Supporting Information

Synthesis of Indolyl Phenyl Diketones through Visible Light Promoted Ni-catalyzed Intramolecular Cyclization/Oxidation Sequence of Ynones

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1. General information.

All reactions were carried out using oven-dried glassware and magnetic stirring under argon unless otherwise stated. Reaction temperatures are reported as the temperature of the bath surrounding the vessel. Analytical thin layer chromatography was performed on silica gel aluminum plates with F-254 indicator and visualized by UV light (254 nm). Column chromatography was performed using 200-300 mesh silica gel. NMR spectra were recorded on AVANCE III HD 400 MHz or Bruker AVANCE III 300 MHz spectrometer. Chemical shifts (δ) are quoted in ppm relative to TMS (^{1}H) and $CFCl_3$ (^{19}F). Coupling constants (J) are quoted in Hz. The following abbreviations were used to show the multiplicities: s: singlet, d: doublet, t: triplet, q: quadruplet, dd: doublet of doublet, m: multiplet. The residual solvent signals were used as references ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm or relative to external $CFCl_3$, δ_F = 0 ppm). High-resolution mass spectrometry (HRMS) was carried out on a Waters Xevo G2-XS QTof.

The Reaction Equipment

The 15 W blue LED (λ_{max}= 475 nm, $\Delta\lambda$ = 10.0 nm) were purchased from the Xuzhou Ai Jia electronic technology Co.LTD (diameter: 18 cm, height: 10 cm). The blue LED irradiance is 20−30 mW/cm^2. The distance from the light source to the Schlenk tube is 1.5 cm. The reactions were conducted in incubator (25 ℃) with fans.

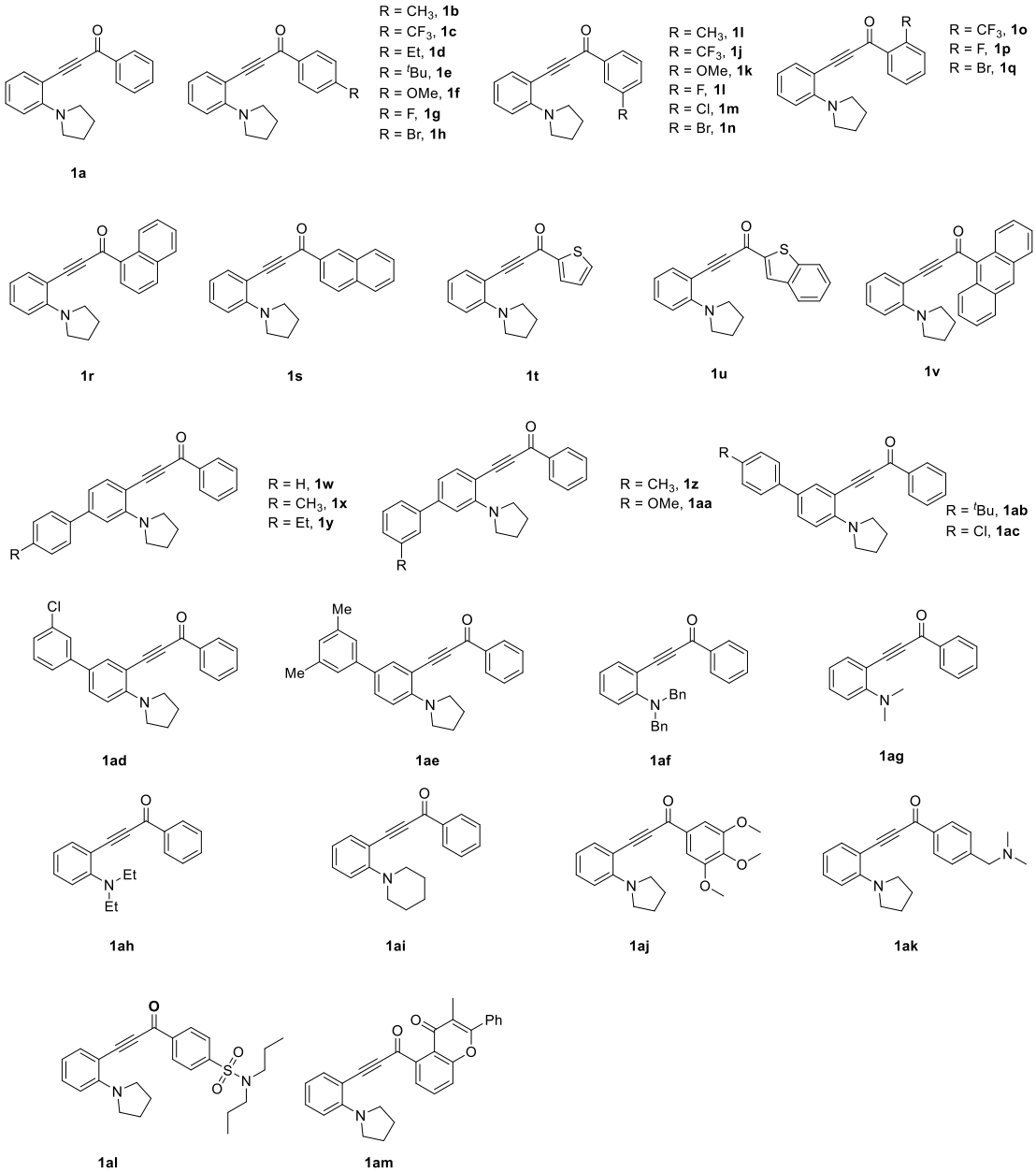
Figure S1. The Reaction Equipment

2. Materials.

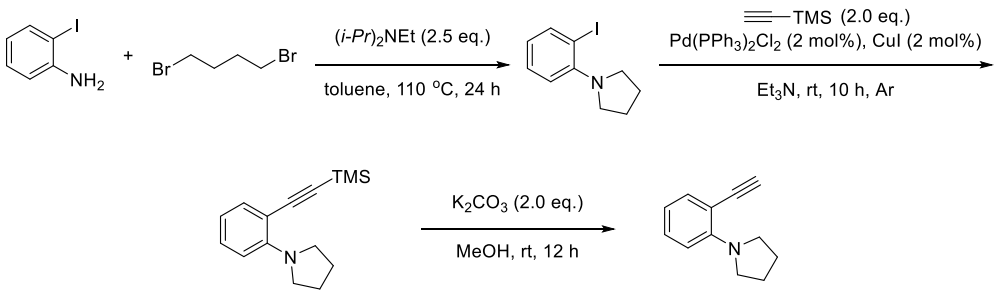
Toluene was distilled over sodium/benzophenone and was degassed before using. Anhydrous THF, DMF were purchased from J&K scientific Ltd. (SuperDry, with molecular sieves, stabilized with 250 ppm BHT, J&K Seal). $Ni(acac)_2$ was purchased from Alfa Aesar, $Pd(PPh_3)_2Cl_2$ was purchased from J&K scientific Ltd., $Pd(PPh_3)_4$ was purchased from Sigma-aldrich, CuI was purchased from Innochem.

3. General procedure for the synthesis of derivatives 1.

List of derivatives 1:



General procedure A (1a-1v) [1]

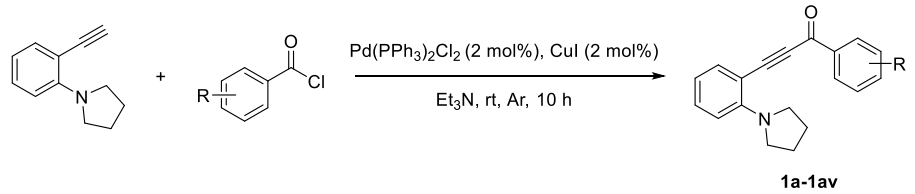


An oven-dried 1.0 L flask equipped with a stirring bar and a reflux condenser was charged with 2-iodoaniline (10.95 g, 50.0 mmol, 1.0 equiv.), 1,4-dibromobutane (16.19 g, 75.0 mmol, 1.5 equiv.), (*i*-Pr)$_2$NEt (16.16 g, 125.0 mmol, 2.5 equiv.) and toluene (500 mL). The resulting reaction mixture was stirred at 110 ℃ (heating mantle) for 24 h. Then the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was diluted with CH_2Cl_2 (100 mL), and 6 M HCl (50 mL) was added dropwise to the above CH_2Cl_2 solution. The resulting mixture was stirred for 1 h at room temperature. After that, the mixture was separated, and aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The resulting crude product was used directly without further purification.

An oven-dried 500 mL flask equipped with a stirring bar was charged with the crude product obtained last step, $Pd(PPh_3)_2Cl_2$ (701.9 mg, 1.0 mmol, 2 mol%), CuI (190.5 mg, 1.0 mmol, 2 mol%), Trimethylsilylacetylene (9.82 g, 100.0 mmol, 2.0 equiv.) and Et_3N (250 mL). Then the resulting reaction mixture was stirred at room temperature under Ar for 10 h. After reaction completed (monitored by TLC), the reaction mixture was diluted with petroleum ether (250 mL). Then the mixture was washed with brine (3 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the crude 1-(2-((trimethylsilyl)ethynyl)phenyl)pyrrolidine as a brown oil, which was used directly without further purification.

An oven-dried 250 mL flask equipped with a stirring bar was charged with the crude product obtained last step, K_2CO_3 (13.8 g, 100.0 mmol, 2.0 equiv.) and MeOH (150 mL). Then the resulting reaction mixture was stirred at room temperature for 12 h. After reaction completed (monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 (100 mL). The mixture was washed with brine (3 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (height 15 cm, width 6.5 cm, eluent: petroleum ether) to afford the desired product as a yellow oil (6.70 g, 78%).

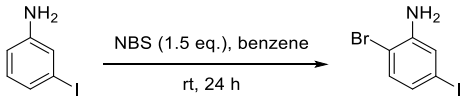
1-(2-ethynylphenyl)pyrrolidine[1] **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.14 (m, 1H), 6.70 – 6.62 (m, 2H), 3.56 (t, *J* = 6.3 Hz, 4H), 3.24 (s, 1H), 1.99 – 1.90 (m, 4H).



1a-1av

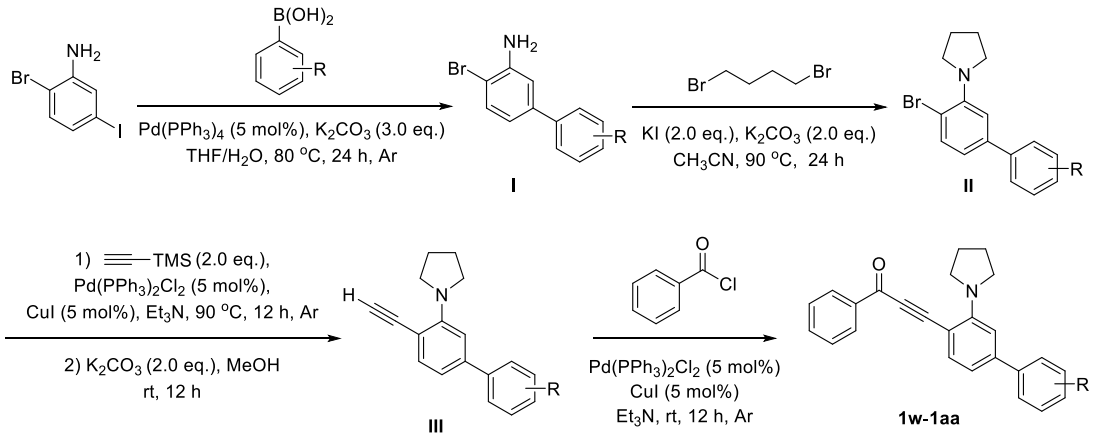
An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with $Pd(PPh_3)_2Cl_2$ (14.0 mg, 0.02 mmol, 2 mol%), CuI (3.8 mg, 0.02 mmol, 2 mol%), 1-(2-ethynylphenyl)pyrrolidine (171.2 mg, 1.0 mmol, 1.0 equiv.), corresponding benzoyl chloride (1.3 mmol, 1.3 equiv.) and Et_3N (10 mL). The resulting reaction mixture was stirred at room temperature under Ar for 10 h. After reaction completed, the reaction mixture was concentrated under reduced pressure. Then the residue was purified by flash column chromatography on silica gel to afford the products **1a-1av**[2].

General procedure B (1w-1aa)[3]



An oven-dried 1.0 L flask equipped with a stirring bar was charged with aniline (21.90 g, 100.0 mmol, 1.0 equiv.), NBS (26.70 g, 150.0 mmol, 1.5 equiv.), and benzene (600 mL). The resulting reaction mixture was stirred at room temperature for 24 h. After reaction completed, the mixture concentrated under reduced pressure. Then the residue was purified by flash column chromatography on silica gel (height 15 cm, width 6.5 cm, eluent: petroleum ether) to afford the desired product as a white solid (7.15 g, 24%).

2-bromo-5-iodoanilin[3a] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.13 – 7.06 (m, 2H), 6.91 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.09 (s, 2H).



An oven-dried 250 mL flask equipped with a stirring bar and a reflux condenser was charged with 2-bromo-5-iodoaniline (2.98 g, 10.0 mmol, 1.0 equiv.), phenylboric acid (15.0 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (577.8 mg, 0.5 mmol, 0.05 equiv.), K_2CO_3 (4.15 g, 30.0 mmol, 3.0 equiv.), THF (60 mL), and H_2O (20 mL). The resulting reaction mixture was stirred at 80 ℃ (heating mantle) under Ar for 24 h. After reaction completed (monitored by TLC), the reaction mixture was extracted with ethyl acetate (3 × 35 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtrated, the filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel to afford the aniline **I**.

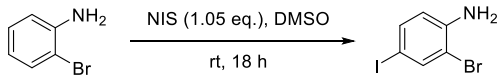
An oven-dried 100 mL flask equipped with a stirring bar and a reflux condenser was charged with aniline intermediate **I** (7.0 mmol, 1.0 equiv.), 1,4-dibromobutane (3.02 g, 14.0 mmol, 2.0 equiv.), KI (2.32 g, 14.0 mmol, 2.0 equiv.), K_2CO_3 (1.93 g, 14.0 mmol, 2.0 equiv.), and CH_3CN (30 mL). Then the resulting reaction mixture was stirred at 90 ℃ (heating mantle) for 24 h. After reaction completed (monitored by TLC), the mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the pyrrolidine product **II**.

An oven-dried 100 mL flask equipped with a stirring bar and a reflux condenser was charged with the pyrrolidine intermediate **II** (2.0 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.1 mmol, 0.05 equiv.), CuI (19.0 mg, 0.1 mmol, 0.05 equiv.), Trimethylsilylacetylene (216.1 mg, 2.2 mmol, 1.1 equiv.) and Et_3N (20 mL). Then the resulting reaction mixture was stirred at 90 ℃ (heating mantle) under Ar for 12 h. After reaction completed, the mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the silylated arylacetylene.

An oven-dried 100 mL flask equipped with a stirring bar was charged with the silylated arylacetylene intermediate (1.5 mmol, 1.0 equiv.), K_2CO_3 (414.6 mg, 3.0 mmol, 2.0 equiv.) and MeOH (10 mL). Then the resulting reaction mixture was stirred at room temperature for 12 h. After reaction completed, the mixture concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the terminal alkyne **III**.

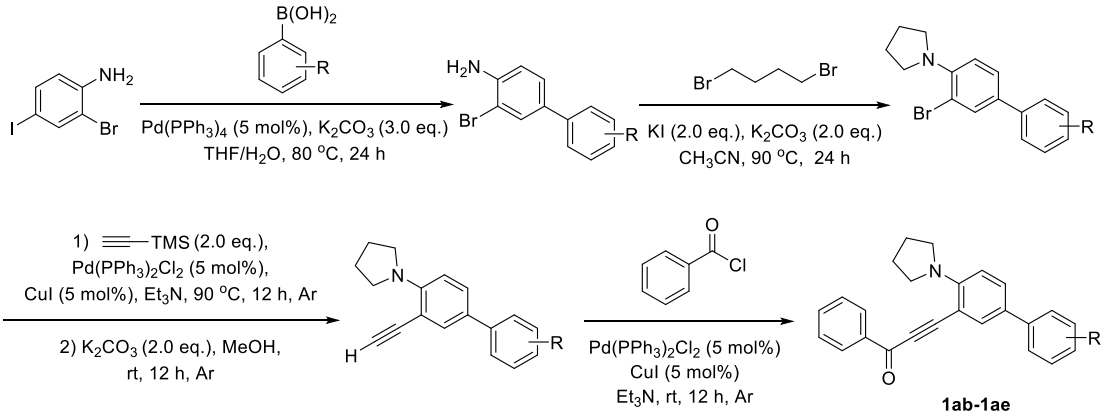
An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with the terminal alkyne intermediate **III** (1.0 mmol, 1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol, 0.05 equiv.), CuI (9.5 mg, 0.05 mmol, 0.05 equiv.), Benzoyl chloride (154.6 mg, 1.1 mmol, 1.1 equiv.) and Et_3N (5 mL). The resulting reaction mixture was stirred at room temperature under Ar for 12 h. After reaction completed, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired products **1w-1aa**.

General procedure C (1ab-1ae):



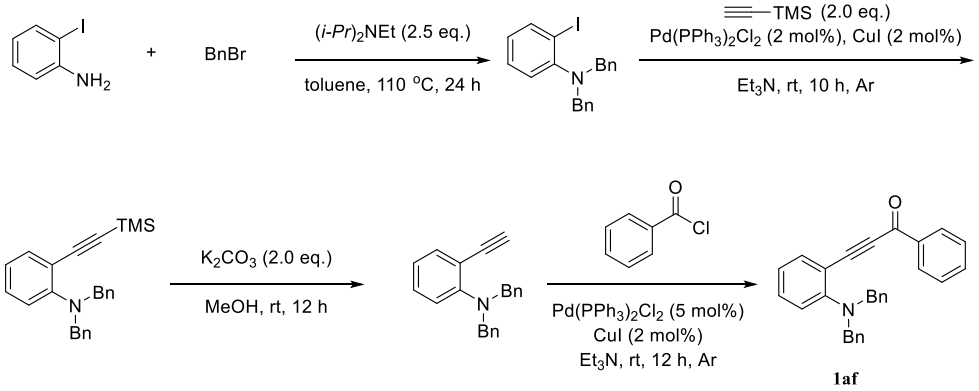
An oven-dried 1.0 L flask equipped with a stirring bar was charged with aniline (5.16 g, 30.0 mmol, 1.0 equiv.), NIS (10.12 g, 45.0 mmol, 1.5 equiv.), and DMSO (250 mL). Then the resulting reaction mixture was stirred at room temperature for 18 h. After reaction completed, the reaction mixture was quenched with aqueous $NaHCO_3$ (500 mL), and the brown suspension was filtered off and washed with water (100 mL), and the mixture was extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtrated, the filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (height 15 cm, width 6.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 10:1) to afford 2-bromo-4-iodoaniline as a brown solid (7.04 g, 79%).

2-bromo-4-iodoaniline[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.0 Hz, 1H), 7.35 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 4.11 (s, 2H).



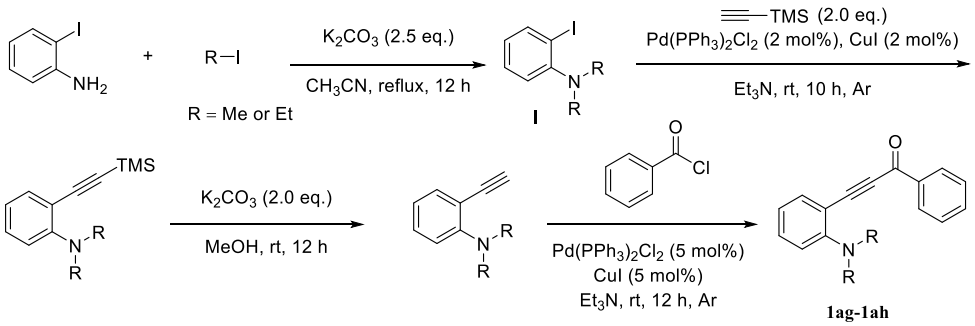
The synthesis of **1ab-1ae** was following the **procedure B** starting from 2-bromo-4-iodoaniline obtained above.

The synthesis of 1af



The synthesis of **1af** was following the **procedure A** starting from 2-bromo-4-iodoaniline obtained above.

The synthesis of 1ag-1ah[5]



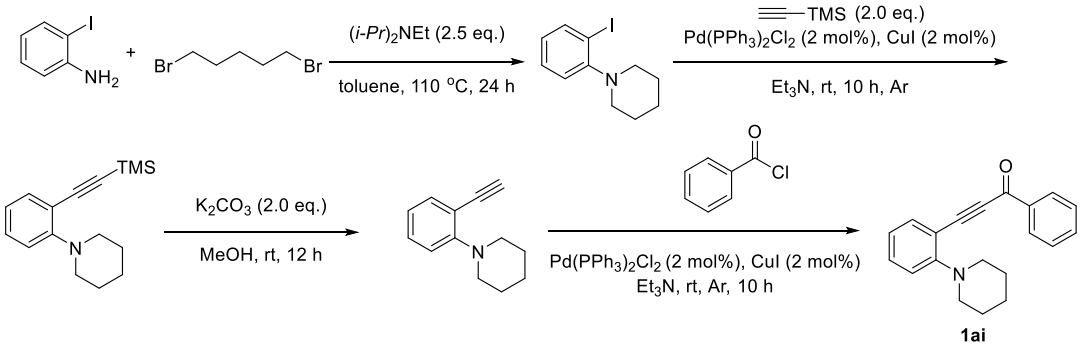
To a mixture of 2-iodoaniline (10 mmol) and K_2CO_3 (3.45g, 25 mmol) in CH_3CN was added iodoethane (5.2g, 30 mmol) dropwise. The reaction was stirred at reflux (heating mantle) for 12 hours. After cooling down to room temperature, the mixture was treated with water and was extracted with Et_2O. The extraction was washed by brine and dried with Na_2SO_4. The solvent was then evaporated in vacuo

and the residue was purified by using silicon gel to afford aniline intermediate **I**

An oven-dried 500 mL flask equipped with a stirring bar was charged with the crude product obtained last step, $Pd(PPh_3)_2Cl_2$ (140.4 mg, 0.2 mmol, 2 mol%), CuI (38.1 mg, 0.2 mmol, 2 mol%), Trimethylsilylacetylene (1.96 g, 20.0 mmol, 2.0 equiv.) and Et_3N (50 mL). Then the resulting reaction mixture was stirred at room temperature under Ar for 10 h. After reaction completed (monitored by TLC), the reaction mixture was diluted with petroleum ether (50 mL). Then the mixture was washed with brine (3 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the crude 1-(2-((trimethylsilyl)ethynyl)phenyl)pyrrolidine as a brown oil, which was used directly without further purification.

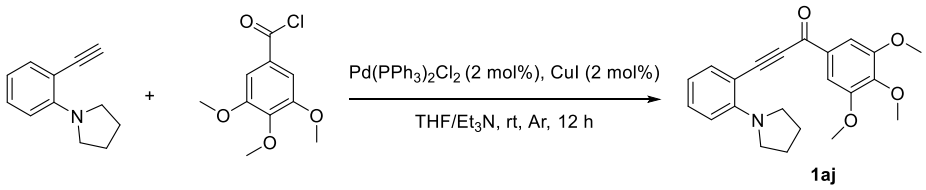
An oven-dried 250 mL flask equipped with a stirring bar was charged with the crude product obtained last step, K_2CO_3 (2.76 g, 20.0 mmol, 2.0 equiv.) and MeOH (20 mL). Then the resulting reaction mixture was stirred at room temperature for 12 h. After reaction completed (monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 (20 mL). The mixture was washed with brine (3 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired products **1ag-1ah**.

The synthesis of 1ai



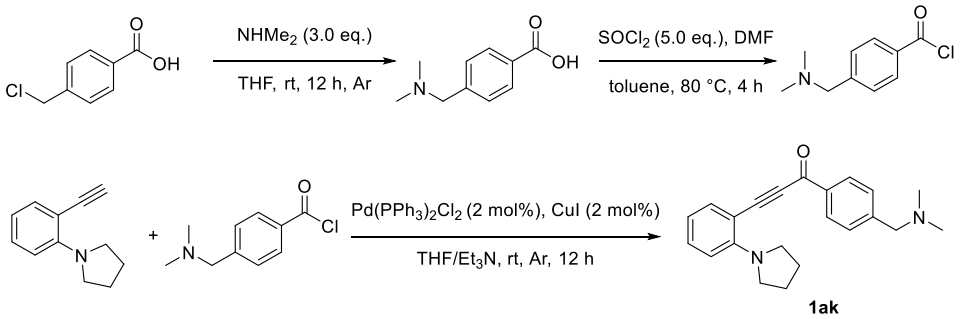
The synthesis of **1ai** was following the **procedure A** starting from 2-bromo-4-iodoaniline obtained above.

The synthesis of 1aj



An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with trimethylgalloyl chloride (276.8 mg, 1.2 mmol, 1.2 equiv.) and THF (5 mL), and the mixture was stirred at room temperature under Ar for 30 min. Then $Pd(PPh_3)_2Cl_2$ (14.0 mg, 0.02 mmol, 2 mol%), CuI (3.8 mg, 0.02 mmol, 2 mol%), 1-(2-ethynylphenyl)pyrrolidine (171.2 mg, 1.0 mmol, 1.0 equiv.) and Et_3N (5 mL) were added to the above mixture. The resulting reaction mixture was stirred at room temperature under Ar for 12 h. After reaction completed, the mixture was filtrated through a pad of celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product **1aj**.

The synthesis of 1ak



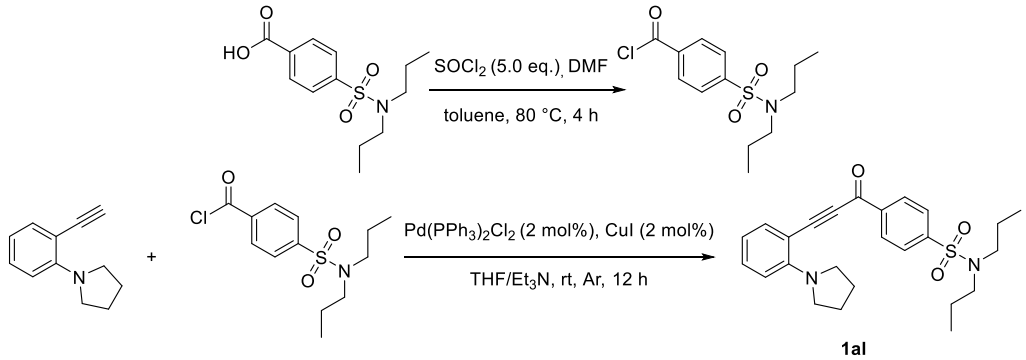
An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with 4-(chloromethyl)benzoic acid (853.0 mg, 5.0 mmol, 1.0 equiv.), $NHMe_2$ (0.76 mL, 15.0 mmol, 3.0 equiv.) and THF (10 mL). Then the resulting mixture was stirred at room temperature under Ar for 12 h. The volume of the reaction was reduced in vacuo and the desired product precipitated as a white solid. The precipitate was collected by filtration, washed with cold EtOH, and dried to afford **4-((dimethylamino)methyl)benzoic acid**[6] as a white solid (35%, 310.1 mg). **^{1}H NMR** (300 MHz, D_2O) δ 7.76 – 7.59 (m, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 4.09 (s, 2H), 2.65 (s, 6H).

An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with 4-((dimethylamino)methyl)benzoic acid (215.1 mg, 1.2 mmol, 1.0 equiv.), $SOCl_2$ (0.44 mL, 6.0 mmol, 5.0 equiv.), toluene (5 mL), and a few drops of DMF were added to the reaction mixture as the catalyst. The reaction was carried out at 80 ℃ (heating mantle) for 4 h. After reaction completed, the mixture was cooled down to room temperature and concentrated under vacuum. The resulting crude product was used directly without further purification.

An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with the crude acyl chloride (1.2 mmol, 1.2 equiv.) and THF (5 mL), and the mixture was stirred at room temperature under Ar for 30 min. Then $Pd(PPh_3)_2Cl_2$ (14.0 mg,

0.02 mmol, 2 mol%), CuI (3.8 mg, 0.02 mmol, 2 mol%), 1-(2-ethynylphenyl)pyrrolidine (171.2 mg, 1.0 mmol, 1.0 equiv.) and Et_3N (5 mL) were added to the above mixture. The resulting reaction mixture was stirred at room temperature under Ar for 12 h. After reaction completed, the mixture was filtrated through a pad of celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product **1ak**.

The synthesis of 1al

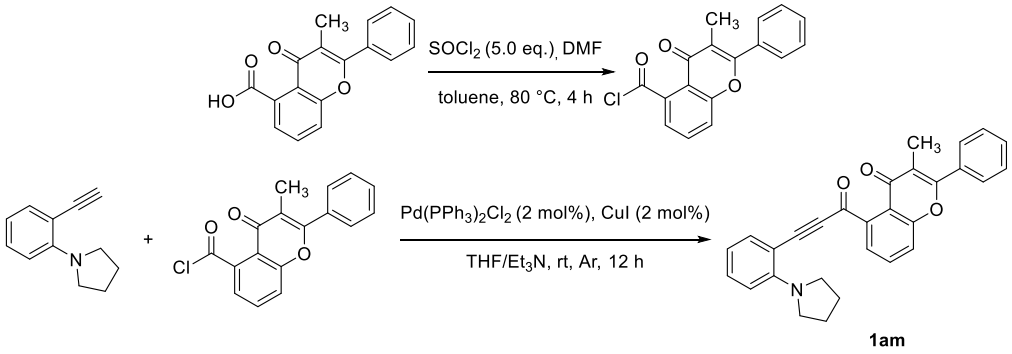


1al

An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with Probenecid (342.1 mg, 1.2 mmol, 1.0 equiv.), $SOCl_2$ (0.44 mL, 6.0 mmol, 5.0 equiv.), toluene (5 mL), and a few drops of DMF were added to the reaction mixture as the catalyst. The reaction was carried out at 80 ℃ (heating mantle) for 4 h. After reaction completed, the mixture was cooled down to room temperature and concentrated under vacuum. The resulting crude product was used directly without further purification.

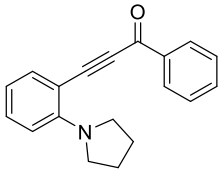
An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with the crude acyl chloride (1.2 mmol, 1.2 equiv.) and THF (5 mL), and the mixture was stirred at room temperature under Ar for 30 min. Then $Pd(PPh_3)_2Cl_2$ (14.0 mg, 0.02 mmol, 2 mol%), CuI (3.8 mg, 0.02 mmol, 2 mol%), 1-(2-ethynylphenyl)pyrrolidine (171.2 mg, 1.0 mmol, 1.0 equiv.) and Et_3N (5 mL) were added to the above mixture. The resulting reaction mixture was stirred at room temperature under Ar for 12 h. After reaction completed, the mixture was filtrated through a pad of celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired product **1al**.

The synthesis of 1am.

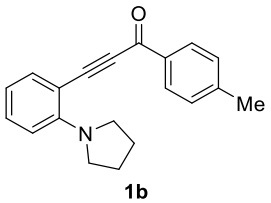


Following the procedure for the synthesis of 1al

4. Purification and characterization of derivatives 1

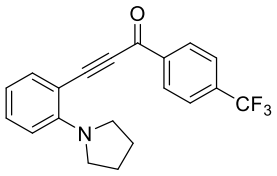


1-phenyl-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1a. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 100:1) as an orange oil (starting from 1-(2-ethynylphenyl)pyrrolidine, 78%, 213.6 mg). R_f (petroleum ether/ethyl acetate = 100:1): 0.19. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.29 – 8.09 (m, 2H), 7.62 – 7.47 (m, 4H), 7.31 – 7.25 (m, 1H), 6.68 (t, *J* = 7.5 Hz, 2H), 3.67 (t, *J* = 6.6 Hz, 4H), 2.07 – 1.90 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.9, 151.5, 137.4, 137.1, 133.5, 132.1, 129.2, 128.4, 116.2, 114.0, 103.2, 97.6, 92.1, 50.5, 25.8. **HRMS** (ESI) calcd for $C_{19}H_{18}NO^+$ *m/z* 276.1383 $[M+H]^+$, Found 276.1384.



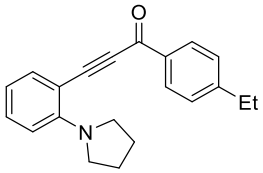
3-(2-(pyrrolidin-1-yl)phenyl)-1-(p-tolyl)prop-2-yn-1-one 1b. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 100:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 70%, 203.2 mg). R_f (petroleum ether/ethyl acetate = 100:1): 0.14. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.32 – 7.25 (m, 3H), 6.74 – 6.62 (m, 2H), 3.68 (t,

J = 6.4 Hz, 4H), 2.45 (s, 3H), 2.06 – 1.90 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.7, 151.5, 144.5, 137.1, 135.1, 132.0, 129.3, 129.2, 116.2, 114.0, 103.5, 96.9, 92.1, 50.5, 25.8, 21.7. **HRMS** (ESI) calcd for $C_{20}H_{20}NO^+$ *m/z* 290.1539 $[M+H]^+$, Found 290.1541.



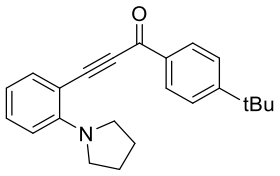
1c

3-(2-(pyrrolidin-1-yl)phenyl)-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one 1c. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 73%, 249.1 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.26. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.55 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.35 – 7.26 (m, 1H), 6.74 – 6.60 (m, 2H), 3.68 (t, *J* = 6.6 Hz, 4H), 2.07 – 1.93 (m, 4H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.5 (s). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.5, 151.8, 140.0, 137.3, 134.6 (q, *J* = 32.3 Hz), 132.6, 129.4, 125.6 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 271.5 Hz), 116.3, 114.1, 102.6, 99.5, 92.1, 50.6, 25.8. **HRMS** (ESI) calcd for $C_{20}H_{17}F_3NO^+$ *m/z* 344.1257 $[M+H]^+$, Found 344.1262.



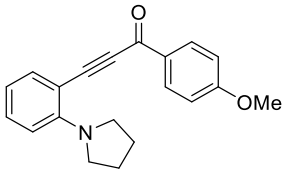
1d

1-(4-ethylphenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1d. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange oil (starting from 1-(2-ethynylphenyl)pyrrolidine, 72%, 218.6 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.27. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.1 Hz, 2H), 7.55 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.34 – 7.27 (m, 3H), 6.72 – 6.63 (m, 2H), 3.67 (t, *J* = 6.6 Hz, 4H), 2.74 (q, *J* = 7.5 Hz, 2H), 2.06 – 1.95 (m, 4H), 1.28 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.7, 151.5, 150.7, 137.1, 135.3, 132.0, 129.4, 128.0, 116.2, 114.0, 103.4, 97.0, 92.1, 50.5, 29.0, 25.8, 15.2. **HRMS** (ESI) calcd for $C_{21}H_{22}NO^+$ *m/z* 304.1696 $[M+H]^+$, Found 304.1690.



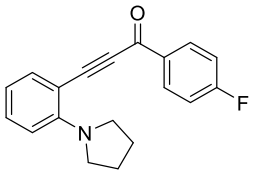
1e

1-(4-(tert-butyl)phenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1e. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange oil (starting from 1-(2-ethynylphenyl)pyrrolidine, 76%, 251.1 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.32. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.58 – 7.50 (m, 3H), 7.30 – 7.24 (m, 1H), 6.75 – 6.61 (m, 2H), 3.67 (t, *J* = 6.6 Hz, 4H), 2.10 – 1.89 (m, 4H), 1.37 (s, 9H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.7, 157.4, 151.5, 137.1, 135.0, 132.0, 129.2, 125.5, 116.2, 113.9, 103.4, 97.0, 92.1, 50.5, 35.2, 31.1, 25.8. **HRMS** (ESI) calcd for $C_{23}H_{26}NO^+$ *m/z* 332.2009 $[M+H]^+$, Found 332.2016.



1f

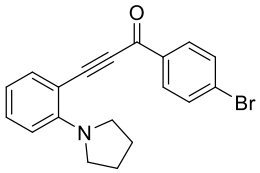
1-(4-methoxyphenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1f. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 100:1 to 20:1) as an orange oil (starting from 1-(2-ethynylphenyl)pyrrolidine, 62%, 190.4 mg). R_f (petroleum ether/ethyl acetate = 20:1): 0.28. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.7 Hz, 2H), 7.54 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.71 – 6.63 (m, 2H), 3.89 (s, 3H), 3.66 (t, *J* = 6.6 Hz, 4H), 2.04 – 1.93 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.7, 164.0, 151.5, 136.9, 131.9, 131.5, 130.7, 116.2, 113.9, 113.7, 103.6, 96.5, 91.8, 55.5, 50.5, 25.8. **HRMS** (ESI) calcd for $C_{20}H_{20}NO_2^+$ *m/z* 306.1489 $[M+H]^+$, Found 306.1493.



1g

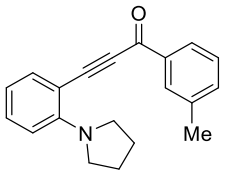
1-(4-fluorophenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1g. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5

cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange oil (starting from 1-(2-ethynylphenyl)pyrrolidine, 68%, 198.4 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.21. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 9.0, 5.4 Hz, 2H), 7.53 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.17 (t, *J* = 8.4 Hz, 2H), 6.75 – 6.61 (m, 2H), 3.66 (t, *J* = 6.6 Hz, 4H), 2.10 – 1.89 (m, 4H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -104.8 (s). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.3, 166.1 (d, *J* = 253.5 Hz), 151.6, 137.0, 133.9 (d, *J* = 3.0 Hz), 132.2, 131.8 (d, *J* = 9.0 Hz), 116.2, 115.6 (d, *J* = 21.8 Hz), 114.0, 103.0, 98.0, 91.8, 50.5, 25.8. **HRMS** (ESI) calcd for $C_{19}H_{17}FNO^+$ *m/z* 294.1289 $[M+H]^+$, Found 294.1299.



1h

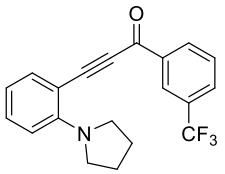
1-(4-bromophenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1h. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 80%, 282.9 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.25. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.33 – 7.27 (m, 1H), 6.76 – 6.57 (m, 2H), 3.66 (t, *J* = 6.6 Hz, 4H), 2.14 – 1.92 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.7, 151.6, 137.1, 136.2, 132.4, 131.8, 130.6, 128.8, 116.2, 114.1, 102.9, 98.4, 91.9, 50.6, 25.8. **HRMS** (ESI) calcd for $C_{19}H_{17}BrNO^+$ *m/z* 354.0488 $[M+H]^+$, Found 354.0481.



1i

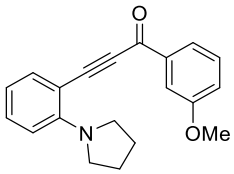
3-(2-(pyrrolidin-1-yl)phenyl)-1-(m-tolyl)prop-2-yn-1-one 1i. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 100:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 83%, 239.6 mg). R_f (petroleum ether/ethyl acetate = 100:1): 0.14. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.10 – 7.87 (m, 2H), 7.56 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.31 – 7.24 (m, 1H), 6.68 (t, *J* = 7.2 Hz, 2H), 3.68 (t, *J* = 6.6 Hz, 4H), 2.45 (s, 3H), 2.07 – 1.92 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 178.1, 151.5, 138.2, 137.4, 137.2, 134.4, 132.1, 129.5,

128.4, 126.6, 116.2, 114.0, 103.3, 97.3, 92.2, 50.5, 25.8, 21.3. **HRMS** (ESI) calcd for $C_{20}H_{20}NO^+$ *m/z* 290.1539 $[M+H]^+$, Found 290.1538.



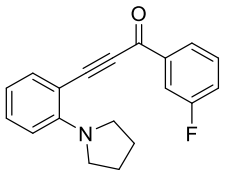
1j

3-(2-(pyrrolidin-1-yl)phenyl)-1-(3-(trifluoromethyl)phenyl)prop-2-yn-1-one 1j. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 65%, 224.3 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.25. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.56 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.34 – 7.26 (m, 1H), 6.78 – 6.59 (m, 2H), 3.68 (t, *J* = 6.6 Hz, 4H), 2.09 – 1.89 (m, 4H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.3 (s). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.1, 151.6, 137.9, 137.4, 132.6, 132.0, 131.0 (q, *J* = 33.8 Hz), 129.7 (q, *J* = 3.8 Hz), 129.2, 126.0, 123.7 (q, *J* = 270.8 Hz), 116.3, 114.1, 102.5, 99.4, 91.9, 50.5, 25.8. **HRMS** (ESI) calcd for $C_{20}H_{17}F_3NO^+$ *m/z* 344.1257 $[M+H]^+$, Found 344.1265.



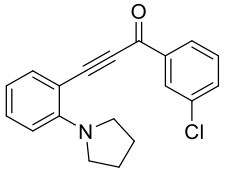
1k

1-(3-methoxyphenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1k. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 100:1 to 20:1) as an orange oil (starting from 1-(2-ethynylphenyl)pyrrolidine, 57%, 173.8 mg). R_f (petroleum ether/ethyl acetate = 20:1): 0.30. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.06 – 7.93 (m, 2H), 7.56 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.31 – 7.26 (m, 1H), 6.71 – 6.61 (m, 2H), 3.68 (t, *J* = 6.6 Hz, 4H), 2.45 (s, 3H), 2.05 – 1.93 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 178.1, 151.5, 138.3, 137.5, 137.2, 134.4, 132.1, 129.6, 128.4, 126.6, 116.3, 114.0, 103.4, 97.3, 92.2, 50.5, 25.8, 21.3. **HRMS** (ESI) calcd for $C_{20}H_{20}NO_2^+$ *m/z* 306.1489 $[M+H]^+$, Found 306.1499.



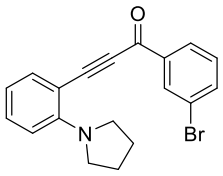
1l

1-(3-fluorophenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1l. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange oil (starting from 1-(2-ethynylphenyl)pyrrolidine, 72%, 211.7 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.20. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 9.3 Hz, 1H), 7.59 – 7.42 (m, 2H), 7.36 – 7.27 (m, 2H), 6.77 – 6.60 (m, 2H), 3.67 (t, *J* = 6.5 Hz, 4H), 2.07 – 1.90 (m, 4H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.6 (s). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.2 (d, *J* = 2.3 Hz), 162.6 (d, *J* = 246.8 Hz), 151.5, 139.4 (d, *J* = 6.8 Hz), 137.1, 132.3, 130.1 (d, *J* = 8.3 Hz), 124.9 (d, *J* = 3.0 Hz), 120.4 (d, *J* = 21.0 Hz), 116.2, 115.4 (d, *J* = 22.5 Hz), 114.0, 102.7, 98.5, 91.9, 50.4, 25.7. **HRMS** (ESI) calcd for $C_{19}H_{17}FNO^+$ *m/z* 294.1289 $[M+H]^+$, Found 294.1280.



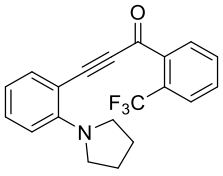
1m

1-(3-chlorophenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1m. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 75%, 232.2 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.23. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21 – 8.11 (m, 1H), 8.08 – 8.02 (m, 1H), 7.59 – 7.52 (m, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.32 – 7.27 (m, 1H), 6.72 – 6.62 (m, 2H), 3.67 (t, *J* = 6.6 Hz, 4H), 2.05 – 1.94 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.3, 151.6, 139.0, 137.3, 134.7, 133.4, 132.5, 129.8, 129.2, 127.2, 116.3, 114.1, 102.7, 98.8, 92.0, 50.6, 25.8. **HRMS** (ESI) calcd for $C_{19}H_{17}ClNO^+$ *m/z* 310.0993 $[M+H]^+$, Found 310.0987.



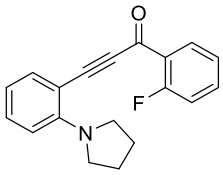
1n

1-(3-bromophenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1n. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 69%, 241.9 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.25. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.29 (t, *J* = 1.8 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 – 7.28 (m, 2H), 6.72 – 6.64 (m, 2H), 3.68 (t, *J* = 6.6 Hz, 4H), 2.05 – 1.96 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.1, 151.6, 139.1, 137.4, 136.2, 132.5, 132.1, 130.1, 127.5, 122.7, 116.3, 114.1, 102.7, 98.9, 91.9, 50.5, 25.8. **HRMS** (ESI) calcd for $C_{19}H_{17}BrNO^+$ *m/z* 354.0488 $[M+H]^+$, Found 354.0489.



1o

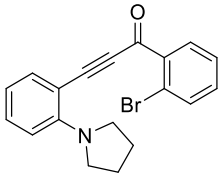
3-(2-(pyrrolidin-1-yl)phenyl)-1-(2-(trifluoromethyl)phenyl)prop-2-yn-1-one 1o. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 70%, 240.6 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.27. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.9 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.71 – 7.57 (m, 2H), 7.45 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.30 – 7.23 (m, 1H), 6.79 – 6.45 (m, 2H), 3.60 (t, *J* = 6.6 Hz, 4H), 2.06 – 1.82 (m, 4H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -58.9 (s). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.7, 151.7, 137.3, 132.7, 131.6, 131.3, 130.5, 127.1 (q, *J* = 5.3 Hz), 123.4 (q, *J* = 272.3 Hz), 116.1, 114.0, 102.3, 100.0, 93.4, 50.5, 25.8, two carbons were overlapped. **HRMS** (ESI) calcd for $C_{20}H_{17}F_3NO^+$ *m/z* 344.1257 $[M+H]^+$, Found 344.1254.



1p

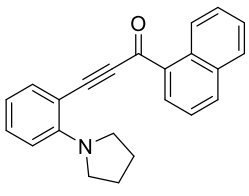
1-(2-fluorophenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1p. The product

was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 100:1) as an orange oil (starting from 1-(2-ethynylphenyl)pyrrolidine, 77%, 226.7 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.20. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.06 (td, *J* = 7.8, 1.8 Hz, 1H), 7.62 – 7.49 (m, 2H), 7.30 – 7.23 (m, 2H), 7.17 (dd, *J* = 10.8, 8.1 Hz, 1H), 6.65 (t, *J* = 7.8 Hz, 2H), 3.66 (t, *J* = 6.6 Hz, 4H), 2.07 – 1.90 (m, 4H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.7 (s). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 173.9, 161.8 (d, *J* = 258.8 Hz), 151.5, 137.3, 134.8 (d, *J* = 9.0 Hz), 132.3, 131.3, 126.1 (d, *J* = 8.3 Hz), 124.0 (d, *J* = 3.8 Hz), 116.8 (d, *J* = 22.5 Hz), 116.0, 113.9, 102.8, 98.1 (d, *J* = 2.3 Hz), 93.8, 50.4, 25.7. **HRMS** (ESI) calcd for $C_{19}H_{17}FNO^+$ *m/z* 294.1289 $[M+H]^+$, Found 294.1282.



1q

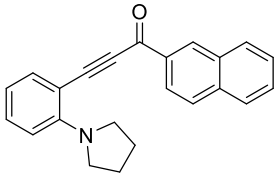
1-(2-bromophenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1q. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 63%, 224.3 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.25. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.22 (m, 4H), 6.76 – 6.53 (m, 2H), 3.63 (t, *J* = 6.6 Hz, 4H), 2.09 – 1.85 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.5, 151.6, 138.2, 137.2, 134.6, 132.6, 132.5, 131.9, 127.2, 120.7, 116.0, 113.9, 102.6, 99.8, 93.2, 50.5, 25.7. **HRMS** (ESI) calcd for $C_{19}H_{17}BrNO^+$ *m/z* 354.0488 $[M+H]^+$, Found 354.0482.



1r

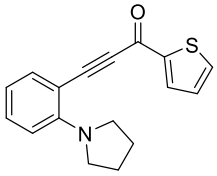
1-(naphthalen-1-yl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1r. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 77%, 249.3 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.19. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.66 – 7.54 (m, 3H),

7.30 (t, *J* = 8.4 Hz, 1H), 6.83 – 6.52 (m, 2H), 3.70 (t, *J* = 5.4 Hz, 4H), 2.00 (t, *J* = 5.4 Hz, 4H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$) δ 177.7, 151.5, 137.2, 135.8, 134.9, 132.4, 132.1, 131.8, 129.6, 128.6, 128.3, 127.8, 126.7, 123.9, 116.2, 114.0, 103.3, 97.6, 92.2, 50.5, 25.8. **HRMS** (ESI) calcd for $C_{23}H_{20}NO^+$ *m/z* 326.1539 $[M+H]^+$, Found 326.1549.



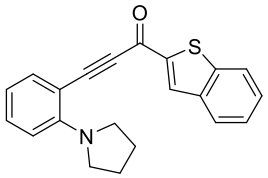
1s

1-(naphthalen-2-yl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1s. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 78%, 254.6 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.20. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.66 – 7.54 (m, 3H), 7.30 (t, *J* = 7.8 Hz, 1H), 6.80 – 6.59 (m, 2H), 3.72 (t, *J* = 6.6 Hz, 4H), 2.02 (t, *J* = 6.6 Hz, 4H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$) δ 177.9, 151.6, 137.2, 135.9, 135.0, 132.5, 132.2, 131.9, 129.7, 128.7, 128.4, 127.9, 126.8, 124.0, 116.3, 114.0, 103.4, 97.6, 92.3, 50.6, 25.8. **HRMS** (ESI) calcd for $C_{23}H_{20}NO^+$ *m/z* 326.1539 $[M+H]^+$, Found 326.1543.



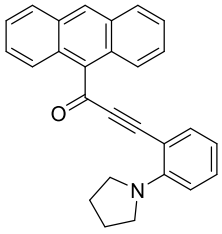
1t

3-(2-(pyrrolidin-1-yl)phenyl)-1-(thiophen-2-yl)prop-2-yn-1-one 1t. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 71%, 200.4 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.20. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 3.6 Hz, 1H), 7.68 (d, *J* = 4.8 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.30 (s, 1H), 7.17 (t, *J* = 4.5 Hz, 1H), 6.67 (t, *J* = 8.1 Hz, 2H), 3.67 (t, *J* = 6.3 Hz, 4H), 1.99 (t, *J* = 6.3 Hz, 4H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$) δ 169.8, 151.4, 145.5, 137.2, 134.2, 133.7, 132.2, 128.2, 116.2, 114.0, 103.0, 96.2, 91.5, 50.5, 25.8. **HRMS** (ESI) calcd for $C_{17}H_{16}NOS^+$ *m/z* 282.0947 $[M+H]^+$, Found 282.0950.



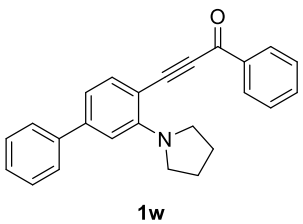
1u

1-(benzo[b]thiophen-2-yl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1u. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 73%, 240.5 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.21. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.40 (m, 2H), 7.33 – 7.28 (m, 1H), 6.80 – 6.60 (m, 2H), 3.69 (t, *J* = 6.3 Hz, 4H), 2.01 (t, *J* = 6.3 Hz, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 171.1, 151.6, 144.9, 142.8, 138.8, 137.2, 132.3, 131.2, 127.6, 126.1, 125.1, 123.0, 116.3, 114.0, 102.9, 97.2, 91.5, 50.6, 25.8. **HRMS** (ESI) calcd for $C_{21}H_{18}NOS^+$ *m/z* 332.1104 $[M+H]^+$, Found 332.1110.



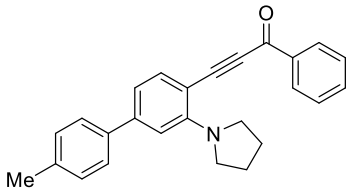
1v

1-(anthracen-9-yl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1v. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 5:1) as an orange solid (starting from 1-(2-ethynylphenyl)pyrrolidine, 13%, 48.9 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.21. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 7.6, 1.6 Hz, 2H), 8.54 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.71 – 7.58 (m, 5H), 7.31 – 7.25 (m, 2H), 6.84 – 6.77 (m, 2H), 3.71 (t, *J* = 6.4 Hz, 4H), 1.99 – 1.95 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 150.2, 135.5, 132.7, 129.8, 128.6, 127.3, 127.0, 126.5, 125.2, 118.5, 117.2, 114.4, 109.1, 103.1, 89.2, 50.6, 25.6, two carbons were overlapped. **HRMS** (ESI) calcd for $C_{27}H_{22}NO^+$ *m/z* 376.1696 $[M+H]^+$, Found 376.1690. **1v** was contaminated with 8% of an inseparable impurity.



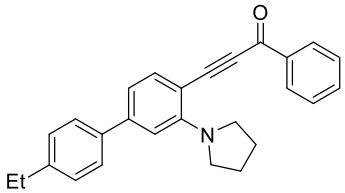
1w

1-phenyl-3-(3-(pyrrolidin-1-yl)-[1,1'-biphenyl]-4-yl)prop-2-yn-1-one 1w. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 2-bromo-5-iodoanilin, overall yield 4%, 143.9 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.36. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 8.1 Hz, 4H), 7.55 – 7.38 (m, 5H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.86 (s, 1H), 3.75 (t, *J* = 6.0 Hz, 4H), 2.03 (t, *J* = 6.3 Hz, 4H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 177.9, 151.8, 145.1, 140.8, 137.6, 137.5, 133.5, 129.2, 128.8, 128.5, 128.0, 127.2, 115.6, 112.6, 102.4, 97.7, 92.7, 50.6, 25.8. **HRMS** (ESI) calcd for $C_{25}H_{22}NO^+$ *m/z* 352.1696 $[M+H]^+$, Found 352.1699.



1x

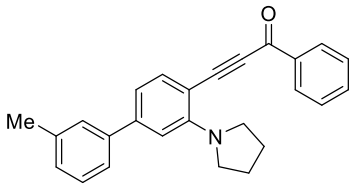
3-(4'-methyl-3-(pyrrolidin-1-yl)-[1,1'-biphenyl]-4-yl)-1-phenylprop-2-yn-1-one 1x. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 2-bromo-5-iodoanilin, overall yield 4%, 146.3 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.32. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.3 Hz, 2H), 7.67 – 7.57 (m, 2H), 7.57 – 7.45 (m, 4H), 7.27 (s, 2H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.84 (s, 1H), 3.74 (t, *J* = 6.3 Hz, 4H), 2.41 (s, 3H), 2.02 (t, *J* = 6.4 Hz, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.8, 151.7, 144.9, 137.8, 137.7, 137.5, 137.4, 133.5, 129.4, 129.1, 128.4, 126.9, 115.3, 112.1, 101.9, 97.9, 92.6, 50.5, 25.7, 21.1. **HRMS** (ESI) calcd for $C_{26}H_{24}NO^+$ *m/z* 366.1852 $[M+H]^+$, Found 366.1861.



1y

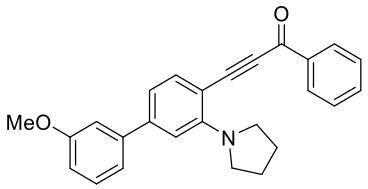
3-(4'-ethyl-3-(pyrrolidin-1-yl)-[1,1'-biphenyl]-4-yl)-1-phenylprop-2-yn-1-one 1y. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 2-bromo-5-iodoanilin, overall yield 3%, 128.9 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.30. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.2 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.56 – 7.49 (m, 4H), 7.29 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.84 (s, 1H), 3.74 (t, *J* = 6.0 Hz, 4H), 2.71 (q, *J* = 7.5 Hz, 2H), 2.02 (t, *J*

= 6.0 Hz, 4H), 1.28 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.8, 151.7, 145.0, 144.2, 138.1, 137.6, 137.4, 133.5, 129.1, 128.4, 128.2, 127.0, 115.4, 112.2, 101.9, 97.9, 92.6, 50.6, 28.5, 25.8, 15.6. **HRMS** (ESI) calcd for $C_{27}H_{26}NO^+$ *m/z* 380.2009 $[M+H]^+$, Found 380.2005.



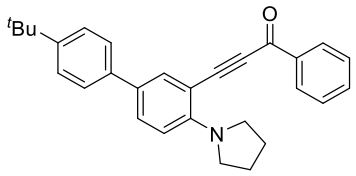
1z

3-(3'-methyl-3-(pyrrolidin-1-yl)-[1,1'-biphenyl]-4-yl)-1-phenylprop-2-yn-1-one 1z. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 2-bromo-5-iodoanilin, overall yield 4%, 138.7 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.29. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.5 Hz, 2H), 7.66 – 7.58 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.31 (m, 3H), 7.20 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.84 (s, 1H), 3.74 (t, *J* = 6.3 Hz, 4H), 2.43 (s, 3H), 2.02 (t, *J* = 6.3 Hz, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.9, 151.7, 145.2, 140.8, 138.4, 137.5, 137.4, 133.5, 129.2, 128.7, 128.6, 128.5, 127.9, 124.3, 115.6, 112.5, 102.2, 97.8, 92.6, 50.6, 25.8, 21.5. **HRMS** (ESI) calcd for $C_{26}H_{24}NO^+$ *m/z* 366.1852 $[M+H]^+$, Found 366.1863.



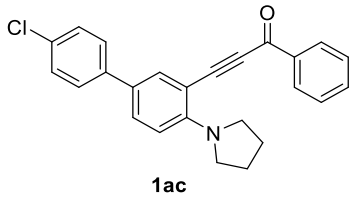
1aa

3-(3'-methoxy-3-(pyrrolidin-1-yl)-[1,1'-biphenyl]-4-yl)-1-phenylprop-2-yn-1-one 1aa. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 10:1) as an orange solid (starting from 2-bromo-5-iodoanilin, overall yield 4%, 152.4 mg). R_f (petroleum ether/ethyl acetate = 20:1): 0.28. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.5 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.18 (m, 2H), 6.99 – 6.93 (m, 2H), 6.88 (s, 1H), 3.90 (s, 3H), 3.77 (t, *J* = 6.0 Hz, 4H), 2.04 (t, *J* = 6.3 Hz, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.7, 159.7, 151.5, 144.7, 142.2, 137.5, 137.3, 133.5, 129.7, 129.1, 128.4, 119.5, 115.4, 112.9, 112.9, 112.4, 102.2, 97.6, 92.5, 55.2, 50.5, 25.7. **HRMS** (ESI) calcd for $C_{26}H_{24}NO_2^+$ *m/z* 382.1802 $[M+H]^+$, Found 382.1797.



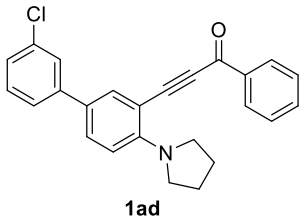
1ab

3-(4'-(tert-butyl)-4-(pyrrolidin-1-yl)-[1,1'-biphenyl]-3-yl)-1-phenylprop-2-yn-1-one 1ab. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 2-bromo-4-iodoanilin, overall yield 4%, 142.5 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.33. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.5 Hz, 2H), 7.78 (s, 1H), 7.62 – 7.45 (m, 8H), 6.74 (d, *J* = 8.7 Hz, 1H), 3.75 – 3.67 (m, 4H), 2.05 – 1.97 (m, 4H), 1.36 (s, 9H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 177.9, 150.7, 149.5, 137.4, 136.9, 135.0, 133.6, 130.9, 129.2, 129.1, 128.5, 125.8, 125.7, 114.5, 103.5, 97.5, 91.9, 50.6, 34.5, 31.4, 25.9. **HRMS** (ESI) calcd for $C_{29}H_{30}NO^+$ *m/z* 408.2322 $[M+H]^+$, Found 408.2338.



1ac

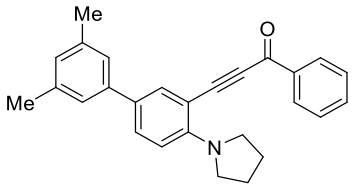
3-(4'-chloro-4-(pyrrolidin-1-yl)-[1,1'-biphenyl]-3-yl)-1-phenylprop-2-yn-1-one 1ac. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 2-bromo-4-iodoanilin, overall yield 4%, 150.2 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.35. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 2.1 Hz, 1H), 7.61 (d, *J* = 6.9 Hz, 1H), 7.54 – 7.45 (m, 5H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 1H), 3.71 (t, *J* = 6.0 Hz, 4H), 2.01 (t, *J* = 6.0 Hz, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.9, 150.7, 138.1, 137.2, 134.9, 133.7, 132.3, 130.6, 129.2, 128.8, 128.5, 127.6, 127.2, 114.6, 103.3, 97.1, 91.9, 50.6, 25.8. **HRMS** (ESI) calcd for $C_{25}H_{21}ClNO^+$ *m/z* 386.1306 $[M+H]^+$, Found 386.1314.



1ad

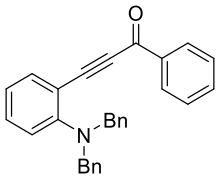
3-(3'-chloro-4-(pyrrolidin-1-yl)-[1,1'-biphenyl]-3-yl)-1-phenylprop-2-yn-1-one 1ad. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an

orange solid (starting from 2-bromo-4-iodoanilin, overall yield 4%, 154.4 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.18. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 2.1 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.54 – 7.40 (m, 5H), 7.35 – 7.25 (m, 2H), 6.70 (d, *J* = 9.0 Hz, 1H), 3.71 (t, *J* = 6.3 Hz, 4H), 2.00 (t, *J* = 6.3 Hz, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.9, 150.9, 141.5, 137.3, 135.1, 134.6, 133.7, 130.7, 130.0, 129.2, 128.5, 127.4, 126.4, 126.1, 124.1, 114.6, 103.4, 97.0, 91.9, 50.6, 25.8. **HRMS** (ESI) calcd for $C_{25}H_{21}ClNO^+$ *m/z* 386.1306 $[M+H]^+$, Found 386.1303.



1ae

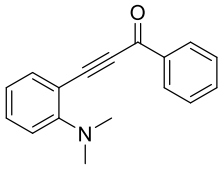
3-(3',5'-dimethyl-4-(pyrrolidin-1-yl)-[1,1'-biphenyl]-3-yl)-1-phenylprop-2-yn-1-one 1ae. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (starting from 2-bromo-4-iodoaniline, overall yield 6%, 227.5 mg). R_f (petroleum ether/ethyl acetate = 50:1): 0.25. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 1.8 Hz, 1H), 7.64 – 7.45 (m, 4H), 7.18 (s, 2H), 6.96 (s, 1H), 6.73 (d, *J* = 9.0 Hz, 1H), 3.72 (t, *J* = 6.0 Hz, 4H), 2.39 (s, 6H), 2.02 (t, *J* = 6.0 Hz, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 150.7, 139.7, 138.3, 135.2, 133.7, 131.1, 129.3, 129.2, 128.9, 128.5, 128.2, 124.1, 114.4, 103.3, 97.6, 91.9, 50.6, 25.9, 21.4, C=O was not detected. **HRMS** (ESI) calcd for $C_{27}H_{26}NO^+$ *m/z* 380.2009 $[M+H]^+$, Found 380.2014.



1af

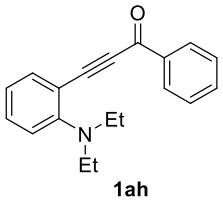
3-(2-(dibenzylamino)phenyl)-1-phenylprop-2-yn-1-one 1af. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (31%, 124.5 mg). R_f (petroleum ether/ethyl acetate = 3:1): 0.25. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.23 (m, 11H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.47 (s, 4H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 178.0, 154.7, 137.5, 137.1, 136.2,

133.8, 131.6, 129.5, 128.5, 128.4, 128.3, 127.2, 121.5, 121.1, 113.4, 93.1, 92.6, 56.0. HRMS (ESI) calcd for $C_{29}H_{24}NO^+$ m/z 402.1852 $[M+H]^+$, Found 402.1852.



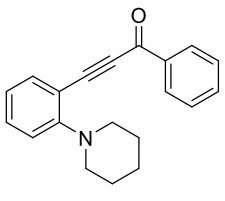
1ag

3-(2-(dimethylamino)phenyl)-1-phenylprop-2-yn-1-one 1ag. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 5:1) as an orange liquid (starting from 2-bromo-4-iodoaniline, overall yield 18%, 443.2 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 – 8.20 (m, 2H), 7.65 – 7.59 (m, 2H), 7.55 – 7.49 (m, 2H), 7.39 – 7.33 (m, 1H), 6.97 – 6.85 (m, 2H), 3.05 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 178.1, 156.7, 137.2, 136.2, 133.8, 131.9, 129.5, 128.5, 120.0, 116.9, 110.6, 94.0, 92.8, 43.6. **HRMS** (ESI) calcd for $C_{19}H_{20}NO^+$ *m/z* 250.1226 $[M+H]^+$, Found 250.1231.



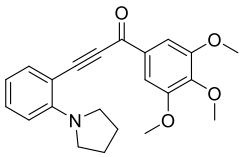
1ah

3-(2-(diethylamino)phenyl)-1-phenylprop-2-yn-1-one 1ah. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 5:1) as an orange solid (starting from 2-bromo-4-iodoaniline, overall yield 14%, 308.6 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.21. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 6.8 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.53 – 7.46 (m, 2H), 7.37 – 7.31 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 3.41 (q, *J* = 7.1 Hz, 4H), 1.14 (t, *J* = 7.2 Hz, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 178.1, 154.7, 137.3, 136.1, 133.7, 131.6, 129.6, 128.4, 120.2, 119.5, 112.3, 94.4, 91.9, 46.2, 12.4. **HRMS** (ESI) calcd for $C_{19}H_{20}NO^+$ *m/z* 278.1539 $[M+H]^+$, Found 278.1538.



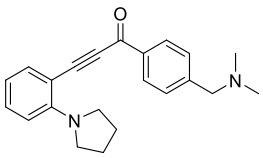
1ai

1-phenyl-3-(2-(piperidin-1-yl)phenyl)prop-2-yn-1-one 1ai. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: PE to 50:1) as an orange solid (69%, 198.6 mg). R_f (petroleum ether/ethyl acetate = 3:1): 0.25. R_f (petroleum ether/ethyl acetate = 50:1): 0.24. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.4 Hz, 2H), 7.66 – 7.58 (m, 2H), 7.55 – 7.47 (m, 2H), 7.42 – 7.35 (m, 1H), 7.04 – 6.93 (m, 2H), 3.23 – 3.11 (m, 4H), 1.82 – 1.72 (m, 4H), 1.63 – 1.54 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 178.0, 157.6, 137.1, 135.5, 133.8, 131.9, 129.8, 128.4, 121.3, 118.3, 113.6, 93.2, 92.2, 53.4, 26.2, 24.1. **HRMS** (ESI) calcd for $C_{20}H_{20}NO^+$ *m/z* 290.1539 $[M+H]^+$, Found 290.1543.



1aj

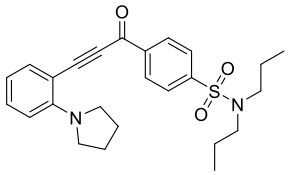
3-(2-(pyrrolidin-1-yl)phenyl)-1-(3,4,5-trimethoxyphenyl)prop-2-yn-1-one 1aj. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as an orange solid (50%, 181.3 mg). R_f (petroleum ether/ethyl acetate = 3:1): 0.25. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.44 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.77 – 6.59 (m, 2H), 4.00 – 3.90 (m, 9H), 3.67 (t, *J* = 6.4 Hz, 4H), 1.99 (t, *J* = 6.4 Hz, 4H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.8, 153.0, 151.6, 143.0, 136.9, 132.8, 132.1, 116.3, 114.0, 106.5, 103.4, 97.4, 91.9, 61.0, 56.2, 50.6, 25.9. **HRMS** (ESI) calcd for $C_{22}H_{24}NO_4^+$ *m/z* 366.1700 $[M+H]^+$, Found 366.1702.



1ak

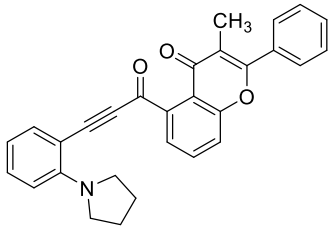
1-(4-((dimethylamino)methyl)phenyl)-3-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 1ak. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 1:1) as an orange oil (59%, 195.0 mg). R_f (petroleum ether/ethyl acetate = 3:1): 0.46. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.53 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.72 – 6.57 (m, 2H), 3.63 (t, *J* = 6.4 Hz, 4H), 3.50 (s, 2H), 2.26 (s, 6H), 2.02 – 1.86 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 177.6, 151.5, 145.3, 137.1, 136.5, 132.1, 129.3, 129.0, 116.2, 114.0, 103.4, 97.3,

92.1, 64.0, 50.5, 45.5, 25.8. **HRMS** (ESI) calcd for $C_{22}H_{25}N_2O^+$ *m/z* 333.1961 $[M+H]^+$, Found 333.1964.



1al

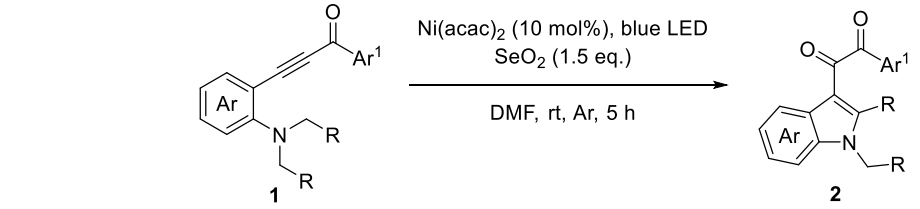
***N*,*N*-dipropyl-4-(3-(2-(pyrrolidin-1-yl)phenyl)propioloyl)benzenesulfonamide 1al.** The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as an orange solid (24%, 105.3 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.20. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.35 – 7.26 (m, 1H), 6.67 (t, *J* = 7.2 Hz, 2H), 3.66 (t, *J* = 6.0 Hz, 4H), 3.11 (t, *J* = 7.5 Hz, 4H), 2.00 (t, *J* = 6.3 Hz, 4H), 1.62 – 1.47 (m, 4H), 0.87 (t, *J* = 7.5 Hz, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.2, 151.8, 144.4, 140.0, 137.2, 132.6, 129.6, 127.1, 116.3, 114.1, 102.5, 99.7, 92.2, 50.6, 49.9, 25.8, 21.9, 11.1. **HRMS** (ESI) calcd for $C_{25}H_{31}N_2O_3S^+$ *m/z* 439.2050 $[M+H]^+$, Found 439.2046.



1am

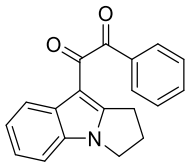
3-methyl-2-phenyl-5-(3-(2-(pyrrolidin-1-yl)phenyl)propioloyl)-4H-chromen-4-one 1am. The product was purified by flash column chromatography on silica gel (height 16 cm, width 2.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 5:1) as an orange solid (64%, 277.3 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.21. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.8 Hz, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.52 – 7.39 (m, 4H), 7.19 (t, *J* = 8.1 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 8.7 Hz, 1H), 6.48 (t, *J* = 7.5 Hz, 1H), 3.56 (t, *J* = 6.3 Hz, 4H), 2.25 (s, 3H), 1.91 (t, *J* = 6.3 Hz, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 178.1, 174.6, 161.1, 154.0, 151.6, 136.9, 135.9, 132.6, 132.2, 130.9, 130.4, 129.3, 128.3, 127.8, 124.0, 123.1, 117.7, 116.0, 113.7, 102.6, 98.7, 93.9, 50.4, 25.7, 11.8. **HRMS** (ESI) calcd for $C_{29}H_{24}NO_3^+$ *m/z* 434.1751 $[M+H]^+$, Found 434.1748.

5. General procedure for the synthesis of derivatives 2.



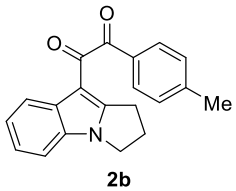
An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with **1** (0.2 mmol, 1.0 equiv.), $Ni(acac)_2$ (5.1 mg, 0.02 mmol, 0.1 equiv.), SeO_2 (33.3 mg, 0.3 mmol, 1.5 equiv.) and DMF (2 mL) under Ar. The reaction mixture was stirred at room temperature under the irradiation of 15 W blue LED for 5 h. Then the volatiles were removed, and the residue was purified by flash column chromatography on silica gel to afford the desired products **2**.

6. Purification and characterization of derivatives 2.



2a

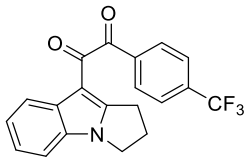
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-phenylethane-1,2-dione 2a. Starting from **1a**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (76%, 43.9 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 6.0 Hz, 1H), 8.15 – 8.01 (m, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.24 (m, 3H), 4.09 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.66 – 2.48 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.1, 188.2, 155.5, 134.3, 133.19, 133.17, 130.6, 130.0, 128.8, 123.18, 123.17, 122.3, 110.1, 106.4, 44.7, 26.5, 26.3. **HRMS** (ESI) calcd for $C_{19}H_{16}NO_2^+$ *m/z* 290.1176 $[M+H]^+$, Found 290.1171.



2b

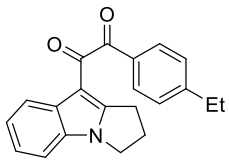
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(p-tolyl)ethane-1,2-dione 2b. Starting from **1b**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (70%, 42.3 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.23. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.8 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.34

– 7.25 (m, 5H), 4.09 (t, *J* = 7.2 Hz, 2H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.63 – 2.50 (m, 2H), 2.42 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.0, 188.5, 155.4, 145.4, 133.2, 130.8, 130.7, 130.2, 129.6, 123.2, 123.2, 122.5, 110.0, 106.5, 44.8, 26.6, 26.4, 21.9. **HRMS** (ESI) calcd for $C_{20}H_{17}NNaO_2^+$ *m/z* 326.1151 $[M+Na]^+$, Found 326.1161.



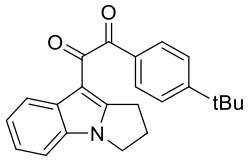
2c

1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(4-(trifluoromethyl)phenyl)ethane-1,2-dione 2c. Starting from **1c**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (57%, 40.7 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.19 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.27 (m, 3H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H), 2.72 – 2.56 (m, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.8 (s). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.5, 186.8, 155.8, 136.0, 135.3 (q, *J* = 33.3 Hz), 133.3, 130.7, 130.4, 125.9 (q, *J* = 4.0 Hz), 123.5 (q, *J* = 274.7 Hz), 123.5, 123.5, 122.4, 110.2, 106.3, 44.8, 26.8, 26.3. **HRMS** (ESI) calcd for $C_{20}H_{14}F_3NNaO_2^+$ *m/z* 380.0869 $[M+Na]^+$, Found 380.0877.



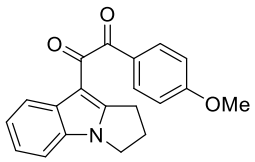
2d

1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(4-ethylphenyl)ethane-1,2-dione 2d. Starting from **1d**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (73%, 46.3 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.21. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.26 (m, 5H), 4.11 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.72 (q, *J* = 7.5 Hz, 2H), 2.64 – 2.52 (m, 2H), 1.26 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 195.0, 188.5, 155.5, 151.5, 133.2, 131.0, 130.7, 130.3, 128.4, 123.2, 123.1, 122.5, 110.0, 106.5, 44.7, 29.1, 26.6, 26.3, 15.0. **HRMS** (ESI) calcd for $C_{21}H_{19}NNaO_2^+$ *m/z* 340.1308 $[M+Na]^+$, Found 340.1307.



