Supporting Information

The Carbomethylation of Arylacrylamide Leading to 3-Ethyl-3-Substituted Indolin-2-one by Cascade Radical Addition/Cyclization

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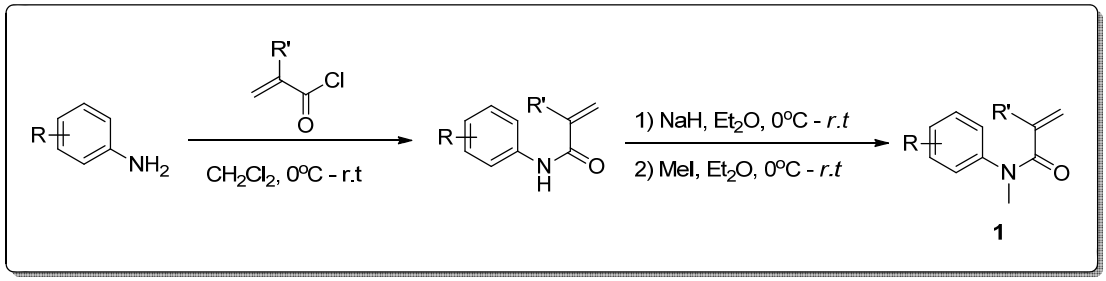
Content:

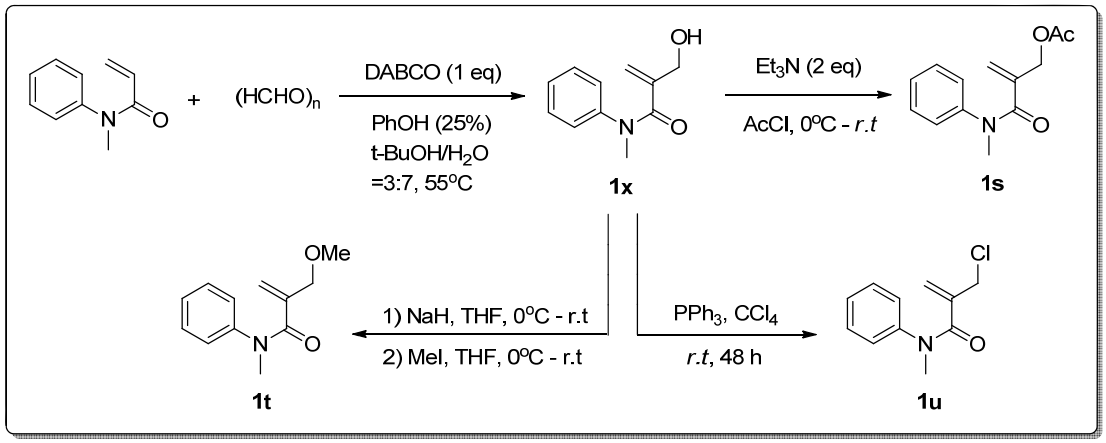
1. General considerations. ……...S2
2. Typical Procedures for the Synthesis of Substrates. ……S2
3. General Procedures for Substrates . ……..……..…….S3
4. Mechanistic studies of the reaction process. ……S3
5. Characterization Data for Products. ……..……S6
6. Reference. … ……S14
7. Copies of ^{1}H, ^{13}C NMR. ……..S15

1. General Considerations. All commercially available compounds were used as received. All reactions were carried out under a nitrogen atmosphere in dried sealed tube with magnetic stirring. Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (particle size 300-400 mesh, purchased from Anhui, China) and eluted with petroleum ether/ethyl acetate. ^{1}H, ^{13}C spectra were recorded on a Bucker Avance-300 MHz (300 MHz for ^{1}H; 75 MHz for ^{13}C) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm in ^{1}H, 77.0 ppm in ^{13}C).

2. Typical Procedures for the Synthesis of Substrates 1: All of Substrates in Figure 1 were synthesized according to the literature, and the NMR spectroscopy were consisted with the reported data.[S1]



The synthesis of substrate **1s**, **1t** and **1u**:



The mixture of paraformaldyde (0.92 g, 30 mmol), DABCO (0.69 g, 6 mmol) and PhOH (141 mg, 1.5 mmol) were put into a 10 mL Schlenk tube under N_2 atmosphere. Then, the solvent of *t*-BuOH/H_2O = 3:7 (2 mL) was added and the solution were heated to 55 ^{o}C. After all the solids were dissolved, *N*, *N*-methyl phenylacrylamide (0.97 g, 6 mmol) was added in portions for 5 min. The mixture was stirred for 3 days at the same temperature. After evaporation of *t*-BuOH, the mixture solution was extracted by CH_2Cl_2, and the organic phase was dried over anhydrous $MgSO_4$. After evaporation solvent, the crude product was subjected to column chromatography (PE/EA = 5:1) to give the desired compound **1x** as white solid (0.60 g, 53%). The spectrum is consistent with the literature. [S1a]

The mixture of **1x** (0.35 g, 2 mmol) and Et_3N (0.57 mL, 4 mmol) were placed in a 10 mL Schlenk tube with 4 mL of CH_2Cl_2 and put into an ice bath, AcCl (0.28 mL, 4 mmol) was added dropwise, the resulting mixture was allowed to warm to room temperature and stirred overnight. Water was added to quench the reaction when the TLC indicate complete disappearance of **1x**, CH_2Cl_2 was added to abstract the organic component, dried over $MgSO_4$ and column chromatography (PE/EA = 6:1) to afford the desired product **1s** (0.26 g, 56%)**.** The spectrum of **1s** is consistent with the literature.[S1b]

A solution of 283.3 mg (1.48 mmol) of **1x** in 8 mL of dry THF was stirred under N_2 at room temperature and treated with 88.8 mg (2.22 mmol) of NaH (60% dispersion in mineral oil). The reaction mixture was stirred for 10 min, and 0.14 mL (2.67 mmol) of MeI was added slowly. The reaction mixture was stirred at room temperature for 2 h, followed by addition of water and extraction with ethyl acetate. The combined extracts were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to obtain the desired product of **1t** (218.5 mg, 73%).

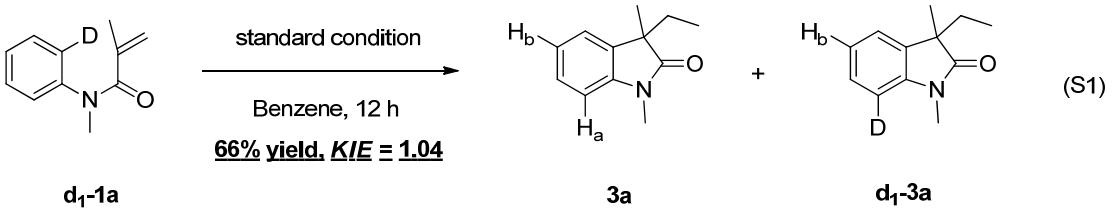
1x (150.0 mg, 0.78 mmol) was dissolved in 0.5 mL of carbon tetrachloride containing PPh_3 (209.9 mg, 0.80 mmol) and the mixture was stirred at ambient temperature for 48 h. the crude product was subjected to column chromatography to give the desired compound **1u** as white solid (77.3 mg, 47%).

3. General Procedures for Cascade Radical Addition/Cyclization of Substrates 1: In a 10 mL sealed tube, anhydrous $FeCl_2$ (5.1 mg, 0.04 mmol) and substrates **1** (0.2 mmol) were added. Then, the anhydrous benzene (1.5 mL) and DTBP (0.5 mmol) were added in turns. The tube was sealed and degassed with nitrogen for three times. The reaction mixture was put into an oil bath of 135 ^oC for 12 h. At last, the mixture was concentrated and subjected to column chromatography to give the product 3, and the results were listed in Figure 1.

4. Mechanistic studies

4-1 Kinetic Isotopic Effect (KIE) Studies:

a) Intramolecular KIE experiment: d-1a were synthesized by deuterated substrates according the literature procedure: [S2] In a 10 mL sealed tube, anhydrous $FeCl_2$ (5.1 mg, 0.04 mmol) and substrate **d-1a** (96% D, 0.2 mmol) were added. Then, the anhydrous benzene (1.5 mL) and DTBP (0.5 mmol) were added in turns. The tube was sealed and degassed with nitrogen for three times. The reaction mixture was put into an oil bath of 135 ^oC for 12 h. At last, the mixture was concentrated and subjected to column chromatography to give the product (Figure S1). The result was summarized in equation S1.



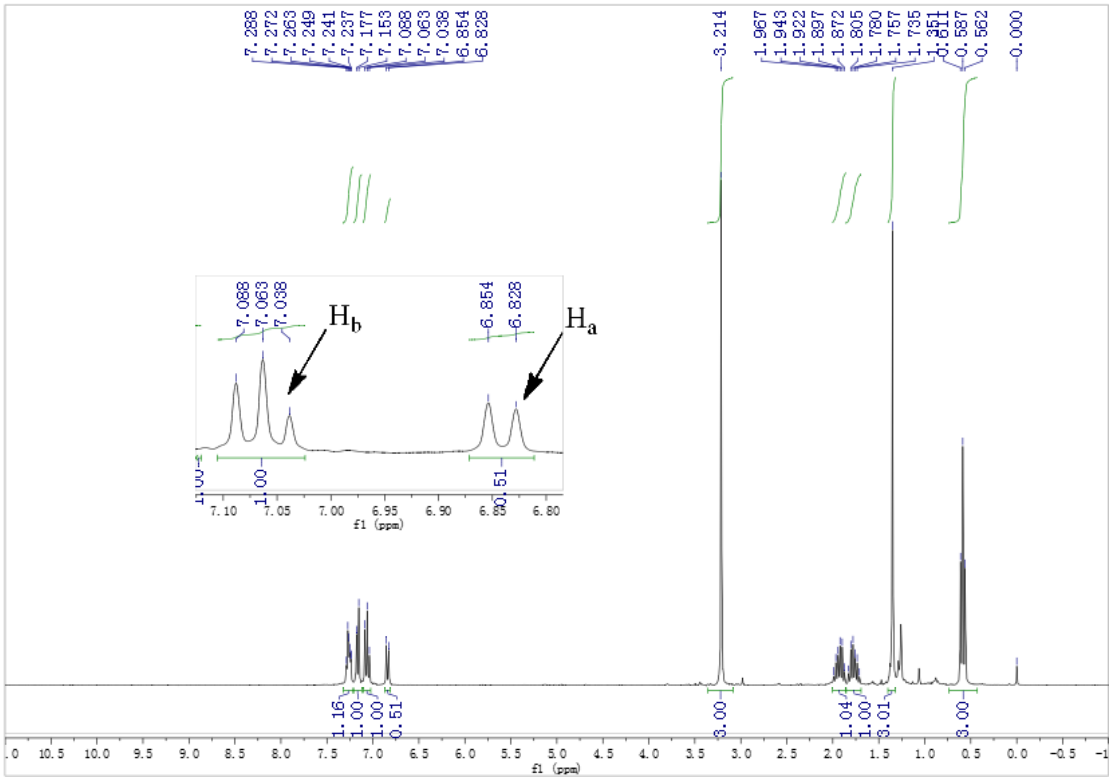
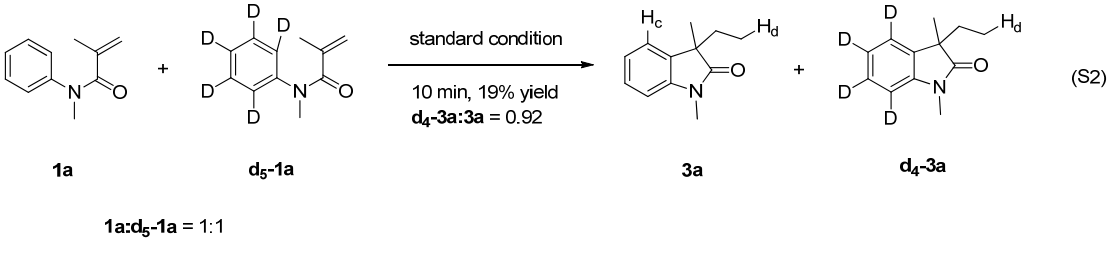


Figure S1. The intramolecular KIE study**.**

b): Intermolecular KIE experiment: d_5-1a was synthesized according the literature procedure. [S2] In a 10 mL sealed tube, anhydrous $FeCl_2$ (5.1 mg, 0.04 mmol), substrates **1a (**0.1 mmol**)** and **d_5-1a** (0.1 mmol) were added. Then, the anhydrous Benzene (1.5 mL) and DTBP (0.5 mmol) were added in turns. The tube was sealed and degassed with nitrogen for three times. The reaction mixture was put into an oil bath of 135 ^{o}C for 10 min. The mixture was concentrated and subjected to column chromatography. The result was summarized in equation S2.



1a:d_5-1a = 1:1

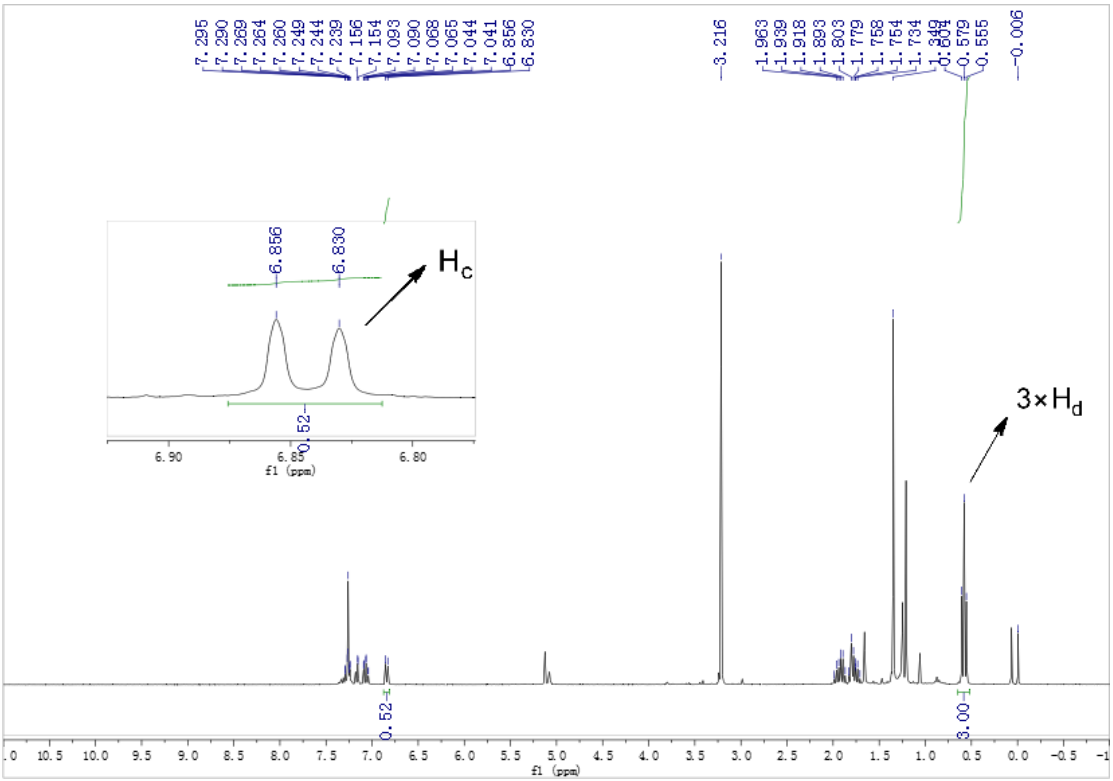
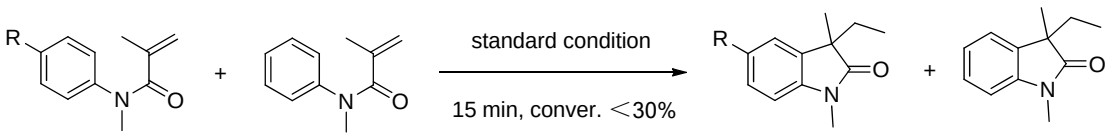


Figure S2. The intermolecular KIE study**.**

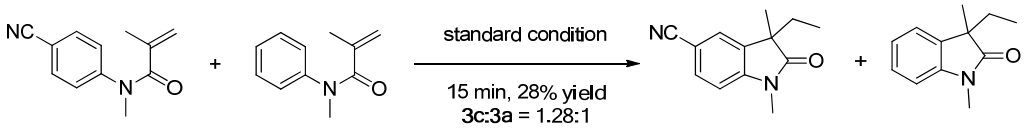
4-2 Competitive Experiments:



1 **1a** **3** **3a**

In order to investigate the detail mechanism, the competition experiments were explored by using *para*-substituted substrate **1** and **1a** (1:1 molar ratio) in standard condition for 15 min with low conversion (less than 30%). The ratios of **3** and **3a** were analyzed by ^{1}H NMR. The results were listed in below (eq S3, S4).

a) Substrates 1c and 1a

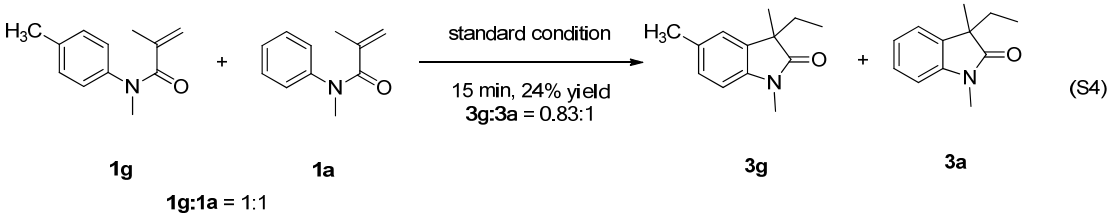


1c **1a** **3c** **3a**

1c:1a = 1:1

(S3)

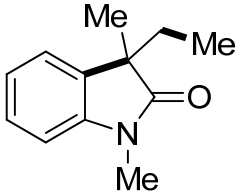
b) Substrates 1g and 1a



The substituent effect on the reaction rate was observed in the competitive experiment, where the electron-withdrawing substituent was beneficial for the reaction. This result is not consistent with the electrophilic aromatic substitution and supports the radical aromatic pathway.

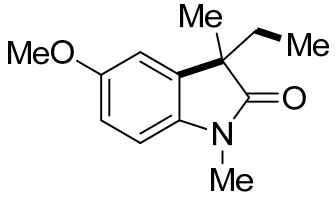
5. Characterization Data for Products

3-ethyl-1,3-dimethylindolin-2-one **3a**[S3]



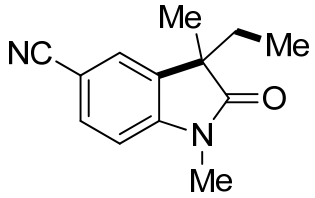
The title compound was prepared according to the general method described above and purified by flash column chromatography in 72% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.39. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.30-7.24 (m, 1 H), 7.18-7.15 (m, 1 H), 7.10-7.04 (m, 1 H), 6.84 (d, *J* = 7.5 Hz, 1 H), 3.22 (s, 3 H), 2.00-1.87 (m, 1 H), 1.84-1.71 (m, 1 H), 1.36 (s, 3 H), 0.59 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.7, 143.4, 133.9, 127.5, 122.4, 122.3, 107.8, 48.9, 31.4, 26.0, 23.3, 8.8.

3-ethyl-5-methoxy-1,3-dimethylindolin-2-one **3b**[S3]



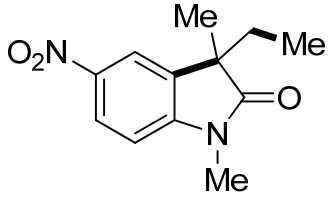
The title compound was prepared according to the general method described above and purified by flash column chromatography in 56% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.35. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.80-6.70 (m, 3 H), 3.80 (s, 3 H), 3.18 (s, 3 H), 1.98-1.85 (m, 1 H), 1.79-1.66 (m, 1 H), 1.32 (s, 3 H), 0.57 (t, *J* = 7.2, 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.3, 156.0, 137.0, 135.3, 111.4, 110.3, 107.9, 55.7, 49.3, 31.4, 26.1, 23.3, 8.8.

3-ethyl-1,3-dimethyl-2-oxoindoline-5-carbonitrile **3c**



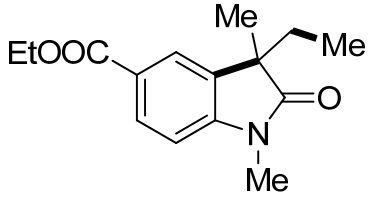
The title compound was prepared according to the general method described above and purified by flash column chromatography in 84% yield. White solid, m.p.: 102-103 ^{o}C. TLC (PE:EA, 5:1): R_f = 0.19. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.60 (d, *J* = 8.1 Hz, 1 H), 7.41 (s, 1 H), 6.90 (d, *J* = 8.1 Hz, 1 H), 3.24 (s, 3 H), 2.01-1.89 (m, 1 H), 1.84-1.71 (m, 1 H), 1.36 (s, 3 H), 0.59 (t, *J* = 7.5, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.3, 147.3, 134.9, 133.1, 125.8, 119.3, 108.2, 105.4, 48.8, 31.3, 26.3, 23.0, 8.7. HRMS (ESI) m/z calcd for $C_{13}H_{15}N_2O$ $(M+H)^+$ 215.1179, found 215.1171.

