Visible-light induced acridine-catalyzed selective *N*-dealkylation of *N*-heterocycles

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Supporting Information

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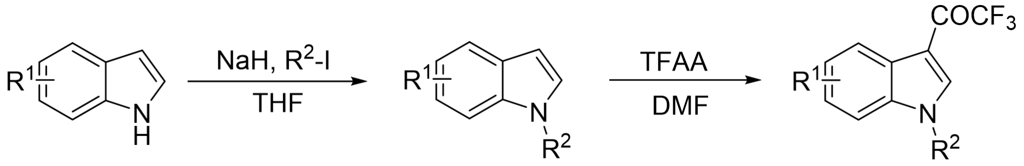
I. General Information

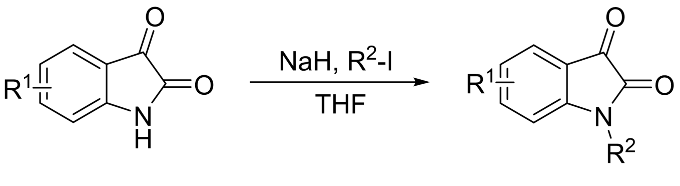
Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers to use without further purification. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. 1H nuclear magnetic resonance (^{1}H NMR) data were acquired at on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, coupling constants J are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 101 MHz on a Bruker Ascend 400 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.16 ppm for $CDCl_3$ as the solvents and tetramethylsilane (TMS) as the internal standard. High resolution mass spectrometry (HRMS) was acquired on a USA-Thermofisher LTQ-Orbitrap XLmass spectrometer.

II. Preparation of Substrates



Add sodium hydride (60% in mineral oil, 15 mmol, 1.5 equiv.) to a well-stirred solution of indole derivative (10 mmol, 1.0 equiv.) in THF (15 mL) at 0 °C. The reaction mixture was warmed to room temperature and allowed to stir for 30 m, After cooling the reaction flask to 0 °C again. alkyl halide (12 mmol, 1.2 equiv.) was added dropwise and the resulting system was stirred at room temperature until the reaction complete (monitor by TLC). The mixture was poured into water and extracted with EtOAc. The organic layer was separated, washed with water and brine, and then dried over anhydrous $MgSO_4$, the solvent was evaporated to afford alkyl-substituted indole crude product. The residue was purified through flash column chromatography on silica gel (petroleum ether:ethyl acetate = 20:1, *v*/*v*) to afford **1j**–**1t**.

A mixture of alkyl-substituted indole crude products was dissolved in DMF (15 mL) and stirred at 0°C, trifluoroacetic anhydride (50 mmol) was added dropwise. After the addition, the reaction mixture was stirred at room temperature until the reaction complete (monitor by TLC), The reaction mixture was poured into water and extracted with EtOAc. The organic layer was separated, washed with water and brine, and then dried over anhydrous $MgSO_4$, the solvent was evaporated and the residue was purified through flash column chromatography on silica gel (petroleum ether:ethyl acetate = 20:1, *v*/*v*) to afford **1a**–**1i**.



Add sodium hydride (60% in mineral oil, 15 mmol, 1.5 equiv.) to a well-stirred solution of indole derivative (10 mmol, 1.0 equiv.) in THF (15 mL) at 0°C.. The reaction mixture was warmed to room temperature and allowed to stir for 30 m, After cooling the reaction flask to 0 °C again. alkyl halide (12 mmol, 1.2 equiv.) was added dropwise and the resulting system was stirred at room temperature until the reaction complete (monitor by TLC). The reaction mixture was poured into water and extracted with

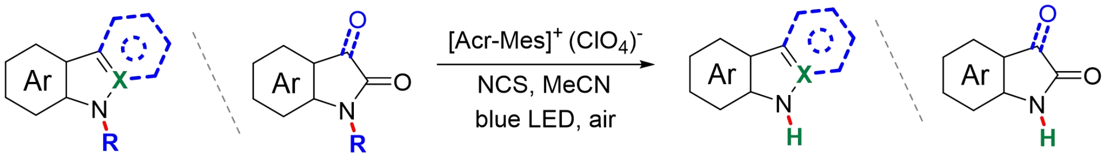
EtOAc. The organic layer was separated, washed with water and brine, and then dried over anhydrous $MgSO_4$, the solvent was evaporated to afford alkyl-substituted indole crude product. The residue was purified through flash column chromatography on silica gel (petroleum ether:ethyl acetate = 10:1, *v*/*v*) to afford **2a**–**2k**.

III. Reaction Results

Table S1 Deviation from the standard conditions[a]

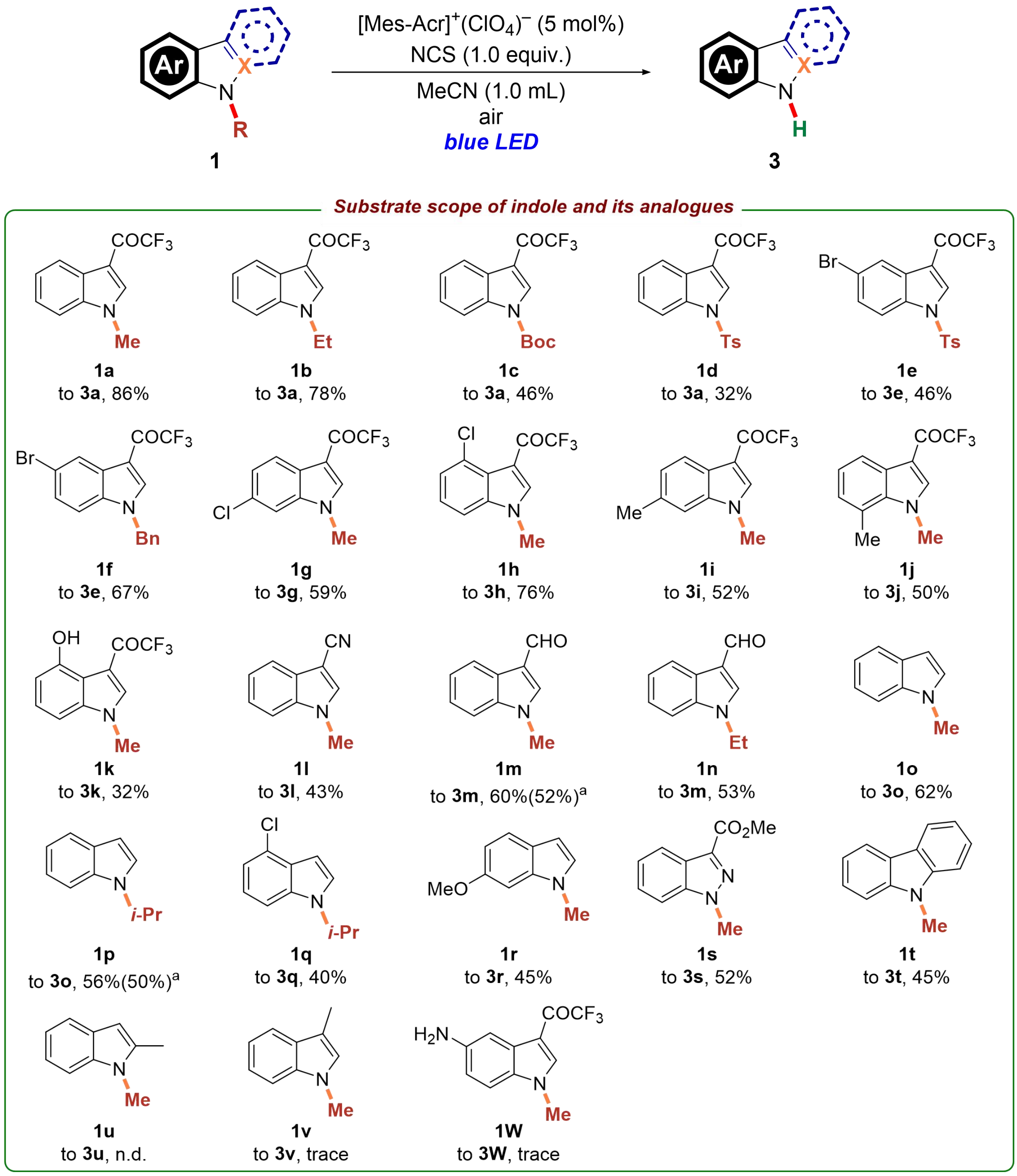
Entry	Deviation from the standard conditions	Yield (%)[b]
1	none	88
2	absence of $[\text{Mes-Acr}]^+\text{ClO}_4^-$	ND
3	absence of light	ND
4	N_2 atmosphere (no air)	ND
5	O_2 atmosphere	62
6	absence of NCS	ND
7	0.5 equiv. of NCS	43
8	absence of H_2O	ND
9	10 μL of H_2O	74 (ND)[c]
10	40 μL of H_2O	36 (trace)[c]
11	0.5 mL of H_2O	trace (72)[c]

[a] Reaction conditions: **1a** (0.10 mmol), NCS (0.10 mmol), and $[\text{Mes-Acr}]^+\text{ClO}_4^-$ (5 mol%) in MeCN (1.0 mL) were stirred at 60 °C for 12 h under air, 400 nm LEDs. [b] Isolated yield reported. [c] Yield of 1-methylindolin-2,3-dione. ND = not detected.



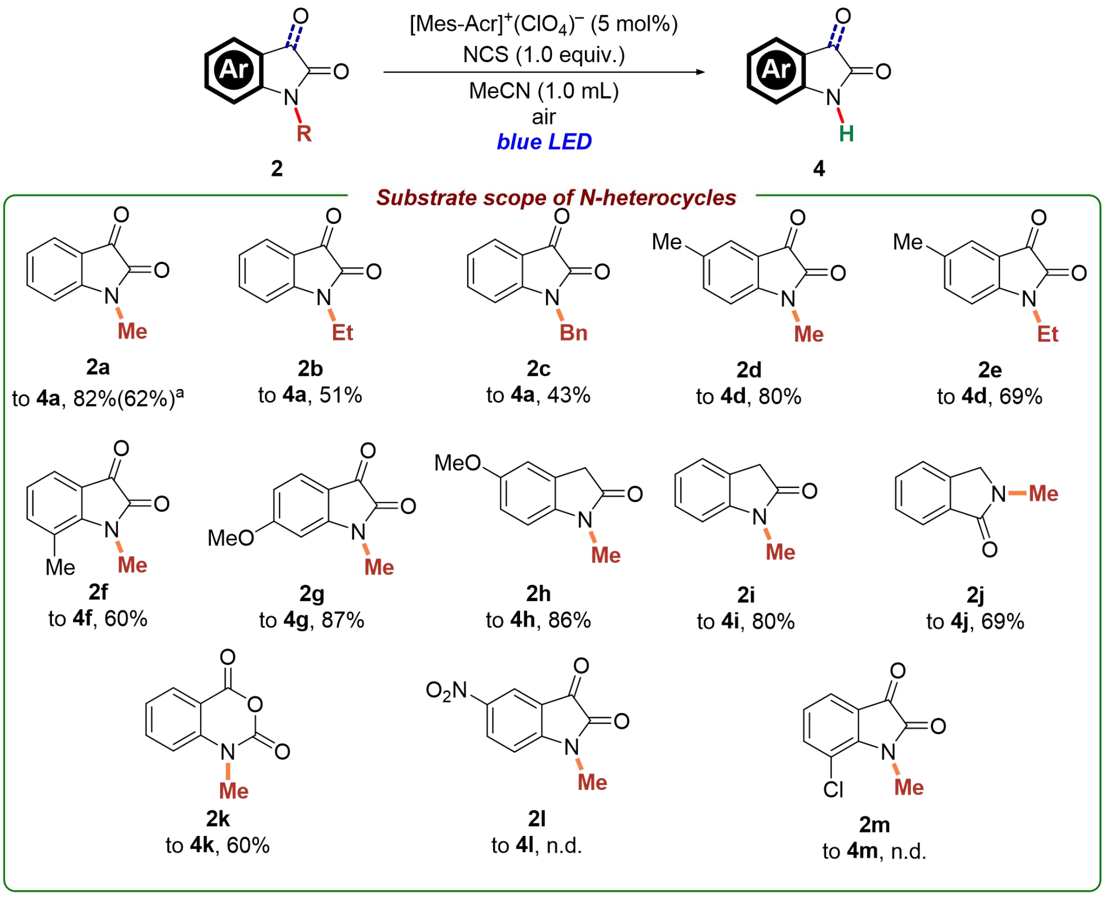
1 **2** **3** **4**

General Procedure for the visible-light induced acridine-catalyzed *N*-dealkylation of *N*-heterocycles: A pressure tube was charged with *N*-heterocycles **1** or **2** (0.1 mmol), $[\text{Mes-Acr}]^+(\text{ClO}_4)^-$ (5 mol%), and NCS (1.0 equiv.) in MeCN. The reaction mixture was stirred under air at 60 °C for 1–12 h under irradiation of 30 W blue LED. Afterwards the product was added with saturated sodium bicarbonate aqueous solution, extracted by ethyl acetate (2×200 mL), and dried over anhydrous Na_2SO_4. After remove;the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel (petroleum ether:ethyl acetate = 20:1, *v*/*v*) to afford **3** or **4**.



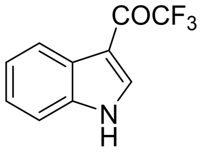
Reaction conditions: **1** (0.10 mmol), NCS (0.10 mmol) and [Mes-Acr]$^+$ClO$_4^-$ (5 mol%) in MeCN (1.0 mL) were stirred at 60 °C for 12 h under air. ^{a} Scaled up to 0.3 mmol.

Scheme S1 Substrate scope of *N*-heterocycles



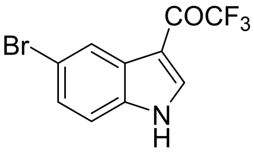
Reaction conditions: **2** (0.10 mmol), NCS (0.10 mmol) and [Mes-Acr]$^+$ClO$_4^-$ (5 mol%) in MeCN (1.0 mL) were stirred at 60 °C for 12 h under air. [a] Scaled up to 0.3 mmol.

Scheme S2 Substrate scope of indole and its analogues



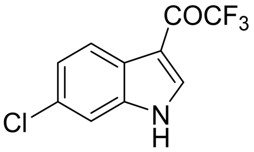
2,2,2-Trifluoro-1-(1*H*-indol-3-yl)ethan-1-one (3a):

White powder (under standard conditions, **1a** gave 18 mg of **3a** in 86% yield, **1b** gave 16 mg of **3a** in 78% yield, **1c** gave 10 mg of **3a** in 46% yield, **1d** gave 9 mg of **3a** in 32% yield; using [Mes-Acr]$^+$BF$_4^-$ as catalyst **1c** gave 8 mg of **3a** in 40% yield; using **Cat-1** as catalyst **1c** gave 7 mg of **3a in** 34% yield). **^{1}H NMR** (400 MHz, DMSO-*d*$_6$): δ = 12.73 (s, 1H), 8.87 – 8.30 (m, 1H), 8.30 – 8.09 (m, 1H), 7.61 (dd, *J* = 6.2, 3.0 Hz, 1H), 7.35 (dt, *J* = 6.7, 3.1 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d*$_6$): δ = 174.39 (q, *J* = 33.8 Hz), 138.11, 137.17, 126.25, 124.85, 123.94, 121.61,117.38 (q, *J* = 290 Hz) 113.52, 109.36 ppm. **^{19}F NMR** (376 MHz, DMSO-*d*$_6$): δ = -71.76 ppm. HRMS (ESI) m/z calculated for $C_{10}H_7F_3NO$ [M+H]$^+$: 214.0474; found 214.0476.



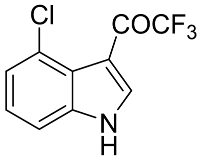
1-(5-Bromo-1*H*-indol-3-yl)-2,2,2-trifluoroethan-1-one (3e):

Yellow powder (**1e** gave 13 mg of **3e** in 46% yield; **1f** gave 19 mg of **3e** in 67% yield). **^{1}H NMR** (400 MHz, DMSO-*d$_6$*): δ = 12.92 (s, 1H), 8.58 (d, *J* = 2.4 Hz, 1H), 8.33 (d, *J* = 1.9 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.53 (dd, *J* = 8.6, 2.0 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d$_6$*): δ = 174.40 (q, J = 34.3 Hz), 138.81, 135.93, 127.97, 127.39 , 123.73, 117.11(q, J = 289 Hz), 116.64, 115.40, 108.85 ppm. **^{19}F NMR** (376 MHz, DMSO-*d$_6$*): δ = -70.98 ppm. HRMS (ESI) m/z calculated for $C_{10}H_6BrF_3NO$ [M+H]$^+$: 291.9579; found 291.9580.



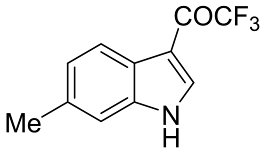
1-(6-Chloro-1*H*-indol-3-yl)-2,2,2-trifluoroethan-1-one (3g):

White powder (59%, 14 mg). **^{1}H NMR** (400 MHz, DMSO-*d$_6$*): δ = 12.81 (s, 1H), 8.54 (s, 1H), 8.27 – 7.97 (m, 1H), 7.66 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d$_6$*): δ = 174.49 (q, *J* = 34.0 Hz), 138.99, 137.71, 129.33, 125.00, 124.19, 122.89, 117.24 (q, *J* = 290 Hz), 113.30, 109.30 ppm. **^{19}F NMR** (376 MHz, DMSO-*d$_6$*): δ = -71.56 ppm. HRMS (ESI) m/z calculated for $C_{10}H_6ClF_3NO$ [M+H]$^+$: 248.0085; found 248.0087.



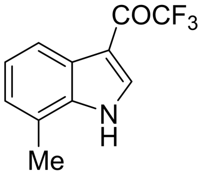
1-(4-Chloro-1*H*-indol-3-yl)-2,2,2-trifluoroethan-1-one (3h):

Yellow powder (76%, 18 mg). **^{1}H NMR** (400 MHz, DMSO-*d$_6$*): δ = 12.76 (s, 1H), 8.36 (s, 1H), 7.39 (d, *J* = 5.2 Hz, 1H), 7.14 (t, *J* = 6.7 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d$_6$*): δ = 172.84 (q, *J* = 33 Hz) , 139.43, 126.19, 125.74, 125.13, 123.42, 117.57 (q, *J* = 293.1 Hz), 112.57, 109.18 ppm. .**^{19}F NMR** (376 MHz, DMSO-*d$_6$*): δ = -70.63 ppm. HRMS (ESI) m/z calculated for $C_{10}H_6ClF_3NO$ [M+H]$^+$: 248.0085; found 248.0084.



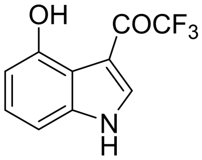
2,2,2-Trifluoro-1-(6-methyl-1*H*-indol-3-yl)ethan-1-one (3i):

Yellow powder (52%, 12 mg). **^{1}H NMR** (400 MHz, DMSO-*d$_6$*): δ = 12.63 (s, 1H), 8.45 (d, *J* = 2.8 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 2.47 (s, 3H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d$_6$*): δ = 174.23 (q, *J* = 34.0 Hz), 137.58, 134.34, 125.46, 124.02, 121.29, 117.74 (q, *J* = 290 Hz), 113.22, 109.38, 21.68 ppm. .**^{19}F NMR** (376 MHz, DMSO-*d$_6$*): δ = -71.86 ppm. HRMS (ESI) m/z calculated for $C_{11}H_9F_3NO$ [M+H]$^+$: 228.0631; found 228.0628.



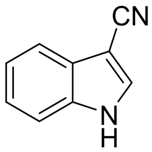
2,2,2-Trifluoro-1-(7-methyl-1*H*-indol-3-yl)ethan-1-one (3j):

White powder (50%, 11 mg). **^{1}H NMR** (400 MHz, DMSO-*d$_6$*): δ = 8.43 (s, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 2.54 (s, 3H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d$_6$*): δ = 174.37 (q, *J* = 33.9 Hz), 137.64, 136.68, 126.15, 125.47, 124.13, 123.10, 119.11, 117.42 (q, *J* = 291.5 Hz), 109.71, 17.12 ppm. **^{19}F NMR** (376 MHz, DMSO-*d$_6$*): δ = -71.81 ppm. HRMS (ESI) m/z calculated for $C_{11}H_9F_3NO$ [M+H]$^+$: 228.0631; found 228.0633.



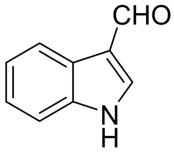
2,2,2-Trifluoro-1-(4-hydroxy-1*H*-indol-3-yl)ethan-1-one (3k):

Yellow powder (32%, 7 mg). **^{1}H NMR** (400 MHz, DMSO-*d$_6$*): δ = 13.24 (s, 1H), 8.68 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.48 (t, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d$_6$*): δ = 173.33 (q, *J* = 33.5 Hz), 156.01, 142.19, 140.71, 139.77, 125.93, 118.12 (q, *J* = 291.5 Hz), 116.53, 113.51, 108.49 ppm. **^{19}F NMR** (376 MHz, DMSO-*d$_6$*): δ = -70.65 ppm. HRMS (ESI) m/z calculated for $C_{10}H_7F_3NO$ [M+H]$^+$: 230.0423; found 230.0428.



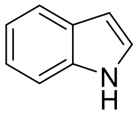
1*H*-Indole-3-carbonitrile (3l):

Yellow oil (under standard conditions, **1l** gave 6 mg of **3l** in 43% yield; using [Mes-Acr]$^+$BF$_4^-$ as catalyst, **1l** gave 5 mg of **3l** in 37% yield; using **Cat-1** as catalyst, **1l** gave 4 mg of **3l** in 31% yield). **^{1}H NMR** (400 MHz, DMSO-*d$_6$*): δ = 12.22 (s, 1H), 8.27 (d, *J* = 1.7 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.19 (m, 2H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d$_6$*): δ = 135.71, 135.00, 127.23, 123.87, 122.19, 118.92, 116.93, 113.45, 84.71 ppm. HRMS (ESI) m/z calculated for $C_9H_7N_2$ [M+H]$^+$: 143.0604; found 143.0605.



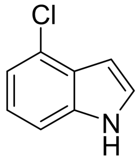
1*H*-Indole-3-carbaldehyde (3m):

Brown powder (**1m** gave 9 mg of **3m** in 60% yield**;** **1n** gave 8 mg of **3m** in 53% yield**,** scaled up **1m** to 0.3 mmol, providing 22 mg of **3m** in 52% yield). **^{1}H NMR** (400 MHz, DMSO-*d$_6$*): δ = 11.98 (s, 1H), 9.98 (s, 1H), 8.31 (s, 1H), 8.17 (d, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d$_6$*): δ = 185.50, 139.00, 137.60, 124.65, 123.98, 122.66, 121.38, 118.70, 112.96 ppm. HRMS (ESI) m/z calculated for C_9H_8NO [M+H]$^+$: 146.0600; found 146.0603.



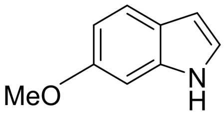
1*H*-Indole (3o):

Brown particles (**1o** gave 7 mg of **3o** in 62% yield, **1p** gave 6 mg of **3o** in 56% yield. scaled up **1p** to 0.3 mmol, providing 15 mg of **3o** in 50% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 8.04 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.28 – 7.24 (m, 1H), 7.22 (t, *J* = 2.9 Hz, 1H), 6.66 (t, *J* = 2.6 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*): δ = 135.87, 127.94, 124.35, 122.10, 120.86, 119.95, 111.22, 102.64 ppm. HRMS (ESI) m/z calculated for C_8H_8N [M+H]$^+$: 118.0651; found 118.0654.



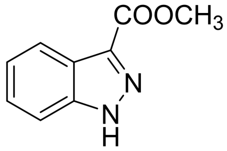
4-Chloro-1*H*-indole (3q):

Yellow oil (40%, 6 mg). ^{1}**H NMR** (400 MHz, DMSO-*d*$_6$): *δ* = 11.52 (s, 1H), 7.48 (d, *J* = 2.8 Hz, 2H), 7.11 (d, *J* = 4.9 Hz, 2H), 6.57 (t, *J* = 2.6 Hz, 1H) ppm. ^{13}**C NMR** (101 MHz, DMSO-*d*$_6$): *δ* = 137.32, 126.87, 124.94, 122.28, 118.97, 111.15, 99.90 ppm. HRMS (ESI) m/z calculated for C_8H_7ClN [M+H]$^+$: 152.0262; found 152.0265.



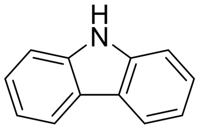
6-Methoxy-1*H*-indole (3r):

Yellow oil (45%, 7 mg). ^{1}**H NMR** (400 MHz, Chloroform-*d*): *δ* = 8.08 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.16 (q, *J* = 2.5 Hz, 1H), 6.91 (ddt, *J* = 13.0, 4.4, 2.4 Hz, 2H), 6.57 (q, *J* = 2.5 Hz, 1H), 3.93 (d, *J* = 3.0 Hz, 3H) ppm. ^{13}**C NMR** (101 MHz, Chloroform-*d*): *δ* = 156.49, 136.62, 123.13, 122.22, 121.34, 109.99, 102.51, 94.61, 55.77 ppm. HRMS (ESI) m/z calculated for $C_9H_{10}NO$ [M+H]$^+$: 147.0757; found 147.0763.



Methyl 1*H*-indazole-3-carboxylate (3s):

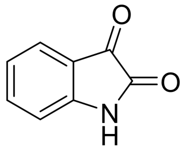
Yellow powder (52%, 9 mg). ^{1}**H NMR** (400 MHz, Chloroform-*d*): *δ* = 13.65 (s, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.70 – 7.45 (m, 1H), 7.45 - 7.12 (m, 1H), 4.14 (d, *J* = 2.5 Hz, 3H) ppm. ^{13}**C NMR** (101 MHz, Chloroform-*d*): *δ* = 163.85, 141.62, 136.05, 127.36, 123.36, 122.37, 121.63, 111.90, 52.23 ppm. HRMS (ESI) m/z calculated for $C_9H_9N_2O_2$ [M+H]$^+$: 177.0659; found 177.0663.



9*H*-Carbazole (3t):

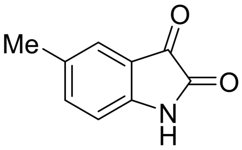
Light yellow powder (45%, 8 mg). ^{1}**H NMR** (400 MHz, DMSO-*d*$_6$): *δ* = 11.27 (s, 1H), 8.12 (d, *J* = 7.9 Hz, 2H), 7.46 (dd, *J* = 41.4, 7.7 Hz, 4H), 7.18 (d, *J* = 7.3 Hz, 2H) ppm.

^{13}C NMR (101 MHz, DMSO-d$_6$): *δ* = 140.23, 125.99, 122.91, 120.63, 118.97, 111.43 ppm. HRMS (ESI) m/z calculated for $C_{12}H_{10}N$ [M+H]$^+$: 168.0808; found 168.0811.



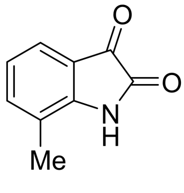
Indoline-2,3-dione (4a):

Orange powder (**2a** gave 12 mg of **4a** in 82% yield, **2b** gave 7 mg of **4a** in 51% yield, **2c** gave 6 mg of **4a** in 43% yield; scaled up **2a** to 0.3 mmol, providing 27 mg of **4a** in 62% yield).**^{1}H NMR** (400 MHz, DMSO-*d*$_6$): *δ* = 11.05 (s, 1H), 7.70 – 7.34 (m, 2H), 7.07 (d, *J* = 3.0 Hz, 1H), 6.96 – 6.65 (m, 1H) ppm. **^{13}C NMR** (101 MHz, DMSO-d$_6$): *δ* = 184.89, 159.85, 151.23, 138.87, 125.18, 123.26, 118.31, 112.71 ppm. HRMS (ESI) m/z calculated for $C_8H_6NO_2$ [M+H]$^+$: 148.0393; found 148.0395.



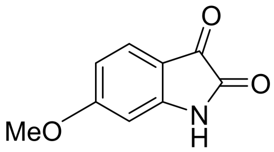
5-Methylindoline-2,3-dione (4d):

Orange powder (80%, 13 mg). **^{1}H NMR** (400 MHz, DMSO-*d*$_6$): *δ* = 10.93 (d, *J* = 4.9 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.30 (s, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 2.26 (d, *J* = 5.0 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, DMSO-d$_6$): *δ* = 185.07, 159.94, 149.04, 139.29, 132.50, 125.27, 118.25, 112.52, 20.58 ppm. HRMS (ESI) m/z calculated for $C_9H_8NO_2$ [M+H]$^+$: 162.0550; found 162.0554.



