Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Intramolecular Trapping of an Iminium Salt: Rapid Construction of Quindoline Derivatives

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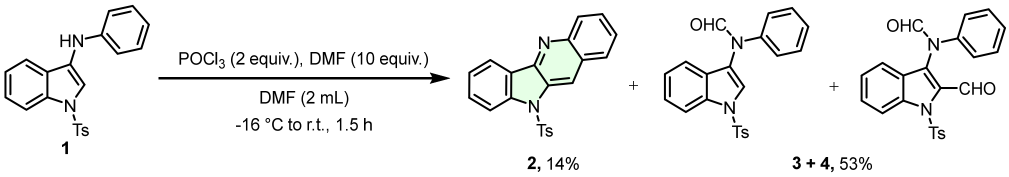
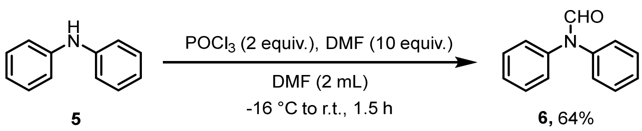
1. Supplementary Notes

Unless otherwise noted, reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh).

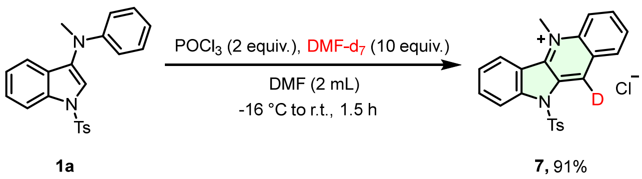
2. Supplementary Discussion



Slowly drop phosphorus oxychloride (4.69 mmol, 436.0 µL) into dry DMF (3.0 ml) at -16 ° C, stir for 0.5 h. Drop it into **1** (2.34 mmol, 850 mg) dissolved in DMF (3.0 ml) at 0 °C, then react at room temperature for 1 h. After the reaction, pour the reaction solution into ice water, stir to precipitate yellow solid, add 10% sodium hydroxide solution, adjust the pH to about 10, stand for 1 h and then filter to obtain green powder. The resulting residue was purified by column chromatography on silica gel with petroleum ether/EtOAc as the eluent to afford the product **2**, **3** and **4**.



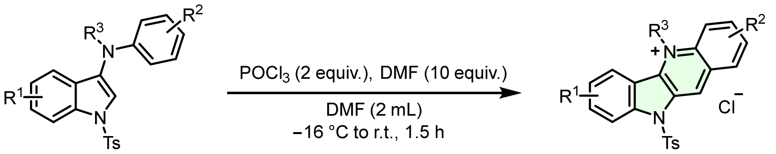
Slowly drop phosphorus oxychloride (10.0 mmol, 930.0 µL) into dry DMF (5.0 ml) at -16 ° C, stir for 0.5 h. Drop it into **5** (5.0 mmol, 846 mg) dissolved in DMF (5.0 ml) at 0 °C, then react at room temperature for 1 h. After the reaction, pour the reaction solution into ice water, stir to precipitate yellow solid, add 10% sodium hydroxide solution, adjust the pH to about 10, stand for 1 h and then filter to obtain white powder **6** in 64% yield.



Slowly drop phosphorus oxychloride (1.0 mmol, 94.0 µL) into dry DMF (0.5 ml) at -16 ° C, stir for 0.5 h. Drop it into **1a** (0.5 mmol, 188.0 mg) dissolved in DMF (0.5 ml) at 0 °C, then react at room temperature for 1 h. After the reaction, pour the reaction solution into ice water, stir to precipitate yellow solid, add 10% sodium hydroxide solution, adjust the pH to about 10, stand for 1 h and then filter to obtain yellow powder **7** in 91% yield.

3. Supplementary Methods

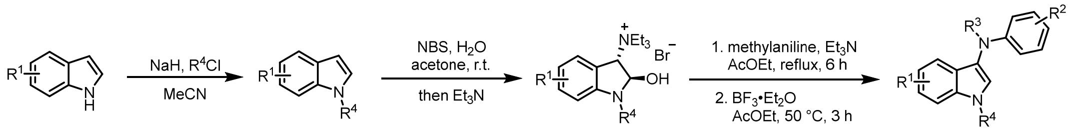
3.1 General procedure for the synthesis of 2.



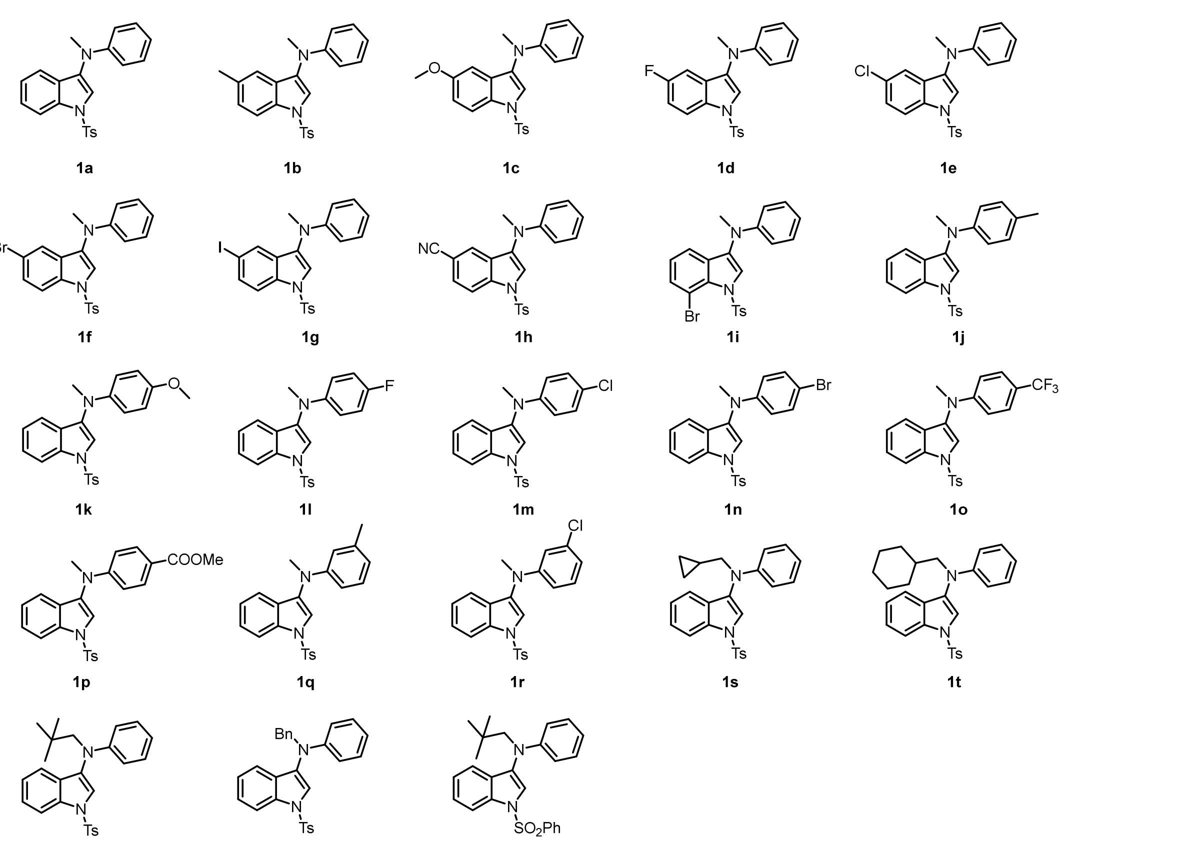
1 2

Slowly drop phosphorus oxychloride (2.0 mmol, 186.0 μL) into dry DMF (1.0 ml) at -16 ° C, stir for 0.5 h. Drop it into **1** (1.0 mmol) dissolved in DMF (1.0 ml) at 0 °C, then react at room temperature for 1 h. After the reaction, pour the reaction solution into ice water, stir to precipitate yellow solid, add 10% sodium hydroxide solution, adjust the pH to about 10, stand for 1 h and then filter to obtain yellow powder.

3.2 General procedure for the synthesis of 1[1].



A B C 1



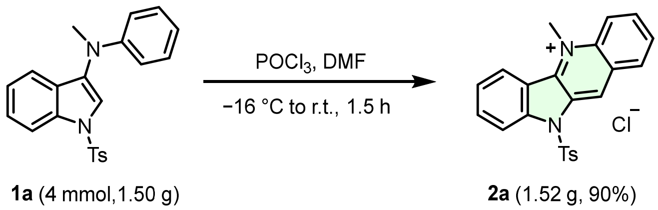
1a 1b 1c 1d 1e 1f 1g 1h 1i 1j 1k 1l 1m 1n 1o 1p 1q 1r 1s 1t 1u 1v 1w

Synthesis of intermediate **B**: dissolve indole (3.51 g, 30 mmol) in acetonitrile (30 ml), slowly add 60% sodium hydride (1.01 g, 40 mmol) in batches at 0 ° C, stir for 10 min and return to room temperature, add *p*-methylbenzene sulfonyl chloride (6.29 g, 33 mmol) until the reaction is completed. Add saturated ammonium chloride aqueous solution to quench the reaction, extract with ethyl acetate and combine the organic phase, Intermediate **B** was obtained by washing with saturated salt water, drying with anhydrous sodium sulfate, distillation under reduced pressure and purification by column chromatography.

Synthesis of intermediate **C**: dissolve intermediate **B** (2.98 g, 11 mmol) and high-purity water (110 mmol) in acetone (110 ml), add NBS (2.14 g, 12 mmol) until the reaction is completed. Add triethylamine (12 mmol) and stir for 1 h to precipitate a large amount of white solid, filter, wash the solid with acetone for several times and dry it.

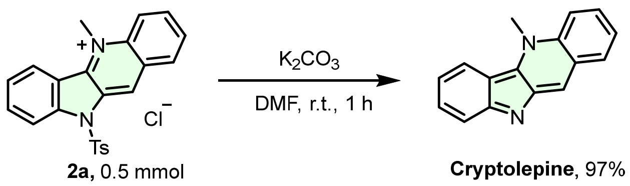
Synthesis of **1**: dissolve intermediate **C** (2.35 g, 5 mmol), *N*-methylaniline (5.5 mmol) and triethylamine (10 mmol) in ethyl acetate (100 ml), heat and reflux for 6 hours. After the reaction, add water and extract with ethyl acetate, combine the organic phase, wash with saturated salt water, dry with anhydrous sodium sulfate, distill under reduced pressure, then dissolve in ethyl acetate, and add boron trifluoride ether (25 mmol) solution, react at 50 ° C for 3 h. Cool to room temperature after the reaction, slowly add saturated sodium bicarbonate solution, extract with ethyl acetate, combine the organic phase, wash with saturated salt aqueous solution, dry anhydrous sodium sulfate, distill under reduced pressure, and purify by column chromatography to obtain the product **1**.

3.3 General procedure for the gram-scale reaction of 2a



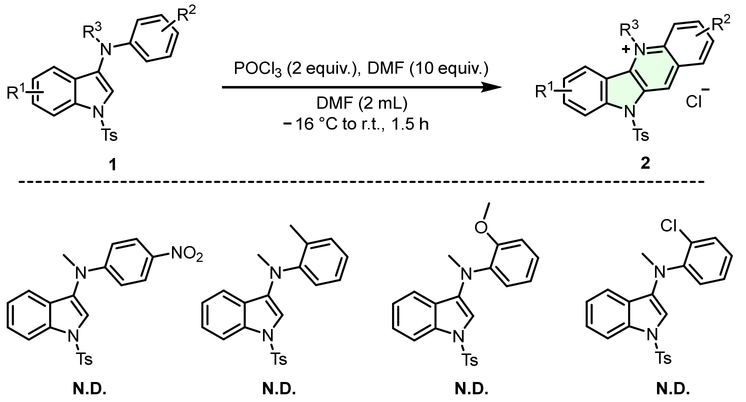
Slowly drop phosphorus oxychloride (8.0 mmol, 745.0 µL) into dry DMF (4.0 ml) at -16 ° C, stir for 0.5 h. Drop it into **1a** (4.0 mmol, 1.50 g) dissolved in DMF (4.0 ml) at 0 °C, then react at room temperature for 1 h. After the reaction, pour the reaction solution into ice water, stir to precipitate yellow solid, add 10% sodium hydroxide solution, adjust the pH to about 10, stand for 1 h and then filter to obtain **2a** in 90% yield.

3.4 General procedure for the Synthesis of cryptolepine[1]



Dissolve **2a** (0.5 mmol, 211 mg) in DMF (5 mL), add potassium carbonate (1.0 mmol, 138 mg), and react at room temperature for 1 h. The reaction mixture was diluted with 5 mL of EtOAc and extracted with three portions of EtOAc. The combined organic phases were concentrated in vacuo, and the resulting residue was purified by column chromatography on silica gel with DCM/MeOH as the eluent to afford the desired product cryptolepine in 97% yield.

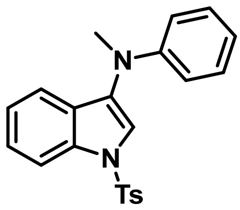
3.5 Unsuccessful substrates for the reaction



4. Supplementary Data

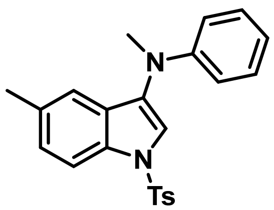
4.1 Characterization Data for Reactants 1.

***N*-methyl-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1a)**



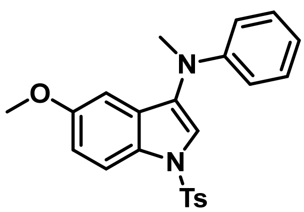
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.34 (s, 1H), 7.29 (t, J = 7.8 Hz, 1H), 7.24 – 7.17 (m, 4H), 7.07 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 7.9 Hz, 1H), 6.88 (t, J = 7.3 Hz, 1H), 6.80 (d, J = 7.8 Hz, 2H), 3.32 (s, 3H), 2.35 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 148.5, 144.9, 135.0, 134.9, 132.9, 129.8, 129.0, 127.2, 126.8, 125.1, 123.0, 120.6, 120.4, 117.8, 117.1, 114.2, 41.8, 21.6.

***N*,5-dimethyl-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1b)**



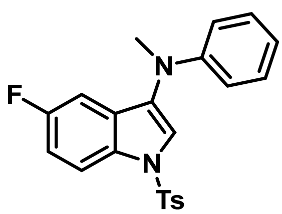
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 – 7.89 (m, 1H), 7.74 (t, J = 6.7 Hz, 2H), 7.32 (d, J = 5.6 Hz, 1H), 7.27 – 7.16 (m, 4H), 7.16 – 7.09 (m, 1H), 6.87 (d, J = 6.6 Hz, 1H), 6.84 – 6.73 (m, 3H), 3.32 (s, 3H), 2.36 (s, 3H), 2.28 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 148.6, 144.8, 134.9, 132.8, 132.7, 129.8, 129.2, 129.0, 127.6, 126.8, 126.5, 120.2, 119.9, 118.2, 117.0, 114.0, 112.7, 77.4, 77.1, 76.7, 41.5, 21.6, 21.3.

5-methoxy-*N*-methyl-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1c)



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, J = 9.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.29 (s, 1H), 7.22 – 7.16 (m, 4H), 6.92 – 6.85 (m, 2H), 6.77 (d, J = 7.7 Hz, 2H), 6.39 (d, J = 2.5 Hz, 1H), 3.60 (s, 3H), 3.31 (s, 3H), 2.35 (s, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 156.1, 148.4, 144.7, 134.8, 133.1, 129.7, 129.7, 129.0, 128.4, 126.8, 120.2, 118.3, 117.5, 115.3, 114.1, 102.7, 55.5, 41.6, 21.6.

5-fluoro-*N*-methyl-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1d)

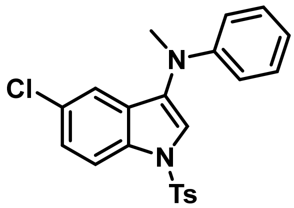


^{1}**H NMR (400 MHz, CDCl$_3$)** δ 8.01 – 7.94 (m, 1H), 7.73 (d, J = 7.8 Hz, 2H), 7.36 (s, 1H), 7.24 – 7.16 (m, 4H), 7.00 (t, J = 9.0 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.77 (d, J = 8.1 Hz, 2H), 6.61 (d, J = 8.7 Hz, 1H), 3.29 (d, J = 2.3 Hz, 3H), 2.35 (s, 3H).

^{13}**C NMR (100 MHz, CDCl$_3$)** δ 148.2, 145.1, 134.6, 131.3, 129.9, 129.1, 126.8, 120.8, 118.7, 117.9, 115.5, 115.4, 113.3, 113.0, 106.4, 106.2, 41.8, 21.6.

^{19}**F NMR (376 MHz, CDCl$_3$)** δ -118.91 – -119.12 (m).

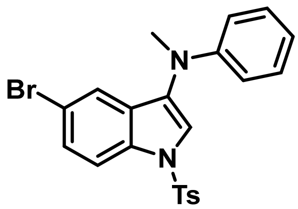
5-chloro-*N*-methyl-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1e)



^{1}**H NMR (400 MHz, CDCl$_3$)** δ 7.97 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.38 (s, 1H), 7.23 – 7.14 (m, 5H), 6.96 (d, J = 1.9 Hz, 1H), 6.86 (t, J = 7.3 Hz, 1H), 6.76 (d, J = 7.9 Hz, 2H), 3.27 (s, 3H), 2.28 (s, 3H).

^{13}**C NMR (100 MHz, CDCl$_3$)** δ 148.3, 145.3, 134.7, 133.4, 132.4, 130.0, 129.2, 129.1, 128.6, 126.9, 125.5, 120.7, 120.2, 118.8, 117.7, 115.5, 41.8, 21.7.

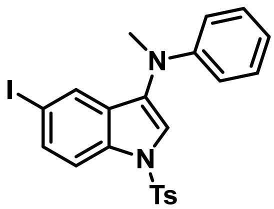
5-bromo-*N*-methyl-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1f)



^{1}**H NMR (400 MHz, CDCl$_3$)** δ 7.91 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.23 – 7.16 (m, 4H), 7.13 (d, J = 1.8 Hz, 1H), 6.88 (t, J = 7.3 Hz, 1H), 6.76 (d, J = 7.9 Hz, 2H), 3.28 (s, 3H), 2.32 (s, 3H).

^{13}**C NMR (100 MHz, CDCl$_3$)** δ 148.2, 145.3, 134.6, 133.7, 132.2, 130.0, 129.2, 129.1, 128.1, 126.9, 123.1, 120.6, 118.7, 117.5, 116.7, 115.8, 77.5, 77.2, 76.9, 41.7, 21.7.

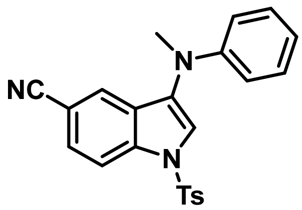
5-iodo-*N*-methyl-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1g)



^{1}**H NMR (400 MHz, CDCl$_3$)** δ 7.80 (d, J = 8.7 Hz, 1H), 7.73 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.7 Hz, 1H), 7.33 (d, J = 13.5 Hz, 2H), 7.24 – 7.16 (m, 4H), 6.88 (t, J = 7.3 Hz, 1H), 6.75 (d, J = 8.1 Hz, 2H), 3.28 (s, 3H), 2.33 (s, 3H).

^{13}**C NMR (100 MHz, CDCl$_3$)** δ 148.2, 145.3, 134.6, 134.2, 133.7, 131.9, 130.0, 129.6, 129.2, 129.2, 126.9, 120.5, 118.5, 117.3, 116.1, 87.5, 41.7, 21.7.

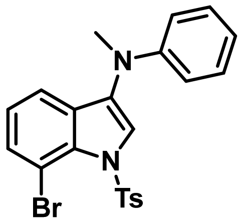
3-(methyl(phenyl)amino)-1-tosyl-1*H*-indole-5-carbonitrile (1h)



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, J = 8.7 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.38 – 7.32 (m, 1H), 7.24 (s, 1H), 7.11 (d, J = 8.2 Hz, 2H), 7.08 – 7.04 (m, 2H), 6.81 (t, J = 7.4 Hz, 1H), 6.69 – 6.63 (m, 2H), 3.16 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 148.0, 145.7, 136.5, 134.5, 132.6, 130.2, 129.3, 128.0, 126.9, 126.9, 125.7, 121.8, 119.2, 118.9, 117.6, 114.9, 106.4, 42.3, 21.7.

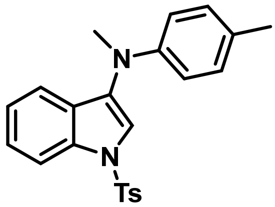
7-bromo-*N*-methyl-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1i)



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 – 7.67 (m, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.23 – 7.14 (m, 4H), 7.11 – 7.04 (m, 2H), 6.71 – 6.61 (m, 3H), 6.30 (d, J = 0.6 Hz, 1H), 3.40 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 143.1, 137.3, 137.1, 136.7, 134.4, 133.4, 132.8, 132.0, 128.6, 128.3, 127.7, 125.9, 124.6, 121.7, 120.6, 119.6, 109.4, 103.1, 30.8, 21.5.

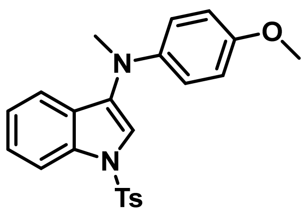
***N*-methyl-*N*-(p-tolyl)-1-tosyl-1*H*-indol-3-amine (1j)**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, J = 4.9 Hz, 1H), 7.74 (d, J = 4.2 Hz, 2H), 7.24 (d, J = 9.5 Hz, 2H), 7.17 (d, J = 4.5 Hz, 2H), 7.04 – 6.97 (m, 3H), 6.93 – 6.87 (m, 1H), 6.79 – 6.71 (m, 2H), 3.26 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 146.3, 144.8, 135.2, 134.9, 133.8, 130.8, 129.8, 129.7, 127.1, 126.8, 125.0, 122.9, 120.9, 119.3, 115.2, 114.3, 42.5, 21.6, 20.7.

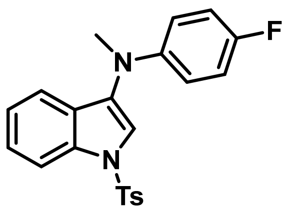
***N*-(4-methoxyphenyl)-*N*-methyl-1-tosyl-1*H*-indol-3-amine (1k)**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.23 (t, J = 7.8 Hz, 1H), 7.19 – 7.14 (m, 3H), 6.97 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 9.0 Hz, 2H), 6.79 – 6.74 (m, 3H), 3.74 (s, 3H), 3.22 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 155.4, 144.7, 142.4, 135.3, 134.8, 134.6, 129.7, 126.8, 126.7, 124.9, 122.8, 122.7, 121.0, 114.4, 114.2, 112.6, 55.5, 43.4, 21.6.

***N*-(4-fluorophenyl)-*N*-methyl-1-tosyl-1*H*-indol-3-amine (1l)**

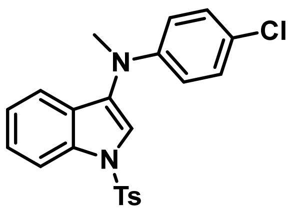


^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 6.7 Hz, 2H), 7.29 (d, J = 1.7 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 7.0 Hz, 2H), 7.00 (t, J = 7.4 Hz, 1H), 6.86 (t, J = 7.2 Hz, 3H), 6.82 – 6.75 (m, 2H), 3.24 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 159.2, 156.8, 145.0, 145.0, 145.0, 135.2, 134.8, 133.5, 130.0, 126.9, 126.8, 126.8, 125.2, 123.1, 120.7, 115.8, 115.6, 115.5, 115.4, 114.4, 114.3, 42.8, 42.7, 21.6.

^{19}F NMR (376 MHz, CDCl$_3$) δ -122.29 – -122.36 (m).

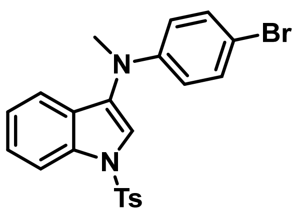
***N*-(4-chlorophenyl)-*N*-methyl-1-tosyl-1*H*-indol-3-amine (1m)**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 7.0 Hz, 2H), 7.37 (d, J = 1.3 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.13 – 7.06 (m, 3H), 6.99 (d, J = 7.8 Hz, 1H), 6.68 (d, J = 7.1 Hz, 2H), 3.29 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 147.1, 145.1, 134.9, 134.8, 132.3, 129.9, 128.9, 126.9, 126.8, 125.3, 124.9, 123.2, 120.4, 118.3, 118.0, 114.3, 114.2, 41.8, 21.7.

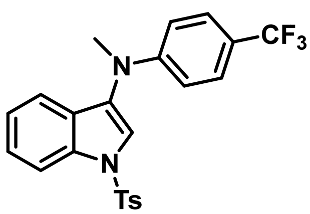
***N*-(4-bromophenyl)-*N*-methyl-1-tosyl-1*H*-indol-3-amine (1n)**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.38 (s, 1H), 7.33 – 7.28 (m, 1H), 7.26 (d, J = 2.1 Hz, 1H), 7.24 (d, J = 1.9 Hz, 2H), 7.21 (s, 1H), 7.12 – 7.08 (m, 1H), 7.01 (d, J = 7.9 Hz, 1H), 6.65 – 6.60 (m, 2H), 3.30 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 147.5, 145.1, 134.8, 134.8, 132.0, 131.8, 129.9, 126.9, 126.9, 125.3, 123.2, 120.3, 118.5, 118.3, 114.3, 112.1, 41.6, 21.7.

***N*-methyl-1-tosyl-*N*-(4-(trifluoromethyl)phenyl)-1*H*-indol-3-amine (1o)**

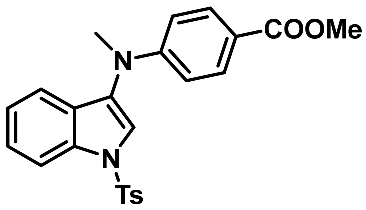


^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.50 (s, 1H), 7.41 – 7.32 (m, 3H), 7.26 (d, J = 7.3 Hz, 2H), 7.19 – 7.10 (m, 2H), 6.71 (d, J = 8.4 Hz, 2H), 3.38 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 150.9, 145.2, 134.9, 134.7, 130.8, 130.0, 127.0, 126.9, 126.3, 126.2, 125.4, 123.4, 120.7, 119.9, 114.3, 114.1, 40.9, 21.6.

^{19}F NMR (376 MHz, CDCl$_3$) δ -61.13 (s).

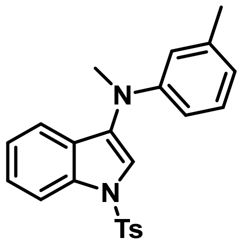
methyl 4-(methyl(1-tosyl-1*H*-indol-3-yl)amino)benzoate (1p)



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.7 Hz, 2H), 7.79 (d, J = 8.1 Hz, 2H), 7.53 (s, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 7.8 Hz, 2H), 7.13 (s, 2H), 6.65 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H), 3.39 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 162.4, 147.3, 140.5, 130.2, 129.9, 126.3, 125.9, 125.3, 122.4, 122.1, 120.7, 118.7, 116.4, 115.1, 114.9, 109.5, 108.8, 46.9, 36.1, 16.9.

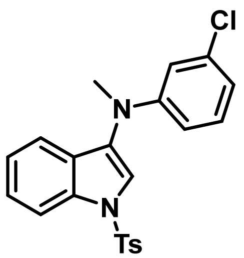
***N*-methyl-*N*-(m-tolyl)-1-tosyl-1*H*-indol-3-amine (1q)**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 7.2 Hz, 2H), 7.33 (d, J = 1.1 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 7.7 Hz, 2H), 7.08 – 6.96 (m, 3H), 6.69 (d, J = 7.4 Hz, 1H), 6.63 (s, 1H), 6.59 (d, J = 8.1 Hz, 1H), 3.27 (s, 3H), 2.26 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 148.7, 144.9, 138.8, 135.1, 135.0, 133.3, 129.9, 128.9, 127.4, 126.9, 125.1, 123.1, 121.5, 120.7, 118.6, 117.1, 115.1, 114.3, 41.9, 21.7, 21.6.

