

Supporting information

Cyanomethylation of Alkenes with C-H Bond Activation of Acetonitrile: In-situ Generated Diazonium Salts as Promoter without Transition-metals

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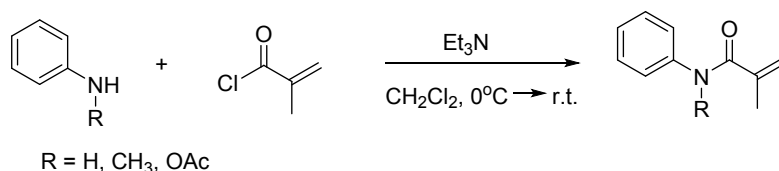
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1. Experimental Section

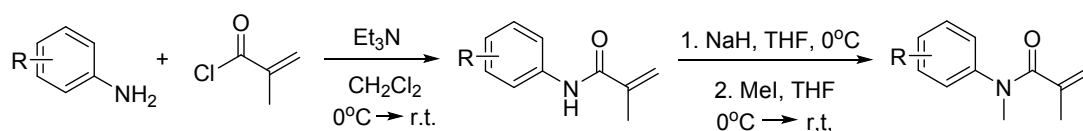
1.1 General information

All reagents were purchased from commercial suppliers and used without further purification. All reactions were conducted in oven-dried schlenk tubes under nitrogen atmosphere. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in CDCl_3 . Data for $^1\text{H-NMR}$ are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for $^{13}\text{C-NMR}$ are reported in terms of chemical shift (δ ppm). Gas chromatography coupled to electron impact ionization/ time-of-flight mass spectrometry (GC/EI-TOF-MS) was performed using a HP6890 gas chromatography with a time of flight mass spectrometry (GCT premier GC-TOFMA, America). Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

1.2 General procedure for the preparation of N-arylacrylamides



In a dry 100 mL round-bottom flask, a mixture of aniline (10 mmol) and Et_3N (30 mmol, 3equiv) in 30 mL of CH_2Cl_2 were stirred in the ice-water bath. The methacryloyl chloride (15 mmol, 1.5 equiv) was added slowly by a syringe. The reaction was monitored by TLC. After the reaction completed, the mixture was evaporated under reduced pressure and extracted by ethyl acetate. The product was purified by silica gel column chromatography.

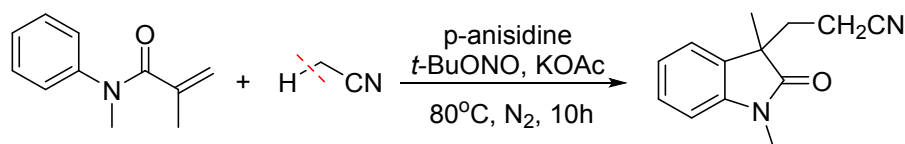


In a dry 100 mL round-bottom flask, a mixture of aniline (10 mmol) and Et_3N (30 mmol, 3equiv) in 30 mL of CH_2Cl_2 were stirred in the ice-water bath. The methacryloyl chloride (15 mmol, 1.5 equiv) was added slowly by a syringe. The reaction was monitored by TLC. After the reaction completed, the mixture was evaporated under reduced pressure and extracted by ethyl acetate. The crude product was purified by silica gel column chromatography.

In a dry 50 mL round-bottom flask, N-phenylmethacrylamide (5 mmol) was dissolved in 15 mL THF and stirred in the ice-water bath. The NaH (7.5 mmol, 1.5 equiv) was added slowly. After 5 mins, the MeI (7.5 mmol, 1.5equiv) was added to the mixture slowly by a syringe. The reaction was monitored by TLC. When the reaction completed, the mixture was evaporated under reduced pressure and extracted by ethyl acetate. The product was purified by silica gel column chromatography.

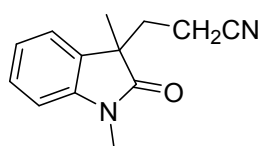
2. Experimental Procedures and Spectral Data

2.1 General procedure for the synthesis of oxoindoles



In a dry 25 mL oven-dried schlenk tubes, N-arylacrylamide (0.5 mmol), aniline (1.5 mmol, 3.0 equiv) and KOAc (1.0 mmol, 2.0 equiv) were dissolved in 4 mL CH₃CN under an atmosphere of dry nitrogen at room temperature. *Tert*-butyl nitrite (1.5 mmol, 3.0 equiv) was then added with a syringe. A fine bubbling was observed and the reaction mixture was heated to 80°C for 10h. Then the solution was cooled to r.t., washed with a saturated aqueous solution of NaCl, extracted by ethyl acetate and dried over by Na₂SO₄. The product was purified by silica gel column chromatography.

2.2 substrate scope of N-Arylacrylamides

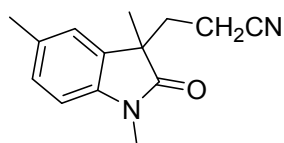


3-(1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ : 7.31 (m, 1H), 7.18 (m, 1H), 7.10 (m, 1H), 6.87 (d, J = 7.6Hz, 1H), 3.22 (s, 3H), 2.32 (m, 1H), 2.05 (m, 3H), 1.39 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 179.1, 143.3, 131.8, 128.9, 123.2, 122.8, 119.0, 108.7, 47.5, 33.6, 26.5, 23.6, 13.0.

HRMS (EI, *m/z*): calcd for C₁₃H₁₄N₂O: 214.1106; found: 214.1100.

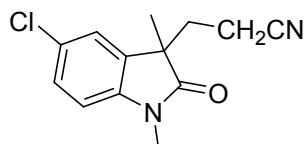


3-(1,3,5-trimethyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ : 7.10 (m, 1H), 7.09 (s, 1H), 6.75 (d, J = 6.3Hz, 1H), 3.18 (s, 3H), 2.35 (s, 3H), 2.30 (m, 1H), 2.03 (m, 3H), 1.37 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 178.7, 140.6, 132.5, 131.5, 128.7, 123.3, 118.8, 108.1, 47.2, 33.3, 26.2, 23.3, 21.0, 12.7.

HRMS (EI, *m/z*): calcd for C₁₄H₁₆N₂O: 228.1263; found: 228.1268.

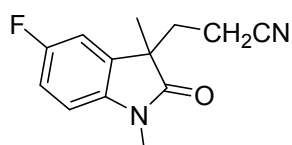


3-(5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ: 7.22 (m, 1H), 7.1 (m, 1H), 6.74 (d, J = 6.6Hz, 1H), 3.13 (s, 3H), 2.25 (m, 1H), 1.98 (m, 3H), 1.32 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ: 178.2, 141.6, 133.3, 128.5, 128.2, 123.1, 118.4, 109.4, 47.4, 33.0, 26.3, 23.2, 12.6.

HRMS (EI, *m/z*): calcd for C₁₃H₁₃ClN₂O: 248.0716; found: 248.0711.

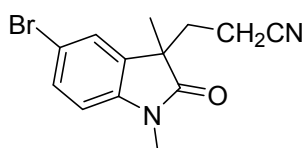


3-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ: 7.01 (m, 1H), 6.94 (m, 1H), 6.80 (m, 1H), 3.19 (s, 3H), 2.29 (m, 1H), 2.02 (m, 3H), 1.38 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ: 178.4, 160.5, 158.1, 138.9, 138.9, 133.3, 133.2, 118.4, 114.9, 114.7, 110.9, 110.7, 109.0, 109.0, 47.6, 47.6, 33.1, 26.3, 23.2, 12.6.

HRMS (EI, *m/z*): calcd for C₁₃H₁₃FN₂O: 232.1012; found: 232.1010.

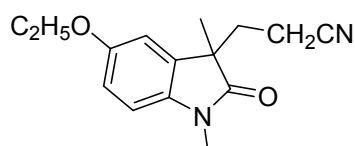


3-(5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ: 7.44 (m, 1H), 7.30 (m, 1H), 6.76 (d, J = 8.3Hz, 1H), 3.20 (s, 3H), 2.33 (m, 1H), 2.06 (m, 3H), 1.40 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ: 178.2, 142.1, 133.7, 131.5, 125.9, 118.4, 115.7, 109.9, 47.4, 33.2, 26.4, 23.4, 12.8.

HRMS (EI, *m/z*): calcd for C₁₃H₁₃BrN₂O: 292.0211; found: 292.0207.

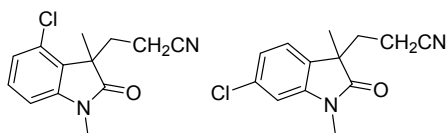


3-(5-ethoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ: 6.79 (m, 3H), 3.99 (q, J = 5.6Hz, 2H), 3.17 (s, 3H), 2.29 (m, 1H), 2.01 (m, 3H), 1.39 (t, J = 5.6Hz, 3H), 1.36 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ: 178.4, 155.6, 136.3, 132.8, 118.7, 113.1, 110.7, 108.7, 64.0, 47.6, 33.3, 26.2, 23.4, 14.7, 12.7.

HRMS (EI, *m/z*): calcd for C₁₅H₁₈N₂O₂: 258.1368; found: 258.1364.

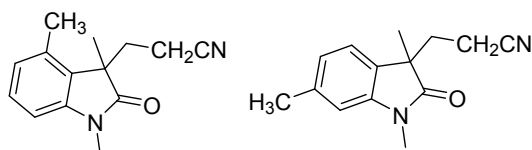


3-(4-chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile 3-(6-chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ : 7.26 (m, 1.3H), 7.10 (m, 1H), 7.04 (m, 1.1H), 6.89 (m, 0.4H), 6.81 (m, 1.1H), 3.23 (s, 3H), 3.21 (s, 1.1H), 2.53 (m, 1.2H), 2.38 (m, 1.7H), 2.03 (m, 3.7H), 1.53 (s, 3H), 1.39 (s, 1.3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 178.7, 178.2, 144.9, 144.2, 134.3, 130.6, 129.9, 129.9, 127.2, 123.7, 123.5, 122.7, 118.5, 118.3, 109.2, 107.0, 48.9, 46.9, 33.0, 30.2, 26.5, 26.3, 23.3, 21.1, 13.0, 12.7.

