Photoinduced efficient synthesis of cyanoalkylsulfonylated oxindoles via sulfur dioxide insertion

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1. General Information

All reactions were carried out in anhydrous solvent and commercially available reagents were used as received unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated aluminium-backed silica gel 60 F_{254} plates (EMD Millipore, 200 μm thickness). Flash column chromatography was performed using Tsingtao silica gel (200-300). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance DRX - 400 spectrometers; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference ($CDCl_3$: δ_H = 7.26 ppm and δ_C = 77.16 ppm). Data for ^{1}H NMR, ^{13}C and ^{19}F NMR are reported as follows: chemical shift (δ, ppm), multiplicity, integration, and coupling constant (Hz).

The Light Source and the Material of the Irradiation Vessel

Manufacturer：Beijin Rogertech Ltd.

Model：RLH-18

Wavelength range: 365 nm – 440 nm

Material of the irradiation vessel：quartz tube

Not use any filters

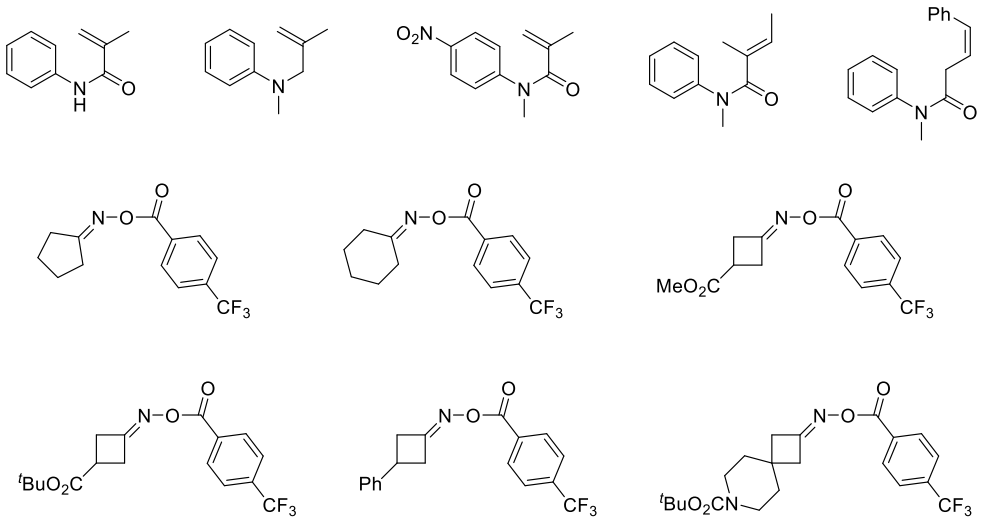
Figure S1

2. Experimental Section

(1) General experimental procedures for compound 3a-3x

In a vial was placed *N*-arylmethacrylamides (0.2 mmol), cycloketone oxime esters (0.3 mmol), $K_2S_2O_5$ (0.4 mmol) and 2 mL MeOH, then the contents were reacted under nitrogen atmosphere and irradiated by 10 W LED for 12 h at room temperature. Upon completion, the reaction mixture was quenched by addition of 10 mL of water. The aqueous layer was extracted three times with EtOAc (10 mL × 3), and the combine organic layers were washed with saturated sodium sulfite solution and dried over anhydrous sodium sulfate, evaporated to dryness, and purified by column chromatography on silica gel (60-120 mesh) using petroleum ether: ethyl acetate = 1:1 as an eluent to afford the desired products.

(2) Unsuccessful substrates



(3) Test of the evolution of SO_2 gas

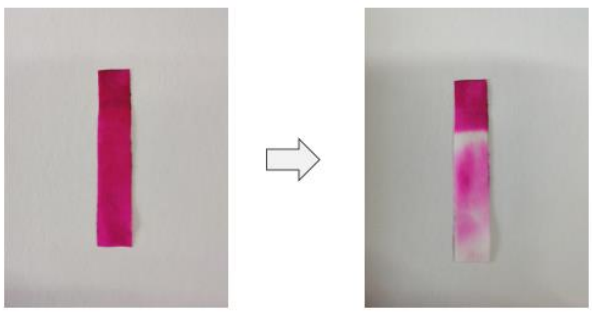
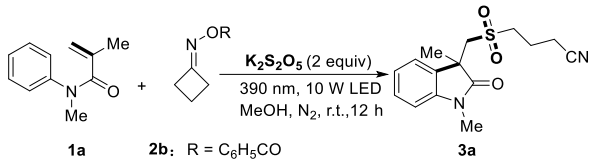


Figure S2

A piece of test strip prepared from magenta solution was put into the reaction tube and sealed. After the completion of the reaction, the magenta was fade rapidly (Figure S2).

(4) Wavelength optimization for 2b-2e

Table S1 the yields of **3a** with irradiation wavelength of visible-light (R = C_6H_5CO)

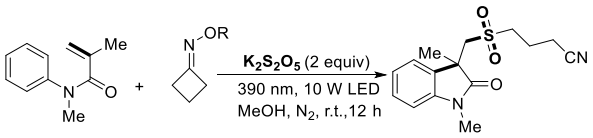


1a **2b**：R = C_6H_5CO **3a**

Entry	Variation from the standard conditions[a]	Yield (%)[b]
1	**None**	**76**
2	365 nm instead of 390 nm	15
3	375 nm instead of 390 nm	21
4	385 nm instead of 390 nm	46
5	395 nm instead of 390 nm	67
6	400 nm instead of 390 nm	57
7	405 nm instead of 390 nm	48
8	410 nm instead of 390 nm	12
9	415 nm instead of 390 nm	8
10	425 nm instead of 390 nm	trace
11	440 nm instead of 390 nm	N.R.
12	In dark	N.R.

[a]Reaction conditions: **1a** (0.2 mmol), **2b** (1.5 equiv), $K_2S_2O_5$ (2 equiv), solvents (1.5 mL), under N_2 at room temperature for 12 h. [b]Isolated yield.

Table S2 the yields of **3a** with irradiation wavelength of visible-light (R = *p*-$NO_2C_6H_5CO$)

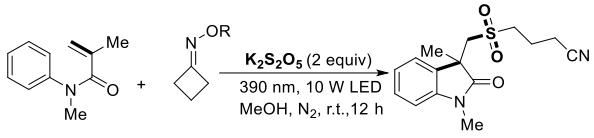


1a **2c**：R = *p*-$NO_2C_6H_4CO$ **3a**

Entry	Variation from the standard conditionsa	Yield (%)b
1	None	36
2	365 nm instead of 390 nm	5
3	375 nm instead of 390 nm	12
4	385 nm instead of 390 nm	35
5	395 nm instead of 390 nm	36
6	400 nm instead of 390 nm	30
7	405 nm instead of 390 nm	18
8	410 nm instead of 390 nm	trace
9	415 nm instead of 390 nm	trace
10	425 nm instead of 390 nm	N.R.
11	440 nm instead of 390 nm	N.R.
12	In dark	N.R.

[a]Reaction conditions: **1a** (0.2 mmol), **2c** (1.5 equiv), $K_2S_2O_5$ (2 equiv), solvents (1.5 mL), under N_2 at room temperature for 12 h. [b]Isolated yield.

Table S3 the yields of **3a** with irradiation wavelength of visible-light (R = *p*-FC_6H_5CO)

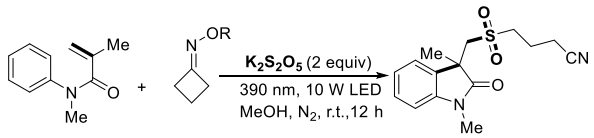


1a **2d**: R = *p*-FC_6H_4CO **3a**

Entry	Variation from the standard conditionsa	Yield (%)b
1	None	29
2	365 nm instead of 390 nm	N.R.
3	375 nm instead of 390 nm	5
4	385 nm instead of 390 nm	14
5	395 nm instead of 390 nm	28
6	400 nm instead of 390 nm	25
7	405 nm instead of 390 nm	10
8	410 nm instead of 390 nm	trace
9	415 nm instead of 390 nm	trace
10	425 nm instead of 390 nm	N.R.
11	440 nm instead of 390 nm	N.R.
12	In dark	N.R.

[a]Reaction conditions: **1a** (0.2 mmol), **2d** (1.5 equiv), $K_2S_2O_5$ (2 equiv), solvents (1.5 mL), under N_2 at room temperature for 12 h. [b]Isolated yield.

Table S4 the yields of **3a** with irradiation wavelength of visible-light (R = *p*-MeC_6H_5CO)

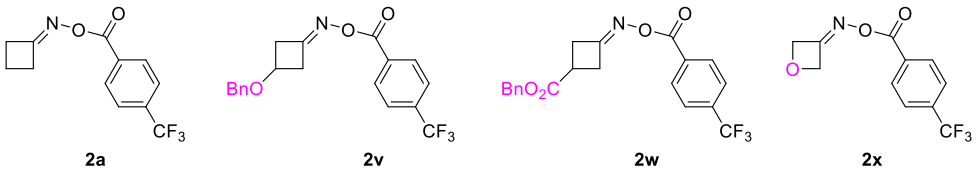


1a **2e**: R = *p*-MeC_6H_4CO **3a**

Entry	Variation from the standard conditionsa	Yield (%)b
1	None	trace
2	365 nm instead of 390 nm	N.R.
3	375 nm instead of 390 nm	N.R.
4	385 nm instead of 390 nm	trace
5	395 nm instead of 390 nm	trace
6	400 nm instead of 390 nm	trace
7	405 nm instead of 390 nm	trace
8	410 nm instead of 390 nm	trace
9	415 nm instead of 390 nm	N.R.
10	425 nm instead of 390 nm	N.R.
11	440 nm instead of 390 nm	N.R.
12	In dark	N.R.

[a]Reaction conditions: **1a** (0.2 mmol), **2e** (1.5 equiv), $K_2S_2O_5$ (2 equiv), solvents (1.5 mL), under N_2 at room temperature for 12 h. [b]Isolated yield.

(5) UV-visible absorption spectra



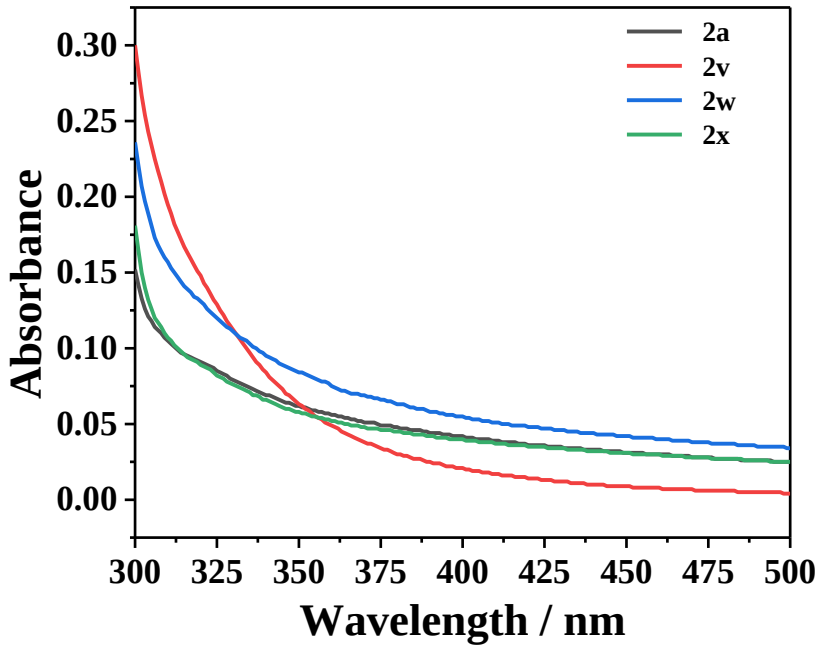
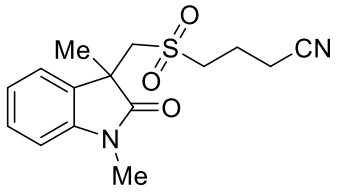


Figure S3 Absorption spectra of **2a**, **2v**, **2w** and **2x** (0.1M dissolved in MeOH)

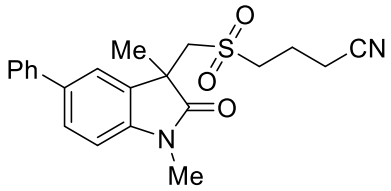
3. Characterization data of products

4-(((1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3a)[1]



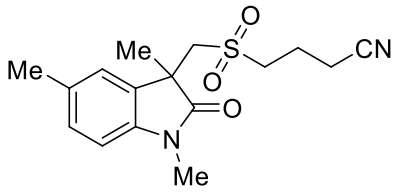
White solid (58.8 mg, 96%), mp: 147.8-148.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.34 (m, 2 H), 7.14 (td, *J* = 7.6 Hz, 0.8 Hz, 1 H), 7.14 (d, *J* = 7.6 Hz, 1 H), 3.72 (d, *J* = 14.8 Hz, 1 H), 3.57 (d, *J* = 14.6 Hz, 1 H), 3.27 (s, 3 H), 2.94 – 2.87 (m, 1 H), 2.84 – 2.76 (m, 1 H), 2.49 (td, *J* = 7.2 Hz, 3.2 Hz, 2 H), 2.11 – 2.04 (m, 2 H), 1.46 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.87, 143.40, 130.11, 129.35, 123.50, 122.92, 118.20, 109.10, 59.65, 53.02, 45.61, 26.79, 25.23, 18.15, 16.32.

4-(((1,3-dimethyl-2-oxo-5-phenylindolin-3-yl)methyl)sulfonyl)butanenitrile (3b)



Yellow solid (62.7 mg, 82%), mp: 125.2-125.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.55 (m, 4 H), 7.43 (t, *J* = 7.6 Hz, 2 H), 7.33 (t, *J* = 7.2 Hz, 1 H), 6.98 (d, *J* = 8.8 Hz, 1 H), 3.74 (d, *J* = 14.8 Hz, 1 H), 3.62 (d, *J* = 14.8 Hz, 1 H), 3.29 (s, 3 H), 2.97 – 2.82 (m, 2 H), 2.45 (t, *J* = 7.2 Hz, 2 H), 2.07 (t, *J* = 7.2 Hz, 2 H), 1.50 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.92, 142.68, 140.67, 136.36, 130.81, 128.99, 128.09, 127.30, 126.99, 122.59, 118.17, 109.25, 59.54, 53.11, 45.79, 26.90, 25.29, 18.11, 16.27; HRMS (ESI) m/z calcd. for $C_{21}H_{23}N_2O_3S$ $[M+H]^+$: 383.1424, found 383.1427.

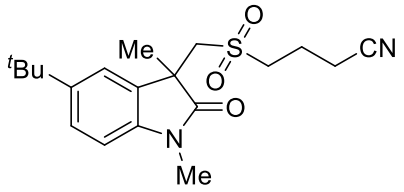
4-(((1,3,5-trimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3c)[1]



White solid (50.6 mg, 79%), mp: 123.9-124.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 – 7.12 (m, 2 H), 7.18 (d, *J* = 1.6 Hz, 1 H), 3.69 (d, *J* = 14.8 Hz, 1 H), 3.54 (d, *J* = 14.8 Hz, 1 H), 3.23 (s, 3 H), 2.94 – 2.87 (m, 1 H), 2.84 – 2.77 (m, 1 H), 2.48 (dt, *J* = 14.8, 2.4 Hz, 2 H), 2.36 (s, 3

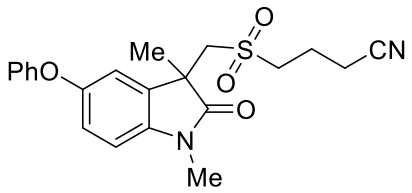
H), 2.07 (t, *J* = 7.6 Hz, 2 H), 1.43 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.75, 140.98, 132.55, 130.24, 129.58, 124.21, 118.18, 108.81, 59.68, 53.04, 45.72, 26.80, 25.31, 21.30, 18.13, 16.33.

4-(((5-(tert-butyl)-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3d)[1]



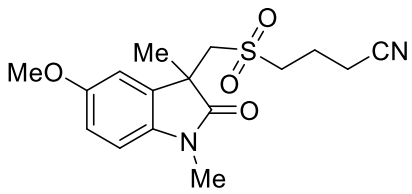
Yellow solid (62.3 mg, 86%), mp: 107.2-107.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.34 (m, 2 H), 6.53 (d, *J* = 8.0 Hz, 1 H), 3.69 (d, *J* = 14.4 Hz, 1 H), 3.61 (d, *J* = 14.8 Hz, 1 H), 3.23 (s, 3 H), 2.91 – 2.84 (m, 1 H) , 2.71 – 2.64 (m, 1 H), 2.48 – 2.40 (m, 2 H), 2.05 – 2.02 (m, 2 H), 1.45 (s, 3 H), 1.31 (s, 9 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.91, 145.97, 140.89, 129.67, 125.68, 120.89, 118.23, 108.35, 59.66, 52.85, 45.73, 34.65, 31.58, 26.69, 25.01, 17.92, 16.18.

4-(((1,3-dimethyl-2-oxo-5-phenoxyindolin-3-yl)methyl)sulfonyl)butanenitrile (3e)[1]



White oil (73.3 mg, 92%);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.28 (m, 2 H), 7.11 (d, *J* = 2.3 Hz, 1 H), 7.05 (t, *J* = 7.4 Hz, 1 H), 7.00 (dd, *J* = 8.4 Hz, 2.4 Hz, 1 H), 6.98 – 6.93 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 1 H), 3.71 (d, *J* = 14.6 Hz, 1 H), 3.53 (d, *J* = 14.6 Hz, 1 H), 3.24 (s, 3 H), 2.99 – 2.84 (m, 2 H), 2.47 (t, *J* = 7.2 Hz, 2 H), 2.10 – 7.02 (m, 2 H), 1.41 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.68, 158.07, 152.35, 139.10, 131.67, 129.78, 122.84, 120.11, 118.31, 117.70, 116.28, 109.61, 58.90, 52.90, 45.71, 26.79, 25.21, 18.03, 16.10.

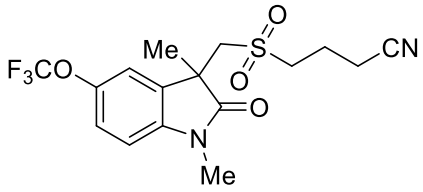
4-(((5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3f)[1]



Yellow oil (54.5 mg, 81%);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 – 6.97 (m, 1 H), 6.89 – 6.81 (m, 2 H), 3.81 (s, 3 H), 3.71 (d, *J* = 14.8 Hz, 1 H), 3.58 (d, *J* = 14.7 Hz, 1 H), 3.24 (s, 3 H),

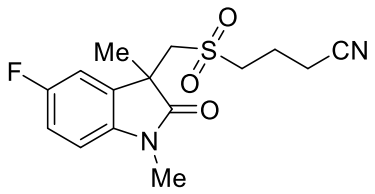
2.98 – 2.82 (m, 2 H), 2.50 (t, *J* = 7.2 Hz, 2 H), 2.12 – 2.05 (m, 2 H), 1.45 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.45, 156.21, 136.72, 131.60, 118.21, 113.09, 111.29, 109.35, 60.51, 55.93, 53.05, 46.07, 26.85, 25.29, 18.14, 16.31.

4-(((1,3-dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)methyl)sulfonyl)butanenitrile (3g)



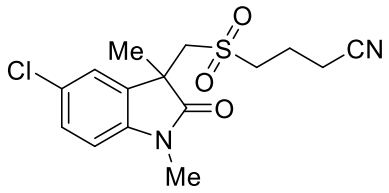
White solid (57.7 mg, 72%, mp: 150.6-151.1 °C);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.22 (m, 2 H), 6.91 (d, *J* = 8.4 Hz, 1 H), 3.75 (d, *J* = 14.6 Hz, 1 H), 3.59 (s, 1 H), 3.27 (s, 3 H), 2.03 – 2.85 (m, 2 H), 2.52 (t, *J* = 7.2 Hz, 2 H), 2.11 (t, *J* = 7.2 Hz, 2 H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.75, 144.84 (t, *J* = 1.9 Hz, 1 C), 142.03, 131.66, 130.64, 122.45, 118.14, 117.93, 109.52, 59.28, 53.17, 45.91, 26.99, 25.17, 18.07, 16.30; ^{19}F NMR (376 MHz, $CDCl_3$): δ -58.29 (s, 3 F); HRMS (ESI) m/z calcd. for $C_{16}H_{18}F_3N_2O_4S$ $[M+H]^+$: 391.0934, found 391.0941.

4-(((5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3h)[1]



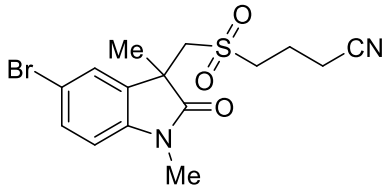
White solid (46.7 mg, 72%, mp: 160.1-160.7 °C);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (dd, *J* = 7.8 Hz, 2.6 Hz, 1 H), 7.05 (td, *J* = 9.0 Hz, 2.6 Hz, 1 H), 6.84 (dd, *J* = 8.6 Hz, 4.2 Hz, 1 H), 3.73 (d, *J* = 14.6 Hz, 1 H), 3.57 (s, 1 H), 3.25 (s, 3 H), 3.05 –2.91 (m, 2 H), 2.53 (t, *J* = 7.2 Hz, 2 H), 2.15 – 2.09 (m, 2 H), 1.46 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.66, 159.34 (d, *J* = 242.6 Hz, 1 C), 139.18, 131.88 (d, *J* = 8.2 Hz, 1 C), 118.20, 115.53 (d, *J* = 23.6 Hz, 1 C), 111.93 (d, *J* = 25.0 Hz, 1 C), 109.60 (d, *J* = 8.2 Hz, 1 C), 59.18, 53.12, 46.07 (d, *J* = 1.5 Hz, 1 C), 26.95, 25.27, 18.11, 16.32; ^{19}F NMR (376 MHz, $CDCl_3$): δ -119.41 (s, 1 F).

