Supporting Information

Transition Metal-free Annulative Vinylene Transfer *via* the 1,3-dipolar reaction of *N*-ylides: Access to Benzo-fused Indolizines

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1. General considerations

Unless otherwise noted, commercial reagents were purchased from Adamas, Alfa, Aladdin, TCI, *J&K* or Macklin and used without further purification. All reactions were carried out using oven-dried glassware and all reactions proceeded without special care. Column chromatography was performed on 200-300 mesh silica gel (Huanghai, China).

^{1}H, ^{19}F and $^{13}C\{^{1}H\}$ NMR spectra were recorded on an Bruker Ascend 400 MHz spectrometer at ambient temperature. ^{1}H NMR spectra are referred to the TMS signal (δ = 0 ppm) and ^{13}C NMR spectra are referred to the residual solvent signal (δ = 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shifts (δ ppm), multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration.

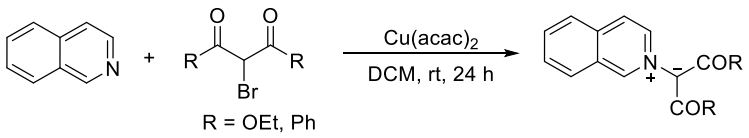
The data of HRMS was carried out on a Agilent 7250 GC/QTOF. Melting point were recorded using a SGW X-4 Melting Point Apparatus.

2. Experimental procedures and characterization data

2.1 Experimental procedures

Synthesis of compounds 1 according to the following procedure:

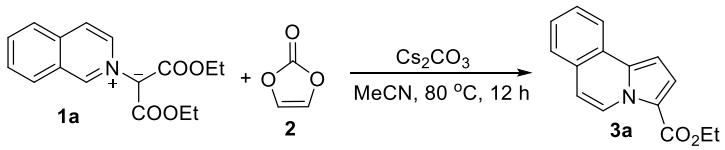
The substrates *N*-ylides **1a-1q** and **4a-4f** are known and were prepared according to the procedures in the literature.[1]



To a solution of $Cu(acac)_2$ (1 mol %) in 5 mL of CH_2Cl_2 were added the corresponding isoquinoline (1.0 mmol) and diethyl 2-bromomalonate (1.2 mmol). The reaction mixture was stirred at room temperature to 40 ℃ for 24 h. After completion of the reaction (monitored by TLC), the solution was concentrated and purified by chromatography on silica gel to give the corresponding isoquinolinium methylides **1a-1q** and **4a-4f**.

Synthesis of products 3 according to the following procedure:

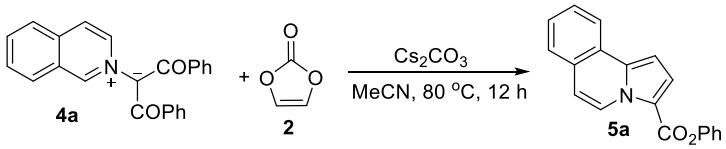
As exemplified for **3a**:



A test tube was charged with a stirring bar, *N*-ylides (**1a**, 86.1 mg, 0.3 mmol), vinylene carbonate (**2**, 38.7 mg, 0.45 mmol) and MeCN (2.0 mL) and Cs_2CO_3 (195.6 mg, 2 equiv.) were added and the mixtures were heated with a heating mantle at 80 °C for 12 h, then cooled to room temperature. The solvent was volatilized and the crude product was separated by column chromatography (PE**:** EA = 15: 1) to give a pure sample of **3a** in 78% yield (55.9 mg).

Synthesis of products 5 according to the following procedure:

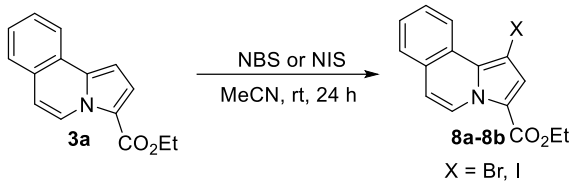
As exemplified for **5a**:



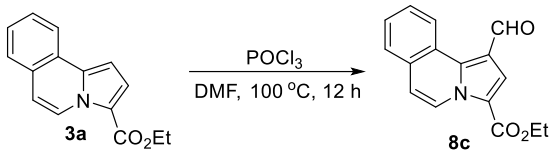
A test tube was charged with a stirring bar, **4a** (105.3 mg, 0.3 mmol), vinylene carbonate (**2**, 38.7 mg, 0.45

mmol) and MeCN (2.0 mL) and Cs_2CO_3 (195.6 mg, 2 equiv.) were added and the mixtures were heated with a heating mantle at 80 °C for 12 h, then cooled to room temperature. The solvent was volatilized and the crude product was separated by column chromatography (PE：EA = 15: 1) to give a pure sample of **5a** in 83% yield (71.5 mg).

Synthesis of products 8a-8d according to the following procedure[2]:

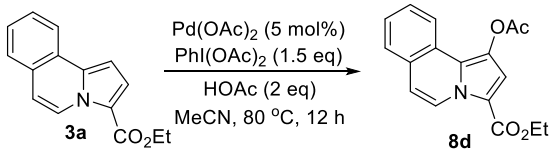


A mixture of the ethyl pyrrolo[2,1-*a*]isoquinoline-3-carboxylate **3a** (71.7 mg, 0.3 mmol), NBS or NIS (1.2 equiv.) in MeCN (2 mL) was stirred 24 h at room temperature. The resulting mixture was filtered, and the filtrate was evaporated in vacuo. The residue was purified by flash column chromatography (PE: EA = 15:1), affording the corresponding halogenated products **8a** and **8b**.



A test tube with 2.0 mL DMF was charged with a stirring bar, ethyl pyrrolo[2,1-*a*]isoquinoline-3-carboxylate **3a** (71.7 mg, 0.3 mmol), $POCl_3$ (68.9 mg, 0.3 mmol) were added. The reaction was heated with a heating mantle at 100 °C for 12 h. Then the water was added. The phases were separated and the aqueous phase was extracted with DCM (10 mL ×2) and the combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Finally, the crude product was purified by flash column chromatography on silica gel (PE: EA = 15:1), affording the corresponding product **8c**.

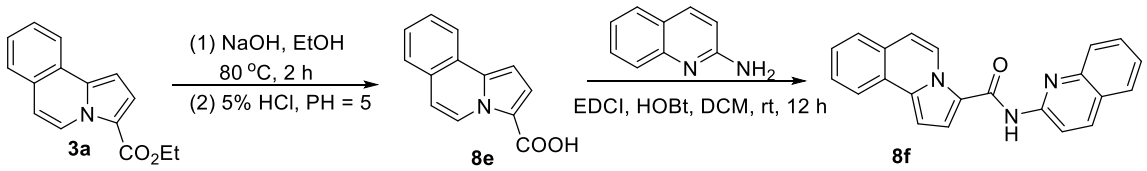
As exemplified for **8d**:



A test tube was charged with a stirring bar, **3a** (71.7 mg, 0.3 mmol), $Pd(OAc)_2$ (5 mol%), $PhI(OAc)_2$ (1.5 equiv.), HOAc (2 equiv.) and MeCN (2.0 mL) was added and the mixtures was heated with a heating mantle at 80 °C for 12 h, then cooled to room temperature. The solvent was volatilized and the crude product was

separated by column chromatography (PE：EA = 10: 1) to give a pure sample of **8d** in 65% yield (71.5 mg).

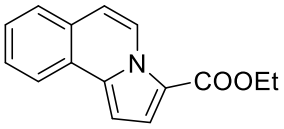
Synthesis of products 8f according to the following procedure:



Dissolve ethyl pyrrolo[2,1-*a*]isoquinoline-3-carboxylate **3a** (71.7 mg, 0.3 mmol), 1M NaOH in ethanol (2 mL). Stirring the mixture for 2 h at 80 °C. The phases were separated and the aqueous phase was acidified by 5% HCl, then the aqueous was extracted with DCM (10 mL ×2) and the combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to give **8e**. Subsequently, reactions were performed with **8e** (0.3 mmol), quinolin-2-amine (1.1 equiv.), HOBt (1.1 equiv.), EDCI (1.1 equiv.) and DCM (2.0 ml) at room temperature for 12 h, the solvent was volatilized and the crude product was separated by column chromatography (PE：EA = 8: 1) to give a pure sample of **8f**.

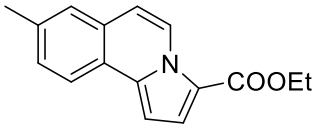
2.2 Characterization data

Ethyl pyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3a)



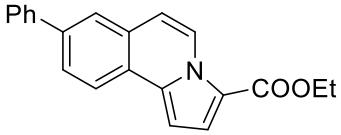
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3a**. Yellow oil (55.9 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.50 (td, *J* = 13.5, 12.5, 7.7 Hz, 3H), 7.00 (d, *J* = 4.8 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 135.5, 128.0, 127.7, 127.4, 127.0, 125.3, 125.1, 123.2, 120.7, 116.7, 112.7, 101.1, 60.1, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{13}NO_2$ [M] $^{+}$ 239.0946; Found 239.0939.

Ethyl 8-methylpyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3b)



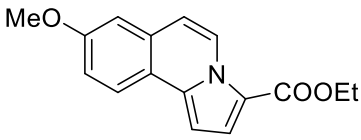
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3b**. White solid (60.7 mg, 80%), mp 125.1-125.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 7.5 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 4.3 Hz, 1H), 7.42 (s, 1H), 7.33 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.94 – 6.88 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 137.4, 135.7, 129.3, 128.1, 126.7, 125.0, 123.1, 123.0, 120.7, 116.3, 112.5, 100.5, 60.0, 21.7, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{16}H_{15}NO_2$ [M] $^{+}$ 253.1103; Found 253.1095.

Ethyl 8-phenylpyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3c)



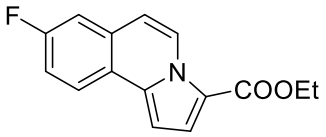
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3c**. White solid (77.5 mg, 82%), mp 168.1-168.8 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 7.5 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 1.7 Hz, 1H), 7.75 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 2H), 7.51 – 7.44 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.00 (dd, *J* = 14.2, 6.0 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 140.5, 140.1, 135.3, 129.0, 128.3, 127.7, 127.3, 126.9, 125.3, 125.0, 124.3, 123.7, 120.8, 116.8, 112.8, 101.2, 60.1, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{21}H_{17}NO_2$ [M] $^{+}$ 315.1259; Found 315.1266.

Ethyl 8-methoxypyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3d)



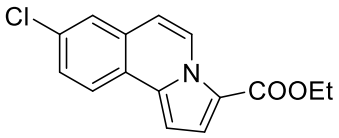
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3d**. Yellow solid (58.1 mg, 72%), mp 183.6-184.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 4.3 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.04 (d, *J* = 2.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 4.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 159.1, 135.8, 129.5, 125.6, 124.9, 121.0, 119.4, 117.6, 115.9, 112.4, 107.8, 99.8, 60.0, 55.6, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{16}H_{15}NO_3$ [M] $^+$ 269.1052; Found 269.1043.

Ethyl 8-fluoropyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3e)



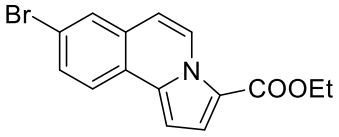
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3e**. Yellow solid (56.3 mg, 73%), mp 173.1-173.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 7.6 Hz, 1H), 8.14 – 8.07 (m, 1H), 7.66 (d, *J* = 6.9 Hz, 1H), 7.57 – 7.44 (m, 4H), 7.43 – 7.32 (m, 3H), 7.01 (d, *J* = 8.7 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 136.9 (d, *J* = 15.6 Hz), 134.2, 130.1, 128.2, 127.7, 126.5 (d, *J* = 330.8 Hz), 127.0 (d, *J* = 25.5 Hz), 125.4, 123.2, 113.2, 112.6, 103.9, 60.0, 14.0. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{12}FNO_2$ [M] $^+$ 257.0853; Found 257.0853.

Ethyl 8-chloropyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3f)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3f**. White solid (58.1 mg, 71%), mp 192.3-193.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.55 – 7.40 (m, 2H), 6.94 (d, *J* = 4.4 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 134.7, 133.1, 129.0, 128.1, 126.2, 126.1, 124.7, 123.6, 120.9, 117.0, 111.6, 101.3, 60.2, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{12}ClNO_2$ [M] $^+$ 273.0557; Found 273.0549.

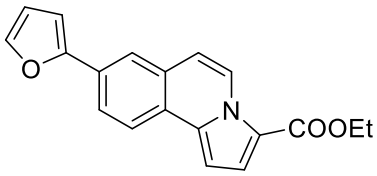
Ethyl 8-bromopyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3g)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3g**. White solid (68.5 mg, 72%), mp 223.1-223.9 °C. ^{1}H NMR (400

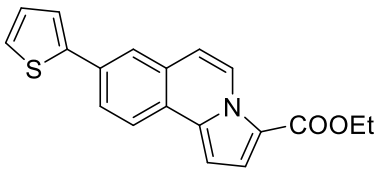
MHz, $CDCl_3$) δ 9.19 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.76 (s, 1H), 7.57 (dt, *J* = 8.6, 1.6 Hz, 1H), 7.47 (dd, *J* = 4.4, 1.1 Hz, 1H), 6.94 (d, *J* = 4.4 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 134.7, 130.7, 129.3, 129.2, 126.0, 124.8, 123.9, 121.1, 120.8, 117.0, 111.5, 101.4, 60.2, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{12}BrNO_2$ $[M]^+$ 317.0051; Found 317.0045.

Ethyl 8-(furan-2-yl)pyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3h)



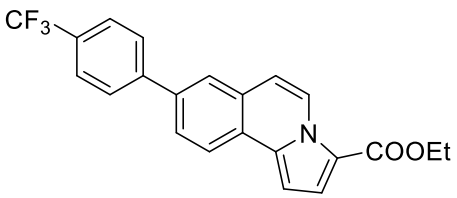
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3h**. Yellow solid (59.5 mg, 65%), mp 187.5-188.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 6.7 Hz, 1H), 8.17 – 8.05 (m, 2H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.29 (s, 1H), 6.99 (t, *J* = 6.9 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 151.7, 138.5, 131.0, 130.6, 129.6, 128.7, 128.4, 127.9, 124.5, 116.4, 113.7, 21.5. HRMS (GC/QTOF) m/z: Calcd for $C_{19}H_{15}NO_3$ $[M]^+$ 305.1052; Found 305.1048.

Ethyl 8-(thiophen-2-yl)pyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3i)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3i**. White solid (60.7 mg, 63%), mp 169.7-170.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.84 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 4.3 Hz, 1H), 7.41 (d, *J* = 3.6 Hz, 1H), 7.32 (d, *J* = 5.1 Hz, 1H), 7.11 (t, *J* = 4.3 Hz, 1H), 6.97 (dd, *J* = 9.2, 6.0 Hz, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 143.9, 135.2, 133.4, 128.4, 128.3, 125.6, 125.5, 125.4, 124.3, 123.8, 123.7, 123.4, 120.8, 116.8, 112.6, 101.3, 60.1, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{19}H_{15}NO_2S$ $[M]^+$ 321.0823; Found 321.0833.

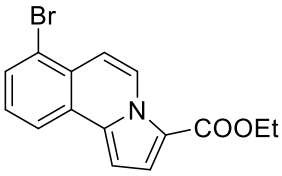
Ethyl 8-(4-(trifluoromethyl)phenyl)pyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3j)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3j**. Black solid (68.9mg, 60%), mp 224.8-225.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J*

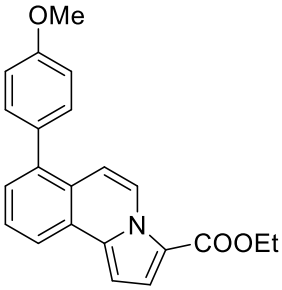
= 8.3 Hz, 1H), 7.85 (s, 1H), 7.74 (t, *J* = 9.5 Hz, 5H), 7.51 (d, *J* = 4.2 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 144.1, 138.5, 135.0, 129.9, 128.3, 127.6, 126.7, 126.0 (q, *J* = 7.1, 3.3 Hz), 125.7, 125.4, 125.0, 124.0, 120.9, 117.1, 112.6, 101.6, 60.2, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{22}H_{16}F_3NO_2$ $[M]^+$ 383.1133; Found 383.1134.

Ethyl 7-bromopyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3k)



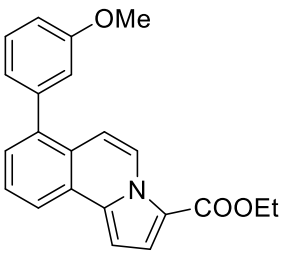
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3k**. Yellow solid (73.2 mg, 77%), mp 156.4-157.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 4.3 Hz, 1H), 7.34 – 7.28 (m, 2H), 6.95 (d, *J* = 4.4 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 134.3, 131.0, 128.1, 127.0, 126.5, 126.0, 122.5, 122.0, 120.9, 116.9, 111.1, 101.7, 60.1, 14.6. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{12}BrNO_2$ $[M]^+$ 317.0051; Found 317.0046.

Ethyl 7-(4-methoxyphenyl)pyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3l)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3l**. Black solid (54.9 mg, 53%), mp 191.4-192.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 4.4 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.06 – 7.02 (m, 3H), 4.38 (q, *J* = 7.0 Hz, 2H), 3.90 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 161.6, 159.3, 139.7, 135.7, 132.5, 131.1, 128.6, 127.3, 125.9, 125.7, 124.9, 122.3, 120.8, 116.6, 114.0, 110.7, 101.4, 60.1, 55.5, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{22}H_{19}NO_3$ $[M]^+$ 345.1365; Found 345.1365.

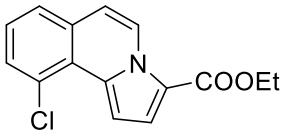
Ethyl 7-(3-methoxyphenyl)pyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3m)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3m**. Brown solid (61.1 mg, 59%), mp 176.9.4-177.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.18 (d, *J* = 4.5 Hz, 1H), 7.07 – 7.02 (m, 2H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.92 (s, 1H), 5.58 (d, *J* = 4.5 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H),

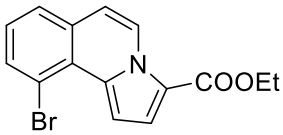
3.82 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 160.0, 144.0, 139.3, 134.3, 130.0, 129.9, 129.0, 126.7, 126.4, 125.1, 123.5, 121.7, 120.0, 115.9, 114.5, 113.8, 113.1, 106.4, 60.0, 55.5, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{22}H_{19}NO_3$ [M] $^+$ 345.1365; Found 345.1366.

Ethyl 10-chloropyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3n)



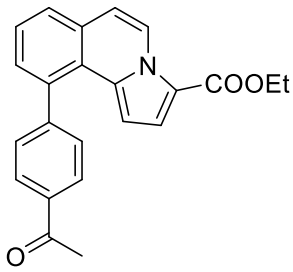
Flash column chromatography on silica gel (eluent: PE/EA = 15/1 v/v) to afford **3n**. White solid (61.4 mg, 75%), mp 152.3-152.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ9.32 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 4.5 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.36 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 132.5, 130.6, 130.5, 130.0, 127.0, 125.9, 125.6, 123.3, 120.4, 116.7, 112.6, 107.8, 60.3, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{12}ClNO_2$ [M] $^+$ 273.0557; Found 273.0555.

Ethyl 10-bromopyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3o)



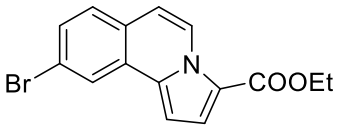
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3o**. White solid (76.1 mg, 80%), mp 164.2-165.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (d, *J* = 7.5 Hz, 1H), 8.09 (d, *J* = 4.5 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 4.5 Hz, 1H), 7.29 – 7.22 (m, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 133.9, 133.0, 130.9, 127.2, 126.6, 125.4, 124.6, 120.0, 119.1, 116.8, 112.7, 107.5, 60.3, 14.6. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{12}BrNO_2$ $[M]^+$ 317.0051; Found 317.0048.

Ethyl 10-(4-acetylphenyl)pyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3p)



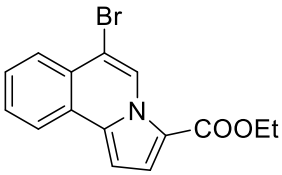
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3p.** Brown solid (79.3 mg, 74%), mp 121.3-122.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, *J* = 7.5 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 3H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 4.5 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 5.51 (d, *J* = 4.5 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.72 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 161.5, 147.8, 138.2, 136.6, 133.9, 129.7, 129.7, 129.1, 128.9, 127.1, 126.5, 125.3, 123.1, 119.9, 116.2, 113.0, 106.3, 60.1, 26.9, 14.6. HRMS (GC/QTOF) m/z: Calcd for $C_{23}H_{19}NO_3$ [M] $^+$ 357.1365; Found 357.1365.

Ethyl 9-bromopyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3q)



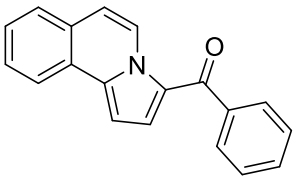
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3q**. Yellow solid (72.3 mg, 76%), mp 213.6-214.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.01 (dd, *J* = 6.2, 3.2 Hz, 1H), 7.95 (dt, *J* = 7.5, 3.4 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.41 (d, *J* = 4.4 Hz, 1H), 6.92 (d, *J* = 4.4 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 133.9, 130.4, 128.5, 126.6, 126.4, 125.7, 125.3, 121.4, 120.7, 117.2, 111.9, 101.6, 60.2, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{12}BrNO_2$ $[M]^+$ 317.0051; Found 317.0049.

Ethyl 6-bromopyrrolo[2,1-*a*]isoquinoline-3-carboxylate (3r)



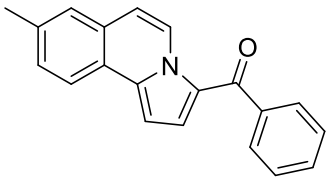
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **3r**. White solid (77.0 mg, 81%), mp 157.7-158.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 7.6 Hz, 1H), 8.18 (s, 1H), 7.56 – 7.43 (m, 3H), 6.91 (dd, *J* = 13.6, 6.0 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 134.4, 128.4, 127.9, 126.6, 126.5, 125.9, 124.9, 123.2, 120.4, 116.5, 108.9, 101.4, 60.2, 14.6. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{12}BrNO_2$ $[M]^+$ 317.0051; Found 317.0050.

Phenyl(pyrrolo[2,1-*a*]isoquinolin-3-yl)methanone (5a)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **5a**. Yellow solid (67.5 mg, 83%), mp 198.3-199.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 7.4 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.50 (dq, *J* = 15.4, 7.4 Hz, 5H), 7.27 (d, *J* = 4.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 140.6, 137.0, 131.2, 131.2, 129.2, 129.0, 128.2, 128.1, 127.7, 126.9, 126.0, 125.9, 124.7, 123.7, 113.4, 102.0. HRMS (GC/QTOF) m/z: Calcd for $C_{19}H_{13}NO$ $[M]^+$ 271.0997; Found 271.0997.

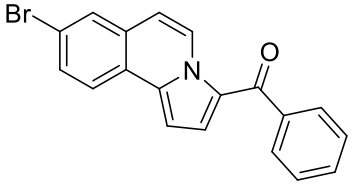
(8-Methylpyrrolo[2,1-*a*]isoquinolin-3-yl)(phenyl)methanone (5b)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **5b**. Black solid (59.0 mg, 69%), mp 209.4-211.1. ^{1}H NMR (400 MHz,

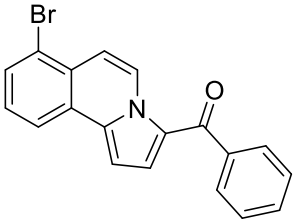
$CDCl_3$) δ 9.60 (d, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.52 (dq, *J* = 14.7, 7.4, 6.9 Hz, 4H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 4.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 4.5 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 140.8, 138.4, 137.4, 131.2, 129.5, 129.3, 129.2, 128.3, 126.8, 126.23, 126.0, 124.5, 123.7, 122.5, 113.4, 101.7, 21.9. HRMS (GC/QTOF) m/z: Calcd for $C_{20}H_{15}NO$ $[M]^+$ 285.1154; Found 285.1145.

(8-Bromopyrrolo[2,1-*a*]isoquinolin-3-yl)(phenyl)methanone (5c)



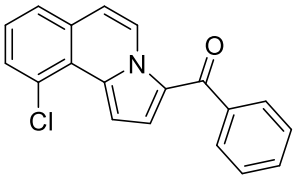
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **5c**. Yellow solid (55.5 mg, 53%), mp 248.7-249.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (dd, *J* = 7.7, 2.4 Hz, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.92 – 7.79 (m, 3H), 7.65 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.57 (td, *J* = 7.0, 6.3, 1.7 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 4.2 Hz, 1H), 7.09 – 6.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 140.4, 136.3, 131.4, 131.0, 130.4, 129.4, 129.2, 128.4, 127.0, 126.2, 125.3, 125.0, 123.5, 122.1, 112.3, 102.3. HRMS (GC/QTOF) m/z: Calcd for $C_{19}H_{12}BrNO$ $[M]^+$ 349.0102; Found 349.0104.

(7-Bromopyrrolo[2,1-*a*]isoquinolin-3-yl)(phenyl)methanone (5d)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **5d**. Yellow solid (58.6 mg, 56%), mp 262.7-263.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.53 (m, 1H), 7.51 (dt, *J* = 7.0, 3.3 Hz, 3H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 4.5 Hz, 1H), 7.07 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 140.4, 136.1, 131.9, 131.5, 130.0, 128.4, 128.4, 128.2, 127.2, 126.3, 126.2, 124.9, 123.2, 122.2, 112.1, 102.7. HRMS (GC/QTOF) m/z: Calcd for $C_{19}H_{12}BrNO$ $[M]^+$ 349.0102; Found 349.0104.

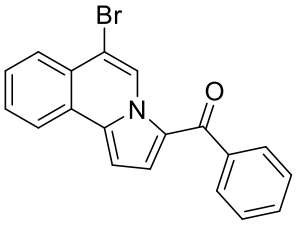
(10-Chloropyrrolo[2,1-*a*]isoquinolin-3-yl)(phenyl)methanone (5e)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **5e**. Yellow solid (52.2 mg, 57%), mp 212.5-213.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 4.7 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.63 (dd, *J* = 7.9, 4.0 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 4.7 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

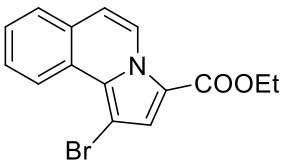
186.0, 140.5, 134.1, 131.7, 131.5, 131.0, 130.1, 129.4, 128.4, 127.7, 126.4, 126.0, 125.7, 124.4, 123.0, 113.4, 108.4. HRMS (GC/QTOF) m/z: Calcd for $C_{19}H_{12}ClNO$ $[M]^+$ 305.0607; Found 305.0604.

(6-Bromopyrrolo[2,1-*a*]isoquinolin-3-yl)(phenyl)methanone (5f)



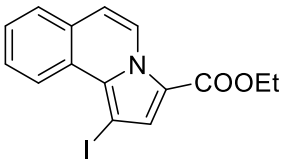
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **5f**. Yellow solid (63.9 mg, 61%), mp 195.2-195.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.22 – 8.14 (m, 1H), 8.10 (d, *J* = 6.8 Hz, 1H), 7.84 (d, *J* = 6.6 Hz, 2H), 7.70 – 7.59 (m, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 4.5 Hz, 1H), 7.06 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.5, 140.3, 136.1, 131.5, 129.2, 128.8, 128.8, 128.4, 127.9, 127.0, 126.9, 125.8, 124.7, 124.6, 123.9, 109.8, 102.5. HRMS (GC/QTOF) m/z: Calcd for $C_{19}H_{12}BrNO$ $[M]^+$ 349.0102; Found 349.0097.

Ethyl 1-bromopyrrolo[2,1-a]isoquinoline-3-carboxylate (8a)



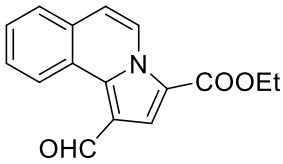
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **8a**. Yellow solid (63.7 mg, 67%), mp 168.2-169.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (dd, *J* = 15.4, 7.9 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.51 (m, 1H), 7.55 – 7.45 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 129.6, 128.5, 127.7, 127.4, 126.9, 125.2, 124.4, 123.7, 123.4, 115.8, 113.5, 90.4, 60.5, 14.6. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{12}BrNO_2$ $[M]^+$ 317.0051; Found 317.0046.

