Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Synthesis of oxindoles via visible light photoredox catalysis

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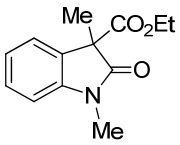
General information

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 MHz spectrometer. The EI-MS spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI. The infrared spectra (IR) were recorded on a Nicolet NEXUS670 FT-IR spectrometer. Melting points were measured on an XT-4 melting point apparatus and were uncorrected. Flash column chromatography was carried out with silica gel (300-350 mesh).Compounds **1a-26a**[1,2,3,4] and photocatalysts ($Ru(bpy)_3Cl$,[5] $Ir(ppy)_2(dtbpy)PF$,[6] *fac*-$(ppy)_3Ir$[7]) were prepared according to literature procedures.

General procedure for the synthesis of substituted oxindoles

To a flame dried 10 mL round bottom flask equipped with a rubber septum and magnetic stir bar was added *fac*-$(ppy)_3Ir$ (1.5 mg, 0.02 equiv.) and α-bromo anilides (**a**) (0.12 mmol, 1.0 equiv). The mixture was degassed through alternating vacuum evacuation and backfilling with Ar (1 min × 4). DMF (2.4 ml, previously degassed with Ar 30 min) was then added into the flask, and the solution was stirred and irradiated under argon atmosphere with a 40 W household fluorescent lamp (distance app. 4 cm) at room temperature for 12-16 hours. After the reaction was complete (indicated by TLC), the reaction mixture was diluted with EtOAc (10 mL), and poured into saturated aqueous NH_4Cl solution (15 mL). The aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine (15 mL × 4) and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residual was treated with silica gel chromatography to give pure product (s) (chromatography of 3-acetyloxindoles was finished in 10 min).

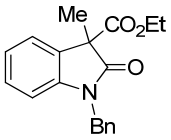
Spectroscopic data for the products



Ethyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (1b)

Colourless oil [8]

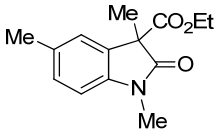
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.33 (dt, J = 1.2 Hz, J = 8.0 Hz, 1H), 7.27-7.25 (m, 1H), 7.07 (dt, J = 1.2 Hz, J = 7.6 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 4.19-4.06 (m, 2H), 3.26 (s, 3H), 1.66 (s, 3H), 1.16 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 175.2, 169.7, 143.6, 130.2, 128.9, 122.9, 122.8, 108.4, 61.9, 55.0, 26.5, 20.1, 13.9; IR (NaCl dep from $CDCl_3$): 3606, 3427, 2983, 1741, 1610, 1470, 1374, 1246, 1110 cm^{-1}; EI-MS m/z (rel. int., %): 233 (M^+, 37), 160 (100), 132 (14).



Ethyl 1-benzyl-3-methyl-2-oxoindoline-3-carboxylate (2b)

White solid: mp. 85–87 °C [8]

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.32-7.28 (m, 4H), 7.27-7.25 (m, 2H), 7.19 (dt, J = 1.2 Hz, J = 7.6 Hz, 1H), 7.02 (dt, J = 1.2 Hz, J = 7.6 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 5.18 (d, J = 15.8 Hz, 1H), 4.73 (d, J = 15.8 Hz, 1H), 4.24-4.18 (m, 1H), 4.16-4.05 (m, 1H), 1.72 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 175.4, 169.7, 142.7, 135.6, 130.2, 128.9, 128.7, 127.6, 127.1, 123.0, 122.9, 109.5, 62.0, 55.1, 43.7, 19.9, 13.8; IR (NaCl dep from $CDCl_3$): 3402, 2920, 1739, 1717, 1608, 1489, 1356, 1236, 1110 cm^{-1}; EI-MS m/z (rel. int., %): 309 (M^+, 49), 236 (56), 208 (21), 159 (14), 158 (14), 91 (100).



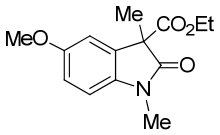
(new compound)

Ethyl 1,3,5-trimethyl-2-oxoindoline-3-carboxylate (3b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.12 (d, J = 7.8 Hz, 1H), 7.08 (s, 1H), 6.76 (d, J = 7.8 Hz, 1H), 4.21-4.05 (m, 2H), 3.24 (s, 3H), 2.34 (s, 3H), 1.65 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 175.2, 169.9, 141.2, 132.5, 130.2, 129.1, 123.7, 108.1, 61.9, 55.1, 26.5, 21.0, 20.2, 13.9; IR (NaCl dep from $CDCl_3$): 3423, 2983, 2935, 1739, 1718, 1617, 1500, 1235, 1112 cm^{-1}; EI-MS m/z (rel. int., %):

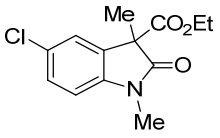
247 (M^+, 41), 174 (100), 159 (10), 131 (10); HRMS (ESI): calcd for $C_{14}H_{17}NO_3$ + H = 248.1281, found: 248.1286.



Ethyl 5-methoxy-1,3-dimethyl-2-oxoindoline-3-carboxylate (4b)

Colourless oil [8]

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 6.88 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 4.20-4.06 (m, 2H), 3.79 (s, 3H), 3.23 (s, 3H), 1.65 (s, 3H), 1.67 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 174.9, 169.7, 156.2, 137.1, 131.4, 113.3, 110.3, 108.7, 61.9, 55.8, 55.4, 26.6, 20.2, 13.9; IR (NaCl dep from $CDCl_3$): 3419, 2983, 2936, 1741, 1713, 1499, 1235, 1115 cm^{-1}; EI-MS m/z (rel. int., %): 263 (M^+, 57), 190 (100), 175 (13), 147 (10).

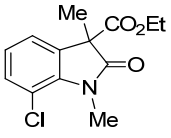


(new compound)

Ethyl 5-chloro-1,3-dimethyl-2-oxoindoline-3-carboxylate (5b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.30 (dd, *J* = 2.0 Hz, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 4.22-4.08 (m, 2H), 3.25 (s, 3H), 1.67 (s, 3H), 1.65 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 174.7, 169.1, 142.2, 131.6, 128.9, 128.2, 123.6, 109.3, 62.2, 55.1, 26.7, 20.1, 13.9; IR (NaCl dep from $CDCl_3$): 3429, 2983, 2936, 1743, 1724, 1609, 1491, 1344, 1246, 1112 cm^{-1}; EI-MS m/z (rel. int., %): 267 (M^+, 38), 269 (11), 194 (100), 196 (30), 159 (21), 131 (14); HRMS (ESI): calcd for $C_{13}H_{14}ClNO_3$ + H = 268.0735, found: 268.0739.



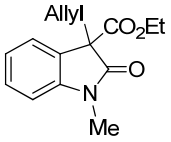
(new compound)

Ethyl 7-chloro-1,3-dimethyl-2-oxoindoline-3-carboxylate (6b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.24 (dd, *J* = 0.8 Hz, *J* = 7.6 Hz, 1H), 7.13 (dd, *J*

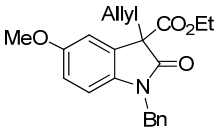
= 0.8 Hz, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 4.20-4.07 (m, 2H), 3.62 (s, 3H), 1.65 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 175.3, 169.2, 139.5, 132.7, 131.3, 123.6, 121.5, 115.7, 62.1, 54.8, 29.9, 20.4, 13.9; IR (NaCl dep from $CDCl_3$): 3438, 2985, 1744, 1726, 1606, 1466, 1367, 1168, 1116 cm^{-1}; EI-MS m/z (rel. int., %): 267 (M^+, 36), 269 (12), 194 (100), 196 (35), 159 (13), 131 (16); HRMS (ESI): calcd for $C_{13}H_{14}ClNO_3$ + H = 268.0735, found: 268.0741.



Ethyl 3-allyl-1-methyl-2-oxoindoline-3-carboxylate (7b)

White solid: mp. 71–72 °C [8]

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.32 (dt, *J* = 1.0 Hz, *J* = 7.6 Hz, 1H), 7.28-7.26 (m, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.43-5.32 (m, 1H), 5.03 (dd, *J* = 1.3 Hz, *J* = 17.0 Hz, 1H), 4.92 (d, *J* = 10.4 Hz, 1H), 4.20-4.08 (m, 2H), 3.23 (s, 3H), 3.05-2.92 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 173.6, 169.0, 144.1, 131.0, 129.0, 127.7, 123.6, 122.7, 119.6, 108.2, 61.9, 59.2, 38.4, 26.3, 13.9; IR (NaCl dep from $CDCl_3$): 3427, 2981, 1740, 1719, 1611, 1470, 1350, 1232 cm^{-1}; EI-MS m/z (rel. int., %): 259 (M^+, 86), 218 (98), 186 (100), 162 (58), 158 (49), 146 (94), 143 (38).

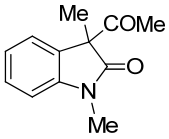


Ethyl 3-allyl-1-benzyl-5-methoxy-2-oxoindoline-3-carboxylate (8b)

Colourless oil [9]

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.30-7.23 (m, 5H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.70 (dd, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 5.46-5.12 (m, 1H), 5.10 (dd, *J* = 1.4 Hz, *J* = 17.0 Hz, 1H), 5.06 (d, *J* = 15.6 Hz, 1H), 4.95 (dd, *J* = 1.4 Hz, *J* = 10.2 Hz, 1H), 4.78 (d, *J* = 15.6 Hz, 1H), 4.25-4.16 (m, 1H), 4.15-4.08 (m, 1H), 3.75 (s, 3H), 3.08-2.99 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 173.6, 169.0, 156.0, 136.7, 135.6, 131.1, 128.9, 128.6, 127.5, 127.2, 119.9, 113.4,

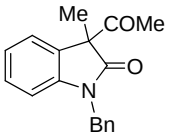
110.7, 109.7, 62.0, 59.6, 55.8, 43.8, 38.0, 13.9; IR (NaCl dep from $CDCl_3$): 3416, 3068, 2982, 2935, 2837, 1739, 1714, 1602, 1495, 1231, 1017 cm^{-1}; EI-MS m/z (rel. int., %): 365 (M^+, 30), 366 (6), 324 (31), 252 (9), 129 (10), 91 (100).



3-Acetyl-1,3-dimethylindolin-2-one (9b)

White solid: mp. 73–75 °C [10]

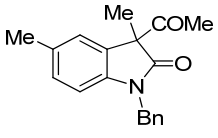
^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.36 (dt, *J* =1.2 Hz, *J* = 7.8 Hz, 1H), 7.16 (dd, *J* =1.2 Hz, *J* = 7.8 Hz, 1H), 7.10 (dt, *J* =0.6 Hz, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.31 (s, 3H), 1.97 (s, 3H), 1.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 201.0, 175.9, 143.7, 129.4, 129.1, 123.5, 123.2, 108.6, 62.0, 26.6, 25.9, 18.9; IR (NaCl dep from $CDCl_3$): 3411, 2981, 2934, 1727, 1701, 1610, 1471, 1348, 1198, 1103 cm^{-1}; EI-MS m/z (rel. int., %): 203 (M^+, 1), 161 (100), 160 (78), 117 (10), 43 (11).



3-Acetyl-1-benzyl-3-methylindolin-2-one (10b)

Colourless oil [11]

^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.34-7.33 (m, 4H), 7.31-7.27 (m, 1H), 7.24 (dt, *J* =1.2 Hz, *J* = 7.6 Hz, 1H), 7.15 (dd, *J* = 0.8 Hz, *J* = 7.6 Hz, 1H), 7.05 (dt, *J* =0.8 Hz, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.05 (d, *J* = 15.4 Hz, 1H), 4.91 (d, *J* = 15.4 Hz, 1H), 1.98 (s, 3H), 1.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 200.9, 176.0, 142.8, 135.5, 129.4, 129.0, 128.9, 127.9, 127.4 123.5, 123.2, 109.6, 61.9, 44.1, 26.1, 19.1; IR (NaCl dep from $CDCl_3$): 3409, 3060, 2931, 2866, 1725, 1706, 1608, 1488, 1353, 1177 cm^{-1}; EI-MS m/z (rel. int., %): 279 (M^+, 6), 237 (100), 159 (40), 91 (90), 43 (8).

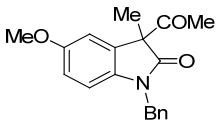


(new compound)

3-Acetyl-1-benzyl-3,5-dimethylindolin-2-one (11b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.33-7.32 (m, 4H), 7.30-7.26 (m, 1H), 7.03 (dd, *J* =1.2 Hz, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.03 (d, *J* = 15.4 Hz, 1H), 4.89 (d, *J* = 15.4 Hz, 1H), 2.29 (s, 3H), 1.98 (s, 3H), 1.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 201.1, 176.0, 140.4, 135.6, 132.9, 129.4, 129.3, 128.8, 127.8, 127.4, 124.3, 109.3, 62.0, 44.1, 26.1, 21.0, 19.1; IR (NaCl dep from $CDCl_3$): 3410, 3031, 2928, 2865, 1723, 1700, 1604, 1494, 1345, 1165, 1085 cm^{-1}; EI-MS m/z (rel. int., %): 293 (M^+, 9), 251 (100), 250 (12), 173 (33), 91 (76), 43 (6); HRMS (ESI): calcd for $C_{19}H_{19}NO_2$ + H = 294.1489, found: 294.1487.

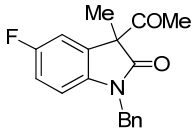


(new compound)

3-Acetyl-1-benzyl-5-methoxy-3-methylindolin-2-one (12b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.34-7.27 (m, 5H), 6.78-6.71 (m, 3H), 5.03 (d, *J* = 15.4 Hz, 1H), 4.89 (d, *J* = 15.4 Hz, 1H), 3.75 (s, 3H), 2.00 (s, 3H), 1.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 201.0, 175.7, 156.4, 136.1, 135.6, 130.6, 128.9, 127.8, 127.4, 113.7, 110.5, 110.1, 62.3, 55.8, 44.2, 26.1, 19.2; IR (NaCl dep from $CDCl_3$): 3405, 3033, 2933, 2837, 1724, 1702, 1601, 1493, 1436, 1347, 1287, 1179, 1044 cm^{-1}; EI-MS m/z (rel. int., %): 309 (M^+, 21), 267 (100), 189 (20), 176 (21), 91 (84), 43 (9); HRMS (ESI): calcd for $C_{19}H_{19}NO_3$ + H = 310.1438, found: 310.1428.



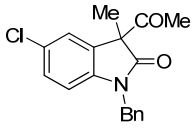
(new compound)

3-Acetyl-1-benzyl-5-fluoro-3-methylindolin-2-one (13b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.37-7.27 (m, 5H), 6.97-6.92 (m, 2H), 6.76-6.73 (m, 1H), 5.03 (d, *J* = 15.4 Hz, 1H), 4.90 (d, *J* = 15.4 Hz, 1H), 2.04 (s, 3H), 1.64 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 200.4, 175.6, 159.4 (d, *J* = 241.0 Hz), 138.6, 135.3, 130.8 (d, *J* = 8.0 Hz), 129.0, 127.7 (d, *J* = 65.0 Hz), 115.4 (d, *J* = 24.0

Hz), 111.8 (d, J = 25.0 Hz), 110.2 (d, J = 6.0 Hz), 62.2, 44.2, 26.2, 19.5; IR (NaCl dep from $CDCl_3$): 3411, 3065, 2932, 2868, 1727, 1709, 1612, 1490 1343, 1173 cm^{-1}; EI-MS m/z (rel. int., %): 297 (M^+, 6), 255 (79), 177 (34), 91 (100), 43 (13); HRMS (ESI): calcd for $C_{18}H_{16}FNO_2$ + H = 298.1238, found: 298.1230.

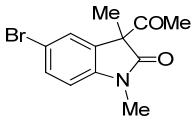


(new compound)

3-Acetyl-1-benzyl-5-chloro-3-methylindolin-2-one (14b)

Colourless oil

^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.36-7.26 (m, 5H), 7.20 (dd, J = 2.0 Hz, J = 8.4 Hz, 1H), 7.15 (d, J = 2.0 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 5.02 (d, J = 15.4 Hz, 1H), 4.89 (d, J = 15.4 Hz, 1H), 2.03 (s, 3H), 1.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 200.2, 175.5, 141.3, 135.1, 131.0, 129.0, 128.7, 128.0, 127.3, 124.2, 110.5, 61.9, 44.2, 26.2, 19.4; IR (NaCl dep from $CDCl_3$): 3414, 3065, 3034, 2931, 2868, 1730, 1705 1607, 1486, 1428, 1340, 1173, 1084 cm^{-1}; EI-MS m/z (rel. int., %): 313 (M^+, 5), 315 (1), 271 (64), 273 (19), 193 (21), 195 (7), 91 (100), 43 (13); HRMS (ESI): calcd for $C_{18}H_{16}ClNO_2$ + H = 314.0942, found: 314.0938.

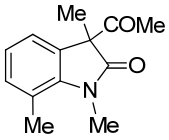


(new compound)

3-Acetyl-5-bromo-1,3-dimethylindolin-2-one (15b)

White solid: mp. 100-102 °C

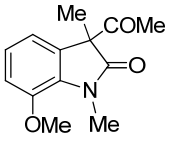
^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.48 (dd, J = 1.8 Hz, J = 8.2 Hz, 1H), 7.29 (d, J = 1.8Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 3.28 (s, 3H), 2.02 (s, 3H), 1.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 200.3, 175.3, 142.6, 131.9, 131.2, 126.9, 115.8, 109.9, 61.9, 26.7, 26.0, 19.3; IR (NaCl dep from $CDCl_3$): 3401, 3097, 2976, 2933, 1714, 1606, 1456, 1356, 1207, 1109 cm^{-1}; EI-MS m/z (rel. int., %): 281 (M^+, 10), 283 (9), 241 (97), 239 (100), 238 (60), 159 (26), 43 (47); HRMS (ESI): calcd for $C_{12}H_{12}BrNO_2$ + H = 282.0125, found: 282.0128.



3-Acetyl-1,3,7-trimethylindolin-2-one (16b)

White solid: mp. 79–81 °C [10]

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.09-7.06 (m, 1H), 6.97-6.96 (m, 2H), 3.58 (s, 3H), 2.62 (s, 3H), 1.95 (s, 3H), 1.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 201.0, 176.6, 141.4, 132.8, 129.9, 123.1, 121.4, 120.2, 61.5, 29.9, 25.8, 19.2, 18.9; IR (NaCl dep from $CDCl_3$): 3582, 3406, 2970, 2935, 1721, 1609, 1468, 1349, 1190 cm^{-1}; EI-MS m/z (rel. int., %): 217 (M^+, 8), 175 (100), 160 (7), 131 (9), 91 (5), 43 (9).

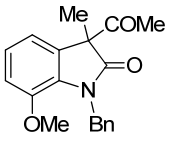


(new compound)

3-Acetyl-7-methoxy-1,3-dimethylindolin-2-one (17b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.02 (dd, *J* =7.6 Hz, *J* = 8.4 Hz, 1H), 6.90 (dd, *J* =0.6 Hz, *J* = 8.4 Hz, 1H), 6.74 (dd, *J* = 0.6 Hz, *J* = 7.6 Hz, 1H), 3.89 (s, 3H), 3.56 (s, 3H), 1.95 (s, 3H), 1.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 200.9, 176.0, 145.5, 131.5, 130.9, 123.7, 116.0, 112.8, 62.1, 55.9, 29.9, 25.8, 19.0; IR (NaCl dep from $CDCl_3$): 3380, 2975, 2939, 2938, 1703, 1162, 1460, 1353, 1251, 1097 cm^{-1}; EI-MS m/z (rel. int., %): 233 (M^+, 15), 191 (100), 190 (36), 176 (19), 148 (15), 43 (10); HRMS (ESI): calcd for $C_{13}H_{15}NO_3$ + H = 234.1125, found: 234.1121.



