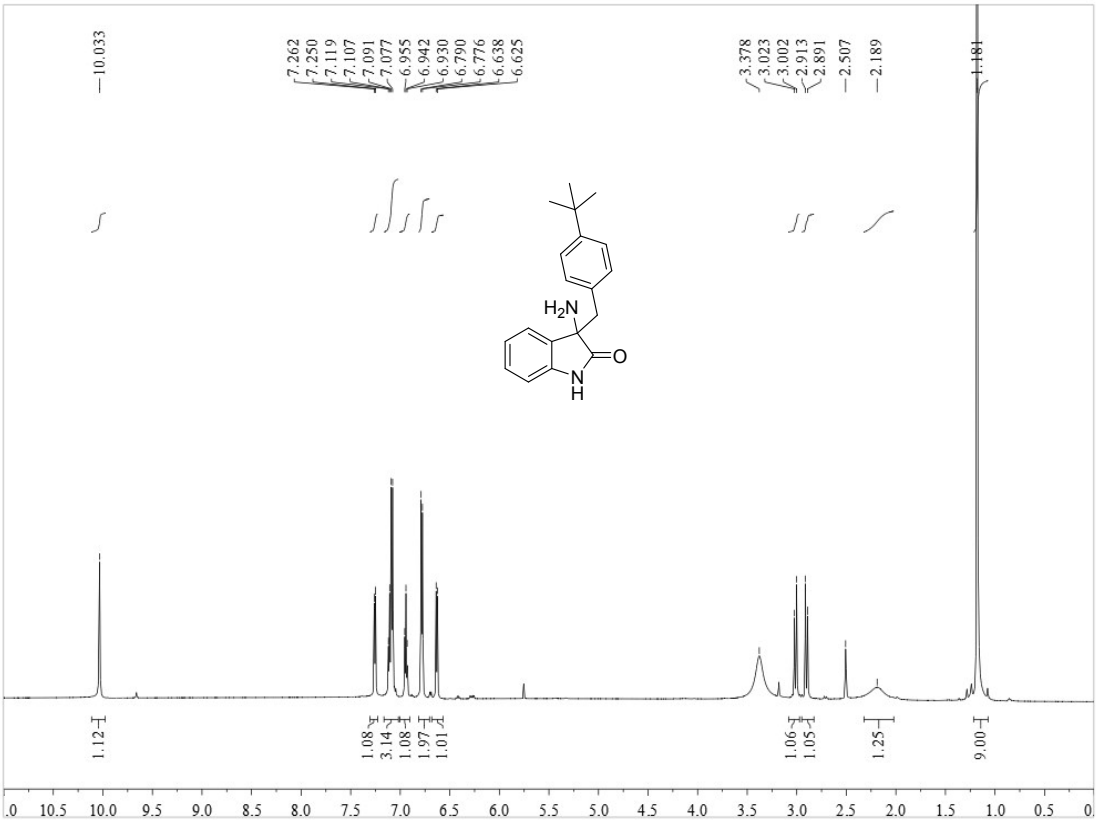



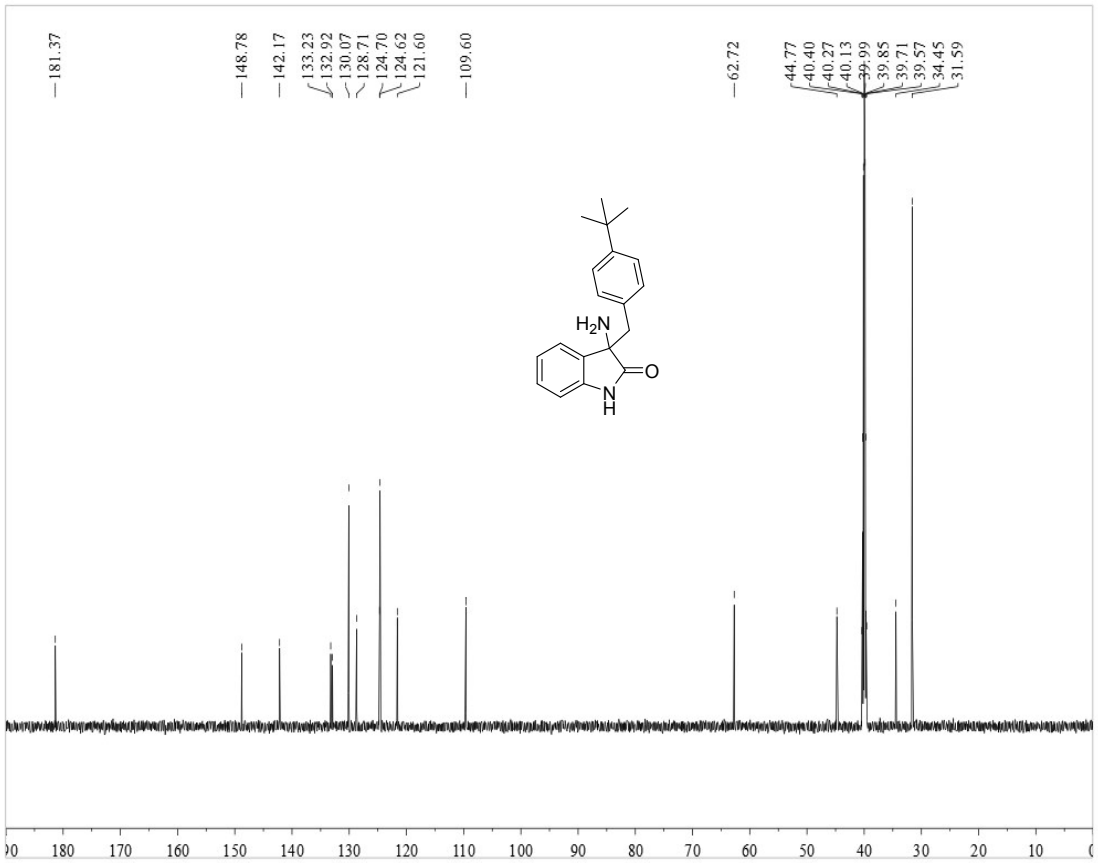
**$^{1}$H and $^{13}$C NMR of 2b**



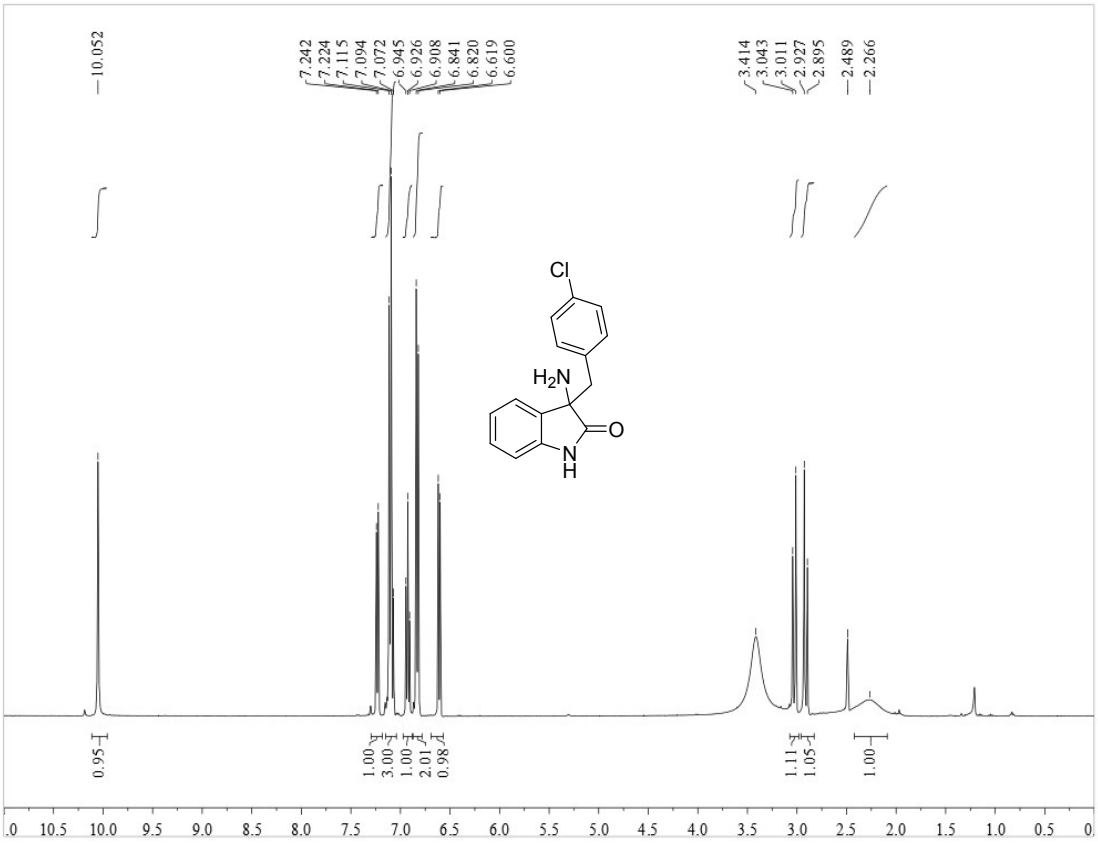



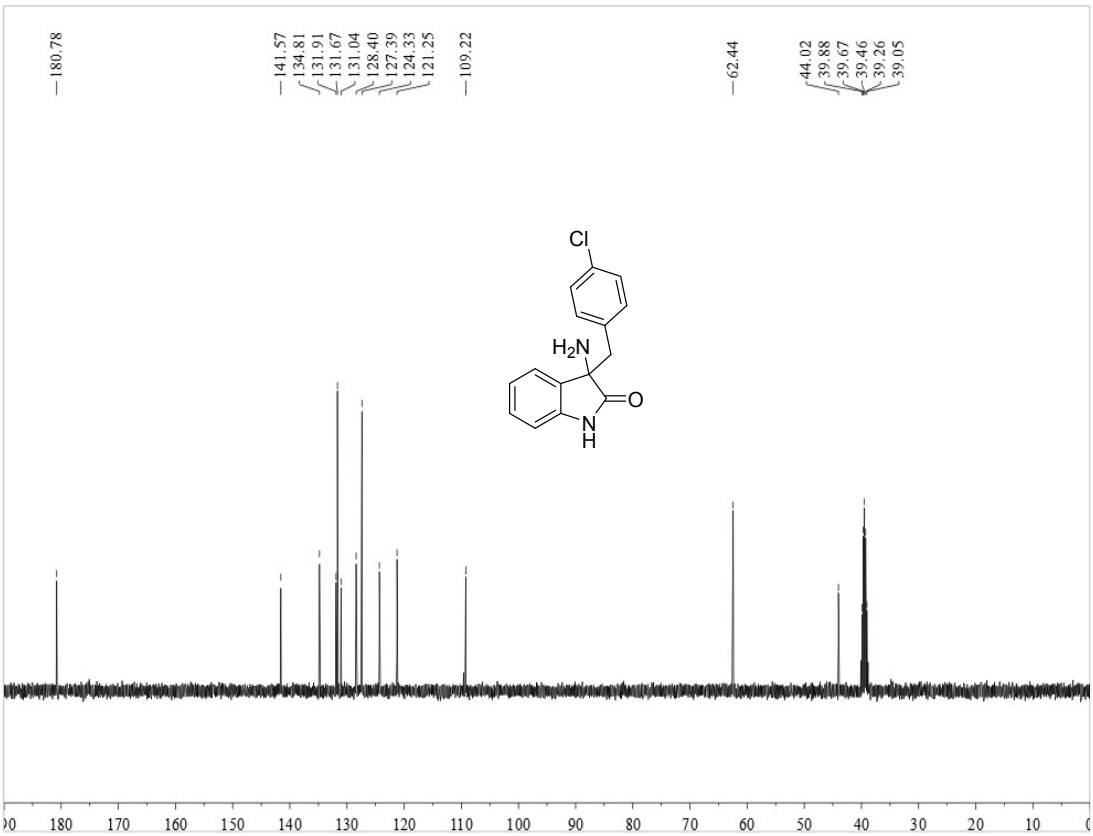
**$^{1}$H and $^{13}$C NMR of 2c**



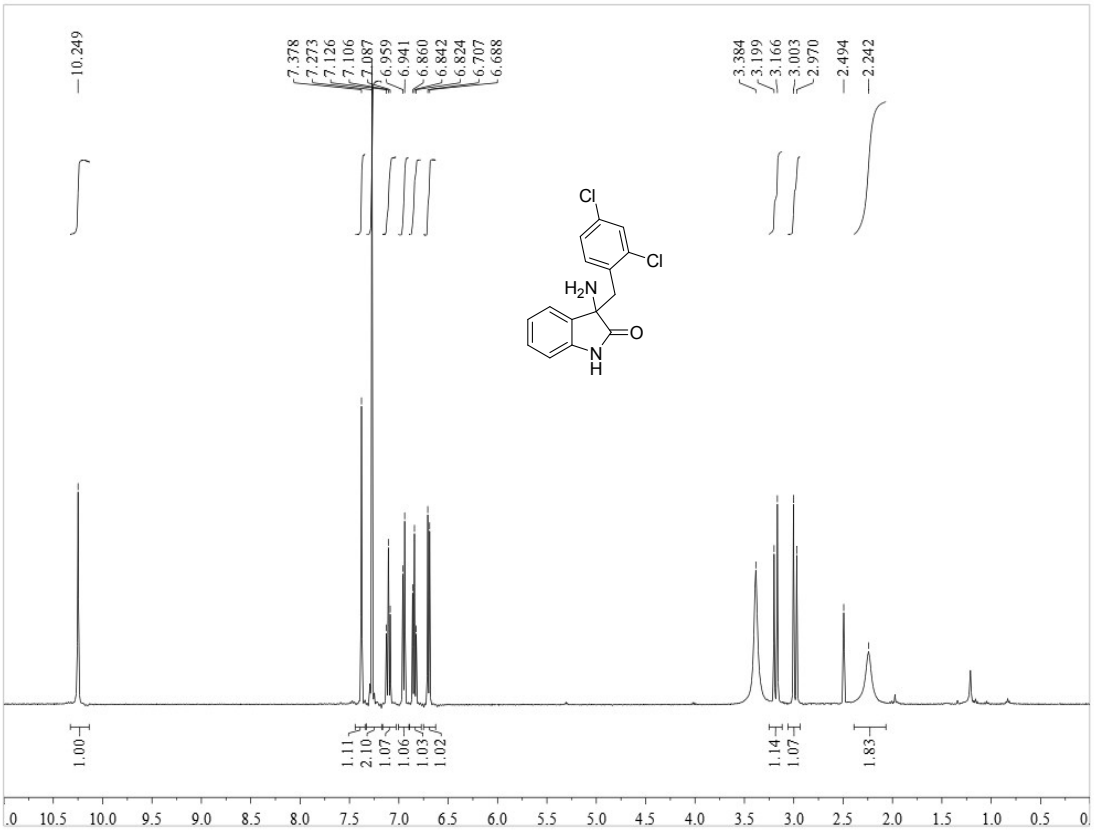



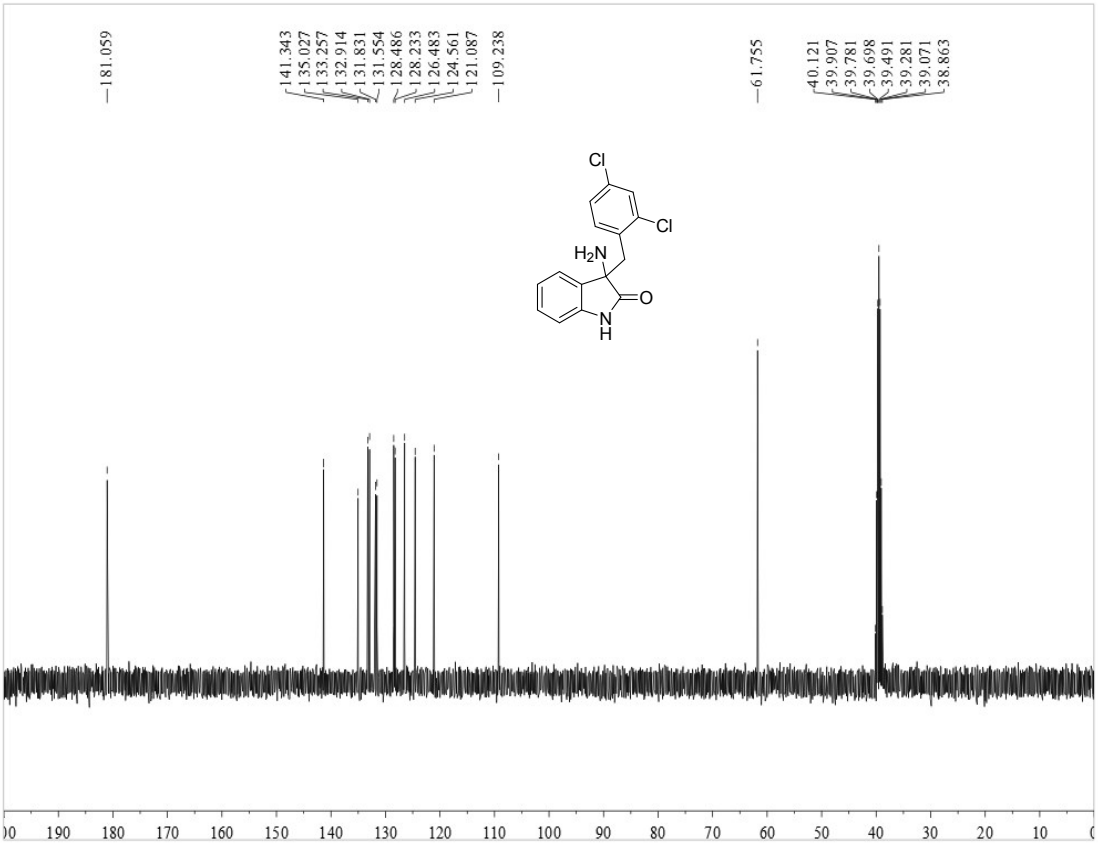
**$^{1}$H and $^{13}$C NMR of 2d**



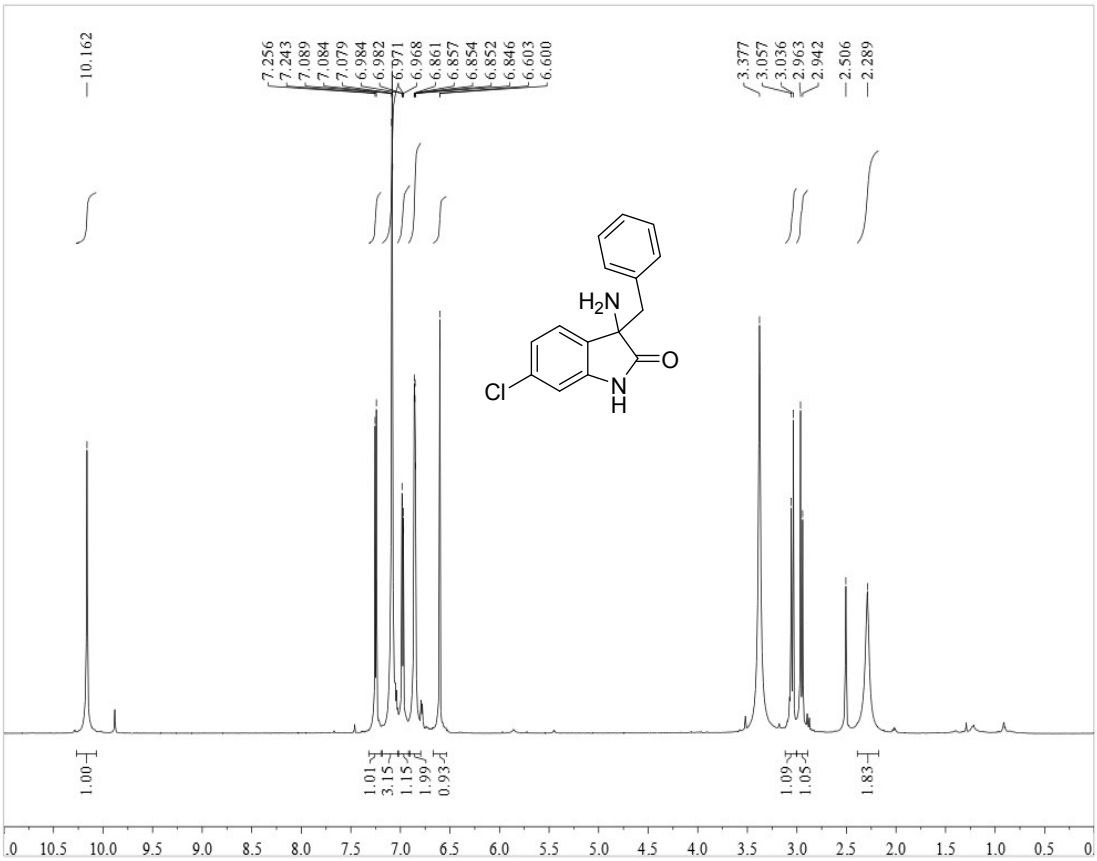