4-(((5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3i)[1]



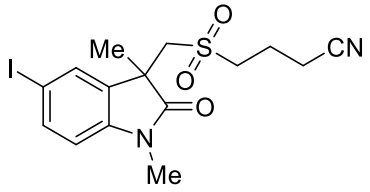
Grey solid (54.4 mg, 72%, mp: 156.0-156.5 °C);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 2 H), 6.83 (d, *J* = 8.4 Hz, 1 H), 3.71 (d, *J* = 14.8 Hz, 1 H), 3.56 (d, *J* = 14.8 Hz, 1 H), 3.24 (s, 3 H), 3.03 – 2.88 (m, 2 H), 2.51 (t, *J* = 7.2 Hz, 2 H), 2.13 – 2.06 (m, 2 H), 1.44 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.45, 141.87, 131.98, 129.14, 128.24, 124.13, 118.21, 109.97, 59.15, 53.14, 45.79, 26.90, 25.25, 18.11, 16.29.

4-(((5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3j)[1]



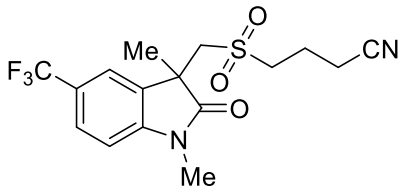
White oil (58.4 mg, 76%);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.40 (m, 2 H), 6.79 (d, *J* = 8.2 Hz, 1 H), 3.72 (d, *J* = 14.8 Hz, 1 H), 3.57 (d, *J* = 14.8 Hz, 1 H), 3.23 (s, 3 H), 3.02 – 2.89 (m, 2 H), 2.51 (t, *J* = 7.2 Hz, 2 H), 2.15 – 2.06 (m, 2 H), 1.44 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.40, 142.35, 132.36, 132.04, 126.85, 118.22, 115.47, 110.49, 59.12, 53.15, 45.74, 26.89, 25.23, 18.12, 16.29.

4-(((5-iodo-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3k)[1]



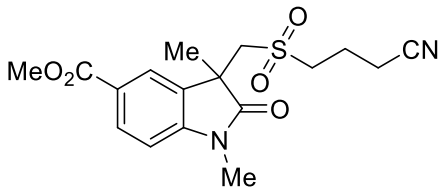
Yellow solid (62.8 mg, 80%, mp: 108.2-108.7 °C);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.54 (m, 2 H), 6.69 (d, *J* = 8.2 Hz, 1 H), 3.71 (d, *J* = 14.8 Hz, 1 H), 3.56 (d, *J* = 14.8 Hz, 1 H), 3.22 (s, 3 H), 2.98 – 2.86 (m, 2 H), 2.51 (t, *J* = 7.2 Hz, 2 H), 2.15 – 2.05 (m, 2 H), 1.43 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.22, 143.06, 137.97, 132.69, 132.33, 118.22, 111.06, 85.20, 59.12, 53.15, 45.53, 26.83, 25.21, 18.13, 16.30.

4-(((1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)methyl)sulfonyl)butanenitrile (3l)[1]



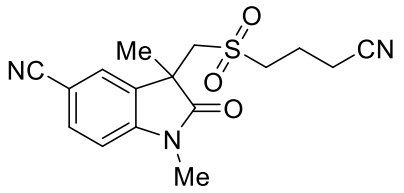
Yellow solid (62.1 mg, 83%, mp: 59.8-60.3 °C);[1]H NMR (400 MHz, $CDCl_3$): δ 7.63 – 7.60 (m, 2 H), 6.98 (d, *J* = 8.4 Hz, 1 H), 3.74 (d, *J* = 14.6 Hz, 1 H), 3.63 (d, *J* = 14.8 Hz, 1 H), 3.28 (s, 3 H), 3.03 – 2.94 (m, 1 H), 2.93 – 2.85 (m, 1 H), 2.48 (t, *J* = 7.2 Hz, 2 H), 2.11 – 2.04 (m, 2 H), 1.46 (s, 3 H); [13]C NMR (101 MHz, $CDCl_3$): δ 177.94, 146.34, 130.88, 126.94 (q, *J* = 3.9 Hz, 1 C), 124.97 (q, *J* = 32.6 Hz, 1 C), 122.98, 120.82 (q, *J* = 3.7 Hz, 1 C), 118.19, 108.80, 59.06, 53.15, 45.49, 26.98, 25.18, 18.03, 16.22; [19]F NMR (376 MHz, $CDCl_3$): δ - 61.31 (s, 3 F).

methyl 3-(((3-cyanopropyl)sulfonyl)methyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3m)



White solid (62.1 mg, 83%, mp: 59.8-60.3 °C);[1]H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, *J* = 8.4 Hz, 1.4 Hz, 1 H), 8.01 (s, 1 H), 6.95 (d, *J* = 8.4 Hz, 1 H), 3.90 (s, 3 H), 3.76 (d, *J* = 14.8 Hz, 1 H), 3.64 (d, *J* = 14.8 Hz, 1 H), 3.29 (s, 3 H), 2.96 – 2.82 (m, 2 H), 2.49 (t, *J* = 7.2 Hz, 2 H), 2.11 – 2.06 (m, 2 H), 1.46 (s, 3 H); [13]C NMR (101 MHz, $CDCl_3$): δ 178.25, 166.70, 147.51, 131.89, 130.25, 124.83, 124.70, 118.14, 108.65, 59.35, 53.14, 52.33, 45.39, 27.02, 25.31, 18.10, 16.29; HRMS (ESI) m/z calcd. for $C_{17}H_{21}N_2O_5S$ $[M+H]^+$: 365.1166, found 365.1171.

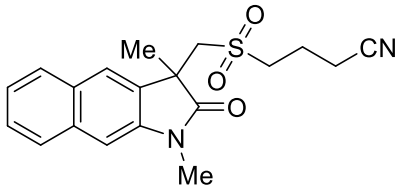
3-(((3-cyanopropyl)sulfonyl)methyl)-1,3-dimethyl-2-oxoindoline-5-carbonitrile (3n)



White solid (47.7 mg, 72%, mp: 116.5-117.2 °C);[1]H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 1 H), 7.64 (s, 1 H), 6.98 (d, *J* = 8.2 Hz, 1 H), 3.76 (d, *J* = 14.6 Hz, 1 H), 3.63 (d, *J* = 14.6 Hz, 1 H), 3.29 (s, 3 H), 3.11– 2.95 (m, 2 H), 2.53 (t, *J* = 7.0 Hz, 2 H), 2.15– 2.08 (m, 2 H), 1.46 (s, 3 H); [13]C NMR (101 MHz, $CDCl_3$): δ 177.83, 147.18, 134.41, 131.43, 127.22,

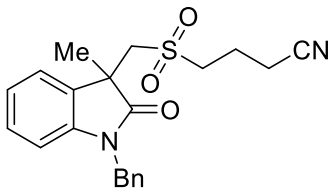
119.10, 118.16, 109.45, 106.06, 58.93, 53.26, 45.33, 27.06, 25.24, 18.10, 16.31; HRMS (ESI) m/z calcd. for $C_{16}H_{18}N_3O_3S$ $[M+H]^+$: 332.1063, found 332.1068.

4-(((1,3-dimethyl-2-oxo-2,3-dihydro-1H-benzo[f]indol-3-yl)methyl)sulfonyl)butanenitrile (3o)



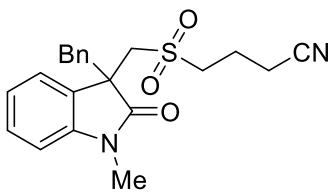
Yellow oil (59.2 mg, 83%);^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 12.2 Hz, 8.6 Hz, 2 H), 7.87 (d, *J* = 8.2 Hz, 1 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.35 (d, *J* = 8.8 Hz, 1 H), 4.20 (d, *J* = 14.4 Hz, 1 H), 3.98 (d, *J* = 14.8 Hz, 1 H), 3.44 (s, 3 H), 2.56 – 2.41 (m, 2 H), 2.21 – 2.12 (m, 2 H), 1.94 – 1.81 (m 2 H), 1.73 (s, 3 H).; ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.93, 141.64, 130.73, 130.25, 129.31, 127.90, 126.95, 123.89, 121.08, 120.88, 118.03, 110.27, 59.44, 52.16, 46.38, 26.95, 24.36, 18.03, 15.81; HRMS (ESI) m/z calcd. for $C_{19}H_{21}N_2O_3S$ $[M+H]^+$: 357.1267, found 357.1270.

4-(((1-benzyl-3-methyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3p)[1]



Yellow oil (60.3 mg, 79%);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 2.29 (m, 6 H), 7.21 – 7.19 (m, 1 H), 7.08 (t, *J* = 7.6 Hz, 1 H), 6.78 (d, *J* = 7.8 Hz, 1 H), 5.03 (d, *J* = 15.8 Hz, 1 H), 4.87 (d, *J* = 15.6 Hz, 1 H), 3.77 (d, *J* = 14.8 Hz, 1 H), 3.64 (d, *J* = 14.8 Hz, 1 H), 2.93 – 2.86 (m, 1 H), 2.83 – 2.77 (m, 1 H), 2.41 (td, *J* = 7.2 Hz, 2.6 Hz, 2 H), 2.03 (s, 2 H), 1.49 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.95, 142.50, 135.66, 130.22, 129.18, 128.77, 127.65, 127.43, 123.51, 122.98, 118.22, 110.12, 59.32, 53.06, 45.72, 44.36, 25.96, 18.19, 16.28.

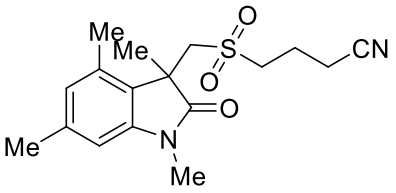
4-(((3-benzyl-1-methyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3q)[1]



Yellow oil (57.3 mg, 75%);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31– 7.25 (m, 2 H), 7.17 – 7.06

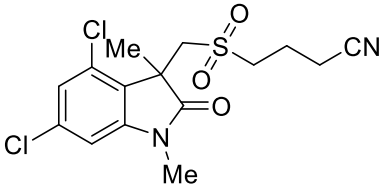
(m, 4 H), 6.81 (d, *J* = 6.8 Hz, 2 H), 6.68 (d, *J* = 8.0 Hz, 1 H), 3.92 (d, *J* = 14.8 Hz, 1 H), 3.72 (d, *J* = 14.8 Hz, 1 H), 3.07 (d, *J* = 3.8 Hz, 2 H), 3.01 (s, 3 H), 2.96 – 2.90 (m, 1 H), 2.89 – 2.80 (m, 1 H), 2.48 (td, *J* = 7.2 Hz, 2.8 Hz, 2 H), 2.10 – 2.03 (m, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.59, 143.80, 133.29, 130.11, 129.28, 127.74, 127.27, 127.23, 124.52, 122.25, 118.29, 108.67, 58.36, 53.11, 50.80, 44.50, 26.30, 18.00, 16.14.

4-(((1,3,4,6-tetramethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3r)



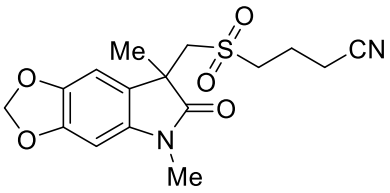
Yellow oil (50.8 mg, 76%);^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (s, 1 H), 6.59 (s, 1 H), 3.82 – 3.70 (m, 2 H), 3.21 (s, 3 H), 2.93 (dt, *J* = 14.4 Hz, 7.2 Hz, 1 H), 2.87 – 2.78 (m, 1 H), 2.46 (t, *J* = 7.2 Hz, 2 H), 2.38 (s, 3 H), 2.33 (s, 3 H), 2.07 – 2.02 (m, 2 H), 1.44 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.13, 143.46, 139.00, 134.29, 125.75, 123.96, 118.28, 107.53, 57.89, 52.26, 45.25, 26.61, 23.11, 21.60, 18.32, 17.76, 16.01; HRMS (ESI) m/z calcd. for $C_{17}H_{23}N_2O_3S$ $[M+H]^+$: 335.1424, found 335.1431.

4-(((4,6-dichloro-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3s)



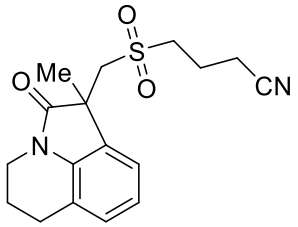
Yellow oil (68.1 mg, 91%);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, *J* = 1.8 Hz, 1 H), 6.83 (d, *J* = 1.8 Hz, 1 H), 4.03 (d, *J* = 14.4 Hz, 1 H), 3.72 (d, *J* = 14.4 Hz, 1 H), 3.22 (s, 3 H), 3.05 – 2.02 (m, 1 H), 2.89 – 2.84 (m, 1 H), 2.51 (t, *J* = 7.2 Hz, 2 H), 3.14 – 2.06 (m, 2 H), 1.51 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.41, 145.99, 135.91, 131.34, 124.87, 123.24, 118.16, 108.59, 57.13, 52.62, 46.03, 27.13, 22.21, 18.05, 16.29; HRMS (ESI) m/z calcd. for $C_{15}H_{17}Cl_2N_2O_3S$ $[M+H]^+$: 375.0331, found 375.0335.

4-(((5,7-dimethyl-6-oxo-6,7-dihydro-5H-[1,3]dioxolo[4,5-f]indol-7-yl)methyl)sulfonyl)butanenitrile (3t)



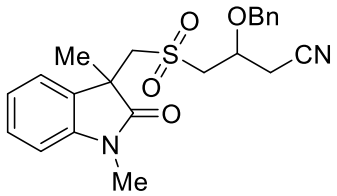
Yellow oil (49.7 mg, 71%);^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (s, 1 H), 6.49 (s, 1 H), 5.93 (s, 2 H), 3.64 (d, *J* = 14.6 Hz, 1 H), 3.52 (d, *J* = 14.6 Hz, 1 H), 3.17 (s, 3 H), 3.14 – 2.06 (m, 2 H), 2.47 (d, *J* = 7.0 Hz, 2 H), 2.06 (d, *J* = 7.2 Hz, 2 H), 1.37 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.97, 148.11, 143.37, 137.63, 121.54, 118.31, 105.03, 101.37, 92.72, 59.17, 52.81, 45.68, 26.79, 25.23, 17.88, 16.12; HRMS (ESI) m/z calcd. for $C_{16}H_{19}N_2O_5S$ $[M+H]^+$: 351.1009, found 351.1013.

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



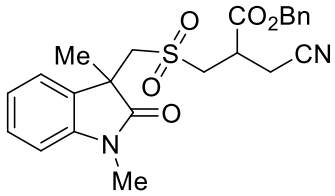
White oil (55.3 mg, 83%);^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 7.3 Hz, 1 H), 7.09 (d, *J* = 7.6 Hz, 1 H), 7.00 (t, *J* = 7.6 Hz, 1 H), 3.77 – 3.70 (m, 2 H), 3.67 (d, *J* = 14.8 Hz, 1 H), 3.57 (d, *J* = 14.8 Hz, 1 H), 2.91 – 2.84 (m, 1 H), 2.81 – 2.73 (m, 3 H), 2.47 (td, *J* = 7.2 Hz, 1.8 Hz, 2 H), 2.08 – 1.99 (m, 4 H), 1.45 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.56, 139.22, 128.56, 128.05, 122.25, 121.28, 121.16, 118.26, 59.51, 52.88, 46.66, 39.23, 24.77, 24.58, 21.03, 18.11, 16.23; HRMS (ESI) m/z calcd. for $C_{17}H_{21}N_2O_3S$ $[M+H]^+$: 333.1267, found 333.1274.

3-(benzyloxy)-4-(((1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3v)[1]



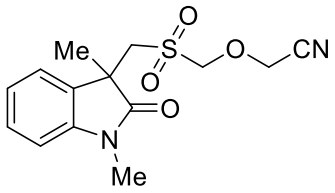
Yellow oil (75.8 mg, 81%, *dr* = 1.6:1);[1]H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.23 (m, 7 H), 7.09 – 7.01 (m, 1 H), 6.82 (d, *J* = 7.8 Hz, 1 H), 4.64 – 4.45 (m, 2 H), 4.15 – 4.09 (m, 1 H), 3.72 – 3.60 (m, 1.5 H), 3.45 (d, *J* = 14.8 Hz, 0.5 H), 3.19 – 3.14 (m, 3.3 H), 3.00 – 2.90 (m, 1 H), 2.67 – 2.55 (m, 2 H), 2.36– 2.32 (m, 0.7 H), 1.24 (s, 1.15 H), 1.15 (s, 1.85 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.04 (2 C), 143.59, 143.31, 136.34, 136.16, 130.30, 129.50, 129.27, 128.89, 128.77, 128.71, 128.59 (2 C), 128.48, 128.37, 128.34, 124.17, 123.60, 122.88, 122.73, 115.88, 108.93 (2 C), 72.99, 72.69, 70.45, 69.77, 61.03, 60.73, 58.71, 57.96, 45.52, 45.45, 26.72, 26.70, 25.15, 24.88, 23.10, 22.64.

benzyl 3-cyano-2-((((1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)methyl)propanoate (3w)[1]



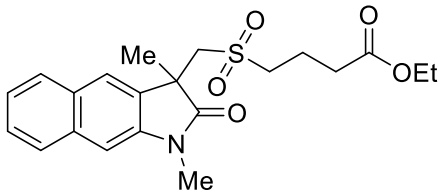
Yellow oil (71.0 mg, 86%, *dr* = 1:1); [1]H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.31 (m, 7 H), 7.08 (q, *J* = 7.2 Hz, 1 H), 6.90 (t, *J* = 8.2 Hz, 1 H), 5.23 – 5.12 (m, 2 H), 3.77 (d, *J* = 14.6 Hz, 1 H), 3.67 – 3.61 (m, 1 H), 3.45 – 3.40 (m, 0.5 H), 3.28 – 3.21 (m, 5 H), 2.87 – 2.78 (m, 2.5 H), 1.43 (s, 1.5 H), 1.43 (s, 1.5 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.78, 177.73, 169.34 (2 C), 143.41, 143.30, 134.61, 134.58, 129.41, 129.26, 128.91(2 C), 128.82 (2 C), 128.81, 128.69, 125.54, 125.50, 123.55, 122.88, 116.61, 116.42, 109.15, 109.06, 68.45, 68.40, 60.62, 60.42, 54.00 (2 C), 45.58, 45.53, 35.74, 35.71, 26.74 (2 C), 25.10, 25.01, 19.36, 19.34.

2-((((1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)methoxy)acetonitrile (3x)[1]



Yellow oil (52.4 mg, 85%);[1]H NMR (400 MHz, $CDCl_3$): δ 7.22 (td, *J* = 7.8 Hz, 1.2 Hz, 1 H), 7.13 – 7.08 (m, 1 H), 7.00 (t, *J* = 7.6 Hz, 1 H), 6.80 (d, *J* = 7.8 Hz, 1 H), 3.94 – 3.85 (d, *J* = 3.8 Hz, 2 H), 3.31 – 3.25 (m, 1 H), 3.20 – 3.15 (m, 1 H), 3.14 (s, 3 H), 3.35 – 3.25 (m, 1 H), 1.96 – 1.90 (m, 1 H), 1.30 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 180.21, 143.22, 132.58, 128.14, 122.58, 122.53, 115.73, 108.30, 68.07, 55.82, 46.31, 36.72, 26.24, 24.40.

ethyl 4-(((1,3-dimethyl-2-oxo-2,3-dihydro-1H-benzo[f]indol-3-yl)methyl)sulfonyl)butanoate (6)



Yellow oil (61.3 mg, 76%);^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 15.4, 8.7 Hz, 2 H), 7.88 (d, *J* = 8.5 Hz, 1 H), 7.64 (t, *J* = 7.3 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.35 (d, *J* = 8.4 Hz, 1 H), 4.21 – 4.10 (m, 3 H), 3.99 (d, *J* = 14.7 Hz, 1 H), 3.46 (s, 3 H), 2.53 – 2.40 (m, 2 H), 2.21 – 2.14 (m, 1 H), 2.10 – 2.04 (m, 1 H), 1.97 – 1.85 (m, 2 H), 1.74 (s, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 179.20, 171.94, 141.74, 130.64, 130.37, 130.23, 129.51, 128.33, 127.83, 123.84, 121.24, 110.26, 60.69, 58.97, 53.37, 46.50, 32.11, 27.02, 24.50, 17.49, 14.25; HRMS (ESI) m/z calcd. for $C_{21}H_{26}NO_5S$ $[M+H]^+$: 404.1526, found 404.1529.

