

Supplementary Information

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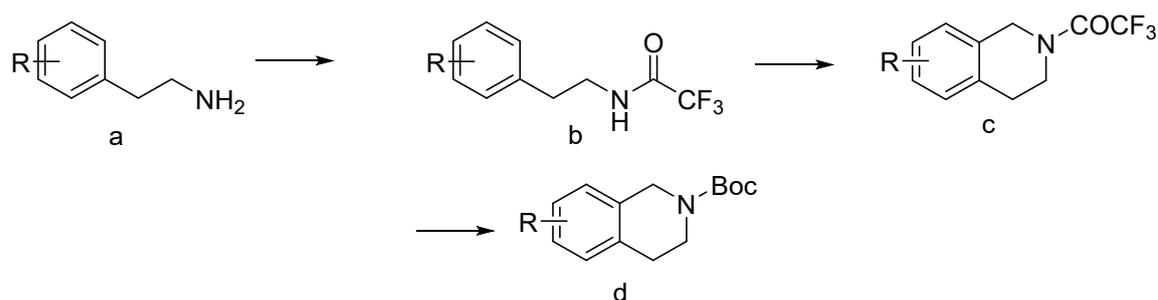
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1. General information

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. Flash column chromatography was carried out using commercially available 300-400 mesh silica gel under pressure with either petrol in ethyl acetate or dichloromethane in methanol as the eluents. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-300 (300 MHz) NMR spectrometer. ^1H NMR spectra are reported in parts per million-(ppm) downfield from an internal standard, tetramethylsilane (0 ppm). ^1H chemical shifts are reported with CDCl_3 (7.27 ppm) as internal standards. ^{13}H chemical shifts are reported with CDCl_3 (77.0 ppm) as internal standards.

2. Experimental Section

2.1 Preparations of the substrates



Substrates **13a-20a** were synthesized according to the literature reported procedure¹ as shown in the above scheme.

Briefly, trifluoroacetic anhydride (5 mmol) was added dropwise to a stirred solution of **a** (4 mmol) and DIEA (8 mmol) in 50 mL of DCM at 0 °C. The solution was stirred at room temperature for 3 hours and then concentrated. The crude product was purified by flash chromatography on 300-400 mesh silica gel with PE/EtOAc (20:1) as the eluent to give **b**.

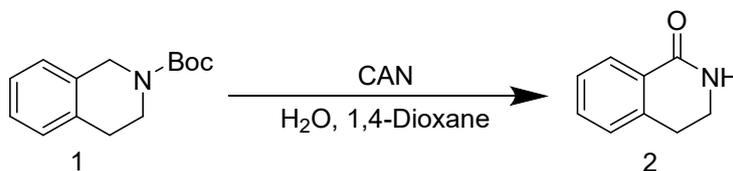
Amide **b** (3 mmol) was dissolved in a mixture of 4 mL of H_2SO_4 and 6 mL of CH_3COOH at 0 °C. After adding paraformaldehyde (4.5 mmol), the solution was stirred at room temperature for 18 hours and then diluted with 50 mL of water. The pH value of the solution was adjusted in 7 by slowly adding NaHCO_3 , then the solution was

extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and then filtered through celite. The solvent was evaporated and the obtained crude product **c** was used in next step without purification.

To a stirred solution of **c** (2 mmol) in 5 mL of ethanol was added 4 mL of 2 N NaOH solution. The mixture was stirred at room temperature for 2 hours and then evaporated to remove EtOH. The residue was suspended in 15 mL of 1,4-dioxane and then Boc₂O (2.2 mmol) was added to this mixture. The mixture was stirred at room temperature for 8 hours, and then extracted with EtOAc (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and then filtered through celite. The solvent was evaporated and the residue was purified by flash chromatography on 300-400 mesh silica gel with PE/EtOAc (20:1) as the eluent to give tetrahydroisoquinoline **d**.

Substrates **21a-25a** were prepared according to literature reported methods^{2,3}.

2.2 Synthesis of 3,4-dihydroisoquinolin-1(2H)-one (**2**) by oxidation of compound **1** by CAN.



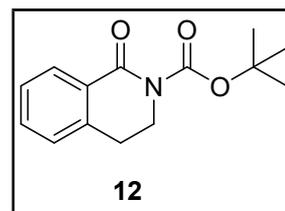
To a stirred mixture of **1** (247 mg, 1 mmol) in 3 mL of H₂O and 3 mL of 1,4-dioxane was added CAN (4 mmol). The mixture was stirred at room temperature until TLC indicated that compound **1** has been completely consumed. The mixture was diluted with 15 mL of water and then extracted with dichloromethane (20 mL × 3). The combined organic layers were washed subsequently with saturated NaHCO₃ solution and brine, dried over anhydrous Na₂SO₄ and filtered through celite. The solvent was evaporated and the residue was purified by flash chromatography on 300-400 mesh silica gel with PE/EtOAc (1:1) as the eluent to give **2** (83 mg, 56%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ: 8.07 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.51 – 7.31 (m, 2H), 7.27 – 7.19 (m, 1H), 3.59 (td, *J* = 6.6 Hz, 2H), 3.00 (t, *J* = 6.6 Hz, 2H); ¹³C NMR (300 MHz, CDCl₃) δ: 160.43, 136.36, 131.11, 128.50, 127.45, 127.26, 127.11, 47.36, 25.03.

2.3 General procedure for co-oxidation of the substrates with CAN-NaBrO₃

To a stirred mixture of the substrate (1 mmol) in 3 mL of H₂O and 3 mL of 1,4-dioxane was added CAN (0.2 mmol) and NaBrO₃ (2 mmol). The mixture was stirred at room temperature or -10 °C until TLC indicated that the substrate has been completely consumed. The mixture was diluted with 15 mL of water and then extracted with dichloromethane (20 mL × 3). The combined organic layers were washed subsequently with saturated NaHCO₃ solution and brine, dried over anhydrous Na₂SO₄ and filtered through celite. The solvent was evaporated and the residue was purified by flash chromatography on 300-400 mesh silica gel with PE/EtOAc as the eluent to give the product.

***tert*-Butyl 1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (12).**

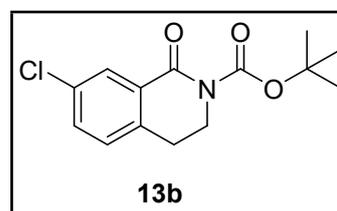
The reaction was run at room temperature. The eluent for chromatography was PE/EA 20/1. Colorless oil, yield 85%. ¹H NMR (300 MHz, CDCl₃) δ: 8.17 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.48 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 –



7.19 (m, 1H), 4.05 – 3.97 (m, 1H), 3.02 (t, *J* = 6.2 Hz, 2H), 1.60 (s, 9H); ¹³C NMR (300 MHz, CDCl₃) δ: 164.01, 153.17, 139.56, 132.89, 129.63, 129.35, 127.24, 127.19, 83.25, 44.46, 28.34, 28.12. MS (ESI) *m/z* calcd. for C₁₄H₁₇NO₃Na [M+Na]⁺: 270.12, found: 270.02.

***tert*-Butyl 7-chloro-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (13b).**

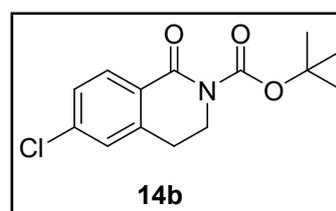
The reaction was run at room temperature. The eluent for chromatography was PE/EA 20/1. Yellow oil, yield 75%. ¹H NMR (300 MHz, CDCl₃) δ: 8.14 (d, *J* = 2.3 Hz, 1H), 7.44 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 4.04 – 3.96



(m, 2H), 2.99 (t, *J* = 6.2 Hz, 2H), 1.60 (s, 9H); ¹³C NMR (300 MHz, CDCl₃) δ: 162.82, 152.84, 137.80, 133.35, 132.84, 130.85, 129.43, 128.71, 83.57, 44.29, 28.08, 27.78. MS (ESI) *m/z* calcd. for C₁₄H₁₆ClNO₃Na [M+Na]⁺: 304.08, found: 304.16.

***tert*-Butyl 6-chloro-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (14b).**

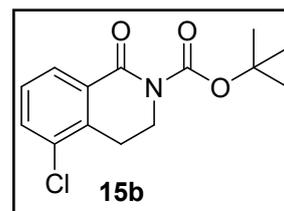
The reaction was run at room temperature. The eluent for



chromatography was PE/EA 20/1. Yellow oil, yield 73%. ^1H NMR (300 MHz, CDCl_3) δ : 8.08 (d, $J = 8.4$ Hz, 1H), 7.31 (dd, $J = 8.4, 2.1$ Hz, 1H), 7.24 – 7.14 (m, 1H), 4.03 – 3.93 (m, 2H), 2.98 (t, $J = 6.2$ Hz, 2H), 1.58 (s, 9H); ^{13}C NMR (300 MHz, CDCl_3) δ : 163.11, 152.84, 141.17, 139.07, 131.21, 127.81, 127.66, 127.19, 83.42, 44.23, 28.14, 28.06. MS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{16}\text{ClNO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 304.08, found: 304.16.

***tert*-Butyl 5-chloro-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (15b).**

The reaction was run at room temperature. The eluent for chromatography was PE/EA 20/1. Yellow oil, yield 74%. ^1H NMR (300 MHz, CDCl_3) δ : 8.11 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.54 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.32 (t, $J = 8.0$ Hz, 1H), 4.04 – 3.95

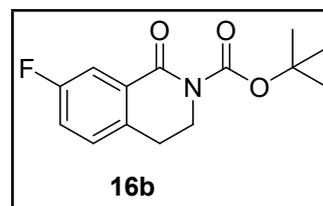


(m, 2H), 3.10 (t, $J = 6.3$ Hz, 2H), 1.59 (s, 9H); ^{13}C NMR (300 MHz, CDCl_3) δ : 162.99, 152.83, 137.45, 133.34, 132.53, 131.28, 128.26, 127.93, 83.55, 43.50, 28.09, 25.74. MS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{16}\text{ClNO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 304.08, found: 304.16.

***tert*-Butyl 7-fluoro-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (16b).**

The reaction was run at room temperature. The eluent for chromatography was PE/EA 20/1. Colorless oil, yield 73%.

^1H NMR (300 MHz, CDCl_3) δ 7.84 (dd, $J = 9.2, 2.3$ Hz, 1H), 7.23 – 7.13 (m, 2H), 4.05 – 3.96 (m, 2H), 2.99 (t, $J =$

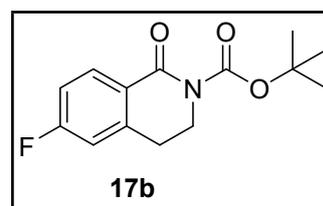


6.2 Hz, 2H), 1.60 (s, 9H); ^{13}C NMR (300 MHz, CDCl_3) δ 163.51, 162.97, 162.93, 160.25, 152.92, 135.27, 135.23, 131.24, 131.14, 128.99, 128.89, 120.29, 120.00, 116.12, 115.81, 83.54, 44.51, 28.09, 27.62. MS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{16}\text{FNO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 288.11, found: 288.10.

***tert*-Butyl 6-fluoro-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (17b).**

The reaction was run at room temperature. The eluent for chromatography was PE/EA 20/1. Colorless oil, yield 71%.

^1H NMR (300 MHz, CDCl_3) δ 8.16 (dd, $J = 8.7, 5.8$ Hz, 1H), 7.02 (td, $J = 8.7, 2.6$ Hz, 1H), 6.90 (dd, $J = 8.7, 2.6$ Hz,

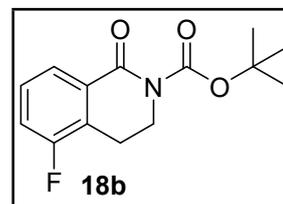


1H), 4.03 – 3.94 (m, 2H), 2.99 (t, $J = 6.2$ Hz, 2H), 1.57 (s, 9H); ^{13}C NMR (300 MHz, CDCl_3) δ 166.98, 163.60, 163.06, 152.95, 142.55, 142.43, 132.65, 132.52, 125.68, 125.65, 114.85, 114.56, 114.04, 113.75, 83.35, 44.28, 28.41, 28.39, 28.06. MS (ESI)

m/z calcd. for $C_{14}H_{16}FNO_3Na$ $[M+Na]^+$: 288.11, found: 288.10.

