Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Ru-catalyzed casecade reaction of α,ω-alkynoic acids and arylethylamines towards the synthesis of aryl-fused heterocycles

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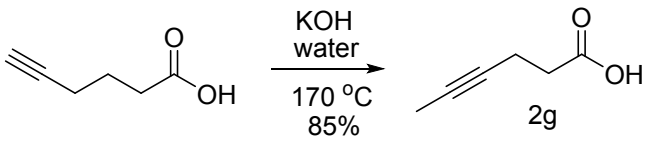
General Experimental

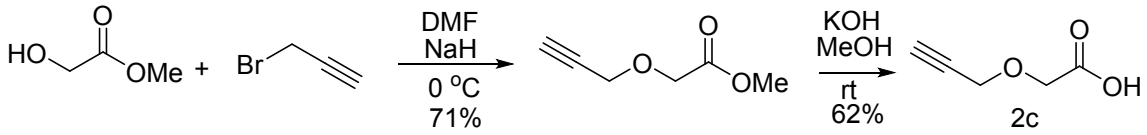
The chemicals and reagents were purchased from Acros, Alfa Aesar, and National Chemical Reagent Group Co. Ltd., P. R. China, and used without further purification. Anhydrous solvents (THF, MeOH, DMF, DCM, and CH_3CN) used in the reactions were dried and freshly distilled before use. Petroleum ether (PE) used had a boiling range of 60−90 °C. All the reactions were carried out under Ar atmosphere, unless otherwise stated else. Oxygen and/or moisture sensitive solids and liquids were transferred appropriately. Concentration of solutions in *vacuo* was accomplished using a rotary evaporator fitted with a water aspirator. Residual solvents were removed under high vacuum (0.1 - 0.2 mm Hg). The progress of the reactions was monitored by TLC (silica-coated glass plates) and visualized under UV light, and by using iodine, ceric ammonium molybdate stain or phosphomolybdic acid. Melting points were measured on a SGW X-4 microscopy melting point apparatus without correction. ^{1}H NMR and ^{13}C NMR spectra were recorded either on a 400 MHz Varian Instrument at 25 °C or 600 MHz Bruker Instrument at 25 °C, using TMS as an internal standard, respectively. Multiplicity is tabulated as s for singlet, d for doublet, dd for doublet of doublet, t for triplet, and m for multiplet. Coupling constants (J) are reported in Hertz. ^{13}C NMR spectra were completely hetero-decoupled and measured at 150 MHz. HRMS spectra were recorded on Finnigan- Mat-95 mass spectrometer, equipped with ESI source.

Experimental Procedures

General Procedure for the Synthesis of Compounds 1e according to the literature. [1]

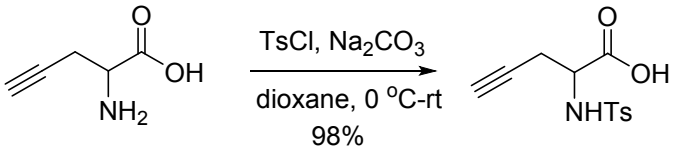


5-Hexynoic acid (2.00 g, 17.9 mmol, 1.0 eq.) was dissolved in 20 mL water and 16.2 g potassium hydroxide (288 mmol, 16 eq.) was added and the mixture was stirred at 170 °C for three hours. After cooling to room temperature and then to 0 °C, the solution was acidified with concentrated HCl solution to a pH value of 12 and the solution was extracted three times with 50 mL dichloromethane. The aqueous layer was acidified with concentrated HCl solution to a pH value of 1 (crystallization of the product starts) and extracted three times with 60 mL dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (PE: EA=4:1, R_f=0.25) to afford the title compound as colorless, crystalline solid in 85% yield (1.70 g, 15.2 mmol). All spectroscopic data were in agreement with those reported in the literature. [2]

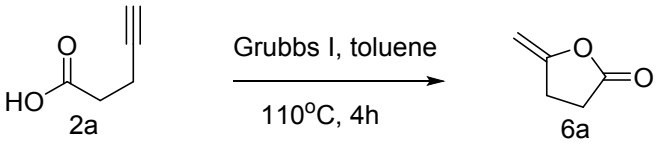


To a stirred solution of methyl 2-hydroxyacetate (9.0 g, 0.1 mol) in dry DMF (100 mL) was added NaH (4.80 g, 0.12 mol, 60% in mineral oil) in portions at 0 °C. After 30 min, propargyl bromide (4.80 g, 0.12 mmol, 80% in toluene) was added and the reaction mixture was allowed to stir for 5 h at room temperature. Water (200 mL) was added and the product was extracted with Et2O (4× 100 mL). The combined organic layer was washed with brine (100 mL) and dried (Na_2SO_4) and concentrated. The crude product was purified by flash column chromatography on silica gel (PE/DCM/EA= 4:1:0.1, R_f=0.24) to yield the title compound as a yellow oil (9.1 g, 71%).

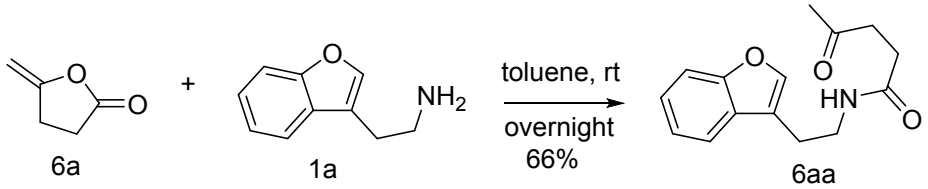
The ester was dissolved in methanol (100 mL), 100 mL of aqueous KOH 1M were added at 0 °C, and the mixture was vigorously stirred at room temperature until completion (TLC, 2 hours). The reaction mixture was washed with Et_2O and this organic layer was discharged. To the aqueous phase was added 5% HCl aqueous solution until pH=2 and was extracted with Et_2O (3x50 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent evaporated under reduced pressure. The desired acid was obtained as a yellow oil (5.1 g, 62%). All spectroscopic data were in agreement with those reported in the literature. [3]



To a solution of 2-amino-4-pentynoic acid (113 mg, 1.0 mmol) in saturated Na_2CO_3 at 0 °C and 4-toluenesulfonyl chloride (228 mg, 1.2 mmol) added in three portions over a period of 1 h. The slurry was then warmed to room temperature and allowed to stir for 48 h. The reaction was acidified with concentrated HCl solution to pH 2, and the product was isolated via filtration. The filter cake was washed with pH 2 buffer and dried in a vacuum oven at 60 °C for 16 h to obtain 265 mg of the product as a white crystalline solid in 99% yield. All spectroscopic data were in agreement with those reported in the literature. [4]



A solution of Grubbs' catalyst (0.032 mmol) in toluene (3 mL) was heated at 110 °C for 1 h. Alkynoic acids (3.20 mmol, 100 equiv.) was added. Subsequently, the reaction vial was sealed, and the reaction mixture was stirred at 110°C for 3h. Water (10 mL) was added and the product was extracted with Et2O (3× 10 mL). The combined organic phase was washed brine, dried with Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography on silica gel (PE/DCM= (2:1), R_f=0.34) to yield the title compound as a colourless liquid (0.32 g, 65%). [4] colorless liquid, **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.75 (q, *J* = 4.8, 1.8 Hz, 1H), 4.32 (q, *J* = 4.8, 1.8 Hz, 1H), 2.90–2.87 (m, 2H), 2.70–2.66 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.26, 154.98, 88.18, 27.39, 24.47. **ESI-MS** (*m*/*z*) 99.2 $[M+H]^+$.[5]



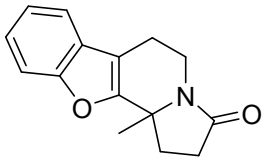
A solution of ester in toluene (3 ml) and amine was added. The mixture was stirred at room temperature for overnight. Water (10 mL) was added and the product was extracted with EA (3× 10 mL). The combined organic phase was washed brine, dried with Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography on silica gel (PE/EA= (1:1), R_f=0.20) to yield the title compound as a white solid (103mg, 66%). White solid (103 mg, yield 66%) mp 88–91 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.52–7.45 (m, 2H), 7.34–7.23 (m, 2H), 5.84 (s, 1H), 3.60–3.53 (m, 2H), 2.91–2.87 (m, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.38 (t, *J* = 6.4 Hz, 2H), 2.16 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.14, 171.34, 154.78, 141.32, 127.21, 123.80, 121.90, 118.87, 116.61, 110.96, 38.27, 37.90, 29.30, 29.26, 23.18. **HRMS** (*m*/*z*): calculated for $C_{15}H_{18}NO_2^+$ $[M+H]^+$: 260.1181, found: 260.1183.

General Procedure for the Synthesis of Compounds 3aa-3da, 3ha-3ia.

To a solution of alkynoic acids (1.2 mmol) in toluene (10 mL) were added Grubbs catalyst I (2 mmol %). After the mixture had been stirred for 1 h at 120°C, amine nucleophiles (1.0 mmol)

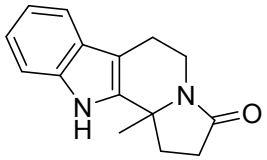
was added. Then CF_3CO_2H (1.1 mmol) was added into the reaction mixture. Subsequently, the reaction vial was sealed, and the mixture was stirred at 120 °C for 4 h. Then the reaction was cooled to ambient temperature, and saturated $NaHCO_3$ solution (10 ml) was added. The mixture obtained was extracted with ethyl acetate (3×20 ml). The combined organic phase was washed brine, dried with Na_2SO_4 and concentrated. Then the mixture was concentrated under reduced pressure, and the resulting reside was purified by flash column chromatography to afford the expected product. As for Compounds **3ea-3ga, 3ja-3la, 4ab-4ah**, the reaction time was required to be overnight.

11b-methyl-1,5,6,11b-tetrahydrobenzofuro[3,2-g] indolizin-3(2H)-one (3aa)



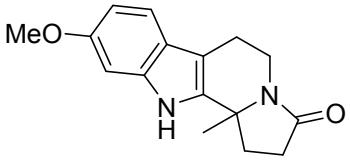
White solid (229mg, yield 95%) mp 100–102 °C. (PE/EA=1.5:1, R_f=0.23) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46–7.43 (m, 2H), 7.29–7.22 (m, 2H), 4.48-4.44 (m, 1H), 3.10–3.05 (m, 1H), 2.84–2.78 (m, 1H), 2.72–2.63 (m, 2H), 2.48–2.43 (m, 1H), 2.32–2.21 (m, 2H), 1.60 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.67, 154.89, 153.94, 126.96, 123.51, 122.23, 118.57, 110.70, 109.43, 59.17, 33.91, 30.68, 29.87, 23.41, 20.46. **HRMS** (*m*/*z*): calculated for $C_{15}H_{16}NO_2^+$ $[M+H]^+$: 242.1176, found: 242.1178.

11b-methyl-1,2,5,6,11,11b-hexahydro-3H-indolizino[8,7-b]indol-3-one (3ba)



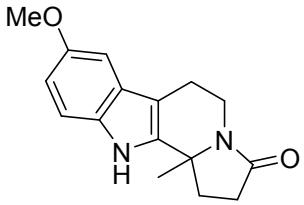
White solid (223 mg, yield 93%) mp 265–267 °C. (PE/EA=1:4, R_f=0.27) **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.07 (s, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.08–7.04 (m, 1H), 6.99–6.95 (m, 1H), 4.22–4.17 (m, 1H), 3.05–3.01 (m, 1H), 2.73–2.69 (m, 1H), 2.63–2.55 (m, 2H), 2.30–2.01 (m, 2H), 2.07–1.98 (m, 1H), 1.54 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 176.45, 143.53, 140.50, 130.84, 125.58, 123.16, 122.57, 115.71, 109.23, 63.46, 38.84, 37.17, 34.66, 29.52, 25.48. **ESI-MS** (*m*/*z*) 241.2 $[M+H]^+$. [6]

9-methoxy-11b-methyl-1,2,5,6,11,11b-hexahydro-3H-indolizino[8,7-b]indol-3-one(3ca)



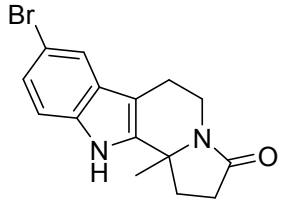
White solid (218 mg, yield 81%) mp 218–220 °C. (PE/EA=1:4, R_f=0.23) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.87 (s, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 6.81 (d, *J* = 2.3 Hz 1H), 6.62 (dd, *J* = 8.5, 2.3 Hz, 1H), 4.19–4.15 (m, 1H), 3.75 (s, 3H), 3.06–2.98 (m, 1H), 2.68–2.52 (m, 3H), 2.28–2.20 (m, 1H), 2.29–2.18 (m, 1H), 2.04–1.95 (m, 1H), 1.51 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 171.71, 155.28, 137.39, 136.49, 120.47, 118.34, 108.13, 104.32, 94.57, 58.69, 55.05, 34.08, 32.44, 29.92, 24.78, 20.75. **ESI-MS** (*m*/*z*) 271.2 $[M+H]^+$. [6]

8-methoxy-11b-methyl-1,2,5,6,11,11b-hexahydro-3H-indolizino[8,7-b]indol-3-one (3da)



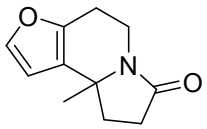
White solid (240mg, yield 89%) mp 190–191 °C. (PE/EA=1:4, R_f=0.24) **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.88 (s, 1H), 7.20 (d, J = 8.7 Hz, 1H), 6.88 (d, J = 2.5 Hz, 1H), 6.69 (dd, J = 8.7, 2.5 Hz, 1H), 4.22–4.17 (m, 1H), 3.74 (s, 3H), 3.07–2.99 (m, 1H), 2.70–2.56 (m, 3H), 2.30–2.20 (m, 2H), 2.07–1.97 (m, 1H), 1.52 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.18, 153.69, 137.96, 130.48, 126.50, 111.48, 111.10, 106.15, 100.03, 58.93, 55.35, 34.35, 32.20, 30.08, 24.85, 20.63. **ESI-MS** (*m*/*z*) 271.2 $[M+H]^+$. [6]

8-bromo-11b-methyl-1,2,5,6,11,11b-hexahydro-3H-indolizino[8,7-b]indol-3-one (3ea)



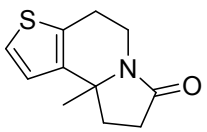
Pale yellow solid (179mg, yield 56%) mp 211–213 °C. (PE/EA=1:3, R_f=0.26) **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.31 (s, 1H), 7.57 (d, J = 2.0 Hz 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.17 (dd, J = 8.5, 1.9 Hz, 1H), 4.21–4.15 (m, 1H), 3.07–2.99 (m, 1H), 2.74–2.68 (m, 1H), 2.66–2.53 (m, 2H), 2.30–2.19 (m, 2H), 2.07–1.99 (m, 1H), 1.53 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.26, 138.50, 134.20, 127.87, 124.24, 120.57, 112.27, 111.85, 105.80, 58.90, 34.29, 32.09, 30.08, 24.79, 20.47. **HRMS** (*m*/*z*): calculated for $C_{15}H_{16}BrN_2O^+$ $[M+H]^+$: 319.0441, found: 319.0459.

9a-methyl-4,8,9,9a-tetrahydrofuro[2,3-g]indolizin-7(5H)-one (3fa)



Colorless oil (122mg, yield 64%). (PE/EA=1:1, R_f=0.26) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 (d, J = 1.9 Hz, 1H), 6.23 (d, J = 1.9 Hz, 1H), 4.44–4.40 (m, 1H), 3.06–3.00 (m, 1H), 2.81–2.74 (m, 1H), 2.66–2.59 (m, 2H), 2.44–2.39 (m, 1H), 2.21–2.17 (m, 1H), 2.04–1.98 (m, 1H), 1.44 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.48, 145.95, 141.20, 123.56, 105.93, 59.15, 33.23, 32.77, 30.04, 25.08, 22.69. **ESI-MS** (*m*/*z*) 192.2 $[M+H]^+$. [6]

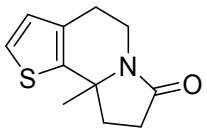
9a-methyl-4,8,9,9a-tetrahydrothieno[2,3-g]indolizin-7(5H)-one (3ga)



Pale yellow solid (117mg, yield 57%) mp 110–112 °C. (PE/EA=1:1, R_f=0.31) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.15 (d, J = 5.3, 1H), 6.80 (d, J = 5.2 Hz, 1H), 4.43–4.39 (m, 1H), 3.08–3.03 (m, 1H), 2.92–2.86 (m, 1H), 2.83–2.74 (m, 1H), 2.68–2.59 (m, 1H), 2.46–2.40 (m, 1H), 2.29–2.25 (m, 1H), 2.08–2.00 (m, 1H), 1.48 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.16, 140.58,

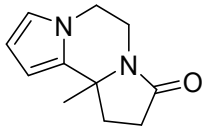
131.34, 123.23, 122.85, 60.56, 33.78, 33.19, 30.08, 25.56, 24.15. **ESI-MS** (*m*/*z*) 208.0 $[M+H]^+$. [6]

9a-methyl-4,8,9,9a-tetrahydrothieno[3,2-g]indolizin-7(5H)-one (3ha)



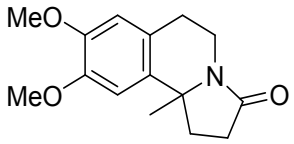
Pale yellow oil (184 mg, yield 88%). (PE/EA=1:1, R_f=0.30) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 4.9 Hz, 1H), 6.74 (d, *J* = 4.9 Hz, 1H), 4.38–4.33 (m, 1H), 3.07–2.99 (m, 1H), 2.80–2.58 (m, 3H), 2.48–2.41 (m, 1H), 2.33–2.25 (m, 1H), 2.20–2.11 (m, 1H), 1.57 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.13, 141.26, 131.68, 126.31, 122.40, 60.60, 34.86, 33.65, 30.20, 27.52, 24.86. **ESI-MS** (*m*/*z*) 208.0 $[M+H]^+$. [6]

10b-methyl-1,5,6,10b-tetrahydrodipyrrolo[1,2-a:2',1'-c]pyrazin-3(2H)-one (3ia)



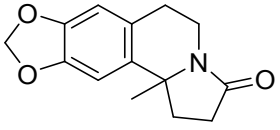
White solid (121mg, yield 70%) mp 108–110 °C. (PE/EA=1:1, R_f=0.26) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.52–6.49 (m, 1H), 6.19–6.15 (m, 1H), 5.94–5.89 (m, 1H), 4.40–4.34 (m, 1H), 3.99–3.85 (m, 2H), 3.34–3.24 (m, 1H), 2.66–2.55 (m, 1H), 2.46–2.19 (m, 3H), 1.53 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.57, 133.85, 118.15, 107.72, 101.75, 58.75, 43.53, 34.46, 33.96, 29.77, 27.03. **ESI-MS** (*m*/*z*) 191.2 $[M+H]^+$. [2]

8,9-dimethoxy-10b-methyl-1,5,6,10b-tetrahydropyrrolo[2,1-a]isoquinolin-3(2H)-one (3ka)



White solid (140mg, yield 54%) mp 138–140 °C**.** (PE/EA=1:1, R_f=0.33) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.57 (s, 2H), 4.34–4.25 (m, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.12–3.04 (m, 1H), 2.94–2.83 (m, 1H), 2.71–2.58 (m, 2H), 2.49–2.32 (m, 2H), 2.13–2.03 (m, 1H), 1.51 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.75, 147.44, 147.22, 134.07, 123.89, 110.94, 107.29, 60.35, 55.52, 55.26, 34.13, 33.45, 30.12, 27.52, 26.70. **ESI-MS** (*m*/*z*) 262.0 $[M+H]^+$. [6]

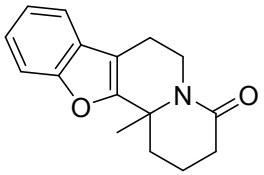
11b-methyl-1,5,6,11b-tetrahydro-[1,3]dioxolo[4,5-g]pyrrolo[2,1-a]isoquinolin-3(2H)-one (3la)



White solid (138mg, yield 45%) mp 133–135 °C. (PE/EA=1.5:1, R_f=0.20) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.58 (s, 1H), 6.54 (s, 1H), 5.92 (s, 2H), 4.29–4.23 (m, 1H), 3.10–3.04 (m, 1H), 2.90–2.80 (m, 1H), 2.68–2.57 (m, 2H), 2.48–2.30 (m, 2H), 2.08–1.99 (m, 1H), 1.48 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.10, 145.96, 145.68, 135.19, 124.88, 108.00, 104.28, 100.34,

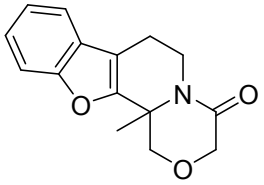
60.58, 34.18, 33.35, 30.11, 28.02, 26.77. **HRMS** (*m*/*z*): calculated for $C_{14}H_{16}NO_3^+$ $[M+H]^+$: 246.1125, found: 246.1125. [6]

12b-methyl-1,2,3,6,7,12b-hexahydro-4H-benzofuro[2,3-a]quinolizin-4-one (4ab)



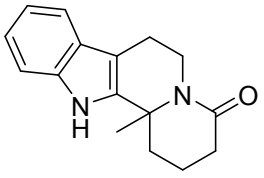
White solid (191mg, yield 75%) mp 103–104 °C. (PE/EA=1:1, R_f=0.33) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.29–7.20 (m, 2H), 5.11–5.05 (m, 1H), 3.02–2.94 (m, 1H), 2.82–2.73 (m, 1H), 2.67–2.52 (m, 2H), 2.45–2.40 (m, 2H), 2.00–1.91 (m, 1H), 1.90–1.79 (m, 2H), 1.65 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 155.60, 153.87, 127.08, 123.36, 122.15, 118.55, 110.68, 110.27, 56.59, 35.25, 32.98, 31.53, 23.74, 20.30, 15.90. **HRMS** (*m*/*z*): calculated for $C_{16}H_{18}NO_2^+$ $[M+H]^+$: 256.1159, found: 256.1165.

12b-methyl-1,6,7,12b-tetrahydrobenzofuro[2',3':3,4]pyrido[2,1-c][1,4]oxazin-4(3H)-one (4ac)



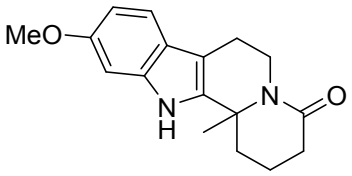
Colorless oil (134mg, yield 52%). (PE/EA=2:1, R_f=0.36) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50–7.46 (m, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.32–7.28 (m, 1H), 7.27–7.24 (m, 1H), 5.04–5.00 (m, 1H), 4.36 (d, *J* = 16.7 Hz, 1H), 4.30 (d, *J* = 11.6 Hz, 1H), 4.20 (d, *J* = 16.7 Hz, 1H), 3.64 (d, *J* = 11.6 Hz, 1H), 3.01–2.93 (m, 1H), 2.85–2.79 (m, 1H), 2.76–2.70 (m, 1H), 1.77 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.46, 154.25, 151.37, 126.64, 123.86, 122.39, 118.64, 111.95, 110.82, 71.27, 67.42, 55.83, 34.25, 21.65, 20.25. **HRMS** (*m*/*z*): calculated for $C_{15}H_{16}NO_3^+$ $[M+H]^+$: 258.1125, found: 258.1126.

12b-methyl-2,3,6,7,12,12b-hexahydroindolo[2,3-a]quinolizin-4(1H)-one (4bb)



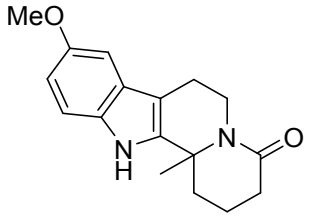
White solid (186mg, yield 73%) mp 260–263 °C. (PE/EA=1:4, R_f=0.30) **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.92 (s, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.09–7.03 (m, 1H), 7.00–6.93 (m, 1H), 4.88–4.83 (m, 1H), 2.97–2.89 (m, 1H), 2.69–2.52 (m, 2H), 2.44–2.22 (m, 3H), 2.00–1.85 (m, 1H), 1.76–1.69 (m, 2H), 1.60 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 172.52, 144.25, 140.54, 130.77, 125.51, 123.10, 122.44, 115.63, 110.37, 60.95, 40.13, 39.34, 36.34, 29.89, 25.58, 20.87. **ESI-MS** (*m*/*z*) 255.2 $[M+H]^+$. [6]

9-methoxy-12b-methyl-2,3,6,7,12,12b-hexahydroindolo[2,3-a]quinolizin-4(1H)-one(4cb)



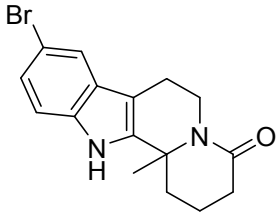
Creamy white solid (184 mg, yield 65 %). mp 226–227 °C. (PE/EA=1:4, R_f=0.23) **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.74 (s, 1H), 7.27–7.22 (m, 1H), 6.80 (s, 1H), 6.65–6.60 (m, 1H), 4.85–4.80 (m, 1H), 3.75 (s, 3H), 2.94–2.85 (m, 1H), 2.61–2.50 (m, 2H), 2.39–2.21 (m, 3H), 1.95–1.83 (m, 1H), 1.73–1.66 (m, 2H), 1.57 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 167.75, 155.23, 138.12, 136.52, 120.42, 118.24, 108.04, 105.44, 94.51, 56.12, 55.02, 35.35, 34.61, 31.60, 25.11, 20.85, 16.11. **ESI-MS** (*m*/*z*) 285.2 $[M+H]^+$. [6]

9-methoxy-12b-methyl-2,3,6,7,12,12b-hexahydroindolo[2,3-a]quinolizin-4(1H)-one (4db)



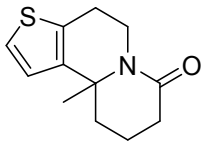
Creamy white solid (200 mg, yield 71 %). mp 199–200 °C. (PE/EA=1:4, R_f=0.27) **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.73 (s, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 6.88 (d, *J* = 2.5 Hz, 1H), 6.69 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.88–4.80 (m, 1H), 3.73 (s, 3H), 2.95–2.86 (m, 1H), 2.65–2.51 (m, 2H), 2.41–2.20 (m, 3H), 1.99–1.84 (m, 1H), 1.76–1.69 (m, 2H), 1.58 (s, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 172.50, 157.76, 144.96, 135.56, 131.08, 116.24, 115.34, 115.26, 110.27, 104.68, 104.59, 60.99, 59.95, 40.17, 39.37, 36.34, 29.94, 25.66, 20.89. **ESI-MS** (*m*/*z*) 285.2 $[M+H]^+$.[6]

9-bromo-12b-methyl-2,3,6,7,12,12b-hexahydroindolo[2,3-a]quinolizin-4(1H)-one (4eb)



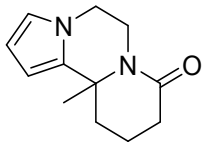
Creamy white solid (98 mg, yield 30 %). mp 229–232 °C. (PE/EA=1:3, R_f=0.26) **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.17 (s, 1H), 7.57 (s, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 8.5,, 1H), 4.85–4.80 (m, 1H), 2.95–2.87 (m, 1H), 2.68–2.62 (m, 1H), 2.57–2.51 (m, 1H), 2.41–2.20 (m, 3H), 1.93–1.85 (m, 1H), 1.76–1.68 (m, 2H), 1.59 (s, 3H). **^{13}C NMR** (150 MHz, CDCl3) δ 168.71, 139.18, 134.13, 127.89, 124.17, 120.52, 112.25, 111.73, 107.20, 56.04, 35.73, 34.83, 31.44, 25.41, 20.49, 16.11. **HRMS** (*m*/*z*): calculated for $C_{16}H_{18}BrN_2O^+$ $[M+H]^+$: 333.0597, found: 333.0612.

10a-methyl-4,5,8,9,10,10a-hexahydro-7H-thieno[2,3-a]quinolizin-7-one (4hb)



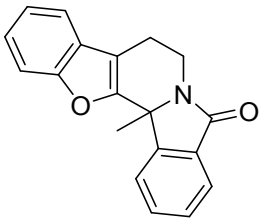
Pale yellow oil (123 mg, yield 56%). (PE/EA=2:1, R_f=0.23) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 5.1 Hz, 1H), 6.73 (d, *J* = 5.1 Hz, 1H), 4.99–4.92 (m, 1H), 2.99–2.90 (m, 1H), 2.78–2.68 (m, 1H), 2.65–2.49 (m, 2H), 2.43–2.33 (m, 1H), 2.24–2.17 (m, 1H), 2.01–1.93 (m, 2H), 1.83–1.78 (m, 1H), 1.65 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.50, 142.51, 132.94, 126.26, 122.21, 57.87, 38.44, 35.11, 31.51, 28.36, 24.97, 16.52. **ESI-MS** (*m*/*z*) 222.0 $[M+H]^+$. [6]

11a-methyl-5,6,9,10,11,11a-hexahydro-8H-pyrido[1,2-a]pyrrolo[2,1-c]pyrazin-8-one (4ib)



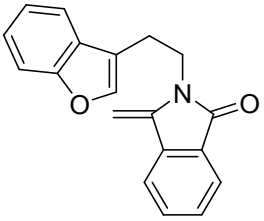
Colorless oil (84 mg, yield 41%). (PE/EA=1:1, R_f=0.23) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.54–6.48 (m, 1H), 6.17–6.11 (m, 1H), 5.88–5.83 (m, 1H), 5.04–4.95 (m, 1H), 3.99–3.86 (m, 2H), 3.26–3.18 (m, 1H), 2.58–2.49 (m, 1H), 2.43–2.34 (m, 1H), 2.29–2.20 (m, 1H), 2.07–1.81 (m, 3H), 1.60 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.71, 134.20, 117.83, 107.71, 101.38, 56.46, 43.77, 36.71, 34.98, 31.30, 27.87, 16.58. **ESI-MS** (*m*/*z*) 205.2 $[M+H]^+$. [2]

13b-methyl-8,13b-dihydrobenzofuro[2',3':3,4]pyrido[2,1-a]isoindol-5(7H)-one (4af)



White solid (93mg, yield 32%) mp 120–122 °C. (PE/EA=10:1, R_f=0.21) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 6.7 Hz, 1H), 7.87 (t, *J* = 6.7 Hz, 1H), 7.67–7.60 (m, 1H), 7.52–7.47 (m, 2H), 7.45–7.40 (m, 1H), 7.27–7.18 (m, 2H), 4.81–4.75 (m, 1H), 3.42–3.33 (m, 1H), 2.96–2.86 (m, 1H), 2.80–2.73 (m, 1H), 1.88 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.87, 154.10, 152.16, 146.92, 131.53, 130.19, 128.17, 126.79, 123.71, 123.40, 122.31, 122.27, 118.78, 110.77, 110.47, 61.52, 34.61, 24.26, 21.30. **HRMS** (*m*/*z*): calculated for $C_{19}H_{16}NO_2^+$ $[M+H]^+$: 290.1176, found: 290.1189.

