Supporting Information

dppb and TfOH promoted cascade reaction of *o*-nitrophenylpropiolamides access to C2-spiro-pseudoindoxyls

Qiongwen Kang,[a] Yan Wang,[a] Zongkang Wang,[a] Nana Fei,[a] Peng He,[a] Lingkai Kong,*[b] and Yanzhong Li *[a]

[a]School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road, Shanghai 200241, China.

[b]School of Chemistry and Chemical Engineering, Linyi University, Shuangling Road, Linyi, Shandong, 276000, China

Fax: (+86) 021-54340096, E-mail: yzli@chem.ecnu.edu.cn

Table of Contents

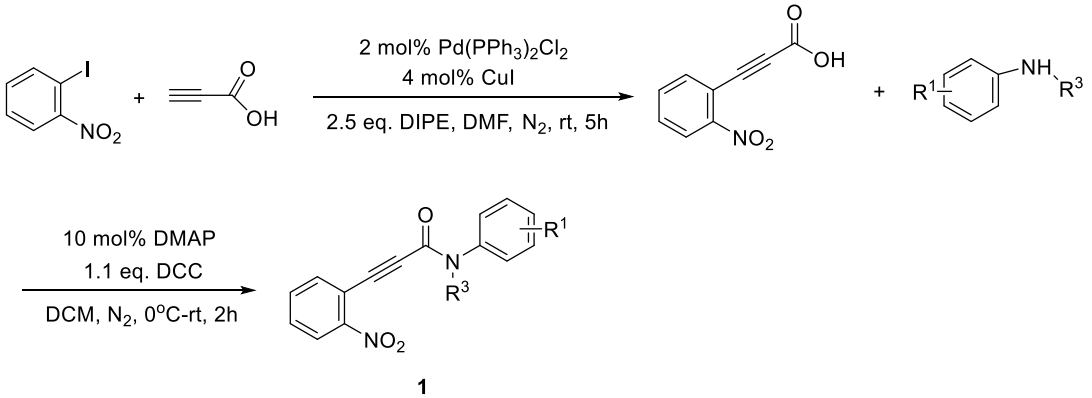
1. General information

Unless noted, all commercial reagents were used without further purification. Reactions were monitored by thin layer chromatography. Column chromatographic purification of products was carried out using silica gel (200~300 mesh). ^{1}H NMR spectra were recorded at 500 MHz or 600 MHz; ^{13}C NMR spectra were recorded at 125 MHz or 150 MHz in $CDCl_3$ (containing 0.03% TMS) or d^6-DMSO solutions. ^{1}H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) or d^6-DMSO (δ = 2.50 ppm) as the internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) or d^6-DMSO (δ = 39.52 ppm) as the internal reference. High-resolution mass spectra were recorded on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single crystal X-raydiffraction data was collected in Bruker SMARTAPEX diffractiometers with molybdenum cathodes.

2. Synthesis of 1

The *o*-nitrophenylpropiolamides **1** were prepared according to the reference [1-4].

General procedure (A) for the preparation of *o*-nitrophenylpropiolamides 1:



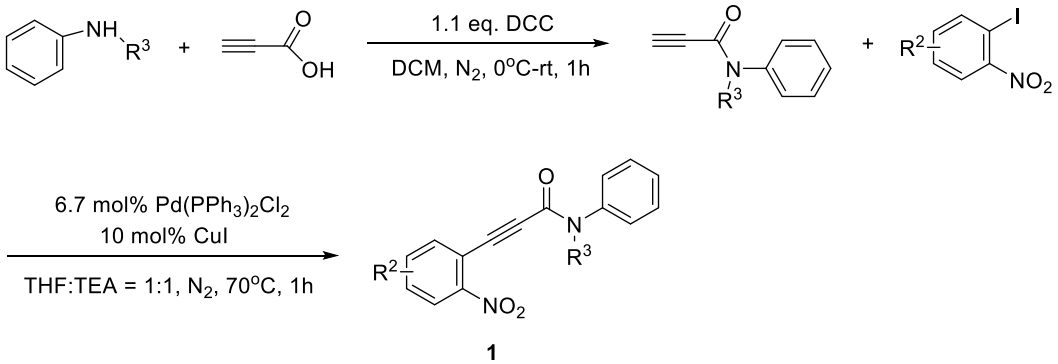
1

To a flame dried round bottom flask was added 1-iodo-2-nitrobenzene (2.5 g, 10 mmol), copper iodide (0.0762 g, 0.4 mmol) and Pd $(PPh_3)_2Cl_2$ (0.1404 g, 0.2 mmol). DMF (14

mL) was added and the resulting solution was purged several times with nitrogen. The flask was cooled to 0 °C, after which propiolic acid (0.76 mL, 12 mmol) and diisopropylethylamine (dropwise; 3.5 mL, 2.5 mmol) were added. The reaction temperature was raised to room temperature for 5 h. Upon completion, the reaction mixture was then quenched by water (20 mL), and the water layers were extracted with ethyl acetate (30 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure.

An oven dried round-bottom flask was charged with phenylpropiolic acid (286.5, 1.5 mmol) and DMAP (183 mg, 0.15 mmol, 10 mol %) and purged with nitrogen. The contents were dissolved in CH_2Cl_2 (3 mL) before the amine was added (1.1 equiv). The mixture was cooled to 0 °C and a CH_2Cl_2 (2 mL) solution of DCC (309.5, 1.5 mmol, 1.0 equiv) was added dropwise. The reaction was warmed to room temperature and stirred until TLC indicated the total consumption of the phenylpropiolic acid. The crude mixture was filtered and washed with CH_2Cl_2, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (petroleum ether/EtOAc = 4:1) to give **1** as a red solid.

General procedure (B) for the preparation of *o*-nitrophenylpropiolamides 1:



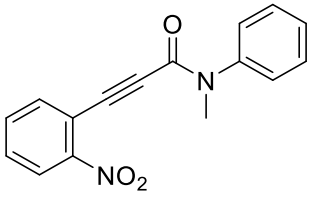
1

To a solution of propiolic acid (0.68 mL, 11 mmol, 1.1 equiv.) and *N*-substituted aniline (10 mmol) in dried CH_2Cl_2 (25 mL) was added gradually DCC (2.2696 g, 11 mmol, 1.1 equiv.) at 0 °C. Then the reaction mixture was stirred at room temperature until TLC indicated the total consumption of the *N*-substituted aniline. The mixture was filtrated

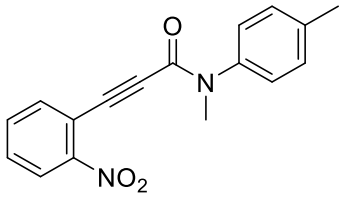
and washed with CH_2Cl_2, dried over Na_2SO_4, and concentrated. The residue was purified by a silica gel column chromatography (petroleum ether/EtOAc = 3:1) to give phenylpropiolamides as a yellow solid.

To a solution of substituted phenylpropiolamides (1.3 mmol, 1.3 equiv) and substituted *o*-iodonitrobenzene (1.0 mmol) in dry Et_3N (8 mL) and THF (8 mL), under a nitrogen atmosphere was added Pd $(PPh_3)_2Cl_2$ (47 mg, 0.067 mmol) and CuI (19 mg, 0.1 mmol) was added. The reaction mixture was heated to 70 °C. After the reaction was completed as monitored by thin-layer chromatography, the resulting mixture was filtered and the filtrate was evaporated to remove the solvent. Then the residue was extracted with EtOAc (50 mL x 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give **1** as a yellow solid.

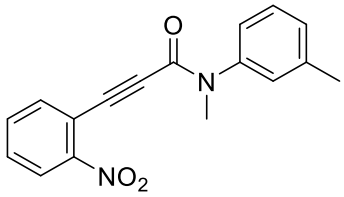
The analytical data of Compounds **1** are as follows.



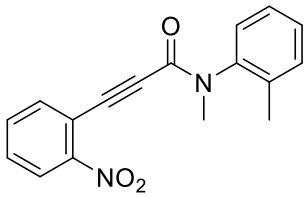
N-methyl-3-(2-nitrophenyl)-N-phenylpropiolamide (1a). Following the general procedure B, compound **1a** was obtained in 4 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); yellow solid, yield: (4 mmol, 941 mg, 84%); m.p. 98-100 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 8.00-7.98 (m, 1H), 7.54-7.51 (m, 1H), 7.49-7.47 (m, 1H), 7.46-7.41 (m, 3H), 7.37-7.35 (m, 3H), 3.40 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.4, 149.4, 142.3, 135.3, 132.8, 130.1, 129.3, 128.1, 127.2, 124.6, 116.1, 88.8, 85.1, 36.5. HRMS (ESI) calcd for $C_{16}H_{12}NaN_2O_3$, $[M+Na]^+$: 303.0740, found: 303.0747.



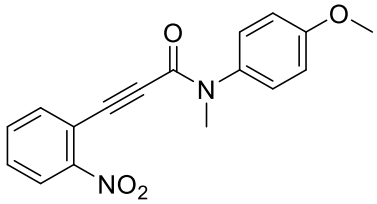
N-methyl-3-(2-nitrophenyl)-N-(p-tolyl)propiolamide (1b). Following the general procedure A, compound **1b** was obtained in 4 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); red solid, yield: (1.5 mmol, 229.8 mg, 52%); m.p. 135-137 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 7.99-7.97 (m, 1H), 7.55-7.51 (m, 1H), 7.49-7.45 (m, 2H), 7.23-7.22 (m, 4H), 3.37 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.5, 149.4, 139.7, 138.1, 135.2, 132.8, 130.0, 129.8, 126.9, 124.5, 116.2, 88.9, 85.0, 36.5, 21.1. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_3$, $[M+Na]^+$: 317.0897, found: 317.0901.



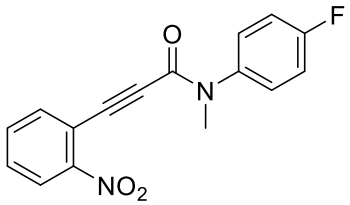
N-methyl-3-(2-nitrophenyl)-N-(m-tolyl)propiolamide (1c). Following the general procedure A, compound **1c** was obtained in 4 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); red solid, yield: (1.2 mmol, 235 mg, 67%); m.p. 75-77 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 8.00-7.98 (m, 1H), 7.55-7.52 (m, 1H), 7.49-7.44 (m, 2H), 7.32-7.27 (m, 1H), 7.17-7.14 (m, 3H), 3.38 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.4, 149.3, 142.2, 139.4, 135.2, 132.8, 130.0, 129.0, 128.8, 127.7, 124.5, 124.1, 116.1, 88.8, 85.0, 36.5, 21.2. HRMS (ESI) calcd for $C_{17}H_{15}N_2O_3$, $[M+H]^+$: 295.1077, found: 295.1079.



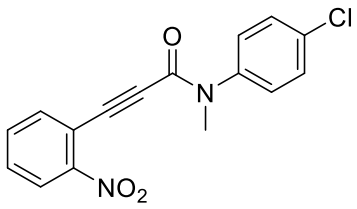
N-methyl-3-(2-nitrophenyl)-N-(o-tolyl)propiolamide (1d). Following the general procedure A, compound **1d** was obtained in 4 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); red solid, yield: (1.2 mmol, 177.5 mg, 50%); m.p. 72-74 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 7.96 (d, *J* = 8.0 Hz, 1H), 7.52-7.44 (m, 2H), 7.37-7.24 (m, 5H), 3.31 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.8, 149.3, 141.1, 136.2, 135.3, 132.8, 131.2, 130.0, 128.8, 128.4, 127.1, 124.5, 116.0, 88.6, 84.2, 35.5, 17.4. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_3$, $[M+Na]^+$: 317.0897, found: 317.0904.



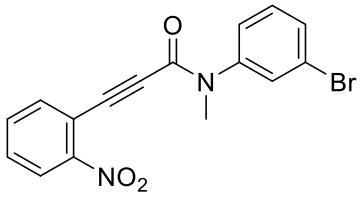
N-(4-methoxyphenyl)-N-methyl-3-(2-nitrophenyl)propiolamide (1e). Following the general procedure A, compound **1e** was obtained in 4 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); red solid, yield: (1.5 mmol, 254.1 mg, 55%); m.p. 76-78 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 7.98-7.96 (m, 1H), 7.55-7.52 (m, 1H), 7.49-7.46 (m, 2H), 7.28-7.25 (m, 2H), 6.95-6.91 (m, 2H), 3.82 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.2, 153.7, 149.5, 135.2, 132.8, 130.0, 128.4, 126.6, 124.5, 116.1, 114.4, 88.8, 85.2, 55.5, 36.7. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_4$, $[M+Na]^+$: 333.0846, found: 333.0850.



N-(4-fluorophenyl)-N-methyl-3-(2-nitrophenyl)propiolamide (1f). Following the general procedure A, compound **1f** was obtained in 4 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1); red solid, yield: (1.2 mmol, 200.8 mg, 56%); m.p. 109-111 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 8.01-7.99 (m, 1H), 7.58-7.54 (m, 1H), 7.52-7.48 (m, 2H), 7.36-7.31 (m, 2H), 7.14-7.09 (m, 2H), 3.38 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.0 (d, J_{C-F} = 246.5 Hz), 153.4, 149.4, 138.3 (d, J_{C-F} = 3.2 Hz), 135.2, 132.9, 130.2, 129.1 (d, J_{C-F} = 8.8 Hz), 124.6, 116.3 (d, J_{C-F} = 22.8 Hz), 115.9, 88.4, 85.5, 36.6. HRMS (ESI) calcd for $C_{16}H_{11}FNaN_2O_3$, $[M+Na]^+$: 321.0646, found: 321.0649.

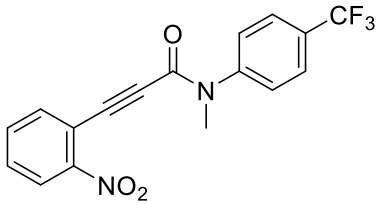


N-(4-chlorophenyl)-N-methyl-3-(2-nitrophenyl)propiolamide (1g). Following the general procedure A, compound **1g** was obtained in 4 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1); red solid, yield: (1.2 mmol, 221 mg, 59%); m.p. 103-105 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 8.02 (d, J = 8.0 Hz, 1H), 7.58-7.55 (m, 1H), 7.52-7.49 (m, 2H), 7.41-7.38 (m, 2H), 7.33-7.30 (m, 2H), 3.38 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.2, 149.4, 140.8, 135.2, 133.9, 132.9, 130.3, 129.5, 128.5, 124.7, 115.8, 88.4, 85.5, 36.5. HRMS (ESI) calcd for $C_{16}H_{11}ClNaN_2O_3$, $[M+Na]^+$: 337.0350, found: 337.0359.

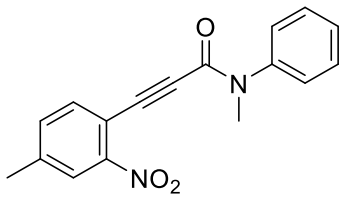


N-(3-bromophenyl)-N-methyl-3-(2-nitrophenyl)propiolamid (1h). Following the general procedure A, compound **1h** was obtained in 4 h and purified by chromatography

on silica gel (petroleum ether/ethyl acetate = 4:1); red solid, yield: (1.2 mmol, 219.1 mg, 51%); m.p. 77-79 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 8.03 (d, *J* = 8.0 Hz, 1H), 7.59-7.49 (m, 5H), 7.36-7.30 (m, 2H), 3.39 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.1, 149.3, 143.5, 135.3, 133.0, 131.2, 130.6, 130.3, 130.2, 126.1, 124.7, 122.4, 115.8, 88.3, 85.7, 36.4. HRMS (ESI) calcd for $C_{16}H_{11}BrNaN_2O_3$, $[M+Na]^+$: 380.9845, found: 380.9841.

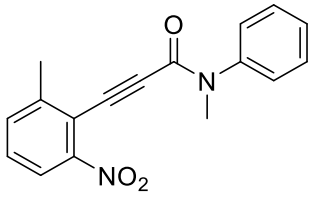


N-methyl-3-(2-nitrophenyl)-N-(4-(trifluoromethyl)phenyl)propiolamide (1i). Following the general procedure B, compound **1i** was obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yellow oil, yield: (1.0 mmol, 102 mg, 29%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ. 8.00 (d, *J* = 7.8 Hz, 1H), 7.71-7.68 (m, 3H), 7.55-7.52 (m, 4H), 3.43 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.0, 149.4, 145.3, 135.2, 132.9, 130.5, 127.4, 126.51, 126.49, 124.7, 115.6, 88.1, 85.6, 36.3. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -61.6. HRMS (ESI) calcd for $C_{17}H_{11}F_3NaN_2O_3$, $[M+Na]^+$: 371.0612, found: 371.0614.

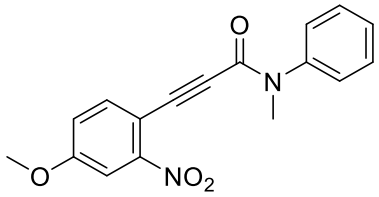


N-methyl-3-(4-methyl-2-nitrophenyl)-N-phenylpropiolamid (1j). Following the general procedure B, compound **1j** was obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); yellow solid, yield: (0.5 mmol, 107.4 mg, 73%); m.p. 106-108 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 7.79 (s, 1H), 7.44-7.41 (m, 2H), 7.36-7.35 (m, 3H), 7.33-7.30 (m, 2H), 3.40 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (125

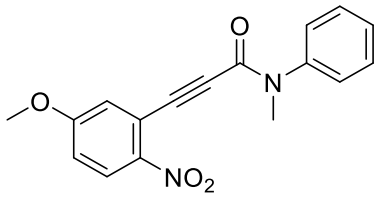
MHz, $CDCl_3$) δ 153.6, 149.2, 142.4, 141.4, 135.1, 133.6, 129.3, 128.0, 127.2, 125.0, 113.1, 88.0, 85.5, 36.5, 21.3. HRMS (ESI) calcd for $C_{17}H_{15}N_2O_3$, $[M+H]^+$: 295.1077, found: 295.1080.



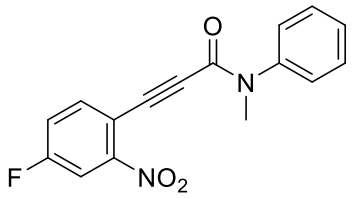
N-methyl-3-(2-methyl-6-nitrophenyl)-N-phenylpropiolamide (1k). Following the general procedure B, compound **1k** was obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); yellow solid, yield: (2.3 mmol, 125.9 mg, 19%); m.p. 134-136 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 7.77 (d, *J* = 8.5 Hz, 1H), 7.44-7.39 (m, 3H), 7.37-7.28 (m, 4H), 3.40 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.4, 150.5, 144.3, 142.5, 133.9, 129.4, 129.2, 128.1, 127.3, 121.9, 115.3, 93.3, 83.8, 36.5, 20.7. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_3$, $[M+Na]^+$: 317.0897, found: 317.0893.



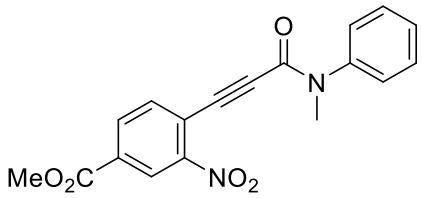
3-(4-methoxy-2-nitrophenyl)-N-methyl-N-phenylpropiolamide (1l). Following the general procedure B, compound **1l** was obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); yellow solid, yield: (1.0 mmol, 182.3 mg, 59%); m.p. 100-102 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 7.47 (d, *J* = 2.5 Hz, 1H), 7.44-7.41 (m, 2H), 7.36-7.31 (m, 4H), 7.05-7.02 (m, 1H), 3.86 (s, 3H), 3.39 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.6, 153.7, 150.5, 142.5, 136.4, 129.2, 128.0, 127.2, 119.3, 109.6, 107.8, 87.3, 85.5, 56.0, 36.5. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_4$, $[M+Na]^+$: 333.0846, found: 333.0848.



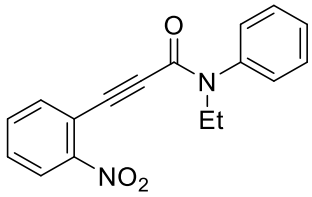
3-(5-methoxy-2-nitrophenyl)-N-methyl-N-phenylpropiolamide (1m). Following the general procedure B, compound **1m** was obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); yellow solid, yield: (1.0 mmol, 241.1 mg, 78%); m.p. 77-79 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 8.03 (d, *J* = 9.5 Hz, 1H), 7.45-7.41 (m, 2H), 7.39-7.33 (m, 3H), 6.92 (dd, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1H), 6.86 (d, *J* = 3.0 Hz, 1H), 3.83 (s, 3H), 3.41 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.7, 153.4, 142.3, 129.3, 128.1, 127.2, 127.0, 125.7, 125.3, 119.3, 116.0, 88.5, 85.7, 56.1, 36.5. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_4$, $[M+Na]^+$: 333.0846, found: 333.0843.



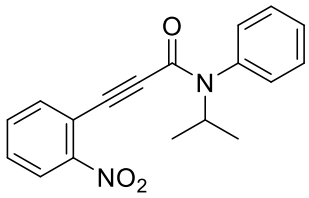
3-(4-fluoro-2-nitrophenyl)-N-methyl-N-phenylpropiolamide (1n). Following the general procedure B, compound **1n** was obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1); yellow solid, yield: (1.0 mmol, 173 mg, 58%); m.p. 69-71 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 7.73-7.71 (m,1H), 7.46-7.42 (m, 3H), 7.38-7.35 (m, 3H), 7.29-7.25 (m, 1H), 3.40 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.1 (d, J_{C-F} = 255.4 Hz), 153.3, 150.2 (d, J_{C-F} = 8.5 Hz), 142.3, 137.0 (d, J_{C-F} = 8.4 Hz), 129.3, 128.2, 127.2, 125.3, 120.6 (d, J_{C-F} = 22.0 Hz), 112.7 (d, J_{C-F} = 27.0 Hz), 112.3 (d, J_{C-F} = 4.1 Hz), 88.6, 84.1, 36.5. HRMS (ESI) calcd for $C_{16}H_{11}FNaN_2O_3$, $[M+Na]^+$: 321.0646, found: 321.0648.



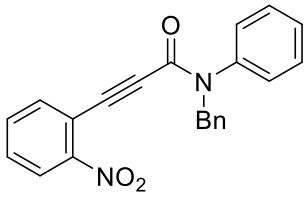
methyl 4-(3-(methyl(phenyl)amino)-3-oxoprop-1-yn-1-yl)-3-nitrobenzoate (1o). Following the general procedure B, compound **1o** was obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); yellow solid, yield: (2.0 mmol, 378.7 mg, 56%); m.p. 142-144 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 8.23 (d, *J* = 7.5 Hz, 1H), 8.12 (s, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.30-7.23 (m, 5H), 3.95 (s, 3H), 3.48 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.8, 164.4, 157.1, 146.4, 141.2, 136.2, 133.9, 133.5, 129.4, 128.6, 125.8, 125.6, 121.9, 115.3, 52.9, 36.7. HRMS (ESI) calcd for $C_{18}H_{14}NaN_2O_5$, $[M+Na]^+$: 361.0795, found: 361.0791.



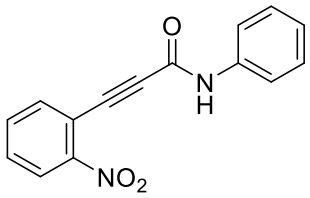
N-ethyl-3-(2-nitrophenyl)-N-phenylpropiolamide (1p). Following the general procedure A, compound **1p** was obtained in 4 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); red solid, yield: (1.2 mmol, 219.3 mg, 62%); m.p. 102-104 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 7.98-7.96 (m, 1H), 7.53-7.50 (m, 1H), 7.48-7.42 (m, 3H), 7.40-7.36 (m, 2H), 7.34-7.27 (m, 2H), 3.88 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.0, 149.3, 140.7, 135.2, 132.8, 130.0, 129.3, 128.4, 128.3, 124.5, 116.1, 89.0, 85.0, 43.7, 12.8. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_3$, $[M+Na]^+$: 317.0897, found: 317.0892.



N-isopropyl-3-(2-nitrophenyl)-N-phenylpropiolamide (1q). Following the general procedure A, compound **1q** was obtained in 4 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); red solid, yield: (1.2 mmol, 67 mg, 18%); m.p. 107-109 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ. 7.95 (d, *J* = 7.8 Hz, 1H), 7.51-7.39 (m, 5H), 7.33-7.32 (m, 1H), 7.27-7.25 (m, 2H), 5.02-4.96 (m, 1H), 1.16 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.4, 149.3, 137.4, 135.2, 132.7, 130.7, 129.9, 129.0, 128.7, 124.5, 116.2, 89.2, 85.3, 46.8, 20.7. HRMS (ESI) calcd for $C_{18}H_{16}NaN_2O_3$, $[M+Na]^+$: 331.1053, found: 331.1057.

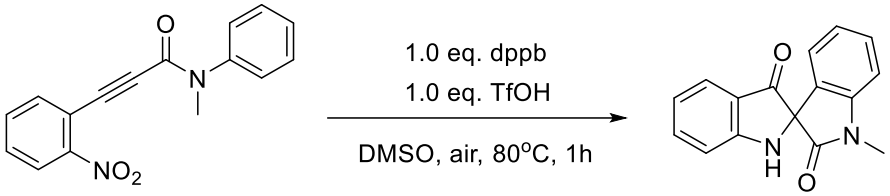


N-benzyl-3-(2-nitrophenyl)-N-phenylpropiolamide (1r). Following the general procedure B, compound **1r** was obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 5:1); yellow solid, yield: (1.4 mmol, 292.2 mg, 59%); m.p. 94-96 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ. 7.98-7.96 (m, 1H), 7.52-7.49 (m, 1H), 7.47-7.44 (m, 1H), 7.39-7.38 (m, 1H), 7.35-7.23 (m, 8H), 7.18-7.15 (m, 2H), 5.00 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 153.5, 149.3, 140.8, 136.3, 135.3, 132.8, 130.1, 129.1, 128.7, 128.5, 128.3, 127.6, 126.7, 124.6, 116.0, 88.7, 85.7, 52.5. HRMS (ESI) calcd for $C_{22}H_{16}NaN_2O_3$, $[M+Na]^+$: 379.1053, found: 379.1051.



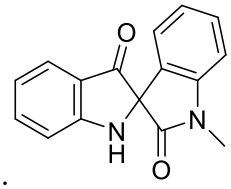
3-(2-nitrophenyl)-N-phenylpropiolamide (1s). Following the general procedure A, compound **1s** was obtained in 4 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); red solid, yield: (0.5 mmol, 67.8 mg, 51%); m.p. 128-130 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 8.14-8.13 (m, 1H), 7.97 (s, 1H), 7.76-7.74 (m, 1H), 7.66-7.63 (m, 1H), 7.60-7.57 (m, 3H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.3, 149.7, 137.1, 135.7, 133.3, 130.7, 129.1, 125.1, 125.0, 120.0, 115.7, 89.5, 80.2. HRMS (ESI) calcd for $C_{15}H_{10}NaN_2O_3$, $[M+Na]^+$: 289.0584, found: 289.0591.

3. Synthesis of 2



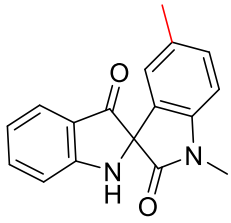
1a **2a**

In a Schlenk tube, o-nitrophenylpropiolamides **1** (52.8 mg, 0.2 mmol), dppb (85.3 mg, 0.2 mmol, 1.0 equiv.), DMSO (2.0 mL), and TfOH (18 uL, 0.2 mmol, 1.0 equiv.) were stirred at 80 ^{o}C in the oil bath for 1h under air. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with EA (20 mL ×3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) afforded desired compound **2a**.

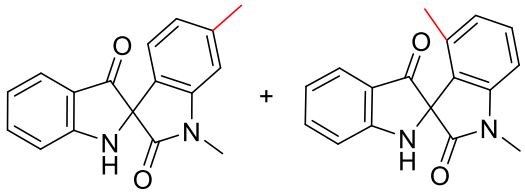


.

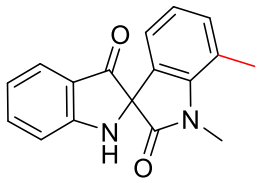
1'-methyl-2,3'-spirobi[indoline]-2',3-dione (2a). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (51.6 mg, 98%); m.p. 250-252 °C. **^{1}H NMR** (500 MHz, d^{6}-DMSO) δ 7.93 (s, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.42-7.39 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.08-7.04 (m, 3H), 6.85 (t, *J* = 7.2 Hz, 1H), 3.19 (s, 3H).**^{13}C NMR** (125 MHz, d^{6}-DMSO) δ 195.7, 171.4, 163.8, 144.9, 138.1, 129.8, 126.3, 125.0, 122.93, 122.86, 118.6, 118.0, 112.7, 109.3, 74.0, 26.6. HRMS (ESI) calcd for $C_{16}H_{13}N_2O_2$, $[M+H]^+$: 265.0972, found: 265.0973.



1',5'-dimethyl-2,3'-spirobi[indoline]-2',3-dione (2b). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (52.9 mg, 95%); m.p. 229-231 °C. **^{1}H NMR** (500 MHz, d^{6}-DMSO) δ 7.92 (s, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.07-7.02 (m, 2H), 6.87-6.83 (m, 2H), 3.17 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (125 MHz, d^{6}-DMSO) δ 195.9, 171.4, 163.7, 142.5, 138.1, 132.1, 129.9, 126.3, 124.9, 123.5, 118.6, 118.1, 112.6, 109.1, 74.0, 26.6, 20.4. HRMS (ESI) calcd for $C_{17}H_{15}N_2O_2$, $[M+H]^+$: 279.1128, found: 279.1129.

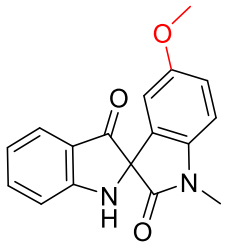


1',6'-dimethyl-2,3'-spirobi[indoline]-2',3-dione and 1',4'-dimethyl-2,3'-spirobi [indoline]-2',3-dione (2c + 2c'). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (53.2 mg, 96%, **2c** : **2c'** = 1.5:1); m.p. 206-208 °C. Major isomer: **^{1}H NMR** (500 MHz, d^{6}-DMSO) δ 7.89 (s, 1H), 7.59-7.55 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.99-6.95 (m, 1H), 6.92-6.82 (m, 3H), 3.17 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (125 MHz, d^{6}-DMSO) δ 195.9, 171.7, 163.7, 145.0, 139.7, 138.1, 134.5, 124.5, 123.2, 122.7,118.6, 118.1, 112.6, 110.1, 73.9, 26.6, 21.5. Minor isomer: **^{1}H NMR** (500 M Hz, d^{6}-DMSO) 7.92 (s, 0.65H), 7.51 (d, *J* = 7.5 Hz, 0.65H), 7.30 (t, *J* = 7.8 Hz, 0.65H), 1.89 (s, 1.95H); other peaks are overlapped with the signals of the other isomer. **^{13}C NMR** (125 MHz, d^{6}-DMSO) δ 195.7, 171.1, 163.0, 145.1, 138.2,129.6, 124.9, 124.6, 123.3, 119.4, 118.5, 112.8, 106.8, 26.7, 16.6; other peaks are overlapped with the signals of the other isomer. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_2$, $[M+Na]^+$: 301.0947, found: 301.0950.

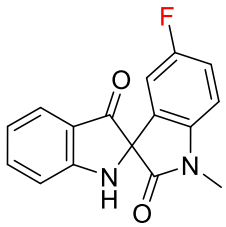


1',7'-dimethyl-2,3'-spirobi[indoline]-2',3-dione (2d). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (47.8 mg, 86%); m.p. 219-221 °C. **^{1}H NMR** (600 MHz, d^{6}-DMSO) δ 7.91 (s, 1H), 7.57 (t, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.85-6.82 (m, 2H), 3.45 (s, 3H), 2.60 (s, 3H). **^{13}C NMR** (150 MHz, d^{6}-DMSO) δ 195.8, 172.0, 163.8, 142.5, 138.1, 133.4, 126.8, 125.0,

122.8, 120.8, 120.6, 118.6, 117.9, 112.6, 73.7, 29.6, 18.4. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_2$, $[M+Na]^+$: 301.0947, found: 301.0955.

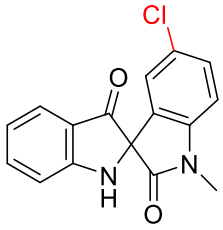


5'-methoxy-1'-methyl-2,3'-spirobi[indoline]-2',3-dione (2e). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (50.0 mg, 85%); m.p. 217-219 °C. **^{1}H NMR** (500 MHz, d^6-DMSO) δ 7.91 (s, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.07-7.05 (m, 2H), 6.97-6.95 (m, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 2.5 Hz, 1H), 3.68 (s, 3H), 3.16 (s, 3H). **^{13}C NMR** (125 MHz, d^6-DMSO) δ 195.6, 171.1, 163.8, 155.8, 138.2, 138.1, 127.4, 125.0, 118.6, 118.1, 114.7, 112.7, 109.9, 109.6, 74.4, 55.7, 26.7. HRMS (ESI) calcd for $C_{17}H_{15}N_2O_3$, $[M+H]^+$: 295.1077, found: 295.1078.

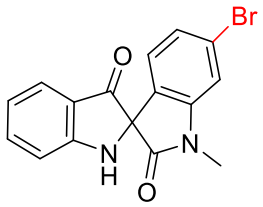


5'-fluoro-1'-methyl-2,3'-spirobi[indoline]-2',3-dione (2f). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (40.1 mg, 71%); m.p. 222-224 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.63 (d, *J* = 7.8 Hz, 1H), 7.56-7.54 (m, 1H), 7.09-7.04 (m, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.87-6.83 (m, 2H), 5.03 (s, 1H), 3.25 (s, 3H). **^{13}C NMR** (125 MHz, d^6-DMSO) δ 195.1, 171.3, 163.8, 158.6 (d, $J_{C\text{-}F}$ = 237.6 Hz), 141.1, 138.2, 127.9 (d, $J_{C\text{-}F}$ = 8.6 Hz), 125.1, 118.8, 118.0, 115.9 (d, $J_{C\text{-}F}$ = 23.1 Hz), 112.8, 111.2 (d, $J_{C\text{-}F}$ = 25.4 Hz), 110.3 (d, $J_{C\text{-}F}$ = 7.9 Hz),

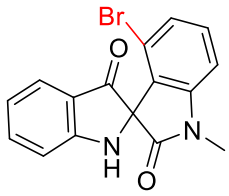
74.2 (d, $J_{C\text{-}F}$ = 1.6 Hz), 26.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -119.3. HRMS (ESI) calcd for $C_{16}H_{11}FNaN_2O_2$, $[M+Na]^+$: 305.0697, found: 305.0695.



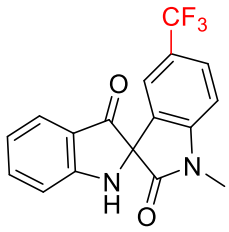
5'-chloro-1'-methyl-2,3'-spirobi[indoline]-2',3-dione (2g). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (51.3 mg, 86%); m.p. 210-212 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 6.99 (d, *J* = 7.5 Hz 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 5.22 (s, 1H), 3.21 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.0, 171.7, 162.7, 143.3, 138.0, 129.8, 128.6, 128.1, 125.9, 123.5, 120.6, 119.1, 113.3, 109.9, 74.3, 27.1. HRMS (ESI) calcd for $C_{16}H_{11}ClNaN_2O_2$, $[M+Na]^+$: 321.0401, found: 321.0410.



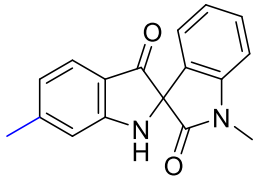
6'-bromo-1'-methyl-2,3'-spirobi[indoline]-2',3-dione (2h). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (26.2 mg, 38%); m.p. 240-242 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.55-7.52 (m, 1H), 7.19 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.08 (d, *J* = 1.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 5.03 (s, 1H), 3.23 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.1, 171.9, 162.6, 146.1, 137.9, 126.1, 125.9, 125.4, 124.3, 123.7, 120.6, 119.3, 113.3, 112.6, 74.2, 27.1. HRMS (ESI) calcd for $C_{16}H_{11}BrNaN_2O_2$, $[M+Na]^+$: 364.9896, found: 364.9901.



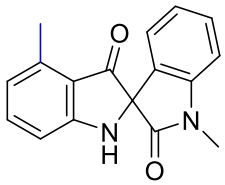
4'-bromo-1'-methyl-2,3'-spirobi[indoline]-2',3-dione (2h'). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (37 mg, 54%); m.p. 195-197 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.57-7.53 (m, 1H), 7.26-7.23 (m, 1H), 7.19-7.17 (m, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.87-6.85 (m, 1H), 4.97 (s, 1H), 3.24 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.8, 171.2, 162.6, 146.8, 137.8, 131.4, 126.9, 125.8, 125.2, 121.2, 120.2, 118.7, 113.4, 107.7, 74.6, 27.1. HRMS (ESI) calcd for $C_{16}H_{11}BrNaN_2O_2$, $[M+Na]^+$: 364.9896, found: 364.9895.



