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Supporting Information

An Efficient Green Synthesis of Versatile Synthon 3-Chlorooxindoles with NaCl/Oxone

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1. General Information

The starting materials and reagents were purchased from various commercial sources and used without further purification. The reactions were performed at room temperature. ACME silica gel (60-120 mesh) was used for column chromatography. Analytical thin-layer chromatography (TLC) was performed on pre-coated TLC plates with silica gel 60-F_{254} plates and visualized by UV-light. ^{1}H NMR and ^{13}C NMR spectra were recorded, using tetramethylsilane (TMS) in the solvent of $CDCl_3$+DMSO as the internal standard on a 300, 500 MHz spectrometer (^{1}H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm, DMSO at 39.43). Chemical shifts (δ) were recorded in ppm with respect to TMS as an internal standard and coupling constants are quoted in Hertz (Hz). Mass spectra were recorded on a mass spectrometer by the electron spray ionization (ESI) and the data acquired in positive ionization mode. HRMS spectra were determined on TOF type mass analyzer. All the starting materials of aliphatic MBH adducts[1], 2-(hydroxy(phenyl)methyl)cyclohex-2-en-1-one[2] and 1-phenylprop-2-en-1-ol[3] have been synthesized according to the reported literature.

2.1 General Procedure:

In a 25 mL round bottom flask, 1H-indole-3-carbaldehyde substrates**1a-1n** (1 equiv), Oxone (2 equiv) and NaCl (2 equiv) were dissolved in CH_3CN:H_2O (1:1). The reaction mixture was stirred 50 ^{o}C temperature for 1-2 h, monitored by TLC. After completion of the reaction, the mixture was diluted with 20 mL of ethyl acetate and then the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate to give the desired product.

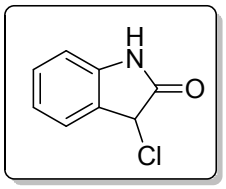
2.2 Gram-scale synthesis of 2a

In a 250 mL round bottom flask, 1H-indole-3-carbaldehyde substrate **1a** (1 equiv, 20mmol, 3g), Oxone (2.0equiv, 41 mmol, 12.7g) and NaCl (2.0equiv, 41mmol, 2.4 g) were dissolved in CH_3CN:H_2O (1:1) 60 ml of solvent. The reaction mixture was stirred at room temperature for 3h as monitored by TLC. After completion of the reaction the reaction mixture was diluted with ethyl

acetate and then the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate to give the desired product **2a**.

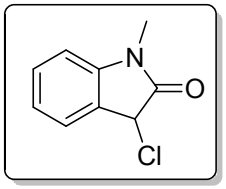
3. Characterization Data for the Products:

3-chloroindolin-2-one (2a)[1-3]:



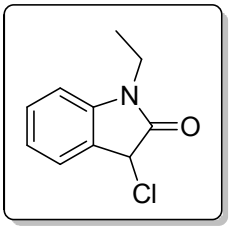
(2a): solid; mp: 134-136°C; Yield: 88%; **IR (KBr):** 3128, 1760, 1620, 1525, 1471, 1342, 1292, 1073, 959, 843, 744cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.72 (brs, 1H), 7.41 (d, J = 7.4 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.11 (t, J = 7.6, 7.4 Hz, 1H), 6.93 (d, J = 7.7 Hz, 1H), 5.17 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 174.6, 140.9, 130.5, 126.2, 125.8, 123.4, 110.6, 51.9; **MS (ESI) *m/z* (%):**168.[M+H]+; HRMS-ESI(m/z)Calcd for C_8H_6ClNO: 168.0270 $[M+H]^+$; Found: 169.0273.

3-chloro-1-methylindolin-2-one (**2b**)[4]:



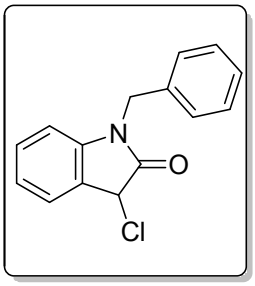
(2b): solid; mp: 97-100°C; Yield: 90%; **IR (KBr):** 3062, 2965, 1721, 1610, 1466, 1370, 1239, 1089, 751, 685 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.42 (d, J = 7.4 Hz, 1H), 7.37 (t, J = 7.8, 7.7 Hz, 1H), 7.12 (t, J = 7.7, 7.4 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 5.13 (s, 1H), 3.23 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.9, 143.6, 130.4, 125.5, 125.4, 123.2, 108.6, 51.4, 26.5; **MS (ESI) *m/z* (%):** 181 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for C_9H_8ClNO: 182.0373 $[M+H]^+$; Found: 182.0373.

3-chloro-1-ethylindolin-2-one (**2c**):



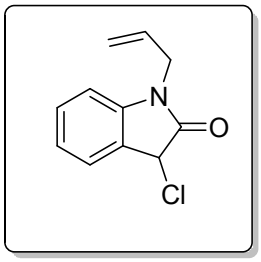
(2c): solid; mp: 126-128°C; Yield: 92%;**IR (KBr):** 3062, 2965, 1721, 1610, 1466, 1370, 1239, 1089, 751, 685 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.4 (d, J = 7.4 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.11 (t, J = 7.8, 7.4 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 5.11 (s, 1H), 3.77 (m, 2H), 1.29 (t, J = 7.3, 7.2 Hz 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.6, 142.9, 130.3, 125.8, 125.7, 123.1, 108.7, 51.5, 35.1 12.4; **MS(ESI) *m/z* (%):** 196 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{10}H_{11}ONCl$: 196.0524 $[M+H]$,$^+$ Found: 196.0523.

1-benzyl-3-chloroindolin-2-one[4] (**2d**):



(2d): solid; **mp:** 145-147°C; Yield: 90%; **IR (KBr):** 3061, 3031, 2955, 1719, 1609, 1486, 1343, 1268, 1157, 1079, 892, 757, 694cm^{-1} ; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.42 (d, J = 7.4 Hz 1H), 7.35 7.28 (m, 5H), 7.22 (t, J = 7.9,10.2 Hz, 1H), 7.08 (t, J = 8.3 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 5.22 (s, 1H), 4.91 (d, 2H) ; **^{13}C NMR (75 MHz, $CDCl_3$):** δ 172.0, 141.7, 130.6, 126.0, 125.4, 123.8, 116.9, 108.5, 50.9, 36.3, 16.2; **MS (ESI) *m/z* (%):** 258 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{15}H_{12}ClNO$ = 258.0683 $[M+H]^+$; Found: 258.0680.

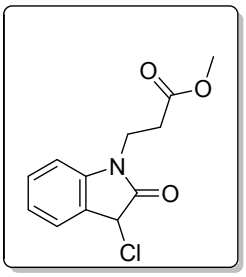
1-allyl-3-chloroindolin-2-one (**2e**):



(2e): solid; mp: 99-101°C; Yield: 91%; **IR (KBr):** 3055, 3022, 2969, 1719, 1611, 1467, 1356, 1179, 922, 751, 681 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.43 (d, J = 7.4 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.11 (t, J = 7.8 ,7.4 Hz,

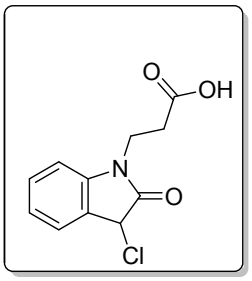
1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.84 (m, 1H), 5.26 (m, 2H),5.16 (s, 1H), 4.35 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.7, 142.9, 130.5, 130.3, 125.6, 123.2, 118.0, 109.5, 51.3, 42.6; **MS (ESI) *m/z* (%):** 208 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{11}H_{11}ONCl$: 208.0525 $[M+H]^+$; Found: 208.0523.

Methyl 3-(3-chloro-2-oxoindolin-1-yl)propanoate (**2f**):



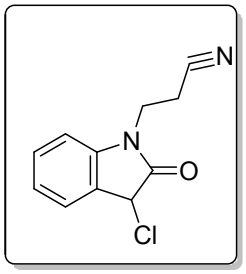
(2f): Colourless Liquid; Yield: 85%; **IR (KBr):** 3020, 2953, 1729, 1610, 1467, 1365, 1201, 1064, 753, 686cm^{-1};**^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.8 , 7.7 Hz, 1H), 7.12 (t, *J* = 7.7 ,7.5 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 5.13 (s, 1H), 4.02 (t, *J*= 7.1, 6.9 2H), 3.67 (s, 3H), 2.73 (t, *J*= 7.1 , 6.9 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.8, 171.1,142.4, 130.3, 125.6, 125.4, 123.2, 108.8, 51.8, 51.1, 36.1, 31.6; **MS (ESI) *m/z* (%):** 350 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{12}H_{12}O_3NCl$: 254.0581 $[M+H]^+$; Found: 254.0581.

3-(3-chloro-2-oxoindolin-1-yl)propanoic acid (**2g**):



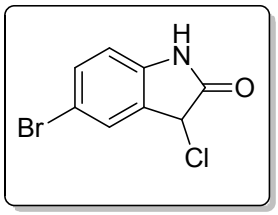
(2g): solid; mp: 130-132^{o}C; Yield: 82%; **IR (KBr):** 3414, 3062, 2954, 1761, 1731, 1681, 1596, 1447, 1264, 1215, 1187, 1018, 990, 798, 688, 638, 616 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 7.58 Hz, 1H), 7.36 (t, *J* = 7.82 , 7.70 Hz, 1H), 7.12 (t, *J* = 8.43 ,7.58 Hz, 1H), 6.95 (d, *J* = 7.82 Hz, 1H), 5.13 (s, 1H), 4.02 (t, *J*= 7.20, 7.09 2H), 2.73 (t, *J*= 7.09 , 6.96 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 187.8, 166.3, 133.8, 132.9, 129.5, 128.5, 64.0, 57.4, 37.2; **MS (ESI) *m/z* (%):** 242 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{11}H_{10}O_3NCl$ = 242.2845 $[M+H]^+$; Found: 242.2845.

3-(3-chloro-2-oxoindolin-1-yl)propanenitrile (**2h**):



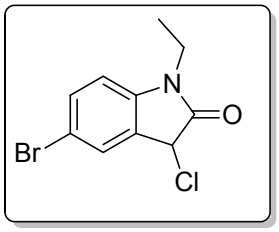
(2h): solid; mp:142-144 ^{o}C; Yield: 84%; **IR (KBr):** 3062, 2926, 2854, 2252, 1728, 1612, 1467, 1361, 1174, 1061, 754, 685 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.46 (d, J = 7.4 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.16 (t, J = 7.9 ,7.4 Hz, 1H), 6.95 (d, J = 7.9 Hz, 1H), 5.18 (s, 1H), 4.03 (t, 2H), 2.79 (m, 2H) ; **^{13}C NMR (75 MHz, $CDCl_3$):**δ 172.0, 141.7, 130.6, 126.0, 125.4, 123.8, 116.9, 108.5, 50.9, 36.3, 16.2;**MS (ESI) *m/z* (%):** 221 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{11}H_{10}ON_2Cl$ = 221.0478 $[M+H]^+$; Found: 221.0476.

5-bromo-3-chloroindolin-2-one (2i):



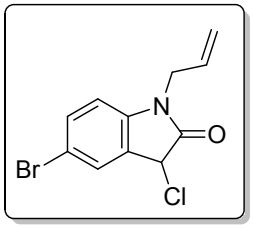
(2i): solid; **mp:** 251-253 ^{o}C; Yield: 90%; **IR (KBr):** 3407, 2926, 1741, 1604, 1482, 1343, 1209, 1104, 816, 794 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.92 (brs, 1H), 7.54 (s, 1H), 7.44 (d, J = 8.3 Hz, 1H), 6.79 (t, J = 8.3 Hz, 1H), 5.31 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 172.2, 140.7, 132.1, 127.6, 127.4, 113.7, 111.2, 50.7; **MS (ESI) *m/z* (%):** 247 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_8H_5ONBrCl$: 247.0887 $[M+H]^+$; Found: 247.0881.

5-bromo-3-chloro-1-ethylindolin-2-one (2j):



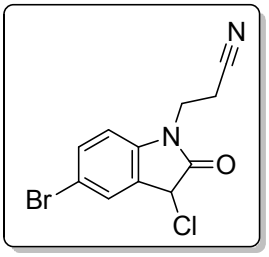
(2j): solid; **mp:** 138-140°C; Yield: 92%; **IR (KBr):** 3144, 2931, 1741, 1683, 1616, 1471, 1386, 1205, 1171, 886, 820, 798, 690 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.55 (s, 1H), 7.48 (d, J = 8.3 Hz, 1H), 6.75 (t, J = 8.3 Hz, 1H), 5.09 (s, 1H), 4.05 (m, 2H), 1.27 (t, J = 7.3, 7.2 Hz 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 170.0, 144.5, 143.1, 130.4, 128.3, 121.3, 111.3, 29.6; **MS (ESI) *m/z* (%):** 275 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{10}H_{10}ONBrCl$: 275.9612 $[M+H]^+$; Found: 275.9612.

1-allyl-5-bromo-3-chloroindolin-2-one (2k):



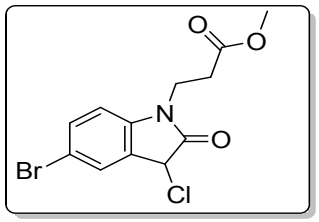
(2k): solid; **mp:** 110-112°C; Yield: 92%; **IR (KBr):**3055, 3022, 2969, 1719, 1611, 1467, 1356, 1179, 922, 751, 681cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.55 (s, 1H), 7.48 (d, J = 8.3 Hz, 1H), 6.75 (t, J = 8.3 Hz, 1H), 5.81 (m, 1H), 5.26 (m, 2H),5.16 (s, 1H), 4.33 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.1, 141.9, 133.1, 130.2, 128.8, 127.4, 118.3, 115.8, 111.0, 50.7, 42.7; **MS (ESI) *m/z* (%):** 284 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{11}HONBrCl$: 284.1747 $[M+H]^+$; Found: 284.1747.

3-(5-bromo-3-chloro-2-oxoindolin-1-yl)propanenitrile (**2l**):



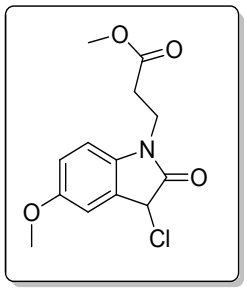
(2l): solid;mp: 145-147°C; Yield: 86%; **IR (KBr):** 3062, 2926, 2854, 2252, 1738, 1622, 1487, 1361, 1174, 1061, 980, 820, 754, 685cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.59 (s, 1H), 7.53 (d, J = 8.3 Hz, 1H), 6.86 (t, J = 8.3 Hz, 1H), 5.16 (s, 1H), 4.02 (m, 2H), 2.78 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.8, 171.1, 142.4, 130.3, 125.6, 125.4, 123.2, 108.8, 51.8, 51.1, 36.1, 31.6; **MS (ESI) *m/z* (%):** 300 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{11}H_8BrClN_2O$: 300.1657 $[M+H]^+$; Found: 300.1686.

Methyl 3-(3-chloro-2-oxoindolin-1-yl)propanoate (**2m**):



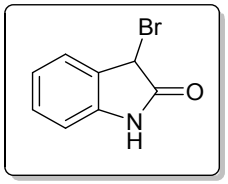
(2m): Solid; mp: 120-122^{o}C; Yield: 86%; **IR (KBr):** 3049, 2949, 1723, 1608, 1482, 1363, 1206, 1169, 1118, 1070, 986, 816, 639 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ7.54 (s, 1H), 7.49 (d, J = 8.3 Hz, 1H), 6.86 (t, J = 8.3 Hz, 1H), 5.10 (s, 1H), 3.99 (t, J= 7.0, 6.8 Hz, 2H), 3.67 (s, 3H), 2.77 (t, J= 7.0 , 6.8 Hz, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.8, 171.1,142.4, 130.3, 125.6, 125.4, 123.2, 108.8, 51.8, 51.1, 36.1, 31.6; **MS (ESI) *m/z* (%):** 333 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{12}H_{11}O_3NBrCl$: 333.9679 $[M+H]^+$; Found: 333.9679.

methyl 3-(3-chloro-5-methoxy-2-oxoindolin-1-yl)propanoate (2n):



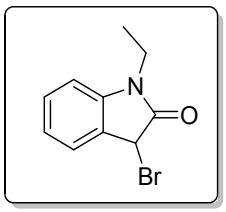
(2n): Colourless Liquid; Yield: 79%; **IR (KBr):** 3042, 2952, 2838, 1729, 1601, 1492, 1438, 1283, 1206, 1174, 1027, 816, 743, 688 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.03 (d, J = 2.3 Hz, 1H), 6.88 (d, J = 2.3 Hz, 1H), 6.86 (s, 1H), 5.09 (s, 1H), 3.99 (t, J = 7.1 Hz, 2H), 3.89 (t, 3H), 3.67 (t, 3H), 2.72 (t, J = 7.1 Hz, 2H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.8, 171.4, 156.3, 135.7, 126.7, 115.2, 112.5, 109.5, 55.7, 51.9, 51.5, 36.4, 31.7; **MS (ESI) *m/z* (%):** 284 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{13}H_{14}O_4NCl$: 284.0689 $[M+H]^+$; Found: 284.0689.

3-Bromoindolin-2-one (3a):



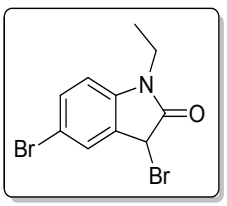
(3a): colourless solid; mp: 138-140°C; Yield: 80%; **IR (KBr):** 3246, 3032, 2849, 1717, 1619, 1471, 1329, 1192, 1168, 1099, 905, 727, 649 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 9.18 (brs, 1H), 7.39 (d, J = 7.4 Hz, 1H), 7.28 (t, J = 7.7, 7.4 Hz, 1H), 7.09 (t, J = 7.6, 7.4 Hz, 1H), 6.94 (d, J = 7.7 Hz, 1H), 5.17 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 174.7, 140.9, 133.3, 130.4, 126.2, 123.4, 110.6, 38.9; **MS (ESI) *m/z* (%):** 211.99$[M+H]^+$; **HRMS-ESI**(m/z)Calcd for C8H6BrN: 212.0089 $[M+H]^+$; Found: 212.0093.

3-Bromo-1-ethylindolin-2-one (3b)[5]:



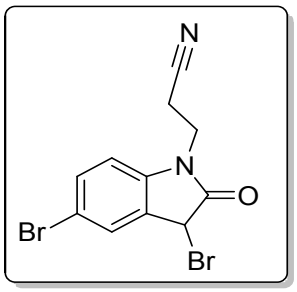
(3b): Colourless solid; mp: 144-146°C; Yield: 75 %; **IR (KBr):** 2978, 2935, 1715, 1615, 1477, 1430, 1338, 1266, 1194, 1106, 809, 745, 683 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.41 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.8, Hz, 1H), 7.10 (t, J = 7.8, 7.5 Hz, 1H), 6.84 (d, J = 7.5 Hz, 1H), 5.25 (s, 1H), 3.78 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 172.0, 142.8, 133.1, 130.2, 126.1, 123.1, 108.8, 38.7, 35.2, 12.4; **MS (ESI) *m/z* (%):** 240 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{10}H_{10}BrNO$: 241.0689 $[M+H]^+$; Found: 241.0695.

3,5-Bibromo-1-ethylindolin-2-one (3c):



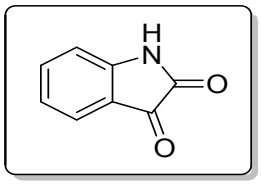
(3c): solid; mp: 160-162^{o}C; Yield: 60 %; **IR (KBr):** 2978, 2935, 1715, 1615, 1477, 1430, 1338, 1266, 1194, 1106, 809, 745, 683 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.53 (s, 1H), 7.46 (dd, J = 8.3 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 5.22 (s, 1H), 3.76 (m, 2H), 1.27 (t, J = 7.2, 7.3 Hz 3H) ; **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.3, 141.8, 133.1, 129.2, 115.5, 110.2, 128.1, 37.6, 35.4, 12.2;**MS (ESI) *m/z* (%):** 317 $[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{10}H_9Br_2NO$: 317.3521 $[M+H]^+$; Found: 317.3525.