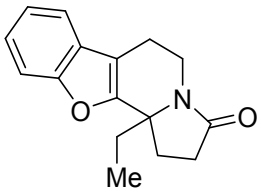
2-(2-(benzofuran-3-yl)ethyl)-3-methyleneisoindolin-1-one (4af')



Pale yellow solid (148mg, yield 51%) mp 127–129 °C. (PE/DCM=1:1, R_f=0.23) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.70–7.65 (m, 2H), 7.58 (td, *J* = 7.5, 1.1 Hz,

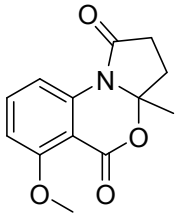
1H), 7.54–7.45 (m, 3H), 7.32–7.28 (m, 1H), 7.27–7.24 (m, 1H), 5.18 (d, *J* = 2.5 Hz, 1H), 4.83 (d, *J* = 2.6 Hz, 1H), 4.13–4.07 (m, 2H), 3.10–3.06 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.44, 154.69, 141.21, 141.09, 135.70, 131.35, 128.94, 128.65, 127.27, 123.78, 122.50, 121.93, 119.29, 118.79, 116.34, 110.96, 87.96, 38.46, 22.08. **HRMS** (*m*/*z*): calculated for $C_{19}H_{16}NO_2^+$ $[M+H]^+$: 290.1176, found: 290.1180.

11b-ethyl-1,5,6,11b-tetrahydrobenzofuro[3,2-g]indolizin-3(2H)-one (4ag)



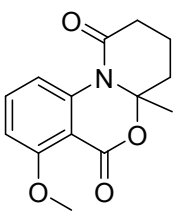
Colorless oil (84 mg, yield 12%). (PE/EA=2:1, R_f=0.24) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.1 Hz, 2H), 7.31–7.22 (m, 2H), 4.52–4.45 (m, 1H), 3.16–3.06 (m, 1H), 2.88–2.78 (m, 1H), 2.73–2.59 (m, 2H), 2.49–2.32 (m, 2H), 2.29–2.19 (m, 1H), 2.08–1.99 (m, 1H), 1.98–1.89 (m, 1H), 1.03 (t, *J* = 7.1, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.51, 154.91, 153.91, 126.94, 123.44, 122.19, 118.54, 110.70, 109.69, 62.52, 34.38, 30.64, 30.36, 27.56, 20.34, 7.79. **HRMS** (*m*/*z*): calculated for $C_{16}H_{17}NO_2Na^+$ $[M+Na]^+$: 278.1152, found: 278.1154.

6-methoxy-3a-methyl-3,3a-dihydro-5H-benzo[d]pyrrolo[2,1-b][1,3]oxazine-1,5(2H)-dione (4ma)



White solid (180mg, yield 79%) mp 111–112 °C. (PE/EA=1:1, R_f=0.27) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.58 (m, 2H), 6.93–6.87 (m, 1H), 3.99 (s, 3H), 2.81–2.64 (m, 2H), 2.63–2.53 (m, 1H), 2.43–2.34 (m, 1H), 1.69 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.31, 160.84, 158.21, 137.20, 135.39, 112.96, 108.59, 104.99, 93.92, 55.80, 31.56, 28.88, 23.77.
HRMS (*m*/*z*): calculated for $C_{13}H_{14}NO_4^+$ $[M+H]^+$: 248.0917, found: 248.0922.

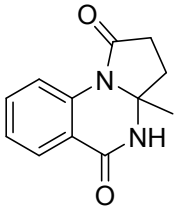
7-methoxy-4a-methyl-2,3,4,4a-tetrahydro-1H,6H-benzo[d]pyrido[2,1-b][1,3]oxazine-1,6-dione (4mb)



White solid (180mg, yield 79%) mp 121–122 °C. (PE/EA=1:1, R_f=0.25) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.55 (m, 1H), 7.34–7.26 (m, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 3.98 (s, 3H), 2.68–2.56 (m, 2H), 2.43–2.37 (m, 1H), 2.13–2.05 (m, 2H), 1.90–1.82 (m, 1H), 1.60 (s, 3H). ^{13}C NMR

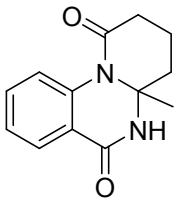
(150 MHz, $CDCl_3$) δ 168.78, 159.81, 158.91, 139.53, 133.81, 118.07, 109.27, 109.00, 90.79, 55.81, 35.36, 32.89, 25.85, 15.97. **HRMS** (*m*/*z*): calculated for $C_{14}H_{16}NO_4^+$ $[M+H]^+$: 262.1074, found: 262.1075.

3a-methyl-2,3,3a,4-tetrahydropyrrolo[1,2-a]quinazoline-1,5-dione (4na)



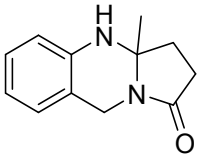
White solid (158 mg, yield 83%), mp 177–178 °C. (PE/EA=1:2, R_f=0.35) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H), 8.10–8.04 (m, 2H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.32–7.25 (m, 1H), 2.72–2.66 (m, 2H), 2.42–2.36 (m, 2H), 1.58 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.10, 162.71, 135.22, 133.24, 127.72, 124.46, 120.15, 118.89, 73.92, 32.35, 29.41, 26.36. **ESI-MS** (*m*/*z*) 217.2 $[M+H]^+$.[6]

4a-methyl-3,4,4a,5-tetrahydro-1H-pyrido[1,2-a]quinazoline-1,6(2H)-dione (4nb)



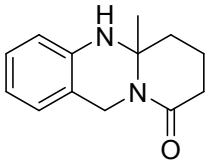
White solid (142 mg, yield 62%), mp 198–199 °C. (PE/EA=1:2, R_f=0.32) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.93 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.59–7.54 (m, 1H), 7.34–7.29 (m, 1H), 2.66–2.59 (m, 2H), 2.22–2.14 (m, 2H), 2.06–2.19 (m, 1H), 1.95–1.88 (m, 1H), 1.52 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.35, 163.57, 137.53, 131.93, 126.73, 125.71, 125.07, 122.55, 70.79, 35.62, 32.95, 28.02, 16.37. **ESI-MS** (*m*/*z*) 231.2 $[M+H]^+$.[6]

3a-methyl-3,3a,4,9-tetrahydropyrrolo[2,1-b]quinazolin-1(2H)-one (4oa)



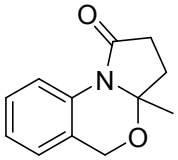
White solid (167mg, yield 83%) mp 141–142 °C. (PE/EA=3:2, R_f=0.32) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08–7.69 (m, 2H), 6.81–6.75 (m, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 5.02 (d, *J* = 16.8 Hz, 1H), 4.18 (d, *J* = 17.1 Hz, 1H), 3.38 (s, 1H), 2.63–2.43 (m, 2H), 2.13–2.04 (m, 2H), 1.54 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.62, 141.15, 126.96, 126.28, 118.65, 116.77, 115.81, 71.27, 37.95, 32.33, 28.93, 24.92. **ESI-MS** (*m*/*z*) 203.2 $[M+H]^+$. [6]

5a-methyl-5,5a,6,7,8,11-hexahydro-9H-pyrido[2,1-b]quinazolin-9-one (4ob)



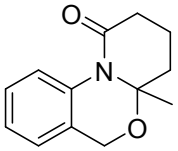
Colorless oil (113 mg, yield 60%). (PE/EA=2:1, R_f=0.32) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09–7.03 (m, 2H), 6.82–6.78 (m, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 5.48 (d, *J* = 17.3 Hz, 1H), 4.18 (d, *J* = 17.2 Hz, 1H), 3.17 (s, 1H), 2.52–2.39 (m, 2H), 2.03–1.95 (m, 3H), 1.80–1.74 (m, 1H), 1.53 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.46, 140.42, 126.78, 126.18, 118.68, 118.23, 115.49, 67.68, 39.16, 36.72, 32.25, 26.23, 16.18. **ESI-MS** (*m*/*z*) 217.2 $[M+H]^+$. [6]

3a-methyl-3,3a-dihydro-5H-benzo[d]pyrrolo[2,1-b][1,3]oxazin-1(2H)-one (4pa)



Colorless oil (77 mg, yield 38%). (PE/EA=5:1, R_f=0.24) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.31–7.24 (m, 1H), 7.16–7.03 (m, 2H), 5.03 (d, *J* = 15.8 Hz, 1H), 4.87 (d, *J* = 15.5 Hz, 1H), 2.68–2.53 (m, 2H), 2.31–2.12 (m, 2H), 1.52 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.74, 132.24, 126.95, 123.48, 123.45, 122.45, 119.92, 89.39, 62.23, 32.40, 29.58, 20.62. **ESI-MS** (*m*/*z*) 204.2 $[M+H]^+$. [6]

4a-methyl-2,3,4,4a-tetrahydro-1H,6H-benzo[d]pyrido[2,1-b][1,3]oxazin-1-one (4pb)



Colorless oil (43 mg, yield 20%). (PE/EA=5:1, R_f=0.22) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.26–7.20 (m, 1H), 7.15–7.10 (m, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 4.92 (s, 2H), 2.70–2.50 (m, 2H), 2.16–1.91 (m, 4H), 1.48 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.99, 133.96, 126.60, 125.78, 125.64, 124.25, 123.11, 85.92, 62.04, 36.36, 33.57, 23.03, 16.12. **ESI-MS** (*m*/*z*) 218.2 $[M+H]^+$. [6]

Reference

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5. K. Melis, T. Opstal, F. Verpoort, *Eur. J. Org. Chem.* 2002, 3779.
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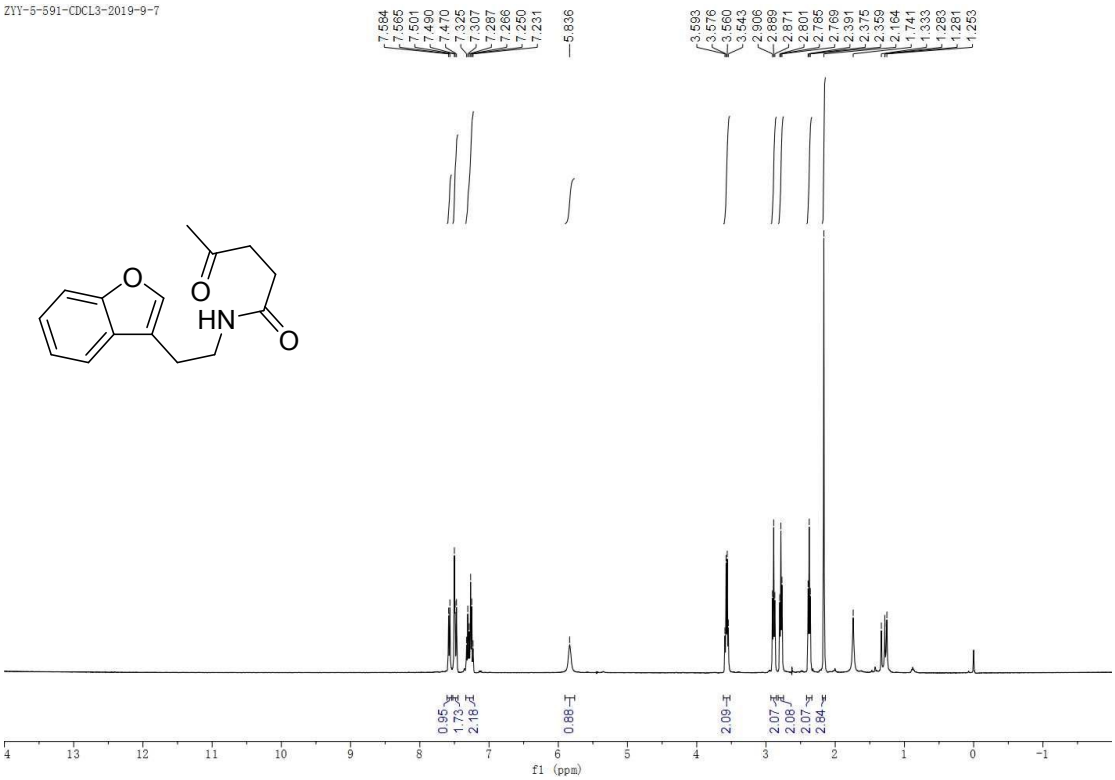
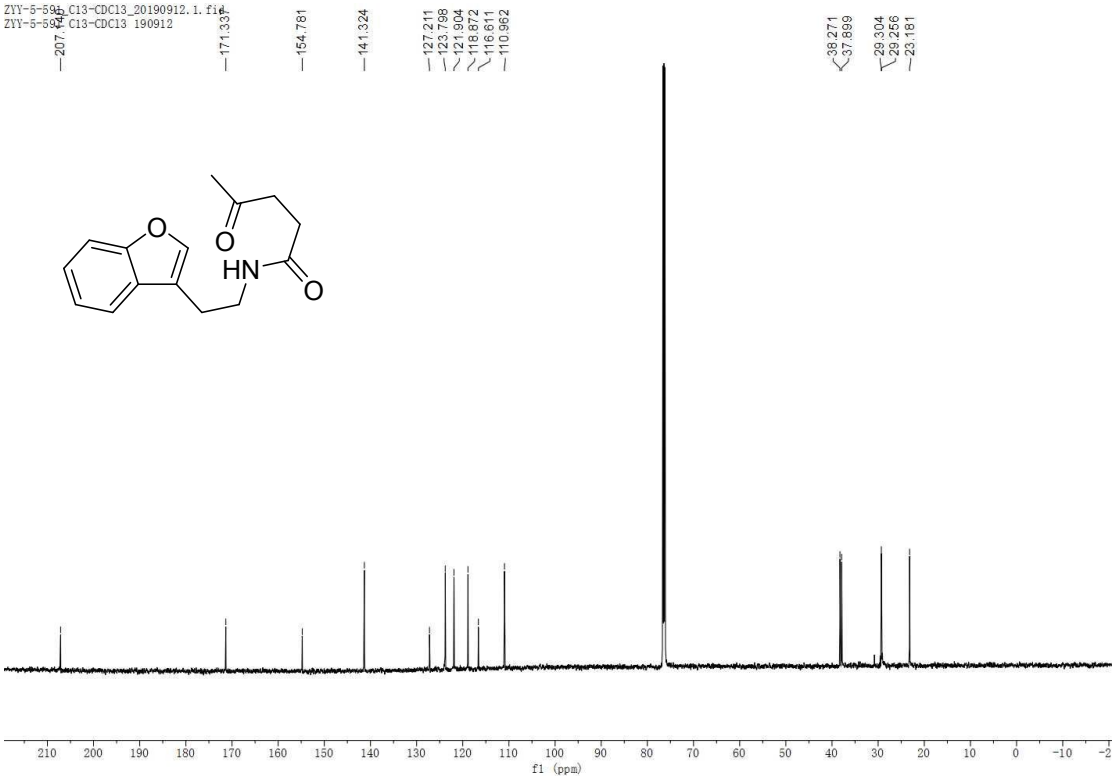
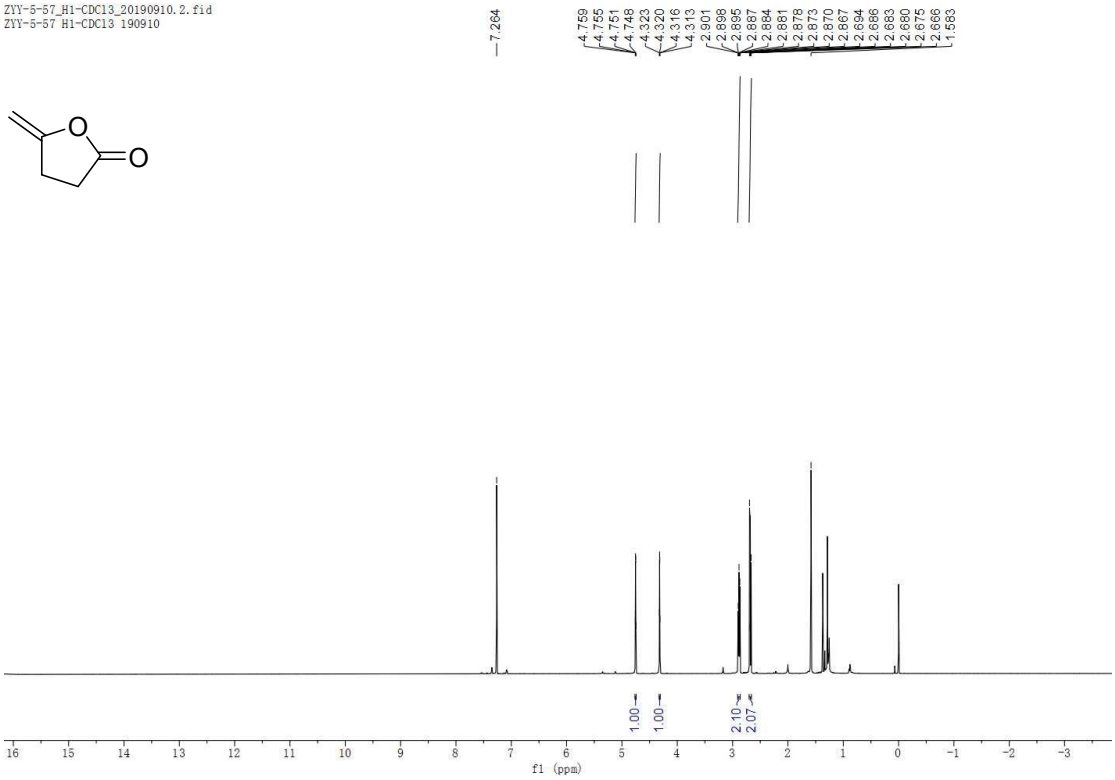
[1]H-NMR spectrum of compound 6aa (400 MHz, $CDCl_3$)



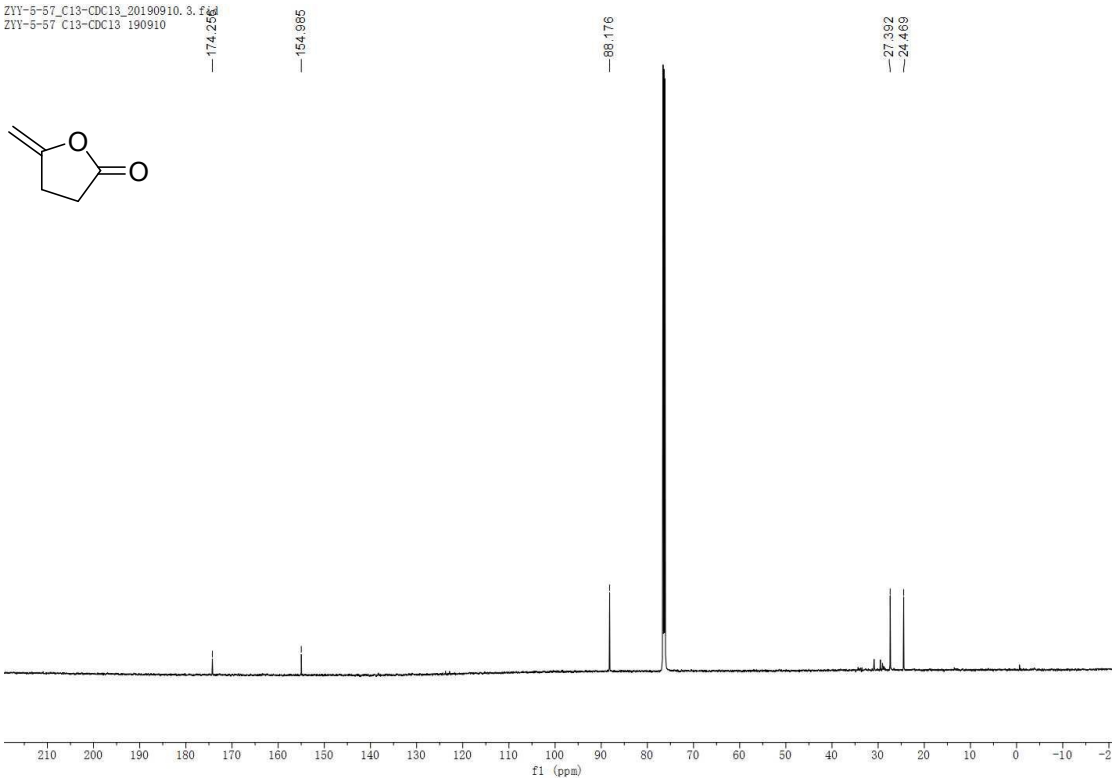
[13]C-NMR spectrum of compound 6aa (150 MHz, $CDCl_3$)



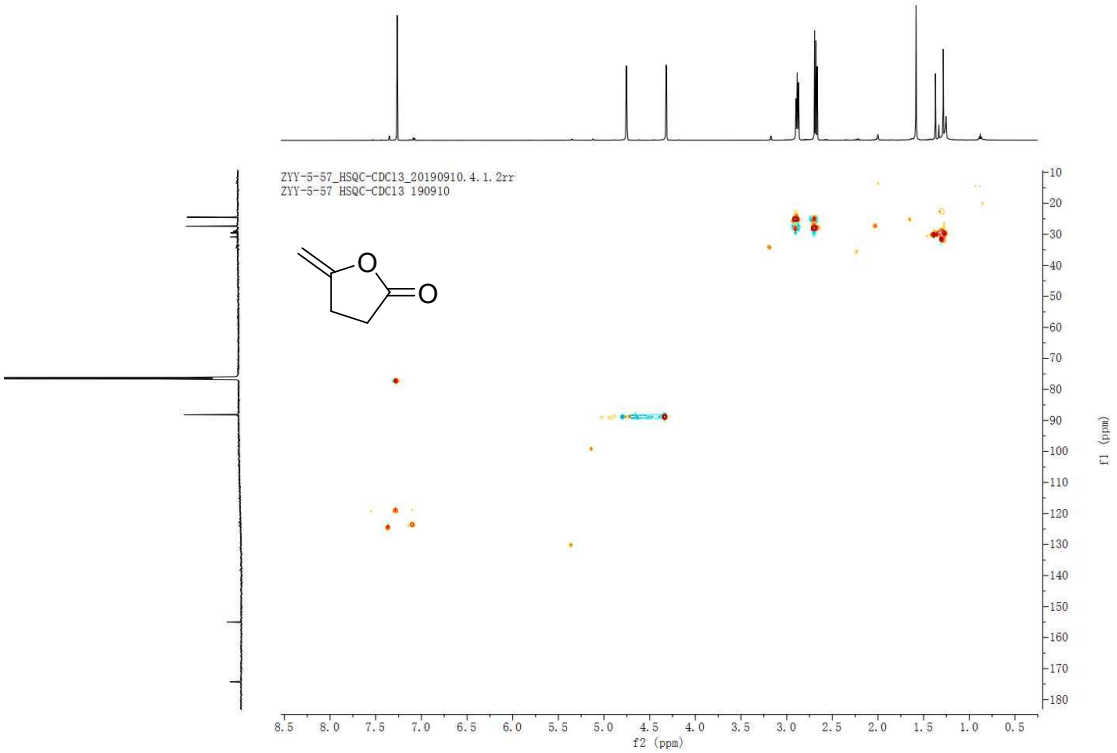
^{1}H-NMR spectrum of compound 6a (600 MHz, $CDCl_3$)



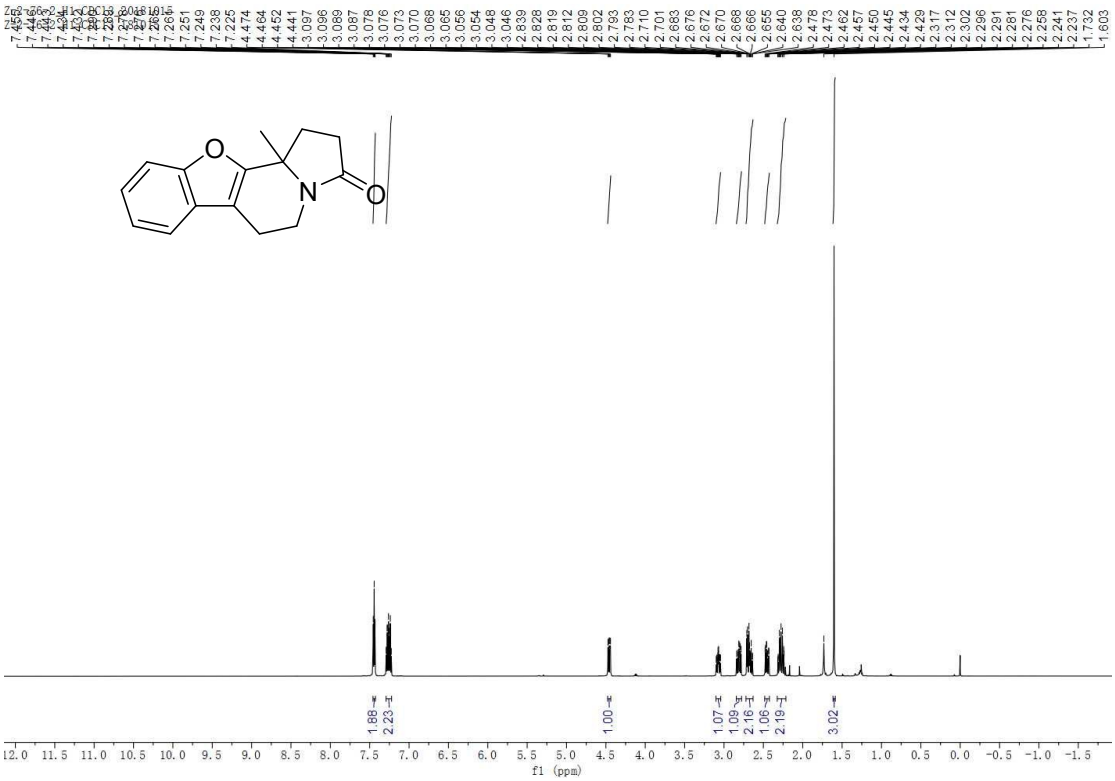
^{13}C-NMR spectrum of compound 6a (150 MHz, $CDCl_3$)



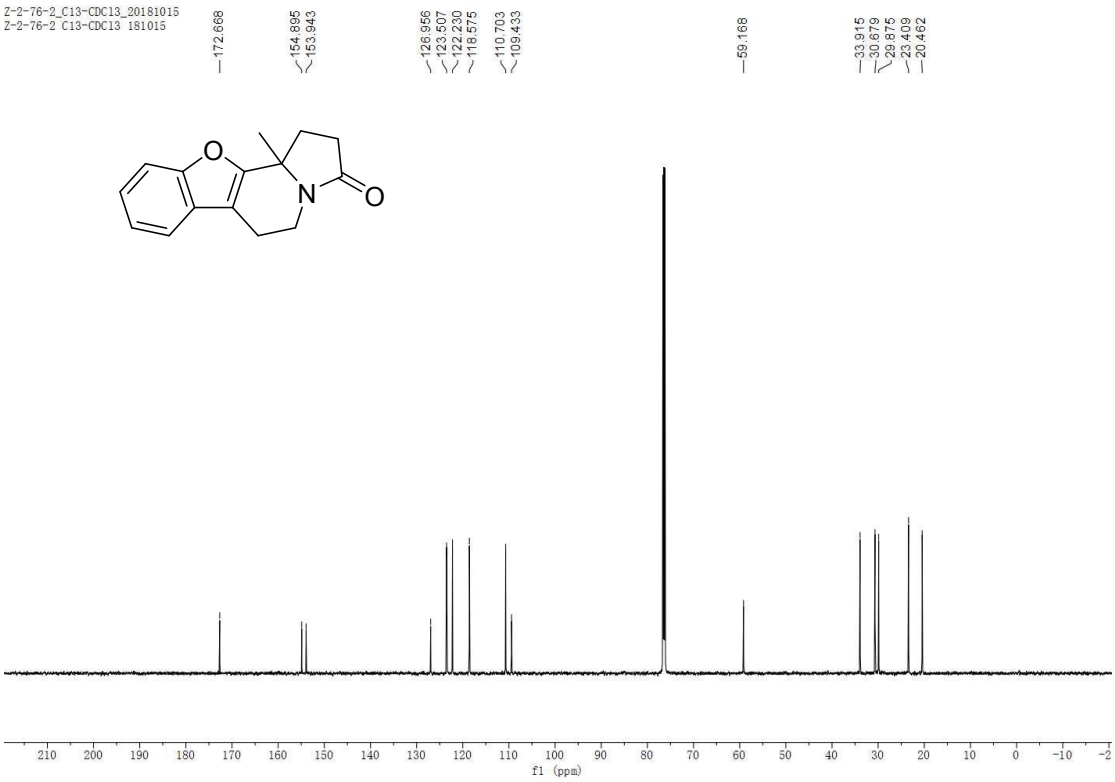
HSQC spectrum of compound 6a (600 MHz, $CDCl_3$)