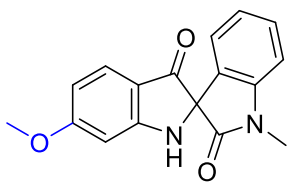
1'-methyl-5'-(trifluoromethyl)-2,3'-spirobi[indoline]-2',3-dione (2i). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (42.3 mg, 64%); m.p. 202-204 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66-7.62 (m, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.31 (s, 1H), 7.05-6.96 (m, 3H), 5.11 (s, 1H), 3.28 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.7, 172.1, 162.7, 147.8, 138.1, 127.7 (q, *J* = 15.0 Hz), 127.3, 126.1, 125.6 (q, *J* = 123.1 Hz), 122.9, 120.9, 120.3 (q, *J* = 13.6 Hz), 119.2, 113.4, 108.8, 74.2, 27.2. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -61.6. HRMS (ESI) calcd for $C_{17}H_{11}F_3NaN_2O_2$, $[M+Na]^+$: 355.0669, found: 355.0665.



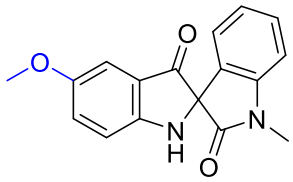
1',6-dimethyl-2,3'-spirobi[indoline]-2',3-dione (2j). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (45.6 mg, 82%); m.p. 263-265 °C. **^{1}H NMR** (500 MHz, d^{6}-DMSO) δ 7.84 (s, 1H), 7.41-7.35 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.06-7.01 (m, 2H), 6.87 (s, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (125 MHz, d^{6}-DMSO) δ 194.8, 171.6, 164.2, 149.5, 144.9, 129.8, 126.5, 124.7, 122.9, 122.8, 120.4, 115.9, 112.5, 109.3, 74.2, 26.6, 22.0. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_2$, $[M+Na]^+$: 301.0947, found: 301.0945.



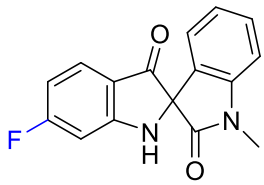
1',4-dimethyl-2,3'-spirobi[indoline]-2',3-dione (2k). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (53.6, 96%); m.p. 227-229 °C. **^{1}H NMR** (500 MHz, d^{6}-DMSO) δ 7.83 (s, 1H), 7.42-7.38 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.06-7.03 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 7.0 Hz, 1H), 3.18 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (125 MHz, d^{6}-DMSO) δ 196.0, 171.7, 164.3, 144.9, 139.6, 137.5, 129.7, 126.7, 122.9, 122.8, 119.9, 116.2, 109.9, 109.3, 74.1, 26.6, 17.7. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_2$, $[M+Na]^+$: 301.0947, found: 301.0957.



6-methoxy-1'-methyl-2,3'-spirobi[indoline]-2',3-dione (2l). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (45.4 mg, 77%); m.p. 262-264 °C. **^{1}H NMR** (500 MHz, d^6-DMSO) δ 7.92 (s, 1H), 7.41-7.36 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.06-7.02 (m, 2H), 6.52-6.51 (m, 1H), 6.43-6.40 (m, 1H), 3.87 (s, 3H), 3.18 (s, 3H). **^{13}C NMR** (125 MHz, d^6-DMSO) δ 192.8, 171.7, 167.8, 166.0, 144.9, 129.7, 126.6, 126.4, 122.83, 122.78, 111.4, 109.2, 109.0, 94.5, 74.4, 55.8, 26.6. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_3$, $[M+Na]^+$: 317.0897, found: 317.0893.

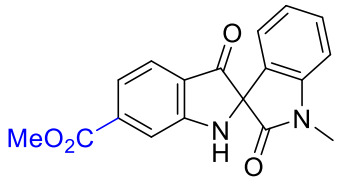


5-methoxy-1'-methyl-2,3'-spirobi[indoline]-2',3-dione (2m). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (51.6 mg, 88%); m.p. 231-233 °C. **^{1}H NMR** (500 MHz, d^6-DMSO) δ 7.55 (s, 1H), 7.41-7.38 (m, 1H), 7.27 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.07-7.01 (m, 3H), 6.94 (d, *J* = 2.5 Hz, 1H), 3.74 (s, 3H), 3.18 (s, 3H). **^{13}C NMR** (125 MHz, d^6-DMSO) δ 195.7, 171.6, 159.8, 152.8, 144.9, 129.7, 128.4, 126.5, 122.9, 122.8, 118.3, 114.3, 109.3, 104.9, 74.9, 55.6, 26.6. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_3$, $[M+Na]^+$: 317.0897, found: 317.0899.

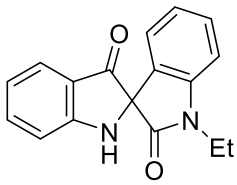


6-fluoro-1'-methyl-2,3'-spirobi[indoline]-2',3-dione (2n). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (50.8 mg, 90%); m.p. 256-258 °C. **^{1}H NMR** (500 MHz, d^6-DMSO) δ 8.19 (s, 1H),

7.57-7.54 (m, 1H), 7.43-7.39 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.08-7.03 (m, 2H), 6.88-6.86 (m, 1H), 6.68-6.64 (m, 1H), 3.19 (s, 3H). **^{13}C NMR** (125 MHz, d^6-DMSO) δ 193.8, 171.1, 169.1 (d, *J* = 252.2 Hz), 165.2 (d, *J* = 15.0 Hz), 144.9, 130.0, 127.8 (d, *J* = 12.9 Hz), 125.9, 123.0, 122.9, 114.9, 109.4, 107.2 (d, *J* = 24.9 Hz), 98.6 (d, *J* = 26.0 Hz), 74.5, 26.7. ^{19}F NMR (470 MHz, d^6-DMSO) δ -99.3. HRMS (ESI) calcd for $C_{16}H_{11}FNaN_2O_2$, $[M+Na]^+$: 305.0697, found: 305.0698.

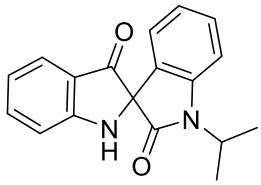


methyl 1'-methyl-2',3-dioxo-2,3'-spirobi[indoline]-6-carboxylate (2o). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (61.2 mg, 95%); m.p. 269-271 °C. **^{1}H NMR** (500 MHz, d^6-DMSO) δ 8.17 (s, 1H), 7.62-7.60 (m, 2H), 7.44-7.40 (m, 1H), 7.37-7.35 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.09-7.04 (m, 2H), 3.90 (s, 3H), 3.20 (s, 3H). **^{13}C NMR** (125 MHz, d^6-DMSO) δ 195.8, 171.0, 165.7, 163.2, 144.9, 137.8, 130.1, 125.8, 125.4, 123.2, 123.0, 121.0, 118.7, 113.2, 109.5, 74.6, 52.7, 26.7. HRMS (ESI) calcd for $C_{18}H_{14}NaN_2O_4$, $[M+Na]^+$: 345.0846, found: 345.0854.

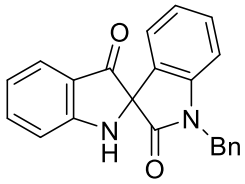


1'-ethyl-2,3'-spirobi[indoline]-2',3-dione (2p). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (54.5 mg, 98%); m.p. 245-247 °C. **^{1}H NMR** (500 MHz, d^6-DMSO) δ 7.97 (s, 1H), 7.59-7.56 (m, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.41-7.36 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.07-7.01 (m, 3H), 6.84 (t, *J* = 7.5 Hz, 1H), 3.75 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz,

3H). **^{13}C NMR** (125 MHz, d^6-DMSO) δ 195.6, 171.1, 163.8, 143.9, 138.1, 129.8, 126.5, 125.0, 123.2, 122.7, 118.6, 118.1, 112.7, 109.4, 74.1, 34.7, 12.5. HRMS (ESI) calcd for $C_{17}H_{14}NaN_2O_2$, $[M+Na]^+$: 301.0947, found: 301.0951.



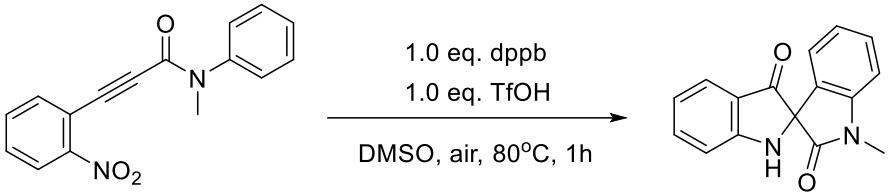
1'-isopropyl-2,3'-spirobi[indoline]-2',3-dione (2q). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 4:1); yield: (47.9 mg, 82%); m.p. 160-162 °C. **^{1}H NMR** (500 MHz, d^6-DMSO) δ 7.96 (s, 1H), 7.57 (t, *J* = 7.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.38-7.34 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.03-7.00 (m, 2H), 6.84 (t, *J* = 7.2 Hz, 1H), 4.53-4.47 (m, 1H), 1.43 (dd, J_1 = 6.5 Hz, J_2 = 2.5 Hz, 6H). **^{13}C NMR** (125 MHz, d^6-DMSO) δ 195.6, 171.1, 163.8, 143.6, 138.1, 129.7, 126.6, 125.0, 123.2, 122.4, 118.6, 118.0, 112.6, 110.5, 74.2, 44.2, 19.5, 18.9. HRMS (ESI) calcd for $C_{18}H_{16}NaN_2O_2$, $[M+Na]^+$: 315.1104, found: 315.1112.



1'-benzyl-2,3'-spirobi[indoline]-2',3-dione (2r). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (58.6 mg, 86%); m.p. 225-227 °C. **^{1}H NMR** (500 MHz, d^6-DMSO) δ. 8.08 (s, 1H), 7.61-7.58 (m, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.40-7.35 (m, 4H), 7.32-7.27 (m, 2H), 7.10-7.06 (m, 2H), 7.03-6.98 (m, 2H), 6.86 (t, *J* = 7.2 Hz, 1H), 5.03-4.89 (m, 2H).**^{13}C NMR** (125 MHz, d^6-DMSO) δ 195.7, 171.7, 163.8, 143.9, 138.2, 135.8, 129.7, 128.6, 127.5,

127.1, 126.3, 125.1, 123.1, 123.0, 118.7, 117.9, 112.7, 110.0, 74.1, 43.0. HRMS (ESI) calcd for $C_{22}H_{16}NaN_2O_2$, $[M+Na]^+$: 363.1104, found: 363.1106.

4. 1.0 mmol Scale reaction



1a **2a**

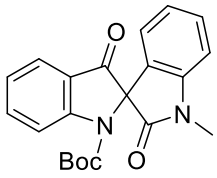
In a Schlenk tube, o-nitrophenylpropiolamides **1** (280.1 mg, 1.0 mmol), dppb (426.3 mg, 1.0 mmol, 1.0 equiv.), DMSO (10 mL), and TfOH (88 uL, 1.0 mmol, 1.0 equiv.) were stirred at 80 °C in the oil bath for 1h under air. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted with EA (20 mL ×3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) afforded desired compound **2a**. (Yellow solid, 216 mg, 82%)

5. Synthesis of 3a

2a **3a**

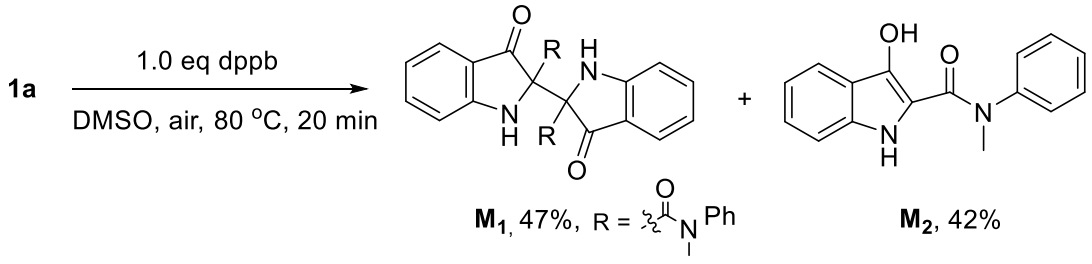
To a solution of the **2a** (0.2 mmol) in DMF (2.0 mL) was added NaH (12 mg, 0.3 mmol, 1.5 equiv, 60%) at 0 °C under a nitrogen atmosphere. After stirring at 0 °C for 30 min, Boc_2O (52.4 mg, 0.24 mmol, 1.2 equiv) was added and the reaction was warmed to room temperature. After the reaction was complete (monitored by TLC), the reaction mixture was then quenched by water, and the water layers were extracted with EA (20

mL ×3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) afforded desired compound **2a**. (White solid, 26.2 mg, 36%)



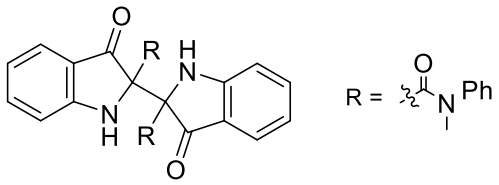
tert-butyl 1'-methyl-2',3-dioxo-2,3'-spirobi[indoline]-1-carboxylate (3a). White solid, obtained in 1.5 h and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 6:1); yield: (0.2 mmol, 26.2 mg, 36%); m.p. 197-199 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 8.39 (s, *J* = 8.5 Hz, 1H), 7.74-7.70 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.04-6.92 (m, 3H), 3.28 (s, 3H), 1.15 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.6, 170.3, 154.8, 149.3, 144.9, 137.8, 129.9, 126.5, 125.2, 123.6, 123.0, 122.0, 121.8, 116.6, 108.8, 82.8, 75.1, 27.6, 26.8. HRMS (ESI) calcd for $C_{21}H_{20}NaN_2O_4$, $[M+Na]^+$: 387.1315, found: 387.1326.

6. Control Experiments



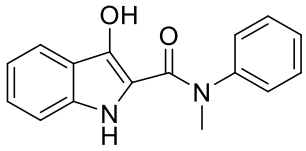
In a Schlenk tube, *o*-nitrophenylpropiolamides **1** (140 mg, 0.5 mmol), dppb (213 mg, 0.5 mmol, 1.0 equiv.), DMSO (5.0 mL) were stirred at 80 °C in the oil bath for 20min under air. After the reaction was completed as monitored by thin-layer chromatography, the reaction mixture was then quenched by water, and the water layers were extracted

with EA (20 mL ×3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 6:1-2:1) afforded desired compounds **M_1** and **M_2**.



M_1

N^2,$N^{2'}$-dimethyl-3,3'-dioxo-N^2,$N^{2'}$-diphenyl-[2,2'-biindoline]-2,2'-dicarboxamide (M_1). Yellow solid, obtained in 20 min and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 2:1); yield: (124.4 mg, 47%); m.p. 184-186 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 7.45-7.44 (m, 1H), 7.16 (s, 1H), 7.03 (t, *J* = 6.2 Hz, 1H), 6.88 (d, *J* = 6.5 Hz, 1H), 6.78 (t, *J* = 6.2 Hz, 1H), 6.60 (s, 1H), 6.51-6.45 (m, 2H), 6.40 (s, 1H), 6.33 (d, *J* = 7.0 Hz, 1H), 3.27 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.8, 168.1, 158.7, 141.4, 136.8, 128.7, 128.2, 127.8, 127.5, 127.4, 123.0, 120.0, 118.5, 112.0, 77.5, 40.6. HRMS (ESI) calcd for $C_{32}H_{26}NaN_4O_4$, $[M+Na]^+$: 553.1846, found: 553.1858.



3-hydroxy-N-methyl-N-phenyl-1H-indole-2-carboxamide (M_2). White solid, obtained in 20 min and purified by chromatography on silica gel (petroleum ether/ethyl acetate = 6:1); yield: (111.7 mg, 42%); m.p. 138-140 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ. 10.87 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.56-7.55 (m, 3H), 7.42-7.40 (m, 2H), 7.19-7.15 (m, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.67 (s, 1H), 3.46 (s,3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.3, 150.2, 142.7, 134.7, 130.4, 129.0, 128.2, 126.6,

119.9, 119.3, 117.2, 111.5, 109.2, 38.1. HRMS (ESI) calcd for $C_{16}H_{14}NaN_2O_2$, $[M+Na]^+$: 298.0947, found: 298.0950.

7. References

[1] Yang, L.; Jiang, L.; Li, Y.; Fu, X.; Zhang, R.; Jin, K.; Duan, C. *Tetrahedron.* **2016**, *72*, 3858-3862.

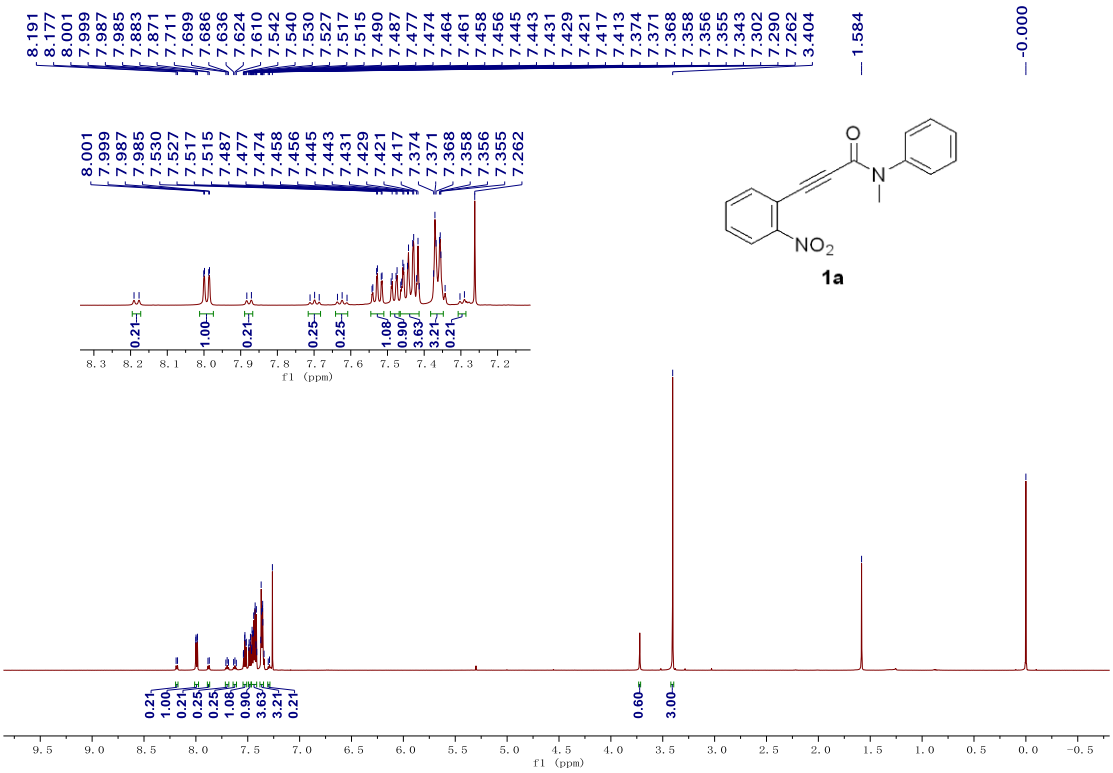
[2] Babu, U. S.; Singam, M. K. R.; Kumar, M. N.; Nanubolu, J. B.; Reddy, M. S. *Org. Lett.* **2022**, *24*, 1598-1603.

[3] Liu, L.; Sun, K.; Su, L.; Dong, J.; Cheng, L.; Zhu, X.; Au, C-T.; Zhou, Y.; Yin, S-F. *Org. Lett.* **2018**, *20*, 4023-4027.

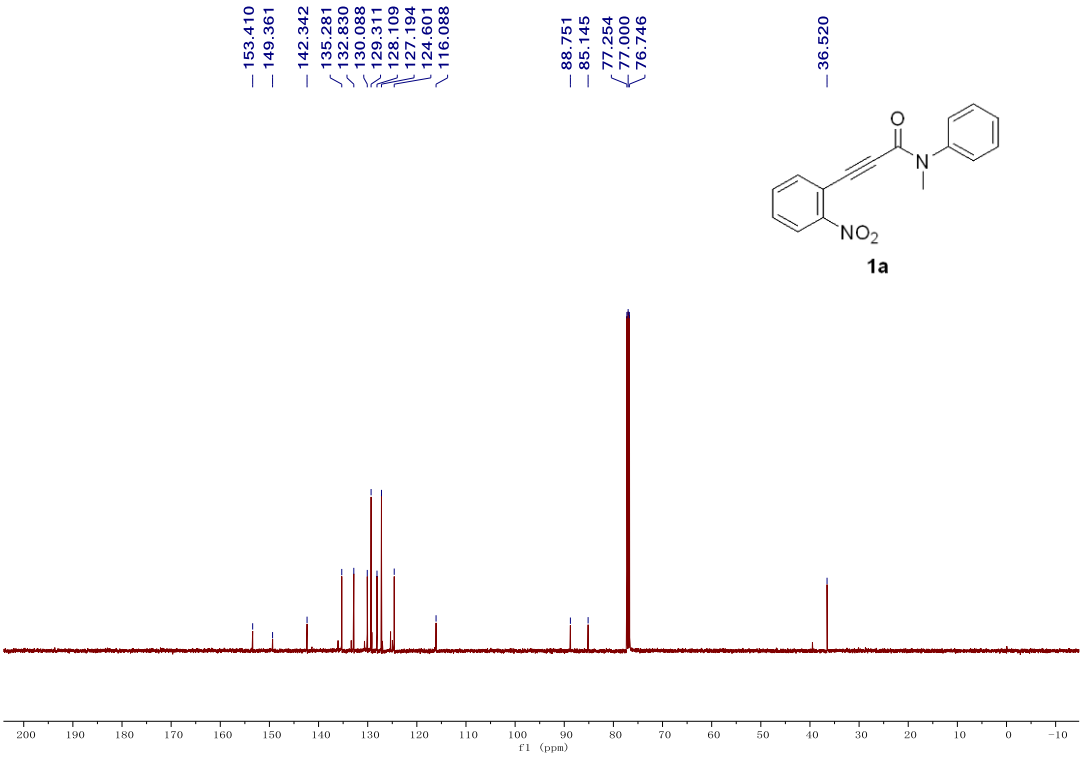
[4] Zhou, M-B.; Wei, W-T.; Xie, Y-X.; Lei, Y.; Li, J-H. *J. Org. Chem.* **2010**, *75*, 5635-5642.

8. Copies of spectra of new products

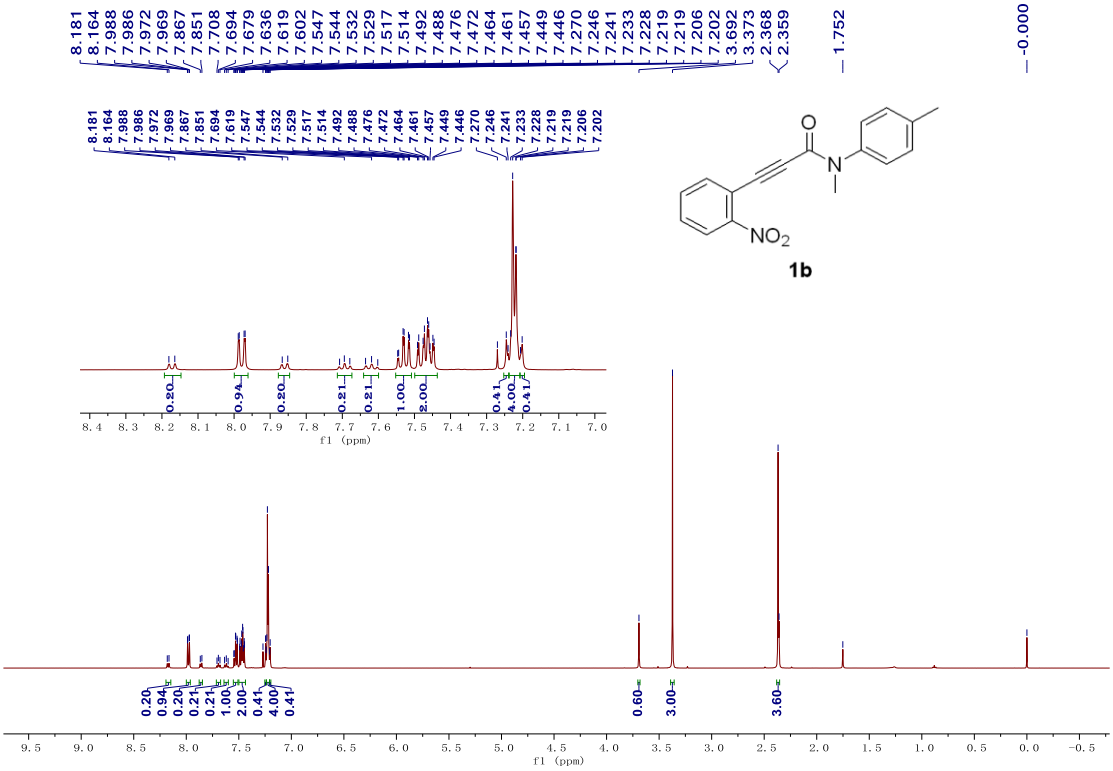
^{1}H NMR (500 MHz, $CDCl_3$)



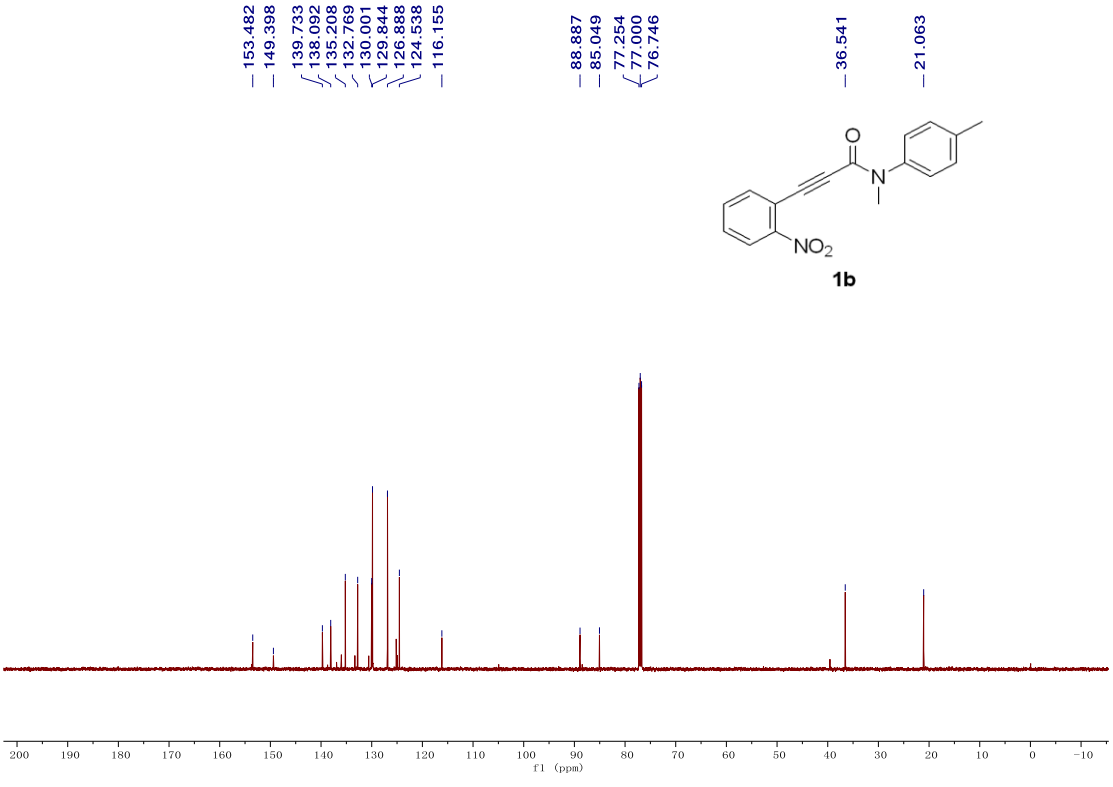
^{13}C NMR (125 MHz, $CDCl_3$)



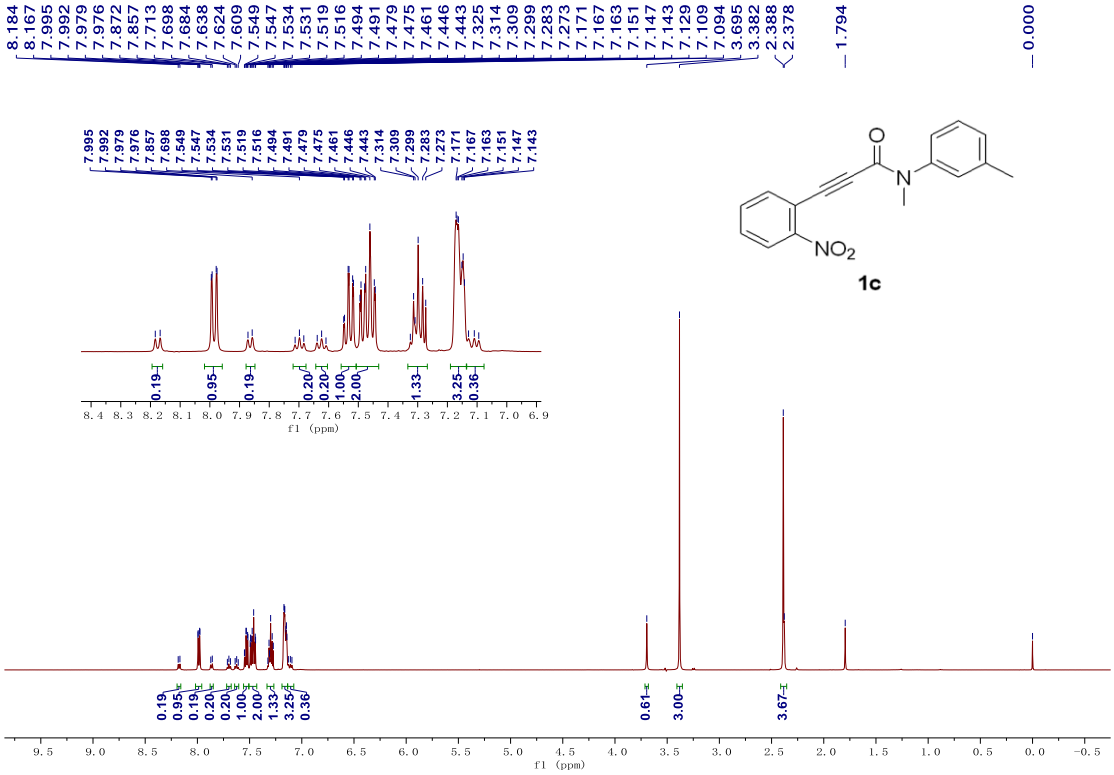
^{1}H NMR (500 MHz, $CDCl_3$)



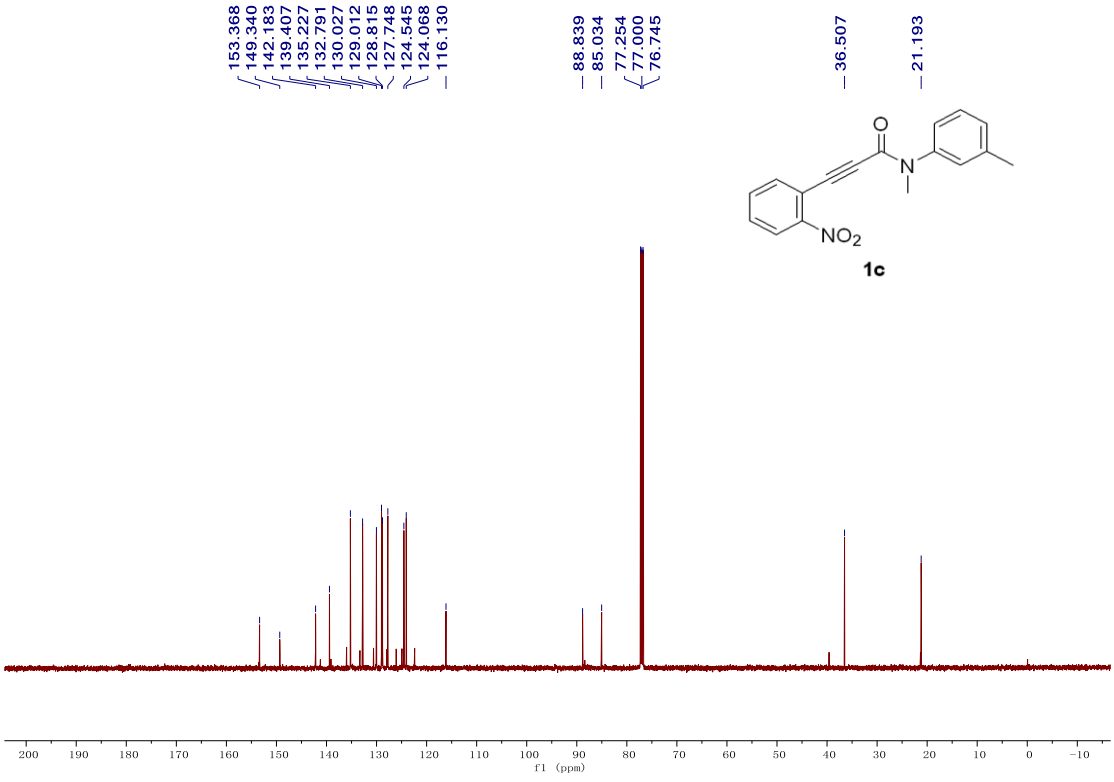
^{13}C NMR (125 MHz, $CDCl_3$)



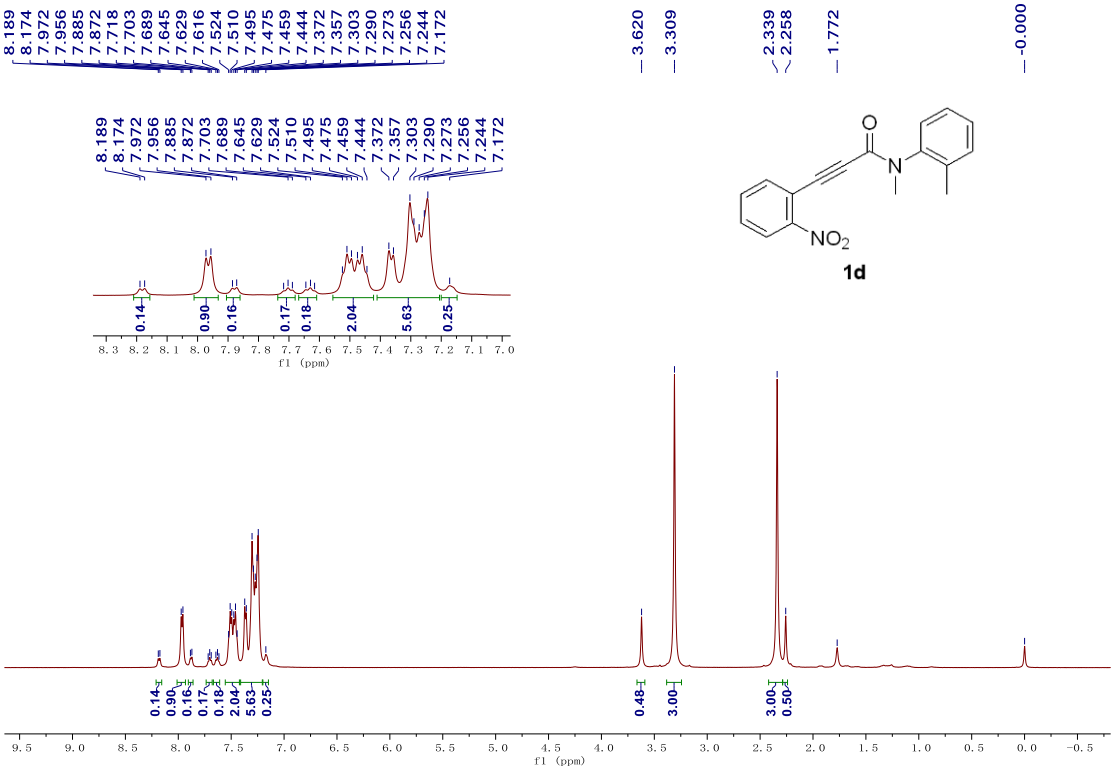
^{1}H NMR (500 MHz, $CDCl_3$)



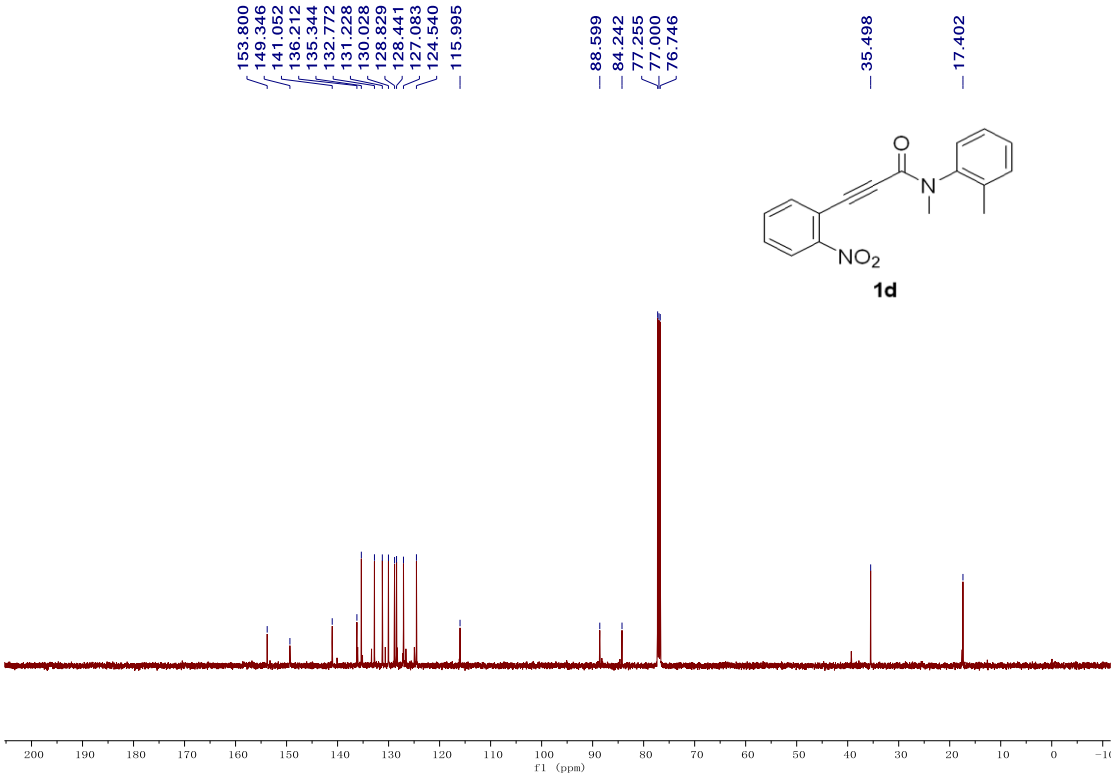
^{13}C NMR (125 MHz, $CDCl_3$)