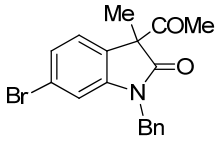
(new compound)

3-Acetyl-1-benzyl-7-methoxy-3-methylindolin-2-one (18b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.36-7.23 (m, 5H), 7.01 (dd, *J* = 7.2 Hz, *J* = 8.4 Hz, 1H), 6.88 (dd, *J* = 0.8 Hz, *J* = 8.4 Hz, 1H), 6.75 (dd, *J* = 0.8 Hz, *J* = 7.2 Hz, 1H), 5.27 (d, *J* = 6.8 Hz, 1H), 5.21 (d, *J* = 6.8 Hz, 1H), 3.78 (s, 3H), 1.90 (s, 3H), 1.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 200.8, 176.2, 145.2, 138.1, 131.0, 130.9,

128.4, 127.5, 127.3, 123.9, 116.0, 112.9, 62.1, 55.7, 45.9, 26.0, 19.2; IR (NaCl dep from $CDCl_3$): 3406, 3032, 2935, 2840, 1724, 1705, 1610, 1494, 1460, 1350, 1259, 1205, 1046 cm^{-1}; EI-MS m/z (rel. int., %): 309 (M^+, 13), 267 (100), 189 (43), 176 (16), 91 (83), 43 (6); HRMS (ESI): calcd for $C_{19}H_{19}NO_3$ + H = 310.1438, found: 310.1431.

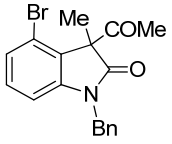


(new compound)

3-Acetyl-1-benzyl-6-bromo-3-methylindolin-2-one (20b)

Colourless oil

^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.38-7.31 (m, 5H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.98 (s, 1H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.87 (d, *J* = 15.6 Hz, 1H), 2.00 (s, 3H), 1.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 200.2, 175.8, 144.1, 135.0, 129.1, 128.3, 128.1, 127.3, 126.1, 124.9, 122.7, 112.9, 61.5, 44.2, 26.1, 19.3; IR (NaCl dep from $CDCl_3$): 3411, 3033, 2932, 2860, 1734, 1709, 1603, 1452, 1331, 1168 cm^{-1}; EI-MS m/z (rel. int., %): 357 (M^+, 1), 359 (1), 317 (26), 315 (27), 239 (9), 237 (10), 91 (100), 43 (11); HRMS (ESI): calcd for $C_{18}H_{16}NO_2$ + H = 358.0437, found: 358.0440.

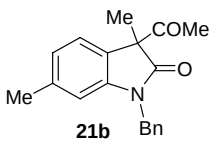


(new compound)

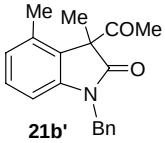
3-Acetyl-1-benzyl-4-bromo-3-methylindolin-2-one (20b')

Colourless oil

^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.36-7.26 (m, 5H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 1.99 (s, 3H), 1.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 198.6, 173.9, 144.7, 135.1, 130.3, 129.5, 129.0, 128.0, 127.2, 126.9, 119.0, 108.6, 63.8, 44.3, 26.4, 17.0; IR (NaCl dep from $CDCl_3$): 3414, 3065, 2926, 2853, 1728, 1602, 1485, 1364, 1175 cm^{-1}; EI-MS m/z (rel. int., %): 357 (M^+, 1), 359 (1), 317 (30), 315 (31), 239 (8), 237 (8), 91 (100), 43 (10); HRMS (ESI): calcd for $C_{18}H_{16}NO_2$ + H = 358.0437, found: 358.0445.



21b



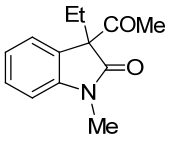
21b'

(mixture, new compounds)

3-Acetyl-1-benzyl-3,6-dimethylindolin-2-one (21b)

3-Acetyl-1-benzyl-3,4-dimethylindolin-2-one (21b')

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.34-7.26 (m, 7.5H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 0.4H), 6.87-6.83 (m, 1.4H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.66 (s, 0.4H), 5.04-4.99 (m, 1.4H), 4.94-4.87 (m, 1.4H), 2.31 (s, 1.2H), 2.16 (s, 3H), 1.96 (s, 1.2H), 1.90 (s, 3H), 1.66 (s, 3H), 1.60 (s, 1.2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 201.1, 200.3, 176.3, 175.4, 143.2, 143.0, 139.4, 135.7, 135.6, 135.0, 128.9, 128.9, 128.8, 128.6, 127.8, 127.4, 127.4, 127.3, 126.6, 125.4, 123.8, 123.3, 110.3, 107.3, 62.6, 61.7, 44.2, 44.0, 26.0, 25.8, 21.8, 19.1, 17.6, 17.0; IR (NaCl dep from $CDCl_3$): 3582, 3407, 3060, 3032, 2983 2931, 2865, 1726, 1707, 1654, 1606, 1458, 1374, 1342, 1200, 1081 cm^{-1}; EI-MS m/z (rel. int., %): b: 293 (M^+, 4), 251 (100), 173 (20), 160 (25), 91 (90), 43 (4); b': 293 (M^+, 6), 251 (100), 173 (23), 160 (19), 91 (97), 43 (5); HRMS (ESI): calcd for $C_{19}H_{19}NO_2$ + H = 294.1489, found: 294.1483.

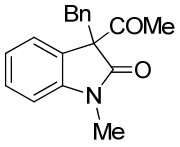


(new compound)

3-Acetyl-3-ethyl-1-methylindolin-2-one (22b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.35 (dt, *J* =1.2 Hz, *J* = 7.6 Hz, 1H), 7.17 (dd, *J* = 0.8 Hz, J = 7.6 Hz, 1H), 7.10 (dt, *J* = 0.8Hz, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.30 (s, 3H), 2.29-2.14 (m, 2H), 2.01 (s, 3H), 0.60 (t, *J* =7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 201.4, 175.0, 144.3, 129.0, 127.3, 123.9, 123.1, 108.3, 67.2, 26.6, 26.6, 26.4, 8.1; IR (NaCl dep from $CDCl_3$): 3387, 3029, 2989, 2933, 2869, 1724, 1700, 1656, 1597, 1457, 1358, 1206, 1094 cm^{-1}; EI-MS m/z (rel. int., %): 217 (M^+, 10), 175 (100), 160 (91), 130 (12), 117 (8), 43 (19); HRMS (ESI): calcd for $C_{13}H_{15}NO_2$ + H = 218.1176, found: 218.1171.

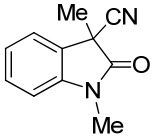


(new compound)

3-Acetyl-3-benzyl-1-methylindolin-2-one (23b)

White solid: mp. 77–79 °C

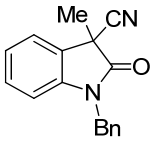
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.27-7.23 (m, 2H), 7.09 (dt, *J* =1.0 Hz, *J* = 8.0 Hz, 1H), 7.03-6.97 (m, 3H), 6.80 (dd, *J* =1.0 Hz, *J* = 8.0 Hz, 2H), 6.30 (d, *J* = 8.0 Hz, 1H), 3.46 (s, 2H), 2.99 (s, 3H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 200.9, 174.3, 144.2, 134.9, 129.7, 129.2, 127.5, 126.7, 126.5, 124.2, 122.8, 108.3, 68.0, 39.0, 26.9, 26.2; IR (NaCl dep from $CDCl_3$): 3397, 3058, 3033, 2930, 1710, 1608, 1471, 1349, 1191, 1088 cm^{-1}; EI-MS m/z (rel. int., %): 279 (M^+, 8), 237 (100), 159 (69), 91 (23), 43 (7); HRMS (ESI): calcd for $C_{18}H_{17}NO_2$ + H = 280.1332, found: 280.1328.



1,3-Dimethyl-2-oxoindoline-3-carbonitrile (24b)

White solid: mp. 70-72 °C [8]

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.45-7.40 (m, 2H), 7.19 (dt, *J* = 0.8 Hz, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 3.27 (s, 3H), 1.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 171.0, 142.5, 130.3, 126.8, 123.8, 123.7, 117.6, 109.2, 42.1, 27.0, 23.4; IR (NaCl dep from $CDCl_3$): 3614, 3439, 3062, 2937, 2241, 1729, 1652, 1612, 1492, 1373, 1129 cm^{-1}; EI-MS m/z (rel. int., %): 187 (M^+, 9), 186 (78), 171 (100), 143 (22), 116 (16), 42 (10).



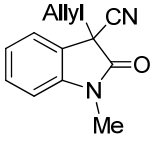
(new compound)

1-Benzyl-3-methyl-2-oxoindoline-3-carbonitrile (25b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.43 (dd, *J* = 0.8 Hz, *J* = 7.6 Hz, 1H), 7.36-7.26 (m, 6H), 7.13 (dt, *J* = 0.8 Hz, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 4.97 (d, *J* =

15.6 Hz, 1H), 4.90 (d, *J* = 15.6 Hz, 1H), 1.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 171.2, 141.6, 134.7, 130.2, 129.0, 128.0, 127.2, 126.8, 123.8, 123.8, 117.6, 110.2, 44.4, 42.2, 23.6; IR (NaCl dep from $CDCl_3$): 3434, 3063, 3033, 2933, 2869, 2242, 1727, 1652, 1610, 1491, 1354, 1181 cm^{-1}; EI-MS m/z (rel. int., %): 262 (M^+, 25), 182 (4), 91 (100), 65 (8); HRMS (ESI): calcd for $C_{17}H_{14}N_2O$ + H = 263.1179, found: 263.1181.



(new compound)

3-Allyl-1-methyl-2-oxoindoline-3-carbonitrile (26b)

Colourless oil

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.43-7.39 (m, 2H), 7.16 (dt, *J* = 1.0 Hz, *J* = 7.6 Hz, 1H), 6.90 (dd, *J* = 0.8 Hz, *J* = 7.6 Hz, 1H), 5.73-5.63 (m, 1H), 5.21-5.15 (m, 2H), 3.25 (s, 3H), 3.00 (dd, *J* = 6.4 Hz, *J* = 13.6 Hz, 1H), 2.74 (dd, *J* = 8.2 Hz, *J* = 13.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 169.9, 143.0, 130.3, 129.1, 124.8, 124.5, 123.5, 121.9, 116.6, 109.0, 46.3, 41.0, 26.9; IR (NaCl dep from $CDCl_3$): 3439, 3064, 2982, 2924, 2242, 1728, 1642, 1611, 1471, 1369, 1256, 1091 cm^{-1}; EI-MS m/z (rel. int., %): 212 (M^+, 26), 213 (4), 172 (14), 171 (100), 116 (14); HRMS (ESI): calcd for $C_{13}H_{12}N_2O$ + H = 213.1023, found: 203.1025.

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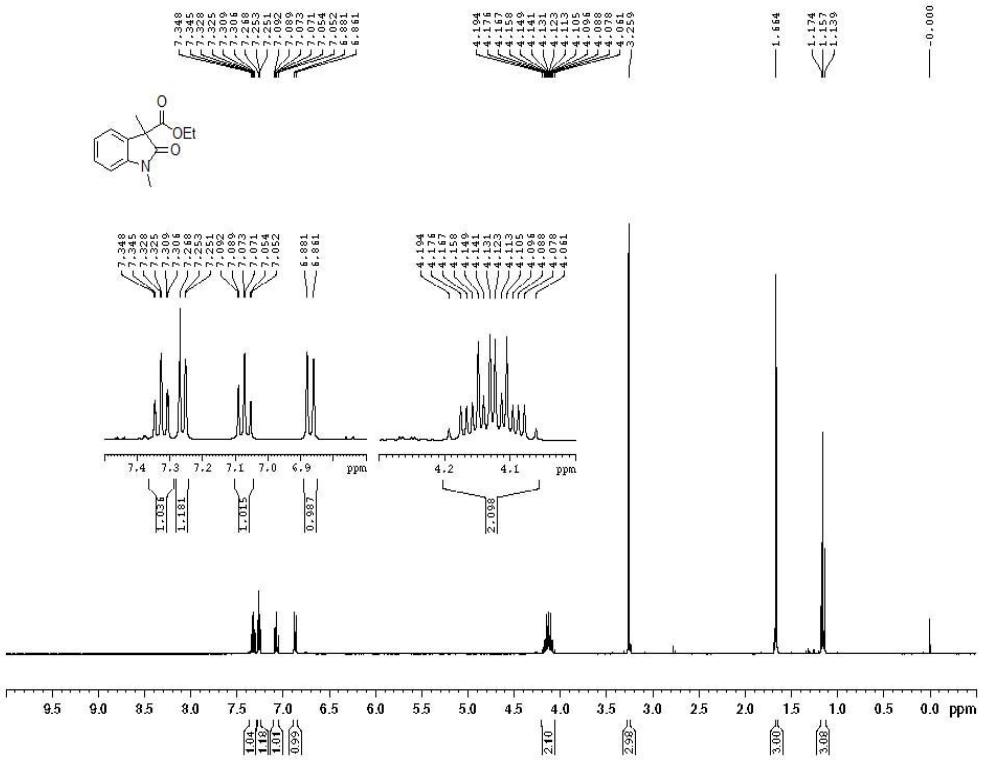
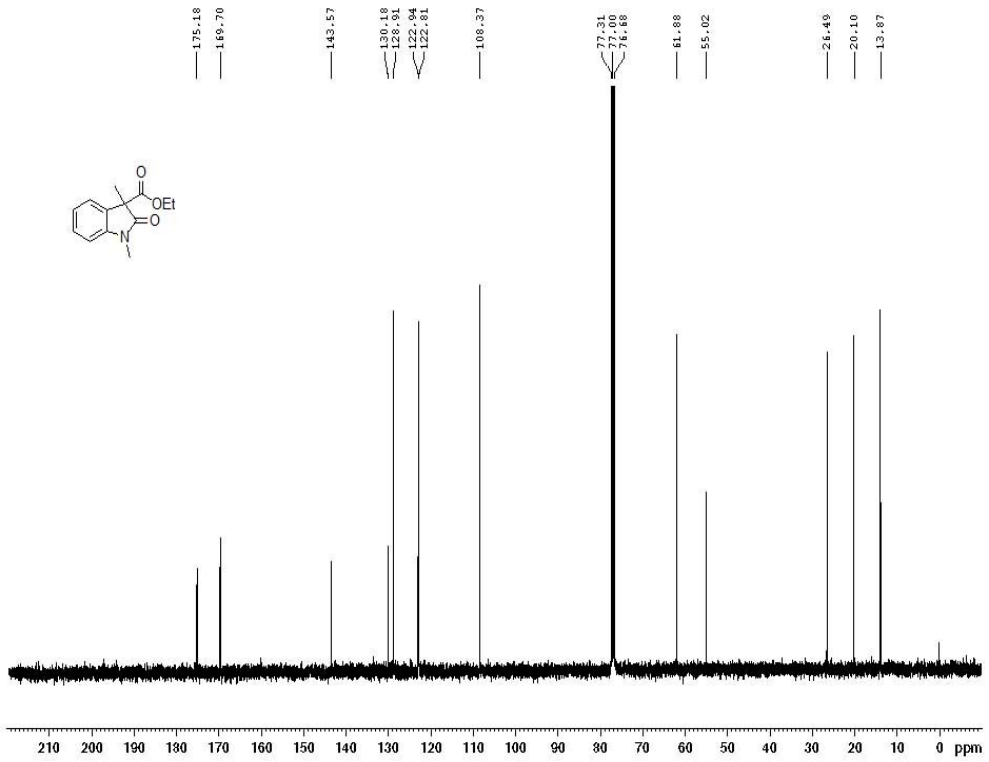
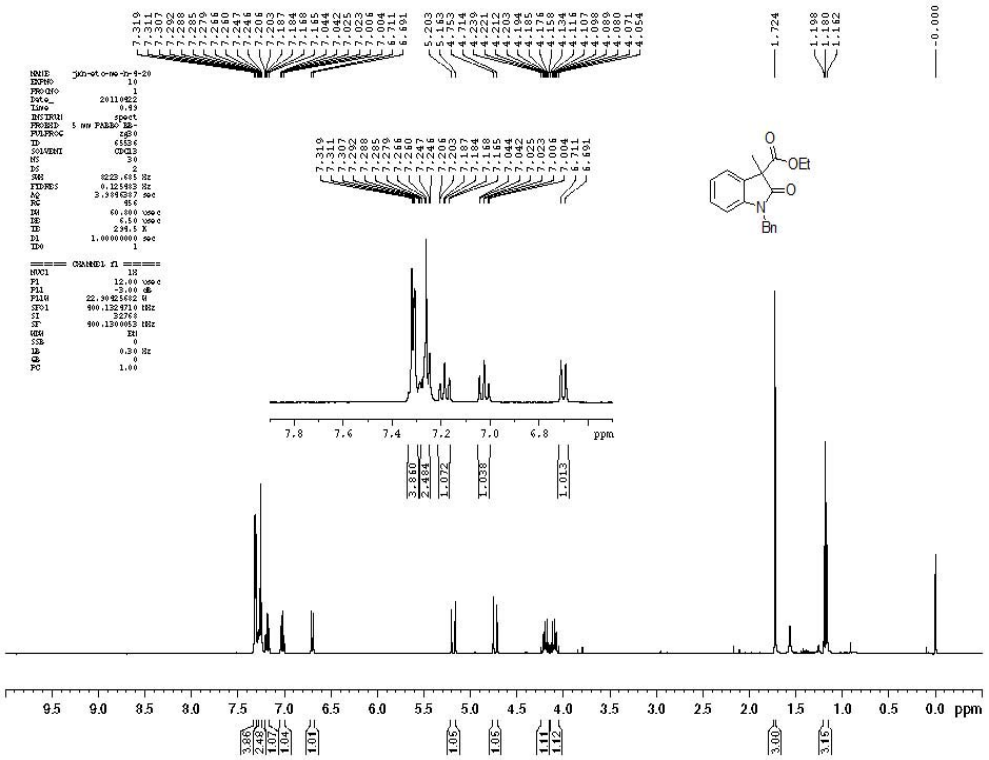
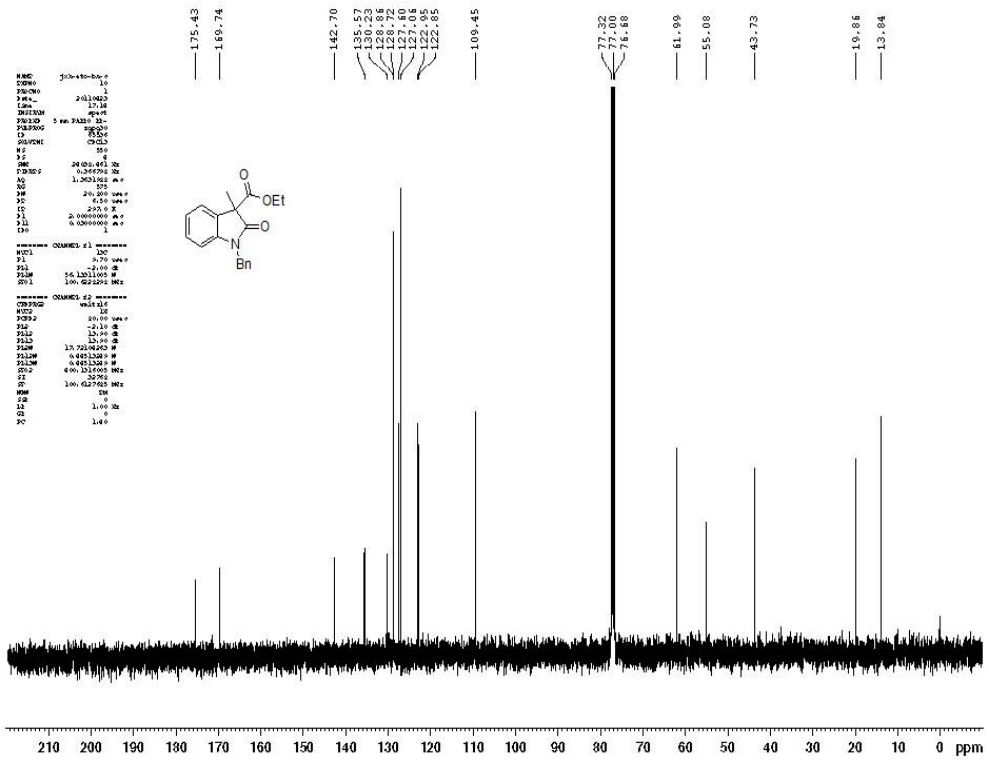
1b