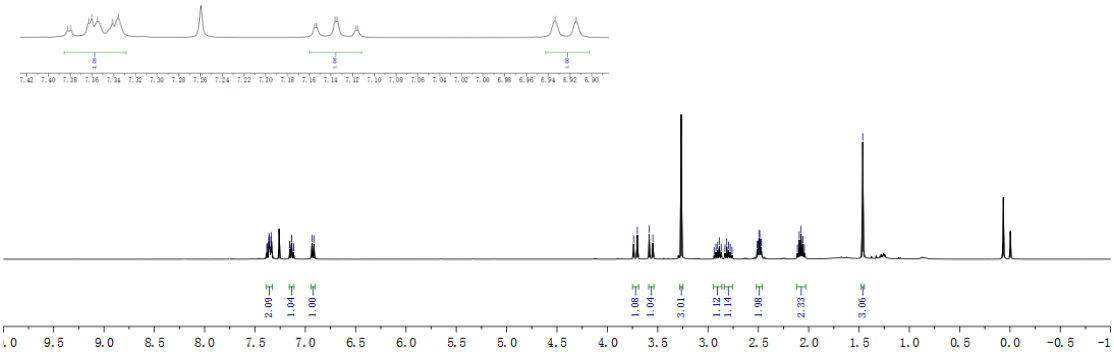
4. References

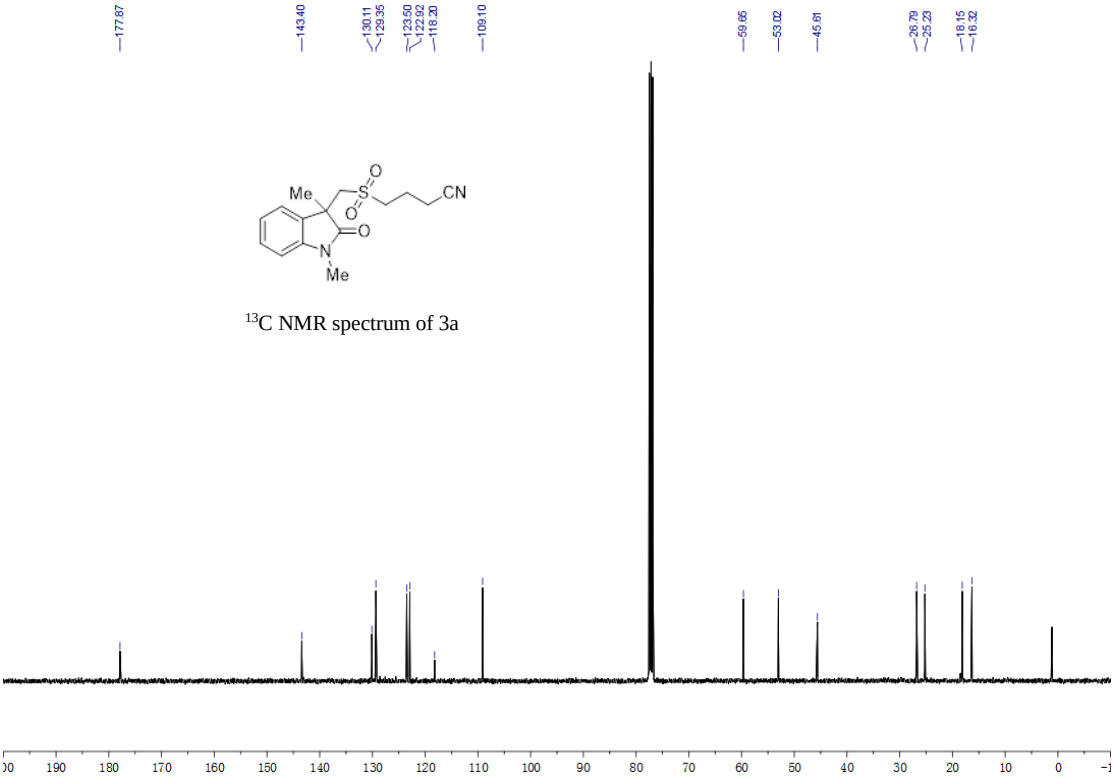
1. Z. Chen; Q. Zhou; Q.-L. Wang; P. Chen; B.-Q. Xiong; Y. Liang; K.-W. Tang; Y. Liu., *Adv. Synth. Catal.* 2020, ***362***, 3004 – 3010.

5. ^{1}H, ^{13}C and ^{19}F NMR spectra of products

4-(((1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3a)

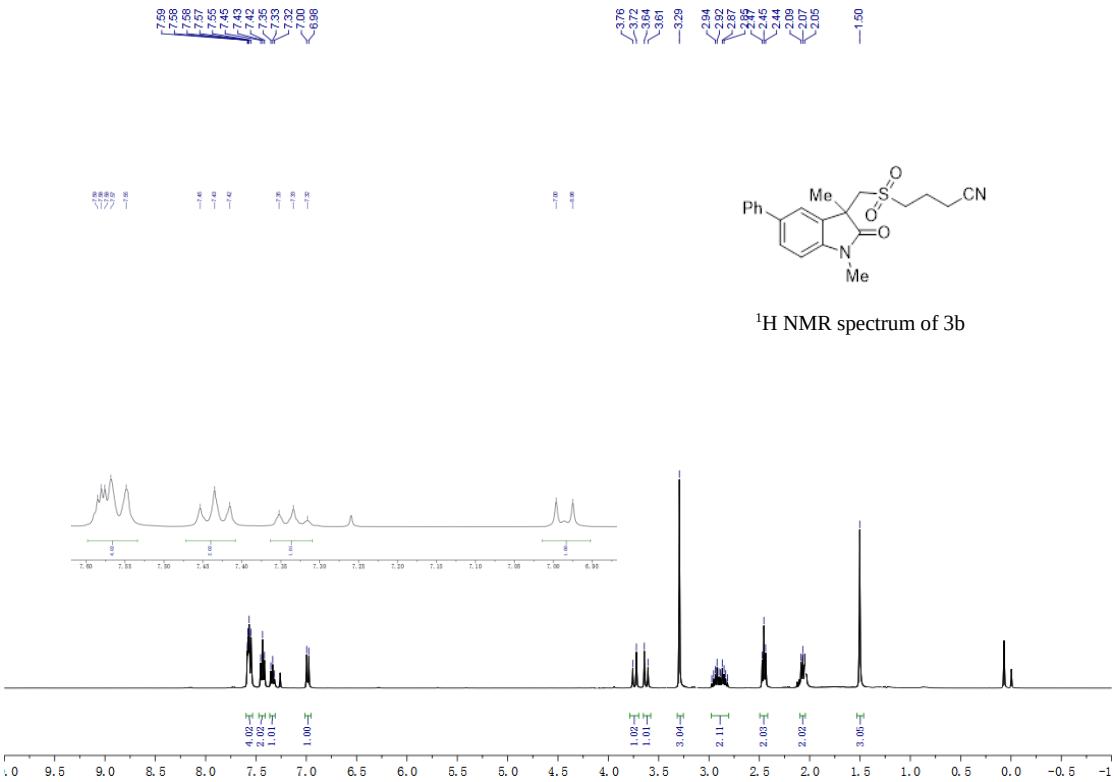
^{1}H NMR spectrum of 3a



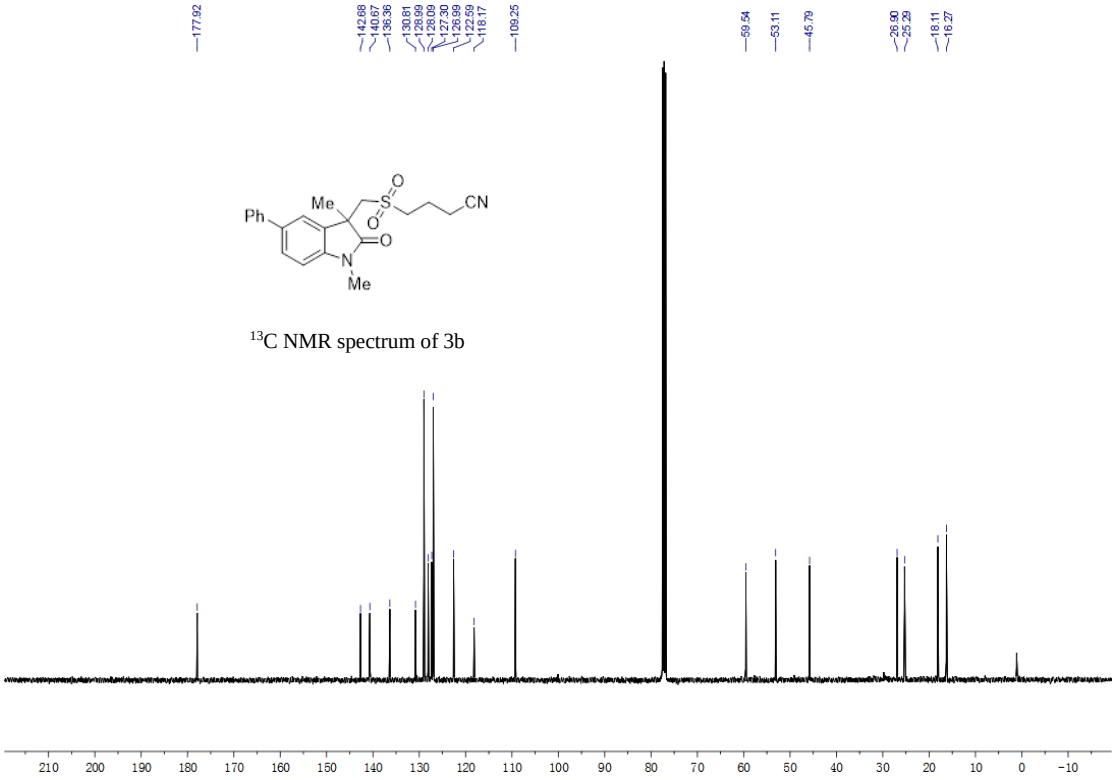


^{13}C NMR spectrum of 3a

4-(((1,3-dimethyl-2-oxo-5-phenylindolin-3-yl)methyl)sulfonyl)butanenitrile (3b)

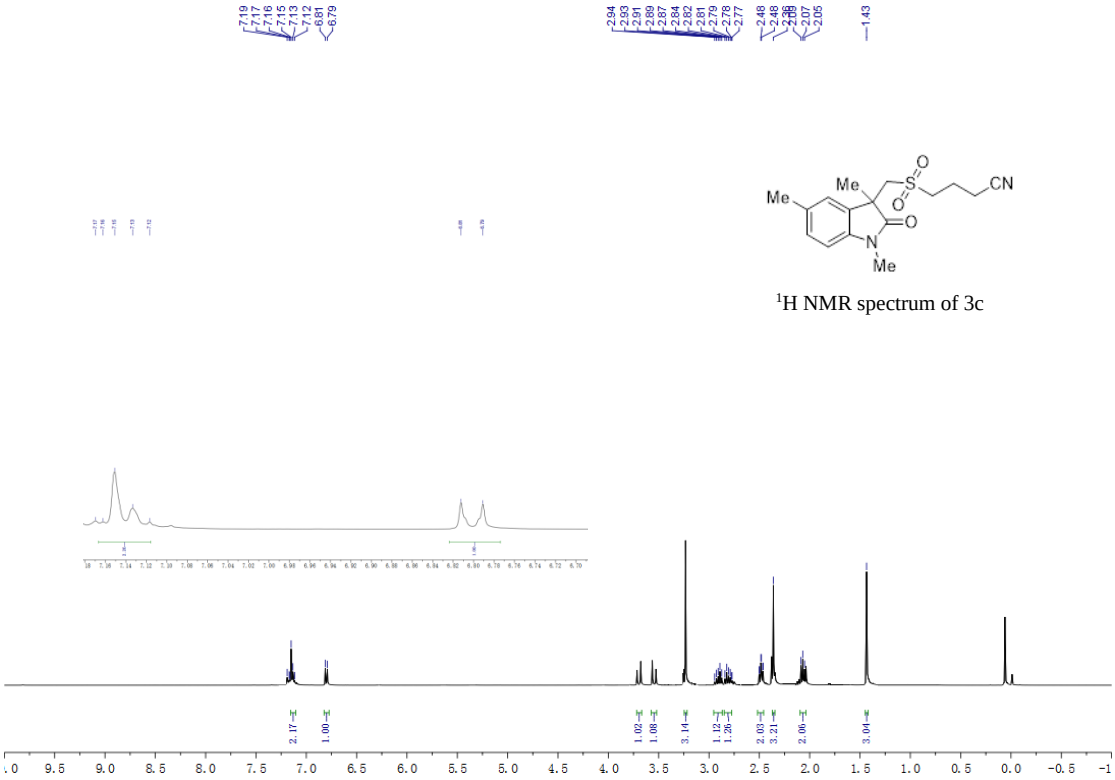


^{1}H NMR spectrum of 3b

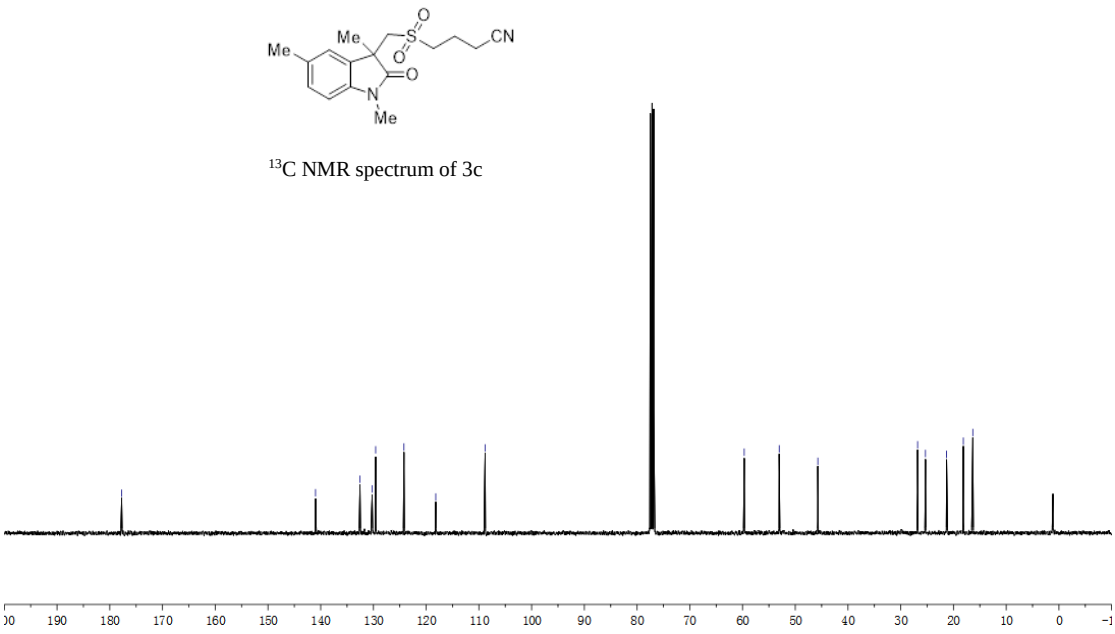


^{13}C NMR spectrum of 3b

4-(((1,3,5-trimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3c)

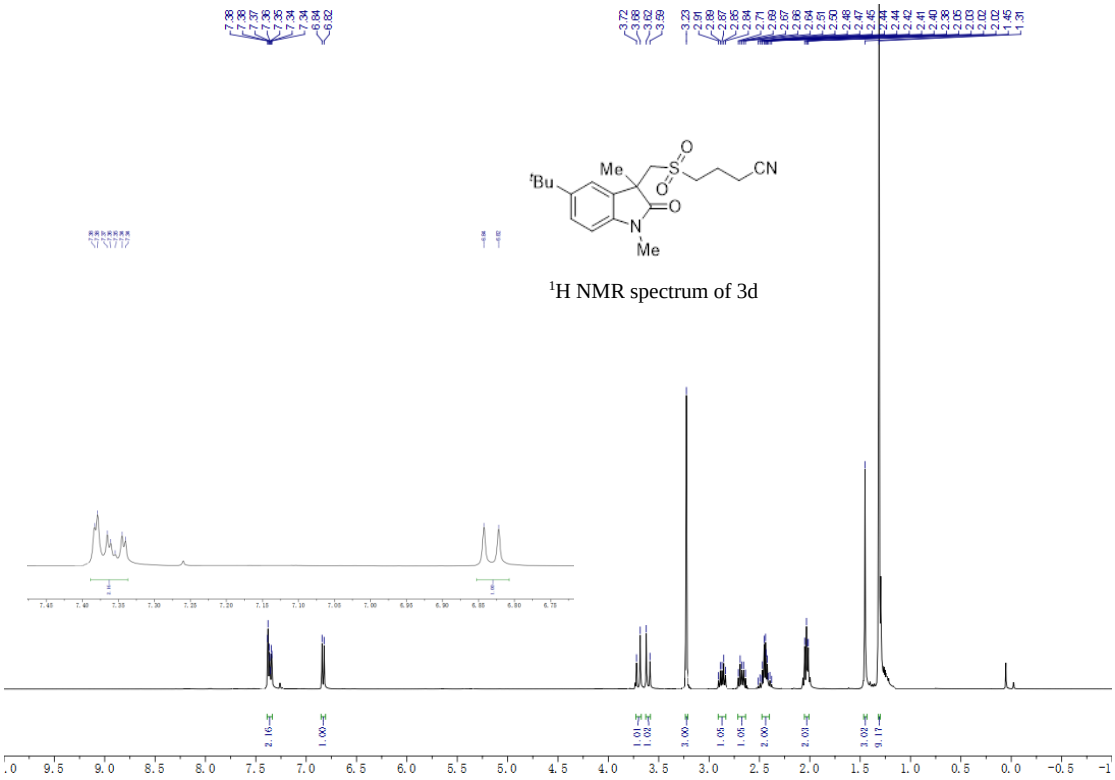


^{1}H NMR spectrum of 3c

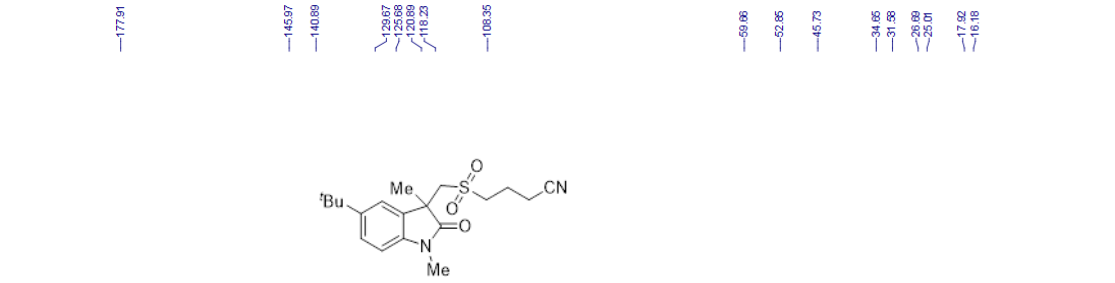


^{13}C NMR spectrum of 3c

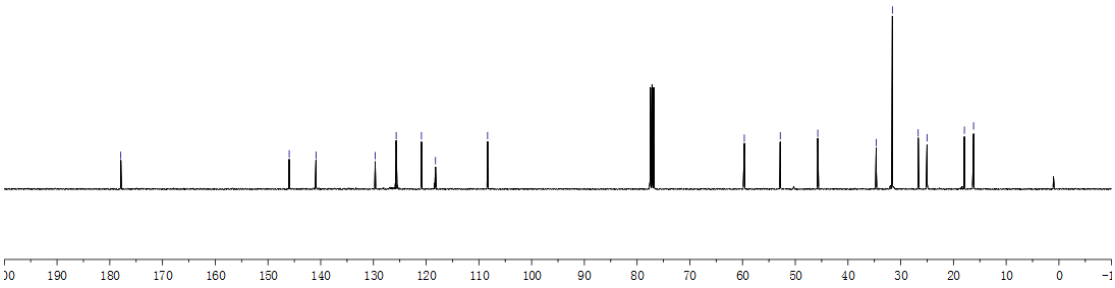
4-(((5-(tert-butyl)-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3d)



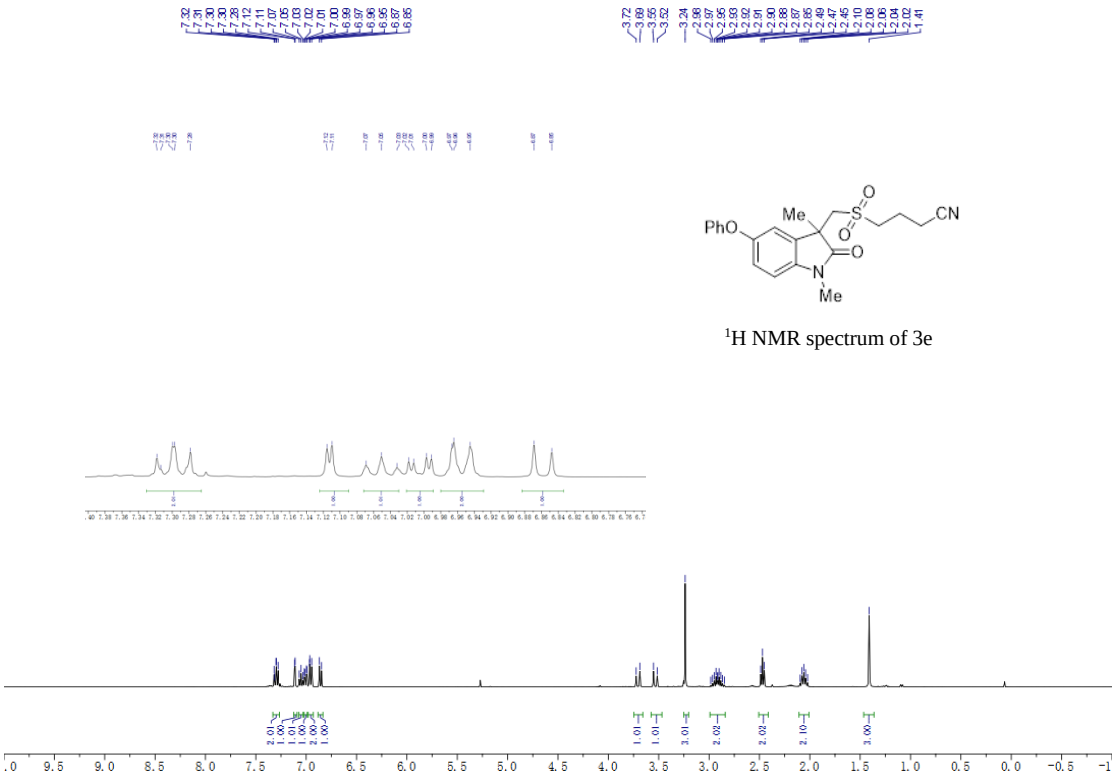
^{1}H NMR spectrum of 3d



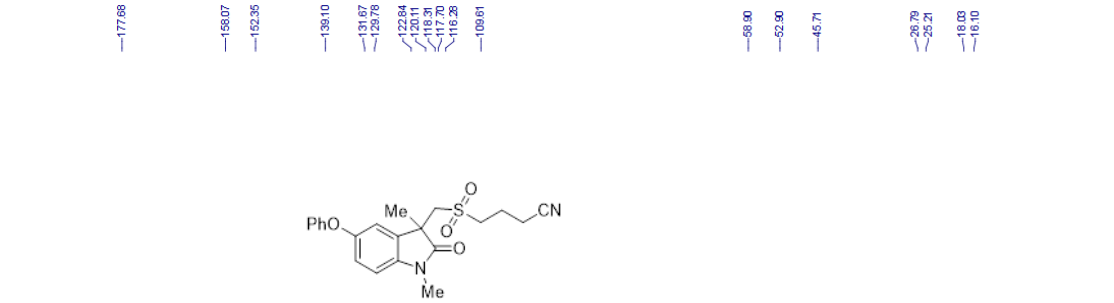
^{13}C NMR spectrum of 3d



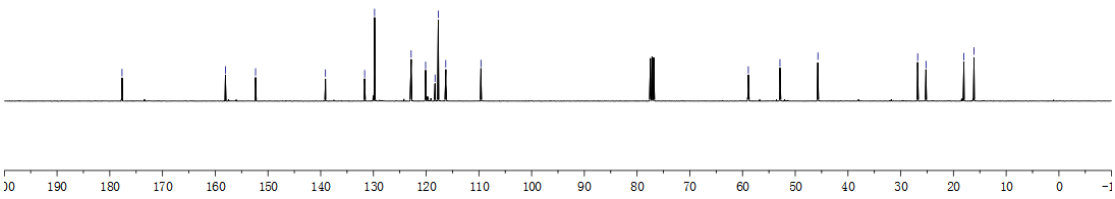
4-(((1,3-dimethyl-2-oxo-5-phenoxyindolin-3-yl)methyl)sulfonyl)butanenitrile (3e)