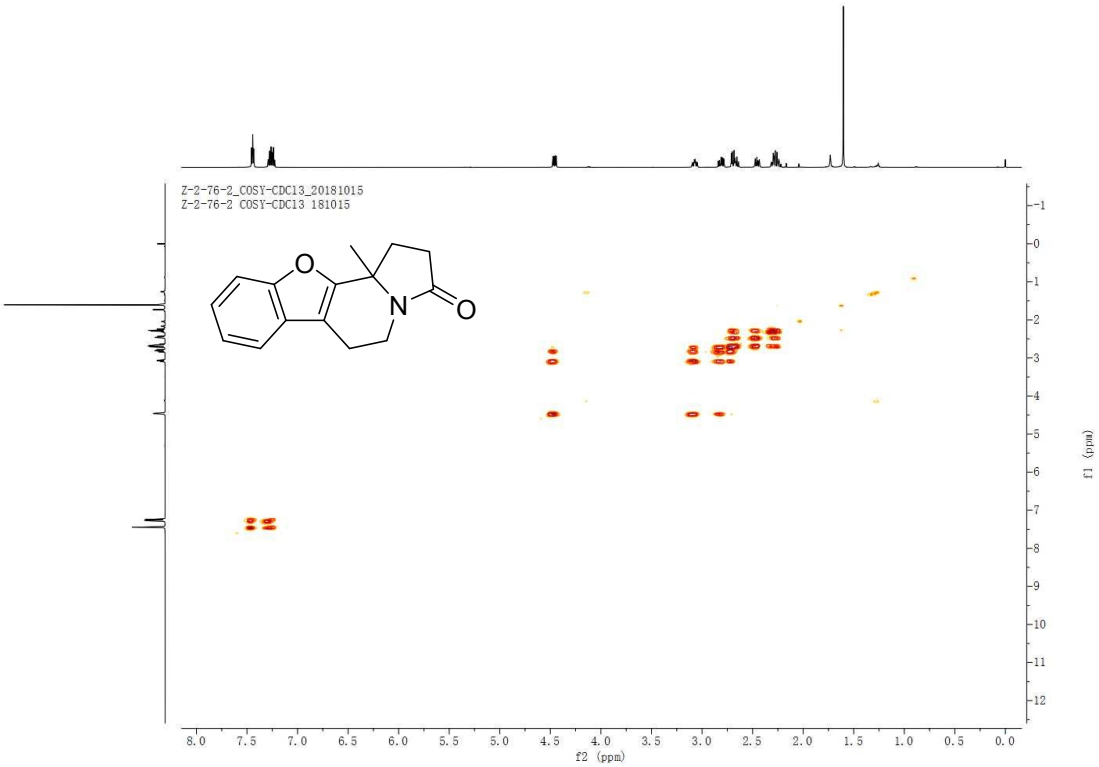
^{1}H NMR spectrum of compound 3aa (600 MHz, $CDCl_3$)



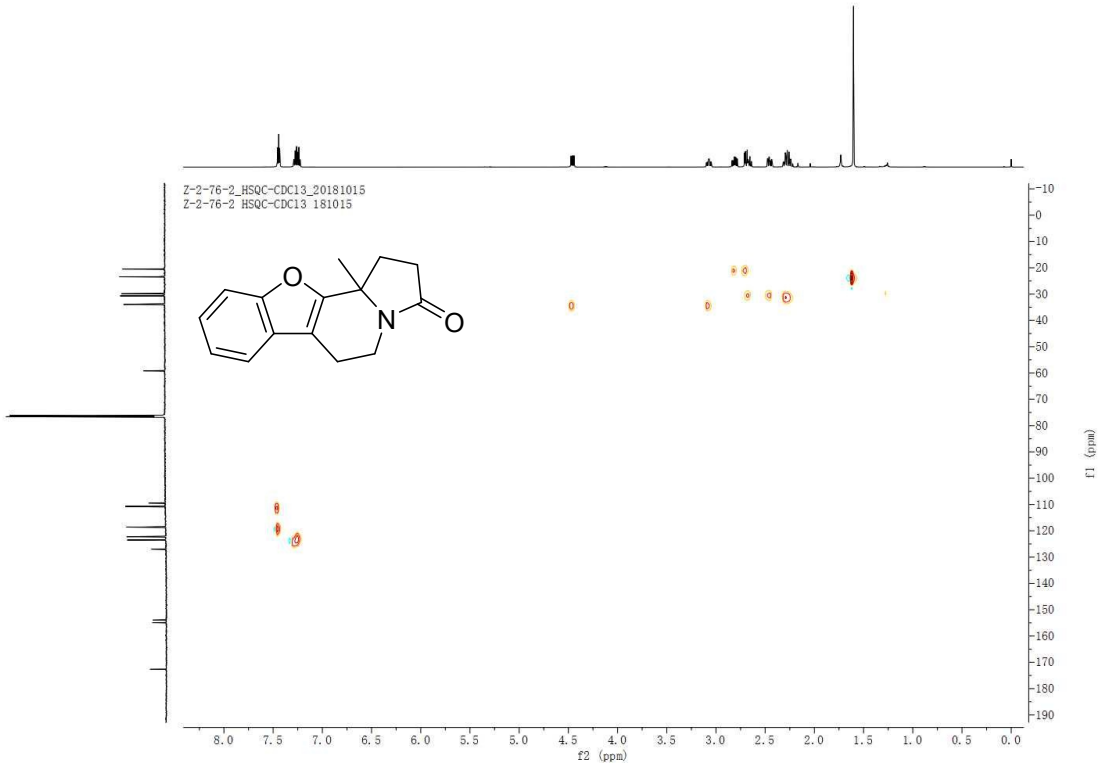
^{13}C-NMR spectrum of compound 3aa (150 MHz, $CDCl_3$)



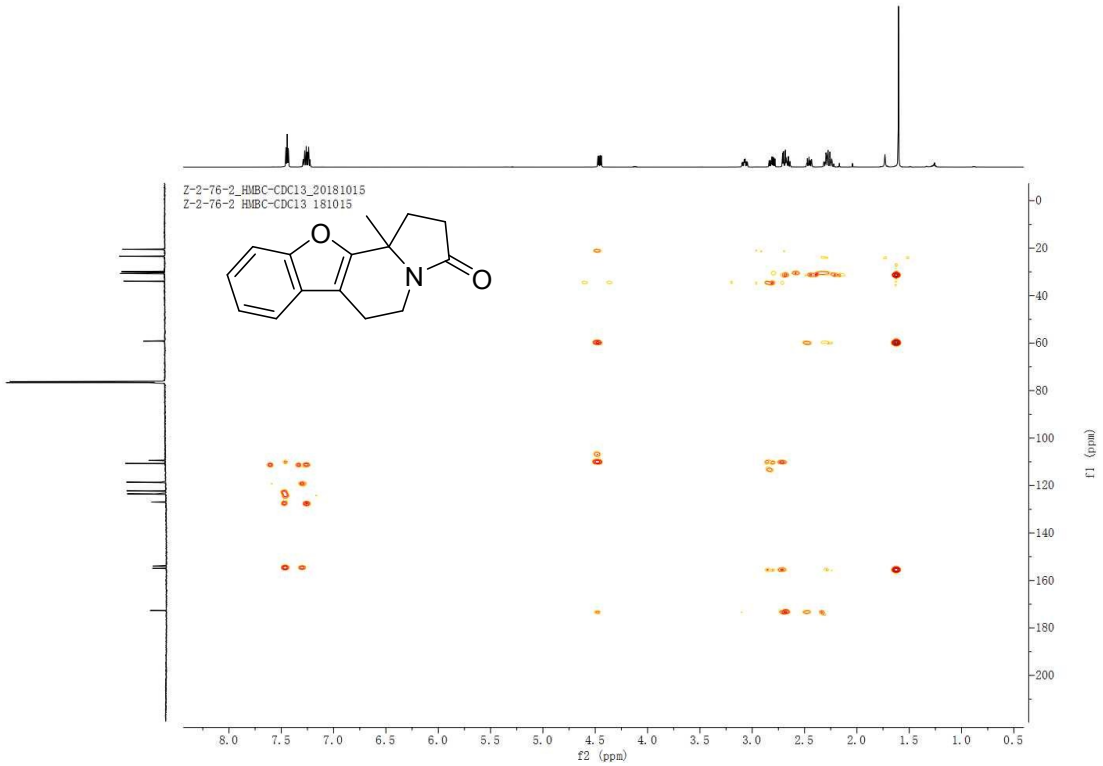
^{1}H-^{1}H COSY spectrum of compound 3aa (600 MHz, $CDCl_3$)



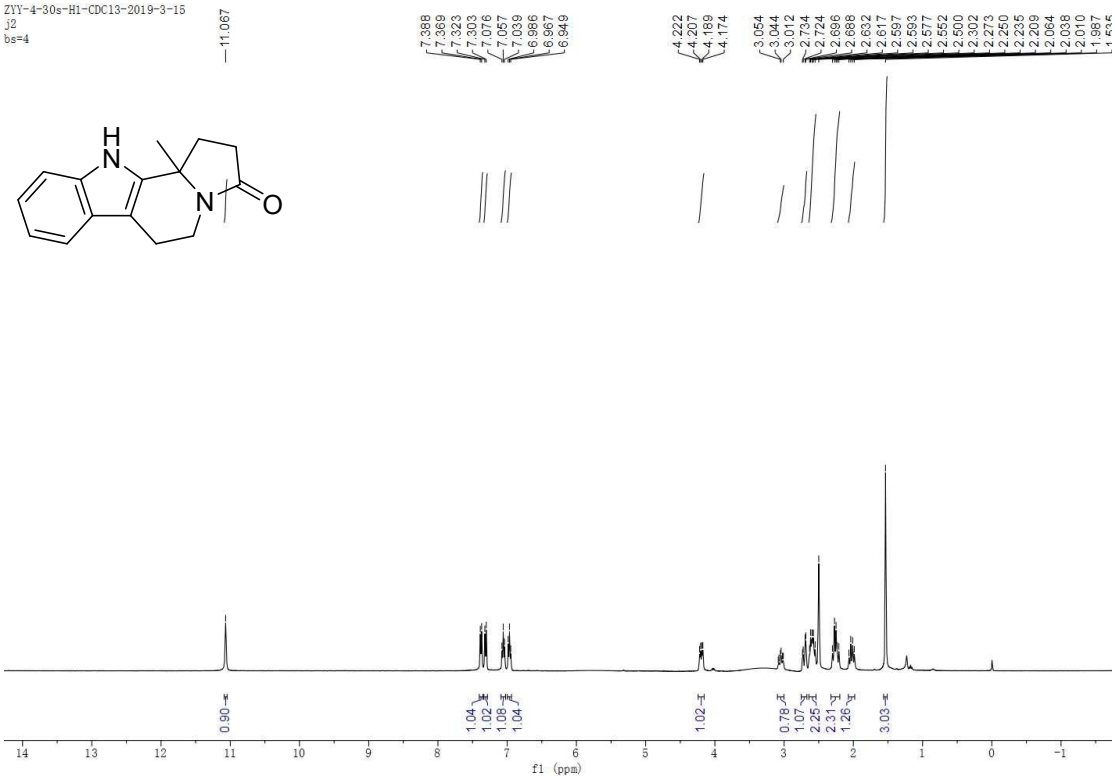
HSQC spectrum of compound 3aa (600 MHz, $CDCl_3$)



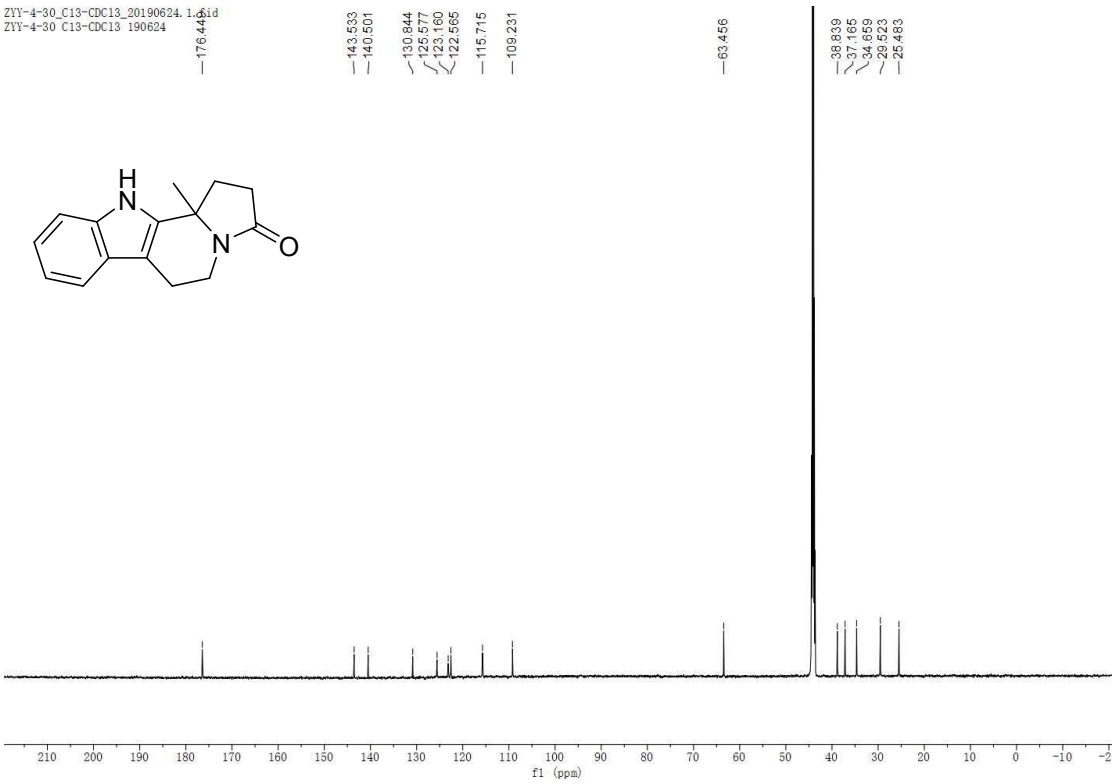
HMBC spectrum of compound 3aa (600 MHz, $CDCl_3$)



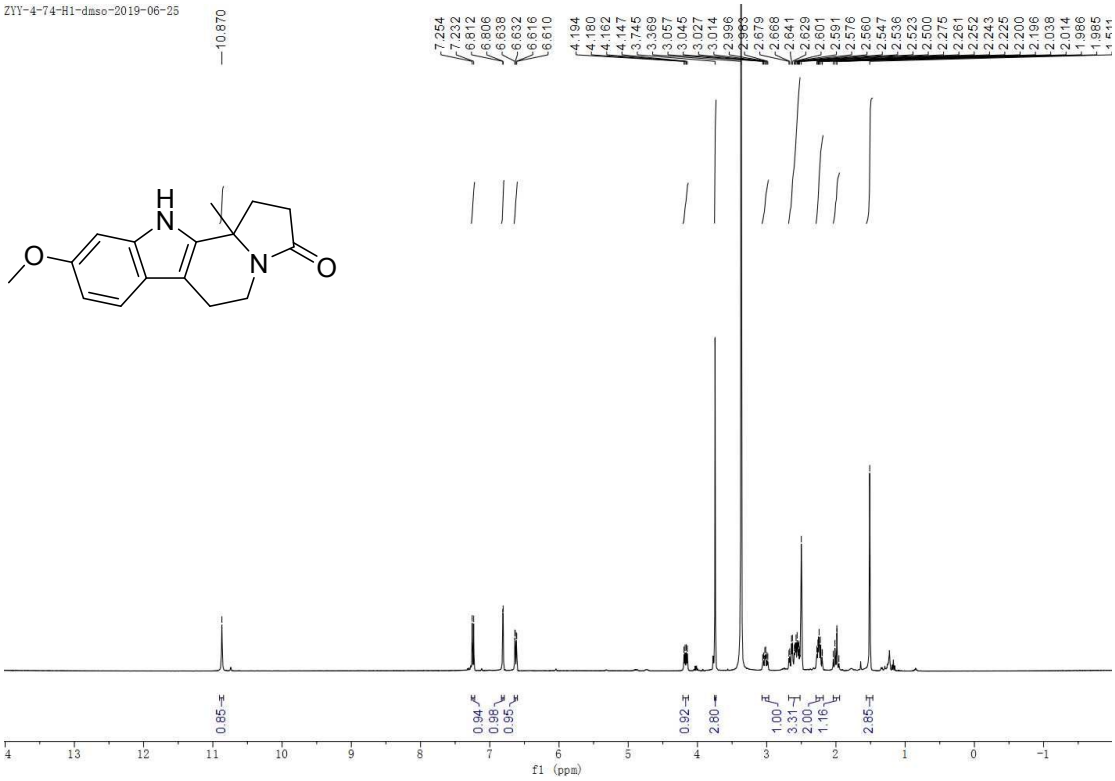
[1]H-NMR spectrum of compound 3ba (400 MHz, DMSO-d6)



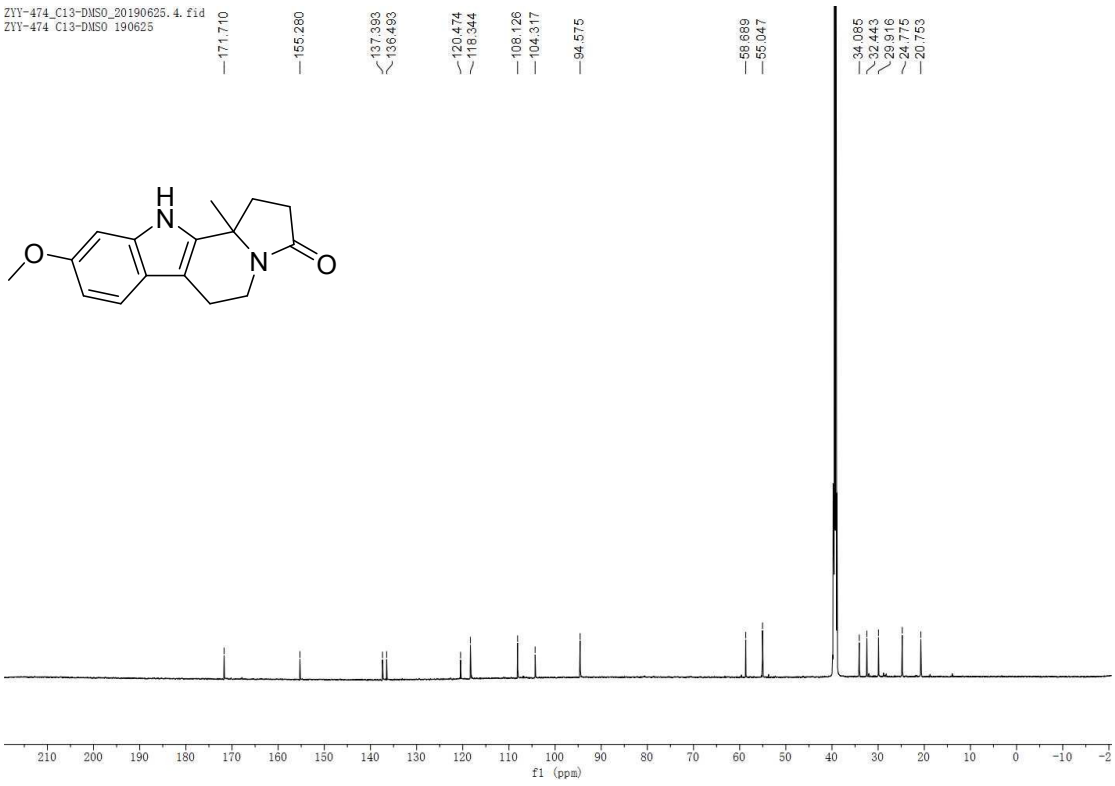
[13]C-NMR spectrum of compound 3ba (150 MHz, DMSO-d6)



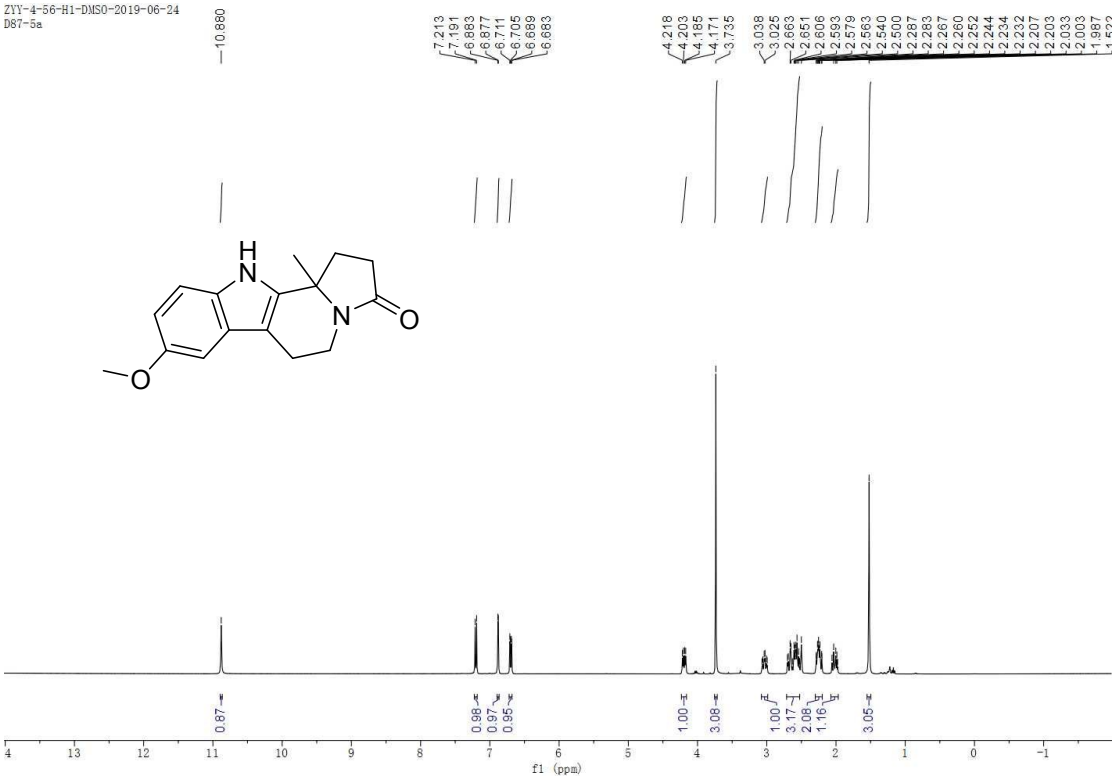
[1]H-NMR spectrum of compound 3ca (400 MHz, DMSO-d6)



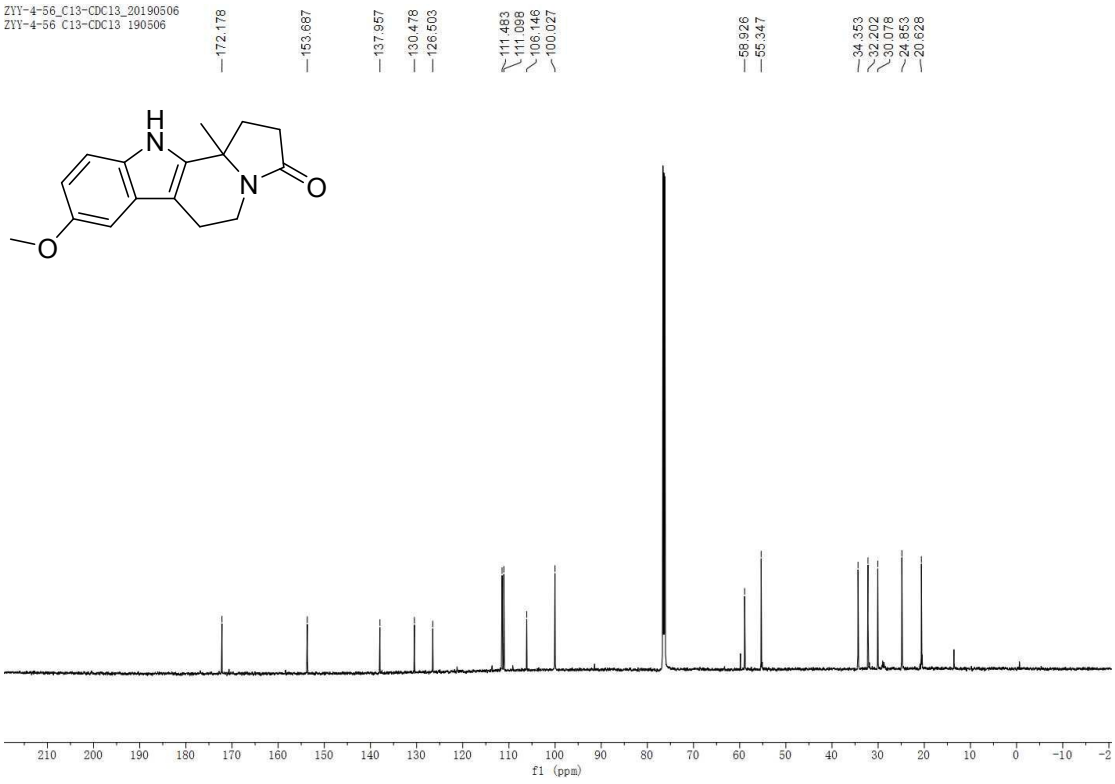
[13]C-NMR spectrum of compound 3ca (150 MHz, DMSO-d6)



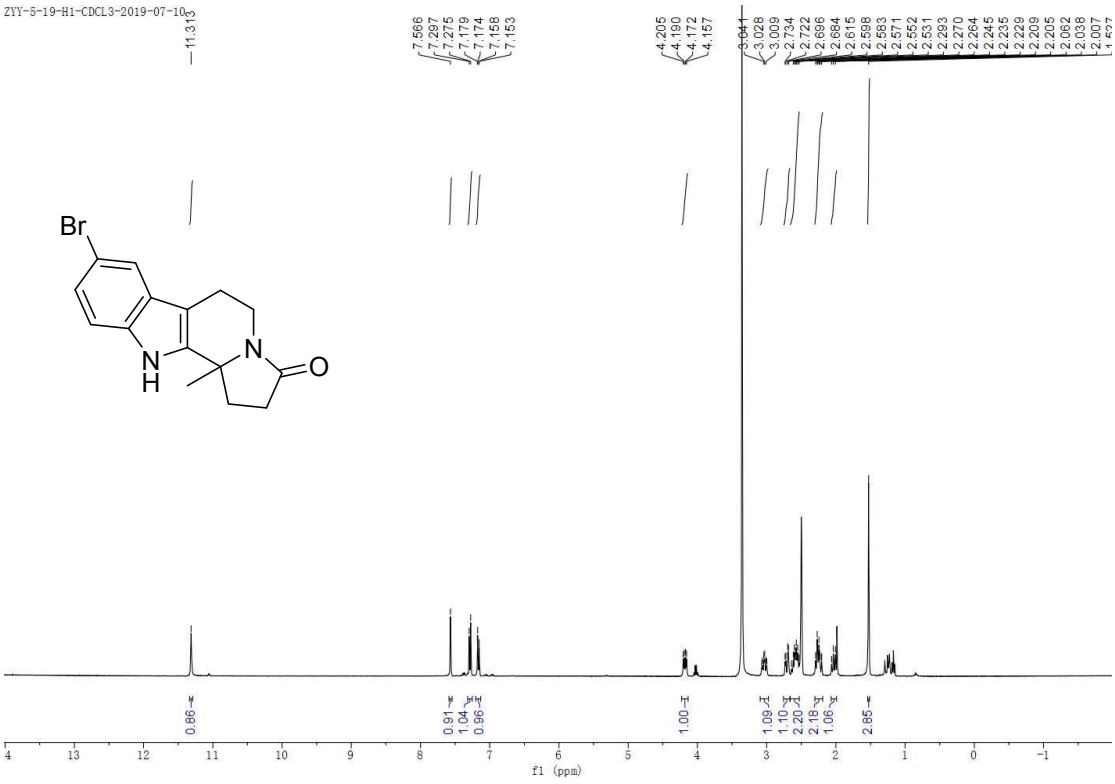
[1]H-NMR spectrum of compound 3da (400 MHz, $CDCl_3$)



