Supporting Information

Visible-Light Induced Radical Tandem Cyanomethylation of *N*-Aryl Acrylamides: Access to Cyanomethylated Oxindoles

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Content

1. General Information

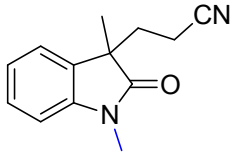
Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Materials were purchased from commercial source and were used without further purification. Solvents were dried using standard methods and distilled before use. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ and spectral data are reported in ppm relative to tetramethylsilane (TMS) as internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. HRMS were performed under ESI ionization technique on a Q-TOF Premier Mass Spectrometer. Flash column chromatography was performed on silica gel (300-400 mesh). All acrylamides **1a-1t** were prepared according to the known procedures.[1]

2. A general procedure for cyclization under visible light

A dried Schlenk tube (25 mL) was equipped with a stirrer bar and evacuated and backfilled with nitrogen, which was charged with *N*-aryl acrylamides (0.5 mmol), Na_2CO_3 (1.0 mmol, 106 mg), *fac*-Ir(ppy)$_3$ (0.01 mmol, 7 mg) and bromoacetonitrile (1.0 mmol). Then 5 mL of CH_3CN was added into the reaction tube via a syringe. The reaction mixture was degassed by the freeze-pump-thaw method and then irradiated with a 23W fluorescent household light bulb (distance app. 5 cm) for 24 h. After the completion of the reaction, it was quenched by water and extracted with ethyl acetate (3 × 15 mL). The organic layers were combined and the pure product was obtained by flash column chromatography on silica gel.

3. Spectral data for products

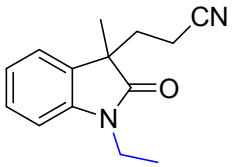
3-(1,3-Dimethyl-2-oxoindolin-3-yl)propanenitrile (**3a**)[2]



3a

Colorless liquid, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.19 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.12 (td, *J* = 7.6, 0.8 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.23 (s, 3H), 2.39 – 2.28 (m, 1H), 2.15 – 1.93 (m, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 142.9, 131.4, 128.4, 122.8, 122.4, 118.6, 108.3, 47.1, 33.1, 26.1, 23.2, 12.6.

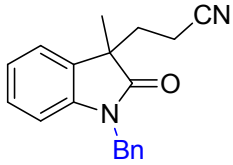
3-(1-Ethyl-3-methyl-2-oxoindolin-3-yl)propanenitrile (**3b**)[3]



3b

Colorless liquid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (td, *J* = 8.0, 1.2 Hz, 1H), 7.19 (d, *J* = 6.8 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 3.84 – 3.69 (m, 2H), 2.38 – 2.26 (m, 1H), 2.12 – 1.91 (m, 3H), 1.38 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 142.1, 131.8, 128.6, 122.8, 122.7, 118.8, 108.6, 47.2, 34.7, 33.4, 23.4, 12.67, 12.65.

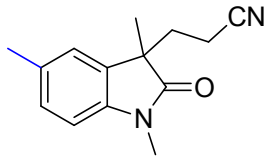
3-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)propanenitrile (**3c**)[4]



3c

Colorless liquid, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 5H), 7.21 – 7.19 (m, 2H), 7.10 – 7.06 (m, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.00 – 4.86 (m, 2H), 2.41 – 2.33 (m, 1H), 2.16 – 1.96 (m, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 142.1, 135.6, 131.5, 128.7, 128.5, 127.6, 127.1, 122.9, 122.6, 118.7, 109.4, 47.2, 43.7, 33.3, 23.6, 12.7.

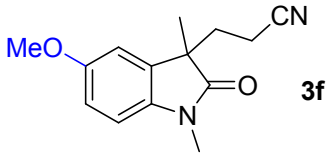
3-(1,3,5-Trimethyl-2-oxoindolin-3-yl)propanenitrile (**3e**)[2]



3e

Colorless liquid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.6 Hz, 1H), 6.99 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 3.19 (s, 3H), 2.35 (s, 3H), 2.32 – 2.26 (m, 1H), 2.12 – 1.92 (m, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 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.

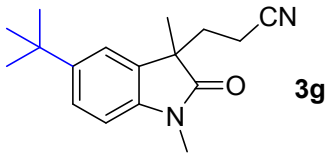
3-(5-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (**3f**)[2]



3f

Yellow liquid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.73 (m, 3H), 3.79 (s, 3H), 3.17 (s, 3H), 2.35 – 2.26 (m, 1H), 2.12 – 1.95 (m, 3H), 1.37 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 156.2, 136.3, 132.8, 118.7, 112.4, 110.1, 108.7, 55.63, 47.6, 33.2, 26.2, 23.3, 12.6.

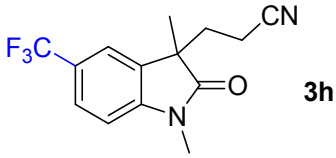
3-(5-(tert-Butyl)-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (**3g**)



3g

Colorless liquid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.20 (s, 3H), 2.37 – 2.28 (m, 1H), 2.15 – 1.97 (m, 4H), 1.40 (s, 3H), 1.33 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 146.3, 140.5, 131.2, 125.1, 119.5, 118.8, 107.8, 47.4, 34.5, 33.3, 31.5, 26.2, 23.3, 12.7. HRMS-ESI (m/z): Calculated for $C_{17}H_{23}N_2O$ $(M + H)^+$: 271.1810, Found: 271.1803.

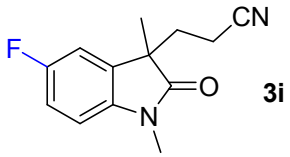
3-(1,3-Dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)propanenitrile (**3h**)[2]



3h

White solid, 88% yield, mp: 69.9 – 71.7 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 1H), 7.424 – 7.420 (m, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 3.26 (s, 3H), 2.41 – 2.31 (m, 1H), 2.18 – 2.02 (m, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 146.1, 132.4, 126.5 (q, $J_{C\text{-}F}$ = 3.9 Hz, 1C), 125.3 (q, $J_{C\text{-}F}$ = 32.5 Hz, 1C), 124.1(q, $J_{C\text{-}F}$ = 269.9 Hz, 1C), 119.7 (q, $J_{C\text{-}F}$ = 3.6 Hz, 1C), 118.3, 108.3, 47.2, 33.1, 26.5, 23.3, 12.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.5.

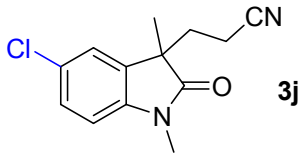
3-(5-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (**3i**)[2]



3i

White solid, 76% yield, mp: 121.4 – 123.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 7.00 (m, 1H), 6.96 – 6.94 (m, 1H), 6.82 – 6.79 (m, 1H), 3.21 (s, 3H), 2.36 – 2.28 (m, 1H), 2.17 – 2.00 (m, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 159.3 (d, *J* = 240.2 Hz), 138.9, 133.1 (d, *J* = 7.7 Hz), 118.4, 114.7 (d, *J* = 23.3 Hz), 110.7 (d, *J* = 24.6 Hz), 109.0 (d, *J* = 8.0 Hz), 47.6, 33.0, 26.3, 23.2, 12.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.5.

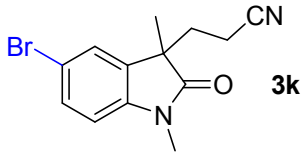
3-(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (**3j**)[2]



3j

White solid, 90% yield, mp: 62.1 – 63.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.17 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 3.20 (s, 3H), 2.36 – 2.28 (m, 1H), 2.16 – 2.02 (m, 3H), 1.40 (s, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 141.5, 133.2, 128.4, 128.2, 123.1, 118.4, 109.4, 47.4, 33.0, 26.3, 23.2, 12.6.

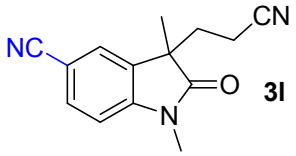
3-(5-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (**3k**)[2]



3k

Pale yellow solid, 90% yield, mp: 88.2 – 89.4 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.30 (d, *J* = 2.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 3.20 (s, 3H), 2.36 – 2.27 (m, 1H), 2.16 – 2.00 (m, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 142.0, 133.5, 131.3, 125.7, 118.3, 115.4, 109.8, 47.2, 32.9, 26.2, 23.2, 12.6.

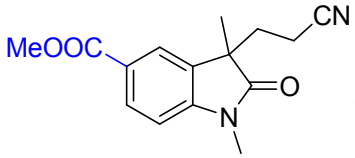
3-(2-Cyanoethyl)-1,3-dimethyl-2-oxoindoline-5-carbonitrile (**3l**)[5]



3l

White solid, 86% yield, mp: 152.4 – 155.0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 (d, *J* = 1.6 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 3.26 (s, 3H), 2.39 – 2.30 (m, 1H), 2.20 – 2.04 (m, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 146.8, 133.8, 132.6, 126.0, 118.7, 118.1, 108.8, 105.7, 46.8, 32.6, 26.4, 23.0, 12.5.

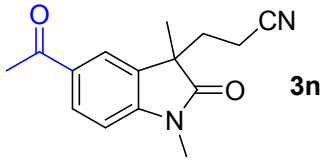
Methyl 3-(2-cyanoethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (**3m**)[2]



3m

White solid, 86% yield, mp: 119.5 – 121.2 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.86 (s, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H), 3.25 (s, 3H), 2.40 – 2.28 (m, 1H), 2.14 – 2.01 (m, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 166.4, 147.1, 131.5, 131.1, 124.7, 123.7, 118.3, 108.0, 52.0, 46.9, 32.9, 26.4, 23.2, 12.6.

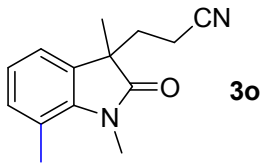
3-(5-Acetyl-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (**3n**)



3n

White solid, 93% yield, mp: 108.6 – 110.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.82 (d, *J* = 1.2 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 3.24 (s, 3H), 2.57 (s, 3H), 2.35 – 2.26 (m, 1H), 2.13 – 2.00 (m, 3H), 1.40 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 179.0, 147.2, 132.3, 131.8, 130.5, 122.3, 118.3, 107.8, 46.9, 32.9, 26.4, 26.2, 23.2, 12.6. HRMS-ESI (m/z): Calculated for $C_{15}H_{17}N_2O_2$ $(M + H)^+$: 257.1290, Found: 257.1289.

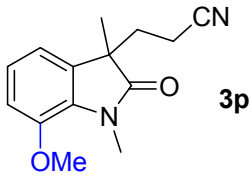
3-(1,3,7-Trimethyl-2-oxoindolin-3-yl)propanenitrile (**3o**)[4]



3o

Pale yellow liquid, 20% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.97 (m, 1H), 3.50 (s, 1H), 2.59 (s, 1H), 2.34 – 2.27 (m, 1H), 2.12 – 1.92 (m, 1H), 1.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ179.6, 140.9, 132.4, 132.3, 123.0, 120.5, 120.2, 118.9, 46.7, 33.7, 29.6, 23.9, 19.0, 12.9.

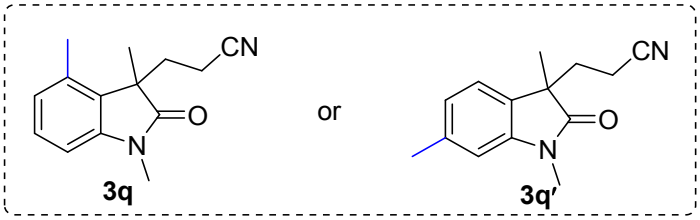
3-(7-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (**3p**)[5]



3p

Colorless liquid, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 7.2 Hz, 1H), 3.86 (s, 3H), 3.47 (s, 3H), 2.35 – 2.25 (m, 1H), 2.11 – 1.90 (m, 3H), 1.36 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 145.5, 133.2, 130.8, 123.6, 118.9, 115.0, 112.2, 55.8, 47.4, 33.6, 29.5, 23.7, 12.8.

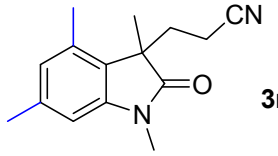
3-(1,3,4-Trimethyl-2-oxoindolin-3-yl)propanenitrile (**3q**) and 3-(1,3,6-Trimethyl-2-oxoindolin-3-yl)propanenitrile (**3q′**)[4]



3q **3q′**

Colorless liquid, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.6 Hz, 0.6H), 7.05 (d, *J* = 7.6 Hz, 0.3H), 6.90 (d, *J* = 7.2 Hz, 0.3H), 6.86 (d, *J* = 7.6 Hz, 0.6H), 6.72 (s, 0.3H), 6.70 (d, *J* = 3.6 Hz, 0.5H), 3.20 (s, 1.44H), 3.19 (s, 0.9H), 2.38 (s, 1H), 2.37 (s, 1.8H), 2.31 – 2.23 (m, 1H), 2.11 – 1.86 (m, 3H), 1.46 (s, 1.8H), 1.36 (s, 0.93H).^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 179.1, 143.7, 143.4, 139.1, 134.6, 128.9, 128.8, 128.3, 125.8, 123.7, 122.6, 119.1, 118.9, 109.7, 106.5, 48.6, 47.4, 33.7, 31.7, 26.6, 26.5, 23.8, 22.1, 18.4, 13.3, 13.0.

3-(1,3,4,6-Tetramethyl-2-oxoindolin-3-yl)propanenitrile (**3r**)[2]

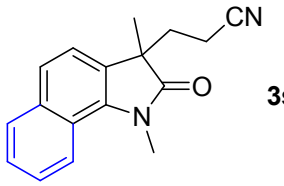


3r

Colorless liquid, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 1H), 6.54 (s, 1H), 3.18 (s, 3H), 2.45 – 2.21 (m, 2H), 2.33 (d, *J* = 5.2 Hz, 6H), 2.01 – 1.85 (m, 2H), 1.44 (s, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 179.5, 143.9, 139.0, 134.4, 126.4, 125.5, 119.1, 107.6, 48.5, 31.9, 26.7, 22.3, 21.9, 18.4, 13.4.

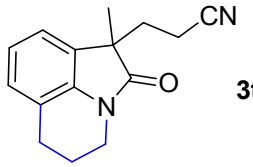
3-(1,3-Dimethyl-2-oxo-2,3-dihydro-1H-benzo[g]indol-3-yl)propanenitrile (**3s**)[2]



3s

Pale yellow liquid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.48 – 7.40 (m, 2H), 6.98 (d, *J* = 7.2 Hz, 1H), 3.54 (s, 3H), 2.86 – 2.79 (m, 1H), 2.27 – 1.99 (m, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 136.0, 135.4, 133.3, 127.0, 126.7, 126.5, 122.7, 122.4, 119.3, 118.9, 108.8, 46.7, 38.0, 31.1, 29.6, 13.5.

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



3t

Colorless liquid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.95 (m, 3H), 3.75 – 3.65 (m, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.32 – 2.24 (m, 1H), 2.15 – 1.97 (m, 5H), 1.38 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 138.7, 130.0, 127.2, 122.2, 120.4, 120.2, 118.7, 48.4, 38.7, 33.0, 24.3, 23.0, 20.9, 12.7.