3-(3,5-dibromo-2-oxoindolin-1-yl)propanenitrile (3d):



(3d): solid; mp: 154-156^{o}C; Yield: 62 %; **IR (KBr):** 3035, 2931, 2227, 1747, 1623, 1495, 1454, 1371, 1214, 1142, 1025, 957, 739, 697 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.57 (s, 1H), 7.50 (dd, J = 8.3, 8.4 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 5.27 (s, 1H), 4.01 (m, 2H), 2.78 (m, 2H) ; **^{13}C NMR (75 MHz, $CDCl_3$):** δ 169.3, 136.9, 134.5, 132.5, 129.5, 117.1, 116.5, 110.5, 42.4, 37.0, 16.1; **MS (ESI) *m/z* (%):** 343$[M+H]^+$; **HRMS-ESI**(*m/z*)Calcd for $C_{11}H_8Br_2N_2O$: 344.5632 $[M+H]^+$; Found: 344.5638.

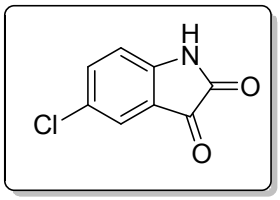
Indoline-2, 3-dione (4a)[6]:



(4a)orange solid; Yield: 84 %; **mp** 198-200 ^{o}C ; **IR (KBr):** 3189, 1728, 1615, 1460, 1328, 1269, 1196, 1091, 769, 658 cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$+d_6-DMSO):** δ 10.7 (s, 1H), 7.53-7.47 (m, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 8.1 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$+d_6-**

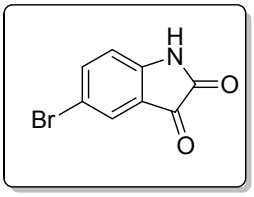
DMSO): δ 184.0, 159.2, 150.8, 138.0, 124.5, 122.8, 117.5, 112.2 ; **MS** (ESI): (m/z) = 170 $(M+Na)^+$. **HRMS** (ESI) $(M+Na)^+$ m/z calcd for $C_8H_5NO_2Na$ = 170.0212, found = 170.0212.

5-chloroindoline-2, 3-dione [6](4b):



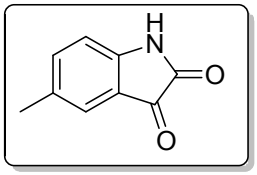
(4b) Orange solid; Yield: 81%; mp 256-258 ^oC :**IR(KBr)**: 3099, 2986, 1747, 1705, 1616, 1450, 1308, 1217, 1119, 845, 746. **^{1}H NMR (500 MHz, $CDCl_3$+d_6-DMSO):**δ 10.94 (s, 1H), 7.46 (m, 2H), 6.90 (d, 1H, J = 8.8 Hz). **^{13}C NMR (75 MHz, d_6-DMSO):** δ 112.9, 117.5, 123.4, 127.0, 136.5, 148.3, 158.0, 182.5. **MS** (ESI): (m/z) = 204 $(M+Na)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_8H_5ClNO_2$ = 182.0003, found = 182.0003.

5-bromoindoline-2, 3-dione[6] (4c):



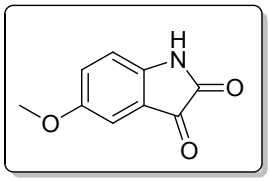
(4c) pale yellow solid; Yield: 85 %; **mp**248-250 ^oC; **IR (KBr):** 3204, 1750, 1709, 1613, 1446, 1269, 1208, 1121, 843, 680 cm^{-1} ; **^{1}H NMR (300 MHz, $CDCl_3$+d_6-DMSO):** δ 10.94 (s, 1H), 7.46 (m, 2H), 6.90 (d, J = 8.8 Hz, 1H); **^{13}C NMR (75 MHz, $CDCl_3$+d_6-DMSO):**δ 182.4, 158.0, 148.7, 139.8, 126.4, 117.9, 114.5, 113.8; **MS** (ESI): (m/z) = 248 $(M+Na)^+$. **HRMS** (ESI) $(M+1)^+$ m/z calcd for $C_8H_5BrNO_2$ = 225.9498, found = 225.9498.

5-methylindoline-2, 3-dione [6](4d):



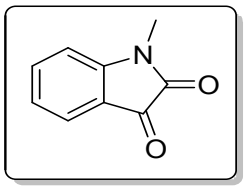
(4d) Orange solid; Yield: 80 %; mp 183-184 ^{o}C. **IR (KBr):** 3286, 1744, 1490, 1302, 1191, 1126, 830, 656 cm^{-1}. **^{1}H NMR (300 MHz, CDCl$_3$+d$_6$-DMSO):** δ 10.5 (s, 1H), 7.3 (s, 2H), 6.80 (d, 1H, J = 8.1 Hz), 2.3 (s, 3H). **^{13}C NMR (75 MHz, d$_6$-DMSO):** δ 184.2, 159.3, 148.1, 138.5, 132.2, 124.7, 117.2, 111.8, 20.0. **MS** (ESI): (m/z) = 184(M+Na)$^{+}$. **HRMS** (ESI) (M+Na)$^{+}$ m/z calcd for $C_9H_7NO_2Na$ = 184.0369, found = 184.0369.

5-methoxyindoline-2, 3-dione[6] (4e):



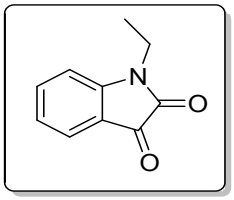
(4e) yellow solid; Yield: 81 %; **mp**196-198 ^{o}C; **IR (KBr):** 2854, 2925, 1733, 1606, 1491, 1241, 1032, 981, 824, 739 cm^{-1} ; **^{1}H NMR (300 MHz, CDCl$_3$+d$_6$-DMSO):** δ 10.6 (s, 1H), 7.53 (s, 1H), 7.1 (m, 1H), 6.84 (d, 1H, J = 8.4 Hz), 3.79 (s, 3H); **^{13}C NMR (75 MHz, CDCl$_3$+d$_6$-DMSO):**δ 183.6, 158.4, 154.4, 143.6, 123.8, 116.6, 112.1, 107.4, 54.3; **MS** (ESI): (m/z) = 200 (M+Na)$^{+}$. **HRMS** (ESI) (M+Na)$^{+}$ m/z calcd for $C_8H_4N_2O_4$ = 200.0318, found = 200.0319.

1-methylindoline-2, 3-dione[6] (4f):



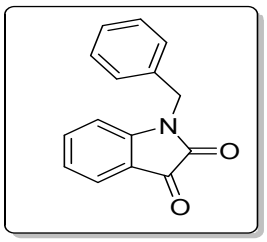
(4f) orange solid; Yield: 78 %; **mp** 134-136 ^{o}C; **IR (KBr):** 2940, 1726, 1606, 1469, 1326, 1159, 1089, 756, 474cm^{-1} ; **^{1}H NMR (300 MHz, CDCl$_3$+d$_6$-DMSO):** δ 7.66-7.58 (m, 2H), 7.15 (t, 1H, J = 7.5 Hz), 6.94 (d, 1H, J = 7.9 Hz), 3.26 (s, 3H); **^{13}C NMR (75 MHz, CDCl$_3$+d$_6$-DMSO):** δ 182.8, 157.6, 150.8, 137.9, 124.4, 123.2, 116.8, 109.5, 25.6; **MS** (ESI): (m/z) = 184 (M+Na)$^{+}$. **HRMS** (ESI) (M+H)$^{+}$ m/z calcd for $C_9H_8NO_2$ = 162.0549, found = 162.0549.

1-ethylindoline-2, 3-dione[6] (4g):



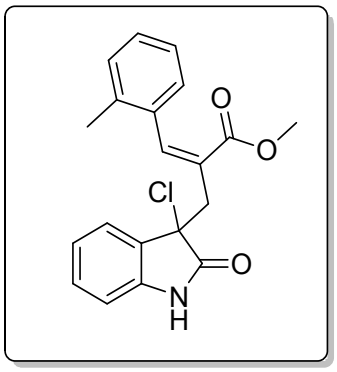
(4g) orange solid, Yield: 80 %, mp 94-96 ^{o}C; **IR(KBr):** 2987, 1727, 1609, 1469, 1352, 1288, 1091, 1051, 868, 759, 472 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$+d_6-DMSO):δ 7.65-7.57 (m, 2H), 7.13 (t, 1H, *J* = 7.5 Hz), 6.96 (d, 1H, *J* = 7.9 Hz), 3.79 (q, 2H), 1.32 (t, 3H, *J* = 7.3 Hz). **^{13}C NMR** (100 MHz, d_6-DMSO): δ 11.8, 34.2, 109.6, 116.8, 123.0, 124.6, 137.9, 149.9, 157.1, 183.1. **MS** (ESI): (m/z) = 198 $(M+Na)^+$. **HRMS** (ESI) $(M+H)^+$ m/z calcd for $C_{10}H_{10}NO_2$ = 176.0706, found = 176.0703.

1-benzylindoline-2, 3-dione[6] (4h):



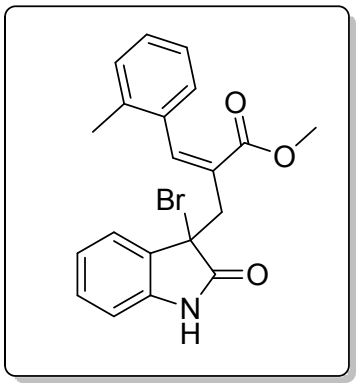
(4h) yellow solid; Yield: 75 %; **mp** 136-138 ^{o}C; **IR (KBr):** 3028, 1732, 1611, 1468, 1346, 1174, 1075, 750, 692,469cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$+d_6-DMSO):** *δ* 7.62 (d, 1H, *J* = 6.7 Hz), 7.48 (t, 1H, *J* = 7.7 Hz), 7.34 (s, 5H), 7.09 (t, 1H, *J* = 7.5 Hz), 6.78 (d, 1H, *J* = 8.1 Hz), 4.93 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$+d_6-DMSO):** *δ* 182.5, 157.5, 149.9, 137.7, 133.9, 128.2, 127.3, 126.6, 124.4, 123.1, 116.7, 110.4, 43.1; **MS** (ESI): (m/z) = 260 $(M+Na)^+$. **HRMS** (ESI) $(M+1)^+$ m/z calcd for $C_{15}H_{12}NO_2$ = 238.0868, found = 238.0881.

(Z)-methyl 2-((3-chloro-2-oxoindolin-3-yl)methyl)-3-(o-tolyl)acrylate (5a):



(5a) solid; mp: 120-122°C; Yield: 85%; IR (KBr): 3128, 2923, 2812, 1850, 1760, 1620, 1525, 1471, 1342, 1292, 1143, 1073, 959, 843, 744cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):**δ 9.0 (d, J = 7.4 Hz, 1H), 7.99 (s, 1H), 7.19 (t, J = 7.7 Hz, 1H), 7.15-7.09 (m, 4H), 6.79 (t, J = 7.9,7.4 Hz, 1H), 6.42 (d, J = 7.7 Hz, 1H), 4.82 (s, 2H) , 3.78 (s, 3H), 2.18 (s, 3H), **^{13}C NMR (75 MHz, $CDCl_3$):**δ 167.2, 166.8, 143.9, 137.7, 133.4, 130.2, 130.0, 128.8, 128.4, 128.4, 125.9, 125.5, 124.9, 121.9, 110.8, 108.2, 52.2, 36.9, 29.6, 19.6; **MS (ESI) *m/z* (%):** 353 $[M+H]^+$; HRMS-ESI(*m/z*)Calcd for $C_{20}H_{18}O_3NCl$: 353.1515 $[M+H]^+$; Found: 353.1515.

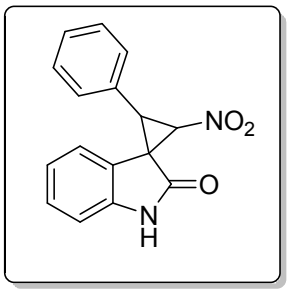
(Z)-methyl 2-((3-bromo-2-oxoindolin-3-yl)methyl)-3-(*o*-tolyl)acrylate (7a):



(7a) solid; mp: 120-122°C; Yield: 81%; IR (KBr): 3128, 2923, 2812, 1850, 1760, 1620, 1525, 1471, 1342, 1292, 1143, 1073, 959, 843, 744cm^{-1}; **^{1}H NMR (300 MHz, $CDCl_3$):**δ 9.0 (d, J = 7.9, 8.8 Hz, 1H), 7.99 (s, 1H), 7.19 (t, J = 7.7, 8.8 Hz, 1H), 7.15-7.09 (m, 4H), 6.79 (t, J = 7.9, 8.6 Hz, 1H), 6.42 (d, J = 7.7 Hz, 1H), 4.82 (s, 2H) , 3.78 (s, 3H), 2.18 (s, 3H), **^{13}C NMR (75 MHz, $CDCl_3$):**δ 167.2, 166.8, 143.9, 137.7, 133.4, 130.2, 130.0, 128.8, 128.4, 128.4, 125.9, 125.5,

124.9, 121.9, 110.8, 108.2, 52.2, 36.9, 29.6, 19.6; **MS (ESI) *m/z* (%):** 400 $[M+H]^+$; **HRMS-ESI(*m/z*):** Calcd for $C_{20}H_{18}O_3BrN$: 401.1535 $[M+H]^+$; Found: 401.1540.

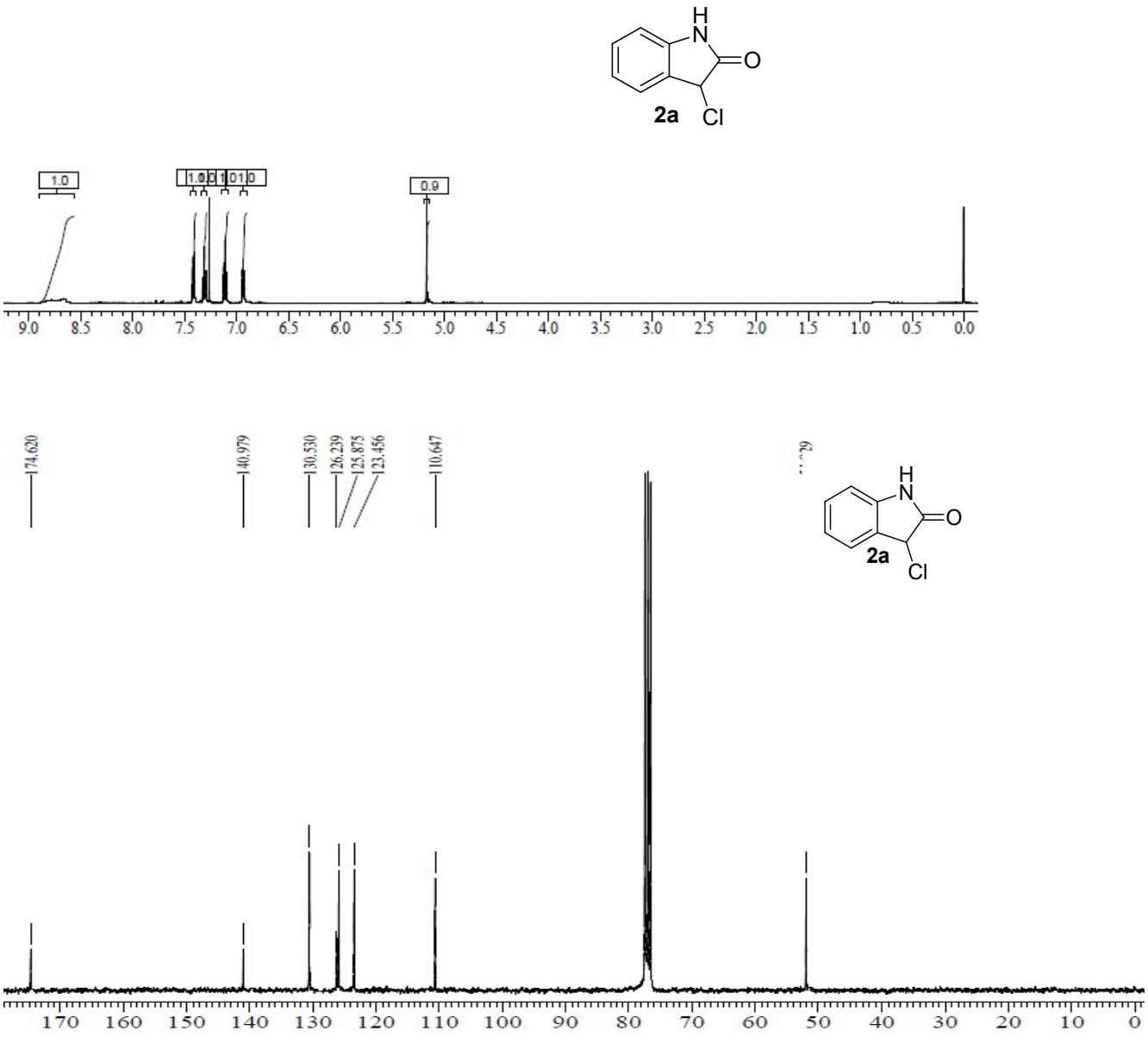
(6a)2-Nitro-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-one[7]:



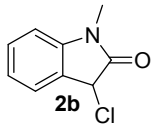
(6a) Solid; Yield: 58%; **^{1}H NMR (500 MHz, CDCl3):**δ 4.35 (d, J = 6.3 Hz, 1H), 5.46 (d, J = 6.3 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 7.10 (t, J = 7.9 Hz, 1H), 7.29-7.34 (m, 6H), 7.38 (d, J = 7.6 Hz, 1H), 8.34 (br s, 1H); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 40.4, 41.8,72.0, 110.3, 122.5, 122.9, 123.4, 128.4, 128.5, 128.8, 129.0, 129.8, 141.4, 171.4; **MS (ESI) *m/z* (%):**279.