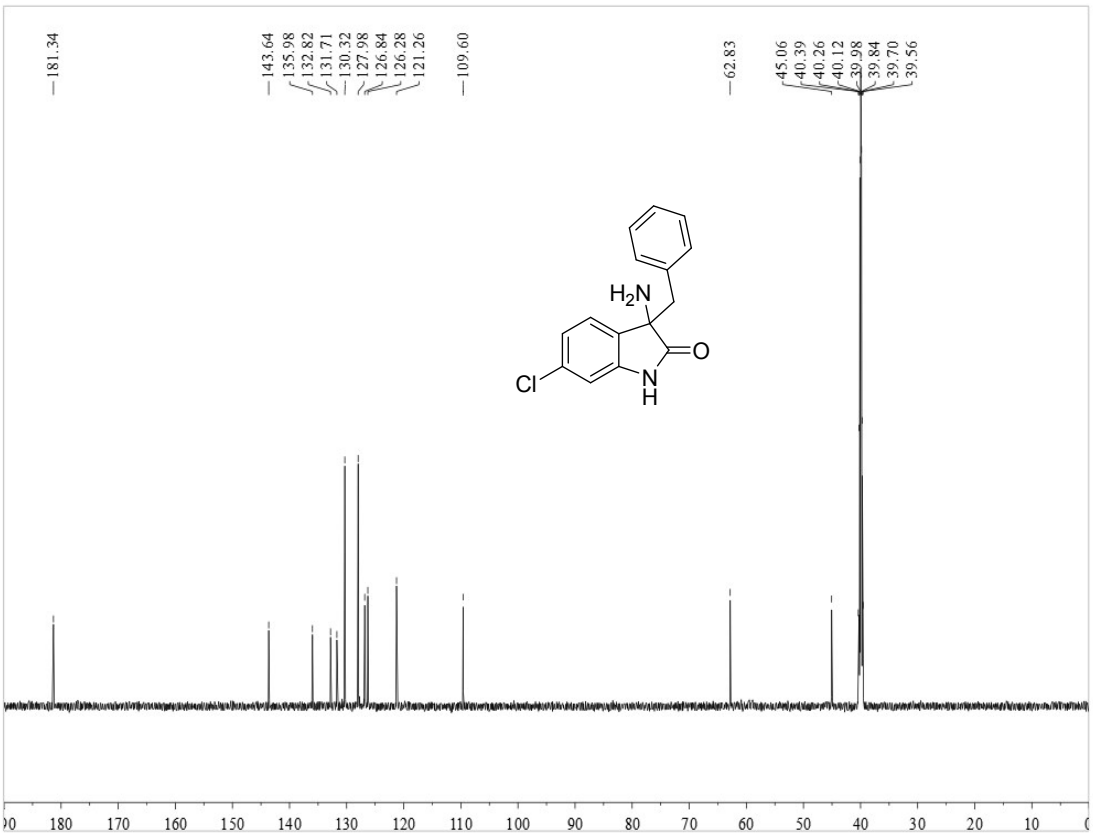
**$^{1}$H and $^{13}$C NMR of 2e**



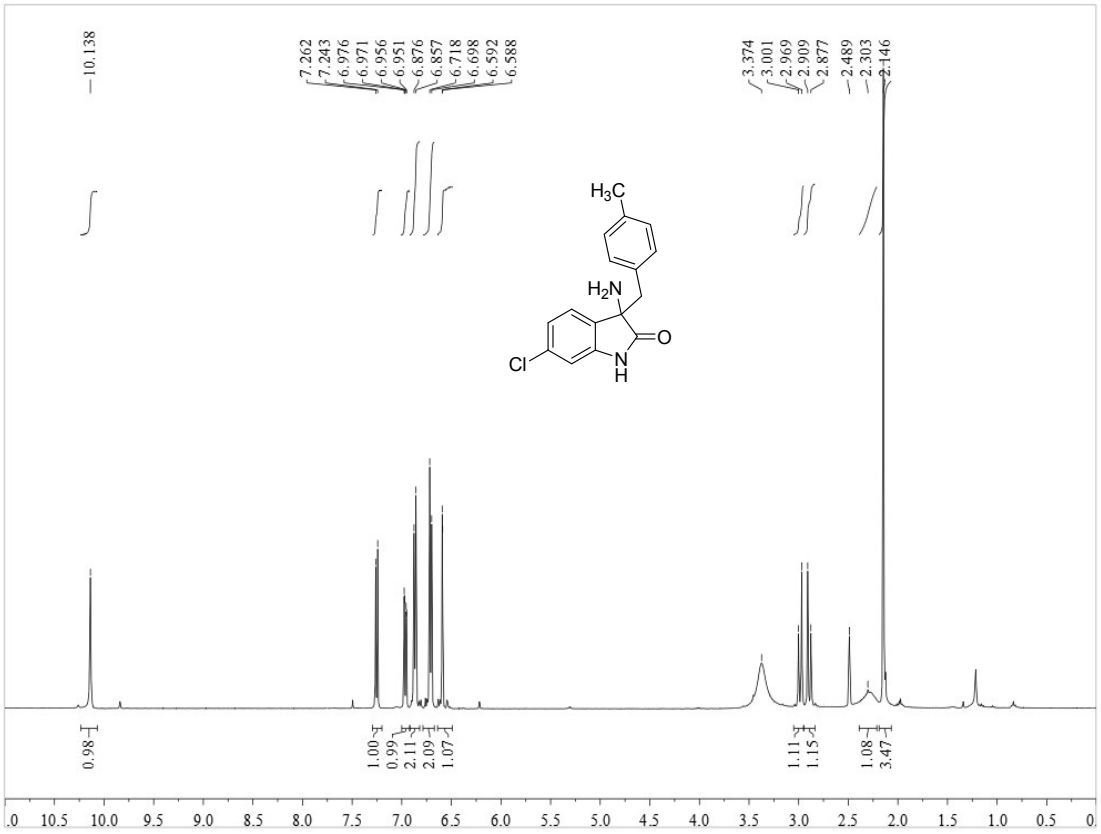



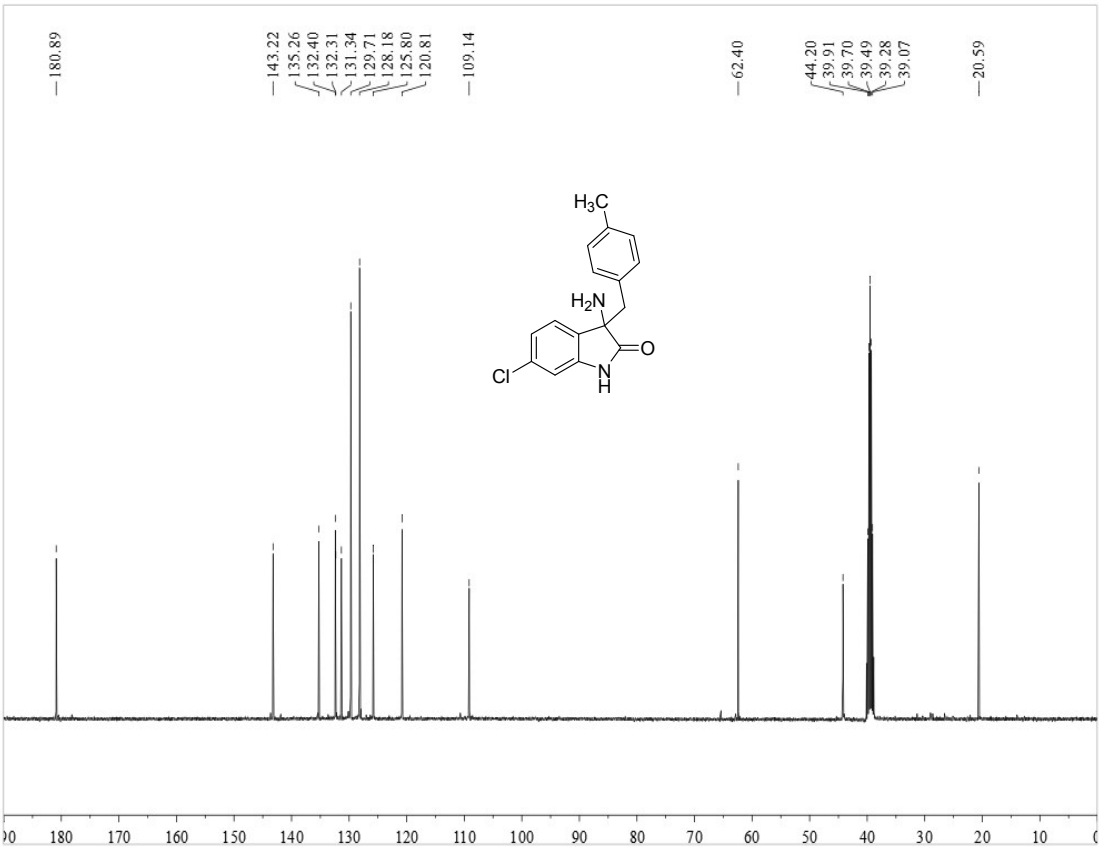
**$^{1}$H and $^{13}$C NMR of 2f**



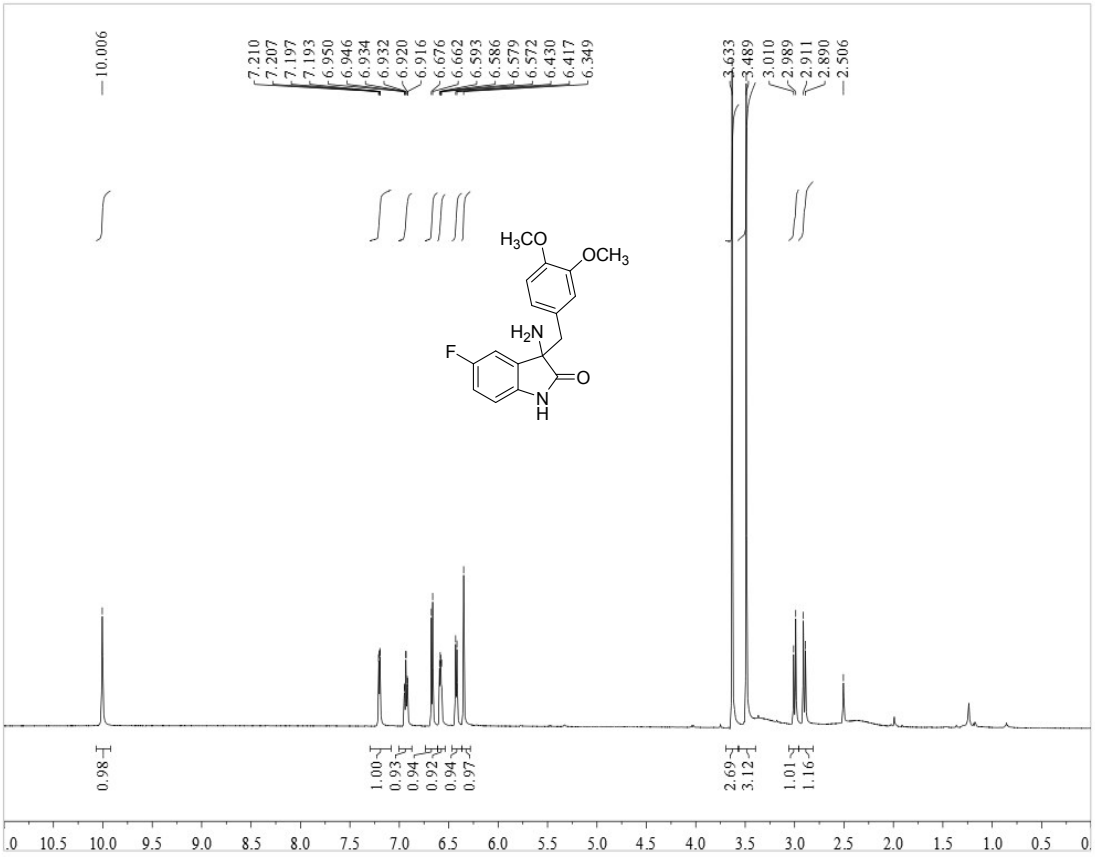



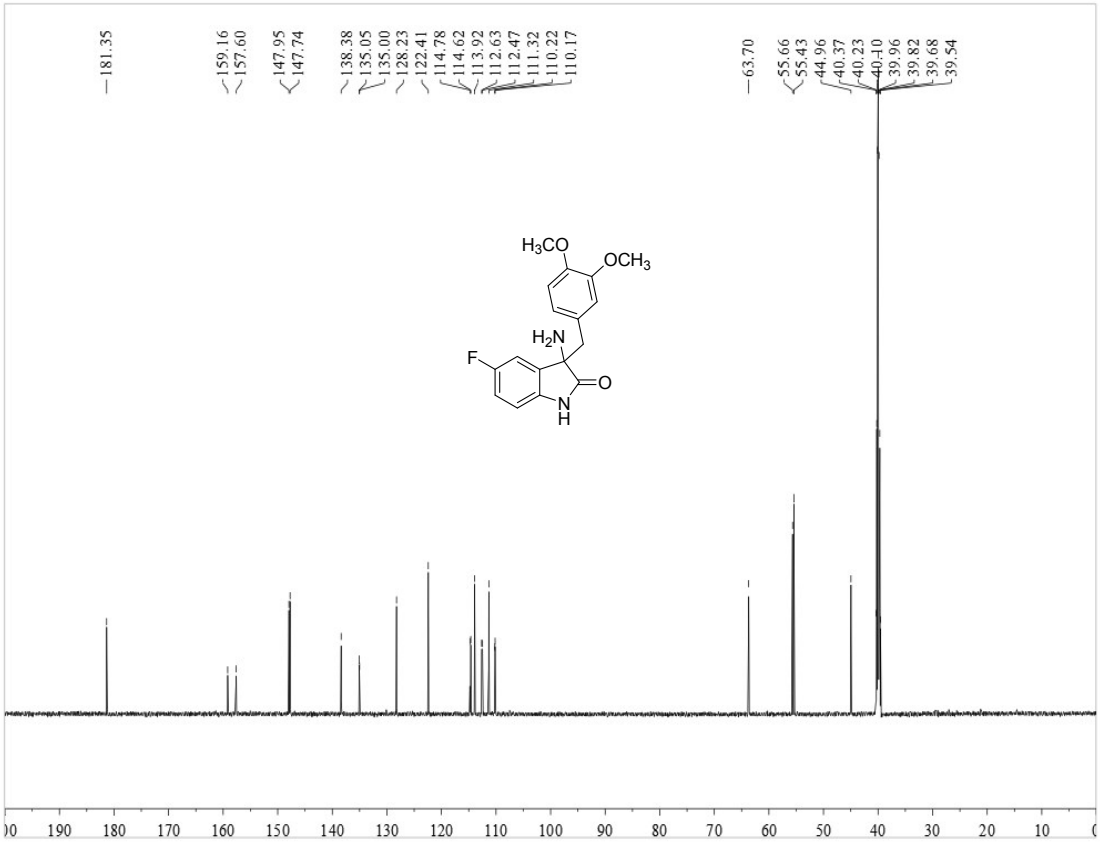
**$^{1}$H and $^{13}$C NMR of 2g**



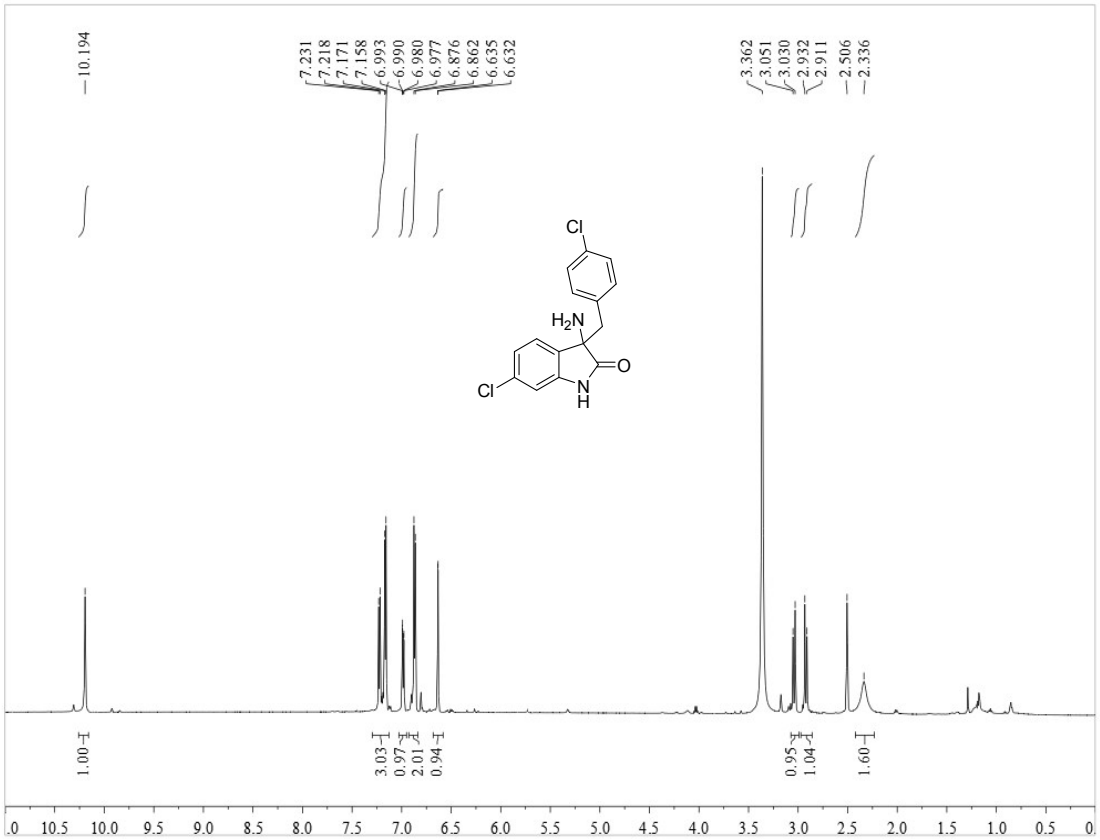