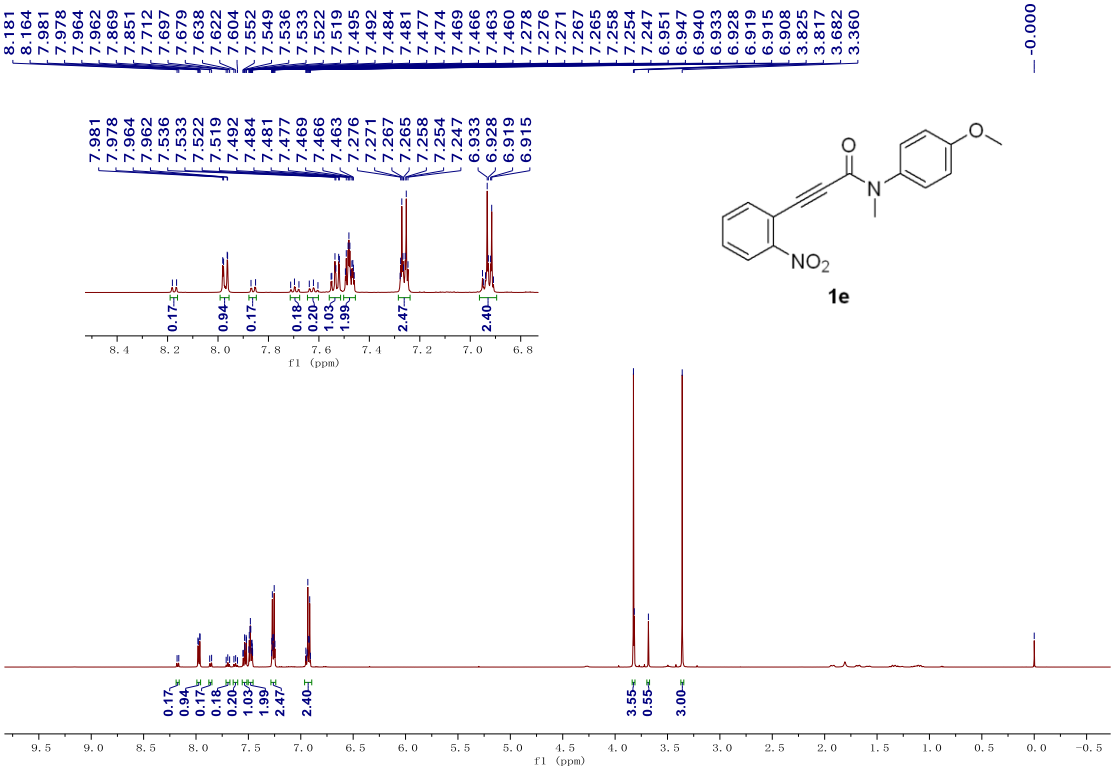
^{1}H NMR (500 MHz, $CDCl_3$)



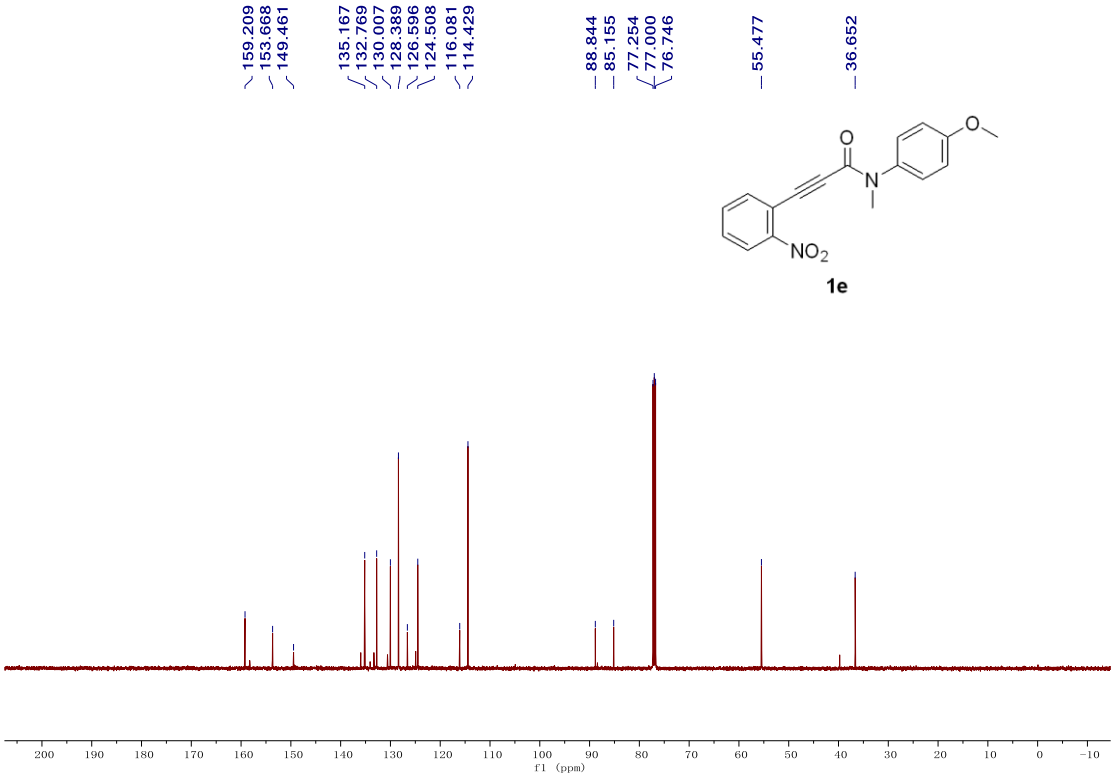
^{13}C NMR (125 MHz, $CDCl_3$)



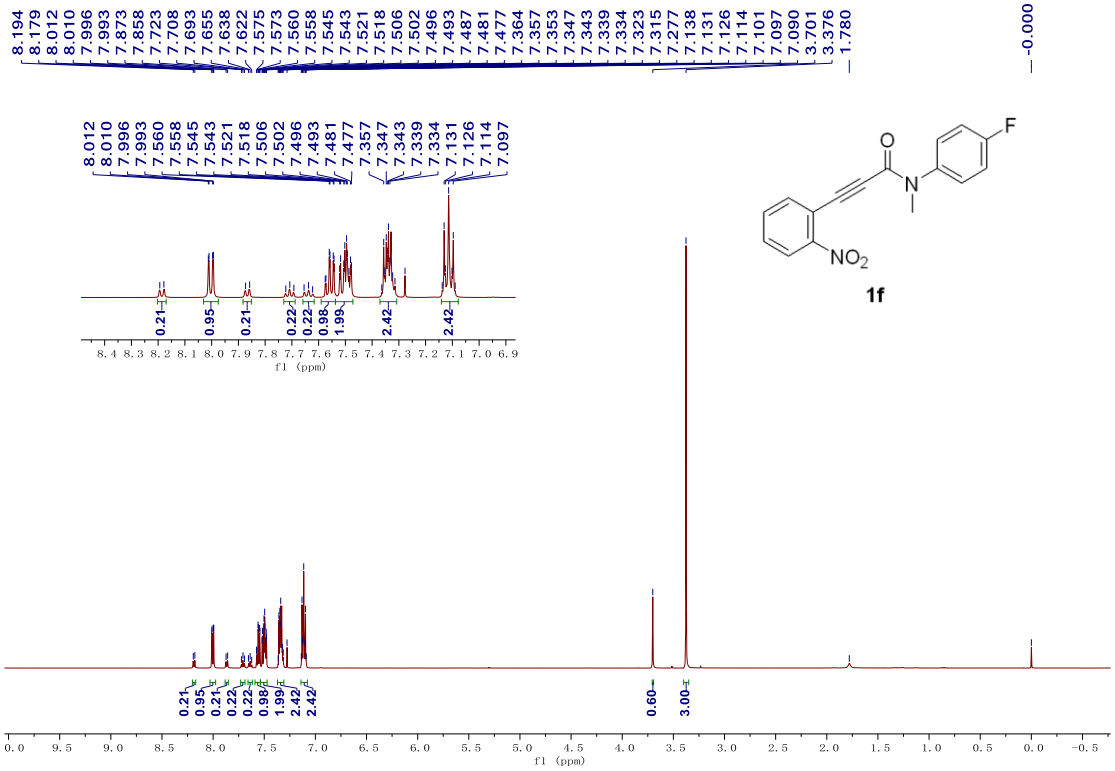
^{1}H NMR (500 MHz, $CDCl_3$)



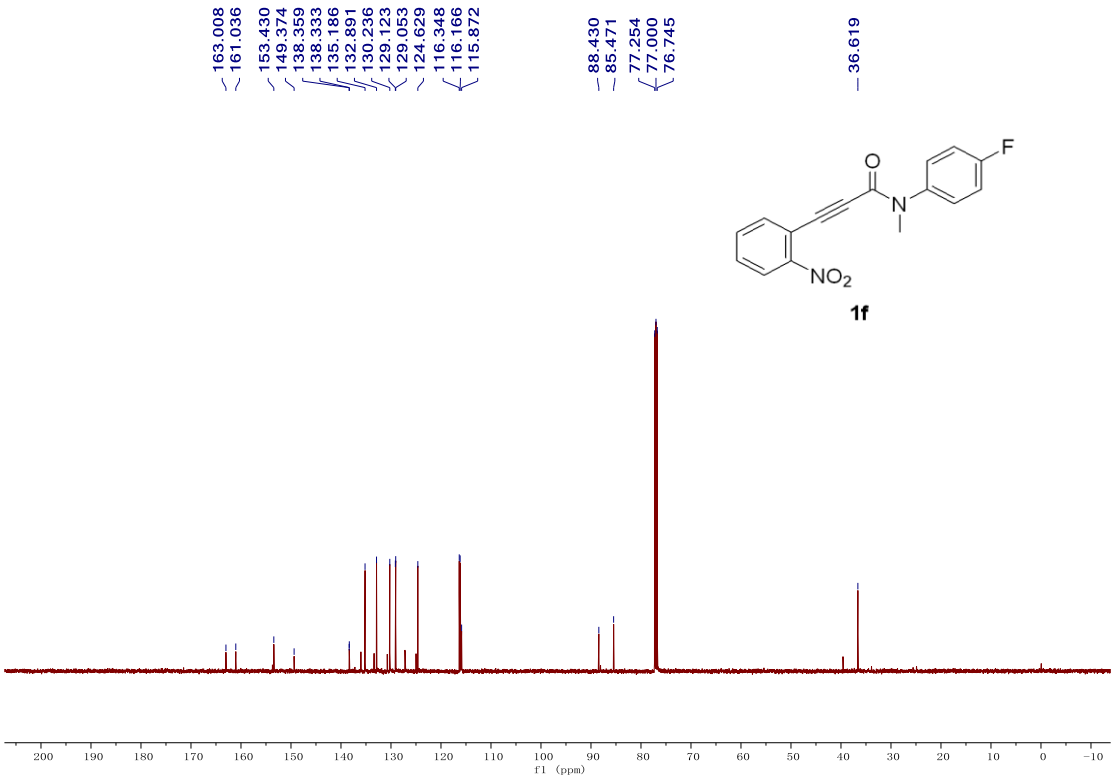
^{13}C NMR (125 MHz, $CDCl_3$)



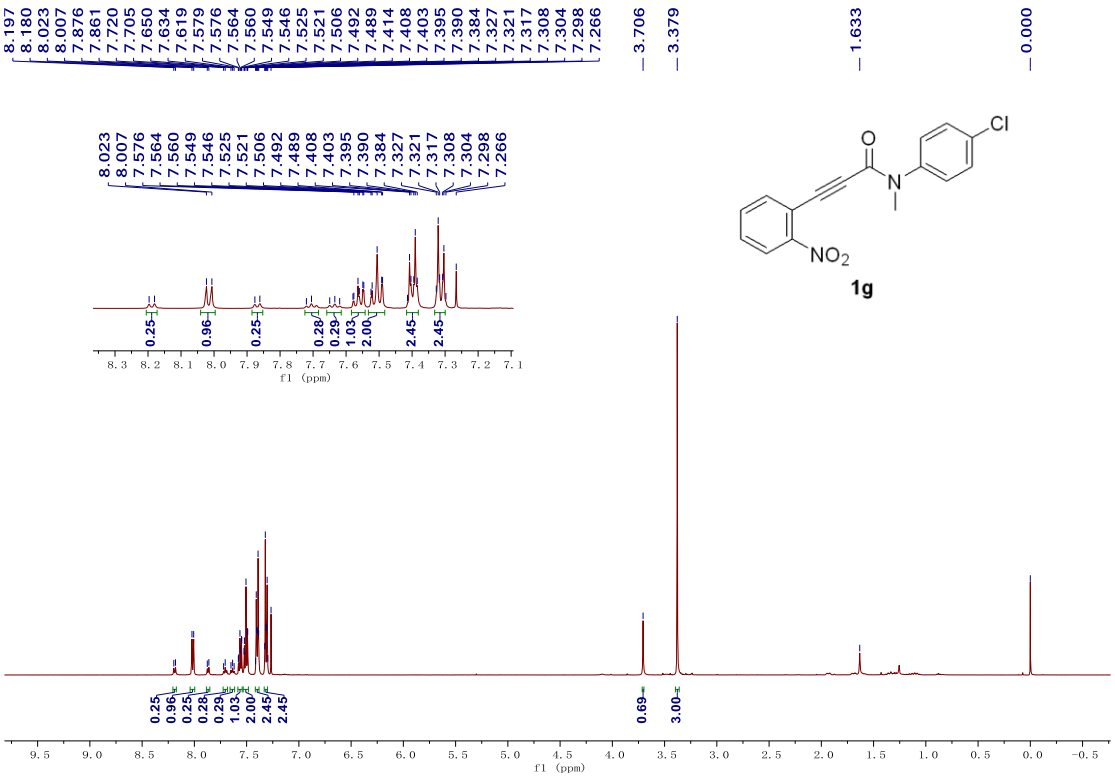
^{1}H NMR (500 MHz, $CDCl_3$)



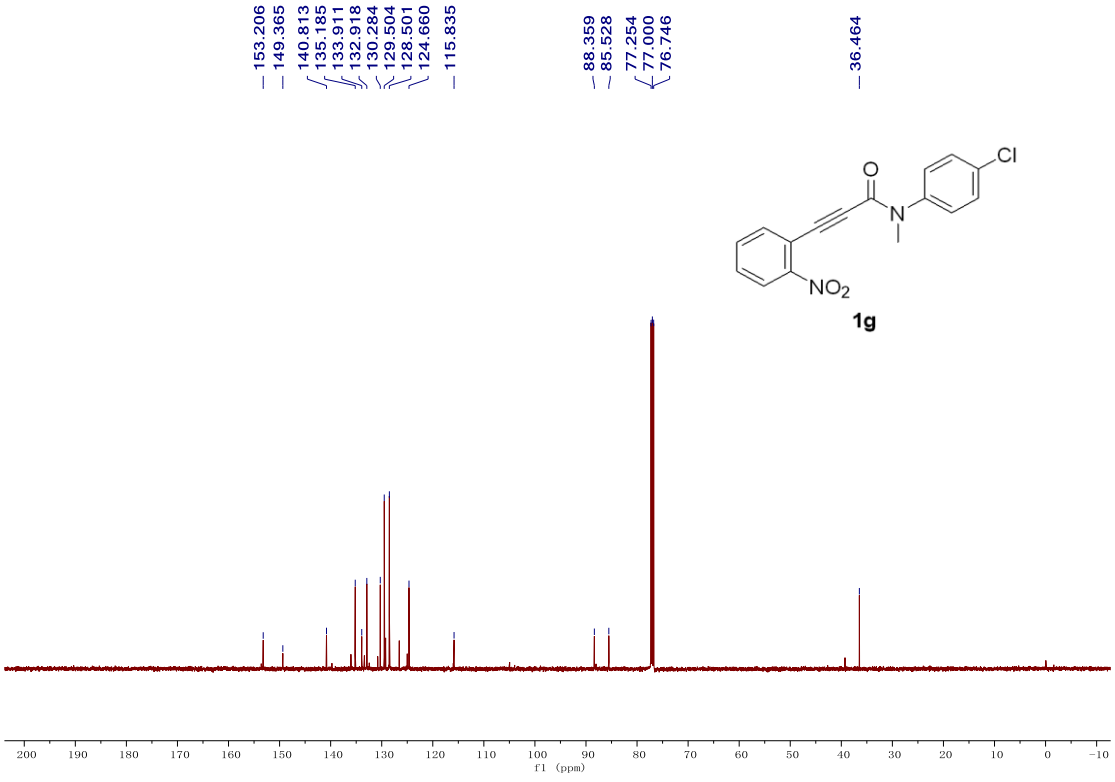
^{13}C NMR (125 MHz, $CDCl_3$)



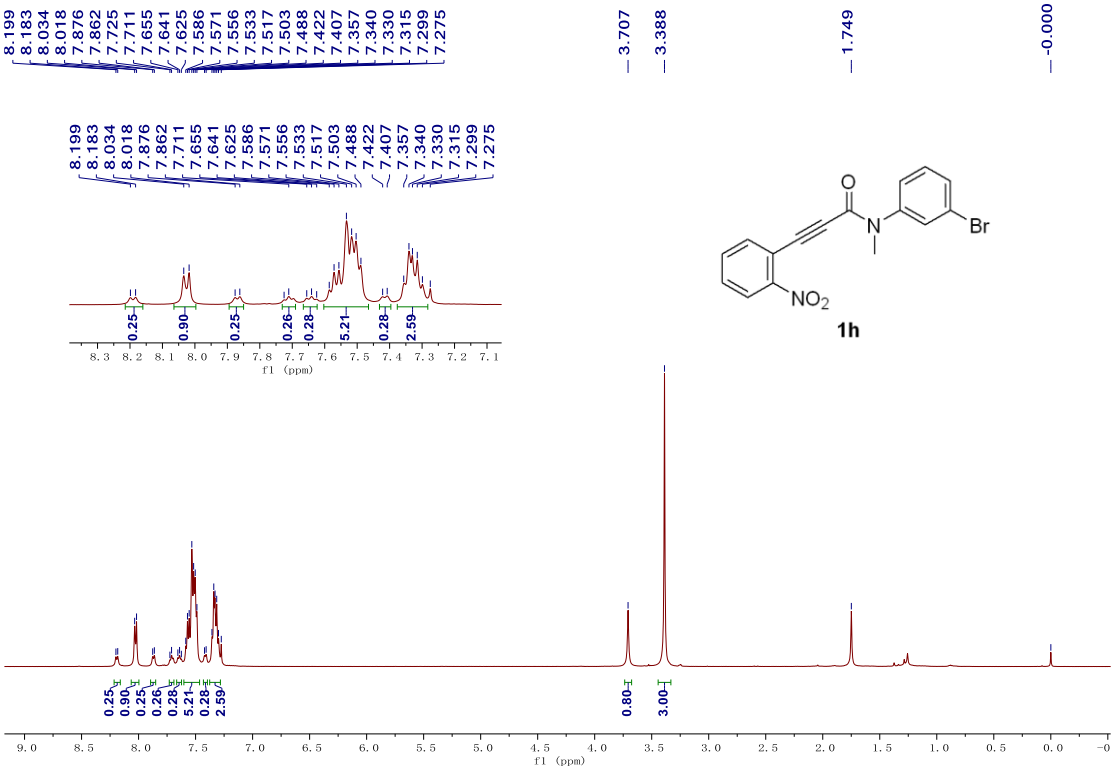
^{1}H NMR (500 MHz, $CDCl_3$)



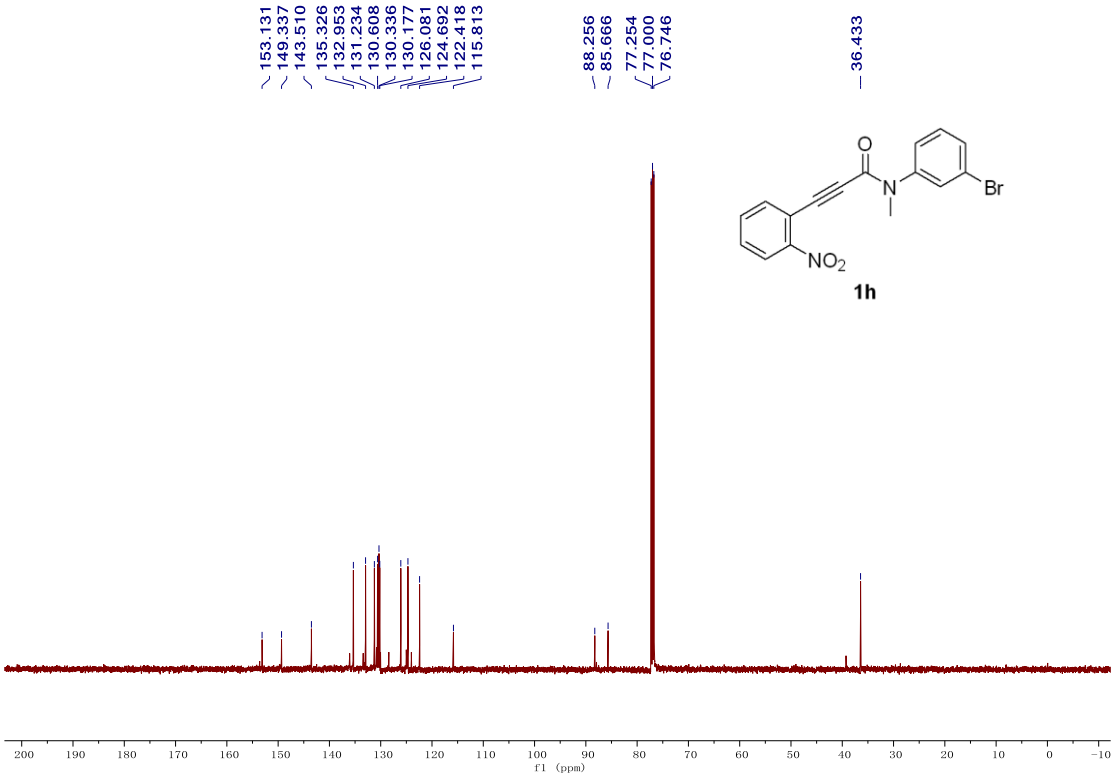
^{13}C NMR (125 MHz, $CDCl_3$)



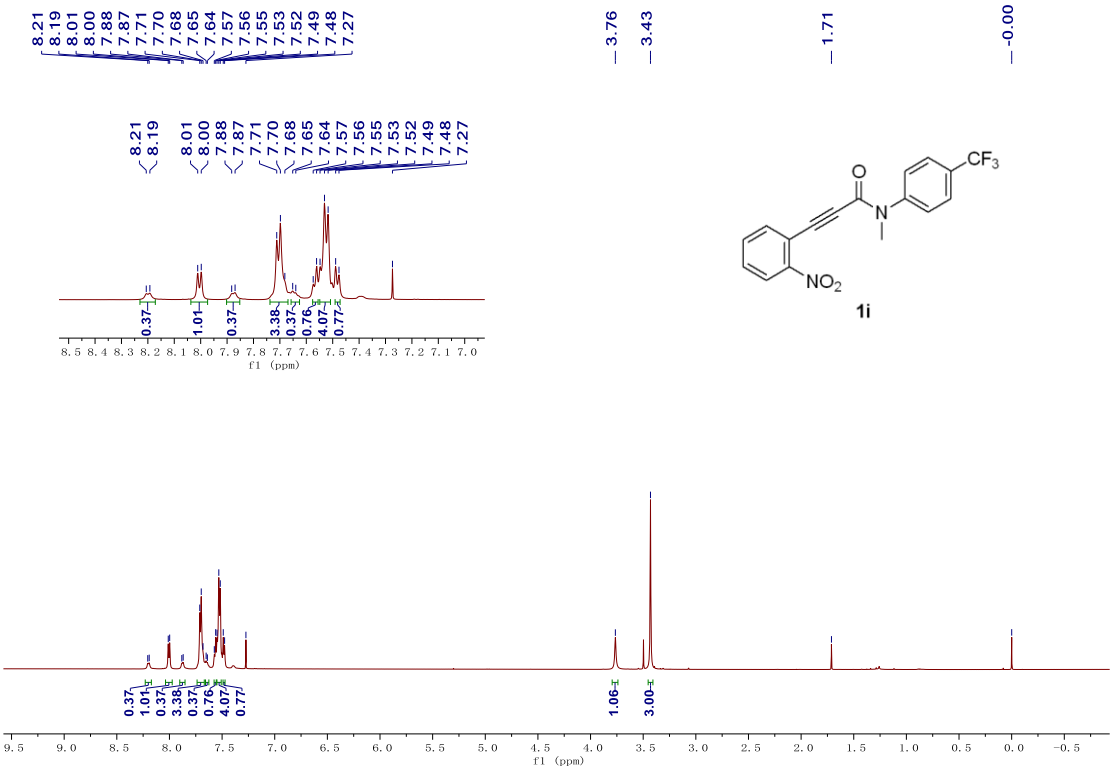
^{1}H NMR (500 MHz, $CDCl_3$)



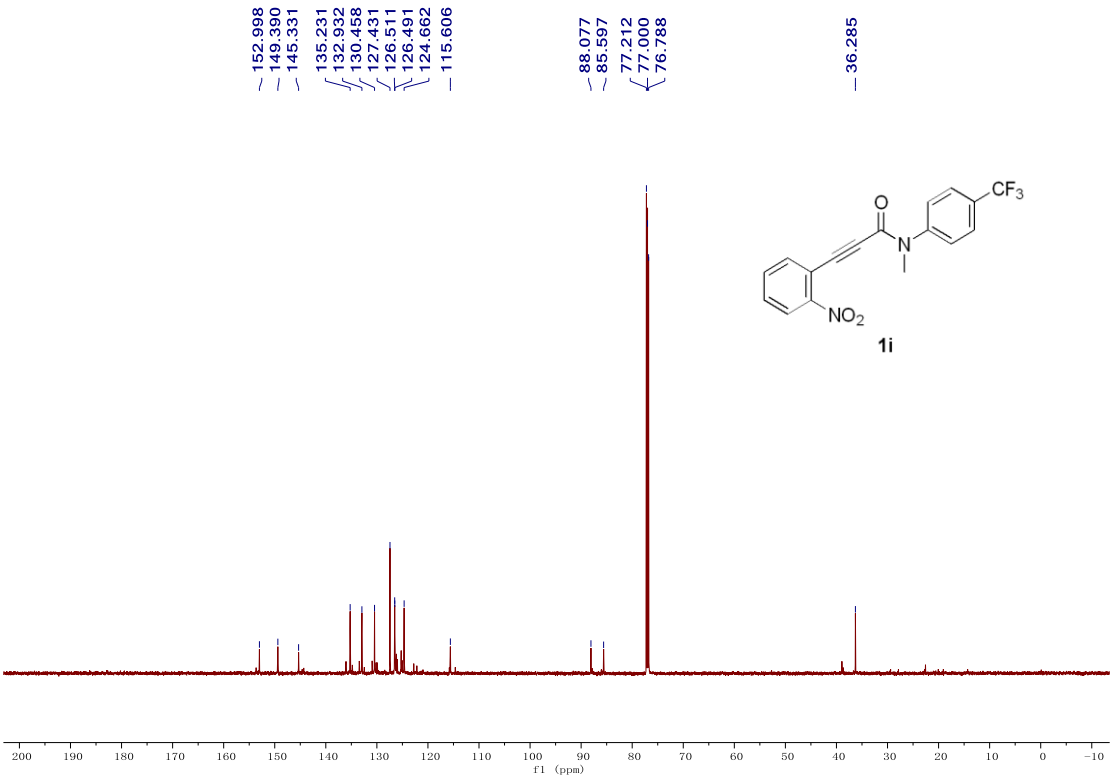
^{13}C NMR (125 MHz, $CDCl_3$)



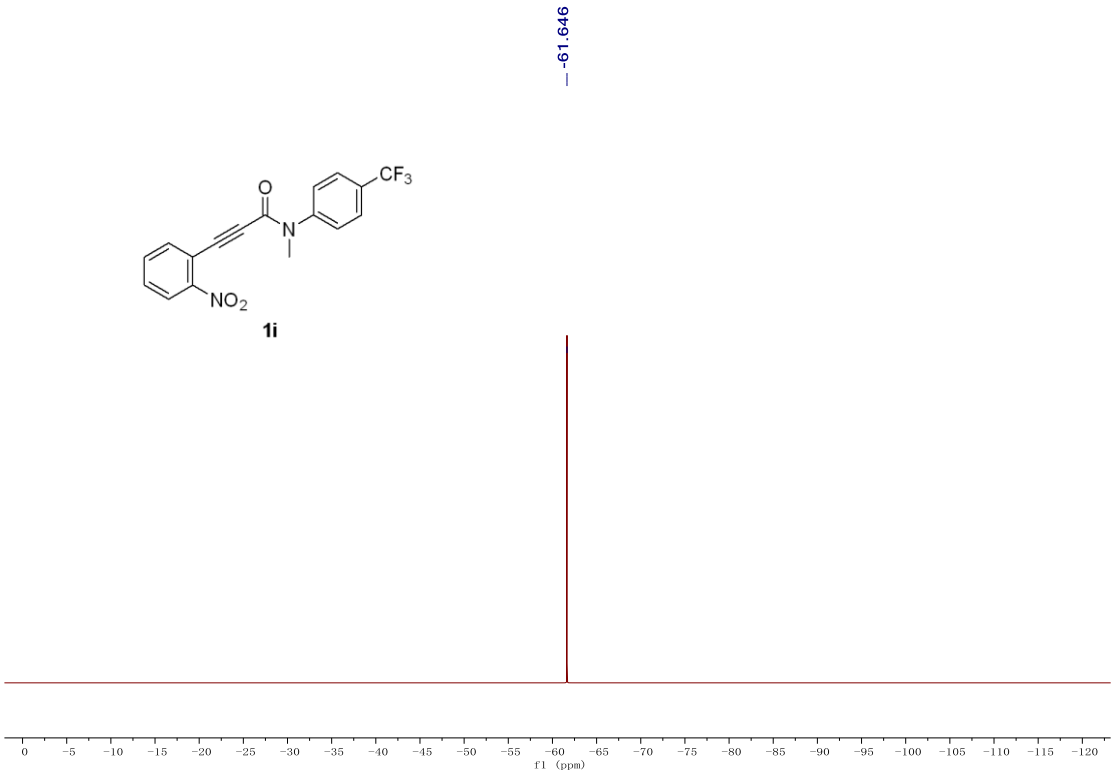
^{1}H NMR (600 MHz, $CDCl_3$)



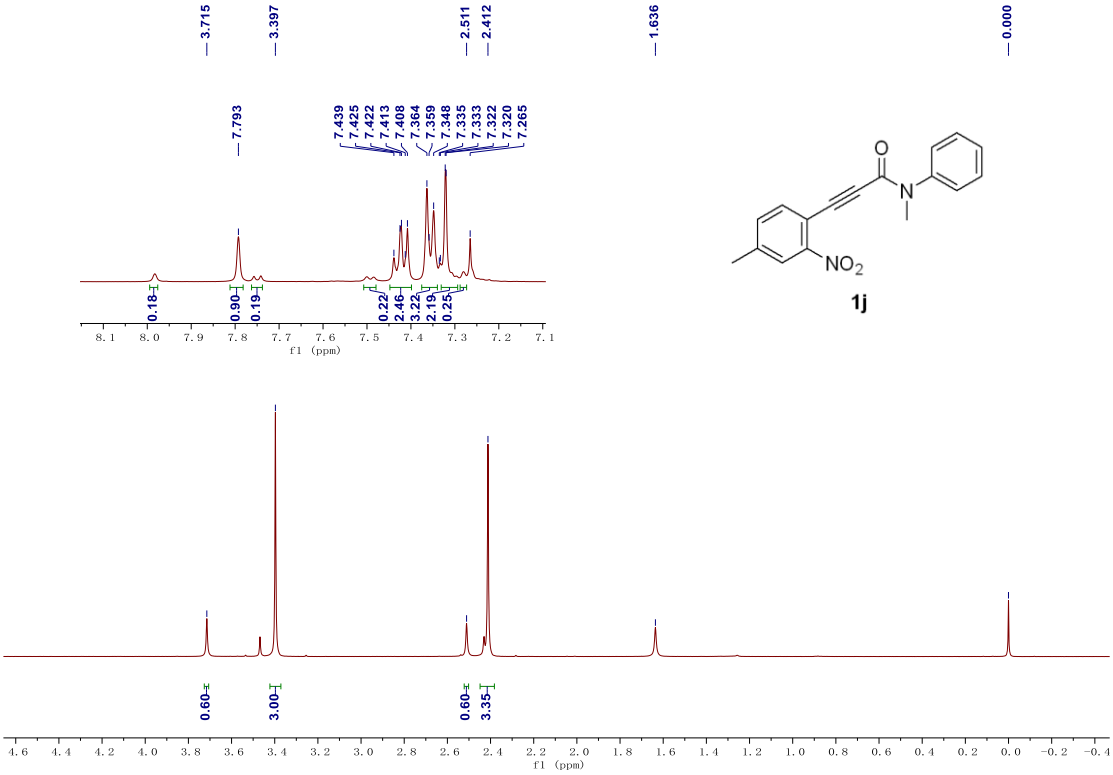
^{13}C NMR (600 MHz, $CDCl_3$)



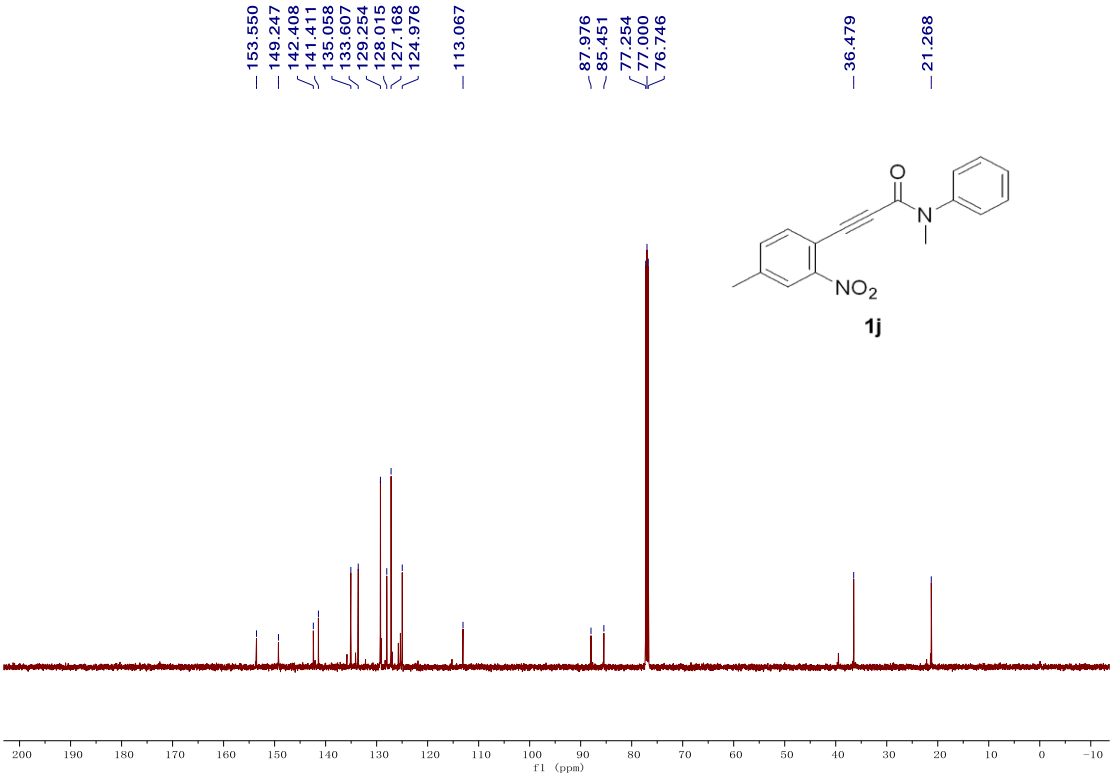
^{19}F NMR (470 MHz, $CDCl_3$)