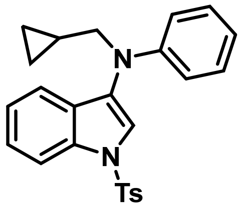
***N*-(3-chlorophenyl)-*N*-methyl-1-tosyl-1*H*-indol-3-amine (1r)**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.43 (s, 1H), 7.34 – 7.28 (m, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.14 – 7.08 (m, 2H), 7.05 (t, J = 8.1 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 6.70 (t, J = 2.1 Hz, 1H), 6.61 – 6.56 (m, 1H), 3.29 (s, 3H), 2.32 (s, 3H).

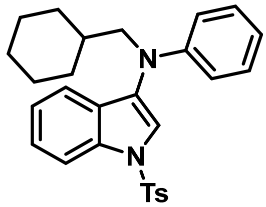
^{13}C NMR (100 MHz, CDCl$_3$) δ 149.8, 145.1, 134.9, 134.9, 134.8, 131.7, 130.0, 127.2, 126.8, 125.3, 123.4, 120.0, 119.7, 119.2, 115.8, 114.3, 114.0, 41.1, 21.6.

***N*-(cyclopropylmethyl)-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1s)**



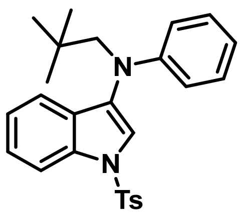
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.40 (s, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 7.9 Hz, 2H), 7.09 (t, J = 7.9 Hz, 2H), 7.02 – 6.95 (m, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 7.8 Hz, 2H), 3.47 (d, J = 6.5 Hz, 2H), 2.27 (s, 3H), 1.22 (s, 1H), 1.11 – 1.00 (m, 1H), 0.83 (t, J = 6.2 Hz, 1H), 0.34 (d, J = 8.0 Hz, 2H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 148.1, 145.0, 135.1, 135.0, 131.5, 129.9, 129.0, 128.0, 126.9, 125.1, 123.2, 120.5, 119.8, 119.5, 116.9, 114.3, 57.7, 21.6, 9.8, 4.0.

***N*-(cyclohexylmethyl)-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1t)**



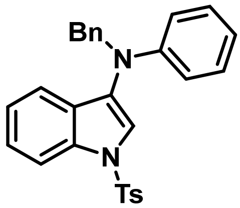
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, J = 8.3 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.34 (d, J = 2.4 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 7.2 Hz, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 7.9 Hz, 1H), 6.81 (t, J = 7.3 Hz, 1H), 6.71 (d, J = 7.6 Hz, 2H), 3.52 – 3.45 (m, 2H), 2.35 (s, 3H), 1.78 (d, J = 13.2 Hz, 2H), 1.68 (d, J = 7.7 Hz, 4H), 1.13 (t, J = 7.9 Hz, 3H), 0.97 – 0.87 (m, 2H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 148.5, 144.8, 135.2, 134.9, 131.8, 129.8, 128.9, 127.7, 126.8, 125.0, 123.1, 120.7, 119.6, 118.7, 117.4, 114.4, 60.9, 36.6, 31.4, 26.6, 26.0, 21.6.

***N*-neopentyl-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1u)**



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.3 Hz, 2H), 7.46 (s, 1H), 7.31 – 7.26 (m, 1H), 7.19 (d, J = 8.2 Hz, 2H), 7.11 – 7.03 (m, 4H), 6.77 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 8.0 Hz, 2H), 3.59 (s, 2H), 2.34 (s, 3H), 0.88 (s, 9H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 149.8, 144.9, 135.1, 135.0, 132.8, 129.8, 128.7, 128.1, 126.8, 125.1, 123.3, 120.6, 120.5, 119.0, 116.4, 114.3, 66.0, 34.7, 28.6, 21.6.

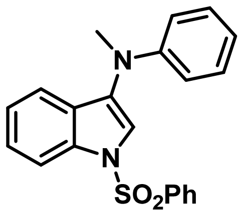
***N*-benzyl-*N*-phenyl-1-tosyl-1*H*-indol-3-amine (1v)**



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.33 – 7.30 (m, 3H), 7.27 – 7.19 (m, 4H), 7.14 – 7.09 (m, 2H), 7.05 – 7.00 (m, 4H), 6.86 – 6.80 (m, 3H), 4.89 (s, 2H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 148.1, 144.8, 138.6, 135.1, 134.7, 131.1, 129.9, 129.2, 128.8, 127.5, 127.2, 126.9, 126.8, 125.2, 123.2, 120.8, 120.6, 118.6, 118.1, 114.4, 58.2, 21.7.

***N*-methyl-*N*-phenyl-1-(phenylsulfonyl)-1*H*-indol-3-amine (1w)**

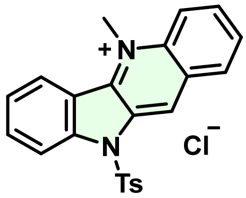


^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.7 Hz, 2H), 7.24 (s, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.08 (t, J = 7.6 Hz, 2H), 6.96 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.9 Hz, 1H), 6.79 (t, J = 7.0 Hz, 1H), 6.70 (d, J = 8.3 Hz, 2H), 3.21 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 148.5, 137.8, 135.1, 133.8, 133.2, 129.2, 129.1, 127.2, 126.8, 125.2, 123.2, 120.7, 120.6, 118.0, 116.9, 114.3, 41.9.

4.2 Characterization Data for Products 2.

5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2a)



Reaction was conducted following the *general procedure*. yellow solid (393.0 mg, 93% yield).

Rf = 0.4 (DCM /MeOH = 10:1);

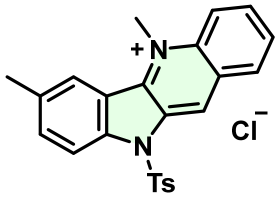
M. p. = 148-149 °C;

^{1}H NMR (400 MHz, DMSO) *δ* 9.98 (d, *J* = 10.7 Hz, 1H), 8.96 – 8.84 (m, 3H), 8.56 – 8.46 (m, 1H), 8.34 – 8.27 (m, 1H), 8.16 – 8.04 (m, 4H), 7.81 – 7.75 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 5.03 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, DMSO) *δ* 147.5, 142.1, 137.6, 136.0, 135.2, 133.0, 131.7, 131.6, 131.1, 129.1, 128.3, 127.7, 127.4, 126.3, 118.9, 118.2, 115.2, 41.7, 21.5.

HRMS (ESI): m/z calcd for $C_{23}H_{19}N_2O_2S^+$ ($[M-Cl]^+$) : 387.1162, found 387.1160.

5,7-dimethyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2b)



Reaction was conducted following the *general procedure*. yellow solid (402.0 mg, 92% yield)

Rf = 0.4 (DCM /MeOH = 10:1);

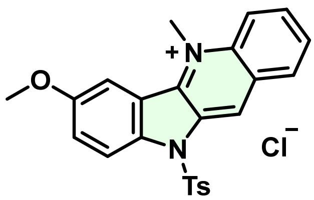
M. p. = 151-152 °C;

^{1}H NMR (400 MHz, DMSO) *δ* 9.98 (s, 1H), 8.84 (d, *J* = 8.8 Hz, 2H), 8.71 (s, 1H), 8.46 (d, *J* = 8.7 Hz, 1H), 8.34 – 8.25 (m, 1H), 8.12 – 8.01 (m, 3H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 4.96 (s, 3H), 2.60 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, DMSO) *δ* 147.4, 142.3, 140.6, 137.6, 137.2, 136.2, 135.1, 133.0, 132.0, 131.7, 131.0, 129.1, 129.0, 128.5, 127.7, 127.4, 126.0, 118.8, 118.5, 115.1, 41.5, 21.5, 21.2.

HRMS (ESI): m/z calcd for $C_{24}H_{21}N_2O_2S^+$ ($[M-Cl]^+$) : 401.1318, found 401.1315.

7-methoxy-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2c)



Reaction was conducted following the *general procedure*. bright orange solid (448.0 mg, 99% yield).

Rf = 0.3 (DCM /MeOH = 10:1);

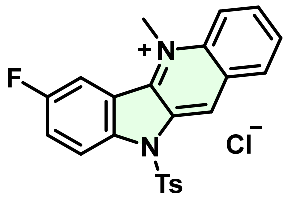
M. p. = 162-163 °C;

^{1}H NMR (400 MHz, DMSO) *δ* 9.94 (s, 1H), 8.91 – 8.82 (m, 2H), 8.42 (d, *J* = 9.3 Hz, 1H), 8.34 – 8.27 (m, 1H), 8.17 (s, 1H), 8.10 – 8.05 (m, 1H), 8.00 (d, *J* = 8.3 Hz, 2H), 7.74 – 7.68 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 5.01 (s, 3H), 4.02 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, DMSO) *δ* 157.4, 147.4, 141.9, 137.7, 136.7, 135.3, 132.9, 132.1, 131.7, 131.0, 129.4, 129.1, 127.6, 127.4, 124.5, 119.2, 118.9, 116.4, 110.1, 56.9, 41.5, 21.5.

HRMS (ESI): m/z calcd for $C_{24}H_{21}N_2O_3S^+$ ($[M\text{-}Cl]^+$) : 417.1267, found 417.1265.

7-fluoro-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2d)



Reaction was conducted following the *general procedure*. yellow solid (379.0 mg, 86% yield).

Rf = 0.3 (DCM /MeOH = 10:1);

M. p. = 160-161 °C;

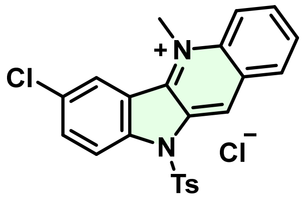
^{1}H NMR (400 MHz, DMSO) *δ* 10.04 (s, 1H), 8.92 – 8.79 (m, 3H), 8.60 (dd, *J* = 9.3, 4.3 Hz, 1H), 8.38 – 8.28 (m, 1H), 8.15 – 7.99 (m, 4H), 7.39 (d, *J* = 8.2 Hz, 2H), 4.97 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, DMSO) *δ* 147.6, 141.7, 138.6, 137.7, 135.6, 132.9, 132.3, 131.7, 131.1, 129.8, 129.3, 127.7, 123.9, 123.6, 119.4, 118.9, 117.1, 114.2, 114.0, 41.4, 21.5.

^{19}F NMR (376 MHz, DMSO) *δ* -115.23 – -115.34 (m).

HRMS (ESI): m/z calcd for $C_{23}H_{18}FN_2O_2S^+$ ($[M\text{-}Cl]^+$) : 405.1068, found 405.1066.

7-chloro-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2e)



Reaction was conducted following the *general procedure*. yellow solid (453.0 mg, 99% yield).

Rf = 0.2 (DCM /MeOH = 10:1);

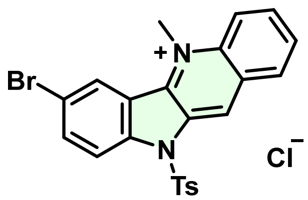
M. p. = 158-159 °C;

^{1}H NMR (400 MHz, DMSO) *δ* 10.05 (s, 1H), 8.97 (s, 1H), 8.87 (d, *J* = 8.2 Hz, 2H), 8.59 (d, *J* = 9.1 Hz, 1H), 8.36 – 8.29 (m, 1H), 8.21 – 8.04 (m, 4H), 7.40 (d, *J* = 8.1 Hz, 2H), 4.98 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, DMSO) *δ* 147.7, 141.2, 140.6, 137.7, 135.6, 135.5, 132.9, 132.1, 131.8, 131.2, 130.8, 129.8, 129.4, 127.8, 127.2, 119.8, 118.9, 116.9, 110.0, 41.6, 21.5.

HRMS (ESI): m/z calcd for $C_{23}H_{18}ClN_2O_2S^+$ ($[M\text{-}Cl]^+$) : 421.0772, found 421.0771.

7-bromo-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2f)



Reaction was conducted following the *general procedure*. yellow solid (472.0 mg, 94% yield).

Rf = 0.5 (DCM /MeOH = 10:1);

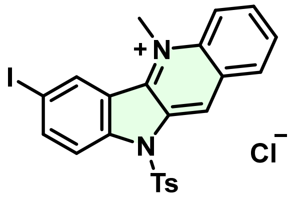
M. p. = 154-155 °C;

^{1}H NMR (400 MHz, DMSO) *δ* 10.04 (s, 1H), 9.06 (s, 1H), 8.87 (d, *J* = 8.2 Hz, 2H), 8.52 (d, *J* = 9.0 Hz, 1H), 8.35 – 8.29 (m, 1H), 8.27 (d, *J* = 9.1 Hz, 1H), 8.14 – 8.07 (m, 3H), 7.39 (d, *J* = 8.3 Hz, 2H), 4.98 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, DMSO) *δ* 147.7, 141.1, 141.0, 138.3, 137.7, 135.6, 132.9, 131.9, 131.7, 131.2, 130.0, 129.7, 129.4, 127.8, 120.2, 118.9, 118.8, 117.1, 41.7, 21.5.

HRMS (ESI): m/z calcd for $C_{23}H_{18}BrN_2O_2S^+$ ($[M-Cl]^+$) : 465.0267, found 465.0269.

7-iodo-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2g)



Reaction was conducted following the *general procedure*. orange solid (505.0 mg, 92% yield)

Rf = 0.2 (DCM /MeOH = 10:1);

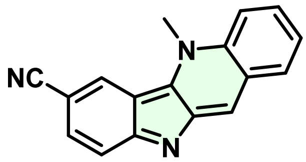
M. p. = 138-139 °C;

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 8.79 (s, 1H), 8.57 – 8.46 (m, 2H), 8.07 (t, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.30 – 7.18 (m, 3H), 4.96 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) *δ* 144.4, 142.9, 141.6, 140.0, 135.2, 134.7, 133.4, 132.7, 132.5, 129.7, 128.9, 127.3, 126.2, 126.1, 125.8, 117.5, 115.5, 114.4, 40.5, 21.4.

HRMS (ESI): m/z calcd for $C_{23}H_{18}IN_2O_2S^+$ ($[M-Cl]^+$) : 513.0128, found 513.0129.

5-methyl-5*H*-indolo[3,2-*b*]quinoline-7-carbonitrile (2h)



Reaction was conducted following the *general procedure*. faint yellow solid (237.0 mg, 92% yield).

Rf = 0.2 (DCM /MeOH = 10:1);

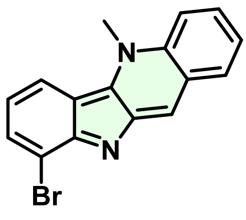
M. p. = 112-113 °C;

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 8.07 (d, *J* = 8.6 Hz, 1H), 7.88 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 3.7 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.28 (s, 1H), 6.72 (d, *J* = 3.7 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) *δ* 145.8, 136.4, 134.8, 130.7, 130.2, 128.4, 127.6, 126.9, 126.4, 119.3, 114.3, 108.5, 106.9, 21.7.

HRMS (ESI): m/z calcd for $C_{17}H_{12}N_3^+$ ($[M+H]^+$) : 258.1026, found 258.1027.

9-bromo-5-methyl-5H-indolo[3,2-b]quinoline (2i)



Reaction was conducted following the *general procedure*. faint yellow solid (298.7 mg, 96% yield).

Rf = 0.3 (DCM /MeOH = 10:1);

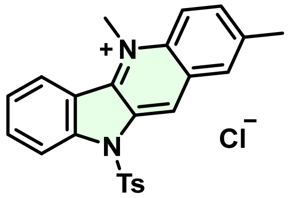
M. p. = 144-145 °C;

^{1}H NMR (400 MHz, DMSO) *δ* 9.75 (s, 1H), 8.89 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 8.22 (d, *J* = 7.5 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 1H), 4.45 (s, 3H).

^{13}C NMR (100 MHz, DMSO) *δ* 143., 141.0, 132.5, 128. 0, 126.7, 126.6, 125.5, 123.2, 121.8, 120.5, 120.4, 118.8, 115.2, 110.9, 99.5, 33.7.

HRMS (ESI): m/z calcd for $C_{16}H_{12}BrN_2^+$ ($[M+H]^+$) : 311.0178, found 311.0177.

2,5-dimethyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2j)



Reaction was conducted following the *general procedure*. chartreuse solid (424.0 mg, 97% yield).

Rf = 0.3 (DCM /MeOH = 10:1);

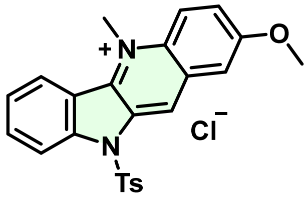
M. p. = 152-153 °C;

^{1}H NMR (400 MHz, DMSO) δ 9.88 (s, 1H), 8.86 (d, J = 8.4 Hz, 1H), 8.72 (d, J = 7.9 Hz, 1H), 8.58 (d, J = 9.2 Hz, 2H), 8.15 (d, J = 9.3 Hz, 1H), 8.13 – 8.09 (m, 1H), 8.07 (d, J = 8.0 Hz, 2H), 7.81 – 7.74 (m, 1H), 7.38 (d, J = 8.1 Hz, 2H), 4.94 (s, 3H), 2.68 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 147.5, 142.1, 141.6, 139.4, 137.2, 136.2, 135.7, 133.1, 131.9, 131.7, 131.1, 130.1, 130.0, 128.3, 128.1, 127.7, 127.7, 126.3, 118.5, 118.5, 115.4, 41.4, 21.5, 21.3.

HRMS (ESI): m/z calcd for $C_{24}H_{21}N_2O_2S^+$ ($[M-Cl]^+$) : 401.1318, found 401.1318.

2-methoxy-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2k)



Reaction was conducted following the *general procedure*. yellow solid (448.0mg, 99% yield).

Rf = 0.3 (DCM /MeOH = 10:1);

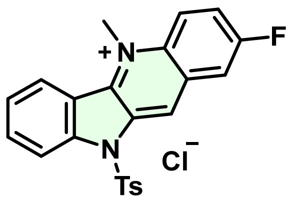
M. p. = 188-189 °C;

^{1}H NMR (400 MHz, DMSO) δ 9.86 (s, 1H), 8.84 (d, J = 8.3 Hz, 1H), 8.77 (d, J = 9.8 Hz, 1H), 8.54 (d, J = 8.6 Hz, 1H), 8.31 (d, J = 2.8 Hz, 1H), 8.06 (d, J = 8.4 Hz, 3H), 7.93 – 7.88 (m, 1H), 7.78 – 7.72 (m, 1H), 7.39 (d, J = 8.3 Hz, 2H), 4.95 (s, 3H), 4.07 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 159.0, 147.5, 141.7, 140.0, 135.3, 133.4, 133.1, 132.2, 131.1, 129.6, 127.8, 127.6, 127.4, 127.2, 126.2, 120.5, 118.5, 115.3, 109.2, 56.8, 41.7, 21.5.

HRMS (ESI): m/z calcd for $C_{24}H_{21}N_2O_3S^+$ ($[M-Cl]^+$) : 417.1267, found 417.1268.

2-fluoro-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2l)



Reaction was conducted following the *general procedure*. yellow solid (410.0mg, 93% yield).

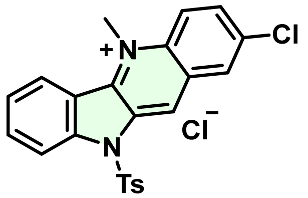
Rf = 0.3 (DCM /MeOH = 10:1);

M. p. = 153-154 °C;

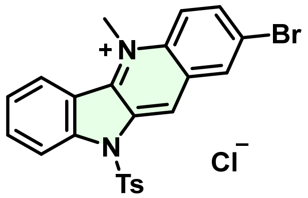
^{1}H NMR (400 MHz, DMSO) δ 10.00 (s, 1H), 8.95 (d, J = 22.6 Hz, 2H), 8.75 (s, 1H), 8.57 (d, J = 7.1 Hz, 1H), 8.27 (s, 1H), 8.10 (s, 3H), 7.79 (s, 1H), 7.41 (s, 2H), 5.00 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 147.6, 142.4, 142.3, 136.2, 134.8, 133.0, 132.6, 131.1, 128.4, 128.2, 127.8, 126.4, 124.8, 124.5, 122.4, 118.2, 115.4, 114.9, 114.7, 42.1, 21.5.

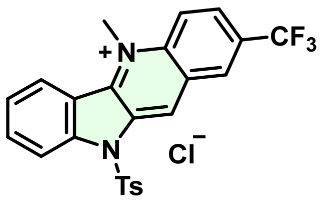
^{19}F NMR (376 MHz, DMSO) *δ* -110.17 – -110.42 (m).
HRMS (ESI): m/z calcd for $C_{23}H_{18}FN_2O_2S^+$ ($[M-Cl]^+$) : 405.1068, found 405.1068.
2-chloro-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2m)



Reaction was conducted following the *general procedure*. green solid (398.0mg, 87% yield).
Rf = 0.4 (DCM /MeOH = 10:1);
M. p. = 178-179 °C;
^{1}H NMR (400 MHz, DMSO) *δ* 9.98 (s, 1H), 9.03 (s, 1H), 8.95 – 8.86 (m, 2H), 8.58 (d, *J* = 8.6 Hz, 1H), 8.32 (d, *J* = 9.6 Hz, 1H), 8.15 (t, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 2H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 4.98 (s, 3H), 2.29 (s, 3H).
^{13}C NMR (100 MHz, DMSO) *δ* 147.6, 142.8, 142.5, 136.4, 136.2, 134.9, 133.6, 133.0, 132.6, 131.1, 129.9, 128.5, 128.3, 128.0, 127.8, 126.4, 121.3, 118.2, 115.4, 100.0, 41.9, 21.5.
HRMS (ESI): m/z calcd for $C_{23}H_{18}ClN_2O_2S^+$ ($[M-Cl]^+$) : 421.0772, found 421.0773.
2-bromo-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2n)

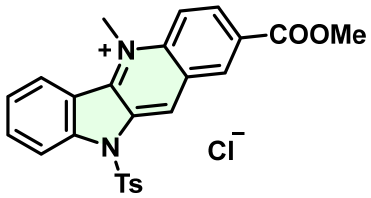


Reaction was conducted following the *general procedure*. yellow solid (478.0 mg, 95% yield).
Rf = 0.4 (DCM /MeOH = 10:1);
M. p. = 167-168 °C;
^{1}H NMR (400 MHz, DMSO) *δ* 9.97 (s, 1H), 9.18 (d, *J* = 2.1 Hz, 1H), 8.91 (d, *J* = 8.3 Hz, 1H), 8.83 (d, *J* = 9.6 Hz, 1H), 8.58 (d, *J* = 8.6 Hz, 1H), 8.41 (d, *J* = 9.5 Hz, 1H), 8.17 – 8.12 (m, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.82 – 7.74 (m, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 4.97 (s, 3H), 2.29 (s, 3H).
^{13}C NMR (100 MHz, DMSO) *δ* 147.6, 142.7, 142.5, 137.4, 136.5, 136.4, 133.2, 133.0, 132.4, 131.1, 128.7, 128.5, 127.9, 127.8, 126.4, 122.2, 121.2, 118.2, 115.4, 41.9, 21.5.
HRMS (ESI): m/z calcd for $C_{23}H_{18}BrN_2O_2S^+$ ($[M-Cl]^+$) : 465.0267, found 465.0268.
5-methyl-10-tosyl-2-(trifluoromethyl)-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2o)

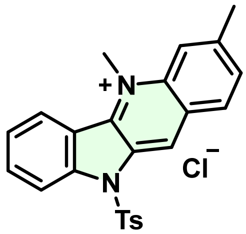


Reaction was conducted following the *general procedure*. yellow solid (481.0 mg, 98% yield).
Rf = 0.4 (DCM /MeOH = 10:1);
M. p. = 165-166 °C;
^{1}H NMR (400 MHz, DMSO) *δ* 10.23 (s, 1H), 9.45 (s, 1H), 9.09 (d, *J* = 9.4 Hz, 1H), 8.97 (d, *J* = 8.3 Hz, 1H), 8.63 (d, *J* = 8.6 Hz, 1H), 8.59 – 8.52 (m, 1H), 8.19 (t, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 2H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 5.03 (s, 3H), 2.30 (s, 3H).

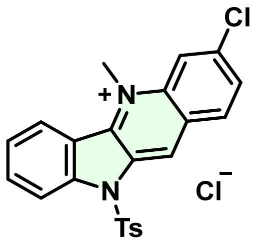
^{13}C NMR (100 MHz, DMSO) *δ* 147.7, 144.2, 142.8, 138.8, 136.9, 133.0, 132.7, 131.2, 129.9, 128.8, 127.8, 126.7, 126.5, 121.0, 118.1, 115.4, 42.0, 21.5.
^{19}F NMR (376 MHz, DMSO) *δ* -61.03 (s).
HRMS (ESI): m/z calcd for $C_{24}H_{18}F_3N_2O_2S^+$ ($[M-Cl]^+$) : 455.1036, found 455.1039.
2-(methoxycarbonyl)-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2p)



Reaction was conducted following the *general procedure*. chartreuse solid (438.0 mg, 91% yield).
Rf = 0.2 (DCM /MeOH = 10:1);
M. p. = 157-158 °C;
^{1}H NMR (400 MHz, DMSO) *δ* 10.21 (s, 1H), 9.54 (s, 1H), 8.94 (t, *J* = 7.8 Hz, 2H), 8.63 (d, *J* = 8.4 Hz, 2H), 8.18 (t, *J* = 8.0 Hz, 3H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 4.99 (s, 3H), 4.04 (s, 3H), 2.29 (s, 3H).
^{13}C NMR (100 MHz, DMSO) *δ* 165.3, 147.7, 143.7, 142.8, 139.2, 136.7, 133.9, 133.3, 133.1, 132.3, 131.1, 130.2, 129.4, 128.6, 127.8, 127.0, 126.4, 119.8, 118.1, 115.4, 53.5, 41.9, 21.5.
HRMS (ESI): m/z calcd for $C_{25}H_{21}N_2O_4S^+$ ($[M-Cl]^+$) : 445.1217, found 445.1216.
3,5-dimethyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2q)



Reaction was conducted following the *general procedure*. chartreuse solid (433.0 mg, 99% yield).
Rf = 0.5 (DCM /MeOH = 10:1);
M. p. = 141-142 °C;
^{1}H NMR (400 MHz, DMSO) *δ* 9.95 (s, 1H), 8.89 (d, *J* = 8.2 Hz, 1H), 8.72 (d, *J* = 8.4 Hz, 1H), 8.68 (s, 1H), 8.57 (d, *J* = 8.6 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 4.94 (s, 3H), 2.76 (s, 3H), 2.28 (s, 3H).
^{13}C NMR (100 MHz, DMSO) *δ* 147.5, 147.1, 142.0, 141.7, 137.9, 135.6, 133.1, 131.2, 131.1, 129.1, 128.1, 127.7, 126.2, 125.9, 118.5, 117.7, 115.4, 41.3, 22.8, 21.5.
HRMS (ESI): m/z calcd for $C_{24}H_{21}N_2O_2S^+$ ($[M-Cl]^+$) : 401.1318, found 401.1318.
3-chloro-5-methyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2r)



Reaction was conducted following the *general procedure*. yellow solid (430.0 mg, 94% yield).
Rf = 0.3 (DCM /MeOH = 10:1);

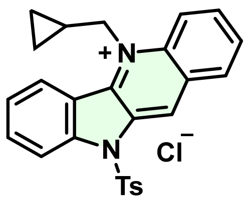
M. p. = 154-155 °C;

^{1}H NMR (400 MHz, DMSO) *δ* 10.05 (s, 1H), 9.02 (s, 1H), 8.96 – 8.85 (m, 2H), 8.59 (d, *J* = 8.6 Hz, 1H), 8.20 – 8.13 (m, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 4.95 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, DMSO) *δ* 147.1, 142.4, 142.0, 139.8, 137.6, 135.9, 132.9, 132.6, 131.5, 130.6, 129.3, 128.6, 127.9, 127.3, 125.9, 125.7, 117.9, 117.7, 114.9, 41.3, 21.0.