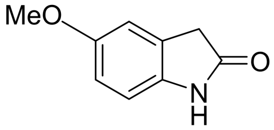
7-Methylindoline-2,3-dione (4f):

Orange powder (80%, 13 mg). **^{1}H NMR** (400 MHz, DMSO-*d*$_6$): *δ* = 11.09 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 2.19 (s, 3H) ppm. **^{13}C NMR** (101 MHz, DMSO-d$_6$): *δ* = 185.23, 160.45, 149.74, 139.95, 123.09, 122.51, 122.06, 118.02, 15.93 ppm. HRMS (ESI) m/z calculated for $C_9H_8NO_2$ [M+H]$^+$: 162.0550; found 162.0551.



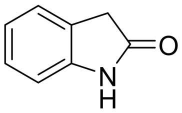
5-Methoxyindoline-2,3-dione (4g):

Orange powder (87%, 15 mg). ^{1}**H NMR** (400 MHz, DMSO-*d*$_6$): δ = 10.97 (s, 1H), 7.58 – 7.16 (m, 1H), 6.98 – 6.50 (m, 1H), 6.39 (t, *J* = 2.3 Hz, 1H), 3.88 (dd, *J* = 4.6, 2.6 Hz, 3H) ppm. ^{13}**C NMR** (101 MHz, DMSO-*d*$_6$): δ = 182.02, 168.24, 161.09, 154.05, 127.78, 111.66, 109.32, 98.30, 56.63 ppm. HRMS (ESI) m/z calculated for $C_9H_8NO_3$ [M+H]$^+$: 178.0499; found 178.0505.



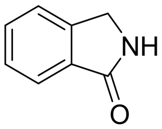
5-Methoxyindolin-2-one (4h):

Reddish-brown powder (86%, 14 mg). ^{1}**H NMR** (400 MHz, DMSO-*d*$_6$): δ = 10.20 (s, 1H), 6.88 (s, 1H), 6.80 – 6.56 (m, 2H), 3.71 (d, *J* = 2.0 Hz, 3H), 3.46 (s, 2H) ppm. ^{13}**C NMR** (101 MHz, DMSO-*d*$_6$): δ = 176.66, 155.06, 137.52, 127.59, 112.66, 111.96, 109.83, 55.90, 36.73 ppm. HRMS (ESI) m/z calculated for $C_9H_{10}NO_2$ [M+H]$^+$: 164.0706; found 164.0710.



Indolin-2-one (4i):

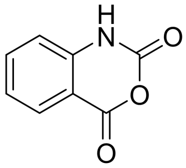
White powder (80%, 11 mg). ^{1}**H NMR** (400 MHz, Chloroform-*d*): δ = 9.15 (s, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 3.58 (s, 2H) ppm. ^{13}**C NMR** (101 MHz, Chloroform-d): δ = 178.22, 142.67, 127.98, 125.35, 124.63, 122.38, 109.91, 36.37 ppm. HRMS (ESI) m/z calculated for C_8H_8NO [M+H]$^+$: 134.0600; found 134.0604.



Isoindolin-1-one (4j):

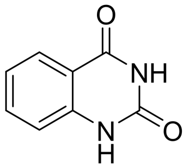
Brown crystals (69%, 9 mg). ^{1}**H NMR** (400 MHz, Chloroform-*d*): δ = 8.38 (s, 1H), 7.93

– 7.85 (m, 1H), 7.59 (td, *J* = 7.5, 1.2 Hz, 1H), 7.54 – 7.44 (m, 2H), 4.50 (s, 2H) ppm. **^{13}C NMR** (101 MHz, Chloroform-*d*): *δ* = 172.50, 143.83, 132.33, 131.72, 123.65, 123.22, 45.94 ppm. HRMS (ESI) m/z calculated for C_8H_8NO $[M+H]^+$: 134.0600; found 134.0601.



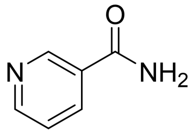
2*H*-Benzo[d][1,3]oxazine-2,4(1*H*)-dione (4k):

Brown powder (60%, 10 mg). **^{1}H NMR** (400 MHz, DMSO-*d*$_6$): *δ* = 11.76 (s, 1H), 8.38 – 7.84 (m, 1H), 7.75 (d, *J* = 4.1 Hz, 1H), 7.55 – 6.80 (m, 2H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d*$_6$): *δ* = 160.38, 147.59, 141.92, 137.44, 129.44, 124.03, 115.86, 110.75 ppm. HRMS (ESI) m/z calculated for $C_8H_6NO_3$ $[M+H]^+$: 164.0342; found 164.0347.



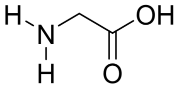
Quinazoline-2,4(1*H*,3*H*)-dione:

Brown powder (76%, 12 mg). **^{1}H NMR** (400 MHz, DMSO-*d*$_6$): *δ* = 11.31 (s, 1H), 11.16 (s, 1H), 7.90 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.64 (td, *J* = 7.7, 7.2, 1.5 Hz, 1H), 7.18 (dt, *J* = 7.3, 3.2 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, Chloroform-d): *δ* = 163.35, 150.82, 141.35, 135.45, 127.45, 122.83, 115.82, 114.82 ppm. HRMS (ESI) m/z calculated for $C_8H_7N_2O_2$ $[M+H]^+$: 163.0502; found 163.0506.



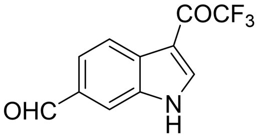
Nicotinamide:

White powder (64%, 8 mg). **^{1}H NMR** (400 MHz, DMSO-*d*$_6$): *δ* = 9.03 (t, *J* = 3.1 Hz, 1H), 8.70 (d, *J* = 4.6 Hz, 1H), 8.30 – 8.15 (m, 1H), 8.16 (s, 1H), 7.61 (s, 1H), 7.49 (p, *J* = 3.7, 3.0 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, DMSO-d$_6$): *δ* = 166.95, 152.36, 149.15, 135.68, 130.19, 123.91 ppm. HRMS (ESI) m/z calculated for $C_6H_7N_2O$ $[M+H]^+$: 123.0553; found 123.0557.



Glycine:

White powder (52%, 5 mg). **^{1}H NMR** (400 MHz, D_2O): δ = 3.50 (s, 2H) ppm. **^{13}C NMR** (101 MHz, D_2O): δ = 172.41, 41.38 ppm. HRMS (ESI) m/z calculated for $C_2H_6NO_2$ $[M+H]^+$: 76.0393; found 76.0398.

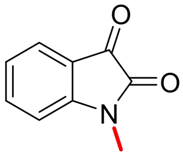


3-(2,2,2-Trifluoroacetyl)-1*H*-indole-6-carbaldehyde (3i')[6]**:**

White powder (byproduct of the demethylation of **1i:** 19%, 5 mg). **^{1}H NMR** (400 MHz, DMSO-*d*$_6$): δ = 10.10 (s, 1H), 8.76 (d, *J* = 2.3 Hz, 1H), 8.35 (d, *J* = 8.2 Hz, 1H), 8.16 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 1H) ppm. **^{13}C NMR** (101 MHz, DMSO-*d*$_6$): δ = 193.29, 174.47 (q, *J* =33.4 Hz), 141.26, 136.91, 133.23, 131.00, 124.05, 121.97, 117.17 (q, *J* = 292 Hz), 116.42, 109.50 ppm. HRMS (ESI) m/z calculated for $C_{11}H_7F_3NO_2$ $[M+H]^+$: 242.0423; found 242.0427.

IV. Mechanistic Studies

4.1 Control experiments



Methylindoline-2,3-dione (2a):

Orange powder (11.6 mg, 72% yield). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.85 – 7.46 (m, 2H), 7.14 (s, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.26 (s, 3H) ppm. **^{13}C NMR** (151 MHz, chloroform-*d*): δ = 183.38, 158.25, 151.48, 138.45, 125.31, 123.87, 117.45, 109.96, 26.25 ppm. HRMS (ESI) m/z calculated for $C_9H_8NO_2$ $[M+H]^+$: 162.0550; found 162.0555.

possible reaction mechanism for 1-methylindoline-2,3-dione

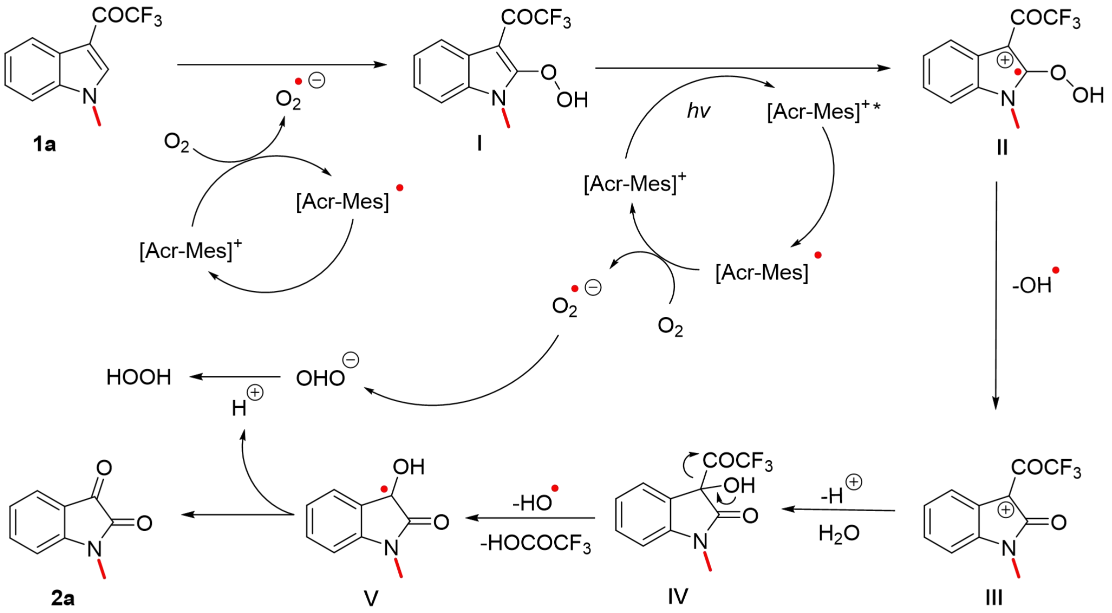


Figure S1 Possible reaction mechanism

4.2 Light on/off experiment

Following the general procedure, four reactions were set up in parallel. Sequentially, the reactons were stopped and quenched after the indicated reaction times. The yield was determined by ^{1}H NMR with CH_2Br_2 as internal standard.

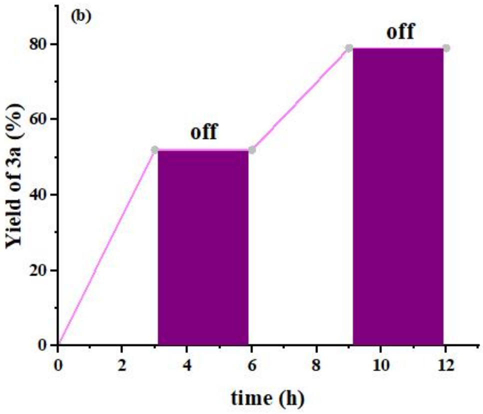


Figure S2 Light on/off experiment

4.3 Fluorescence quenching experiments

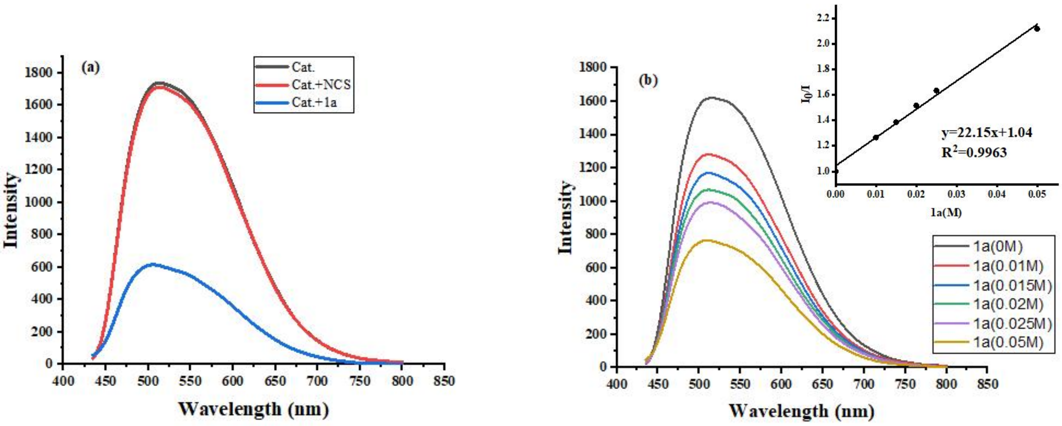


Figure S3 Luminescence quenching study

Emission intensities were recorded using an F-4600 FL, spectrophotometer. First, the emissionintensity of [Mes-Acr]$^+$ClO$_4^-$ solutions was observed at 510 nm. The solutions were irradiated at 400 nm (Maximum absorption wavelength of [Mes-Acr]$^+$ClO$_4^-$ and fluorescence was measured from 420 nm to 800 nm. In a typical experiment, the emission spectrum of a 5 x10^{-3} M solution of [Mes-Acr]$^+$ClO$_4^-$ with **1a** and NCS in MeCN in 10 mm path length quartz cuvette was collected. Figure S3-a) the emission spectra of 5 x 10^{-3} M solutions of [Mes-Acr]$^+$ClO$_4^-$ with reactants (**1a** and NCS) in MeCN; b) the emission spectra of a 5 x10^{-3} M solution of [Mes-Acr]$^+$ClO$_4^-$ with various concentrations of **1a** in MeCN and the linear relationship between I_0/I and the increasing concentration of **1a** (I_0 and I are the fluorescence intensities before and after the increasing the concentration of **1a**, respectively).

4.4 Set of experiment

Table S2 Sensitivity assessment experiments[a]

Parameter	Variation		Description	Yield[b]	Deviation[c]
Concentration (c)	High c	c+10% c	0.9 mL MeCN	86%	-2%
	Low c	c-10% c	1.1 mL MeCN	84%	-4%
Temperature (T)	High T	T+10 °C	70 °C	37%	-51%
	Low T	T-10 °C	50 °C	33%	-55%
Light intensity (I)	High I	1.5 I	45 W	83%	-5%
	Low I	0.5 I	15 W	ND	-88%
catalyst level (Cat.)	High Cat.		10 mol%	87%	-1%
	Low Cat.		5 mol%	18%	-70%
wavelength of light (W)	Purple Light		365 nm	ND	-88%

[a] Reaction conditions: **1a** (0.10 mmol), NCS (0.10 mmol) and $[\text{Mes-Acr}]^+\text{ClO}_4^-$ (5mol%) in MeCN (1.0 mL) were stirred at 60 °C for 12 h under air, 425 nm LEDs, isolated yield reported. [b] The average yield of three parallel reactions. [c] Deviation from the yield of standard reaction.

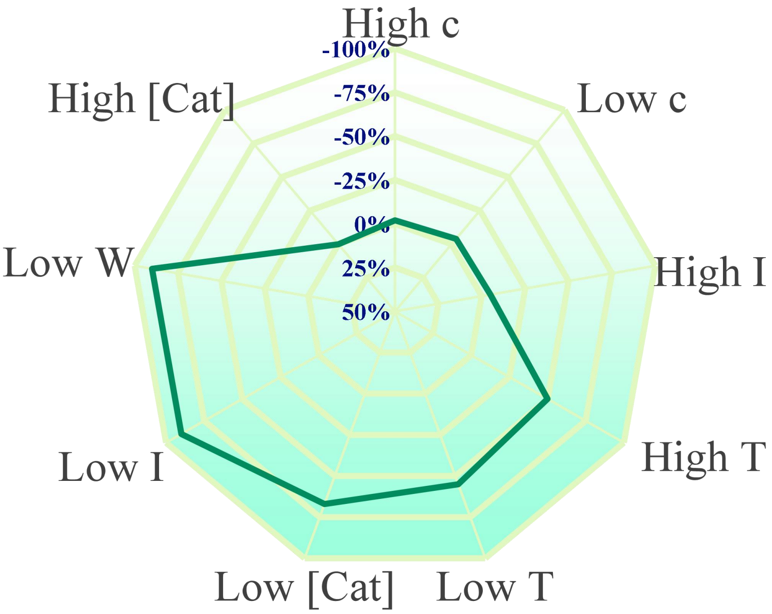
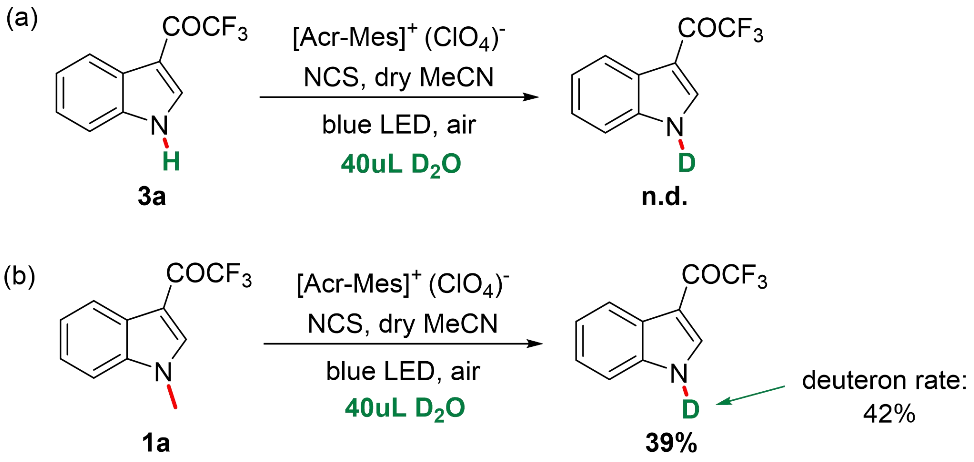


Figure S4 Sensitivity assessment

4.5 Investigation of proton source



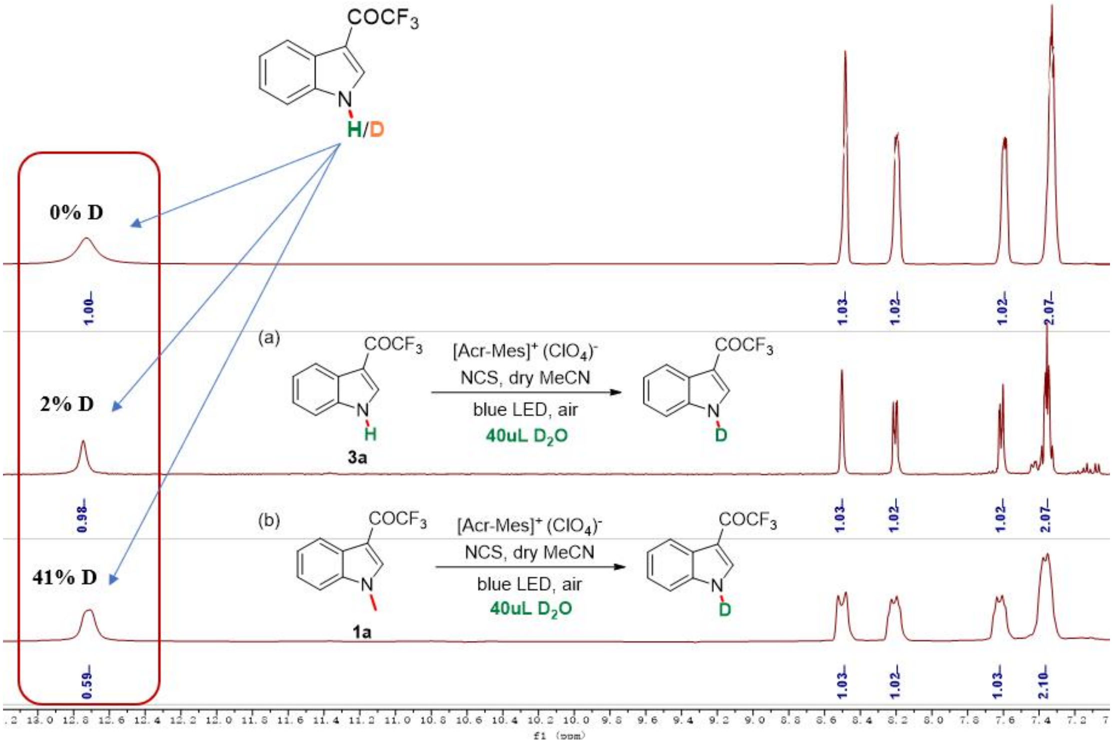
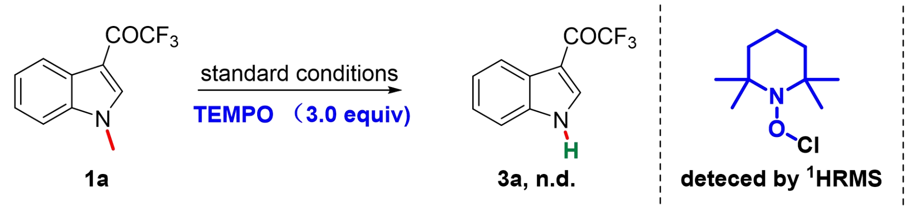
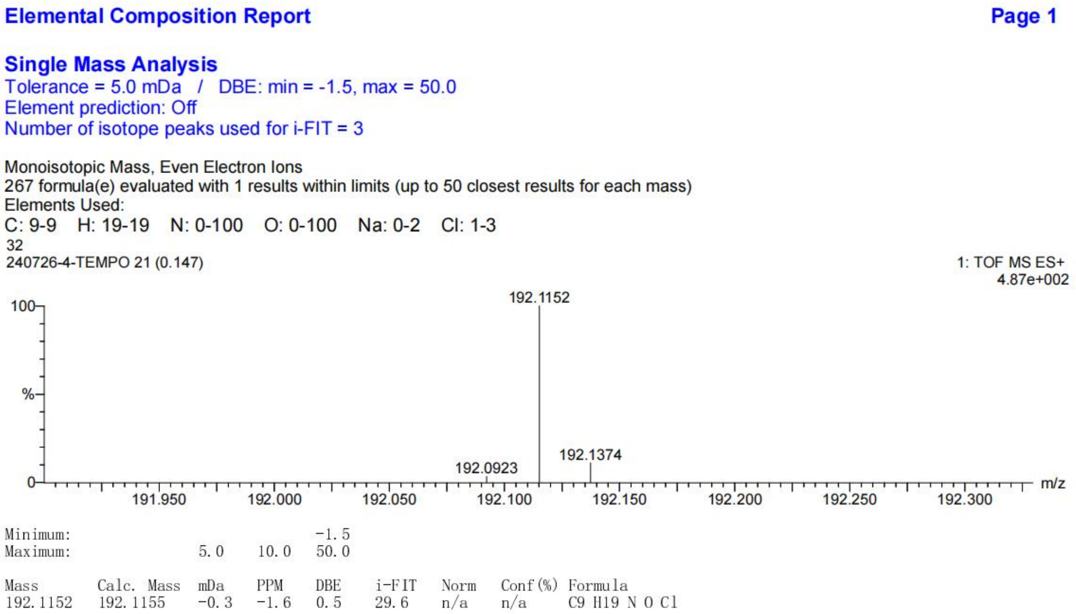


Figure S5 Proton source investigation

4.6 HRMS data analysis



m/z: $[M+H]^+$ Calcd for $C_9H_{18}ClNO$ 192.1155, found 192.1152



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
267 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 9-9 H: 19-19 N: 0-100 O: 0-100 Na: 0-2 Cl: 1-3
32
240726-4-TEMPO 21 (0.147)

1: TOF MS ES+
4.87e+002

```
Minimum:                                -1.5
Maximum:                5.0     10.0    50.0

Mass       Calc. Mass   mDa     PPM     DBE     i-FIT   Norm    Conf(%) Formula
192.1152   192.1155     -0.3    -1.6    0.5     29.6    n/a     n/a     C9 H19 N O Cl
```

Figure S6 Radical intermediate capture and determination

V. References

1 S. D. Shinde, A. Chhetri, S. Ghosh, A. Debnath, P. Joshi and D. Kumar, *J. Org. Chem.,* 2024, **89**, 15995−16003.

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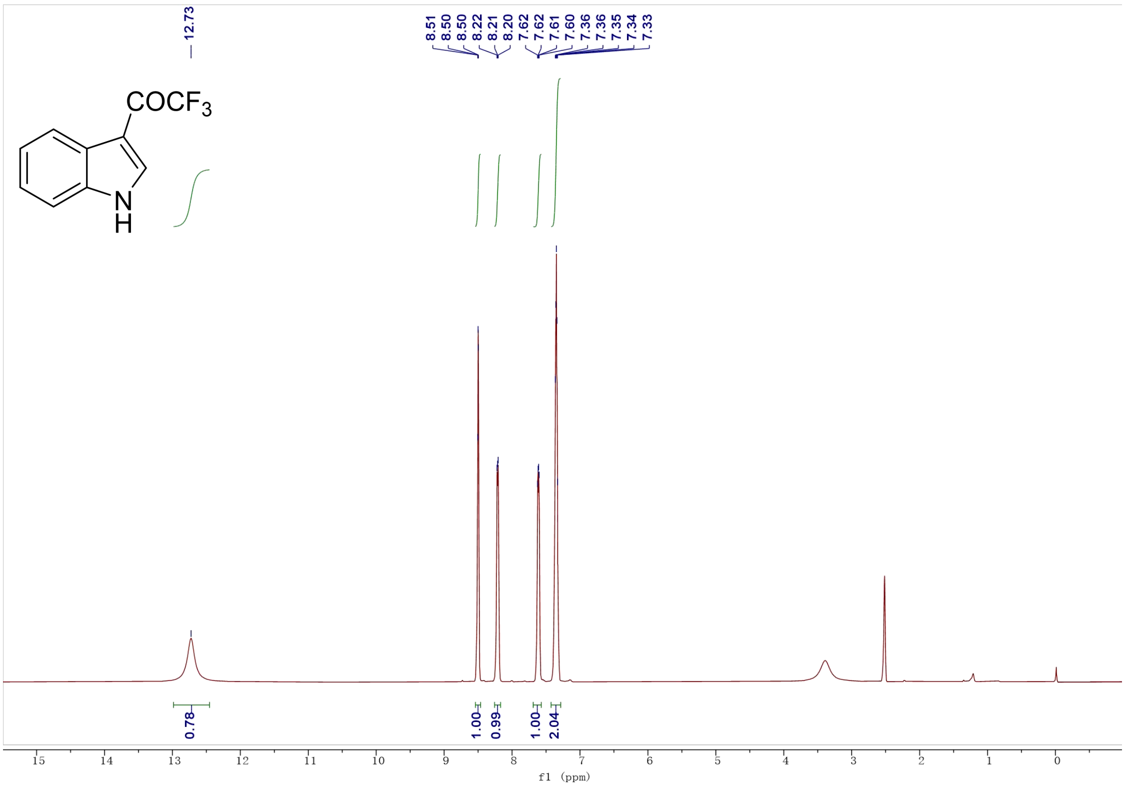
5 H. Zhu, F. Zeng, X. Chen, K. Sun, H. Li, X. Yuan, L. Qu and B. Yu, *Org. Lett.,* 2021, **23**, 2976−2980.