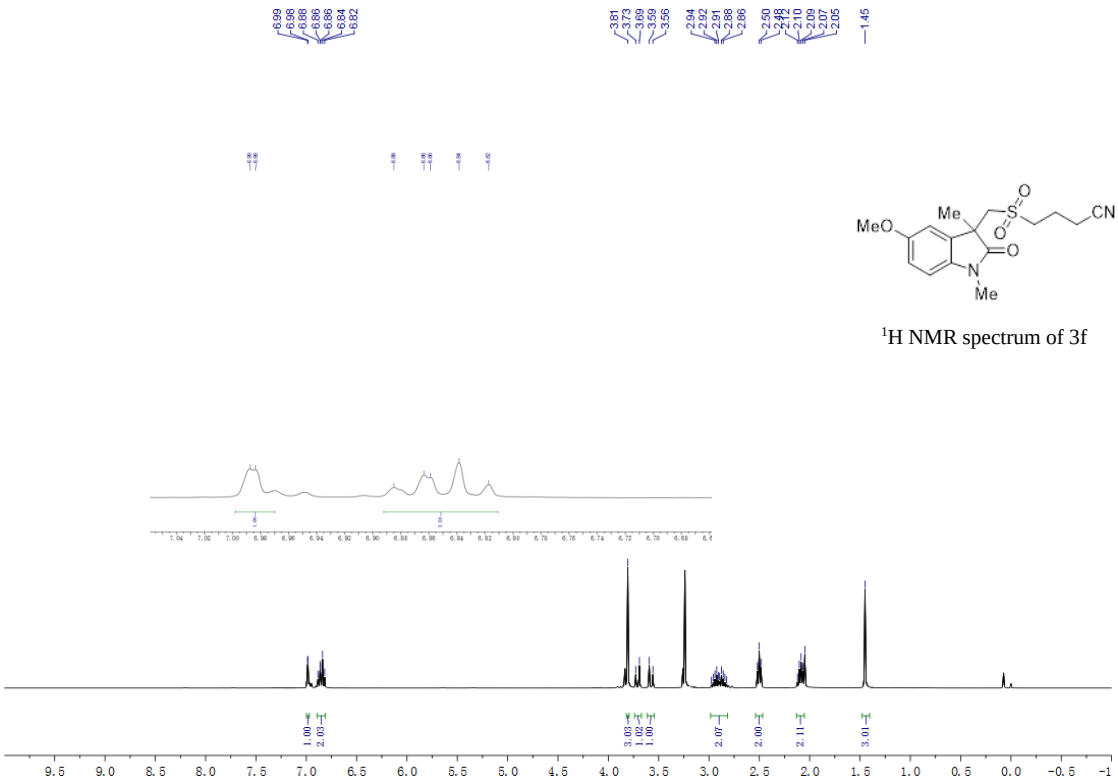
^{1}H NMR spectrum of 3e



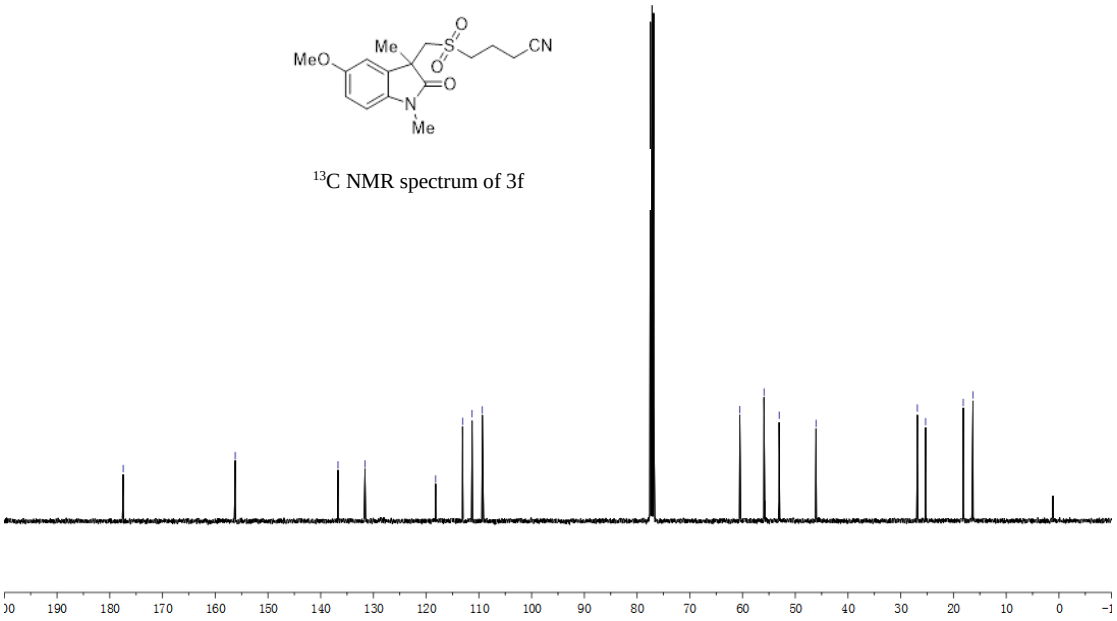
^{13}C NMR spectrum of 3e



4-(((5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3f)

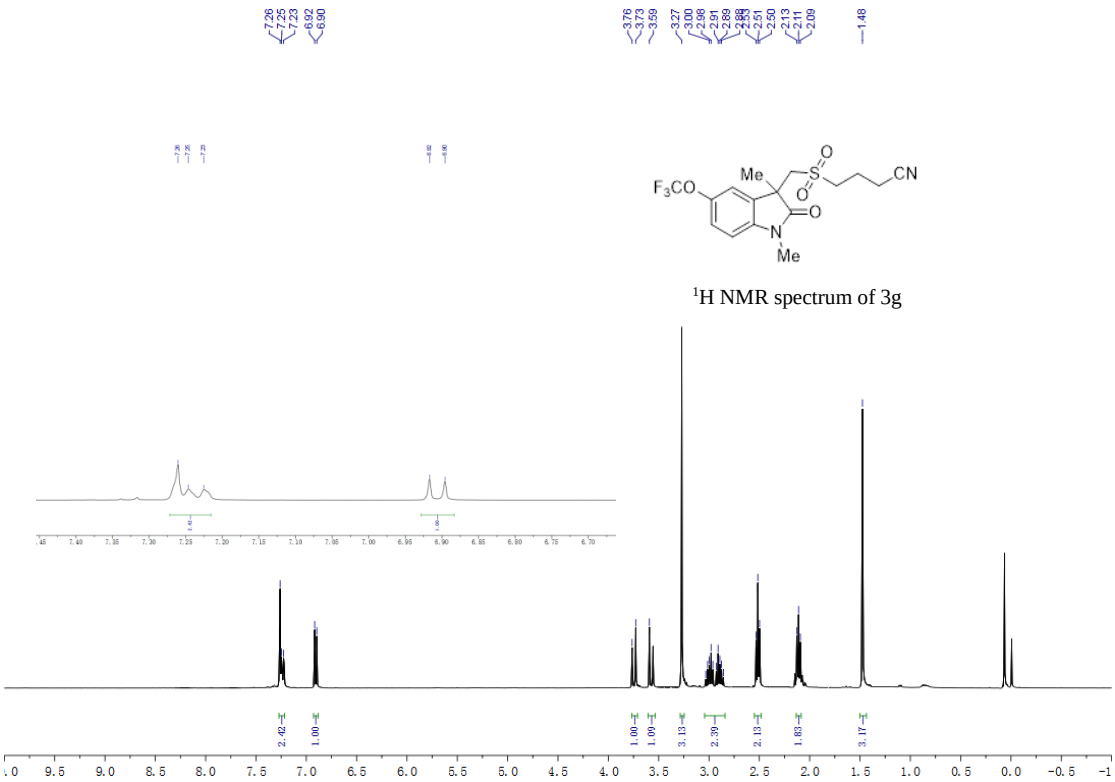


^{1}H NMR spectrum of 3f

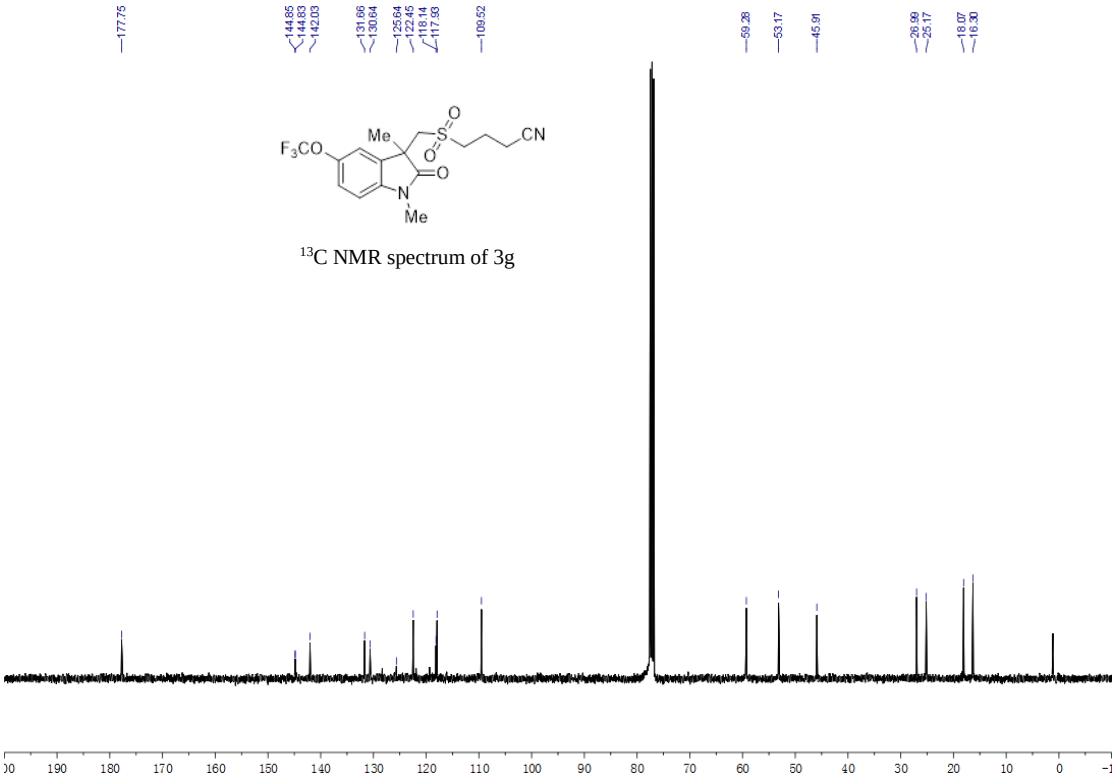


^{13}C NMR spectrum of 3f

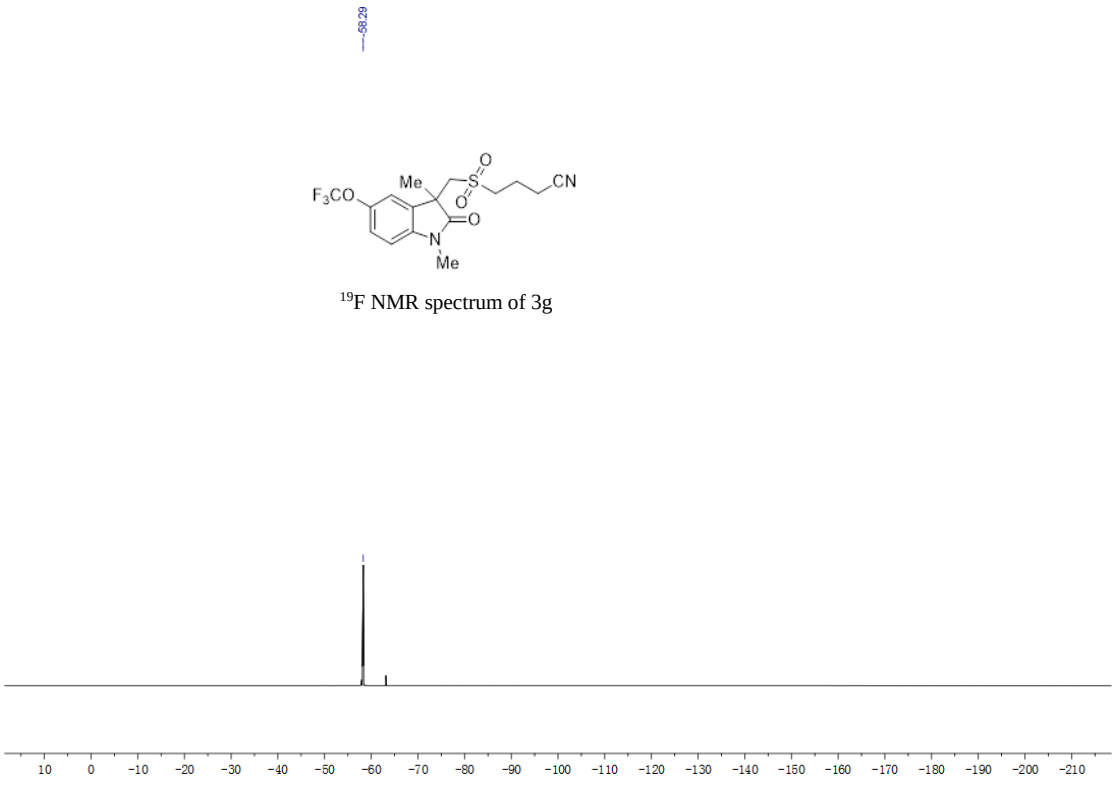
4-(((1,3-dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)methyl)sulfonyl)butanenitrile (3g)



^{1}H NMR spectrum of 3g

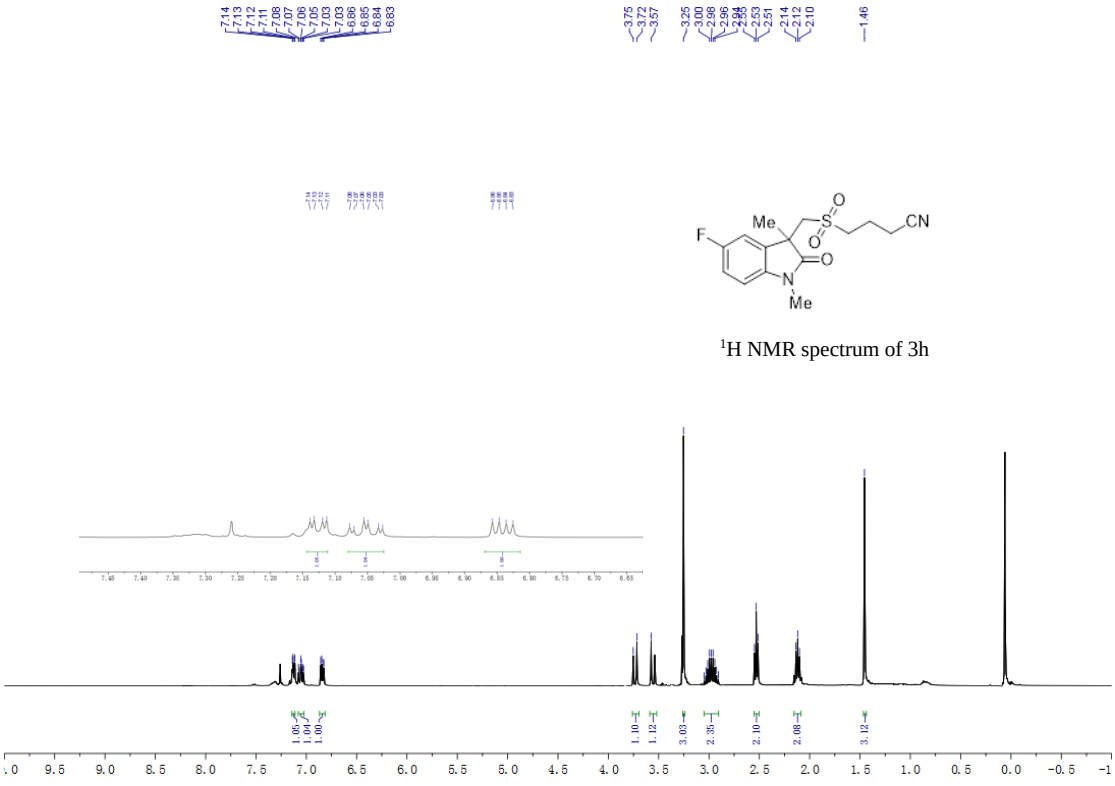


^{13}C NMR spectrum of 3g

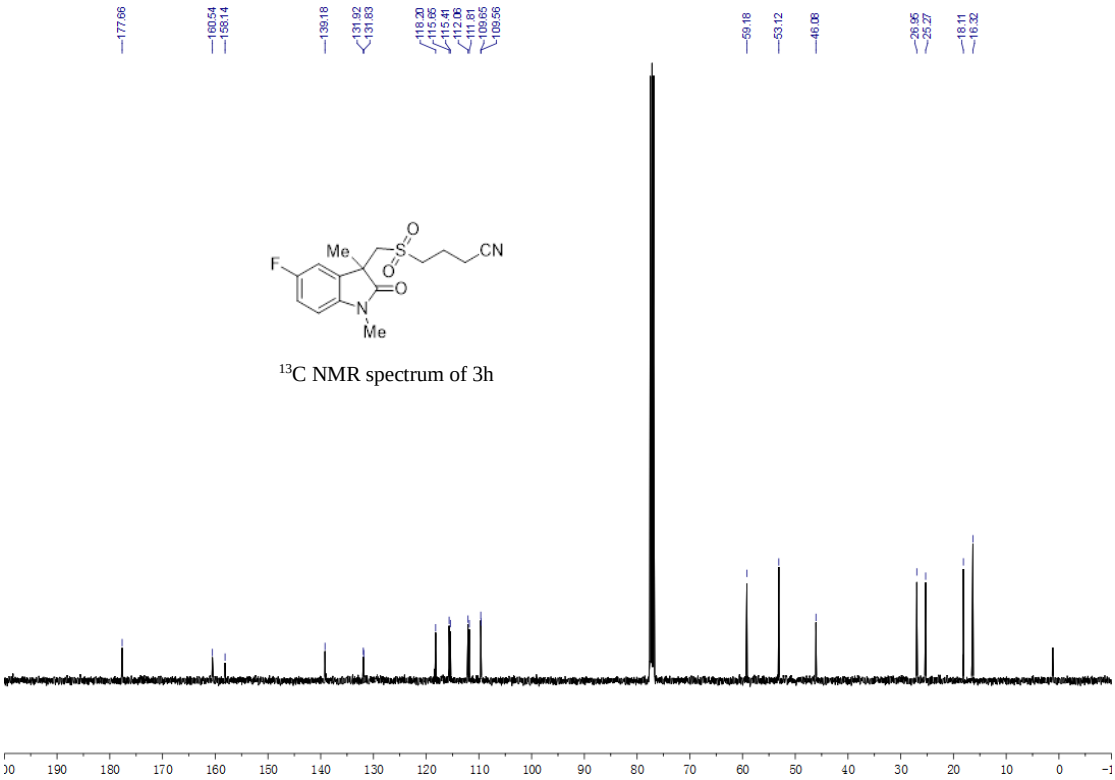


^{19}F NMR spectrum of 3g

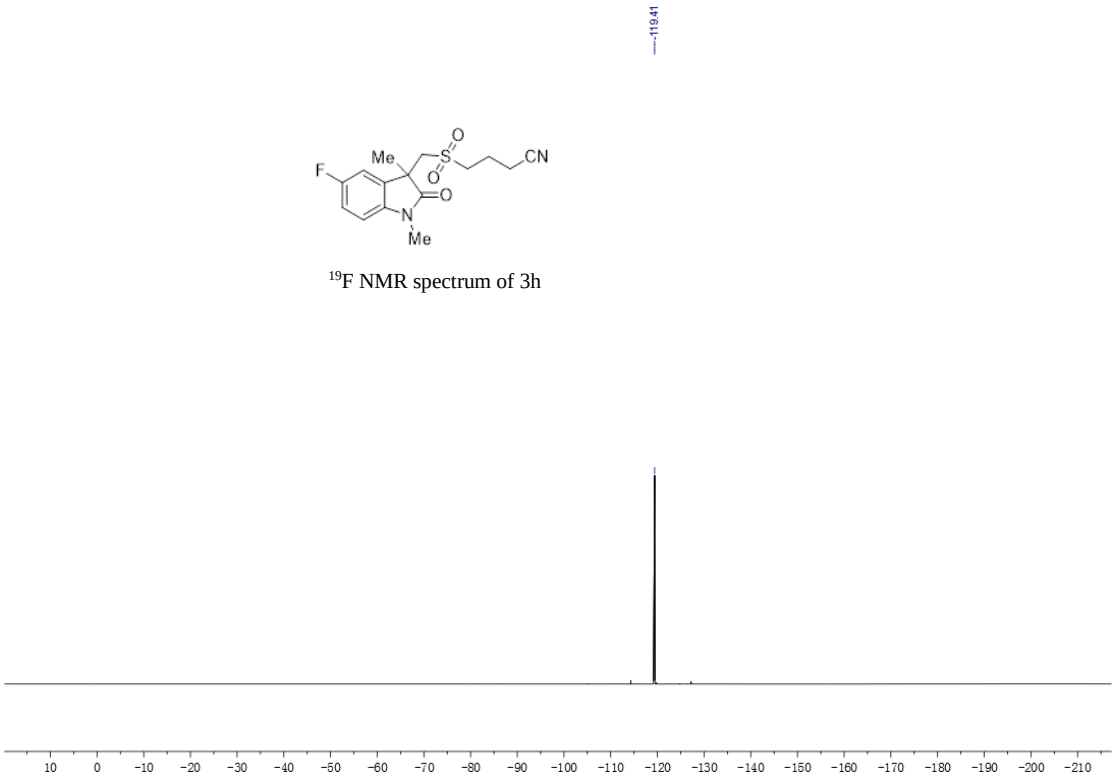
4-(((5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3h)



