Supporting Information

Electrochemical difunctionalization of indolizines with glyoxylic acid and halide salts

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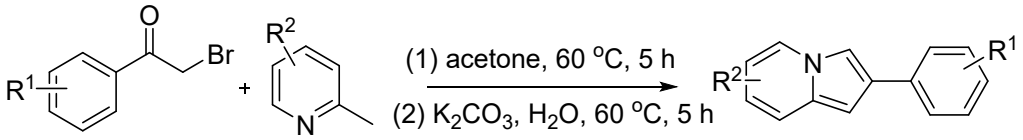
contents

1. General Information

All reagents were obtained from commercial suppliers and were used without further purification. The reactions were monitored by thin layer chromatography. Cyclic voltammetry experiments were carried out on CHI600e electrochemical workstation. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (377 MHz) spectra were recorded on Bruker AVANCE NEO 400MHz spectrometers with tetramethylsilane (TMS) as internal standard. High-resolution mass spectrometry data were obtained on a Bruker Ultrafle Xtreme MALDI TOF/TOF mass spectrometer (ESI-MS). Preparative thin layer chromatography was performed on silica gel plates about 0.50 mm, using UV light (UV 254) for visualization. Melting point data were obtained on Buchi M565 melting point instrument.

2. Experimental Procedures

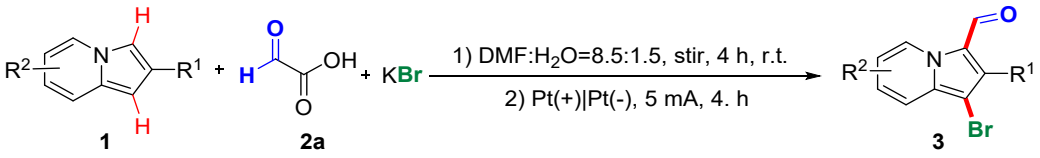
General procedure for the preparation of 1a-1z



S1 **S2** **1a-1z**

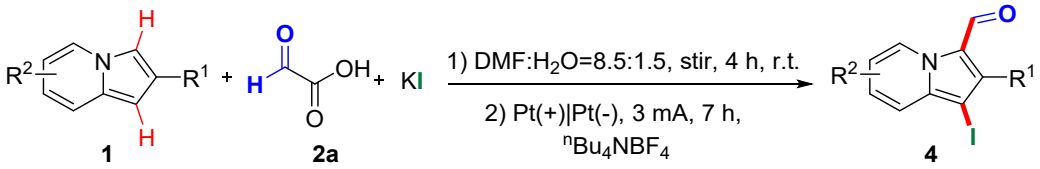
The indolizine derivatives **1a-1z** were synthesized according to literature procedures.[1] A solution of 2-bromoacetophenones (**S1**, 10 mmol) and 2-picolines (**S2**, 10 mmol) in acetone (50 mL) was heated at 60 ℃ for 5 h. The resulting precipitate was isolated via filtration and redissolved in 30 mL of hot water (60 ℃). Then, K_2CO_3 (10 mmol) was added, and the mixture was heated at 60 ℃ for 4 h. After filtration and drying in vacuum the compounds **1a-1z** were obtained without further purification needed. All compounds had spectral and physical data identical to those reported.

General procedure for preparing C1-brominated and C3-formylated indolizines



Indolizines (**1**, 0.2 mmol), glyoxylic acid (**2a**, 0.3 mmol), KBr (1.0 mmol) and DMF/H_2O (10 mL, v/v = 8.5:1.5) were added to a 25 mL undivided three-necked flask with a stir bar. The three-necked flask was equipped with a platinum plate anode (1.5 cm×1.5 cm) and a platinum plate cathode (1.5 cm×1.5 cm). Firstly, the mixture was stirred for 4 h at room temperature (step 1). Subsequently, the electrolysis was carried out at a constant current of 5 mA for 4 h (step 2). After completion of the reaction (monitored by TLC), the mixture was diluted with ethyl acetate and washed with saturated NaCl solution. The aqueous phase was extracted with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuum, and the product was isolated by purification of the residue by thin layer chromatography using petroleum ether/ethyl acetate (v/v=10:1) as eluent.

General procedure for preparing C1- iodinated and C3-formylated indolizines



Indolizines (**1**, 0.2 mmol), glyoxylic acid (**2a**, 0.3 mmol), KI (0.3 mmol), $^{n}Bu_4NBF_4$ (1.0 mmol) and DMF/H_2O (10 mL, v/v = 8.5:1.5) were added to a 25 mL undivided three-necked flask with a stir bar. The three-necked flask was furnished with a platinum plate anode (1.5 cm×1.5 cm) and a platinum plate cathode (1.5 cm×1.5 cm). Firstly, the mixture was stirred for 4 h at room temperature (step 1). Subsequently, the electrolysis was carried out at 3 mA for 7 h (step 2). At the end of the reaction (monitored by TLC), the mixture was diluted with ethyl acetate and washed with saturated NaCl solution. The aqueous phase was extracted with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuum, and the product was isolated by purification of the residue by thin layer chromatography using petroleum ether/ethyl acetate (v/v=10:1) as eluent.

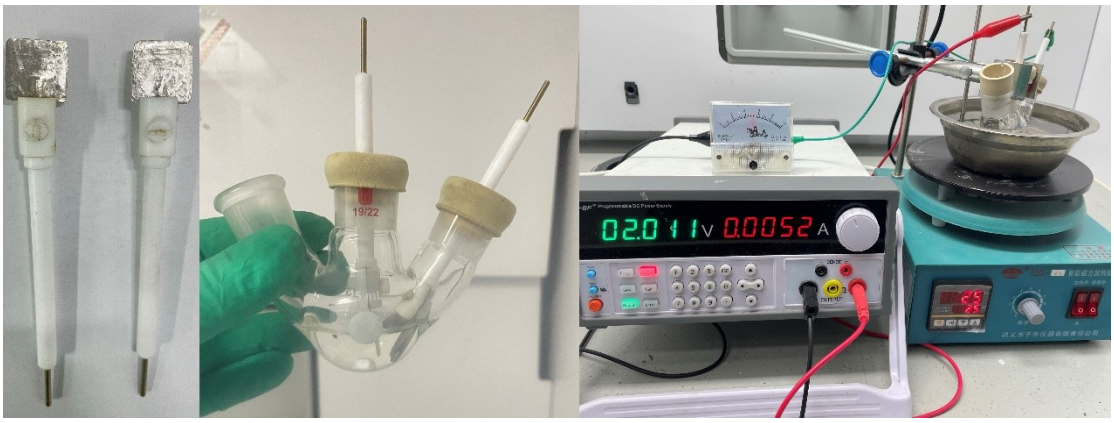
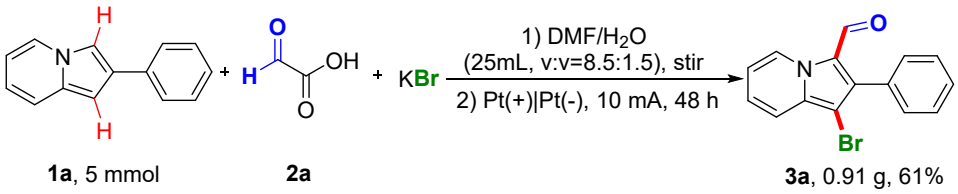


Figure S1 Electrolysis setup.

Cyclic voltammetry analysis

Cyclic voltammetry experiments were carried out on CHI600e electrochemical workstation at room temperature. An L-type Pt electrode (3.0 mm diameter) and a Pt plate (1.5 cm × 1.5 cm) were employed as the working electrode and counter electrode, respectively. Ag/Ag^+ electrode (0.1 M $AgNO_3$ in CH_3CN) was the reference electrode. Cyclic voltammograms recorded in 0.05 M $^nBu_4NBF_4$/ DMF+H_2O (15 mL, v/v=13.5:1.5) from 0 V to 0.6 V or 1.0 V at a scan rate of 50 mV/s.

Gram scale synthesis



2-Phenylindolizines (**1a**, 5 mmol, MW=193.3, 0.966 g), glyoxylic acid monohydrate (**2a**, 7.5 mmol, MW=92.0, 0.690 g), KBr (7.5 mmol, MW= 119.0, 0.893 g) and DMF/H_2O (25 mL, v/v=8.5:1.5, 20.148 g/3.75 g) were added to a beaker with a stir bar. The beaker was equipped with a platinum plate anode (1.5 cm×3.0 cm) and a platinum plate cathode (1.5 cm×3.0 cm). Firstly, the mixture was stirred at room temperature (step 1). After completion of the step 1 (monitored by TLC), the solution was electrolyzed at 10 mA for 48 h (step 2). The mixture was diluted with ethyl acetate

and washed with saturated NaCl solution. The aqueous phase was extracted with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuum, and the residue was purified by column chromatography analysis using petroleum ether/ethyl acetate as the eluent to afford the product.

As shown in Scheme S1, the superior solubility of DMF enables a significant reduction in solvent volume for gram-scale reactions. Consequently, our method performs satisfactorily in terms of sustainability indicators (E-factor, PMI and RME). Furthermore, the main by-products in the system are limited to carbon dioxide and hydrogen gas, and the yield of the product is also satisfactory. Therefore, in terms of atomic efficiency and carbon efficiency, the system maintains a good level in these aspects as well.

$$\text{E-factor} = \frac{\text{Total mass of wastes}}{\text{Mass of product}} = \frac{0.996\,g+0.690g+0.893\,g+20.148\,g-0.91\,g}{0.91\,g} = 23.97$$

$$\text{PMI} = \frac{\text{Total mass of input material in the whole process}}{\text{Mass of product}} = \frac{0.996\,g+0.690g+0.893\,g+20.148\,g}{0.91\,g} = 24.97$$

$$\text{RME}(\%) = \frac{\text{Mass of product}}{\text{Total mass of input material in the whole process}} \times 100\,\% = \frac{0.91\,g}{0.996\,g+0.690g+0.893\,g+20.148\,g} \times 100\,\% = 4.0\,\%$$

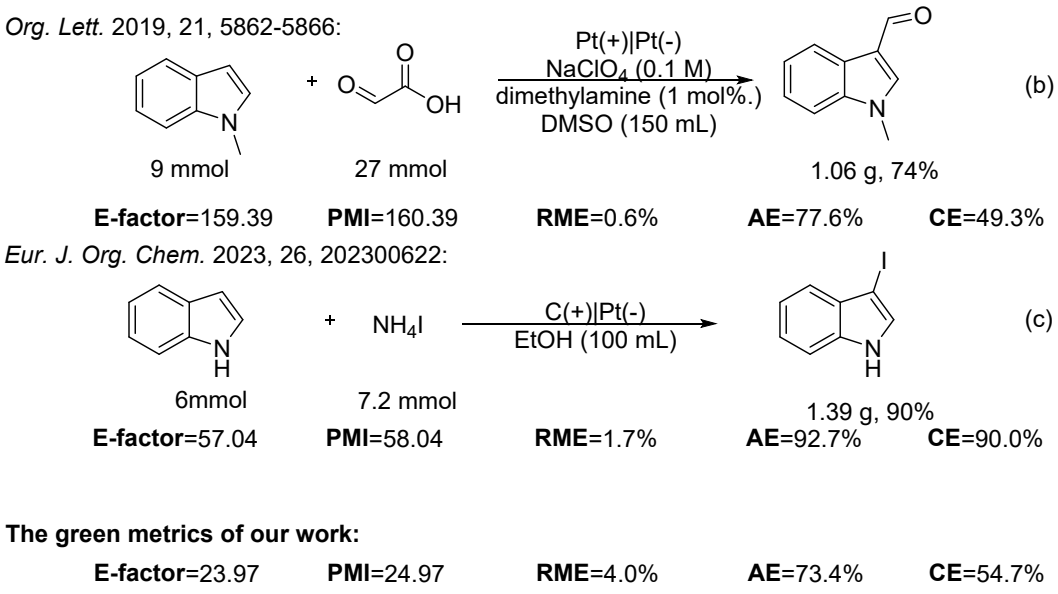
$$\text{AE}\,(\%) = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100\,\% = \frac{300.2}{193.3+92.0+119.0} \times 100\,\% = 74.3\,\%$$

$$\text{CE}\,(\%) = \frac{\text{Amount of carbon in product}}{\text{Total amount of carbon}} \times 100\,\% = \frac{3.1\times15}{5\times14+7.5\times2} \times 100\,\% = 54.7\,\%$$

(The water is generally excluded from the calculation.)

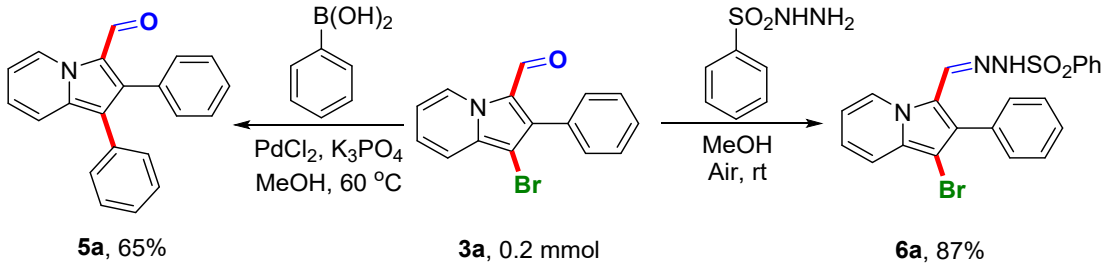
Scheme S1. The green chemistry metrics evaluation of our work

As shown in Scheme S2, compared to formylation or halogenation reactions of indole substrates, our strategy demonstrates superior performance across most green chemistry metrics.



Scheme S2. The green chemistry metrics of two independent reactions

Further transformation of 3a



(1) 1-Bromo-2-phenylindolizine-3-carbaldehyde (**3a**, 0.2 mmol), phenylboronic acid (0.24 mmol), K_3PO_4 (1.0 mmol), $PdCl_2$ (5 mol %) and methanol (3 mL) were added to a Schlenk tube with a stir bar. The reaction mixture was warmed to 60 °C in an oil bath. After completion of the reaction (monitored by TLC), the mixture was diluted with ethyl acetate (10 mL) and washed with saturated NaCl solution (30 mL). The aqueous phase was extracted with ethyl acetate (2×10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuum, and the product **5a** was obtained by purification of the residue by thin layer chromatography using petroleum ether/ethyl acetate(v/v=20:1) as eluent.

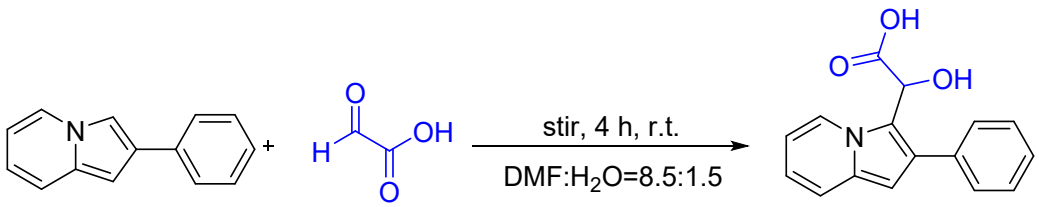
The characteristics of **5a**: m.p.= 171-173 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.93 (d, *J* = 7.0 Hz, 1H), 9.68 (s, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.42 – 7.20 (m, 12H), 7.01 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.9, 139.4, 136.7,

133.2, 132.4, 131.4, 130.3, 128.6, 128.3, 127.9, 126.8, 126.0, 121.0, 117.6, 116.9, 114.7.

(2) 1-Bromo-2-phenylindolizine-3-carbaldehyde (**3a**, 0.2 mmol), benzenesulfonohydrazide (0.24 mmol) and methanol (4 mL) were added to a tube with a stir bar. The reaction was carried out in room temperature. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum, the product **6a** was obtained by purification of the residue by thin layer chromatography using petroleum ether/ethyl acetate (v/v=3:1) as eluent.

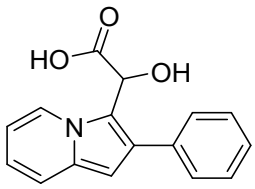
The characteristics of **6a**: m.p.= 142-144 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.41 – 9.23 (m, 1H), 8.05 – 7.92 (m, 2H), 7.86 (s, 1H), 7.67 (s, 1H), 7.59 – 7.46 (m, 4H), 7.46 – 7.31 (m, 5H), 7.15 – 7.03 (m, 1H), 6.92 – 6.73 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.1, 138.1, 134.6, 134.0, 133.3, 131.9, 130.8, 129.1, 128.4, 128.2, 128.1, 127.9, 122.4, 117.3, 115.2, 113.6, 89.4.

General procedure for preparing A



1a,0.2 mmol **2a**, 0.2 mmol **A**

Indolizines (**1**, 0.2 mmol), glyoxylic acid (**2a**, 0.3 mmol) and DMF/H_2O (10 mL, v/v = 8.5:1.5) were added to a 25 mL undivided three-necked flask with stirring for 4 h at room temperature. As it was not possible to isolate **A**, the solvent was replaced by DMSO-d_6 to carry out the subsequent characterization.



2-hydroxy-2-(2-phenylindolizin-3-yl)acetic acid (**A**)

The characteristics of **A**: ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.38 – 8.30 (m, 1H), 7.67 – 7.58 (m, 3H), 7.51 – 7.44 (m, 4H), 7.37 – 7.32 (m, 2H), 6.81 – 6.74 (m, 1H),

6.63 – 6.58 (m, 1H), 6.54 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 172.9, 135.7, 132.2, 129.1, 129.0, 128.6, 126.7, 125.1, 118.7, 118.2, 117.6, 110.1, 98.7, 64.9. HRMS (ESI) calculated for $C_{16}H_{14}NO_3^+$ [M+H]$^+$: 268.0968; found: 268.0969

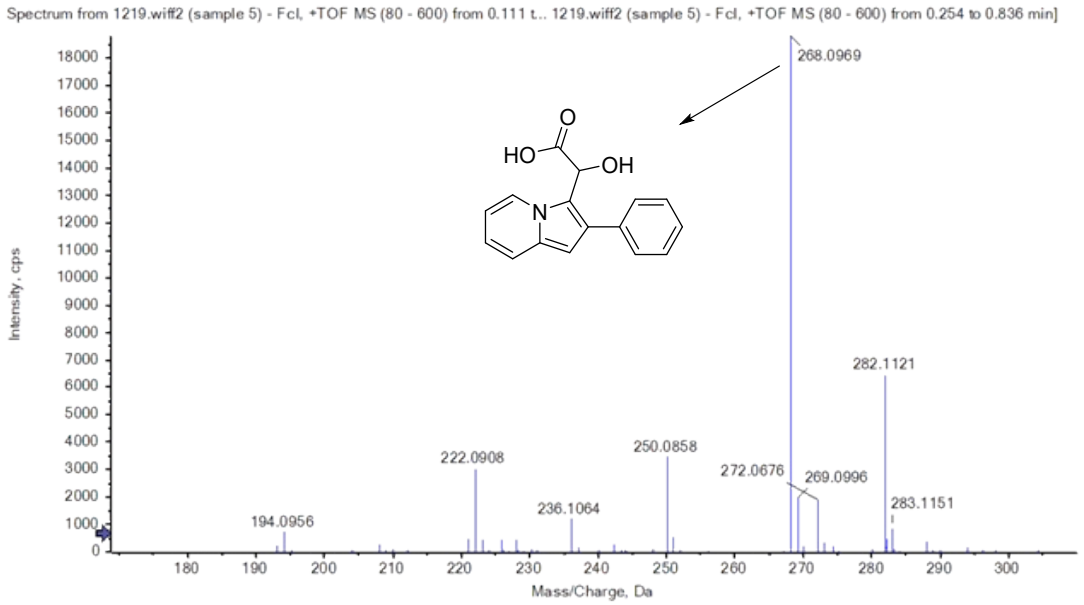


Figure S2 HRMS analysis of **A**.

The CV of the radical scavenger BHT

As shown in Figure S3, the oxidation potential of BHT is more positive than that of the bromide ions. The result indicates that BHT can play the role of a radical scavenger in this system.

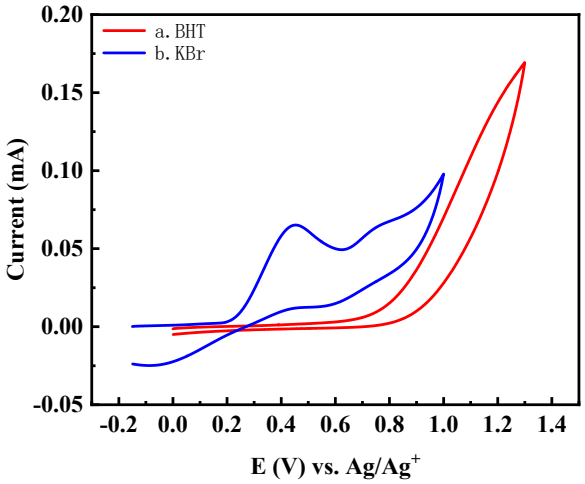
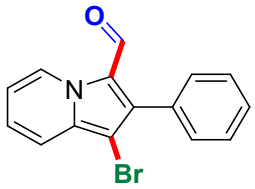
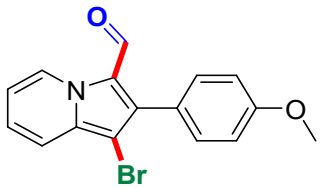


Figure S3. CV of BHT and KBr

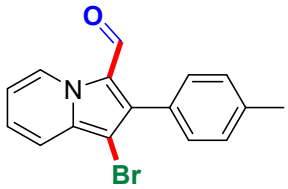
3. Characterization Data of Products



1-bromo-2-phenylindolizine-3-carbaldehyde (3a) — Yellow solid m.p.= 141-143 °C. (48.6 mg, 0.162 mmol, 81% yield) ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.83 (d, *J* = 7.0 Hz, 1H), 9.59 (s, 1H), 7.71 – 7.62 (m, 1H), 7.57 – 7.41 (m, 5H), 7.38 – 7.28 (m, 1H), 7.09 – 6.93 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.4, 139.9, 136.1, 131.2, 131.1, 128.7, 128.5, 128.4, 126.4, 121.1, 117.4, 115.1, 91.2. HRMS (ESI) calculated for $C_{15}H_{11}BrNO^{+}$ $[M+H]^{+}$: 300.0019; found: 300.0029.

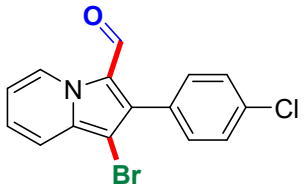


1-bromo-2-(4-methoxyphenyl)indolizine-3-carbaldehyde (3b) — Yellow solid m.p.= 123-126°C. (50.8 mg, 0.154 mmol, 77% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 (d, *J* = 7.0 Hz, 1H), 9.58 (s, 1H), 7.78 – 7.59 (m, 1H), 7.56 – 7.44 (m, 2H), 7.37 – 7.29 (m, 1H), 7.07 – 7.00 (m, 2H), 7.00 – 6.88 (m, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 160.1, 136.1, 132.3, 128.5, 126.4, 123.2, 121.0, 117.24, 114.9, 114.0, 91.1, 55.4. HRMS (ESI) calculated for $C_{16}H_{13}BrNO_{2}^{+}$ $[M+H]^{+}$: 330.0124; found: 330.0132.

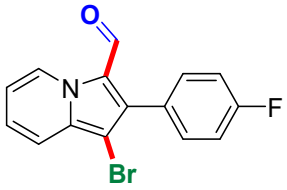


1-bromo-2-(p-tolyl)indolizine-3-carbaldehyde (3c) — Yellow solid m.p.= 129-131 °C. (47.1 mg, 0.150 mmol, 75% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.83 (d, *J*

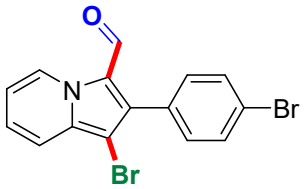
= 7.0 Hz, 1H), 9.59 (s, 1H), 7.74 – 7.59 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.24 (m, 3H), 7.10 – 6.91 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.41, 140.0, 138.7, 136.1, 130.9, 129.2, 128.5, 128.1, 126.4, 121.0, 117.3, 115.0, 91.1, 21.5. HRMS (ESI) calculated for $C_{16}H_{13}BrNO^+$ $[M+H]^+$: 314.0175; found: 314.0183.



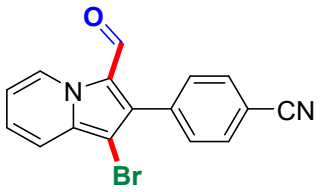
1-bromo-2-(4-chlorophenyl)indolizine-3-carbaldehyde (3d) — Yellow solid m.p.= 142-145 °C. (46.2 mg, 0.138 mmol, 69 % yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 (d, *J* = 7.0 Hz, 1H), 9.55 (s, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 4H), 7.39 – 7.30 (m, 1H), 7.11 – 6.96 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 138.6, 136.1, 135.1, 132.3, 129.5, 128.8, 128.5, 126.6, 120.9, 117.4, 115.4, 91.2. HRMS (ESI) calculated for $C_{15}H_{10}BrClNO^+$ $[M+H]^+$: 333.9629; found: 333.9635.



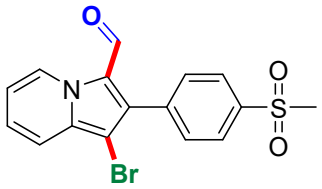
1-bromo-2-(4-fluorophenyl)indolizine-3-carbaldehyde (3e) — Yellow solid m.p.= 140-142 °C. (45.2 mg, 0.142 mmol, 72% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.06 – 9.67 (m, 1H), 9.55 (s, 1H), 7.76 – 7.61 (m, 1H), 7.54 – 7.47 (m, 2H), 7.39 – 7.29 (m, 1H), 7.20 (t, *J* = 8.6 Hz, 2H), 7.05 – 6.91 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.0, 163.1 (d, *J* = 248.8 Hz), 138.8, 136.1, 132.8 (d, *J* = 8.1 Hz), 128.5, 127.1 (d, *J* = 3.3 Hz), 126.6, 121.0, 117.4, 115.6 (d, *J* = 21.8 Hz), 115.3, 91.2. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -112.52. HRMS (ESI) calculated for $C_{15}H_{10}BrFNO^+$ $[M+H]^+$: 317.9924; found: 317.9922.



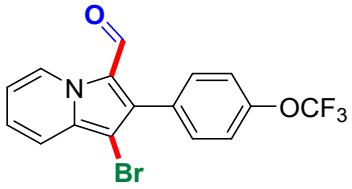
1-bromo-2-(4-bromophenyl)indolizine-3-carbaldehyde (3f) — Yellow solid m.p.= 162-164 °C. (45.5 mg, 0.120 mmol, 60% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.81 (d, *J* = 6.9 Hz, 1H), 9.55 (s, 1H), 7.85 – 7.62 (m, 3H), 7.44 – 7.32 (m, 3H), 7.01 (td, *J* = 6.9, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 138.5, 136.1, 132.6, 131.8, 130.0, 128.5, 126.6, 123.3, 120.9, 117.4, 115.4, 91.1. HRMS (ESI) calculated for $C_{15}H_{10}Br_2NO^+$ $[M+H]^+$: 379.9103; found: 379.9110.



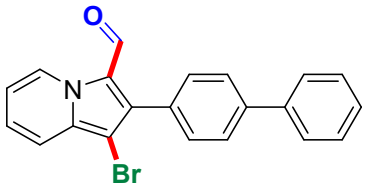
4-(1-bromo-3-formylindolizin-2-yl)benzonitrile (3g) — Yellow solid m.p.= 179-181 °C. (34.5 mg, 0.106 mmol, 53% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.83 (d, *J* = 7.0 Hz, 1H), 9.54 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.74 – 7.57 (m, 3H), 7.45 – 7.36 (m, 1H), 7.16 – 6.98 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.4, 137.5, 136.2, 136.1, 132.2, 131.8, 128.5, 126.9, 120.8, 118.6, 117.6, 115.8, 112.6, 91.2. HRMS (ESI) calculated for $C_{16}H_{10}BrN_2O^+$ $[M+H]^+$: 324.9971; found: 324.9980.



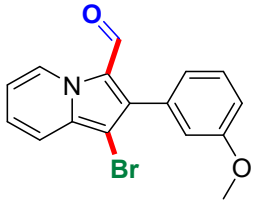
1-bromo-2-(4-(methylsulfonyl)phenyl)indolizine-3-carbaldehyde (3h) — Yellow solid m.p.= 176-179 °C. (29.5 mg, 0.078 mmol, 39% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.91 – 9.76 (m, 1H), 9.61 (s, 1H), 7.73 – 7.55 (m, 1H), 7.47 – 7.29 (m, 2H), 7.17 – 6.92 (m, 4H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.5, 140.7, 137.5, 137.1, 136.2, 132.0, 128.6, 127.6, 127.0, 121.0, 117.7, 115.9, 91.3, 44.7. HRMS (ESI) calculated for $C_{16}H_{10}BrNO_3^+$ $[M+H]^+$: 377.9794; found: 377.9802.



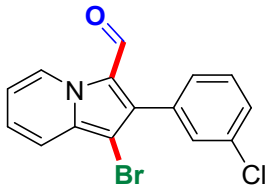
1-bromo-2-(4-(trifluoromethoxy)phenyl)indolizine-3-carbaldehyde (3i) — Yellow solid m.p.= 95-96 °C. (40.7 mg, 0.106 mmol, 53% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 (d, *J* = 7.0 Hz, 1H), 9.56 (s, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.41 – 7.32 (m, 3H), 7.11 – 6.96 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 149.6, 138.3, 136.1, 132.5, 129.8, 128.5, 126.7, 121.0, 120.9, 120.6 (d, *J* = 256.6 Hz), 117.5, 115.4, 91.2. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -57.66. HRMS (ESI) calculated for $C_{16}H_{10}BrF_3NO^+$ $[M+H]^+$: 383.9842; found: 383.9848.



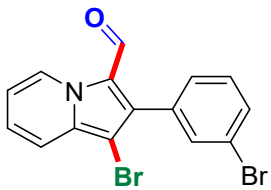
2-([1,1'-biphenyl]-4-yl)-1-bromoindolizine-3-carbaldehyde (3j) — Yellow solid m.p.= 172-174 °C. (32.4 mg, 0.086 mmol, 43% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.86 (d, *J* = 7.0 Hz, 1H), 9.66 (s, 1H), 7.93 – 7.55 (m, 8H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.28 (m, 2H), 7.09 – 6.94 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 141.6, 140.5, 139.5, 136.2, 131.5, 130.0, 129.0, 128.5, 127.8, 127.3, 127.2, 126.5, 121.1, 117.4, 115.2, 91.2. HRMS (ESI) calculated for $C_{21}H_{15}BrNO^+$ $[M+H]^+$: 376.0332; found: 376.0339.



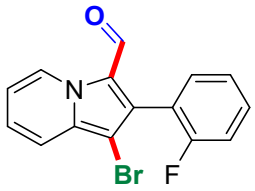
1-bromo-2-(3-methoxyphenyl)indolizine-3-carbaldehyde (3k) — Yellow solid m.p.= 127-129 °C. (46.9 mg, 0.142 mmol, 71% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.03 – 9.73 (m, 1H), 9.56 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.89 – 7.58 (m, 3H), 7.51 – 7.35 (m, 1H), 7.12 – 6.94 (m, 1H), 3.15 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 159.5, 139.7, 136.1, 132.3, 129.5, 128.5, 126.5, 123.6, 121.0, 117.4, 116.6, 115.2, 114.4, 91.1, 55.5. HRMS (ESI) calculated for $C_{16}H_{13}BrNO_2^+$ $[M+H]^+$: 330.0124; found: 330.0131.