***tert*-Butyl 5-fluoro-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (18b).**

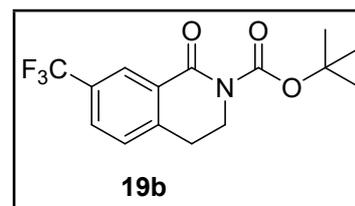
The reaction was run at room temperature. The eluent for chromatography was PE/EA 20/1. Colorless oil, yield 72%. 1H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 1H), 7.35 (td, J = 8.3, 5.4 Hz, 1H), 7.24 (td, J = 8.3, 1.1 Hz, 1H), 4.05 – 3.98 (m,



2H), 3.04 (t, J = 6.3 Hz, 2H), 1.60 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 163.00, 160.43, 152.97, 131.36, 131.30, 128.09, 127.98, 126.82, 126.57, 125.29, 125.24, 119.55, 119.27, 83.55, 43.80, 28.10, 21.29, 21.25. MS (ESI) m/z calcd. for $C_{14}H_{16}FNO_3Na$ $[M+Na]^+$: 288.11, found: 288.10.

***tert*-Butyl 1-oxo-7-(trifluoromethyl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (19b).**

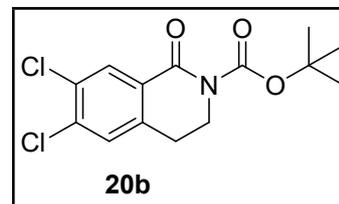
The reaction was run at room temperature. The eluent for chromatography was PE/EA 20/1. Colorless oil, yield 68%. 1H NMR (300 MHz, $CDCl_3$) δ 8.48 – 8.45 (m, 1H), 7.73 (dd, J = 7.9, 1.5 Hz, 1H), 7.38 (d, J = 7.9 Hz, 1H),



4.08 – 3.99 (m, 2H), 3.10 (t, J = 6.2 Hz, 2H), 1.61 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 162.70, 152.81, 143.15, 130.25, 130.02, 129.81, 129.30, 129.26, 129.21, 129.16, 128.03, 126.88, 126.83, 126.78, 125.47, 121.81, 83.75, 44.00, 28.26, 28.07. MS (ESI) m/z calcd. for $C_{15}H_{16}F_3NO_3Na$ $[M+Na]^+$: 338.11, found: 338.01.

***tert*-Butyl 6,7-dichloro-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (20b).**

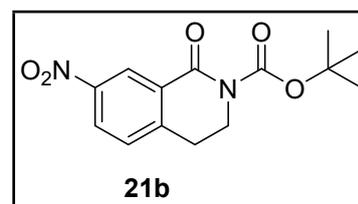
The reaction was run at room temperature. The eluent for chromatography was PE/EA 20/1. Yellow oil, yield 35%. 1H NMR (300 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.34 (s, 1H), 4.03 – 3.95 (m, 2H), 2.97 (t, J = 6.2 Hz, 2H), 1.58 (s, 9H);



^{13}C NMR (300 MHz, $CDCl_3$) δ 162.12, 152.60, 138.95, 137.18, 131.81, 131.40, 129.14, 129.11, 83.73, 44.15, 28.43, 28.05, 27.59. MS (ESI) m/z calcd. for $C_{14}H_{15}Cl_2NO_3Na$ $[M+Na]^+$: 338.04, found: 338.05.

***tert*-Butyl 7-nitro-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (21b).**

The reaction was run at room temperature. The eluent for

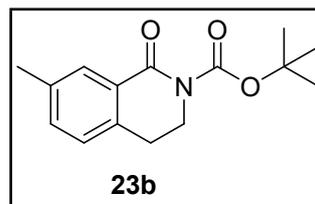


chromatography was PE/EA 20/1. Yellow oil, yield 38%. ^1H NMR (300 MHz, CDCl_3) δ 9.01 (d, $J = 2.4$ Hz, 1H), 8.32 (dd, $J = 8.3, 2.4$ Hz, 1H), 7.49 – 7.41 (m, 1H), 4.10 – 4.02 (m, 2H), 3.15 (t, $J = 6.2$ Hz, 2H), 1.61 (s, 9H); ^{13}C NMR (300 MHz, CDCl_3) δ 161.84, 152.52, 147.56, 146.08, 130.81, 128.71, 127.09, 124.91, 84.07, 43.76, 28.43, 28.06. MS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 315.11, found: 315.01.

***tert*-Butyl 7-methyl-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (23b).**

The reaction was run at room temperature. The eluent for chromatography was PE/EA 20/1. Colorless oil, yield 62%.

^1H NMR (300 MHz, CDCl_3) δ 7.98 (s, 1H), 7.31 – 7.25 (m, 1H), 7.11 (d, $J = 7.7$ Hz, 1H), 4.01 – 3.93 (m, 2H), 2.96 (t,

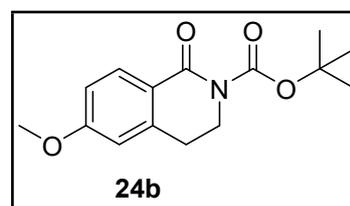


$J = 6.2$ Hz, 2H), 2.38 (s, 3H), 1.59 (s, 9H); ^{13}C NMR (300 MHz, CDCl_3) δ 164.24, 153.20, 136.94, 136.63, 133.75, 129.84, 129.07, 127.10, 83.12, 44.60, 28.11, 27.93, 21.06. MS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 284.14, found: 284.04.

***tert*-Butyl 6-methoxy-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (24b).**

The reaction was run at -10 °C. The eluent for chromatography was PE/EA 20/1. Colorless oil, yield

41%. ^1H NMR (300 MHz, CDCl_3) δ 8.10 (d, $J = 8.8$ Hz, 1H), 6.85 (dd, $J = 8.8, 2.6$ Hz, 1H), 6.66 (d, $J = 2.6$ Hz,

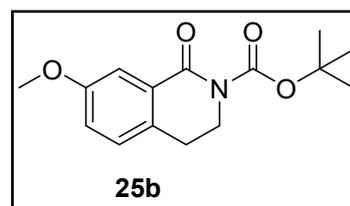


1H), 4.00 – 3.92 (m, 2H), 3.84 (s, 3H), 2.96 (t, $J = 6.2$ Hz, 2H), 1.58 (s, 9H); ^{13}C NMR (300 MHz, CDCl_3) δ 163.82, 163.16, 153.27, 141.87, 131.92, 122.05, 113.15, 111.75, 82.97, 55.46, 44.44, 28.70, 28.12. MS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 300.13, found: 300.03.

***tert*-Butyl 7-methoxy-1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate (25b).**

The reaction was run at -10 °C. The eluent for chromatography was PE/EA 20/1. Colorless oil. (40%,

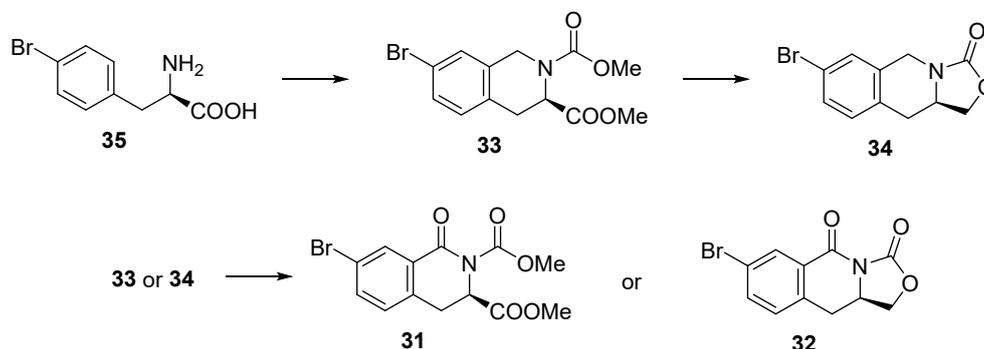
206mg); ^1H NMR (300 MHz, CDCl_3) δ 7.68 (d, $J = 2.7$ Hz, 1H), 7.13 (d, $J = 8.3$ Hz, 1H), 7.04 (dd, $J = 8.3, 2.7$



Hz, 1H), 4.03 – 3.94 (m, 2H), 3.85 (s, 3H), 3.00 – 2.90 (m, 2H), 1.60 (s, 9H); ^{13}C NMR (300 MHz, CDCl_3) δ 164.02, 158.78, 153.30, 131.96, 130.20, 128.36, 120.86, 112.17, 83.25, 55.54, 44.76, 28.12, 27.47. MS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$:

300.13, found: 300.02.

2.4 Synthesis of compounds 31 and 32



Dimethyl (*R*)-7-bromo-3,4-dihydroisoquinoline-2,3(1H)-dicarboxylate (33). A solution of compound **35** (50 g, 0.21 mol) in 300 mL of methanol was cooled to $-25\text{ }^{\circ}\text{C}$. To this solution was added 31 mL of SOCl_2 (0.43 mol) via dropping funnel. After the adding was finished, the solution was warmed to room temperature, stirred overnight and then concentrated. The residue was dissolved in 300 mL of water and the resulted solution was neutralized with NaHCO_3 until the pH was 8. To this mixture was added 200 mL of 1,4-dioxane, 26 g NaHCO_3 (0.32 mol) and 23.8 g methyl chloroformate (0.25 mol). The mixture was stirred at room temperature overnight and then extracted with ethyl acetate (300 mL \times 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered through celite. The solvent was evaporated and the residue was purified by flash chromatography on 300-400 mesh silica gel with PE/EtOAc (10:1) as the eluent to give a sticky oil. This oil was dissolved in 120 mL of acetic acid. To this solution was slowly added 80 mL of concentrated sulfuric acid and then followed by 12.6 g paraformaldehyde at $0\text{ }^{\circ}\text{C}$. The mixture was stirred at room temperature for 24 hours and then poured onto 500 g of ice. The mixture was stirred until the ice has completely melted. The mixture was extracted with EtOAc (300 mL \times 3). The combined organic layers were washed subsequently with 300 mL of water, 300 mL of saturated NaHCO_3 solution, and 300 mL of brine. Then the solution was dried over anhydrous Na_2SO_4 and filtered through celite. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (15:1) as the eluent to give compound **33** (42.5 g, 62% over three steps) as a colorless oil⁴. ^1H NMR (300 MHz, CDCl_3) δ 7.32 – 7.23 (m, 2H), 7.03 (d, $J = 8.0$ Hz, 1H), 5.08 (m, 1H), 4.76 (dd,

$J = 16.7, 7.9\text{Hz}, 1\text{H}$), 4.52 (dd, $J = 16.7, 7.9\text{ Hz}, 1\text{H}$), 3.79 (d, $J = 15.3\text{ Hz}, 3\text{H}$), 3.64 (s, 3H), 3.29 – 3.02 (m, 2H). MS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{14}\text{BrNO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 350.01, found: 350.10.

(R)-7-Bromo-1,5,10,10a-tetrahydro-3H-oxazolo[3,4-b]isoquinolin-3-one (34).

To a solution of compound **33** (24 g, 73.5 mmol) in 200 mL of dry THF was slowly added 45 mL of LiBH_4 solution (2 M in THF, 90 mmol) at 0°C . After the mixture was stirred at room temperature for 24 h, 20 mL of water was added dropwise to quench the reaction. The solvent was evaporated and the residue was dissolved in 200 mL of ethyl acetate. The solution was washed with brine, dried over anhydrous Na_2SO_4 and then filtered through celite. The filtrate was concentrated and the residue was purified by flash chromatography with PE/EtOAc (5:1) as the eluent to give compound **34** (16.7 g, 85%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.33 (d, $J = 8.2\text{ Hz}, 2\text{H}$), 7.04 (d, $J = 8.0\text{ Hz}, 1\text{H}$), 4.83 (d, $J = 17.2\text{ Hz}, 1\text{H}$), 4.61 (dd, $J = 8.7, 7.9\text{ Hz}, 1\text{H}$), 4.35 (d, $J = 17.2\text{ Hz}, 1\text{H}$), 4.17 (dd, $J = 8.7, 4.8\text{ Hz}, 1\text{H}$), 3.97 (ddt, $J = 10.7, 7.8, 4.5\text{ Hz}, 1\text{H}$), 2.99 – 2.76 (m, 2H). MS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{10}\text{BrNO}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 289.99, found: 290.00.

Dimethyl (R)-7-bromo-1-oxo-3,4-dihydroisoquinoline-2,3(1H)-dicarboxylate (31).

Compound **33** (16 g, 49 mmol) was oxidized according to the general oxidation method to give compound **31** (11.8 g, 71%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 8.27 (d, $J = 2.2\text{ Hz}, 1\text{H}$), 7.60 (dd, $J = 8.1, 2.2\text{ Hz}, 1\text{H}$), 7.11 (d, $J = 8.1\text{ Hz}, 1\text{H}$), 5.34 (dd, $J = 5.0, 3.4\text{ Hz}, 1\text{H}$), 3.97 (s, 3H), 3.64 (s, 3H), 3.44 – 3.28 (m, 2H). ^{13}C NMR (300 MHz, CDCl_3) δ 170.38, 160.95, 154.95, 136.40, 134.53, 132.37, 130.66, 129.29, 121.81, 56.51, 54.65, 52.49, 30.19. MS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{12}\text{BrNO}_5\text{Na}$ $[\text{M}+\text{Na}]^+$: 363.99, found: 364.10.

