Supporting Information

Fe-promoted radical cyanomethylation/arylation of arylacrylamides to access oxindoles via cleavage of the sp^3 C–H of acetonitrile and the sp^2 C–H of phenyl group

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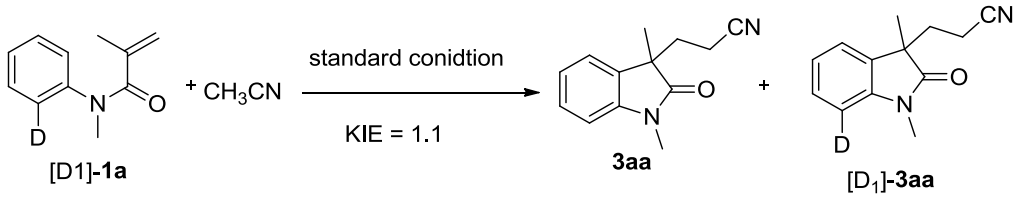
Experimental

1. General experimental details

^{1}H NMR and ^{13}C NMR spectra were measured on 400 MHz spectrometer, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants J are given in Hz. HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

Typical procedure for radical cyanomethylation/arylation of arylacrylamide to access oxindole: To a sealed tube, the mixture of **1a** (0.2 mmol), $Fe(acac)_2$ (5 mol %, 2.5 mg), DTBP (0.6 mmol) and CH_3CN (2.0 mL) were added into the flask. The reaction mixture was vigorously stirred at 120 ^{o}C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by preparative TLC on GF254 to afford the products **3aa**.

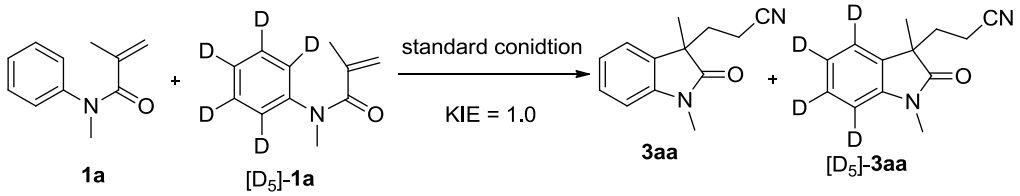
Intramolecular competition experiment isotopically labeled [D_1]-1a



To a sealed tube, the mixture of **[D_1]-1a** (0.2 mmol) $Fe(acac)_2$ (5 mol %, 2.5 mg), DTBP (0.6 mmol) and CH_3CN (2.0 mL) were added into the flask. The reaction mixture was vigorously stirred at 120 ^{o}C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by preparative TLC on GF254 to afford the products **3aa** and **[D_1]-3aa**.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.31 (m, 1H), 7.19 (dd, J = 1.2, 7.4 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 7.8 Hz, 0.54H), 3.23 (s, 3H), 2.38-2.30 (m, 1H), 2.13-1.98 (m, 3H), 1.40 (s, 3H).

Intermolecular competition experiment with isotopically labeled [D_5]-1a

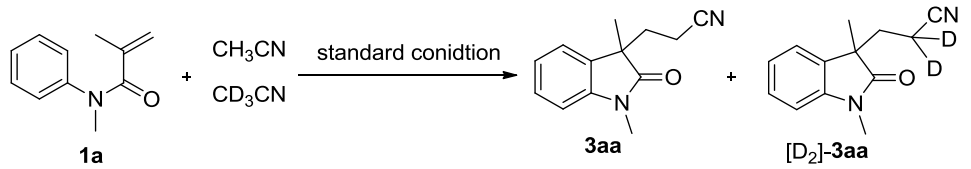


To a sealed tube, the mixture of **[D_5]-1a** (0.2 mmol) $Fe(acac)_2$ (5 mol %, 2.5 mg), DTBP (0.6 mmol) and CH_3CN (2.0 mL) were added into the flask. The reaction mixture was vigorously stirred at 120 ^{o}C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by preparative TLC on GF254 to afford the products **3aa** and **[D_5]-3aa**.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (t, J = 7.7 Hz, 0.5H), 7.19 (d, J = 6.6 Hz, 0.5H),

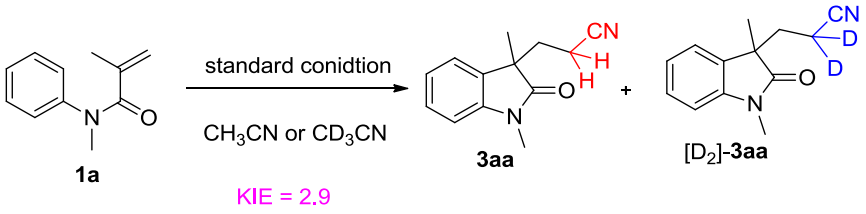
7.12 (t, J = 7.4 Hz, 0.5H), 6.89 (d, J = 7.8 Hz, 0.5H), 3.23 (s, 3H), 2.35-2.30 (m, 1H), 2.13-1.97 (m, 3H), 1.40 (s, 3H).

The KIE studies on solvent (competition reaction):

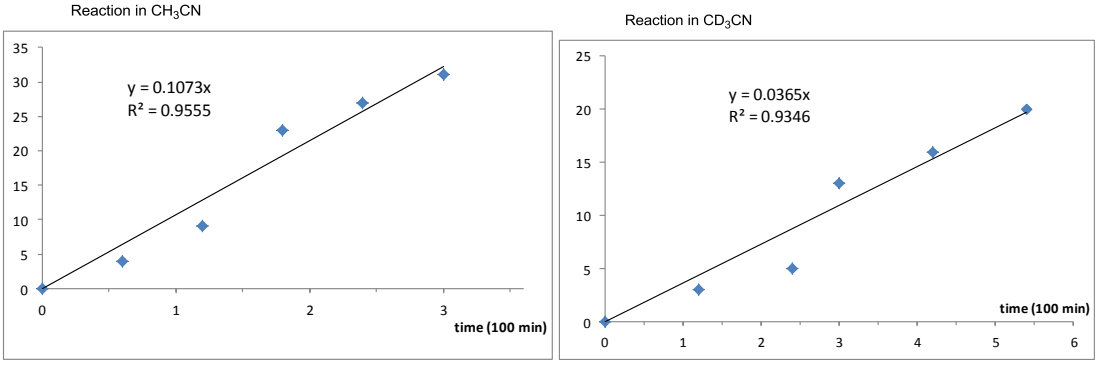


To a sealed tube, the mixture of **1a** (0.2 mmol), $Fe(acac)_2$ (5 mol %, 2.5 mg), DTBP (0.6 mmol), CH_3CN (1.0 mL) and CD_3CN (1.0 mL) were added into the flask. The reaction mixture was vigorously stirred at 120 ^oC for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by preparative TLC on GF254 to afford the products **3aa** and **[D_2]-3aa**.
^1H NMR ($CDCl_3$, 400 MHz): δ 7.32 (t, J = 7.7 Hz, 1H), 7.19 (d, J = 7.3 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.23 (s, 3H), 2.35-2.30 (m, 1H), 2.14-1.97 (m, 2.78H), 1.40 (s, 3H).

The Kinetic Isotopic Effect Studies on Solvent (parallel reaction): In ten parallel sealed tubes, the mixture of **1a** (0.2 mmol) was treated by standard condition in acetonitrile or D_3-acetonitrile (five experiments for each). Then the reaction was quenched by addition internal standard in Et_2OAc in specified time. The mixture was analyzed by GC-MS to give the yield of product. A significant intermolecular kinetic isotope effect (k_H/k_D = 2.9) was observed. The results were listed below:

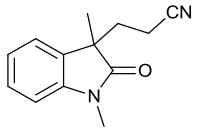


[D_2]-3aa: ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 3.22 (s, 3H), 2.32 (d, J = 13.7 Hz, 1H), 2.06 (d, J = 13.7 Hz, 1H).



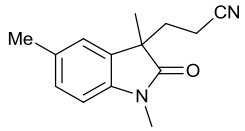
2. Experimental characterization data for compounds

3-(1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3aa)[1]



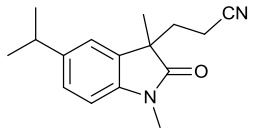
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H), 2.35-2.30 (m, 1H), 2.14-1.97 (m, 3H), 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.9, 143.2, 131.7, 128.7, 123.0, 122.6, 118.8, 108.5, 47.3, 33.4, 26.3, 23.5, 12.8.

3-(1,3,5-trimethyl-2-oxoindolin-3-yl)propanenitrile(3ba)[1]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.11 (d, *J* = 7.9 Hz, 1H), 7.00 (s, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 3.20 (s, 3H), 2.36 (s, 3H), 2.33-2.27 (m, 1H), 2.14-1.96 (m, 3H), 1.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.8, 140.7, 132.7, 131.7, 123.4, 118.9, 108.2, 47.4, 33.5, 26.3, 23.5, 21.1, 12.8.

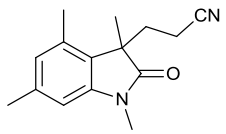
3-(5-isopropyl-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3ca)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10 (dd, *J* =1.5, 8.0 Hz, 1H), 6.97 (d, *J* =1.7 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.13 (s, 3H), 2.87-2.80 (m, 1H), 2.30-2.20 (m, 1H), 2.06-1.89 (m, 3H), 1.32 (s, 3H), 1.19 (s, 3H), 1.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.9, 144.1, 141,0, 131.7, 126.3, 120.8, 118.9, 108.3, 47.5, 33.9, 33.5, 26.3, 24.3, 24.2, 23.4, 12.8.

HRMS (ESI) *m/z* calcd for $C_{16}H_{20}N_2NaO$ $(M+Na)^+$ 279.1468, found 279.1469.

3-(1,3,4,6-tetramethyl-2-oxoindolin-3-yl)propanenitrile (3da)[1]

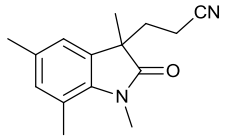


^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.69 (s, 1H), 6.55 (s, 1H), 3.19 (s, 3H), 2.42-2.21 (m, 8H), 2.02-1.82 (m, 2H), 1.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.2, 143.6,

[1] T. Wu, X. Mu and G. Liu, *Angew. Chem., Int. Ed.*, 2011, **50**, 12578.

138.7, 134.0, 126.1, 125.1, 118.7, 107.2, 48.2, 31.6, 26.4, 22.0, 21.6, 18.1, 13.0.

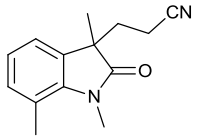
3-(1,3,5,7-tetramethyl-2-oxoindolin-3-yl)propanenitrile (3ea)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.84-6.81 (m, 2H), 3.47 (s, 3H), 2.53 (s, 3H), 2.34-2.28 (m, 4H), 2.00-1.97 (m, 3H), 1.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.5, 138.4, 132.7, 132.5, 132.4, 121.1, 119.9, 118.9, 46.7, 33.7, 29.5, 23.9, 20.7, 18.8, 12.8.

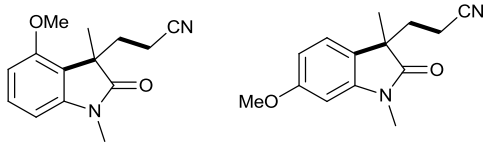
HRMS (ESI) *m/z* calcd for $C_{15}H_{18}N_2NaO$ $(M+Na)^+$ 265.1311, found 265.1314.

3-(1,3,7-trimethyl-2-oxoindolin-3-yl)propanenitrile (3fa) [1]



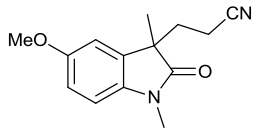
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.05-6.97 (m, 3H), 3.50 (s, 3H), 2.59 (s, 3H), 2.34-2.27 (m, 1H), 2.07-1.95 (m, 3H), 1.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.6, 140.9, 132.3, 122.9, 120.4, 120.2, 118.8, 46.6, 33.7, 29.6, 23.9, 19.0, 12.8.

3-(4-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile and 3-(6-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3ga)



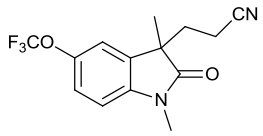
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (t, *J* = 8.3 Hz, 0.7H), 7.08 (d, *J* = 8.1 Hz, 0.31H), 6.65 (d, *J* = 8.4 Hz, 0.63H), 6.61 (d, *J* = 8.1 Hz, 0.31H), 6.54 (d, *J* = 7.7 Hz, 0.63H), 6.46 (d, *J* = 2.2 Hz, 0.31H), 3.87 (s, 2H), 3.83 (s, 1H), 3.20 (s, 3H), 2.42-2.21 (m, 2H), 2.08-1.94 (m, 2H), 1.44 (s, 2H), 1.37 (s, 1H).

3-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3ha) [1]



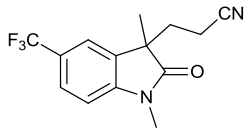
^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.85-6.77 (m, 3H), 3.81 (s, 3H), 3.20 (s, 3H), 2.38-2.28 (m, 1H), 2.14-1.97 (m, 3H), 1.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.5, 156.4, 136.5, 133.0, 118.8, 112.6, 110.3, 108.9, 55.8, 47.8, 33.5, 26.4, 23.5, 12.8.

3-(1,3-dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)propanenitrile (3ia) [1]



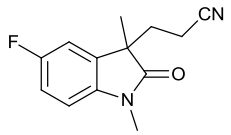
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.21 (d, *J* = 8.4 Hz, 1H), 7.09 (s, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.23 (s, 3H), 2.37-2.31 (m, 1H), 2.14-2.03 (m, 3H), 1.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.6, 145.0, 141,8, 133.3, 121.8, 119.2, 118.4, 116.7, 109.0, 47.6, 33.2, 26.5, 23.3, 12.8.

3-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)propanenitrile(3ja)[1]



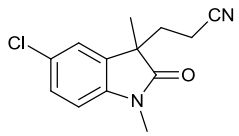
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, *J* = 0.9, 8.2 Hz, 1H), 7.43 (d, *J* = 1.1 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.26 (s, 3H), 2.41-2.32 (m, 1H), 2.16-2.05 (m, 3H), 1.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.8, 146.2, 141,8, 132.4, 126.5 (q, $J_{C\text{-}F}$= 3.9 Hz), 125.3 (q, $J_{C\text{-}F}$= 32.6 Hz), 124.2 (q, $J_{C\text{-}F}$= 270.0 Hz), 119.7 (q, $J_{C\text{-}F}$= 3.6 Hz), 118.3, 108.3, 47.2, 33.1, 26.5, 23.3, 12.8.

3-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3ka) [1]



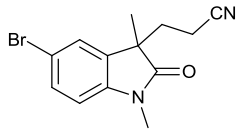
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.05-7.01 (m, 1H), 6.97-6.95 (m, 1H), 6.83-6.80 (m, 1H), 3.22 (s, 3H), 2.36-2.28 (m, 1H), 2.14-2.01 (m, 3H), 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.5, 159.5 (d, $J_{C\text{-}F}$ = 240.4 Hz), 139.0 (d, $J_{C\text{-}F}$ = 1.9 Hz), 133.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 118.5, 115.0 (d, $J_{C\text{-}F}$ = 23.3 Hz), 110.0 (d, $J_{C\text{-}F}$ = 24.6 Hz), 109.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 47.8 (d, $J_{C\text{-}F}$ = 1.7 Hz), 33.3, 23.4, 12.8.

3-(5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3la) [1]



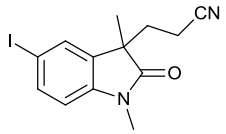
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 (dd, *J* = 2.1, 8.4 Hz, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 3.21 (s, 1H), 2.34-2.30 (m, 1H), 2.12-2.01 (m, 3H), 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.4, 141.7, 133.4, 128.6, 128.5, 123.2, 118.5, 109.5, 47.5, 33.2, 26.5, 23.4, 12.8.

3-(5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3ma) [1]



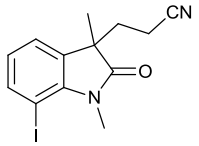
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (dd, *J* =1.8, 8.2 Hz, 1H), 7.31 (d, *J* =1.8 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 3.21 (s, 3H), 2.35-2.30 (m, 1H), 2.12-2.01 (m, 3H), 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.2, 142.2, 133.8, 131.5, 125.9, 118.5, 115.7, 110.0, 47.5, 33.2, 26.4, 23.4, 12.8.

3-(5-iodo-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3na) [1]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* = 1.6, 8.2 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 6.67 (d, *J* = 8.2Hz, 1H), 3.20 (s, 3H), 2.35-2.28 (m, 1H), 2.11-2.00 (m, 3H), 1.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.1, 142.9, 137.5, 134.2, 131.5, 118.5, 110.6, 85.6, 47.3, 33.2, 26.4, 23.4, 12.8.

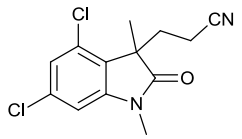
3-(7-iodo-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3oa)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, *J* = 1.0, 8.1 Hz, 1H), 7.13 (d, *J* = 1.0, 8.3 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 2.35-2.28 (m, 1H), 2.13-1.99 (m, 3H), 1.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.5, 143.5, 141.3, 134.8, 124.7, 122.4, 118.6, 72.1, 46.8, 33.6, 30.2, 23.8, 12.8.

HRMS (ESI) *m/z* calcd for $C_{13}H_{13}IN_2NaO$ $(M+Na)^+$ 362.9965, found 362.9967.

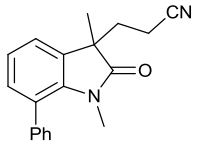
3-(4,6-dichloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3pa)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.06 (d, *J* = 1.6 Hz, 1H), 6.81 (d, *J* = 1.6 Hz, 1H), 3.21 (s, 3H), 2.52-2.34 (m, 2H), 2.07-2.02 (m, 2H), 1.52 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.3, 145.9, 135.4, 131.2, 125.9, 123.4, 118.2, 108.0, 48.8, 30.2, 26.7, 21.3, 13.2.

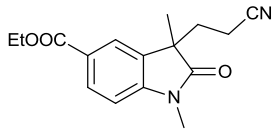
HRMS (ESI) *m/z* calcd for $C_{13}H_{12}Cl_2N_2NaO$ $(M+Na)^+$ 305.0219, found 305.0221.

3-(1,3-dimethyl-2-oxo-7-phenylindolin-3-yl)propanenitrile (3qa) [1]



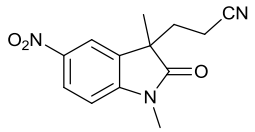
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42-7.33 (m, 5H), 7.20-7.17 (m, 1H), 7.15-7.09 (m, 2H), 2.73 (s, 3H), 2.42-2.31 (m, 1H), 2.15-2.06 (m, 3H), 1.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.9, 140.0, 138.5, 132.7, 131.6, 129.8, 127.9, 127.8, 125.9, 122.3, 121.6, 118.8, 46.6, 33.7, 30.2, 23.8, 12.8.

ethyl 3-(2-cyanoethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3ra)



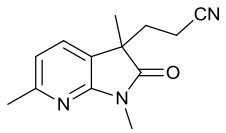
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (dd, *J* = 1.6, 8.2 Hz, 1H), 7.87 (s, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 4.41-4.36 (m, 2H), 3.26 (s, 3H), 2.39-2.32 (m, 1H), 2.14-2.05 (m, 3H), 1.44-1.40 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.2, 166.1, 147.1, 131.7, 131.3, 125.3, 123.8, 118.5, 108.0, 61.1, 47.1, 33.1, 26.5, 23.4, 14.3, 12.8.
HRMS (ESI) *m/z* calcd for $C_{16}H_{18}N_2NaO_3$ $(M+Na)^+$ 309.1210, found 309.1211.

3-(1,3-dimethyl-5-nitro-2-oxoindolin-3-yl)propanenitrile (3sa) [1]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (dd, *J* = 2.2, 8.6 Hz, 1H), 8.12 (d, *J* = 2.2 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.31 (s, 3H), 2.41-2.34 (m, 1H), 2.19-2.12 (m, 3H), 1.48 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.0, 148.8, 143.7, 132.7, 126.0, 118.7, 118.1, 108.2, 47.3, 32.9, 26.8, 23.4, 12.8.

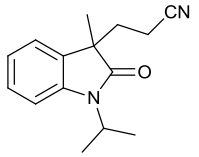
3-(1,3,6-trimethyl-2-oxo-2,3-dihydro-1*H*-pyrrolo[2,3-b]pyridin-3-yl)propanenitrile (3ta)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (d, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.4 Hz, 1H), 3.29 (s, 3H), 2.52 (s, 3H), 2.33-2.28 (m, 1H), 2.21-2.01 (m, 3H), 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.2, 157.3, 156.1, 130.4, 122.6, 118.6, 117.5, 46.8, 32.9, 25.4, 24.2, 23.0, 12.8.

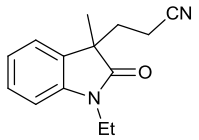
HRMS (ESI) *m/z* calcd for $C_{13}H_{15}N_3NaO$ $(M+Na)^+$ 252.1107, found 252.1107.

3-(1-isopropyl-3-methyl-2-oxoindolin-3-yl)propanenitrile (4aa)



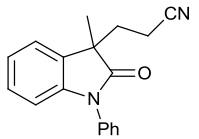
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.26 (m, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.67-4.60 (m, 1H), 2.35-2.29 (m, 1H), 2.10-1.91 (m, 3H), 1.48 (dd, *J* = 1.7, 7.0 Hz, 6H), 1.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.5, 142.8, 132.1, 128.4, 122.9, 122.5, 118.8, 110.2, 47.0, 43.9, 33.6, 23.7, 19.5, 19.4, 12.7.
HRMS (ESI) *m/z* calcd for $C_{15}H_{18}N_2NaO$ $(M+Na)^+$ 265.1311, found 265.1312.

3-(1-ethyl-3-methyl-2-oxoindolin-3-yl)propanenitrile (4ba)



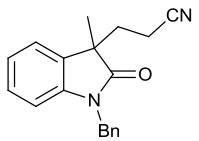
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.29 (m, 1H), 7.20 (d, *J* = 6.8 Hz, 1H), 7.12-7.08 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.82-3.71 (m, 2H), 2.38-2.27 (m, 1H), 2.12-2.94 (m, 3H), 1.39 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.5, 142.2, 131.9, 128.6, 122.9, 122.8, 118.8, 108.6, 47.2, 34.7, 33.5, 23.5, 12.8, 12.7
HRMS (ESI) *m/z* calcd for $C_{14}H_{16}N_2NaO$ $(M+Na)^+$ 251.1155, found 251.1154.

3-(3-methyl-2-oxo-1-phenylindolin-3-yl)propanenitrile (4ca) [1]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.51 (m, 2H), 7.44-7.39 (m, 3H), 7.25-7.22 (m, 2H), 7.16-7.12 (m, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 2.46-2.38 (m, 1H), 2.27-2.11 (m, 3H), 1.52 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.4, 143.1, 134.1, 131.5, 129.7, 128.6, 128.3, 126.4, 123.5, 122.9, 118.8, 109.9, 47.5, 33.7, 23.9, 12.9.

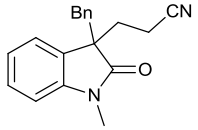
3-(1-benzyl-3-methyl-2-oxoindolin-3-yl)propanenitrile (4da)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.26 (m, 5H), 7.23-7.19 (m, 1H), 7.08 (t, *J* = 7.5

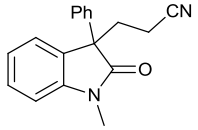
Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 4.91 (q, 2H), 2.42-2.34 (m, 1H), 2.16-1.95 (m, 3H), 1.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.0, 142.2, 135.7, 131.7, 128.9, 128.6, 127.8, 127.3, 123.1, 122.7, 118.8, 109.5, 47.3, 43.8, 33.5, 23.8, 12.8.
HRMS (ESI) *m/z* calcd for $C_{19}H_{18}N_2NaO$ $(M+Na)^+$ 313.1311, found 313.1313.

3-(3-benzyl-1-methyl-2-oxoindolin-3-yl)propanenitrile (4ea) [1]



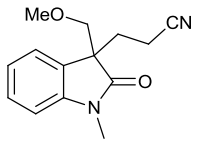
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25-7.21 (m, 1H), 7.14-7.02 (m, 5H), 6.80-6.78 (m, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 3.12 (d, *J* = 12.8 Hz, 1H), 3.01 (d, *J* = 12.8 Hz, 1H), 2.96 (s, 3H), 2.54-2.46 (m, 1H), 2.25-2.18 (m, 1H), 2.11-2.03 (m, 1H), 1.97-1.88 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.5, 143.8, 134.7, 129.8, 128.8, 128.6, 127.6, 126.8, 123.6, 122.6, 118.8, 108.3, 53.7, 44.4, 31.9, 25.9, 12.9.

3-(1-methyl-2-oxo-3-phenylindolin-3-yl)propanenitrile (4fa) [1]



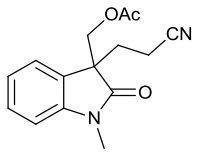
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.25 (m, 7H), 7.19-7.14 (m, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 3.24 (s, 3H), 2.86-2.78 (m, 1H), 2.52-2.45 (m, 1H), 2.21-2.07 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.0, 143.7, 138.4, 130.0, 129.2, 128.9, 127.9, 126.6, 124.7, 123.2, 118.7, 108.9, 55.4, 33.2, 26.6, 13.1.