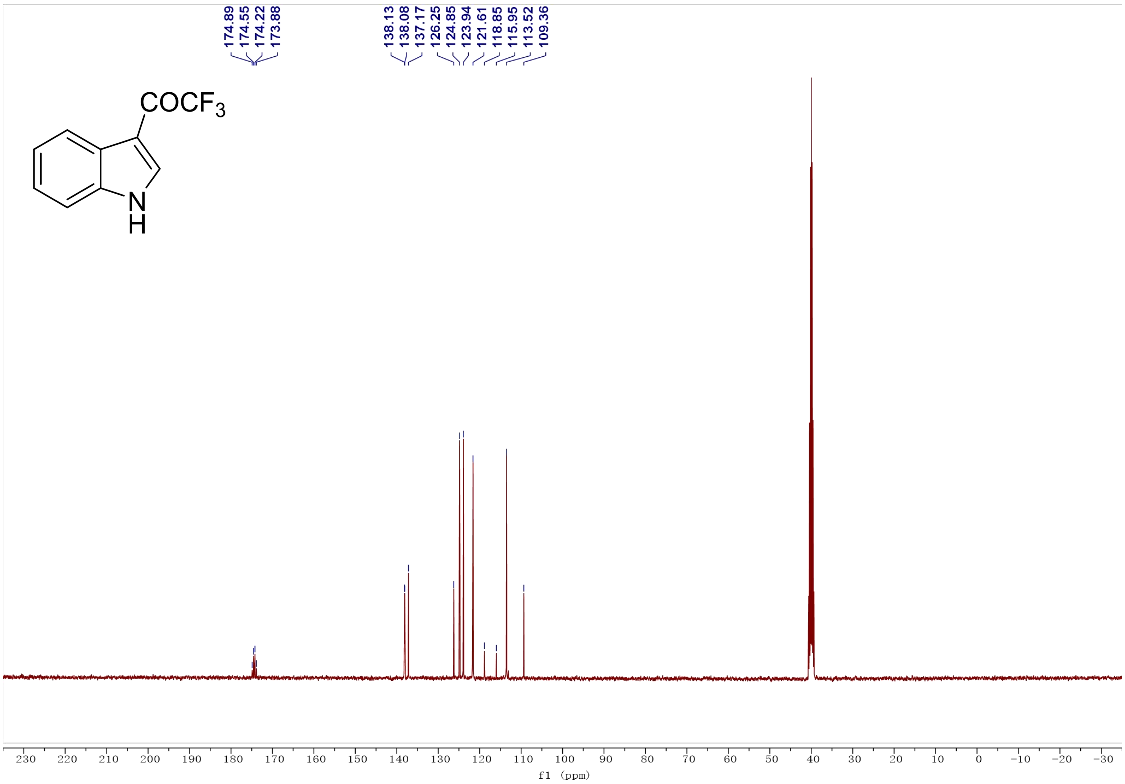
6 For a very similar example concerning photocatalyzed oxidation of benzylic into aldehyde, see: (a) K. Ohkubo, K. Suga, K. Morikawa and S. Fukuzumi, *J. Am. Chem. Soc.,* 2003, **125**, 12850−12859; (b) M. Uygur, J. H. Kuhlmann, M. C. Pérez-Aguilar, D. G. Piekarski and O. G. Mancheño, *Green Chem.*, 2021, **23**, 3392−3399; (c) Y. Itabashi, H. Asahara and K. Ohkubo, *Chem. Commun.*, 2023, **59**, 7506−7517; (d) S. Liu, X. Zhou, L.-Y. Jiao, C. Li and Z. Wang, *Chem. Eur. J.* 2023, **29**, e202300978; (e) K. Ohkubo and S. Fukuzumi, *Org. Lett.* 2000, **2**, 3647−3650.

VI. ^{1}H, ^{13}C, and ^{19}F NMR Spectra of Products

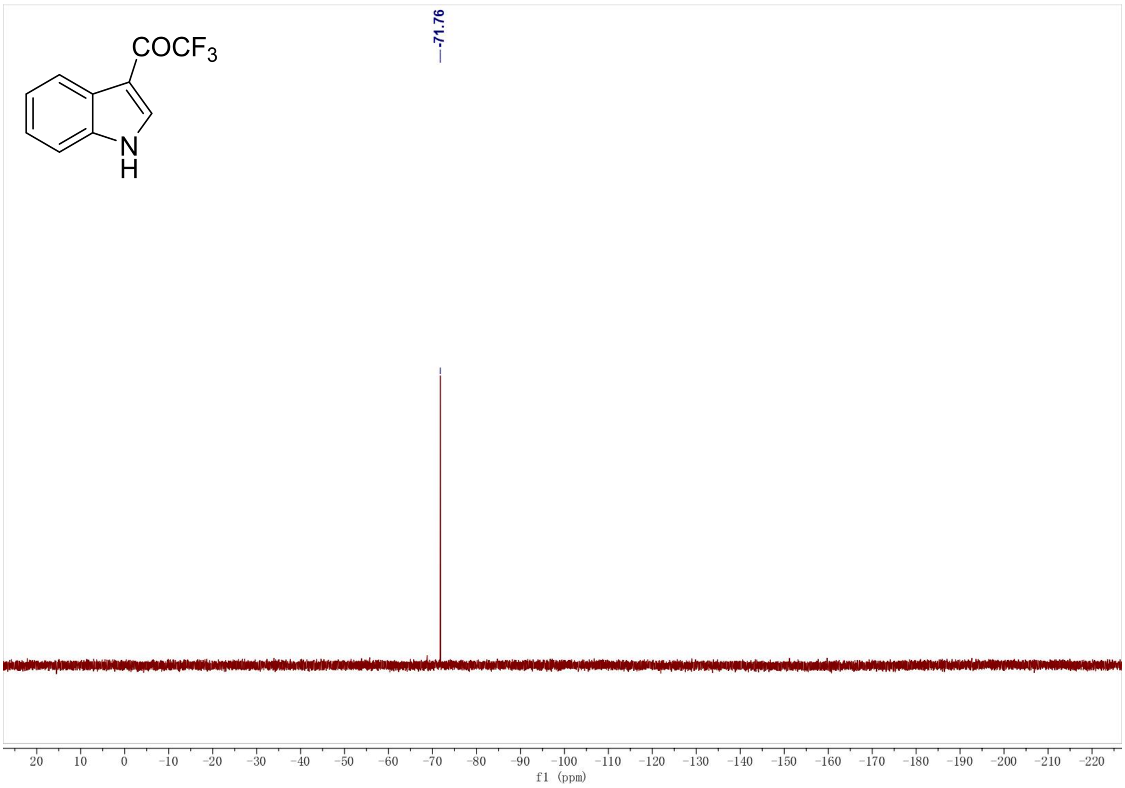
^{1}H NMR spectrum of compound **3a** (400 MHz, DMSO-d_6)



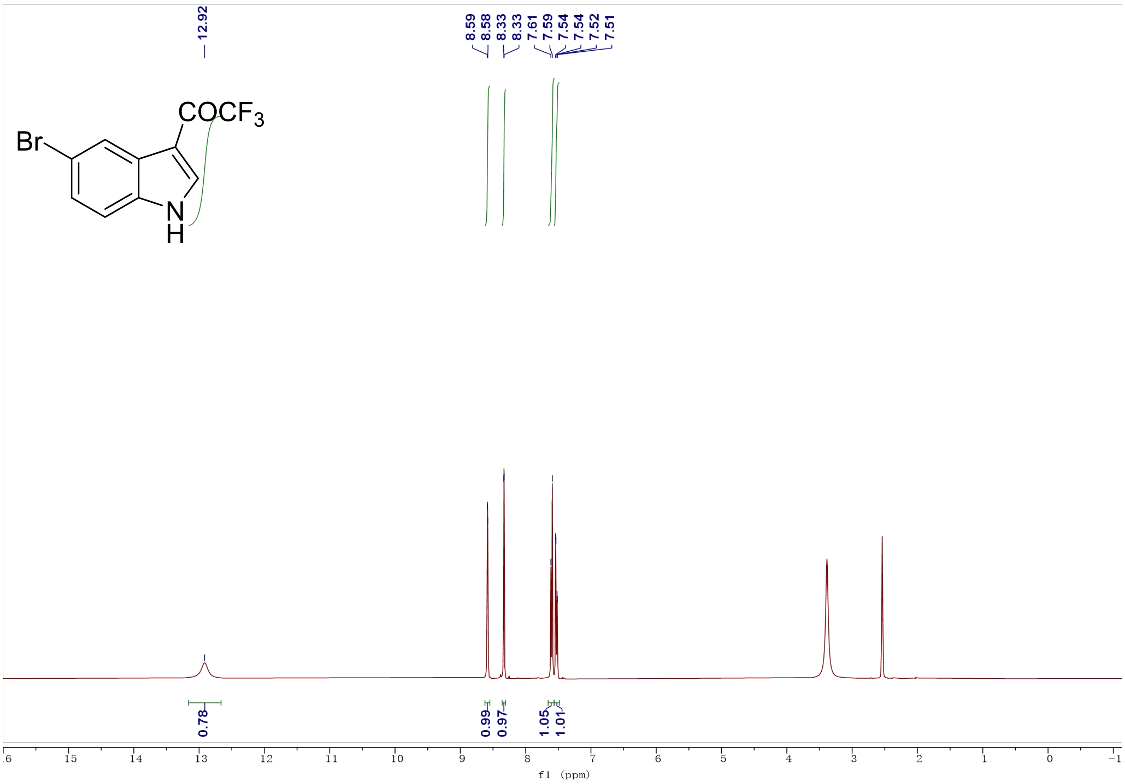
^{13}C NMR spectrum of compound **3a** (101 MHz, DMSO-d_6)



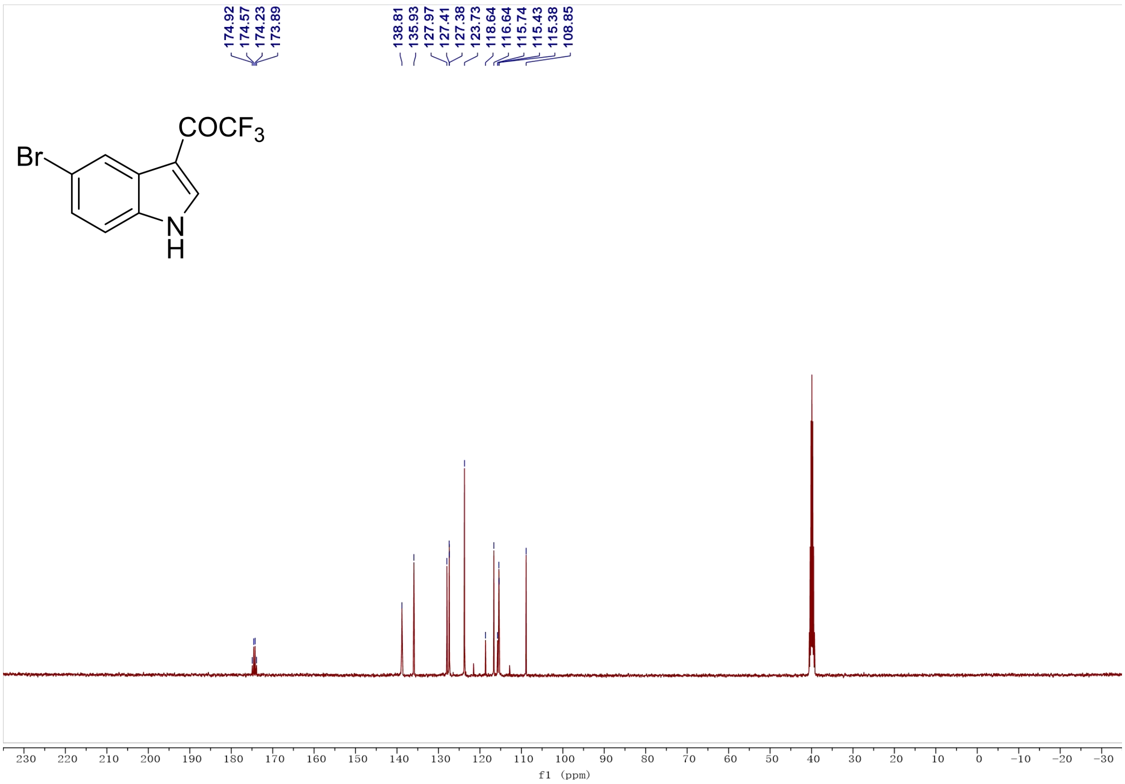
^{19}F NMR spectrum of compound **3a** (376 MHz, DMSO-d_6)



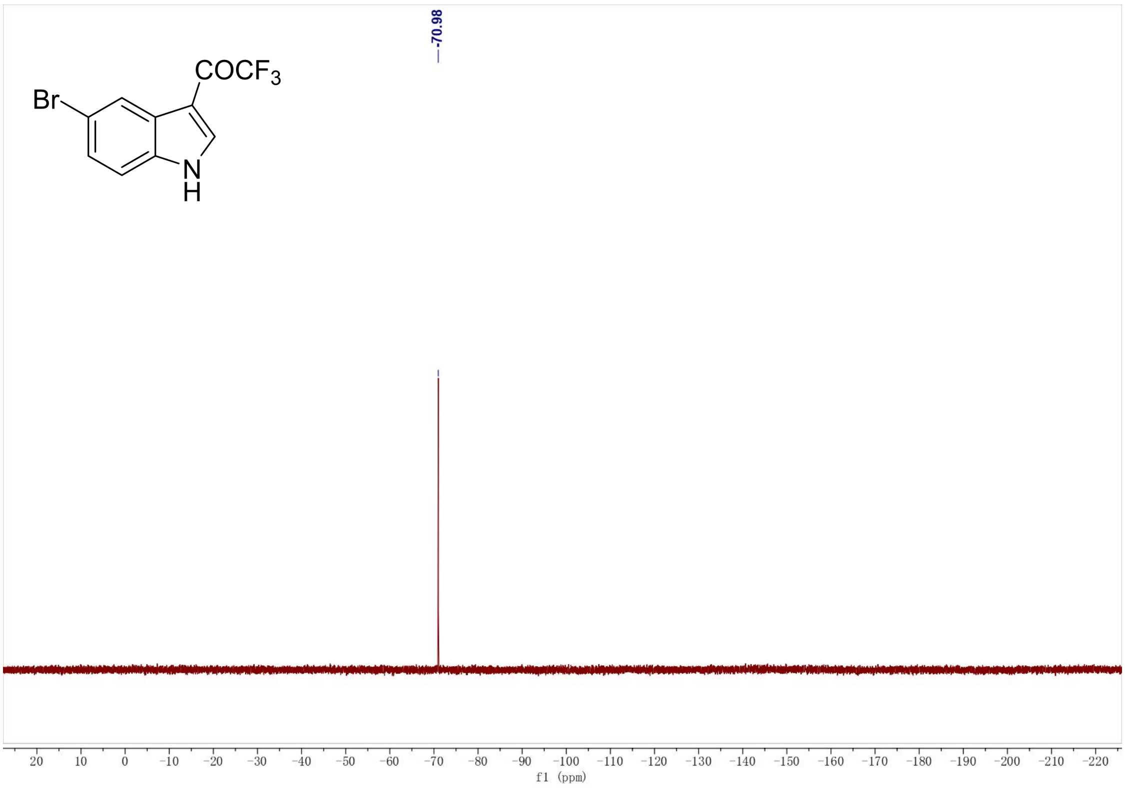
^{1}H NMR spectrum of compound **3e** (400 MHz, DMSO-d_6)



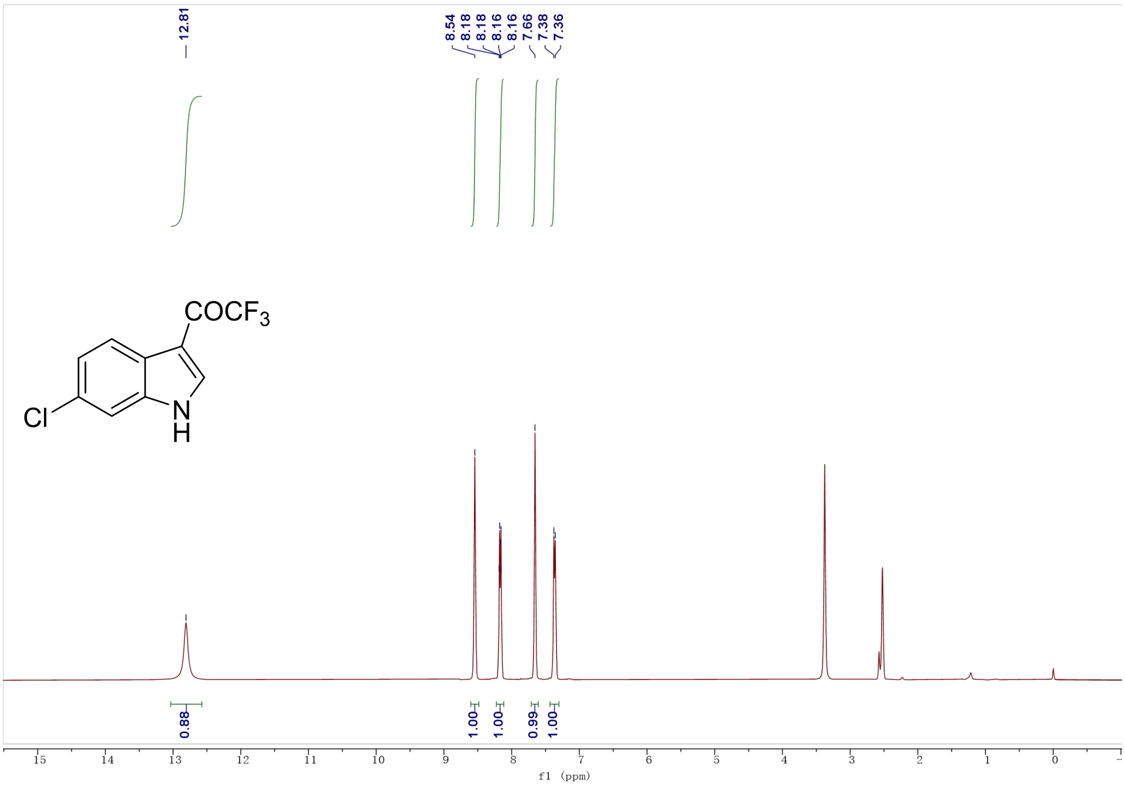
^{13}C NMR spectrum of compound **3e** (101 MHz, DMSO-d_6)



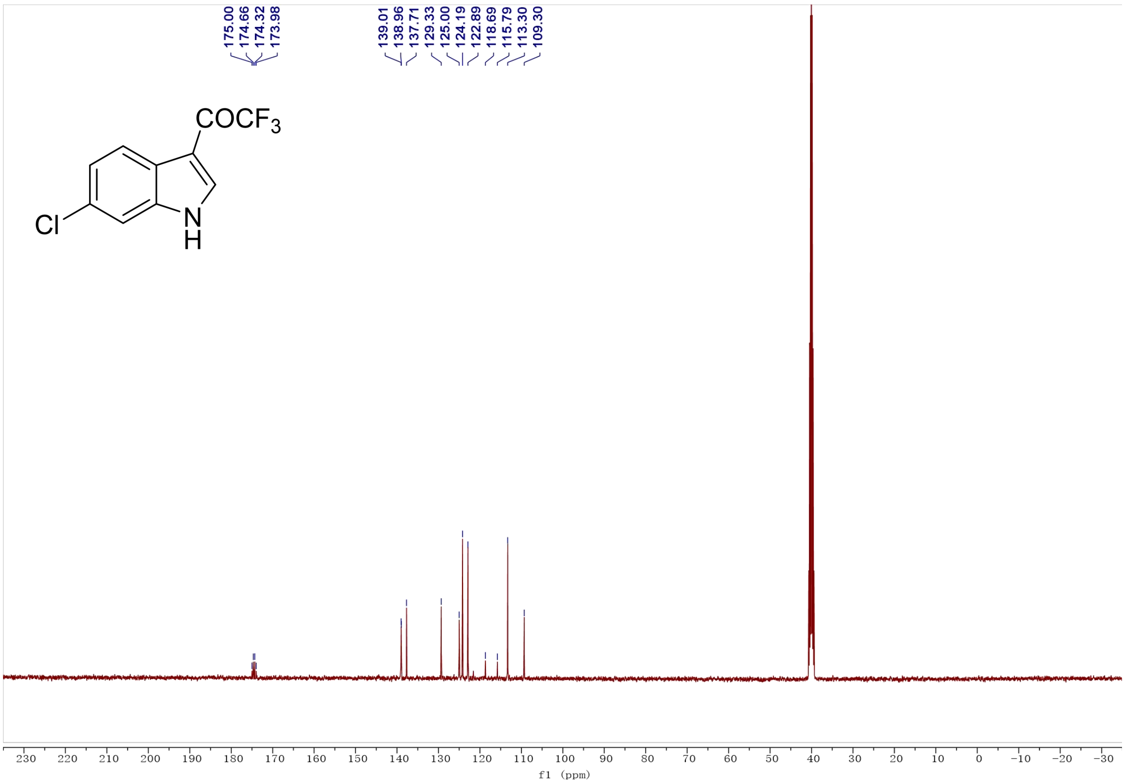
^{19}F NMR spectrum of compound **3e** (376 MHz, DMSO-d_6)



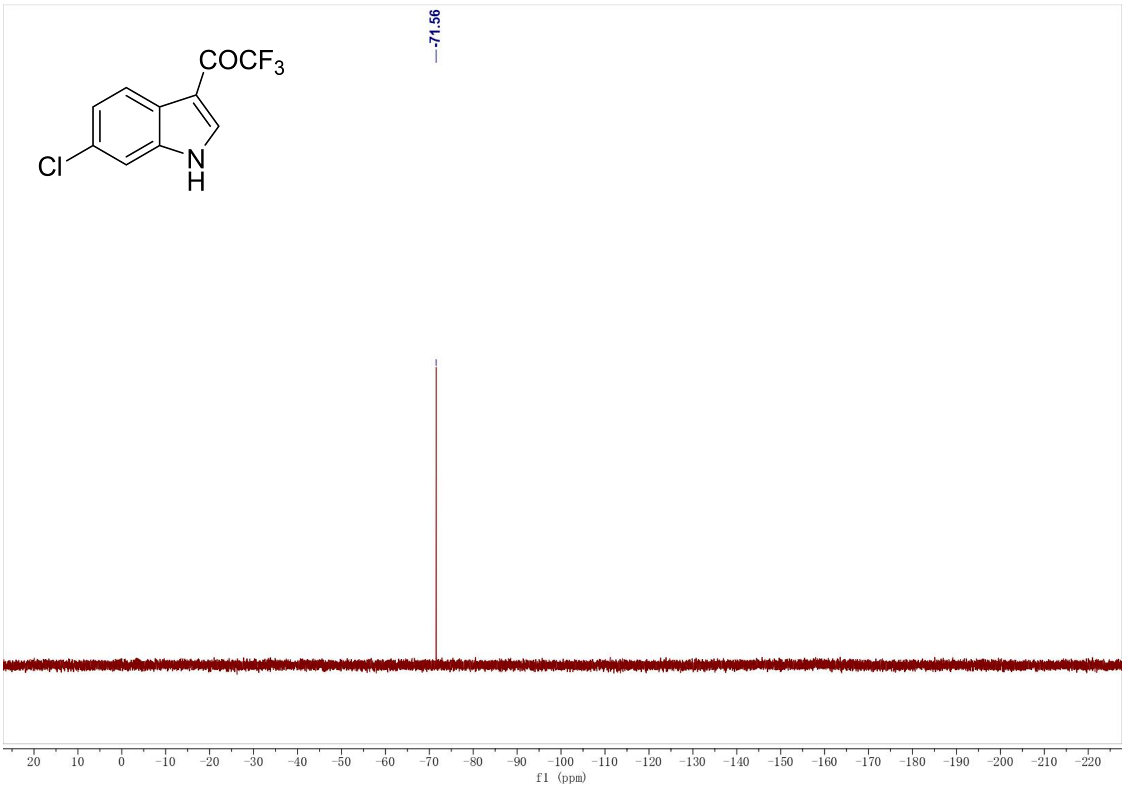
^{1}H NMR spectrum of compound **3g** (400 MHz, DMSO-*d*$_6$)



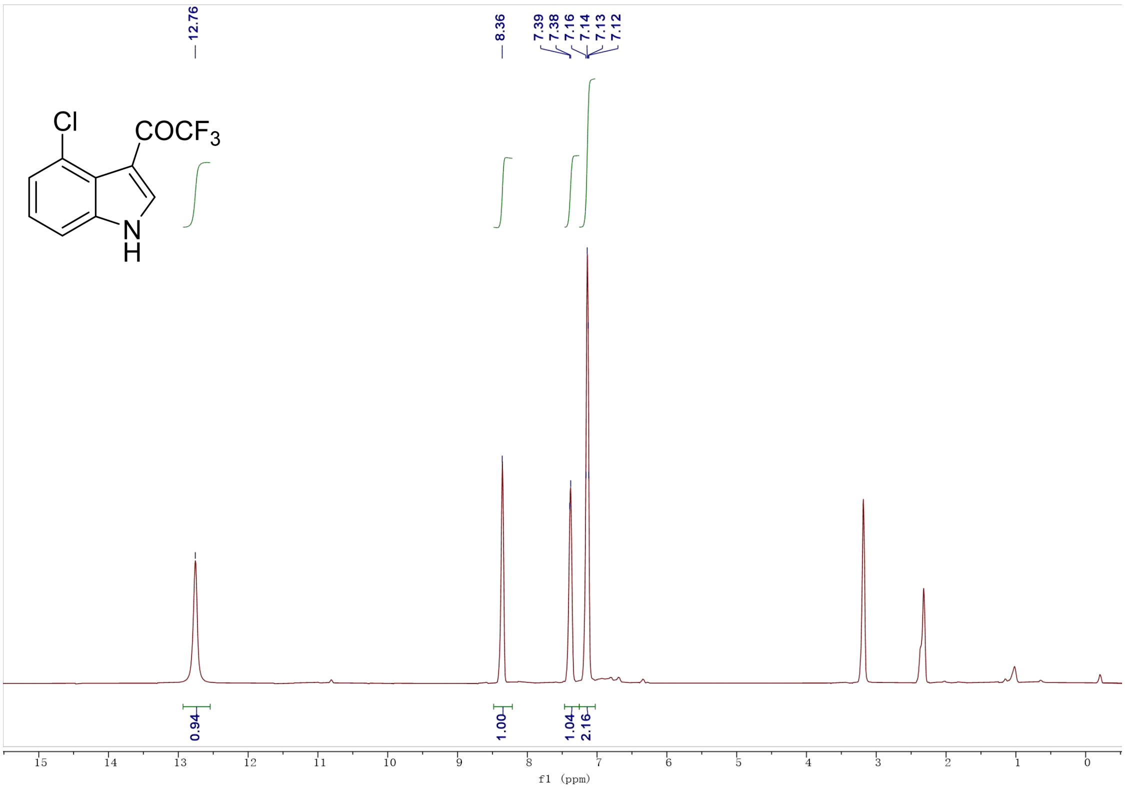
^{13}C NMR spectrum of compound **3g** (101 MHz, DMSO-*d*$_6$)



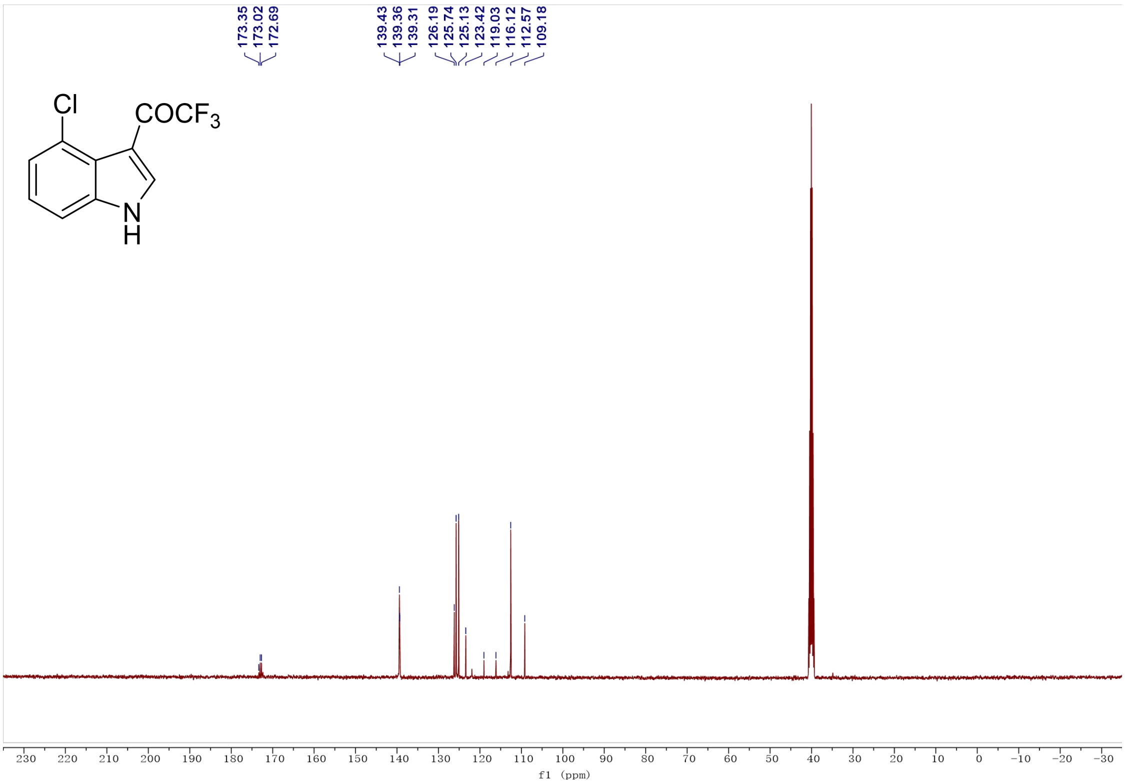
^{19}F NMR spectrum of compound **3g** (376 MHz, DMSO-d_6)