3-ethyl-1,3-dimethyl-5-nitroindolin-2-one **3d**



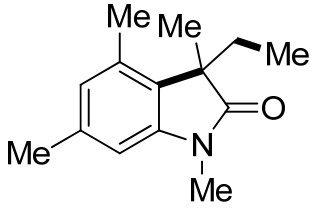
The title compound was prepared according to the general method described above and purified by flash column chromatography in 67% yield. Yellow solid, m.p.: 102-103 ^{o}C. TLC (PE:EA, 5:1): R_f = 0.25. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.24 (d, *J* = 8.6 Hz, 1 H), 8.04 (s, 1 H), 6.92 (d, *J* = 8.4 Hz, 1 H), 3.27 (s, 3 H), 2.03-1.91 (m, 1 H), 1.88-1.77 (m, 1 H), 1.39 (s, 3 H), 0.59 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 179.6, 148.1, 142.4, 133.7, 124.1, 117.6, 106.3, 48.0, 30.3, 25.4, 22.0, 7.7. HRMS (ESI) m/z calcd for $C_{12}H_{15}N_2O_3$ $(M+H)^+$ 235.1077, found 235.1079.

ethyl 3-ethyl-1,3-dimethyl-2-oxoindoline-5-carboxylate **3e**



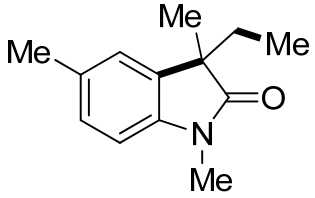
The title compound was prepared according to the general method described above and purified by flash column chromatography in 74% yield. Light yellow oil, TLC (PE:EA, 5:1): R_f = 0.37. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.01 (d, *J* = 8.1 Hz, 1 H), 7.82 (s, 1 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 3.23 (s, 3 H), 2.00-1.88 (m, 1 H), 1.86-1.74 (m, 1 H), 1.41-1.36 (t, *J* = 7.2 Hz, 3 H), 1.35 (s, 3 H), 0.55 (t, *J* = 7.2, 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.9, 166.5, 147.5, 133.7, 130.4, 124.6, 123.7, 107.2, 60.8, 48.8, 31.3, 26.2, 23.2, 14.3, 8.7. HRMS (ESI) m/z calcd for $C_{15}H_{20}NO_3$ $(M+H)^+$ 262.1438, found 262.1431.

3-ethyl-1,3,4,6-tetramethylindolin-2-one **3f**



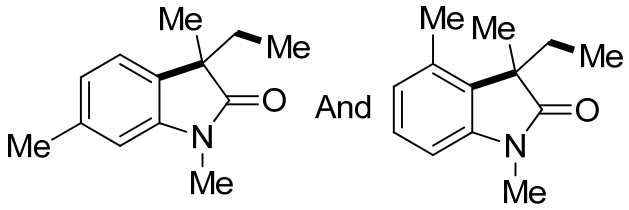
The title compound was prepared according to the general method described above and purified by flash column chromatography in 49% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.52. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.65 (s, 1 H), 6.52 (s, 1 H), 3.18 (s, 3 H), 2.34 (s, 3 H), 2.31 (s, 3 H), 1.98 (q, *J* = 7.5 Hz, 2 H), 1.40 (s, 3 H), 0.48 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 181.0, 143.8, 137.4, 133.8, 127.3, 125.4, 106.6, 49.9, 29.4, 26.1, 22.2, 21.5, 17.9, 9.2. HRMS (ESI) m/z calcd for $C_{14}H_{20}NO$ $(M+H)^+$ 218.1539, found 218.1536.

3-ethyl-1,3,5-trimethylindolin-2-one **3g**[S3]



The title compound was prepared according to the general method described above and purified by flash column chromatography in 50% yield. Colorless oil, TLC (PE:EA, 3:1): R_f = 0.72. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.05 (d, *J* = 7.8 Hz, 1 H), 6.97 (s, 1 H), 6.72 (d, *J* = 7.8 Hz, 3 H), 3.19 (s, 3 H), 2.35 (s, 3 H), 1.97-1.85 (m, 1 H), 1.80-1.68 (m, 1 H), 1.33 (s, 3 H), 0.57 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.7, 141.1, 133.9, 131.8, 127.8, 123.3, 107.5, 49.0, 31.4, 26.0, 23.3, 21.1, 8.8.

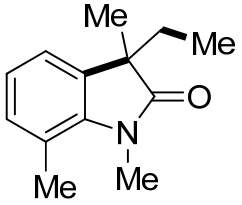
3-ethyl-1,3,6-trimethylindolin-2-one **3h**
3-ethyl-1,3,4-trimethylindolin-2-one **3h'**



The title compound was prepared according to the general method described above and purified by flash column chromatography in 61% yield(3:5). Colorless oil, TLC (PE:EA, 2:1): R_f = 0.75. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.15 (t, *J* = 7.8 Hz, 1 H), 7.03 (d, *J* = 7.5 Hz, 0.6 H), 6.86 (d, *J* = 7.5 Hz, 0.6 H), 6.82 (d, *J* = 7.8 Hz, 1 H), 6.68 (d, *J* = 7.5 Hz, 1.6 H), 3.19 (s, 3 H), 3.18 (s, 1.8 H), 2.38 (s, 1.8 H), 2.34 (s, 3 H), 2.00 (t, *J* = 7.2 Hz, 2 H), 1.93-1.83 (m, 0.6 H), 1.79-1.67 (m, 0.6 H), 1.41 (s, 3 H), 1.32 (s, 1.8 H), 0.57 (t, *J* = 7.5 Hz, 3 H), 0.47 (t, J = 7.5, 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 181.1, 180.7, 143.7, 143.5, 137.6, 134.1, 130.9, 130.3, 127.5, 125.0, 122.9, 122.3, 108.8, 105.6, 50.2, 48.7, 31.4, 29.4, 26.2, 26.0, 23.4, 22.1, 21.8,

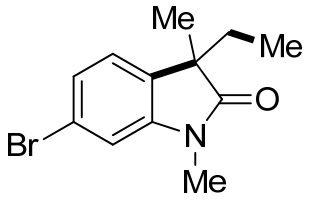
18.1, 9.2, 8.9. HRMS (ESI) m/z calcd for $C_{13}H_{17}NO$ $(M+H)^+$ 204.1383, found 204.1372.

3-ethyl-1,3,7-trimethylindolin-2-one **3i**



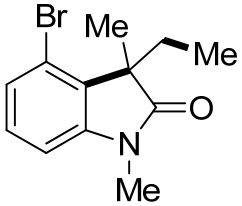
The title compound was prepared according to the general method described above and purified by flash column chromatography in 61% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.63. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.00-6.91 (m, 3 H), 3.49 (s, 3 H), 2.58 (s, 3 H), 1.98-1.86 (m, 1 H), 1.78-1.66 (m, 1 H), 1.32 (s, 3 H), 0.56 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.4, 140.1, 133.5, 130.3, 121.2, 119.3, 118.4, 47.2, 30.7, 28.3, 22.8, 18.0, 7.8. HRMS (ESI) m/z calcd for $C_{13}H_{18}NO$ $(M+H)^+$ 204.1383, found 204.1382.

6-bromo-3-ethyl-1,3-dimethylindolin-2-one **3j**



The title compound was prepared according to the general method described above and purified by flash column chromatography in 21% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.65. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.19 (d, *J* = 7.8 Hz, 1 H), 7.01 (d, *J* = 7.8 Hz, 1 H), 6.98 (s, 1 H), 3.18 (s, 3 H), 1.97-1.85 (m, 1 H), 1.79-1.67 (m, 1 H), 1.32 (s, 3 H), 0.57 (t, *J* = 7.2, 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.4, 144.8, 132.8, 125.1, 123.8, 121.0, 111.3, 48.8, 31.3, 26.1, 23.2, 8.8. HRMS (ESI) m/z calcd for $C_{12}H_{14}BrNO$ $(M+Na)^+$ 290.0151, found 290.0141.

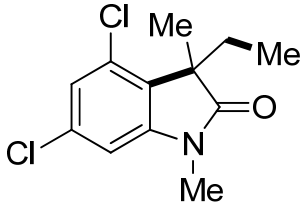
4-bromo-3-ethyl-1,3-dimethylindolin-2-one **3j'**



The title compound was prepared according to the general method described above and purified by flash column chromatography in 54% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.60. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.16-7.08 (m, 2 H), 6.76 (d, *J* = 7.1 Hz, 1 H), 3.19 (s, 3 H), 2.39-2.27 (m, 1 H), 1.94-1.82 (m, 1 H), 1.47 (s, 3 H), 0.46 (t, *J* = 7.5, 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 179.9, 145.4, 131.0, 129.1, 126.6, 118.7, 106.8, 51.5, 28.2, 26.1, 21.0, 9.0. HRMS (ESI) m/z

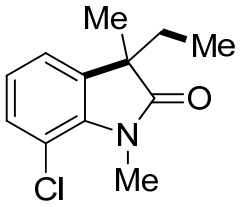
calcd for $C_{12}H_{14}BrNO$ $(M+H)^+$ 268.0332, found 268.0321.

4,6-dichloro-3-ethyl-1,3-dimethylindolin-2-one **3k**



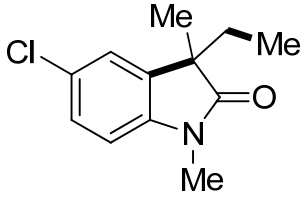
The title compound was prepared according to the general method described above and purified by flash column chromatography in 72% yield. White solid, m.p.: 44-45 ^oC. TLC (PE:EA, 5:1): R_f = 0.62. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.99 (s, 1 H), 6.74 (s, 1 H), 3.18 (s, 3 H), 2.28-2.16 (m, 1 H), 1.99-1.87 (m, 1 H),1.45 (s, 3 H), 0.49 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 179.9, 146.0, 134.1, 130.9, 127.9, 122.9, 107.2, 50.7, 28.5, 26.3, 21.1, 9.1. HRMS (ESI) m/z calcd for $C_{12}H_{14}Cl_2NO$ $(M+H)^+$ 258.0447, found 258.0440.

7-chloro-3-ethyl-1,3-dimethylindolin-2-one **3l**



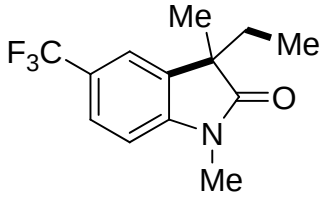
The title compound was prepared according to the general method described above and purified by flash column chromatography in 69% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.75. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.17 (d, *J* = 8.0 Hz, 1 H), 7.04-6.93 (m, 2 H), 3.57 (s, 3 H), 1.99-1.87 (m, 1 H), 1.78-1.66 (m, 1 H), 1.32 (s, 3 H), 0.56 (t, *J* = 7.2, 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.8, 139.3, 136.7, 129.9, 123.1, 120.9, 115.3, 48.7, 31.7, 29.3, 23.7, 8.8. HRMS (ESI) m/z calcd for $C_{12}H_{15}ClNO$ $(M+H)^+$ 224.0837, found 224.0832.

5-chloro-3-ethyl-1,3-dimethylindolin-2-one **3m**[S3]



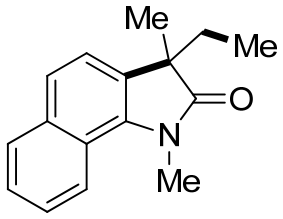
The title compound was prepared according to the general method described above and purified by flash column chromatography in 74% yield. Colorless oil, TLC (PE:EA, 3:1): R_f = 0.62. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.22 (d, *J* = 8.4 Hz, 1 H), 7.12 (s, 1 H), 6.75 (d, *J* = 8.4 Hz, 3 H), 3.18 (s, 3 H), 1.98-1.86 (m, 1 H), 1.79-1.67 (m, 1 H), 1.32 (s, 3 H), 0.57 (t, *J* = 7.2, 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.1, 142.0, 135.6, 127.7, 127.5, 123.0, 108.7, 49.2, 31.3, 26.1, 23.2, 8.8.

3-ethyl-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one **3n**



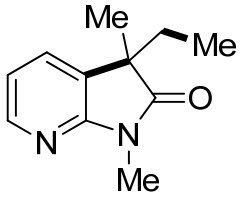
The title compound was prepared according to the general method described above and purified by flash column chromatography in 69% yield. White solid, m.p.: 34-35 ^{o}C. TLC (PE:EA, 3:1): R_f = 0.70. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.55 (d, *J* =8.1 Hz, 1 H), 7.38 (s, 1 H), 6.90 (d, *J* = 8.1 Hz, 1 H), 3.24 (s, 3 H), 2.02-1.90 (m, 1 H), 1.85-1.73 (m, 1 H), 1.37 (s, 3 H), 0.58 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.6, 146.4, 134.5, 125.5 (q, *J* = 4.1 Hz), 124.6 (q, *J* = 32.3 Hz),124.5 (q, *J* = 270.0 Hz), 119.5 (q, *J* = 3.6 Hz), 107.5, 49.0, 31.3, 26.2, 23.1, 8.8. HRMS (ESI) m/z calcd for $C_{13}H_{14}F_3NO$ $(M+H)^+$ 280.0920, found 280.0912.

3-ethyl-1,3-dimethyl-1H-benzo[g]indol-2(3H)-one **3o**



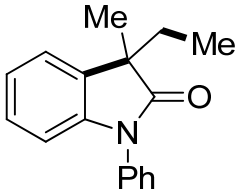
The title compound was prepared according to the general method described above and purified by flash column chromatography in 67% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.63. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.72 (d, *J* =8.1 Hz, 1 H), 7.57-7.50 (m, 2 H), 7.45-7.40 (m, 2 H), 3.54 (s, 3 H), 2.44-2.32 (m, 1 H), 1.92-1.80 (m, 1 H), 1.70 (s, 3 H), 0.62 (t, *J* = 7.5, 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 173.5, 138.1, 136.9, 133.2, 127.0, 126.2, 125.8, 122.6, 122.3, 120.0, 108.1, 48.1, 38.0, 30.0, 29.5, 9.7. HRMS (ESI) m/z calcd for $C_{16}H_{17}NO$ $(M+H)^+$ 240.1383, found 240.1374.

3-ethyl-1,3-dimethyl-1H-pyrrolo[2,3-b]pyridin-2(3H)-one **3p**[S3]



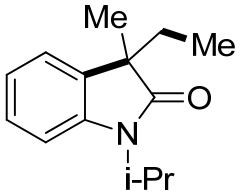
The title compound was prepared according to the general method described above and purified by flash column chromatography in 73% yield. Colorless oil, TLC (PE:EA, 3:1): R_f = 0.50. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.15 (dd, *J* = 5.4, 1.5 Hz, 1 H), 7.37 (dd, *J* = 7.2, 1.5 Hz, 1 H), 6.93 (dd, *J* = 7.2, 5.4 Hz, 3 H), 3.27 (s, 3 H), 1.98-1.86 (m, 1 H), 1.82-1.70 (m, 1 H), 1.34 (s, 3 H), 0.60 (t, *J* = 7.2, 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.3, 157.0, 146.5, 129.8, 128.2, 118.0, 48.5, 30.9, 25.1, 22.6, 8.8.

3-ethyl-3-methyl-1-phenylindolin-2-one **3q**[S3]



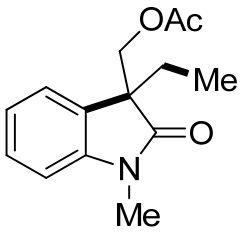
The title compound was prepared according to the general method described above and purified by flash column chromatography in 84% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.56. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.54-7.48 (m, 2 H), 7.42-7.35 (m, 3 H), 7.24-7.15 (m, 2 H), 7.12-7.07 (m, 1 H), 6.84-6.82 (m, 1 H), 2.11-1.99 (m, 1 H), 1.91-1.79 (m, 1 H), 1.47 (s, 3 H), 0.71 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.1, 143.3, 134.6, 133.6, 129.5 (2C), 127.8, 127.5, 126.5 (2C), 122.8, 122.7, 109.1, 49.0, 32.0, 23.6, 8.9.

3-ethyl-1-isopropyl-3-methylindolin-2-one **3r**[S3]



The title compound was prepared according to the general method described above and purified by flash column chromatography in 66% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.75. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.25-7.14 (m, 2 H), 7.06-7.00 (m, 2 H), 4.67 (Hept, *J* = 6.9 Hz, 1 H), 1.98-1.87 (m, 1 H), 1.79-1.67 (m, 1 H), 1.32 (s, 3 H), 1.46 (d, *J* = 7.1 Hz, 6 H), 1.32 (s, 3 H),0.53 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.3, 142.0, 134.3, 127.2, 122.6, 121.8, 109.6, 48.4, 43.4, 31.7, 23.5, 19.5, 19.3, 8.7.

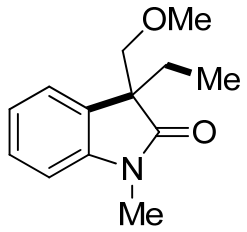
(3-ethyl-1-methyl-2-oxoindolin-3-yl)methyl acetate **3s**



The title compound was prepared according to the general method described above and purified by flash column chromatography in 76% yield. Colorless oil, TLC (PE:EA, 2:1): R_f = 0.62. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.28 (t, *J* = 7.8 Hz, 1 H), 7.18 (d, J = 6.8 Hz, 1 H), 7.05 (t, *J* = 7.8 Hz, 1 H), 6.84 (d, *J* = 7.8 Hz, 1 H), 4.50 (d, *J* = 10.8 Hz, 1 H), 4.16 (d, *J* = 10.8 Hz, 1 H), 3.21 (s, 3 H), 1.98-1.87 (m, 1 H), 1.86-1.75 (m, 1 H), 1.82 (s, 3 H), 0.57 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 177.4, 170.4, 144.2, 129.2, 128.3, 123.1, 122.5, 107.8, 67.1, 53.0, 26.7, 26.1, 20.5, 7.9. HRMS (ESI) m/z calcd for $C_{14}H_{17}NO_3$ $(M+H)^+$ 248.1281, found

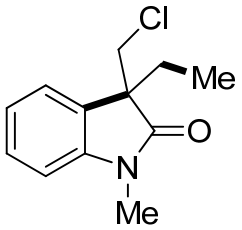
248.1281.

3-ethyl-3-(methoxymethyl)-1-methylindolin-2-one **3t**



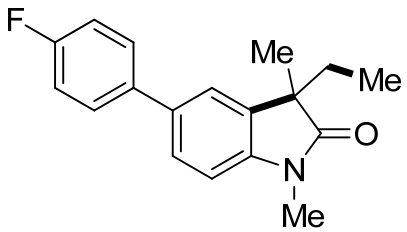
The title compound was prepared according to the general method described above and purified by flash column chromatography in 62% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.32-7.23 (m, 2 H), 7.11-7.06 (m, 1 H), 6.85 (d, *J* = 7.8 Hz, 1 H), 3.66 (q, *J* = 9, 3.9 Hz, 2 H), 3.23 (s, 3 H), 3.22 (s, 3 H), 1.96-1.87 (m, 1 H), 1.85-1.75 (m, 1 H), 0.57 (t, *J* = 7.2, 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 178.3, 144.3, 130.8, 127.9, 123.0, 122.3, 107.8, 76.8, 59.5, 54.5, 26.8, 26.1, 8.0. HRMS (ESI) m/z calcd for $C_{13}H_{17}NO_2$ $(M+H)^+$ 220.1332, found 220.1323.

3-(chloromethyl)-3-ethyl-1-methylindolin-2-one **3u**



The title compound was prepared according to the general method described above and purified by flash column chromatography in 72% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.45. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.36-7.26 (m, 2 H), 7.14-7.09 (m, 1 H), 6.88 (d, *J* = 7.8 Hz, 1 H), 3.84-3.75 (m, 2 H), 3.24 (s, 3 H), 2.02-1.83 (m, 2 H), 0.61 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 177.0, 144.3, 129.3, 128.6, 123.2, 122.7, 108.0, 54.8, 48.3, 28.4, 26.2, 8.5. HRMS (ESI) m/z calcd for $C_{12}H_{14}ClNO$ $(M+Na)^+$ 246.0656, found 246.0656.