3-(3-(methoxymethyl)-1-methyl-2-oxoindolin-3-yl)propanenitrile (4ga) [1]



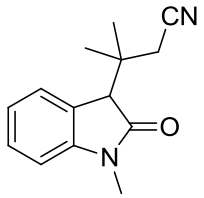
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.30 (m, 2H), 7.11 (d, *J* =7.5 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.66 (d, *J* = 8.8 Hz, 1H), 3.50 (d, *J* = 8.8 Hz, 1H), 3.26 (s, 3H), 3.22 (s, 3H), 2.37-2.30 (m, 1H), 2.22-2.02 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.5, 143.8, 129.0, 128.9, 123.8, 123.0, 118.8, 108.4, 75.8, 59.5, 52.5, 29.0, 26.3, 12.4.

(3-(2-cyanoethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (4ha) [1]



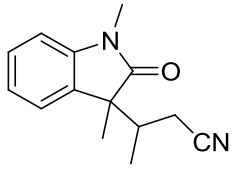
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 10.9 Hz, 1H), 4.14 (d, *J* = 10.9 Hz, 1H), 3.25 (s, 3H), 2.43-2.34 (m, 1H), 2.24-2.02 (m, 3H), 1.95 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 175.7, 170.1, 143.9, 129.4, 127.3, 123.7, 123.2, 118.4, 108.6, 66.5, 51.3, 28.9, 26.4, 20.5, 12.4.

3-methyl-3-(1-methyl-2-oxoindolin-3-yl)butanenitrile (4ia)



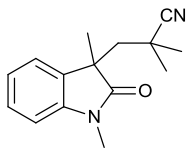
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.29 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.7 Hz, 1H), 3.43 (s, 3H), 2.88-2.82 (m, 1H), 2.79-2.76 (m, 1H), 2.56-2.50 (m, 1H), 1.45 (s, 3H), 1.18 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.4, 138.4, 133.4, 128.1, 124.3, 123.9, 119.0, 115.5, 48.8, 36.2, 30.2, 25.9, 22.4, 14.2.
HRMS (ESI) *m/z* calcd for $C_{14}H_{16}N_2NaO$ $(M+Na)^+$ 251.1155, found 251.1157.

3-(1,3-dimethyl-2-oxoindolin-3-yl)butanenitrile (4ja: 4ja' = 1.4:1 d.r.)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (t, *J* = 7.6 Hz, 1H), 7.21-7.15 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 3.21 (d, *J* = 2.4 Hz, 3H), 2.54-2.11 (m, 3H), 1.40 (d, *J* = 0.9 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 1.76H), 1.05 (d, *J* = 6.8 Hz, 1.24H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.9, 178.6, 143.2, 143.1, 131.8, 128.5, 128.4, 123.0, 123.0, 122.9, 122.8, 118.7, 108.4, 50.2, 50.0, 37.9, 37.5, 26.1, 21.7, 20.9, 20.2, 19.8, 14.7, 14.4.
HRMS (ESI) *m/z* calcd for $C_{14}H_{16}N_2NaO$ $(M+Na)^+$ 251.1155, found 251.1158.

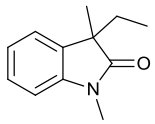
3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3ab)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.31 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 3.25 (s, 3H), 2.33 (d, *J* = 14.6 Hz, 1H), 2.17 (d, *J* = 14.6 Hz, 1H), 1.35 (s, 3H), 1.16 (s, 3H), 1.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.6, 143.1, 130.9, 128.6, 124.7, 123.9, 122.5, 108.5, 46.9, 46.5, 30.7, 29.6, 27.4, 26.6, 26.4.

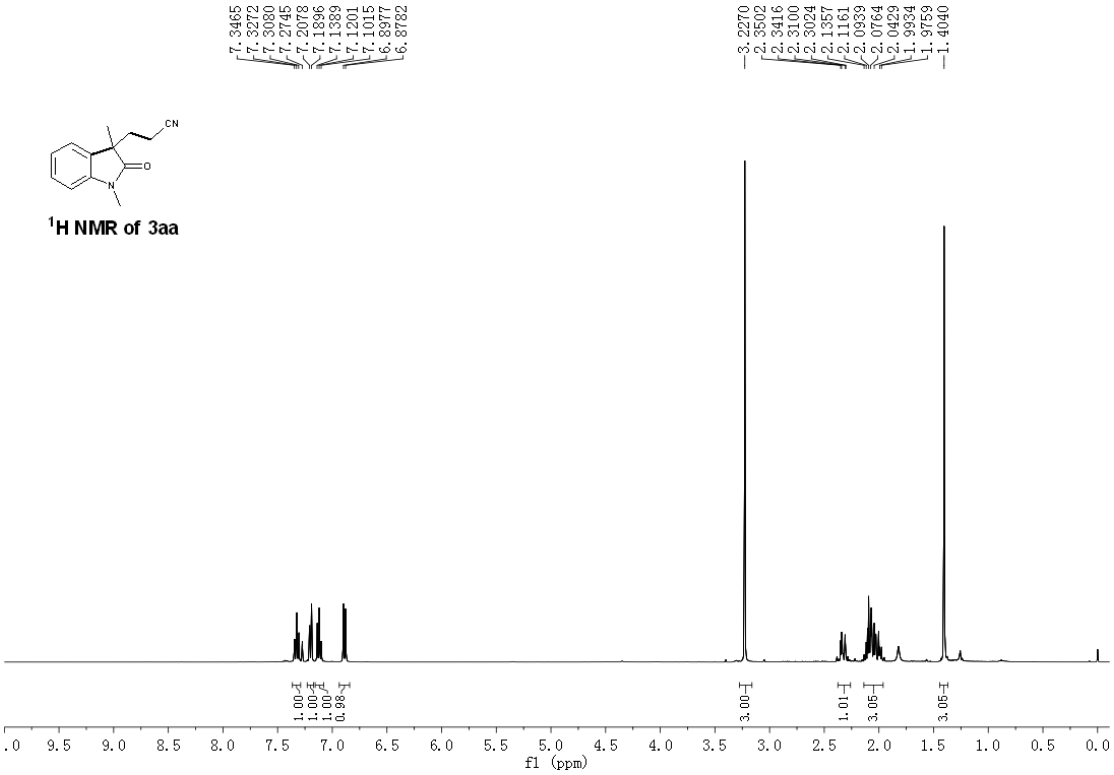
HRMS (ESI) *m/z* calcd for $C_{15}H_{18}N_2NaO$ $(M+Na)^+$ 265.1311, found 265.1310.

3-ethyl-1,3-dimethylindolin-2-one (5aa)[2]

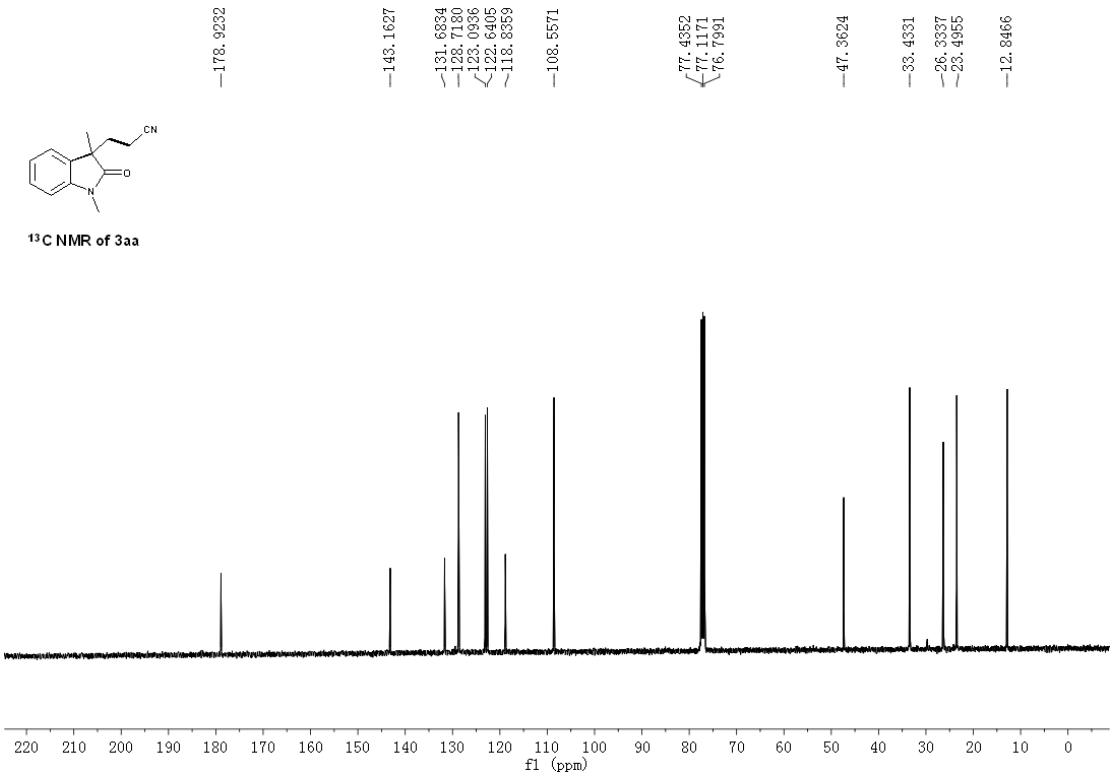


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 3.21 (s, 3H), 1.97-1.88 (m, 1H), 1.82-1.82 (m, 1H), 1.35 (s, 3H), 0.58 (t, *J* = 7.4 Hz, 3H).

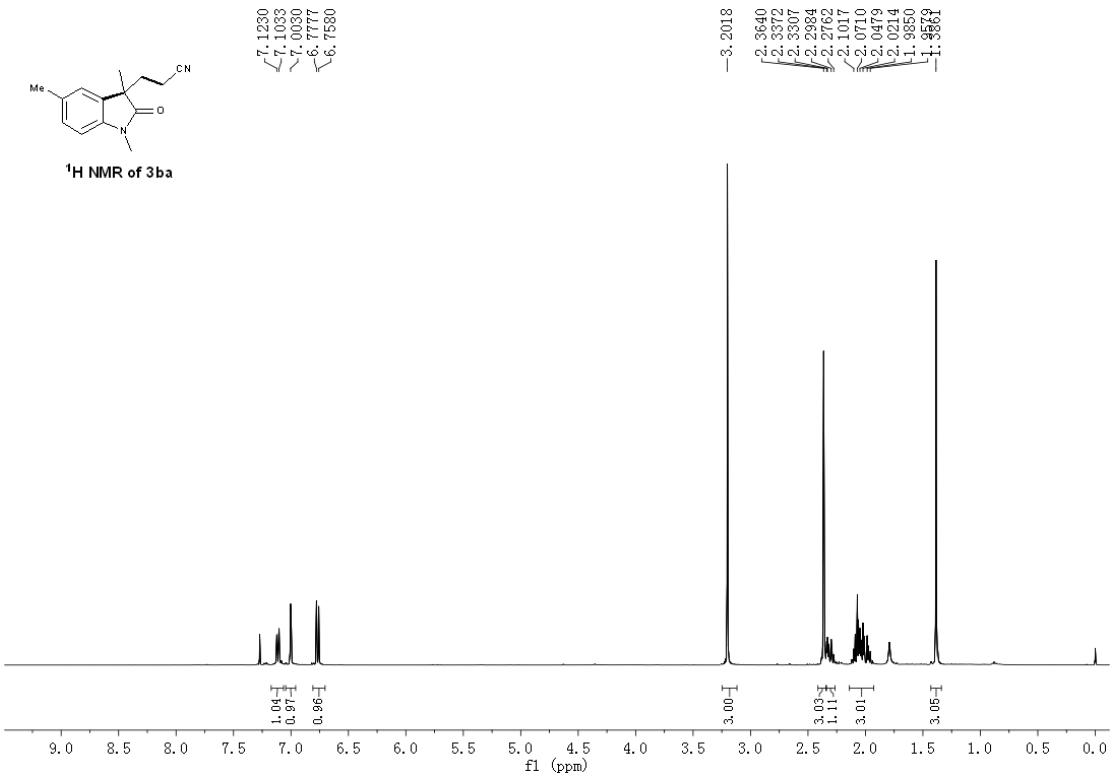
[2] Q. Dai, J.-T. Yu, Y. Jiang, S. Guo, H. Yang and J. Cheng, *Chem. Commun.*, 2014, **50**, 3865.