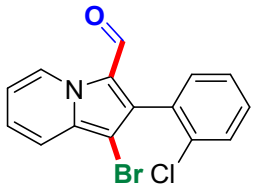
1-bromo-2-(3-chlorophenyl)indolizine-3-carbaldehyde (3l) — Yellow solid m.p.= 170-172 °C. (32.8 mg, 0.098 mmol, 49% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.83 (d, *J* = 7.0 Hz, 1H), 9.57 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.53 (q, *J* = 1.5 Hz, 1H), 7.48 – 7.31 (m, 4H), 7.11 – 6.83 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 138.3, 136.1, 134.5, 132.9, 131.0, 129.8, 129.3, 128.9, 128.5, 126.7, 121.0, 117.5, 115.5. HRMS (ESI) calculated for $C_{15}H_{10}BrClNO^+$ $[M+H]^+$: 333.9629; found: 333.9634.



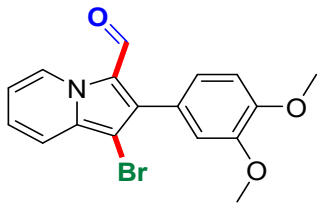
1-bromo-2-(3-bromophenyl)indolizine-3-carbaldehyde (3m) — Yellow solid m.p.= 163-165 °C. (30.3 mg, 0.080 mmol, 40% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.89 – 9.75 (m, 1H), 9.57 (s, 1H), 7.72 – 7.65 (m, 2H), 7.63 – 7.56 (m, 1H), 7.49 – 7.43 (m, 1H), 7.41 – 7.34 (m, 2H), 7.10 – 6.95 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 138.2, 136.2, 133.8, 133.2, 131.9, 130.0, 129.7, 128.5, 126.7, 122.5, 121.0, 117.6, 115.5, 91.3. HRMS (ESI) calculated for $C_{15}H_{10}Br_2NO^+$ $[M+H]^+$: 379.9103; found: 379.9106.



1-bromo-2-(2-fluorophenyl)indolizine-3-carbaldehyde (3n) — Yellow solid m.p.= 156-158 °C. (49.0 mg, 0.154 mmol, 77% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.81 (d, *J* = 7.0 Hz, 1H), 9.53 (d, *J* = 2.0 Hz, 1H), 7.70 – 7.61 (m, 1H), 7.55 – 7.40 (m, 2H), 7.39 – 7.20 (m, 3H), 7.06 – 6.96 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.8 (d, *J* = 1.5 Hz), 160.0 (d, *J* = 249.0 Hz), 136.2, 133.7, 133.1 (d, *J* = 2.3 Hz), 131.1 (d, *J* = 8.3 Hz), 128.3, 126.3, 124.2 (d, *J* = 3.6 Hz), 120.9, 119.0 (d, *J* = 15.8 Hz), 117.4, 116.2 (d, *J* = 21.9 Hz), 115.3, 92.3. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -112.65. HRMS (ESI) calculated for $C_{15}H_{10}BrFNO^{+}$ $[M+H]^{+}$: 317.9924; found: 317.9922.

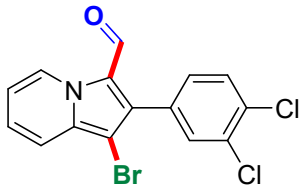


1-bromo-2-(2-chlorophenyl)indolizine-3-carbaldehyde (3o) — Yellow solid m.p.= 152-155 °C. (381 mg, 0.114 mmol, 57% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.83 – 9.75 (m, 1H), 9.38 (s, 1H), 7.73 – 7.62 (m, 1H), 7.59 – 7.52 (m, 1H), 7.49 – 7.32 (m, 4H), 7.08 – 6.98 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.7, 137.5, 136.1, 134.5, 132.9, 130.5, 130.4, 123.0, 128.5, 126.7, 126.3, 121.0, 117.5, 115.4, 92.5. HRMS (ESI) calculated for $C_{15}H_{10}BrClNO^{+}$ $[M+H]^{+}$: 333.9629; found: 333.9639.

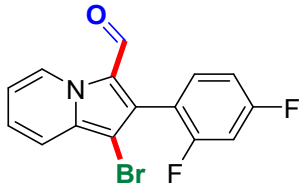


1-bromo-2-(3,4-dimethoxyphenyl)indolizine-3-carbaldehyde (3p) — Yellow solid m.p.= 145-147 °C. (51.8 mg, 0.144 mmol, 72% yield) ^{1}H NMR (400 MHz, Chloroform-

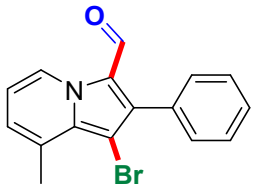
d) δ 9.82 (d, *J* = 7.0 Hz, 1H), 9.61 (s, 1H), 7.67 – 7.59 (m, 1H), 7.38 – 7.29 (m, 1H), 7.08 (d, *J* = 6.5 Hz, 2H), 7.03 – 6.93 (m, 2H), 3.94 (d, *J* = 10.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 149.8, 148.8, 139.8, 136.2, 128.5, 126.5, 123.9, 123.5, 121.0, 117.3, 115.0, 114.1, 111.1, 91.1, 56.1, 56.0. HRMS (ESI) calculated for $C_{17}H_{15}BrNO_3^+$ $[M+H]^+$: 360.0230; found: 360.0238.



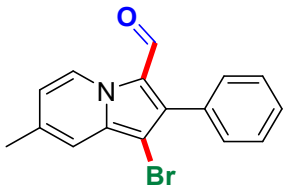
1-bromo-2-(3,4-dichlorophenyl)indolizine-3-carbaldehyde (3q) — Yellow solid m.p.= 170-173 °C. (48.1 mg, 0.130 mmol, 65% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.87 – 9.77 (m, 1H), 9.56 (s, 1H), 7.72 – 7.54 (m, 3H), 7.42 – 7.32 (m, 2H), 7.09 – 6.95 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.5, 137.1, 136.1, 133.3, 132.9, 132.7, 131.1, 130.6, 130.3, 128.5, 126.8, 120.9, 117.5, 115.6, 91.2. HRMS (ESI) calculated for $C_{15}H_9BrCl_2NO^+$ $[M+H]^+$: 367.9239; found:367.9241.



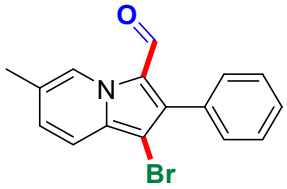
1-bromo-2-(2,4-difluorophenyl)indolizine-3-carbaldehyde (3r) — Yellow solid m.p.= 130-132 °C. (46.4 mg, 0.138 mmol, 69% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.86 – 9.72 (m, 1H), 9.48 (d, *J* = 1.9 Hz, 1H), 7.71 – 7.60 (m, 1H), 7.50 – 7.28 (m, 2H), 7.11 – 6.94 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.4, 163.6 (dd, J = 251.8, 12.0 Hz), 160.3 (dd, J = 252.2, 13.1 Hz), 136.2, 133.9, 132.8, 128.4, 126.4, 121.0, 117.5, 115.5, 115.2 (dd, *J* = 15.7, 4.0 Hz), 111.8 (dd, *J* = 21.3, 3.8 Hz), 104.7 (t, *J* = 25.7 Hz), 92.4. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -107.82 (d, *J* = 8.4 Hz), -108.05 (d, *J* = 8.3 Hz). HRMS (ESI) calculated for $C_{15}H_9BrF_2NO^+$ $[M+H]^+$: 335.9830; found: 335.9835.



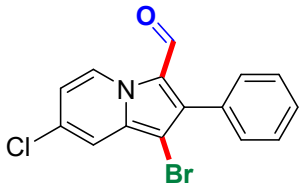
1-bromo-8-methyl-2-phenylindolizine-3-carbaldehyde (3s) — Yellow solid m.p.= 123-127 °C. (45.8 mg, 0.146 mmol, 73% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.79 (d, *J* = 6.9 Hz, 1H), 9.49 (s, 1H), 7.65 – 7.34 (m, 5H), 7.11 – 6.97 (m, 1H), 6.84 (t, *J* = 7.0 Hz, 1H), 2.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.3, 141.0, 134.5, 131.4, 131.2, 128.9, 128.6, 128.3, 127.2, 126.6, 121.1, 114.7, 90.8, 20.7. HRMS (ESI) calculated for $C_{16}H_{13}BrNO^{+}$ $[M+H]^{+}$: 314.0175; found: 314.0183.



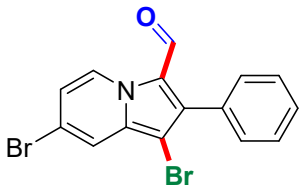
1-bromo-7-methyl-2-phenylindolizine-3-carbaldehyde (3t) — Yellow solid m.p.= 126-128 °C. (32.0 mg, 0.102 mmol, 51% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.72 (d, *J* = 7.1 Hz, 1H), 9.51 (s, 1H), 7.59 – 7.35 (m, 6H), 6.91 – 6.77 (m, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.8, 140.3, 138.1, 136.6, 131.2, 131.0, 128.7, 128.4, 128.1, 120.7, 117.7, 116.0, 90.1, 21.7. HRMS (ESI) calculated for $C_{16}H_{13}BrNO^{+}$ $[M+H]^{+}$: 314.0175; found: 314.0184.



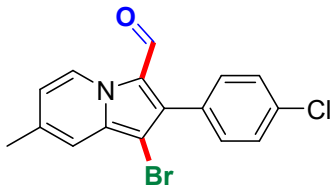
1-bromo-6-methyl-2-phenylindolizine-3-carbaldehyde (3u) — Yellow solid m.p.= 125-128 °C. (39.6 mg, 0.126 mmol, 63% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.68 (q, *J* = 1.3 Hz, 1H), 9.54 (s, 1H), 7.61 – 7.39 (m, 6H), 7.21 (dd, *J* = 9.0, 1.5 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.2, 139.4, 135.0, 131.3, 131.1, 129.5, 128.6, 128.4, 126.5, 125.3, 120.8, 116.7, 90.9, 18.6. HRMS (ESI) calculated for $C_{16}H_{13}BrNO^{+}$ $[M+H]^{+}$: 314.0175; found: 314.0185.



1-bromo-7-chloro-2-phenylindolizine-3-carbaldehyde (3v) — Yellow solid m.p.= 180-183 °C. (28.8 mg, 0.086 mmol,43 % yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.76 (d, *J* = 7.4 Hz, 1H), 9.57 (s, 1H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.55 – 7.47 (m, 5H), 6.98 – 6.90 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.6, 140.9, 136.2, 133.0, 131.0, 130.6, 129.1, 129.0, 128.6, 121.1, 116.5, 116.4, 90.9. HRMS (ESI) calculated for $C_{15}H_{10}BrClNO^{+}$ $[M+H]^{+}$: 333.9629; found: 333.9638.

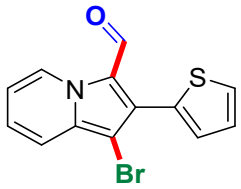


1,7-dibromo-2-phenylindolizine-3-carbaldehyde (3w) — Yellow solid m.p.= 176-178 °C. (23.5 mg, 0.062 mmol, 31% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.68 (d, *J* = 7.4 Hz, 1H), 9.59 (s, 1H), 7.83 (d, *J* = 2.1 Hz, 1H), 7.59 – 7.41 (m, 5H), 7.06 (dd, *J* = 7.4, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.7, 140.7, 136.4, 131.0, 130.6, 129.0, 128.8, 128.6, 121.1, 120.5, 119.8, 118.8, 90.7. HRMS (ESI) calculated for $C_{15}H_{10}Br_2NO^{+}$ $[M+H]^{+}$: 379.9103; found: 379.9110.

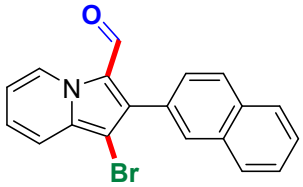


1-bromo-2-(4-chlorophenyl)-7-methylindolizine-3-carbaldehyde (3x) — Yellow solid m.p.= 155-157 °C. (30.7 mg, 0.088 mmol, 44% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.70 (d, *J* = 7.1 Hz, 1H), 9.48 (s, 1H), 7.47 (s, 4H), 7.41 (s, 1H), 6.85 (dd, *J* = 7.1, 1.9 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.3,

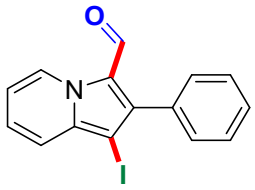
138.8, 138.3, 136.6, 135.0, 132.3, 129.7, 128.8, 128.0, 120.6, 117.9, 116.0, 90.0, 21.7. HRMS (ESI) calculated for $C_{16}H_{12}BrClNO^+$ $[M+H]^+$: 347.9785; found: 347.9790.



1-bromo-2-(thiophen-2-yl)indolizine-3-carbaldehyde (3y) — Yellow solid m.p.= 131-133 °C. (41.1 mg, 0.134 mmol, 67% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.87 – 9.75 (m, 2H), 7.66 – 7.57 (m, 1H), 7.57 – 7.51 (m, 1H), 7.38 – 7.28 (m, 2H), 7.24 – 7.17 (m, 1H), 7.03 – 6.93 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.2, 136.2, 132.6, 131.1, 130.3, 128.4, 128.3, 127.6, 126.6, 121.1, 117.4, 115.3, 91.7. HRMS (ESI) calculated for $C_{13}H_9BrNOS^+$ $[M+H]^+$: 305.9583; found: 305.9590.

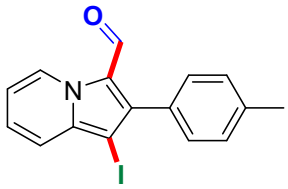


1-bromo-2-(naphthalen-2-yl)indolizine-3-carbaldehyde (3z) — Yellow solid m.p.= 176-179 °C. (41.3 mg, 0.118 mmol, 59% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.87 (d, *J* = 6.9 Hz, 1H), 9.66 (s, 1H), 8.04 – 7.87 (m, 4H), 7.72 – 7.62 (m, 2H), 7.61 – 7.51 (m, 2H), 7.39 – 7.31 (m, 1H), 7.08 – 6.94 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 139.9, 136.2, 133.1, 133.0, 130.8, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 126.9, 126.8, 126.5, 121.2, 117.4, 115.2, 91.4. HRMS (ESI) calculated for $C_{19}H_{13}BrNO^+$ $[M+H]^+$: 350.0175; found: 350.0172.

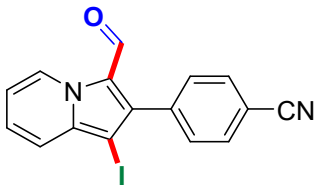


1-iodo-2-phenylindolizine-3-carbaldehyde (4a) — Yellow solid m.p.= 122-124 °C. (38.9 mg, 0.112 mmol, 56% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.84 – 9.79

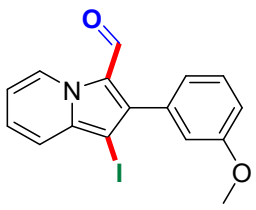
(m, 1H), 9.56 (s, 1H), 7.66 – 7.59 (m, 1H), 7.49 (d, *J* = 2.7 Hz, 5H), 7.37 – 7.30 (m, 1H), 7.03 – 6.95 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 144.4, 138.7, 132.6, 131.0, 130.2, 128.7, 128.4, 126.8, 122.7, 119.3, 115.1, 61.3. HRMS (ESI) calculated for $C_{15}H_{11}INO^+$ $[M+H]^+$: 347.9880; found: 347.9887.



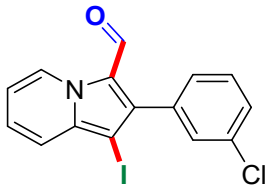
1-iodo-2-(p-tolyl)indolizine-3-carbaldehyde (4b) — Yellow solid m.p.= 123-126 °C. (33.9 mg, 0.094 mmol, 47% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.88 – 9.76 (m, 1H), 9.57 (s, 1H), 7.67 – 7.57 (m, 1H), 7.43 – 7.22 (m, 5H), 7.04 – 6.93 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.5, 144.5, 138.7, 130.9, 129.6, 129.1, 128.8, 126.8, 122.8, 119.3, 115.1, 61.3, 21.5. $C_{16}H_{13}INO^+$ $[M+H]^+$: 362.0036; found: 362.0041.



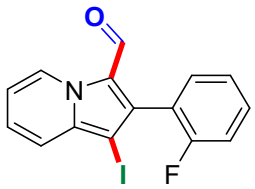
4-(1-iodo-3-formylindolizin-2-yl)benzonitrile (4c) — Yellow solid m.p.= 155-159 °C. (26.8 mg, 0.072 mmol, 36% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 (d, *J* = 7.0 Hz, 1H), 9.51 (s, 1H), 7.85 – 7.75 (m, 2H), 7.68 – 7.57 (m, 3H), 7.44 – 7.35 (m, 1H), 7.05 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.5, 142.0, 138.8, 137.6, 132.2, 131.8, 128.8, 127.4, 122.6, 119.5, 118.6, 115.9, 112.7, 61.0. $C_{16}H_{10}INO^+$ $[M+H]^+$: 372.9832; found: 372.9831.



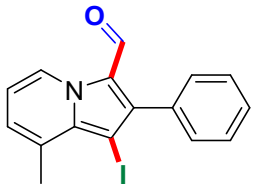
1-iodo-2-(3-methoxyphenyl)indolizine-3-carbaldehyde (4d) — Yellow solid m.p.= 114-116 °C. (37.7 mg, 0.100 mmol, 50% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.88 – 9.77 (m, 1H), 9.59 (s, 1H), 7.68 – 7.56 (m, 1H), 7.50 – 7.27 (m, 2H), 7.13 – 6.92 (m, 4H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.5, 159.4, 144.3, 138.7, 133.9, 129.4, 128.8, 126.9, 123.6, 122.7, 119.3, 116.6, 115.2, 114.4, 61.2, 55.5. $C_{16}H_{13}INO_2^+$ $[M+H]^+$: 377.9986; found: 377.9990.



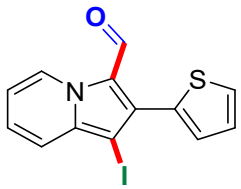
1-iodo-2-(3-chlorophenyl)indolizine-3-carbaldehyde (4e) — Yellow solid m.p.= 167-169 °C. (26.7 mg, 0.070 mmol, 35% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.87 – 9.78 (m, 1H), 9.55 (s, 1H), 7.69 – 7.60 (m, 1H), 7.51 – 7.33 (m, 5H), 7.08 – 6.98 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.0, 142.8, 138.7, 134.5, 134.4, 131.0, 129.7, 129.3, 128.9, 128.8, 127.1, 122.8, 119.5, 115.5, 61.2. $C_{15}H_{10}ClINO^+$ $[M+H]^+$: 381.9490; found: 381.9480.



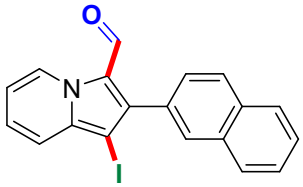
1-iodo-2-(2-fluorophenyl)indolizine-3-carbaldehyde (4f) — Yellow solid m.p.= 151-153 °C. (27.1 mg, 0.074 mmol, 37% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.80 (d, *J* = 7.0 Hz, 1H), 9.49 (d, *J* = 1.8 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.53 – 7.20 (m, 5H), 7.06 – 6.96 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 159.9 (d, *J* = 248.4 Hz), 138.9, 138.6, 133.1 (d, *J* = 2.8 Hz), 131.1 (d, *J* = 8.1 Hz), 128.7, 126.8, 124.2 (d, *J* = 3.6 Hz), 122.8, 120.7 (d, *J* = 15.7 Hz), 119.3, 116.2 (d, *J* = 21.8 Hz), 115.4, 62.2. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -117.14. $C_{15}H_{10}FINO^+$ $[M+H]^+$: 365.9786; found: 365.9778.



1-iodo-8-methyl-2-phenylindolizine-3-carbaldehyde (4g) — Yellow solid m.p.= 115-118 °C. (26.2 mg, 0.072 mmol, 36% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.85 (d, *J* = 6.9 Hz, 1H), 9.44 (s, 1H), 7.53 – 7.37 (m, 5H), 7.10 – 7.02 (m, 1H), 6.87 (t, *J* = 7.0 Hz, 1H), 2.99 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.6, 146.2, 136.0, 133.6, 131.2, 129.1, 128.7, 128.3, 127.6, 127.2, 123.1, 114.7, 58.4, 22.0. $C_{16}H_{13}INO^{+}$ $[M+H]^{+}$: 362.0036; found: 362.0035.



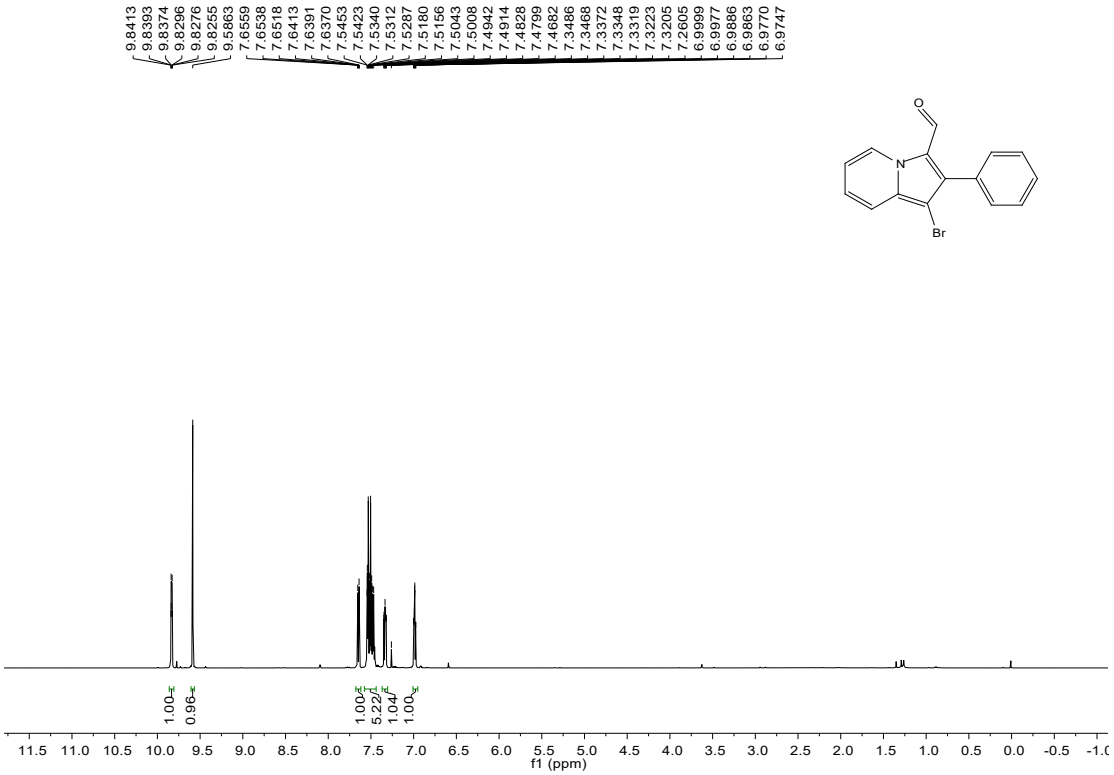
1-iodo-2-(thiophen-2-yl)indolizine-3-carbaldehyde (4h) — Yellow solid m.p.= 115-117 °C. (30.4 mg, 0.086 mmol, 43% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.87 – 9.69 (m, 2H), 7.66 – 7.51 (m, 2H), 7.37 – 7.16 (m, 3H), 7.03 – 6.95 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.3, 138.9, 137.2, 132.6, 130.4, 128.6, 128.2, 127.5, 127.0, 123.0, 119.5, 115.4, 62.2. $C_{13}H_{9}INOS^{+}$ $[M+H]^{+}$: 353.9444; found:353.9440.



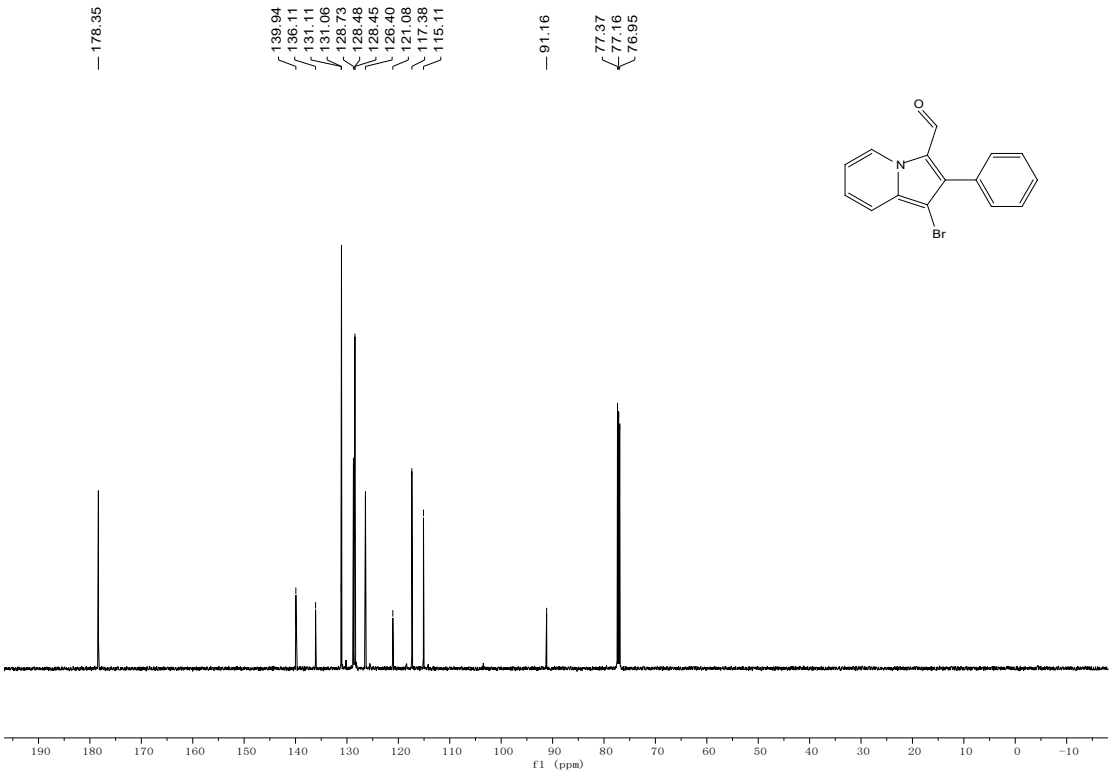
1-iodo-2-(naphthalen-2-yl)indolizine-3-carbaldehyde (4i) — Yellow solid m.p.= 160-163 °C. (21.4 mg, 0.054 mmol, 27% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.89 – 9.83 (m, 1H), 9.62 (s, 1H), 8.00 – 7.88 (m, 4H), 7.71 – 7.52 (m, 4H), 7.42 – 7.34 (m, 1H), 7.07 – 6.99 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.6, 144.4, 138.8, 133.2, 133.0, 130.7, 130.1, 128.9, 128.4, 128.1, 128.0, 127.0, 126.9, 126.8, 123.0, 119.4, 115.3, 61.5. $C_{19}H_{13}INO^{+}$ $[M+H]^{+}$: 398.0036; found:398.0038.