HRMS (EI, *m/z*): calcd for C₁₃H₁₃ClN₂O: 248.0716; found: 248.0720.

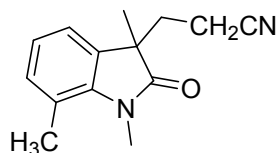


3-(1,3,4-trimethyl-2-oxoindolin-3-yl)propanenitrile 3-(1,3,6-trimethyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ : 7.19 (t, *J* = 6.3Hz, 1H), 7.04 (d, *J* = 6Hz, 0.6H), 6.89 (d, *J* = 6Hz, 0.7H), 6.84 (d, *J* = 6.2Hz, 1H), 6.70 (m, 1.5H), 3.17 (m, 4.4H), 2.36 (m, 5.3H), 2.26 (m, 1.9H), 2.00 (m, 4.7H), 1.45 (s, 3H), 1.35 (s, 1.8H).

¹³C NMR (CDCl₃, 100 MHz) δ : 179.0, 178.7, 143.3, 143.0, 138.6, 134.2, 128.4, 128.3, 127.9, 125.3, 123.3, 122.1, 118.7, 118.5, 109.3, 106.1, 48.7, 46.9, 33.2, 31.2, 26.2, 26.0, 23.3, 21.6, 21.6, 18.0, 12.8, 12.6.

HRMS (EI, *m/z*): calcd for C₁₄H₁₆N₂O: 228.1263; found: 228.1260.

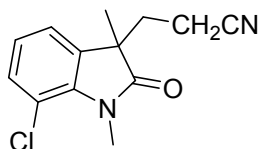


3-(1,3,7-trimethyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ : 6.99 (m, 3H), 3.49 (s, 3H), 2.57 (s, 3H), 2.30 (m, 1H), 2.00 (m, 3H), 1.36 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 179.5, 140.7, 132.2, 132.1, 122.8, 120.3, 120.1, 118.8, 46.5, 33.5, 29.5, 23.7, 18.9, 12.7.

HRMS (EI, *m/z*): calcd for C₁₄H₁₆N₂O: 228.1263; found: 228.1259.

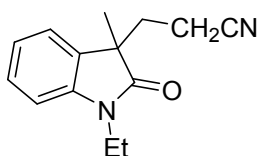


3-(7-chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ : 7.25 (m, 1H), 7.07 (m, 1H), 7.01 (m, 1H), 3.59 (s, 3H), 2.33 (m, 1H), 2.06 (m, 3H), 1.40 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 179.0, 139.0, 134.5, 131.0, 123.8, 121.1, 118.5, 116.0, 47.1, 33.5, 29.6, 23.8, 12.8.

HRMS (EI, *m/z*): calcd for C₁₃H₁₃ClN₂O: 248.0716; found: 248.0722.

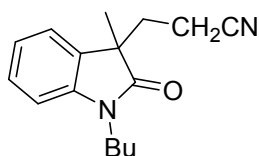


3-(1-ethyl-3-methyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ : 7.29 (m, 1H), 7.17 (m, 1H), 7.09 (m, 1H), 6.89 (d, *J* = 6.2Hz, 1H), 3.75 (m, 2H), 2.30 (m, 1H), 2.05 (m, 3H), 1.37 (s, 3H), 1.25 (t, *J* = 5.8Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 178.3, 142.0, 131.7, 128.5, 122.7, 122.6, 118.7, 108.5, 47.1, 34.6, 33.3, 23.3, 12.6, 12.5.

HRMS (EI, *m/z*): calcd for C₁₄H₁₆N₂O: 228.1263; found: 228.1269.

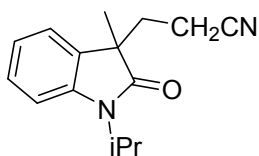


3-(1-butyl-3-methyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ : 7.30 (m, 1H), 7.18 (m, 1H), 7.08 (m, 1H), 6.88 (d, *J* = 6.2Hz, 1H), 3.7 (t, *J* = 6.0Hz, 2H), 2.31 (m, 1H), 2.08 (m, 3H), 1.64 (t, *J* = 6.9Hz, 2H), 1.37 (m, 4H), 0.96 (t, *J* = 5.9Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 178.7, 142.5, 131.8, 128.6, 122.8, 122.7, 118.9, 108.8, 47.2, 39.8, 33.4, 29.5, 23.6, 20.1, 13.7, 12.8.

HRMS (EI, *m/z*): calcd for C₁₆H₂₀N₂O: 256.1576; found: 256.1570.

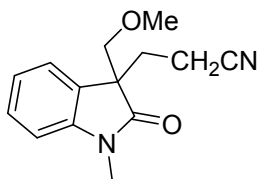


3-(1-isopropyl-3-methyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ : 7.27 (m, 1H), 7.18 (m, 1H), 7.09 (m, 1H), 7.05 (m, 1H), 4.62 (m, 1H), 2.33 (m, 1H), 2.30 (m, 3H), 1.47 (m, 6H), 1.37 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 178.4, 141.7, 132.0, 128.3, 122.8, 122.4, 118.8, 110.1, 46.9, 43.8, 33.5, 23.6, 19.4, 19.3, 12.6.

HRMS (EI, *m/z*): calcd for C₁₅H₁₈N₂O: 242.1419; found: 242.1415.

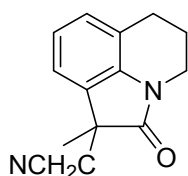


3-(3-(methoxymethyl)-1-methyl-2-oxoindolin-3-yl)propanenitrile

¹H NMR (CDCl₃, 400 MHz) δ : 7.24 (m, 2H), 7.04 (t, J = 6.0Hz, 1H), 6.80 (d, J = 6.2Hz, 1H), 3.59 (d, J = 7.1Hz, 1H), 3.42 (d, J = 7.1Hz, 1H), 3.19 (s, 3H), 3.14 (s, 3H), 2.26 (m, 1H), 2.02 (m, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 176.4, 143.7, 128.9, 128.8, 123.7, 122.9, 118.7, 108.3, 75.7, 59.4, 52.4, 28.9, 26.2, 12.3.

HRMS (EI, *m/z*): calcd for C₁₄H₁₆N₂O₂: 244.1212; found: 244.1211.

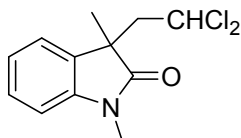


2-(1-methyl-2-oxo-1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-*ij*]quinolin-1-yl)acetonitrile

¹H NMR (CDCl₃, 400 MHz) δ : 7.02 (m, 3H), 3.72 (m, 2H), 2.79 (t, J = 6.0Hz, 2H), 2.28 (m, 1H), 2.06 (m, 5H), 1.40 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 177.6, 138.8, 130.0, 127.3, 122.3, 120.5, 120.3, 118.8, 48.5, 38.7, 33.1, 24.4, 23.1, 21.0, 12.8.

HRMS (EI, *m/z*): calcd for C₁₄H₁₄N₂O: 226.1106; found: 226.1100.

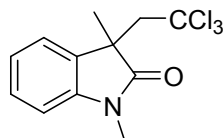


3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one

¹H NMR (CDCl₃, 400 MHz) δ : 7.46 (m, 1H), 7.32 (m, 1H), 7.09 (m, 1H), 7.03 (m, 1H), 5.58 (q, J = 5.2 Hz, 1H), 3.11 (s, 3H), 2.94 (m, 1H), 2.78 (m, 1H), 1.27 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ : 178.9, 143.6, 131.0, 128.8, 123.9, 122.7, 109.1, 71.5, 49.4, 47.1, 26.7, 26.7.

HRMS (EI, *m/z*): calcd for C₁₂H₁₃Cl₂NO: 257.0374; found: 257.0370.



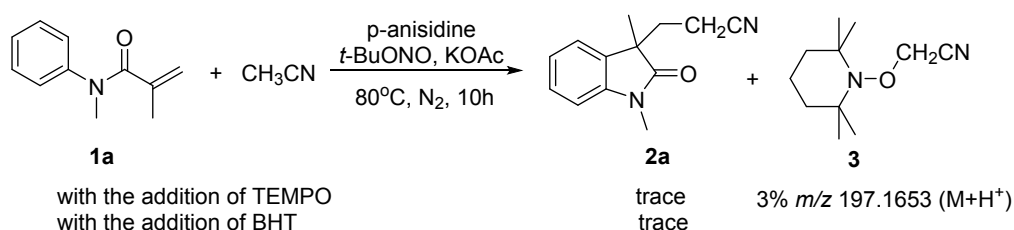
1,3-dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ : 7.54 (m, 1H), 7.28 (m, 1H), 7.03 (m, 2H), 3.71 (m, 1H), 3.43 (m, 1H), 3.14 (s, 3H), 1.29 (s, 3H).