4. Reference

1. Z. Ni, X. Huang, J. Wang and Y. Pan, *RSC Advances*, 2016, **6**, 522-526.
2. T. Wu, X. Mu and G. Liu, *Angew. Chem. Int. Ed.*, 2011, **50**, 12578-12581.
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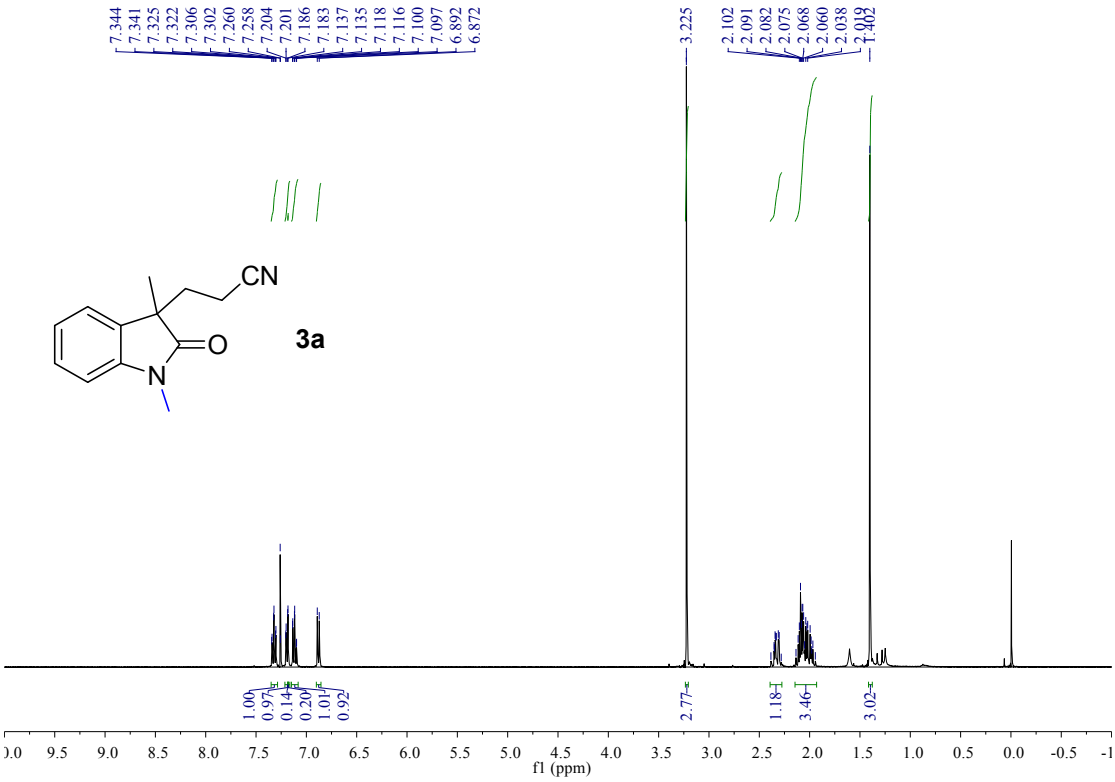
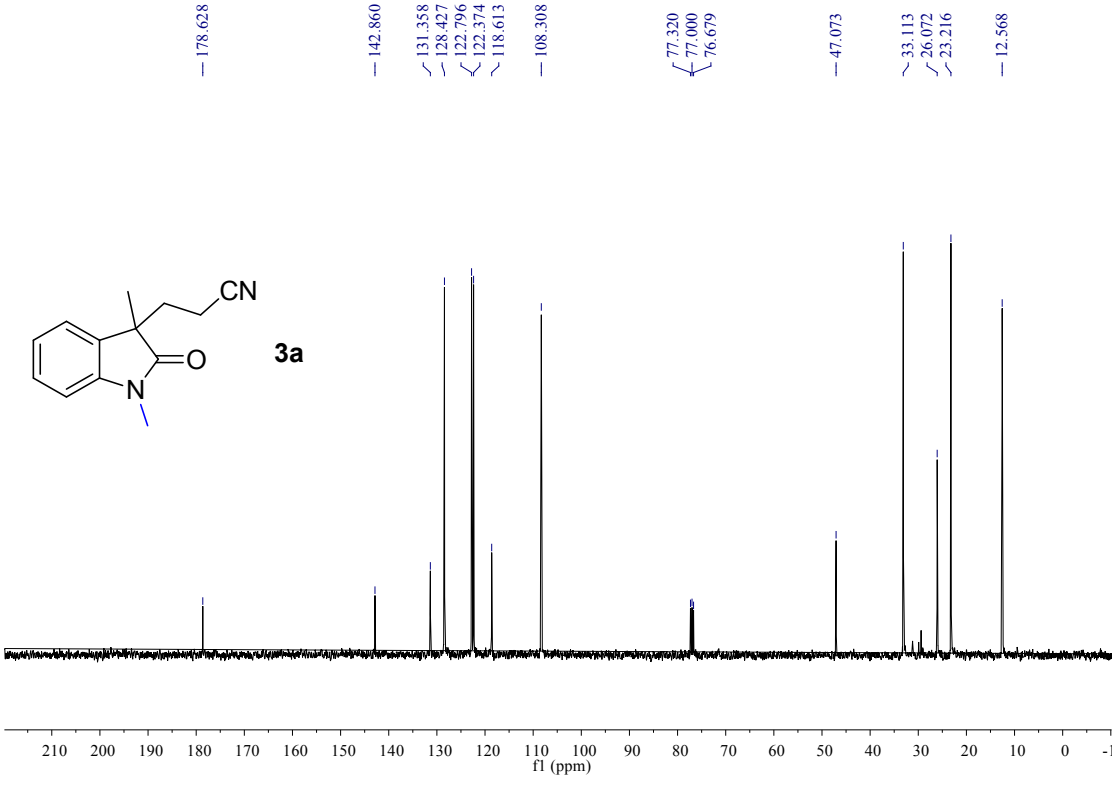
5. NMR spectra of products

3-(1,3-Dimethyl-2-oxoindolin-3-yl)propanenitrile (3a)





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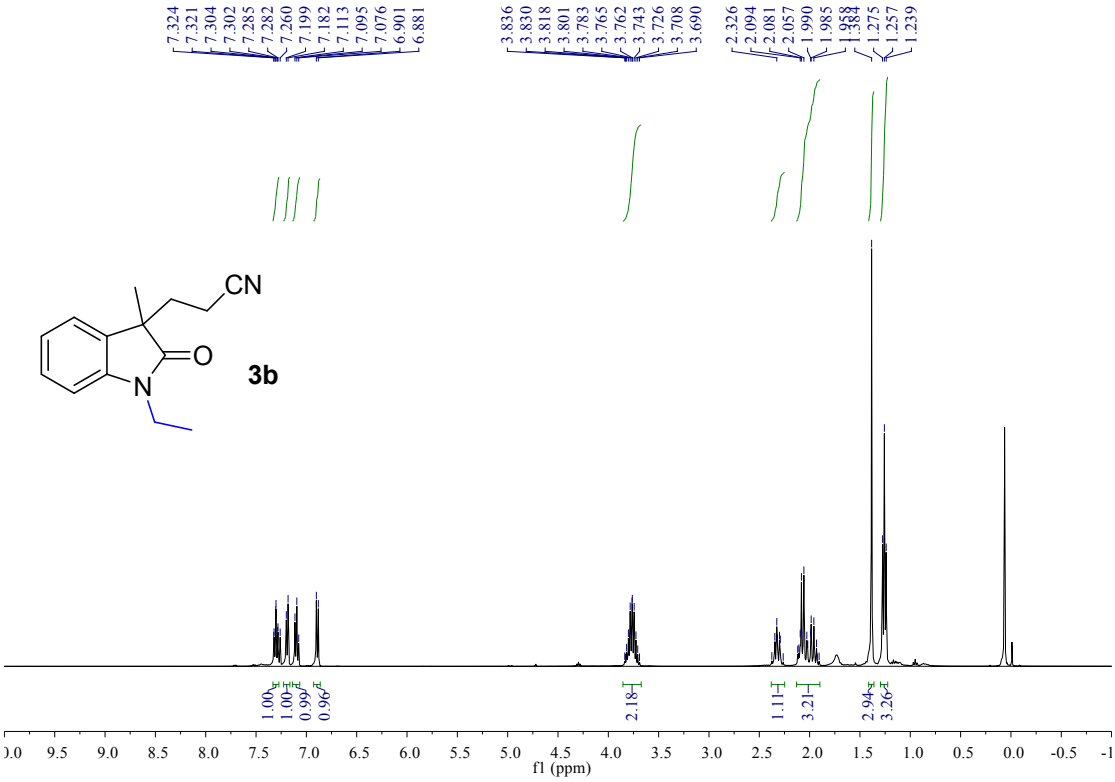
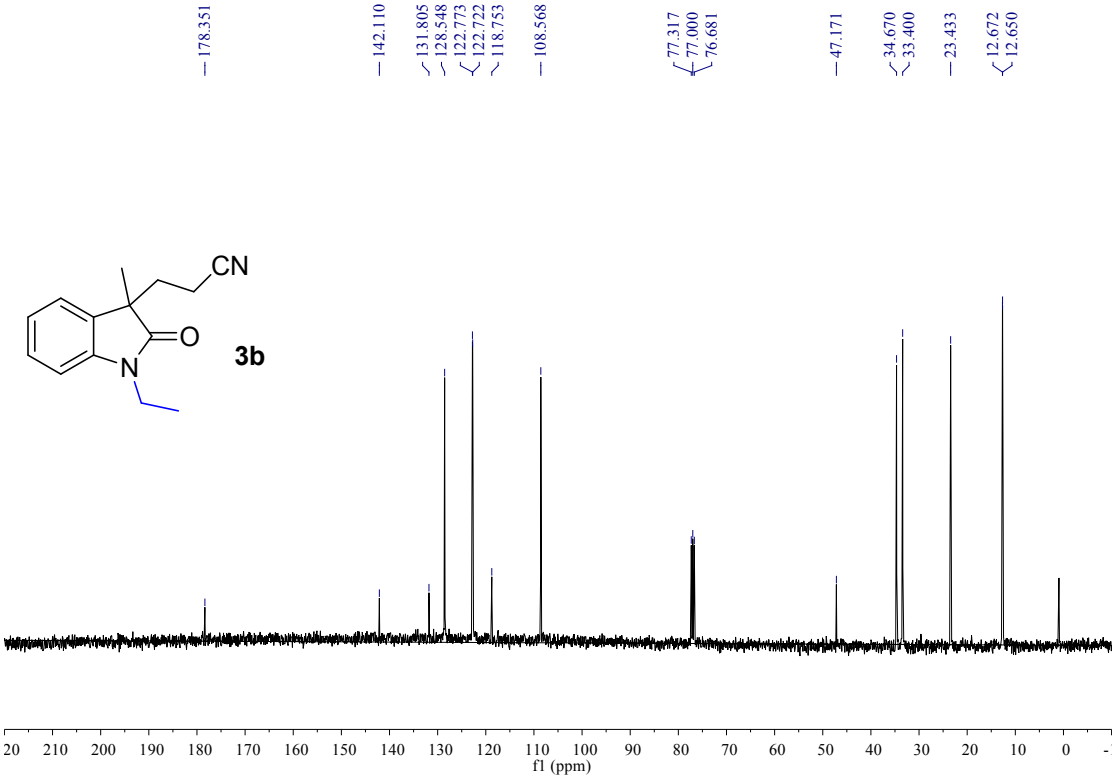
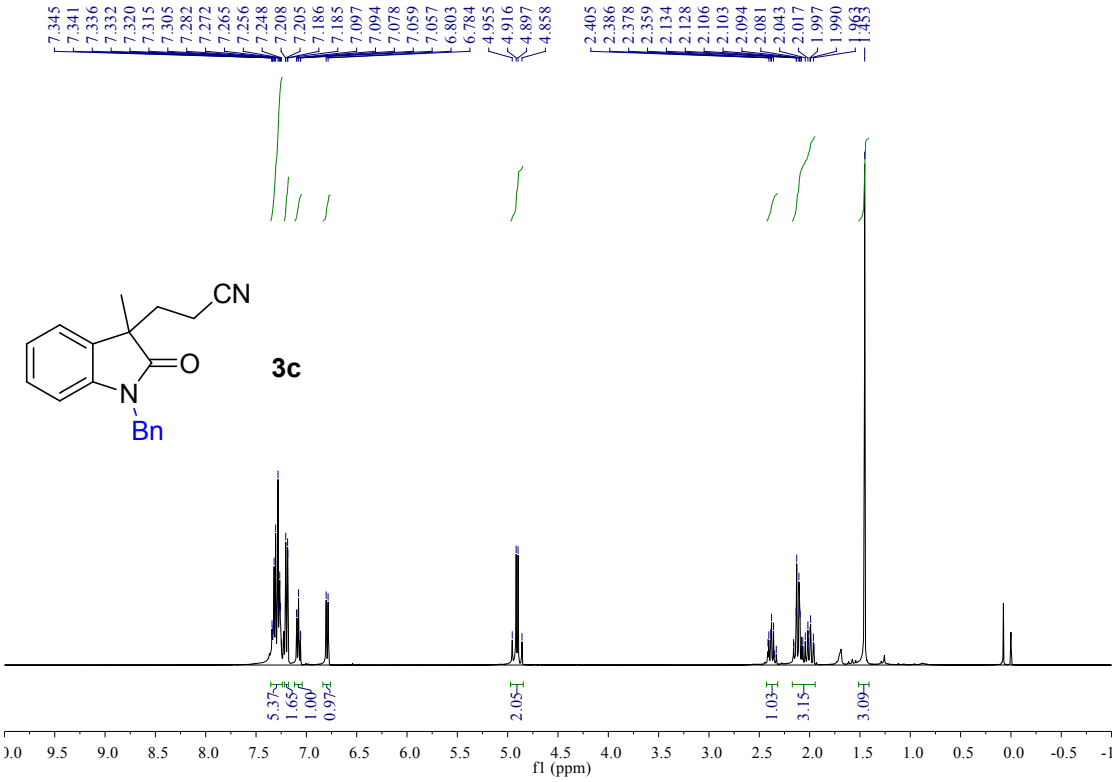
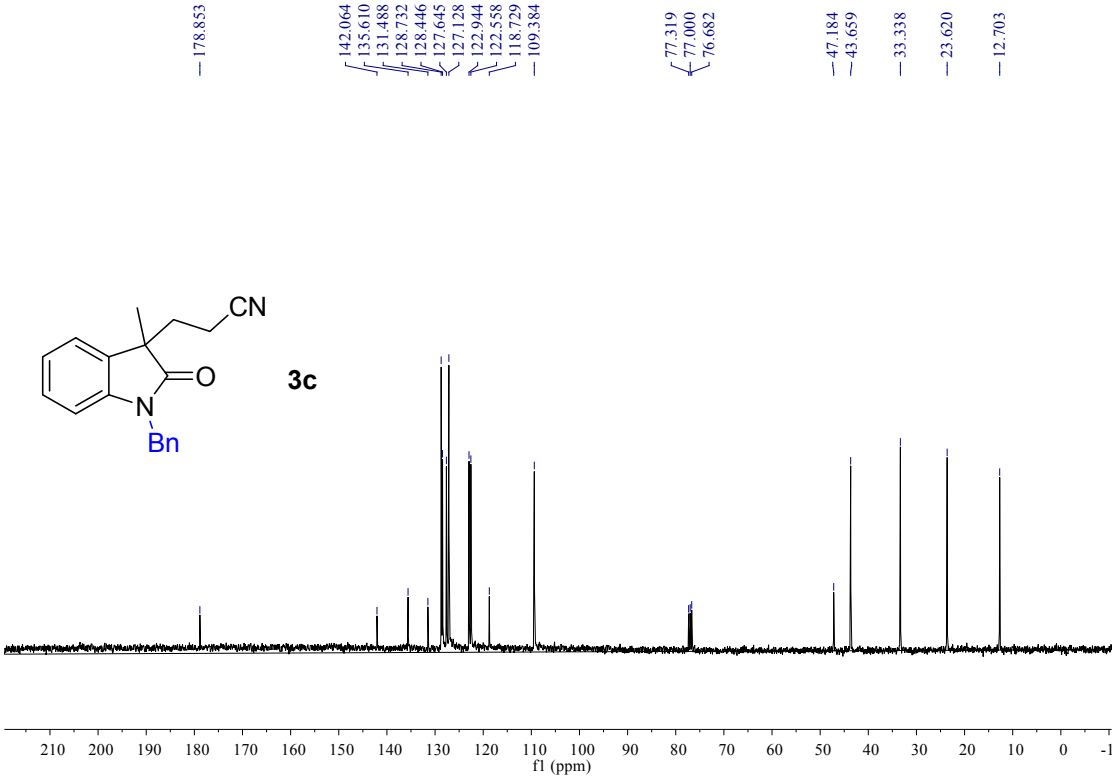




