$B(C_6F_5)_3$-Catalyzed *β*-Functionalization of Pyrrolidines using Isatins via Borrowing Hydrogen: Divergent Access to Substituted Pyrrolidines and Pyrroles

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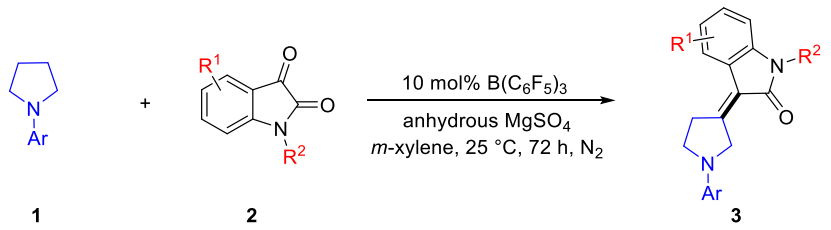
1. General Information

^{1}H and **^{13}C NMR** spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra (**HRMS**) were obtained on Agilent 1260-6224 LC-MS TOF using ESI (electrospray ionization). For thin layer chromatography (**TLC**), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with I_2. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

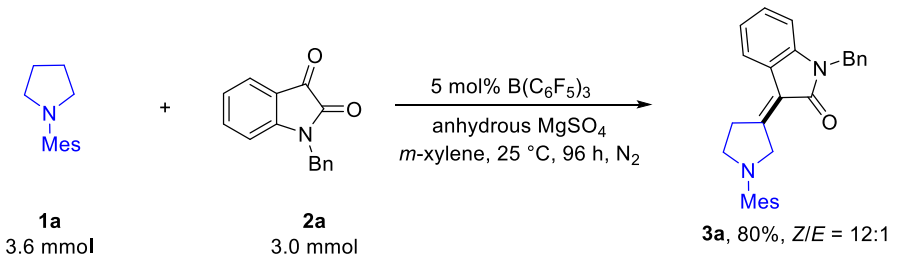
All reactions were carried out under nitrogen atmosphere. All commercially available reagents were used as received for the reactions without any purification. All solvents were dried on alumina columns using a solvent dispensing system. $B(C_6F_5)_3$ were purchased from TCI or Alfa. Tertiary amines[1] were synthesized following the reported procedure.

2. General procedure for the synthesis of 3-substituted pyrrolidines 3 and the reaction in large scale



To a Schlenk tube equipped with a dried stir bar was added $B(C_6F_5)_3$ (0.02 mmol), *N*-protected pyrrolidines **1** (0.24 mmol), isatins **2** (0.20 mmol), anhydrous $MgSO_4$ (50 mg) and *m*-xylene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 25 °C for 72 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:80) to afford the desired functionalized pyrrolidines **3**.

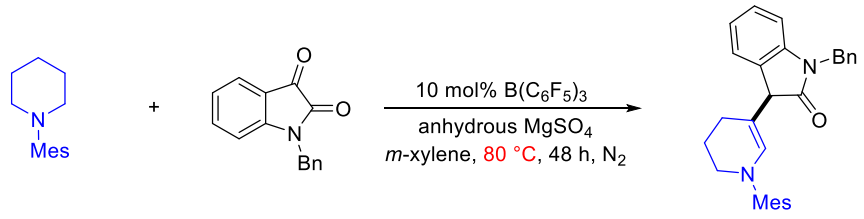
Reaction of 1a and 2a in a large scale



To a Schlenk tube equipped with a dried stir bar was added $B(C_6F_5)_3$ (0.15 mmol), *N*-protected pyrrolidine **1a** (3.6 mmol), isatin **2a** (3.0 mmol), anhydrous $MgSO_4$ (750 mg) and *m*-xylene (10.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 25 °C for 96 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:80) to afford **3a** (978.1 mg, 80% yield, *Z*/*E* = 12:1).

3. Procedure for the synthesis of 3-substituted tetrahydropyridine 5 and 3-substituted pyrrolidine 7

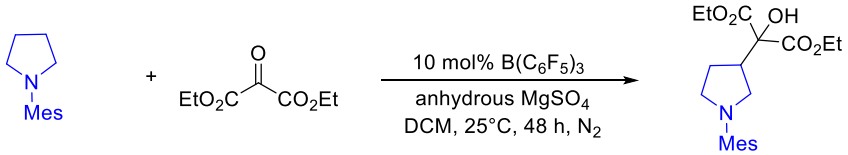
Procedure for the synthesis of 3-substituted tetrahydropyridine 5



4 **2a** **5**, 53%

To a Schlenk tube equipped with a dried stir bar was added $B(C_6F_5)_3$ (0.02 mmol), *N*-protected piperidine **4** (0.24 mmol), isatin **2a** (0.20 mmol), anhydrous $MgSO_4$ (50 mg) and *m*-xylene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 80 °C in oil bath for 48 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:80) to afford 3-substituted tetrahydropyridine **5** in 53% yield.

Procedure for the synthesis of 3-substituted pyrrolidine 7

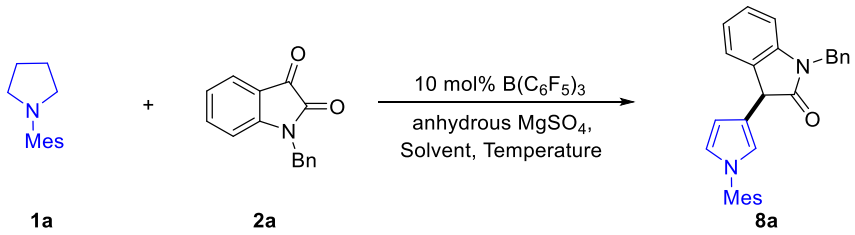


1a **6** **7**, 86%

To a Schlenk tube equipped with a dried stir bar was added $B(C_6F_5)_3$ (0.02 mmol), *N*-protected pyrrolidine **1a** (0.24 mmol), diethyl ketomalonate **6** (0.20 mmol), anhydrous $MgSO_4$ (50 mg) and DCM (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 25 °C for 48 hours. The crude reaction mixture was directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:30) to afford functionalized pyrrolidine **7** in 86% yield. This result indicated that the nucleophilic addition to enamine **II** follow by protonation to form intermediate **IV** in proposed catalytic cycle was reasonable. It should be noticed that the reaction without $MgSO_4$ as additive gave similar yield of **7**.

4. Optimization and general procedure for the synthesis of 3-substituted pyrroles 8

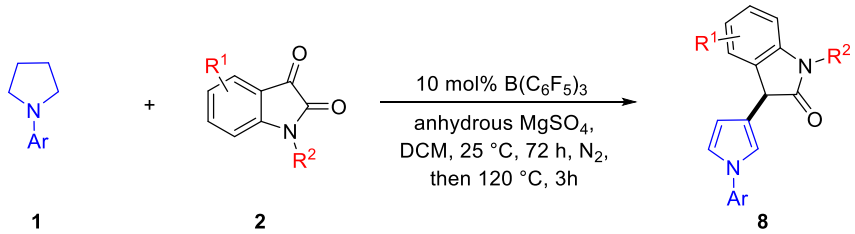
Table S1. Optimization for C(3)-substituted pyrrole 8a synthesis



Entry	Solvent	Temperature (°C)	Yield (%)
1	*m*-xylene	120	49
2	DCM	120	50
3	Tol	25 then 120	47
4	1,4-diox	25 then 120	49
5	THF	25 then 120	42
6	MeCN	25 then 120	27
7	*m*-xylene	25 then 120	73
8	DCM	25 then 120	87

The reactions were carried out by stirring **1a** (0.24 mmol), **2a** (0.2 mmol), $B(C_6F_5)_3$ (0.02 mmol) and anhydrous $MgSO_4$ (50 mg) in 1 mL of solvent at 120 °C for 24 hours under N_2, or 25 °C for 72 hours follow by 120 °C for 3 hours under N_2.

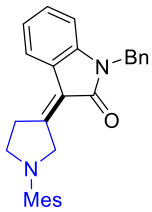
General procedure for the synthesis of C(3)-substituted pyrroles 8



To a Schlenk tube equipped with a dried stir bar was added $B(C_6F_5)_3$ (0.02 mmol), *N*-protected pyrrolidines **1** (0.24 mmol), isatins **2** (0.20 mmol), anhydrous $MgSO_4$ (50 mg) and *m*-xylene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 25 °C for 72 hours then 120 °C in oil bath for 3 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:80) to afford the desired functionalized pyrroles **8**.

5. Analytical data for products 3, 5, 7, 8

(*Z*)-1-benzyl-3-(1-mesitylpyrrolidin-3-ylidene)indolin-2-one (3a):



3a

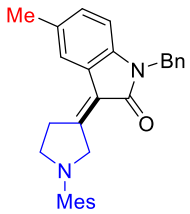
Light yellow solid, 70.4 mg, 86% yield, *Z*/*E* = 12:1, m.p.: 120~121 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.36–7.33 (m, 4H), 7.29–7.26 (m, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.90 (s, 2H), 6.78 (d, *J* = 7.7 Hz, 1H), 5.01 (s, 2H), 4.69 (s, 2H), 3.56 (t, *J*= 6.5 Hz, 2H), 3.28 (t, *J* = 5.9 Hz, 2H), 2.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 159.7, 142.0, 140.8, 137.9, 136.4, 135.2, 129.5, 128.7, 127.8, 127.3, 123.1, 122.5, 121.8, 118.8, 108.8, 56.0, 49.3, 43.3, 34.0, 20.8, 18.9.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{29}N_2O, M+H]^+$: 409.2274; Found: 409.2275.

(*Z*)-1-benzyl-3-(1-mesitylpyrrolidin-3-ylidene)-5-methylindolin-2-one (3b):



3b

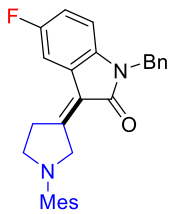
Yellow oil, 70 mg, 83% yield, *Z*/*E* = 9:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.27 (m, 5H), 7.25–7.21 (m, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.87 (s, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.95 (s, 2H), 4.66 (s, 2H), 3.53 (t, *J* = 6.6 Hz, 2H), 3.21 (t, *J* = 6.5 Hz, 2H), 2.36 (s, 3H), 2.28 (s, 6H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 159.3, 140.8, 139.8, 137.9, 136.4, 135.1, 131.1, 129.5, 128.6, 128.6, 128.1, 127.3, 127.2, 123.3, 123.2, 108.5, 55.9, 49.1, 43.3, 34.0, 21.3, 20.8, 18.9.

HRMS (ESI): m/z Calcd. for $[C_{29}H_{31}N_2O, M+H]^+$: 423.2431; Found: 423.2439.

(*Z*)-1-benzyl-5-fluoro-3-(1-mesitylpyrrolidin-3-ylidene)indolin-2-one (3c):



3c

Yellow solid, 52.0 mg, 61% yield, *Z*/*E* = 19:1, m.p.: 220~221 °C.

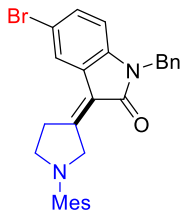
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.29 (m, 1H), 7.28–7.24 (m, 4H), 7.20 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.89–6.83 (m, 3H), 6.62 (dd, *J* = 8.6, 4.3 Hz, 1H), 4.95 (s, 2H), 4.66 (s, 2H), 3.53 (t, *J* = 6.6 Hz, 2H), 3.21 (t, *J* = 6.5 Hz, 2H), 2.27 (s, 6H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 161.5, 158.9 (d, *J* = 236.7 Hz), 140.5, 137.9, 136.1, 135.3, 129.5, 128.7, 127.5, 127.2, 124.1 (d, *J* = 8.8 Hz), 118.6 (d, *J* = 2.5 Hz), 113.8 (d, *J* = 23.5 Hz), 110.1 (d, *J* = 25.6 Hz), 109.1 (d, *J* = 8.2 Hz), 56.1, 49.2, 43.42, 33.9, 20.8, 18.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -123.22.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{28}FN_2O, M+H]^+$: 427.2180; Found: 427.2180.

(*Z*)-1-benzyl-5-bromo-3-(1-mesitylpyrrolidin-3-ylidene)indolin-2-one (3d):



3d

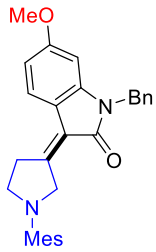
Yellow solid, 57.3 mg, 59% yield, *Z*/*E* > 20:1, m.p.: 150~151 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 1.5 Hz, 1H), 7.35–7.27 (m, 6H), 6.90 (s, 2H), 6.63 (d, *J* = 8.3 Hz, 1H), 4.98 (s, 2H), 4.70 (s, 2H), 3.57 (t, *J* = 6.5 Hz, 2H), 3.27 (t, *J* = 6.5 Hz, 2H), 2.31 (s, 6H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 159.8, 156.4, 143.4, 140.9, 137.9, 136.3, 135.1, 129.5, 128.7, 127.4, 127.2, 123.3, 118.3, 116.3, 105.8, 96.7, 55.7, 49.3, 43.3, 33.8, 20.8, 18.9.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{28}BrN_2O, M+H]^+$: 487.1380; Found: 487.1371.

(*Z*)-1-benzyl-3-(1-mesitylpyrrolidin-3-ylidene)-6-methoxyindolin-2-one (3e):



3e

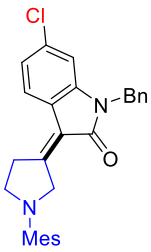
Yellow solid, 57.8 mg, 66% yield, *Z*/*E* = 8:1, m.p.: 149~151 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.4 Hz, 1H), 7.32–7.29 (m, 4H), 7.25–7.20 (m, 1H), 6.86 (s, 2H), 6.56 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.33 (d, *J* = 1.9 Hz, 1H), 4.94 (s, 2H), 4.61 (s, 2H), 3.75 (s, 3H), 3.51 (t, *J* = 6.6 Hz, 2H), 3.18 (t, *J* = 6.5 Hz, 2H), 2.28 (s, 3H), 2.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 161.9, 140.8, 140.5, 137.9, 135.9, 135.3, 130.26, 129.5, 128.7, 127.6, 127.2, 125.4, 124.9, 117.9, 114.5, 110.1, 56.1, 49.2, 43.35, 34.2, 20.8, 18.9.

HRMS (ESI): m/z Calcd. for $[C_{29}H_{30}N_2O_2Na, M+Na]^+$: 461.2199; Found: 461.2199.

(*Z*)-1-benzyl-6-chloro-3-(1-mesitylpyrrolidin-3-ylidene)indolin-2-one (3f):



3f

Yellow solid, 57.5 mg, 65% yield, *Z*/*E* = 5:1, m.p.: 168~170 °C.

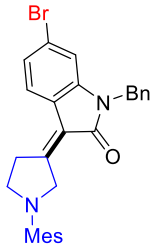
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.2 Hz, 1H), 7.30–7.23 (m, 5H), 7.01 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.85 (s, 2H), 6.72 (d, *J* = 1.7 Hz, 1H), 4.92 (s,

2H), 4.62 (s, 2H), 3.51 (t, J = 6.6 Hz, 2H), 3.19 (t, J = 6.5 Hz, 2H), 2.26 (s, 3H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 160.6, 142.9, 140.5, 137.9, 135.8, 135.3, 133.5, 129.5, 128.8, 127.6, 127.2, 123.2, 121.7, 121.6, 117.9, 109.2, 56.1, 49.2, 43.4, 34.1, 20.8, 18.9.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{28}ClN_2O, M+H]^+$: 443.1885; Found: 443.1889.

(*Z*)-1-benzyl-6-bromo-3-(1-mesitylpyrrolidin-3-ylidene)indolin-2-one (3g):



3g

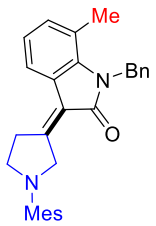
Yellow solid, 52.5 mg, 54% yield, Z/E > 20:1, m.p.: 169~170 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.2 (m, 6H), 7.20 (dd, J = 8.1, 1.7 Hz, 1H), 6.90 (d, J = 1.5 Hz, 1H), 6.88 (s, 2H), 4.95 (s, 2H), 4.64 (s, 2H), 3.54 (t, J = 6.6 Hz, 2H), 3.21 (t, J = 6.6 Hz, 2H), 2.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 160.9, 143.1, 140.5, 137.9, 135.8, 135.3, 129.5, 128.8, 127.6, 127.2, 124.7, 123.5, 122.0, 121.4, 118.0, 111.9, 56.1, 49.2, 43.4, 34.1, 20.8, 18.9.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{28}BrN_2O, M+H]^+$: 487.1380; Found: 487.1380.

(*Z*)-1-benzyl-3-(1-mesitylpyrrolidin-3-ylidene)-7-methylindolin-2-one (3h):



3h

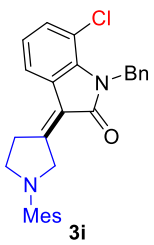
Yellow solid, 70.0 mg, 83% yield, Z/E = 9:1, m.p.: 141~142 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 7.3 Hz, 1H), 7.26–7.21 (m, 2H), 7.16 (d, J = 6.8 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 6.93–6.86 (m, 2H), 6.80 (s, 2H), 5.20 (s, 2H), 4.61 (s, 2H), 3.48 (t, J = 6.6 Hz, 2H), 3.20 (t, J = 6.6 Hz, 2H), 2.24 (s, 3H), 2.22 (s, 6H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 159.5, 140.8, 140.1, 138.3, 137.9, 135.1, 131.8, 129.5, 128.7, 126.9, 125.6, 123.8, 121.8, 120.7, 119.5, 118.6, 56.3, 49.4, 44.6, 34.1, 26.5, 20.7, 18.9.

HRMS (ESI): m/z Calcd. for $[C_{29}H_{31}N_2O, M+H]^+$: 423.2431; Found: 423.2438.

(*Z*)-1-benzyl-7-chloro-3-(1-mesitylpyrrolidin-3-ylidene)indolin-2-one (3i):



3i

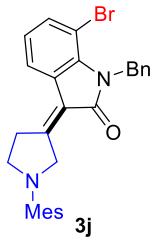
Colorless oil, 54.4mg, 63% yield, Z/E > 20:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 8.2 Hz, 1H), 7.25–7.15 (m, 5H), 6.95 (dd, J = 8.1, 1.8 Hz, 1H), 6.79 (s, 2H), 6.66 (d, J = 1.8 Hz, 1H), 4.86 (s, 2H), 4.56 (s, 2H), 3.45 (t, J = 6.6 Hz, 2H), 3.13 (t, J = 6.5 Hz, 2H), 2.20 (s, 6H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 160.6, 143.0, 140.6, 137.9, 135.8, 135.3, 133.5, 129.5, 128.8, 127.6, 127.2, 123.2, 121.7, 121.6, 118.0, 109.2, 56.1, 49.2, 43.4, 34.1, 20.8, 18.9.

HRMS (ESI): m/z Calcd. for $[C_{30}H_{48}ClN_2O, M+H]^+$: 433.1885; Found: 433.1888.

(*Z*)-1-benzyl-7-bromo-3-(1-mesitylpyrrolidin-3-ylidene)indolin-2-one (3j):



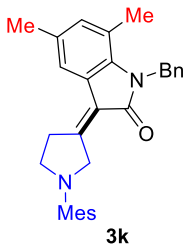
Yellow solid, 63.2 mg, 65% yield. *Z*/*E* > 20:1, m.p.: 125~126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.17–7.12 (m, 3H), 6.87 (t, *J* = 7.9 Hz, 1H), 6.80 (s, 2H), 5.42 (s, 2H), 4.60 (s, 2H), 3.47 (t, *J* = 6.6 Hz, 2H), 3.18 (t, *J* = 6.5 Hz, 2H), 2.20 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 161.7, 140.5, 139.3, 138.1, 137.8, 135.3, 133.6, 129.5, 129.2, 128.4, 126.8, 126.3, 122.9, 121.6, 117.8, 108.1, 102.5, 56.5, 49.3, 44.1, 34.3, 20.8, 18.9.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{28}BrN_2O, M+H]^+$: 487.1380; Found: 487.1377.

1-benzyl-3-(1-mesitylpyrrolidin-3-ylidene)-5,7-dimethylindolin-2-one (3k):



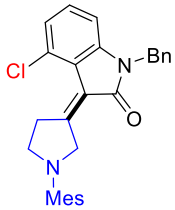
Yellow solid, 63.6 mg, 73% yield, *Z*/*E* = 4:1 in a mixture, m.p.: 146~148 °C.

Z isomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (t, *J* = 7.2 Hz, 2H), 7.24 (q, *J* = 3.8 Hz, 2H), 7.17 (t, *J* = 9.0 Hz, 2H), 6.89 (s, 2H), 6.80 (s, 1H), 5.26 (s, 2H), 4.68 (s, 2H), 3.56 (t, *J* = 6.4 Hz, 2H), 3.29 (t, *J* = 6.4 Hz, 2H), 2.36 (s, 3H), 2.34 (s, 3H), 2.30 (s, 6H), 2.28 (s, 3H). **^{13}C NMR** (100MHz, $CDCl_3$): δ 167.9, 159.2, 140.9, 138.4, 137.9, 135.1, 132.4, 131.1, 129.6, 129.4, 128.7, 126.9, 125.6, 123.9, 121.4, 119.2, 118.7, 56.2, 49.4, 44.6, 34.2, 21.0, 20.7, 18.9, 18.8.

E isomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34–7.29 (m, 2H), 7.26–7.22(m, 2H), 7.20 (d, *J* = 6.6 Hz, 2H), 6.96 (s, 2H), 6.77 (s, 1H), 5.30 (s, 2H), 4.49 (s, 2H), 3.64–3.48 (m, 4H), 2.34 (s, 6H), 2.33 (s, 3H), 2.28 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.4, 159.3, 140.9, 138.3, 137.9, 135.7, 132.4, 131.3, 129.6, 128.7, 126.9, 125.6, 123.7, 121.6, 119.1, 118.6, 56.7, 49.9, 44.6, 33.6, 20.9, 20.8, 18.8, 18.6.

HRMS (ESI): m/z Calcd. for $[C_{30}H_{33}N_2O, M+H]^+$: 437.2587; Found: 452.2587.

1-benzyl-4-chloro-3-(1-mesitylpyrrolidin-3-ylidene)indolin-2-one (3l):



3l

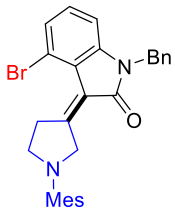
Colorless oil, 29.1mg, 33% yield. *Z/E* = 1.7:1 in a mixture.

Z isomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25–7.14 (m, 5H), 7.00–6.94 (m, 1H), 6.86 (dd, *J* = 8.2, 0.7 Hz, 1H), 6.70 (s, 2H), 6.50 (d, *J* = 7.7 Hz, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 4.68 (d, *J* = 15.6 Hz, 1H), 3.76 (dd, *J* = 15.9, 4.2 Hz, 1H), 3.60–3.38 (m, 1H), 3.30–3.02 (m, 2H), 2.85–2.67 (m, 2H), 2.12 (s, 3H), 2.08 (s, 6H). **^{13}C NMR** (100 MHz, d_6-Acetone): δ 176.0, 146.3, 143.2, 138.6, 137.6, 135.4, 131.0, 130.6, 130.2, 129.7, 128.6, 127.3, 123.8, 108.7, 52.6, 51.0, 47.2, 40.1, 21.1, 18.9.

E isomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.26–7.14 (m, 5H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 8.2, 0.7 Hz, 1H), 6.77 (s, 2H), 6.55 (d, *J* = 7.7 Hz, 1H), 4.94 (d, *J* = 15.5 Hz, 1H), 4.73 (d, *J* = 15.5 Hz, 1H), 3.89–3.83 (m, 1H), 3.45–3.35 (m, 1H), 3.30–3.03 (m, 3H), 2.84–2.67 (m, 1H), 2.19 (s, 6H), 2.17 (s, 3H). **^{13}C NMR** (100 MHz, d_6-Acetone): δ 176.2, 146.5, 143.4, 138.8, 137.7, 135.3, 131.0, 130.6, 130.3, 129.8, 128.7, 127.3, 123.9, 108.8, 52.7, 51.0, 47.0, 40.1, 21.1, 19.1.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{28}ClN_2O, M+H]^+$: 443.1885; Found: 443.1883.

1-benzyl-4-bromo-3-(1-mesitylpyrrolidin-3-ylidene)indolin-2-one (3m):



3m

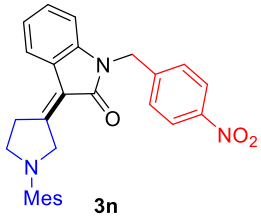
Colorless oil, 32.3mg, 33% yield. *Z/E* = 1.7:1 in a mixture.

Z isomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34–7.22 (m, 5H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.78 (s, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.75 (d, *J* = 15.6 Hz, 1H), 3.77 (dd, *J* = 18.7, 4.0 Hz, 2H), 3.39–3.09 (m, 2H), 2.97–2.69 (m, 2H), 2.20 (s, 3H), 2.16 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.4, 144.8, 142.1, 138.0, 135.6, 134.7, 129.3, 129.2, 128.8, 128.3, 127.7, 127.3, 126.1, 118.8, 107.7, 51.5, 47.5, 43.8, 38.7, 20.7, 18.5.

E isomer: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34–7.22 (m, 5H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.85 (s, 2H), 6.67 (d, *J* = 7.8 Hz, 1H), 5.02 (d, *J* = 15.8 Hz, 1H), 4.80 (d, *J* = 15.8 Hz, 1H), 3.99 (t, *J* = 8.7 Hz, 1H), 3.74–3.66 (m, 1H), 3.39–3.09(m, 3H), 2.97–2.69 (m, 1H), 2.28 (s, 6H), 2.25 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.5, 144.9, 142.3, 138.2, 135.6, 134.6, 129.4, 129.2, 128.8, 128.3, 127.7, 127.3, 126.2, 118.9, 107.8, 51.8, 47.4, 43.8, 38.8, 20.8, 18.7.

HRMS (ESI): m/z Calcd. for [$C_{28}H_{28}BrN_2O$, M+H]$^+$: 487.1380; Found: 487.1374.

(*Z*)-3-(1-mesitylpyrrolidin-3-ylidene)-1-(4-nitrobenzyl)indolin-2-one (3n):



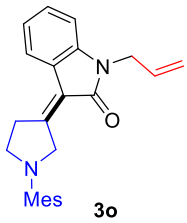
Yellow solid, 65.2 mg, 72% yield, *Z*/*E* > 20:1, m.p.: 163~164 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.89 (s, 2H), 6.68 (d, *J* = 7.7 Hz, 1H), 5.08 (s, 2H), 4.68 (s, 2H), 3.56 (t, *J* = 6.6 Hz, 2H), 3.29 (t, *J* = 6.5 Hz, 2H), 2.30 (s, 6H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 160.8, 147.3, 143.9, 141.2, 140.5, 137.8, 135.3, 129.5, 127.88, 128.9, 123.9, 123.1, 122.8, 122.3, 118.3, 108.3, 56.0, 49.2, 42.7, 34.1, 20.7, 18.9.

HRMS (ESI): m/z Calcd. for [$C_{28}H_{27}N_3O_3$, M+H]$^+$: 454.2125; Found: 454.2128.

(*Z*)-1-allyl-3-(1-mesitylpyrrolidin-3-ylidene)indolin-2-one (3o):



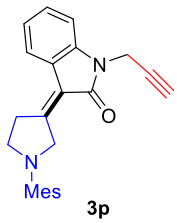
Yellow oil, 60.1 mg, 84% yield. *Z*/*E* = 5:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.5 Hz, 1H), 7.33–7.28 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.00–6.86 (m, 3H), 5.98–5.87 (m, 1H), 5.31–5.25 (m, 2H), 4.69 (s, 2H), 4.50–4.45 (m, 2H), 3.58 (t, *J* = 6.5 Hz, 2H), 3.29 (t, *J* = 6.5 Hz, 2H), 2.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 159.5, 142.0, 140.7, 137.9, 135.2, 131.9, 129.4, 127.7, 123.0, 122.4, 121.7, 118.8, 117.1, 108.6, 55.9, 49.3, 41.9, 33.9, 20.8, 18.9.

HRMS (ESI): m/z Calcd. for [$C_{24}H_{27}N_2O$, M+H]$^+$: 359.2118; Found: 359.2118.

(*Z*)-3-(1-mesitylpyrrolidin-3-ylidene)-1-(prop-2-yn-1-yl)indolin-2-one (3p):



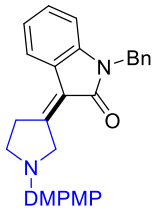
Yellow solid, 53.4 mg, 75% yield, *Z*/*E* = 10:1, m.p.: 110~111 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.17–7.09 (m, 2H), 6.89 (s, 2H), 4.64 (s, 2H), 4.59 (d, *J* = 2.5 Hz, 2H), 3.53 (t, *J* = 6.5 Hz, 2H), 3.25 (t, *J* = 6.6 Hz, 2H), 2.29 (s, 9H), 2.23 (t, *J* = 2.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 160.2, 140.9, 140.6, 137.9, 135.2, 129.5, 127.8, 123.0, 122.5, 122.2, 118.5, 108.7, 77.4, 71.8, 55.9, 49.2, 34.0, 28.7, 20.8, 18.9.

HRMS (ESI): m/z Calcd. for [$C_{24}H_{25}N_2O$, M+H]$^+$: 357.1961; Found: 357.1963.

(*Z*)-1-benzyl-3-(1-(4-methoxy-2,6-dimethylphenyl)pyrrolidin-3-ylidene)indolin-2-one



3q

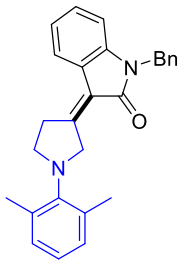
(3q): Yellow solid, 74.0 mg, 87% yield, *Z*/*E* = 8:1, m.p.: 140~141 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.5 Hz, 1H), 7.31–7.28 (m, 4H), 7.25–7.22 (m, 1H), 7.18–7.14 (m, 1H), 7.07–7.01 (m, 1H), 6.75–6.72 (m, 1H), 6.59 (s, 2H), 4.97 (s, 2H), 4.64 (s, 2H), 3.76 (s, 3H), 3.50 (t, *J* = 6.6 Hz, 2H), 3.24 (t, *J* = 6.5 Hz, 2H), 2.29 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 159.8, 156.9, 141.9, 139.5, 136.4, 128.6, 127.8, 127.4, 137.2, 123.1, 122.5, 121.8, 118.8, 113.7, 112.9, 108.8, 56.1, 55.2, 49.4, 43.3, 34.0, 19.2.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{29}N_2O_2, M+H]^+$: 425.2224; Found: 425.2224.

(*Z*)-1-benzyl-3-(1-(2,6-dimethylphenyl)pyrrolidin-3-ylidene)indolin-2-one (3r):



3r

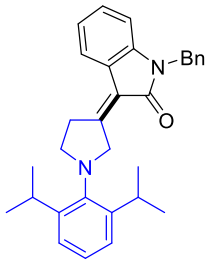
Yellow solid, 54.4 mg, 69% yield, *Z*/*E* = 12:1, m.p.:103~104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.24–7.17 (m, 5H), 7.10 (q, *J* = 7.5 Hz, 1H), 7.02–6.95 (m, 4H), 6.69 (d, *J* = 7.8 Hz, 1H), 4.91 (s, 2H), 4.62 (s, 2H), 3.49 (t, *J* = 6.6 Hz, 2H), 3.19 (t, *J* = 6.5 Hz, 2H), 2.26 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 159.5, 143.4, 141.9, 138.1, 136.3, 128.8, 128.6, 127.8, 127.4, 127.2, 125.7, 123.1, 122.5, 121.8, 118.8, 108.8, 55.9, 49.1, 43.3, 34.0, 19.1.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{27}N_2O, M+H]^+$: 395.2118; Found: 395.2114.

(*Z*)-1-benzyl-3-(1-(2,6-diisopropylphenyl)pyrrolidin-3-ylidene)indolin-2-one (3s):



3s

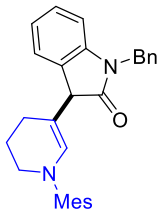
Yellow solid, 70.4 mg, 78% yield, *Z*/*E* = 17:1, m.p.: 143~144 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.5 Hz, 1H), 7.39–7.33 (m, 4H), 7.32–7.28 (m, 2H), 7.24–7.18 (m, 3H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.04 (s, 2H), 4.77 (s, 2H), 3.66–3.62 (m, 2H), 3.39–3.35 (m, 4H), 1.30 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 159.0, 149.5, 141.7, 140.5, 136.0, 128.3, 127.5, 127.1, 126.9, 126.6, 123.7, 122.8, 122.2, 121.5, 118.6, 108.5, 58.1, 51.4, 43.0, 33.5, 28.0, 24.1.

HRMS(ESI): m/z Calcd. for $[C_{31}H_{35}N_2O, M+H]^+$: 451.2744; Found: 451.2748.

1-benzyl-3-(1-mesityl-1,4,5,6-tetrahydropyridin-3-yl)indolin-2-one (5):



5

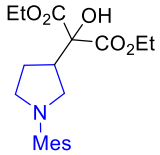
Colorless oil, 44.7 mg, 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 4H), 7.18 – 7.12 (m, 2H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.79 (s, 2H), 6.60 (d, *J* = 7.7 Hz, 1H), 5.93 (s, 1H), 4.93 (d, *J* = 15.6 Hz, 1H), 4.76 (d, *J* = 15.6 Hz, 1H), 3.90 (s, 1H), 3.23 – 3.07 (m, 2H), 2.20 (s, 3H), 2.18 (s, 3H), 2.17 (s, 3H), 1.95 – 1.79 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.7, 143.5, 143.1, 137.0, 136.6, 136.2, 135.7, 134.0, 129.3, 129.2, 129.1, 128.7, 127.7, 127.4, 127.2, 124.3, 122.3, 108.7, 99.3, 52.3, 47.1, 43.7, 22.7, 22.1, 20.8, 18.3, 18.2.

HRMS (ESI): m/z Calcd. for $[C_{29}H_{31}N_2O, M+H]^+$: 423.2431; Found: 423.2431.

diethyl 2-hydroxy-2-(1-mesitylpyrrolidin-3-yl)malonate (7):



7

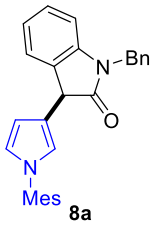
Colorless oil, 62.4 mg, 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 4.38 – 4.19 (m, 5H), 3.34 – 3.16 (m, 5H), 2.26 (s, 6H), 2.25 (s, 3H), 2.04 (dt, *J* = 12.5, 5.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 170.1, 141.7, 137.8, 134.9, 129.4, 79.9, 62.5, 62.4, 50.5, 49.9, 43.1, 26.5, 20.7, 18.7, 14.0, 13.9.

HRMS (ESI): m/z Calcd. for $[C_{20}H_{30}NO_5, M+H]^+$: 364.2118; Found: 364.2117.

1-benzyl-3-(1-mesityl-1*H*-pyrrol-3-yl)indolin-2-one (8a):



8a

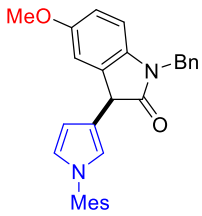
Yellow solid, 69.7 mg, 87% yield, m.p.: 140~141 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.14 (m, 6H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.83 (s, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 12.8 Hz, 2H), 6.24 (s, 1H), 4.92 (d, *J* = 15.7 Hz, 1H), 4.80 (d, *J* = 15.7 Hz, 1H), 4.65 (s, 1H), 2.22 (s, 3H), 1.95 (s, 3H), 1.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 143.2, 137.6, 137.2, 136.0, 135.8, 135.7, 129.5, 128.6, 128.5, 128.5, 127.7, 127.4, 127.1, 124.7, 122.3, 122.2, 119.9, 118.5, 108.9, 108.1, 44.9, 43.6, 20.9, 17.3, 17.2.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{27}N_2O, M+H]^+$: 407.2118; Found: 407.2115.

1-benzyl-3-(1-mesityl-1*H*-pyrrol-3-yl)-5-methoxyindolin-2-one (8b):



8b

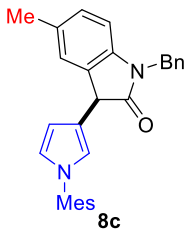
Yellow oil, 71.5 mg, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.17 (m, 5H), 6.92 (d, 1H), 6.87 (s, 2H), 6.65 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 6.53 (t, *J* = 2.4 Hz, 1H), 6.51–6.50 (m, 1H), 6.28–6.27 (m, 1H), 4.95 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.67 (s, 1H), 3.69 (s, 3H), 2.27 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 155.8, 137.6, 137.2, 136.7, 136.1, 135.8, 135.7, 130.9, 128.6, 128.5, 128.5, 127.4, 127.1, 122.3, 119.9, 118.5, 112.3, 111.9, 109.1, 108.1, 55.6, 45.4, 43.7, 20.9, 17.3, 17.2.

HRMS (ESI): m/z Calcd. for $[C_{29}H_{28}N_2O_2Na, M+Na]^+$: 459.2043; Found: 459.2047.

1-benzyl-3-(1-mesityl-1*H*-pyrrol-3-yl)-5-methylindolin-2-one (8c):



8c

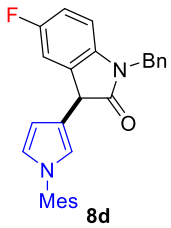
Yellow solid, 67.8 mg, 85% yield, m.p.: 150~151 °C.