HRMS (ESI): m/z calcd for $C_{23}H_{18}ClN_2O_2S^+$ ([M-Cl]$^+$) : 421.0772, found 421.0773.

5-(cyclopropylmethyl)-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2s)



Reaction was conducted following the *general procedure*. yellow solid (458.0 mg, 99% yield).

Rf = 0.3 (DCM /MeOH = 10:1);

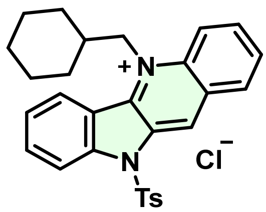
M. p. = 113-114 °C;

^{1}H NMR (400 MHz, DMSO) *δ* 10.06 (s, 1H), 8.86 (t, *J* = 9.8 Hz, 2H), 8.79 (d, *J* = 8.1 Hz, 1H), 8.59 (d, *J* = 8.3 Hz, 1H), 8.32 (t, *J* = 7.7 Hz, 1H), 8.19 – 8.05 (m, 4H), 7.84 (t, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 5.52 (d, *J* = 4.9 Hz, 2H), 2.30 (s, 3H), 1.51 (s, 1H), 0.82 (s, 2H), 0.66 (d, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, DMSO) *δ* 147.5, 142.5, 141.5, 137.2, 136.0, 135.3, 133.3, 132.3, 131.9, 131.1, 129.7, 129.2, 127.8, 127.4, 126.6, 119.0, 117.5, 115.6, 54.7, 21.6, 10.6, 4.6.

HRMS (ESI): m/z calcd for $C_{26}H_{23}N_2O_2S^+$ ([M-Cl]$^+$) : 427.1475, found 427.1474.

5-(cyclohexylmethyl)-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2t)



Reaction was conducted following the *general procedure*. yellow solid (495.0 mg, 98% yield).

Rf = 0.2 (DCM /MeOH = 10:1);

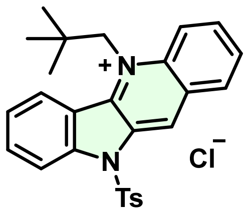
M. p. = 142-143 °C;

^{1}H NMR (400 MHz, DMSO) *δ* 10.07 (s, 1H), 8.96 (d, *J* = 9.2 Hz, 1H), 8.87 (d, *J* = 7.9 Hz, 1H), 8.64 – 8.56 (m, 2H), 8.32 – 8.25 (m, 1H), 8.17 – 8.06 (m, 4H), 7.83 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 5.44 (d, *J* = 92.5 Hz, 2H), 2.89 (s, 1H), 2.72 (s, 1H), 2.51 (s, 1H), 2.30 (s, 3H), 2.09 (s, 1H), 1.83 (s, 1H), 1.62 – 1.53 (m, 2H), 1.43 – 1.34 (m, 2H), 1.19 – 1.04 (m, 2H).

^{13}C NMR (100 MHz, DMSO) *δ* 147.5, 142.4, 141.7, 137.7, 135.8, 135.1, 133.2, 132.4, 131.8, 131.1, 129.8, 129.2, 127.8, 127.7, 127.2, 126.6, 119.4, 117.7, 115.6, 56.2, 38.0, 36.3, 31.2, 26.0, 21.5.

HRMS (ESI): m/z calcd for $C_{29}H_{29}N_2O_2S^+$ ([M-Cl]$^+$) : 469.1944, found 469.1946.

5-neopentyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2u)



Reaction was conducted following the *general procedure*. yellow solid (455.0 mg, 95% yield).

Rf = 0.2 (DCM /MeOH = 10:1);

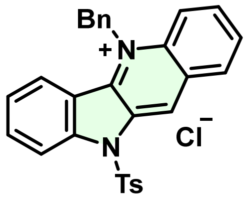
M. p. = 127-129 °C;

^{1}H NMR (400 MHz, DMSO) *δ* 10.12 (s, 1H), 9.09 (d, *J* = 7.6 Hz, 1H), 9.01 – 8.83 (m, 2H), 8.56 (d, *J* = 7.9 Hz, 1H), 8.26 (s, 1H), 8.11 – 7.94 (m, 4H), 7.77 (s, 1H), 7.35 (d, *J* = 7.0 Hz, 2H), 5.77 (s, 1H), 5.55 (d, *J* = 14.7 Hz, 1H), 2.27 (s, 3H), 0.85 (s, 9H).

^{13}C NMR (100 MHz, DMSO) *δ* 147.5, 142.9, 142.4, 138.7, 135.9, 134.5, 132.9, 132.6, 131.7, 131.0, 129.3, 128.2, 127.9, 127.7, 126.2, 120.7, 118.6, 115.9, 59.0, 37.4, 28.6, 21.5.

HRMS (ESI): m/z calcd for $C_{27}H_{27}N_2O_2S^+$ ($[M-Cl]^+$) : 443.1788, found 443.1790.

5-benzyl-10-tosyl-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2v)



Reaction was conducted following the *general procedure*. yellow solid (494.0 mg, 99% yield).

Rf = 0.3 (DCM /MeOH = 10:1);

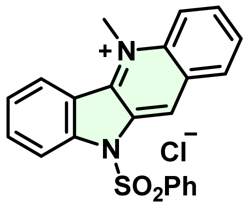
M. p. = 156-157 °C;

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 9.87 (s, 1H), 8.61 (d, *J* = 9.1 Hz, 1H), 8.55 (d, *J* = 8.6 Hz, 1H), 8.50 (d, *J* = 8.1 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 8.17 (t, *J* = 7.5 Hz, 1H), 7.99 – 7.92 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 5.2 Hz, 3H), 7.31 – 7.26 (m, 6H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) *δ* 147.5, 143.3, 141.9, 137.7, 136.0, 133.0, 132.1, 131.9, 130.8, 130.7, 130.0, 129.7, 129.5, 128.8, 127.2, 127.0, 126.7, 126.6, 125.9, 119.3, 116.9, 115.7, 57.5, 21.7.

HRMS (ESI): m/z calcd for $C_{29}H_{23}N_2O_2S^+$ ($[M-Cl]^+$) : 463.1475, found 463.1476.

5-methyl-10-(phenylsulfonyl)-10*H*-indolo[3,2-*b*]quinolin-5-ium chloride (2w)



Reaction was conducted following the *general procedure*. yellow solid (466.0 mg, 97% yield).

Rf = 0.3 (DCM /MeOH = 10:1);

M. p. = 140-141 °C;

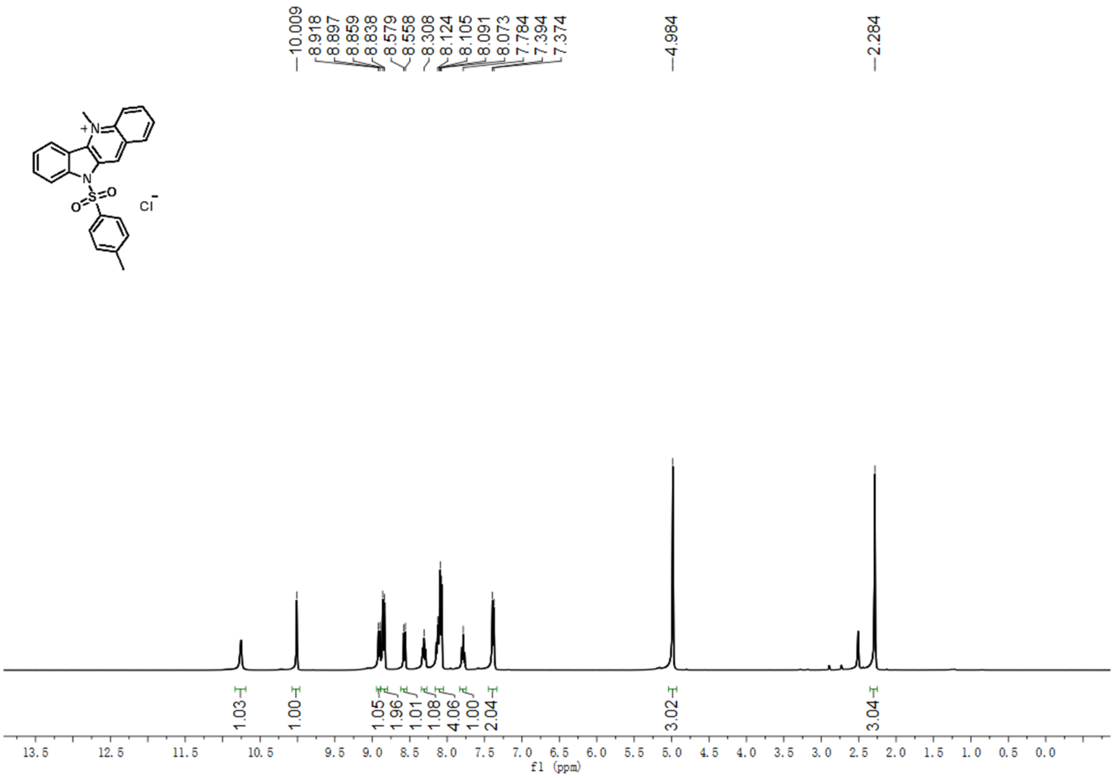
^{1}H NMR (400 MHz, DMSO-*d$_6$*) *δ* 10.03 (s, 1H), 8.92 (d, J = 8.2 Hz, 1H), 8.85 (d, J = 8.6 Hz, 2H), 8.58 (d, J = 8.5 Hz, 1H), 8.31 (t, J = 7.6 Hz, 1H), 8.21 (d, J = 7.7 Hz, 2H), 8.16 – 8.07 (m, 2H), 7.79 (t, J = 7.7 Hz, 1H), 7.74 (t, J = 7.4 Hz, 1H), 7.60 (t, J = 7.7 Hz, 2H), 4.98 (s, 3H).

^{13}C NMR (100 MHz, DMSO-*d$_6$*) *δ* 142.4, 142.2, 137.6, 136.4, 136.0, 135.2, 131.8, 131.7, 130.7, 129.2, 129.1, 128.4, 127.7, 127.5, 126.4, 118.8, 118.4, 115.4, 110.0, 41.5.

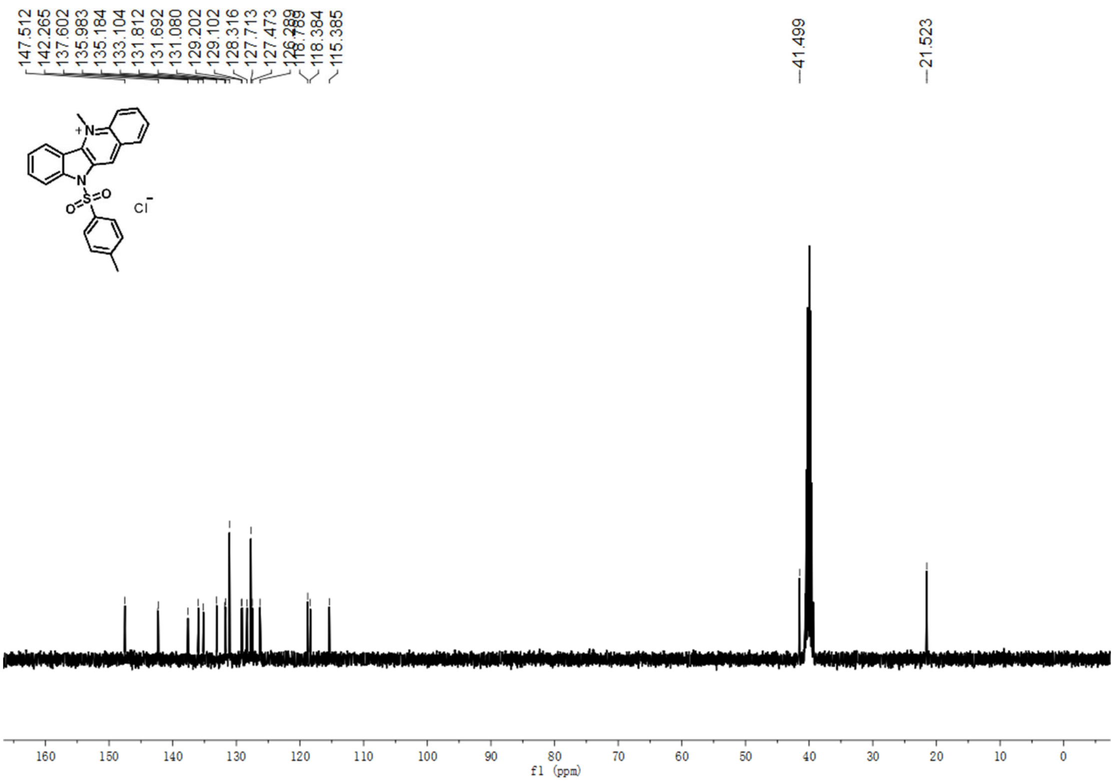
HRMS (ESI): m/z calcd for $C_{22}H_{17}N_2O_2S^+$ ($[M-Cl]^+$) : 373.1005, found 373.1004.