3-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)propanenitrile (3c)





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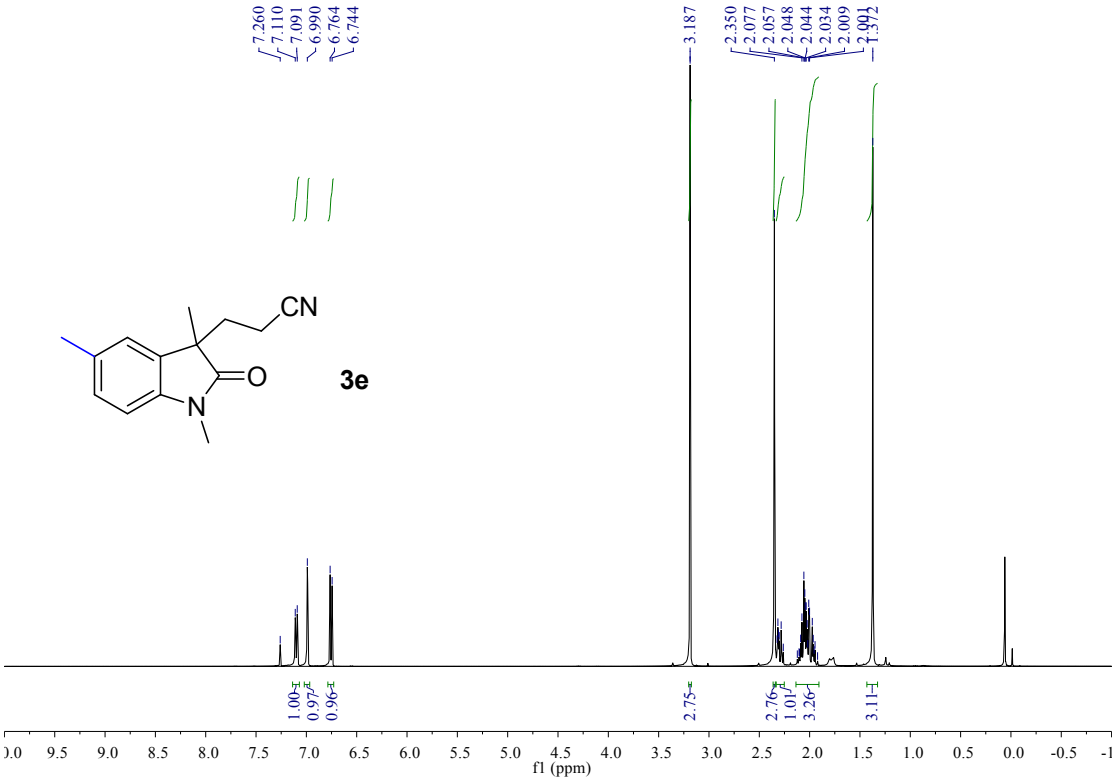
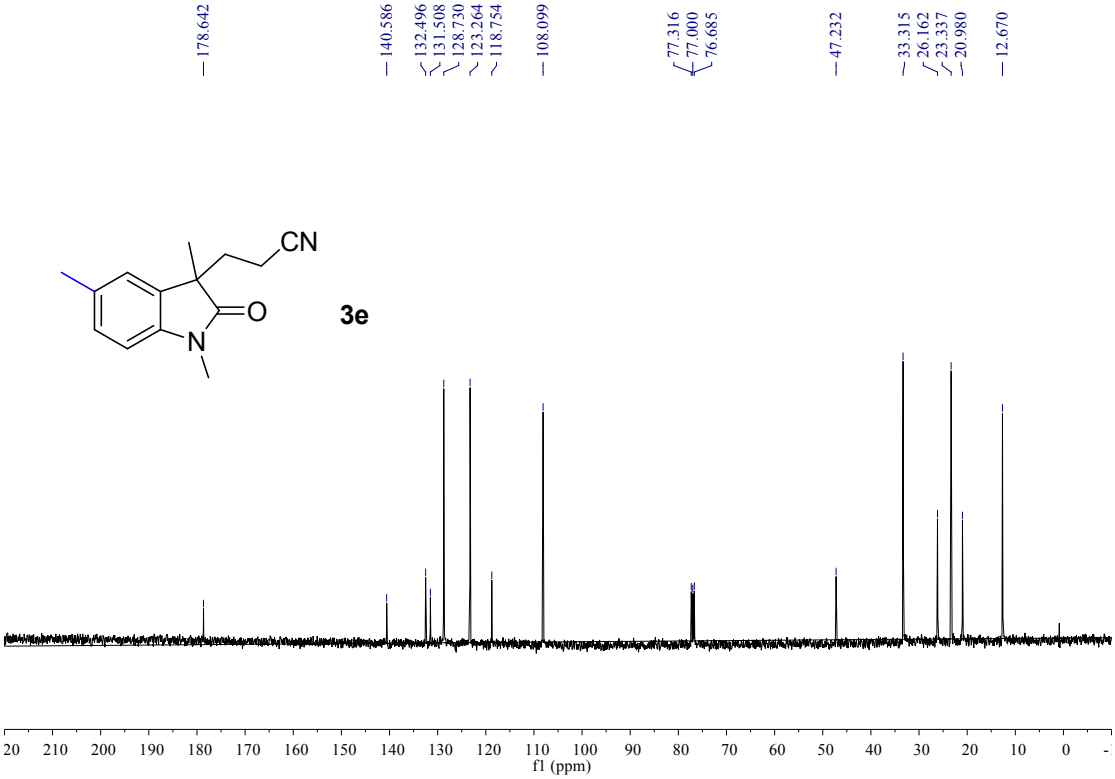
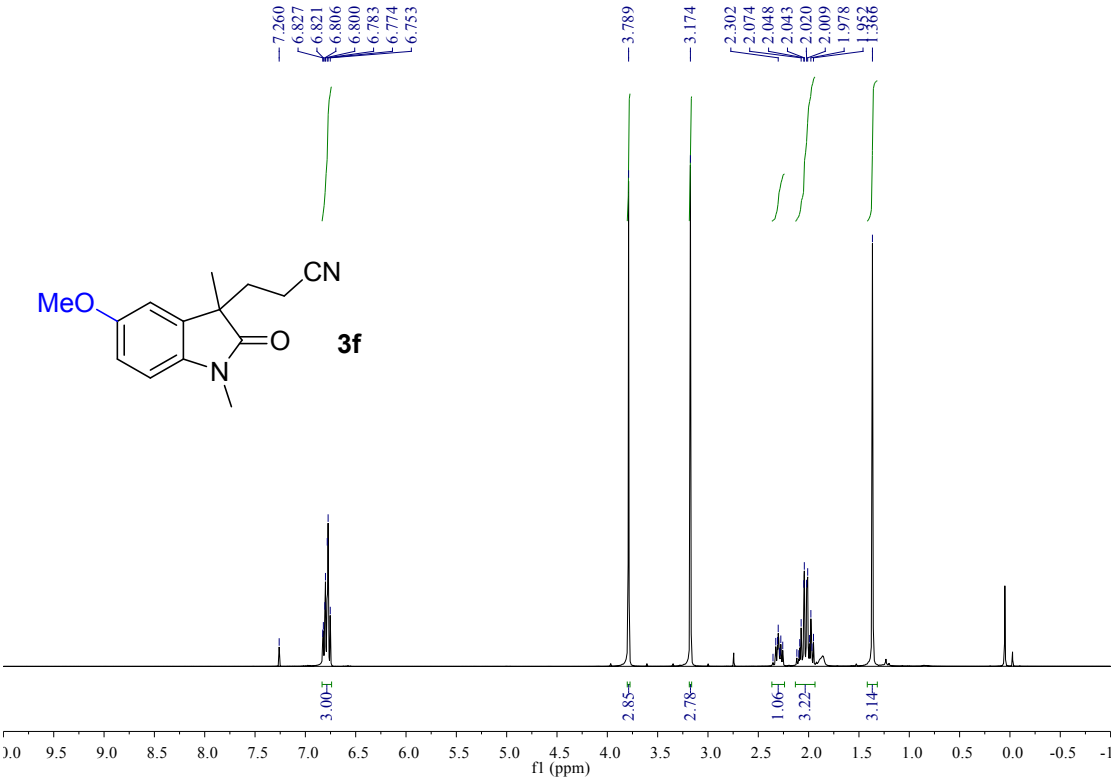
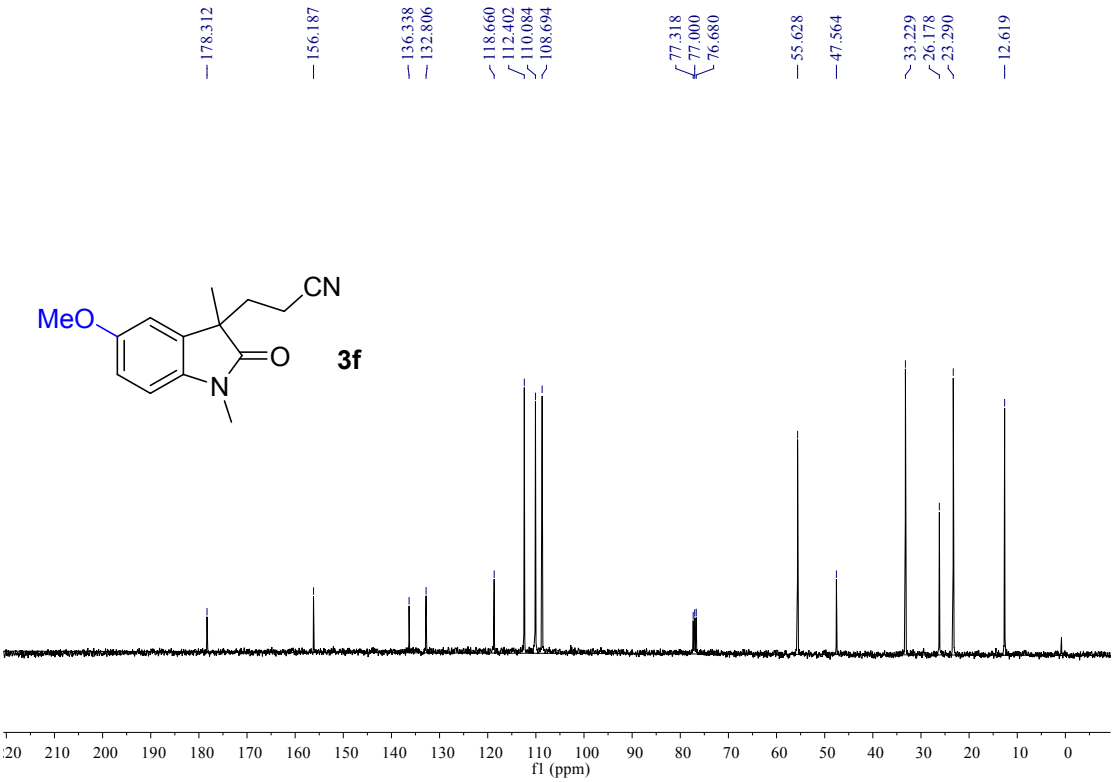




3-(5-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3f)