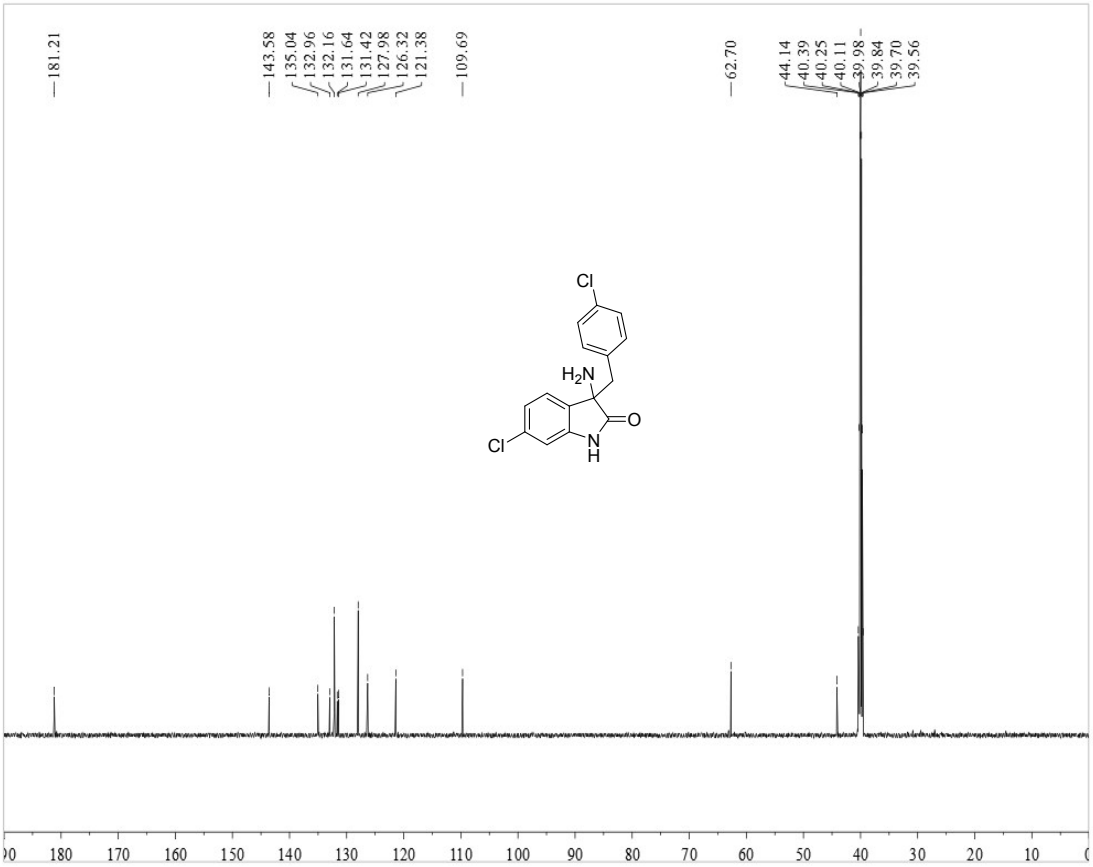
**$^{1}$H and $^{13}$C NMR of 2h**



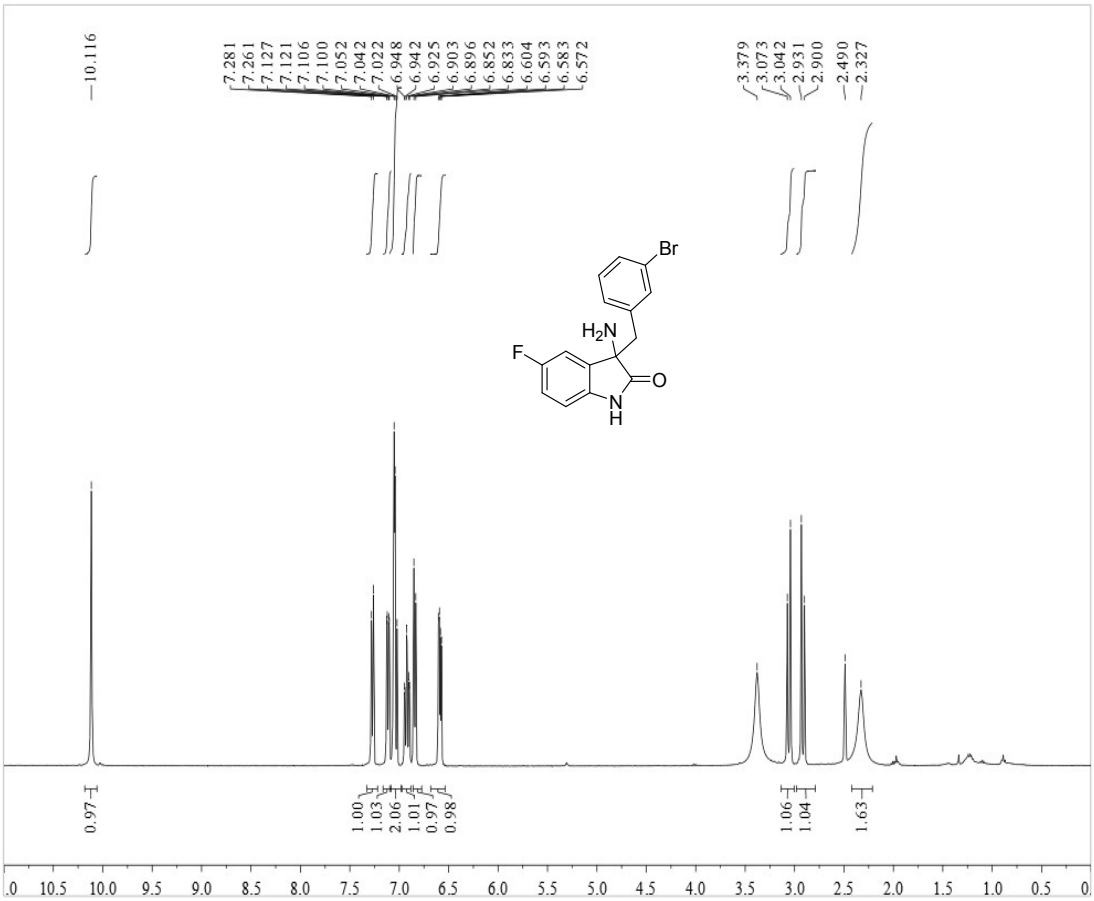



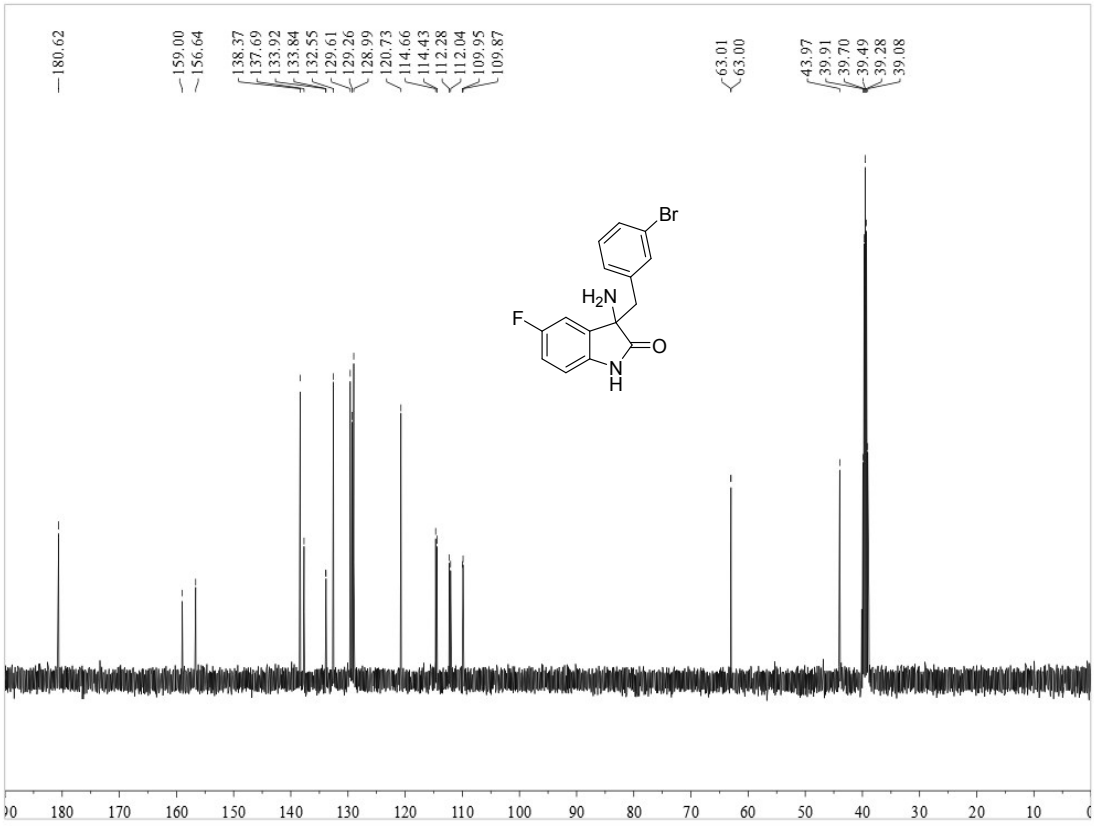
**$^{1}$H and $^{13}$C NMR of 2i**



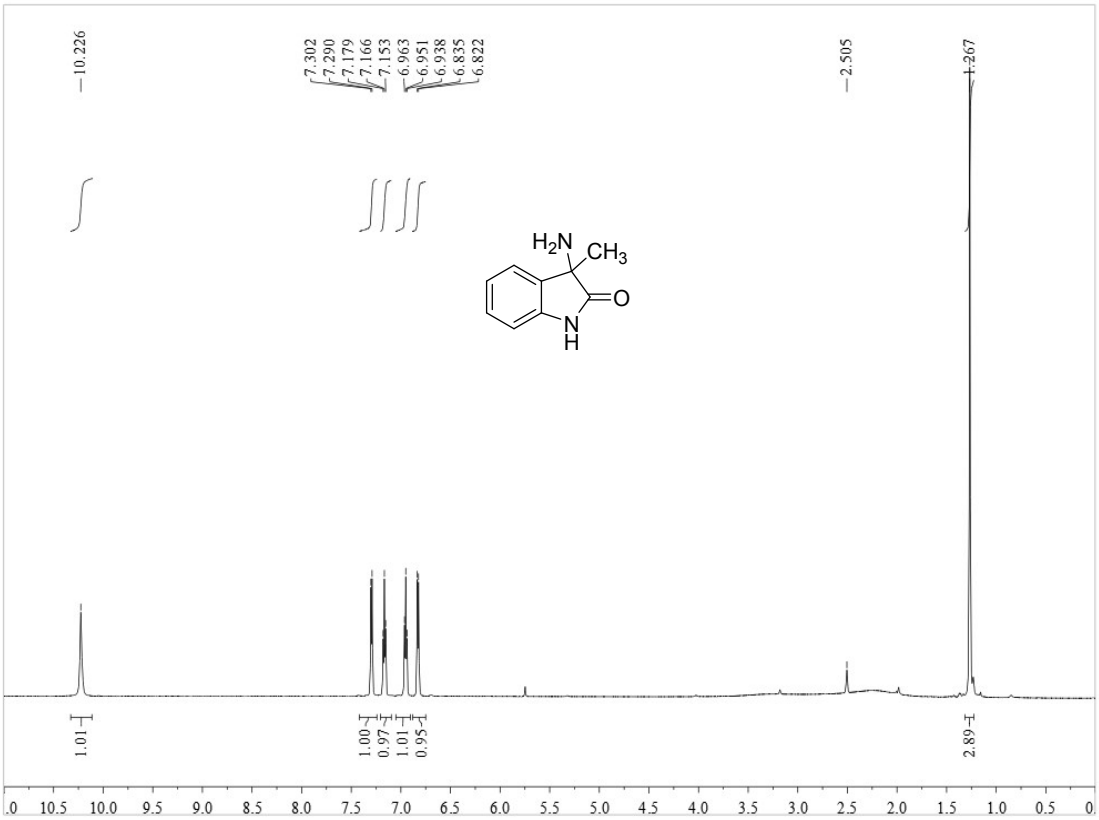



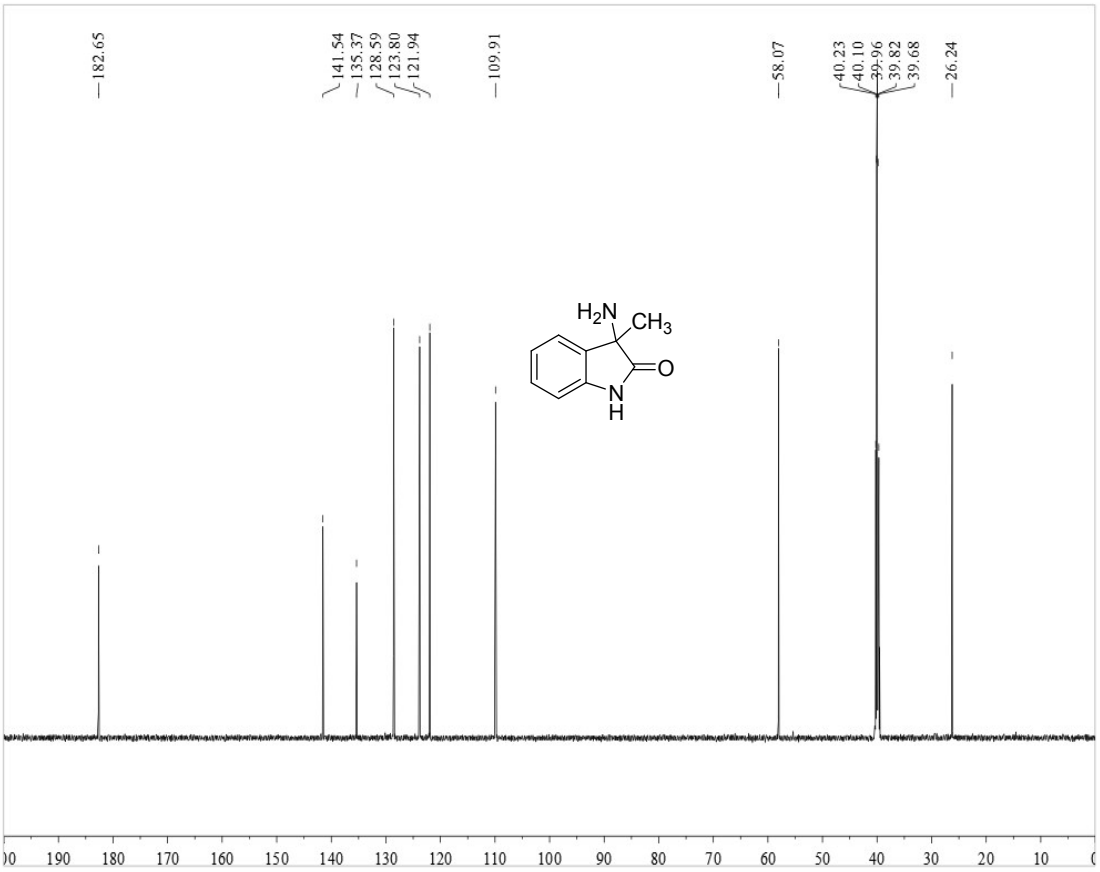
**$^{1}$H and $^{13}$C NMR of 2j**



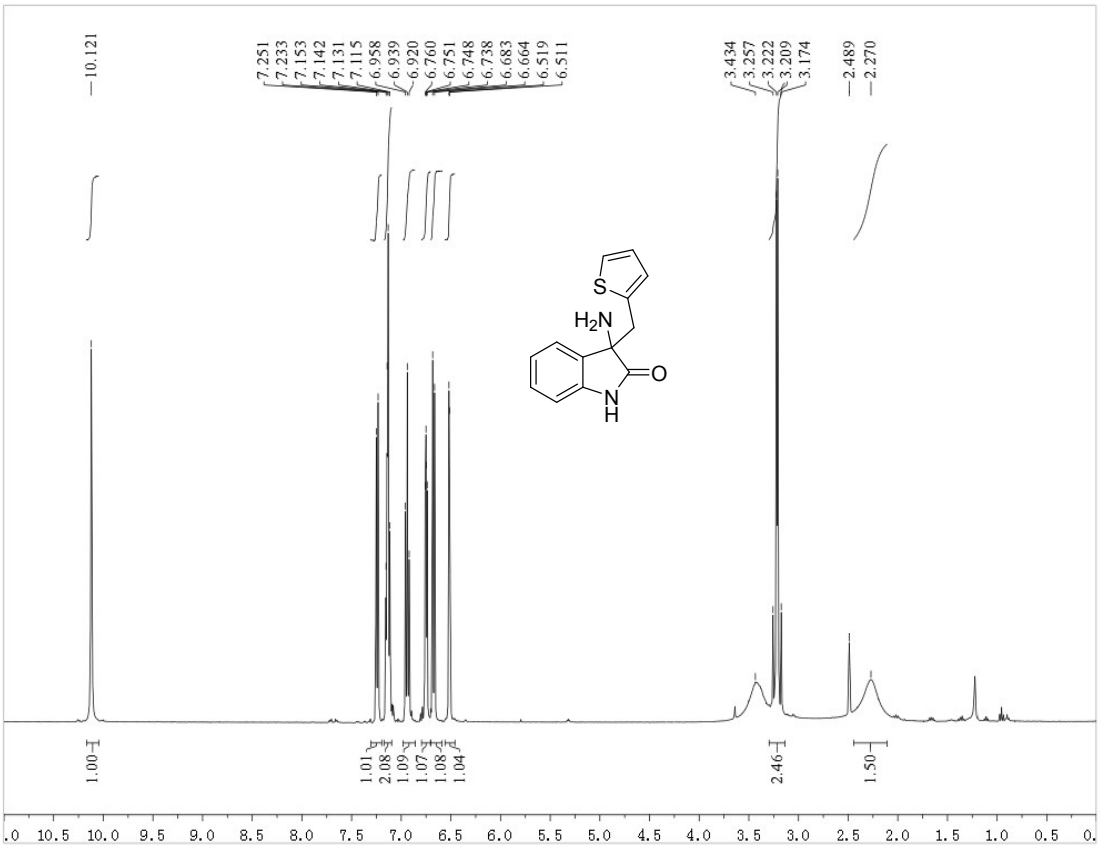