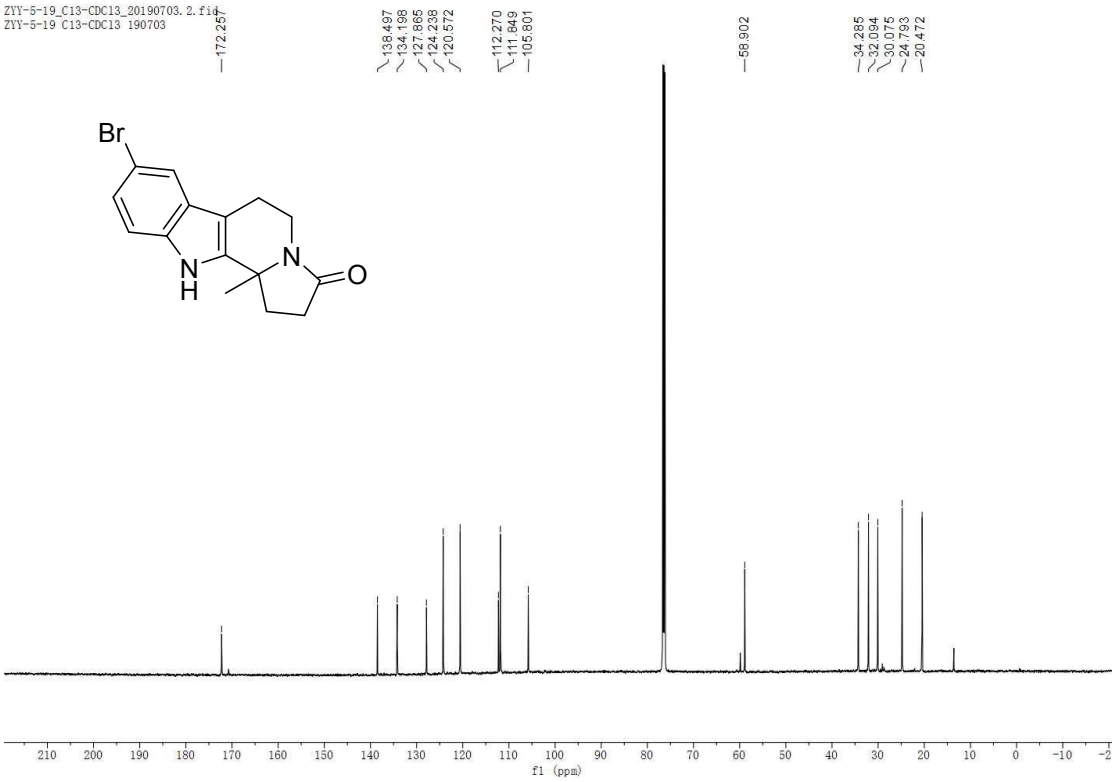
[13]C-NMR spectrum of compound 3da (150 MHz, $CDCl_3$)



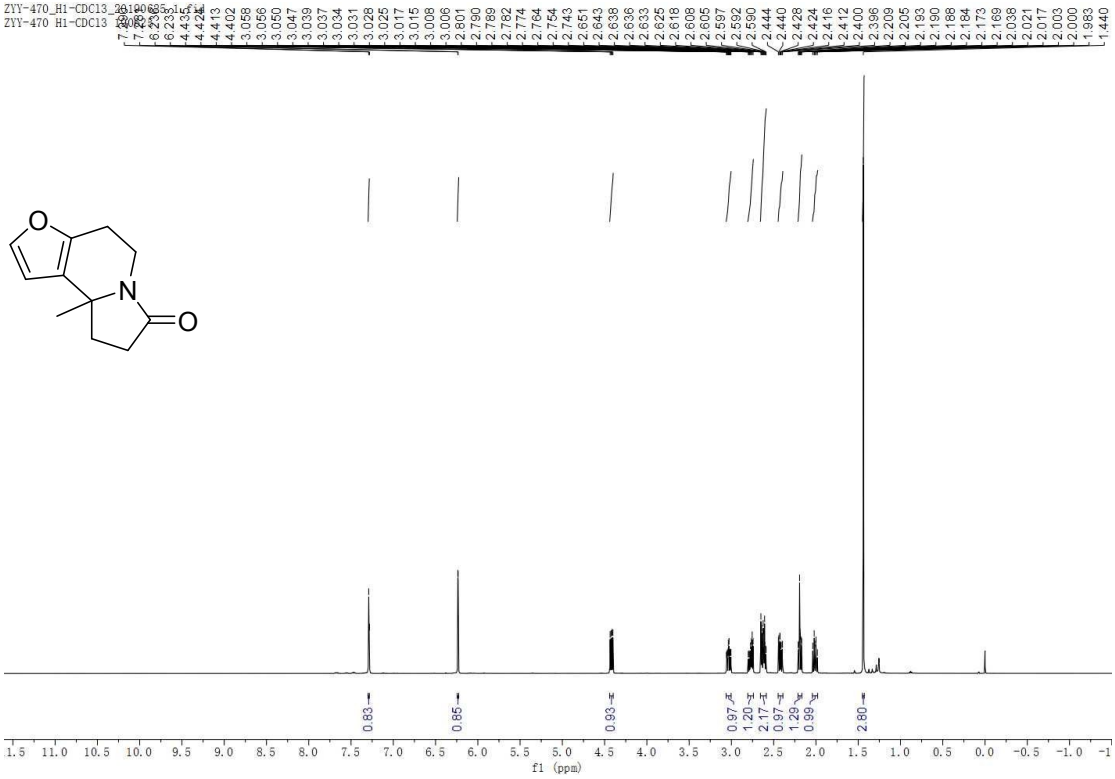
[1]H-NMR spectrum of compound 3ea (400 MHz, DMSO-d6)



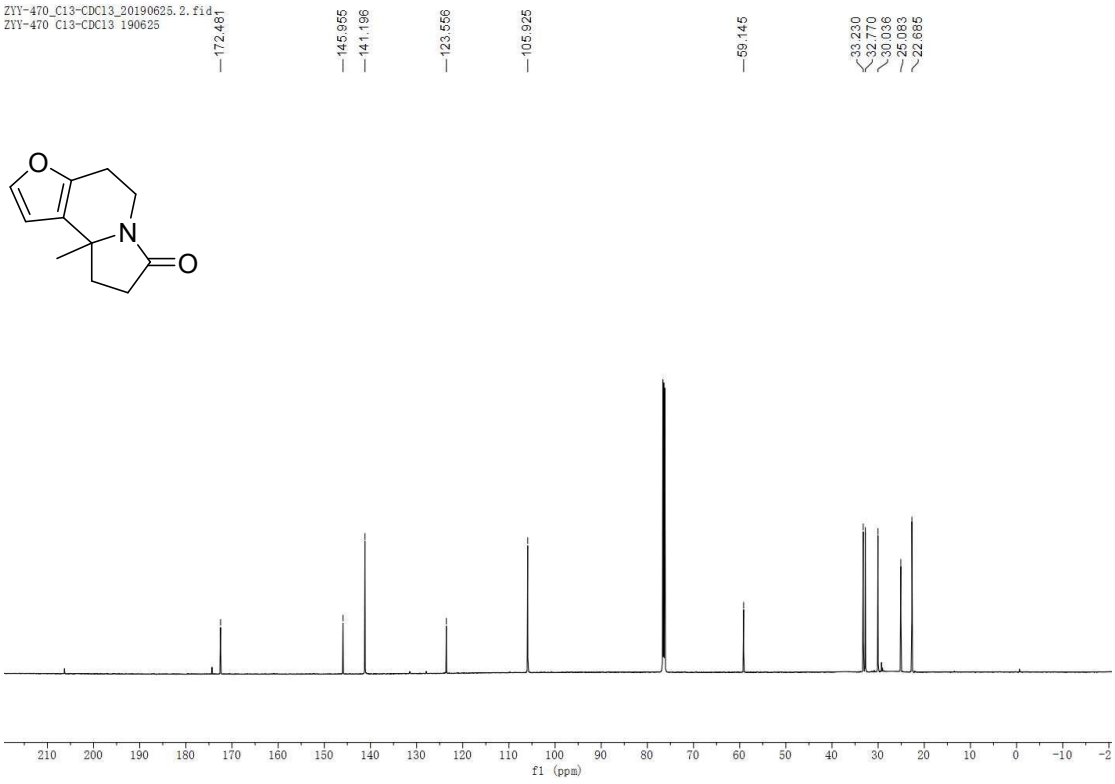
[13]C-NMR spectrum of compound 3ea (150 MHz, $CDCl_3$)



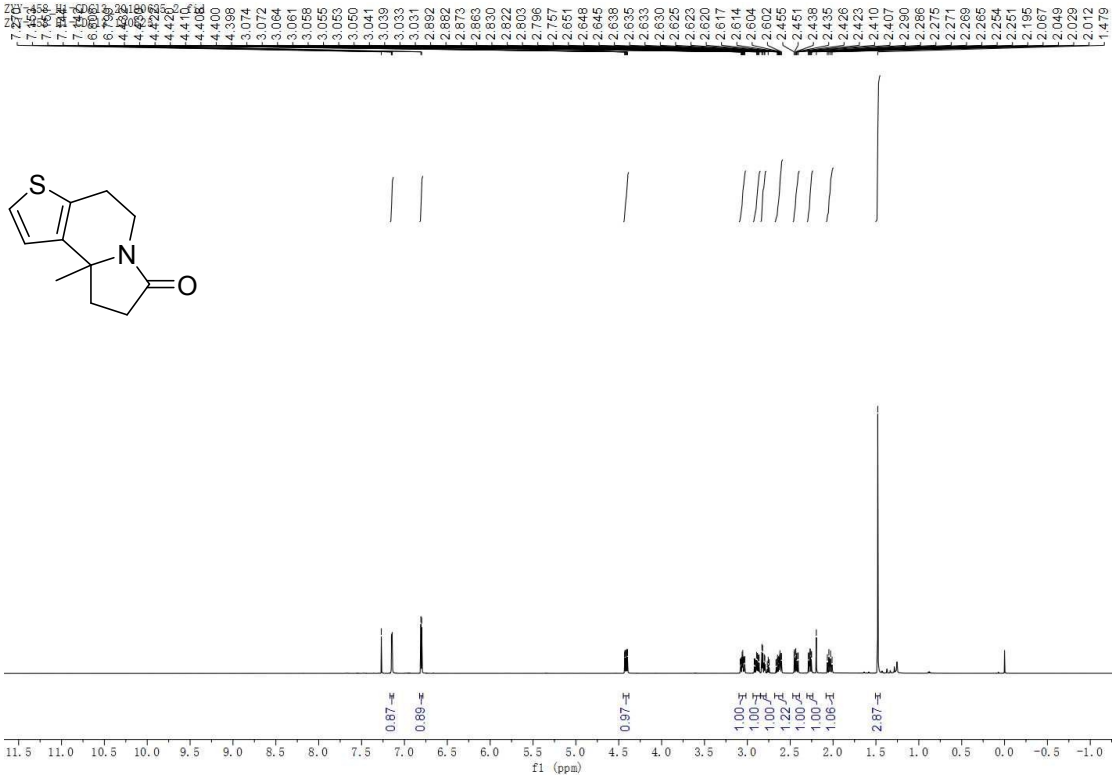
^{1}H-NMR spectrum of compound 3fa (600 MHz, $CDCl_3$)



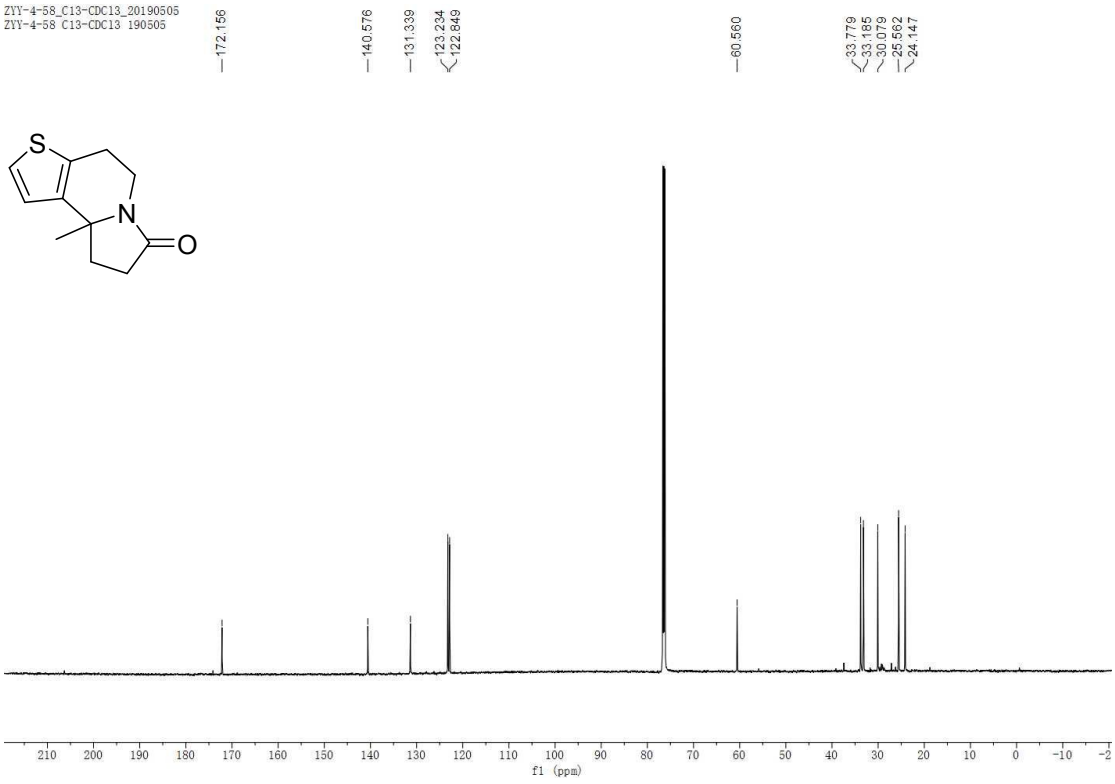
^{13}C-NMR spectrum of compound 3fa (150 MHz, $CDCl_3$)



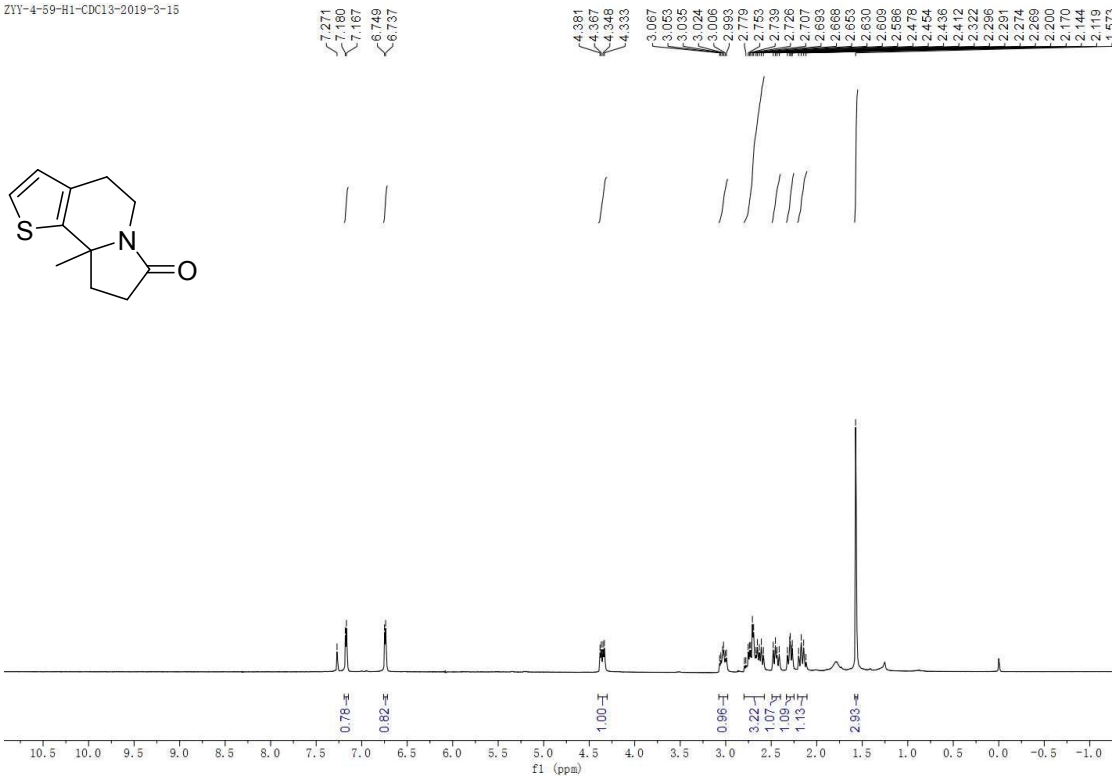
^{1}H-NMR spectrum of compound 3ga (600 MHz, $CDCl_3$)



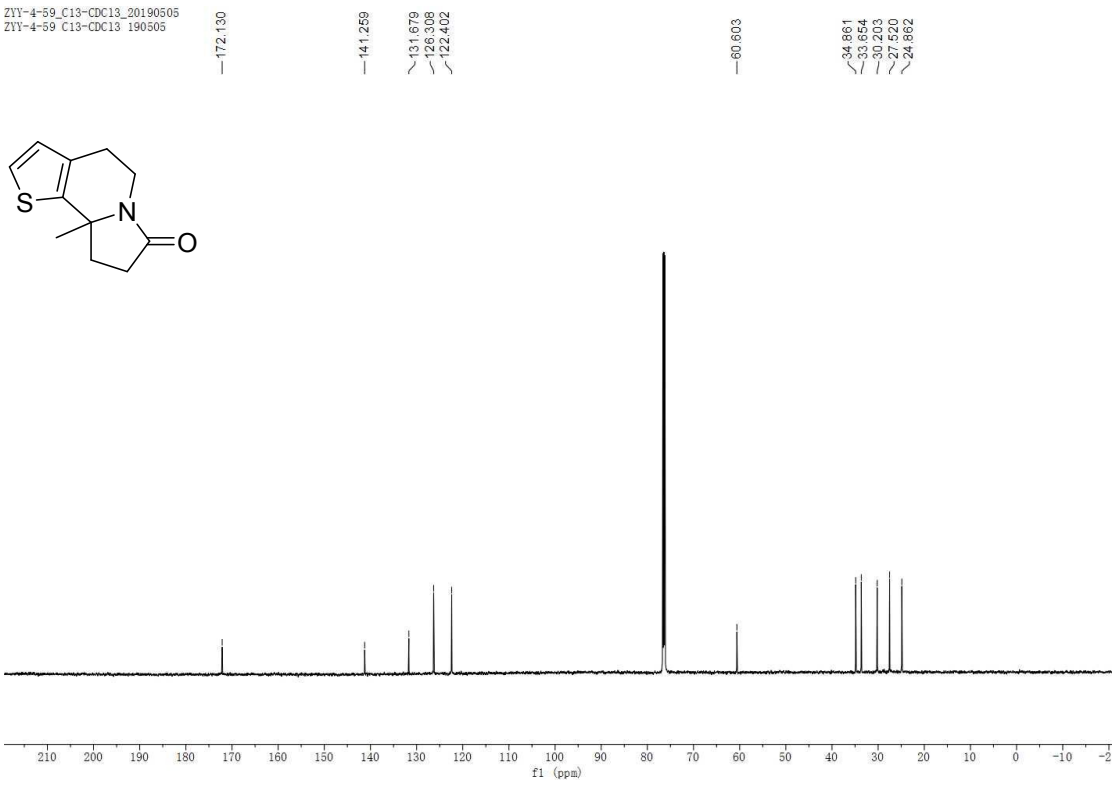
^{13}C-NMR spectrum of compound 3ga (150 MHz, $CDCl_3$)



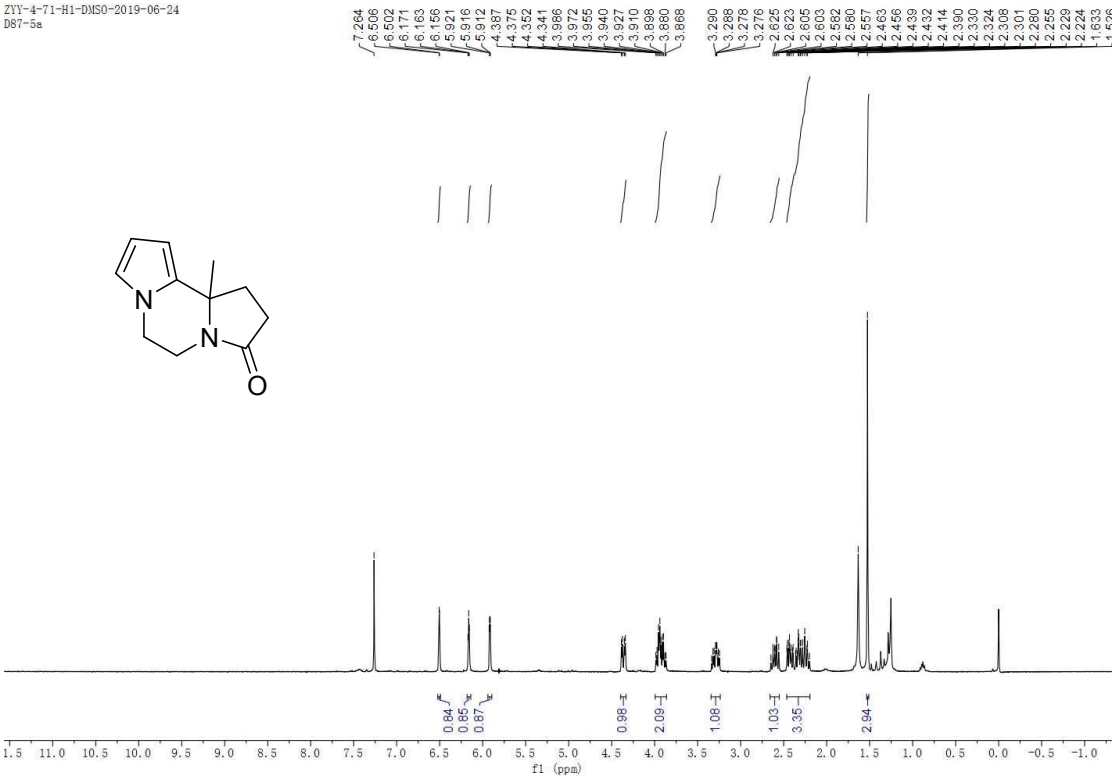
[1]H-NMR spectrum of compound 3ha (400 MHz, $CDCl_3$)



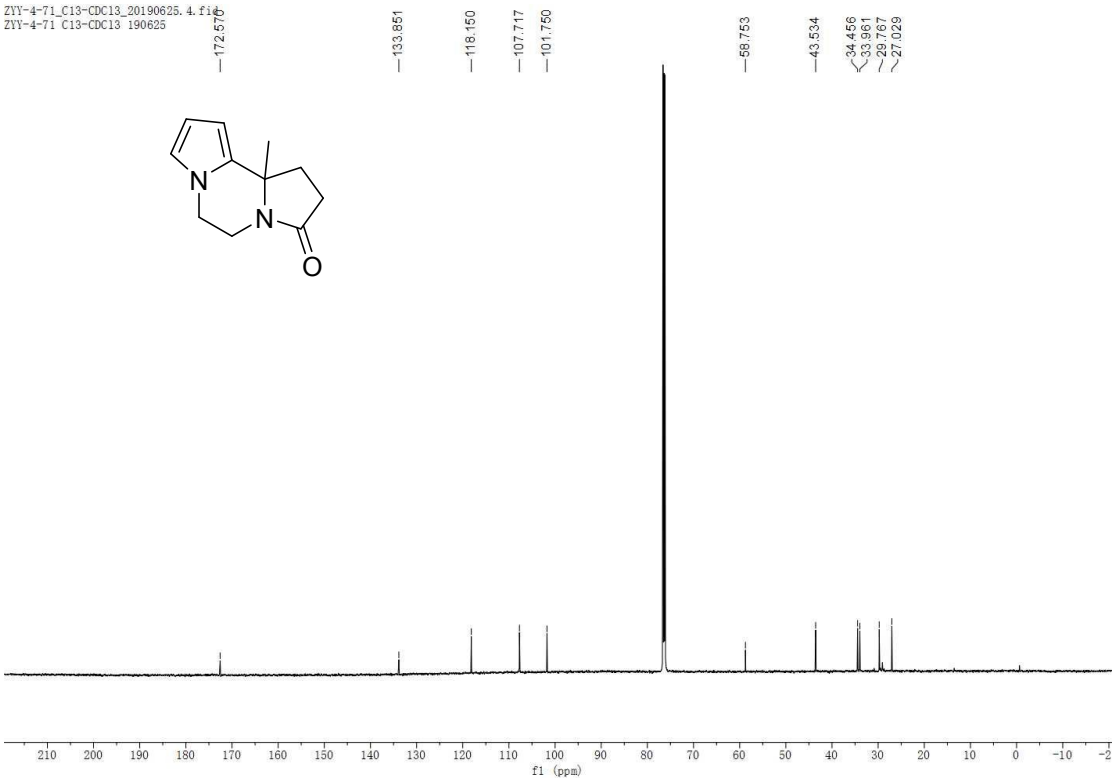
[13]C-NMR spectrum of compound 3ha (150 MHz, $CDCl_3$)



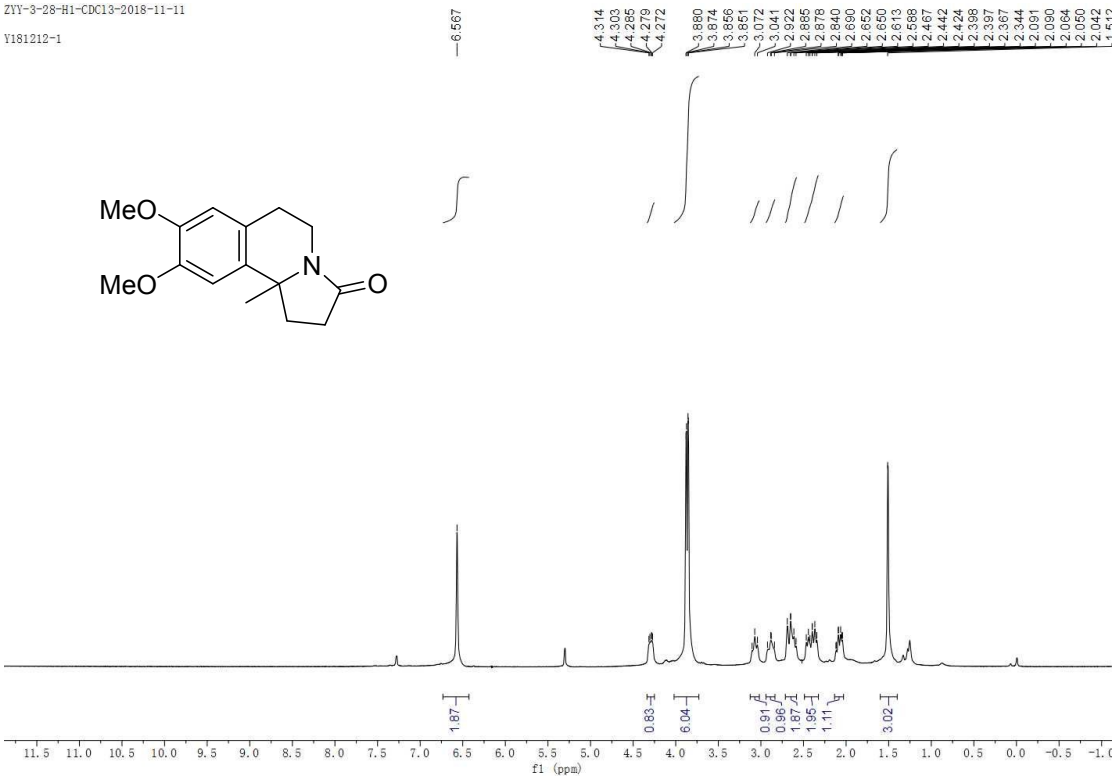
^{1}H-NMR spectrum of compound 3ia (400 MHz, $CDCl_3$)



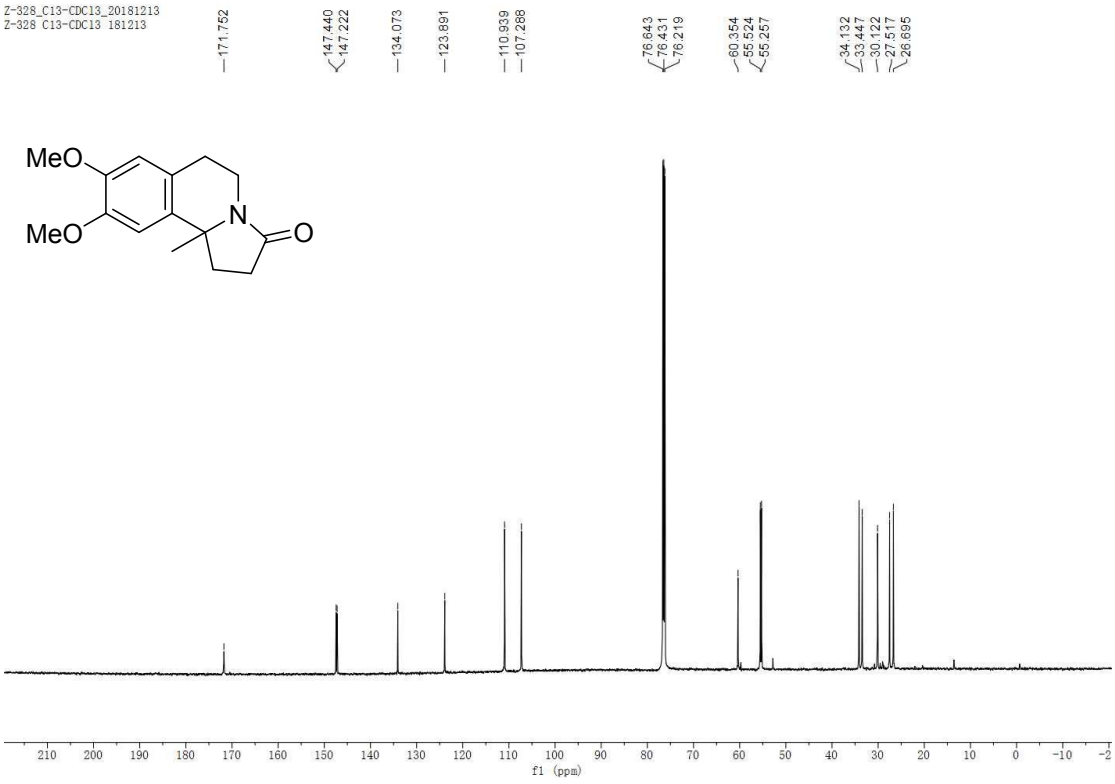
^{13}C-NMR spectrum of compound 3ia (150 MHz, $CDCl_3$)