(R)-7-Bromo-10,10a-dihydro-3H-oxazolo[3,4-b]isoquinoline-3,5(1H)-dione (32).

Compound **34** (15 g, 56 mmol) was oxidized according to the general oxidation method to give compound **32** (11.5 g, 73%) as a colorless oil. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.03 (d, $J = 2.2\text{ Hz}, 1\text{H}$), 7.82 (dd, $J = 8.1, 2.2\text{ Hz}, 1\text{H}$), 7.41 (d, $J = 8.1\text{ Hz}, 1\text{H}$), 4.71 – 4.56 (m, 2H), 4.25 – 4.08 (m, 1H), 3.22 – 3.00 (m, 2H). ^{13}C NMR (300 MHz, $\text{DMSO}-d_6$) δ 160.04, 151.79, 138.13, 136.62, 131.22, 131.19, 130.86, 120.81,

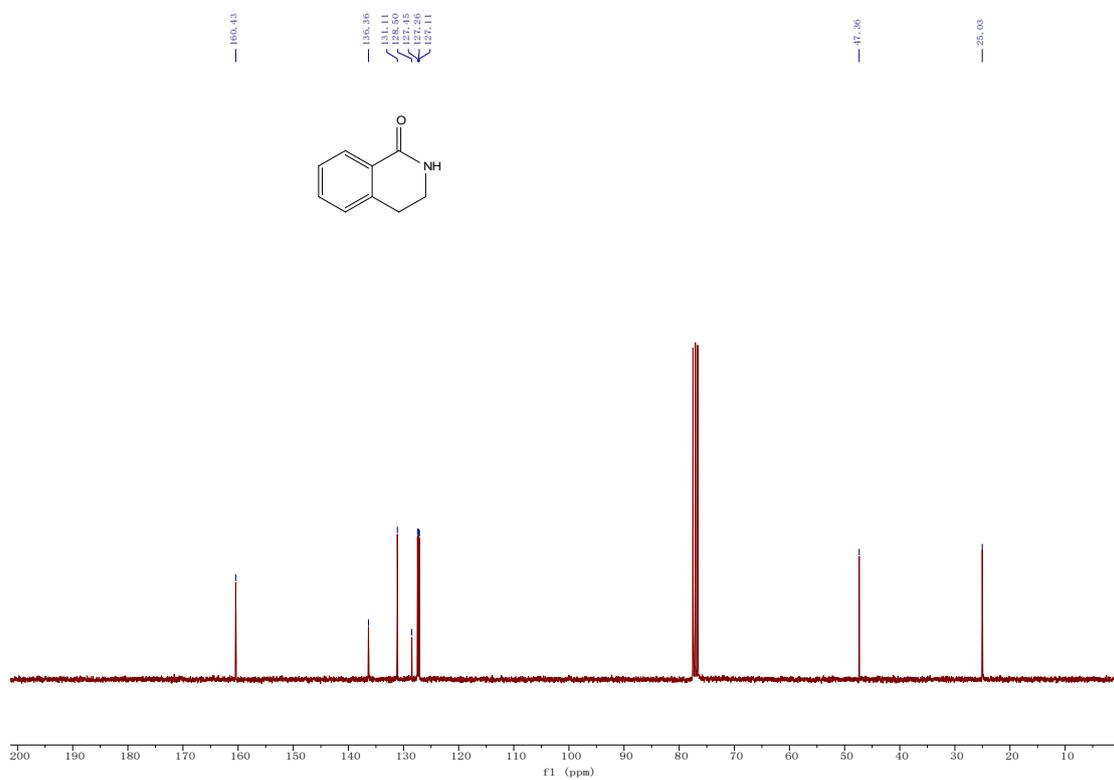
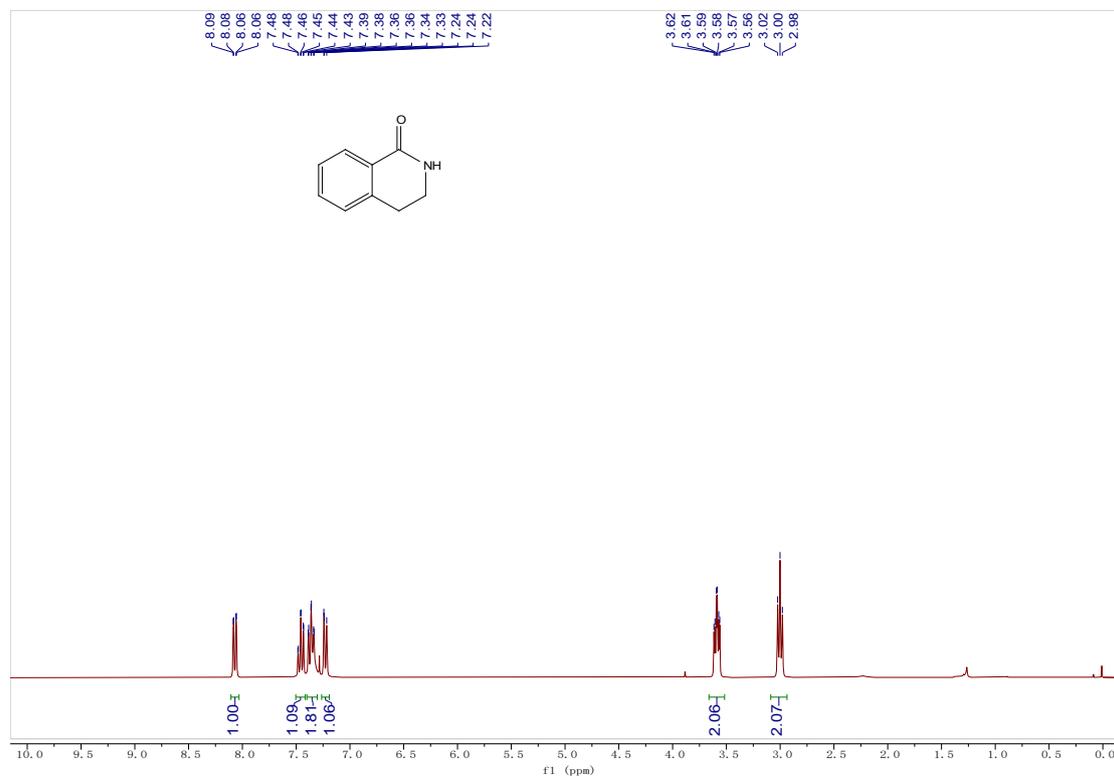
68.02, 53.38, 31.33. MS (ESI) m/z calcd. for $C_{11}H_8BrNO_3Na$ $[M+Na]^+$: 303.97, found: 304.10.

3. References

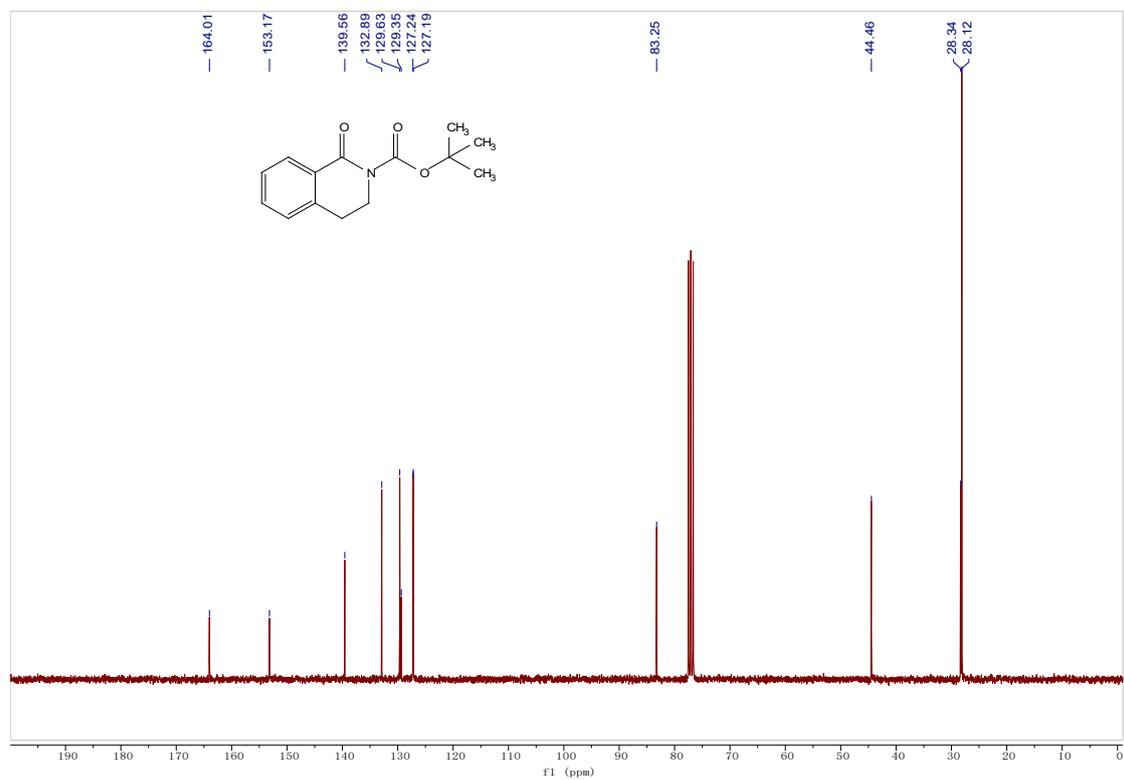
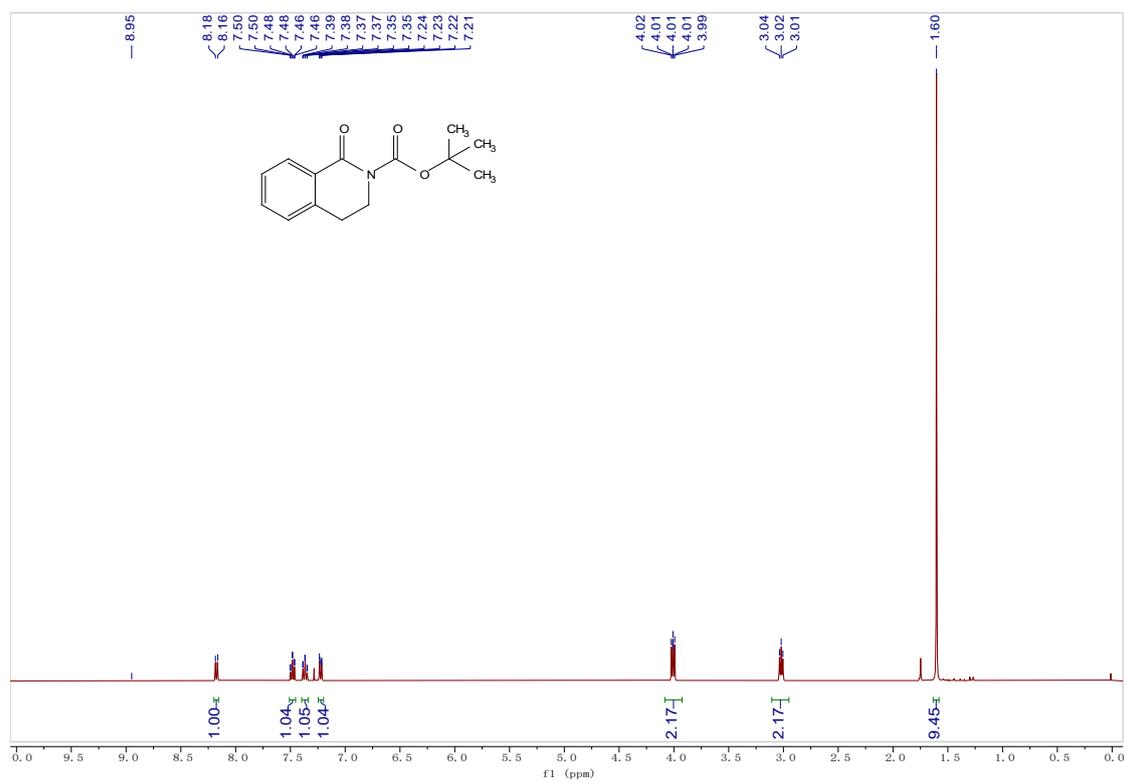
1. (a) A. Eberhard, E. Karl, G. Norbert, H. Albrecht, L. Gisela and R. Harald. WO 2019/088057 A1, 2019. (b) J.-Q. Li, S.-P. Peng and W.-P. Cai, CN 101712675 B, 2008.
2. (a) V. Boeckel, V. Galen and Rewinkel., WO 98/47876, 1998.
3. Buolamwini. John. K., WO 2004/060902 A2, 2004.
4. F. DEY, D. Ding, H.-T. Xu, W. Zhu and G. Zou., WO 2021/094301 A1, 2021