Ethyl 1-iodopyrrolo[2,1-*a*]isoquinoline-3-carboxylate (8b)



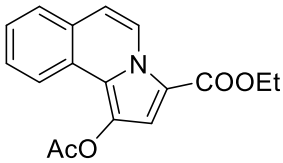
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **8c**. Yellow solid (77.5 mg, 71%), mp 159.8-160.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, *J* = 8.2 Hz, 1H), 9.16 (d, *J* = 6.7 Hz, 1H), 7.63 – 7.48 (m, 3H), 7.44 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 4.34 (q, *J* = 7.0 Hz, 2H), 1.39 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 131.1, 129.9, 128.5, 127.7, 126.9, 126.9, 125.2, 124.3, 122.9, 117.8, 113.5, 60.4, 52.7, 14.6. HRMS (GC/QTOF) m/z: Calcd for $C_{15}H_{12}INO_2$ $[M]^+$ 364.9913; Found 364.9913.

Ethyl 1-formylpyrrolo[2,1-*a*]isoquinoline-3-carboxylate (8c)



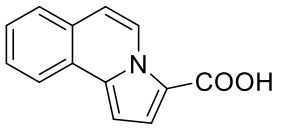
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **8c**. Yellow solid (56.1 mg, 70%), mp 155.1-156.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.50 (m, *J* = 7.7 Hz, 3H), 7.00 (d, *J* = 4.6 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.43 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 135.5, 127.9, 127.7, 127.4, 126.9, 126.9, 125.3, 125.0, 123.2, 120.6, 116.7, 112.7, 101.1, 60.1, 14.7. HRMS (GC/QTOF) m/z: Calcd for $C_{16}H_{13}NO_3$ $[M]^+$ 267.0895; Found 267.0900.

Ethyl 1-acetoxypyrrolo[2,1-*a*]isoquinoline-3-carboxylate (8d)



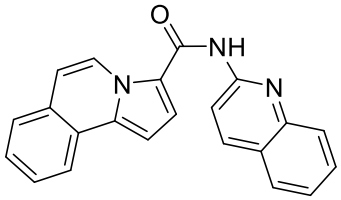
Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **8d**. Yellow oil (57.9 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, *J* = 7.6 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.49 (m, 1H), 7.48 (d, *J* = 10.2 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.48 (s, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 161.4, 130.9, 128.1, 127.8, 127.3, 126.8, 124.5, 124.2, 123.4, 123.4, 113.0, 112.7, 112.5, 60.3, 21.5, 14.6. HRMS (GC/QTOF) m/z: Calcd for $C_{17}H_{15}NO_4$ $[M]^+$ 297.1001; Found 297.0997.

Pyrrolo[2,1-*a*]isoquinoline-3-carboxylic acid (8e)



Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **8e**. White solid (56.3 mg, 89%), mp 190.4-191.3. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.62 (s, 1H), 9.20 (dd, *J* = 7.6, 3.5 Hz, 1H), 8.33 (dd, *J* = 8.0, 3.4 Hz, 1H), 7.82 (d, *J* = 4.5 Hz, 1H), 7.67 – 7.54 (m, 2H), 7.46 (d, *J* = 4.0 Hz, 1H), 7.36 – 7.18 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ 162.7, 134.8, 128.4, 127.9, 127.6, 127.4, 125.1, 124.9, 123.7, 120.8, 117.2, 112.9, 101.9. HRMS (GC/QTOF) m/z: Calcd for $C_{13}H_9NO_2$ $[M]^+$ 211.0633; Found 211.0629.

***N*-(quinolin-2-yl)pyrrolo[2,1-*a*]isoquinoline-3-carboxamide (8f)**

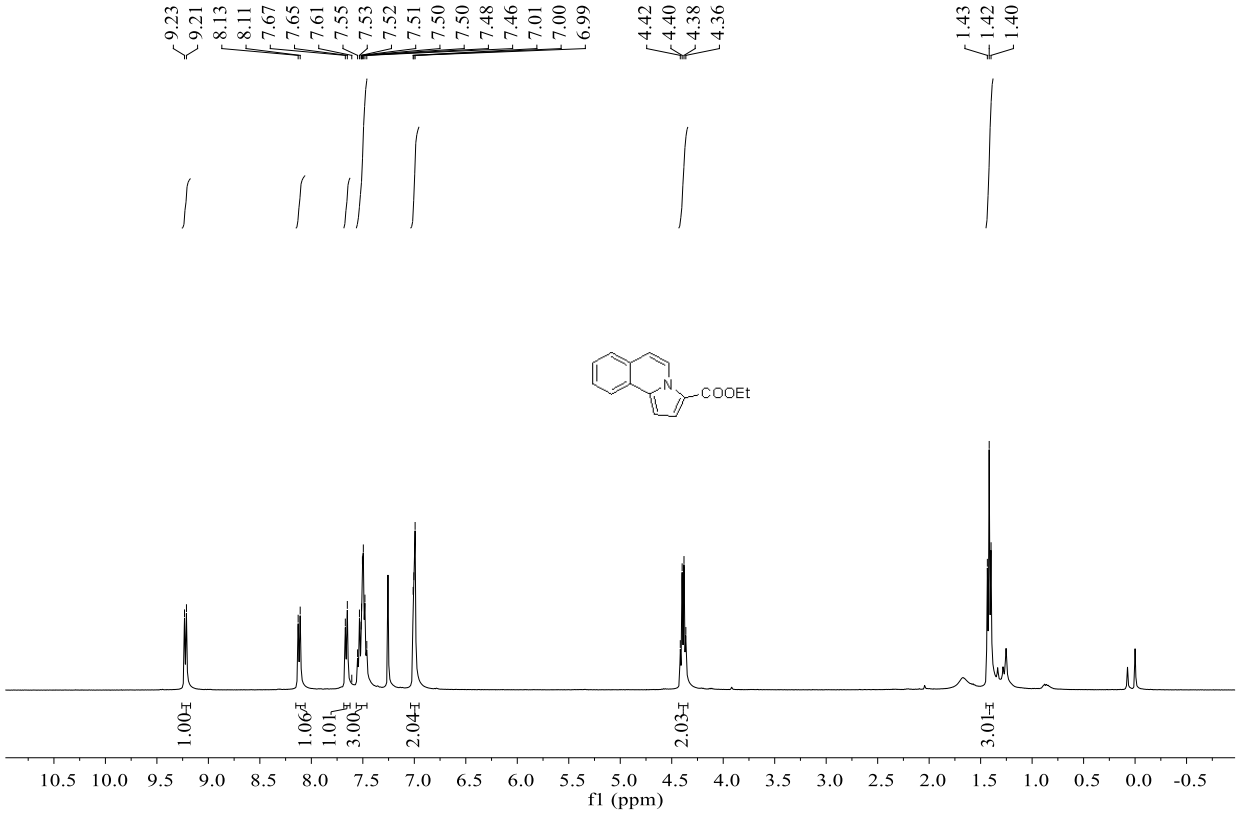


Flash column chromatography on silica gel (eluent: PE/EA = 15/1, v/v) to afford **8f**. Black solid (45.5 mg, 45%), mp 227.5-228.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, *J* = 7.6 Hz, 1H), 8.60 (d, *J* = 9.0 Hz, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.62 – 7.42 (m, 5H), 7.06 (dd, *J* = 11.6, 6.0 Hz, 2H). ^{13}C NMR (100

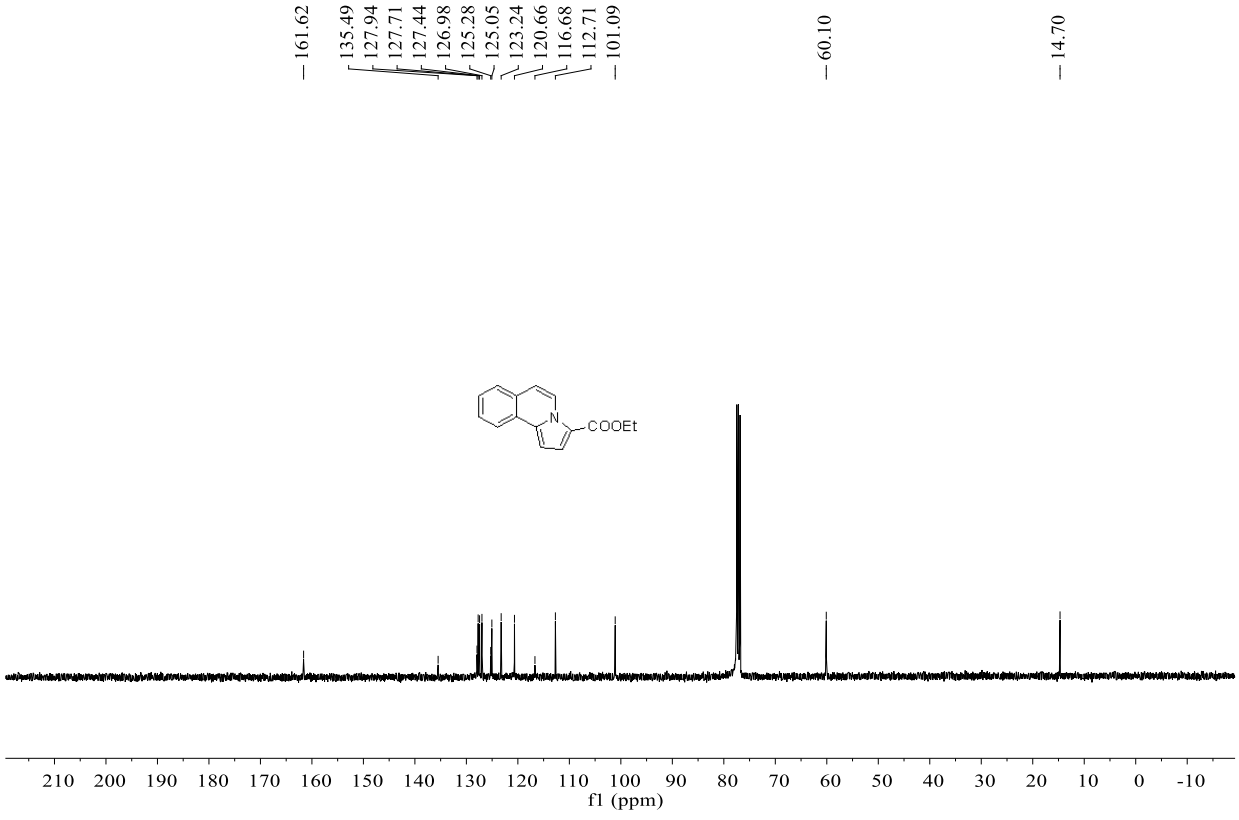
MHz, $CDCl_3$) δ 169.1, 151.6, 139.3, 136.0, 130.6, 128.2, 128.1, 127.8, 127.7, 126.9, 126.4, 126.0, 125.4, 125.3, 125.2, 124.1, 123.3, 118.5, 117.7, 114.7, 113.1, 101.5. HRMS (GC/QTOF) m/z: Calcd for $C_{22}H_{15}N_3O$ $[M]^+$ 337.1215; Found 337.1213.

3. NMR spectra for new compounds

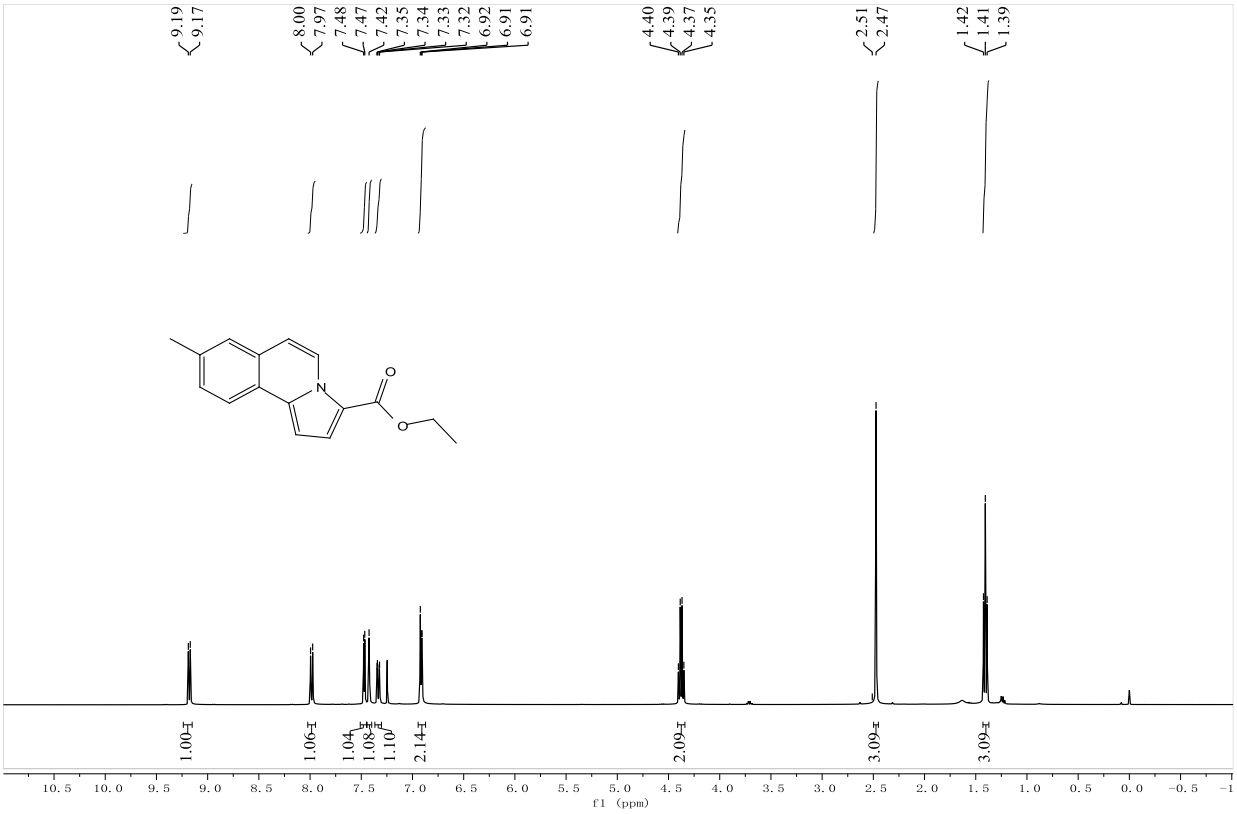
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3a**



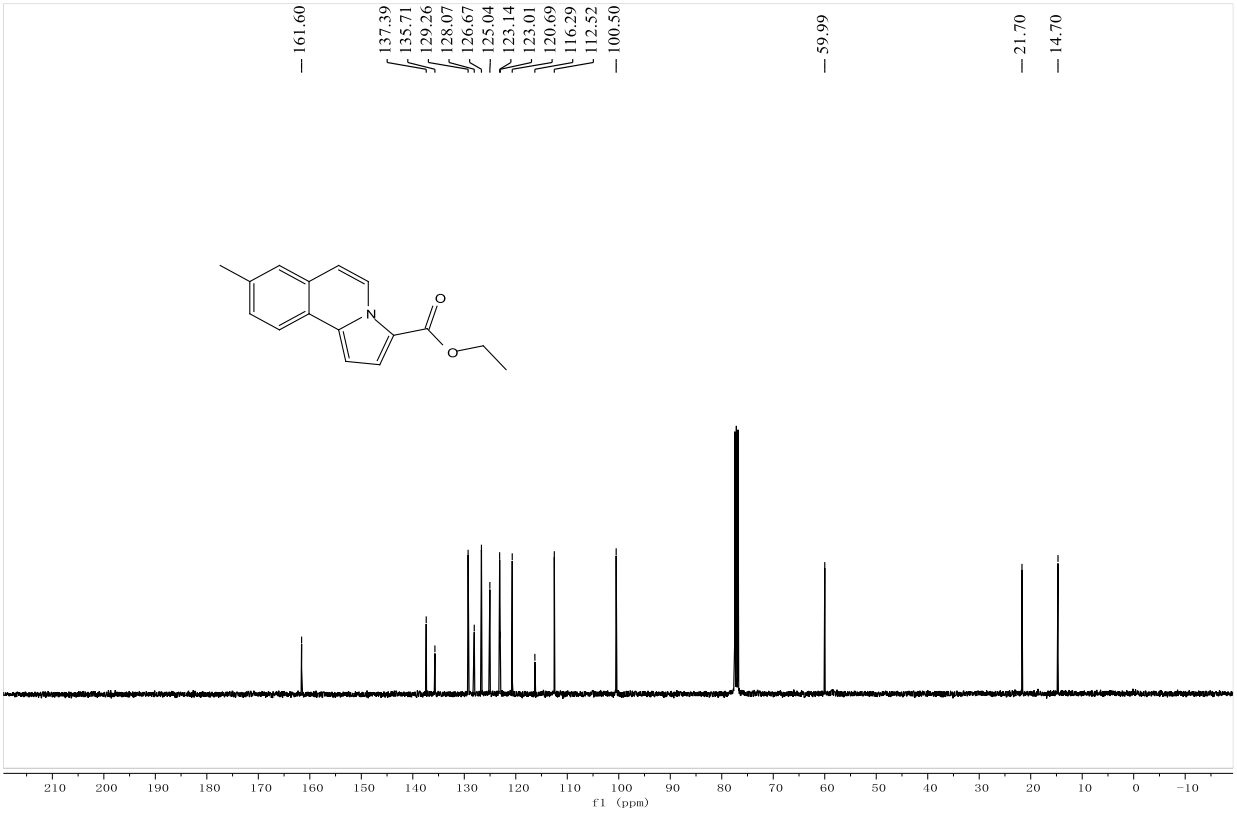
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3a**



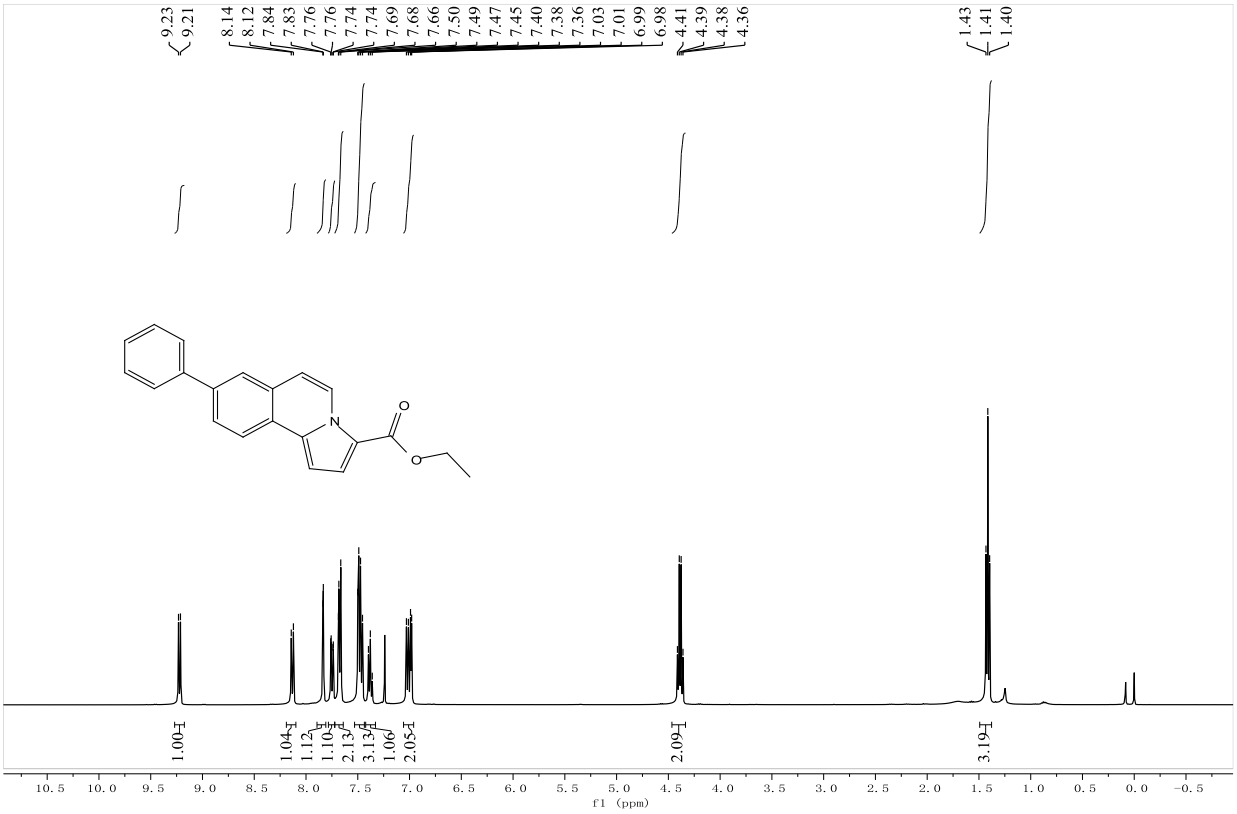
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**



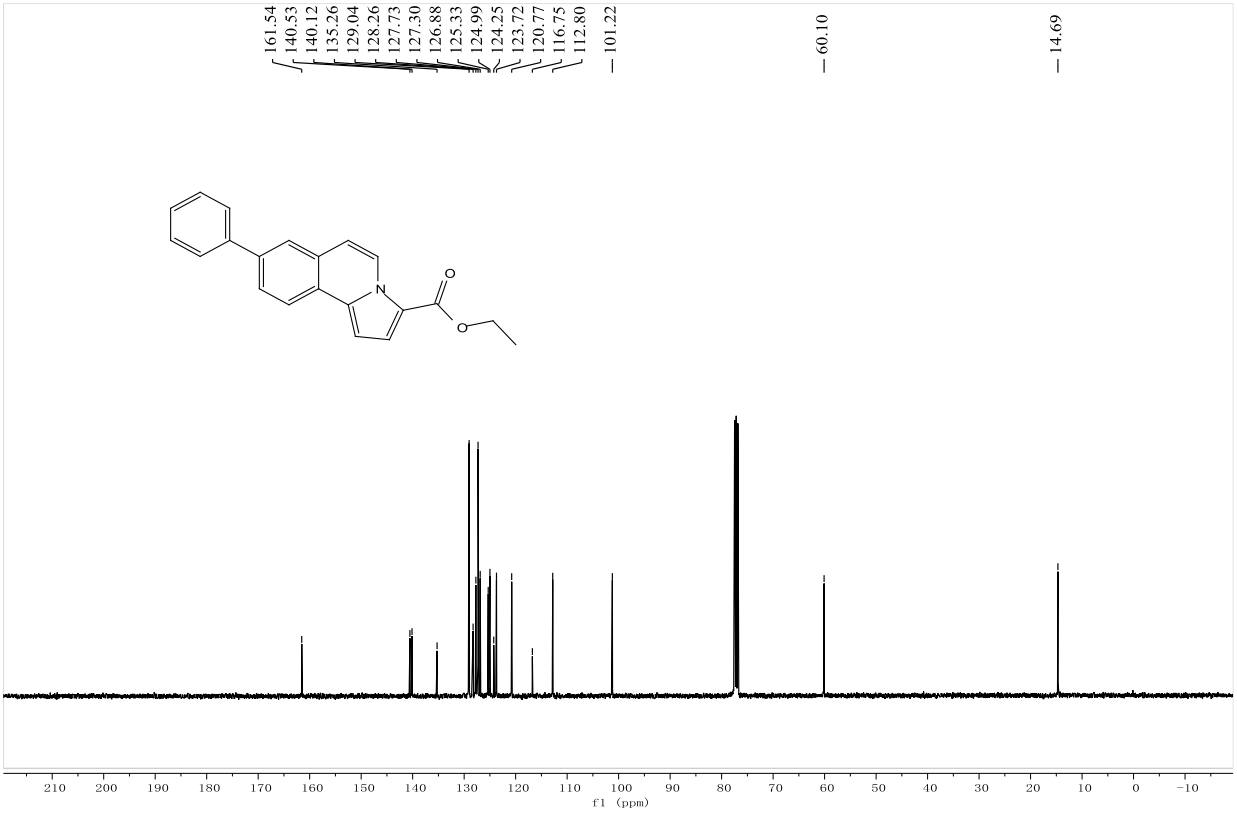
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3b**



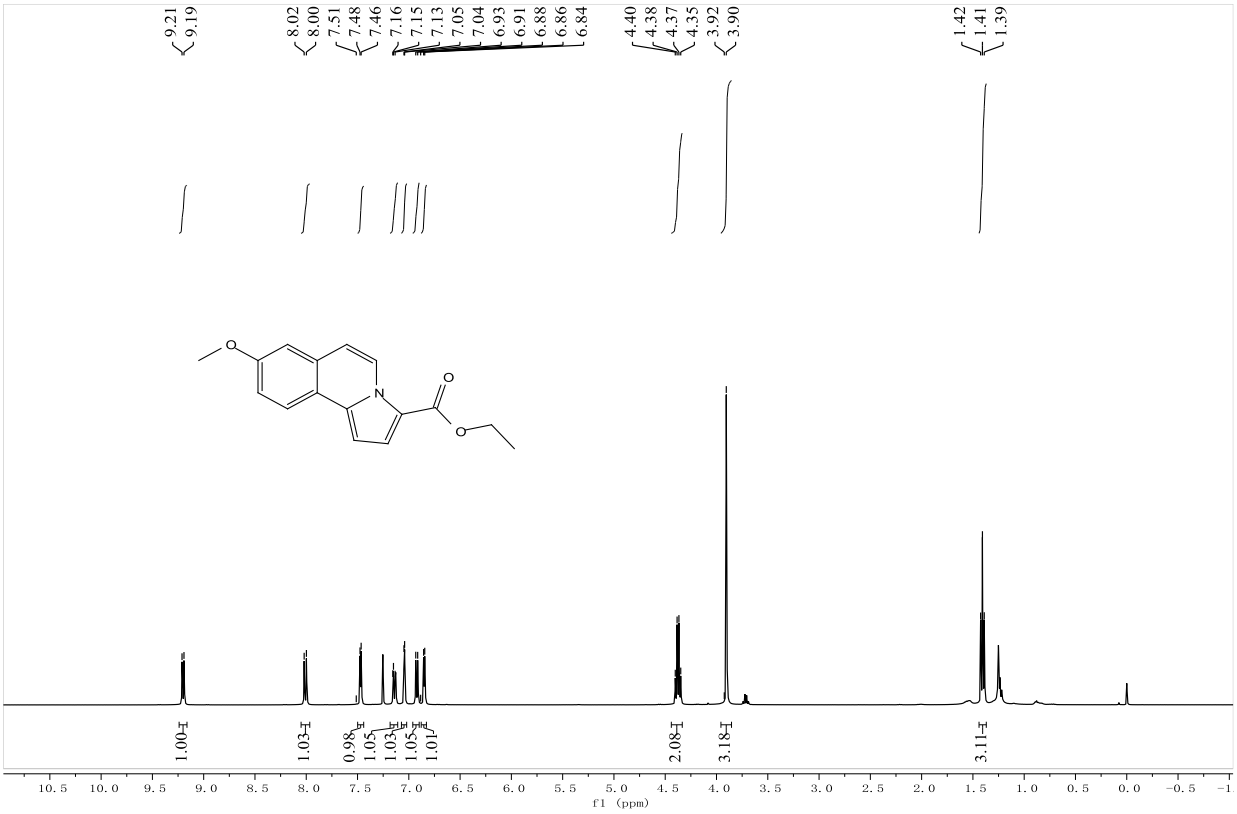
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3c**



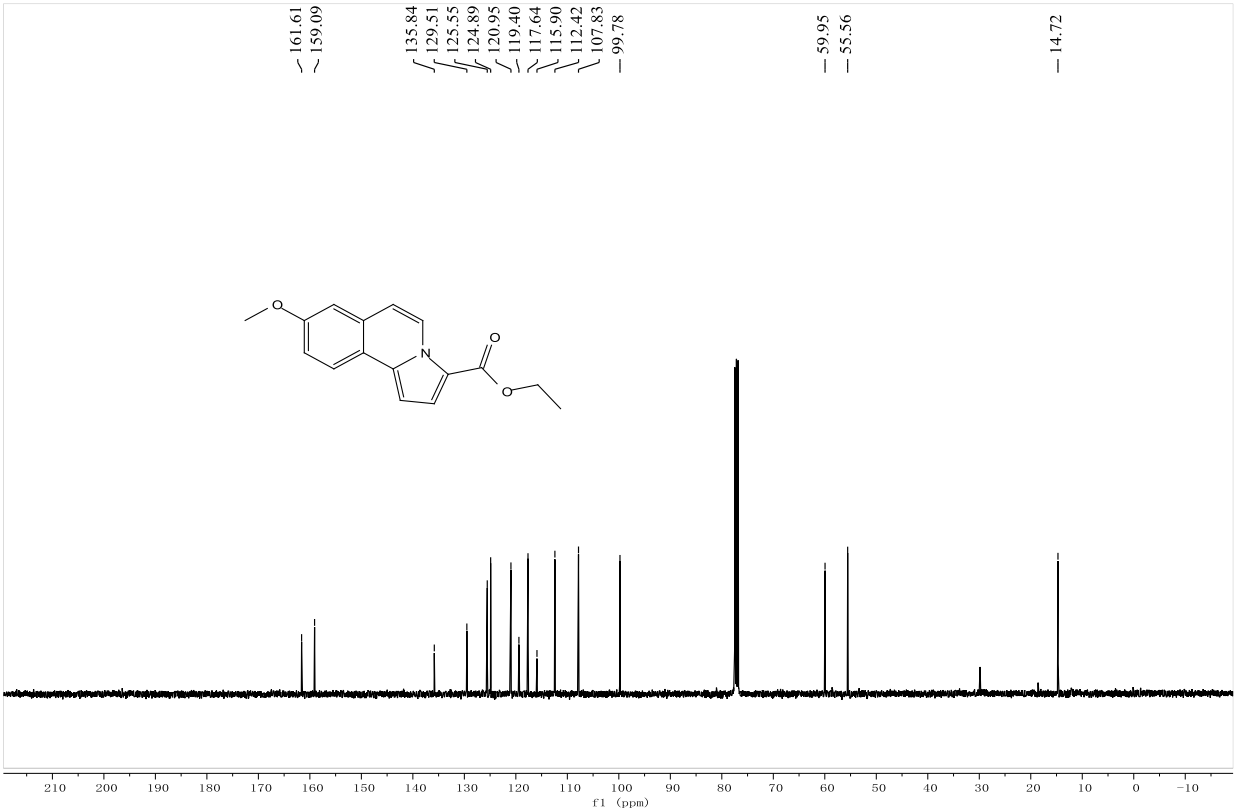
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3c**