4. ^{1}H NMR and ^{13}C NMR Spectra of the Products

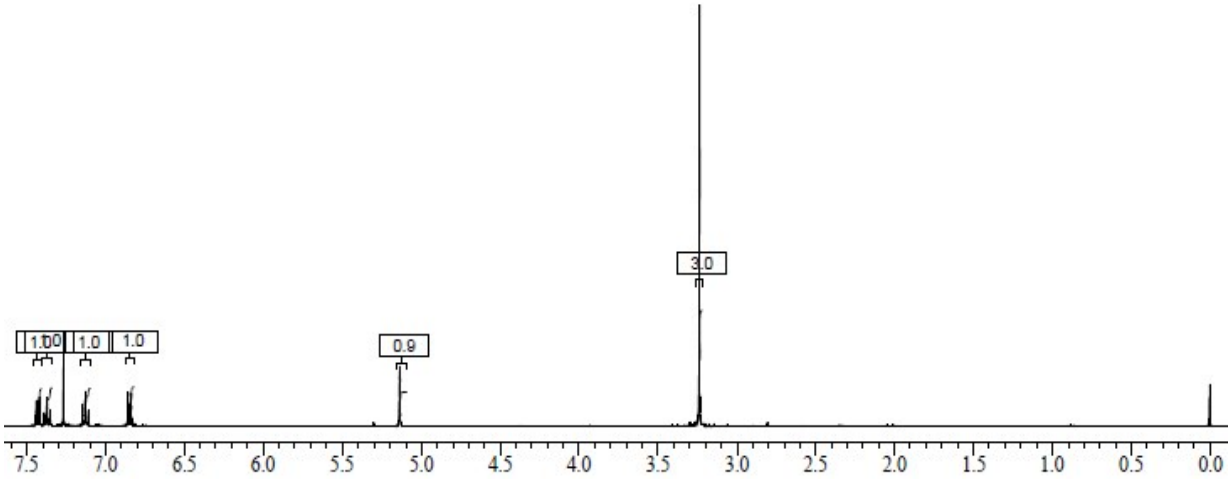
^{1}H &^{13}CNMR of compound 2a:



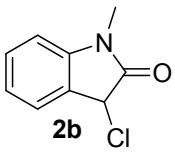
^{1}H &^{13}C NMR of compound 2b:


N
O
Cl

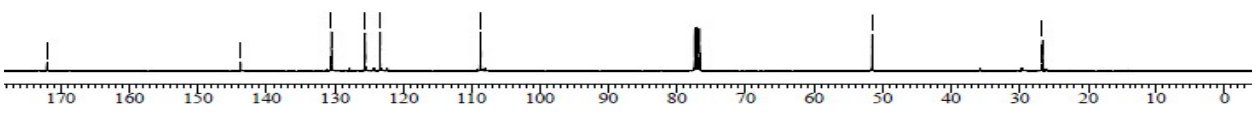
2b


1.00
1.0
1.0
0.9
3.0
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

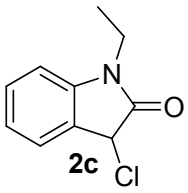

171.947
143.691
130.409
125.560
125.494
123.294
108.626
51.403
26.581

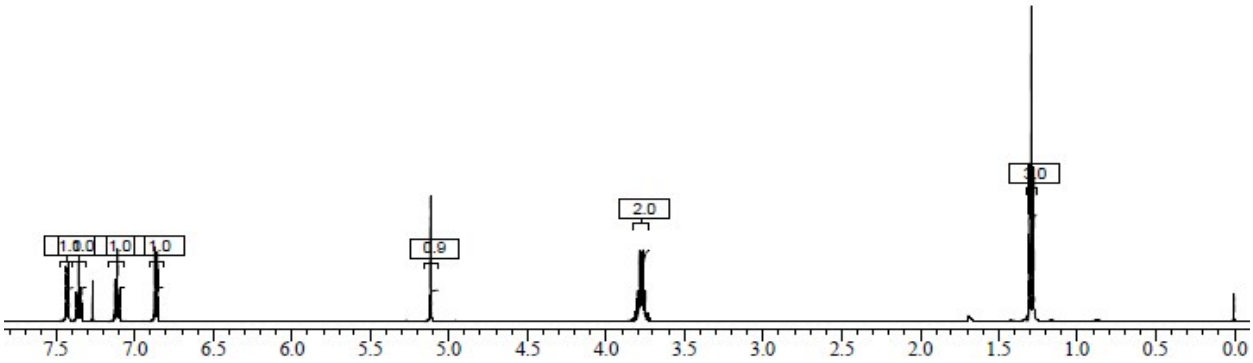

N
O
Cl

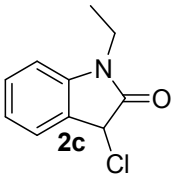
2b

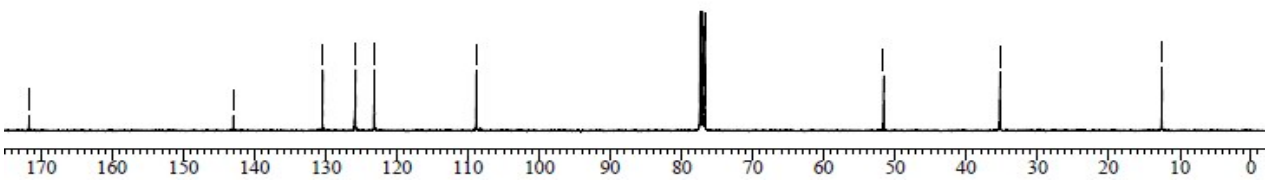

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H &^{13}C NMR of compound 2c:

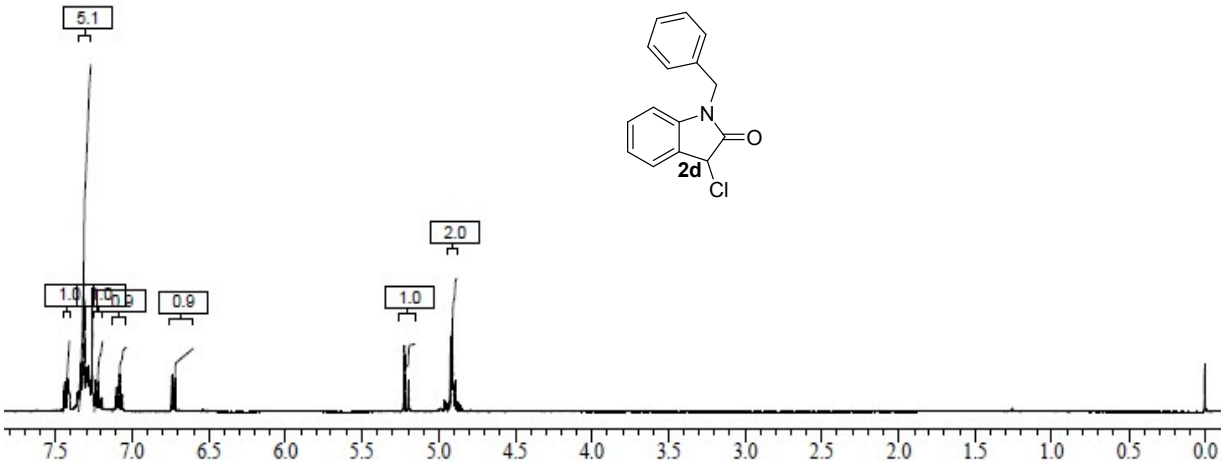


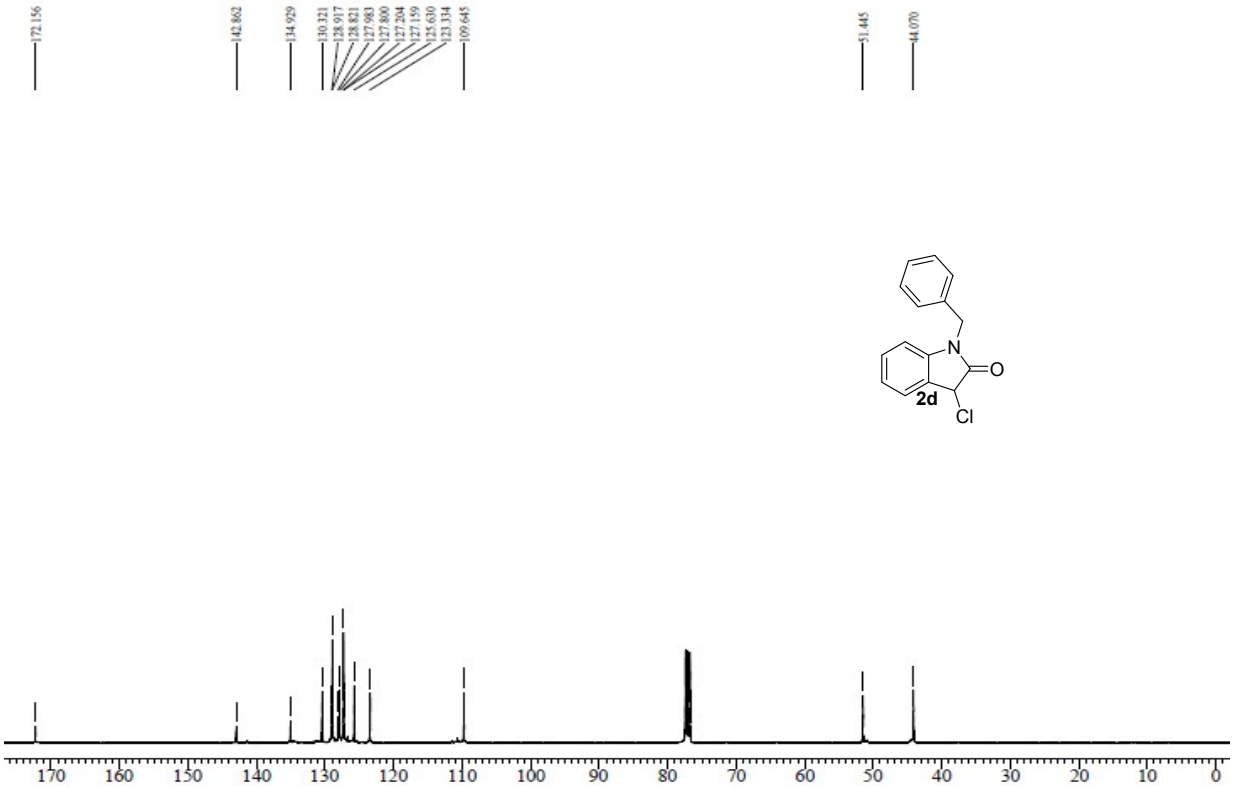




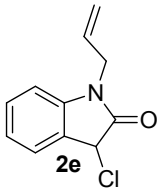


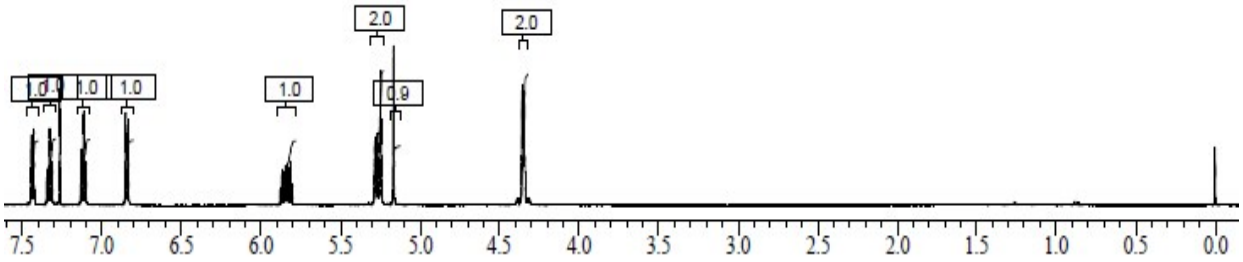
^{1}H &^{13}C NMR of compound 2d:

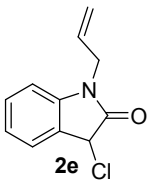


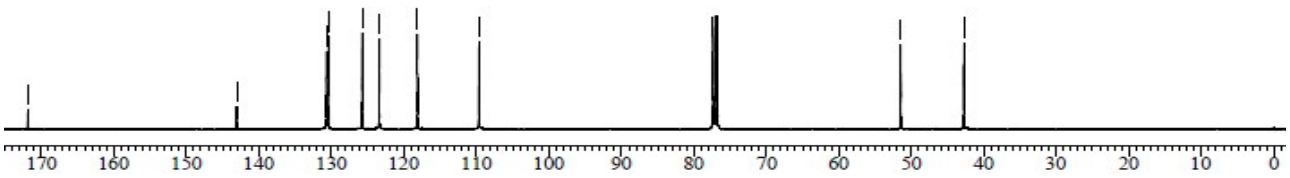


^{1}H &^{13}C NMR of compound 2e:









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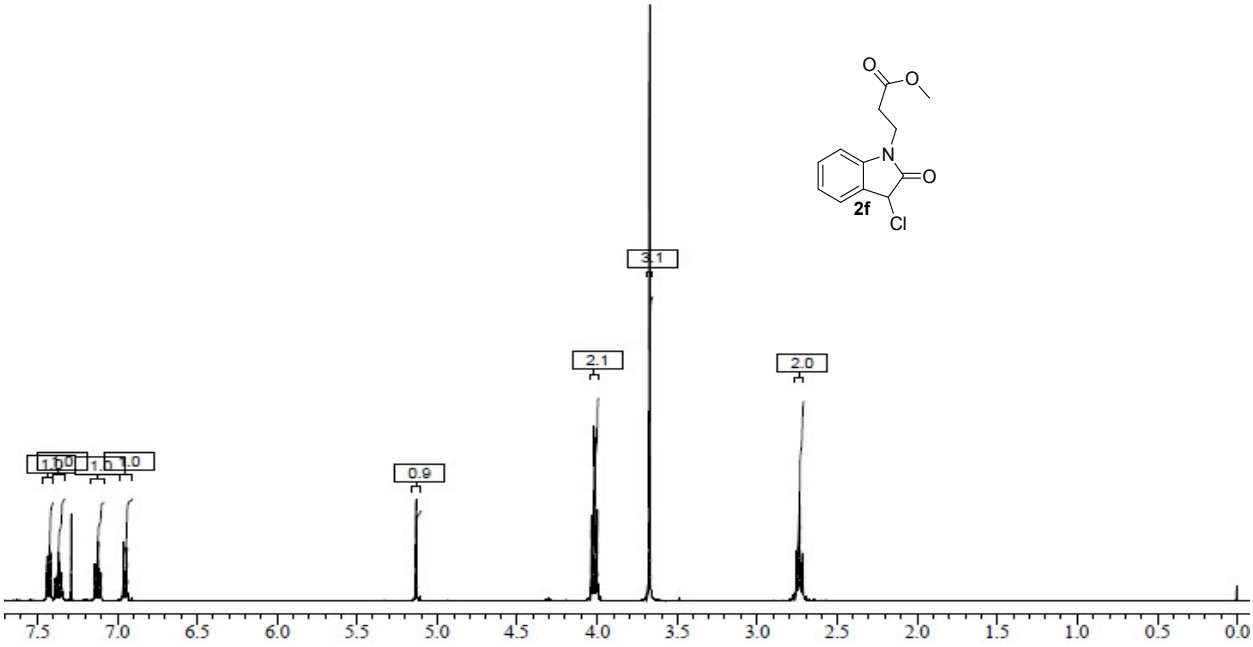

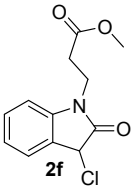

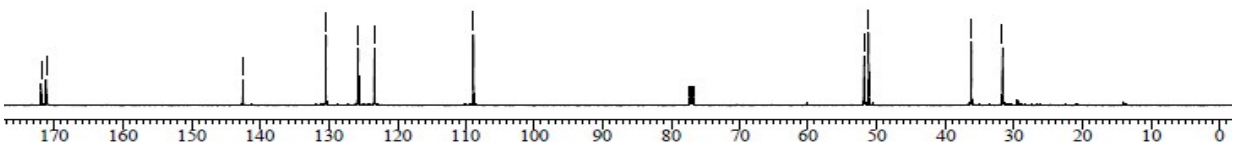

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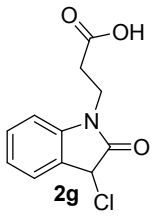
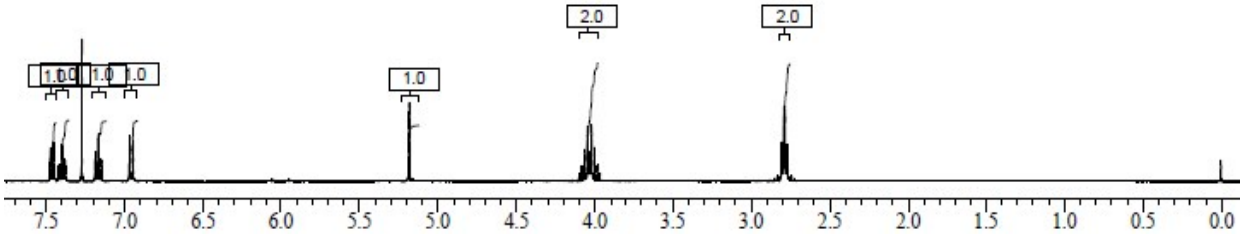
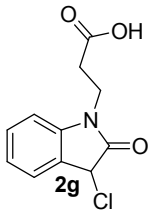
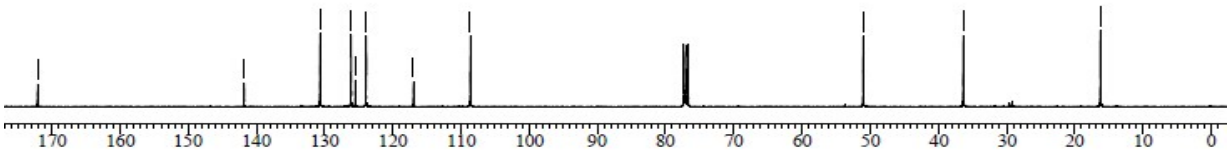
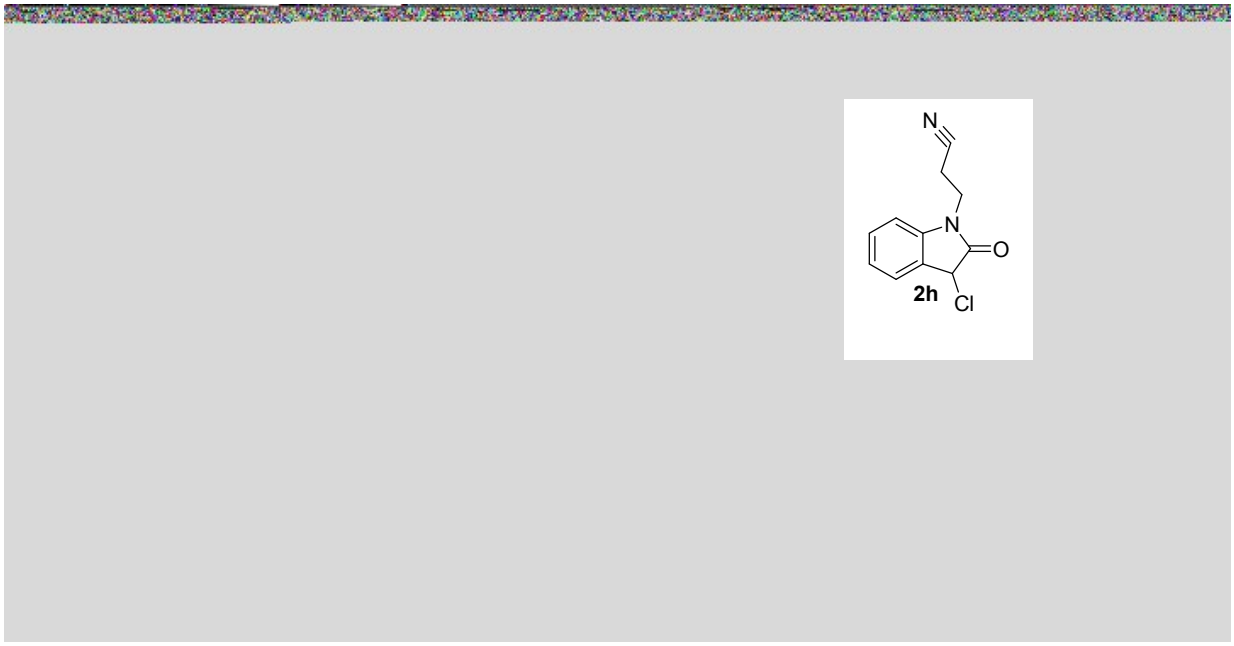


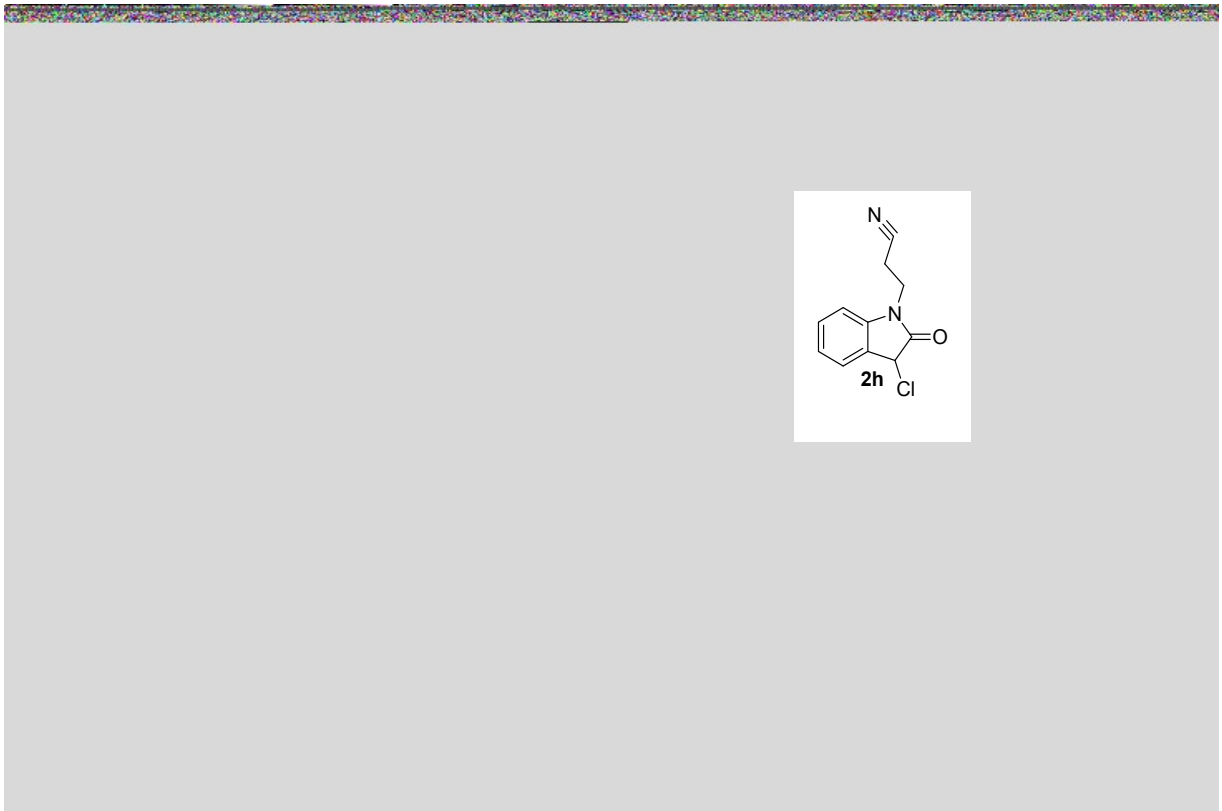






^{1}H &^{13}C NMR of compound 2h:





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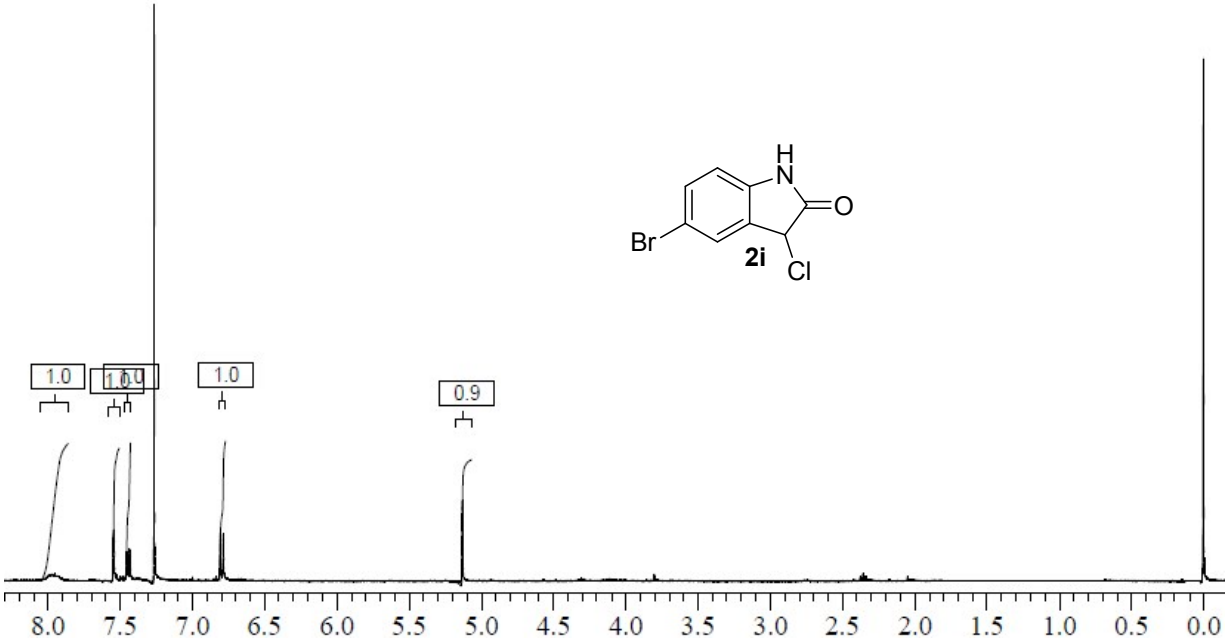

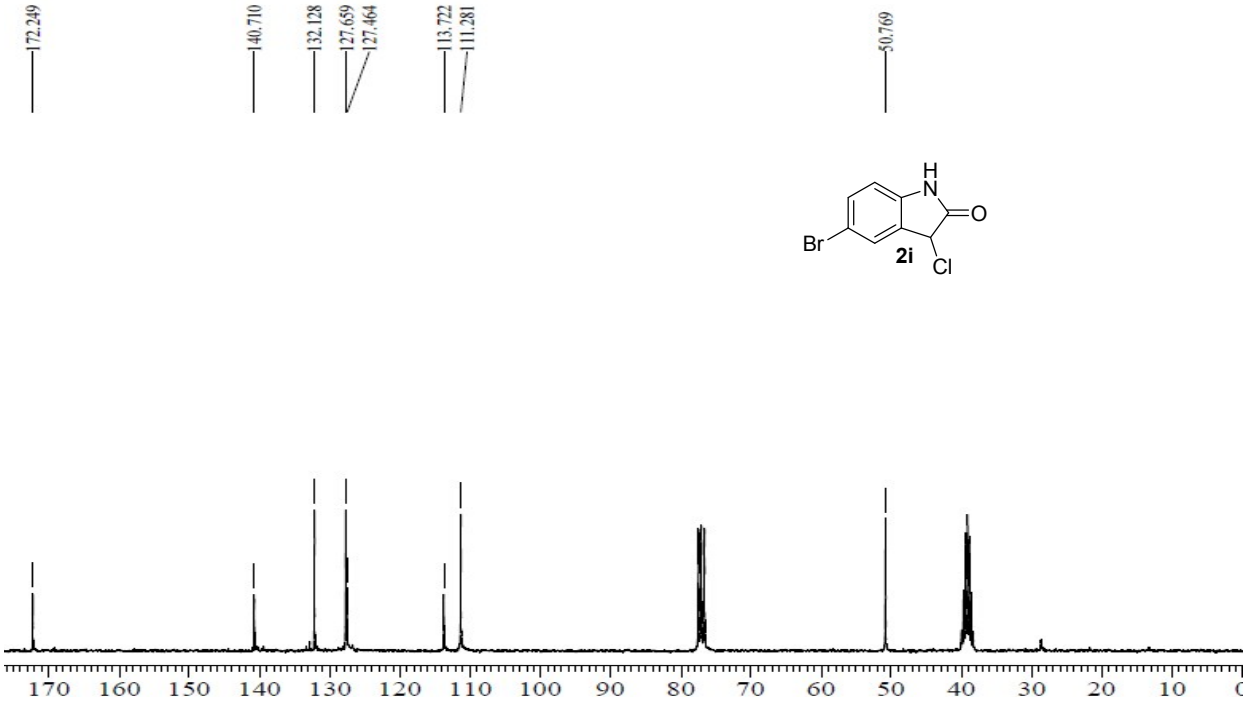

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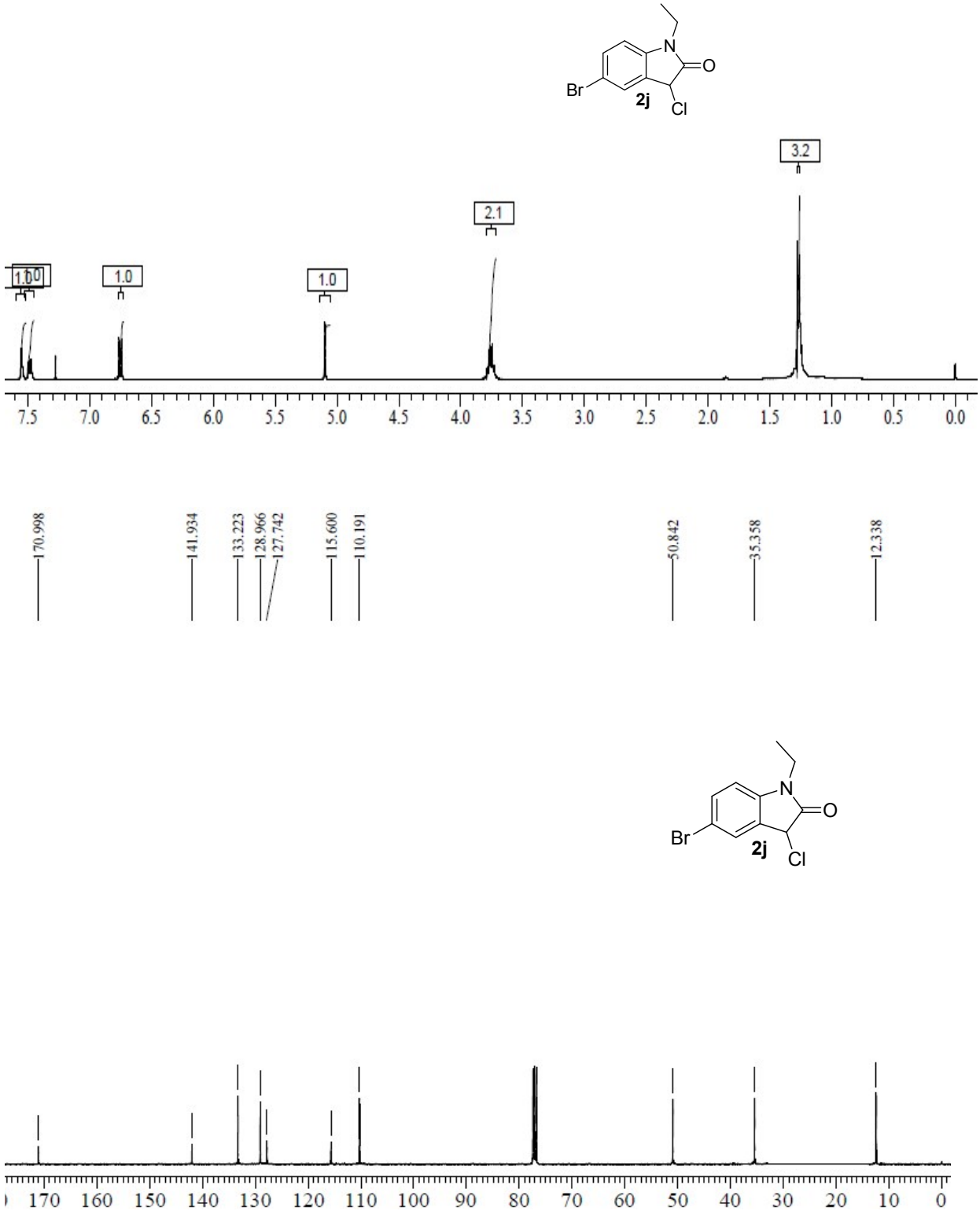

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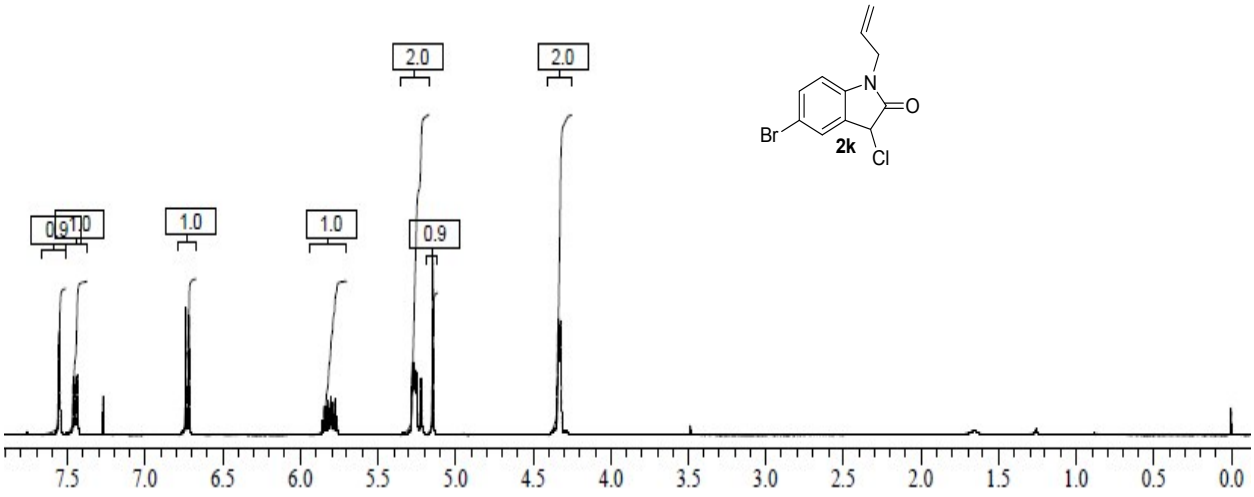

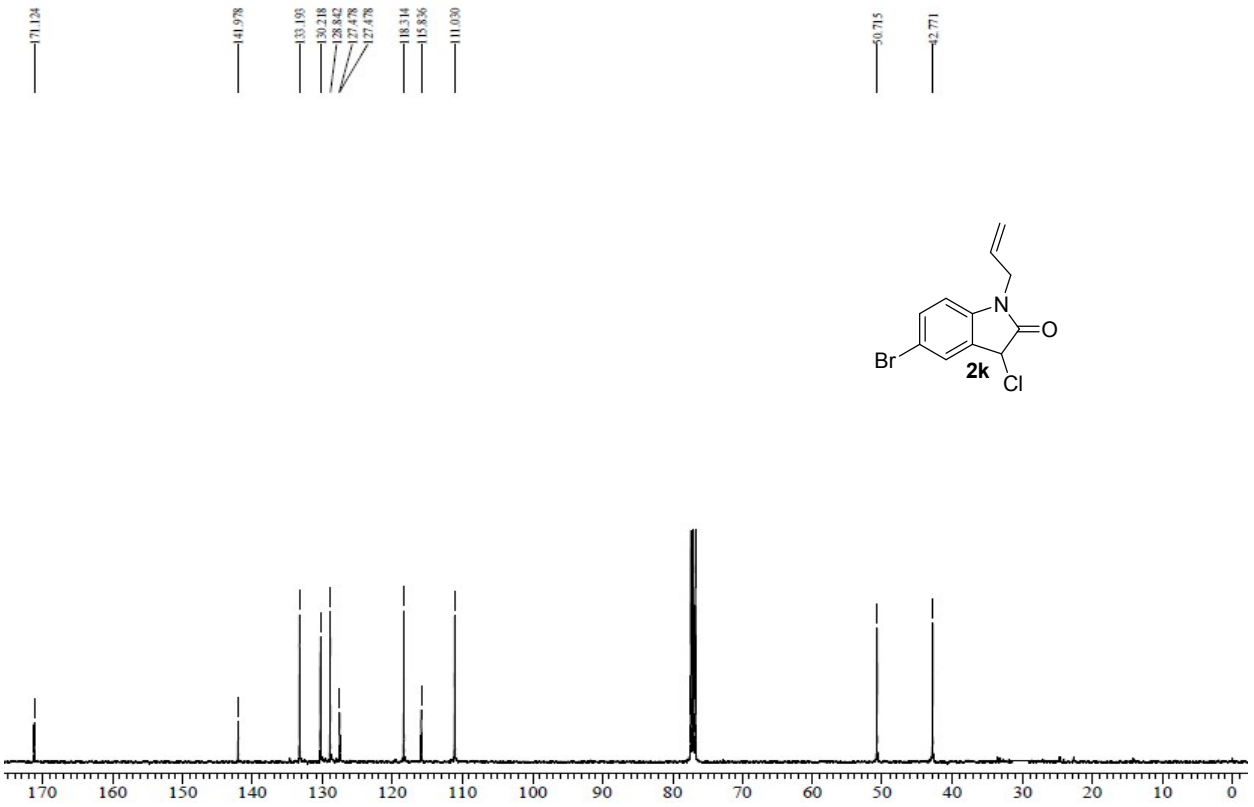

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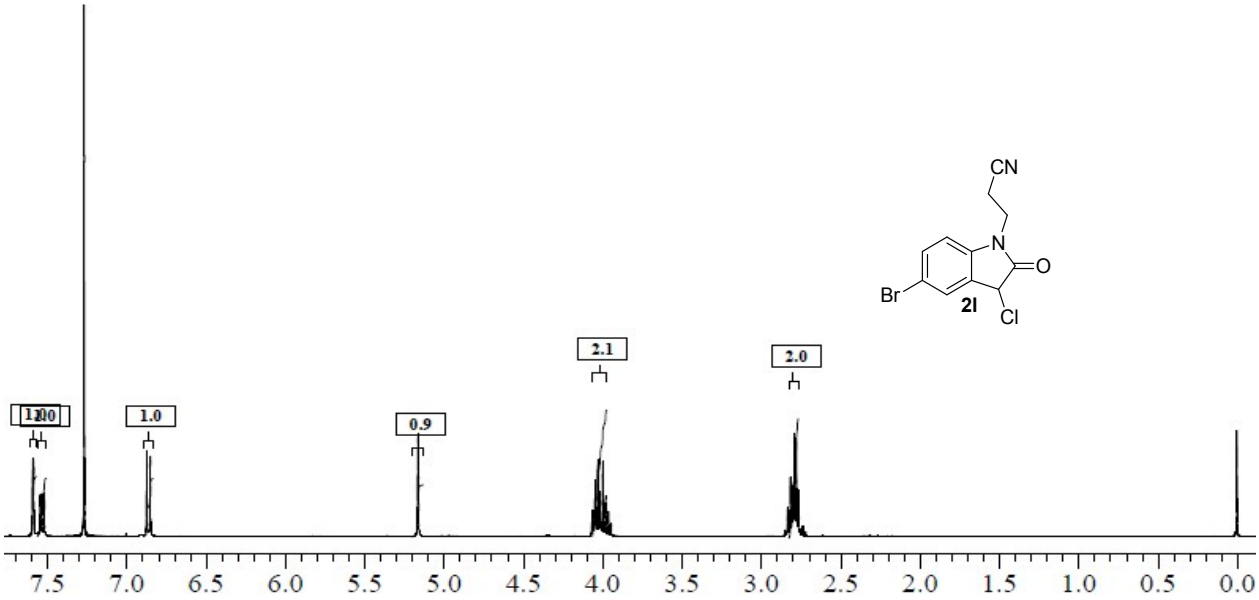

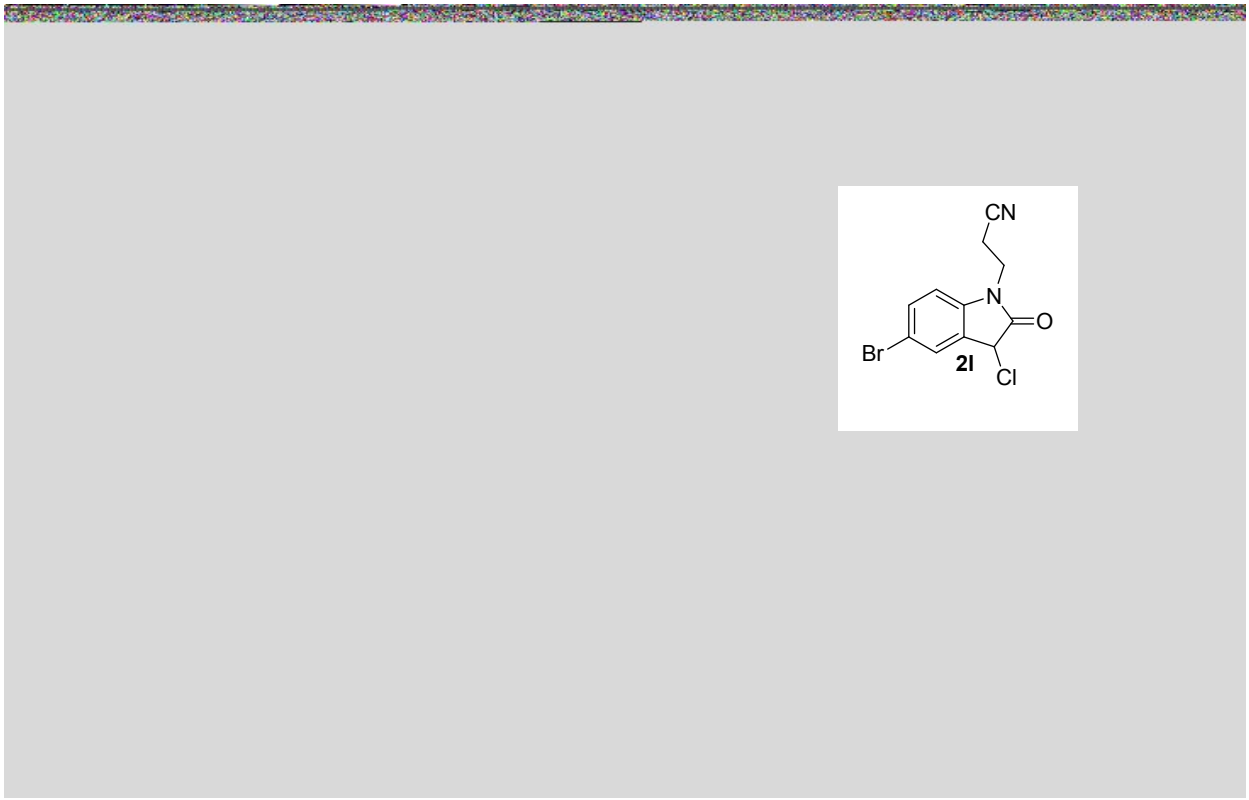

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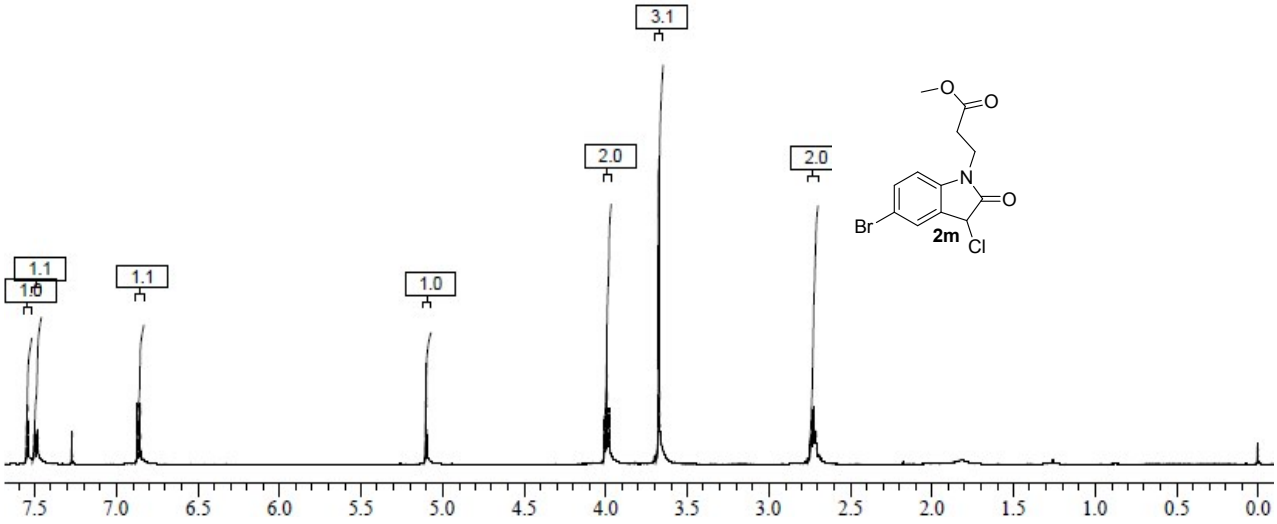