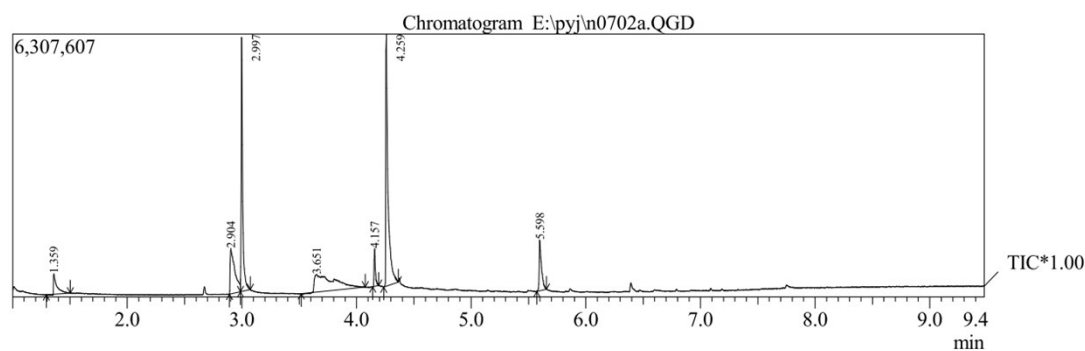
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ : 178.4, 143.5, 129.8, 128.8, 125.3, 122.0, 109.1, 97.3, 59.1, 47.9, 26.8, 26.7.

HRMS (EI, m/z): calcd for $\text{C}_{12}\text{H}_{12}\text{Cl}_3\text{NO}$: 290.9984; found: 290.9988.

3. Control Experiments.



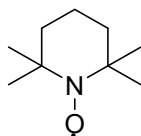
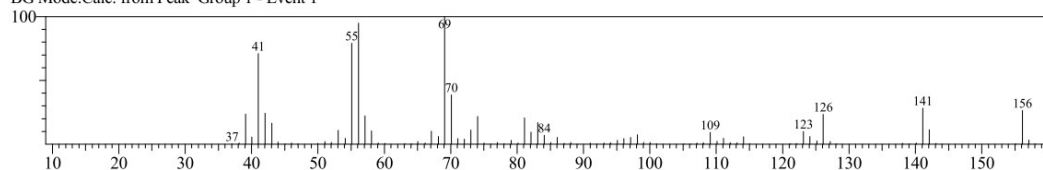
In a dry 25 mL oven-dried schlenk tubes, N-arylacrylamide (0.5 mmol), aniline (1.5 mmol, 3.0 equiv), KOAc (1.0 mmol, 2.0 equiv) and TEMPO (or BHT) (1.5 mmol, 3.0 equiv) were dissolved in 4 mL CH_3CN under an atmosphere of dry nitrogen at room temperature. *Tert*-butyl nitrite (1.5 mmol, 3.0 equiv) was then added with a syringe. The reaction mixture was heated to 80°C for 10h. Then the solution was cooled to r.t., washed with a saturated aqueous solution of NaCl, extracted by ethyl acetate and dried over by Na_2SO_4 . The mixture was detected by GC-MS and the exact molecular weight of compound **3** was confirmed by HRMS.



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3	2.997	2.987	3.073	5371754	21.64	6095996	37.49	0.88	V	Pip
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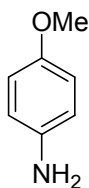
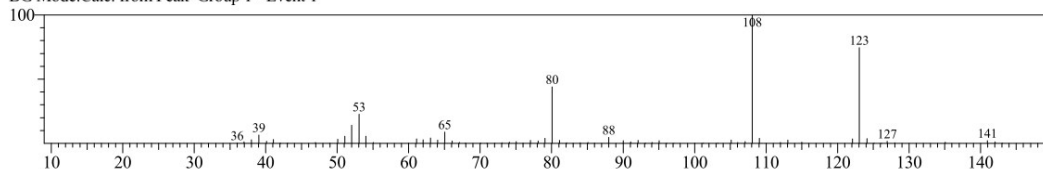
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BG Mode:Calc. from Peak Group 1 - Event 1



Chemical Formula: C₉H₁₈NO⁺
Exact Mass: 156.14

<< Target >>

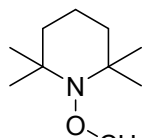
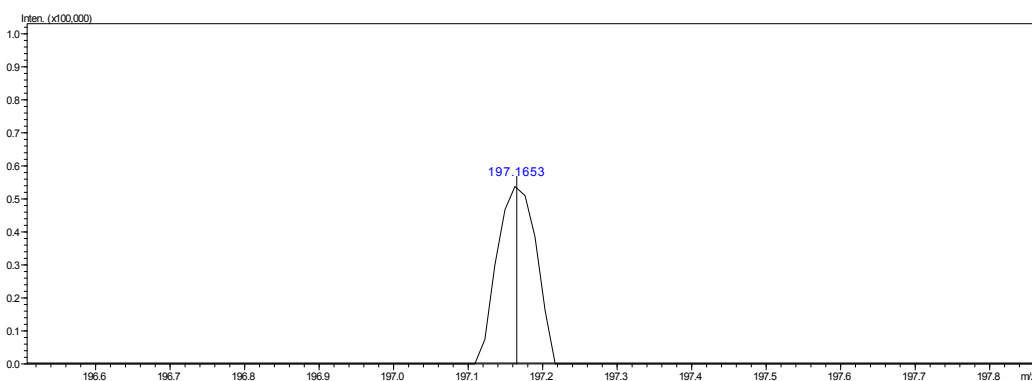
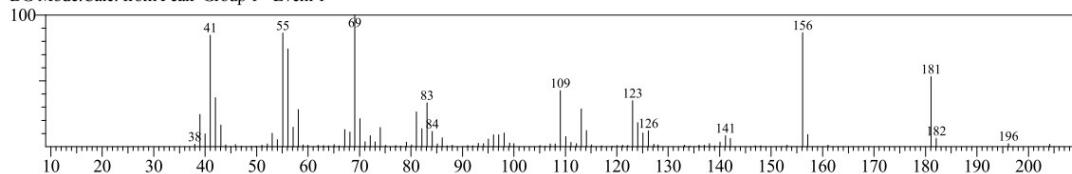
Line#:4 R.Time:3.650(Scan#:796) MassPeaks:73
RawMode:Averaged 3.647-3.653(795-797) BasePeak:108.05(114539)
BG Mode:Calc. from Peak Group 1 - Event 1



Chemical Formula: C₇H₉NO
Exact Mass: 123.07

<< Target >>

Line#:5 R.Time:4.157(Scan#:948) MassPeaks:99
RawMode:Averaged 4.153-4.160(947-949) BasePeak:69.10(67542)
BG Mode:Calc. from Peak Group 1 - Event 1



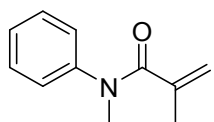
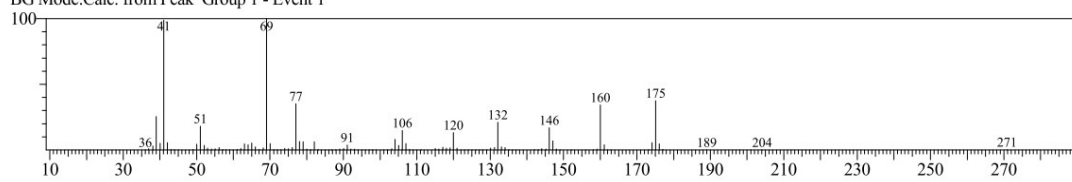
HRMS (ESI, *m/z*): calcd for C₁₁H₂₁N₂O⁺: 197.1648; found: 197.1653.

<< Target >>

Line#6 R.Time:4.260(Scan#:979) MassPeaks:122

RawMode:Averaged 4.257-4.263(978-980) BasePeak:69.05(972640)