^{1}H NMR spectrum of 3h

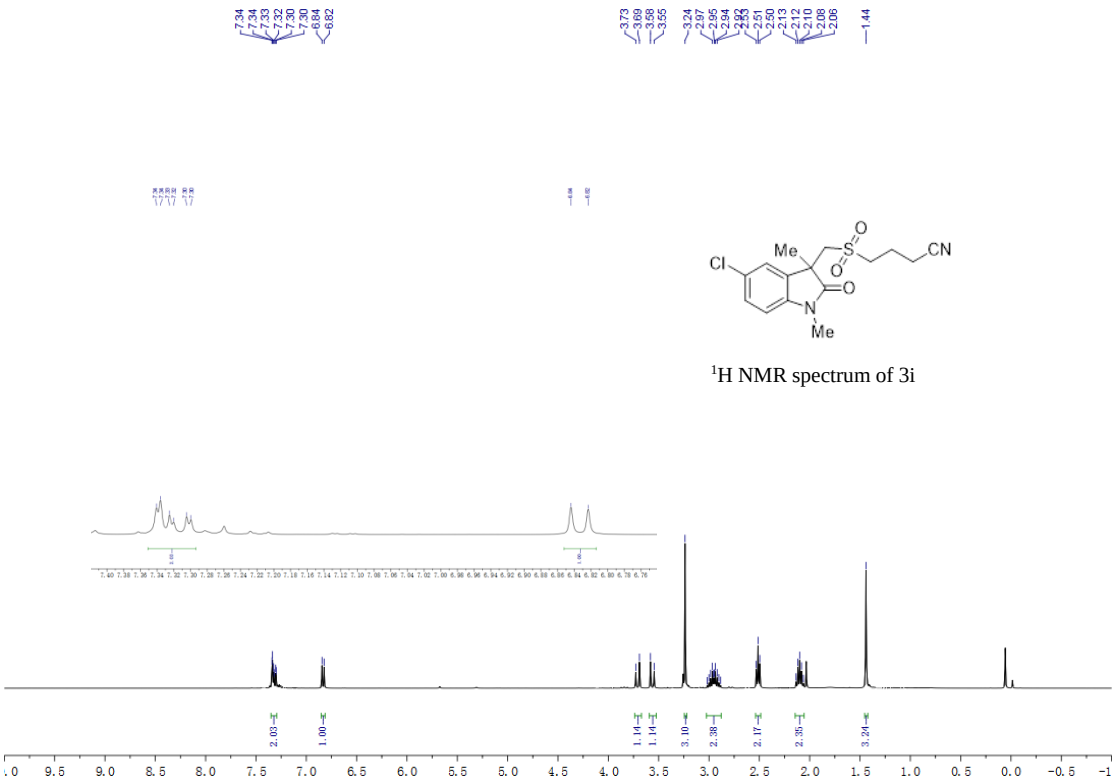


^{13}C NMR spectrum of 3h

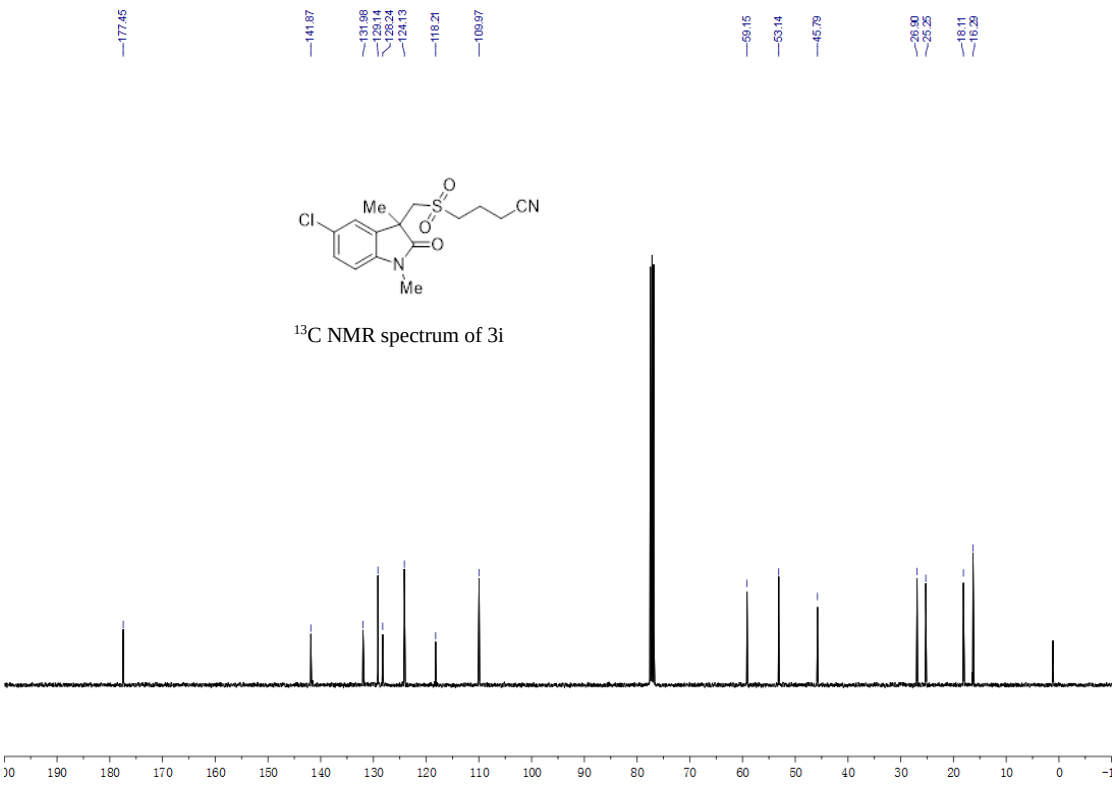


^{19}F NMR spectrum of 3h

4-(((5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3i)

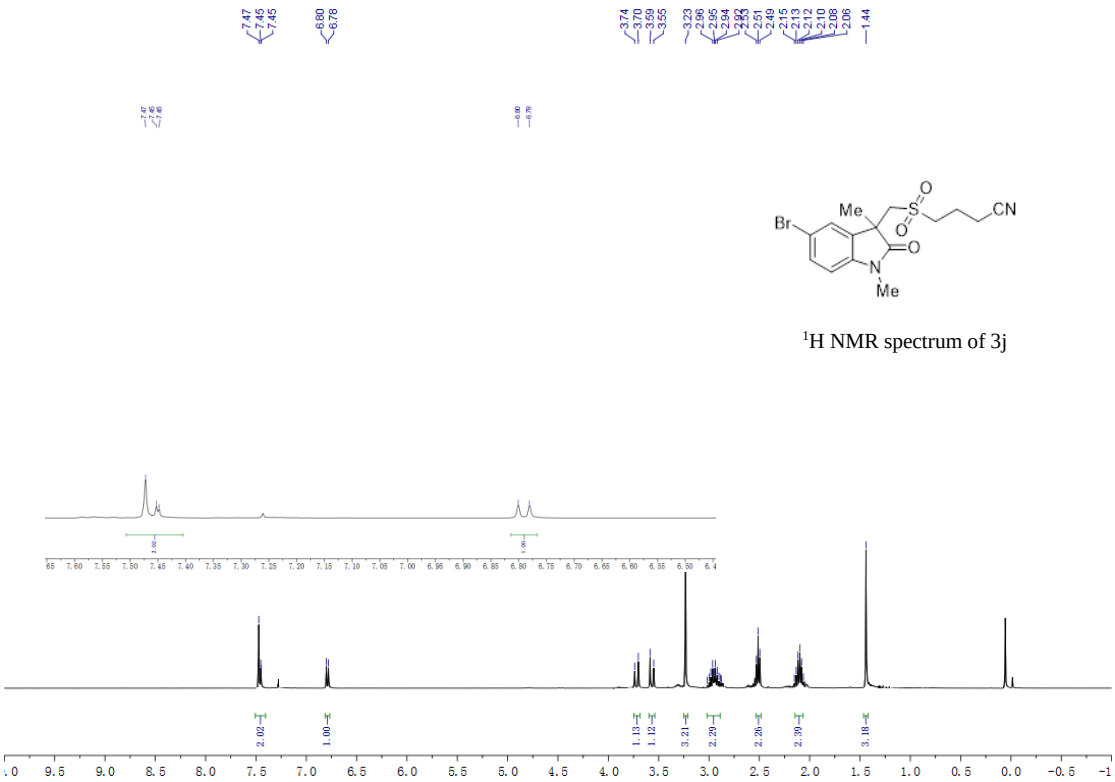


^{1}H NMR spectrum of 3i

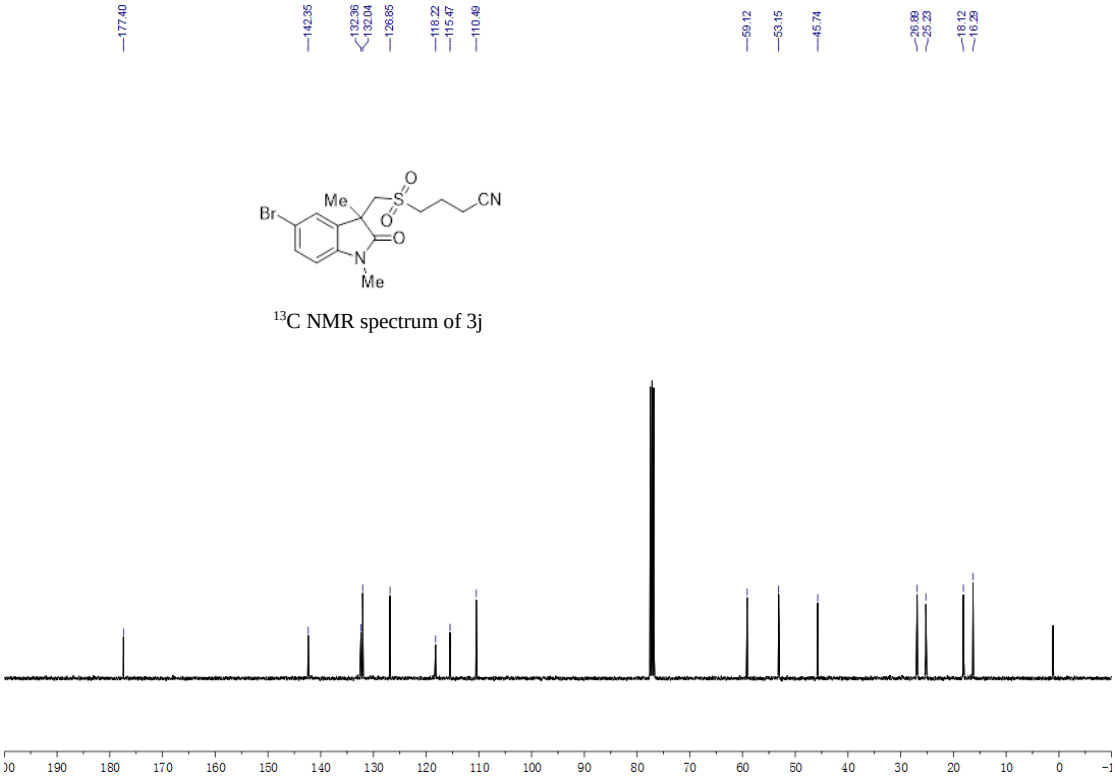


^{13}C NMR spectrum of 3i

4-(((5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3j)

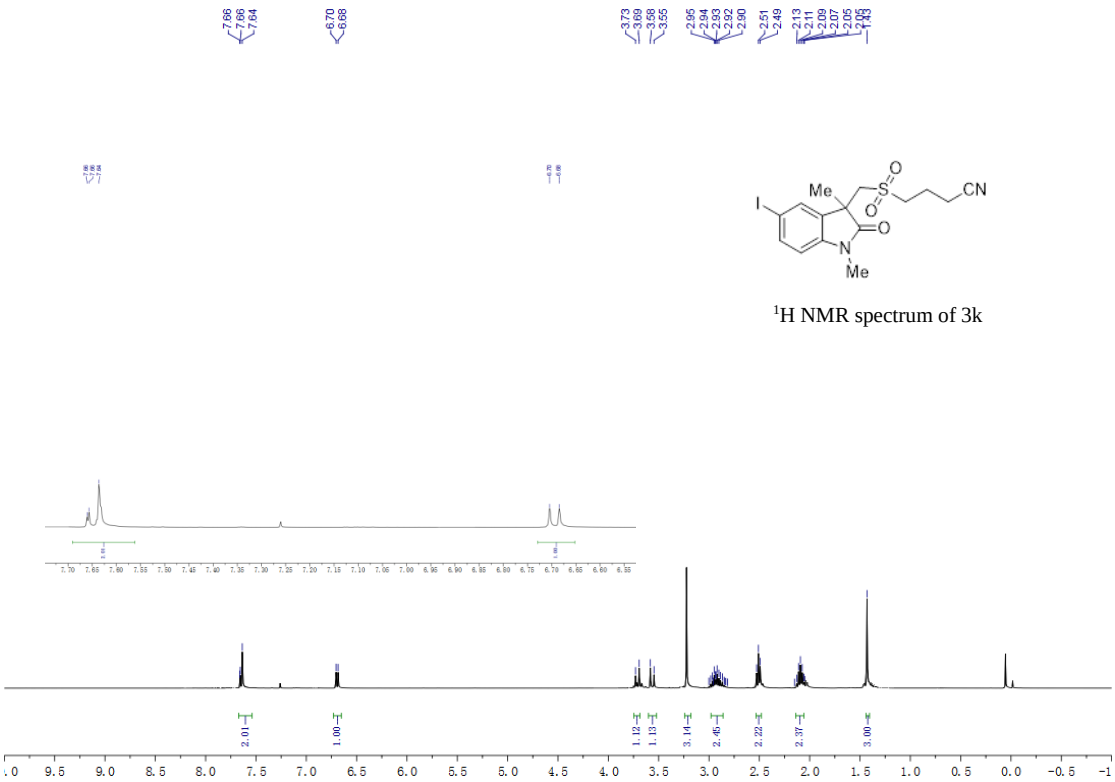


^{1}H NMR spectrum of 3j

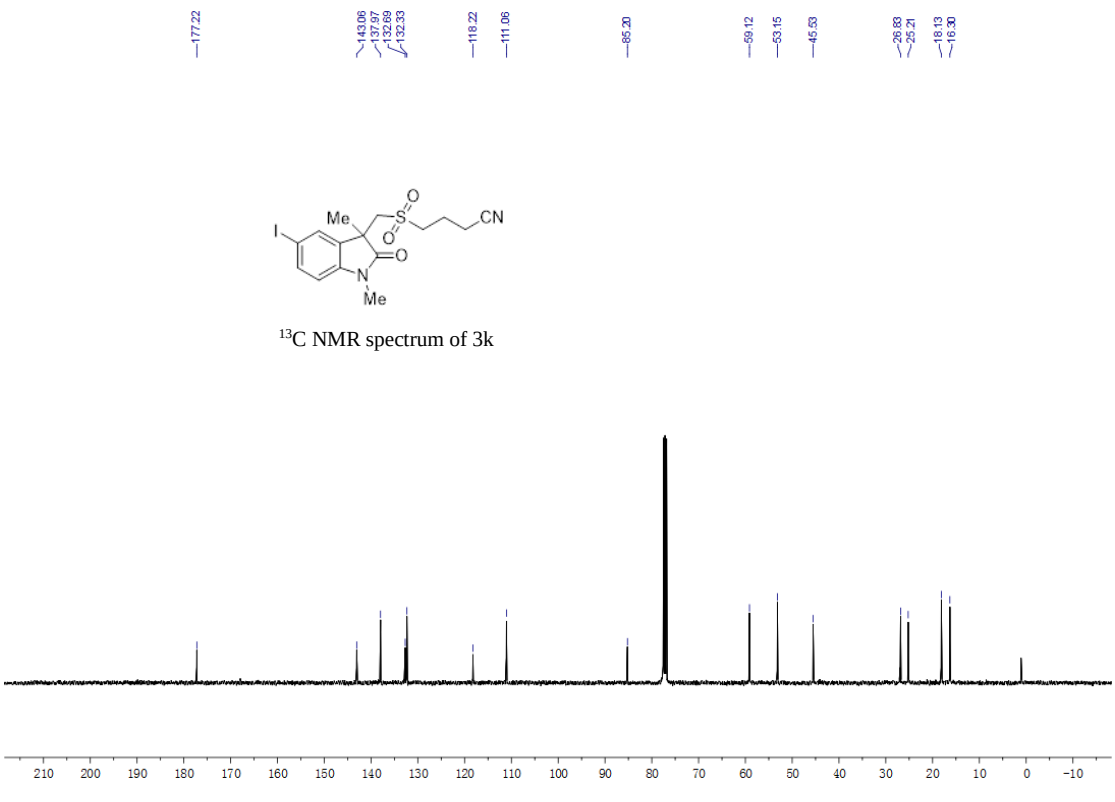


^{13}C NMR spectrum of 3j

4-(((5-iodo-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3k)

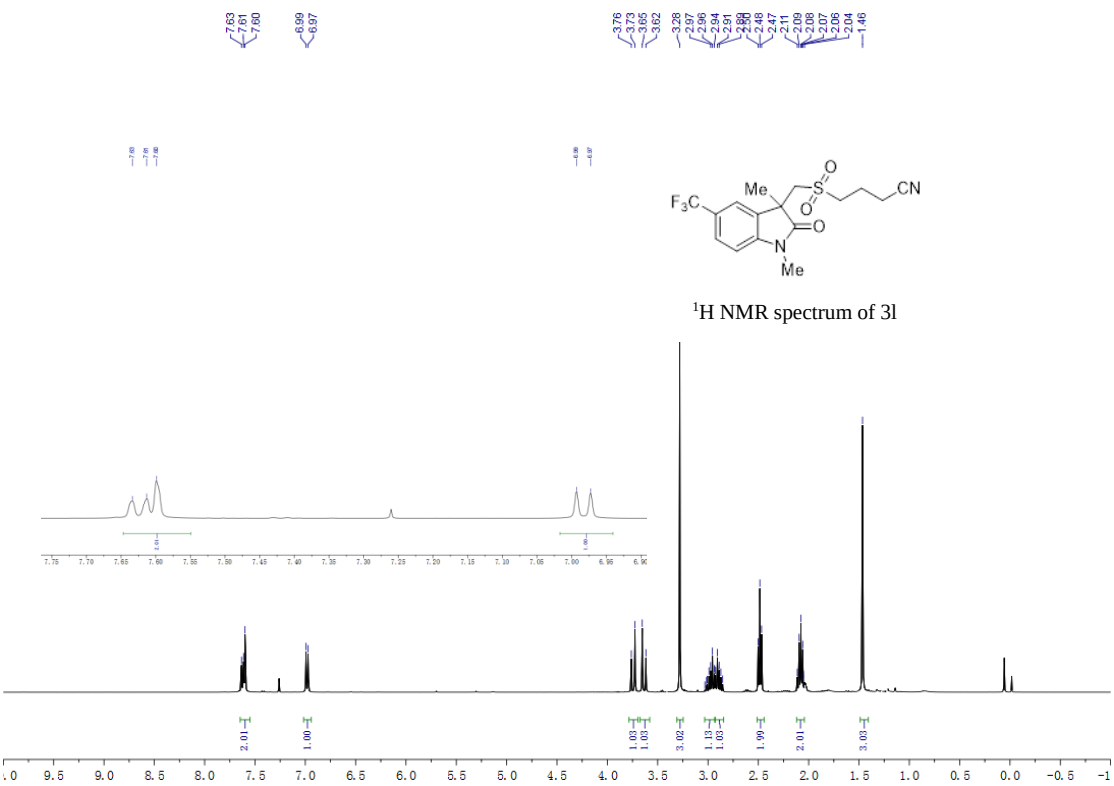


^{1}H NMR spectrum of 3k

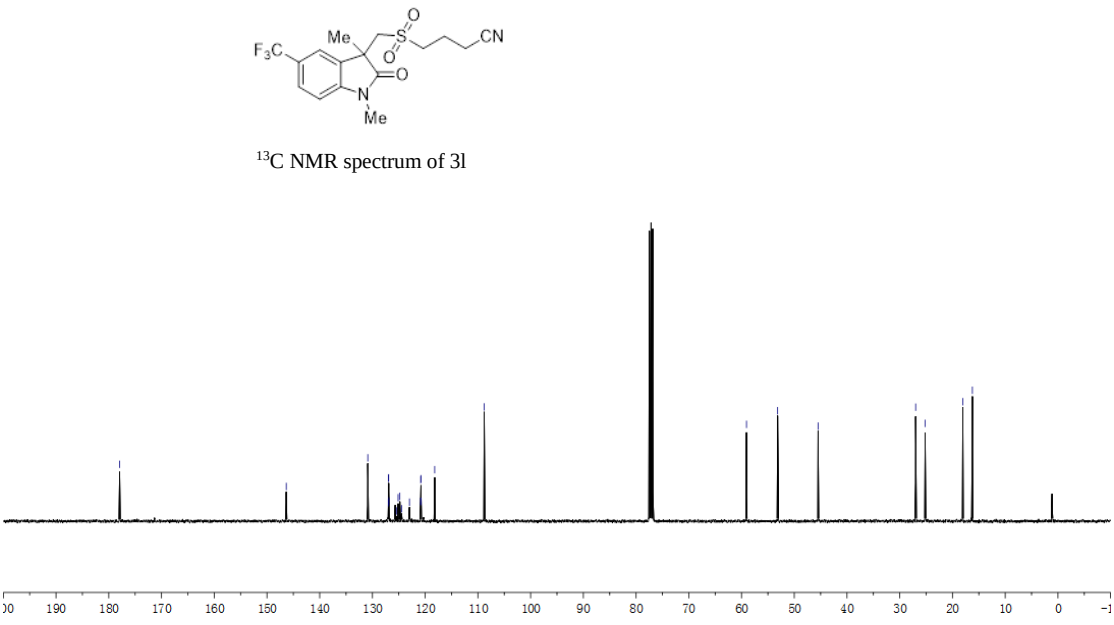


^{13}C NMR spectrum of 3k

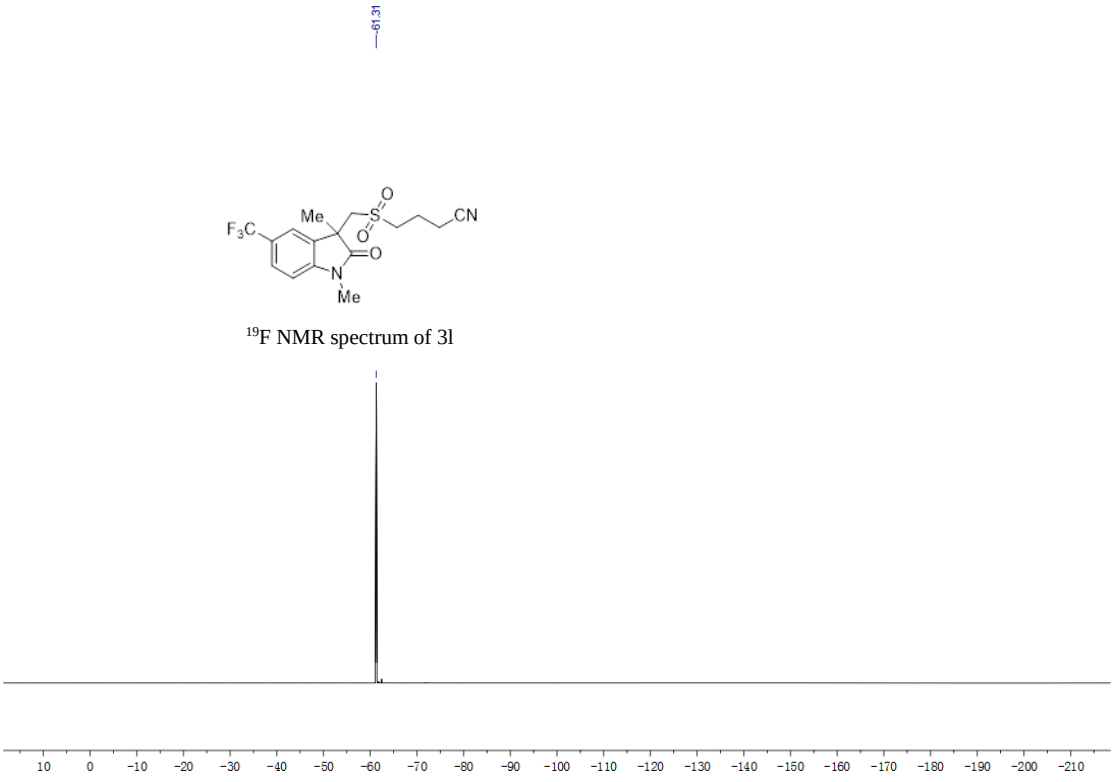
4-(((1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)methyl)sulfonyl)butanenitrile (3l)