^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.37–7.35 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.18 (s, 1H), 6.99–6.96 (m, 3H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.62 (t, *J* = 2.2 Hz, 1H), 6.59 (t, *J* = 2.4 Hz, 1H), 6.24 (d, *J* = 2.3 Hz, 1H), 5.01 (d, *J* = 15.7 Hz, 1H), 4.88 (d, *J* = 15.7 Hz, 1H), 4.69 (s, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 140.9, 137.7, 137.2, 136.2, 135.9, 135.8, 131.8, 129.6, 128.6, 128.6, 128.5, 128.0, 127.4, 127.2, 125.6, 122.2, 120.0, 118.7, 108.6, 108.1, 45.1, 43.7, 21.1, 20.9, 17.3, 17.3.

HRMS (ESI): m/z Calcd. for $[C_{29}H_{28}N_2ONa, M+Na]^+$: 443.2094; Found: 443.2095.

1-benzyl-5-fluoro-3-(1-mesityl-1*H*-pyrrol-3-yl)indolin-2-one (8d):



8d

Yellow solid, 69.6 mg, 82% yield, m.p.: 250~251 °C.

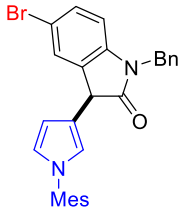
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.15 (m, 5H), 7.01 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.85 (s, 2H), 6.79 (td, *J* = 9.0, 2.6 Hz, 1H), 6.56 (dd, *J* = 8.6, 4.2 Hz, 1H), 6.51 (t, *J* = 2.4 Hz, 1H), 6.48 (t, *J* = 1.9 Hz, 1H), 6.22–6.21(m, 1H), 4.93 (d, *J* = 15.7 Hz, 1H), 4.81 (d, *J* = 15.7 Hz, 1H), 4.66 (s, 1H), 2.25 (s, 3H), 1.97 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 159.1 (d, *J* = 238.6 Hz), 139.1 (d, *J* = 1.5 Hz), 137.7, 137.1, 135.8, 135.7, 135.7, 131.3 (d, *J* = 8.5 Hz), 128.7, 128.6, 128.5, 127.54, 127.1, 122.4, 119.9, 117.9, 114.0 (d, *J* = 23.5 Hz), 112.8 (d, *J* = 24.6 Hz), 109.3 (d, *J* = 8.1 Hz), 108.0, 45.3, 43.8, 20.9, 17.3, 17.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -120.83.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{26}FN_2O, M+H]^+$: 425.2024; Found: 443.2024.

1-benzyl-5-bromo-3-(1-mesityl-1*H*-pyrrol-3-yl)indolin-2-one (8e):



8e

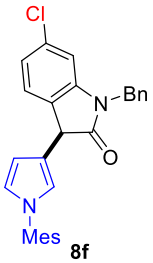
Yellow solid, 53.3 mg, 55% yield, m.p.: 170~171 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, *J* = 1.5 Hz, 1H), 7.24–7.18 (m, 6H), 6.87 (s, 2H), 6.55–6.52 (m, 2H), 6.49 (t, *J* = 1.9 Hz, 1H), 6.21 (t, *J* = 1.2 Hz, 1H), 4.94 (d, *J* = 15.7 Hz, 1H), 4.81 (d, *J* = 15.7 Hz, 1H), 4.67 (s, 1H), 2.26 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 142.3, 137.8, 137.1, 135.8, 135.7, 135.6, 131.7, 130.7, 128.8, 128.6, 128.5, 128.0, 127.6, 127.1, 122.5, 120.0, 117.7, 115.1, 110.4, 108.0, 45.0, 43.8, 20.9, 17.3, 17.2.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{25}N_2OBrNa, M+Na]^+$: 507.1042; Found: 507.1043.

1-benzyl-6-chloro-3-(1-mesityl-1*H*-pyrrol-3-yl)indolin-2-one (8f):



8f

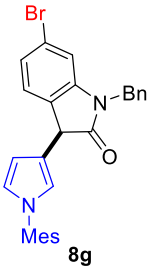
Yellow solid, 62.5mg, 71% yield. m.p.: 170~171 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.29 (m, 6H), 7.07 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.99 (s, 2H), 6.81 (d, *J* = 1.8 Hz, 1H), 6.64 (t, *J* = 2.4 Hz, 1H), 6.59 (t, *J* = 2.1 Hz, 1H), 6.34 (t, *J* = 2.0 Hz, 1H), 5.05 (d, *J* = 15.7 Hz, 1H), 4.93 (d, *J* = 15.7 Hz, 1H), 4.77 (s, 1H), 2.39 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 144.5, 137.8, 137.1, 135.8, 135.7, 133.5, 128.8, 128.6, 128.5, 128.0, 127.7, 127.2, 126.9, 125.7, 122.5, 122.3, 119.9, 118.0, 109.5, 108.0, 44.6, 43.8, 20.9, 17.3, 17.2.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{26}N_2OCl, M+H]^+$: 441.1728; Found: 441.1726.

1-benzyl-6-bromo-3-(1-mesityl-1*H*-pyrrol-3-yl)indolin-2-one (8g):



8g

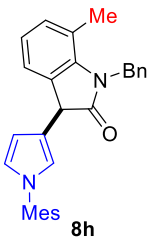
Yellow oil, 55.2 mg, 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.27 (m, 5H), 7.18 (s, 1H), 7.17 (d, *J* = 1.4 Hz, 1H), 6.92 (s, 2H), 6.88 (s, 1H), 6.57 (t, *J* = 2.2 Hz, 1H), 6.52–6.51 (m, 1H), 6.28–6.26 (m, 1H), 4.98 (d, *J* = 15.7 Hz, 1H), 4.86 (d, *J* = 15.7 Hz, 1H), 4.67 (s, 1H), 2.32 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6, 144.7, 137.8, 137.1, 135.8, 135.7, 135.5, 129.3, 128.8, 128.6, 128.5, 127.7, 127.1, 126.1, 125.3, 122.4, 121.3, 119.9, 117.9, 112.2, 108.0, 44.6, 43.7, 20.9, 17.3, 17.2.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{26}N_2OBr, M+H]^+$: 485.1223; Found: 485.1228.

1-benzyl-3-(1-mesityl-1*H*-pyrrol-3-yl)-7-methylindolin-2-one (8h):



8h

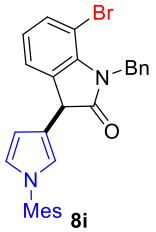
Yellow oil, 70.4 mg, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.16 (m, 4H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.91–6.87 (m, 4H), 6.54 (t, *J* = 2.4 Hz, 1H), 6.50 (t, *J* = 2.0 Hz, 1H), 6.31 (t, *J* = 2.0 Hz, 1H), 5.29 (d, *J* = 16.8 Hz, 1H), 5.11 (d, *J* = 16.8 Hz, 1H), 4.70 (s, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.8, 141.3, 137.9, 137.6, 137.2, 135.8, 135.7, 131.7, 130.2, 128.7, 128.5, 128.5, 127.0, 125.6, 122.9, 122.4, 122.2, 119.9, 119.6, 119.0, 108.2, 44.9, 44.6, 20.9, 18.8, 17.3, 17.2.

HRMS (ESI): m/z Calcd. for [$C_{29}H_{29}N_2O$, M+H]$^+$: 421.2274; Found: 421.2276.

1-benzyl-7-bromo-3-(1-mesityl-1H-pyrrol-3-yl)indolin-2-one (8i):



8i

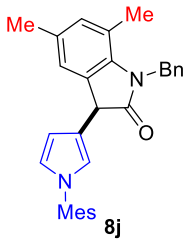
Yellow oil, 84.2 mg, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.2 Hz, 1H), 7.20–7.14 (m, 3H), 7.12–7.09 (m, 3H), 6.81–6.78 (m, 3H), 6.47–6.46 (m, 1H), 6.42–6.41 (m, 1H), 6.18 (dt, *J* = 2.6, 1.3 Hz, 1H), 5.39 (d, *J* = 16.4 Hz, 1H), 5.30 (d, *J* = 16.4 Hz, 1H), 4.64 (s, 1H), 2.21 (s, 3H), 1.92 (s, 3H), 1.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4, 140.7, 137.8, 137.6, 137.1, 135.8, 135.7, 133.7, 132.8, 128.6, 128.5, 128.4, 126.9, 126.3, 124.0, 123.7, 122.5, 120.0, 118.2, 108.1, 102.3, 44.8, 44.4, 20.1, 17.30, 17.2.

HRMS (ESI): m/z Calcd. for [$C_{28}H_{26}N_2OBr$, M+Na]$^+$: 507.1042; Found: 507.1043.

1-benzyl-3-(1-mesityl-1*H*-pyrrol-3-yl)-5,7-dimethylindolin-2-one (8j):



8j

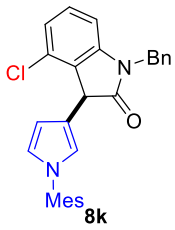
Yellow oil, 68.7 mg, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.24(m, 2H), 7.22–7.18 (m, 1H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.03 (s, 1H), 6.91 (s, 2H), 6.74 (s, 1H), 6.57 (t, *J* = 2.4 Hz, 1H), 6.55–6.54 (m, 1H), 6.33 (dd, *J* = 2.7, 1.8 Hz, 1H), 5.29 (d, *J* = 16.8 Hz, 1H), 5.12 (d, *J* = 16.8 Hz, 1H), 4.70 (s, 1H), 2.31 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.8, 138.9, 138.0, 137.6, 137.3, 135.9, 135.8, 132.1, 131.8, 130.33, 128.7, 128.6, 128.5, 126.9, 125.6, 123.6, 122.2, 120.0, 119.3, 119.1, 108.2, 44.9, 44.7, 20.9, 20.8, 18.6, 17.4, 17.3.

HRMS (ESI): m/z Calcd. for [$C_{30}H_{31}N_2O$, M+H]$^+$: 435.2431; Found: 435.2431.

1-benzyl-4-chloro-3-(1-mesityl-1*H*-pyrrol-3-yl)indolin-2-one (8k):



8k

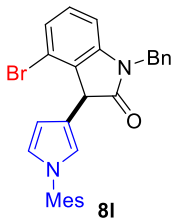
Colorless oil, 46.6 mg, 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.16 (m, 5H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 2H), 6.57 (d, *J* = 7.7 Hz, 1H), 6.49 (t, *J* = 2.5 Hz, 1H), 6.41 (t, *J* = 1.9 Hz, 1H), 6.18–6.17 (m, 1H), 5.01 (d, *J* = 15.7 Hz, 1H), 4.75 (d, *J* = 15.7 Hz, 1H), 4.69 (s, 1H), 2.25 (s, 3H), 1.98 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 144.8, 137.7, 137.2, 136.0, 135.8, 135.7, 131.2, 129.1, 128.7, 128.5, 128.4, 127.6, 127.3, 127.1, 123.2, 122.1, 120.6, 116.6, 107.9, 107.3, 45.2, 43.8, 20.9, 17.3, 17.2.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{26}N_2OCl, M+H]^+$: 441.1728; Found:441.1722.

1-benzyl-4-bromo-3-(1-mesityl-1*H*-pyrrol-3-yl)indolin-2-one (8l):



8l

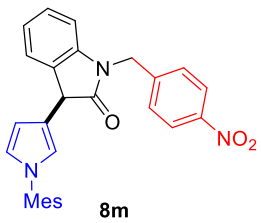
Colorless oil, 48.0 mg, 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.17 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.98 (t, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 3.0 Hz, 2H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.50 (t, *J* = 2.4 Hz, 1H), 6.40 (t, *J* = 1.6 Hz, 1H), 6.17–6.16 (m, 1H), 5.01 (d, *J* = 15.7 Hz, 1H), 4.73 (d, *J* = 15.7 Hz, 1H), 4.62 (s, 1H), 2.26 (s, 3H), 2.00 (s, 3H), 1.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.0, 144.9, 137.7, 137.2, 136.0, 135.8, 135.7, 129.4, 129.3, 128.7, 128.5, 128.4, 127.6, 127.1, 126.2, 122.2, 120.8, 119.9, 116.6, 108.0, 107.8, 46.6, 43.8, 20.9, 17.3, 17.2.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{26}N_2OBr, M+H]^+$: 485.1223; Found: 485.1227.

3-(1-mesityl-1*H*-pyrrol-3-yl)-1-(4-nitrobenzyl)indolin-2-one (8m):



8m

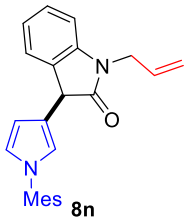
Brown solid, 76.6 mg, 80% yield, m.p.: 160~161 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 15.4 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.93 (s, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.59 (t, *J* = 2.4 Hz, 1H), 6.54 (s, 2H), 6.30 (t, *J* = 1.88 Hz, 1H), 5.12 (d, *J* = 16.3 Hz, 1H), 4.98 (d, *J* = 16.3 Hz, 1H), 4.78 (s, 1H), 2.32 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9, 147.4, 143.6, 142.6, 137.8, 137.1, 135.7, 135.6, 129.5, 128.6, 128.6, 127.9, 127.9, 125.2, 124.0, 122.9, 122.4, 119.9, 118.2, 108.4, 108.0, 44.9, 43.1, 20.9, 17.3, 17.2.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{26}N_3O_3, M+H]^+$: 452.1969; Found: 452.1970.

1-allyl-3-(1-mesityl-1*H*-pyrrol-3-yl)indolin-2-one (8n):



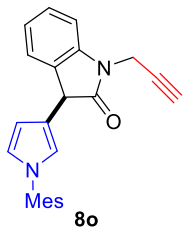
Yellow oil, 60.5 mg, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 2.1 Hz, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.51–6.38 (m, 2H), 6.17 (d, *J* = 2.1 Hz,, 1H), 5.76 (ddt, *J* = 17.1, 10.3, 5.2 Hz, 1H), 5.13–5.08 (m, 2H), 4.56 (s, 1H), 4.29–4.26 (m, 2H), 2.20 (s, 3H), 1.91 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.4, 143.4, 137.6, 137.2, 135.8, 135.7, 131.5, 129.6, 128.5, 128.5, 127.7, 124.8, 122.3, 122.1, 119.9, 118.4, 117.1, 108.8, 108.0, 44.9, 42.2, 20.9, 17.3, 17.2.

HRMS (ESI): m/z Calcd. for $[C_{24}H_{25}N_2O, M+H]^+$: 357.1961; Found: 357.1963.

3-(1-mesityl-1*H*-pyrrol-3-yl)-1-(prop-2-yn-1-yl)indolin-2-one (8o):



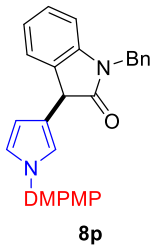
Yellow oil, 53.7 mg, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.31 (m, 2H), 7.10 (t, *J* = 7.3 Hz, 2H), 6.92 (d, *J* = 1.7 Hz, 2H), 6.56–6.54 (m, 2H), 6.26 (t, *J* = 2.0 Hz, 1H), 4.68 (s, 1H), 4.60 (d, *J* = 2.5 Hz, 1H), 4.51 (d, *J* = 2.5 Hz, 1H), 2.32 (s, 3H), 2.24 (t, *J* = 2.4 Hz, 1H), 2.02 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 142.3, 137.7, 137.2, 135.8, 135.7, 129.4, 128.5, 128.5, 127.8, 124.8, 122.7, 122.2, 120.0, 117.9, 109.0, 108.0, 77.1, 72.1, 44.9, 29.3, 20.9, 17.3.

HRMS (ESI): m/z Calcd. for $[C_{24}H_{22}N_2ONa, M+Na]^+$: 377.1624; Found: 377.1628.

1-benzyl-3-(1-(4-methoxy-2,6-dimethylphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (8p):



Yellow solid, 71.7 mg, 85% yield, m.p.: 150~151 °C.

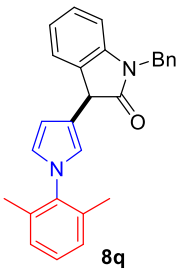
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 7.3 Hz, 1H), 7.24–7.16 (m, 5H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.57 (s, 2H), 6.51 (t, *J* = 2.4 Hz, 1H), 6.47 (s, 1H), 6.26 (t, *J* = 1.3 Hz, 1H), 4.95 (d, *J* = 15.7 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 4.68 (s, 1H), 3.74 (s, 3H), 1.99 (s, 3H), 1.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 158.6, 143.3, 137.4, 137.3, 136.0, 132.8, 129.6, 128.6, 127.7, 127.4, 127.2, 124.8, 122.5, 122.3, 120.2, 118.5, 112.8, 108.9, 108.1, 55.3, 45.0, 43.6,

17.9, 17.6.

HRMS (ESI): m/z Calcd. for $[C_{28}H_{27}N_2O_2, M+H]^+$: 423.2067; Found: 423.2069.

1-benzyl-3-(1-(2,6-dimethylphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (8q):



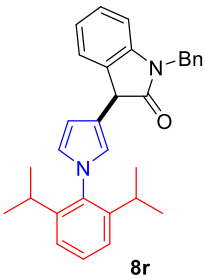
Yellow solid, 66.6 mg, 85% yield, m.p.: 120~121 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.4 Hz, 1H), 7.36–7.35 (m, 4H), 7.34-7.30 (m, 1H), 7.25–7.21 (m, 2H), 7.17–7.15 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.65 (t, *J* = 2.5 Hz, 1H), 6.61 (t, *J* = 2.0 Hz, 1H), 6.44–6.37 (m, 1H), 5.07 (d, *J* = 15.7 Hz, 1H), 4.96 (d, *J* = 15.7 Hz, 1H), 4.80 (s, 1H), 2.14 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 146.9, 146.8, 143.3, 136.8, 136.0, 129.5, 128.8, 128.7, 127.8, 127.4, 127.2, 124.7, 123.6, 123.3, 123.3, 122.4, 121.4, 118.3, 109.0, 108.1, 44.9, 43.7, 27.9, 24.5.

HRMS (ESI): m/z Calcd. for $[C_{27}H_{24}N_2ONa, M+Na]^+$: 415.1781; Found: 415.1781.

1-benzyl-3-(1-(2,6-diisopropylphenyl)-1*H*-pyrrol-3-yl)indolin-2-one (8r):



Yellow solid, 75.3 mg, 84% yield, m.p.: 142~143 °C.

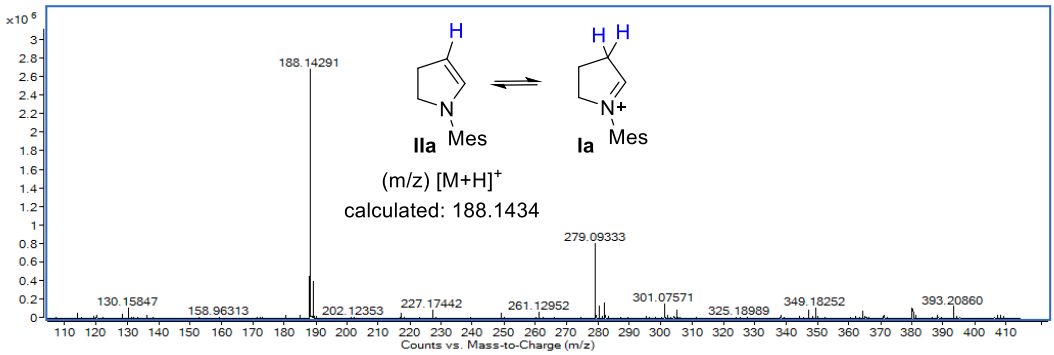
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.27 (m, 7H), 7.24–7.18 (m, 3H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.66 (t, *J* = 2.4 Hz, 1H), 6.59 (t, *J* = 2.0 Hz, 1H), 6.39 (t, *J* = 2.2 Hz, 1H), 5.09 (d, *J* = 15.7 Hz, 1H), 4.92 (d, *J* = 15.7 Hz, 1H), 4.79 (s, 1H), 2.60–2.45 (m, 2H), 1.19 (d, *J* = 4.9 Hz, 3H), 1.18 (d, *J* = 4.2 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.14 (d, *J* = 8.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 146.9, 146.8, 143.3, 136.8, 136.0, 129.5, 128.8, 128.7, 127.8, 127.4, 127.2, 124.7, 123.6, 123.3, 123.3, 122.4, 121.4, 118.3, 109.0, 108.1, 44.9, 43.7, 27.9, 27.9, 24.7, 24.6, 24.5.

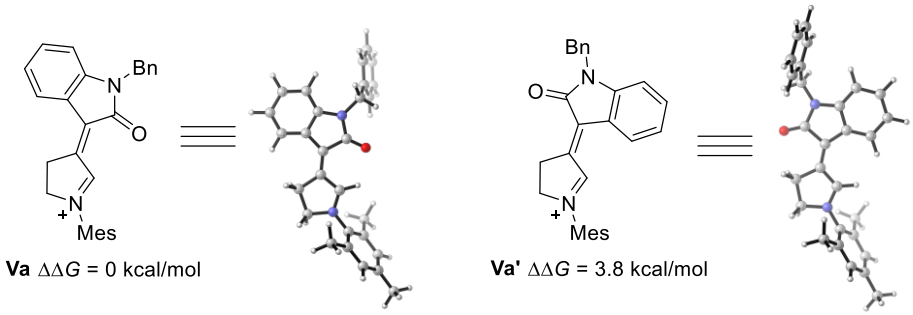
HRMS (ESI): m/z Calcd. for $[C_{31}H_{33}N_2O, M+H]^+$: 449.2587; Found: 449.2599.

6. Mechanism study

Experimental procedure: To a Schlenk tube equipped with a dried stir bar was added $B(C_6F_5)_3$ (0.02 mmol), pyrrolidines **1a** (0.24 mmol), isatin **2a** (0.20 mmol), anhydrous $MgSO_4$ (50 mg) and *m*-xylene (1.0 mL) in the glovebox. The Schlenk tube was sealed with a Teflon screw cap. The reaction mixture was taken outside the glovebox and allowed to stir at 25 °C for 10 hours. The crude reaction mixture was analyzed by HRMS. Iminium **Ia** or enamine **IIa** was observed in the crude reaction mixture.



DFT calculations: The result shows that intermediate **Va** was more stable than **Va'**, which will convert to **3a** with high *Z*/*E* ratio.



Complete reference for Gaussian 09

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.;

Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, **2013**.

Computational Methods.

All DFT calculations were carried out with the GAUSSIAN 09 series of programs. Density functional B3-LYP[2] with a standard 6-31G(d) basis set was used for geometry optimizations. Harmonic frequency calculations were performed for all stationary points to confirm them as local minima and to derive the thermochemical corrections for the enthalpies and free energies. All minima have zero imaginary frequency. The solvent effects were considered by single point calculations on the gas-phase stationary points with a continuum solvation model SMD.[3] The DFT method M06[4] functional with the 6-311+G(d) basis set was used to calculate the single point energies with *m*-xylene as solvent and provide highly accurate energy information. The energies given in this report are the M06 calculated Gibbs free energies in *m*-xylene solvent. The optimized structures were displayed using CYLview.[5]

B3LYP and M06 absolute calculation energies, enthalpies, and free energies.

Geometry	$E_{(elec\text{-}B3LYP)}$[1]	$H_{(corr\text{-}B3LYP)}$[2]	$G_{(corr\text{-}B3LYP)}$[3]	$E_{(solv\text{-}M11\text{-}L)}$[4]	IF[5]
Va	-1267.772071	0.513467	0.422673	-1267.161951	-
Va'	-1267.765400	0.513343	0.422737	-1267.156007	-

[1]The electronic energy calculated by B3LYP in gas phase. [2]The thermal correction to enthalpy calculated by B3LYP in gas phase. [3]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase. [4]The electronic energy calculated by M06 in *m*-xylene solvent. [5]The B3LYP calculated imaginary frequencies for the transition states.

B3LYP geometries for all the optimized compounds.

Va

C	1.23057800	-0.12714700	0.82789200
C	2.97429300	1.27453200	0.37458200
C	4.24424500	1.82506300	0.28619700
C	4.36690300	3.07688200	-0.33202600
C	3.25732900	3.76122800	-0.84926200
C	1.98581900	3.20134900	-0.76105000
C	1.83445100	1.94723700	-0.14683500
H	5.11577700	1.30339000	0.66312400
H	5.35255300	3.52564900	-0.41275500
H	3.39230200	4.72898300	-1.32052000
H	1.13034800	3.73463600	-1.16095300
O	0.59448000	-1.09483400	1.21798300
N	2.59122800	0.05572000	0.95046900
C	3.47558600	-0.90519500	1.61849100
H	4.01439400	-0.38094600	2.41568500
H	2.80417100	-1.62802800	2.09137200
C	4.45215000	-1.59526700	0.68384400
C	5.82298200	-1.58078500	0.96328300
C	3.99343300	-2.28498500	-0.44633900
C	6.72519200	-2.24252900	0.12644900
H	6.18872300	-1.05965800	1.84592500
C	4.89291600	-2.94131100	-1.28510100
H	2.92855500	-2.31547700	-0.66489700
C	6.26151000	-2.92096500	-1.00073000
H	7.78663900	-2.22602800	0.35639500
H	4.52691900	-3.47544100	-2.15744500
H	6.96083000	-3.43529900	-1.65346200
C	0.69423100	1.11025700	0.10702200
C	-0.62957700	1.27917800	-0.19229700
C	-1.65322600	0.34908700	0.15455700
C	-1.29839300	2.43887700	-0.91368500
C	-2.78359800	2.01687900	-1.00209300
H	-0.86797300	2.59853200	-1.90792200
H	-1.18020200	3.37404300	-0.35455900
H	-3.12384600	1.82629800	-2.02428000
H	-3.47073600	2.72928700	-0.54197800
N	-2.84008900	0.73008500	-0.25254300
H	-1.50557500	-0.57476400	0.70065800
C	-4.05678000	-0.03709400	-0.11640100
C	-4.19287500	-1.21936500	-0.87031900
C	-5.06137600	0.42666200	0.75268100
C	-5.38578800	-1.93321300	-0.73411900
C	-6.22709100	-0.33722600	0.85226400
C	-6.41513200	-1.51197900	0.11573800
H	-5.51303900	-2.84610600	-1.31032400
H	-7.00746100	-0.00631100	1.53313200
C	-3.11068600	-1.72232400	-1.80019400
H	-2.69823400	-0.92672600	-2.43171600
H	-2.27357800	-2.17389900	-1.25295100
H	-3.51131500	-2.49234000	-2.46399100
C	-4.91055400	1.68249500	1.58120000
H	-3.88218800	1.83685300	1.92459100
H	-5.21577200	2.57739300	1.02270400
H	-5.54838700	1.63151500	2.46760200
C	-7.70120600	-2.29415200	0.22022300
H	-8.43219500	-1.93922500	-0.51787200
H	-7.53917200	-3.35991000	0.03230300
H	-8.15737400	-2.18552000	1.20897400

Va'

C	-1.85242700	-0.78425700	-1.12493400
C	-2.60476000	1.21060500	-0.33031200
C	-3.43001200	2.27296500	0.02004300
C	-2.83794200	3.38468300	0.62560100
C	-1.45783600	3.43945600	0.87967300
C	-0.63912700	2.37205200	0.53071500
C	-1.20226800	1.23908000	-0.08136400
H	-4.49902300	2.23507500	-0.15173100
H	-3.46468600	4.22504500	0.90892000
H	-1.03082800	4.31744700	1.35265700
H	0.42427400	2.43377500	0.73694900
O	-1.82268200	-1.89331600	-1.63227800
N	-2.96607500	0.01083200	-0.94904600
C	-4.30734500	-0.36812100	-1.40609500
H	-4.66565500	0.39928800	-2.10175100
H	-4.16054400	-1.28980300	-1.97724400
C	-5.30786800	-0.57364400	-0.28375600
C	-6.53589100	0.09661500	-0.30654600
C	-5.03497500	-1.46187400	0.76520200
C	-7.47824500	-0.11289300	0.70346200
H	-6.76394700	0.77825800	-1.12362000
C	-5.97208300	-1.66777600	1.77659600
H	-4.09014700	-1.99996200	0.78571000
C	-7.19609600	-0.99303800	1.74825000
H	-8.42900400	0.41140900	0.67195500

H	-5.75175800	-2.36048600	2.58394300
H	-7.92644500	-1.15722500	2.53521600
C	-0.66526800	-0.00934900	-0.56415100
C	0.58901200	-0.56285600	-0.61156800
C	1.78871600	0.02915100	-0.12688400
C	0.96821500	-1.92896200	-1.17695500
C	2.49983600	-2.00179200	-0.99168400
H	0.67419600	-2.02324000	-2.22532900
H	0.44981300	-2.73293700	-0.64726000
H	3.05767400	-2.03698900	-1.93235000
H	2.83004200	-2.83786800	-0.37123000
N	2.84594600	-0.72733200	-0.30257700
H	1.90344100	0.99113100	0.35624400
C	4.20338500	-0.36021300	0.03083300
C	4.85437100	0.60086500	-0.76775300
C	4.82861000	-0.98733700	1.12372400
C	6.17207700	0.92346800	-0.43644900
C	6.14540500	-0.61499700	1.40903600
C	6.83756600	0.32846900	0.64244300
H	6.69445400	1.65966100	-1.04221800
H	6.64138800	-1.07496400	2.26007000
C	4.18157200	1.26791700	-1.94712800
H	3.65482100	0.55147500	-2.58790300
H	3.45107900	2.02558700	-1.63521900
H	4.92315200	1.77776700	-2.56690500
C	4.12977400	-2.01399800	1.98590200
H	3.06490000	-1.79587700	2.11906900
H	4.21216500	-3.02298300	1.56076600
H	4.58534800	-2.05127500	2.97896900
C	8.27114400	0.68138900	0.95451600
H	8.95931300	0.08178100	0.34479000
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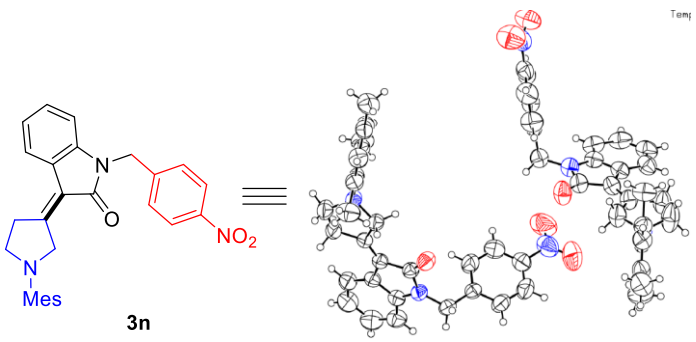
H	8.51242800	0.49018700	2.00428500

7. X-Ray crystallography data



Thermal ellipsoids are drawn on 50% probability level

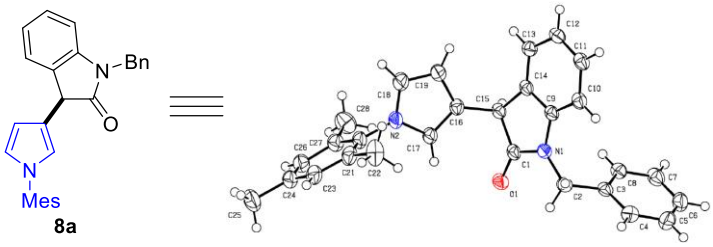
The single-crystal diffraction data were collected on a Rigaku XtaLAB synergy four-circle diffractometer with Cu-*K*α radiation (λ = 1.54184 Å), with the CrysAlisPro software (version 1.171.39.34b) for data reduction and analysis. The crystal was kept at 293 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were generated geometrically.

Table S2. Crystal data and structure refinement for **3n** (CCDC 2016599)

Empirical formula	$C_{28}H_{27}N_3O_3$
Formula weight	453.52
Temperature / K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	34.6336(3)
b / Å	9.30770(10)
c / Å	15.67260(10)
α/°	90
β/°	91.6510(10)
γ/°	90
V / Å^3	5050.11(8)
Z	8
F(000)	1920.0
D_c./ g cm^{-3}	1.193
μ / mm^{-1}	0.628
Reflns coll.	50400

Independent reflns	10299
R_{int}	0.0291
$^{a}R_1$ [I≥2σ(I)]	0.0537
$^{b}wR_2$ (all data)	0.1608
GOF	1.056

$^{a}R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^{b}wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.



Thermal ellipsoids are drawn on 50% probability level

The single-crystal diffraction data were collected on a Rigaku XtaLAB synergy four-circle diffractometer with Cu-*K*α radiation (λ = 1.54184 Å), with the CrysAlisPro software (version 1.171.39.34b) for data reduction and analysis. The crystal was kept at 100 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were generated geometrically.

Table S3. Crystal data and structure refinement for **8a** (CCDC 2004862).

Empirical formula	$C_{28}H_{26}N_2O$
Formula weight	406.51
Temperature / K	99.94(10)
Crystal system	triclinic
Space group	*P-1*
a / Å	8.2189(3)
b / Å	8.2436(3)
c / Å	16.0834(6)
α / °	90.216(3)
β / °	90.280(3)
γ / °	99.017(3)
V / Å^3	1076.21(7)
Z	2
F(000)	432.0
D_c./ g cm^{-3}	1.254
μ / mm^{-1}	0.592

Reflns coll.	10546
Independent reflns	4306
R_{int}	0.0575
$^{a}R_1$ [I≥2σ(I)]	0.0540
$^{b}wR_2$ (all data)	0.1494
GOF	1.050

$^{a}R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^{b}wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

8. References

(1) Takasu, N.; Oisaki, K.; Kanai, M. Iron-Catalyzed Oxidative C(3)-H Functionalization of Amines. *Org. Lett.* **2013**, *15*, 1918−1921.

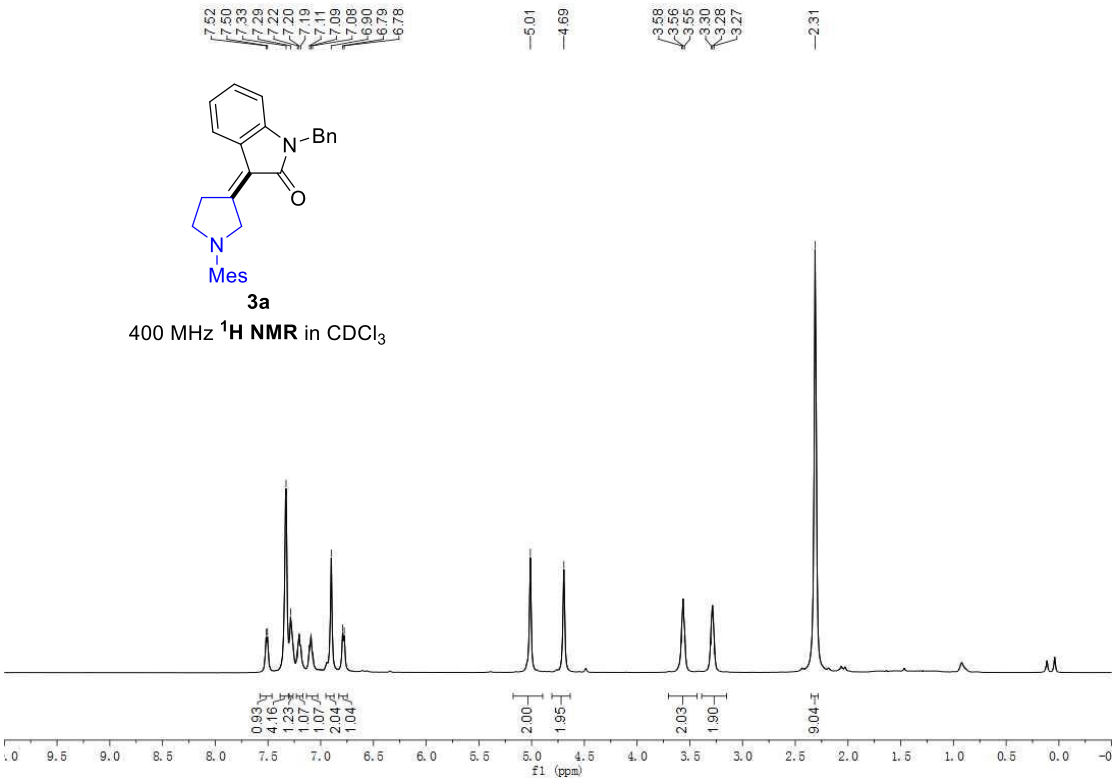
(2) (a) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *37*, 785−789.

(3) (a) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Ab initio* study of solvated molecules: a new implementation of the polarizable continuum model. *Chem. Phys. Lett.* **1996**, *255*, 327−335. (b) Cances, E.; Mennucci, B.; Tomasi, J. A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics. *J. Chem. Phys.* **1997**, *107*, 3032−3041. (c) Barone, V.; Cossi, M.; Tomasi, J. Geometry optimization of molecular structures in solution by the polarizable continuum model. *J. Comput. Chem.* **1998**, *19*, 404−417. (d) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B.* **2009**, *113*, 6378−6396.

(4) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215−241.