4. NMR Spectra

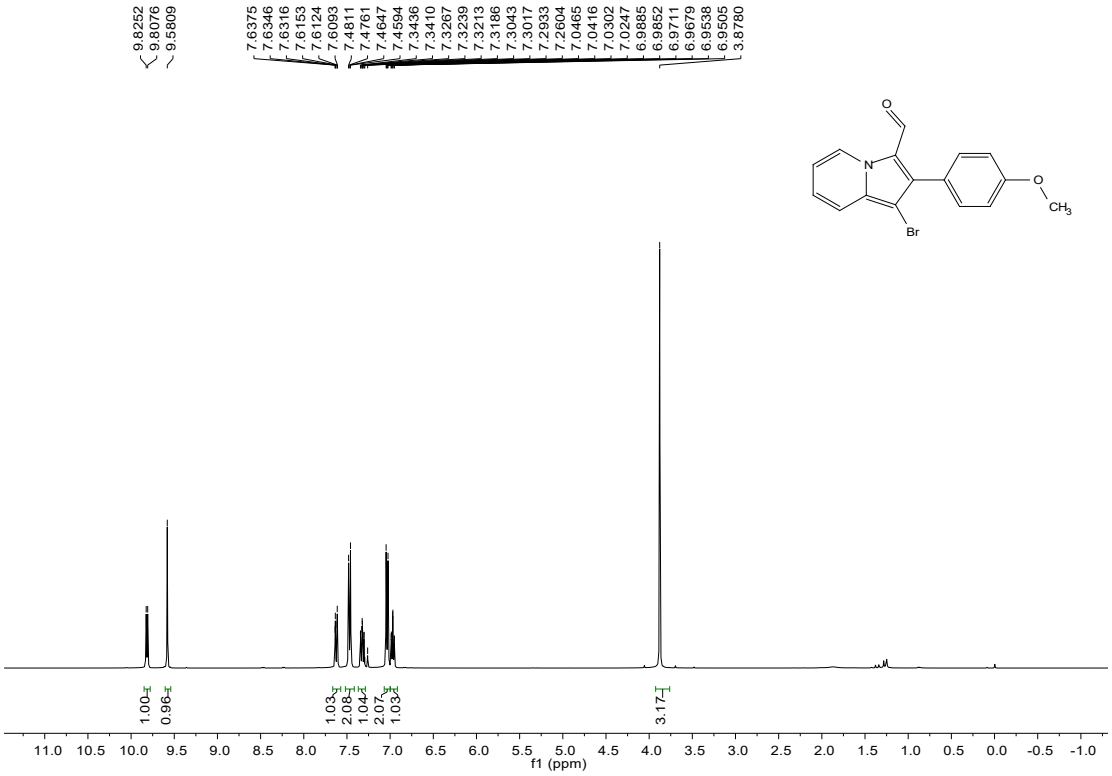
3a ^{1}H NMR (600 MHz, $CDCl_3$)



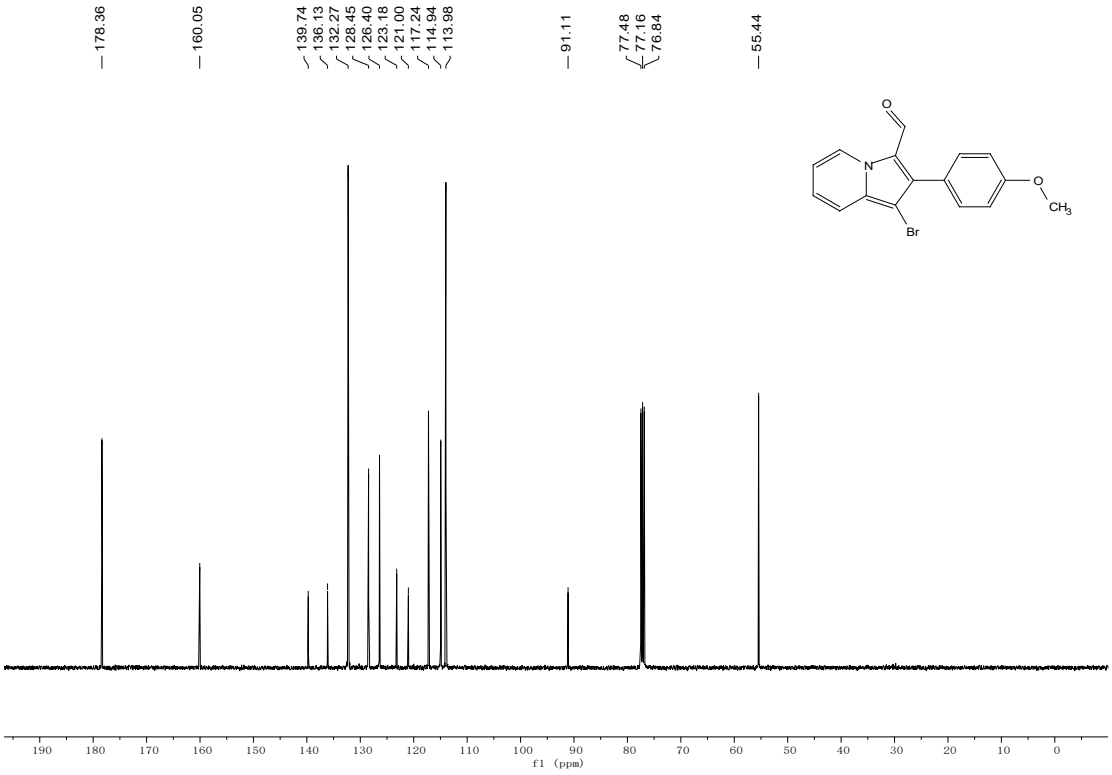
3a ^{13}C NMR (151 MHz, $CDCl_3$)



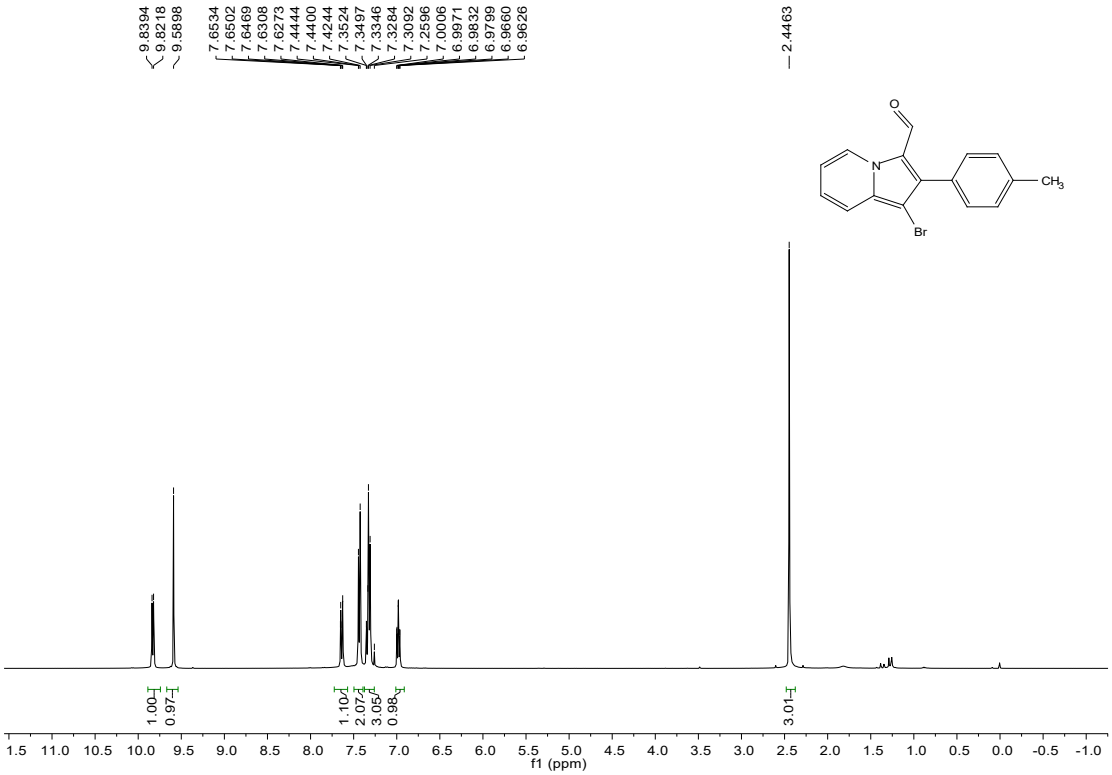
3b ^{1}H NMR (400 MHz, $CDCl_3$)



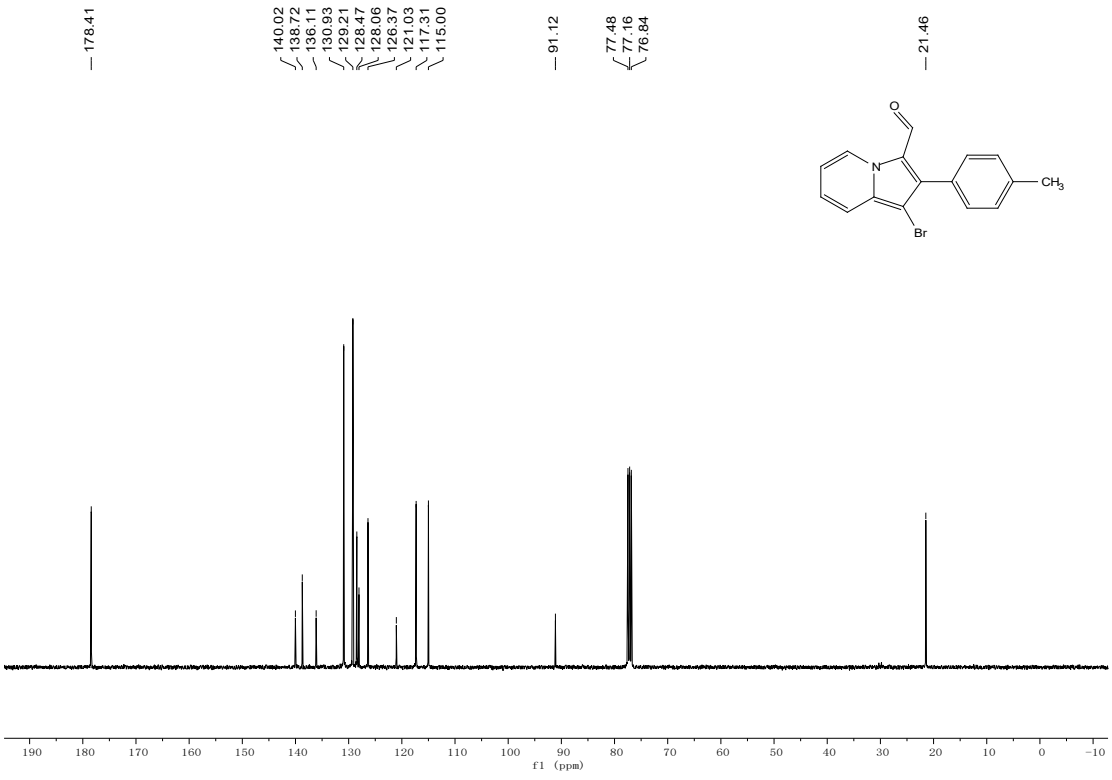
3b ^{13}C NMR (101 MHz, $CDCl_3$)



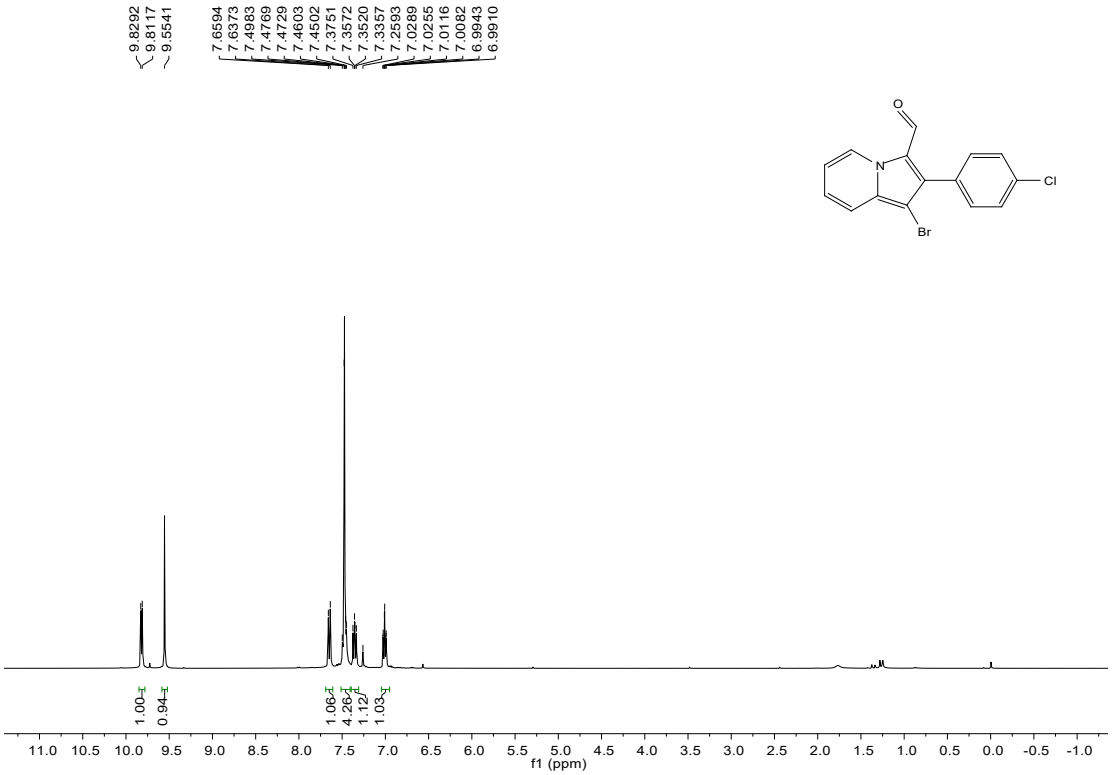
3c ^{1}H NMR (400 MHz, $CDCl_3$)



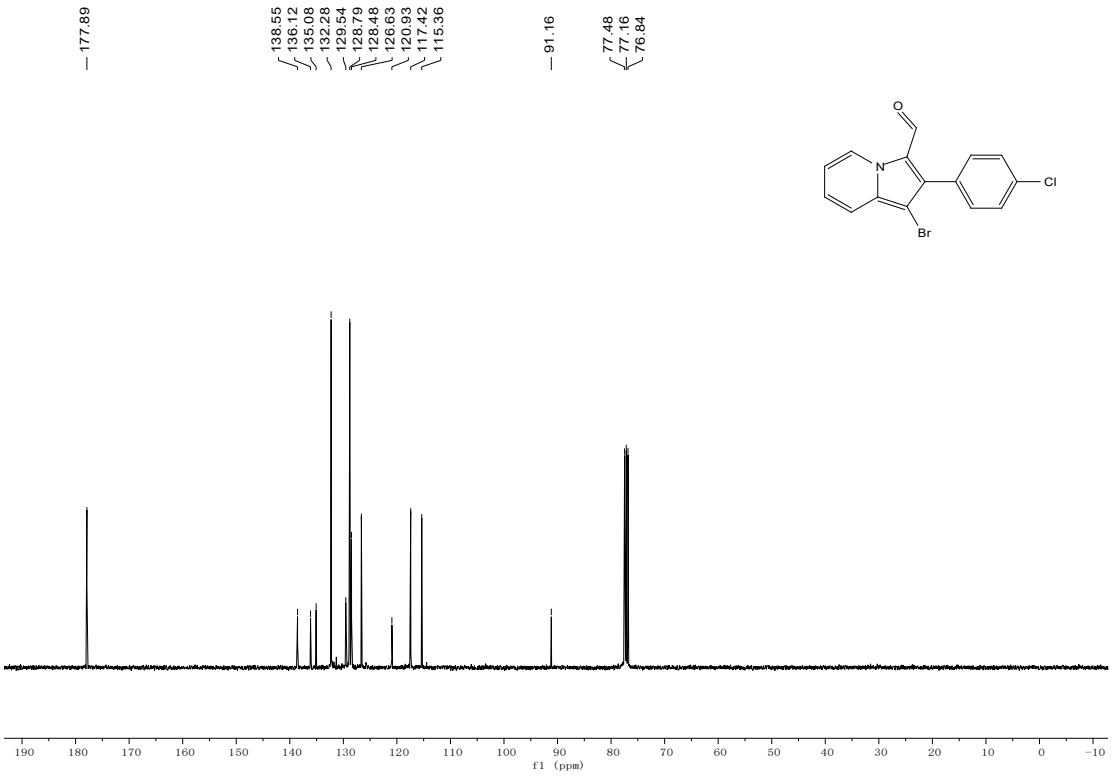
3c ^{13}C NMR (101 MHz, $CDCl_3$)



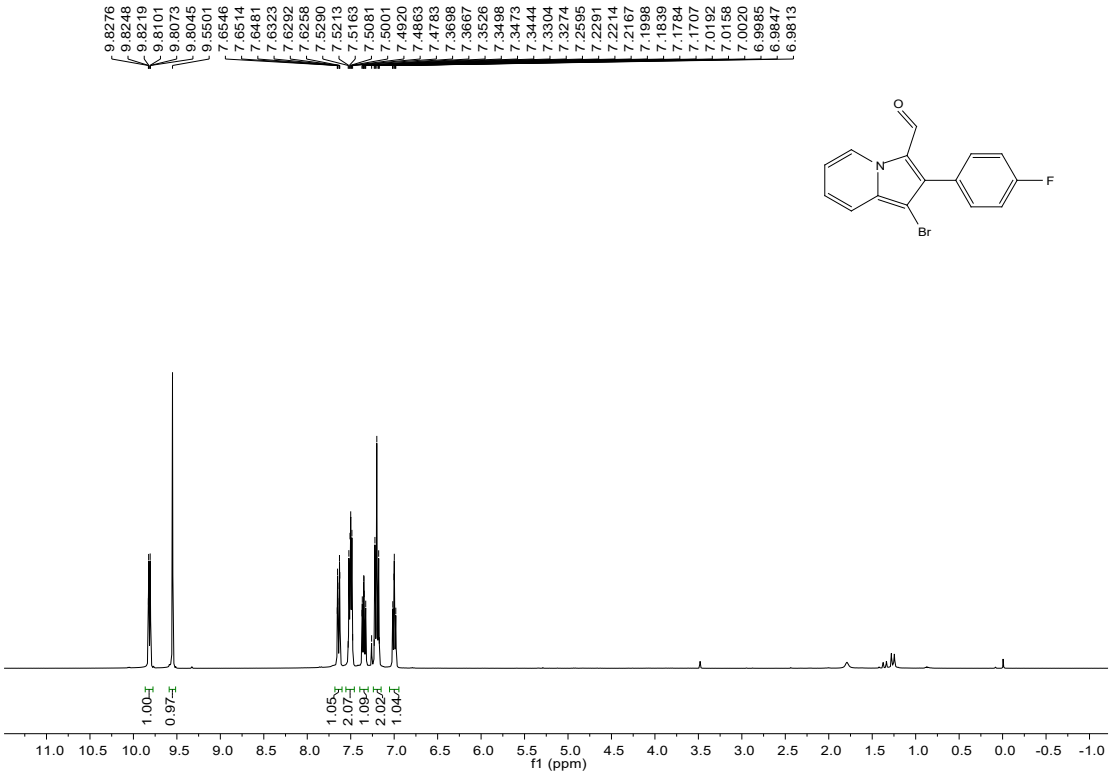
3d ^{1}H NMR (400 MHz, $CDCl_3$)



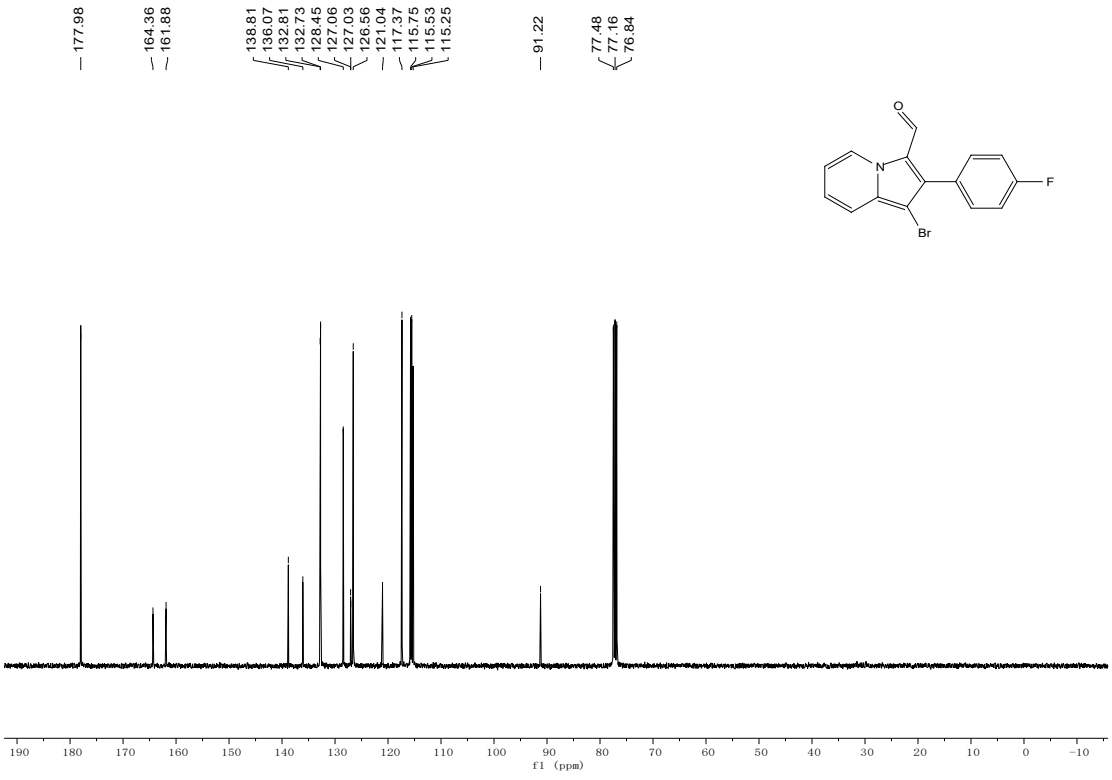
3d ^{13}C NMR (101 MHz, $CDCl_3$)



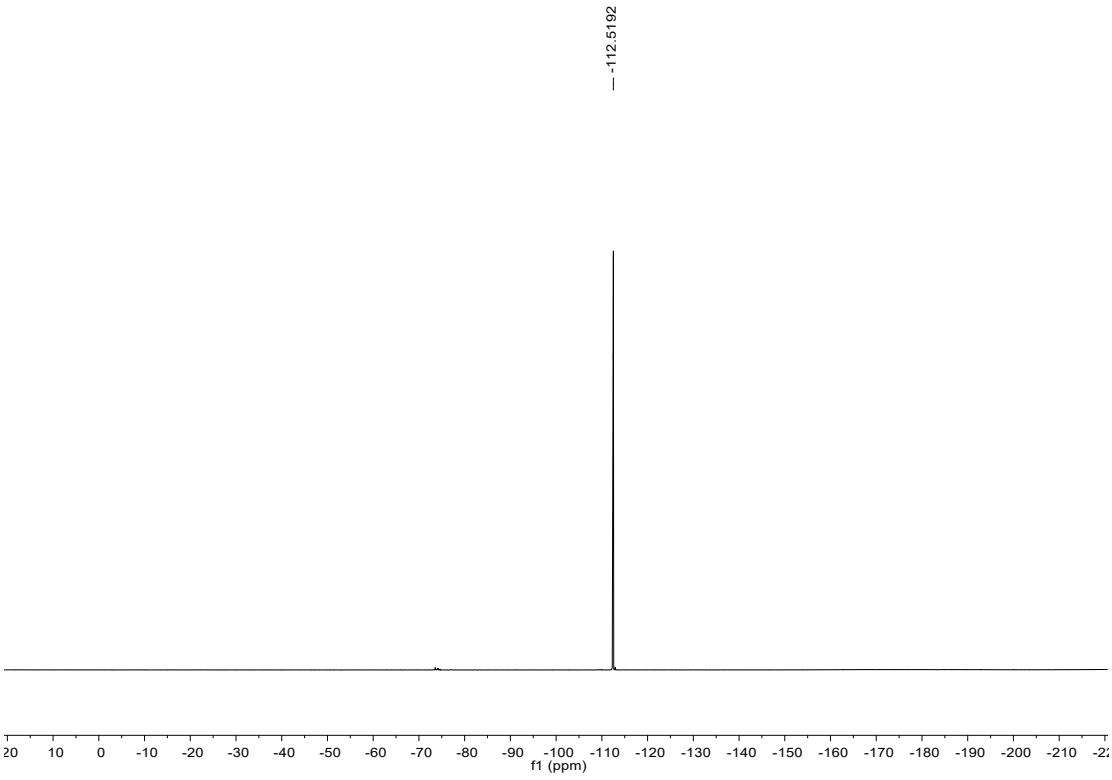
3e ^{1}H NMR (400 MHz, $CDCl_3$)



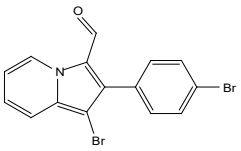
3e ^{13}C NMR (101 MHz, $CDCl_3$)

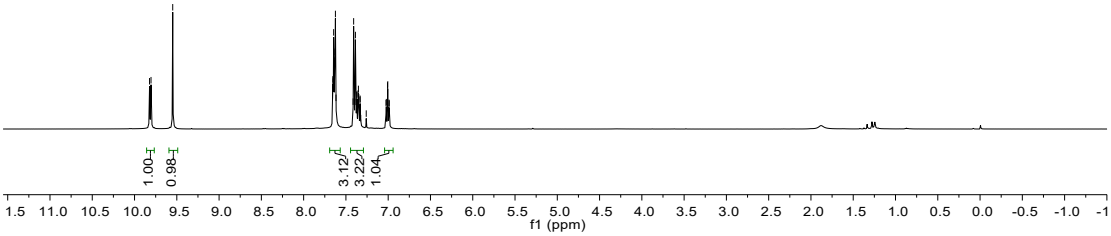


3e ^{19}F NMR (377 MHz, $CDCl_3$)

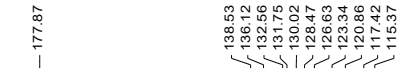


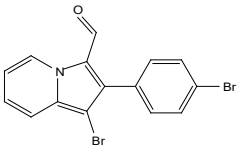
3f ^{1}H NMR (400 MHz, $CDCl_3$)

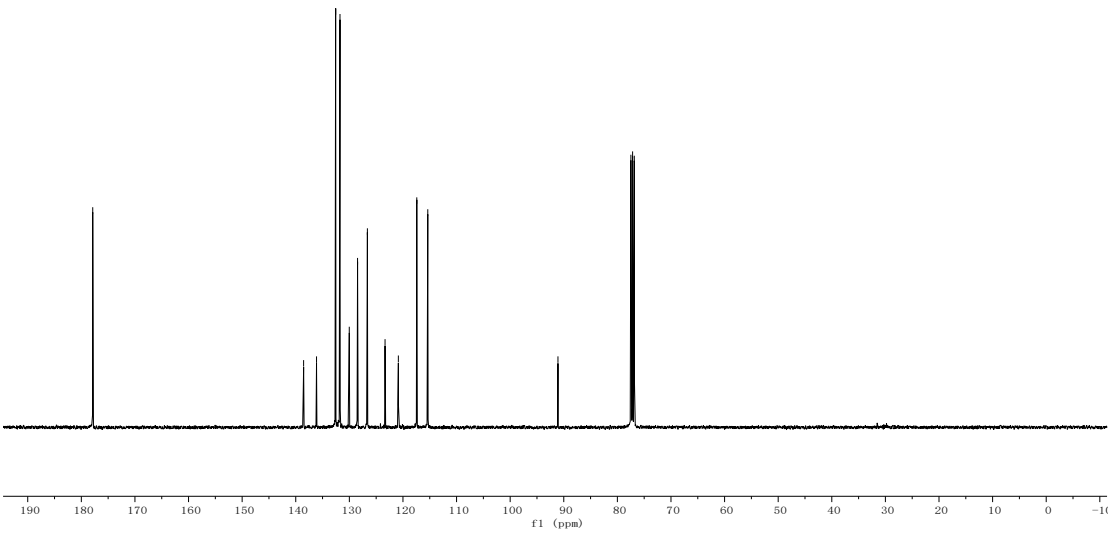




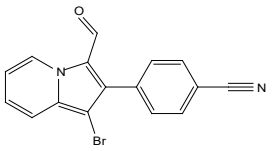
3f ^{13}C NMR (101 MHz, $CDCl_3$)

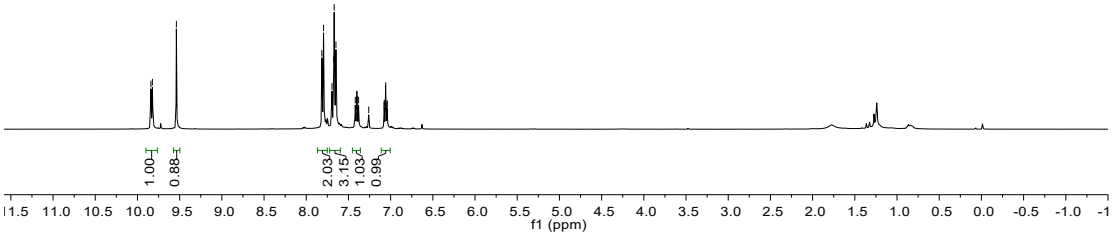




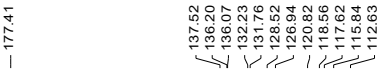


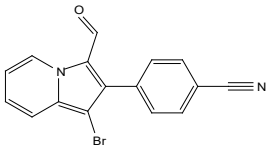
3g ^{1}H NMR (400 MHz, $CDCl_3$)

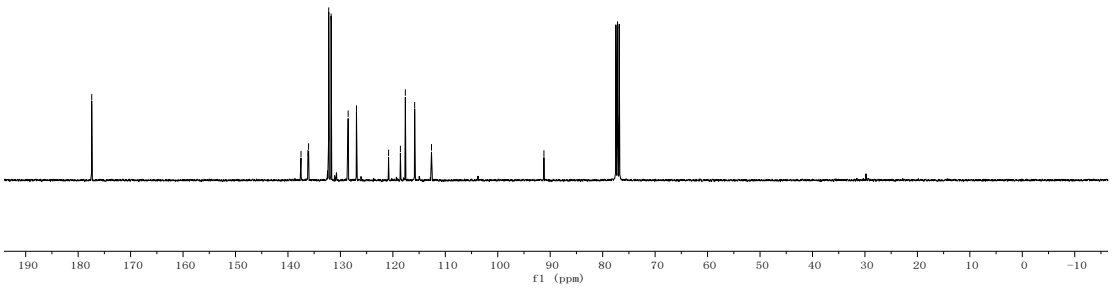




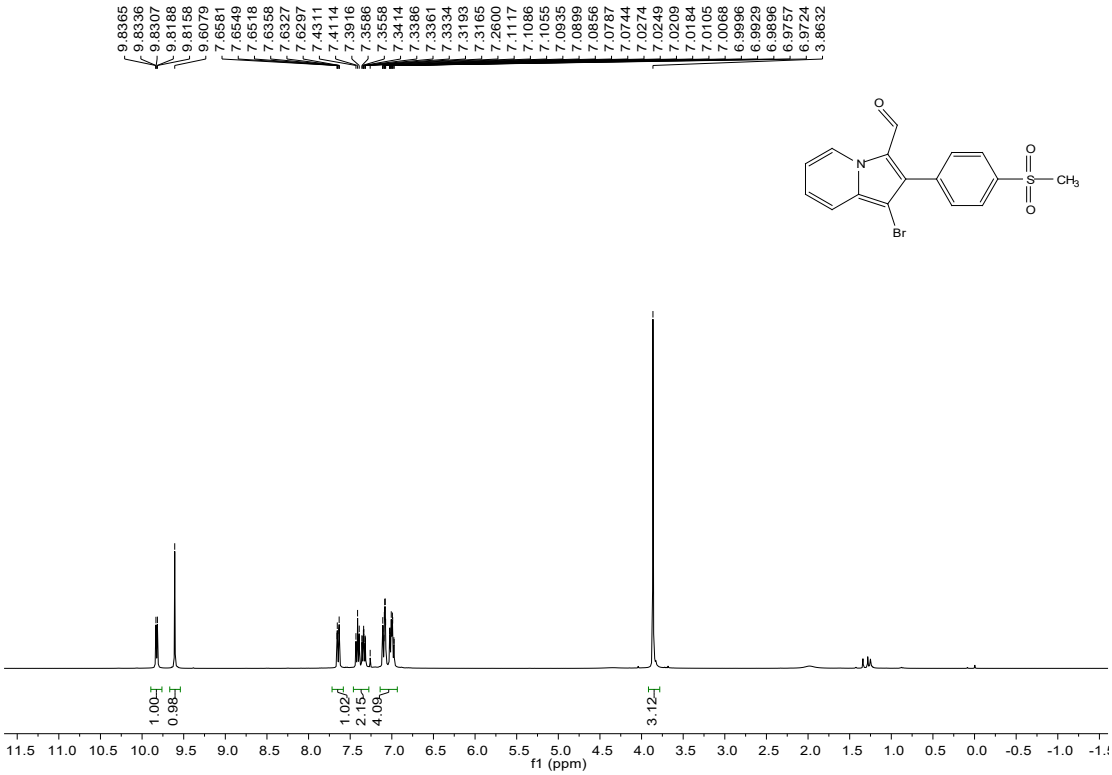
3g ^{13}C NMR (101 MHz, $CDCl_3$)



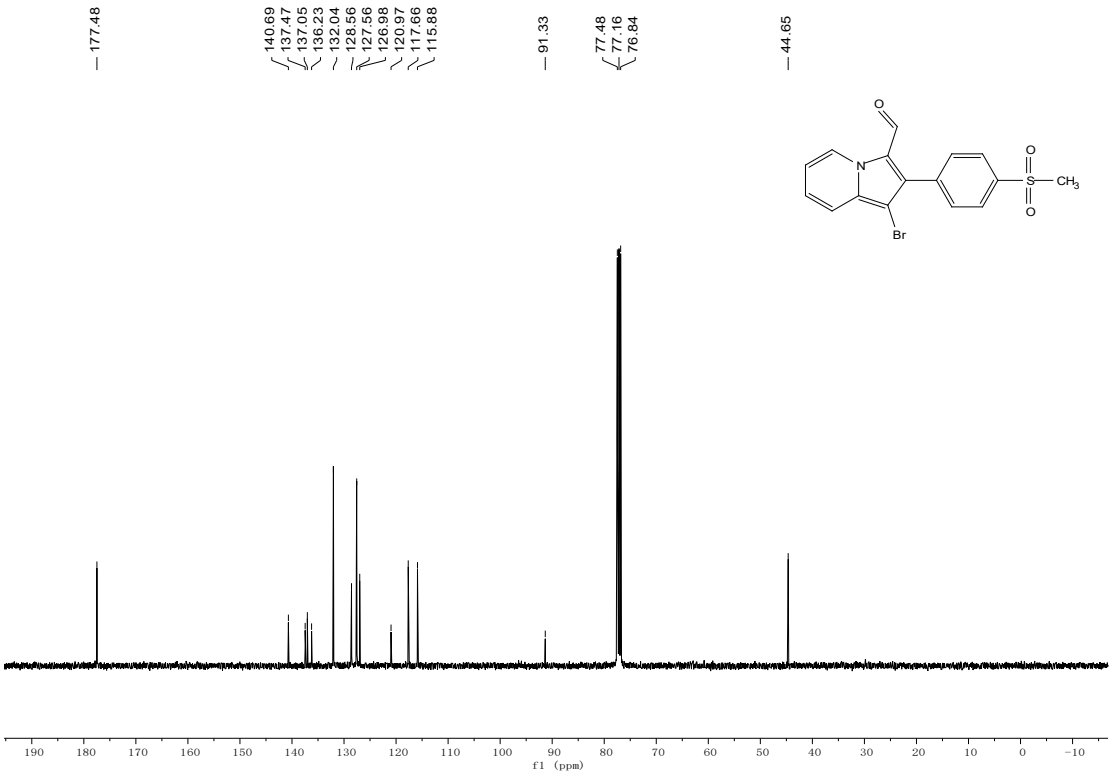




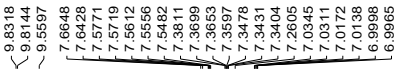
3h ^{1}H NMR (400 MHz, $CDCl_3$)