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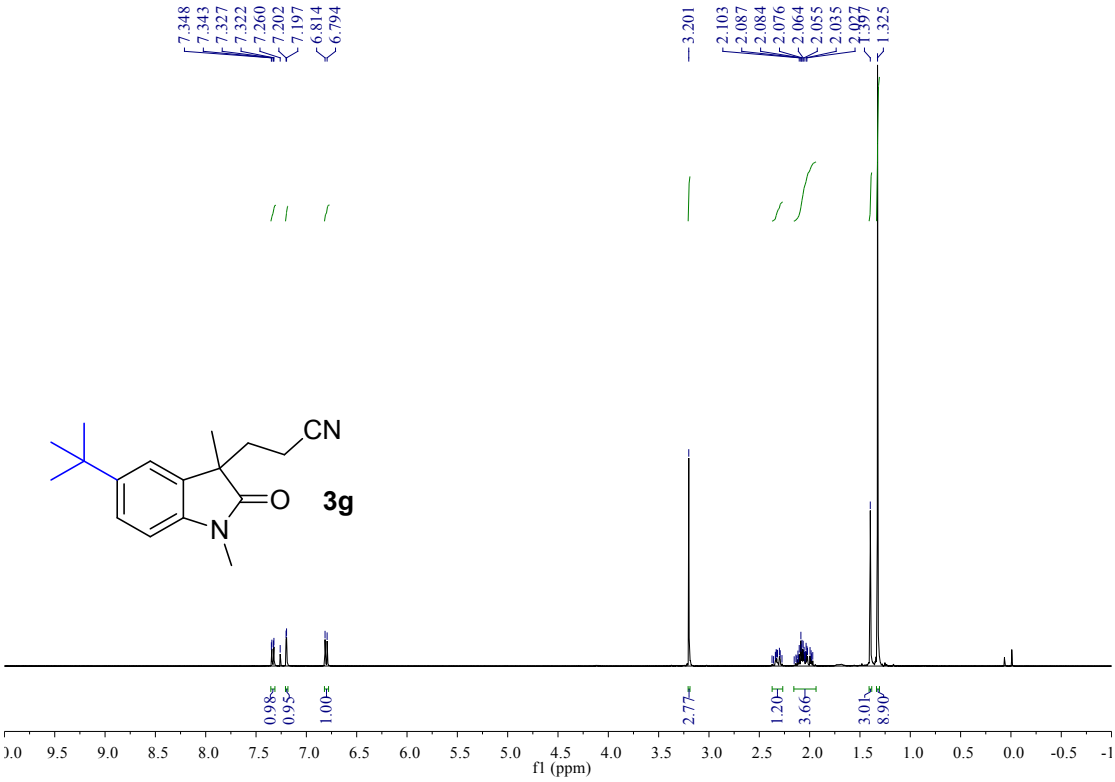
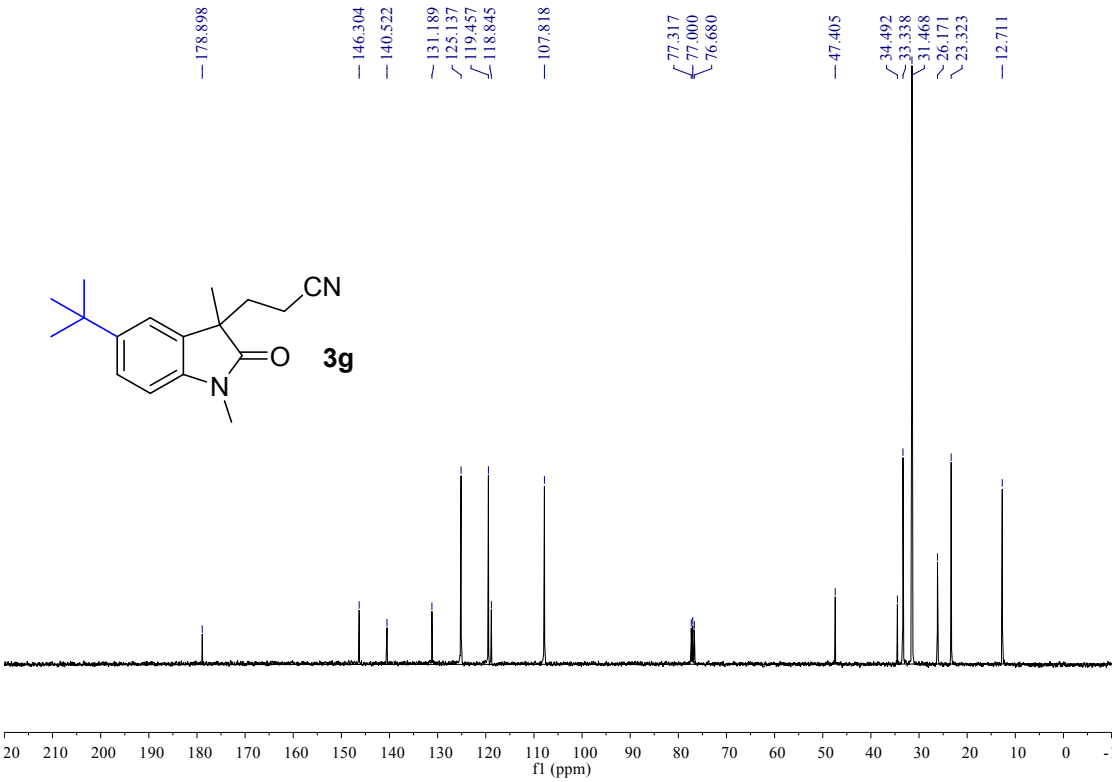
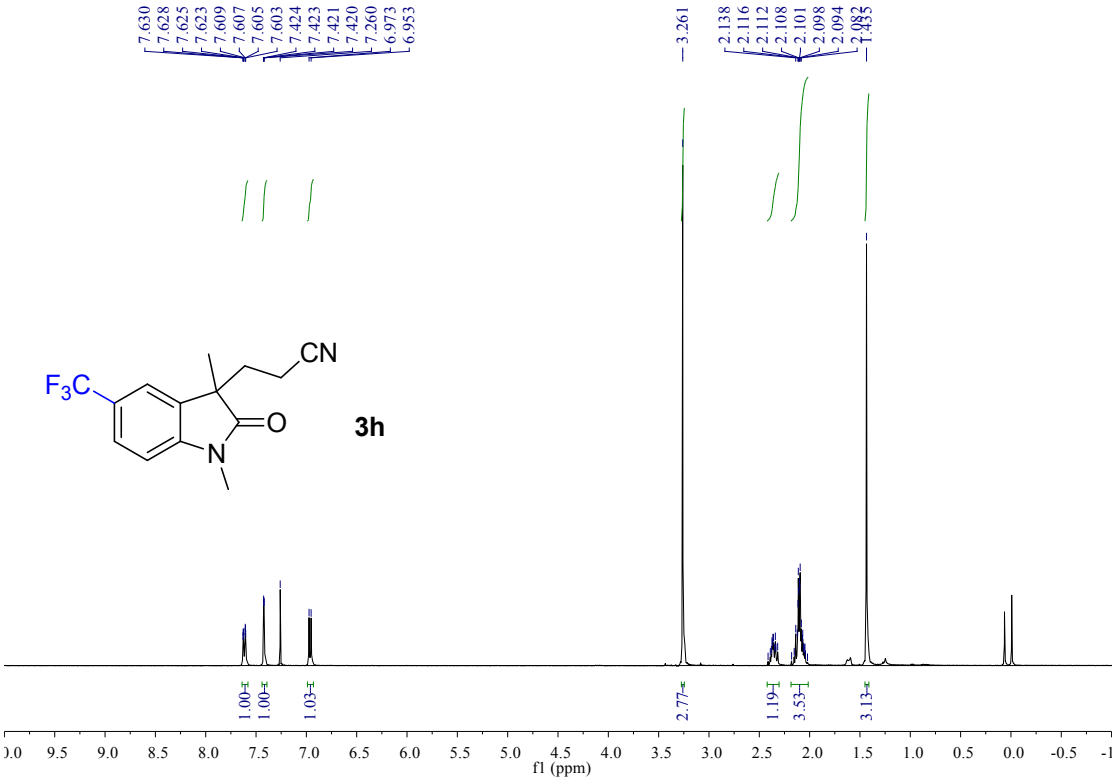
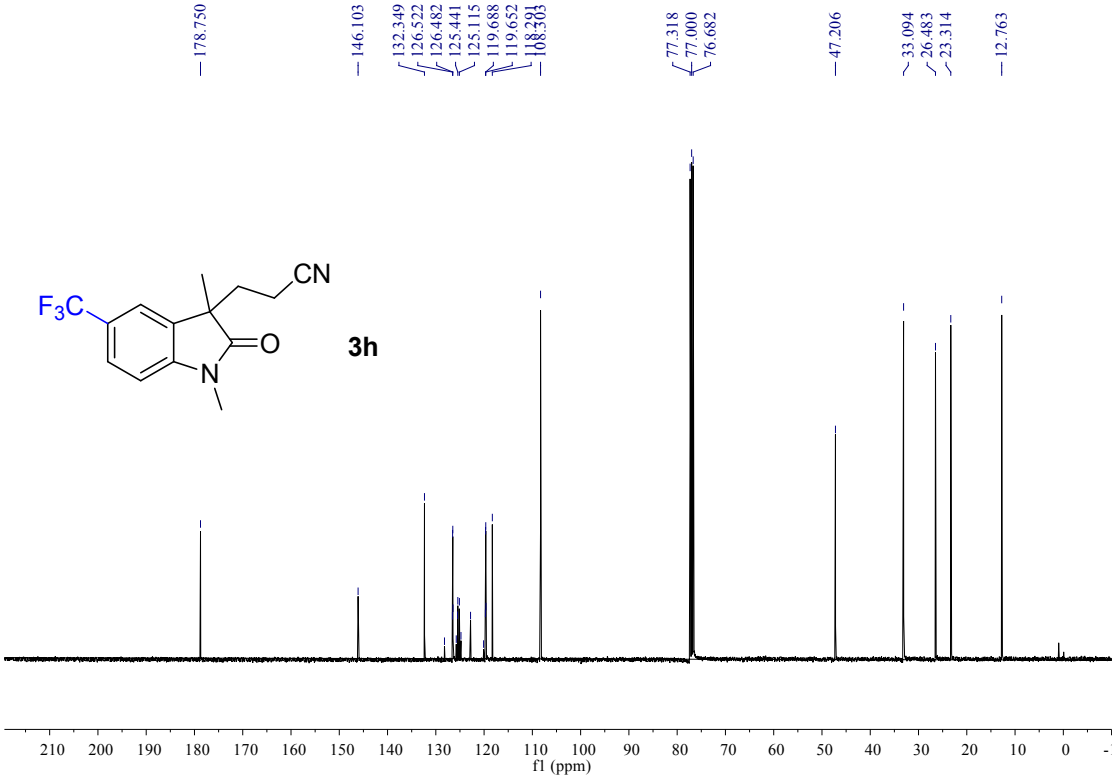
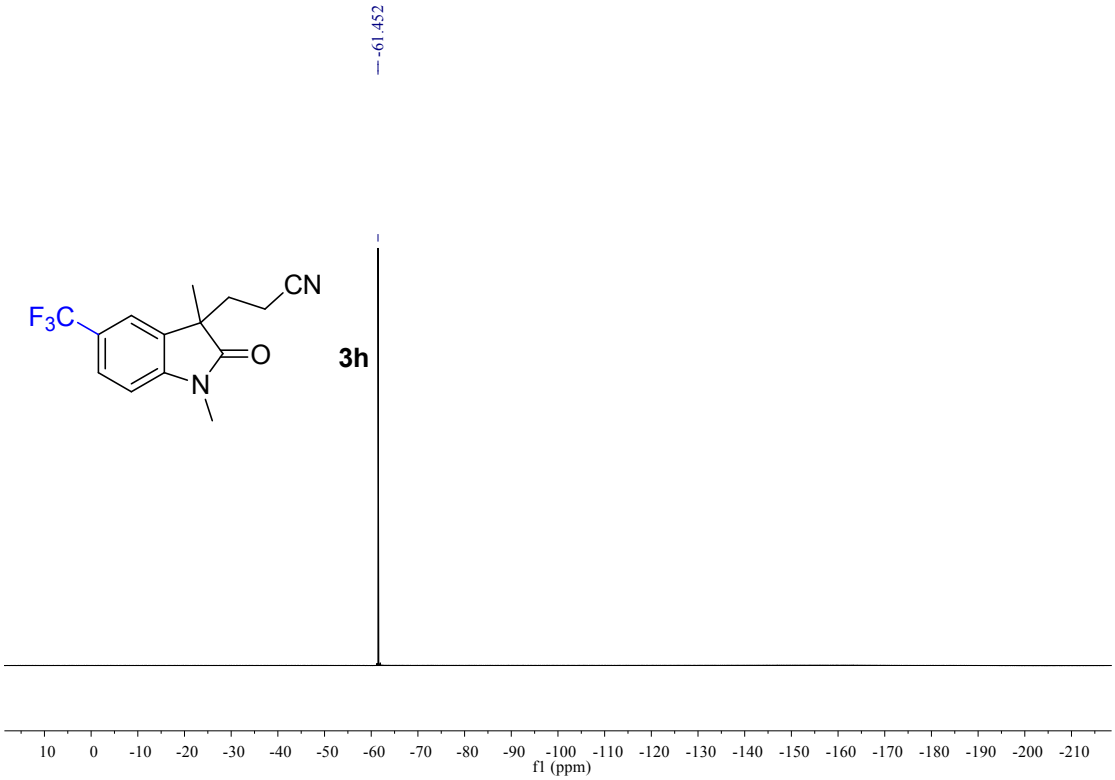




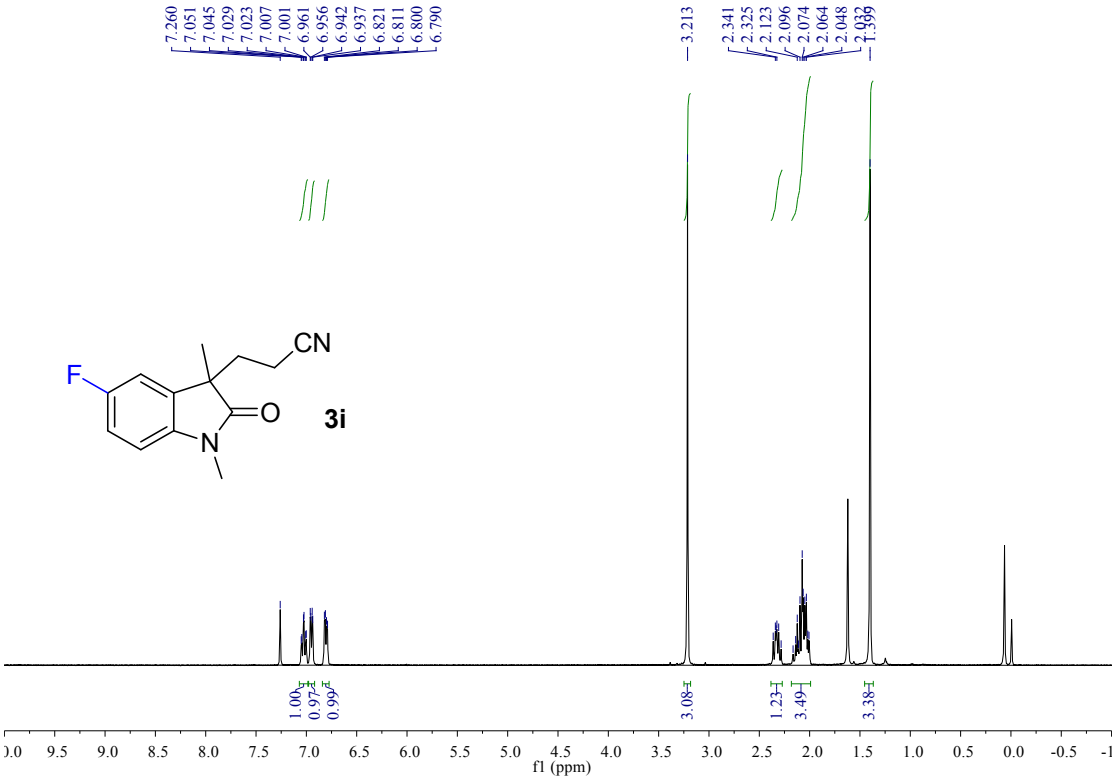
3-(1,3-Dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)propanenitrile (3h)