4.3 Spectra of prepared compounds

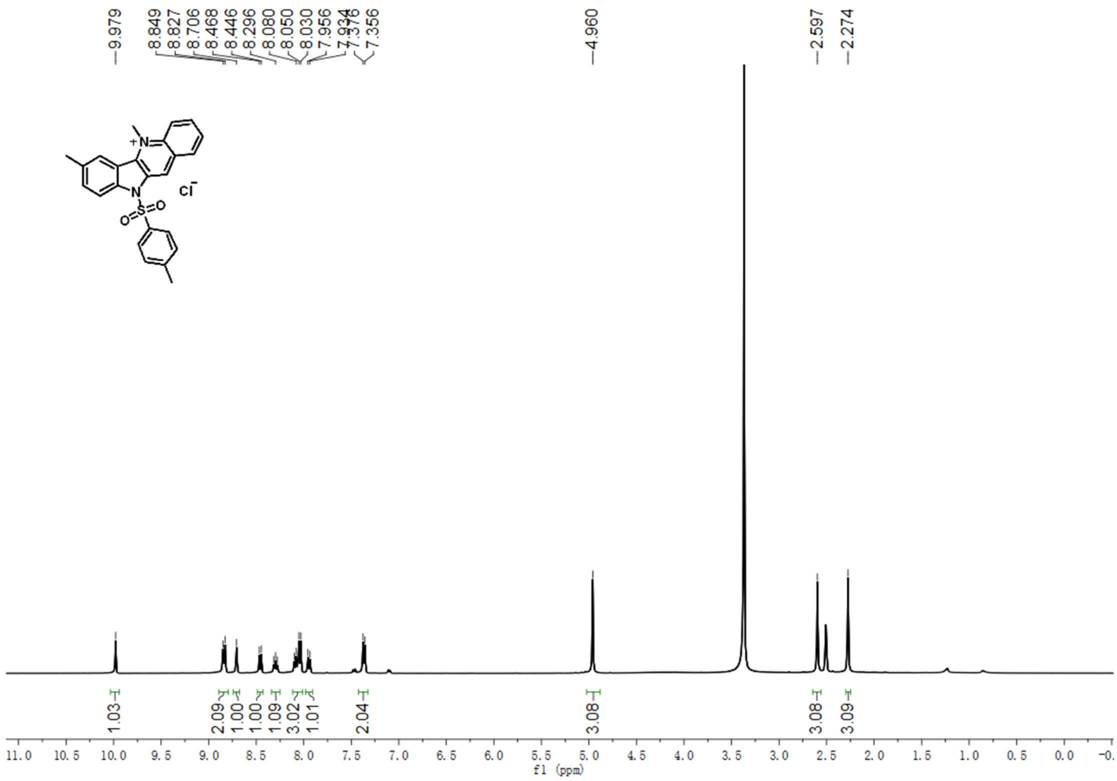
^{1}H NMR spectrum of compound **2a**



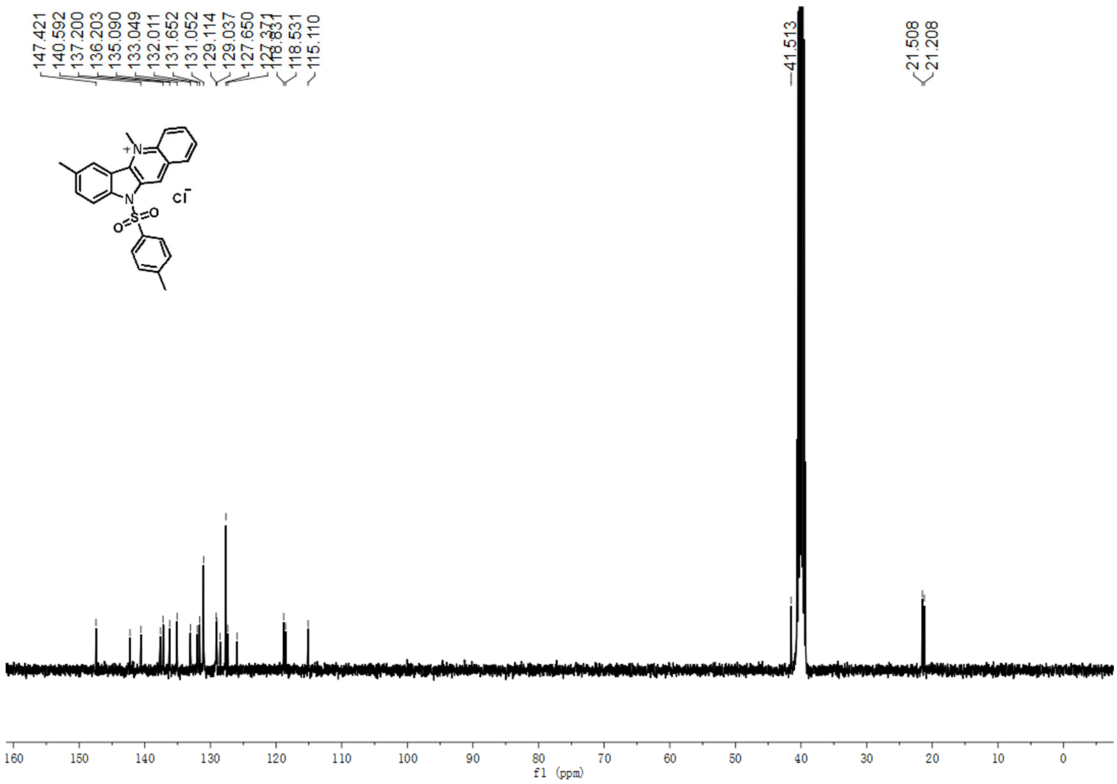
^{13}C NMR spectrum of compound **2a**



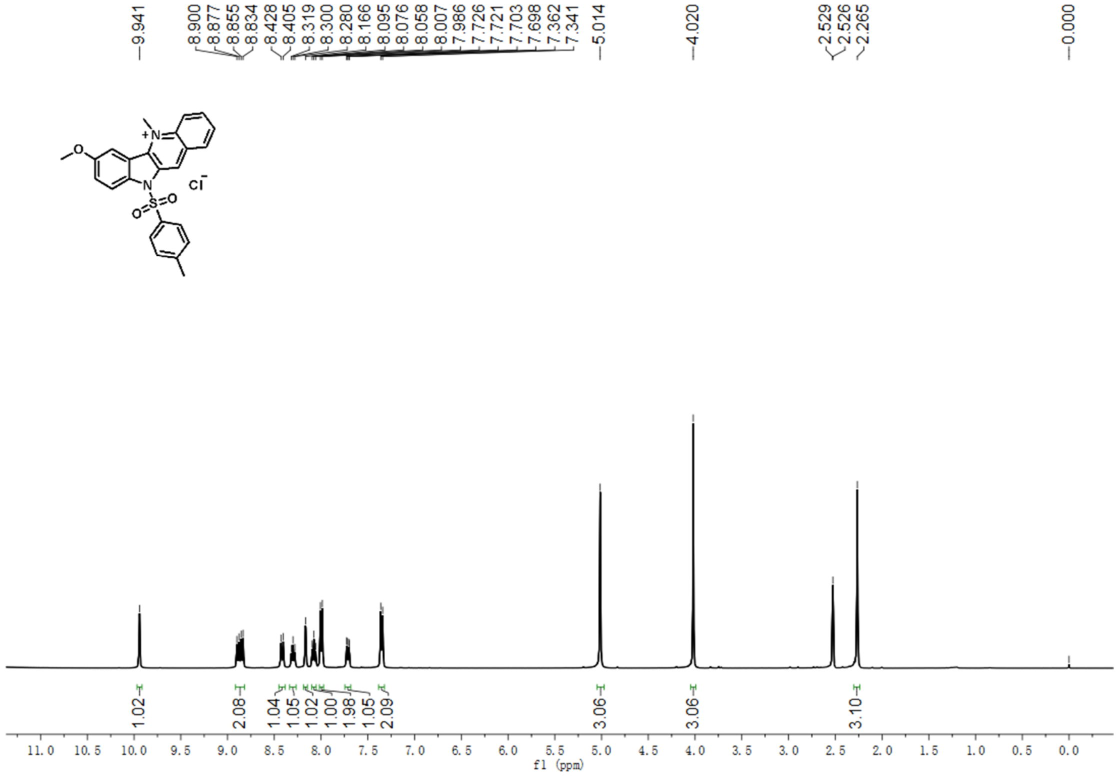
[1]H NMR spectrum of compound **2b**



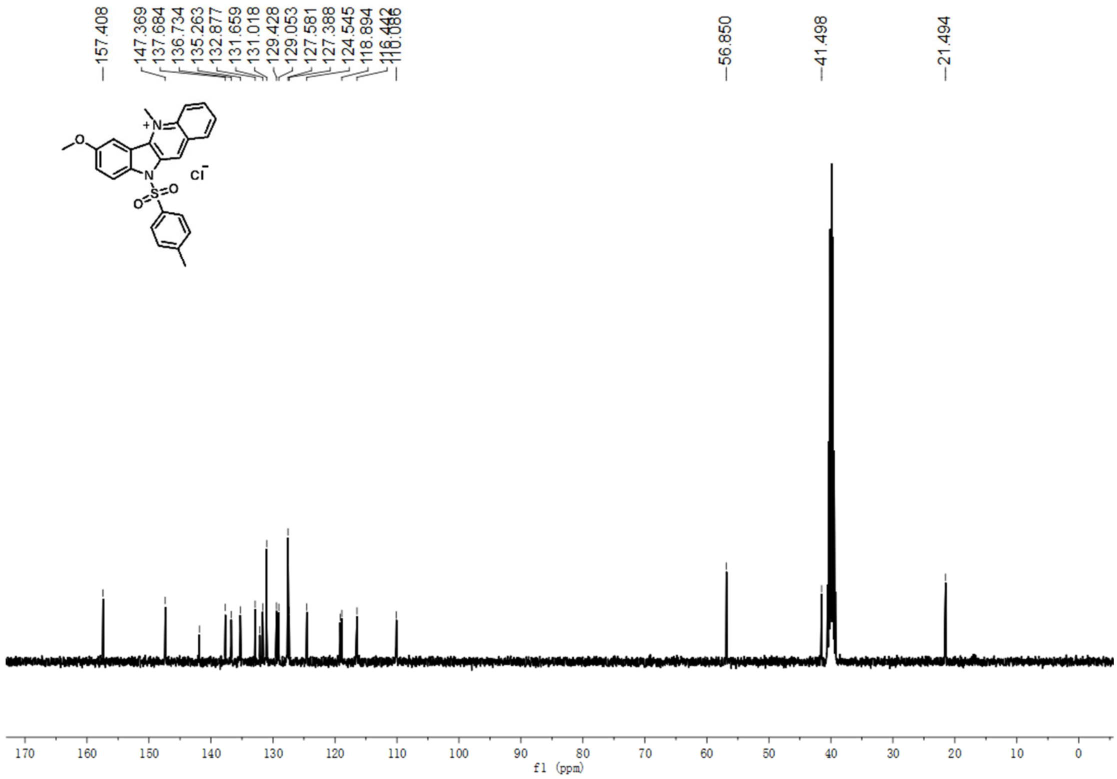
[13]C NMR spectrum of compound **2b**



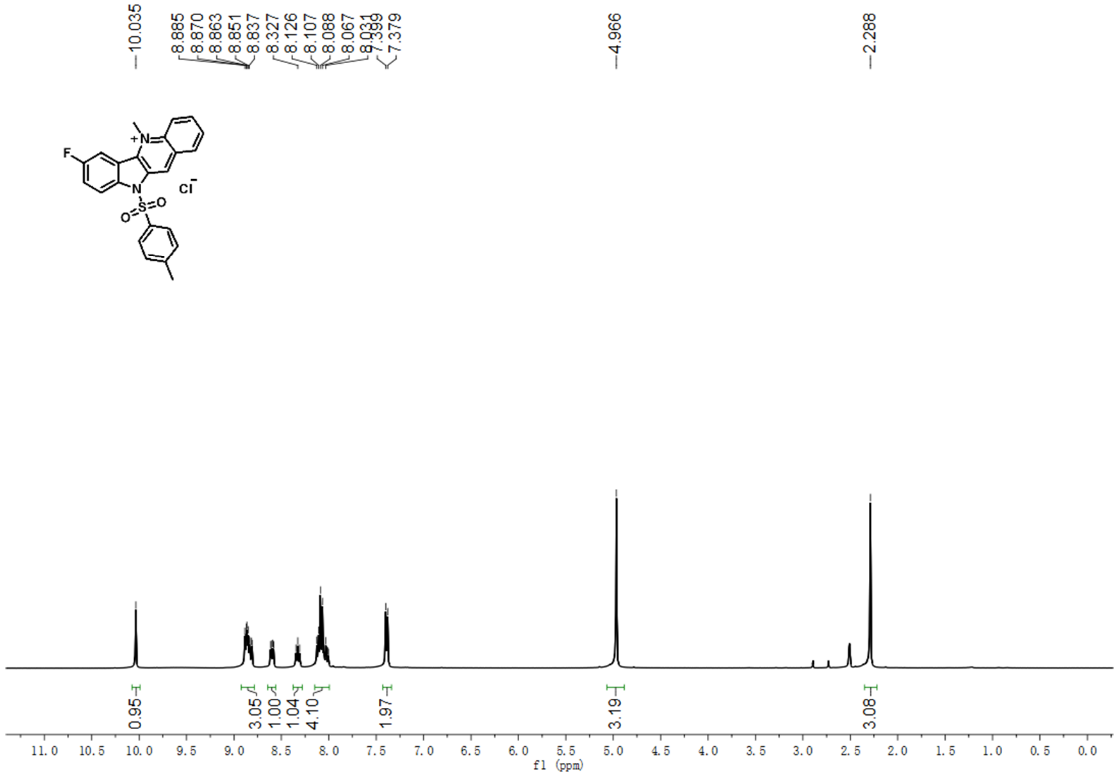
[1]H NMR spectrum of compound **2c**



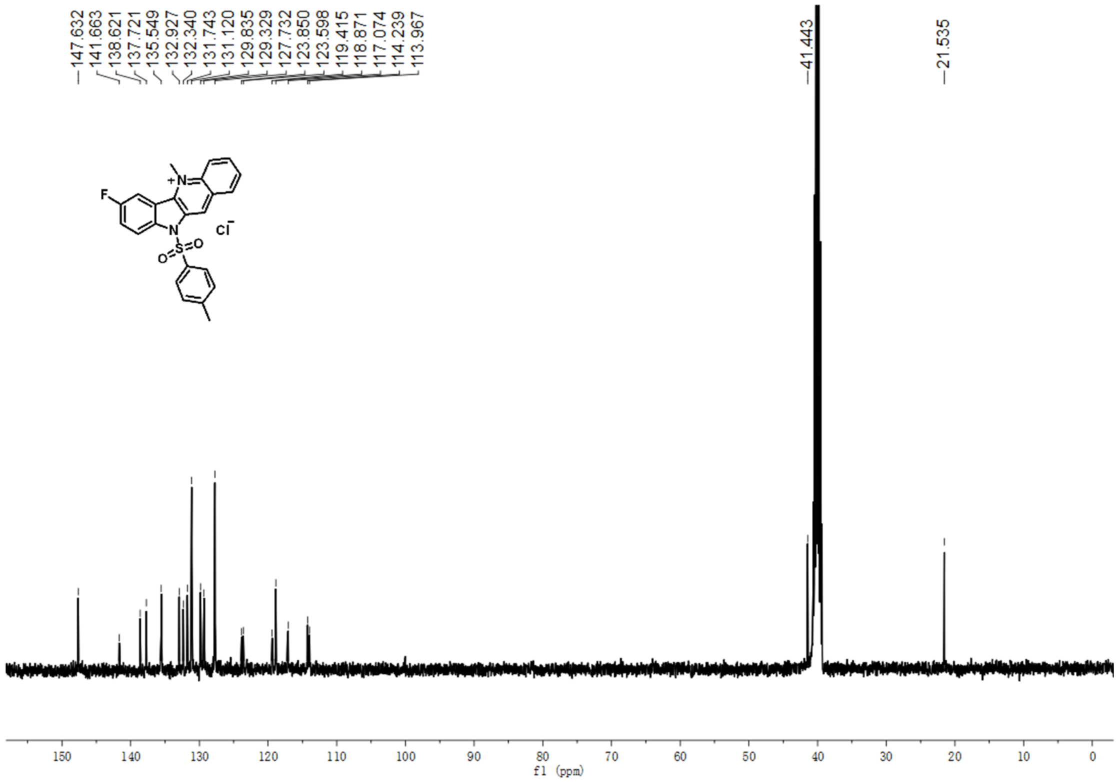
[13]C NMR spectrum of compound **2c**



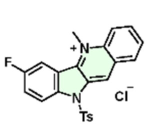
^{1}H NMR spectrum of compound **2d**

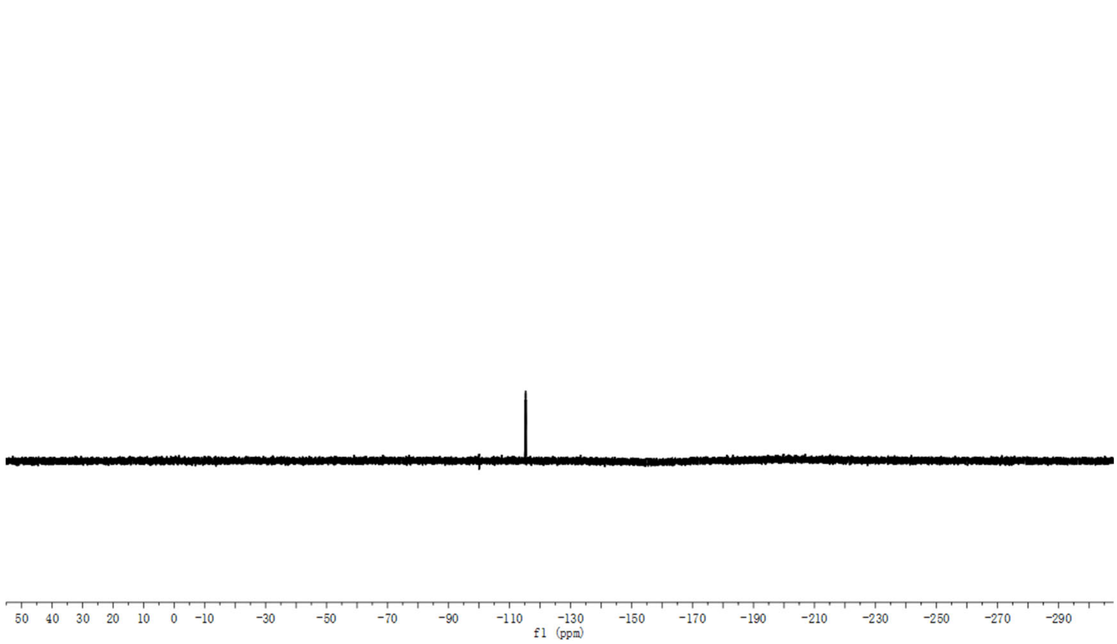


^{13}C NMR spectrum of compound **2d**

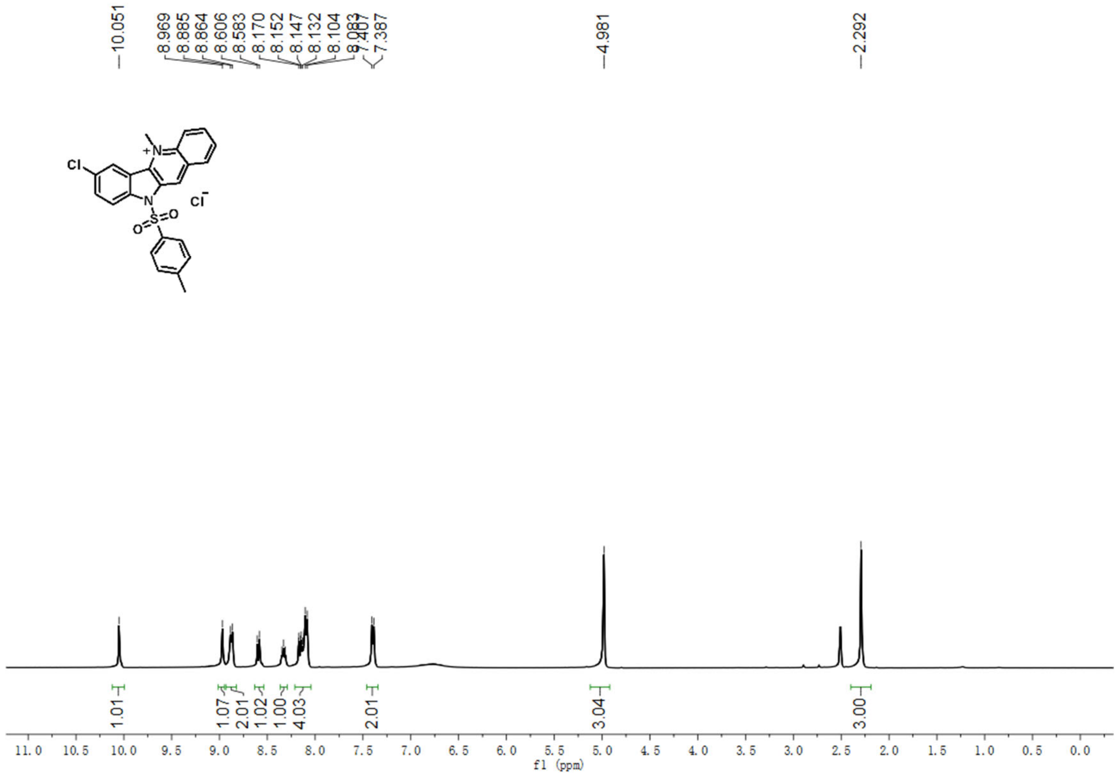


^{19}F NMR spectrum of compound **2d**

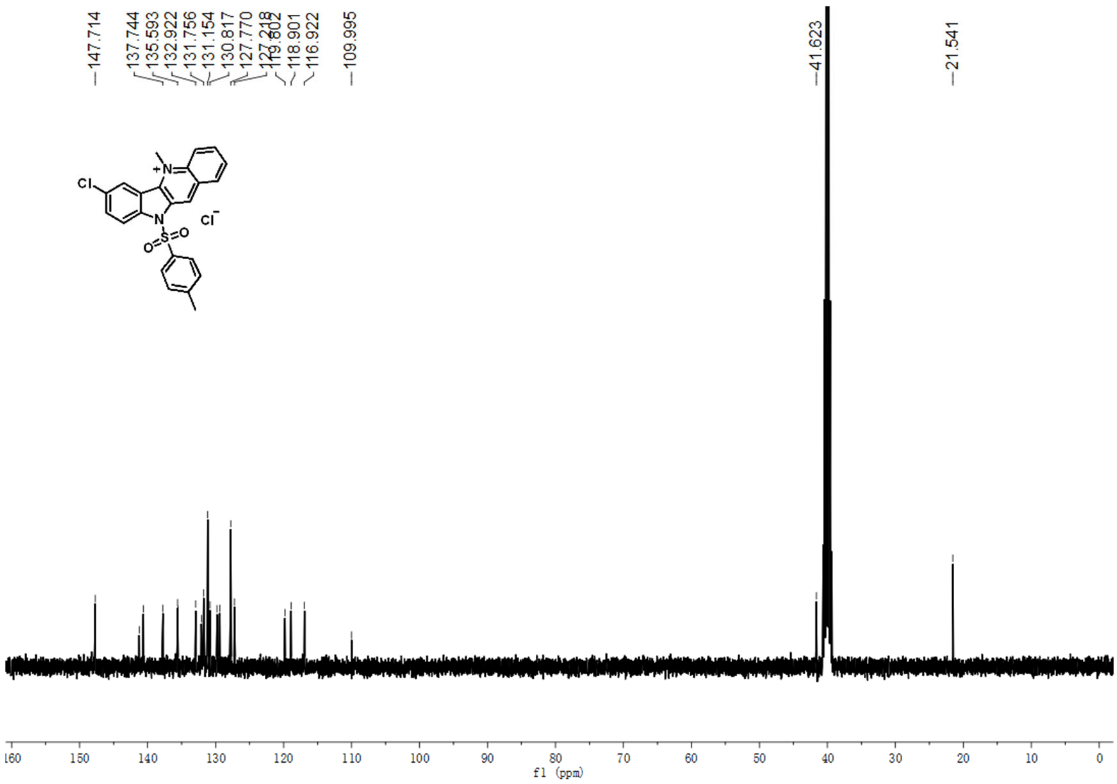




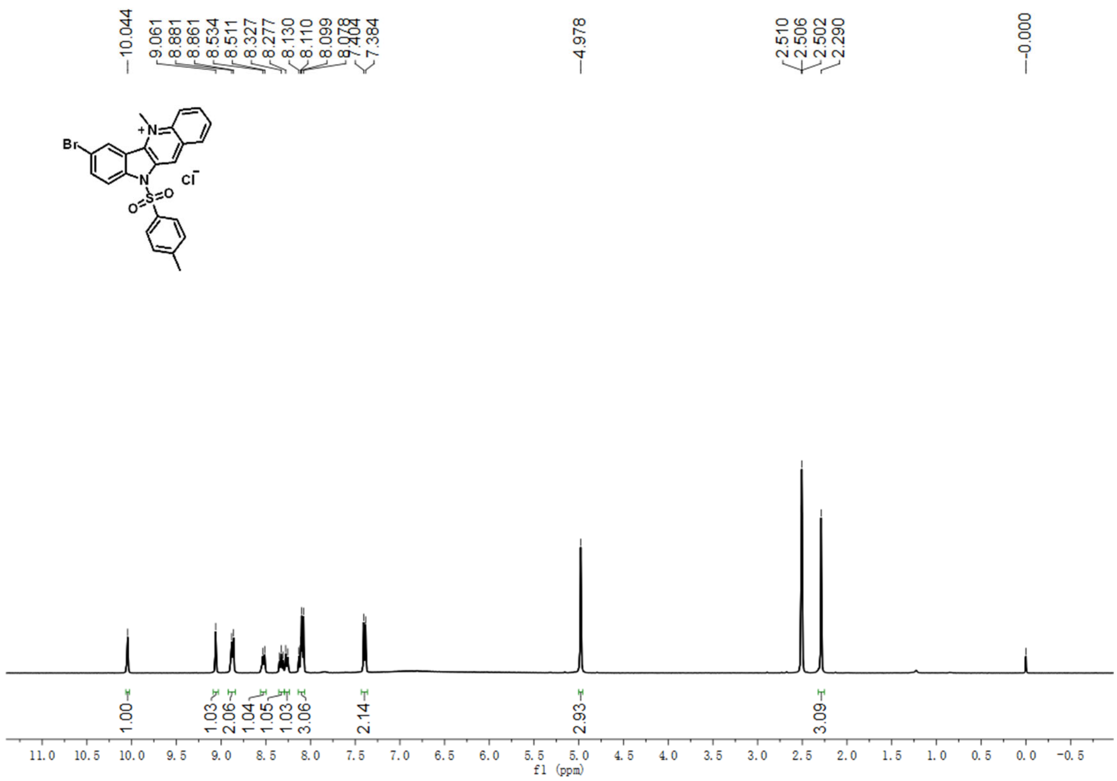
[1]H NMR spectrum of compound **2e**



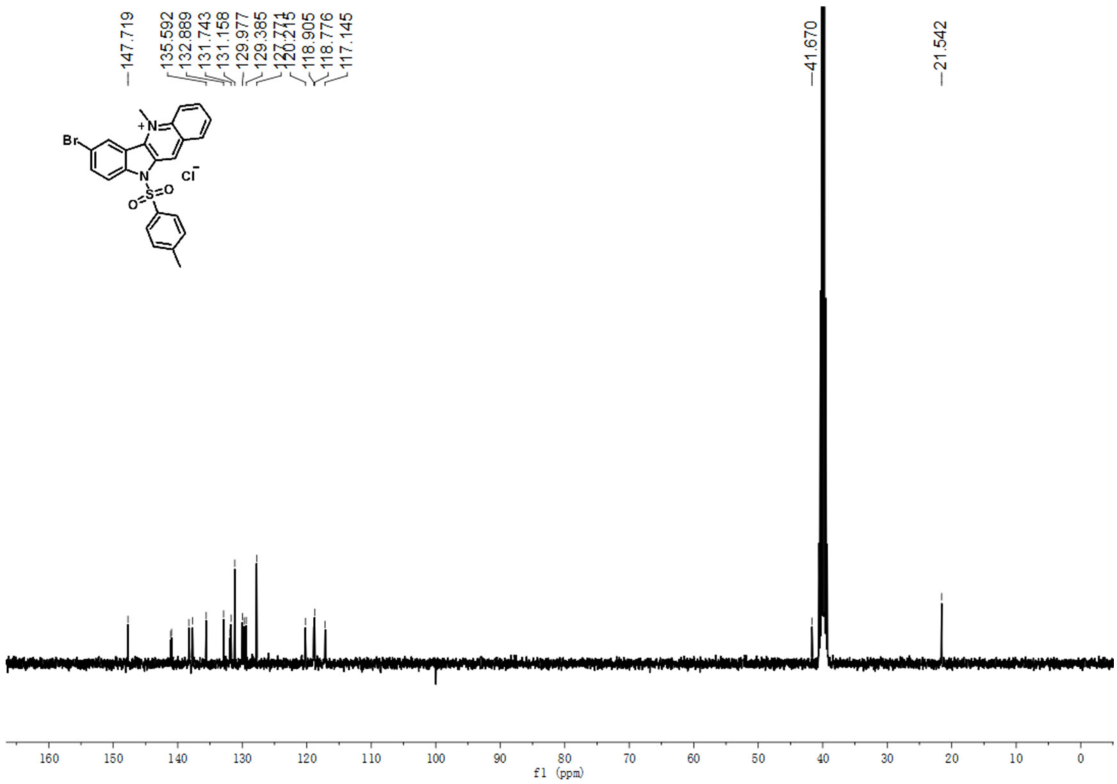
[13]C NMR spectrum of compound **2e**