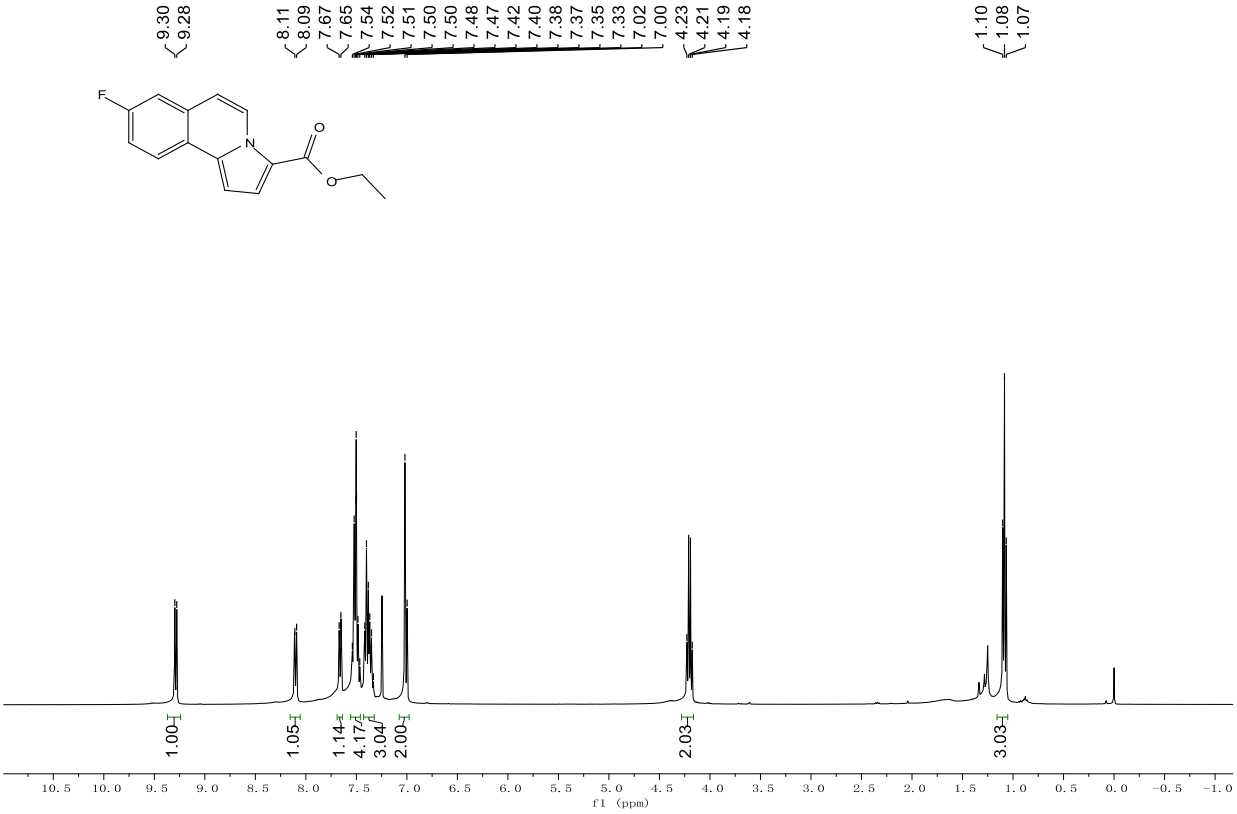
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**



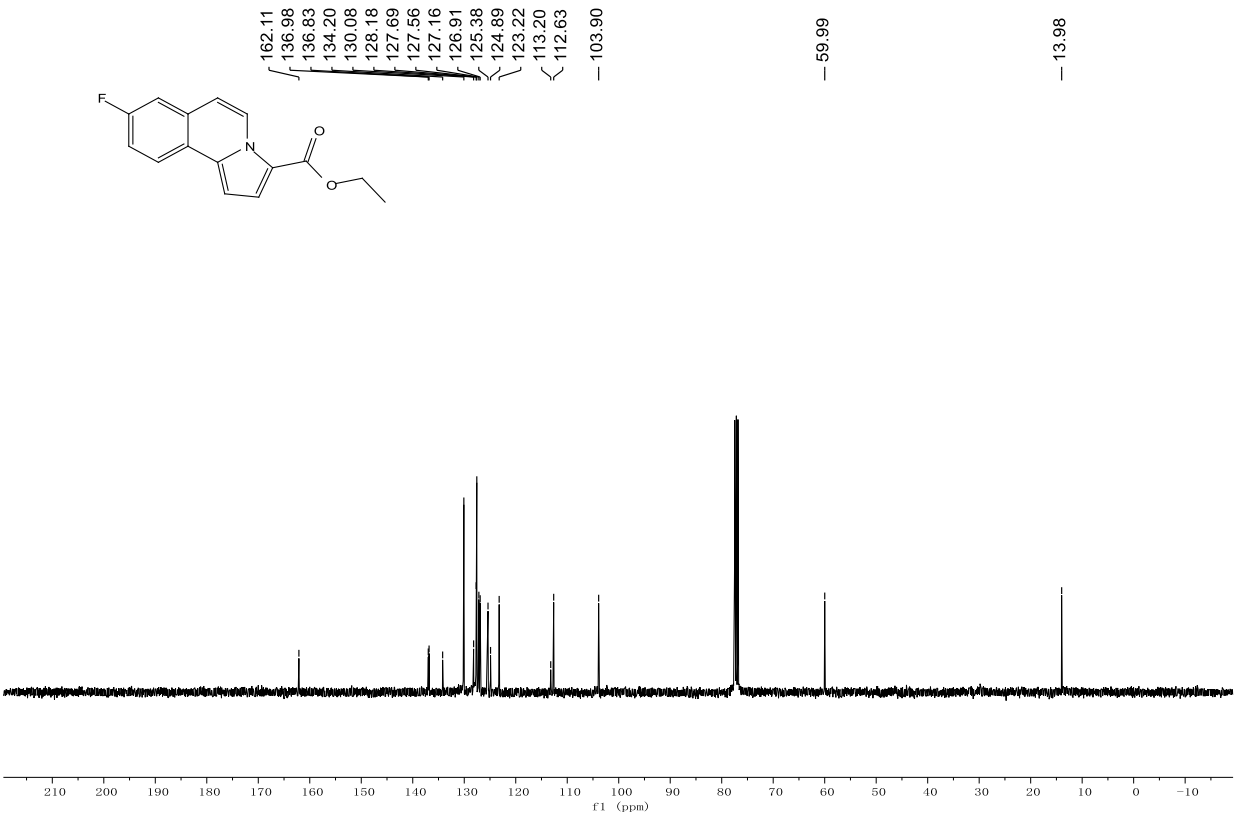
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3d**



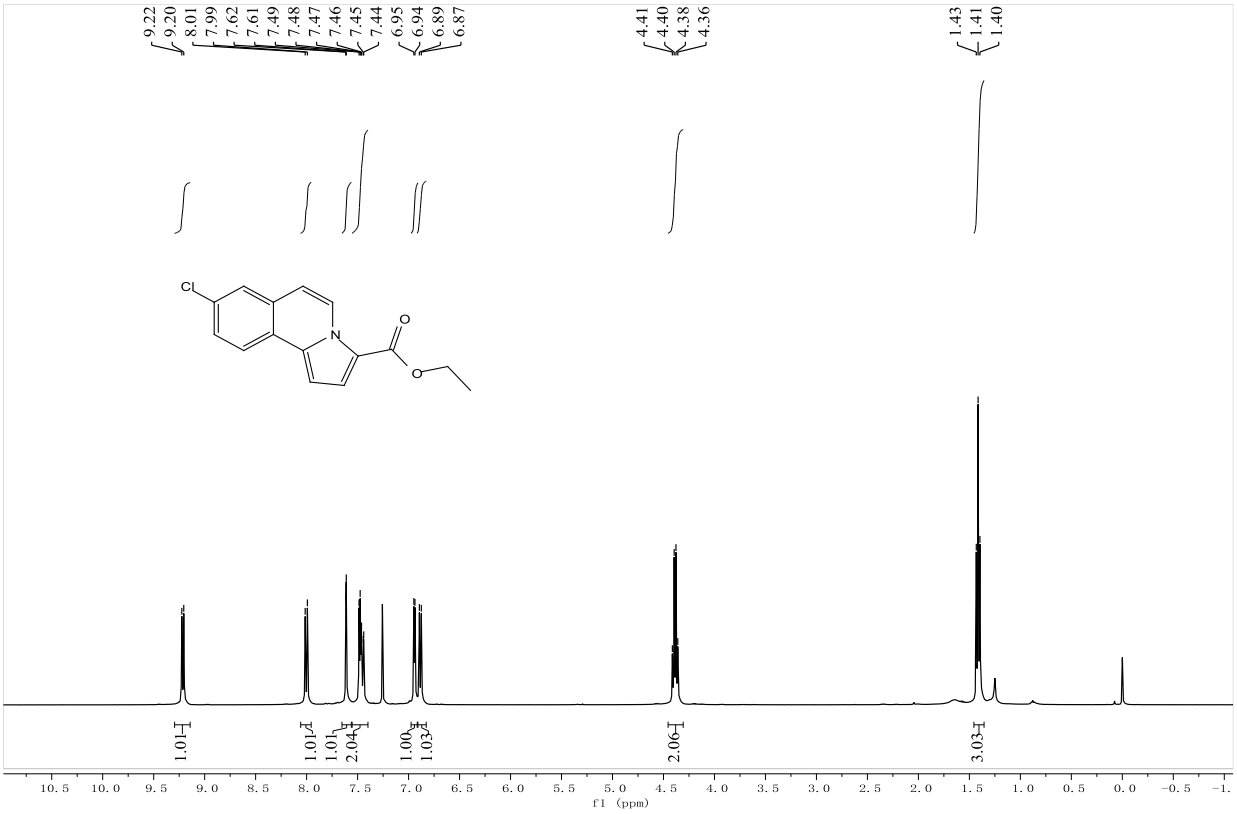
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**



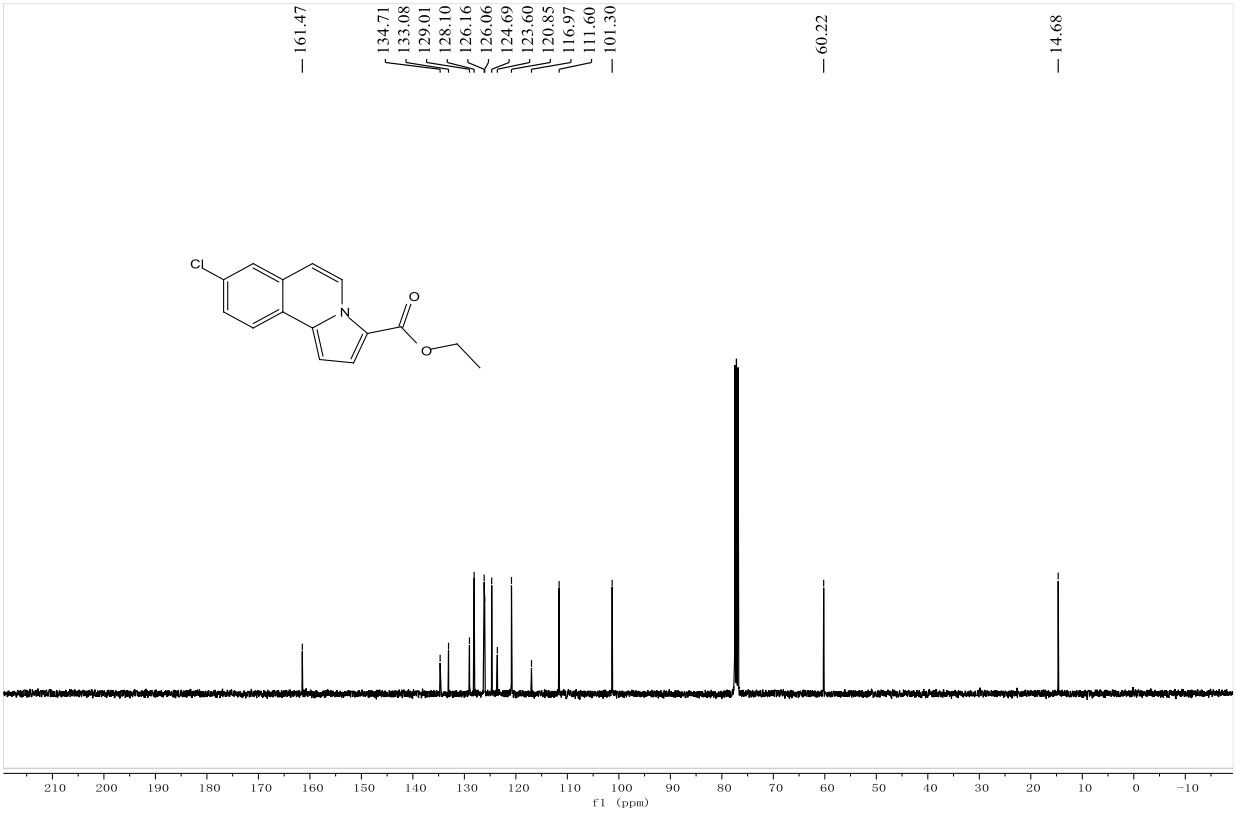
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**



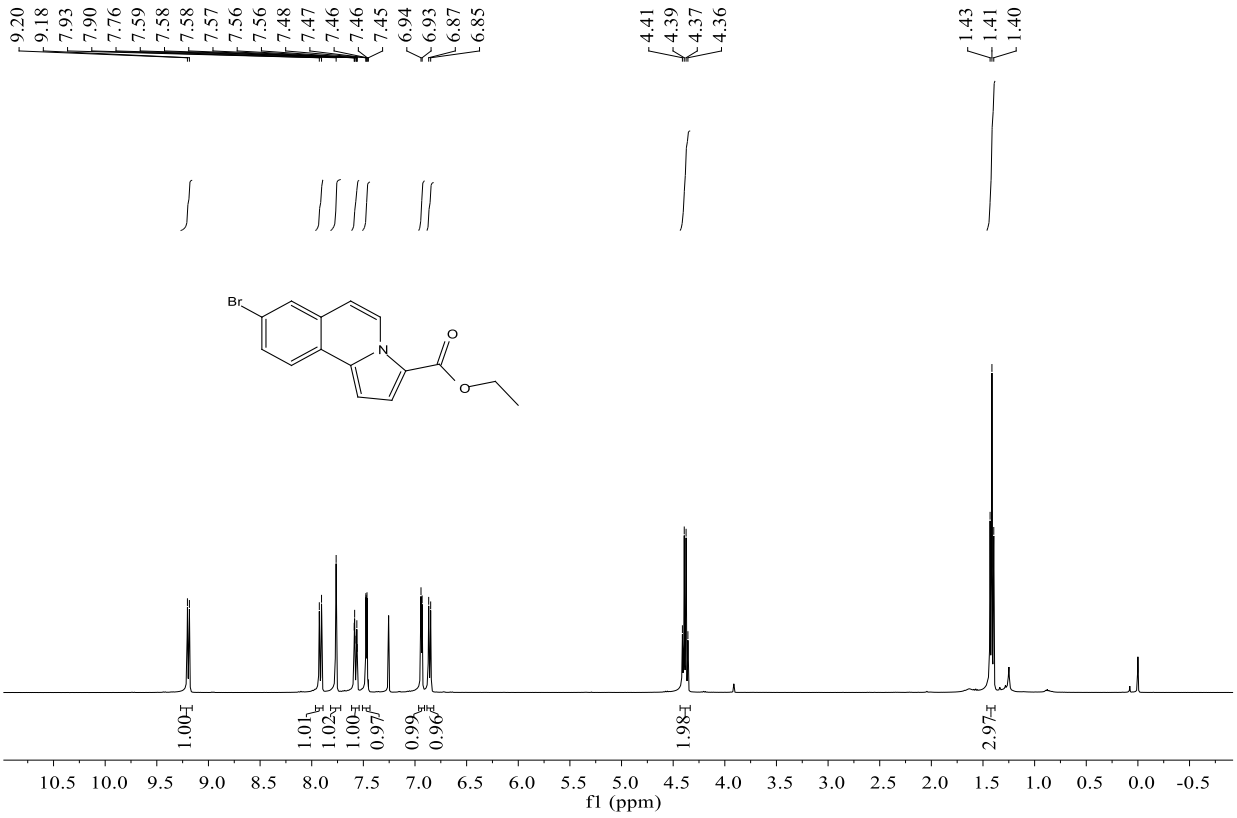
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3f**



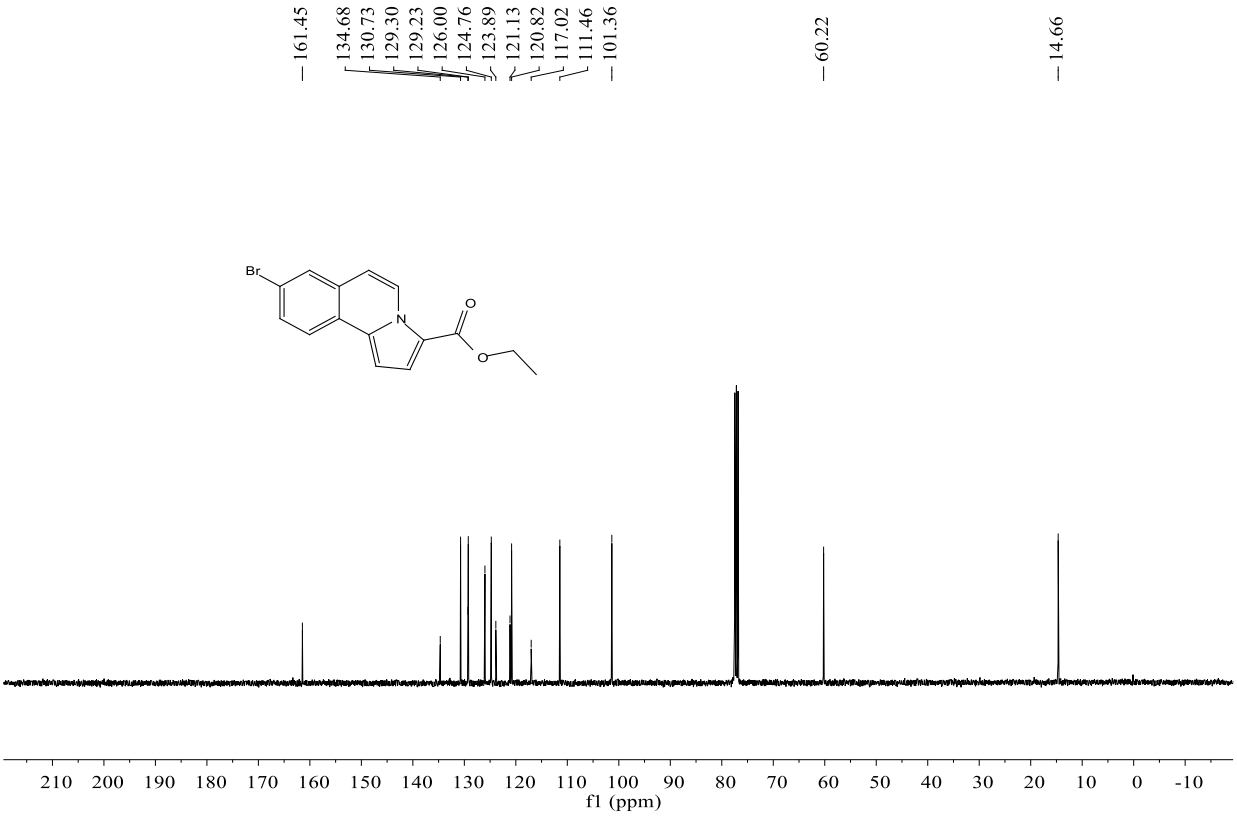
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3f**



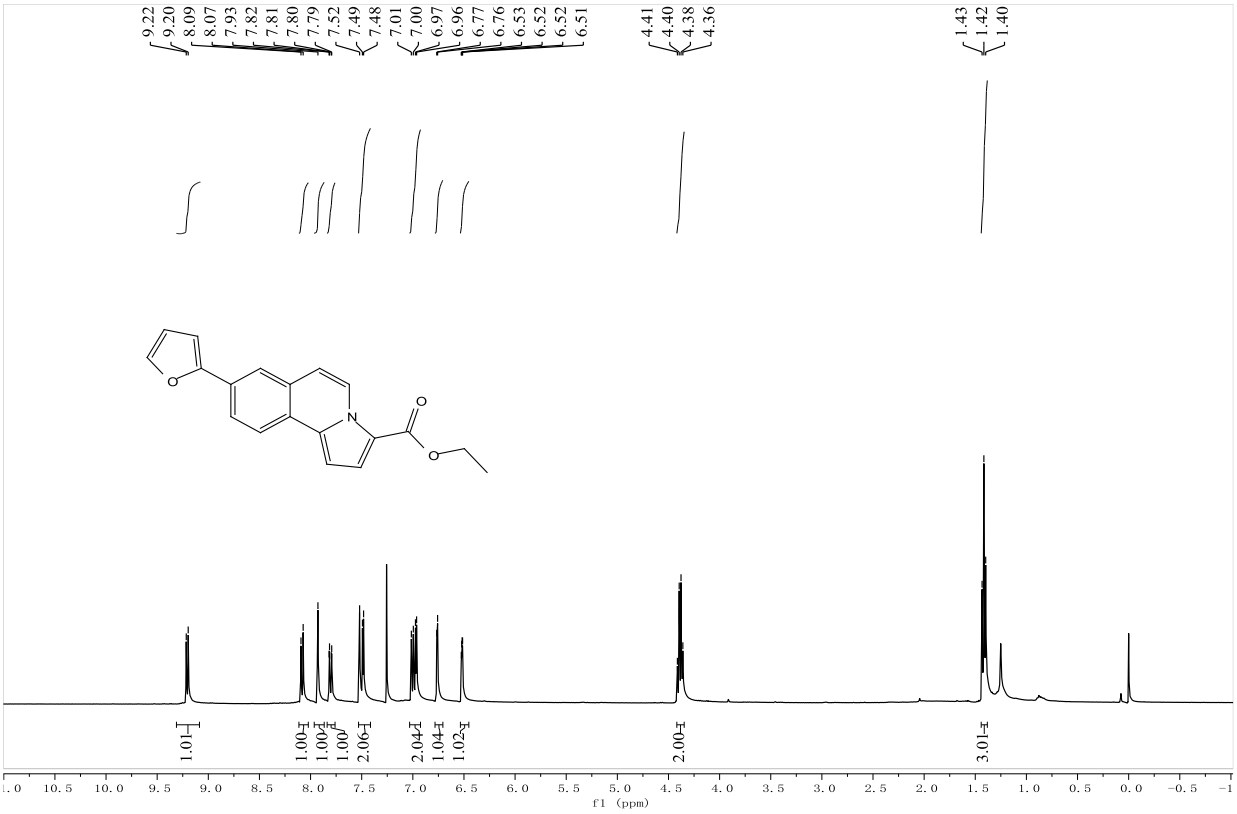
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3g**



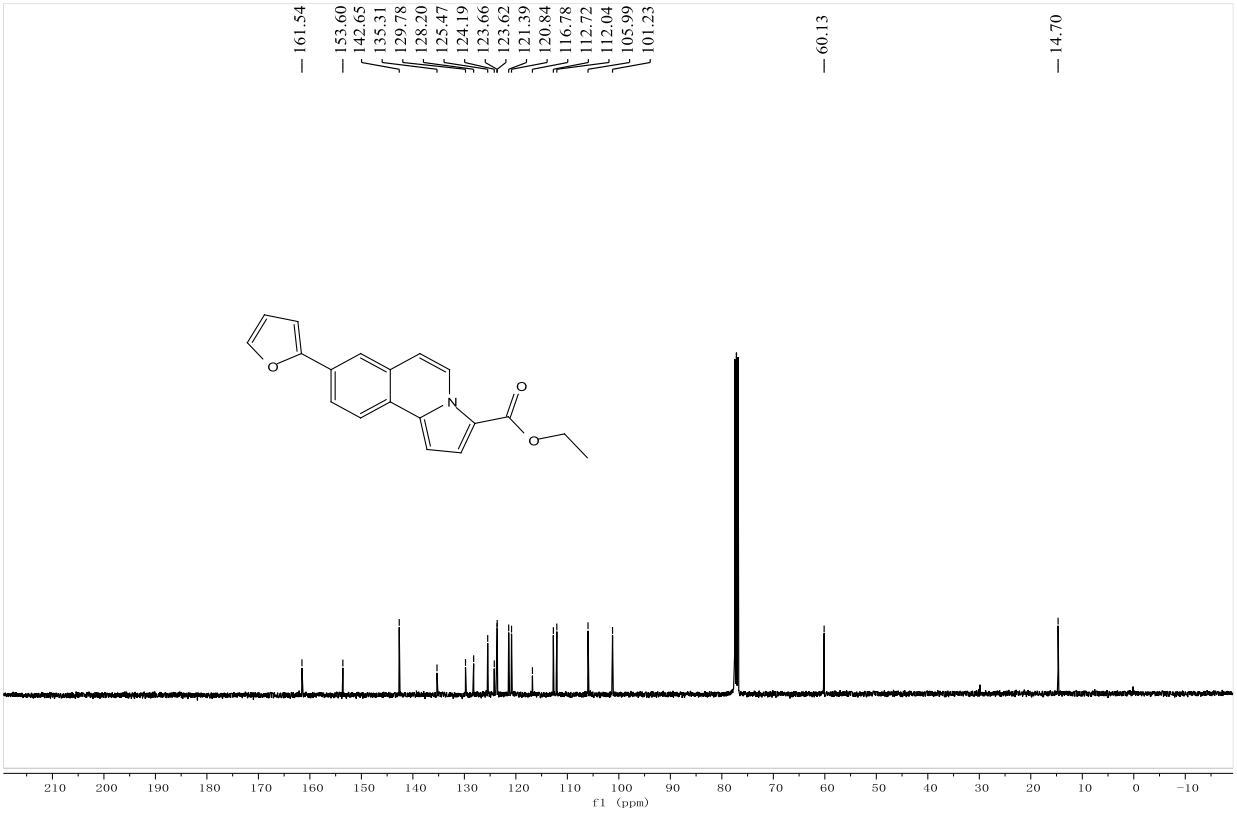
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3g**