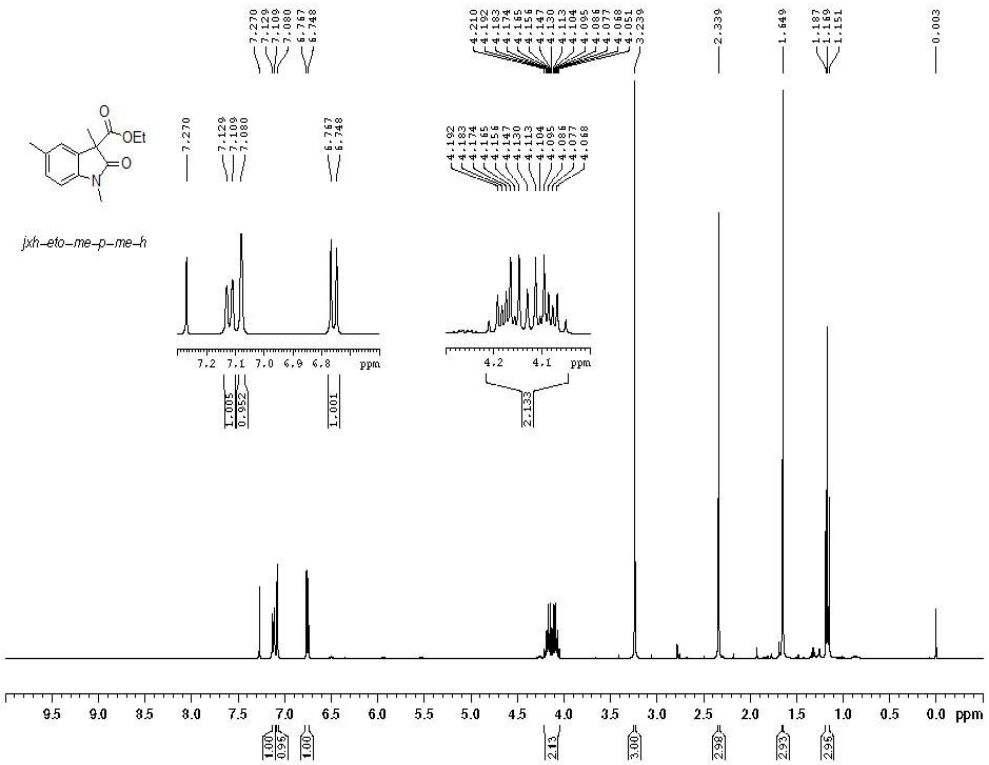


2b





3b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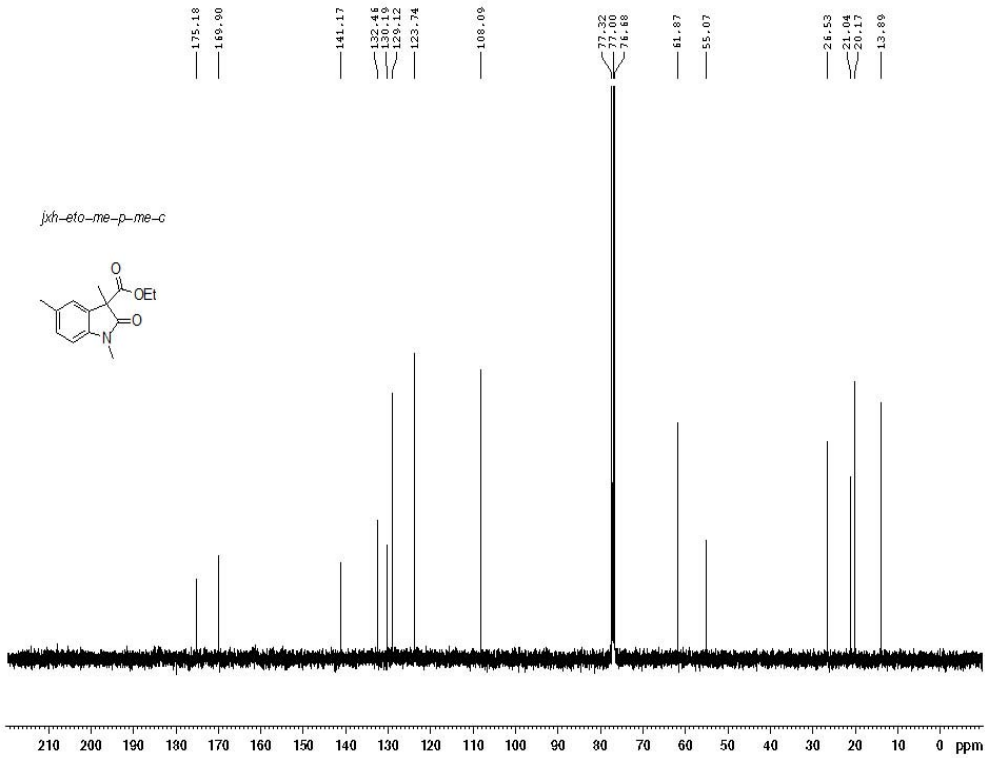
2.95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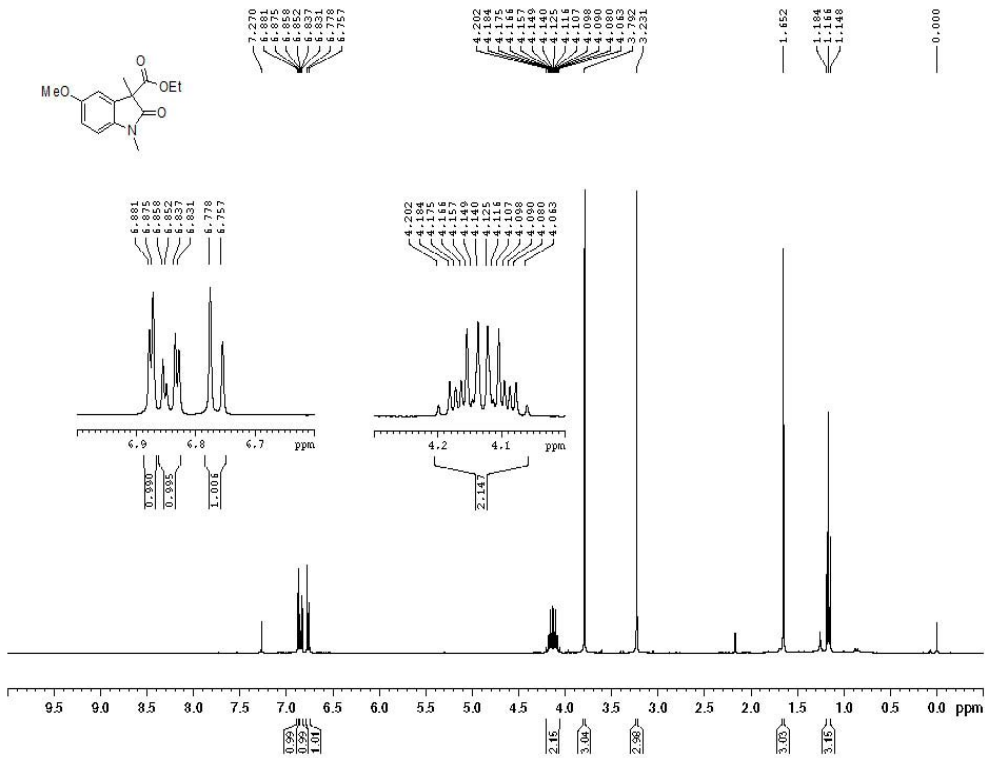
4b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6.8
6.7
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1.006
2.143
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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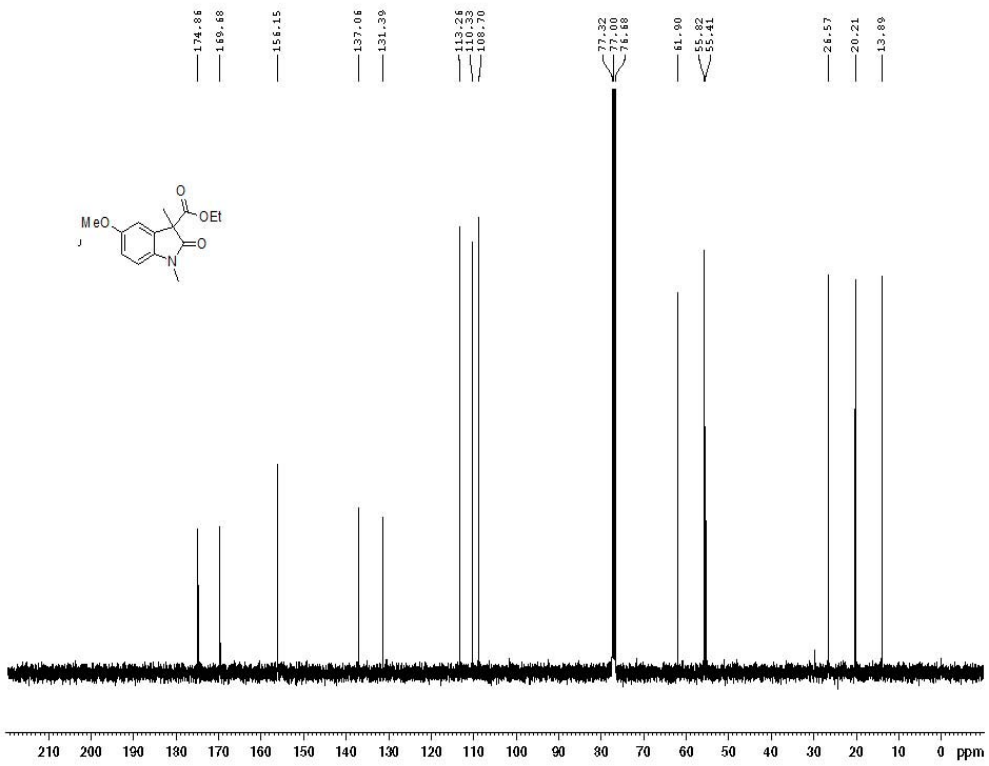
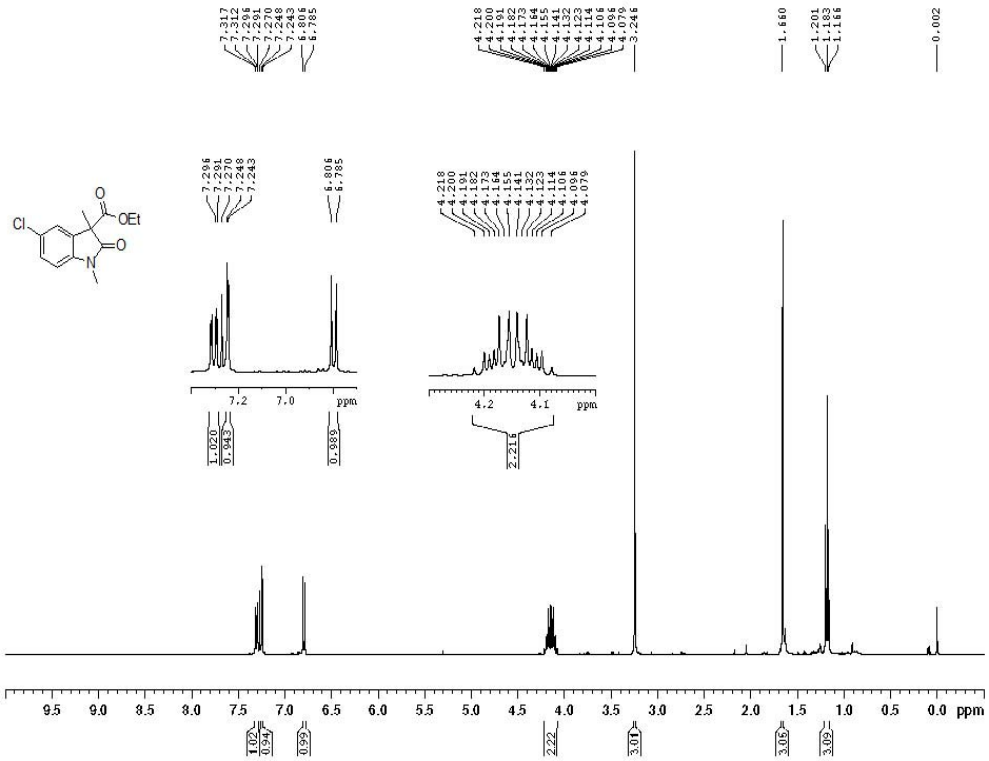
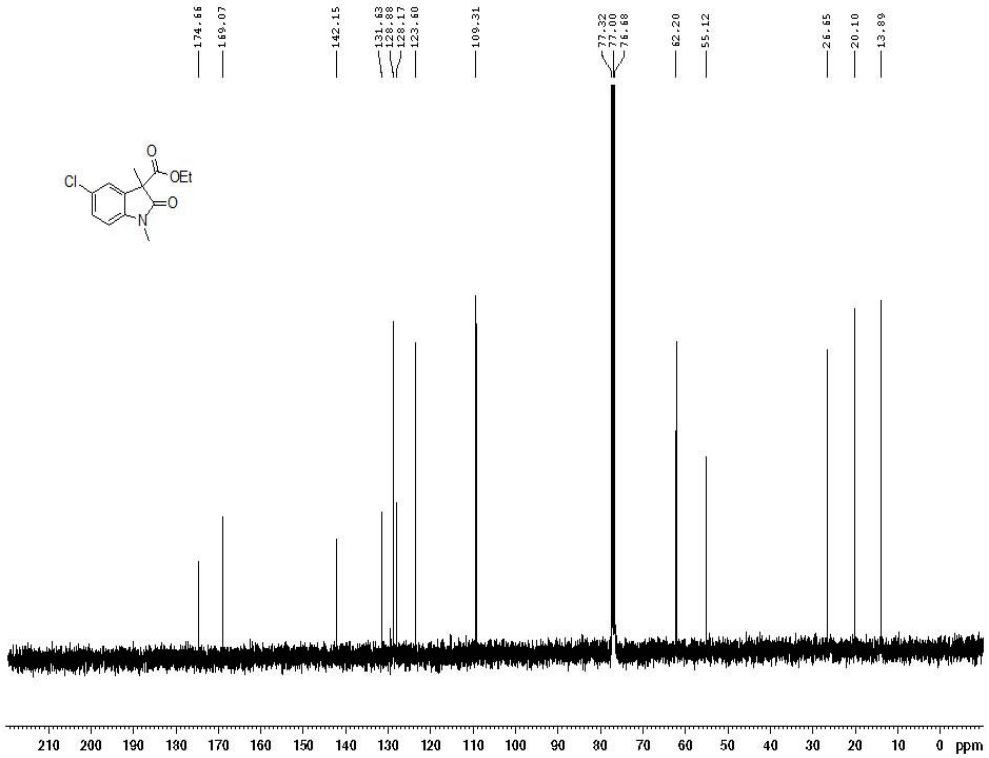
3.04
2.98
3.05
3.16

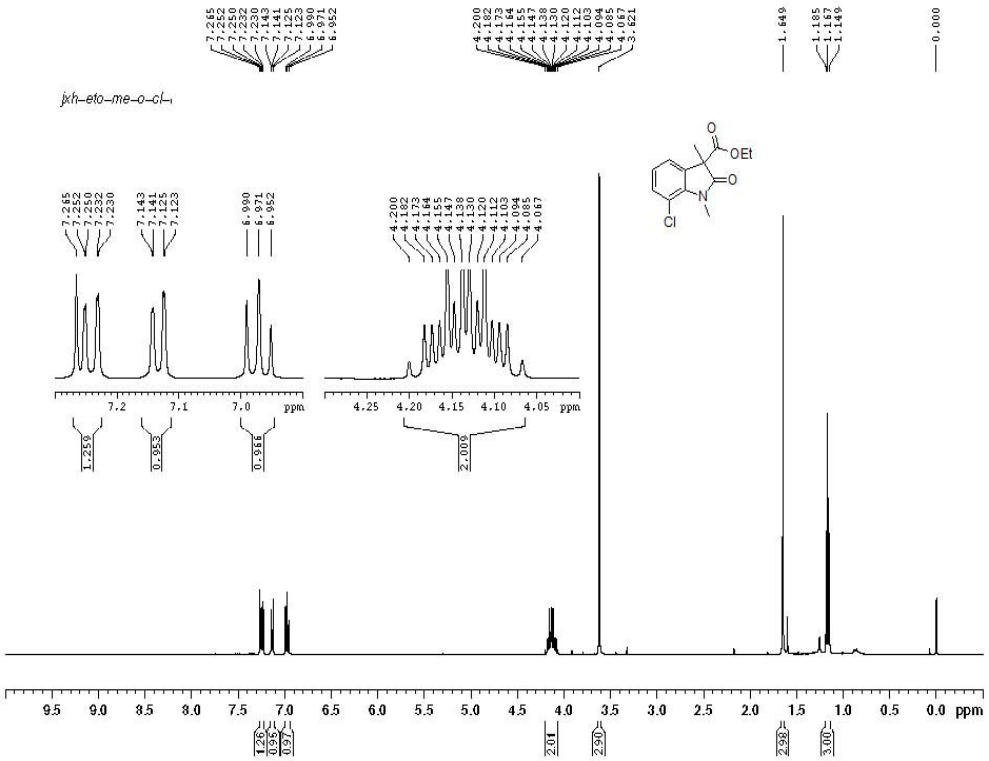

174.86
169.68
156.15
137.06
131.39
113.26
110.33
108.70
77.32
77.00
76.68
61.90
55.82
55.41
26.57
20.21
13.89
MeO
OEt
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