3-ethyl-5-(4-fluorophenyl)-1,3-dimethylindolin-2-one **3w**



The title compound was prepared according to the general method described above and purified by flash column chromatography in 73% yield. Colorless oil, TLC (PE:EA, 5:1): R_f = 0.25. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.54-7.49 (m, 2 H), 7.44 (dd, *J* = 1.8, 8.1 Hz, 1 H), 7.34 (d, *J* = 1.8 Hz, 1 H), 7.16-7.08 (m, 1 H), 6.90 (d,

J = 8.1 Hz, 2 H), 3.25 (s, 3 H), 2.04-1.91 (m, 1 H), 1.88-1.76 (m, 1 H),1.40 (s, 3 H), 0.63 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.6, 162.1 (d, J_{C-F} = 244.5 Hz), 142.9, 137.2 (d, J_{C-F} = 3.2 Hz), 134.8, 134.6, 128.3 (d, 2C, J_{C-F} = 7.9 Hz), 126.3, 121.2, 115.6 (d, 2C, J_{C-F} = 21.3 Hz), 108.0, 49.1, 31.5, 26.1, 23.3, 8.9. HRMS (ESI) m/z calcd for $C_{18}H_{18}FNO$ $(M+H)^+$ 284.1145, found 284.1438.

Reference:

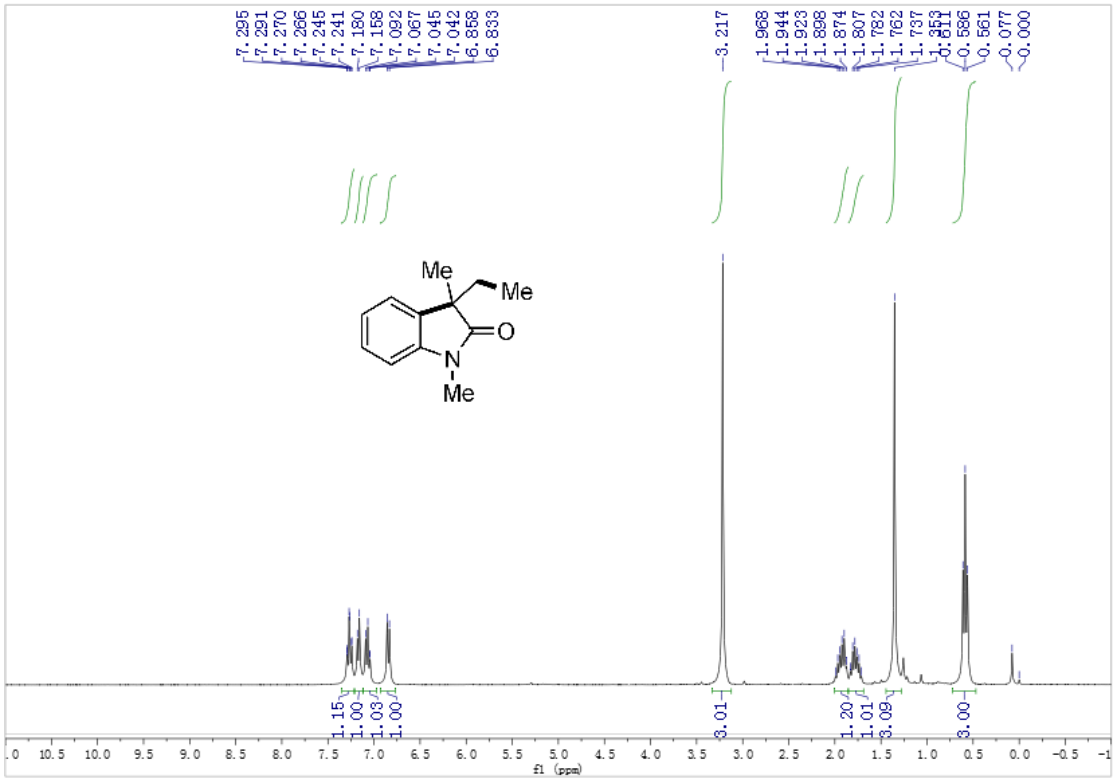
[S1] (a) Mu, X.; Wu, T.; Wang, H.-y.; Guo, Y.-l.; Liu, G. *J. Am. Chem.Soc.* **2012**, *134*, 878−881. (b) Pinto, A.; Jia, Y.; Neuville, L.; Zhu, J. *Chem. Eur. J.* **2007**, *13*, 961-967. (c) Jones, K.; Thompson, M.; Wright, C. *J. Chem. Soc., Chem. Commun.* **1986**, 715-716. (d) Wei, H.; Piou, T.; Dufour, J.; Neuville, L.; Zhu, J. *Org. Lett.* **2011**, *13*, 2244-2247.

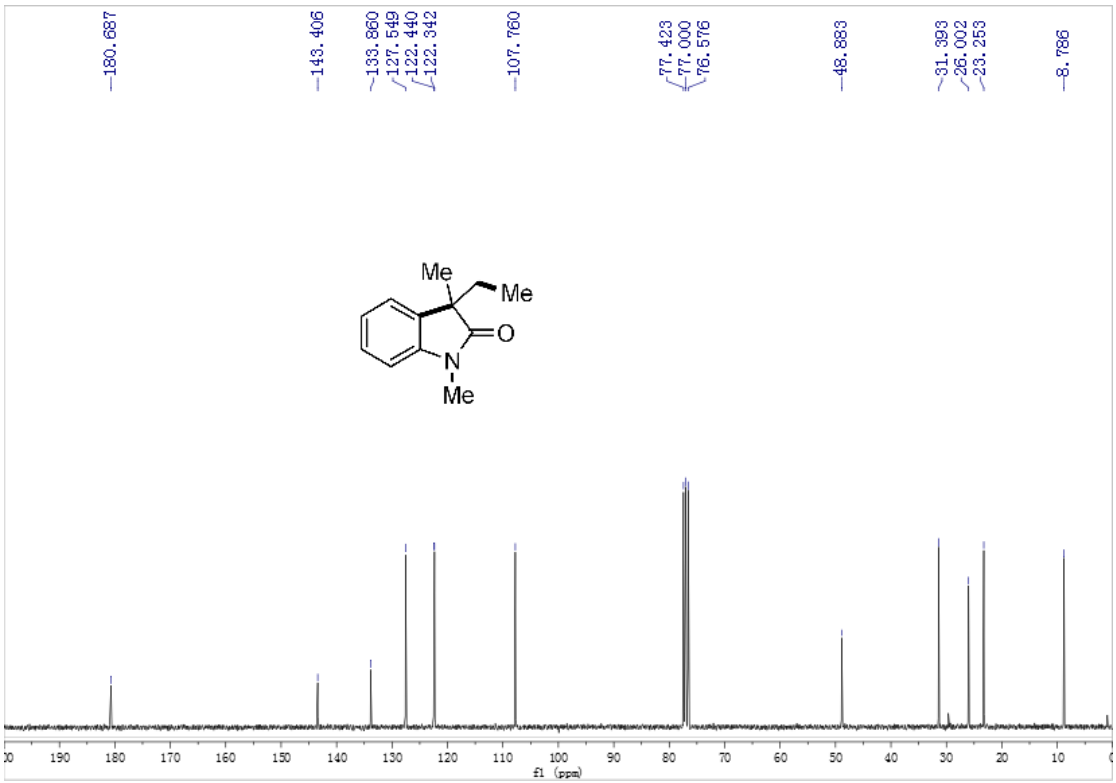
[S2] (a) Pinto, A.; Neuville, L.; Retailleau, P.; Zhu, J. *Org. Lett.* **2006**, *8*, 4927-4930. (b) Fairlamb, I. J. S.; Kapdi, A. R.; Lee, A. F.; Mcglacken, G. P.; Weissburger, F.; de Vries, A. H. M.; van de Vondervoort, L. S. *Chem. Eur. J.* **2006**, *12*, 8750-8761.

[S3] Xie, J.; Xu, P.; Li, H.; Xue, Q.; Jin, H.; Cheng, Y.; Zhu, C. *Chem. Commun*. **2013**, *49*, 5672-5674.

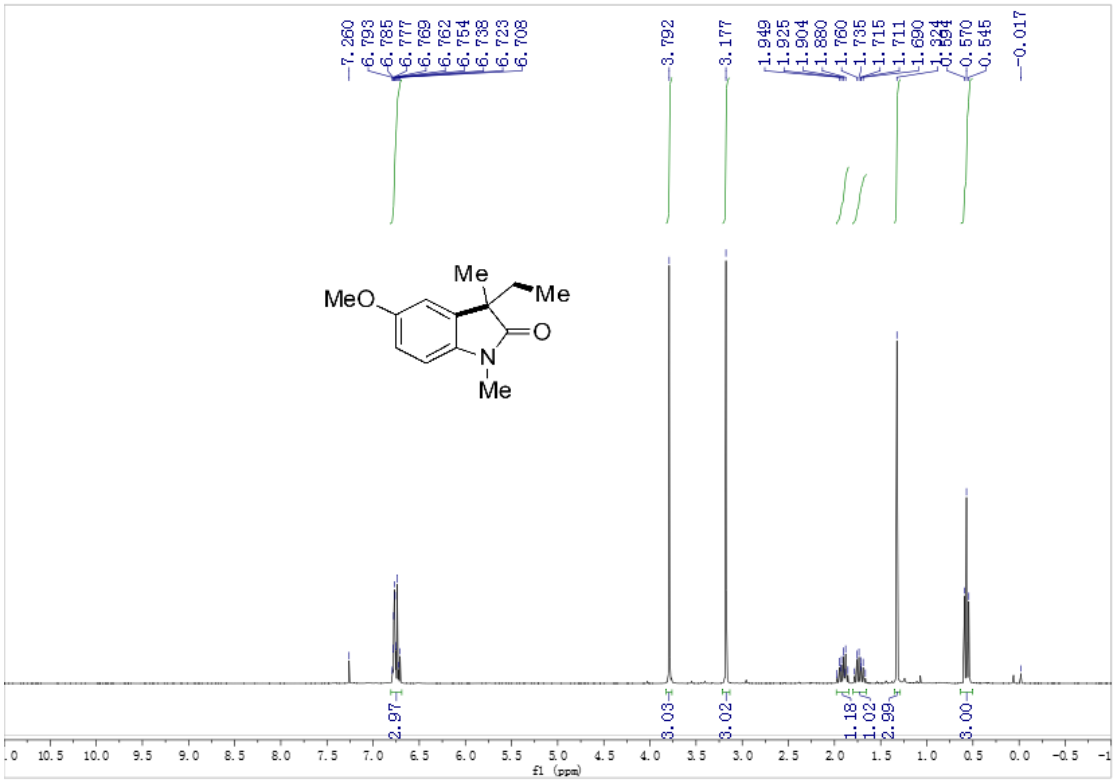
Copies of the ^{1}H, ^{13}C NMR

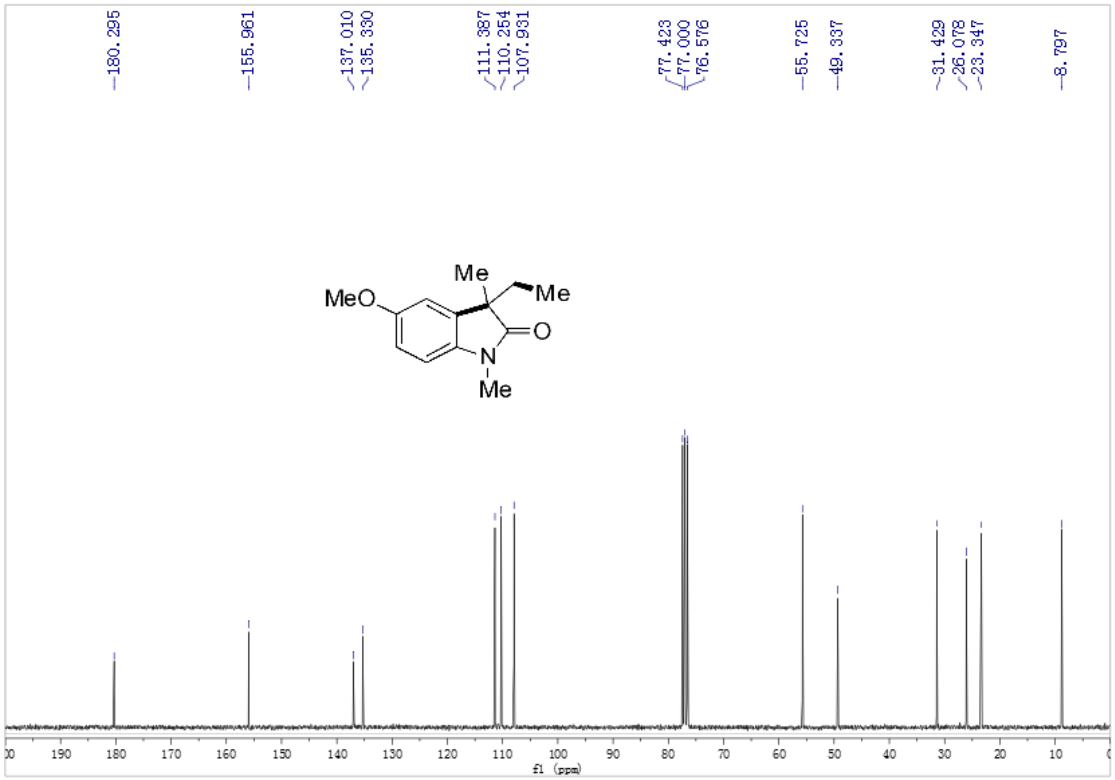
3-ethyl-1,3-dimethylindolin-2-one **3a**



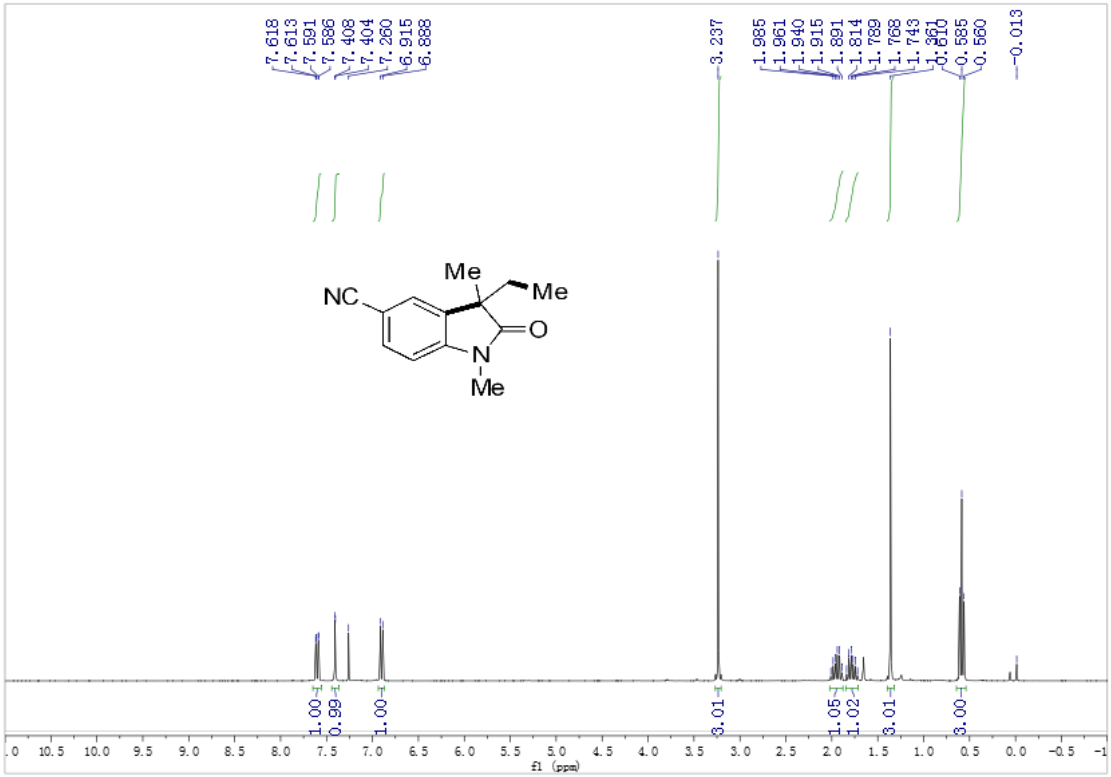


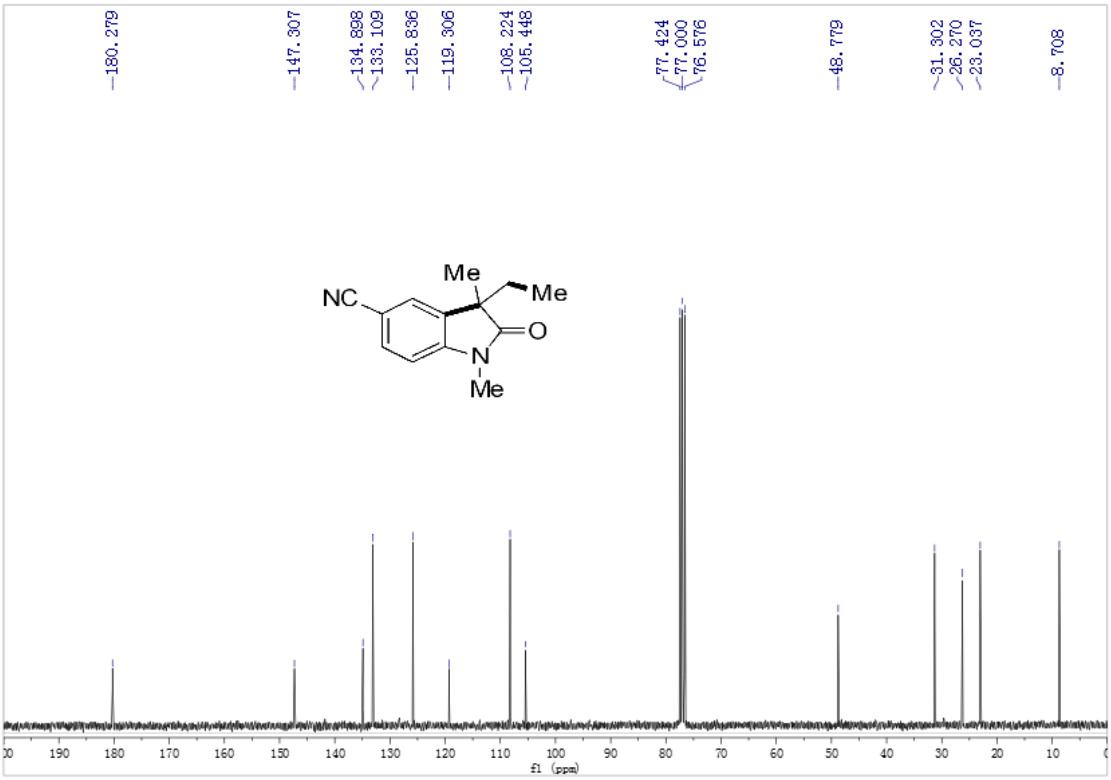
3-ethyl-5-methoxy-1,3-dimethylindolin-2-one **3b**