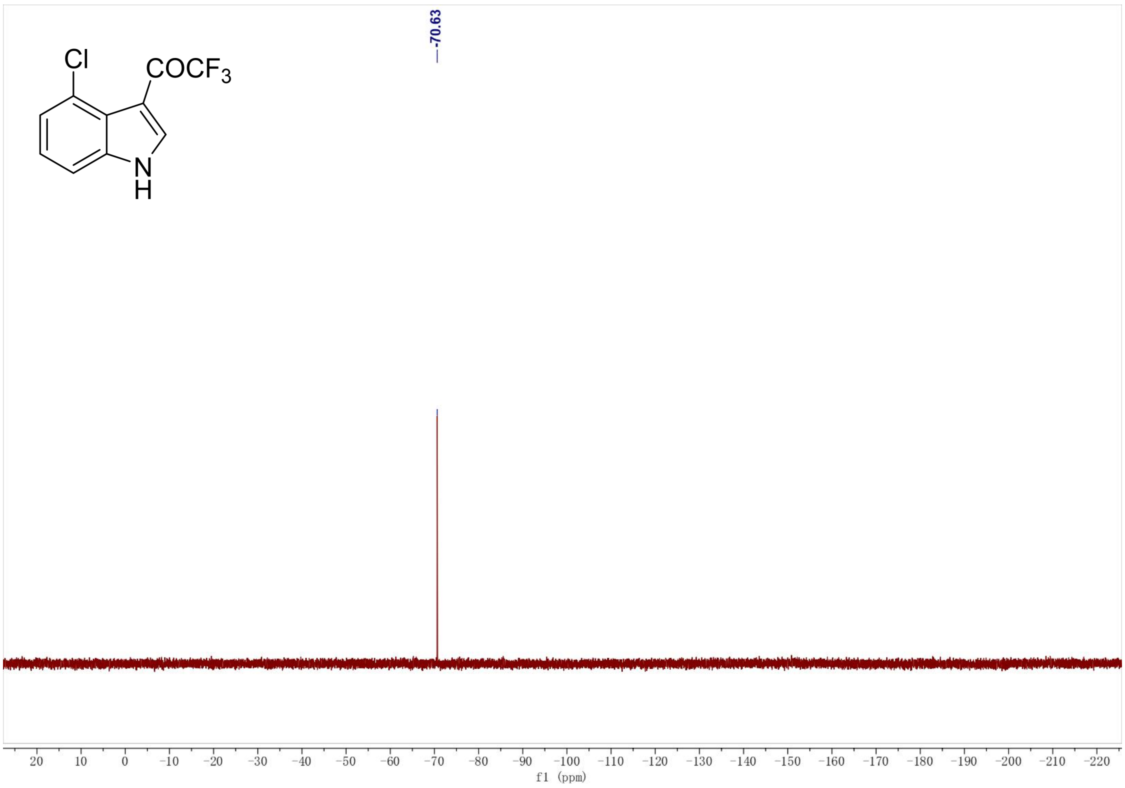
^{1}H NMR spectrum of compound **3h** (400 MHz, DMSO-d_6)



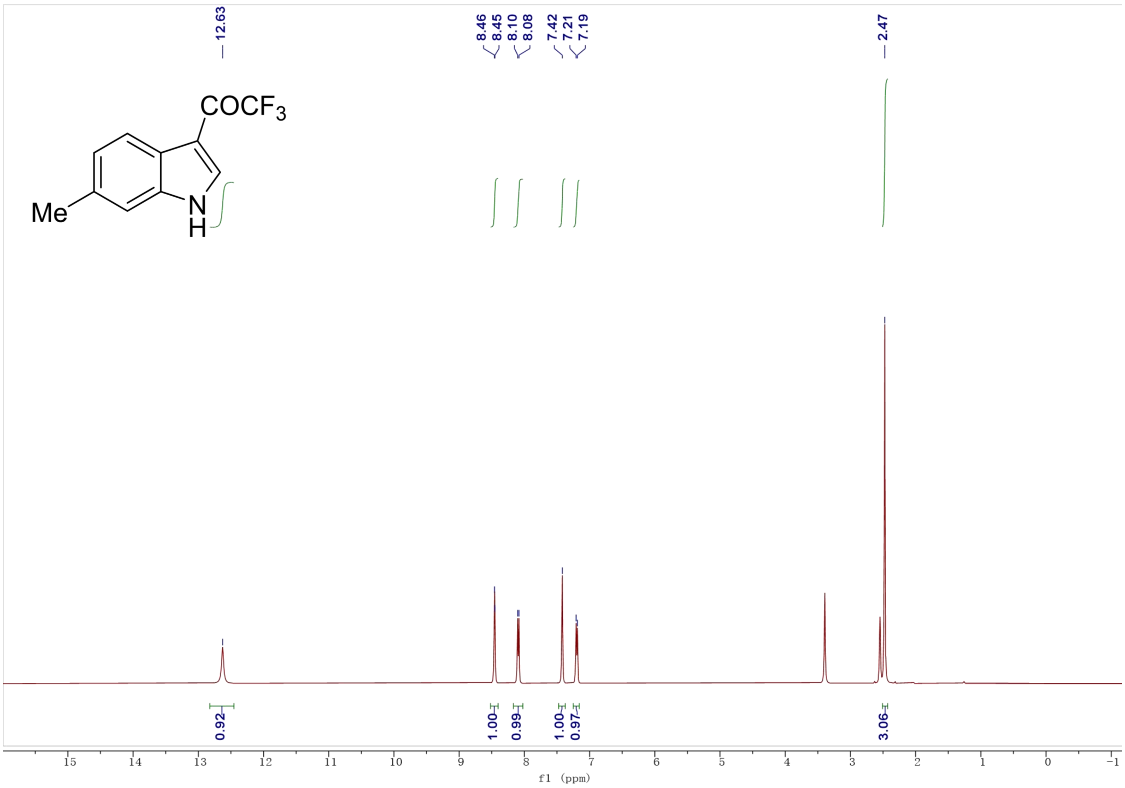
^{13}C NMR spectrum of compound **3h** (101 MHz, DMSO-*d*$_6$)



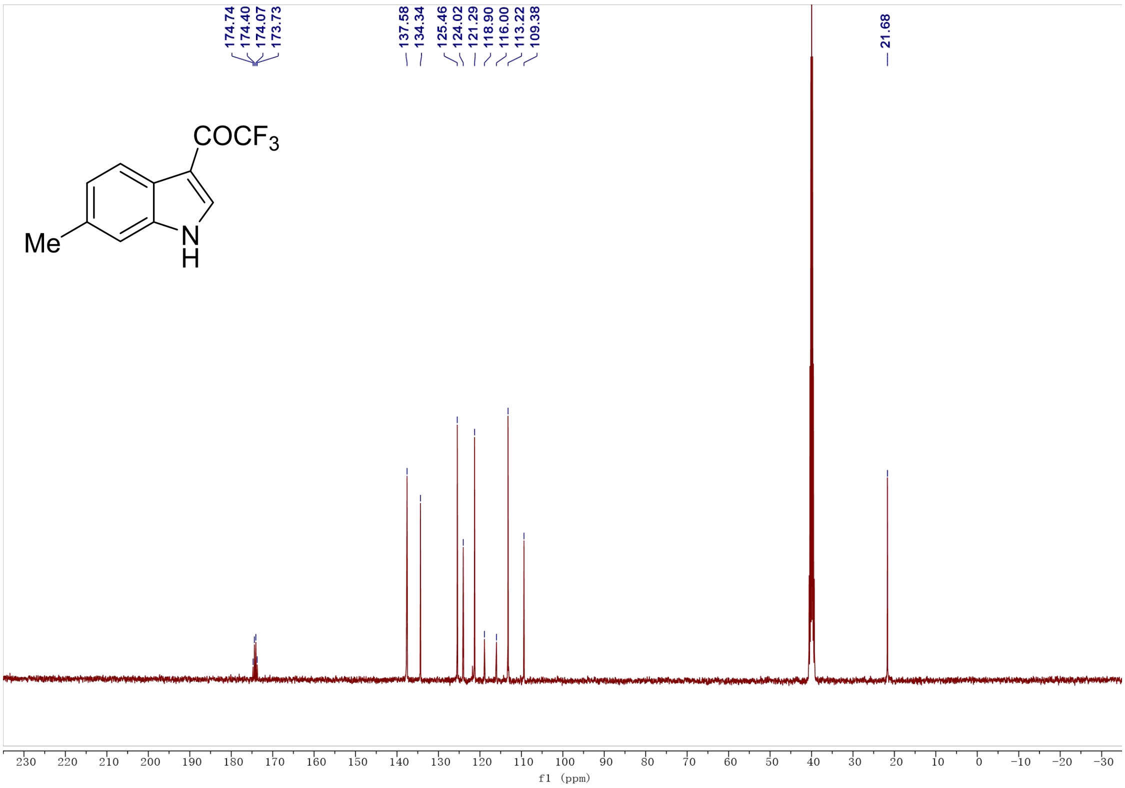
^{19}F NMR spectrum of compound **3h** (376 MHz, DMSO-*d*$_6$)



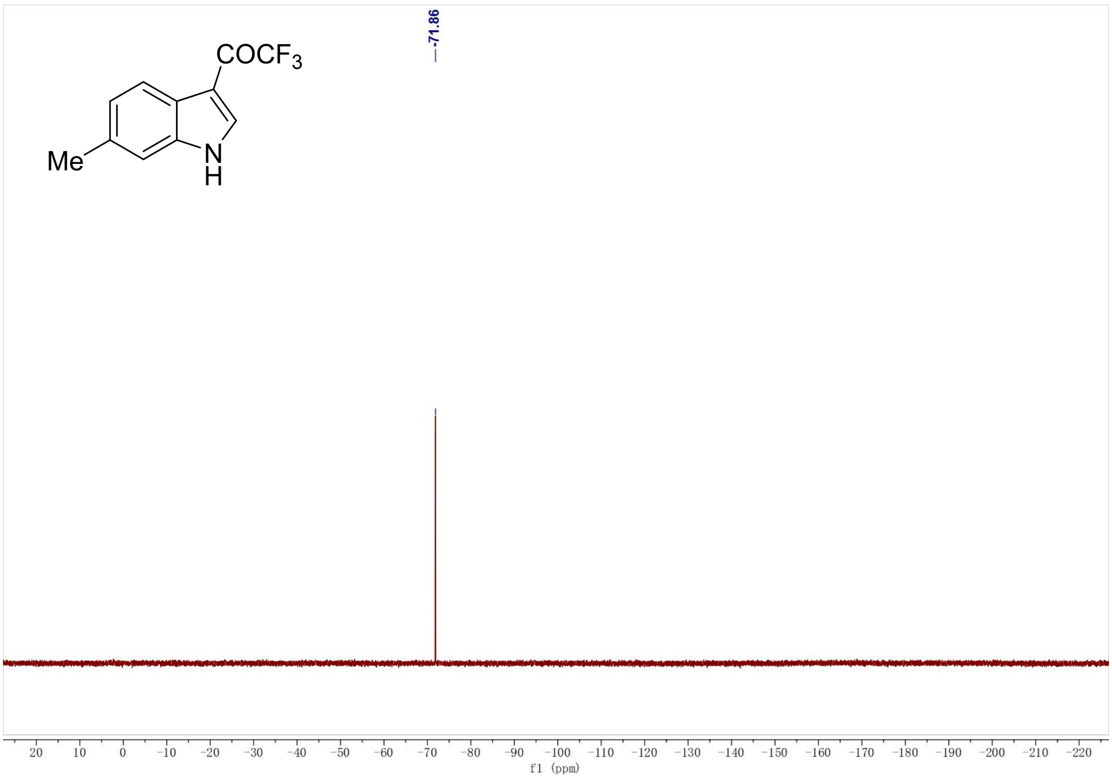
^{1}H NMR spectrum of compound **3i** (400 MHz, DMSO-d_6)



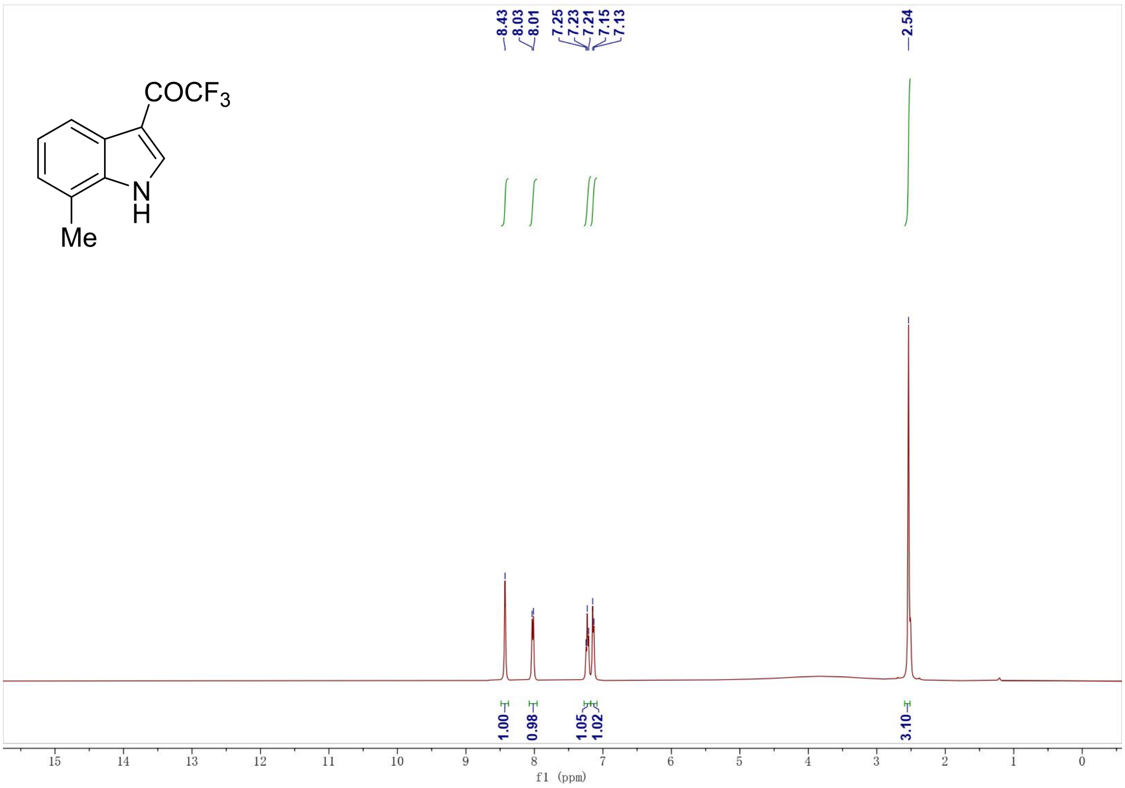
^{13}C NMR spectrum of compound **3i** (101 MHz, DMSO-d_6)



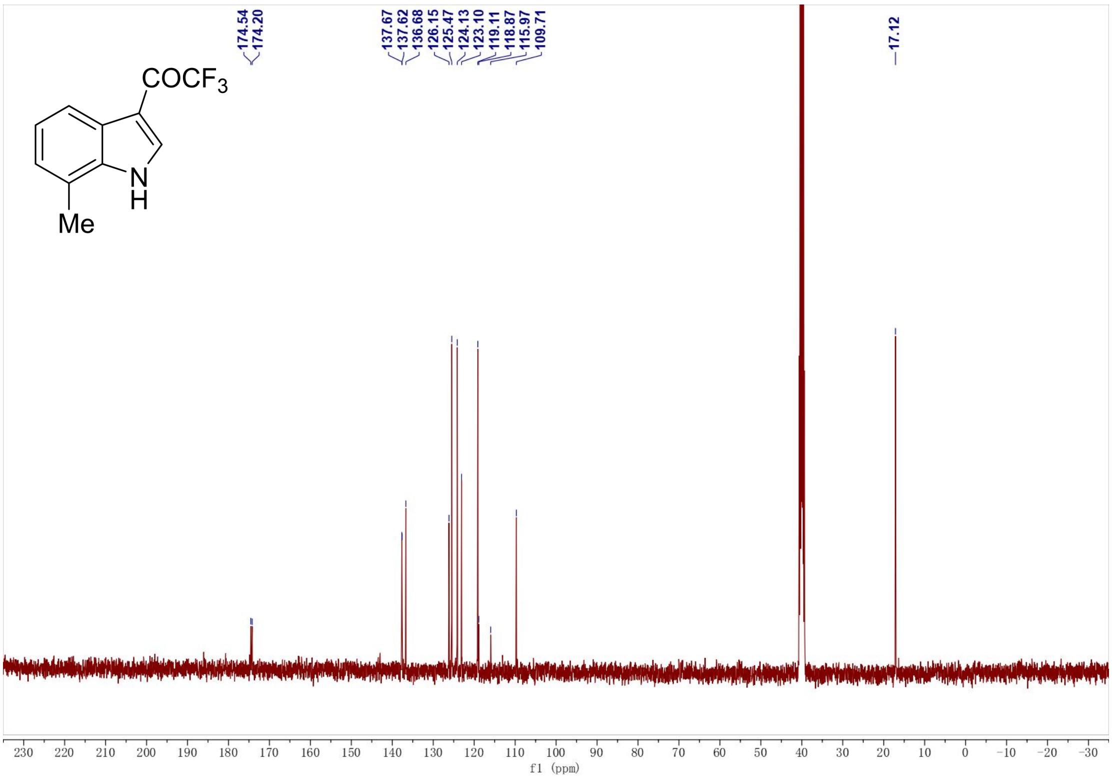
^{19}F NMR spectrum of compound **3i** (376 MHz, DMSO-*d_6*)



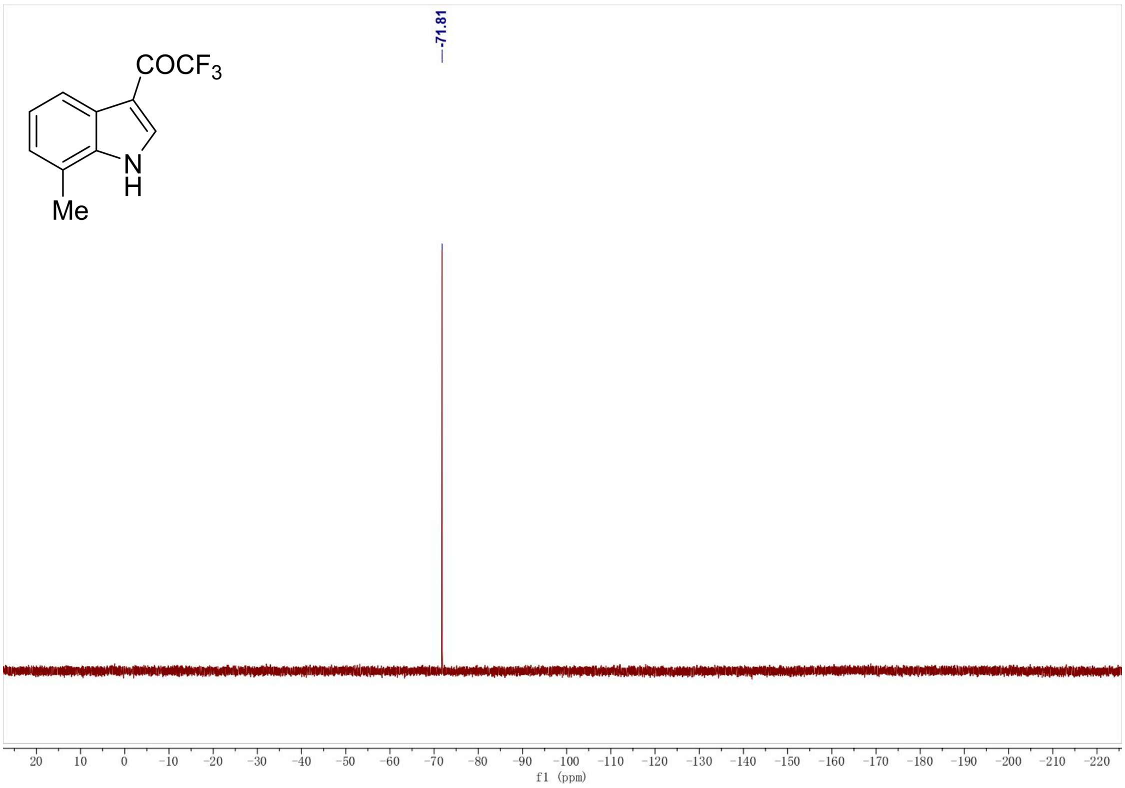
^{1}H NMR spectrum of compound **3j** (400 MHz, DMSO-*d_6*)



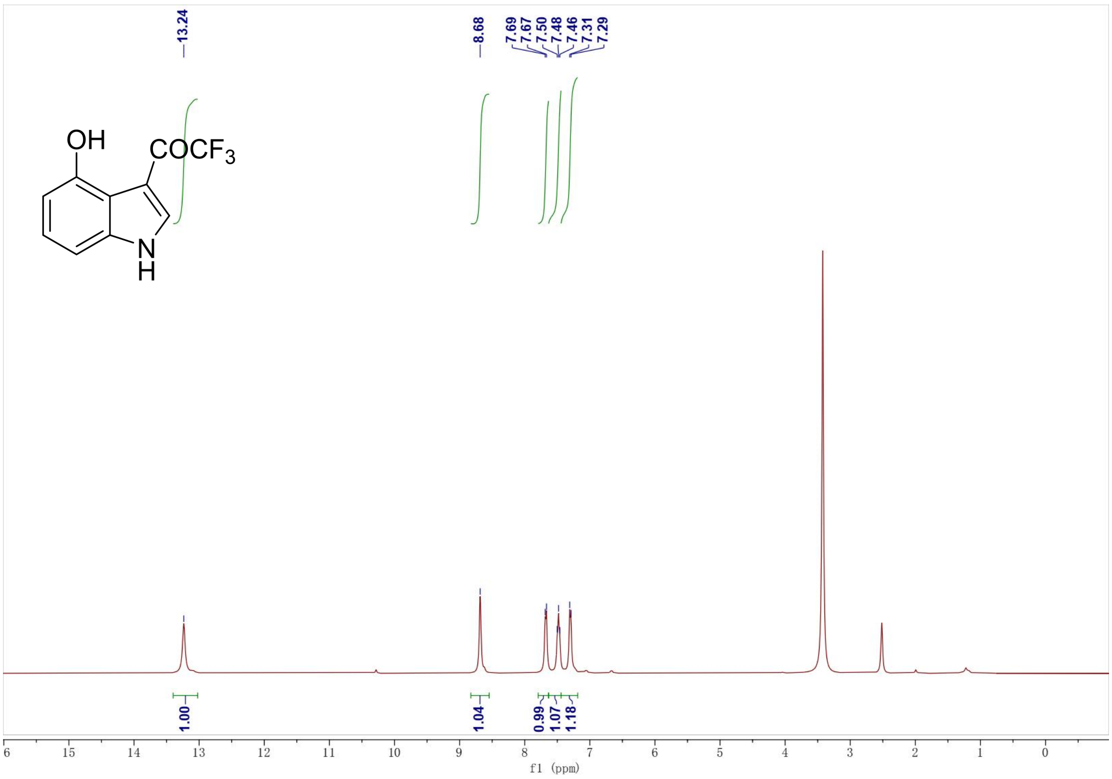
^{13}C NMR spectrum of compound **3j** (101 MHz, DMSO-*d*$_6$)



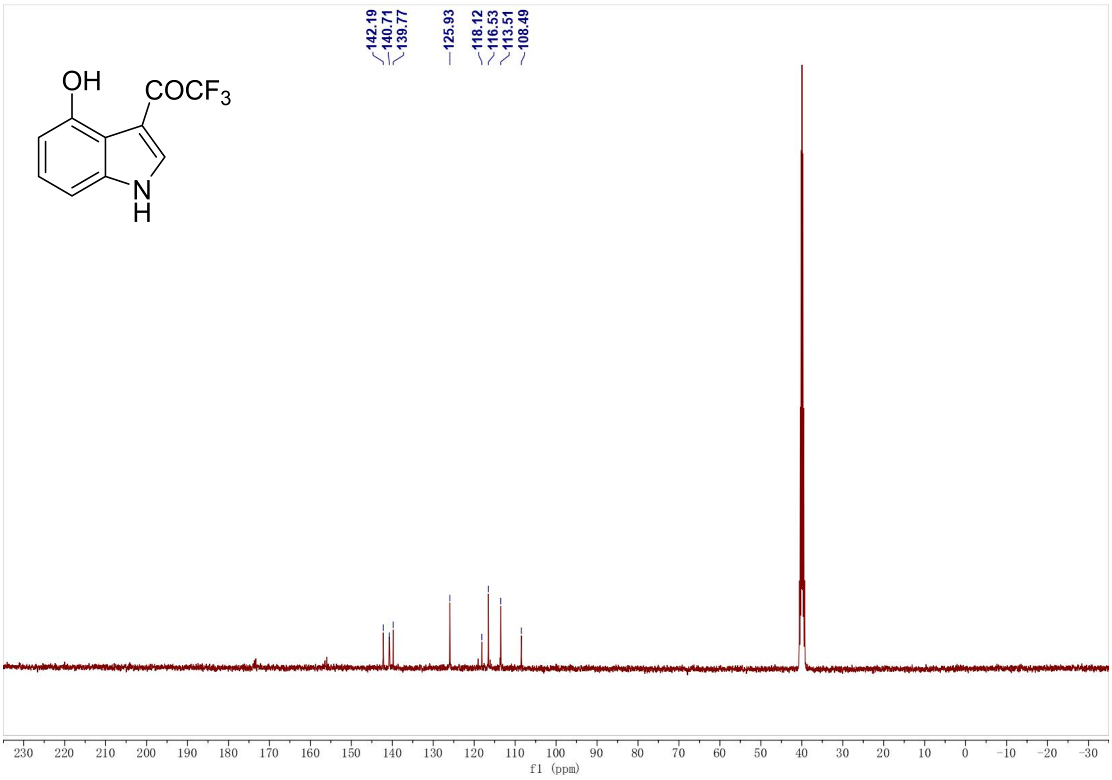
^{19}F NMR spectrum of compound **3j** (376 MHz, DMSO-*d*$_6$)



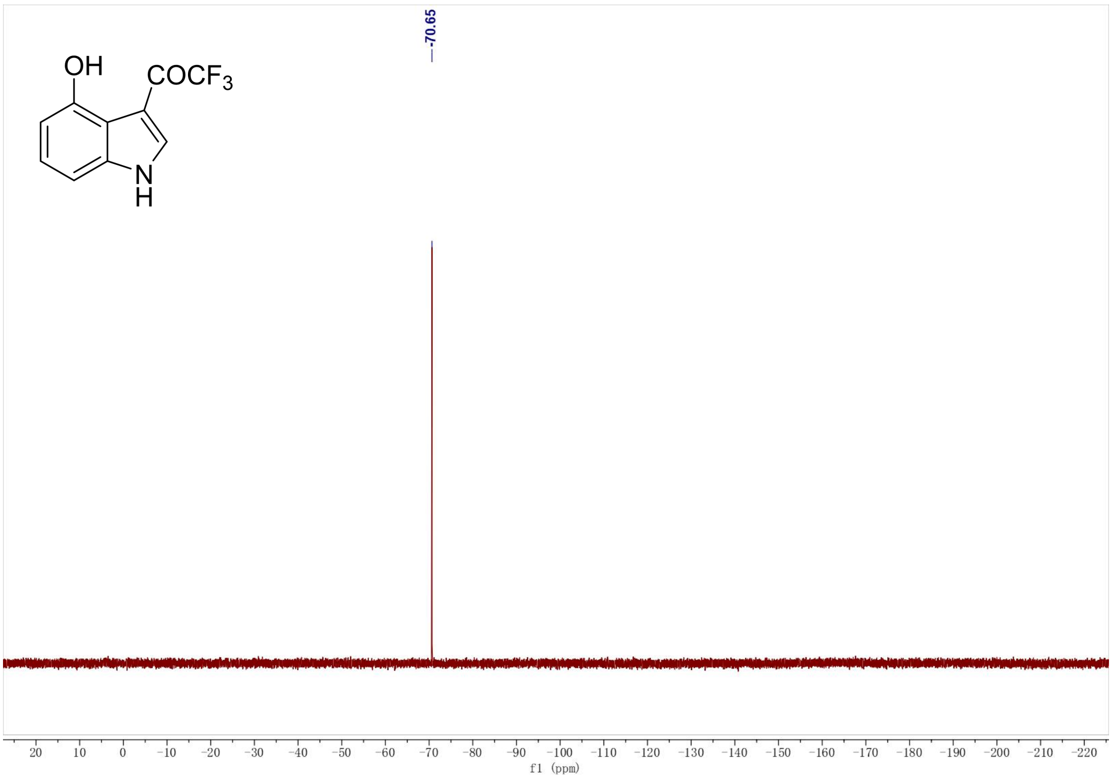
^{1}H NMR spectrum of compound **3k** (400 MHz, DMSO-d_6)