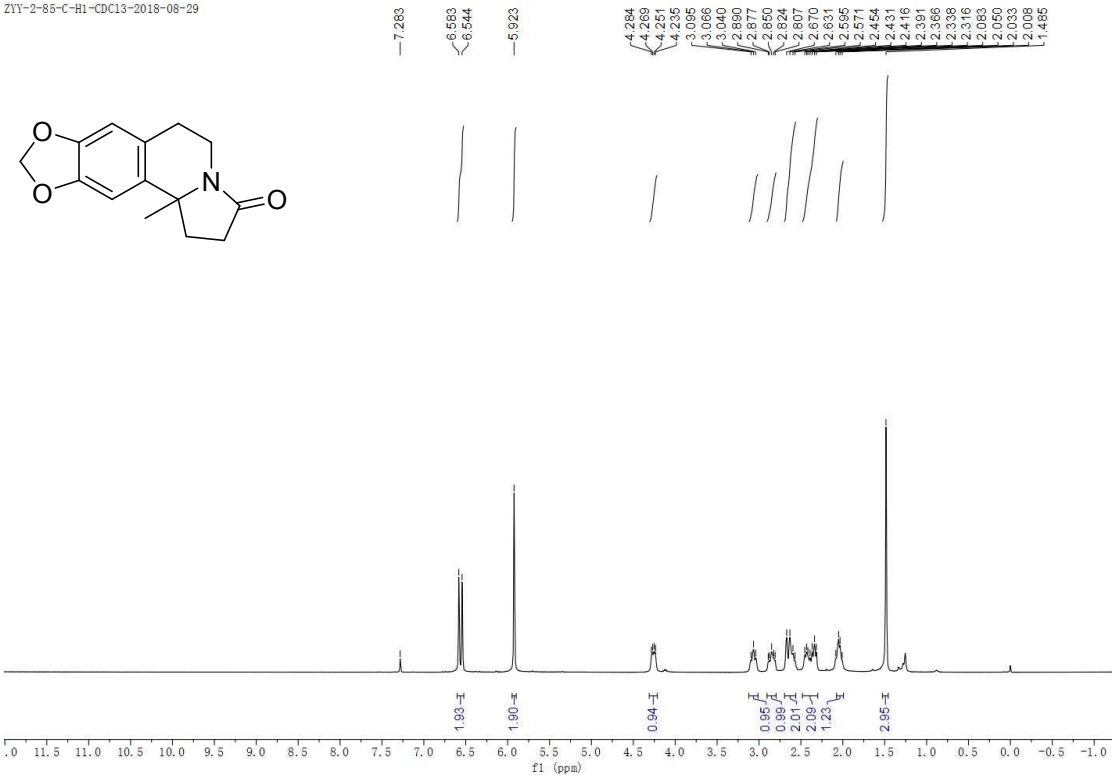
[1]H-NMR spectrum of compound 3ka (400 MHz, $CDCl_3$)



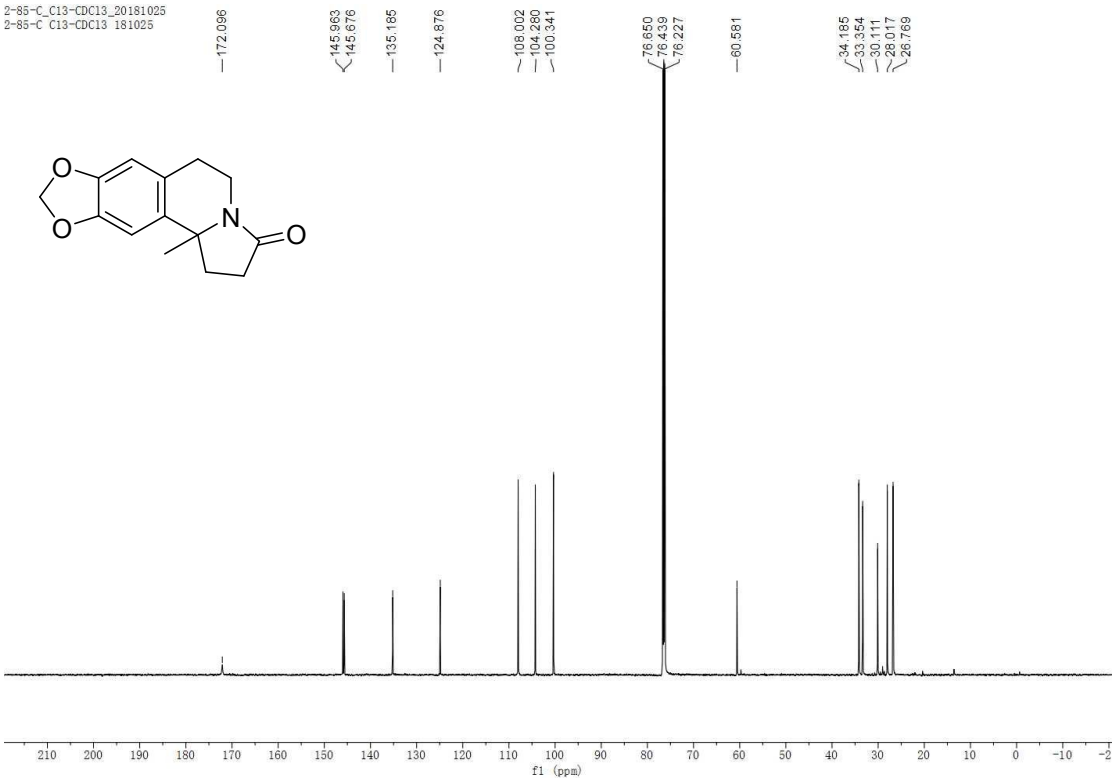
[13]C-NMR spectrum of compound 3ka (150 MHz, $CDCl_3$)



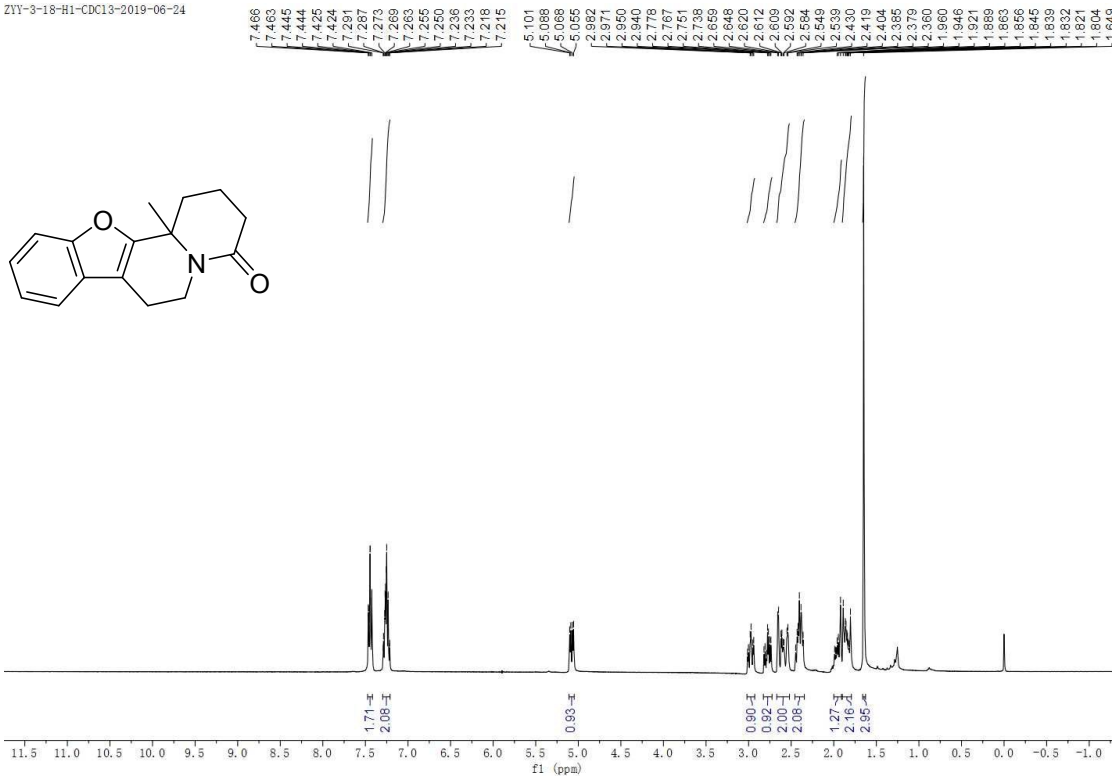
[1]H-NMR spectrum of compound 3la (400 MHz, $CDCl_3$)



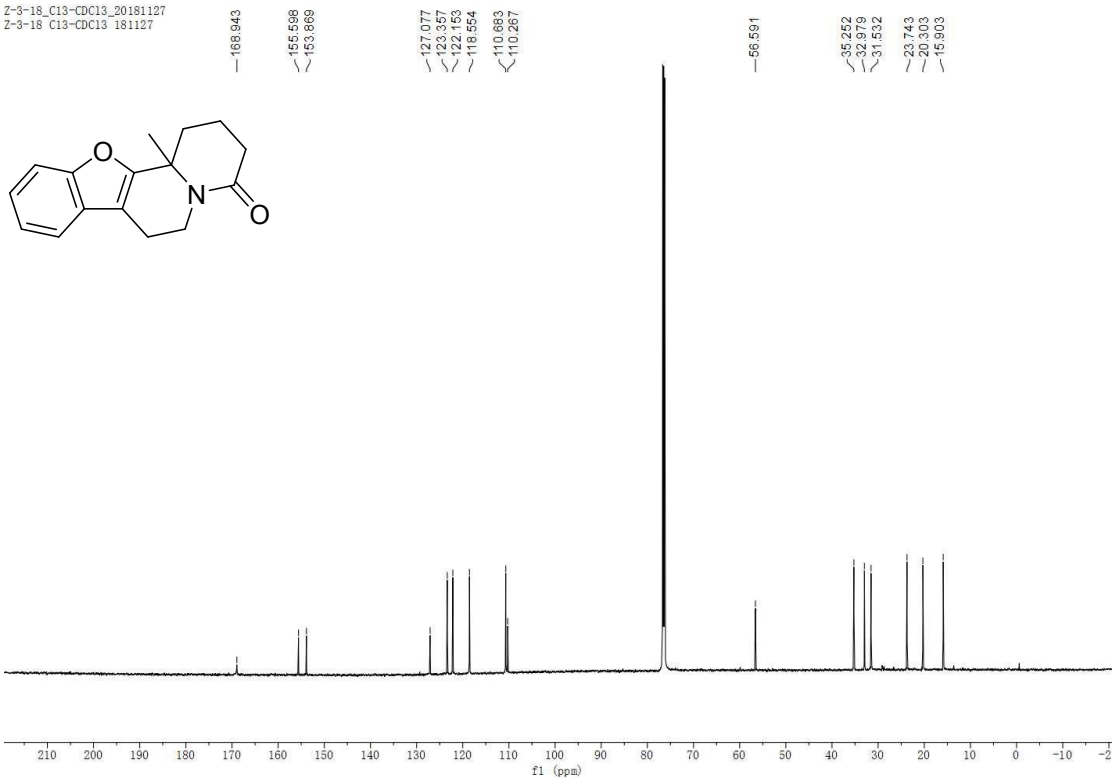
[13]C-NMR spectrum of compound 3la (150 MHz, $CDCl_3$)



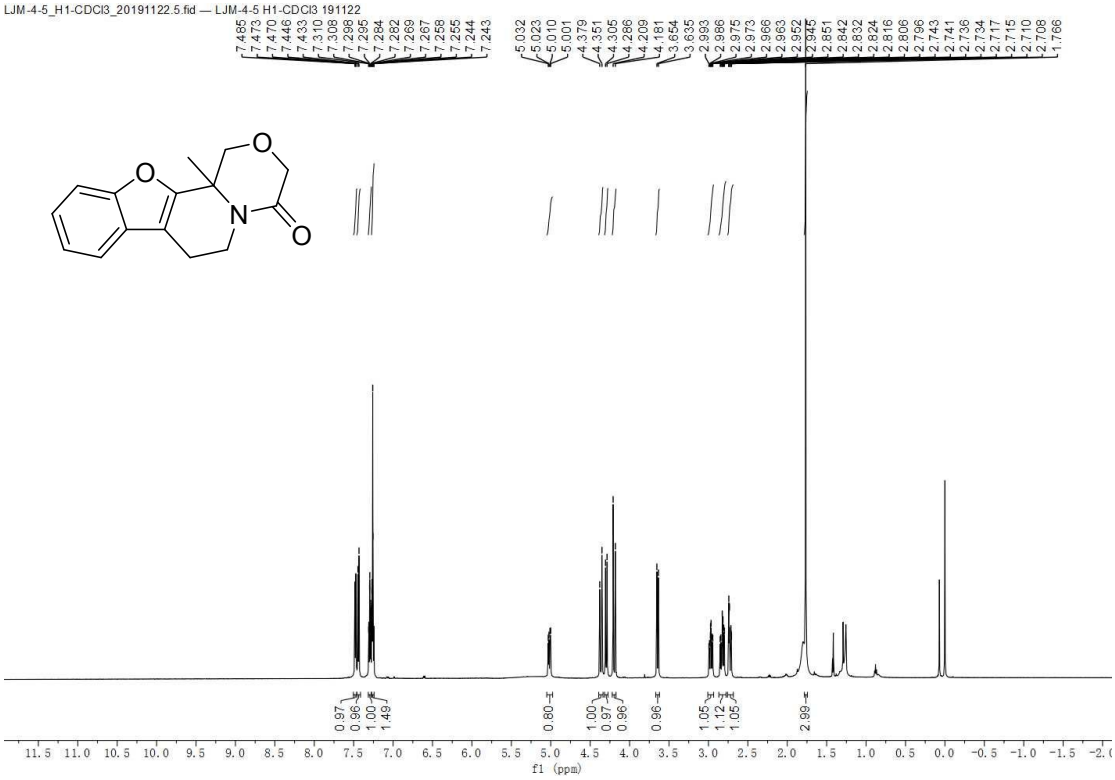
[1]H-NMR spectrum of compound 4ab (400 MHz, $CDCl_3$)



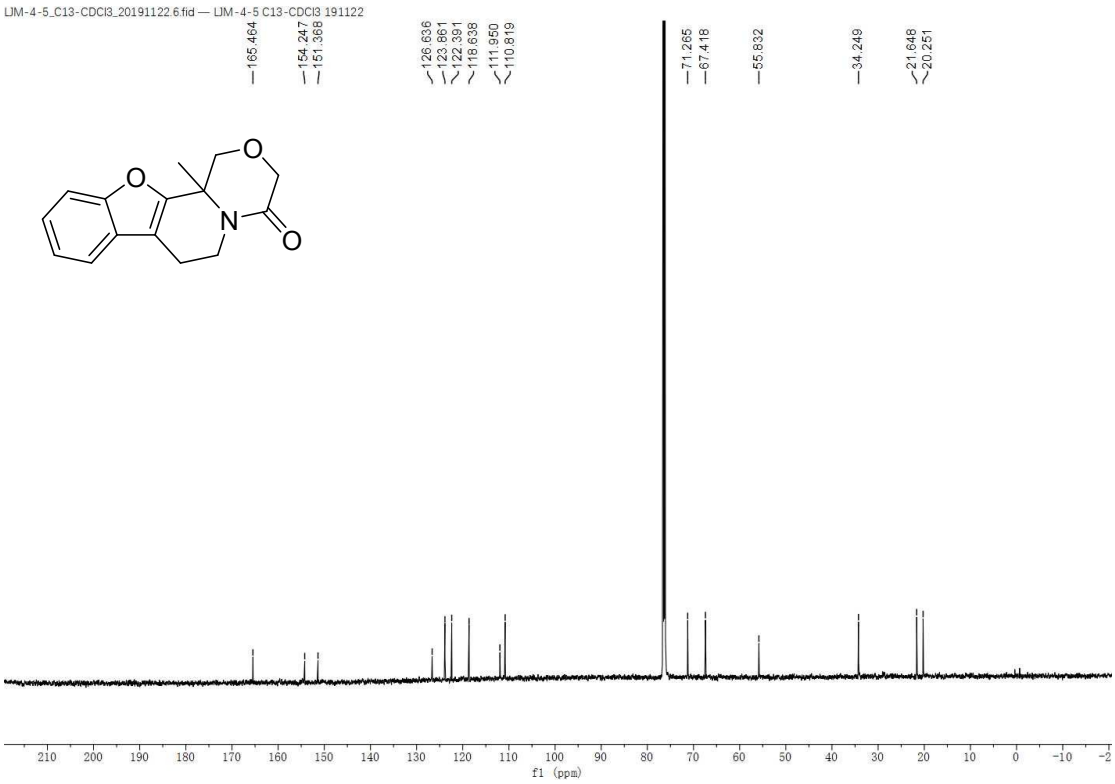
[13]C-NMR spectrum of compound 4ab (150 MHz, $CDCl_3$)



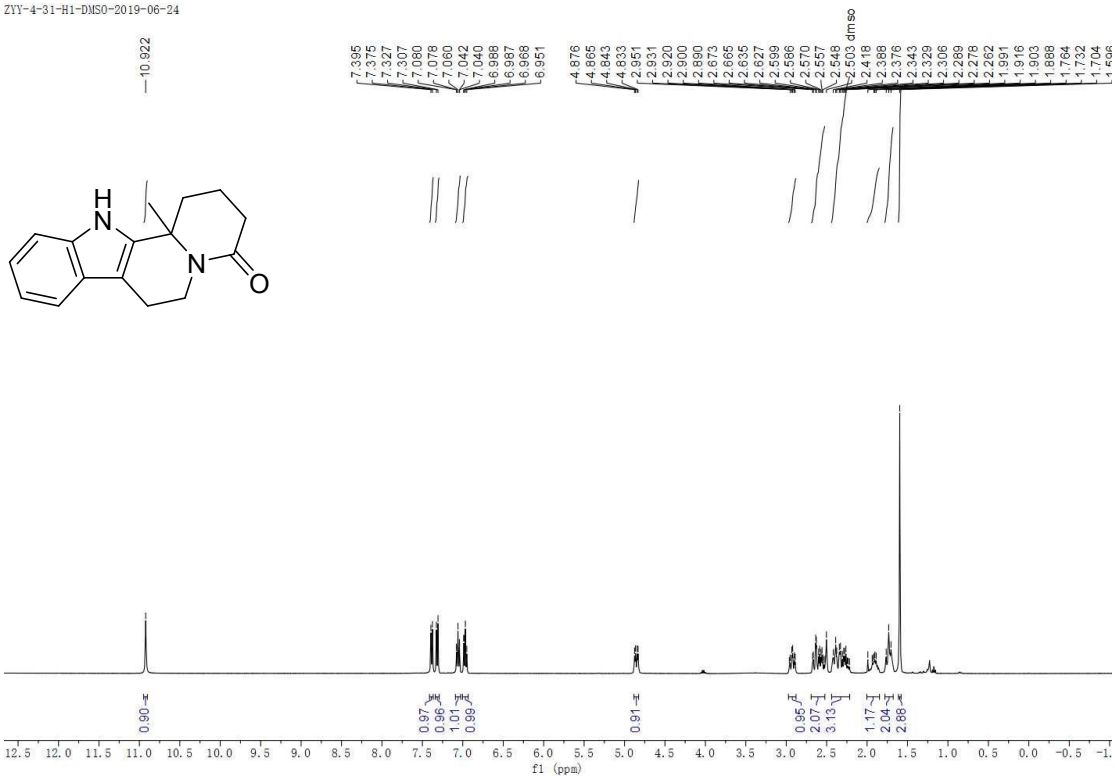
[1]H-NMR spectrum of compound 4ac (600 MHz, $CDCl_3$)



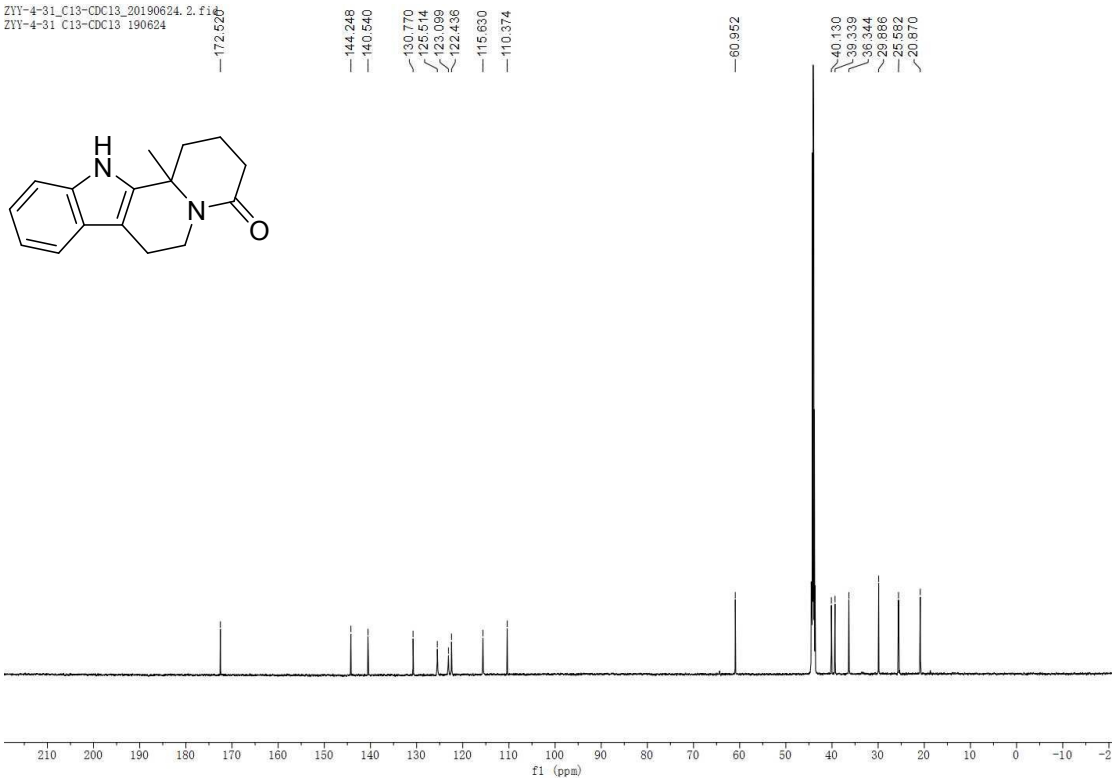
[13]C-NMR spectrum of compound 4ac (150 MHz, $CDCl_3$)



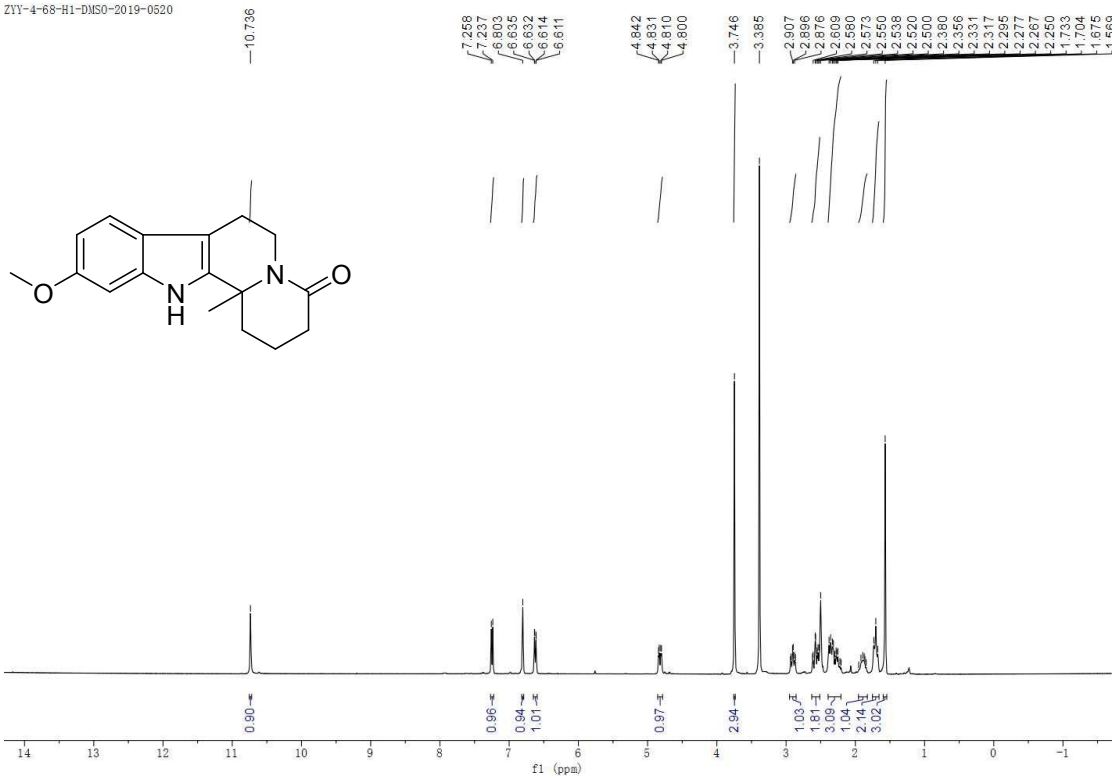
[1]H-NMR spectrum of compound 4bb (400 MHz, DMSO-d6)



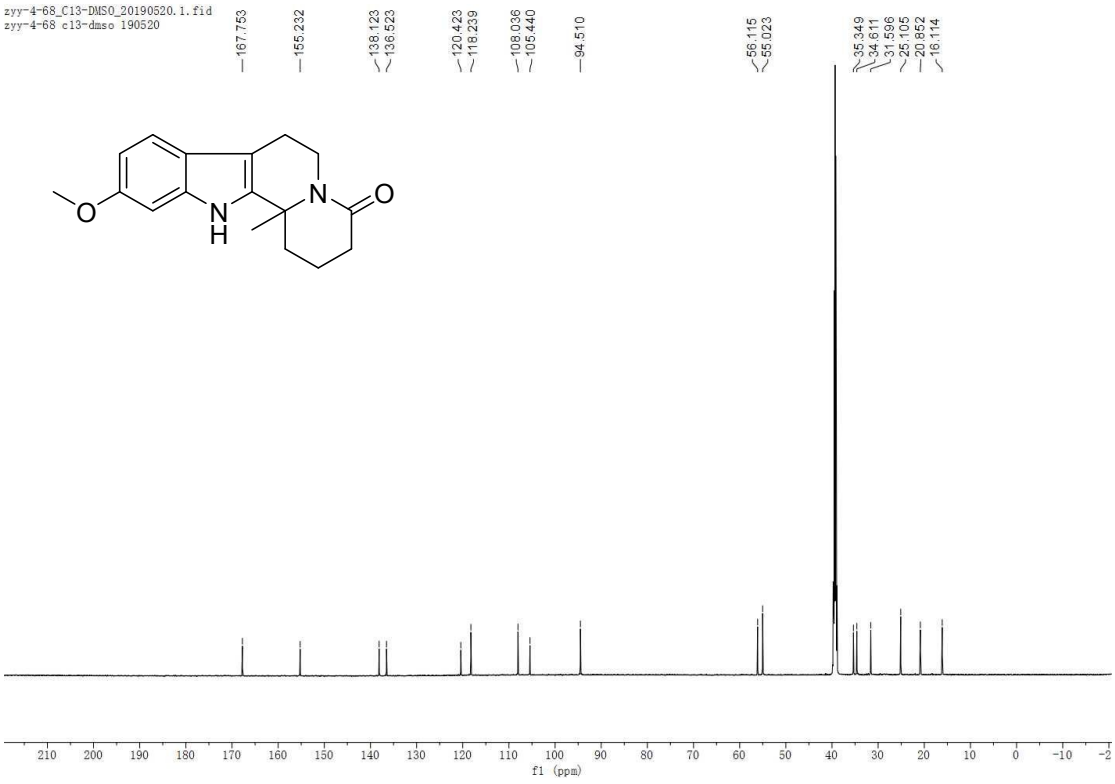
[13]C-NMR spectrum of compound 4bb (150 MHz, DMSO-d6)



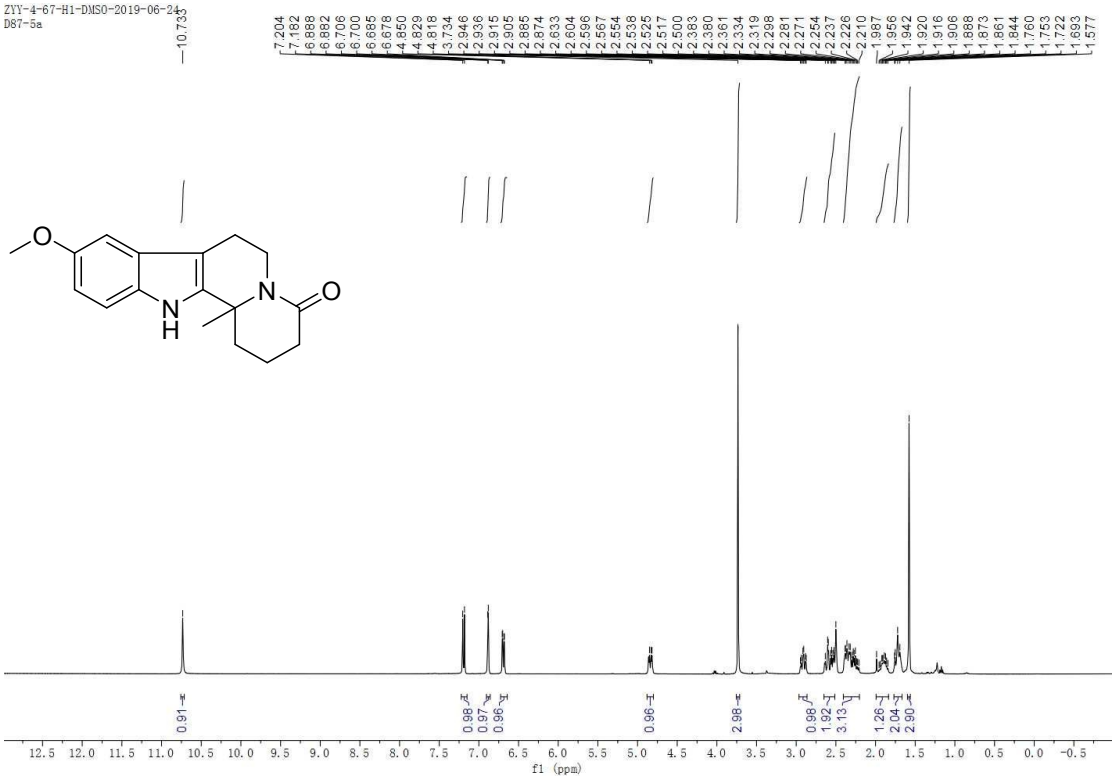
[1]H-NMR spectrum of compound 4cb (400 MHz, DMSO-d6)