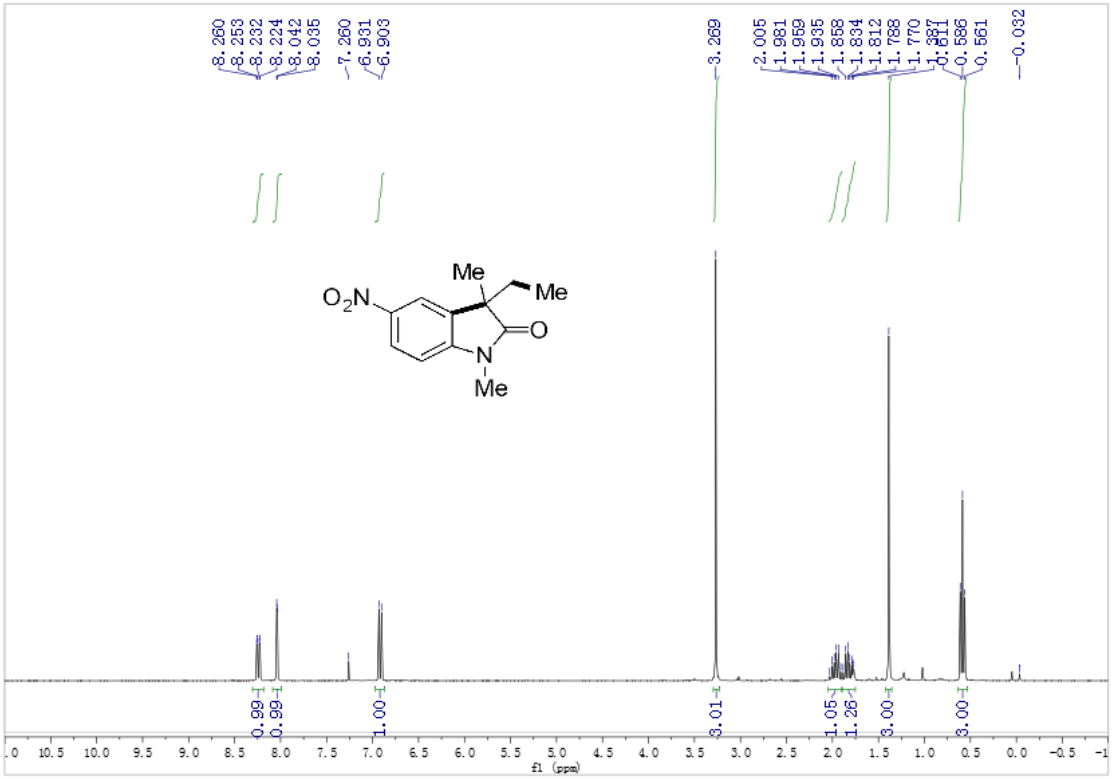


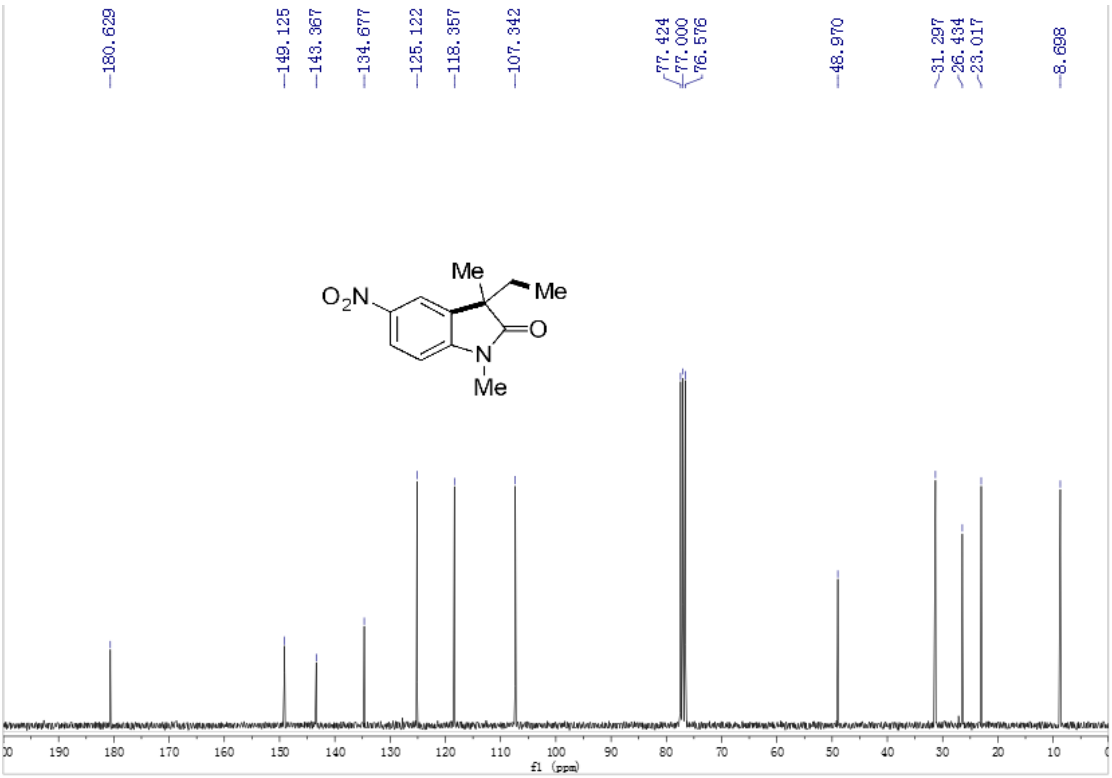
3-ethyl-1,3-dimethyl-2-oxoindoline-5-carbonitrile **3c**



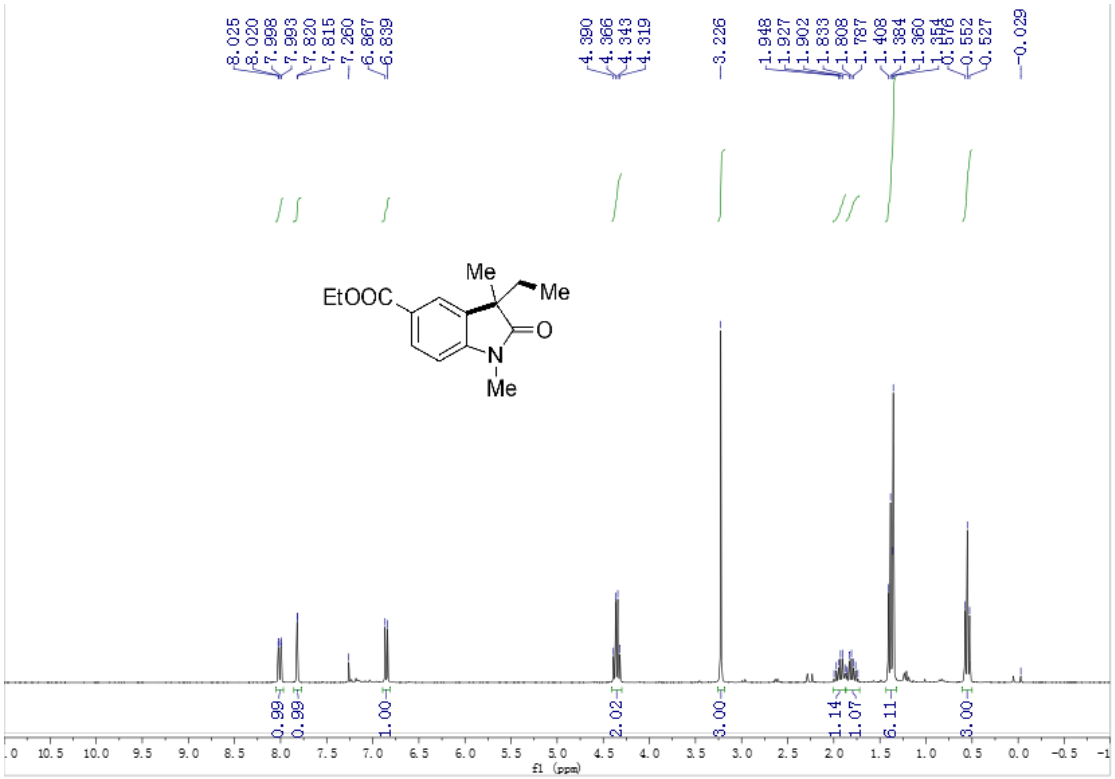


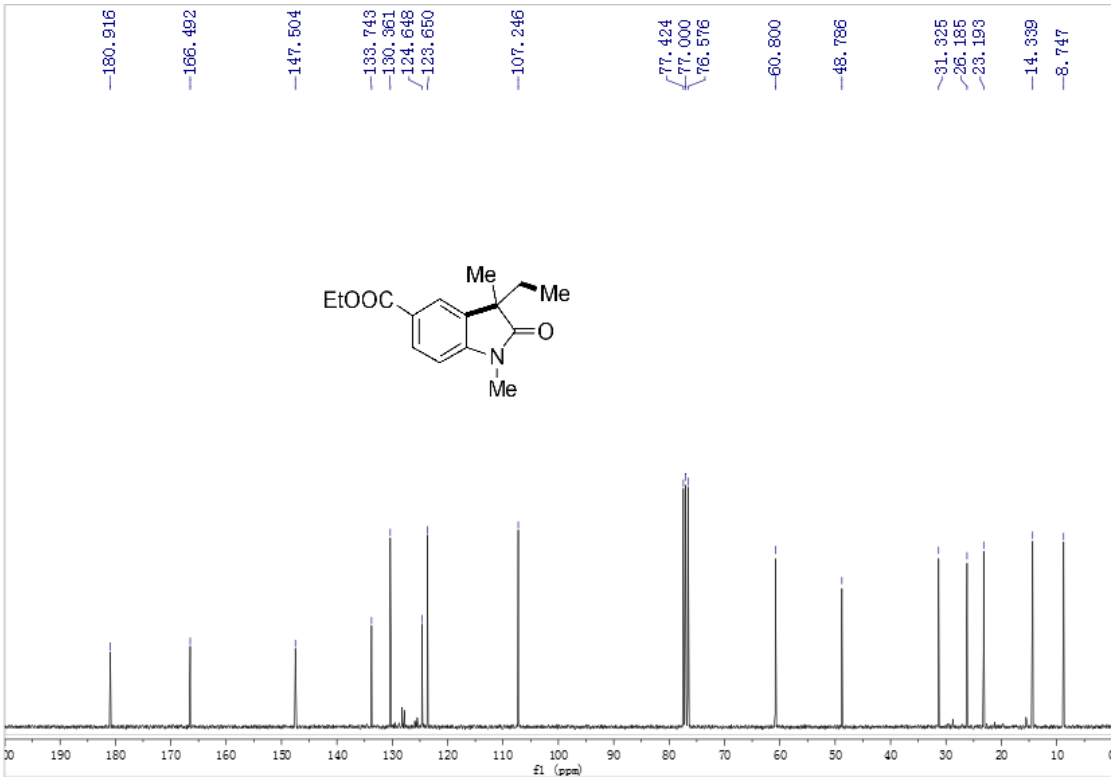
3-ethyl-1,3-dimethyl-5-nitroindolin-2-one **3d**



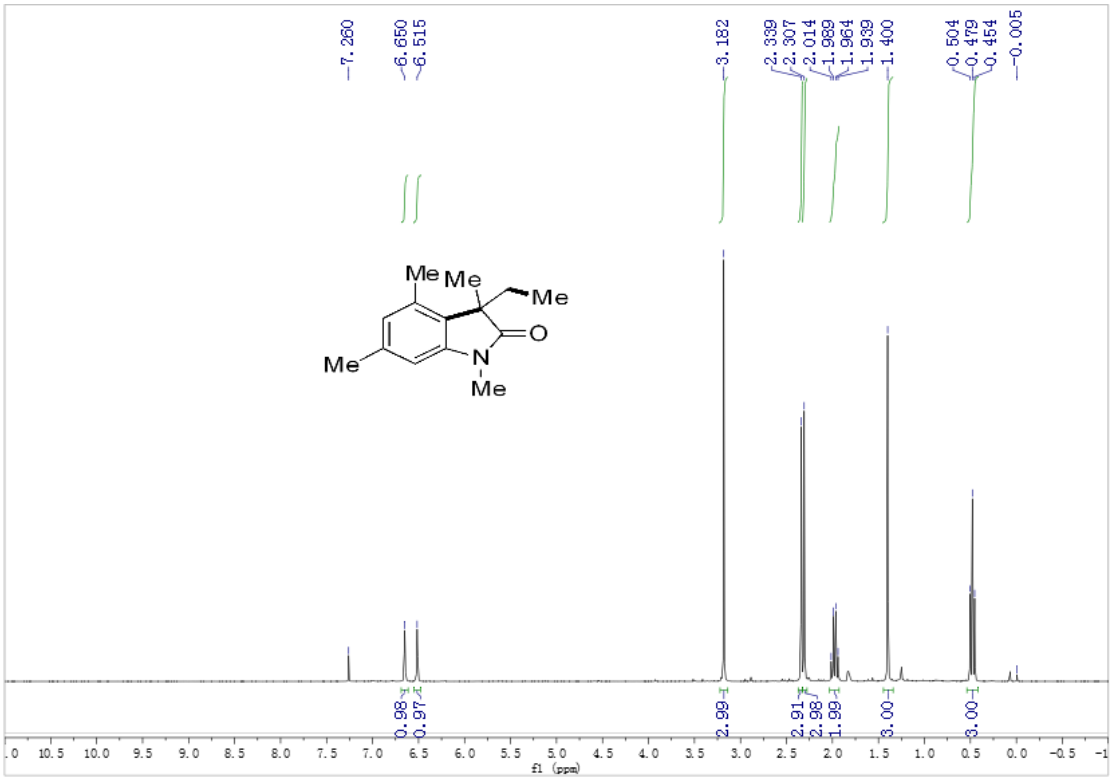


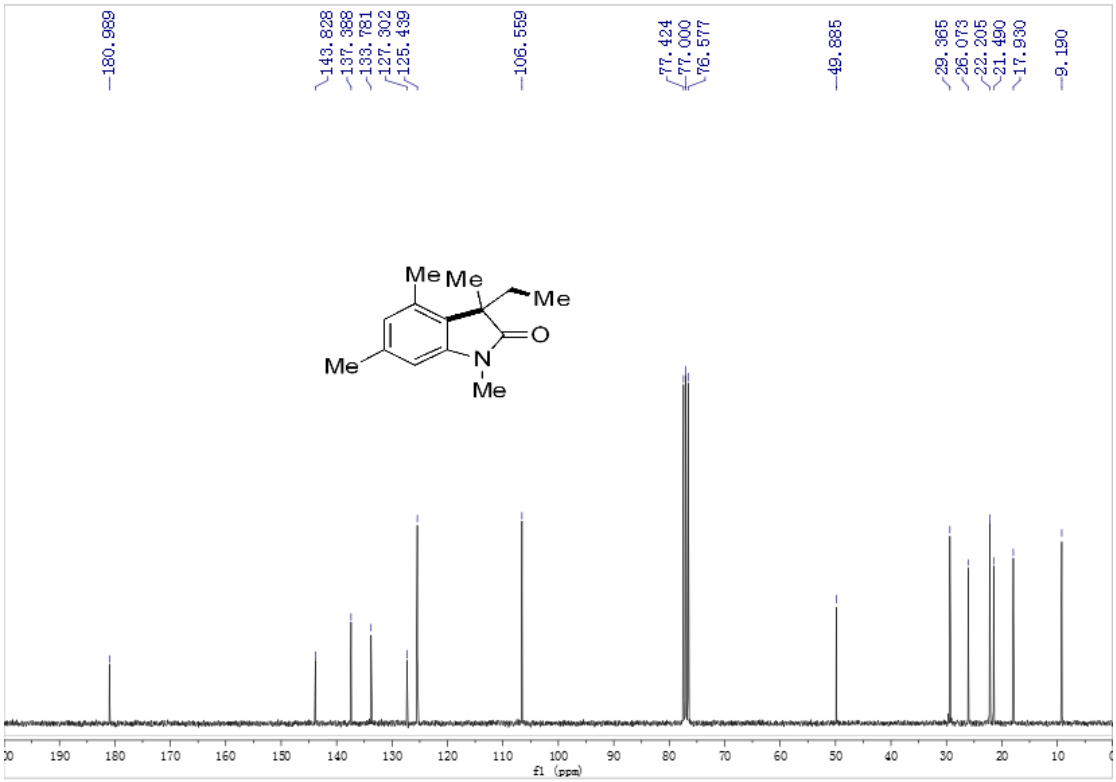
ethyl 3-ethyl-1,3-dimethyl-2-oxoindoline-5-carboxylate **3e**



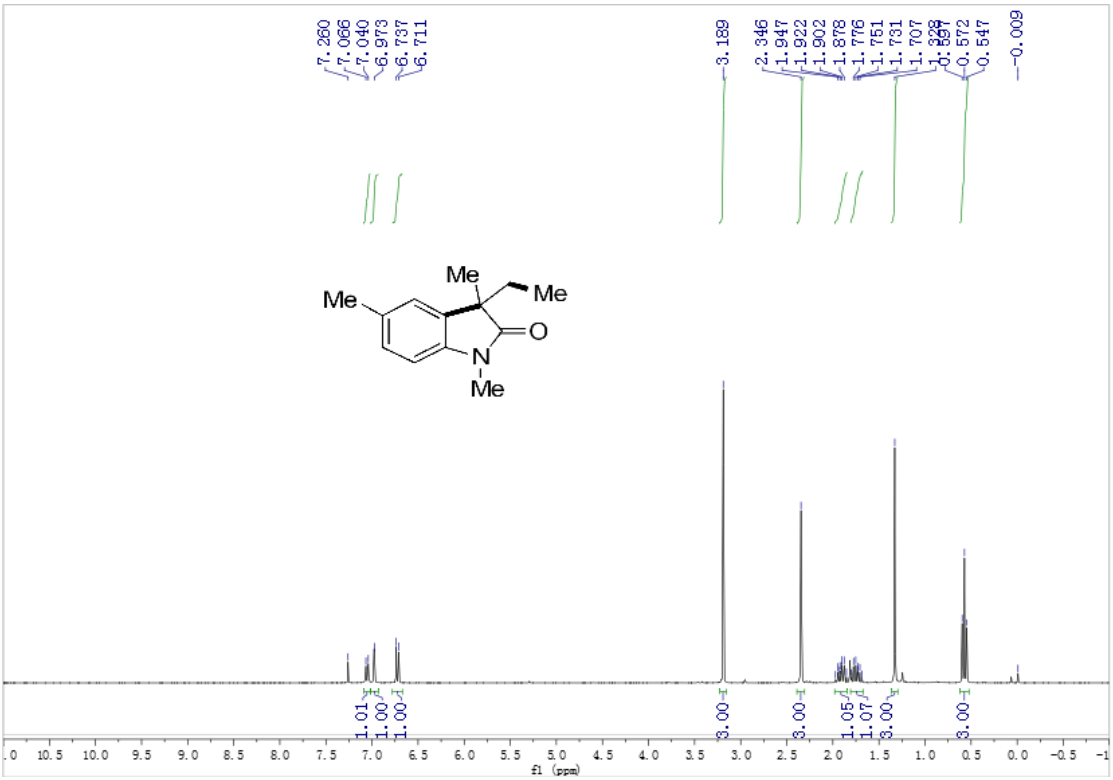


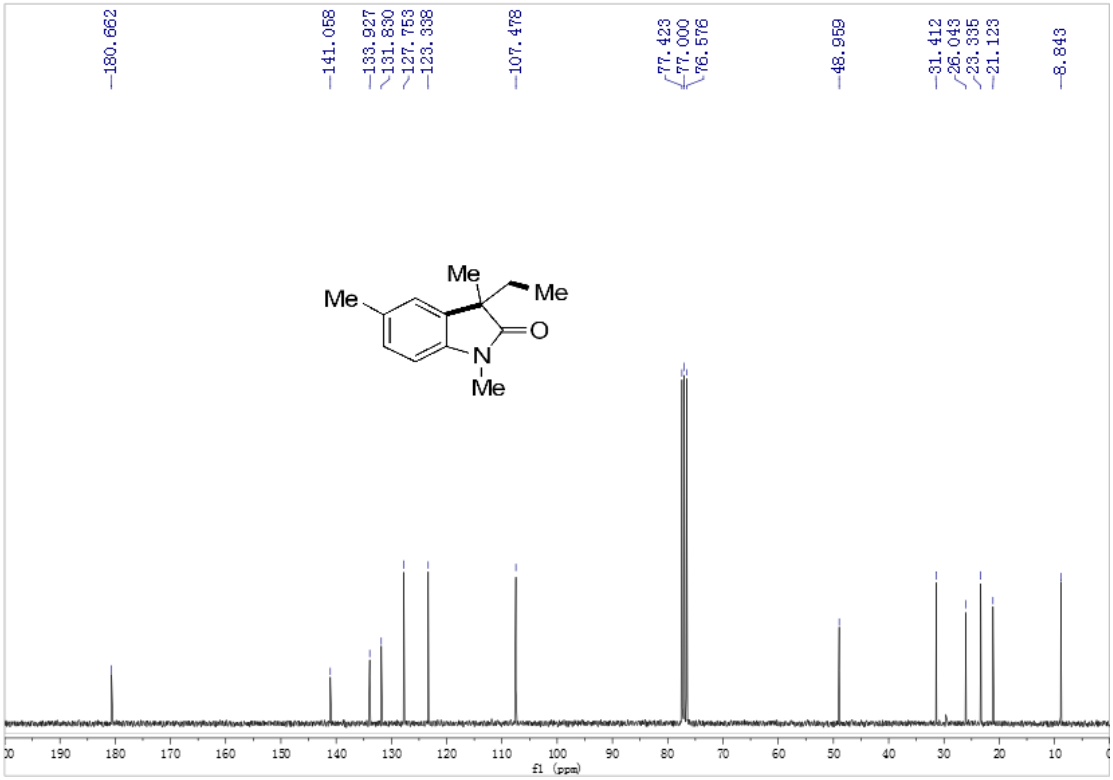
3-ethyl-1,3,4,6-tetramethylindolin-2-one **3f**