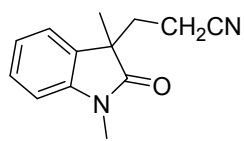
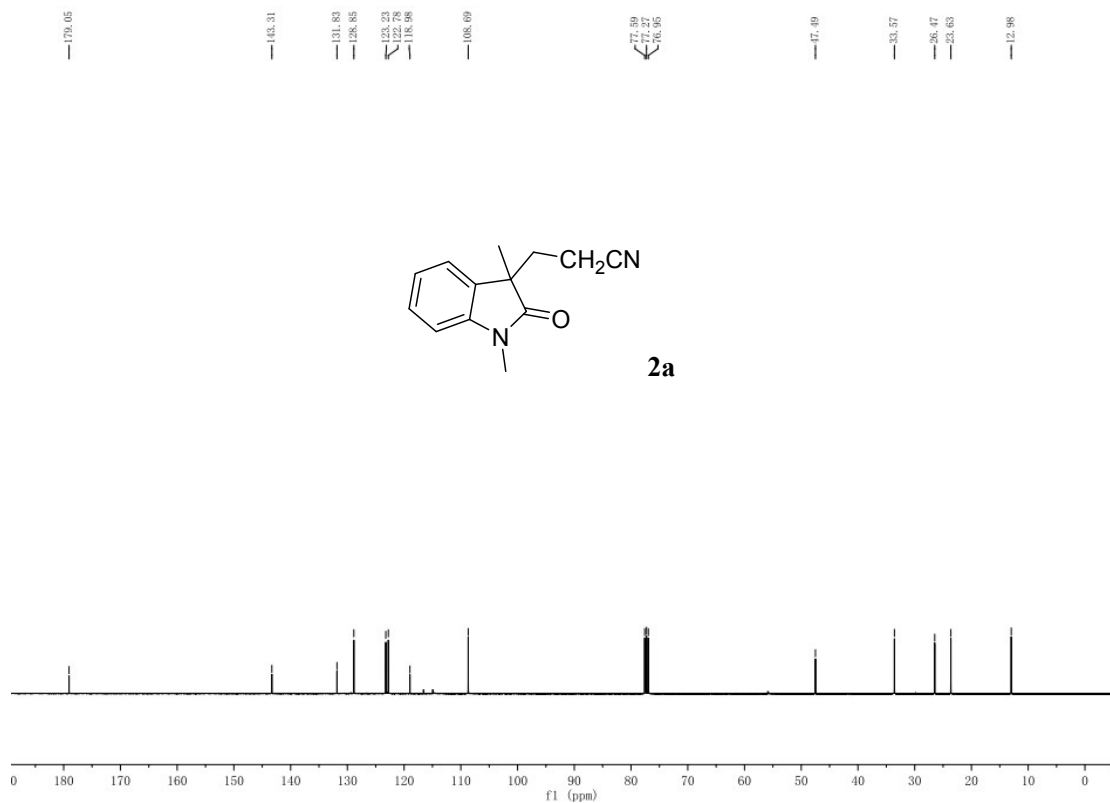
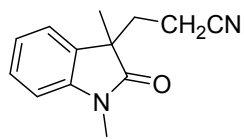
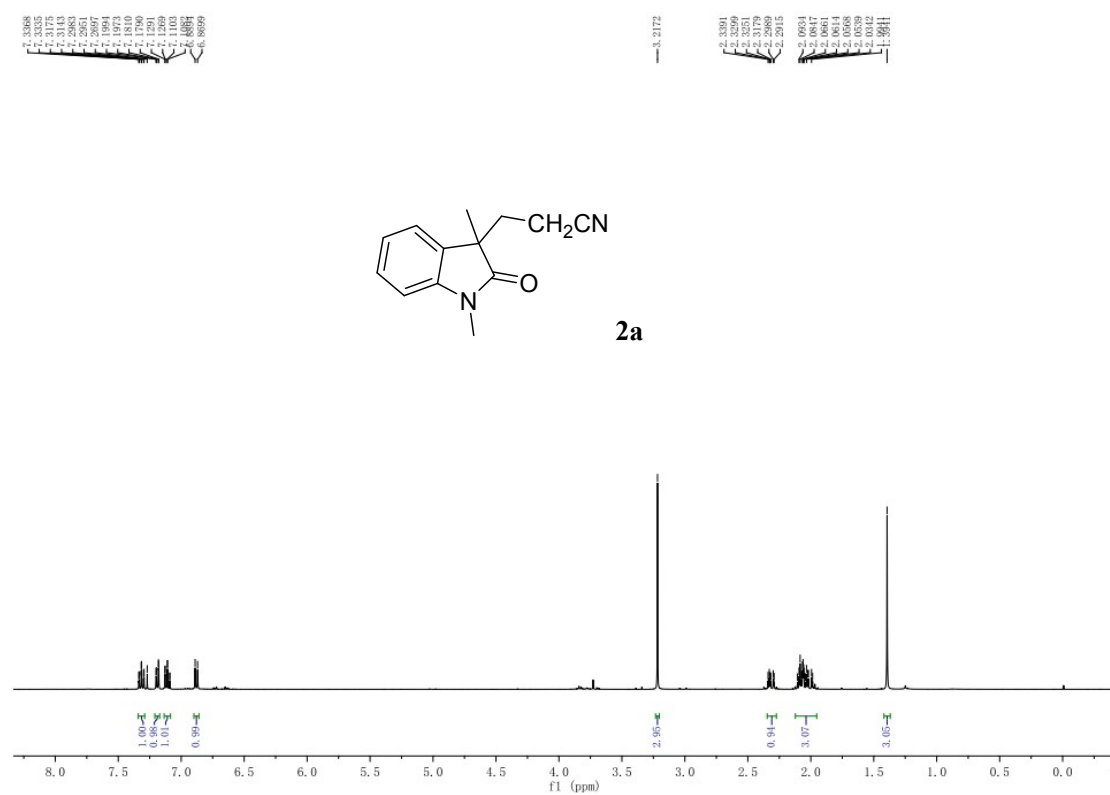
BG Mode:Calc. from Peak Group 1 - Event 1

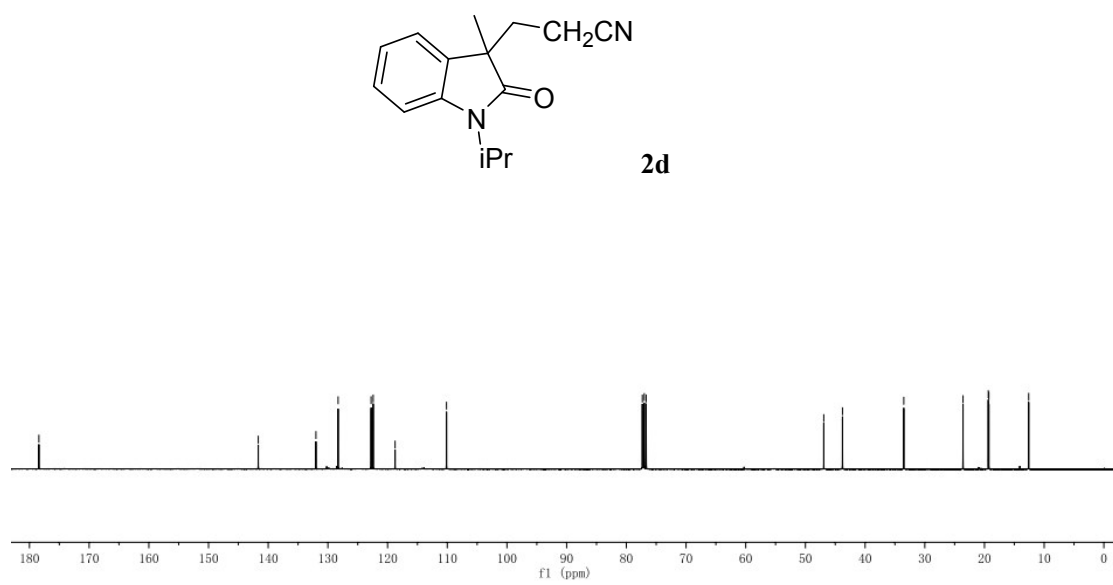
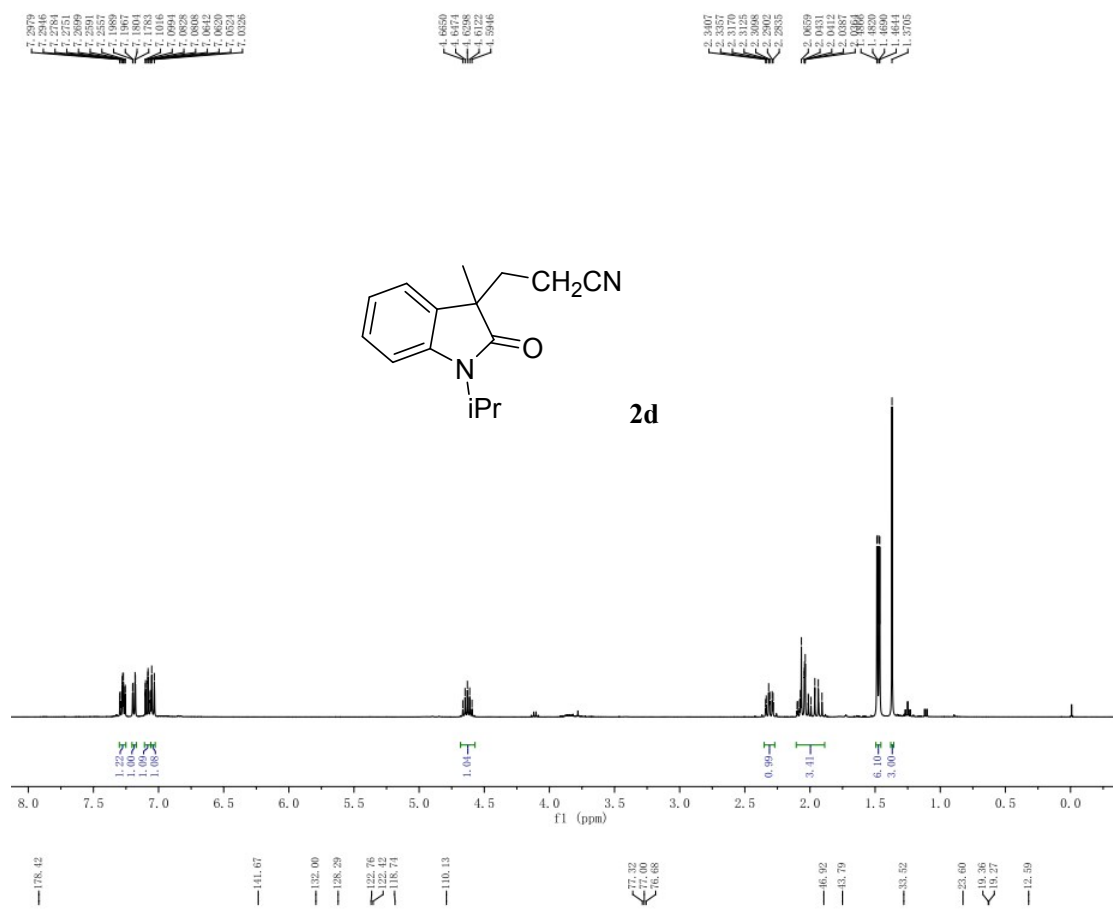