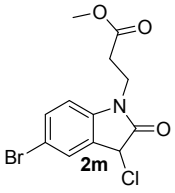

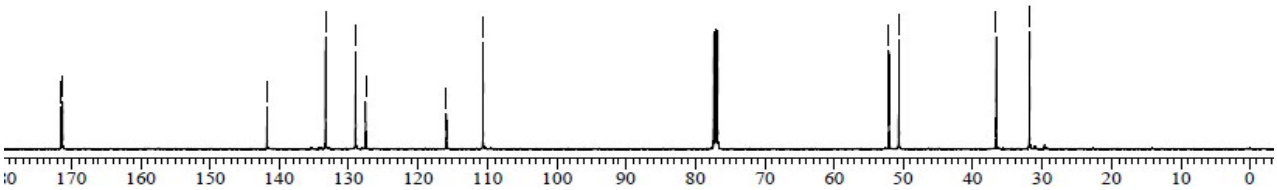

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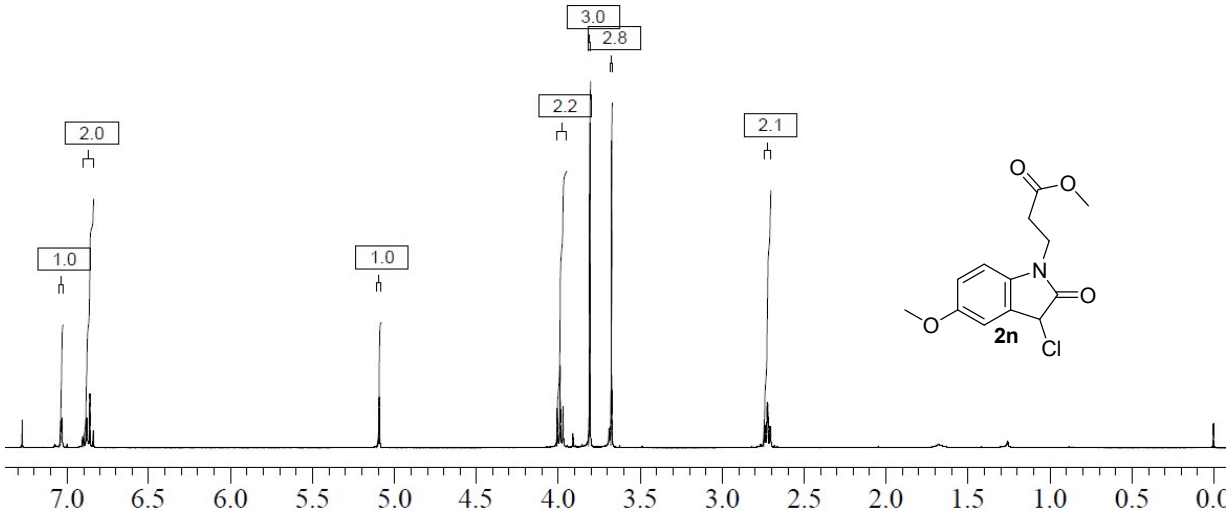
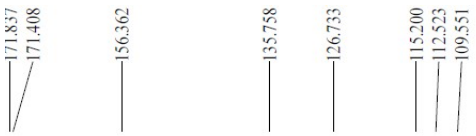
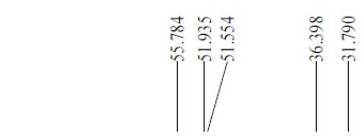
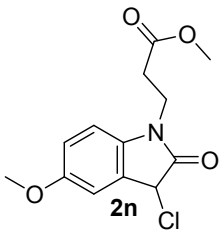
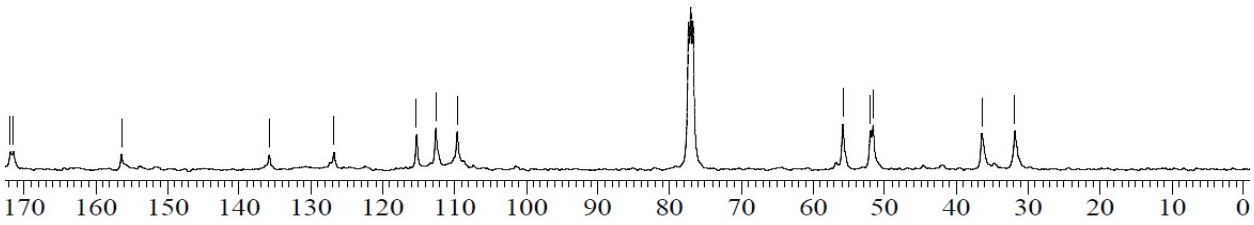


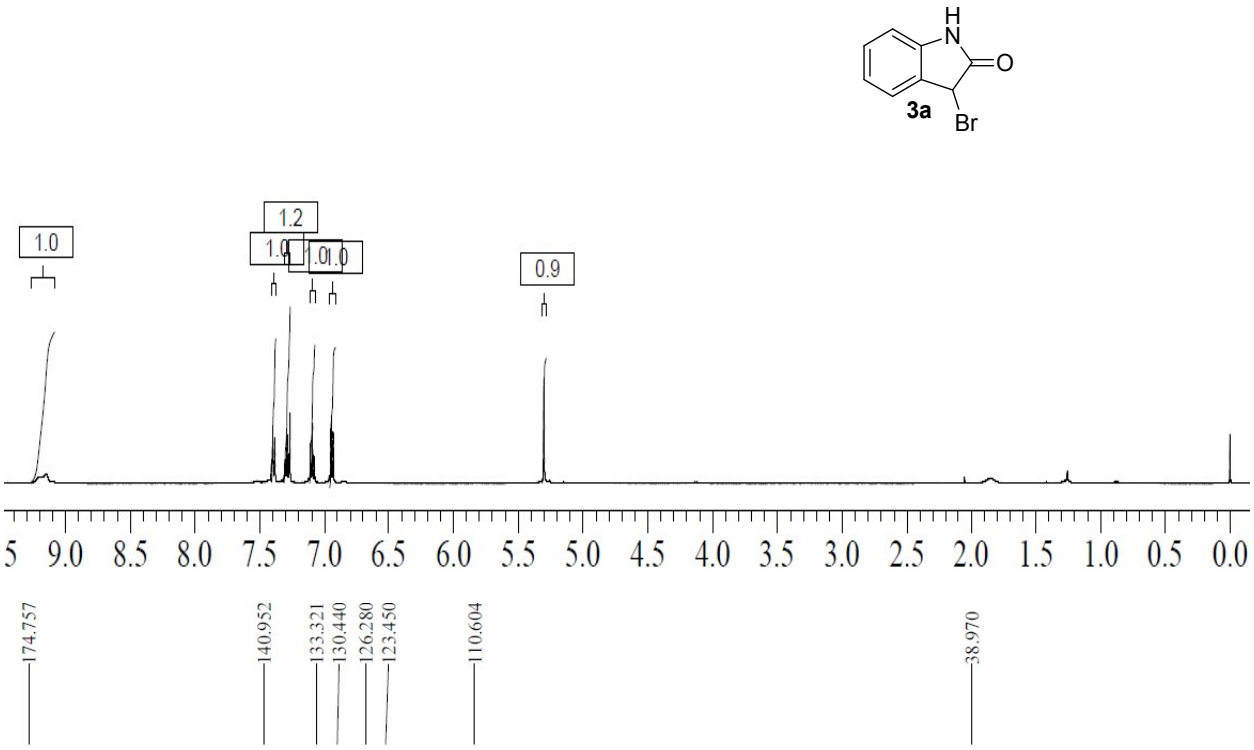


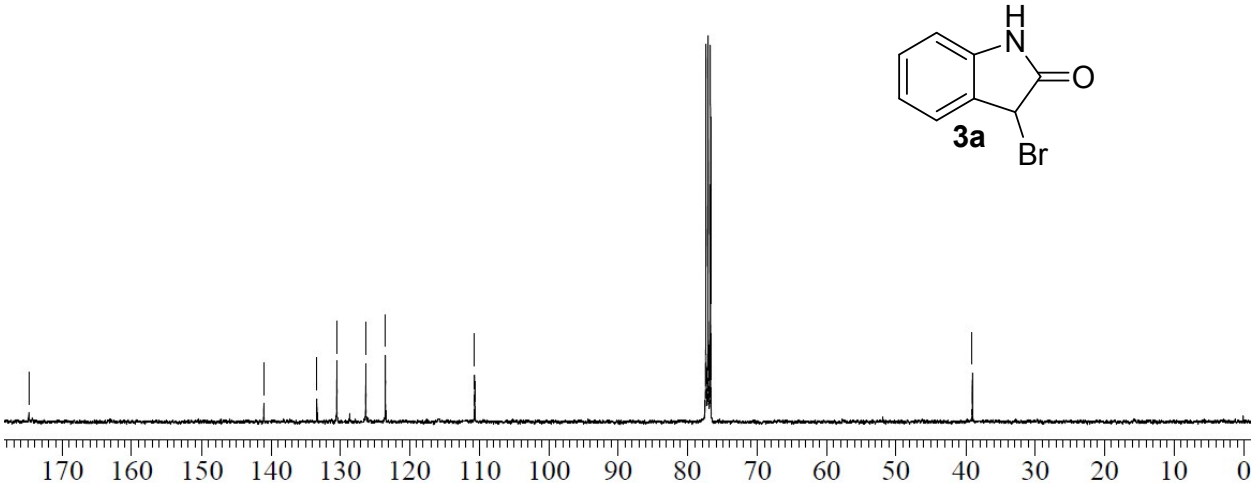






^{1}H &^{13}C NMR of compound 3a:





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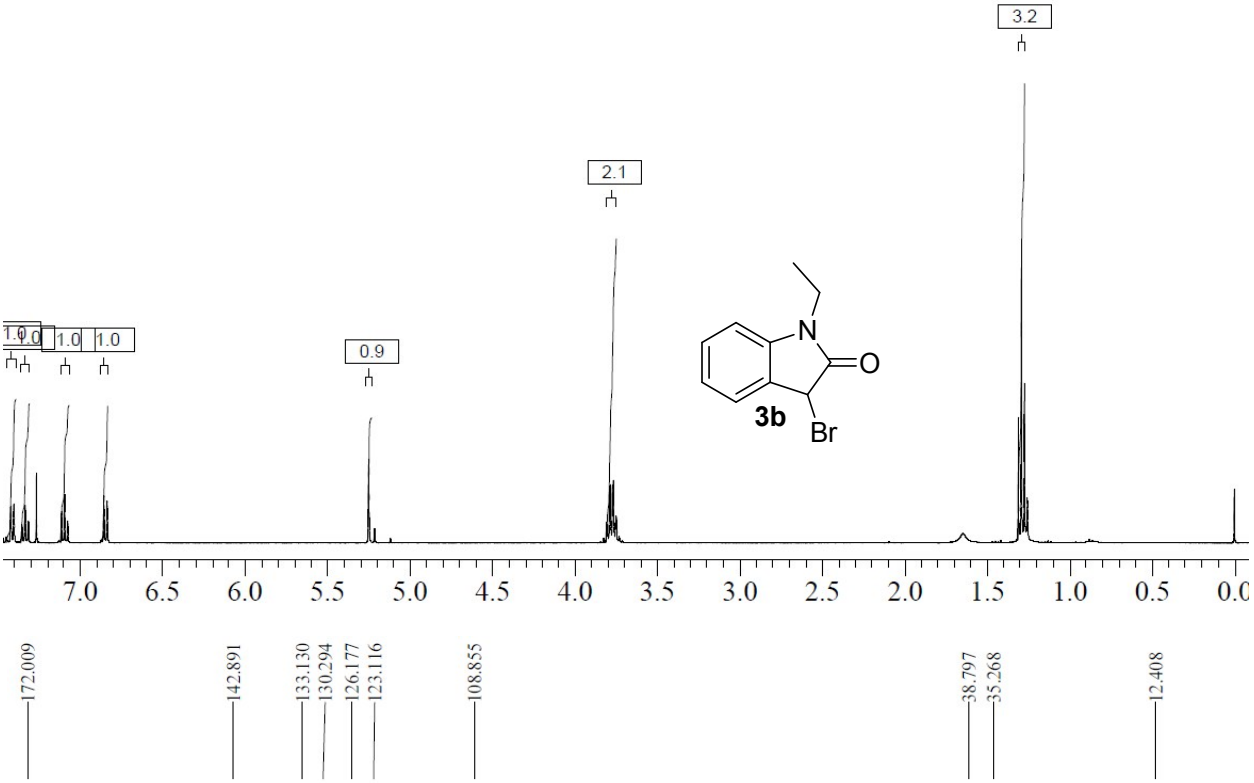

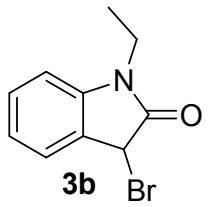

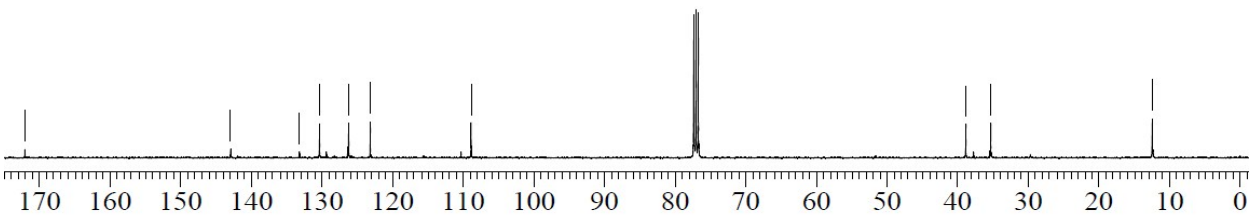

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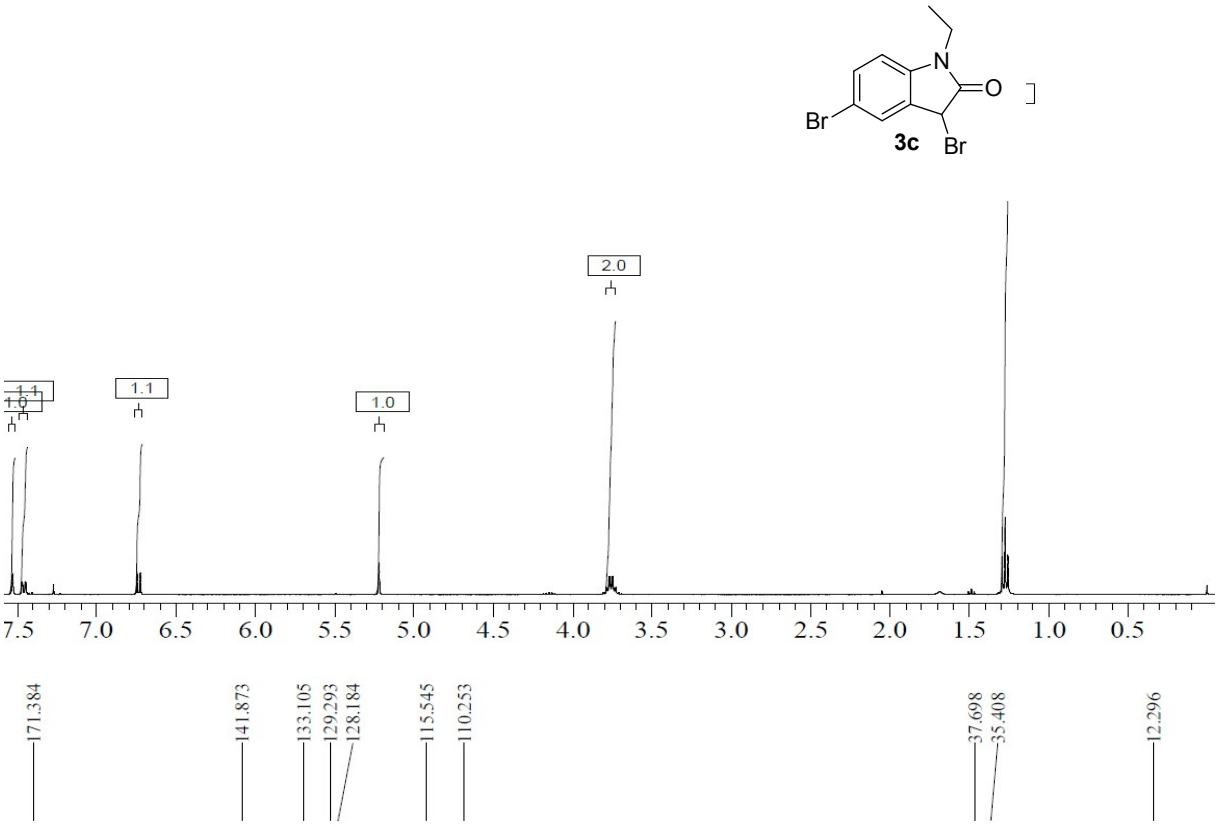