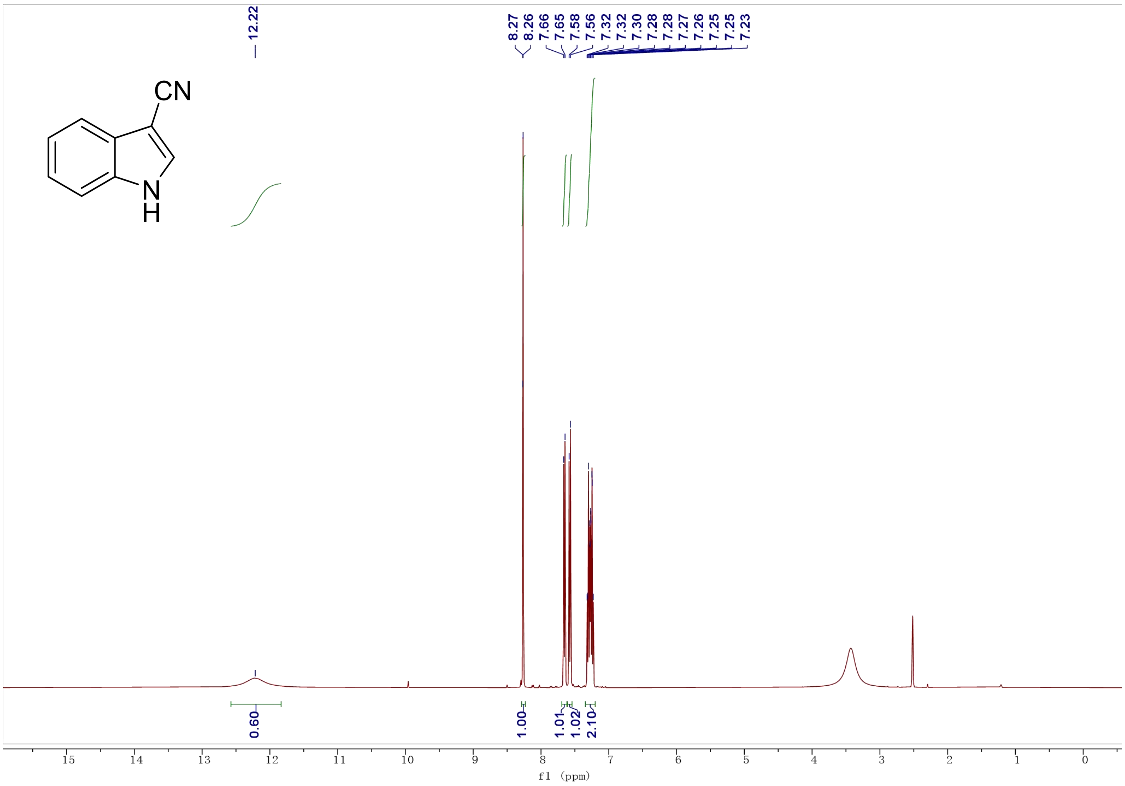
^{13}C NMR spectrum of compound **3k** (101 MHz, DMSO-d_6)



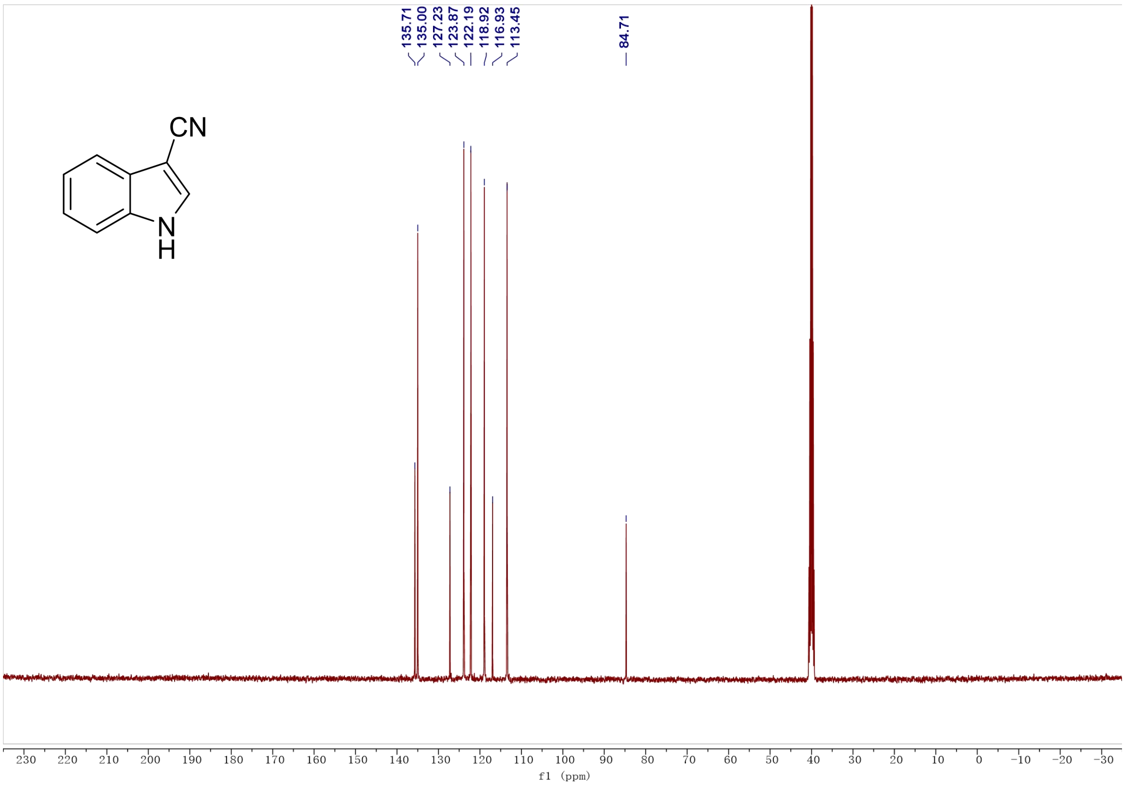
^{19}F NMR spectrum of compound **3k** (376 MHz, DMSO-*d*$_6$)



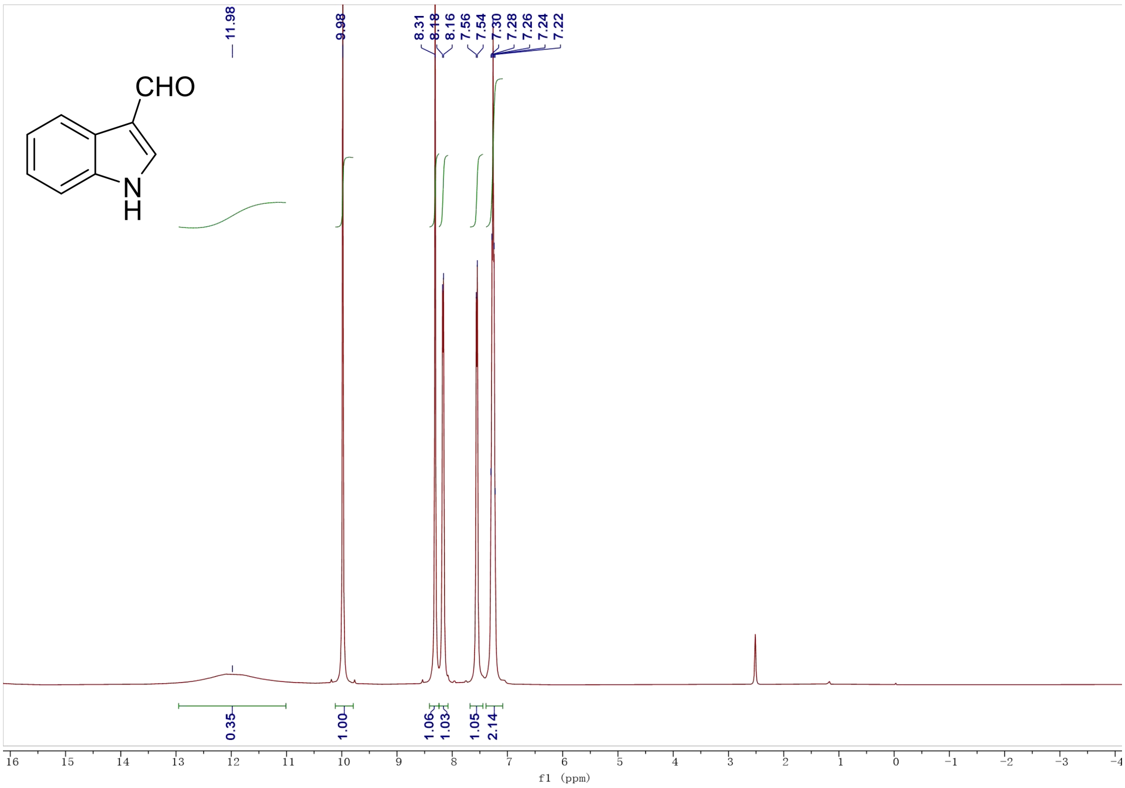
^{1}H NMR spectrum of compound **3l** (400 MHz, DMSO-*d*$_6$)



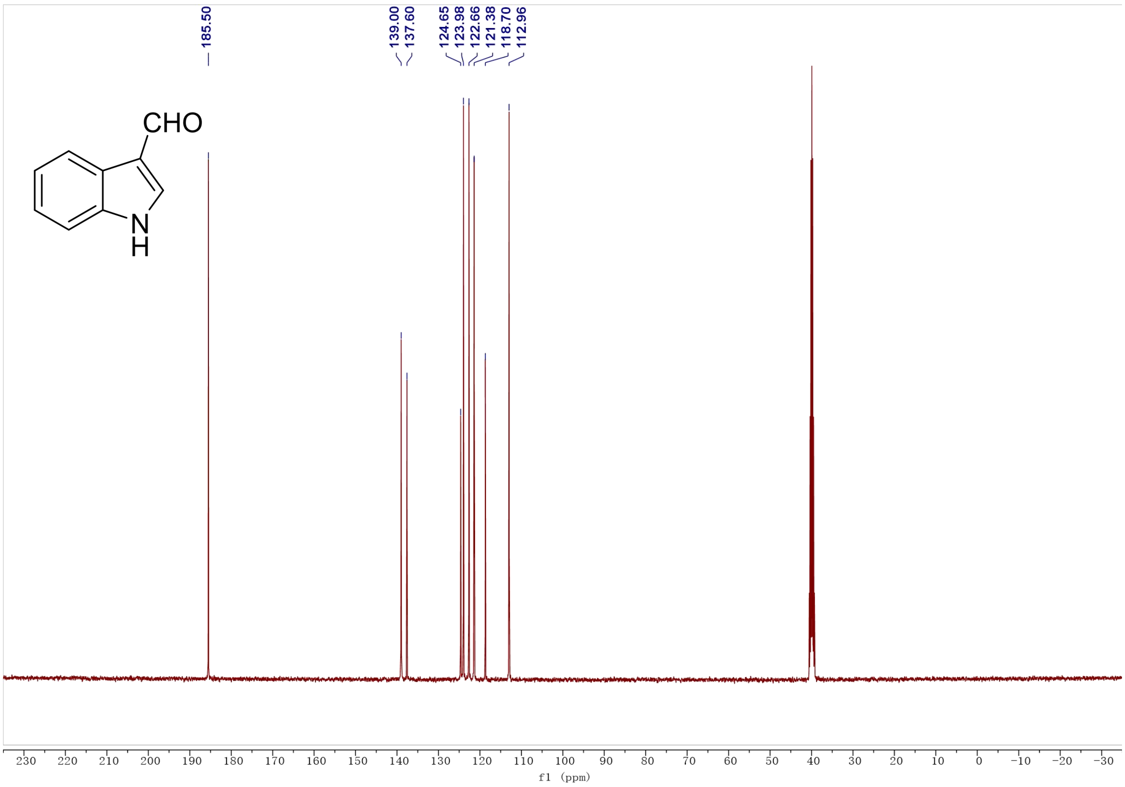
^{13}C NMR spectrum of compound **3l** ((101 MHz, DMSO-d_6)



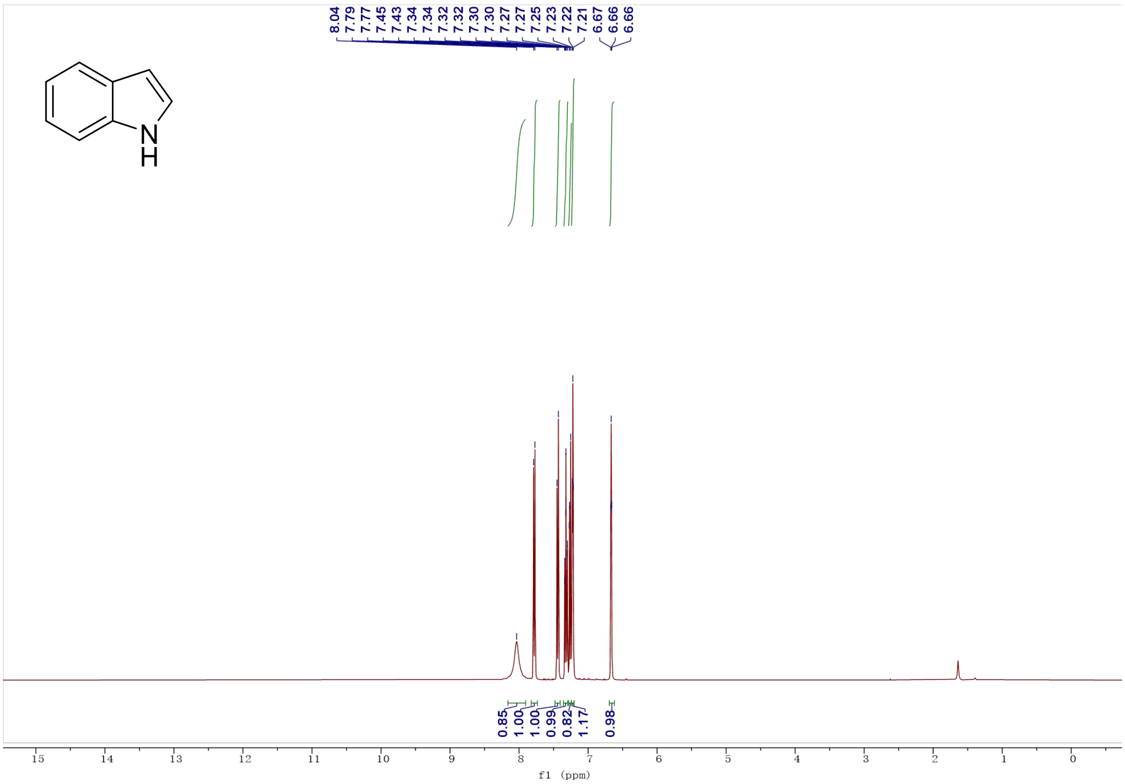
^{1}H NMR spectrum of compound **3m** (400 MHz, DMSO-d_6)



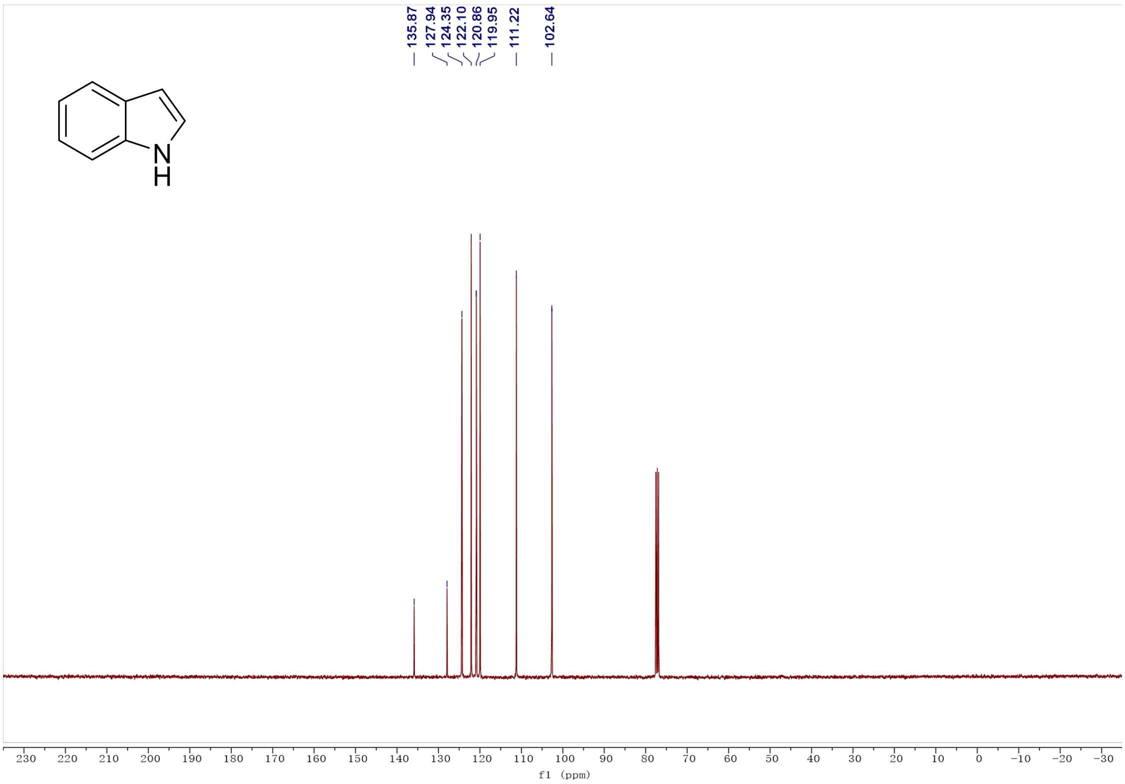
^{13}C NMR spectrum of compound **3m** (101 MHz, DMSO-d_6)



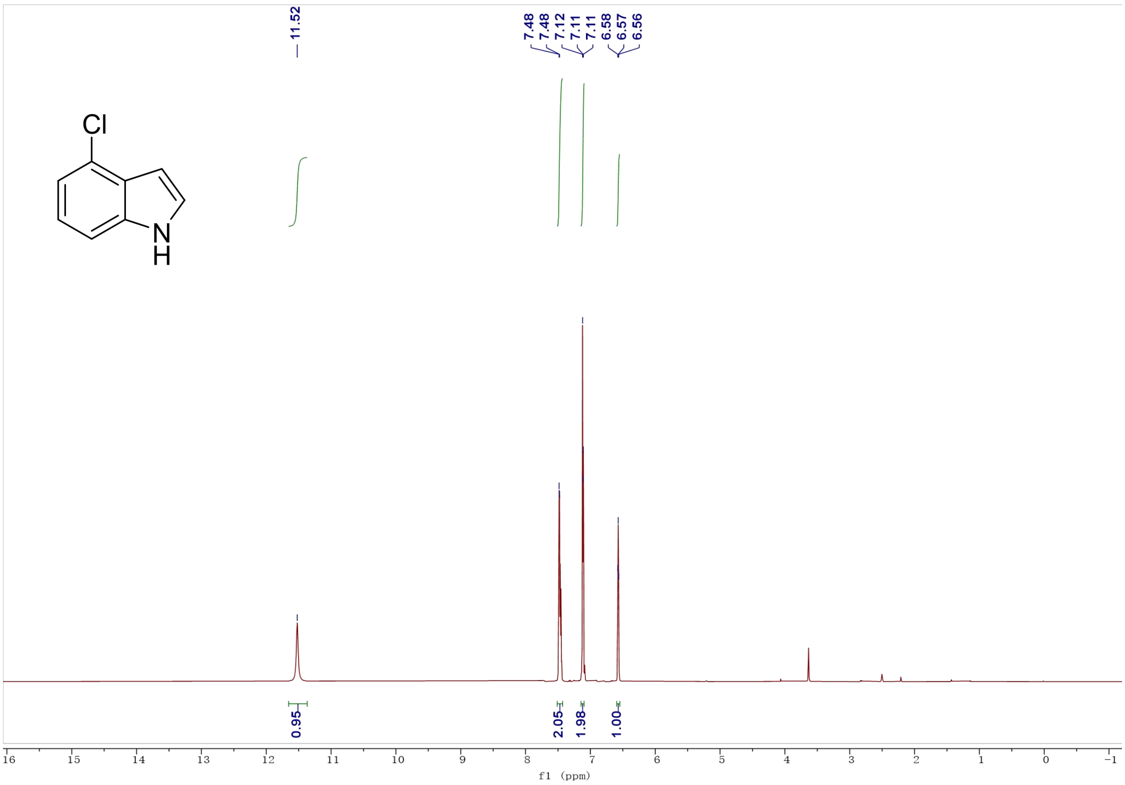
^{1}H NMR spectrum of compound **3o** (400 MHz, CDCl$_3$)



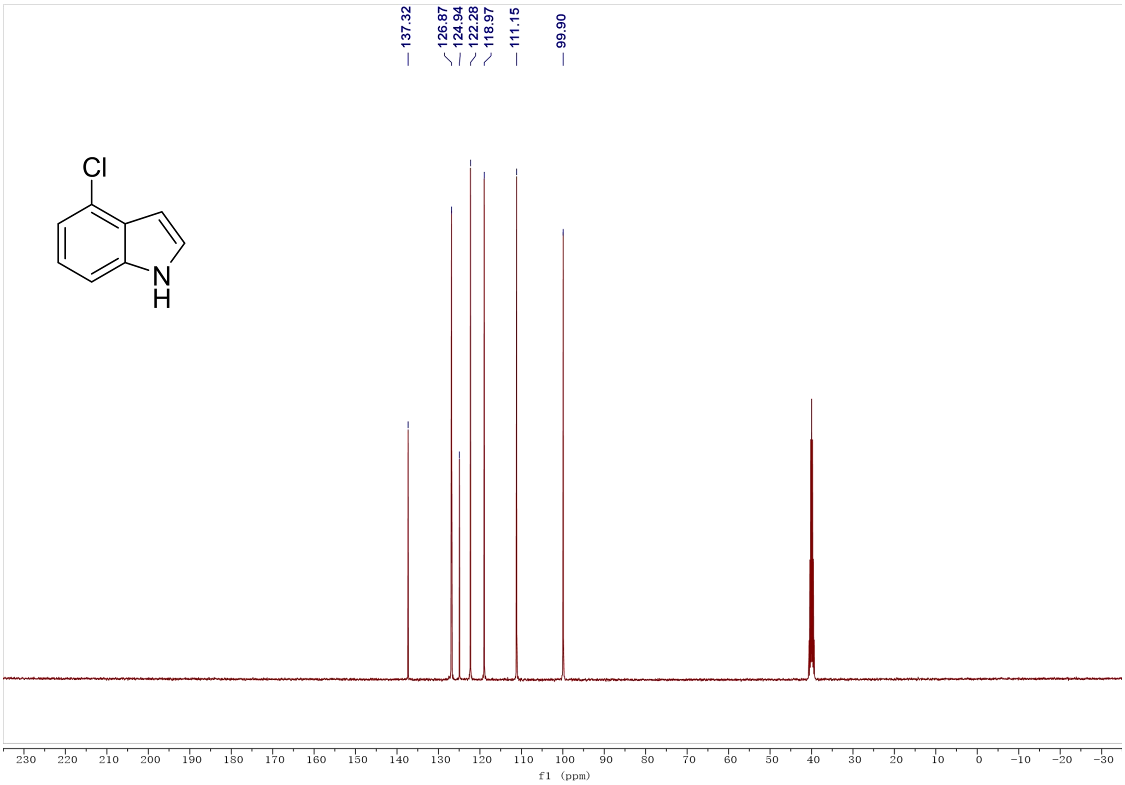
^{13}C NMR spectrum of compound **3o** (101 MHz, $CDCl_3$)



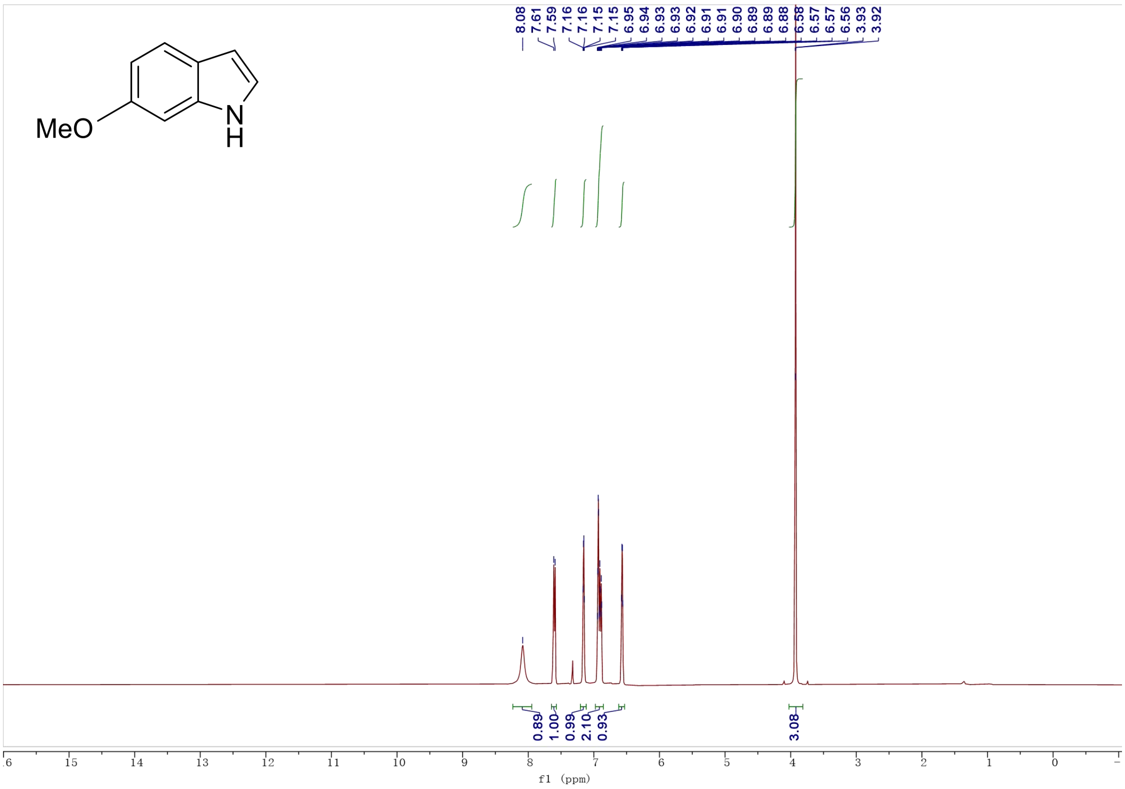
^{1}H NMR spectrum of compound **3q** (400 MHz, DMSO-d_6)



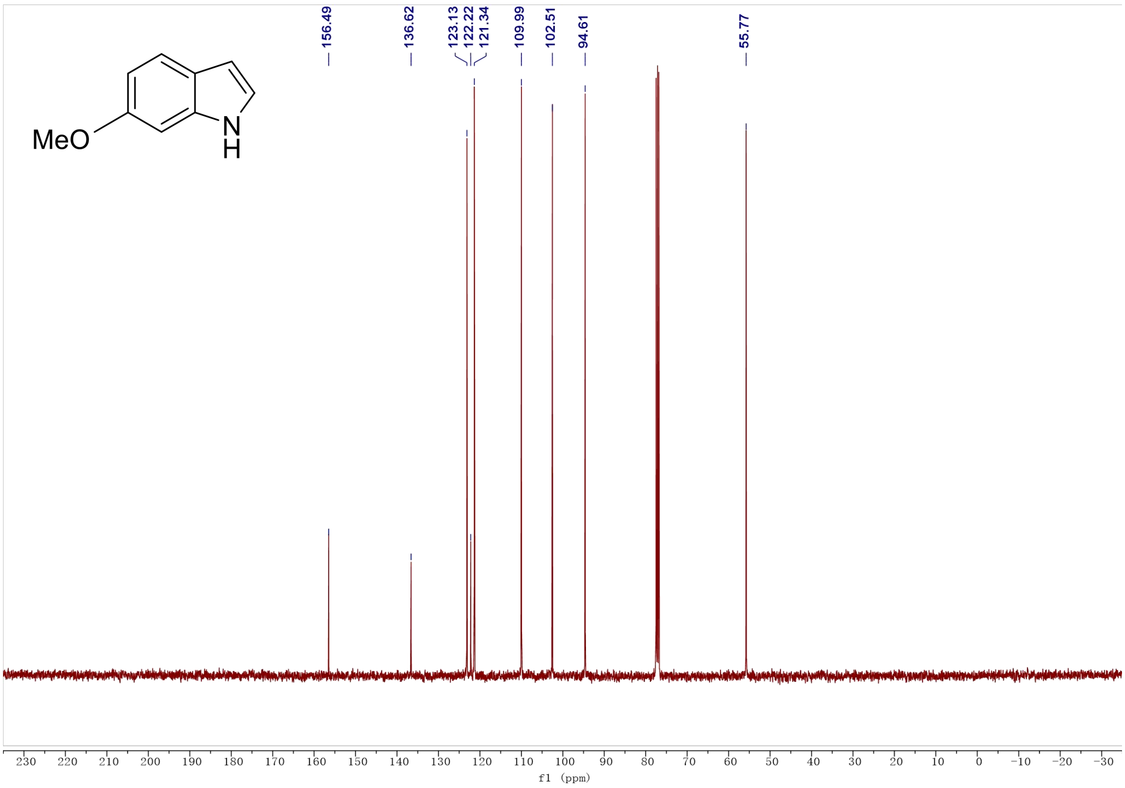
^{13}C NMR spectrum of compound **3q** (101 MHz, DMSO-*d*$_6$)