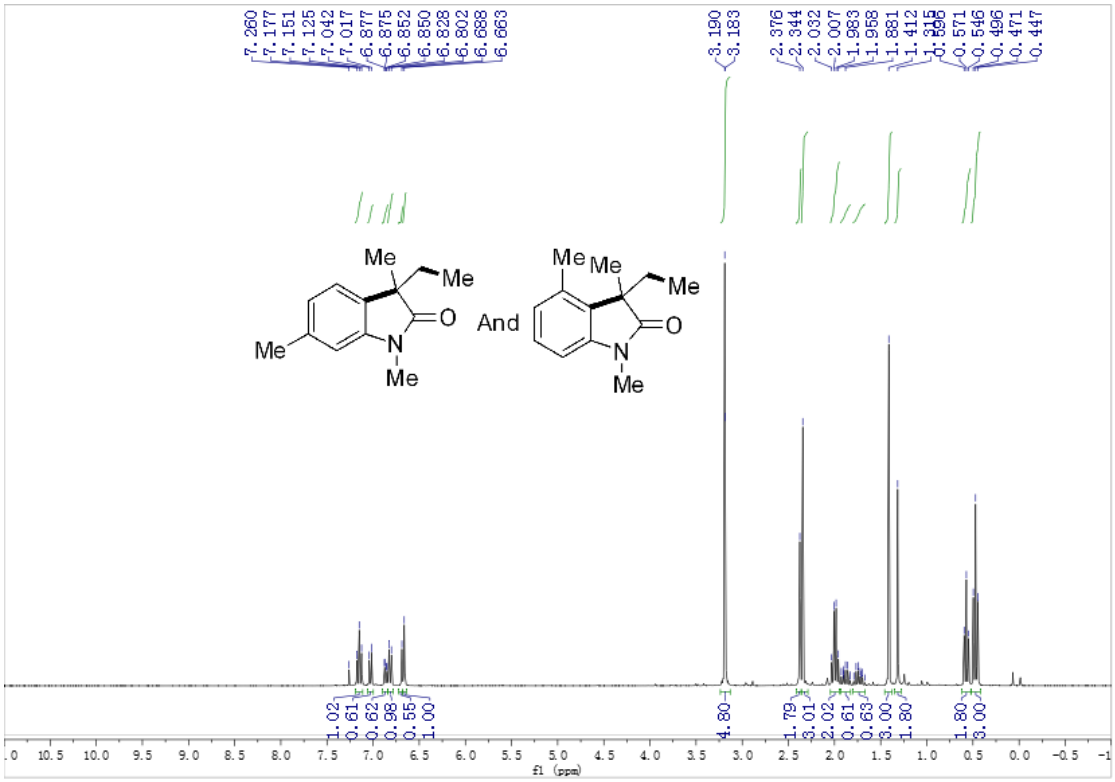


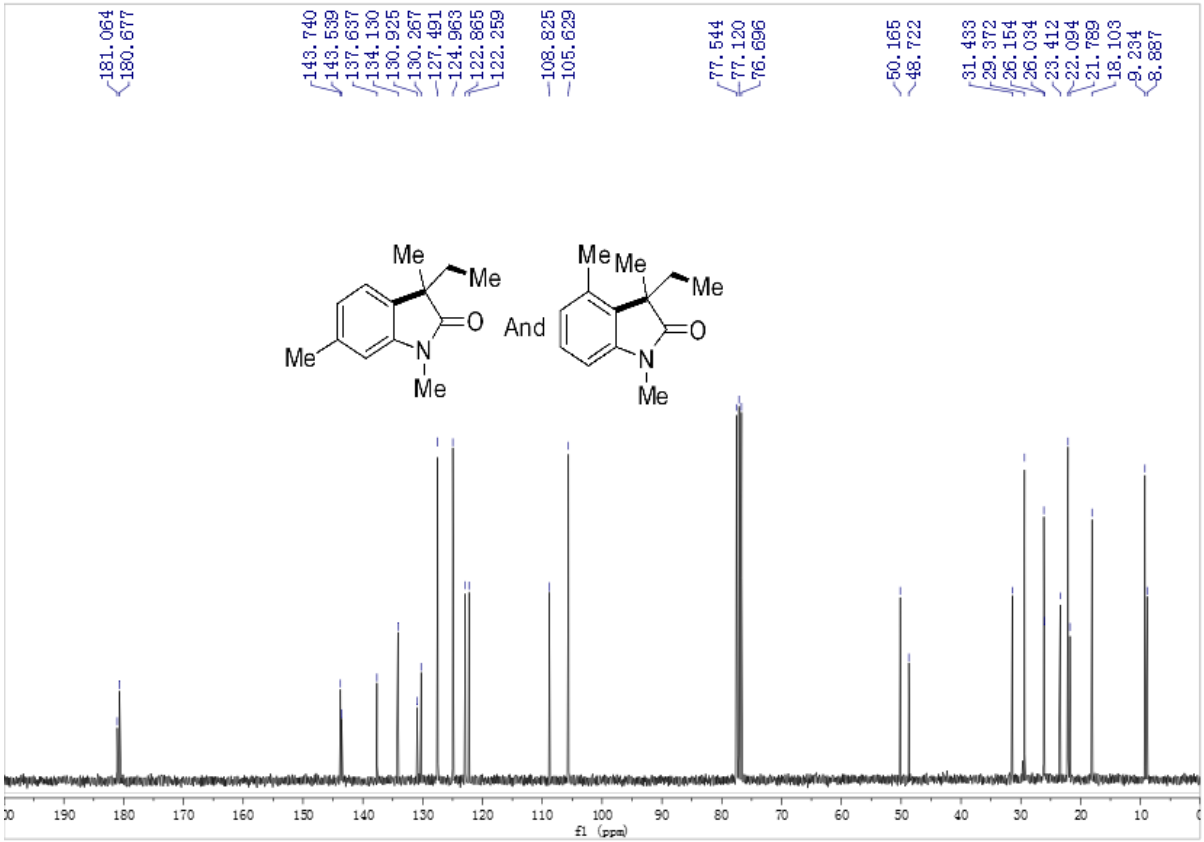
3-ethyl-1,3,5-trimethylindolin-2-one **3g**



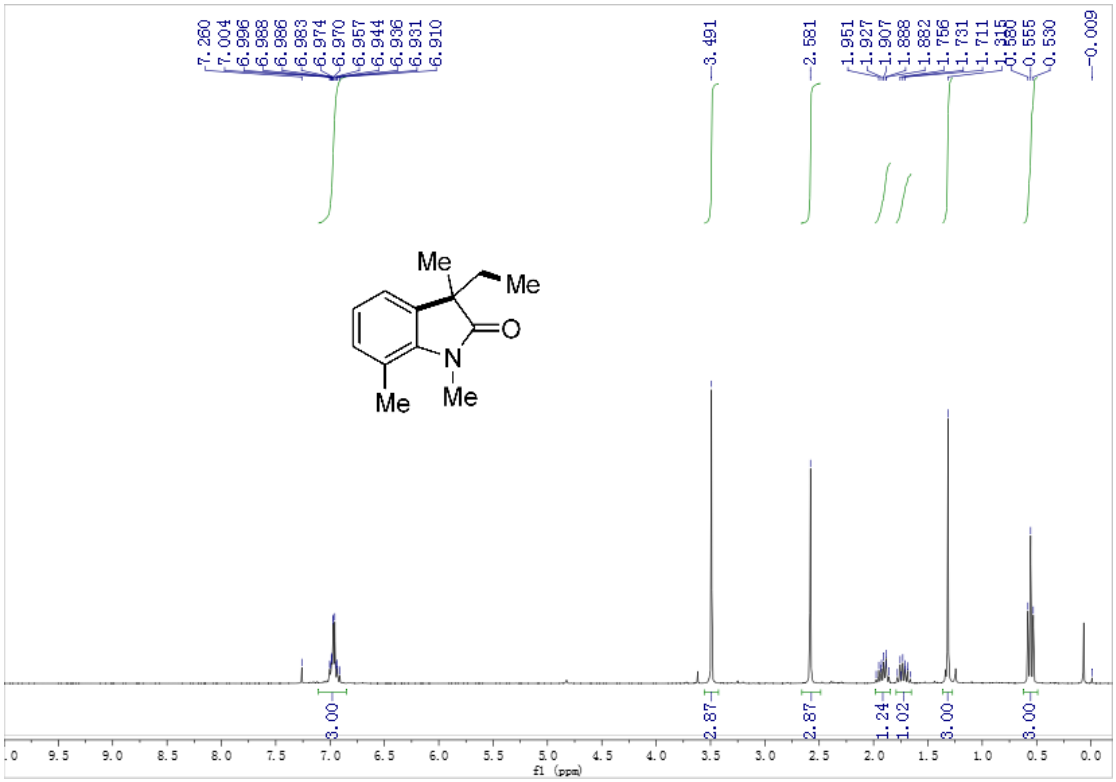


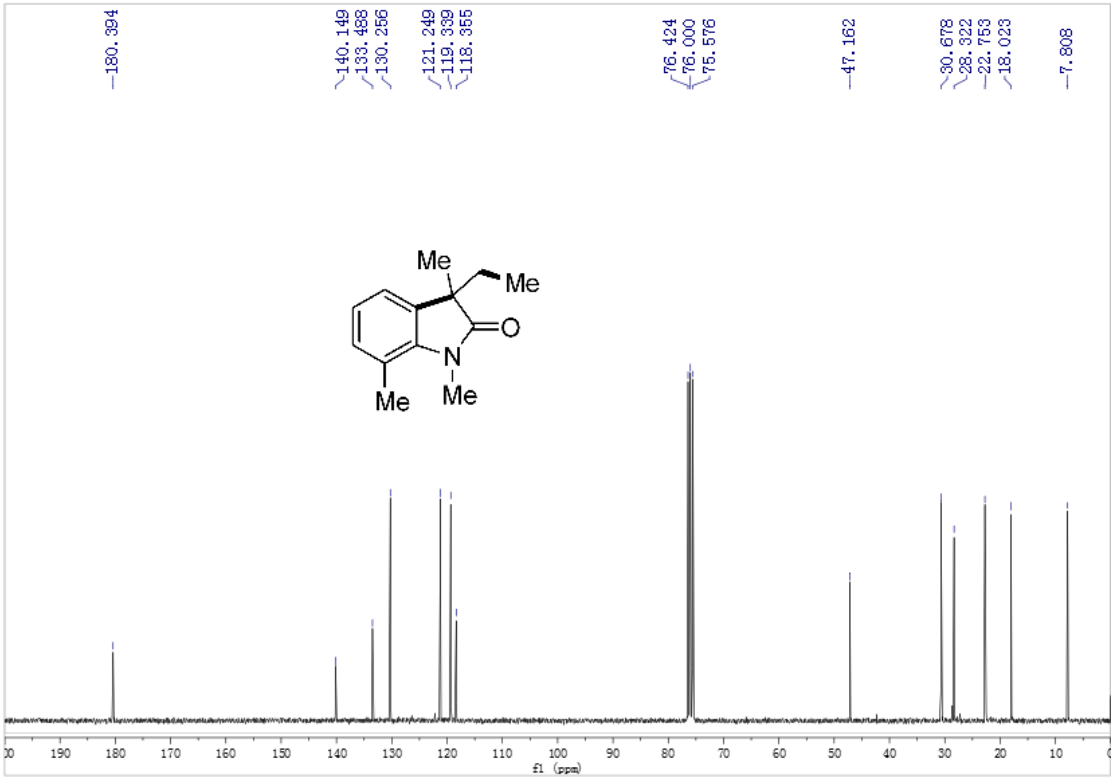
3-ethyl-1,3,6-trimethylindolin-2-one **3h**
3-ethyl-1,3,4-trimethylindolin-2-one **3h'**



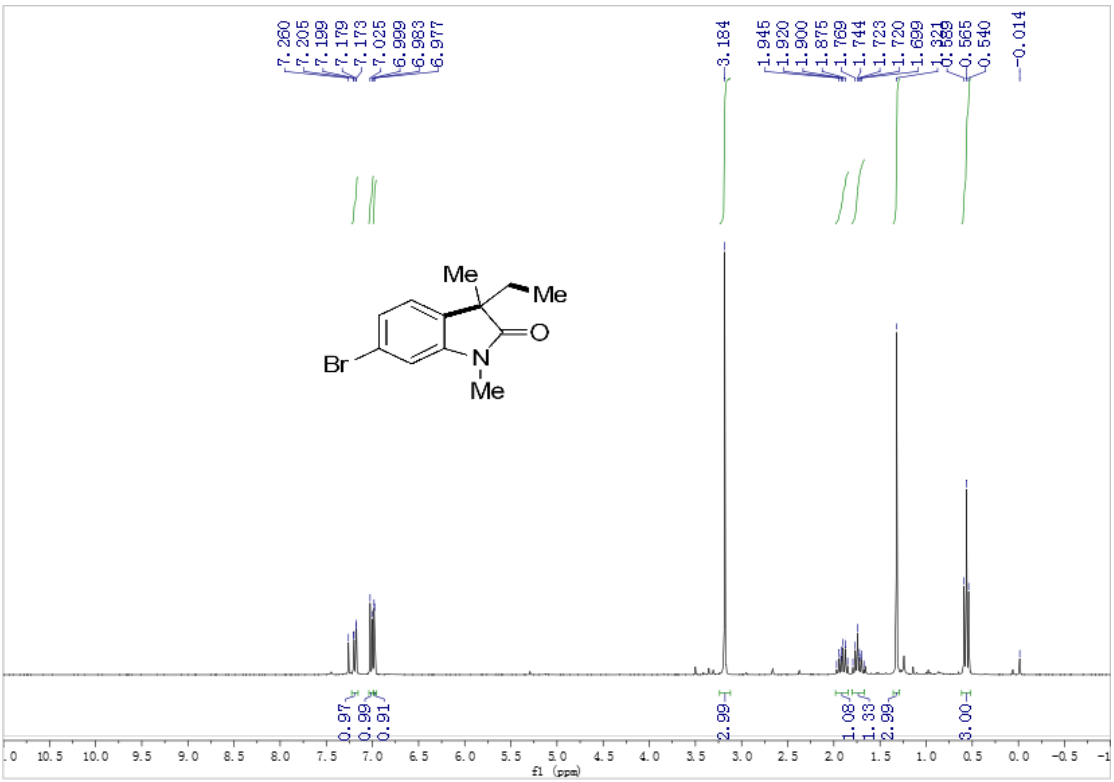


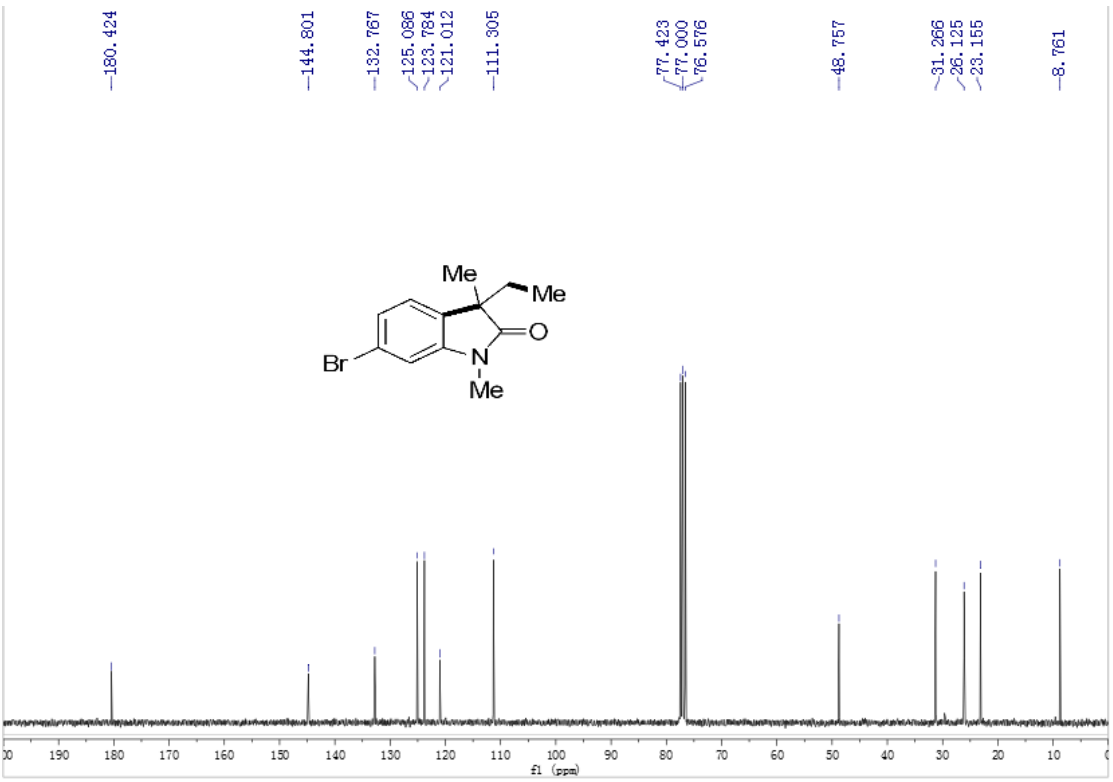
3-ethyl-1,3,7-trimethylindolin-2-one **3i**



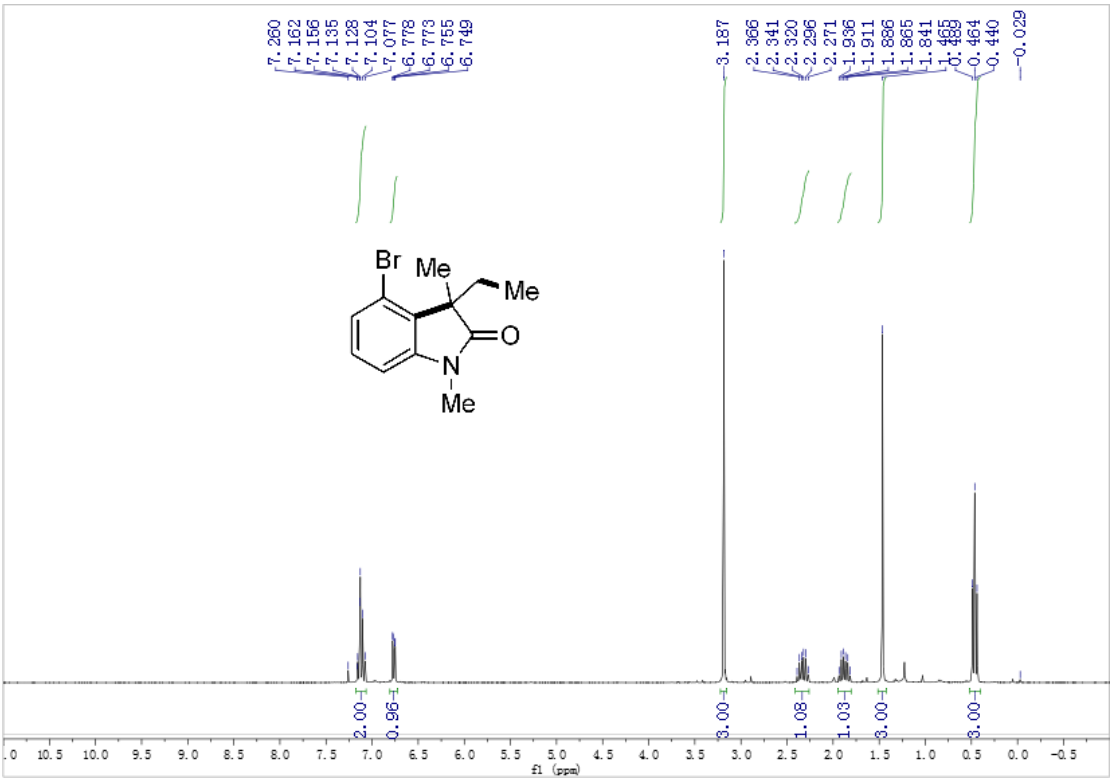


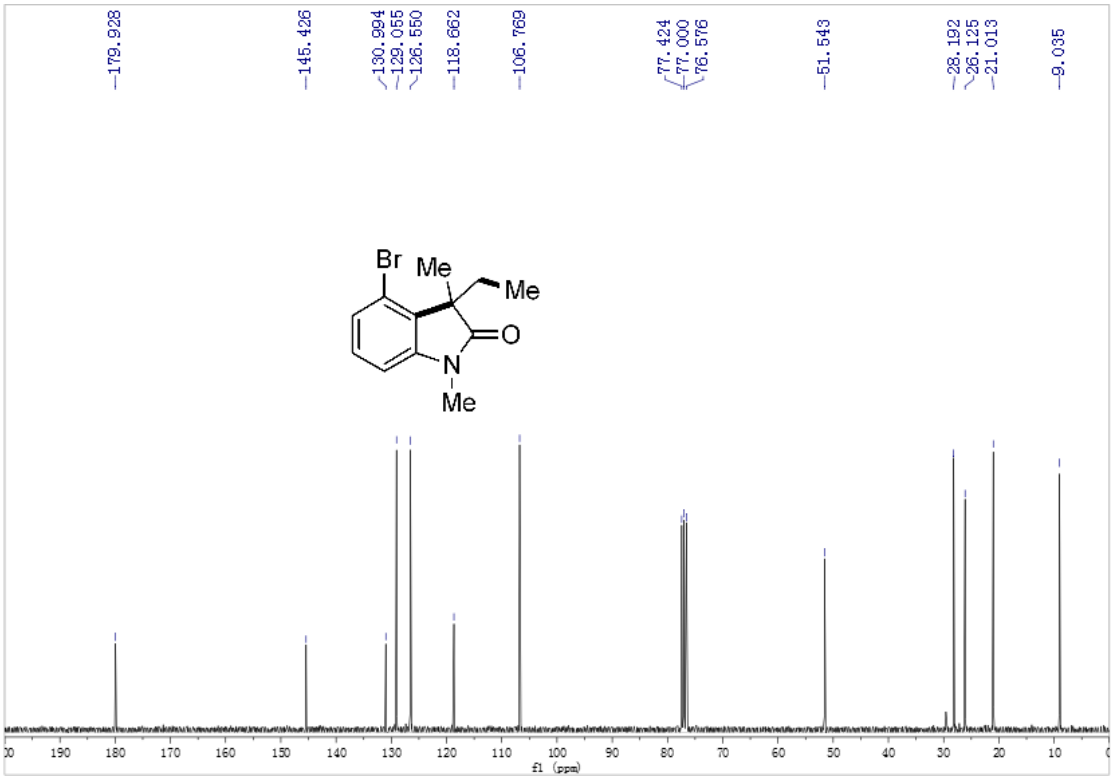
6-bromo-3-ethyl-1,3-dimethylindolin-2-one **3j**