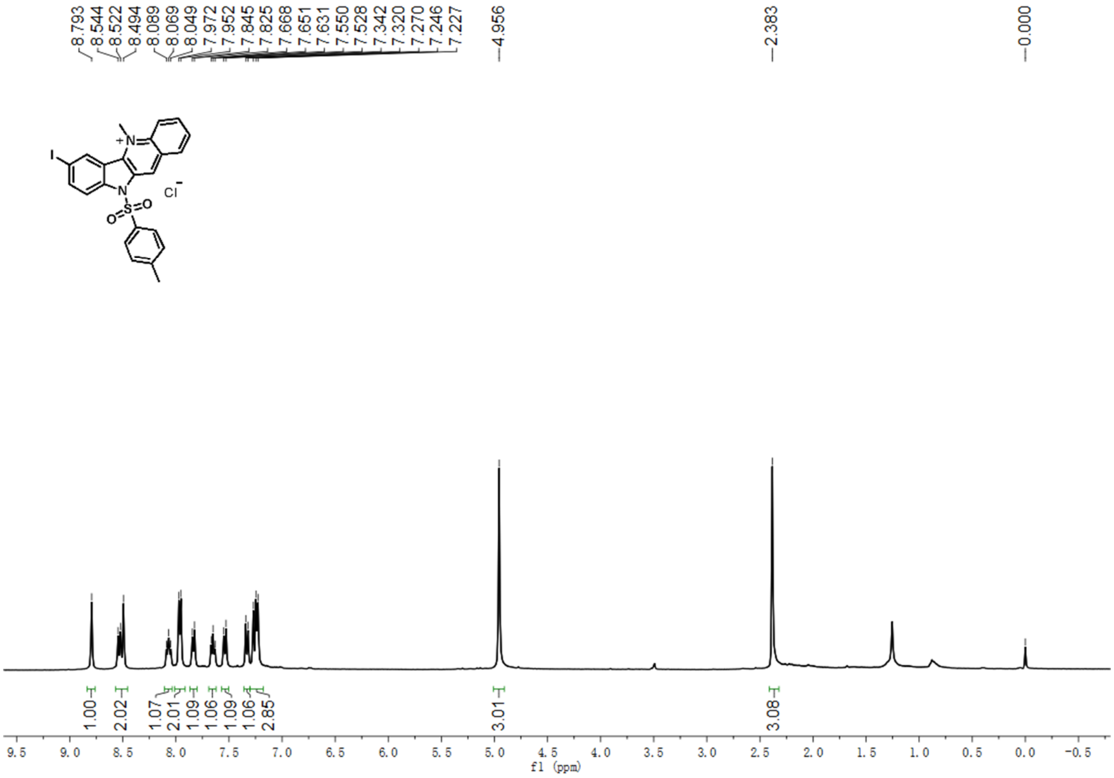
^{1}H NMR spectrum of compound **2f**



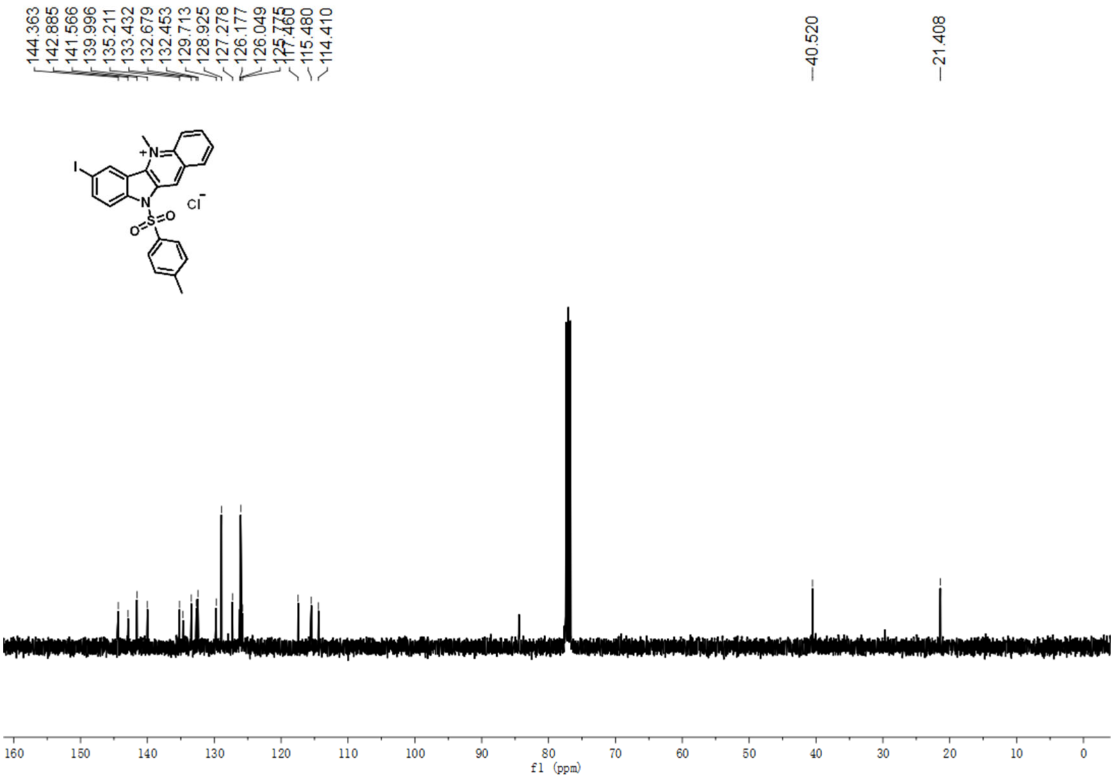
^{13}C NMR spectrum of compound **2f**



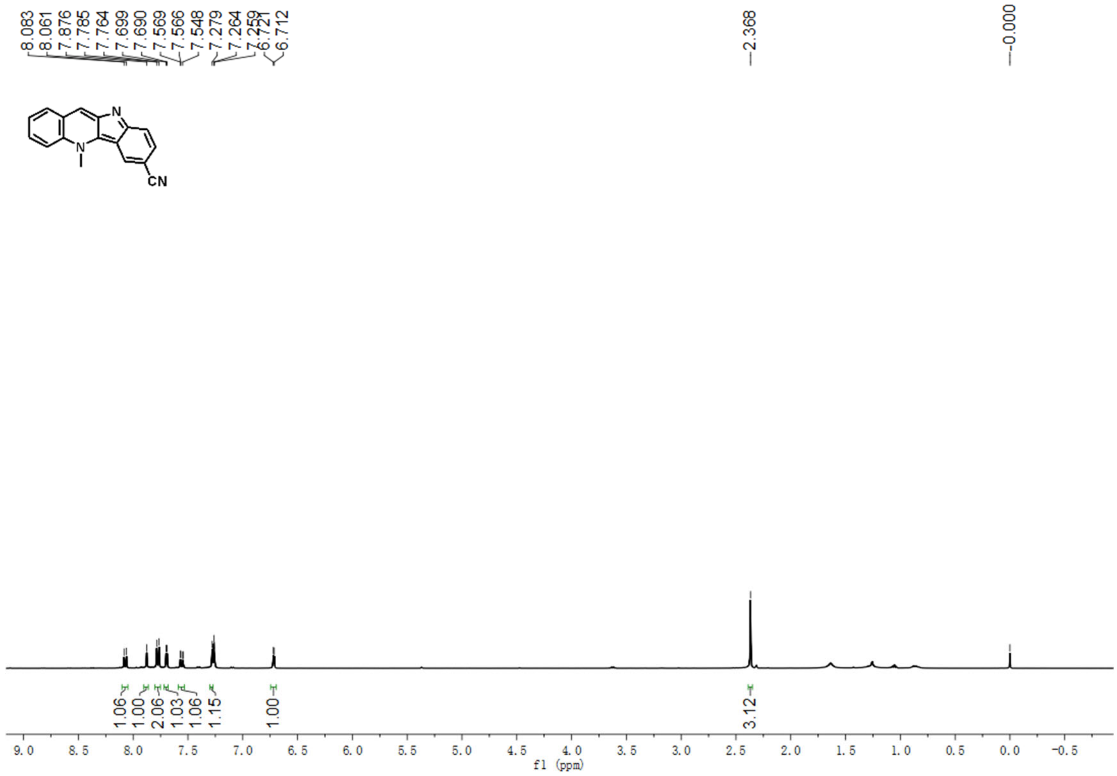
[1]H NMR spectrum of compound **2g**



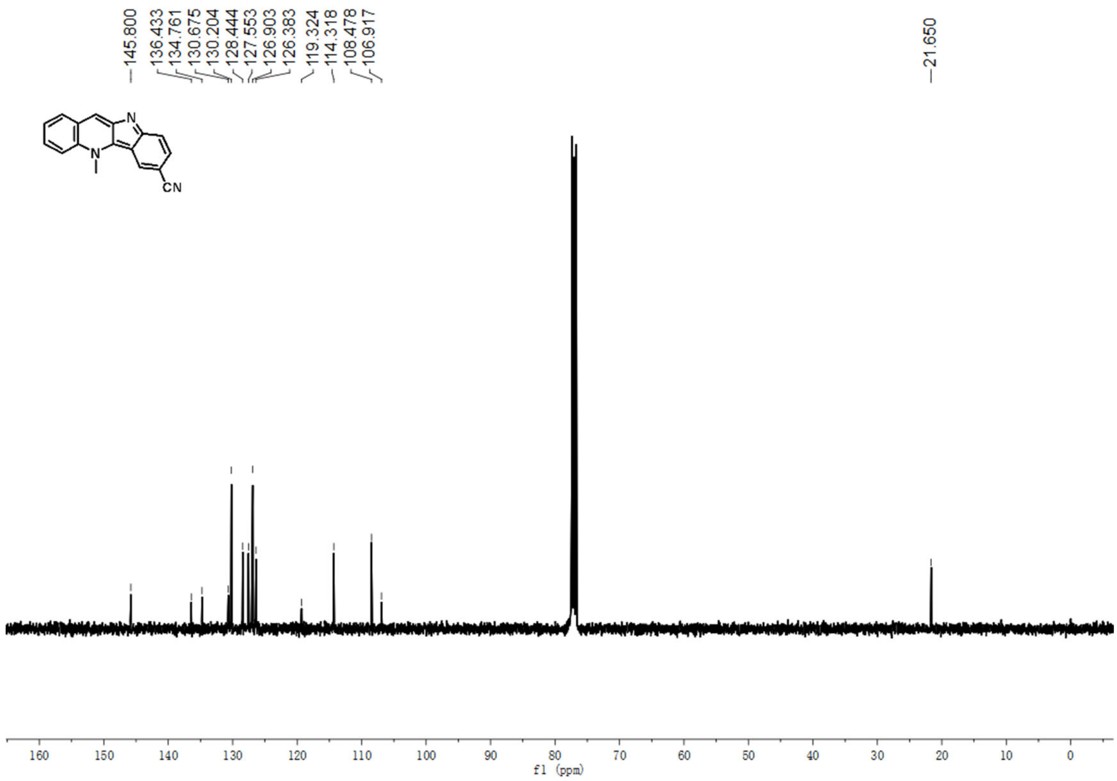
[13]C NMR spectrum of compound **2g**



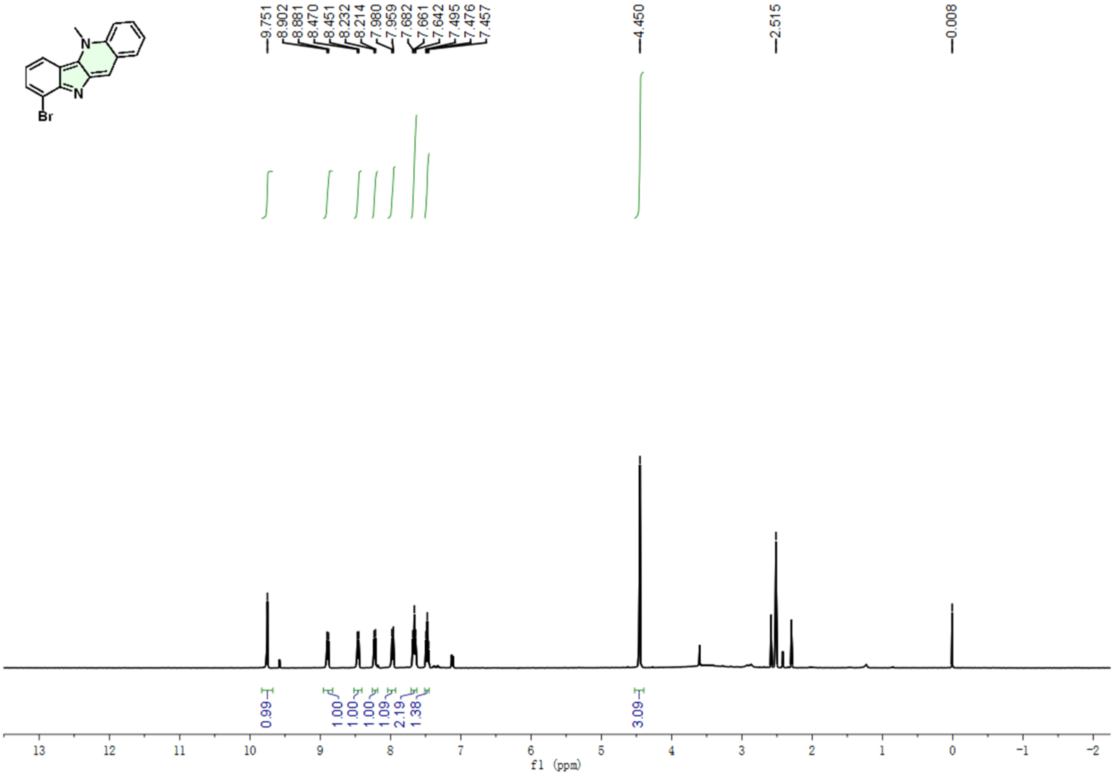
^{1}H NMR spectrum of compound **2h**



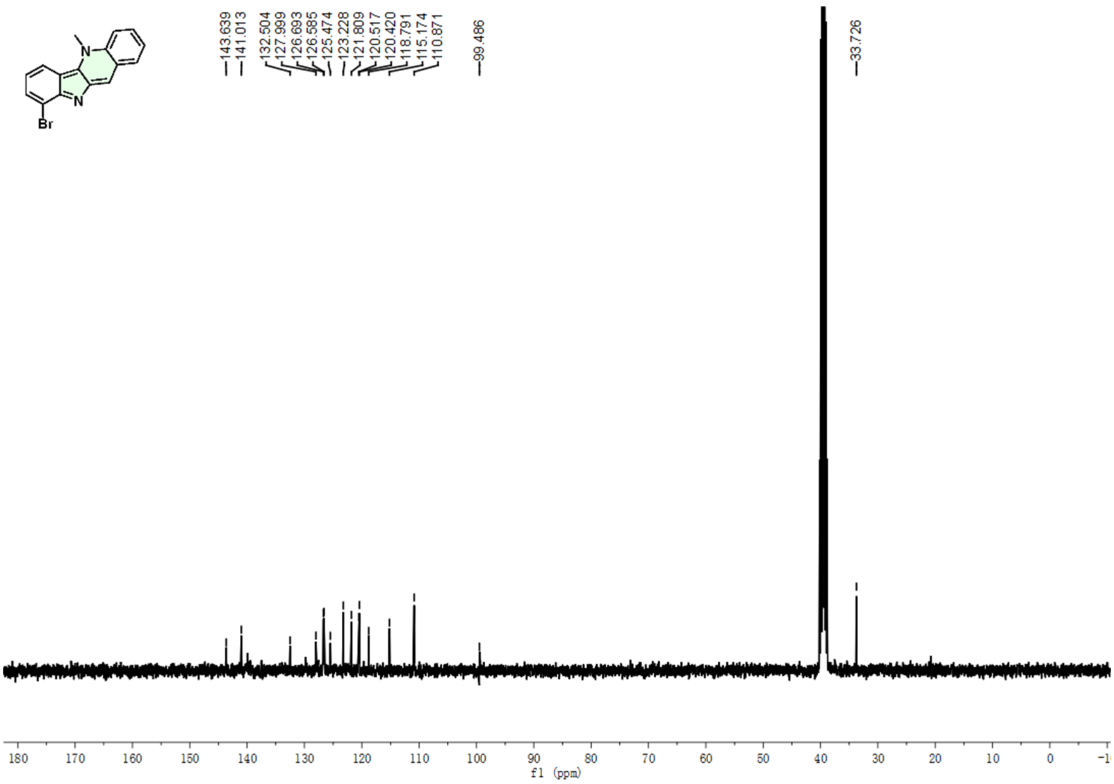
^{13}C NMR spectrum of compound **2h**



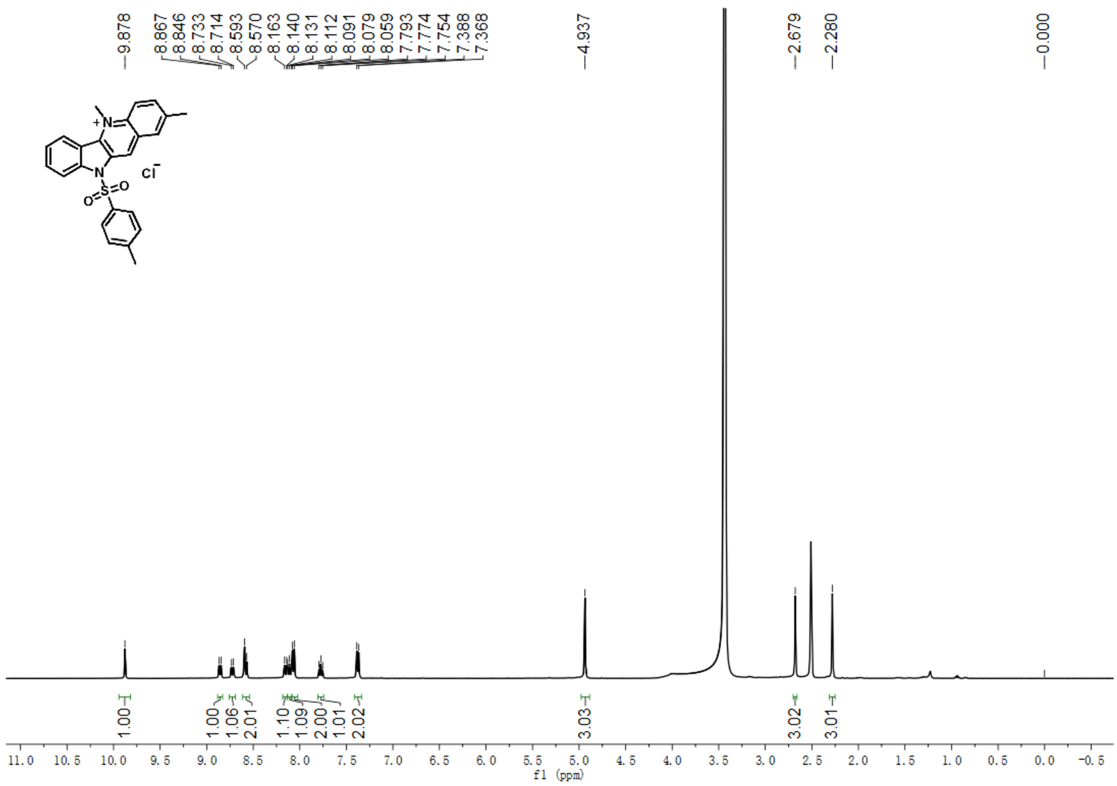
^{1}H NMR spectrum of compound **2i**



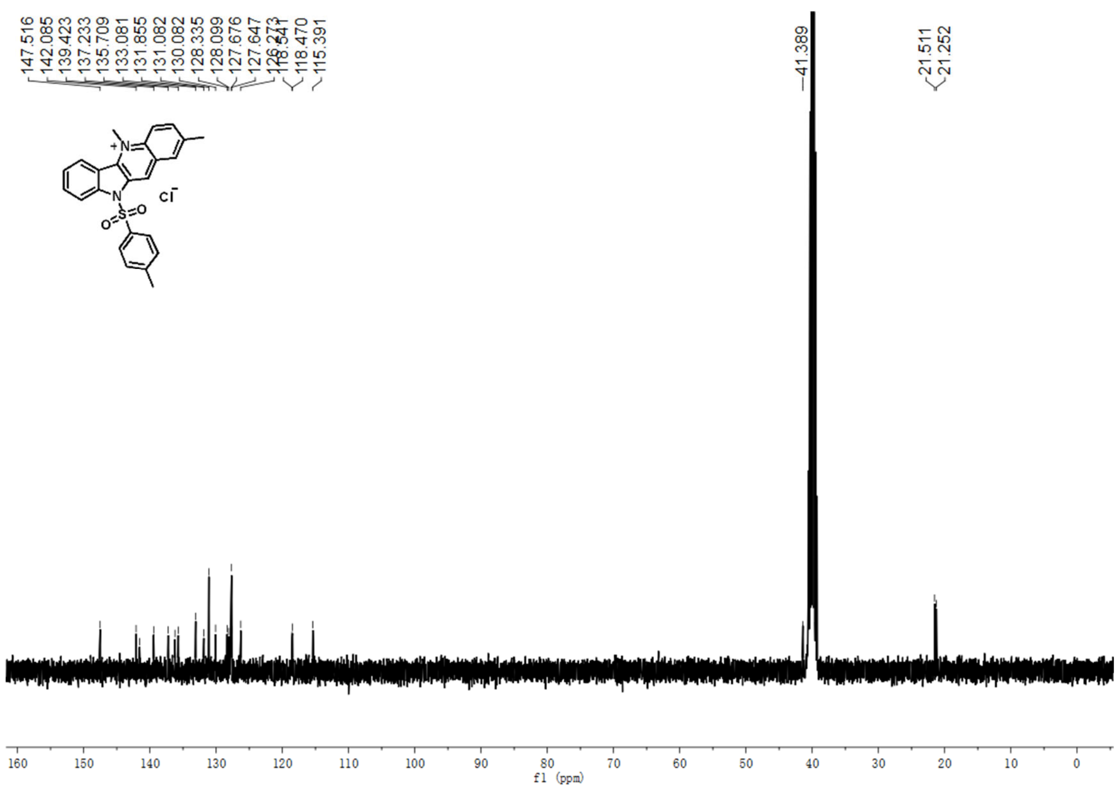
^{13}C NMR spectrum of compound **2i**



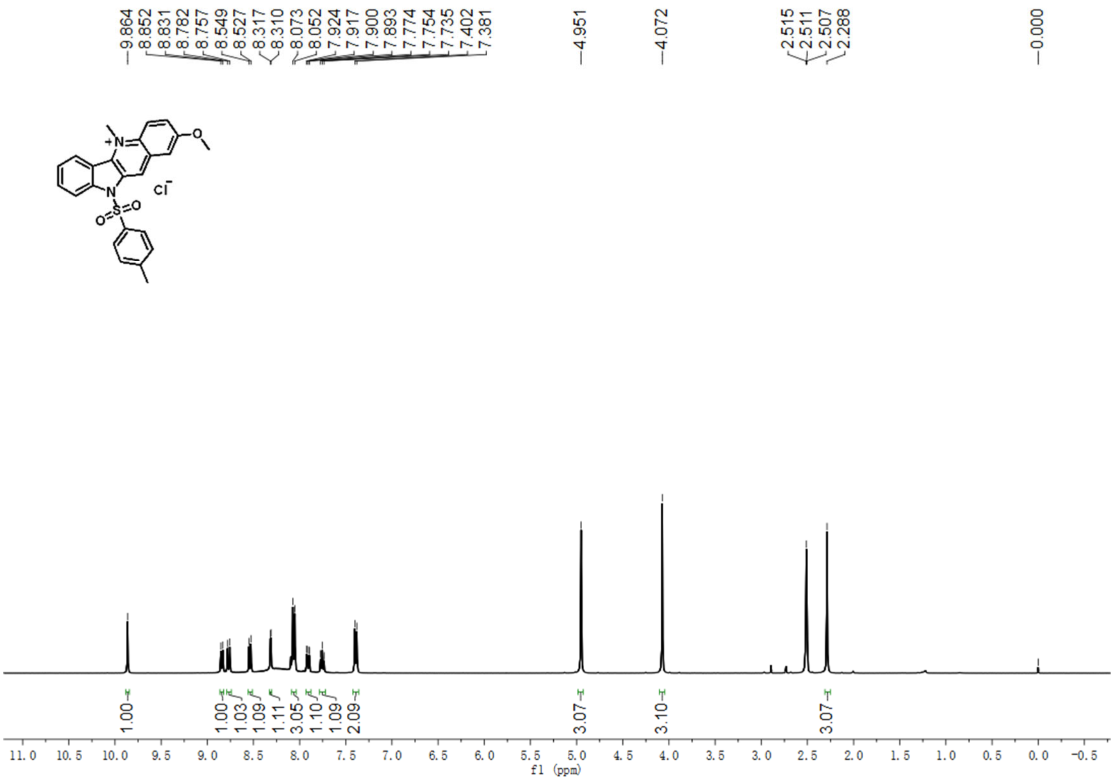
[1]H NMR spectrum of compound **2j**



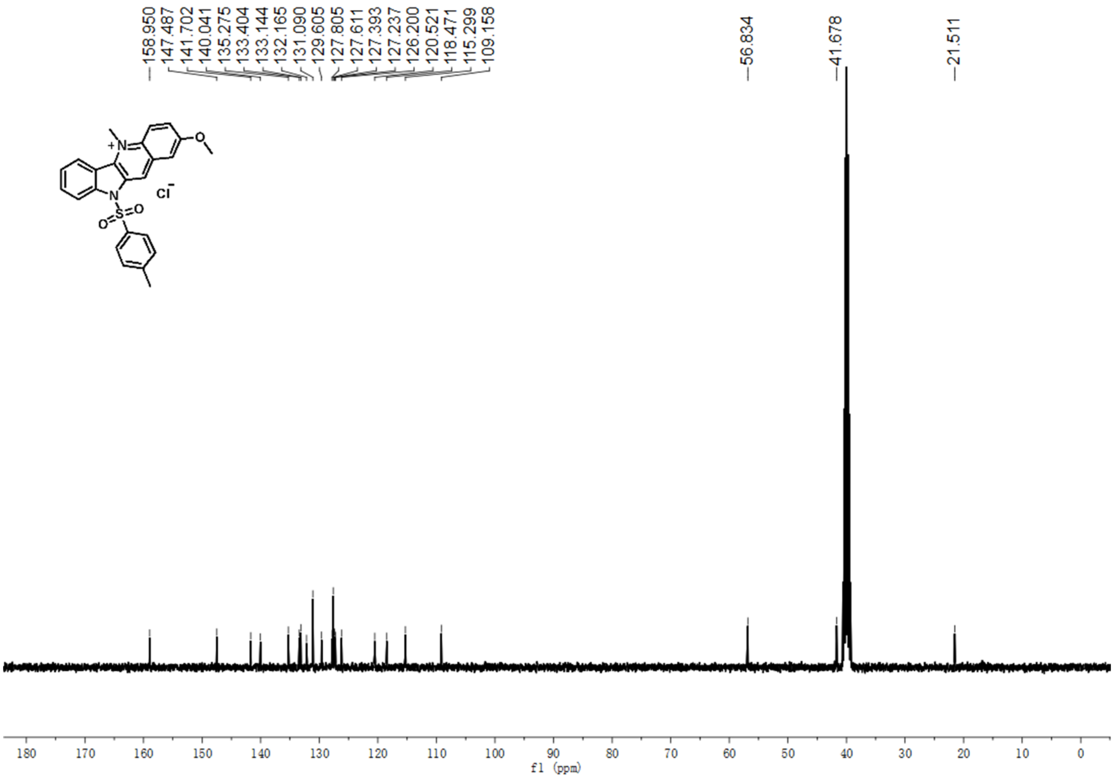
[13]C NMR spectrum of compound **2j**



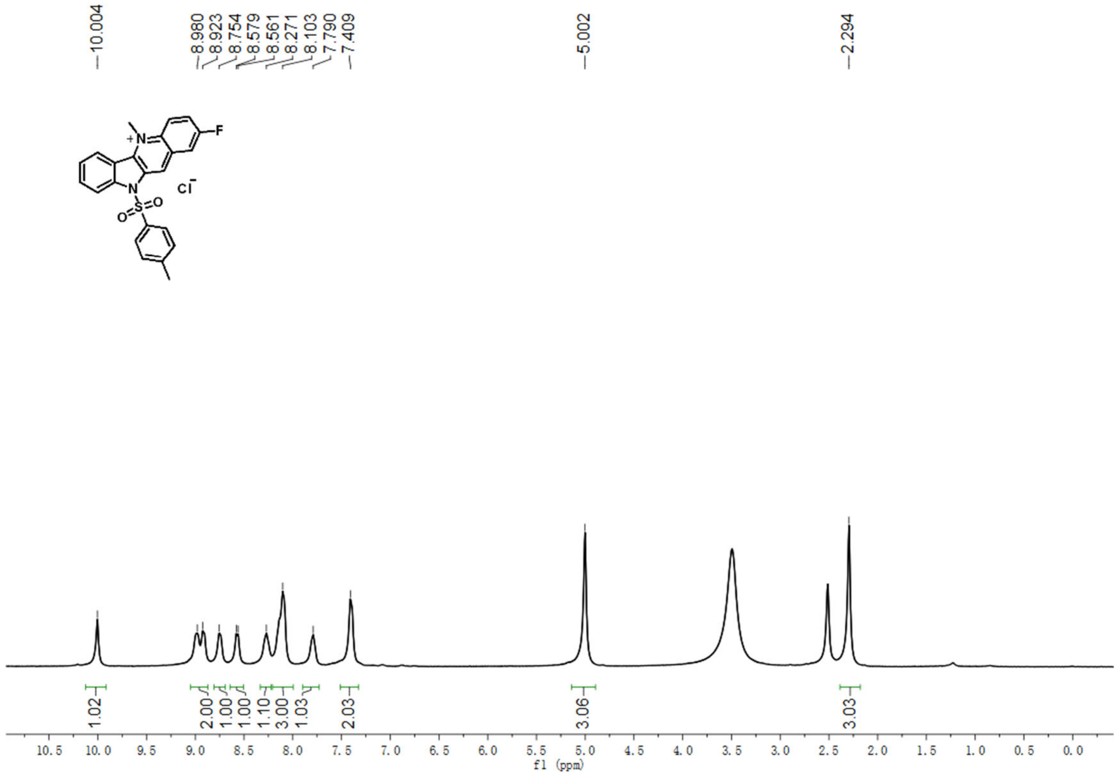
[1]H NMR spectrum of compound **2k**



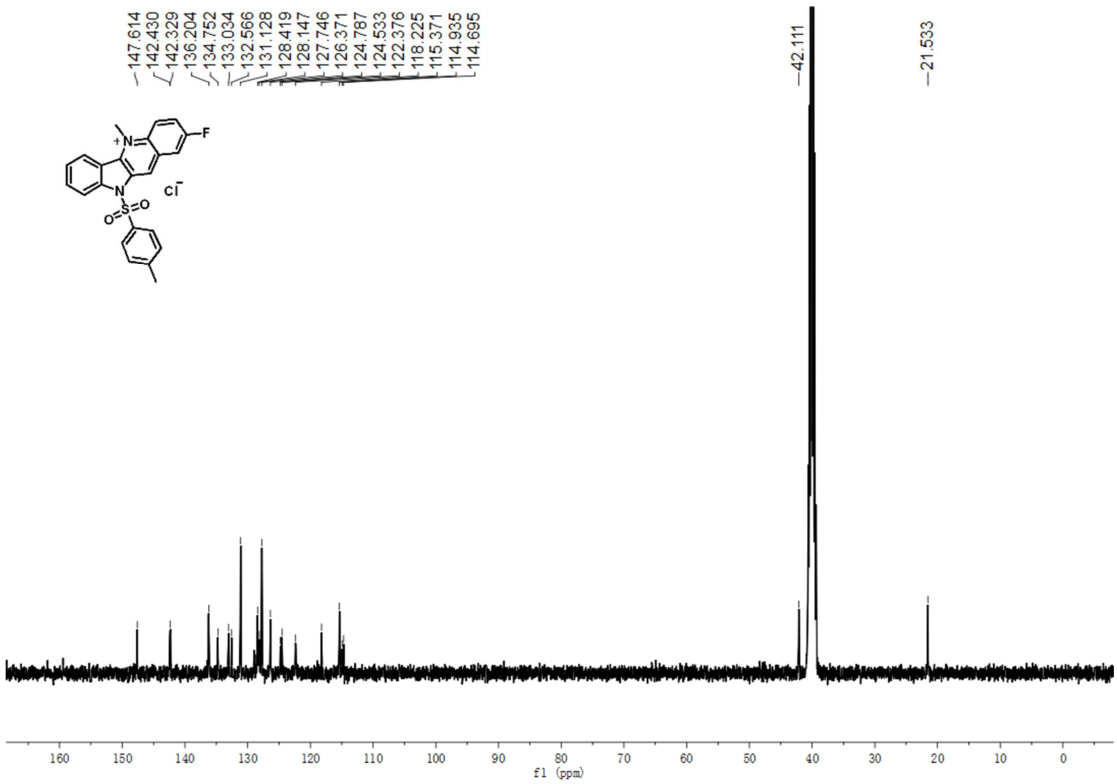
[13]C NMR spectrum of compound **2k**



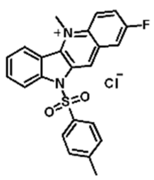