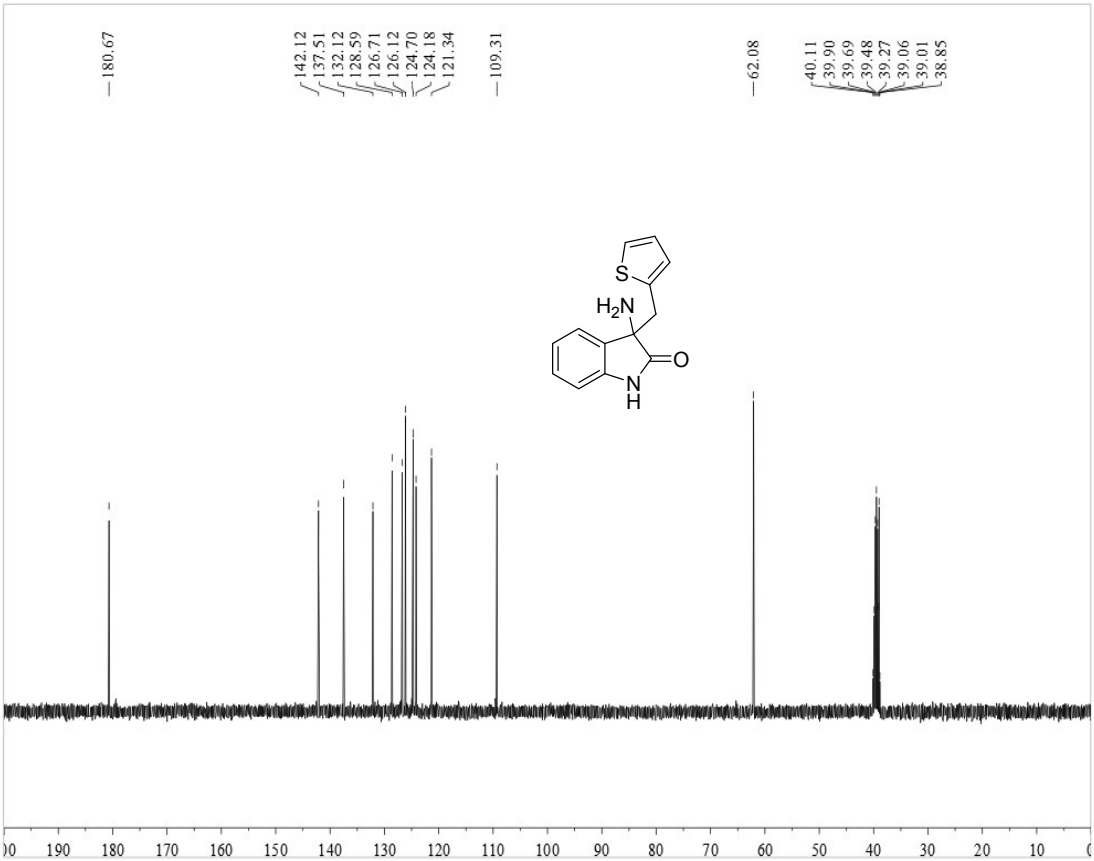
**$^{1}$H and $^{13}$C NMR of 2k**



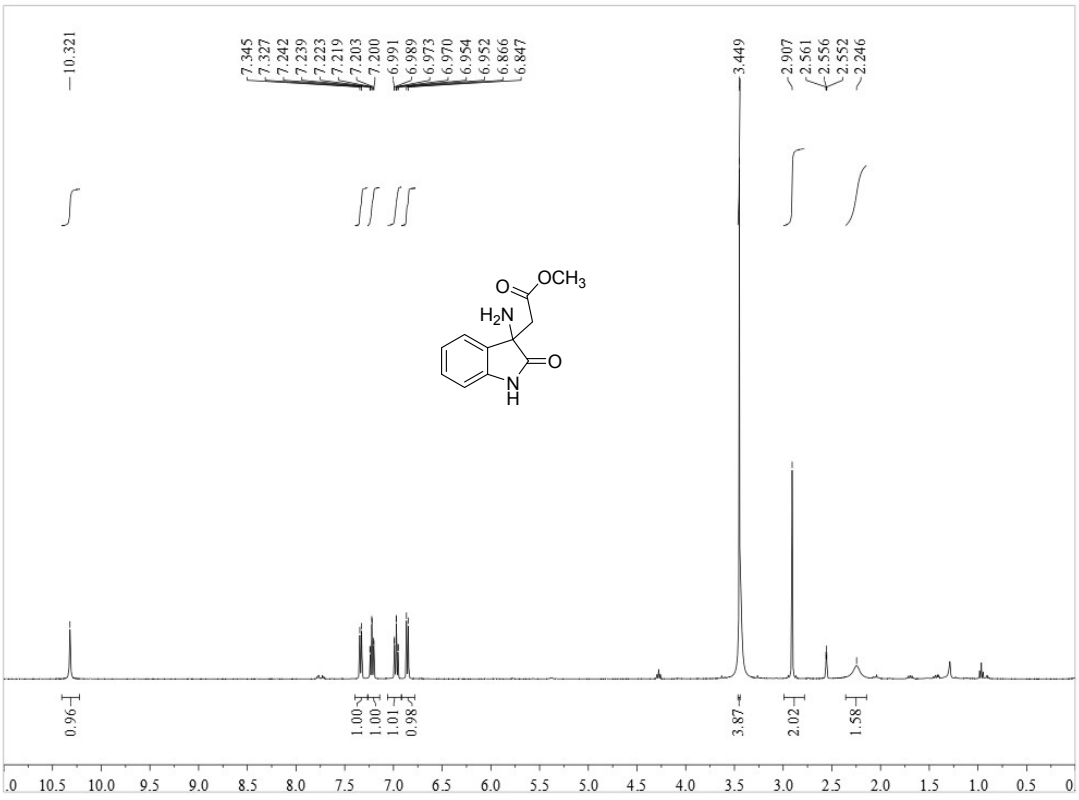



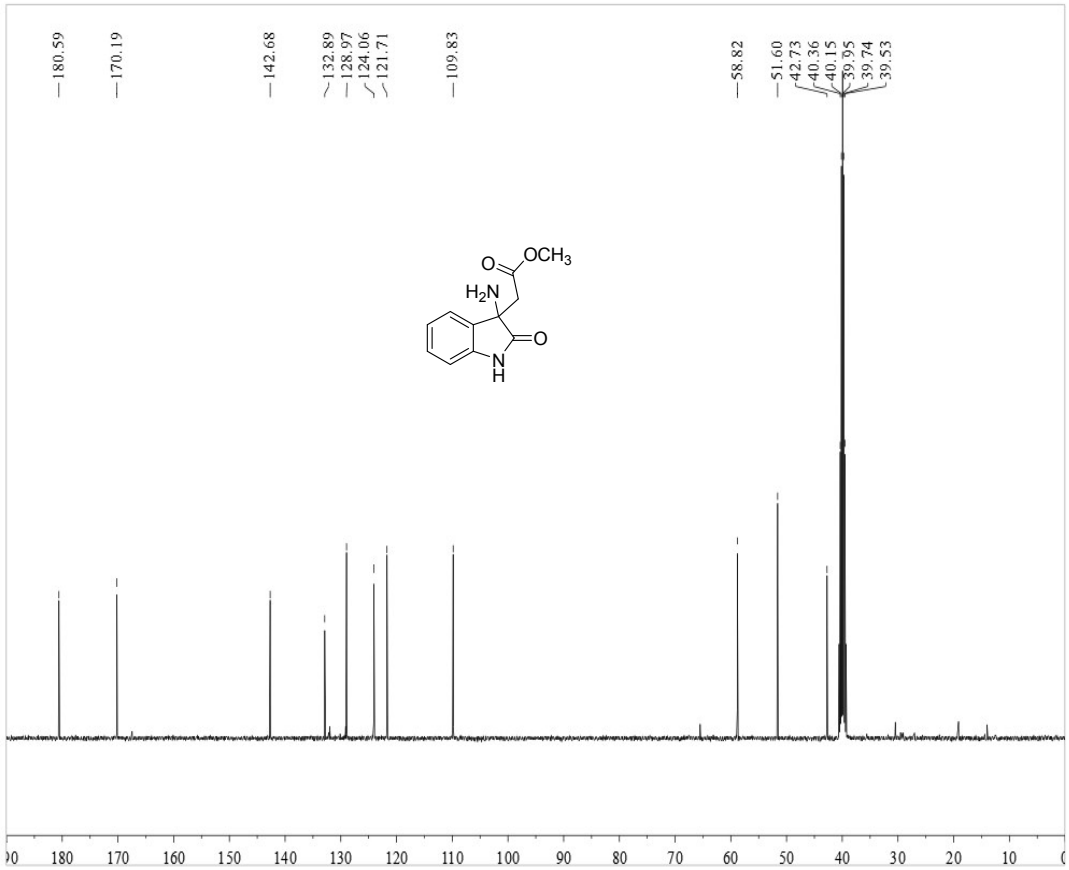
**$^{1}$H and $^{13}$C NMR of 2l**



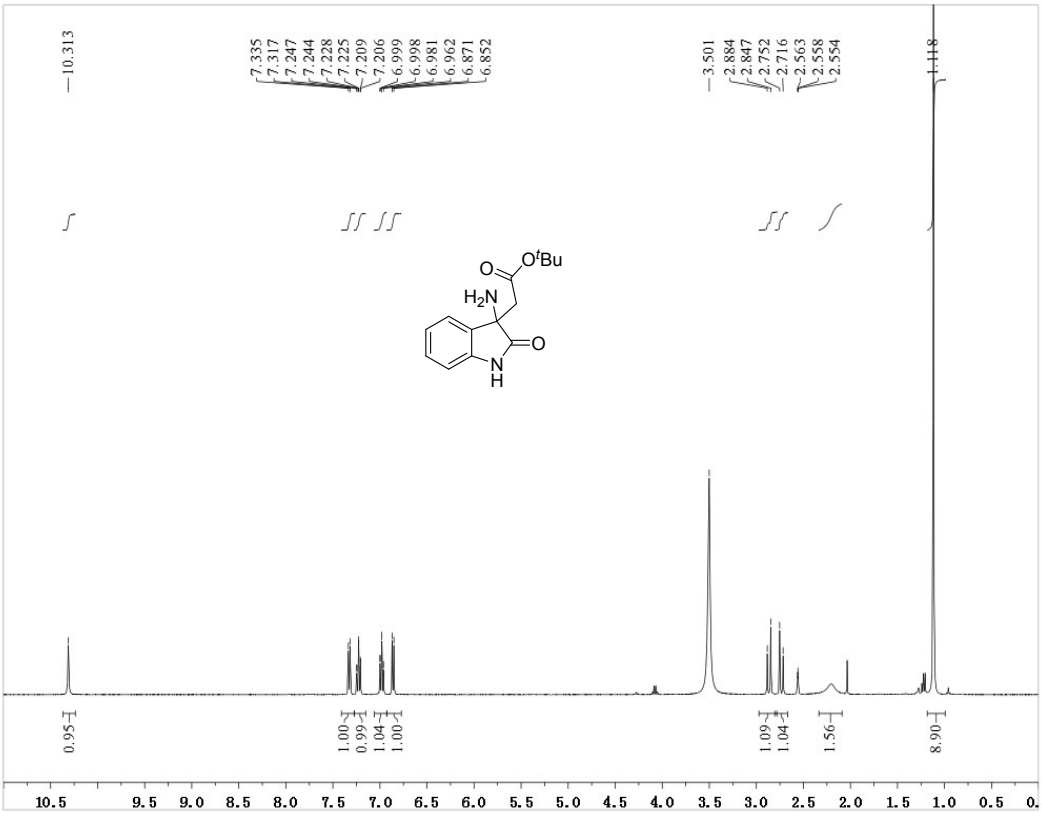



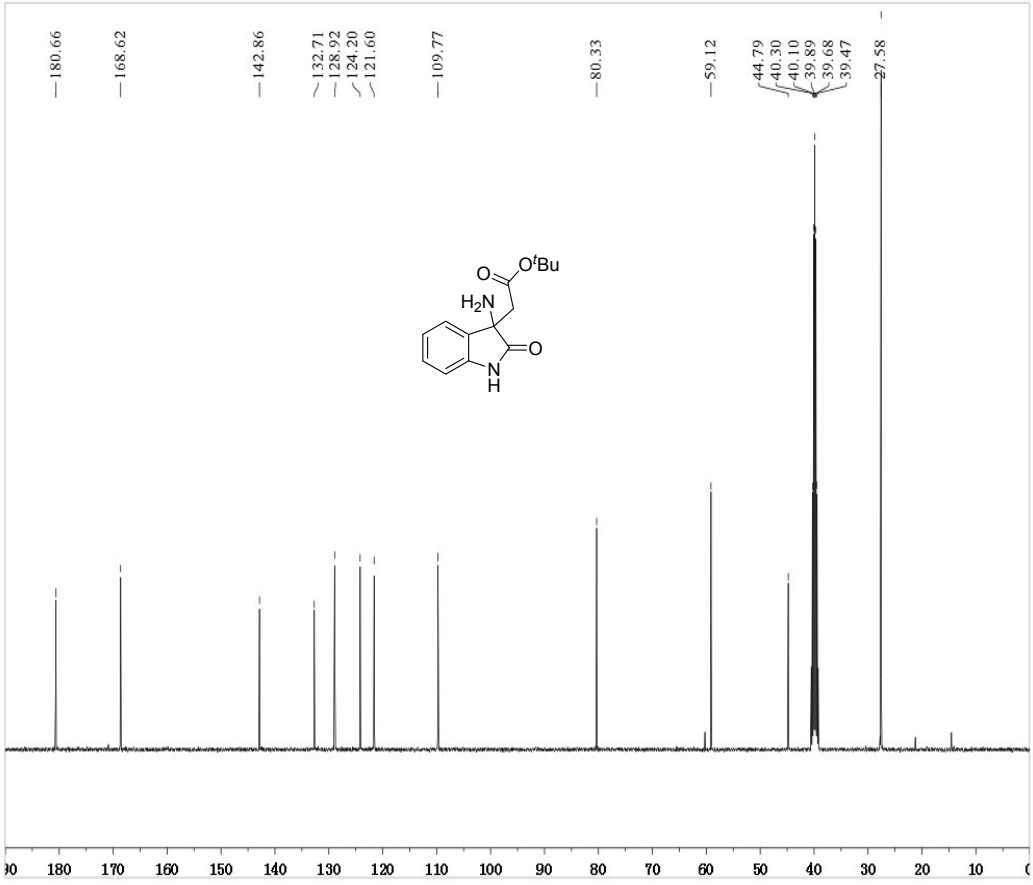
**$^{1}$H and $^{13}$C NMR of 2m**



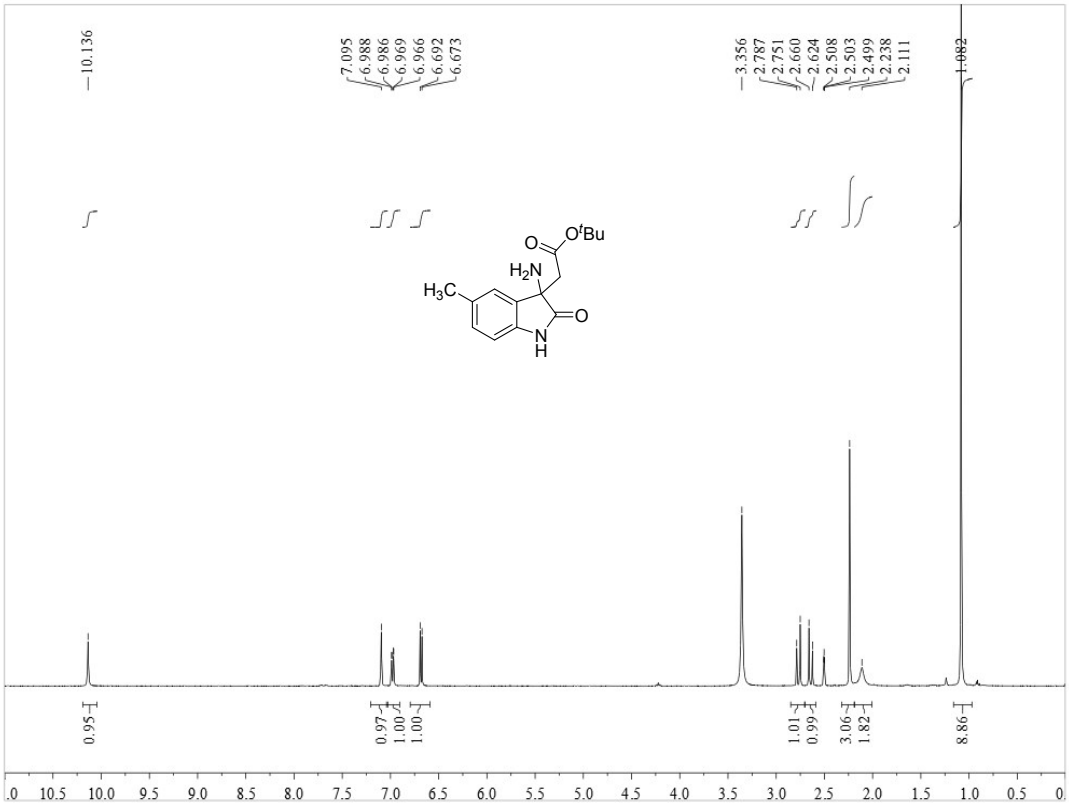