^{1}H NMR spectrum of 3l

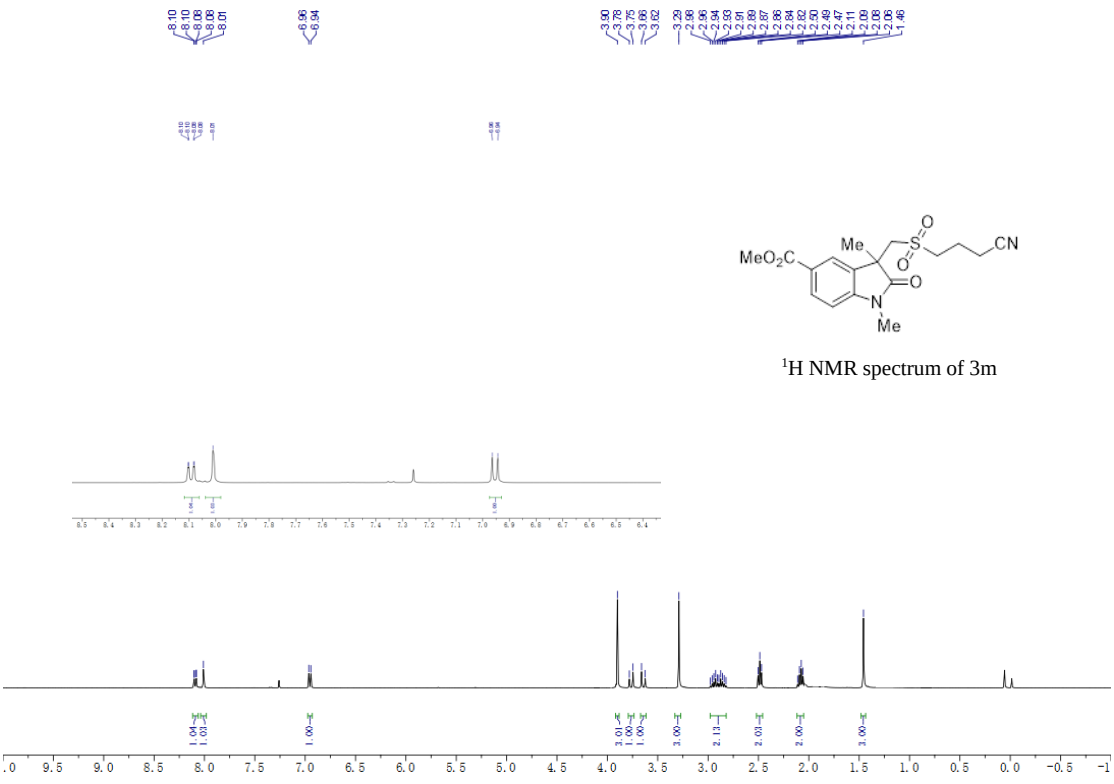


^{13}C NMR spectrum of 3l

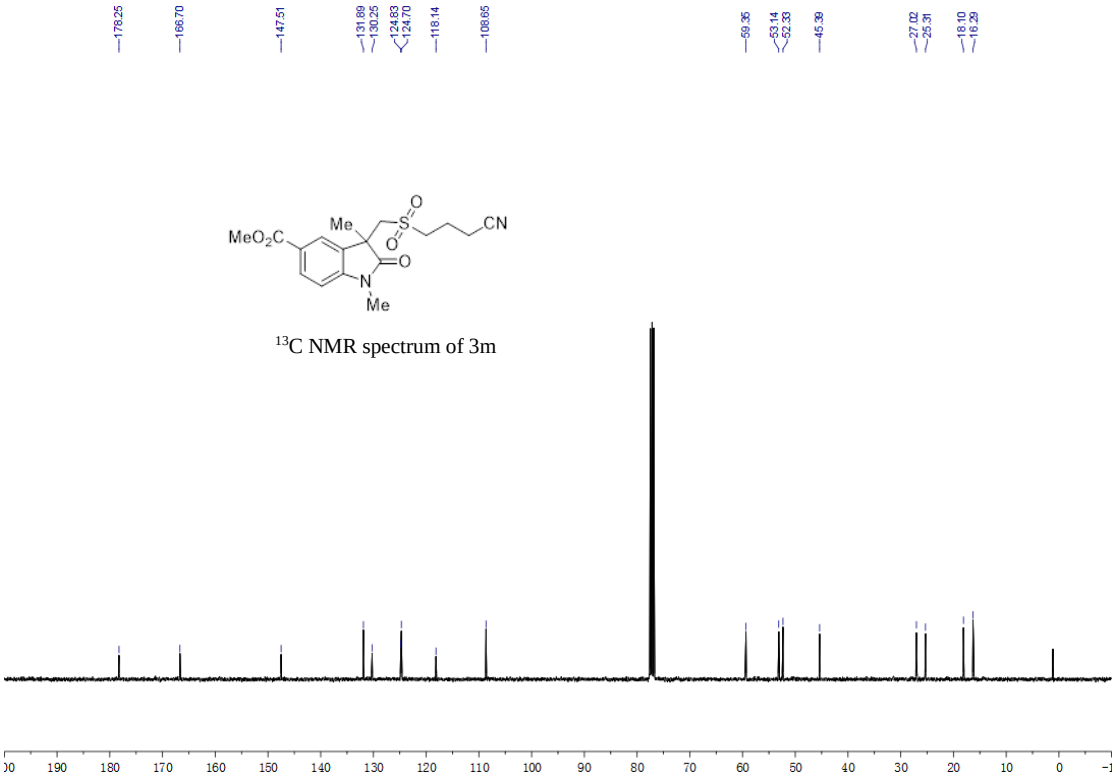


^{19}F NMR spectrum of 3l

methyl 3-(((3-cyanopropyl)sulfonyl)methyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3m)

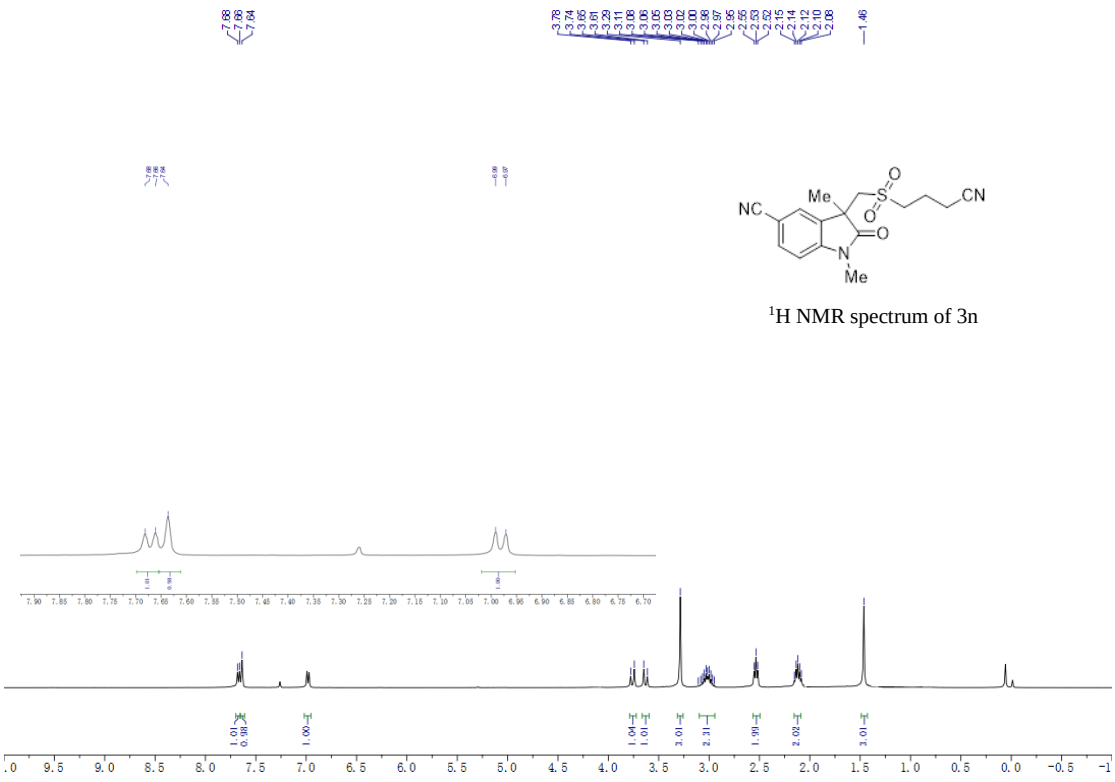


^{1}H NMR spectrum of 3m

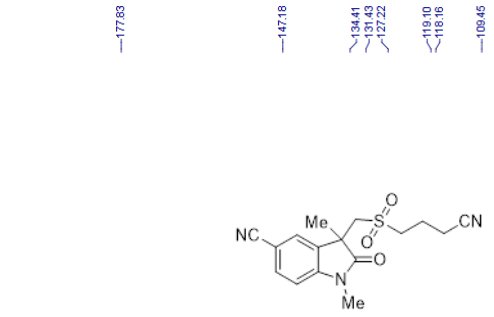


^{13}C NMR spectrum of 3m

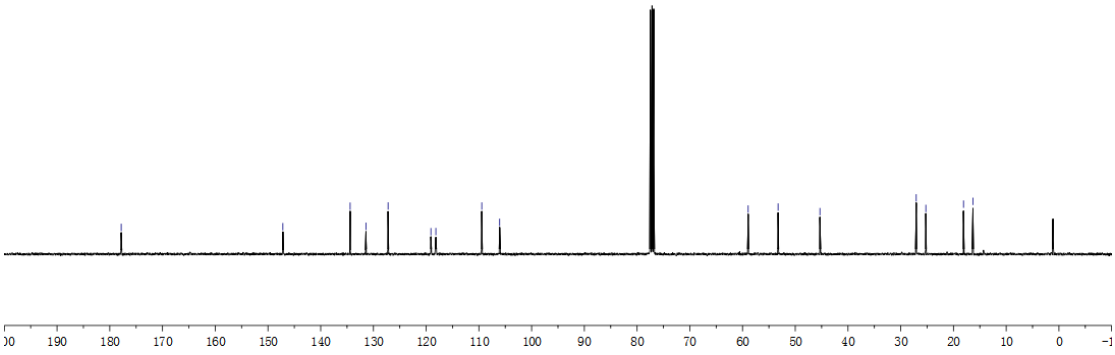
3-(((3-cyanopropyl)sulfonyl)methyl)-1,3-dimethyl-2-oxoindoline-5-carbonitrile (3n)



^{1}H NMR spectrum of 3n

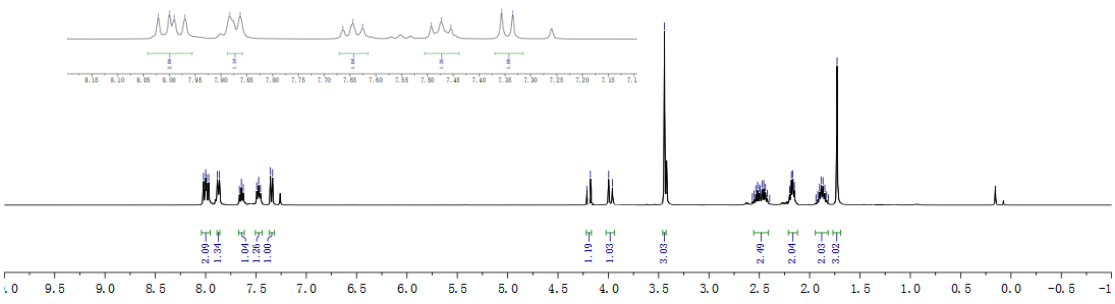


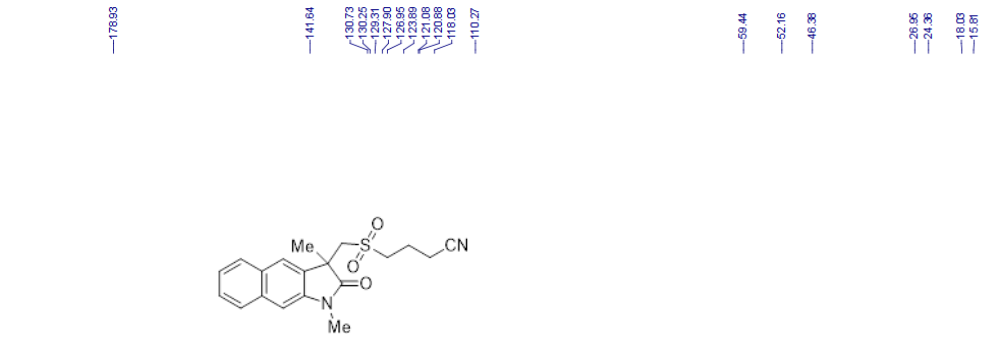
^{13}C NMR spectrum of 3n



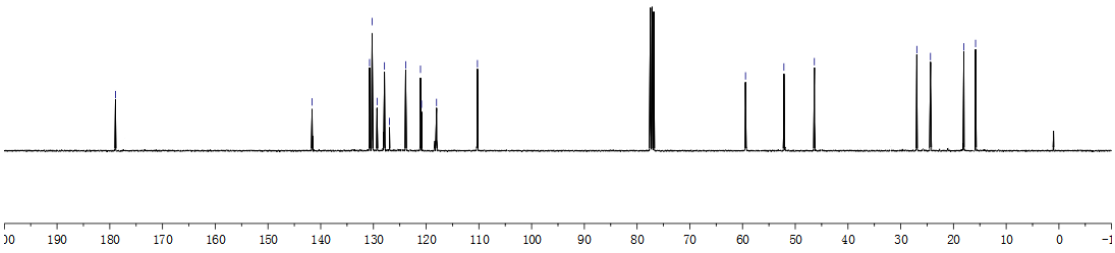
4-(((1,3-dimethyl-2-oxo-2,3-dihydro-1H-benzo[f]indol-3-yl)methyl)sulfonyl)butanenitrile (3o)

^{1}H NMR spectrum of 3o

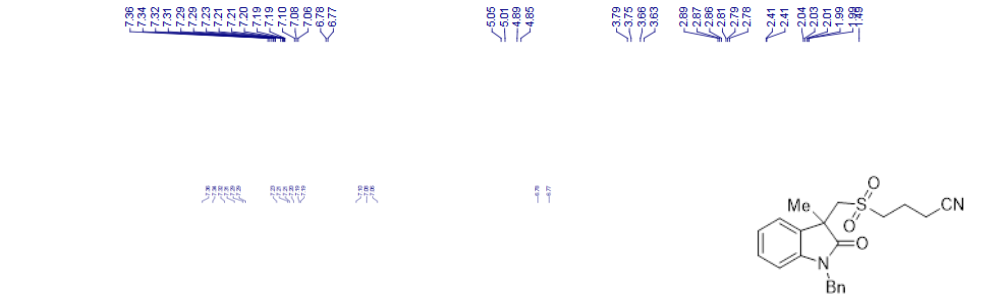




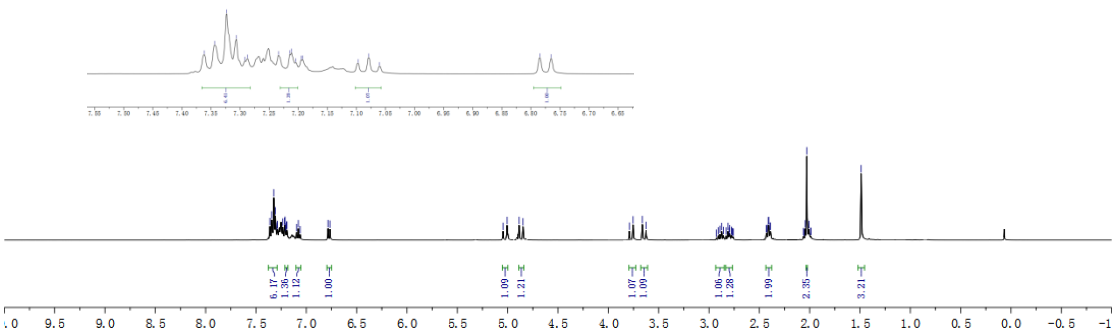
^{13}C NMR spectrum of 3o

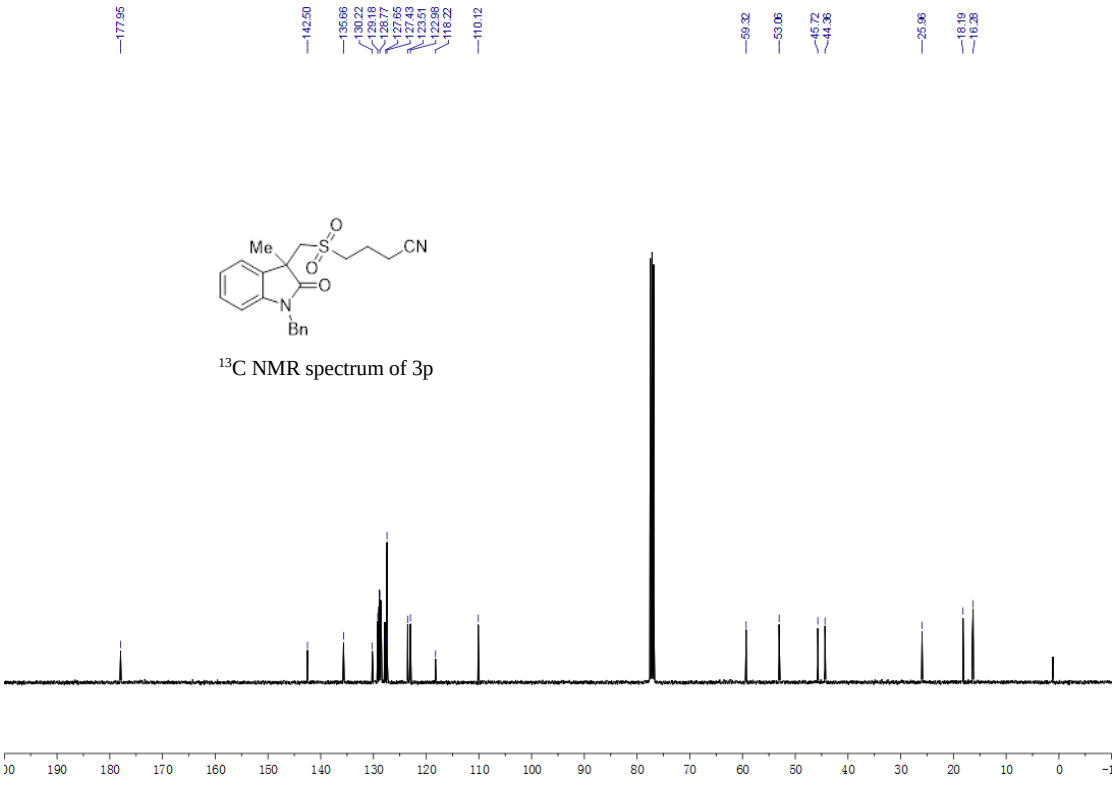


4-(((1-benzyl-3-methyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3p)