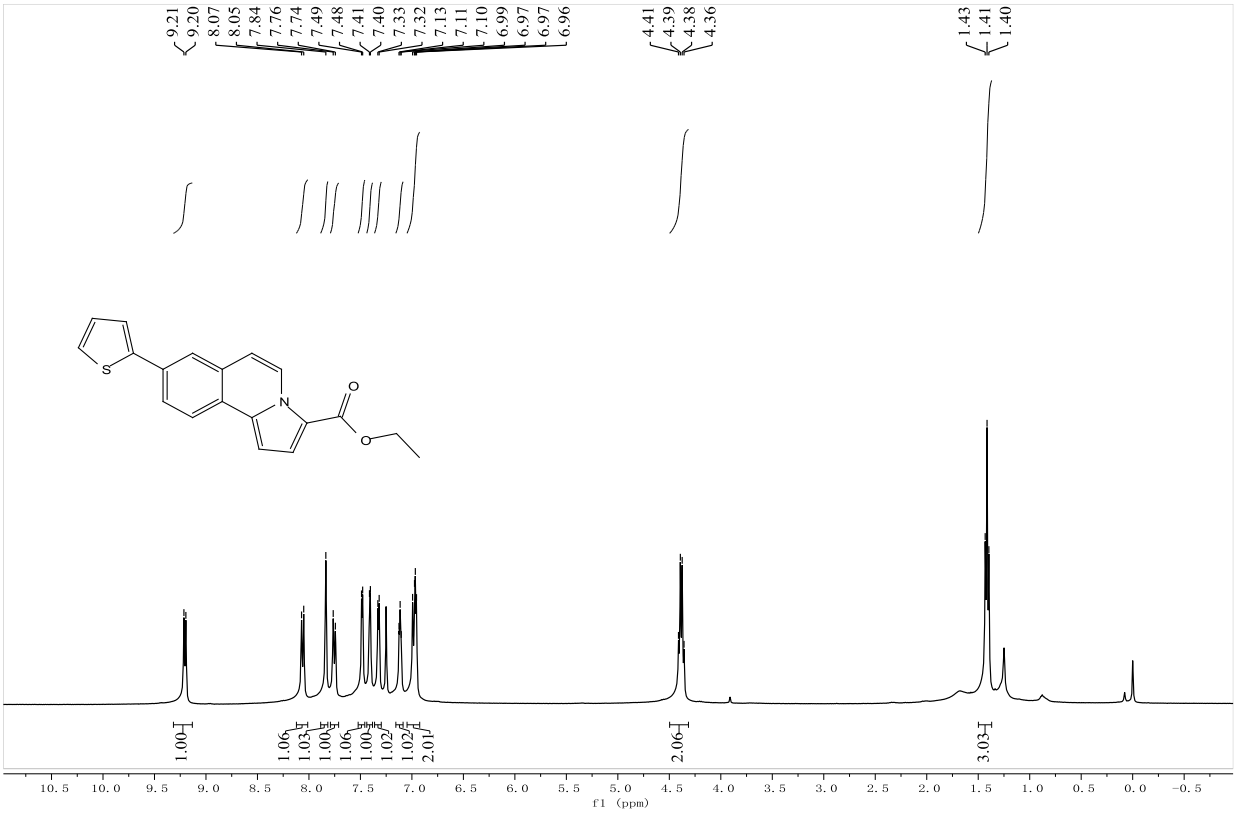
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**



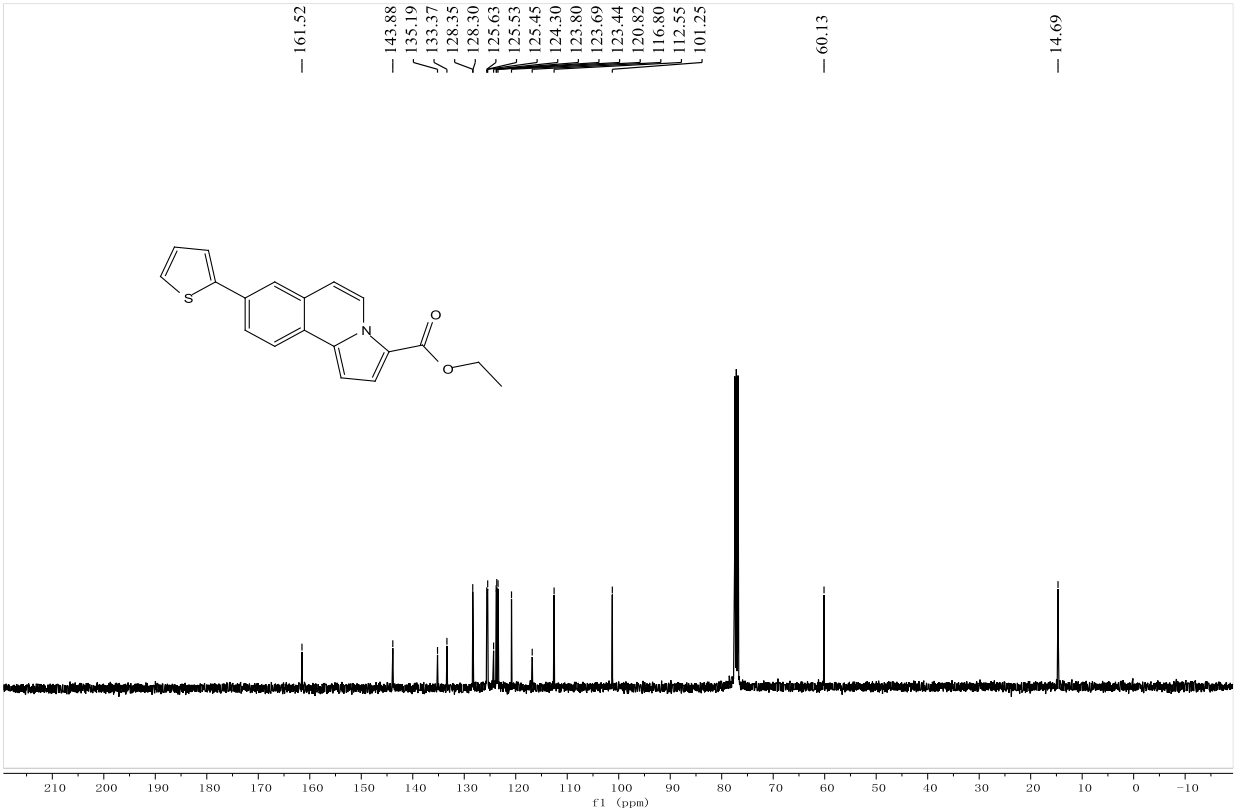
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3h**



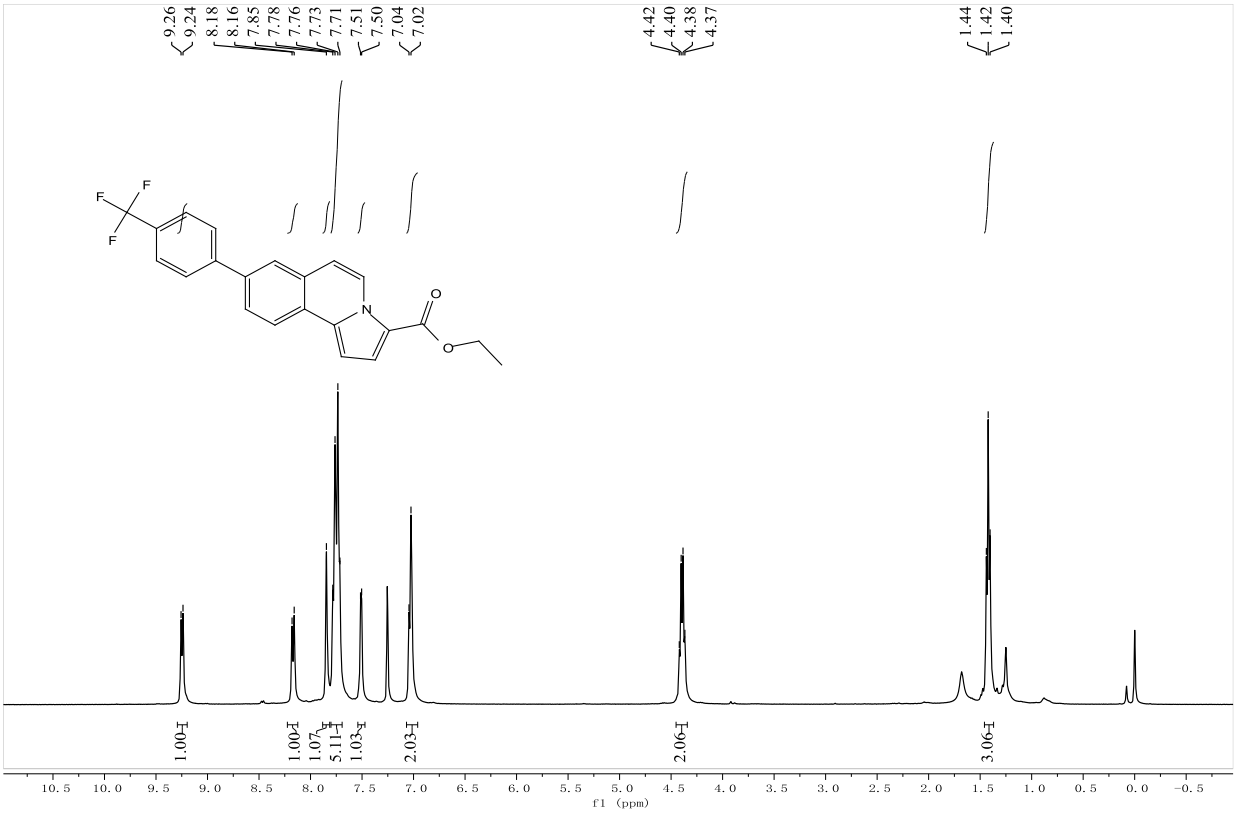
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3i**



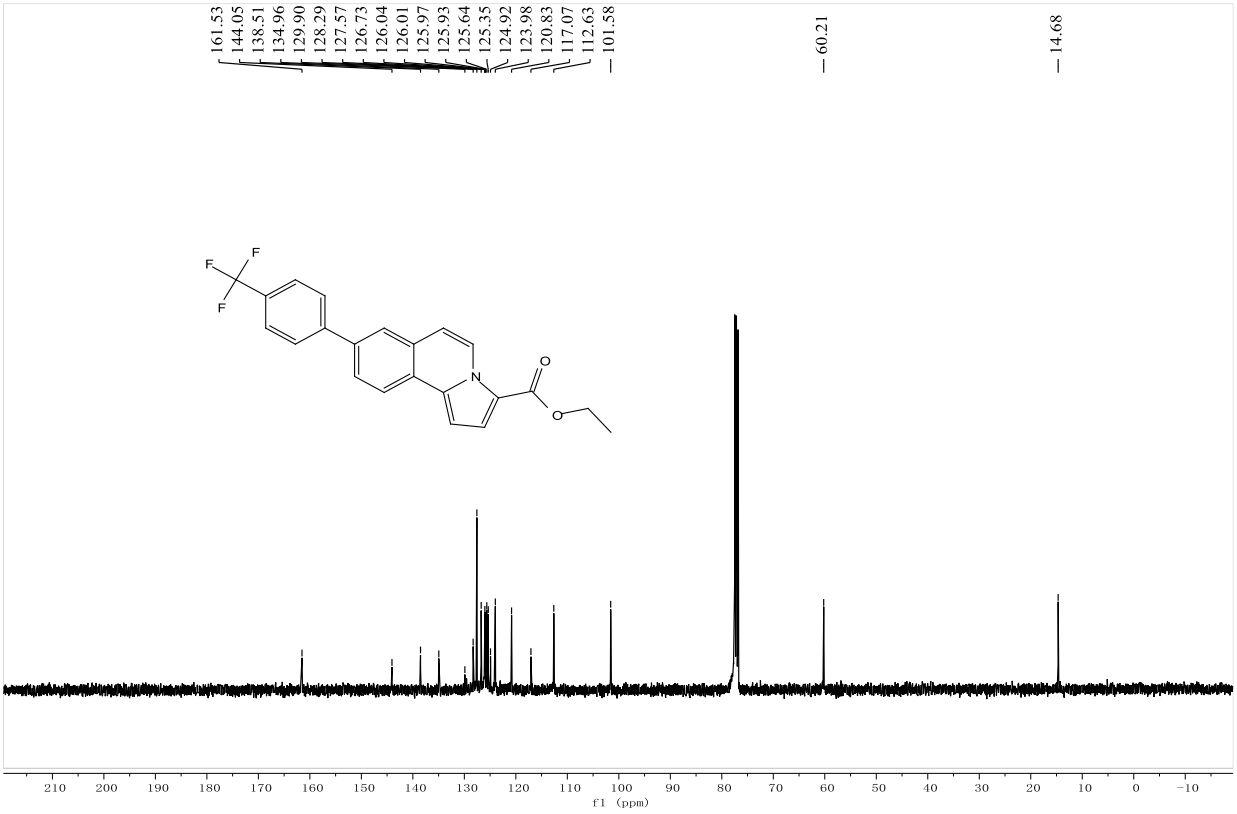
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3i**



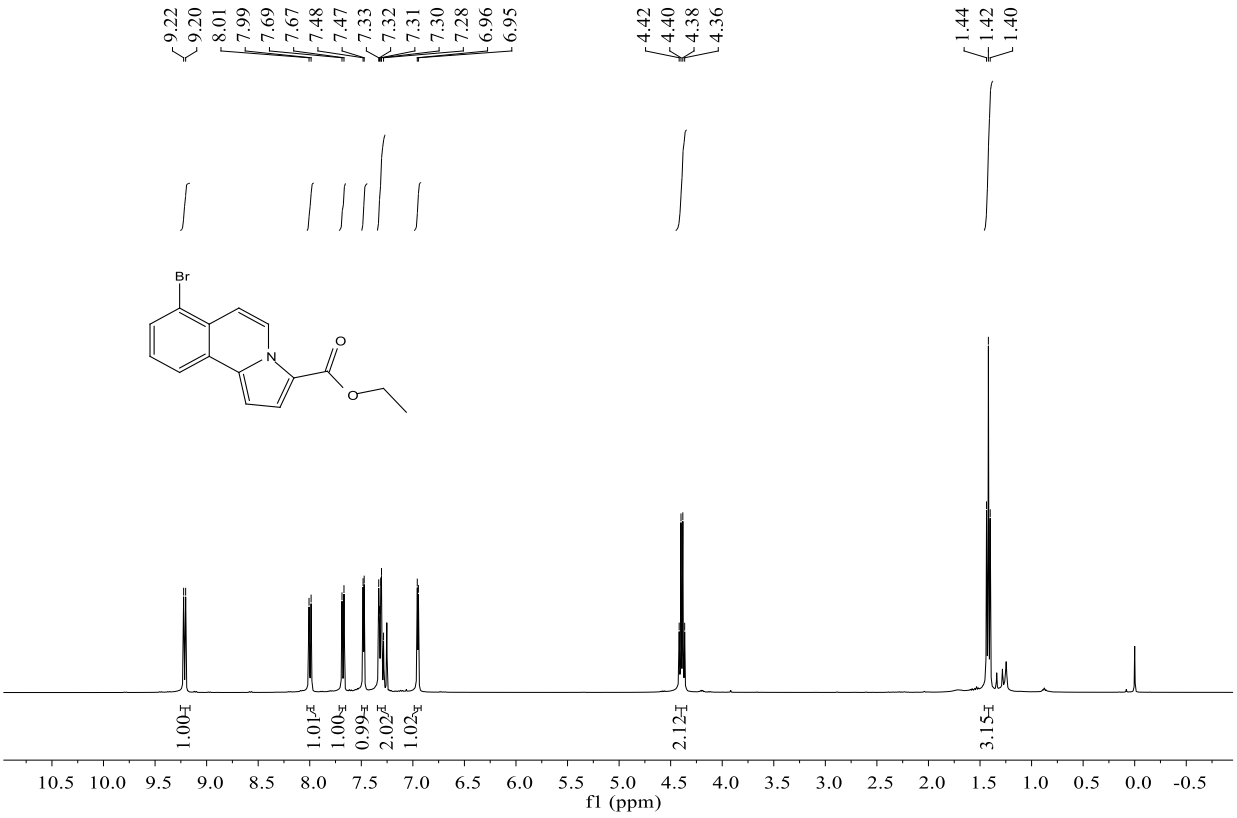
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**



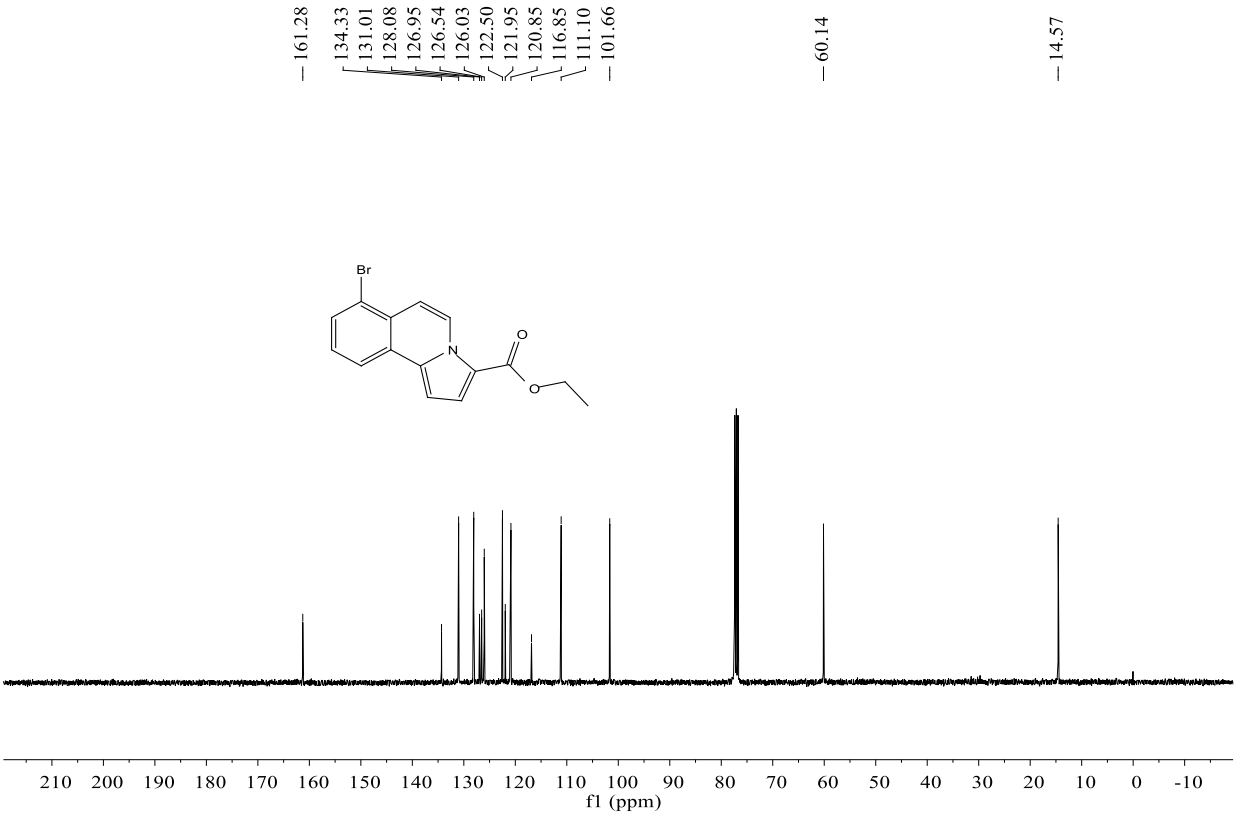
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3j**



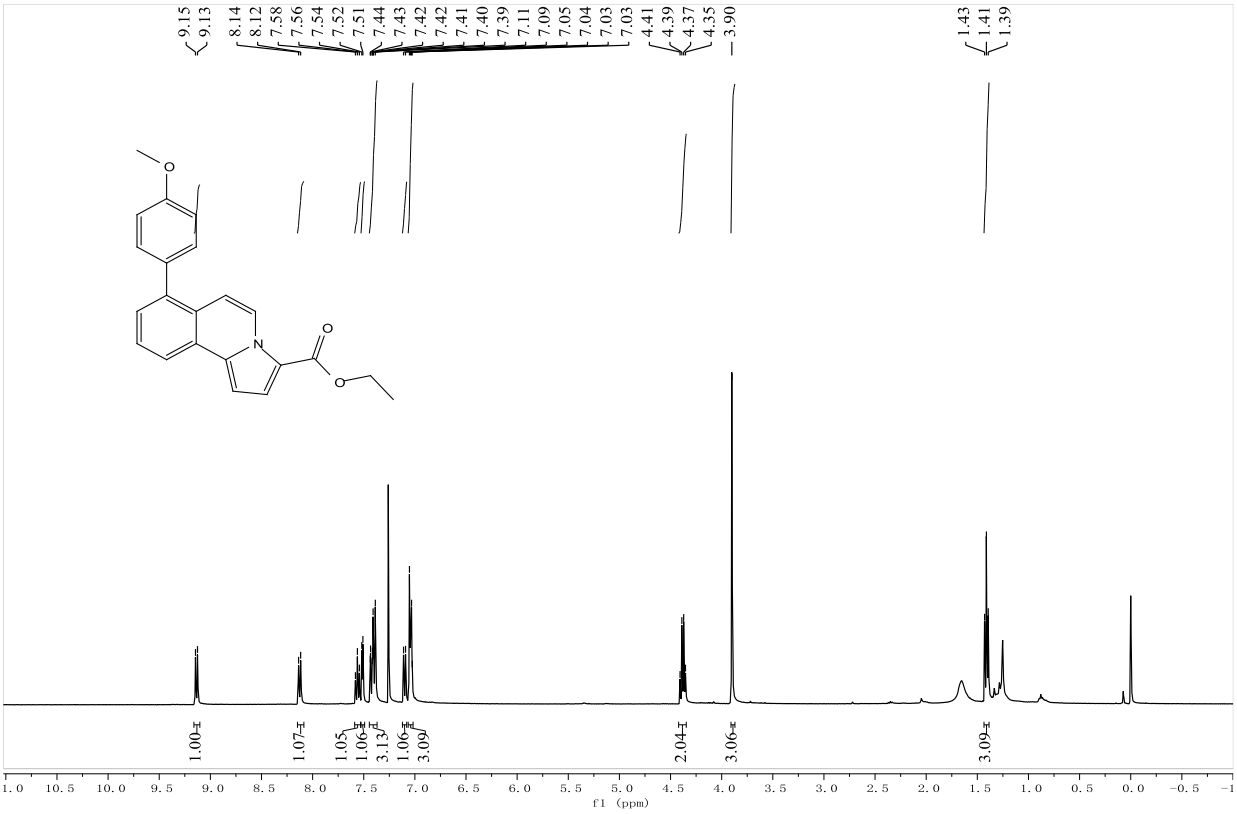
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3k**



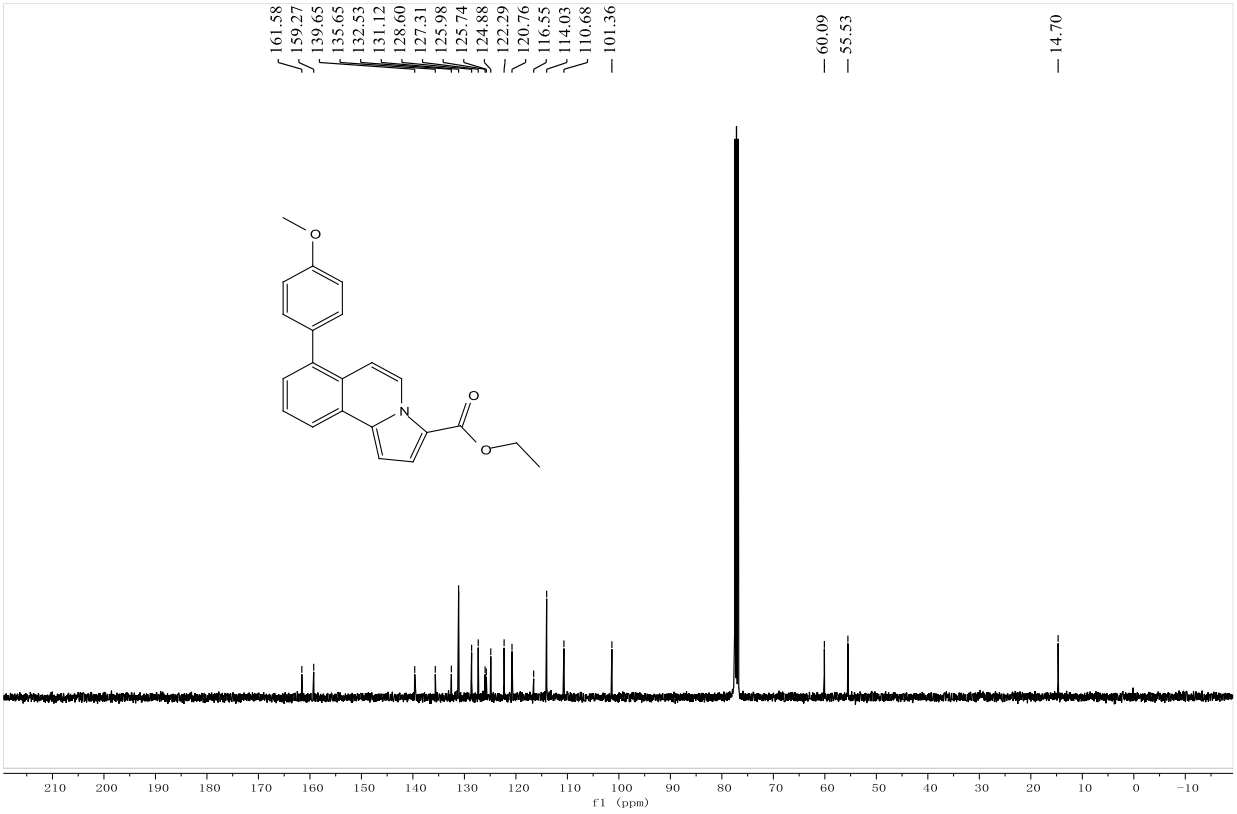
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3k**



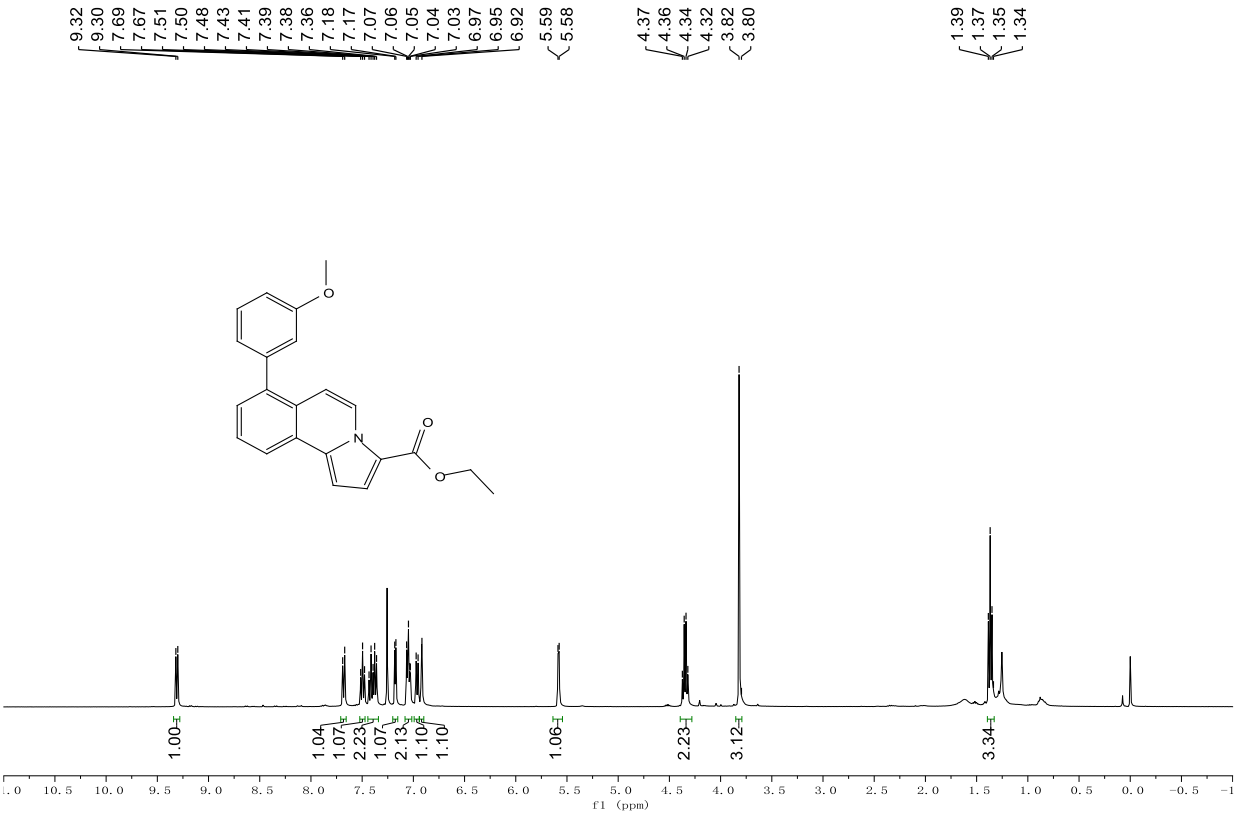
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**