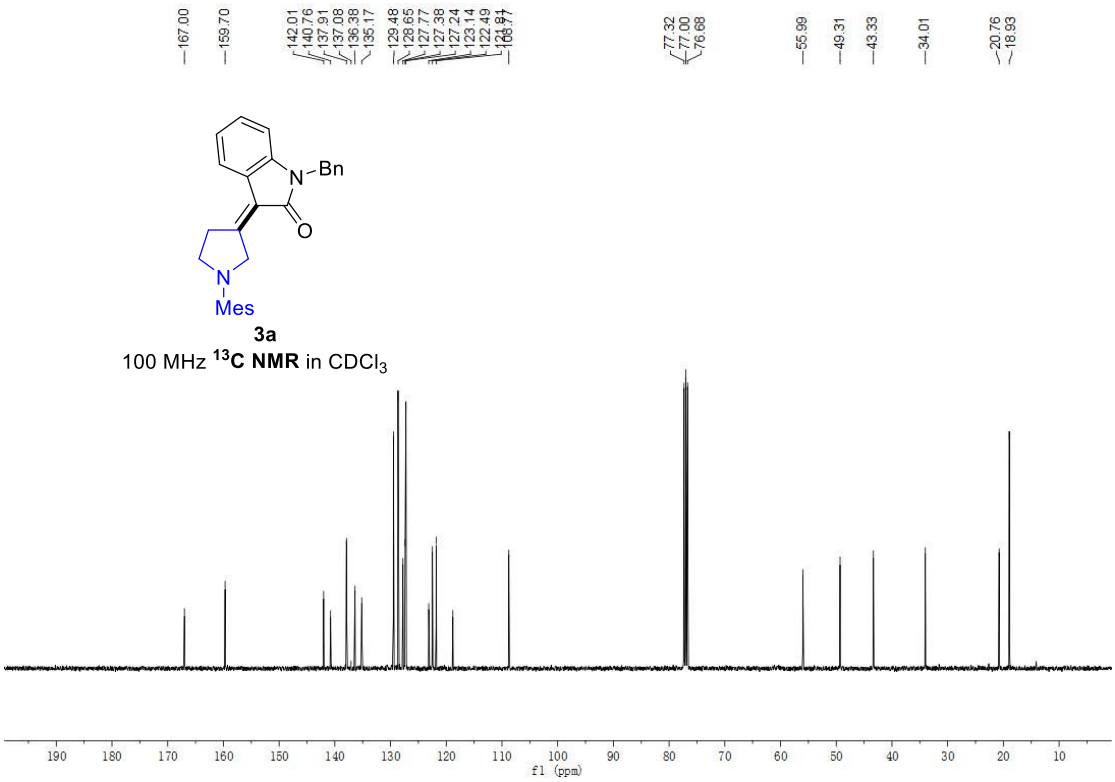
(5) Legault, C. Y.; CYLView, 1.0b; Université de Sherbrooke, Canada, **2009**. http://www.cylview.org (Date of access: 1/10/2017).

9. NMR spectra of products



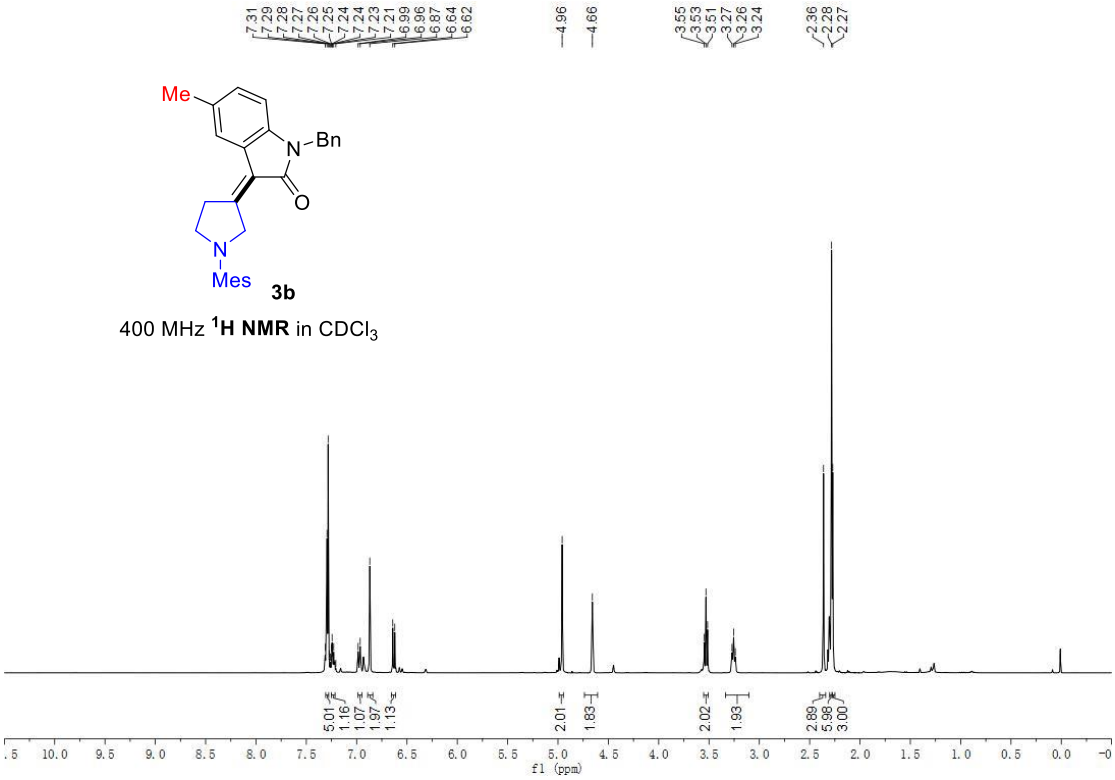
3a

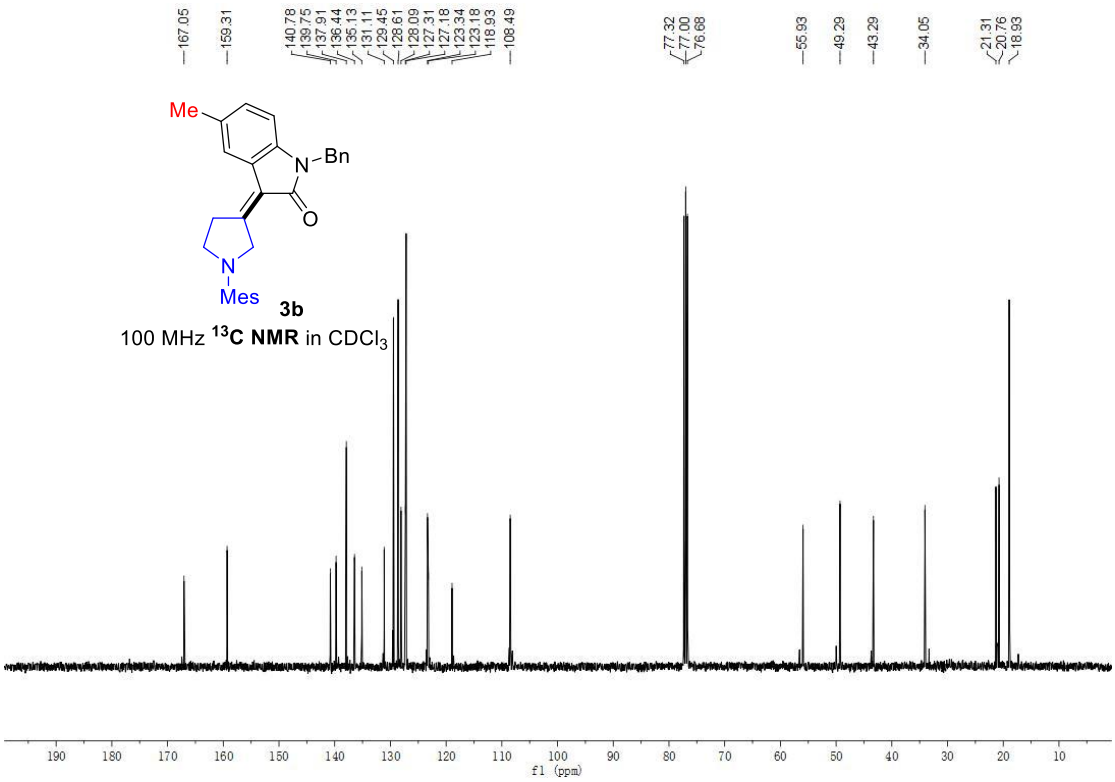
400 MHz **^{1}H NMR** in $CDCl_3$

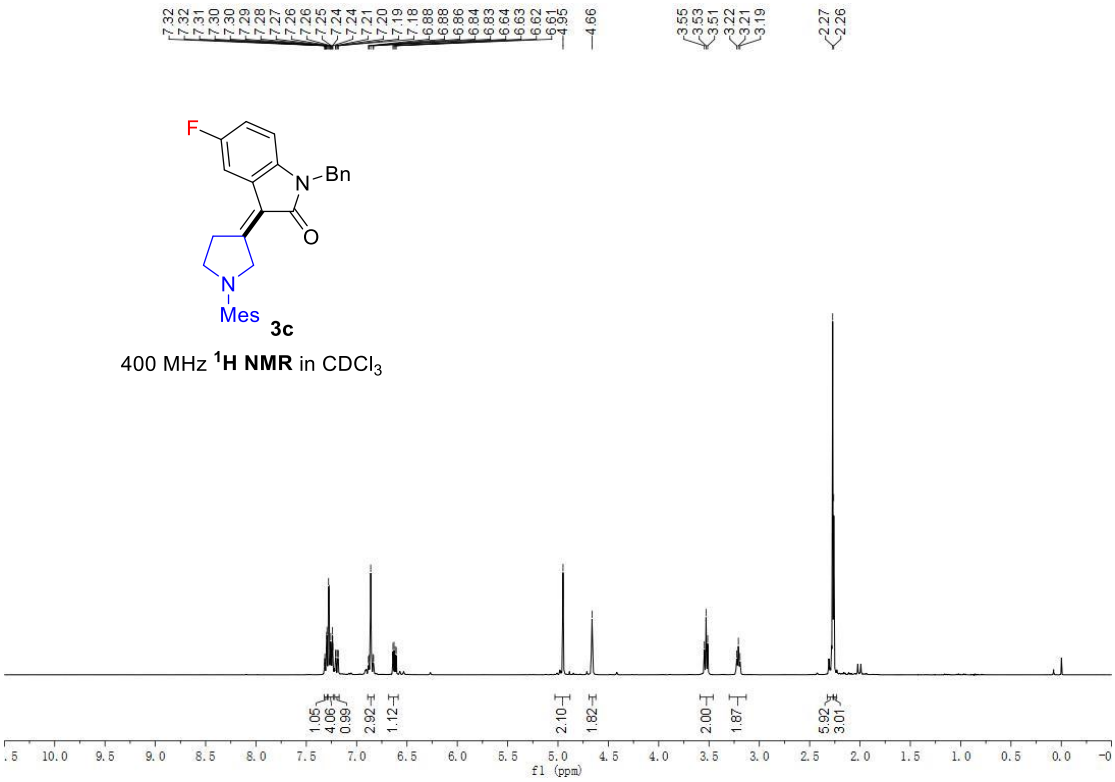


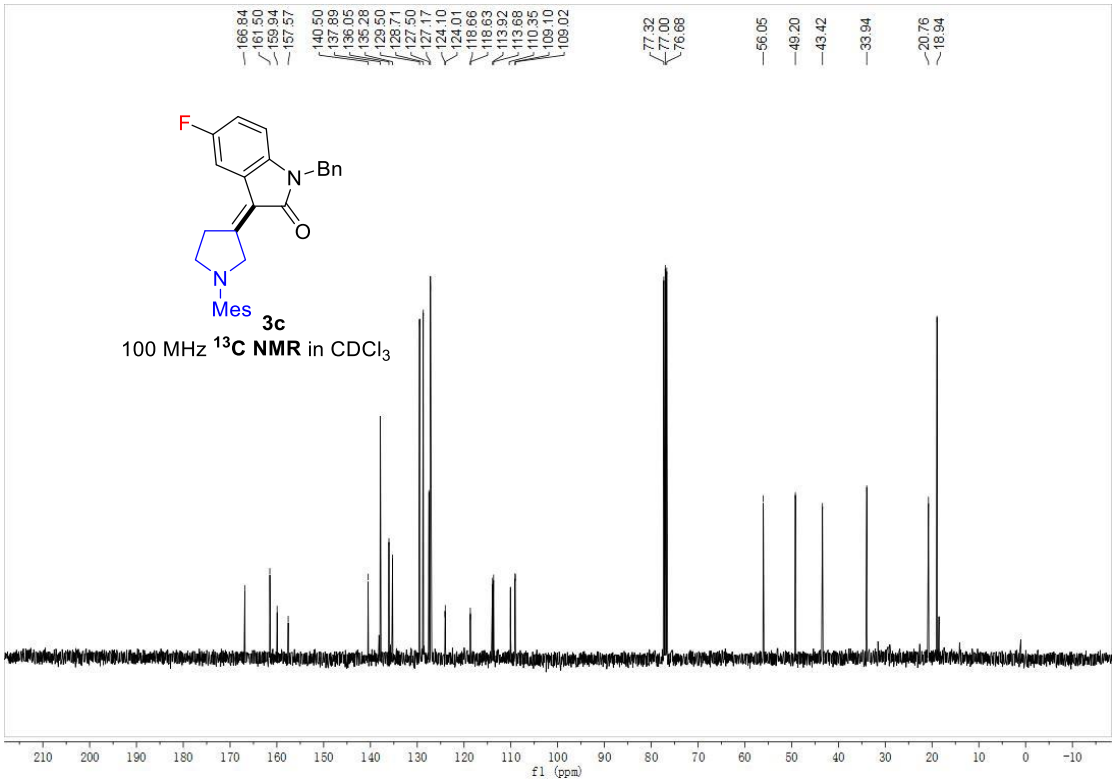
3a

100 MHz **^{13}C NMR** in $CDCl_3$


Me
N
Bn
O
N
Mes
3b
400 MHz ¹H NMR in CDCl₃
7.31
7.29
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.21
6.99
6.96
6.87
6.64
6.62
4.96
4.66
3.55
3.53
3.51
3.27
3.26
3.24
2.36
2.28
2.27
5.01
1.16
1.07
1.97
1.13
2.01
1.83
2.02
1.93
2.89
5.98
3.00
f1 (ppm)

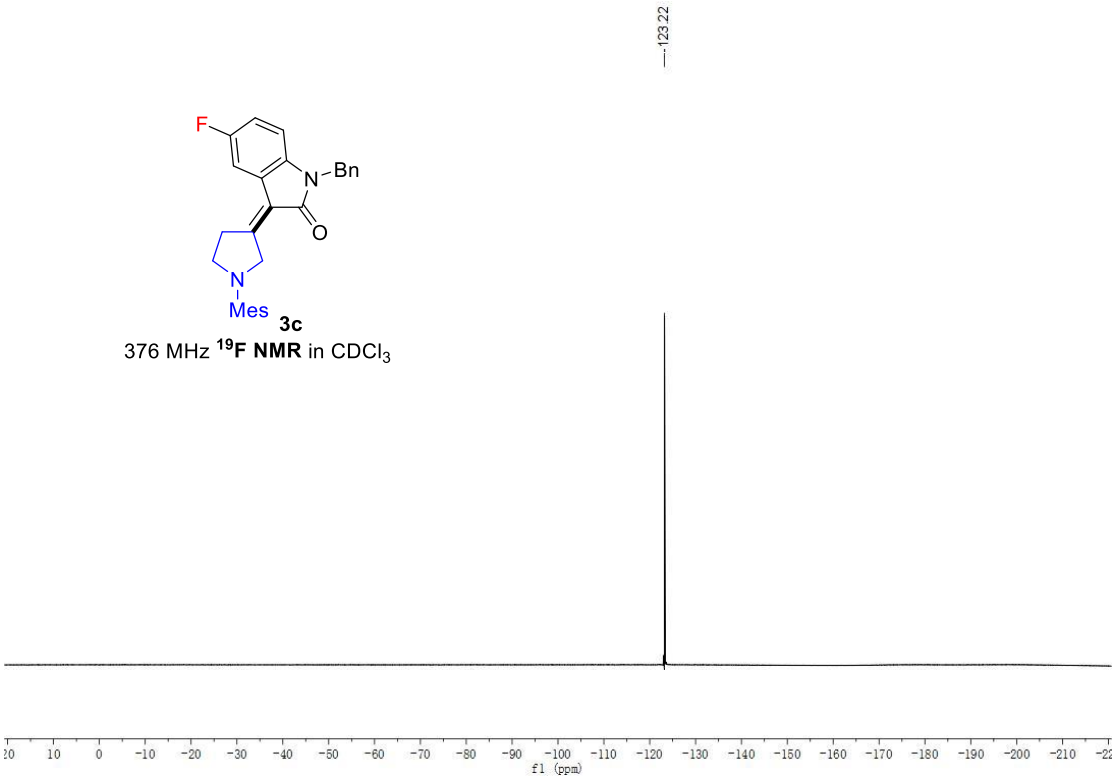

Me
N
Bn
O
N
Mes
3b
100 MHz ¹³C NMR in CDCl₃
167.05
159.31
140.78
139.75
137.91
136.44
135.13
131.11
129.45
128.61
128.09
127.31
127.18
123.34
123.18
118.93
108.49
77.32
77.00
76.68
55.93
49.29
43.29
34.05
21.31
20.76
18.93
f1 (ppm)


F
N
Bn
O
N
Mes
3c
400 MHz ¹H NMR in CDCl₃
f1 (ppm)


F
N
Bn
O
N
Mes
3c
100 MHz ¹³C NMR in CDCl₃
f1 (ppm)