4. ^1H and ^{13}C NMR Spectra of Compounds

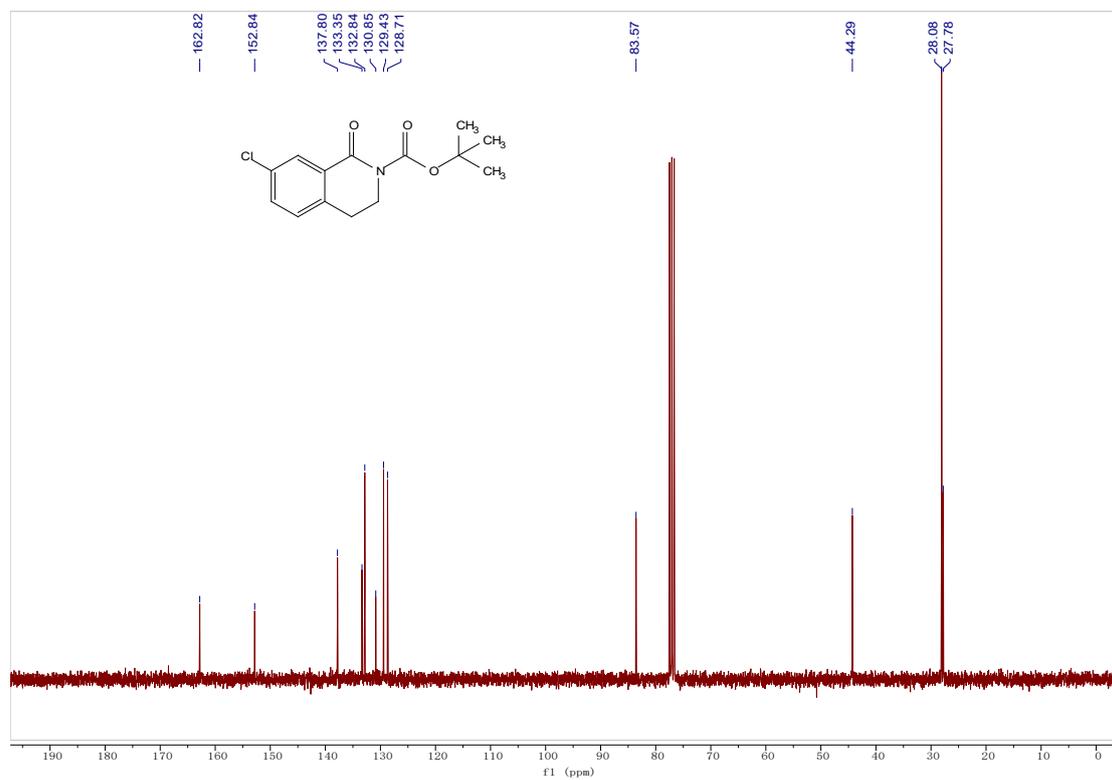
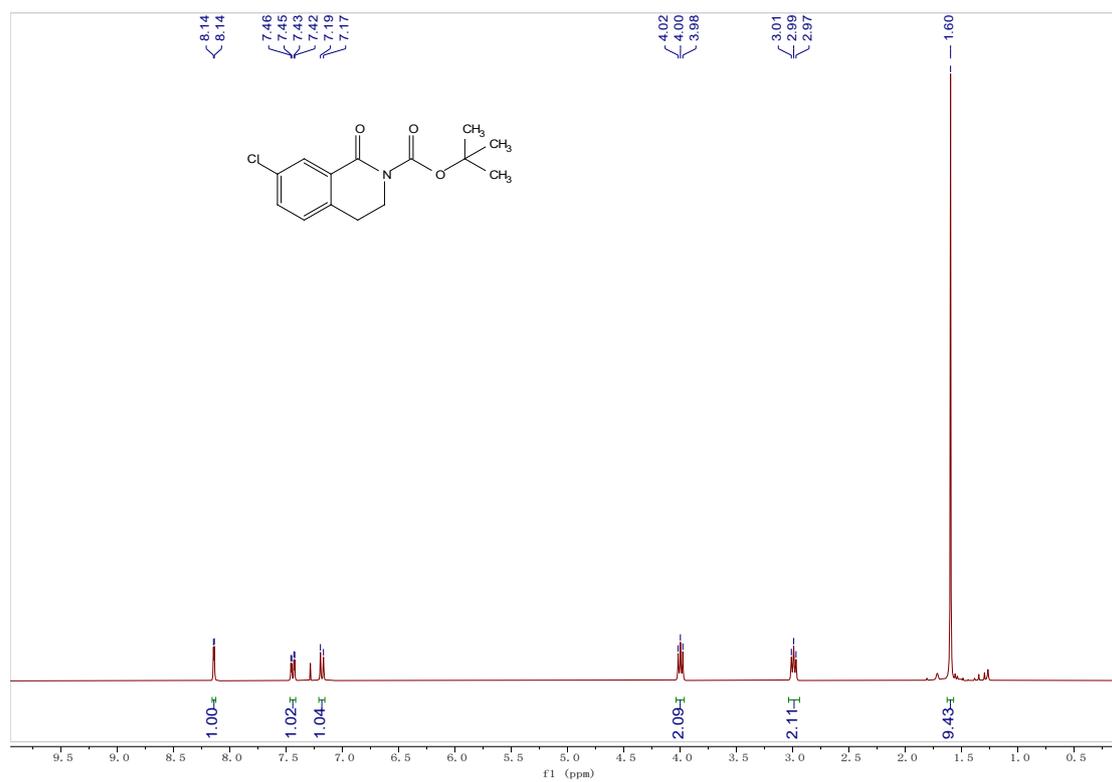
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **2**



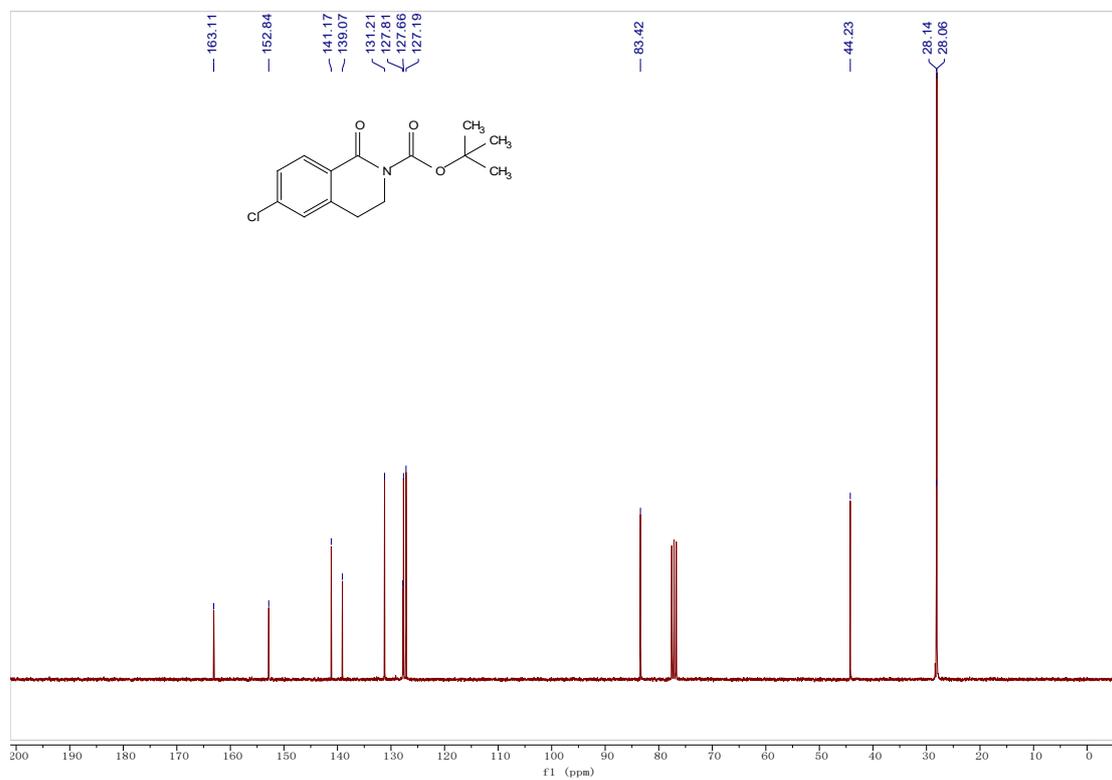
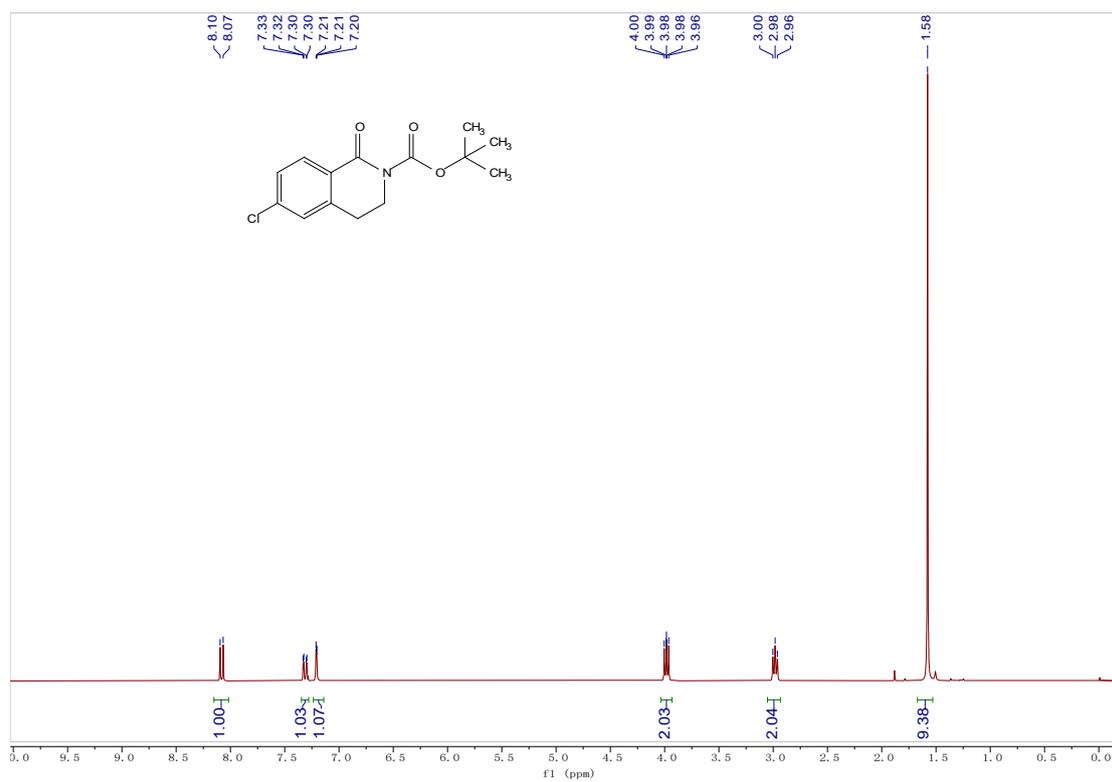
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **12**