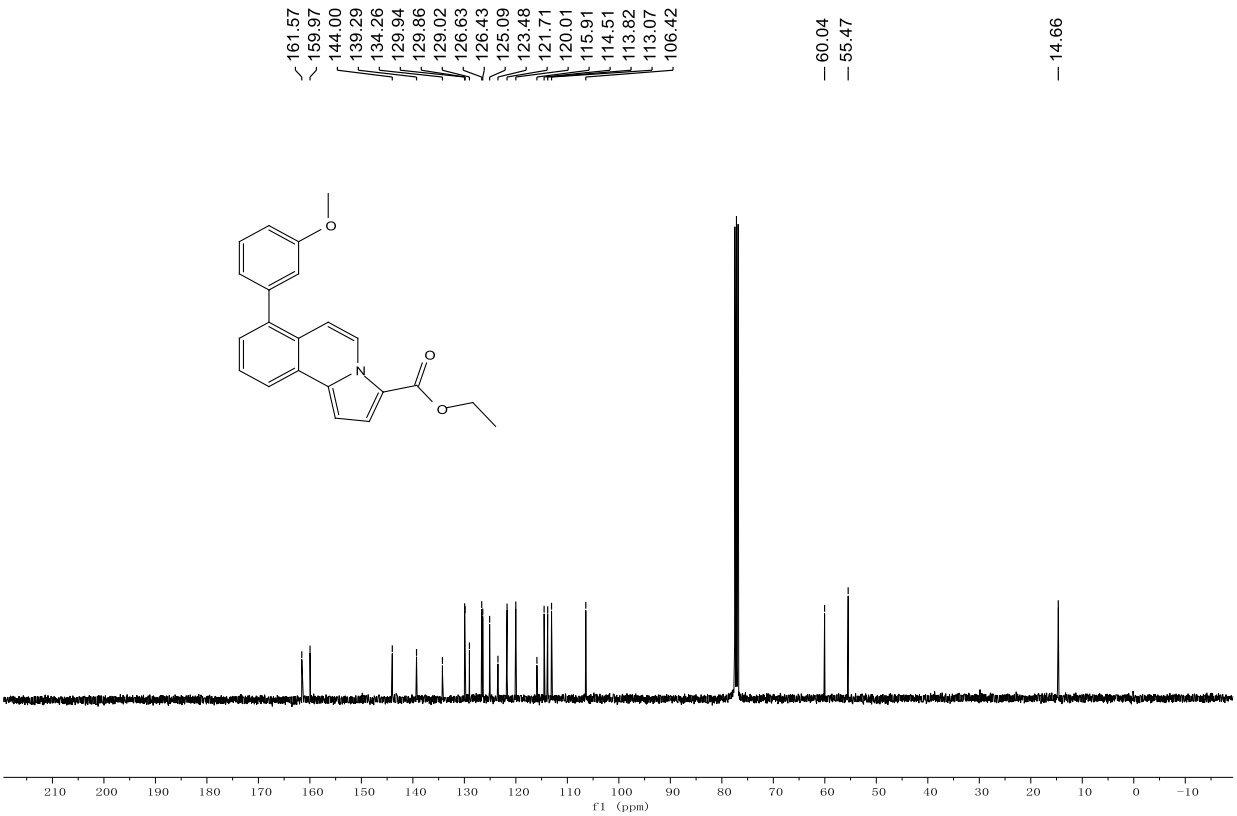
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3l**



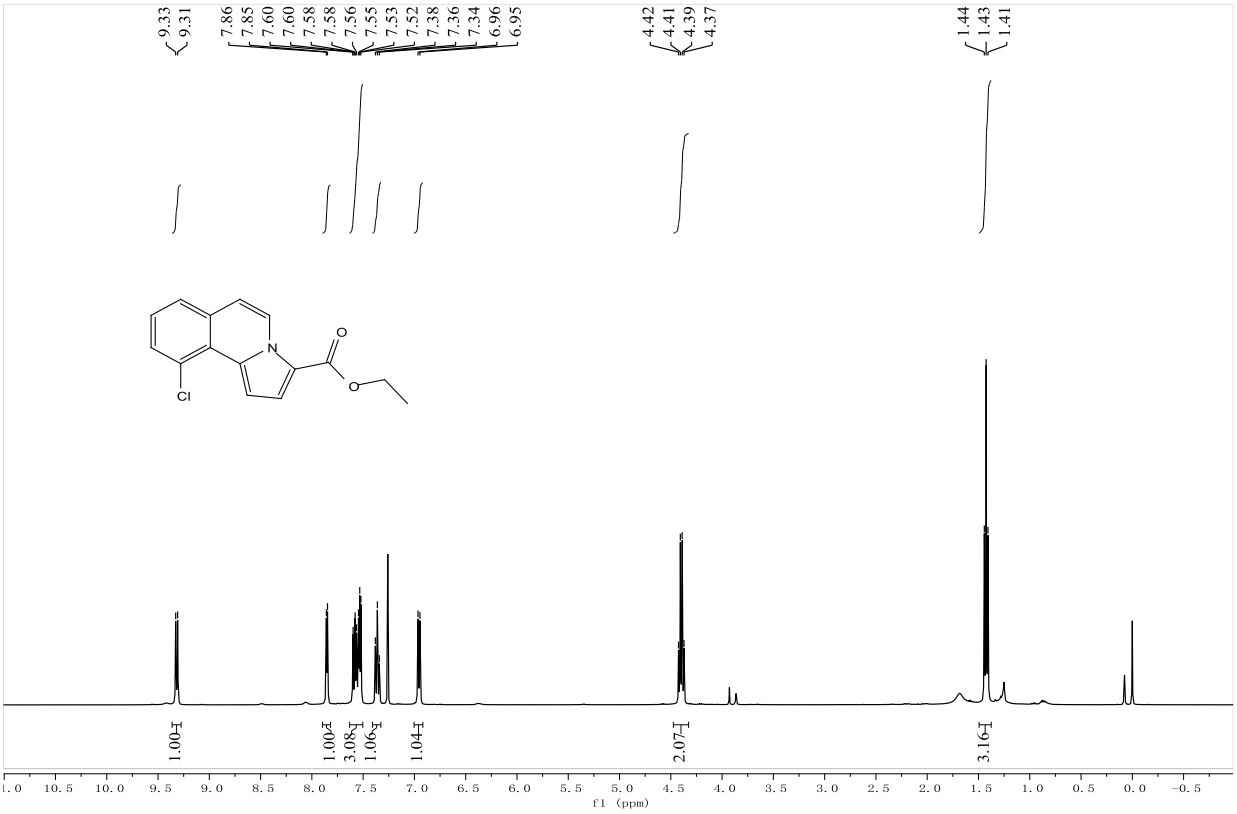
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**



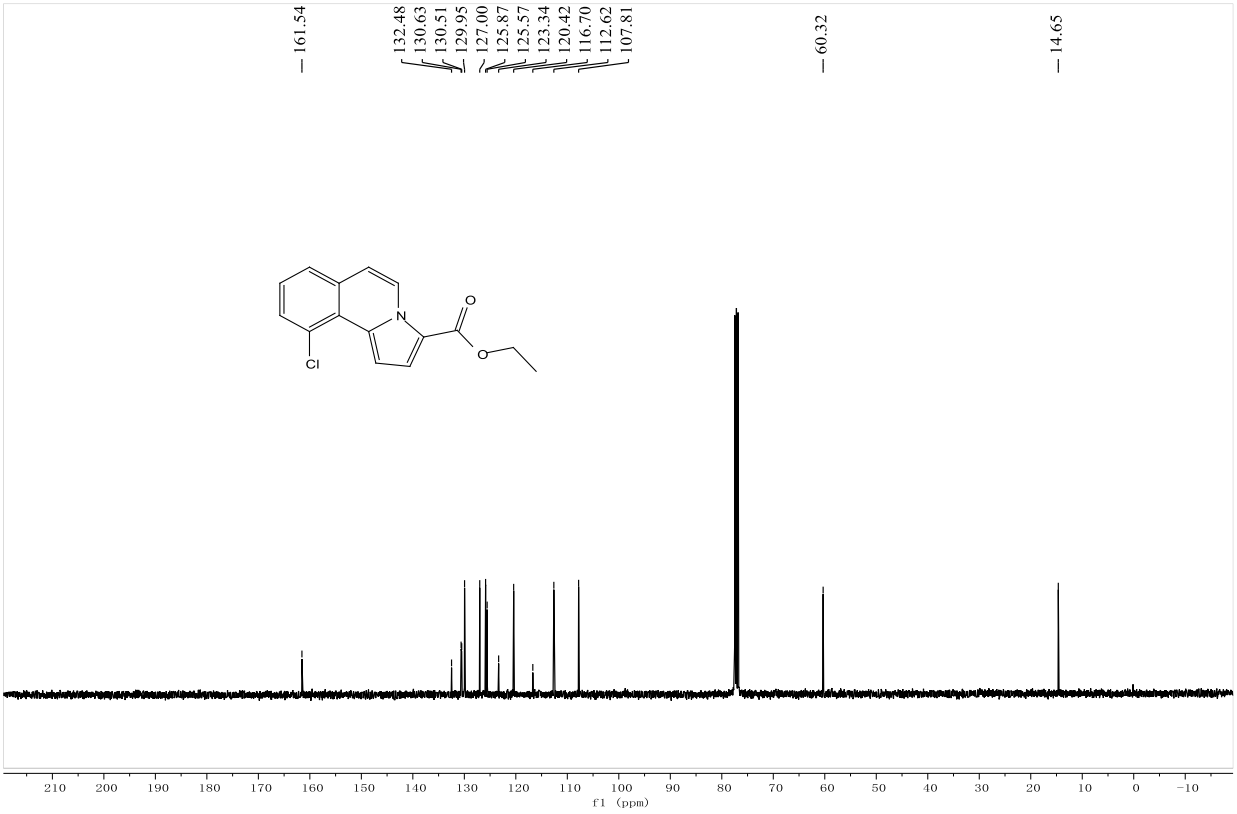
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3m**



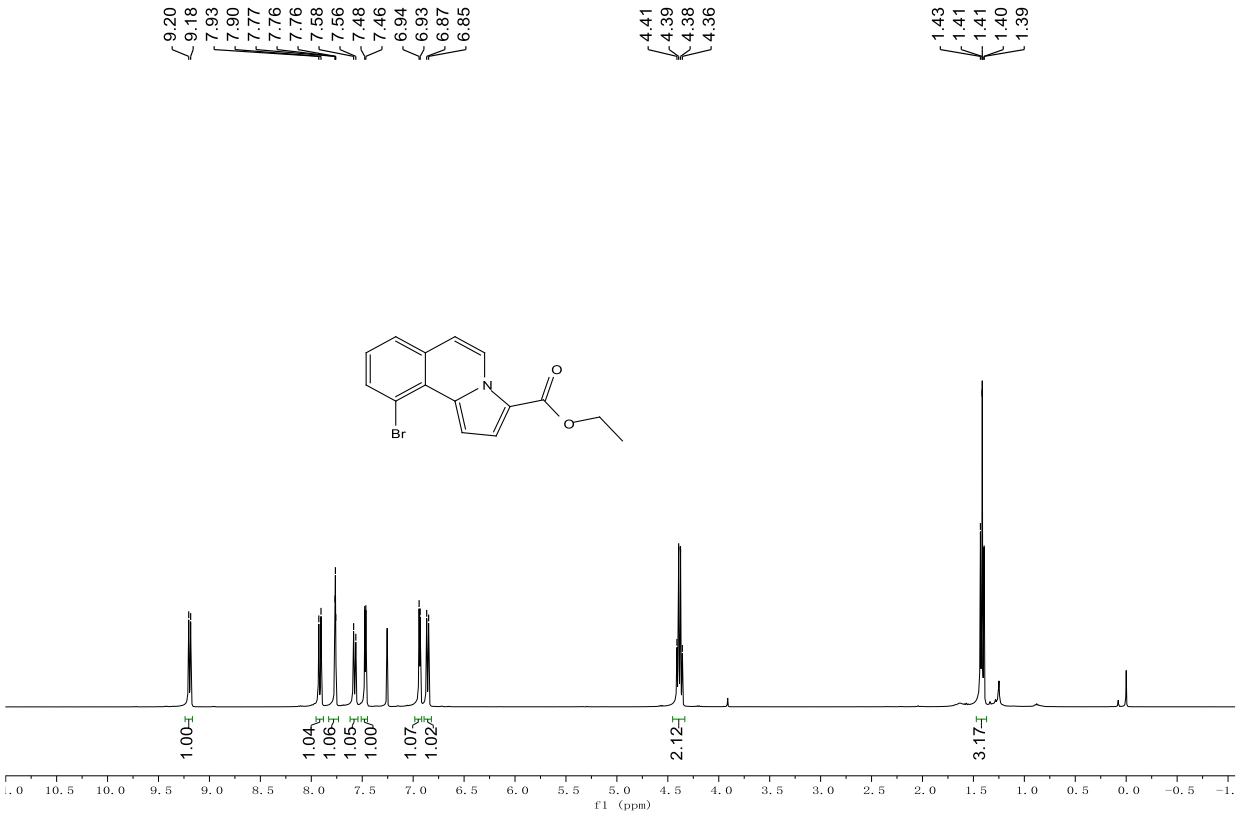
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**



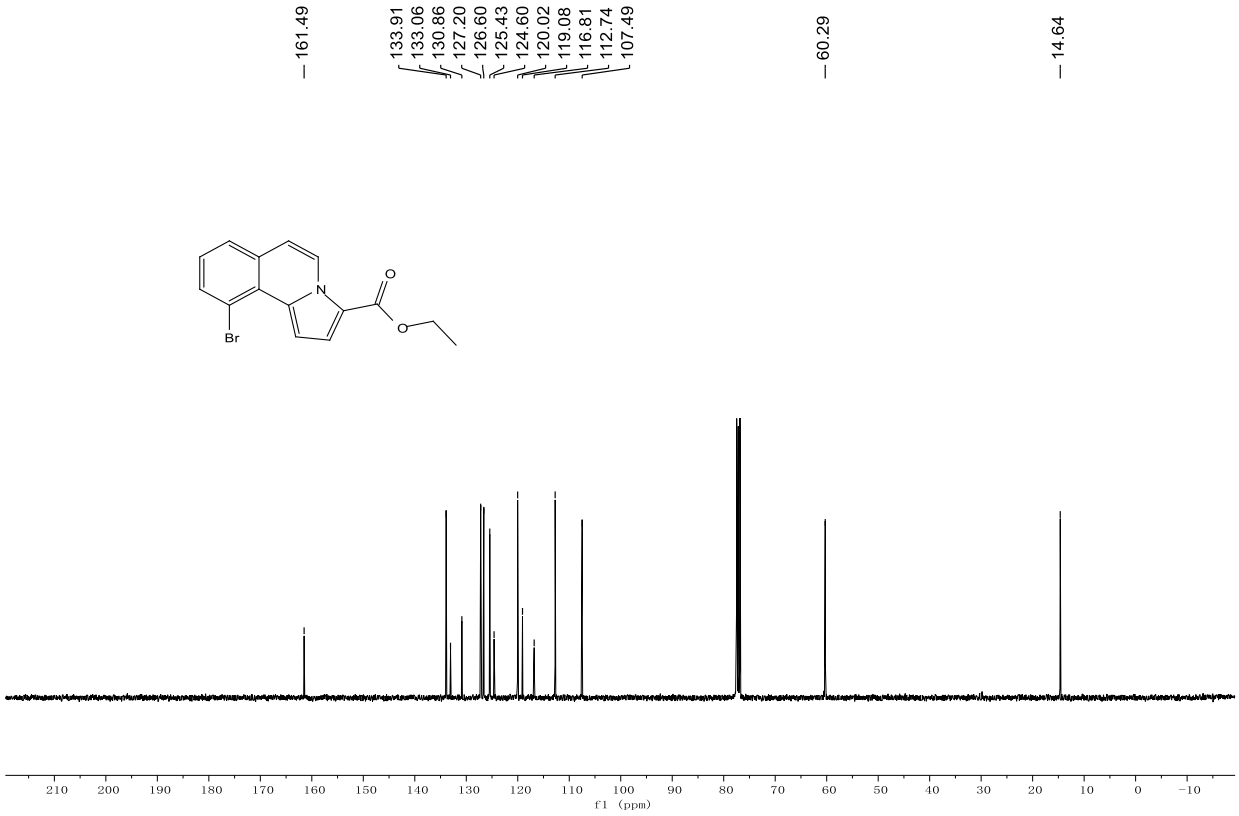
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3n**



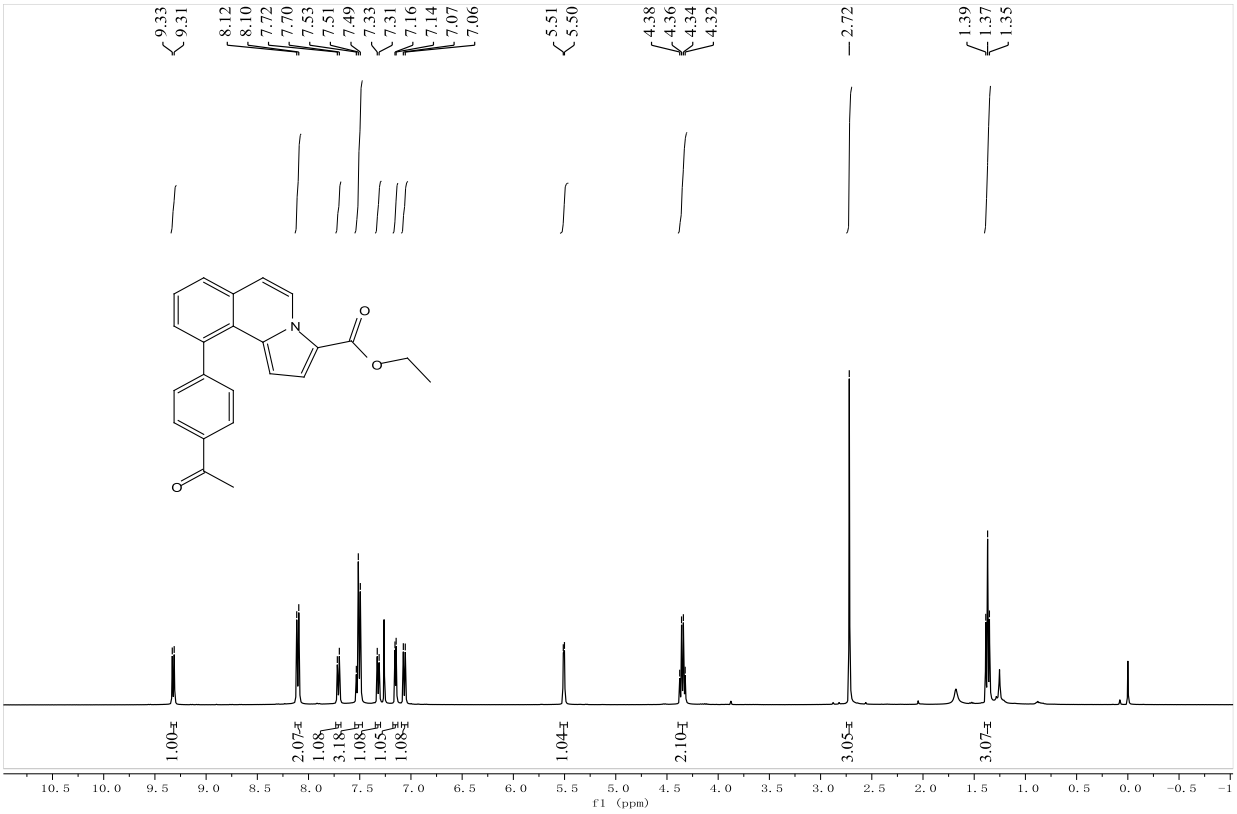
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**



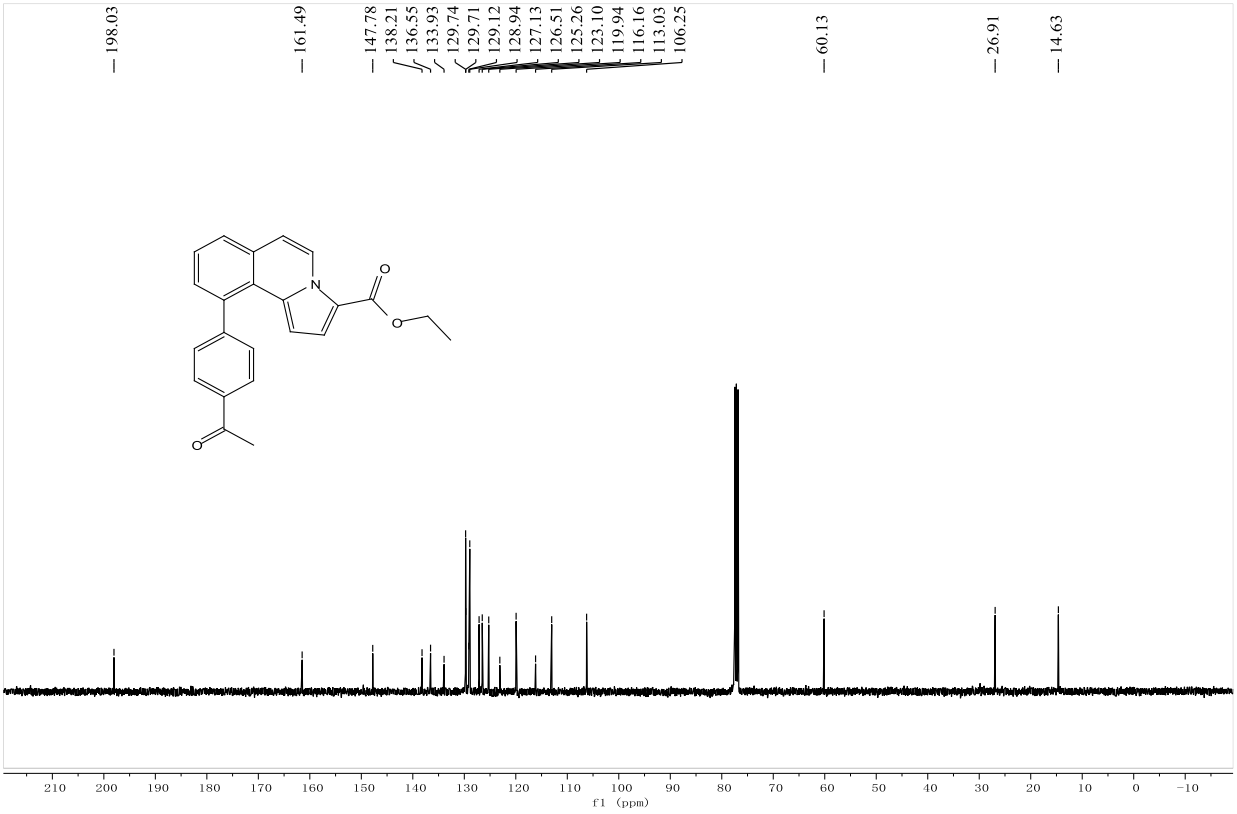
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3o**



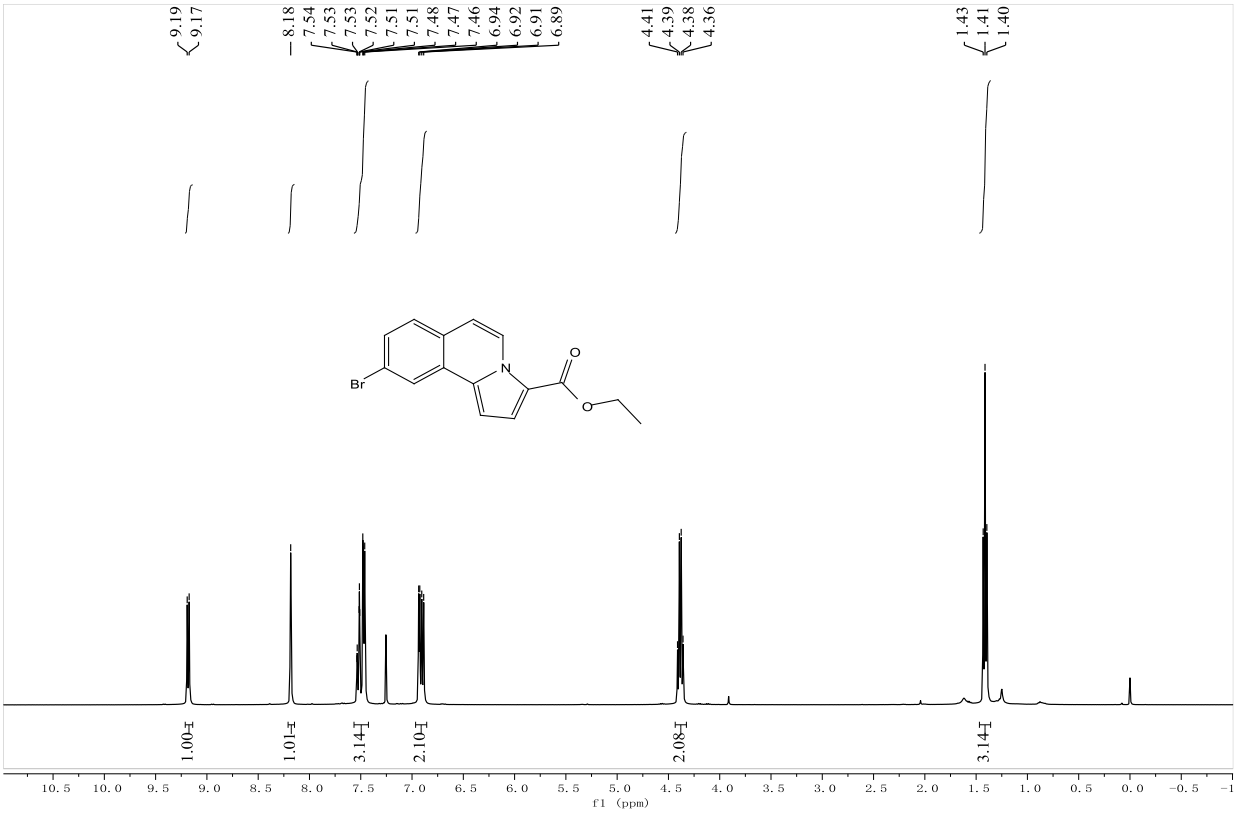
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3p**



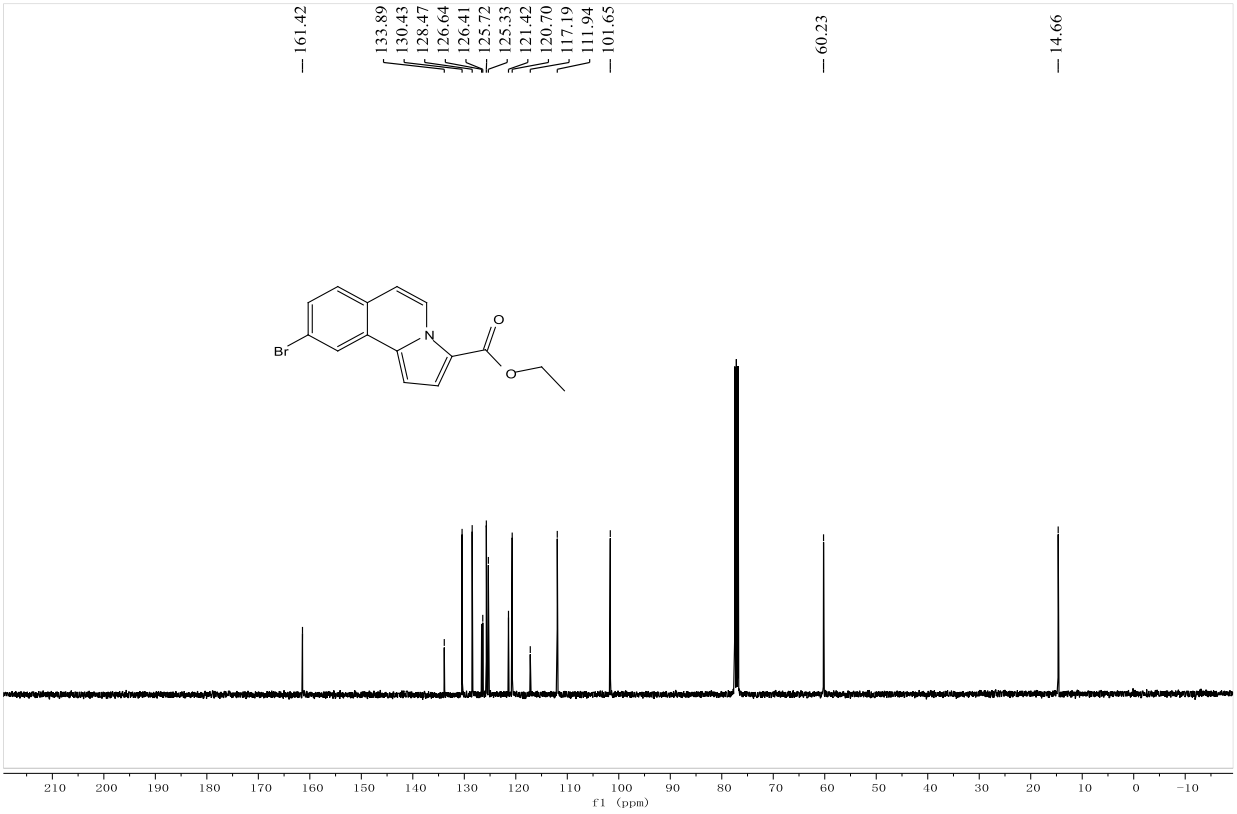
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3p**