^{1}H NMR spectrum of compound **2l**

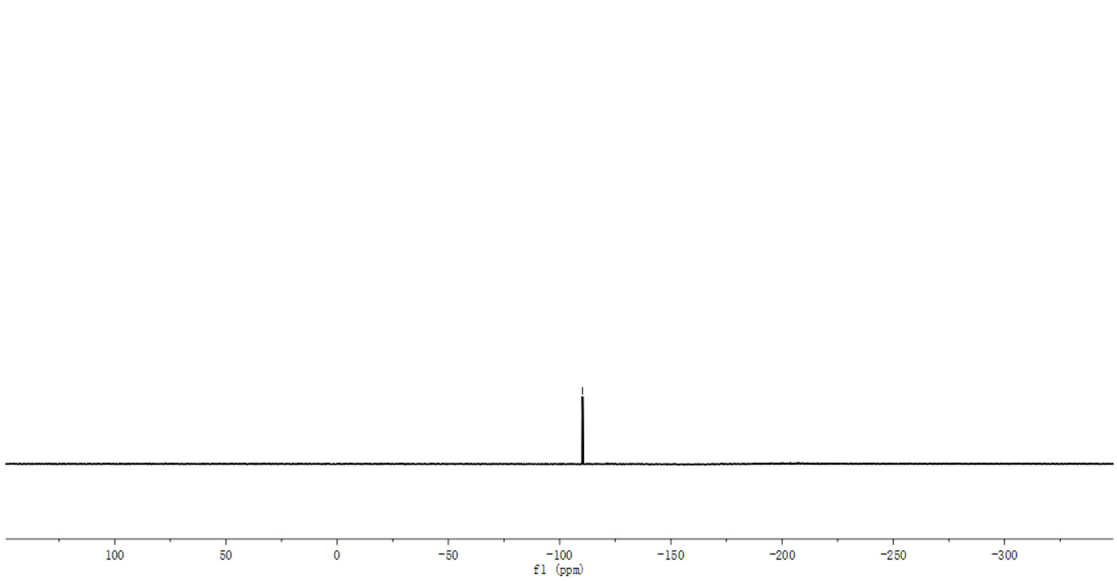


^{13}C NMR spectrum of compound **2l**

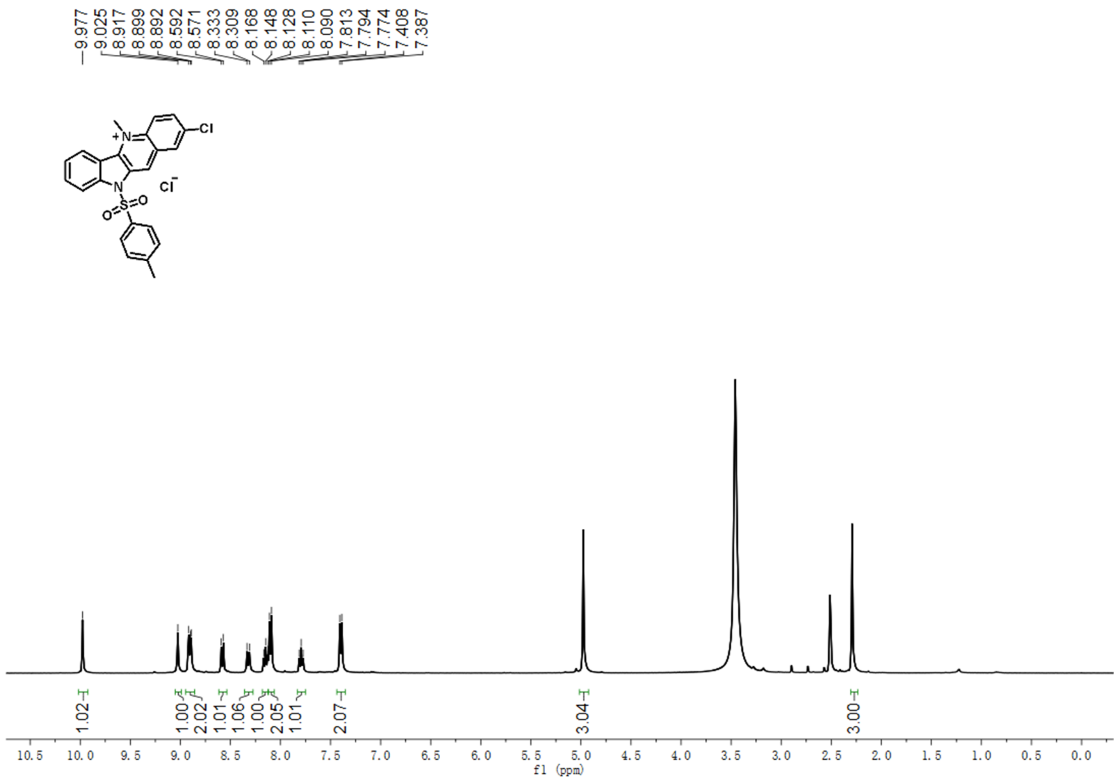


[19]F NMR spectrum of compound **2l**

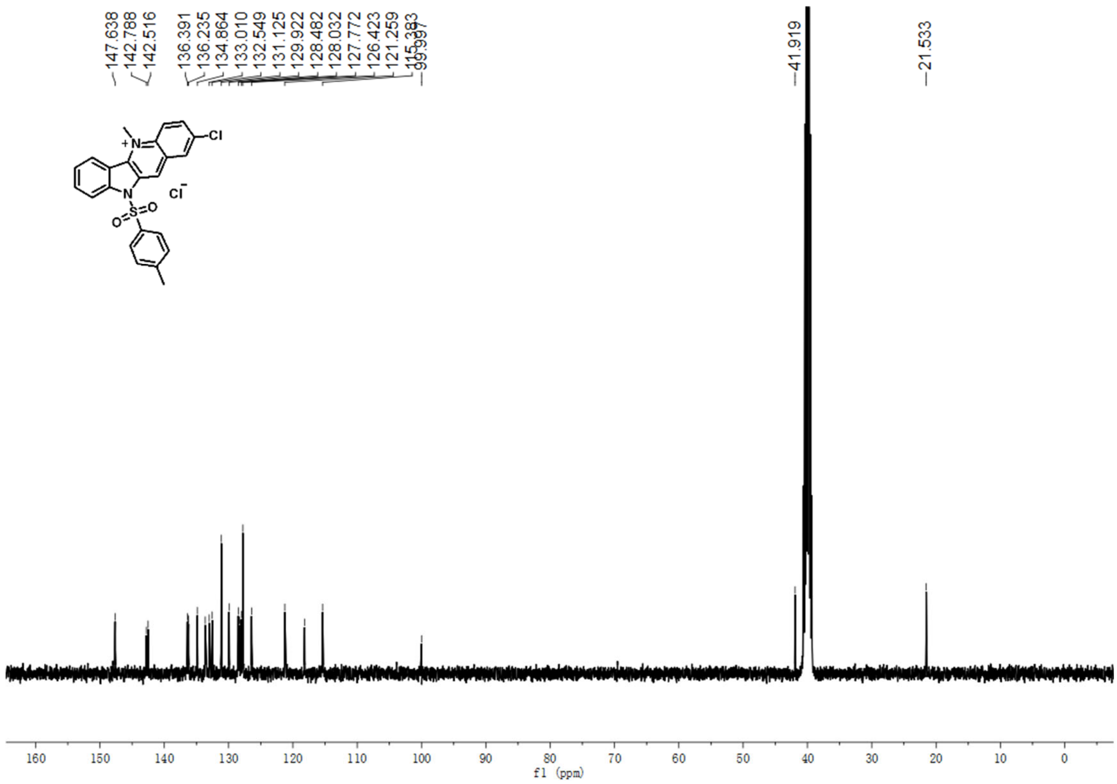




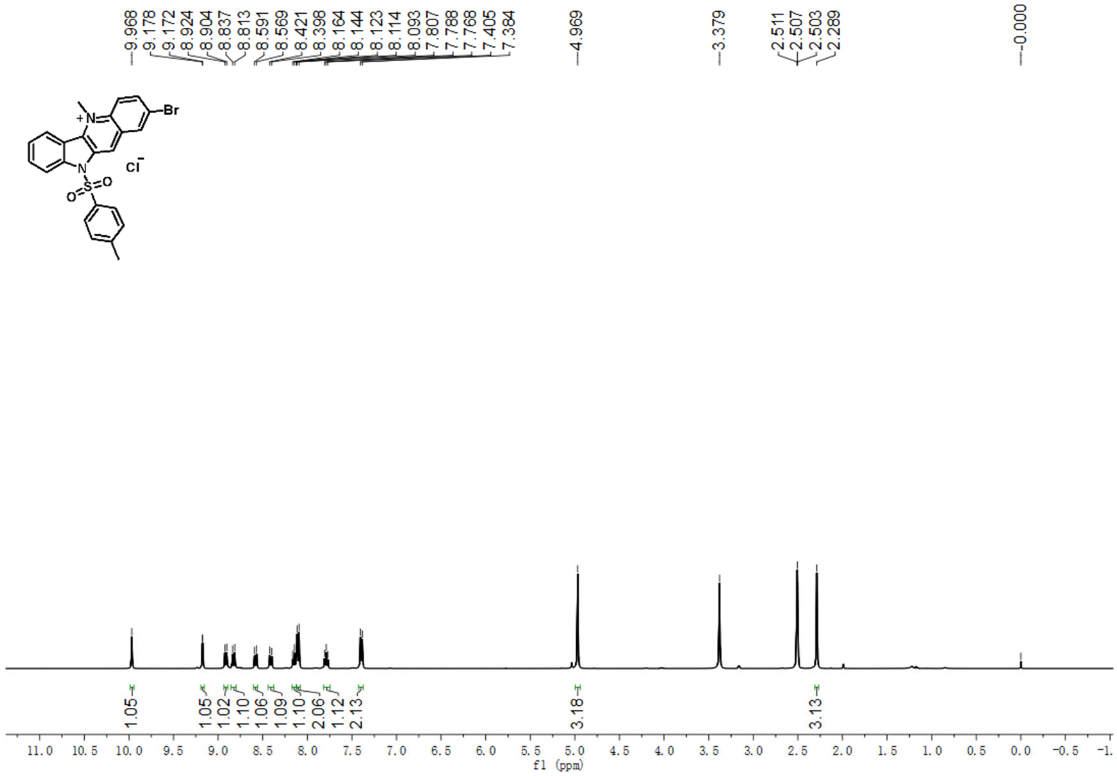
^{1}H NMR spectrum of compound **2m**



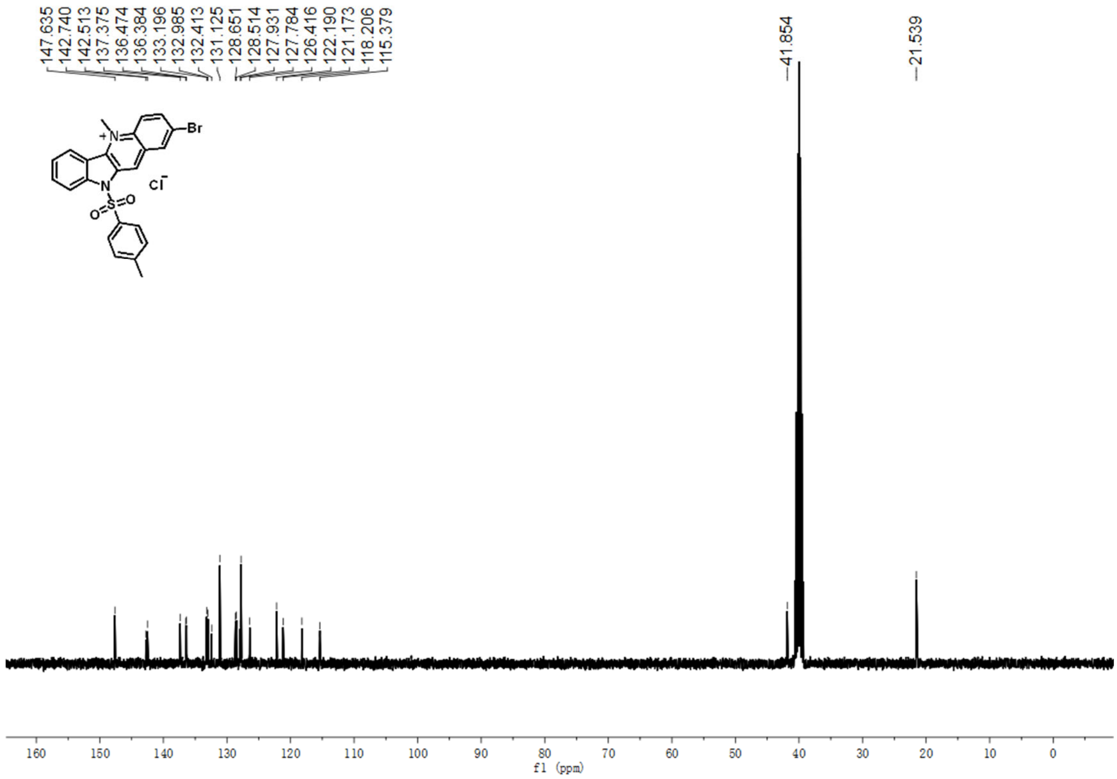
^{13}C NMR spectrum of compound **2m**



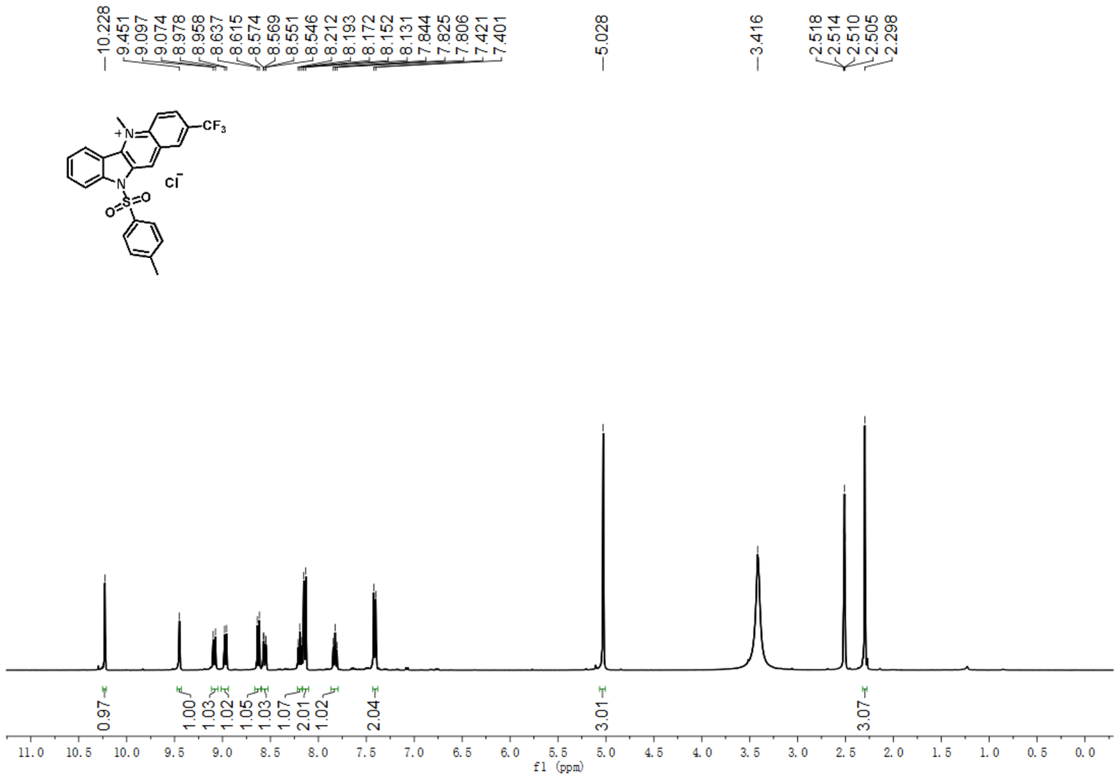
[1]H NMR spectrum of compound **2n**



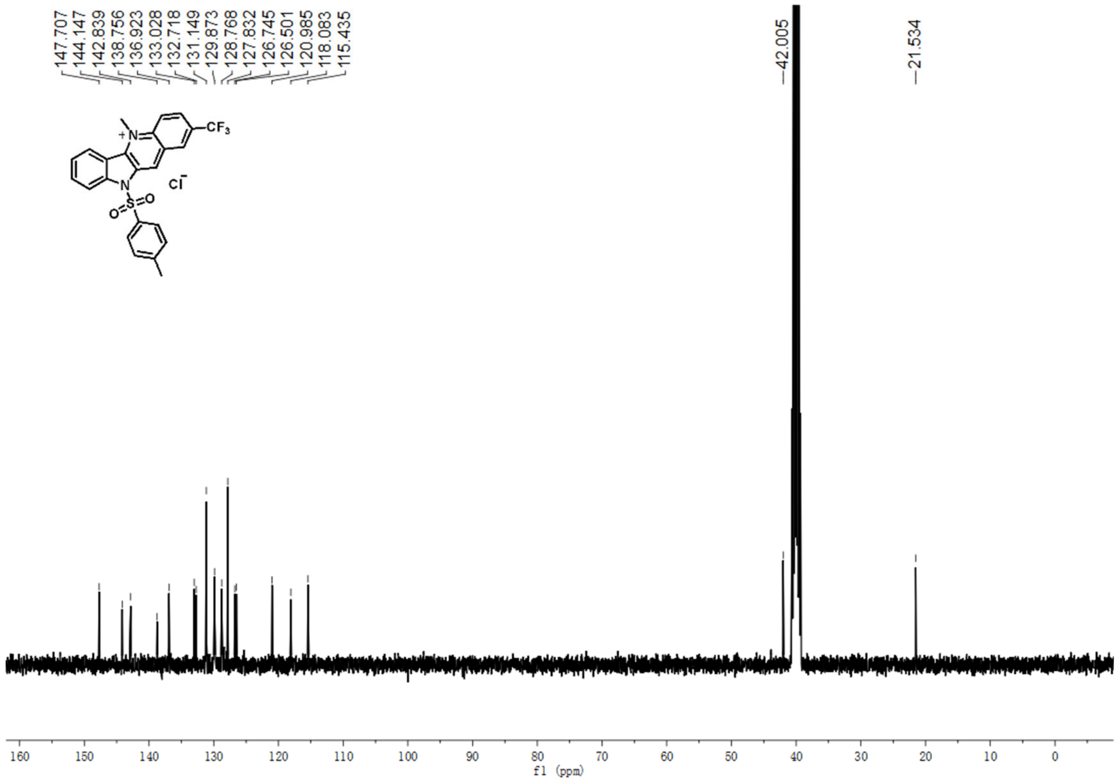
[13]C NMR spectrum of compound **2n**



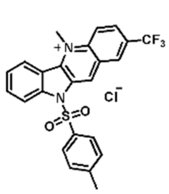
[1]H NMR spectrum of compound **2o**

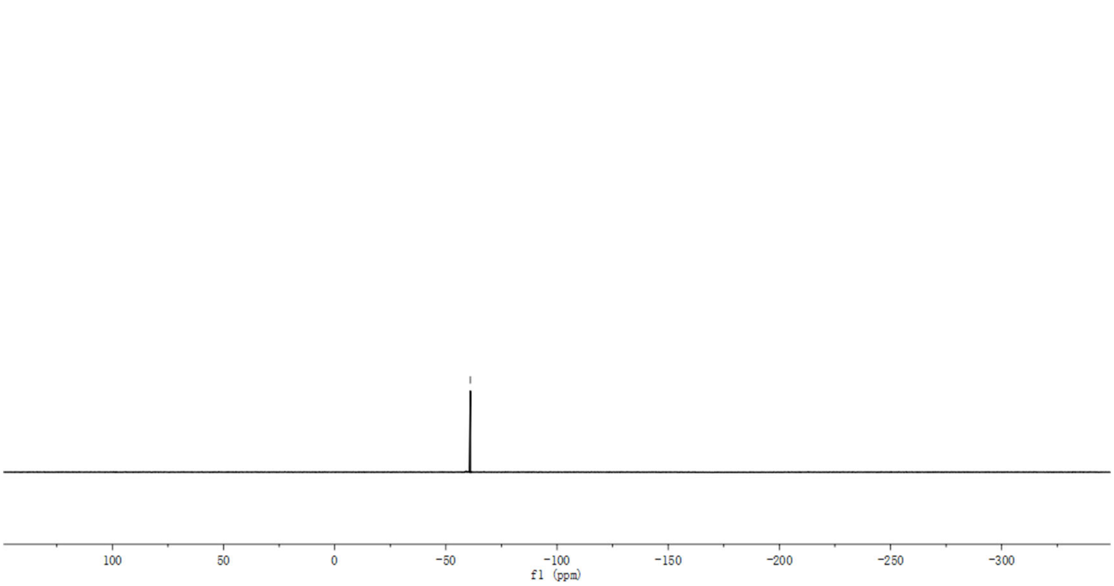


[13]C NMR spectrum of compound **2o**

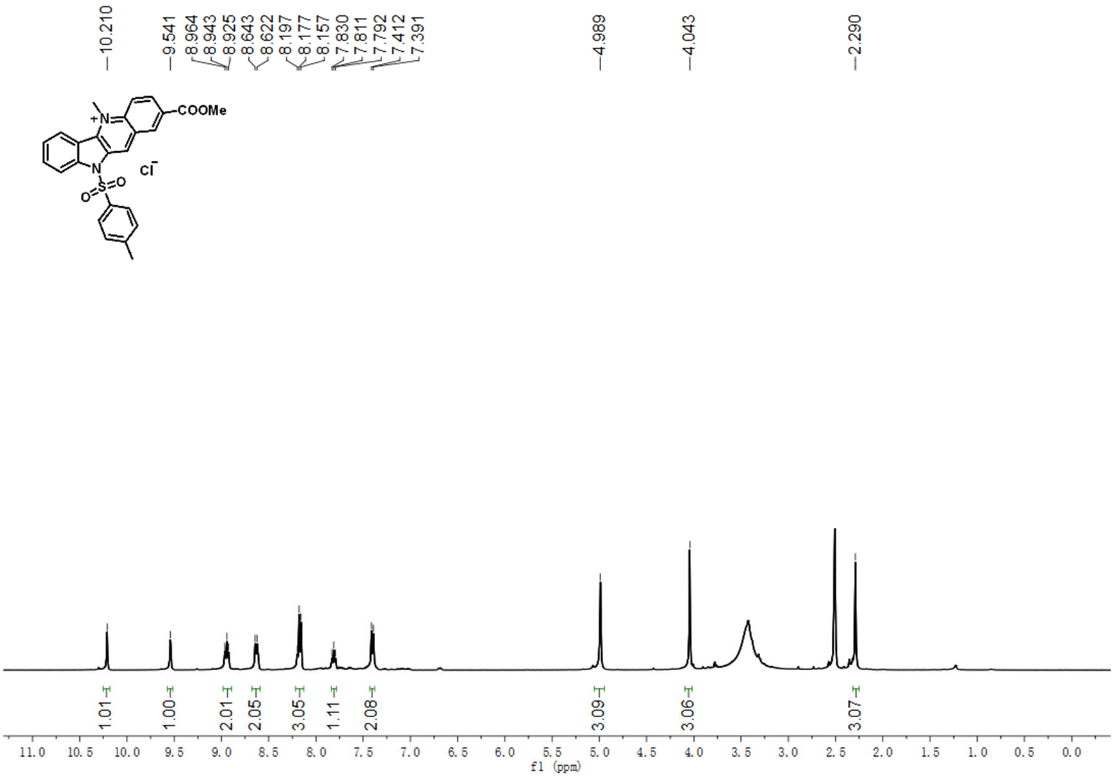


^{19}F NMR spectrum of compound **2o**

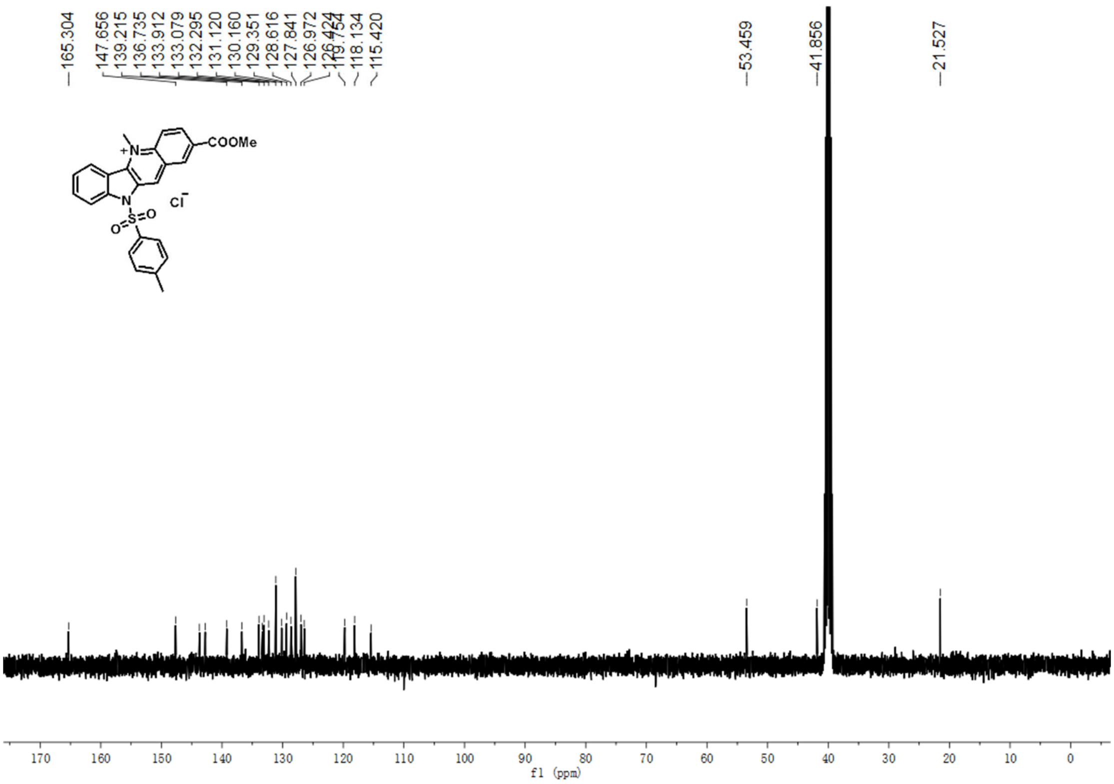




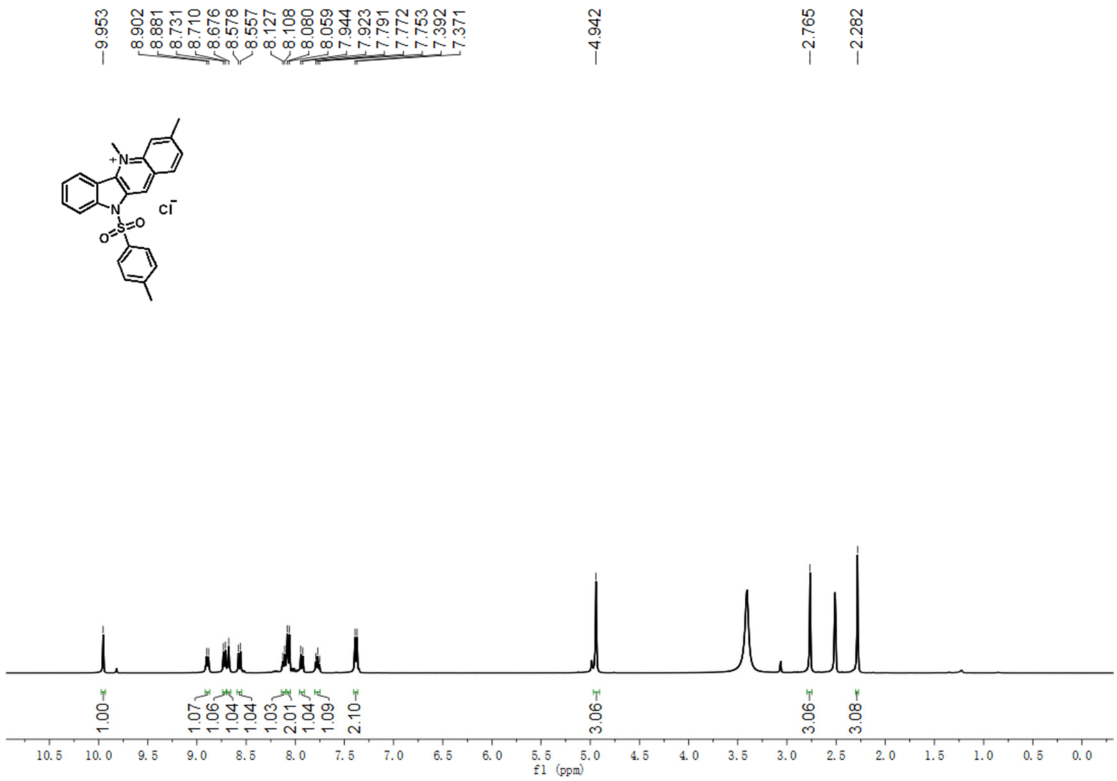
[1]H NMR spectrum of compound **2p**



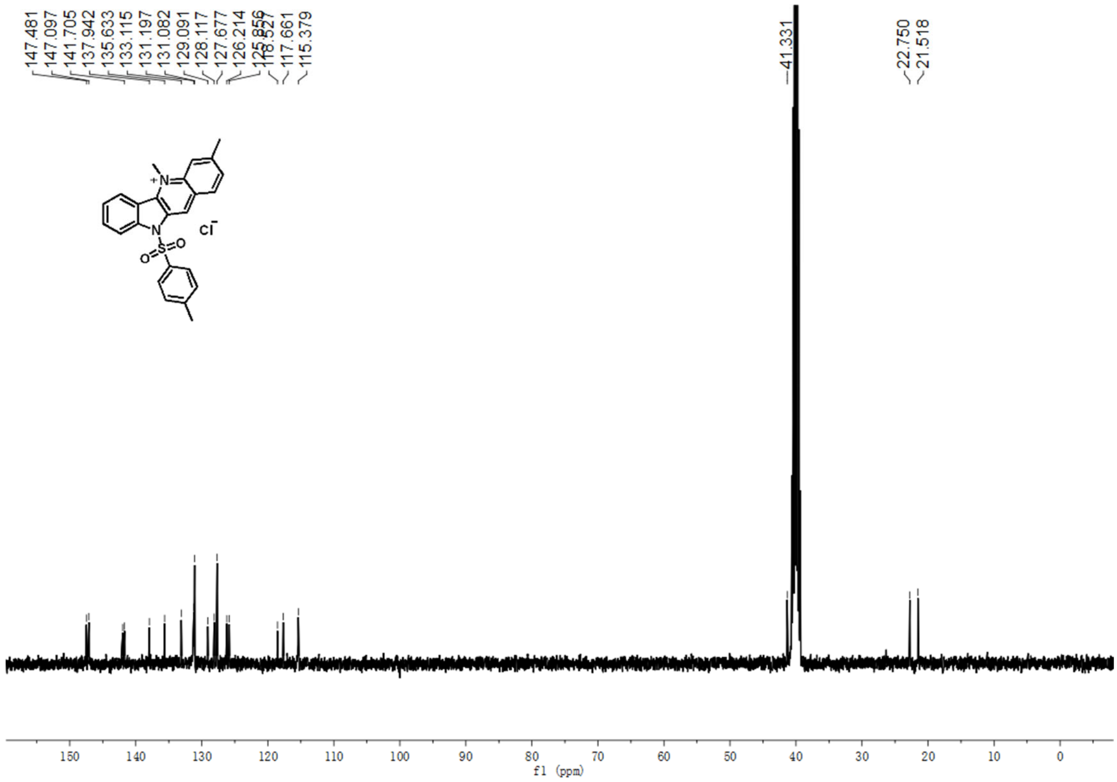