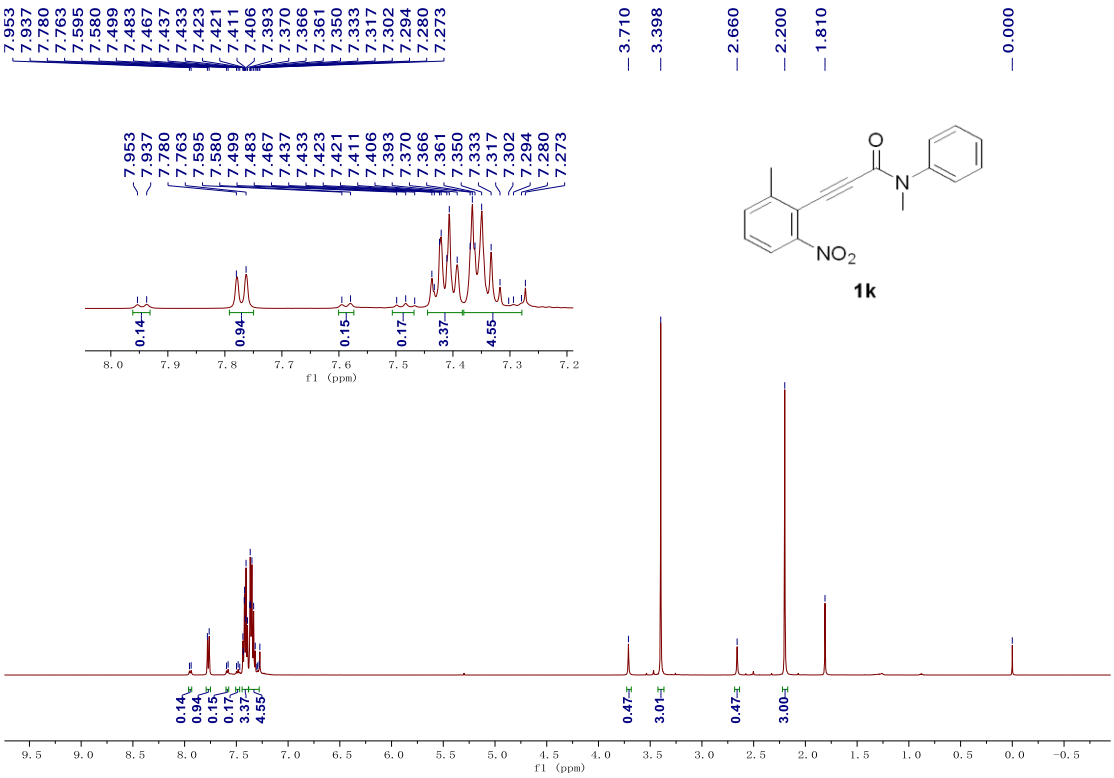
^{1}H NMR (500 MHz, $CDCl_3$)



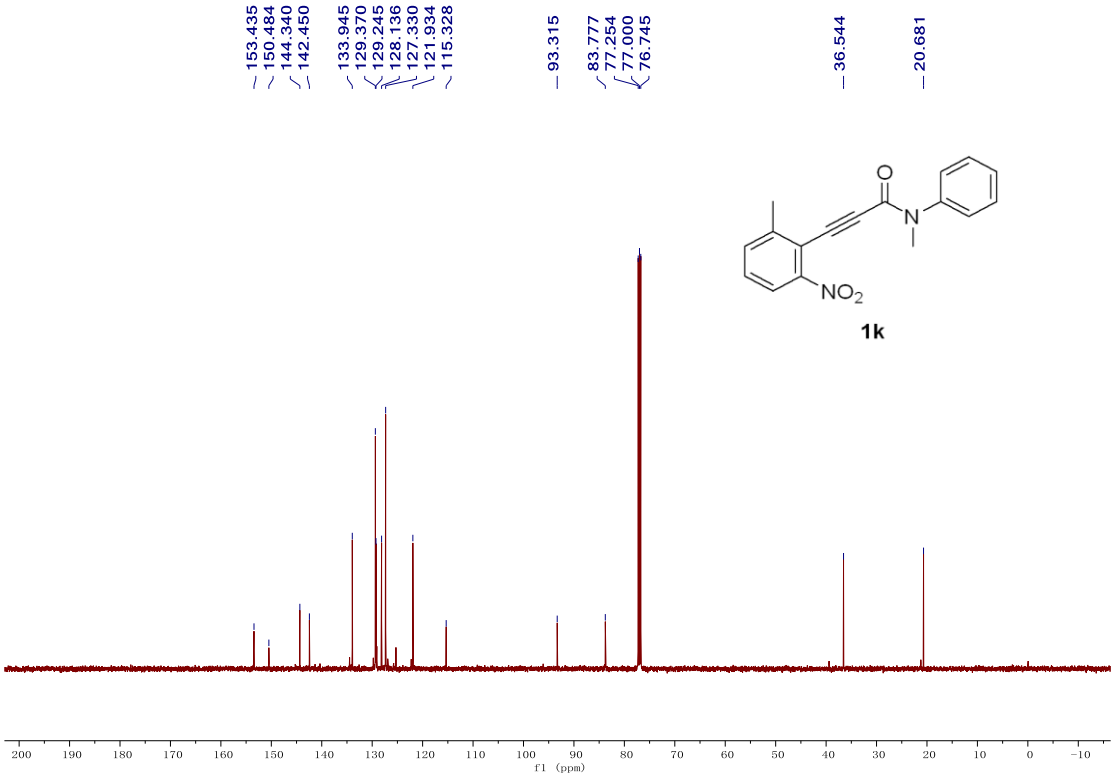
^{13}C NMR (125 MHz, $CDCl_3$)



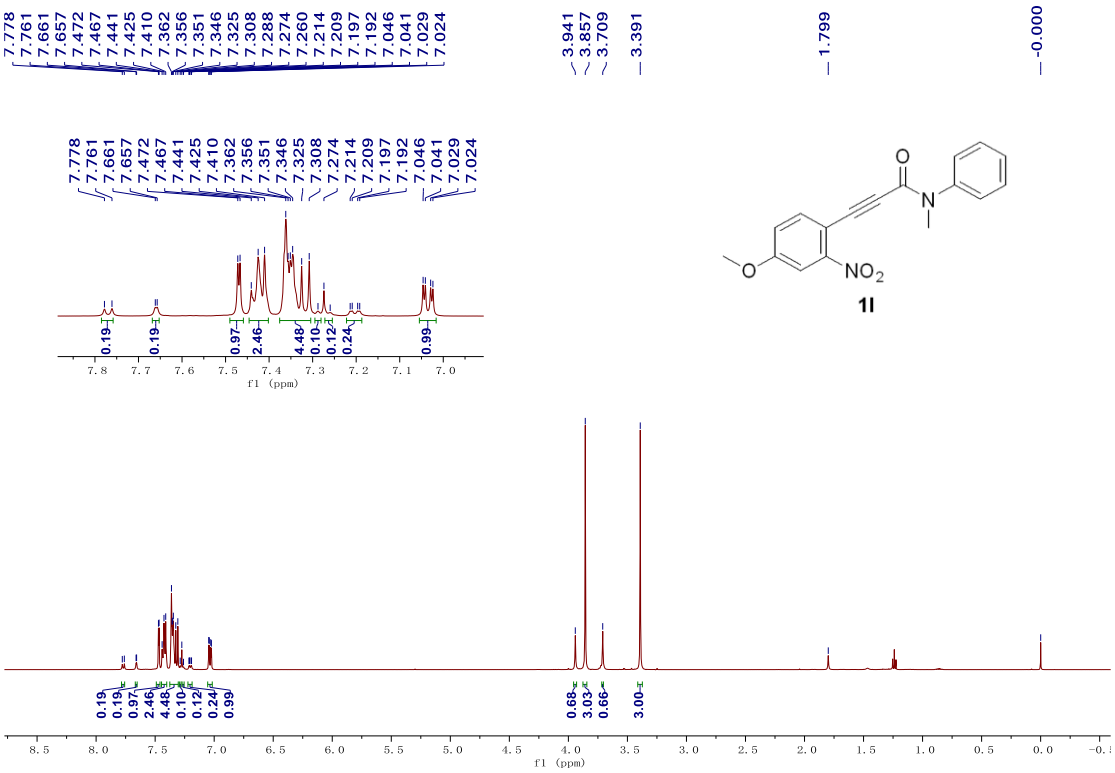
^{1}H NMR (500 MHz, $CDCl_3$)



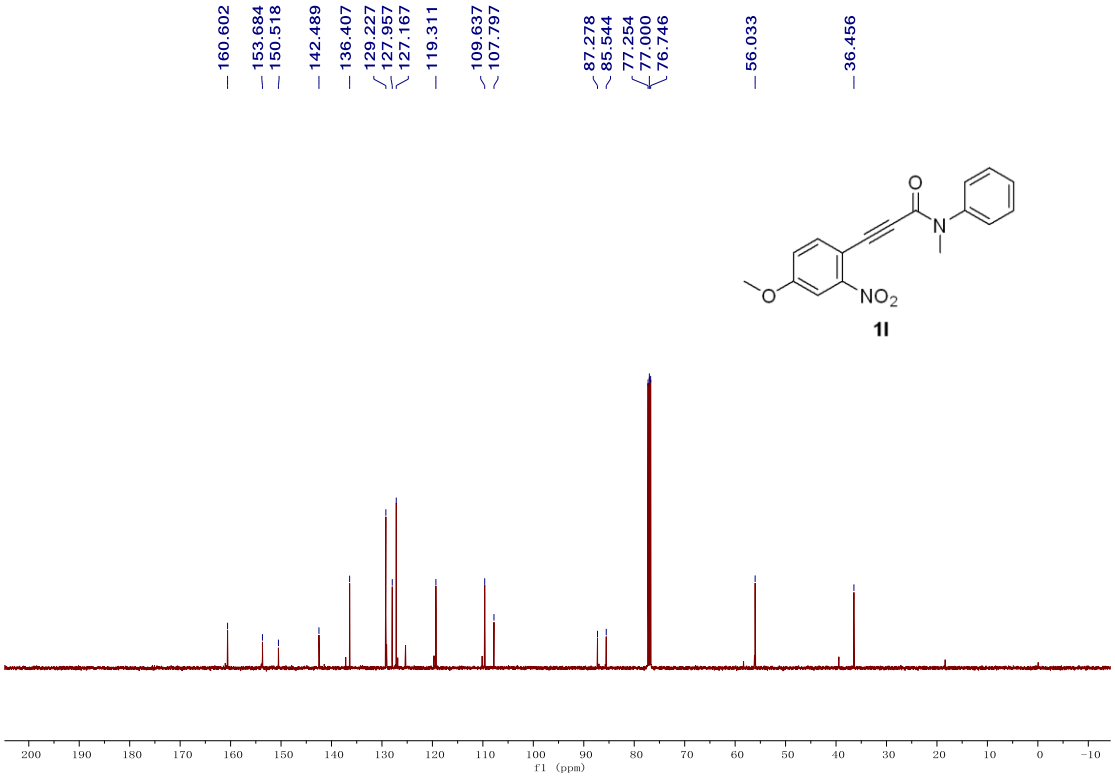
^{13}C NMR (125 MHz, $CDCl_3$)



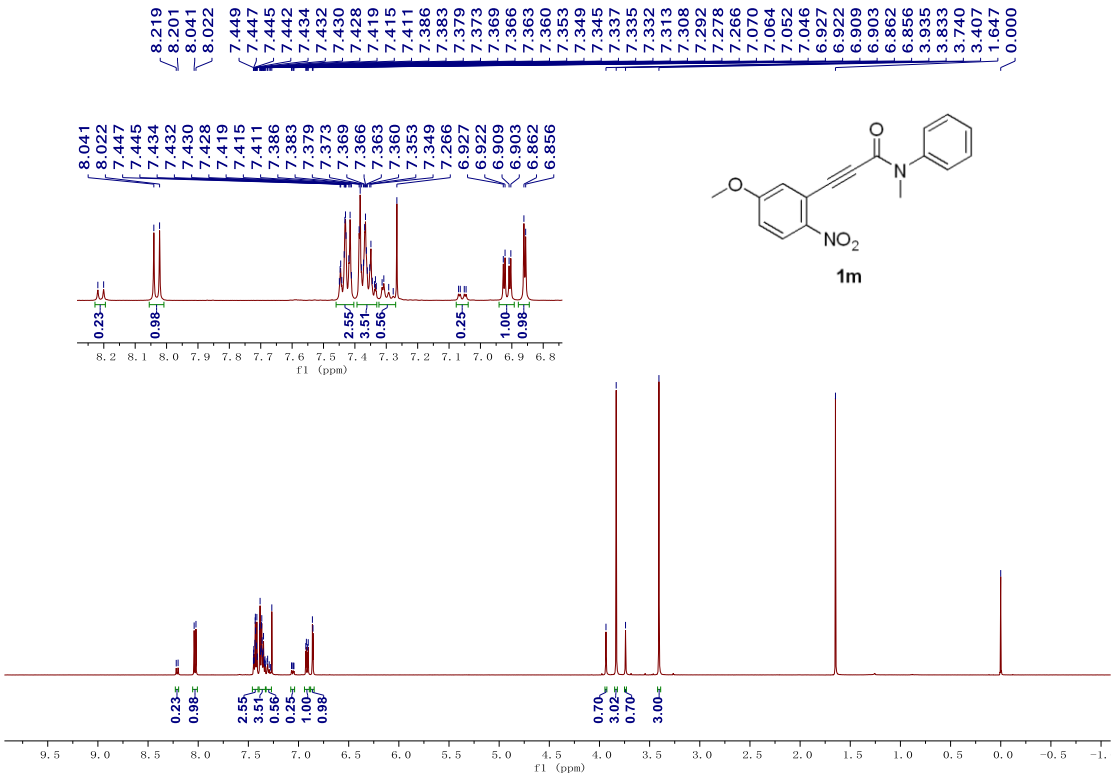
^{1}H NMR (500 MHz, $CDCl_3$)



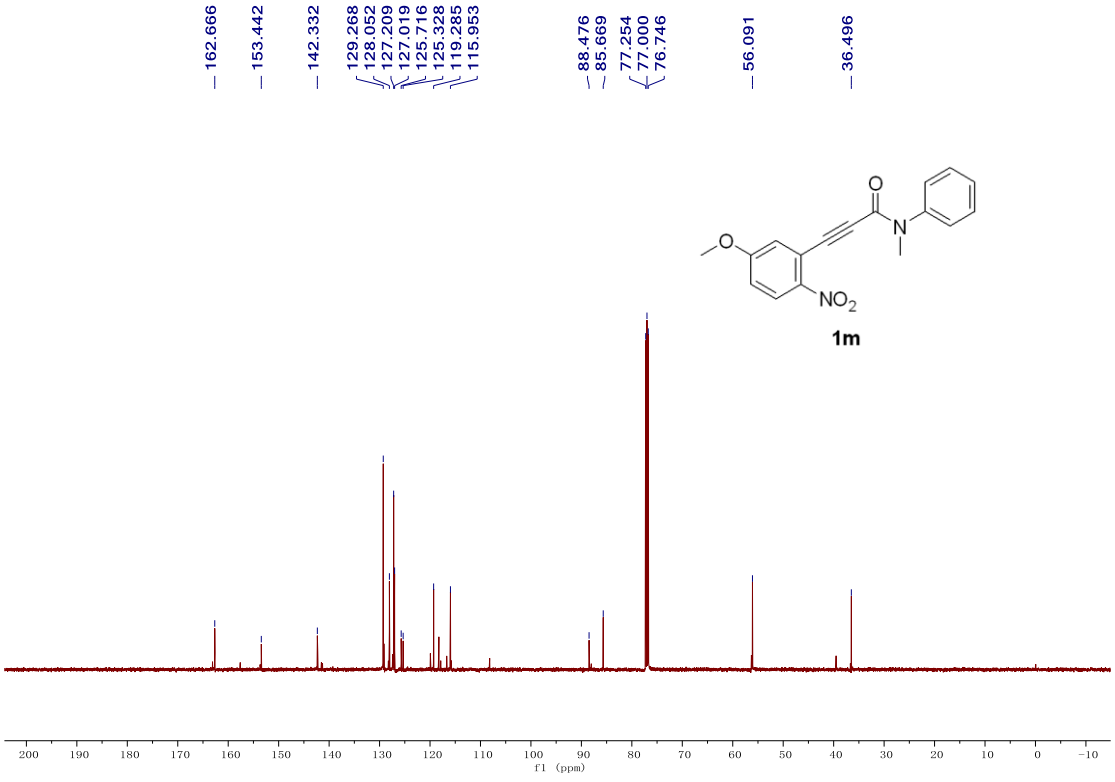
^{13}C NMR (125 MHz, $CDCl_3$)



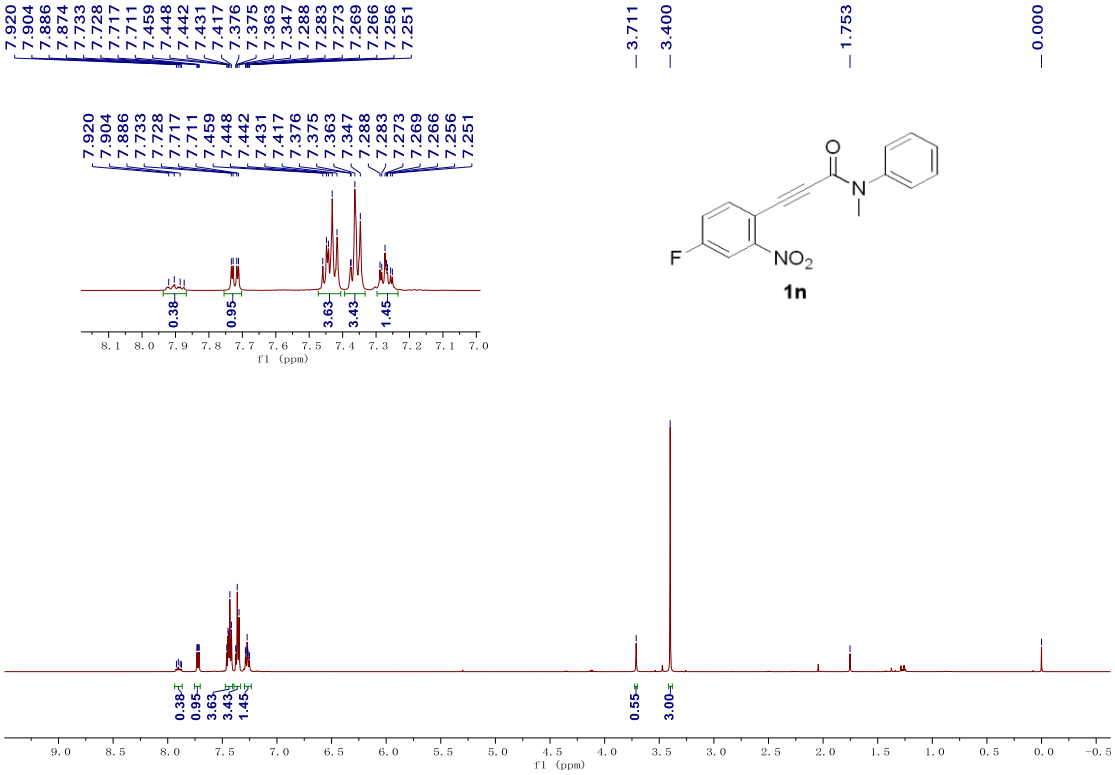
^{1}H NMR (500 MHz, $CDCl_3$)



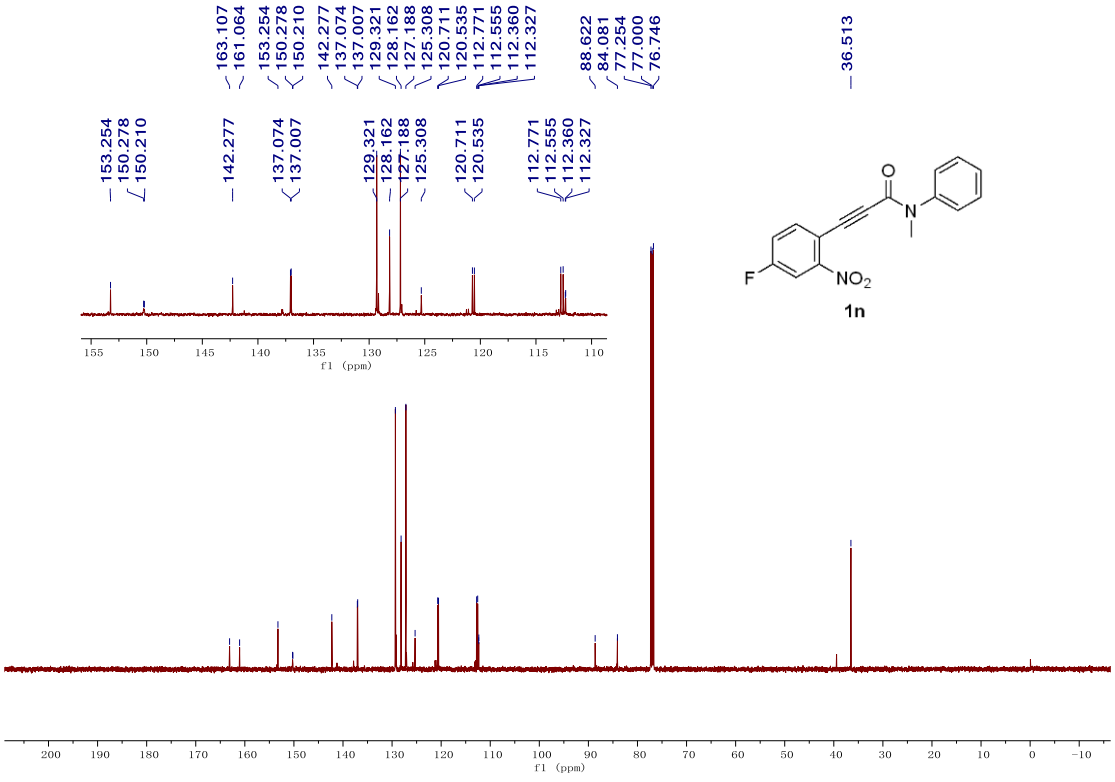
^{13}C NMR (125 MHz, $CDCl_3$)



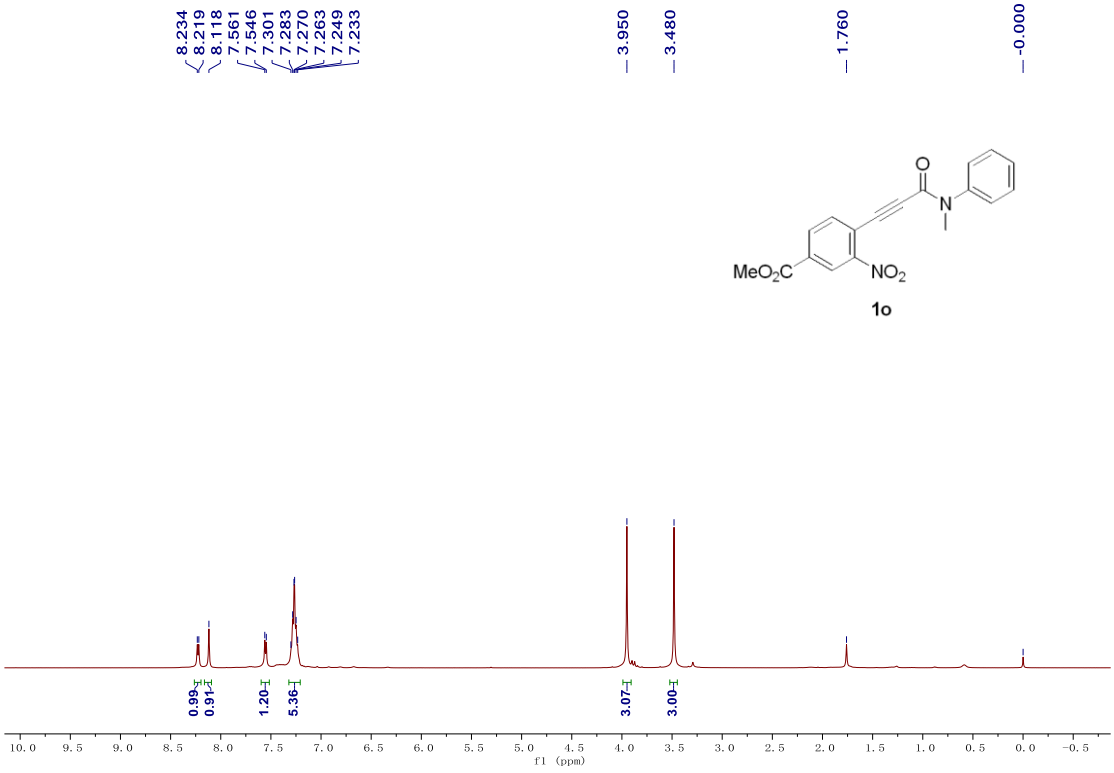
^{1}H NMR (500 MHz, $CDCl_3$)



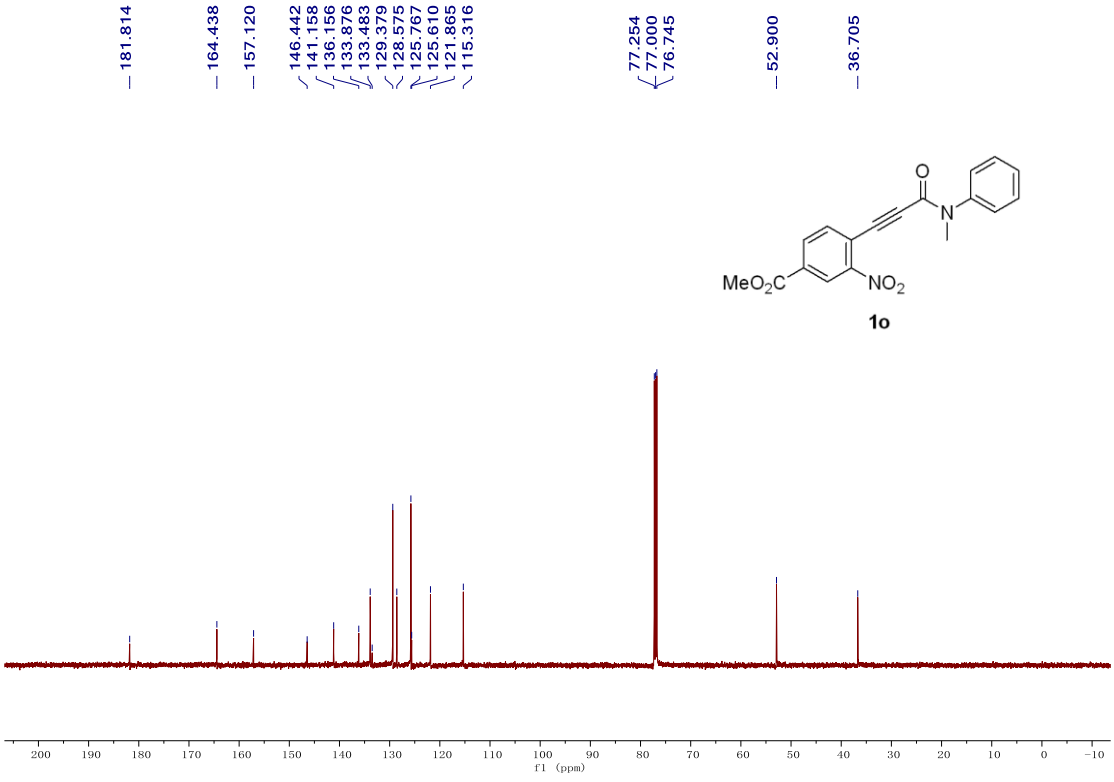
^{13}C NMR (125 MHz, $CDCl_3$)



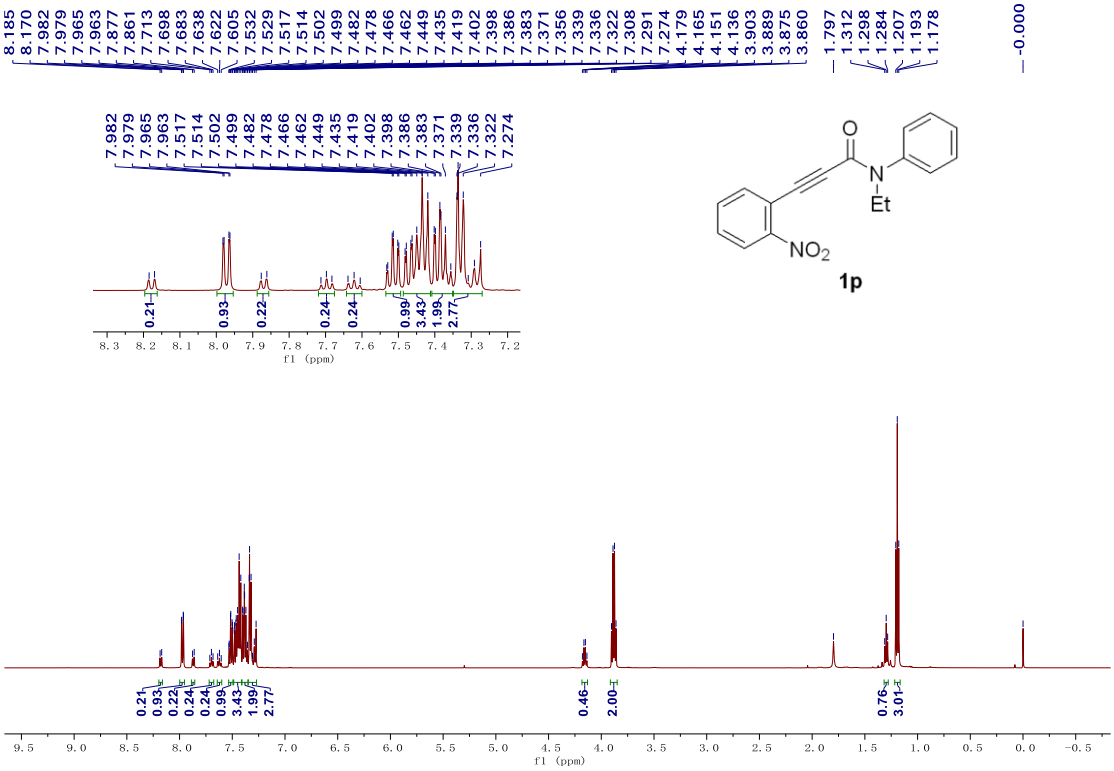
^{1}H NMR (500 MHz, $CDCl_3$)



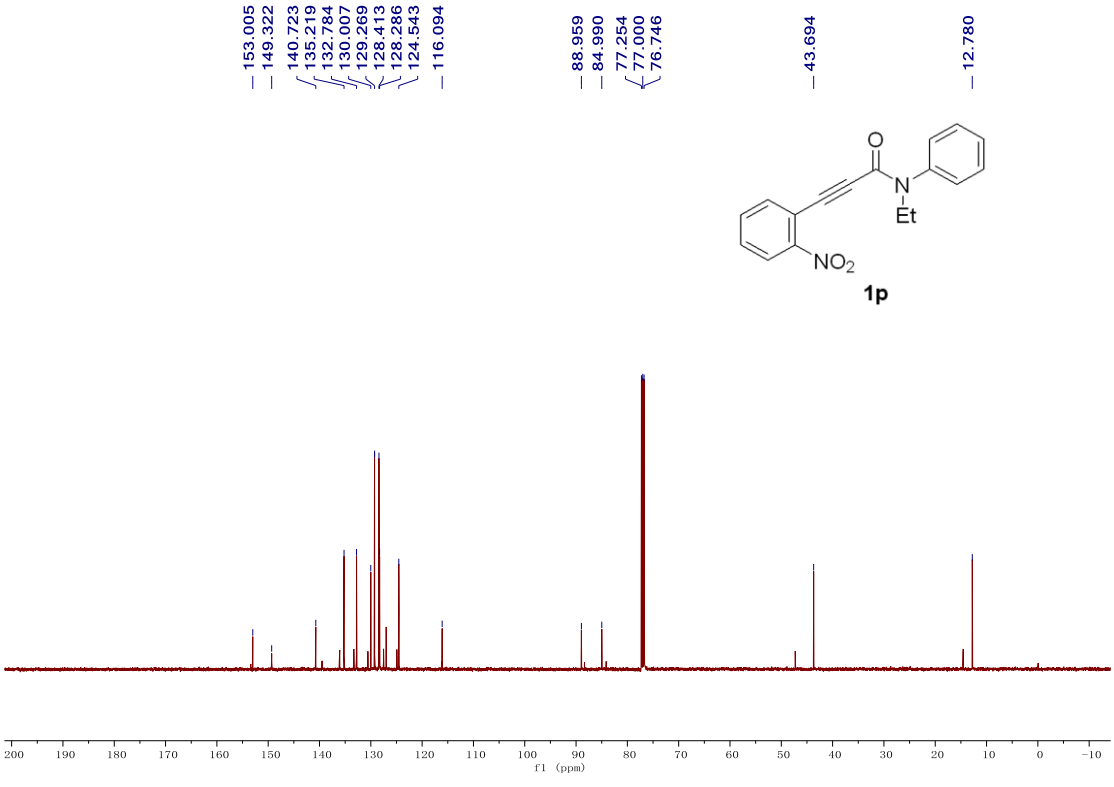
^{13}C NMR (125 MHz, $CDCl_3$)



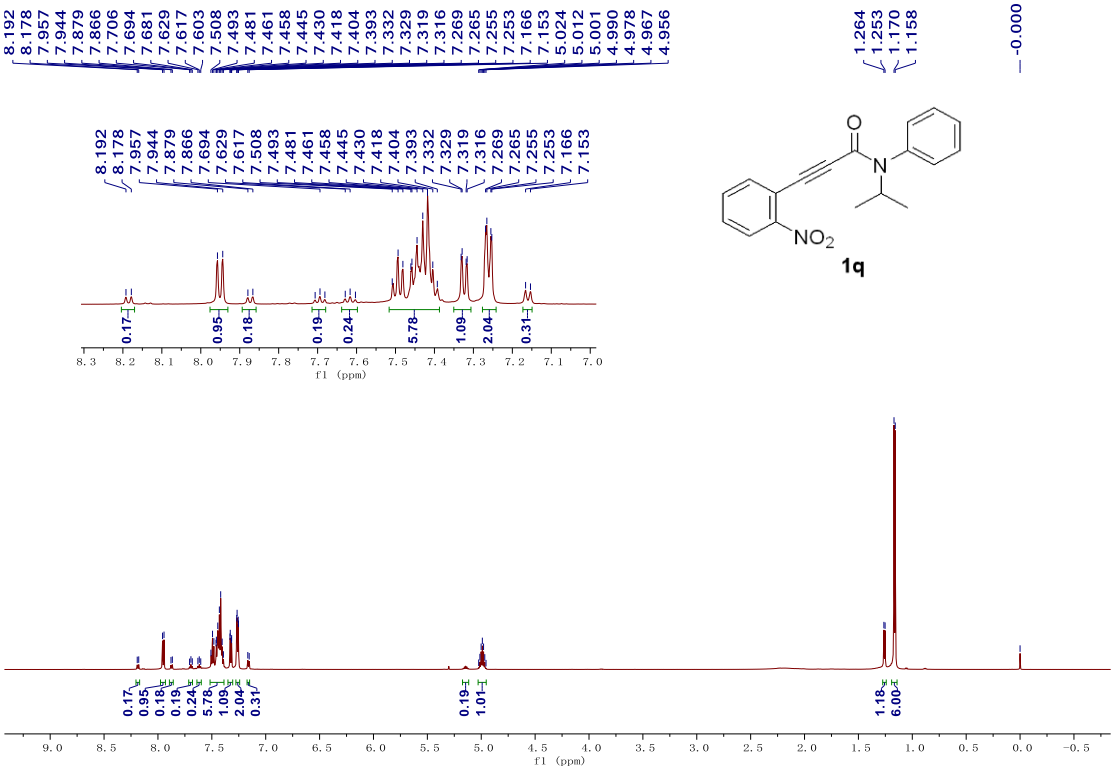
^{1}H NMR (500 MHz, $CDCl_3$)



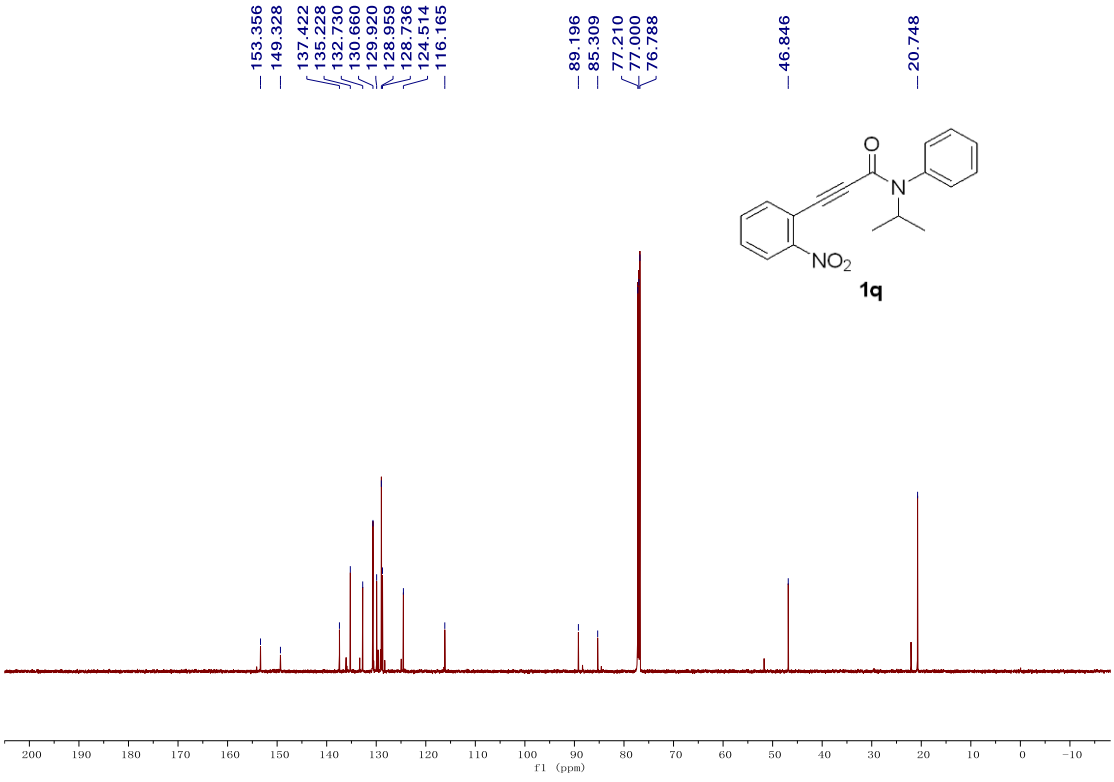
^{13}C NMR (125 MHz, $CDCl_3$)