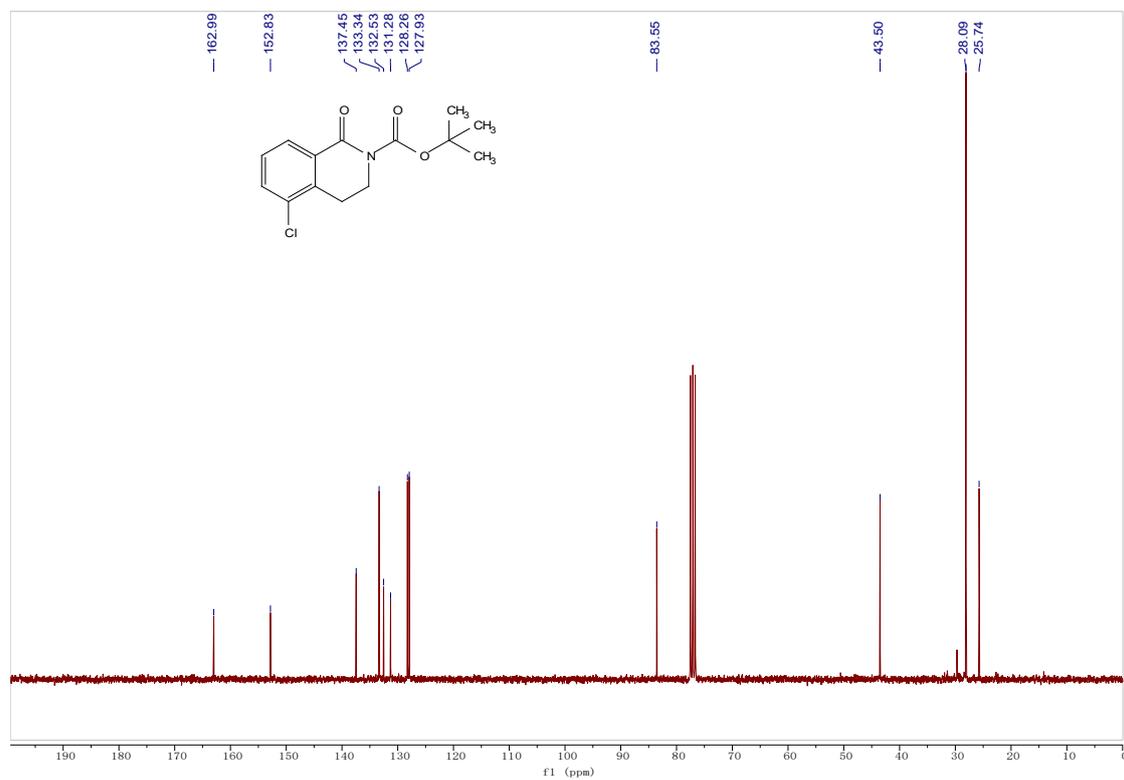
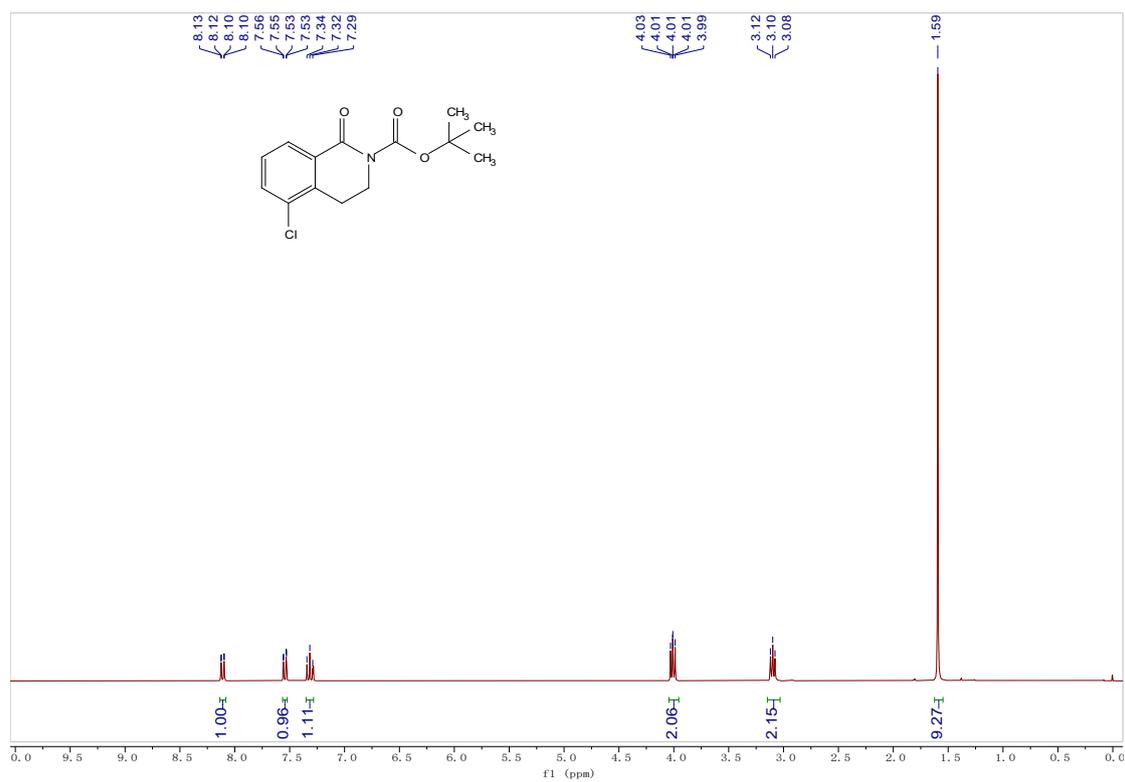
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **13b**



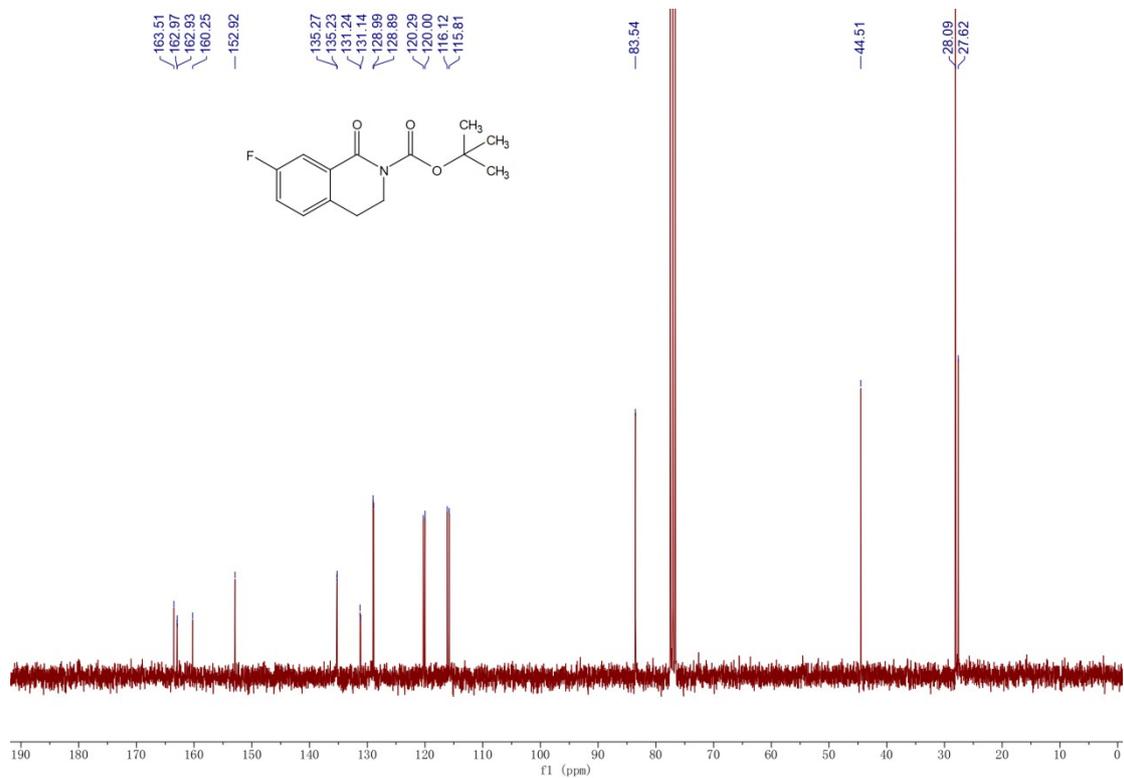
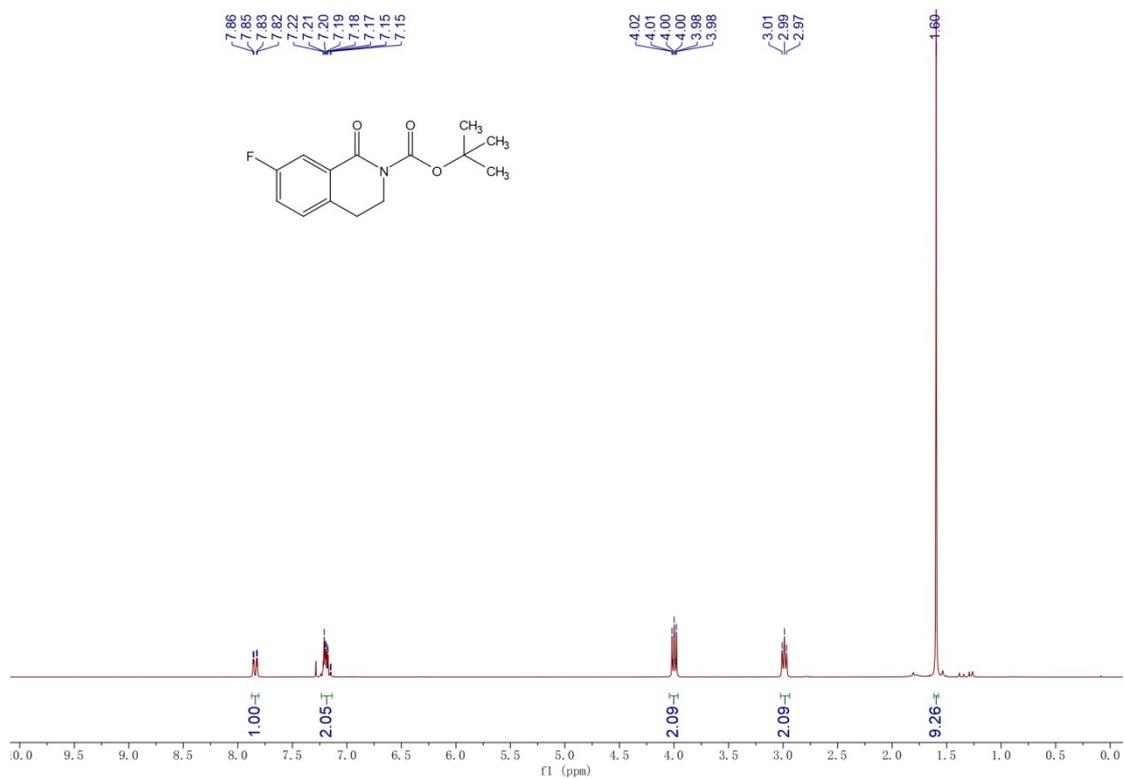
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **14b**



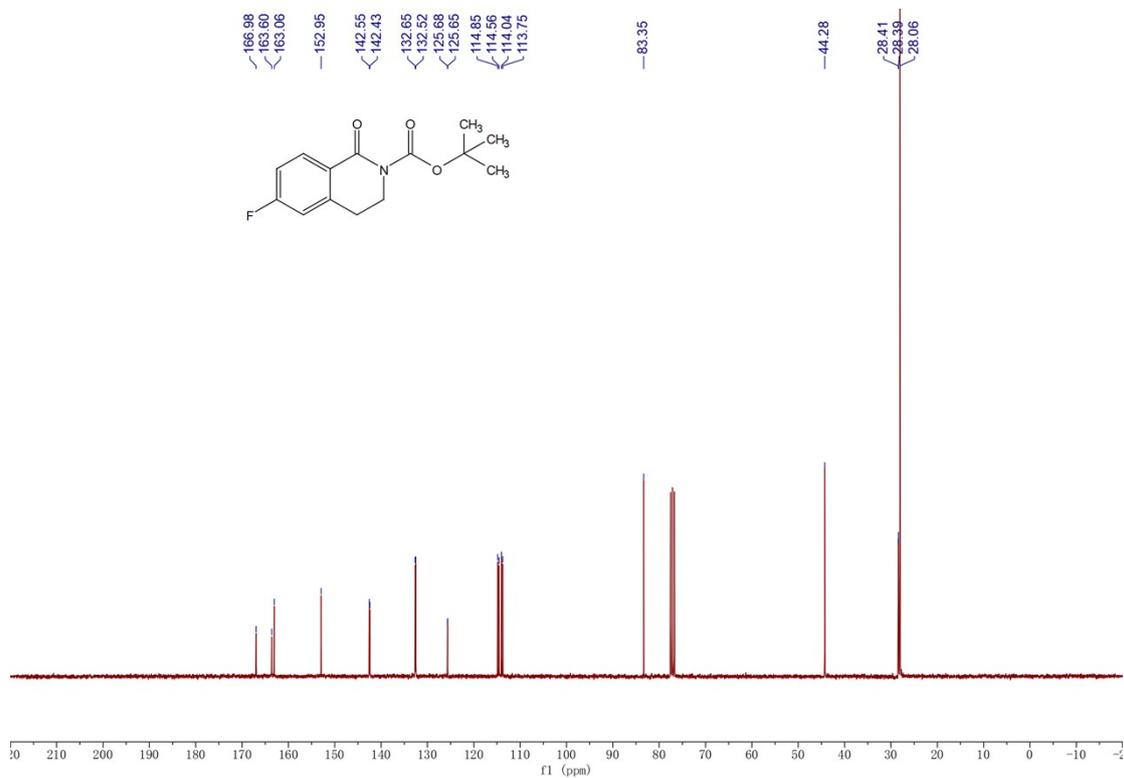
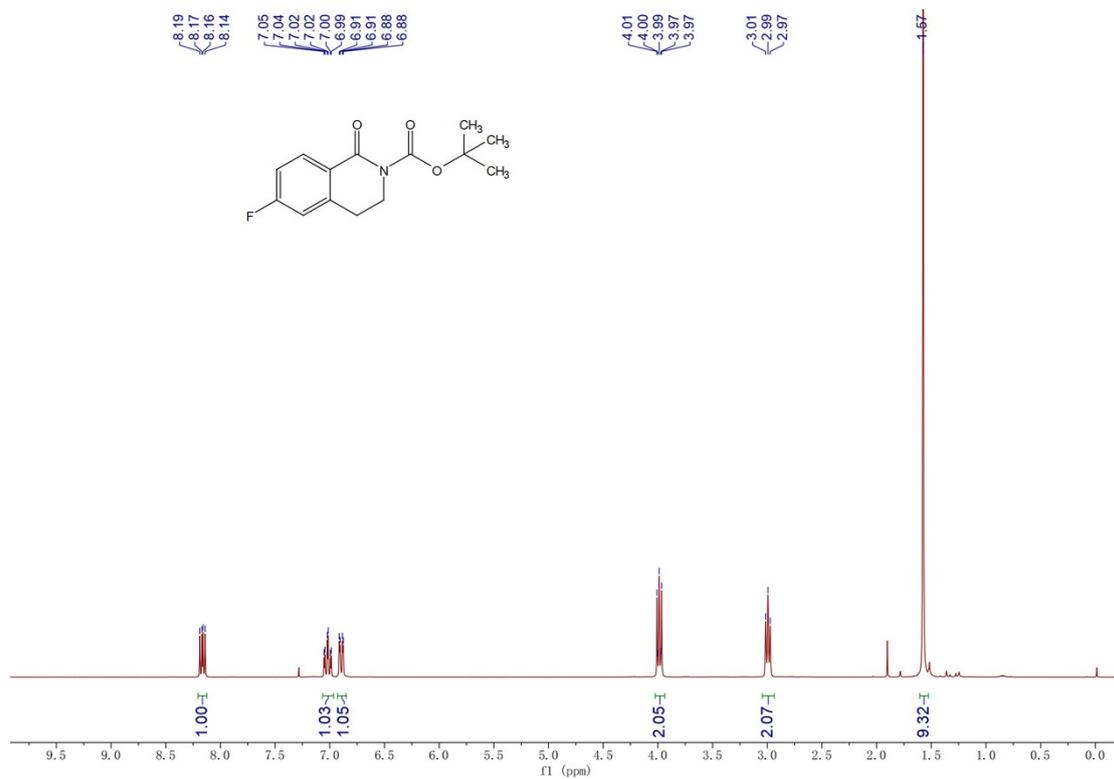
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **15b**