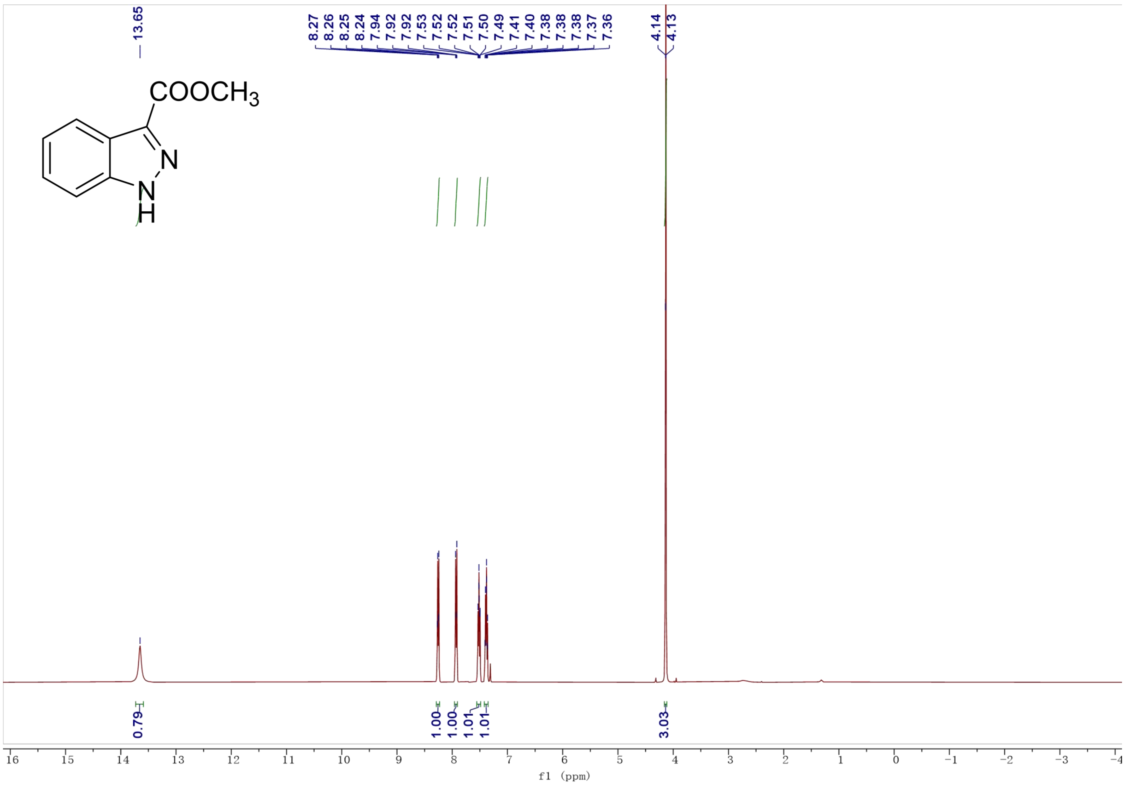
^{1}H NMR spectrum of compound **3r** (400 MHz, CDCl$_3$)



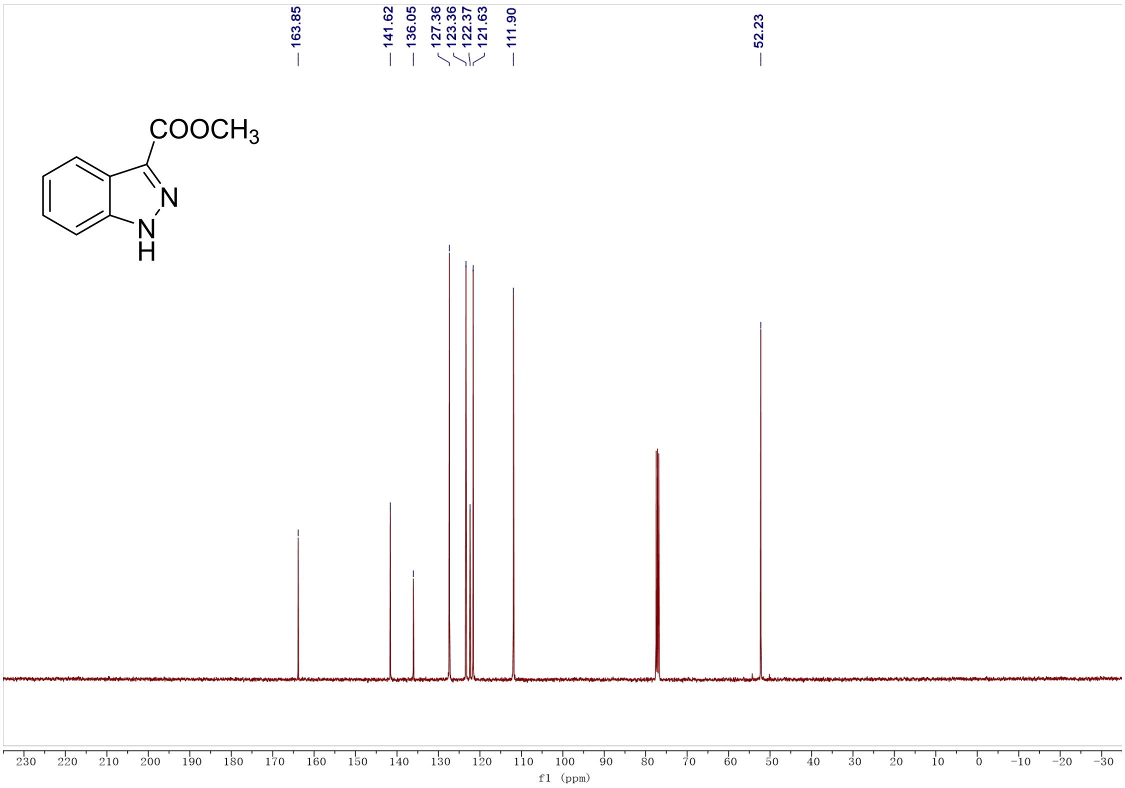
^{13}C NMR spectrum of compound **3r** (101 MHz, CDCl$_3$)



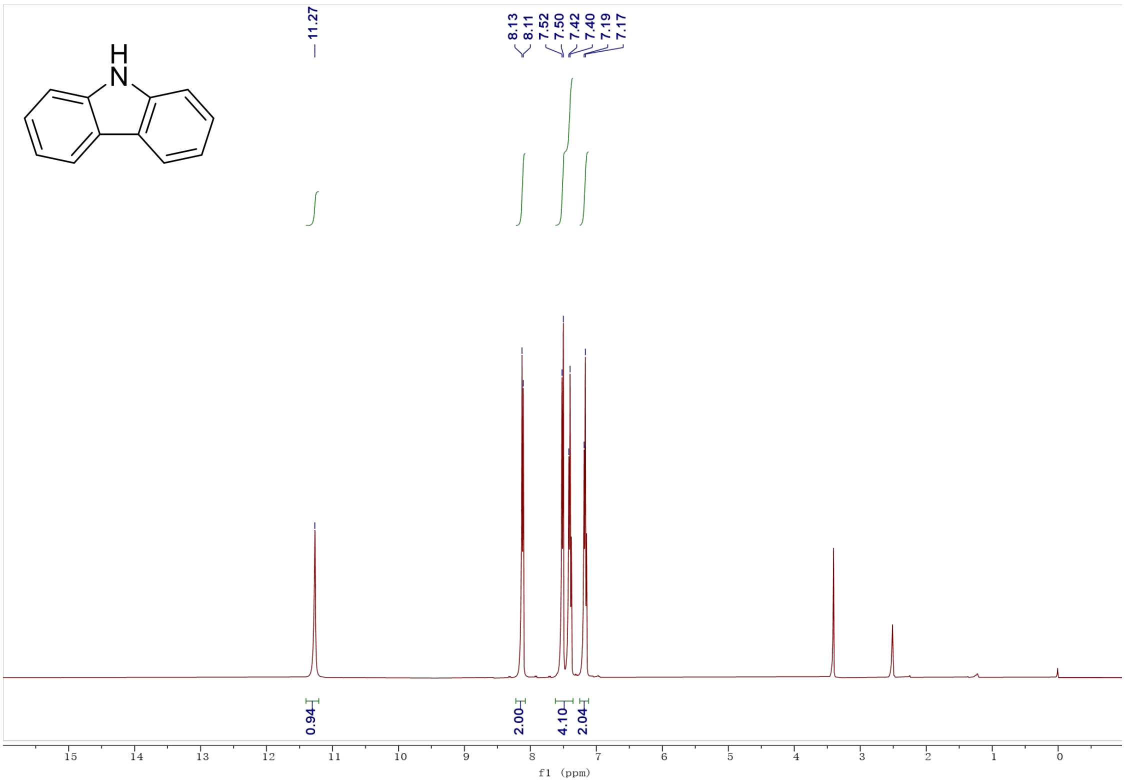
^{1}H NMR spectrum of compound **3s** (400 MHz, CDCl$_3$)



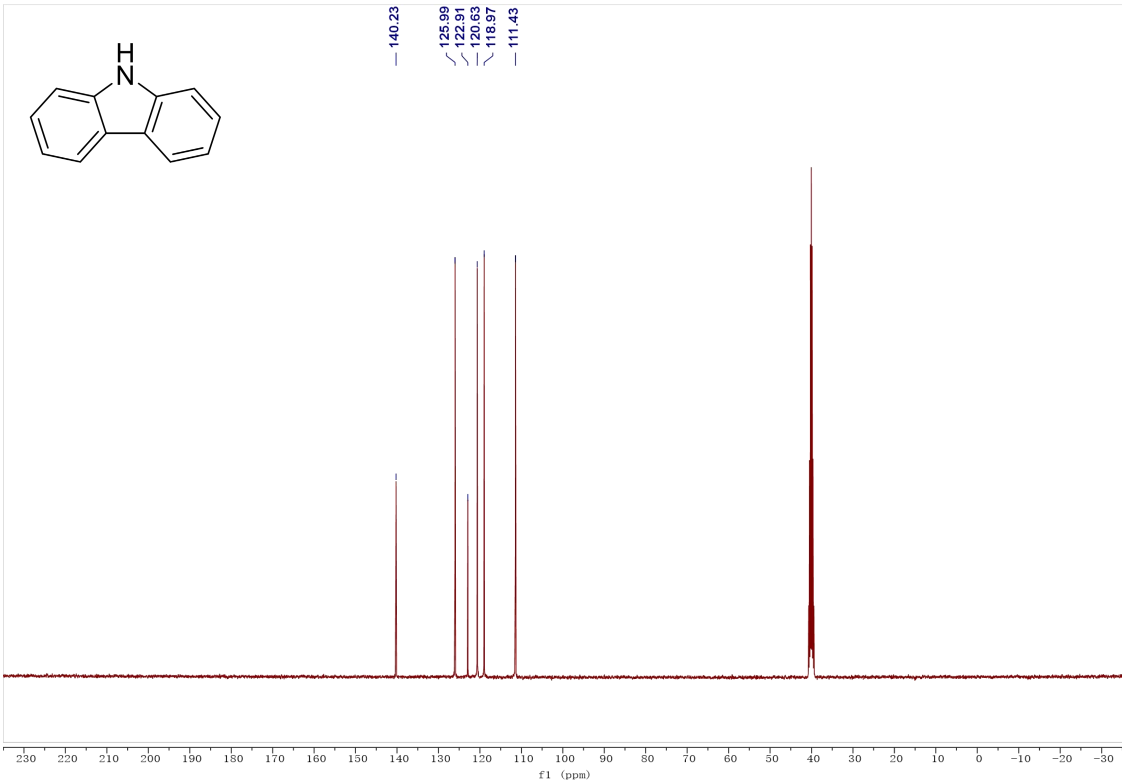
^{13}C NMR spectrum of compound **3s** (101 MHz, $CDCl_3$)



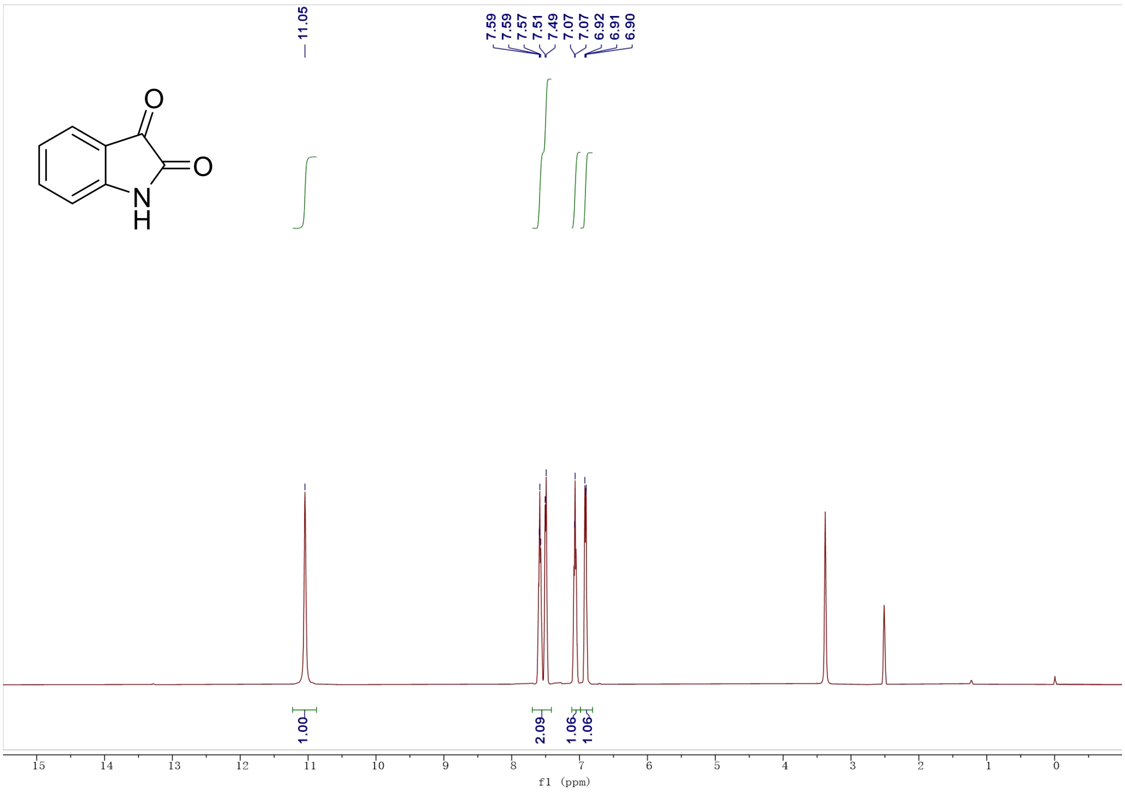
^{1}H NMR spectrum of compound **3t** (400 MHz, DMSO-d_6)



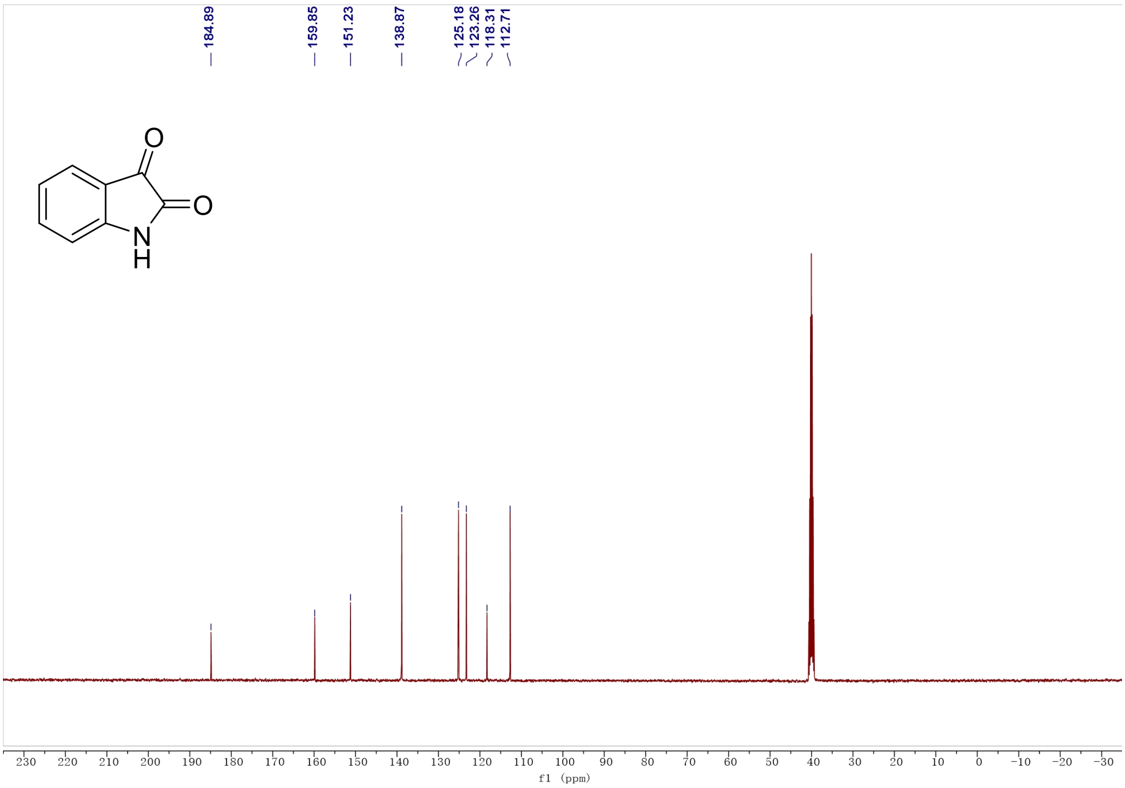
^{13}C NMR spectrum of compound **3t** (101 MHz, DMSO-d_6)



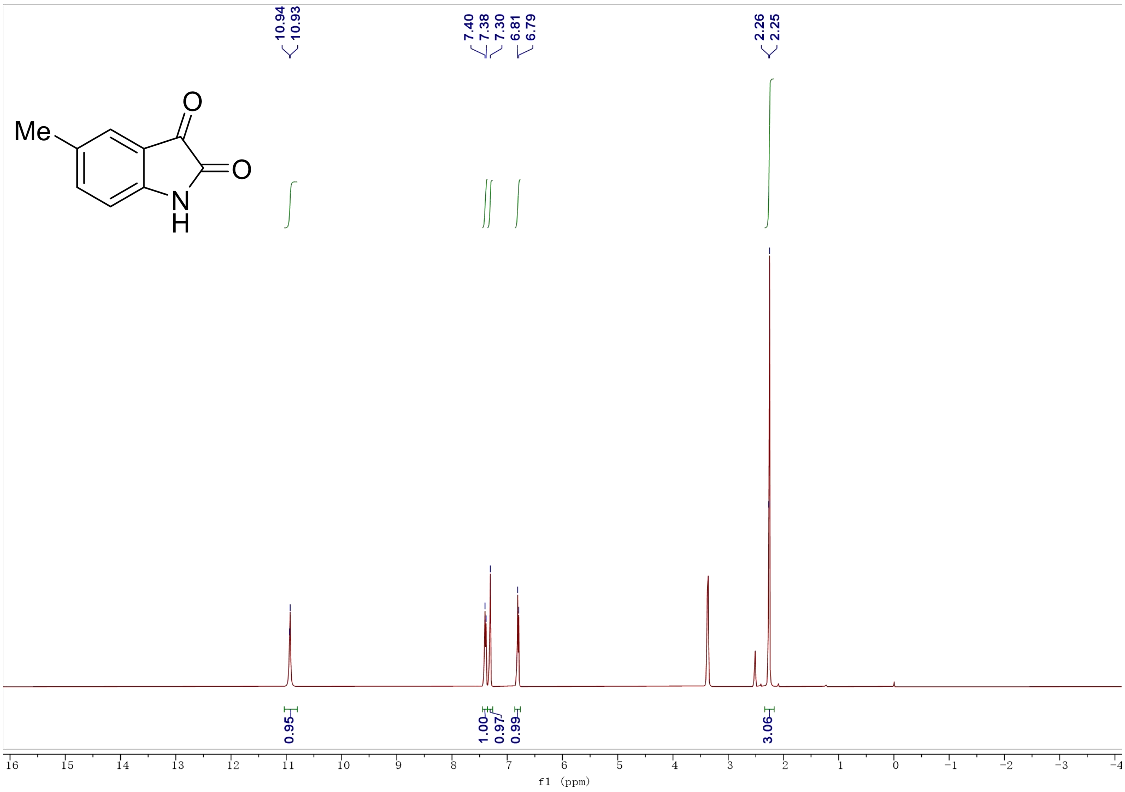
^{1}H NMR spectrum of compound **4a** (400 MHz, DMSO-d_6)



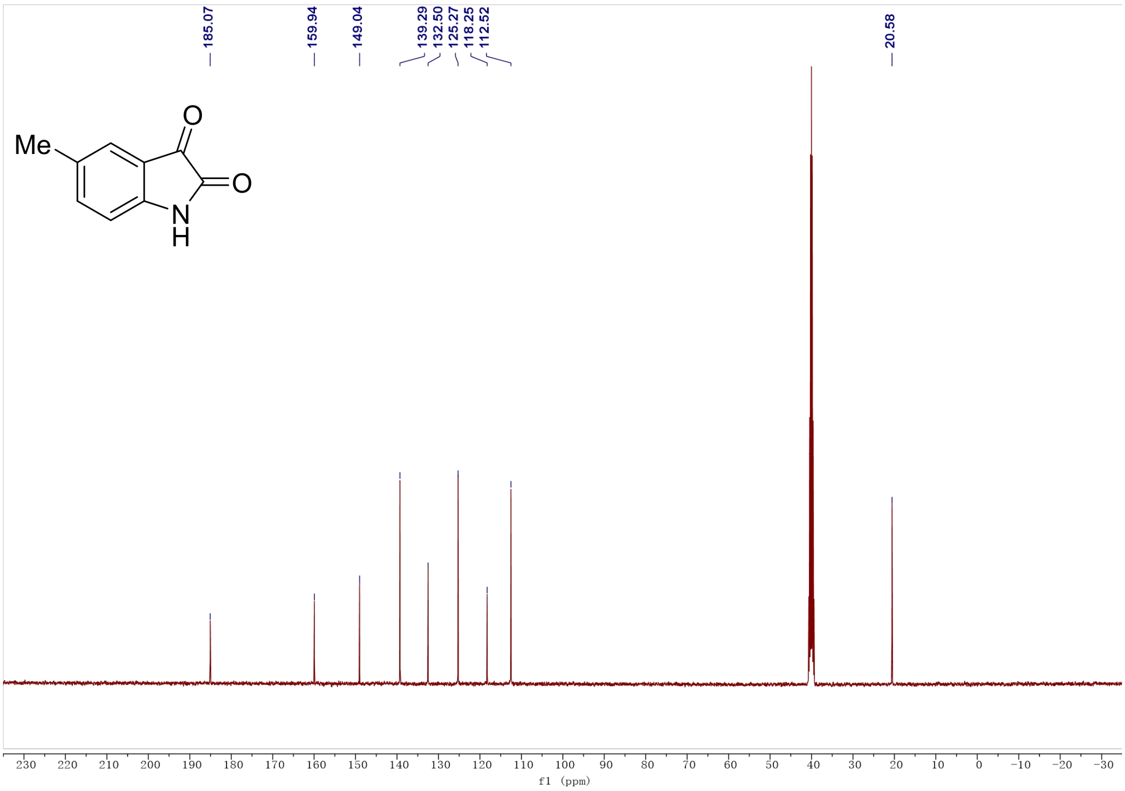
^{13}C NMR spectrum of compound **4a** (101 MHz, DMSO-*d_6*)



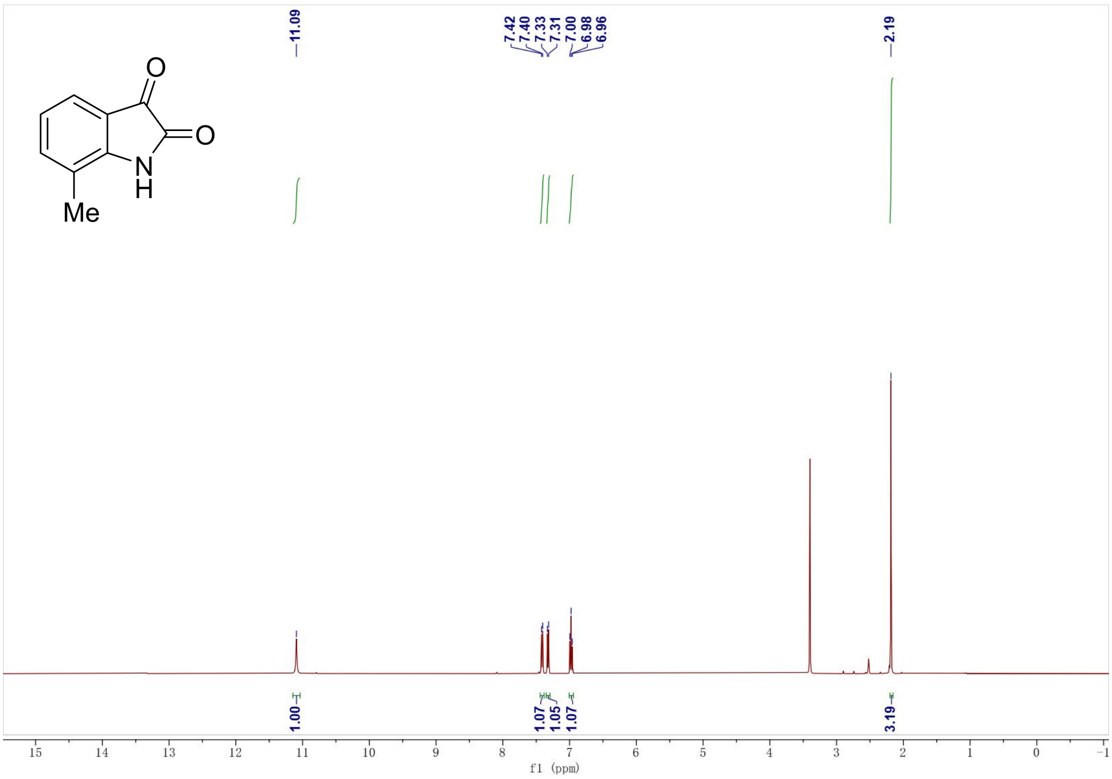
^{1}H NMR spectrum of compound **4d** (400 MHz, DMSO-*d_6*)