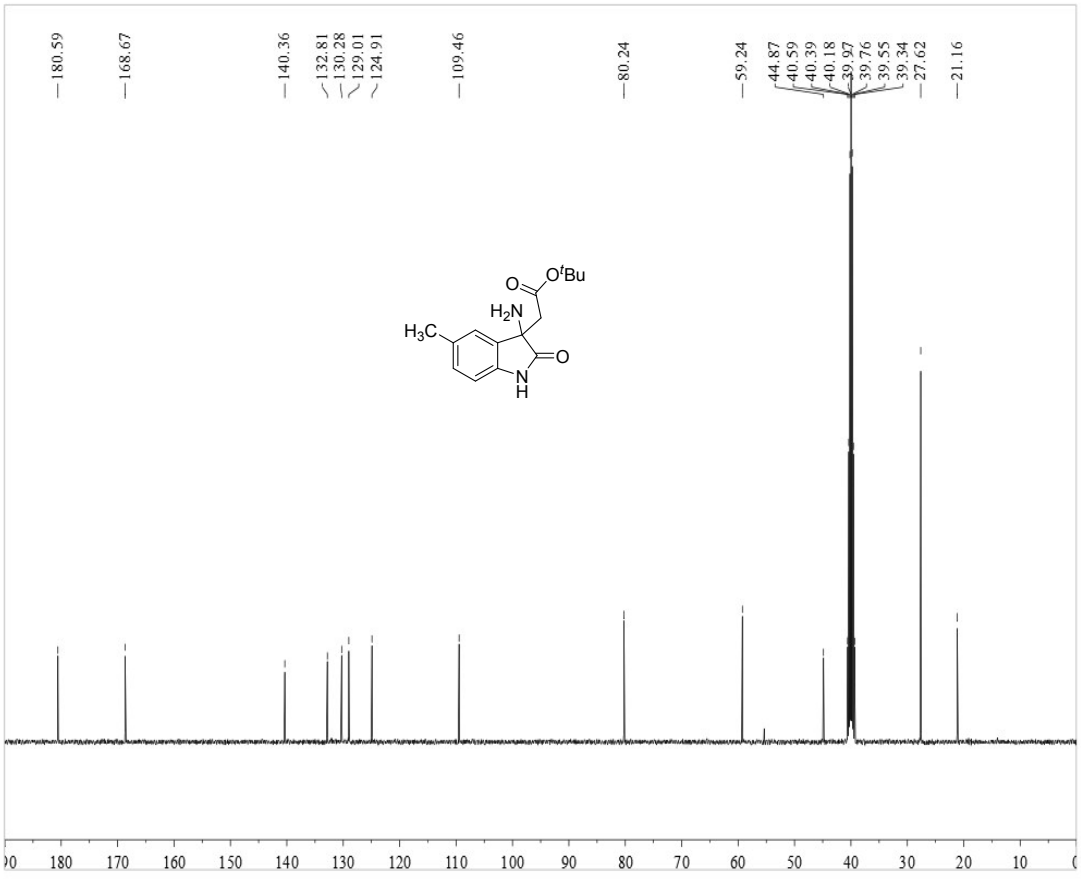
**$^{1}$H and $^{13}$C NMR of 2n**



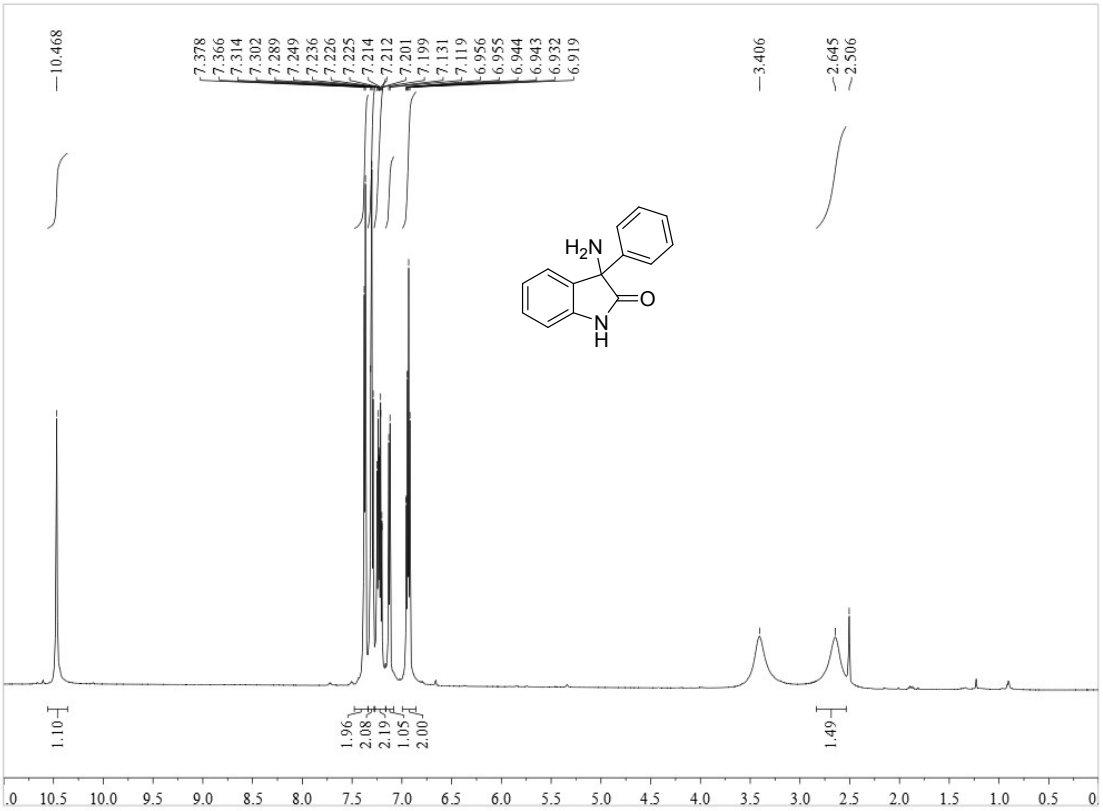



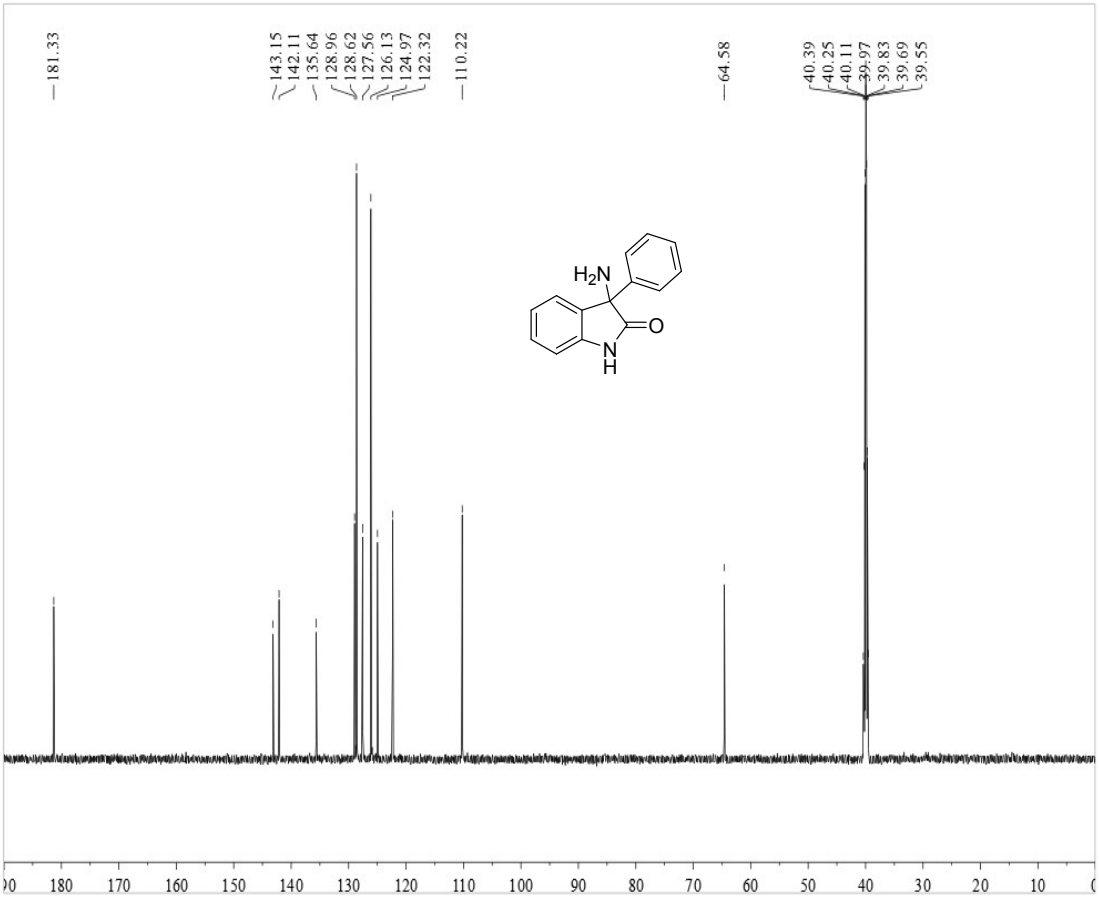
**$^{1}$H and $^{13}$C NMR of 2n**



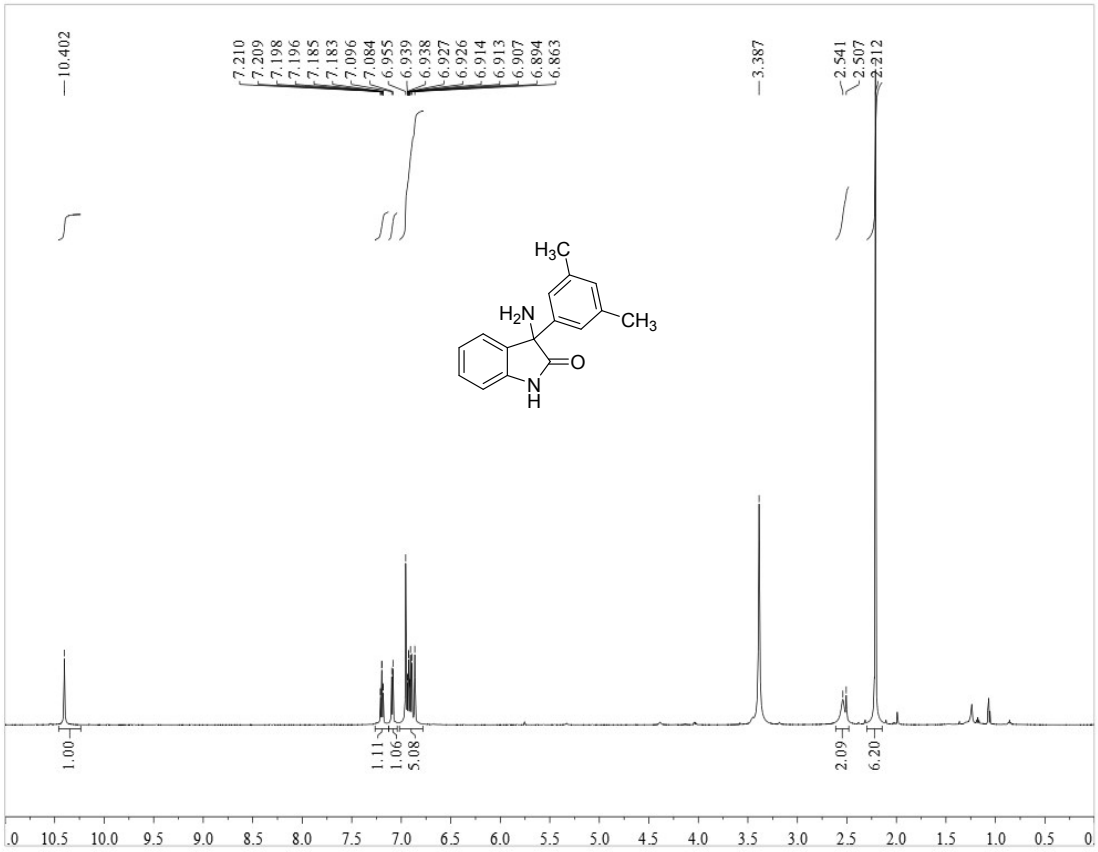



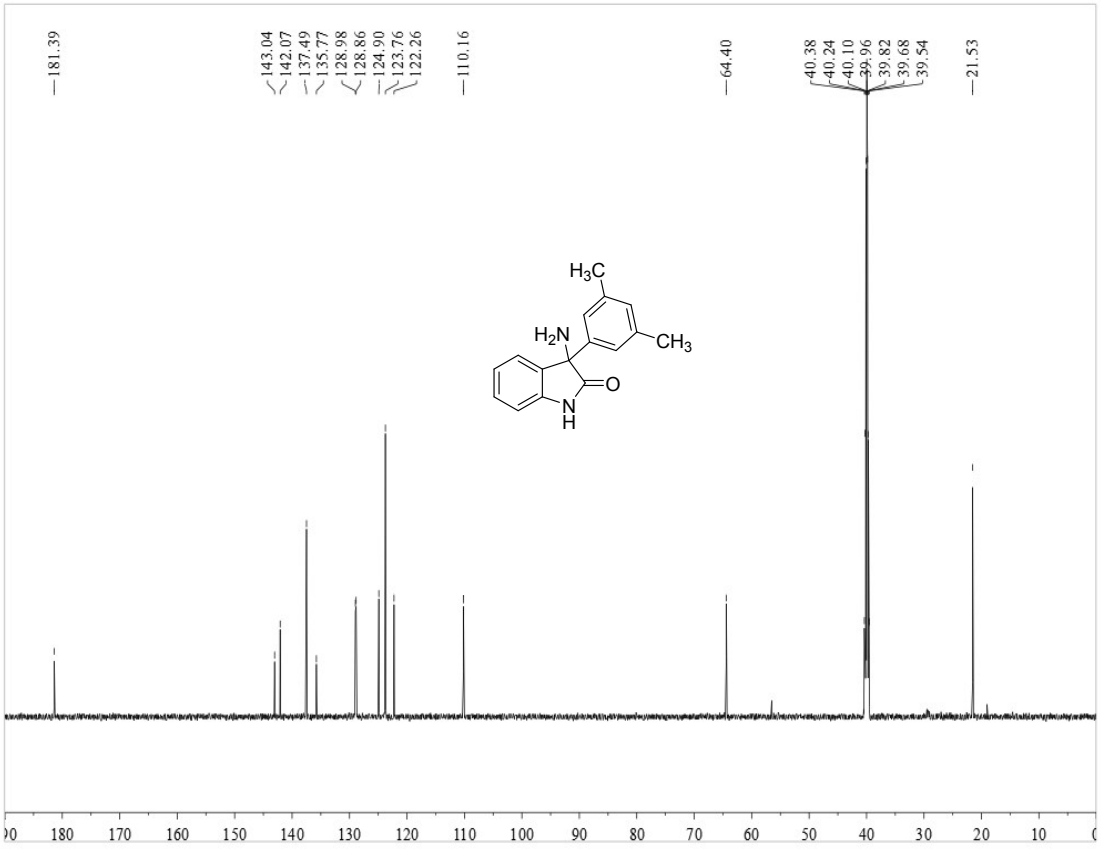
**$^{1}$H and $^{13}$C NMR of 2p**



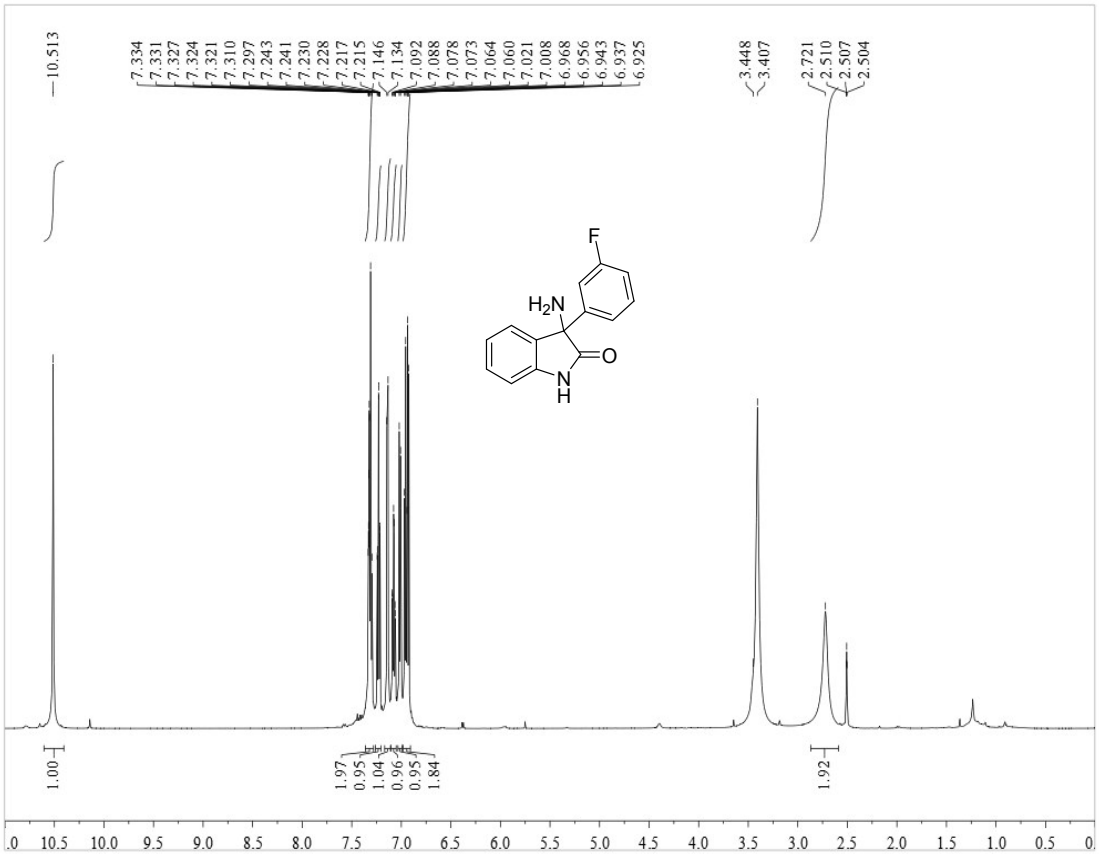