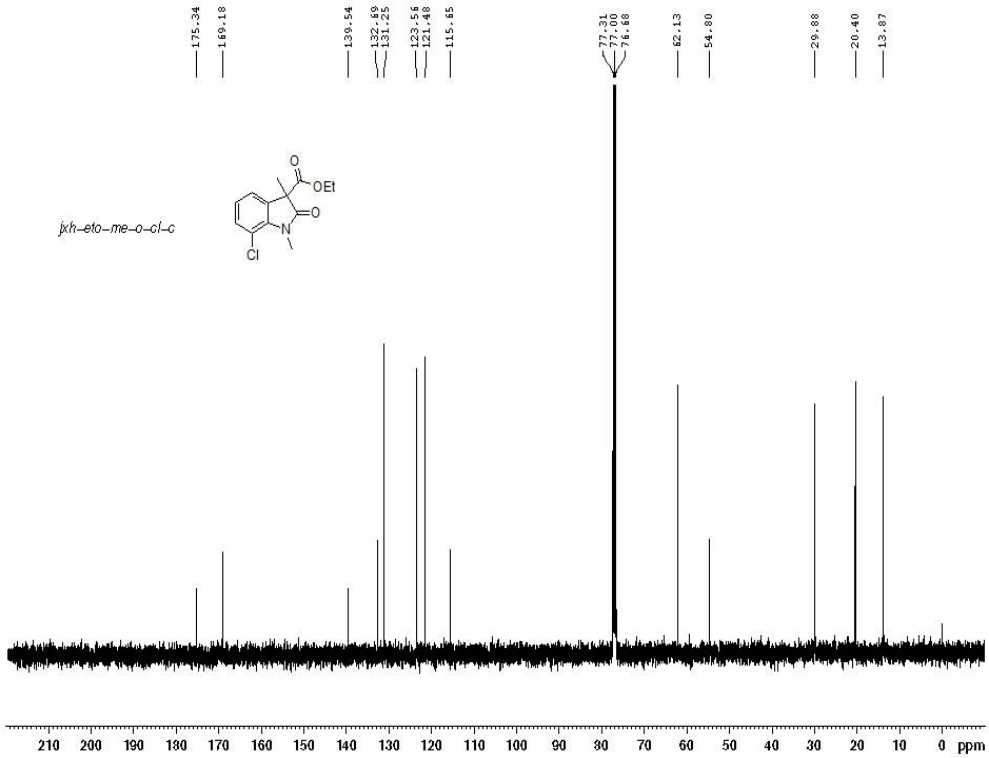
5b


7.317
7.312
7.296
7.291
7.270
7.248
7.243
6.806
6.785
4.218
4.200
4.191
4.182
4.173
4.164
4.155
4.141
4.132
4.123
4.114
4.106
4.096
4.079
3.246
1.660
1.201
1.183
1.166
0.002
Cl
OEt
O
N
7.2
7.0
ppm
4.2
4.1
ppm
1.020
0.943
0.989
2.216
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 ppm
1.02
0.94
0.99
2.22
3.01
3.05
3.09

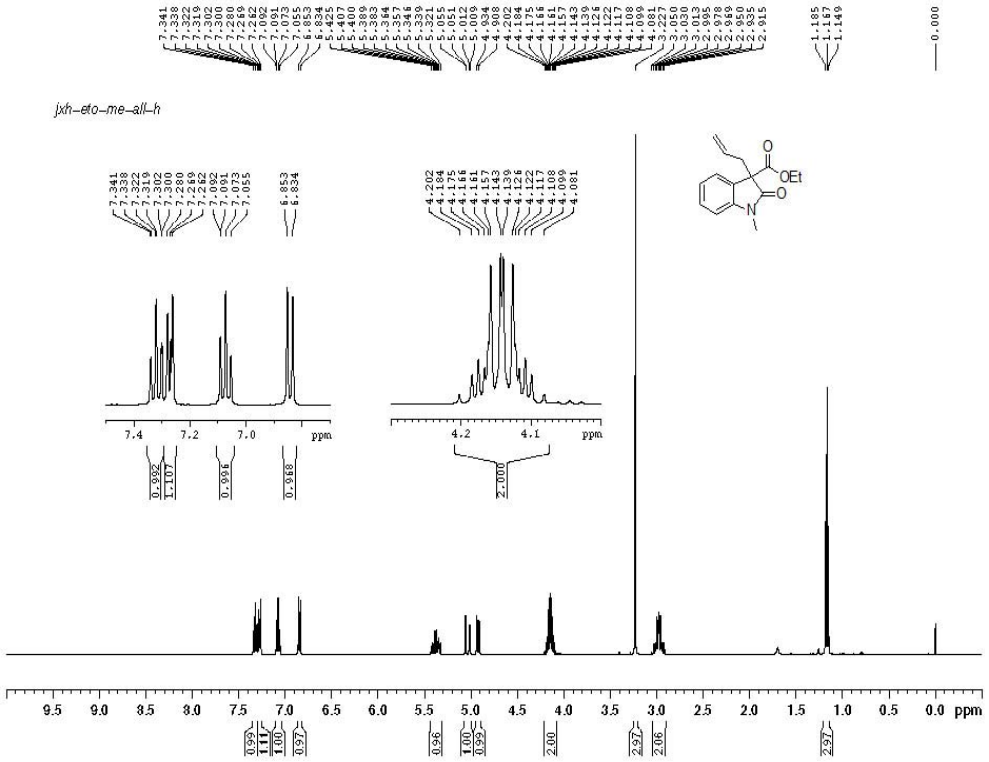

174.66
169.07
142.15
131.63
128.88
128.17
123.60
109.31
77.32
77.00
76.68
62.20
55.12
26.85
20.10
13.89
Cl
OEt
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