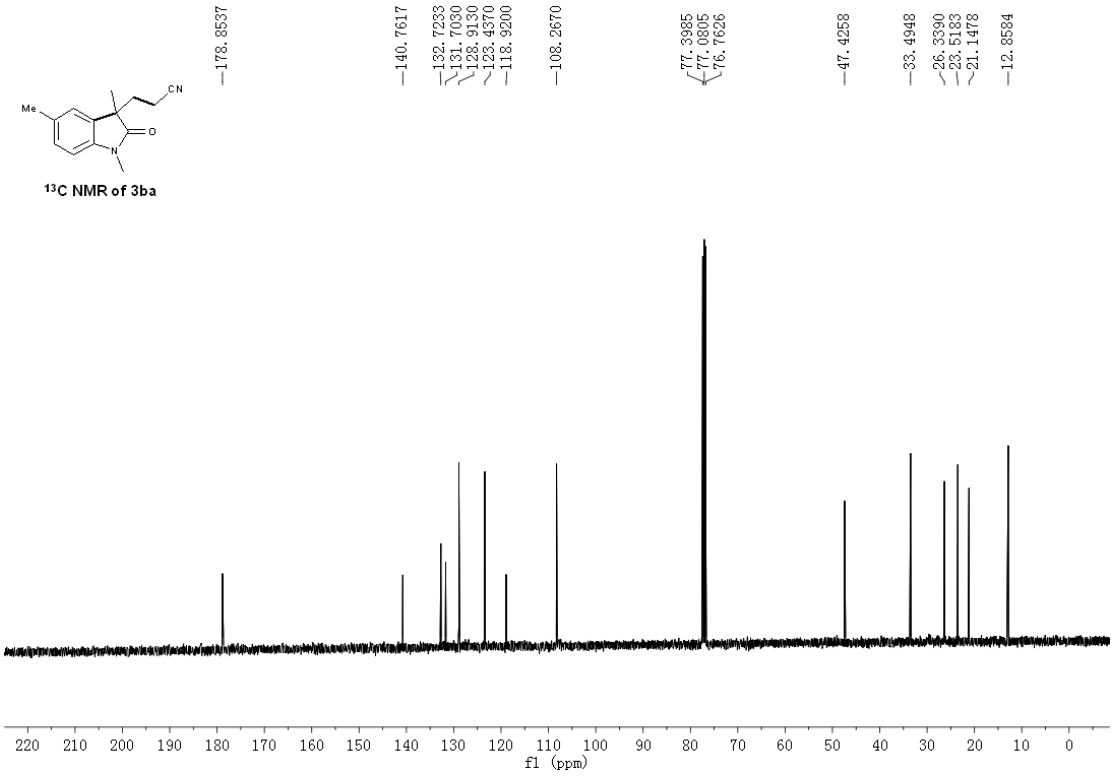
^{1}H NMR of 3aa



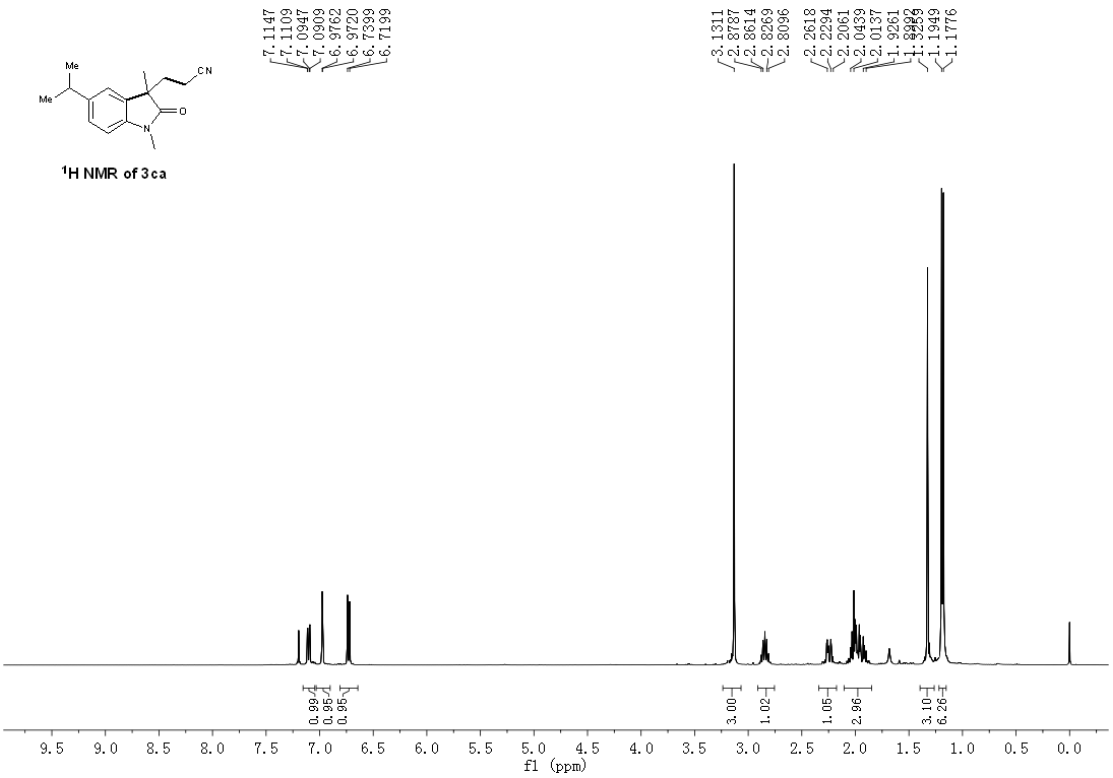
^{13}C NMR of 3aa



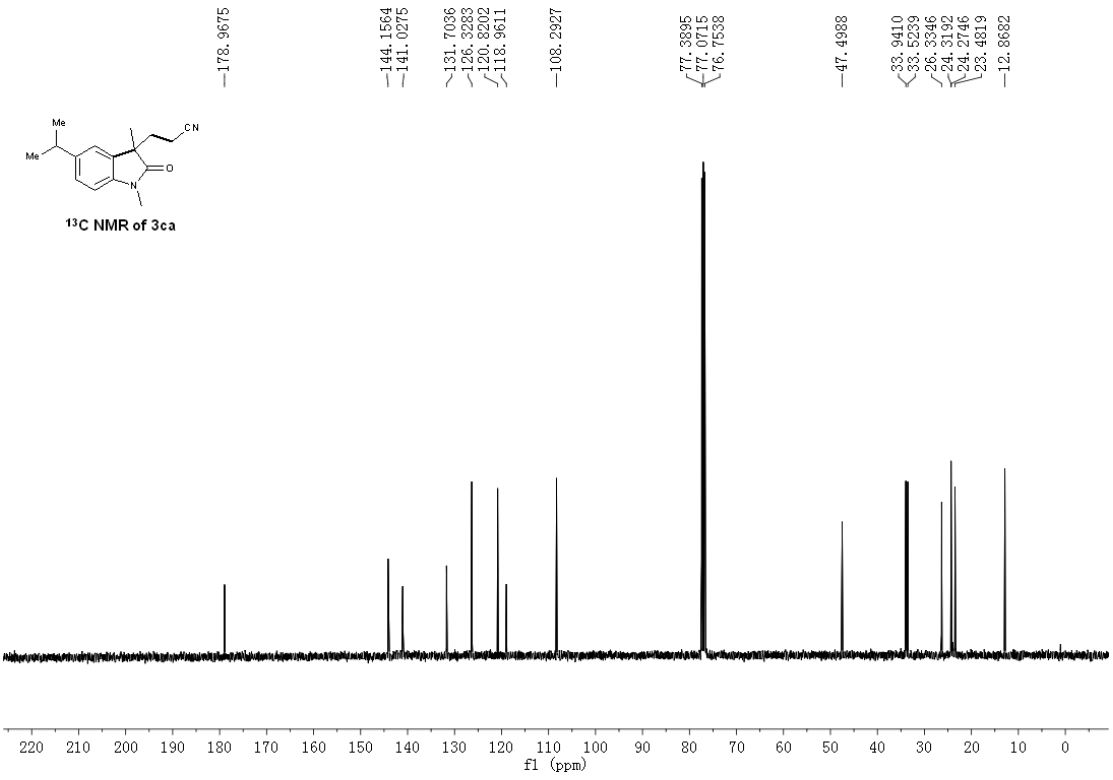
^{1}H NMR of 3ba



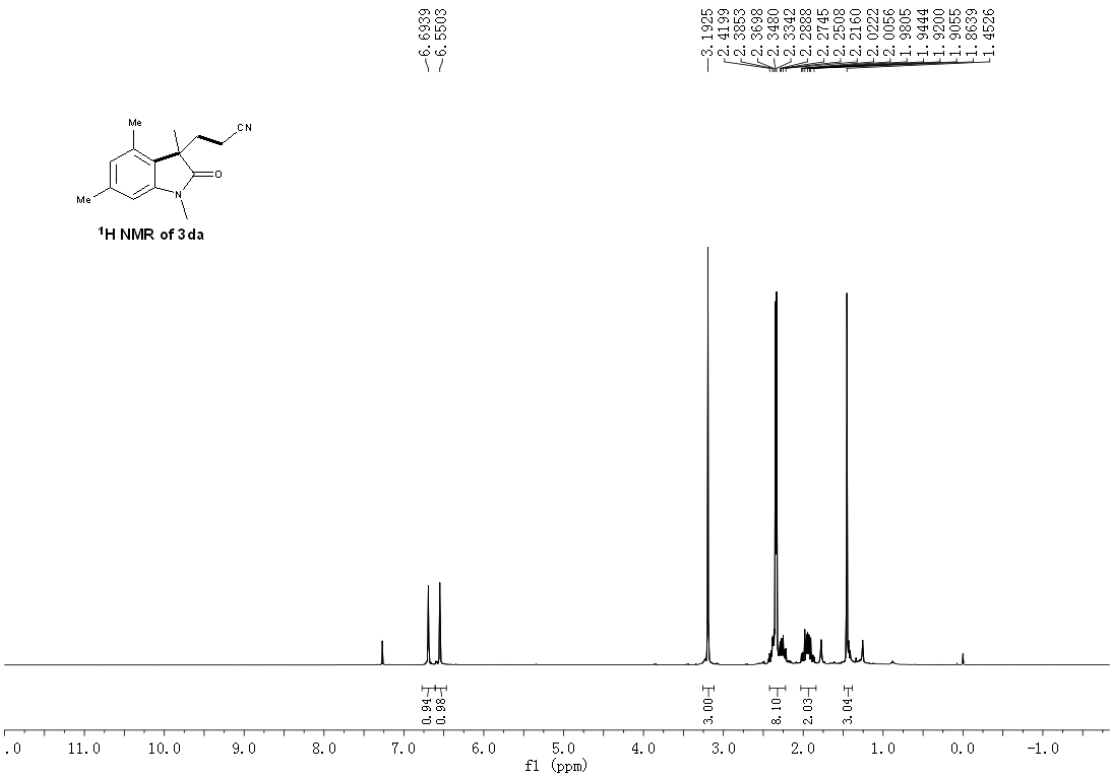
^{13}C NMR of 3ba



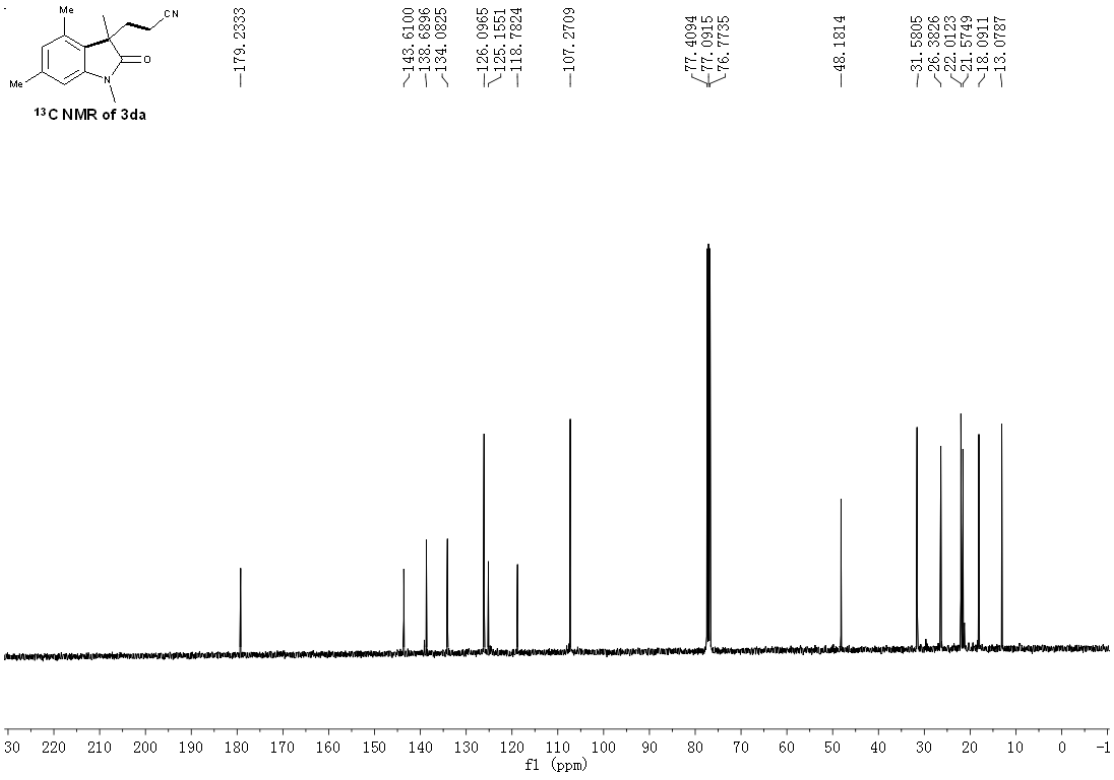
^{1}H NMR of 3ca



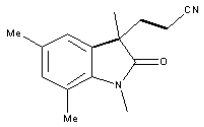
^{13}C NMR of 3ca



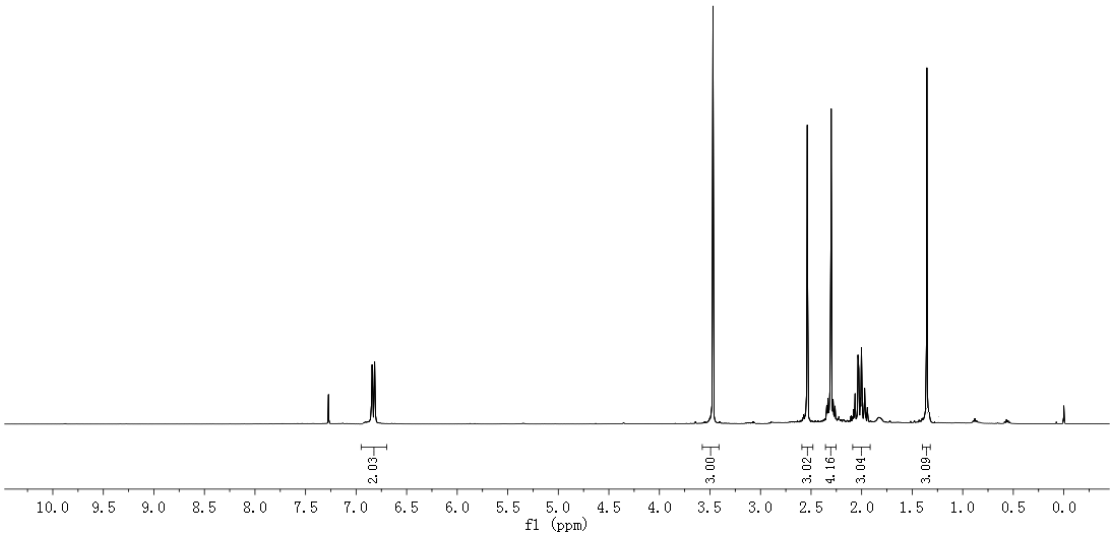
^{1}H NMR of 3da

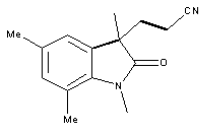


^{13}C NMR of 3da

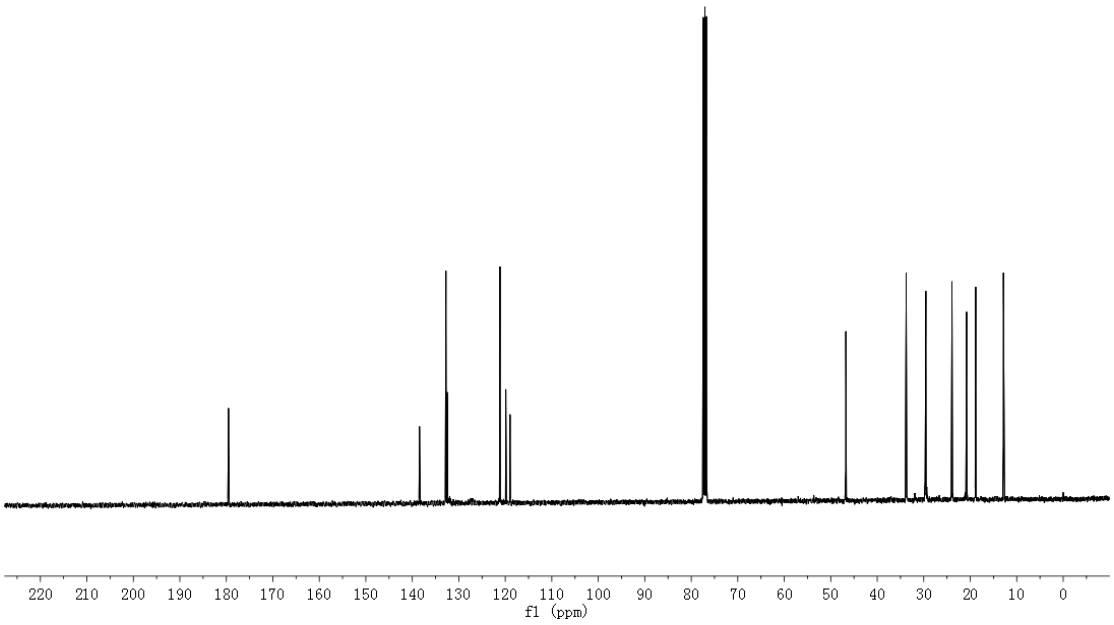


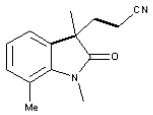
^{1}H NMR of 3ea

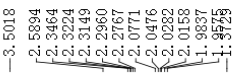




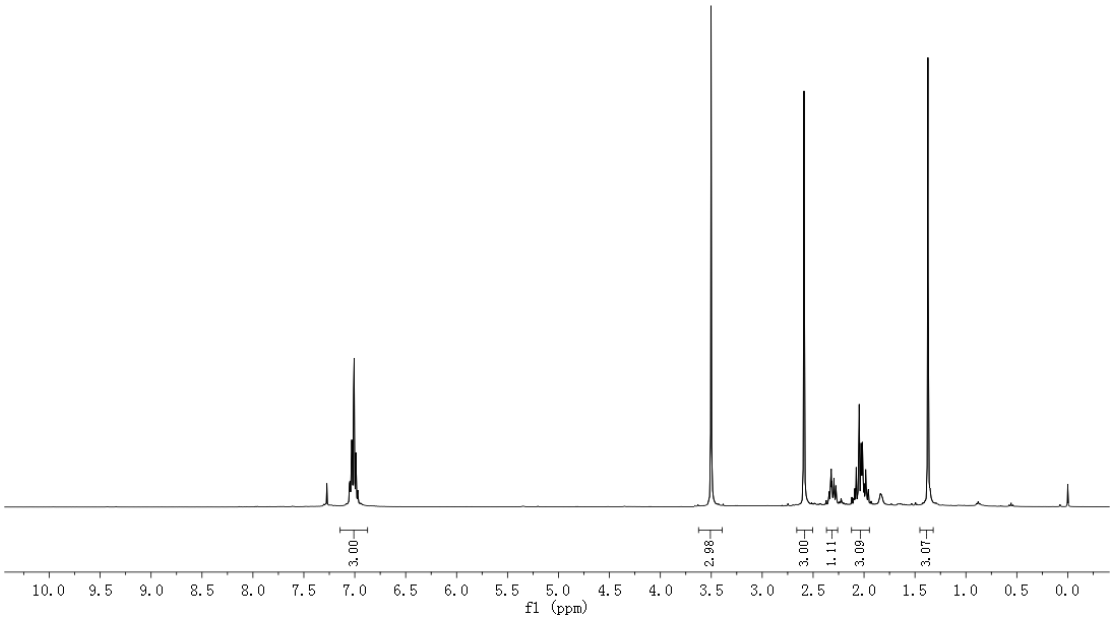
^{13}C NMR of 3ea

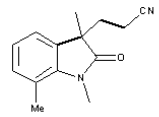




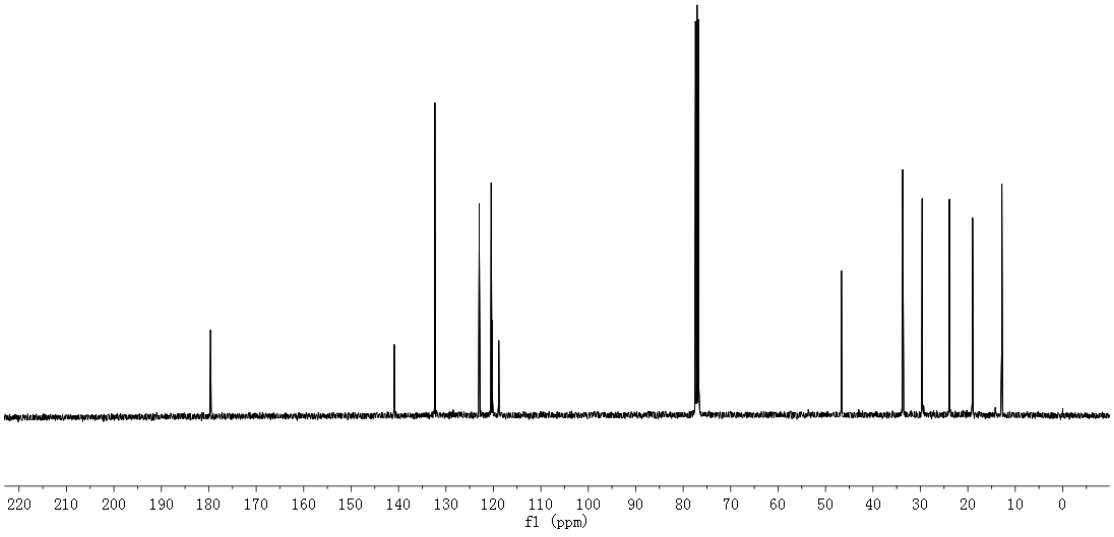


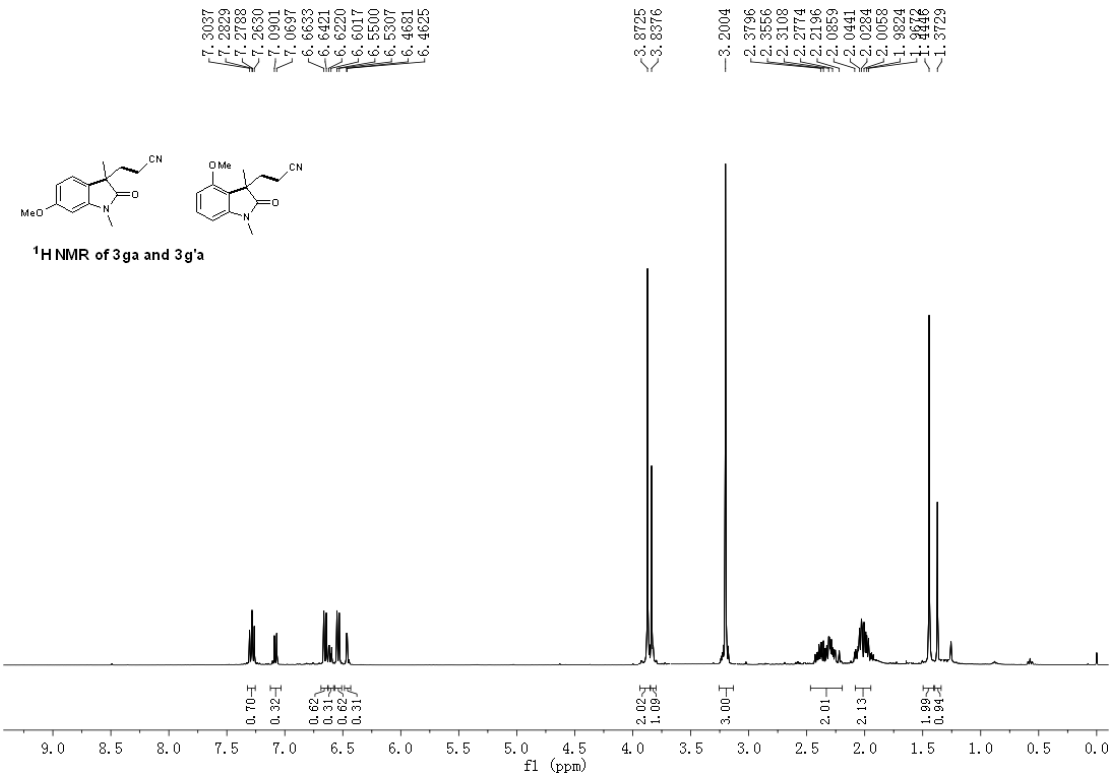
^{1}H NMR of 3fa



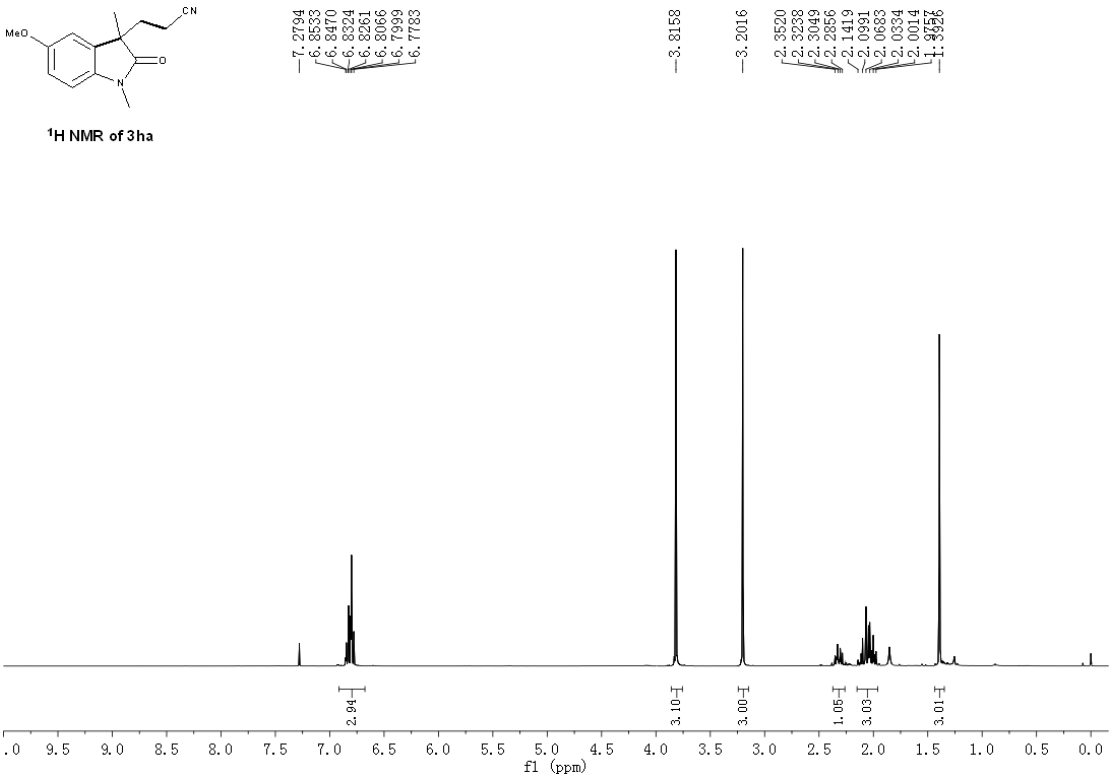


^{13}C NMR of 3fa

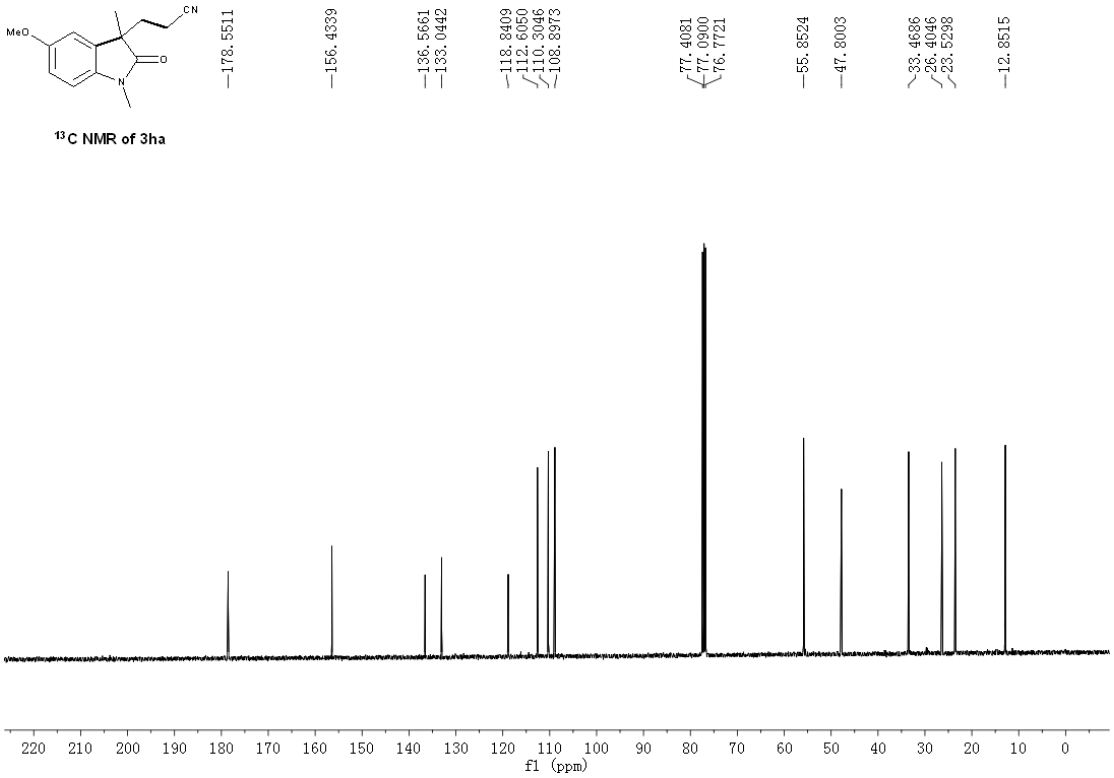




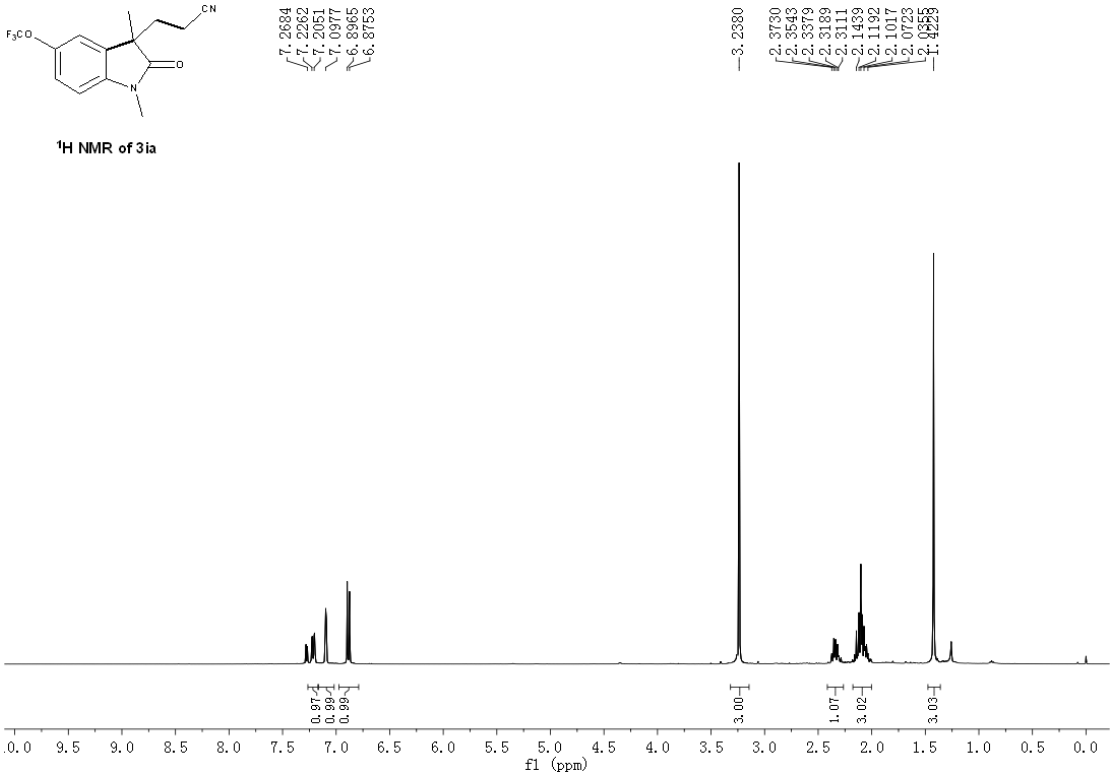
^{1}H NMR of 3ga and 3g'a



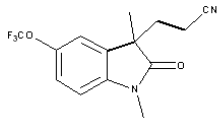
^{1}H NMR of 3ha



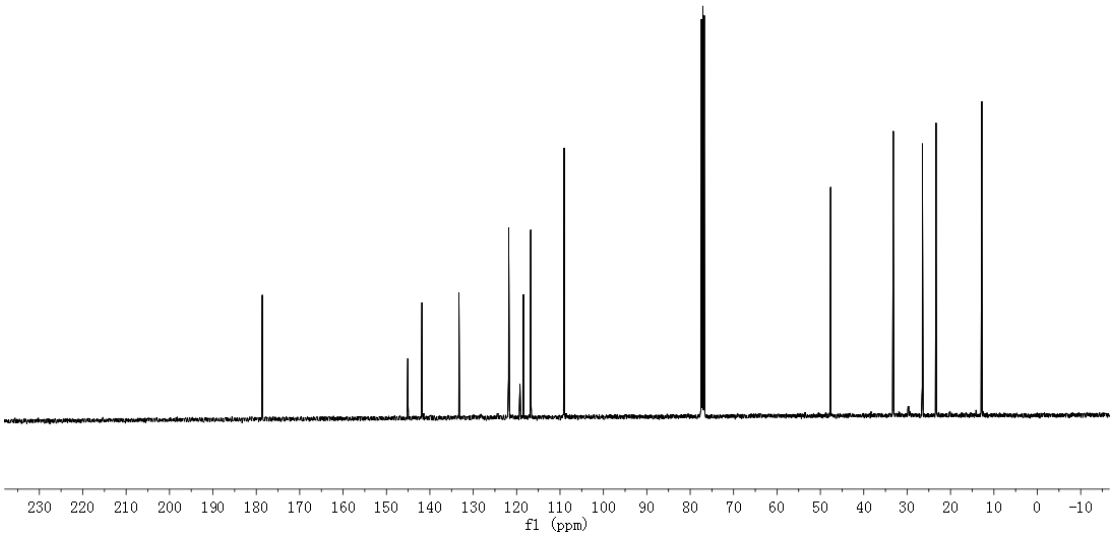
^{13}C NMR of 3ha



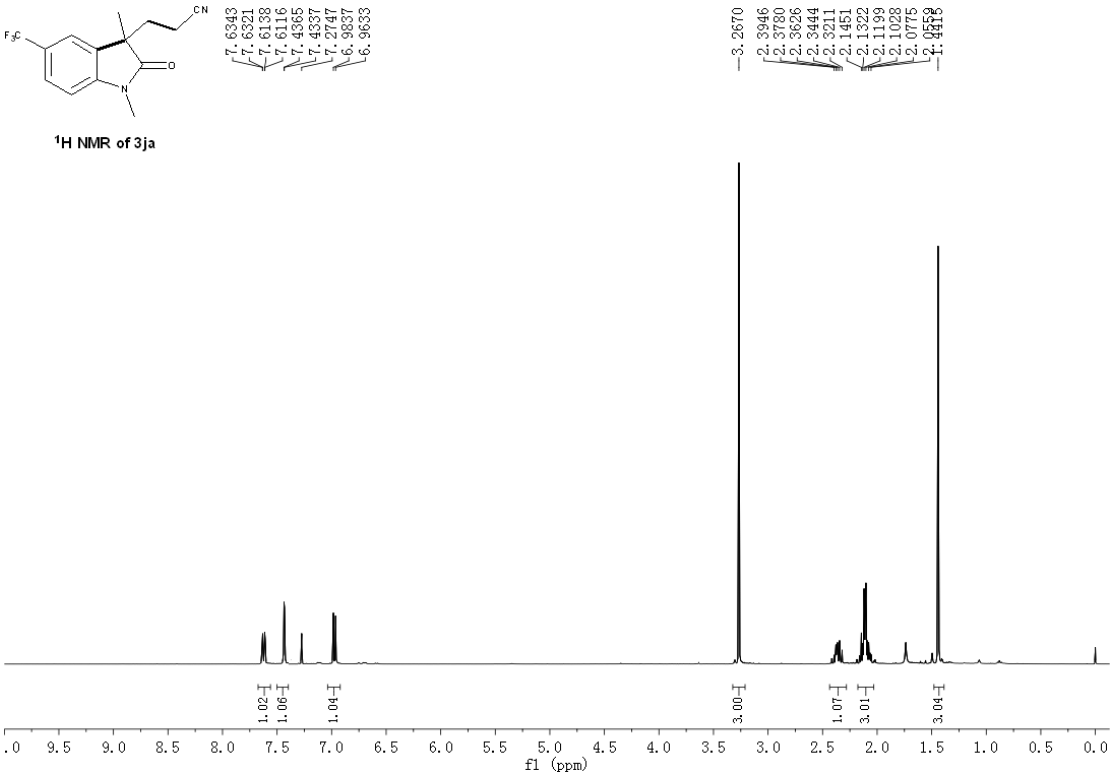
^{1}H NMR of 3ia

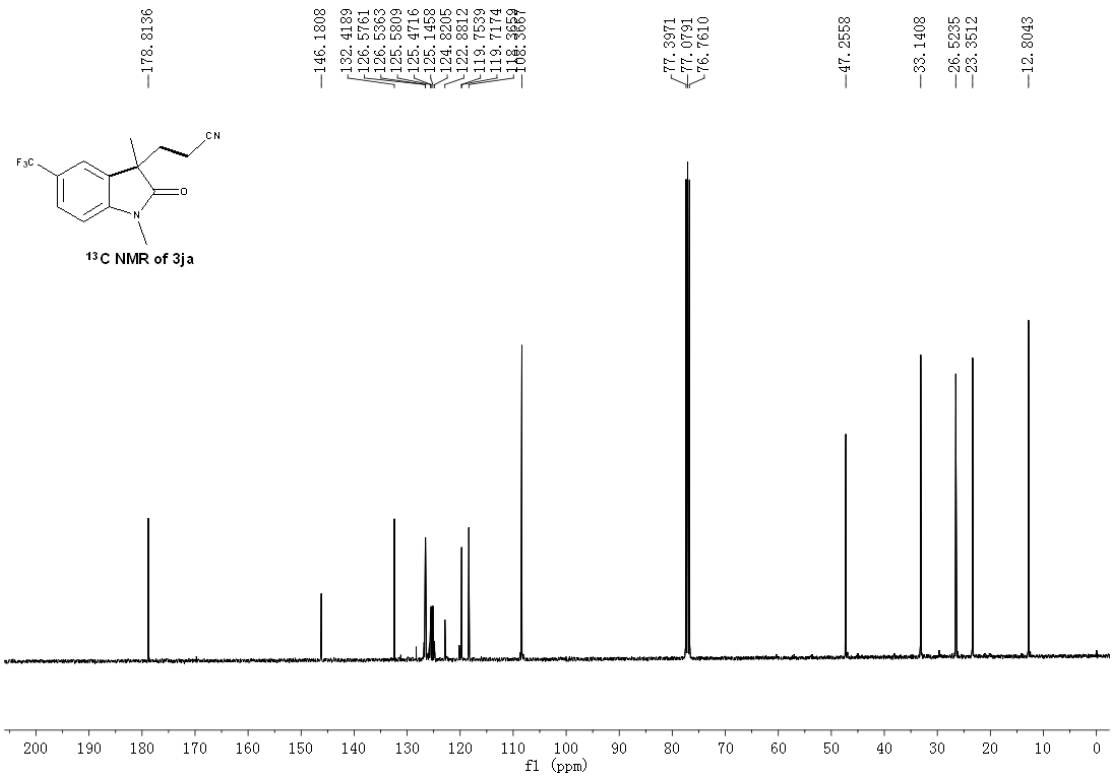


^{13}C NMR of 3ia



^{1}H NMR of 3ja

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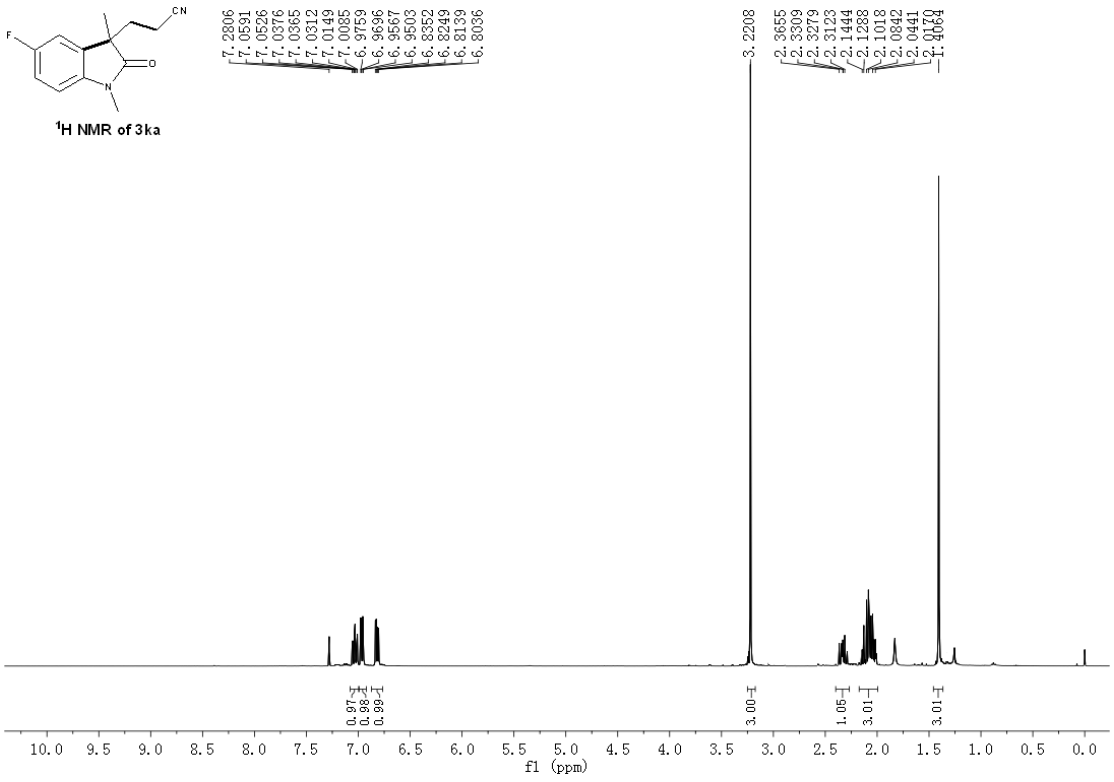
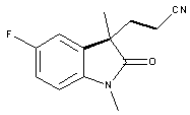
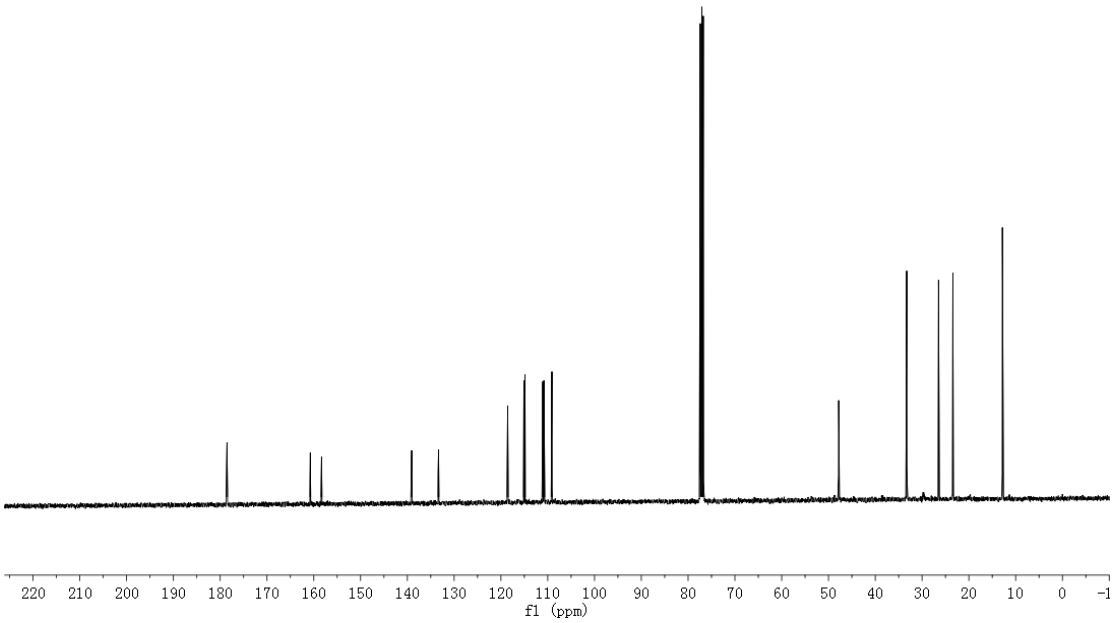
146.1808
132.4189
126.5761
126.5363
125.5809
125.4716
125.1458
124.8205
122.8812
119.7539
119.7174
108.3659
108.3681
77.3971
77.0791
76.7610
47.2558
33.1408
26.5235
23.3512
12.8043
CN
F3C
O
N
13C NMR of 3ja