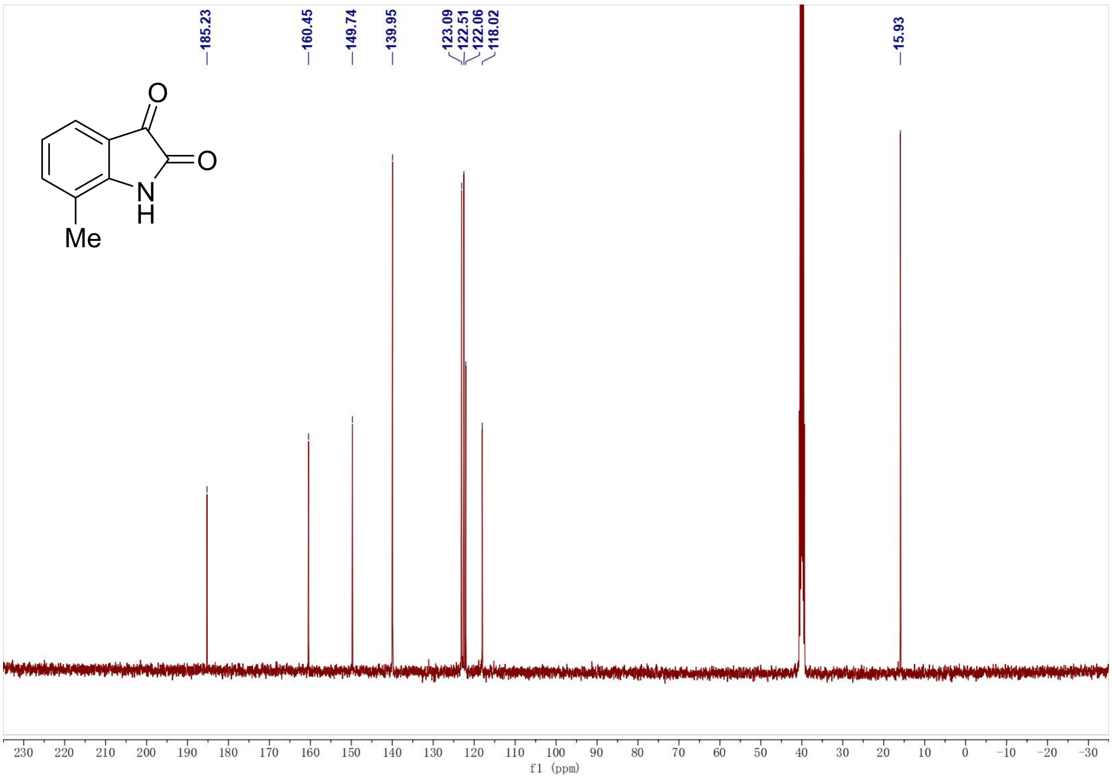
^{13}C NMR spectrum of compound **4d** (101 MHz, DMSO-d_6)



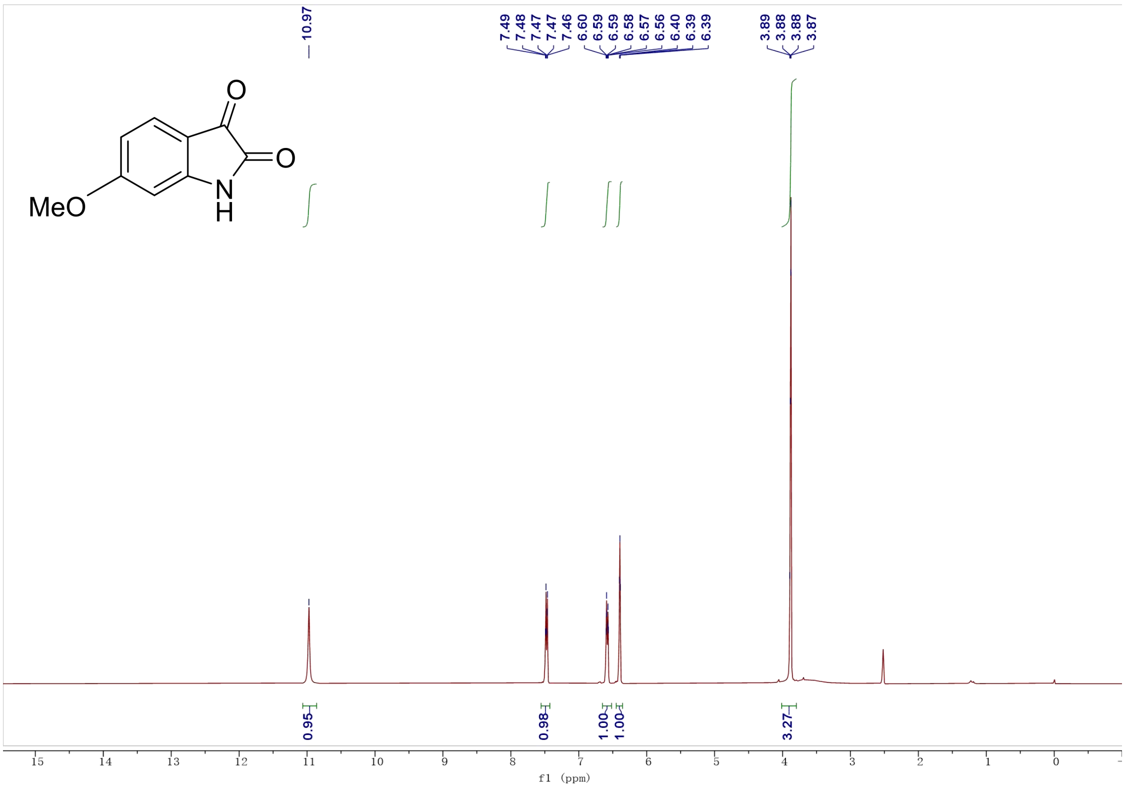
^{1}H NMR spectrum of compound **4f** (400 MHz, DMSO-d_6)



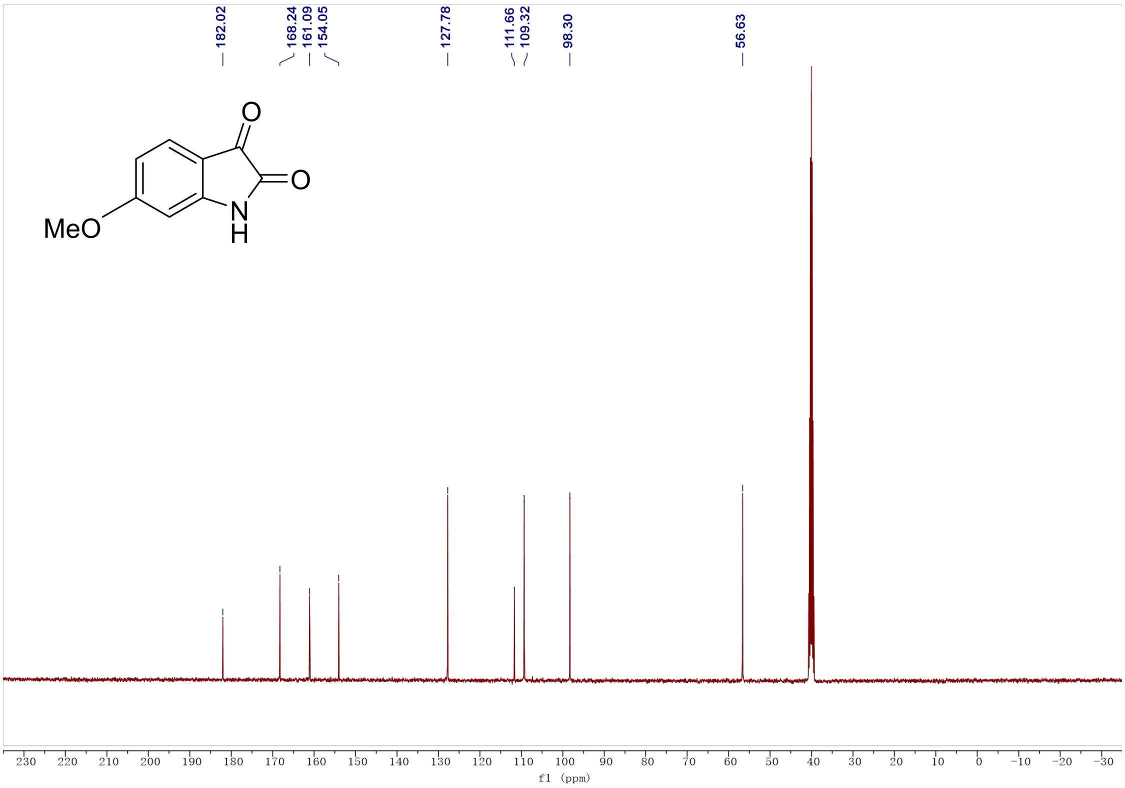
^{13}C NMR spectrum of compound **4f** (101 MHz, DMSO-d_6)



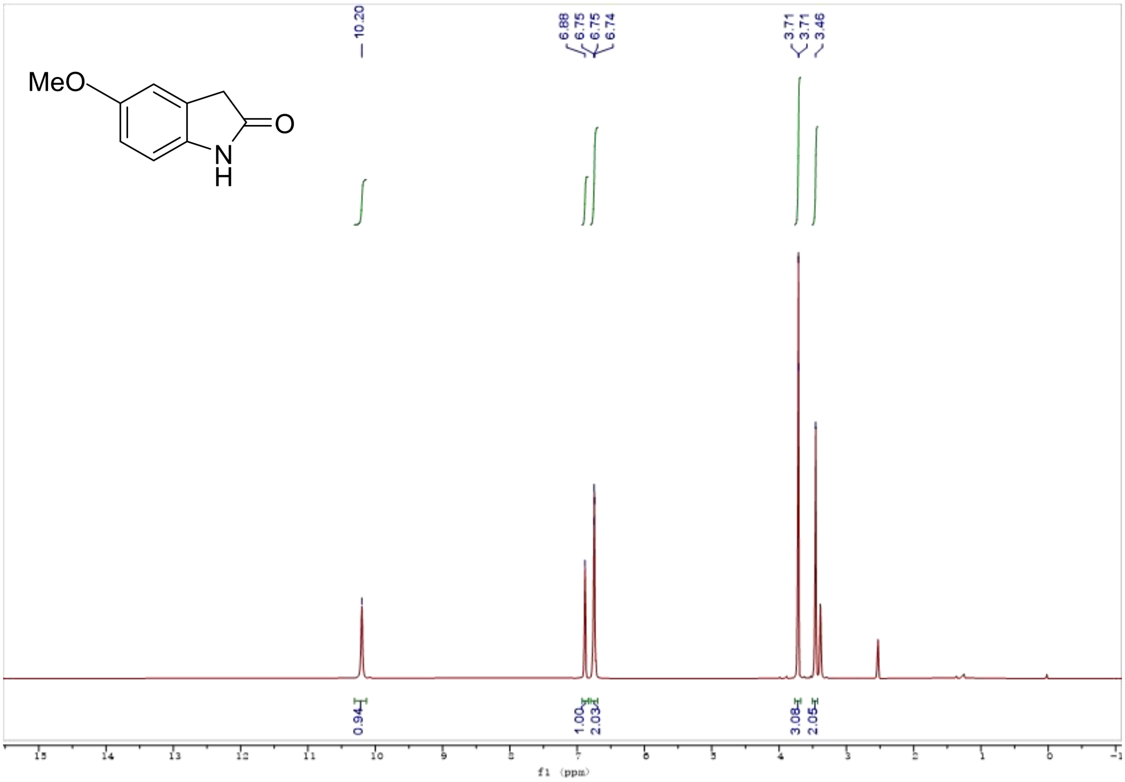
^{1}H NMR spectrum of compound **4g** (400 MHz, DMSO-d_6)



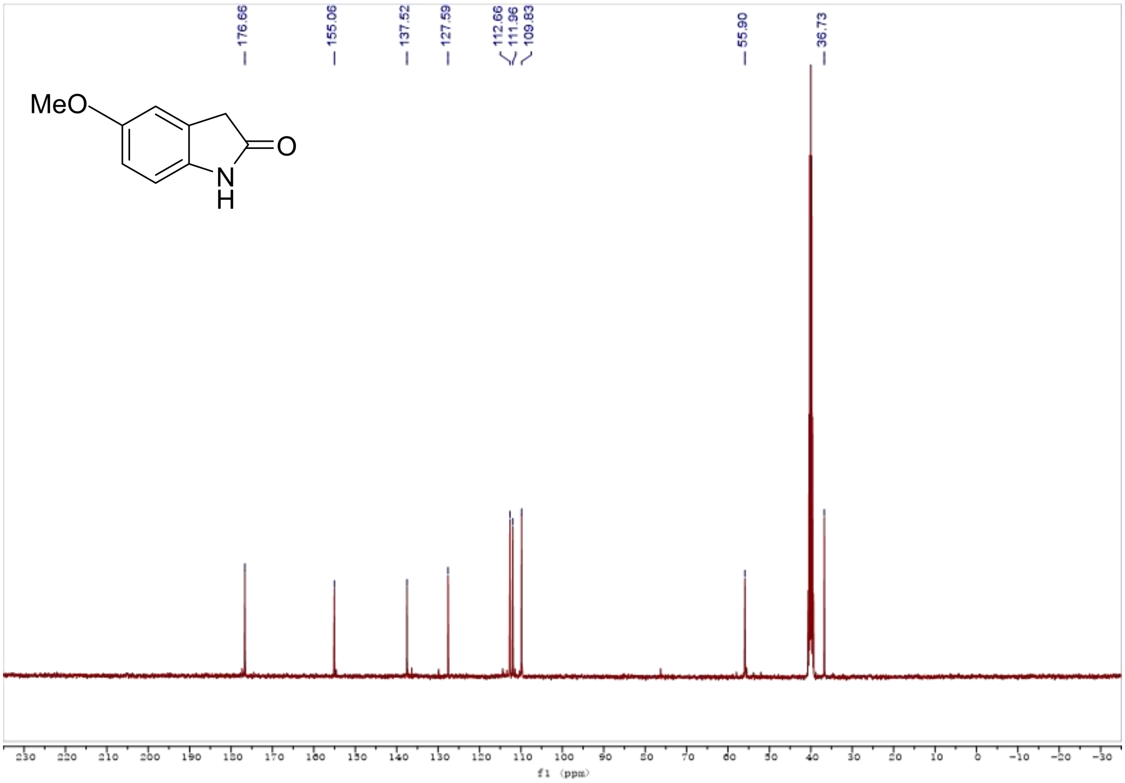
^{13}C NMR spectrum of compound **4g** (101 MHz, DMSO-d_6)



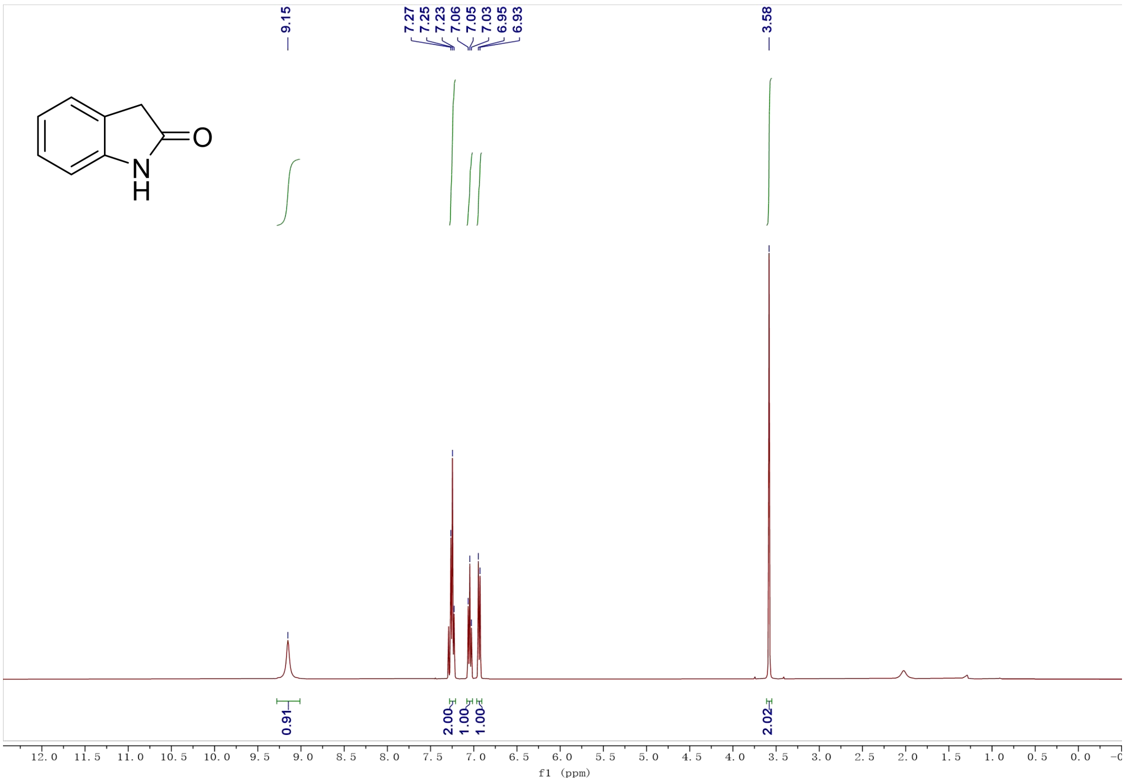
^{1}H NMR spectrum of compound **4h** (400 MHz, CDCl$_3$)



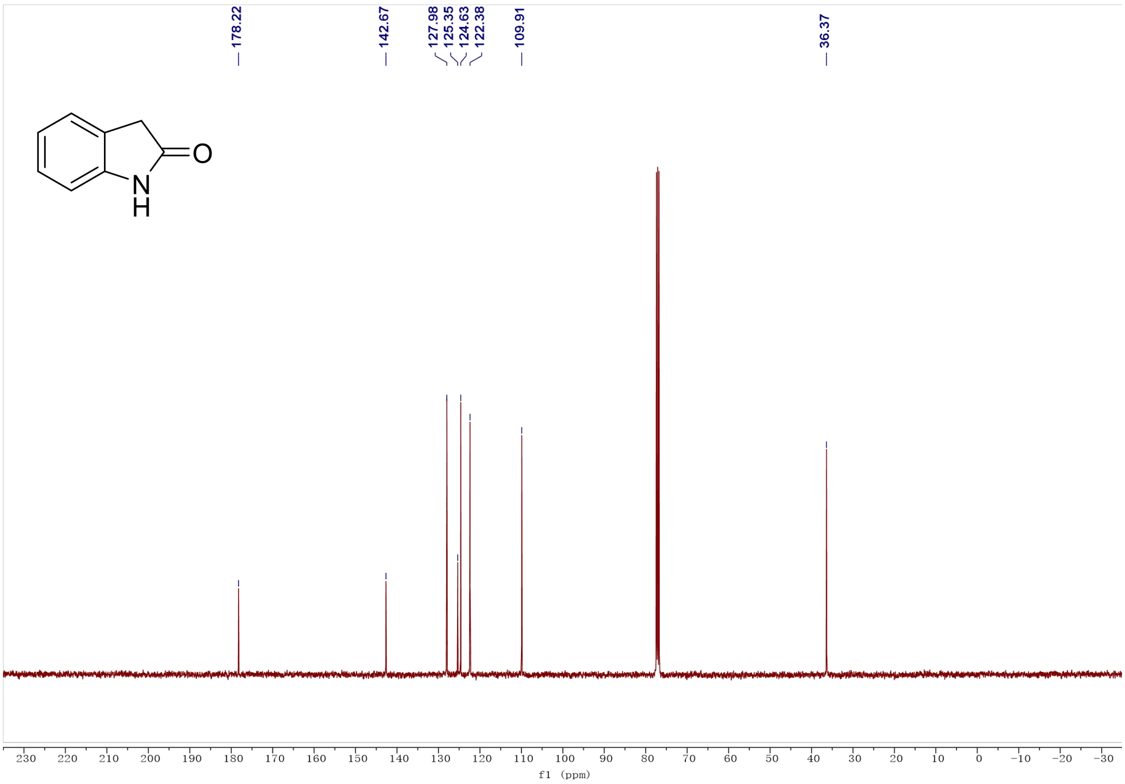
^{13}C NMR spectrum of compound **4h** (101 MHz, DMSO-d_6)



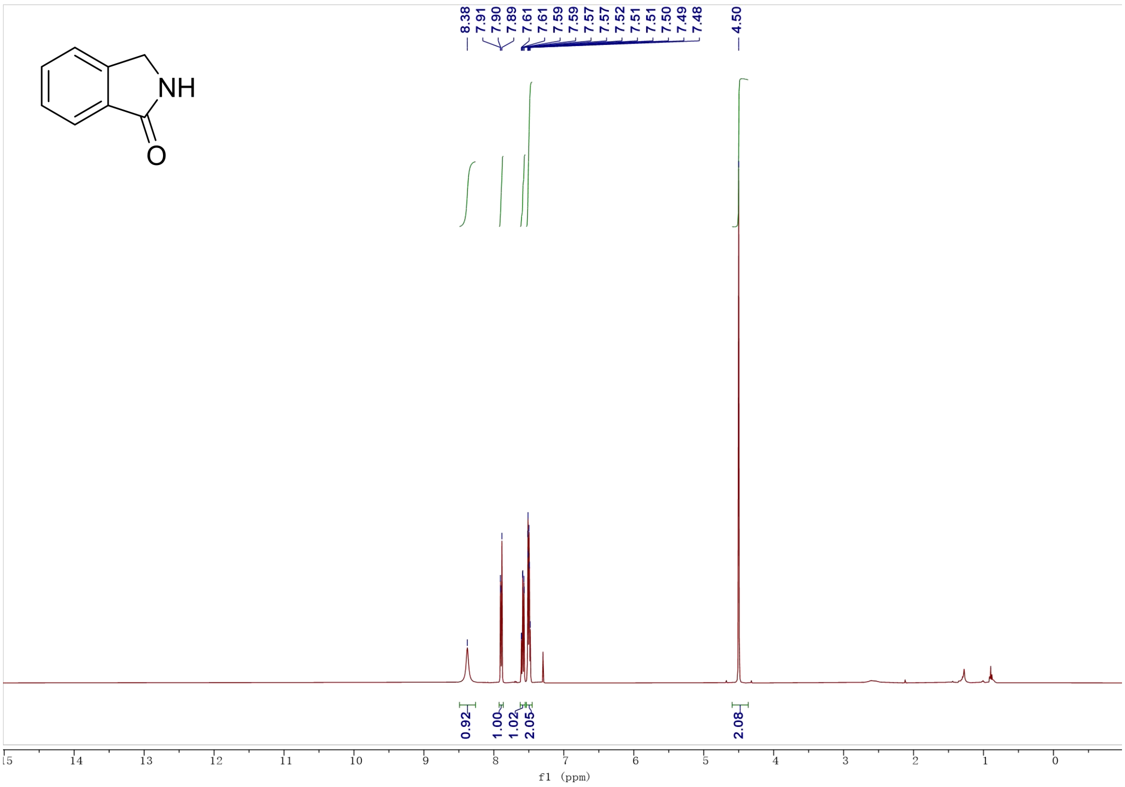
^{1}H NMR spectrum of compound **4i** (400 MHz, $CDCl_3$)



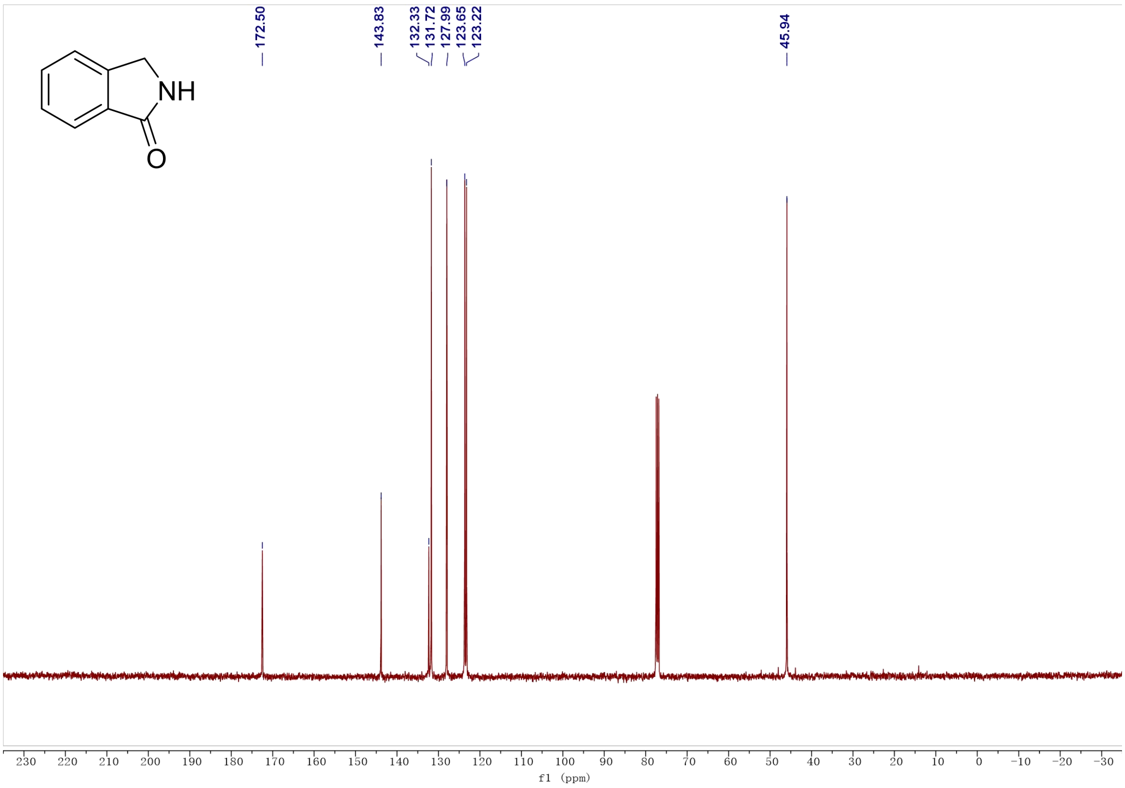
^{13}C NMR spectrum of compound **4i** (101 MHz, $CDCl_3$)



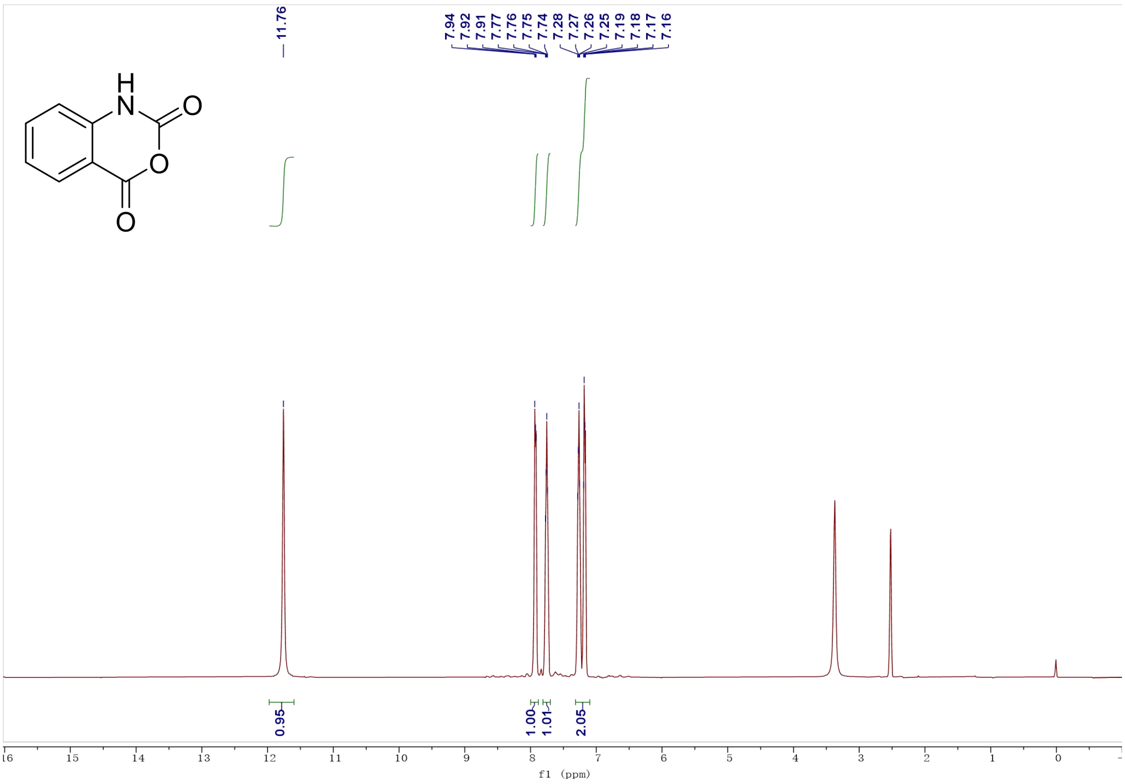
^{1}H NMR spectrum of compound **4j** (400 MHz, $CDCl_3$)