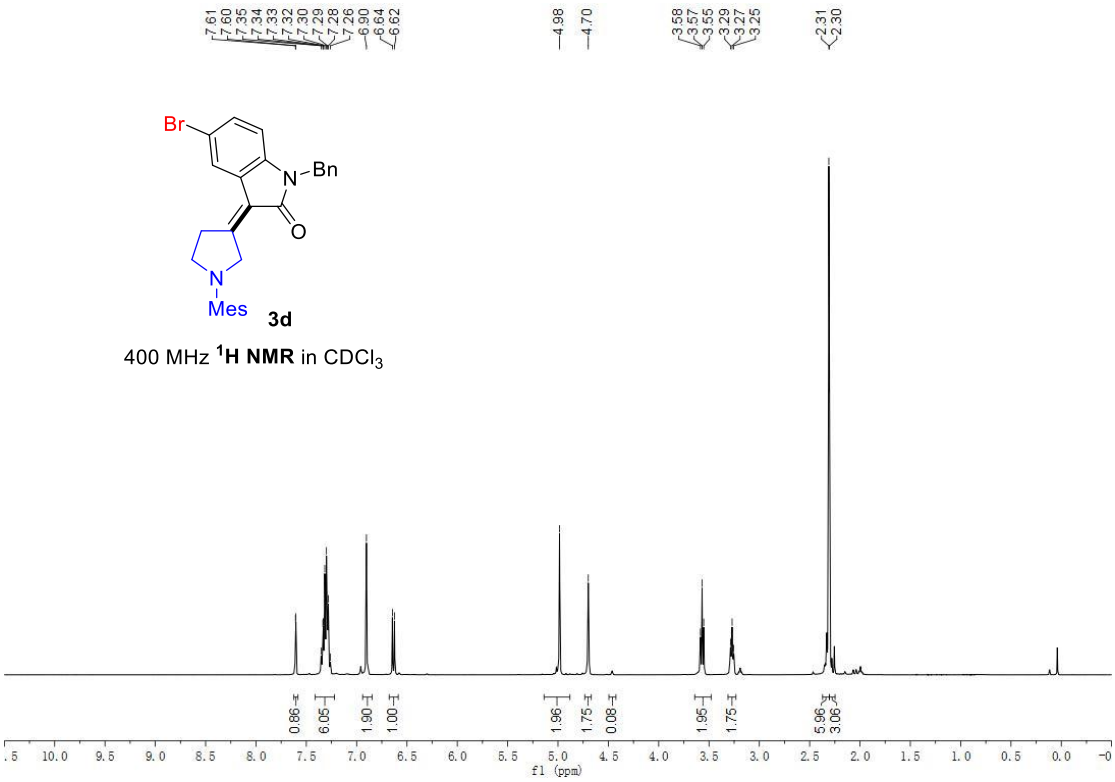
3c

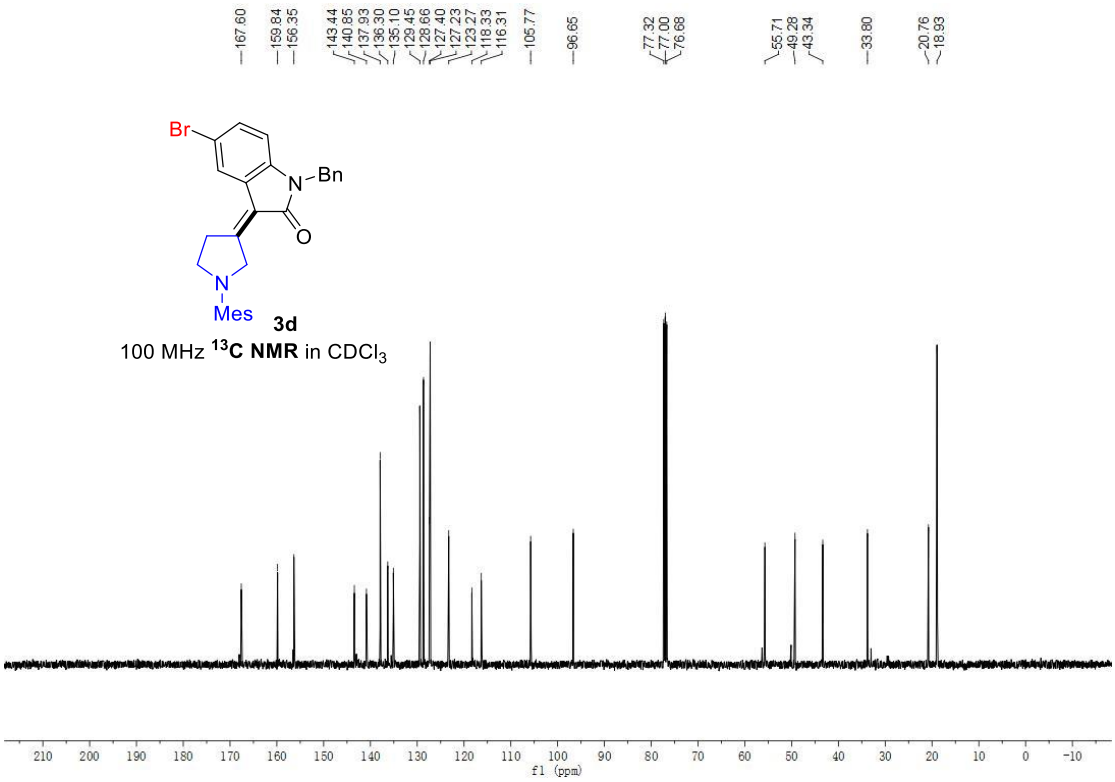
376 MHz **^{19}F NMR** in $CDCl_3$



3d

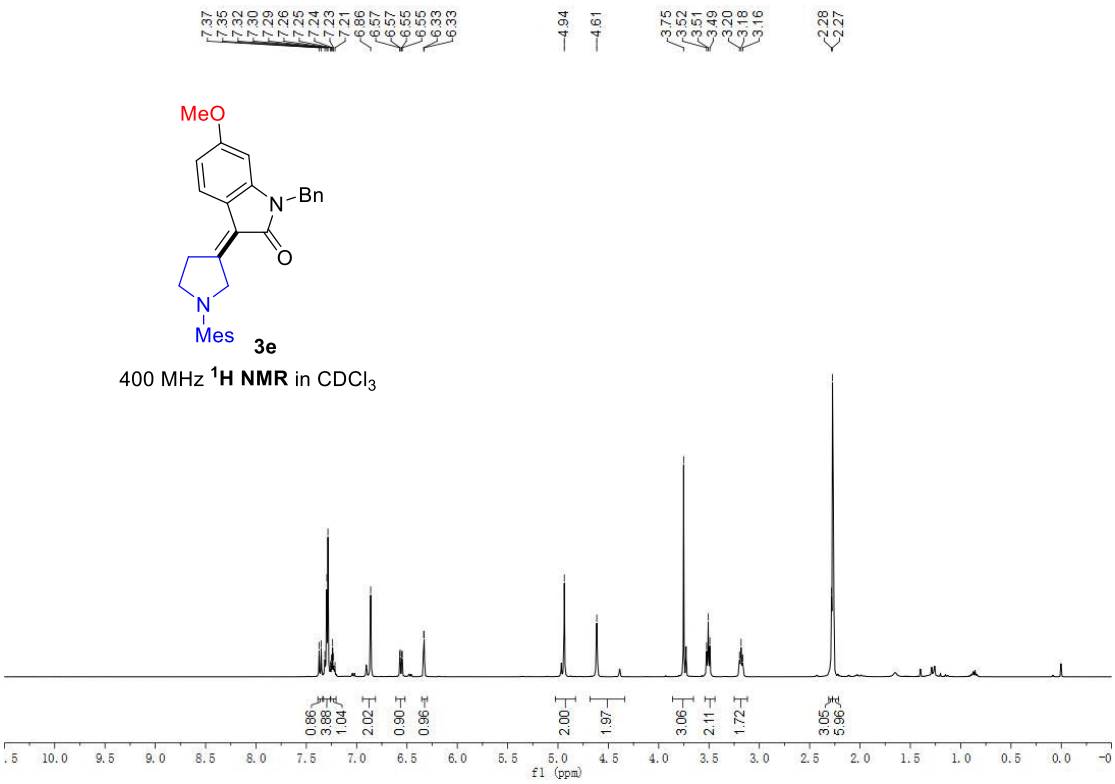
400 MHz **^{1}H NMR** in $CDCl_3$





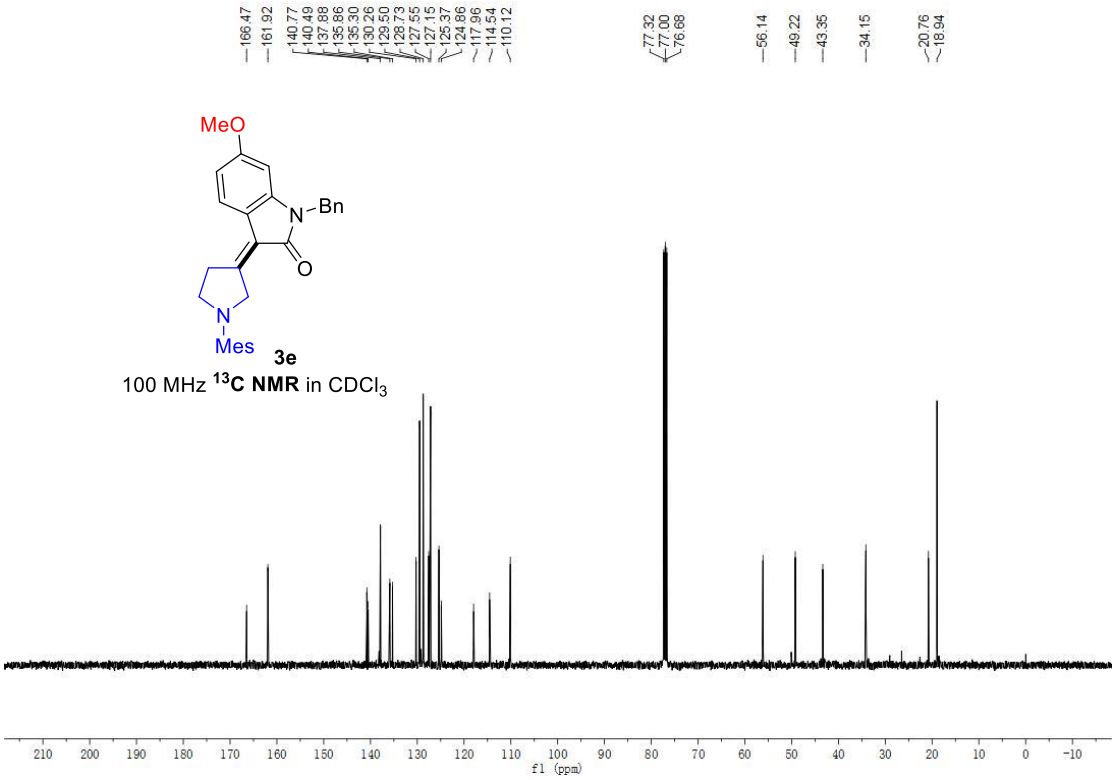
3d

100 MHz ^{13}**C NMR** in $CDCl_3$

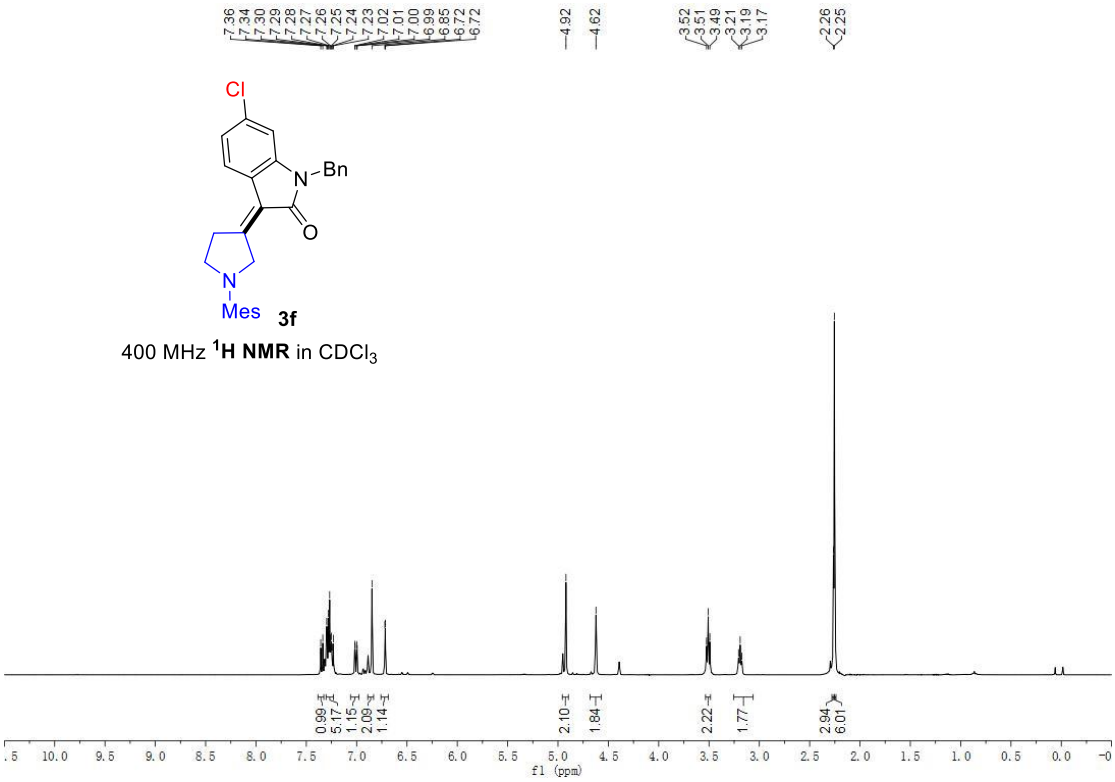


3e

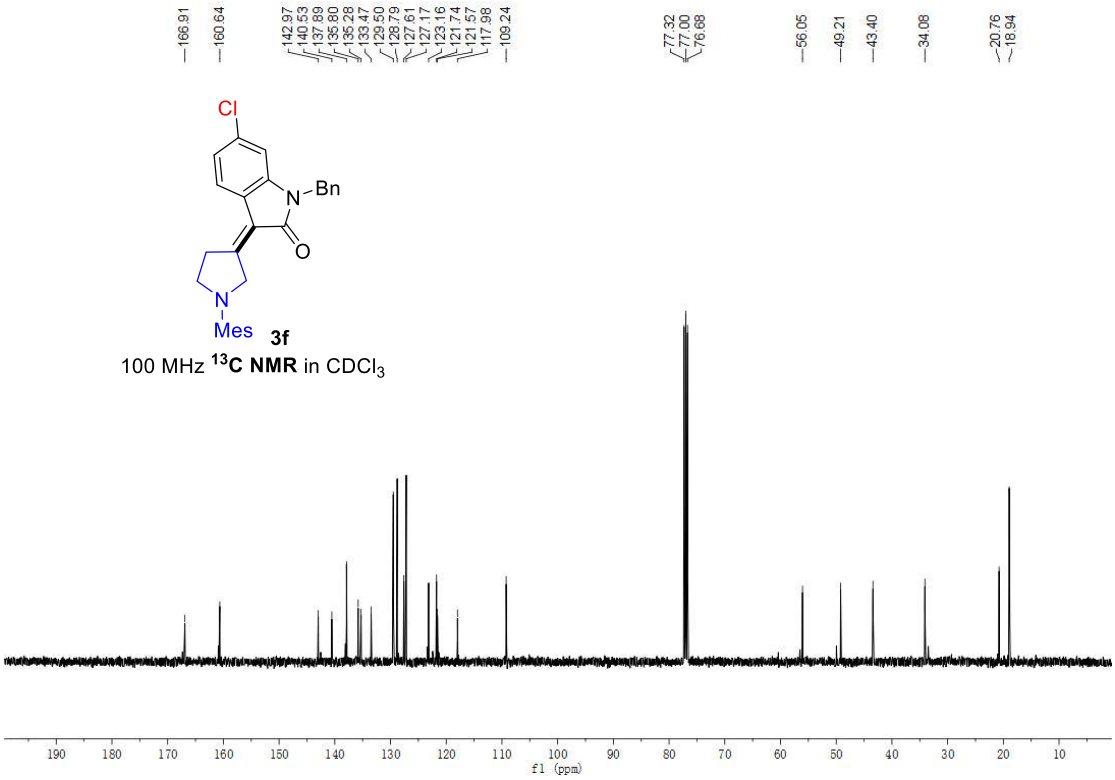
400 MHz ^{1}**H NMR** in $CDCl_3$

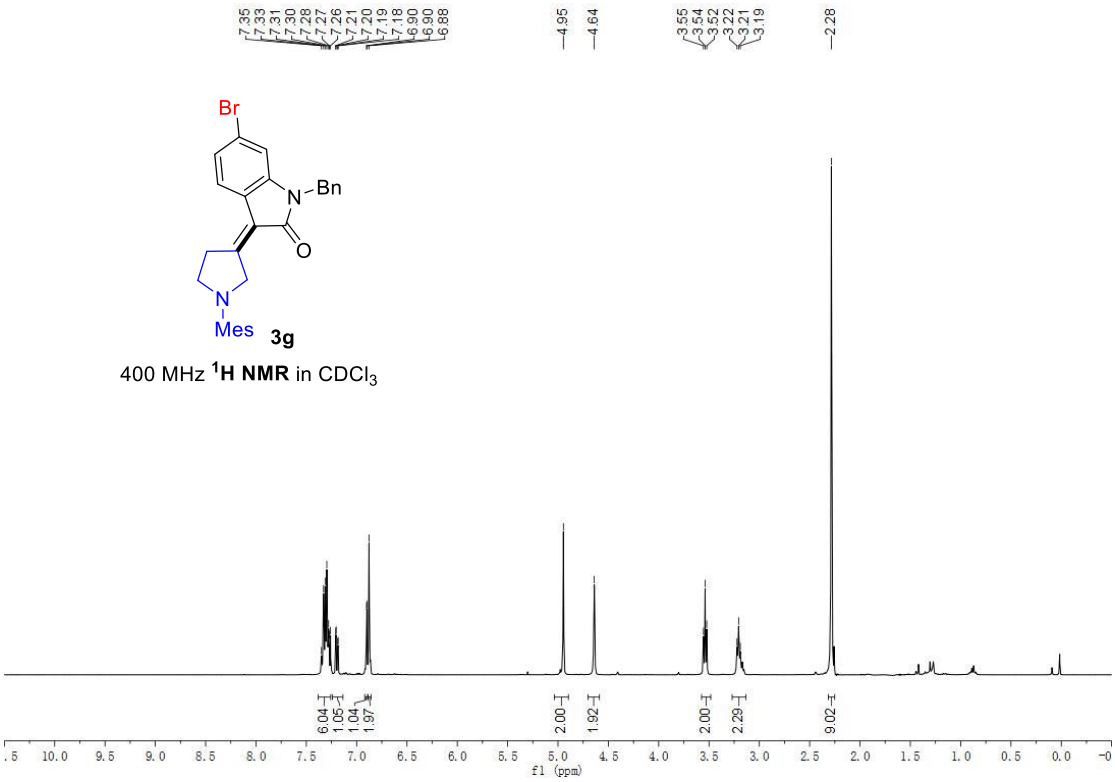


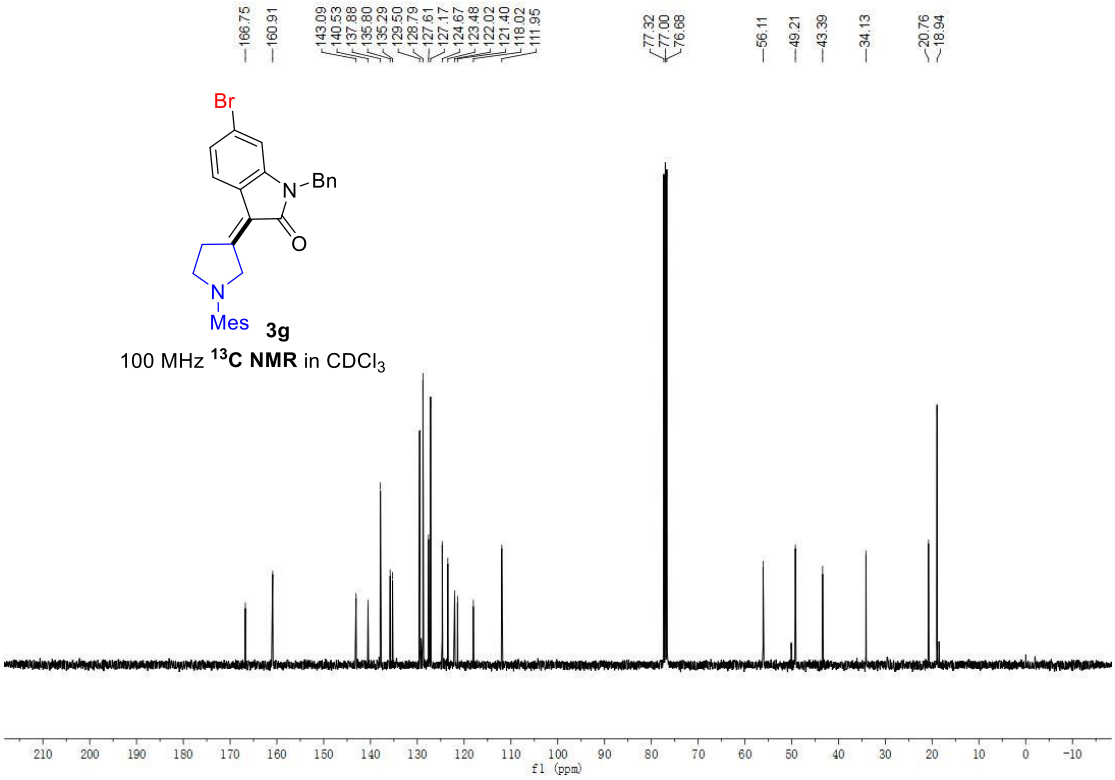
100 MHz ^{13}**C NMR** in $CDCl_3$



400 MHz ^{1}**H NMR** in $CDCl_3$


166.91
160.64
142.97
140.53
137.89
135.80
135.28
133.47
129.50
128.79
127.61
127.17
123.16
121.74
121.57
117.98
109.24
77.32
77.00
76.68
56.05
49.21
43.40
34.08
20.76
18.94
Cl
N
Bn
O
N
Mes
3f
100 MHz 13C NMR in CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.35
7.33
7.31
7.30
7.28
7.27
7.26
7.21
7.20
7.19
7.18
6.90
6.90
6.88
4.95
4.64
3.55
3.54
3.52
3.22
3.21
3.19
2.28
Br
N
Bn
O
N
Mes
3g
400 MHz 1H NMR in CDCl3
6.04
1.05
1.04
1.97
2.00
1.92
2.00
2.29
9.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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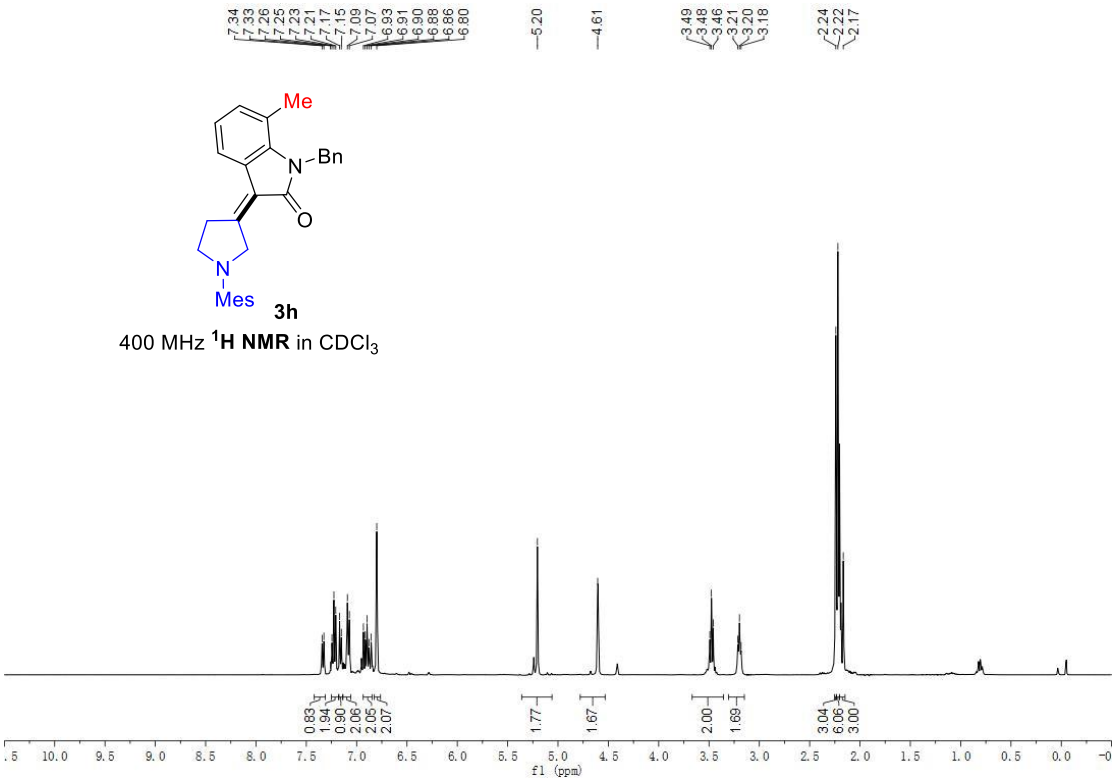
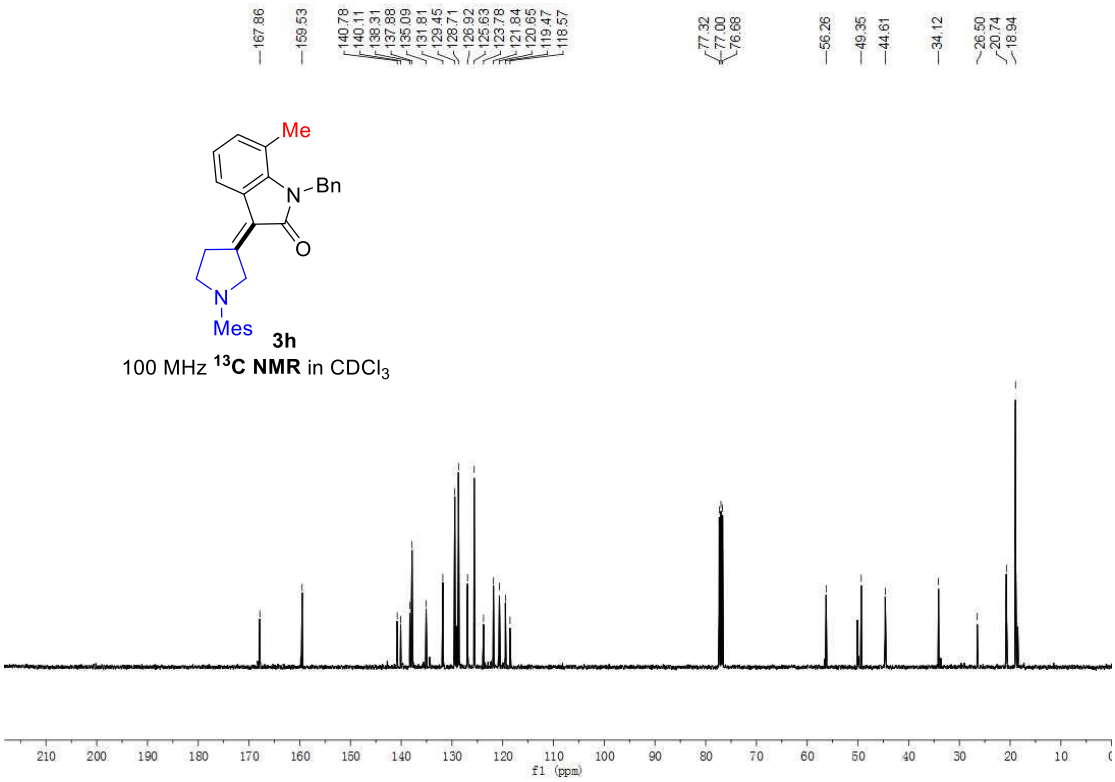
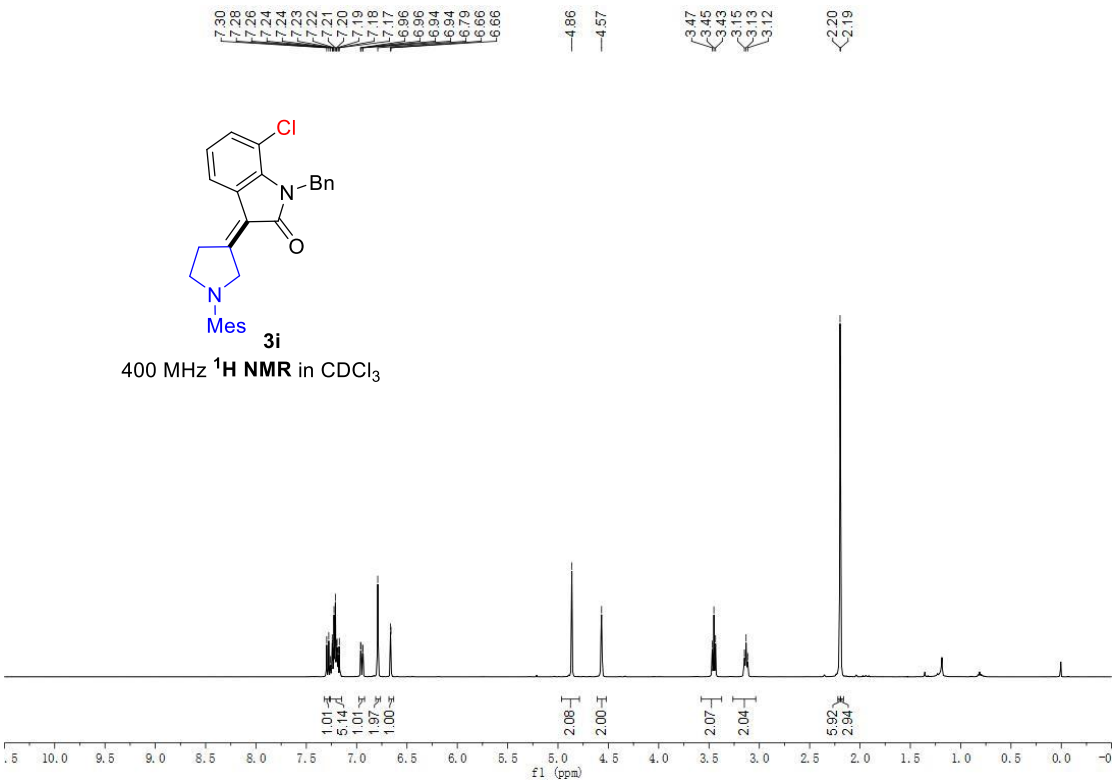
140.53
137.88
135.80
135.29
129.50
128.79
127.61
127.17
124.67
123.48
122.02
121.40
118.02
111.95
77.32
77.00
76.68
56.11
49.21
43.39
34.13
20.76
18.94
Br
N
Bn
O
N
Mes
3g
100 MHz 13C NMR in CDCl3
f1 (ppm)


7.34
7.33
7.26
7.25
7.23
7.21
7.17
7.15
7.09
7.07
6.93
6.91
6.90
6.88
6.86
6.80
5.20
4.61
3.49
3.48
3.46
3.21
3.20
3.18
2.24
2.22
2.17
Me
N
Bn
O
N
Mes
3h
400 MHz 1H NMR in CDCl3
0.83
1.94
0.90
2.06
2.05
2.07
1.77
1.67
2.00
1.69
3.04
6.06
3.00
f1 (ppm)



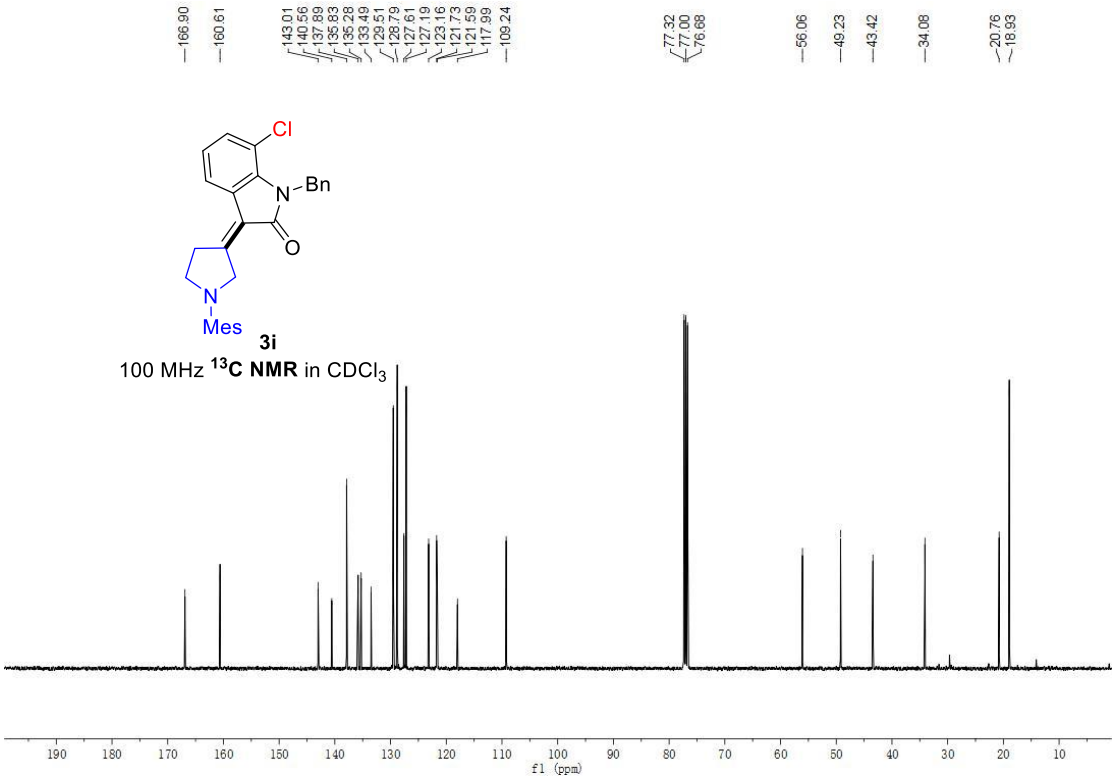
3h

100 MHz ^{13}**C NMR** in $CDCl_3$



3i

400 MHz ^{1}**H NMR** in $CDCl_3$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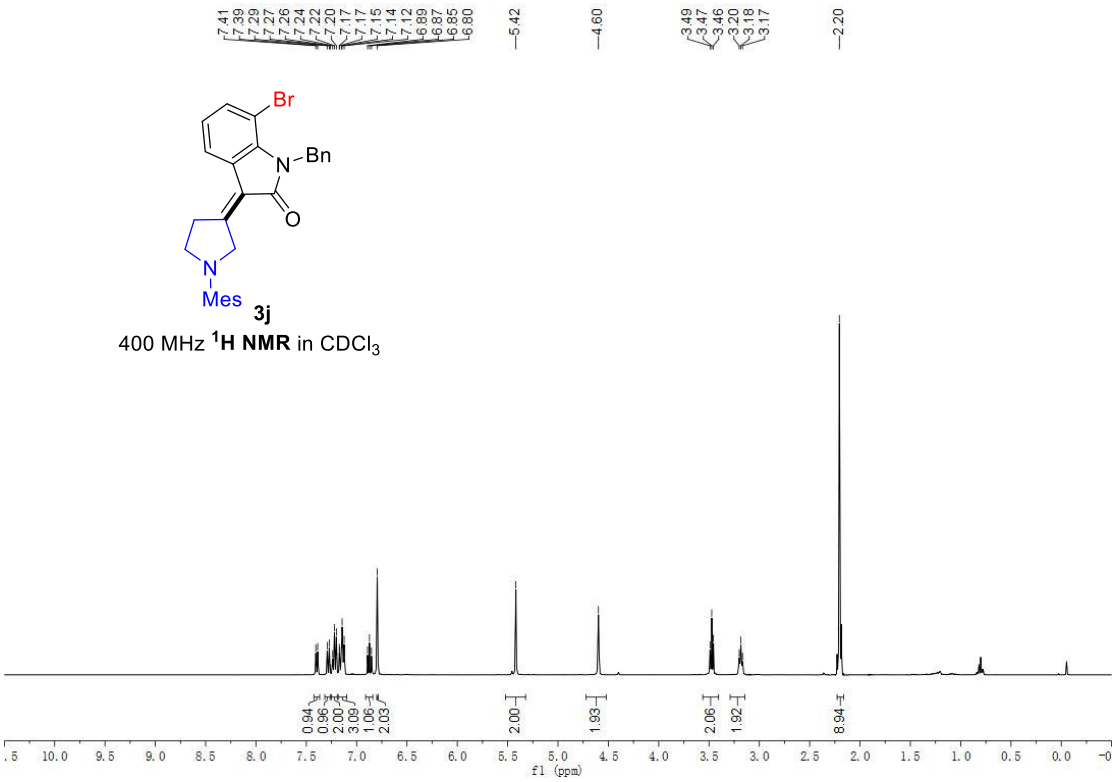
143.01
140.56
137.89
135.83
135.28
133.49
129.51
128.79
127.61
127.19
123.16
121.73
121.59
117.99
109.24
77.32
77.00
76.68
56.06
49.23
43.42
34.08
20.76
18.93
Cl
N
Bn
O
N
Mes
3i
100 MHz 13C NMR in CDCl3
f1 (ppm)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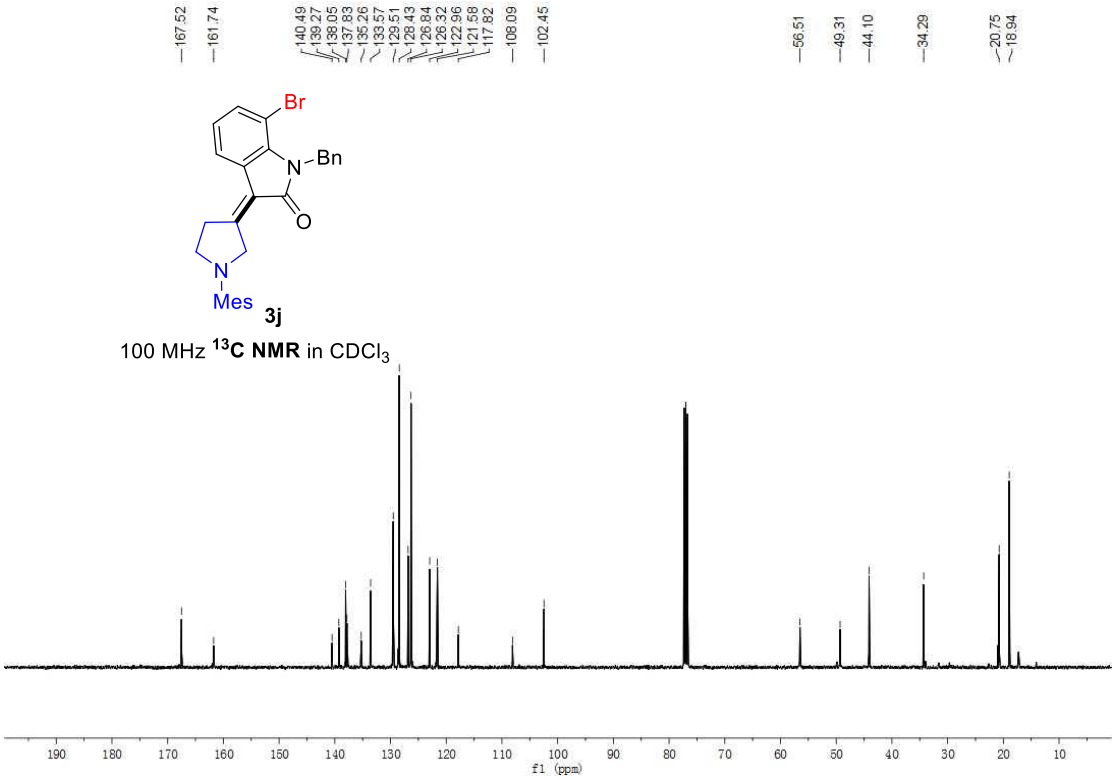
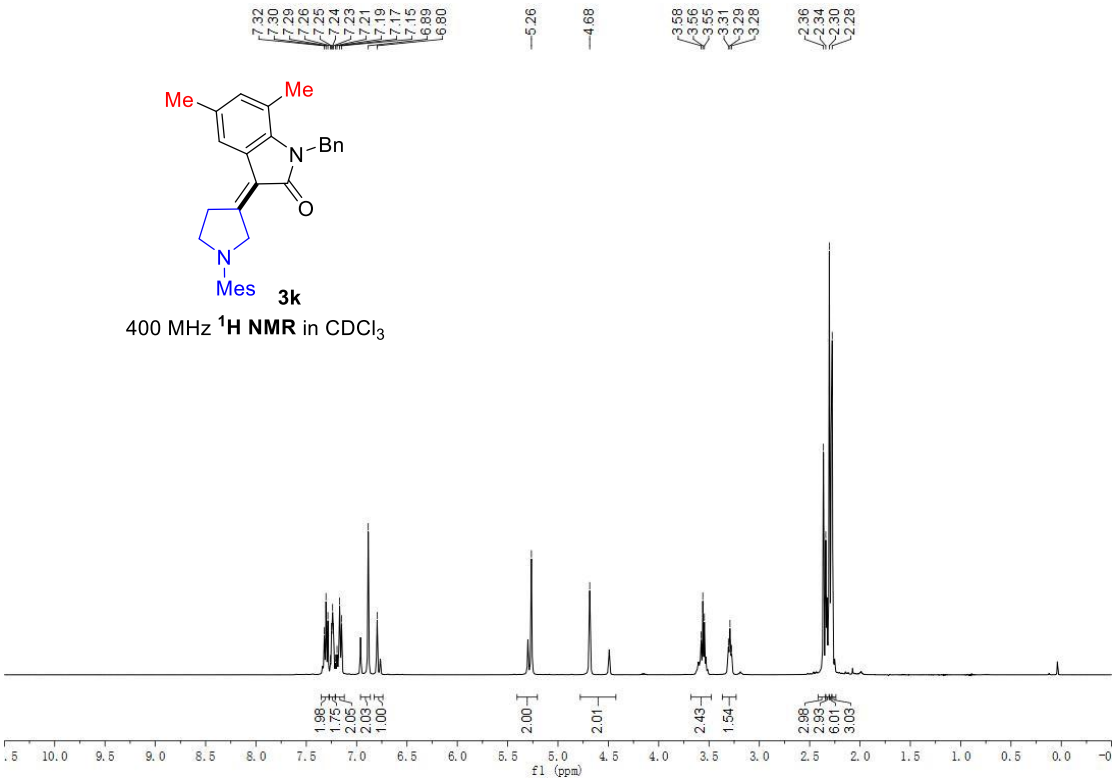
7.39
7.29
7.27
7.26
7.24
7.22
7.20
7.17
7.17
7.15
7.14
7.12
6.89
6.87
6.85
6.80
5.42
4.60
3.49
3.47
3.46
3.20
3.18
3.17
2.20
Br
N
Bn
O
N
Mes
3j
400 MHz 1H NMR in CDCl3
0.94
0.96
2.00
3.09
1.06
2.03
2.00
1.93
2.06
1.92
8.94
f1 (ppm)


167.52
161.74
140.49
139.27
138.05
137.83
135.26
133.57
129.51
128.43
126.84
126.32
122.96
121.58
117.82
108.09
102.45
56.51
49.31
44.10
34.29
20.75
18.94
Br
N
Bn
O
N
Mes
3j
100 MHz 13C NMR in CDCl3
f1 (ppm)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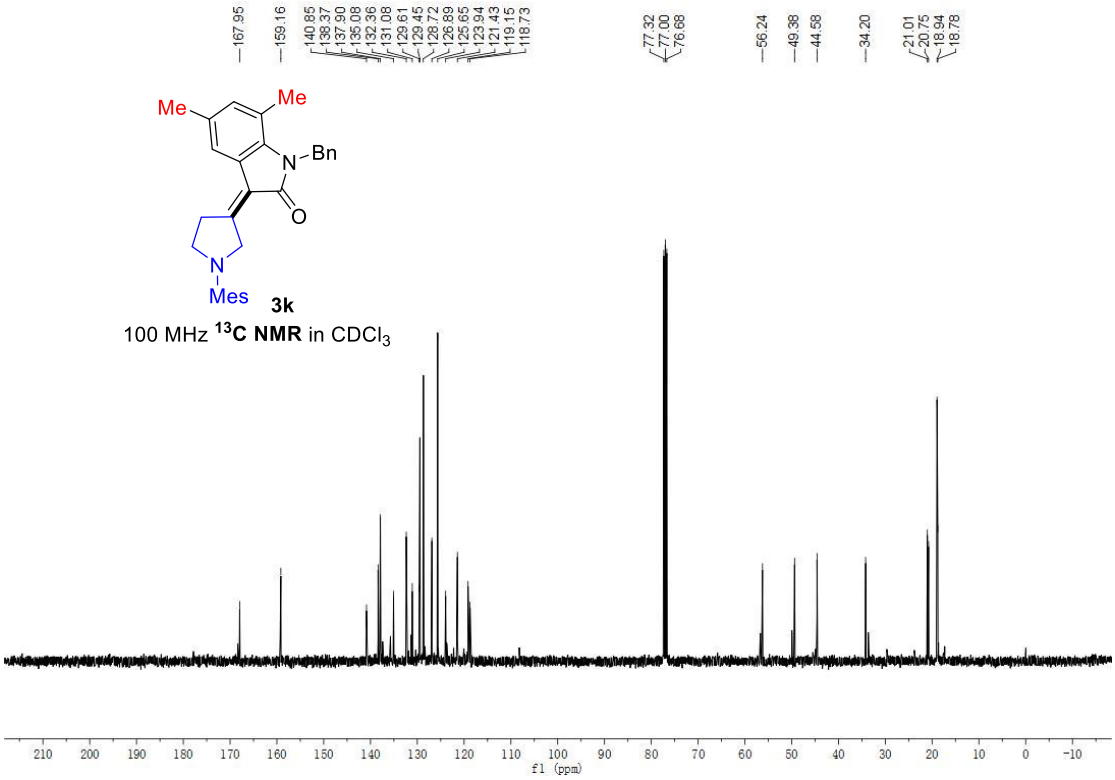
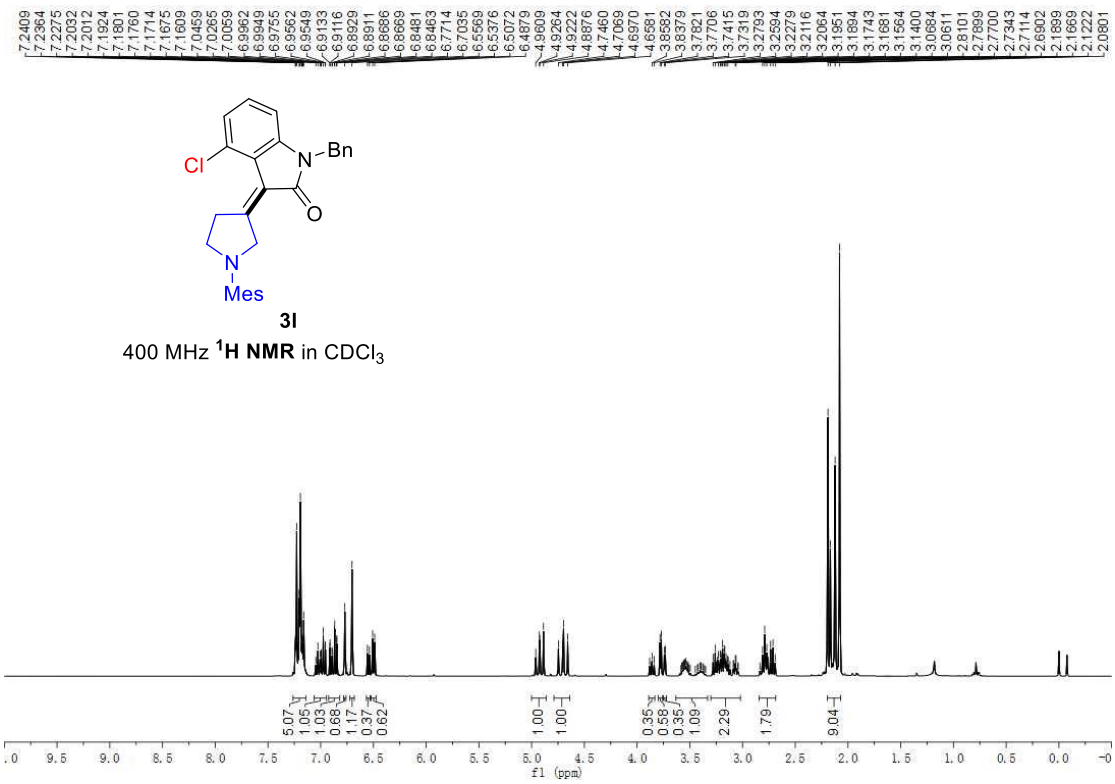
7.30
7.29
7.26
7.25
7.24
7.23
7.21
7.19
7.17
7.15
6.89
6.80
5.26
4.68
3.58
3.56
3.55
3.31
3.29
3.28
2.36
2.34
2.30
2.28
Me
Me
N
Bn
O
N
Mes
3k
400 MHz 1H NMR in CDCl3
1.98
1.75
2.05
2.03
1.00
2.00
2.01
2.43
1.54
2.98
2.93
6.01
3.03
f1 (ppm)



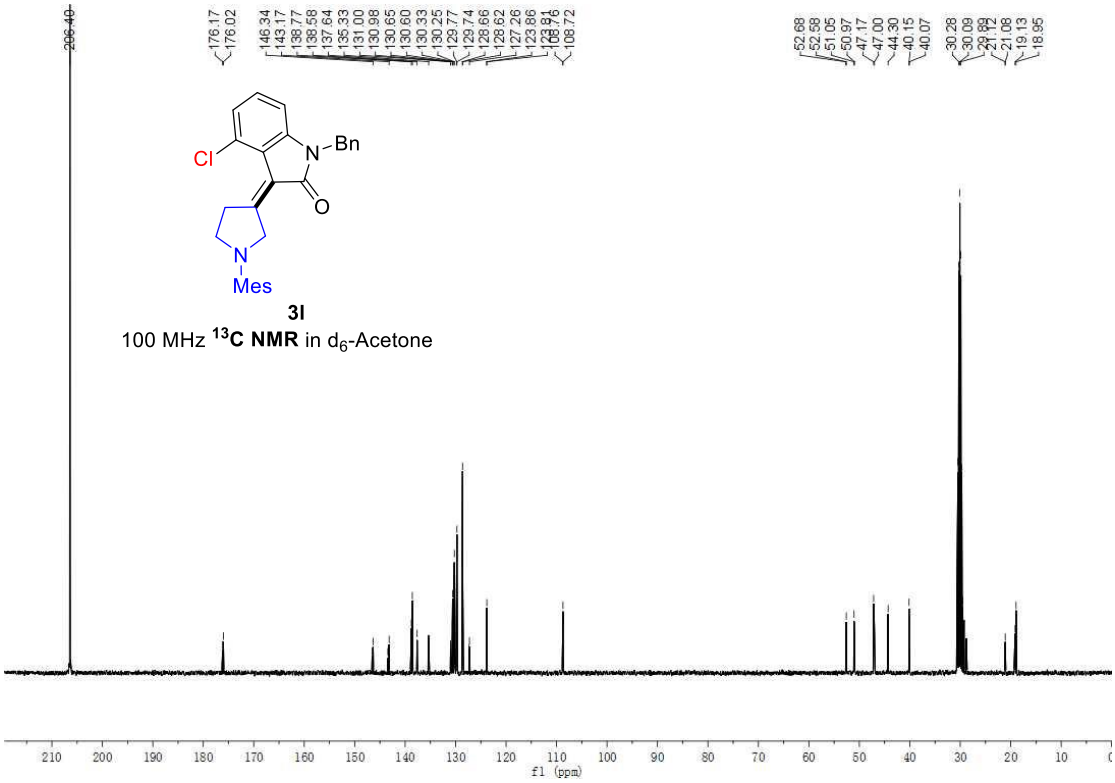
3k

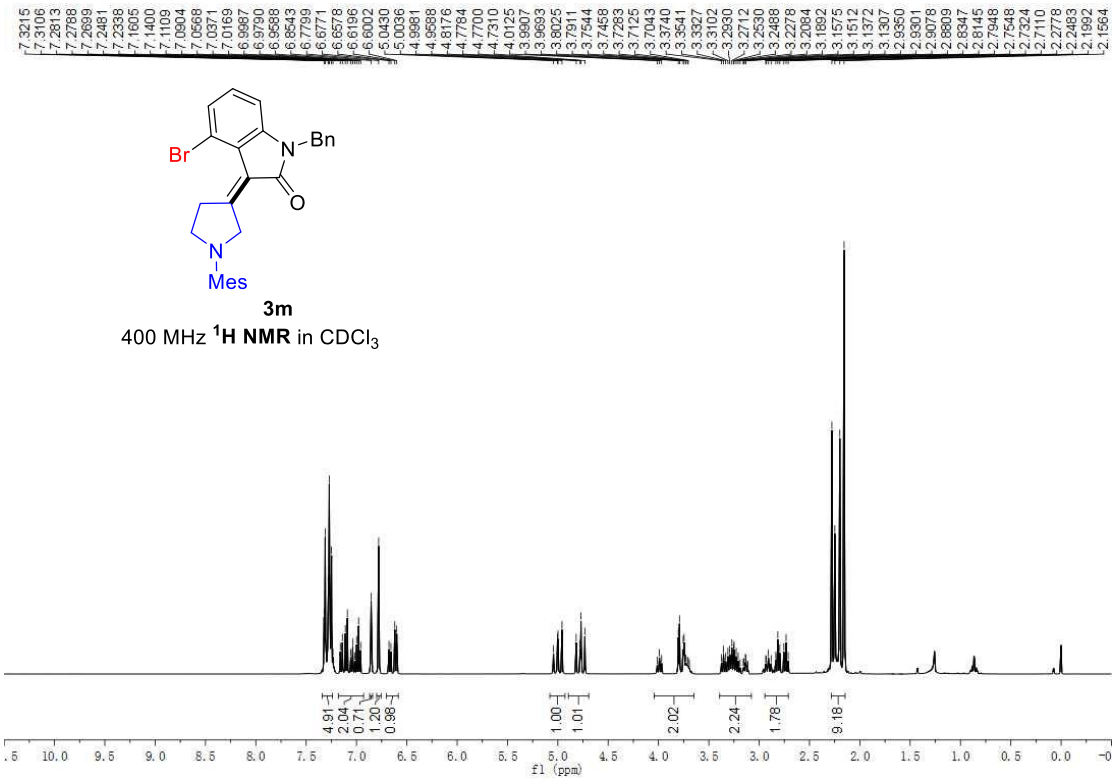
100 MHz ^{13}**C NMR** in $CDCl_3$

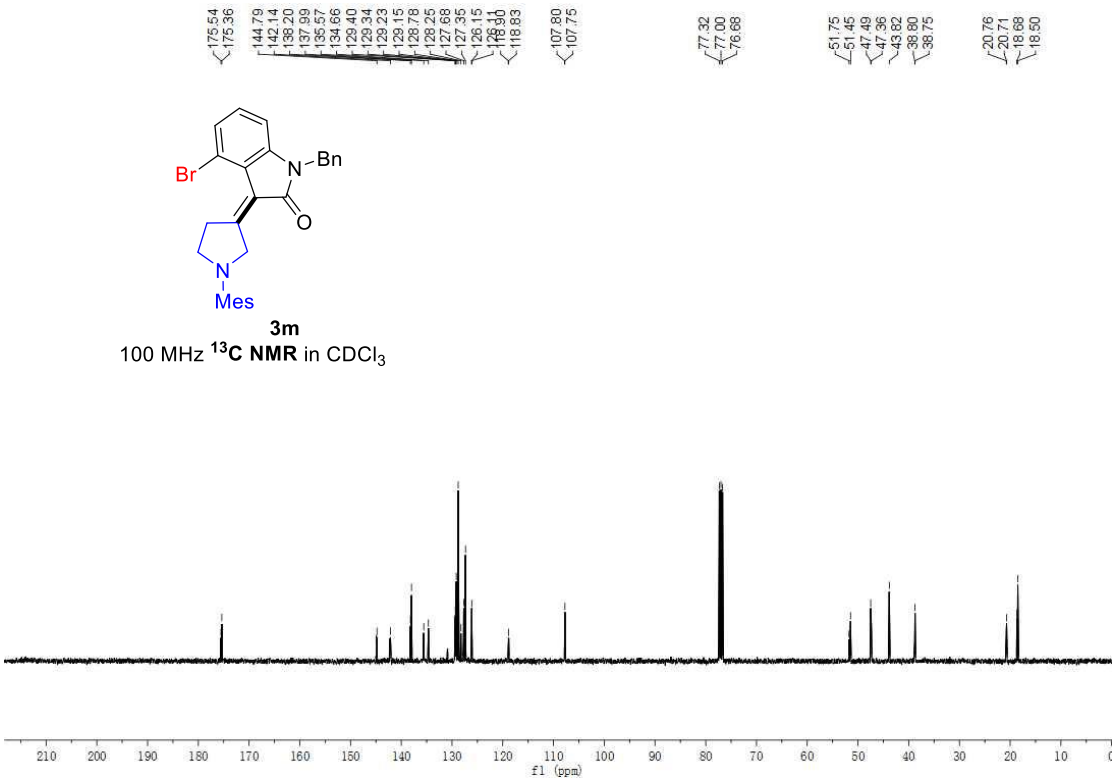


3l

400 MHz ^{1}**H NMR** in $CDCl_3$

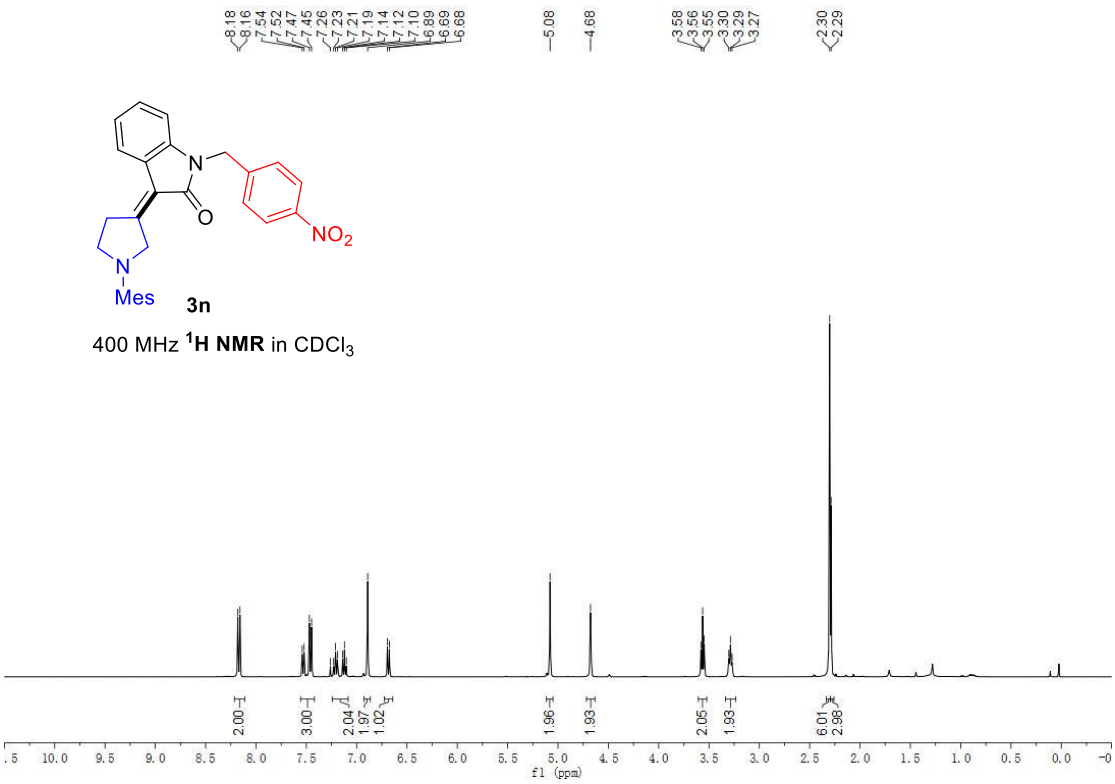

Cl
N
Bn
O
N
Mes
3l
100 MHz 13C NMR in d6-Acetone
f1 (ppm)