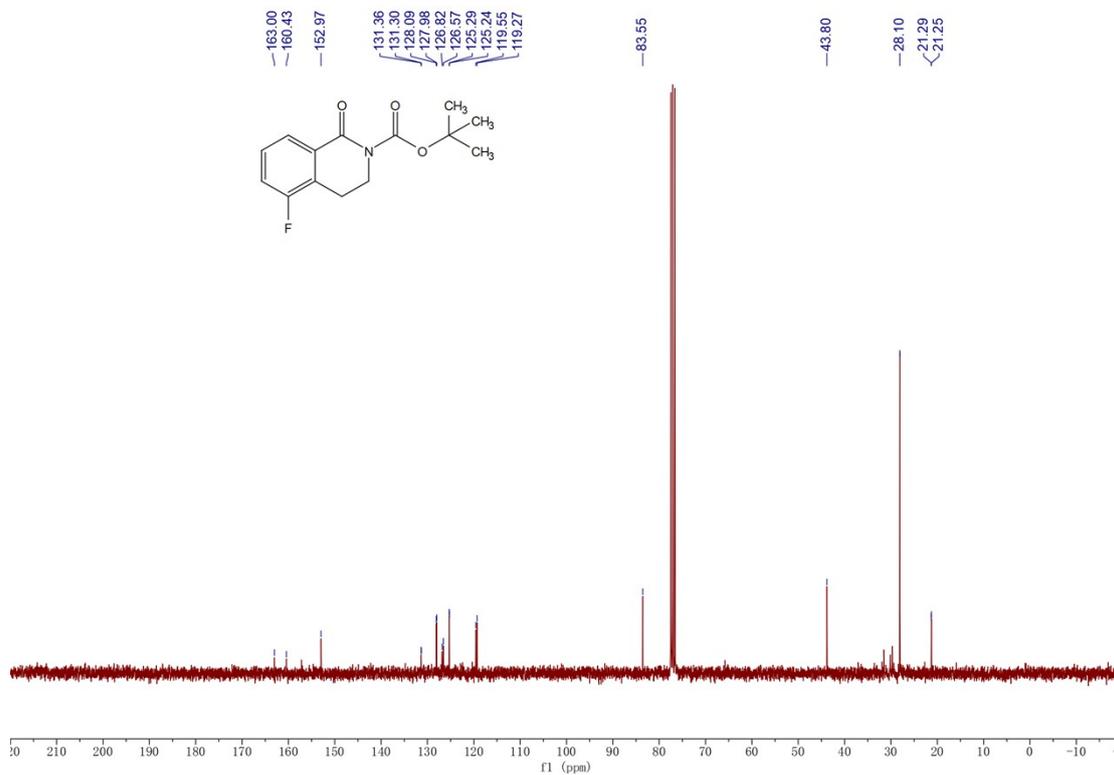
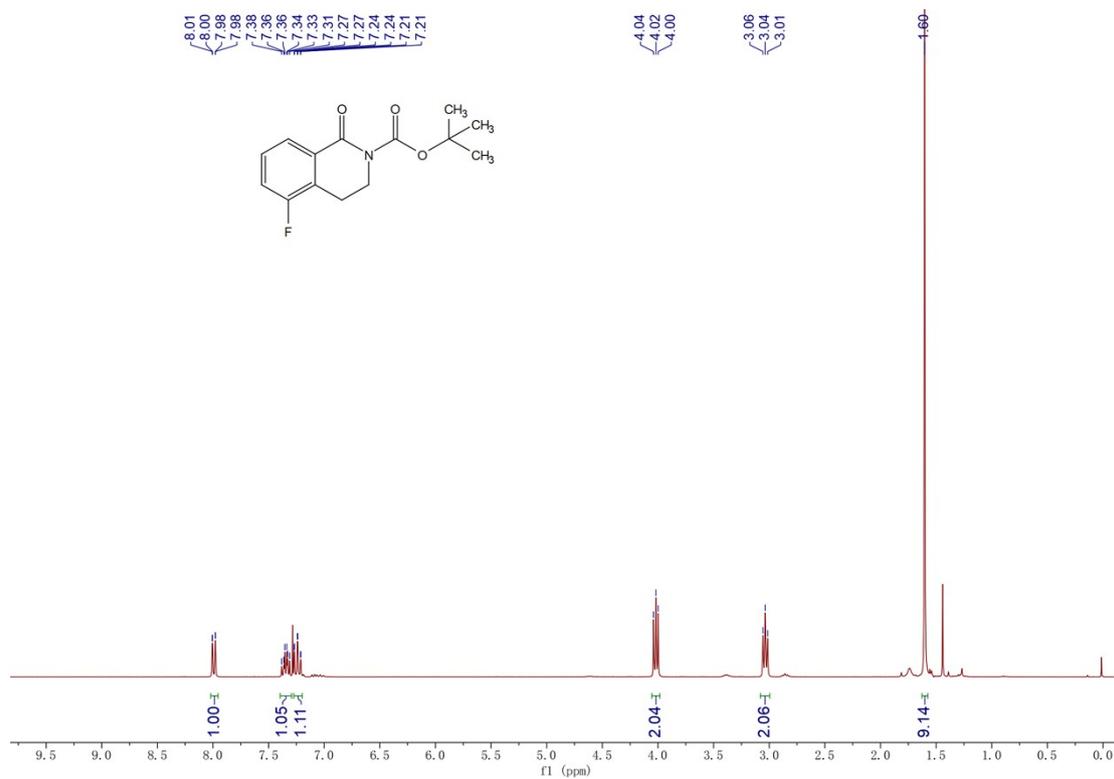
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **16b**



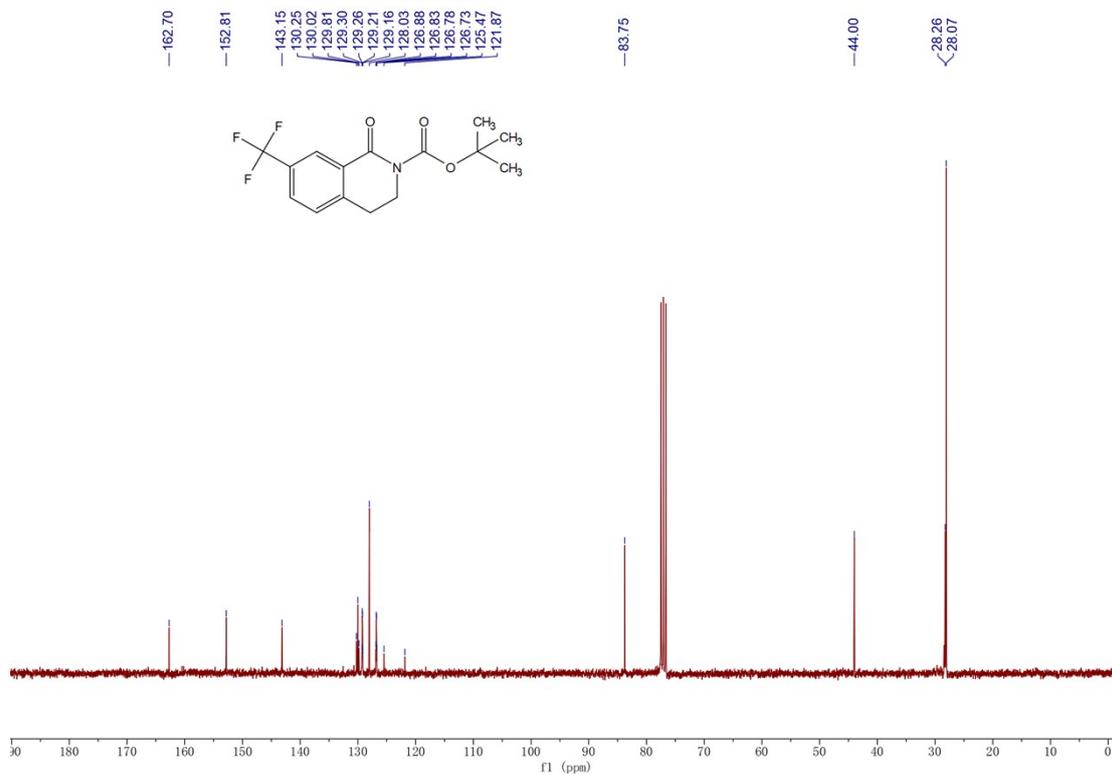
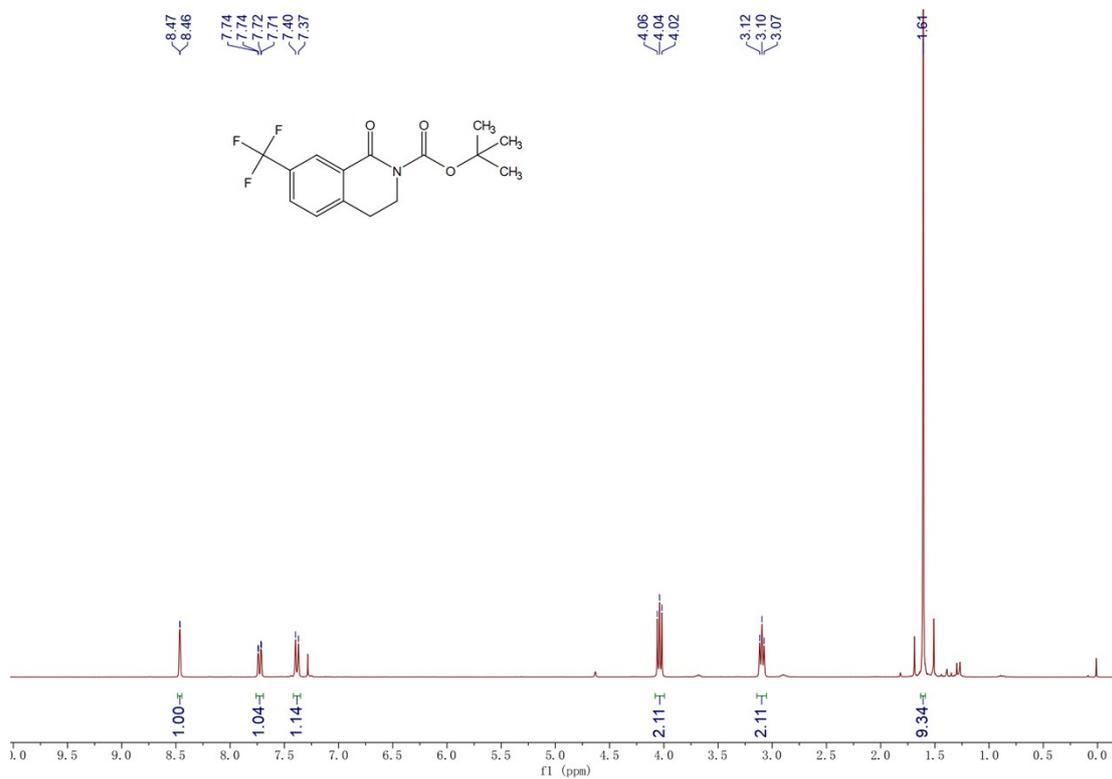
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **17b**