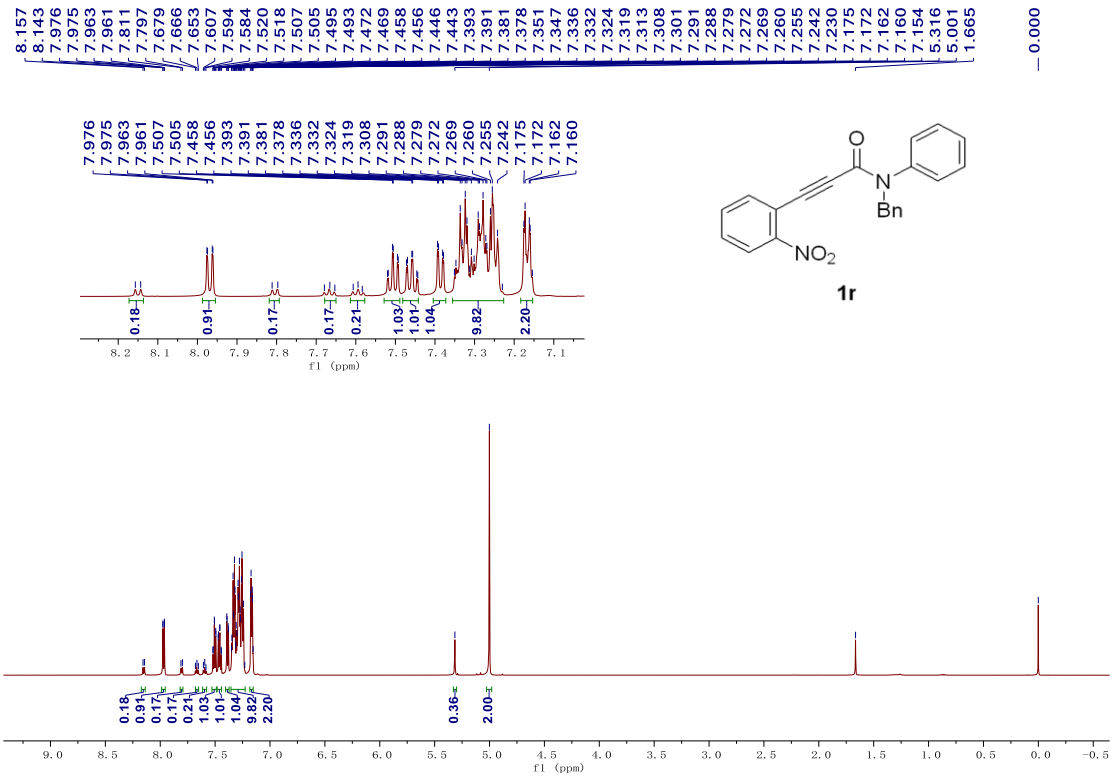
^{1}H NMR (600 MHz, $CDCl_3$)



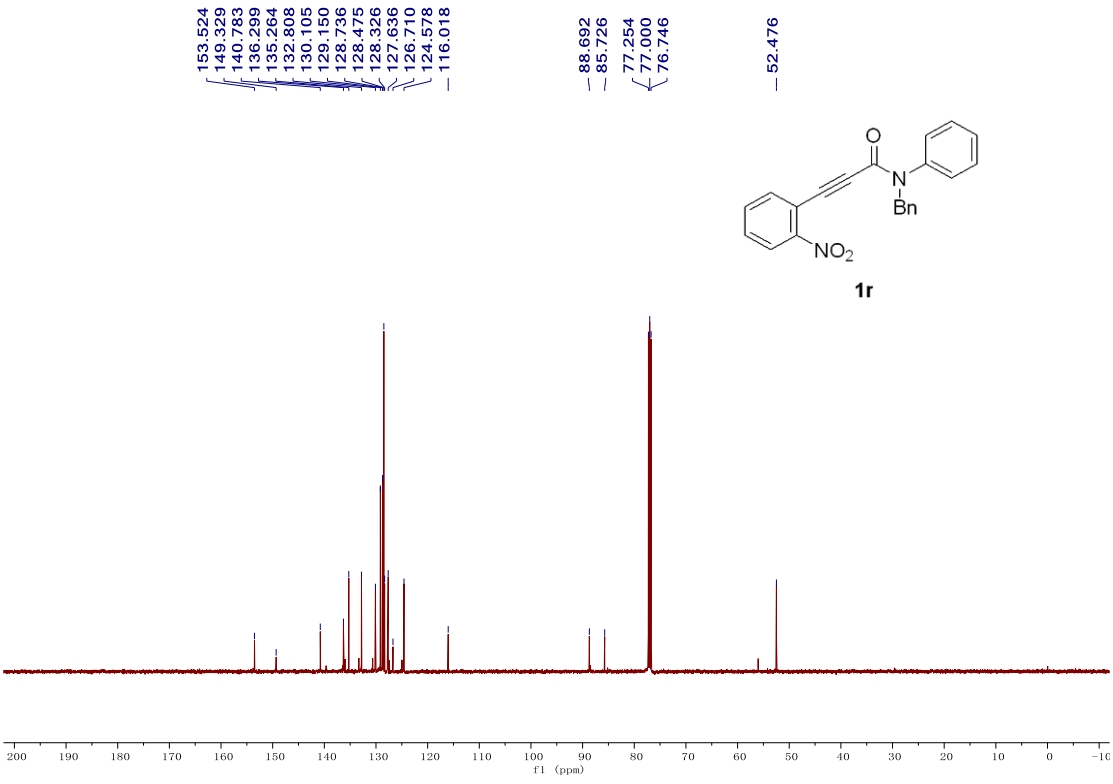
^{13}C NMR (150 MHz, $CDCl_3$)



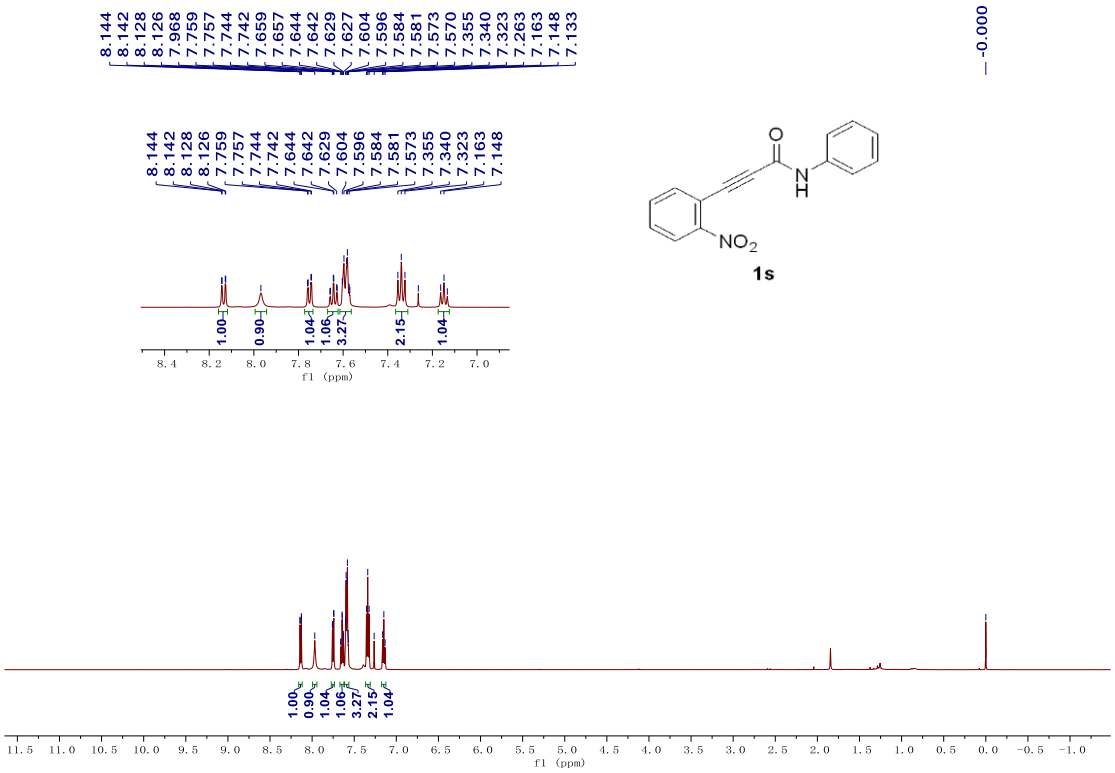
^{1}H NMR (600 MHz, $CDCl_3$)



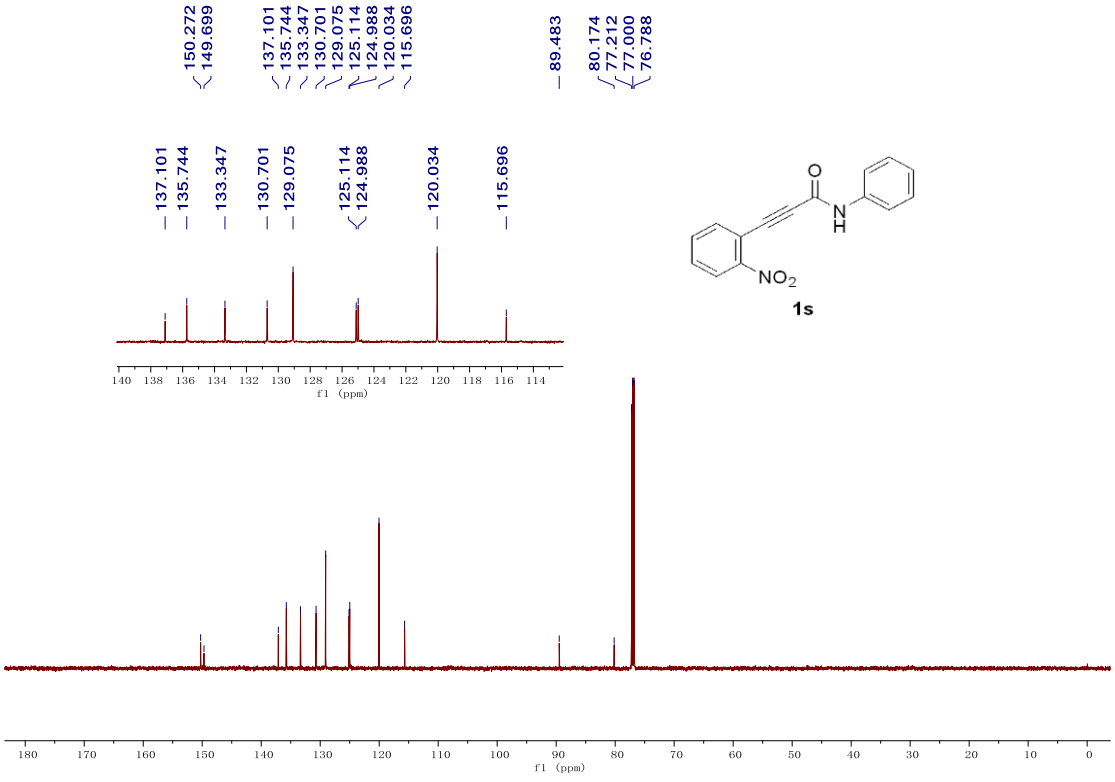
^{13}C NMR (150 MHz, $CDCl_3$)



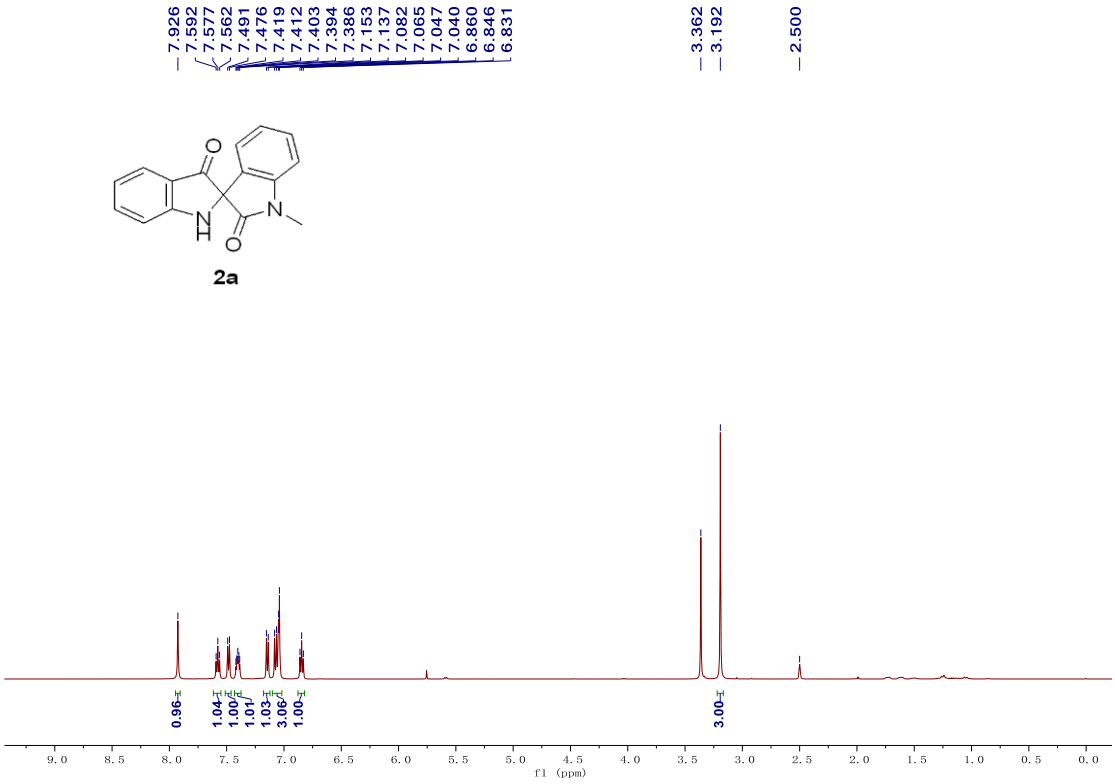
^{1}H NMR (500 MHz, $CDCl_3$)



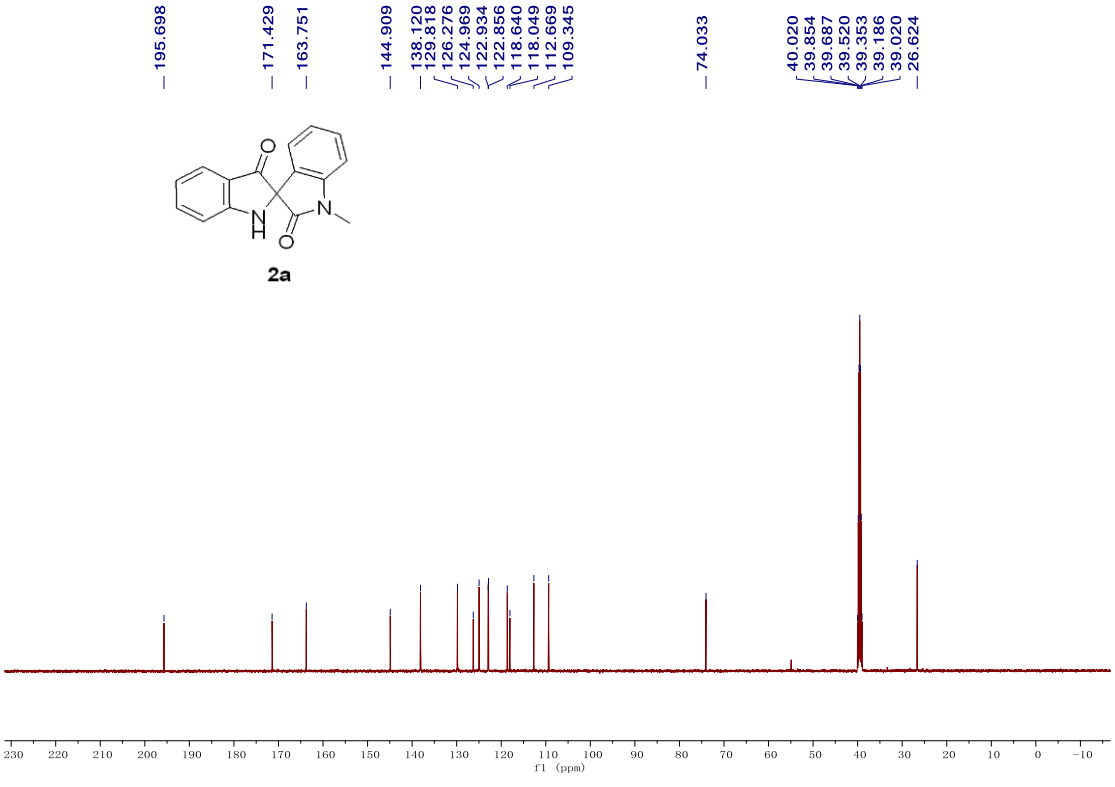
^{13}C NMR (125 MHz, $CDCl_3$)



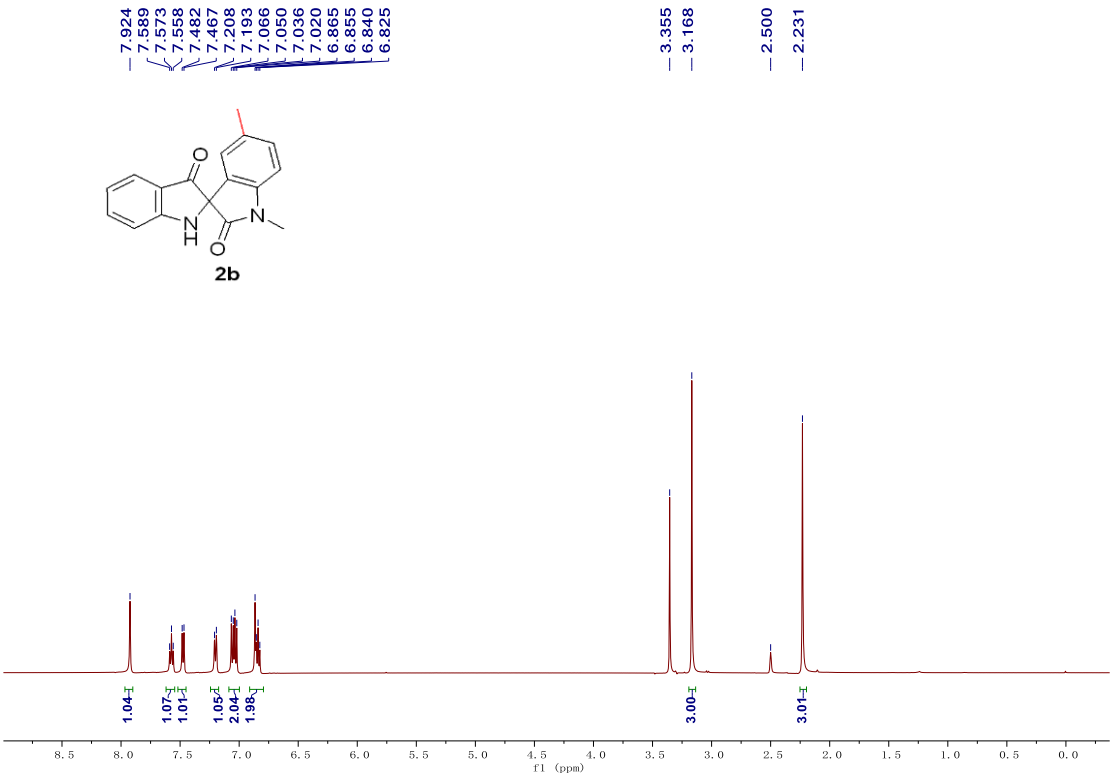
^{1}H NMR (500 MHz, d^{6}-DMSO)



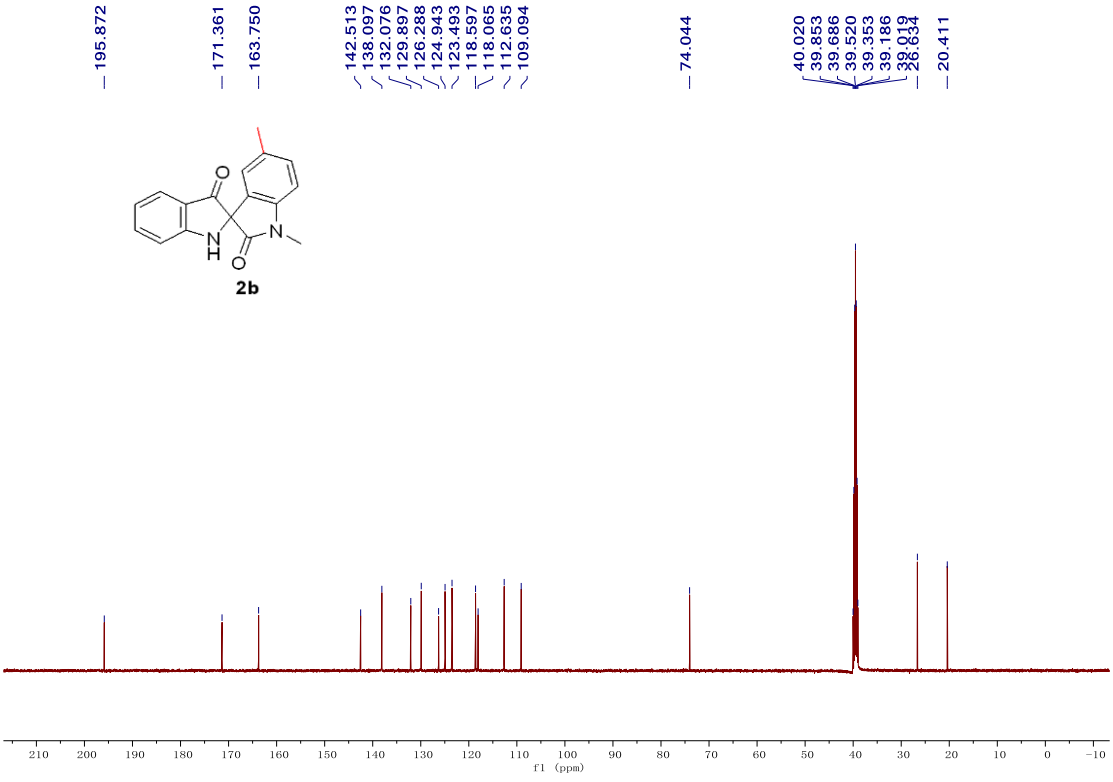
^{13}C NMR (125 MHz, d^{6}-DMSO)



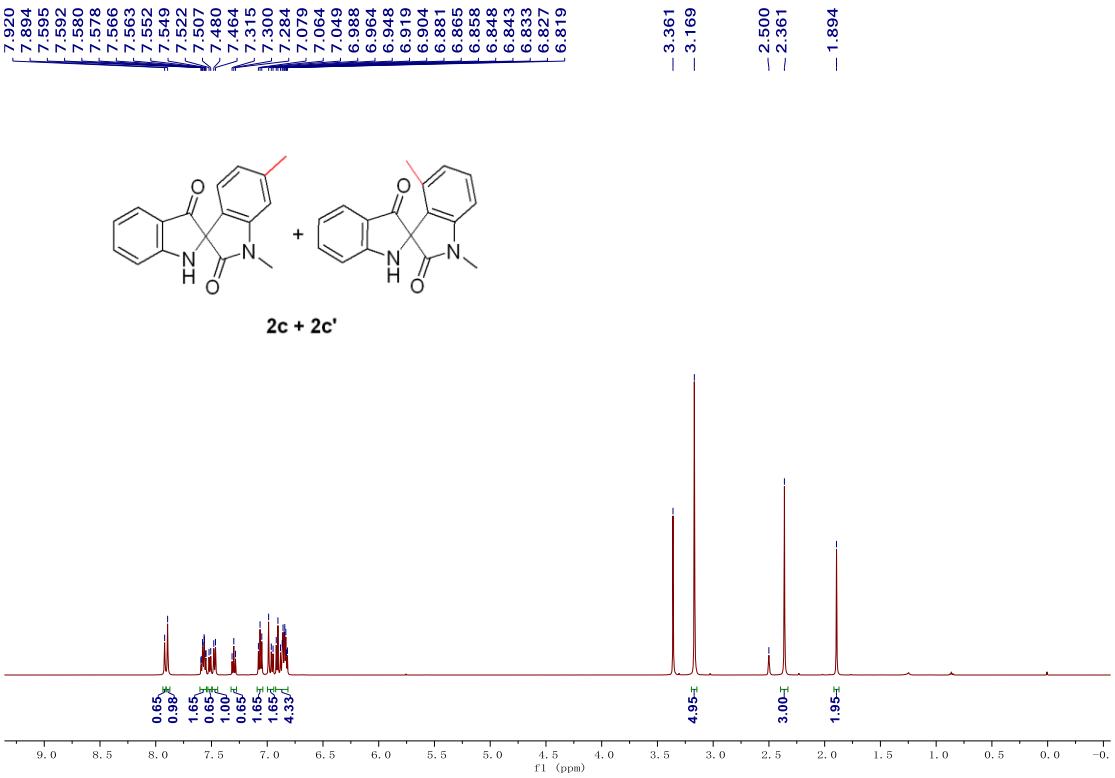
^{1}H NMR (500 MHz, d^{6}-DMSO)



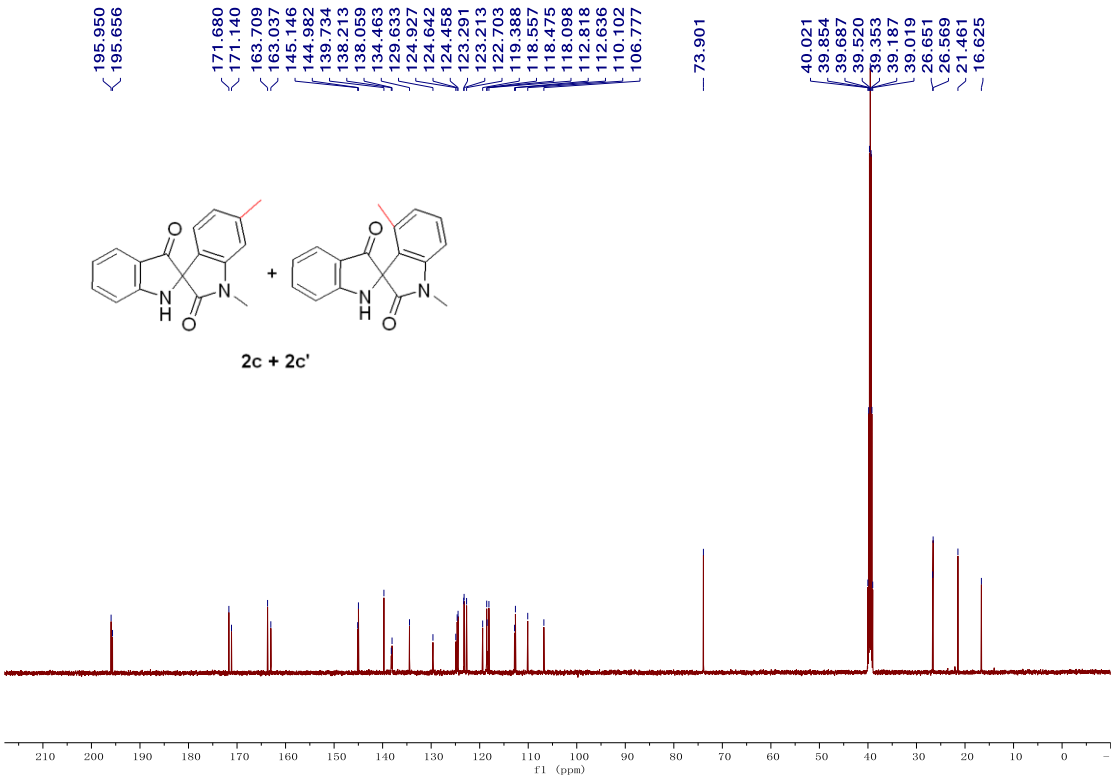
^{13}C NMR (125 MHz, d^{6}-DMSO)



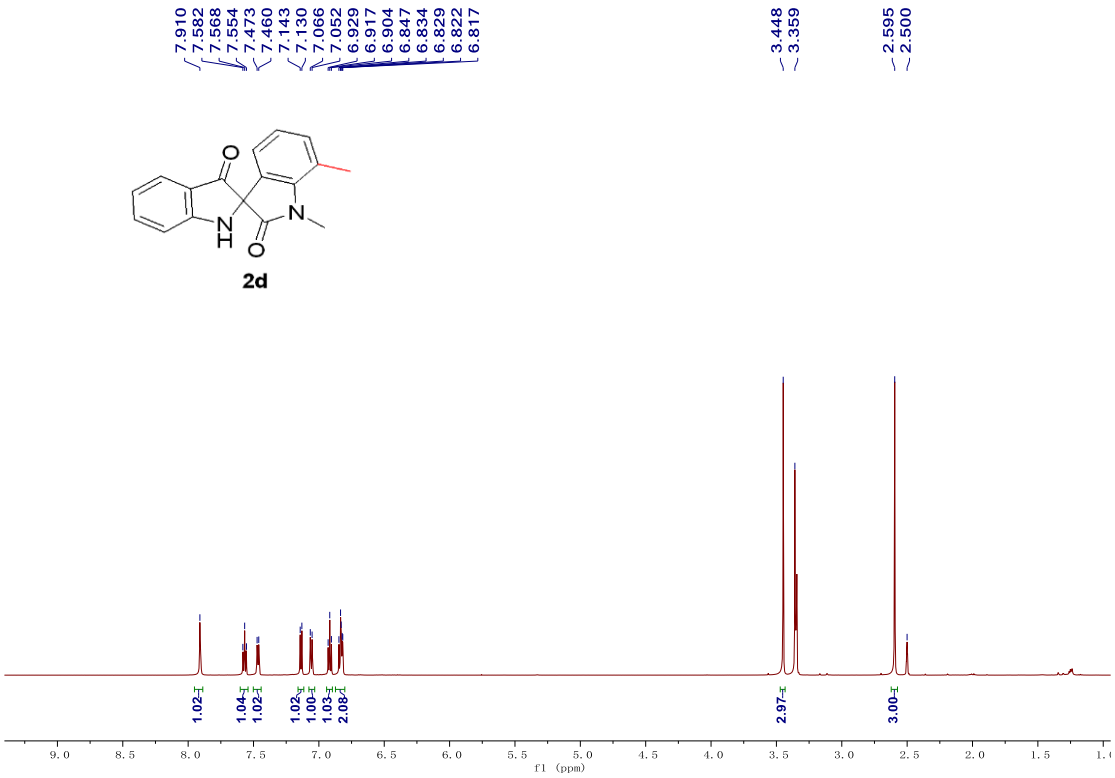
^{1}H NMR (500 MHz, d^{6}-DMSO)



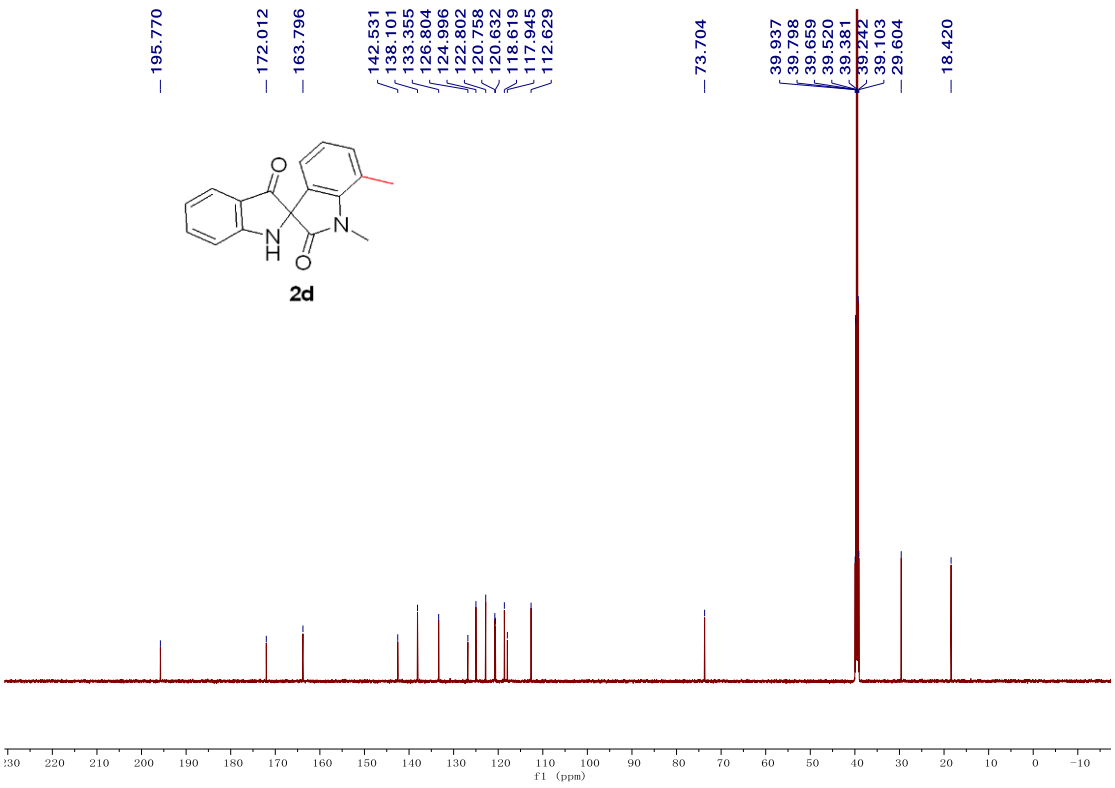
^{13}C NMR (125 MHz, d^{6}-DMSO)



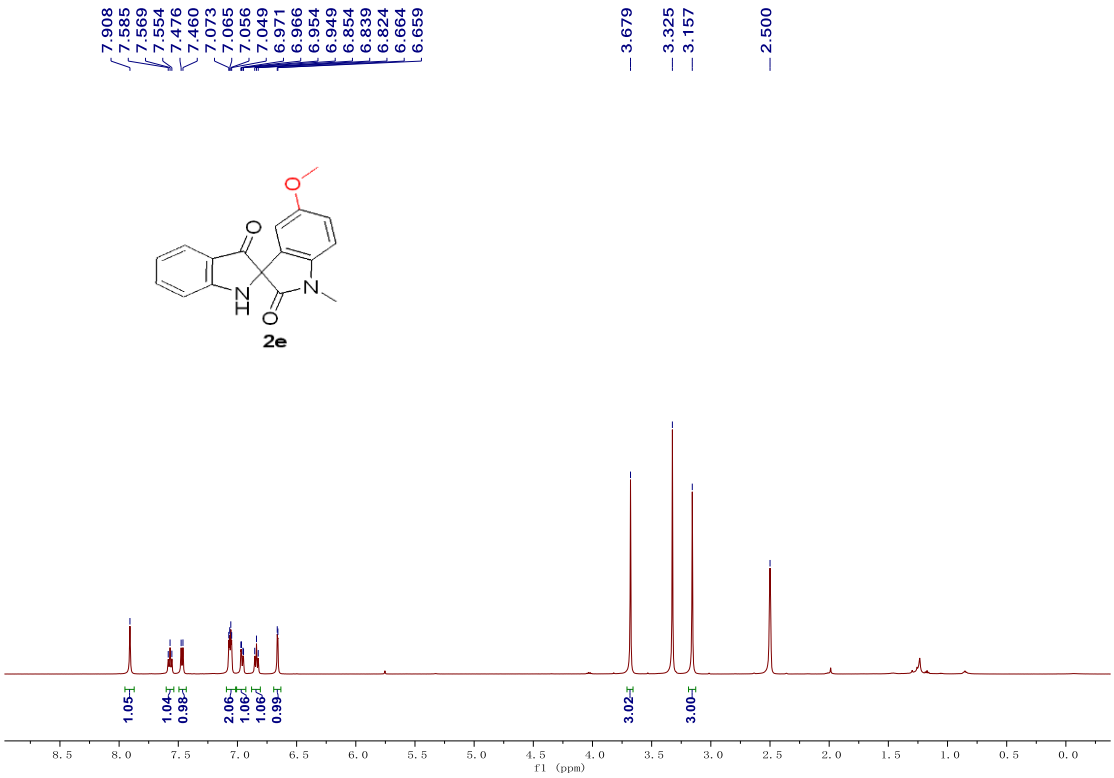
^{1}H NMR (600 MHz, d^{6}-DMSO)