Br
N
Bn
O
N
Mes
3m
400 MHz 1H NMR in CDCl3
f1 (ppm)



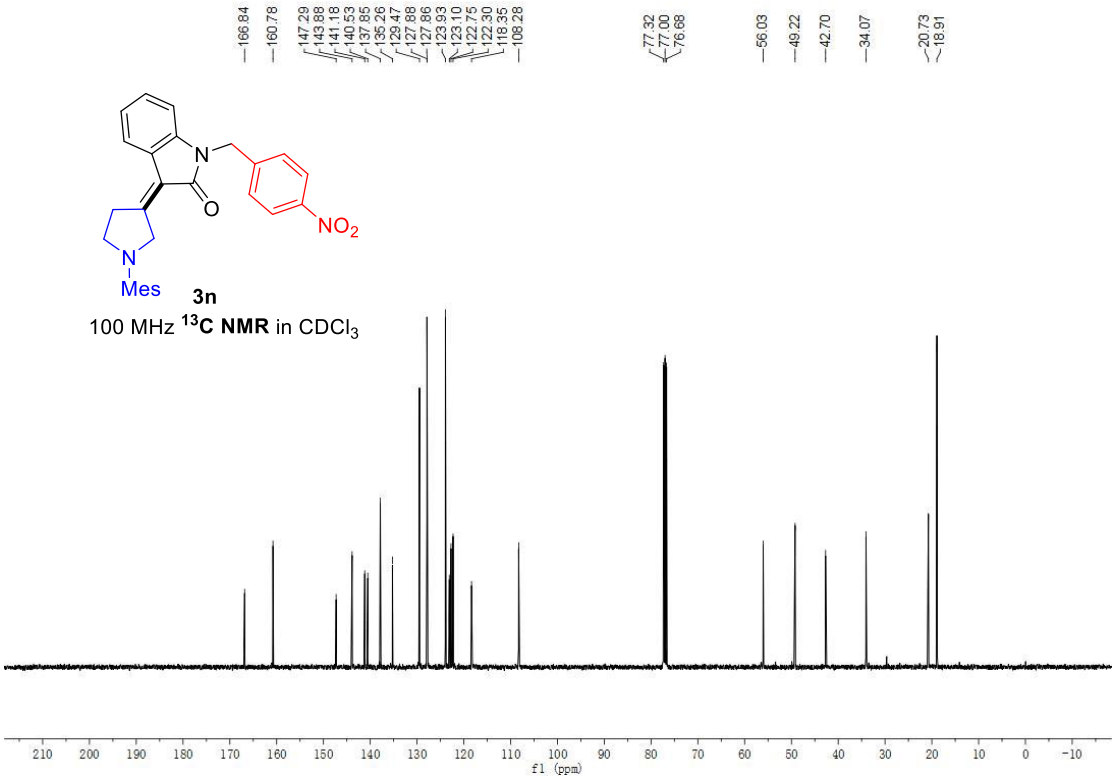
3m

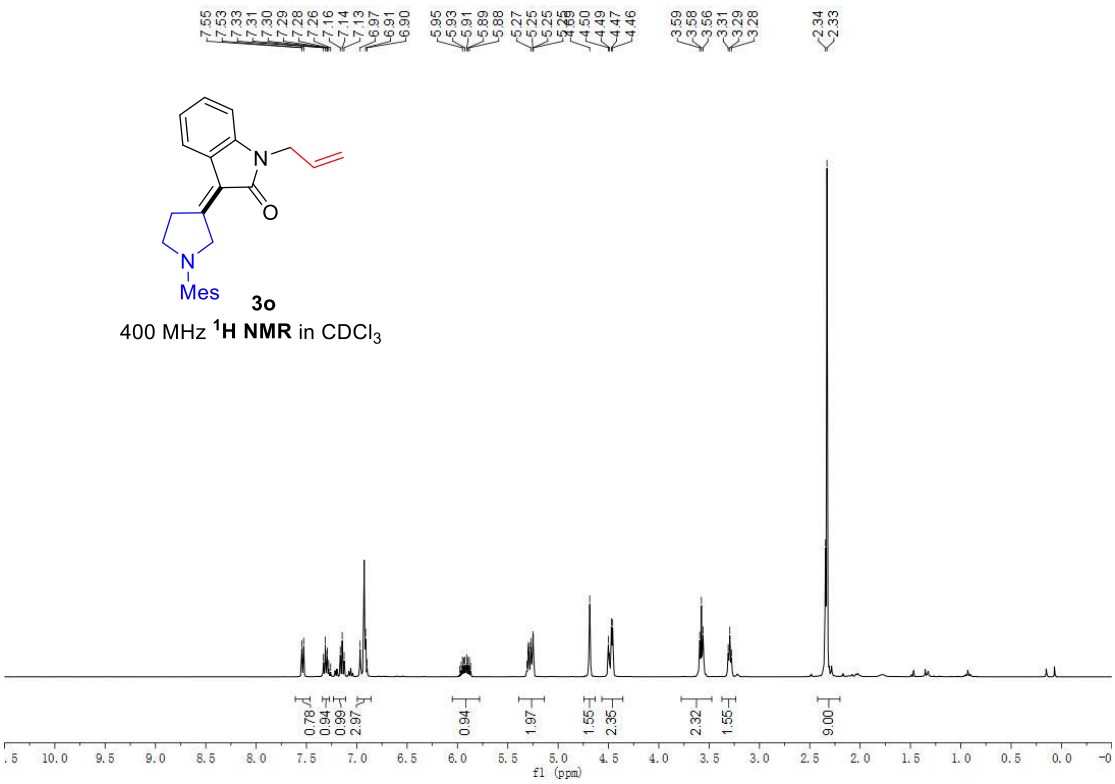
100 MHz ^{13}**C NMR** in $CDCl_3$

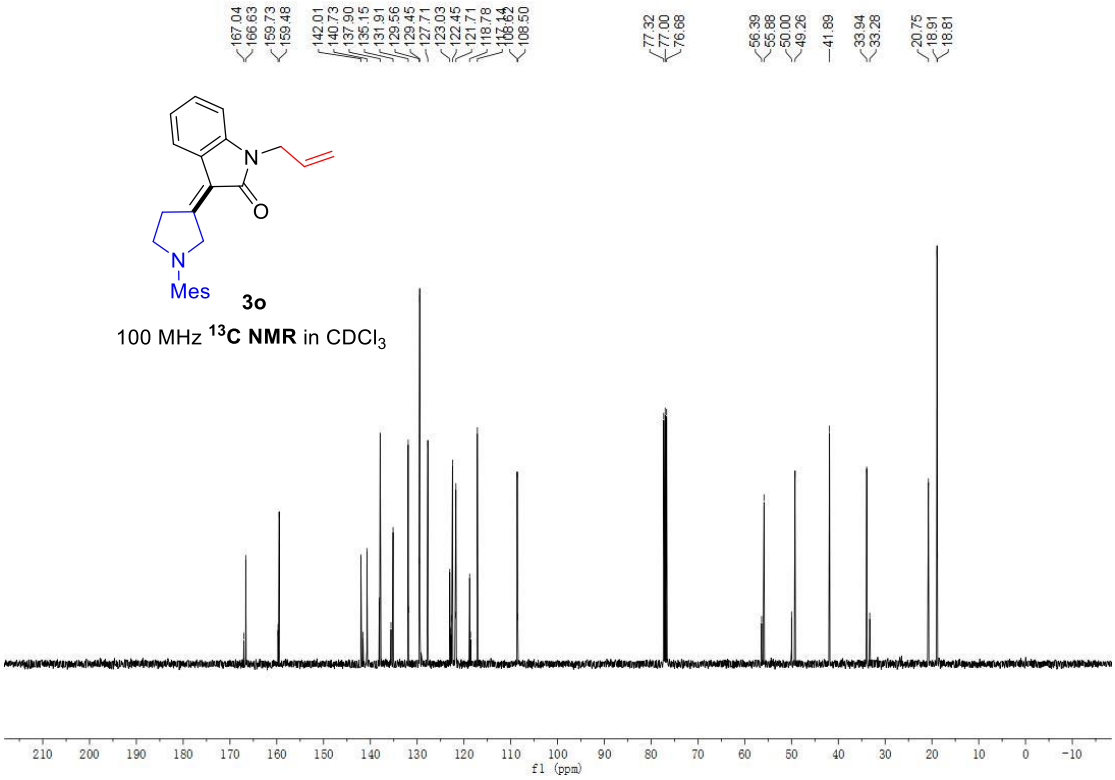


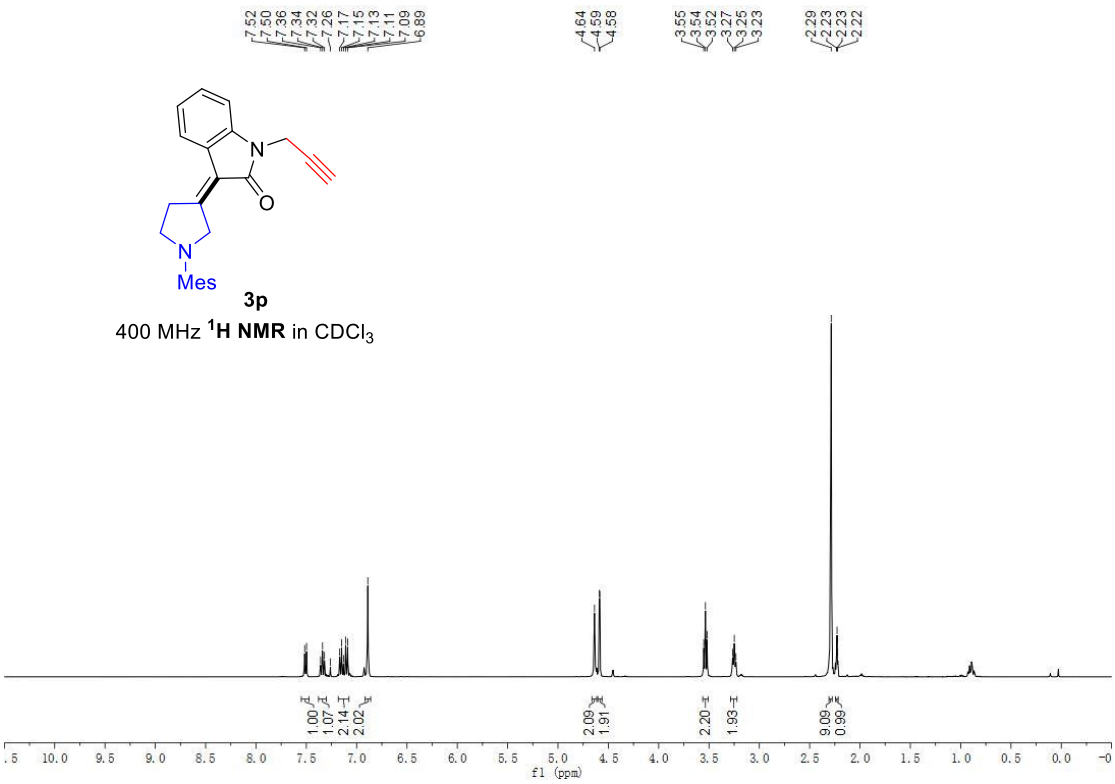
3n

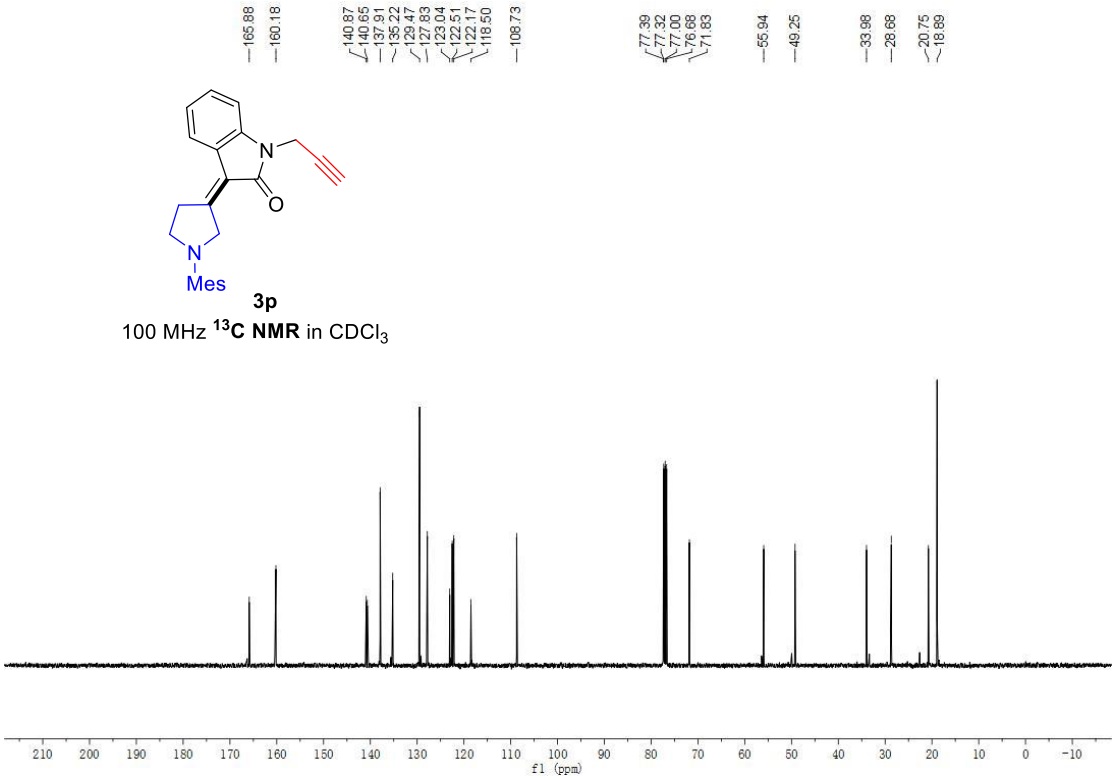
400 MHz ^{1}**H NMR** in $CDCl_3$


166.84
160.78
147.29
143.88
141.18
140.53
137.85
135.26
129.47
127.88
127.86
123.93
123.10
122.75
122.30
118.35
108.28
77.32
77.00
76.68
56.03
49.22
42.70
34.07
20.73
18.91
N
O
NO2
N
Mes
3n
100 MHz 13C NMR in CDCl3
f1 (ppm)


7.55
7.53
7.33
7.31
7.30
7.29
7.28
7.26
7.16
7.14
7.13
6.97
6.91
6.90
5.95
5.93
5.91
5.89
5.88
5.27
5.25
5.25
4.50
4.49
4.47
4.46
3.59
3.58
3.56
3.31
3.29
3.28
2.34
2.33
N
O
N
Mes
3o
400 MHz 1H NMR in CDCl3
0.78
0.94
0.99
2.97
0.94
1.97
1.55
2.35
2.32
1.55
9.00
f1 (ppm)

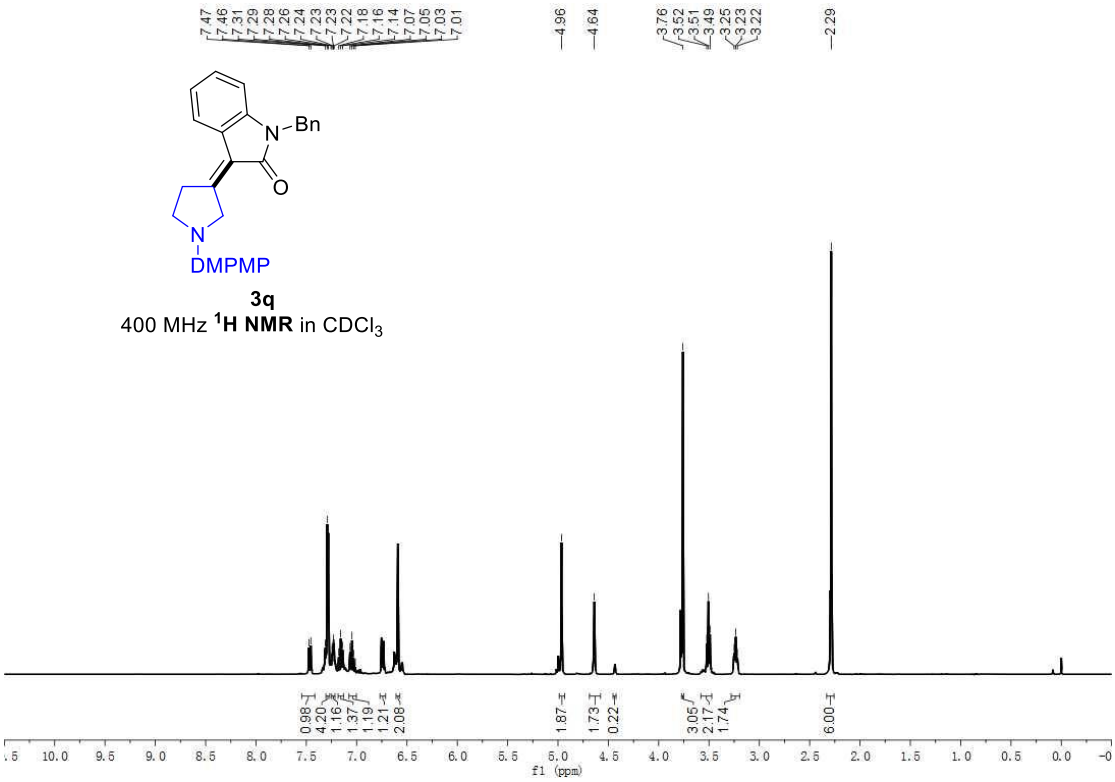

167.04
166.63
159.73
159.48
142.01
140.73
137.90
135.15
131.91
129.56
129.45
127.71
123.03
122.45
121.71
118.78
108.62
108.50
77.32
77.00
76.68
56.39
55.88
50.00
49.26
41.89
33.94
33.28
20.75
18.91
18.81
N
O
N
Mes
3o
100 MHz 13C NMR in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.52
7.50
7.36
7.34
7.32
7.26
7.17
7.15
7.13
7.11
7.09
6.89
4.64
4.59
4.58
3.55
3.54
3.52
3.27
3.25
3.23
2.29
2.23
2.23
2.22
N
O
N
Mes
3p
400 MHz 1H NMR in CDCl3
1.00
1.07
2.14
2.02
2.09
1.91
2.20
1.93
9.09
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