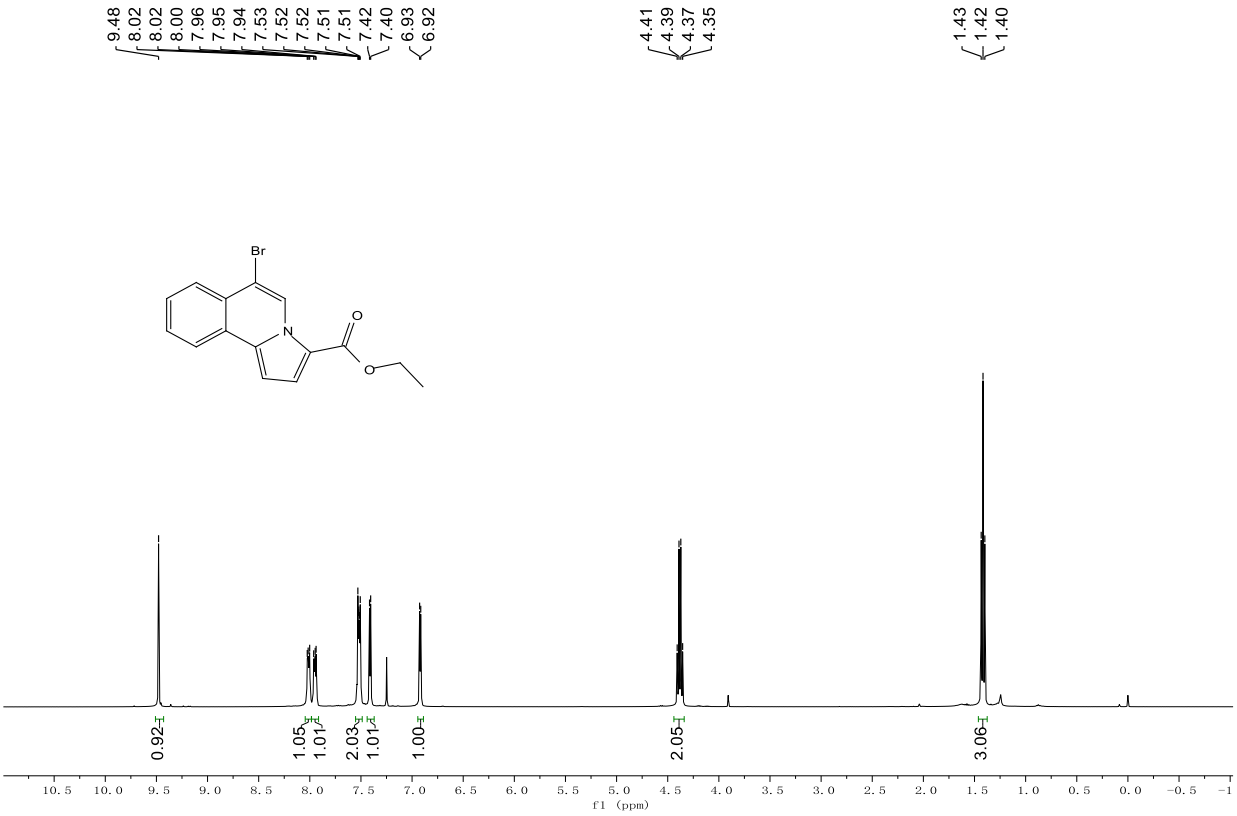
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3q**



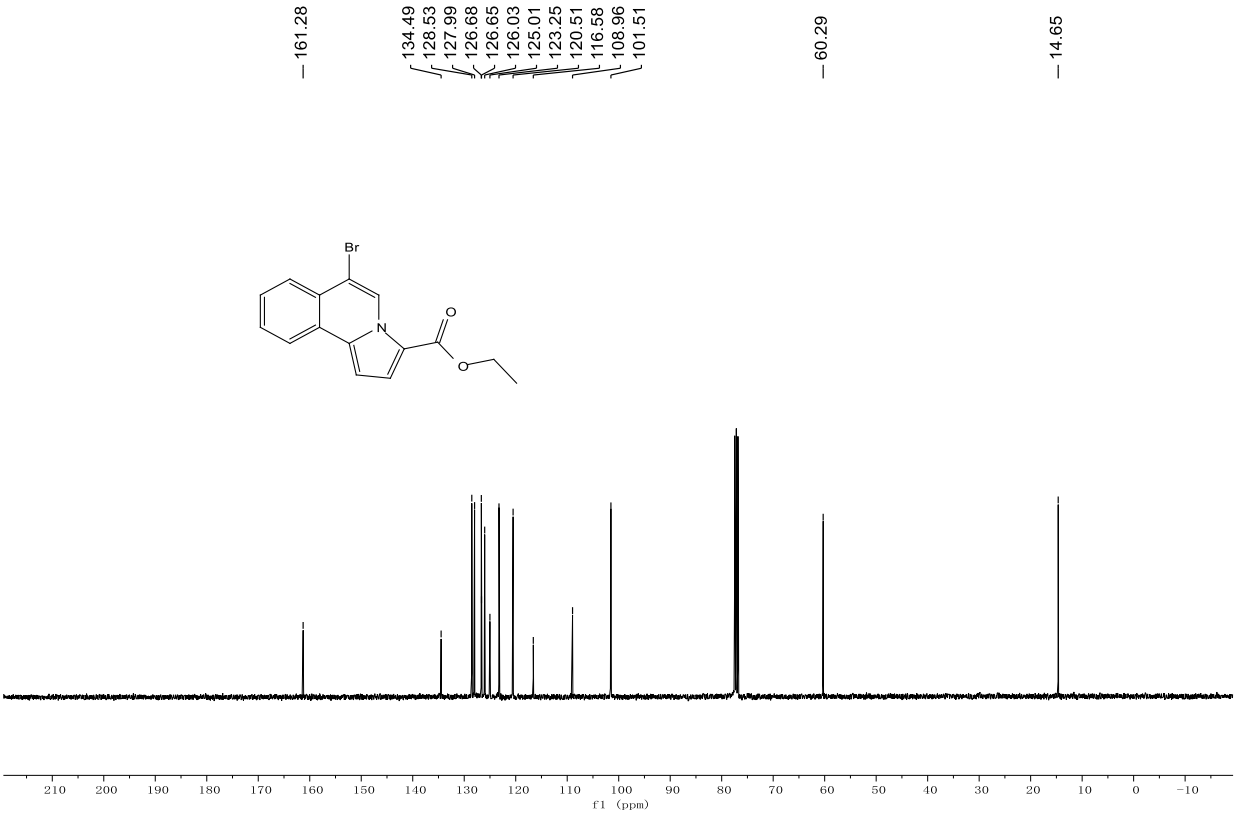
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3q**



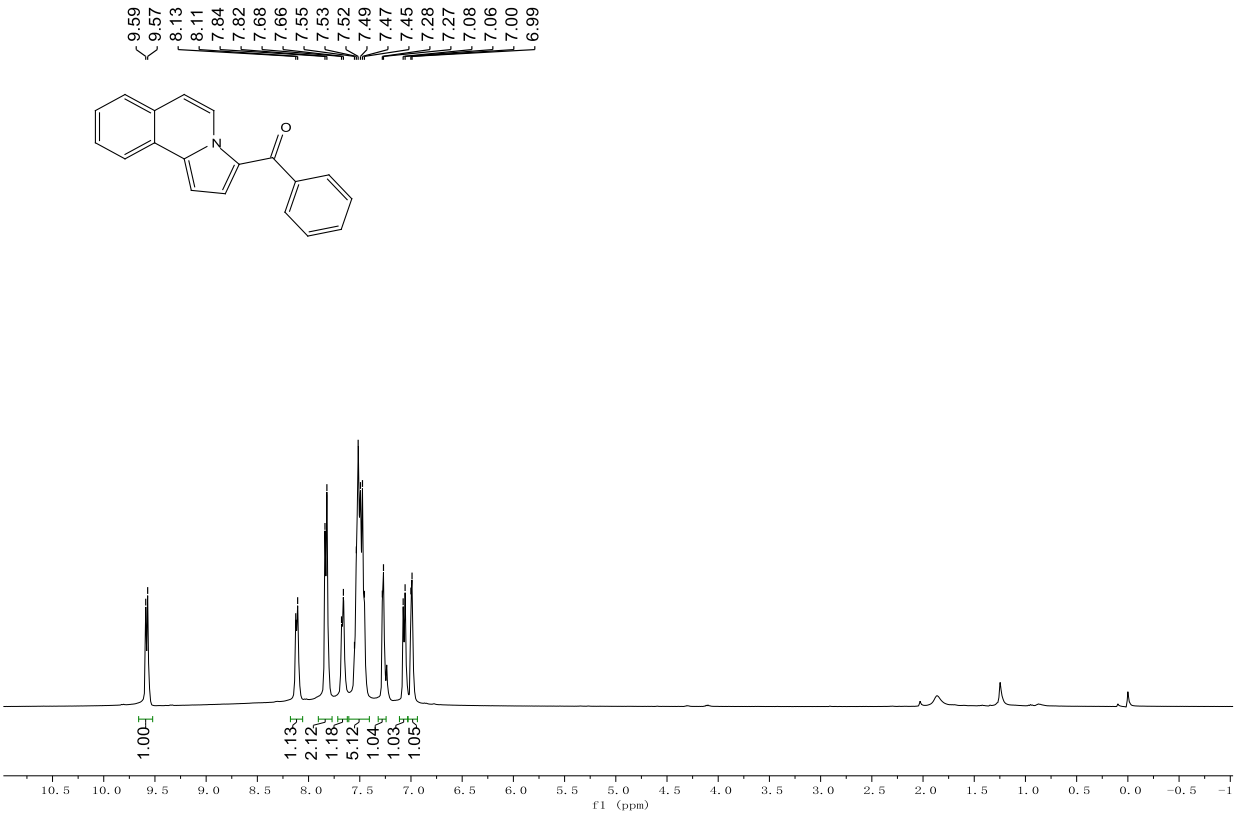
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3r**



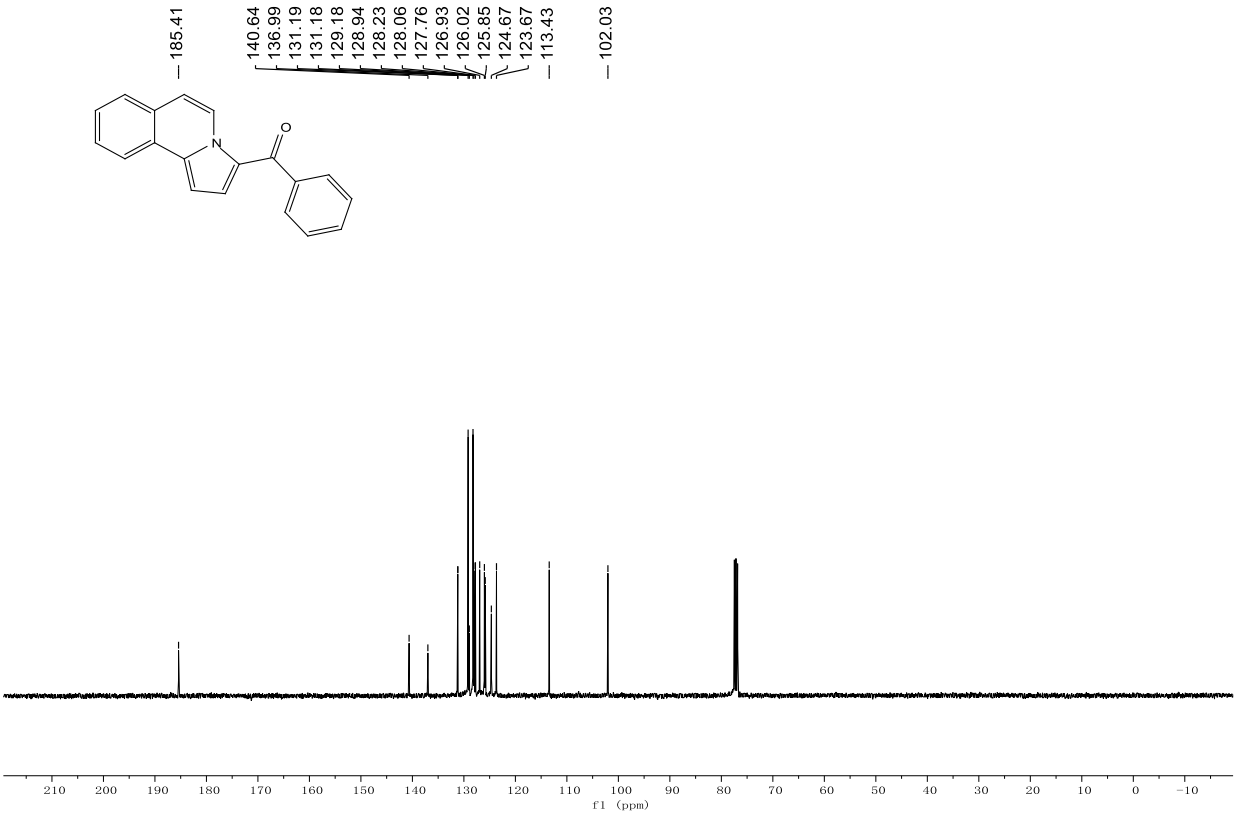
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3r**



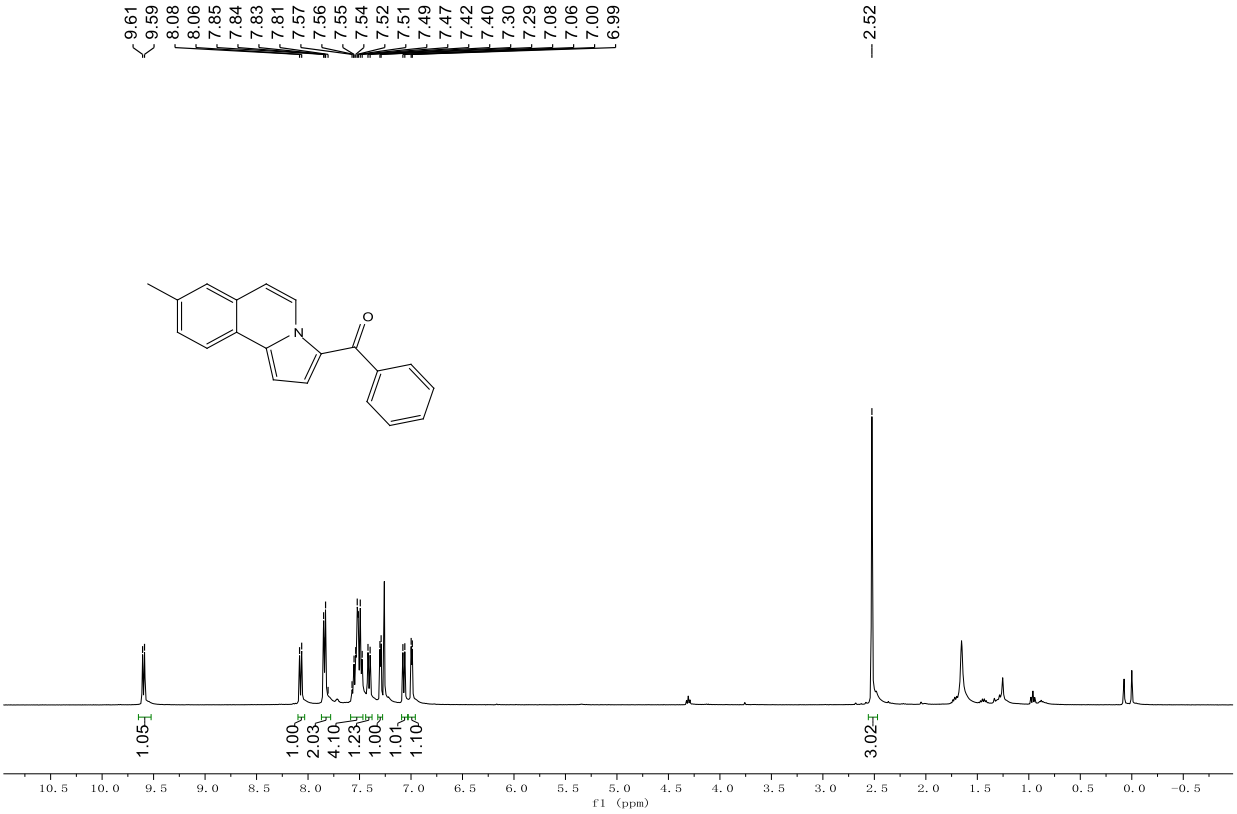
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5a**



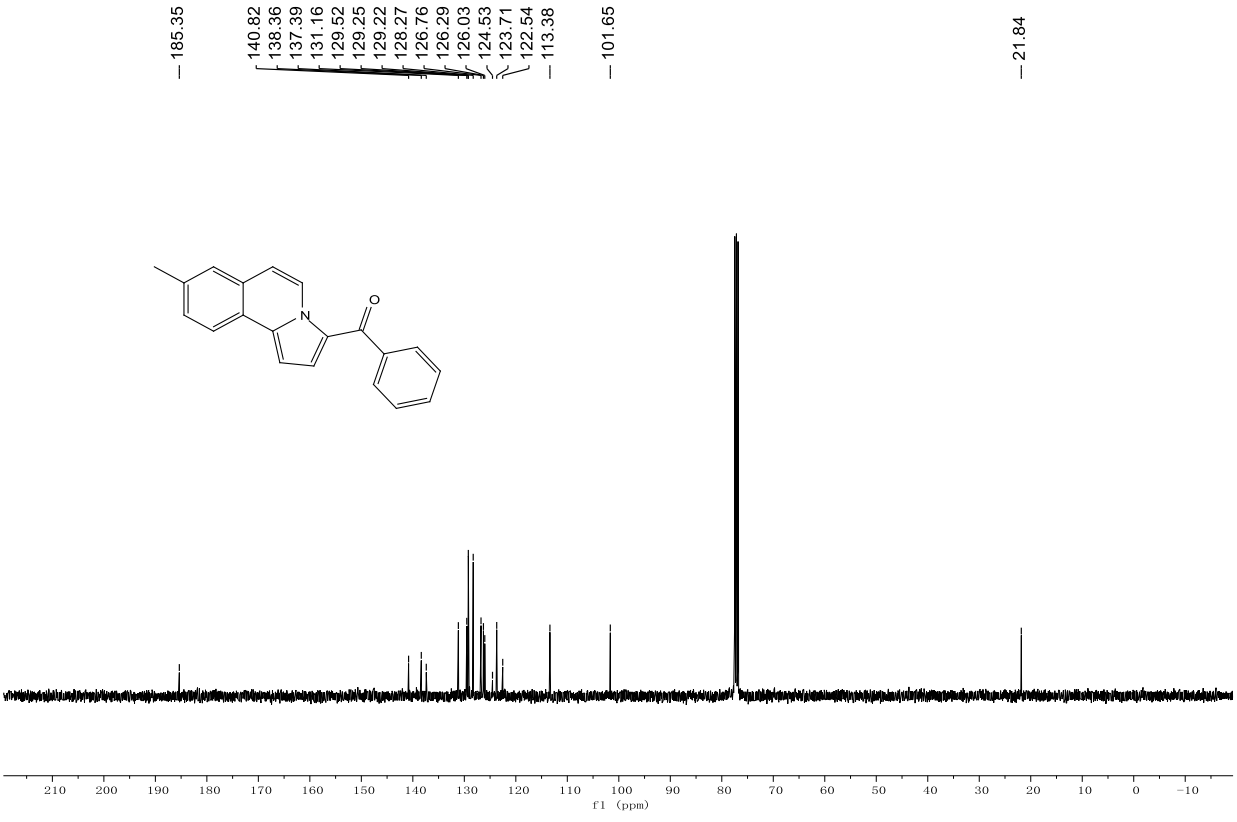
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5a**



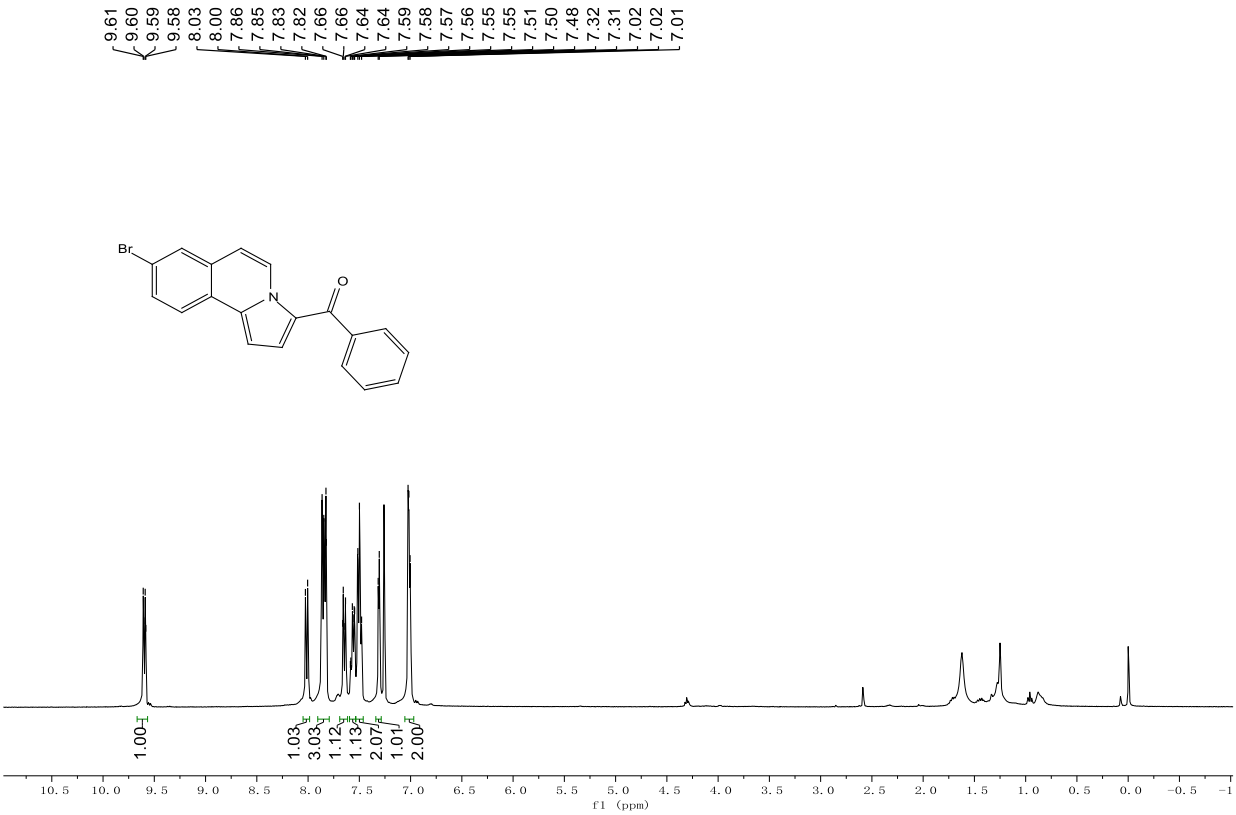
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5b**



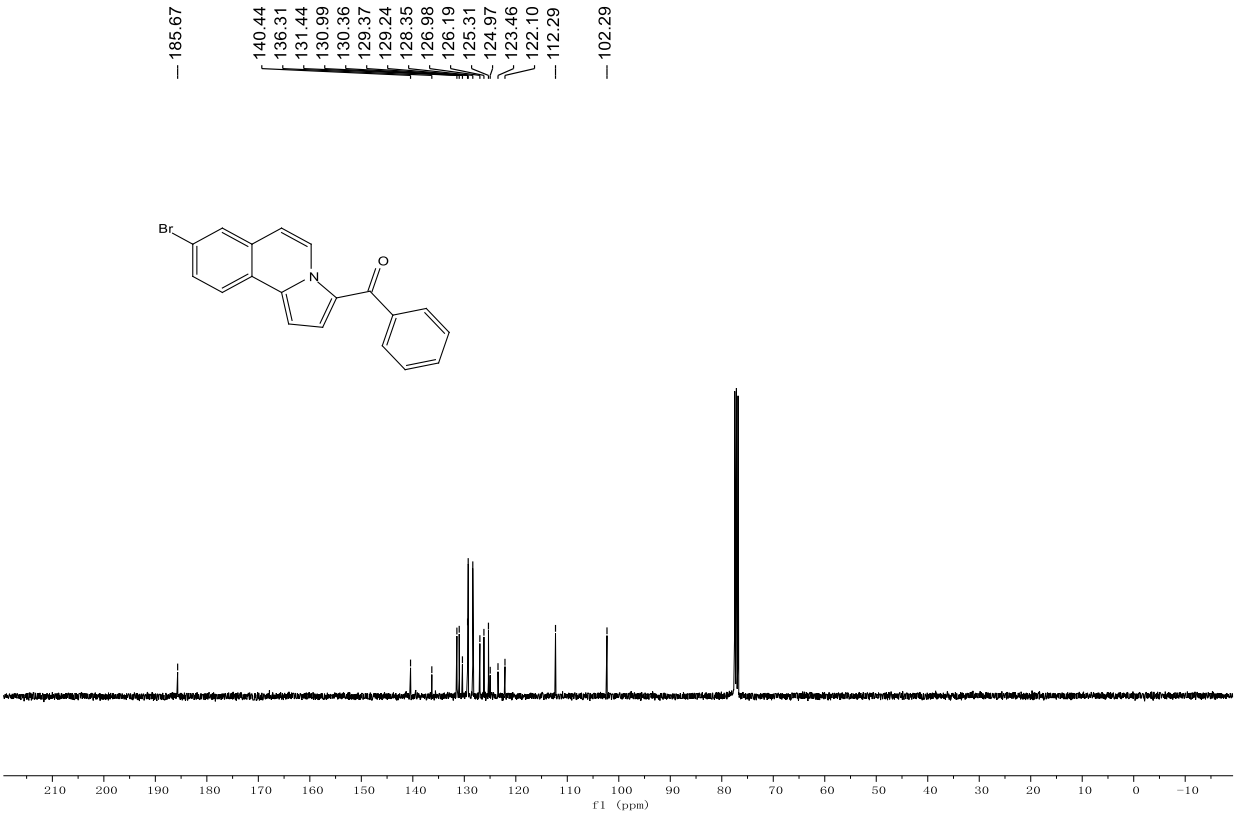
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5b**



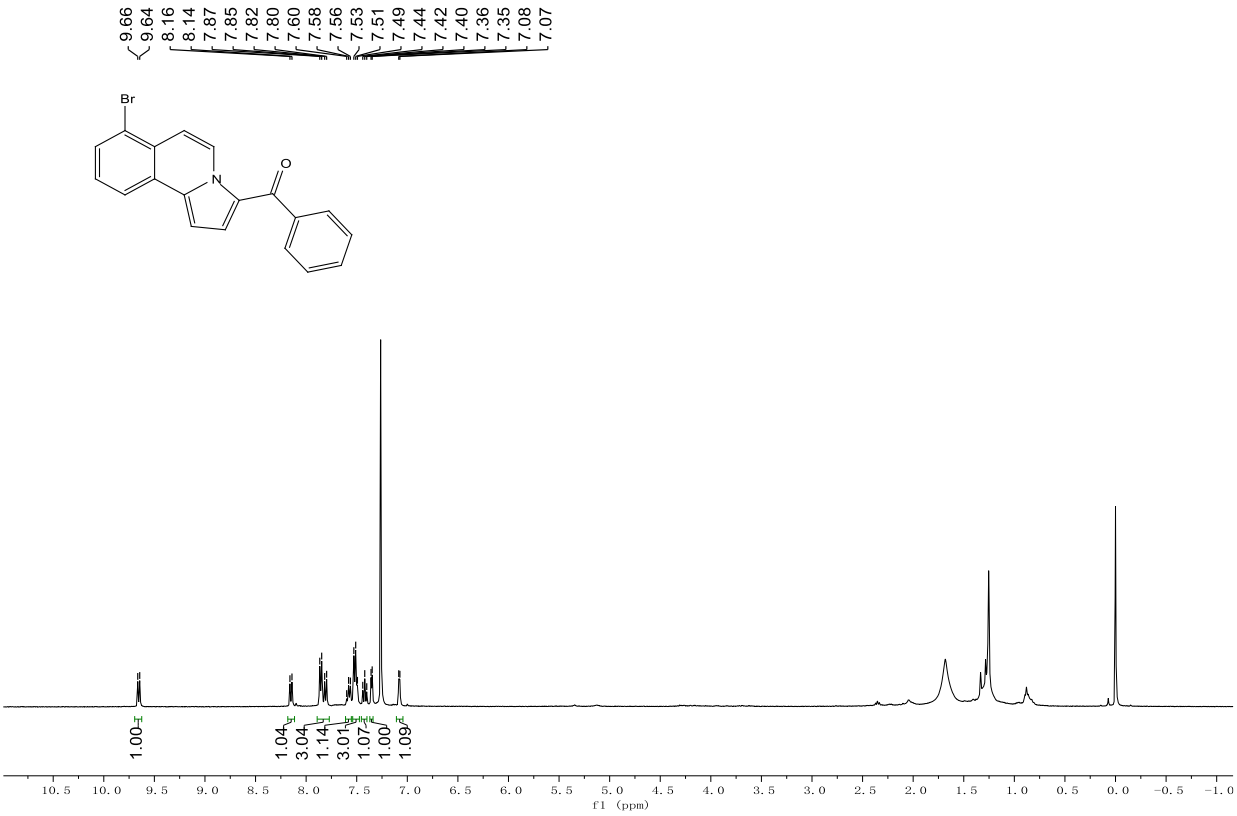
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5c**