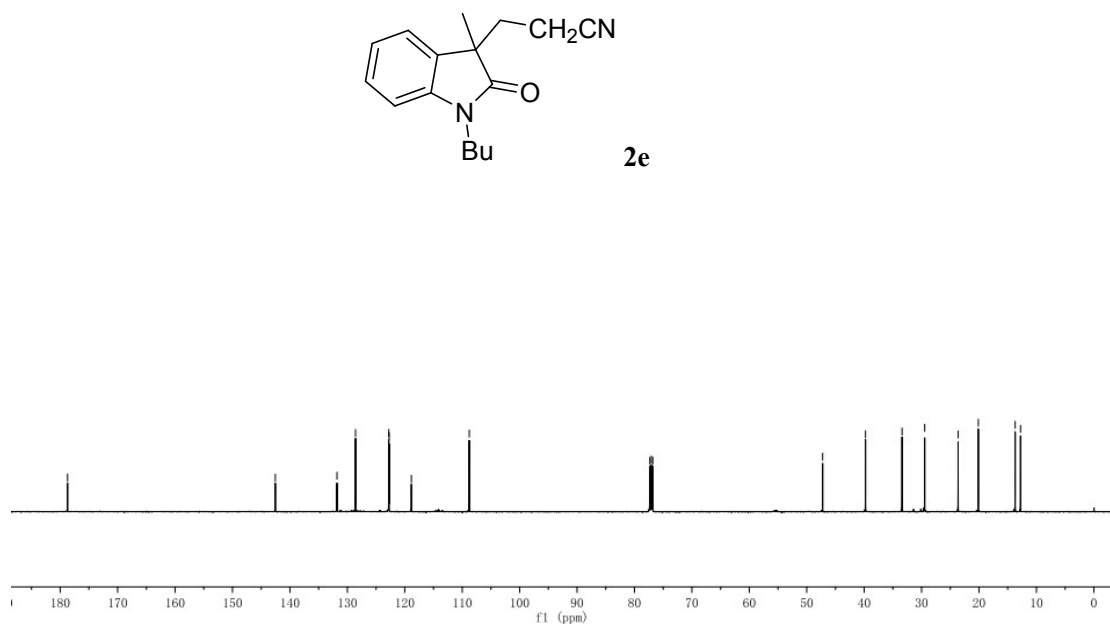
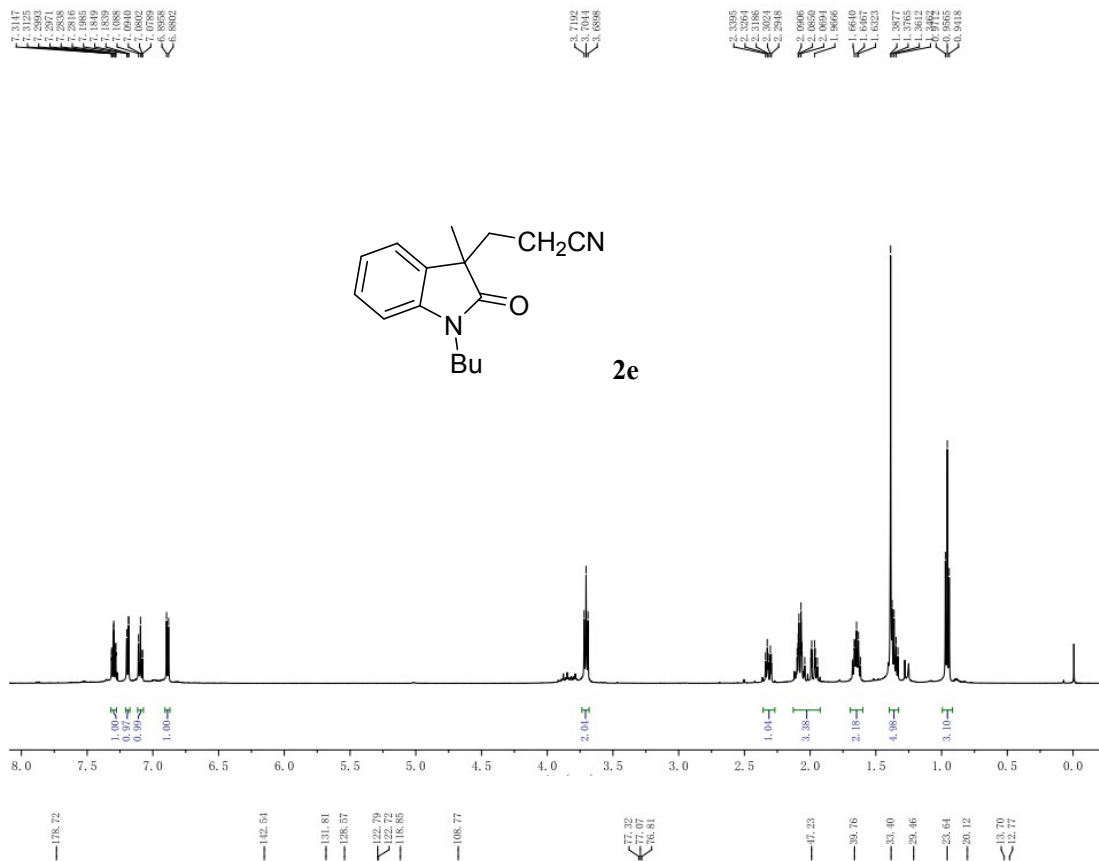
Chemical Formula: C₁₁H₁₃NO

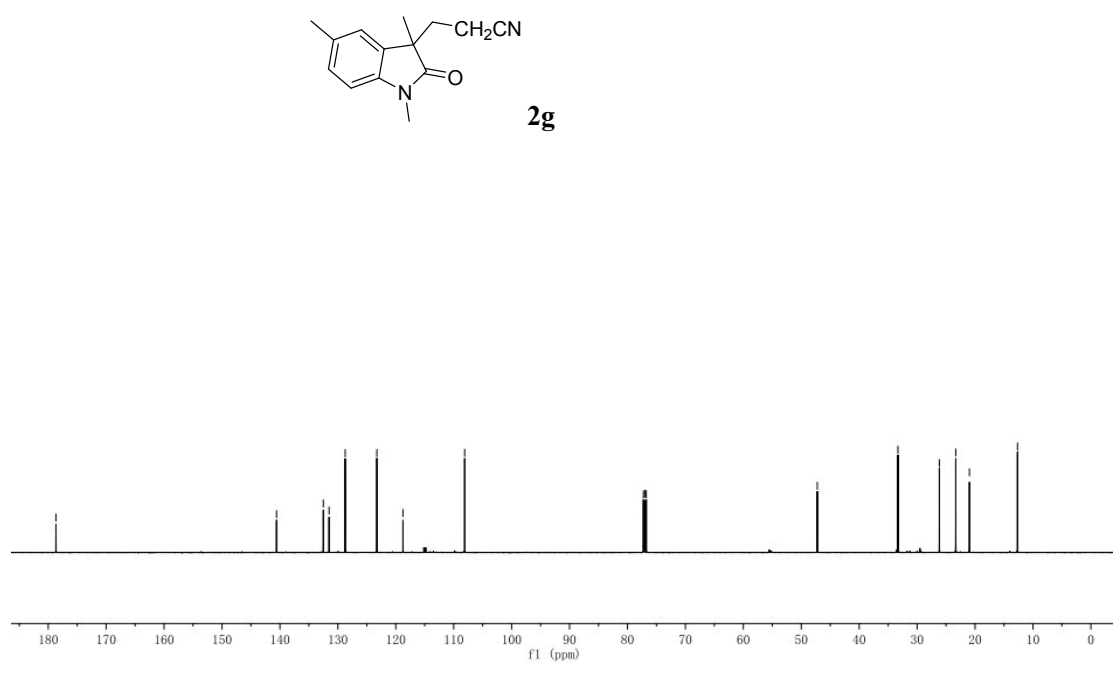
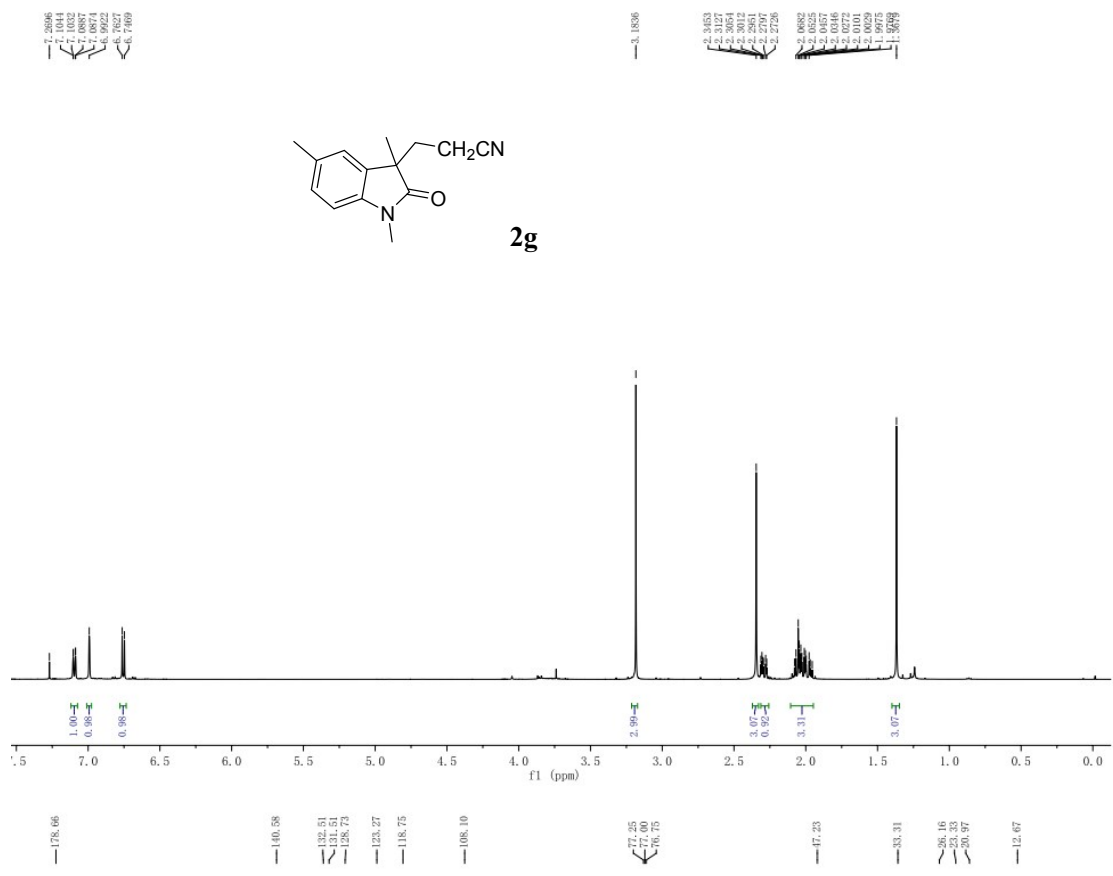
Exact Mass: 175.10