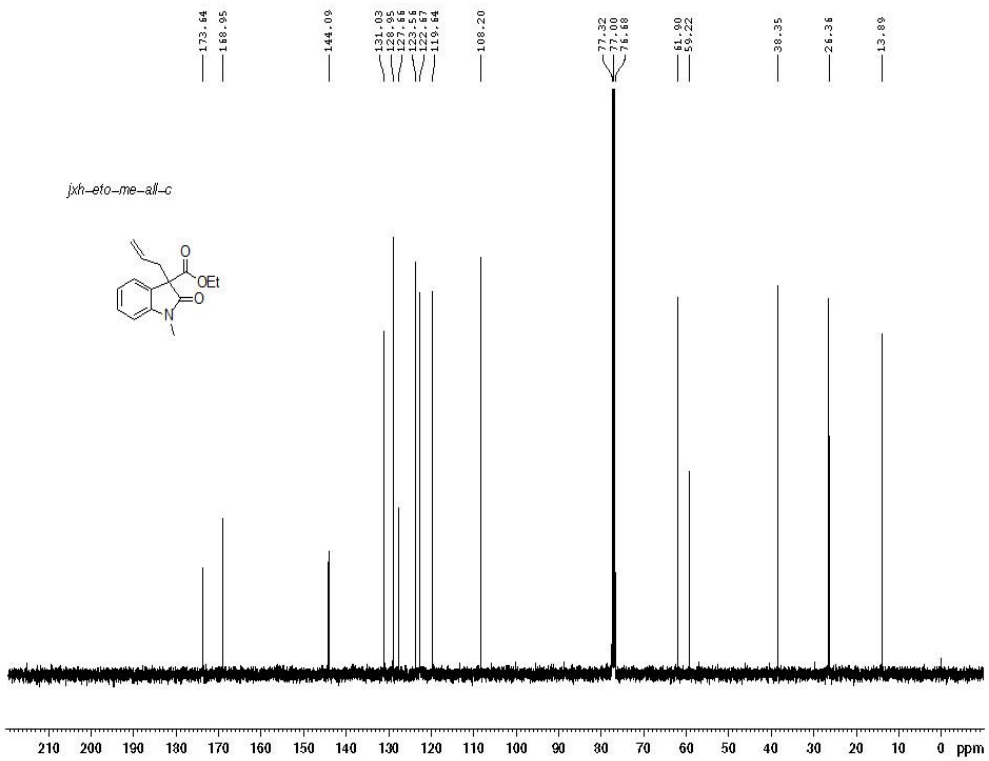
6b



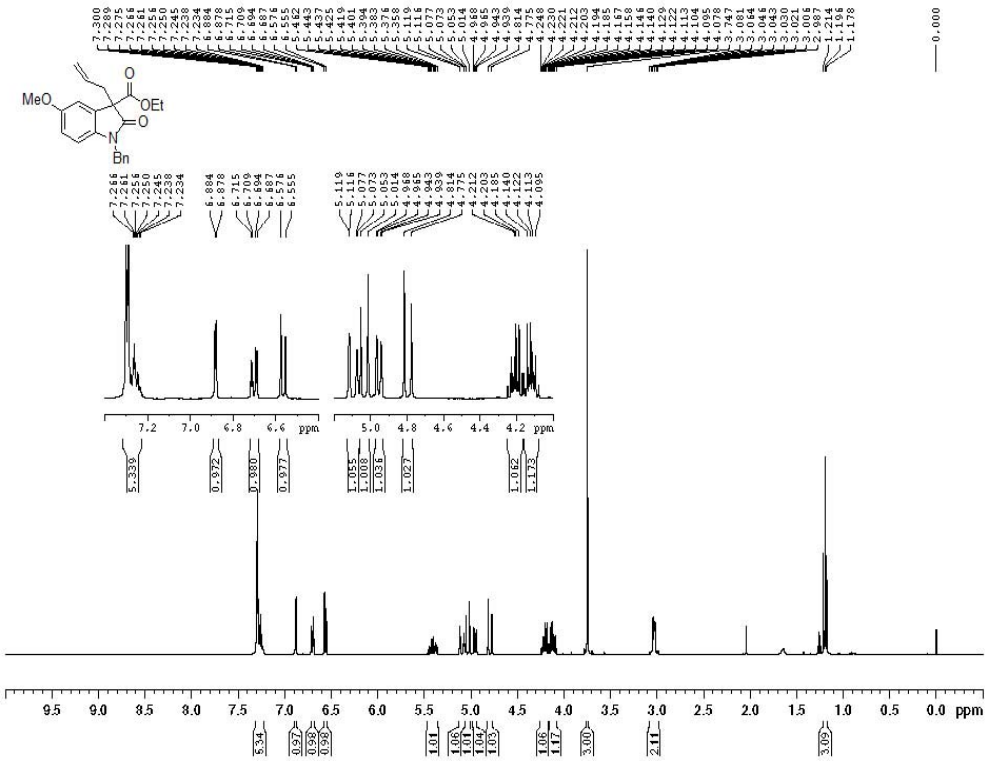


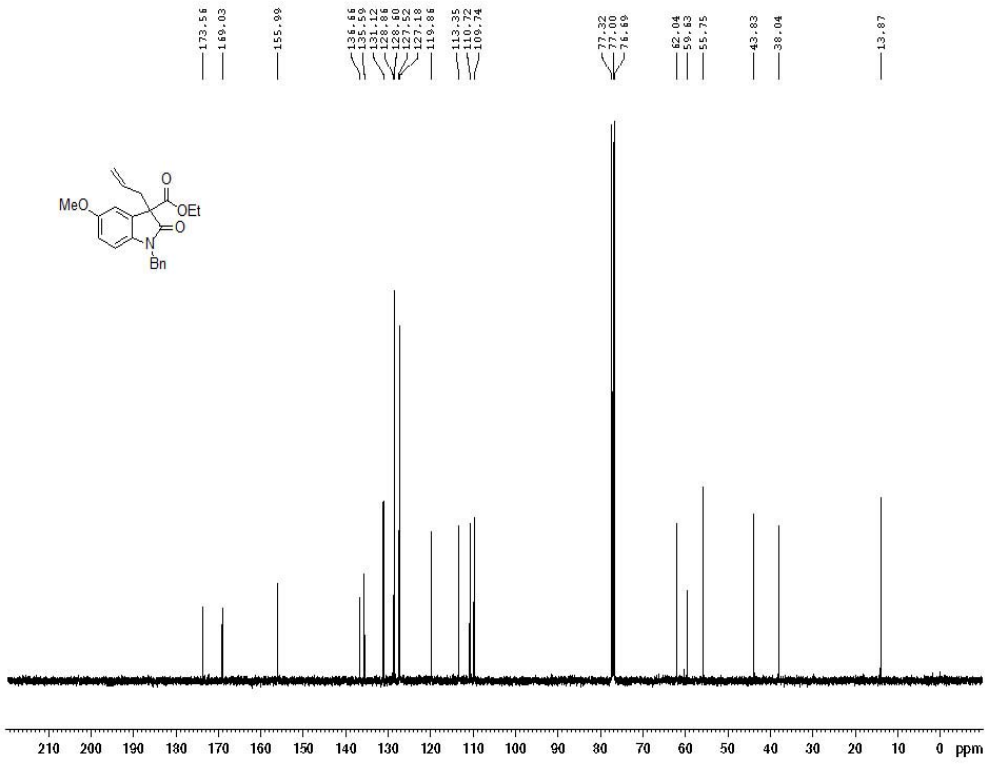
7b



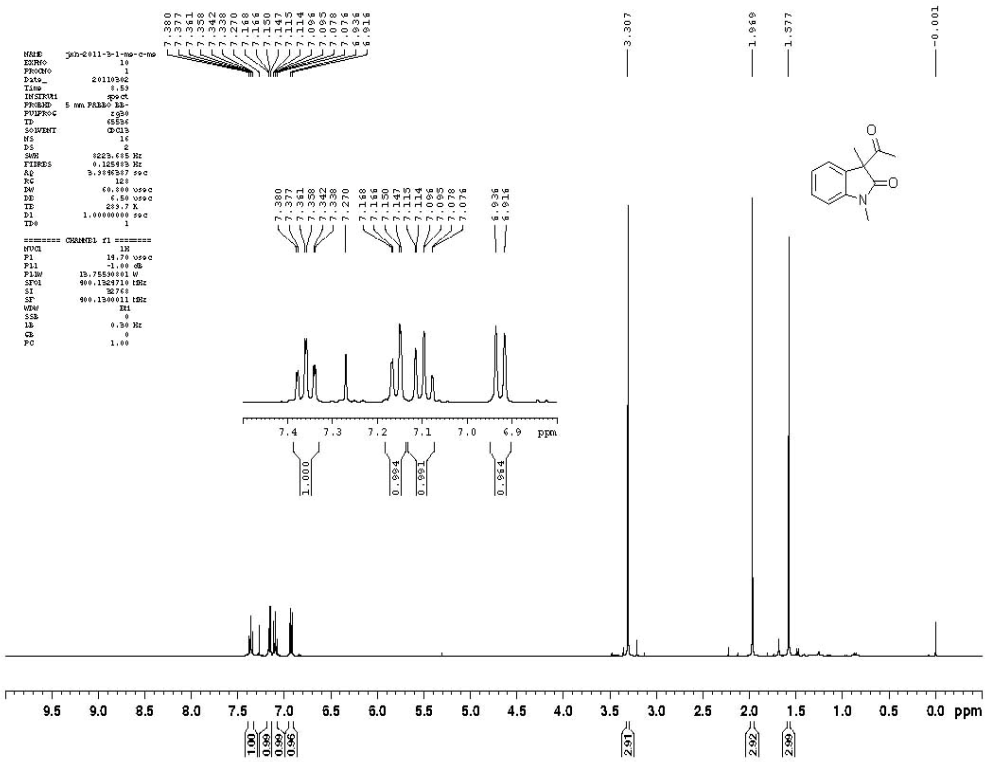


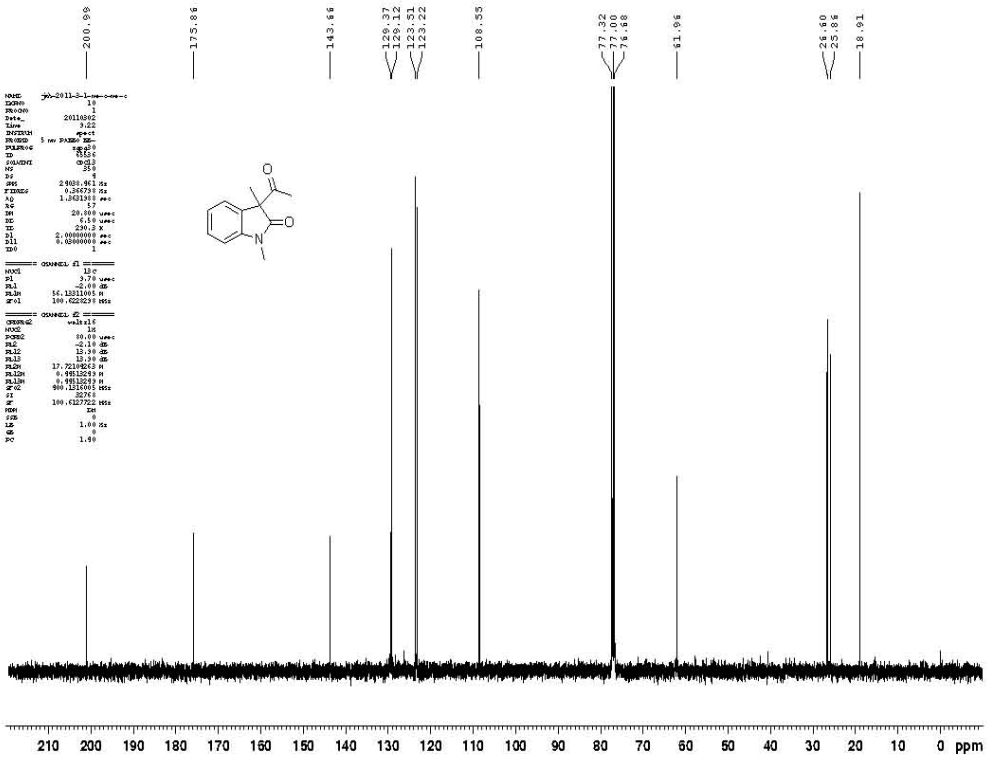
8b



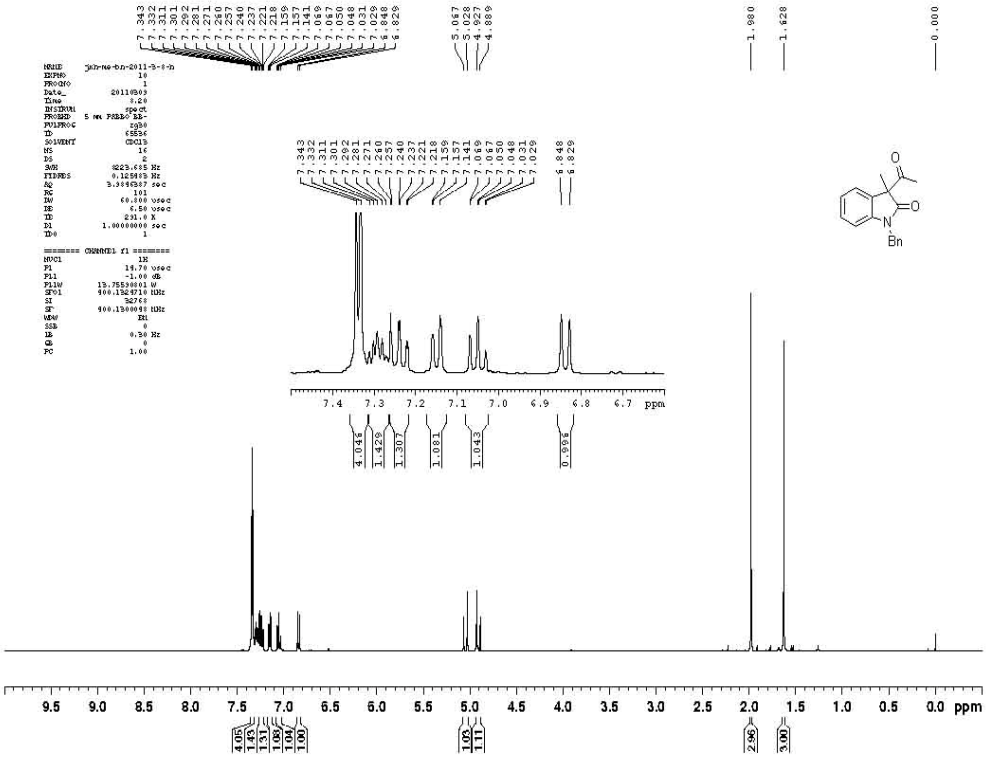


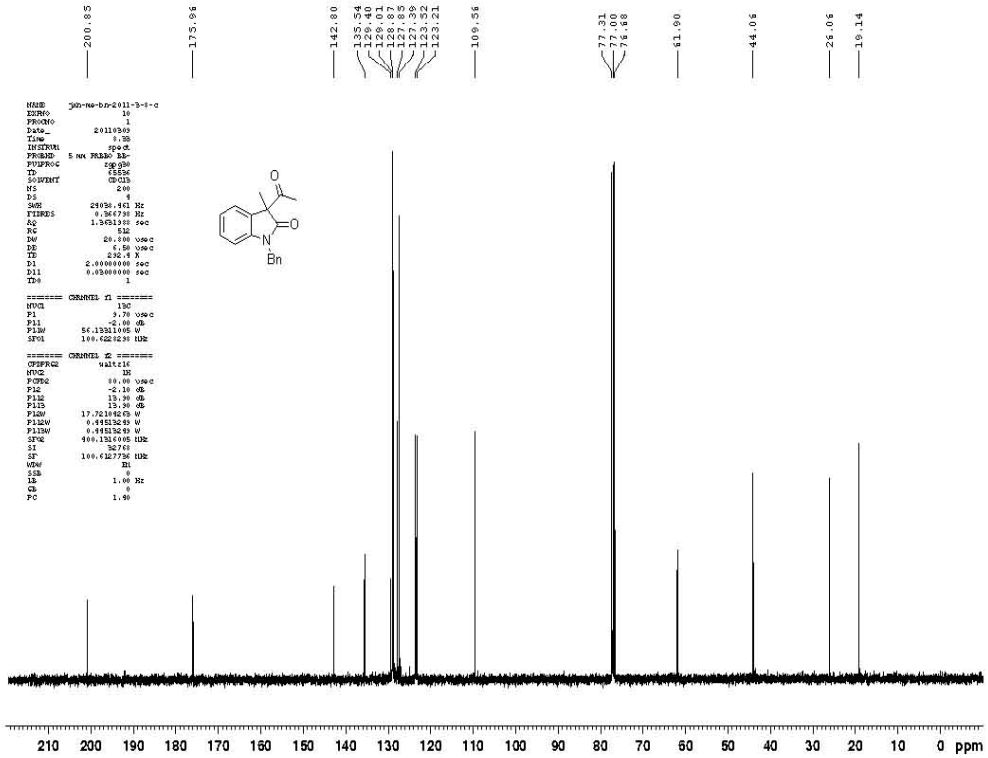
9b



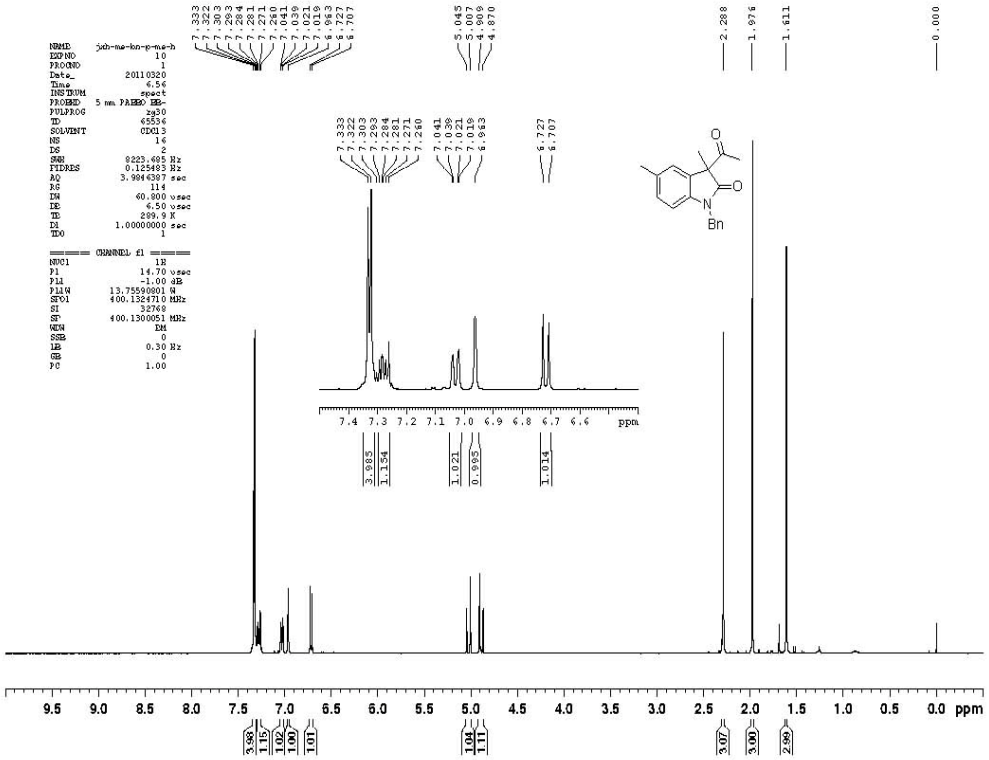


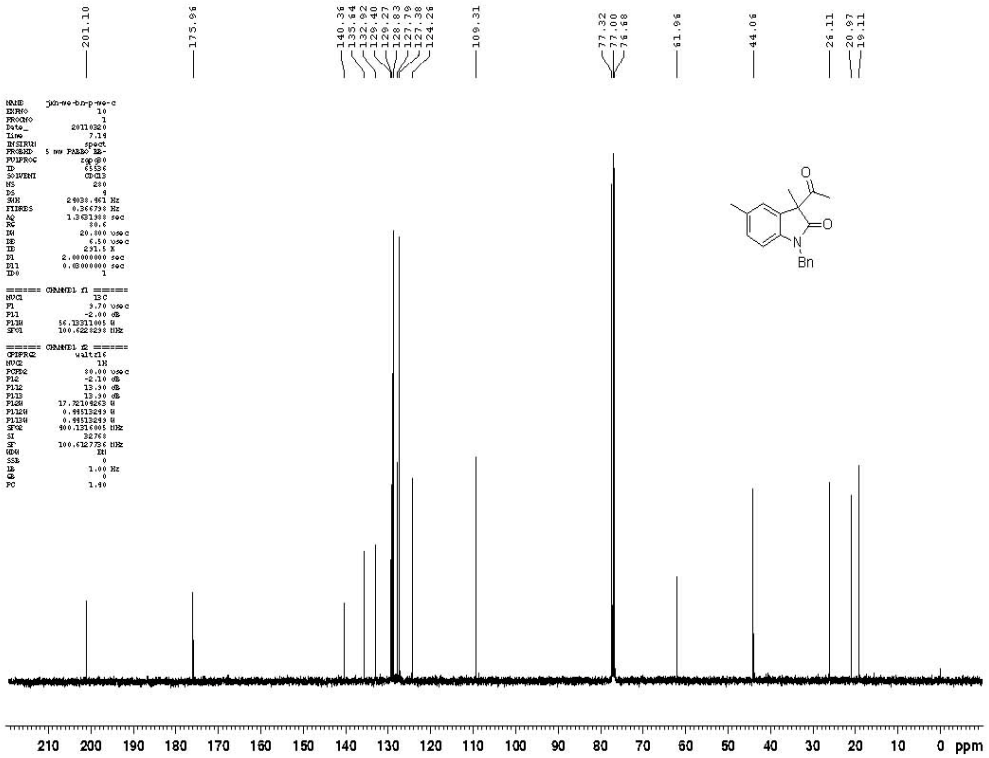
10b



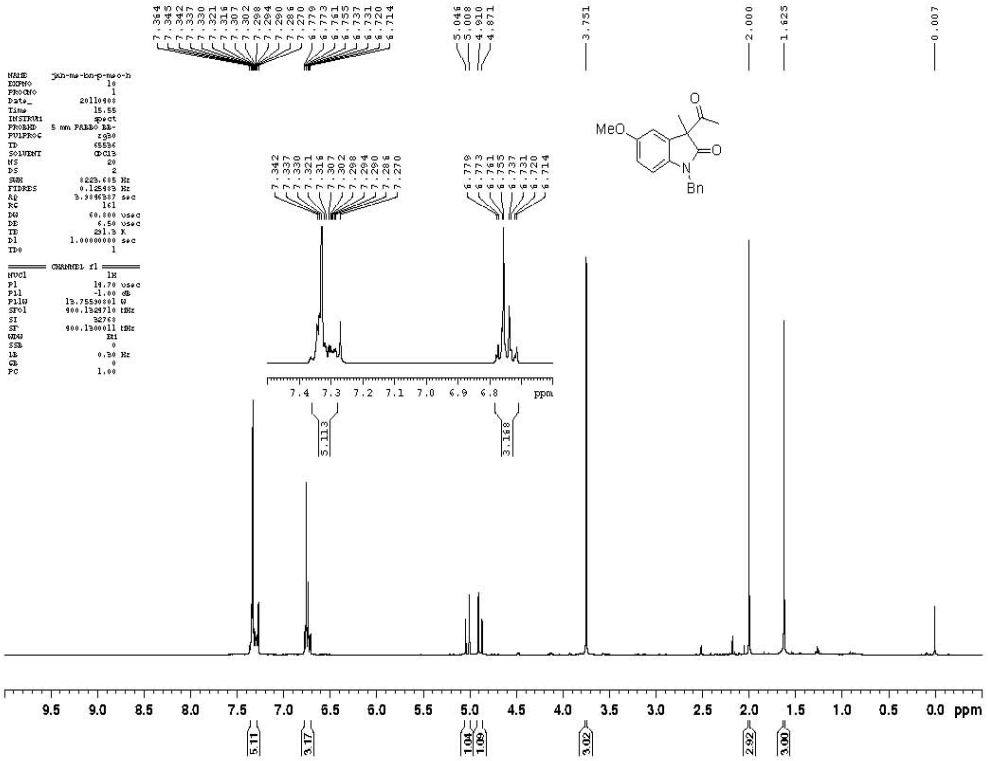


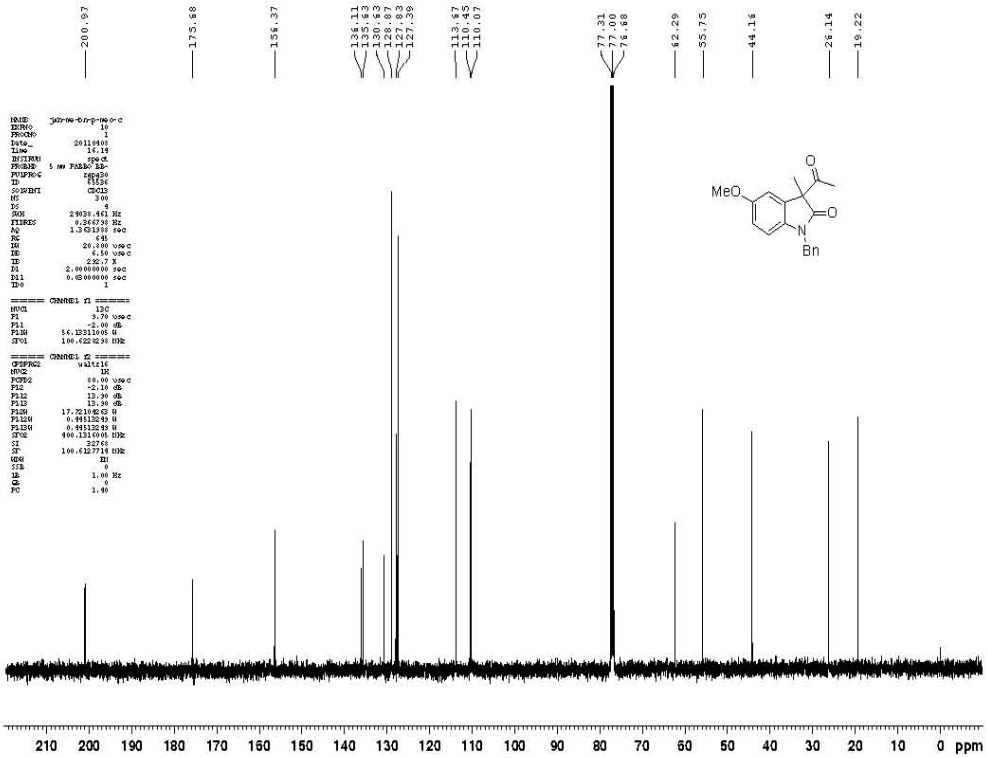
11b



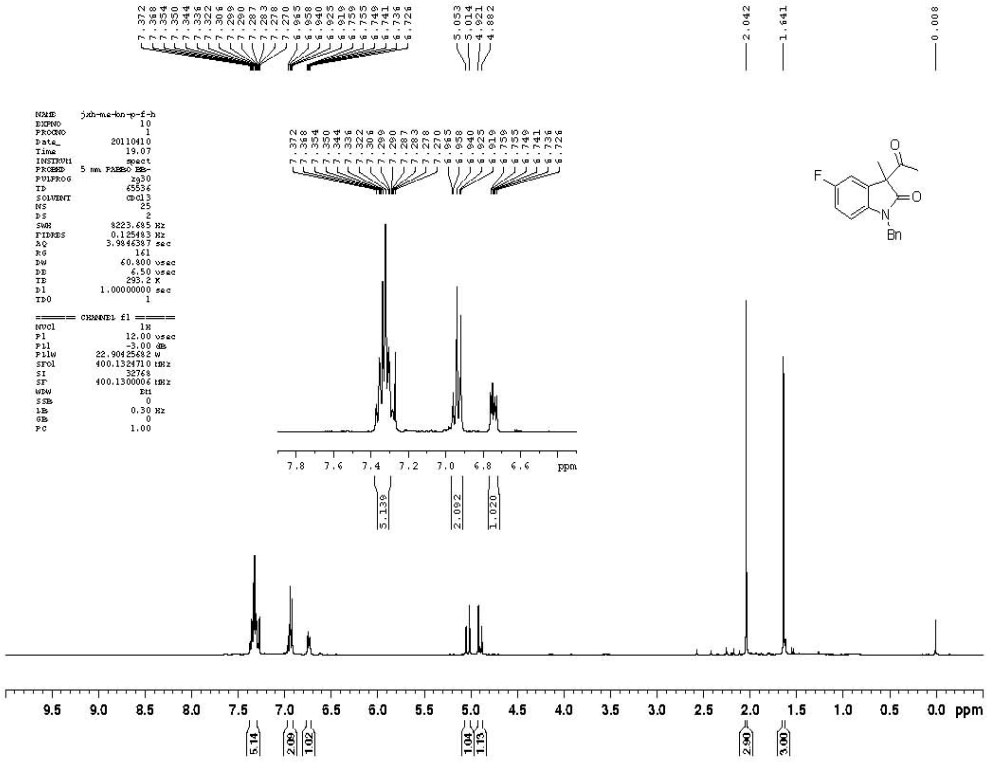


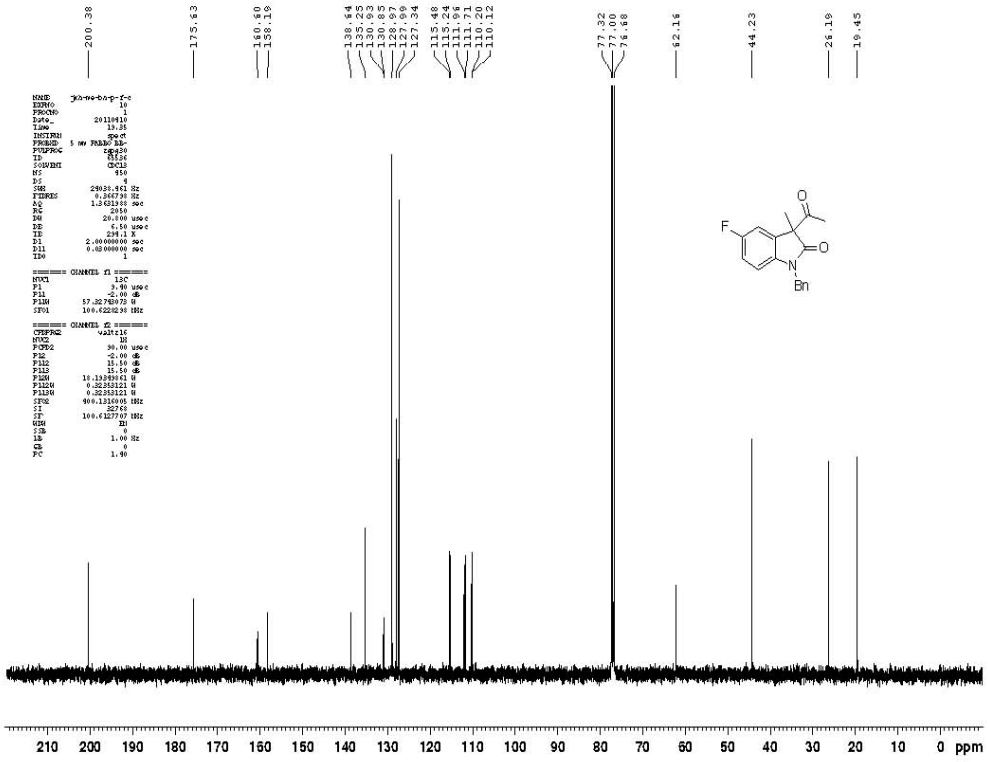
12b



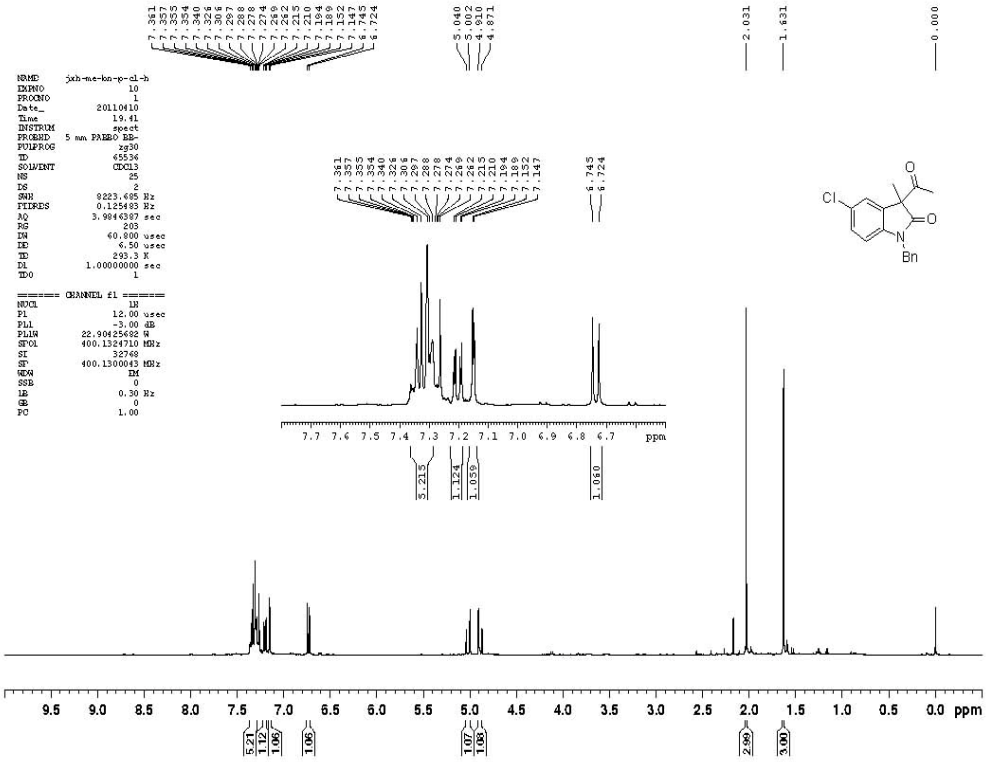


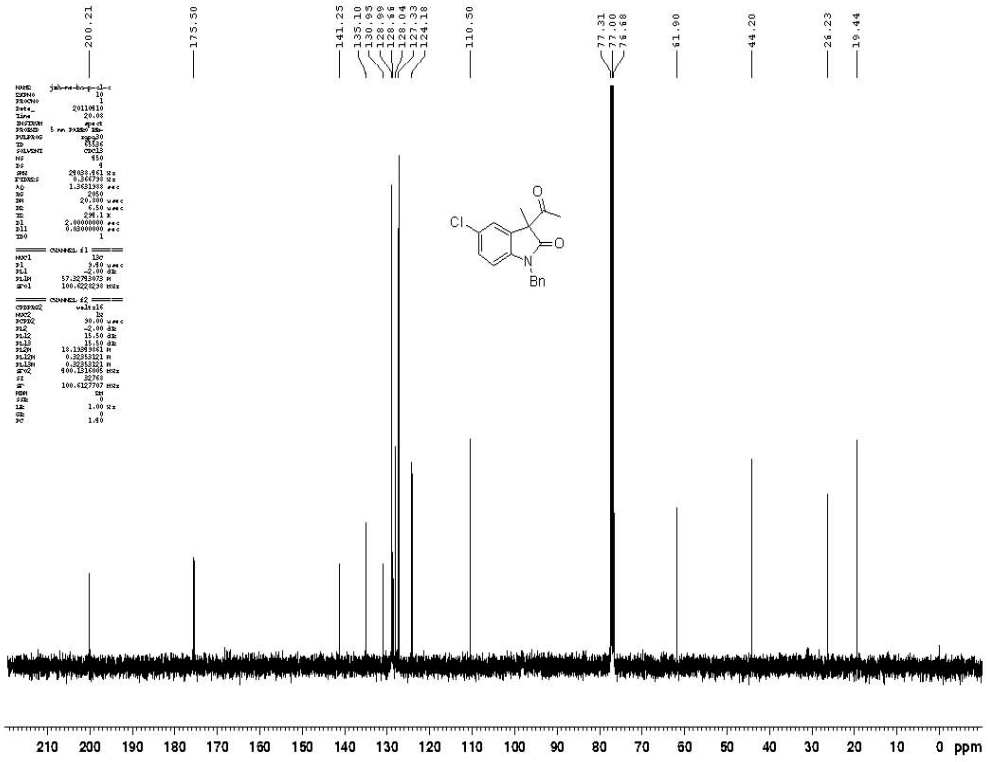
13b



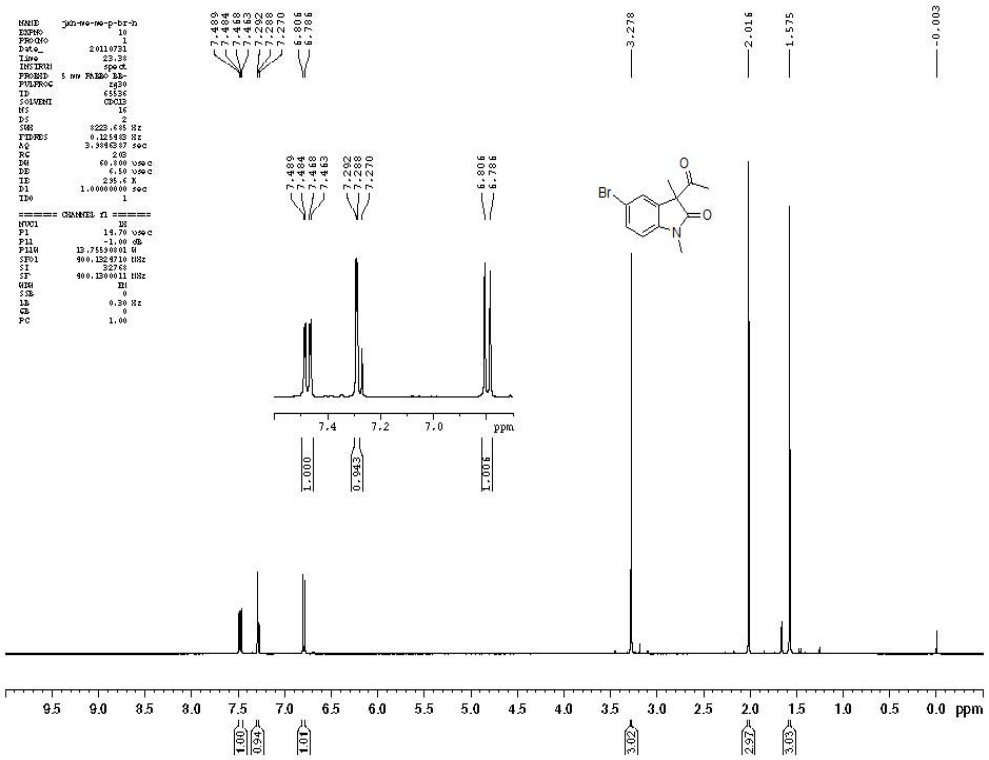


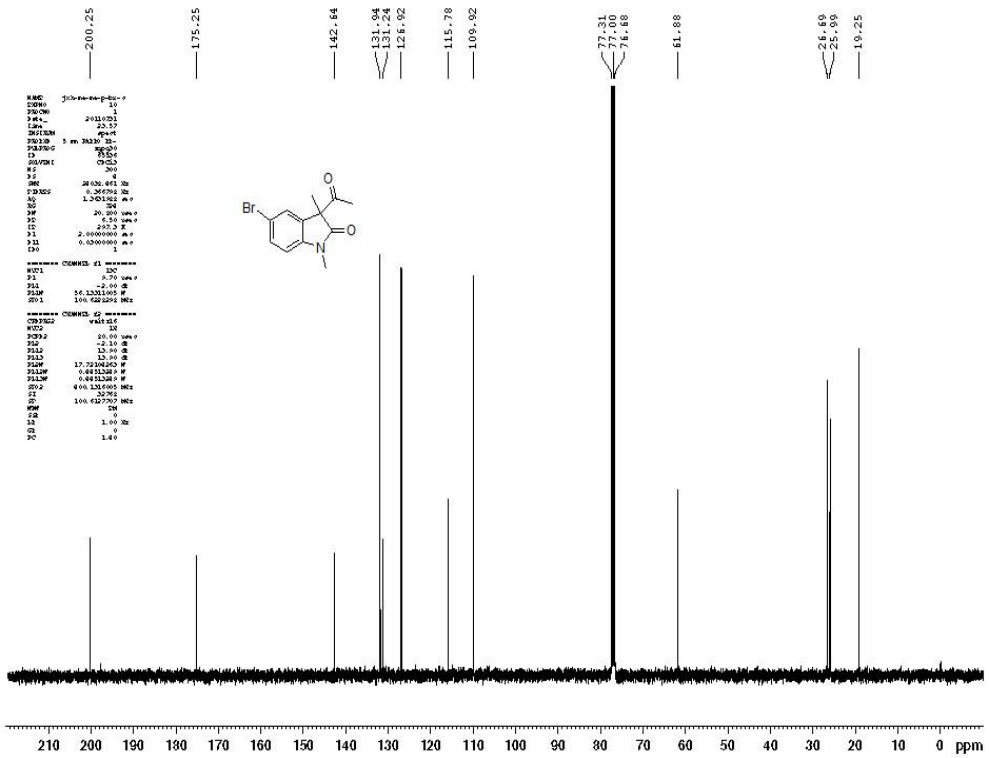
14b



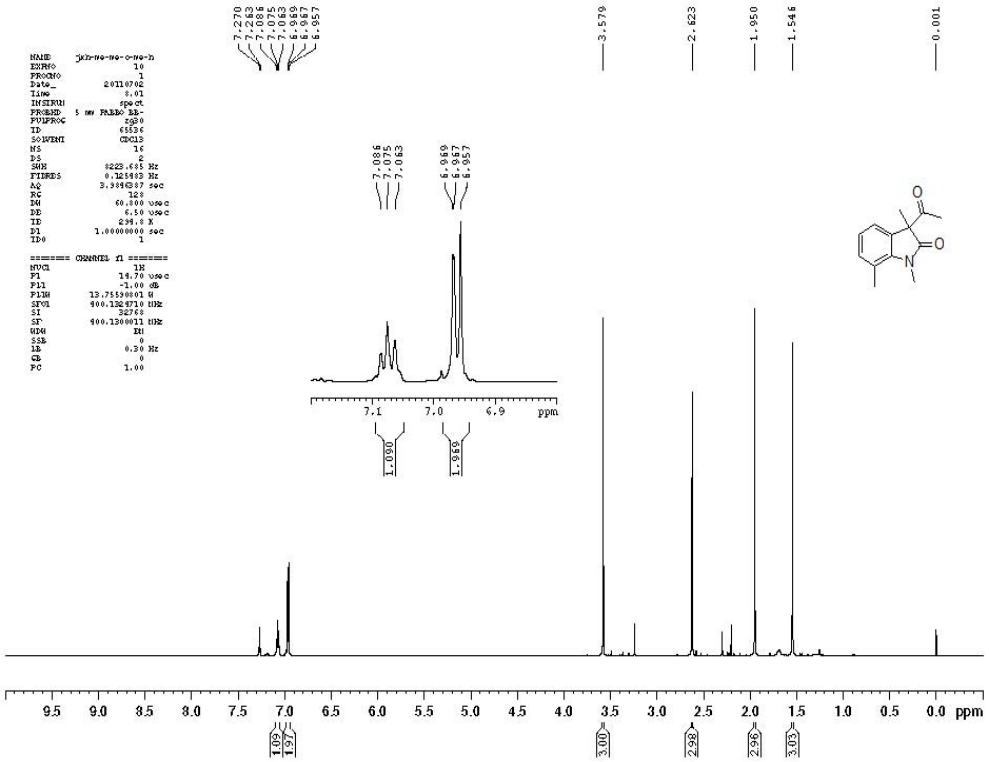


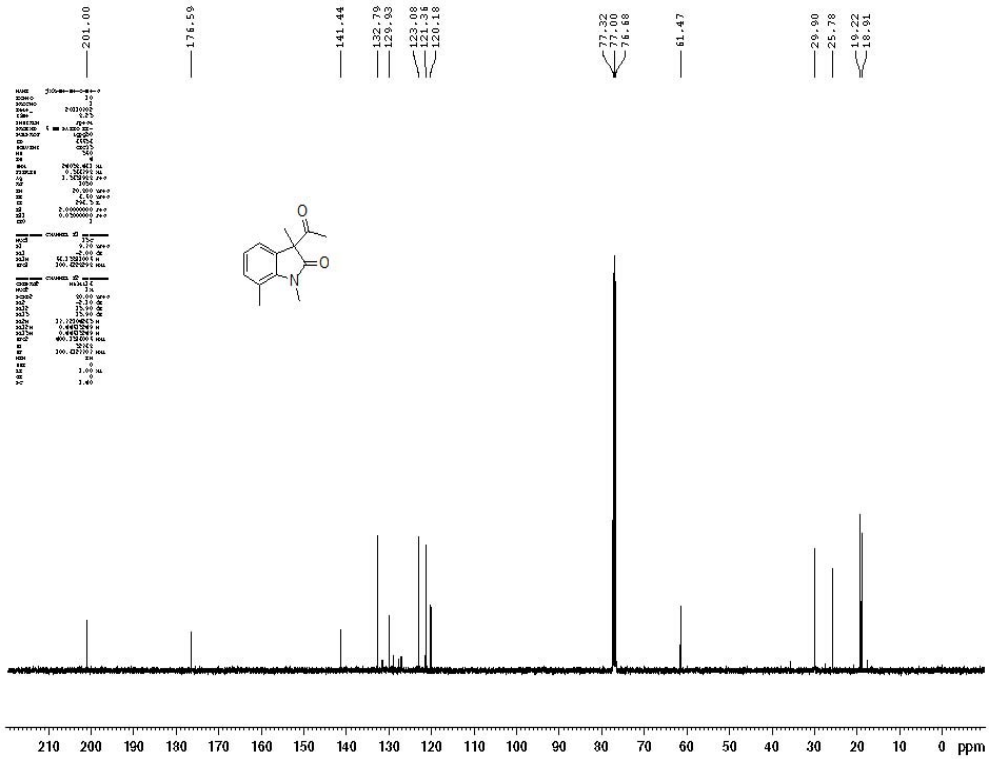
15b


7.489