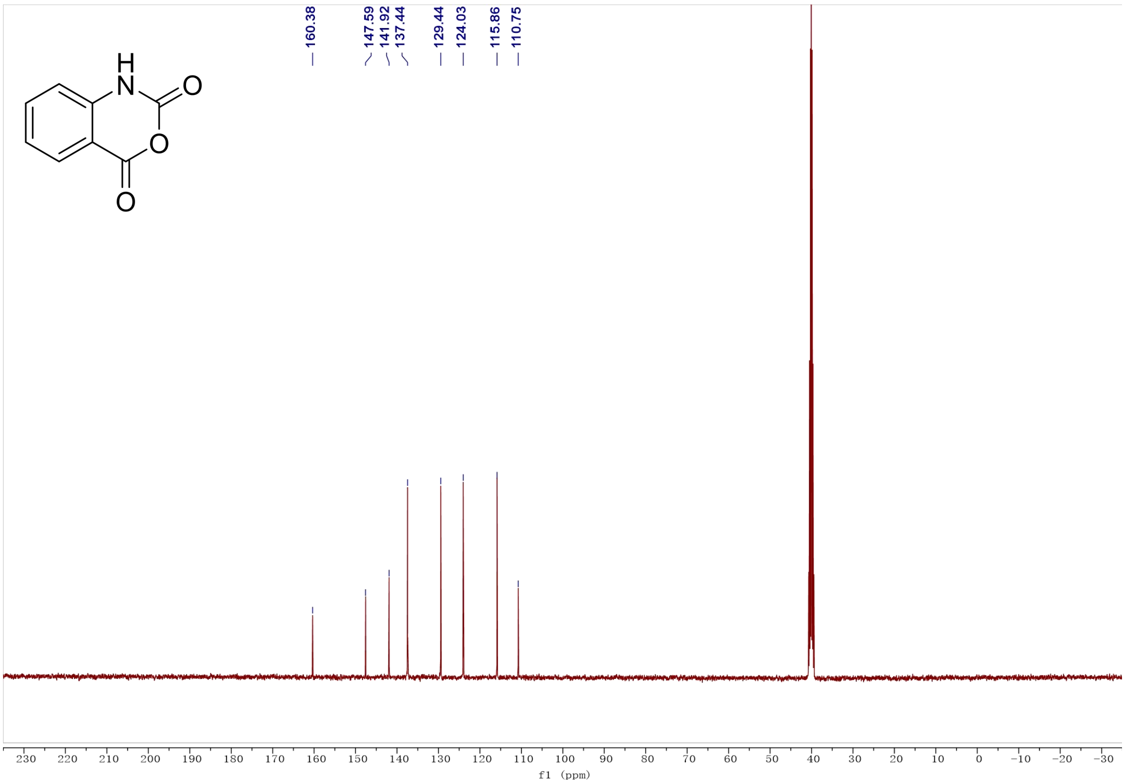
^{13}C NMR spectrum of compound **4j** (101 MHz, $CDCl_3$)



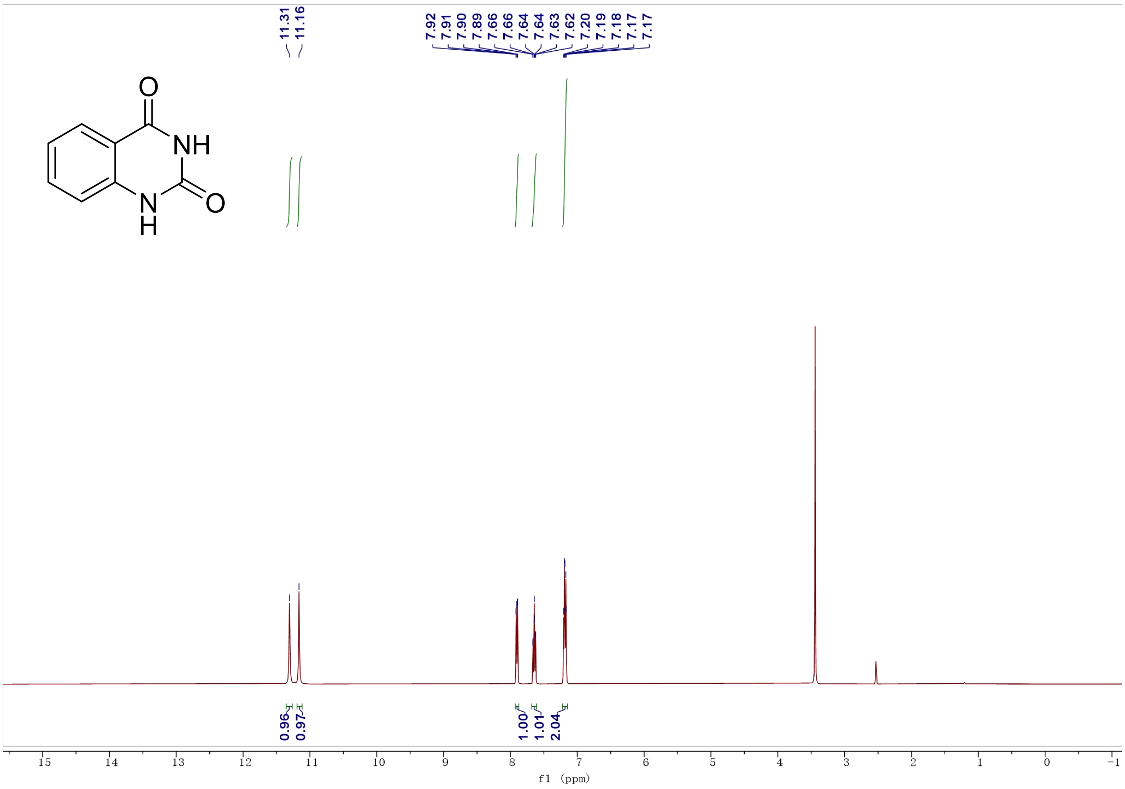
^{1}H NMR spectrum of compound **4k** (400 MHz, DMSO-d_6)



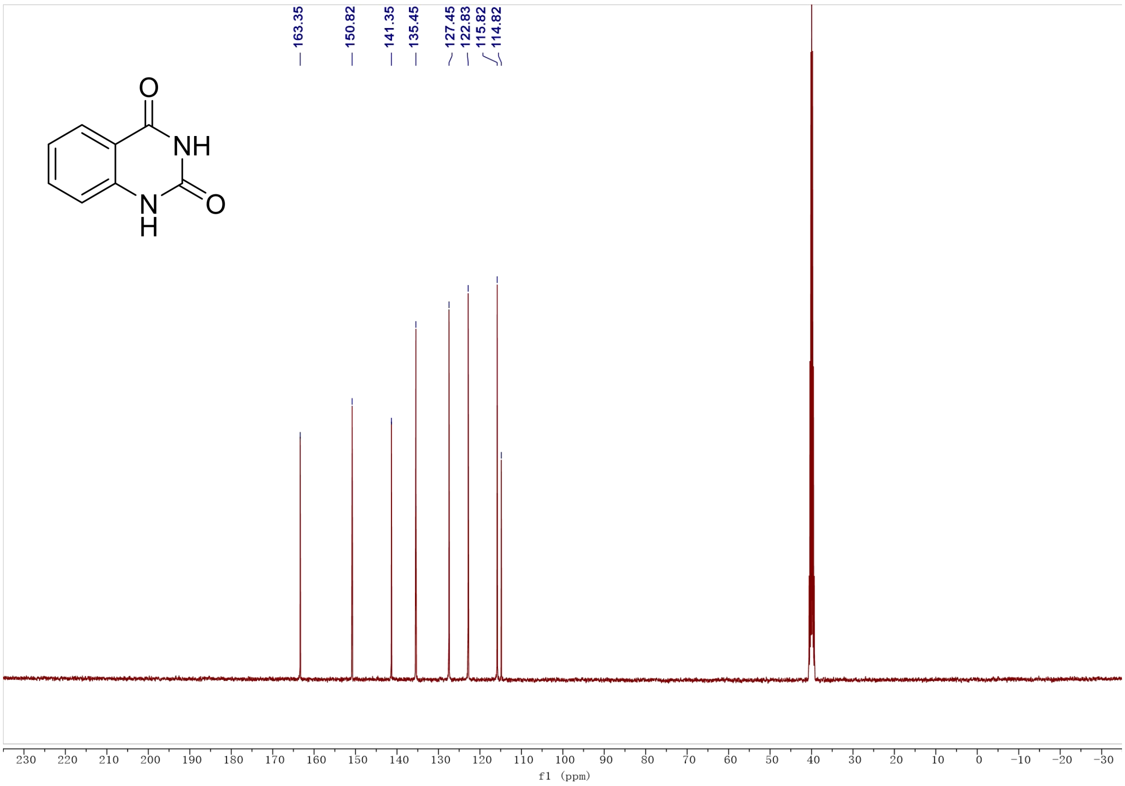
^{13}C NMR spectrum of compound **4k** (101 MHz, DMSO-d_6)



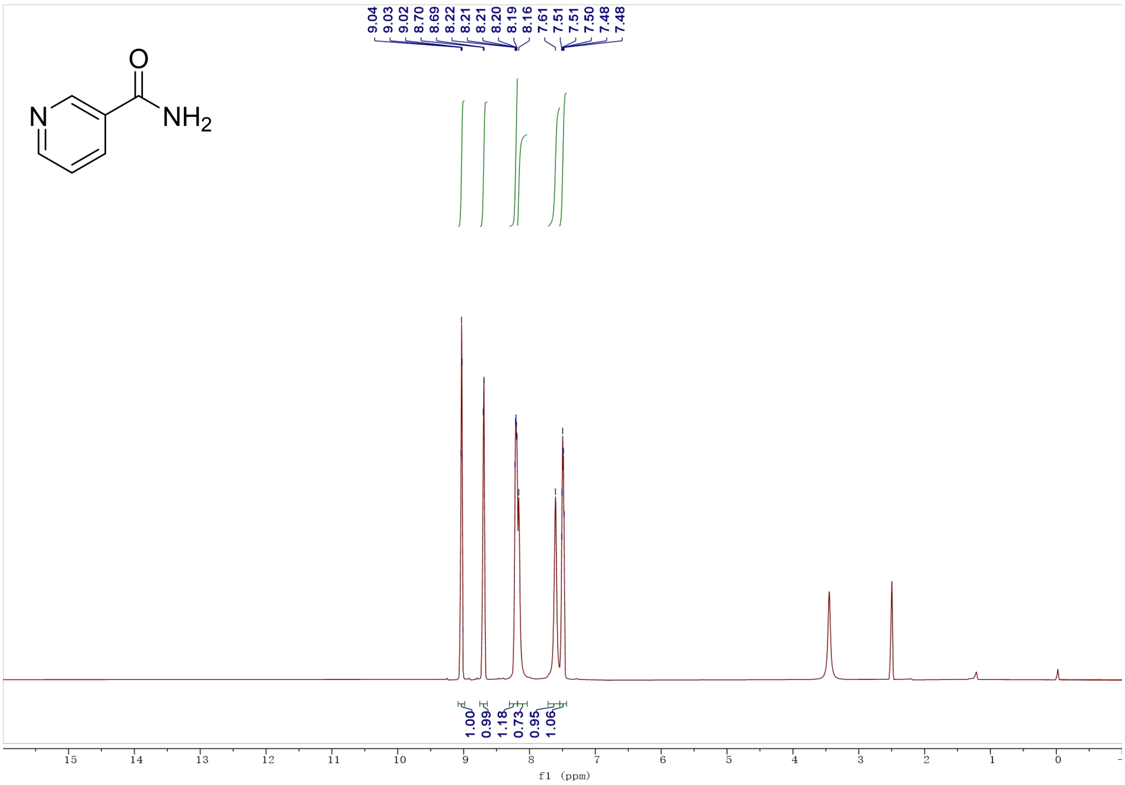
^{1}H NMR spectrum of **quinazoline-2,4(1*H*,3*H*)-dione** (400 MHz, DMSO-d_6)



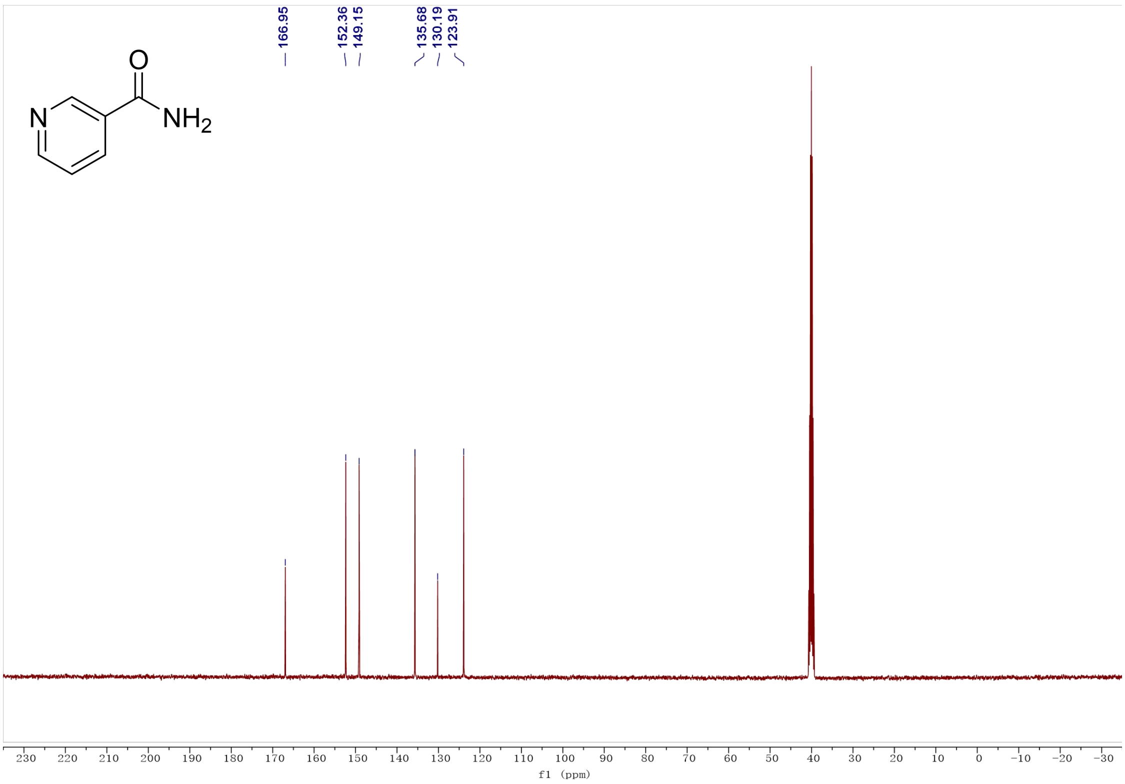
^{13}C NMR spectrum of **quinazoline-2,4(1*H*,3*H*)-dione** (101 MHz, DMSO-d_6)



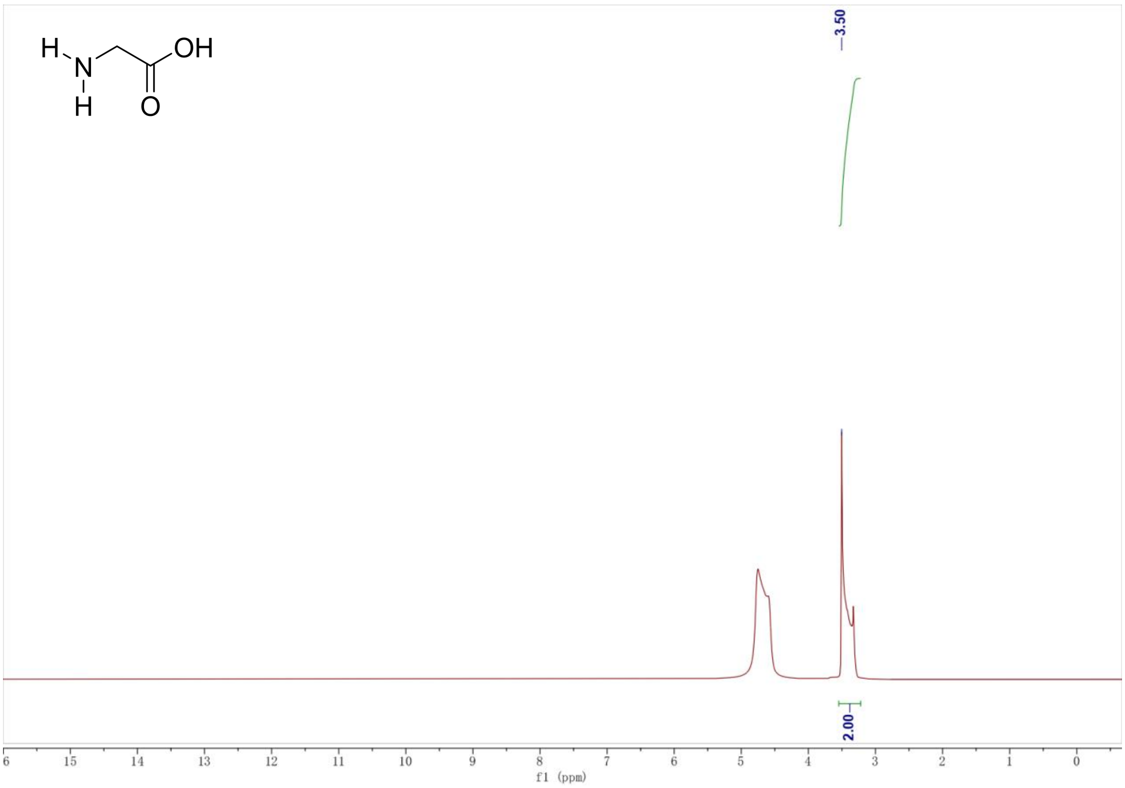
^{1}H NMR spectrum of **nicotinamide** (400 MHz, DMSO-d_6)



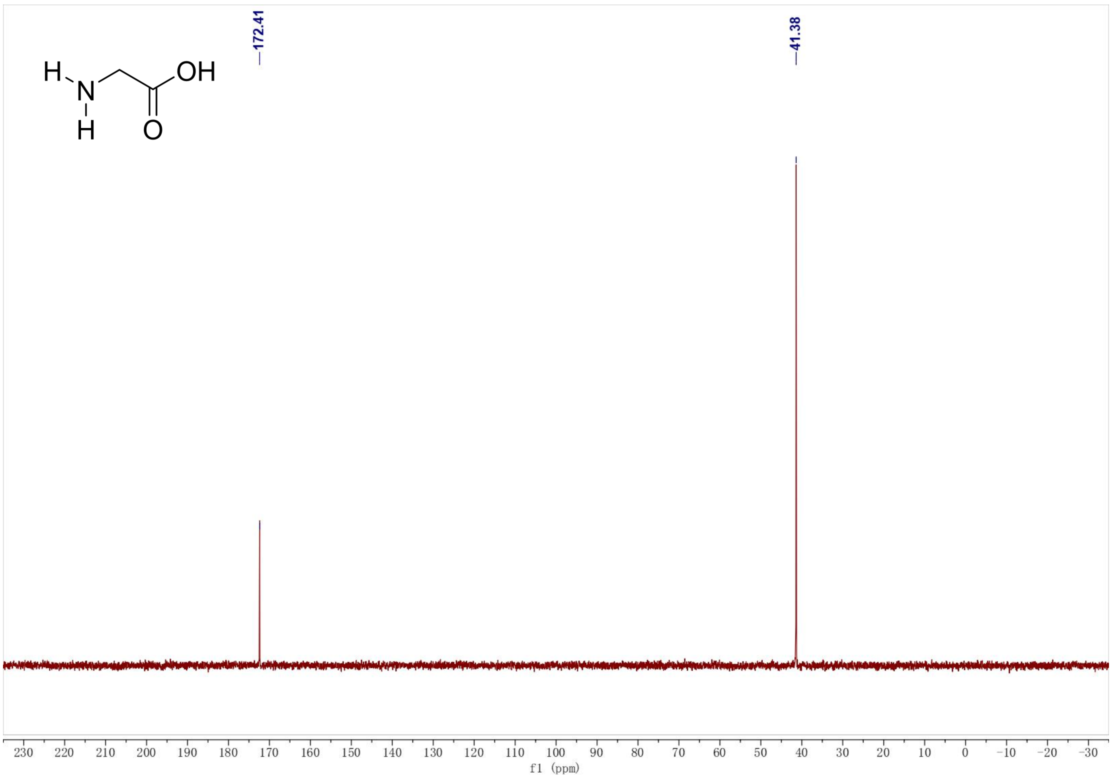
^{13}C NMR spectrum of **nicotinamide** (101 MHz, DMSO-d_6)



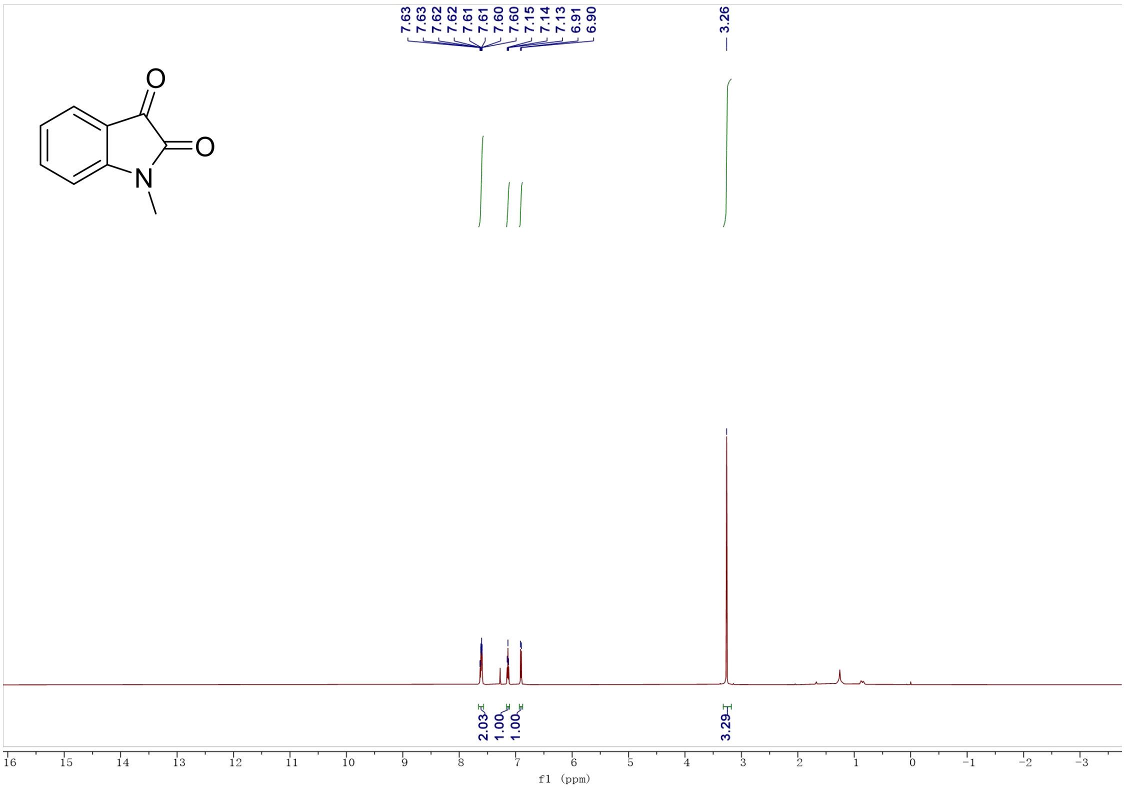
^{1}H NMR spectrum of **Glycine** (400 MHz, D_2O)



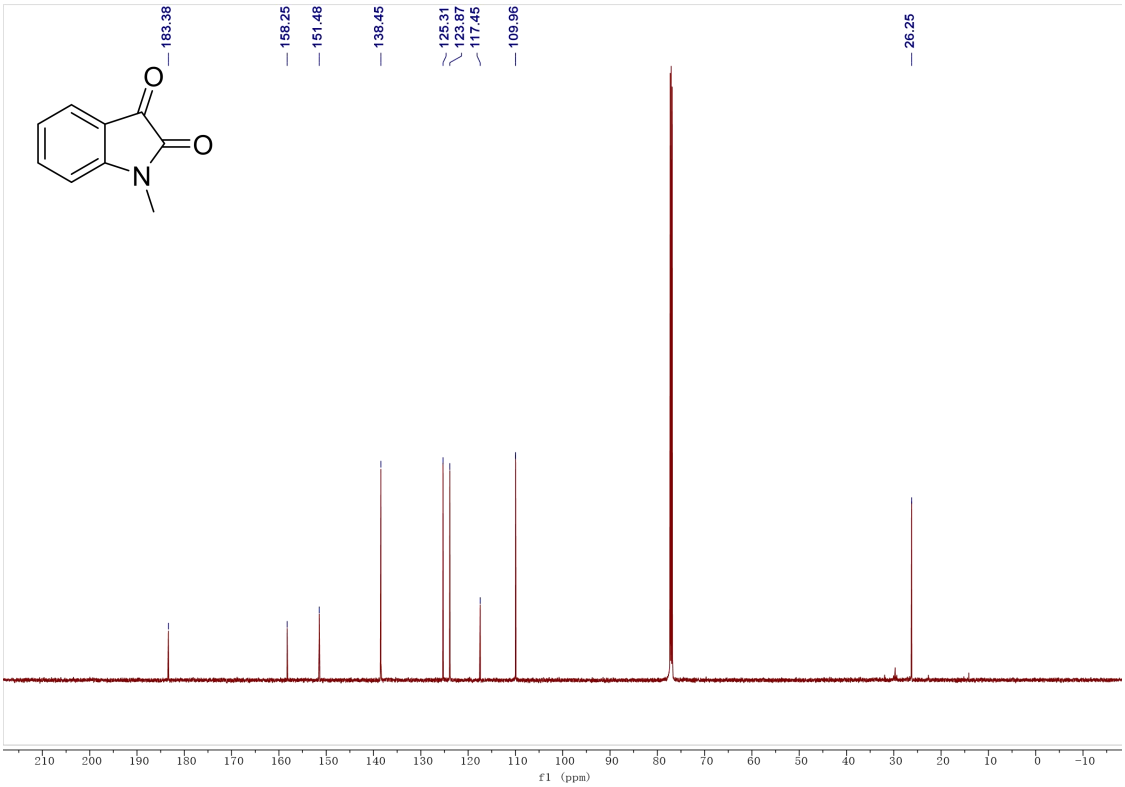
^{13}C NMR spectrum of **Glycine** (101 MHz, D_2O)



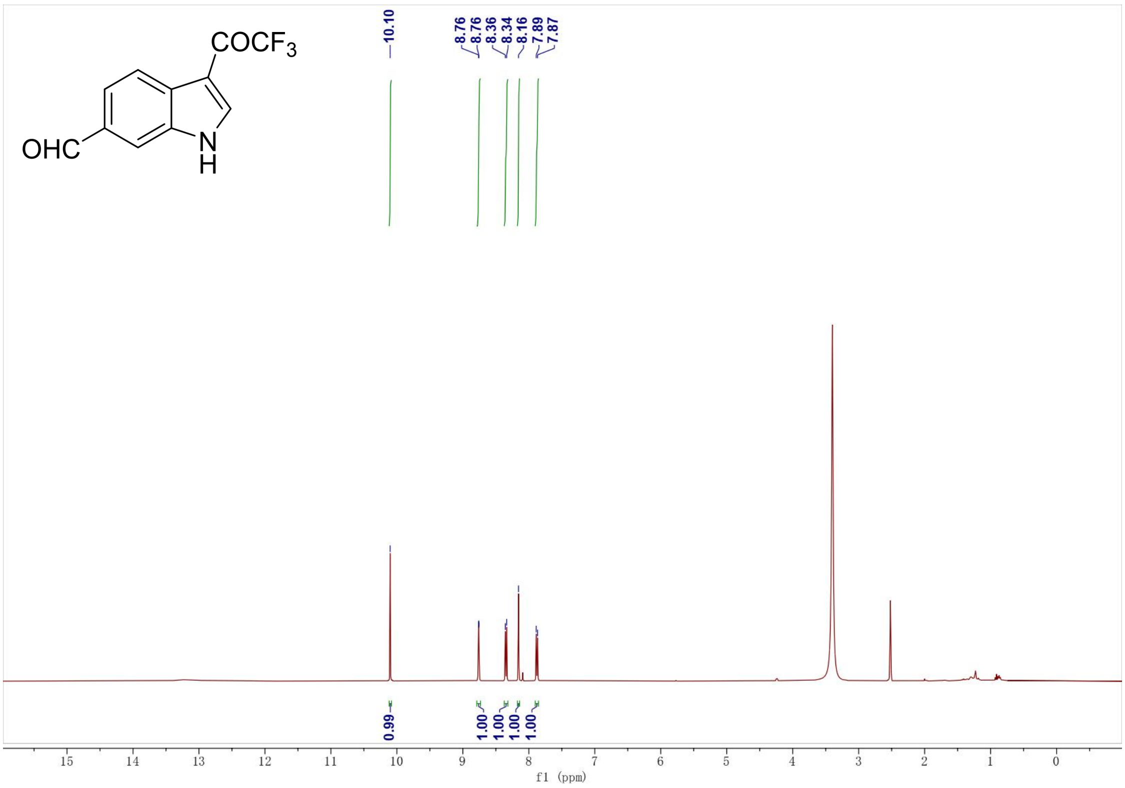
^{1}H NMR spectrum of compound **2a** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **2a** (151 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **3i'** (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of compound **3i'** (101 MHz, DMSO-d_6)