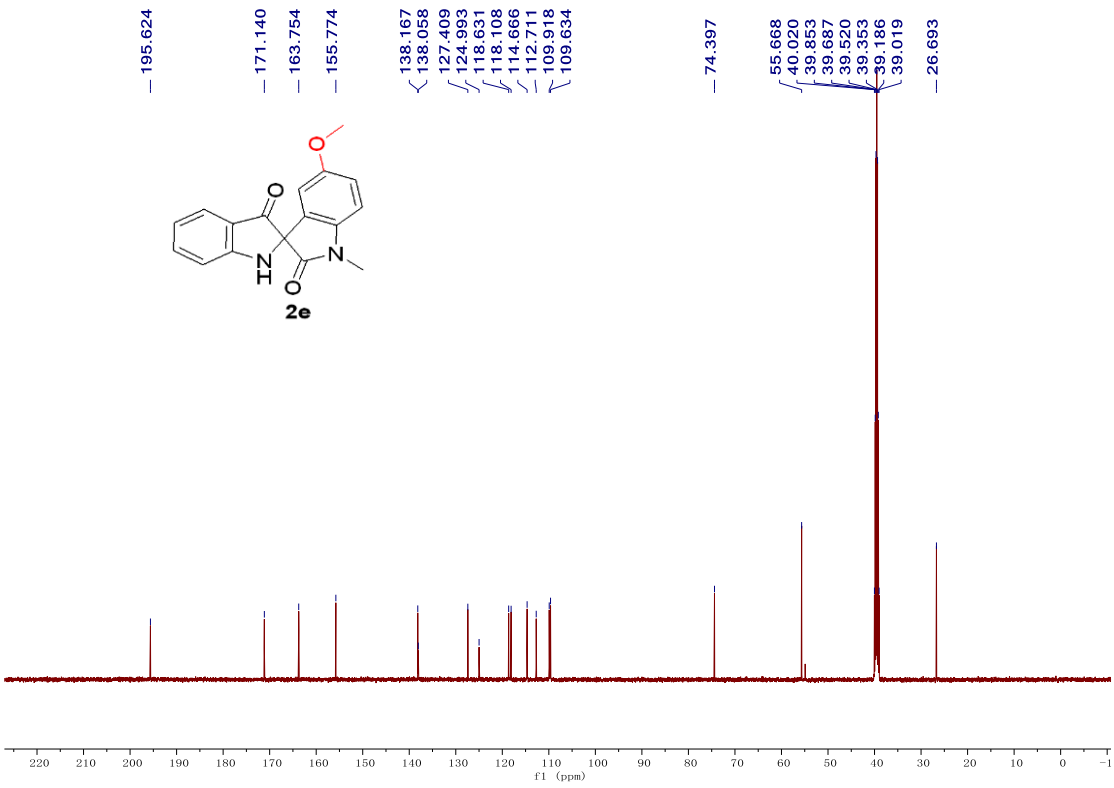
^{13}C NMR (150 MHz, d^{6}-DMSO)



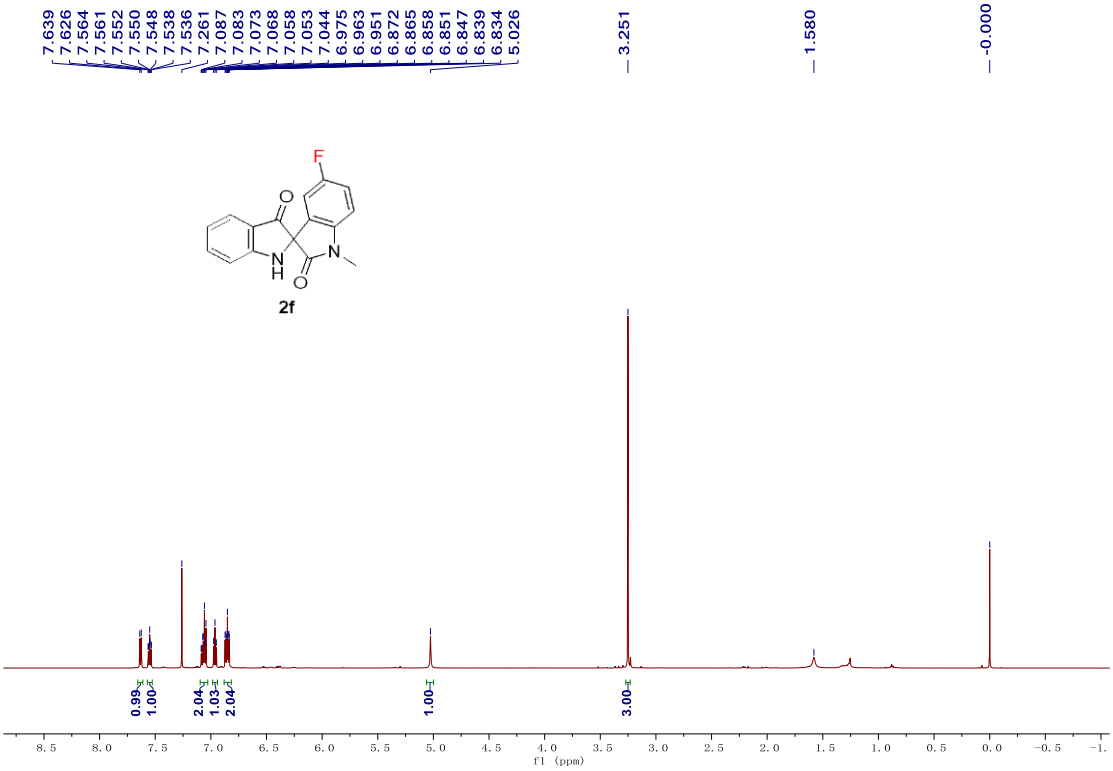
^{1}H NMR (500 MHz, d^{6}-DMSO)



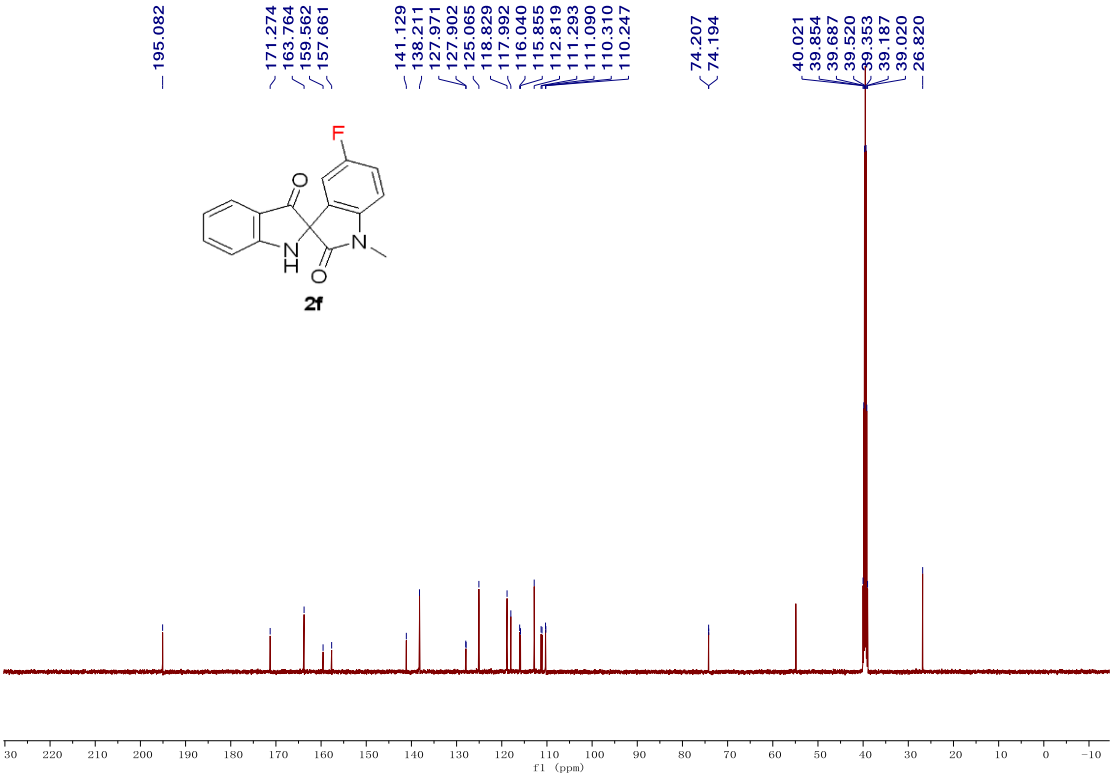
^{13}C NMR (125 MHz, d^{6}-DMSO)



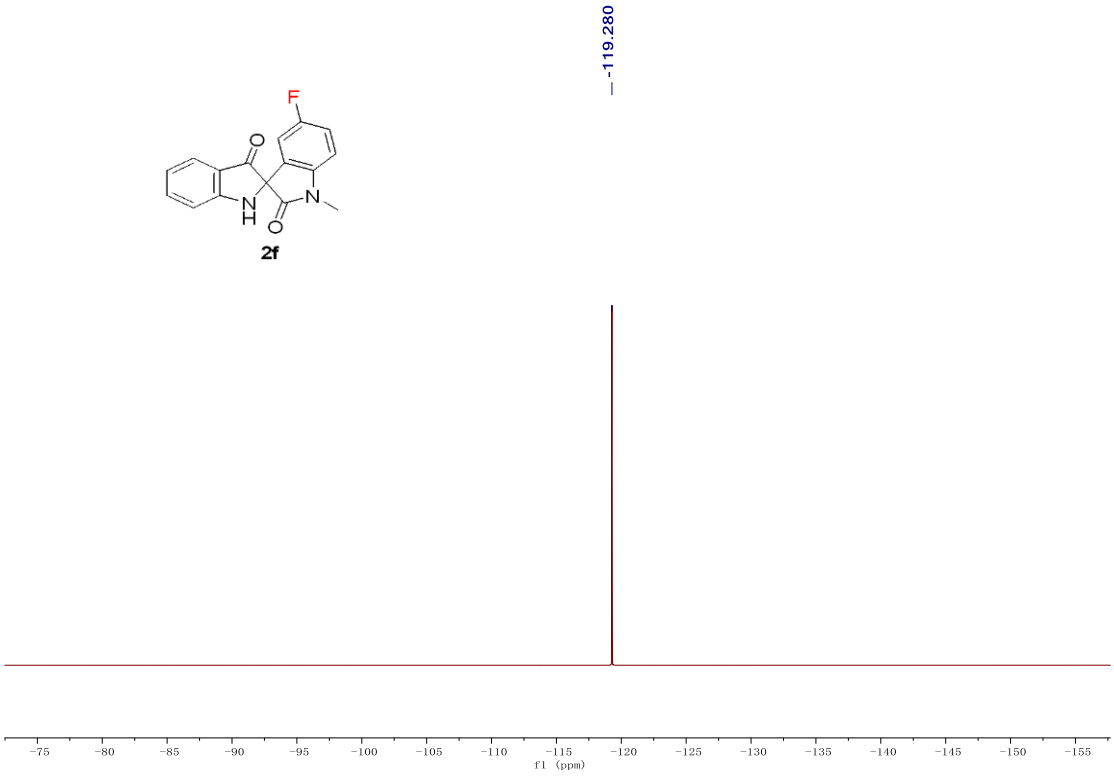
^{1}H NMR (600 MHz, $CDCl_3$)



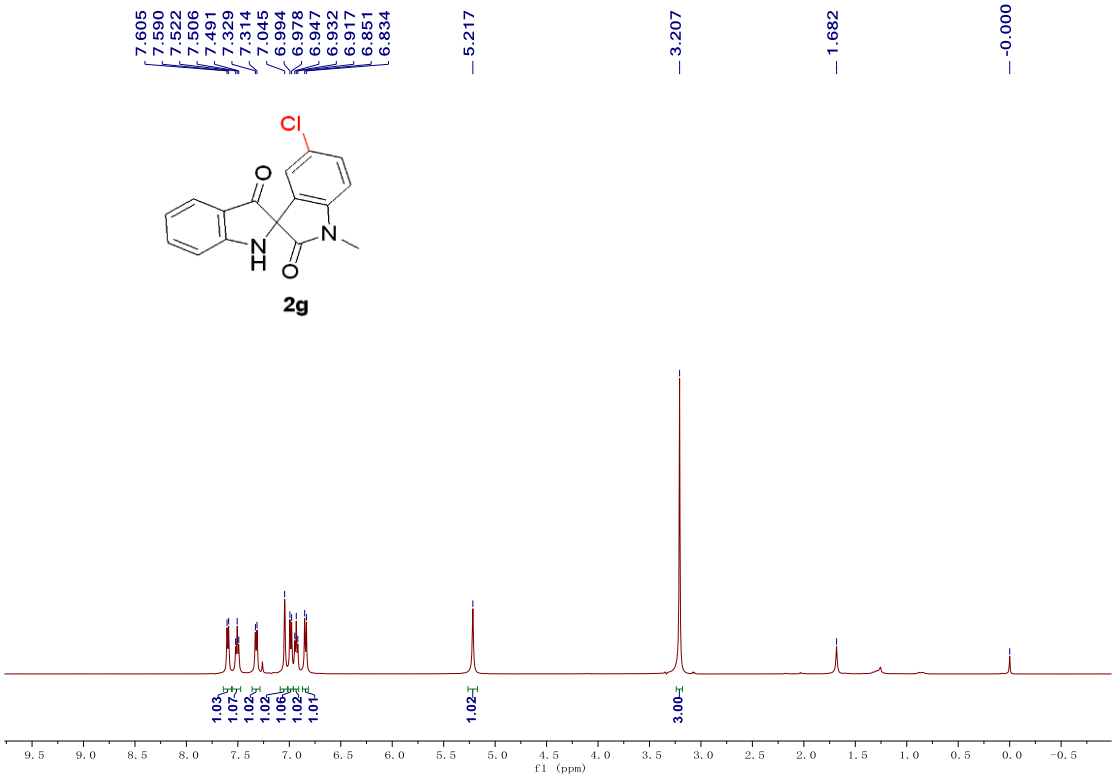
^{13}C NMR (125 MHz, d^6-DMSO)



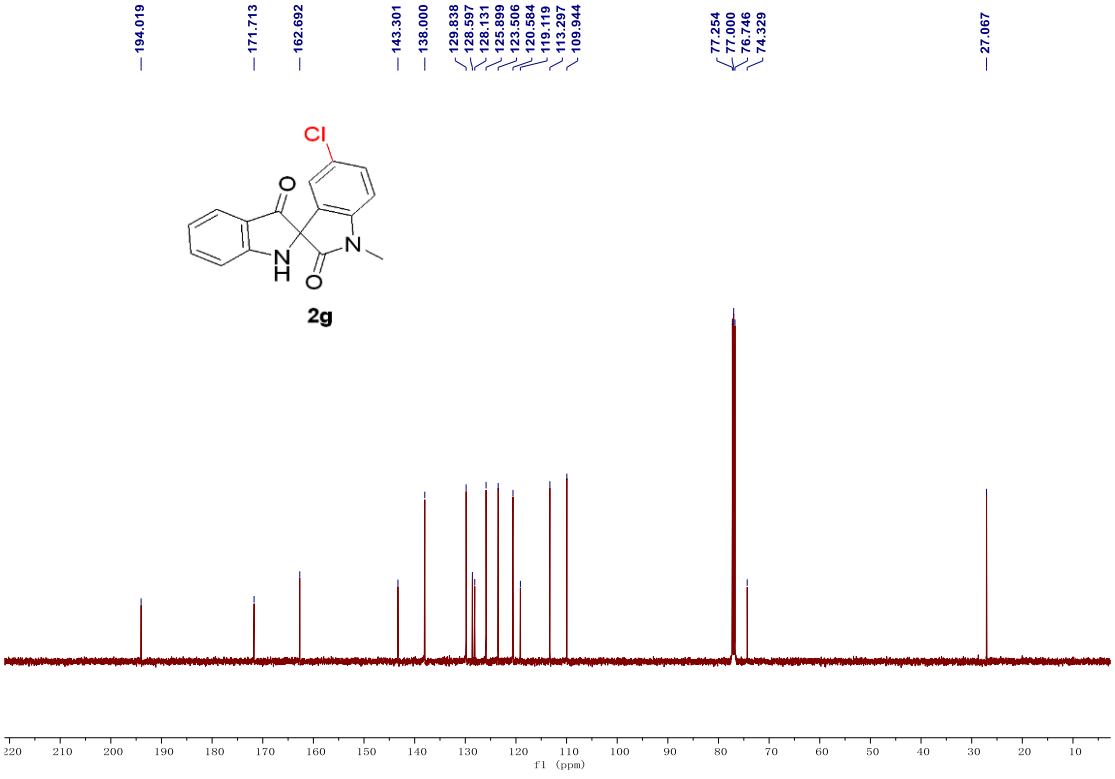
^{19}F NMR (470 MHz, $CDCl_3$)



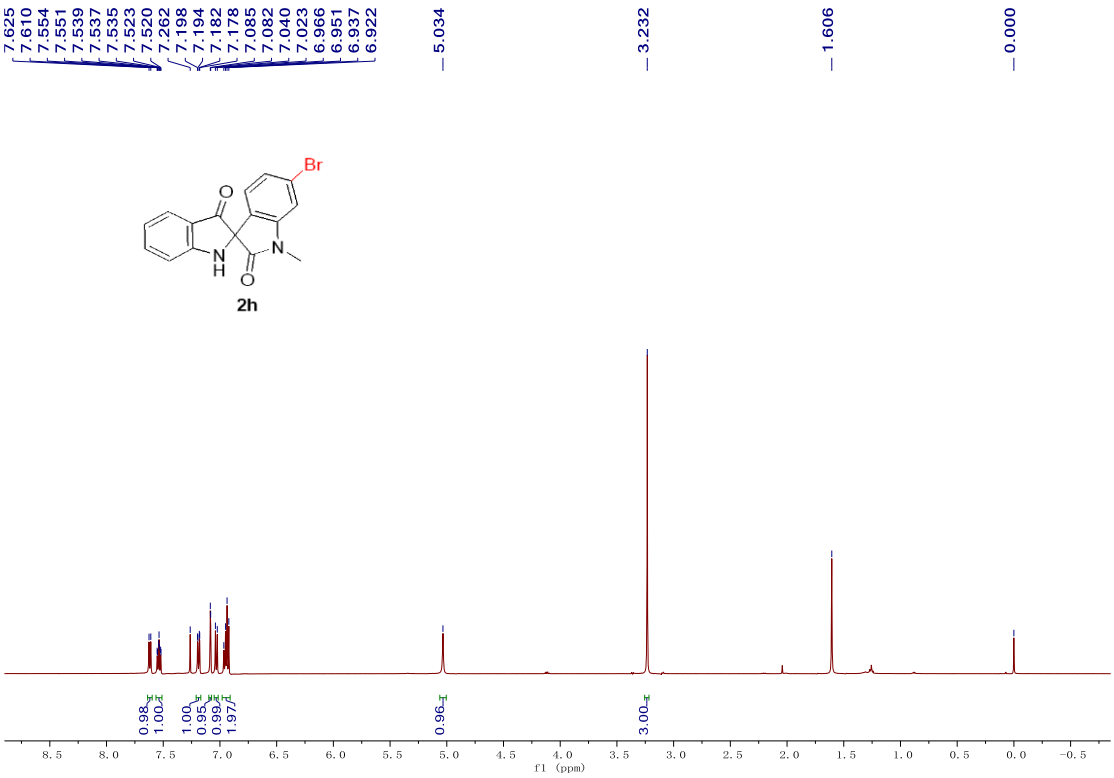
^{1}H NMR (500 MHz, $CDCl_3$)



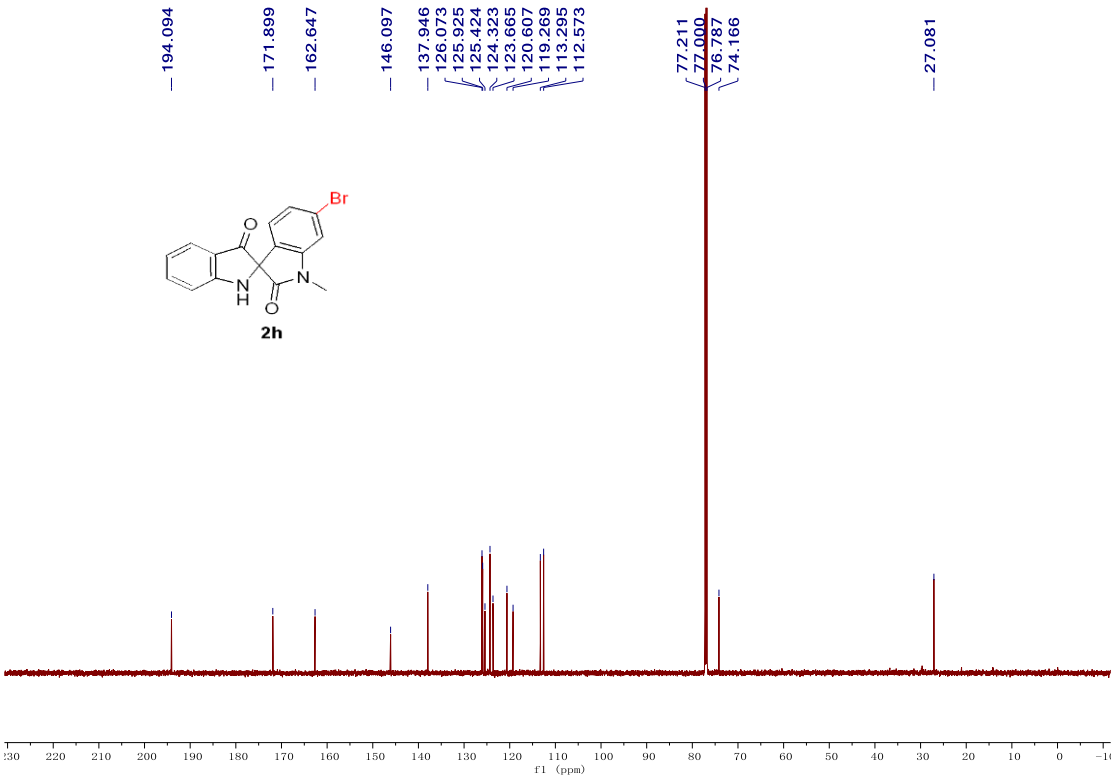
^{13}C NMR (125 MHz, $CDCl_3$)



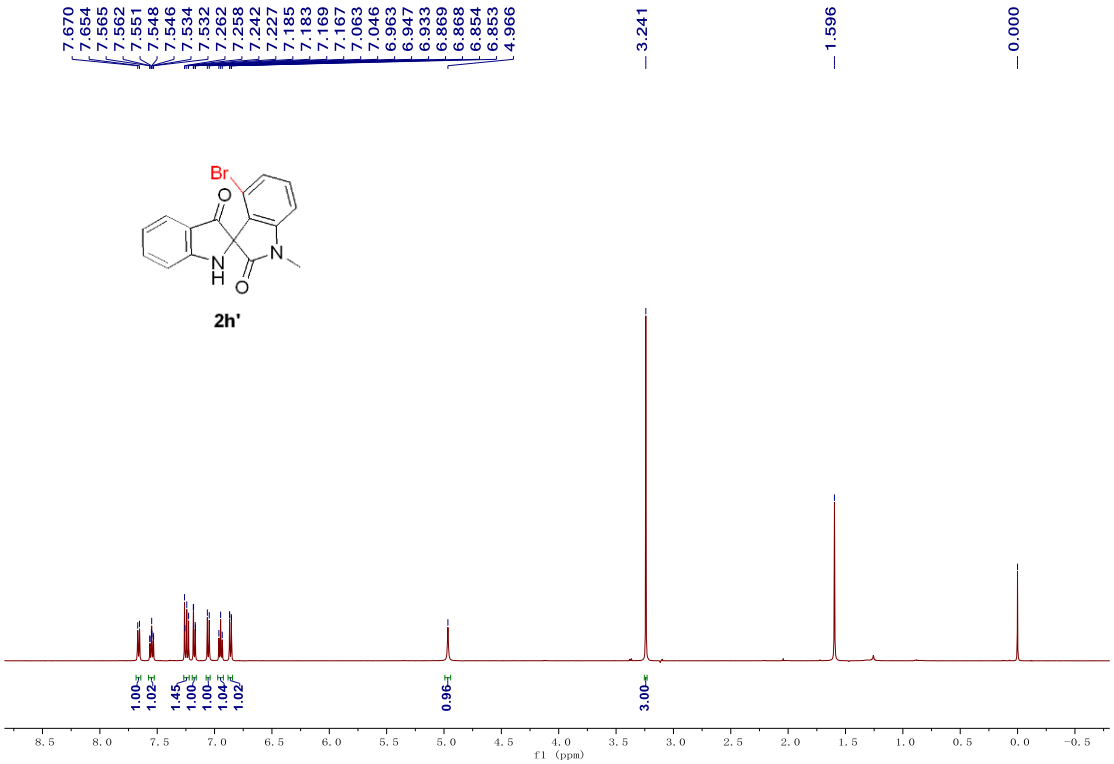
^{1}H NMR (500 MHz, $CDCl_3$)



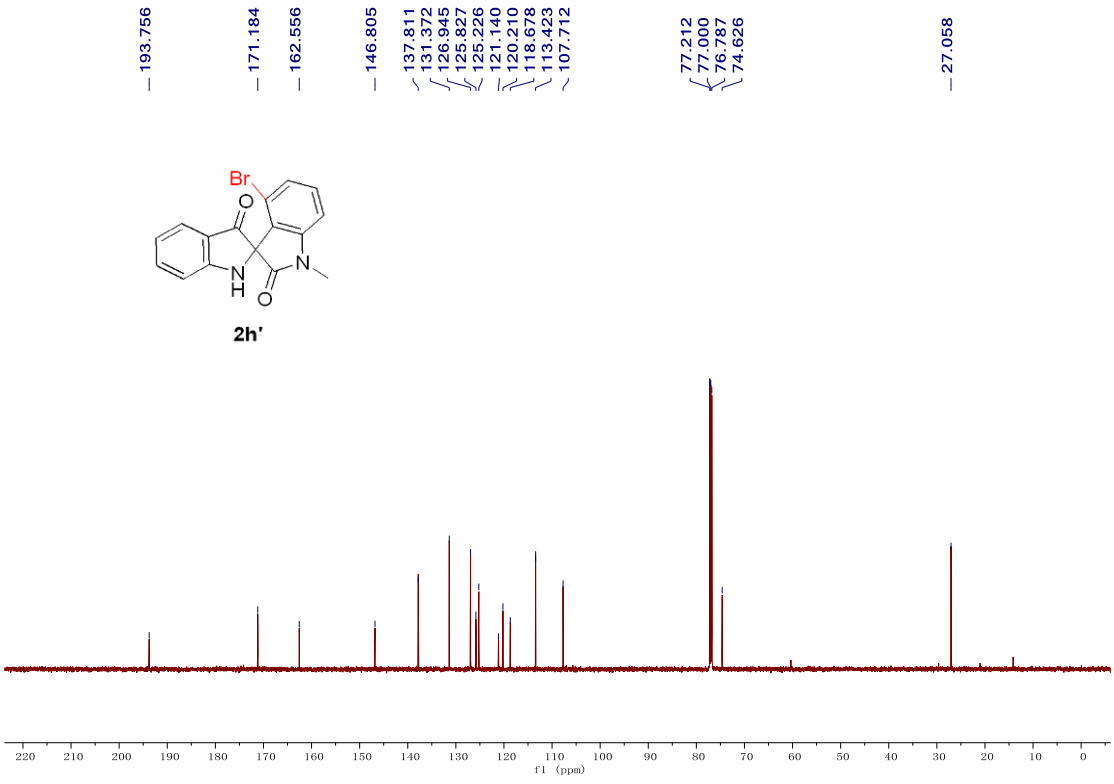
^{13}C NMR (125 MHz, $CDCl_3$)



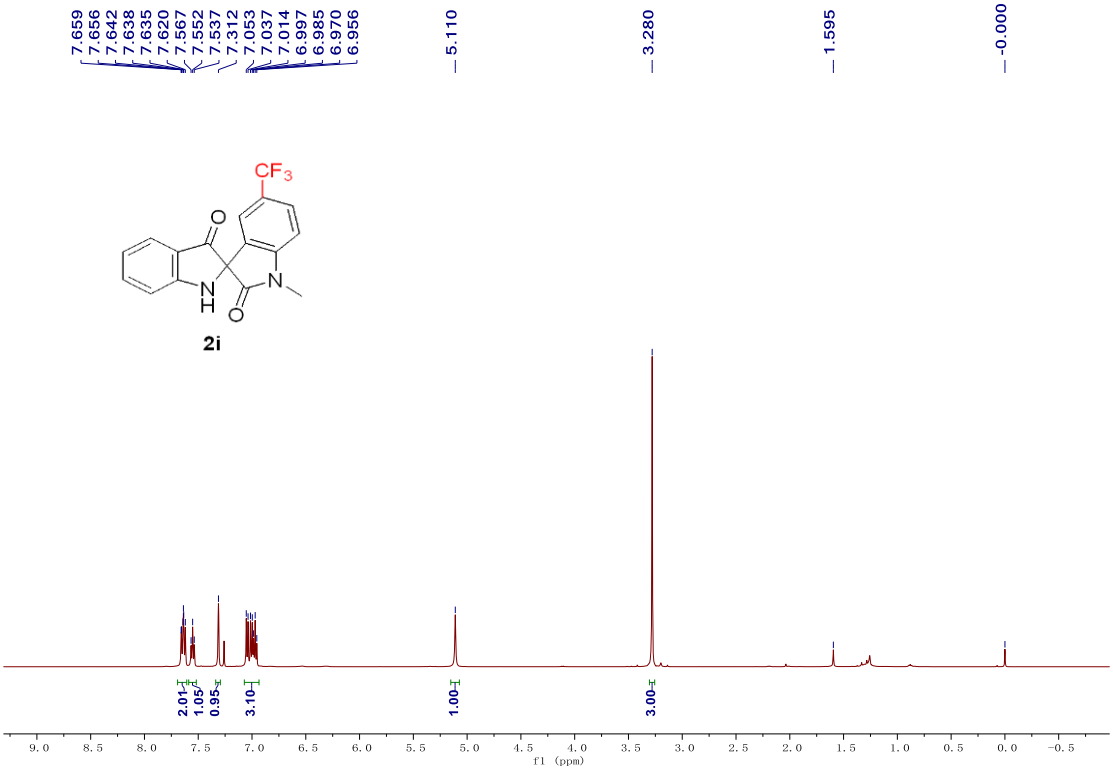
^{1}H NMR (500 MHz, $CDCl_3$)



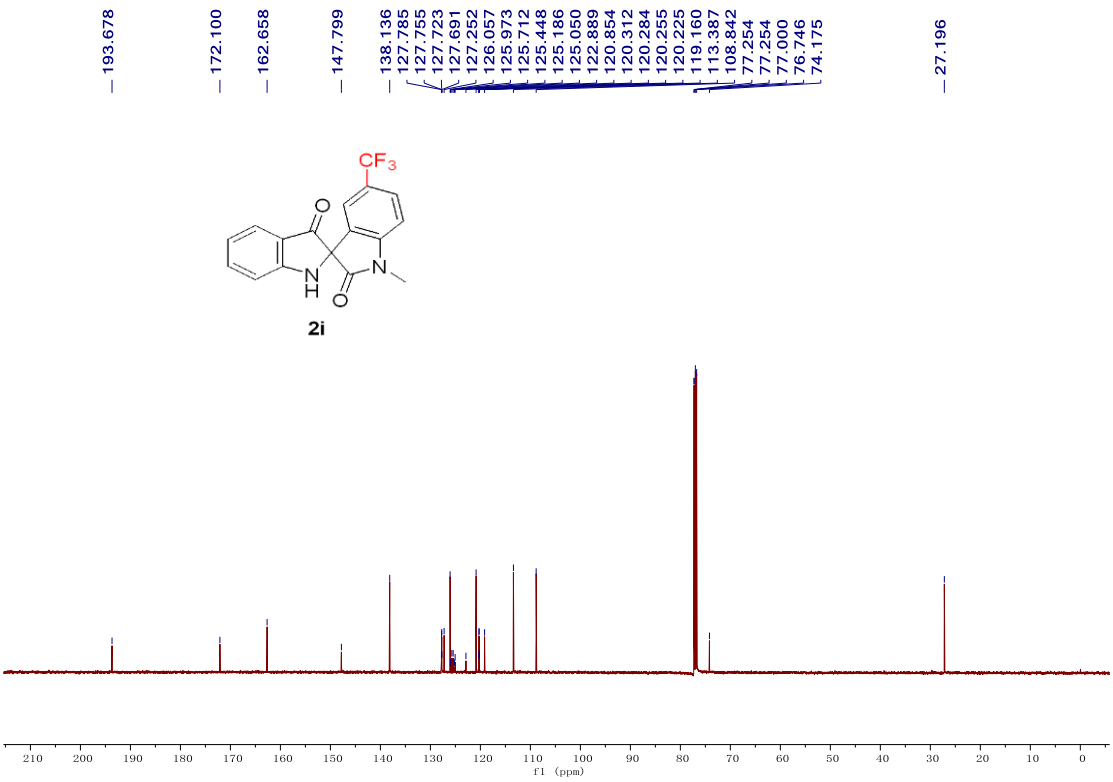
^{13}C NMR (125 MHz, $CDCl_3$)



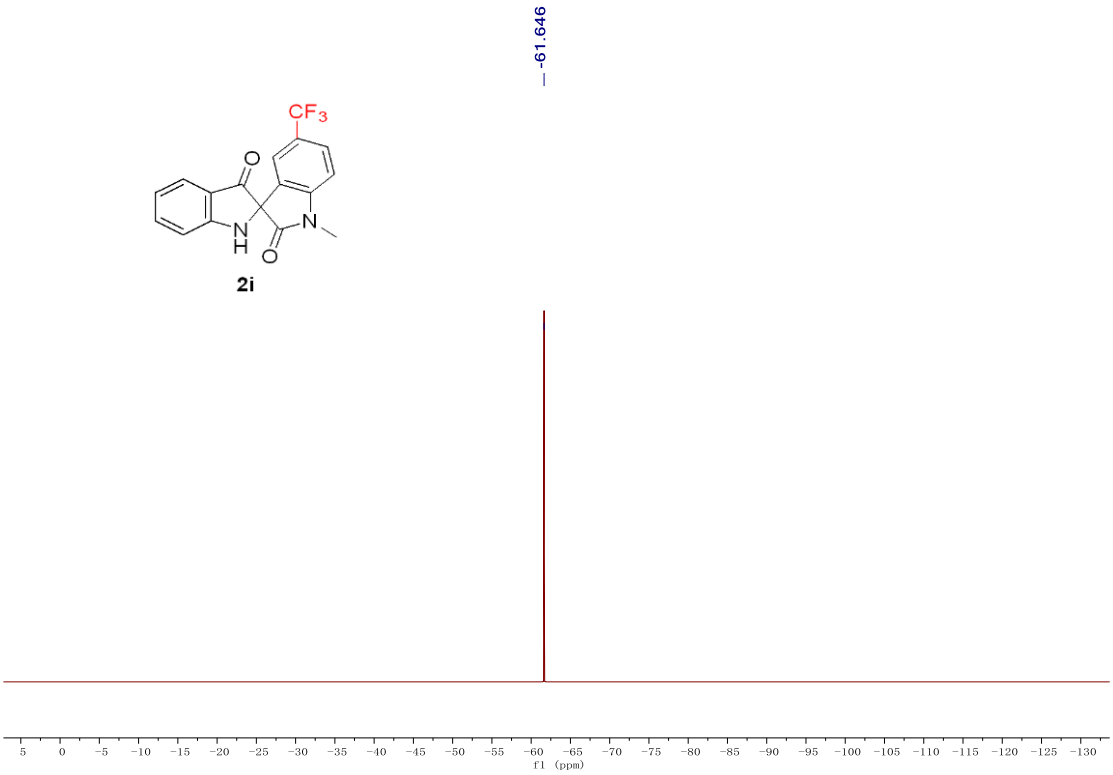
H NMR (500 MHz, $CDCl_3$)



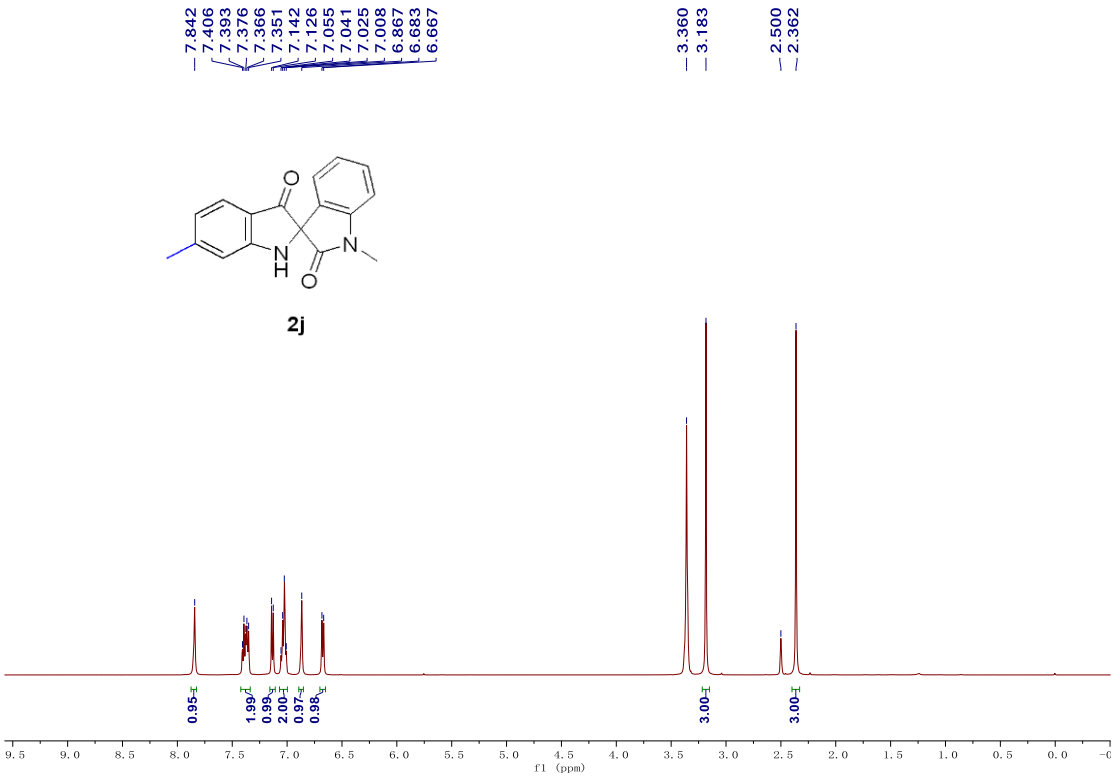
^{13}C NMR (125 MHz, $CDCl_3$)