7.484
7.468
7.463
7.292
7.288
7.270
6.806
6.786
3.278
2.016
1.575
-0.003
Br
O
N
7.4
7.2
7.0
ppm
1.000
0.943
1.006
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 ppm
1.00
0.94
1.01
3.02
2.97
3.03

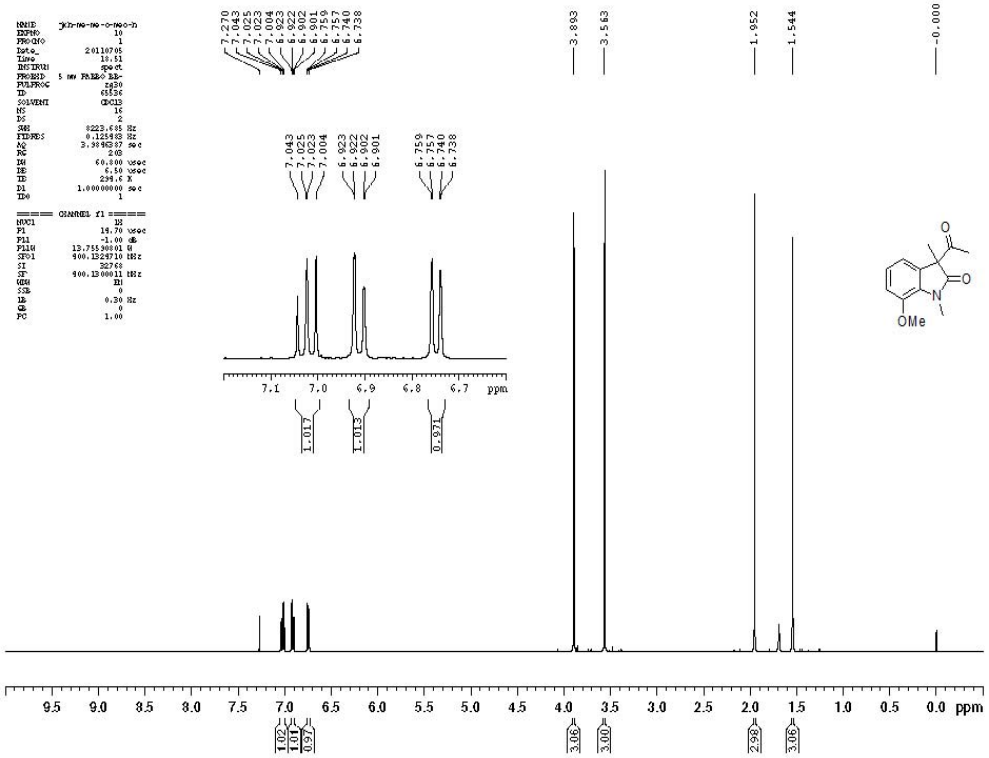

200.25
175.25
142.64
131.94
131.24
126.92
115.78
109.92
77.31
77.00
76.68
61.88
26.69
25.99
19.25
Br
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

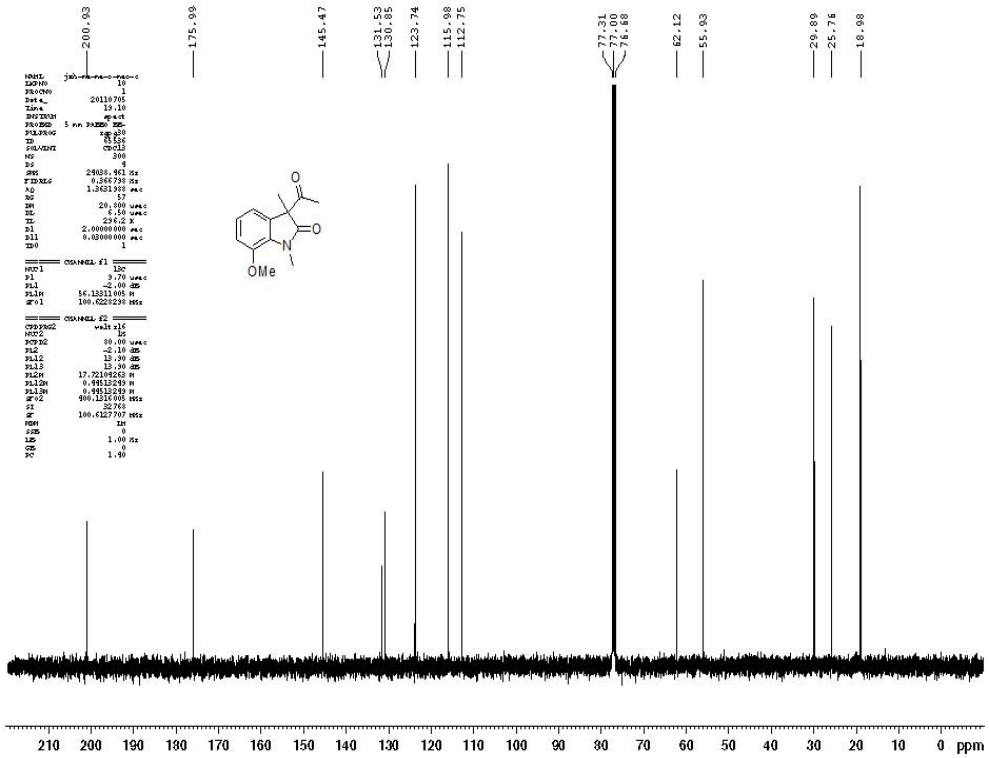
16b


7.270
7.263
7.256
7.075
7.063
6.969
6.957
3.579
2.623
1.950
1.546
0.001
7.086
7.075
7.063
6.969
6.957
6.957
7.1
7.0
6.9
ppm
1.090
1.969
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 ppm
1.09
1.97
3.00
2.98
2.96
3.03

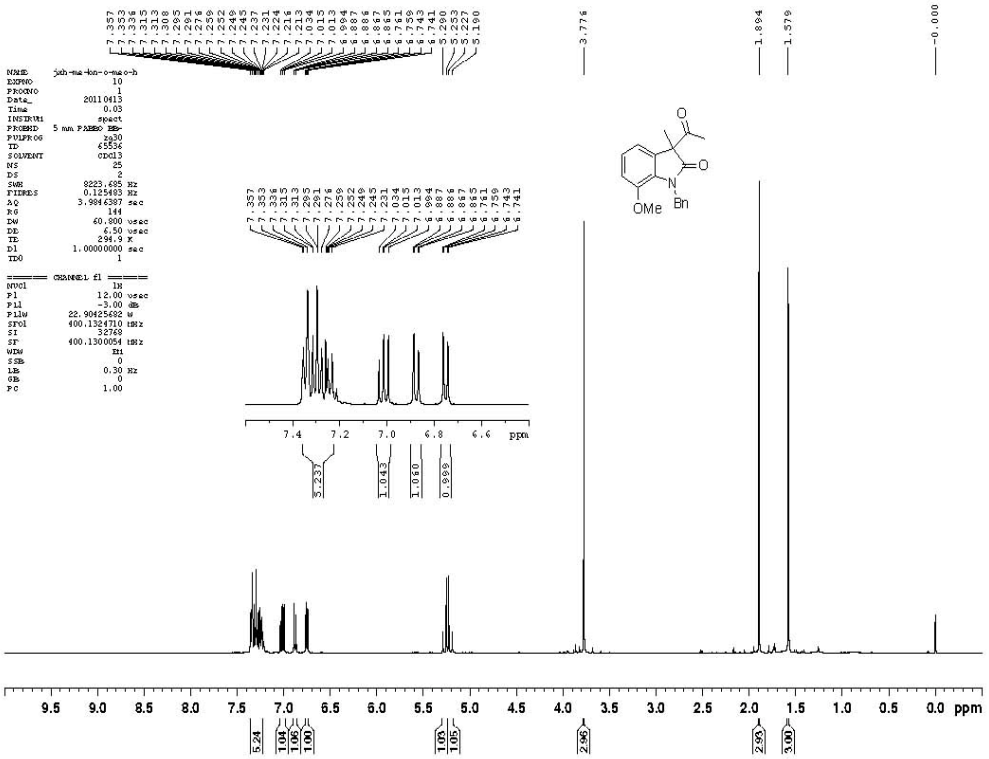

201.00
176.59
141.44
132.79
129.03
123.08
121.36
120.18
77.32
77.00
76.68
61.47
29.90
25.78
19.22
18.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