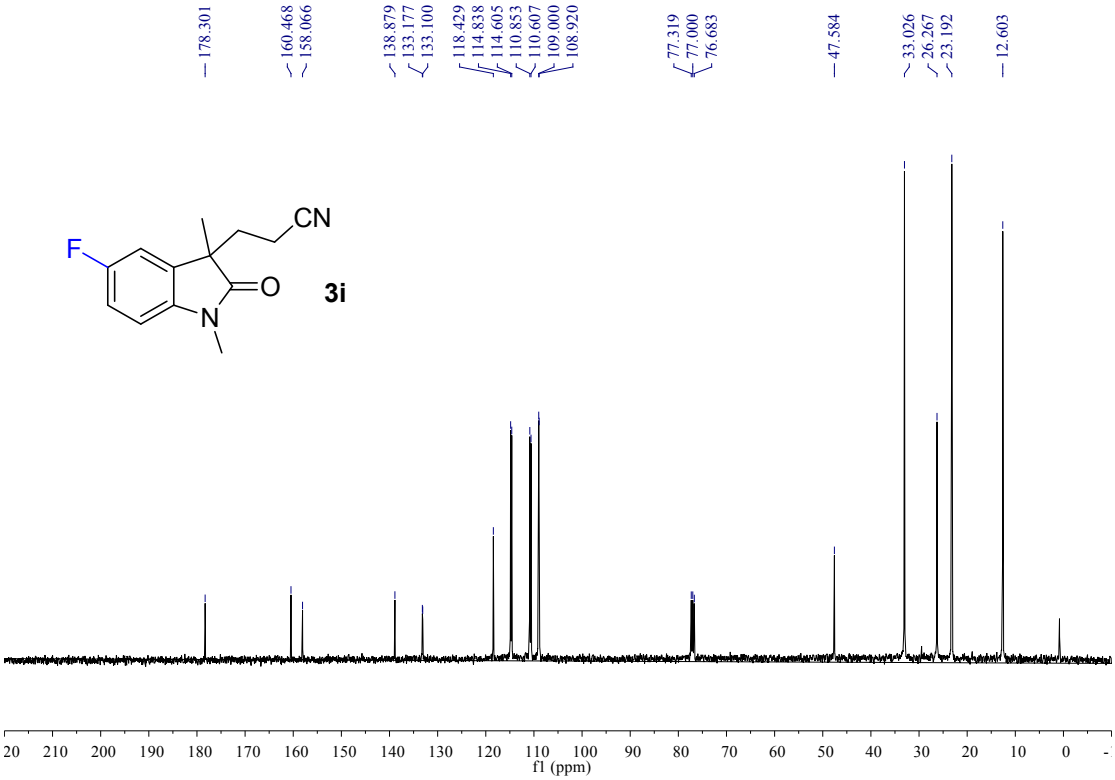






3-(5-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3i)

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158.066
138.879
133.177
133.100
118.429
114.838
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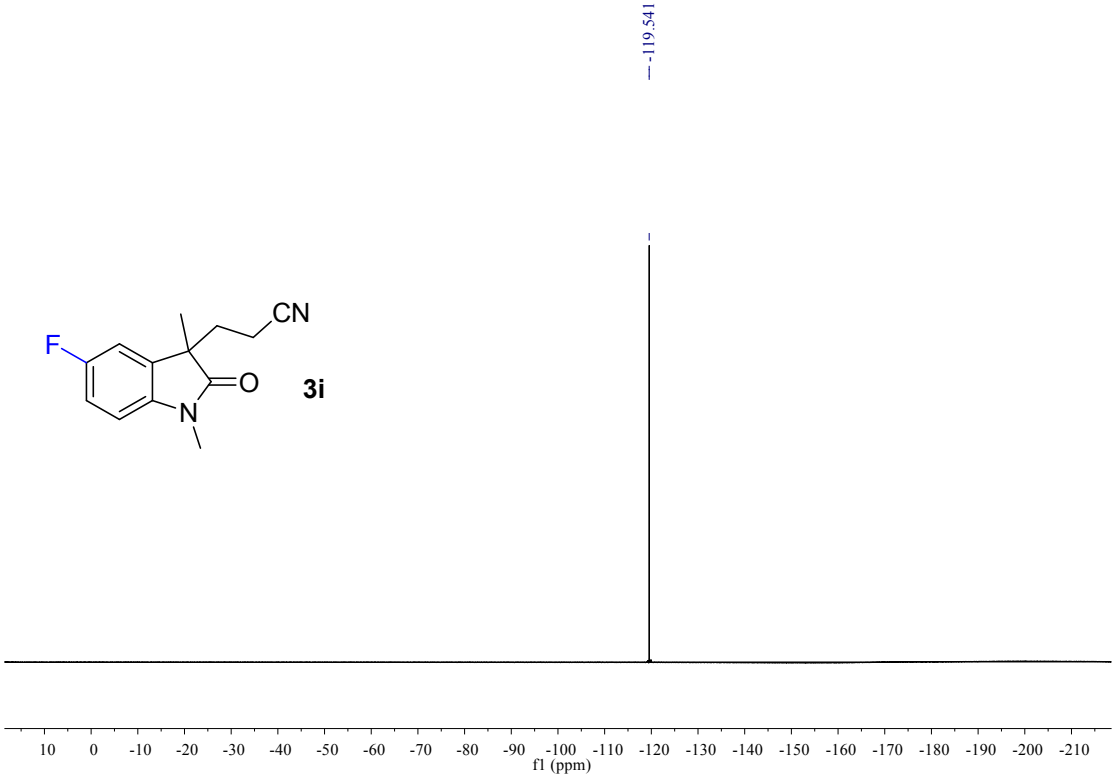
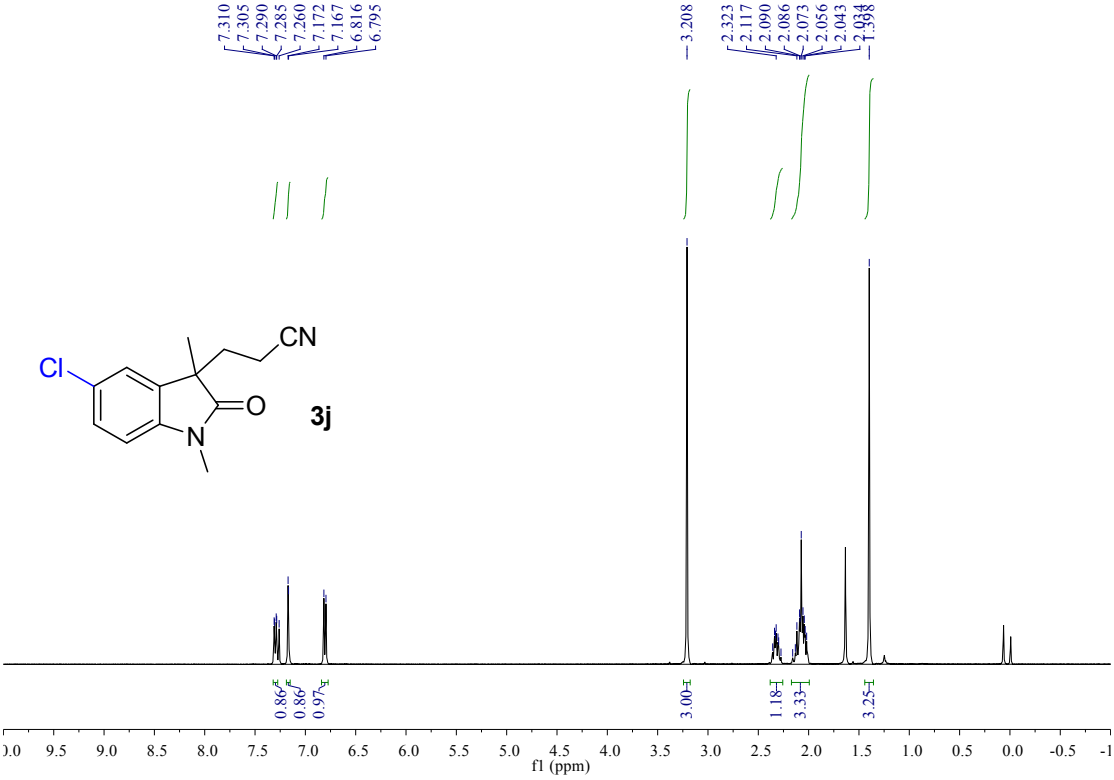
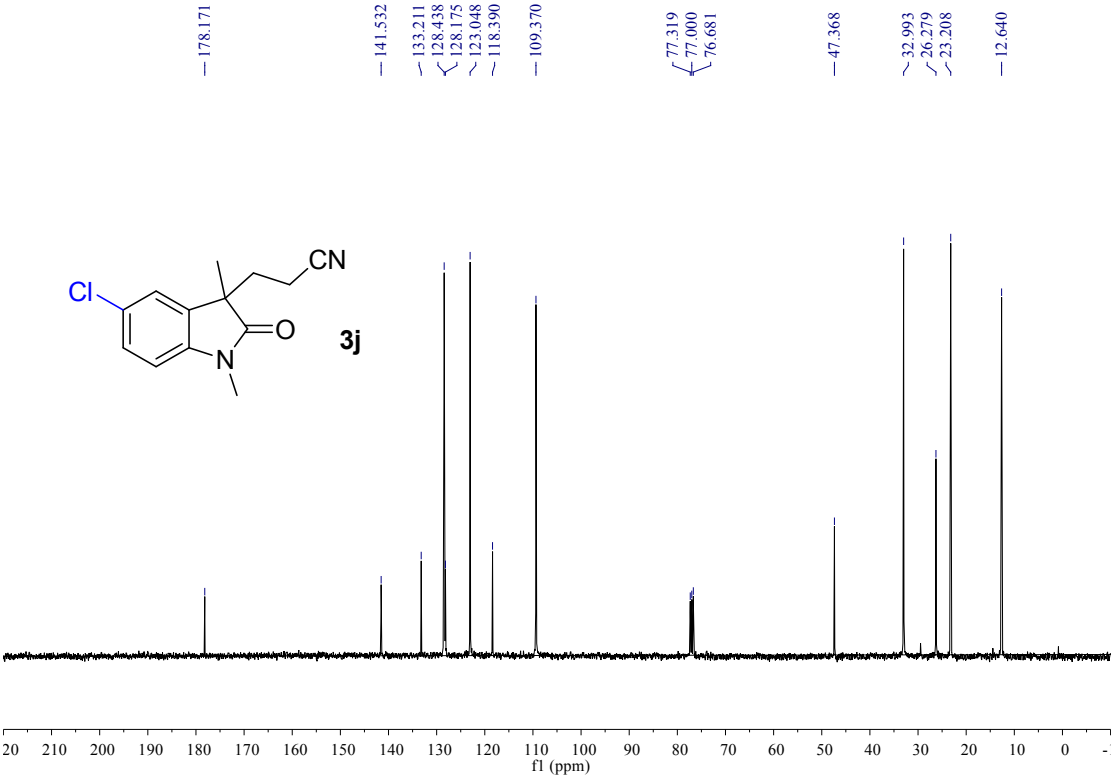
110.853
110.607
109.000
108.920
77.319
77.000
76.683
47.584
33.026
26.267
23.192
12.603
CN
F
O
N
3i
f1 (ppm)

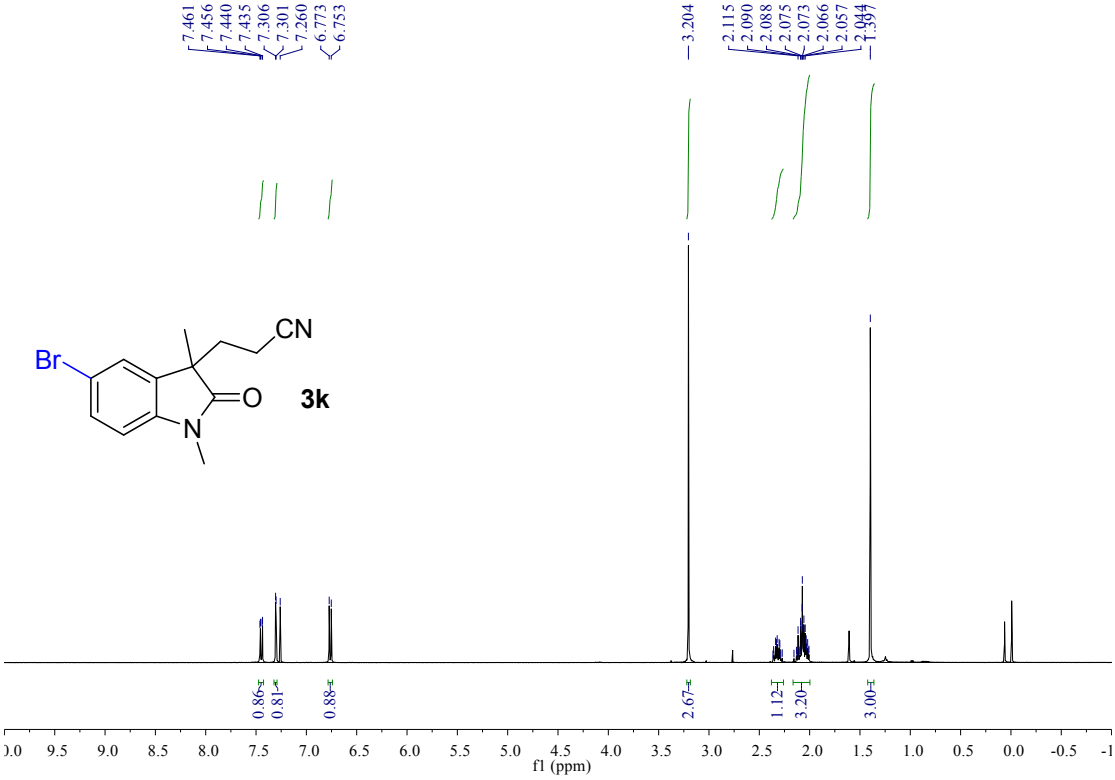

-119.541
CN
F
O
N
3i
f1 (ppm)

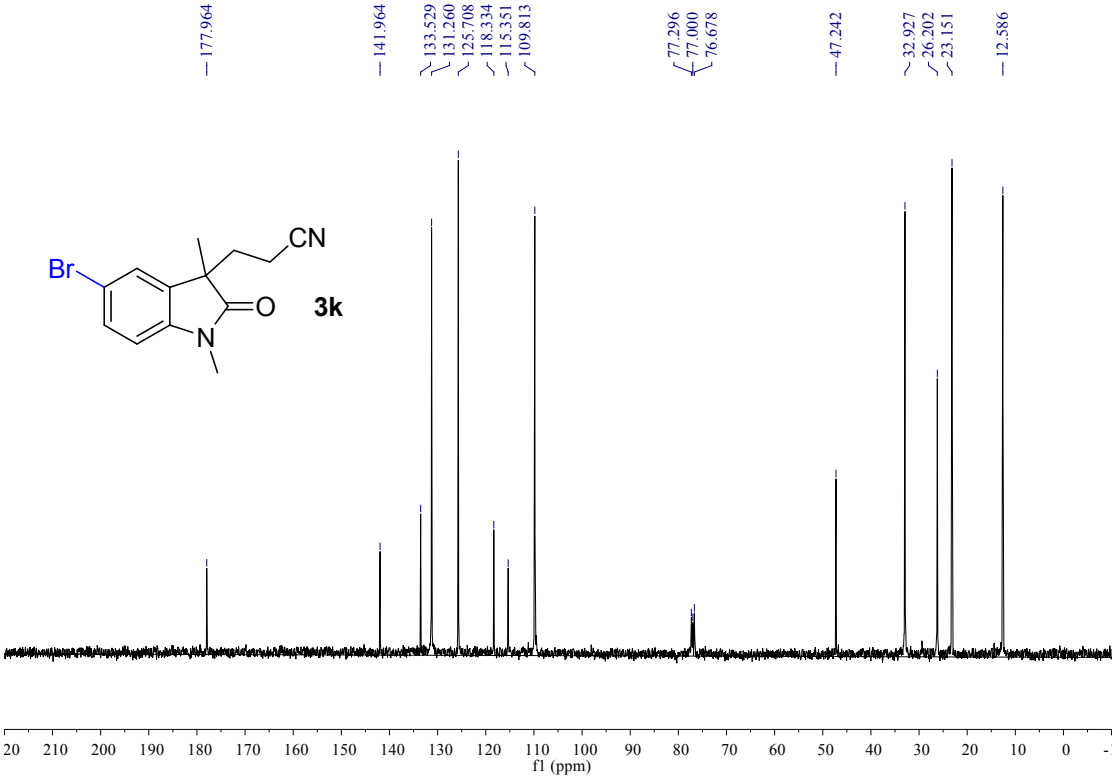
3-(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3j)