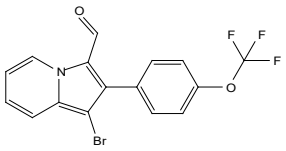


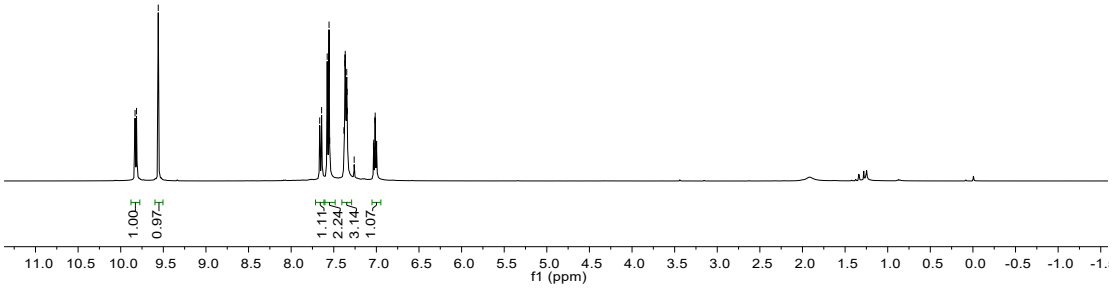
3h ^{13}C NMR (101 MHz, $CDCl_3$)



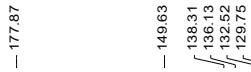
3i ^{1}H NMR (400 MHz, $CDCl_3$)

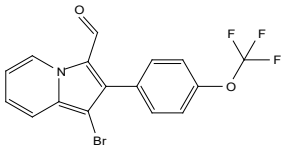




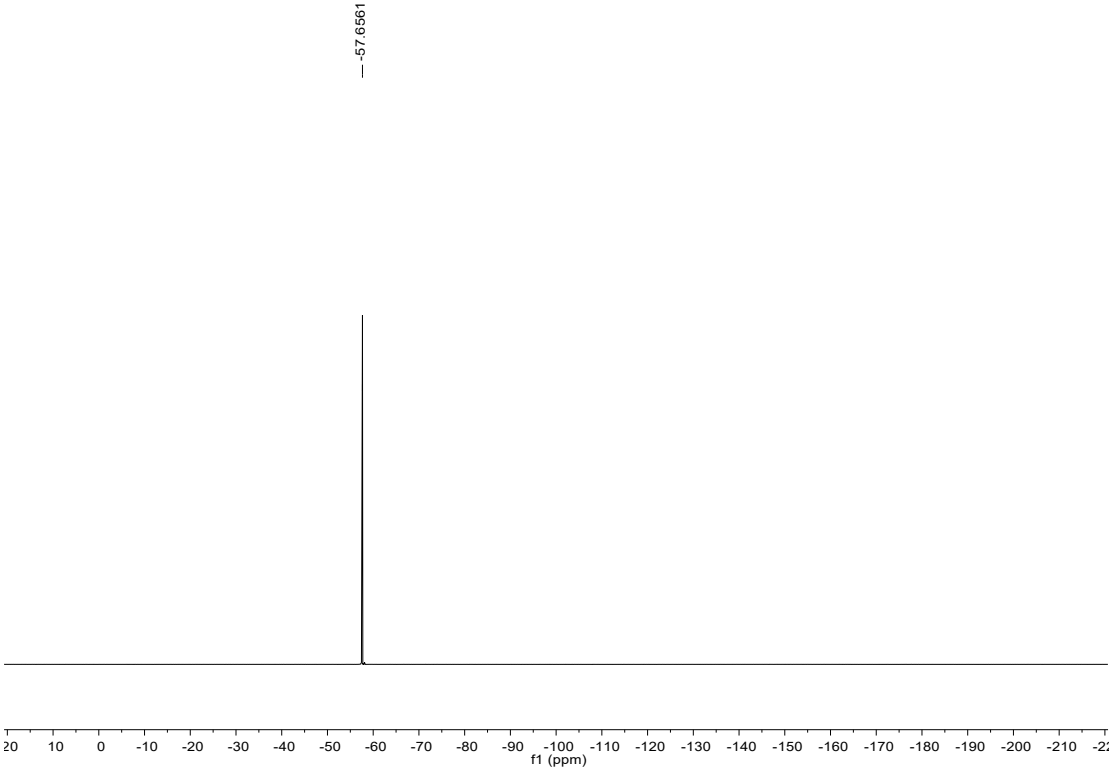


3i ^{13}C NMR (101 MHz, $CDCl_3$)

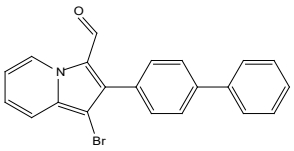


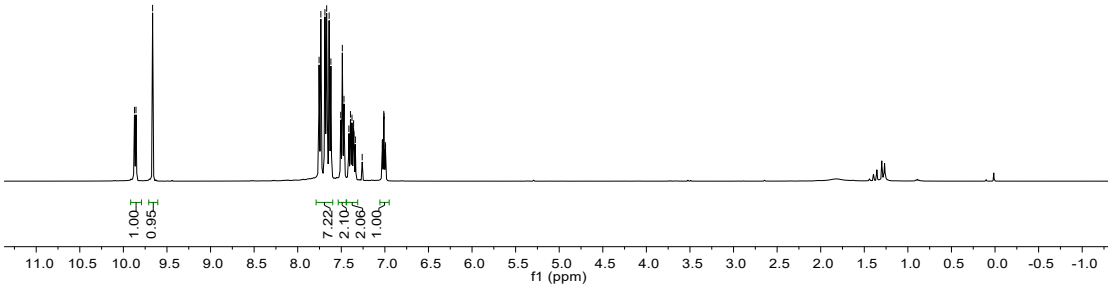


3i ^{19}F NMR (377 MHz, $CDCl_3$)

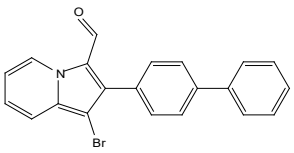


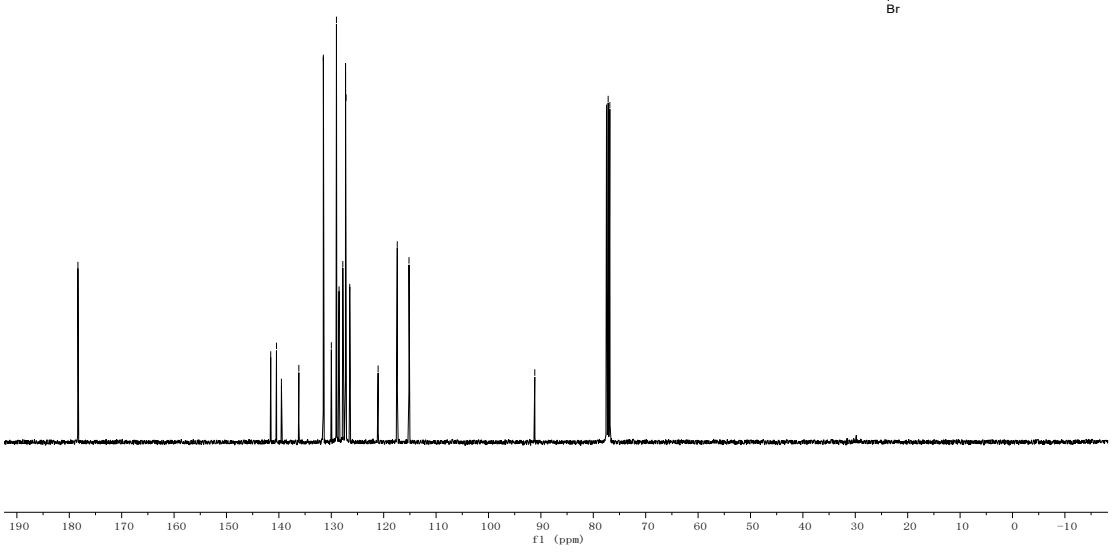
3j ^{1}H NMR (400 MHz, $CDCl_3$)



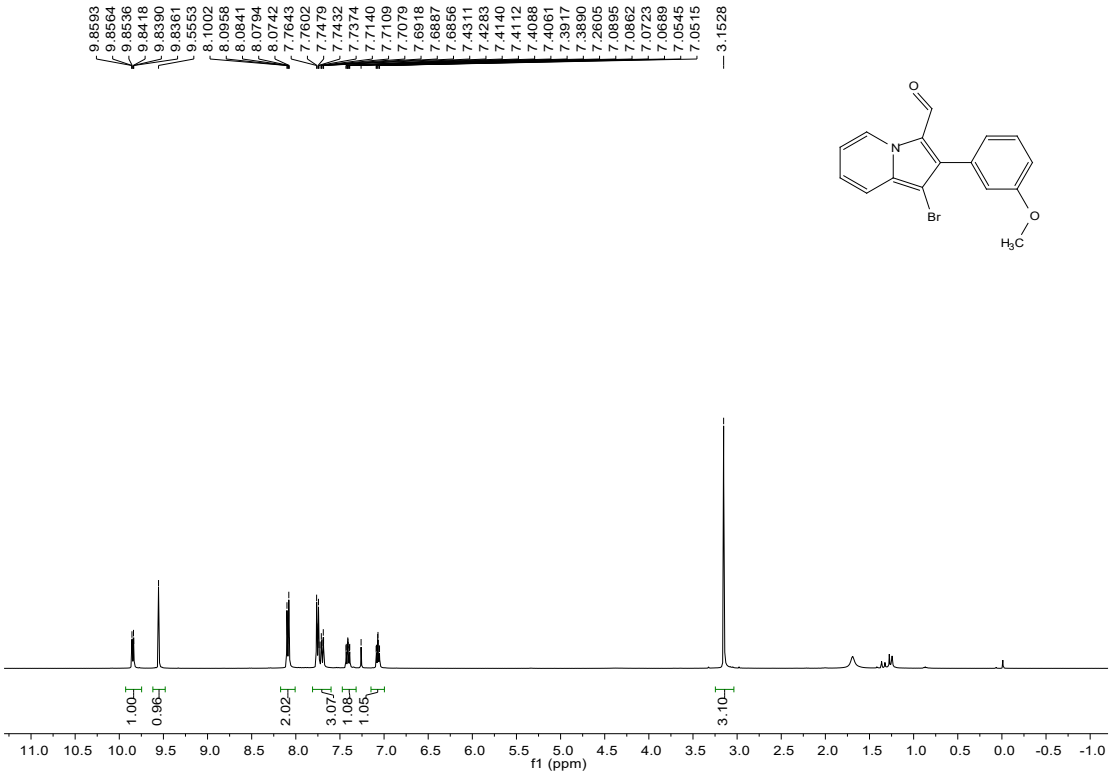


3j ^{13}C NMR (101 MHz, $CDCl_3$)

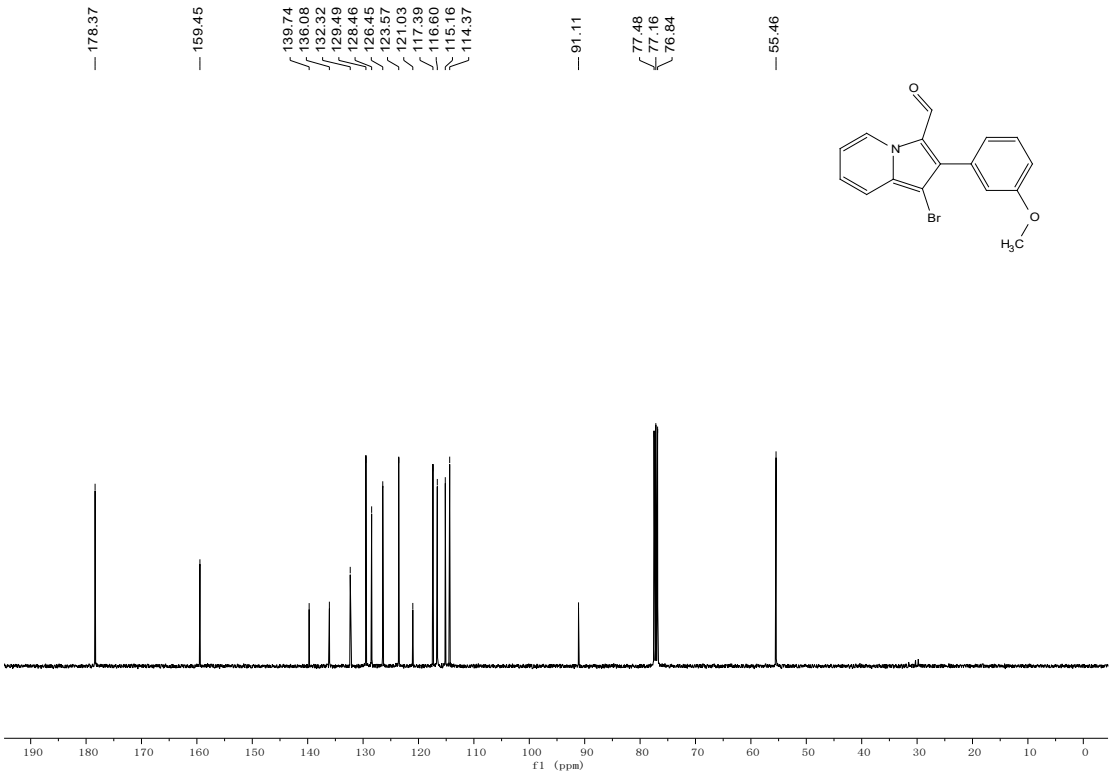




3k ^{1}H NMR (400 MHz, $CDCl_3$)



3k ^{13}C NMR (101 MHz, $CDCl_3$)



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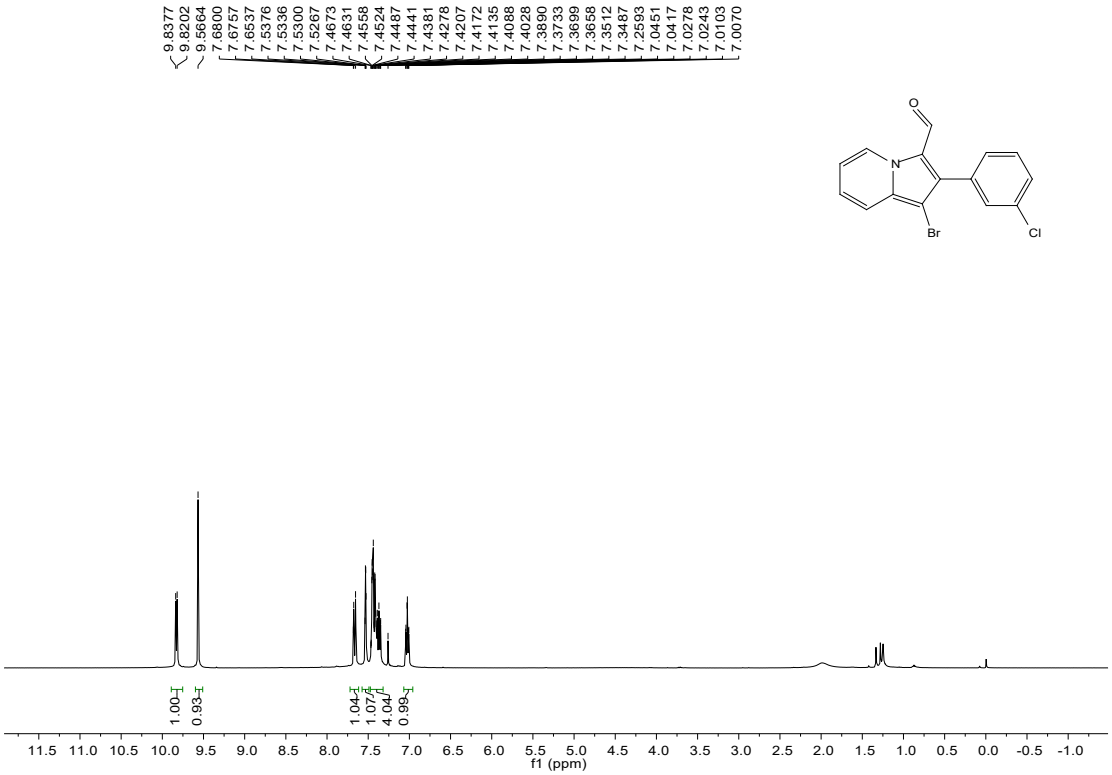
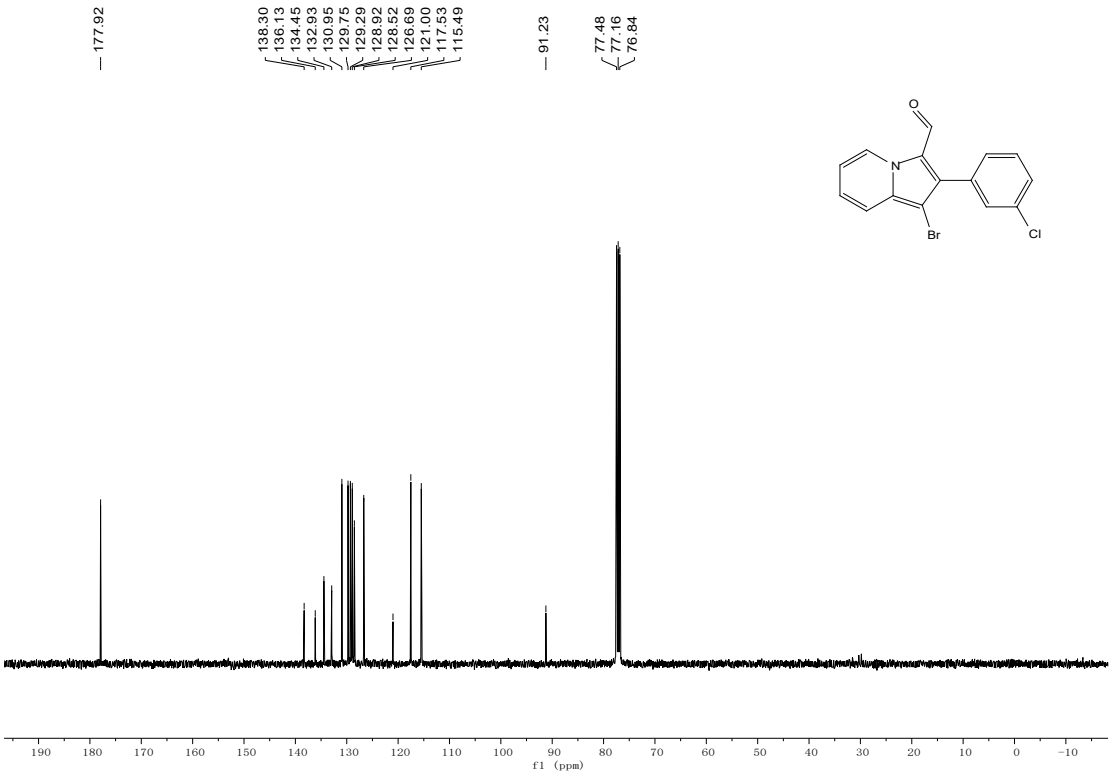


3l ^{13}C NMR (101 MHz, $CDCl_3$)



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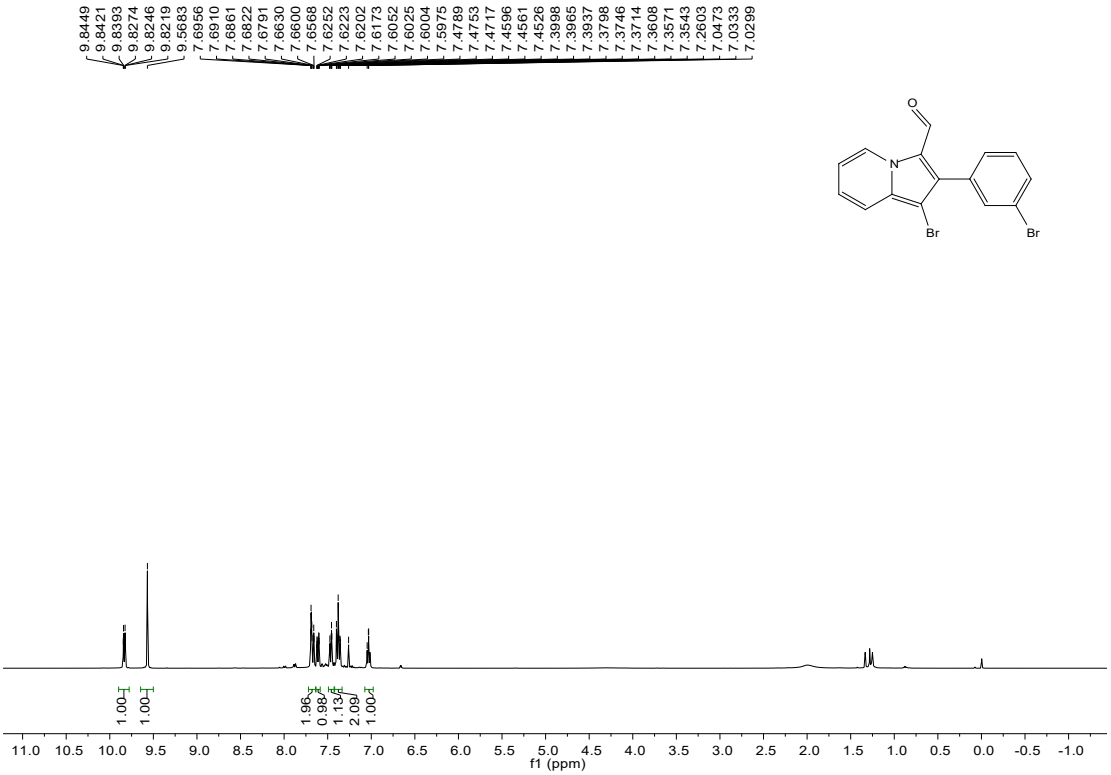
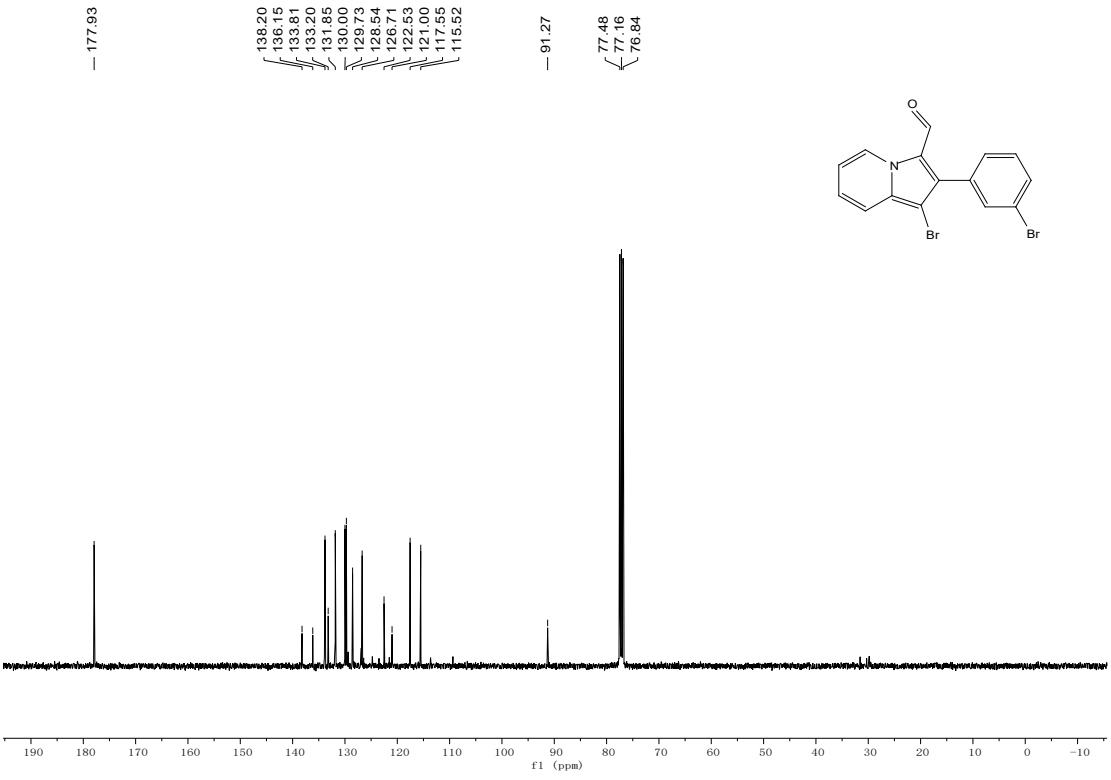
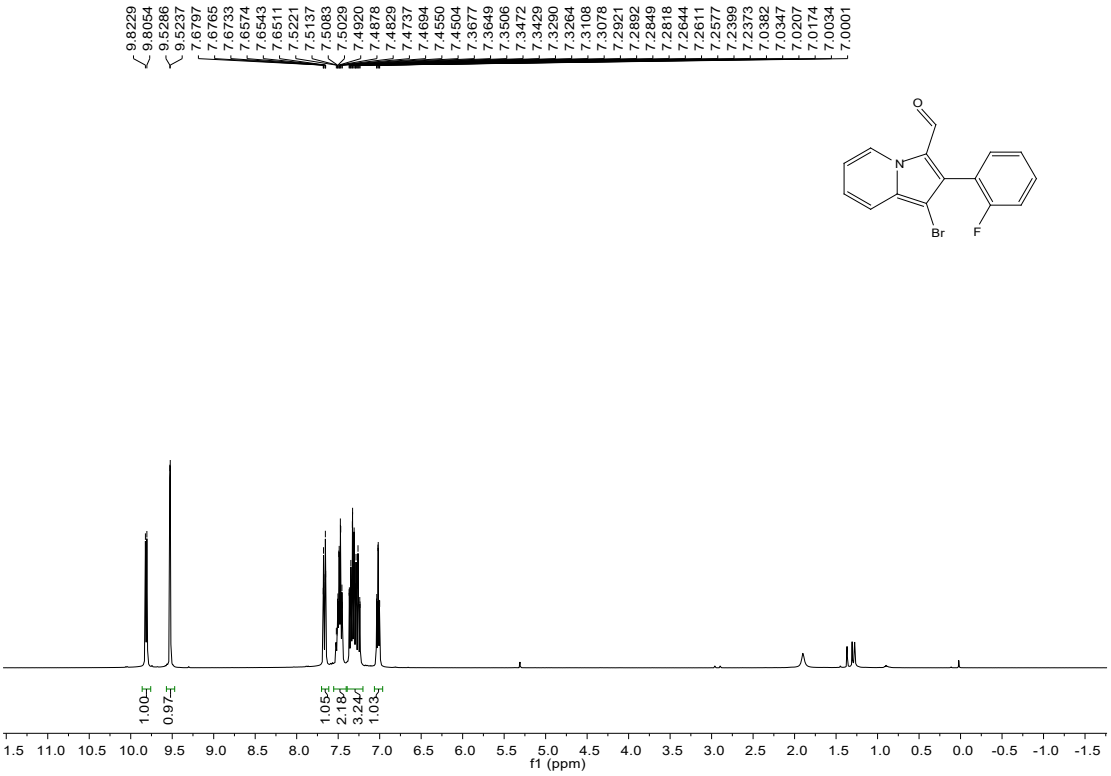


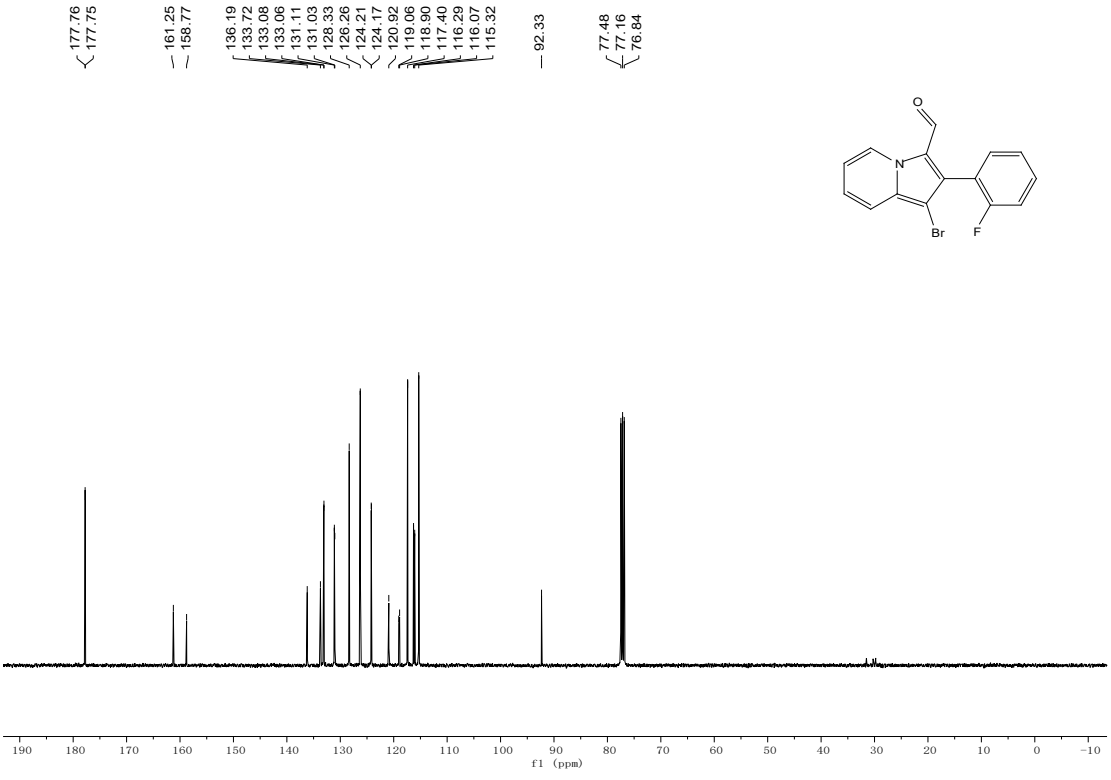
3m ^{13}C NMR (101 MHz, $CDCl_3$)