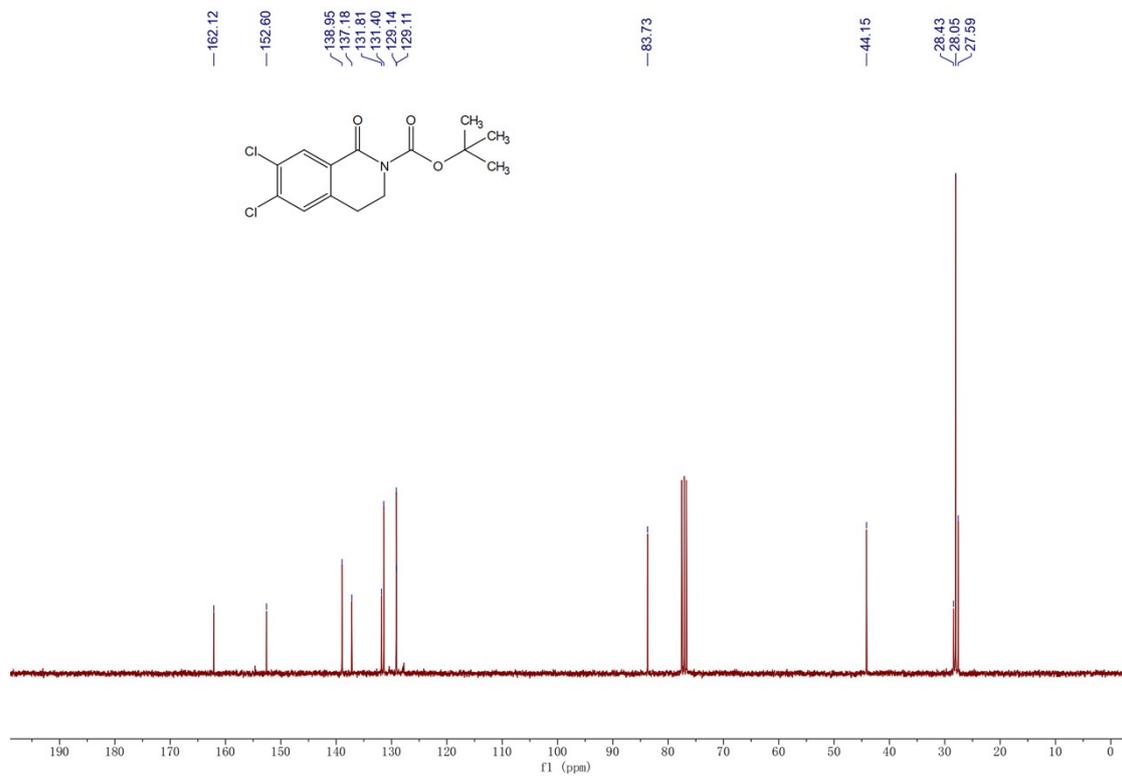
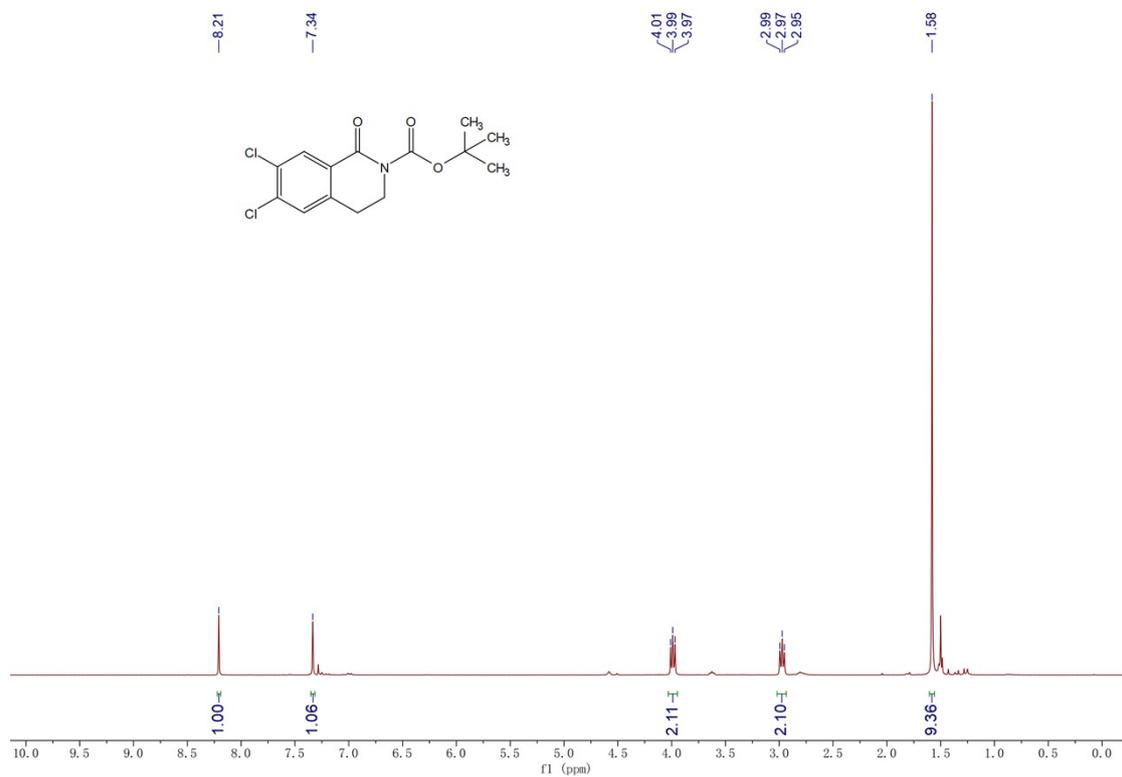
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **18b**



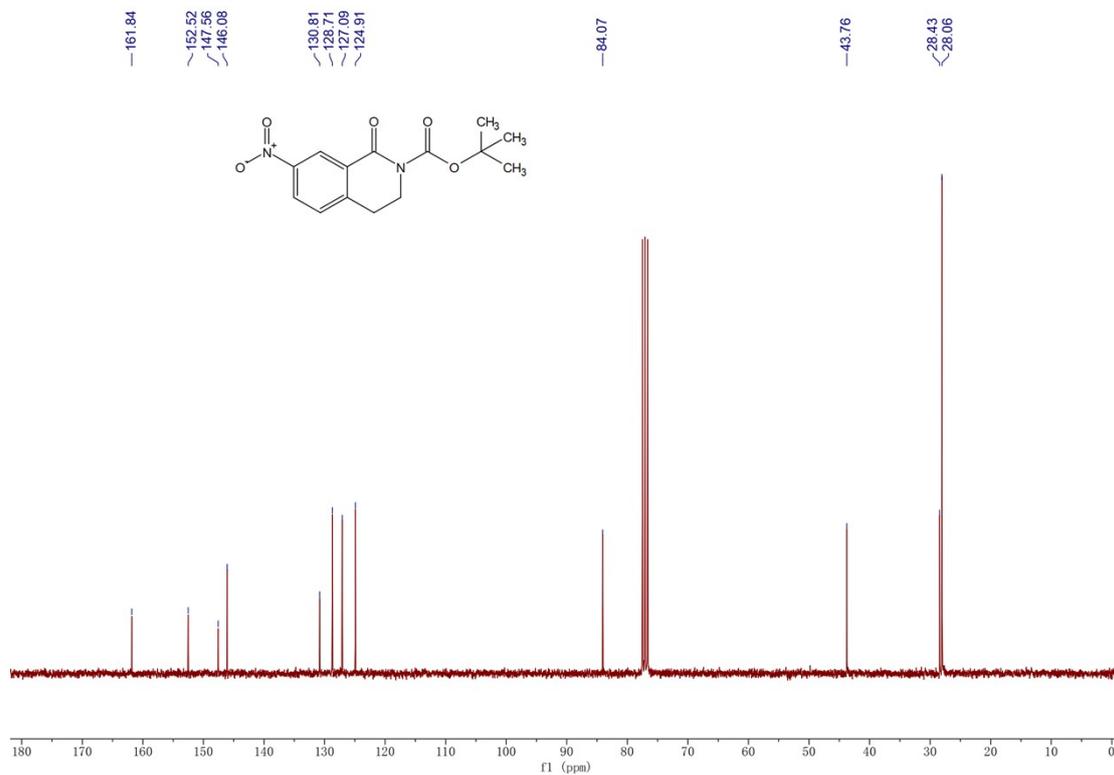
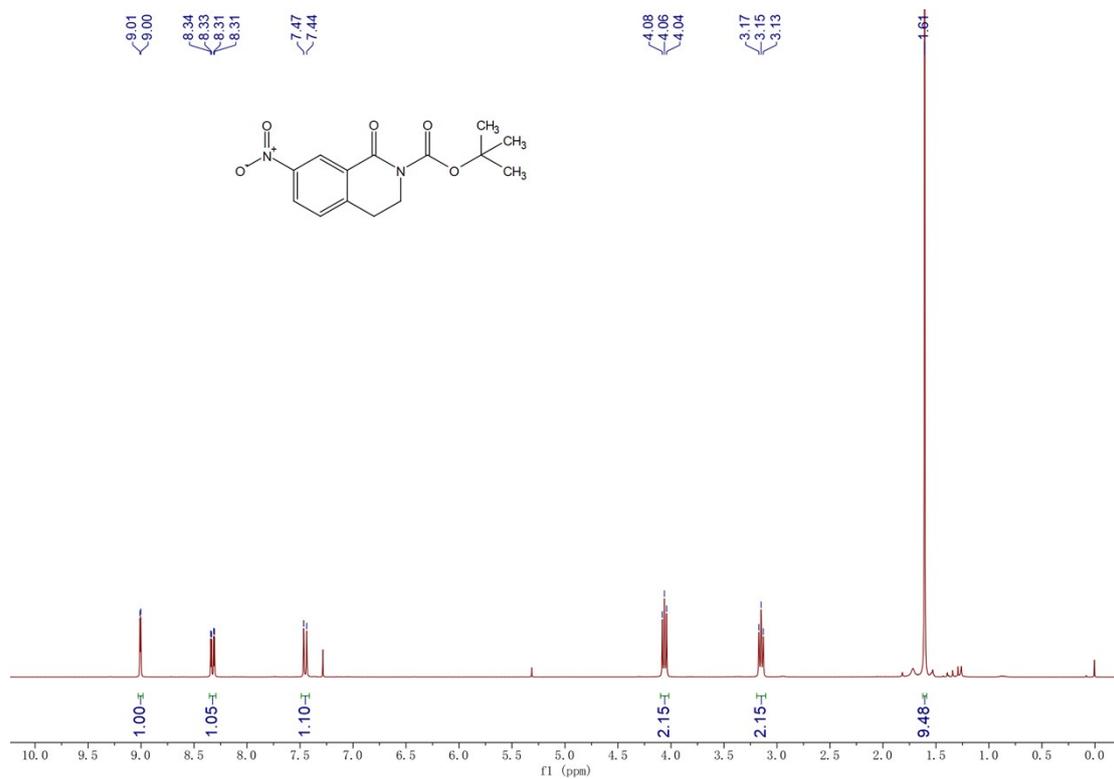
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **19b**