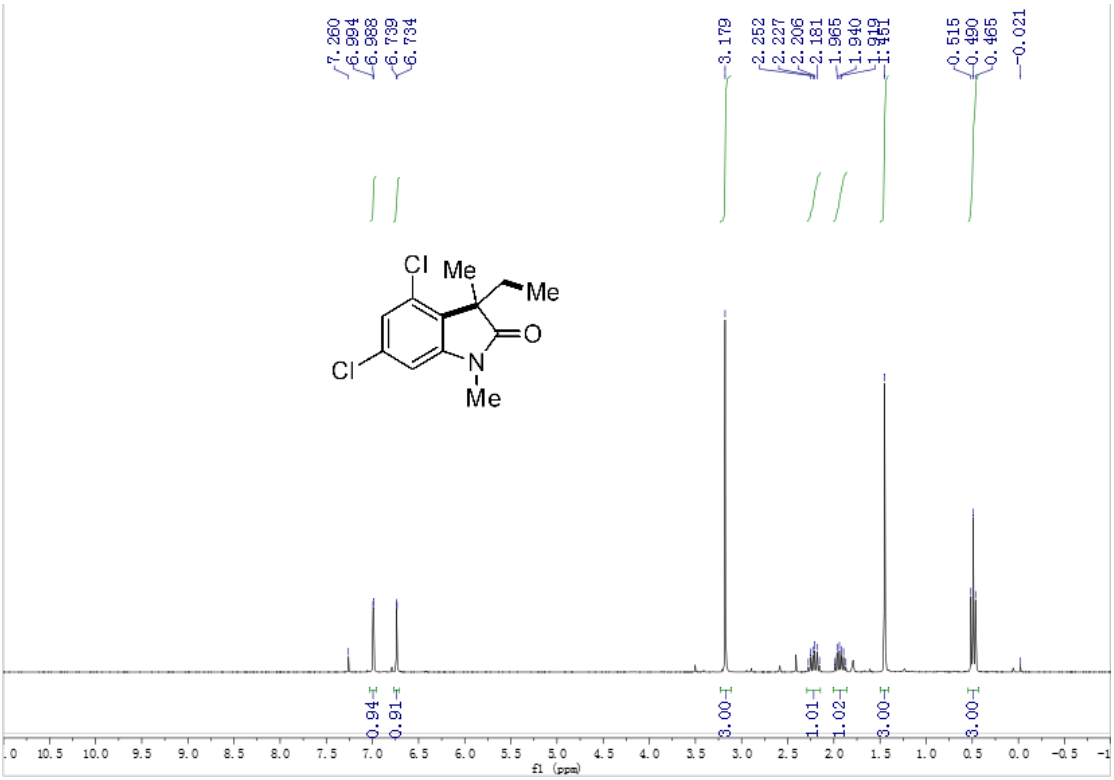


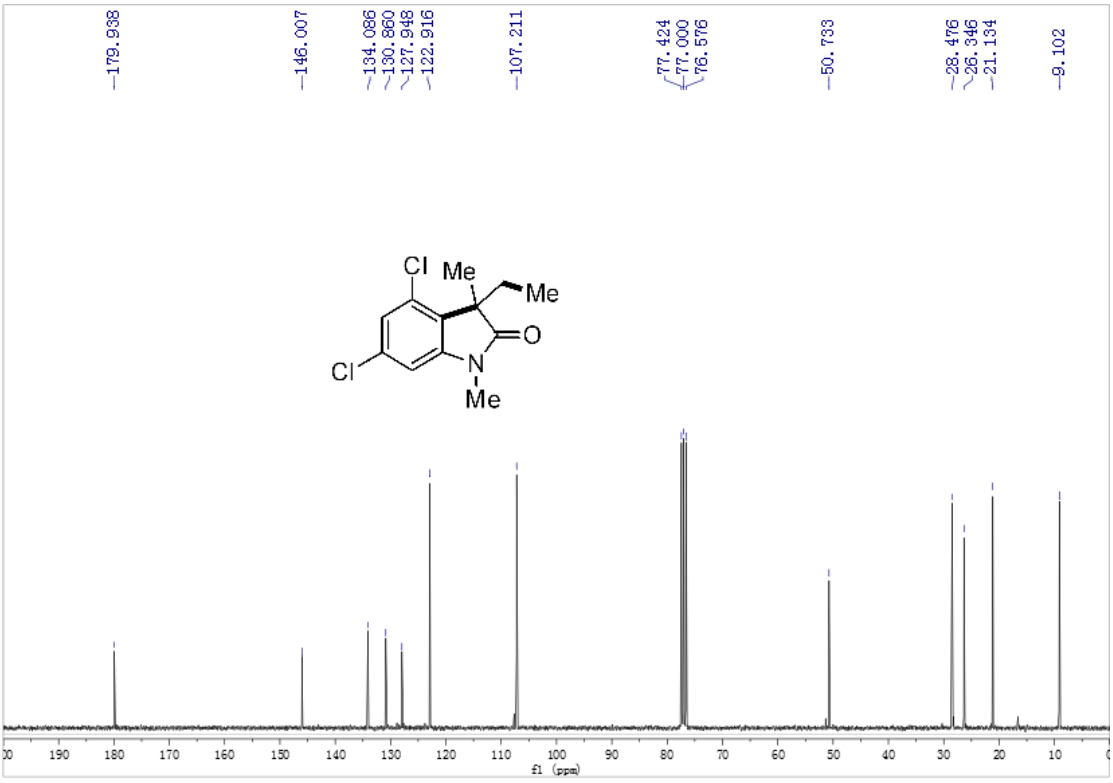
4-bromo-3-ethyl-1,3-dimethylindolin-2-one **3j'**



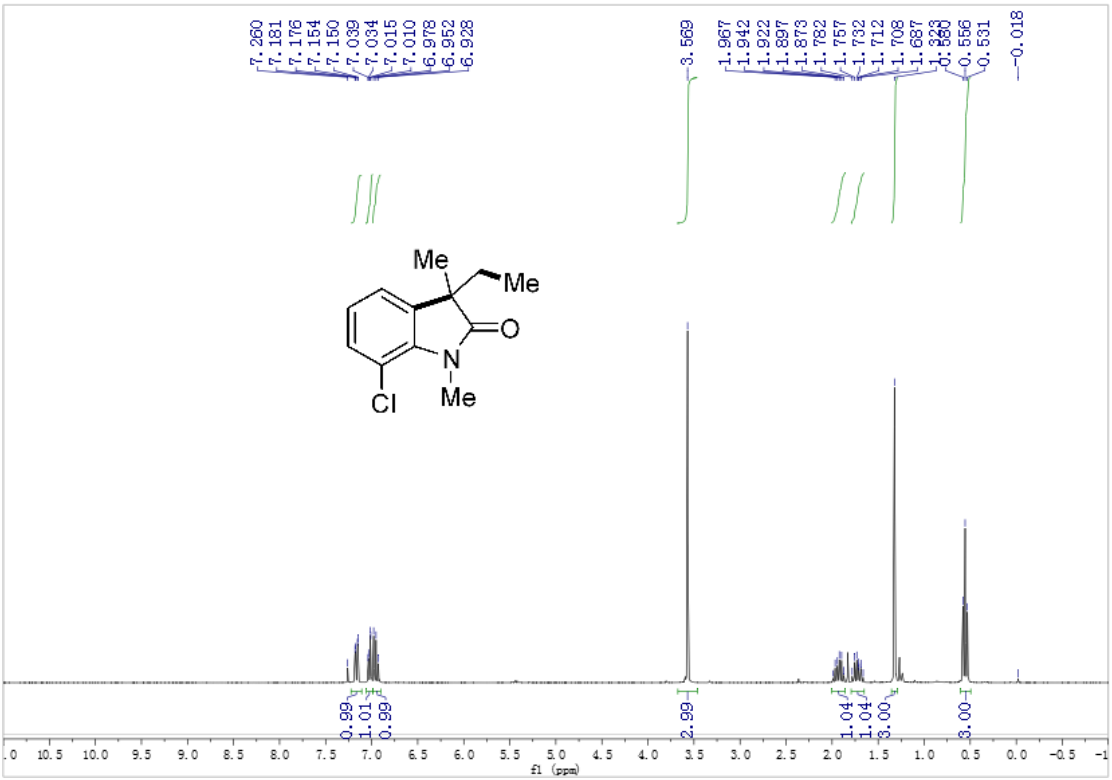


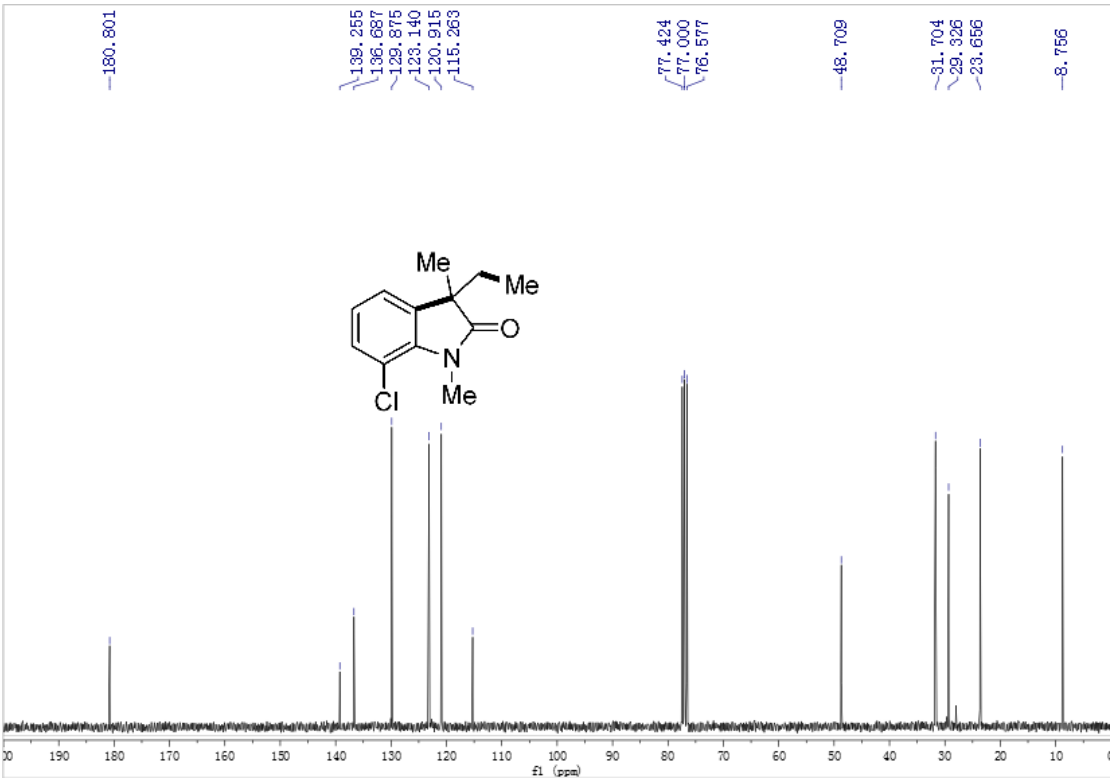
4,6-dichloro-3-ethyl-1,3-dimethylindolin-2-one **3k**



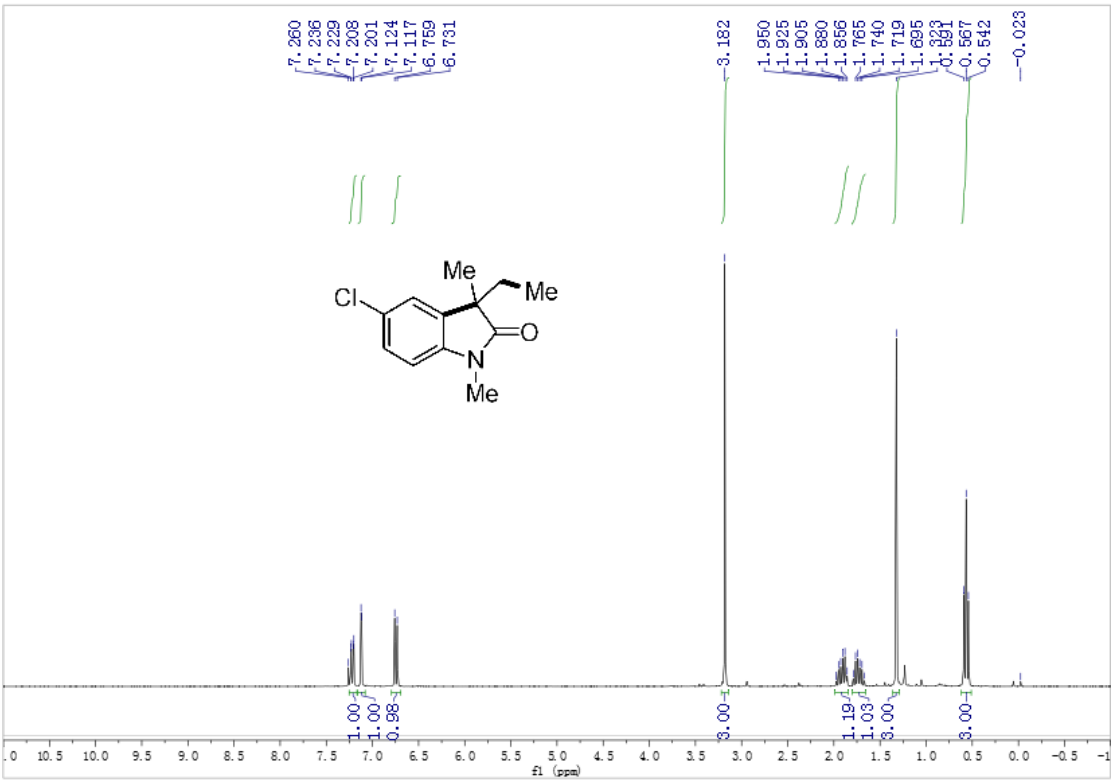


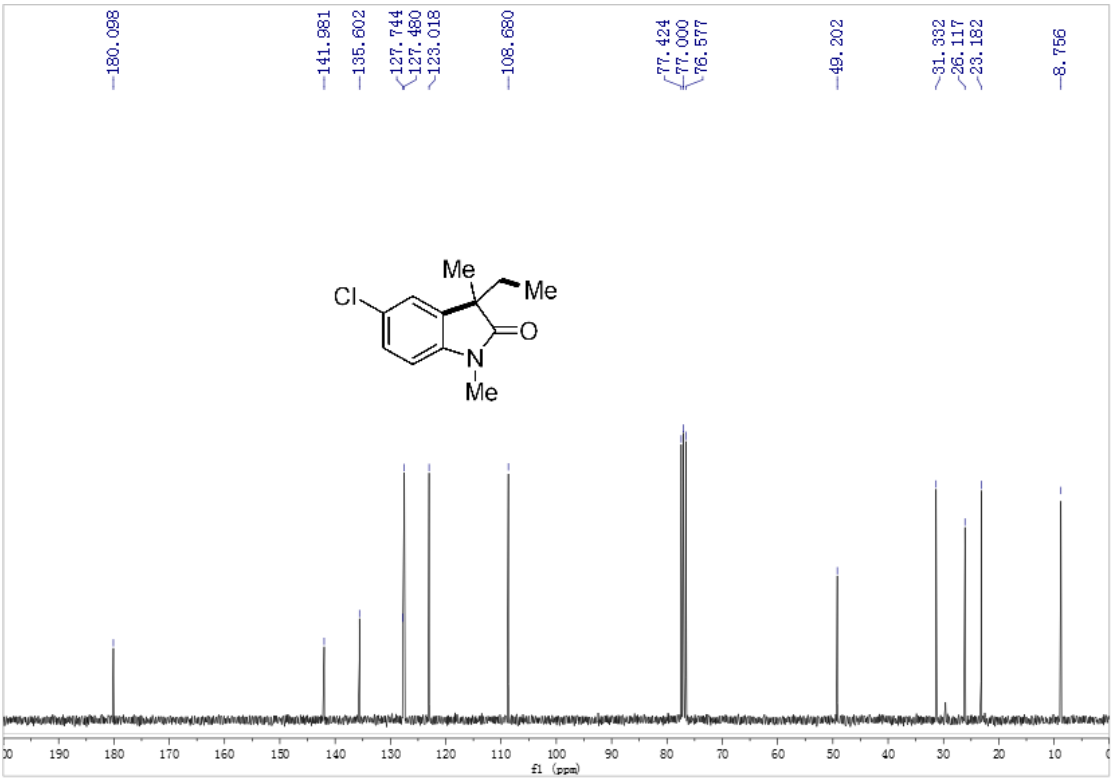
7-chloro-3-ethyl-1,3-dimethylindolin-2-one **3l**



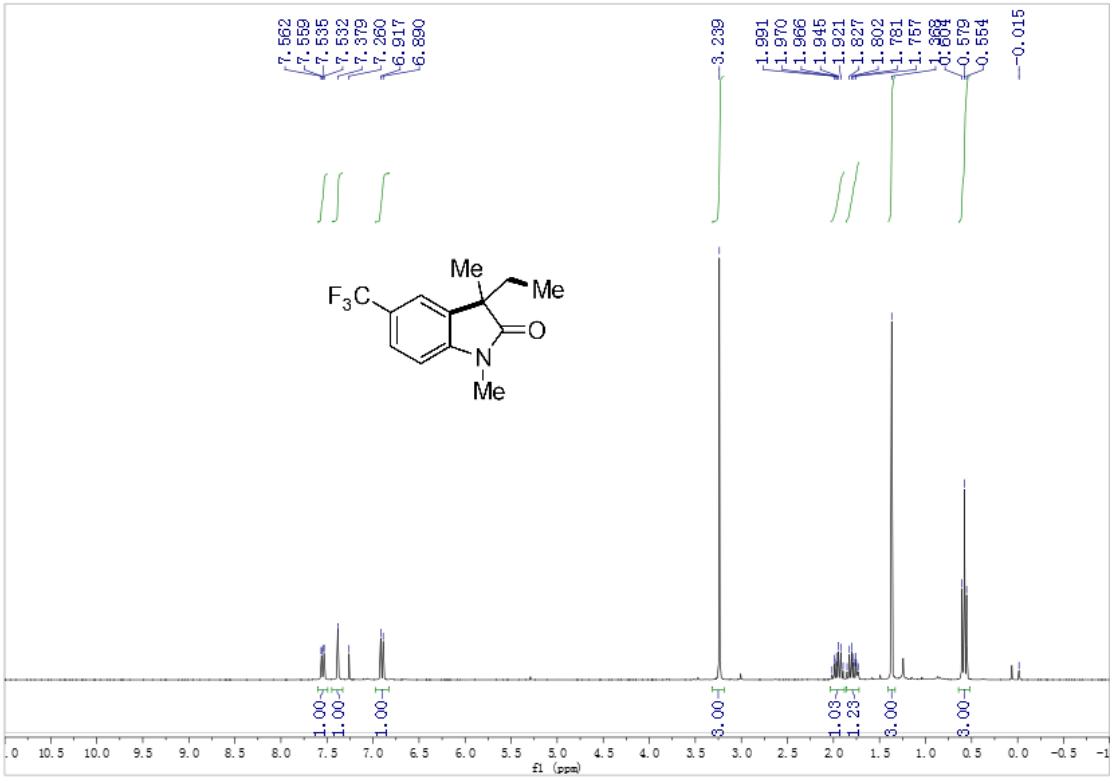


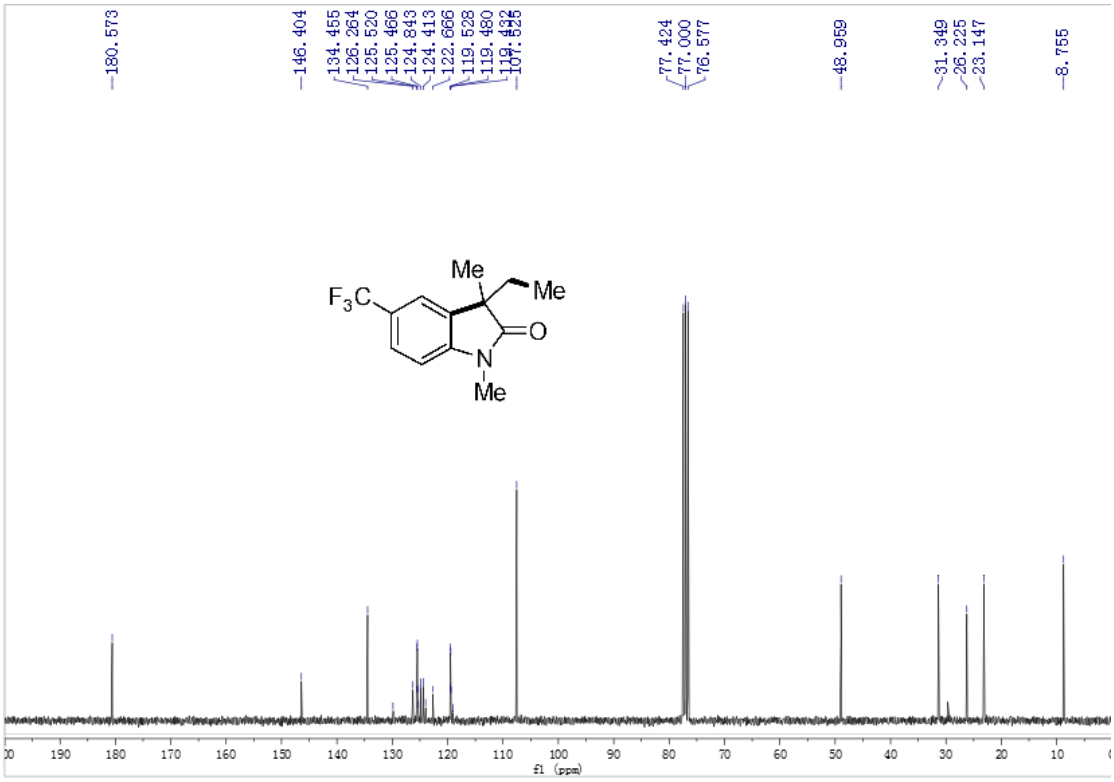
5-chloro-3-ethyl-1,3-dimethylindolin-2-one **3m**