[13]C NMR spectrum of compound **2p**



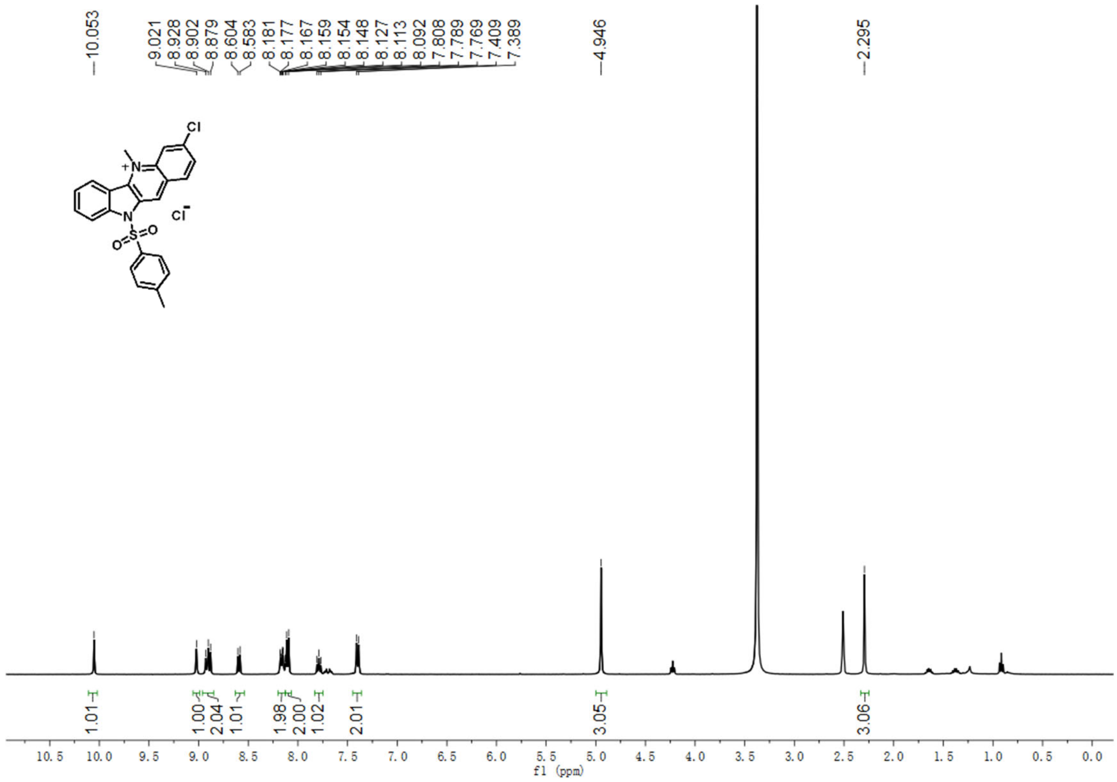
^{1}H NMR spectrum of compound **2q**



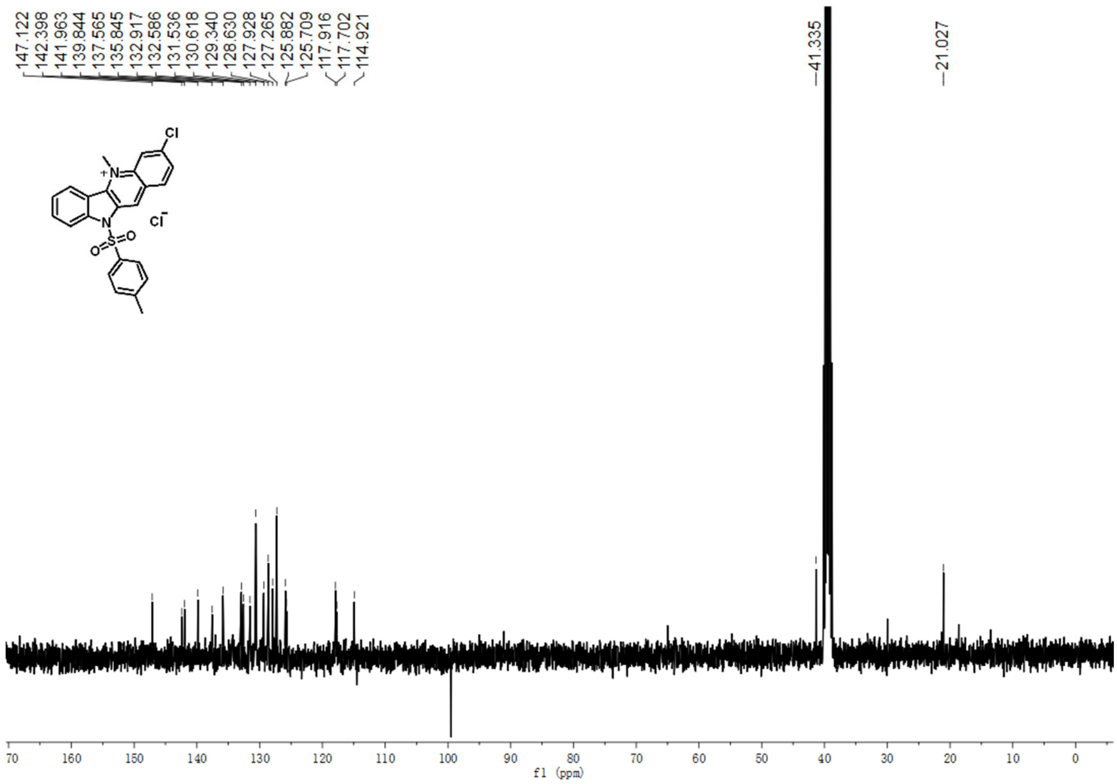
^{13}C NMR spectrum of compound **2q**



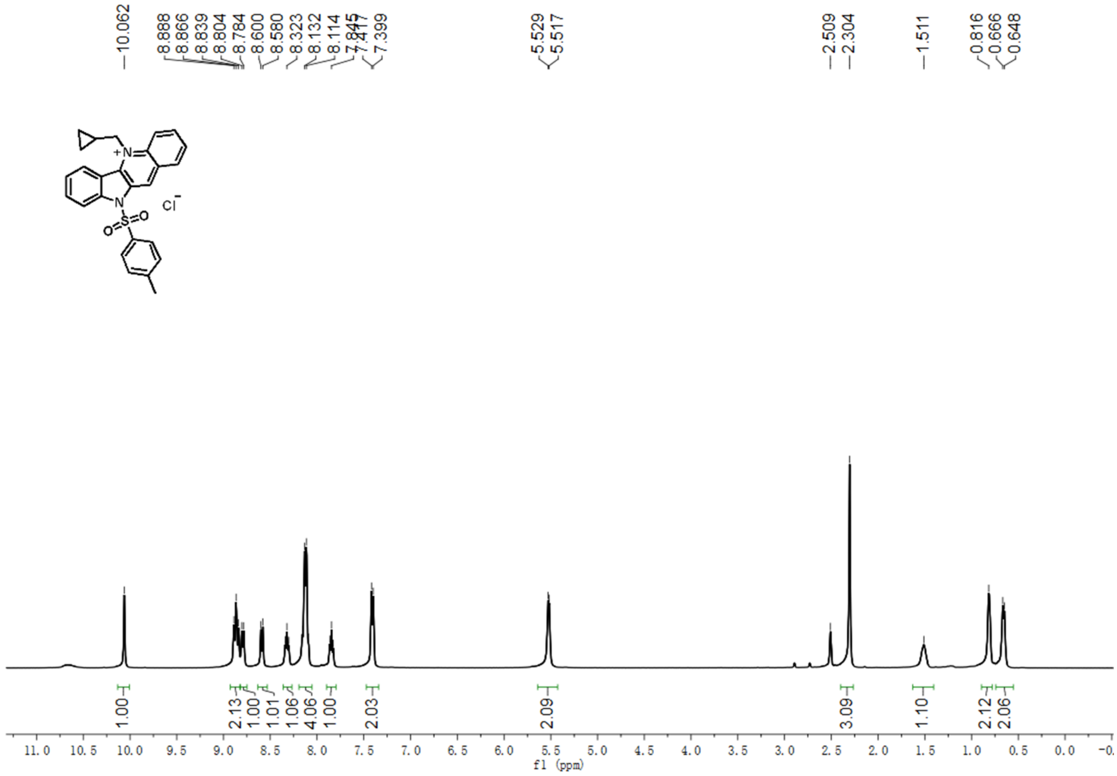
[1]H NMR spectrum of compound **2r**



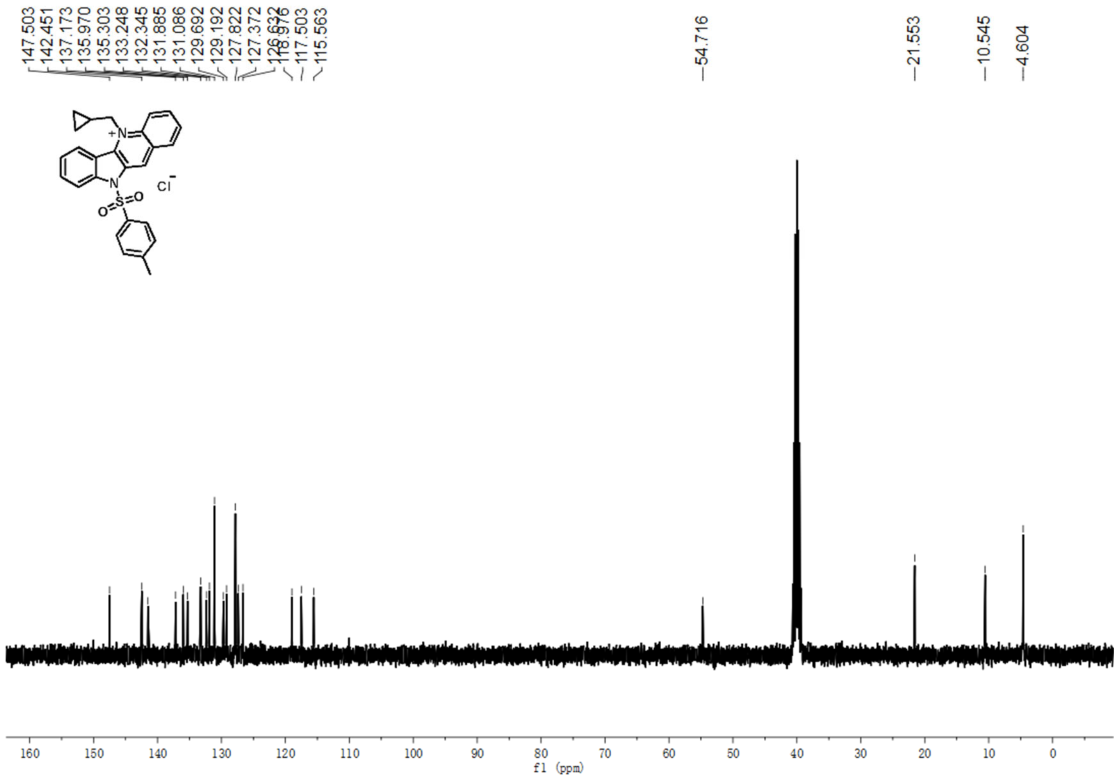
[13]C NMR spectrum of compound **2r**



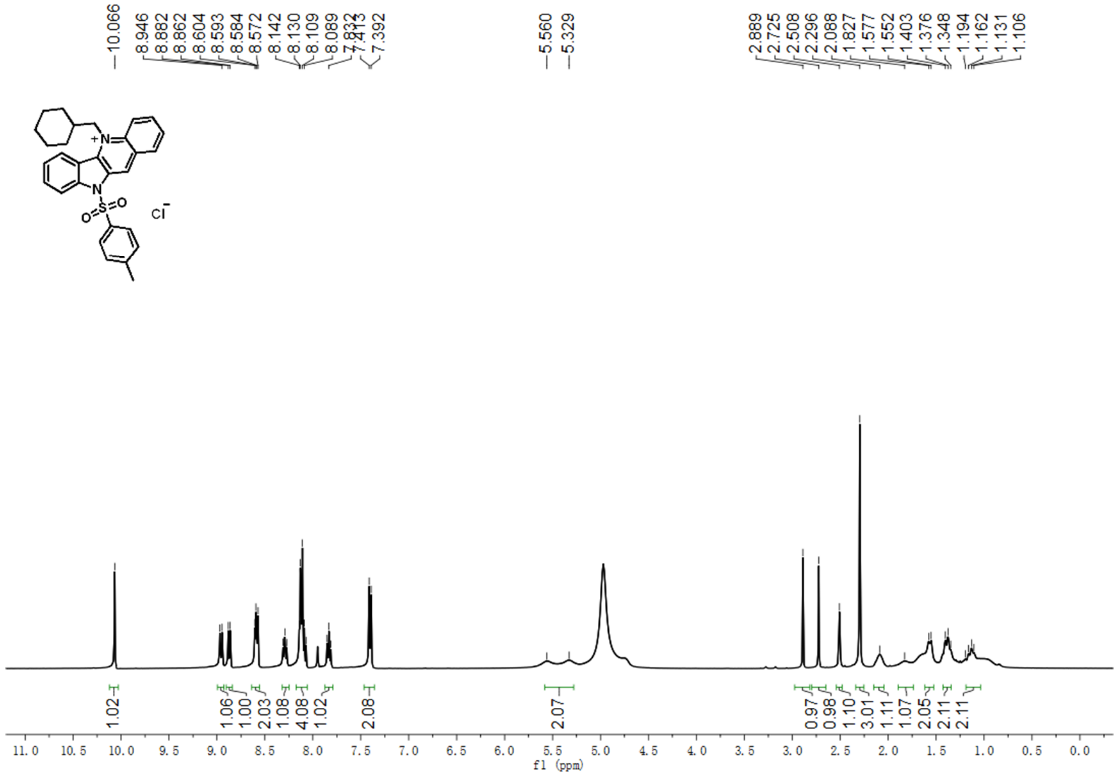
[1]H NMR spectrum of compound **2s**



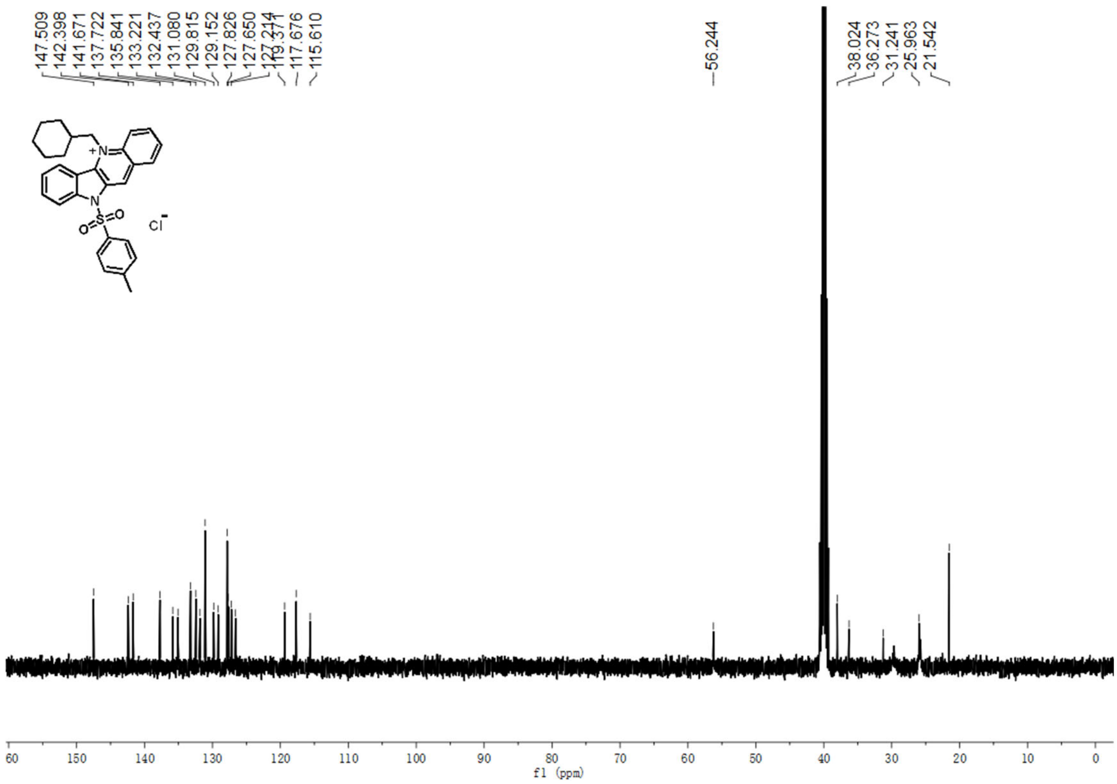
[13]C NMR spectrum of compound **2s**



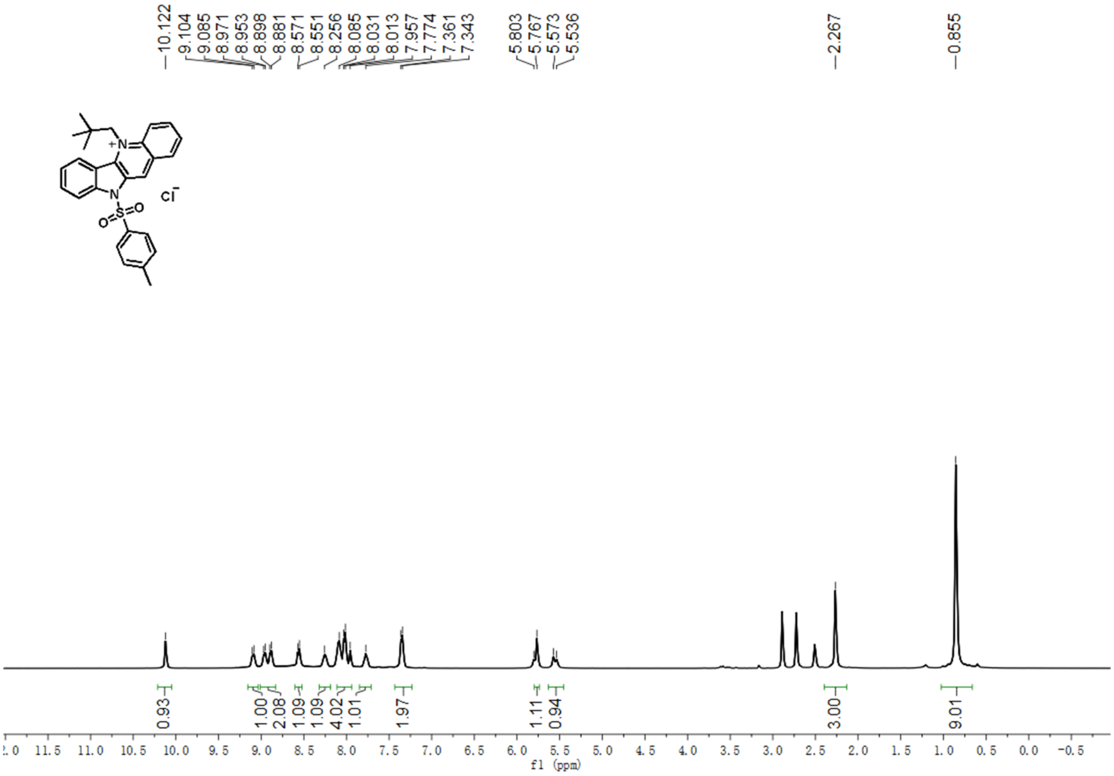
[1]H NMR spectrum of compound **2t**



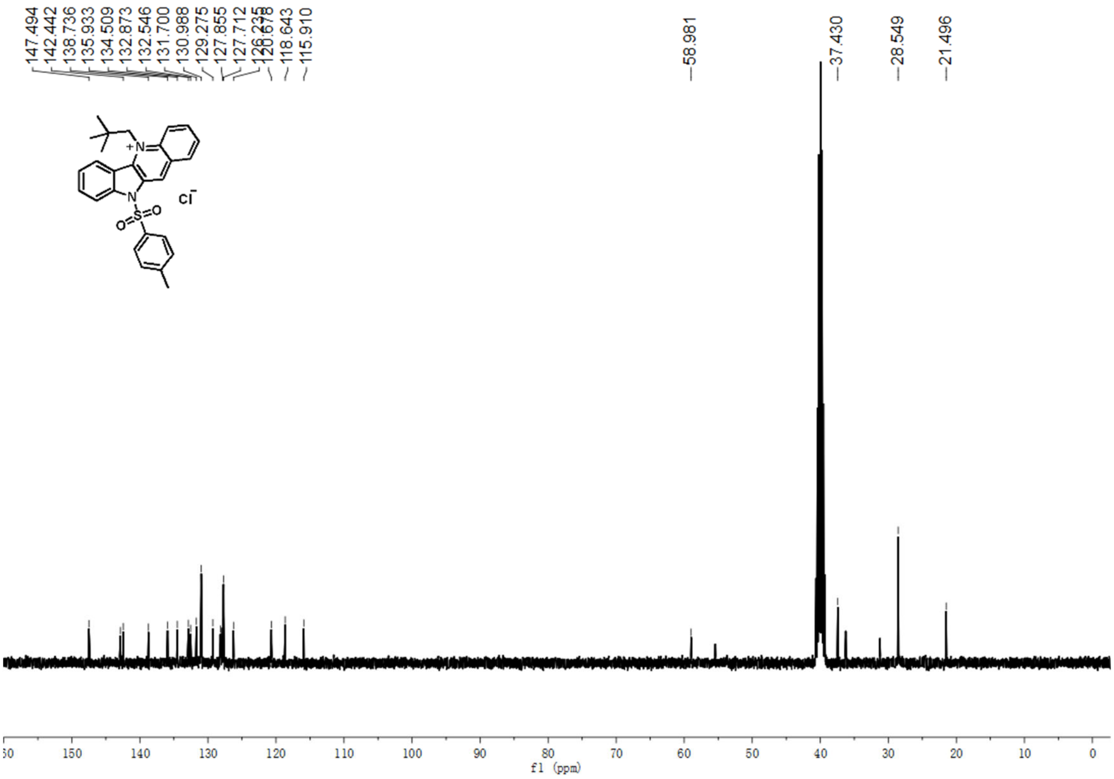
[13]C NMR spectrum of compound **2t**



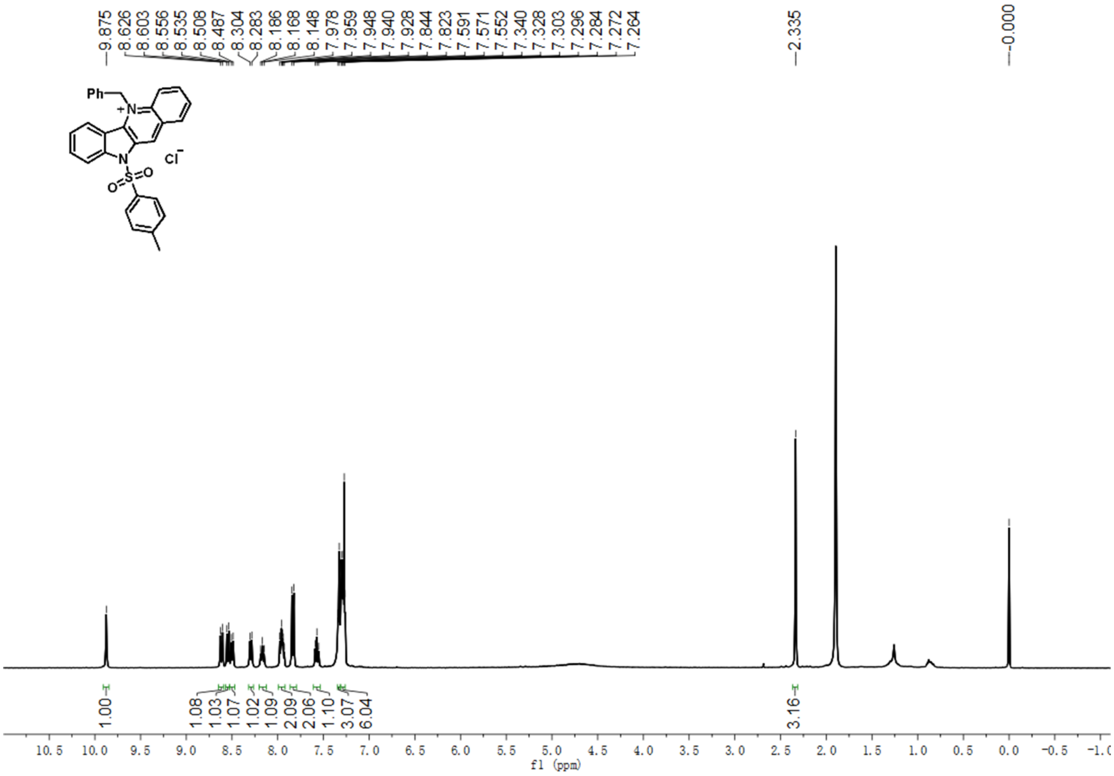
[1]H NMR spectrum of compound **2u**



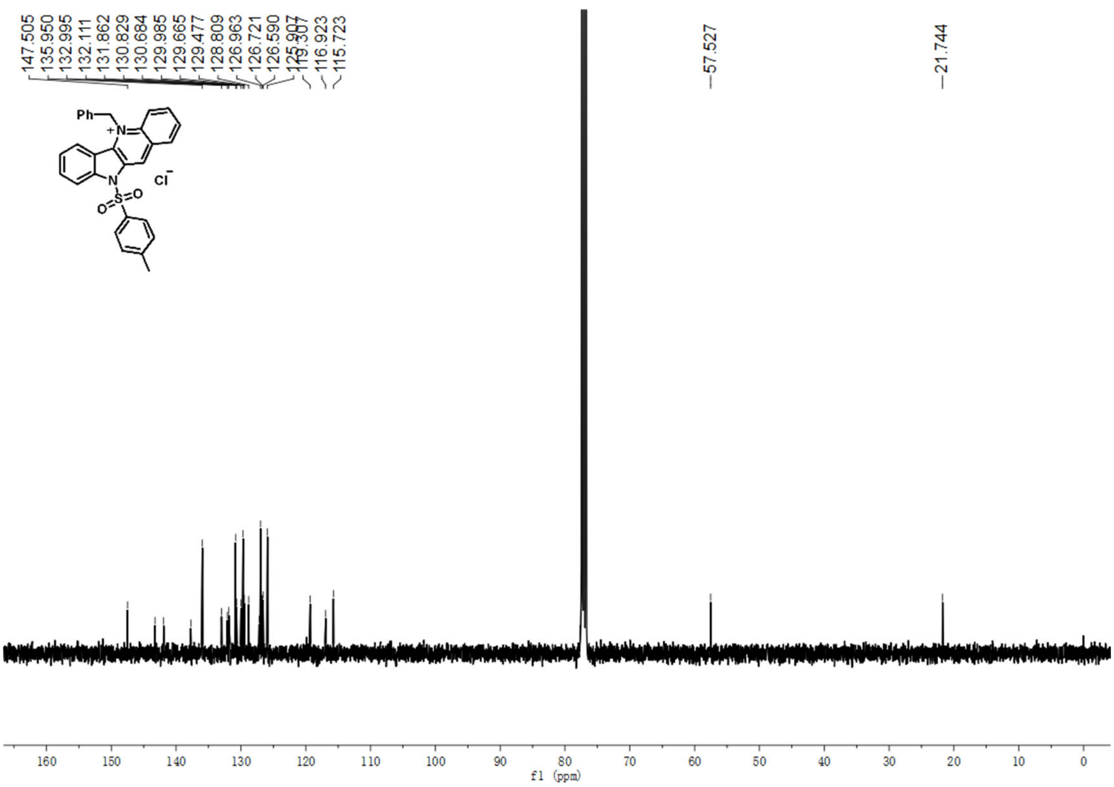
[13]C NMR spectrum of compound **2u**



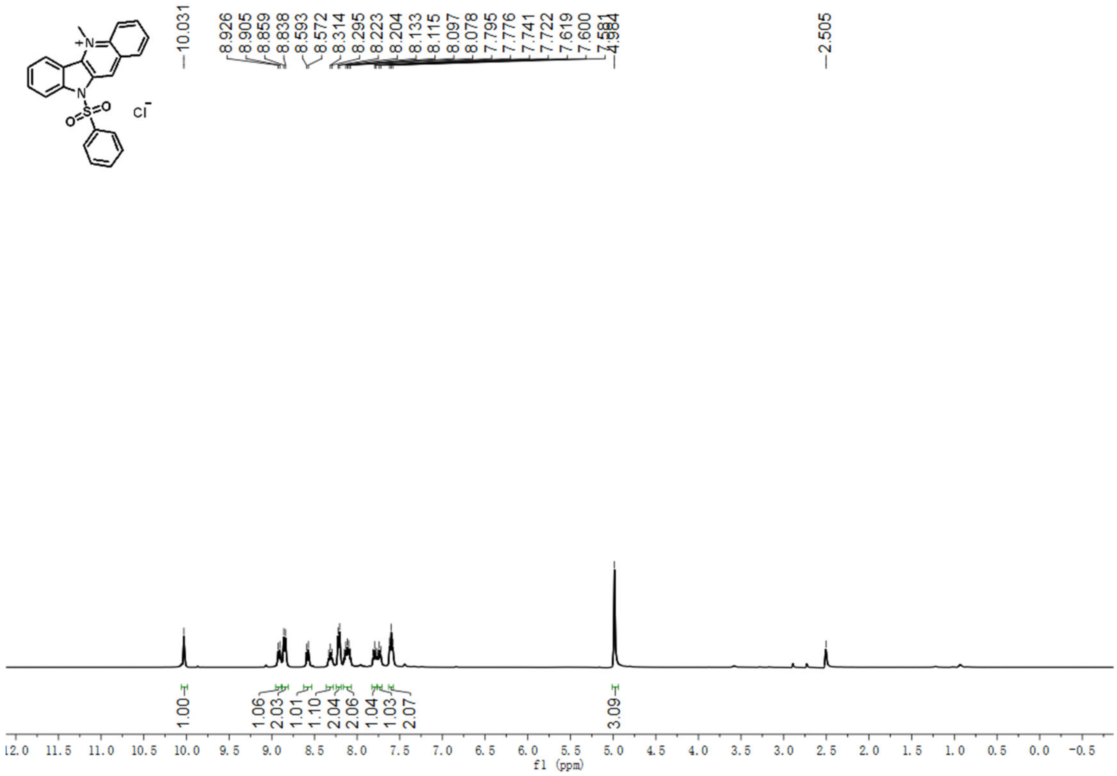
[1]H NMR spectrum of compound **2v**



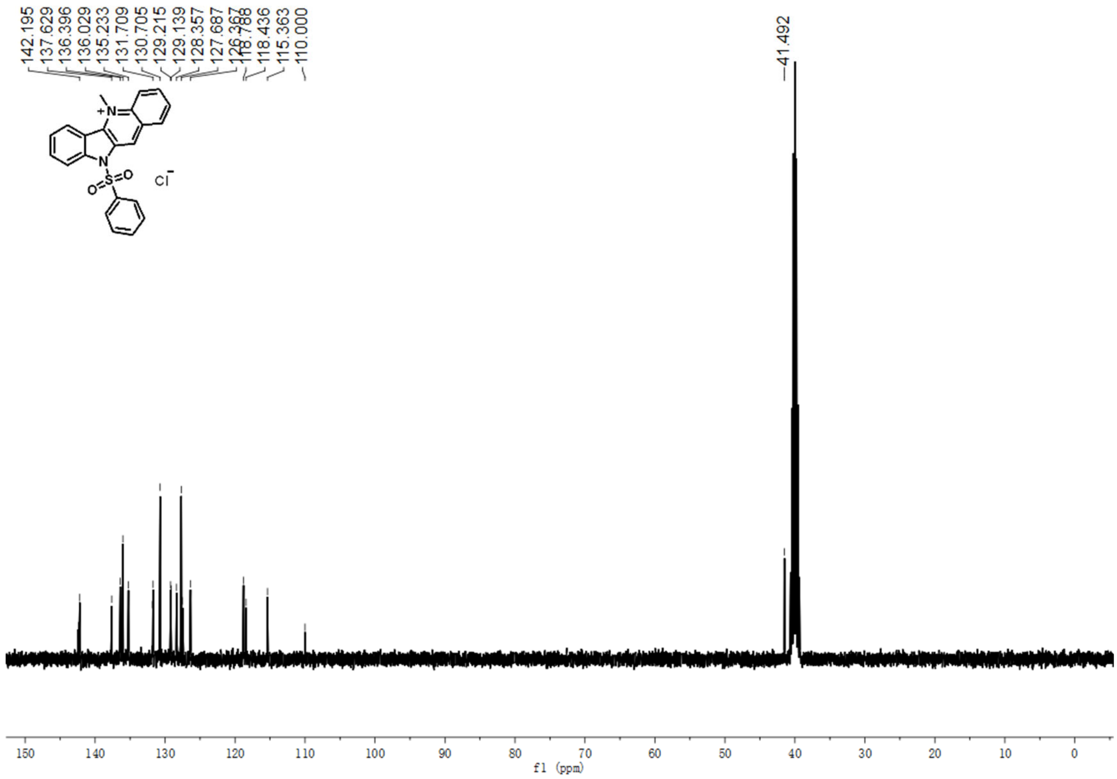