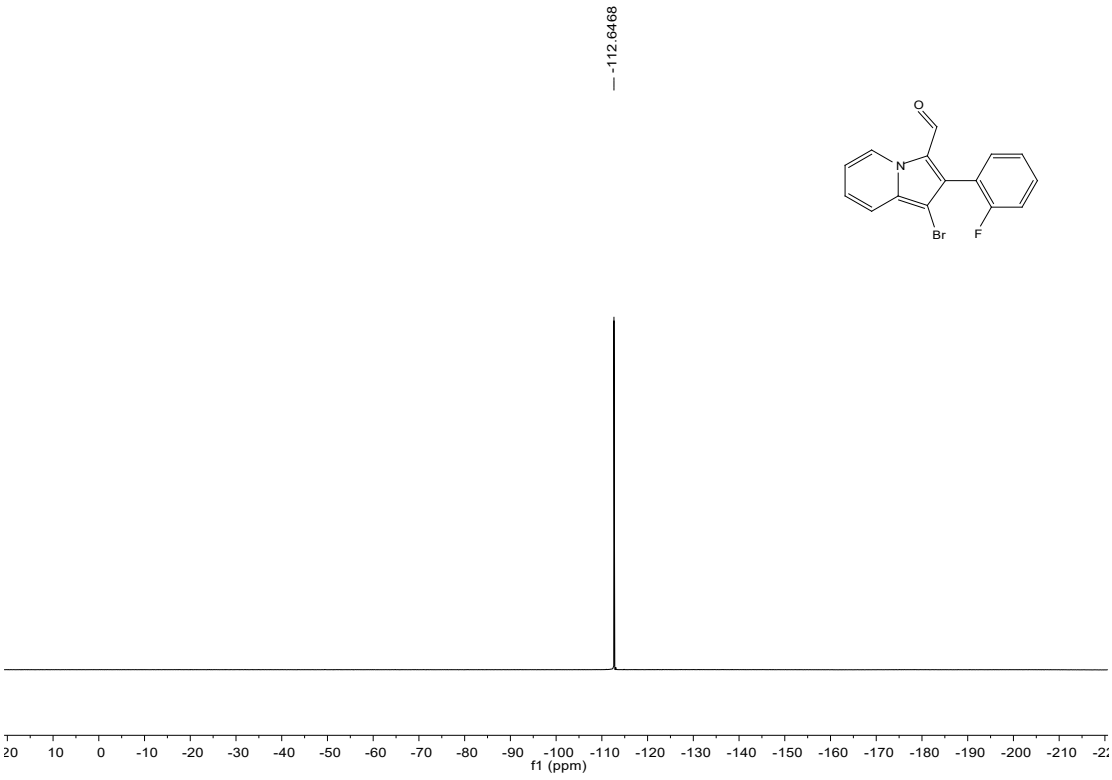
3n ^{1}H NMR (400 MHz, $CDCl_3$)



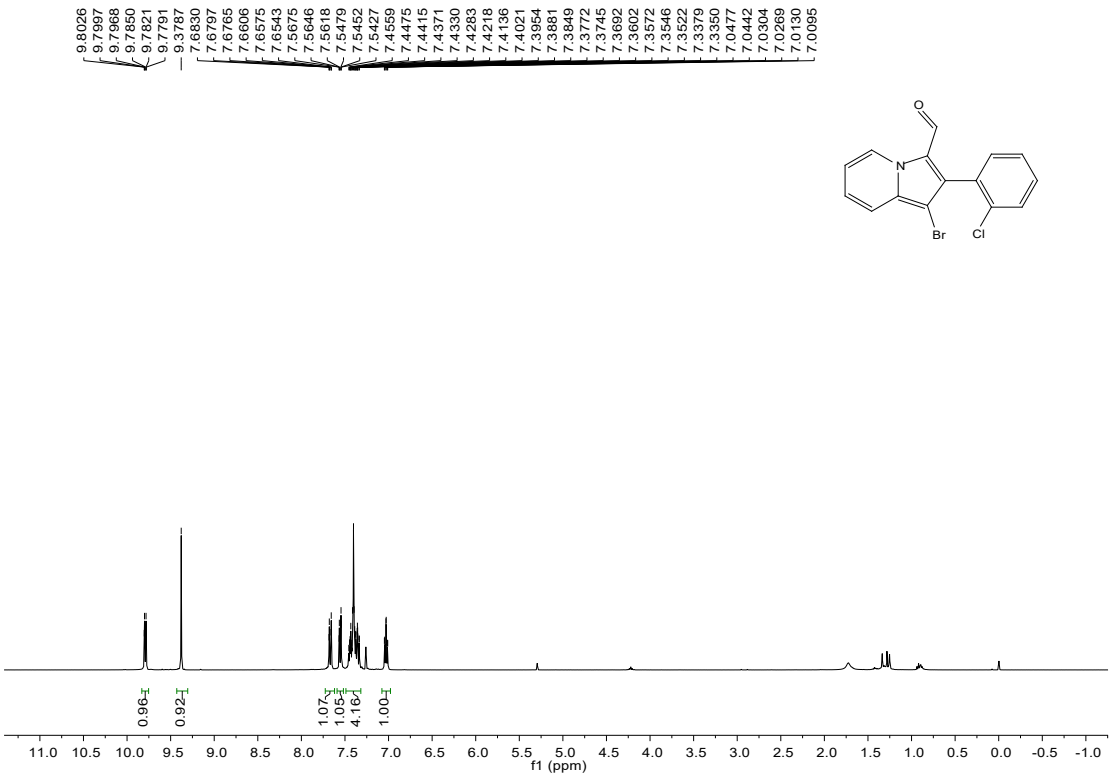
3n ^{13}C NMR (101 MHz, $CDCl_3$)



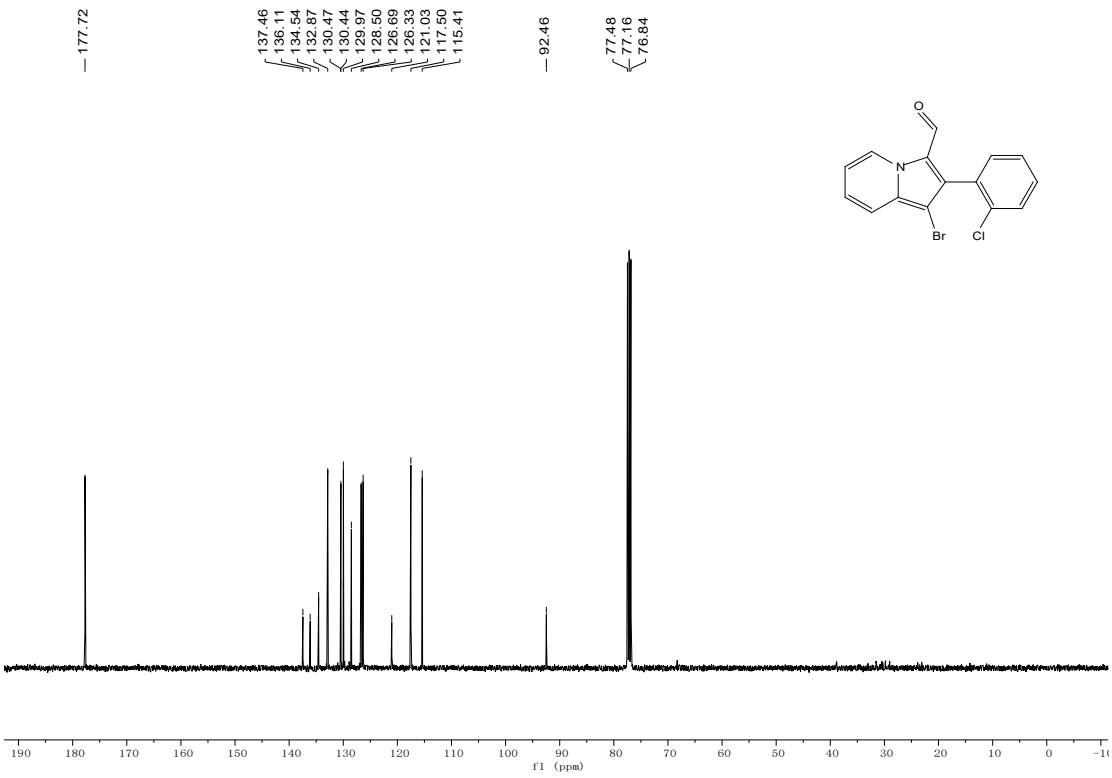
3n ^{19}F NMR (377 MHz, $CDCl_3$)



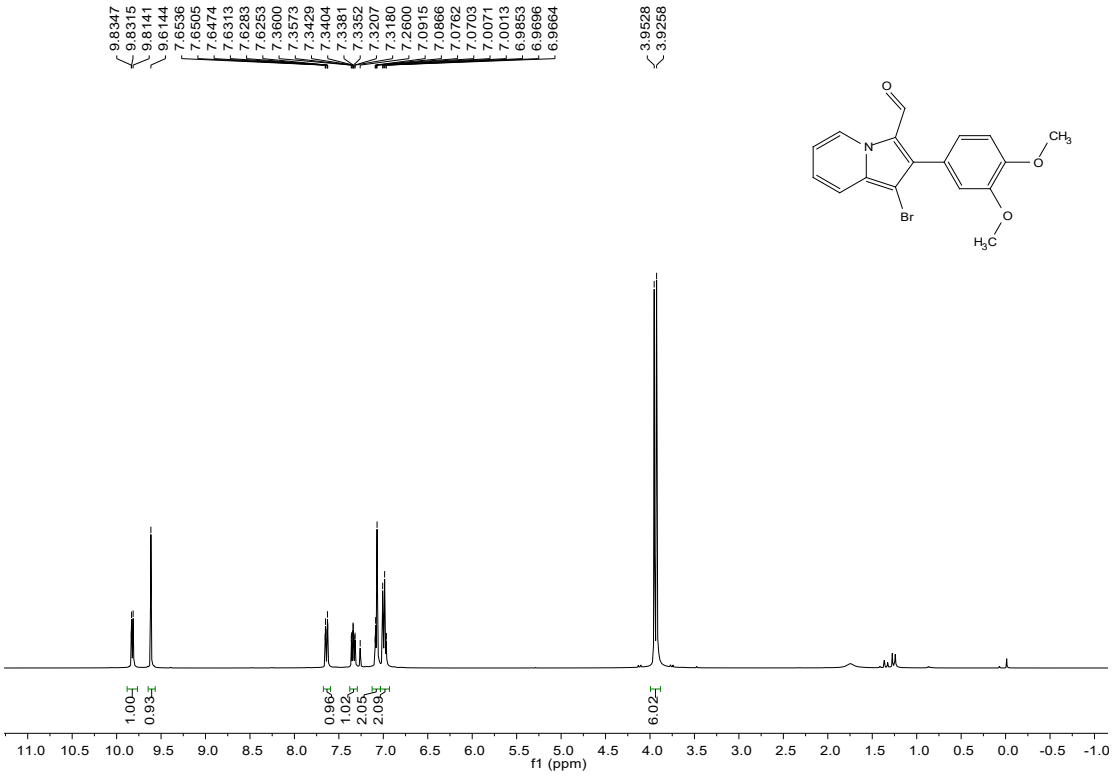
3o ^{1}H NMR (400 MHz, $CDCl_3$)



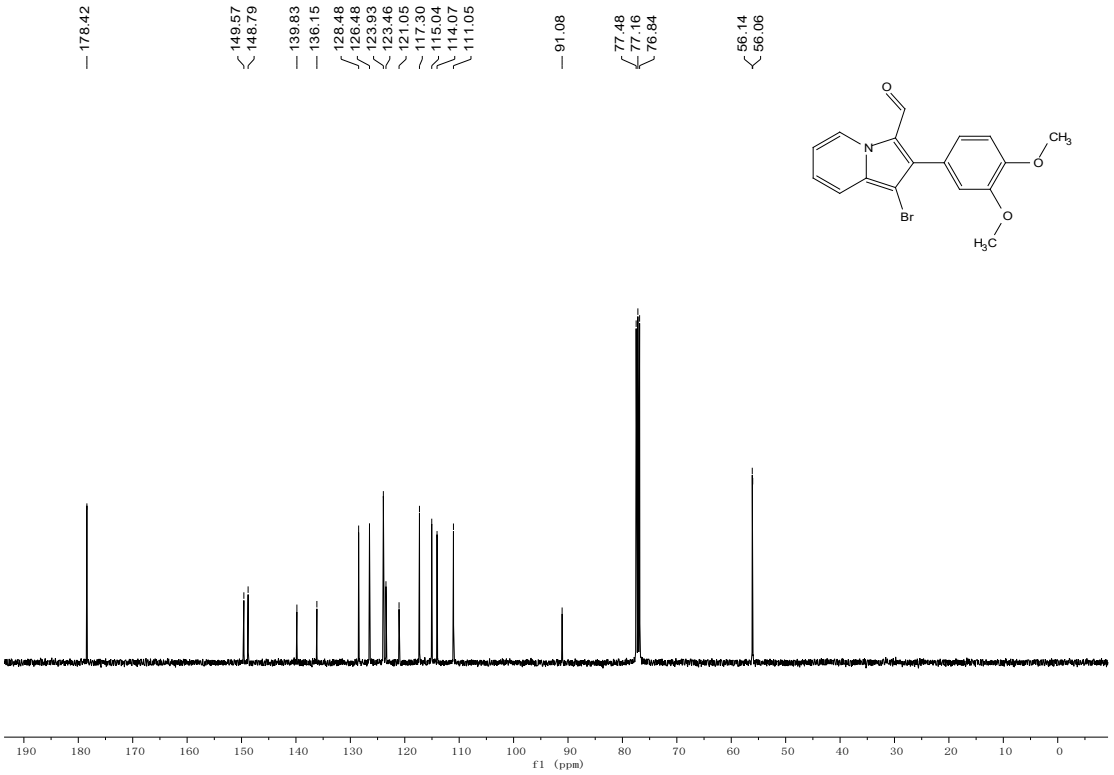
3o ^{13}C NMR (101 MHz, $CDCl_3$)



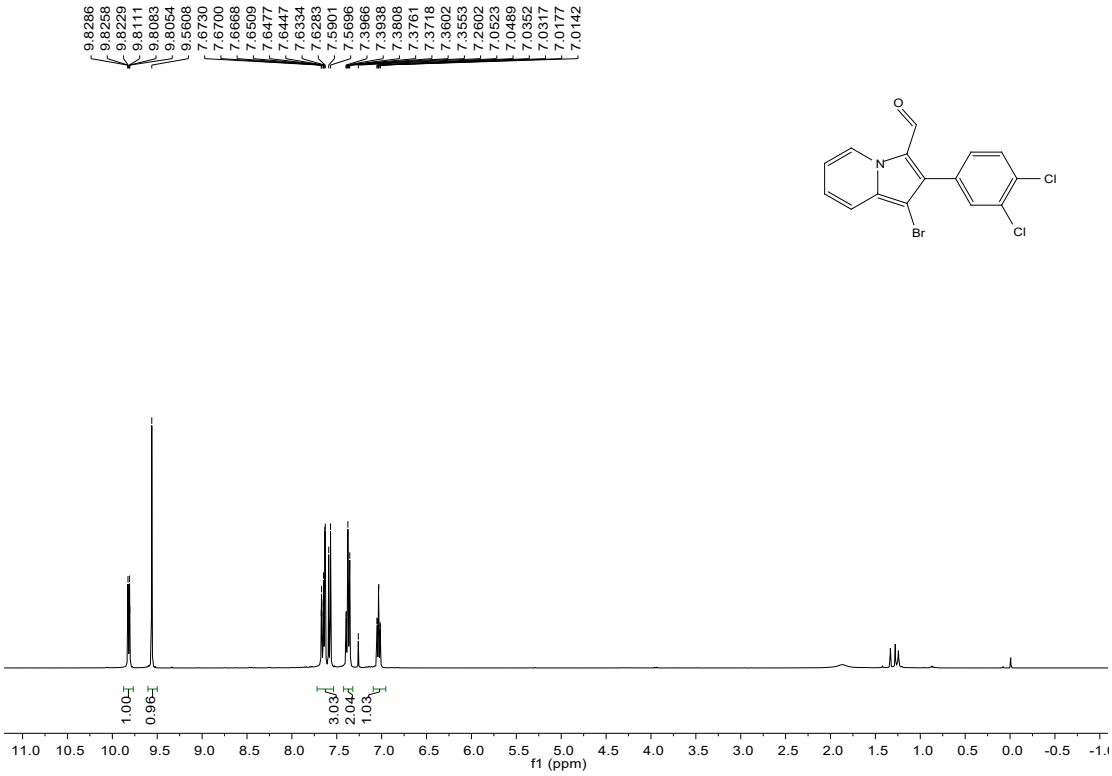
3p ^{1}H NMR (400 MHz, $CDCl_3$)



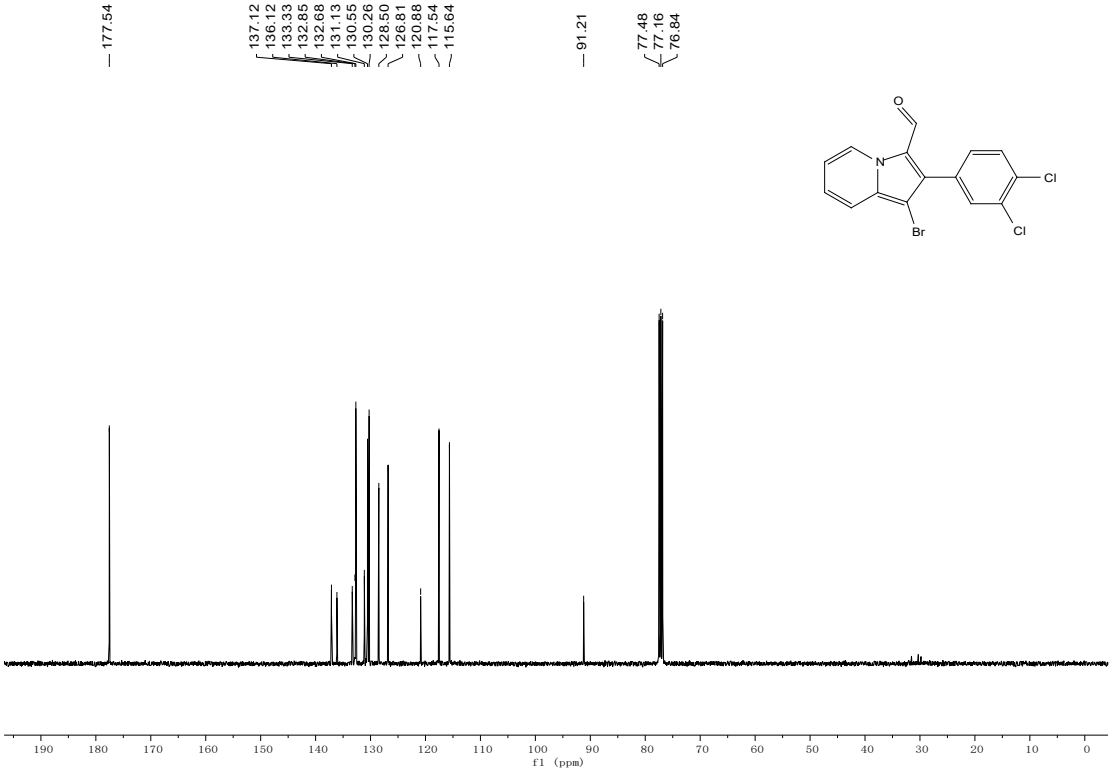
3p ^{13}C NMR (101 MHz, $CDCl_3$)



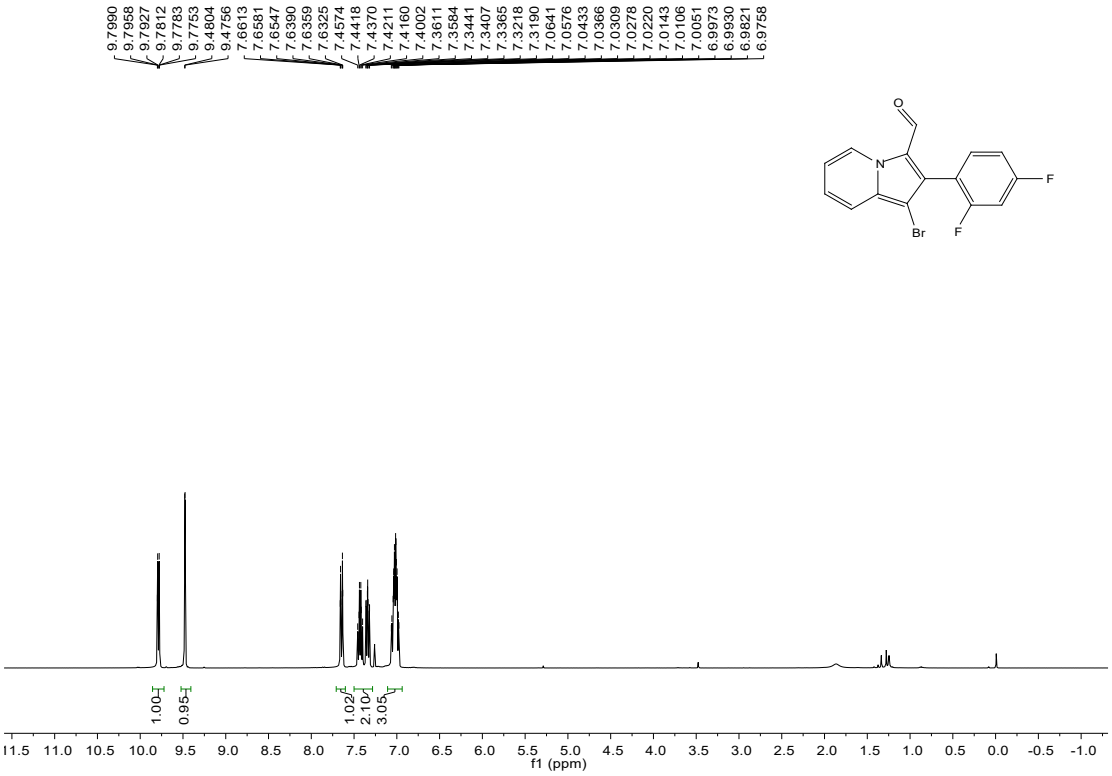
3q ^{1}H NMR (400 MHz, $CDCl_3$)



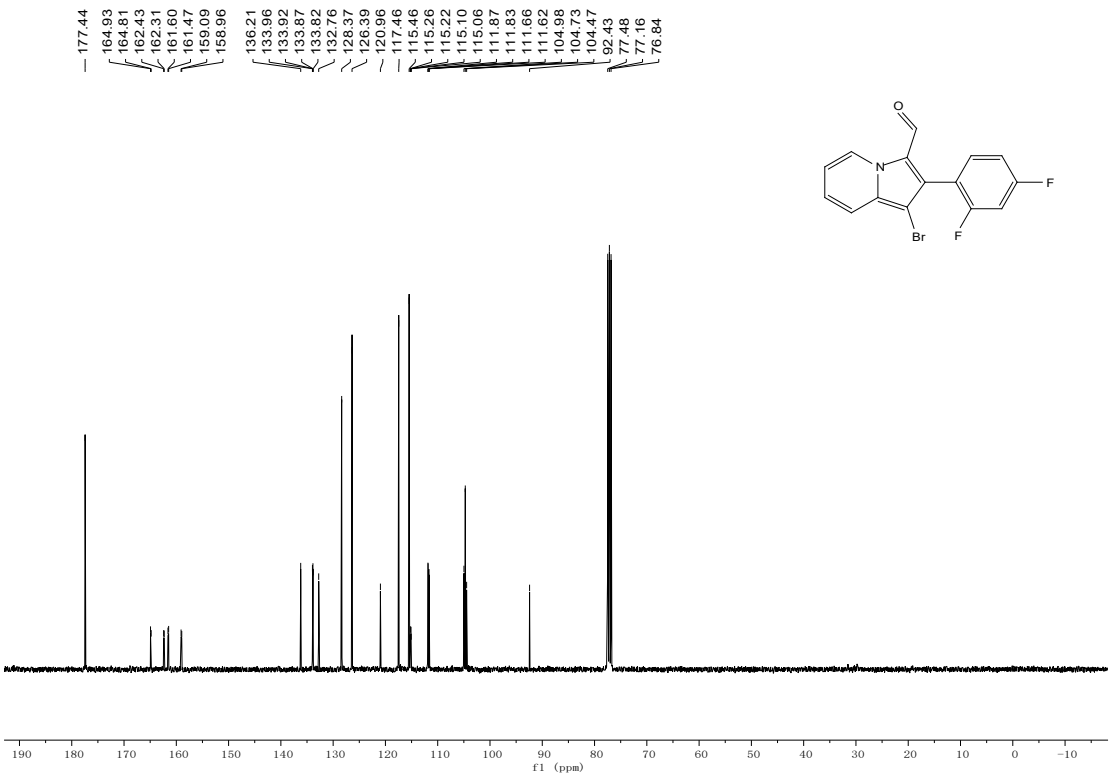
3q ^{13}C NMR (101 MHz, $CDCl_3$)



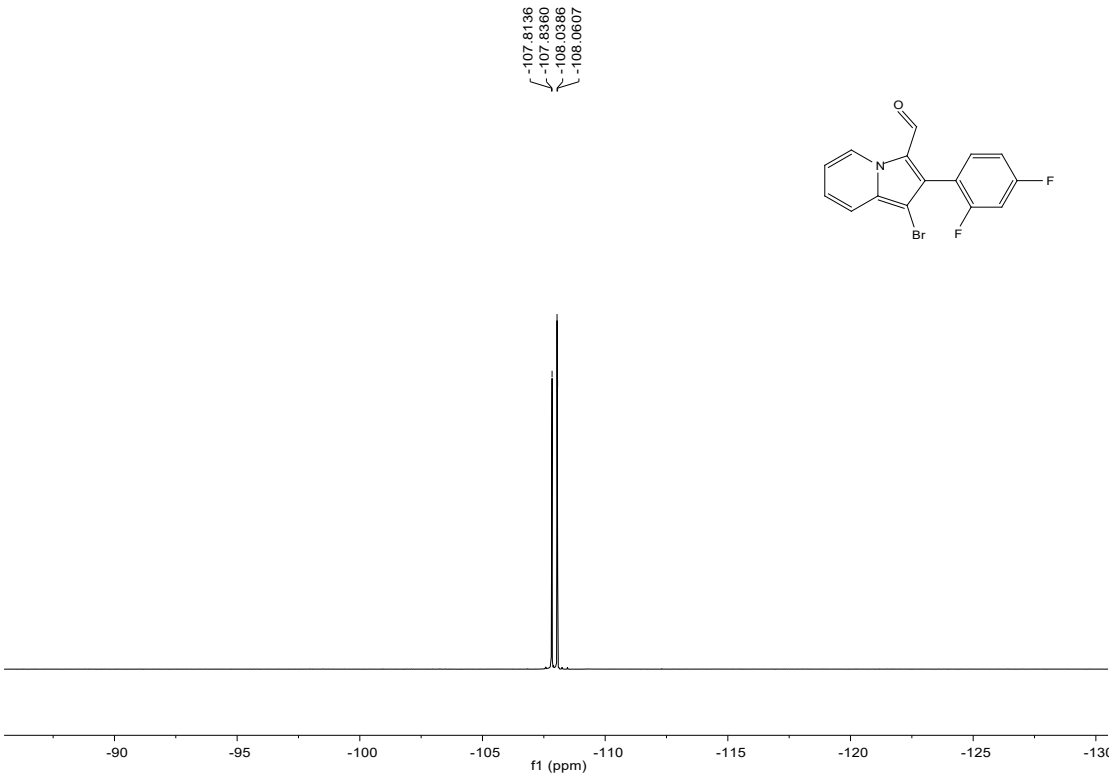
3r ^{1}H NMR (400 MHz, $CDCl_3$)



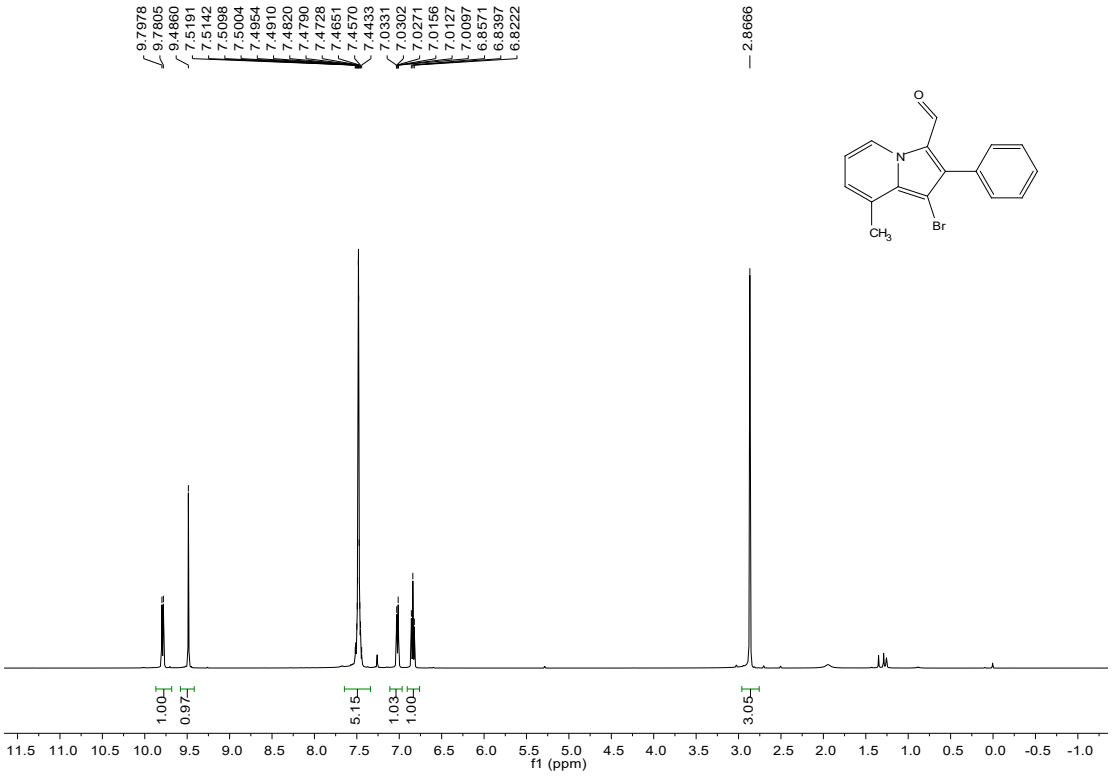
3r ^{13}C NMR (101 MHz, $CDCl_3$)