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CN
F
O
N
1H NMR of 3ka
7.2806
7.0591
7.0526
7.0376
7.0365
7.0312
7.0149
7.0085
6.9759
6.9696
6.9567
6.9503
6.8352
6.8249
6.8139
6.8036
3.2208
2.3655
2.3309
2.3279
2.3123
2.1444
2.1288
2.1018
2.0842
2.0441
2.0070
1.4064
0.97
0.88
0.89
3.00
1.05
3.01
3.01
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)



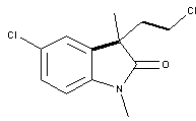
178.5443
160.7403
158.3354
139.0837
139.0648
133.4087
133.3321
118.5587
115.0924
114.8589
111.0527
110.8068
109.1849
109.1039
77.4031
77.0849
76.7671
47.8089
47.7920
33.2813
26.4782
23.4199
12.8195

^{13}C NMR of 3ka



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

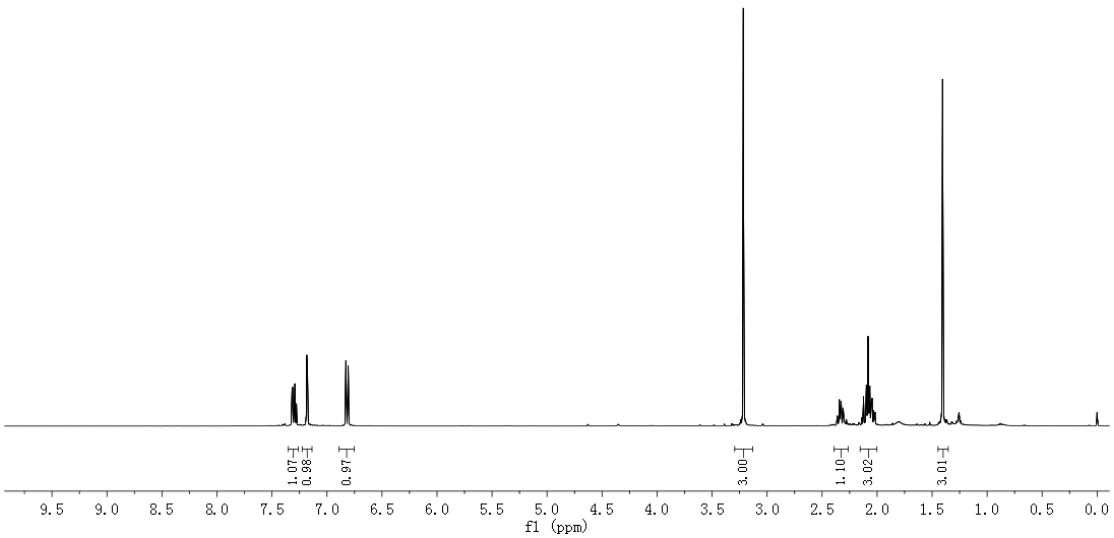
f1 (ppm)



7.3174
7.3122
7.2966
7.2914
7.2782
7.1840
7.1789
6.8281
6.8073

3.2158
2.3432
2.3343
2.3270
2.3095
2.3024
2.1236
2.0973
2.0827
2.0664
2.0305

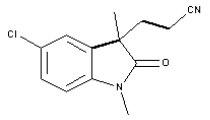
^{1}H NMR of 3la



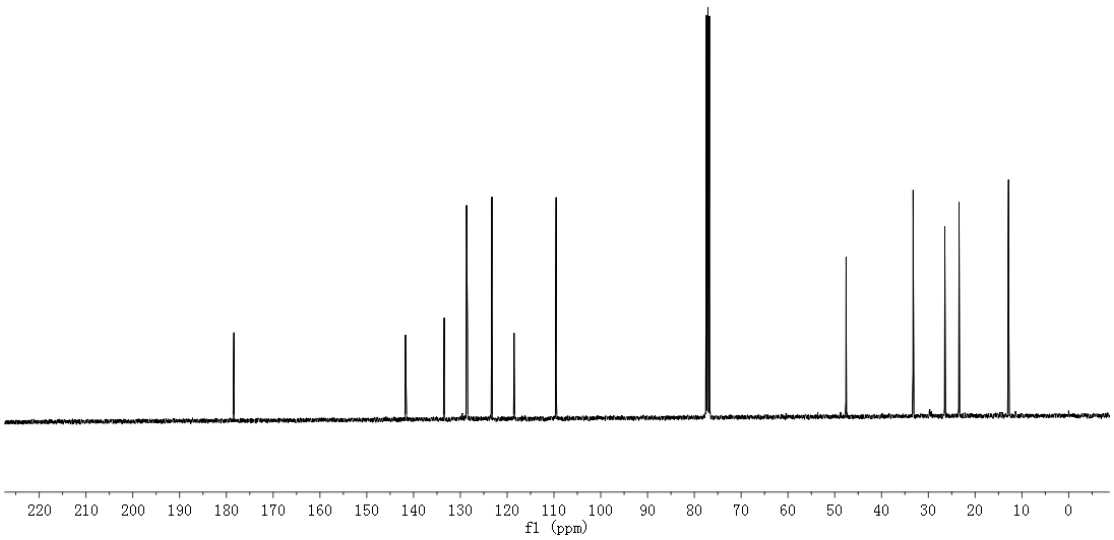
1.07
0.98
0.97
3.00
1.10
3.02
3.01

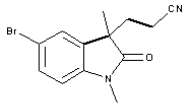
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

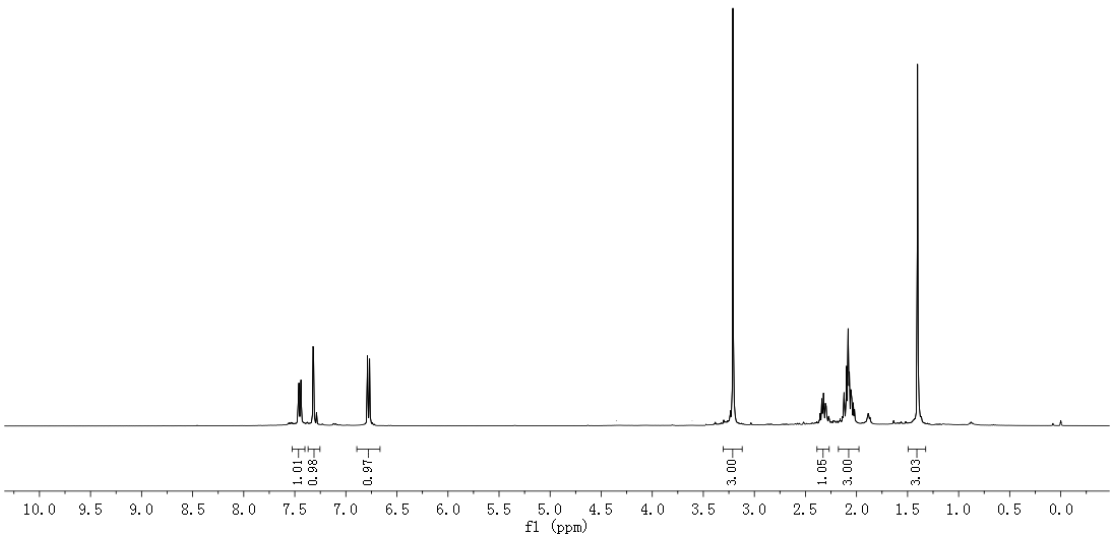


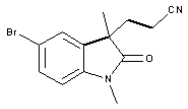
^{13}C NMR of 3la





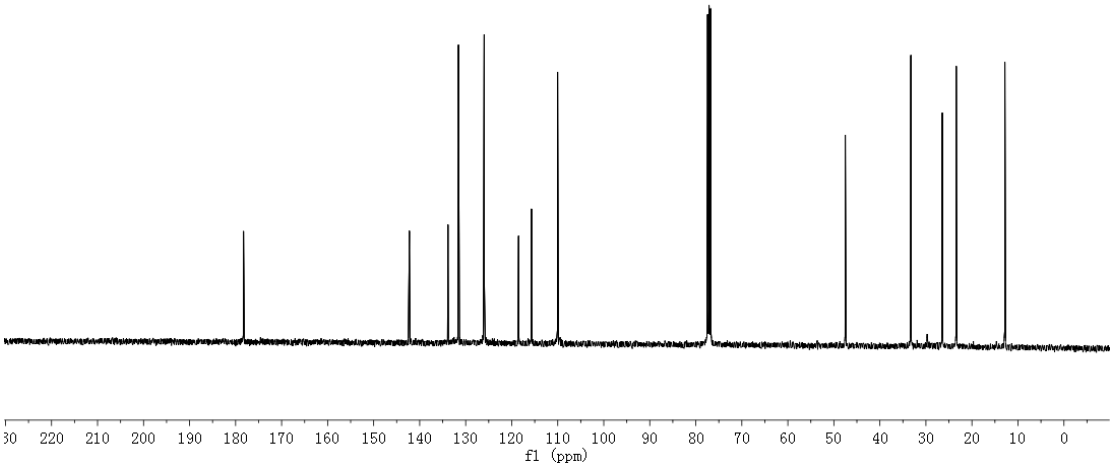
^{1}H NMR of 3ma

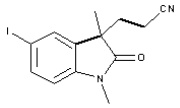




178.2748
142.2432
133.8506
131.5733
125.9894
118.4998
115.7074
110.0225
77.4300
77.1118
76.7939
47.5106
33.2574
26.4345
23.4080
12.8339

^{13}C NMR of 3ma

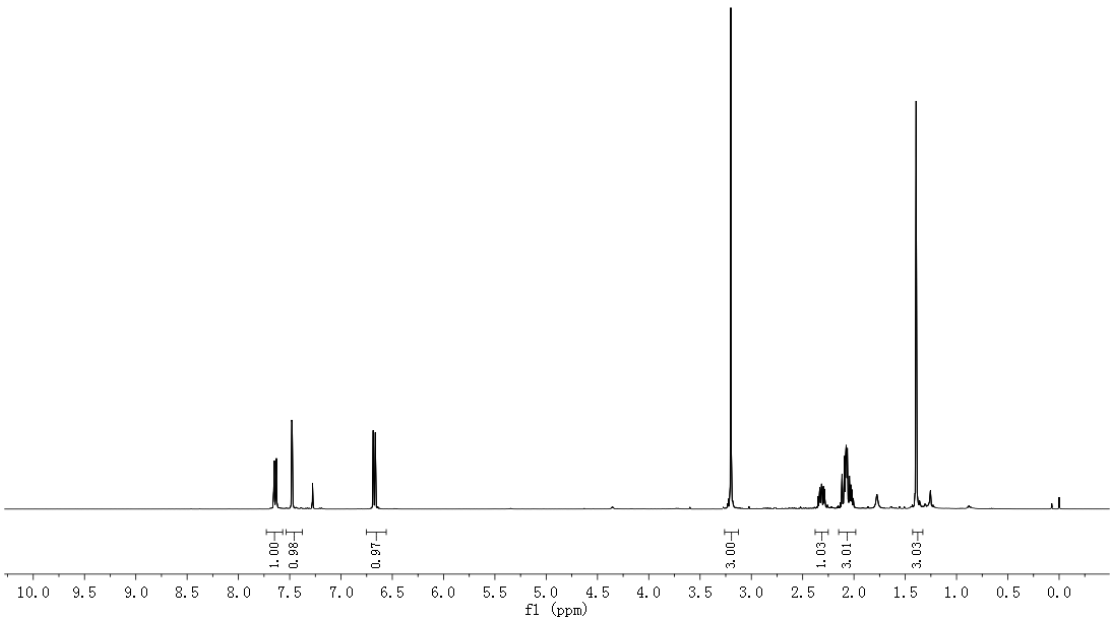




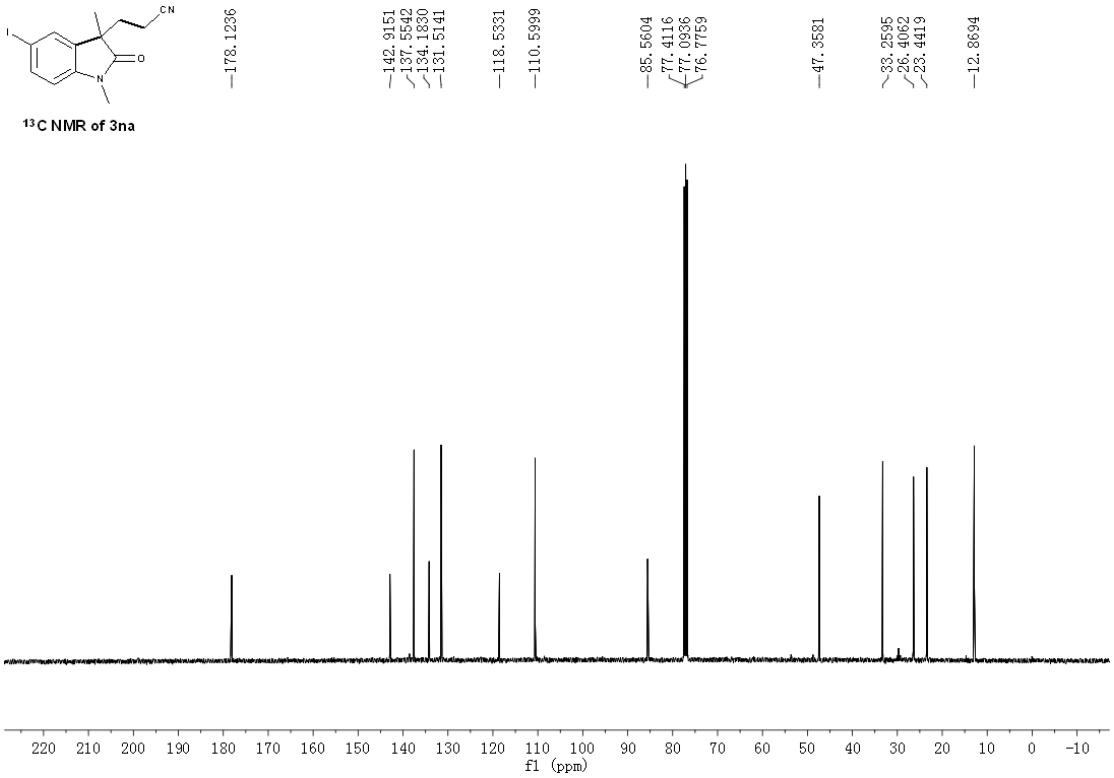
7.6544
7.6502
7.6339
7.6297
7.4799
7.4757
7.2776
6.6860
6.6655

3.2008
2.3506
2.3319
2.3152
2.2869
2.1165
2.0916
2.0644
2.0443
2.0314
2.0068
1.3942