[13]C NMR spectrum of compound **2v**



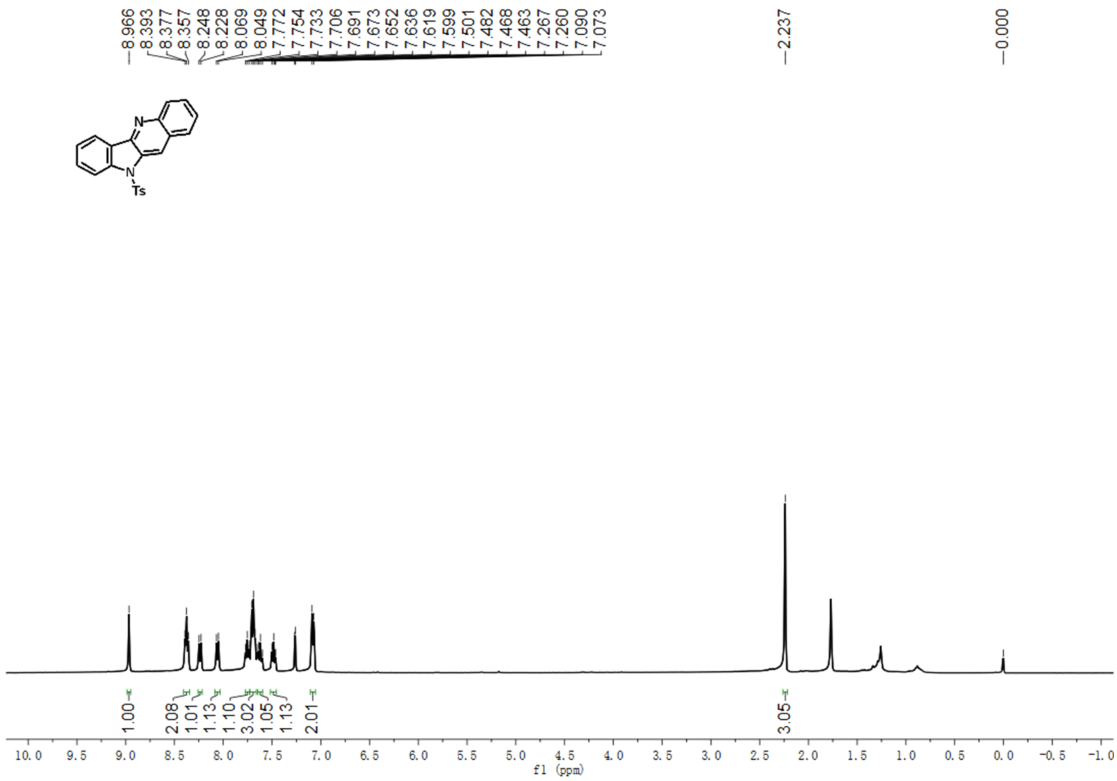
[1]H NMR spectrum of compound **2w**



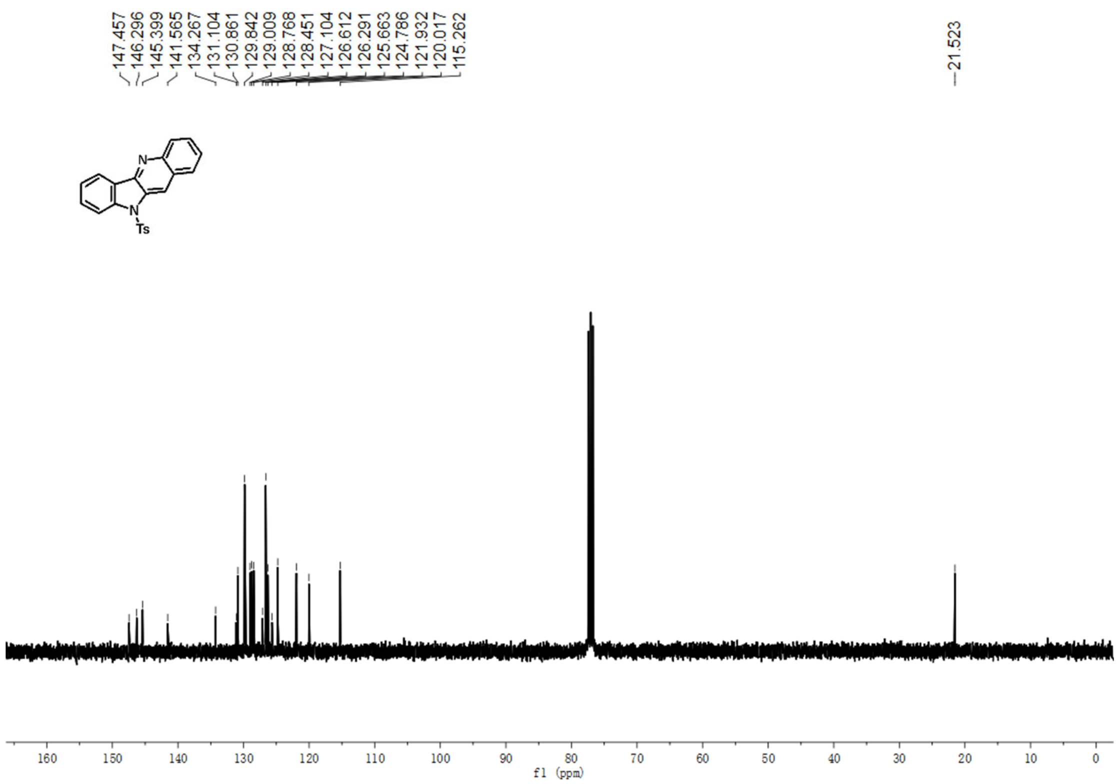
[13]C NMR spectrum of compound **2w**



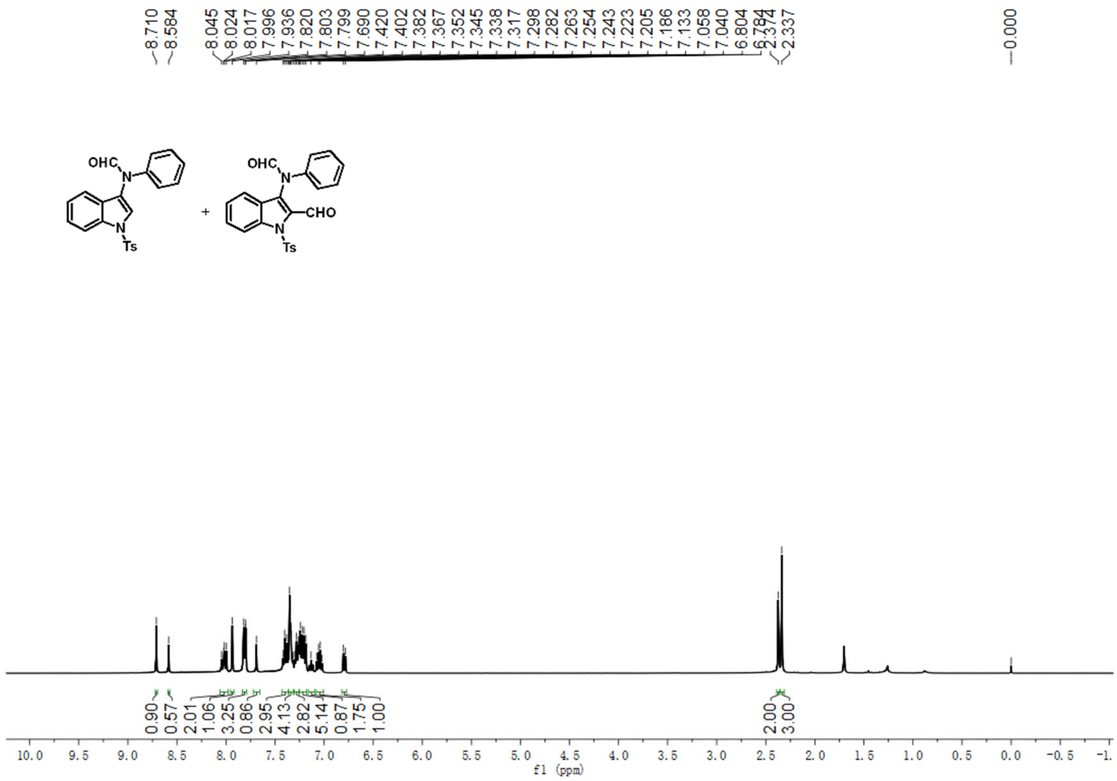
^{1}H NMR spectrum of compound **2**



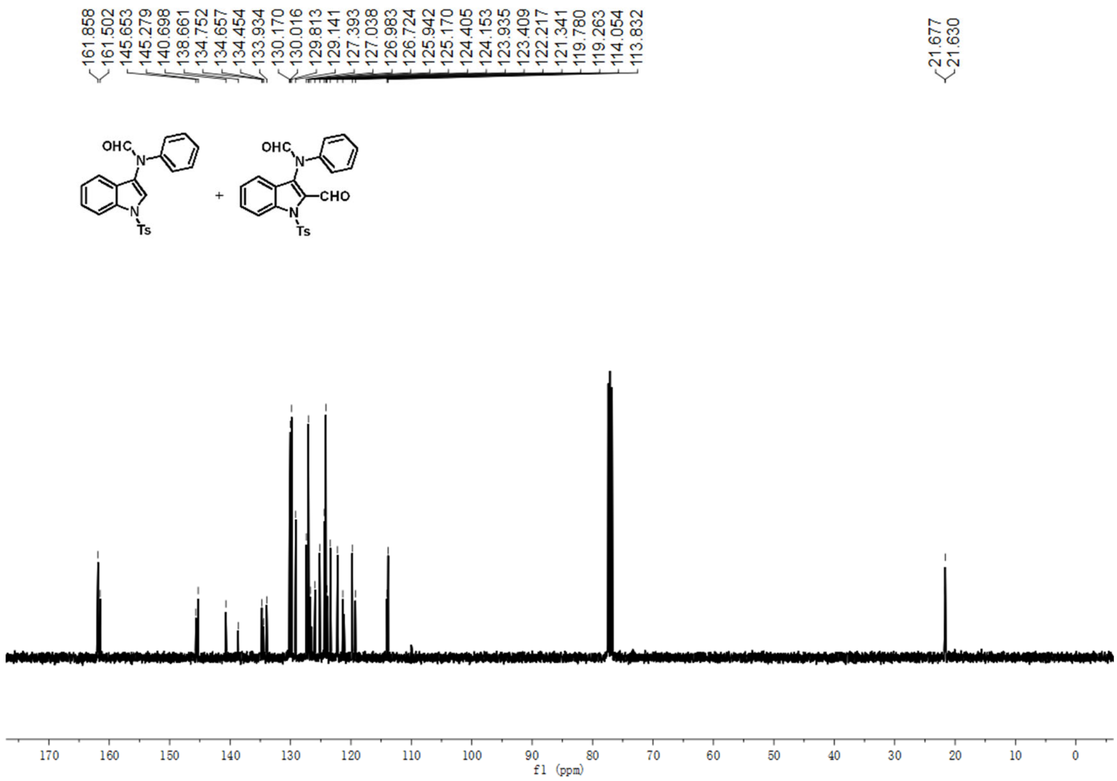
^{13}C NMR spectrum of compound **2**



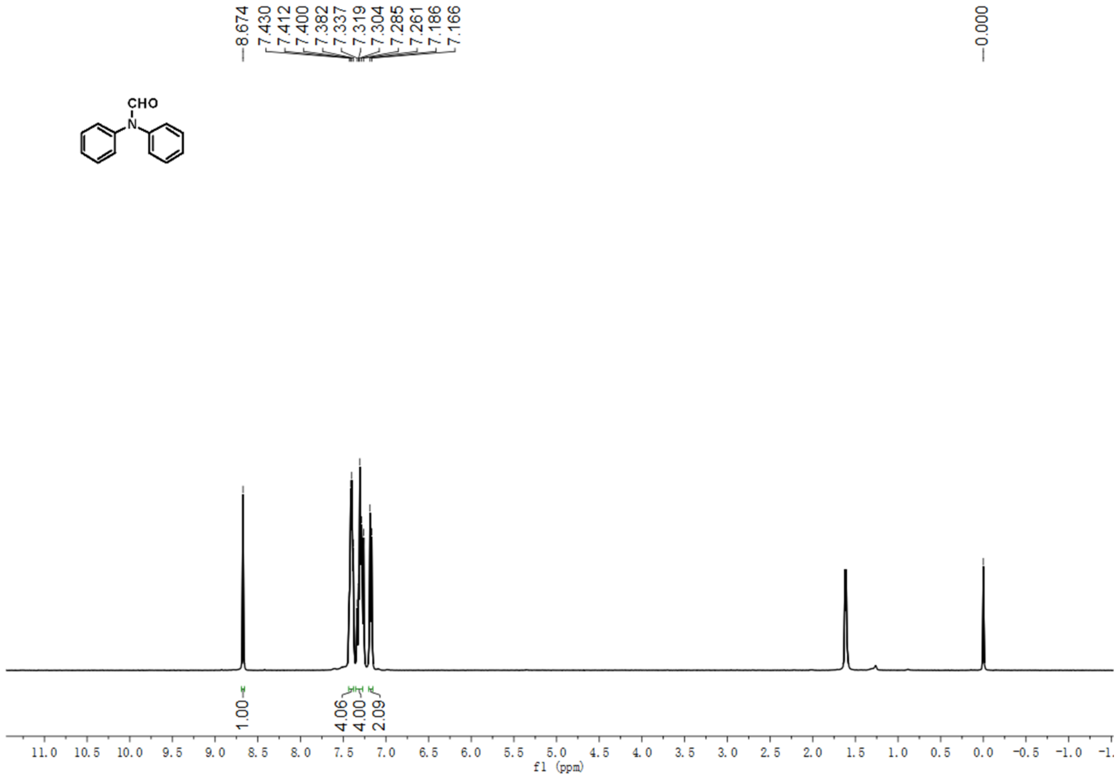
^{1}H NMR spectrum of compound **3** and **4**



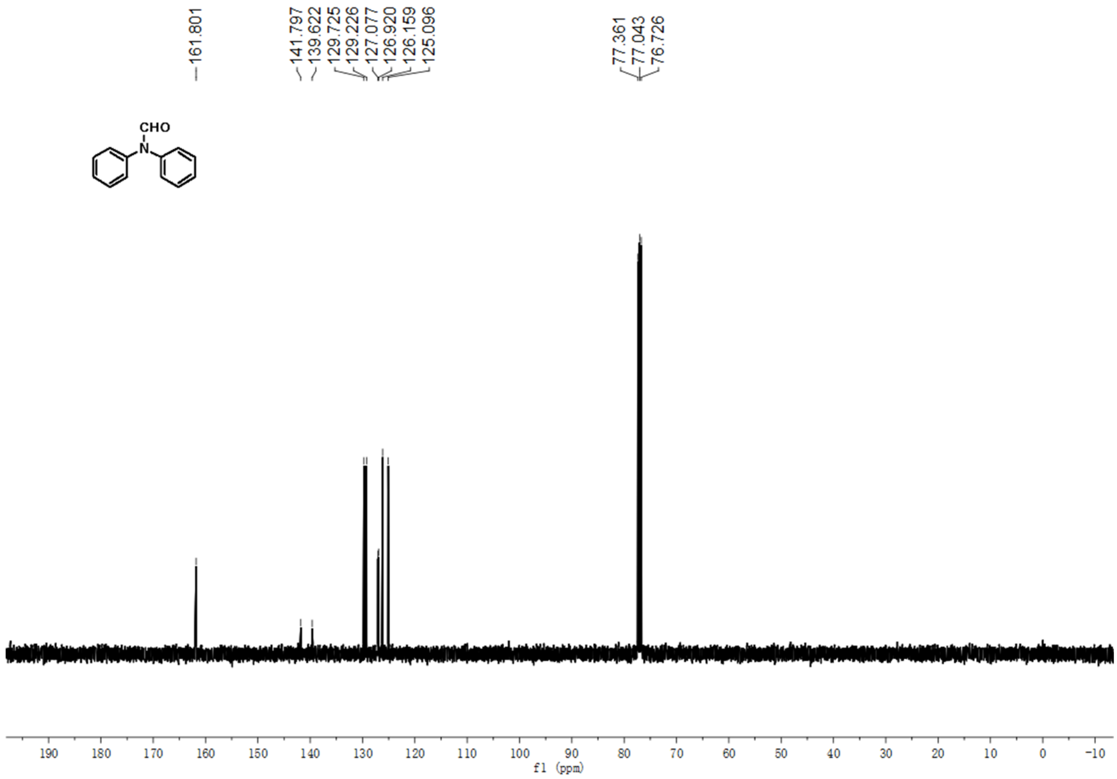
^{13}C NMR spectrum of compound **3** and **4**



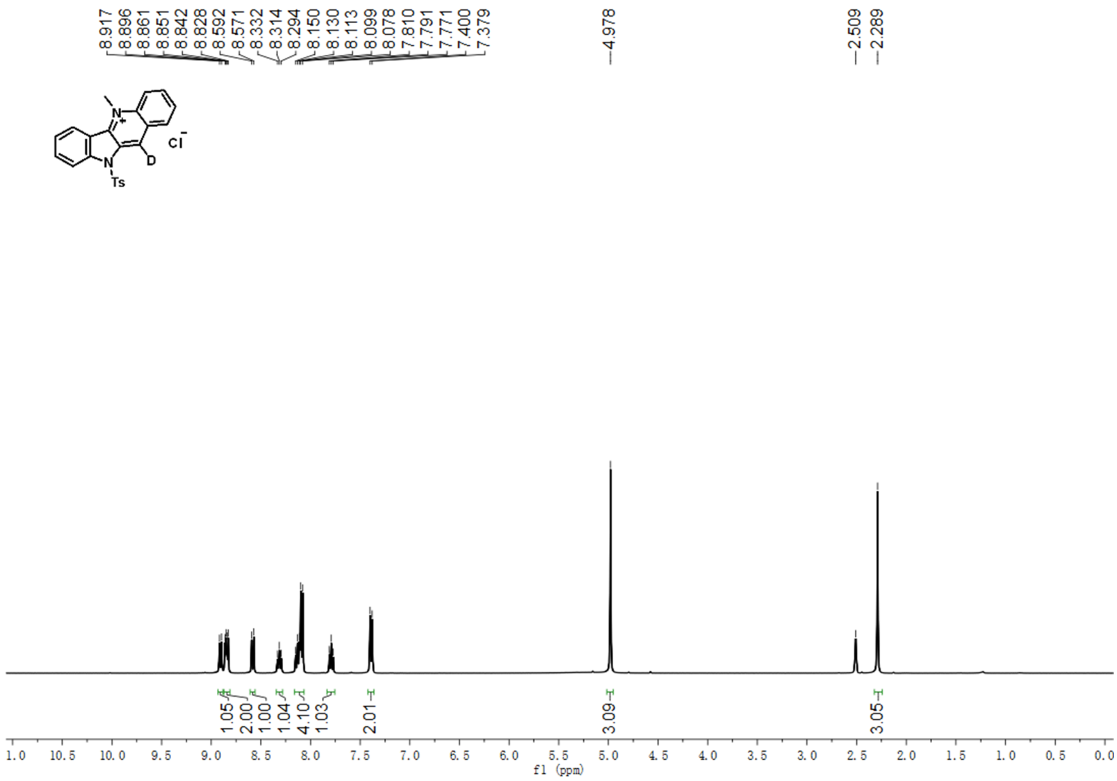
^{1}H NMR spectrum of compound **6**



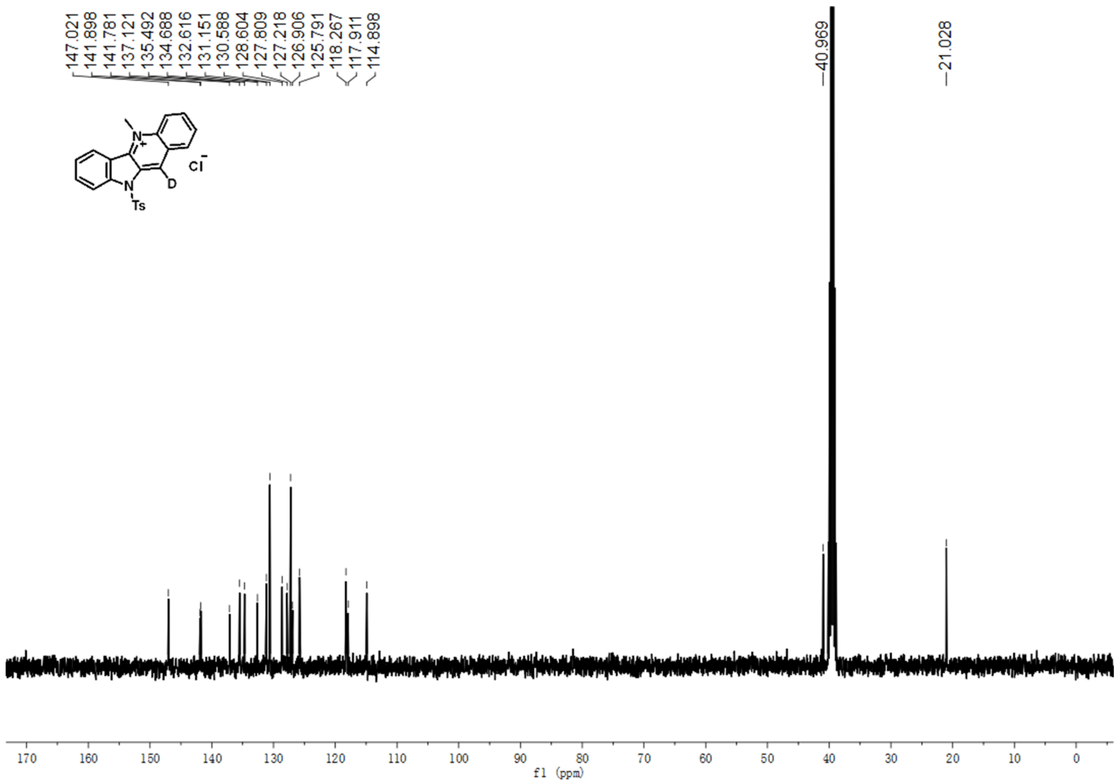
^{13}C NMR spectrum of compound **6**



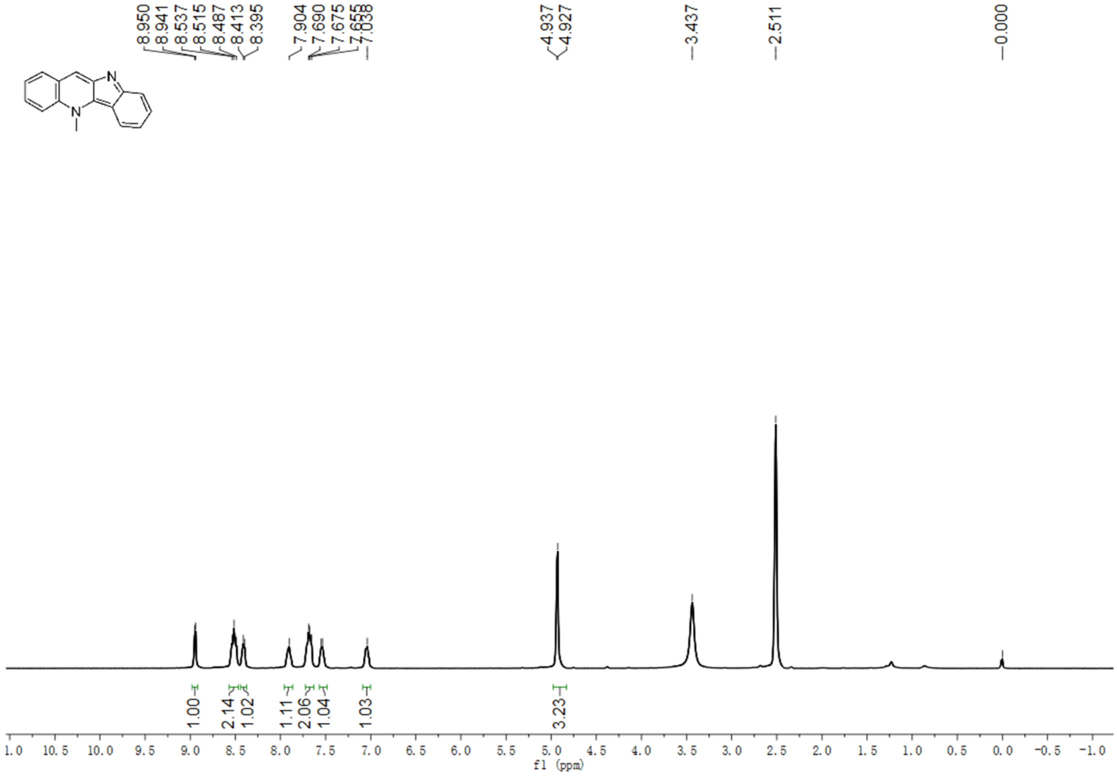
[1]H NMR spectrum of compound **7**



[13]C NMR spectrum of compound **7**



[1]H NMR spectrum of compound **Cryptolepine**



5. Supplementary References

1 T. Abe, T. Suzuki, M. Anada, S. Matsunaga, K. Yamada, *Org. Let.* **2017**, *19*, 4275-4278.