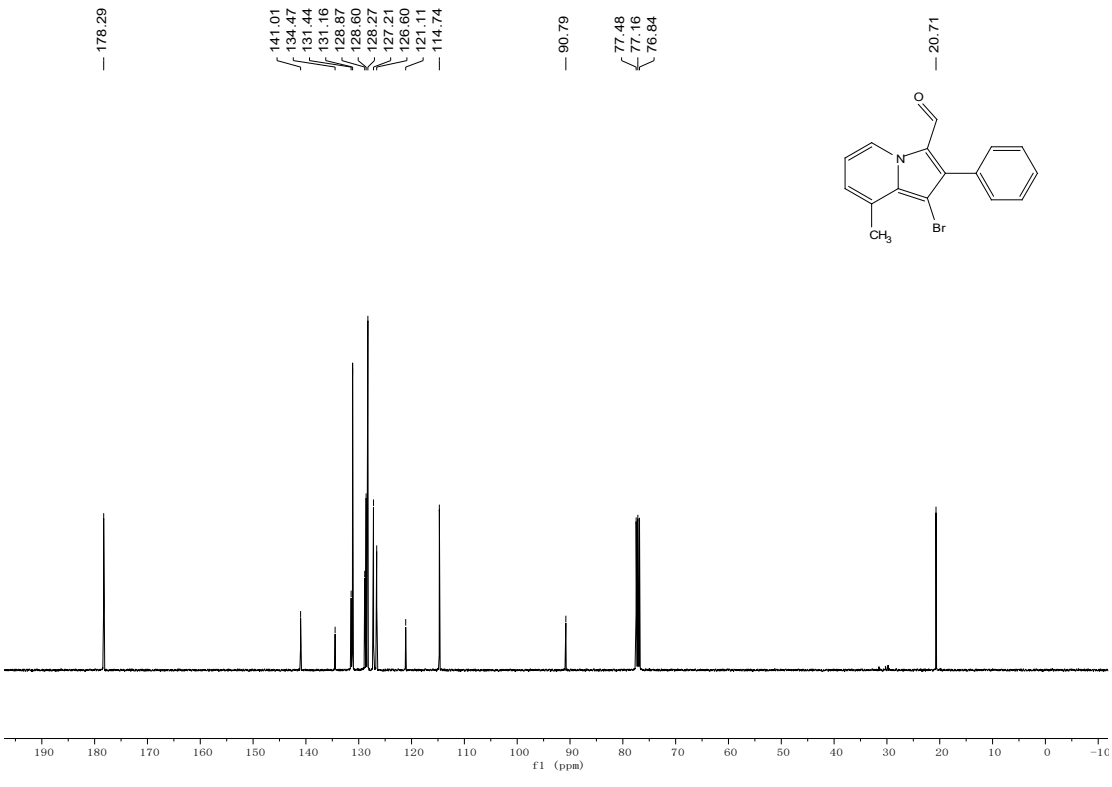
3r ^{19}F NMR (377 MHz, $CDCl_3$)



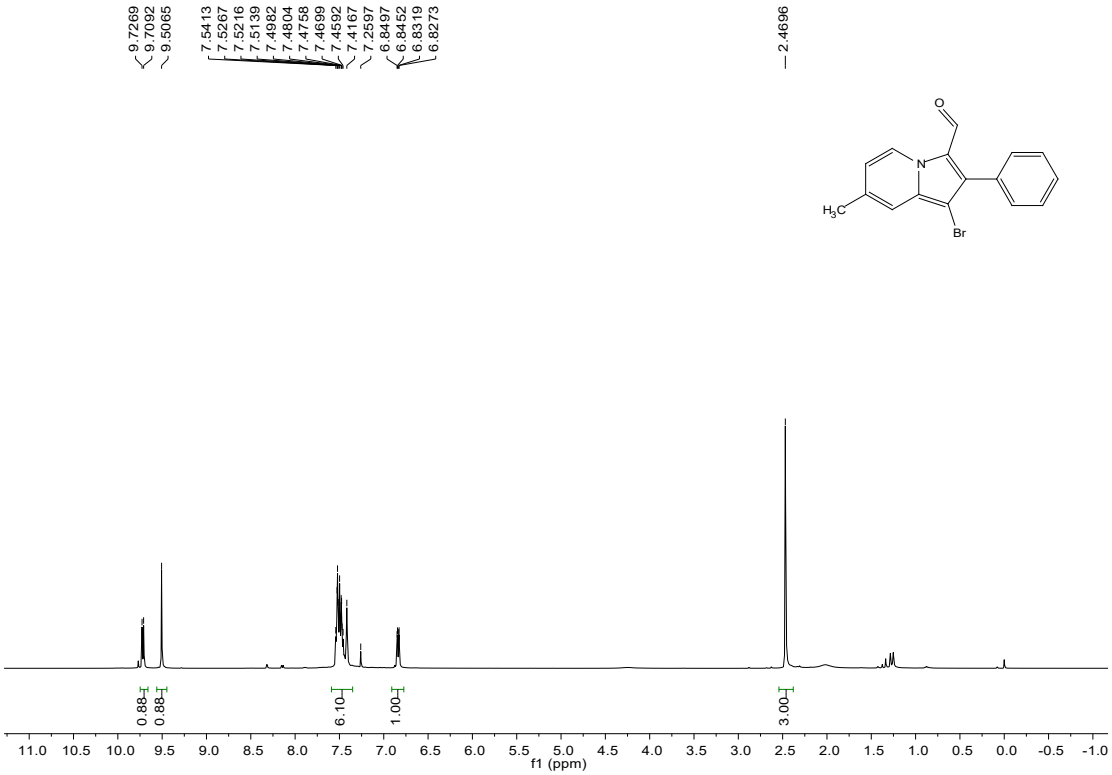
3s ^{1}H NMR (400 MHz, $CDCl_3$)



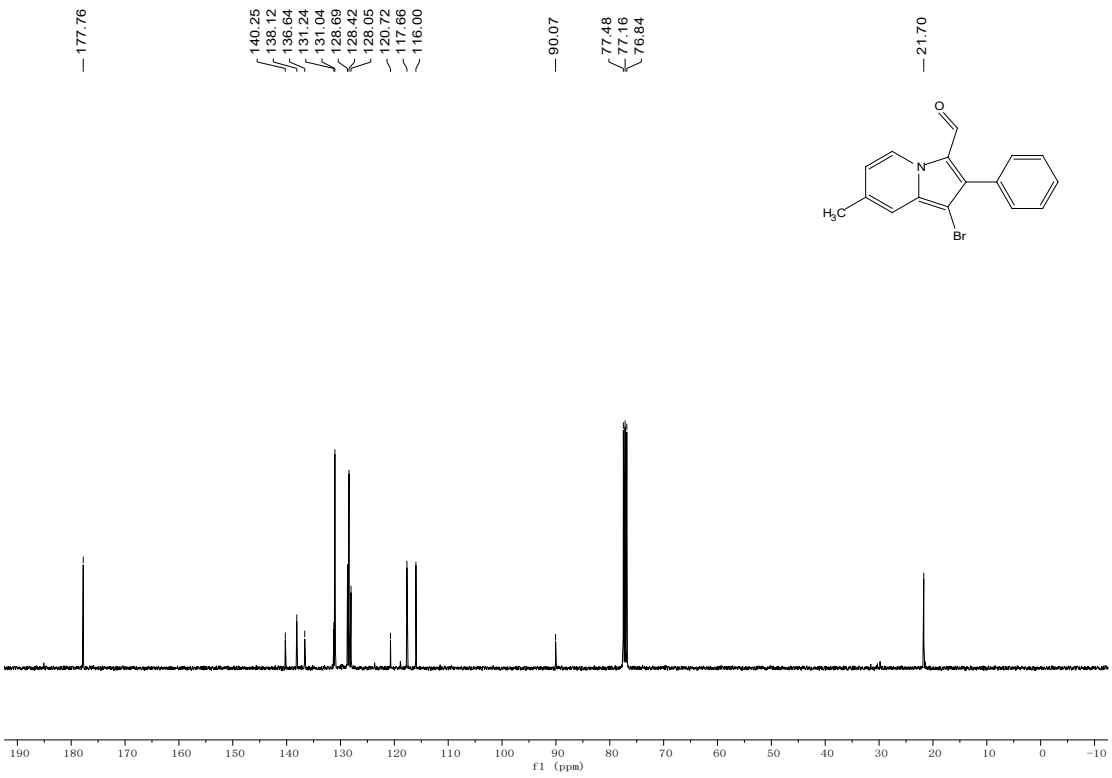
3s ^{13}C NMR (101 MHz, $CDCl_3$)



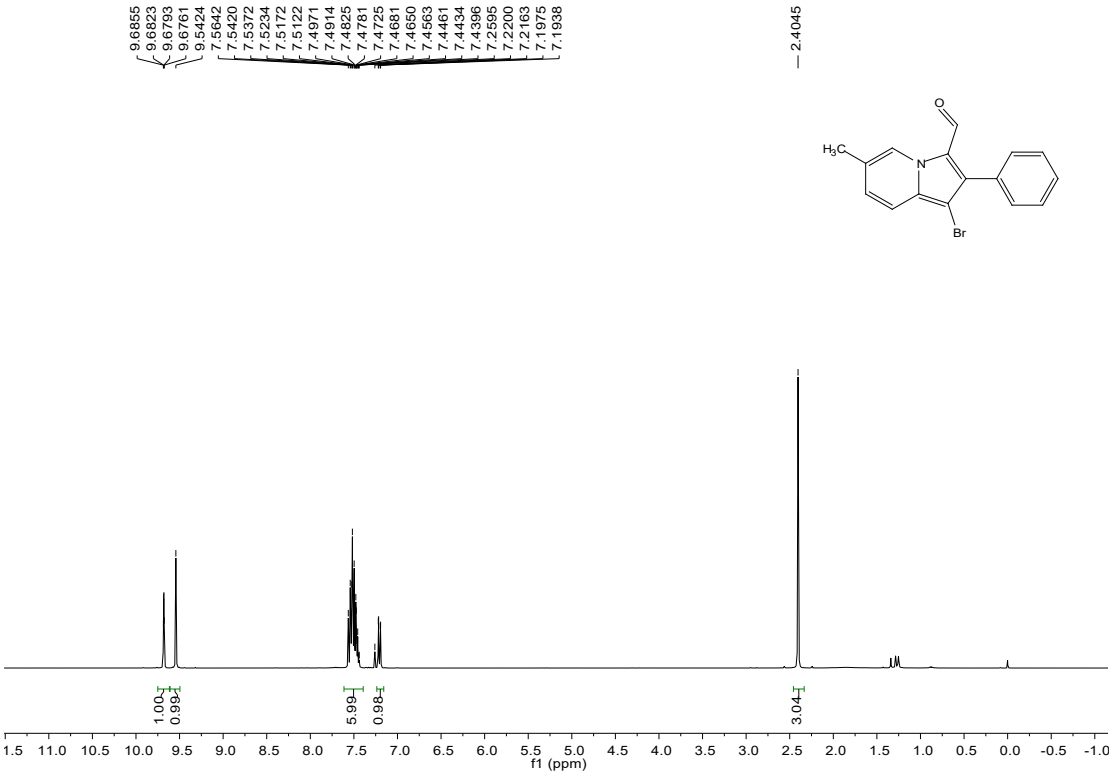
3t ^{1}H NMR (400 MHz, $CDCl_3$)



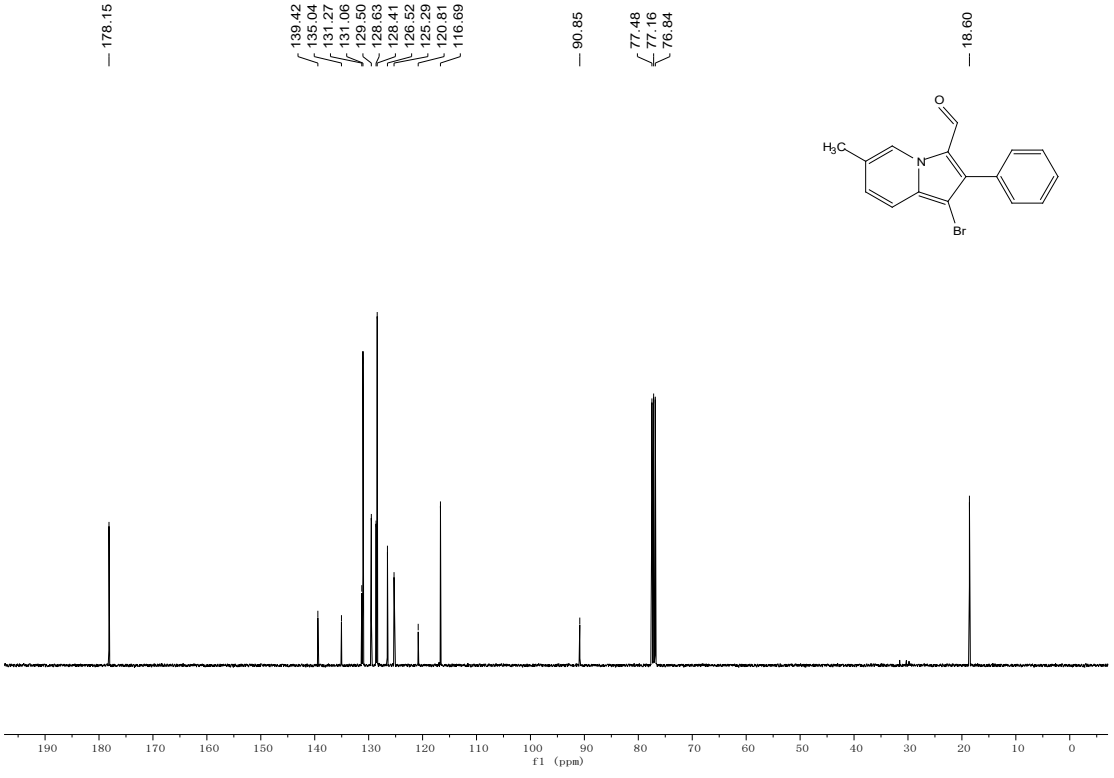
3t ^{13}C NMR (101 MHz, $CDCl_3$)



3u ^{1}H NMR (400 MHz, $CDCl_3$)



3u ^{13}C NMR (101 MHz, $CDCl_3$)



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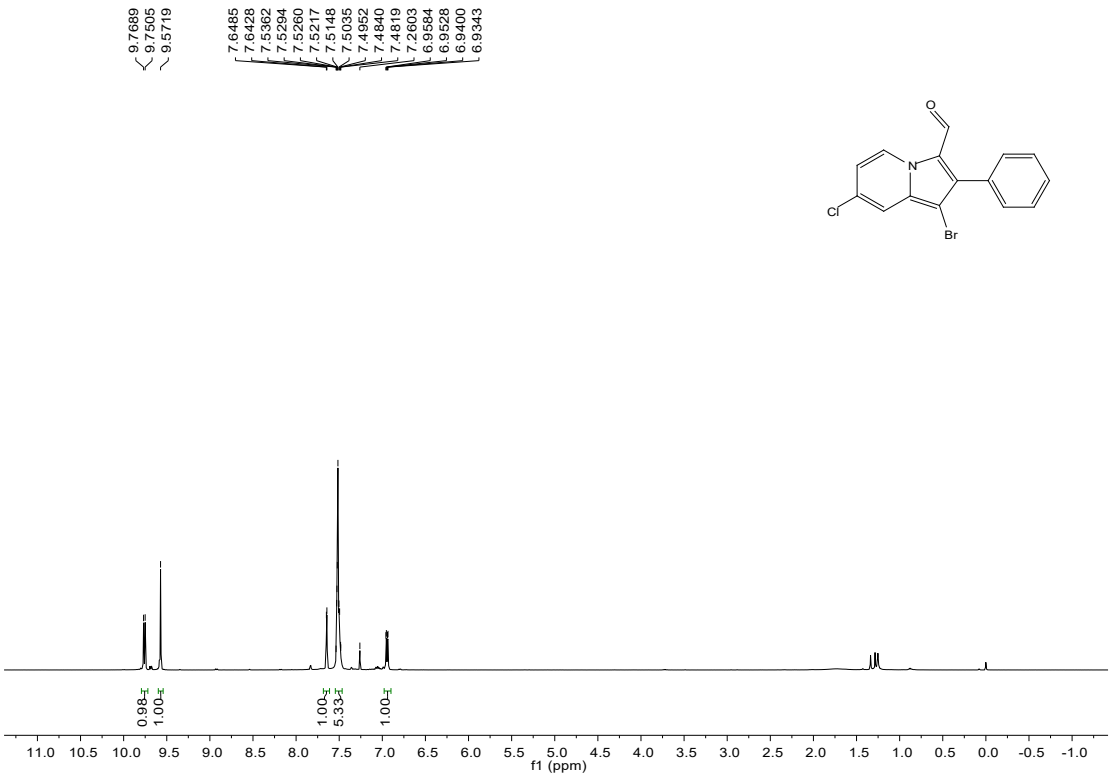

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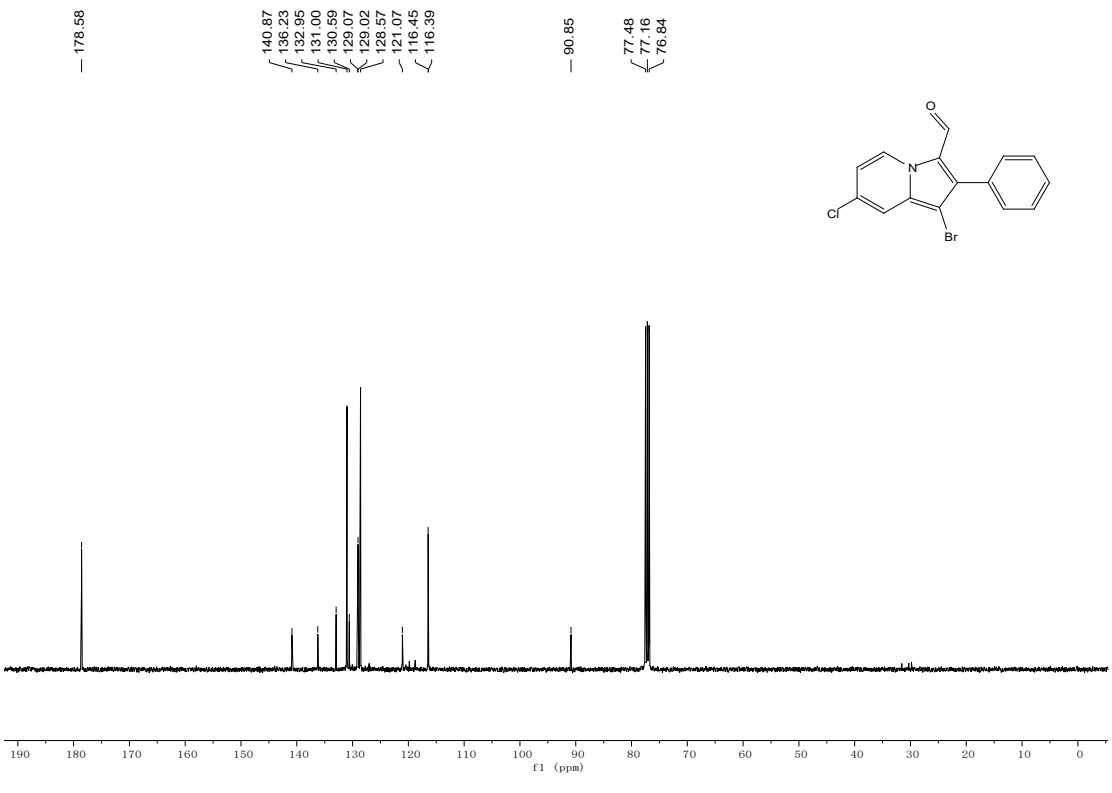
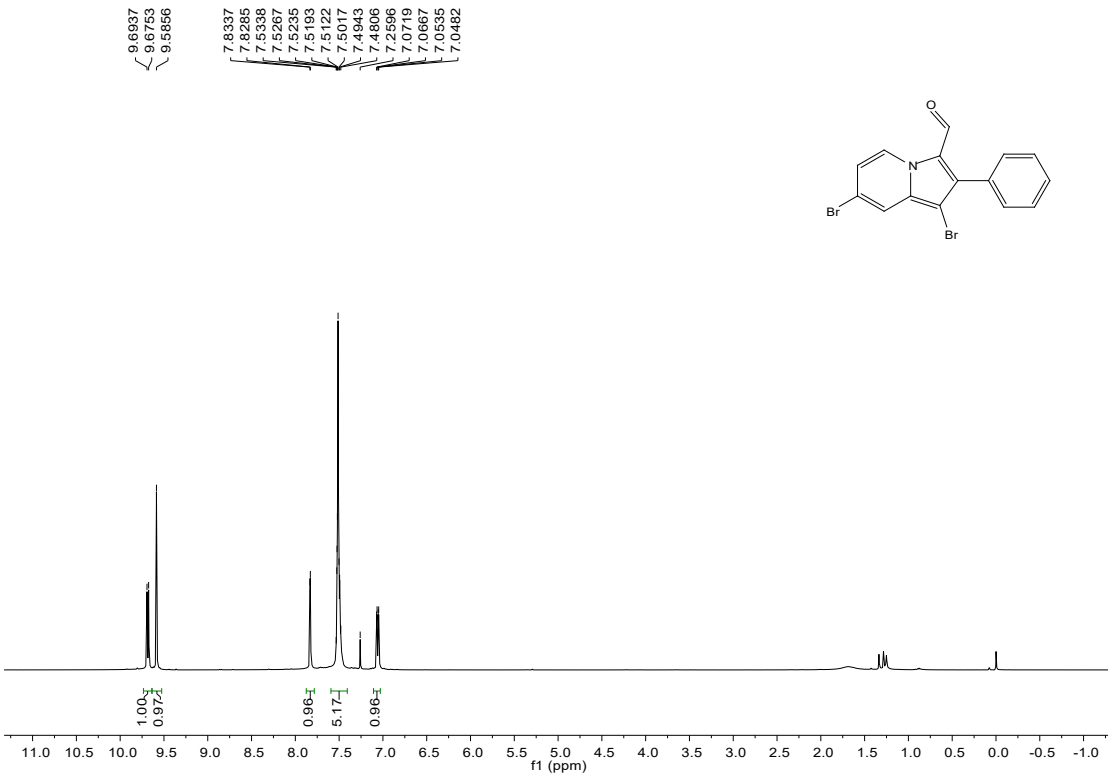
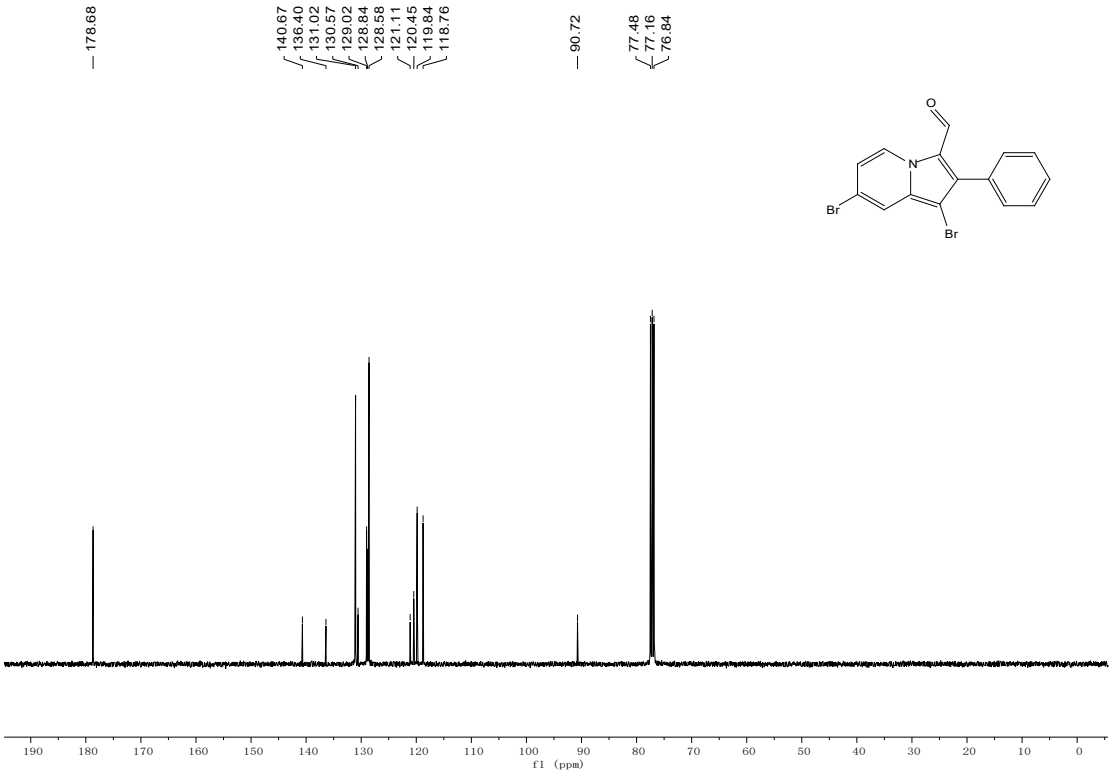


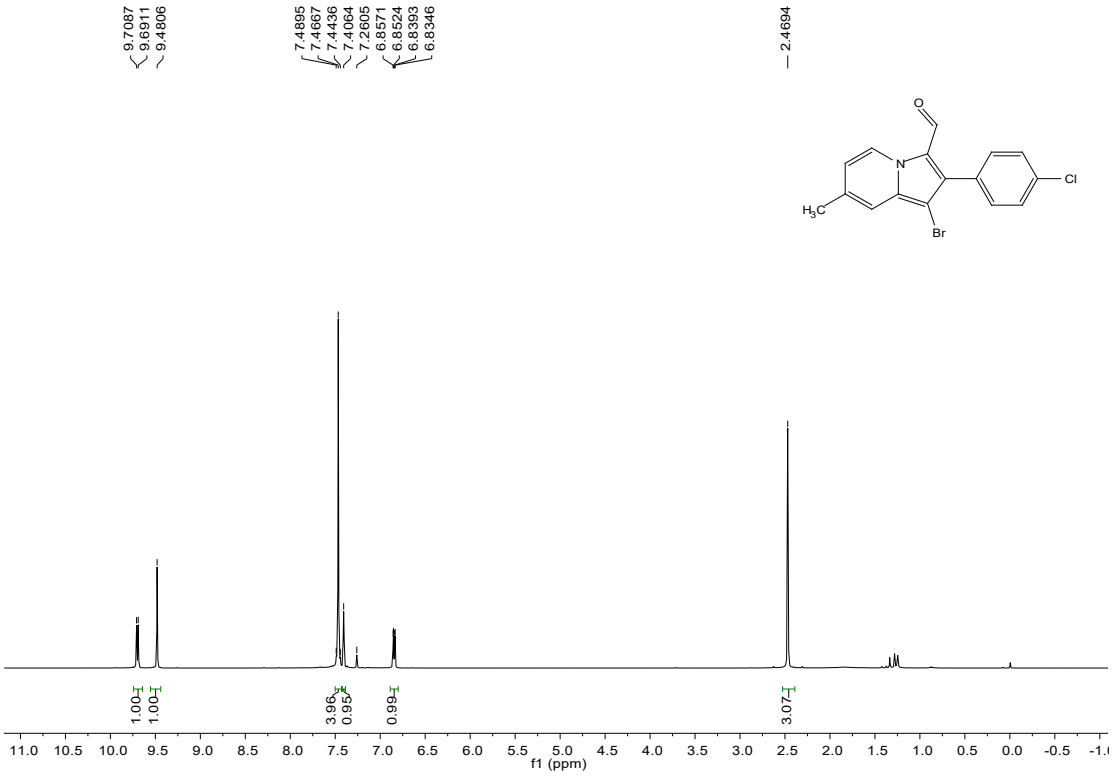
3w ^{1}H NMR (400 MHz, $CDCl_3$)



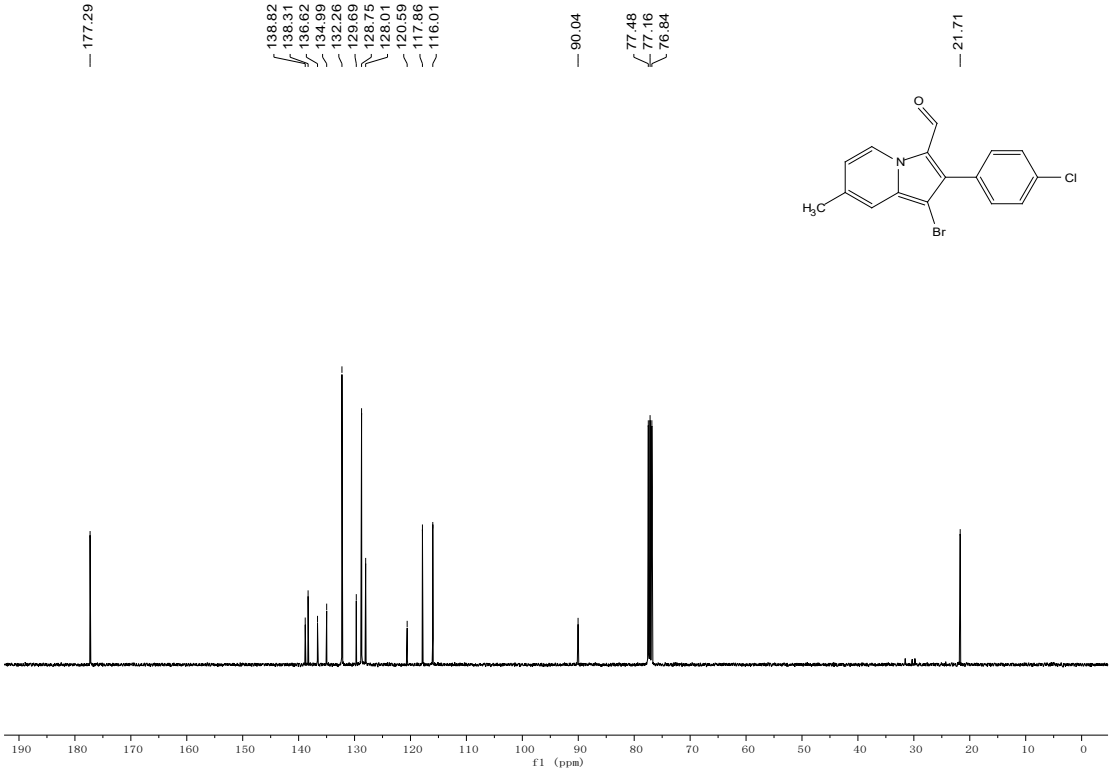
3w ^{13}C NMR (101 MHz, $CDCl_3$)



3x ^{1}H NMR (400 MHz, $CDCl_3$)



3x ^{13}C NMR (101 MHz, $CDCl_3$)