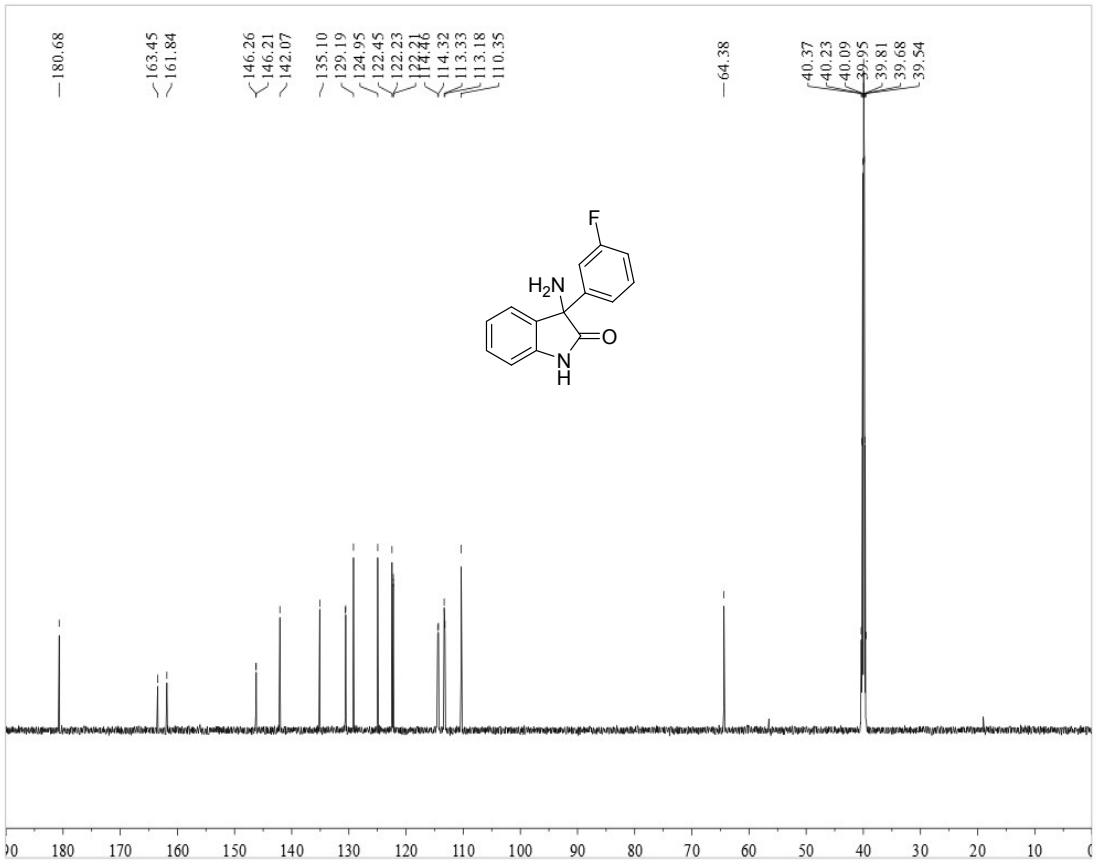
**$^{1}$H and $^{13}$C NMR of 2q**



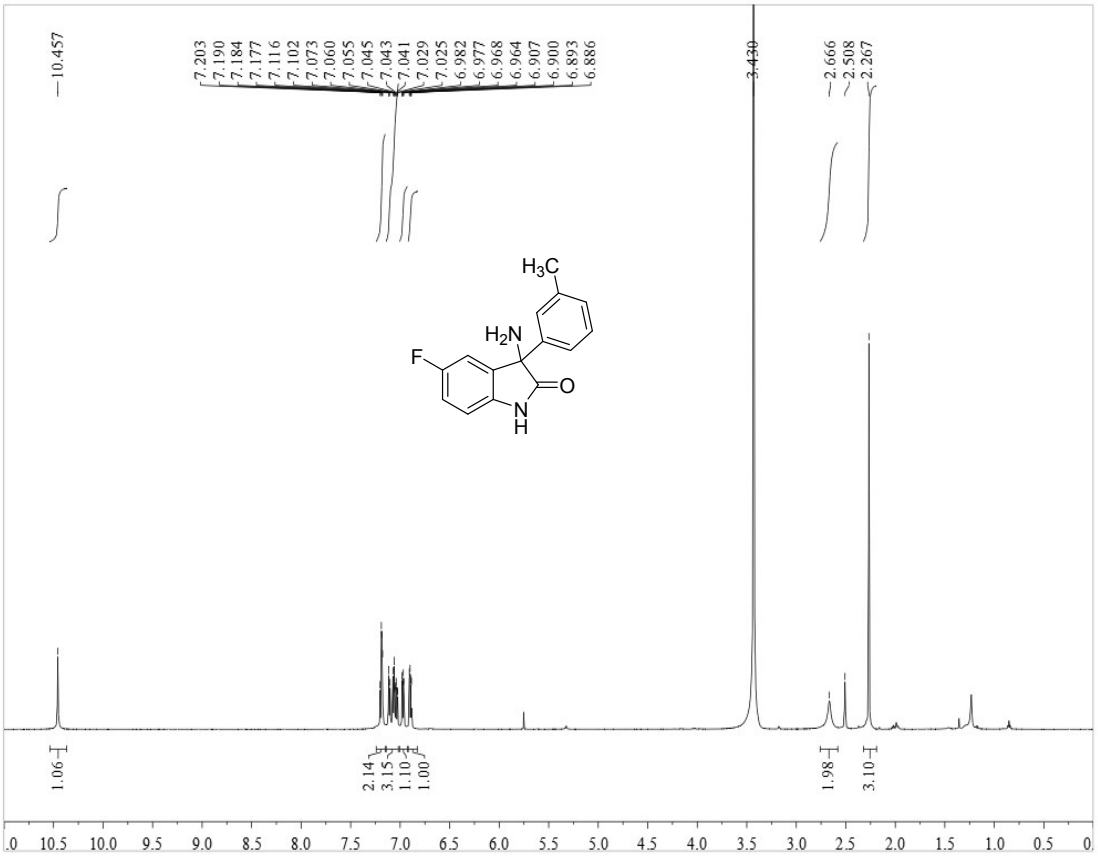



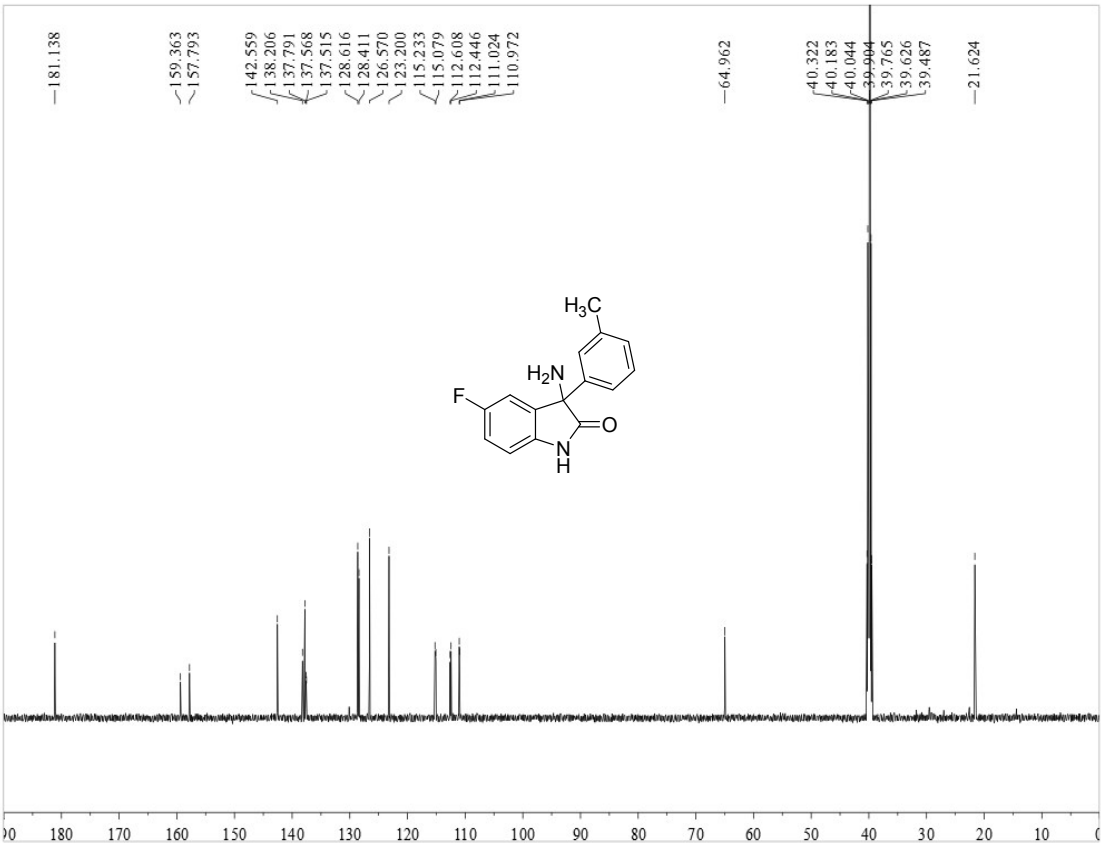
**$^{1}$H and $^{13}$C NMR of 2r**



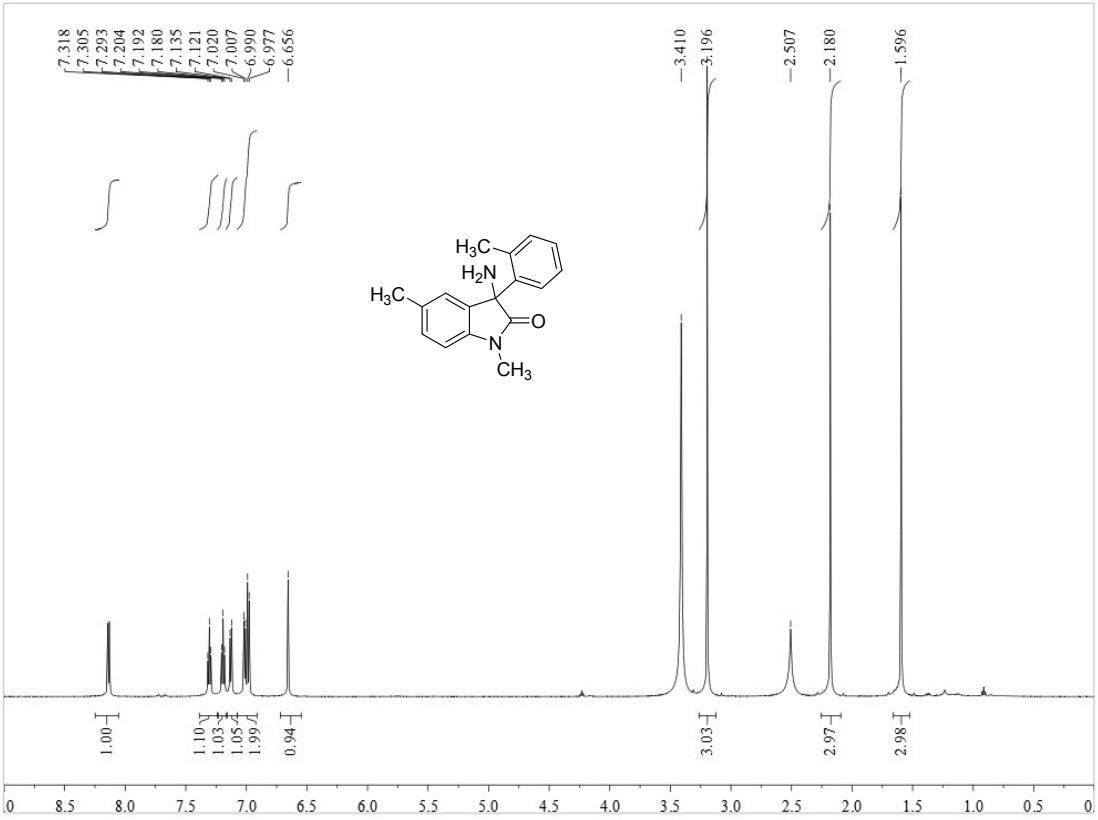



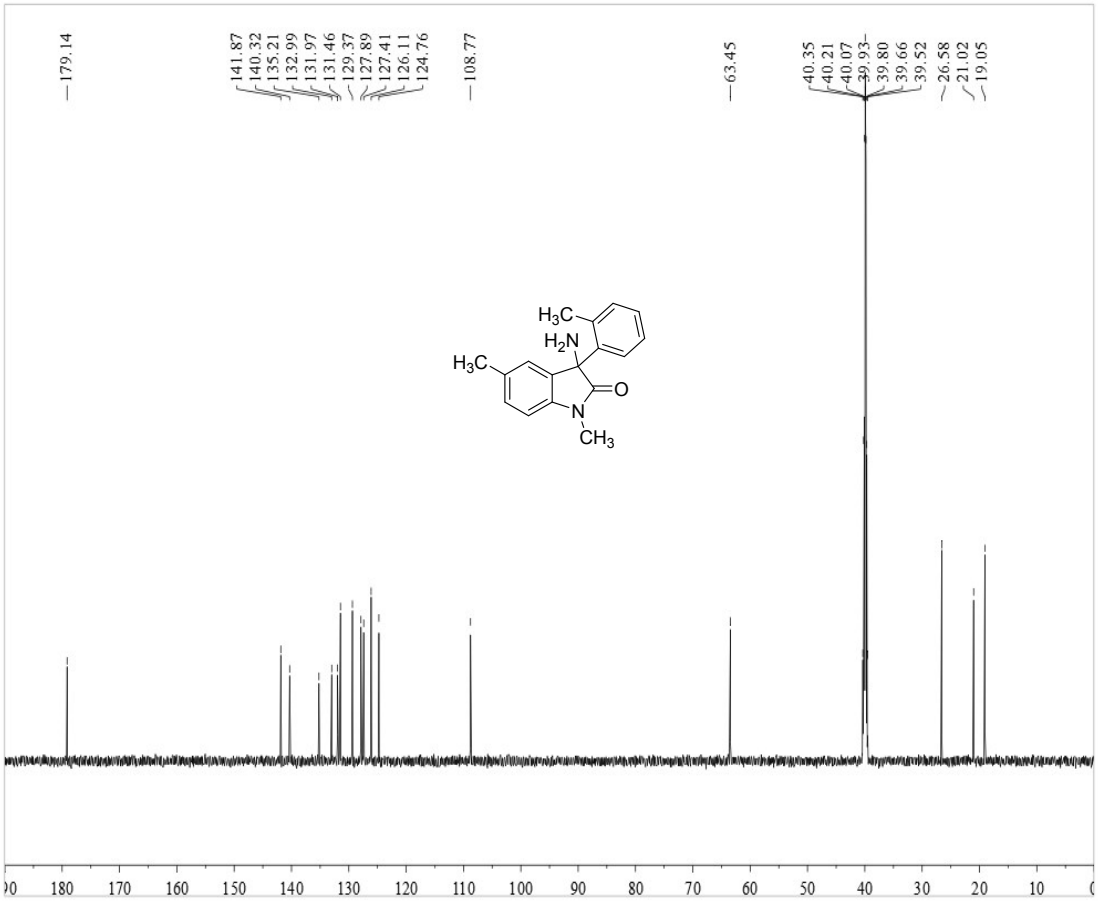
**$^{1}$H and $^{13}$C NMR of 2s**



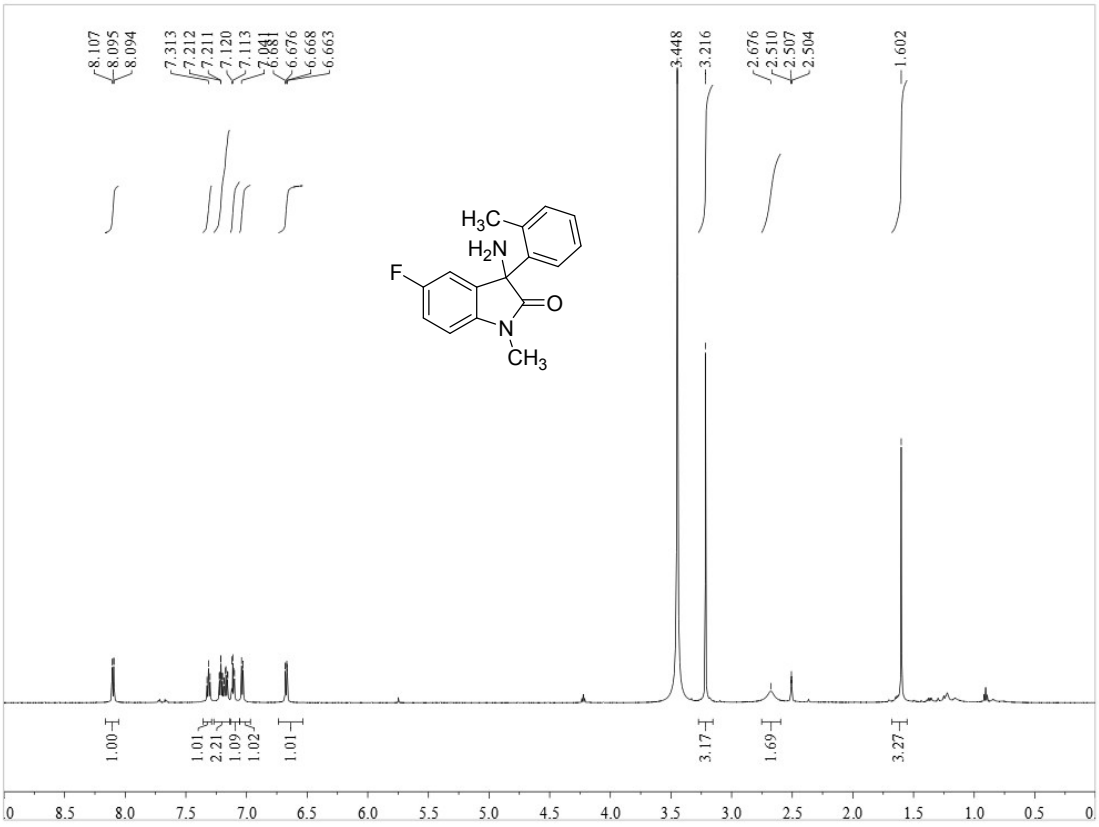