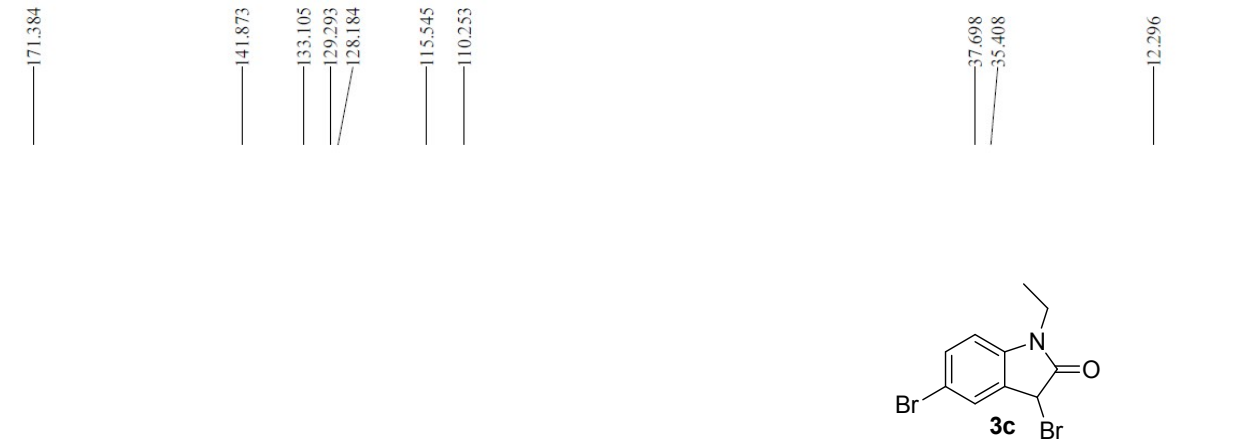

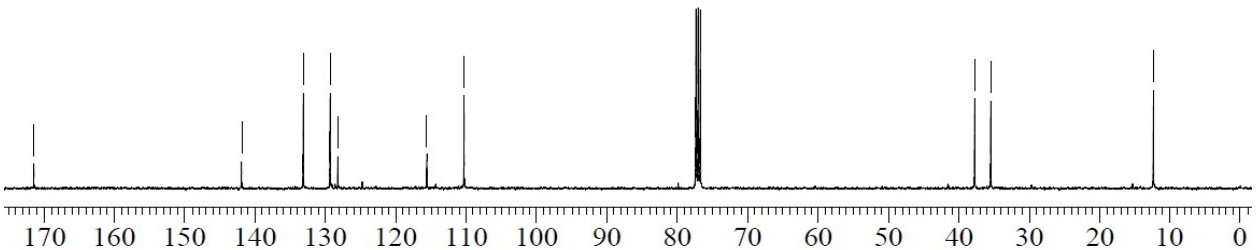

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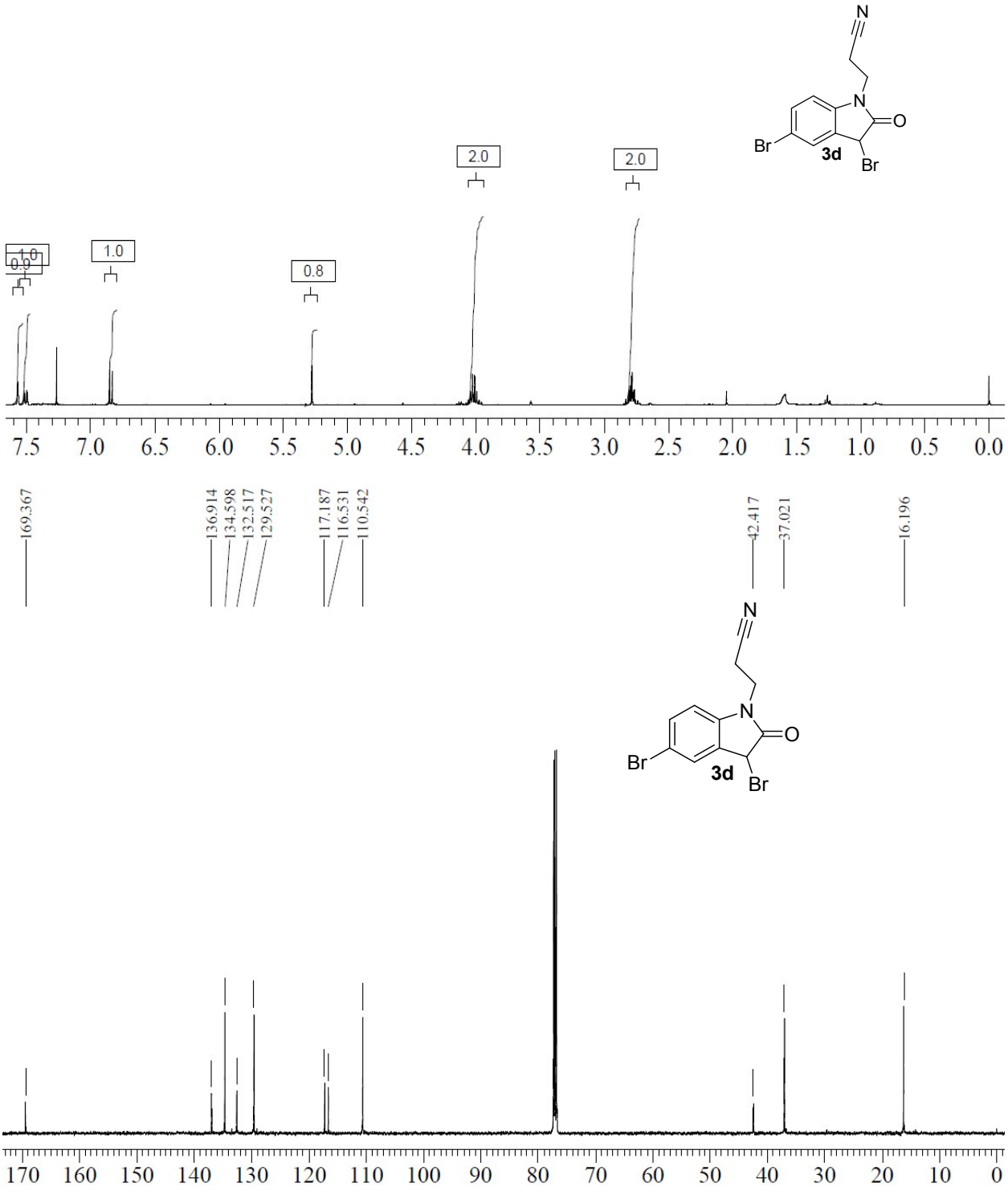
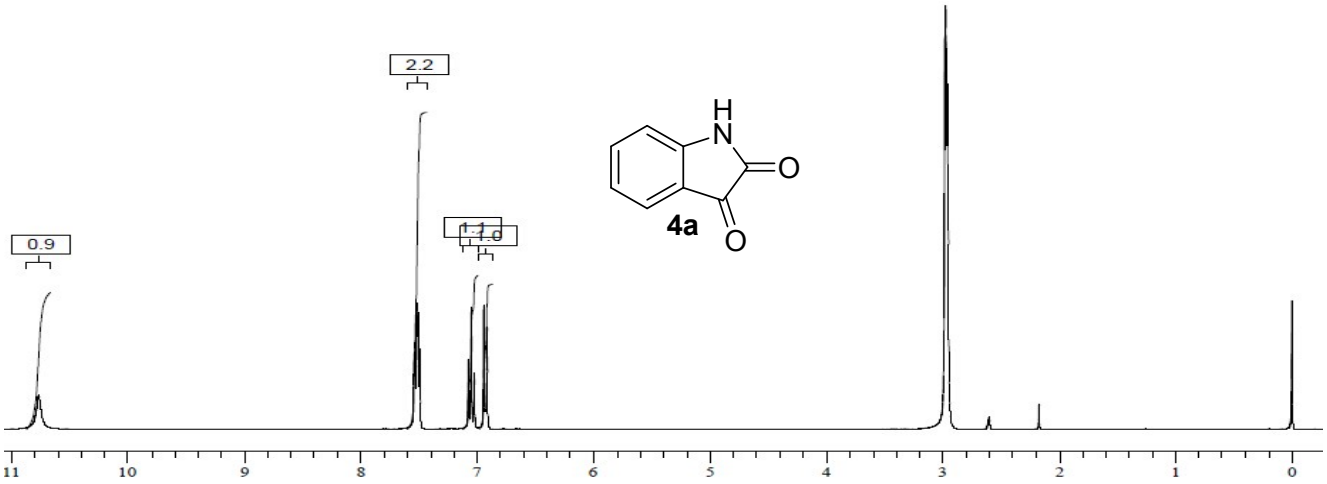
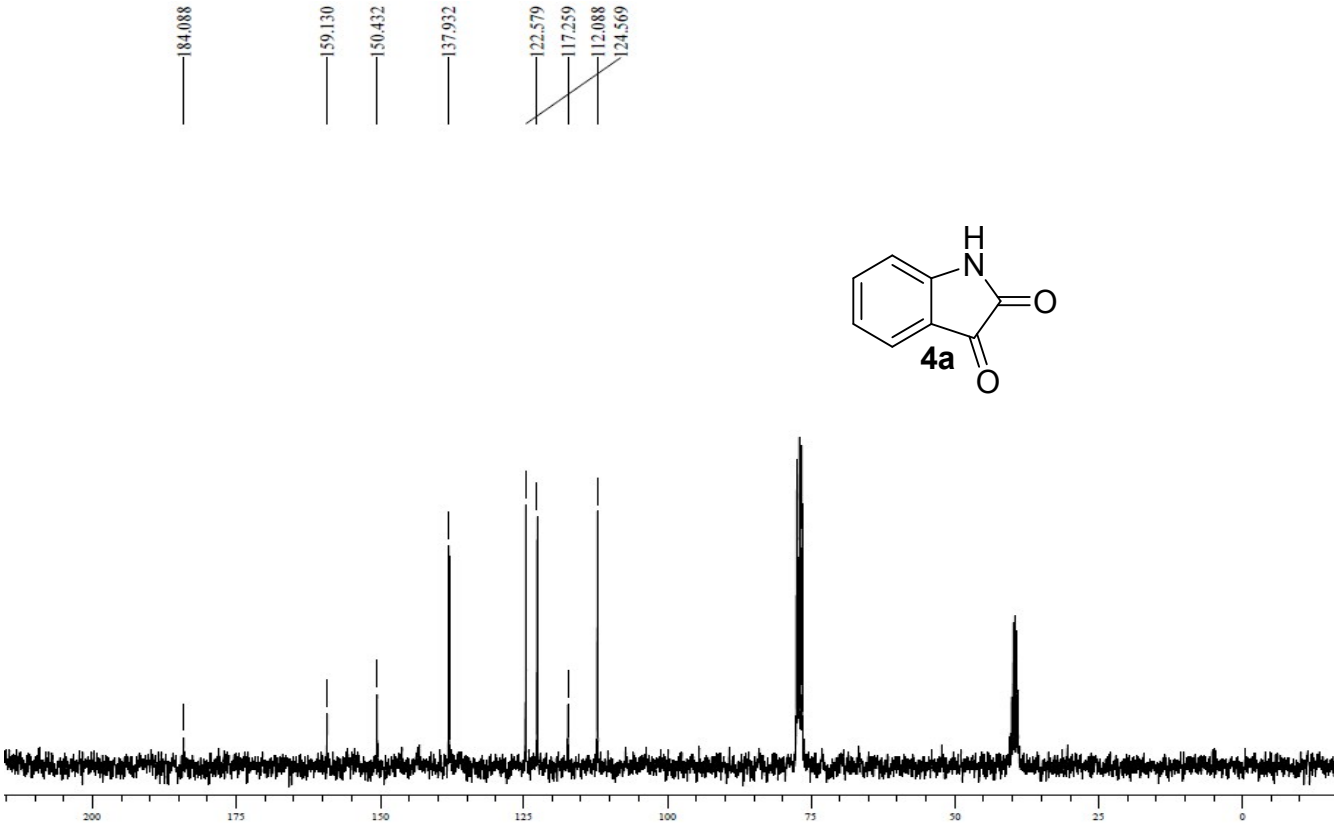


^{1}H &^{13}C NMR of compound 4a:





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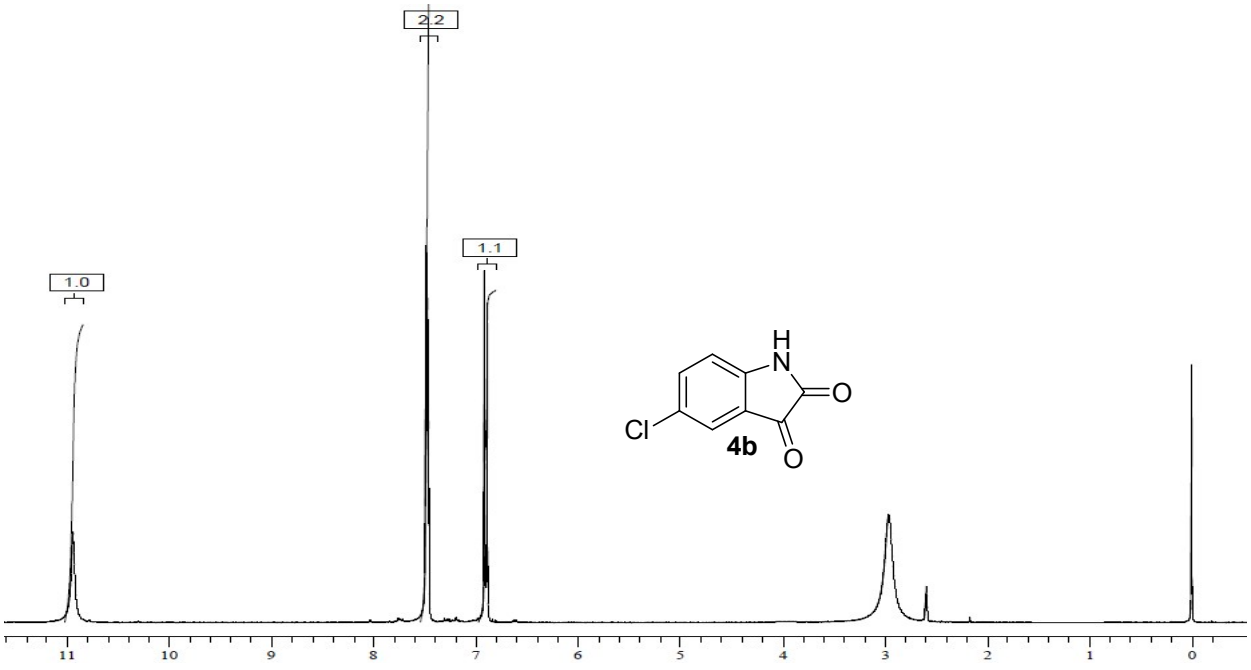

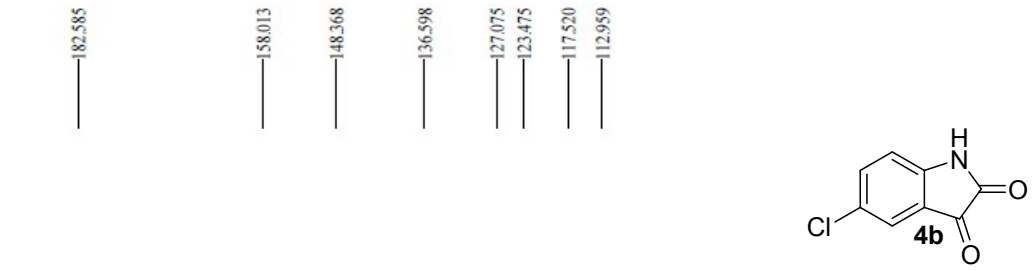

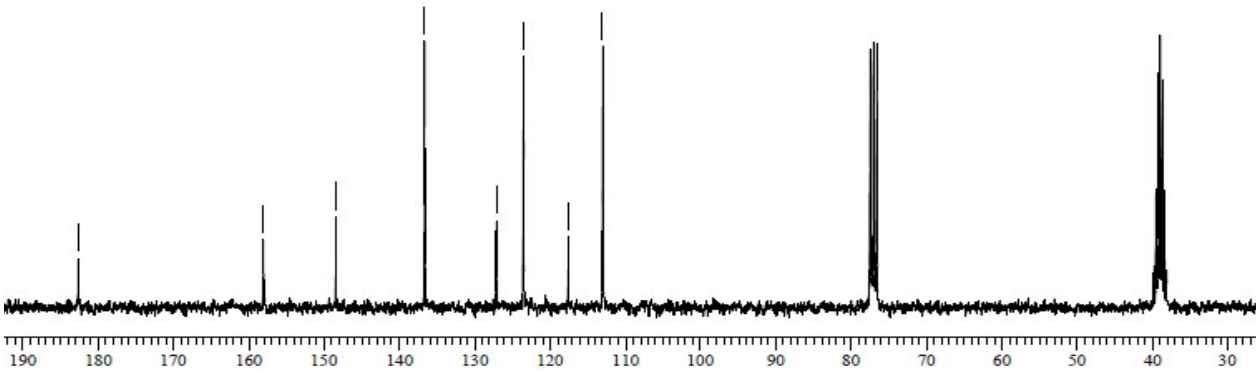

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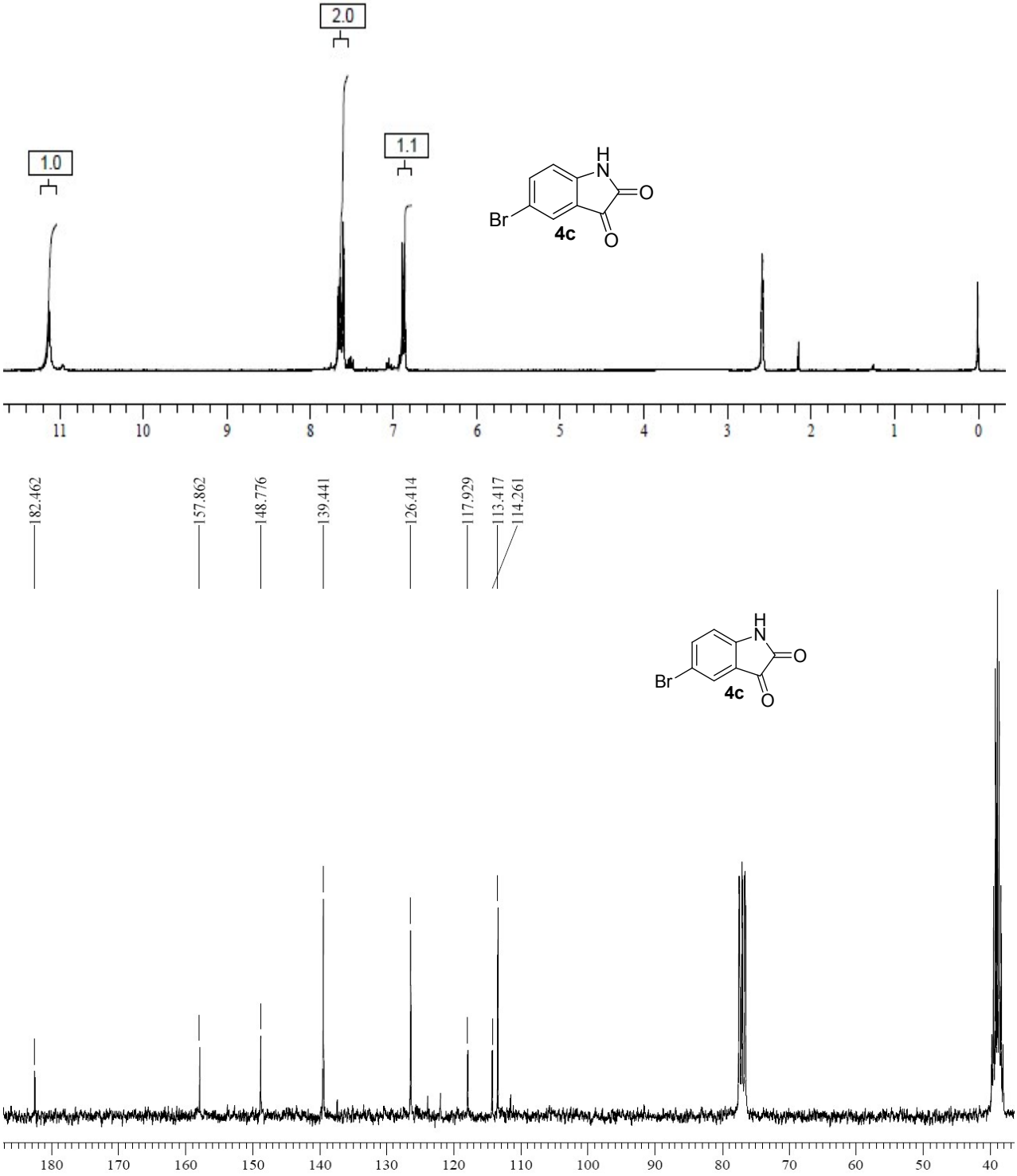