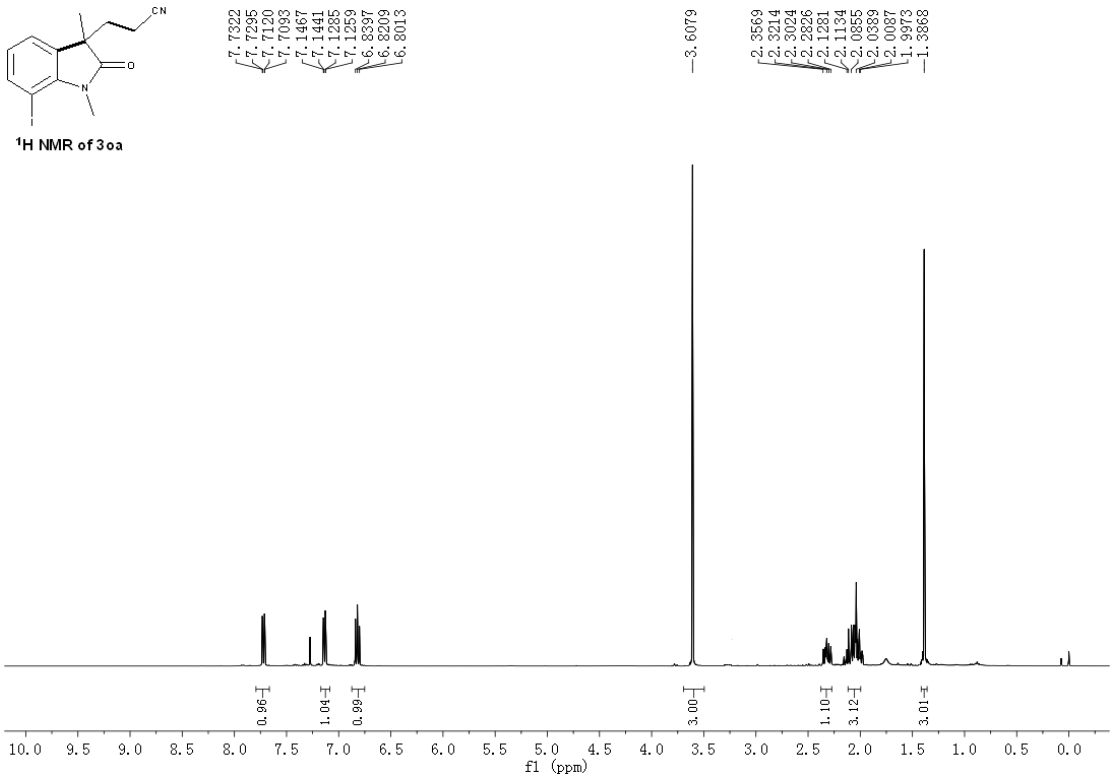
^{1}H NMR of 3na

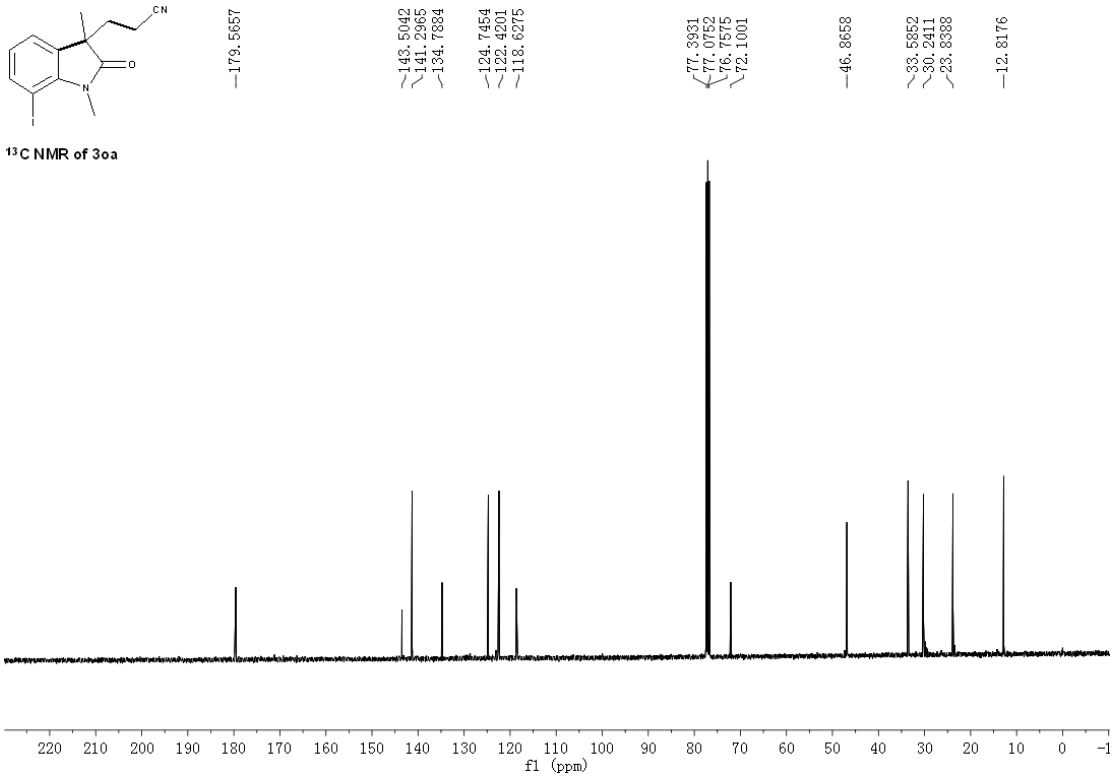


^{13}C NMR of 3na

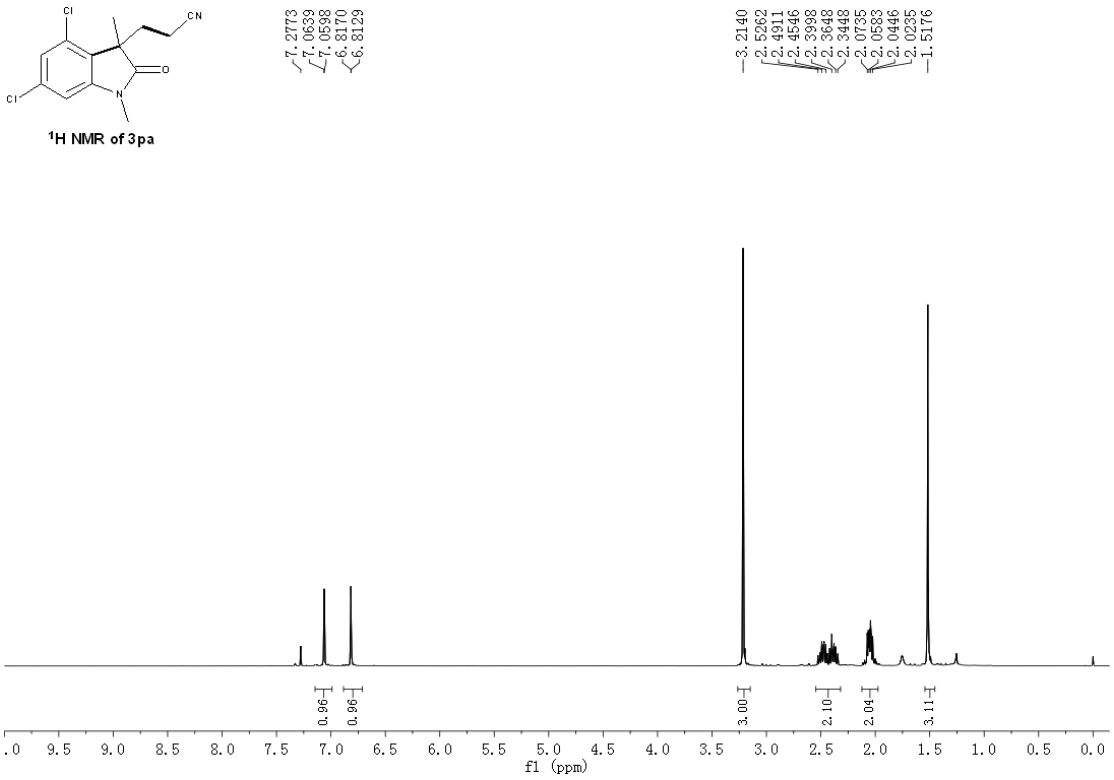


^{1}H NMR of 3oa

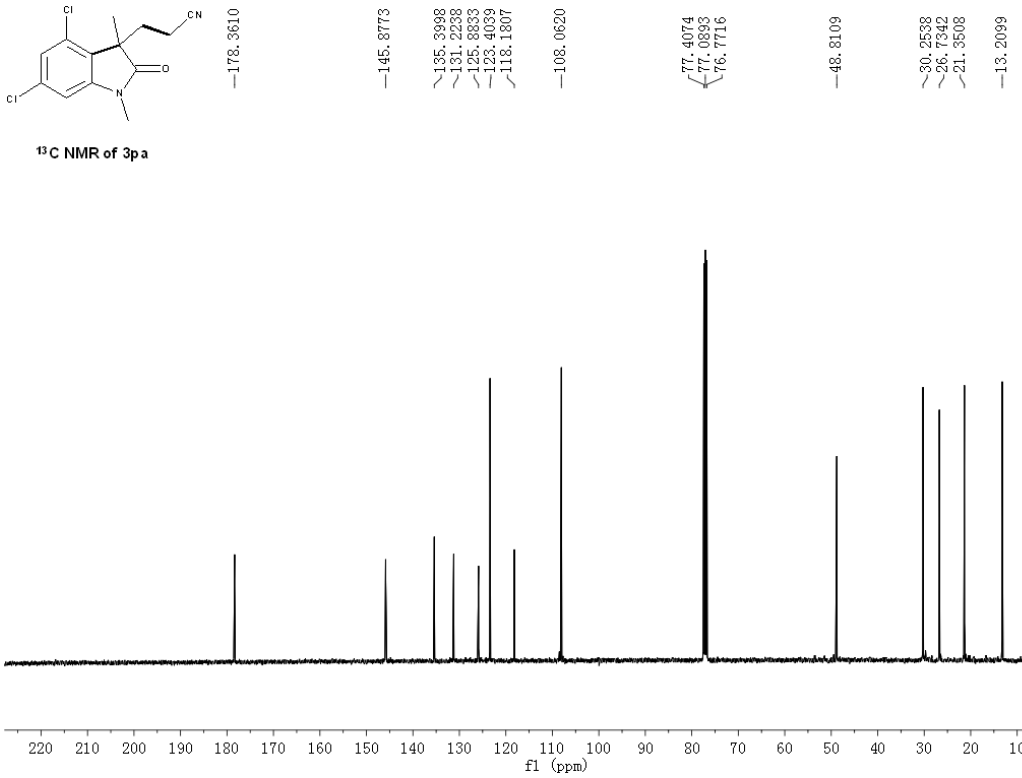




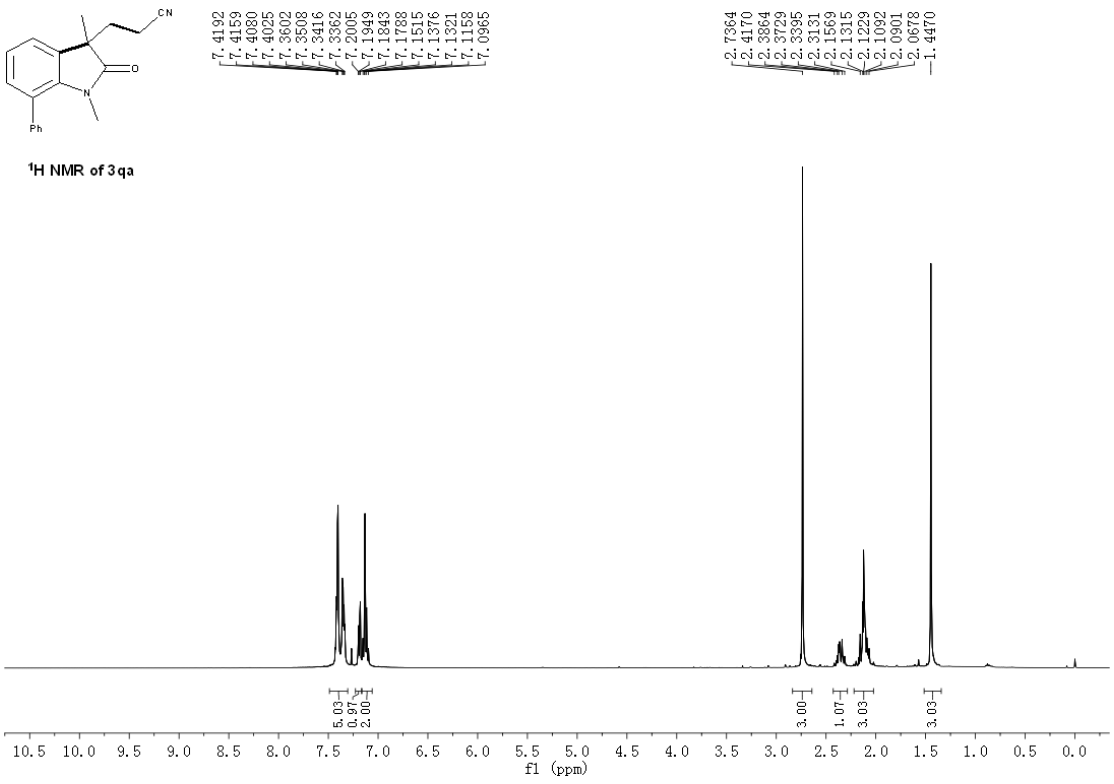
^{13}C NMR of 3oa



^{1}H NMR of 3pa

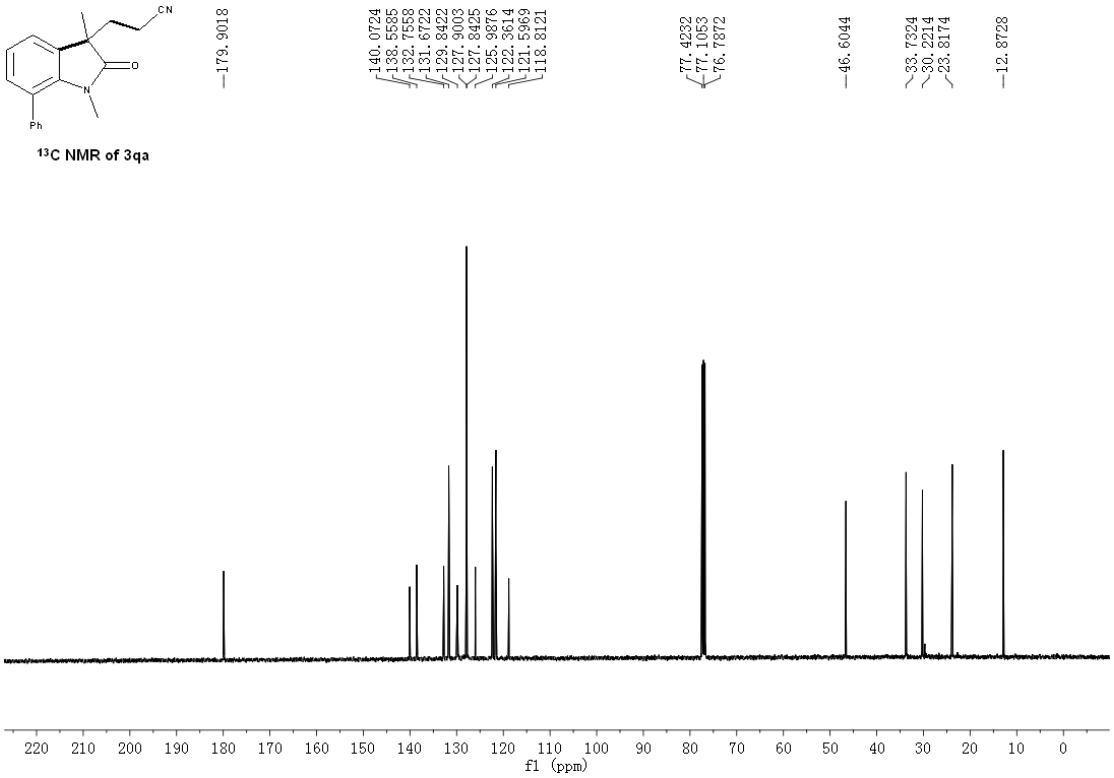


^{13}C NMR of 3pa

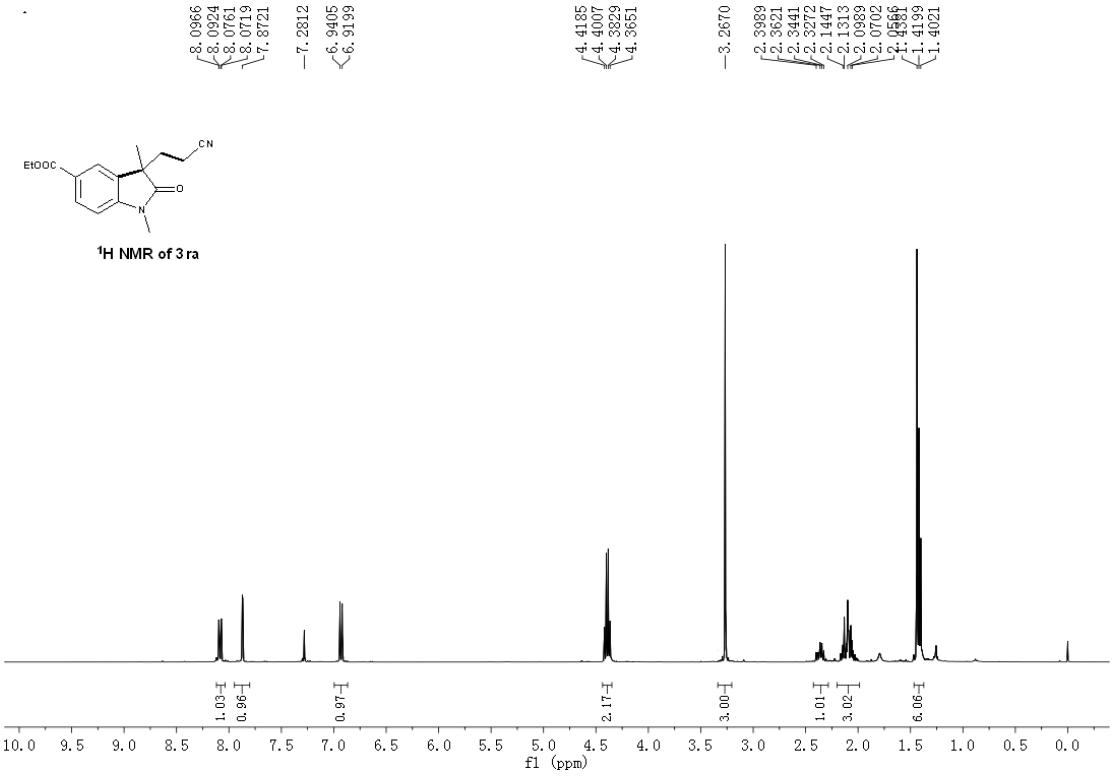


^{1}H NMR of 3qa

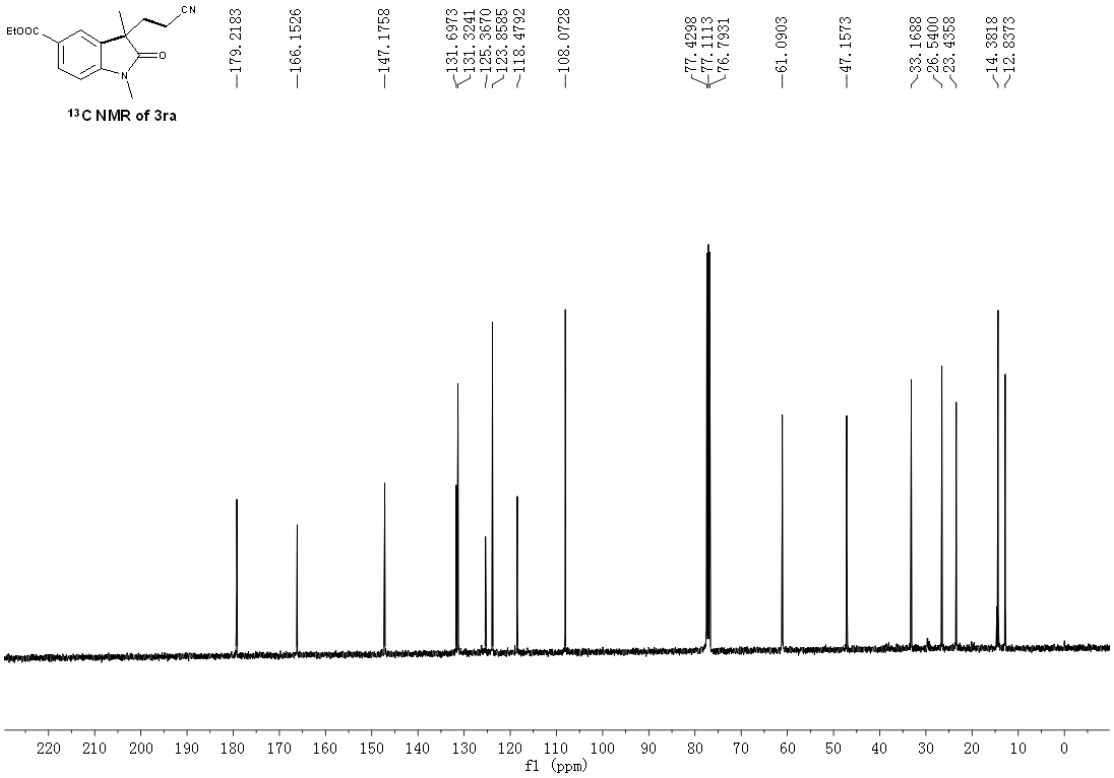
^{13}C NMR of 3qa

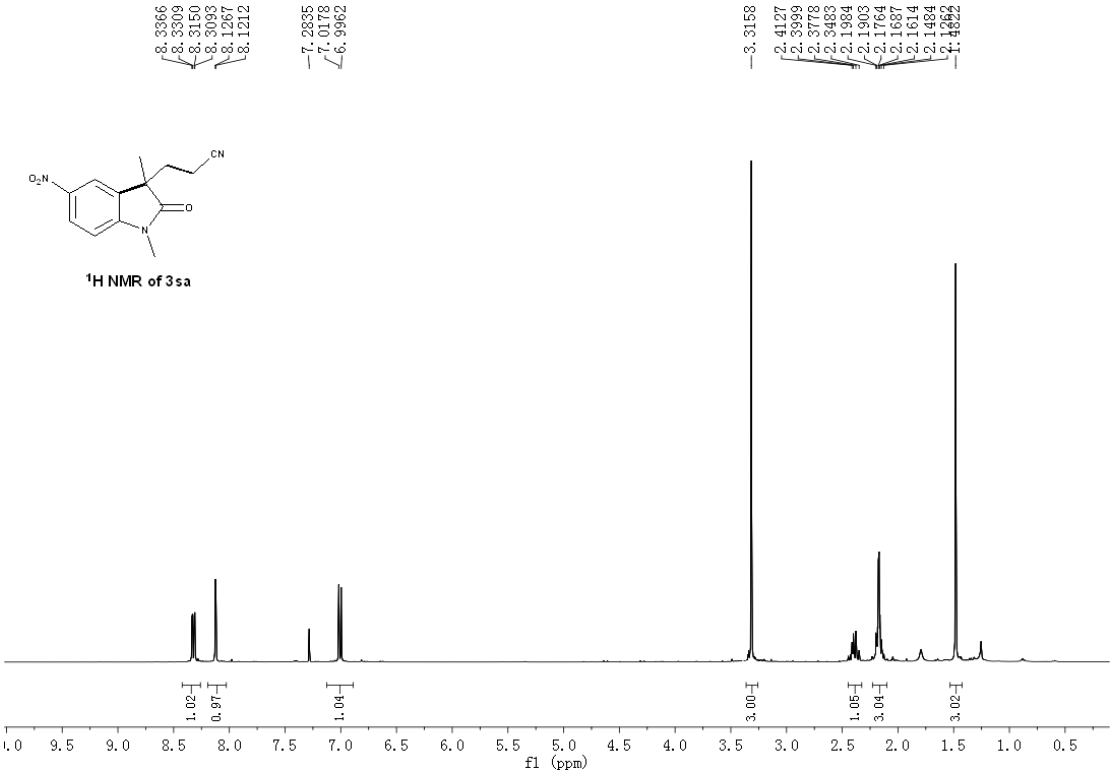


^{1}H NMR of 3ra



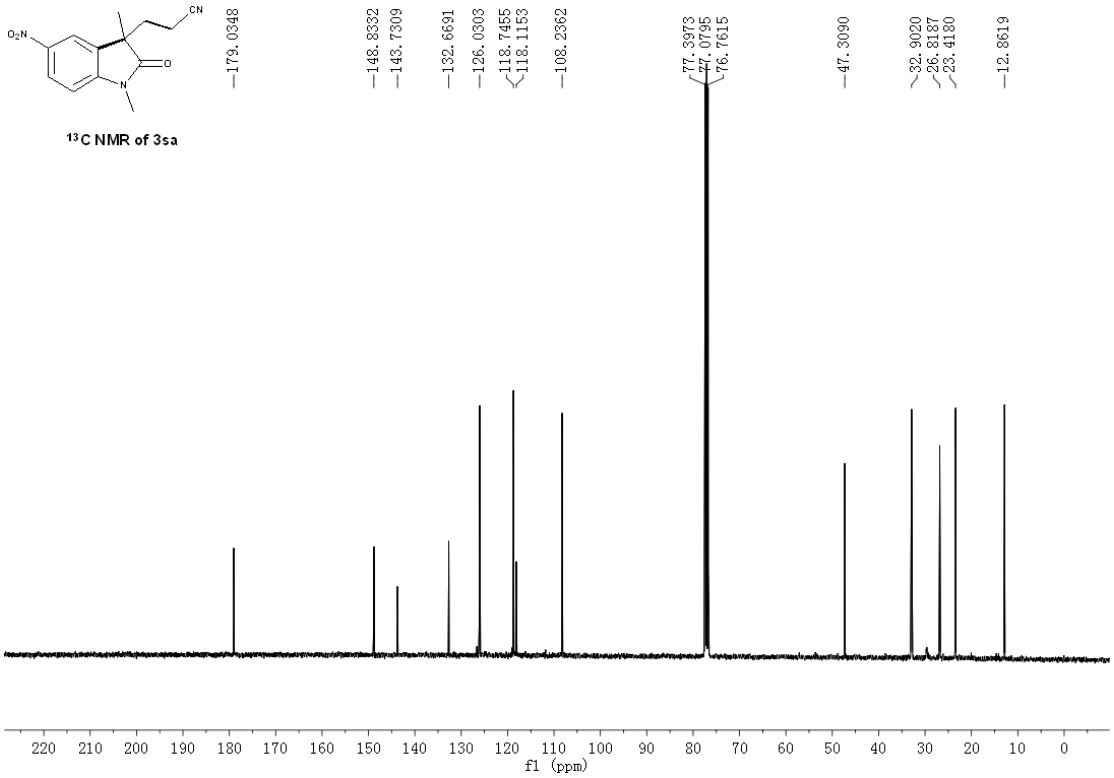
^{13}C NMR of 3ra



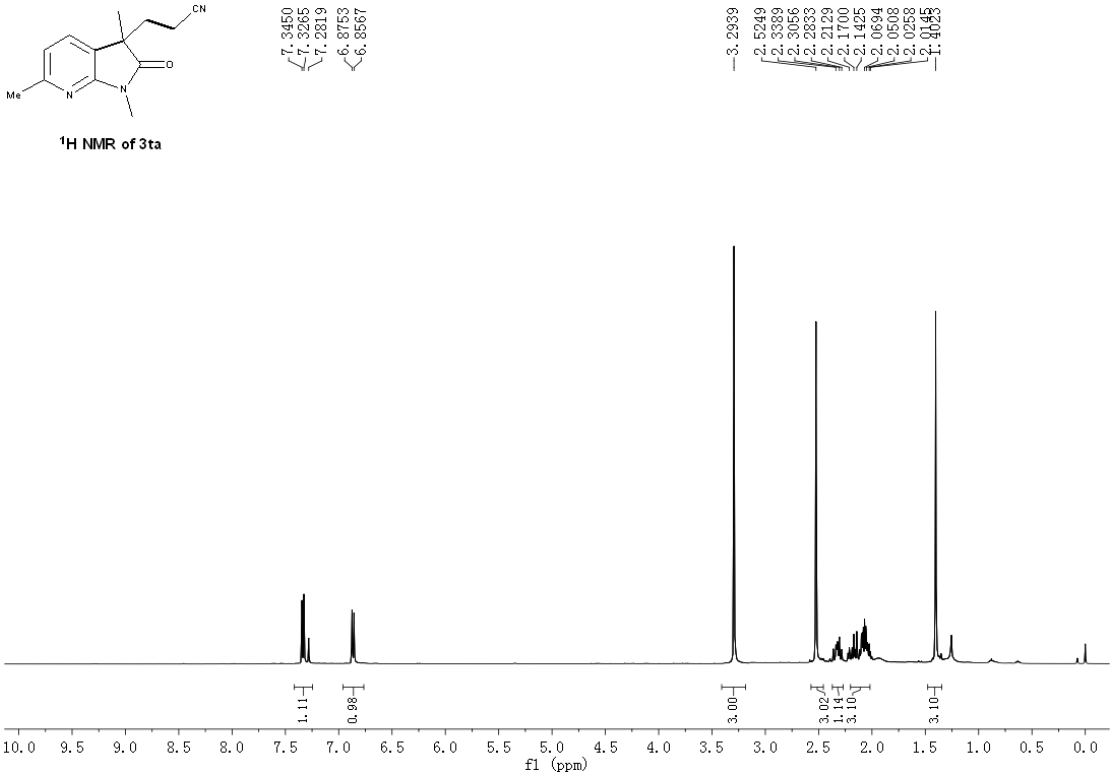


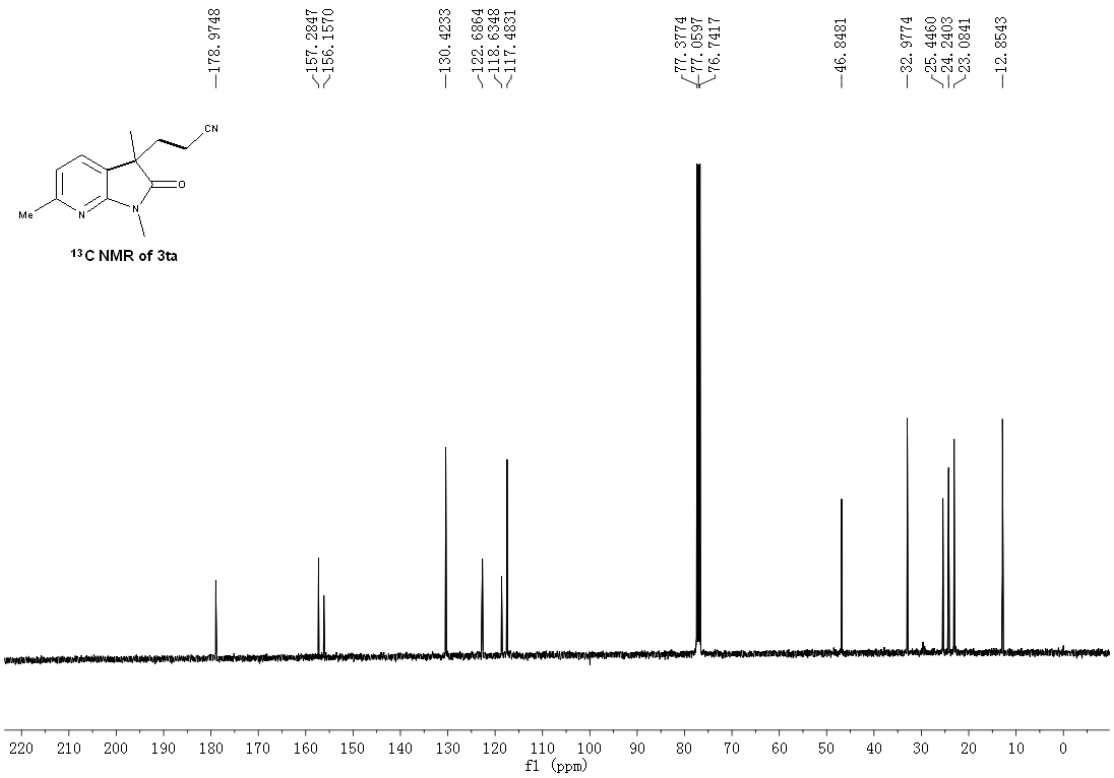
^{1}H NMR of 3sa

^{13}C NMR of 3sa

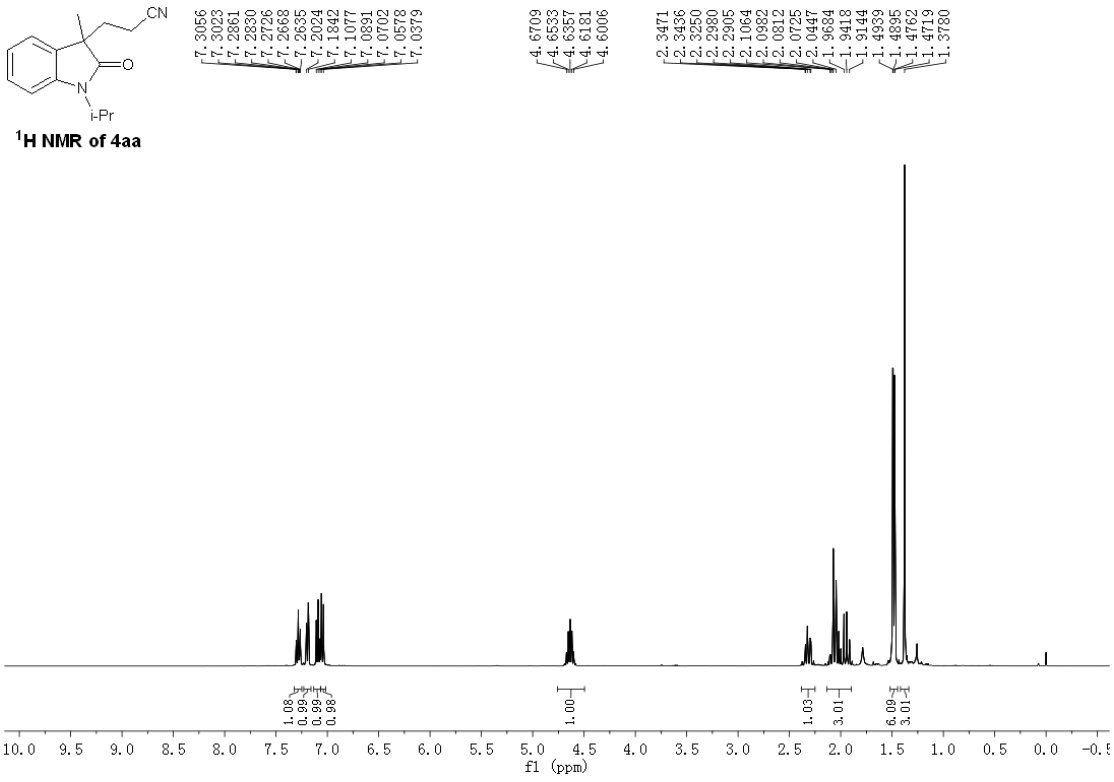


^{1}H NMR of 3ta