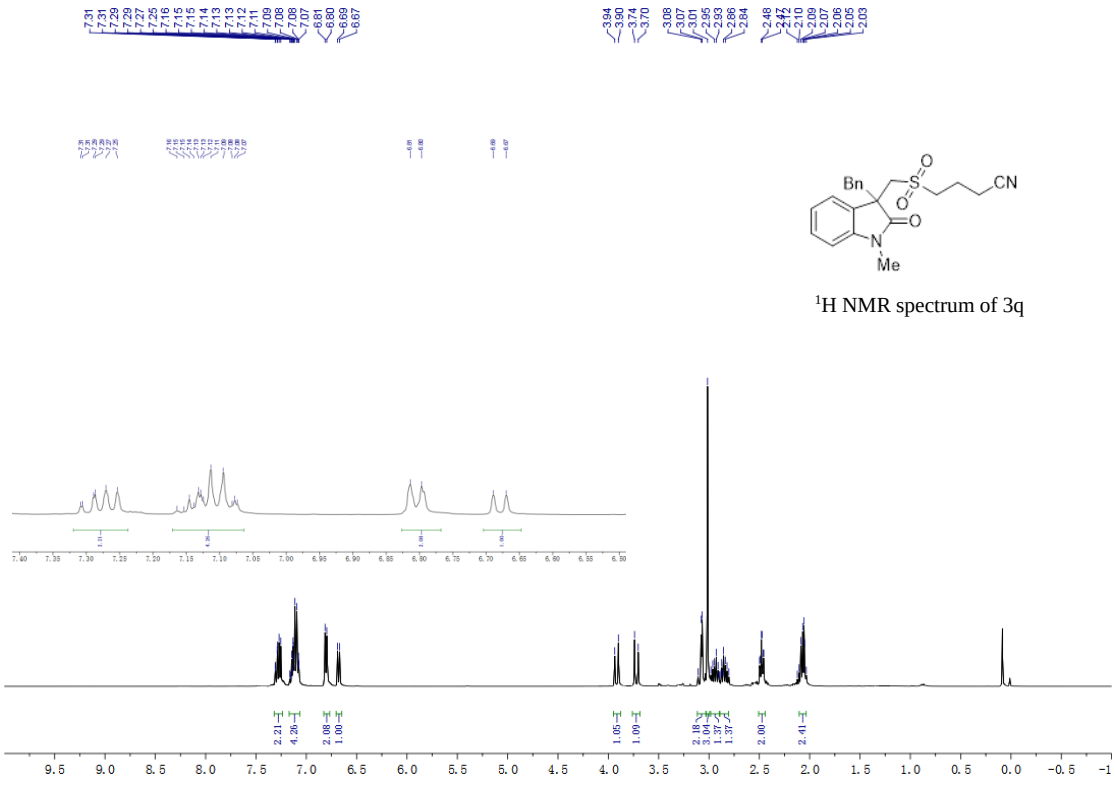
^{1}H NMR spectrum of 3p



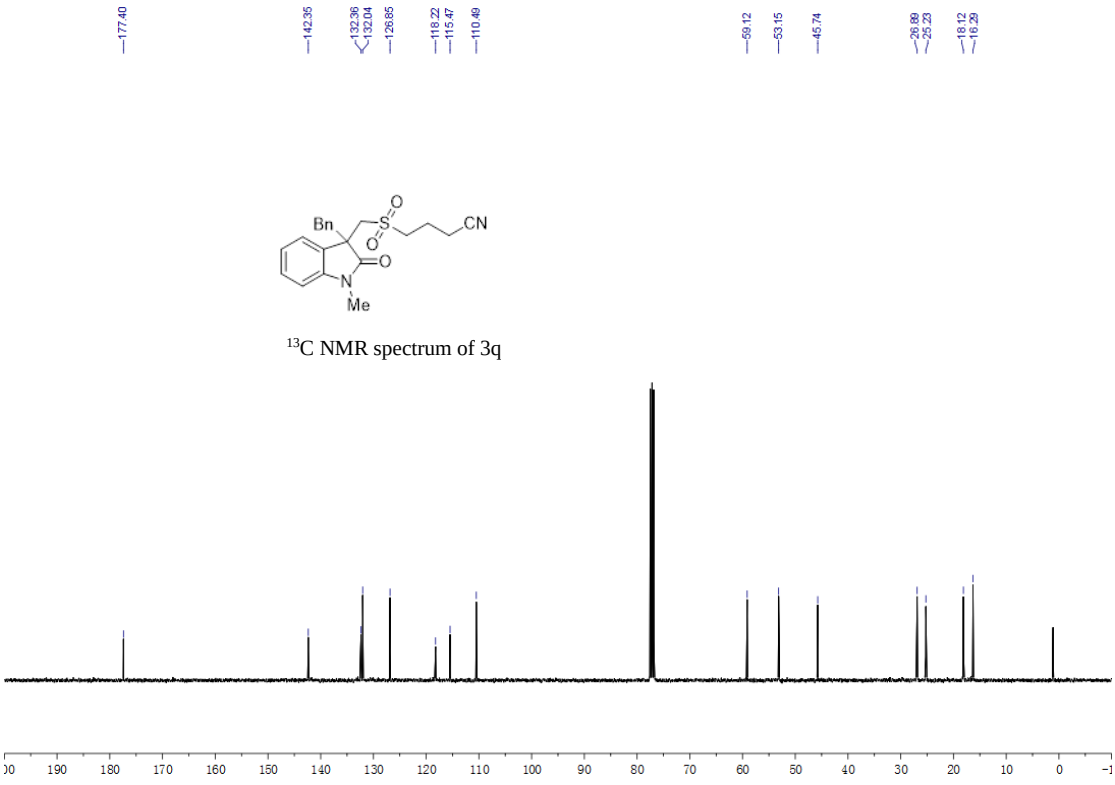


^{13}C NMR spectrum of 3p

4-(((3-benzyl-1-methyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3q)

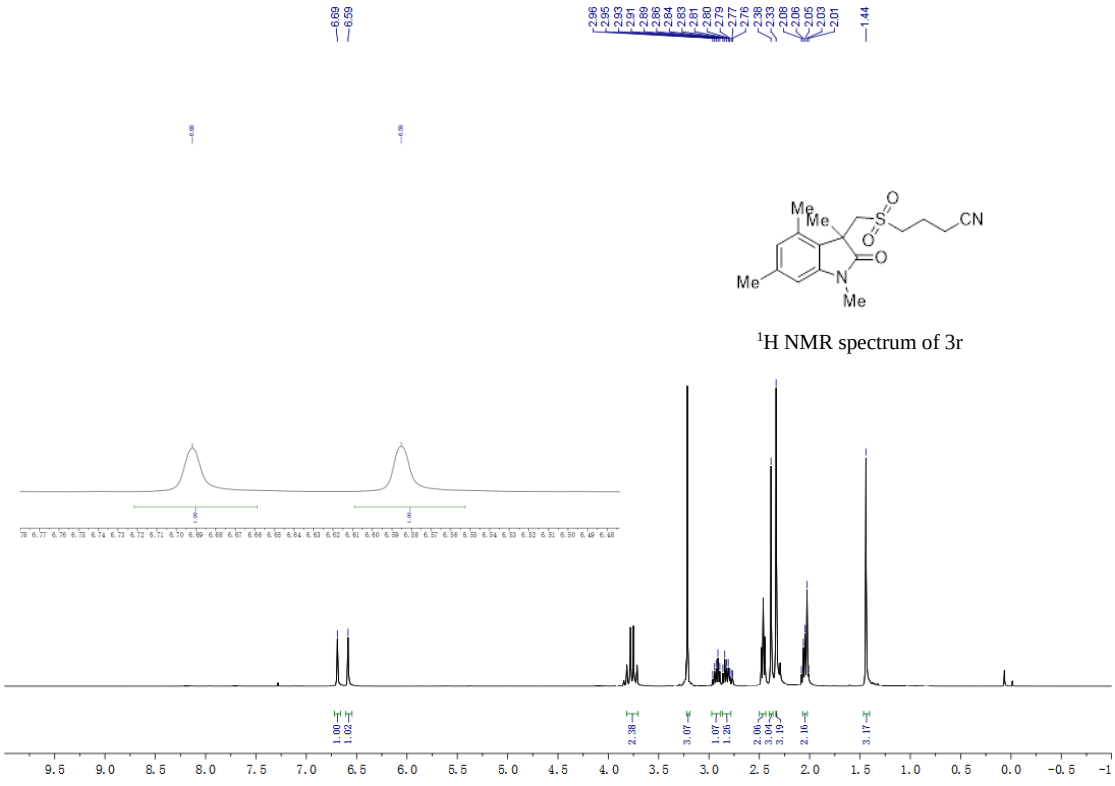


^{1}H NMR spectrum of 3q

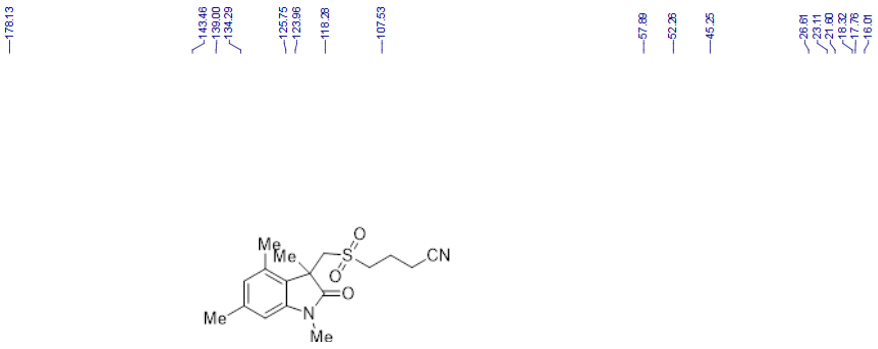


^{13}C NMR spectrum of 3q

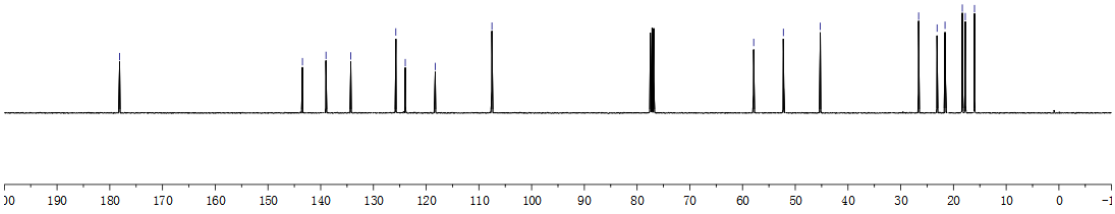
4-(((1,3,4,6-tetramethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3r)



^{1}H NMR spectrum of 3r

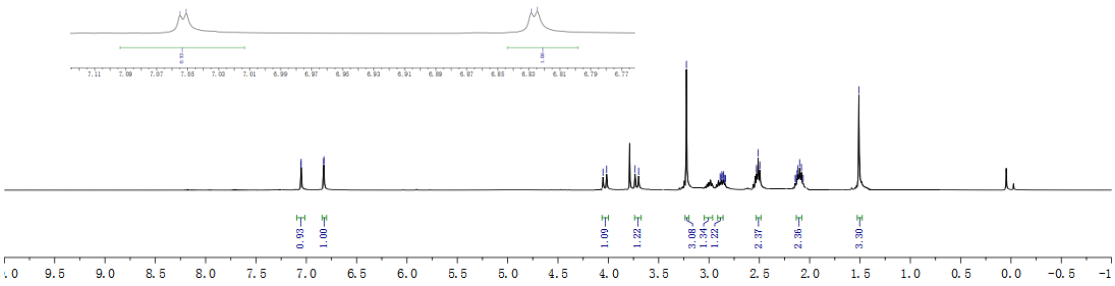


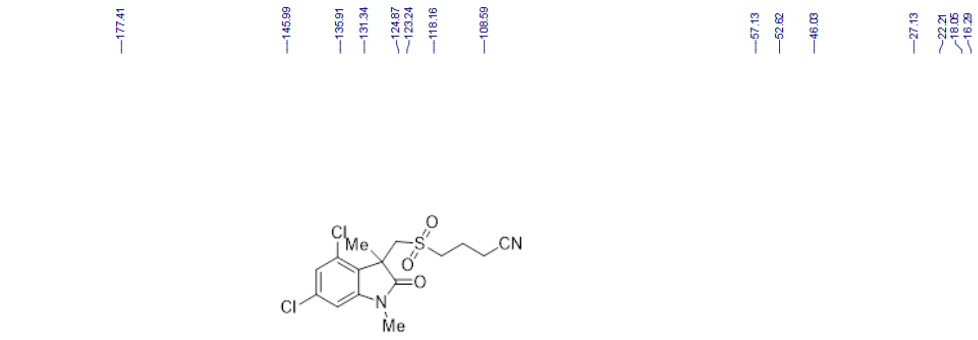
^{13}C NMR spectrum of 3r



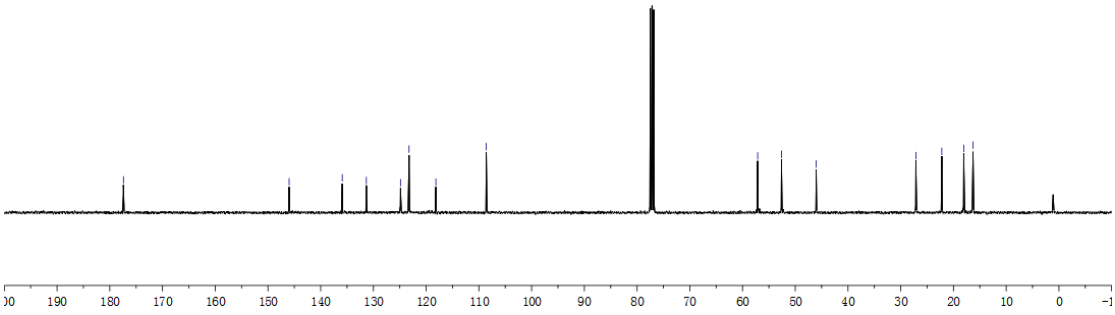
4-(((4,6-dichloro-1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3s)

^{1}H NMR spectrum of 3s

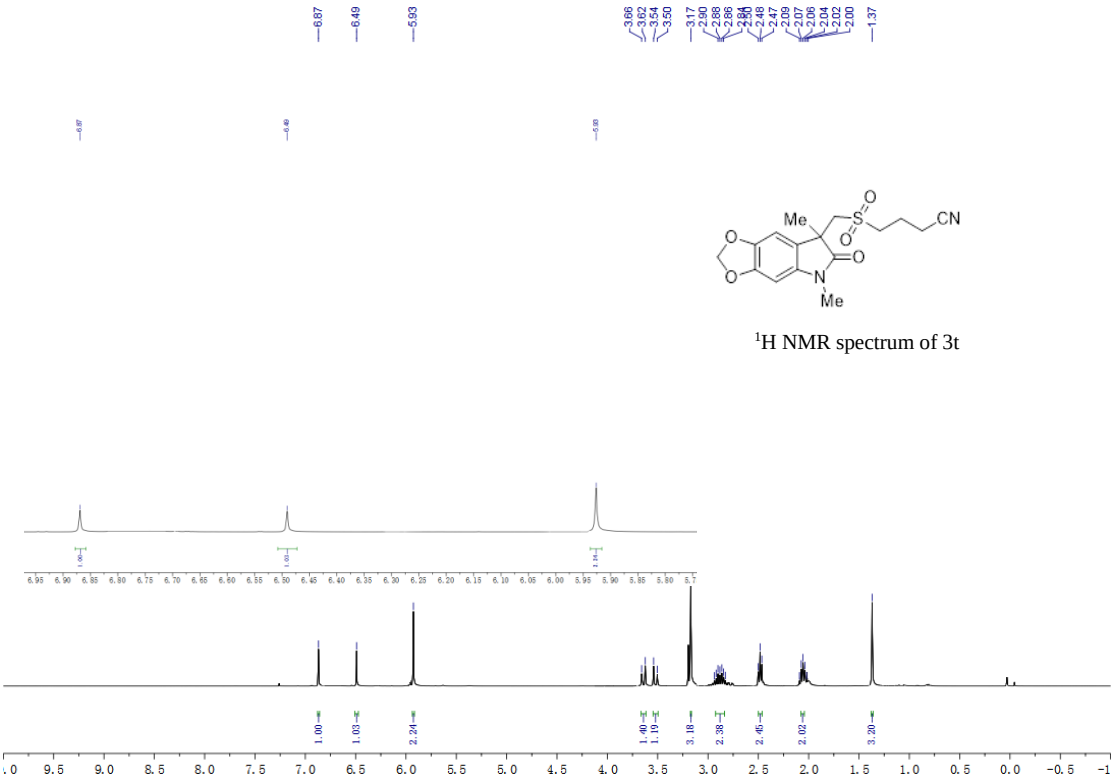




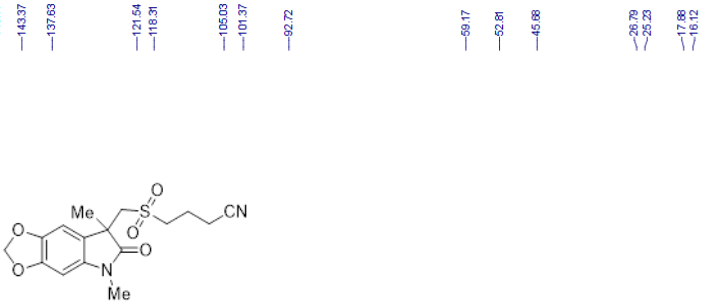
^{13}C NMR spectrum of 3s



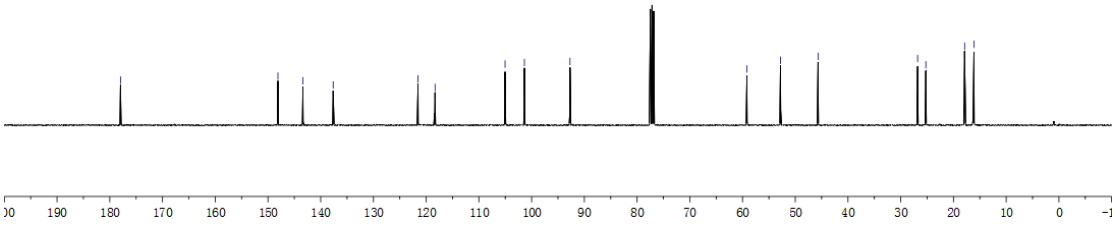
4-(((5,7-dimethyl-6-oxo-6,7-dihydro-5H-[1,3]dioxolo[4,5-f]indol-7-yl)methyl)sulfonyl)butanenitrile (3t)



^{1}H NMR spectrum of 3t

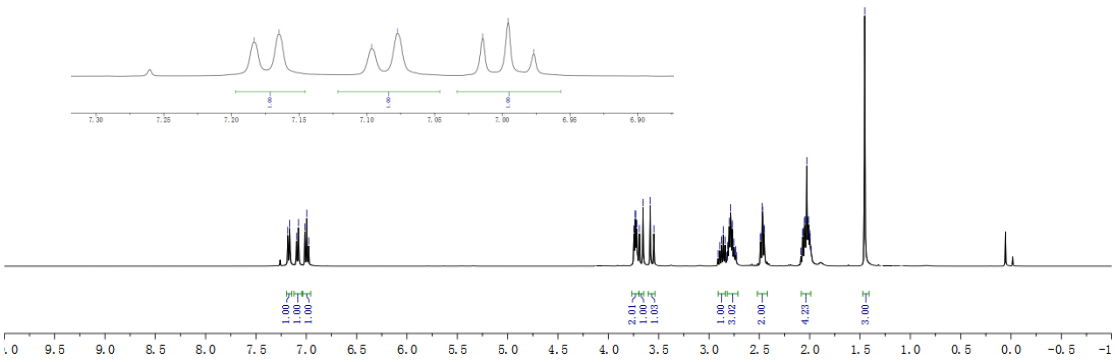


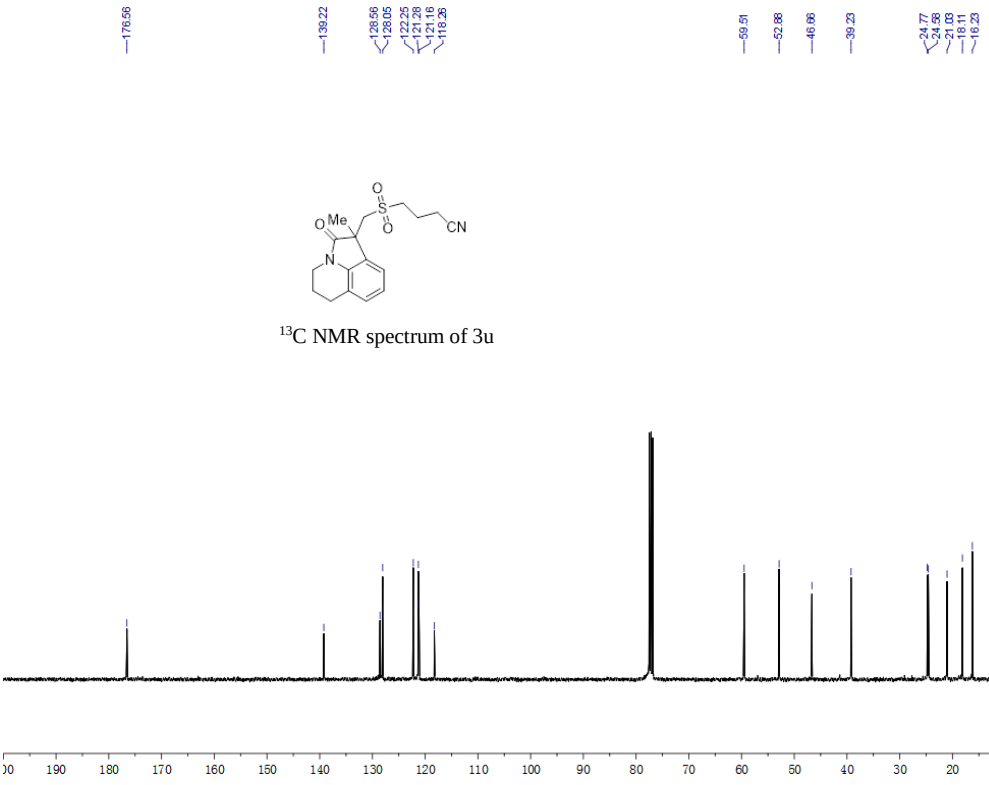
^{13}C NMR spectrum of 3t



4-(((1-methyl-2-oxo-1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolin-1-yl)methyl)sulfonyl)butanenitrile e (3u)