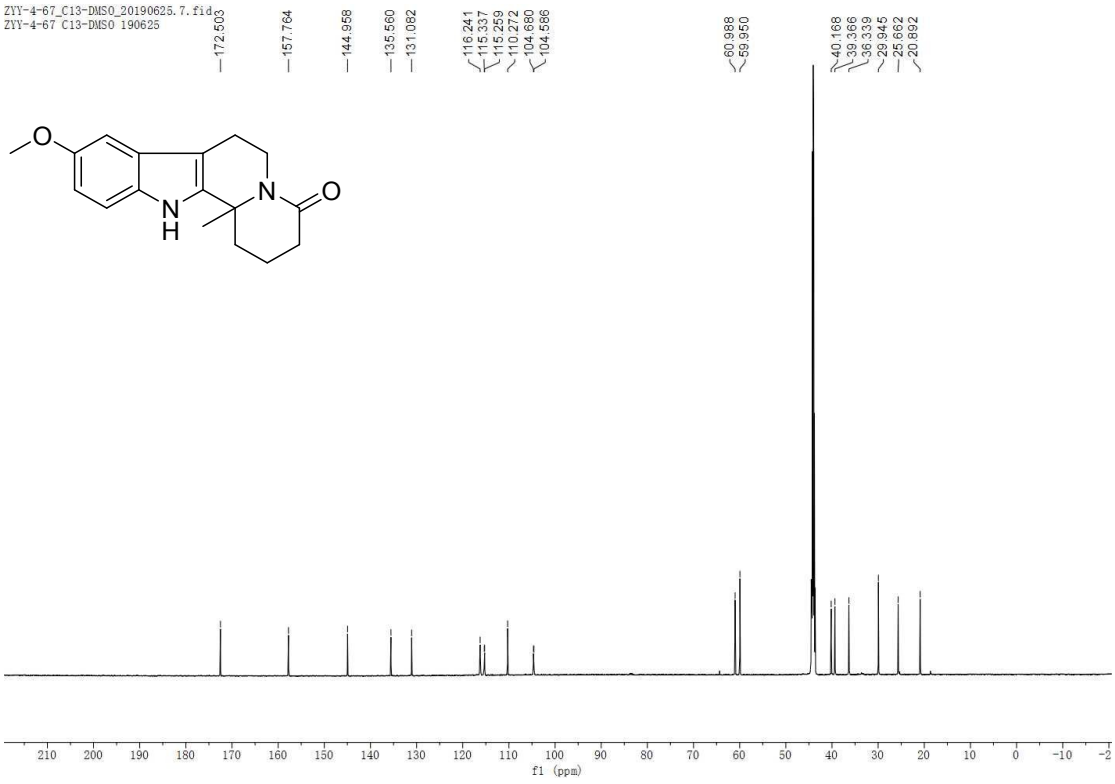
[13]C-NMR spectrum of compound 4cb (150 MHz, DMSO-d6)



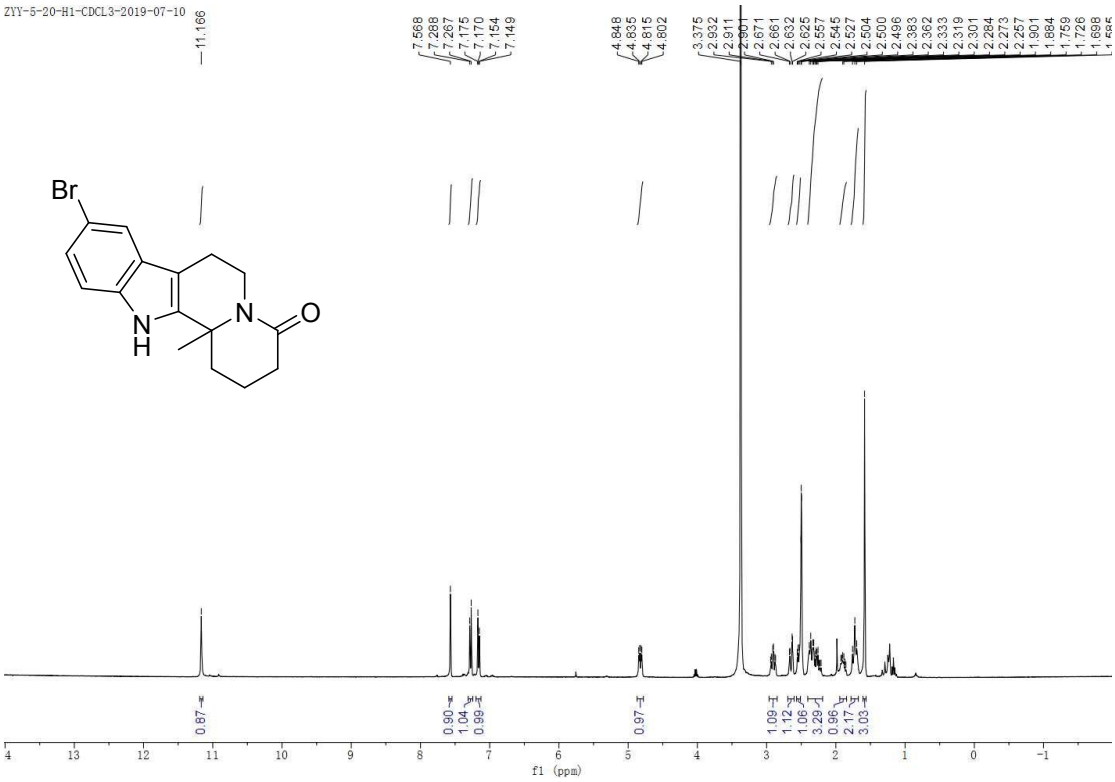
[1]H-NMR spectrum of compound 4db (400 MHz, DMSO-d6)



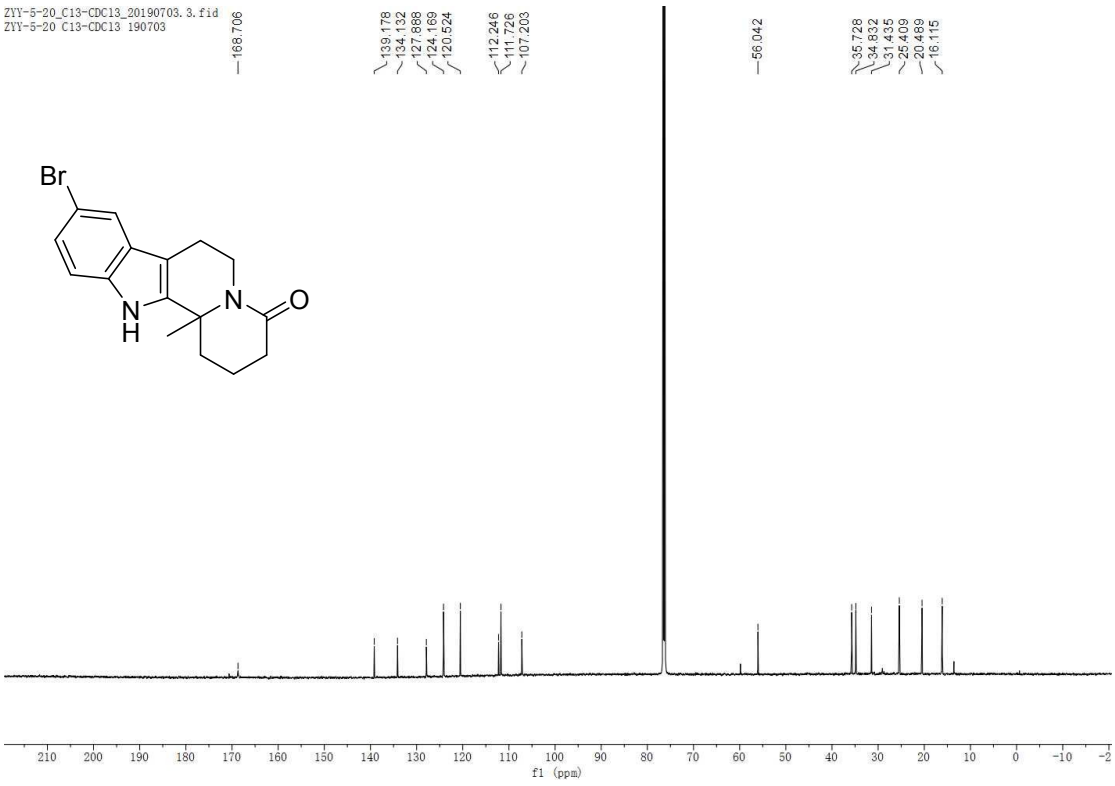
[13]C-NMR spectrum of compound 4db (150 MHz, DMSO-d6)



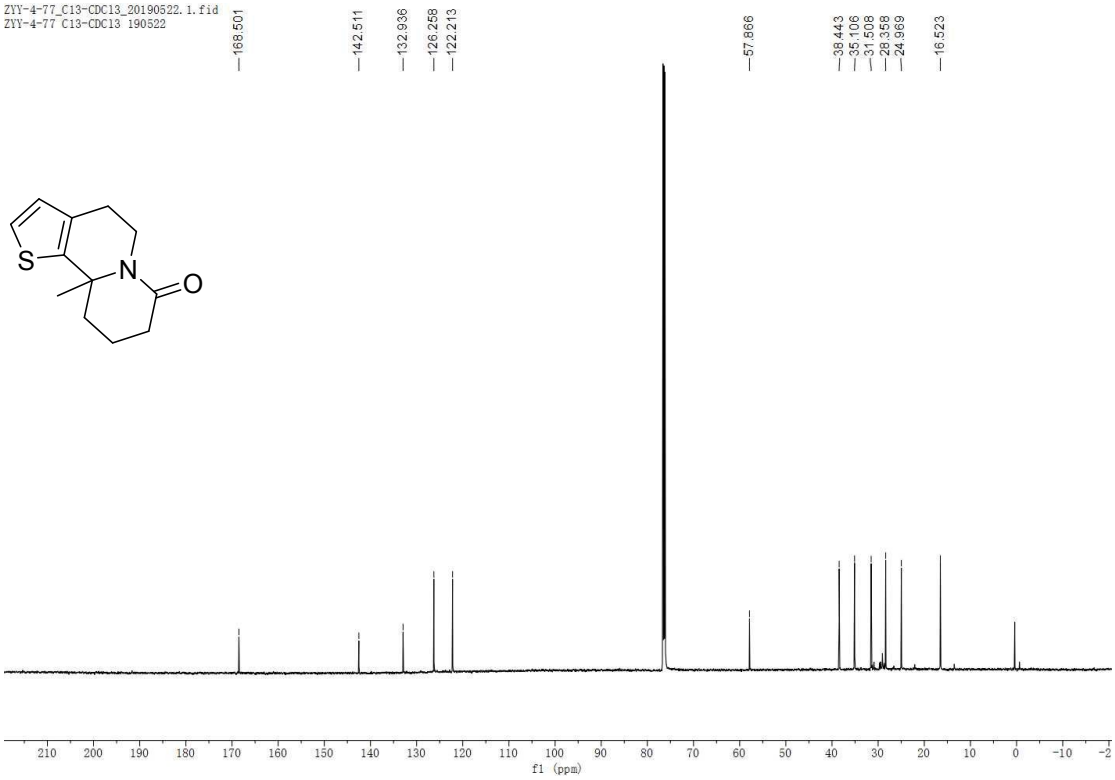
[1]H-NMR spectrum of compound 4eb (400 MHz, $CDCl_3$)



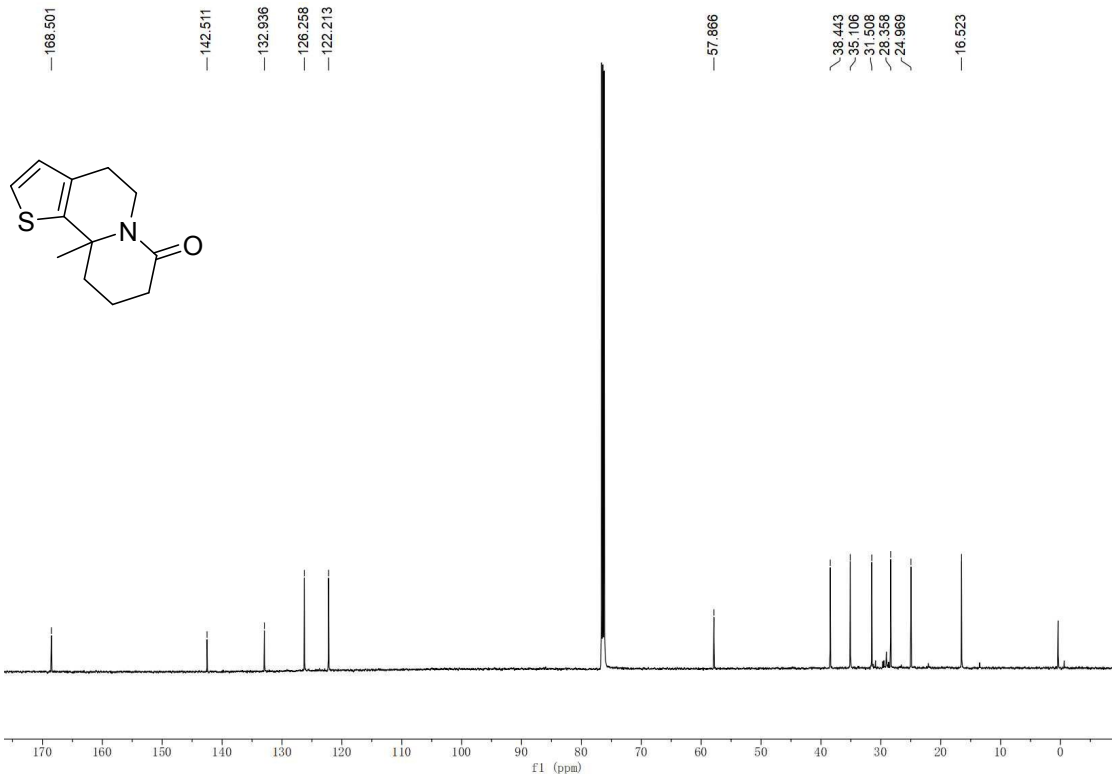
[13]C-NMR spectrum of compound 4eb (150 MHz, $CDCl_3$)



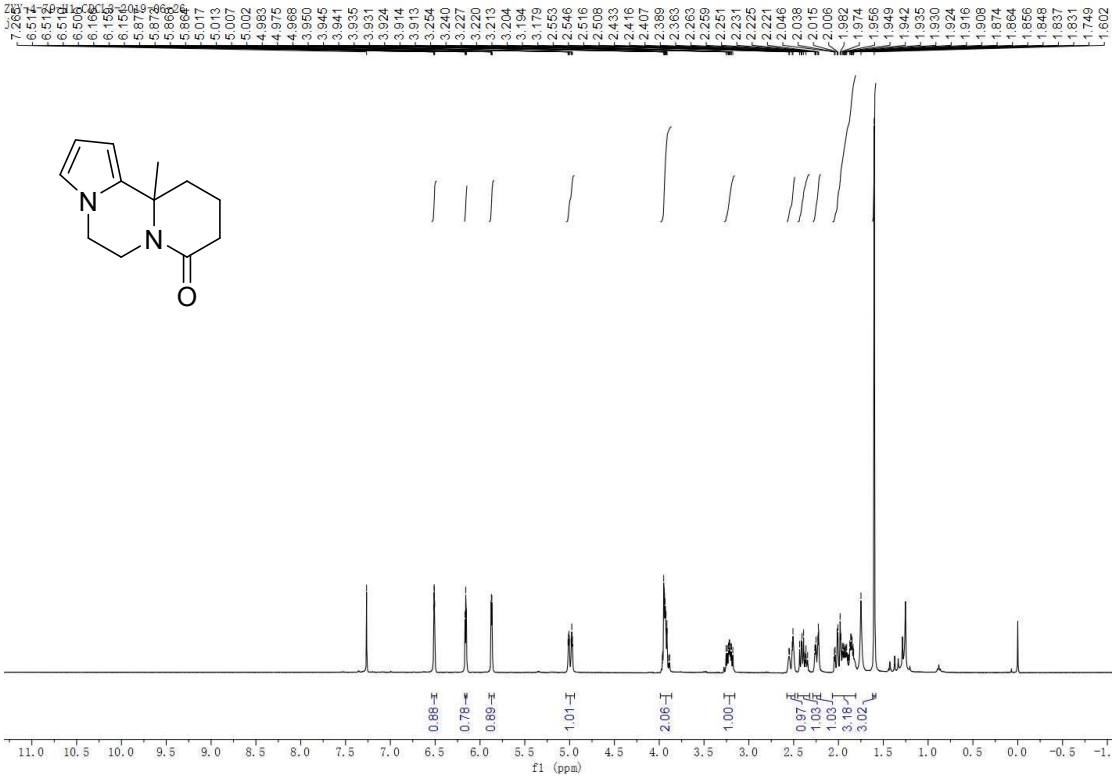
[1]H-NMR spectrum of compound 4gb (400 MHz, $CDCl_3$)



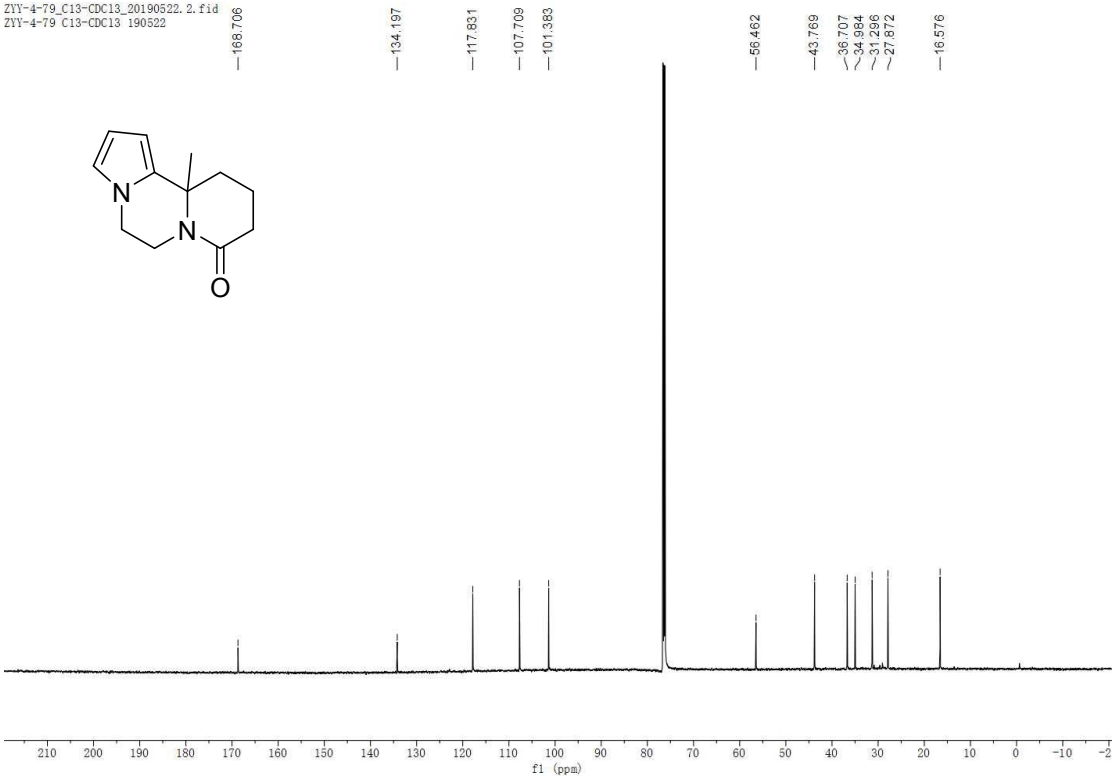
[13]C-NMR spectrum of compound 4gb (150 MHz, $CDCl_3$)



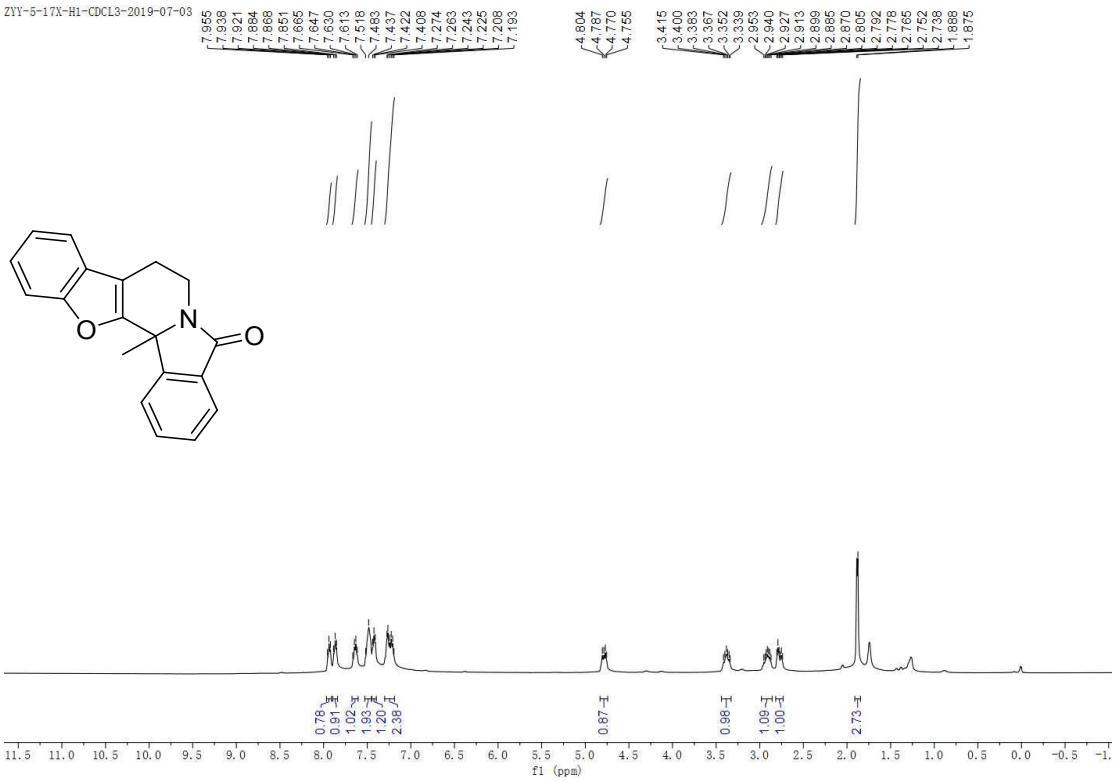
[1]H-NMR spectrum of compound 4ib (400 MHz, $CDCl_3$)



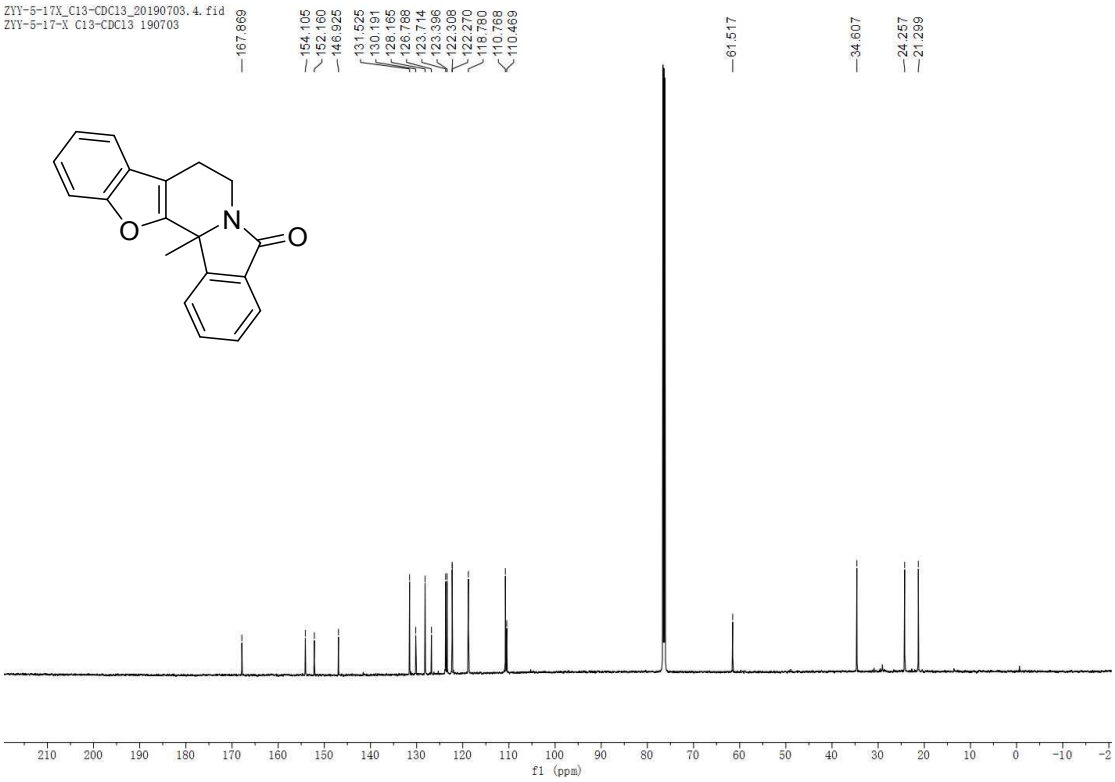
[13]C-NMR spectrum of compound 4ib (150 MHz, $CDCl_3$)



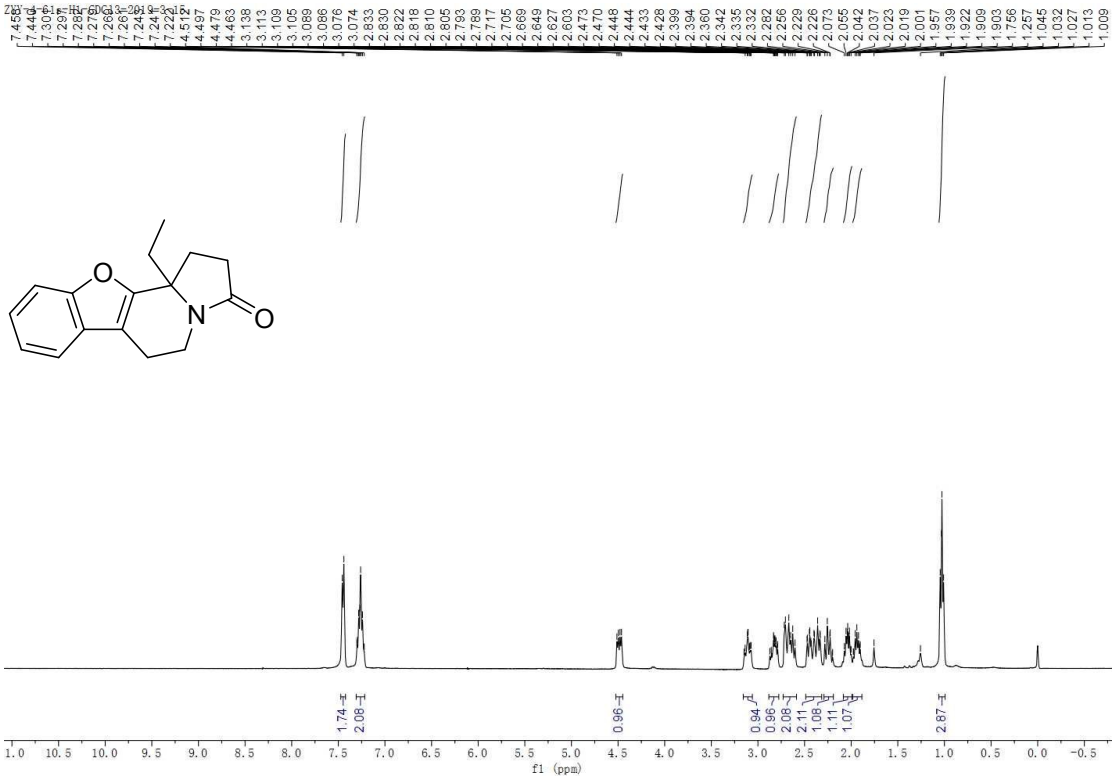
[1]H-NMR spectrum of compound 4af (400 MHz, $CDCl_3$)