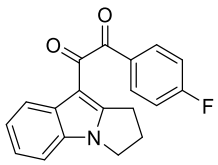
2e

1-(4-(tert-butyl)phenyl)-2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione 2e. Starting from **1e**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (71%, 49.0 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.24. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 6.6 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.25 (m, 3H), 4.12 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H), 2.67 – 2.51 (m, 2H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 195.0, 188.5, 158.2, 155.5, 133.2, 130.8, 130.7, 130.0, 125.8, 123.2, 123.1, 122.5, 110.0, 106.5, 44.7, 35.3, 31.0, 26.6, 26.4. **HRMS** (ESI) calcd for $C_{23}H_{23}NNaO_2^+$ *m/z* 368.1621 $[M+Na]^+$, Found 368.1624.



2f

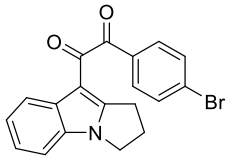
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(4-methoxyphenyl)ethane-1,2-dione 2f. Starting from **1f**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (64%, 40.8 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.14. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 2H), 7.34 – 7.25 (m, 3H), 6.95 (d, *J* = 8.7 Hz, 2H), 4.10 (t, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.65 – 2.51 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 194.0, 188.7, 164.5, 155.4, 133.2, 132.4, 130.7, 126.2, 123.1, 123.1, 122.4, 114.2, 110.0, 106.5, 55.5, 44.7, 26.5, 26.3. **HRMS** (ESI) calcd for $C_{20}H_{18}NO_3^+$ *m/z* 320.1281 $[M+H]^+$, Found 320.1281.



2g

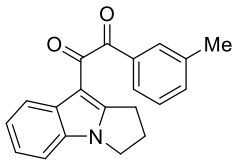
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(4-fluorophenyl)ethane-1,2-dione 2g. Starting from **1g**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (65%, 39.9 mg). R_f (petroleum ether/ethyl acetate = 5:1):

0.24. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.17 – 8.05 (m, 2H), 7.36 – 7.26 (m, 3H), 7.16 (t, *J* = 8.4 Hz, 2H), 4.12 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.67 – 2.53 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.1 (s). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.4, 187.7, 166.5 (d, *J* = 258.6 Hz), 155.6, 133.2, 132.8 (d, *J* = 10.1 Hz), 130.7, 129.7 (d, *J* = 3.0 Hz), 123.3, 123.3, 122.4, 116.1 (d, *J* = 22.2 Hz), 110.1, 106.4, 44.8, 26.7, 26.3. **HRMS** (ESI) calcd for $C_{19}H_{15}FNO_2^+$ *m/z* 308.1081 $[M+H]^+$, Found 308.1089.



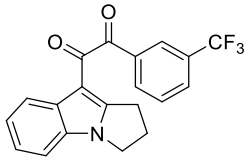
2h

1-(4-bromophenyl)-2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione 2h. Starting from **1h**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (62%, 45.5 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.09 – 7.87 (m, 2H), 7.69 – 7.42 (m, 2H), 7.38 – 7.22 (m, 3H), 4.10 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.69 – 2.45 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 193.7, 187.4, 155.6, 140.8, 133.2, 132.2, 131.6, 131.4, 131.4, 129.2, 123.3, 122.4, 110.1, 106.3, 44.8, 26.7, 26.3. **HRMS** (ESI) calcd for $C_{19}H_{14}BrNNaO_2^+$ *m/z* 390.0100 $[M+Na]^+$, Found 390.0094.



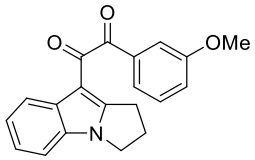
2i

1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(m-tolyl)ethane-1,2-dione 2i. Starting from **1i**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (70%, 42.4 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.23. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.36 (d, *J* = 6.3 Hz, 1H), 7.93 – 7.79 (m, 2H), 7.55 – 7.12 (m, 5H), 4.11 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.5 Hz, 2H), 2.65 – 2.51 (m, 2H), 2.40 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 195.4, 188.4, 155.5, 138.7, 135.1, 133.18, 133.18, 130.7, 130.4, 128.7, 127.2, 123.17, 123.15, 122.4, 110.0, 106.4, 44.7, 26.5, 26.3, 21.2. **HRMS** (ESI) calcd for $C_{20}H_{17}NNaO_2^+$ *m/z* 326.1151 $[M+Na]^+$, Found 326.1148.



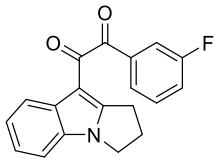
2j

1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(3-(trifluoromethyl)phenyl)ethane-1,2-dione 2j. Starting from **1j**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (65%, 46.4 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.55 – 8.05 (m, 3H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.48 – 7.25 (m, 3H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.5 Hz, 2H), 2.77 – 2.50 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.8 (s). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.1, 186.7, 155.8, 134.0, 133.4, 133.3, 131.6 (q, *J* = 33.3 Hz), 130.7, 130.5 (q, *J* = 4.0 Hz), 129.5, 126.6 (q, *J* = 4.0 Hz), 123.53 (q, *J* = 273.7 Hz), 123.48, 123.46, 122.5, 110.2, 106.3, 44.8, 26.8, 26.3. **HRMS** (ESI) calcd for $C_{20}H_{15}F_3NO_2^+$ *m/z* 358.1049 $[M+H]^+$, Found 358.1050.



2k

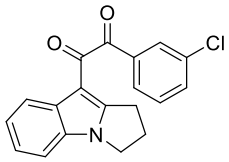
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(3-methoxyphenyl)ethane-1,2-dione 2k. Starting from **1k**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (70%, 44.7 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.15. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.87 (d, *J* = 6.0 Hz, 2H), 7.47 – 7.27 (m, 5H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.66 – 2.54 (m, 2H), 2.40 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.5, 188.4, 155.5, 138.7, 135.2, 133.2, 130.7, 130.4, 128.8, 127.3, 123.2, 123.2, 122.5, 110.0, 106.5, 46.0, 44.8, 26.6, 26.4, one carbon was overlapped. **HRMS** (ESI) calcd for $C_{20}H_{17}NNaO_3^+$ *m/z* 342.1101 $[M+Na]^+$, Found 342.1104.



2l

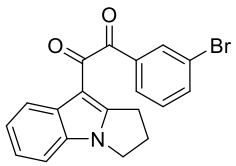
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(3-fluorophenyl)ethane-1,2-dione 2l. Starting from **1l**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient:

20:1 to 5:1) as a yellow solid (65%, 39.9 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.24. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.53 – 7.41 (m, 1H), 7.37 – 7.24 (m, 4H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.68 – 2.50 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.7 (s). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.6, 187.2, 162.9 (d, *J* = 250.5 Hz), 155.7, 135.4 (d, *J* = 6.1 Hz), 133.3, 130.7, 130.6 (d, *J* = 7.1 Hz), 126.1 (d, *J* = 3.0 Hz), 123.4, 123.4, 122.4, 121.4 (d, *J* = 22.2 Hz), 116.3 (d, *J* = 22.2 Hz), 110.1, 106.3, 44.8, 26.7, 26.3. **HRMS** (ESI) calcd for $C_{19}H_{14}FNNaO_2^+$ *m/z* 330.0901 $[M+Na]^+$, Found 330.0904.



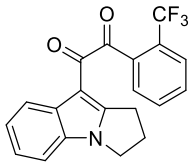
2m

1-(3-chlorophenyl)-2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione 2m. Starting from **1m**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (63%, 40.7 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.05 (s, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.27 (m, 3H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.67 – 2.55 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 193.5, 187.1, 155.7, 135.2, 134.9, 134.2, 133.3, 130.7, 130.2, 129.7, 128.3, 123.4, 123.4, 122.5, 110.1, 106.3, 44.8, 26.7, 26.3. **HRMS** (ESI) calcd for $C_{19}H_{15}ClNO_2^+$ *m/z* 324.0786 $[M+H]^+$, Found 324.0779.



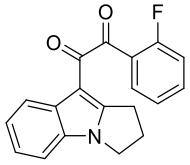
2n

1-(3-bromophenyl)-2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione 2n. Starting from **1n**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (64%, 47.1 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.23. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.20 (t, *J* = 1.5 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.41 – 7.26 (m, 4H), 4.12 (t, *J* = 7.2 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.68 – 2.52 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.4, 187.0, 155.7, 137.1, 135.0, 133.2, 132.6, 130.6, 130.4, 128.7, 123.4, 123.3, 123.1, 122.4, 110.1, 106.2, 44.8, 26.7, 26.3. **HRMS** (ESI) calcd for $C_{19}H_{15}BrNO_2^+$ *m/z* 368.0281 $[M+H]^+$, Found 368.0272.



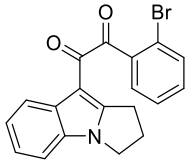
2o

1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(2-(trifluoromethyl)phenyl)ethane-1,2-dione 2o. Starting from **1o**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (60%, 42.8 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.39 (d, *J* = 5.7 Hz, 1H), 7.97 – 7.62 (m, 4H), 7.43 – 7.25 (m, 3H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.29 (t, *J* = 7.2 Hz, 2H), 2.86 – 2.55 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.9 (s). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.8, 184.8, 156.1, 135.5 (q, *J* = 1.0 Hz), 133.2, 131.7, 131.6, 131.3, 131.1, 128.7 (q, *J* = 33.3 Hz), 126.9 (q, *J* = 5.1 Hz), 123.5 (q, *J* = 274.7 Hz), 123.31, 123.25, 122.6, 110.1, 105.9, 44.8, 27.4, 26.3. **HRMS** (ESI) calcd for $C_{20}H_{15}F_3NO_2^+$ *m/z* 358.1049 $[M+H]^+$, Found 358.1052.



2p

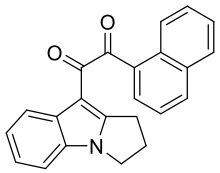
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(2-fluorophenyl)ethane-1,2-dione 2p. Starting from **1p**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (57%, 35.0 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.24. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.54 – 8.12 (m, 1H), 8.02 (t, *J* = 7.2 Hz, 1H), 7.66 – 7.52 (m, 1H), 7.38 – 7.27 (m, 3H), 7.16 – 6.95 (m, 2H), 4.12 (t, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.5 Hz, 2H), 2.67 – 2.50 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.9 (s). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 196.4, 186.6, 143.2, 140.2, 135.7, 132.9, 132.0, 130.7, 130.3, 129.2, 127.8, 127.3 (d, *J* = 6.8 Hz), 122.8 (d, *J* = 5.3 Hz), 109.7, 106.5, 44.6, 27.2, 26.4, one carbon was overlapped. **HRMS** (ESI) calcd for $C_{19}H_{15}FNO_2^+$ *m/z* 308.1081 $[M+H]^+$, Found 308.1084.



2q

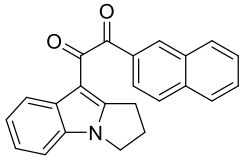
1-(2-bromophenyl)-2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione 2q. Starting from **1q**. The product was purified by flash column chromatography on

silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (60%, 44.0 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 3.6 Hz, 1H), 7.78 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.45 – 7.34 (m, 2H), 7.31 – 7.24 (m, 3H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.19 (t, *J* = 7.2 Hz, 2H), 2.68 – 2.56 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 194.5, 185.6, 155.6, 136.5, 133.8, 133.5, 133.2, 132.6, 131.2, 127.5, 123.1, 123.1, 122.5, 121.4, 110.0, 106.2, 44.8, 27.3, 26.4. **HRMS** (ESI) calcd for $C_{19}H_{15}BrNO_2^+$ *m/z* 368.0281 $[M+H]^+$, Found 368.0290.



2r

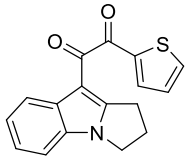
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(naphthalen-1-yl)ethane-1,2-dione 2r. Starting from **1r**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (67%, 45.4 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.7 Hz, 1H), 8.37 (s, 1H), 8.11 (t, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.27 (m, 3H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.63 – 2.44 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 197.8, 188.7, 155.5, 135.3, 134.8, 134.1, 133.2, 131.4, 129.1, 128.8, 128.7, 126.8, 126.1, 124.5, 123.2, 123.2, 122.5, 110.0, 106.7, 44.8, 26.6, 26.4, one carbon was overlapped. **HRMS** (ESI) calcd for $C_{23}H_{18}NO_2^+$ *m/z* 340.1332 $[M+H]^+$, Found 340.1329.



2s

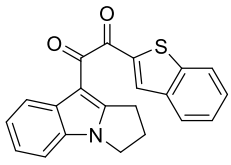
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(naphthalen-2-yl)ethane-1,2-dione 2s. Starting from **1s**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (65%, 44.1 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.41 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.04 – 7.77 (m, 3H), 7.69 – 7.47 (m, 2H), 7.44 – 7.27 (m, 3H), 4.10 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.63 – 2.44 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.4, 188.4, 155.6, 136.2, 133.4, 133.2, 132.4, 130.7, 130.5, 129.9, 129.1, 128.9,

127.8, 126.9, 124.0, 123.3, 123.2, 122.5, 110.1, 106.6, 44.8, 26.6, 26.3. **HRMS** (ESI) calcd for $C_{23}H_{18}NO_2^+$ *m/z* 340.1332 $[M+H]^+$, Found 340.1332.



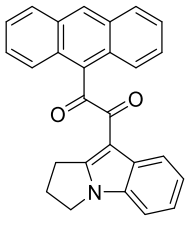
2t

1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(thiophen-2-yl)ethane-1,2-dione 2t. Starting from **1t**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (74%, 43.7 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.19. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 3.9 Hz, 1H), 7.78 (d, *J* = 5.1 Hz, 1H), 7.40 – 7.26 (m, 3H), 7.16 (t, *J* = 4.2 Hz, 1H), 4.12 (t, *J* = 7.2 Hz, 2H), 3.12 (t, *J* = 7.5 Hz, 2H), 2.69 – 2.51 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 186.9, 186.0, 155.9, 140.1, 136.3, 136.0, 133.2, 131.0, 128.6, 123.2, 123.2, 122.5, 110.0, 105.9, 44.8, 27.0, 26.3. **HRMS** (ESI) calcd for $C_{17}H_{14}NO_2S^+$ *m/z* 296.0740 $[M+H]^+$, Found 296.0739.



2u

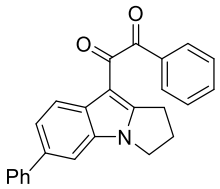
1-(benzo[b]thiophen-2-yl)-2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione 2u. Starting from **1u**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (53%, 36.6 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.40 (d, *J* = 6.3 Hz, 1H), 8.16 (s, 1H), 7.99 – 7.79 (m, 2H), 7.58 – 7.27 (m, 5H), 4.12 (t, *J* = 7.2 Hz, 2H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.68 – 2.53 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 188.8, 185.7, 156.0, 143.3, 139.8, 139.1, 134.3, 133.2, 130.9, 128.1, 126.5, 125.2, 123.4, 123.3, 123.0, 122.6, 110.1, 106.0, 44.8, 27.0, 26.3. **HRMS** (ESI) calcd for $C_{21}H_{15}NNaO_2S^+$ *m/z* 368.0716 $[M+Na]^+$, Found 368.0715.



2v

1-(anthracen-9-yl)-2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione

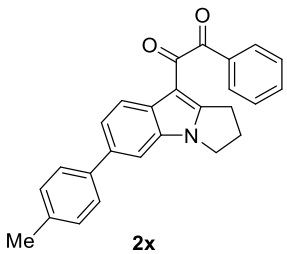
2v. Starting from **1v**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (50%, 38.9 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.19. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.39 (m, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.26 – 7.21 (m, 3H), 7.20 – 6.81 (m, 3H), 4.11 (t, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.5 Hz, 2H), 2.69 – 2.47 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 196.4, 186.6, 143.2, 140.2, 135.7, 132.9, 132.0, 130.7, 130.3, 129.2, 127.8, 127.3, 127.2, 122.8, 122.8, 122.5, 109.7, 106.5, 44.6, 27.2, 26.4.



2w

1-phenyl-2-(6-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione

2w. Starting from **1w**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (71%, 51.8 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.21. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.08 (d, *J* = 7.2 Hz, 2H), 7.73 – 7.31 (m, 10H), 4.17 (t, *J* = 6.9 Hz, 2H), 3.03 (t, *J* = 6.3 Hz, 2H), 2.72 – 2.50 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.1, 188.1, 156.1, 141.5, 136.8, 134.3, 133.8, 133.2, 130.1, 128.9, 128.8, 127.3, 127.0, 122.9, 122.6, 108.5, 106.5, 44.8, 26.7, 26.4, one carbon was overlapped. **HRMS** (ESI) calcd for $C_{25}H_{20}NO_2^+$ *m/z* 366.1489 $[M+H]^+$, Found 366.1490.

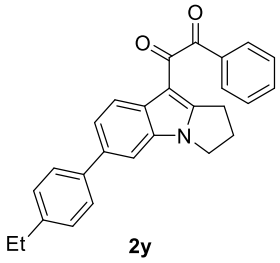


2x

1-phenyl-2-(6-(p-tolyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione

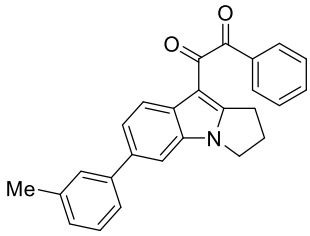
2x. Starting from **1x**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (73%, 55.4 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.69 – 7.42 (m, 7H), 7.27 (d, *J* = 7.5 Hz, 2H), 4.17 (t, *J* = 6.9 Hz, 2H), 3.03 (t, *J* = 6.9 Hz,

2H), 2.74 – 2.53 (m, 2H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.2, 188.1, 156.0, 138.6, 136.8, 136.8, 134.3, 133.9, 133.2, 130.1, 129.7, 129.5, 128.9, 127.1, 122.8, 122.6, 108.3, 106.5, 44.8, 26.7, 26.4, 21.1. **HRMS** (ESI) calcd for $C_{26}H_{22}NO_2^+$ *m/z* 380.1645 $[M+H]^+$, Found 380.1642.



2y

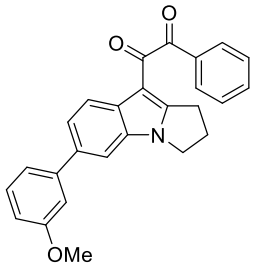
1-(6-(4-ethylphenyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-phenylethane-1, 2-dione 2y. Starting from **1y**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (78%, 61.3 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.20. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.77 – 7.34 (m, 7H), 7.28 – 7.22 (m, 2H), 4.13 (t, *J* = 7.2 Hz, 2H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.76 – 2.51 (m, 4H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.2, 188.1, 156.0, 143.2, 138.8, 136.8, 134.3, 133.8, 133.2, 130.0, 129.7, 128.9, 128.3, 127.2, 122.8, 122.5, 108.3, 106.5, 46.1, 44.8, 28.5, 26.7, 26.4. **HRMS** (ESI) calcd for $C_{27}H_{24}NO_2^+$ *m/z* 394.1802 $[M+H]^+$, Found 394.1811.



2z

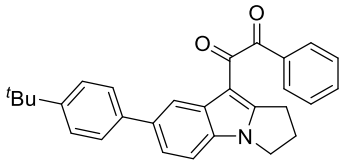
1-phenyl-2-(6-(m-tolyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione 2z. Starting from **1z**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (51%, 38.7 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.21. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 2H), 7.67 – 7.45 (m, 7H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 4.17 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.69 – 2.56 (m, 2H), 2.45 (s, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.2, 188.1, 156.0, 141.4, 138.4, 136.9, 134.3, 133.8, 133.2, 130.1, 128.9, 128.7, 128.1, 127.8, 124.4, 122.9, 108.5, 44.8, 26.7, 26.4, 21.6, three carbons

were overlapped. **HRMS** (ESI) calcd for $C_{26}H_{22}NO_2^+$ *m/z* 380.1645 $[M+H]^+$, Found 380.1635.



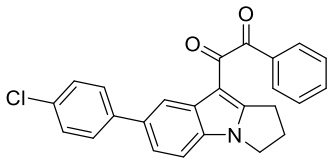
2aa

1-(6-(3-methoxyphenyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-phenylethane-1,2-dione 2aa. Starting from **1aa**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 3:1) as a yellow solid (60%, 47.4 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.16. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 2H), 7.66 – 7.47 (m, 5H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.16 (m, 2H), 6.91 (d, *J* = 6.9 Hz, 1H), 4.16 (t, *J* = 6.9 Hz, 2H), 3.89 (s, 3H), 3.03 (t, *J* = 6.9 Hz, 2H), 2.67 – 2.54 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.1, 188.1, 159.9, 156.1, 143.0, 142.2, 136.6, 134.3, 133.7, 133.2, 130.0, 129.8, 128.9, 122.9, 122.6, 119.8, 113.2, 112.3, 108.6, 106.4, 55.3, 44.8, 26.7, 26.4. **HRMS** (ESI) calcd for $C_{26}H_{22}NO_3^+$ *m/z* 396.1594 $[M+H]^+$, Found 396.1603.



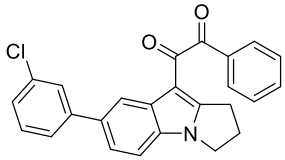
2ab

1-(7-(4-(tert-butyl)phenyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-phenylethane-1,2-dione 2ab. Starting from **1ab**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (63%, 53.1 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.69 – 7.59 (m, 3H), 7.56 – 7.45 (m, 5H), 7.32 (d, *J* = 8.4 Hz, 1H), 4.15 (t, *J* = 6.9 Hz, 2H), 3.02 (t, *J* = 6.9 Hz, 2H), 2.69 – 2.52 (m, 2H), 1.38 (s, 9H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.1, 188.1, 155.9, 149.8, 138.8, 136.6, 134.3, 133.2, 132.5, 131.3, 130.1, 128.9, 127.1, 125.6, 122.7, 120.9, 110.2, 106.7, 44.9, 34.5, 31.4, 26.7, 26.4. **HRMS** (ESI) calcd for $C_{29}H_{27}NNaO_2^+$ *m/z* 444.1934 $[M+Na]^+$, Found 444.1928.



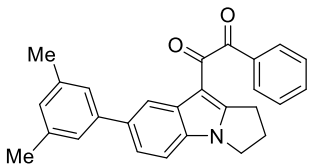
2ac

1-(7-(4-chlorophenyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-phenylethane-1,2-dione 2ac. Starting from **1ac**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (61%, 48.7 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.23. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 3H), 7.50 (t, *J* = 8.1 Hz, 3H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 4.15 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.69 – 2.53 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.0, 188.2, 156.2, 140.2, 135.5, 134.4, 133.2, 132.8, 132.8, 131.4, 130.1, 128.9, 128.8, 128.7, 122.6, 121.0, 110.4, 106.7, 44.9, 26.7, 26.4. **HRMS** (ESI) calcd for $C_{25}H_{19}ClNO_2^+$ *m/z* 400.1099 $[M+H]^+$, Found 400.1108.



2ad

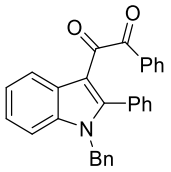
1-(7-(3-chlorophenyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-phenylethane-1,2-dione 2ad. Starting from **1ad**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (60%, 47.9 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.23. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.78 – 7.44 (m, 6H), 7.43 – 7.27 (m, 3H), 4.16 (t, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H), 2.71 – 2.52 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.0, 188.2, 156.2, 143.6, 135.3, 134.5, 134.4, 133.2, 132.9, 131.4, 130.1, 129.9, 128.9, 127.5, 126.8, 125.7, 122.7, 121.2, 110.4, 106.8, 44.9, 26.7, 26.4. **HRMS** (ESI) calcd for $C_{25}H_{19}ClNO_2^+$ *m/z* 400.1099 $[M+H]^+$, Found 400.1103.



2ae

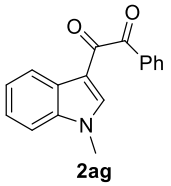
1-(7-(3,5-dimethylphenyl)-2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-phenylethane-1,2-dione 2ae. Starting from **1ae**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum

ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (64%, 50.3 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.20. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.59 – 7.41 (m, 3H), 7.38 – 7.26 (m, 3H), 6.99 (s, 1H), 4.13 (t, *J* = 6.6 Hz, 2H), 3.00 (t, *J* = 6.9 Hz, 2H), 2.70 – 2.52 (m, 2H), 2.40 (s, 6H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 195.1, 188.2, 155.9, 141.6, 138.1, 137.0, 134.3, 133.2, 132.6, 131.2, 130.1, 128.9, 128.5, 125.4, 122.9, 121.0, 110.1, 106.7, 44.9, 26.7, 26.4, 21.4. **HRMS** (ESI) calcd for $C_{27}H_{24}NO_2^+$ *m/z* 394.1802 $[M+H]^+$, Found 394.1808.



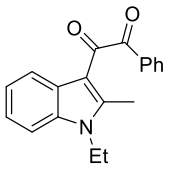
2af

1-(1-benzyl-2-phenyl-1H-indol-3-yl)-2-phenylethane-1,2-dione 2af. Starting from **1af**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) as a yellow solid (79%, 65.9 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.51. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.34 – 7.16 (m, 8H), 7.02 (d, *J* = 4.4 Hz, 4H), 6.88 (d, *J* = 4.8 Hz, 2H), 5.12 (s, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.6, 191.2, 149.9, 136.6, 136.0, 133.6, 133.4, 131.0, 129.7, 129.3, 128.7, 128.7, 128.2, 127.8, 127.6, 126.6, 126.0, 124.3, 123.7, 122.7, 113.0, 110.9, 47.8. **HRMS** (ESI) calcd for $C_{29}H_{22}NO_2^+$ *m/z* 416.1645 $[M+H]^+$, Found 416.1656.



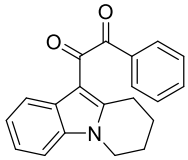
2ag

1-(1-methyl-1H-indol-3-yl)-2-phenylethane-1,2-dione 2ag. Starting from **1ag**, 12 h. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 5:1) as a yellow solid (73%, 38.4 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.24. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56– 8.37 (m, 1H), 8.16 – 8.00 (m, 2H), 7.80 (s, 1H), 7.67 – 7.59 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.33 (m, 3H), 3.83 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.7, 187.5, 139.5, 137.7, 134.3, 133.4, 130.3, 128.7, 126.3, 124.2, 123.5, 122.7, 112.8, 110.0, 33.8. **HRMS** (ESI) calcd for $C_{17}H_{13}NNaO_2^+$ *m/z* 286.0838 $[M+Na]^+$, Found 286.0838.



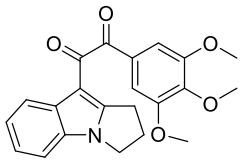
2ah

1-(1-ethyl-2-methyl-1H-indol-3-yl)-2-phenylethane-1,2-dione 2ah. Starting from **1ah**, 12 h. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 3:1) as a yellow solid (62%, 36.1 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.26. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.13 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.68 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 195.4, 190.0, 146.7, 136.0, 134.3, 133.4, 130.1, 128.9, 126.4, 123.0, 123.0, 121.0, 110.7, 109.6, 38.2, 14.6, 12.5. **HRMS** (ESI) calcd for $C_{19}H_{17}NNaO_2^+$ *m/z* 314.1151 $[M+Na]^+$, Found 314.1153.



2ai

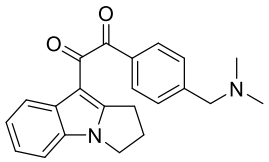
1-phenyl-2-(6,7,8,9-tetrahydropyrido[1,2-a]indol-10-yl)ethane-1,2-dione 2ai. Starting from **1ai**, 24 h. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 5:1) as a brown solid (79%, 47.9 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.22. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 7.92 (m, 3H), 7.69 – 7.61 (m, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.36 – 7.20 (m, 3H), 4.12 (t, *J* = 6.0 Hz, 2H), 3.20 (t, *J* = 6.4 Hz, 2H), 2.19 – 2.03 (m, 2H), 1.98 – 1.83 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 195.5, 189.3, 148.4, 136.5, 134.3, 133.3, 130.0, 128.9, 126.2, 123.4, 122.8, 120.9, 109.6, 109.3, 42.7, 24.9, 22.0, 19.6. **HRMS** (ESI) calcd for $C_{20}H_{18}NO_2^+$ *m/z* 304.1332 $[M+H]^+$, Found 304.1343.



2aj

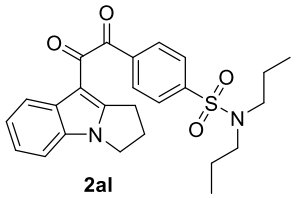
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(3,4,5-trimethoxyphenyl)ethane-1, 2-dione 2aj. Starting from **1aj**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum

ether/ethyl acetate, gradient: 20:1 to 3:1) as a yellow solid (65%, 49.3 mg). R_f (petroleum ether/ethyl acetate = 3:1): 0.43. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.37 – 7.23 (m, 5H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 3.90 (s, 6H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.67 – 2.54 (m, *J* = 7.4 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 194.0, 187.9, 155.6, 153.3, 143.6, 133.1, 130.7, 128.2, 123.2, 123.1, 122.4, 110.0, 107.2, 106.4, 60.9, 56.3, 44.7, 26.6, 26.3. **HRMS** (ESI) calcd for $C_{22}H_{22}NO_5^+$ *m/z* 380.1492 $[M+H]^+$, Found 380.1502.



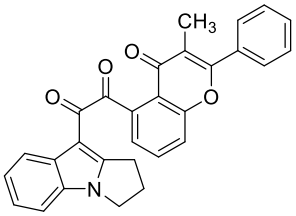
2ak

1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(4-((dimethylamino)methyl)phenyl)ethane-1,2-dione 2ak. Starting from **1ak**. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 3:1) as a yellow solid (88%, 60.9 mg). R_f (petroleum ether/ethyl acetate = 3:1): 0.43. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.35 – 7.23 (m, 3H), 6.66 (d, *J* = 8.8 Hz, 2H), 4.09 (t, *J* = 7.2 Hz, 2H), 3.20 – 2.88 (m, 10H), 2.62 – 2.50 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.7, 189.8, 155.3, 154.1, 133.1, 132.2, 130.8, 122.9, 122.8, 122.4, 120.8, 110.8, 109.9, 106.7, 44.6, 40.0, 26.4, 26.3. one carbon was overlapped. **HRMS** (ESI) calcd for $C_{22}H_{23}N_2O_3^+$ *m/z* 347.1754 $[M+H]^+$, Found 347.1756.



2al

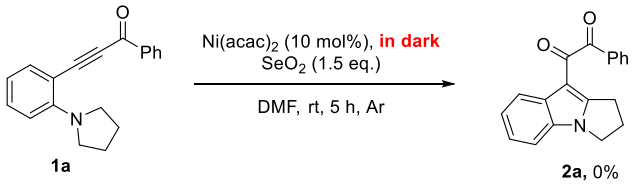
4-(2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-oxoacetyl)-N,N-dipropylbenzen esulfonamide 2al. Starting from **1al**, 40 °C (heating mantle), 12 h. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 5:1) as a yellow solid (74%, 66.9 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.15. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.17 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.24 (m, 3H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.10 (t, *J* = 7.6 Hz, 4H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.67 – 2.53 (m, 2H), 1.62 – 1.49 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 193.3, 186.8, 155.9, 145.1, 136.0, 133.3, 130.6, 127.3, 123.5, 122.4, 110.2, 106.3, 50.0, 44.9, 26.8, 26.3, 22.0, 11.1, two carbon was overlapped. **HRMS** (ESI) calcd for $C_{25}H_{29}N_2O_4S^+$ *m/z* 453.1843 $[M+H]^+$, Found 453.1848.



2am

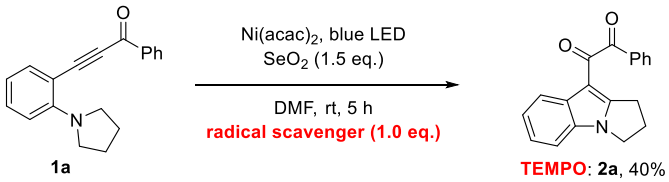
1-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-(3-methyl-4-oxo-2-phenyl-4H-chromen-5-yl)ethane-1,2-dione 2am. Starting from **1am**, 24 h. The product was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 3:1) as a yellow solid (41%, 36.6 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.12. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.29 (d, *J* = 6.8 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 9.2, 5.2 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.16 – 7.02 (m, 3H), 6.71 (s, 2H), 3.92 (t, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.43 – 2.31 (m, 2H), 2.07 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 192.9, 186.1, 177.9, 161.0, 154.6, 135.6, 133.4, 131.9, 131.6, 129.5, 128.6, 127.5, 125.6, 124.8, 123.3, 123.1, 122.8, 118.1, 110.0, 105.7, 44.6, 26.7, 26.3, 11.6, three carbons were overlapped. **HRMS** (ESI) calcd for $C_{29}H_{21}NNaO_4^+$ *m/z* 470.1363 $[M+Na]^+$, Found 470.1371.

7. Procedure for the control experiment.



1a **2a**, 0%

An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with **1a** (55.1 mg, 0.2 mmol, 1.0 equiv.), $Ni(acac)_2$ (5.1 mg, 0.02 mmol, 0.1 equiv.), SeO_2 (33.3 mg, 0.3 mmol, 1.5 equiv.) and DMF (2 mL) under Ar. The reaction mixture was stirred at room temperature in dark for 5 h. No product was detected by the TLC.

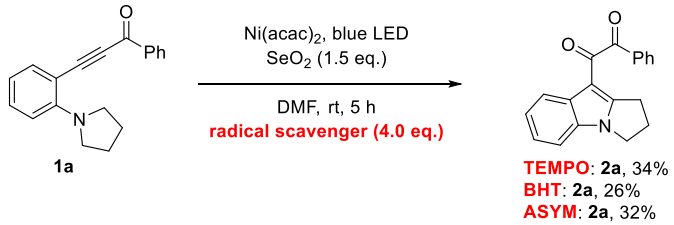


1a

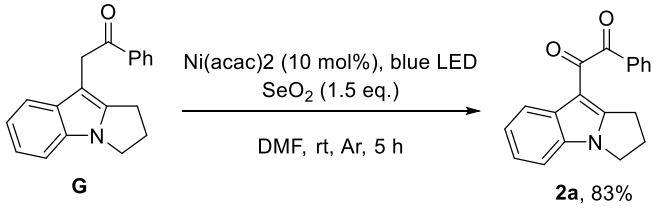
TEMPO: **2a**, 40%
BHT: **2a**, 21%
ASYM: **2a**, 30%

An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with **1a** (55.1 mg, 0.2 mmol, 1.0 equiv.), $Ni(acac)_2$ (5.1 mg, 0.02 mmol, 0.1 equiv.), SeO_2 (33.3 mg, 0.3 mmol, 1.5 equiv.) and DMF (2 mL), followed by radical scavenger (TEMPO, 31.3 mg, 0.2 mmol, 1.0 equiv.; or BHT, 44.1 mg, 0.2 mmol, 1.0

equiv.; or ASYM, 36.1 mg, 0.2 mmol, 1.0 equiv.). The Schlenk tube was vacuumed and purged with air three times before it was tightly screw capped. The reaction mixture was stirred at room temperature under the irradiation of 15 W blue LED for 5 h. Then the volatiles were removed, and the residue was purified by flash column chromatography on silica gel eluting with petroleum ether and ethyl acetate (5:1) to afford the desired product **2a** (when with TEMPO, 23.1 mg, 40%; when with BHT, 12.1 mg, 21%; when with ASYM, 17.3 mg, 30%).



An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with **1a** (55.1 mg, 0.2 mmol, 1.0 equiv.), $Ni(acac)_2$ (5.1 mg, 0.02 mmol, 0.1 equiv.), SeO_2 (33.3 mg, 0.3 mmol, 1.5 equiv.) and DMF (2 mL), followed by radical scavenger (TEMPO, 125.2 mg, 0.8 mmol, 4.0 equiv.; or BHT, 176.4 mg, 0.8 mmol, 4.0 equiv.; or ASYM, 144.4 mg, 0.8 mmol, 4.0 equiv.). The Schlenk tube was vacuumed and purged with air three times before it was tightly screw capped. The reaction mixture was stirred at room temperature under the irradiation of 15 W blue LED for 5 h. Then the volatiles were removed, and the residue was purified by flash column chromatography on silica gel eluting with petroleum ether and ethyl acetate (5:1) to afford the desired product **2a** (when with TEMPO, 19.7 mg, 34%; when with BHT, 15.0 mg, 26%; when with ASYM, 18.5 mg, 32%).



An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with intermediate **G** (0.2 mmol, 1.0 equiv.), $Ni(acac)_2$ (5.1 mg, 0.02 mmol, 0.1 equiv.), SeO_2 (33.3 mg, 0.3 mmol, 1.5 equiv.) and DMF (2 mL) under Ar. The reaction mixture was stirred at room temperature under the irradiation of 15 W blue LED for 5 h. Then the volatiles were removed, and the residue was purified by flash column chromatography on silica gel to afford the desired products **2a**.

2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-1-phenylethan-1-one G. G was isolated from reaction mixture after reaction was set up for 1 h. **^{1}H NMR** (300 MHz,

$CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.68 – 7.38 (m, 4H), 7.27 – 7.06 (m, 3H), 4.35 (s, 2H), 4.02 (t, *J* = 6.9 Hz, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.65 – 2.49 (m, 2H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$) δ 197.6, 142.7, 136.7, 132.8, 132.5, 132.1, 128.5, 128.5, 120.3, 119.0, 118.2, 109.4, 98.1, 43.6, 35.4, 27.6, 23.6. **HRMS** (ESI) calcd for $C_{19}H_{18}NO^+$ *m/z* 276.1383 $[M+H]^+$, Found 276.1377.

EPR experiment

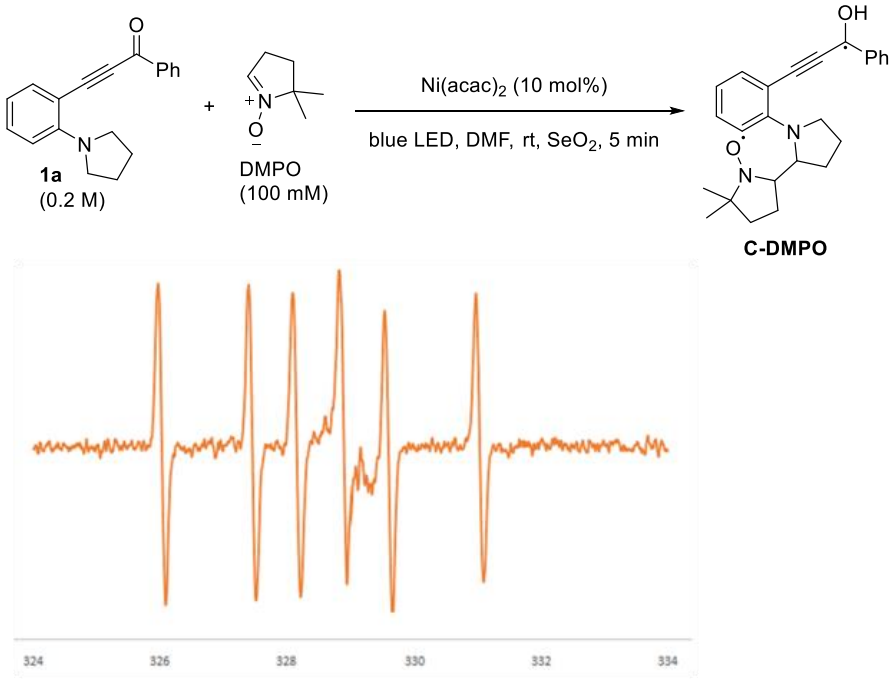


Figure S2. EPR experiment

Spectrophotometric experiments

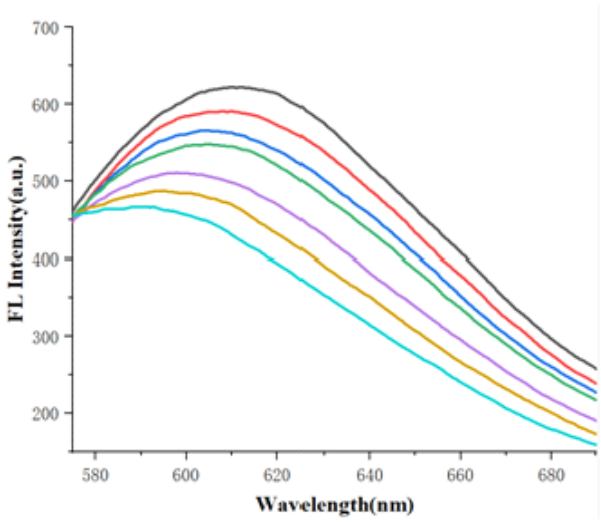
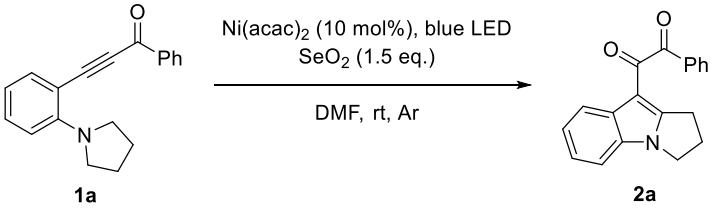


Figure S3. Fluorescent spectra of **1a** (1.00×10^{-1} M) with the addition of various concentration of Ni^{2+} in DMF.

8. Procedure for the ON-OFF Experiments



Ten **1a** as substrate reactions were carried under irradiation of blue LED at room temperature. After 1 h, the blue LED was turned off, one reaction tube was removed from the light source for LC analysis. The remaining nine were kept stirring for another 1 h under blue LED irradiation off. Then another tube was removed for analysis. The remaining eight continued irradiation under blue light for another 1 h. The experiments were cycled as described above.

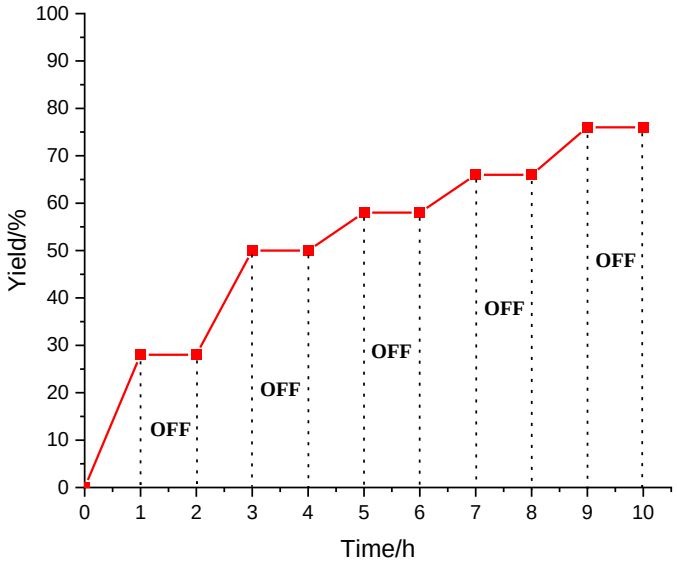
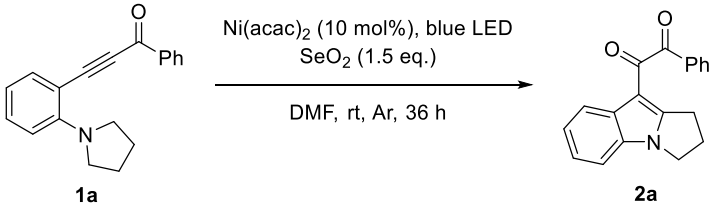


Figure S4. ON/OFF experiments.

9. Procedure for the synthesis of 2a on gram scale.



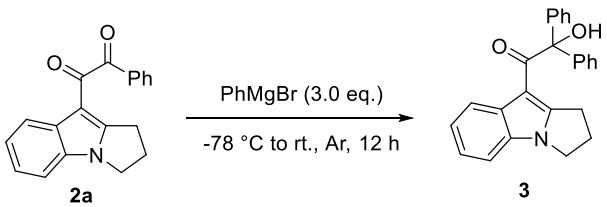
An oven-dried 500 mL Schlenk tube equipped with a stirring bar was charged with **1a** (6.0 mmol, 1.0 equiv.), SeO_2 (998.6 mg, 9.0 mmol, 1.5 equiv.) and DMF (240 mL) under Ar. The mixture was degassed for 1 h. Then, the $Ni(acac)_2$ (154.1 mg, 0.6 mmol, 0.1 equiv.) was added. The reaction mixture was stirred at room temperature

under the irradiation of 15 W blue LED for 36 h. The volatiles were removed, and the residue was purified by flash column chromatography on silica gel to afford the desired product **2a**.

Before reaction **In reaction** **End of reaction**

Figure S5. Procedure for the synthesis of 2a on gram scale.

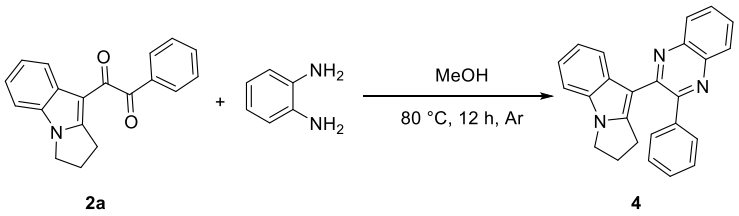
10. Procedure for the synthesis of derivative 3.



To a solution of **2a** (0.2 mmol, 1.0 equiv.) in anhydrous THF (2 mL) at –78 ℃, PhMgBr (1 M in THF, 3.0 equiv.) was added dropwise. The reaction mixture was stirred at room temperature for 12 h. After quenching with H_2O (5 mL), the mixture was extracted with EtOAc (3 × 10 mL), and the combined organic layer was washed with brine (20 mL), then dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (height 23 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 50:1 to 5:1) to afford the corresponding product **3** as a yellow solid (69%, 50.7 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.24**.**

2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-2-hydroxy-1,2-diphenylethan-1-one.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.10 (m, 1H), 7.54 – 7.44 (m, 4H), 7.38 – 7.27 (m, 6H), 7.24 – 7.15 (m, 3H), 5.09 (s, 1H), 4.03 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.46 – 2.32 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 194.9, 153.7, 142.7, 134.3, 132.8, 131.9, 130.0, 128.8, 128.3, 128.1, 127.7, 123.3, 122.6, 122.5, 109.8, 109.6, 107.6, 84.2, 44.4, 28.4, 26.3. **HRMS** (ESI) calcd for $C_{25}H_{22}NO_2^+$ *m/z* 368.1645 $[M+H]^+$, Found 368.1654.

11. Procedure for the synthesis of derivative 4.

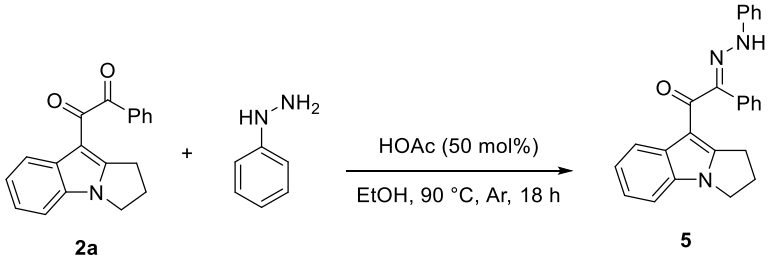


2a **4**

An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with **2a** (57.9 mg, 0.2 mmol, 0.1 equiv.), *o*-Phenylenediamine (43.3 mg, 0.4 mmol, 2.0 equiv.), and MeOH (2 mL). Then the resulting reaction mixture was stirred at 80 ℃ under Ar for 12 h. After that, the volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 20:1 to 5:1) to afford the desired product **4** as a white solid (91%, 65.9 mg). R_f (petroleum ether/ethyl acetate = 10:1): 0.17.

9-(3-phenylquinoxalin-2-yl)-2,3-dihydro-1H-pyrrolo[1,2-a]indole 4. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.63 (m, 4H), 7.35 (d, *J* = 5.2 Hz, 3H), 7.29 – 7.15 (m, 3H), 4.00 (t, *J* = 6.9 Hz, 2H), 2.38 – 2.24 (m, 2H), 2.09 (t, *J* = 7.2 Hz, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 153.5, 149.8, 145.8, 141.5, 140.3, 139.9, 133.2, 131.8, 129.5, 129.5, 129.0, 128.8, 128.7, 128.6, 128.4, 121.4, 120.9, 120.5, 109.4, 106.3, 43.9, 27.7, 24.9. **HRMS** (ESI) calcd for $C_{25}H_{20}N_3^+$ *m/z* 362.1652 $[M+H]^+$, Found 362.1648.

12. Procedure for the synthesis of derivative 5.

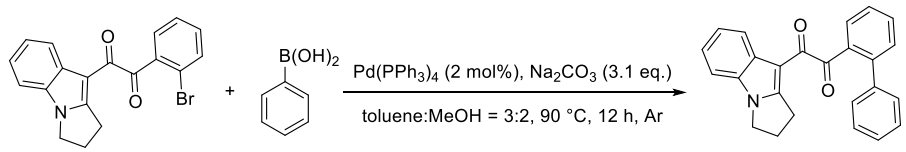


2a **5**

An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with **2a** (57.8 mg, 0.2 mmol, 1.0 equiv.), phenylhydrazine (43.3 mg, 0.26 mmol, 1.5 equiv.), HOAc (6.0 mg, 0.1 mmol, 50 mol%) and EtOH (2 mL). Then the resulting reaction mixture was stirred at 90 ℃ under Ar for 18 h. After that, the volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 100:1 to 10:1) to afford the desired product **5** as a yellow solid (74%, 65.9 mg). R_f (petroleum ether/ethyl acetate = 5:1): 0.51.

(Z)-2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)-1-phenyl-2-(2-phenylhydrazono) ethan-1-one. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.23 (m, 8H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 7.6 Hz, 1H), 4.06 (t, *J* = 7.2 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.56 – 2.36 (t, *J* = 7.5 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 187.6, 155.0, 144.5, 143.6, 135.6, 133.3, 130.7, 129.2, 128.5, 128.1, 126.1, 123.3, 122.6, 120.6, 113.2, 110.1, 109.4, 44.7, 26.3, 26.1. **HRMS** (ESI) calcd for $C_{25}H_{22}N_3O^+$ *m/z* 380.1757 $[M+H]^+$, Found 380.1768.

13. Procedure for the synthesis of derivative 6.



2q **6**

An oven-dried 25 mL Schlenk tube equipped with a stirring bar was charged with **3p** (73.6 mg, 0.2 mmol, 1.0 equiv.), phenylboronic acid (36.6 mg, 0.3 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (4.6 mg, 0.004 mmol, 2 mol%), Na_2CO_3 (65.7 mg, 0.62 mmol, 3.1 equiv.), and toluene/MeOH (3:2, 3 mL). Then the resulting mixture was stirred at 90 ℃ under Ar for 12 h. After reaction completed, water (2 mL) was added to the mixture which was further extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (height 16 cm, width 1.5 cm, eluent: petroleum ether/ethyl acetate, gradient: 30:0 to 10:1) to afford the desired product **6** as a white solid (84%, 61.3 mg). R_f (petroleum ether/ethyl acetate = 10:1): 0.19.

1-([1,1'-biphenyl]-2-yl)-2-(2,3-dihydro-1H-pyrrolo[1,2-a]indol-9-yl)ethane-1,2-dione 6. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.38 (m, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 3.0 Hz, 3H), 7.18 – 6.92 (m, 3H), 4.11 (t, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.5 Hz, 2H), 2.68 – 2.51 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 196.4, 186.6, 155.3, 143.2, 140.2, 135.7, 132.9, 132.0, 130.7, 130.3, 129.2, 127.8, 127.3, 127.2, 122.8, 122.8, 122.5, 109.7, 106.5, 44.6, 27.2, 26.4, one carbon was overlapped. **HRMS** (ESI) calcd for $C_{25}H_{20}NO_2^+$ *m/z* 366.1489 $[M+H]^+$, Found 366.1494.

14. Testing of the wavelength of the light source used

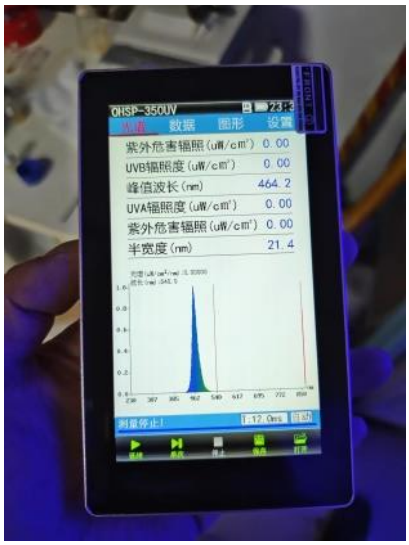


Figure S6. Wavelength test of the blue LED

15. References.

[1] Chen, D.; Han, Z.; He, Y.; Yu, J.; Gong, L. Metal-Free Oxidation/C(sp^3)-H Functionalization of Unactivated Alkynes Using Pyridine-*N*-Oxide as the External Oxidant. *Angew. Chem. Int. Ed.* **2012**, *51*, 12307-12310.

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[3] a) Garfunkle, J.; Kimball, F. S.; Trzupek, J. D.; Takizawa, S.; Shimamura, H.; Tomishima, M.; Boger, D. L. Total Synthesis of Chloropeptin II (Complestatin) and Chloropeptin I. *J. Am. Chem. Soc*. **2009**, *131*, 16036-16038. b) Xu, B.; Li, M.-L.; Zuo, X.-D.; Zhu, S.-F.; Zhou, Q.-L. Catalytic asymmetric arylation of α-aryl-α-diazoacetates with aniline derivatives. *J. Am. Chem. Soc*. **2015**, *137*, 8700-8703. c) Han, X.-Q.; Wang, L.; Yang, P.; Liu, J.-Y.; Xu, W.-Y.; Zheng, C.; Liang, R.-X.; You, S.-L.; Zhang, J.; Jia, Y.-X. Enantioselective Dearomative Mizoroki–Heck Reaction of Naphthalenes. *ACS Catal.* **2022**, *12*, 655-661.

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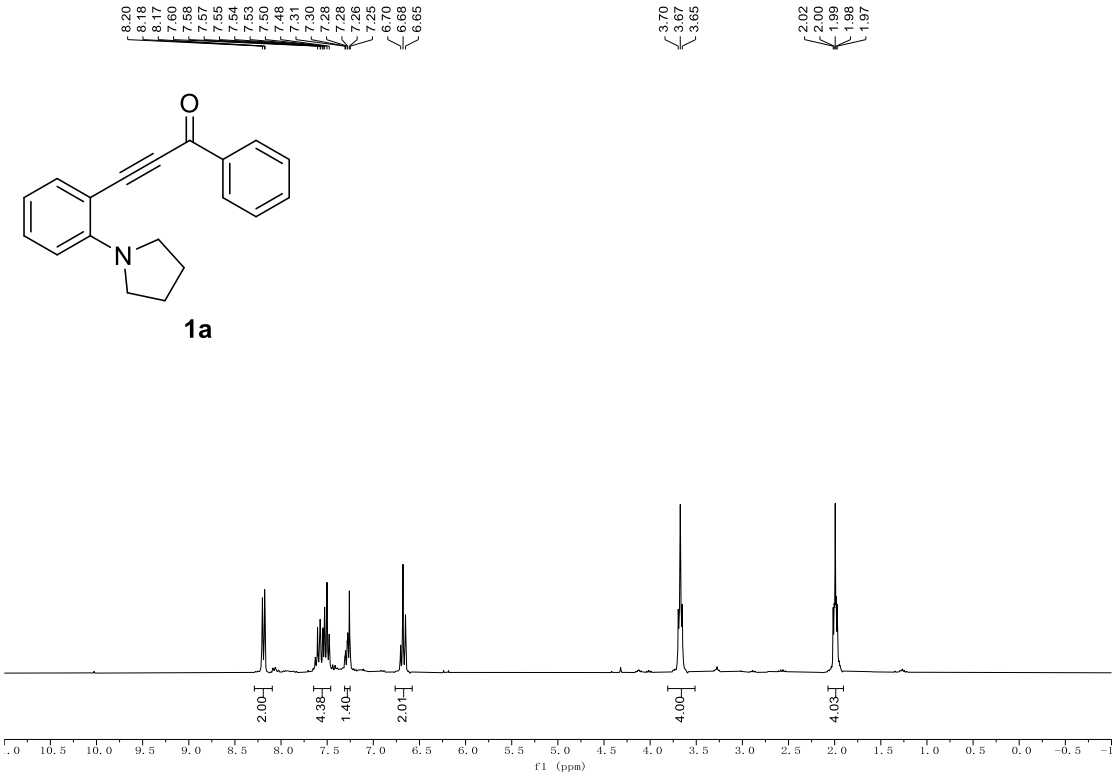
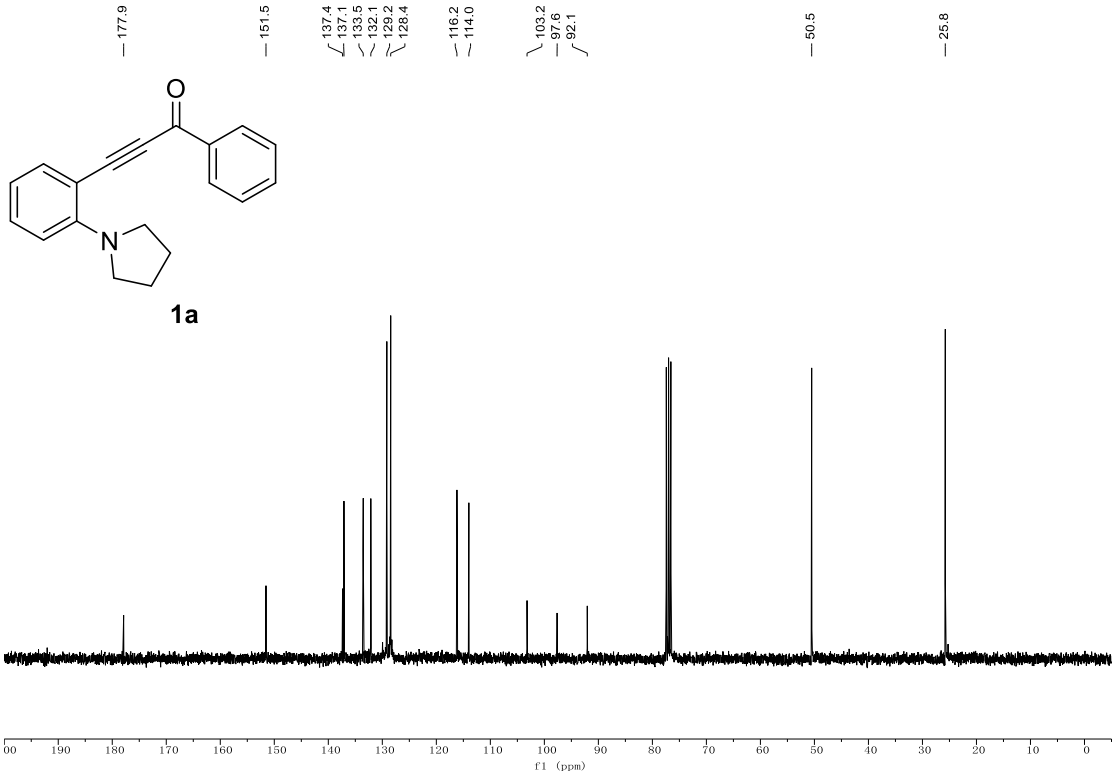
[6] Zamora, A.; Gandioso, A.; Massaguer, A.; Buenestado, S.; Calvis, C.; Hernández, J. L.; Mitjans, F.; Rodríguez, V.; Ruiz, J.; Marchán, V. Toward Angiogenesis Inhibitors Based on the Conjugation of Organometallic Platinum(II) Complexes to RGD Peptides. *ChemMedChem* **2018**, *13*, 1755-1762.

16. NMR spectra copies of the products.

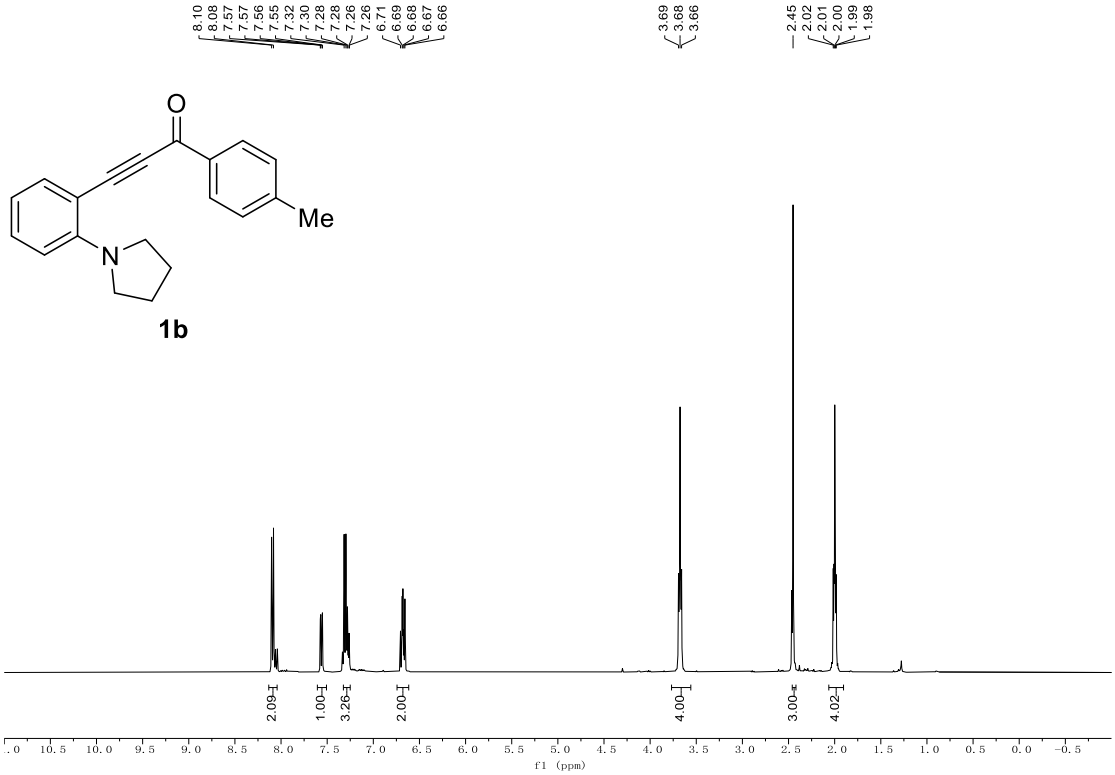
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1a**:



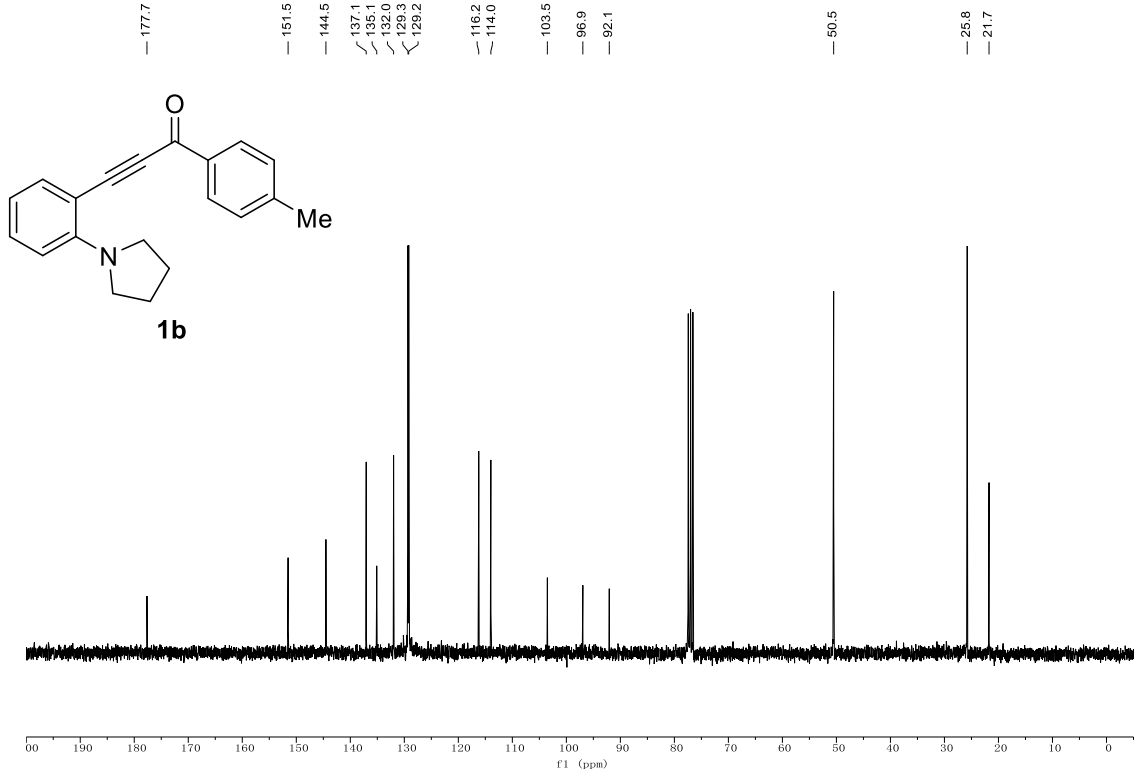
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1a**:



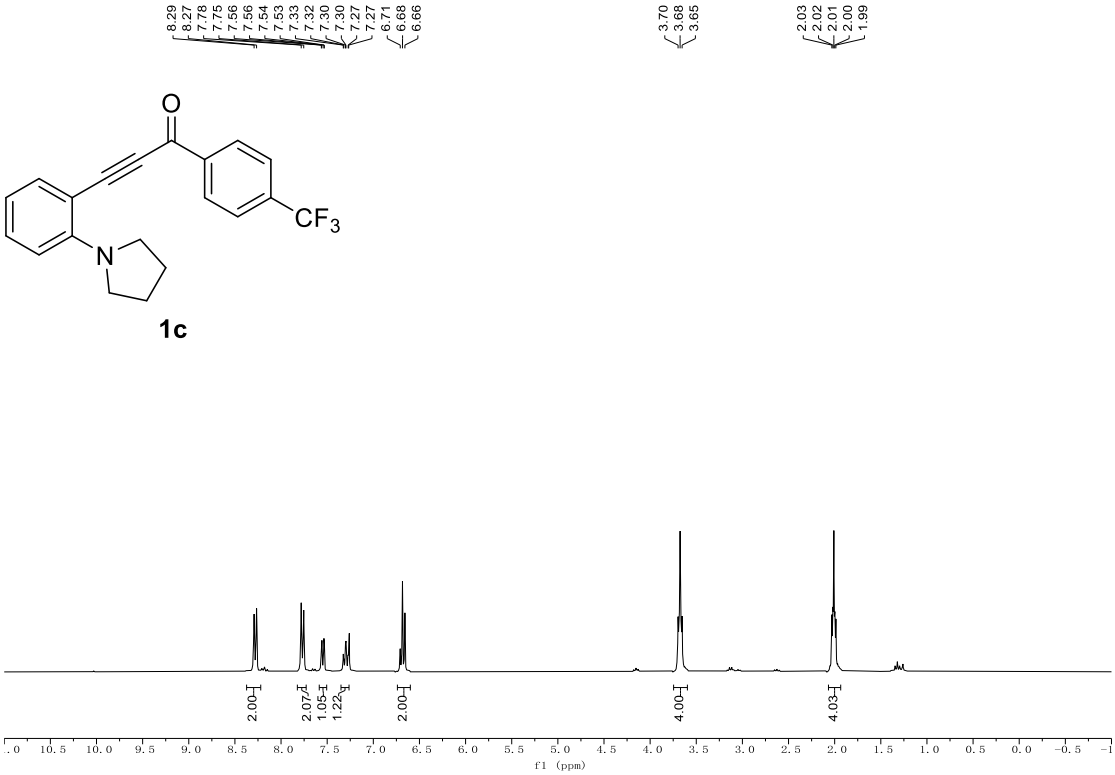
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **1b**:



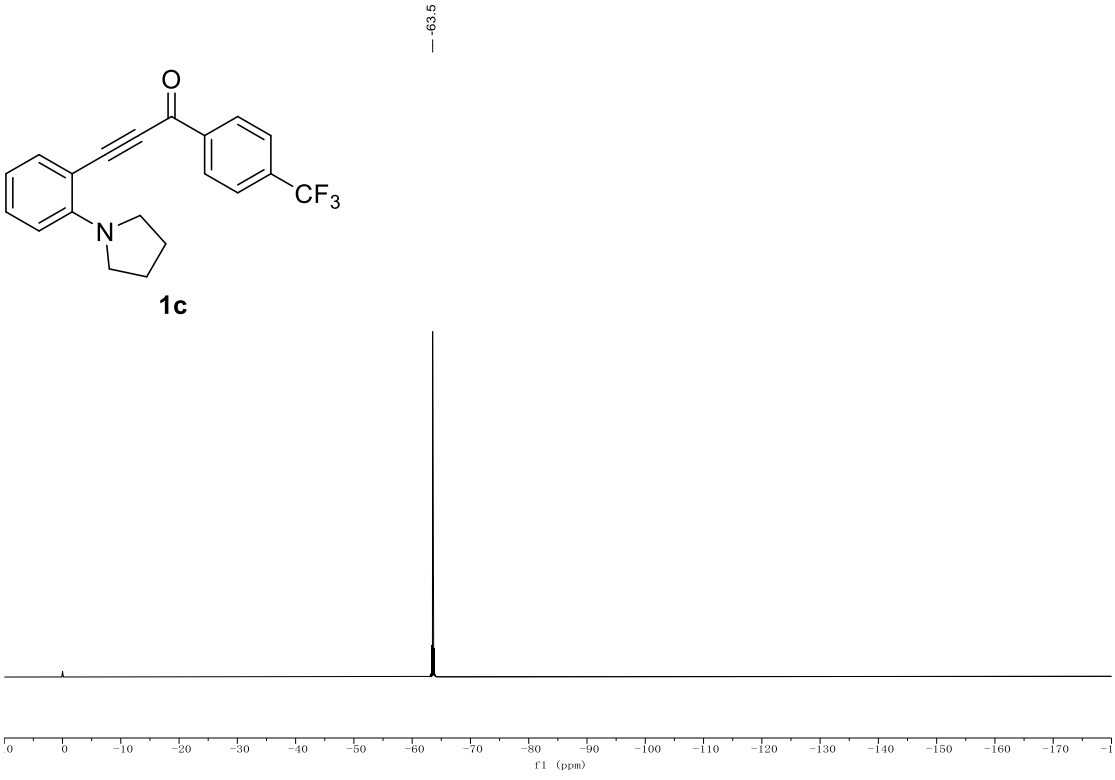
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1b**:



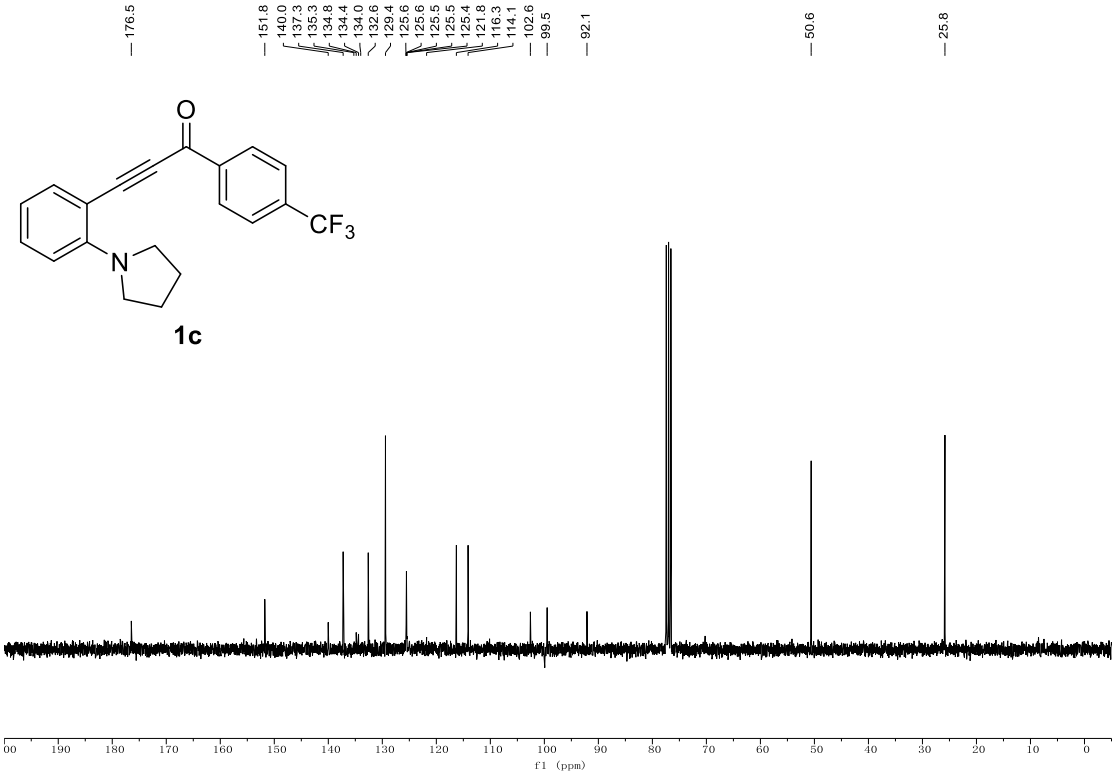
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1c**:



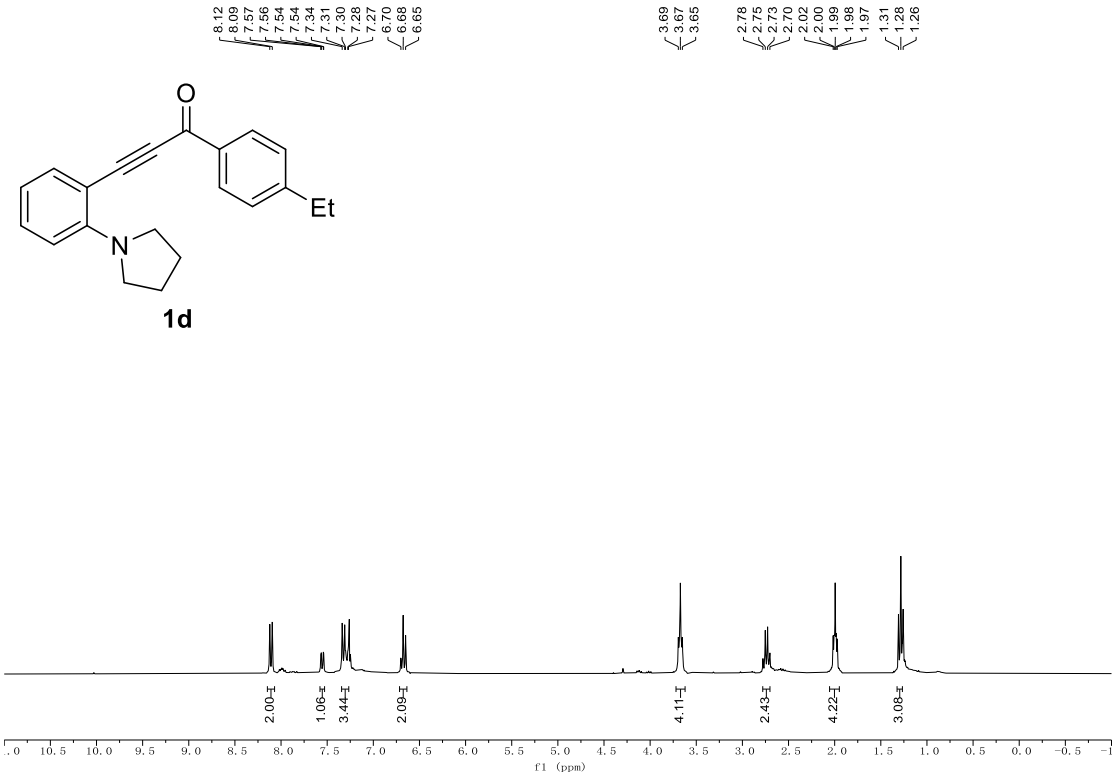
^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) spectra of compound **1c**:



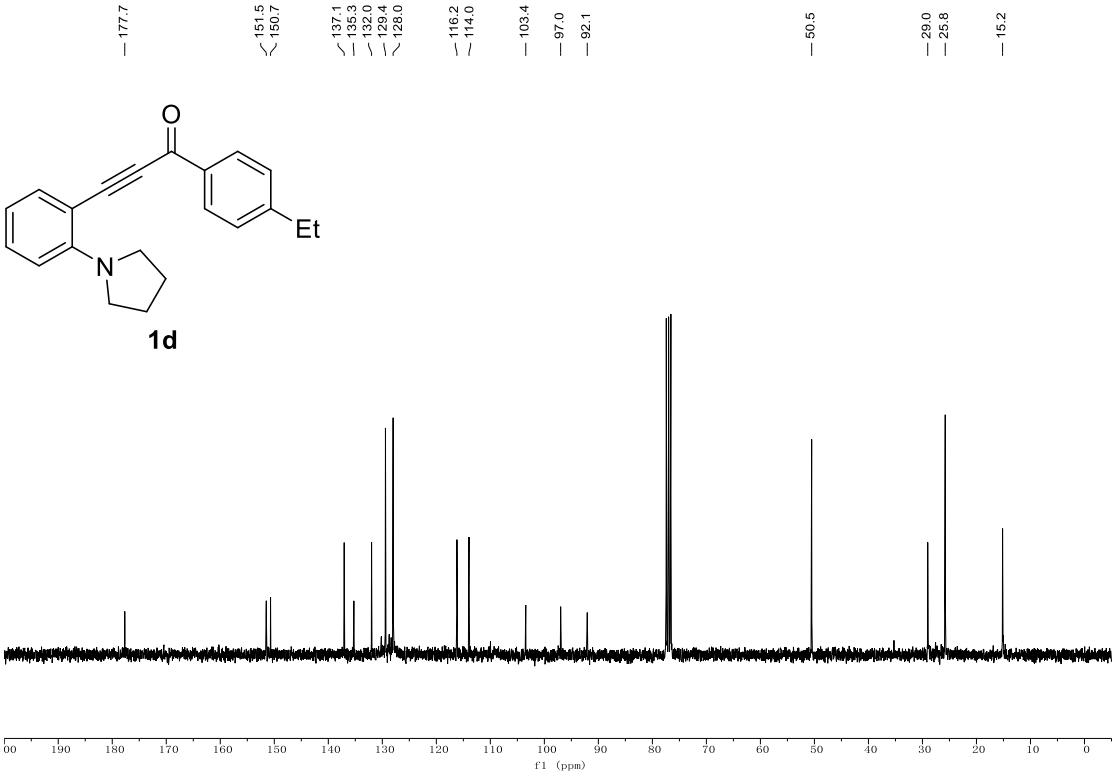
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **1c**:



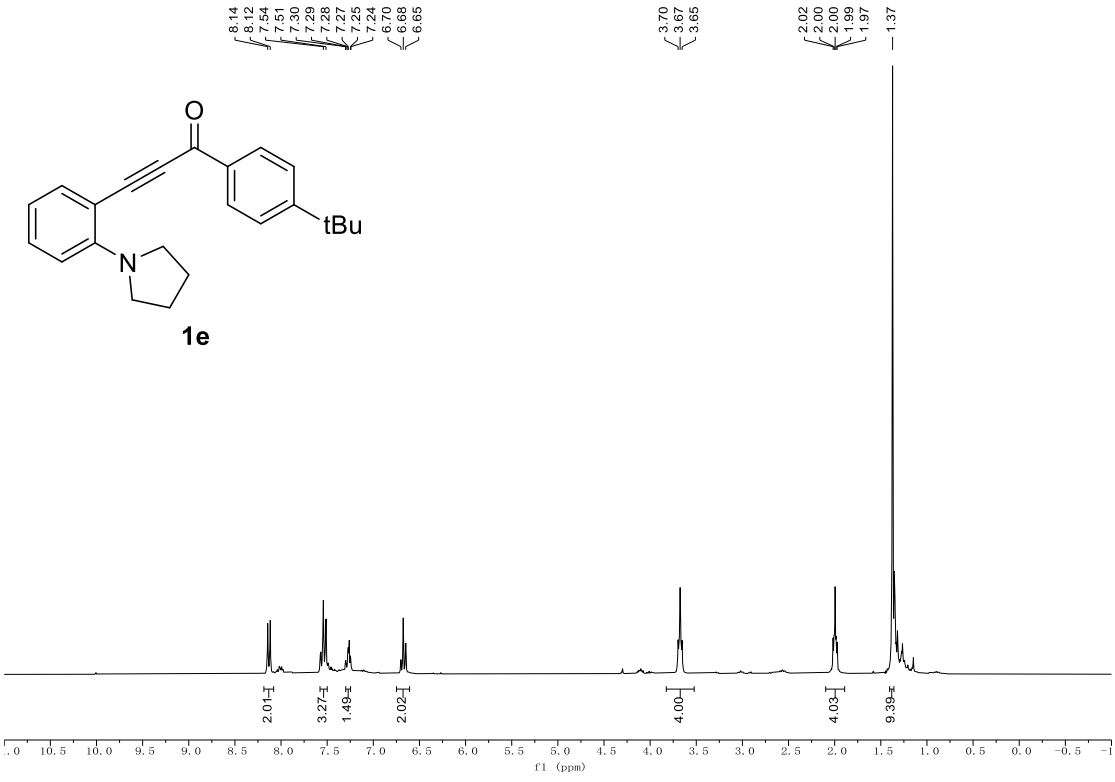
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1d**:



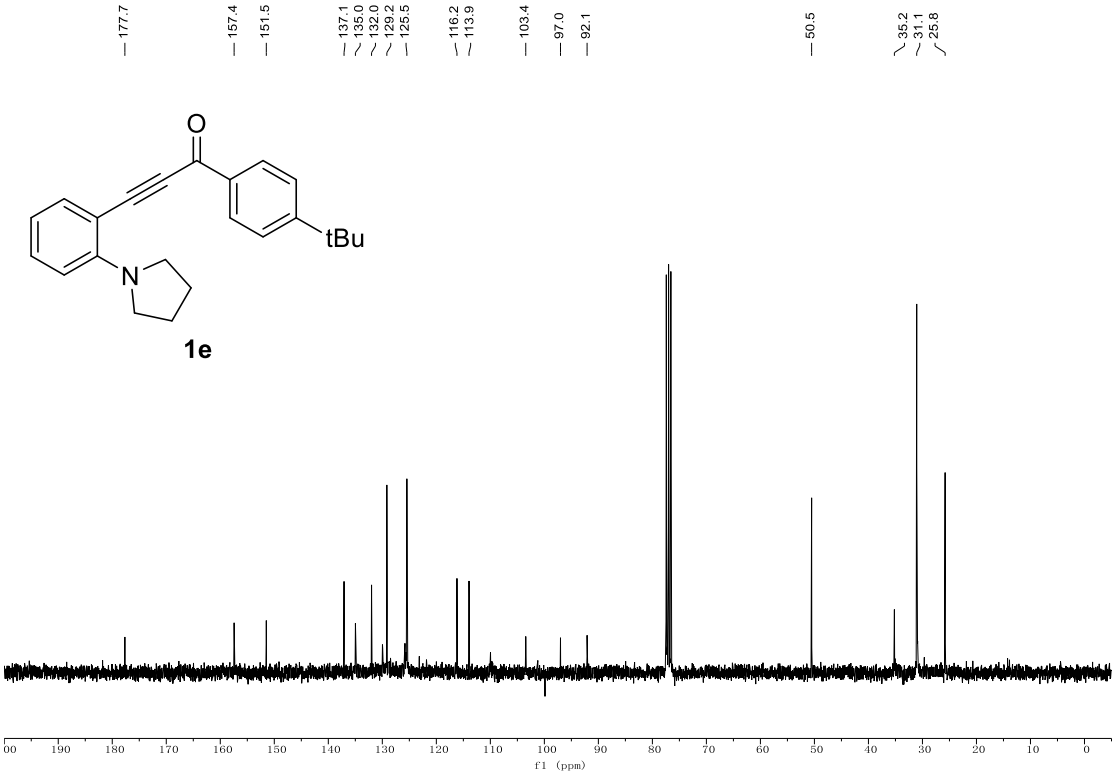
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **1d**:



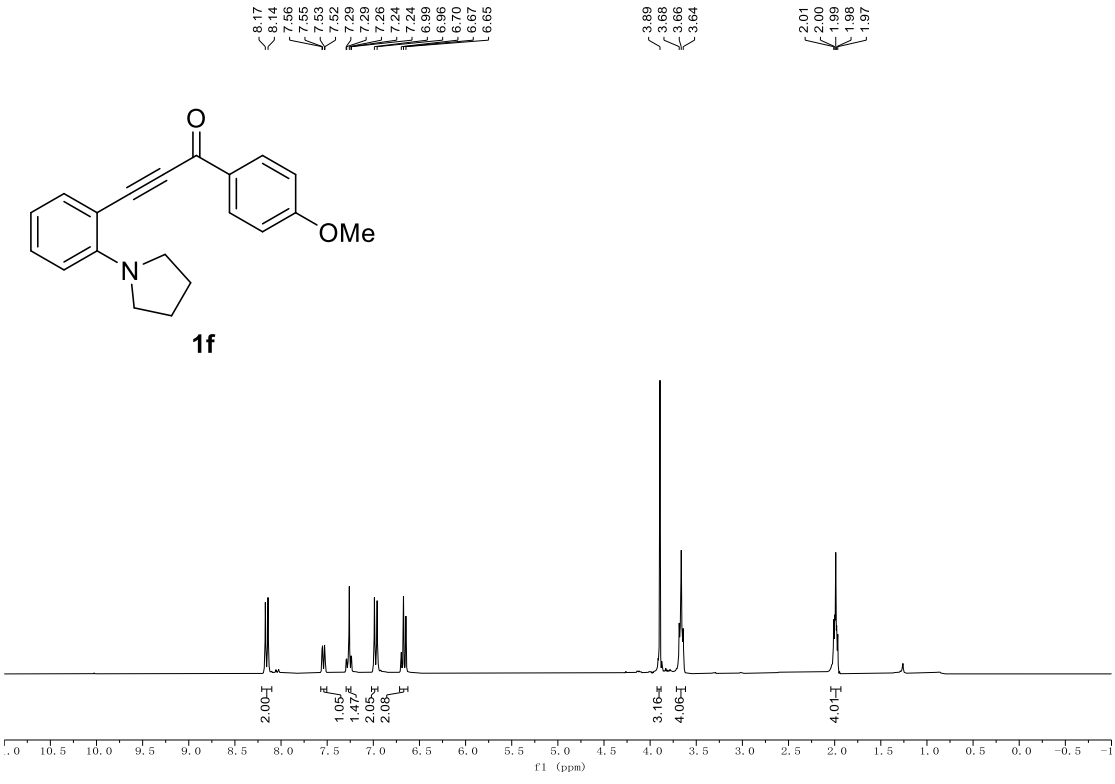
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1e**:



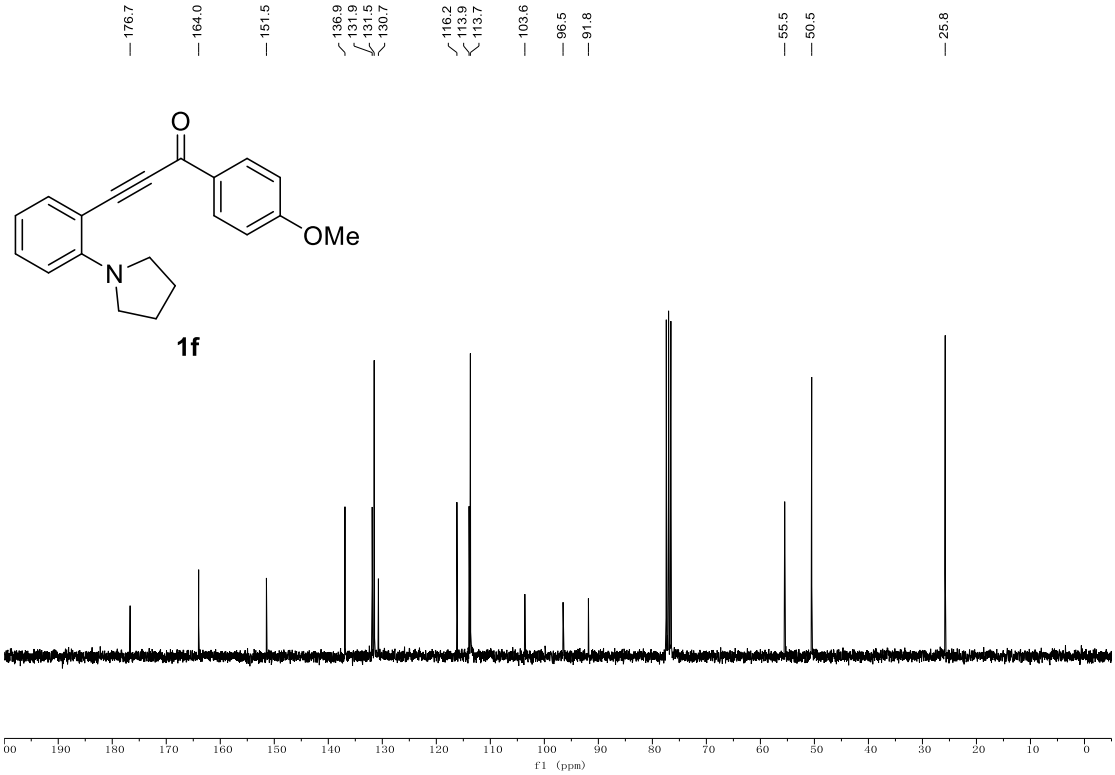
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **1e**:



^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1f**:

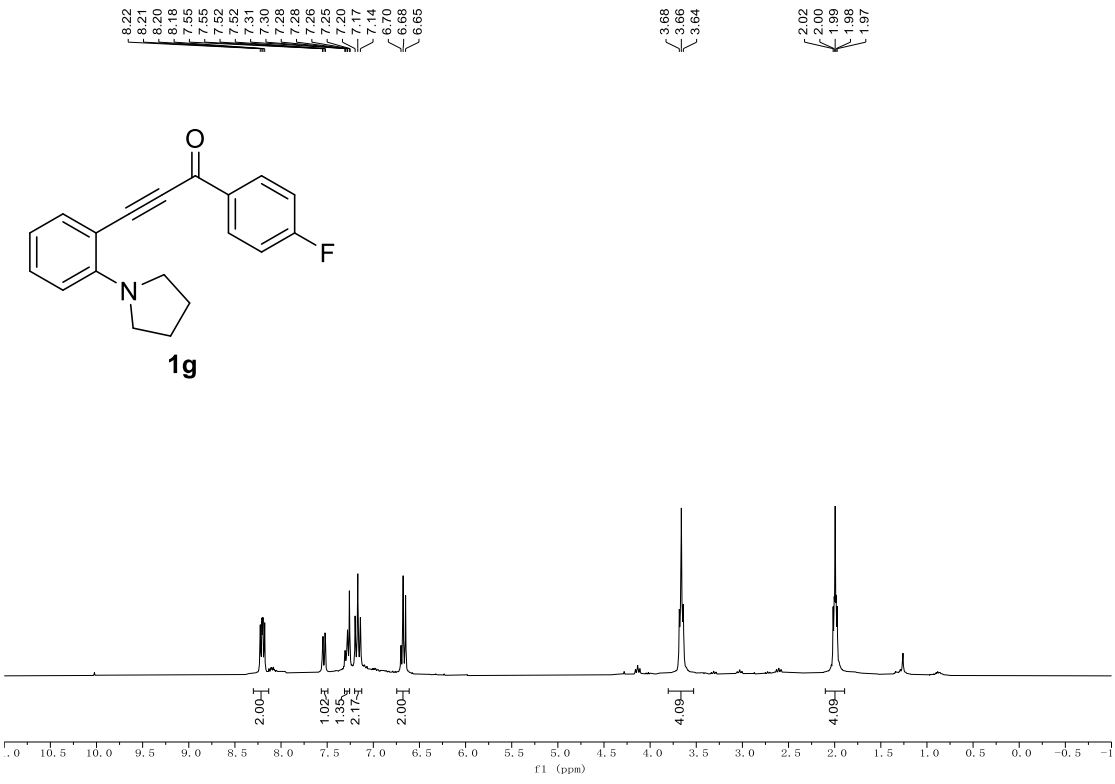


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **1f**:



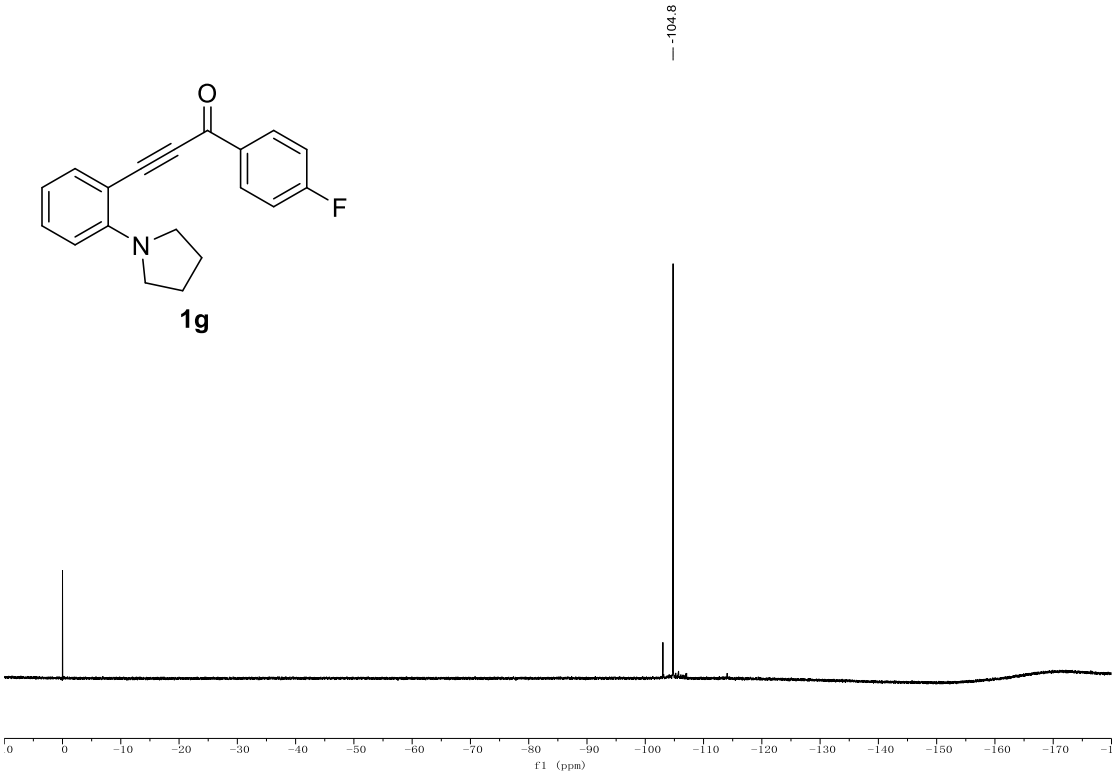
1f

^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1g**:

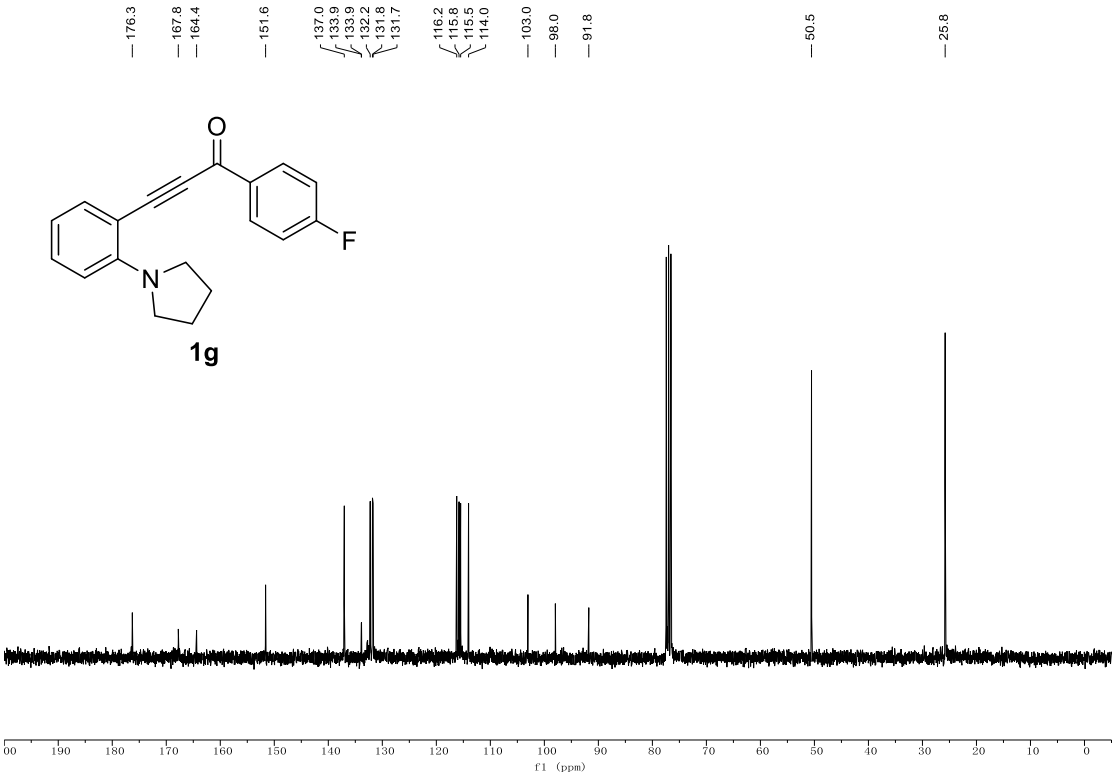


1g

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) spectra of compound **1g**:

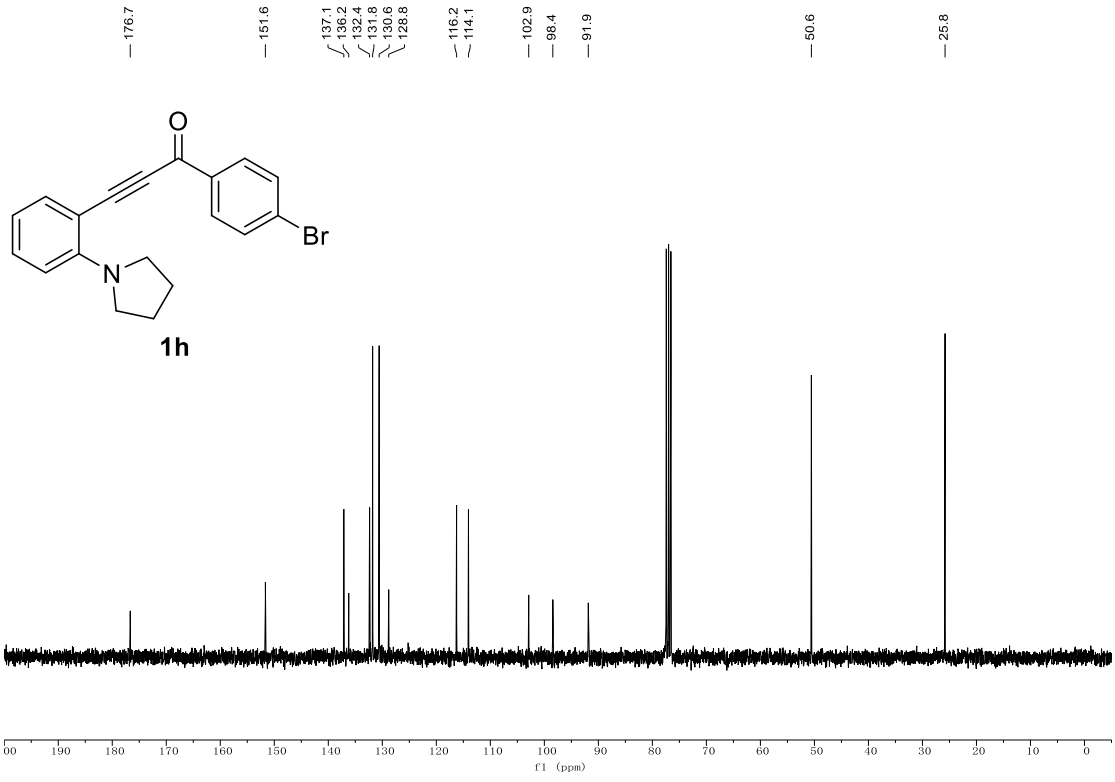


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **1g**:

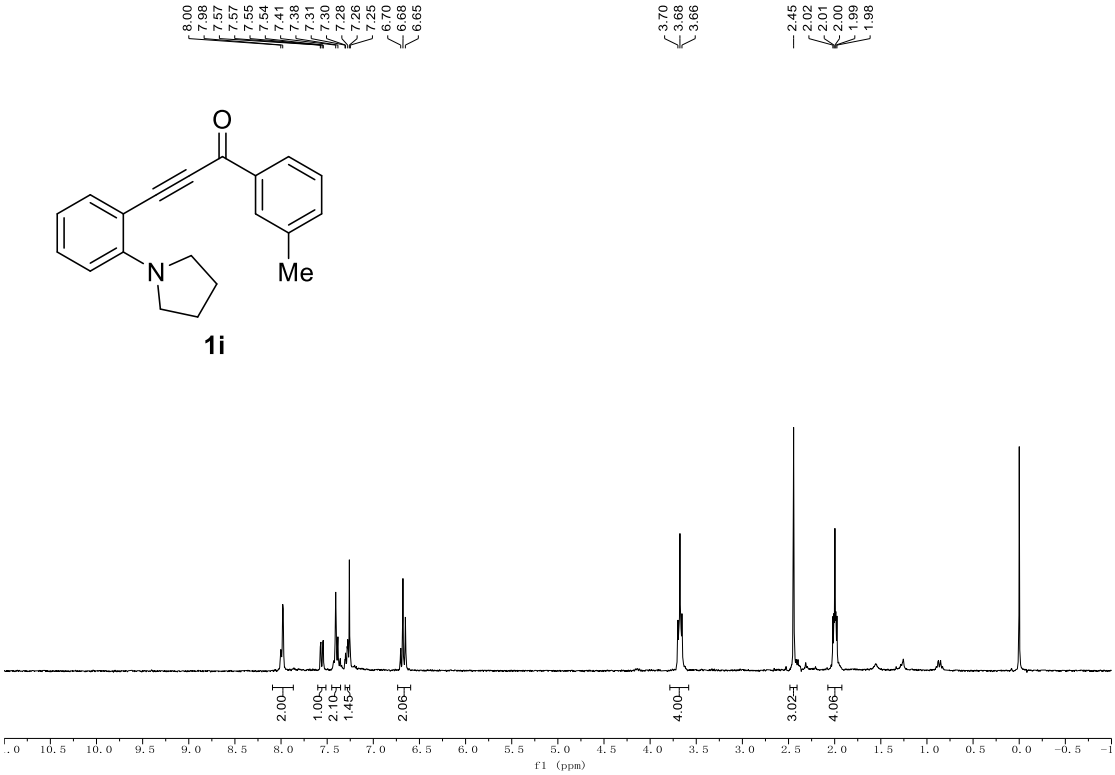


^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1h**:

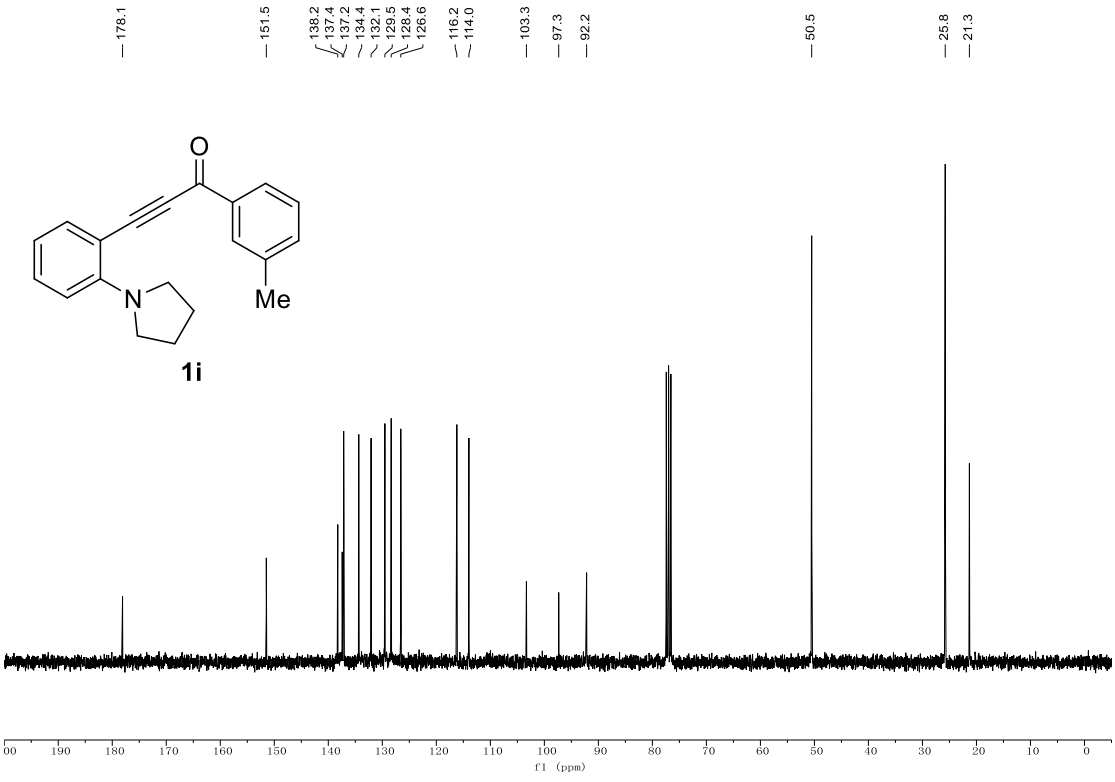
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1h**:



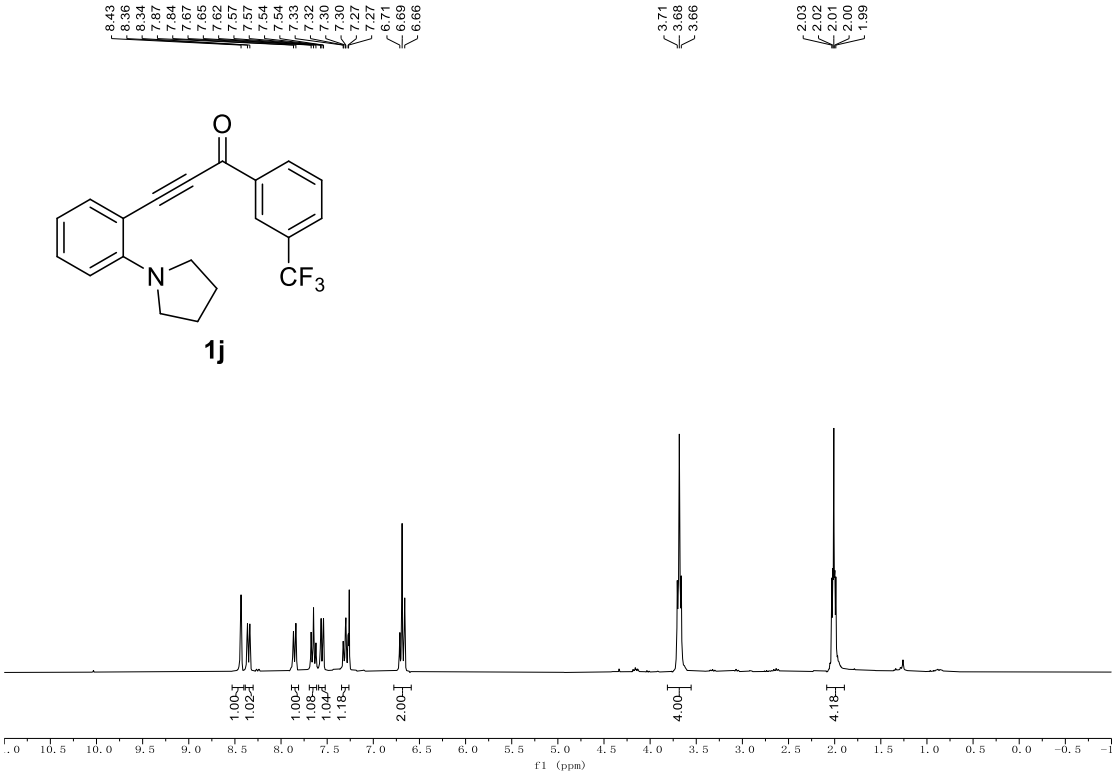
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1i**:



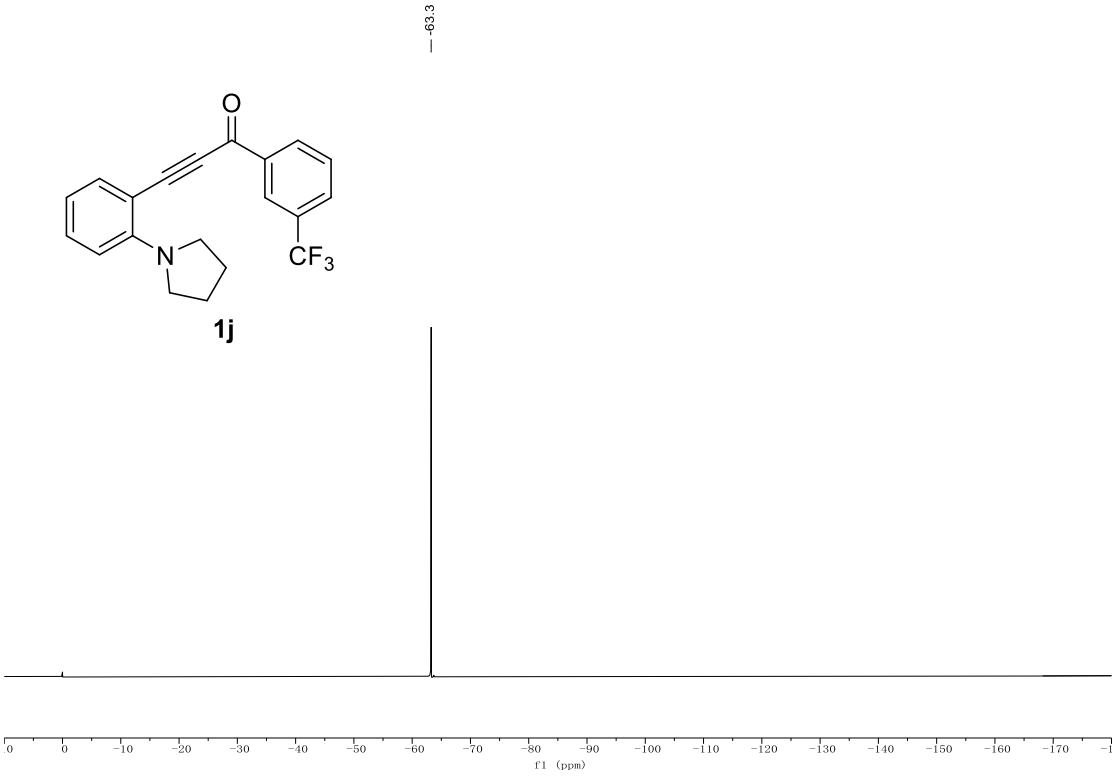
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1i**:



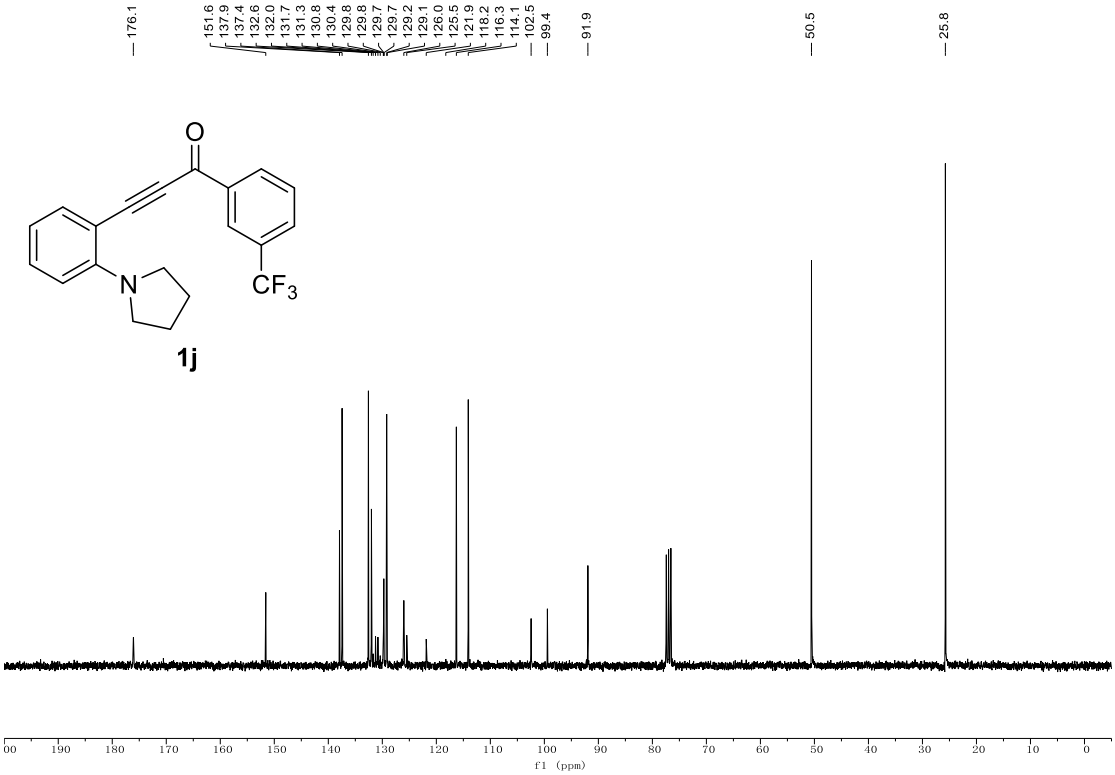
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1j**:



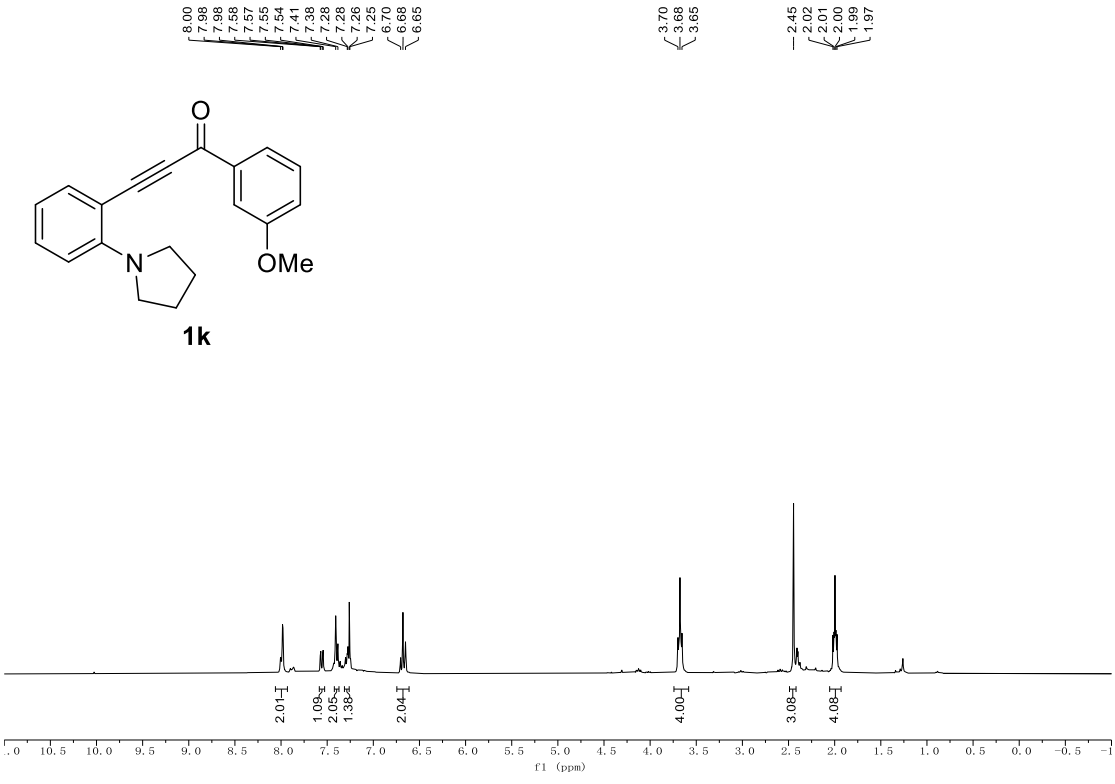
^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) spectra of compound **1j**:



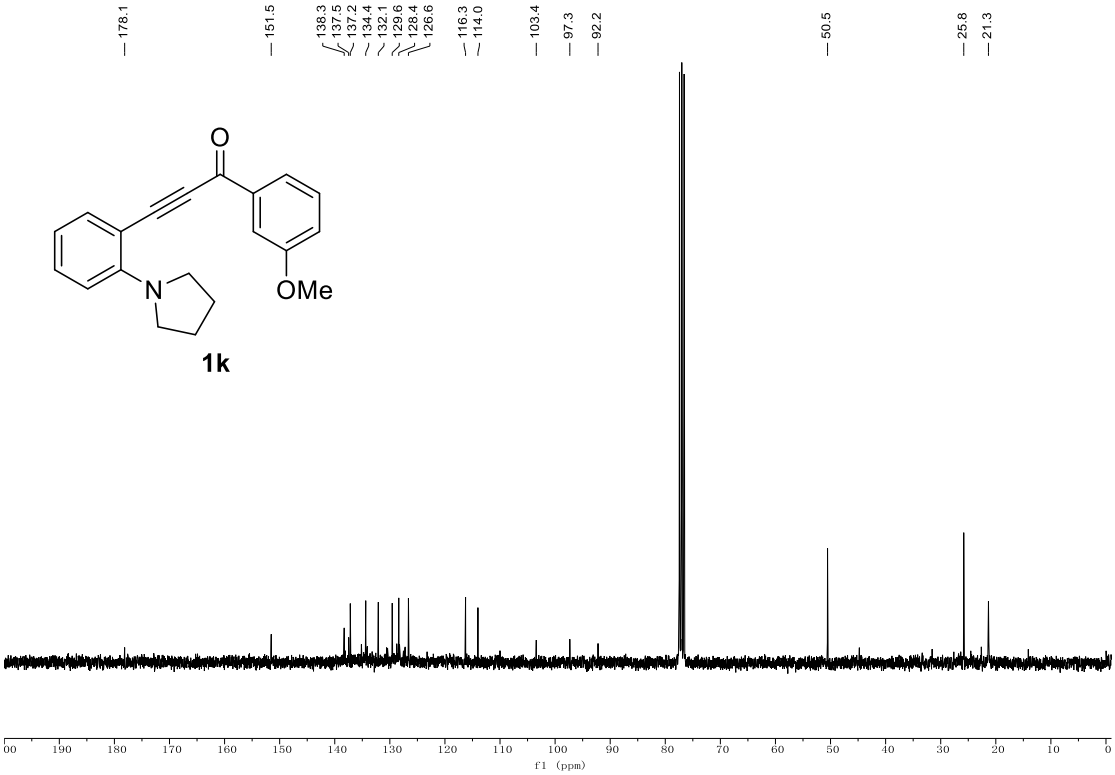
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **1j**:



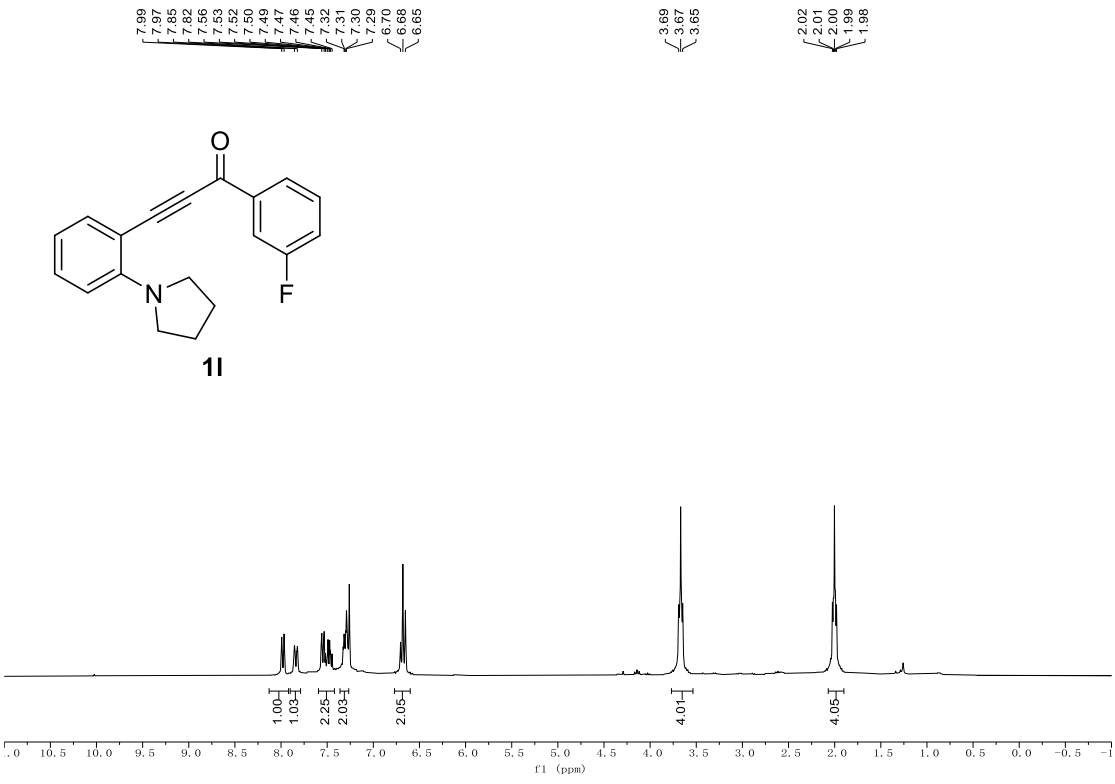
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1k**:



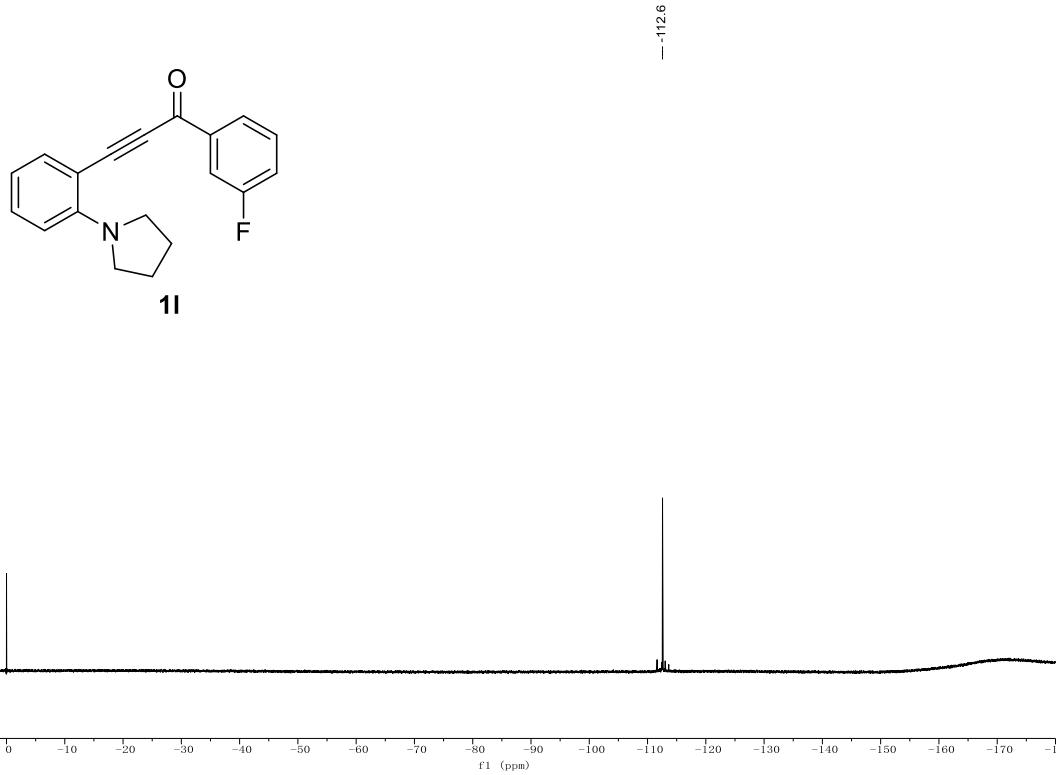
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **1k**:



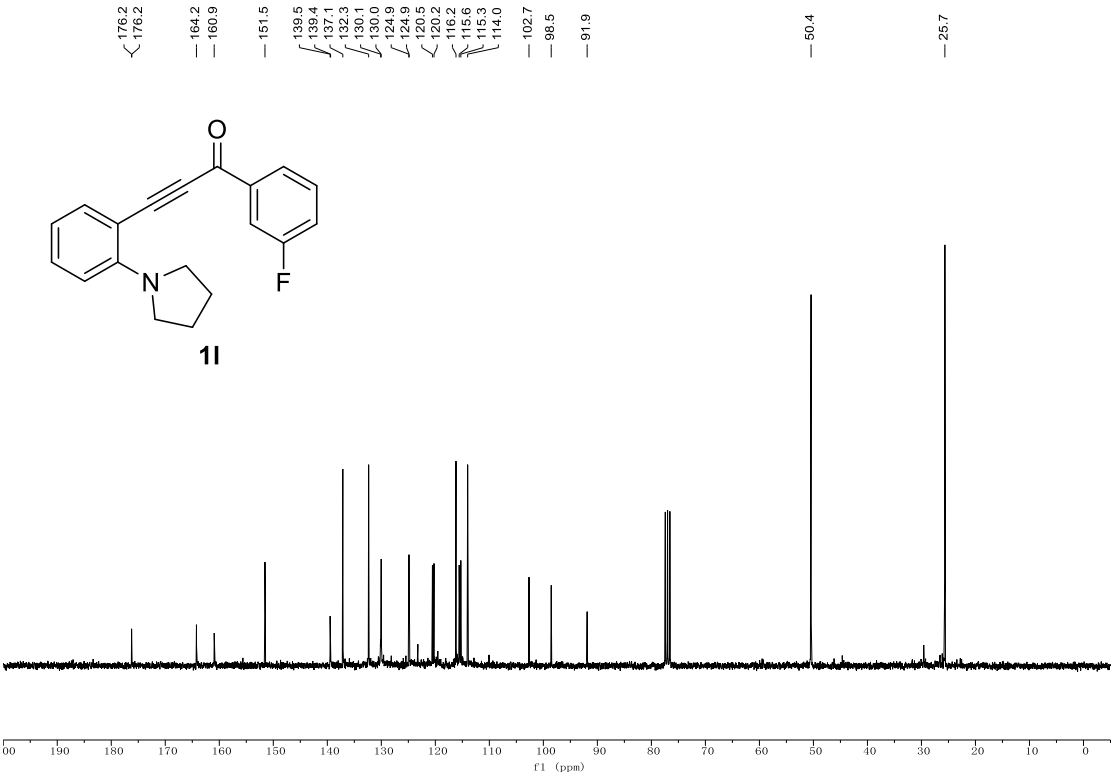
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1l**:



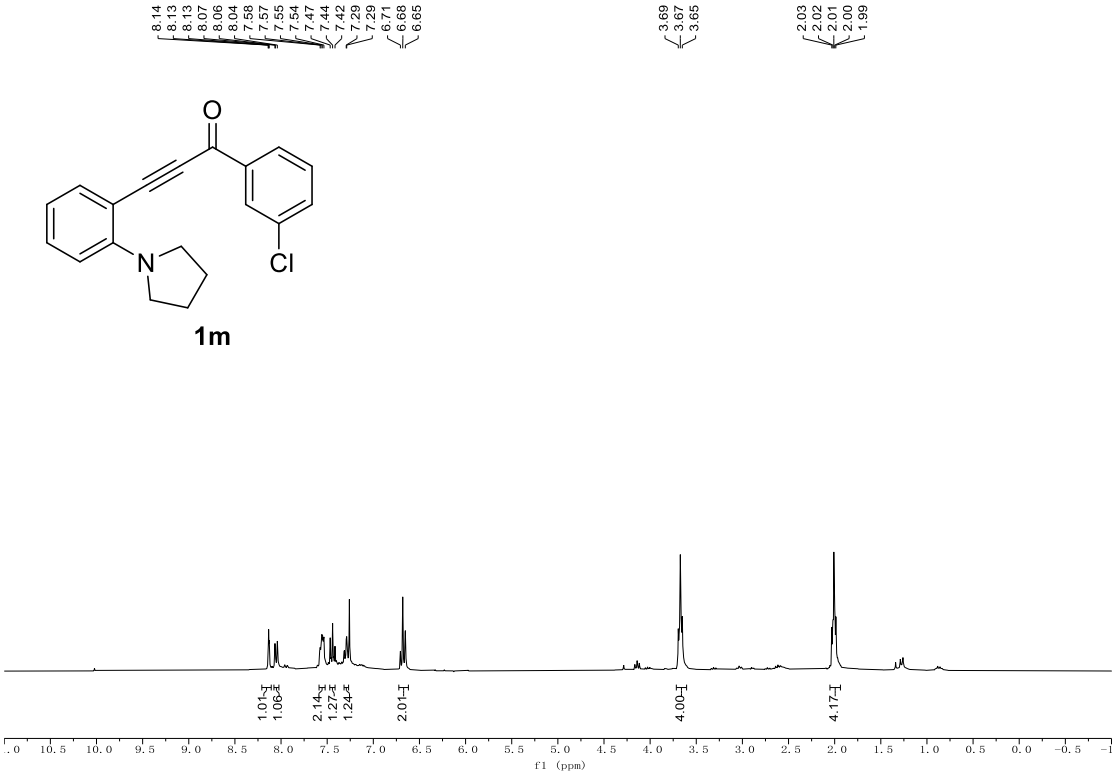
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) spectra of compound **1l**:



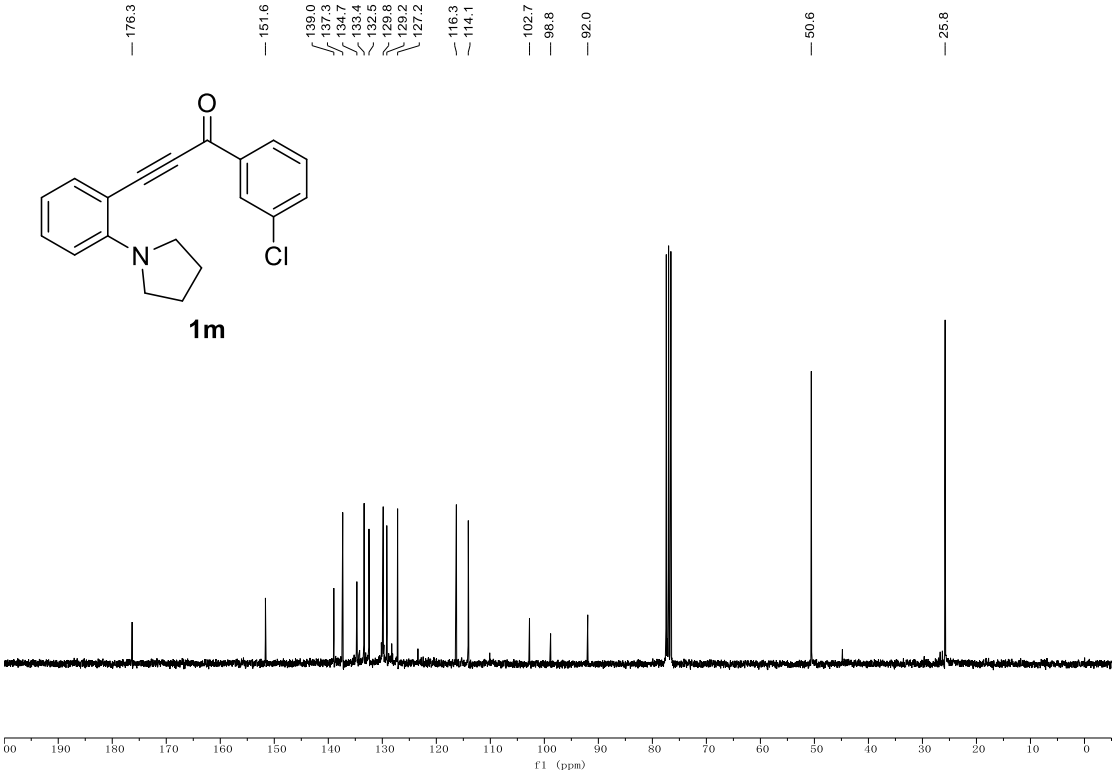
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **1l**:



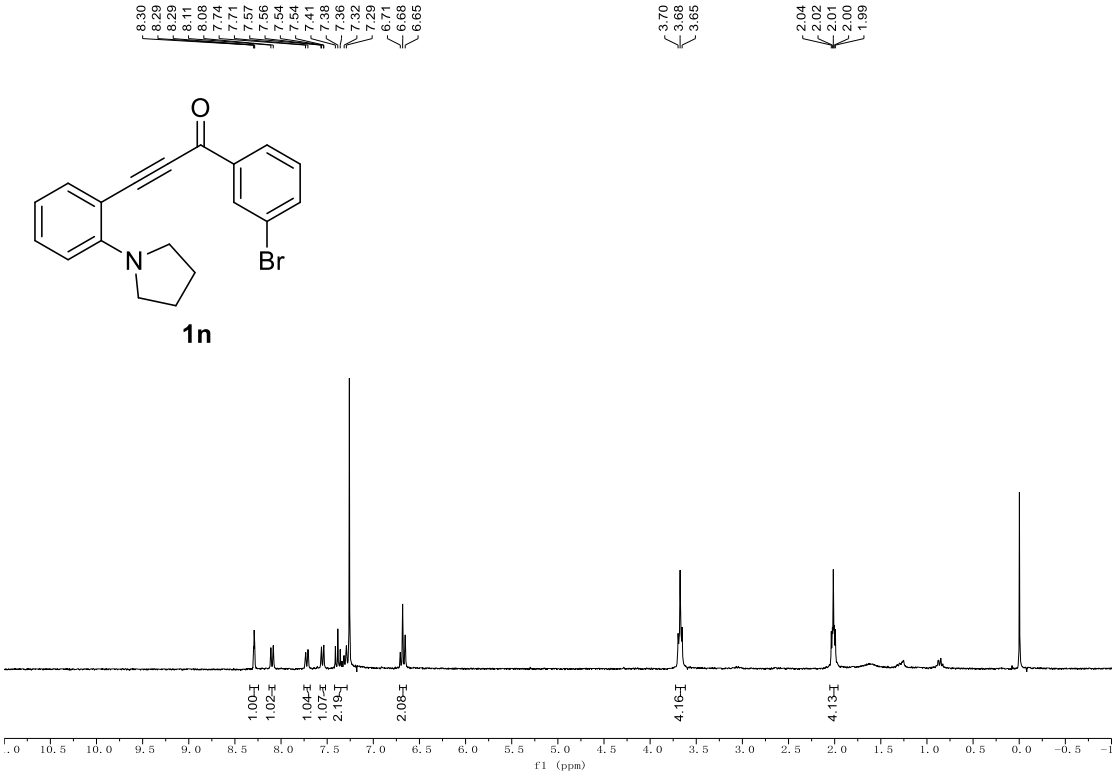
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1m**:



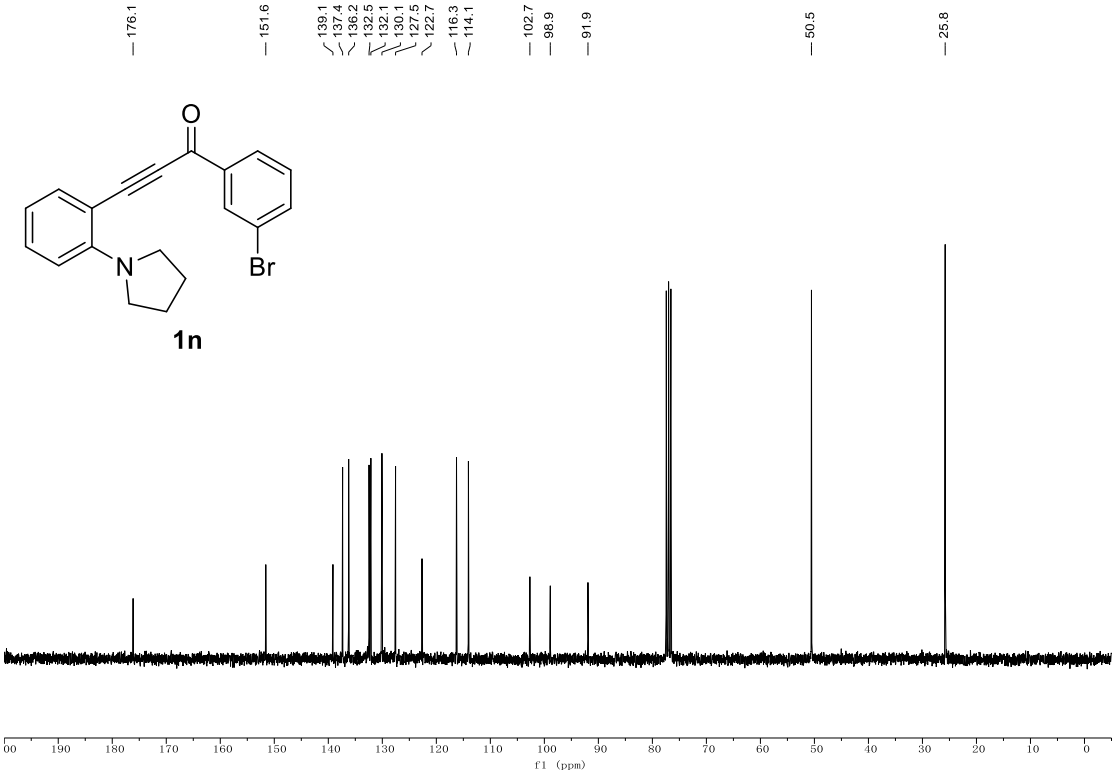
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1m**:



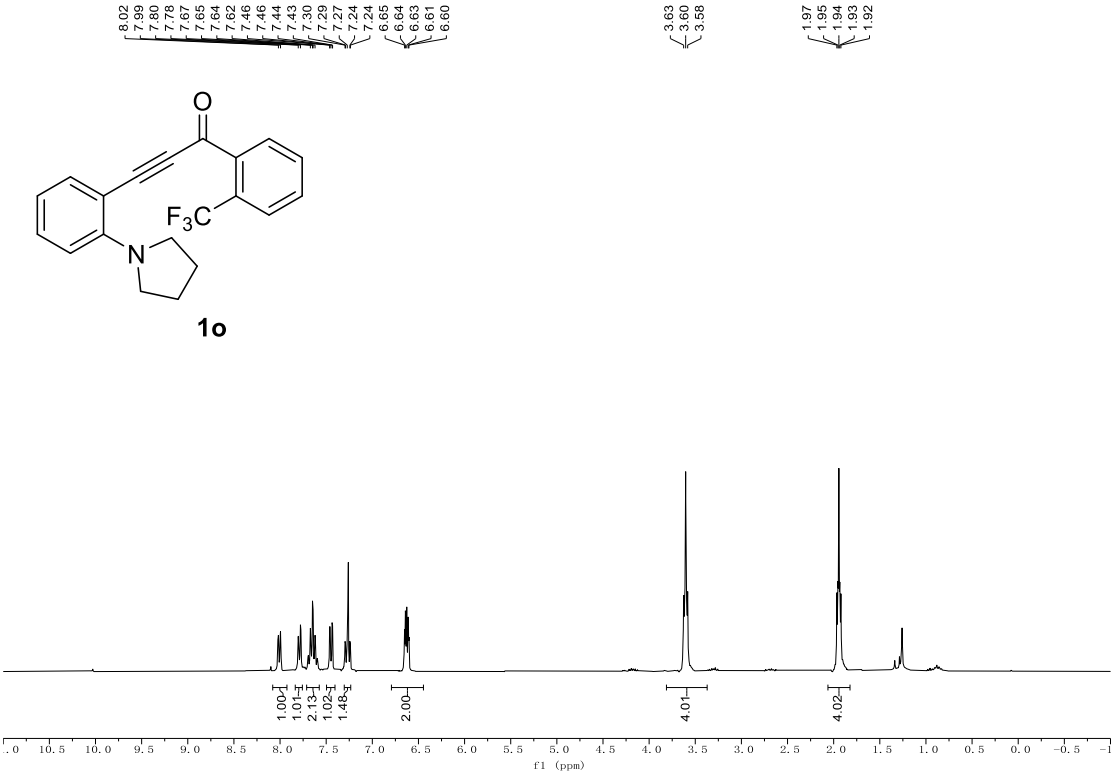
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1n**:



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1n**:



^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1o**:



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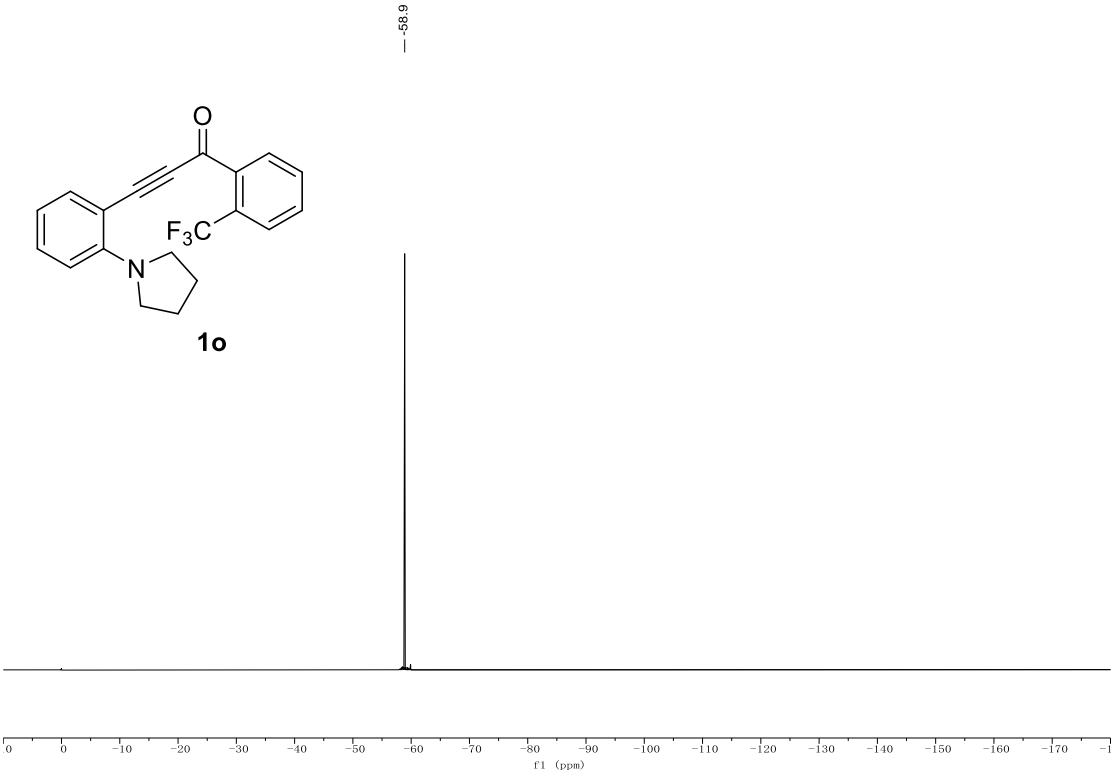
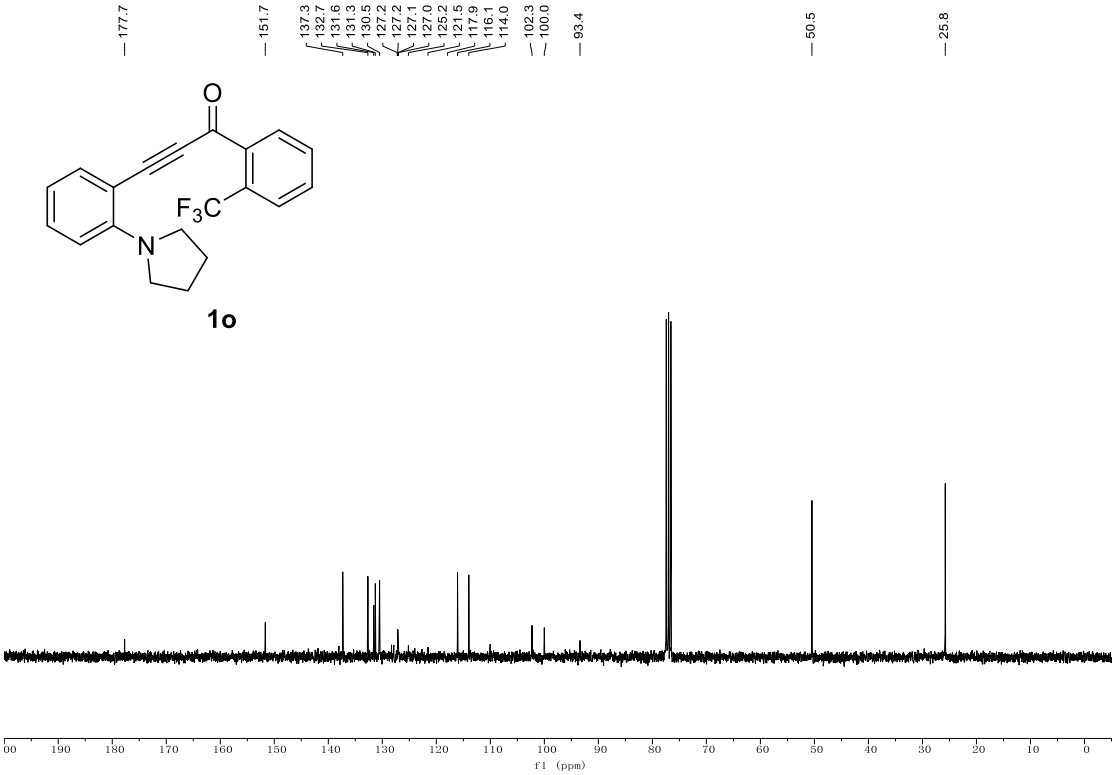
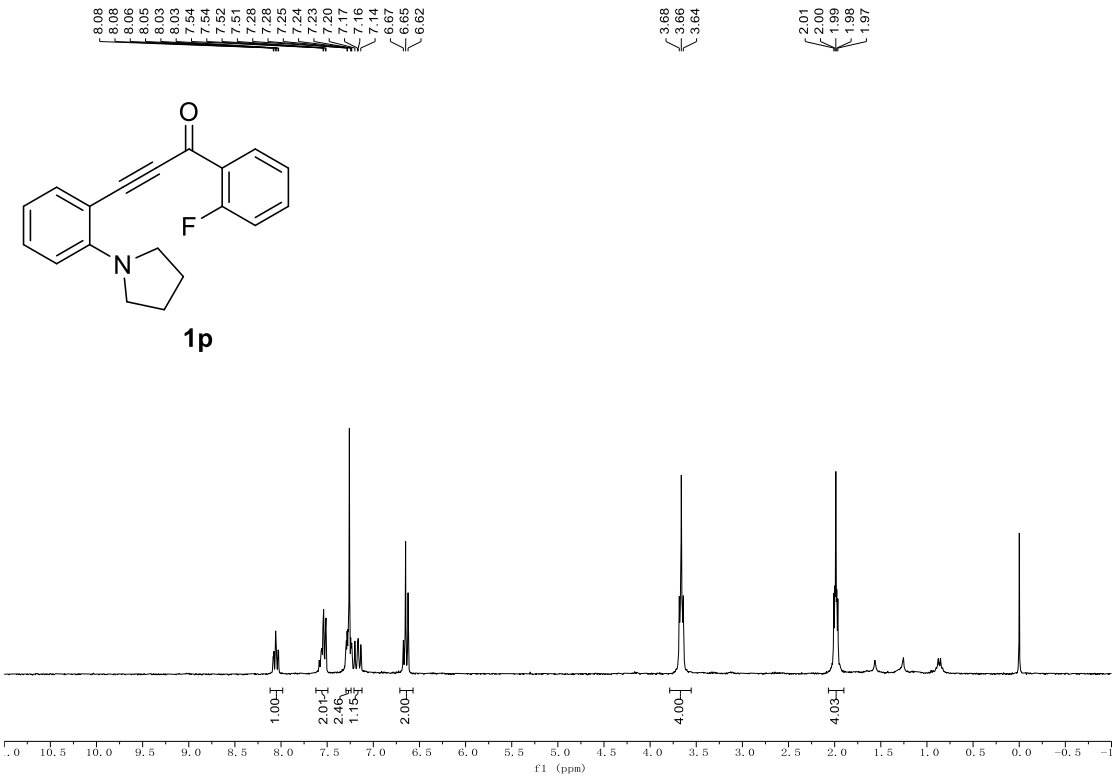


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **1o**:



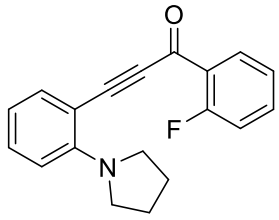
1o

^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1p**:



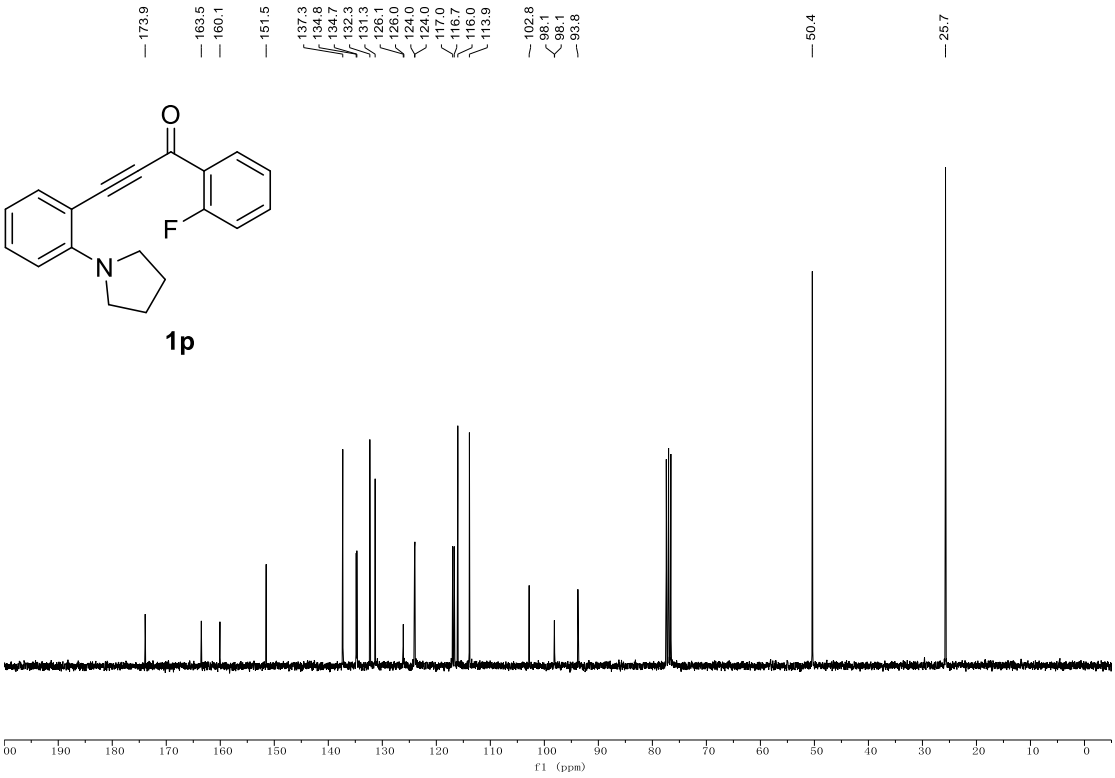
1p

$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) spectra of compound **1p**:



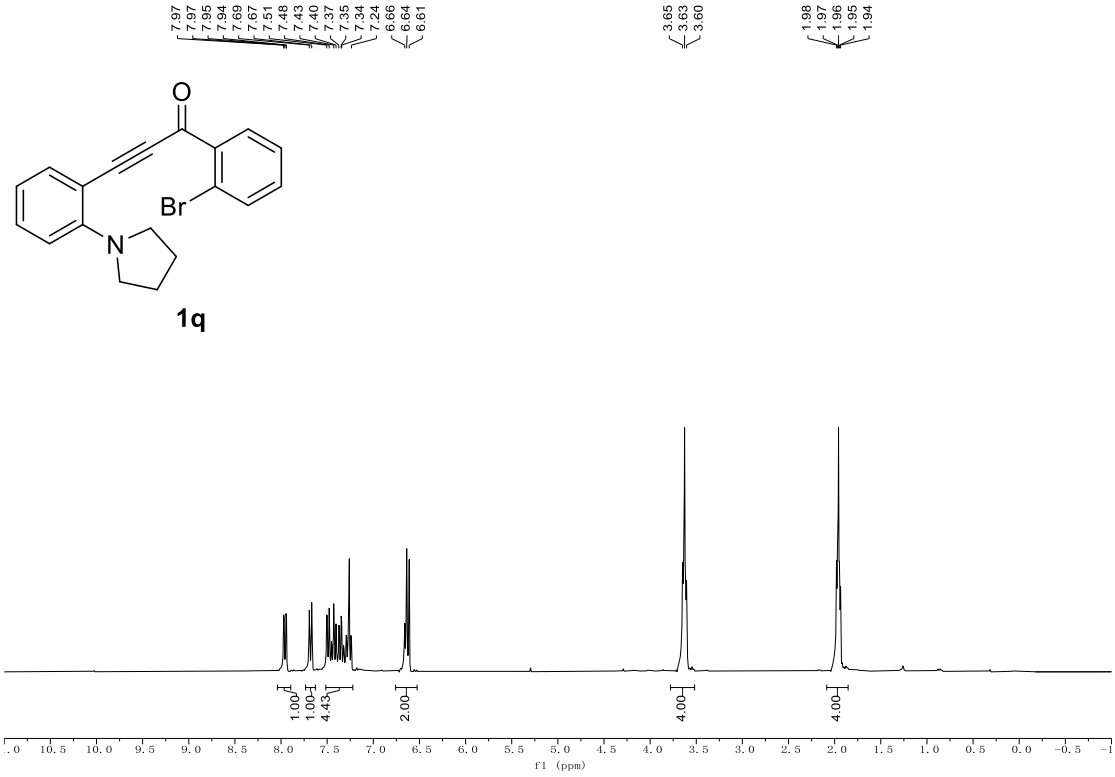
1p

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **1p**:

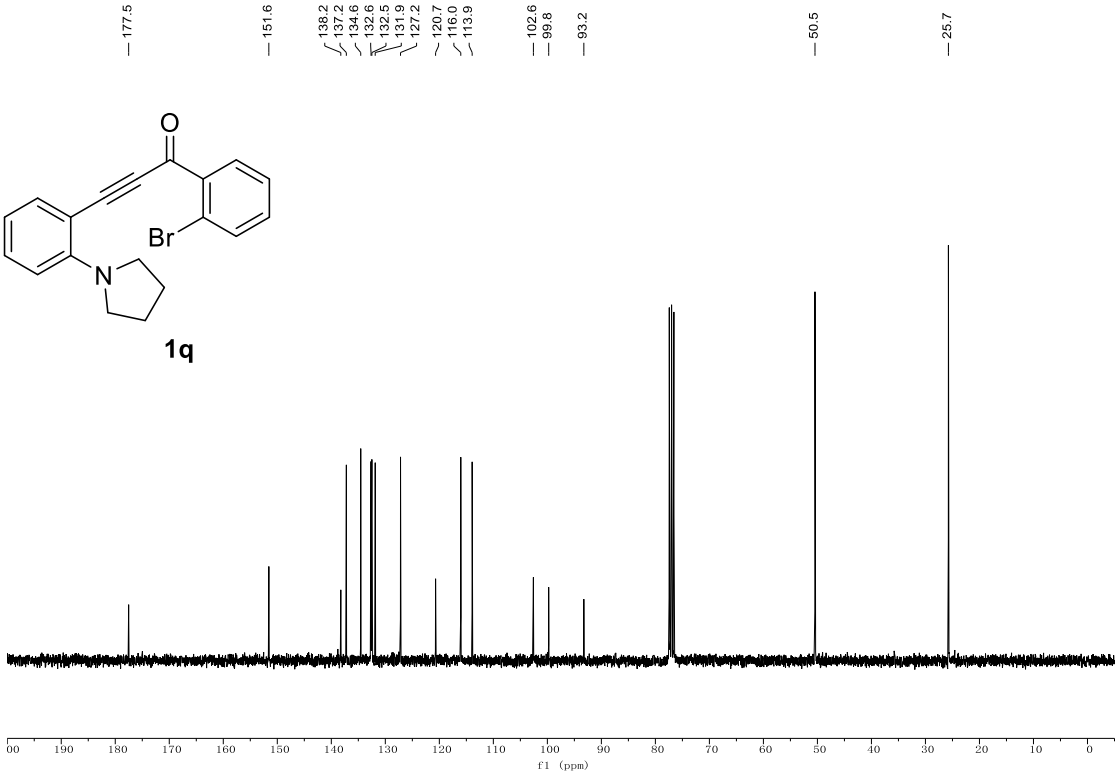


1p

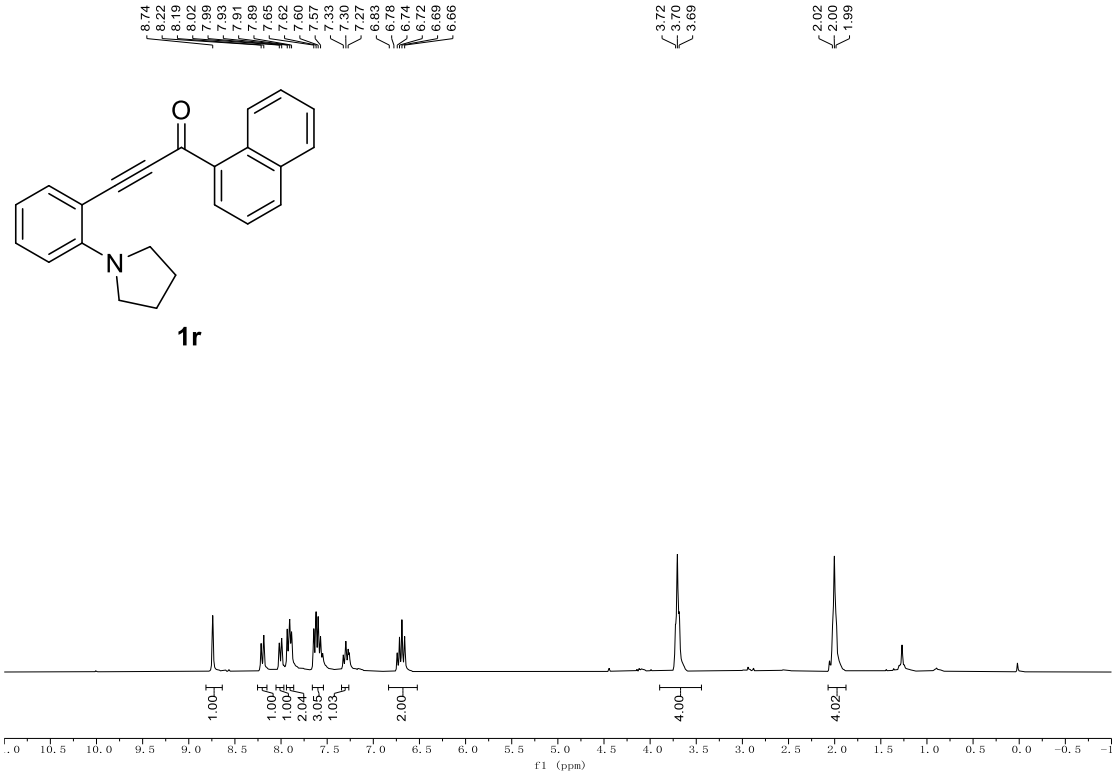
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1q**:



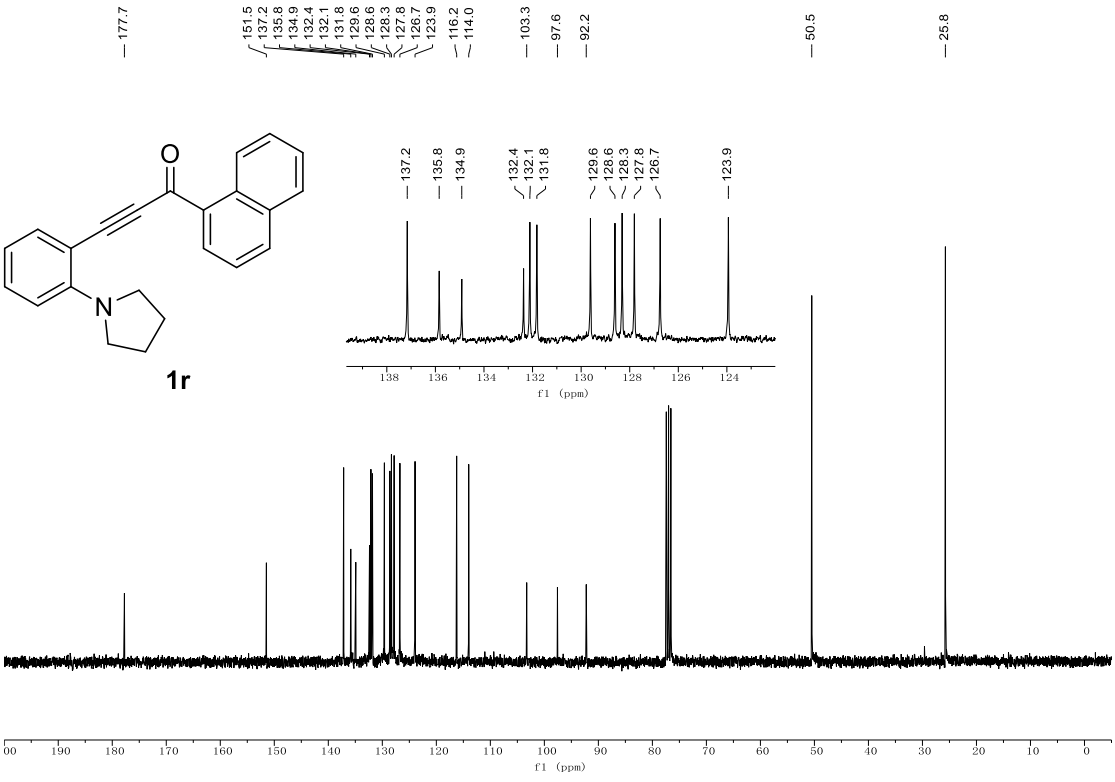
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1q**:



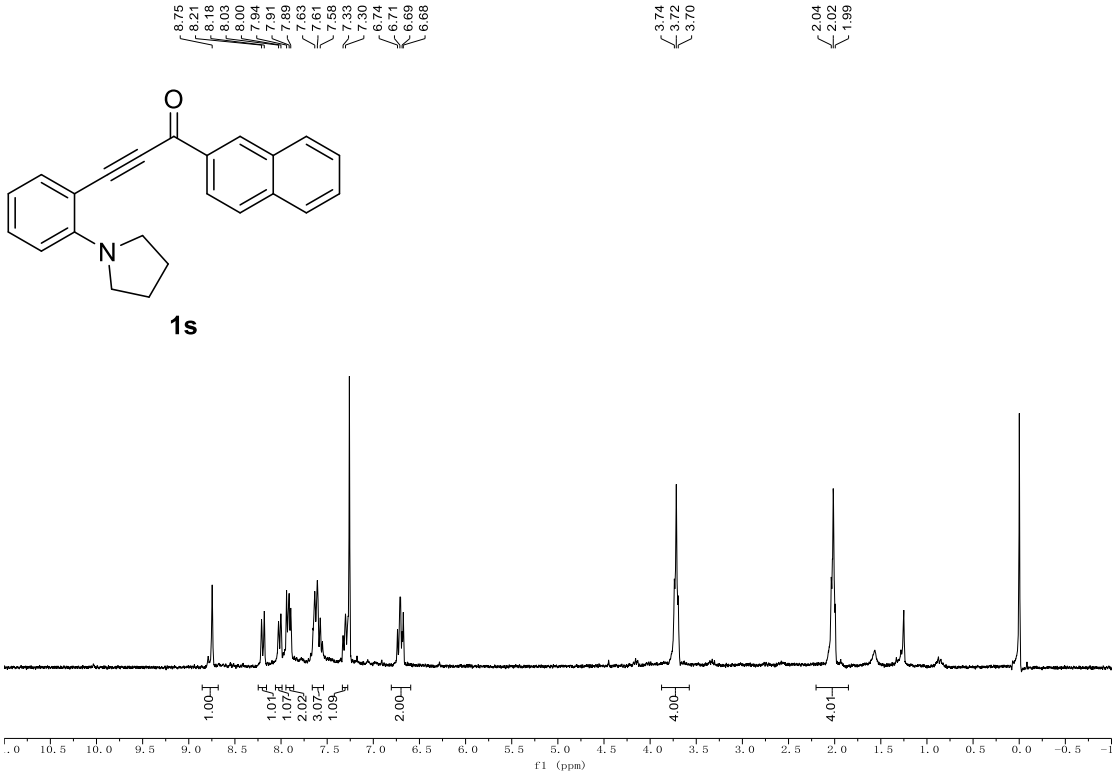
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1r**:



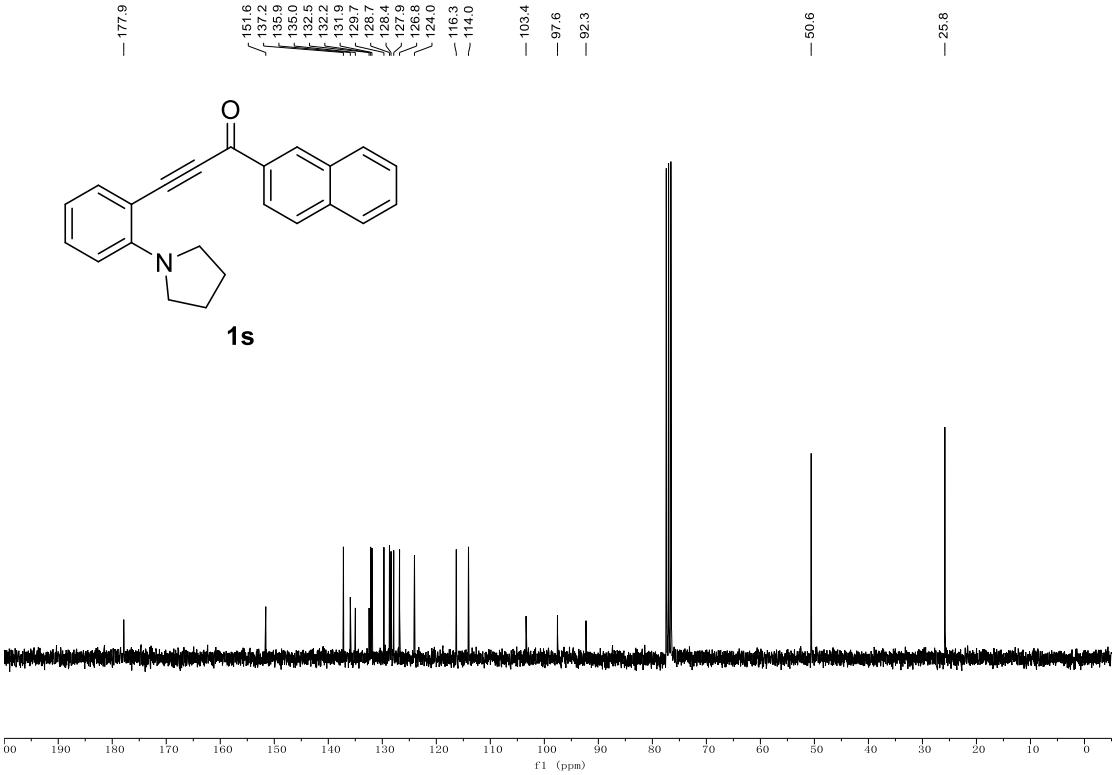
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1r**:



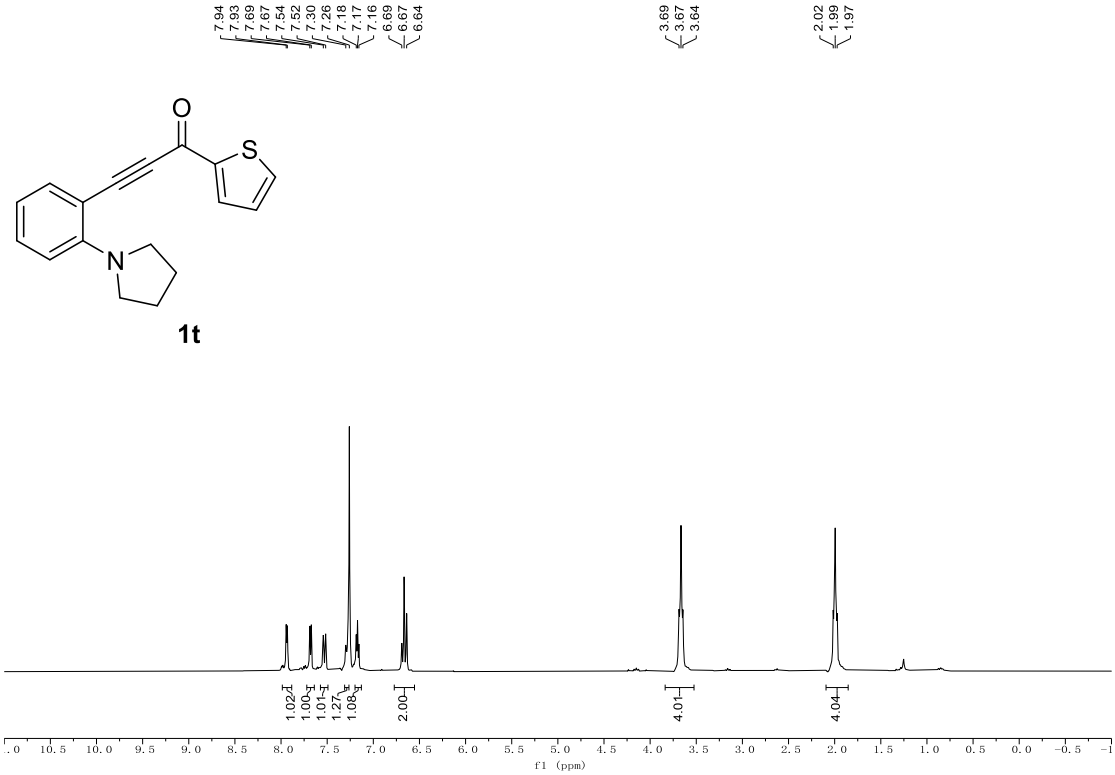
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1s**:



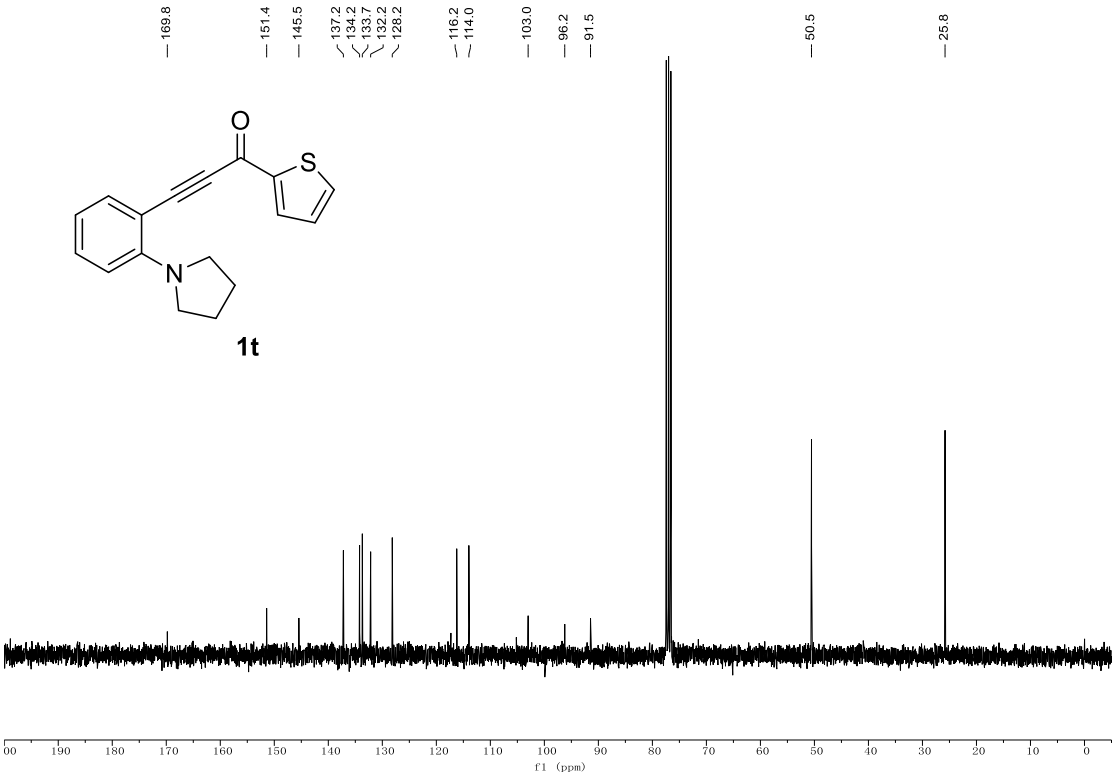
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1s**:



^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1t**:

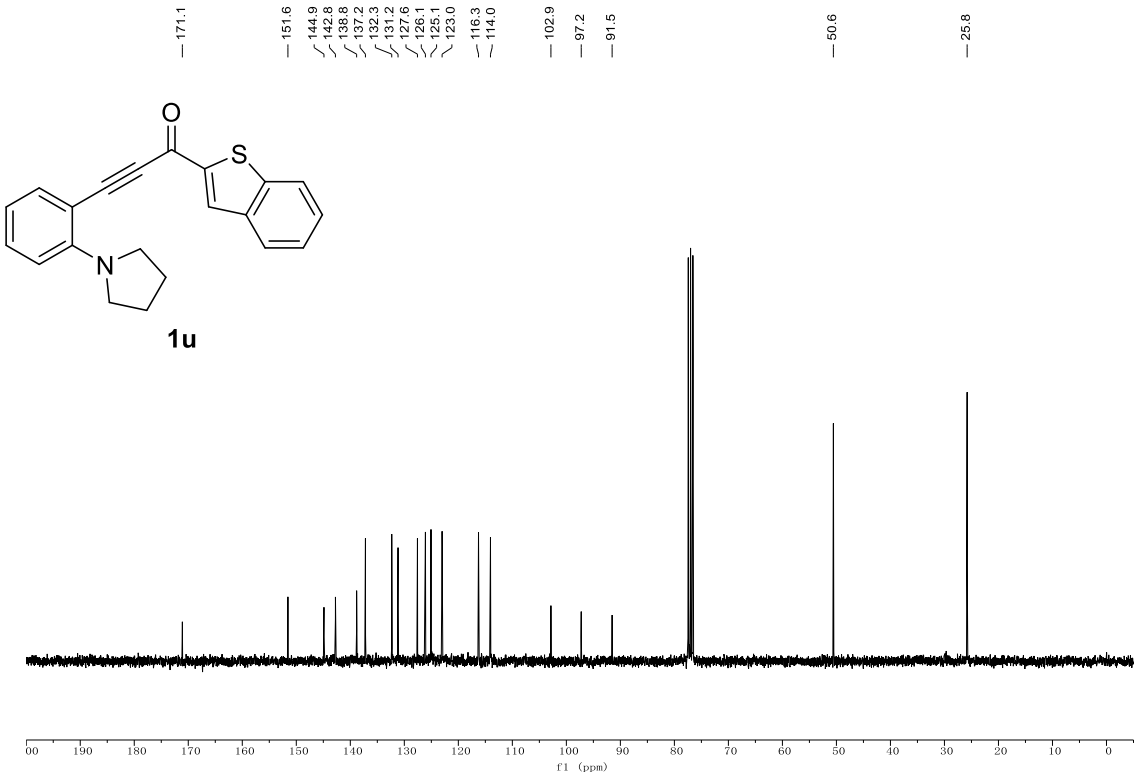


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1t**:

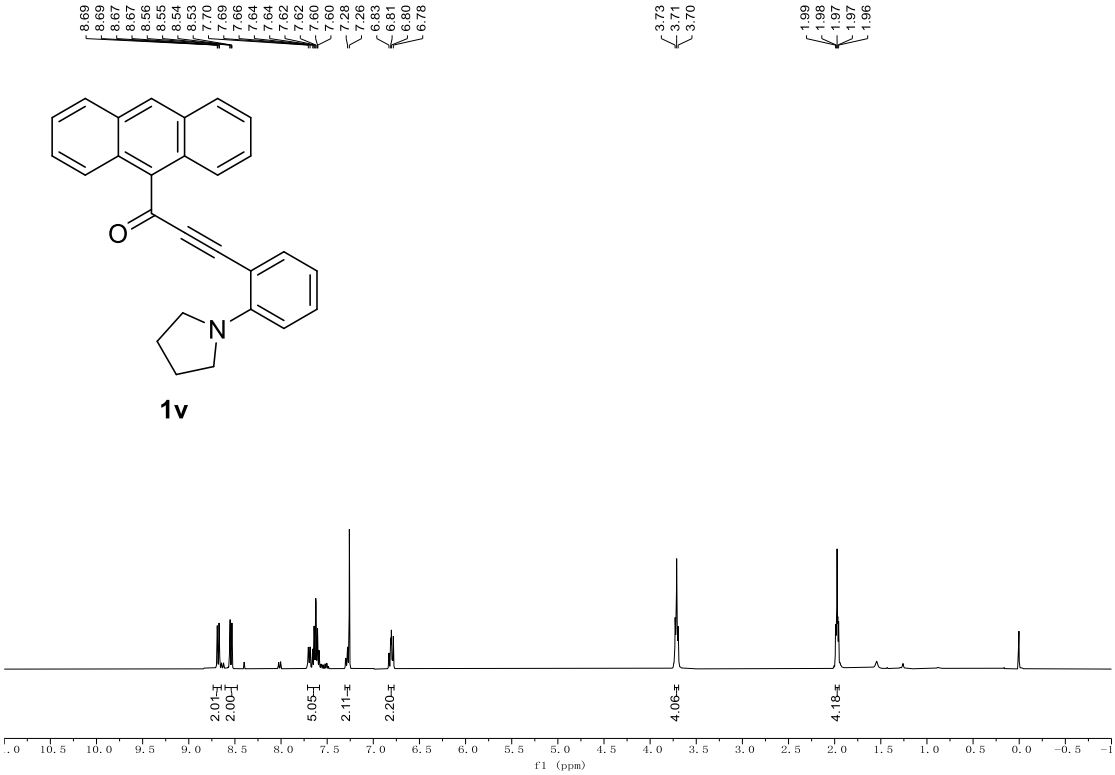


^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1u**:

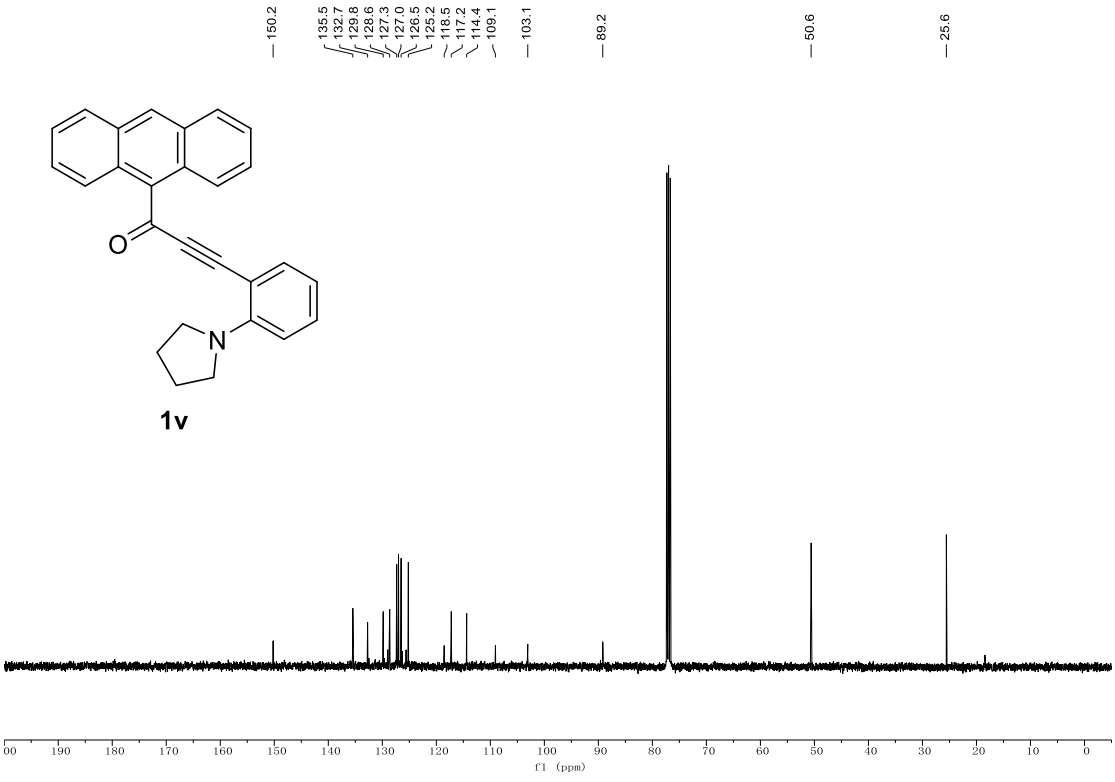
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1u**:



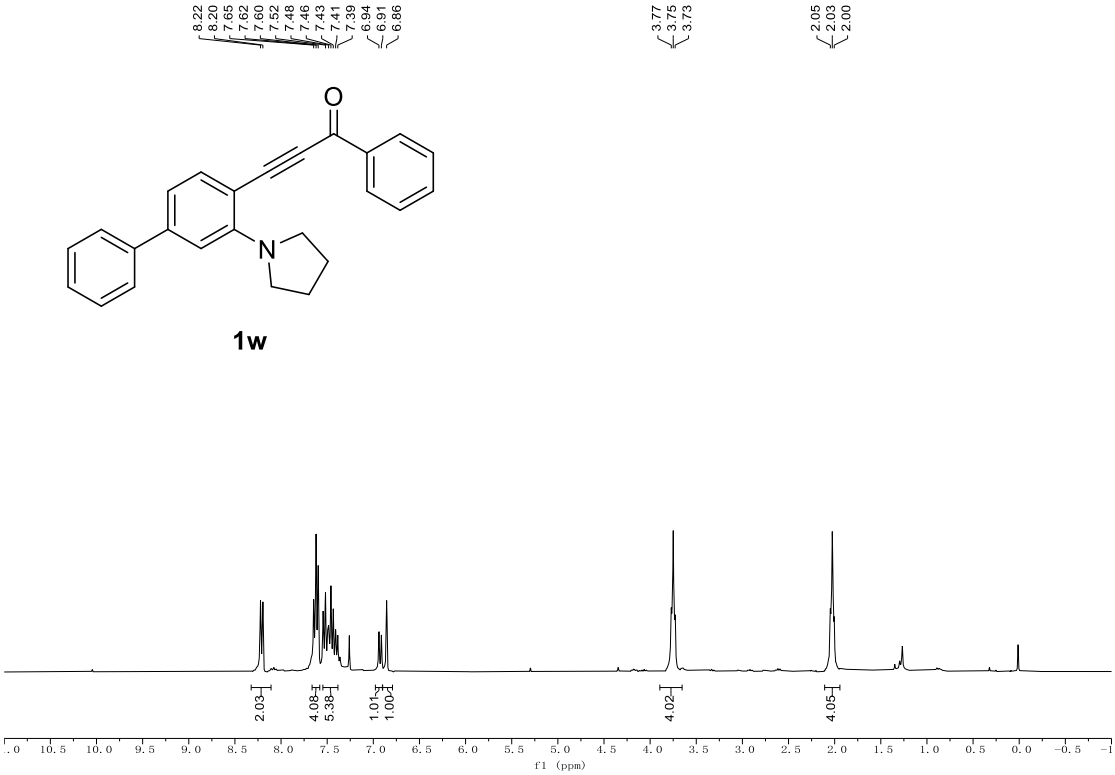
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **1v**:



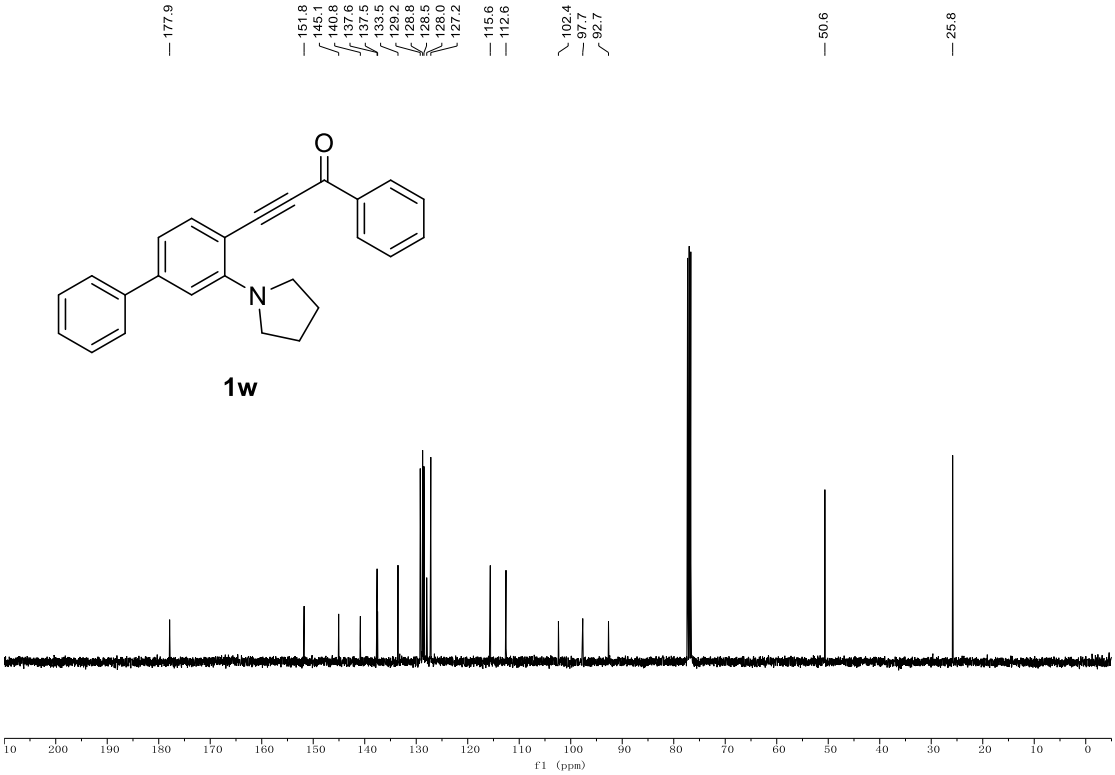
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **1v**:



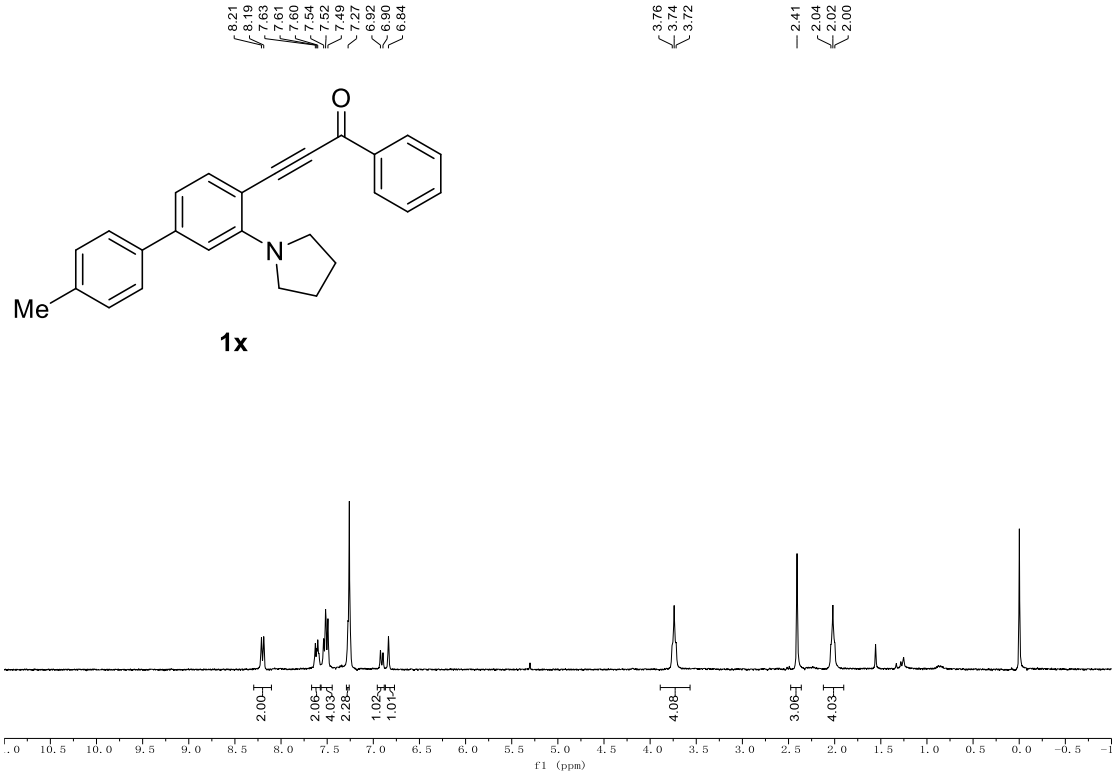
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1w**:



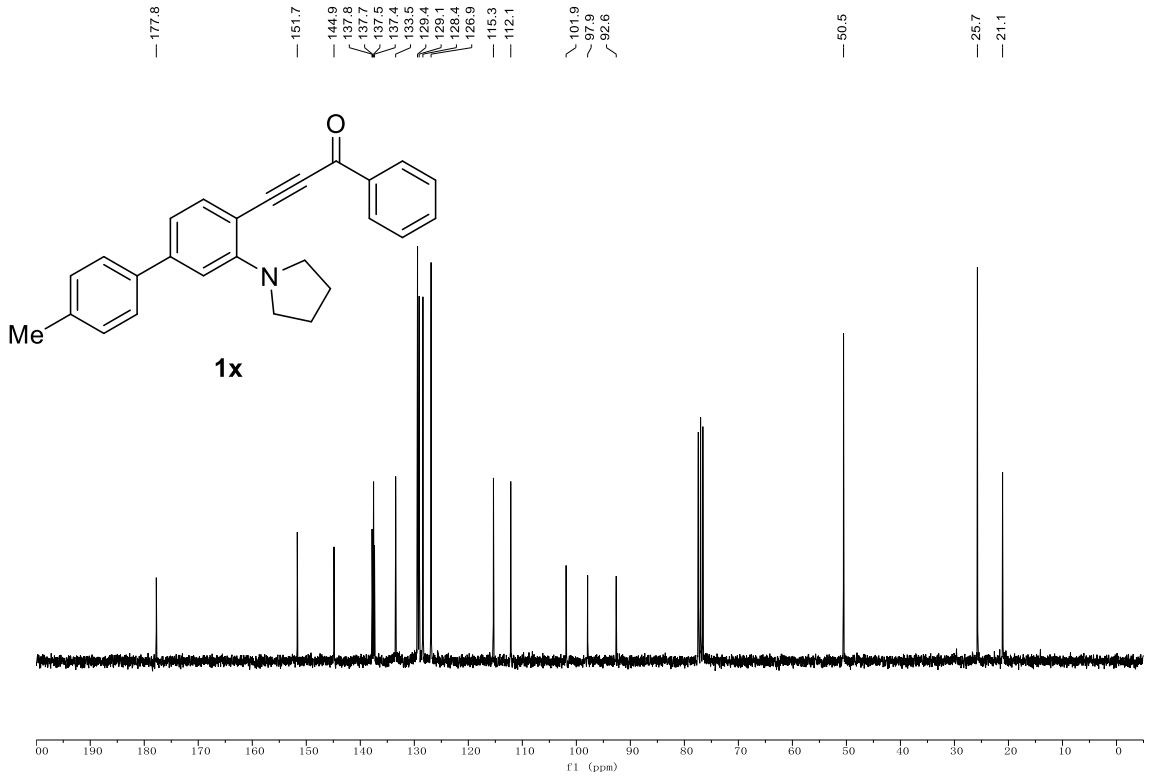
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **1w**:



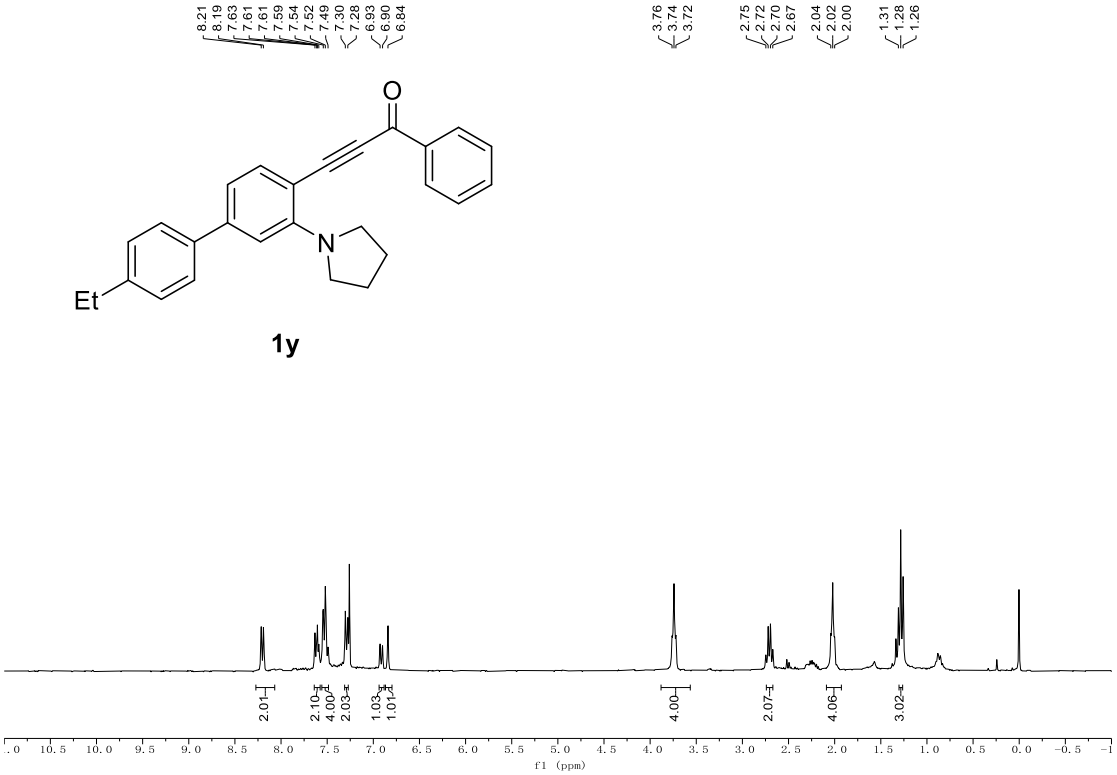
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1x**:



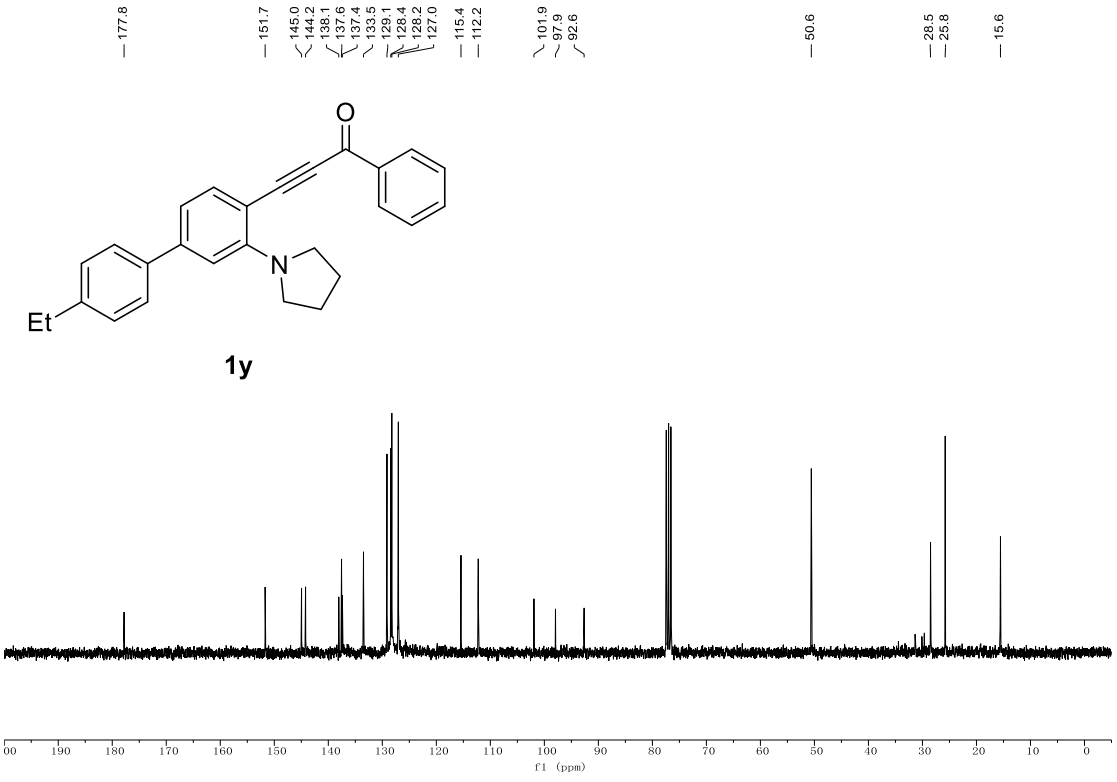
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1x**:



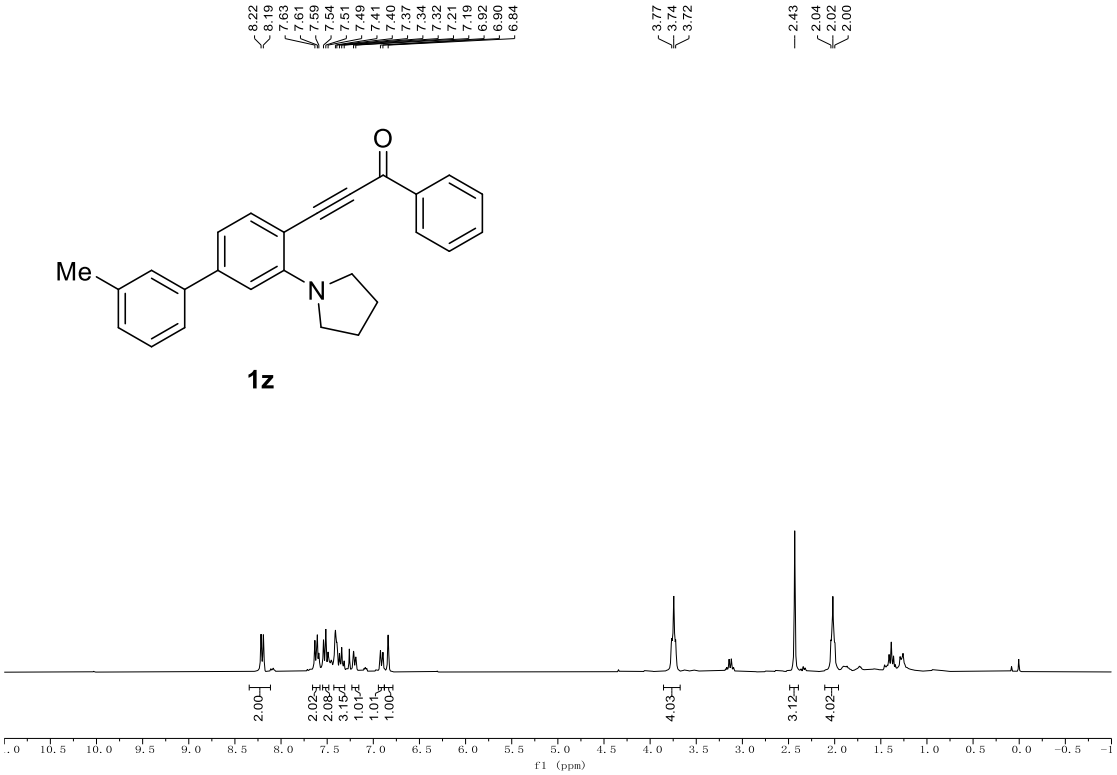
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1y**:



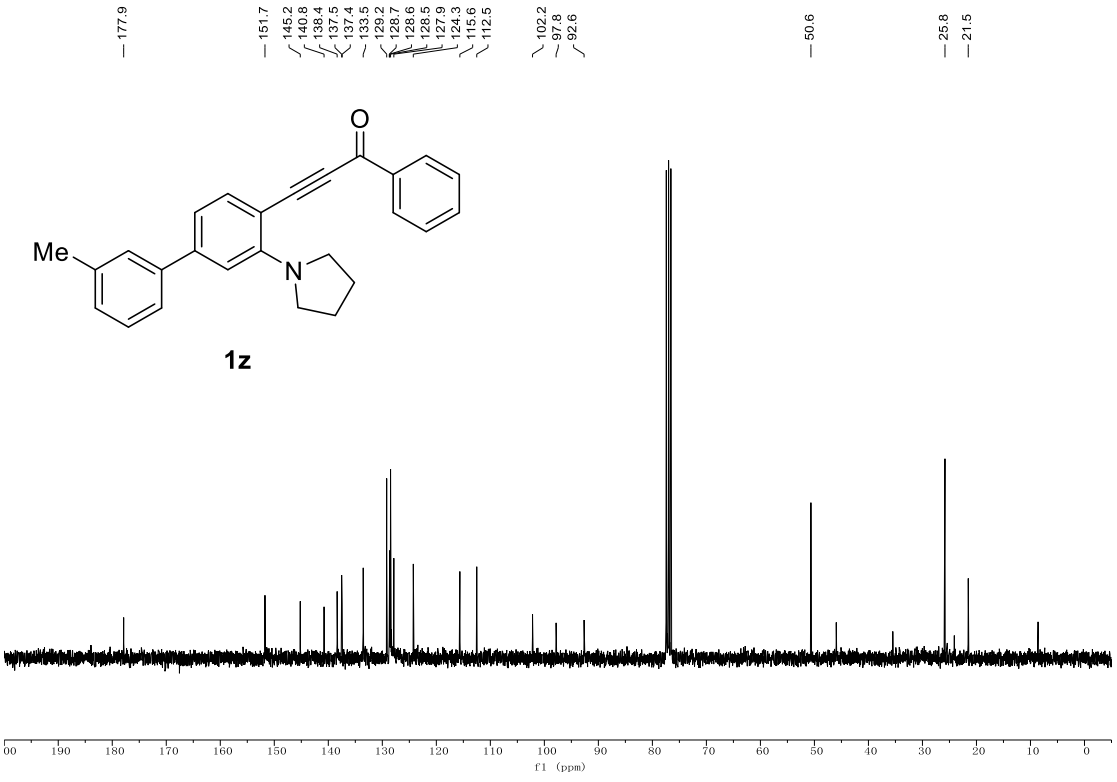
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1y**:



^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1z**:

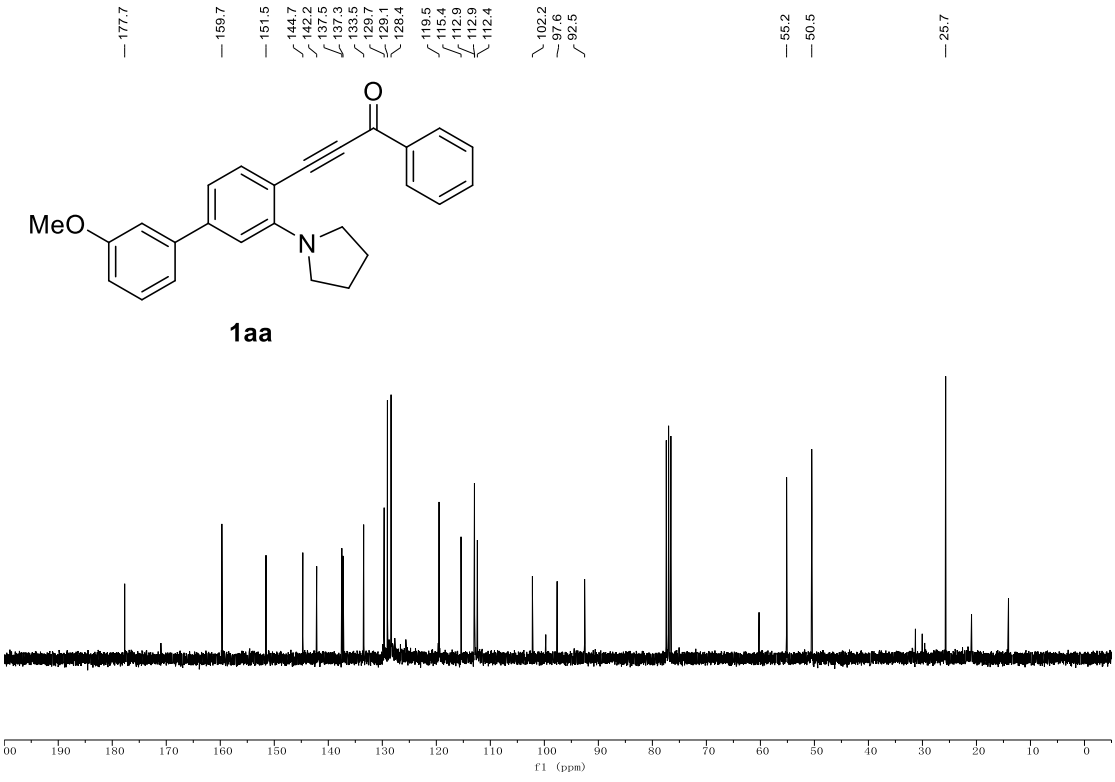


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1z**:

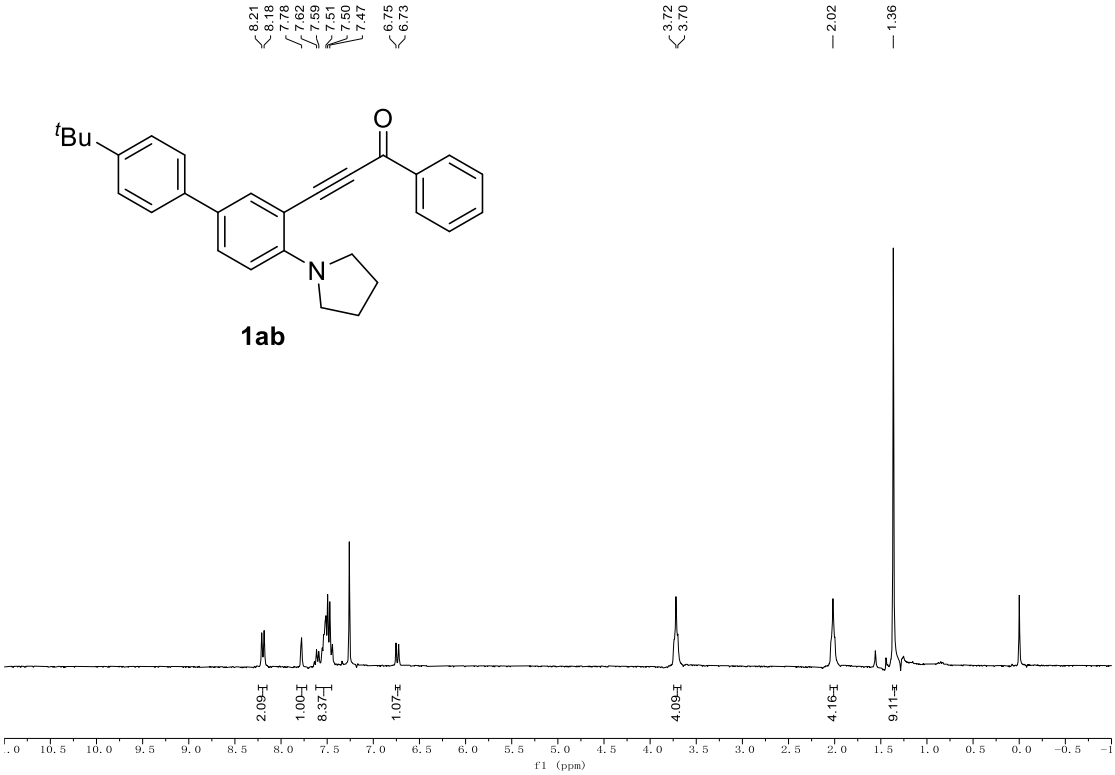


^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1aa**:

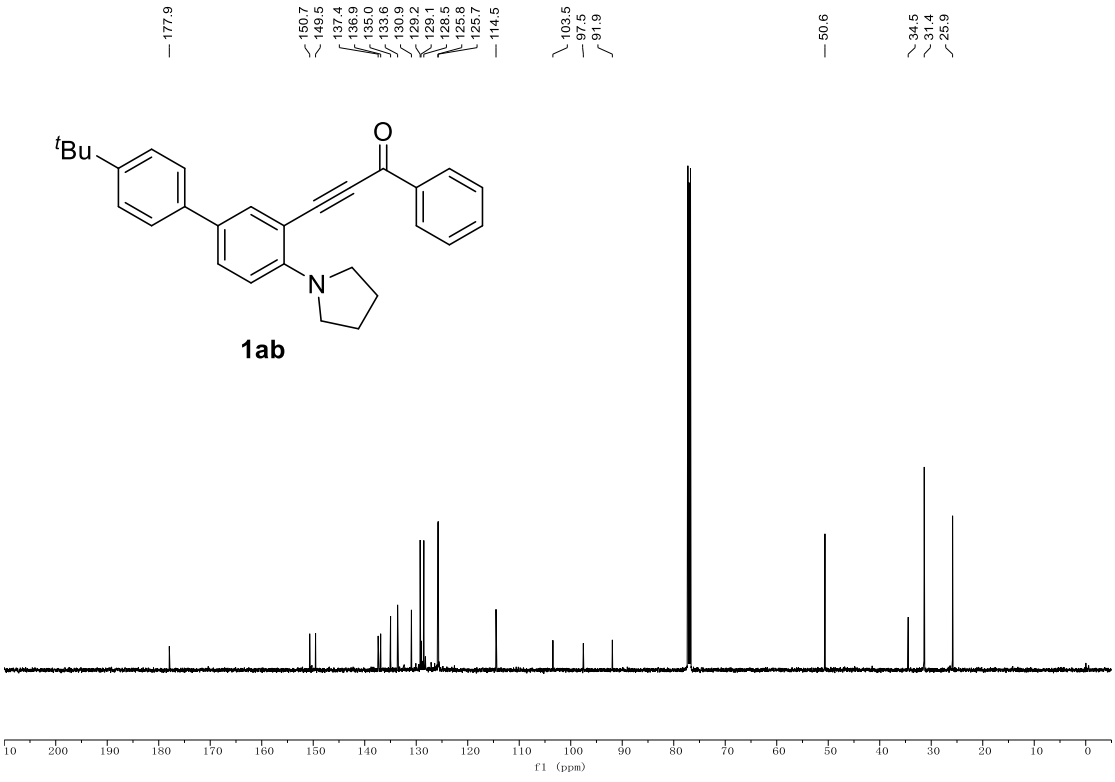
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1aa**:



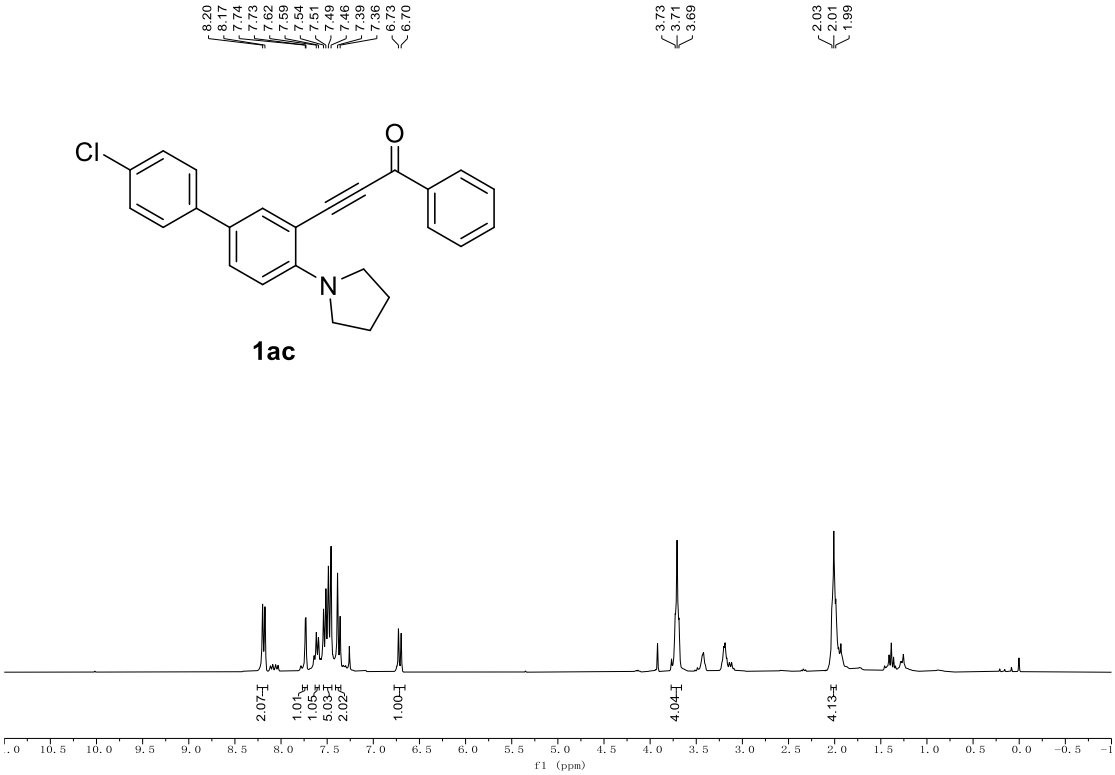
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1ab**:



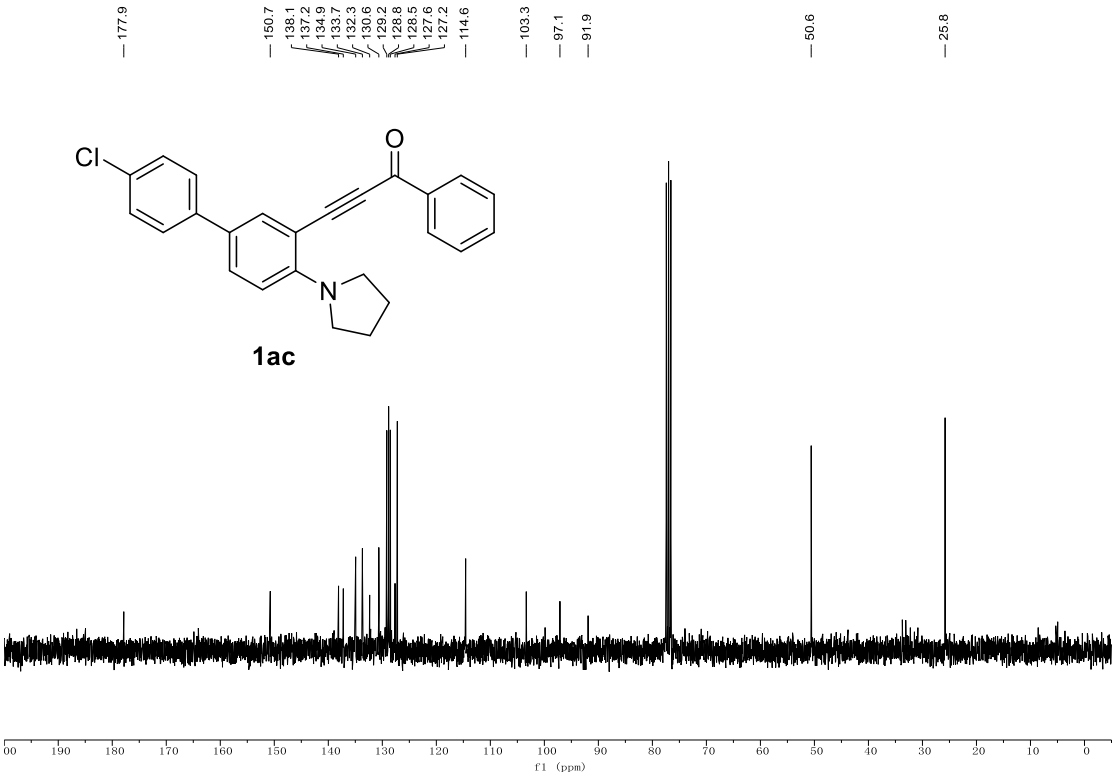
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectra of compound **1ab**:



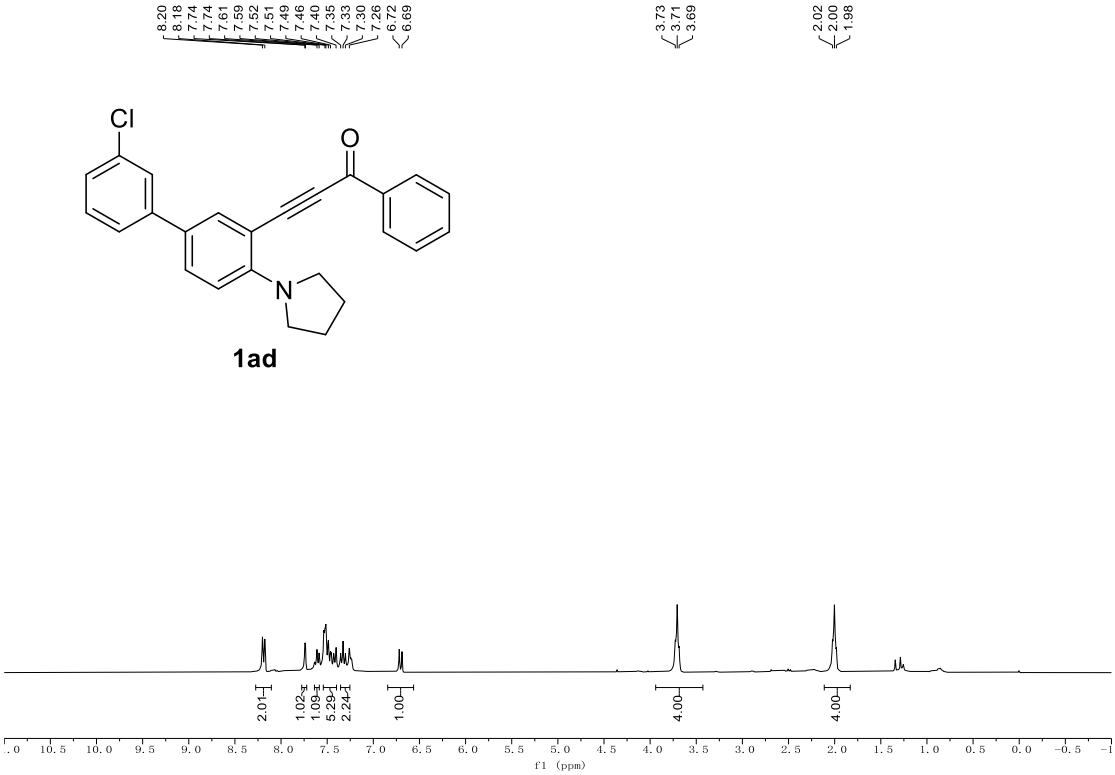
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1ac**:



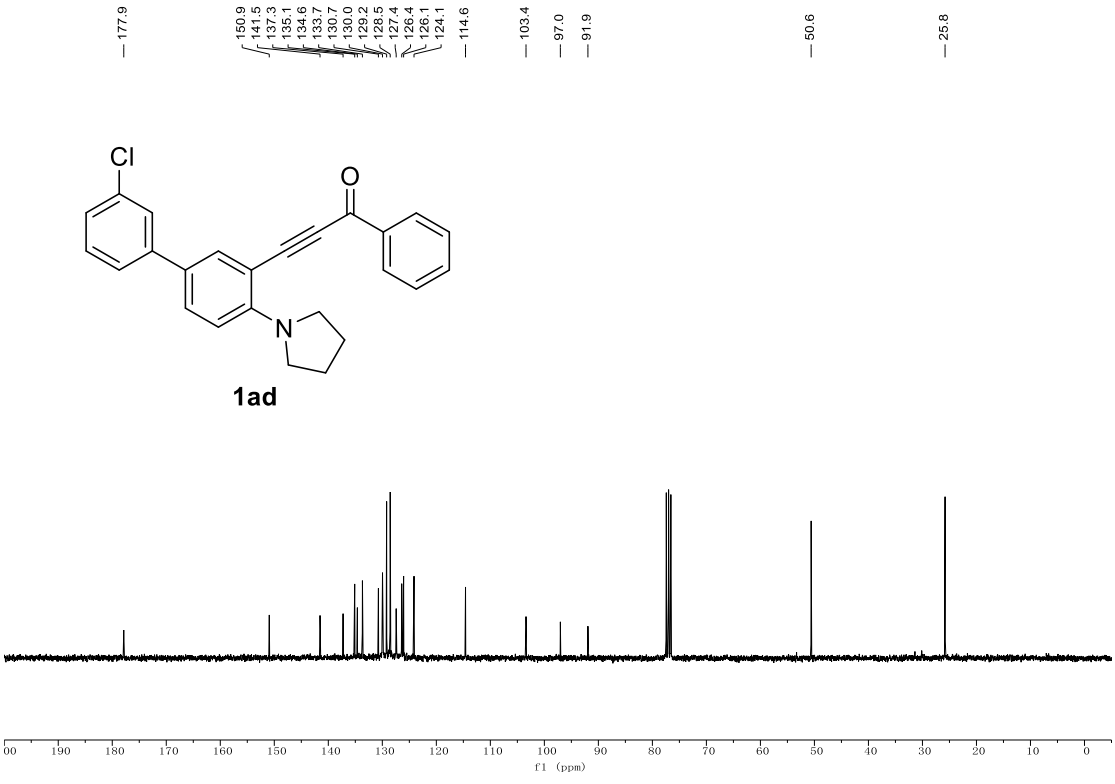
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1ac**:



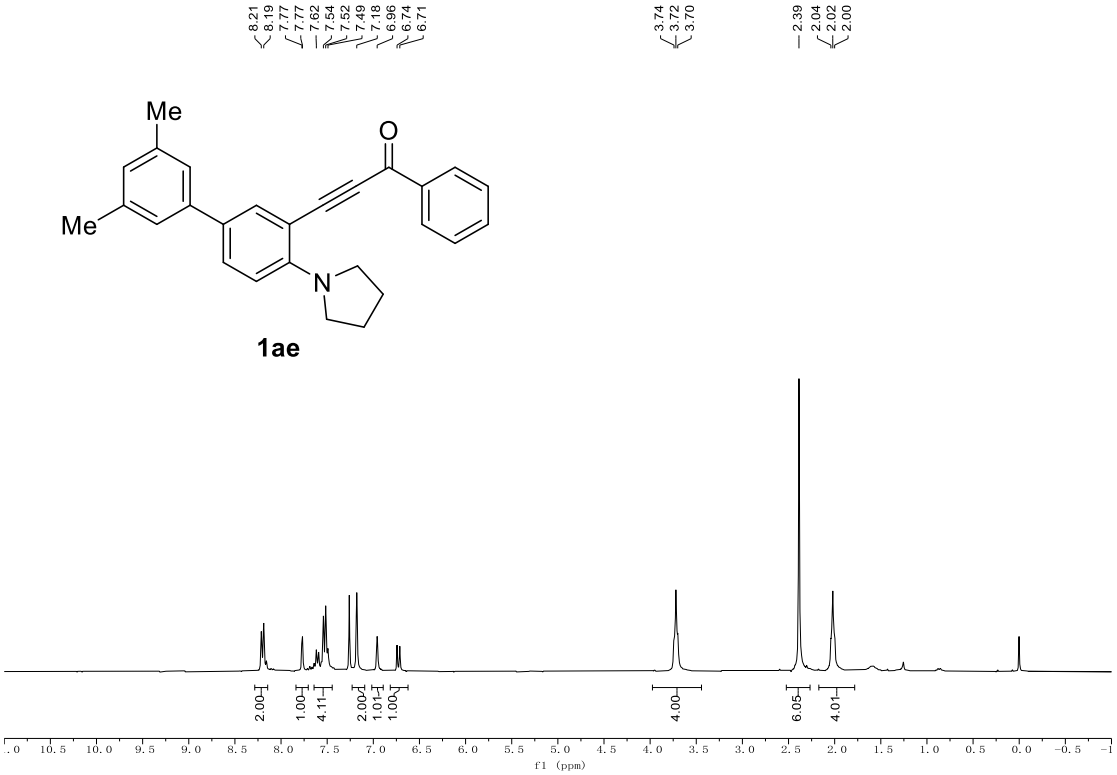
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1ad**:



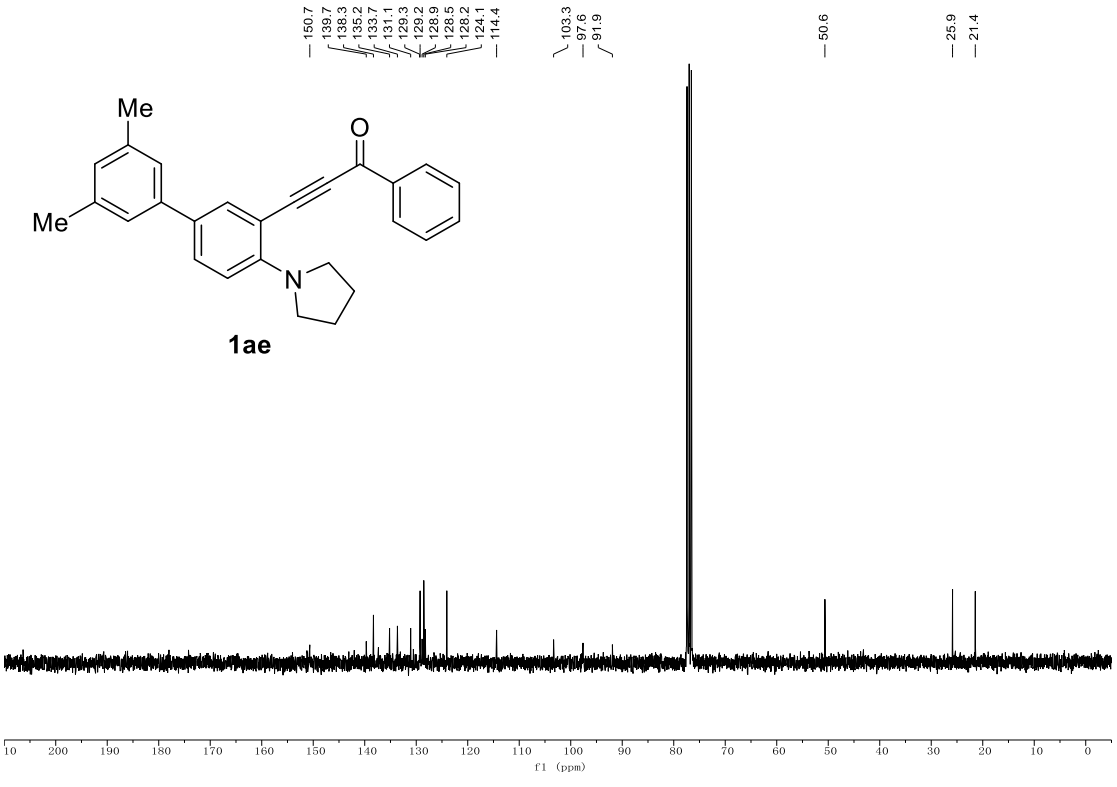
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1ad**:



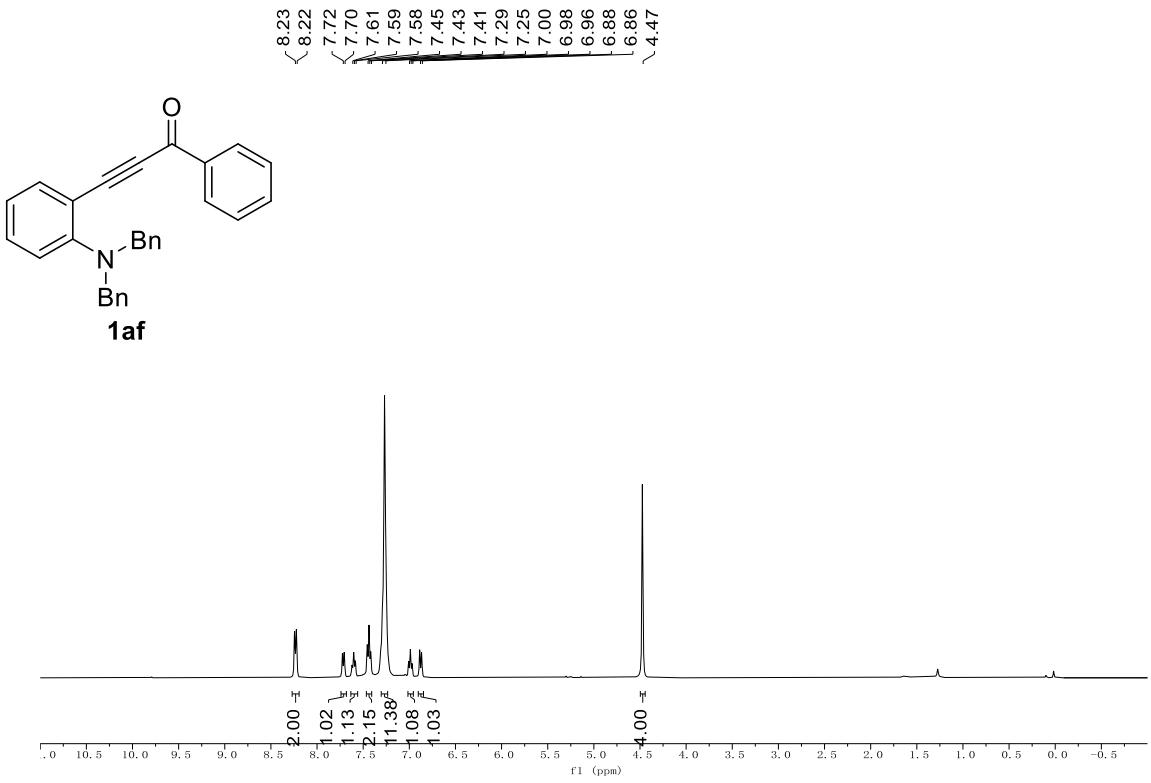
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1ae**:



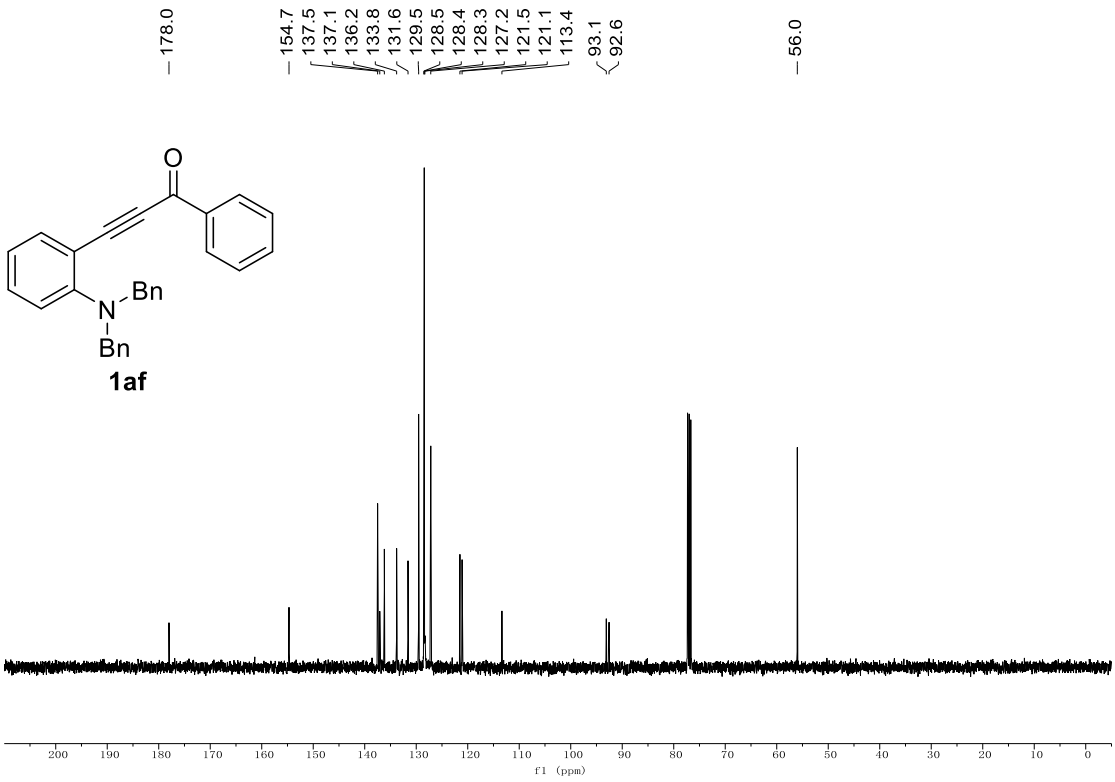
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1ae**:



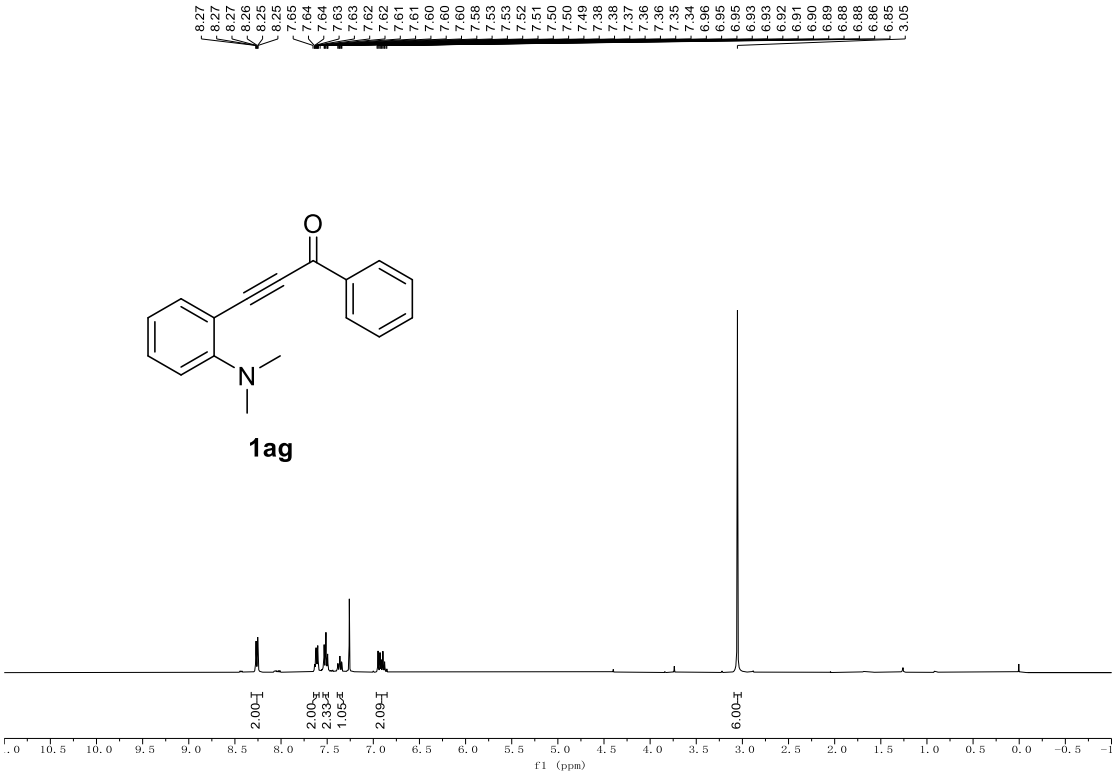
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1af**:



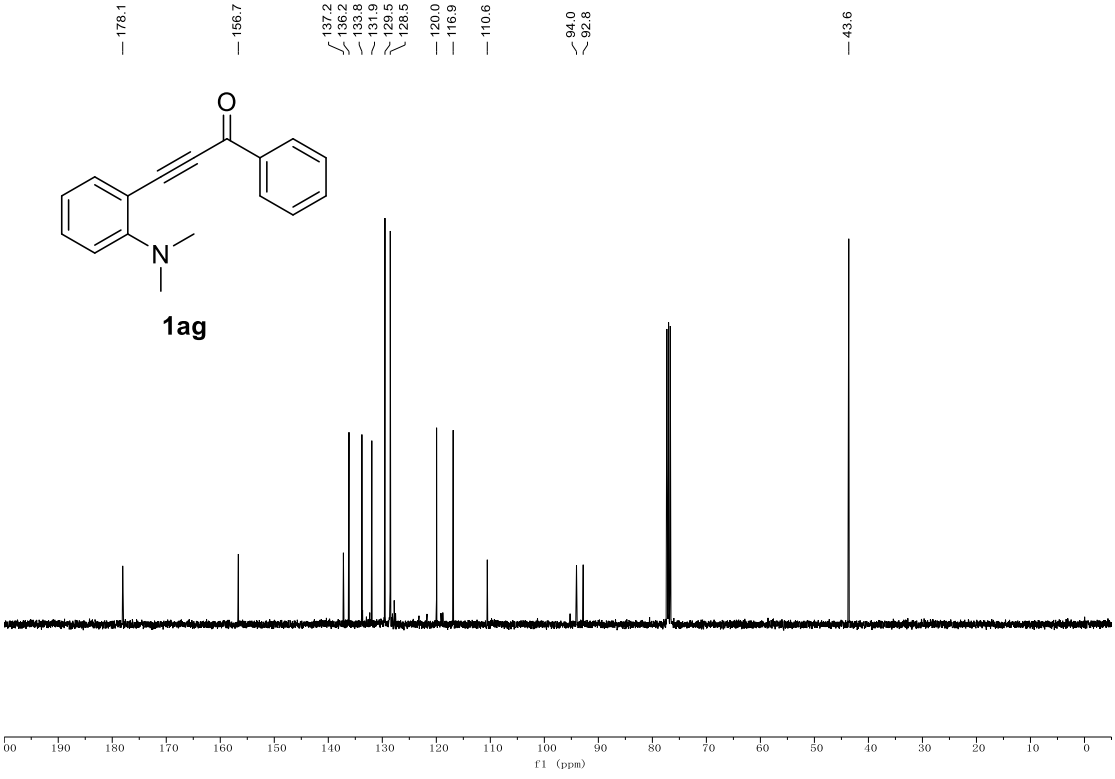
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1af**:



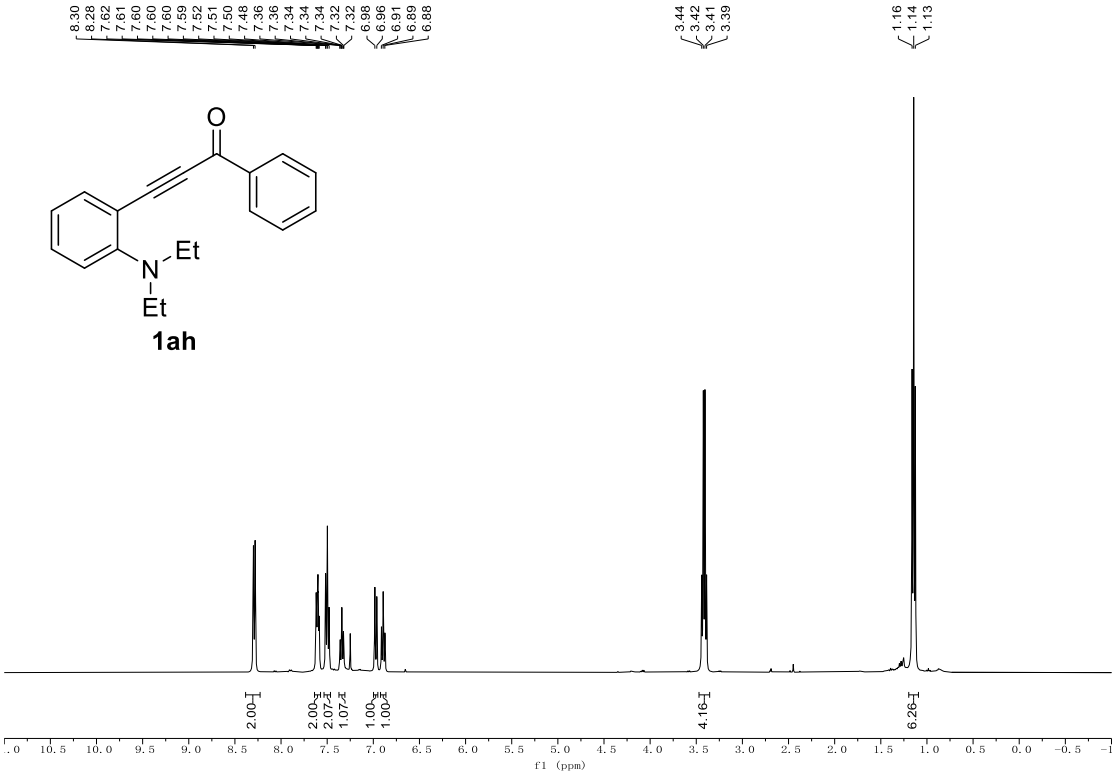
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **1ag**:



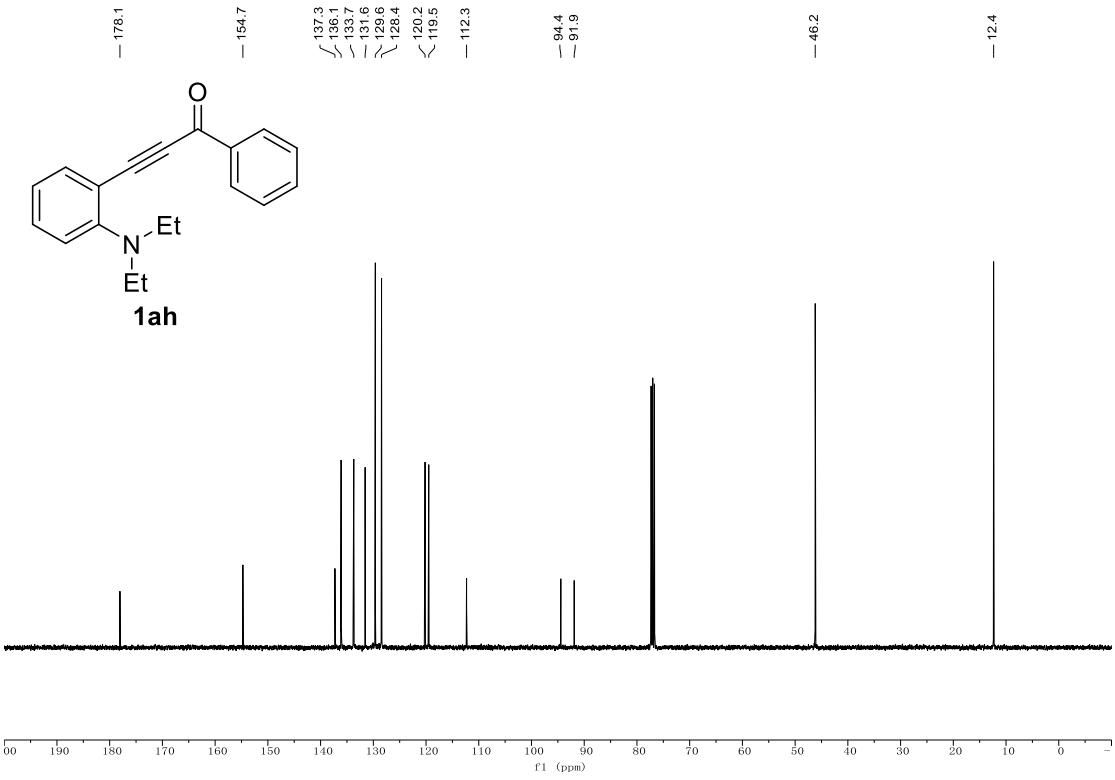
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **1ag**:



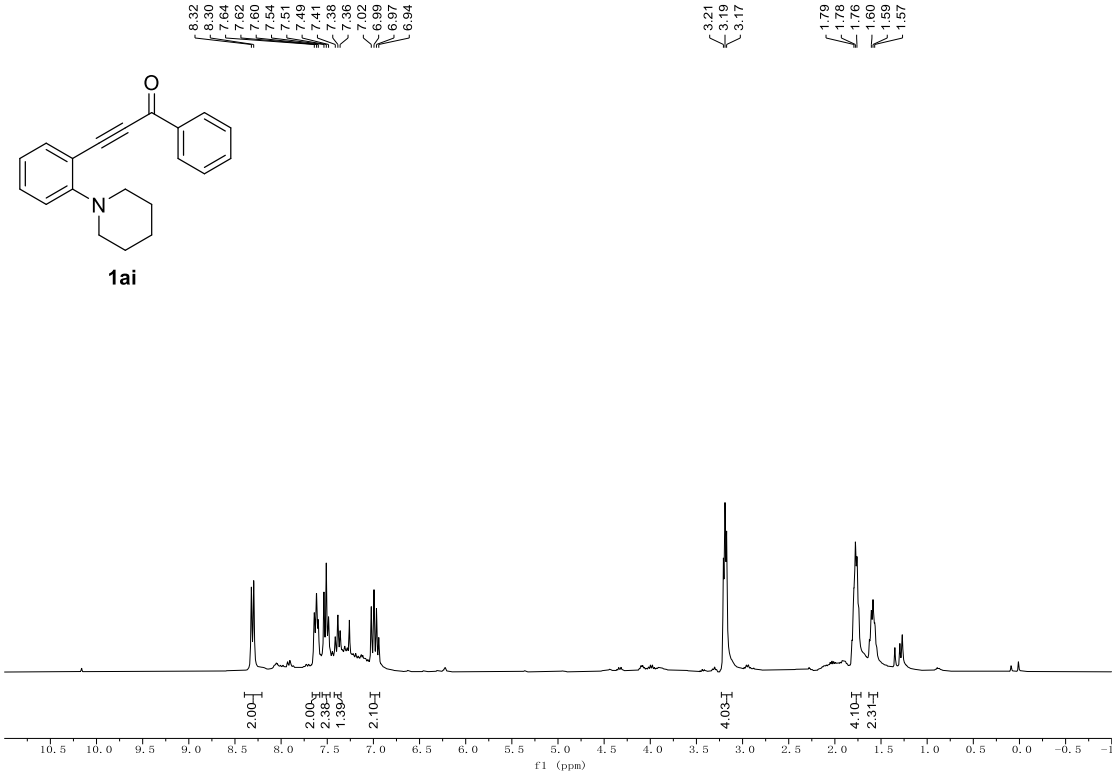
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **1ah**:



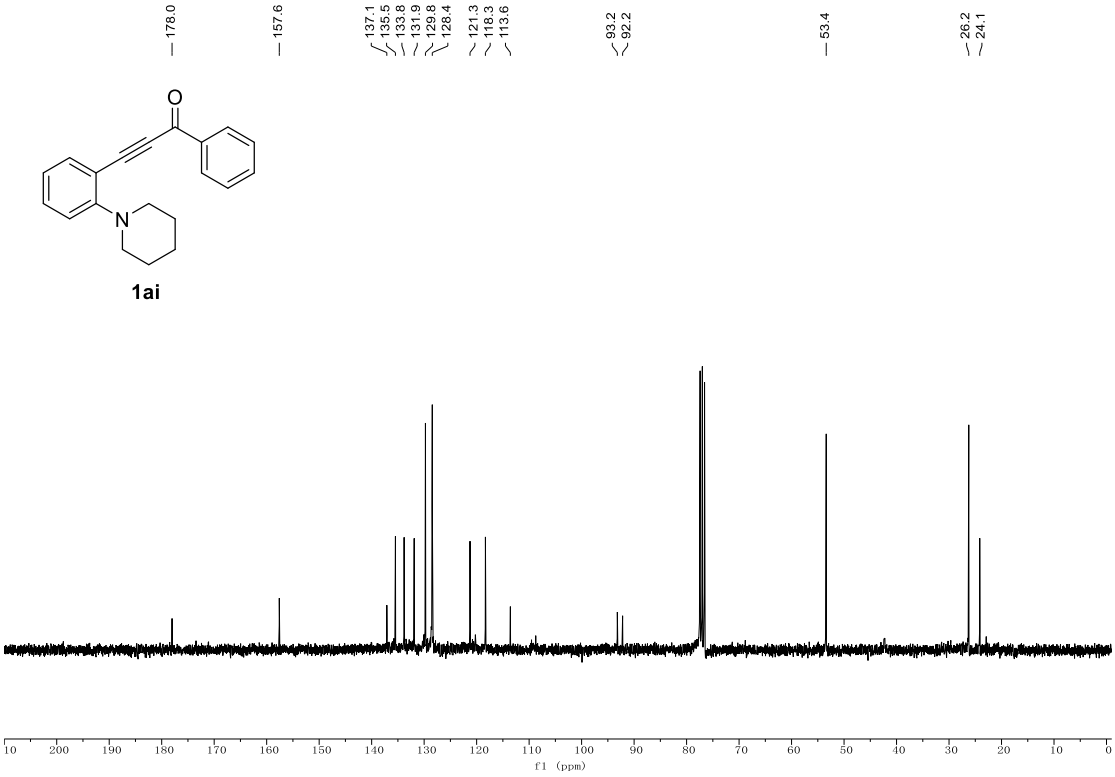
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **1ah**:



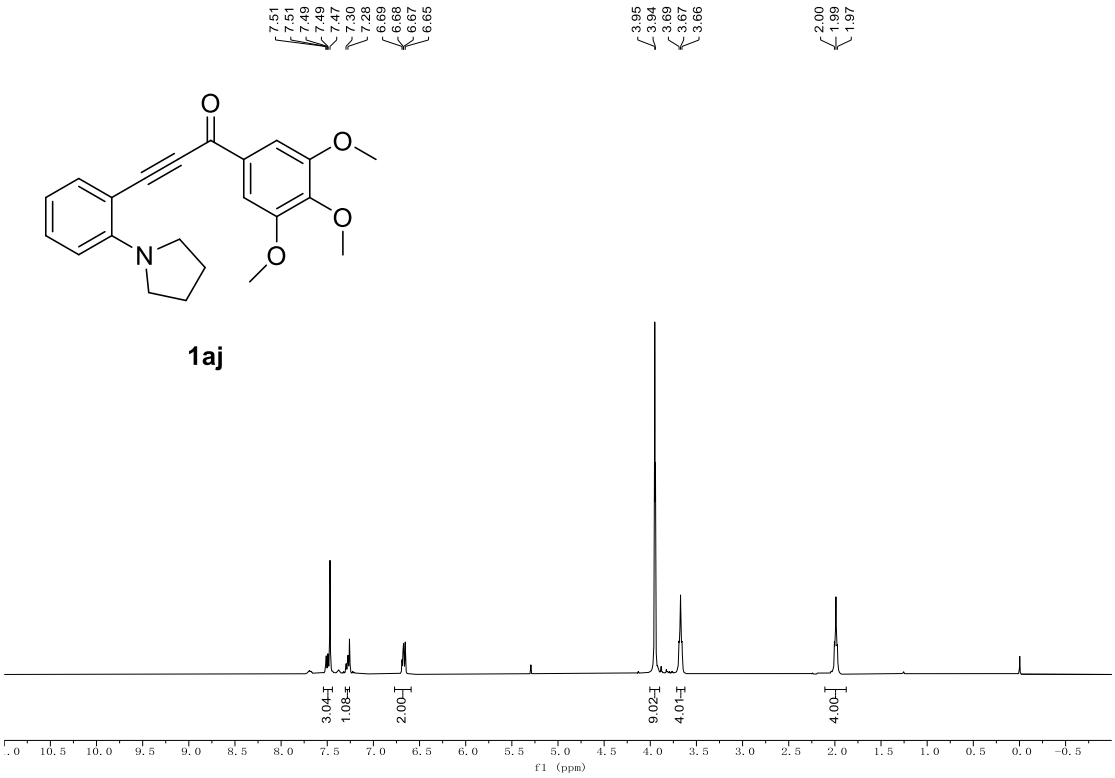
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **1ai**:



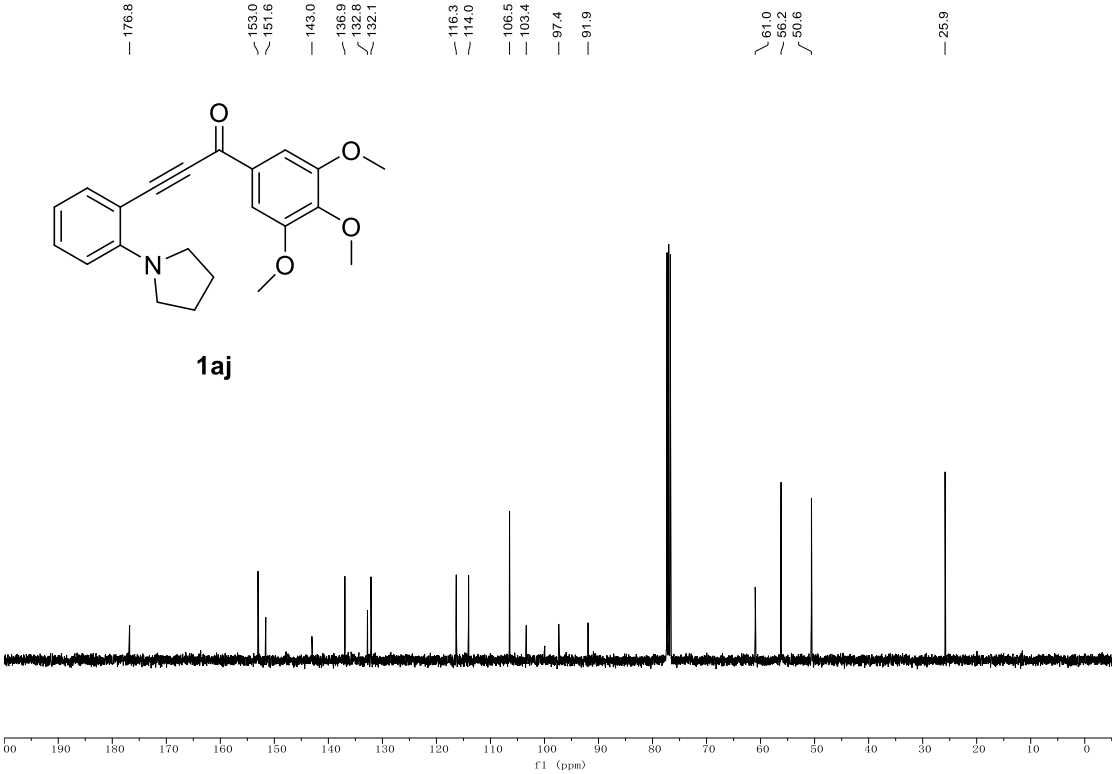
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **1ai**:



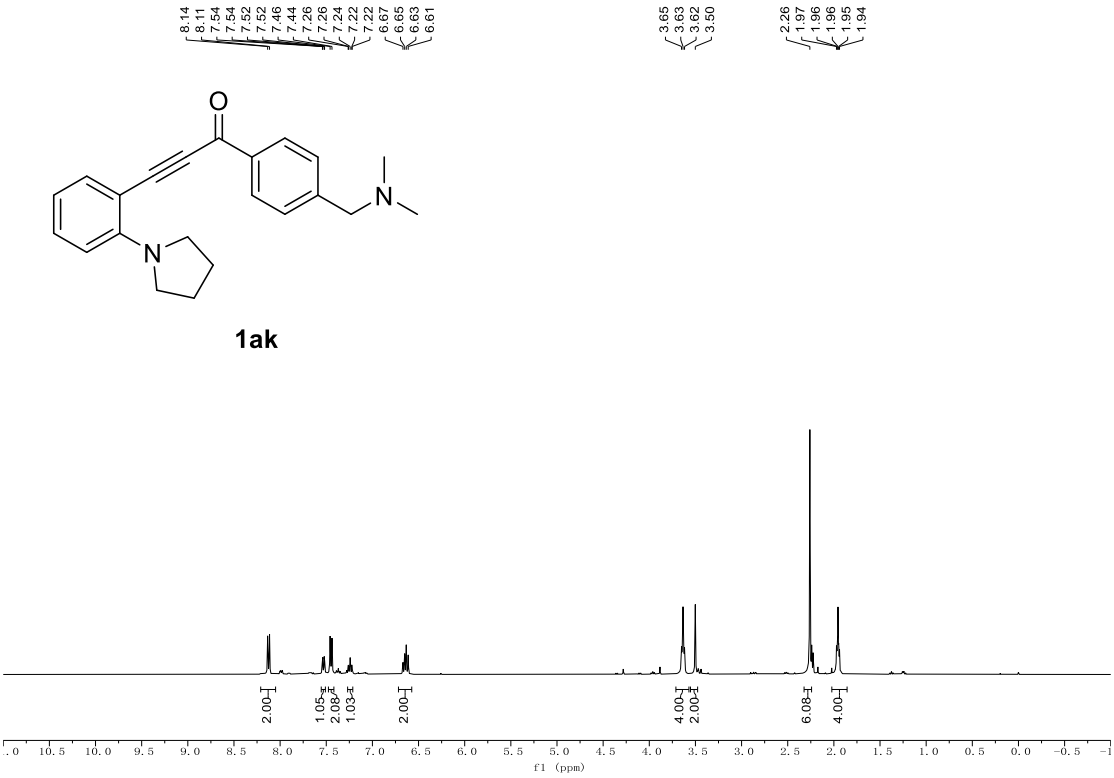
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **1aj**



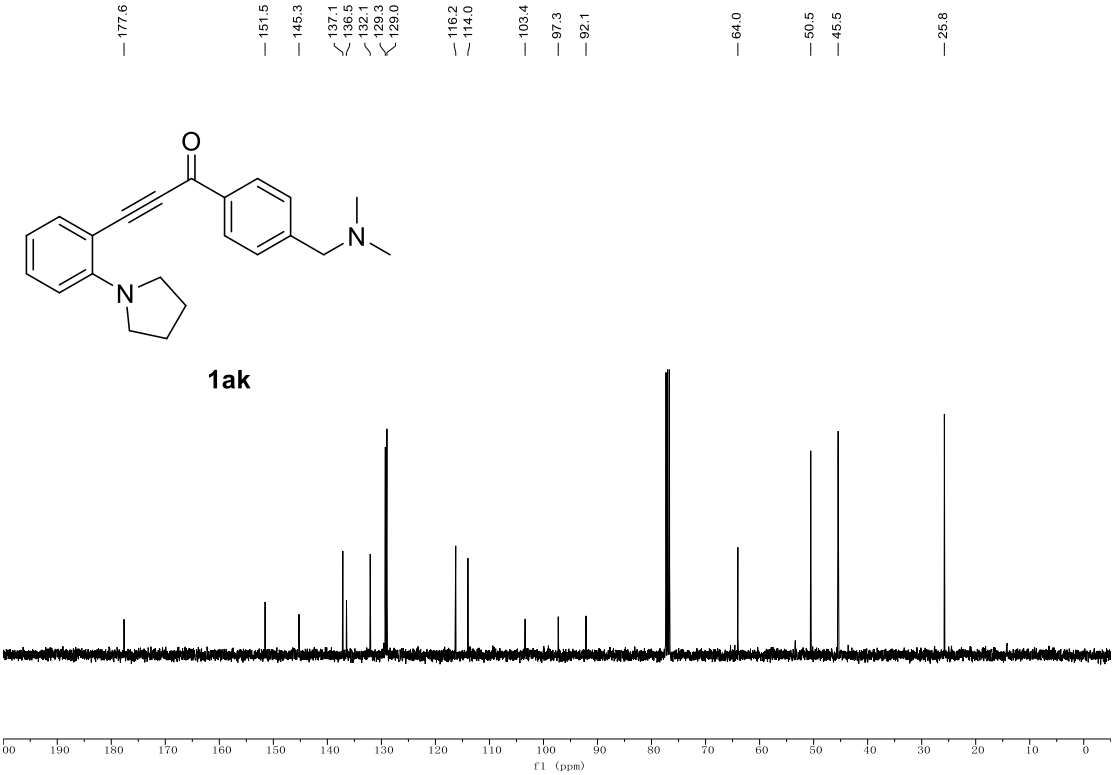
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **1aj**:



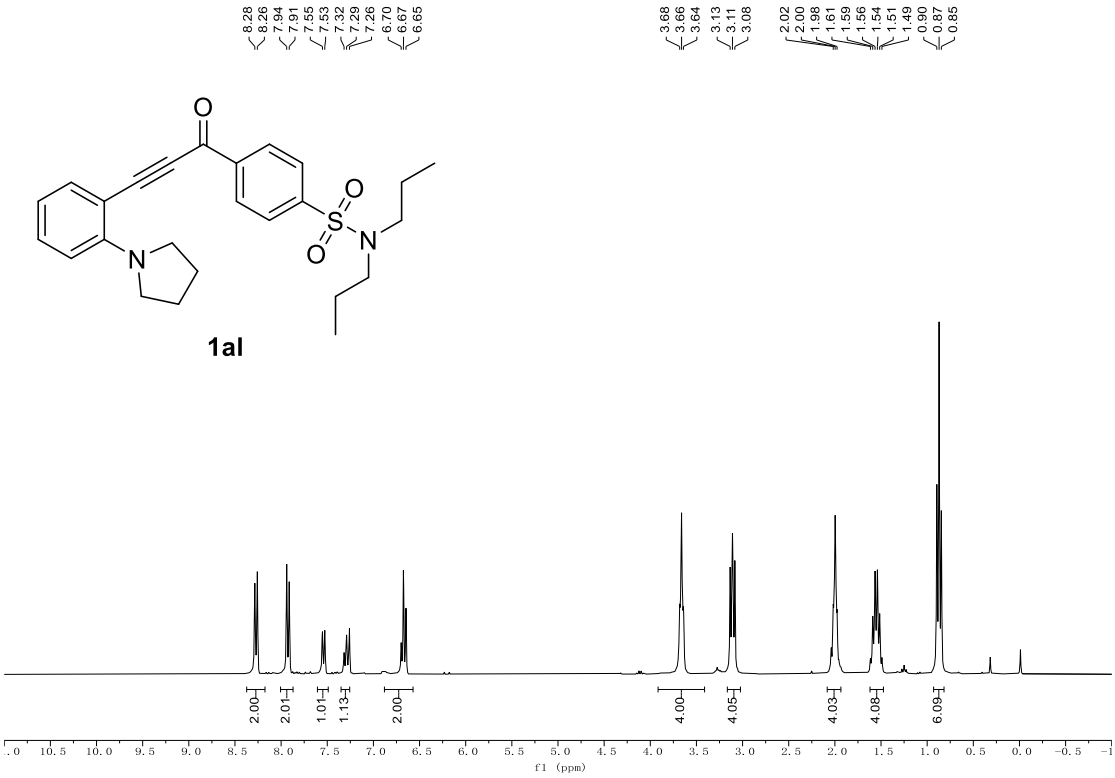
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **1ak**:



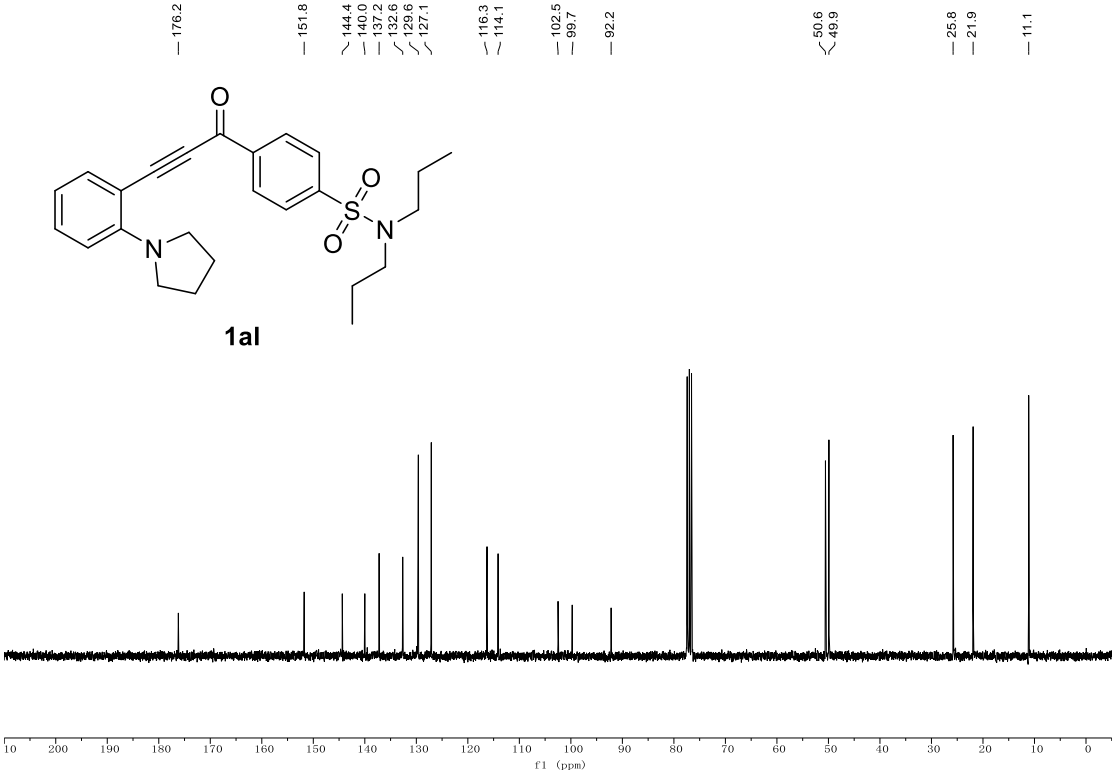
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **1ak**:



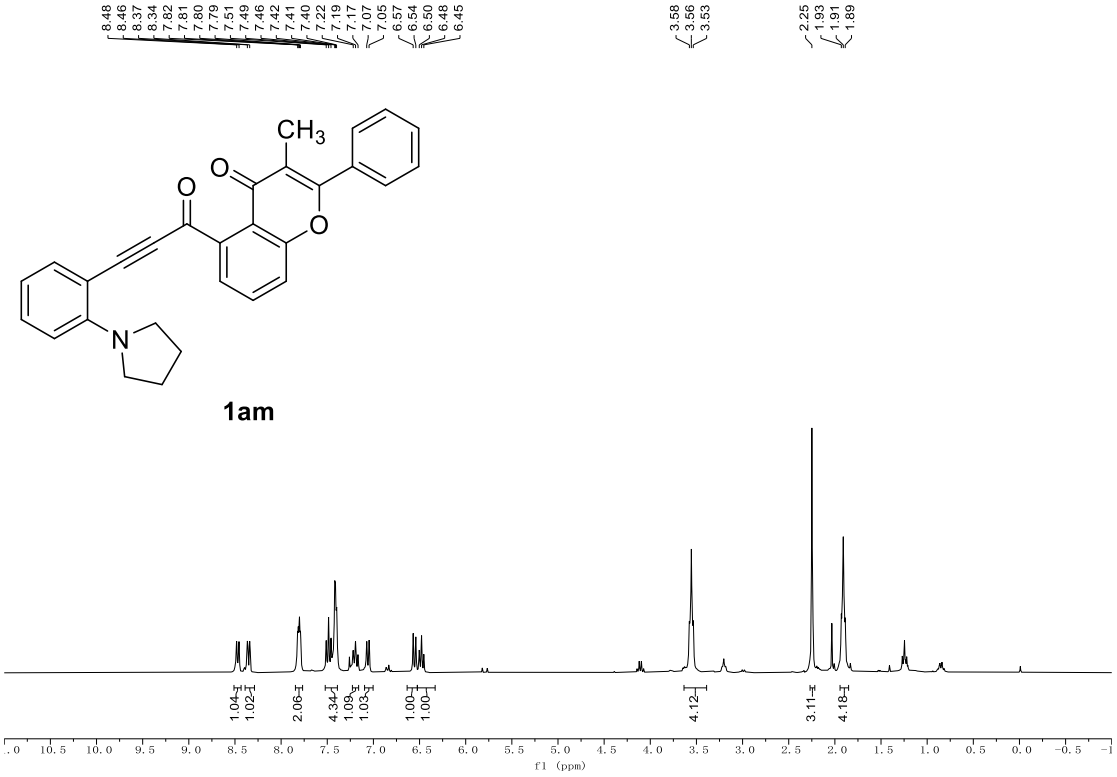
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1al**:



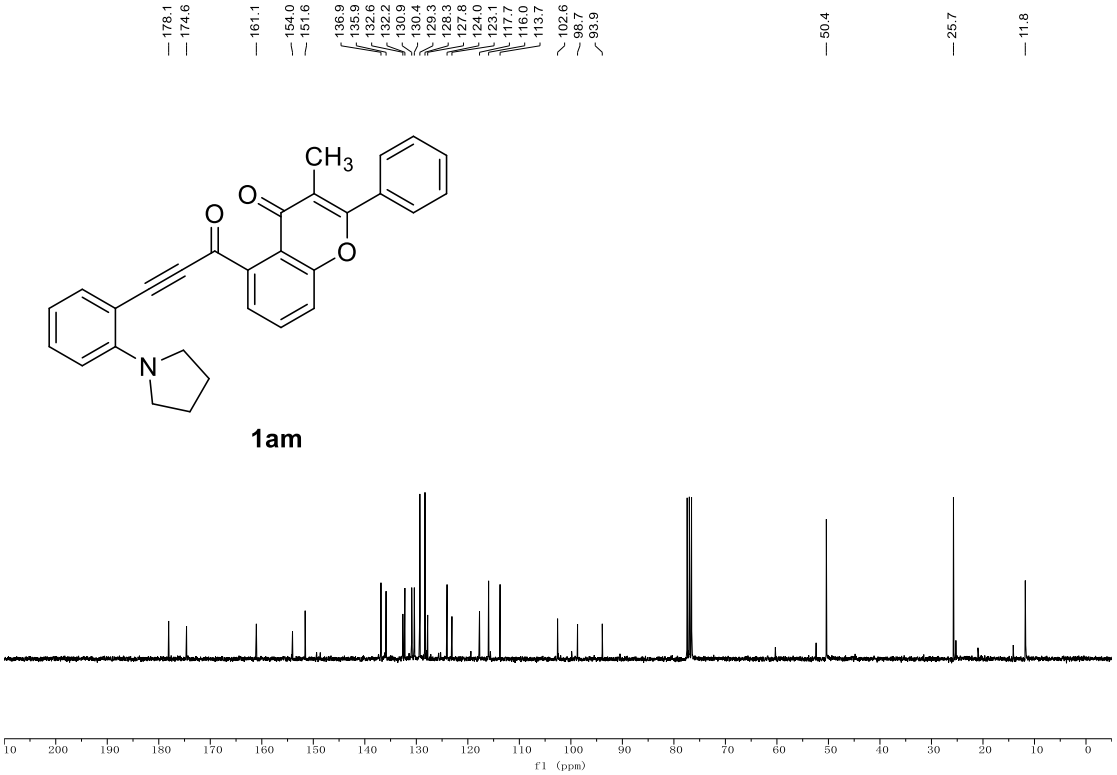
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1al**:



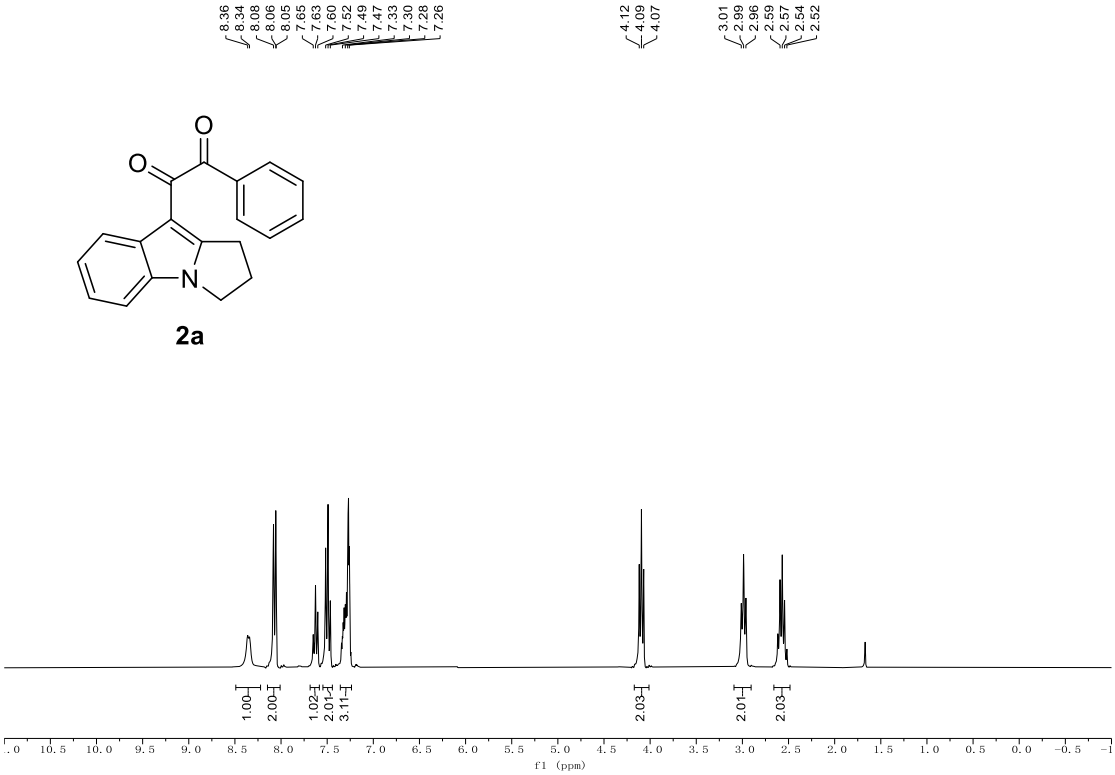
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **1am**:



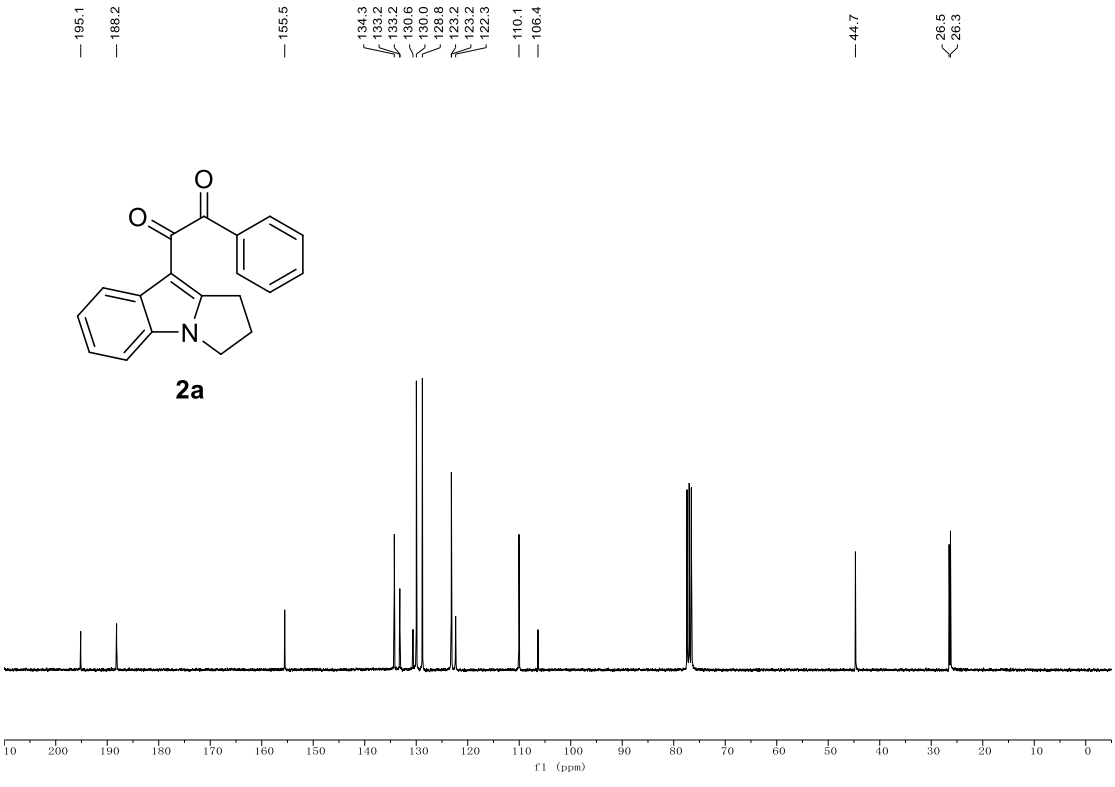
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **1am**:



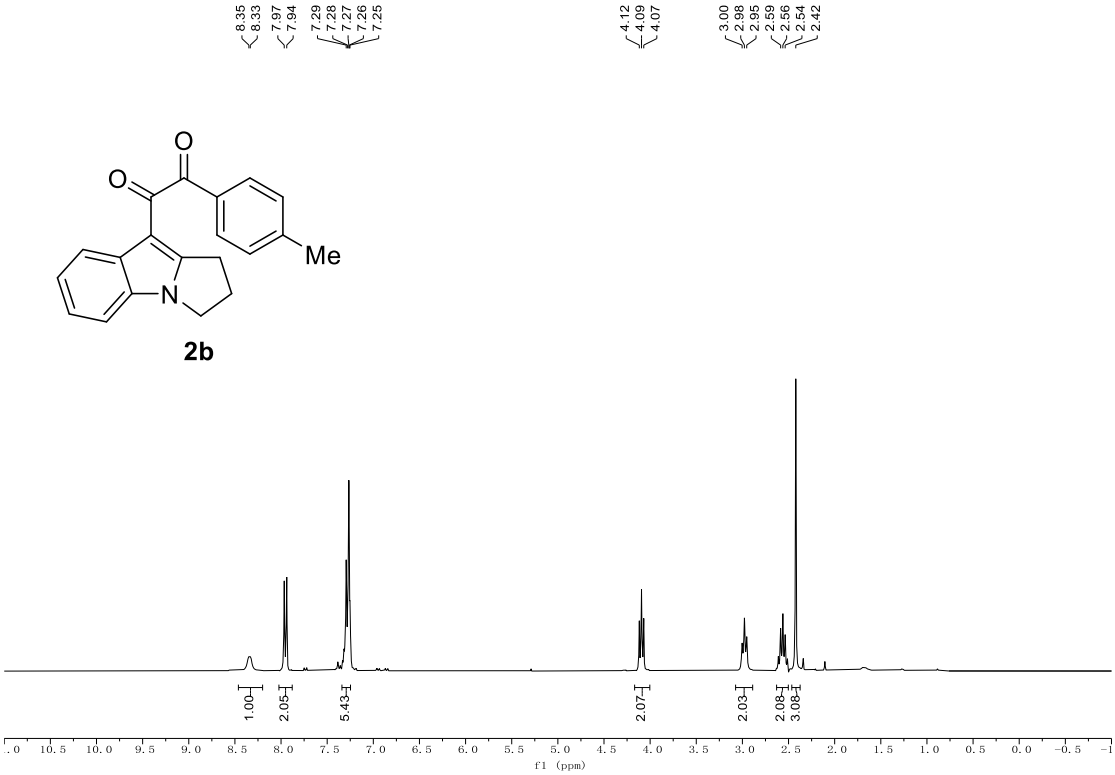
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2a**:



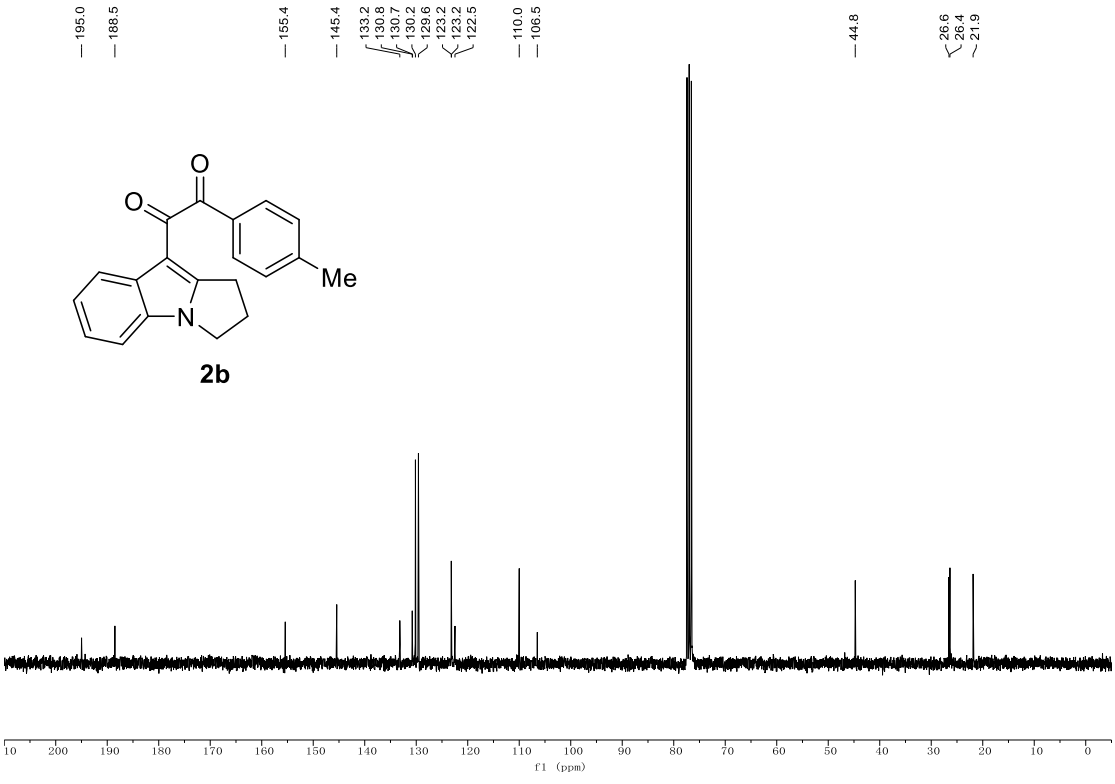
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2a**:



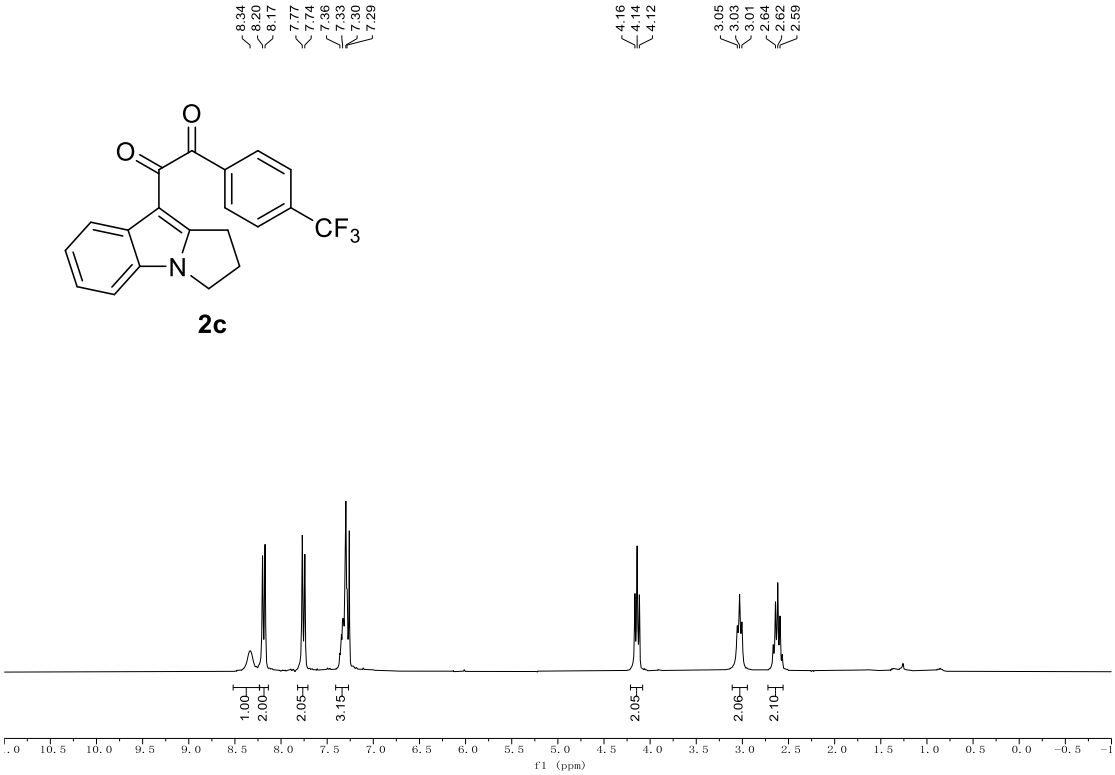
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2b**:



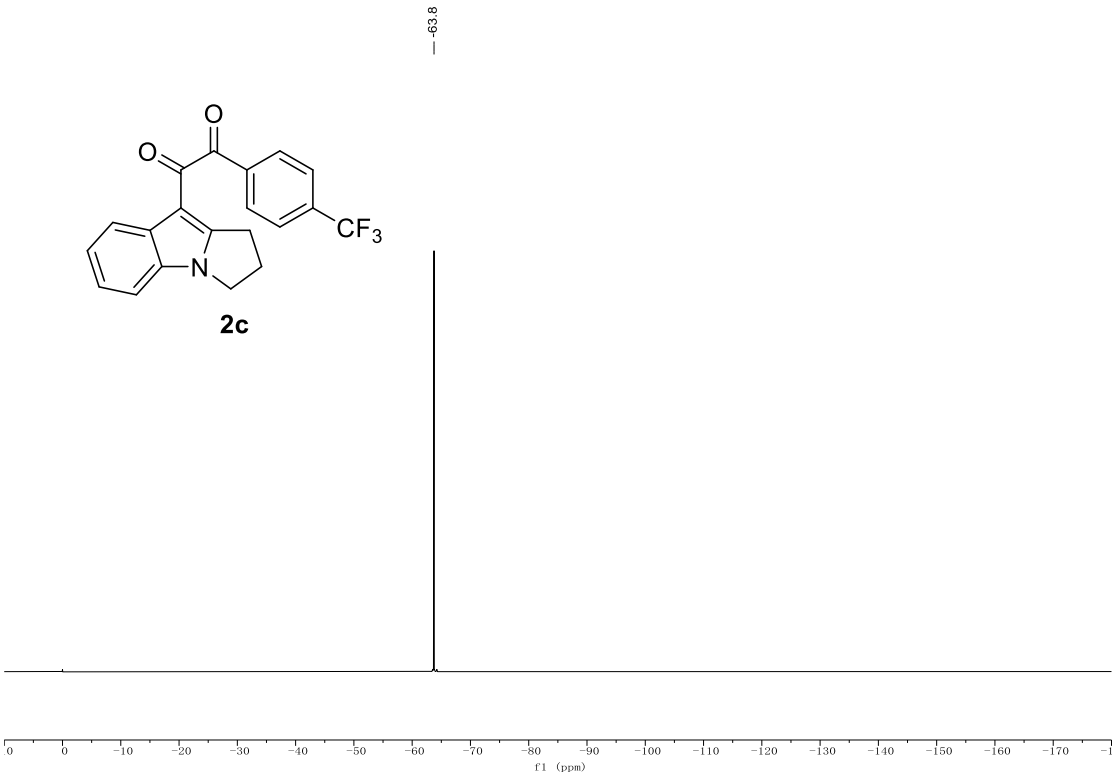
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2b**:



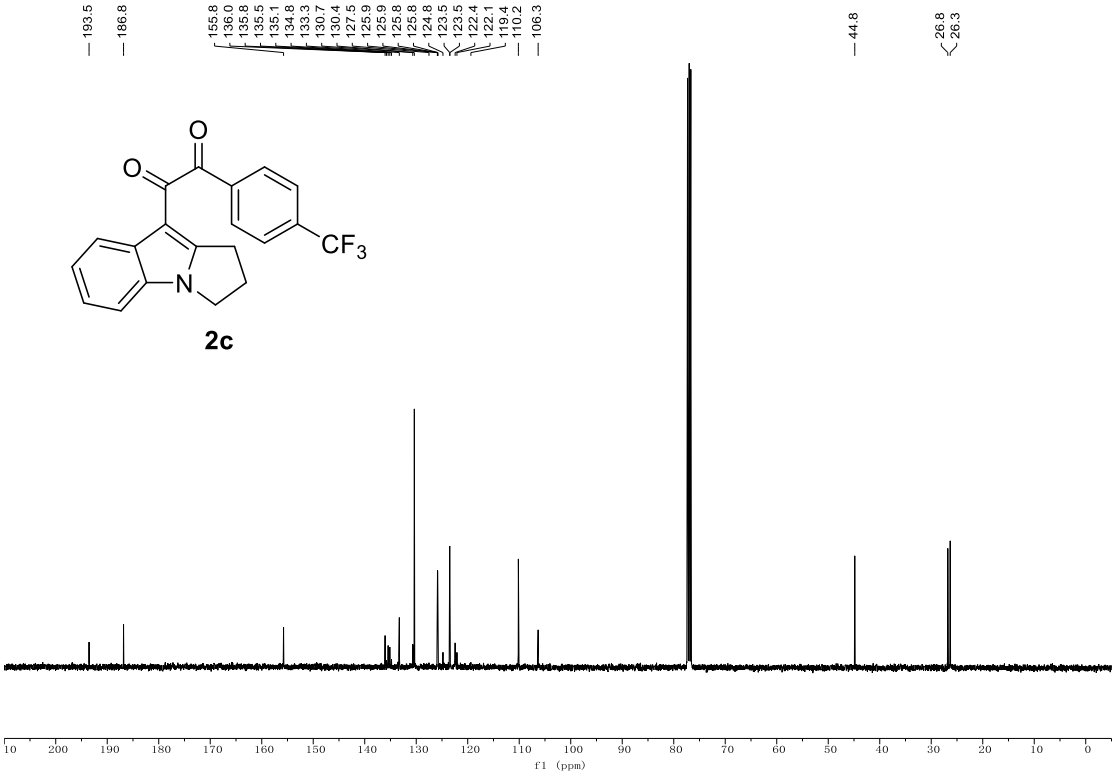
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2c**:



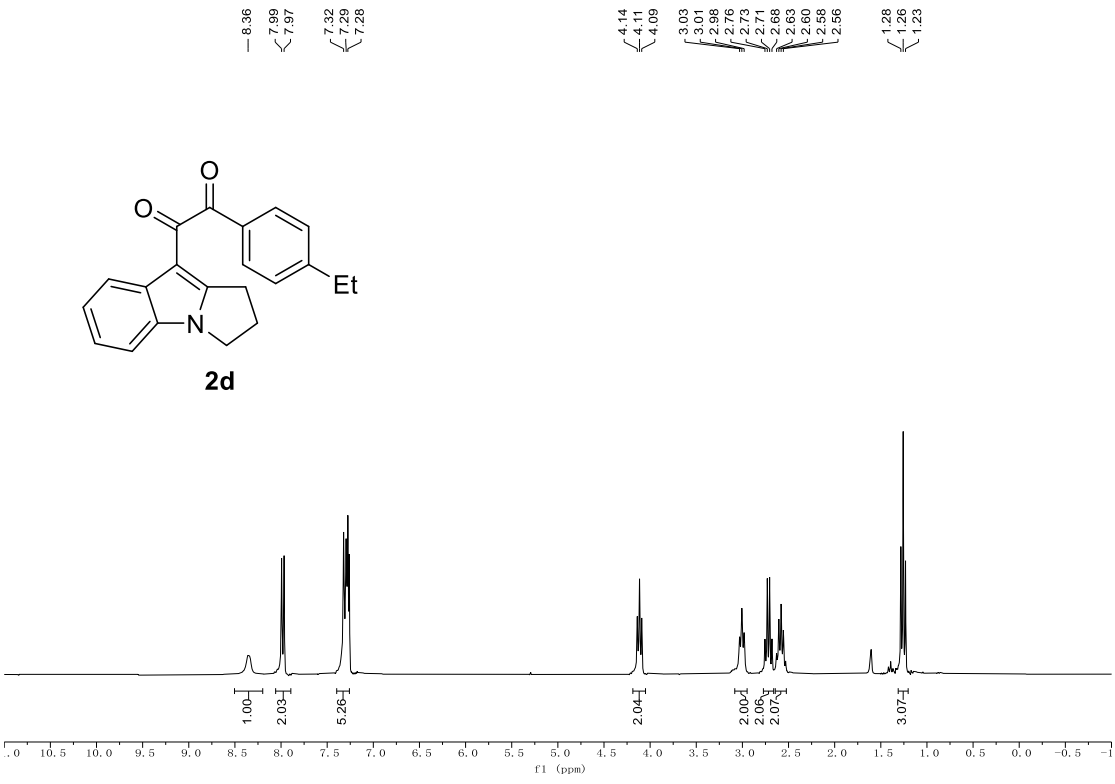
^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) spectra of compound **2c**:



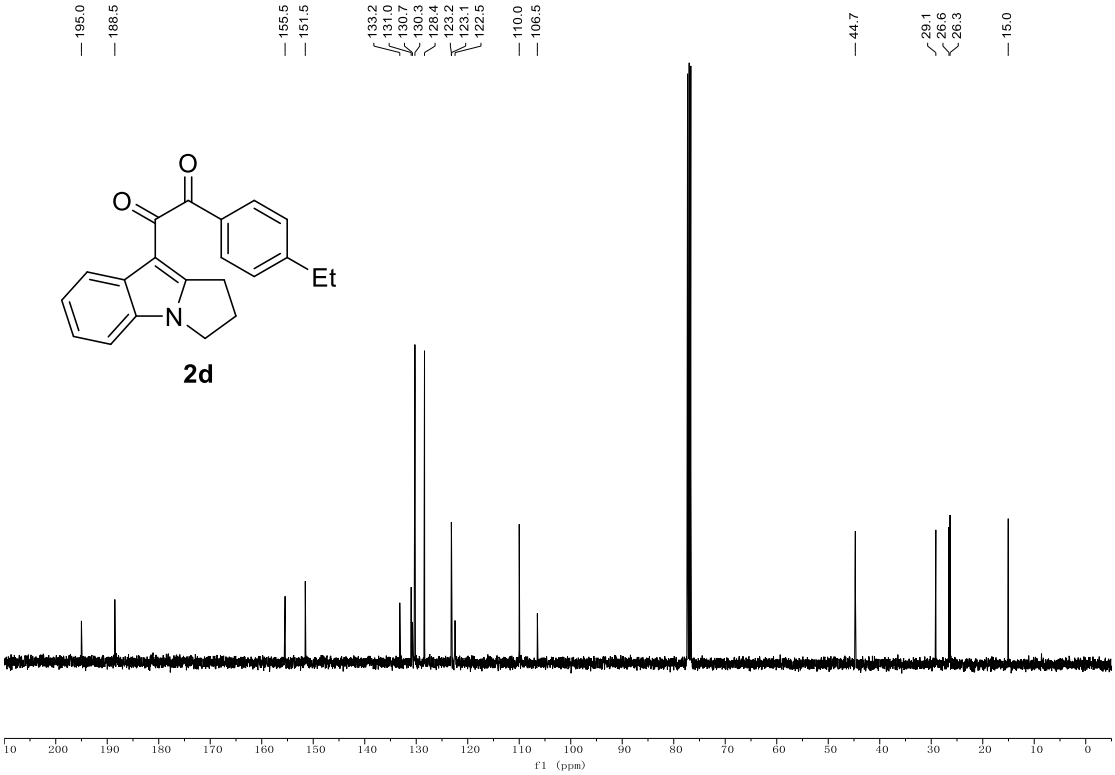
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of compound **2c**:



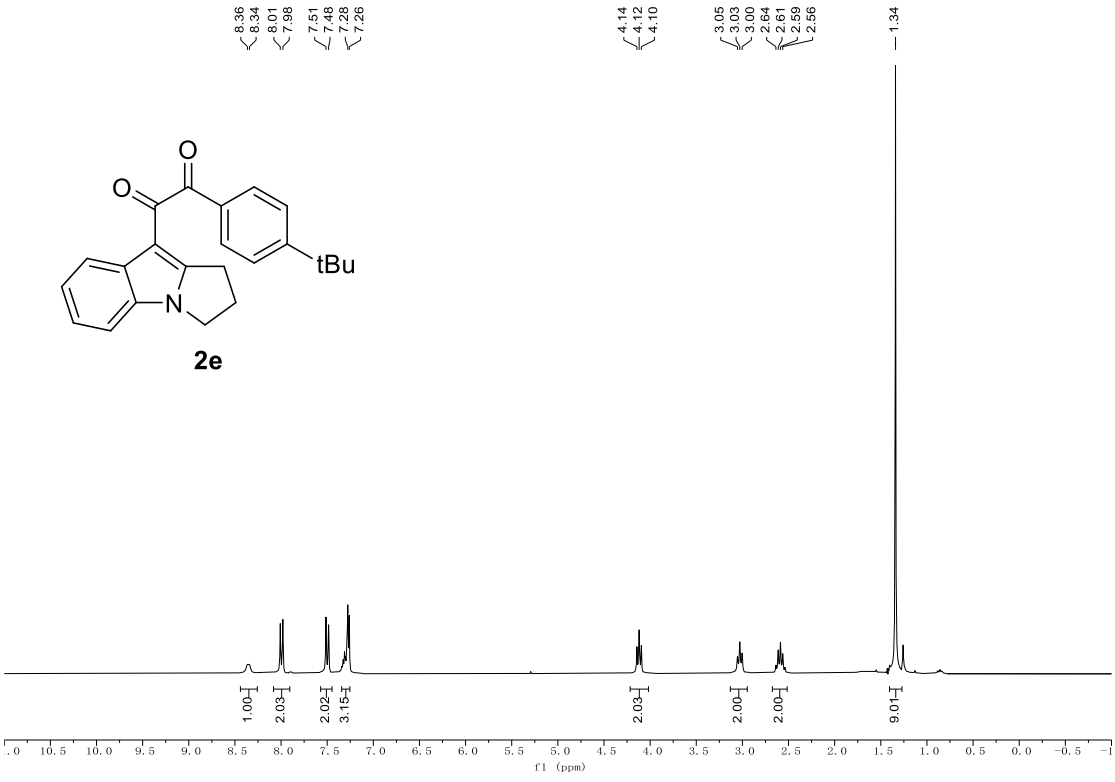
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2d**:



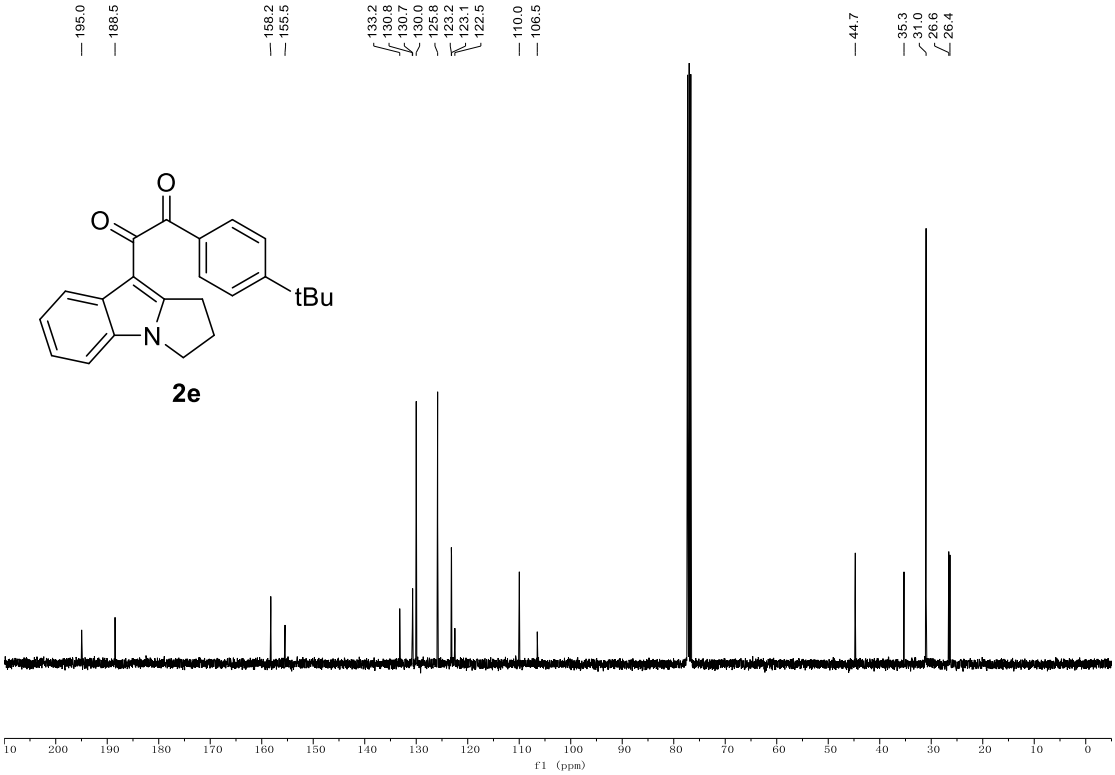
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of compound **2d**:



^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2e**:

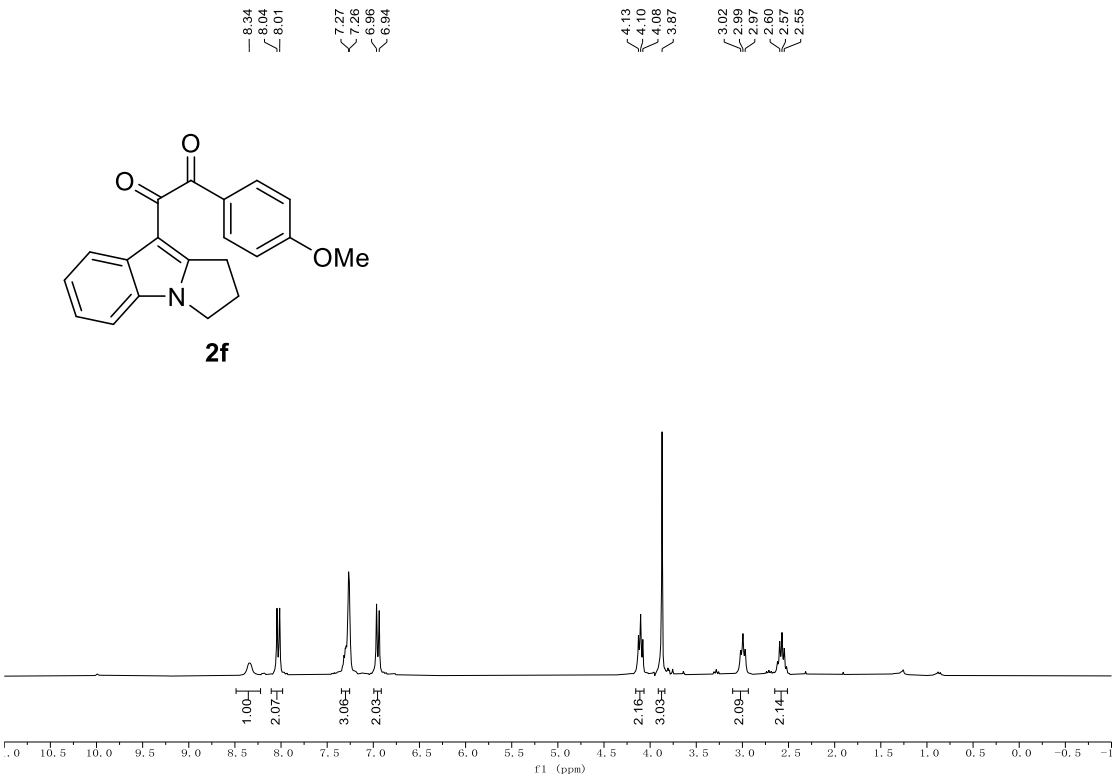


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of compound **2e**:



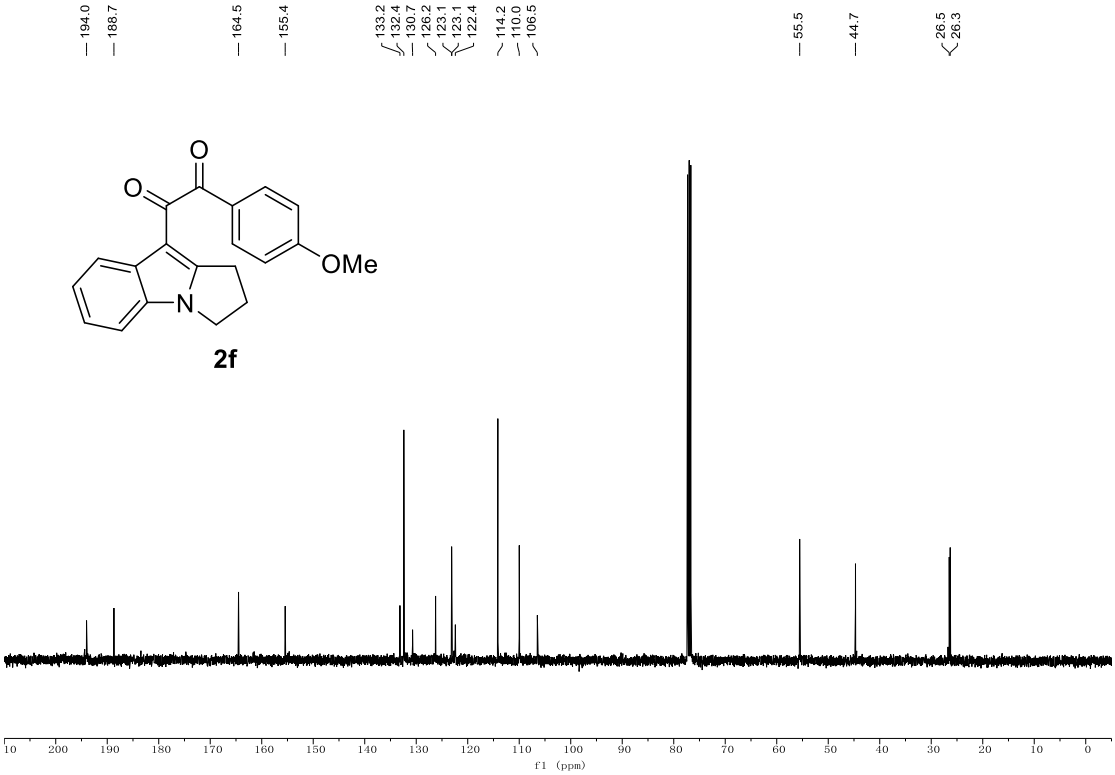
2e

^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2f**:



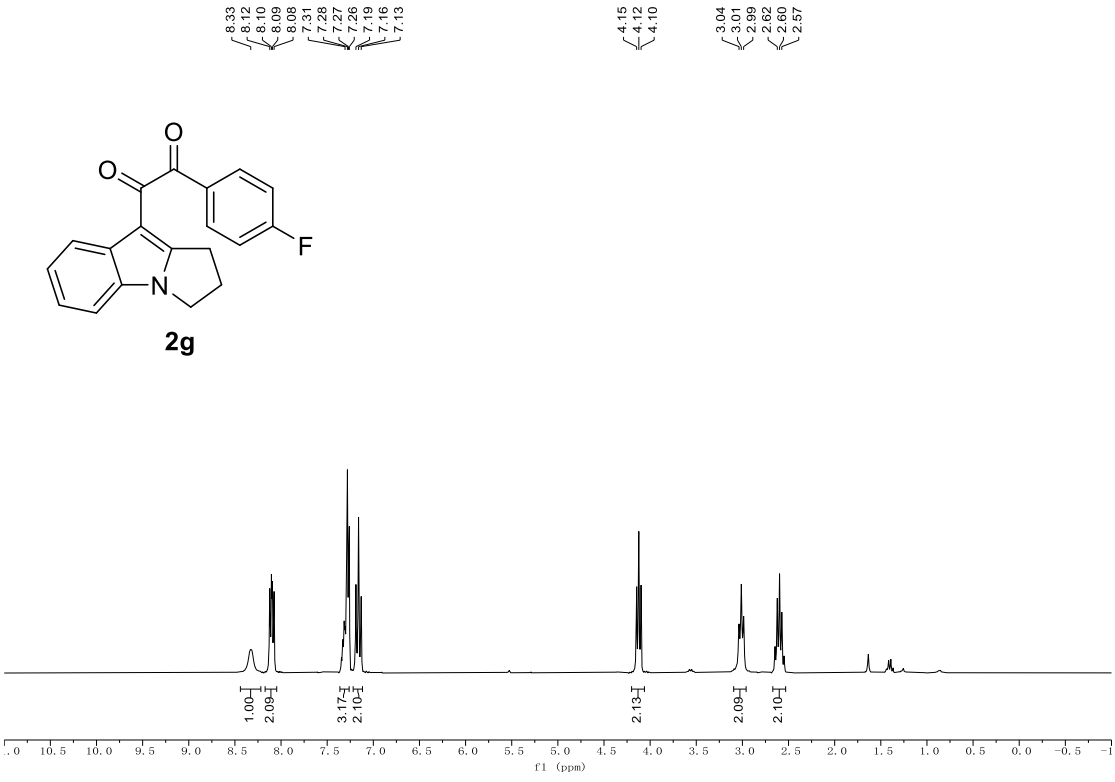
2f

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of compound **2f**:



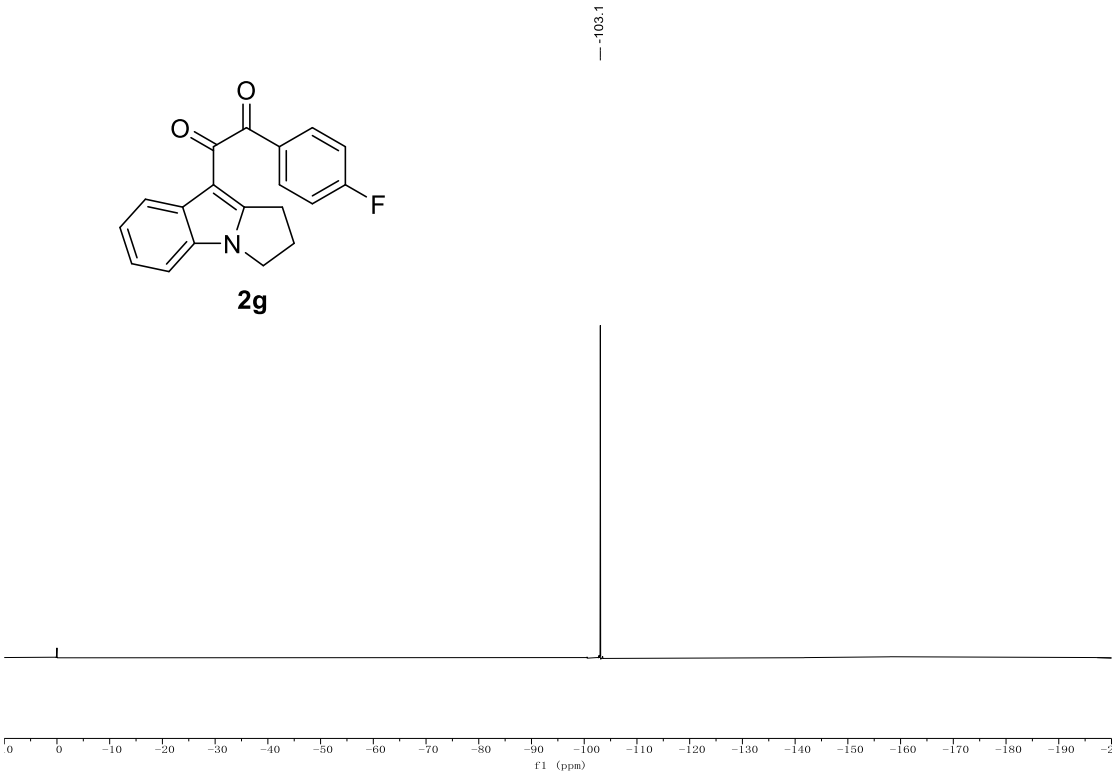
2f

^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2g**:

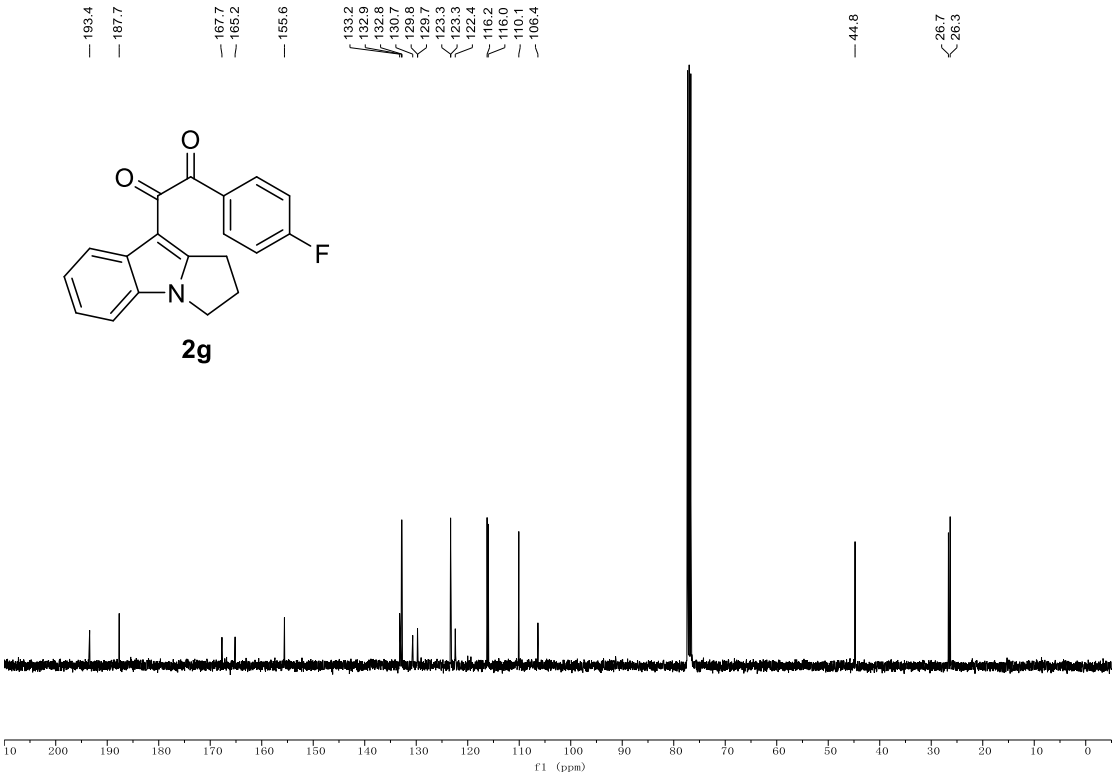


2g

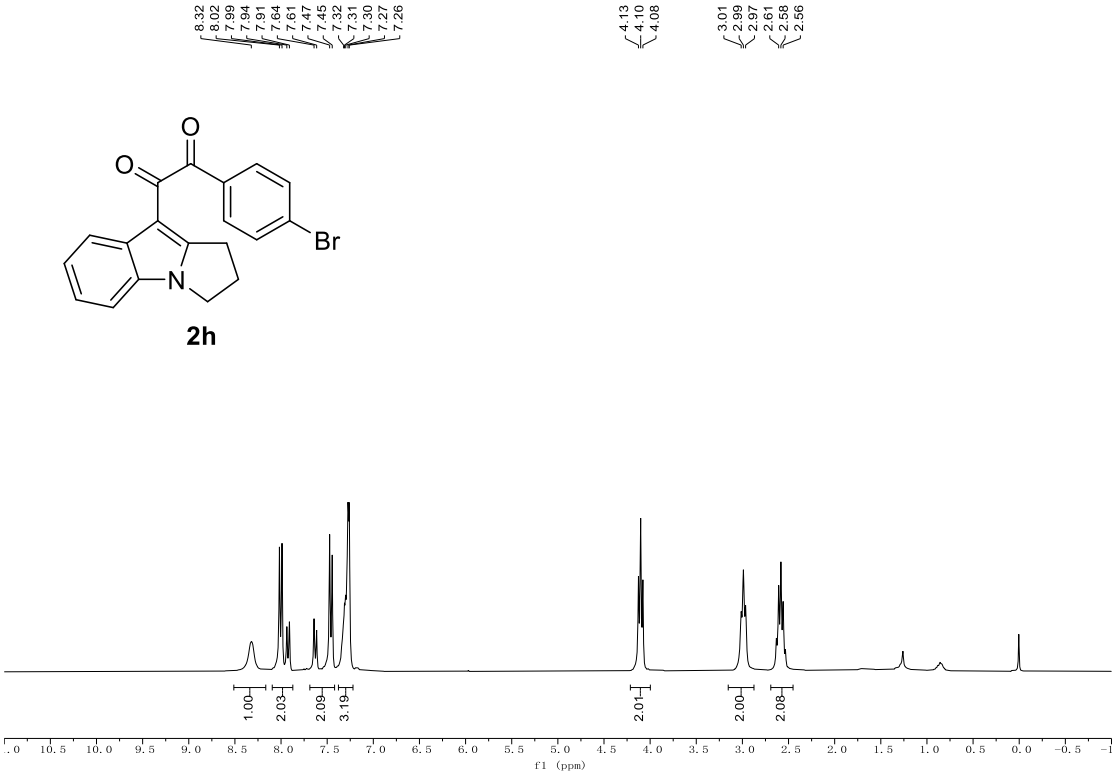
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectra of compound **2g**:



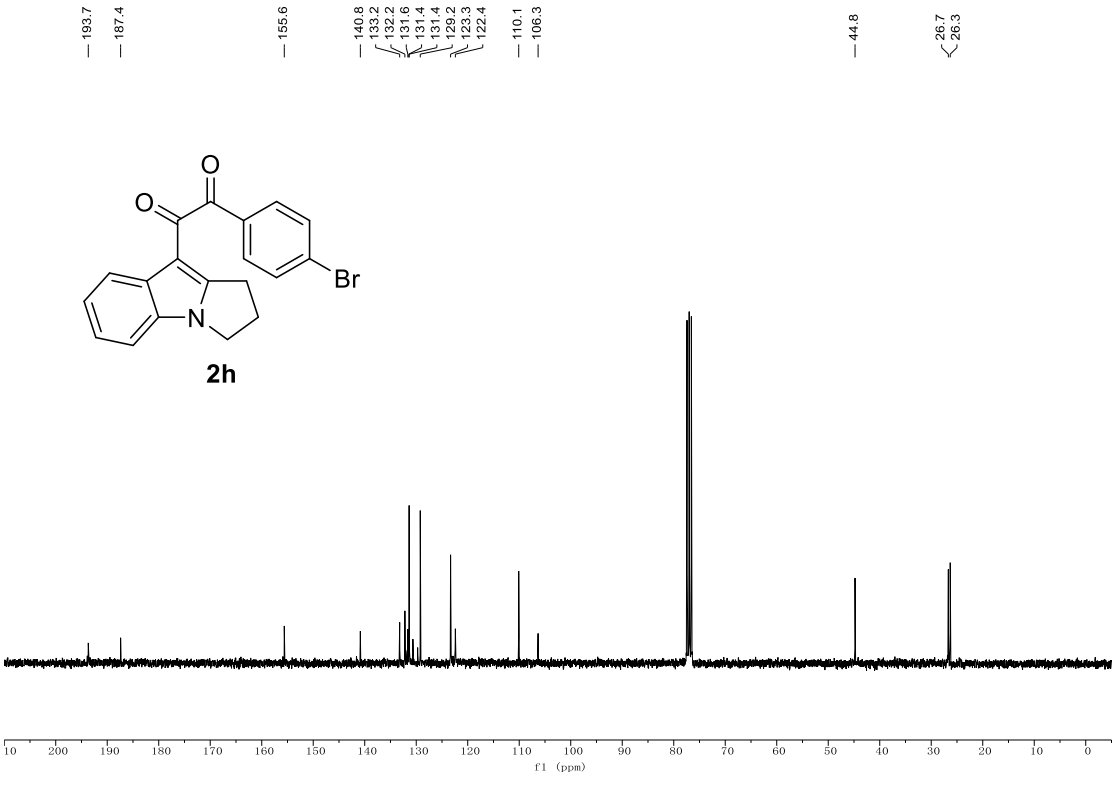
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of compound **2g**:



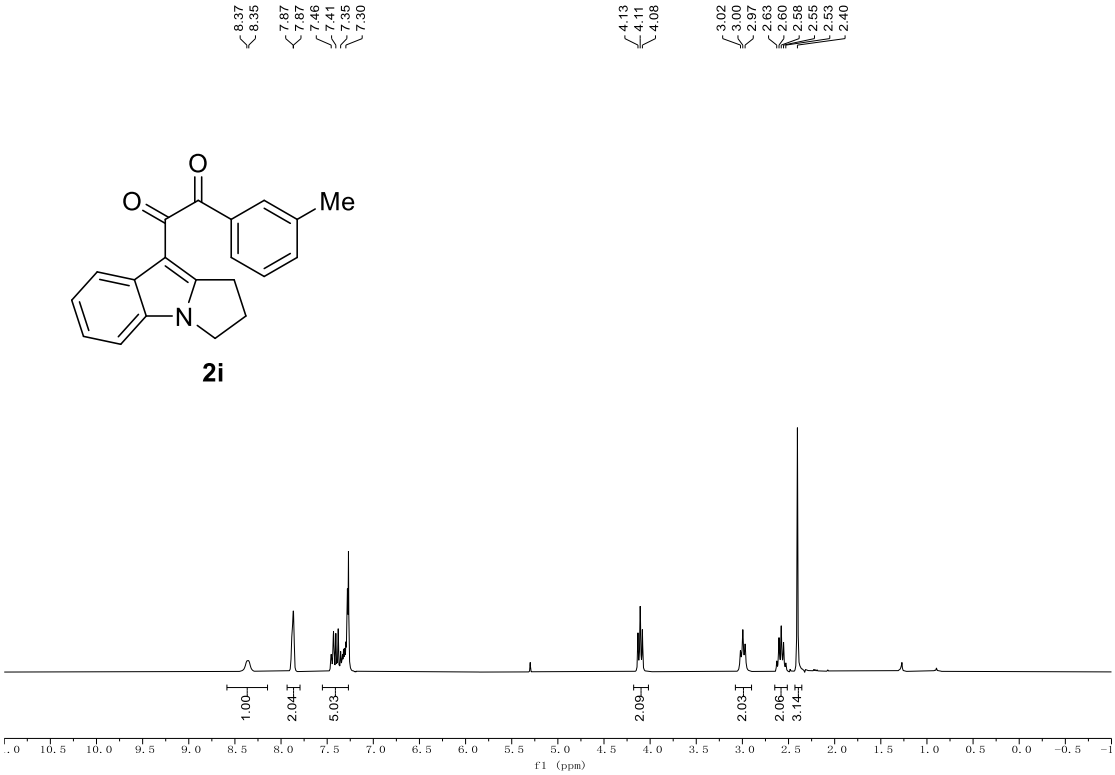
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2h**:



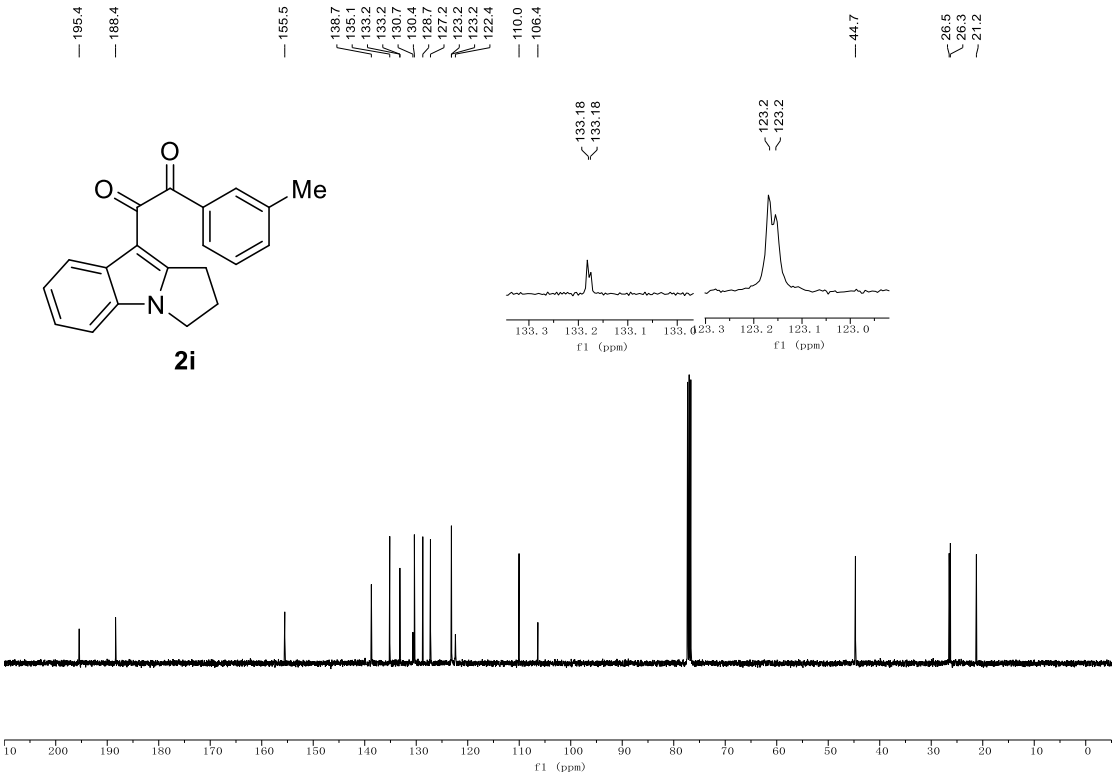
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2h**:



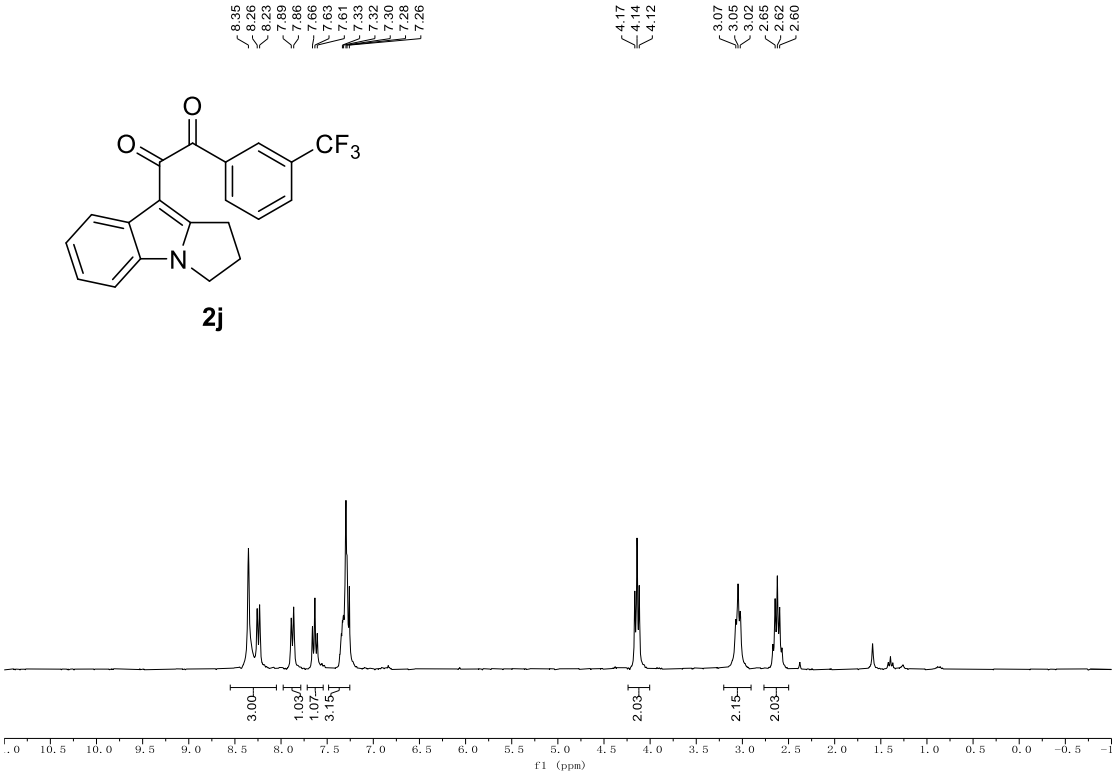
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2i**:



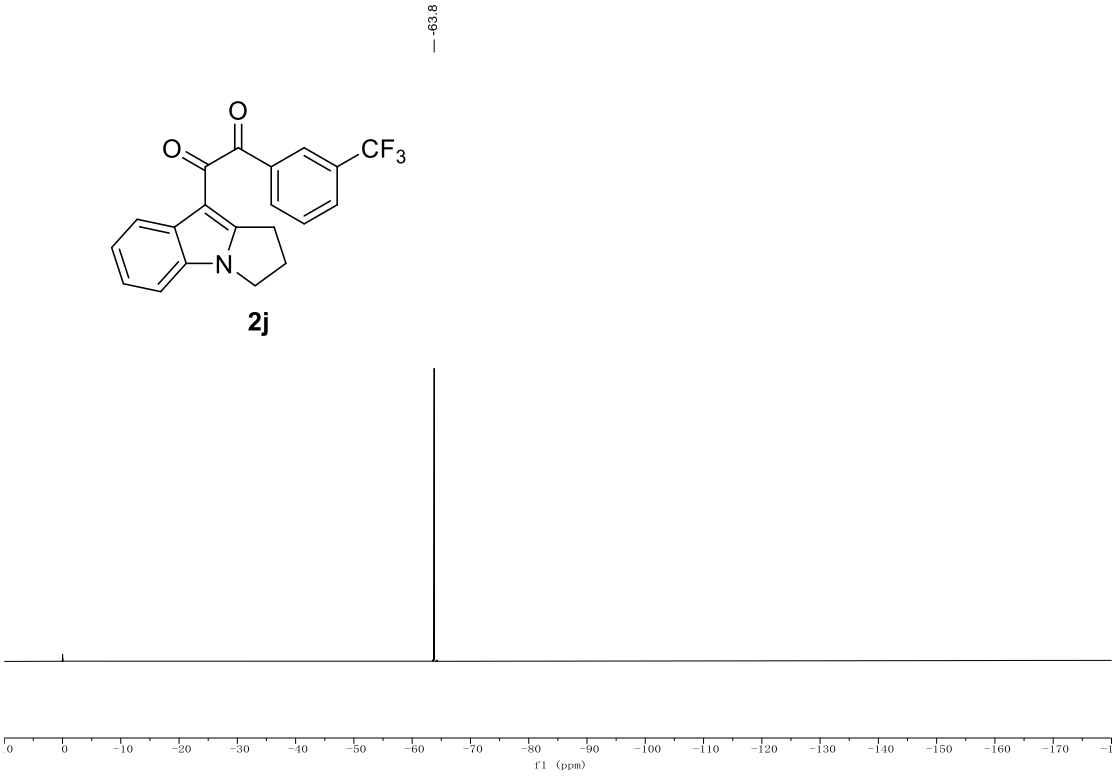
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2i**:



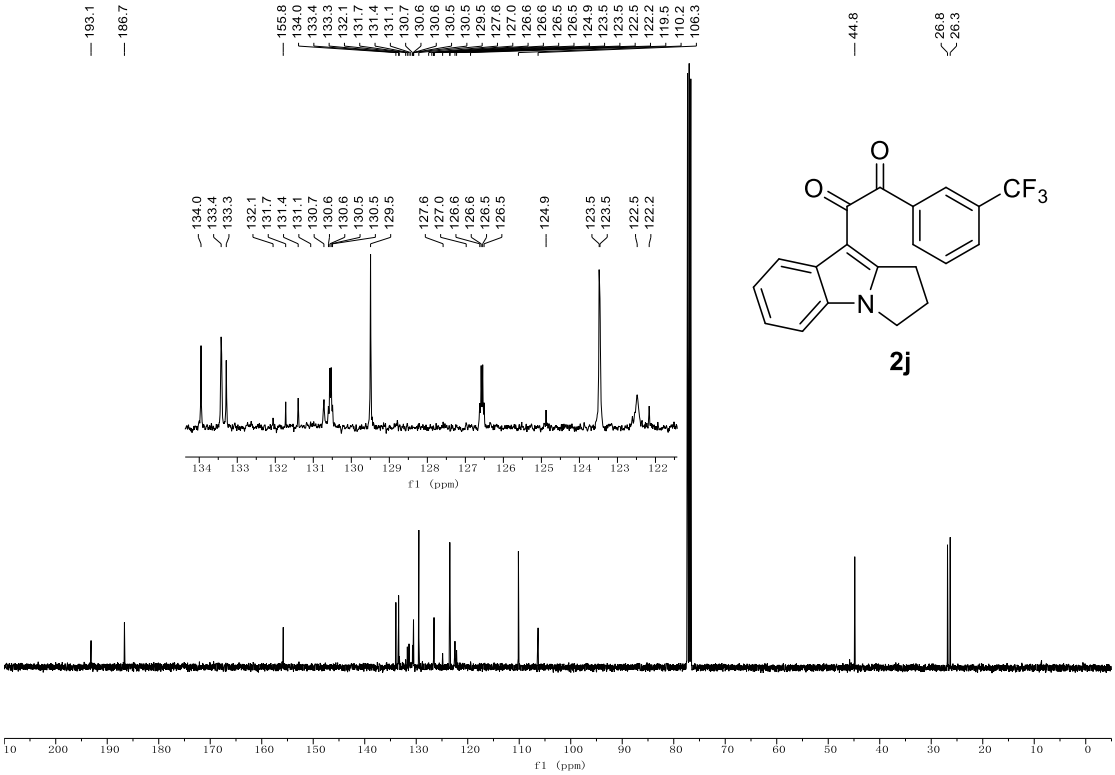
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2j**:



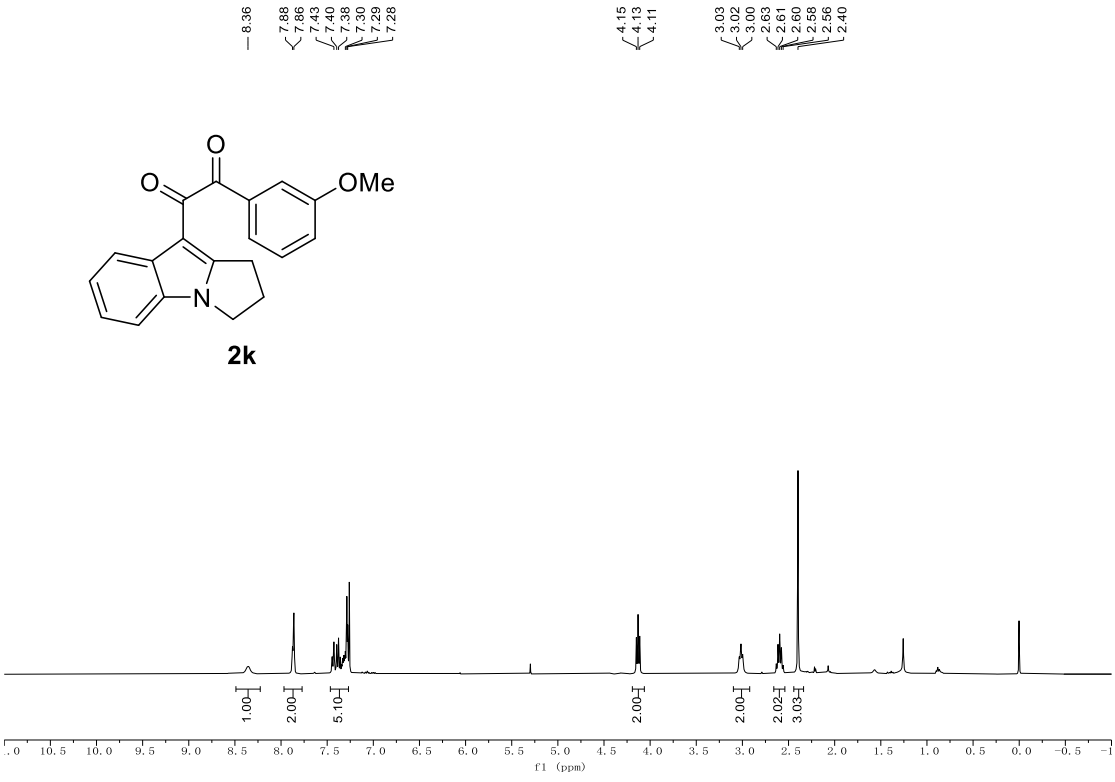
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) spectra of compound **2j**:



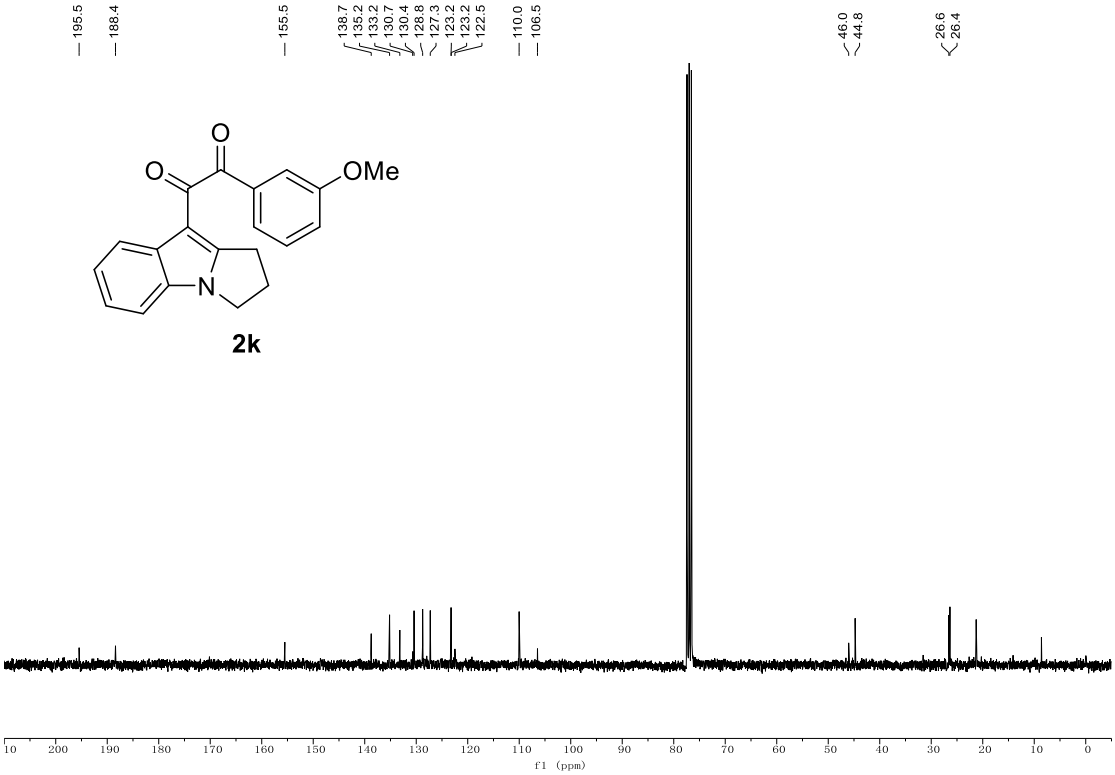
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of compound **2j**:



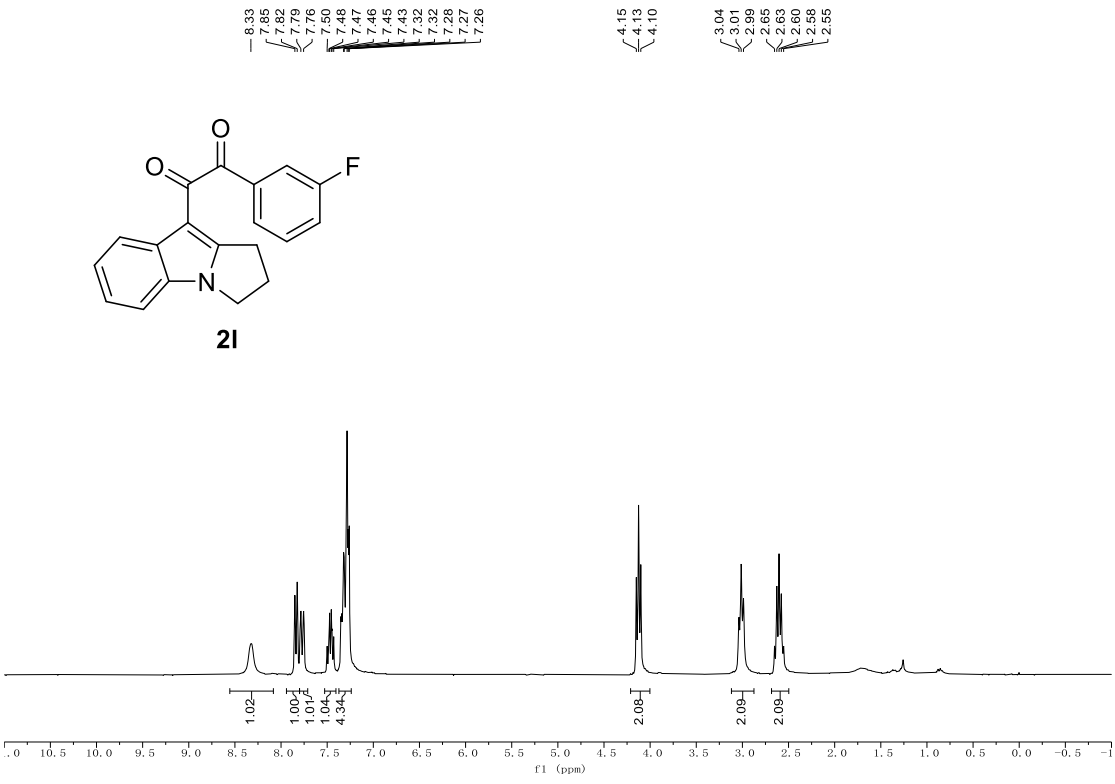
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2k**:



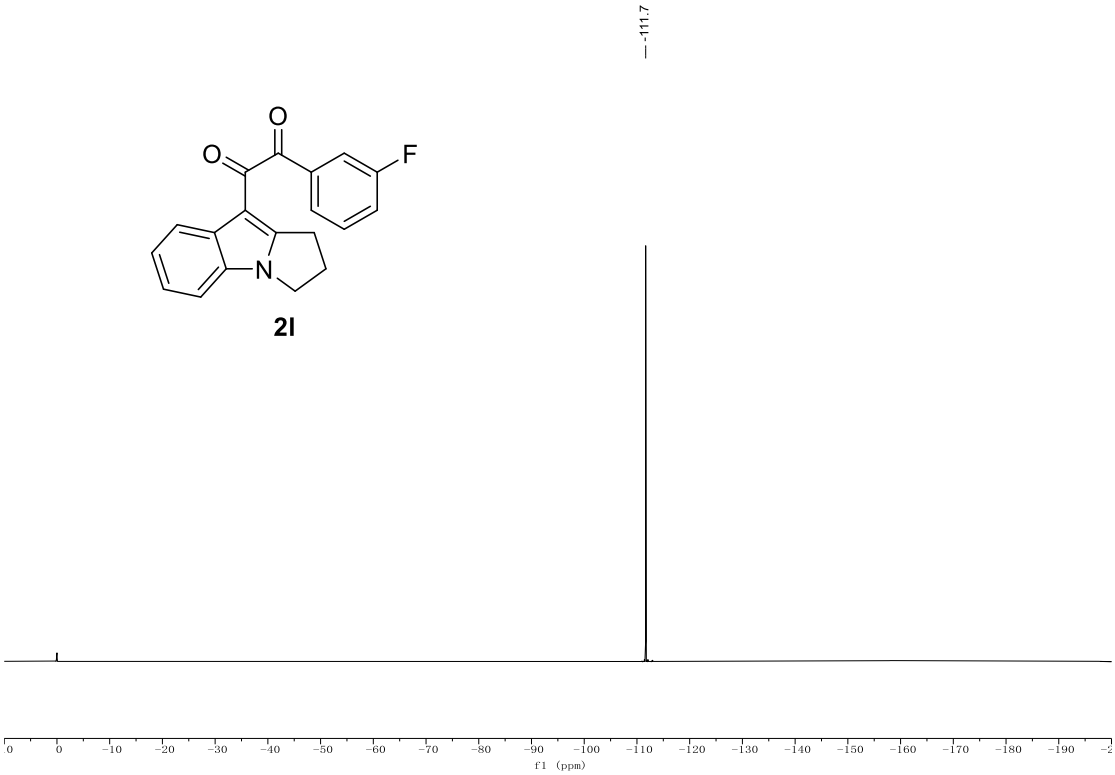
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **2k**:



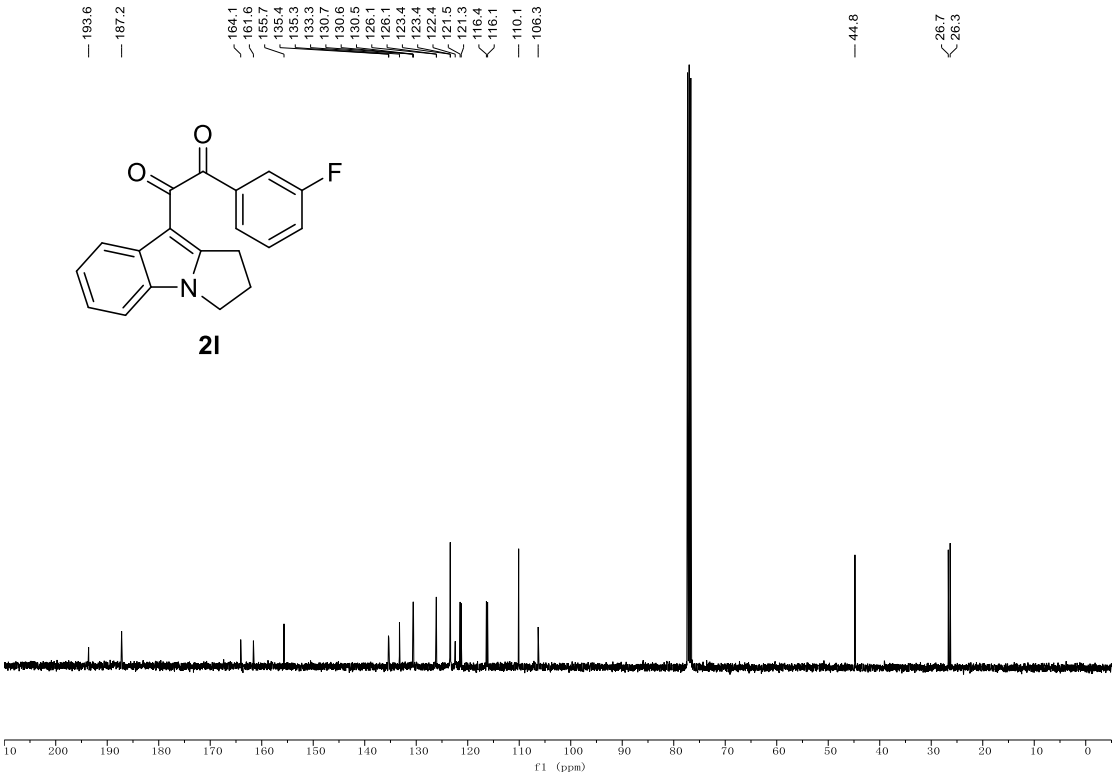
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2l**:



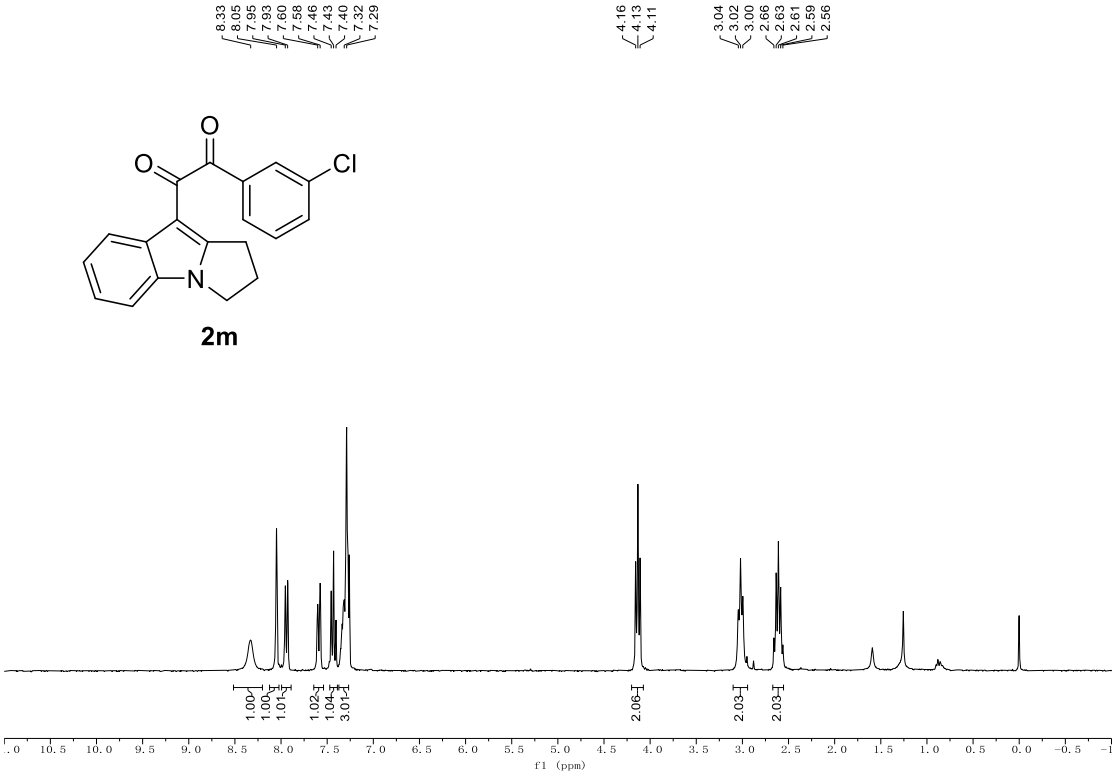
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectra of compound **2l**:



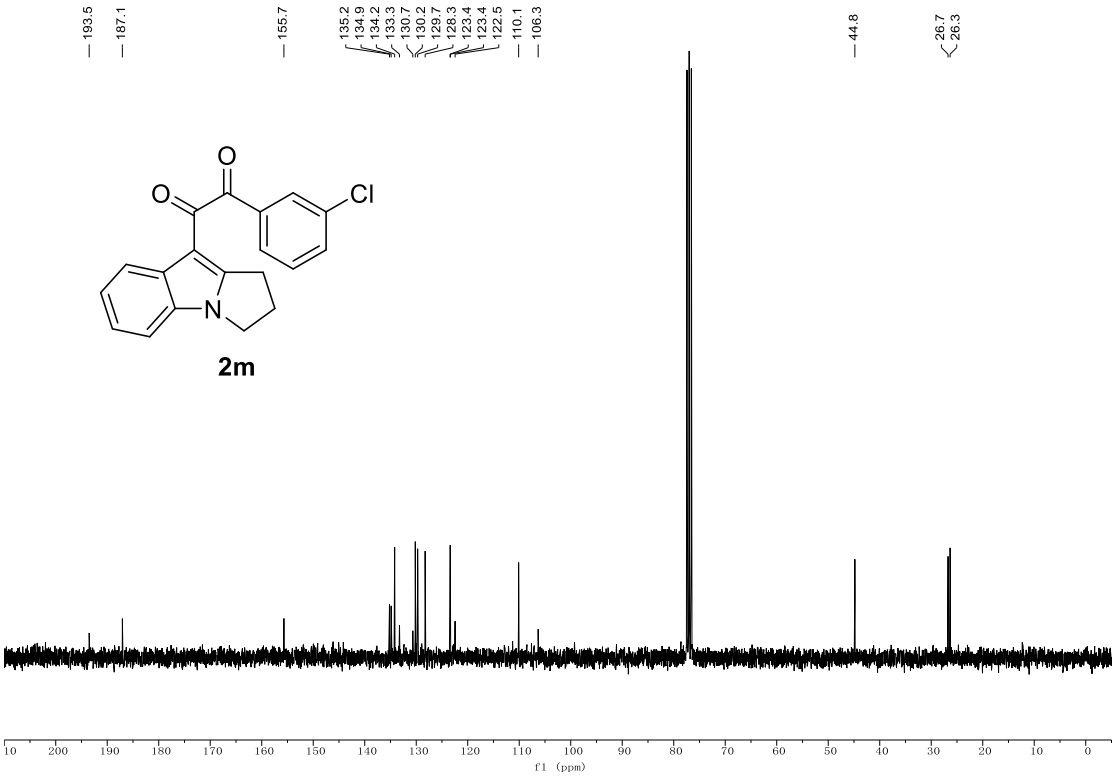
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of compound **2l**:



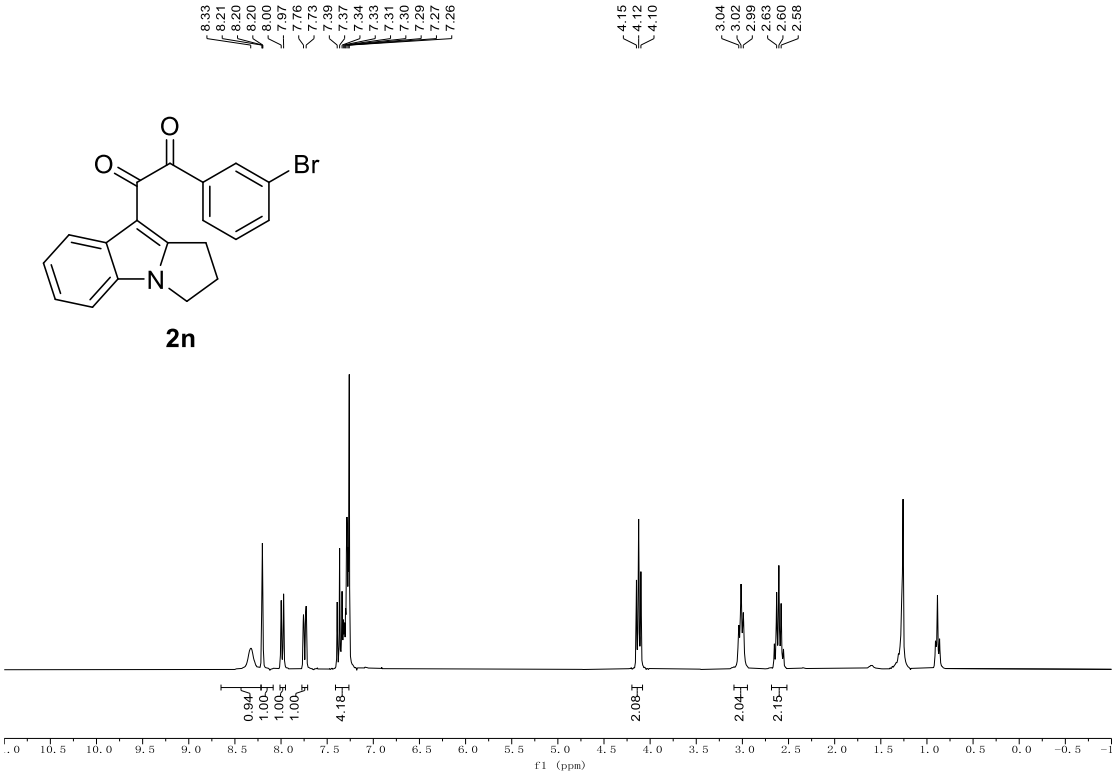
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2m**:



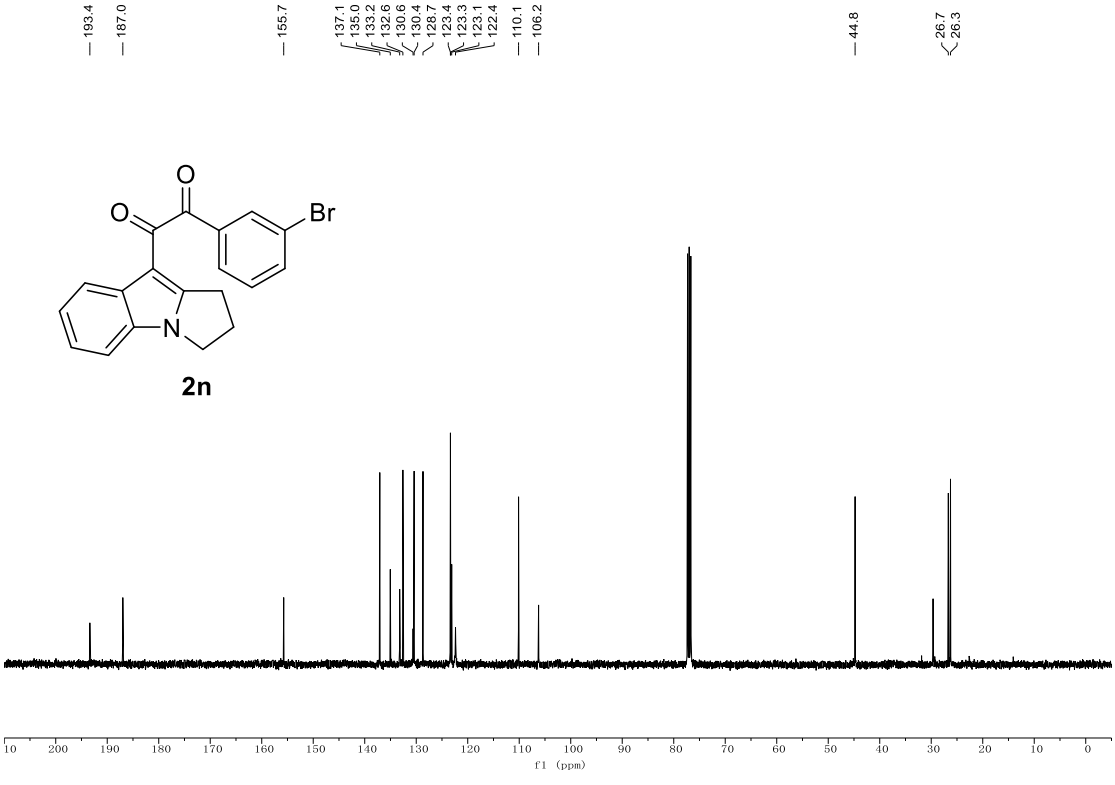
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2m**:



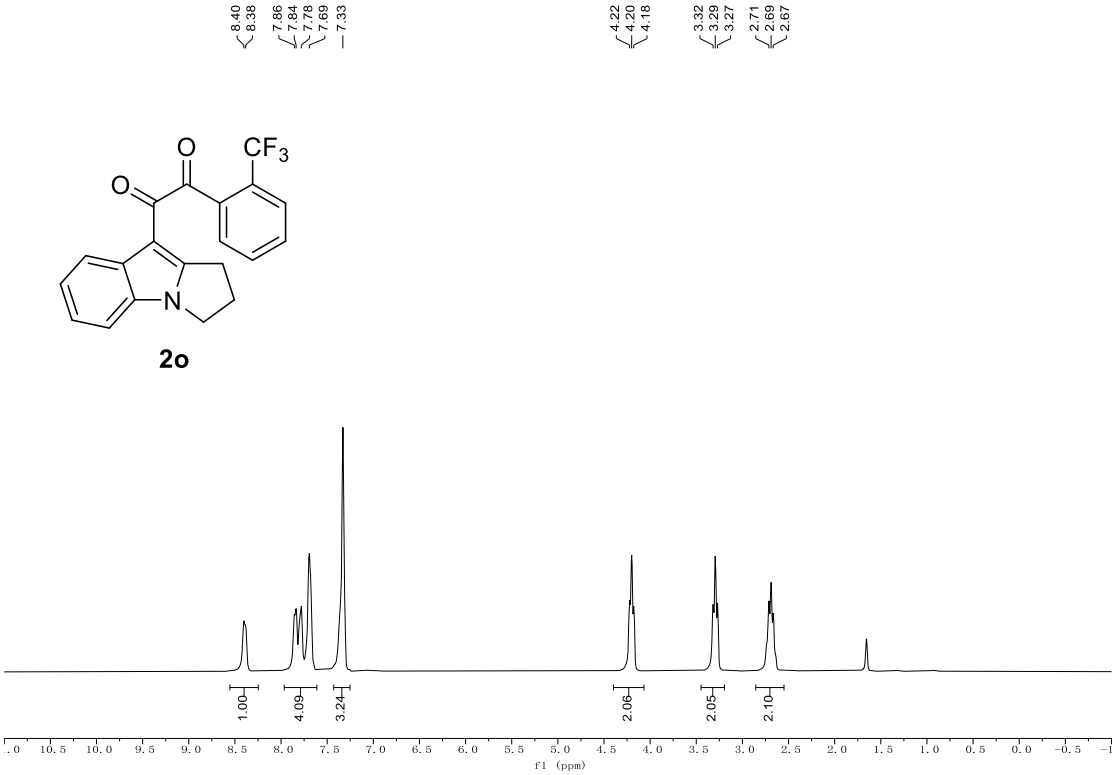
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2n**:



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2n**:

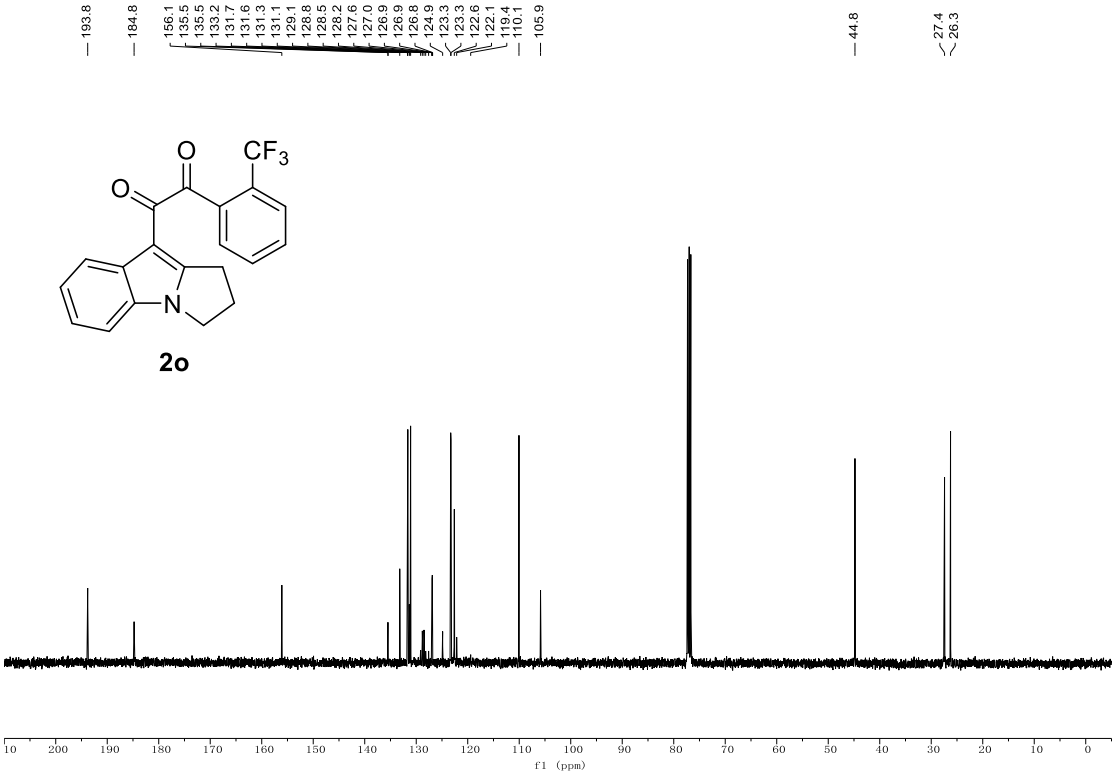


^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2o**:

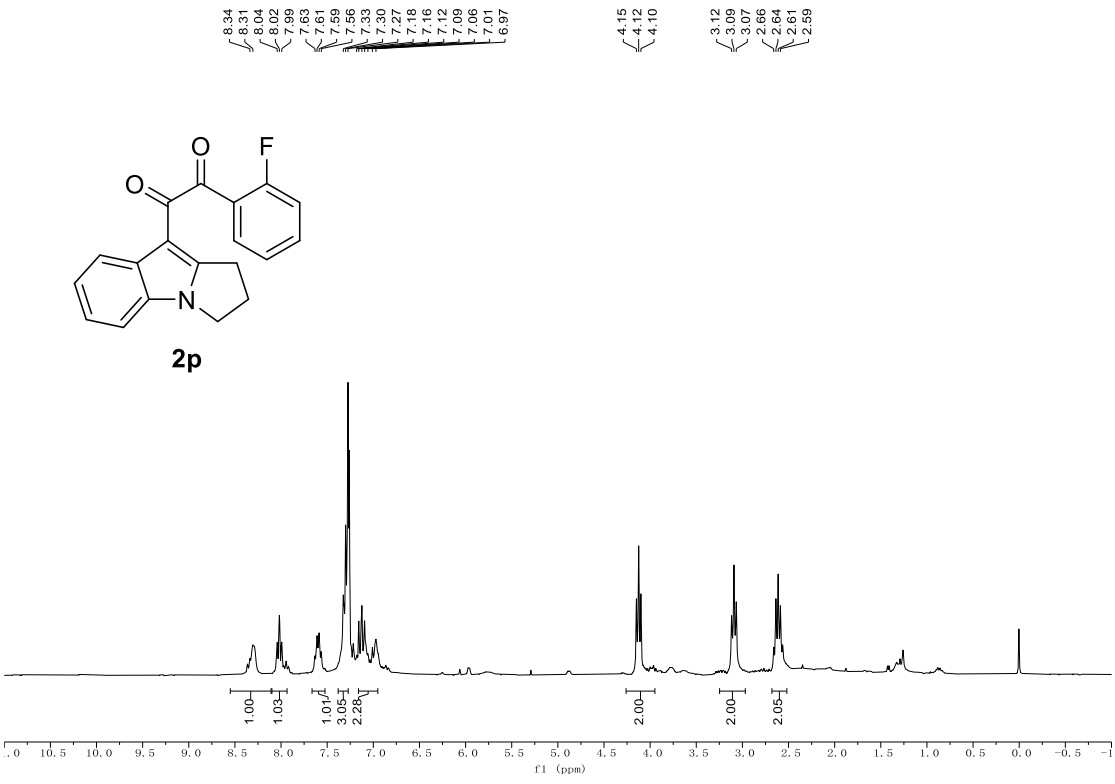


^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) spectra of compound **2o**:

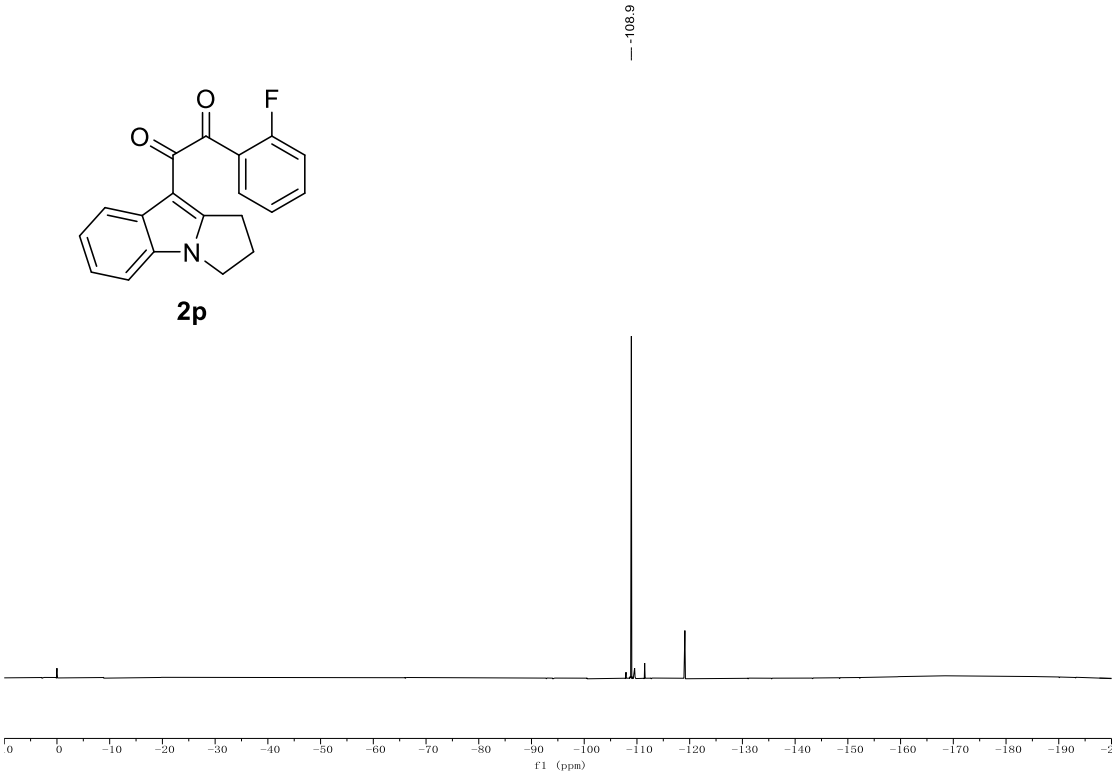
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectra of compound **2o**:



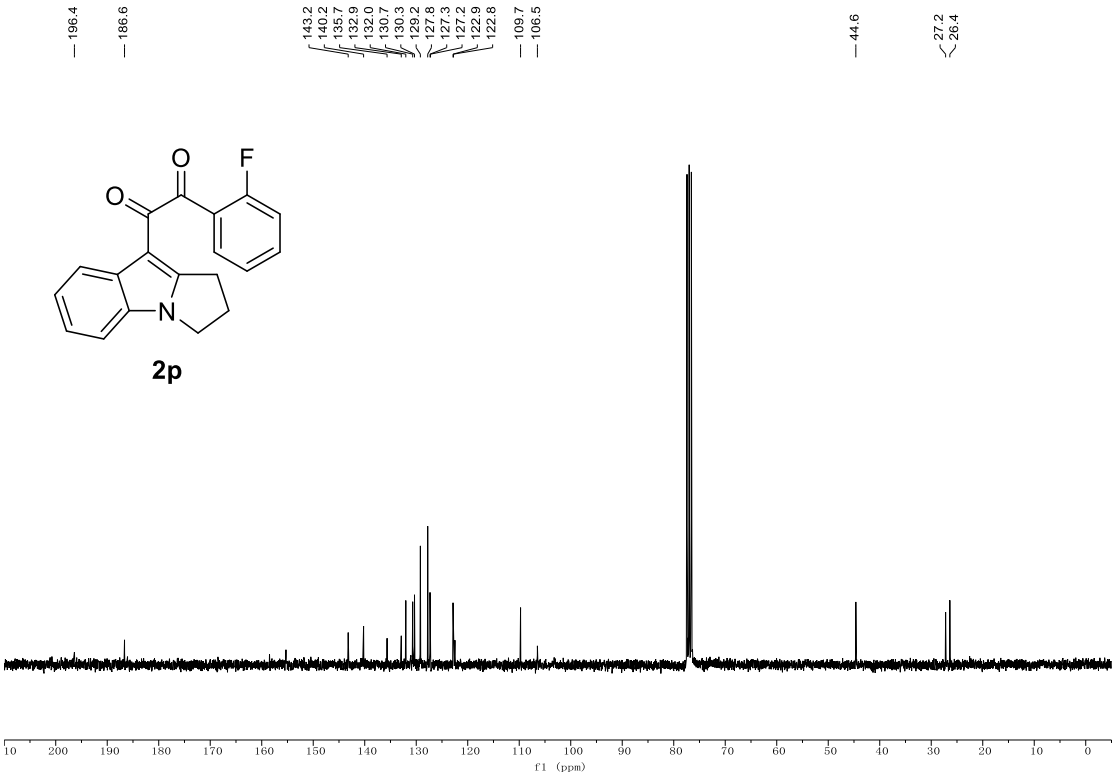
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2p**:



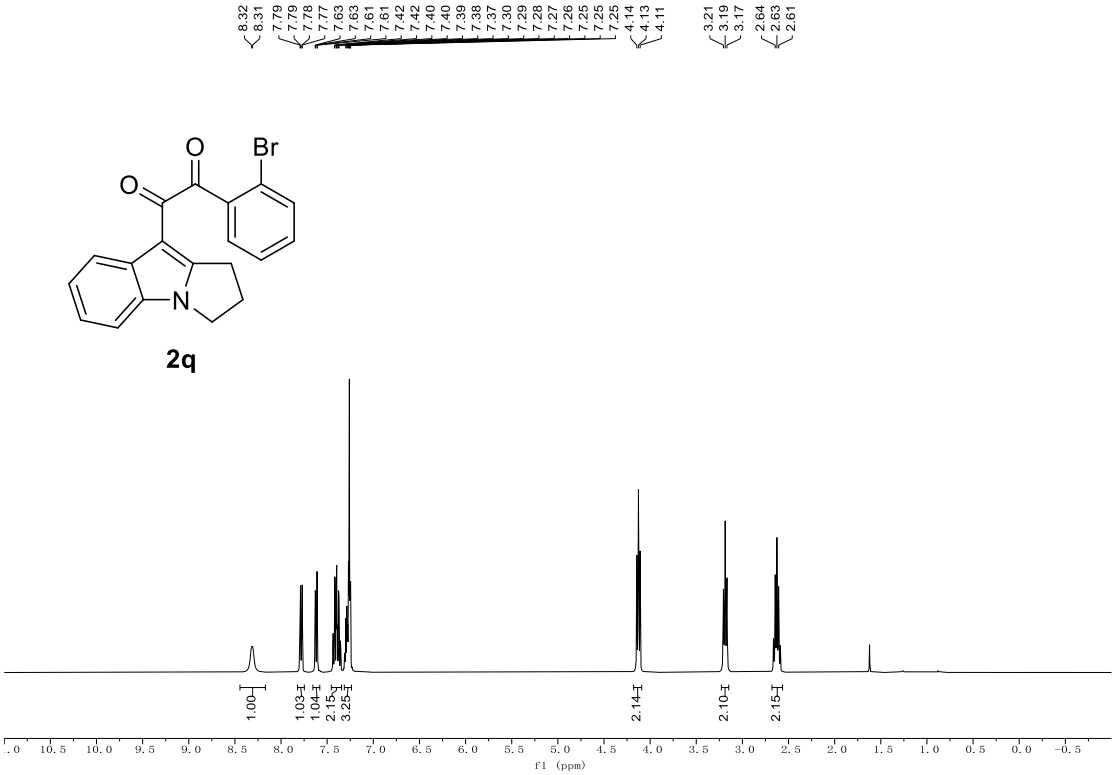
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectra of compound **2p**:



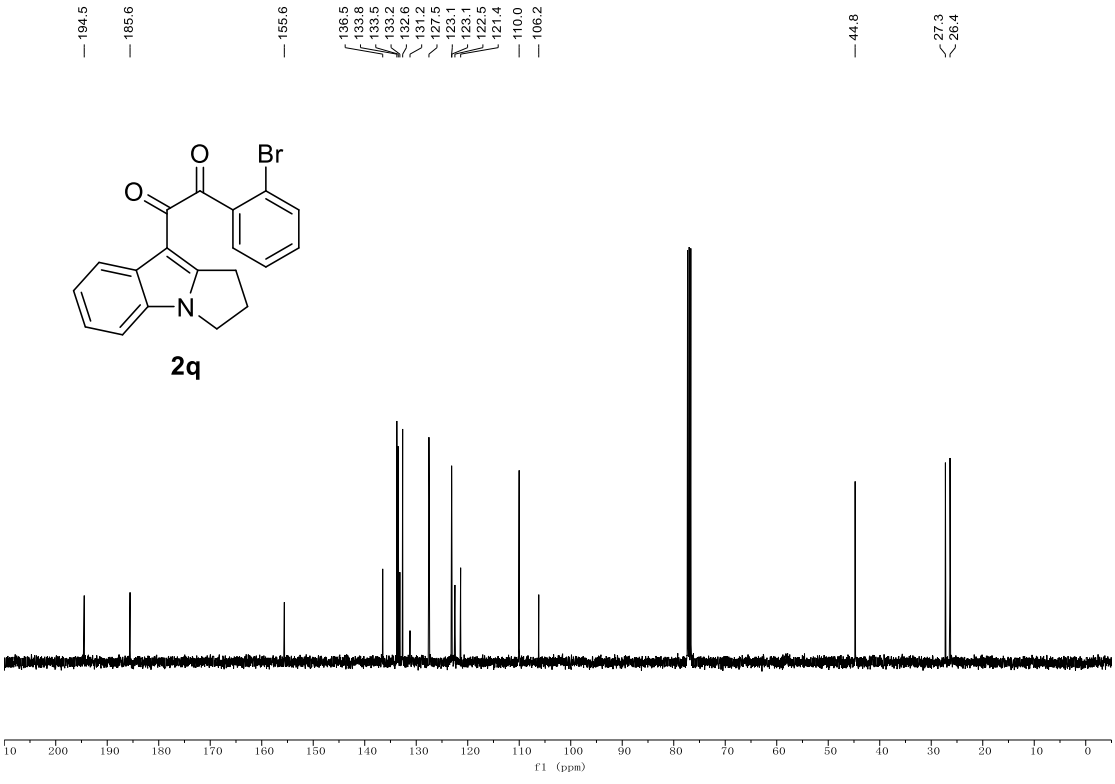
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) spectra of compound **2p**:



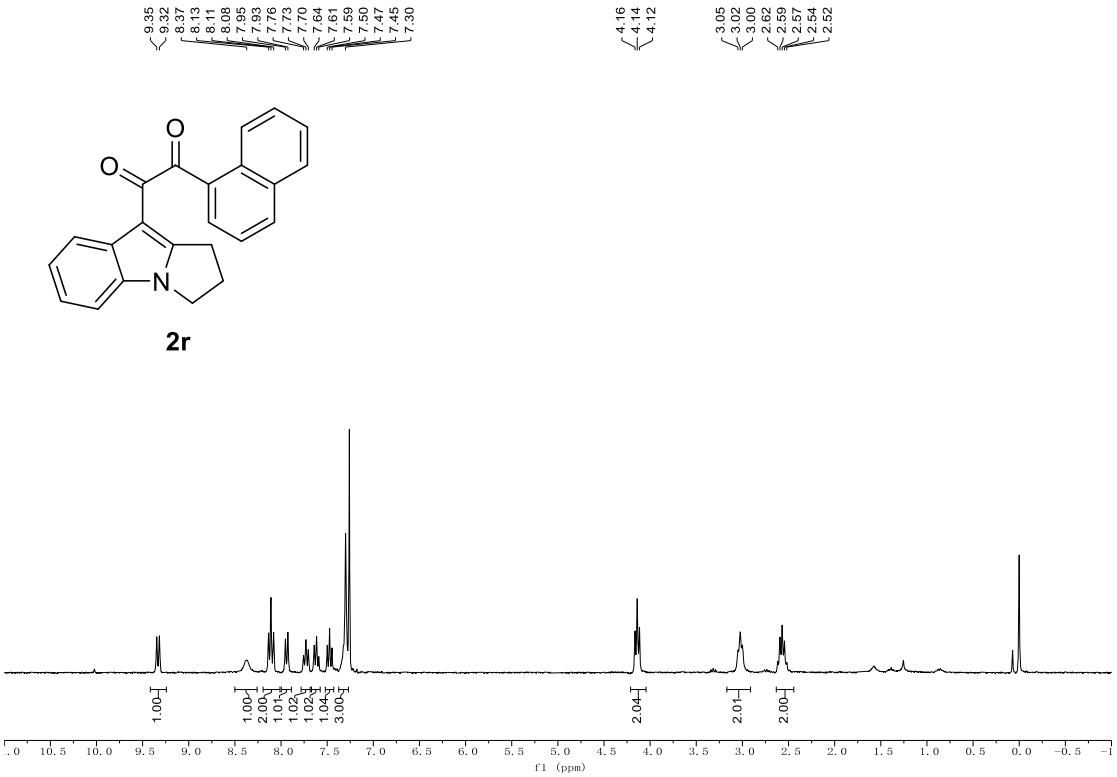
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2q**:



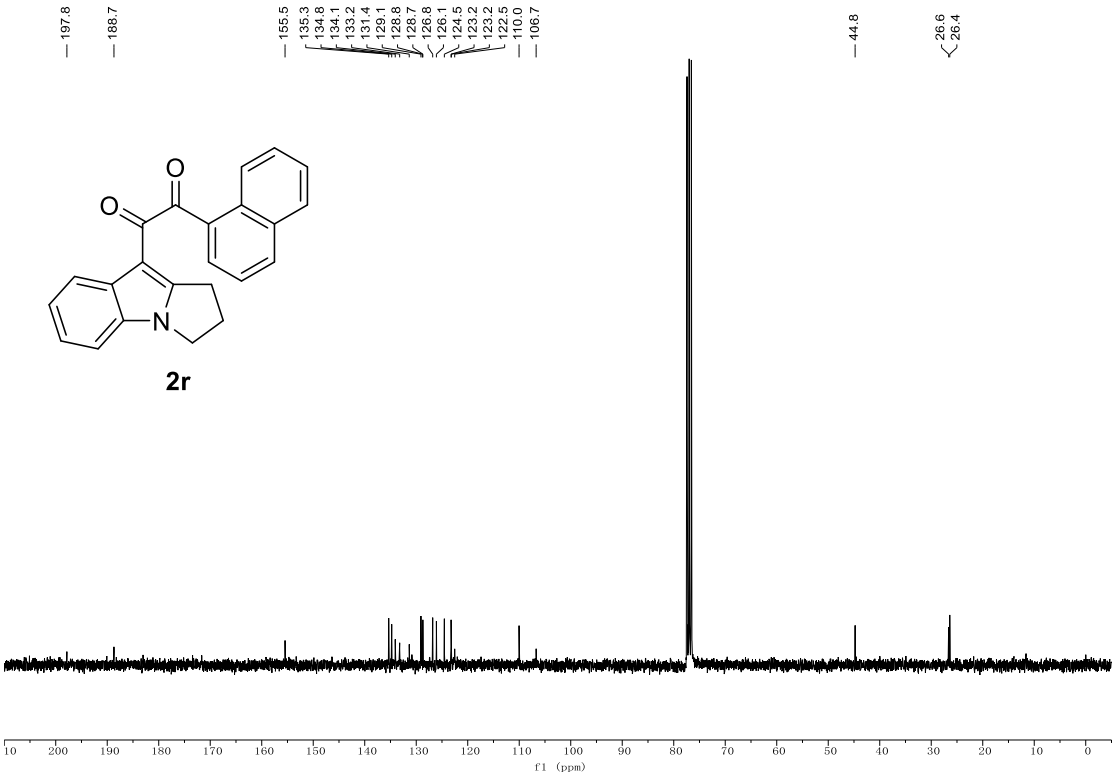
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2q**:



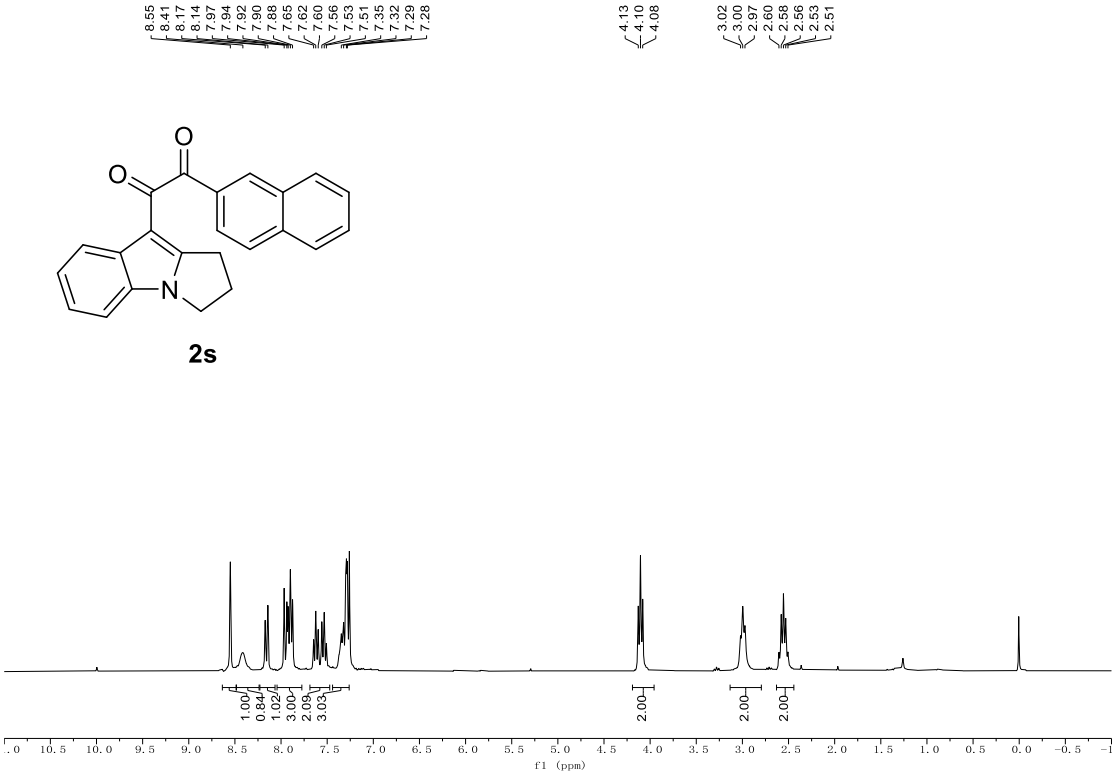
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2r**:



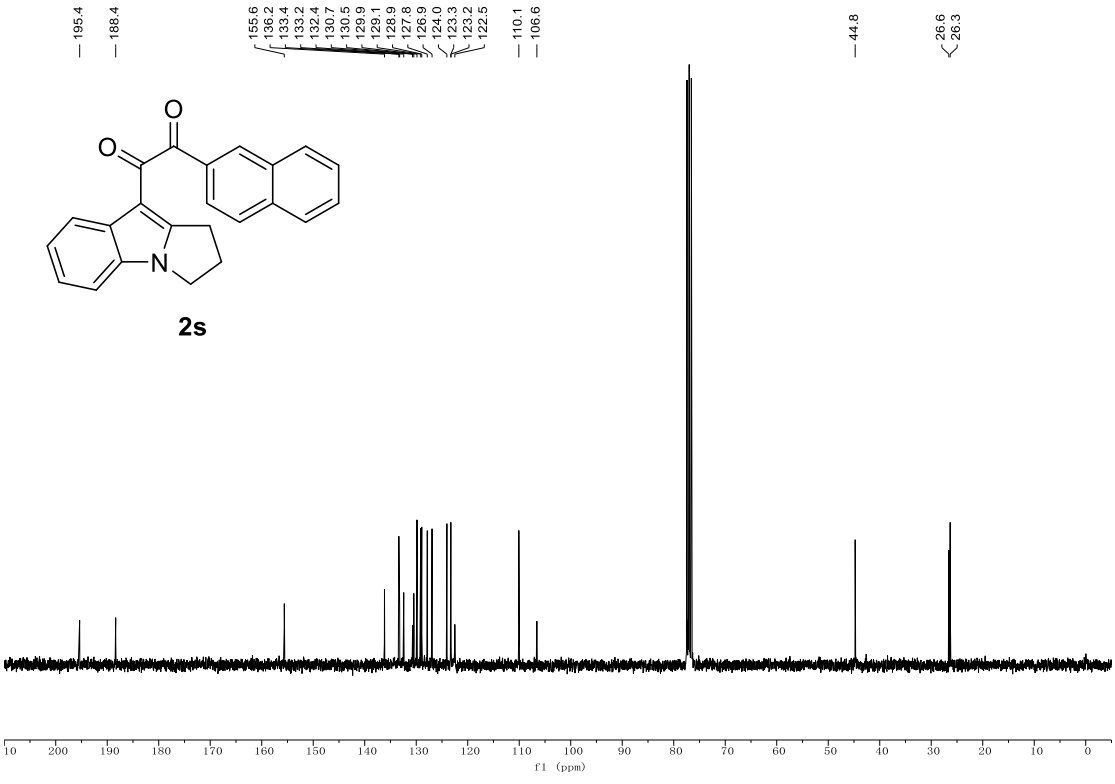
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2r**:



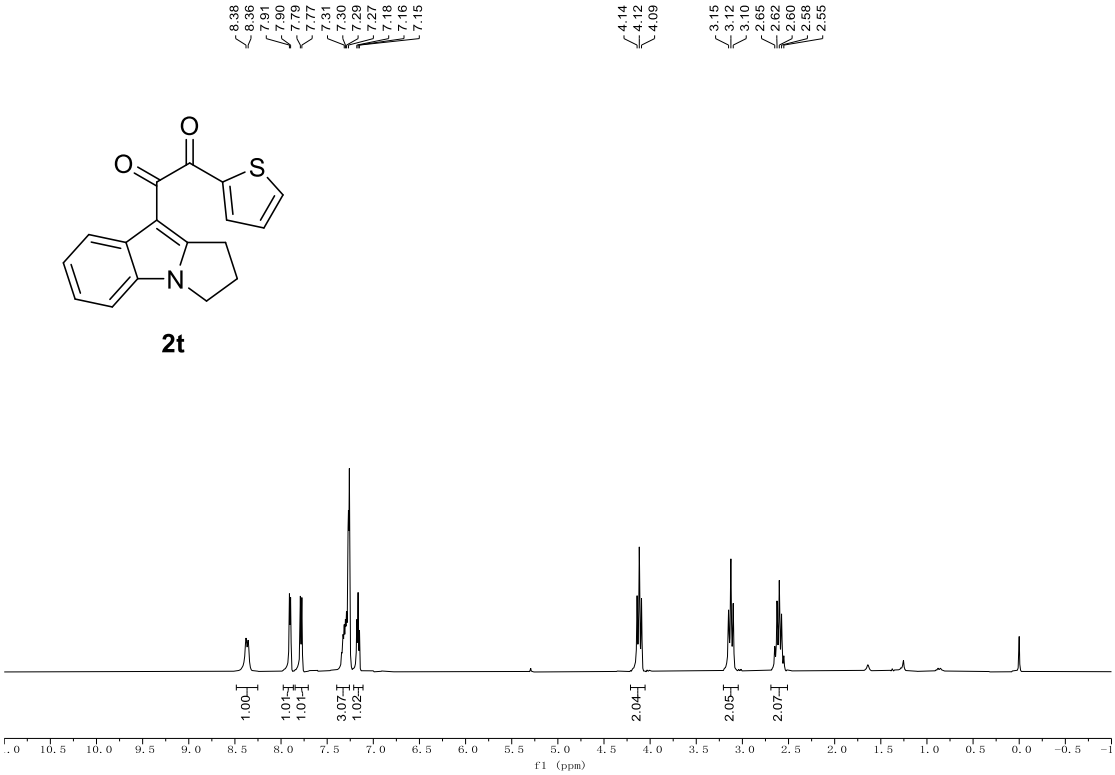
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2s**:



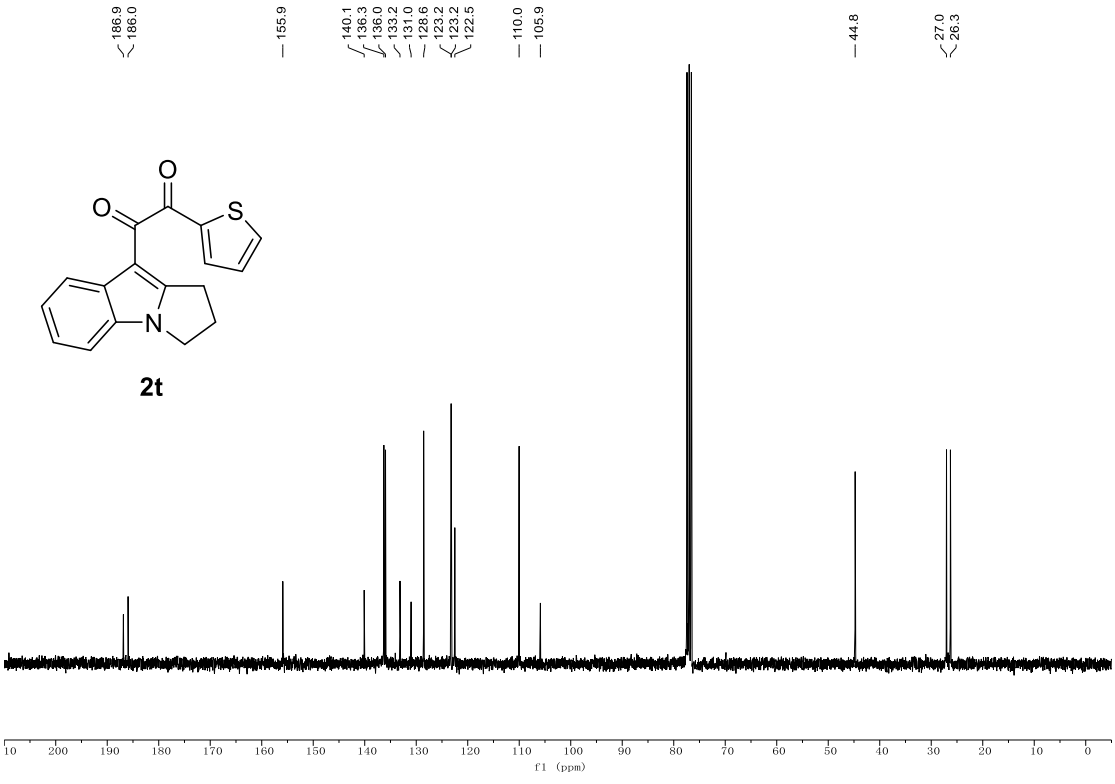
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2s**:



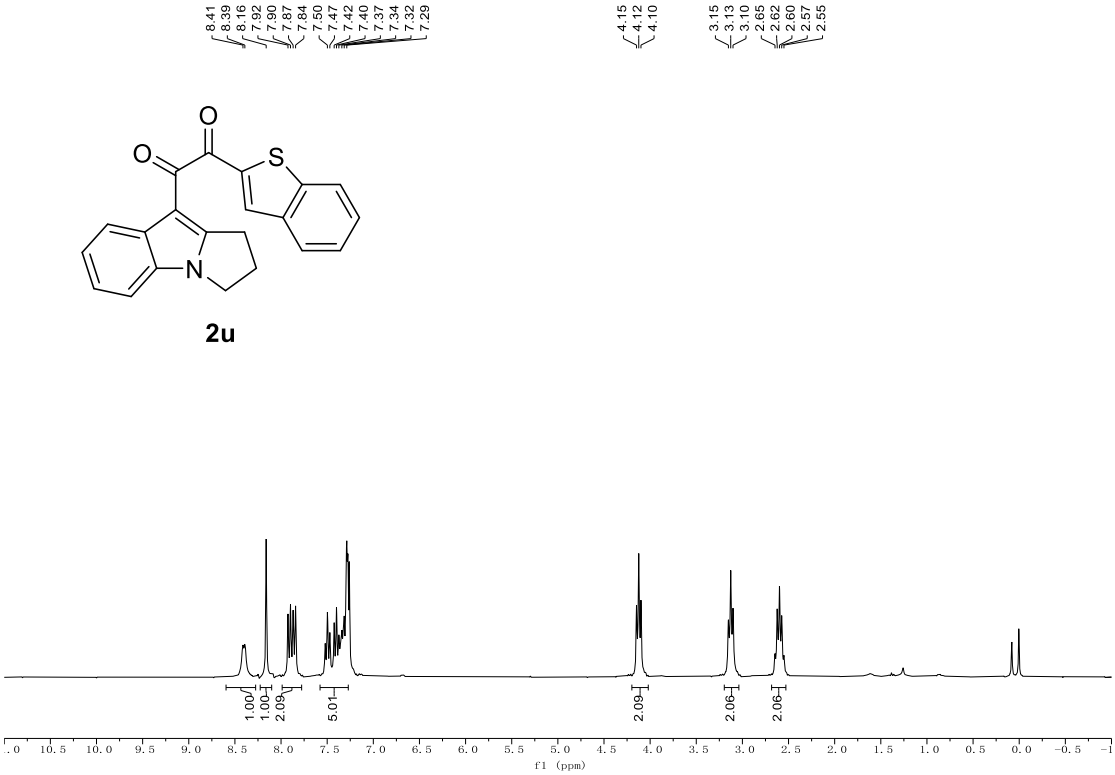
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2t**:



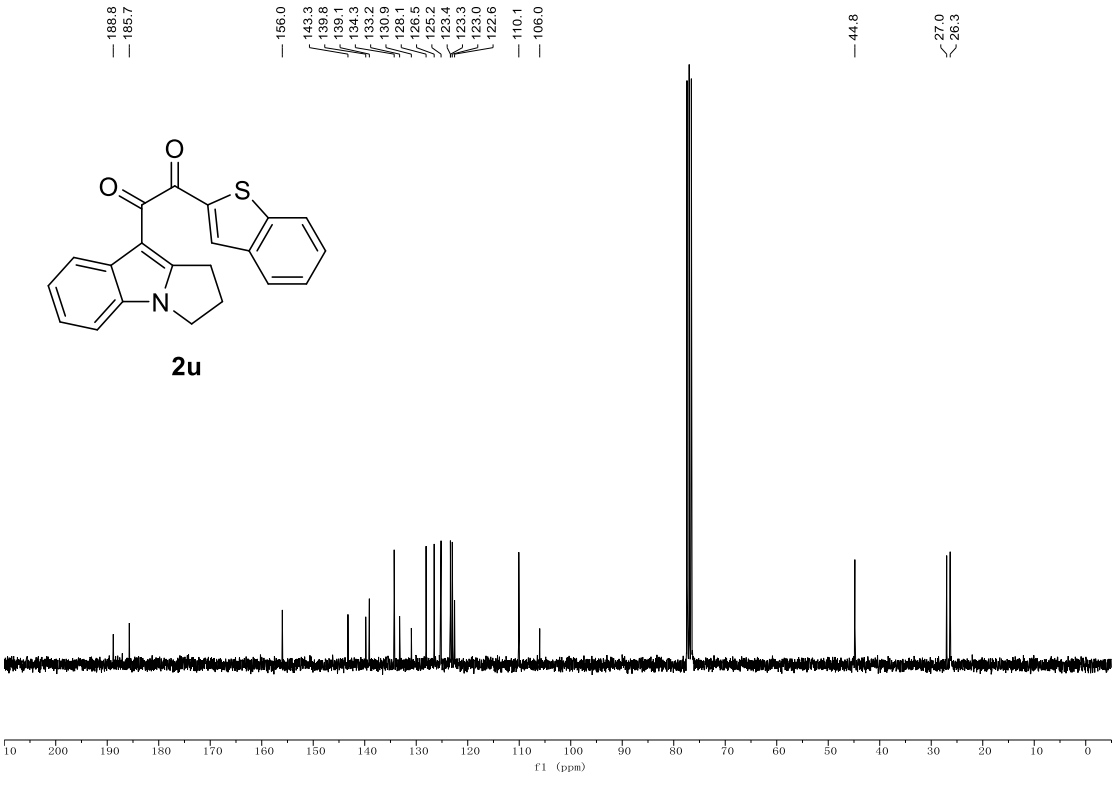
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2t**:



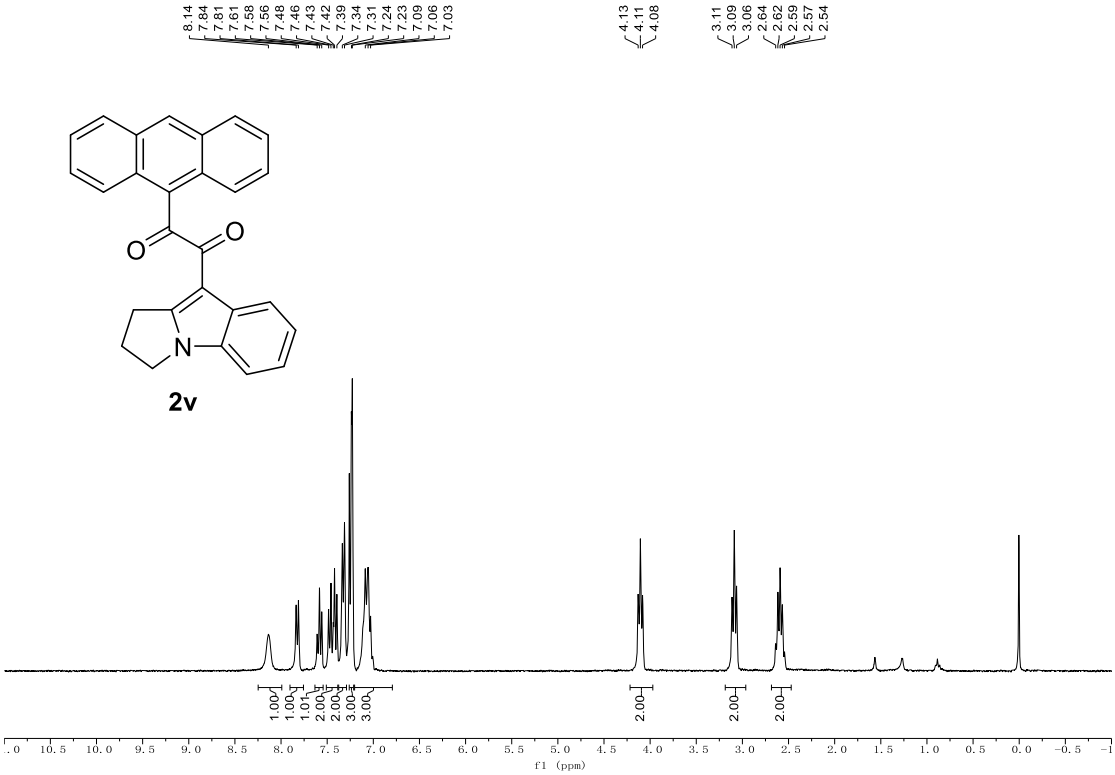
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2u**:



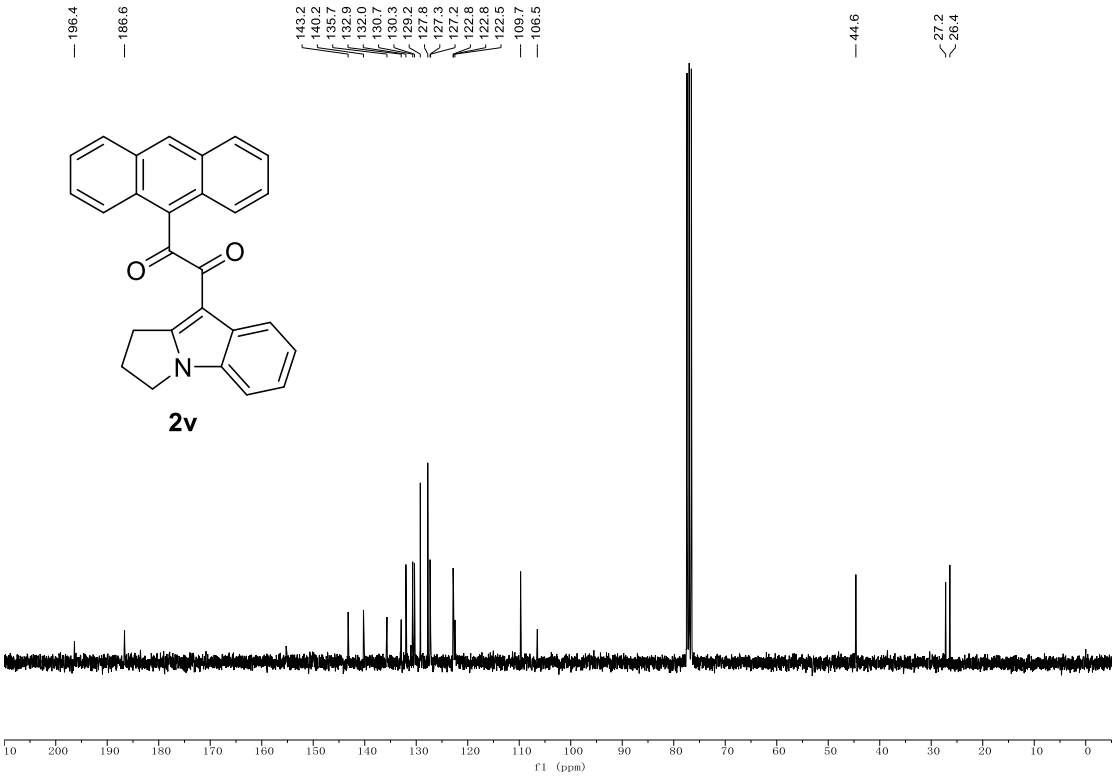
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2u**:



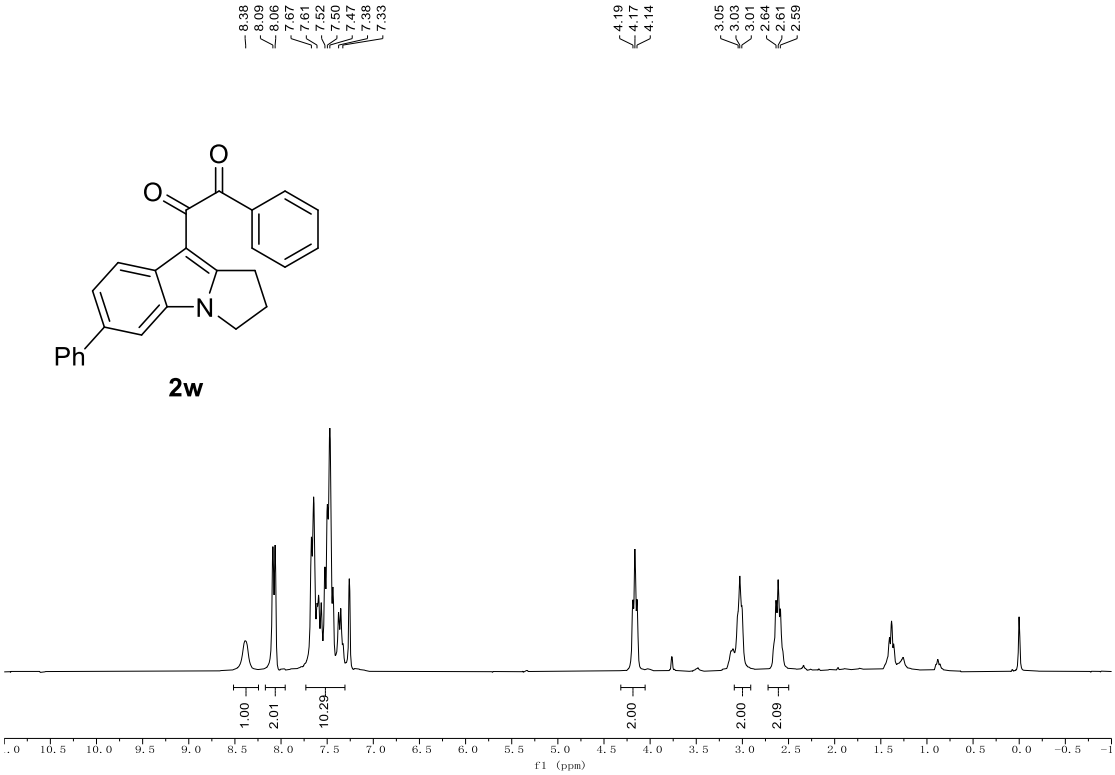
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2v**:



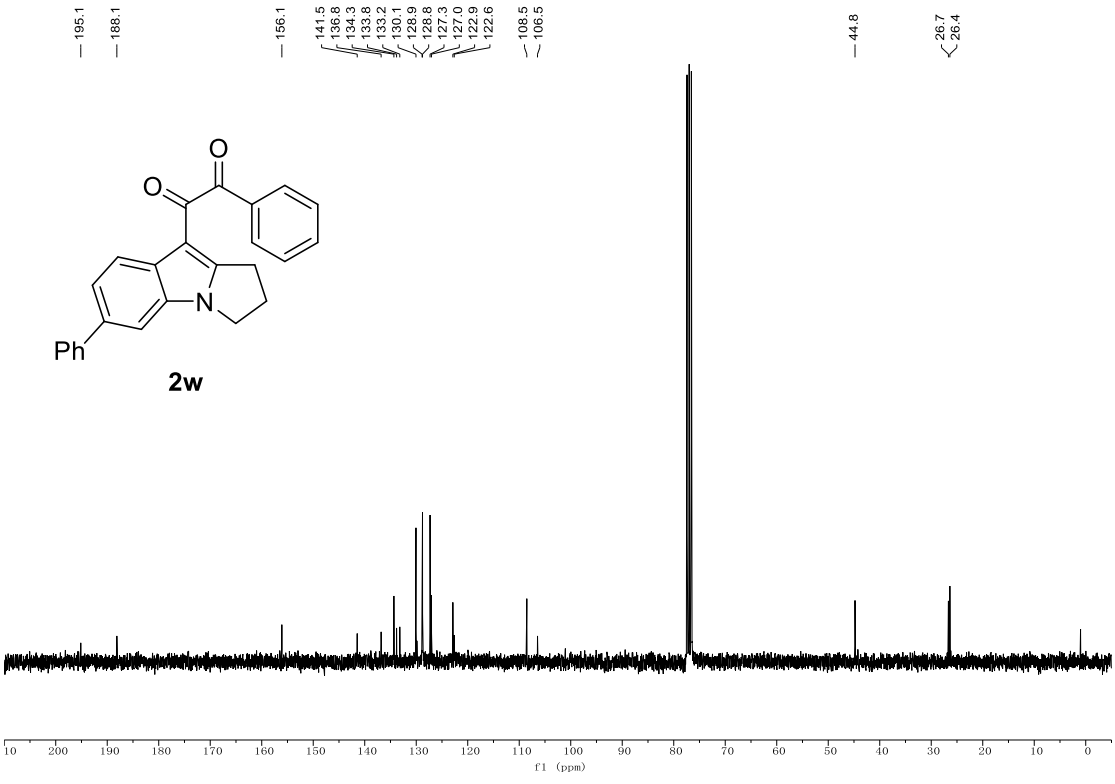
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2v**:



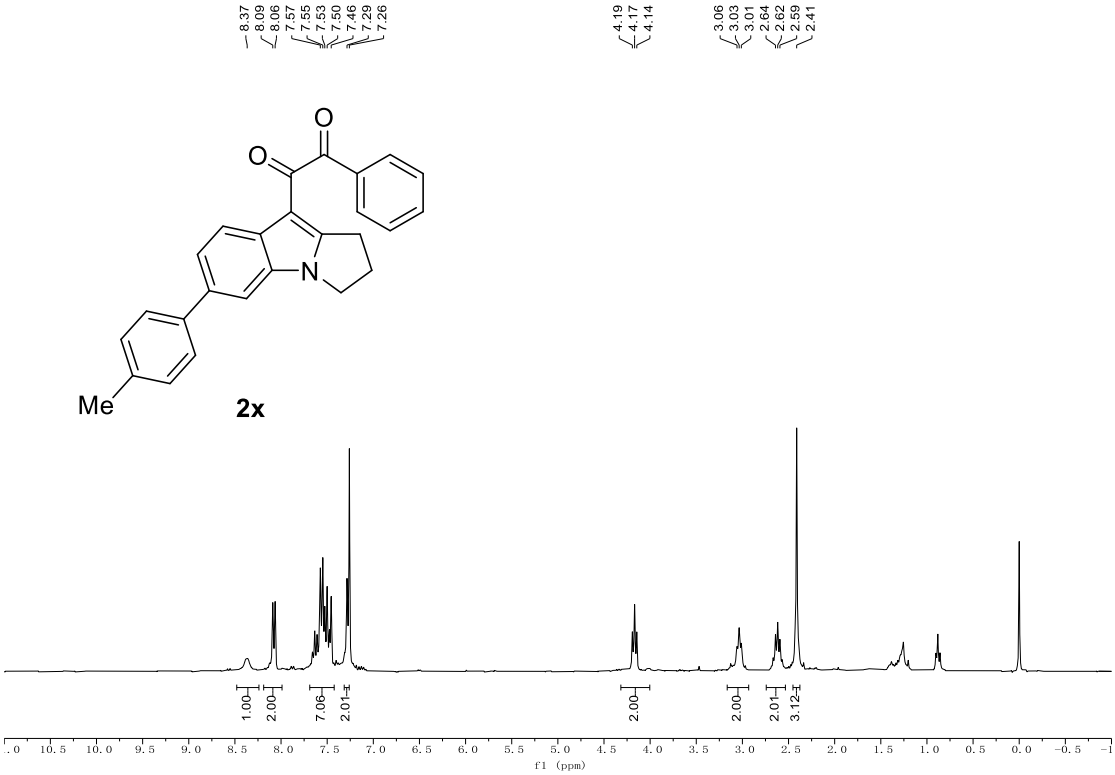
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2w**:



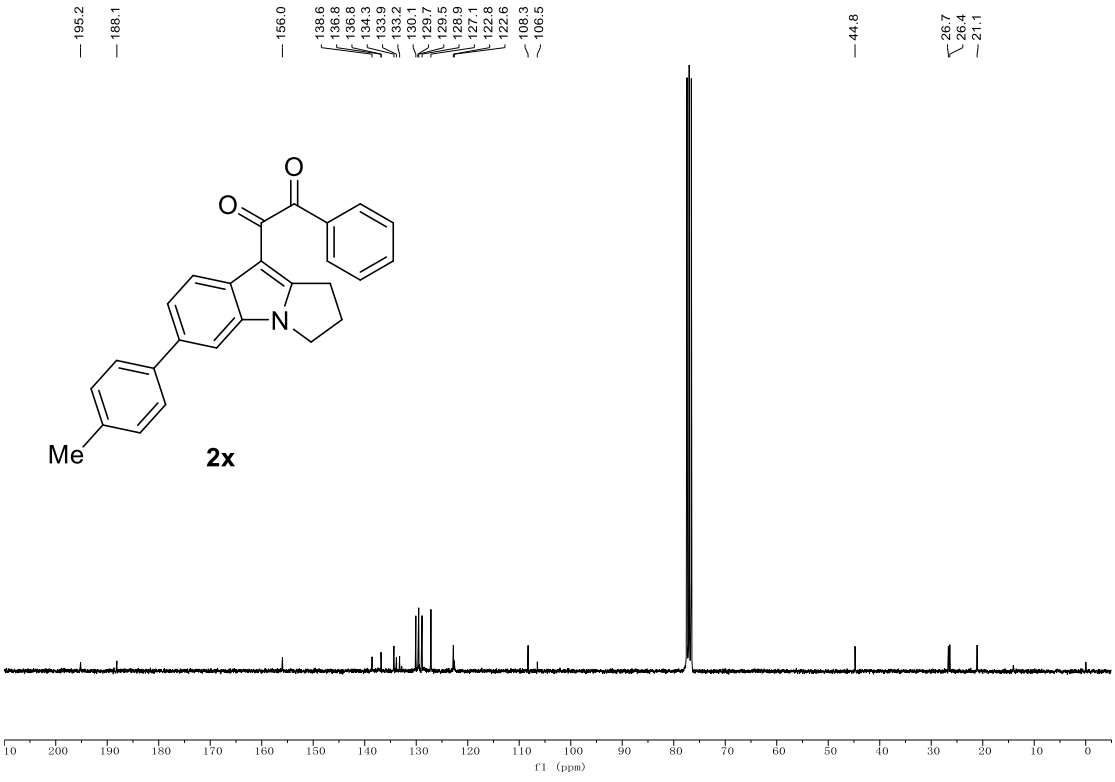
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2w**:



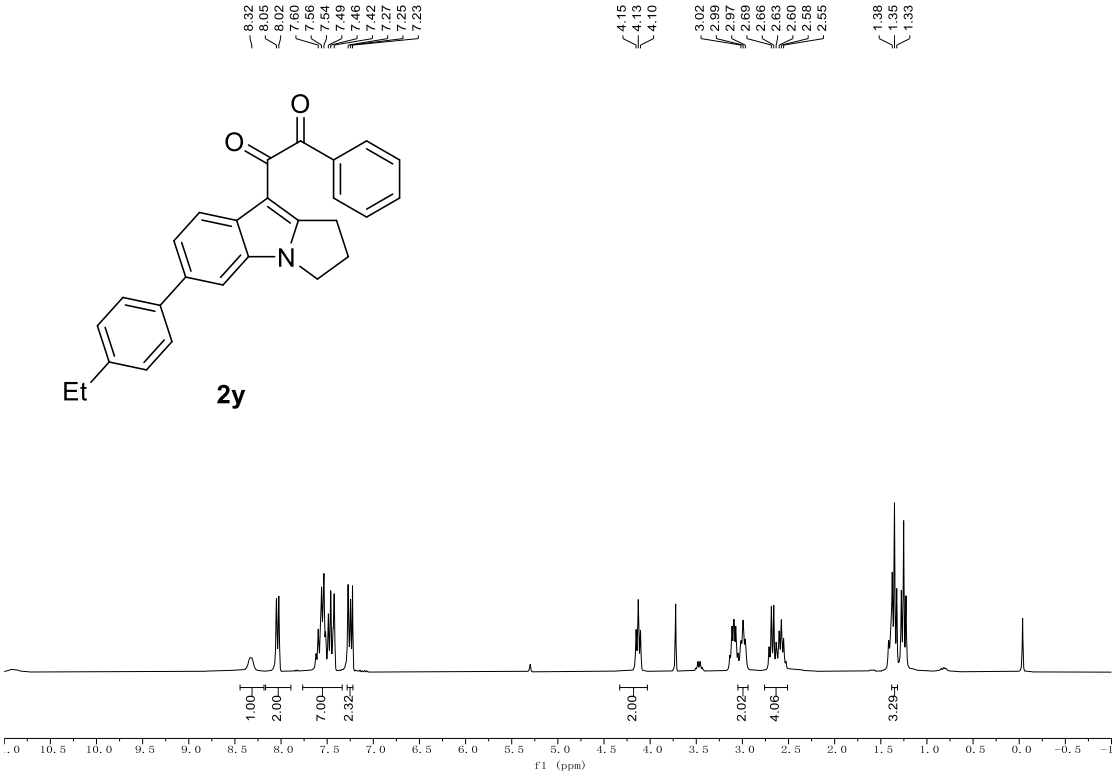
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2x**:



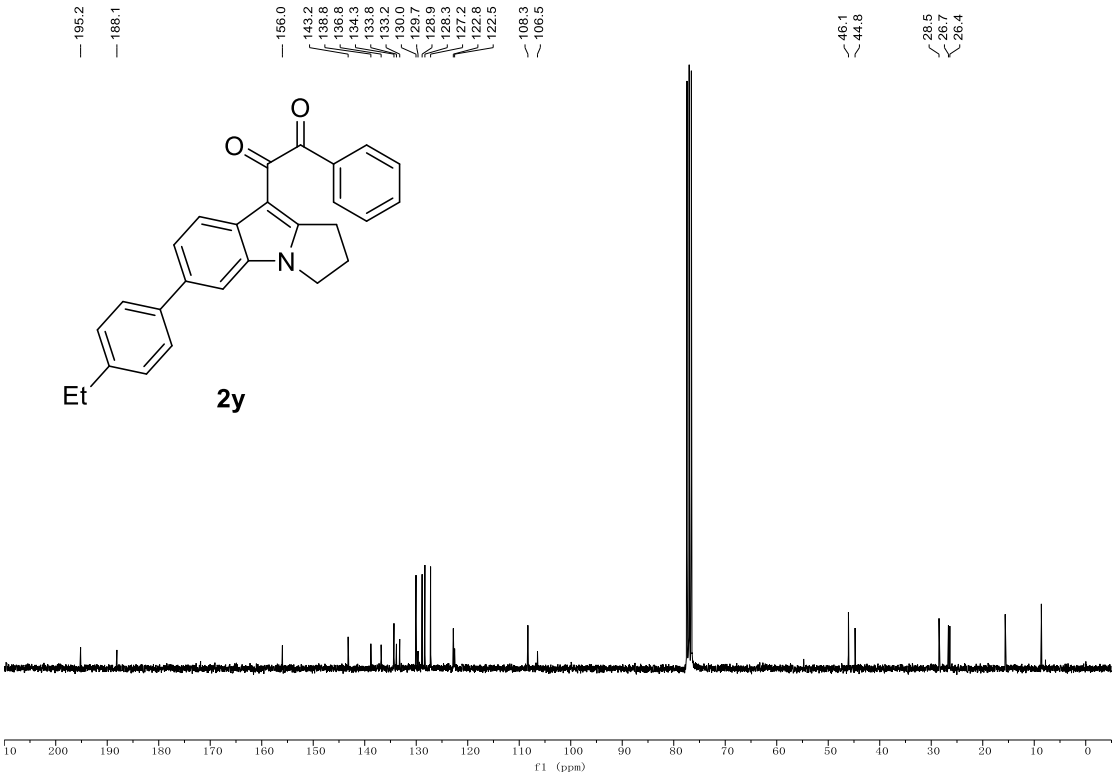
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2x**:



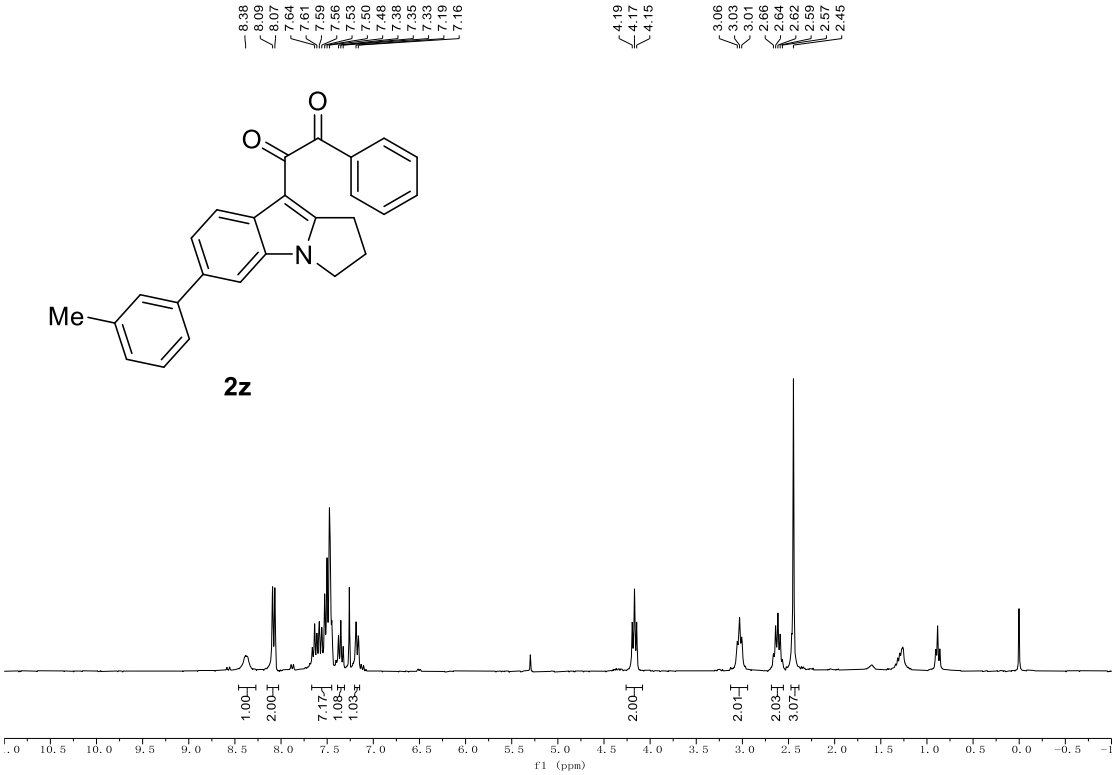
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2y**:



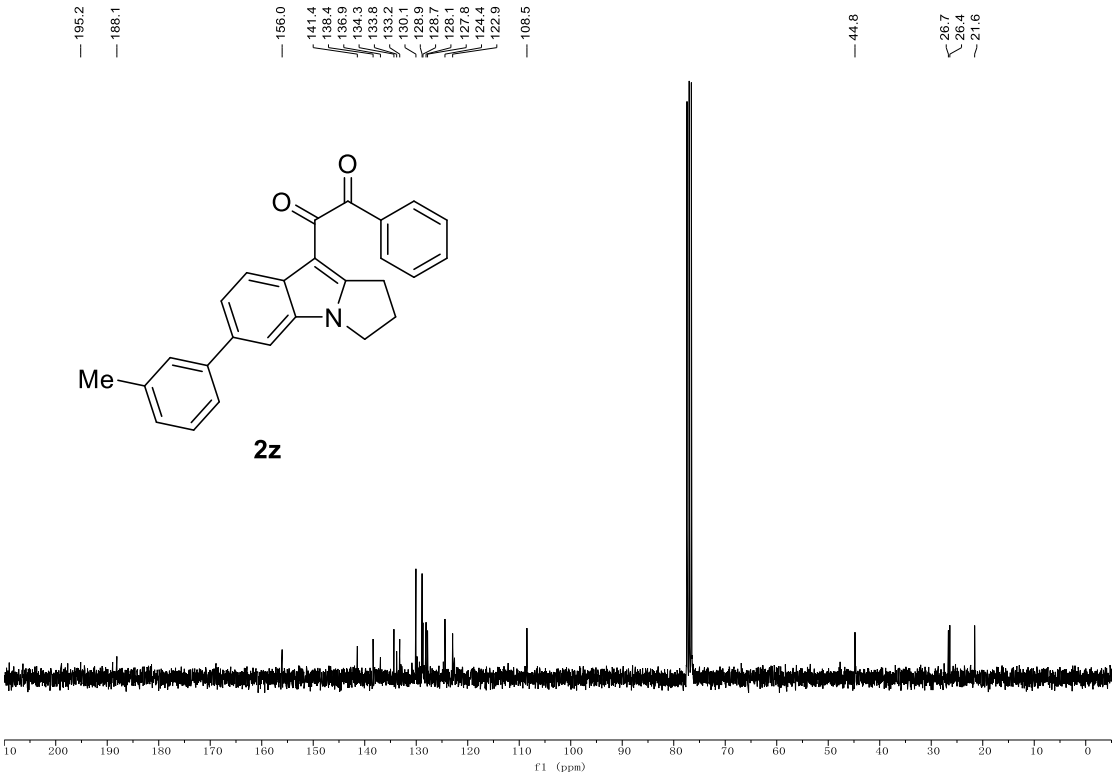
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2y**:



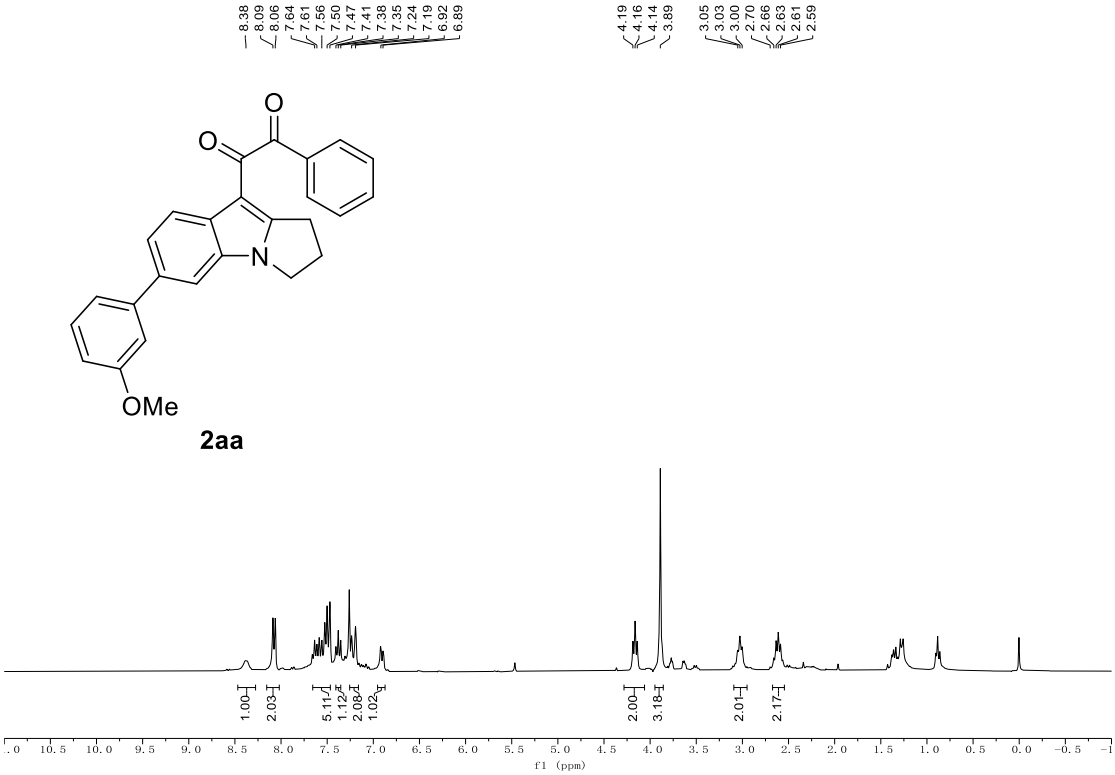
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2z**:



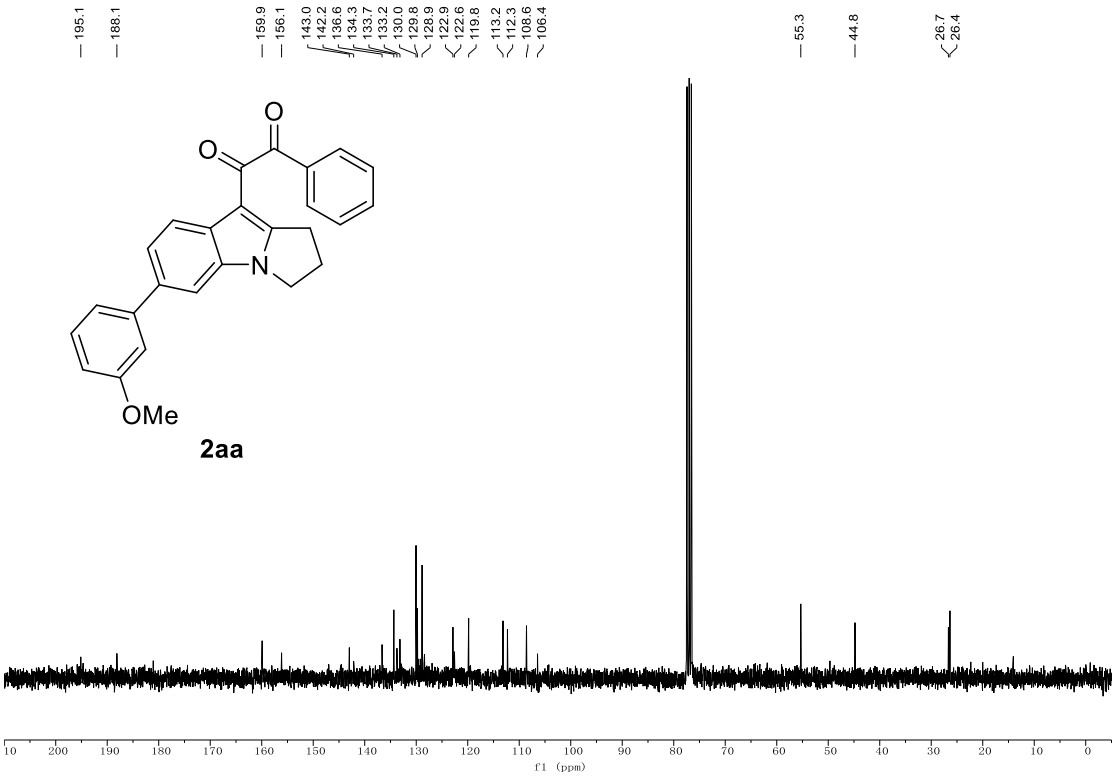
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2z**:



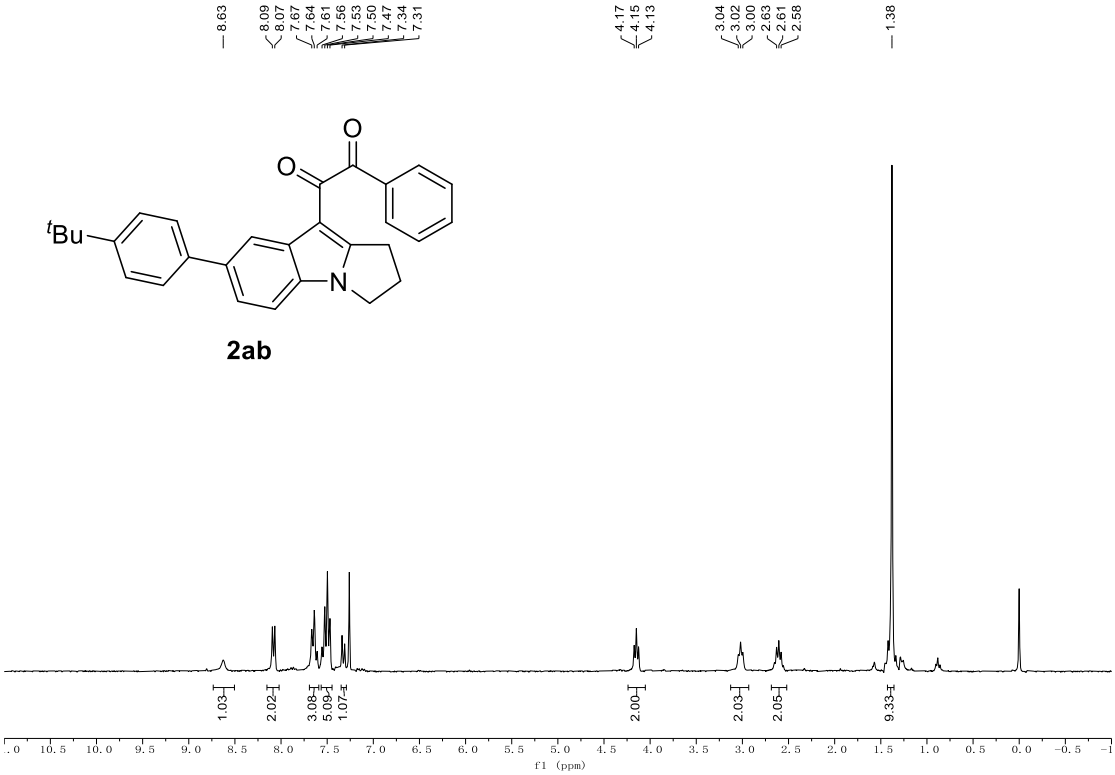
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2aa**:



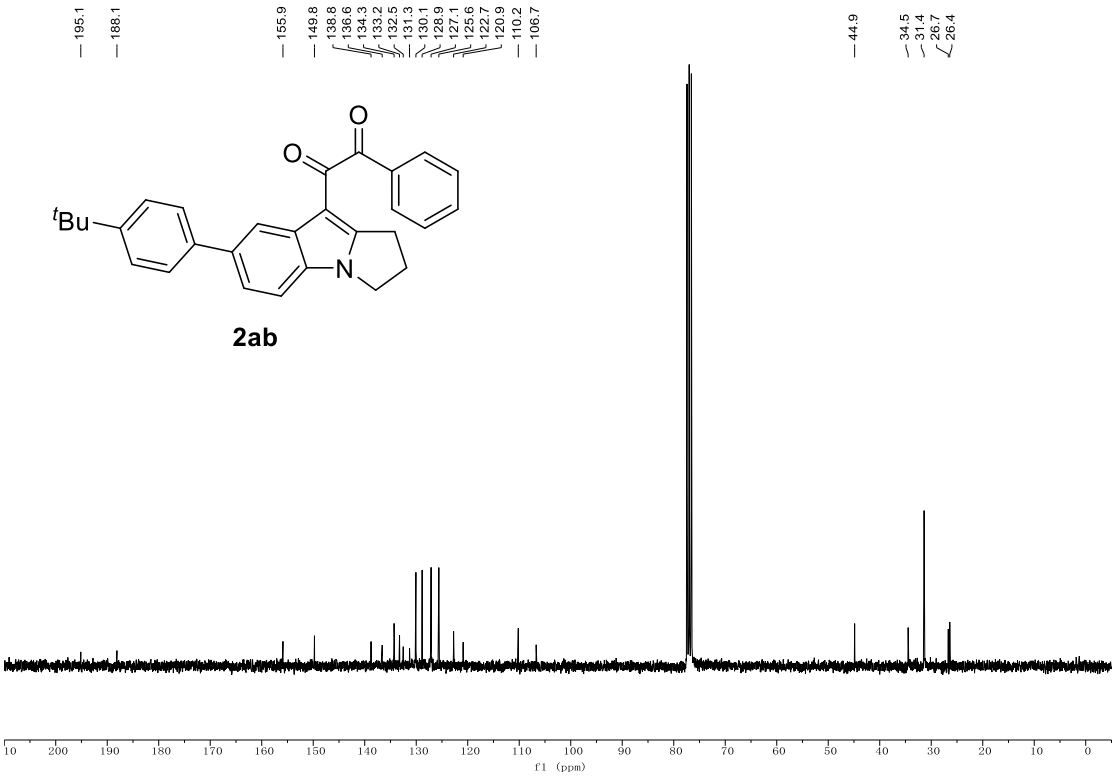
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2aa**:



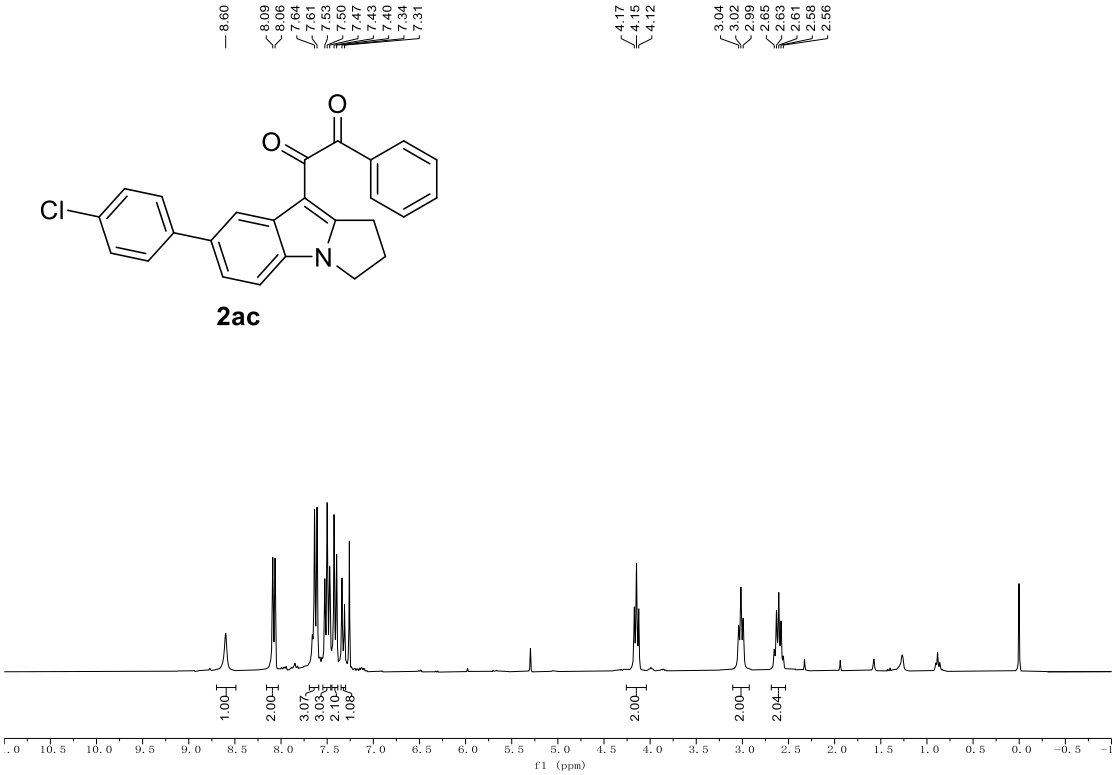
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2ab**:



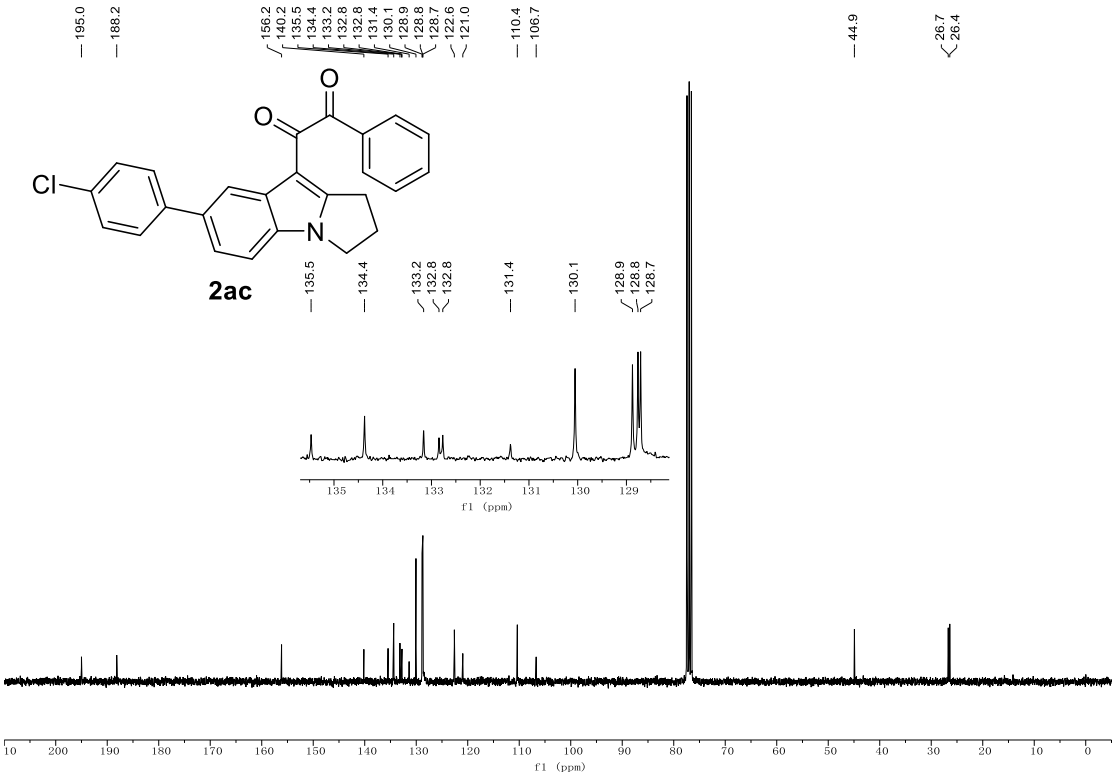
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2ab**:



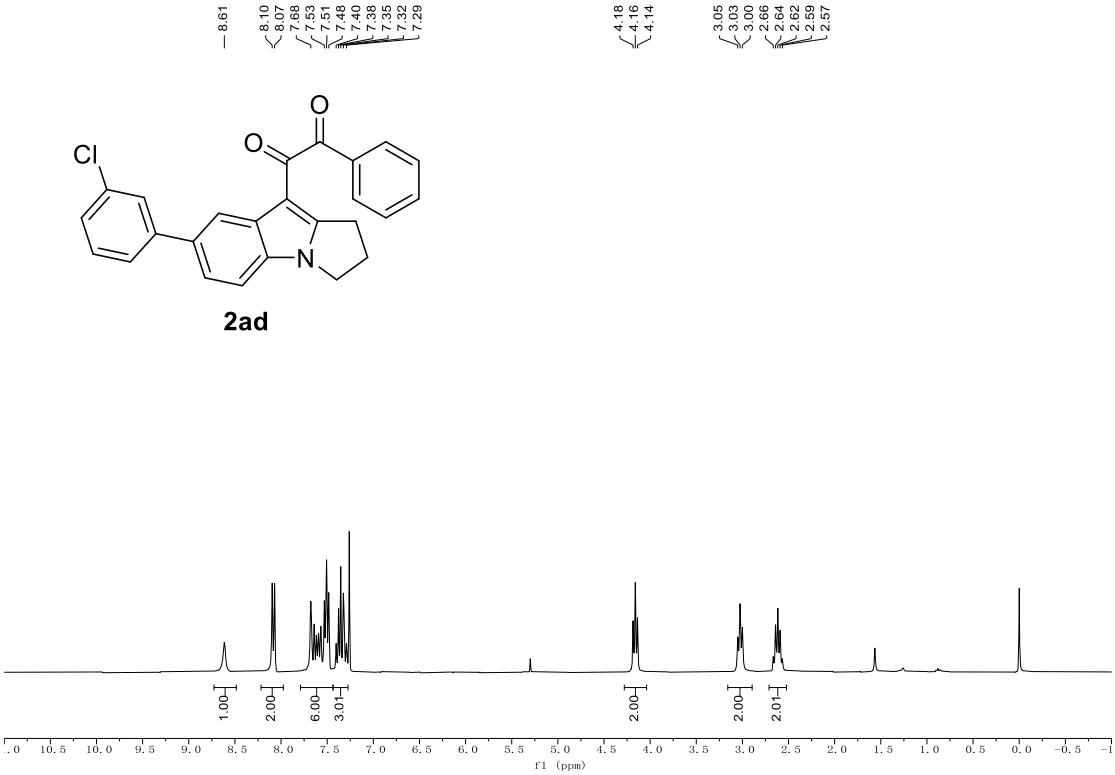
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2ac**:



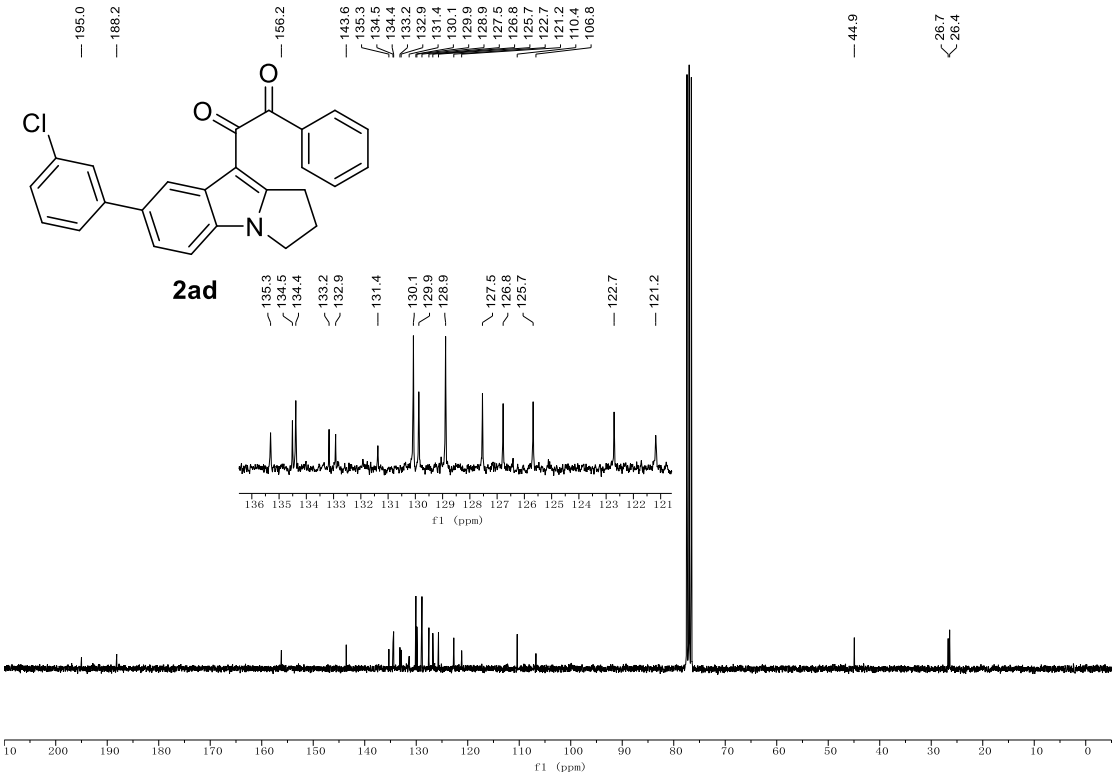
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2ac**:



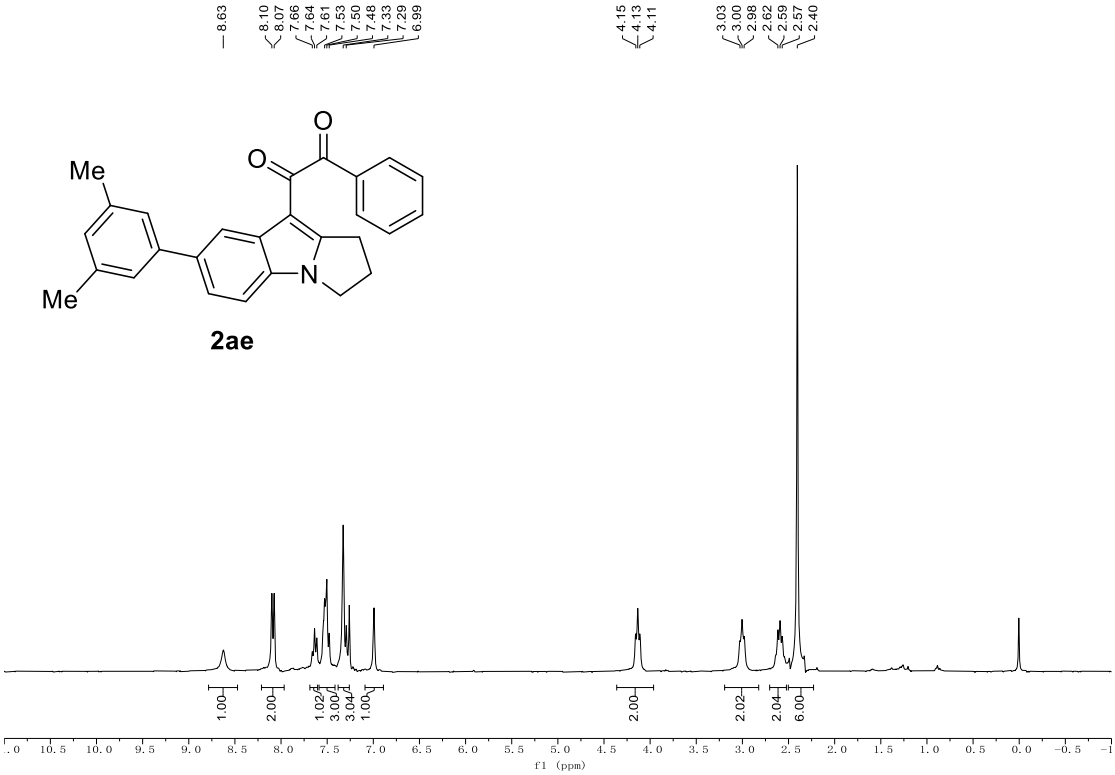
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2ad**:



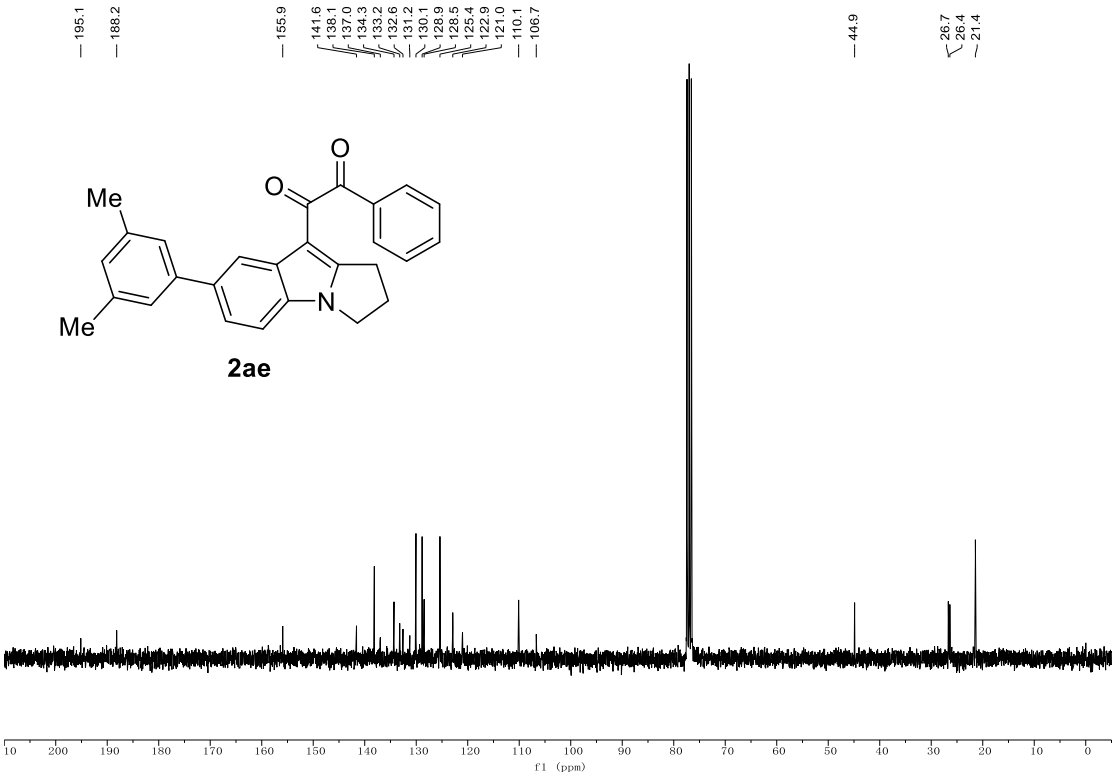
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2ad**:



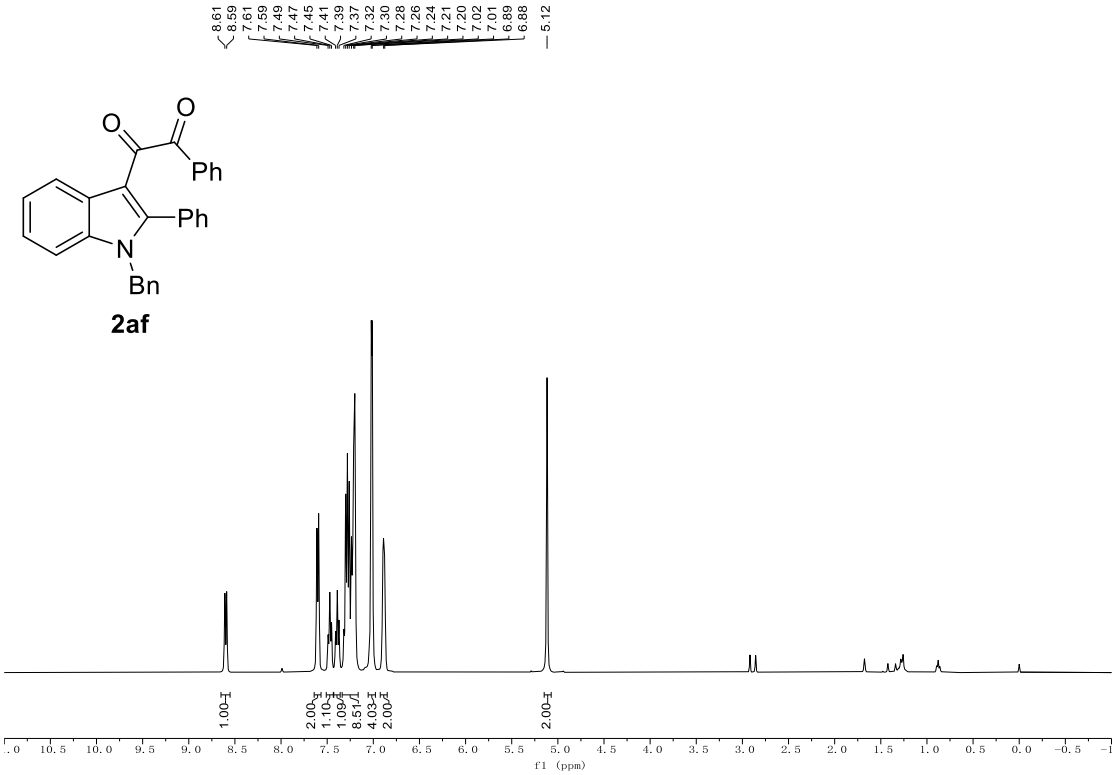
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **2ae**:



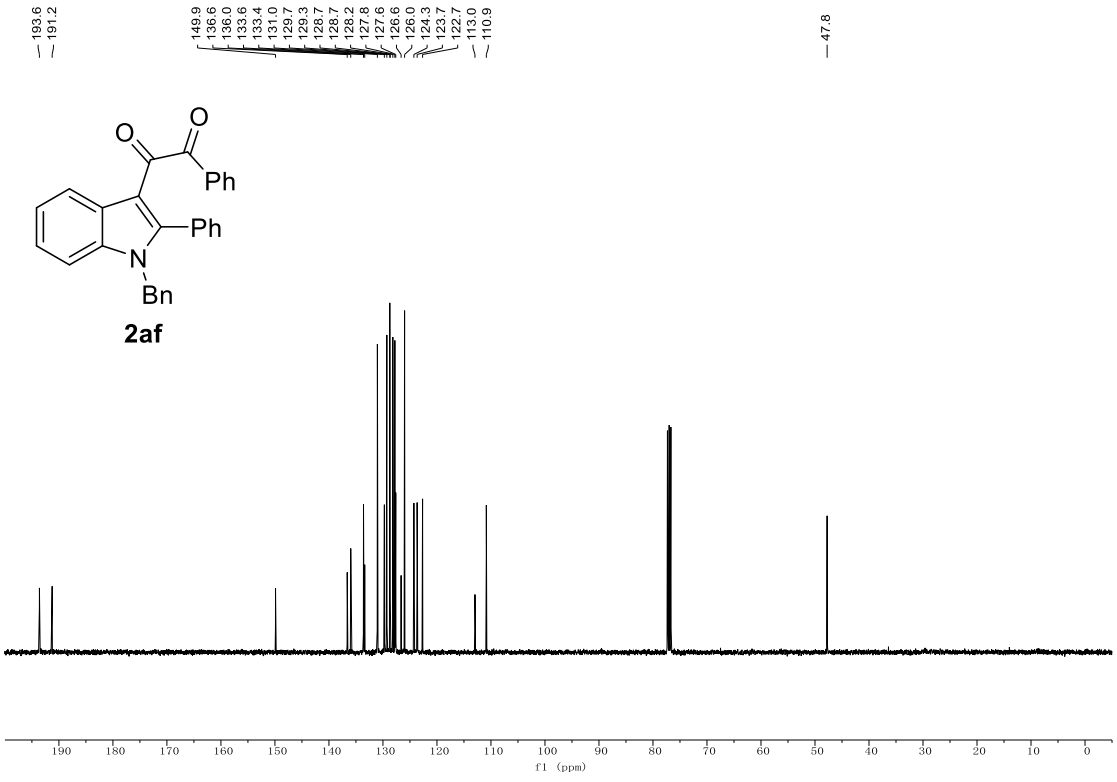
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **2ae**:



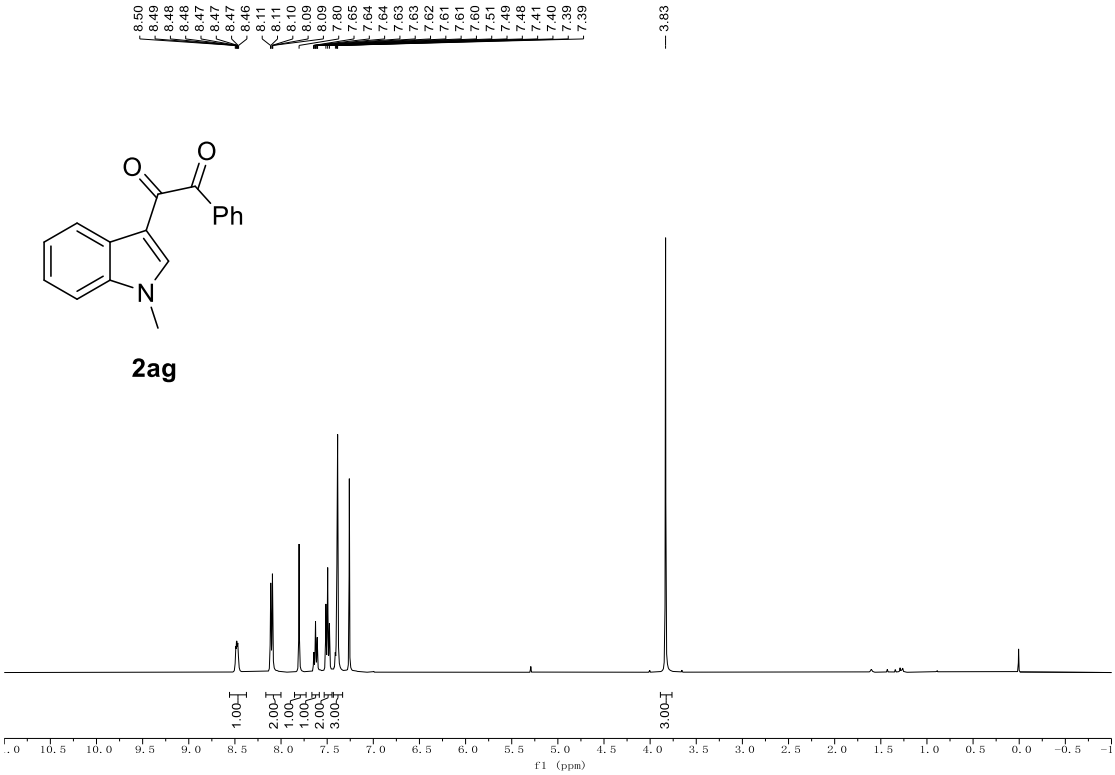
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2af**:



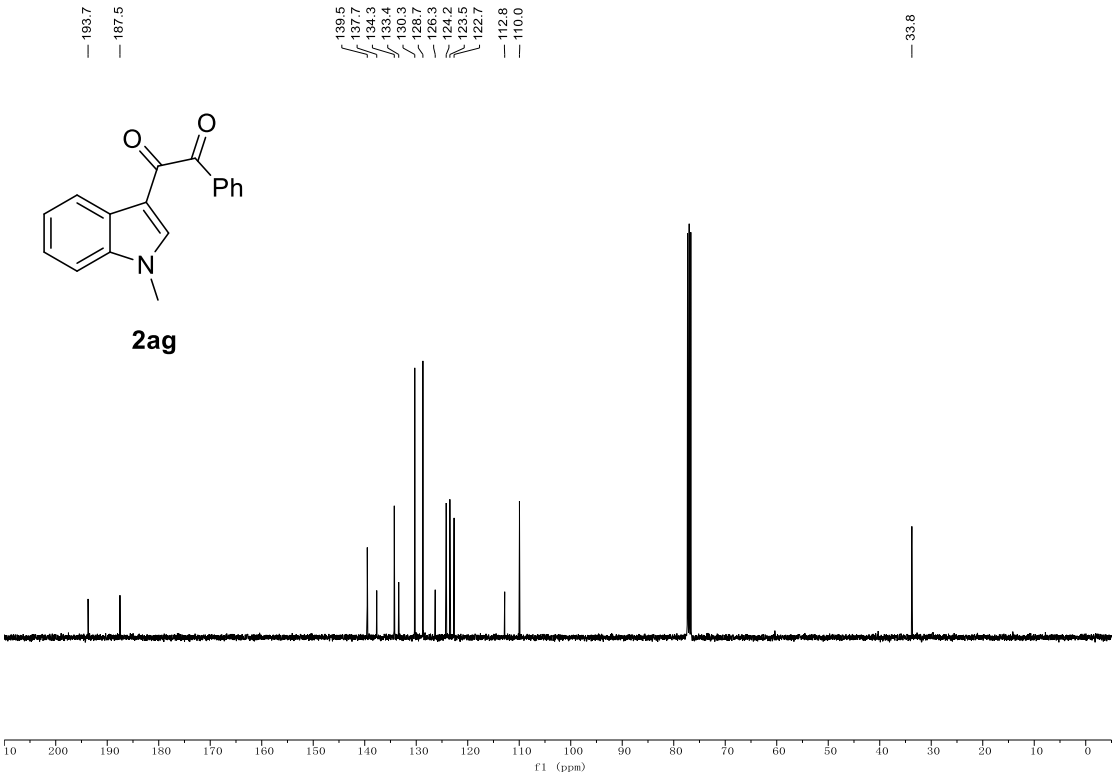
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2af**:



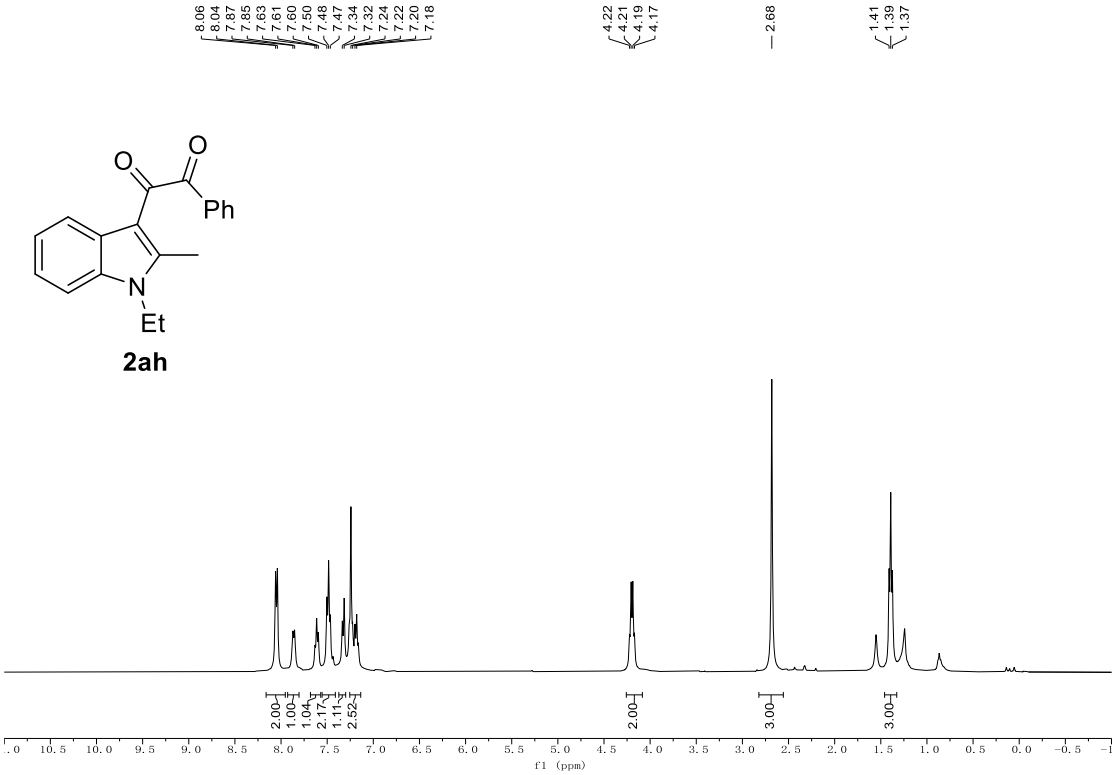
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2ag**:



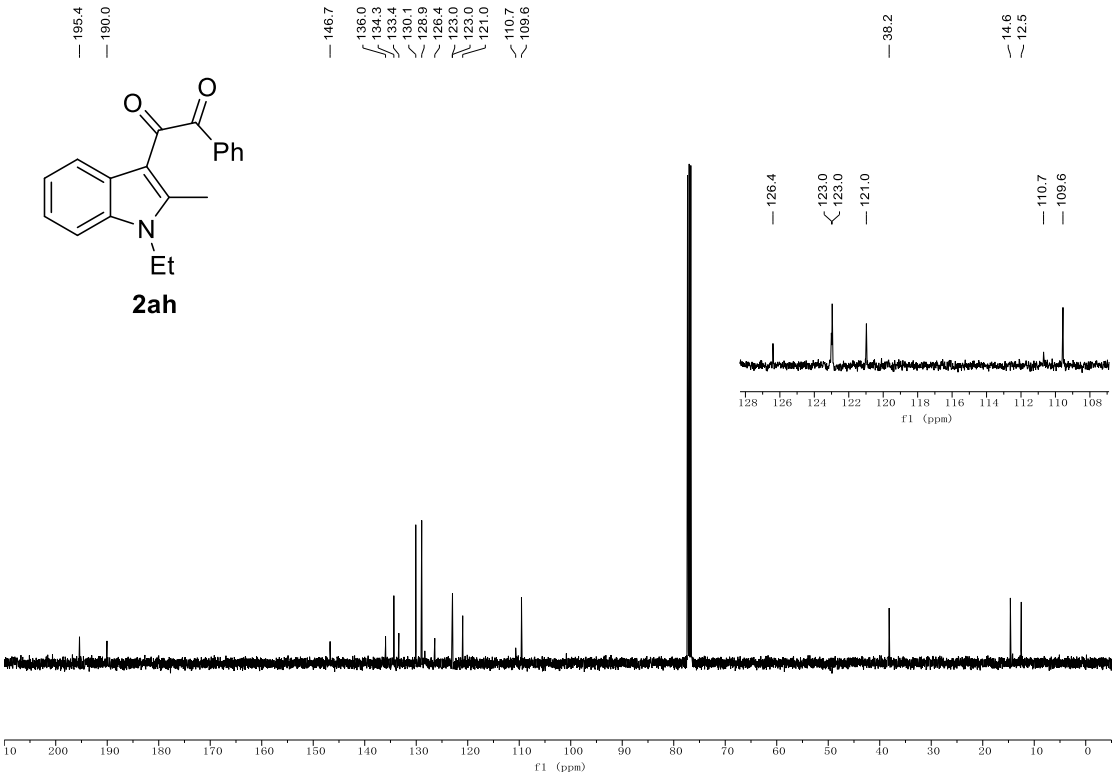
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2ag**:



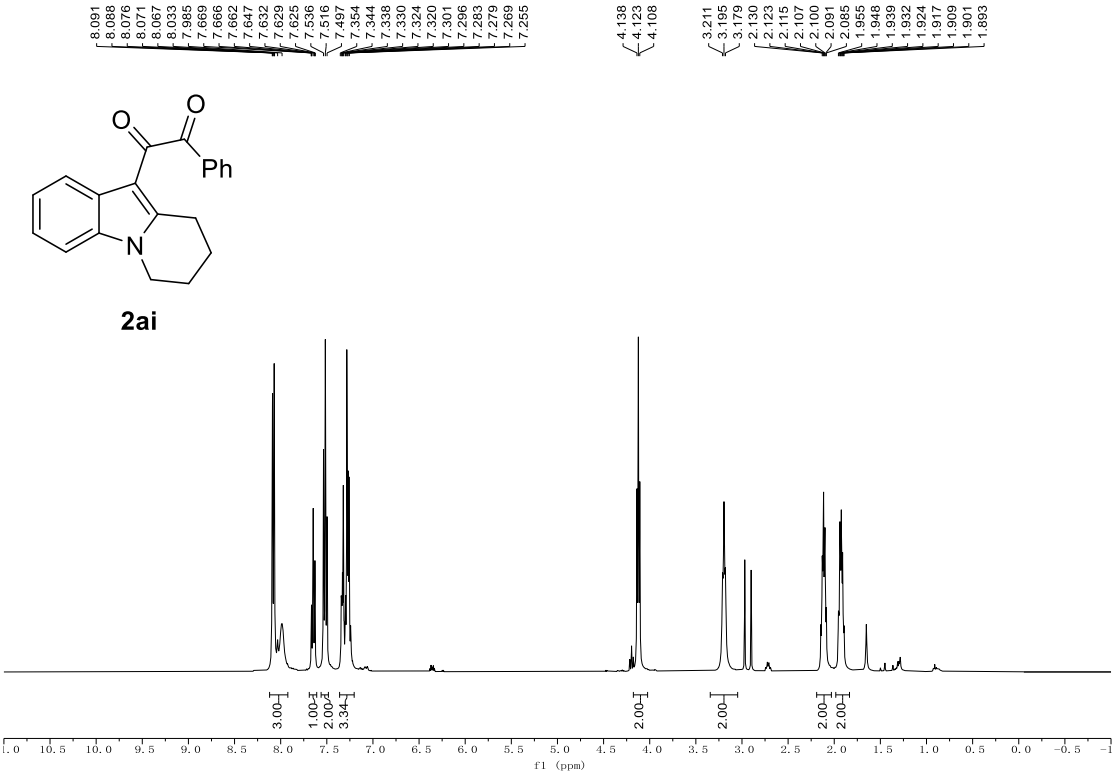
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2ah**:



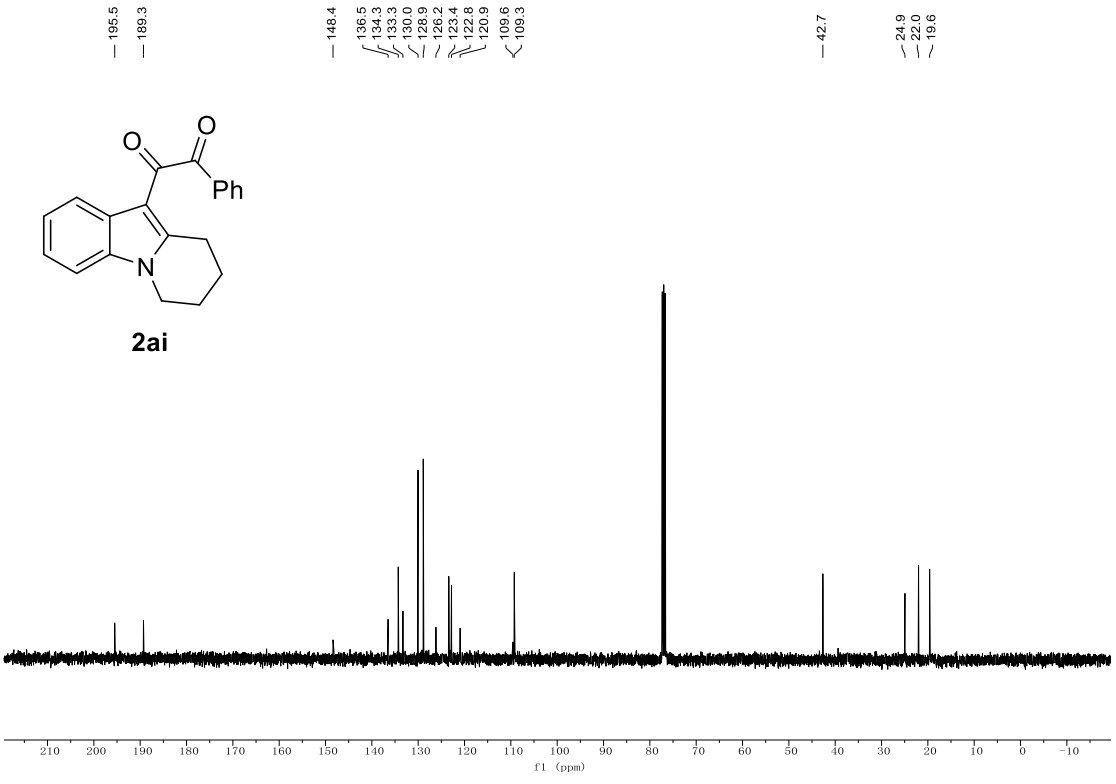
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2ah**:



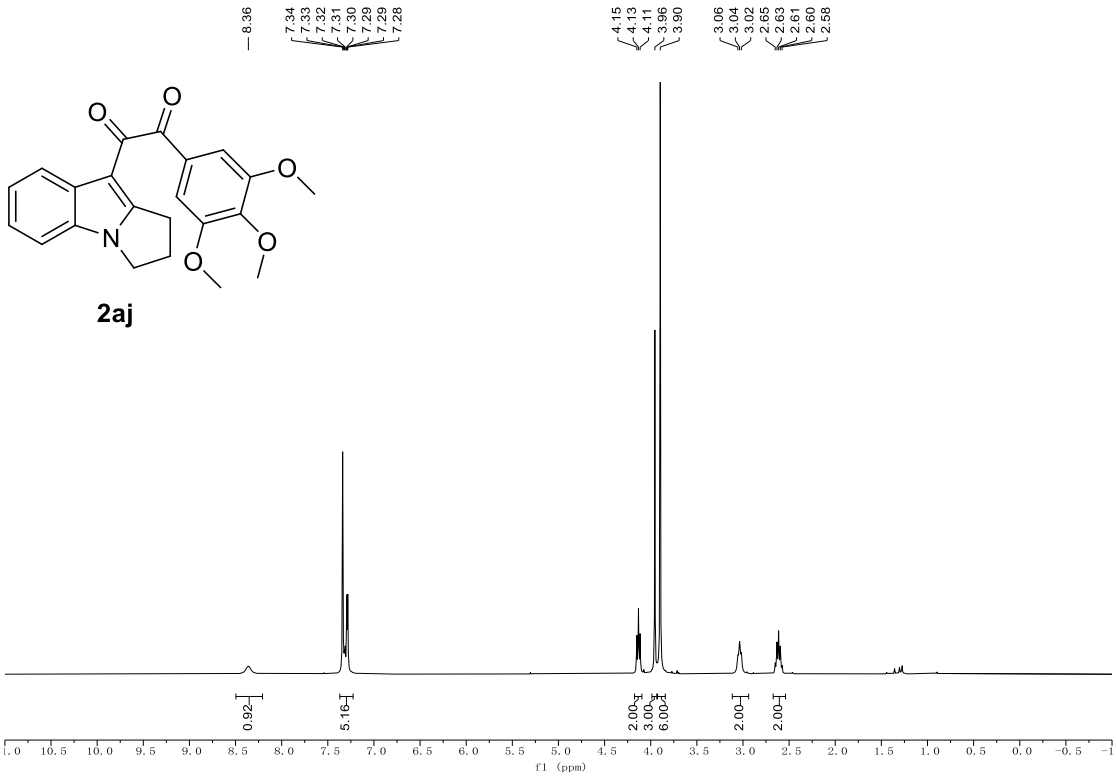
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2ai**:



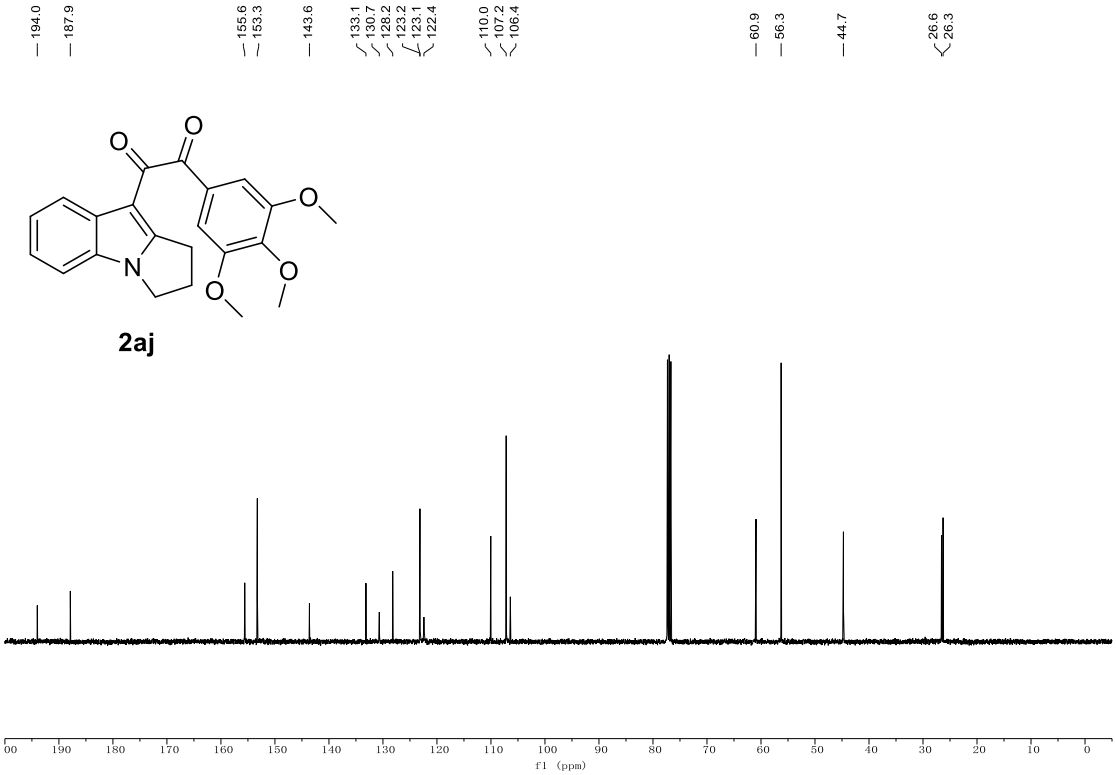
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2ai**:



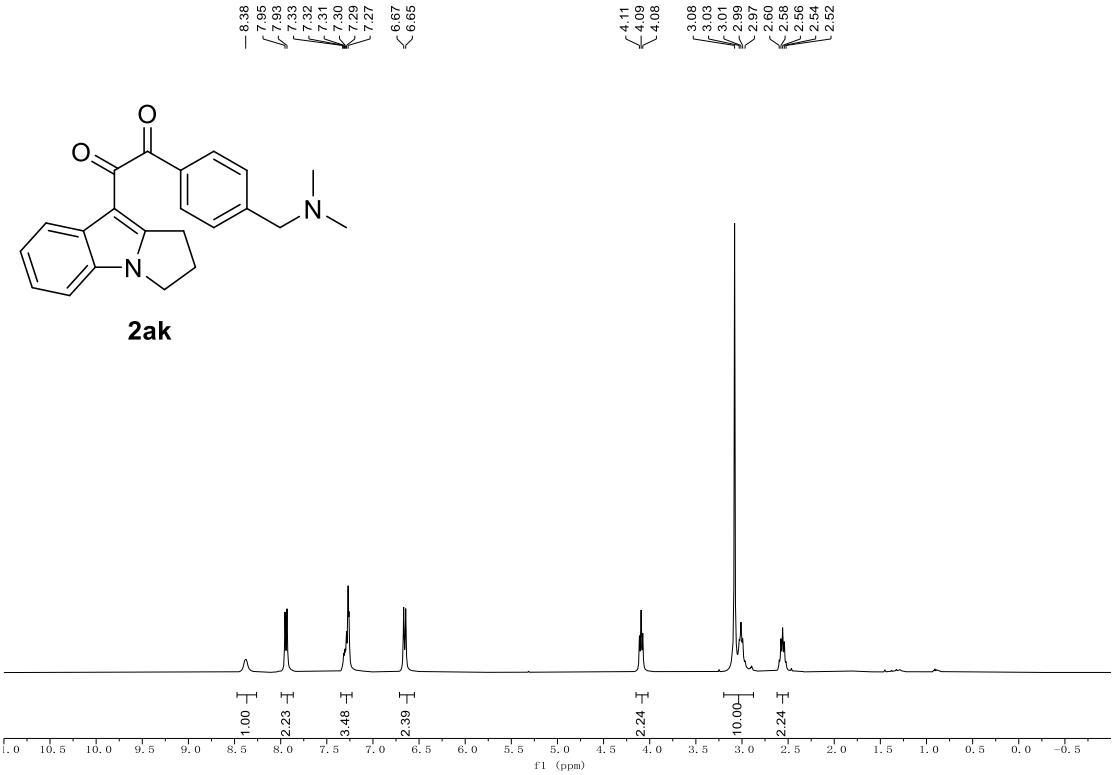
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2aj**:



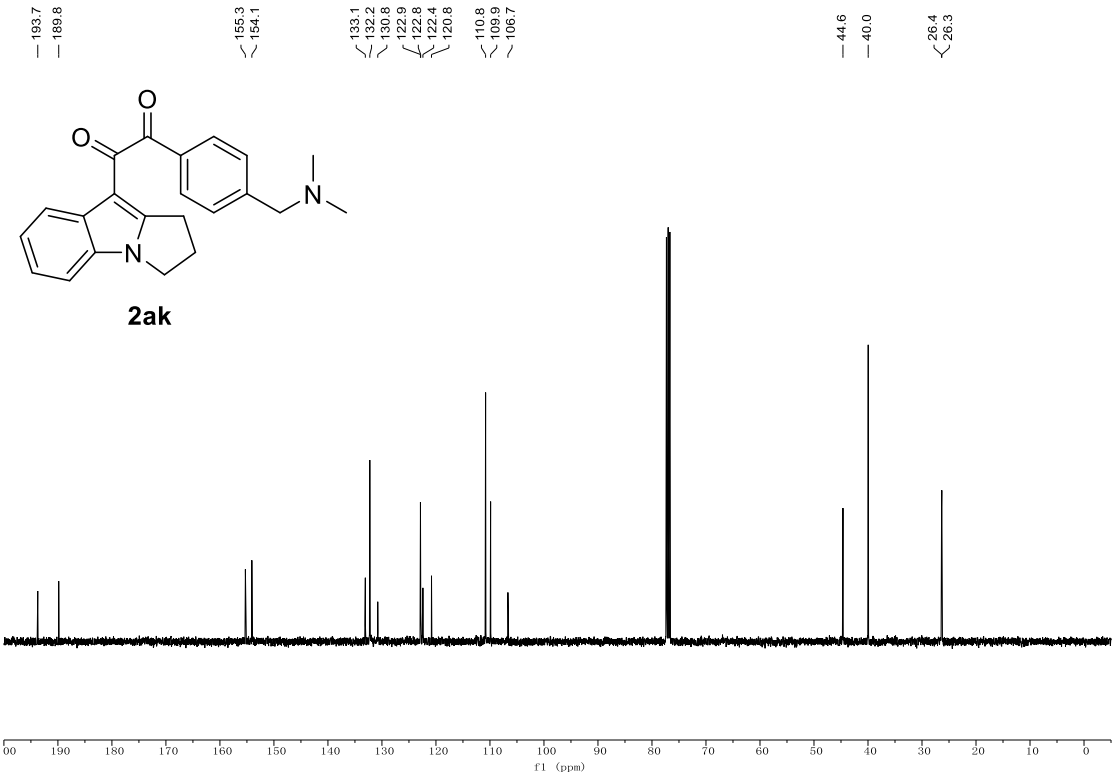
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2aj**:



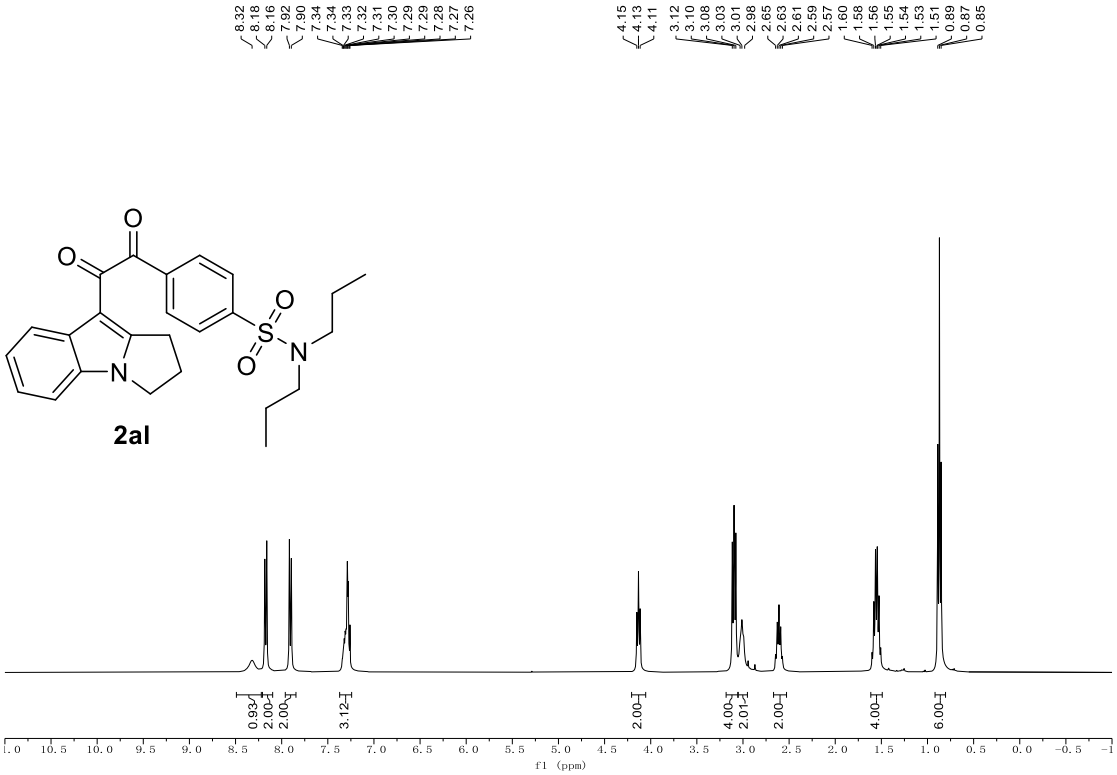
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2ak**:



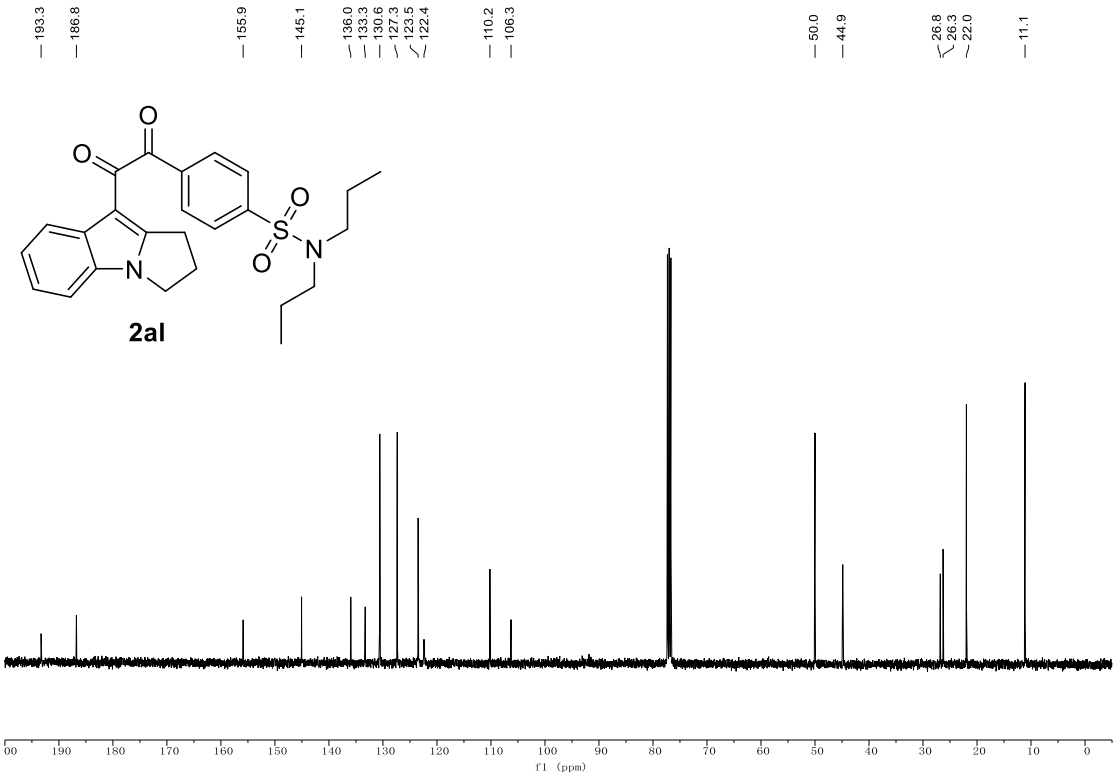
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2ak**:



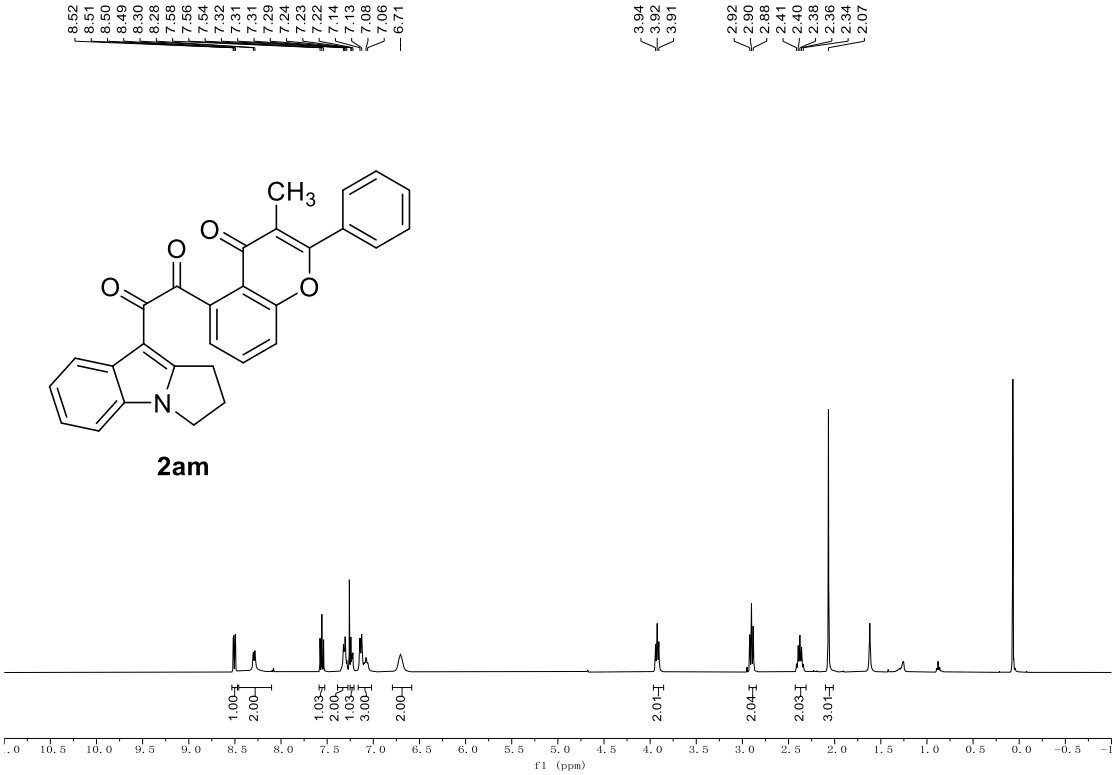
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2al**:



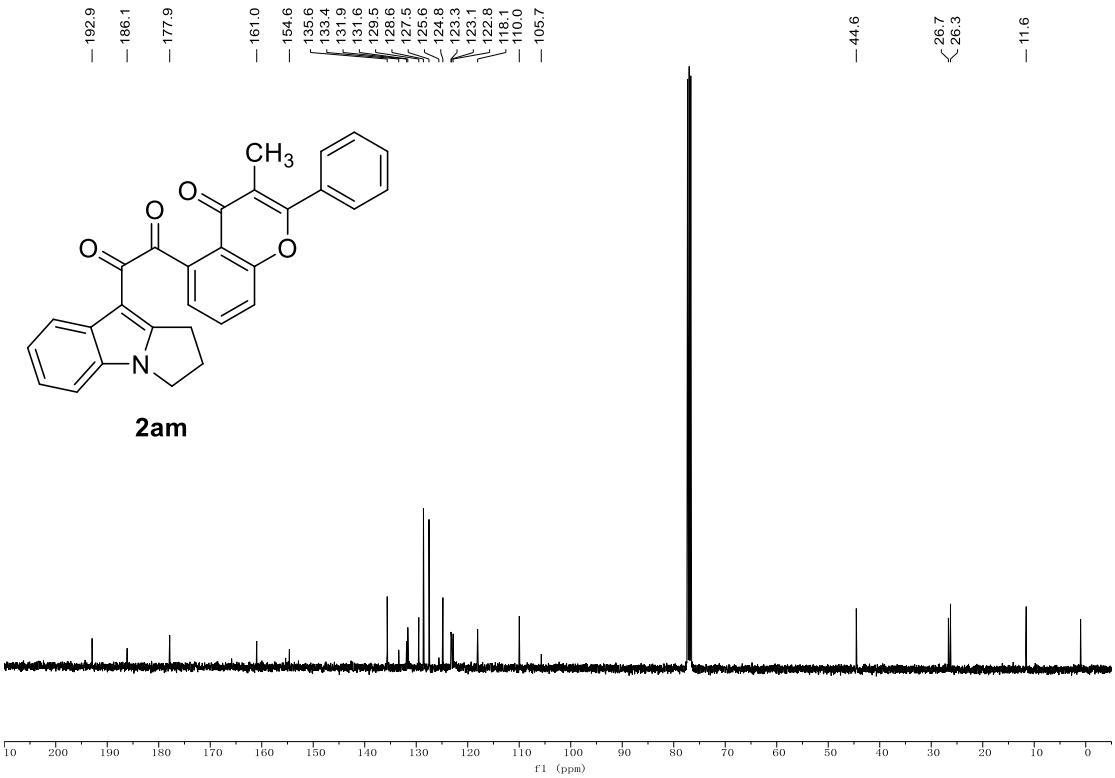
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2al**:



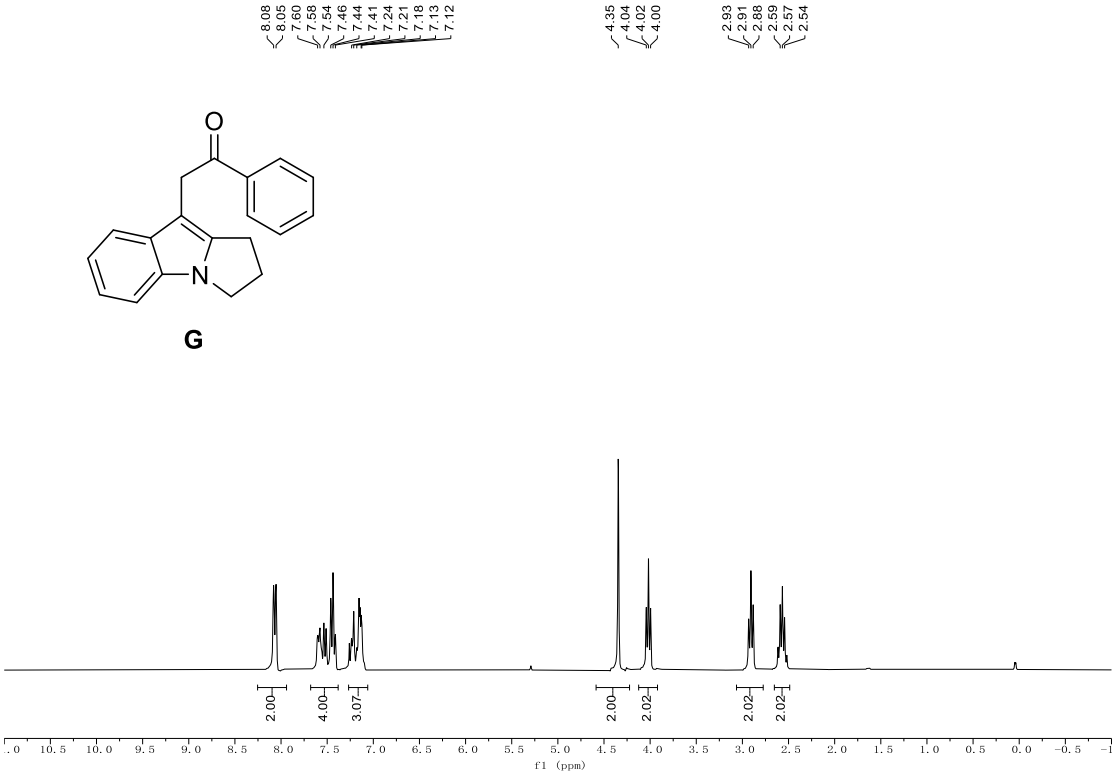
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2am**:



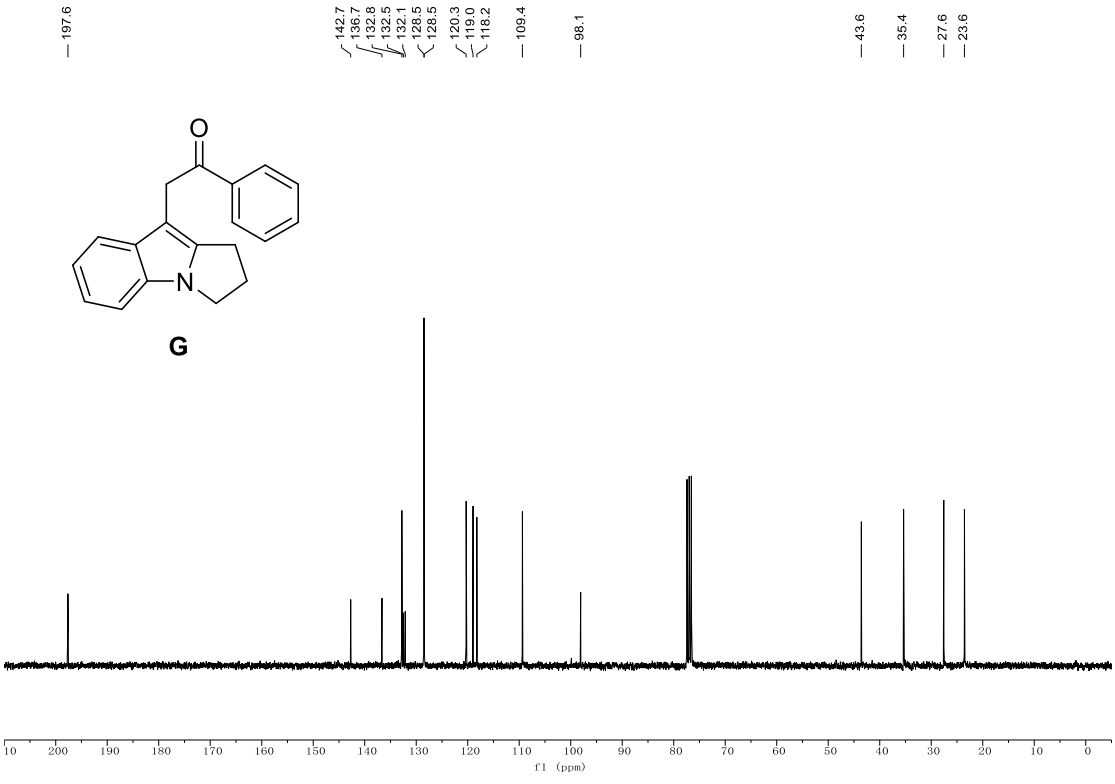
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **2am**:



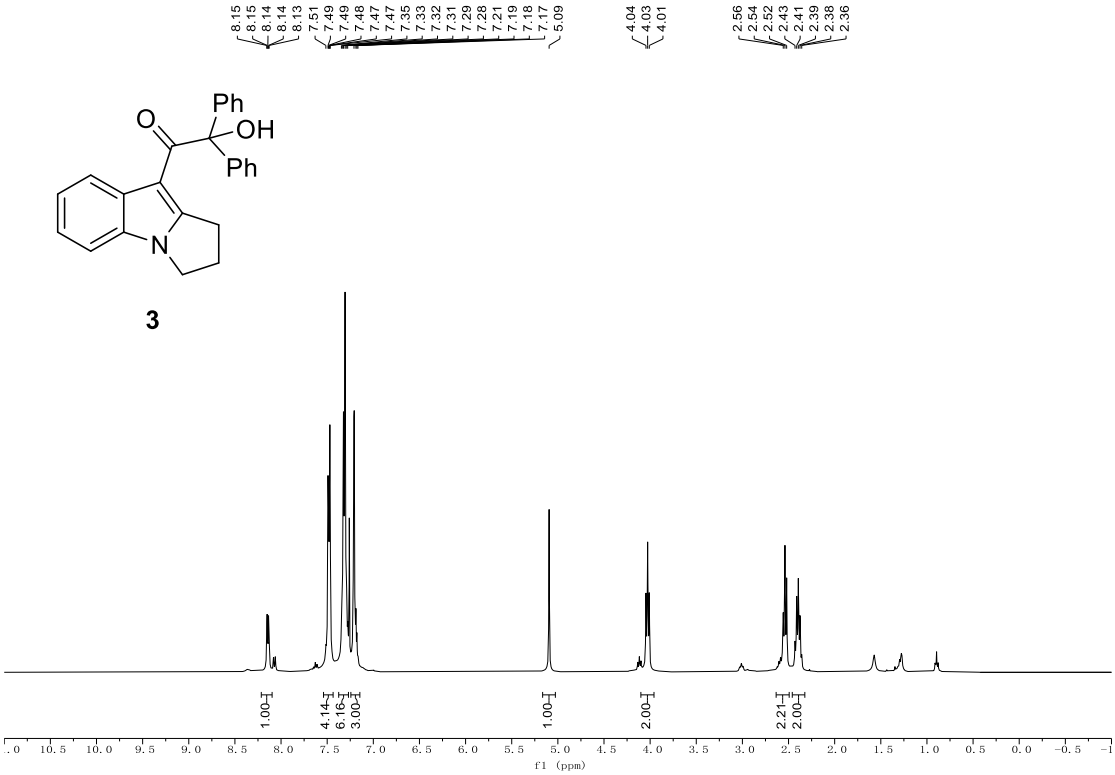
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **G**:



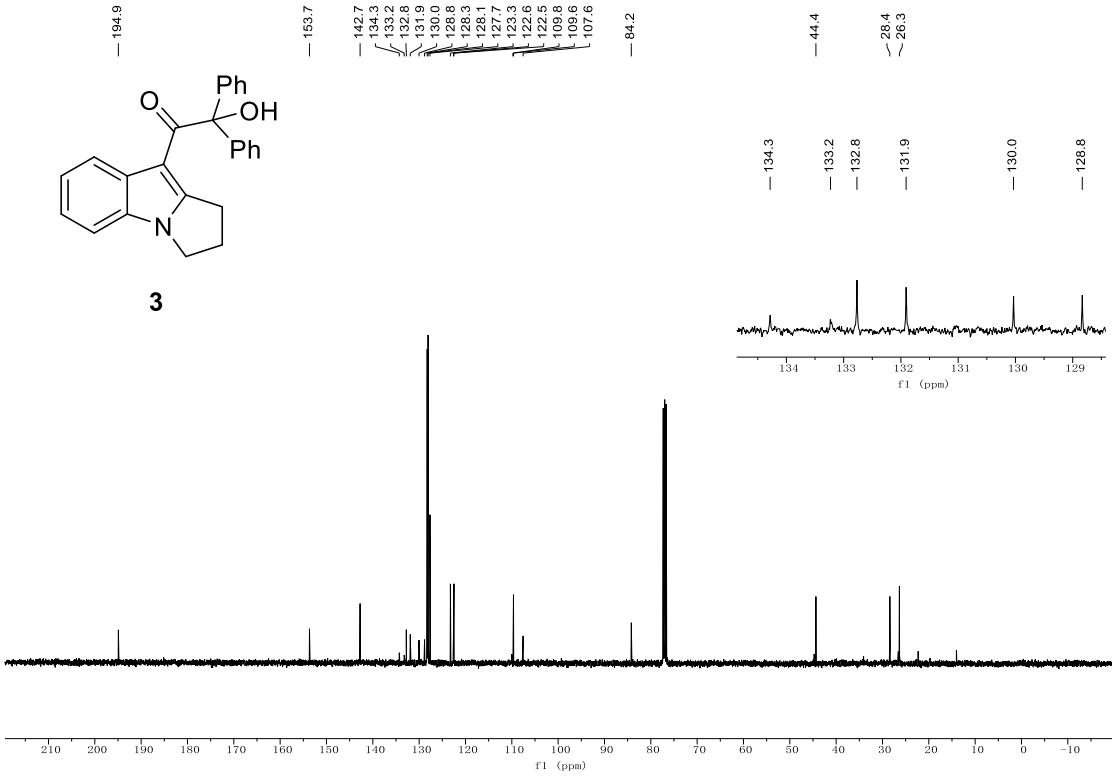
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **G**:



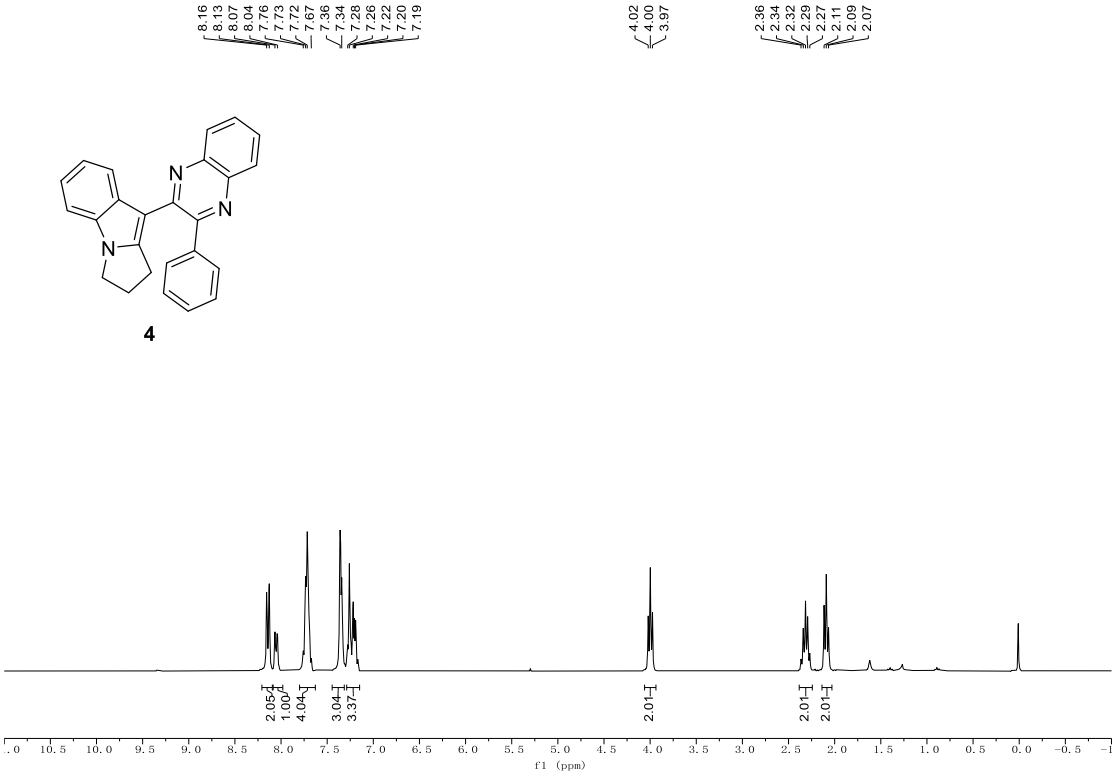
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3**:



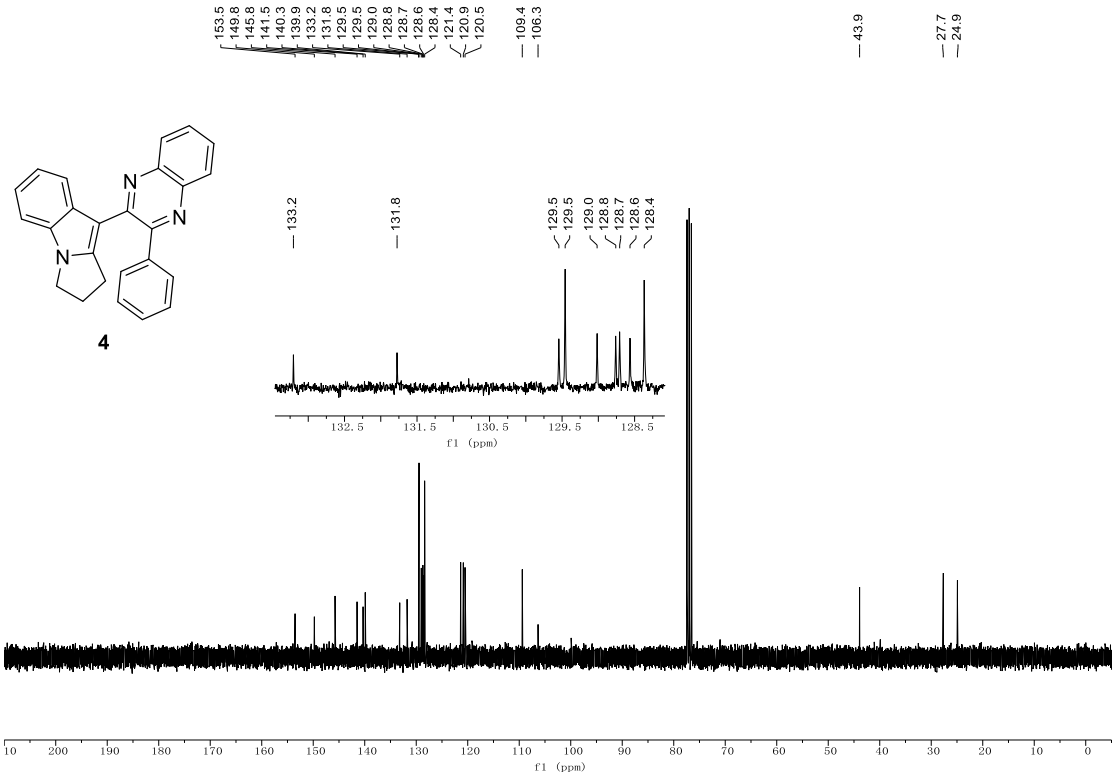
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3**:



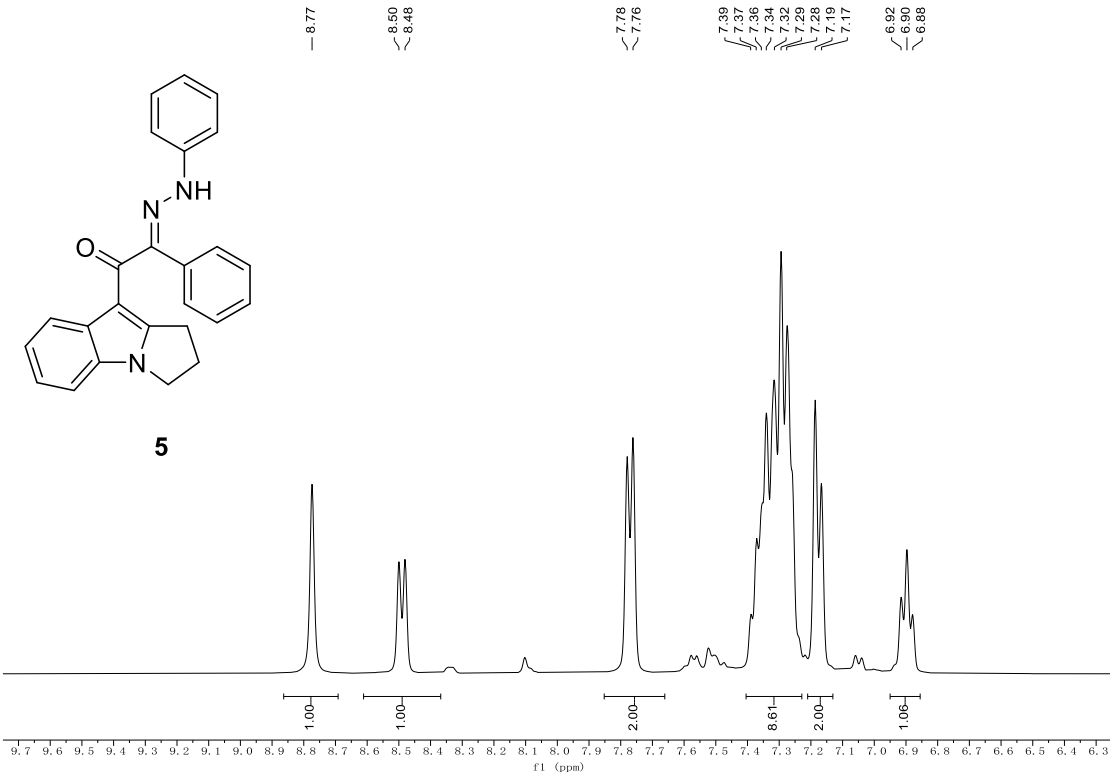
^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **4**:



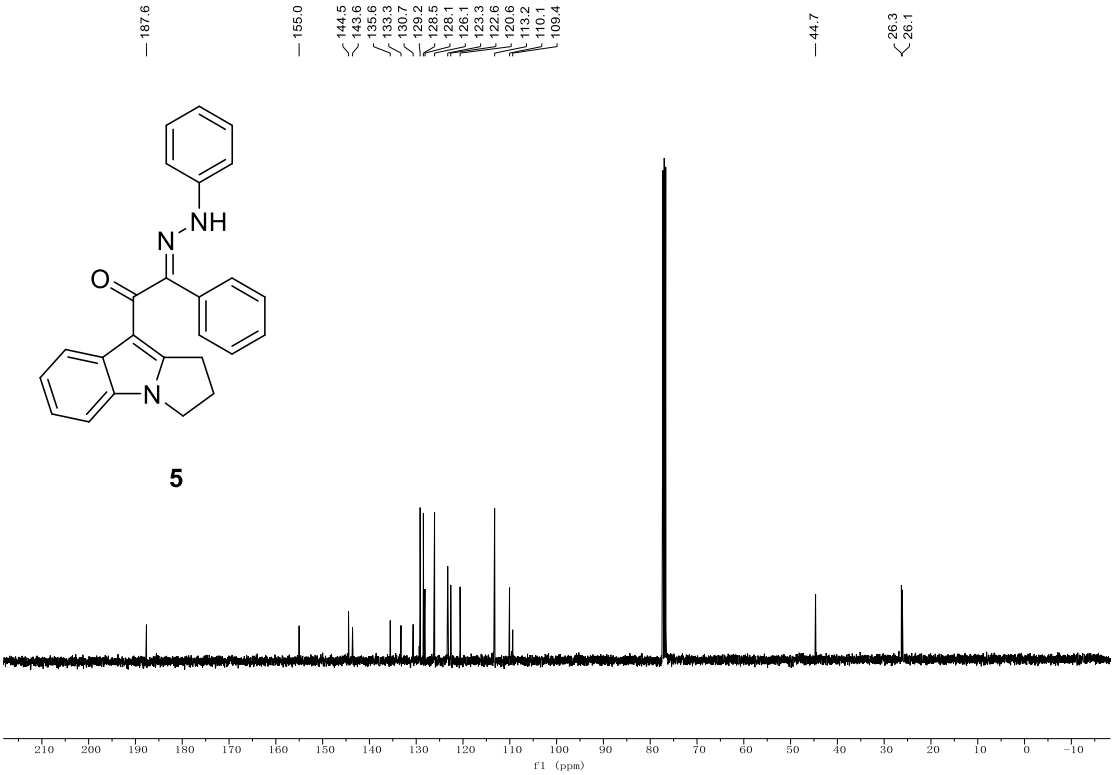
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **4**:



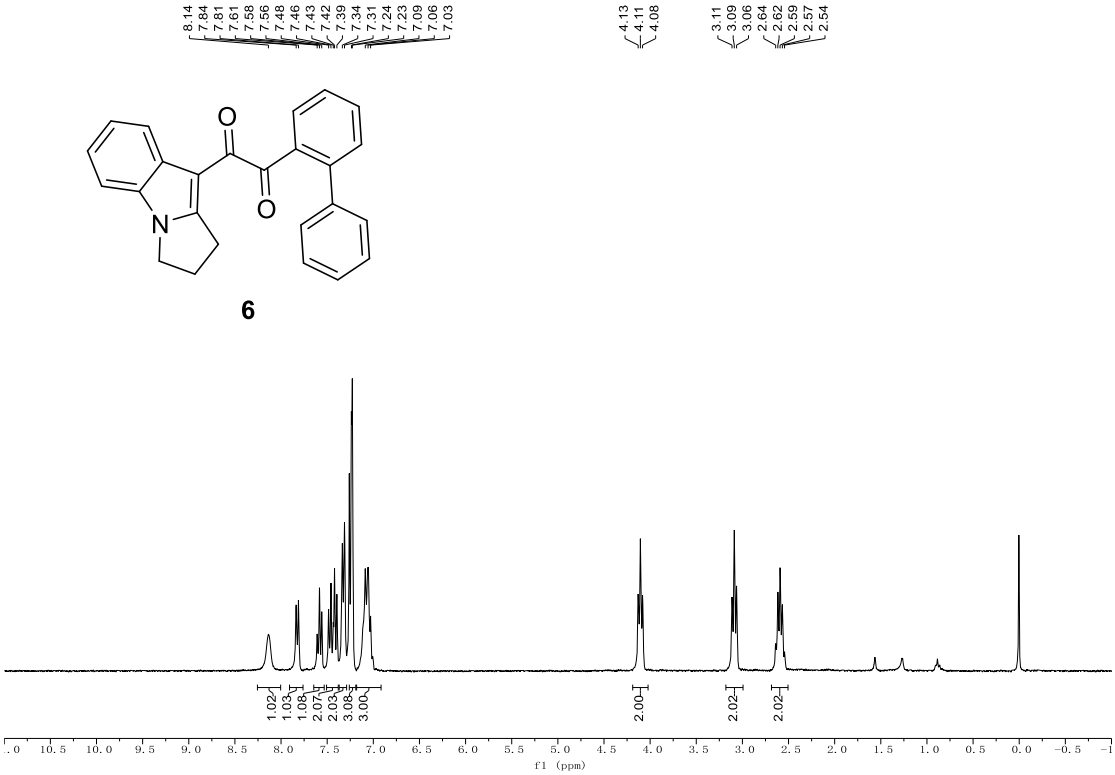
、^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5**:



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5**:



^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **6**:



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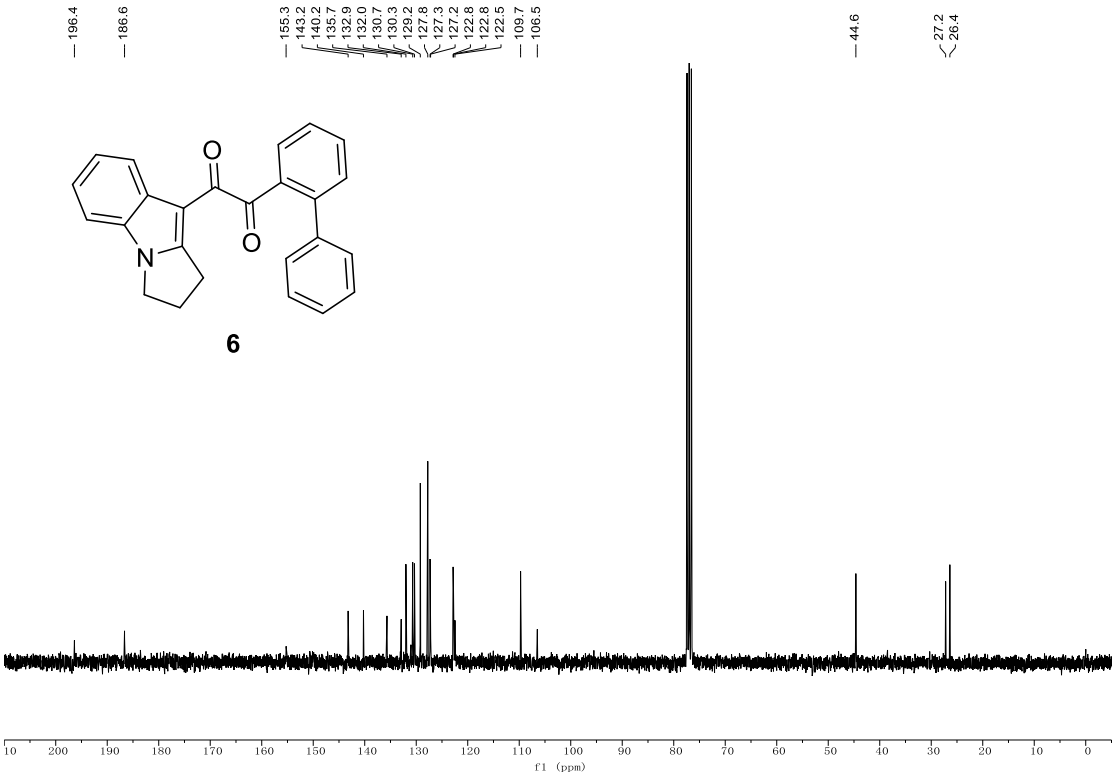
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) spectra of compound **6**:



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