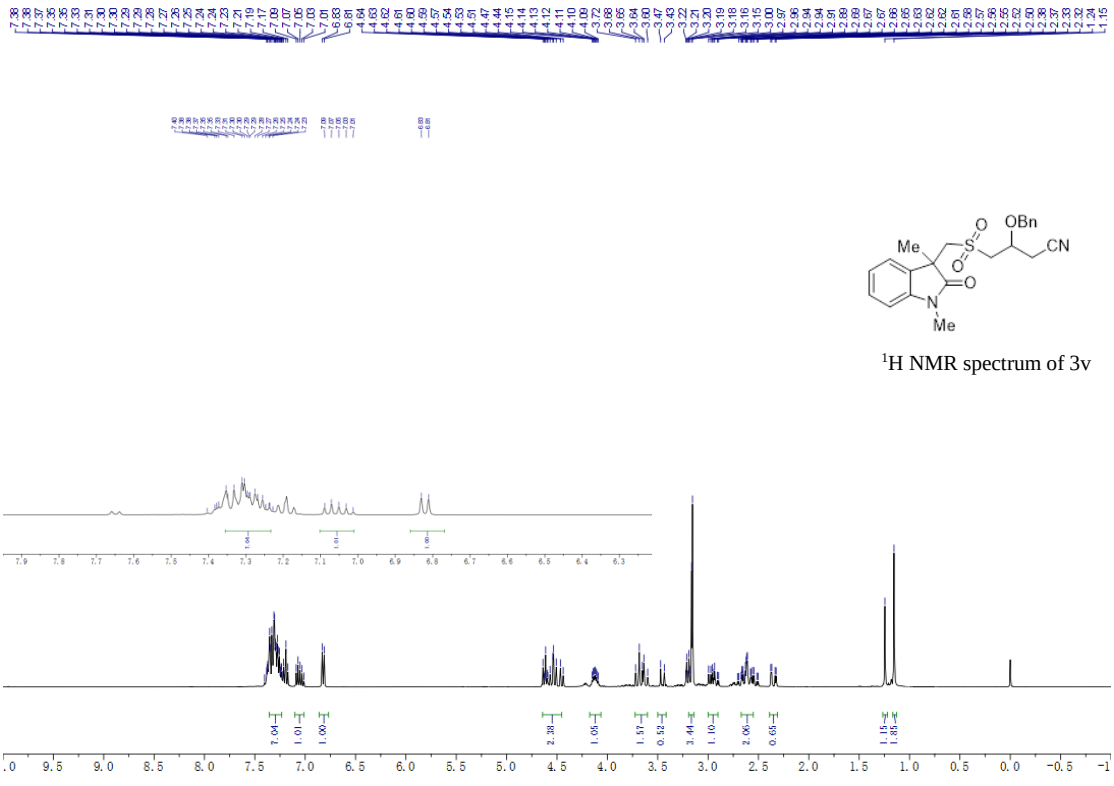
^{1}H NMR spectrum of 3u



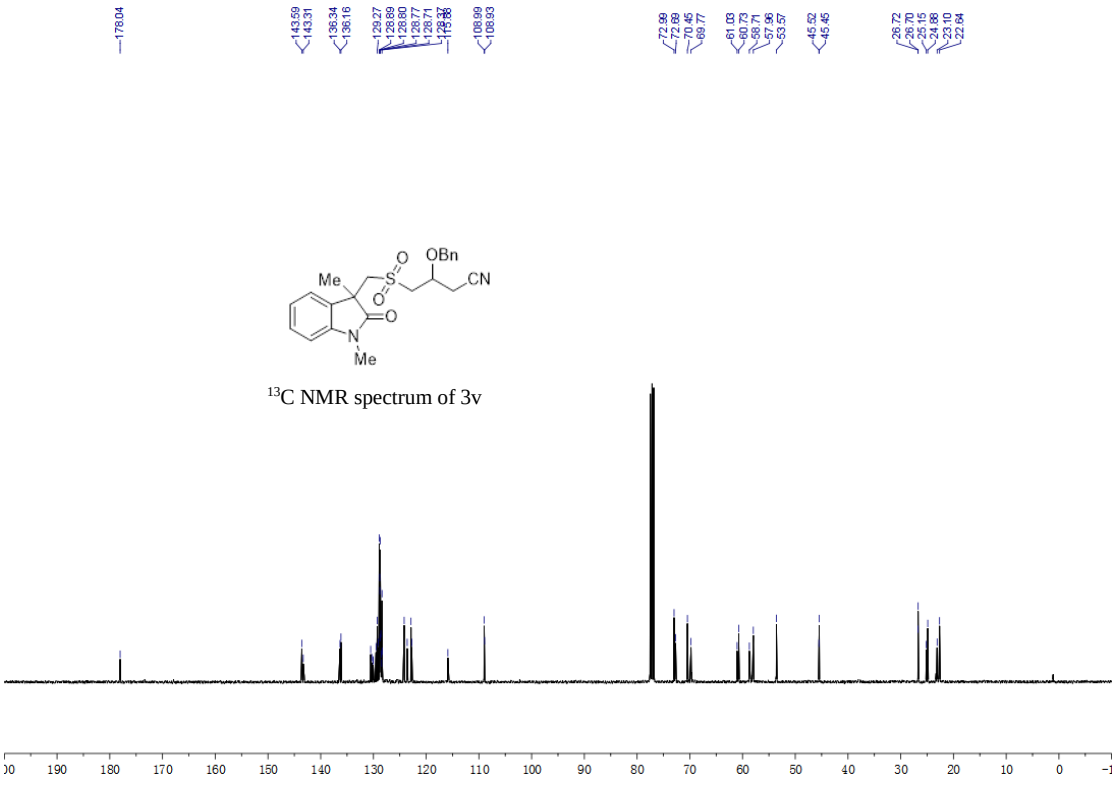


^{13}C NMR spectrum of 3u

3-(benzyloxy)-4-(((1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)butanenitrile (3v)

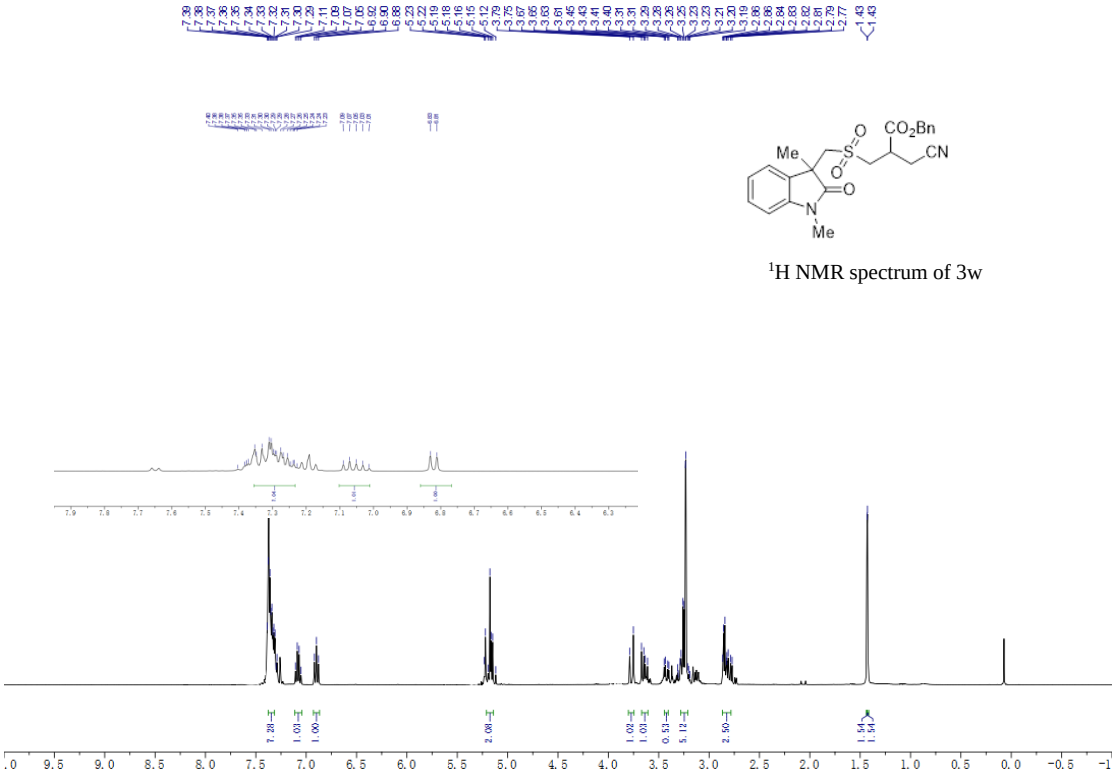


^{1}H NMR spectrum of 3v

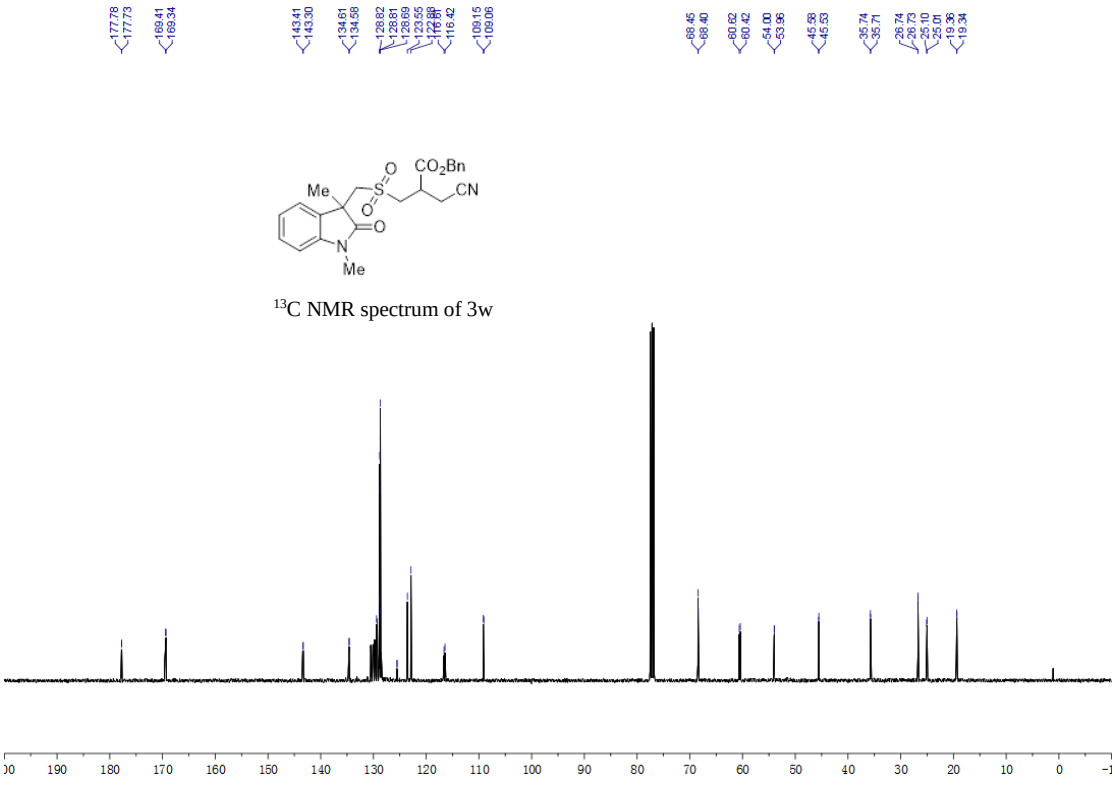


^{13}C NMR spectrum of 3v

benzyl 3-cyano-2-((((1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)methyl)propanoate (3w)

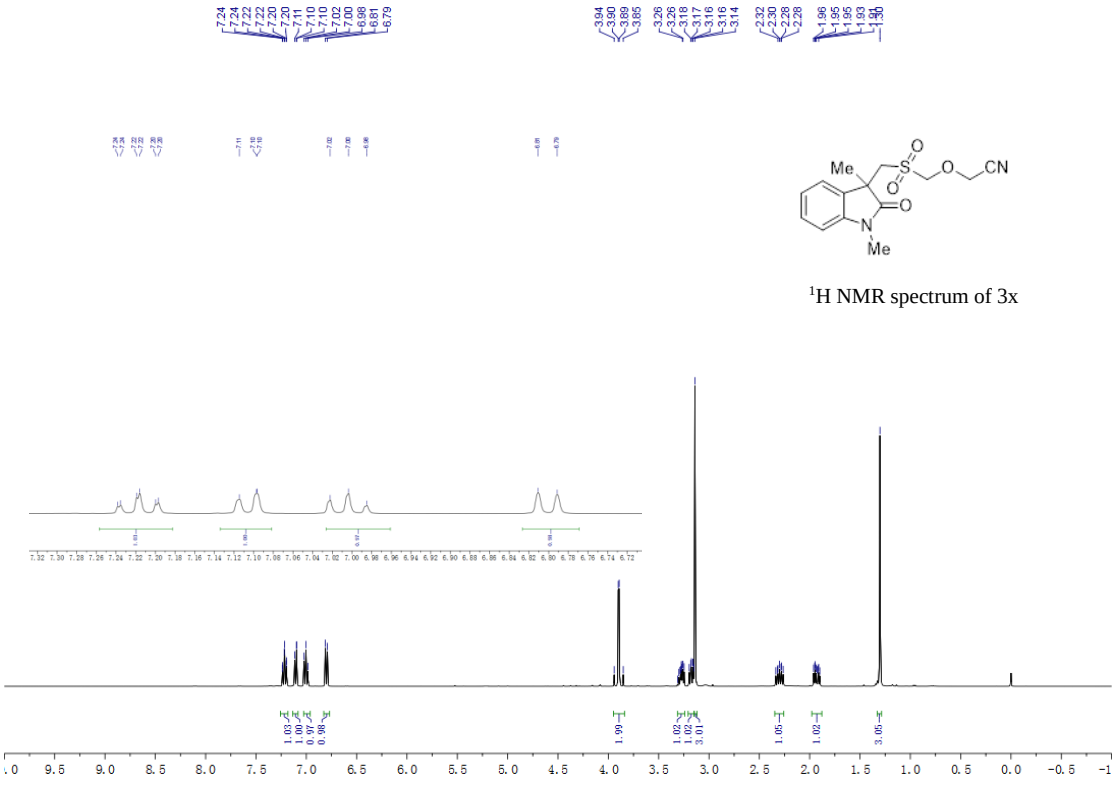


^{1}H NMR spectrum of 3w

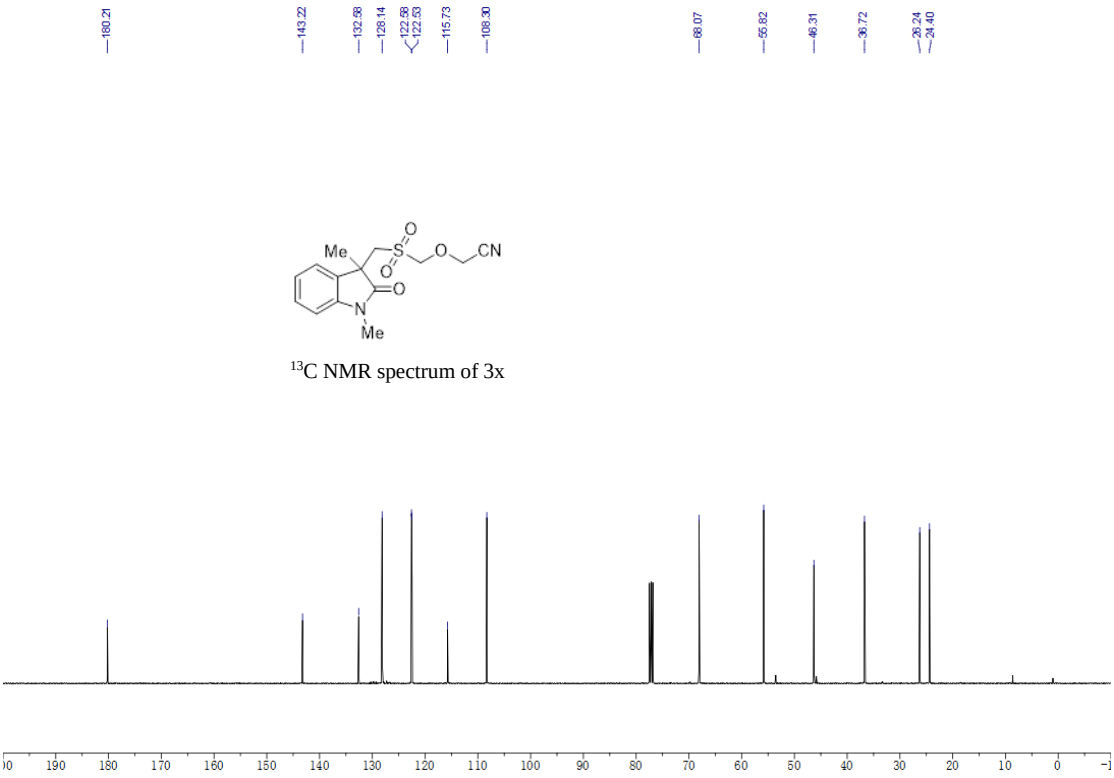


^{13}C NMR spectrum of 3w

2-((((1,3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)methoxy)acetonitrile (3x)

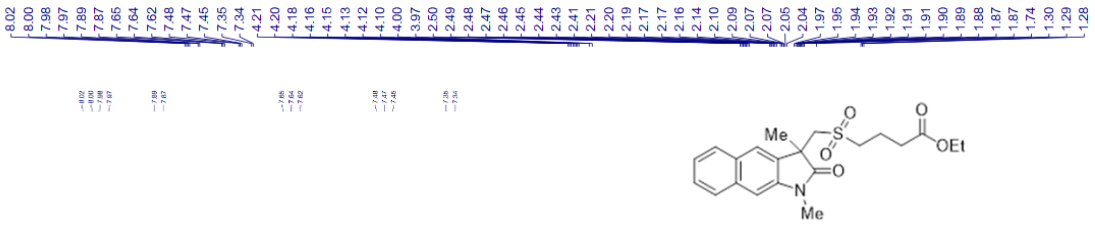


^{1}H NMR spectrum of 3x

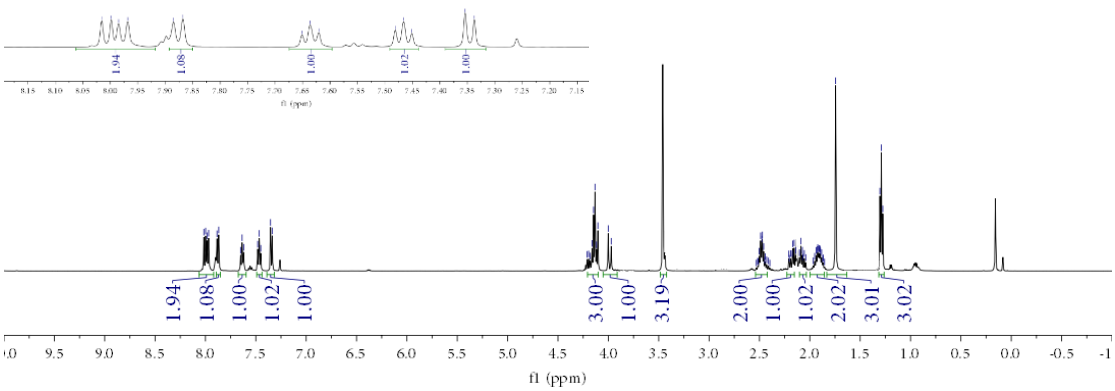


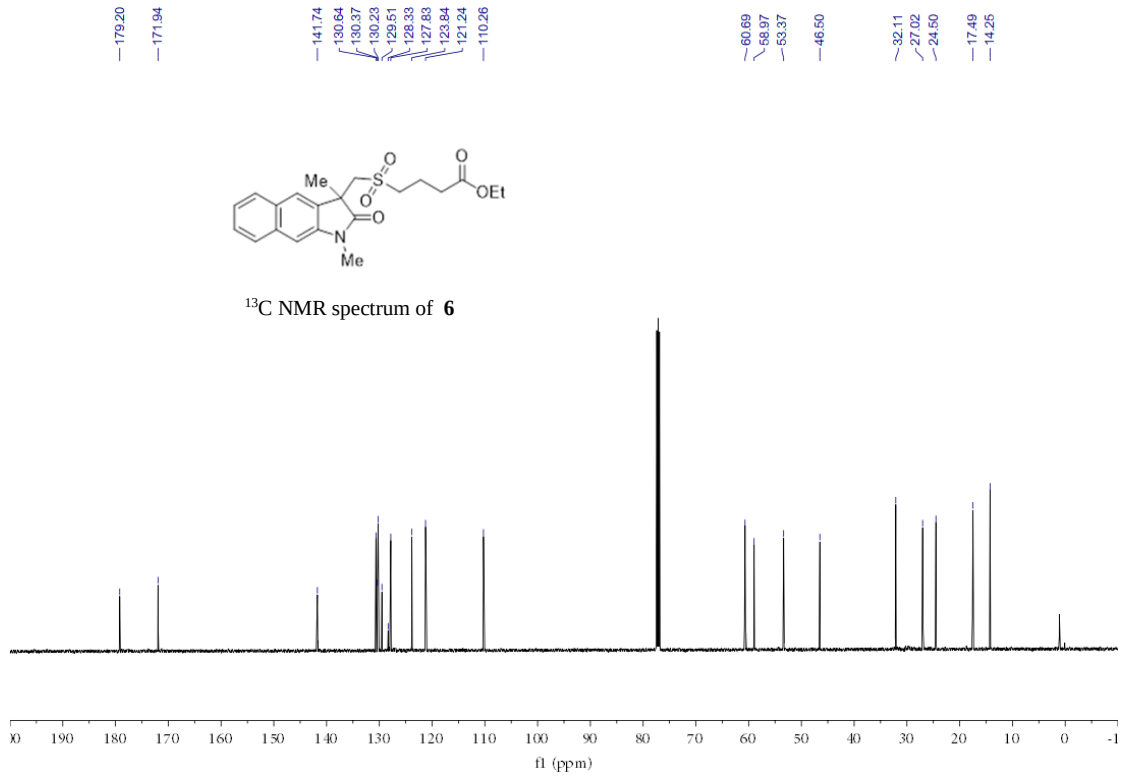
^{13}C NMR spectrum of 3x

ethyl 4-(((1,3-dimethyl-2-oxo-2,3-dihydro-1H-benzo[f]indol-3-yl)methyl)sulfonyl)butanoate (6)



^{1}H NMR spectrum of **6**





^{13}C NMR spectrum of **6**