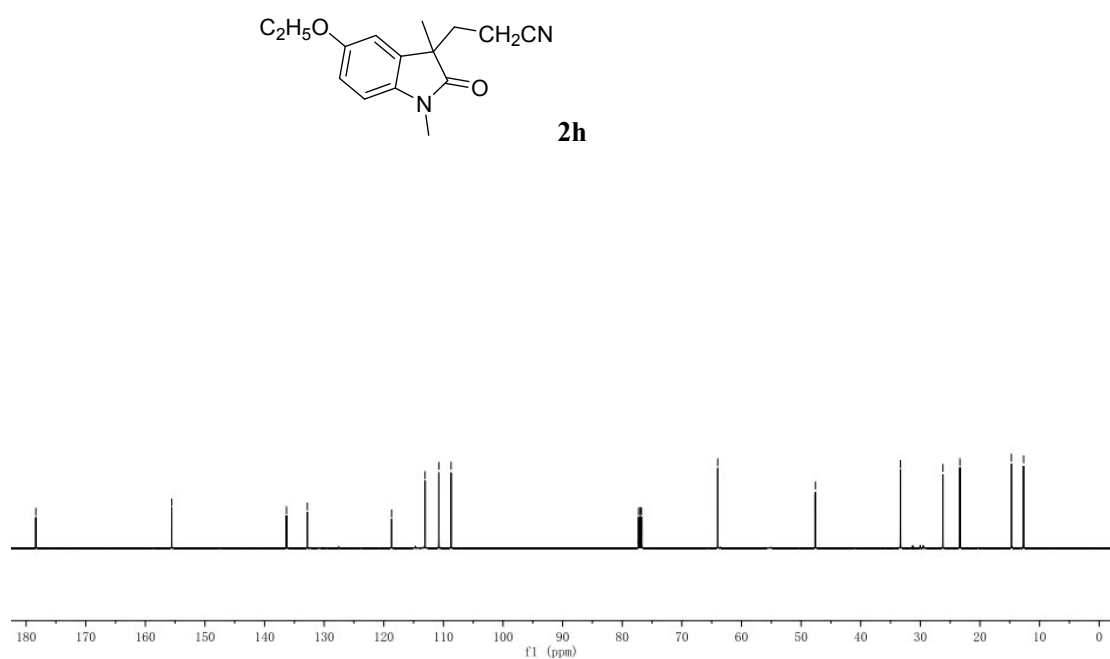
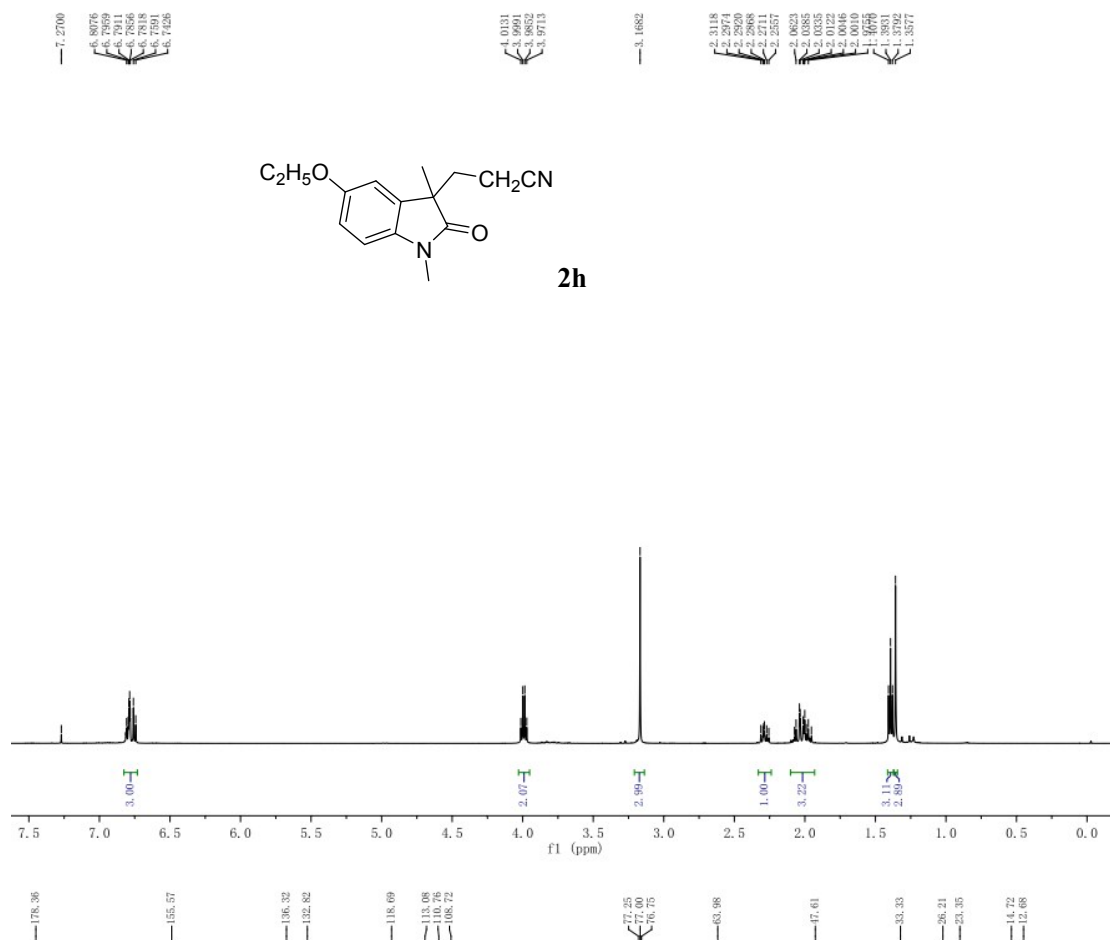
4. NMR Spectra

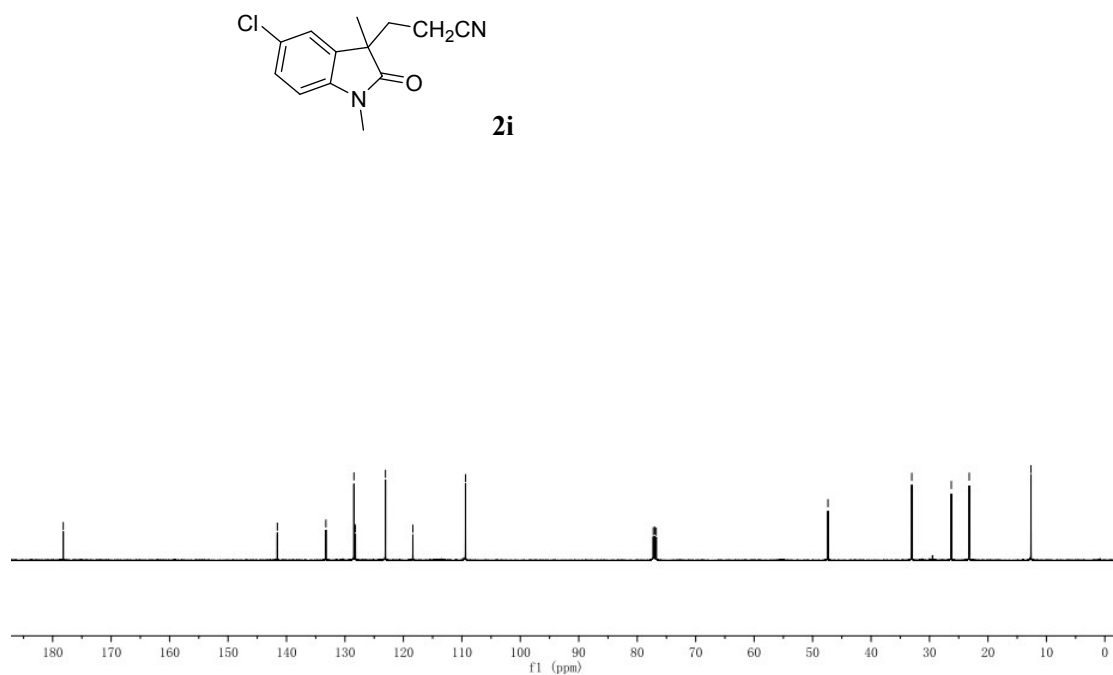
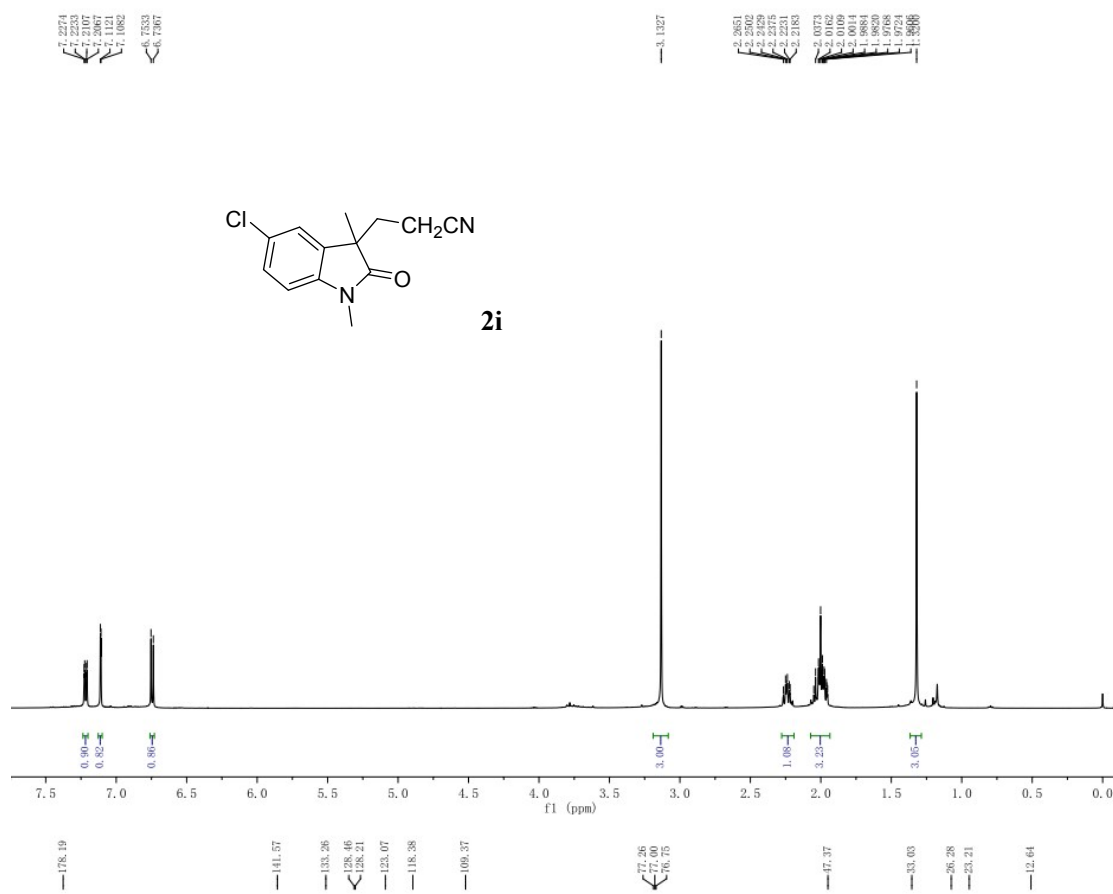