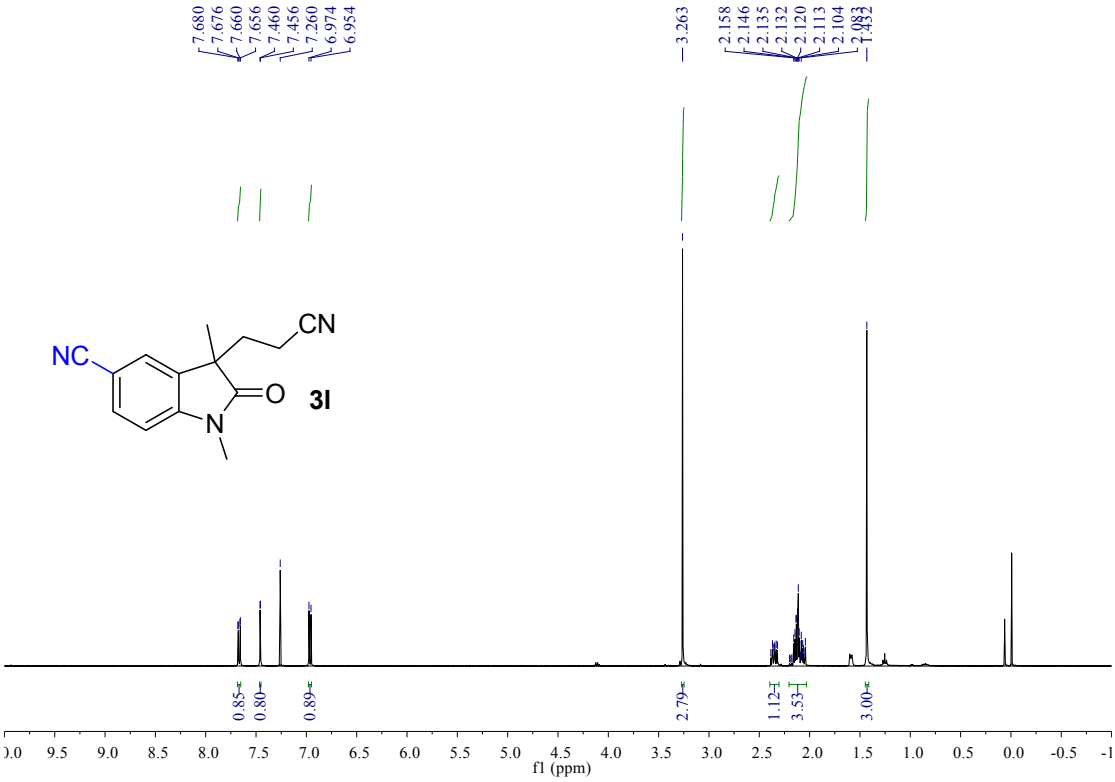


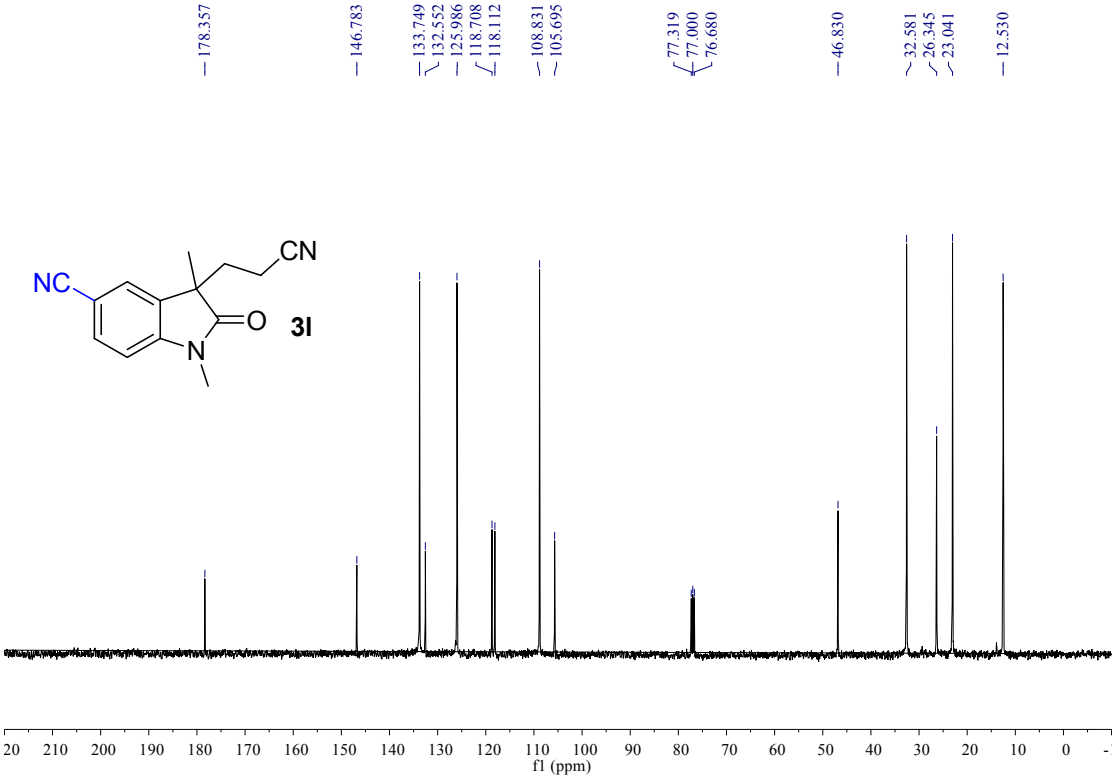
3-(5-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3k)



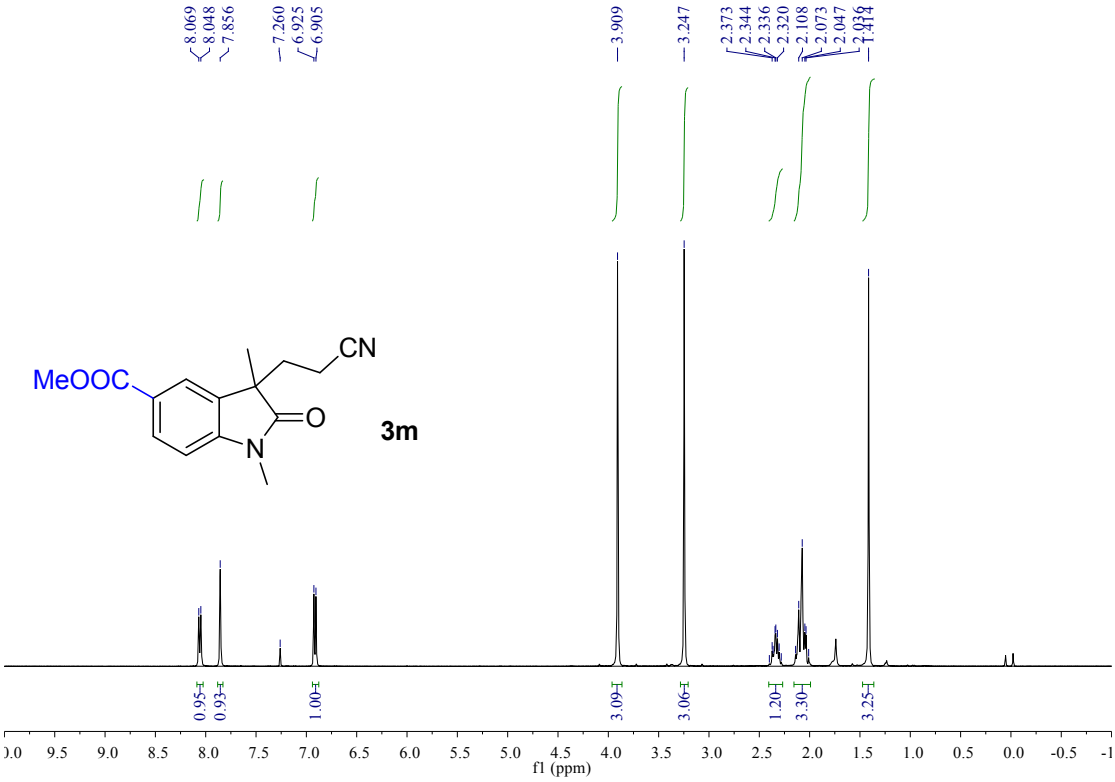


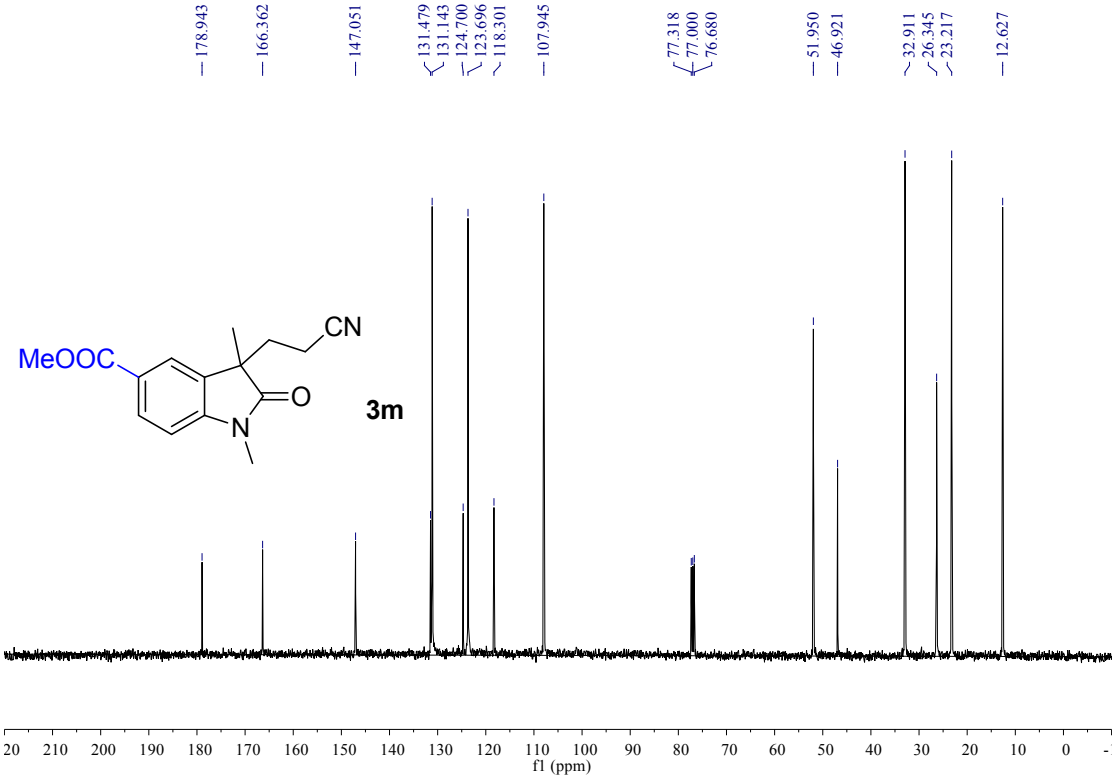
3-(2-Cyanoethyl)-1,3-dimethyl-2-oxoindoline-5-carbonitrile (3l)



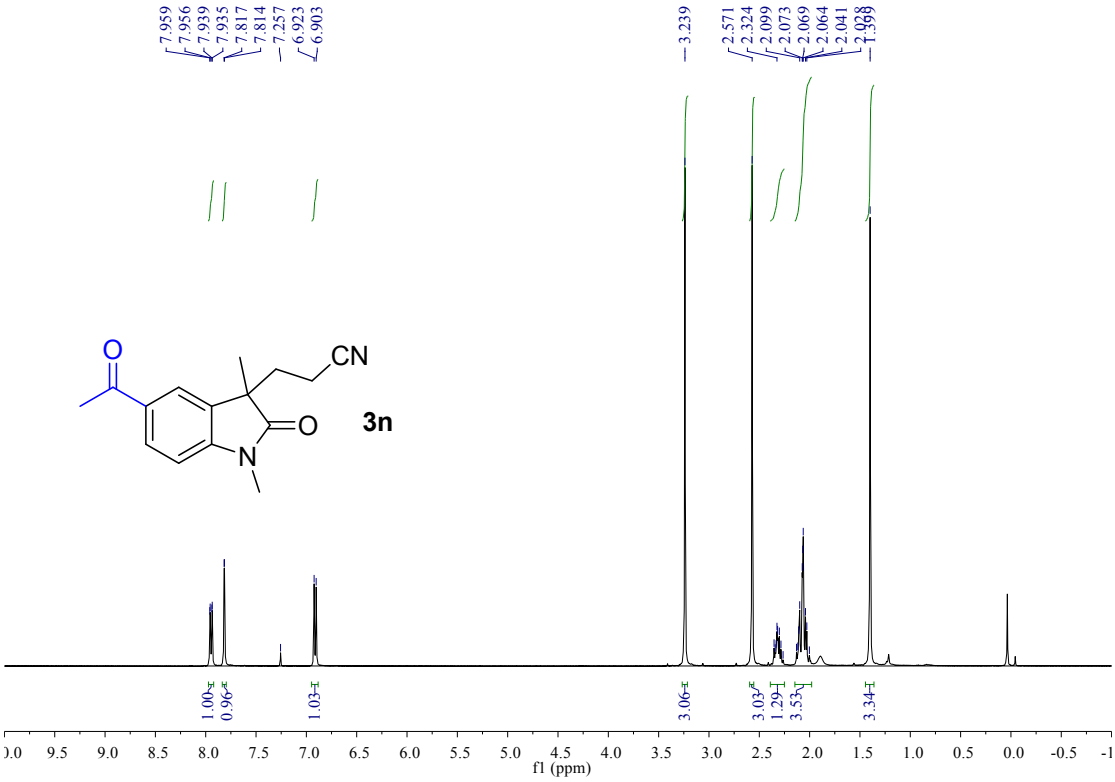


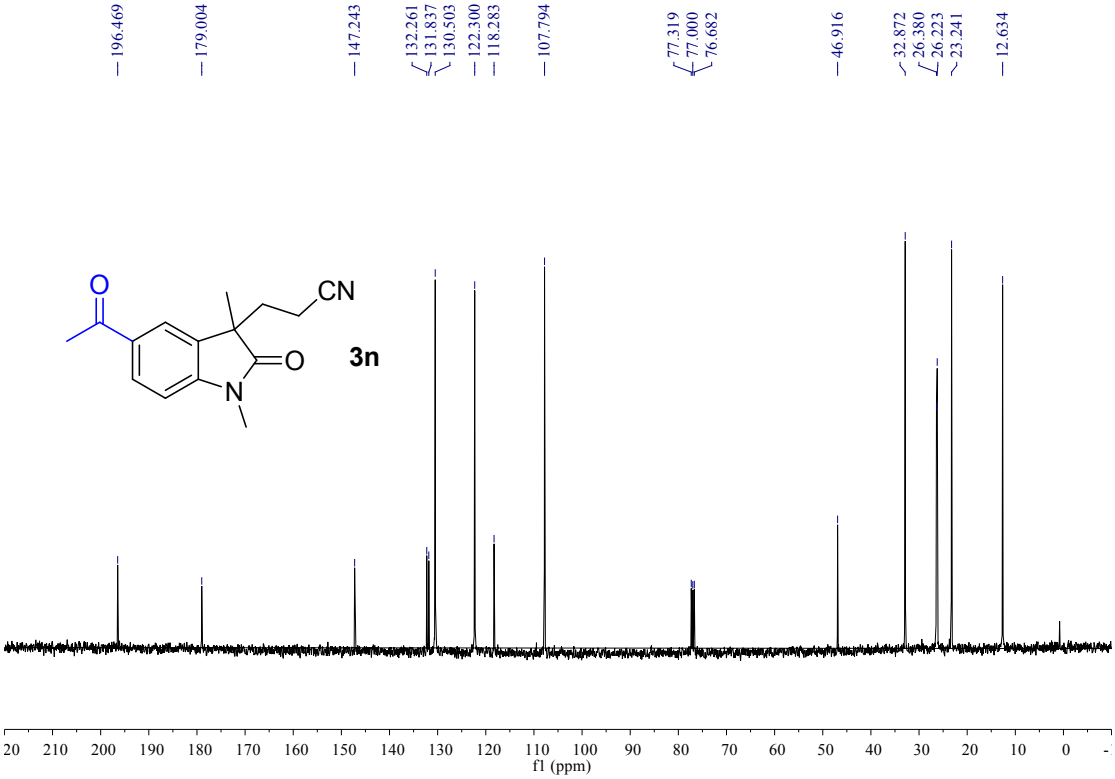
Methyl 3-(2-cyanoethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3m)