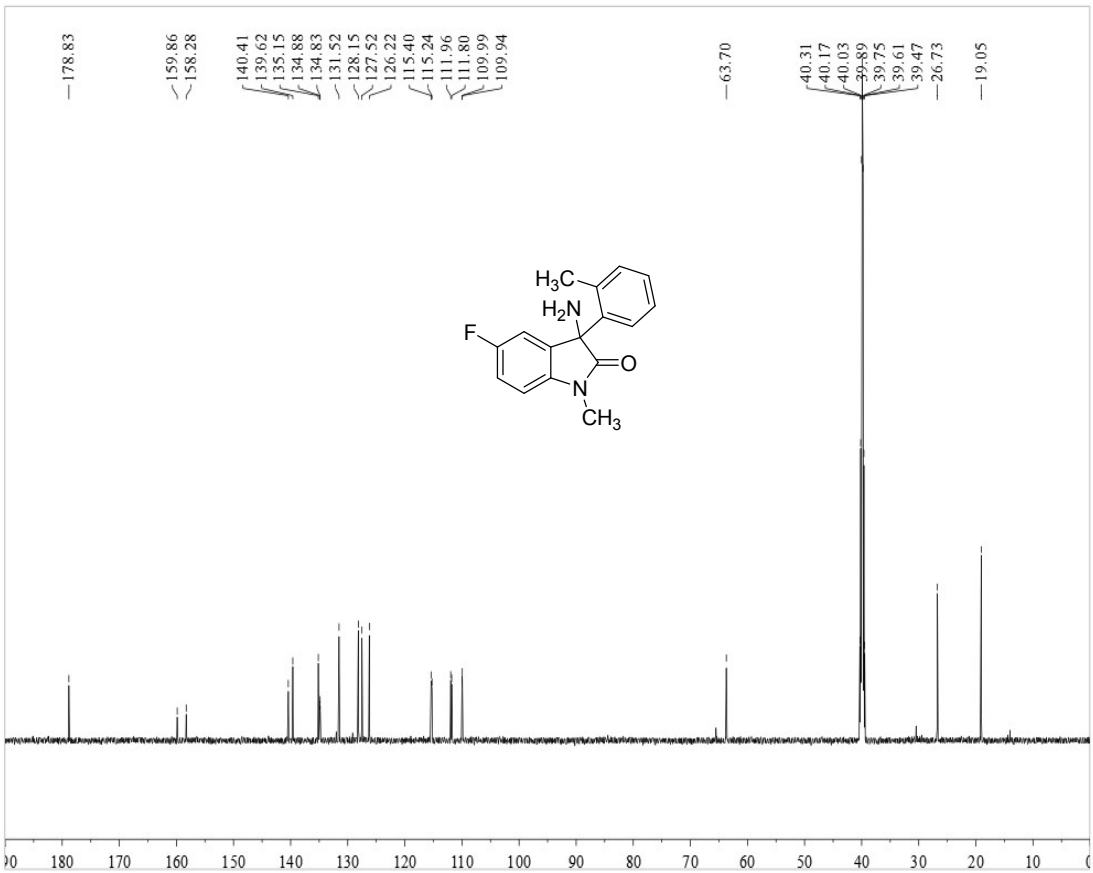
**$^{1}$H and $^{13}$C NMR of 2t**



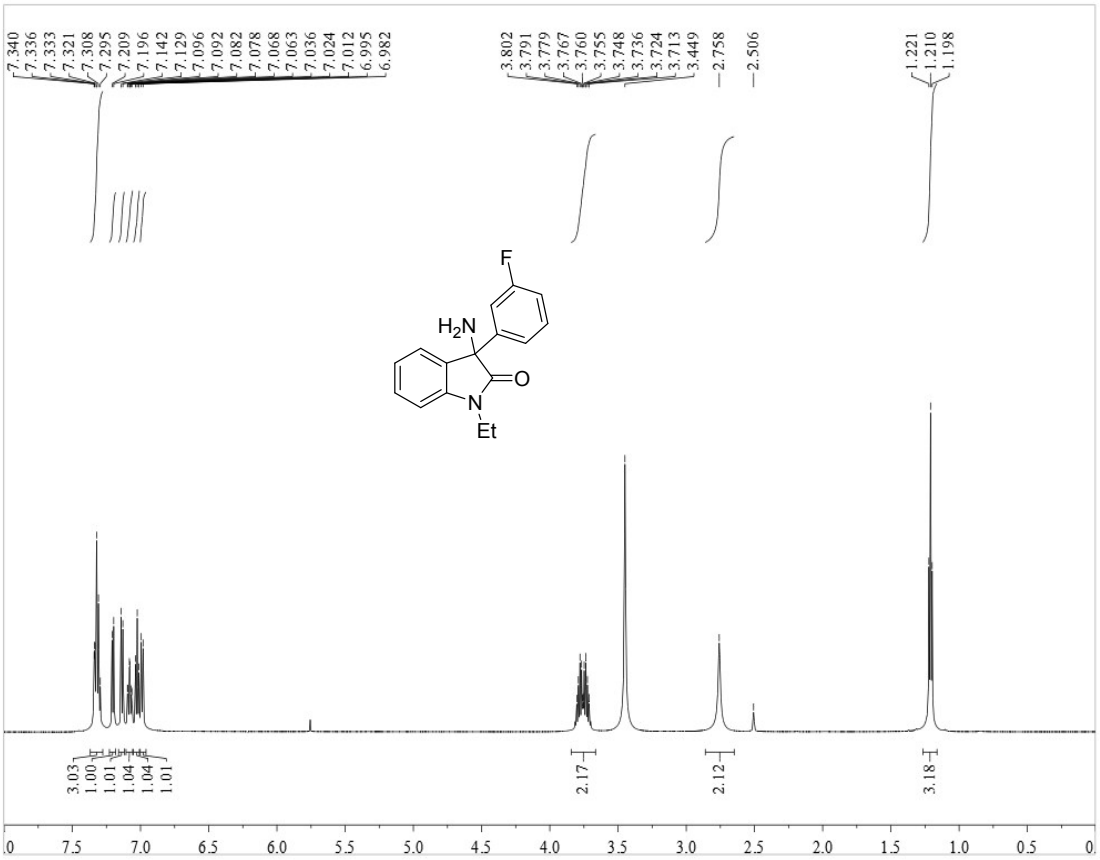



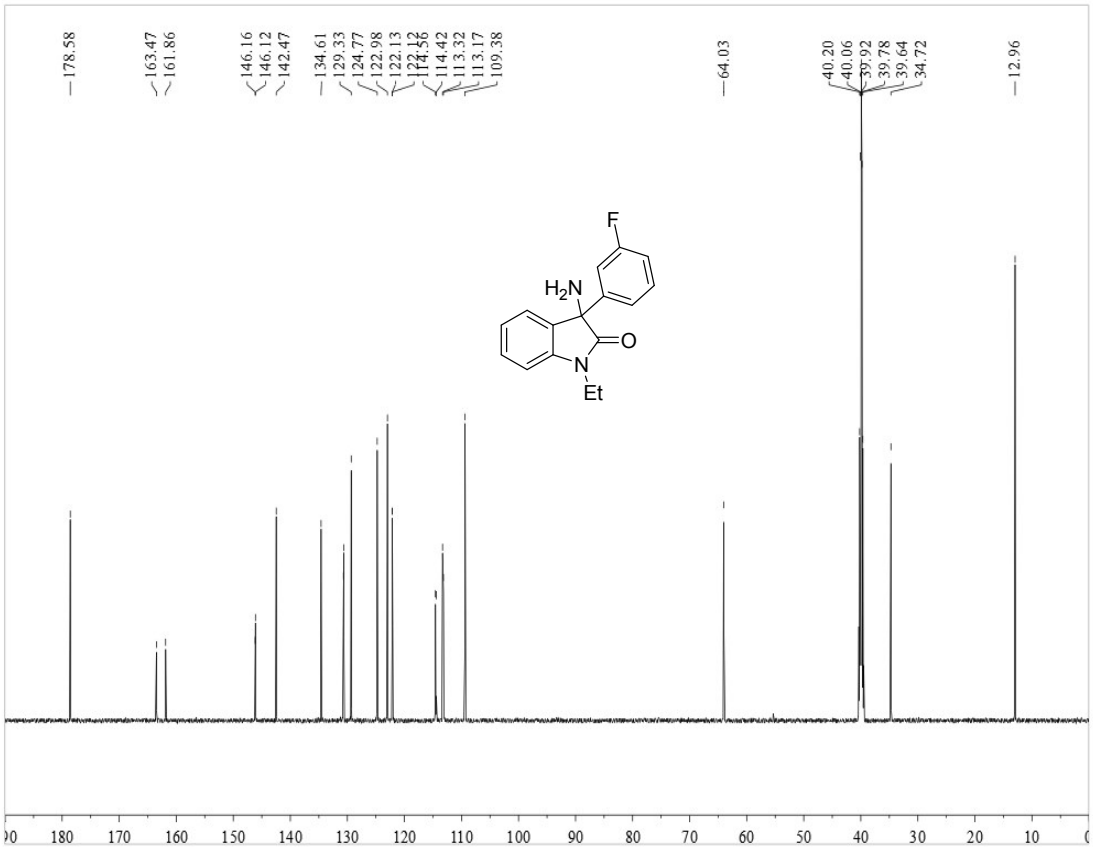
**$^{1}$H and $^{13}$C NMR of 2u**



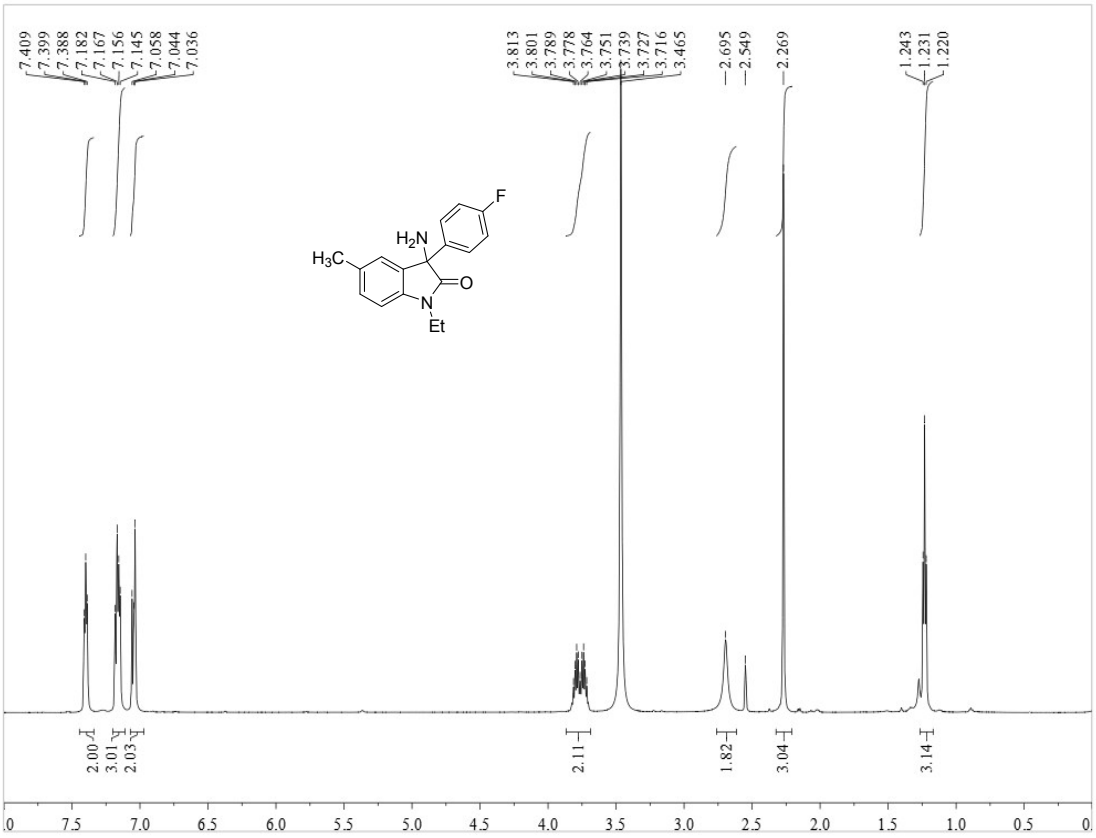



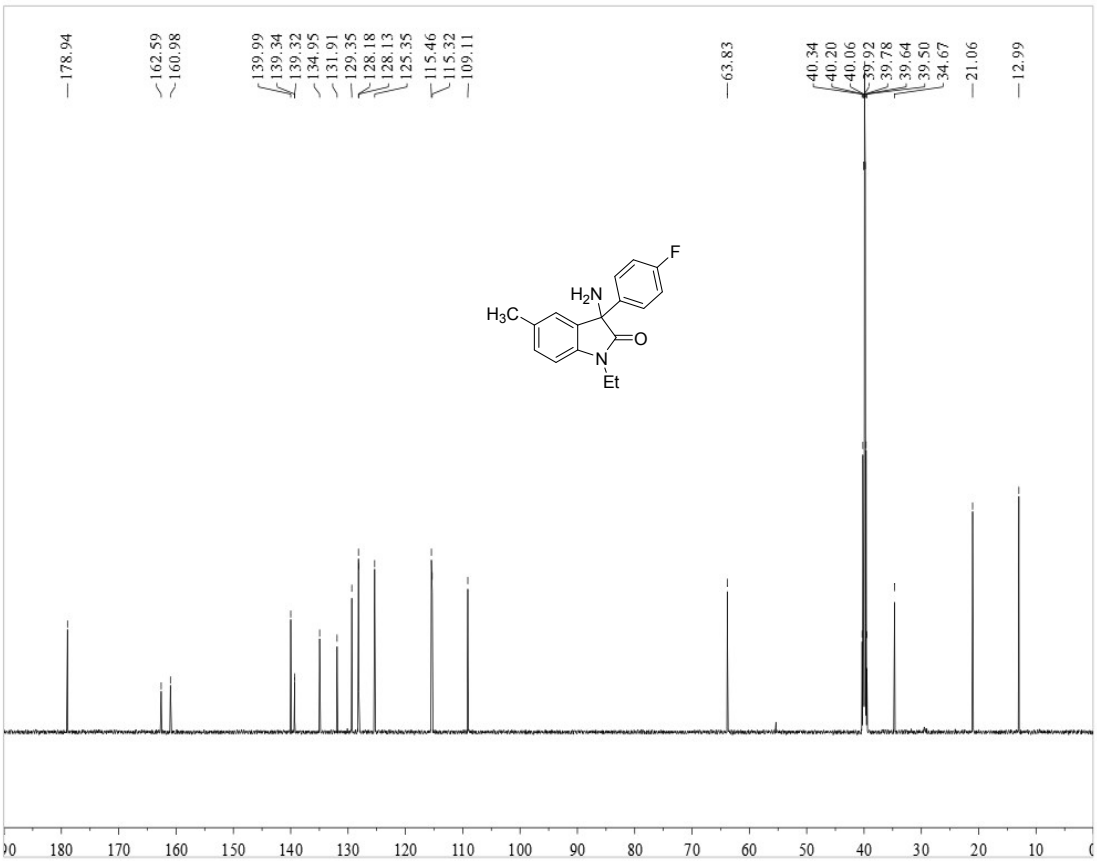
**$^{1}$H and $^{13}$C NMR of 2v**



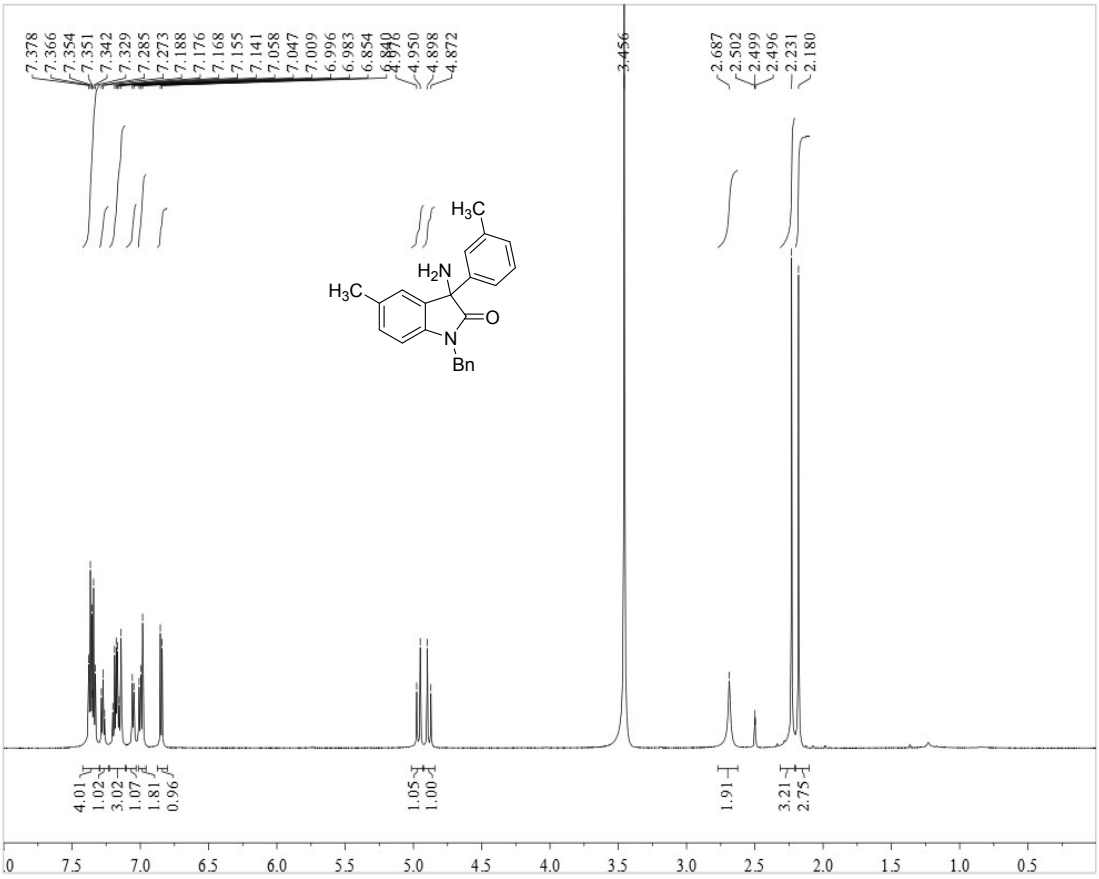