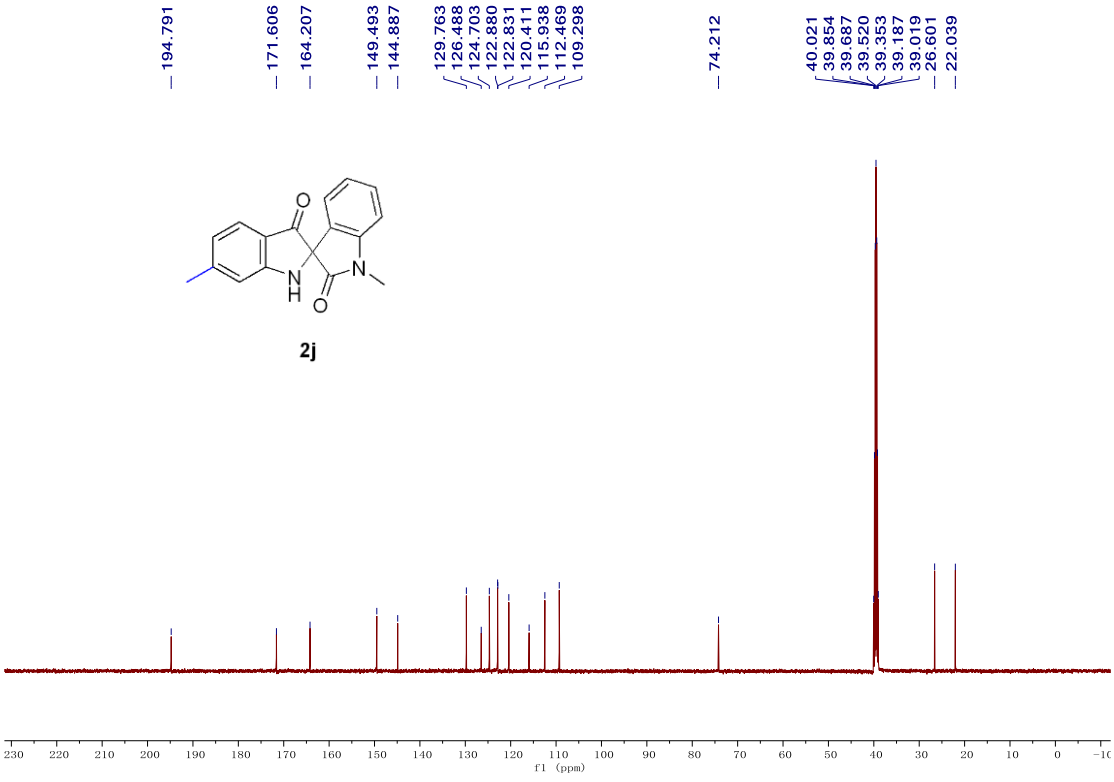
^{19}F NMR (470 MHz, $CDCl_3$)



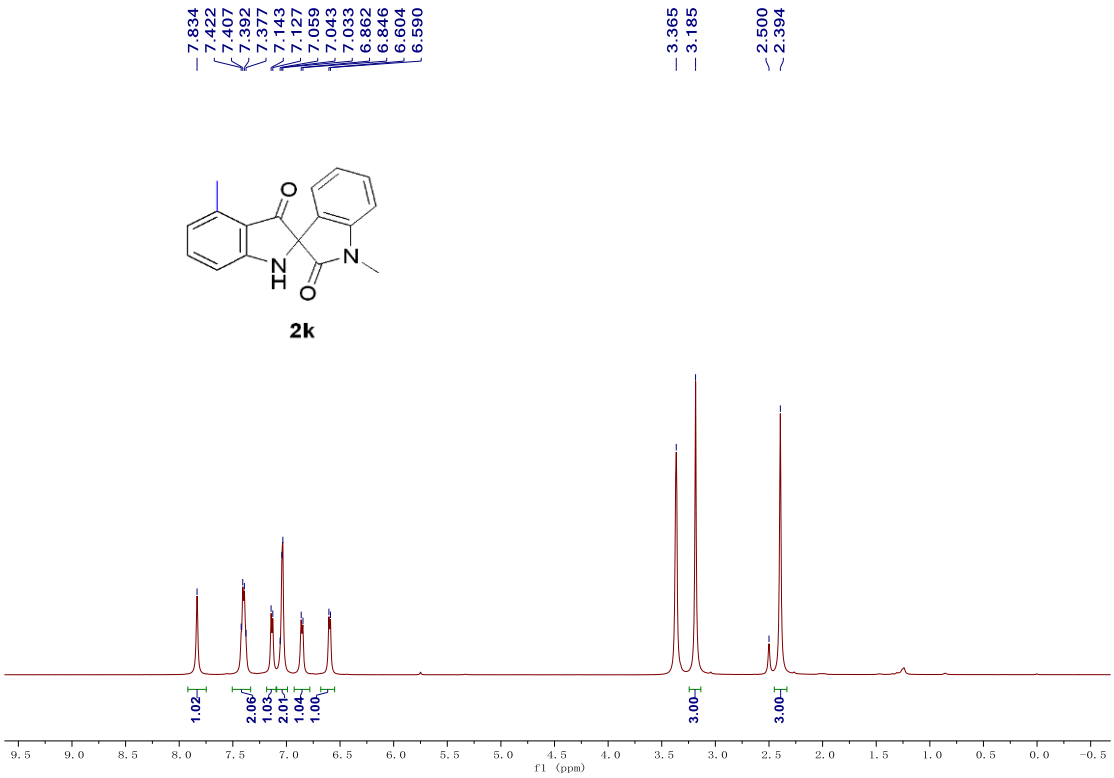
^{1}H NMR (500 MHz, d^{6}-DMSO)



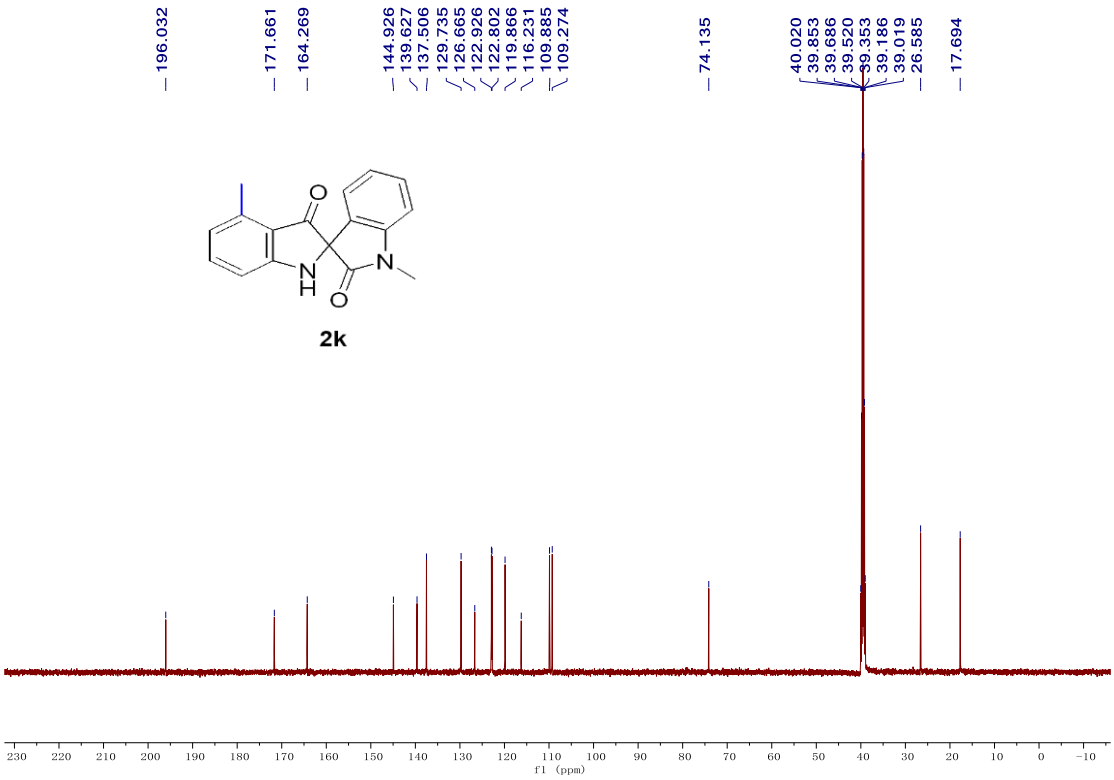
^{13}C NMR (125 MHz, d^{6}-DMSO)



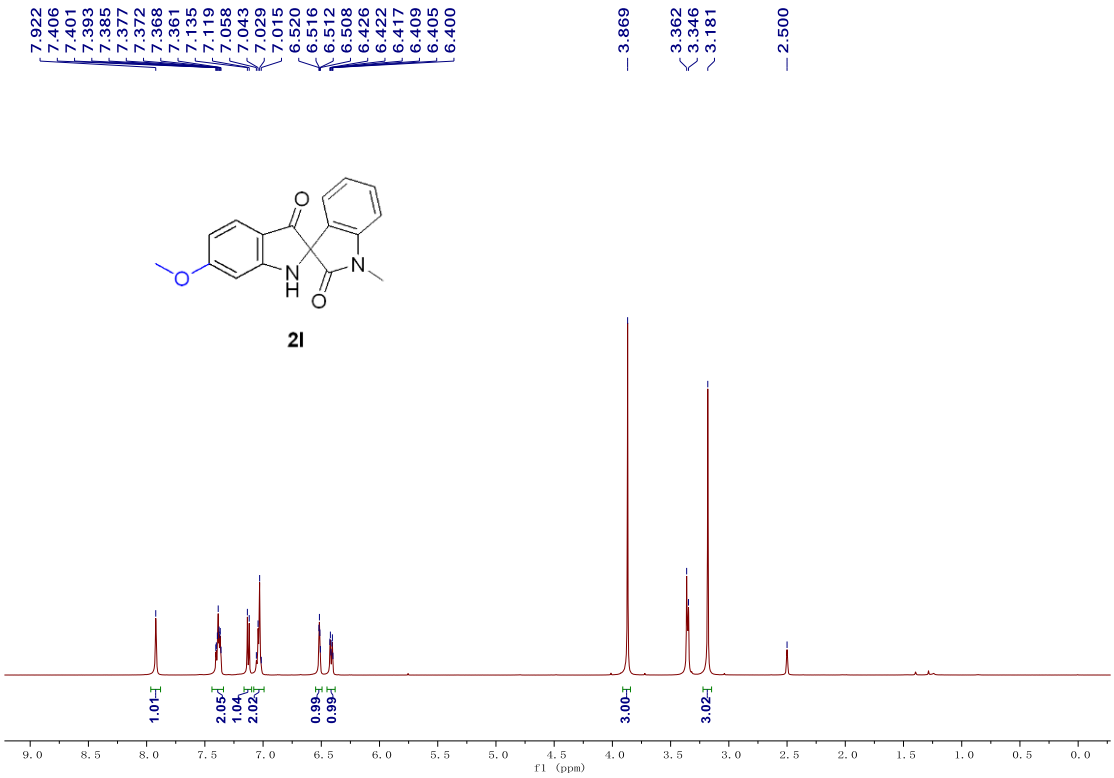
^{1}H NMR (500 MHz, d^{6}-DMSO)



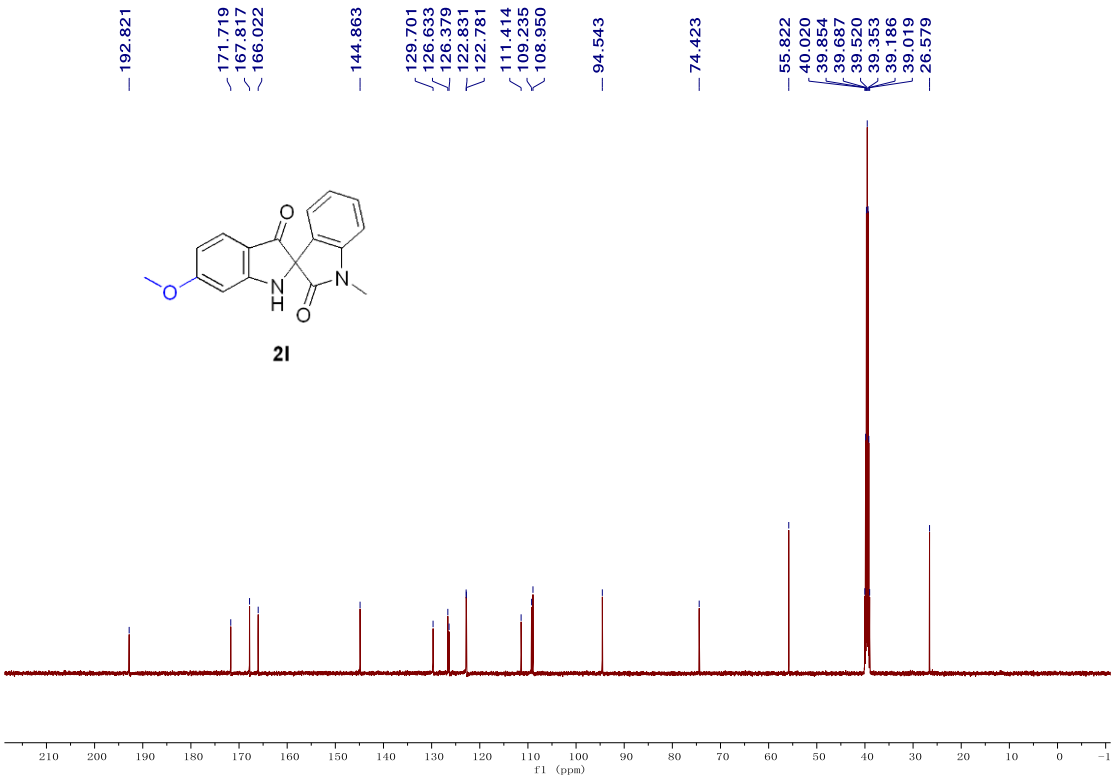
^{13}C NMR (125 MHz, d^{6}-DMSO)



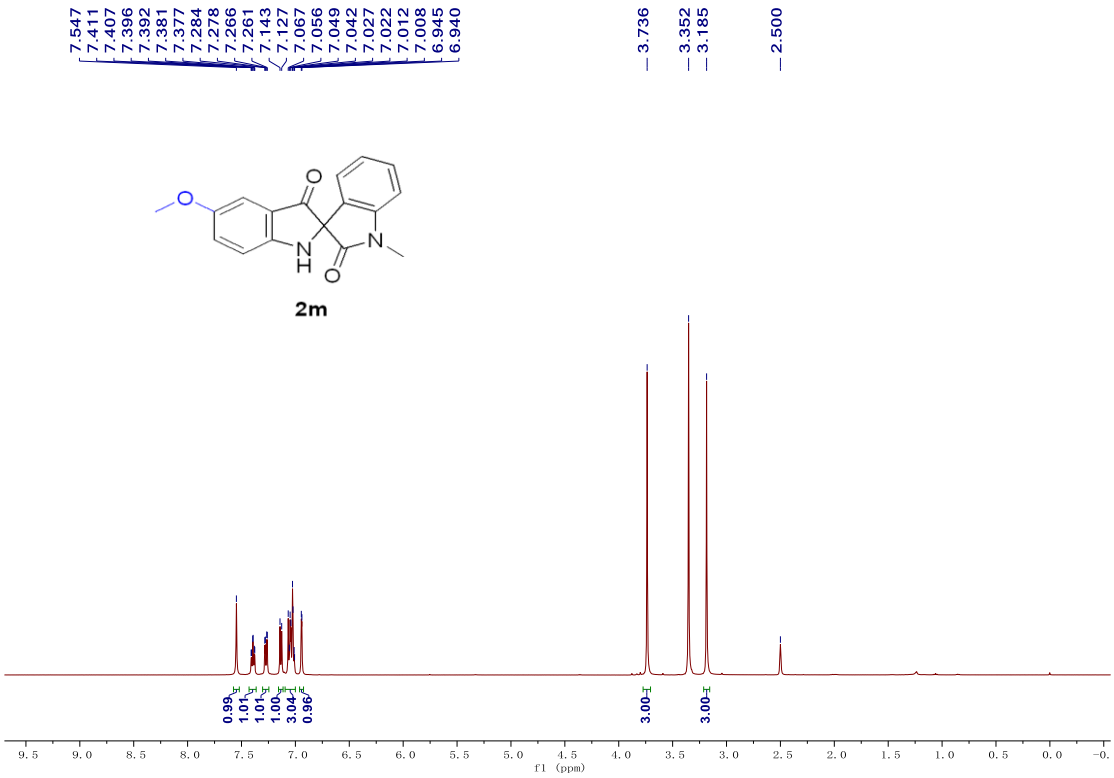
^{1}H NMR (500 MHz, d^{6}-DMSO)



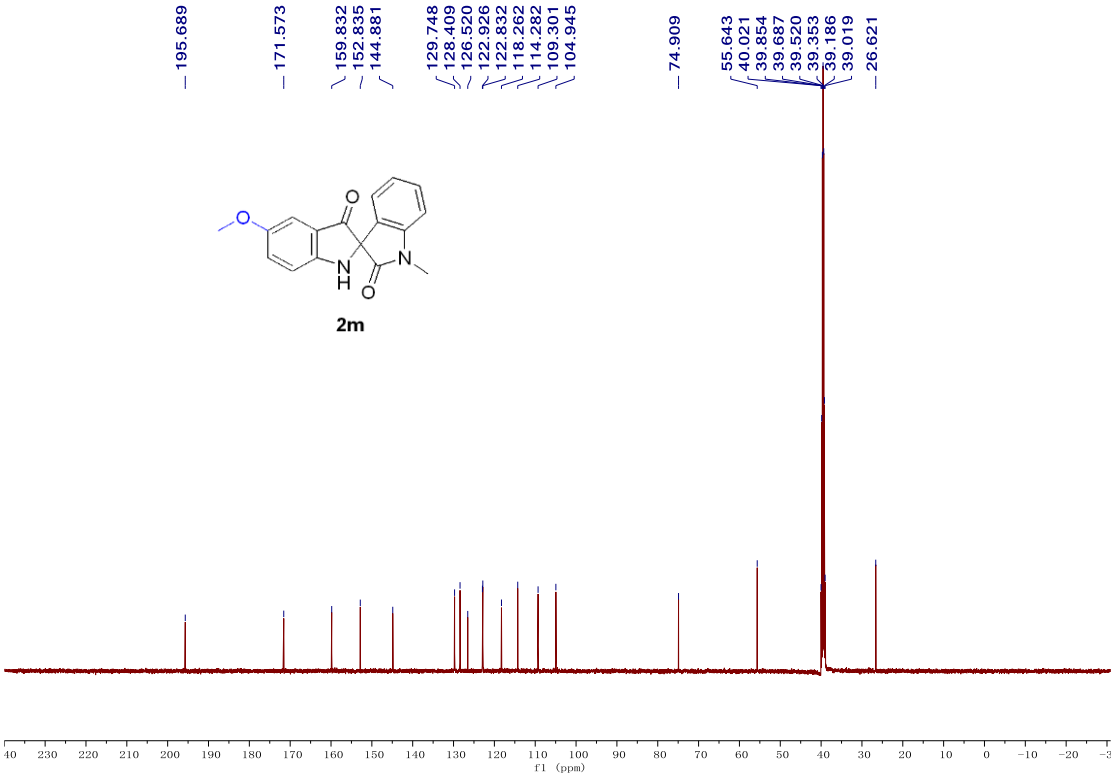
^{13}C NMR (125 MHz, d^{6}-DMSO)



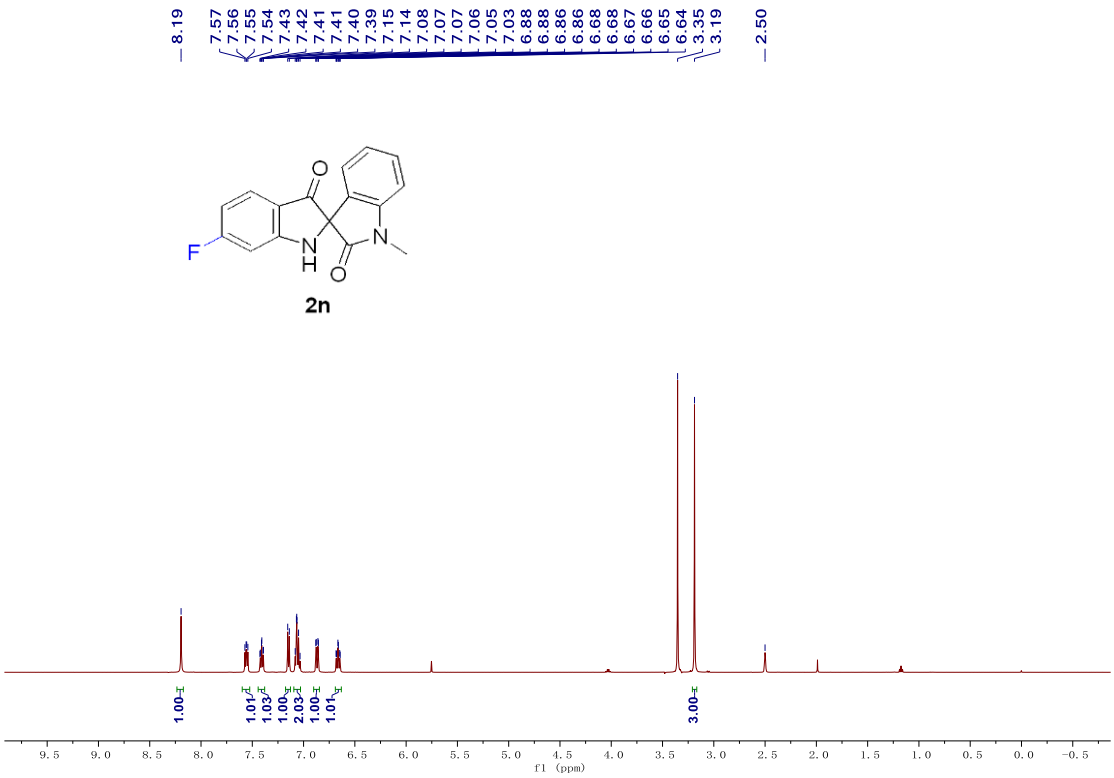
^{1}H NMR (500 MHz, d^{6}-DMSO)



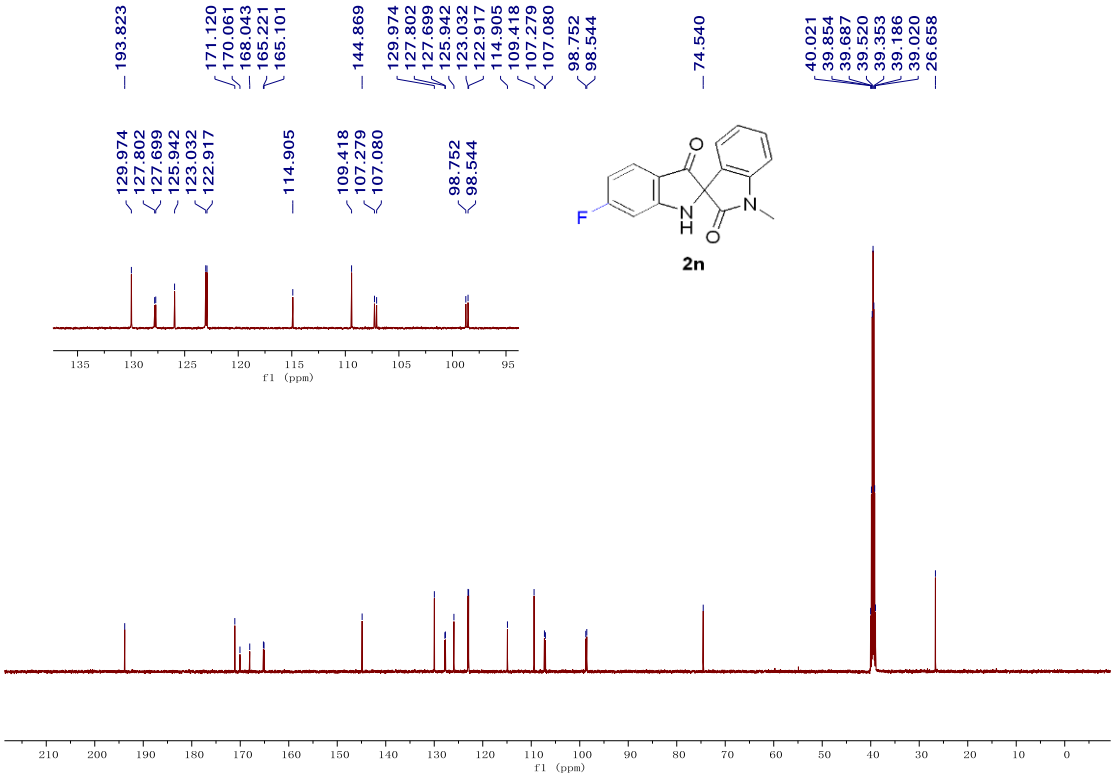
^{13}C NMR (125 MHz, d^{6}-DMSO)



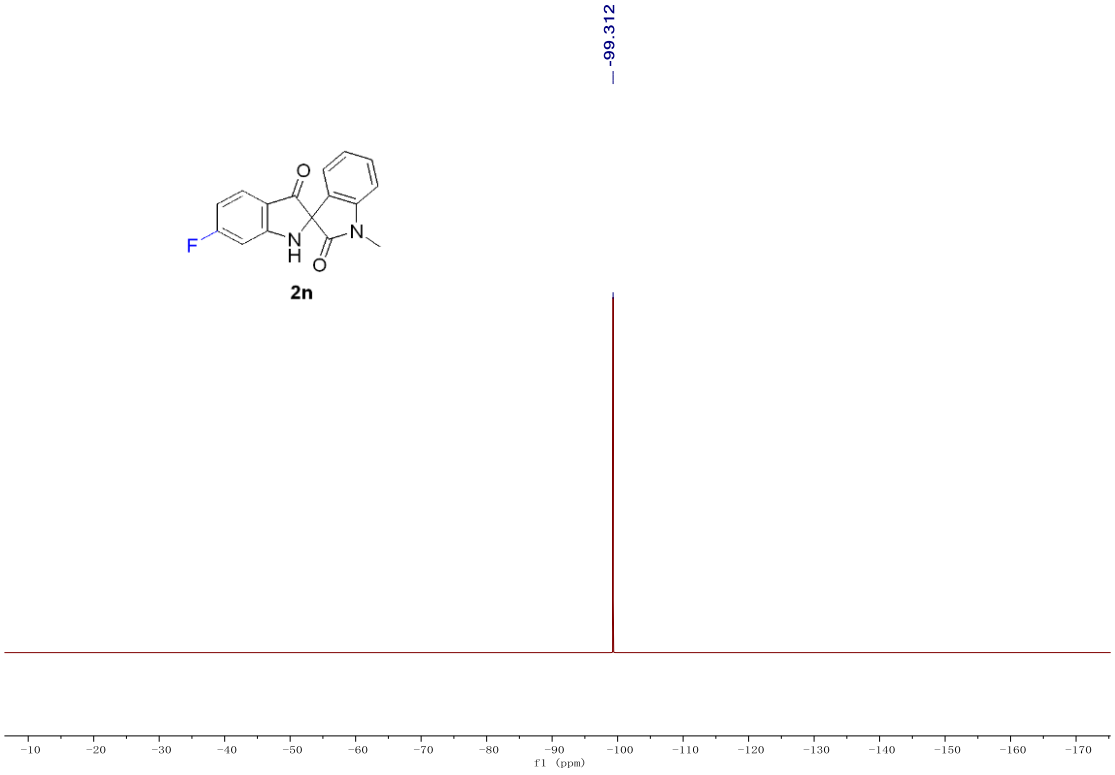
^{1}H NMR (500 MHz, d^{6}-DMSO)



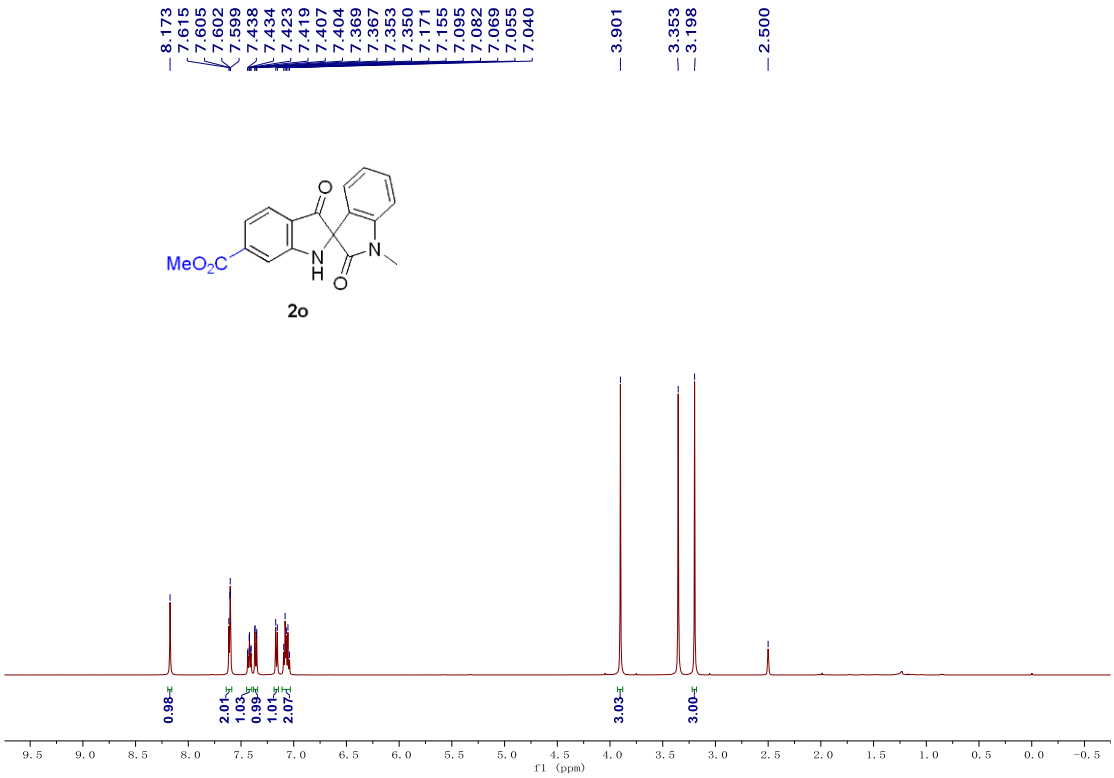
^{13}C NMR (125 MHz, d^{6}-DMSO)



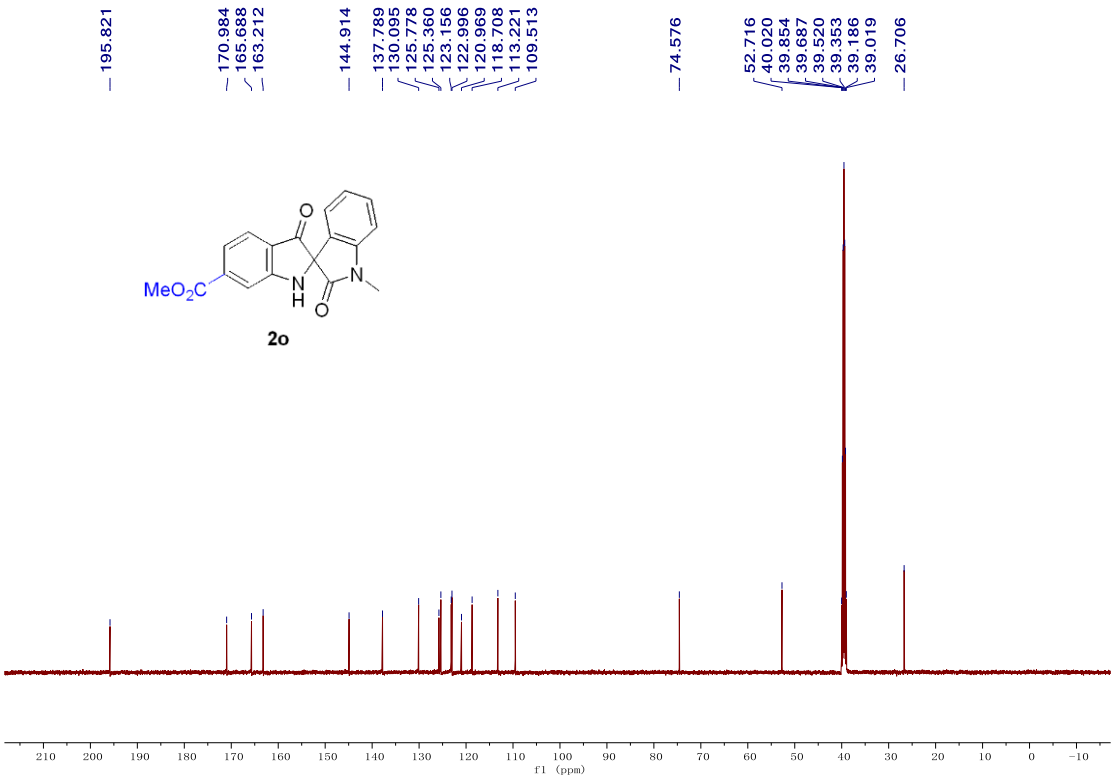
^{19}F NMR (470 MHz, d^{6}-DMSO)



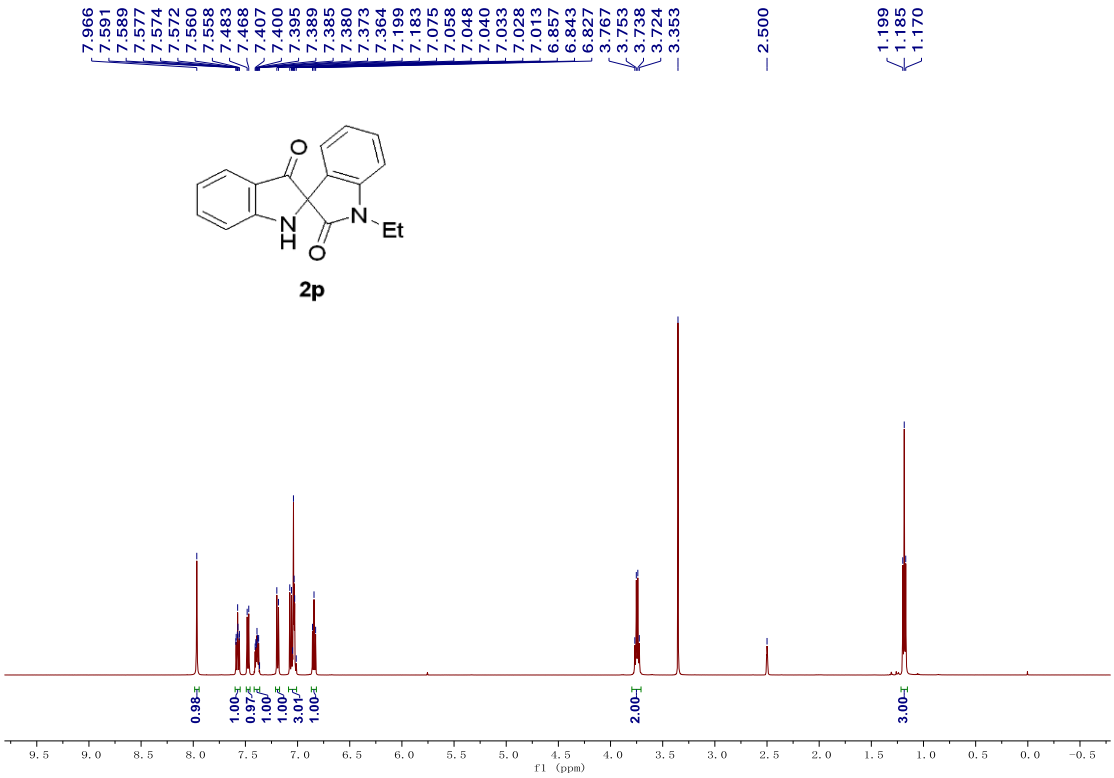
^{1}H NMR (500 MHz, d^{6}-DMSO)



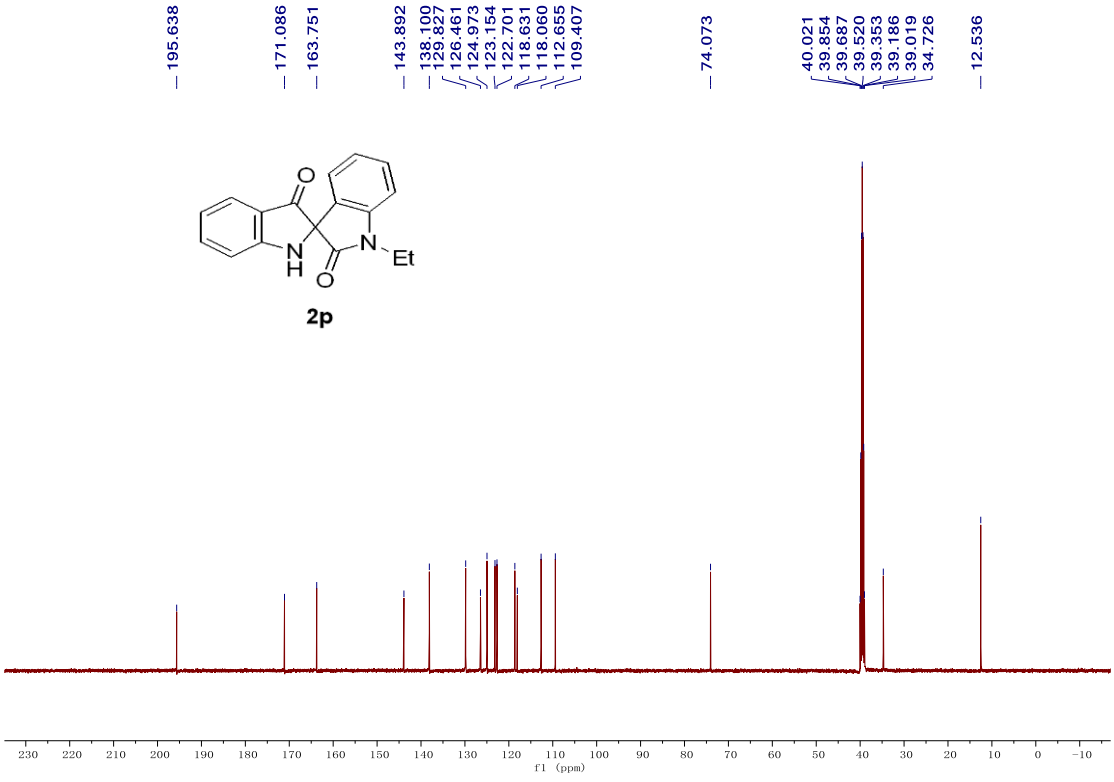
^{13}C NMR (125 MHz, d^{6}-DMSO)