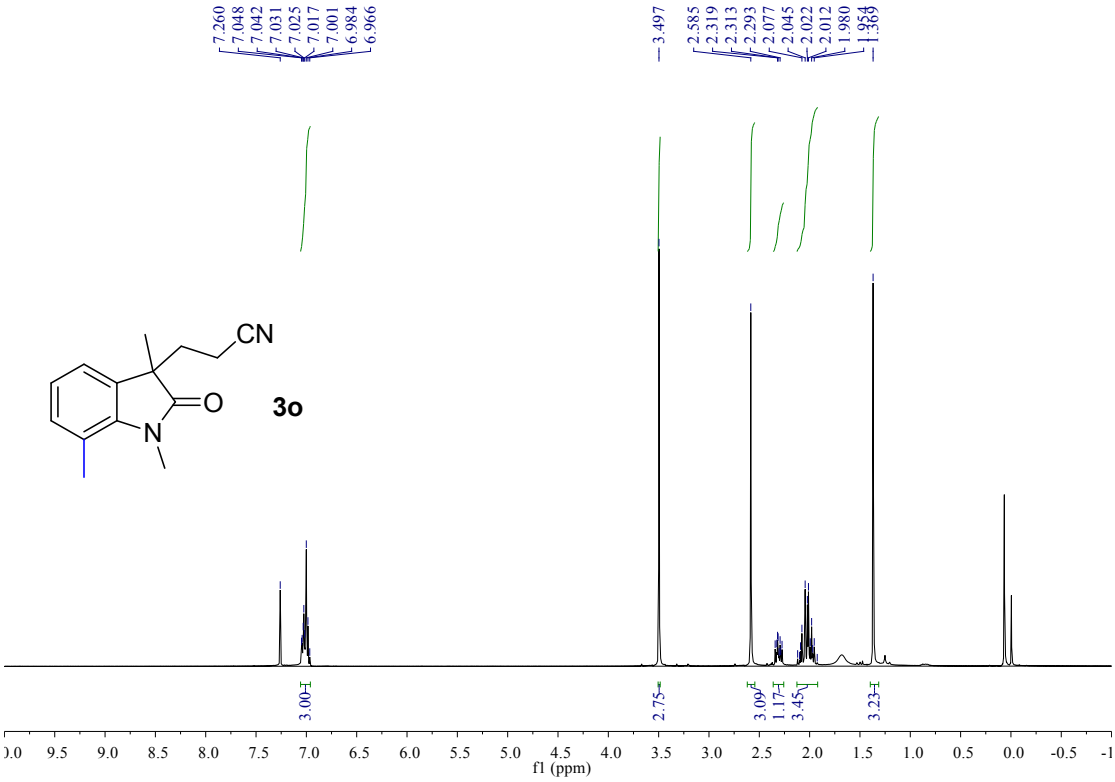


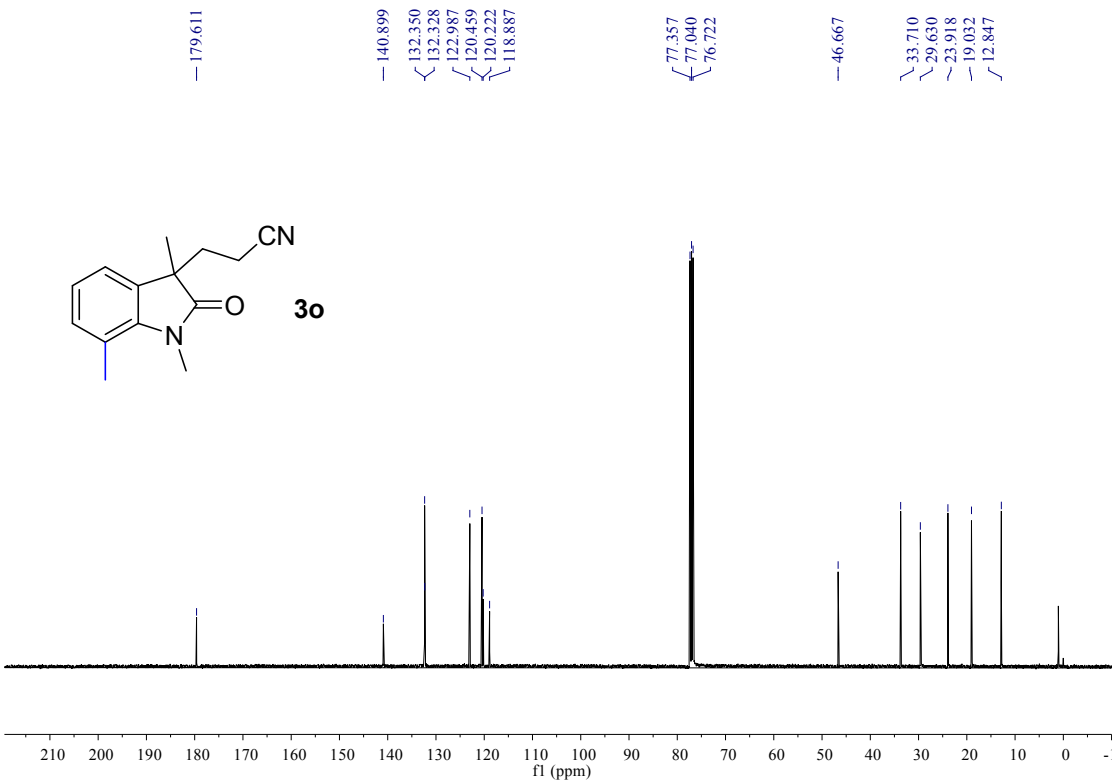
3-(5-Acetyl-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3n)



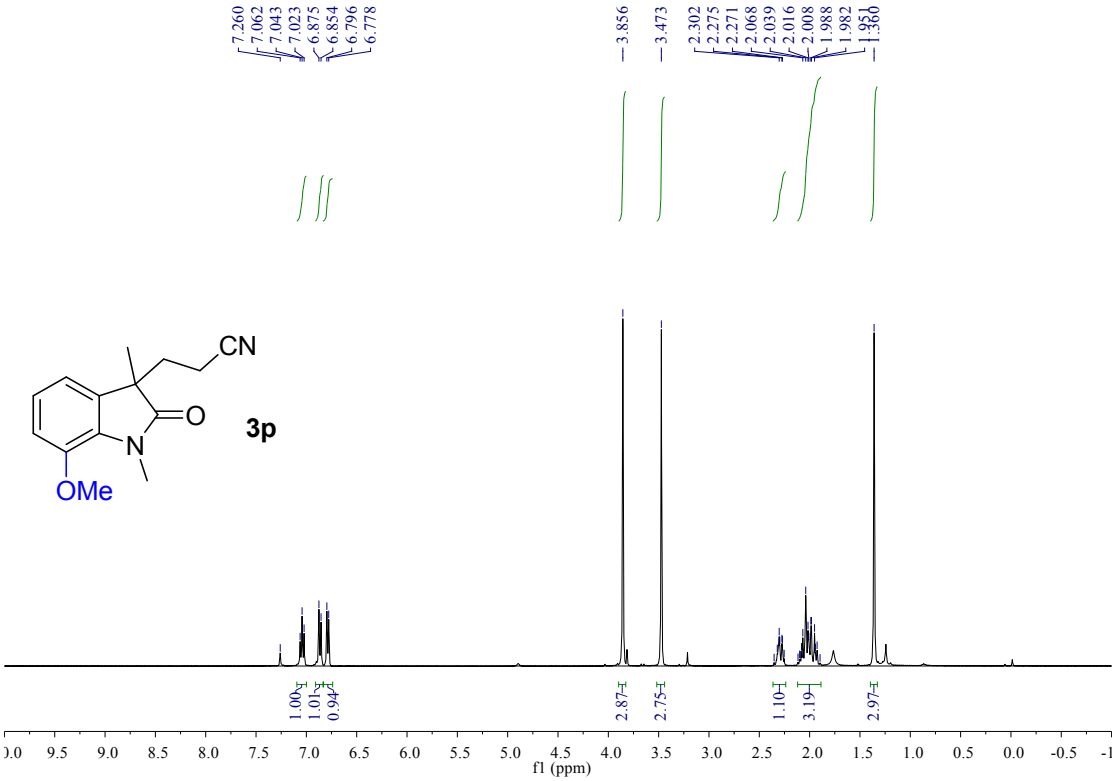


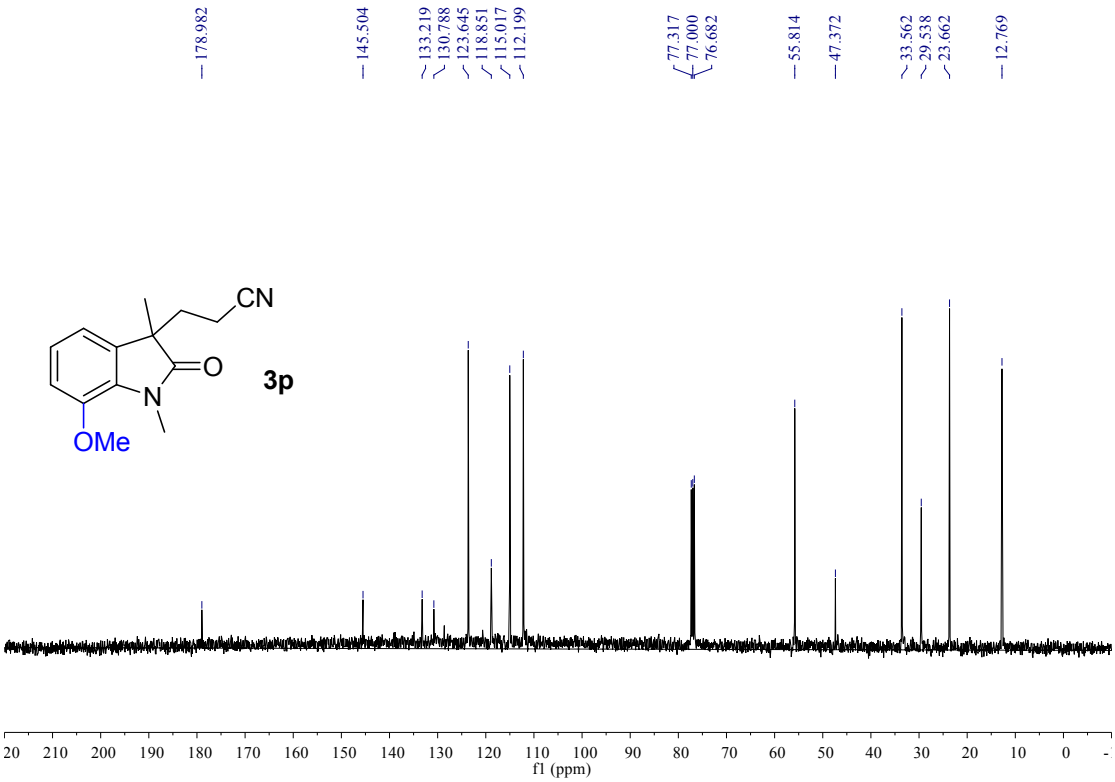
3-(1,3,7-Trimethyl-2-oxoindolin-3-yl)propanenitrile (3o)