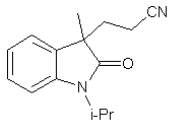




^{13}C NMR of 3ta

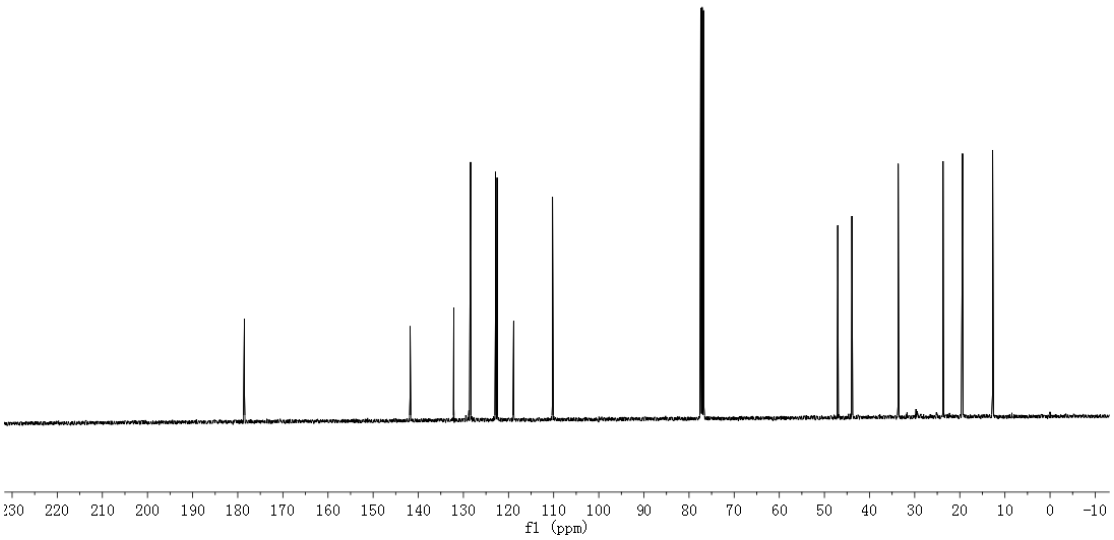


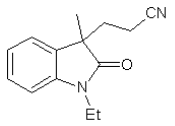
^{1}H NMR of 4aa



178.5334
141.7970
132.1340
128.4090
122.8809
122.5336
118.8595
110.2438
77.4049
77.0871
76.7691
47.0453
43.9120
33.6498
23.7190
19.4875
19.3933
12.7146

^{13}C NMR of 4aa





7.3344
7.3315
7.3151
7.3122
7.2958
7.2929
7.2745
7.2107
7.1938
7.1242
7.1056
7.0883
6.9133
6.8937

3.8291
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3.7938
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3.7721
3.7540
3.7363
3.7187

2.3366
2.3294
2.3097
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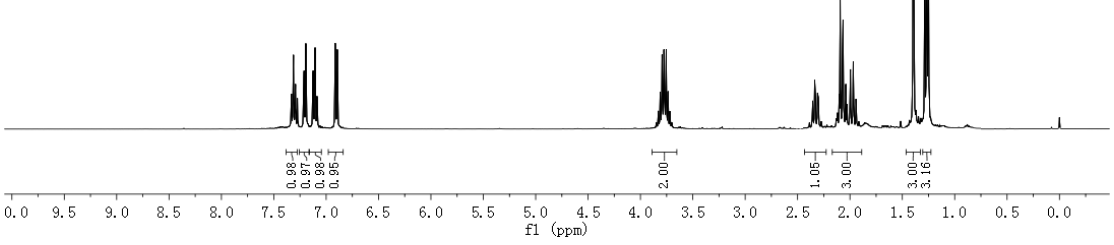
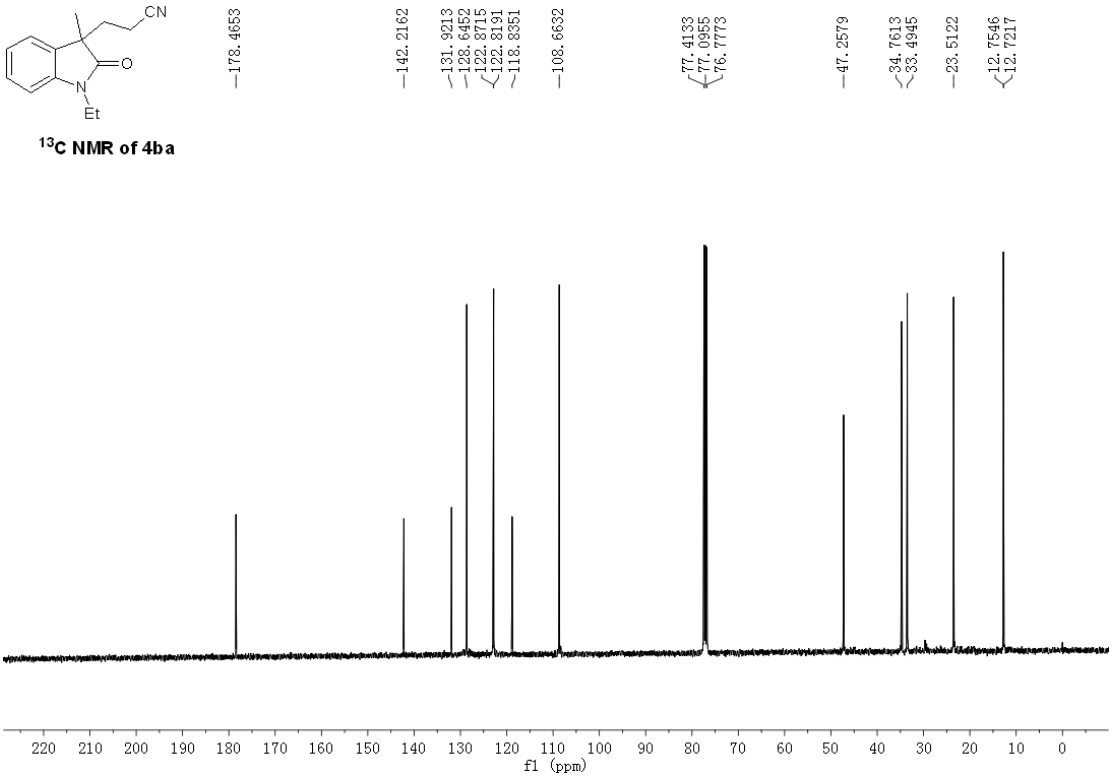
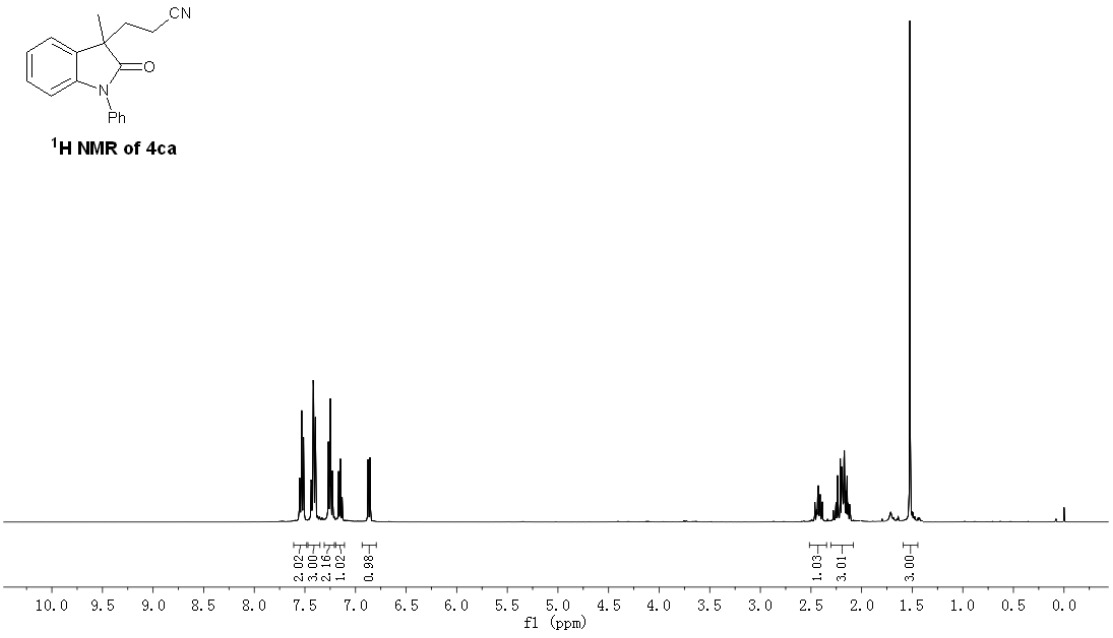
1.2495