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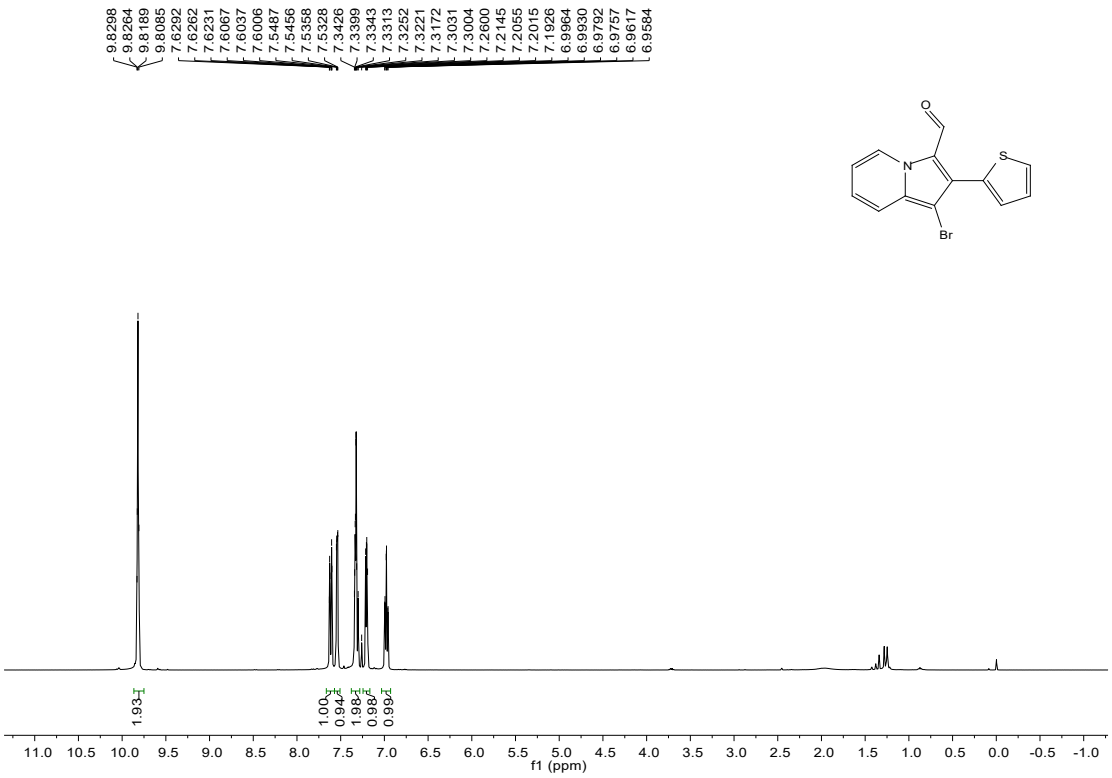
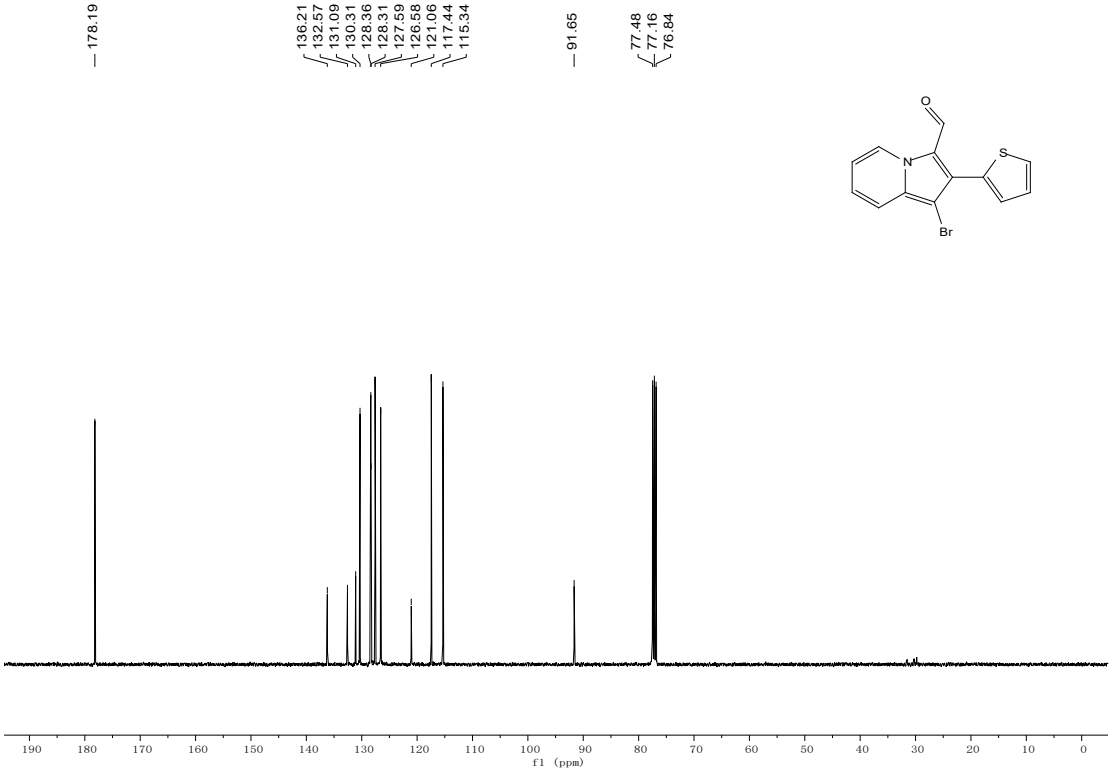


3y ^{13}C NMR (101 MHz, $CDCl_3$)



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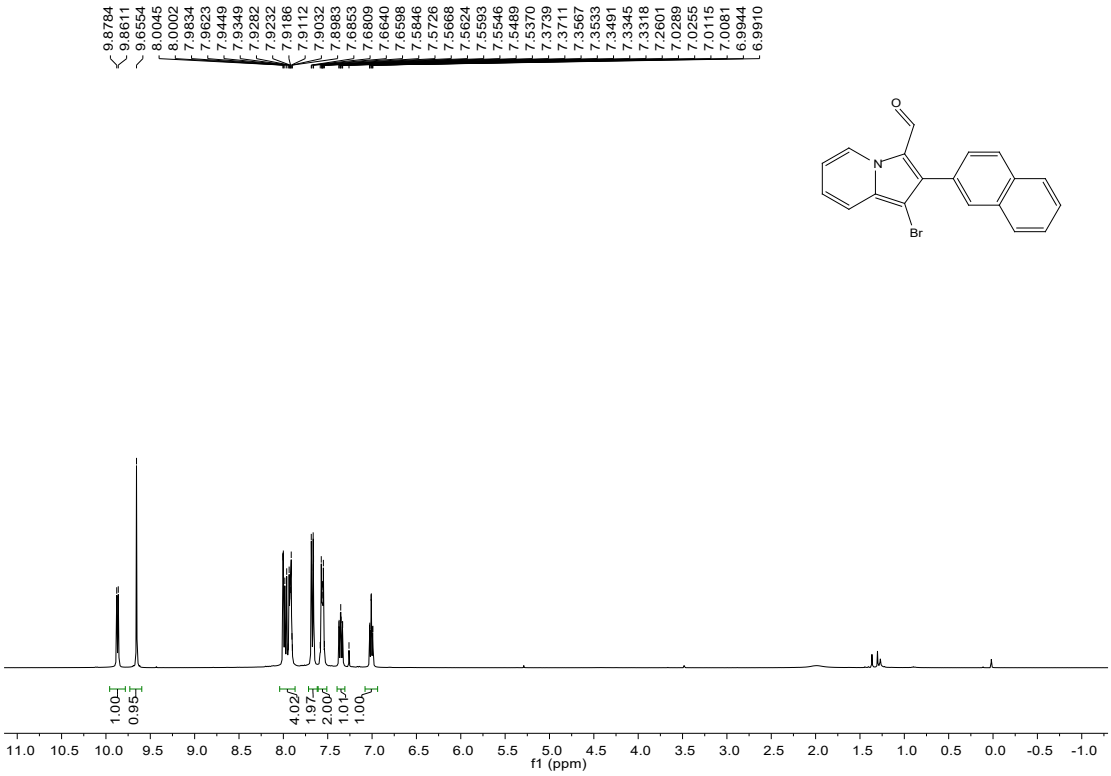

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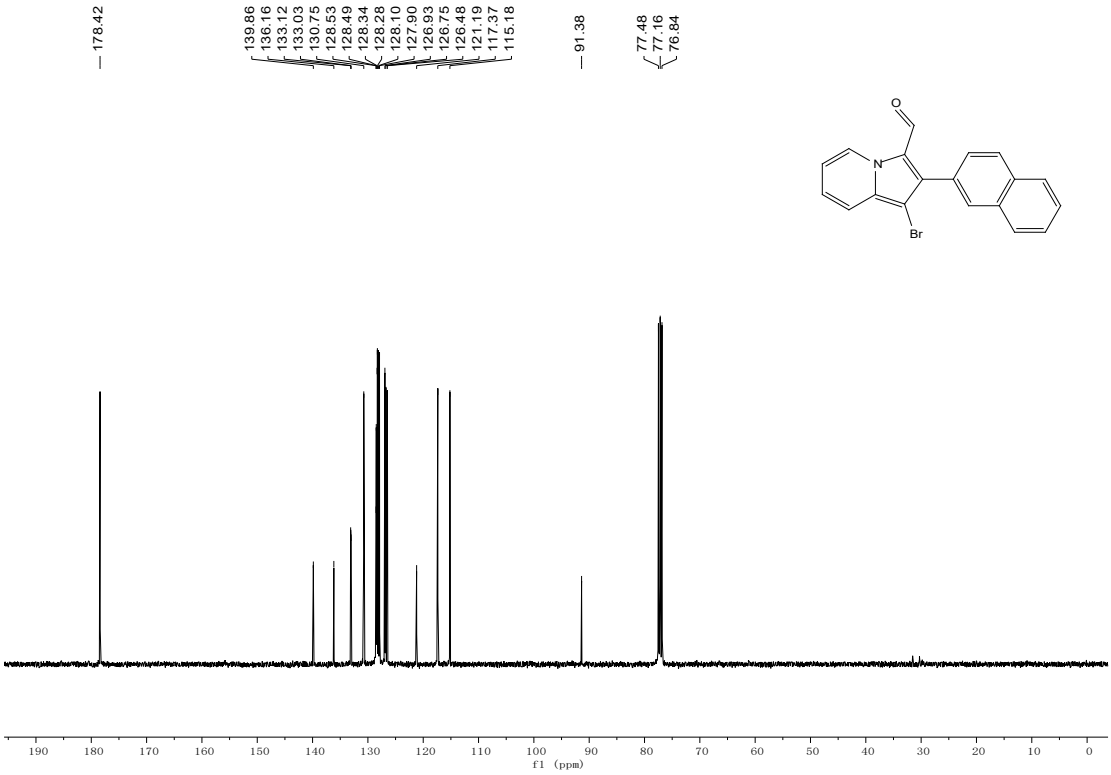
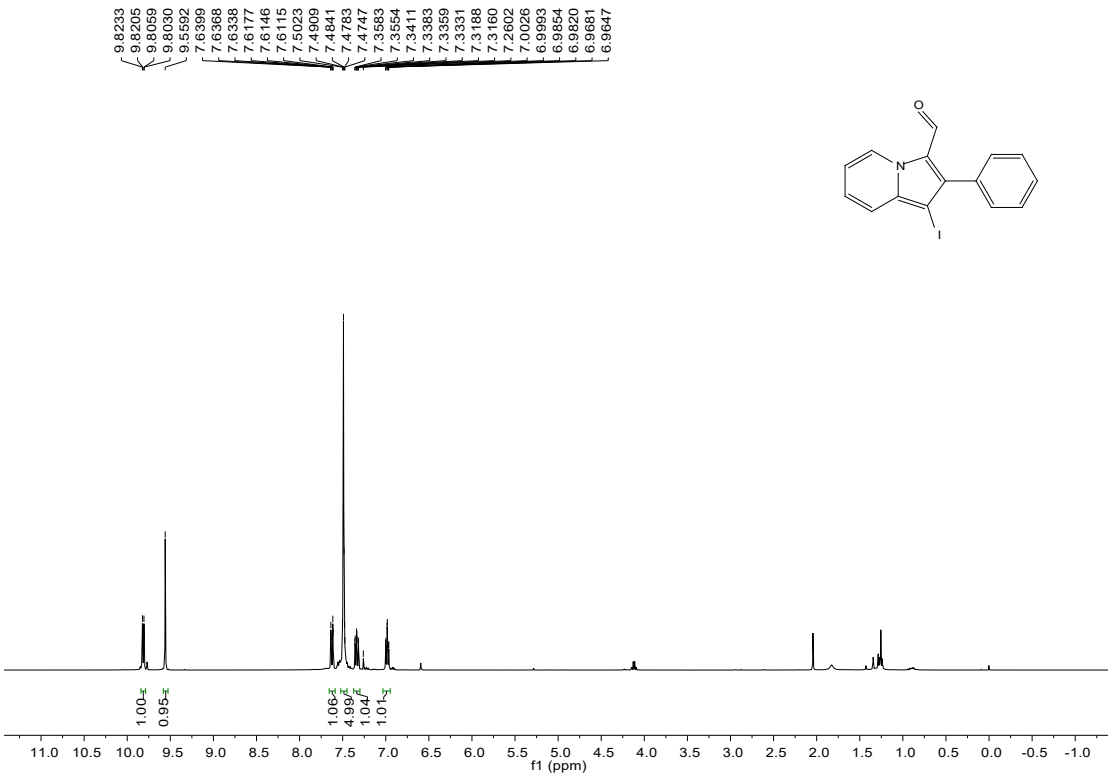
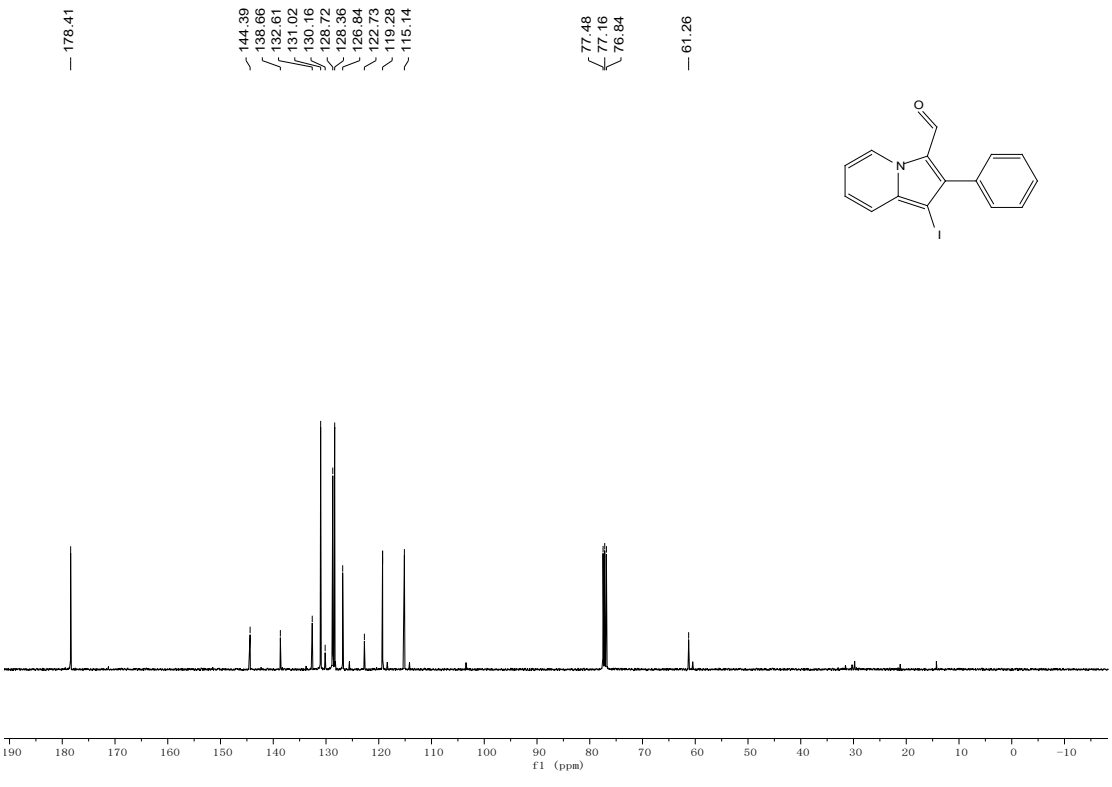


4a ^{1}H NMR (400 MHz, $CDCl_3$)



4a ^{13}C NMR (101 MHz, $CDCl_3$)



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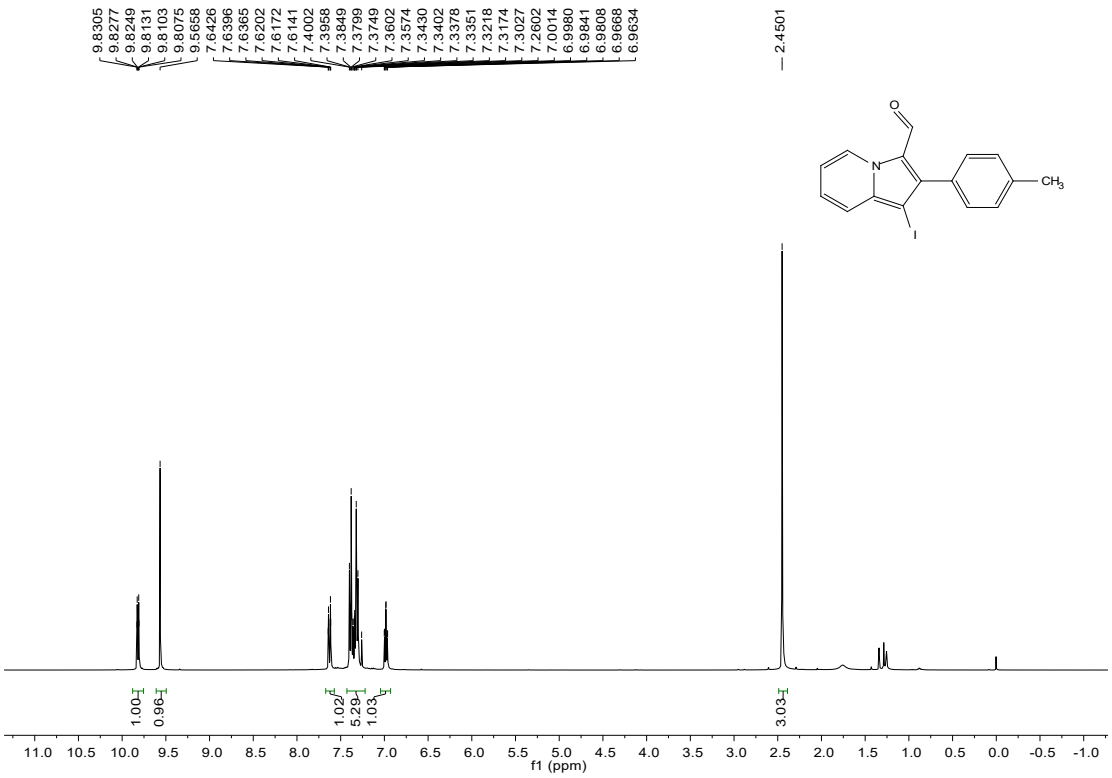
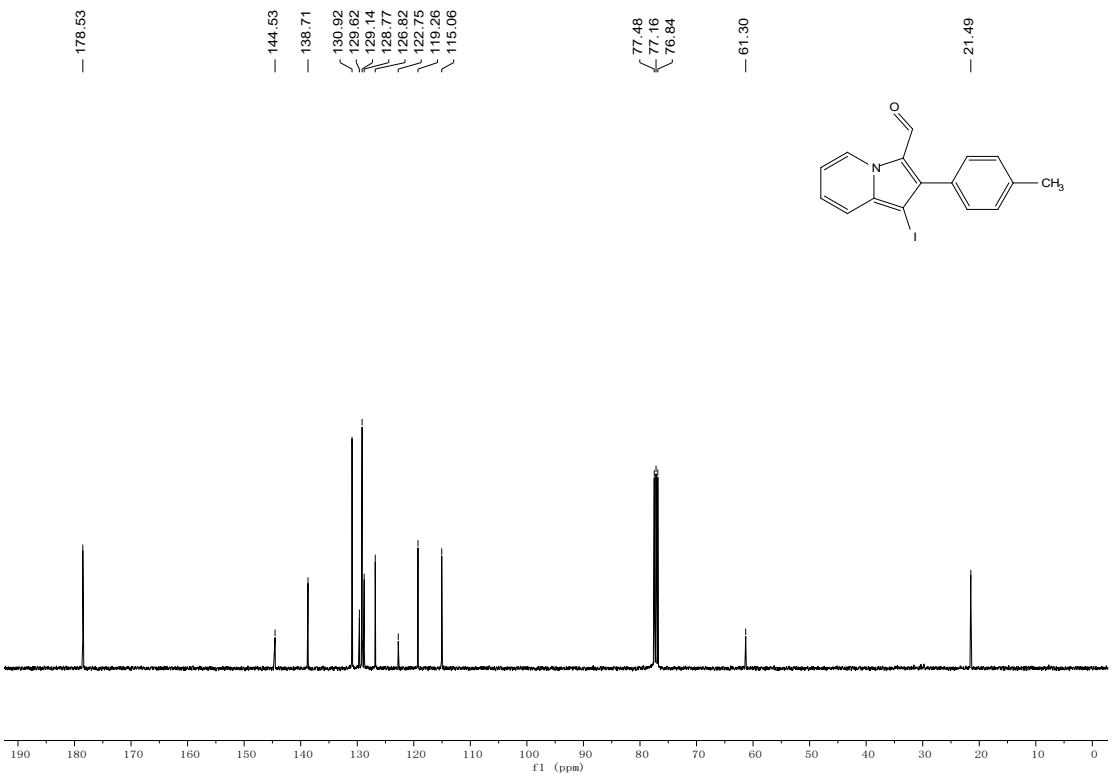
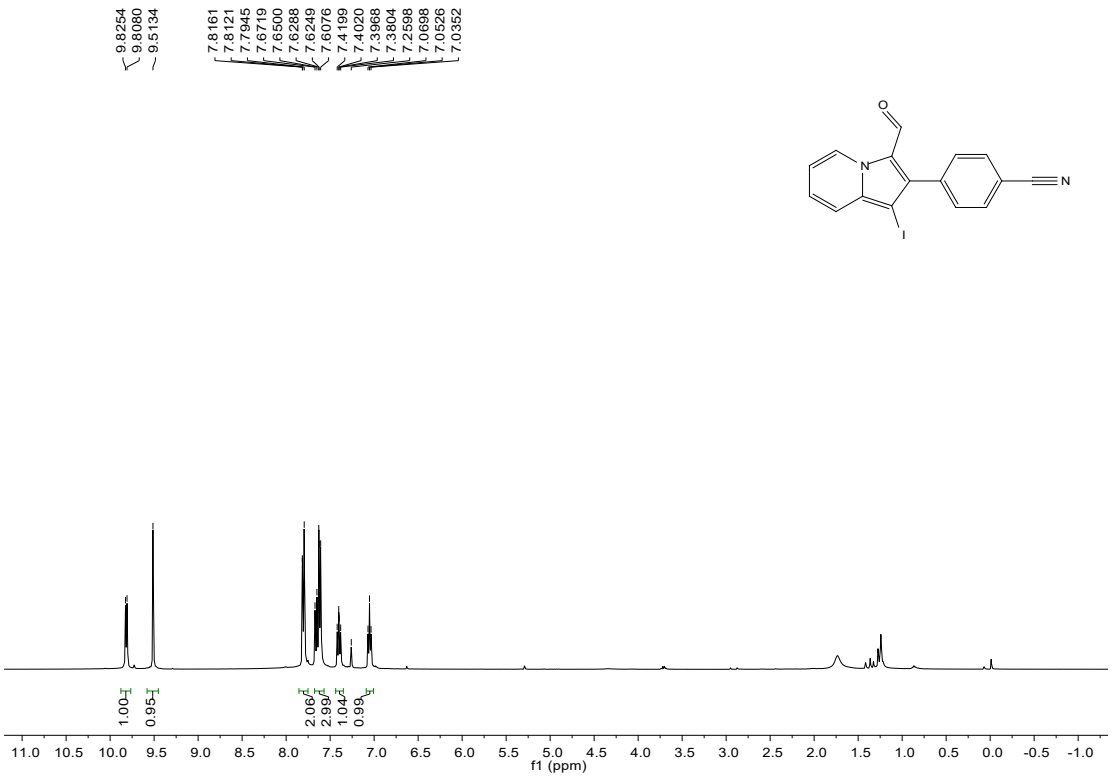


4b ^{13}C NMR (101 MHz, $CDCl_3$)



4c ^{1}H NMR (400 MHz, $CDCl_3$)



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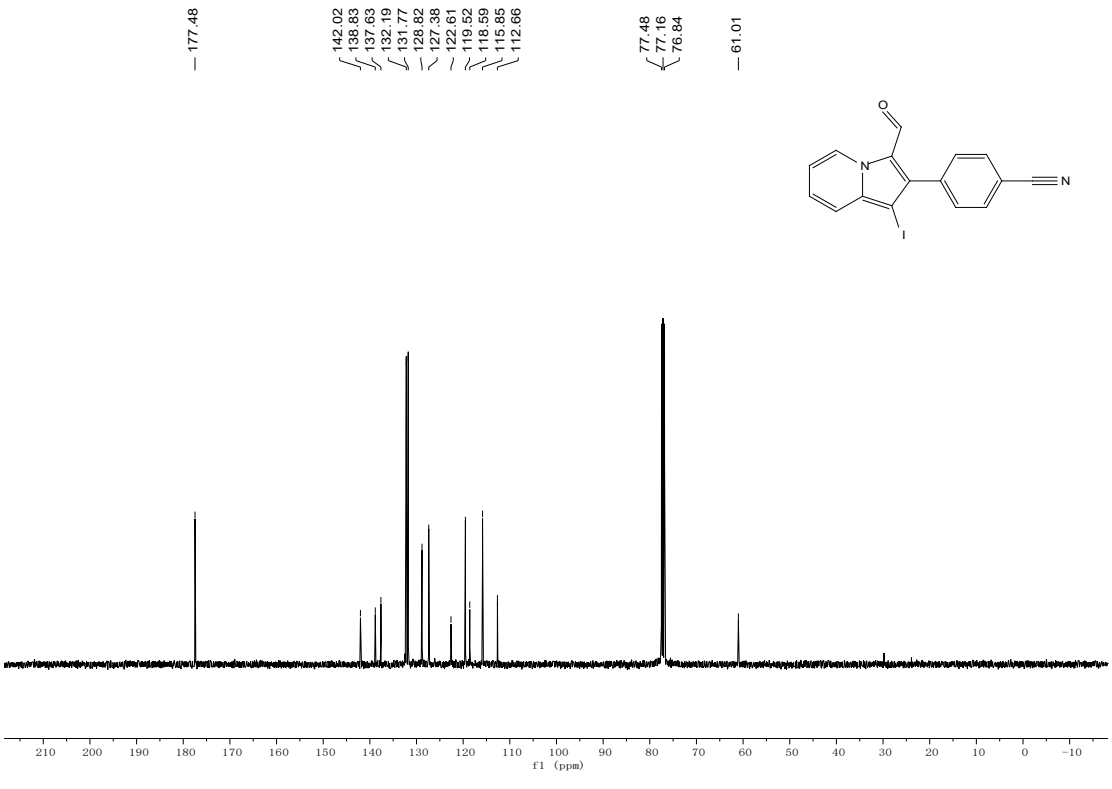
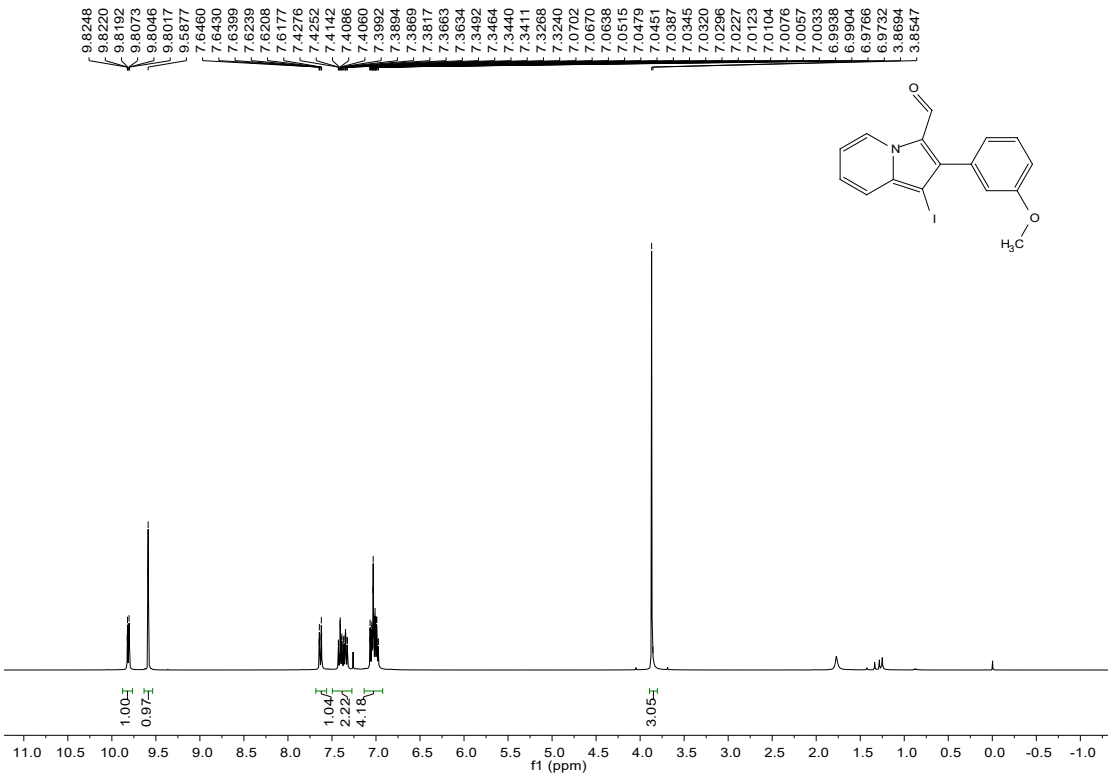
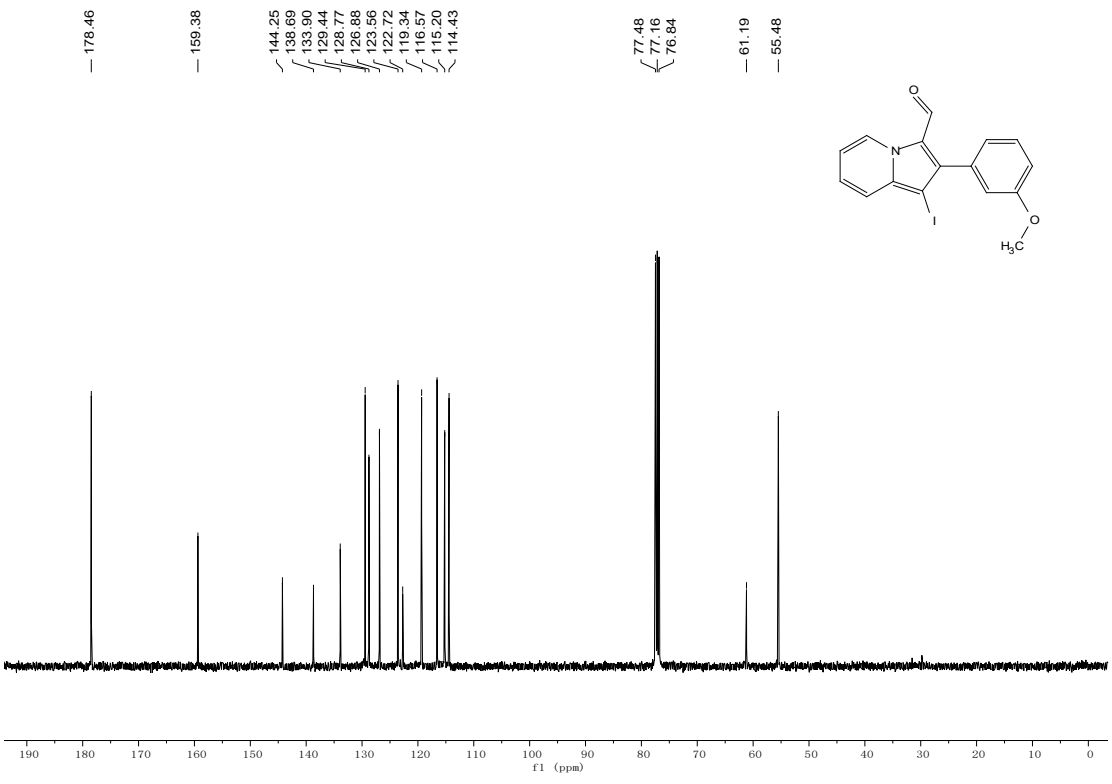