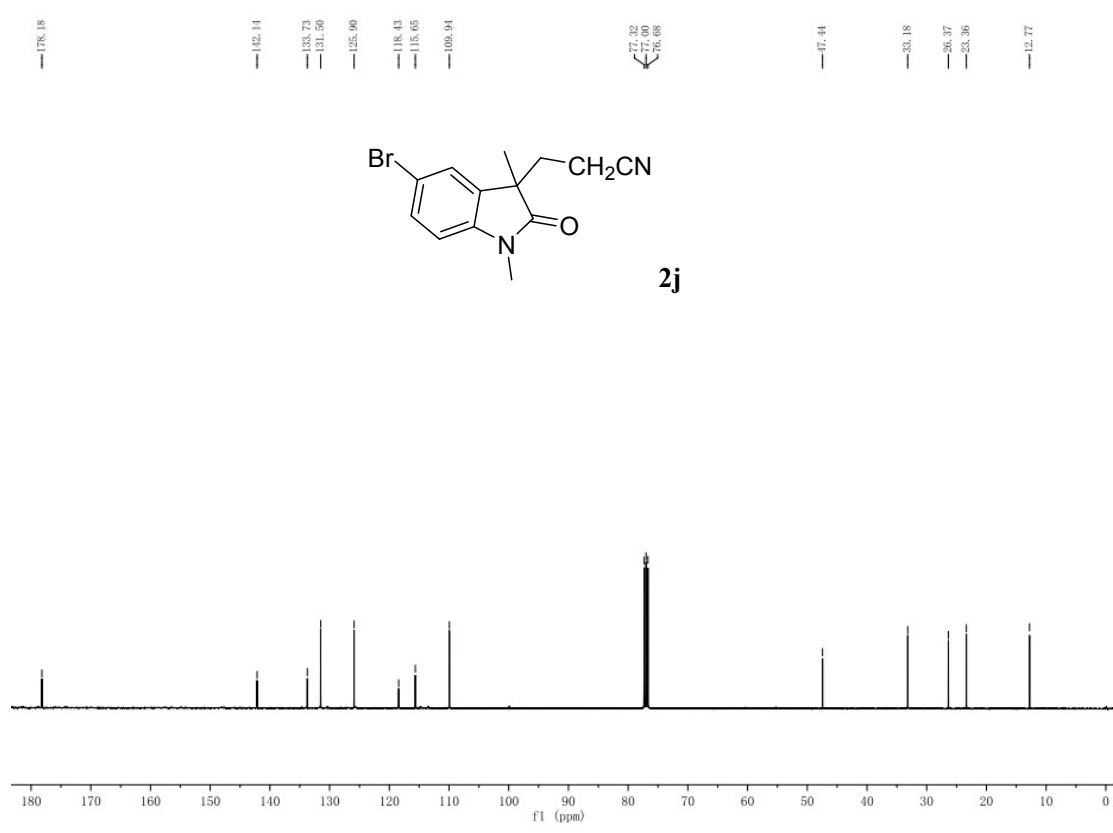
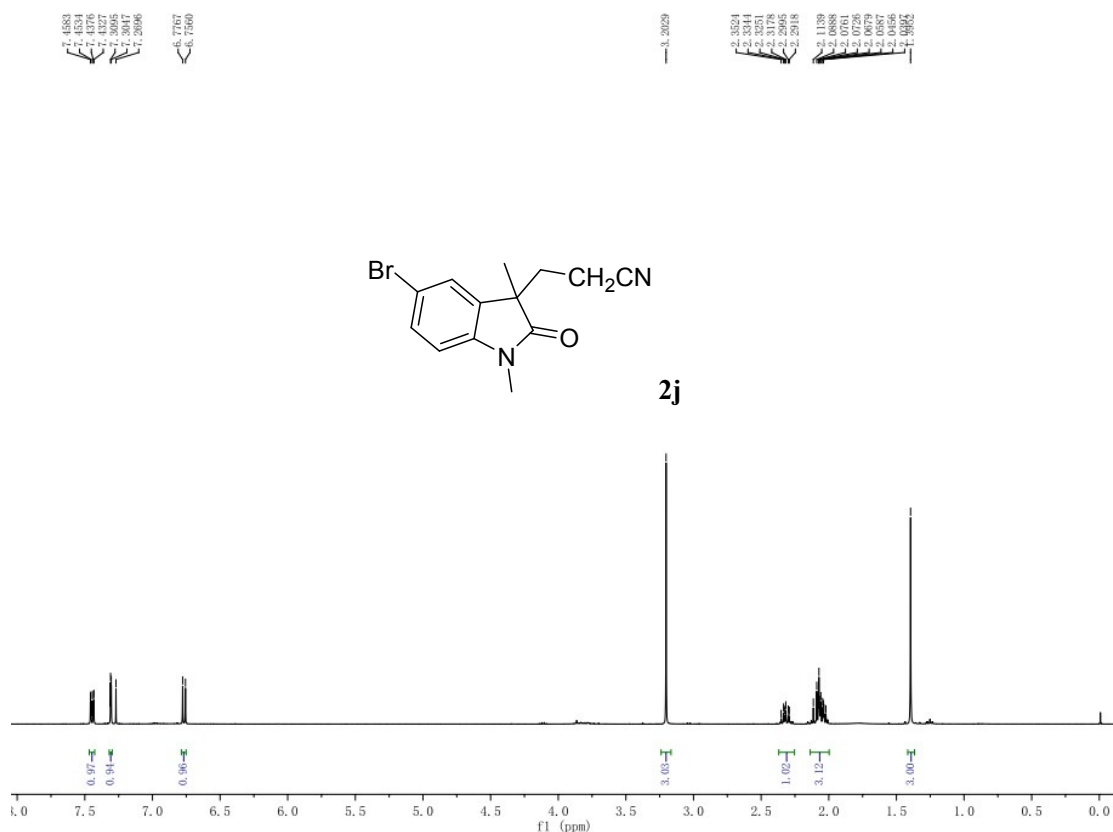