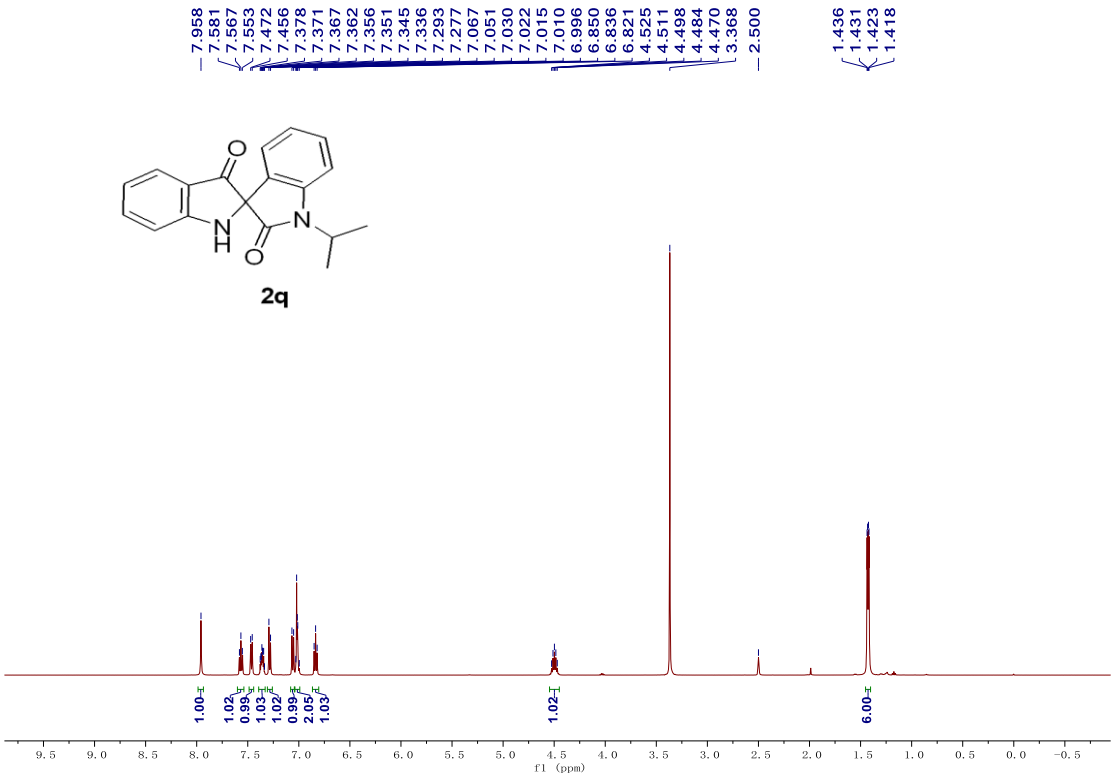
^{1}H NMR (500 MHz, d^{6}-DMSO)



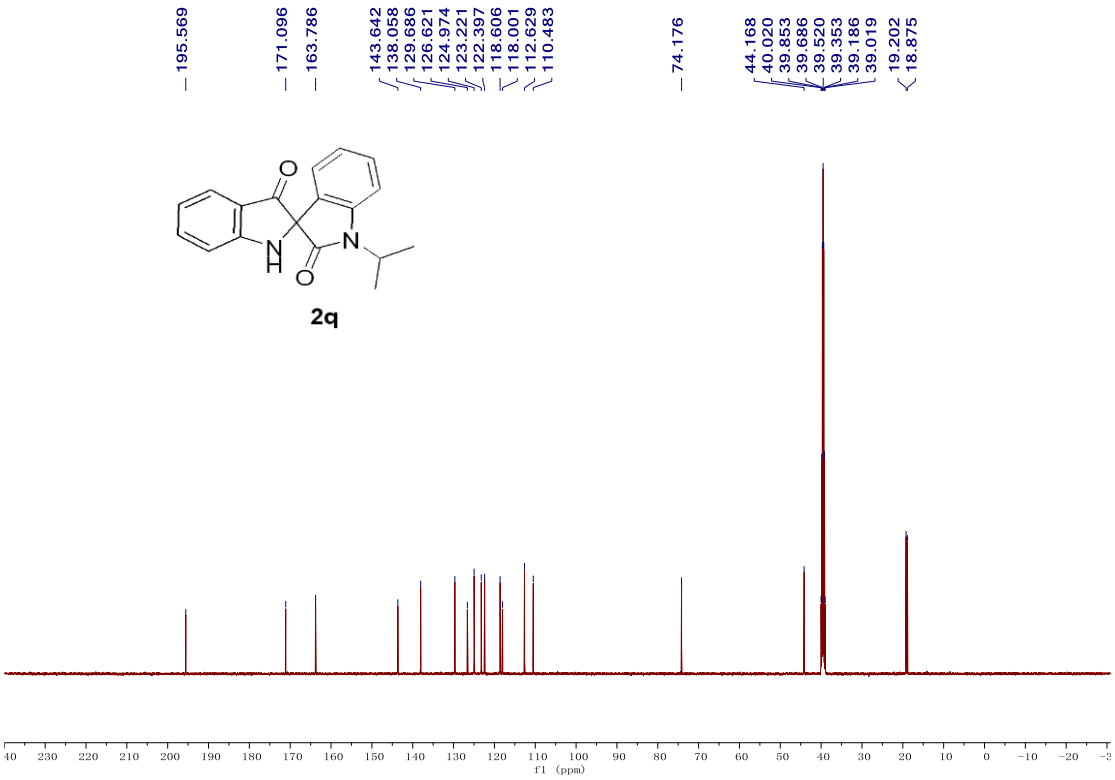
^{13}C NMR (125 MHz, d^{6}-DMSO)



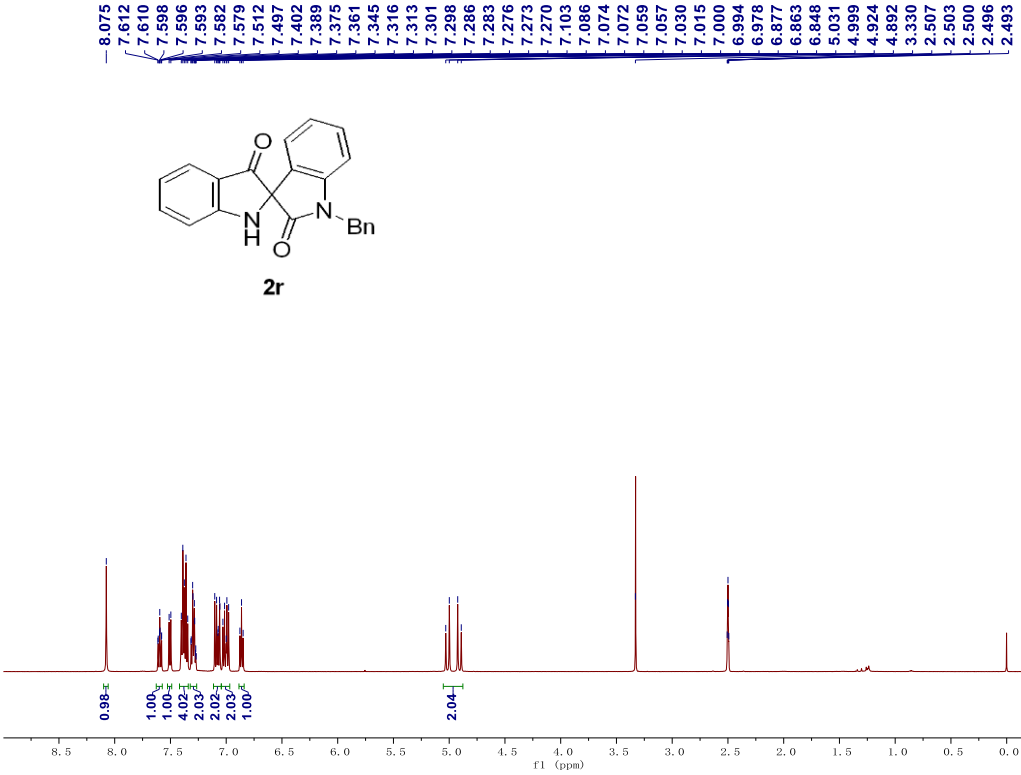
H NMR (500 MHz, d^6-DMSO)



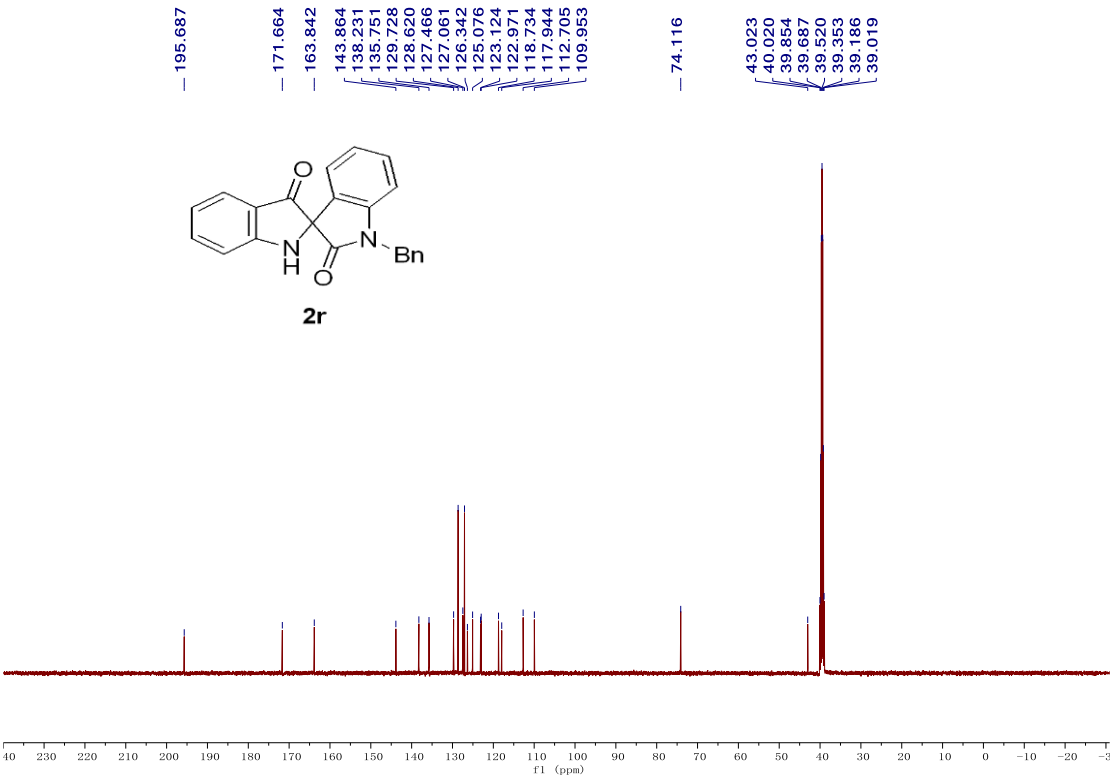
^{13}C NMR (125 MHz, d^6-DMSO)



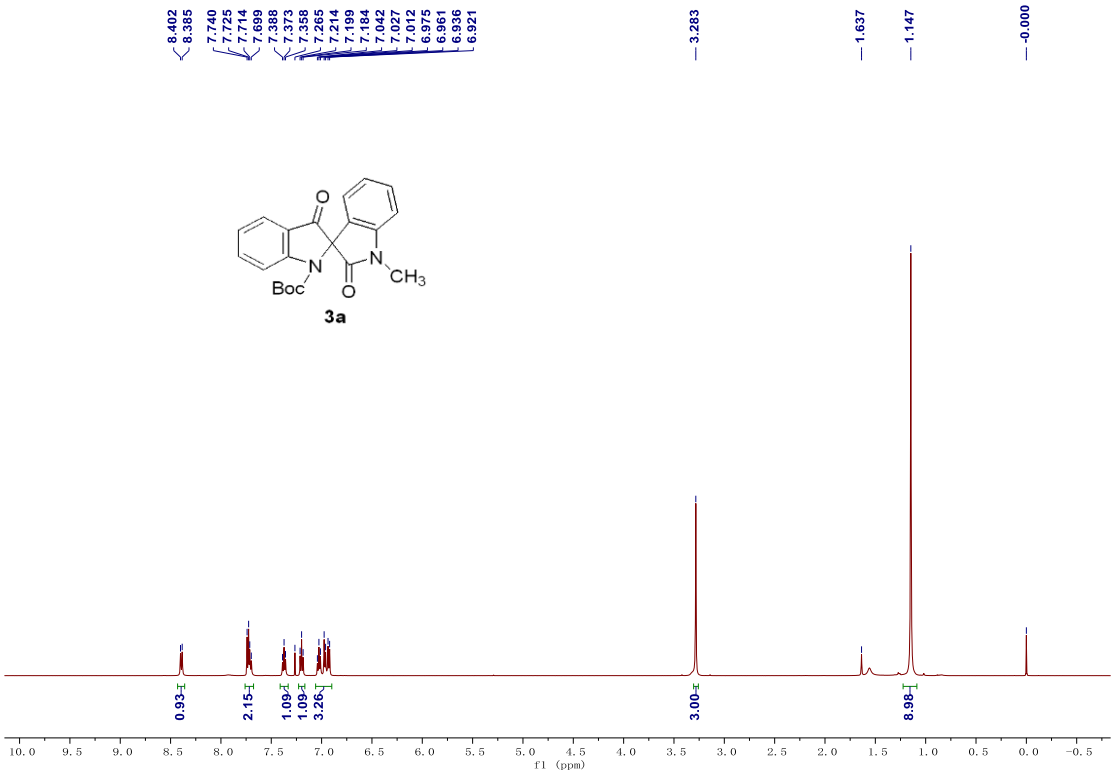
^{1}H NMR (500 MHz, d^{6}-DMSO)



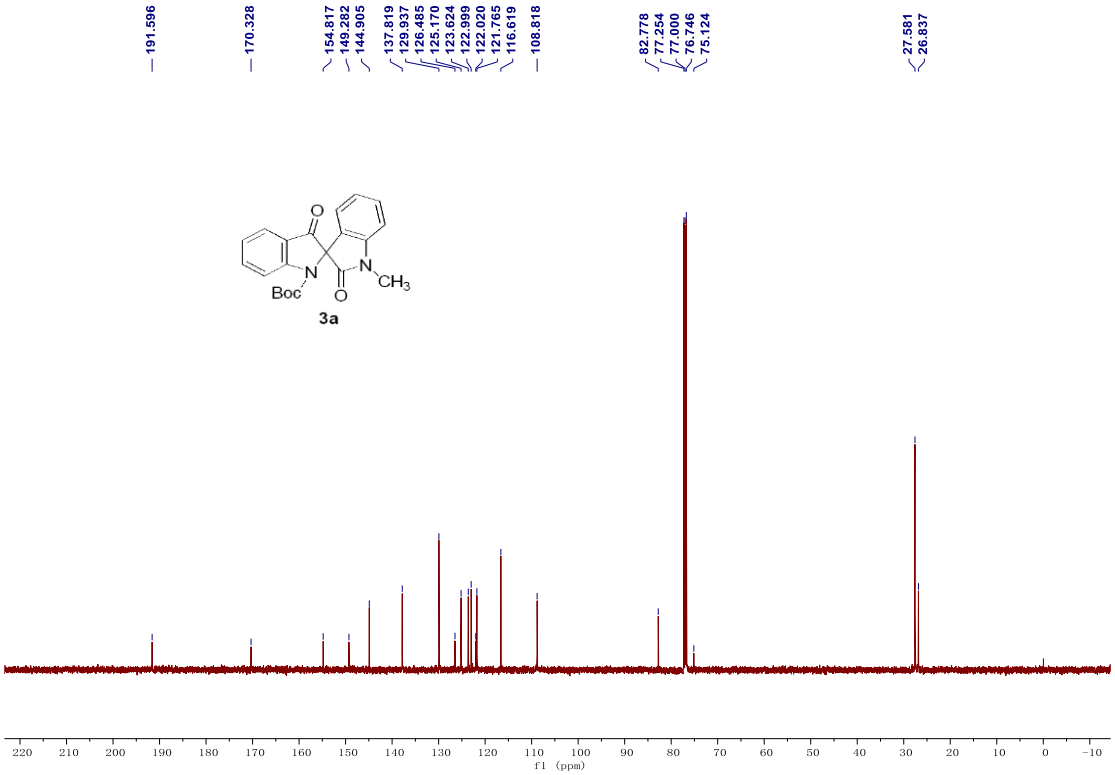
^{13}C NMR (125 MHz, d^{6}-DMSO)



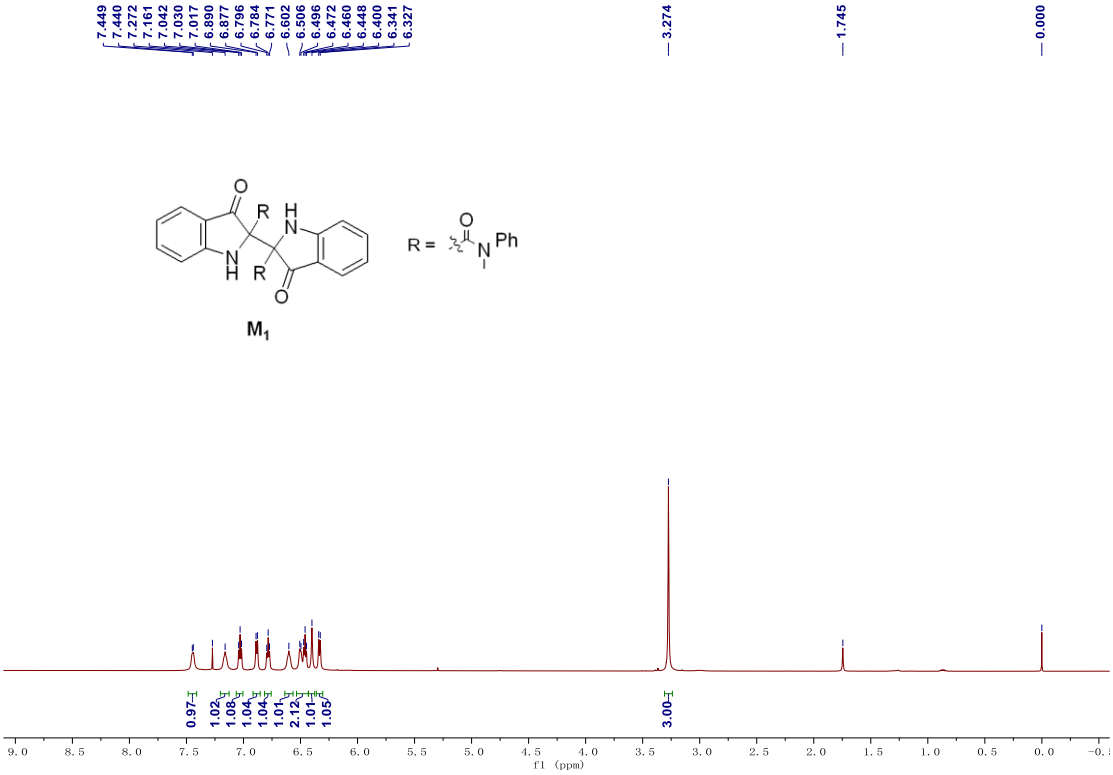
^{1}H NMR (500 MHz, $CDCl_3$)



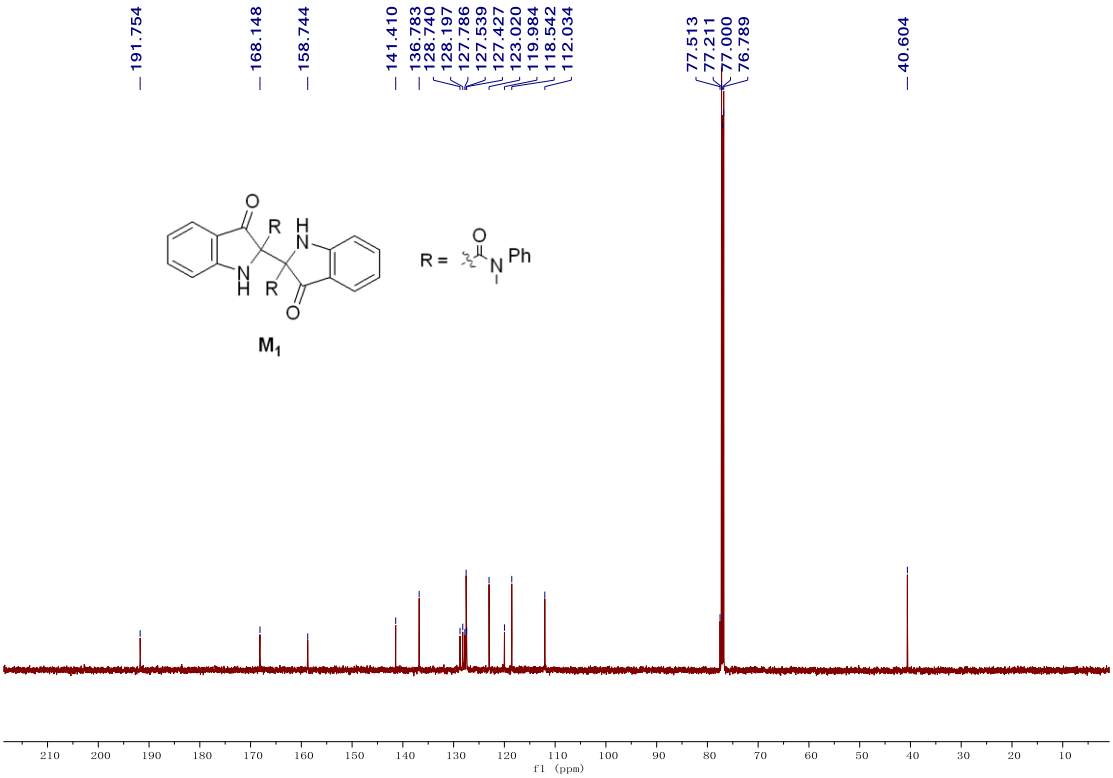
^{13}C NMR (500 MHz, $CDCl_3$)



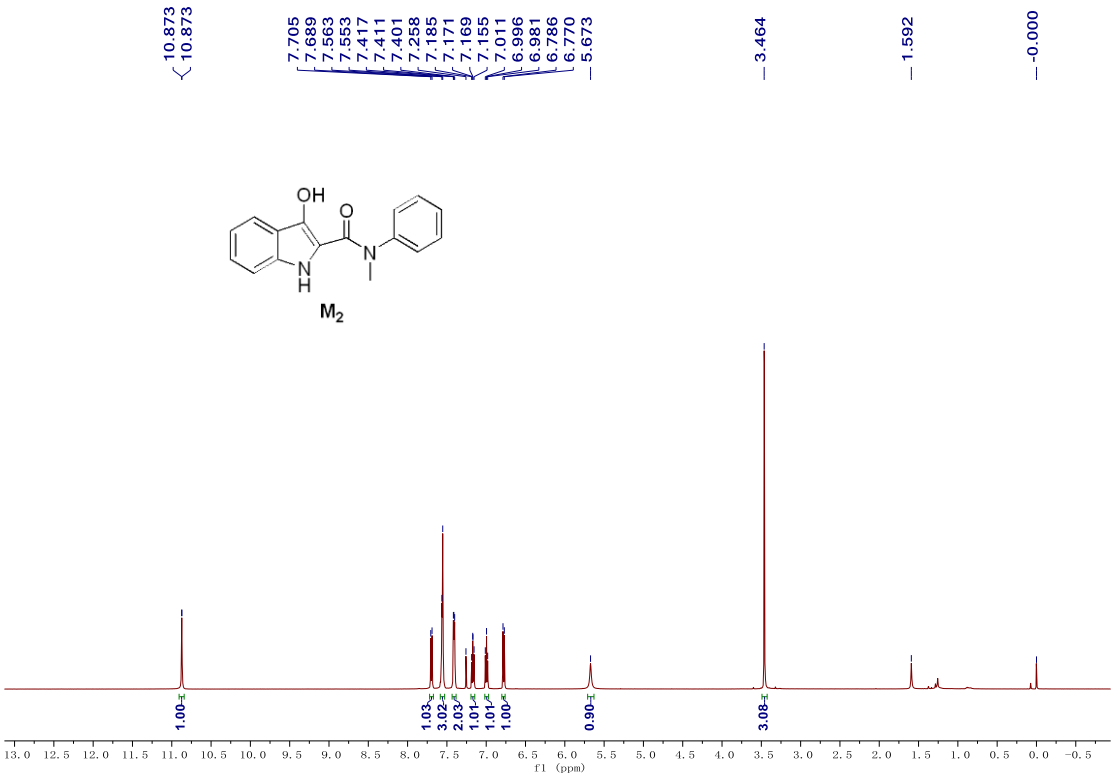
^{1}H NMR (500 MHz, $CDCl_3$)



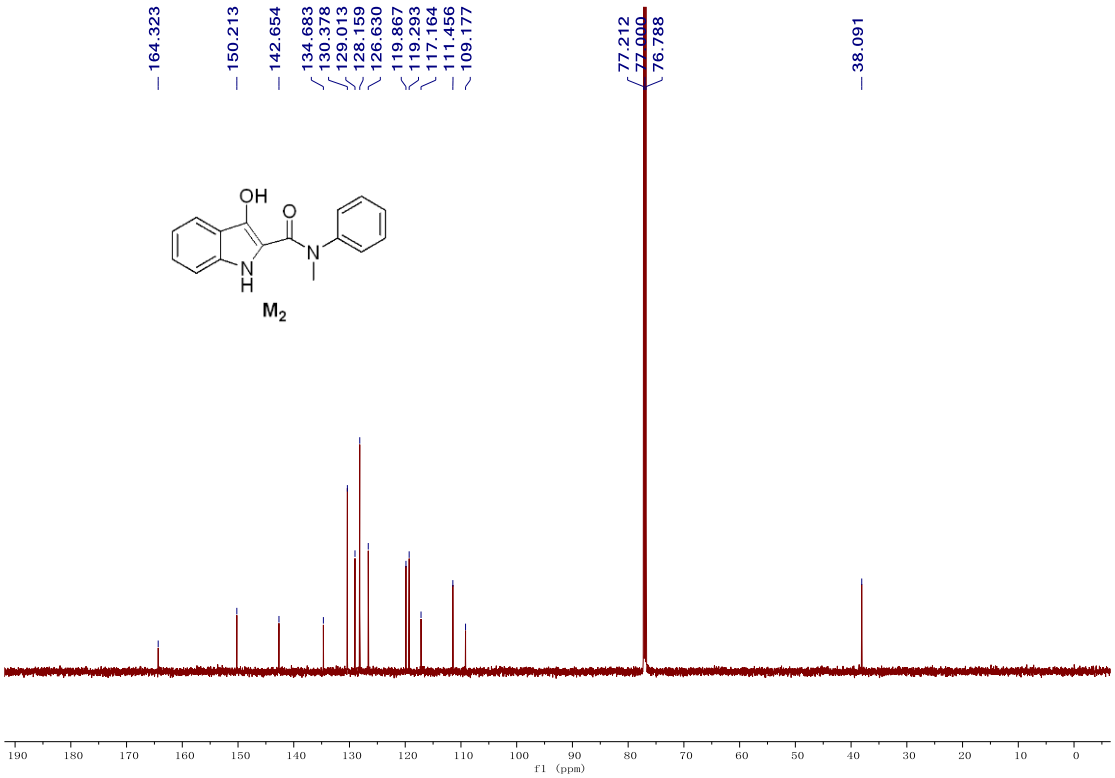
^{13}C NMR (500 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (500 MHz, $CDCl_3$)

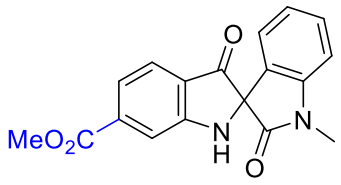


9.X-ray crystallography of compounds 2o, M_1 and M_2.

methyl 1'-methyl-2',3-dioxo-2,3'-spirobi[indoline]-6-carboxylate (**2o**, mo_d8v23354_0m.)

(Ortep ellipsoids are depicted at the 50% level)

Sample preparation for crystal growth: Compound **2o** (50 mg) was dissolved in the mixed solvent of dichloromethane/petroleum ether = 3 ml/6 ml in a 50 mL roundbottom flask. The white single crystal of **2o** was obtained by slowly evaporating mixed solvent at room temperature under air.

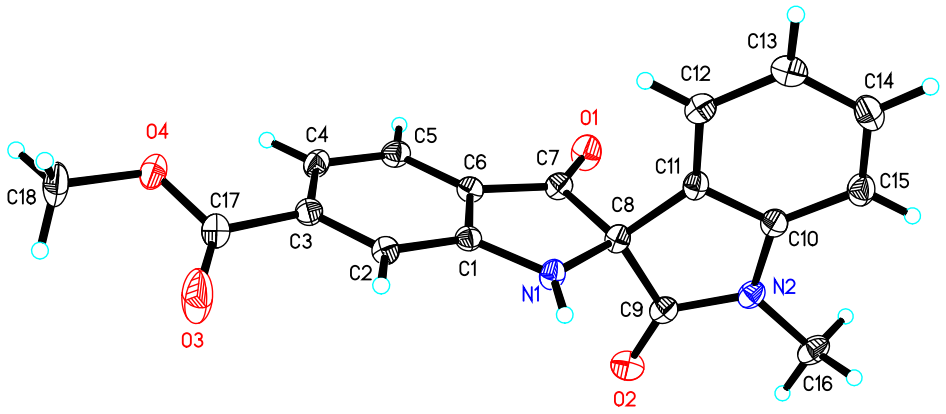


2o

Table S1. Crystal data and structure refinement for 2o.

Identification code	**2o**
Empirical formula	$C_{18}H_{14}N_2O_4$
Formula weight	322.31
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21
Unit cell dimensions	a = 5.5407(4) Å α= 90°. b = 13.5218(9) Å β= 99.771(2)°. c = 10.3493(7) Å γ = 90°.
Volume	764.12(9) $Å^3$

Z	2
Density (calculated)	1.401 Mg/m^3
Absorption coefficient	0.101 mm^{-1}
F(000)	336
Crystal size	0.200 x 0.130 x 0.100 mm^3
Theta range for data collection	3.013 to 25.999°.
Index ranges	-6<=h<=6, -16<=k<=16, -12<=l<=12
Reflections collected	8348
Independent reflections	2955 [R(int) = 0.0545]
Completeness to theta = 25.242°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5754
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2955 / 1 / 220
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.0986
R indices (all data)	R1 = 0.0493, wR2 = 0.1040
Absolute structure parameter	-0.1(8)
Extinction coefficient	0.114(19)
Largest diff. peak and hole	0.258 and -0.282 $e.Å^{-3}$

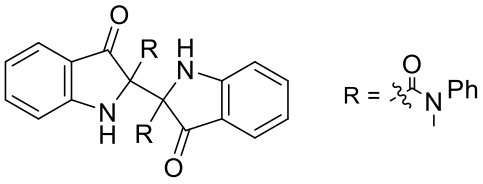


N^2,$N^{2'}$-dimethyl-3,3'-dioxo-N^2,$N^{2'}$-diphenyl-[2,2'-biindoline]-2,2'-dicarboxamide

(**M_1**, d8v23376.)

(Ortep ellipsoids are depicted at the 50% level)

Sample preparation for crystal growth: Compound **M_1** (50 mg) was dissolved in the mixed solvent of dichloromethane/petroleum ether = 3 ml/6 ml in a 50 mL roundbottom flask. The white single crystal of **M_1** was obtained by slowly evaporating mixed solvent at room temperature under air.



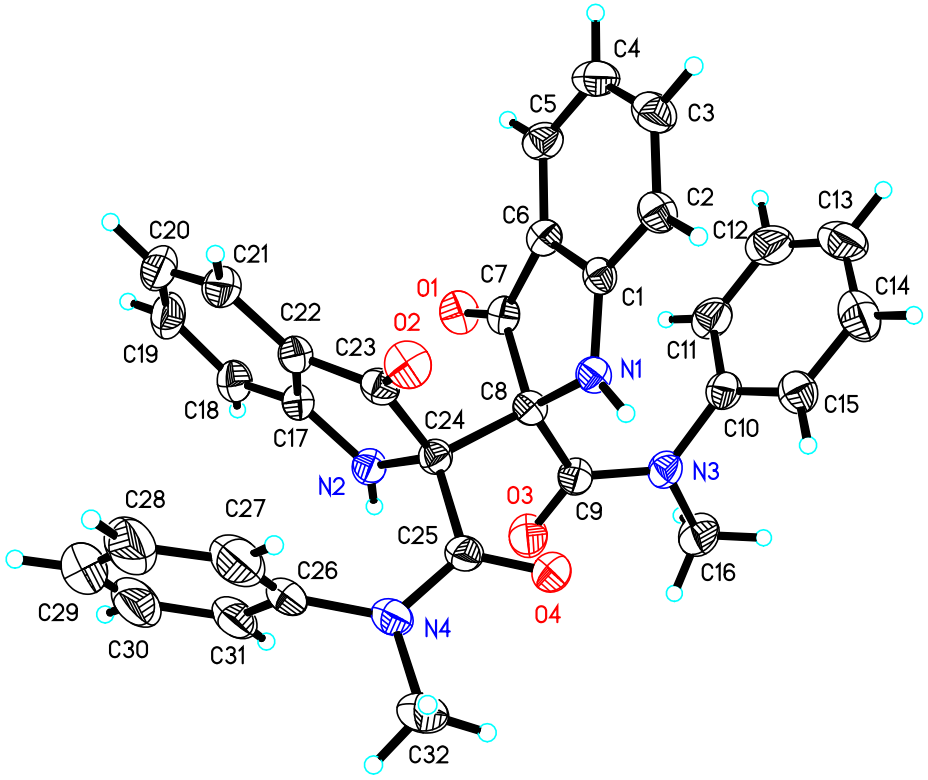
M_1

Table S2. Crystal data and structure refinement for M_1.

Identification code	**M_1**
Empirical formula	$C_{32}H_{26}N_4O_4$
Formula weight	530.57
Temperature	293(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 12.3359(8) Å α= 90°. b = 19.7652(13) Å β= 109.454(2)°. c = 12.0310(7) Å γ = 90°.
Volume	2765.9(3) $Å^3$
Z	4
Density (calculated)	1.274 Mg/m^3
Absorption coefficient	0.086 mm^{-1}
F(000)	1112
Crystal size	0.170 x 0.140 x 0.100 mm^3
Theta range for data collection	3.074 to 25.500°.
Index ranges	-14<=h<=14, -23<=k<=20, -14<=l<=14
Reflections collected	20565
Independent reflections	5121 [R(int) = 0.0558]
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6255
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5121 / 0 / 364
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0684, wR2 = 0.1508
R indices (all data)	R1 = 0.1146, wR2 = 0.1792

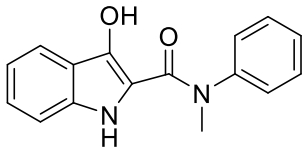
Extinction coefficient	0.016(2)
Largest diff. peak and hole	0.565 and -0.328 e.Å^{-3}



3-hydroxy-N-methyl-N-phenyl-1H-indole-2-carboxamide (**M2**, mo_d8v23188_0m.)

(Ortep ellipsoids are depicted at the 50% level)

Sample preparation for crystal growth: Compound **M2** (50 mg) was dissolved in the mixed solvent of dichloromethane/petroleum ether = 3 ml/6 ml in a 50 mL roundbottom flask. The white single crystal of **M2** was obtained by slowly evaporating mixed solvent at room temperature under air.



M2

Table S3. Crystal data and structure refinement for M2.

Identification code	**M_2**
Empirical formula	$C_{16}H_{14}N_2O_2$
Formula weight	266.29
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 8.0941(4) Å α= 90°. b = 16.8363(7) Å β= 111.720(2)°. c = 0.3616(5) Å γ = 90°.
Volume	1311.77(11) $Å^3$
Z	4
Density (calculated)	1.348 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
F(000)	560
Crystal size	0.170 x 0.150 x 0.120 mm^3
Theta range for data collection	2.709 to 25.996°.
Index ranges	-9<=h<=9, -20<=k<=20, -12<=l<=12
Reflections collected	13345
Independent reflections	2562 [R(int) = 0.0734]
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4830

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2562 / 0 / 184
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1331
R indices (all data)	R1 = 0.0730, wR2 = 0.1463
Absolute structure parameter	-0.1(8)
Extinction coefficient	0.021(6)
Largest diff. peak and hole	0.293 and -0.211 e.$Å^{-3}$