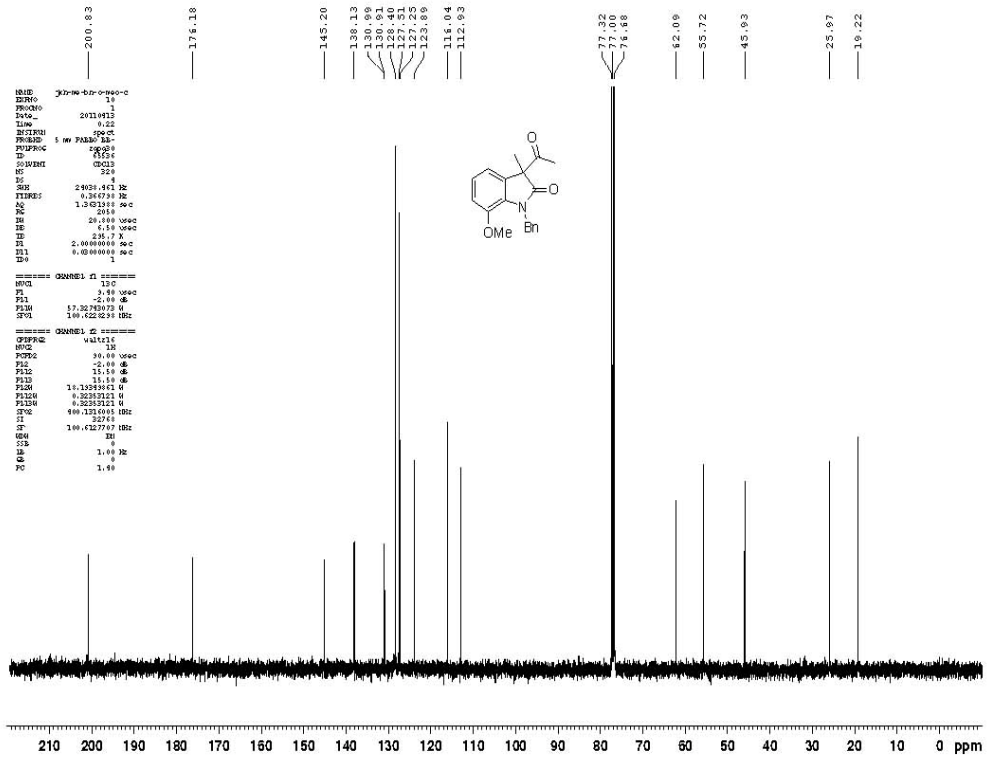
17b


7.270
7.043
7.025
7.023
7.004
6.923
6.922
6.902
6.901
6.759
6.757
6.740
6.738
3.893
3.583
1.952
1.544
0.000
OMe
7.1
7.0
6.9
6.8
6.7
ppm
1.017
1.013
0.971
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 ppm
1.02
1.01
0.97
3.06
3.00
2.98
3.06

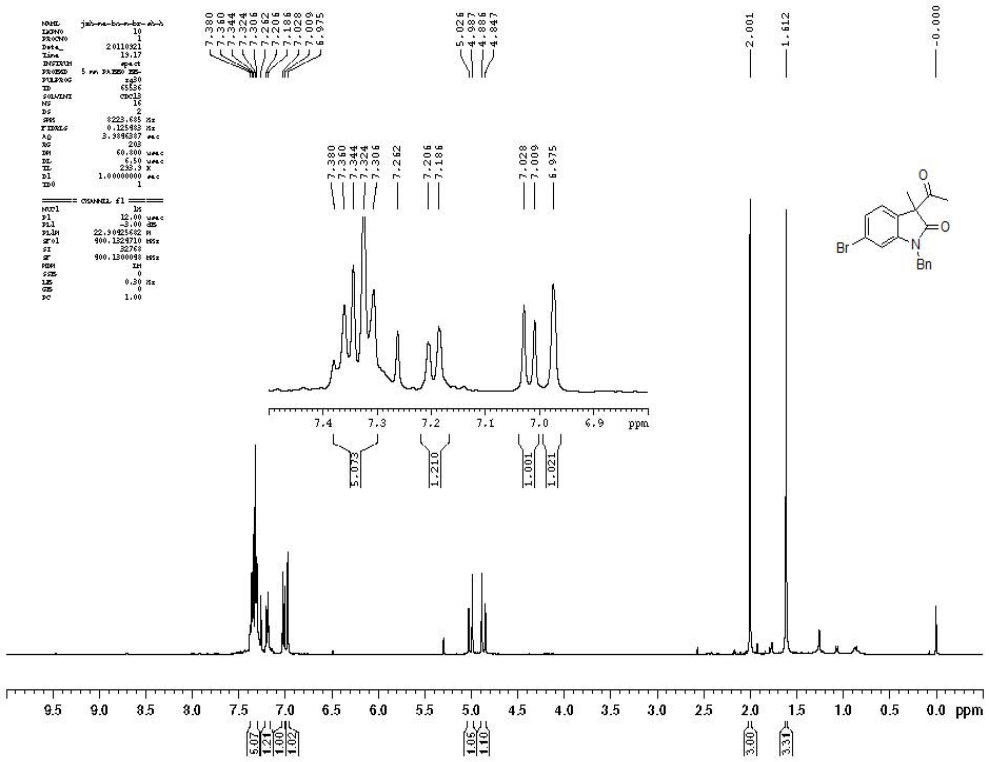

200.93
175.99
145.47
131.53
130.85
123.74
115.98
112.75
77.31
77.00
76.68
62.12
55.93
29.89
25.76
18.98
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

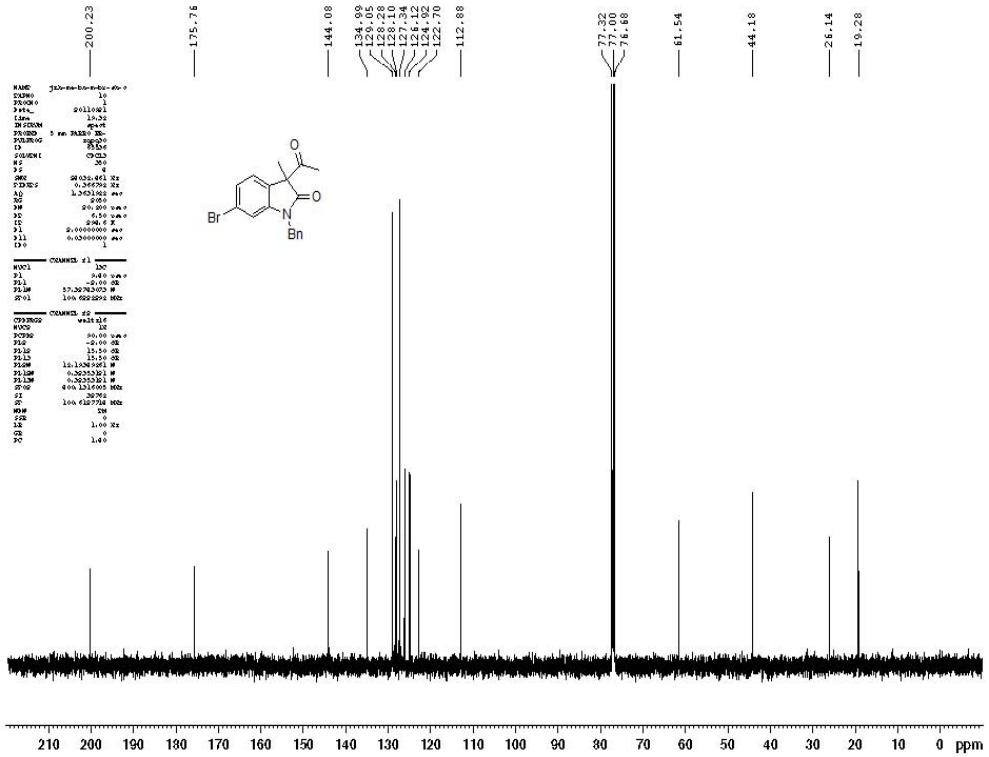
18b



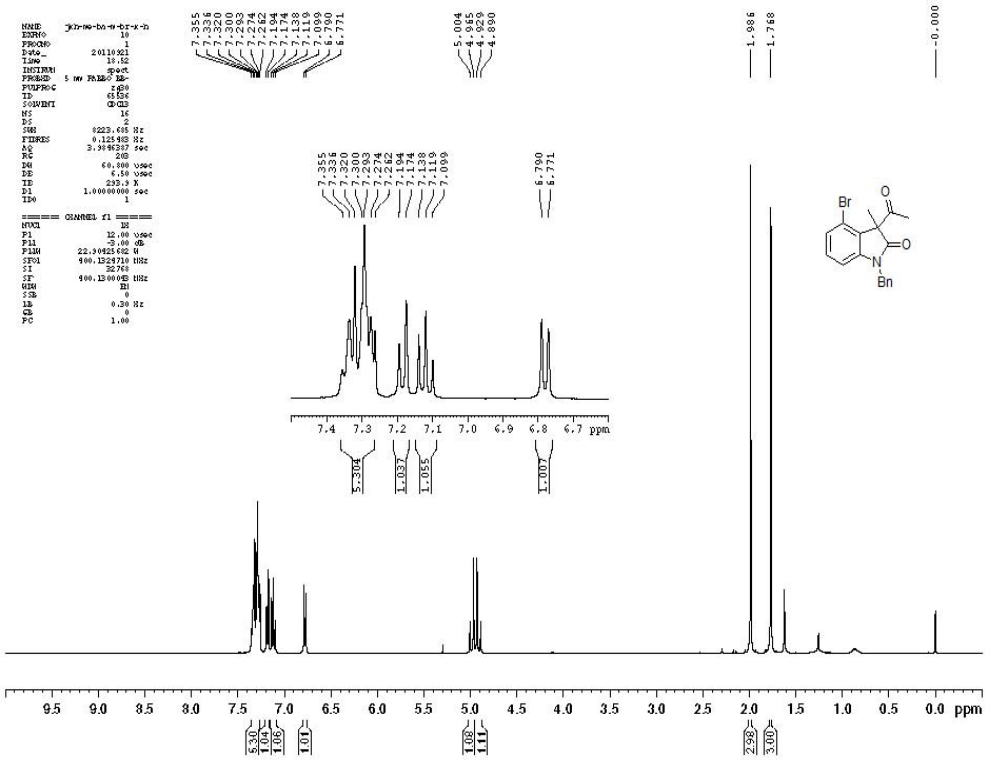


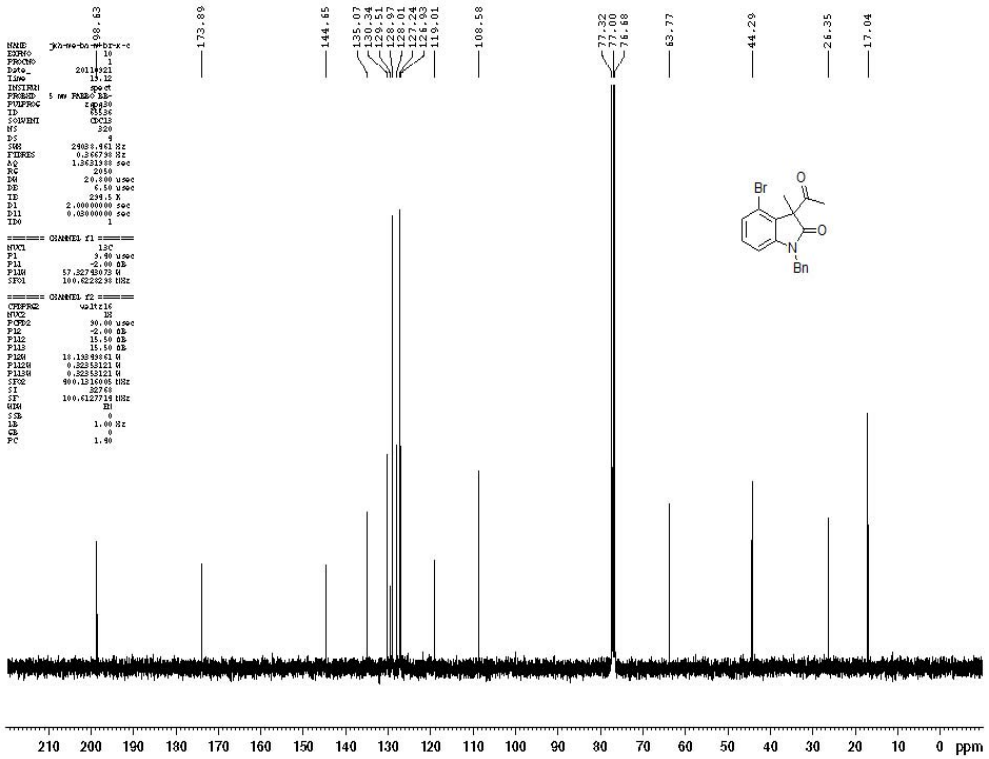
20b


7.380
7.360
7.344
7.324
7.306
7.262
7.206
7.186
7.028
7.009
6.975
5.025
4.887
4.866
4.847
2.001
1.612
0.000
Br
N
Bn
O
ppm
5.073
1.210
1.001
1.021
5.07
1.21
1.00
1.02
1.08
1.10
3.00
3.31

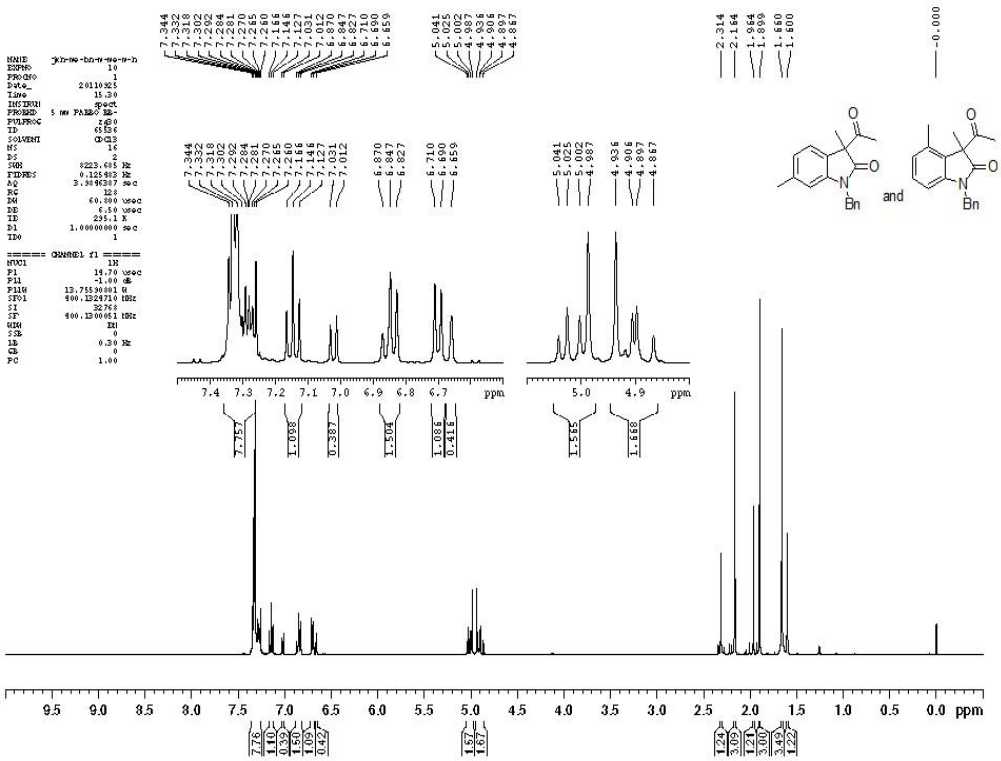

200.23
175.76
144.08
134.99
134.05
128.28
128.10
127.34
124.62
122.70
112.88
77.32
77.00
76.68
61.54
44.18
26.14
19.28
Br
N
Bn
O
ppm

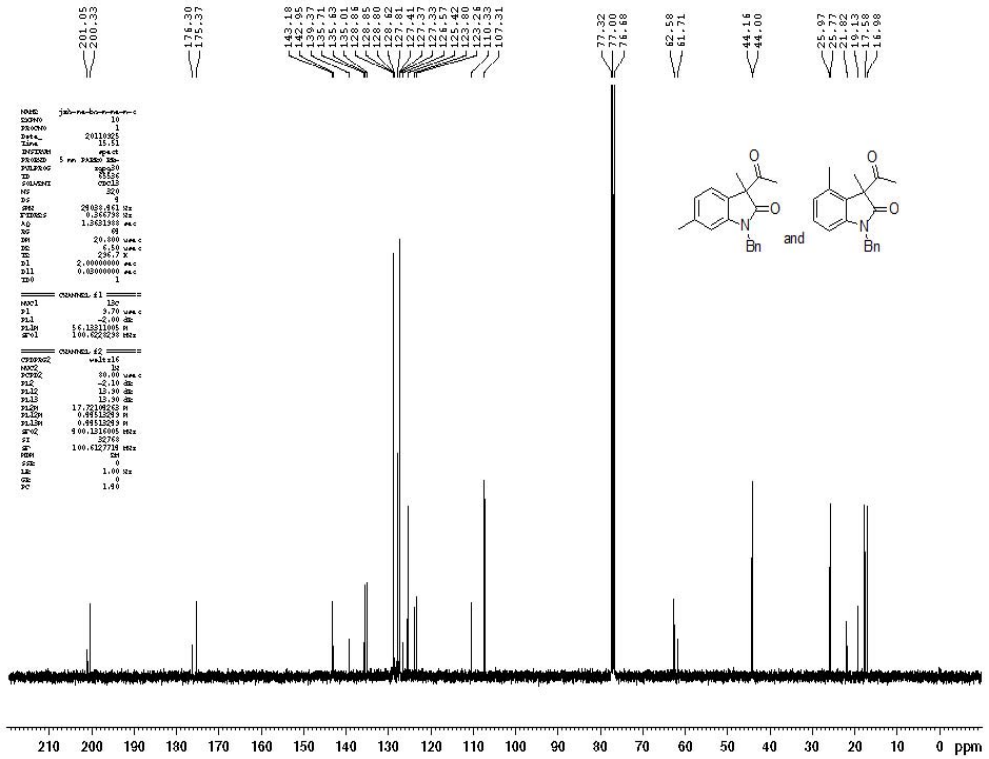
20b’


7.355
7.336
7.320
7.300
7.293
7.274
7.262
7.194
7.174
7.138
7.119
7.099
6.790
6.771
5.004
4.965
4.929
4.890
1.986
1.768
0.000
Br
O
O
N
Bn
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 ppm
5.30
1.03
1.05
1.01
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 ppm
1.00
1.11
2.98
3.00