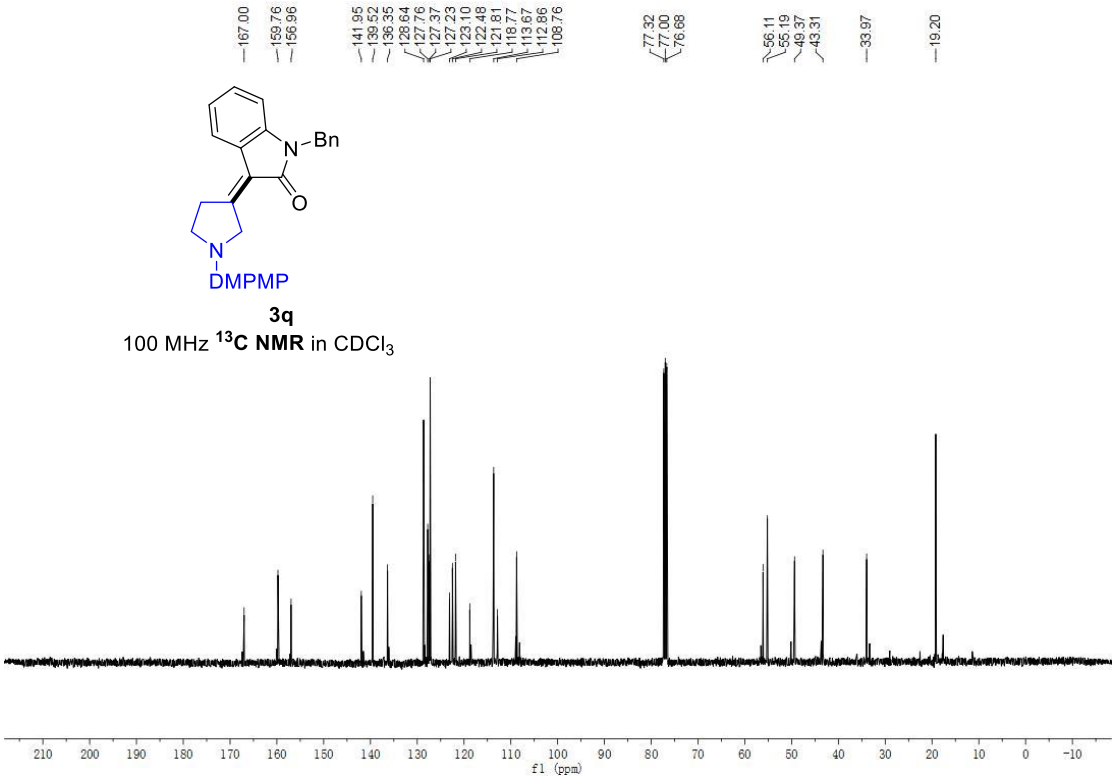
3p

100 MHz **^{13}C NMR** in $CDCl_3$



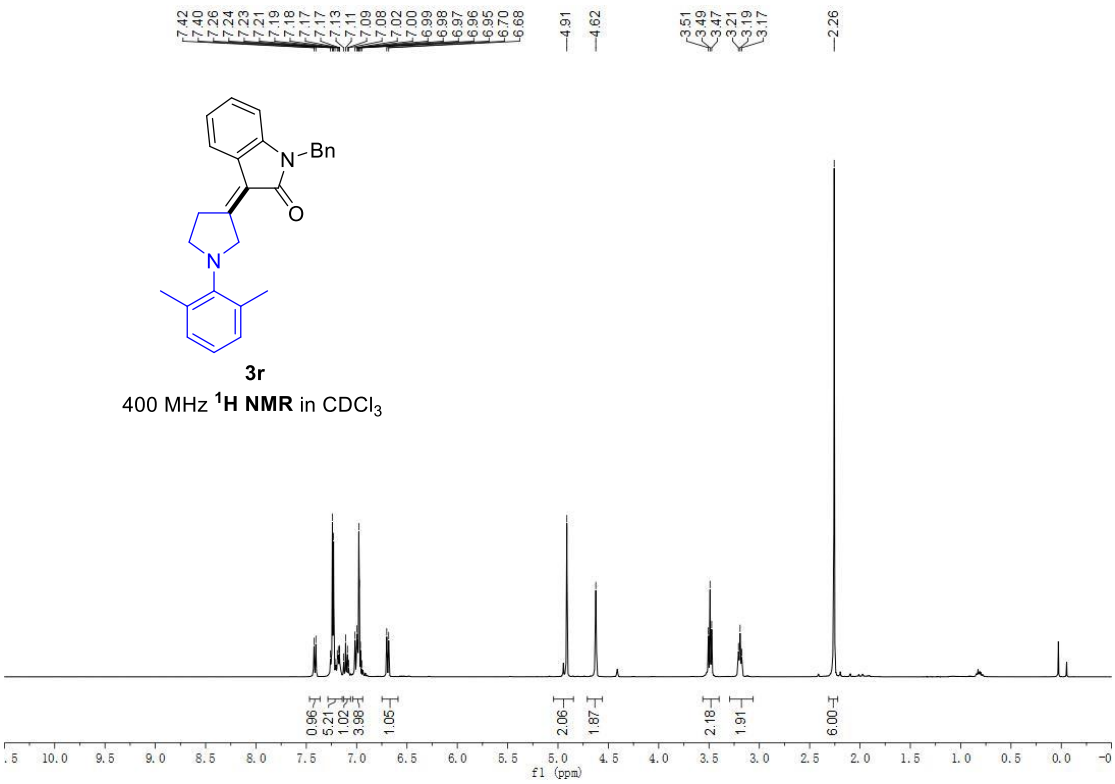
3q

400 MHz **^{1}H NMR** in $CDCl_3$



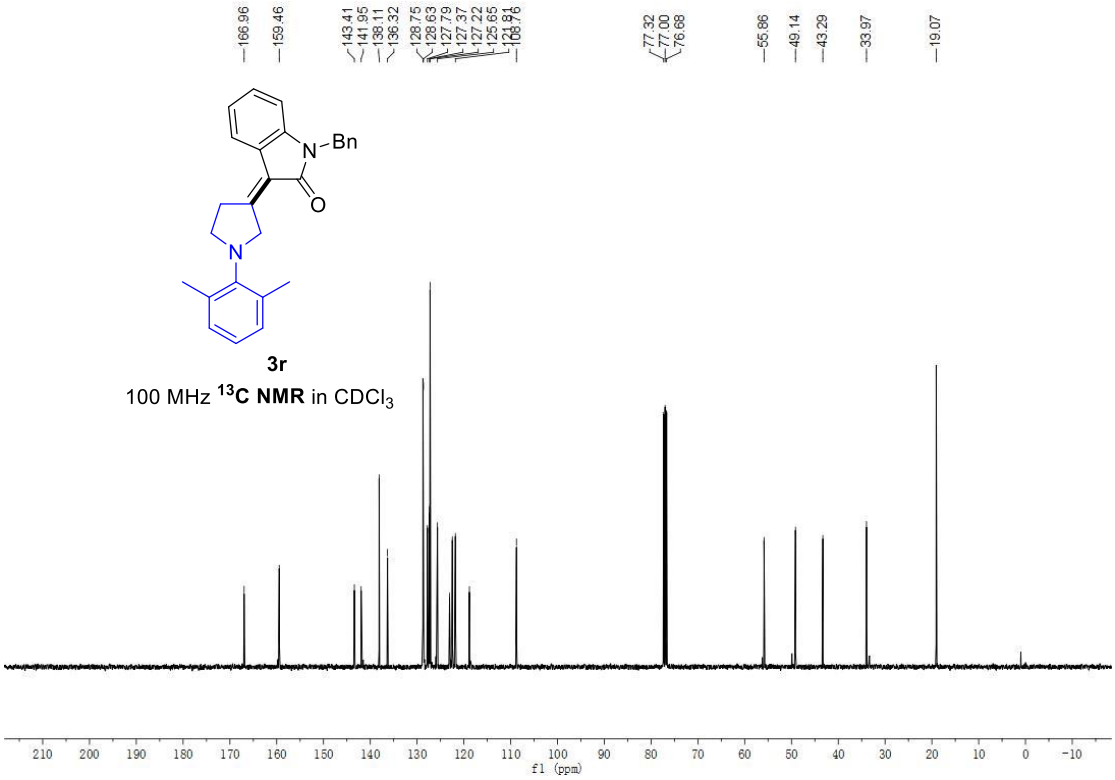
3q

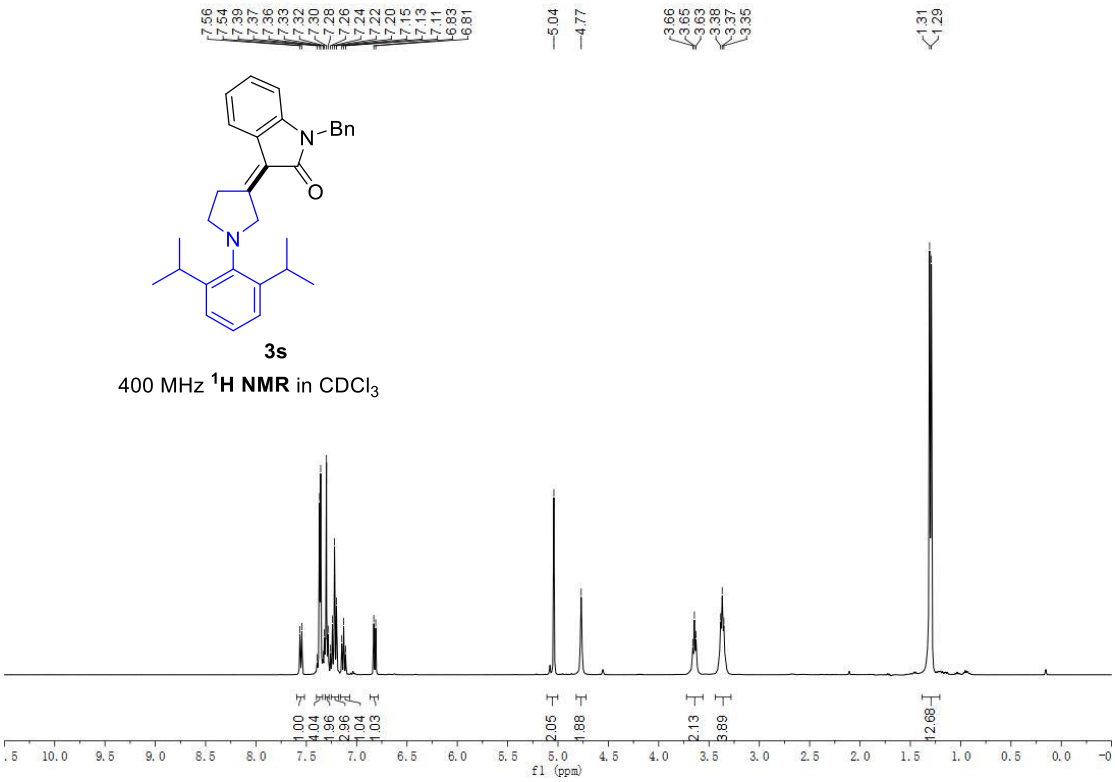
100 MHz ^{13}**C NMR** in $CDCl_3$



3r

400 MHz ^{1}**H NMR** in $CDCl_3$


166.96
159.46
143.41
141.95
138.11
136.32
128.75
128.63
127.79
127.37
127.22
125.65
123.91
108.76
77.32
77.00
76.68
55.86
49.14
43.29
33.97
19.07
N-Bn
O
N
3r
100 MHz 13C NMR in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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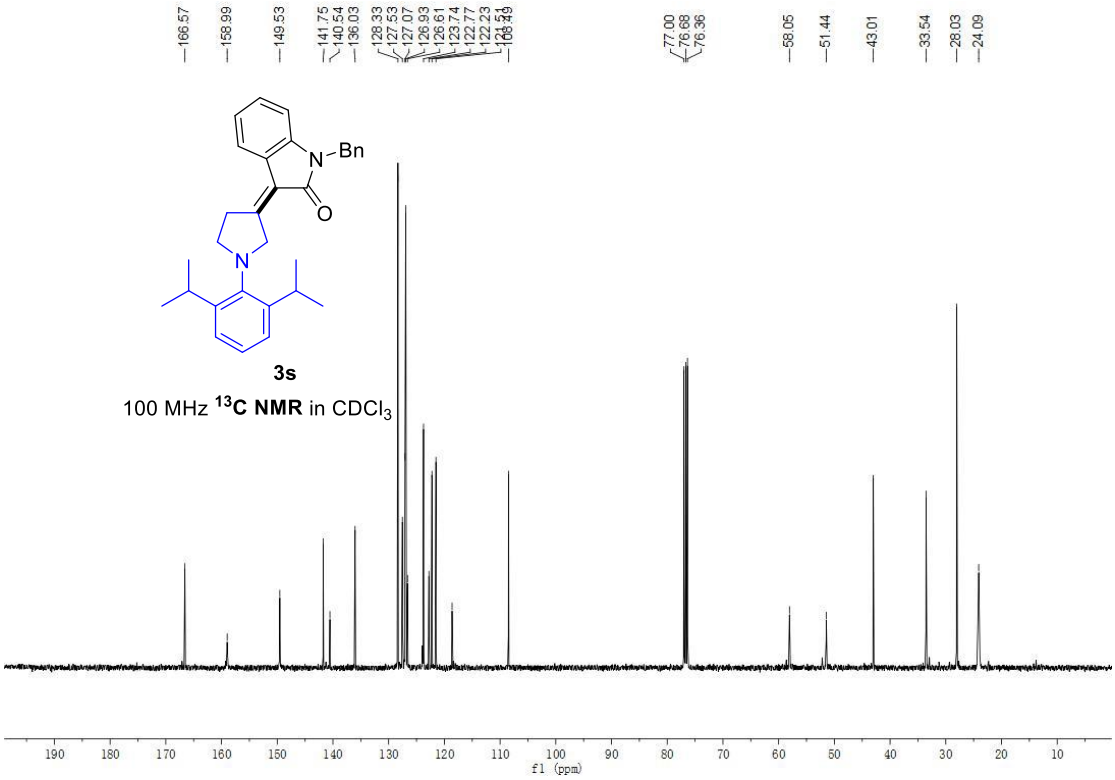
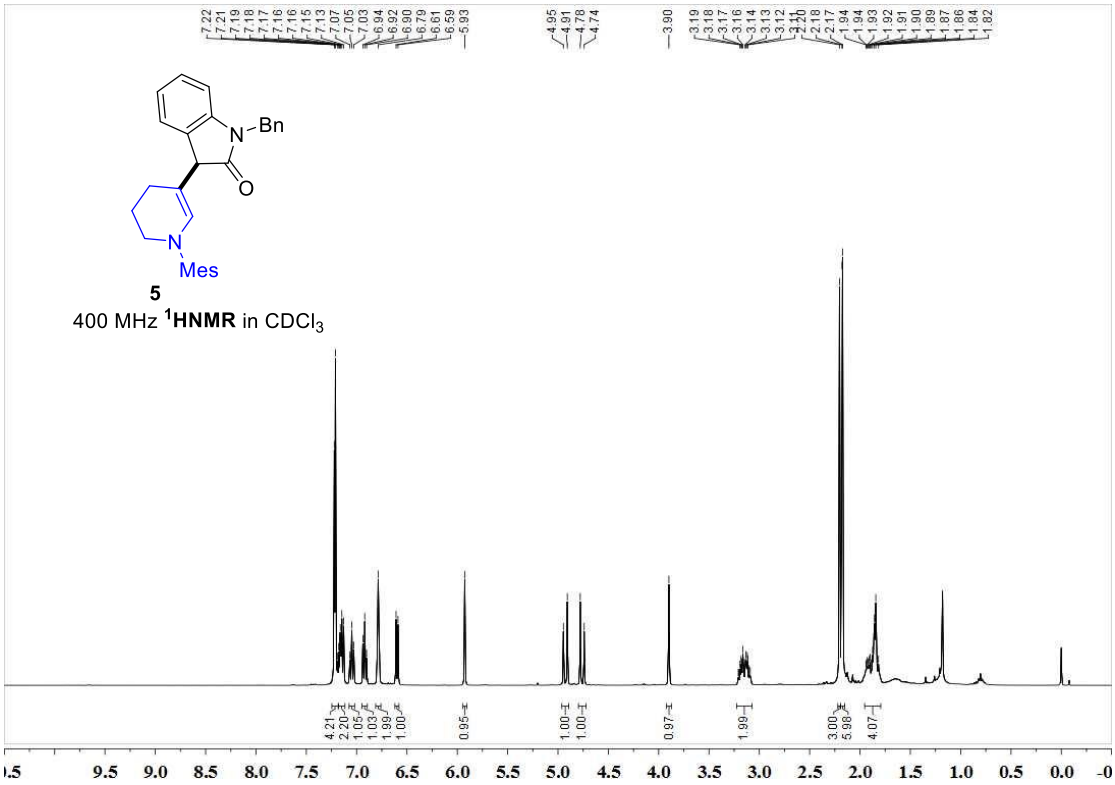
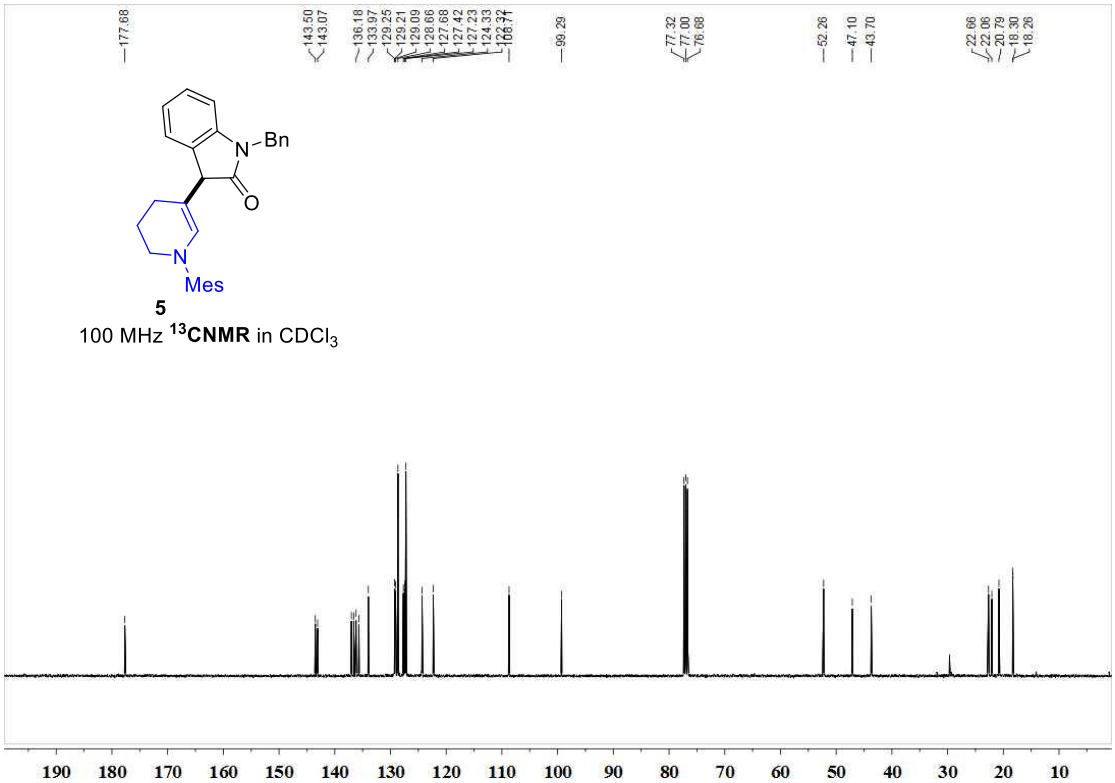
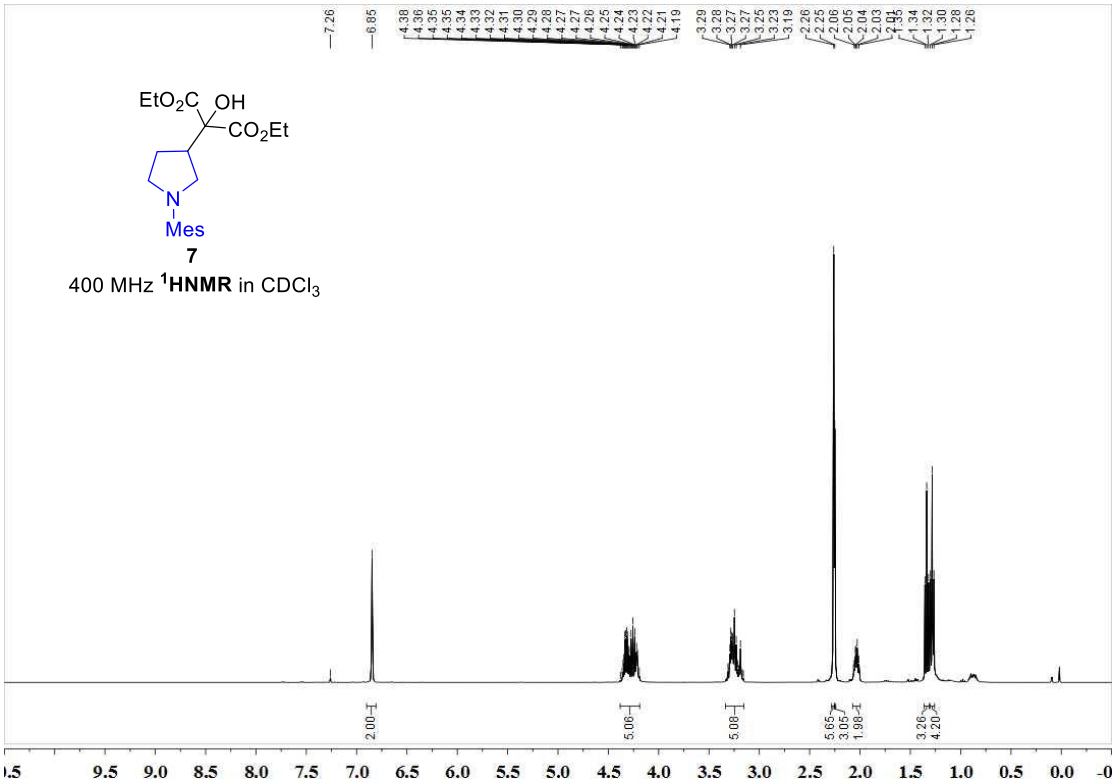
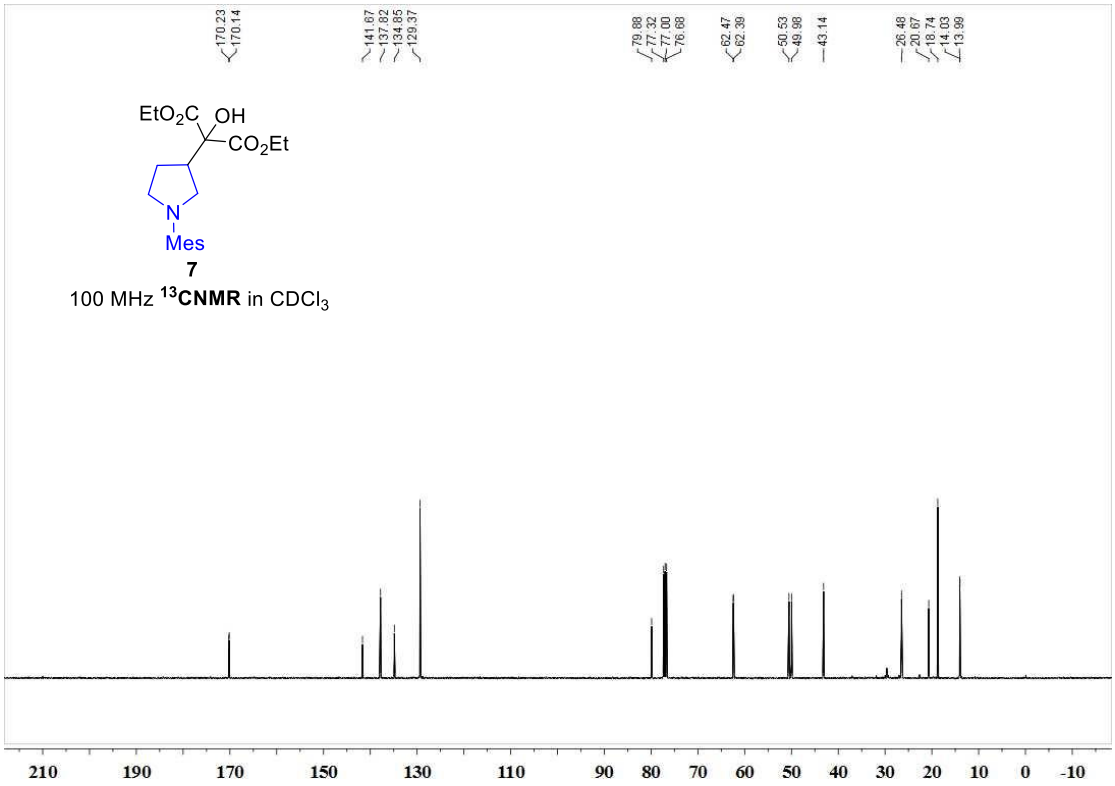
7.54
7.39
7.37
7.36
7.33
7.32
7.30
7.28
7.26
7.24
7.22
7.20
7.15
7.13
7.11
6.83
6.81
5.04
4.77
3.66
3.65
3.63
3.39
3.37
3.35
1.31
1.29
N-Bn
O
N
3s
400 MHz 1H NMR in CDCl3
1.00
4.04
1.96
2.96
1.04
1.03
2.05
1.88
2.13
3.89
12.68
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

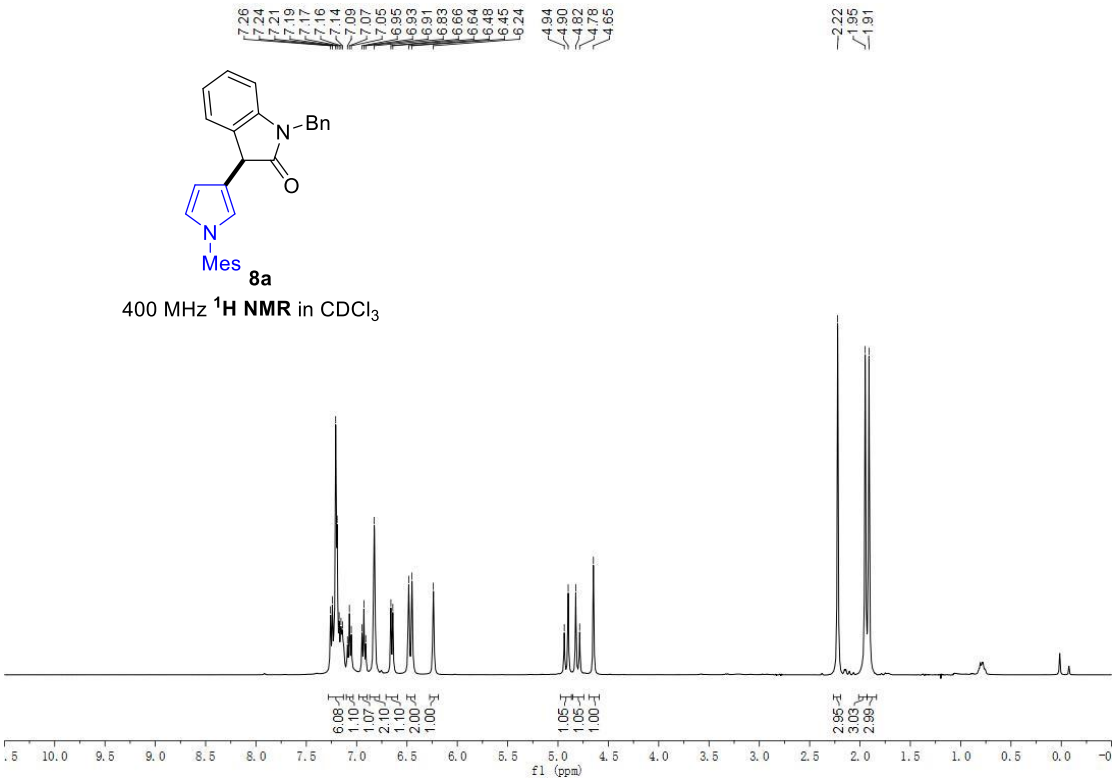

166.57
158.99
149.53
141.75
140.54
136.03
128.33
127.53
127.07
126.93
126.61
123.74
122.77
122.23
121.51
108.49
77.00
76.68
76.36
58.05
51.44
43.01
33.54
28.03
24.09
N-Bn
O
N
3s
100 MHz 13C NMR in CDCl3
f1 (ppm)

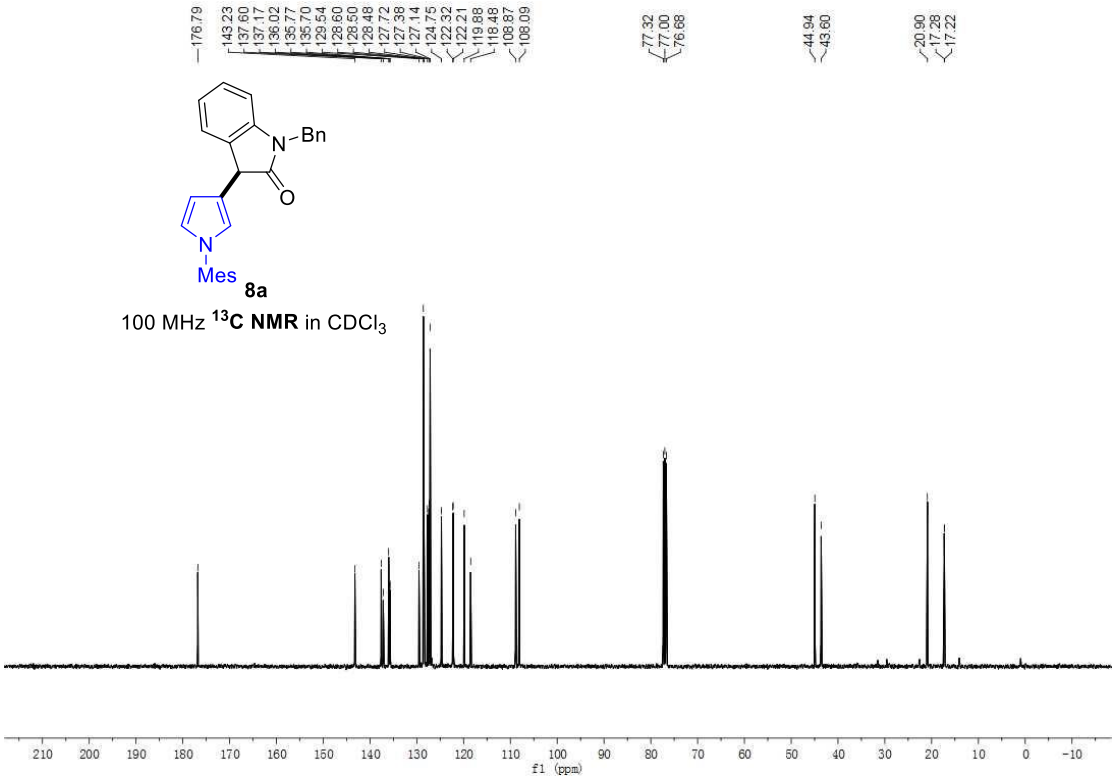

N-Bn
O
N
Mes
5
400 MHz 1HNMR in CDCl3

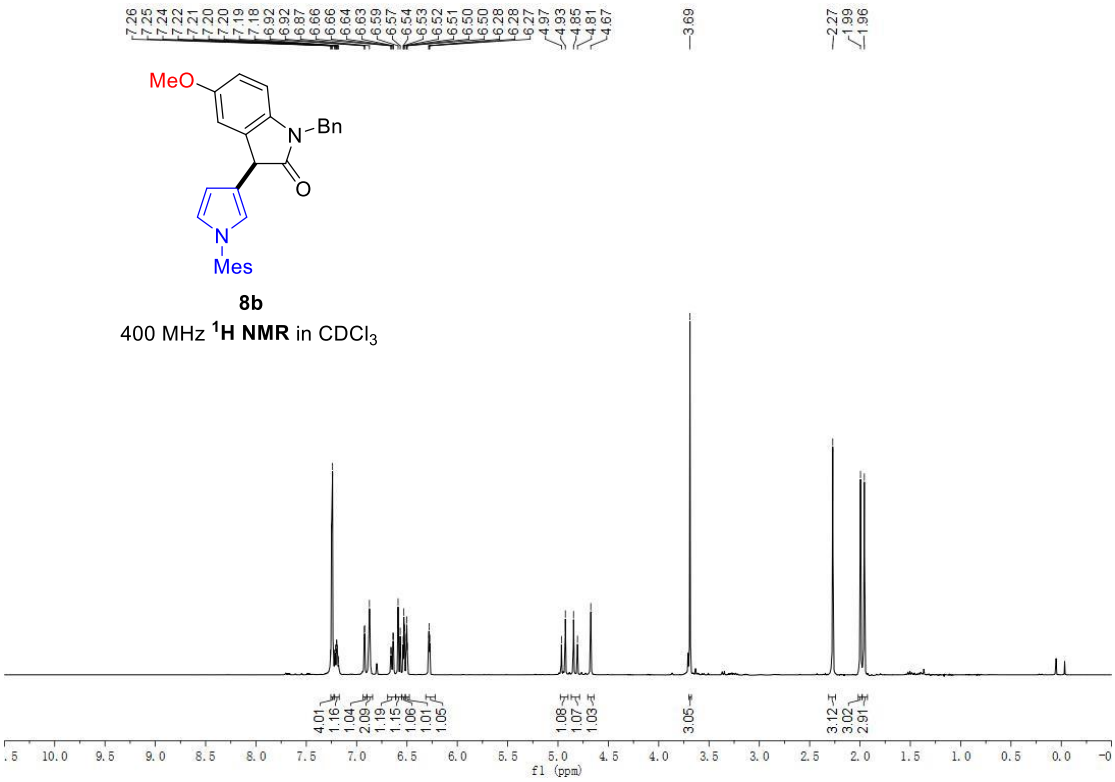

177.68
143.50
143.07
136.18
133.97
129.25
129.21
129.09
128.66
127.68
127.42
127.23
124.33
122.32
108.71
99.29
77.32
77.00
76.68
52.26
47.10
43.70
22.66
22.06
20.79
18.30
18.26
N
Bn
O
N
Mes
5
100 MHz 13CNMR in CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

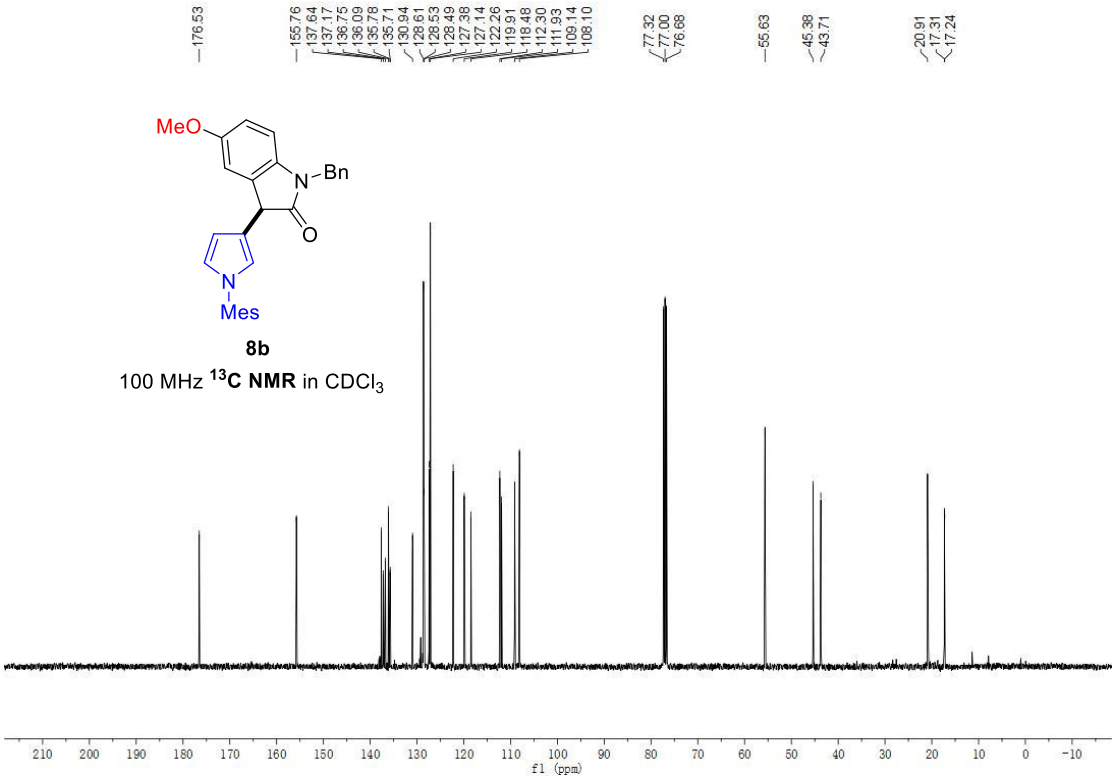

7.26
6.85
4.38
4.36
4.35
4.35
4.34
4.33
4.32
4.31
4.30
4.29
4.28
4.27
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.19
3.29
3.28
3.27
3.27
3.25
3.23
3.19
2.26
2.25
2.06
2.05
2.04
2.03
2.01
1.35
1.34
1.32
1.30
1.28
1.26
EtO2C
OH
CO2Et
N
Mes
7
400 MHz 1HNMR in CDCl3
2.00
5.06
5.08
5.65
3.05
1.98
3.26
4.20
9.5 9.0 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

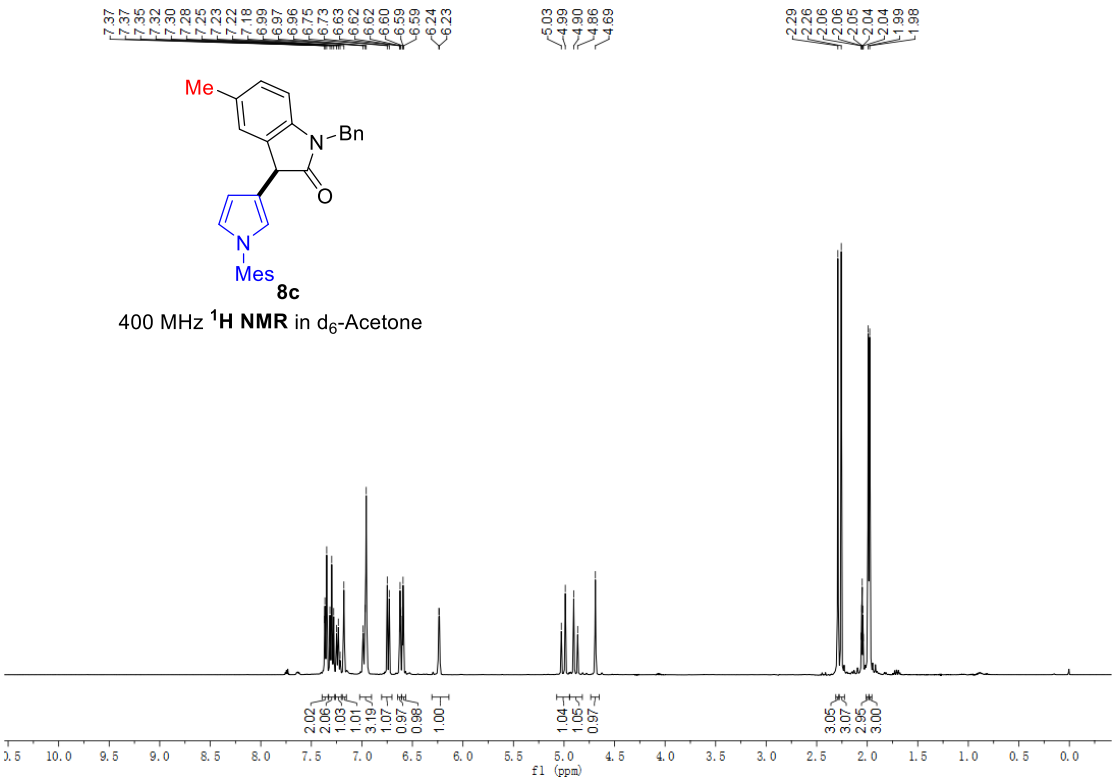

170.23
170.14
141.67
137.82
134.85
129.37
79.88
77.32
77.00
76.68
62.47
62.39
50.53
49.98
43.14
26.48
20.67
18.74
14.03
13.99
EtO2C
OH
CO2Et
N
Mes
7
100 MHz 13CNMR in CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10

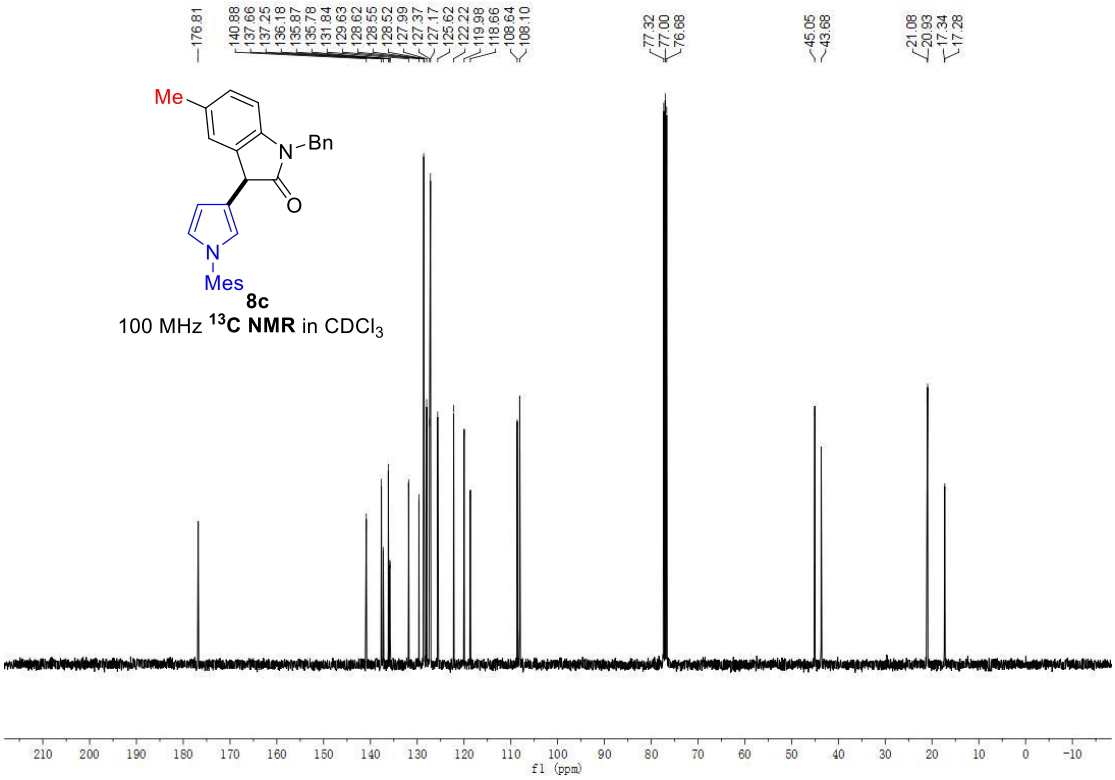

7.26
7.24
7.21
7.19
7.17
7.16
7.14
7.09
7.07
7.05
6.95
6.93
6.91
6.83
6.66
6.64
6.48
6.45
6.24
4.94
4.90
4.82
4.78
4.65
2.22
1.95
1.91
N
Bn
O
N
Mes
8a
400 MHz 1H NMR in CDCl3
6.08
1.10
1.07
2.10
1.10
2.00
1.00
1.05
1.05
1.00
2.95
3.03
2.99
f1 (ppm)

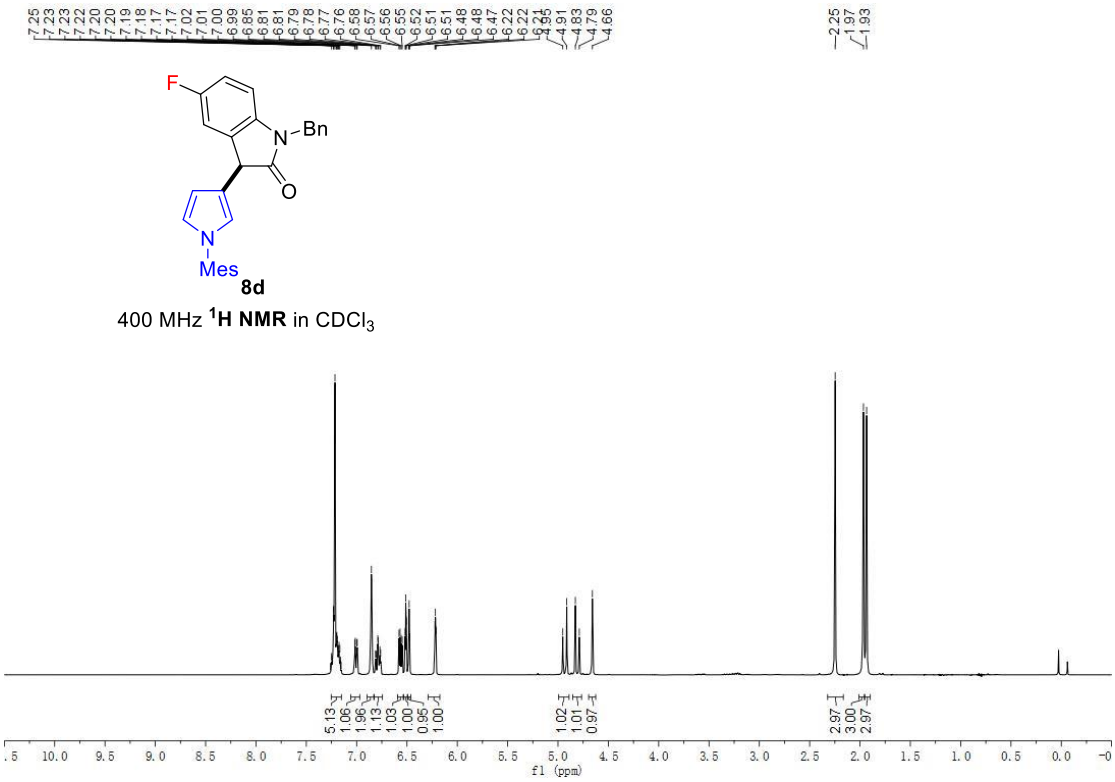

176.79
143.23
137.60
137.17
136.02
135.77
135.70
129.54
128.60
128.50
128.48
127.72
127.38
127.14
124.75
122.32
122.21
119.88
119.48
108.87
108.09
77.32
77.00
76.68
44.94
43.60
20.90
17.28
17.22
N
Bn
O
N
Mes
8a
100 MHz 13C NMR in CDCl3
f1 (ppm)

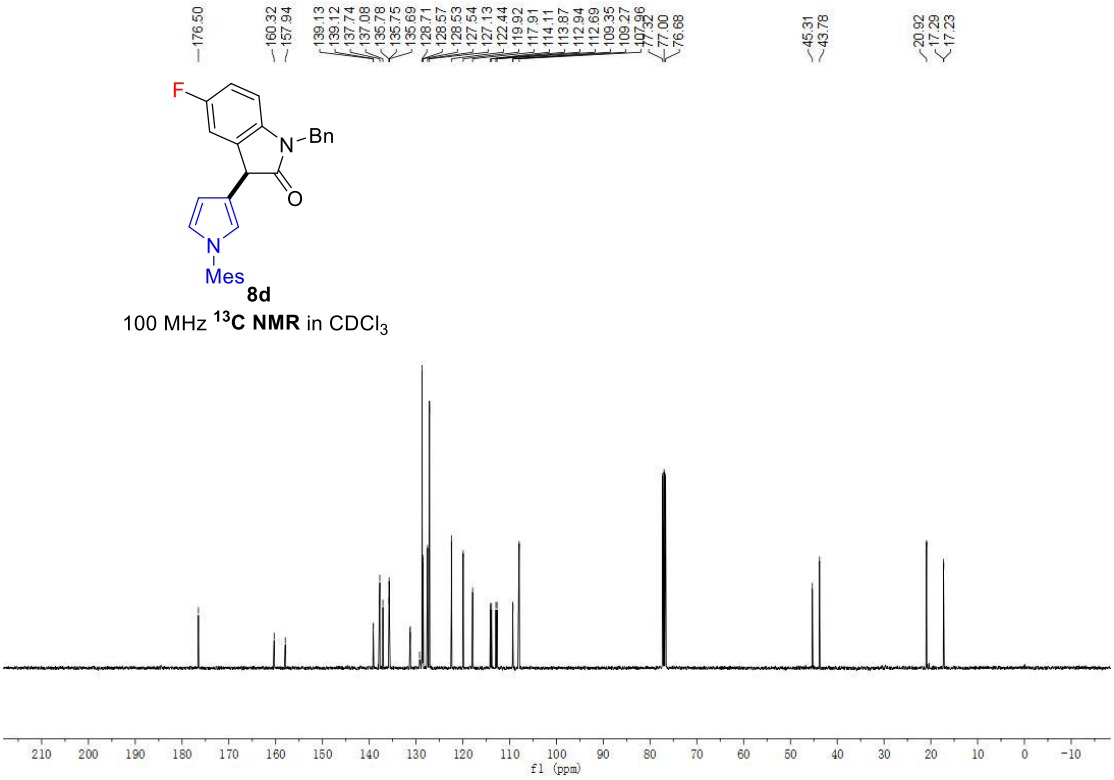

7.26
7.25
7.24
7.22
7.21
7.20
7.20
7.19
7.18
6.92
6.92
6.87
6.66
6.66
6.64
6.63
6.59
6.57
6.54
6.53
6.52
6.51
6.50
6.50
6.28
6.28
6.27
4.97
4.93
4.85
4.81
4.67
3.69
2.27
1.99
1.96
MeO
N
Bn
O
N
Mes
8b
400 MHz 1H NMR in CDCl3
4.01
1.16
1.04
2.09
1.19
1.15
1.06
1.01
1.05
1.08
1.07
1.03
3.05
3.12
3.02
2.91
f1 (ppm)


MeO
N
Bn
O
N
Mes
8b
100 MHz 13C NMR in CDCl3
f1 (ppm)

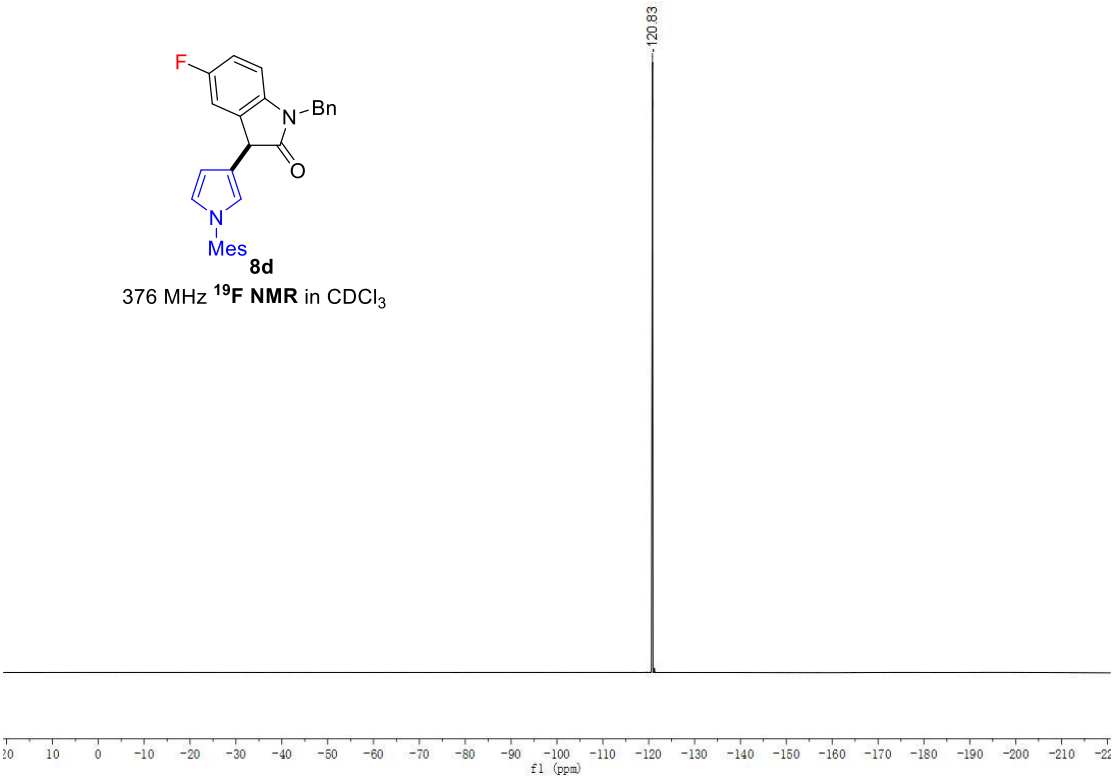

Me
N
Bn
O
N
Mes
8c
400 MHz 1H NMR in d6-Acetone
f1 (ppm)


Me
N
Bn
O
N
Mes
8c
100 MHz 13C NMR in CDCl3
f1 (ppm)

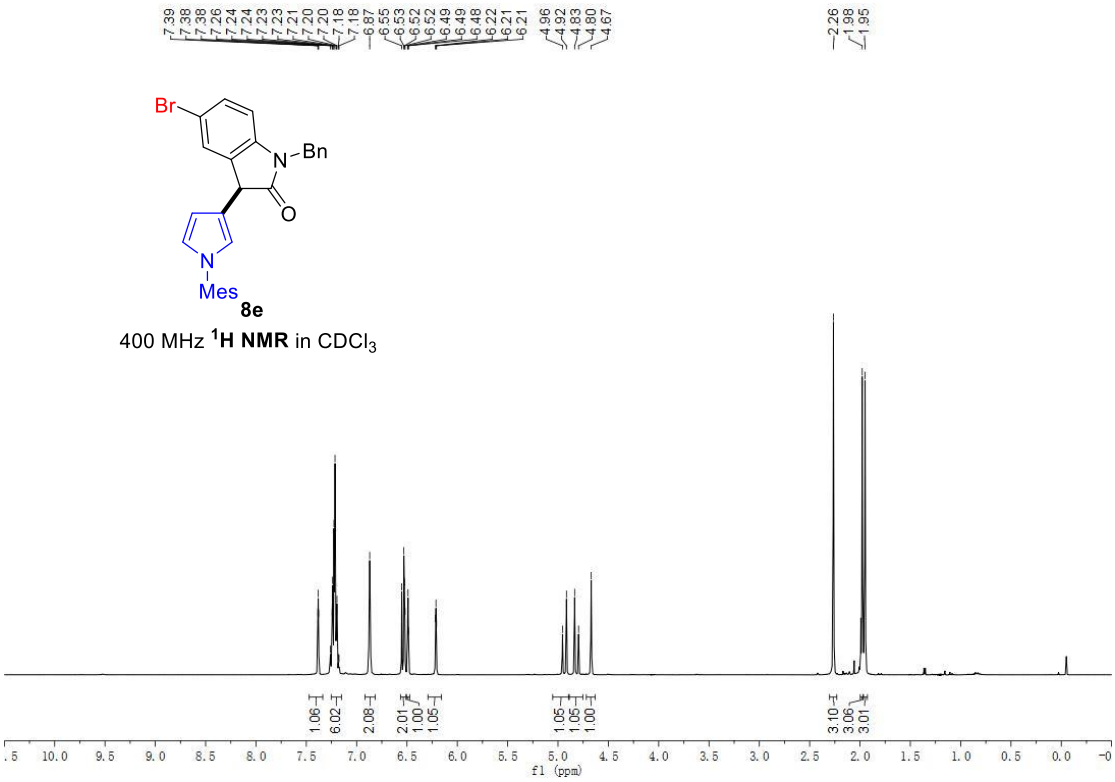

F
N
Bn
O
N
Mes
8d
400 MHz 1H NMR in CDCl3
f1 (ppm)