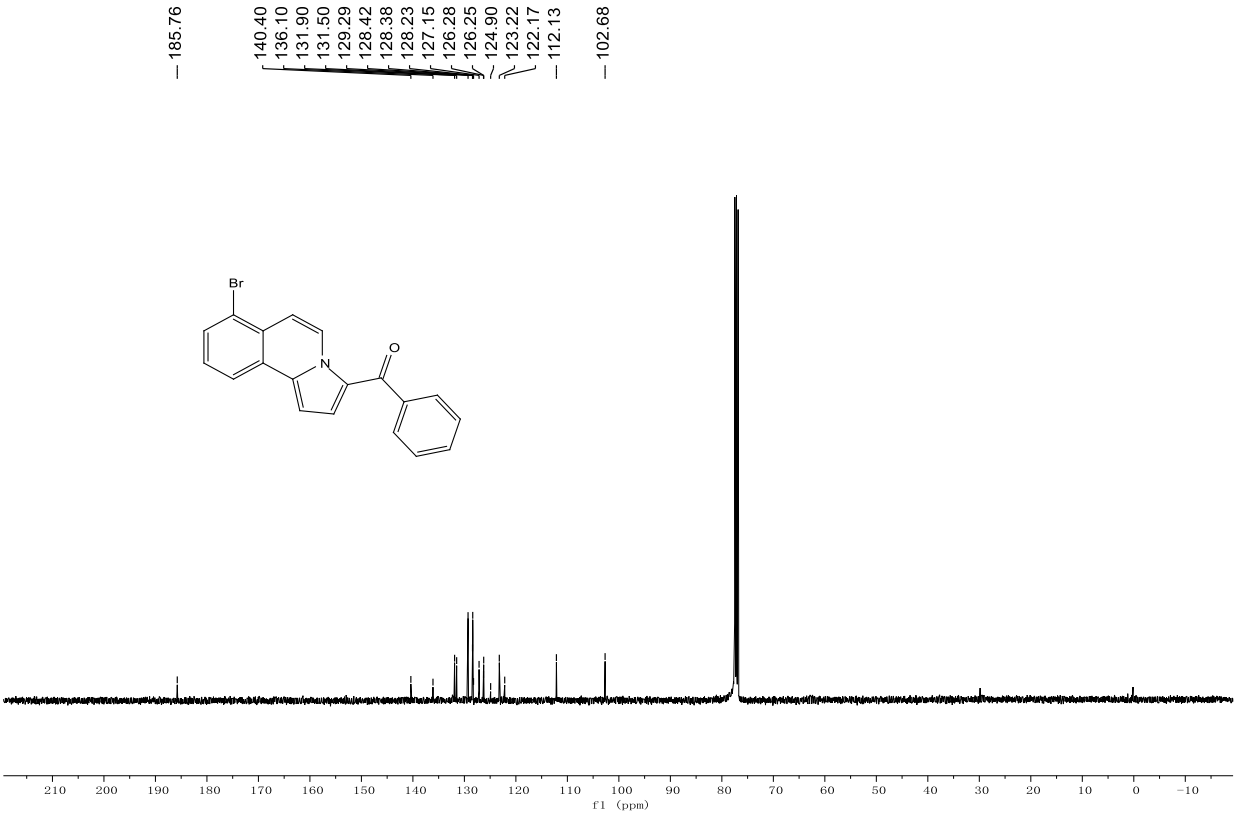
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5c**



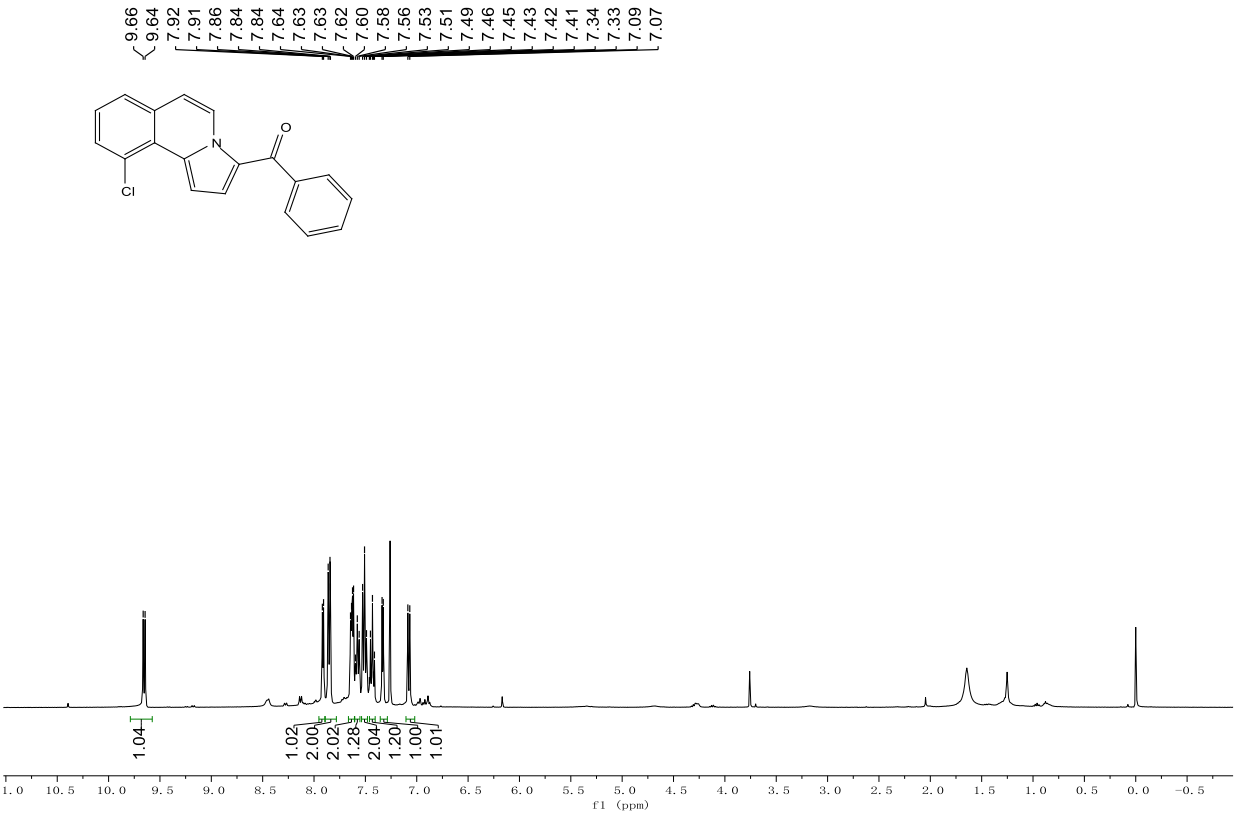
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5d**



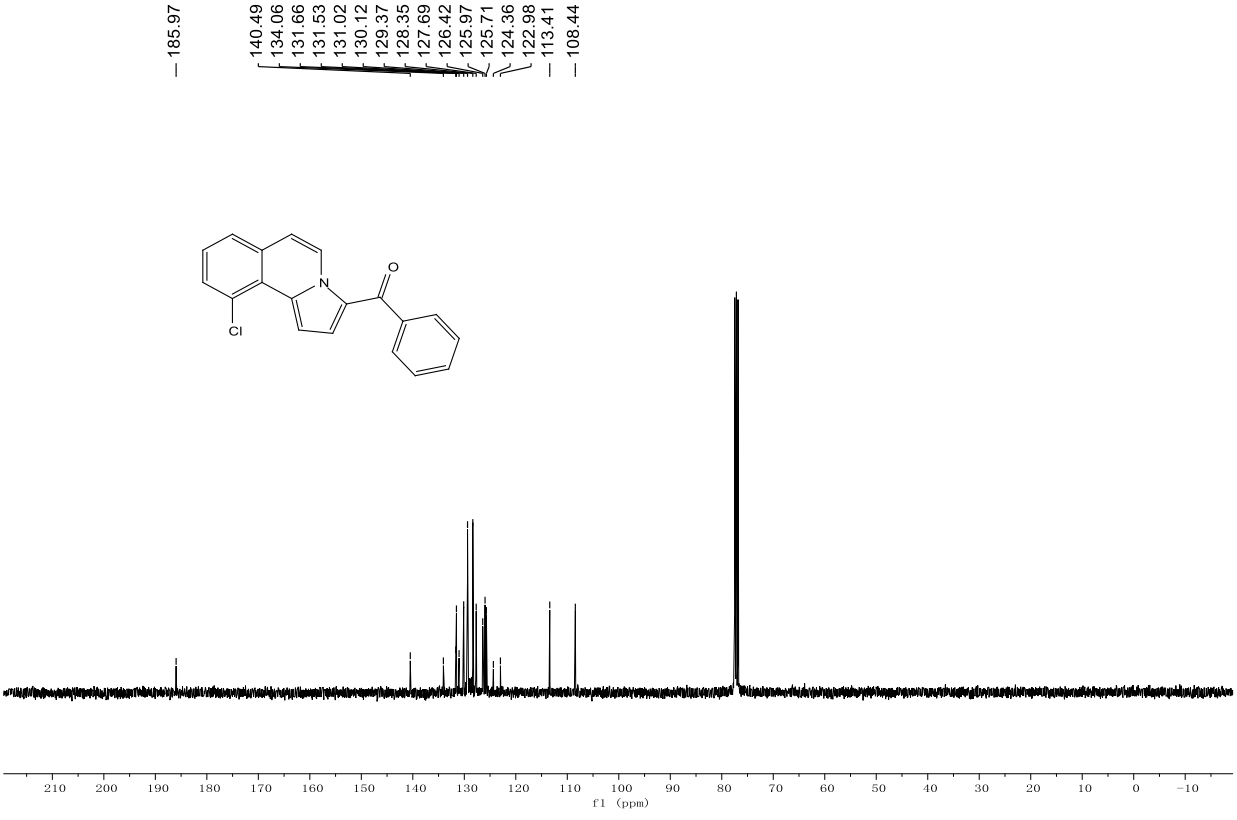
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5d**



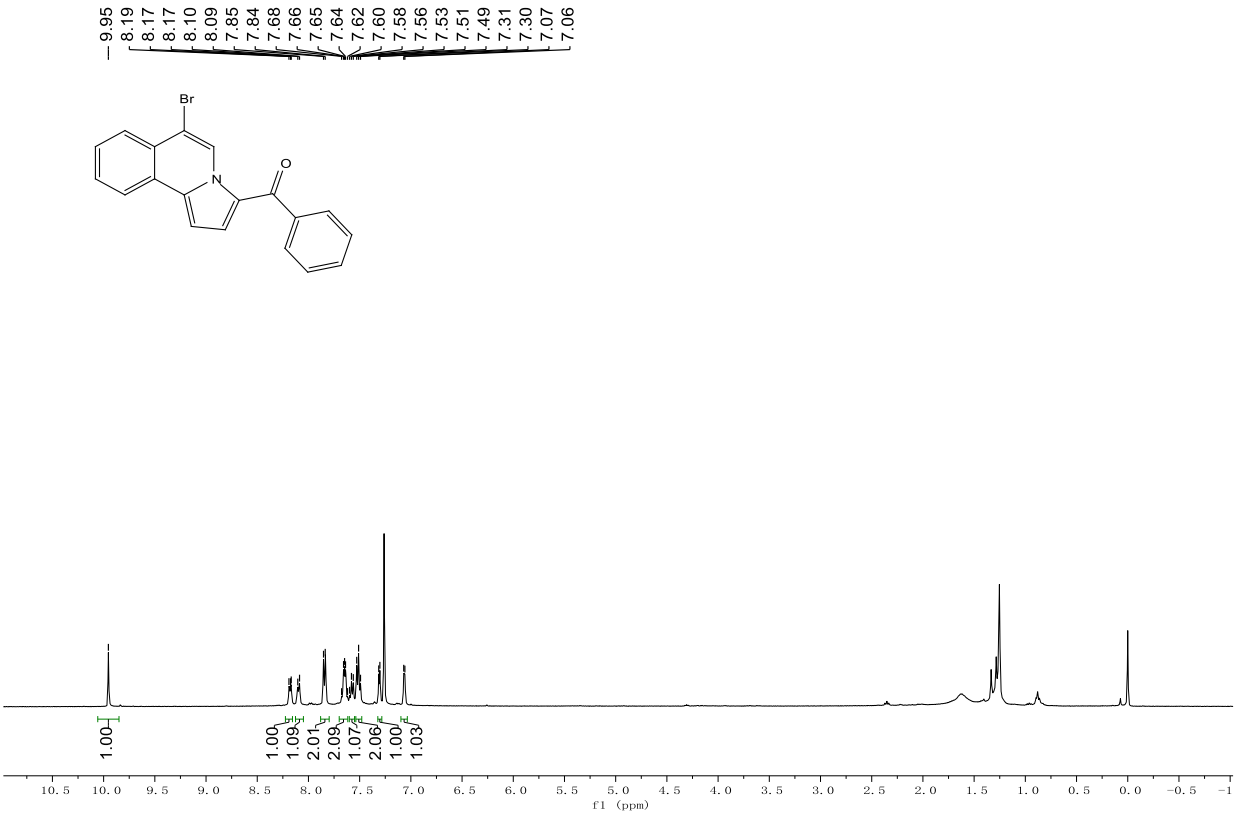
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5e**



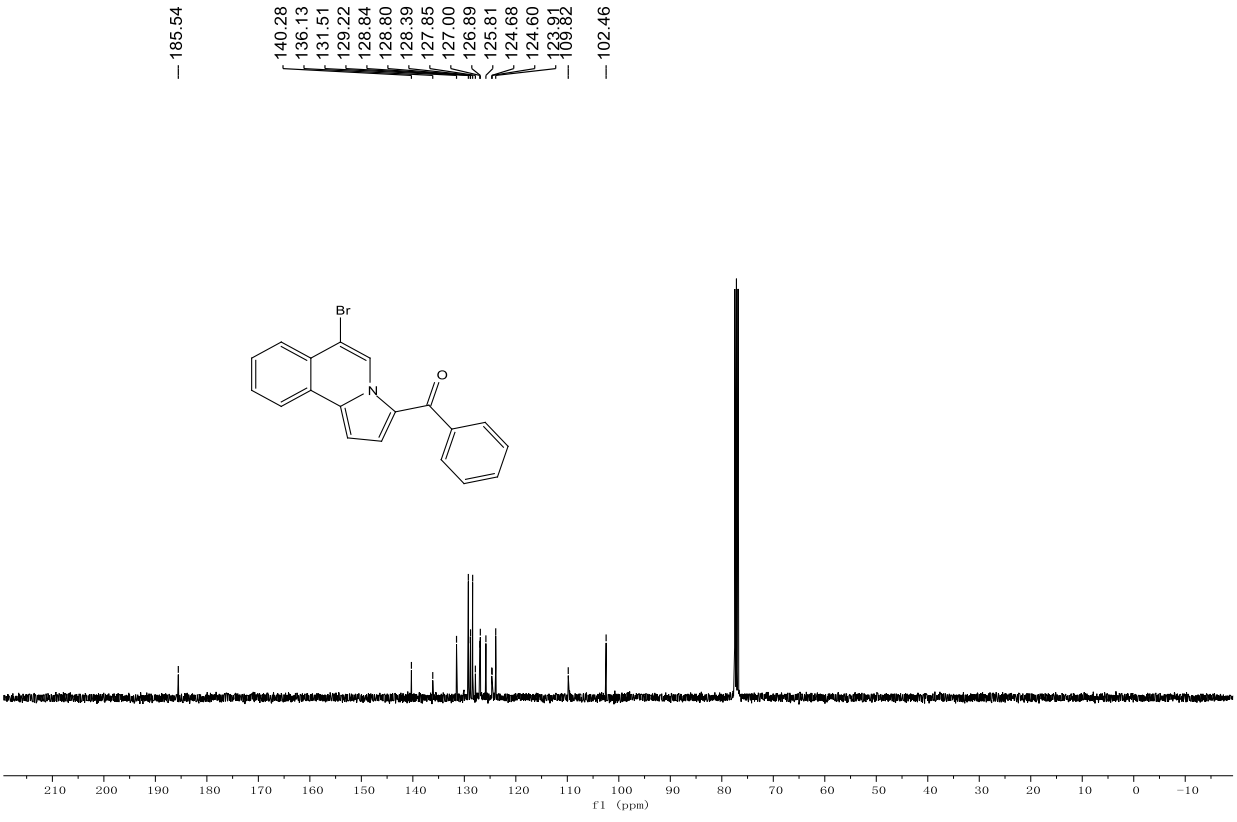
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5e**



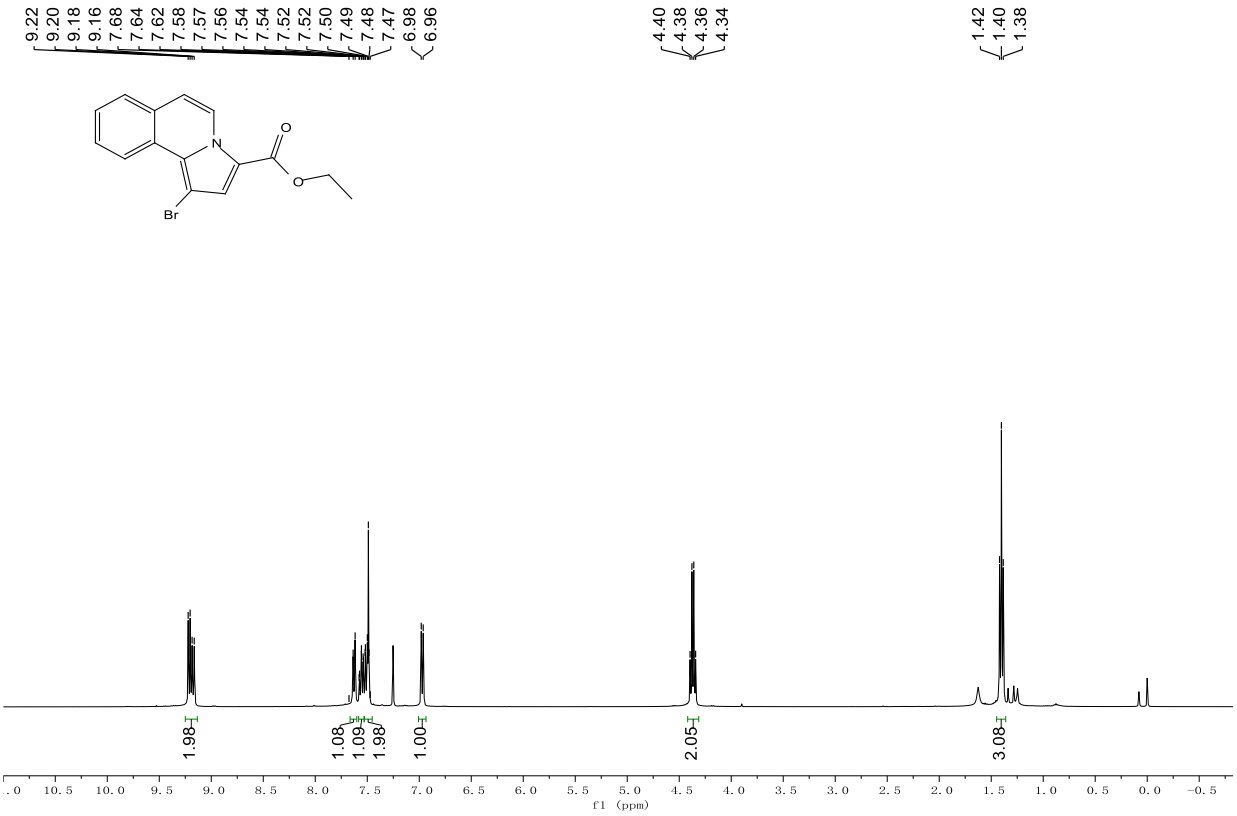
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5f**



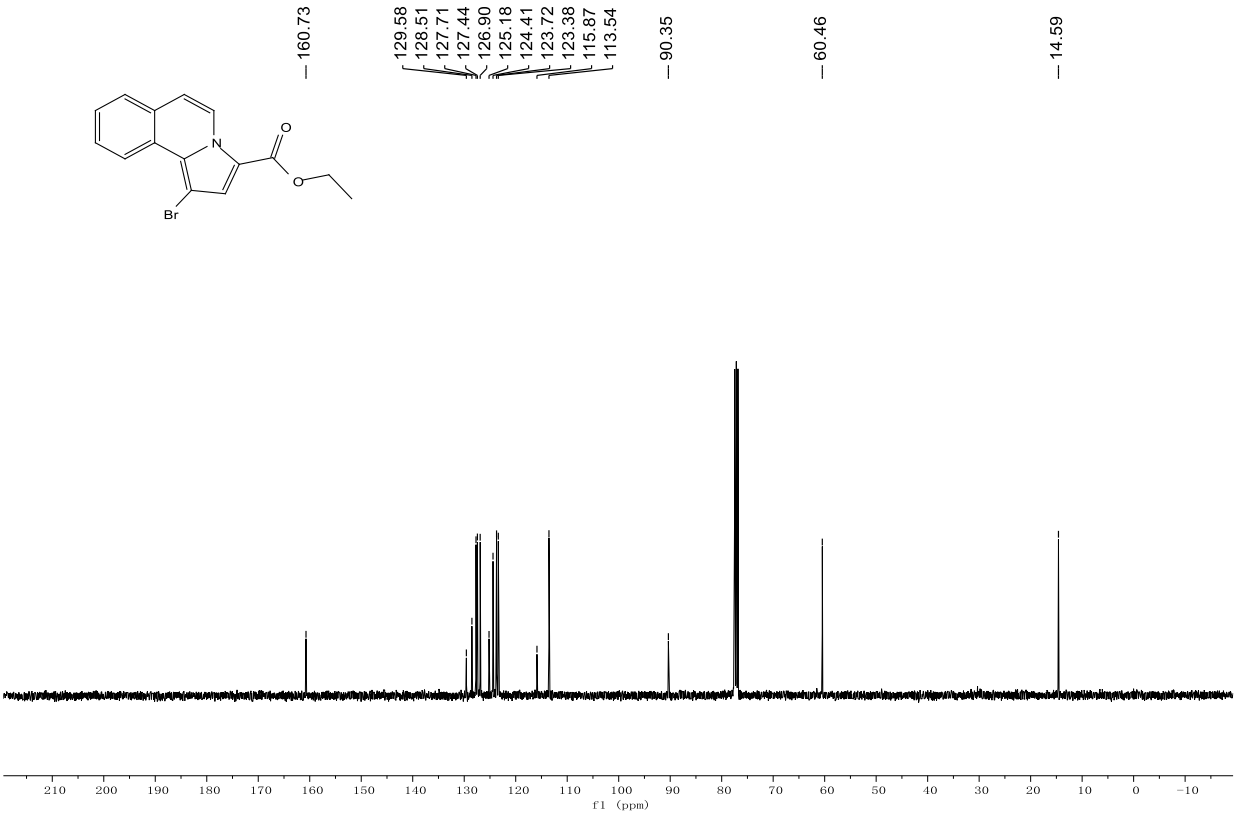
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5f**



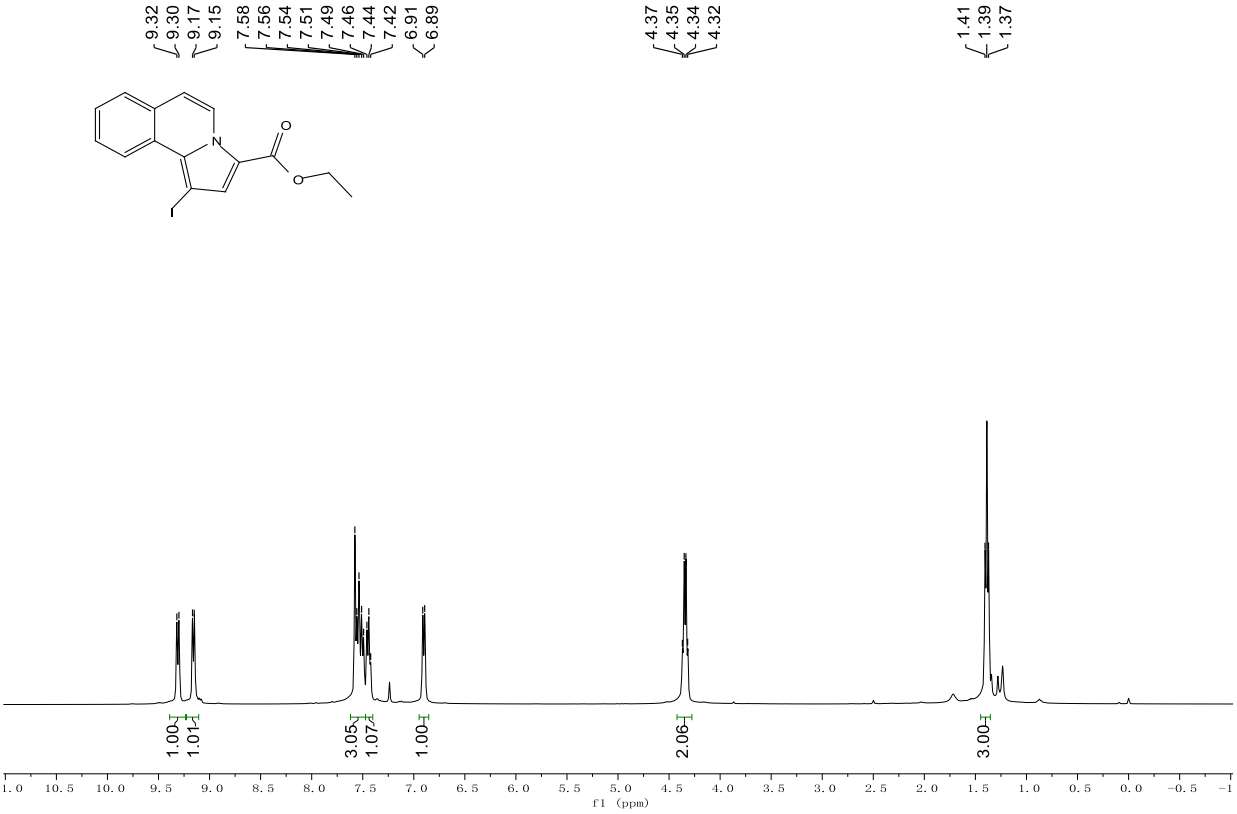
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8a**