^{1}H NMR of 4ba

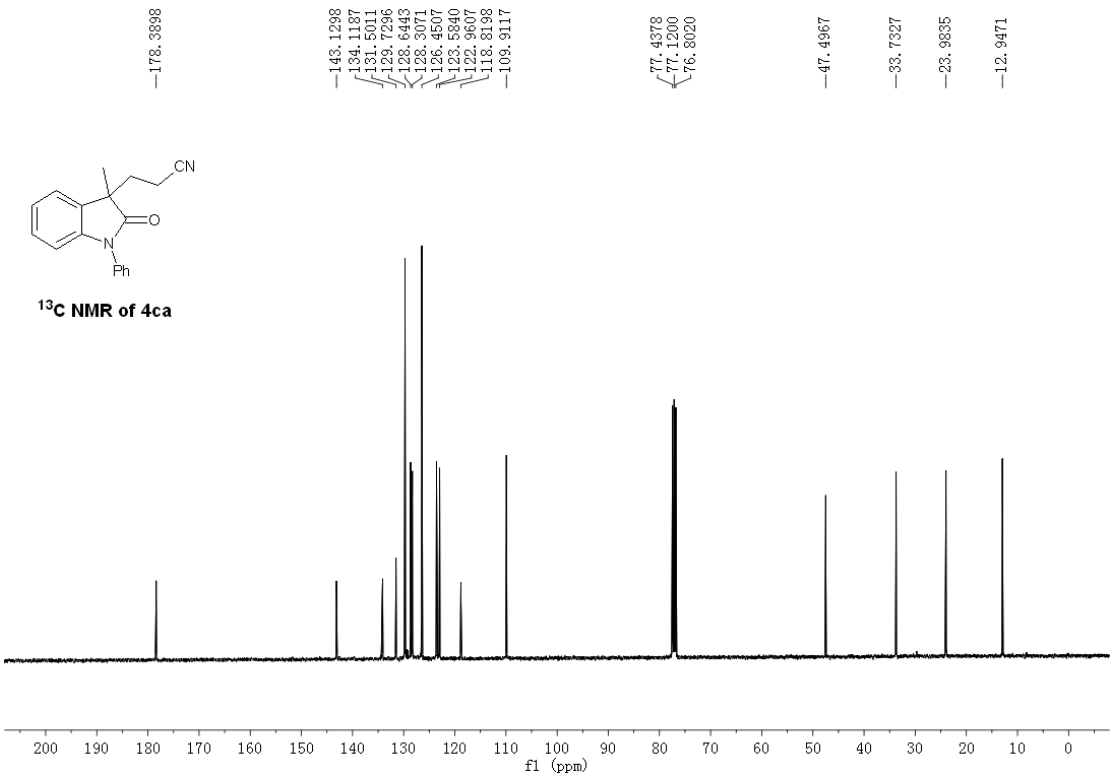




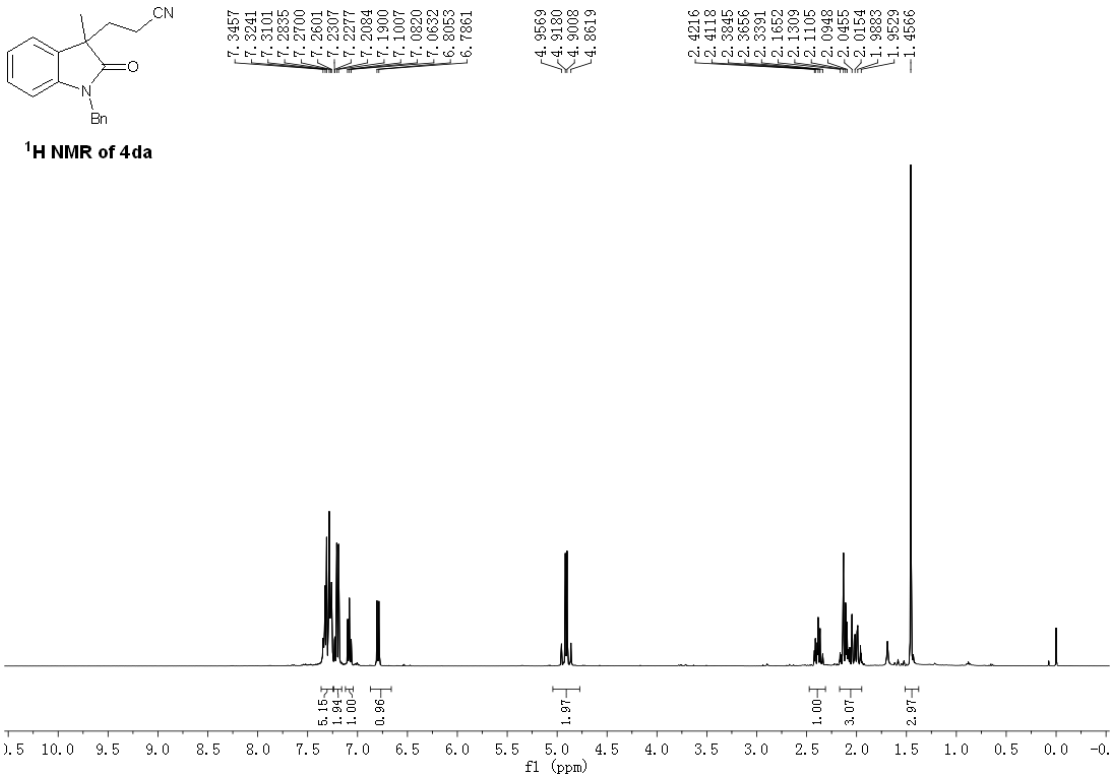
^{13}C NMR of 4ba



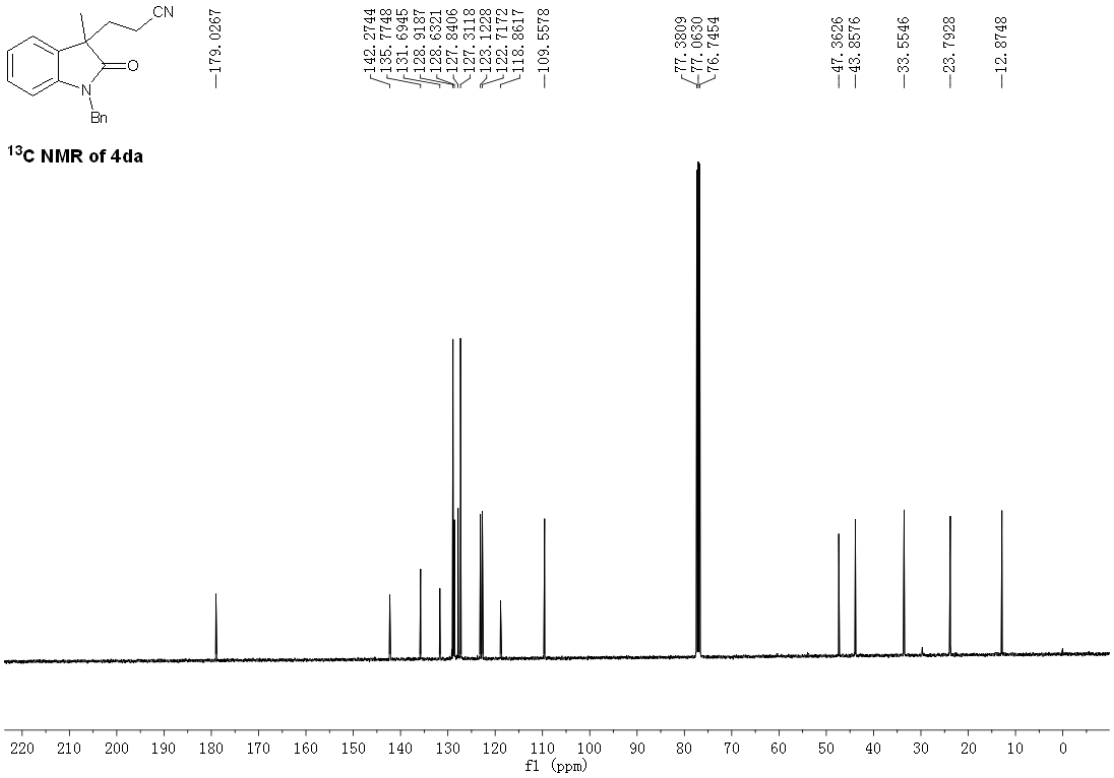
^{1}H NMR of 4ca



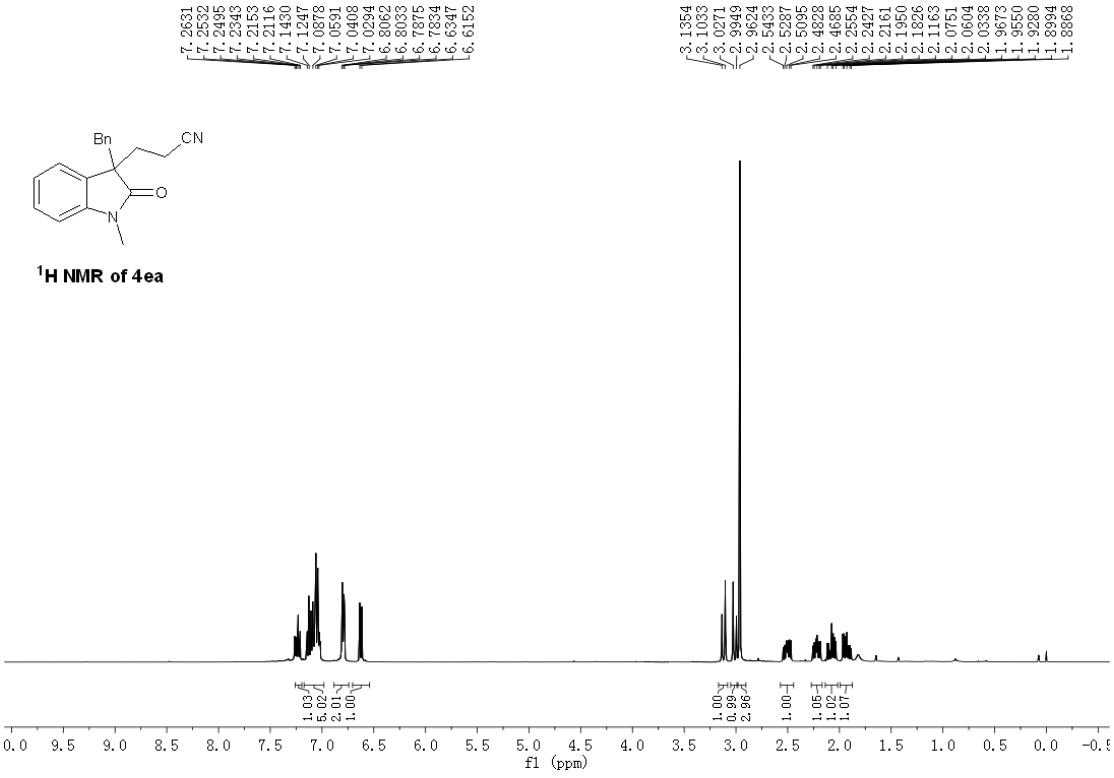
^{13}C NMR of 4ca



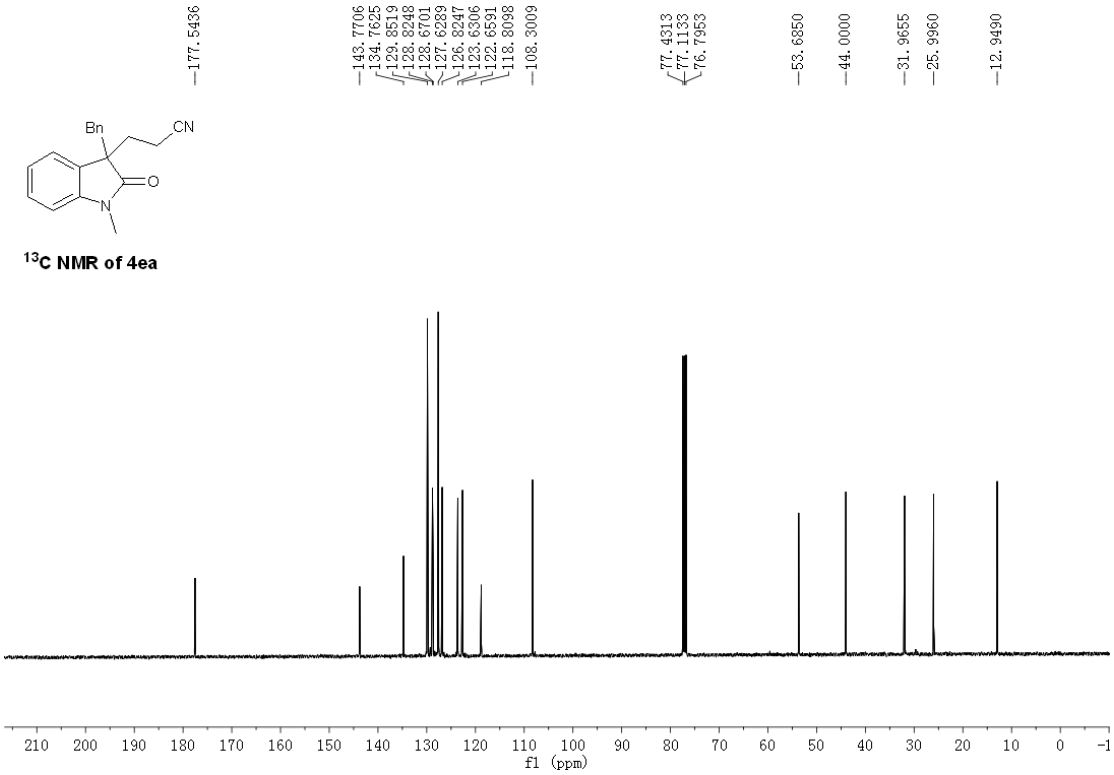
^{1}H NMR of 4da



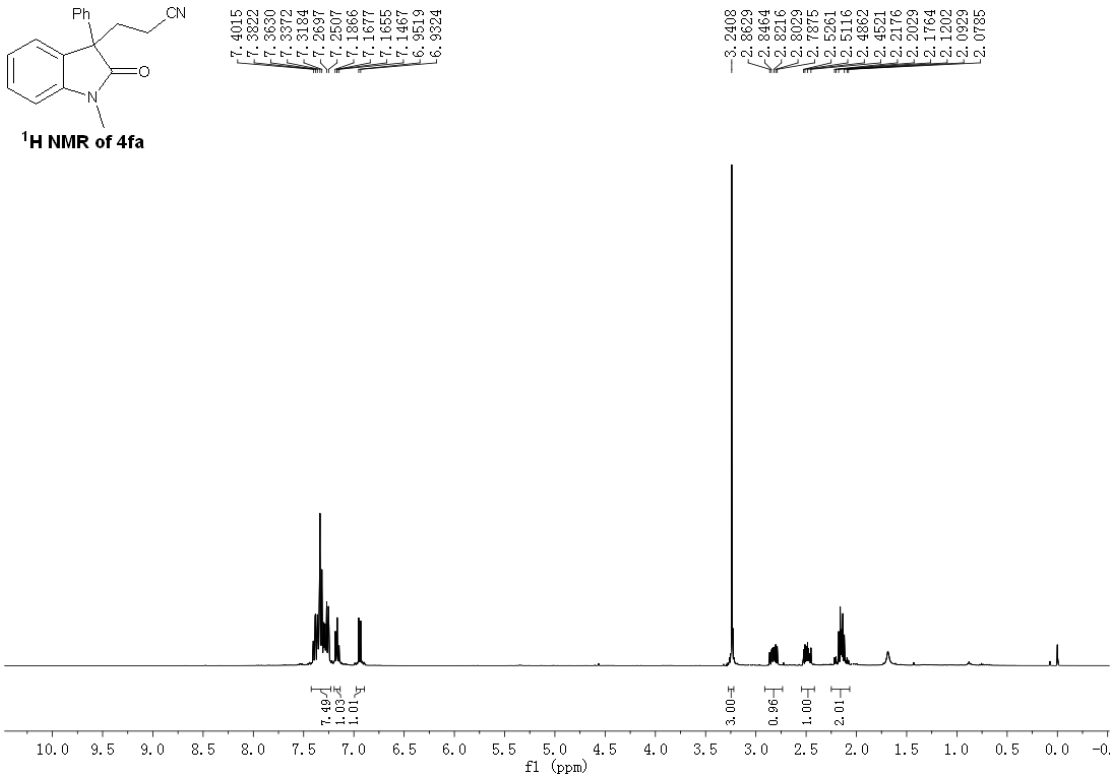
^{13}C NMR of 4da



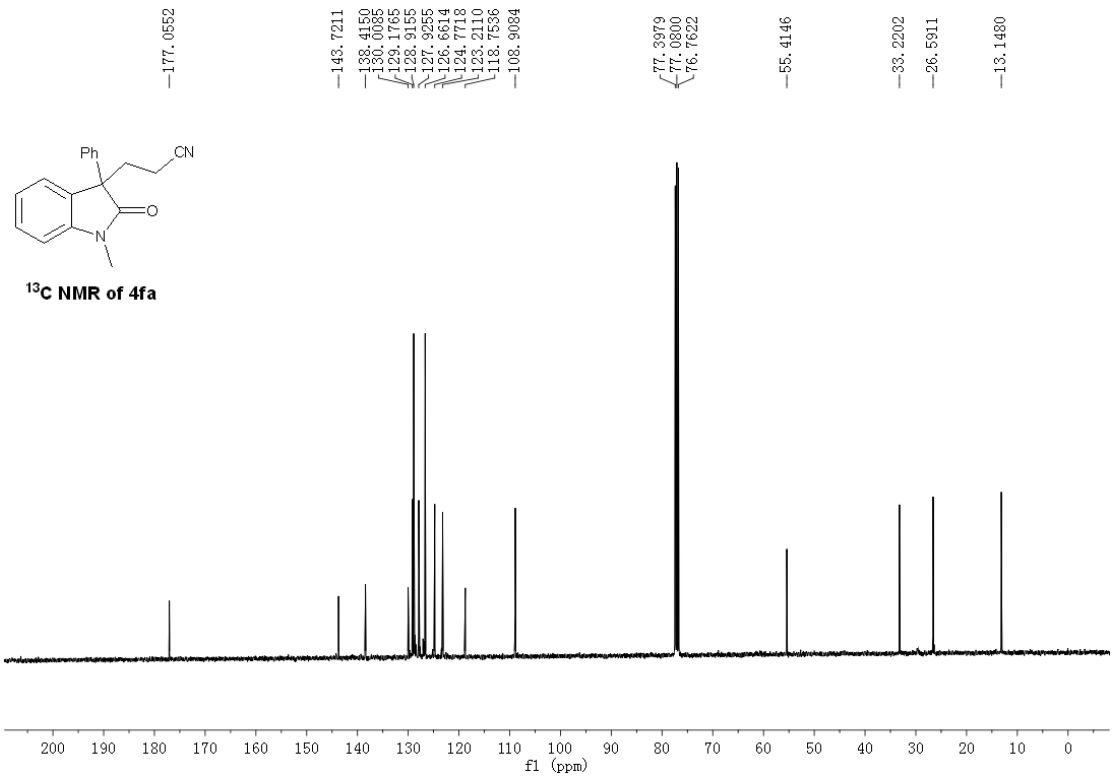
^{1}H NMR of 4ea



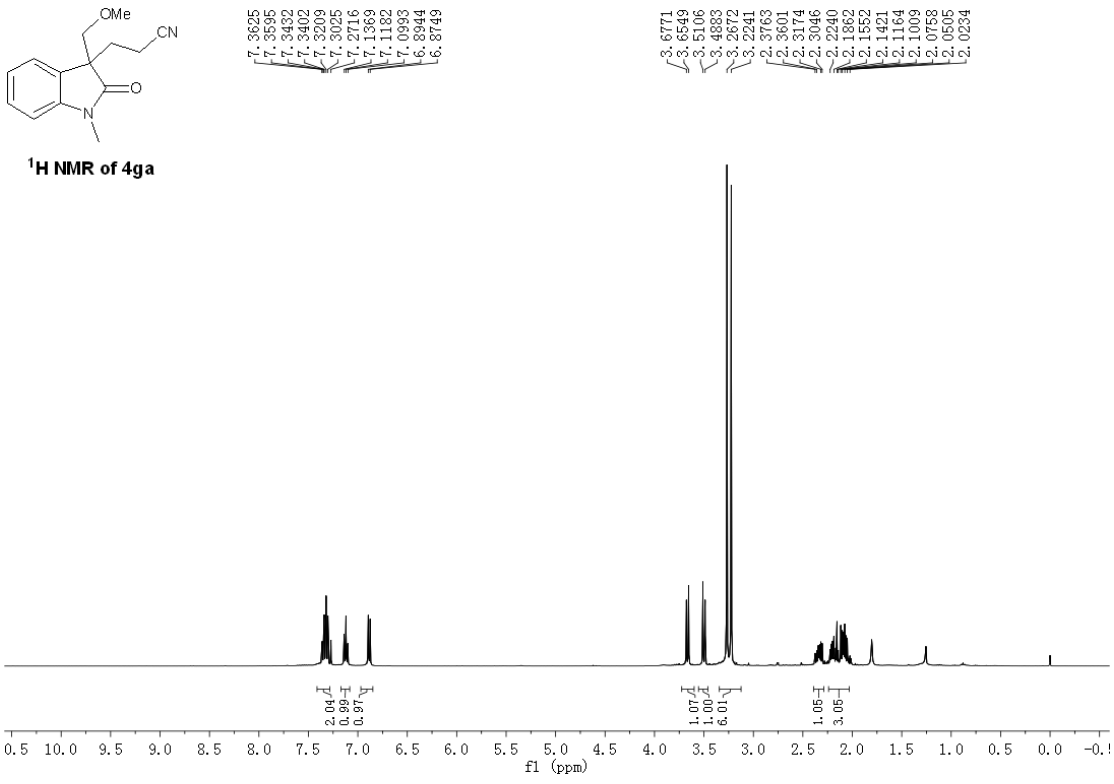
^{13}C NMR of 4ea



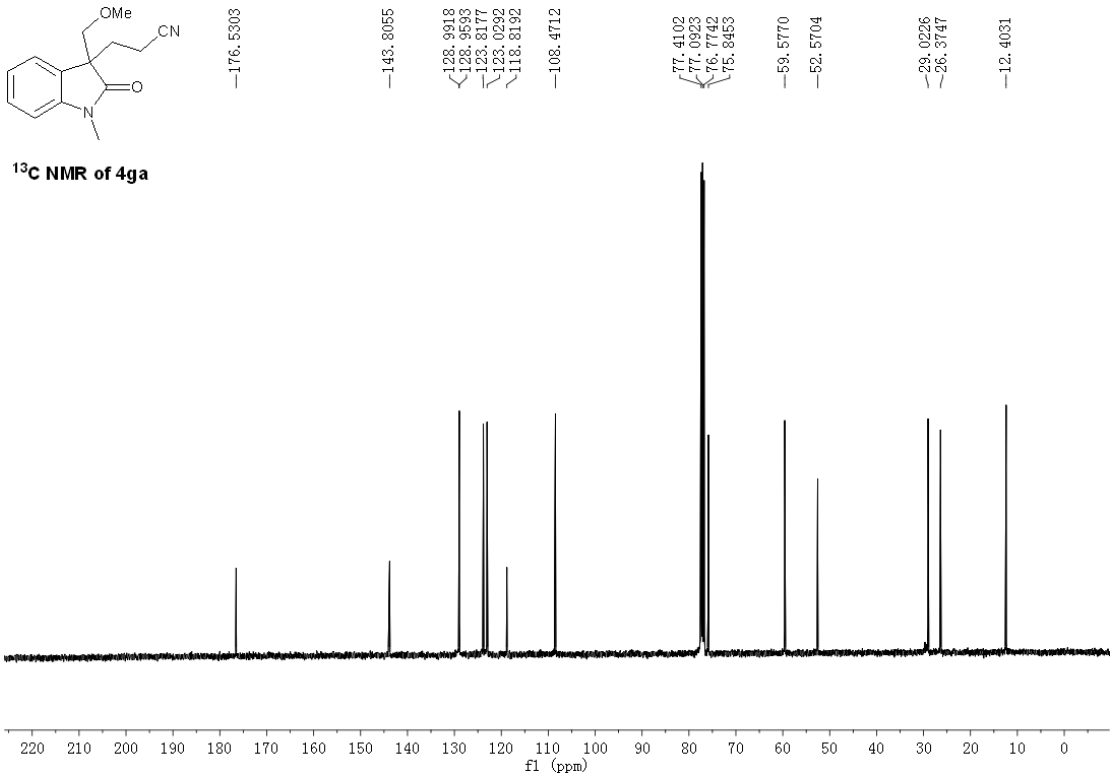
^{1}H NMR of 4fa



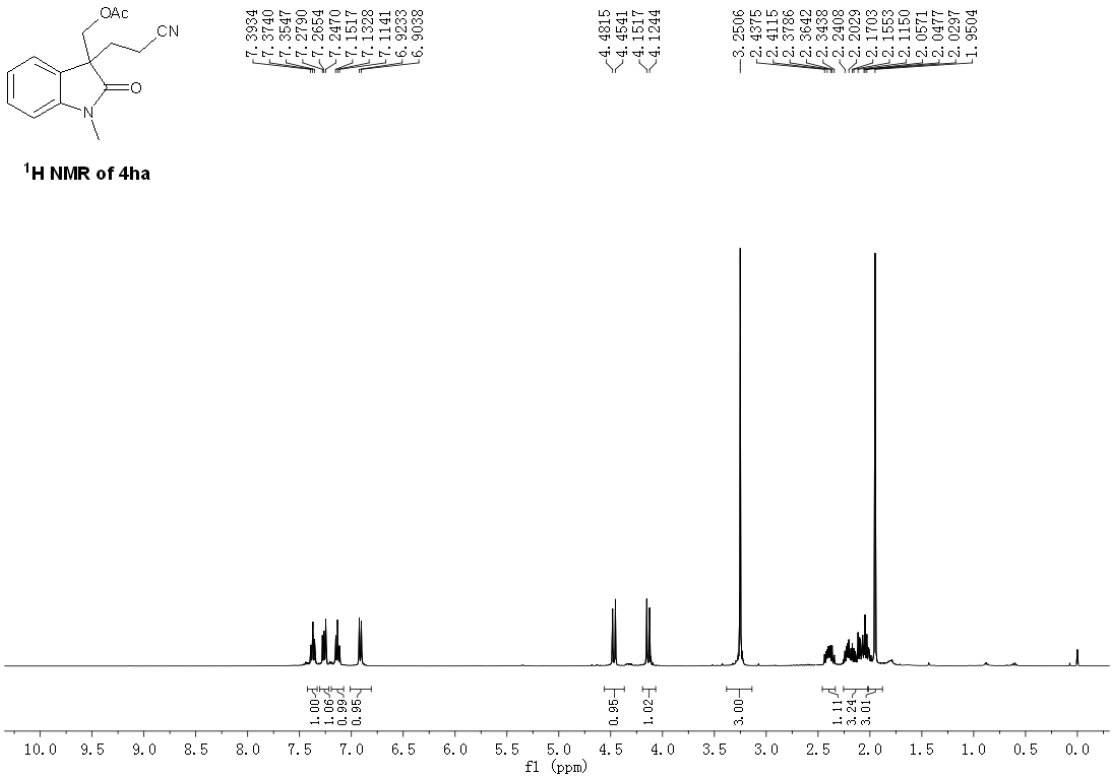
^{13}C NMR of 4fa



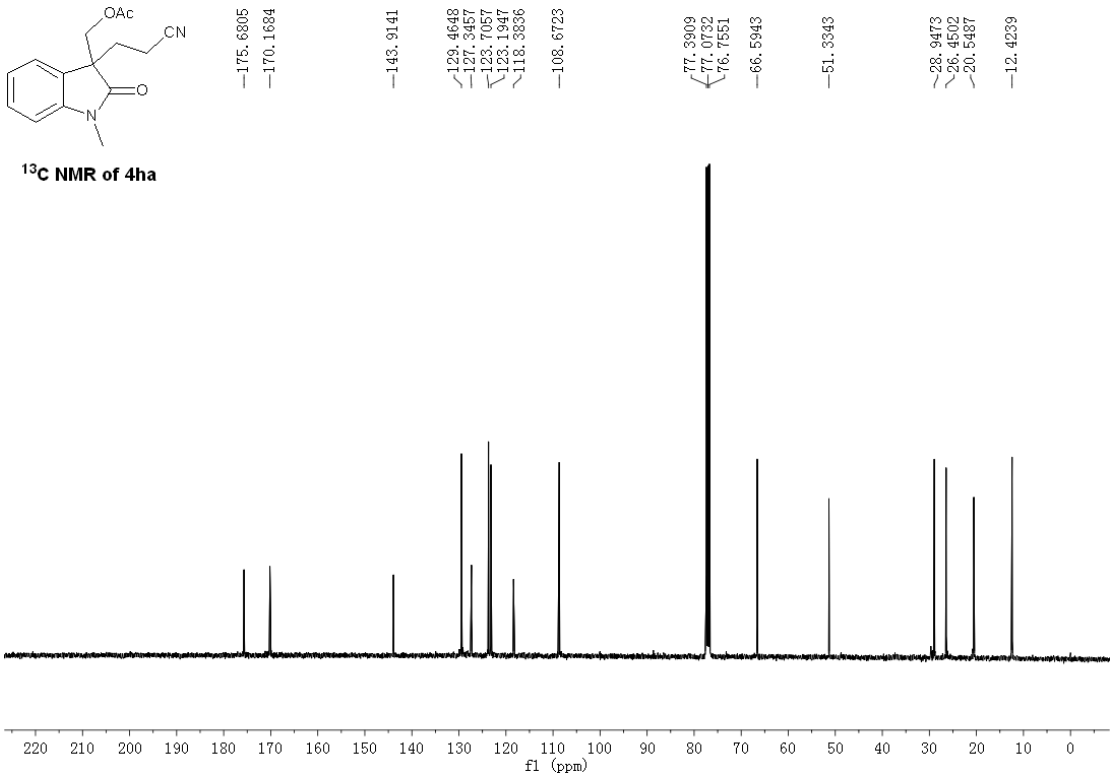
^{1}H NMR of 4ga



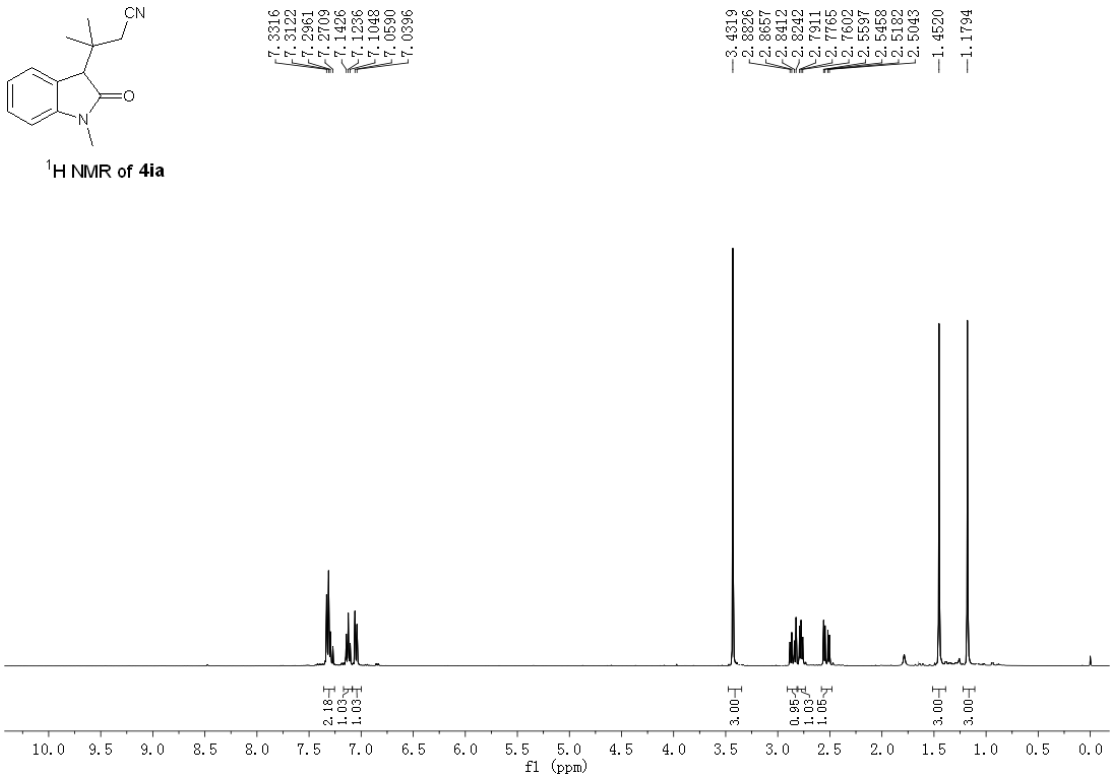
^{13}C NMR of 4ga



^{1}H NMR of 4ha

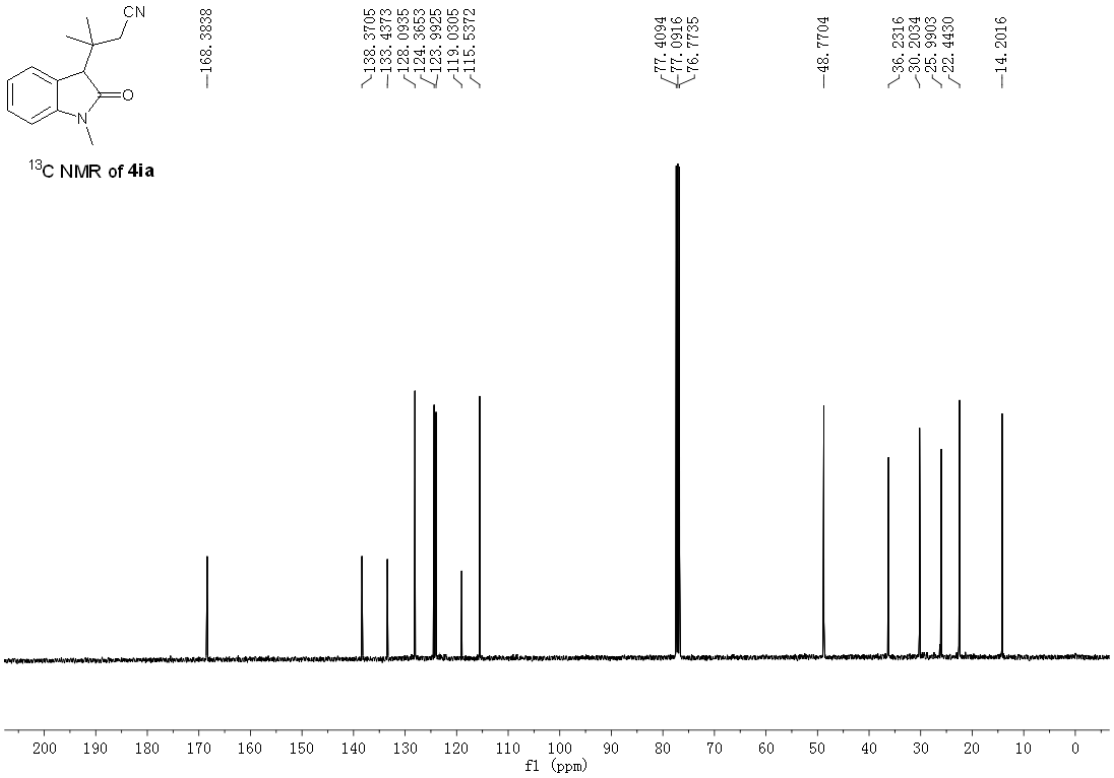


^{13}C NMR of **4ha**

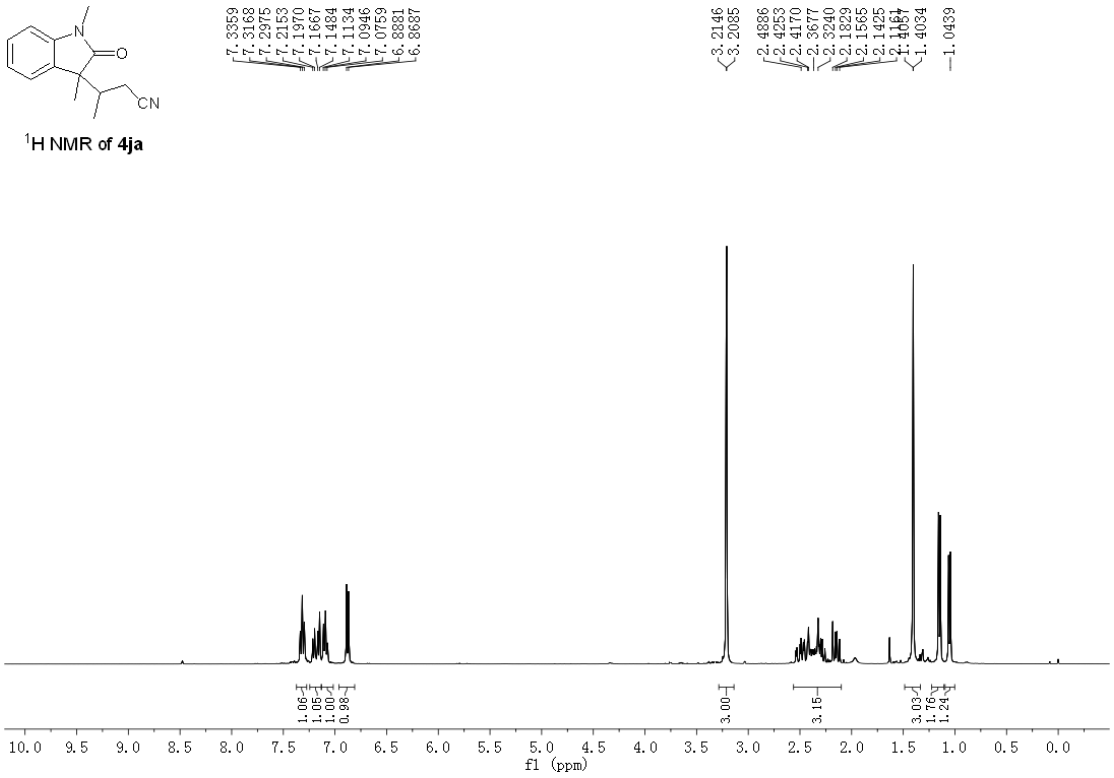


^{1}H NMR of **4ia**

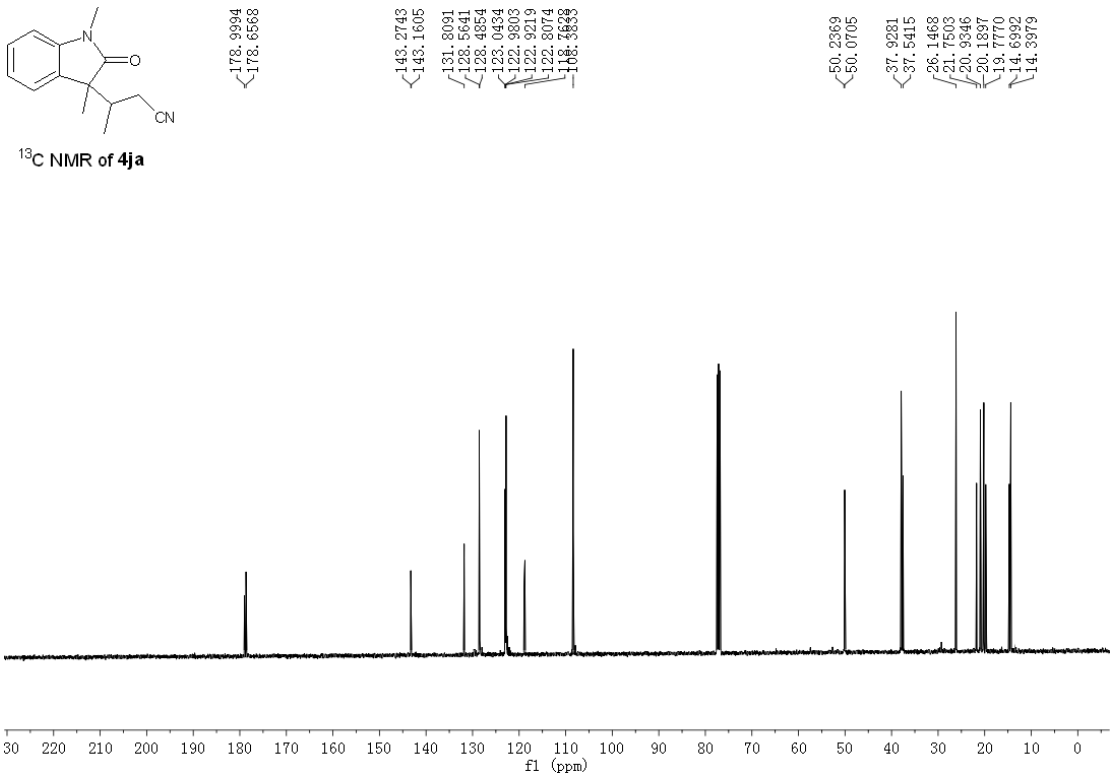