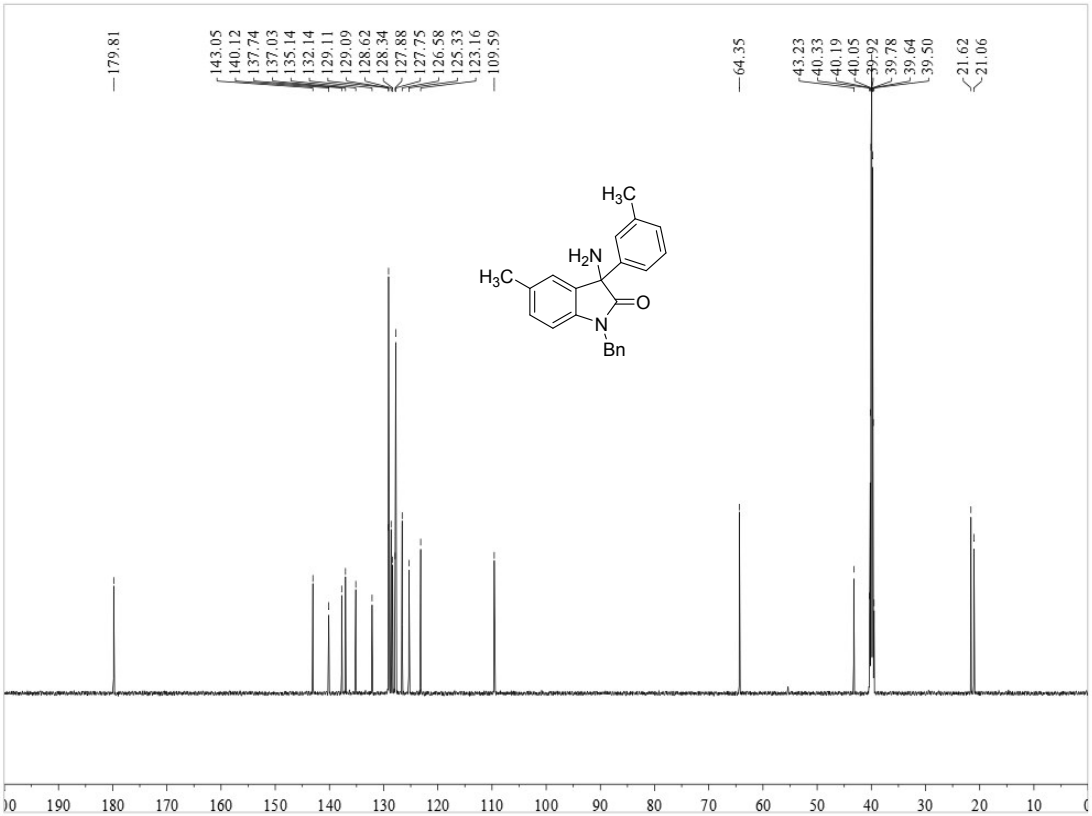
**$^{1}$H and $^{13}$C NMR of 2w**



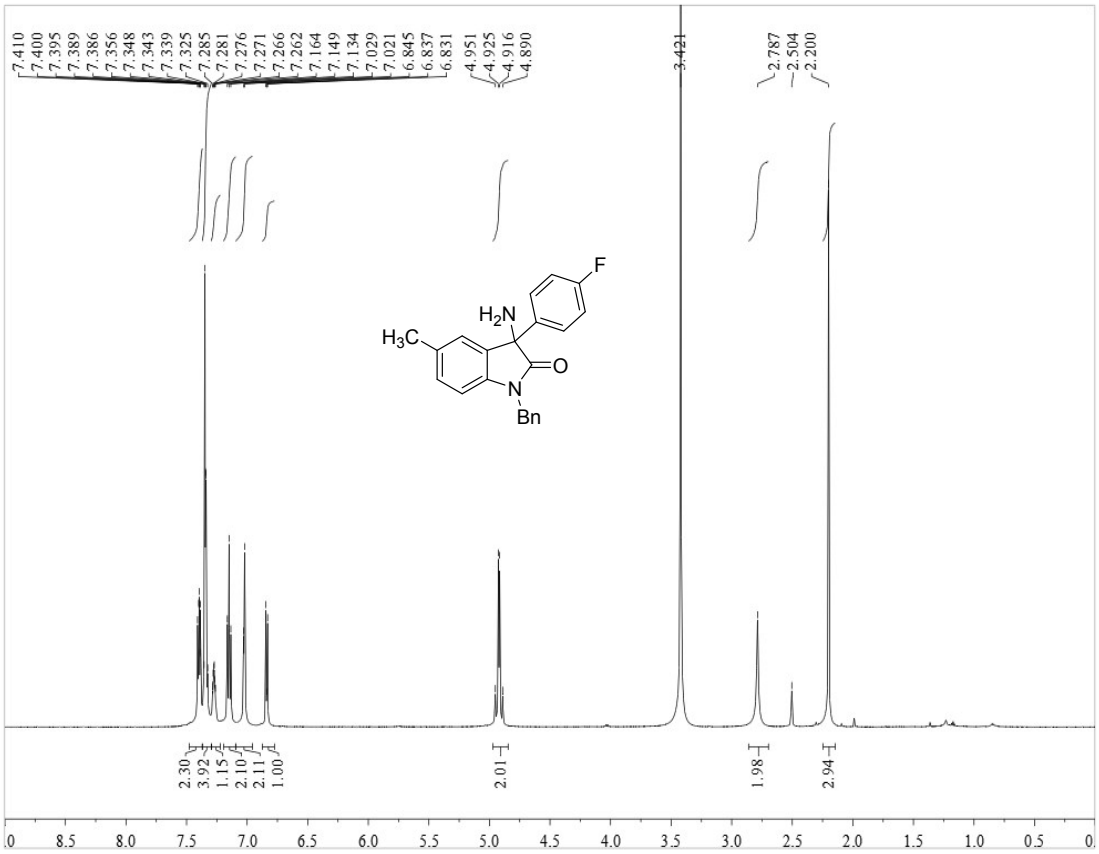



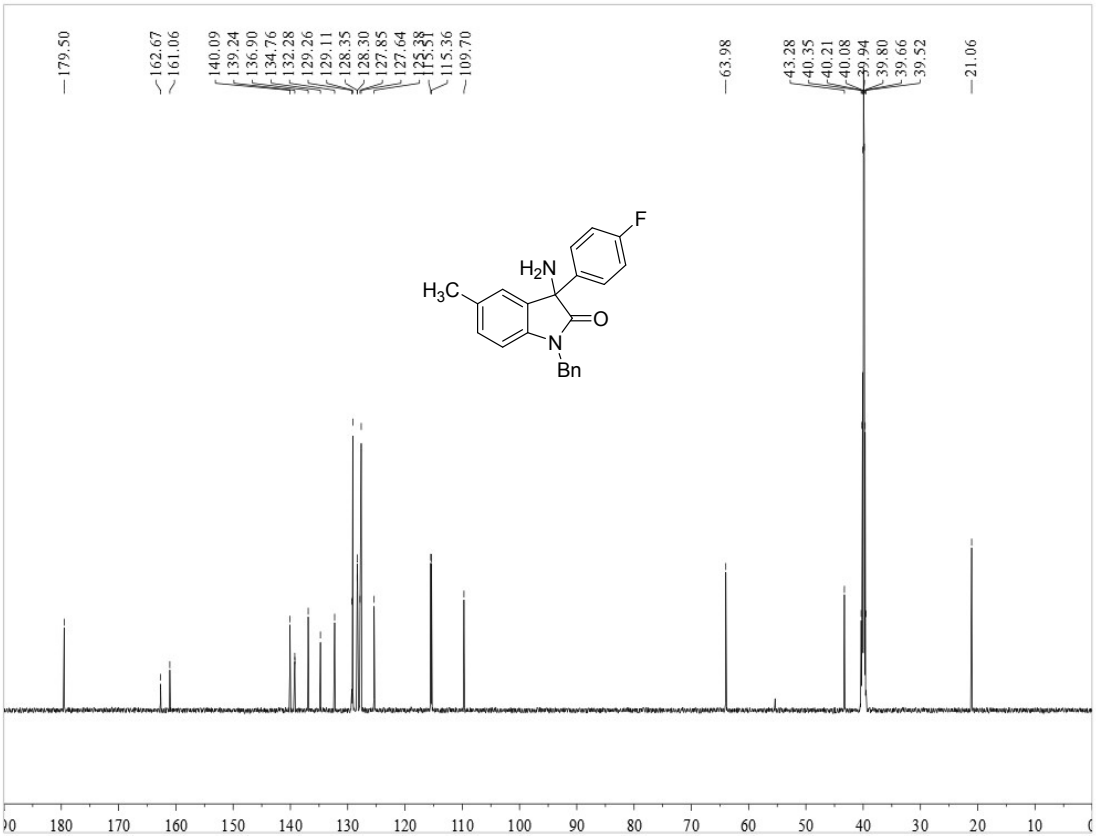
**$^{1}$H and $^{13}$C NMR of 2x**



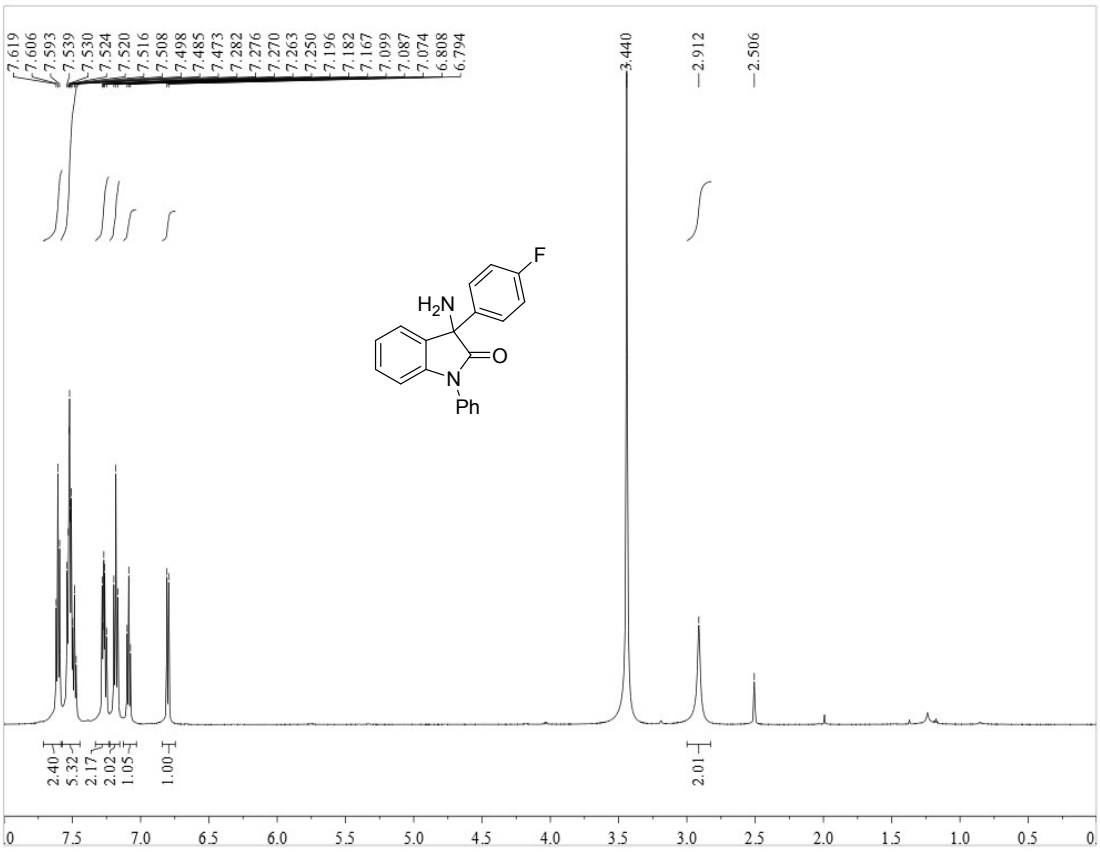



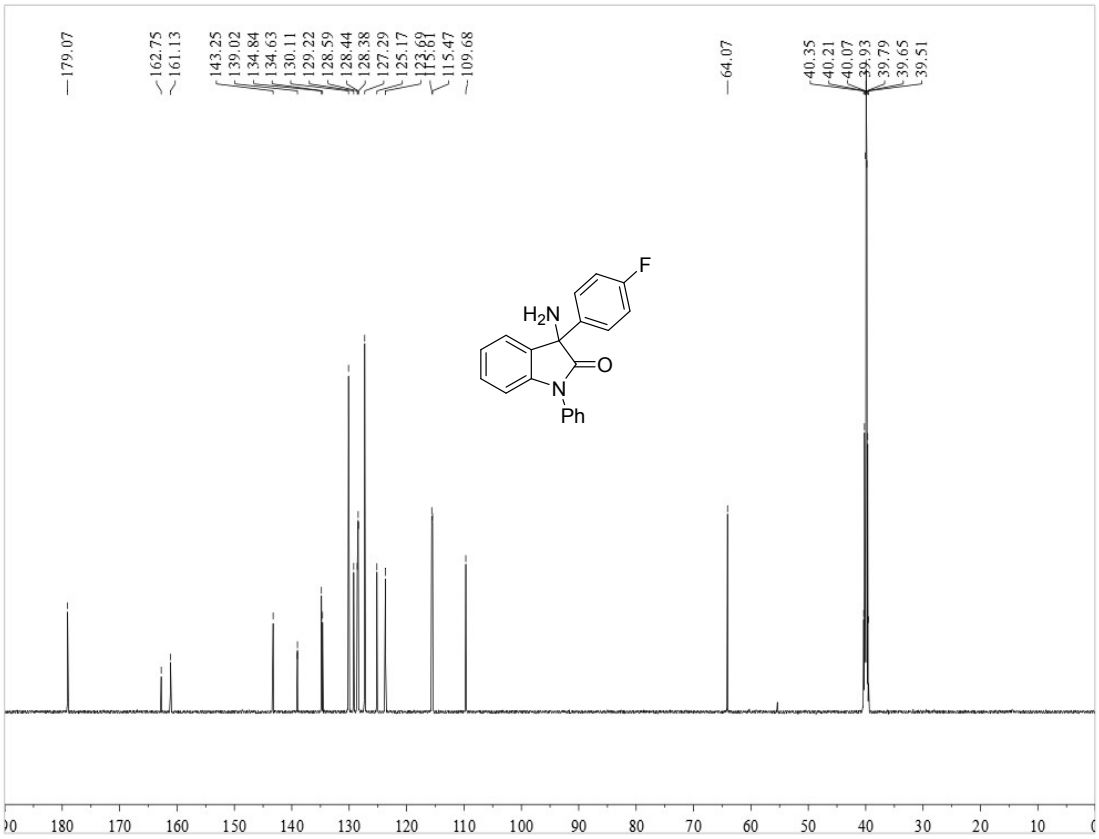
**$^{1}$H and $^{13}$C NMR of 2y**



**$^{1}$H and $^{13}$C NMR of 2z**



**$^{1}$H and $^{13}$C NMR of 2za**