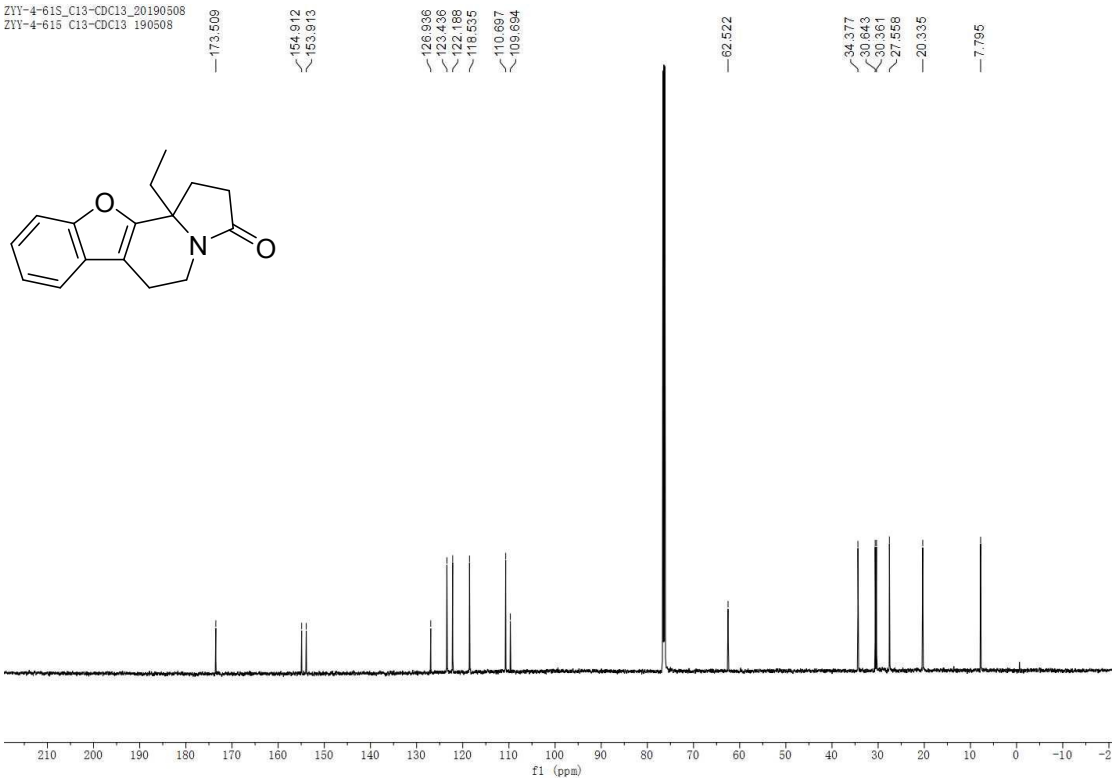
[13]C-NMR spectrum of compound 4af (150 MHz, $CDCl_3$)



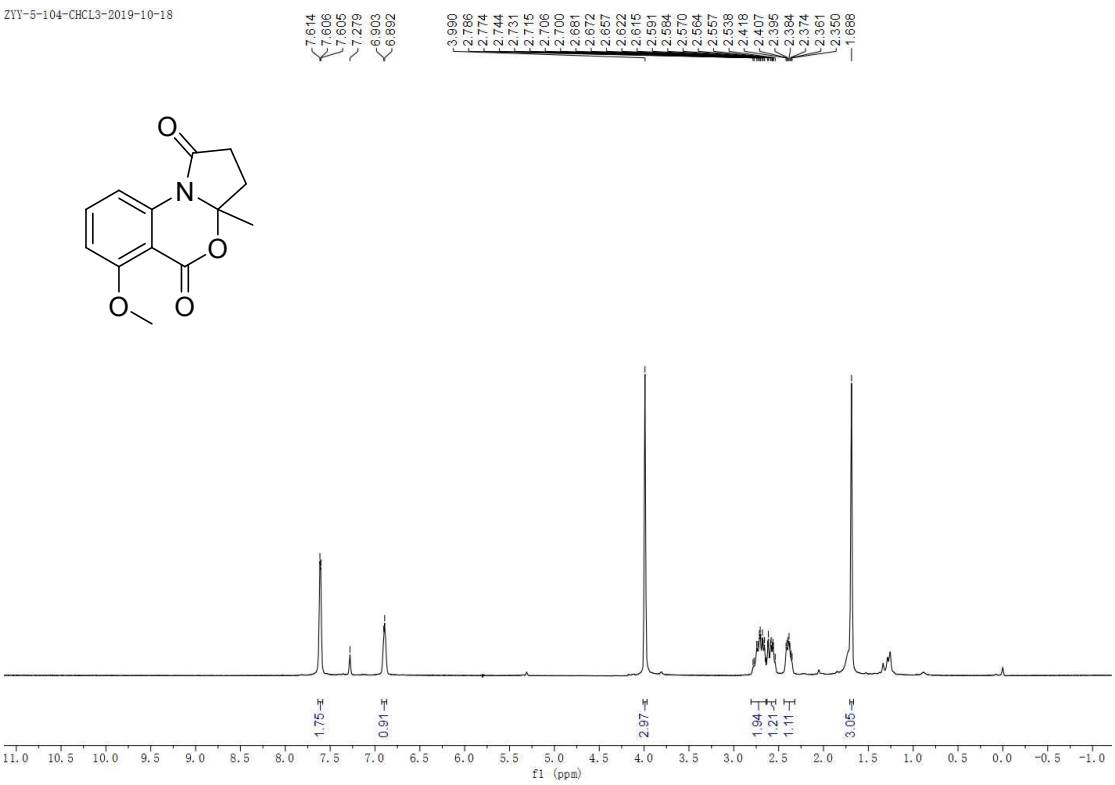
^{1}H-NMR spectrum of compound 4ag (400 MHz, $CDCl_3$)



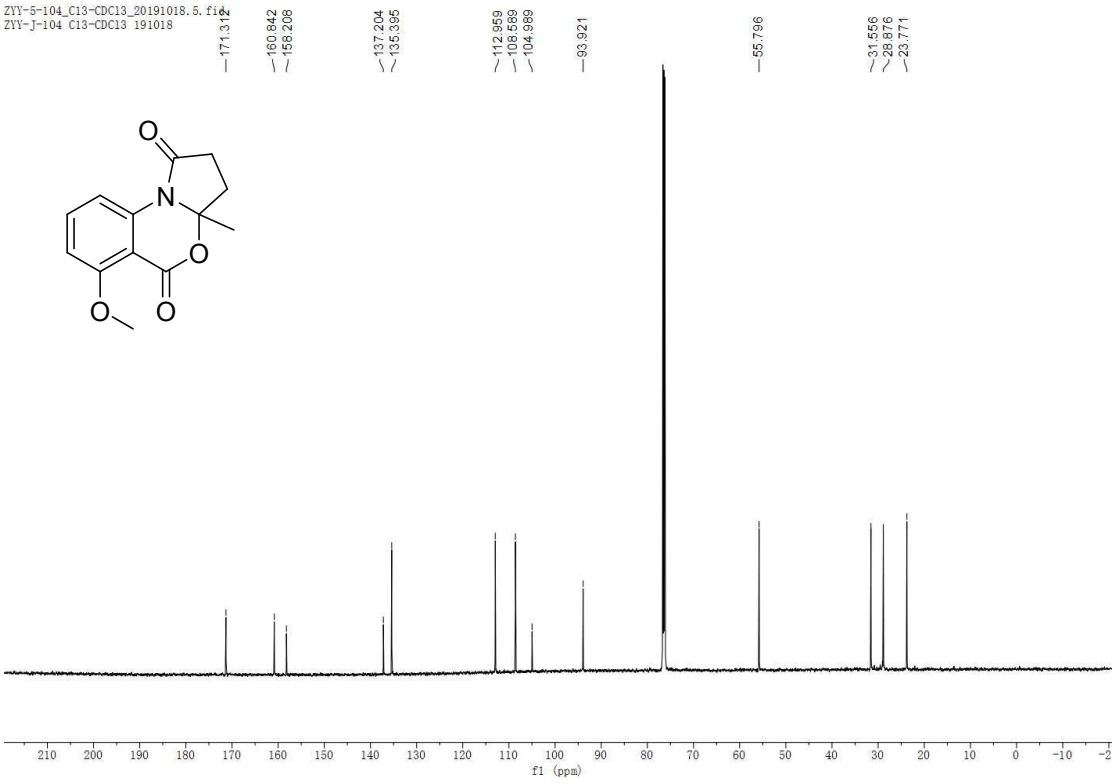
^{13}C-NMR spectrum of compound 4ag (150 MHz, $CDCl_3$)



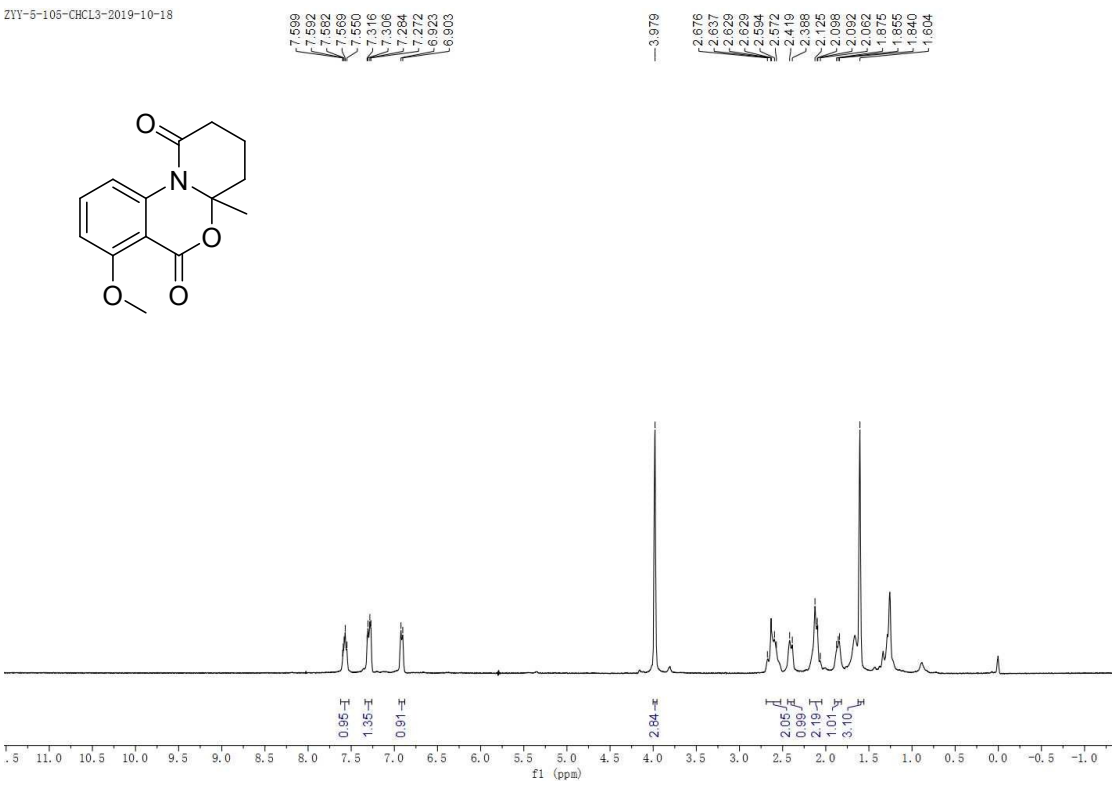
[1]H-NMR spectrum of compound 4ma (400 MHz, $CDCl_3$)



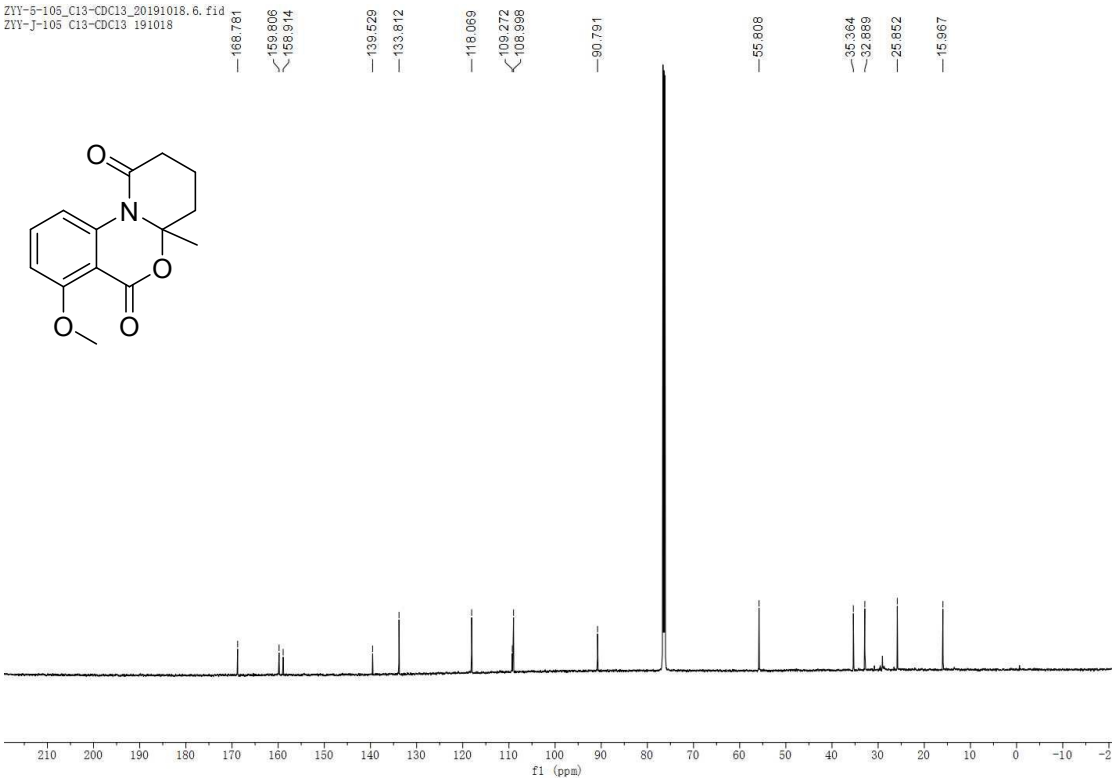
[13]C-NMR spectrum of compound 4ma (150 MHz, $CDCl_3$)



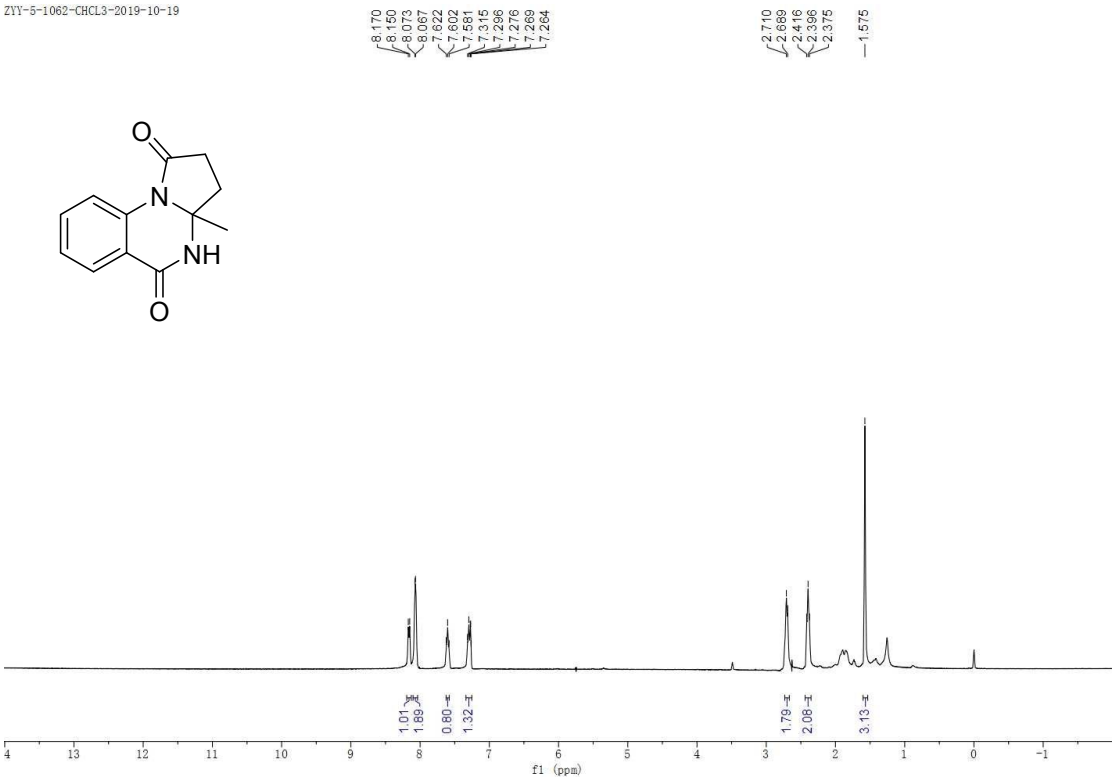
^{1}H-NMR spectrum of compound 4mb (400 MHz, $CDCl_3$)



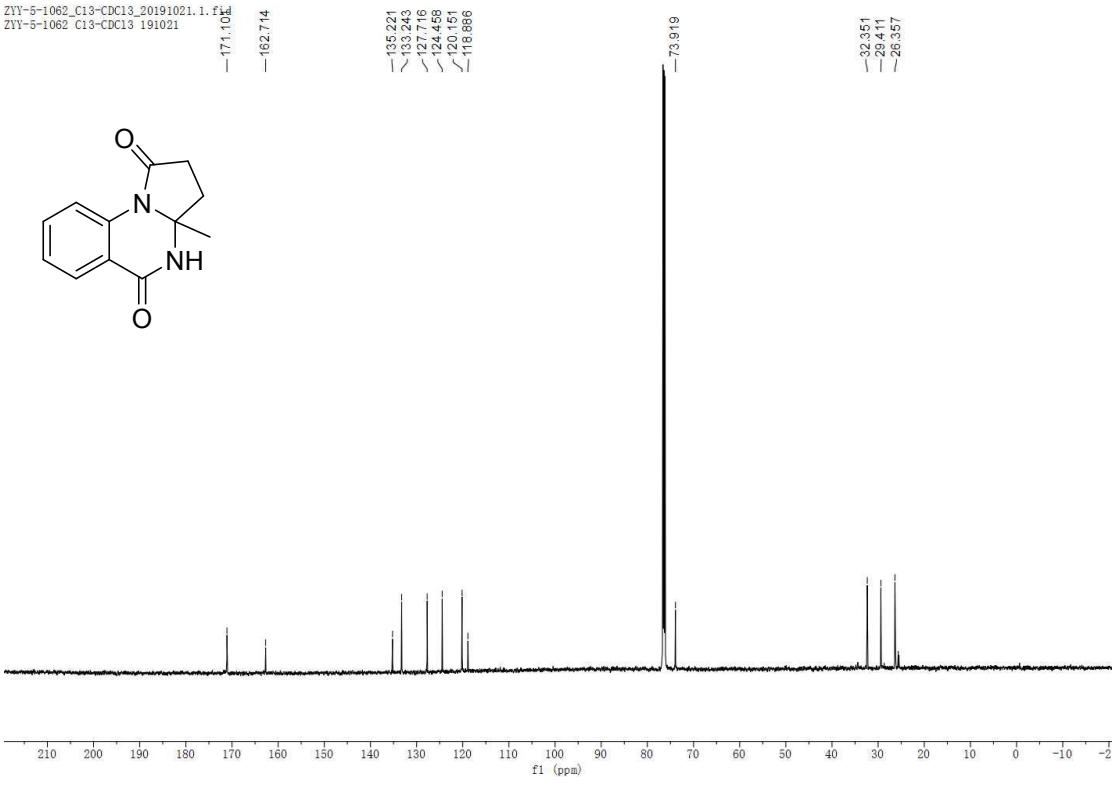
^{13}C-NMR spectrum of compound 4mb (150 MHz, $CDCl_3$)



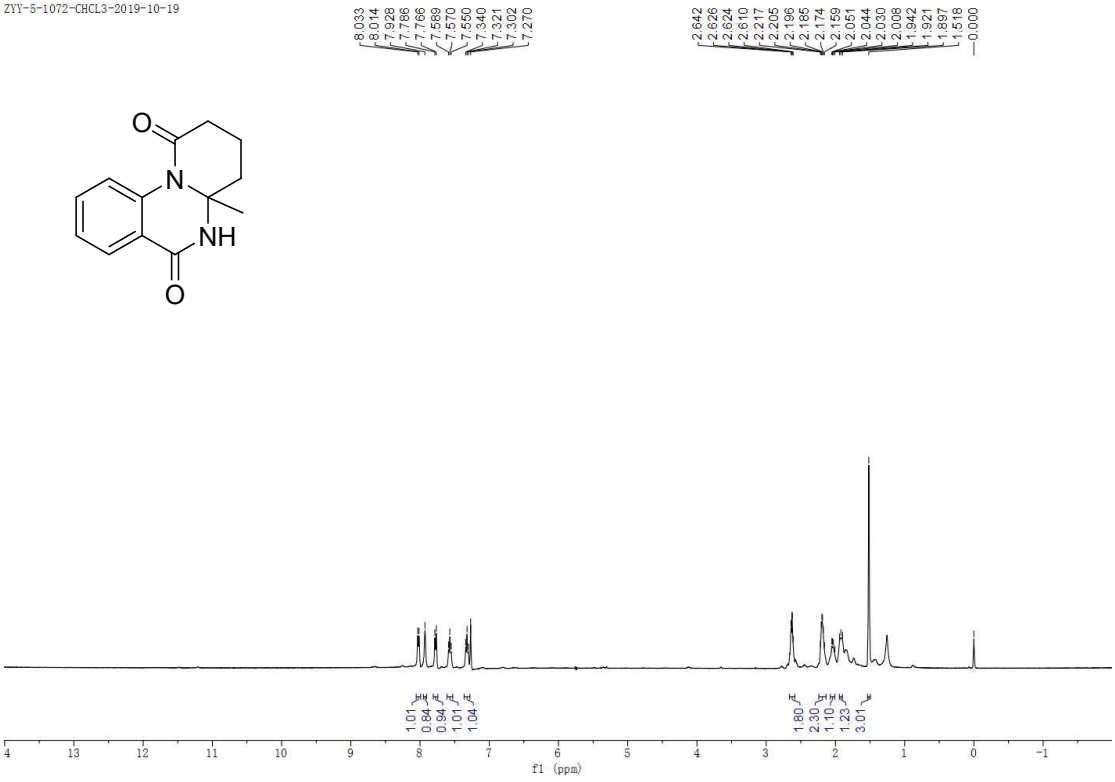
[1]H-NMR spectrum of compound 4na (400 MHz, $CDCl_3$)



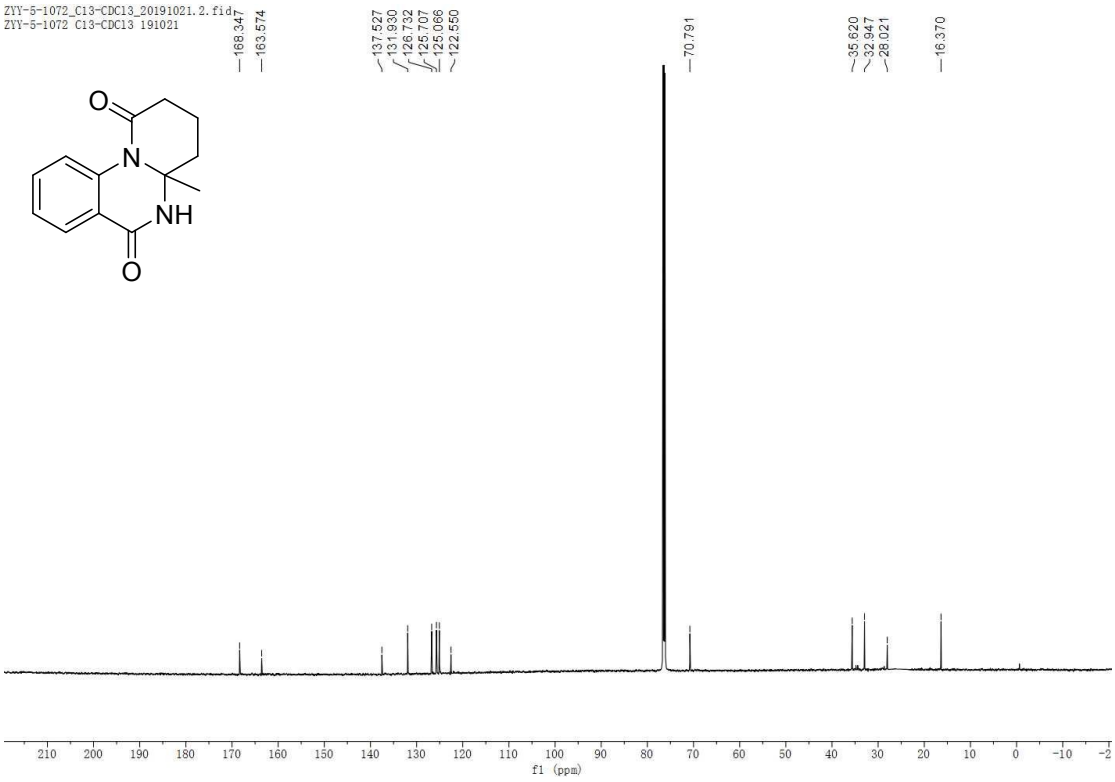
[13]C-NMR spectrum of compound 4na (150 MHz, $CDCl_3$)



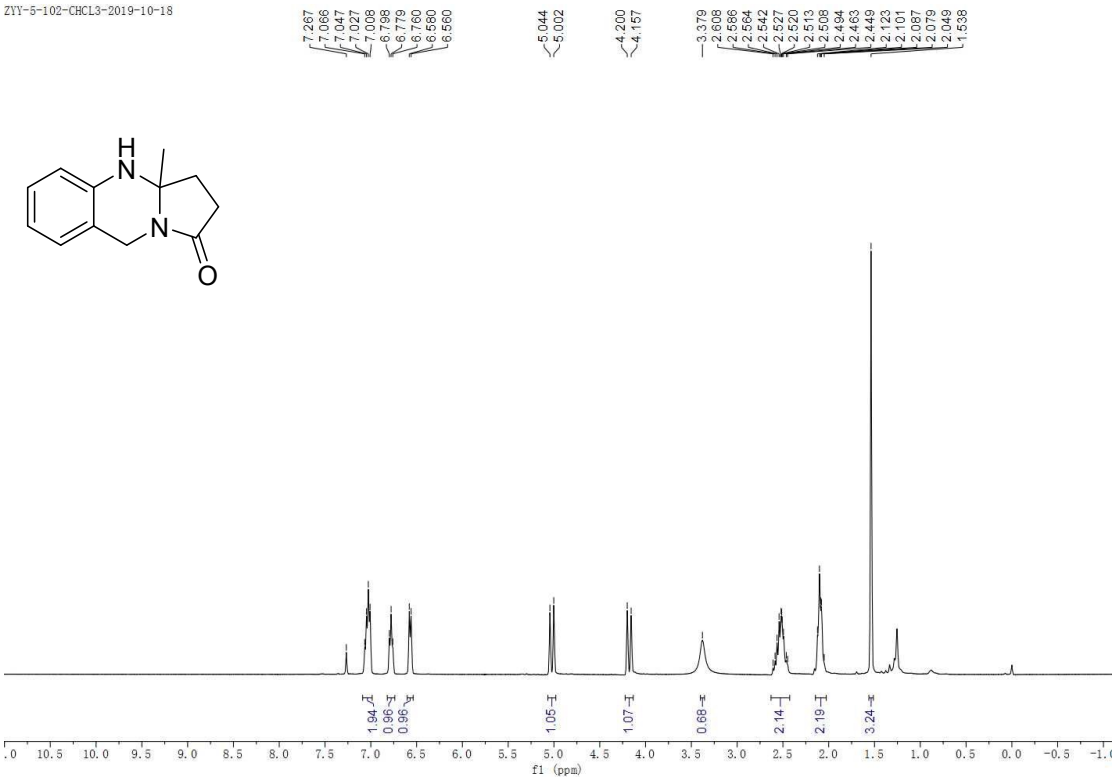
^{1}H-NMR spectrum of compound 4nb (400 MHz, $CDCl_3$)



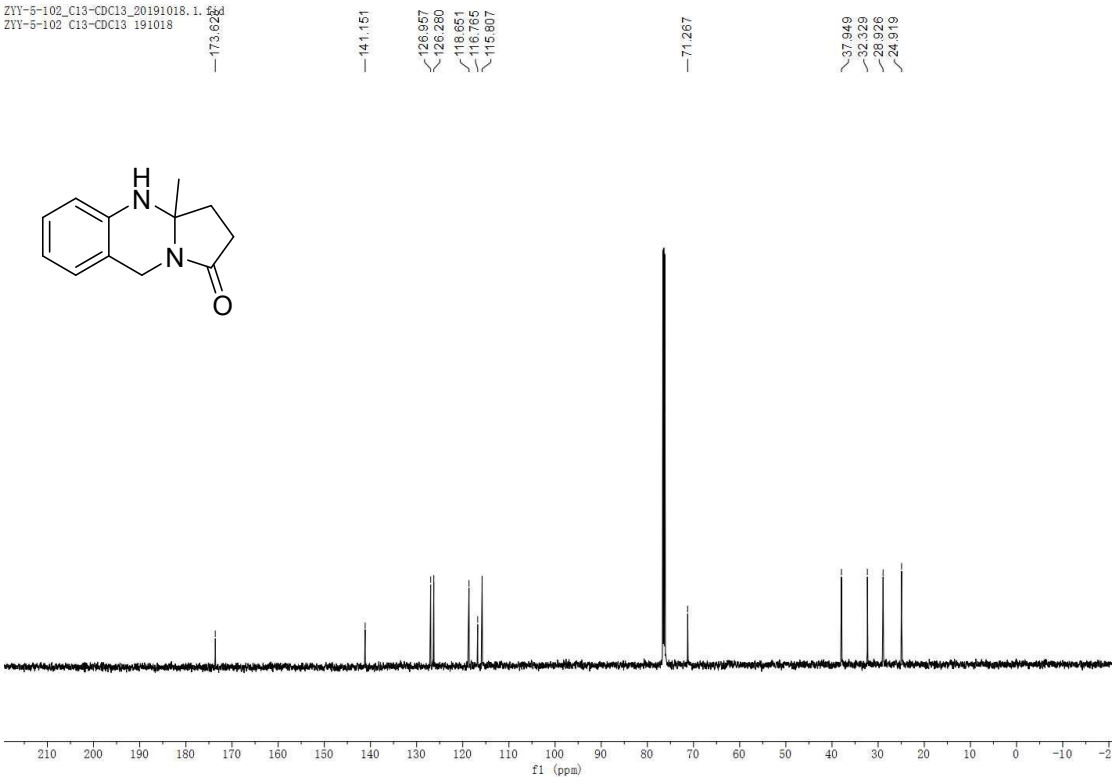
^{13}C-NMR spectrum of compound 4nb (150 MHz, $CDCl_3$)