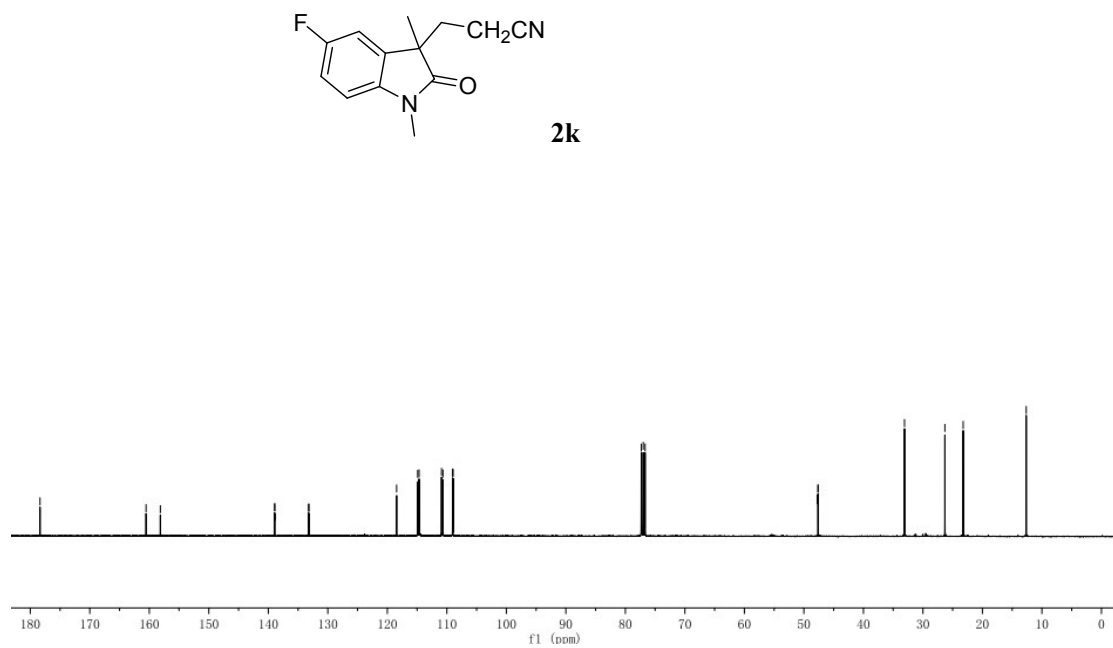
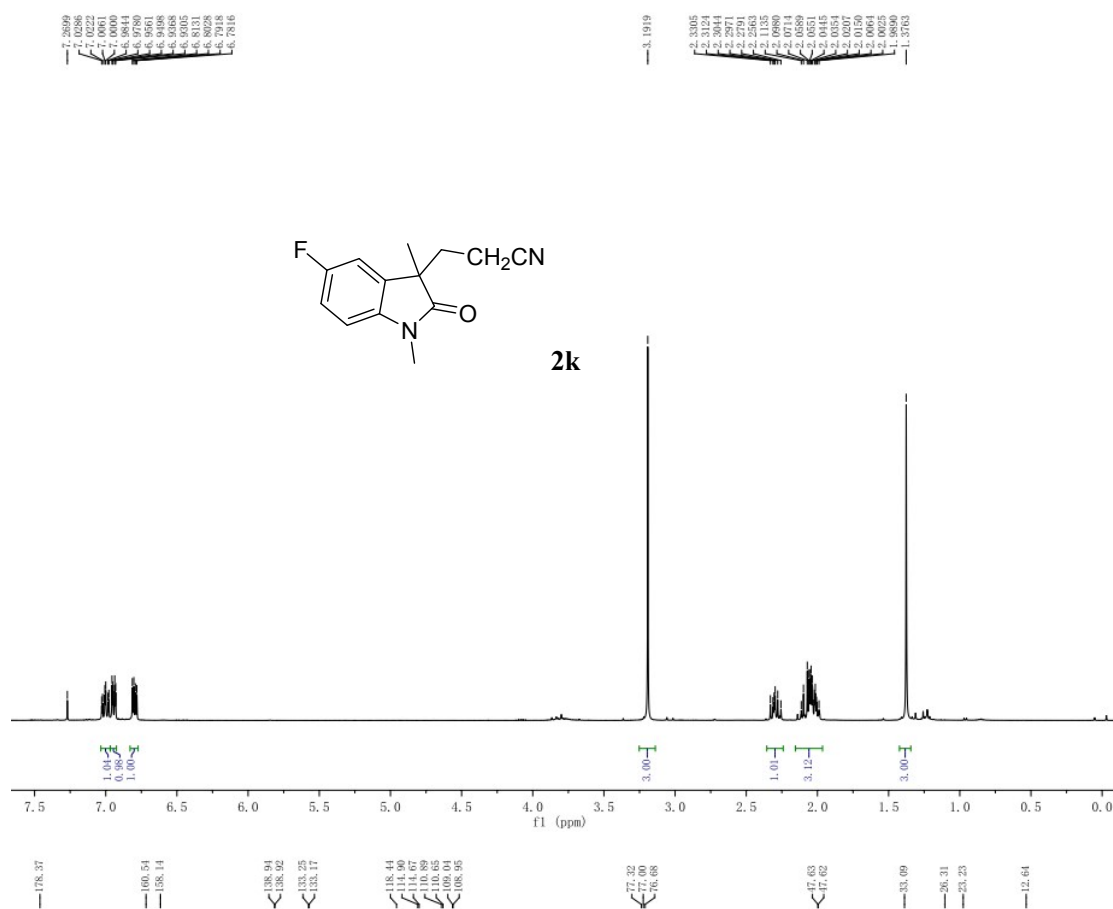






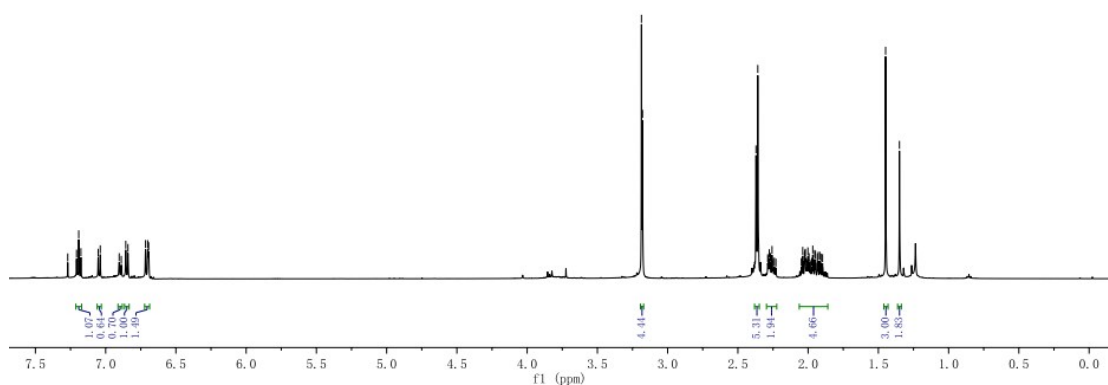
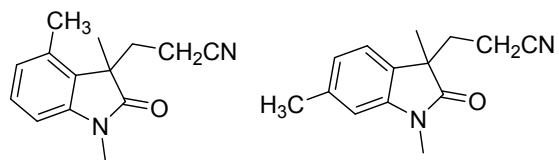




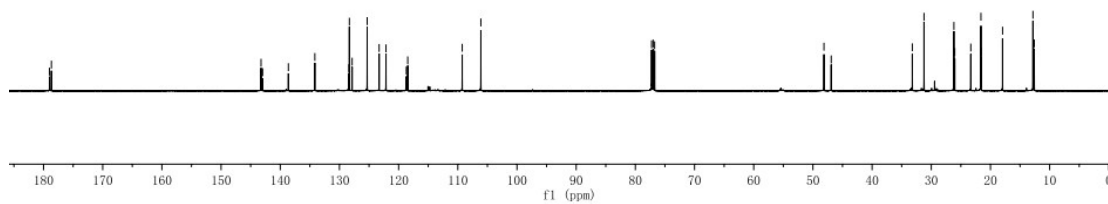
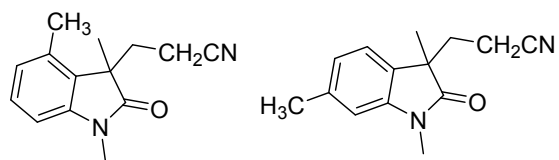


7.2098
7.1916
7.1849
7.0231
6.9837
6.8569
6.8413
6.7101
6.6942

3.1863
3.1787
2.3709
2.3581
2.2938
2.2766
2.2573
2.2485
2.2387
2.2295
2.0384
2.0322
2.0199
1.9835
1.9669
1.9535
1.9476
1.4881
1.3500

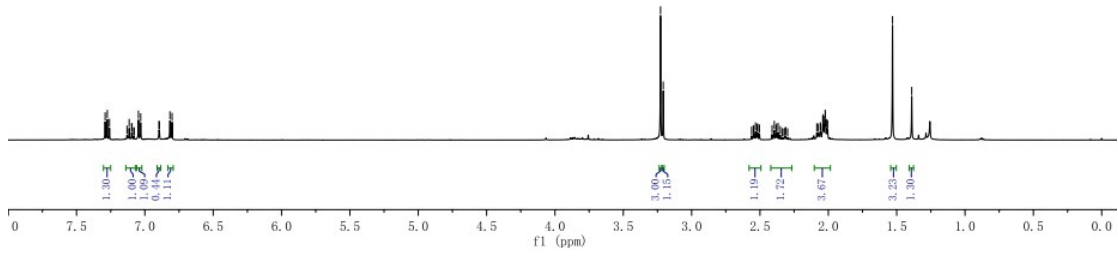
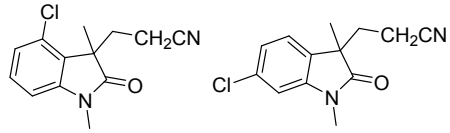


178.99
178.67
143.25
142.98
138.63
134.16
128.41
128.32
127.86
125.29
122.14
118.40
109.26
106.10
77.26
77.00
76.75
48.13
46.91
33.20
31.22
26.18
25.44
23.32
21.61
17.95
17.85
12.82
12.59



7.5987
7.5750
7.5591
7.5306
7.5089
7.4808
7.4941
7.4810
7.4770
7.4006
6.8807
6.8155
6.8008

3.2273
3.2076
2.5983
2.5449
2.5376
2.5327
2.5167
2.5040
2.4853
2.3832
2.3792
2.3675
2.0007
2.0282
2.0259
2.0115
2.0115
1.9904
1.3899



178.06
178.20

144.92
144.22

134.32
129.85
129.88
129.86
127.71
123.48
122.68

109.18
106.97

27.25
26.94

48.87
46.94

33.04
30.18
26.46
23.30
21.12

13.02
12.65