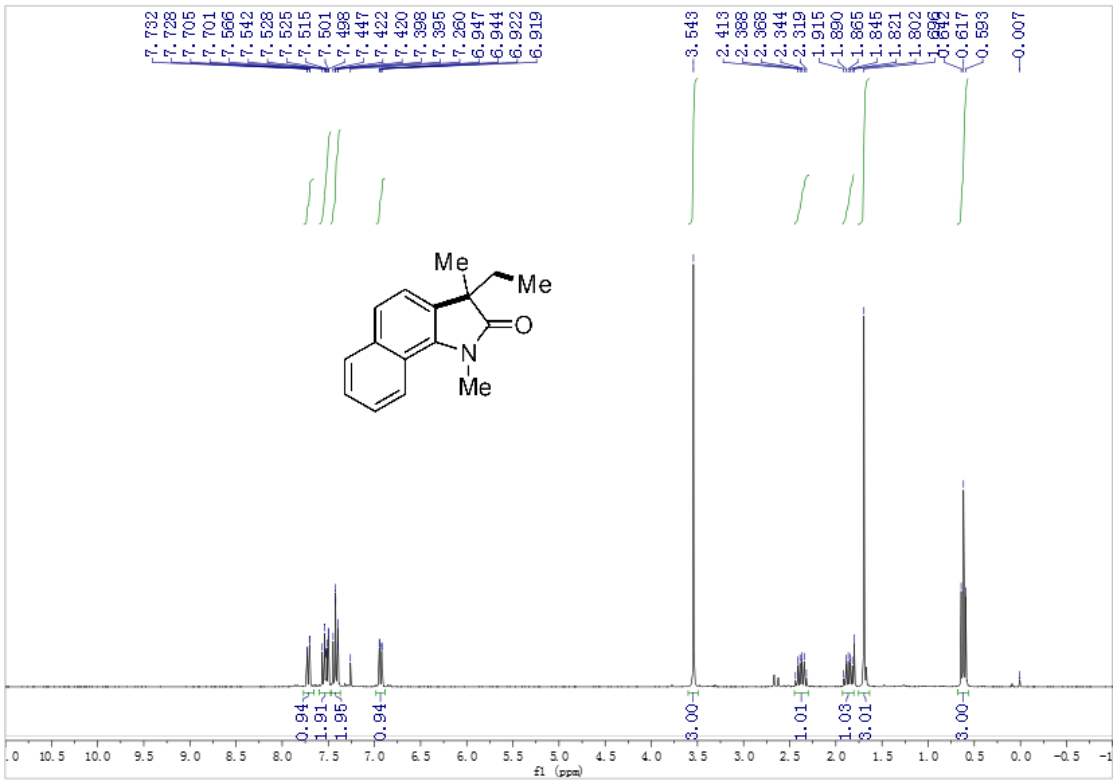


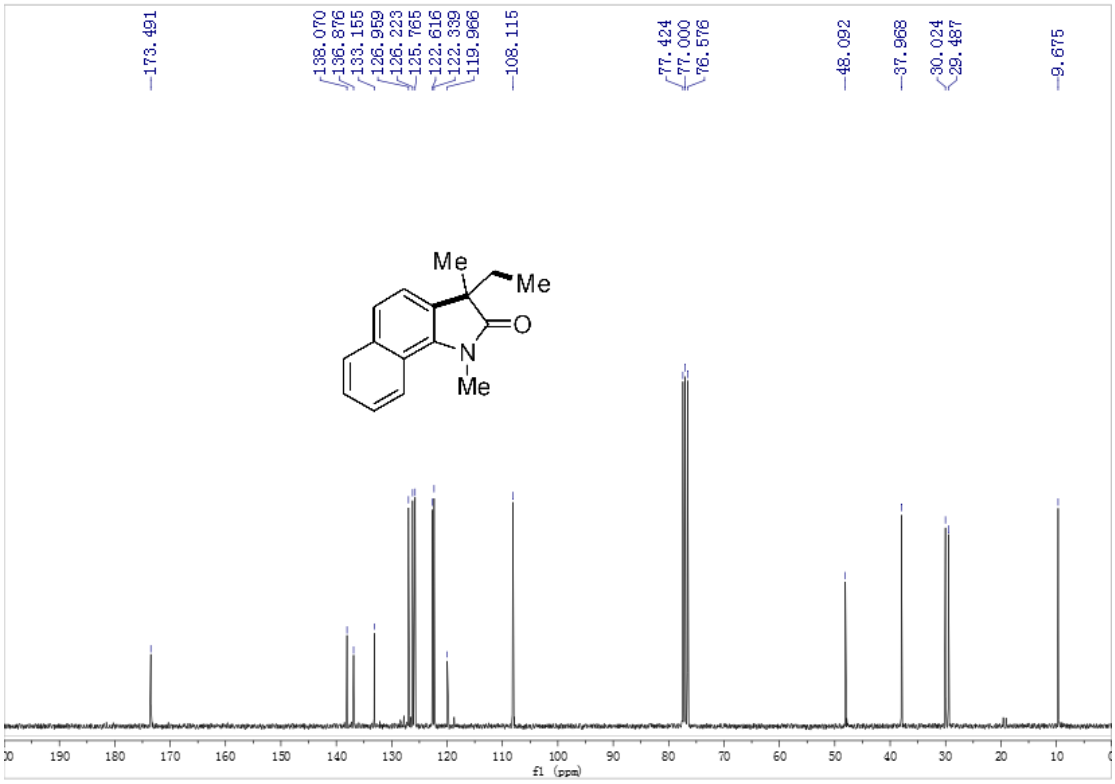
3-ethyl-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one **3n**



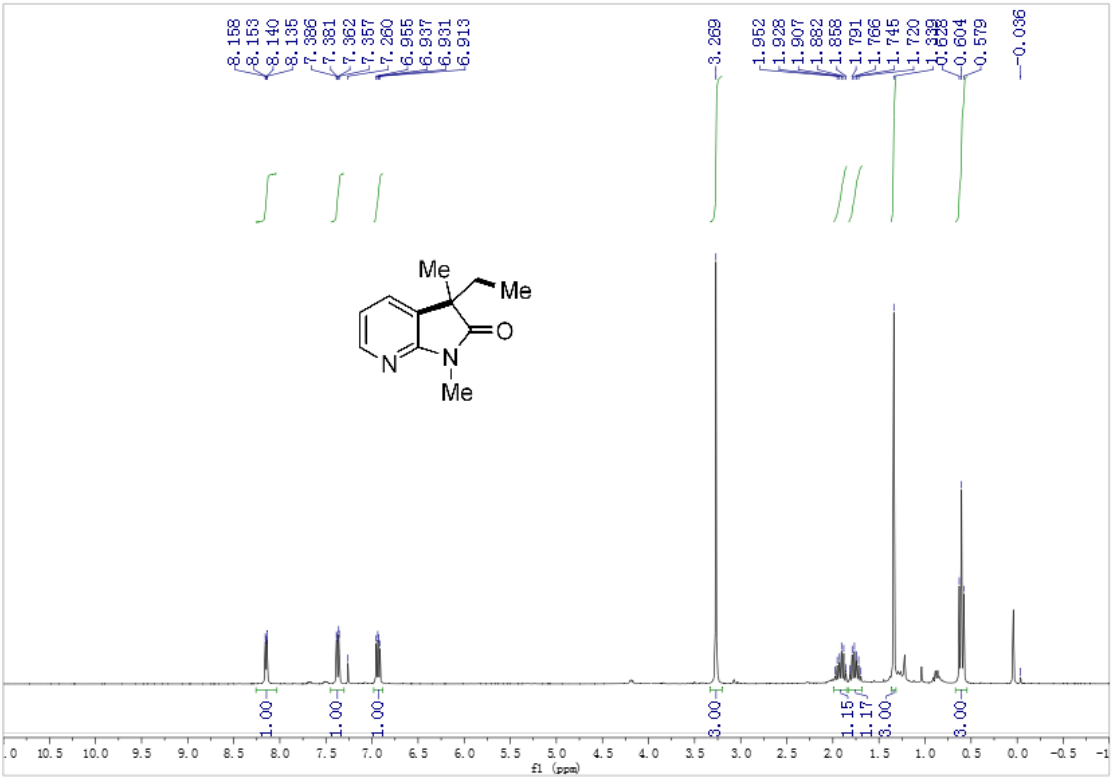


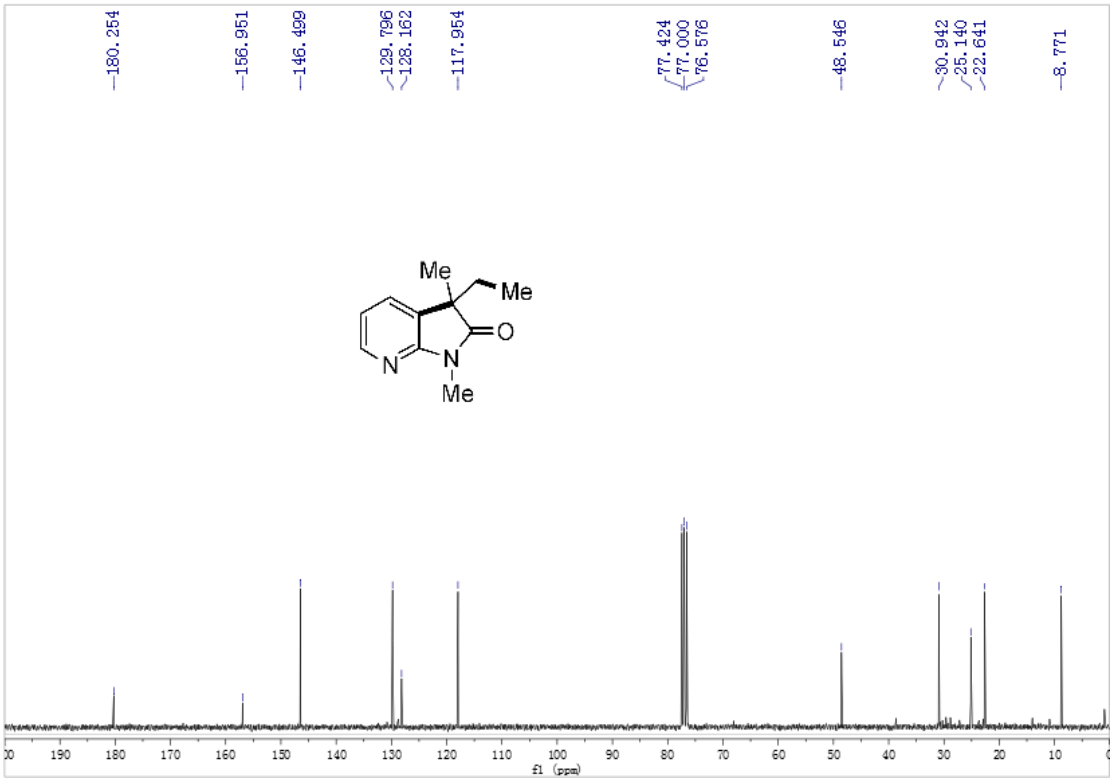
3-ethyl-1,3-dimethyl-1H-benzo[g]indol-2(3H)-one **3o**



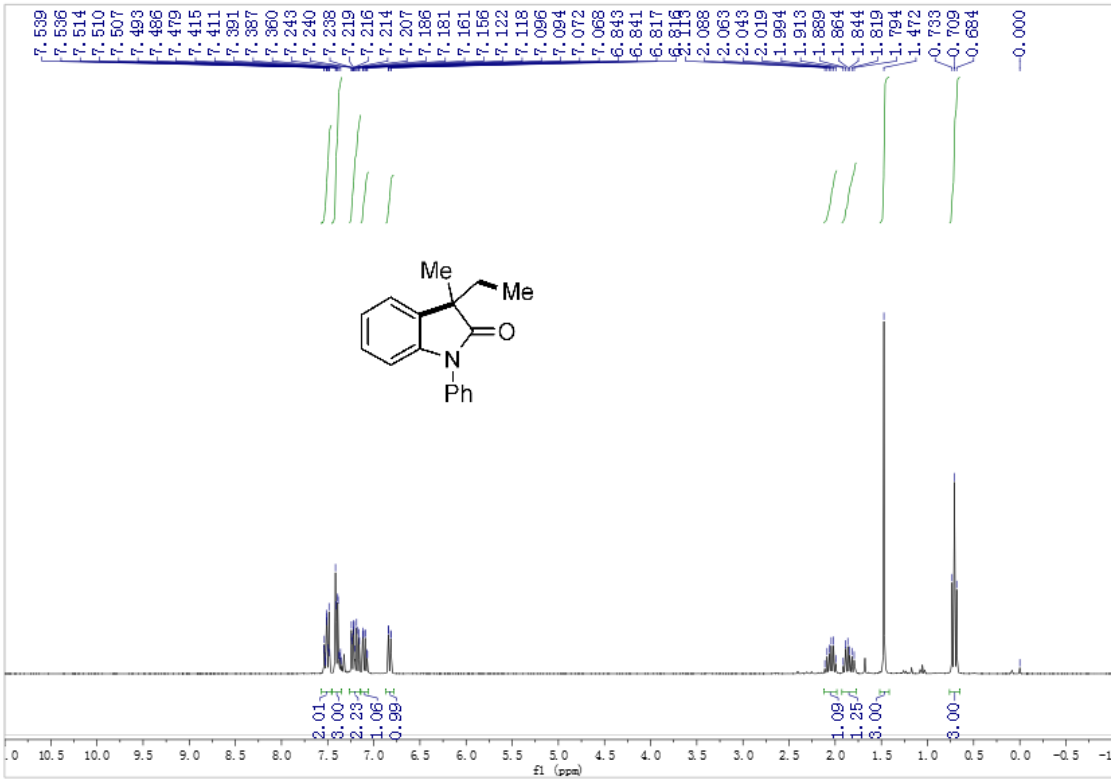


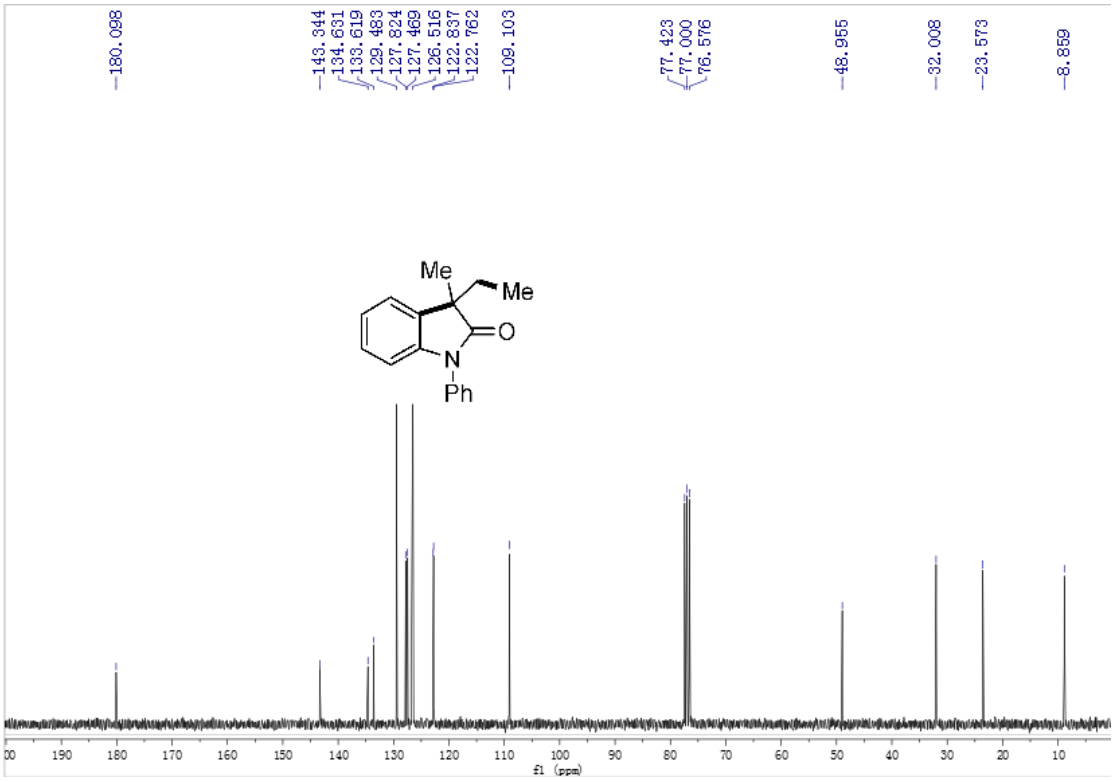
3-ethyl-1,3-dimethyl-1H-pyrrolo[2,3-b]pyridin-2(3H)-one **3p**