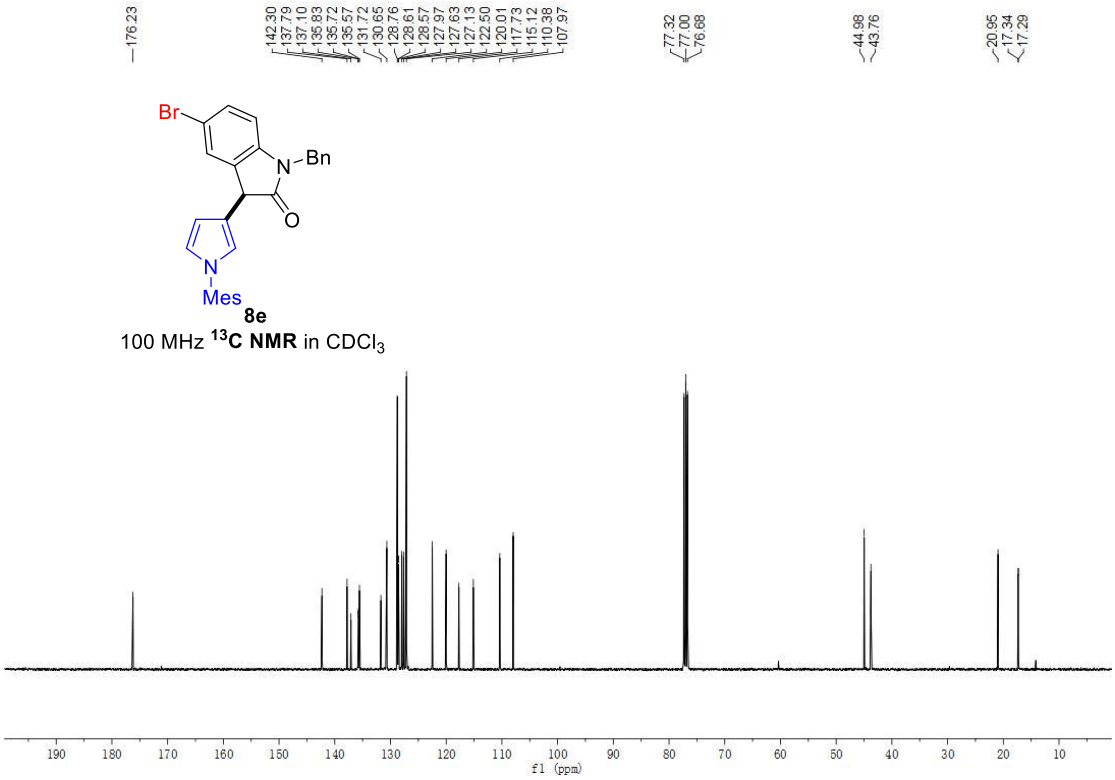


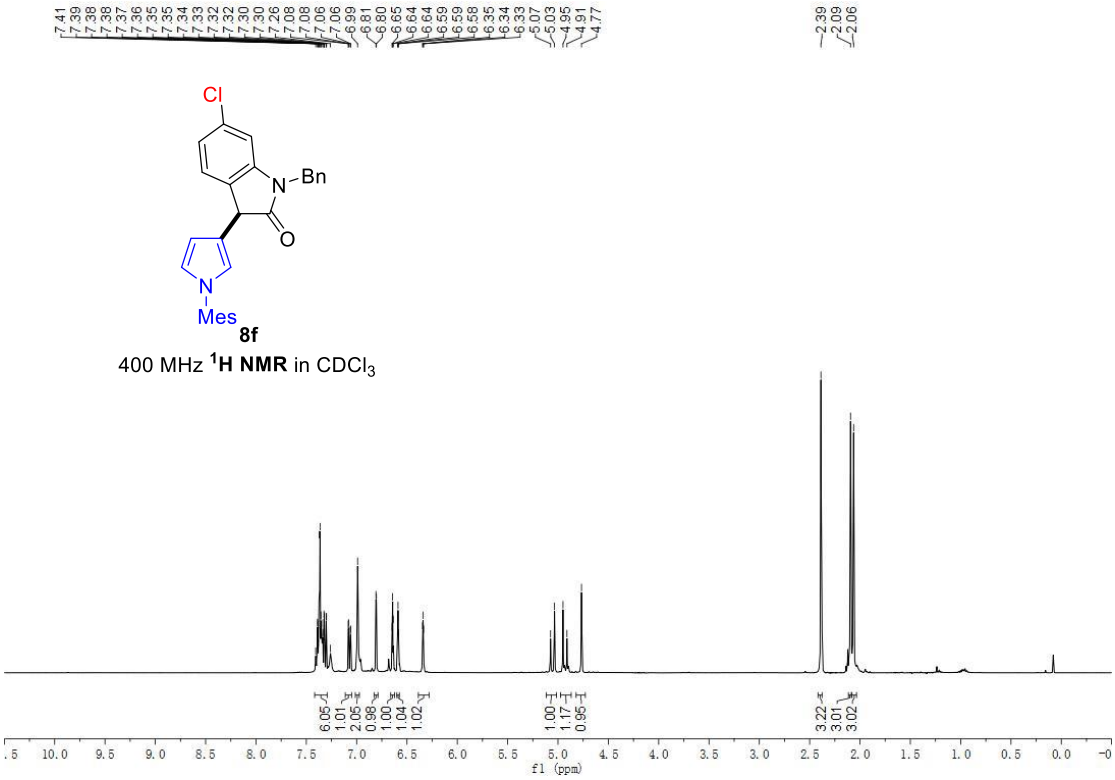
100 MHz ^{13}**C NMR** in $CDCl_3$

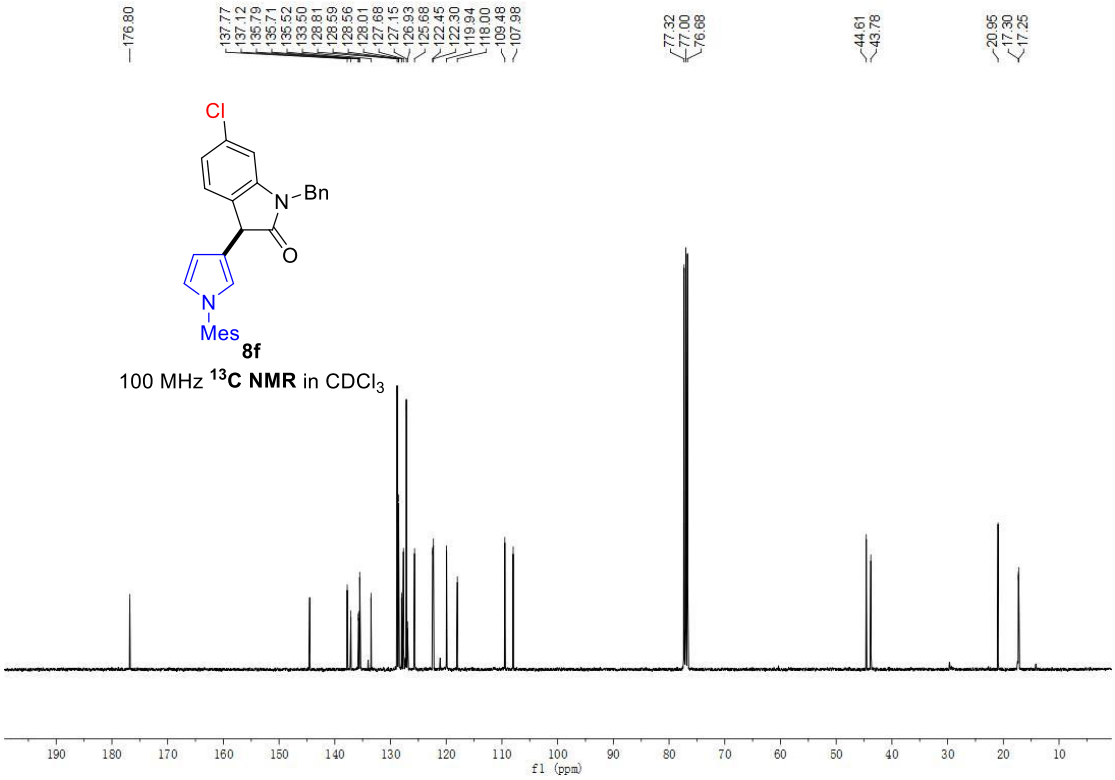


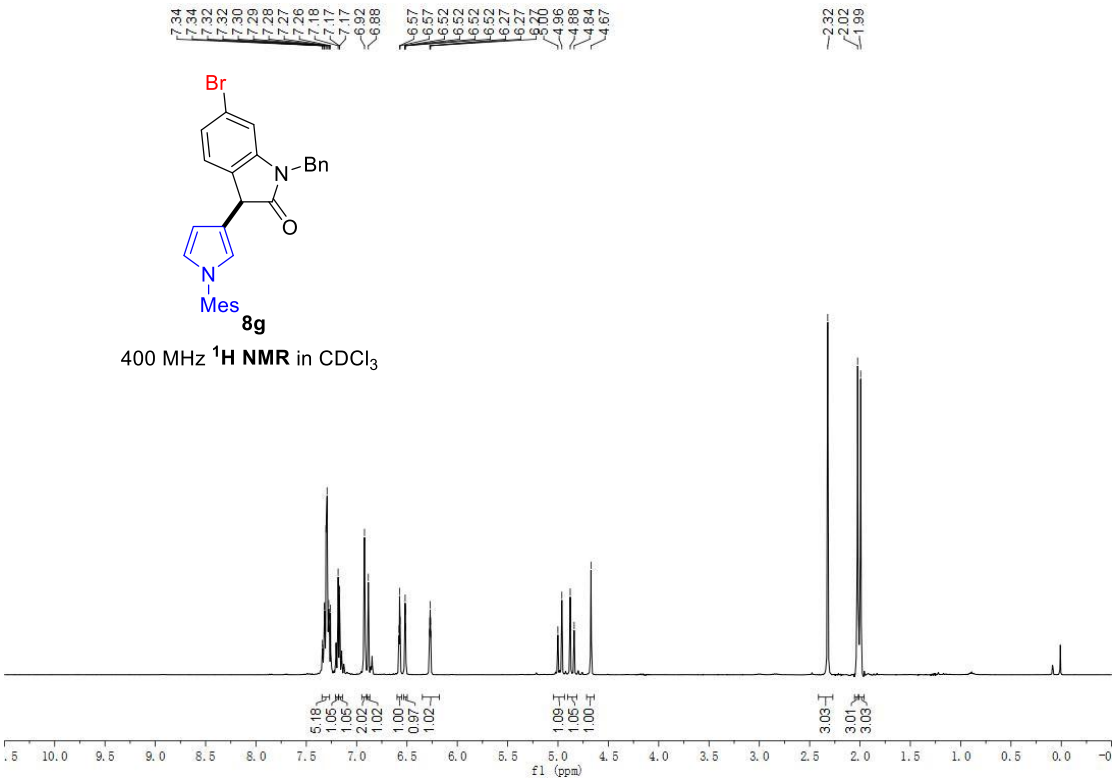
376 MHz ^{19}**F NMR** in $CDCl_3$

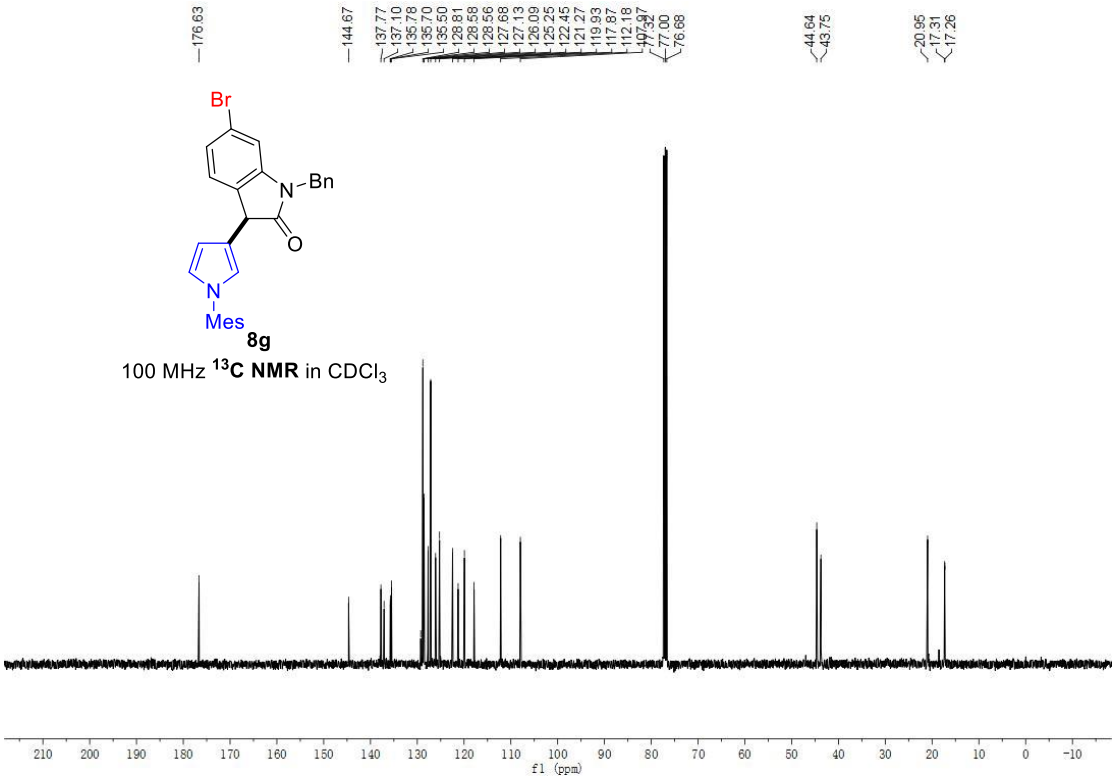

Br
N
Bn
O
N
Mes
8e
400 MHz ¹H NMR in CDCl₃
f1 (ppm)

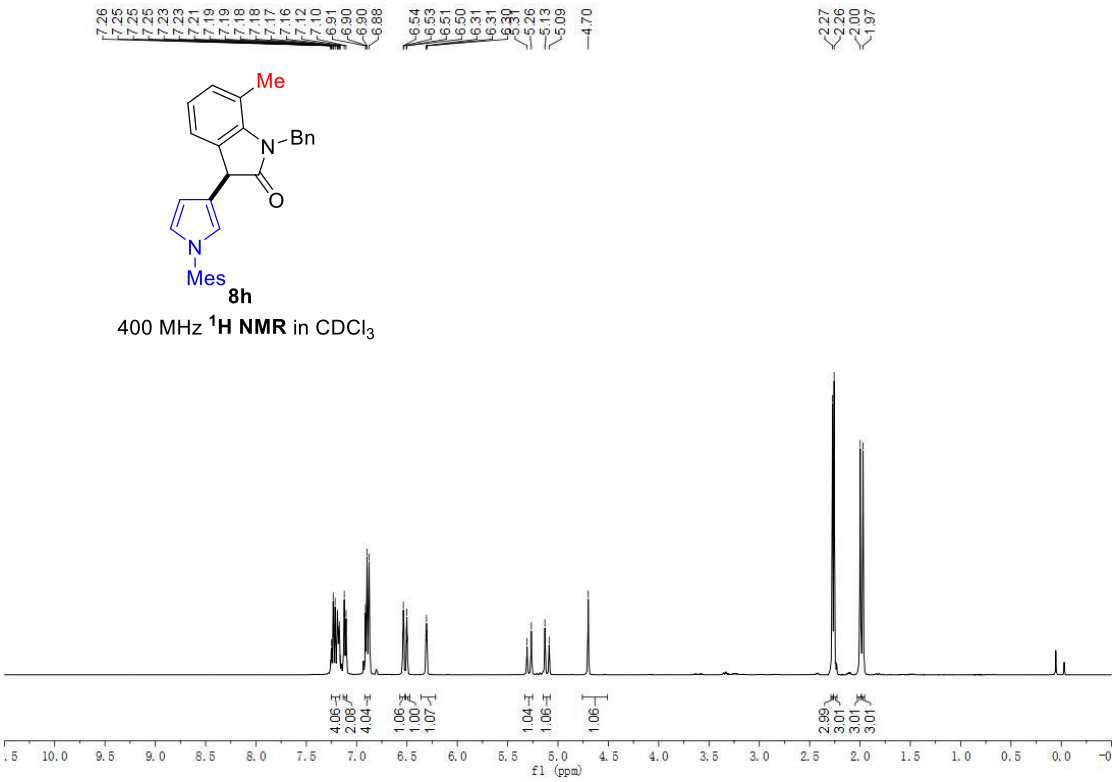

Br
N
Bn
O
N
Mes
8e
100 MHz ¹³C NMR in CDCl₃
f1 (ppm)

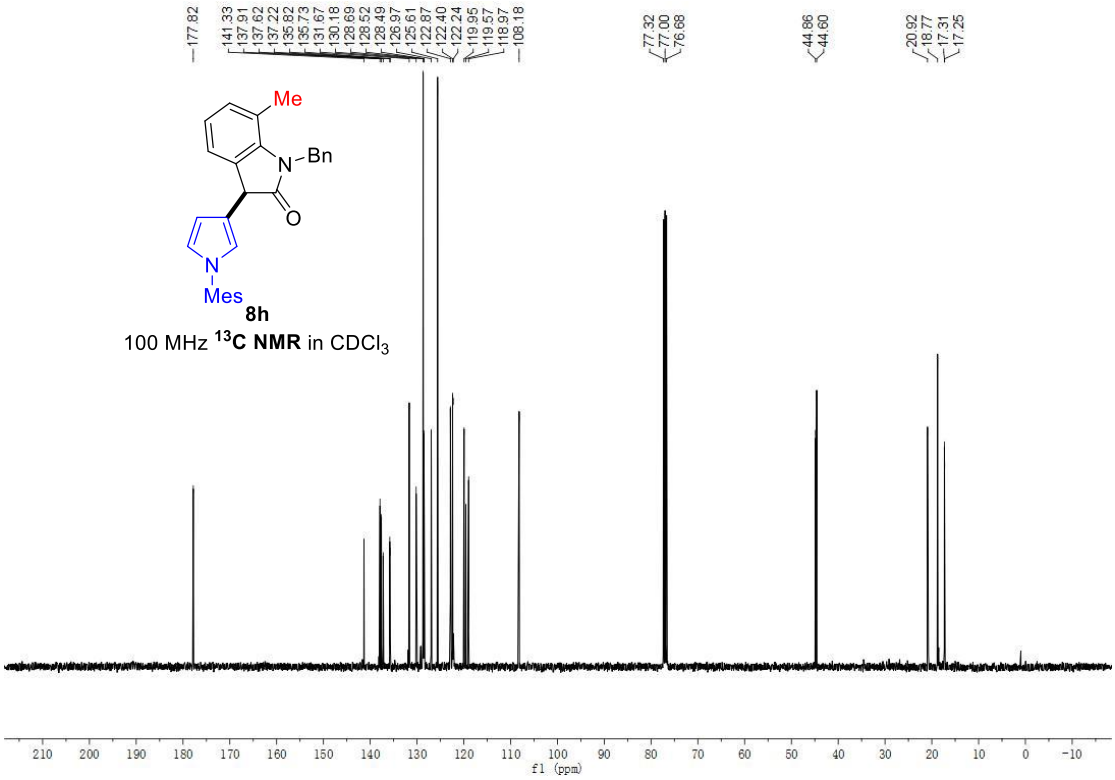

Cl
N
Bn
O
N
Mes
8f
400 MHz ¹H NMR in CDCl₃
f1 (ppm)


Cl
N
Bn
O
N
Mes
8f
100 MHz ¹³C NMR in CDCl₃
f1 (ppm)

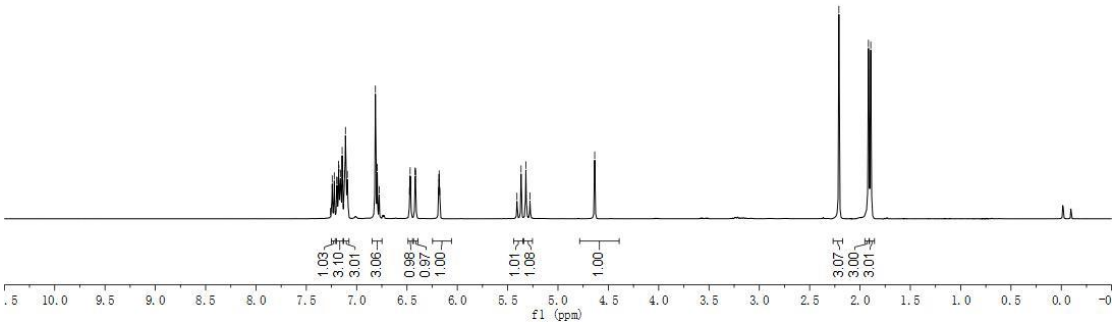

Br
N
Bn
O
N
Mes
8g
400 MHz ¹H NMR in CDCl₃
f1 (ppm)

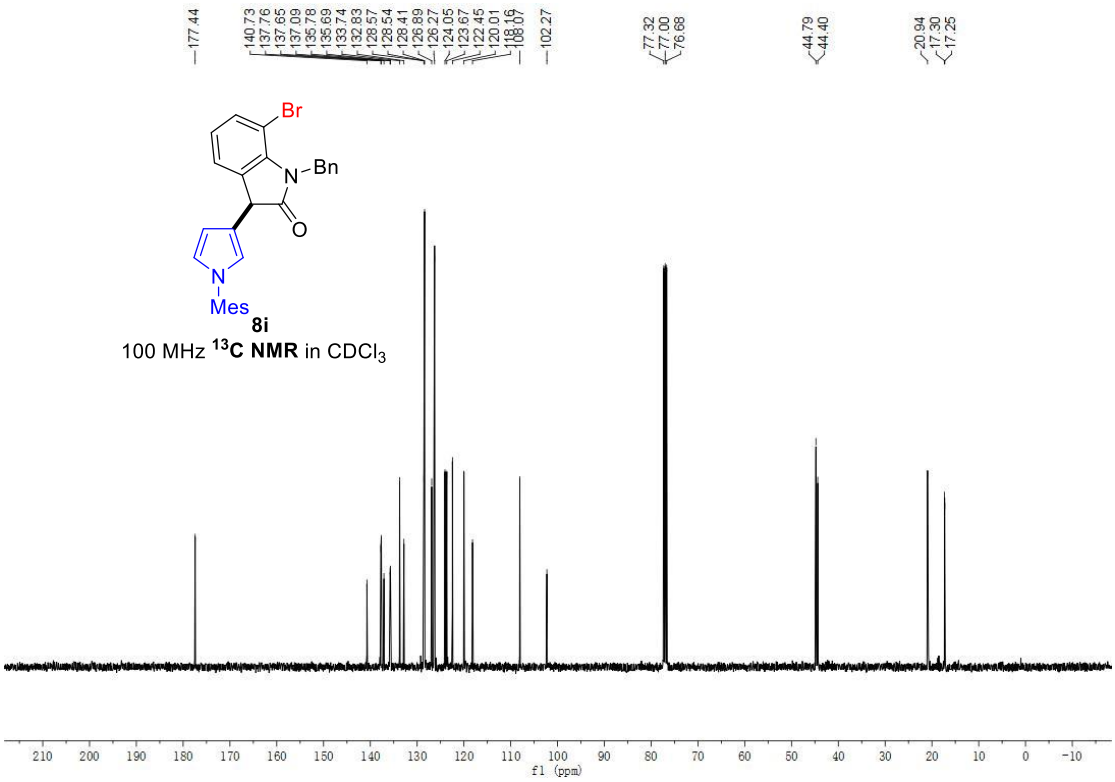

Br
N
Bn
O
N
Mes
8g
100 MHz ¹³C NMR in CDCl₃
f1 (ppm)


Me
N-Bn
O
N
Mes
8h
400 MHz ¹H NMR in CDCl₃
f1 (ppm)

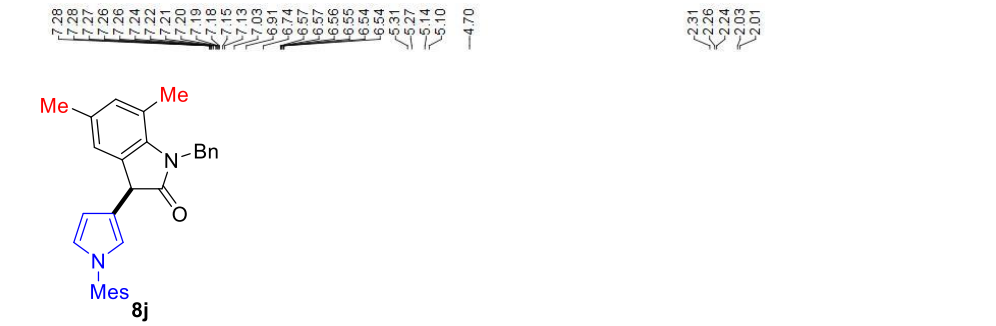

Me
N-Bn
O
N
Mes
8h
100 MHz ¹³C NMR in CDCl₃
f1 (ppm)