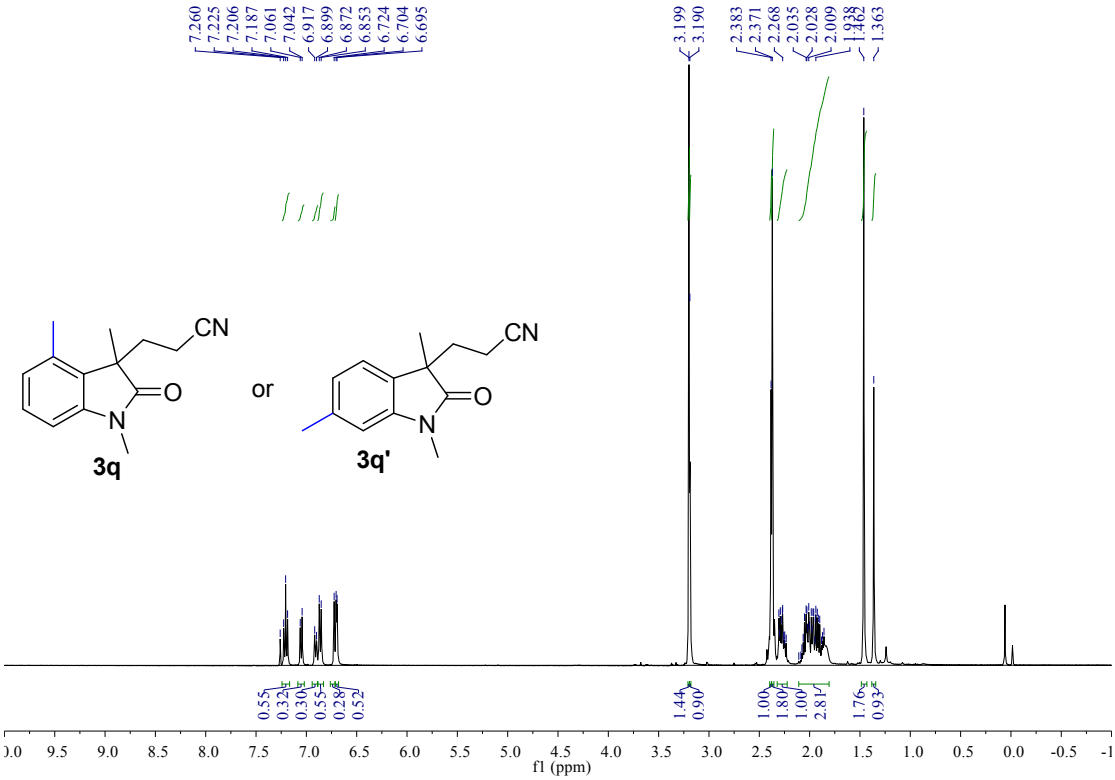


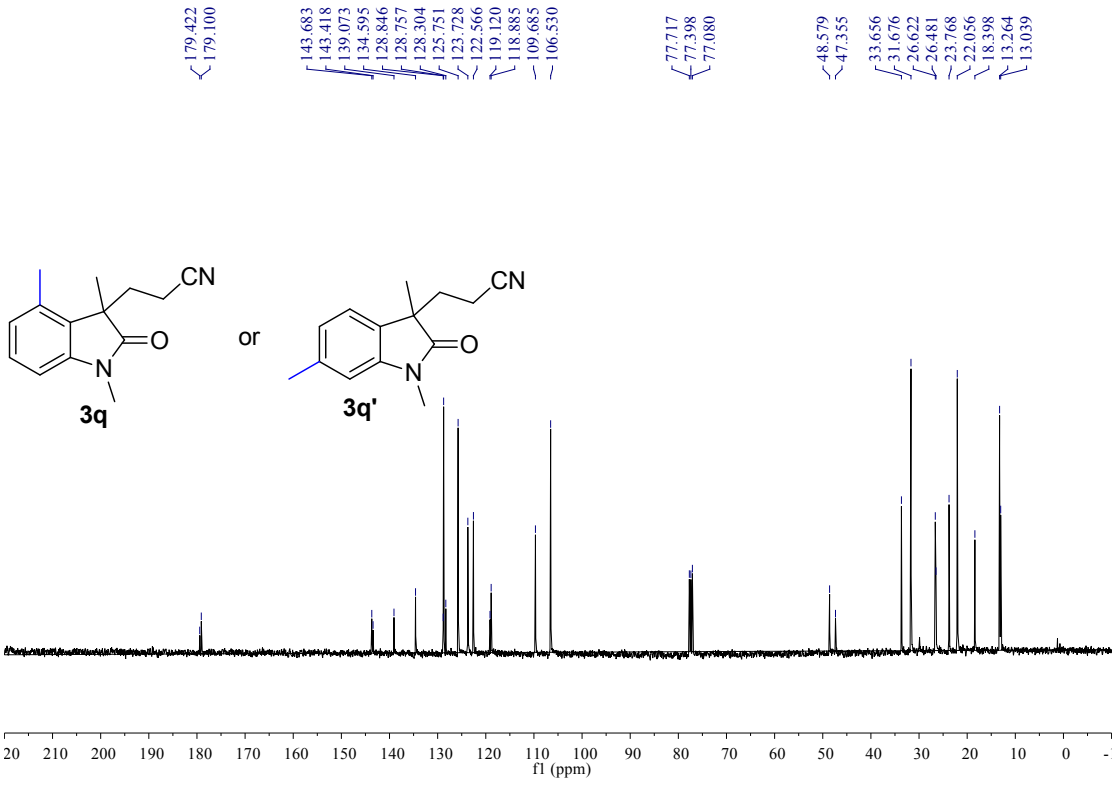
3-(7-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3p)



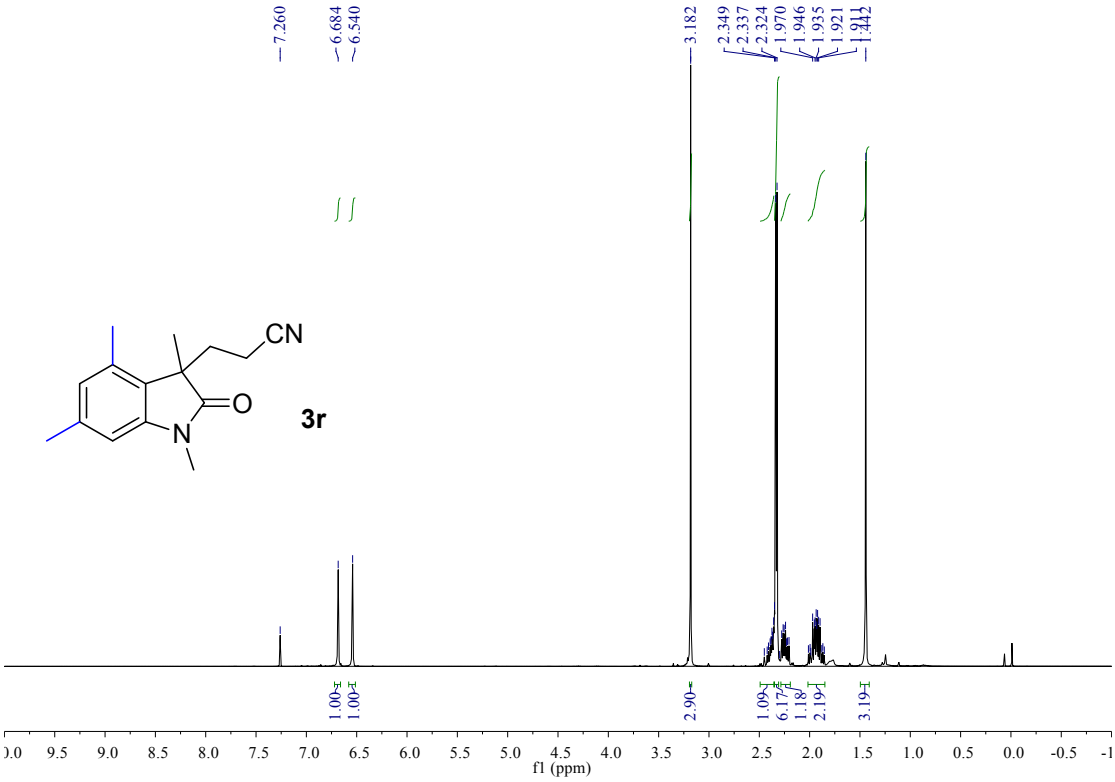


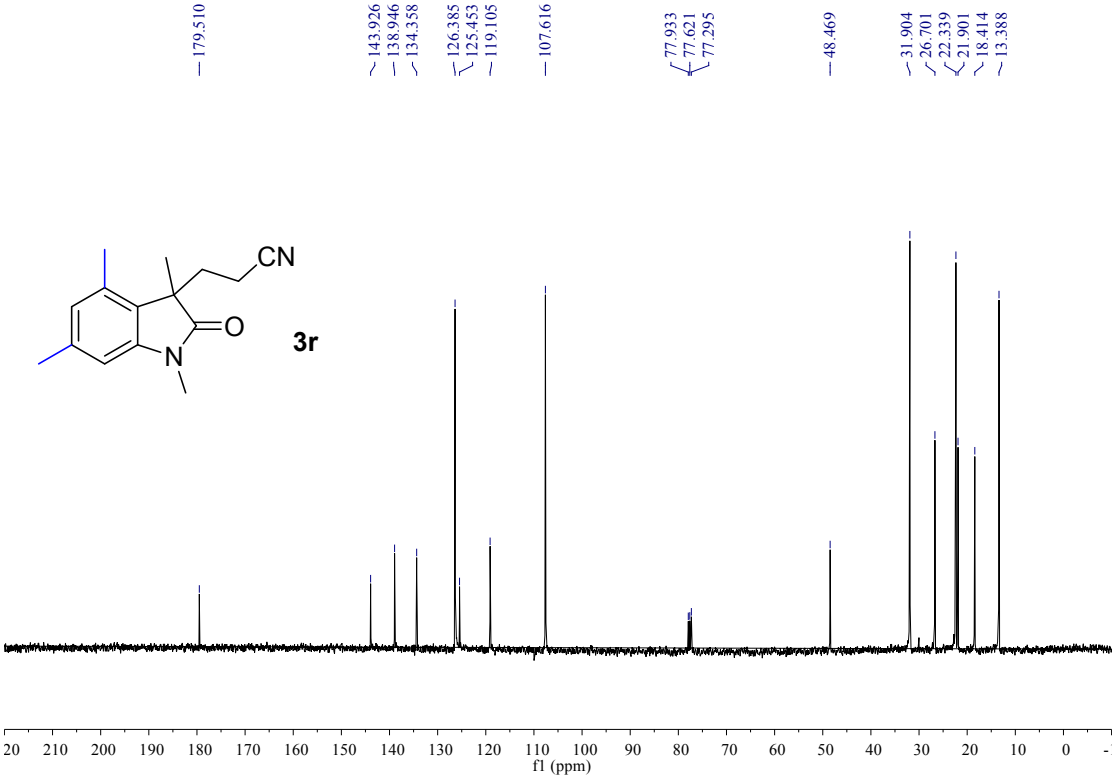
3-(1,3,4-Trimethyl-2-oxoindolin-3-yl)propanenitrile (3q) and 3-(1,3,6-Trimethyl-2-oxoindolin-3-yl)propanenitrile (3q′)



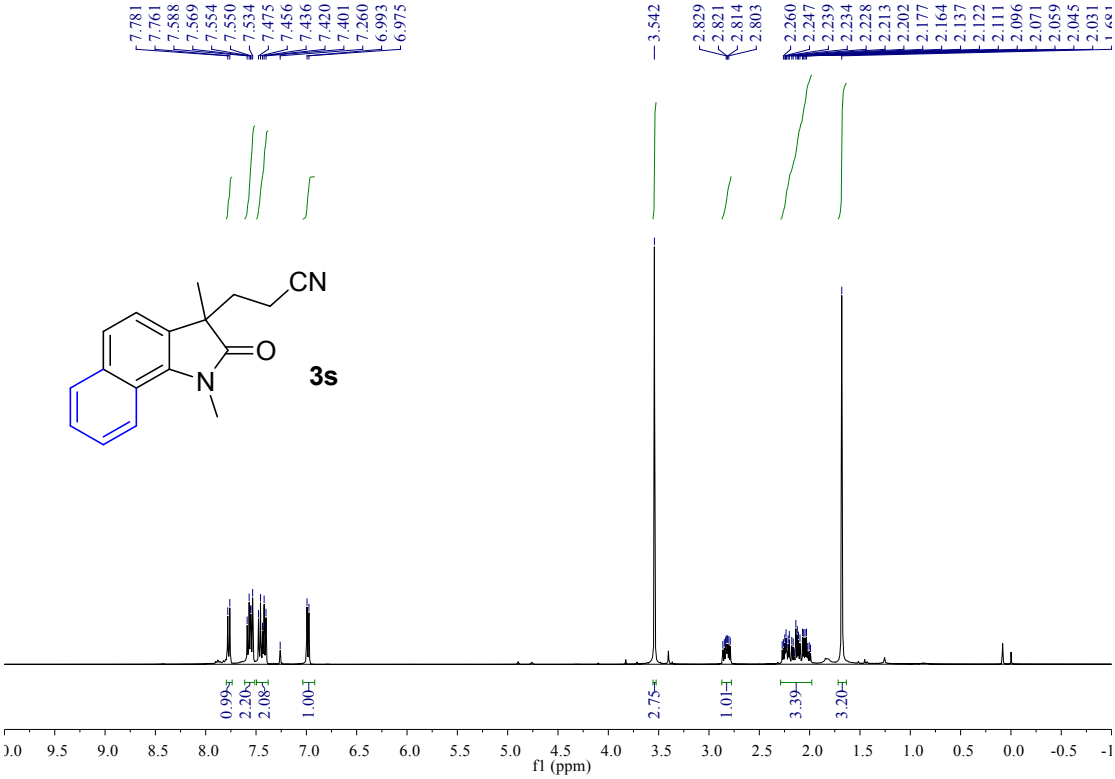


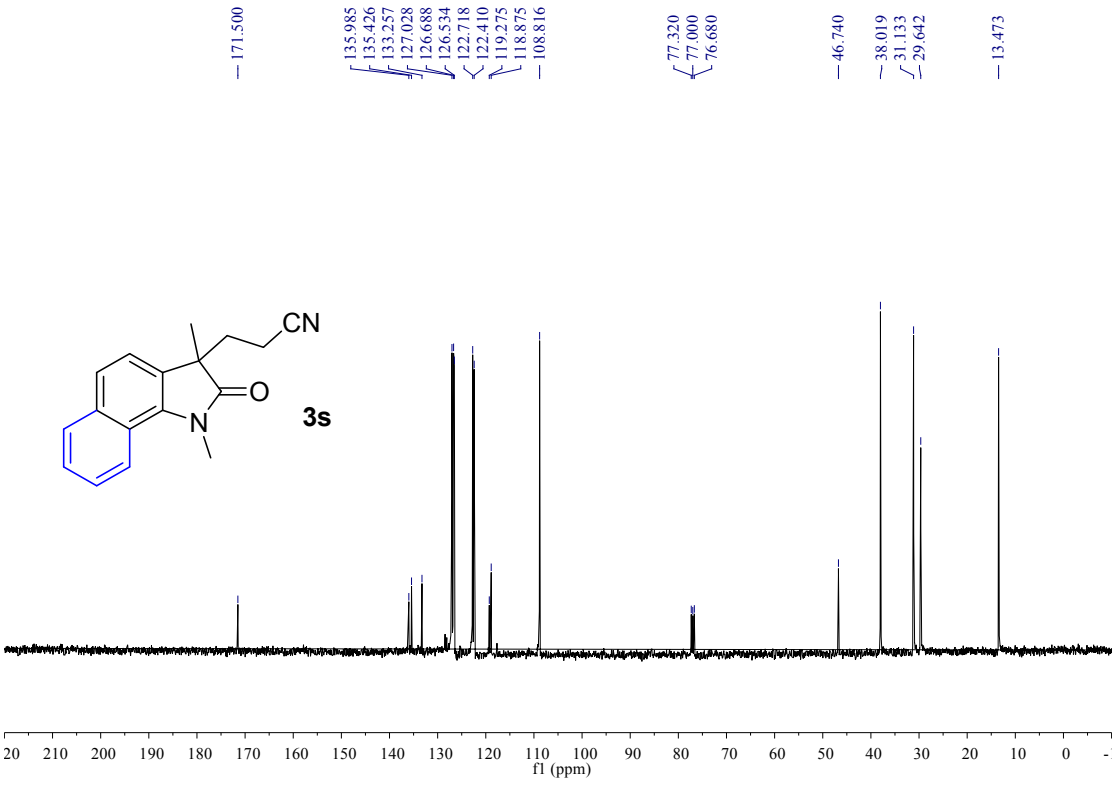
3-(1,3,4,6-Tetramethyl-2-oxoindolin-3-yl)propanenitrile (3r)





3-(1,3-Dimethyl-2-oxo-2,3-dihydro-1H-benzo[g]indol-3-yl)propanenitrile (3s)





3-(1-Methyl-2-oxo-2,4,5,6-tetrahydro-1H-pyrrolo[3,2,1-ij]quinolin-1-yl)propanenitrile (3t)