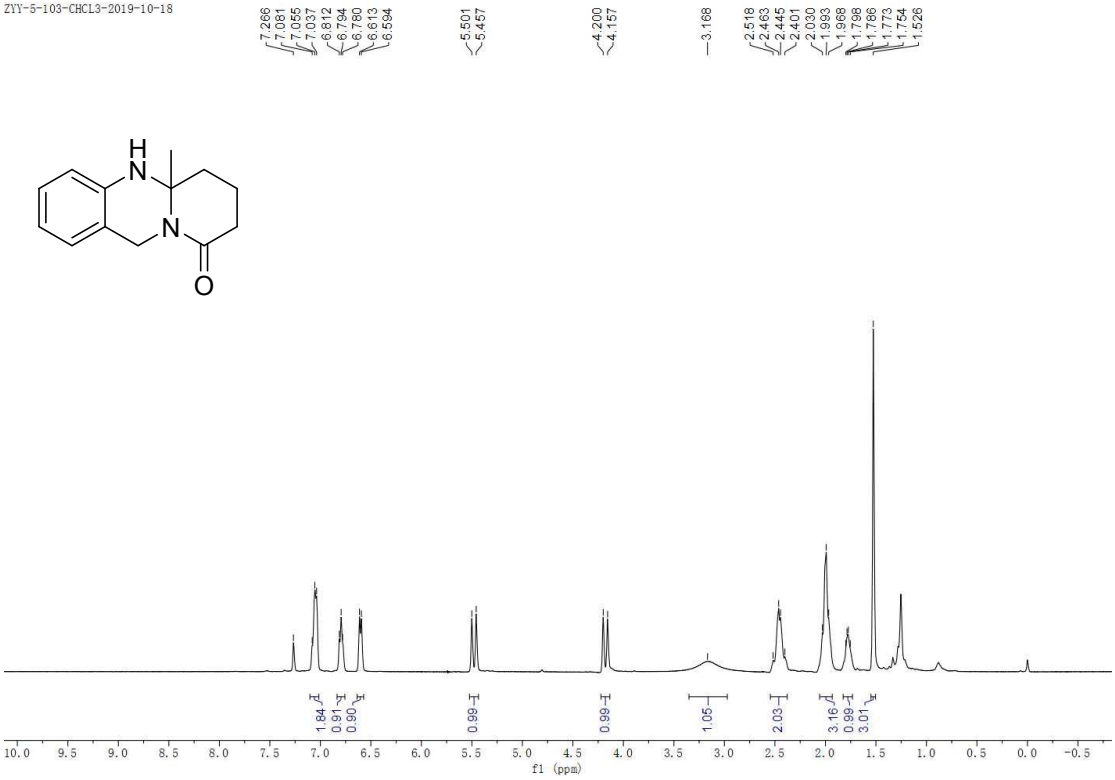
[1]H-NMR spectrum of compound 4oa (400 MHz, $CDCl_3$)



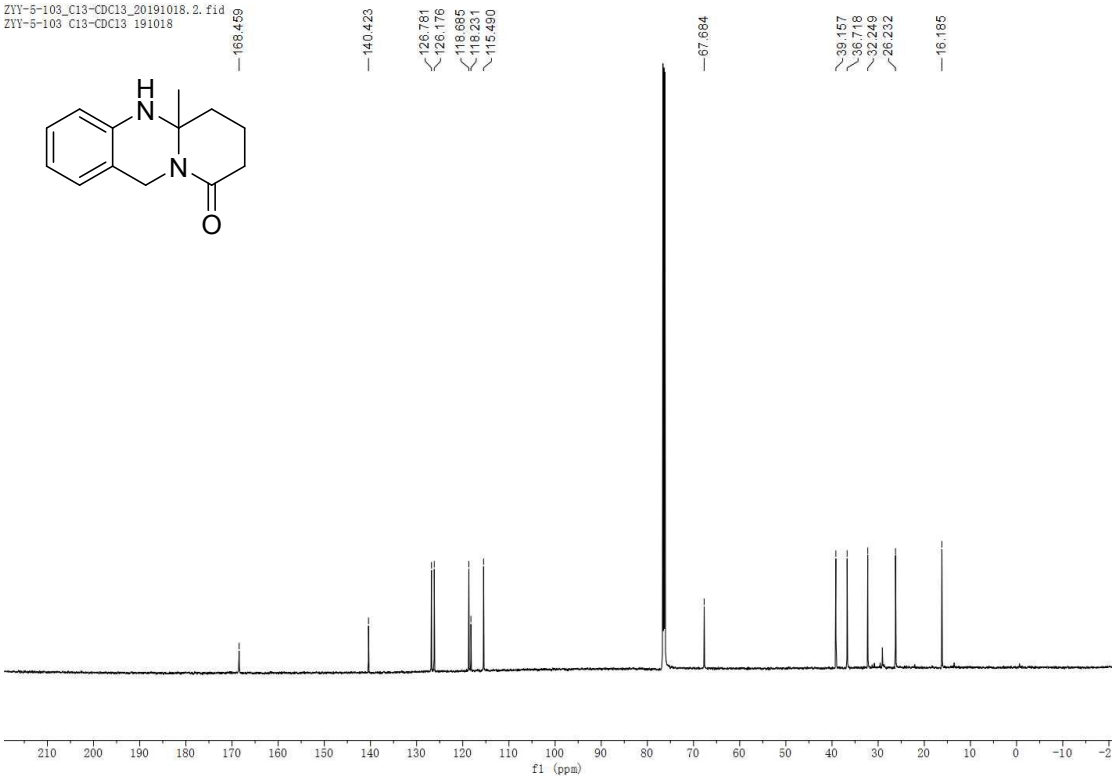
[13]C-NMR spectrum of compound 4oa (150 MHz, $CDCl_3$)



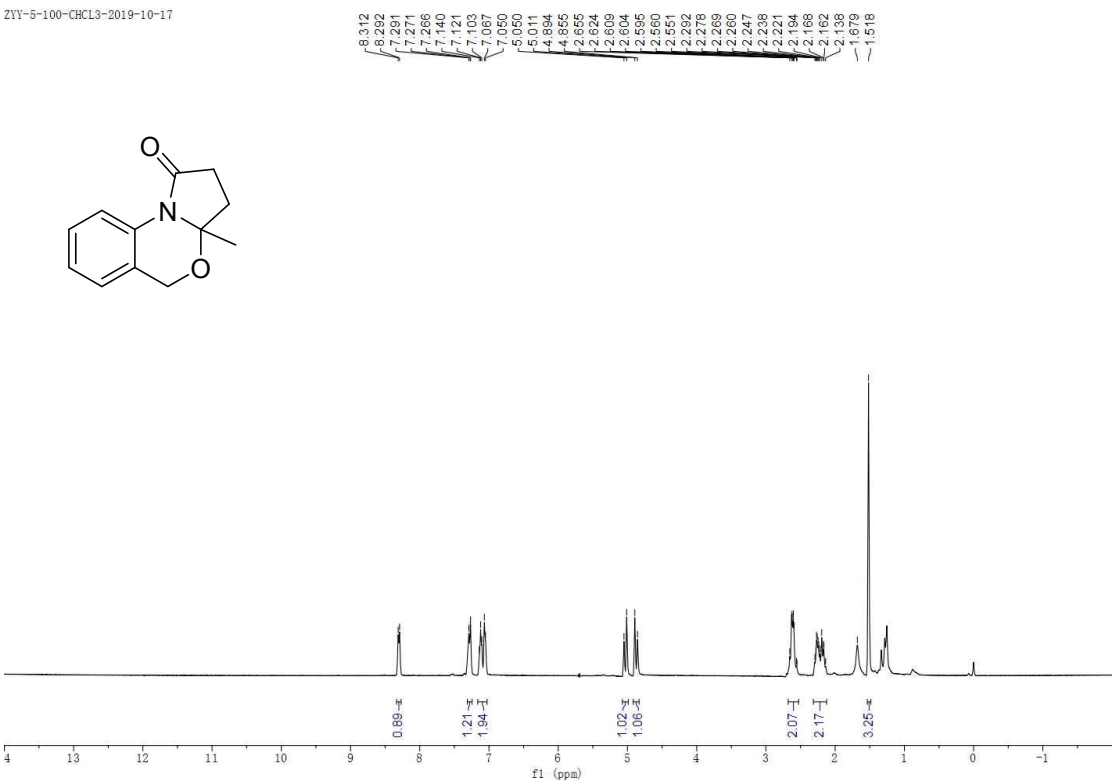
[1]H-NMR spectrum of compound 4ob (400 MHz, $CDCl_3$)



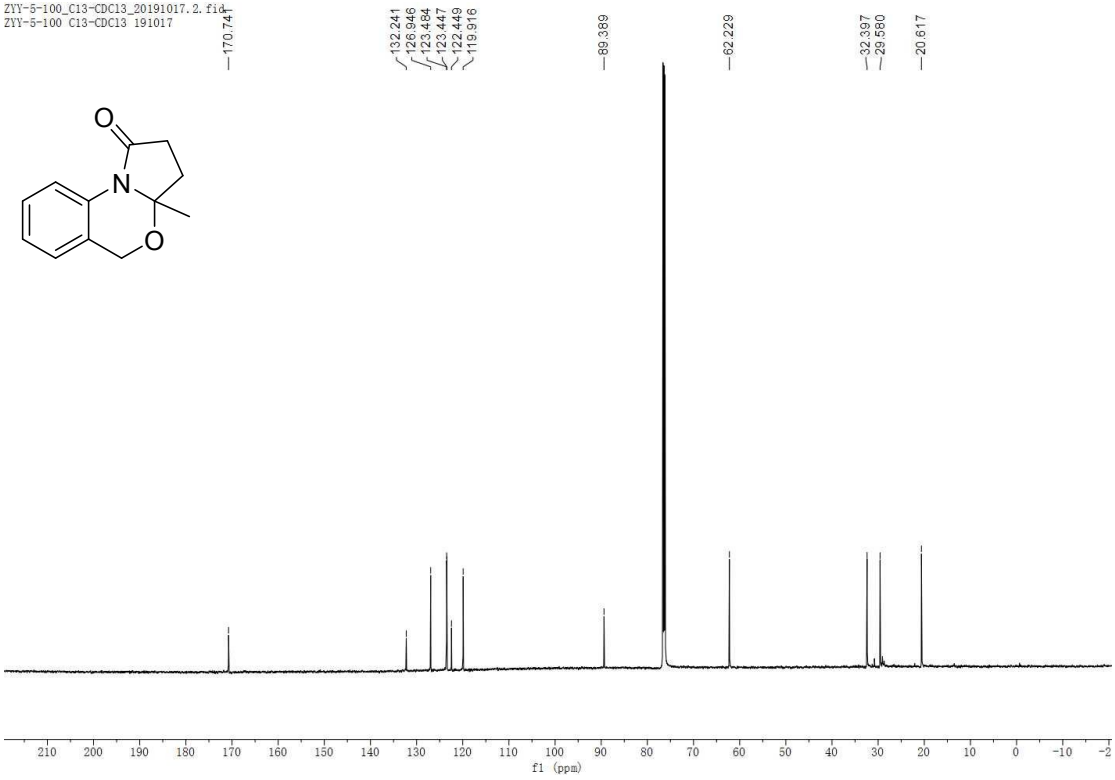
[13]C-NMR spectrum of compound 4ob (150 MHz, $CDCl_3$)



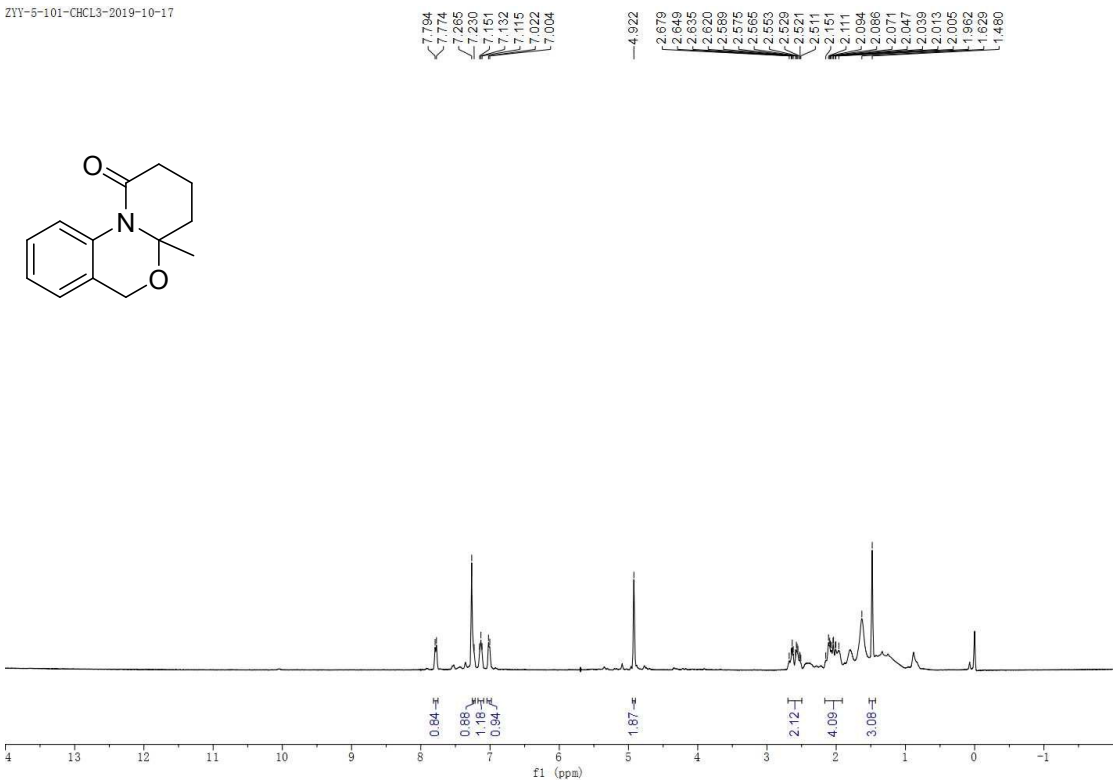
[1]H-NMR spectrum of compound 4pa (400 MHz, $CDCl_3$)



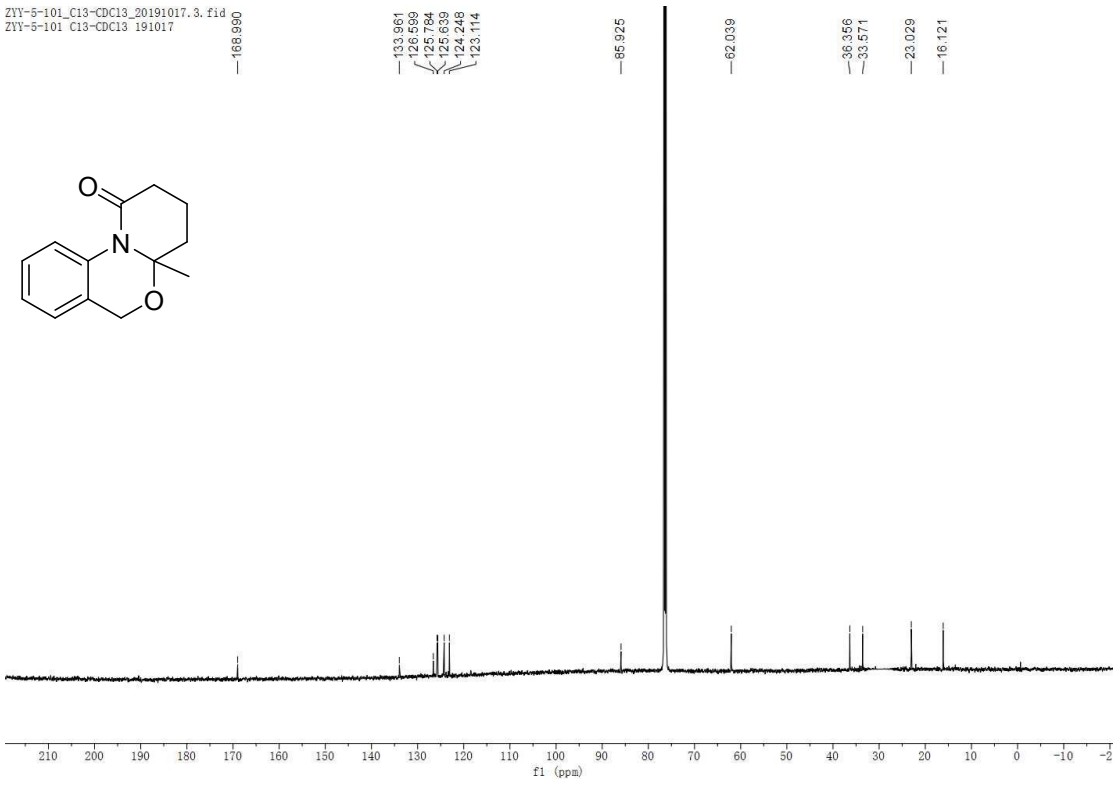
[13]C-NMR spectrum of compound 4pa (150 MHz, $CDCl_3$)



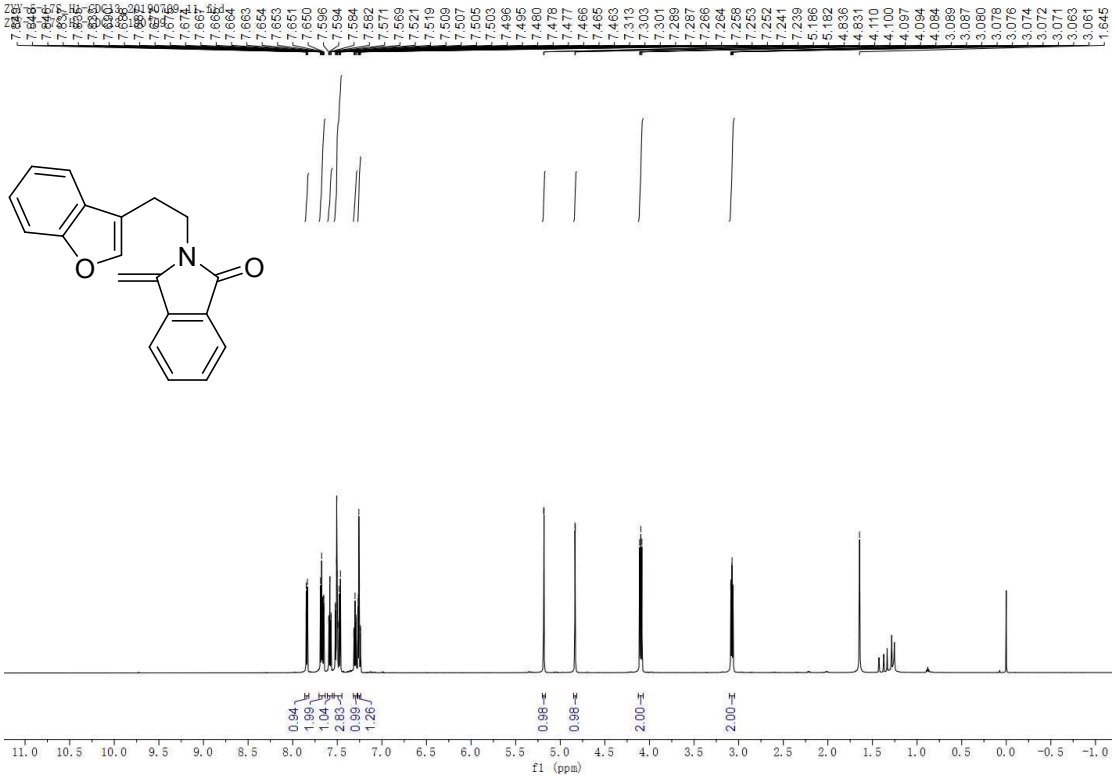
[1]H-NMR spectrum of compound 4pb (400 MHz, $CDCl_3$)



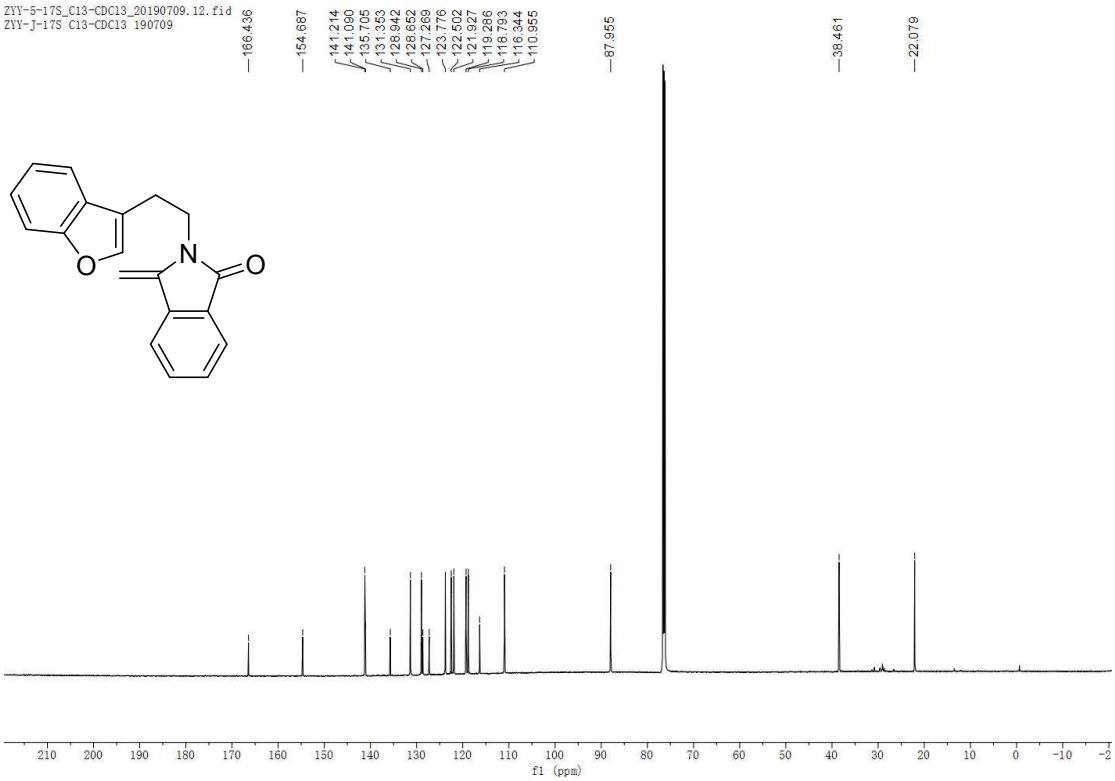
[13]C-NMR spectrum of compound 4pb (150 MHz, $CDCl_3$)



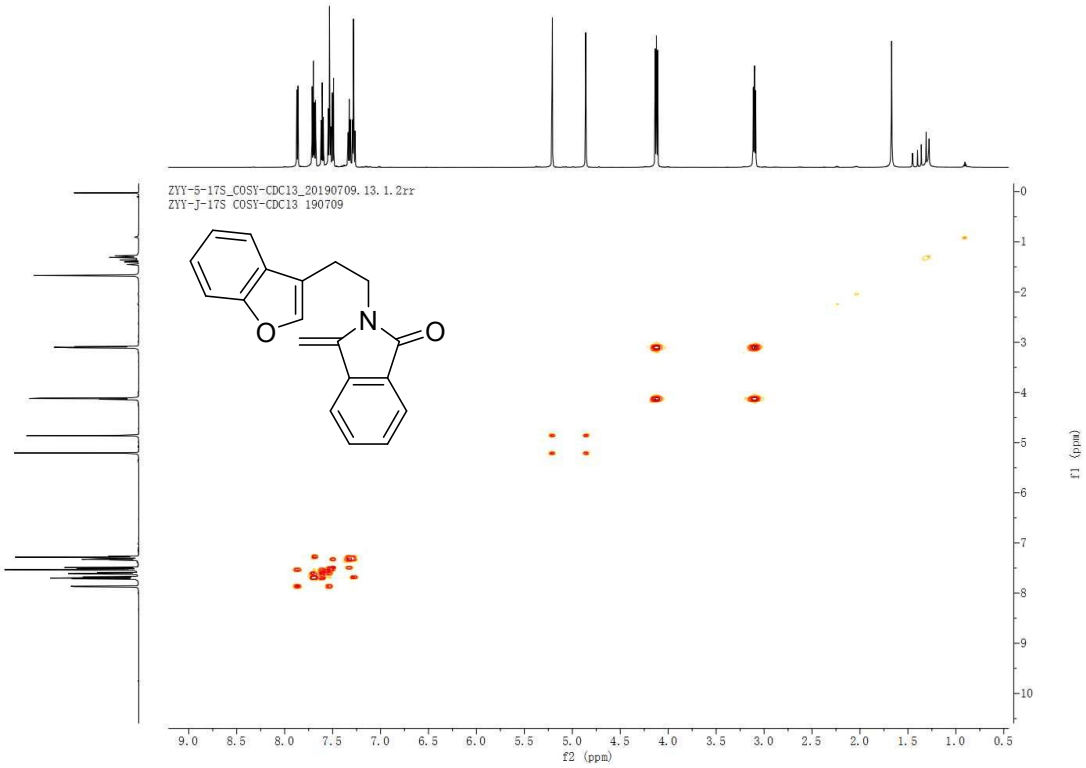
^{1}H-NMR spectrum of compound 4af' (600 MHz, $CDCl_3$)



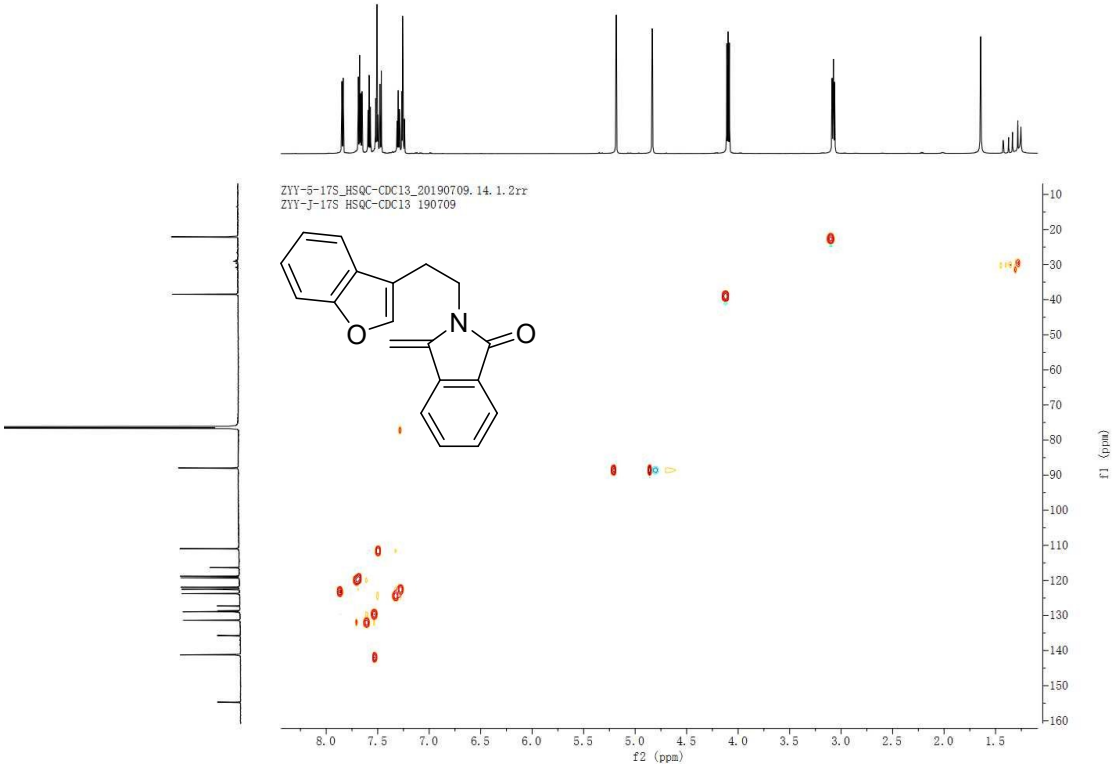
^{13}C-NMR spectrum of compound 4af' (150 MHz, $CDCl_3$)



^{1}H-^{1}H COSY spectrum of compound 4af' (600 MHz, $CDCl_3$)



HSQC spectrum of compound 4af' (600 MHz, $CDCl_3$)



HMBC spectrum of compound 4af' (600 MHz, $CDCl_3$)