^{13}C NMR of **4ia**



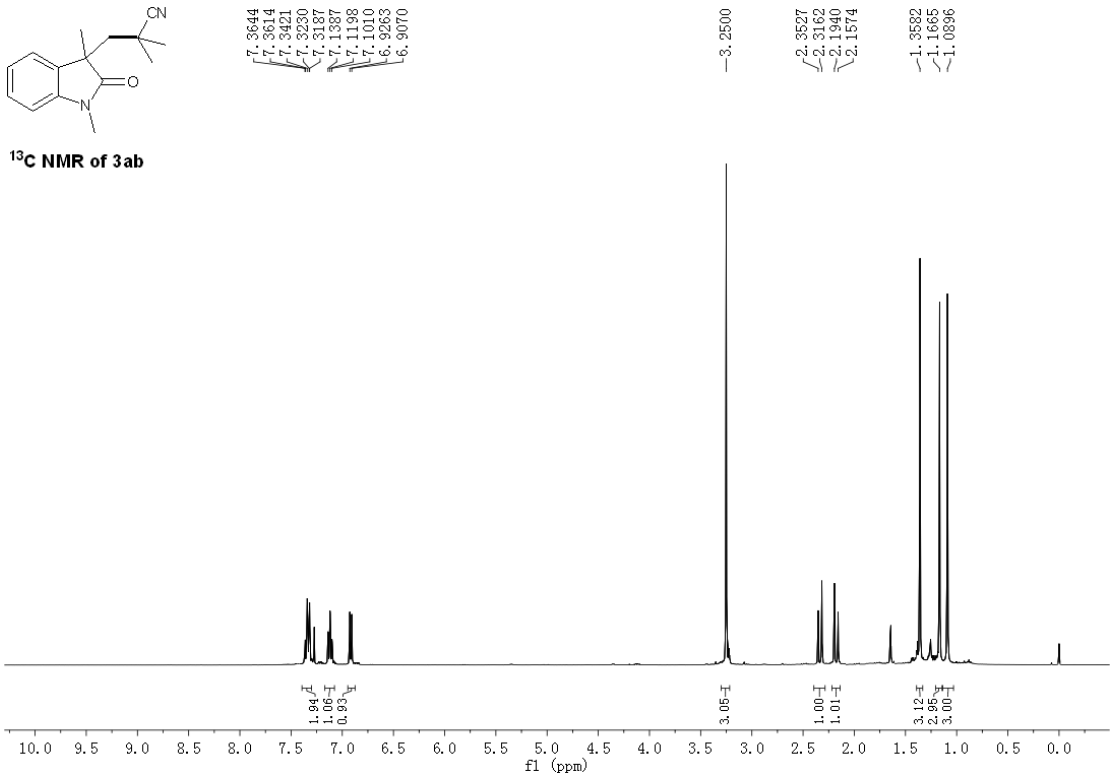
^{1}H NMR of **4ja**

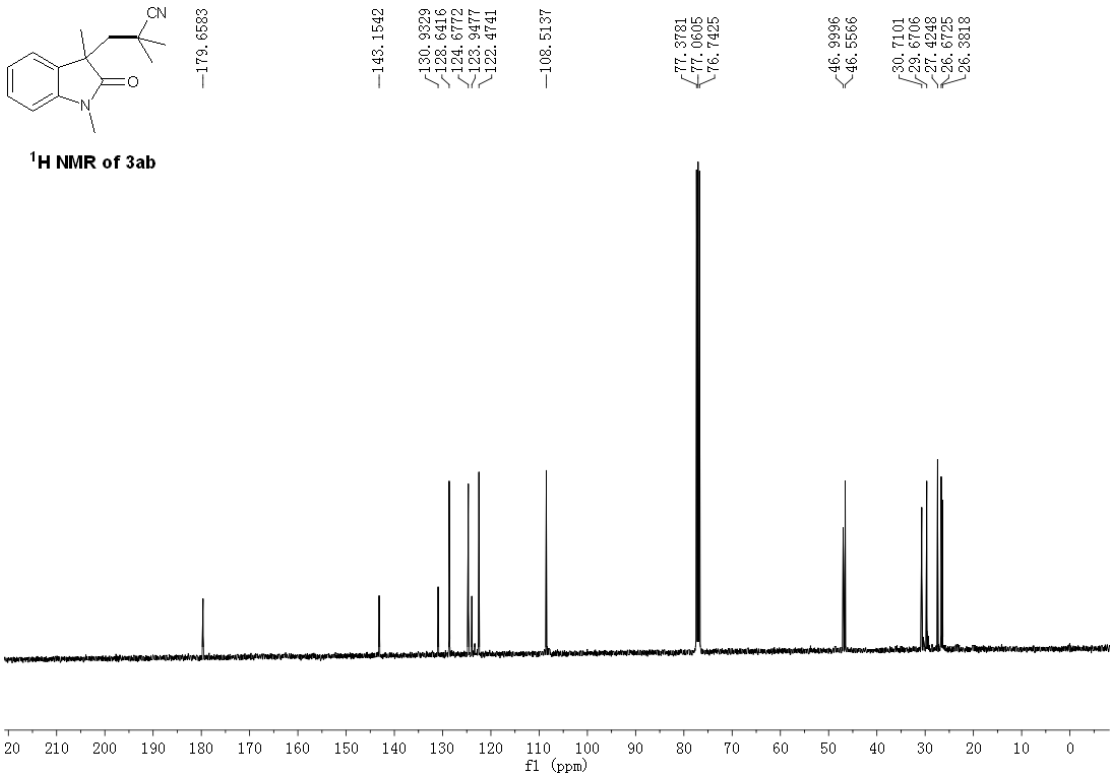


^{13}C NMR of **4ja**

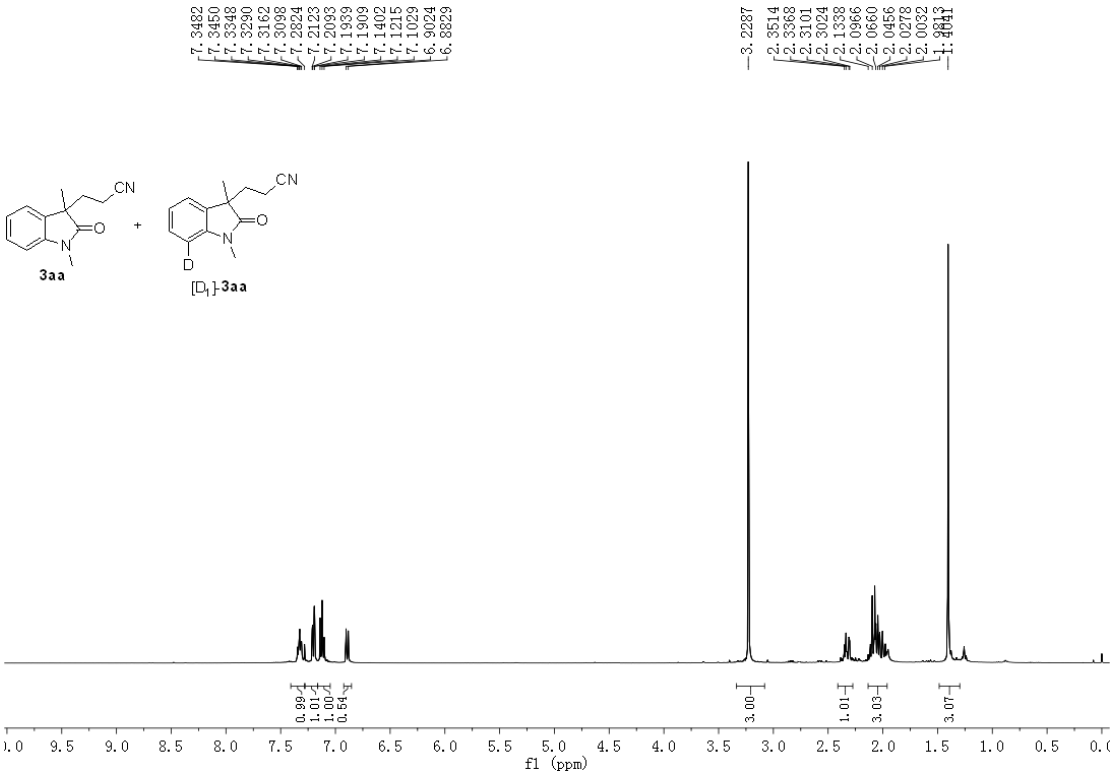


^{13}C NMR of **3ab**

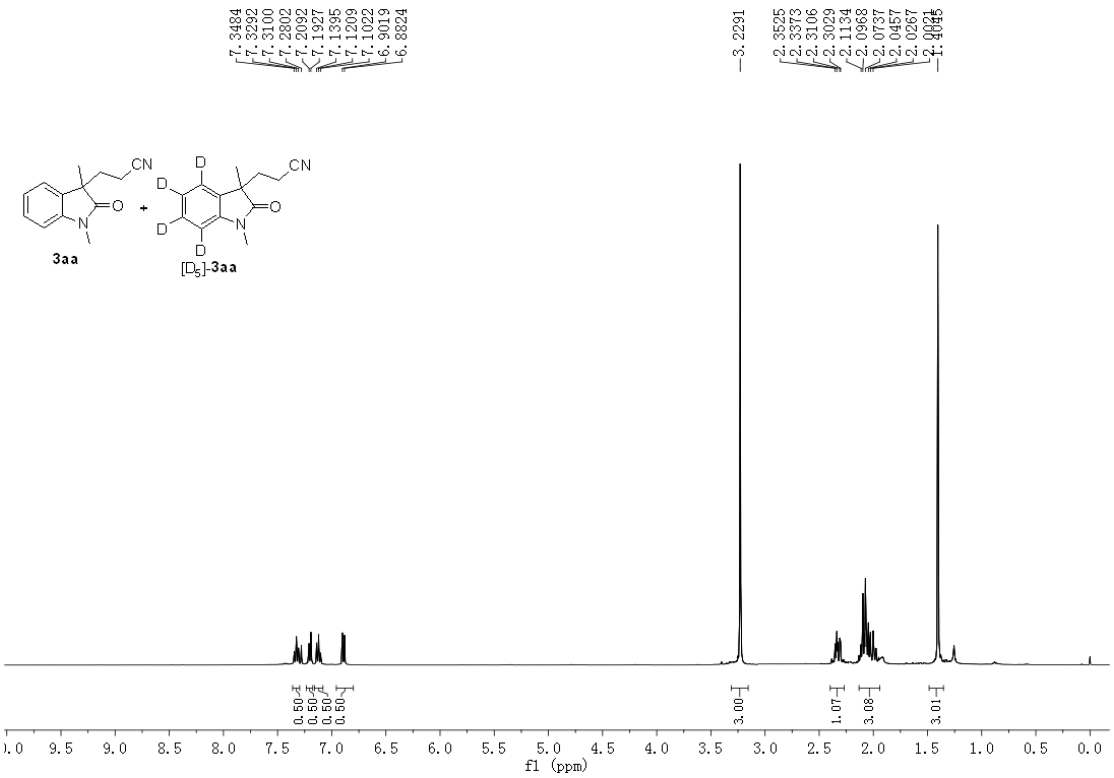


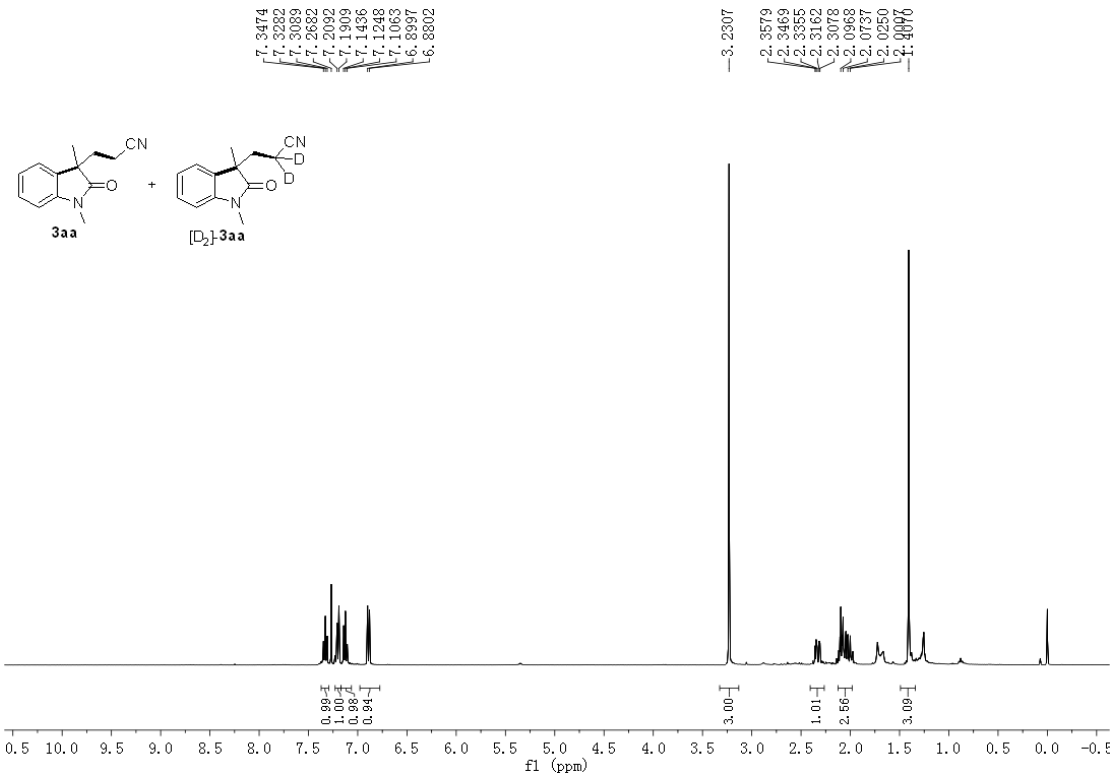


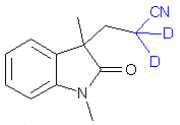
^{1}H NMR of 3ab



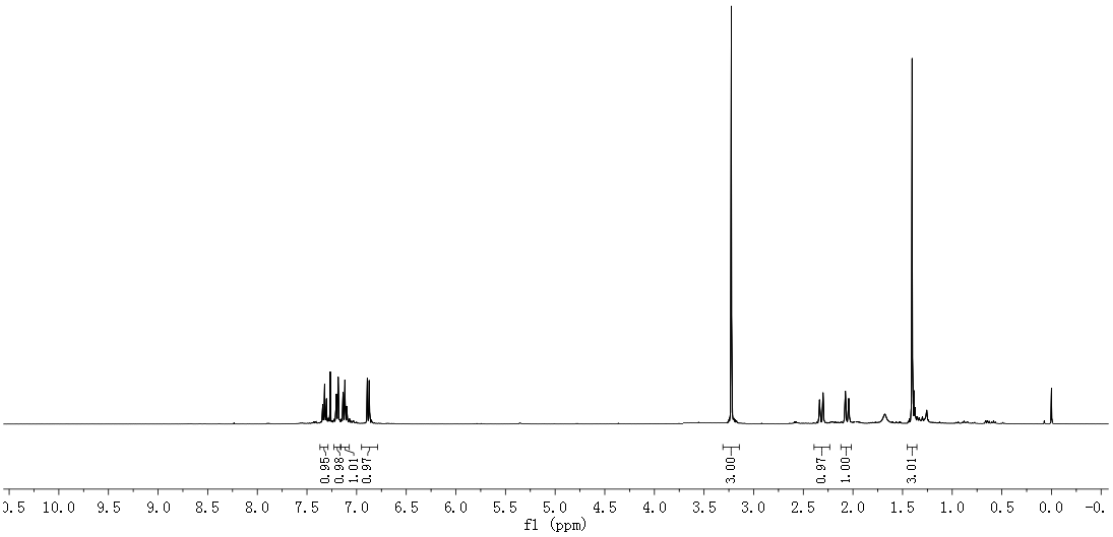
3aa + **[D$_1$]-3aa**


7.3484
7.3292
7.3100
7.2802
7.2092
7.1927
7.1395
7.1209
7.1022
6.9019
6.8824
3.2291
2.3525
2.3373
2.3106
2.3029
2.1134
2.0968
2.0737
2.0457
2.0267
CN
O
N
D
3aa
[D5]-3aa
0.60
0.60
0.60
3.00
1.07
3.08
3.01
f1 (ppm)


7.3474
7.3282
7.3089
7.2682
7.2092
7.1909
7.1436
7.1248
7.1063
6.8997
6.8802
3.2307
2.3579
2.3469
2.3355
2.3162
2.3078
2.0968
2.0737
2.0250
CN
O
N
D
3aa
[D2]-3aa
0.99
1.00
0.98
0.94
3.00
1.01
2.56
3.09
f1 (ppm)



^{1}H NMR of [D_2]-**3aa**



^{1}H NMR of **5aa**