400 MHz **^{1}H NMR** in $CDCl_3$

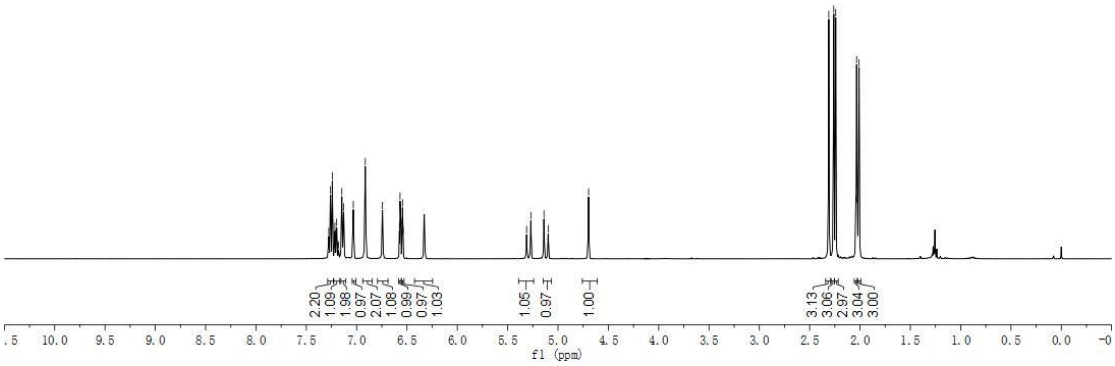


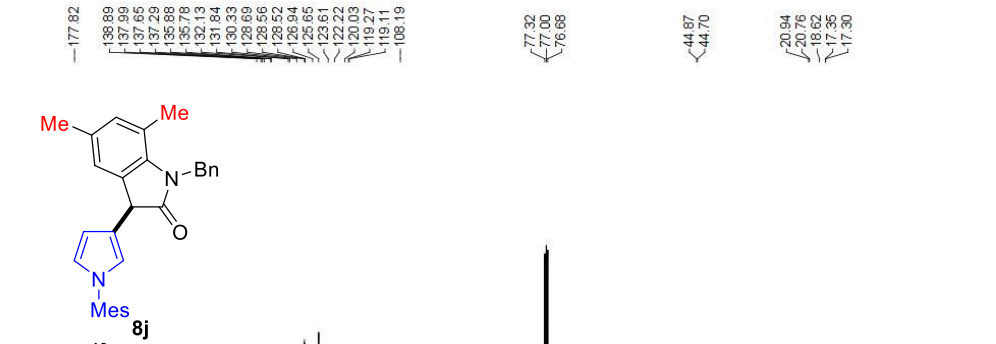


100 MHz **^{13}C NMR** in $CDCl_3$

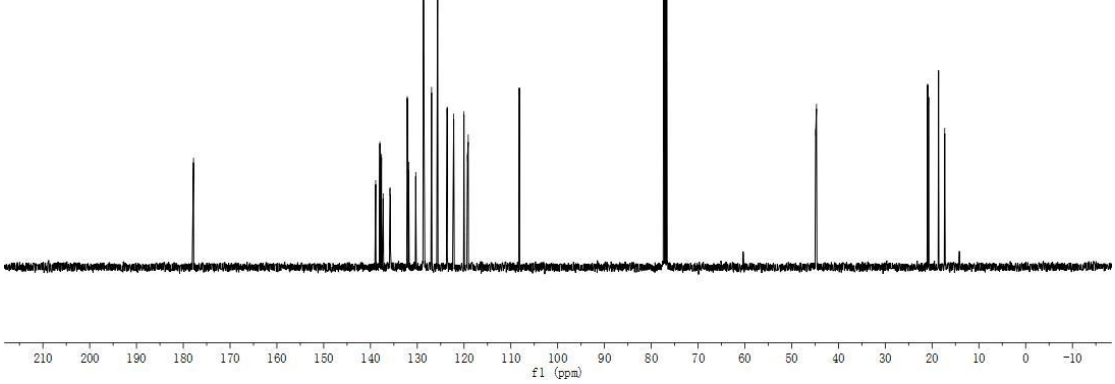


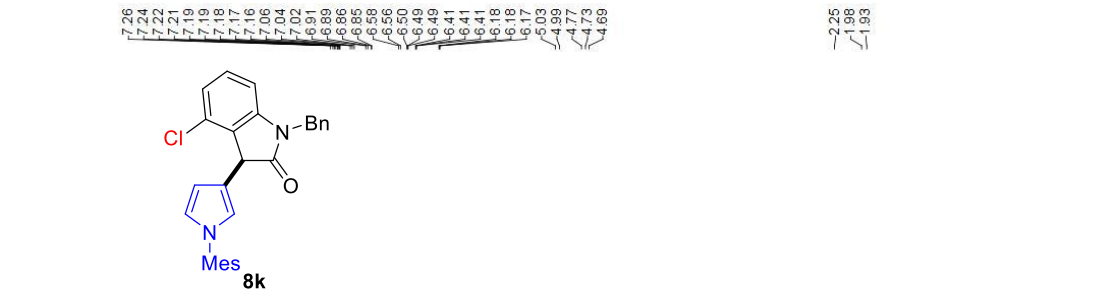
400 MHz **^{1}H NMR** in $CDCl_3$





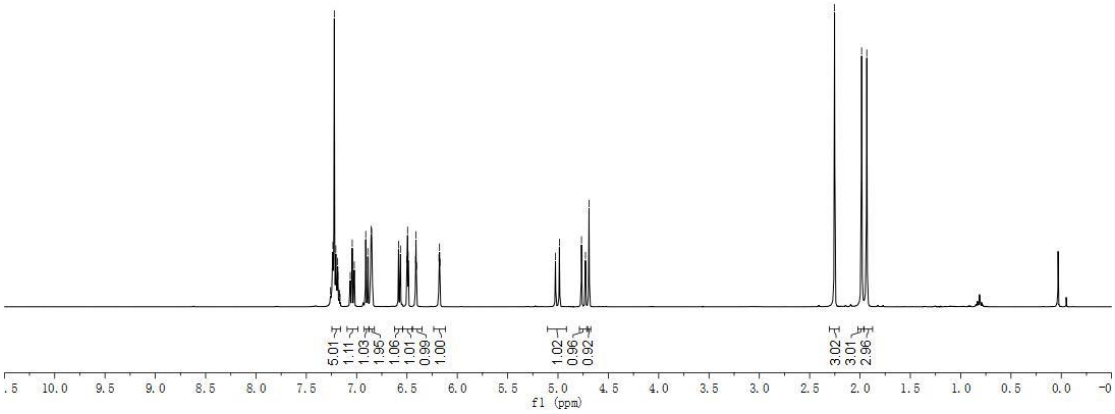
100 MHz **^{13}C NMR** in $CDCl_3$

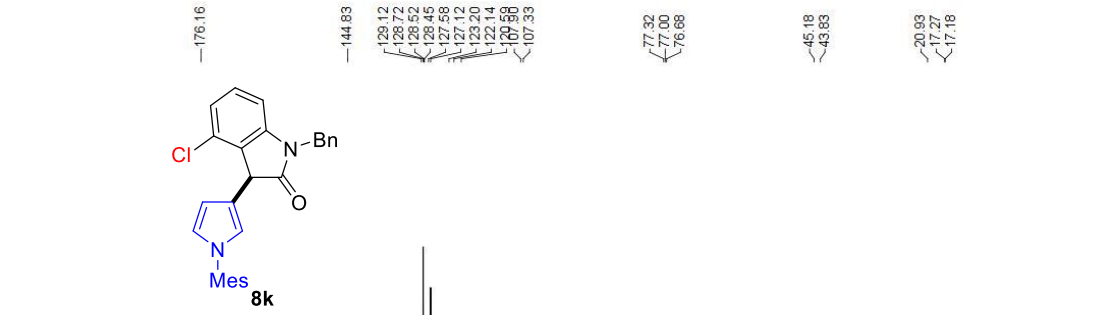




8k

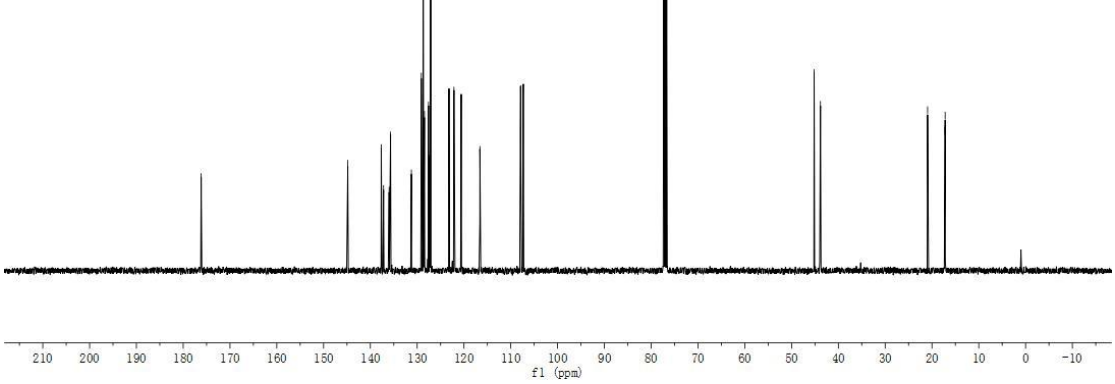
400 MHz **^{1}H NMR** in $CDCl_3$

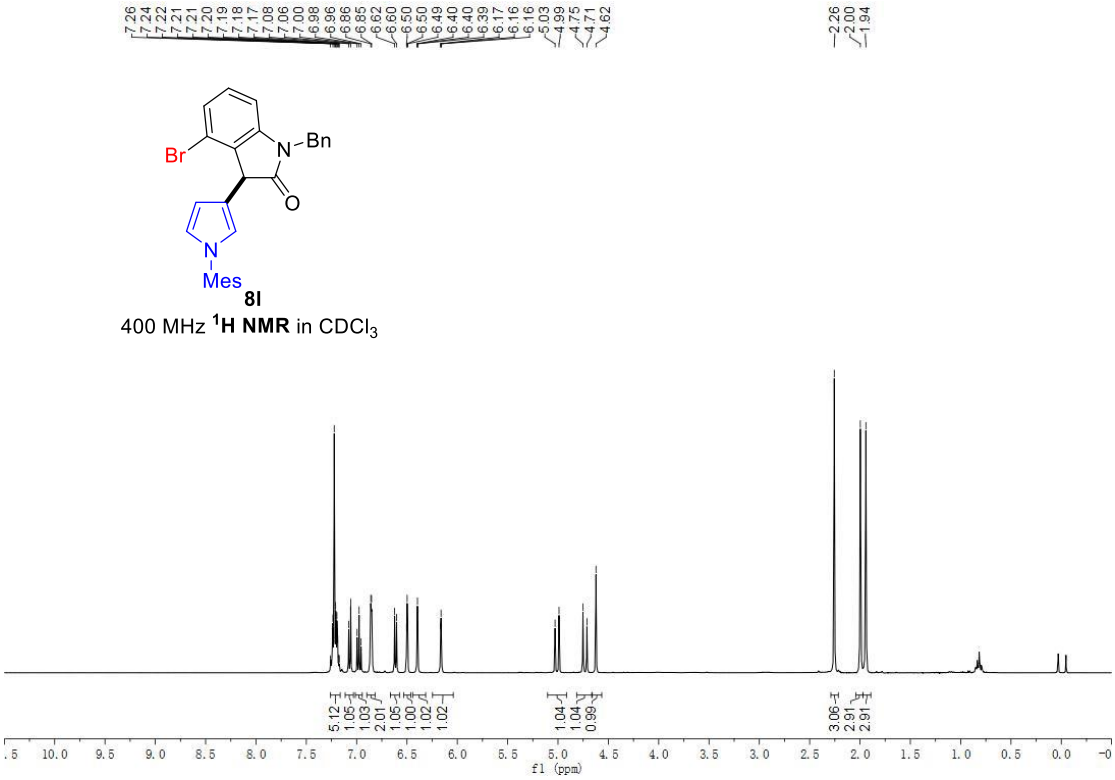


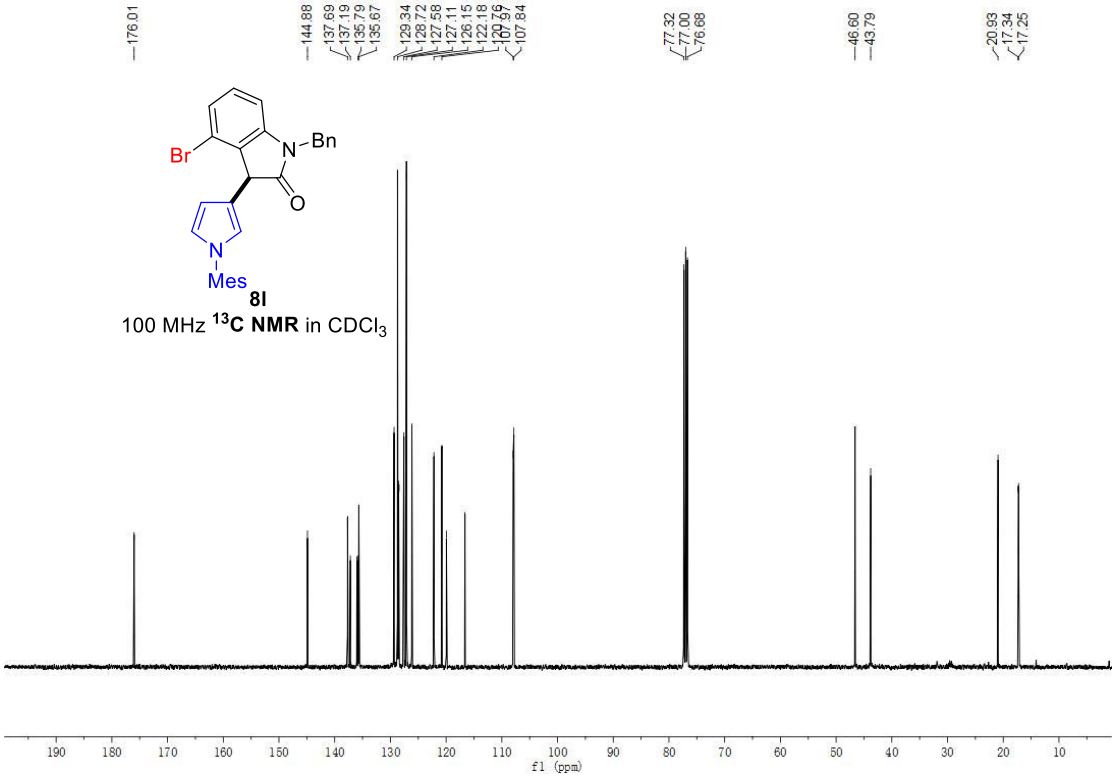


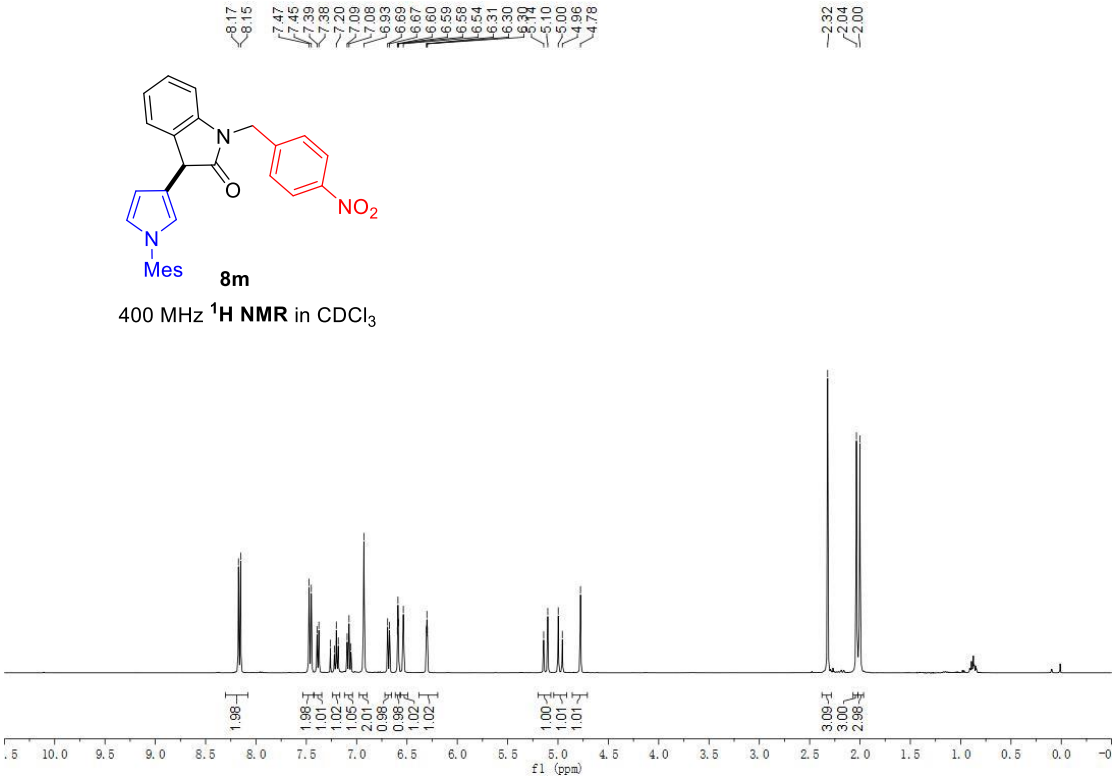
8k

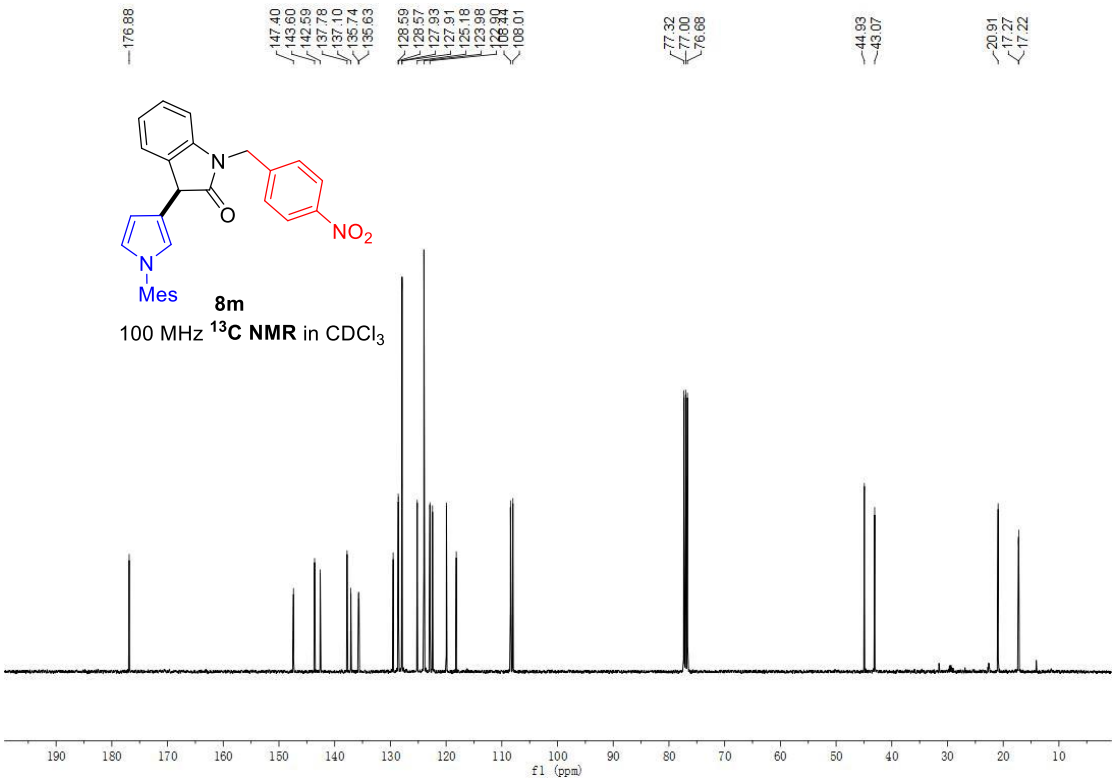
100 MHz **^{13}C NMR** in $CDCl_3$

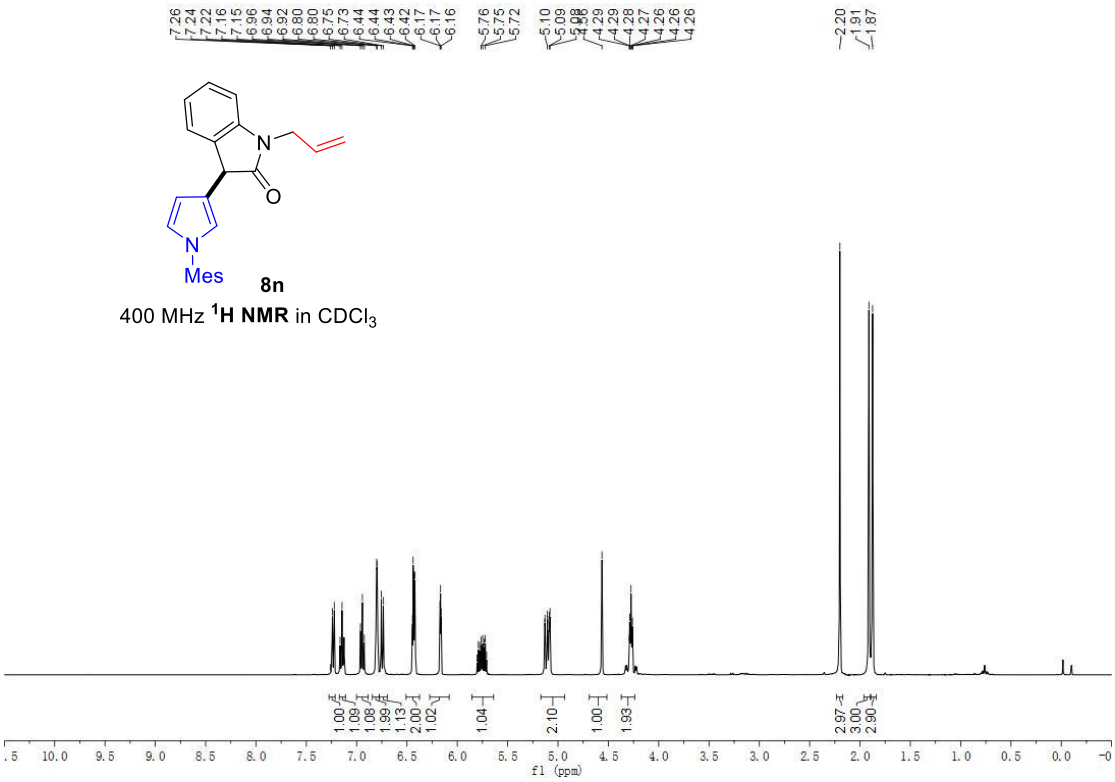


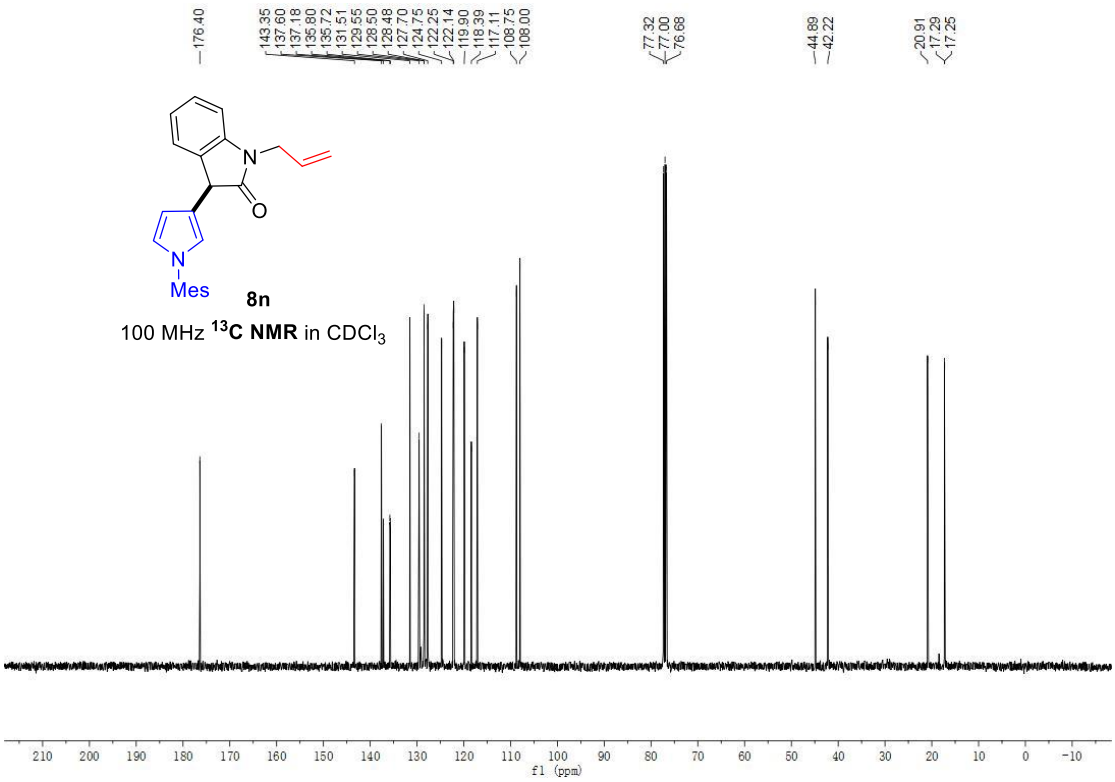

Br
N
Bn
O
N
Mes
8l
400 MHz ¹H NMR in CDCl₃
f1 (ppm)

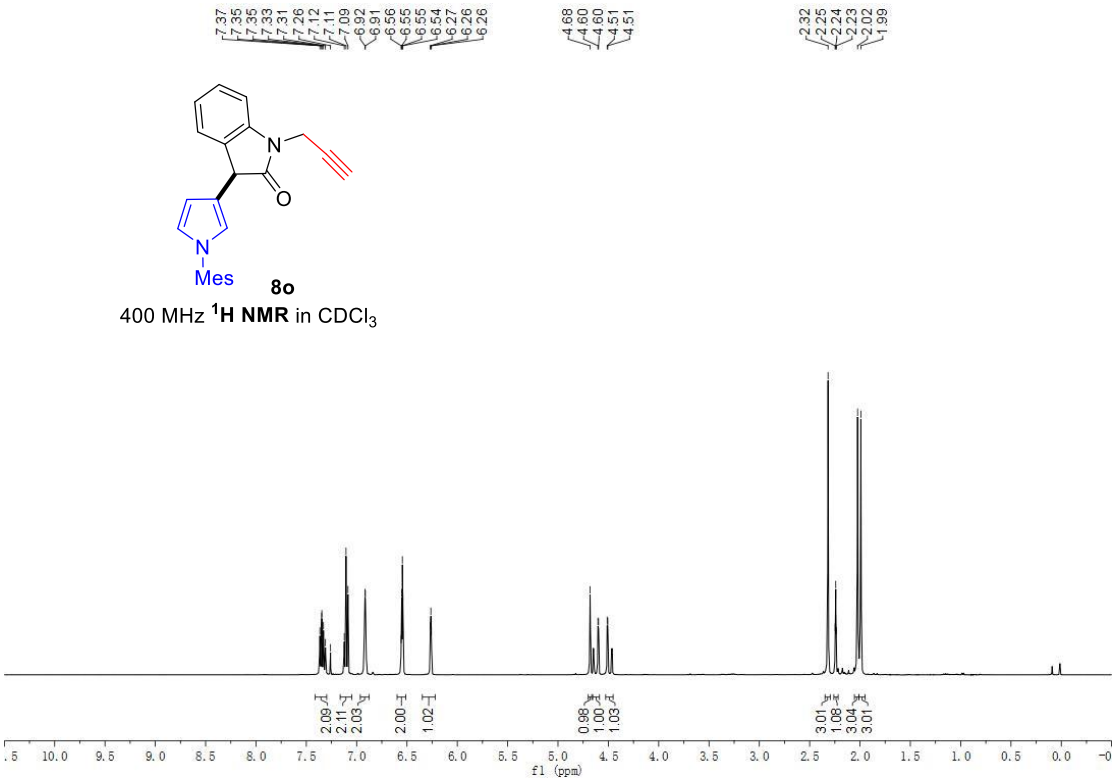

Br
N
Bn
O
N
Mes
8l
100 MHz ¹³C NMR in CDCl₃
f1 (ppm)


8.17
8.15
7.47
7.45
7.39
7.38
7.20
7.09
7.08
6.93
6.69
6.67
6.60
6.59
6.58
6.54
6.31
6.30
5.14
5.10
5.00
4.96
4.78
2.32
2.04
2.00
N
O
NO2
N
Mes
8m
400 MHz 1H NMR in CDCl3
1.98
1.98
1.01
1.02
1.05
2.01
0.98
0.98
1.02
1.02
1.00
1.01
1.01
3.09
3.00
2.98
f1 (ppm)

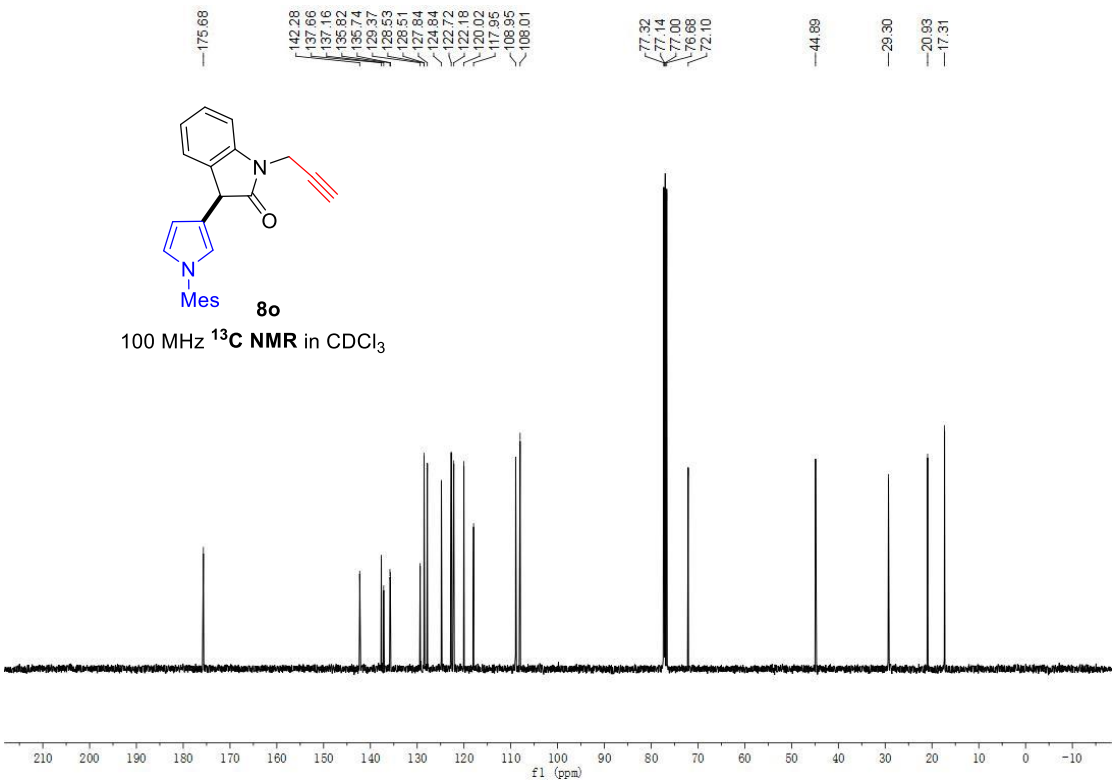

176.88
147.40
143.60
142.59
137.78
137.10
135.74
135.63
128.59
128.57
127.93
127.91
125.18
123.98
108.01
77.32
77.00
76.68
44.93
43.07
20.91
17.27
17.22
N
O
NO2
N
Mes
8m
100 MHz 13C NMR in CDCl3
f1 (ppm)


Mes
8n
400 MHz ¹H NMR in CDCl₃
f1 (ppm)

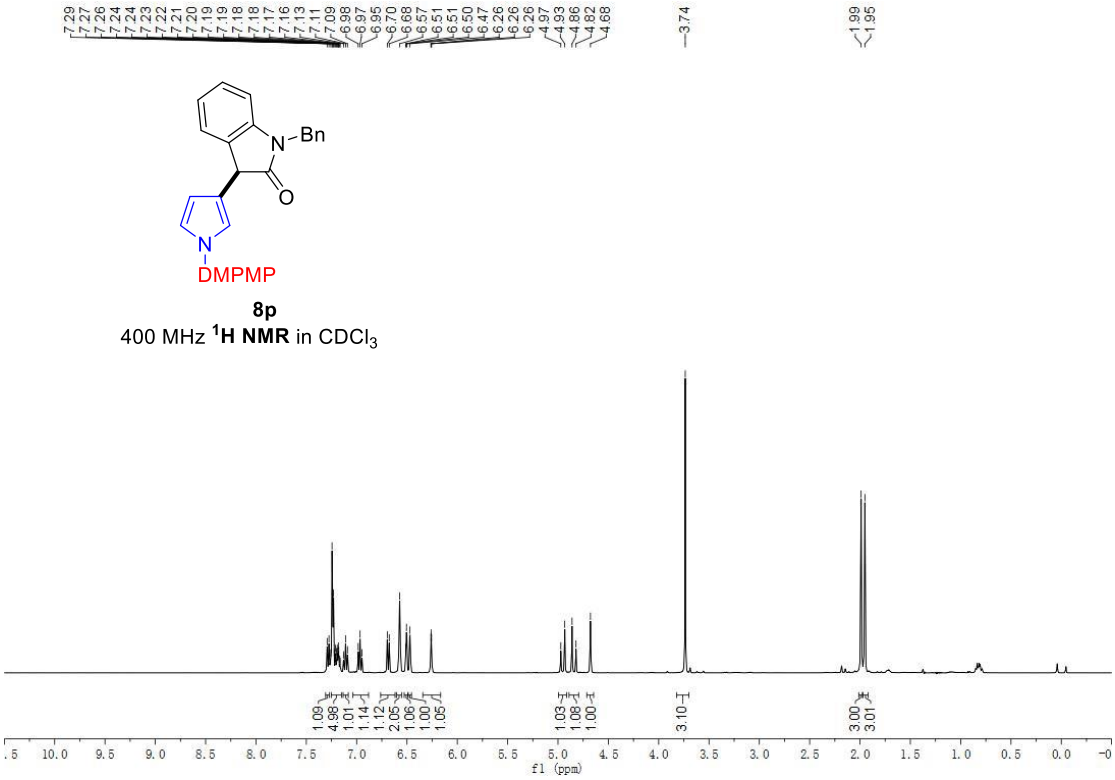

Mes
8n
100 MHz ¹³C NMR in CDCl₃
f1 (ppm)

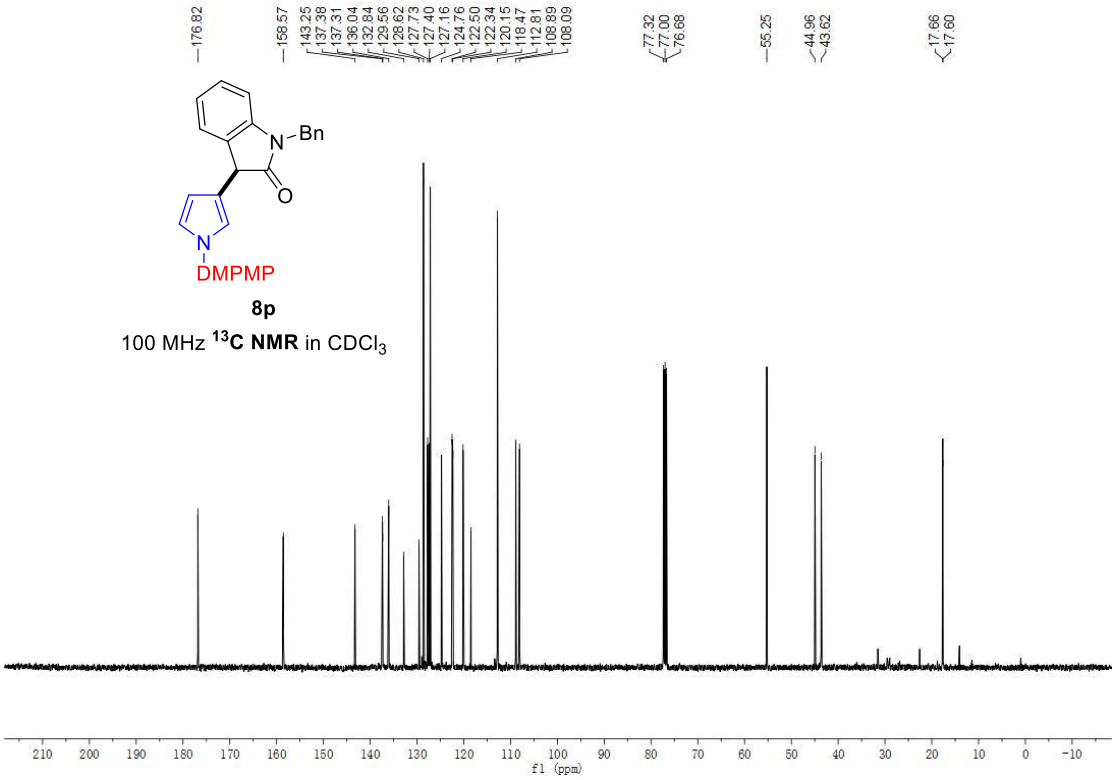


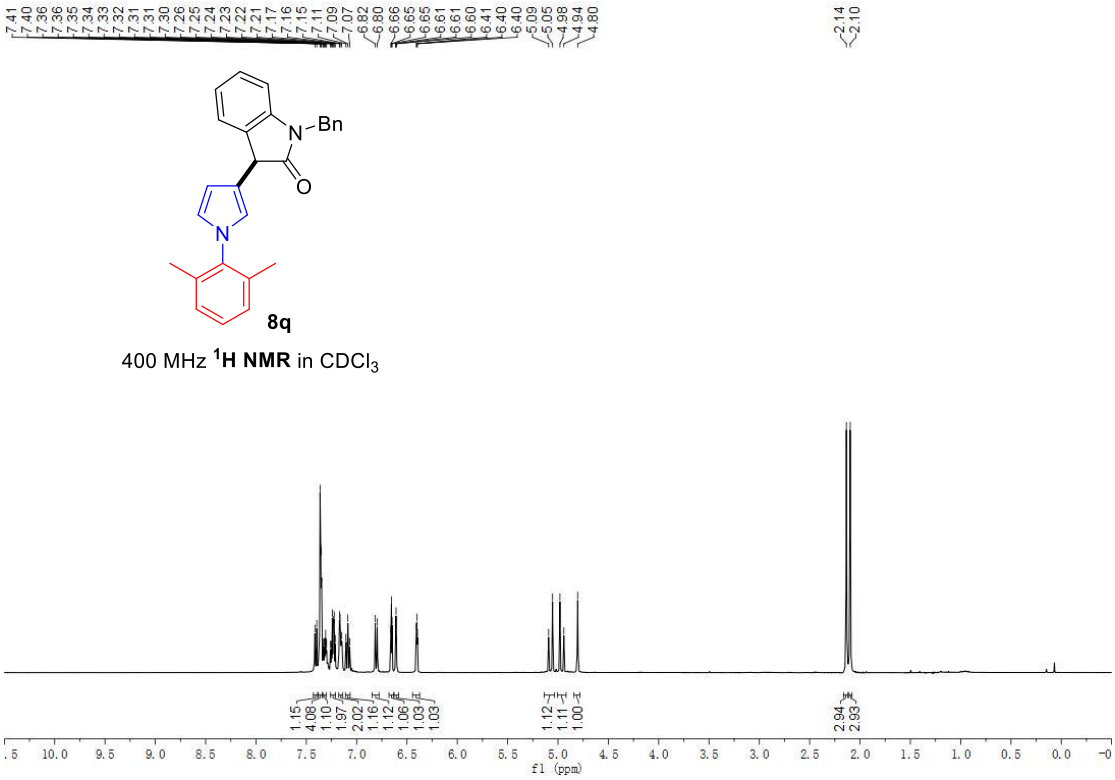
400 MHz ^{1}**H NMR** in $CDCl_3$



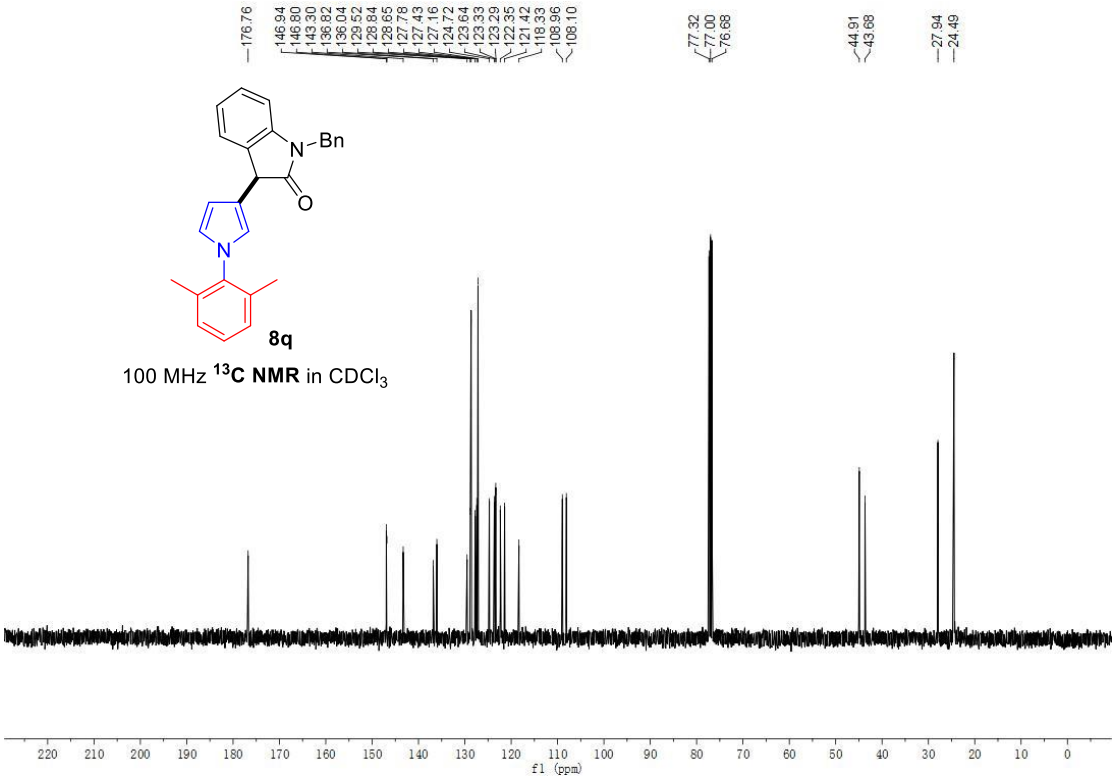
100 MHz ^{13}**C NMR** in $CDCl_3$


N-Bn
O
N
DMPMP
8p
400 MHz ¹H NMR in CDCl₃
f1 (ppm)

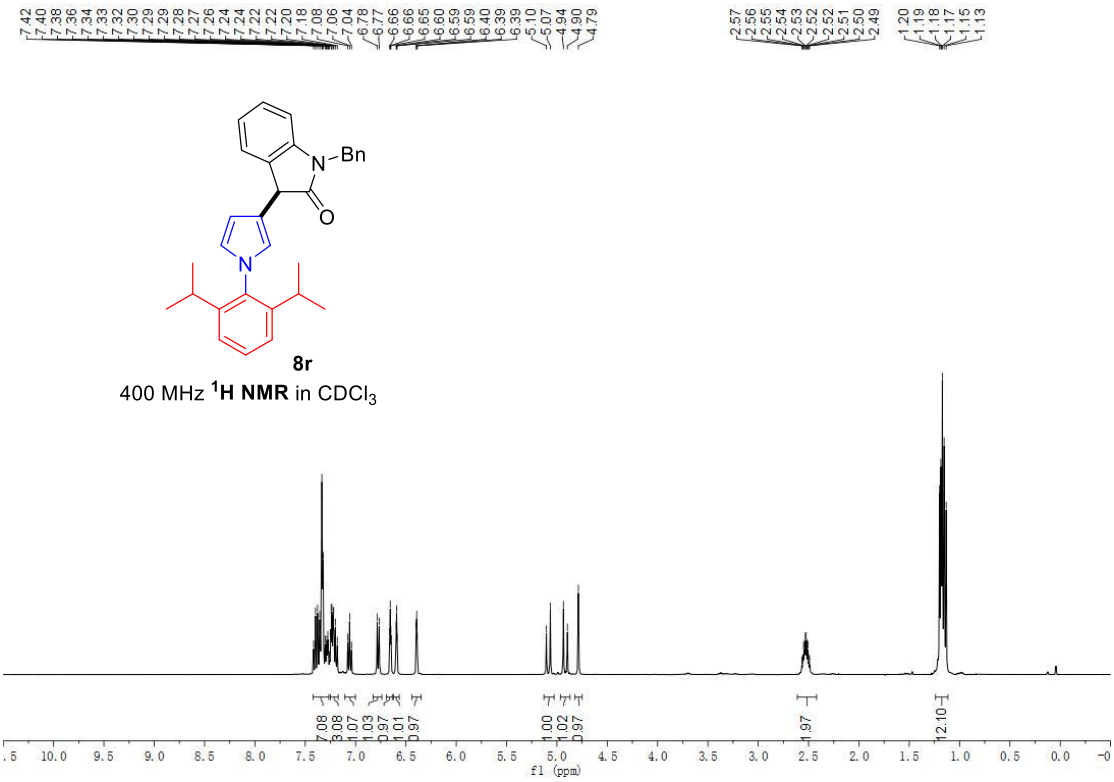

N-Bn
O
N
DMPMP
8p
100 MHz ¹³C NMR in CDCl₃
f1 (ppm)

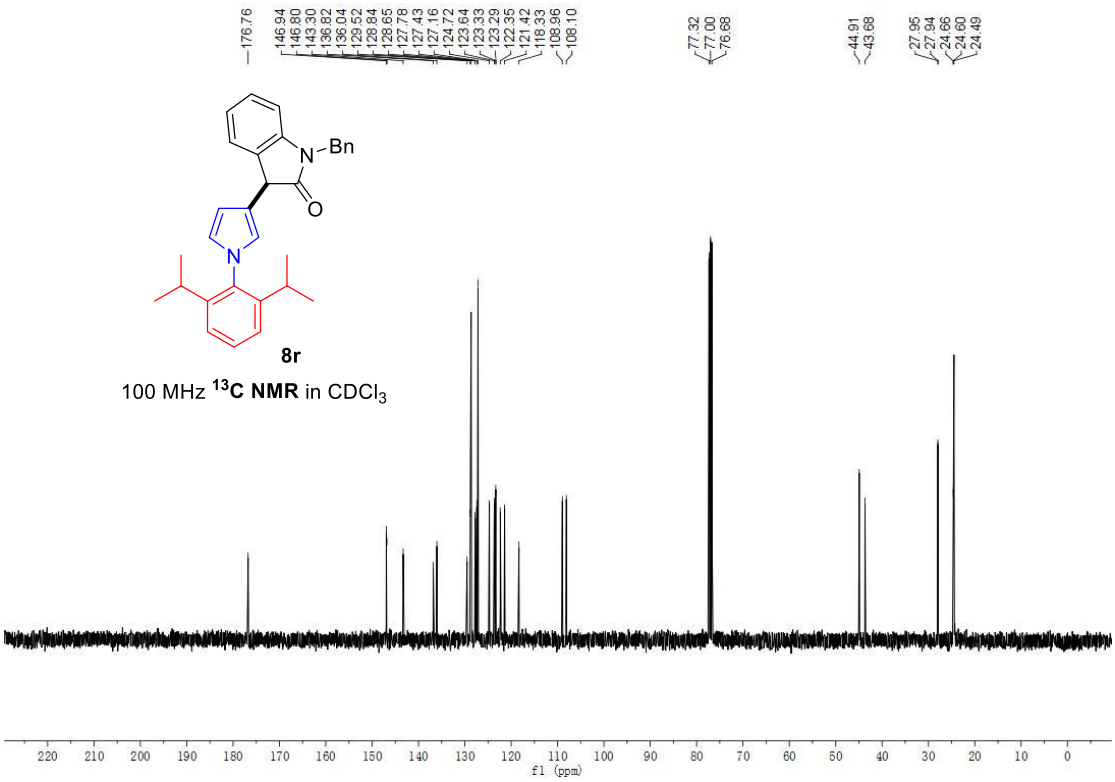


400 MHz **^{1}H NMR** in $CDCl_3$



100 MHz **^{13}C NMR** in $CDCl_3$


N-Bn
O
N
8r
400 MHz ¹H NMR in CDCl₃
f1 (ppm)


N-Bn
O
N
8r
100 MHz ¹³C NMR in CDCl₃
f1 (ppm)