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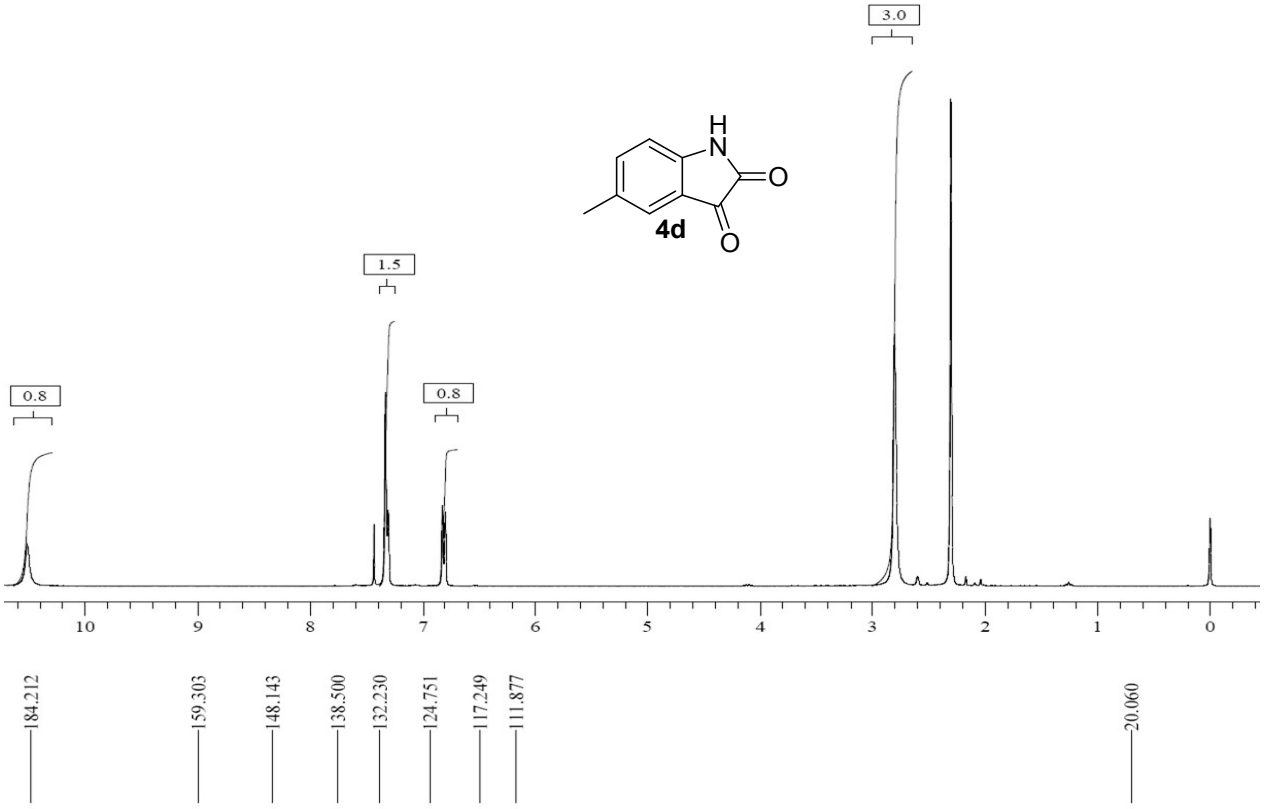

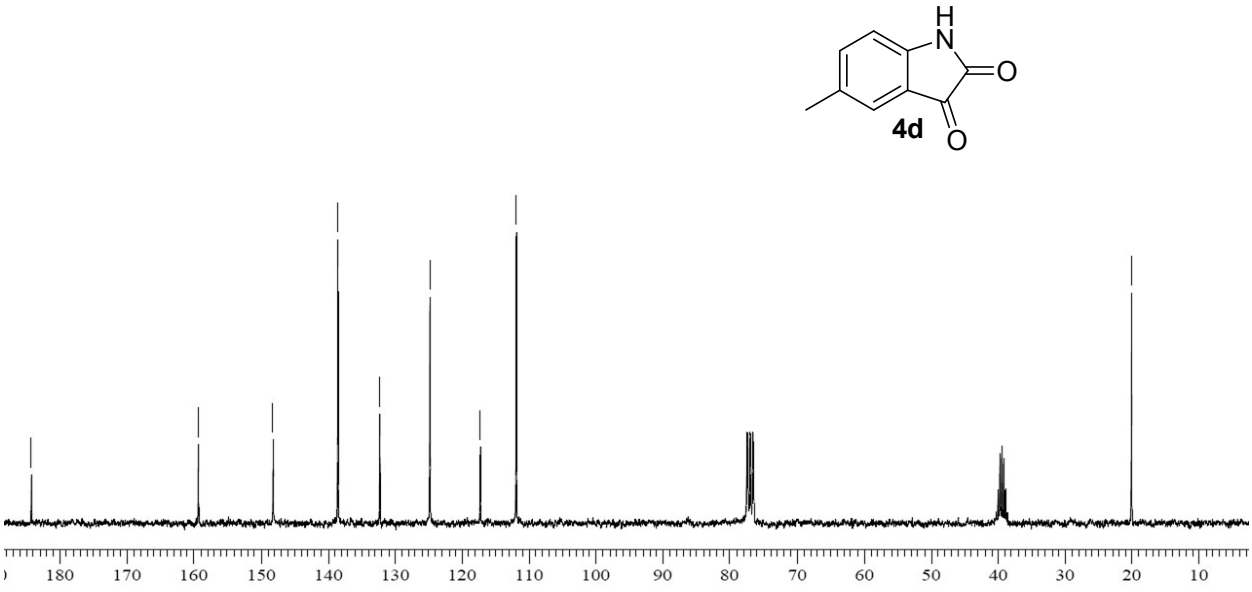

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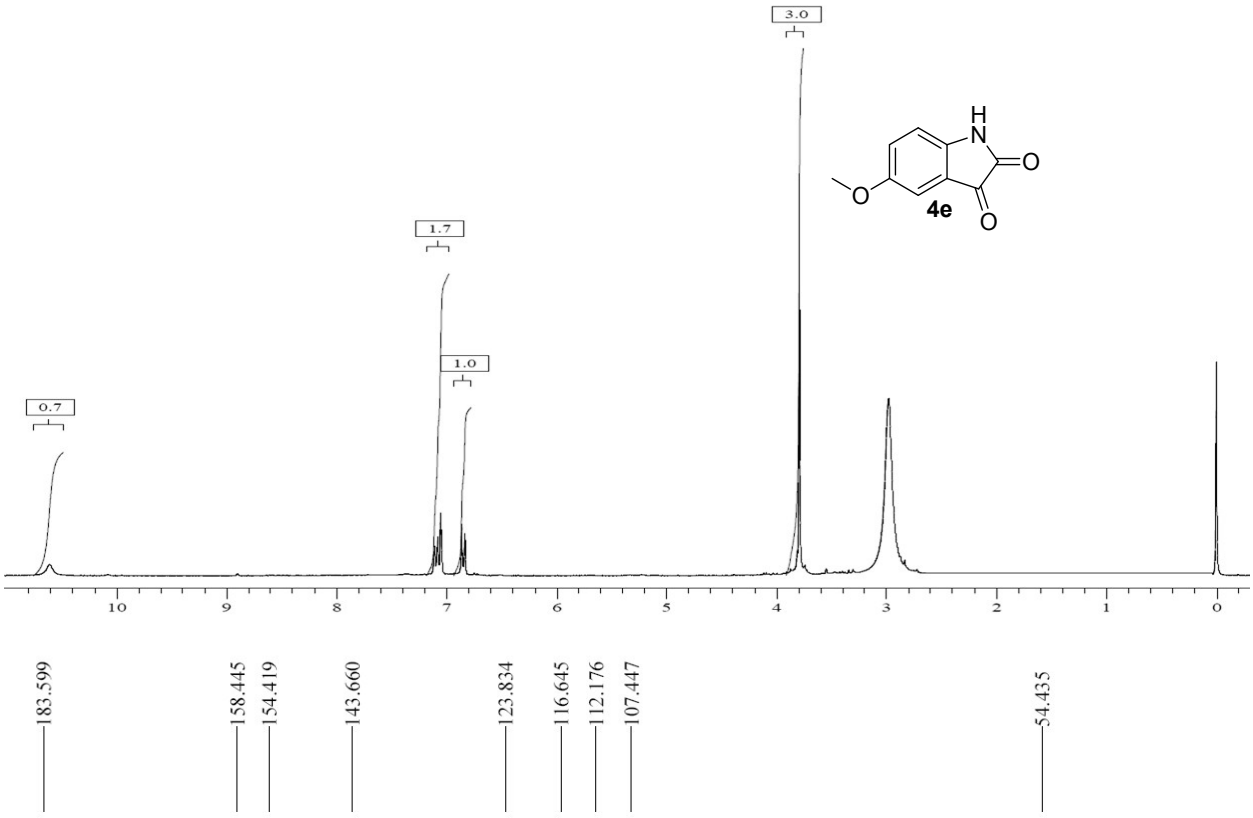
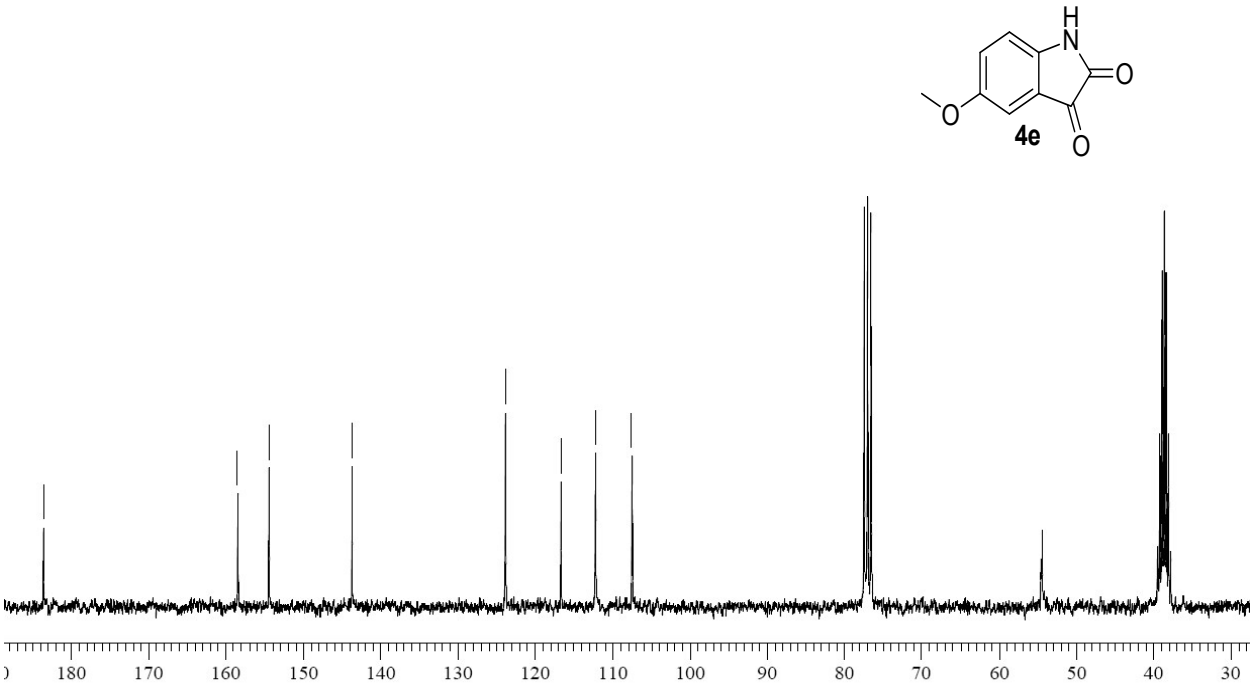
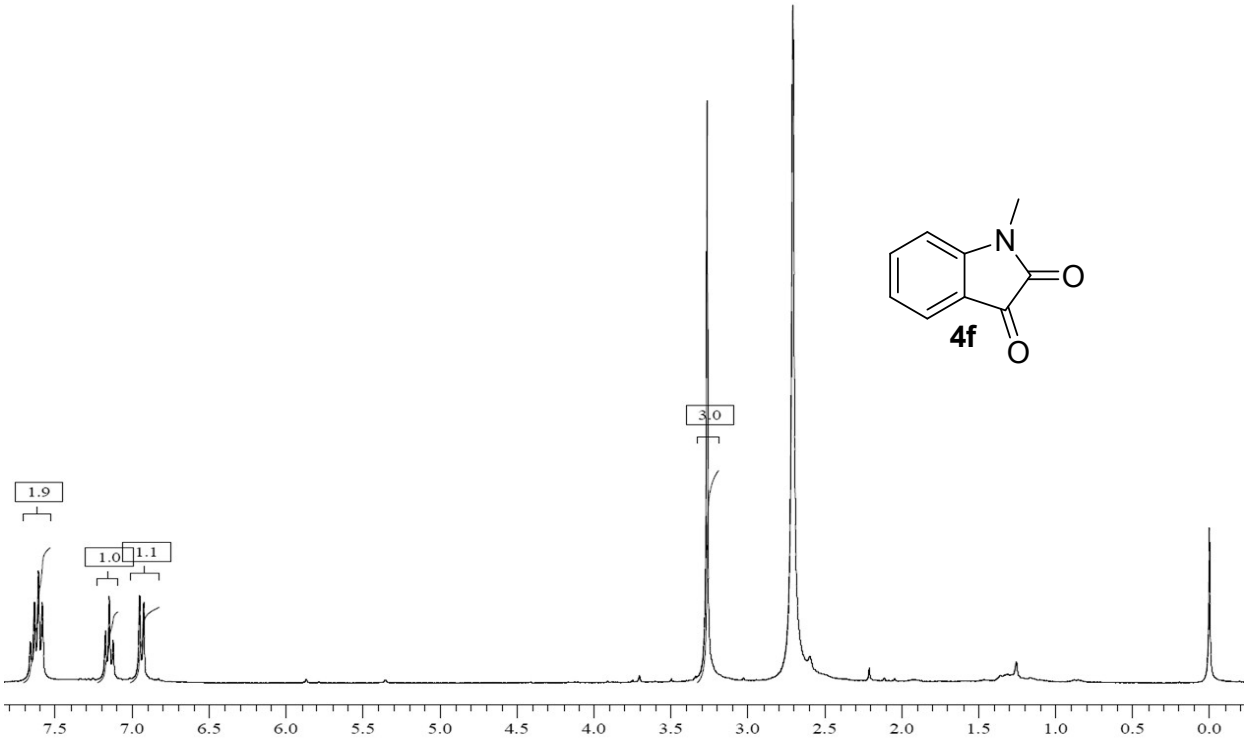
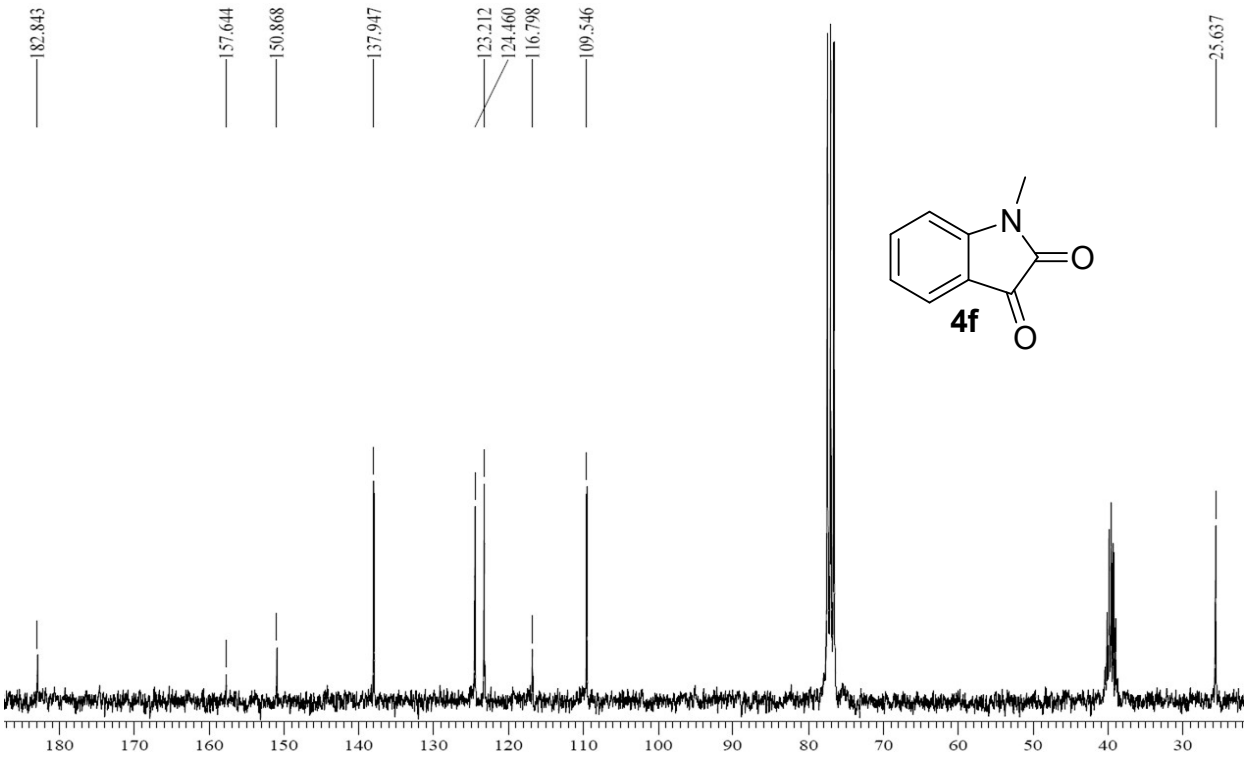


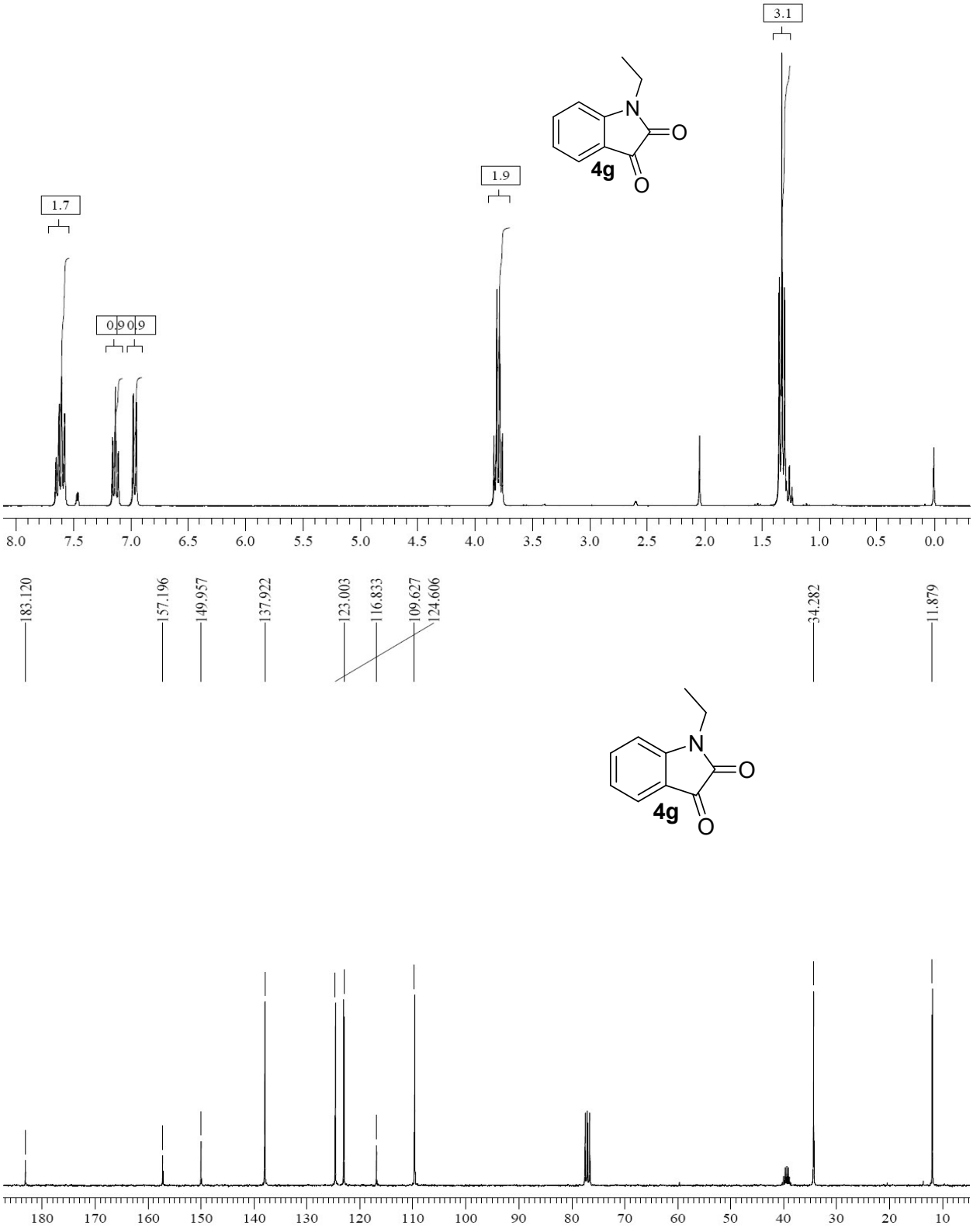


^{1}H &^{13}C NMR of compound 4f:





^{1}H &^{13}C NMR of compound 4g:



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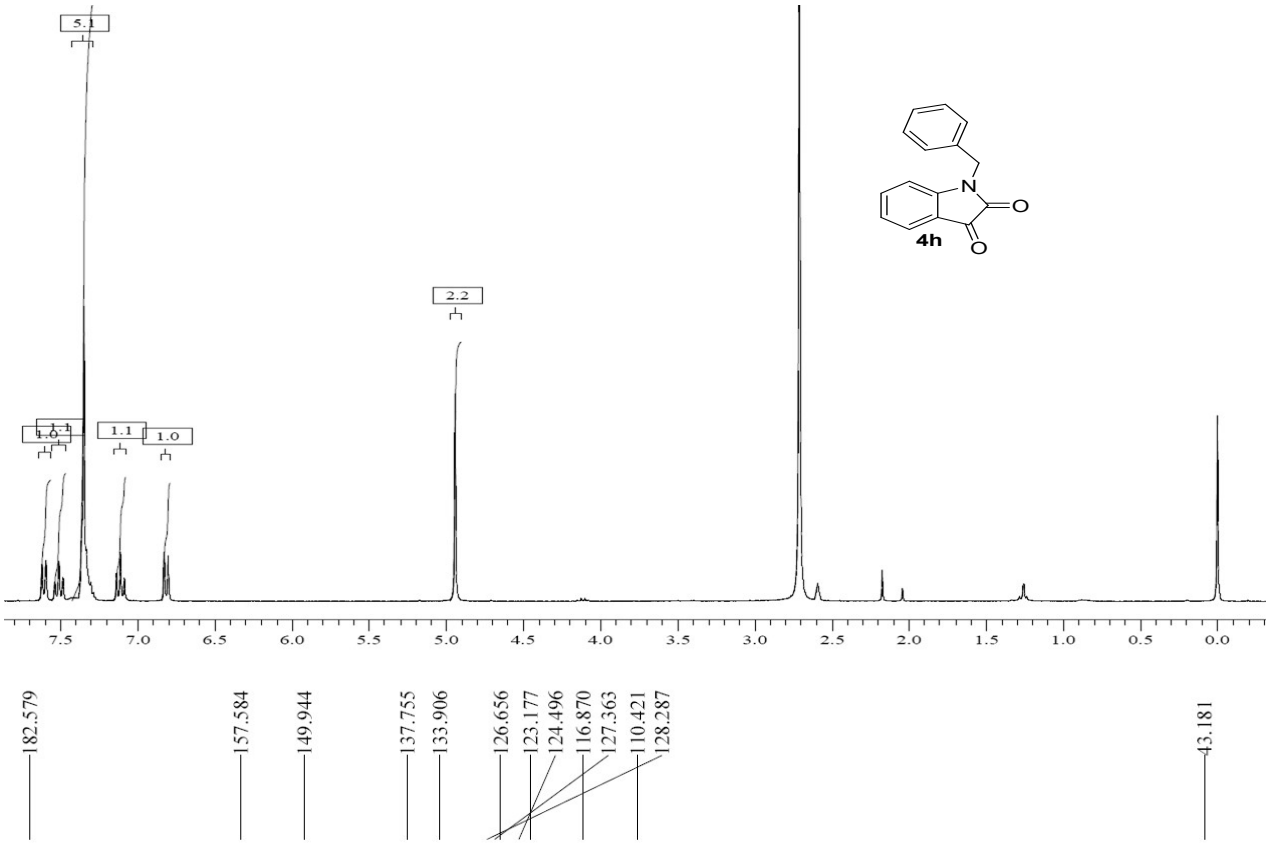
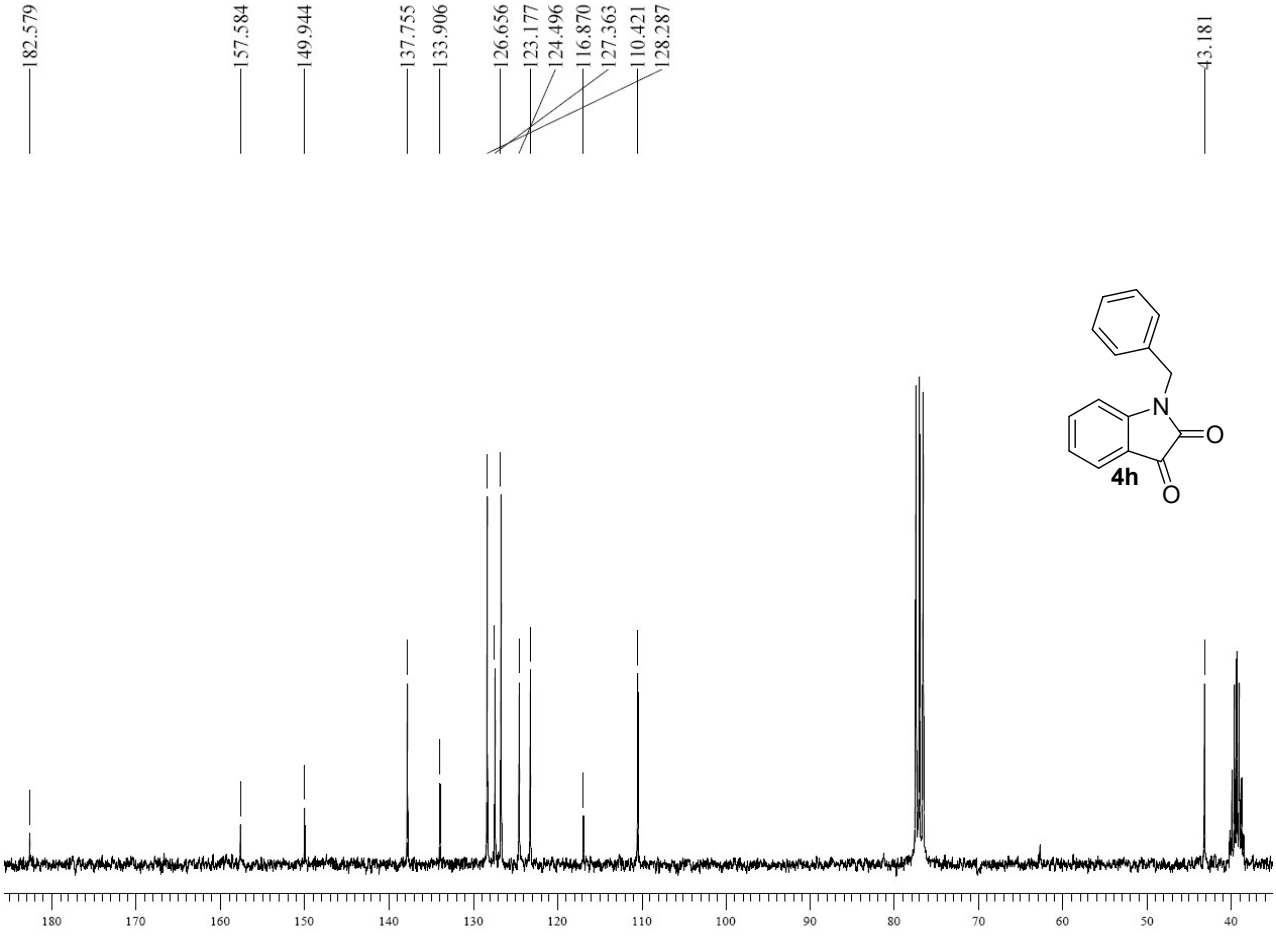
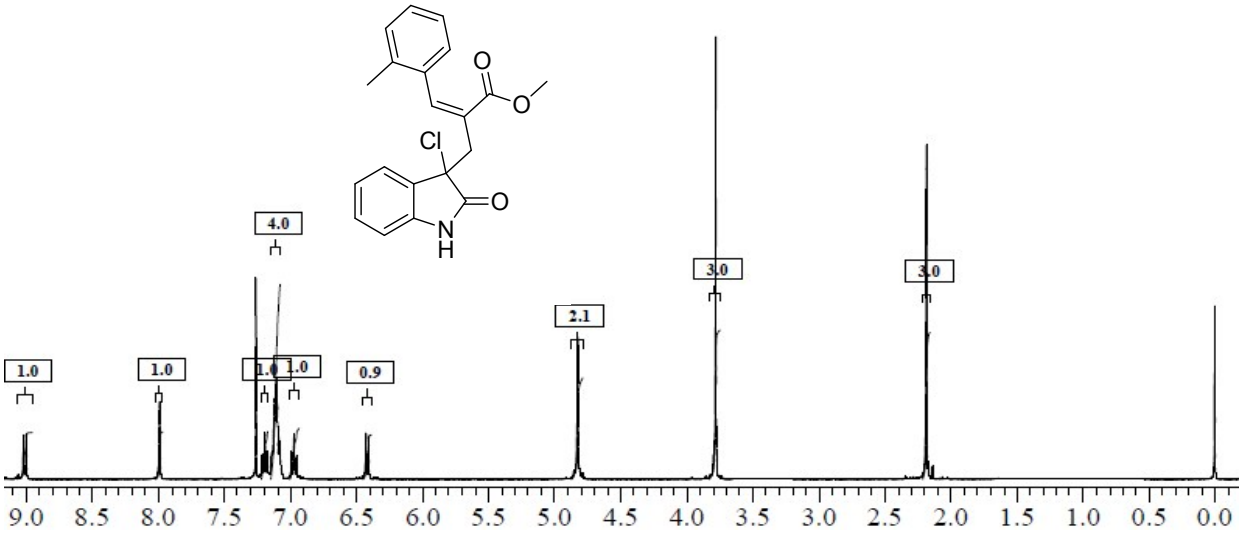
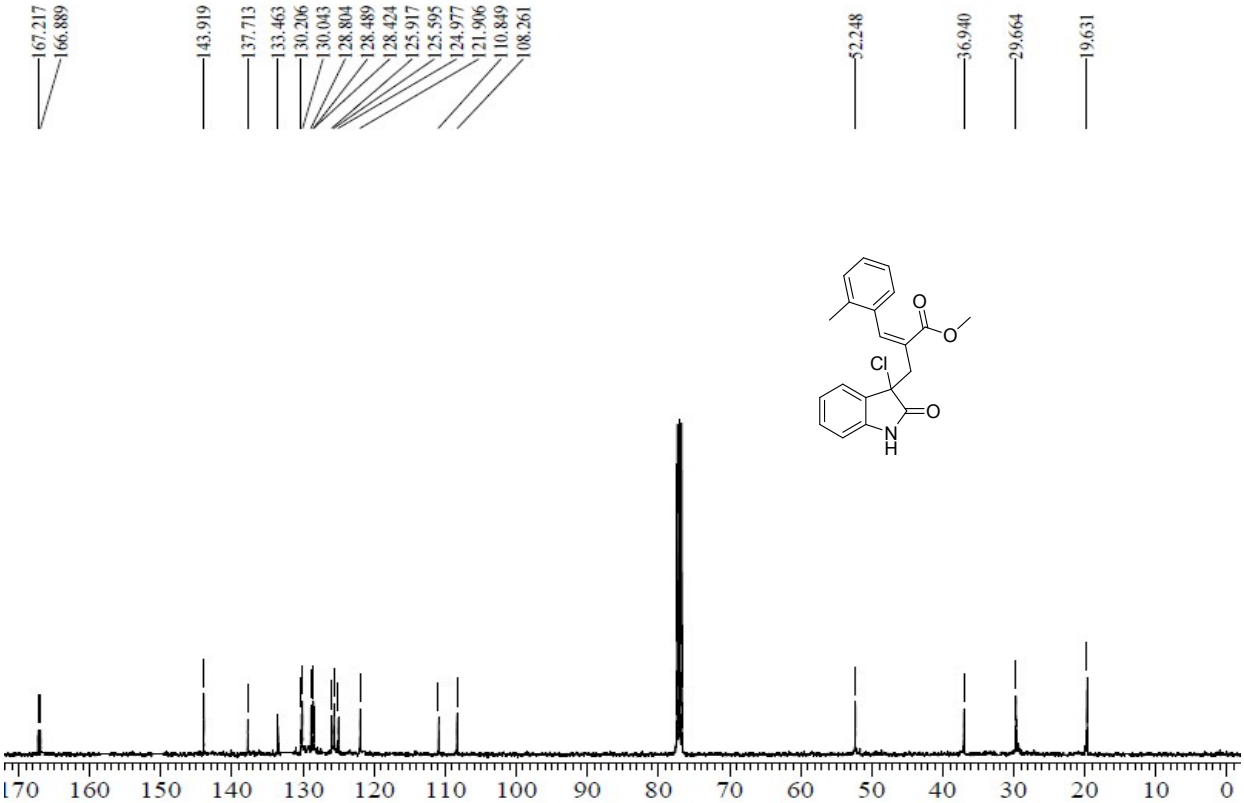




^{1}H &^{13}C NMR of compound 5a:





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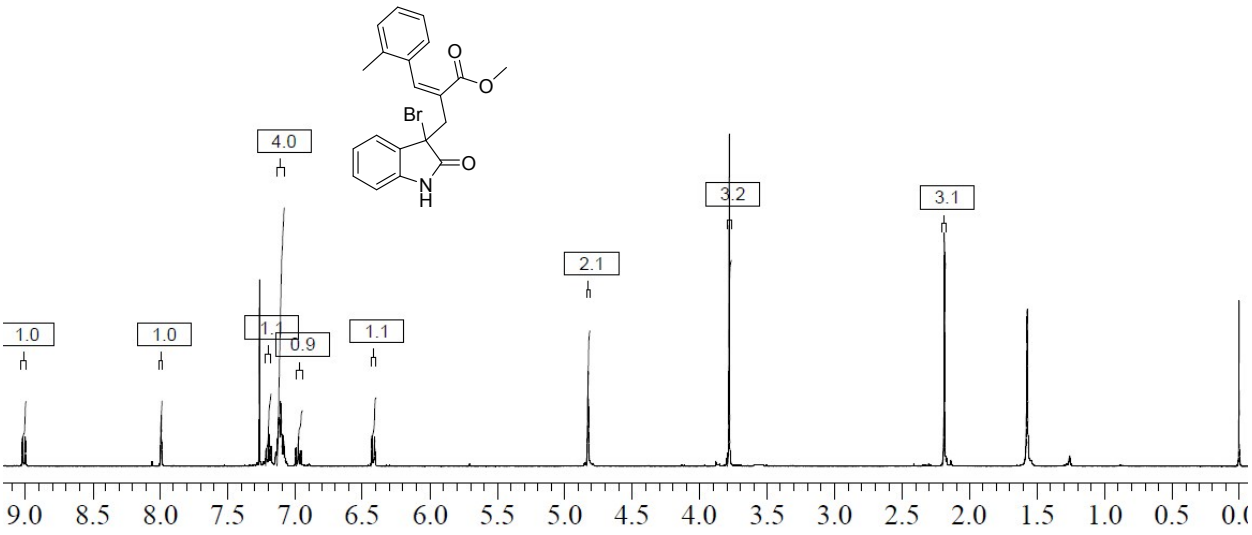

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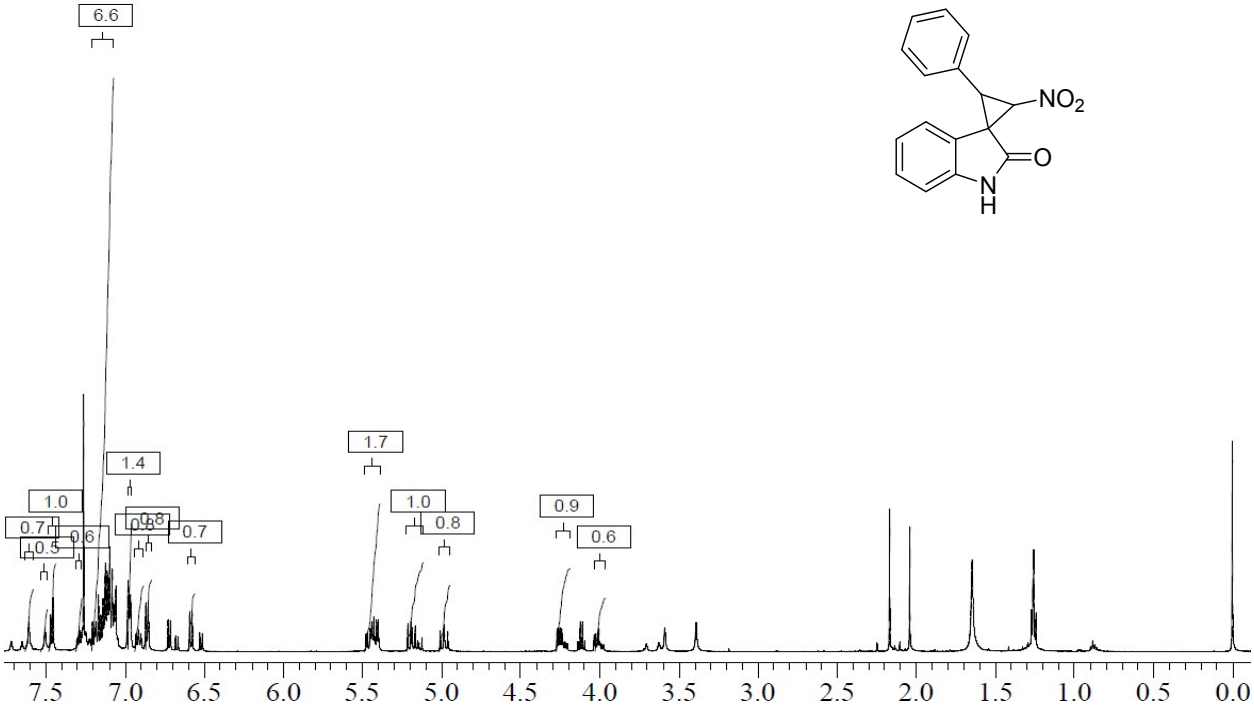

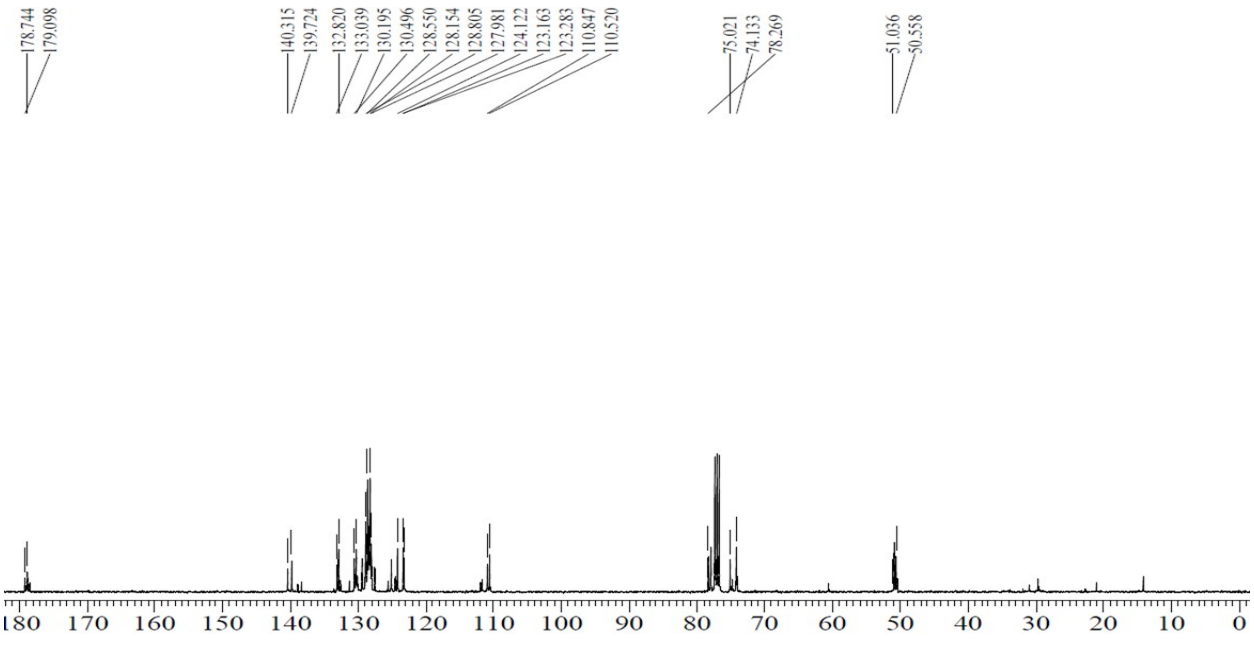

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