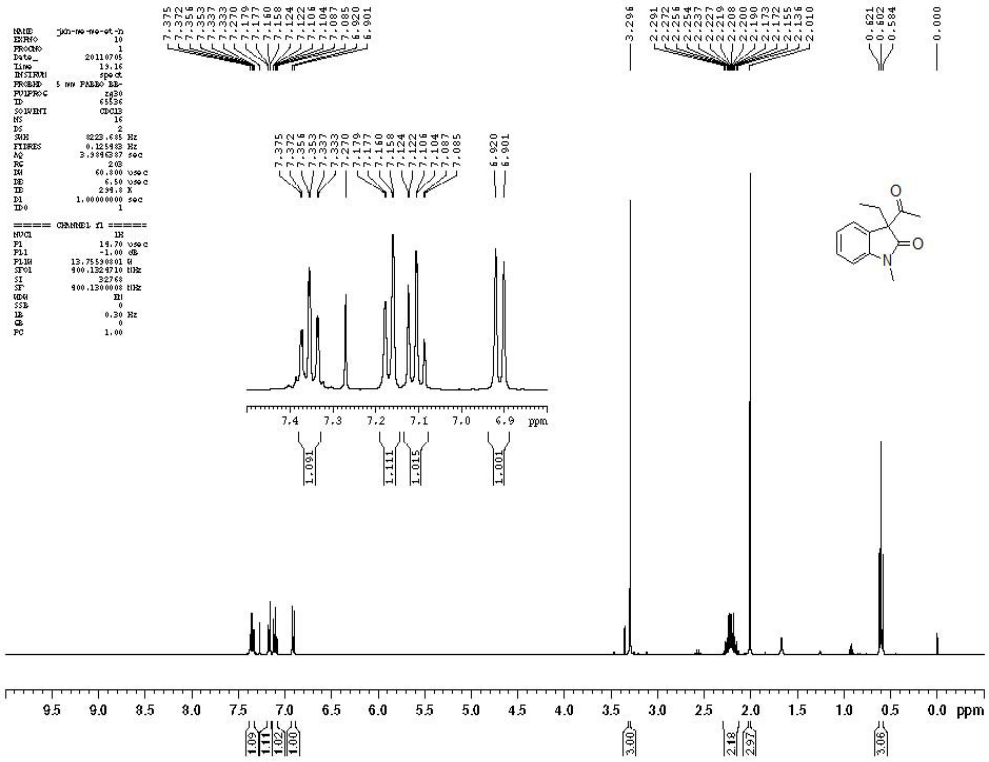

173.89
144.65
135.07
130.34
129.51
128.97
127.01
122.84
121.93
119.01
108.58
77.32
77.00
76.68
63.77
44.29
26.35
17.04
Br
O
O
N
Bn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

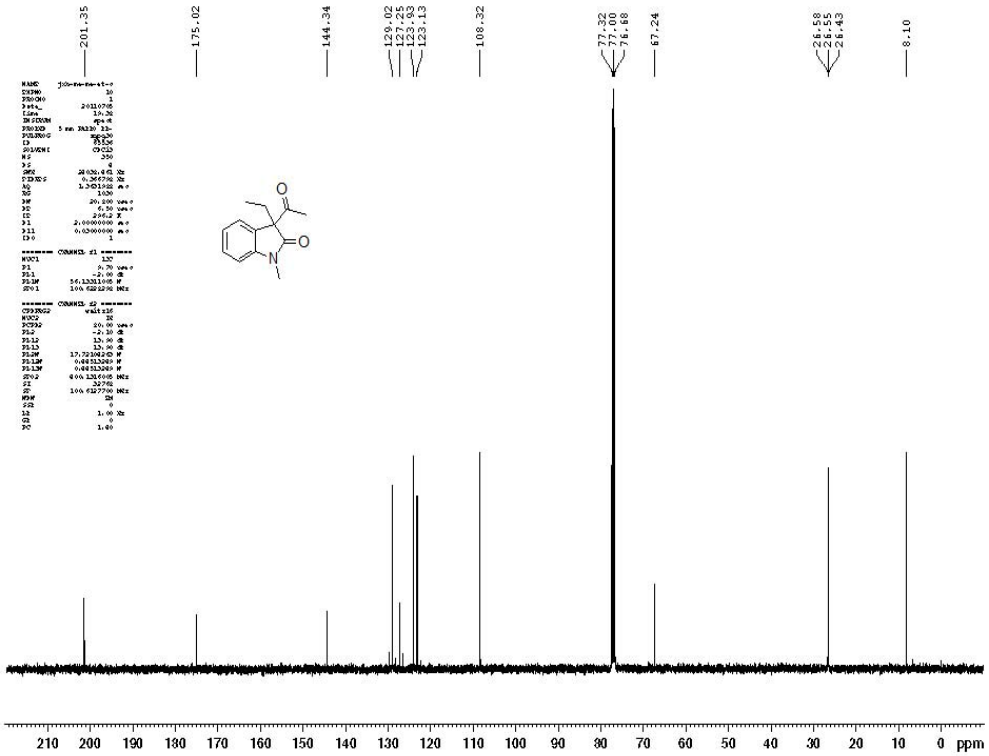
21b, 21b’



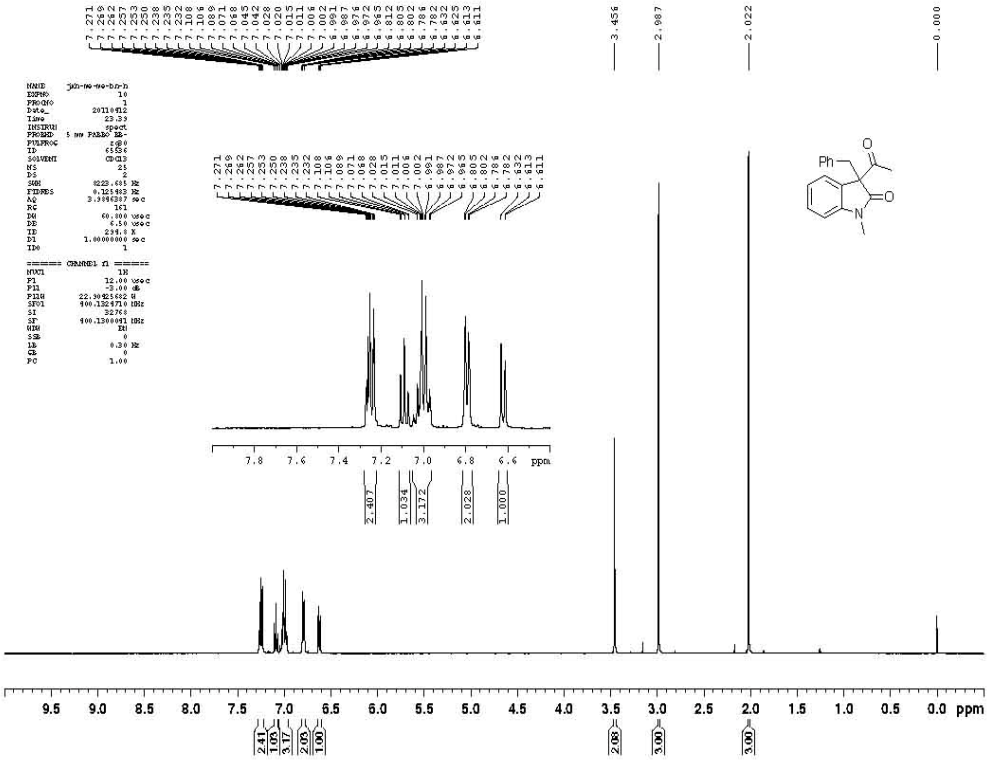


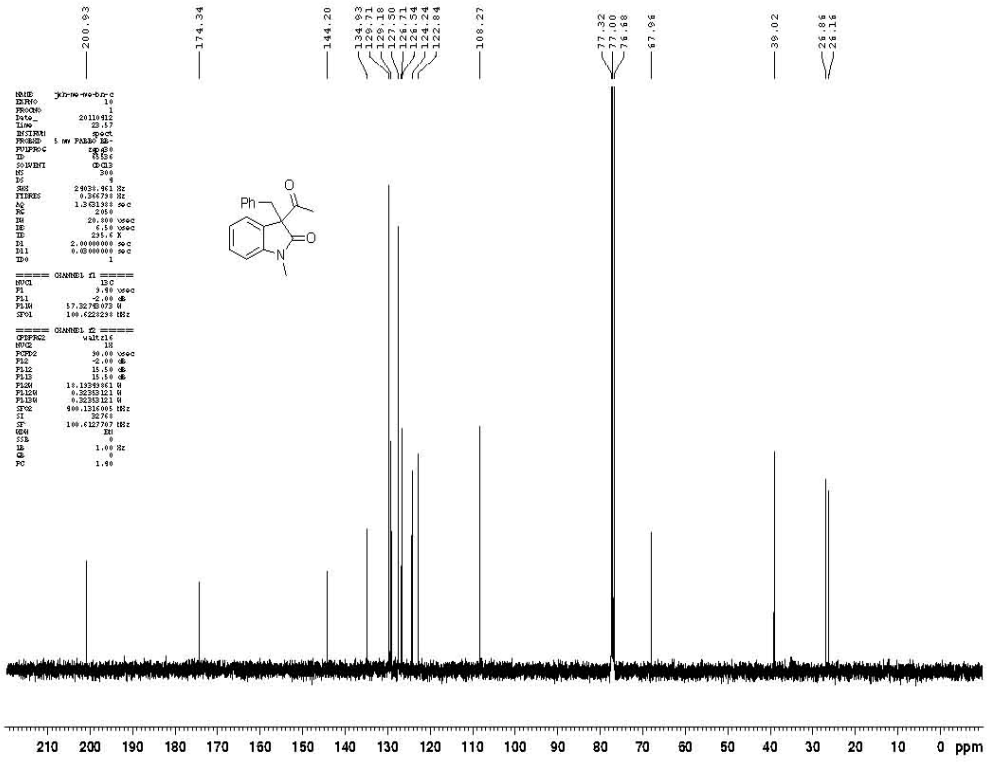
22b



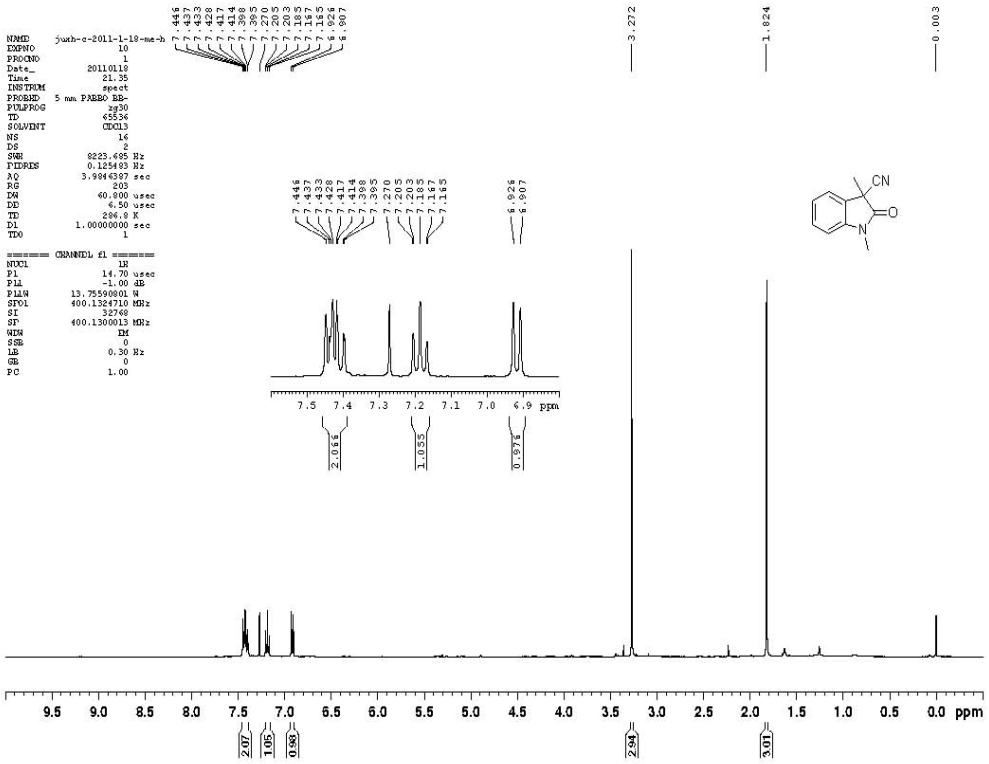


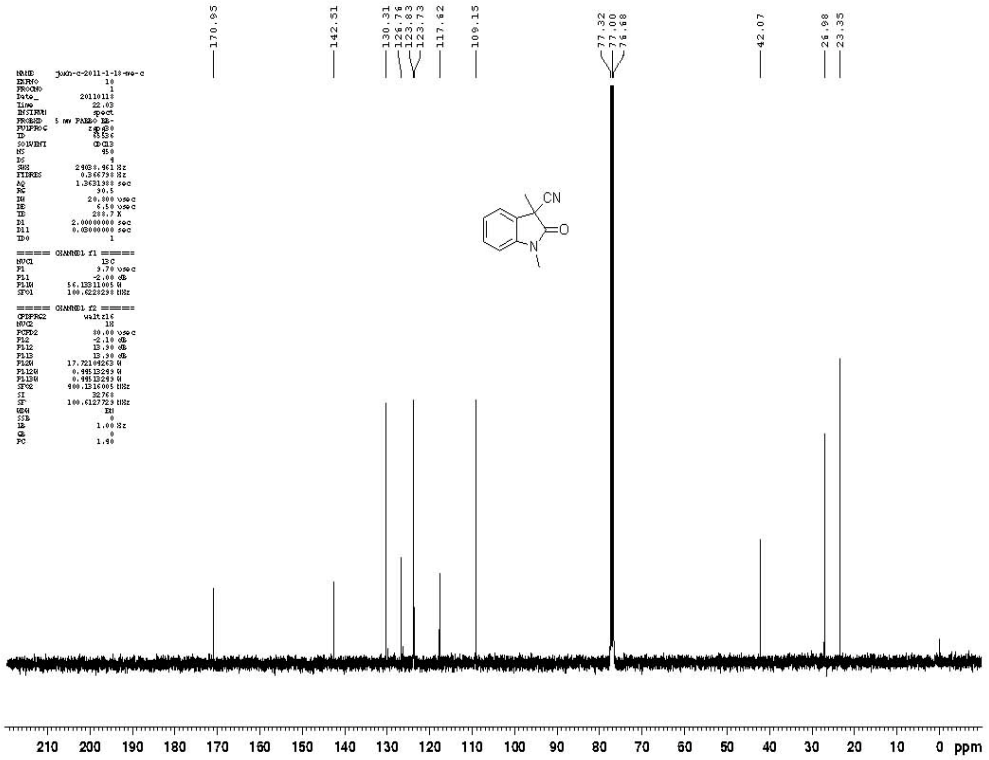
23b



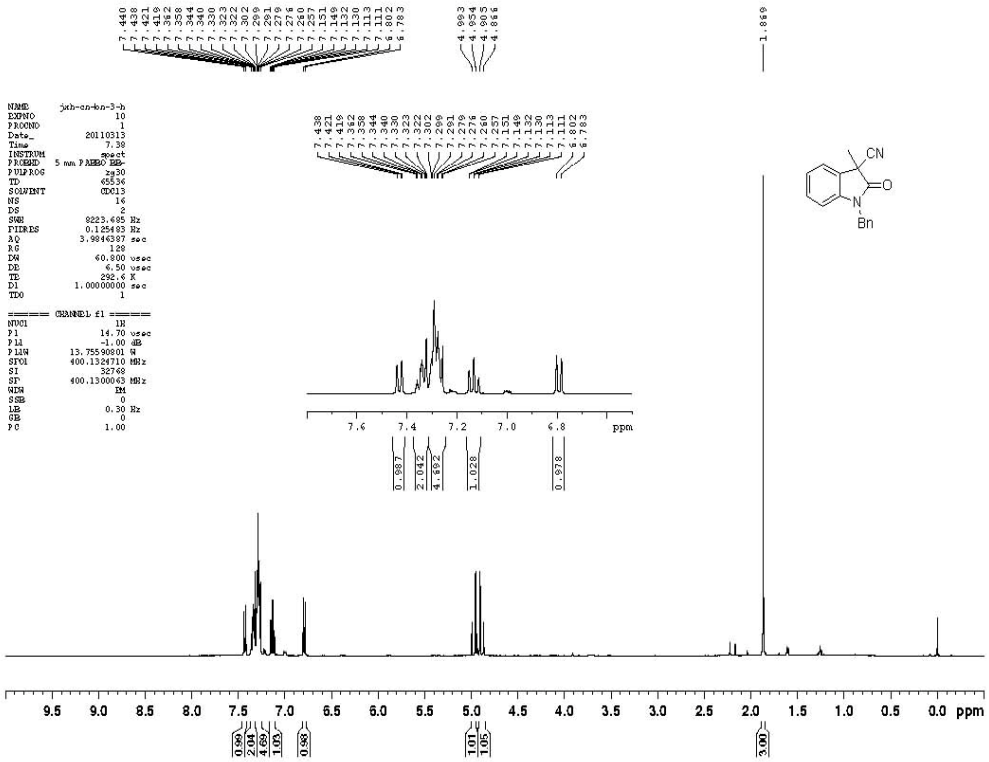


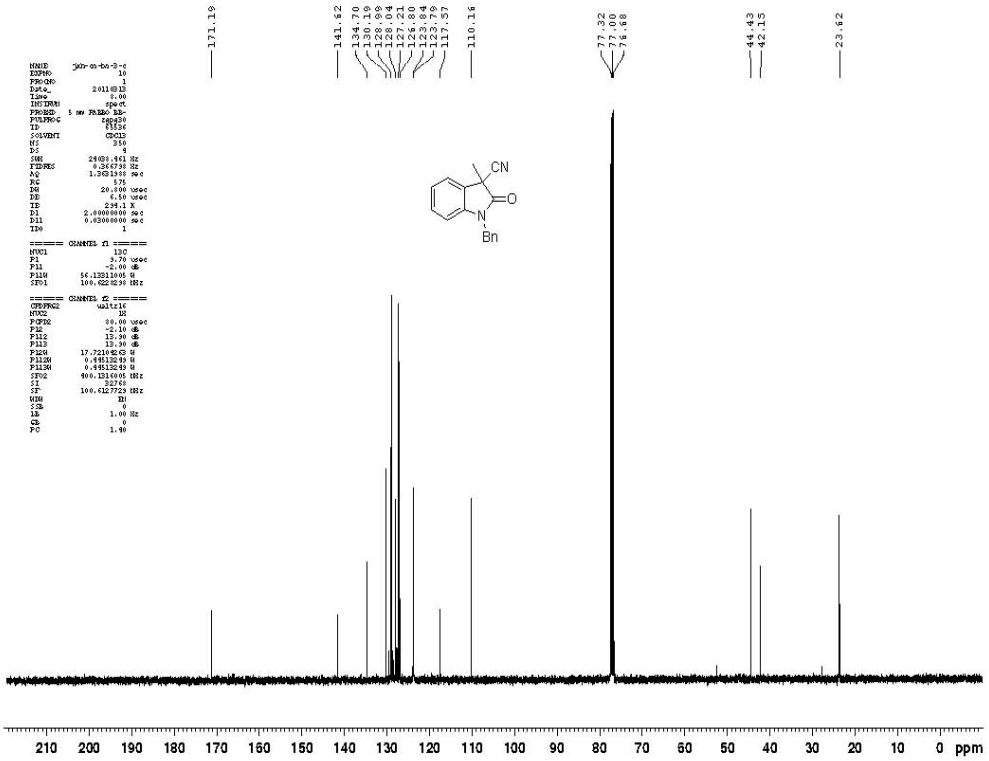
24b


7.446
7.437
7.433
7.428
7.417
7.414
7.398
7.395
7.270
7.203
7.185
7.167
6.926
6.907
3.272
1.024
0.003
CN
O
N
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 ppm
2.07
1.05
0.80
2.94
3.01


170.95
142.91
130.31
126.76
123.83
123.73
117.62
109.15
77.32
77.00
76.68
42.07
26.98
23.35
CN
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

25b





26b