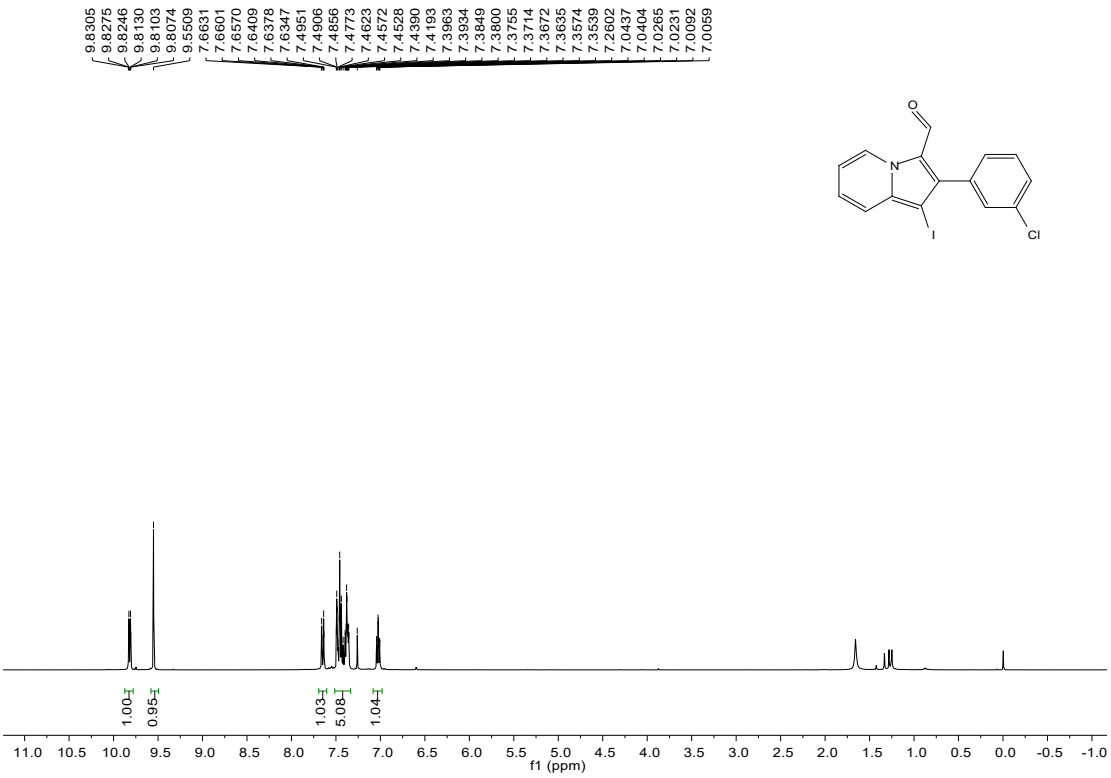
4d ^{1}H NMR (400 MHz, $CDCl_3$)



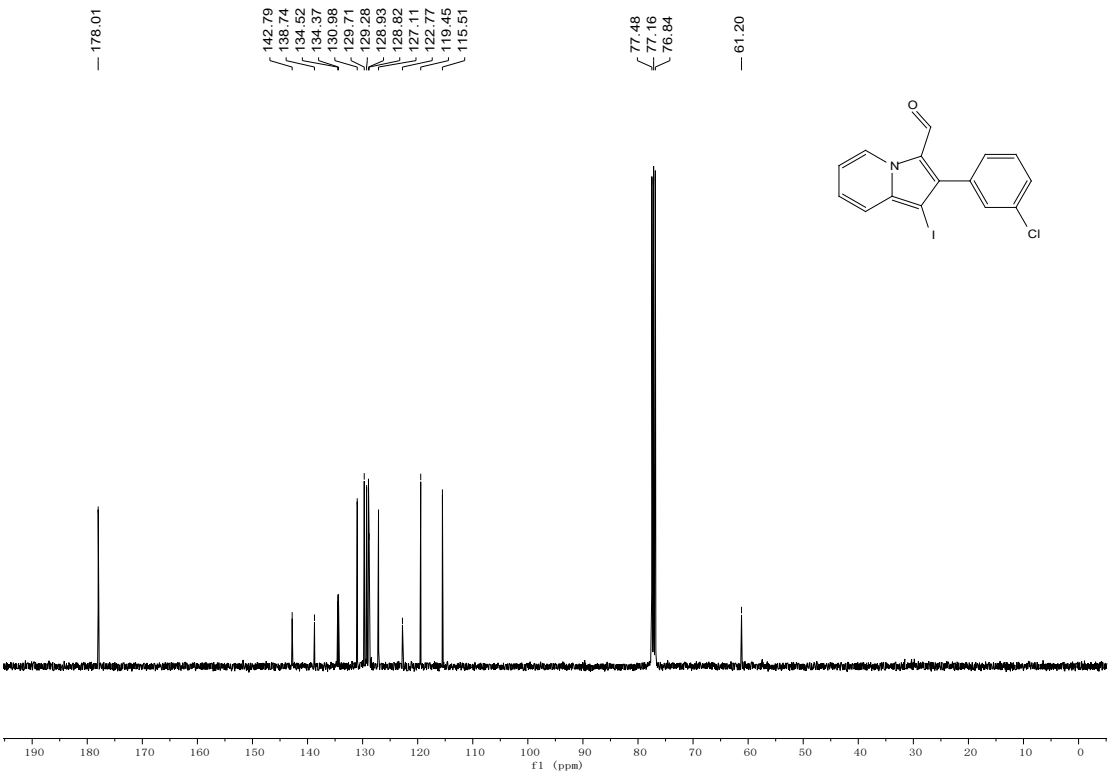
4d ^{13}C NMR (101 MHz, $CDCl_3$)



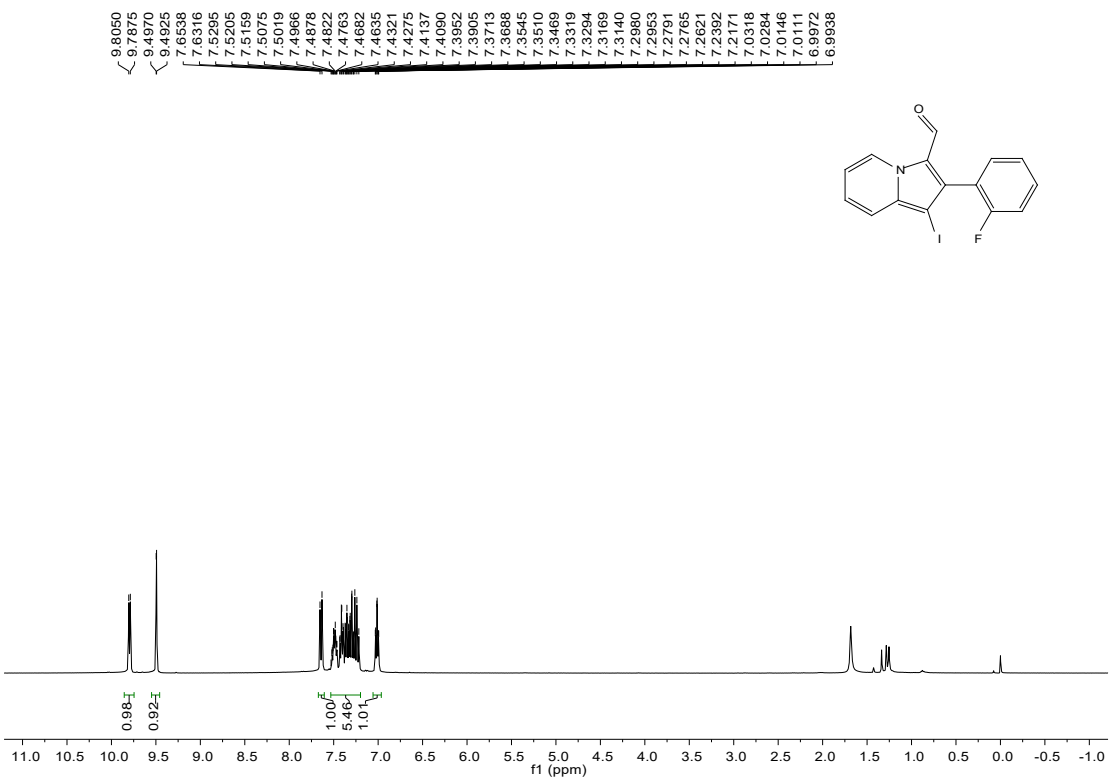
4e ^{1}H NMR (400 MHz, $CDCl_3$)



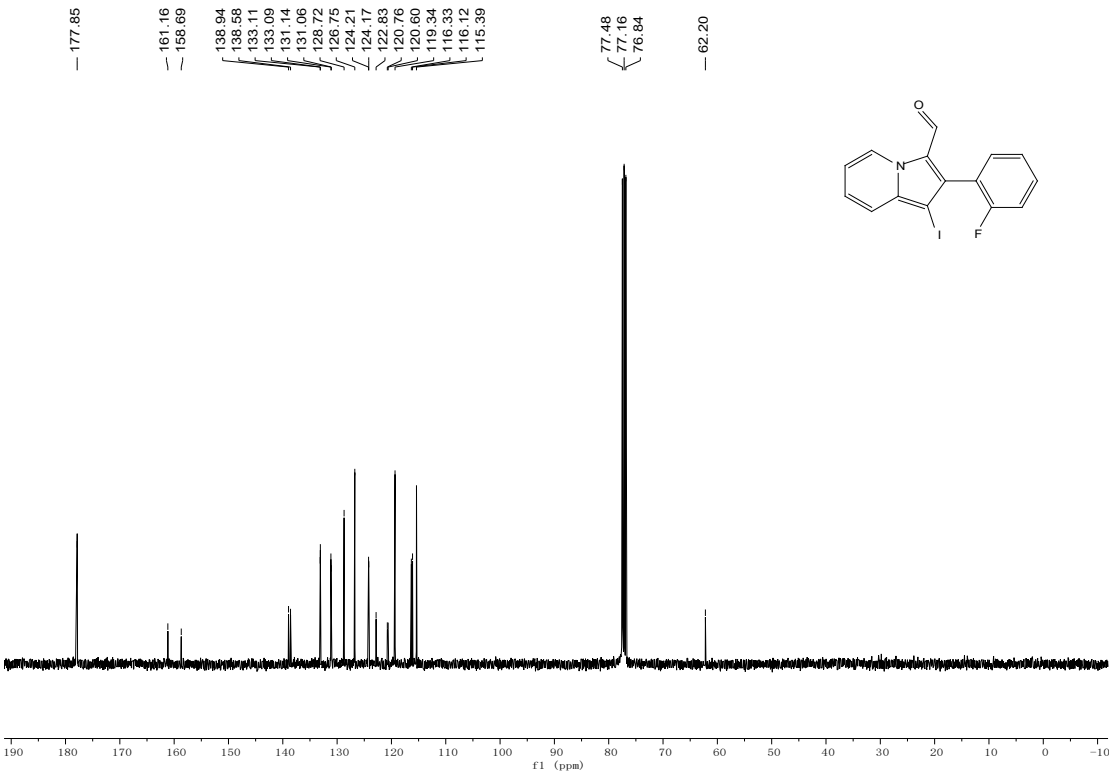
4e ^{13}C NMR (101 MHz, $CDCl_3$)



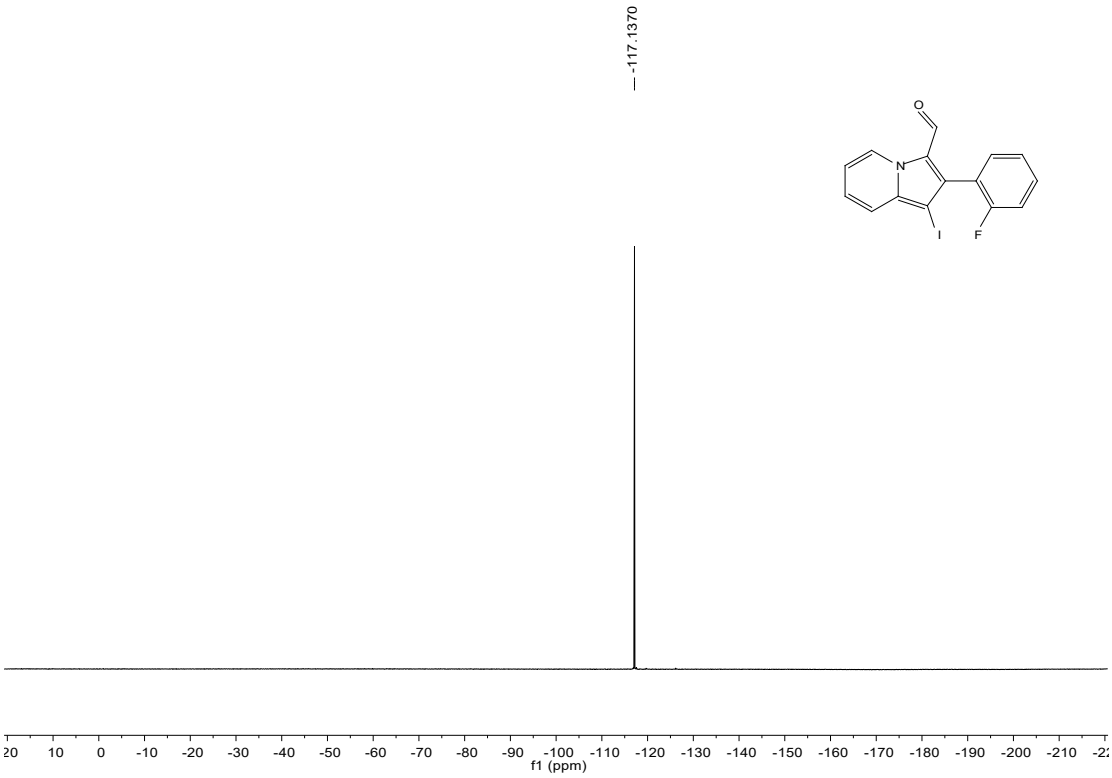
4f ^{1}H NMR (400 MHz, $CDCl_3$)



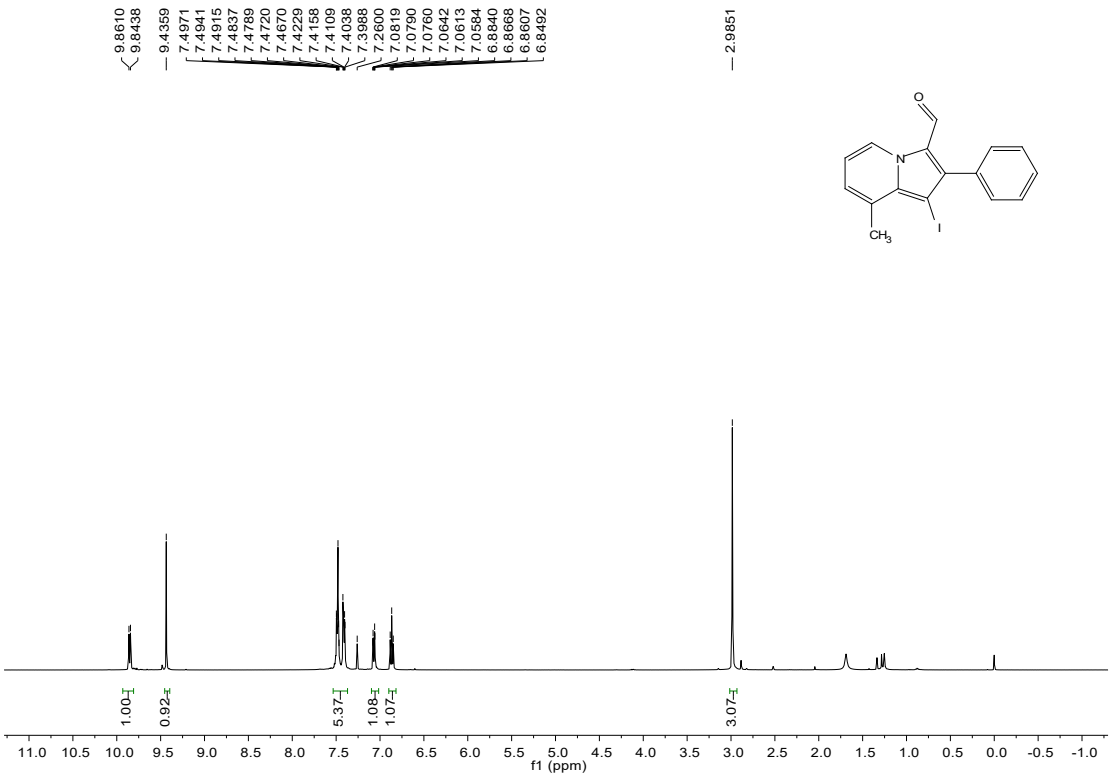
4f ^{13}C NMR (101 MHz, $CDCl_3$)



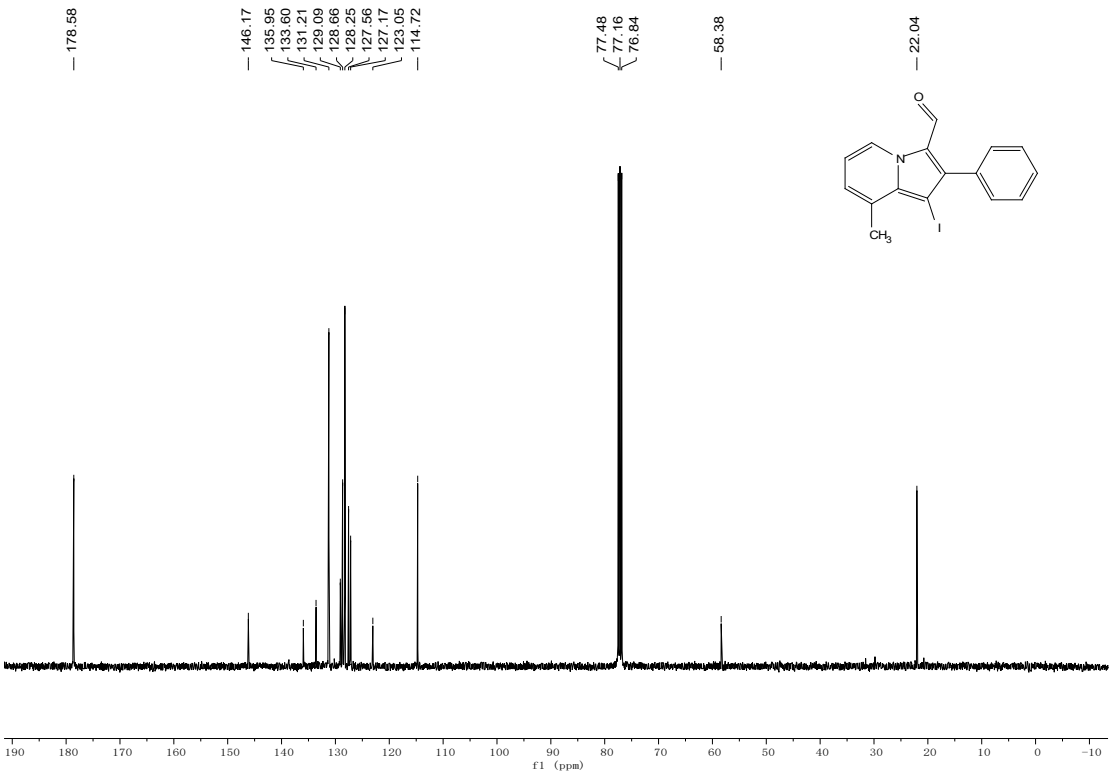
4f ^{19}F NMR (377 MHz, $CDCl_3$)



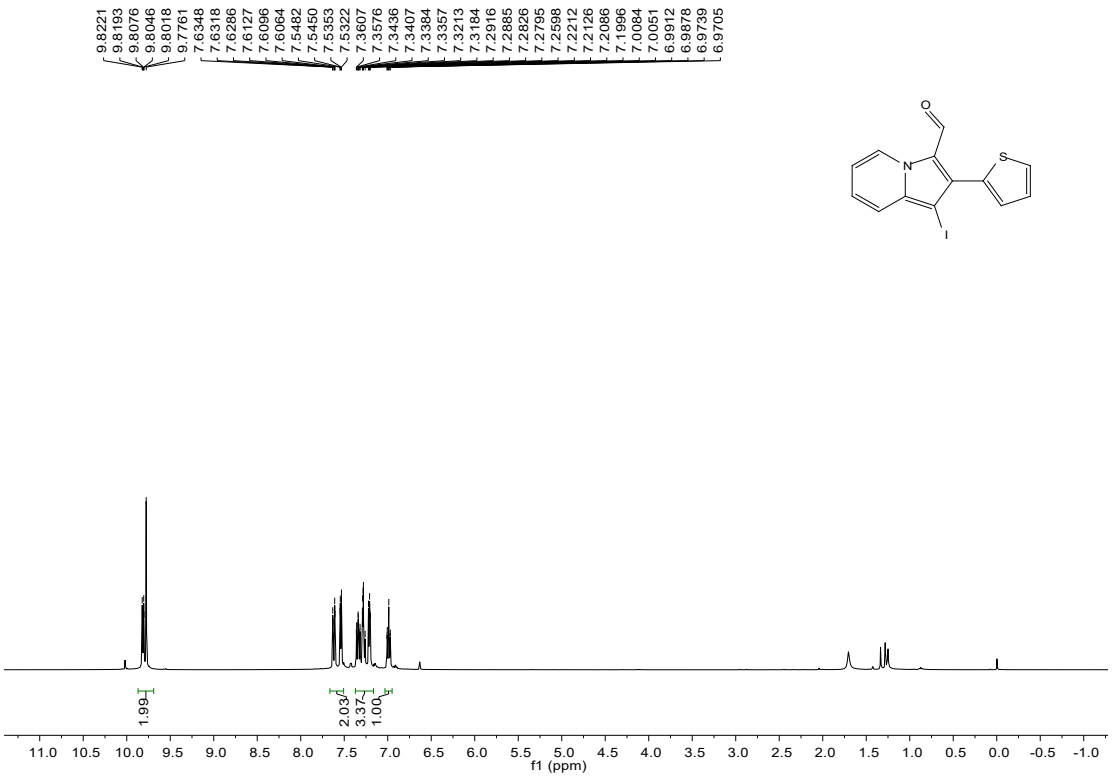
4g ^{1}H NMR (400 MHz, $CDCl_3$)



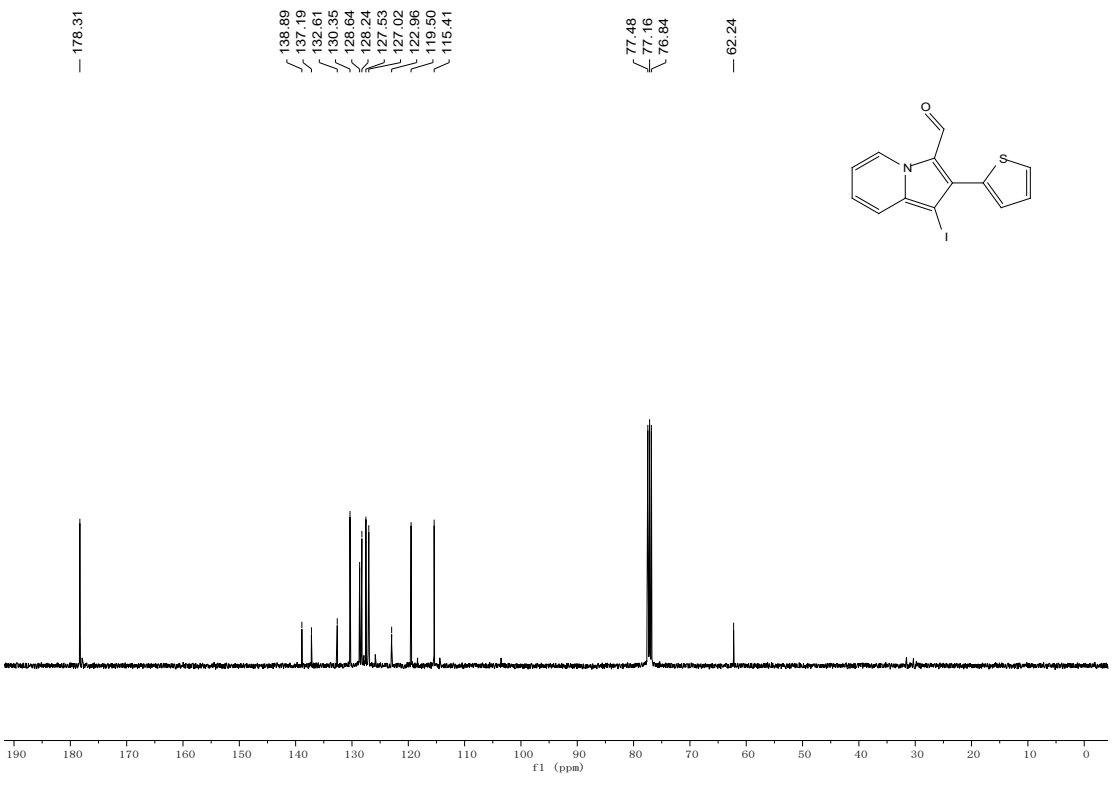
4g ^{13}C NMR (101 MHz, $CDCl_3$)



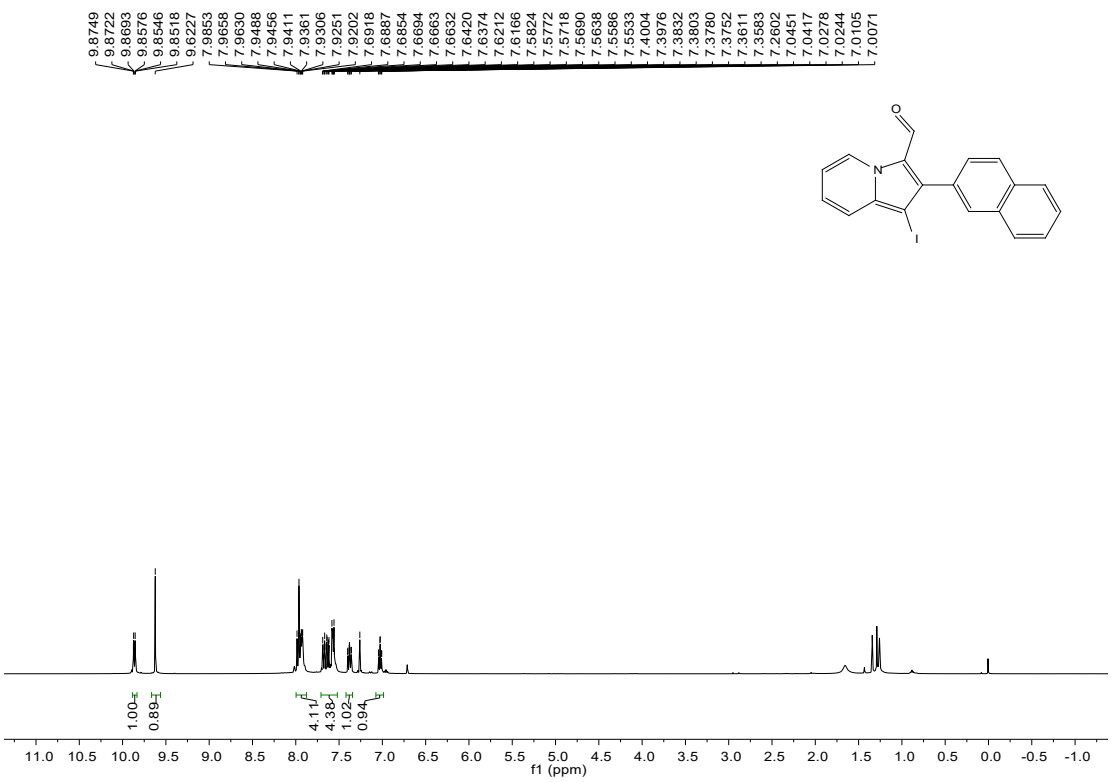
4h ^{1}H NMR (400 MHz, $CDCl_3$)



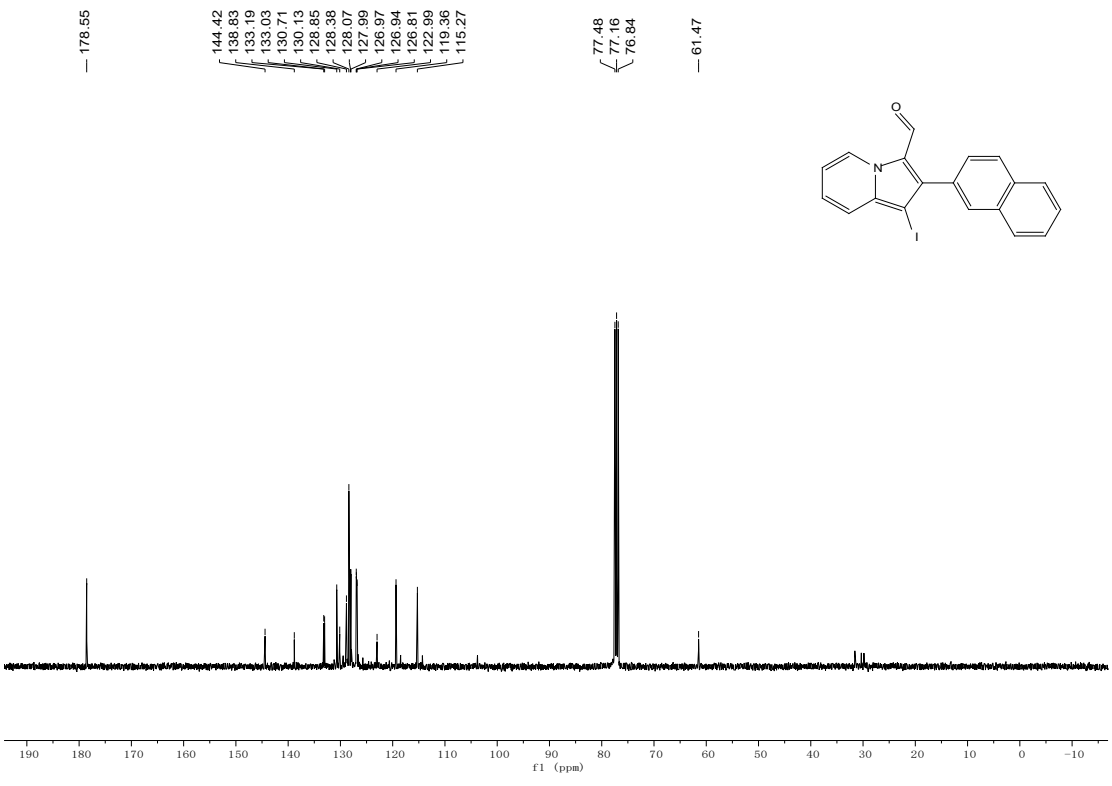
4h ^{13}C NMR (101 MHz, $CDCl_3$)



4i ^{1}H NMR (400 MHz, $CDCl_3$)



4i ^{13}C NMR (101 MHz, $CDCl_3$)



5. Reference

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