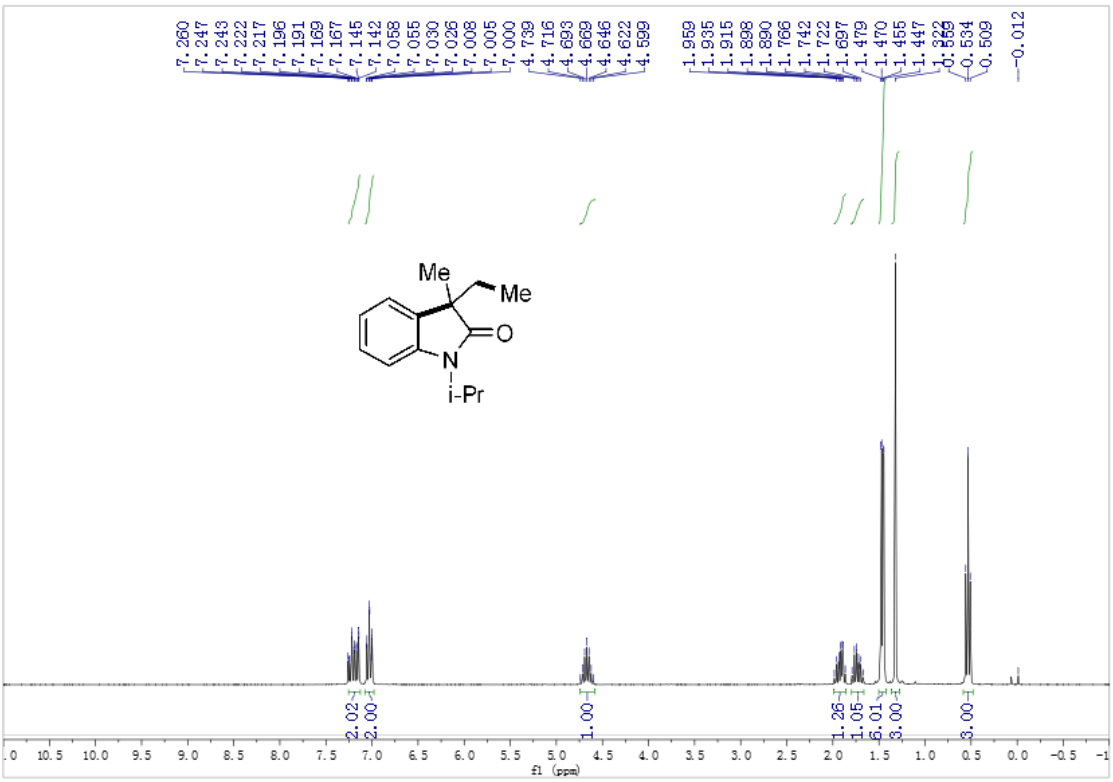


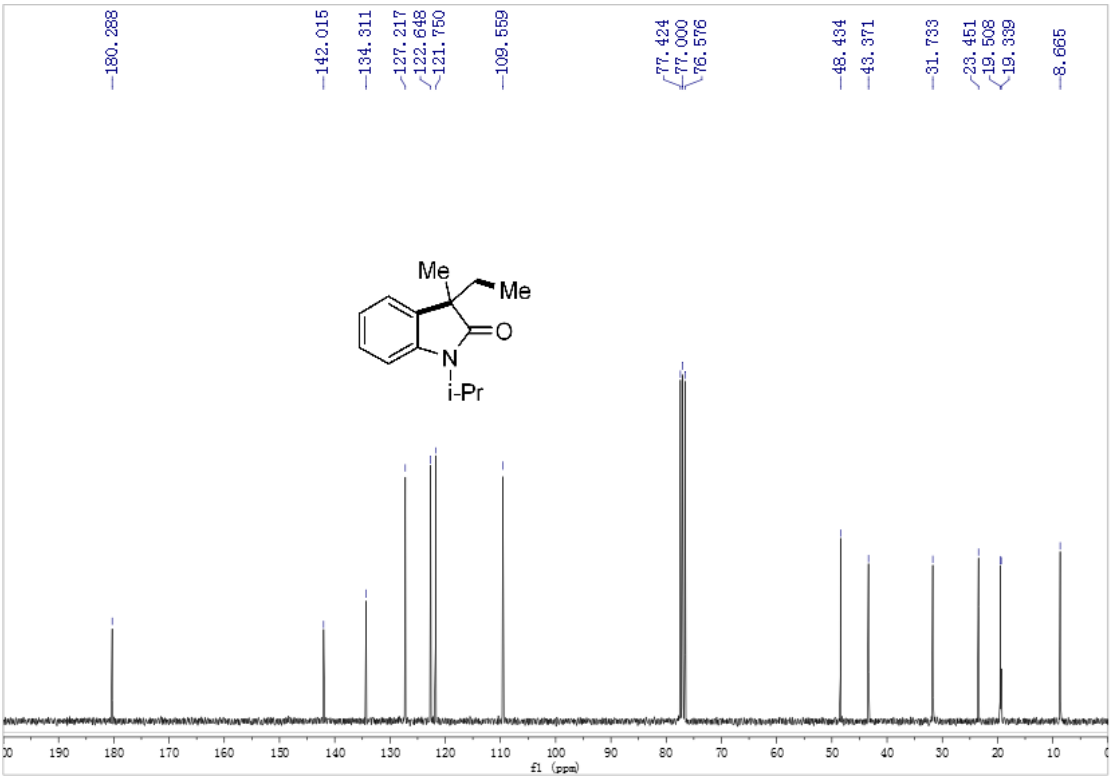
3-ethyl-3-methyl-1-phenylindolin-2-one **3q**



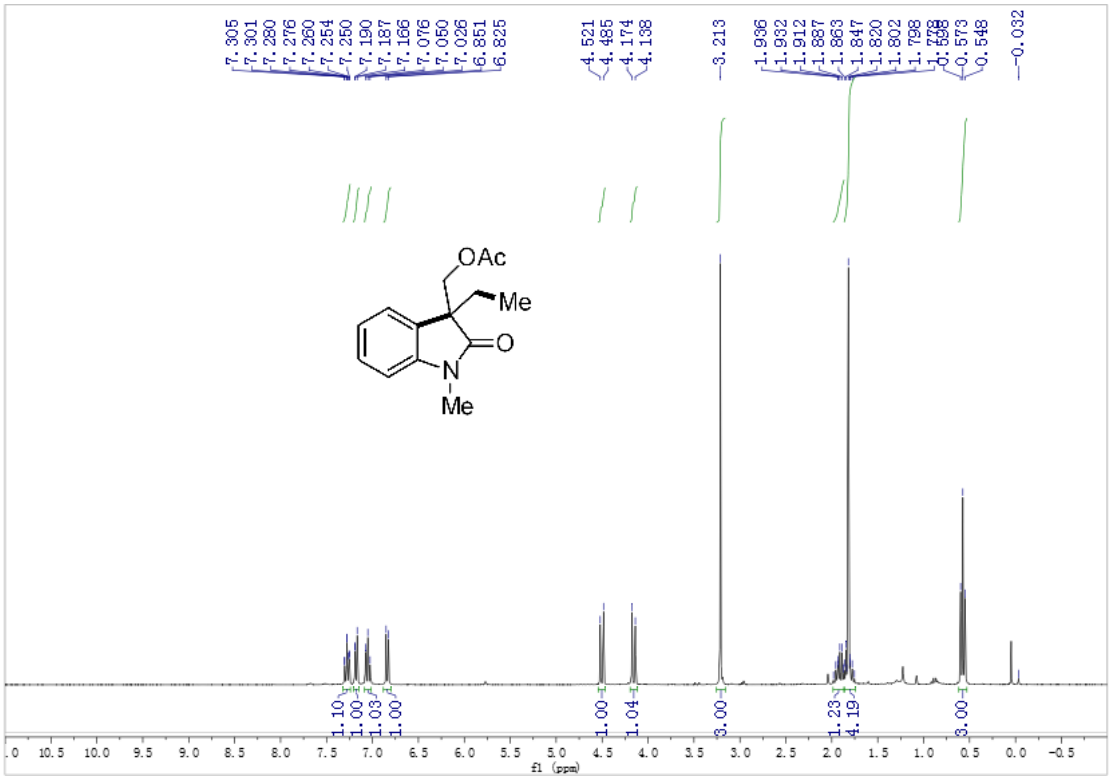


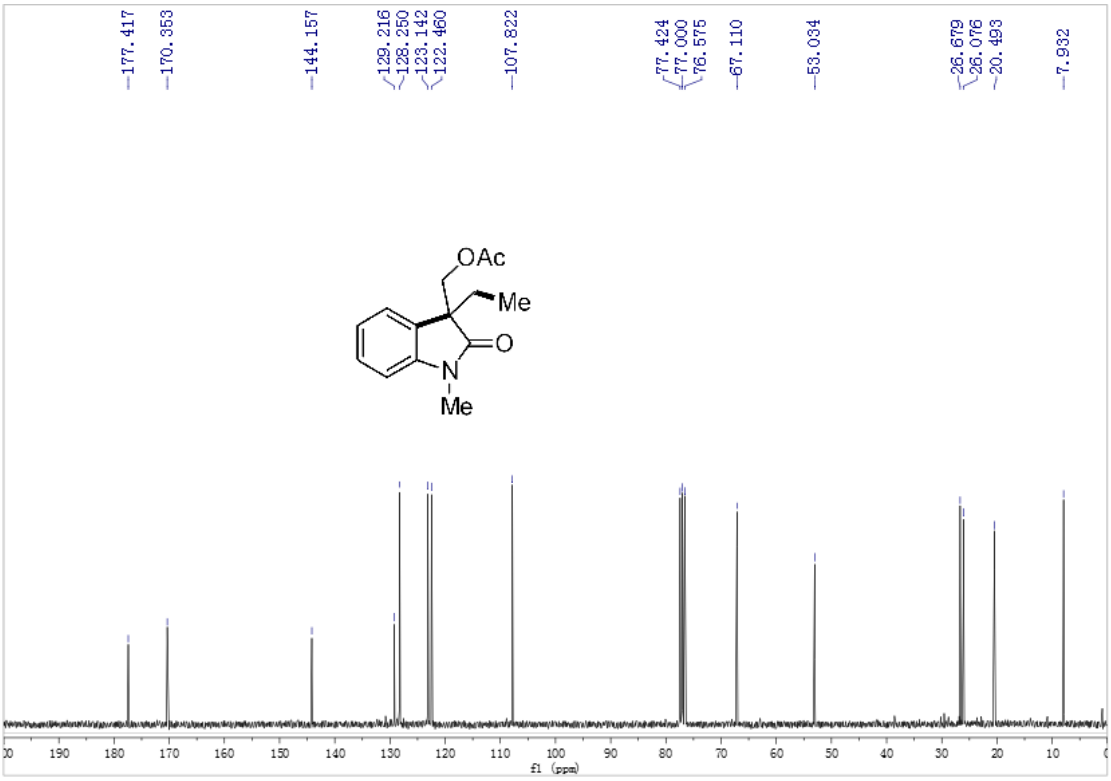
3-ethyl-1-isopropyl-3-methylindolin-2-one **3r**



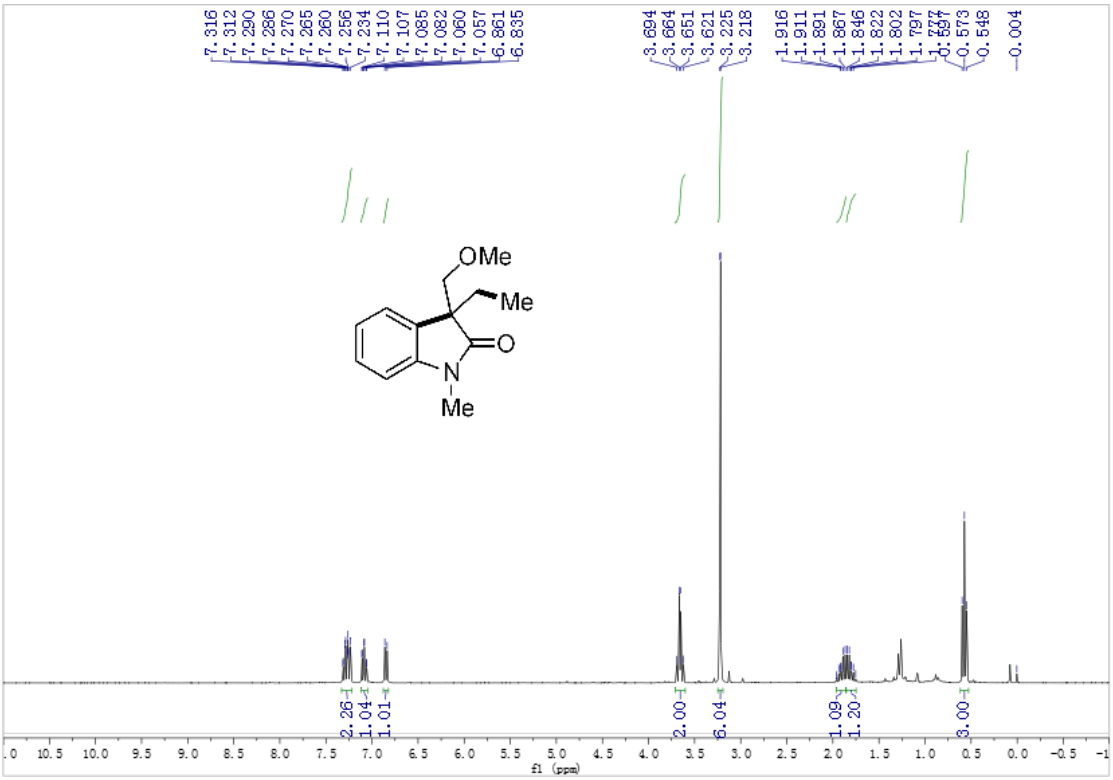


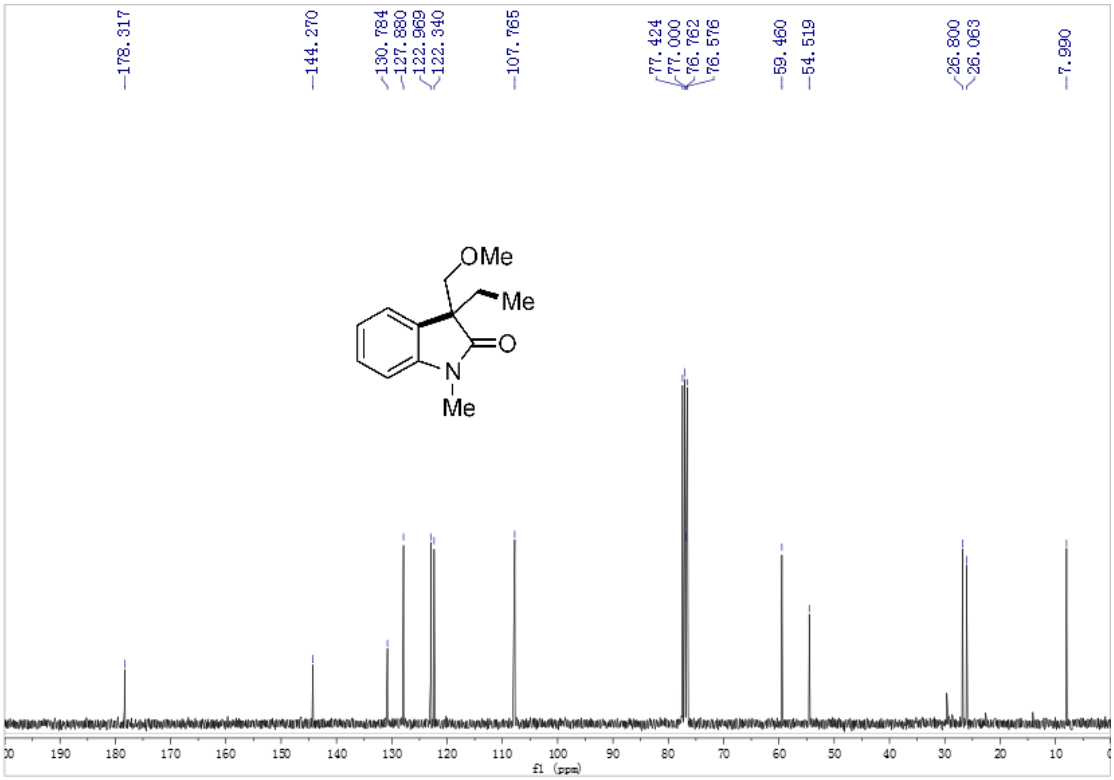
(3-ethyl-1-methyl-2-oxoindolin-3-yl)methyl acetate **3s**



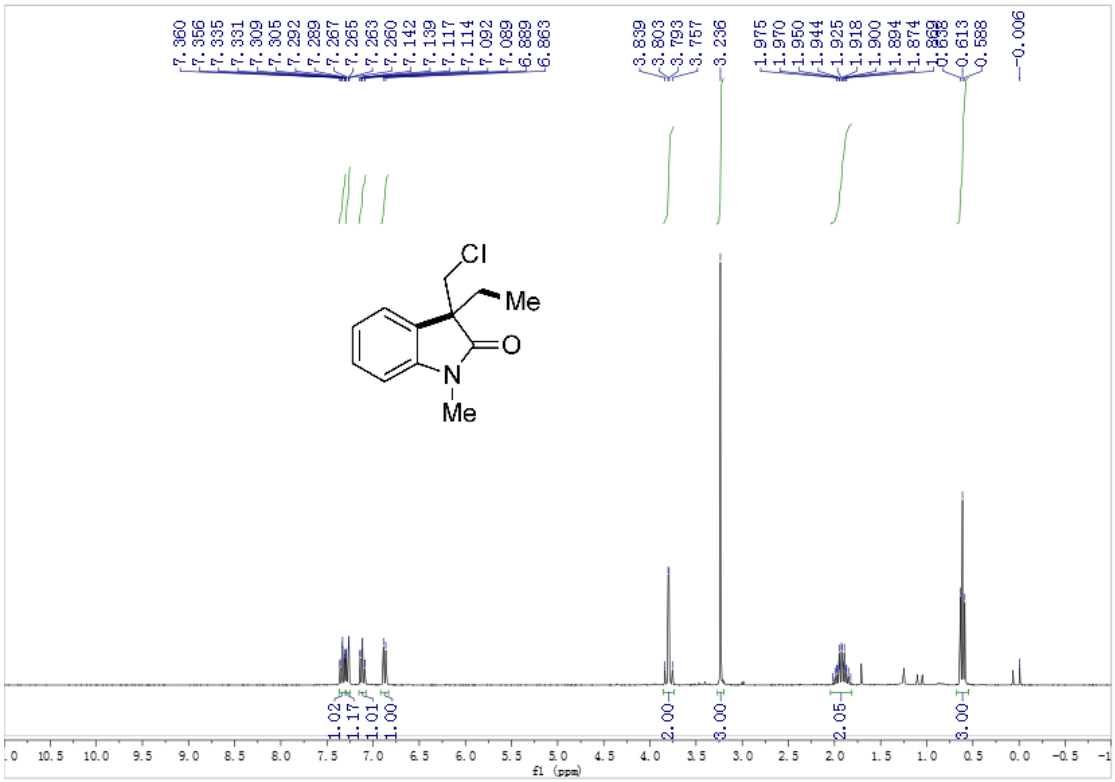


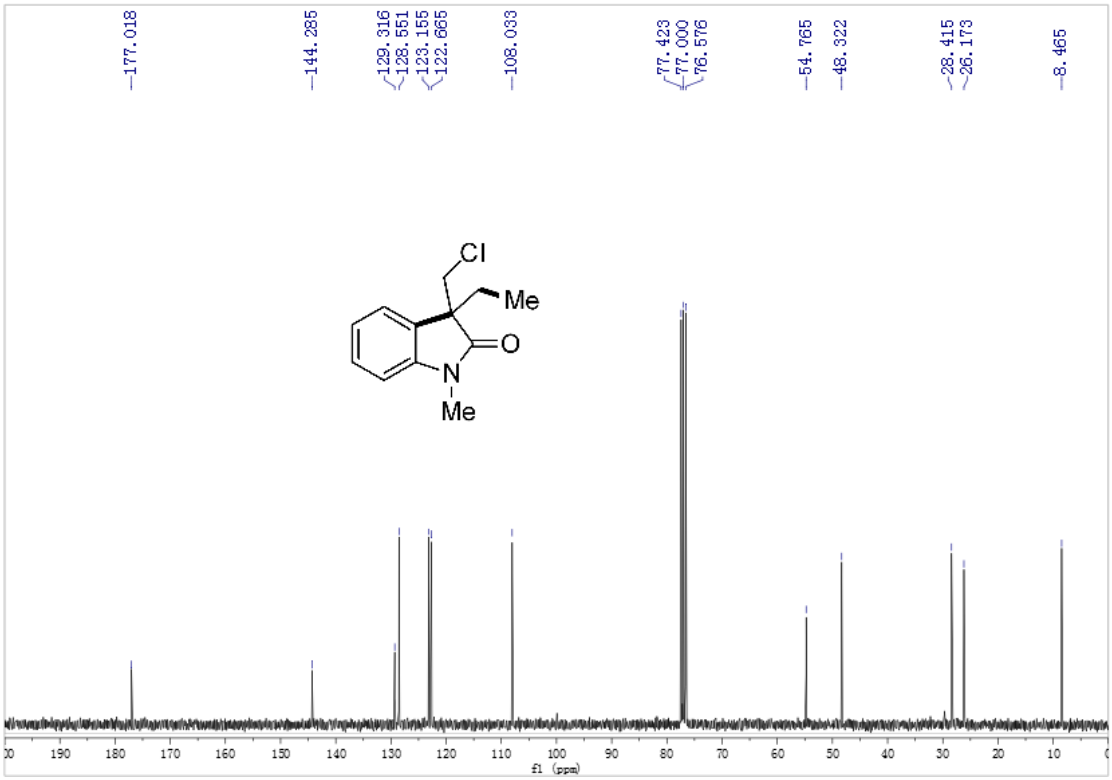
3-ethyl-3-(methoxymethyl)-1-methylindolin-2-one **3t**





3-(chloromethyl)-3-ethyl-1-methylindolin-2-one **3u**





3-ethyl-5-(4-fluorophenyl)-1,3-dimethylindolin-2-one **3w**