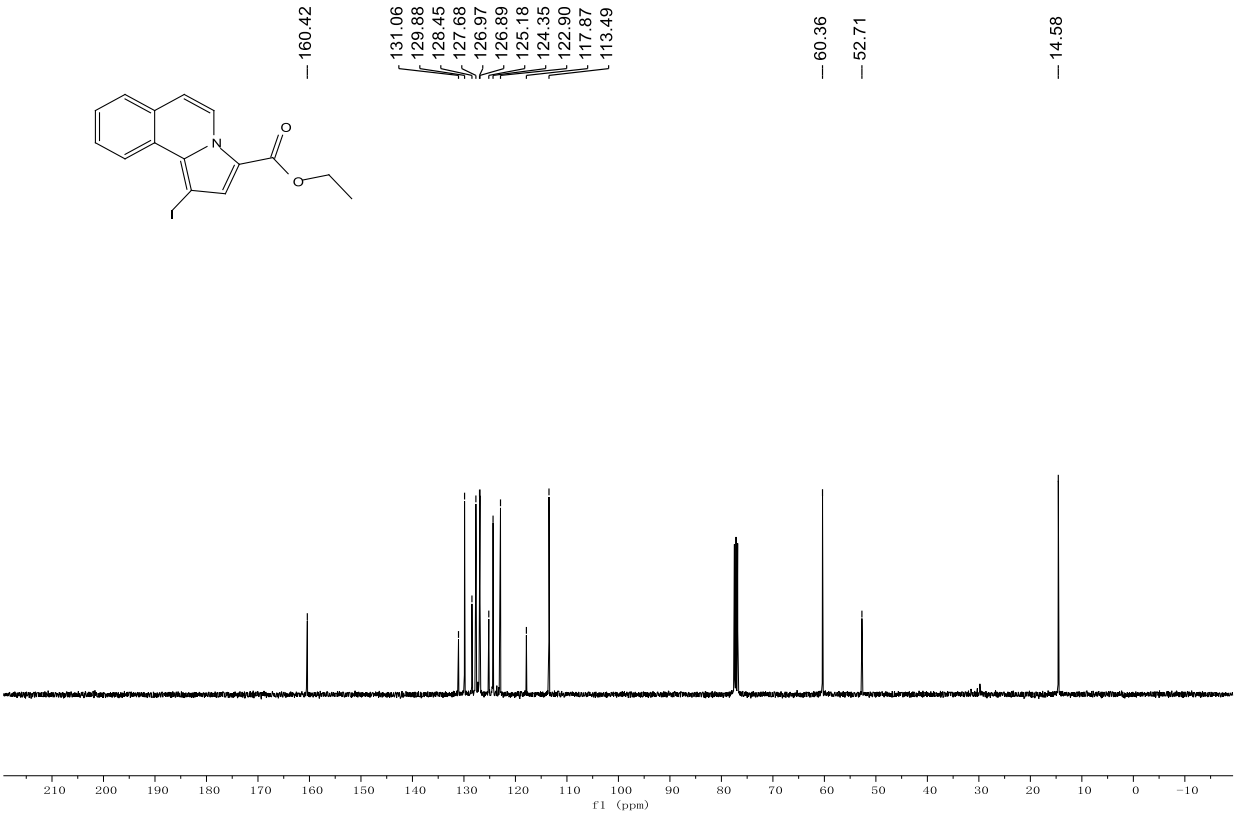
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8a**



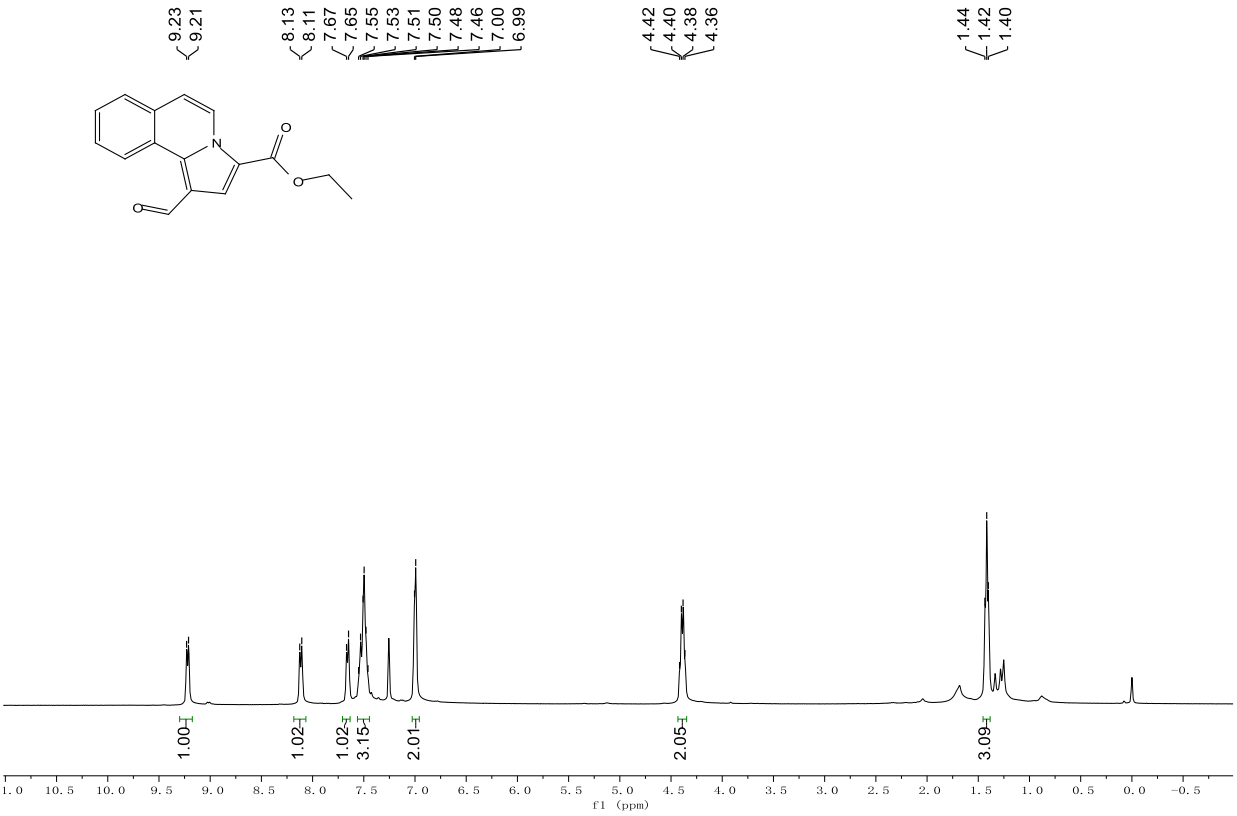
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8b**



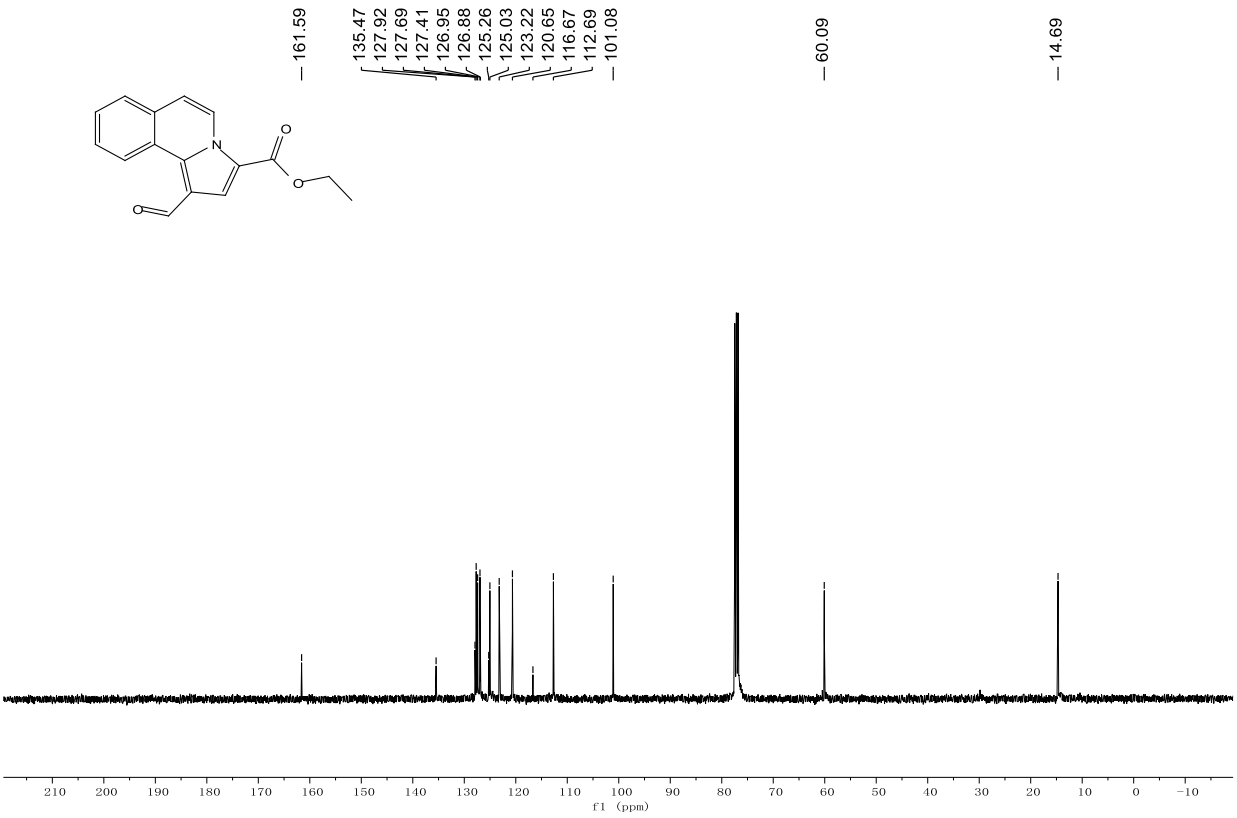
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8b**



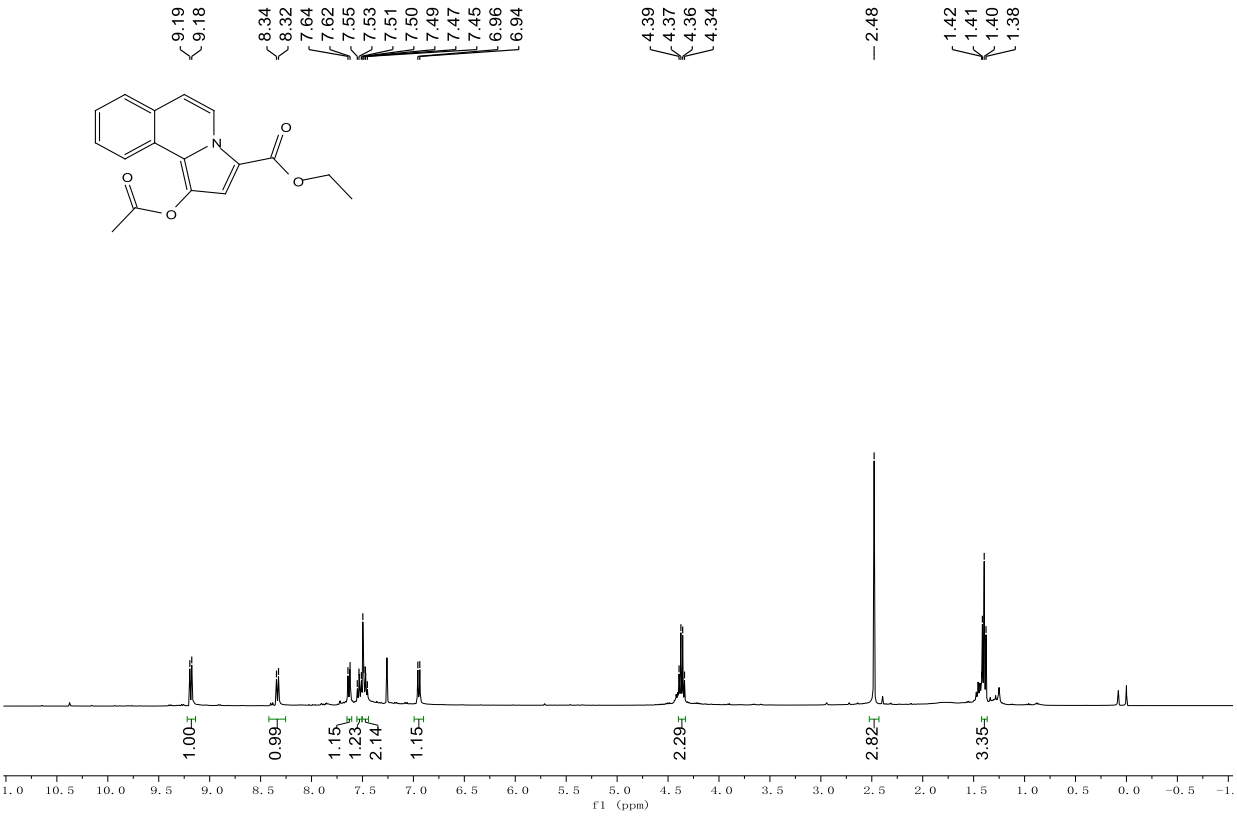
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8c**



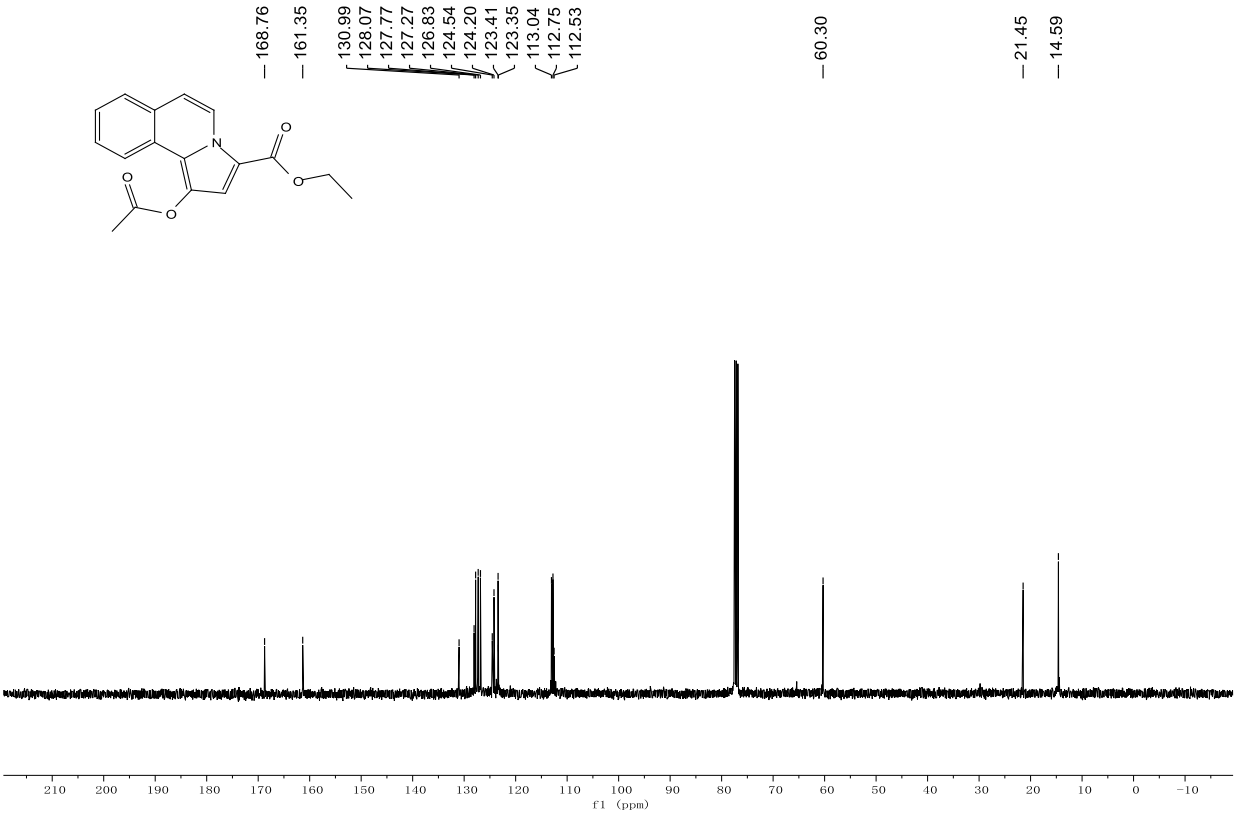
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8c**



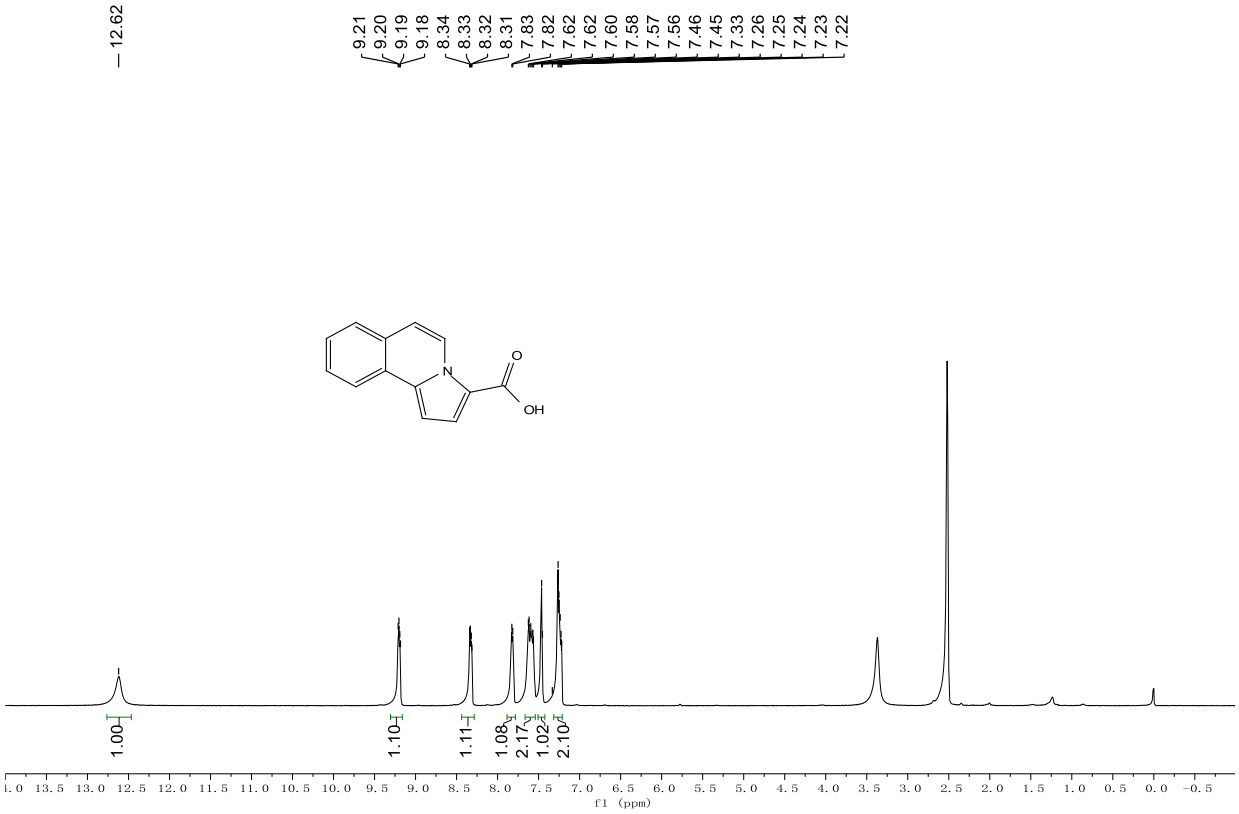
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8d**



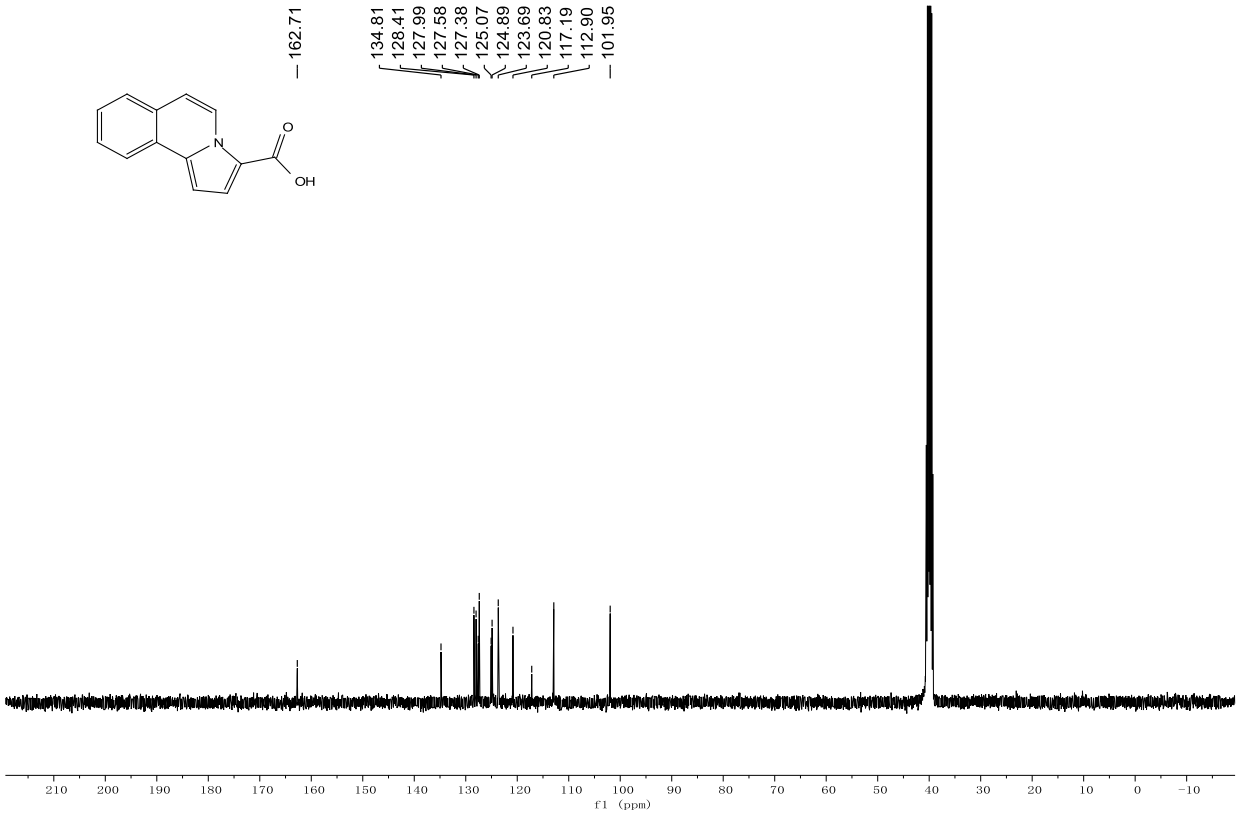
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8d**



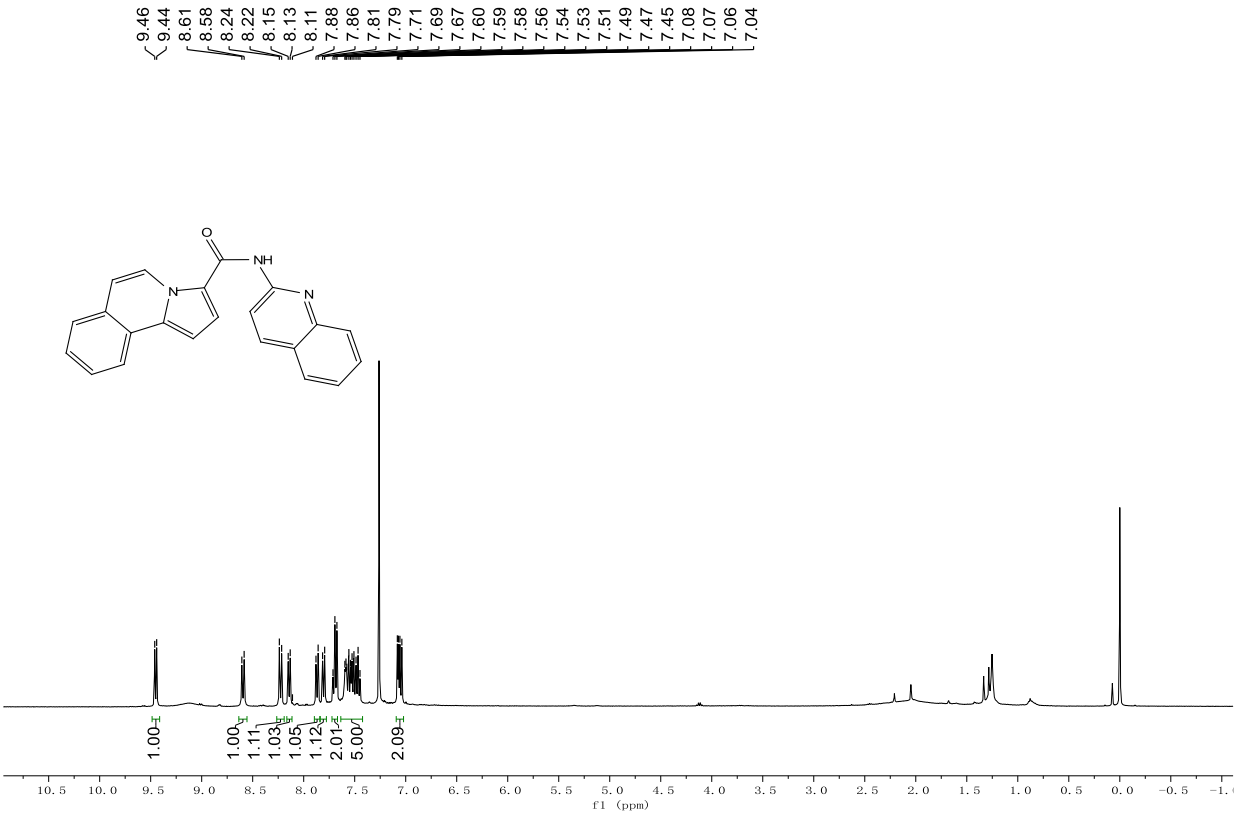
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8e**



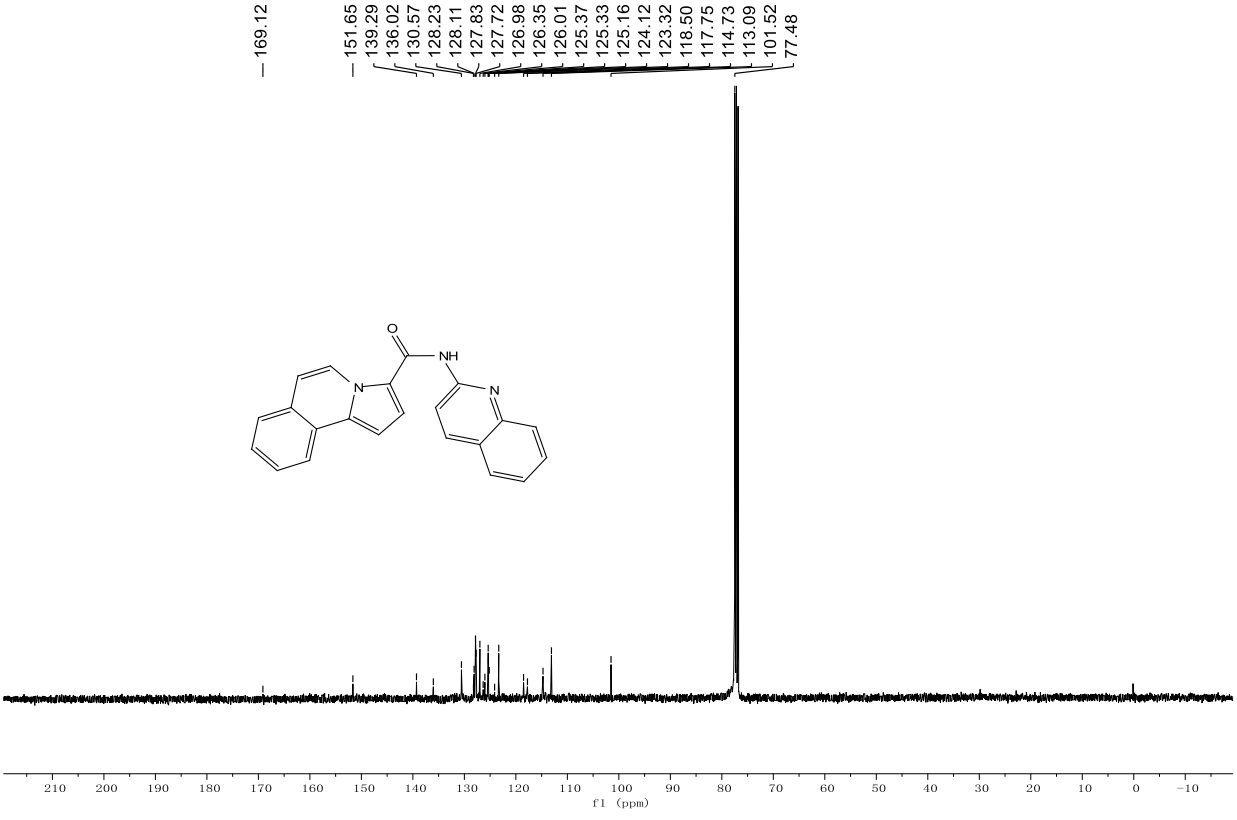
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8e**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8f**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8f**



4. References

1. Z.-J. Jia, C. G. Daniliuc, A. P. Antonchick and H. Waldmann, Phosphine-catalyzed dearomatizing [3+2] annulations of isoquinolinium methylides with allenes. *Chem. Commun.*, **2015**, *51*, 1054–1057.

2. K.Tanji, T. Sasahara, J. Suzuki, T. Higashino, Pyrazolopyridines. 1. Formylation and Acylation of Pyrazolo[1,5-*a*]pyridines. *Heterocycles*, **1993**, *35*, 915.