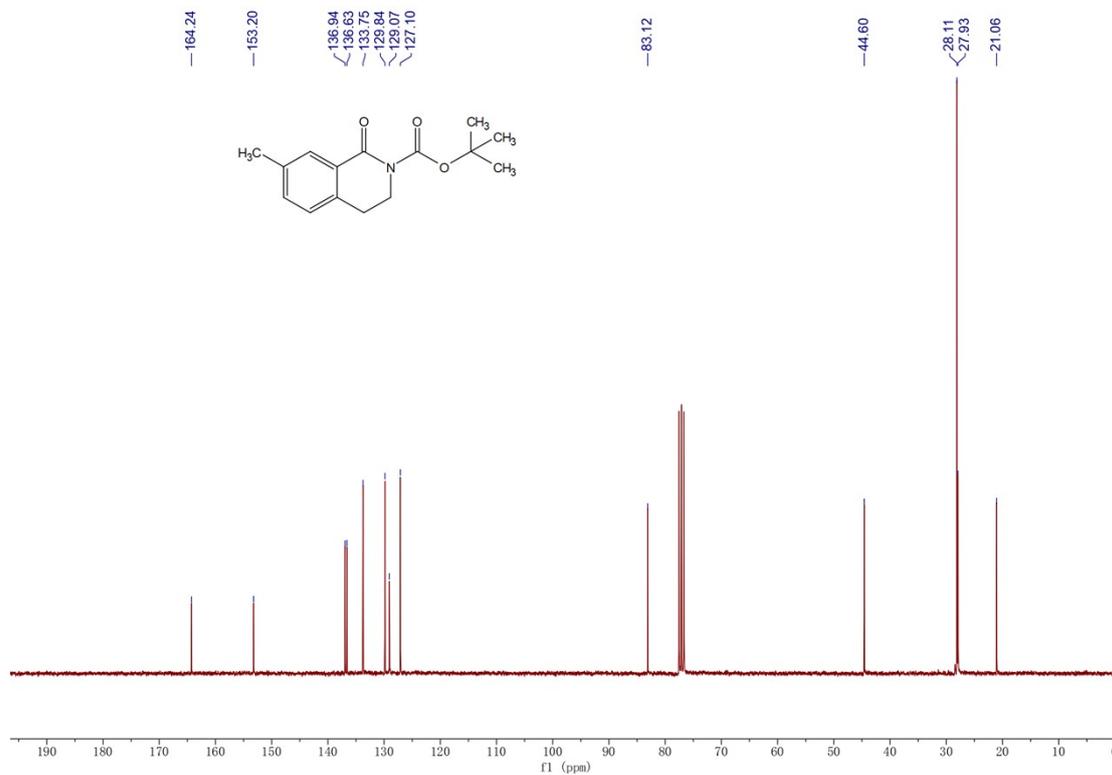
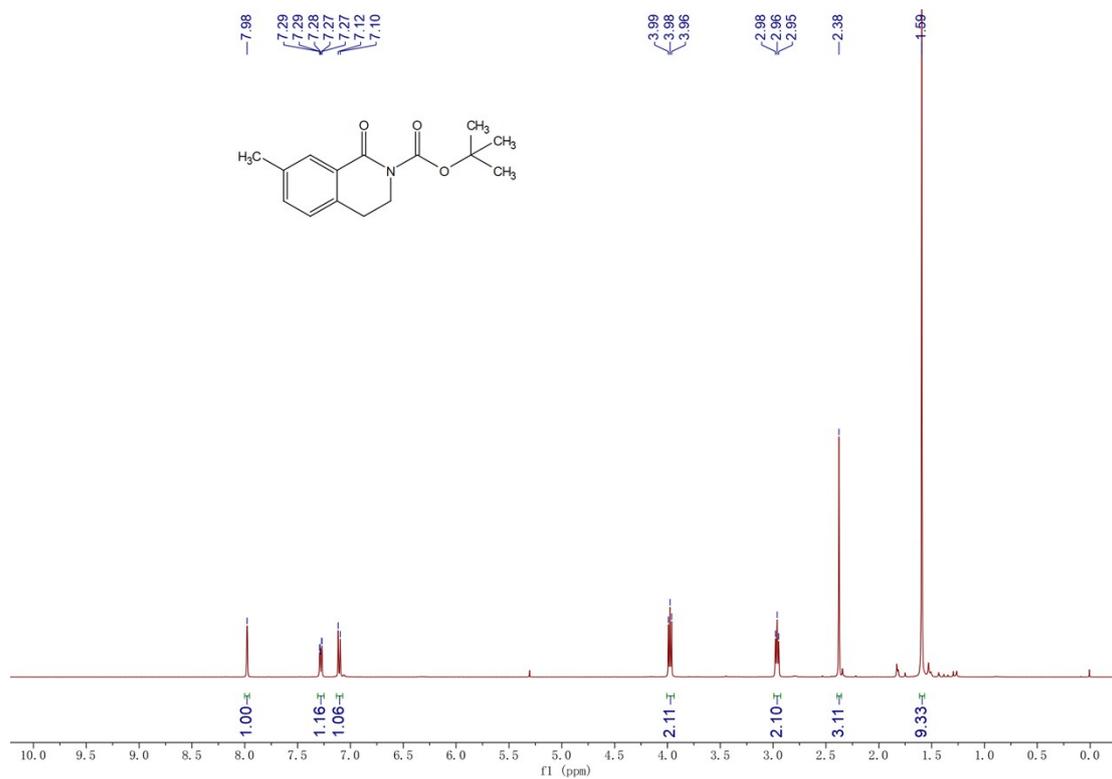
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **20b**



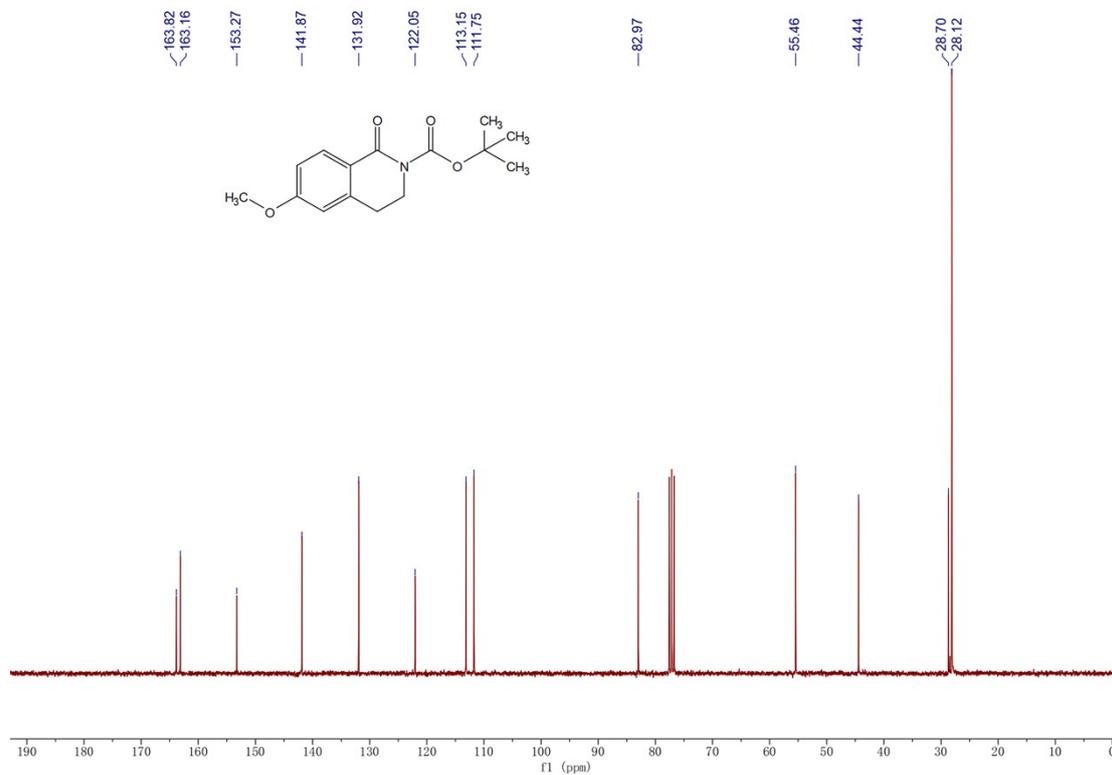
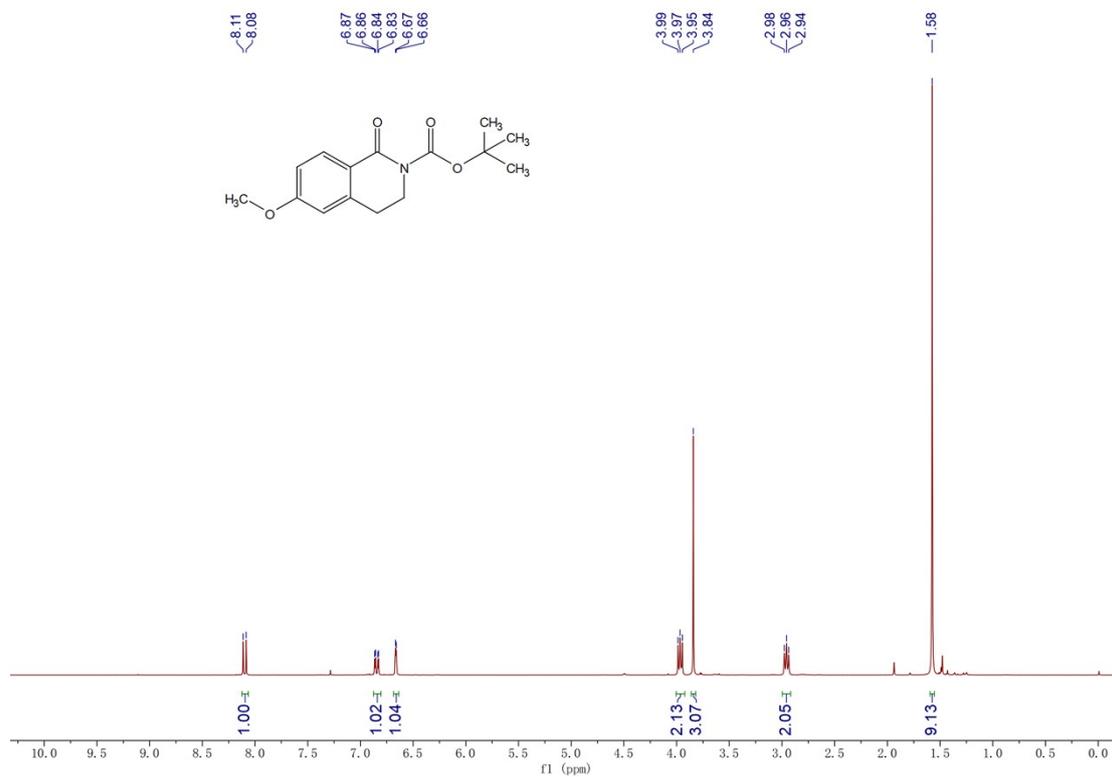
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **21b**



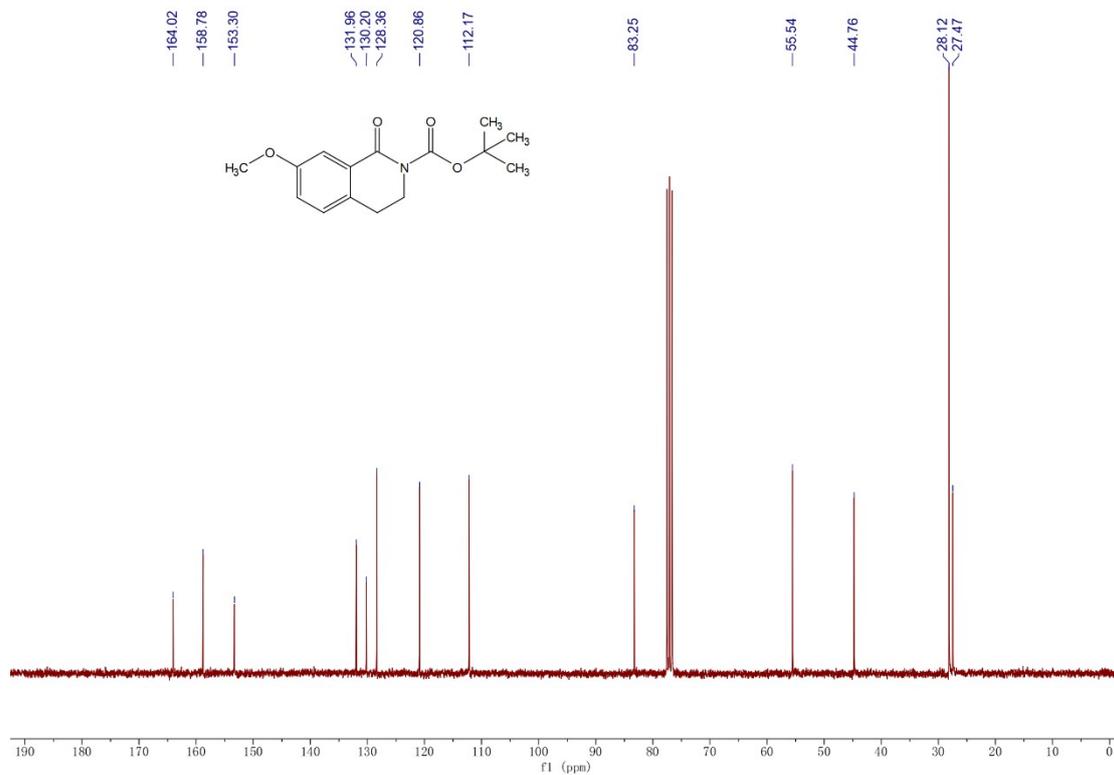
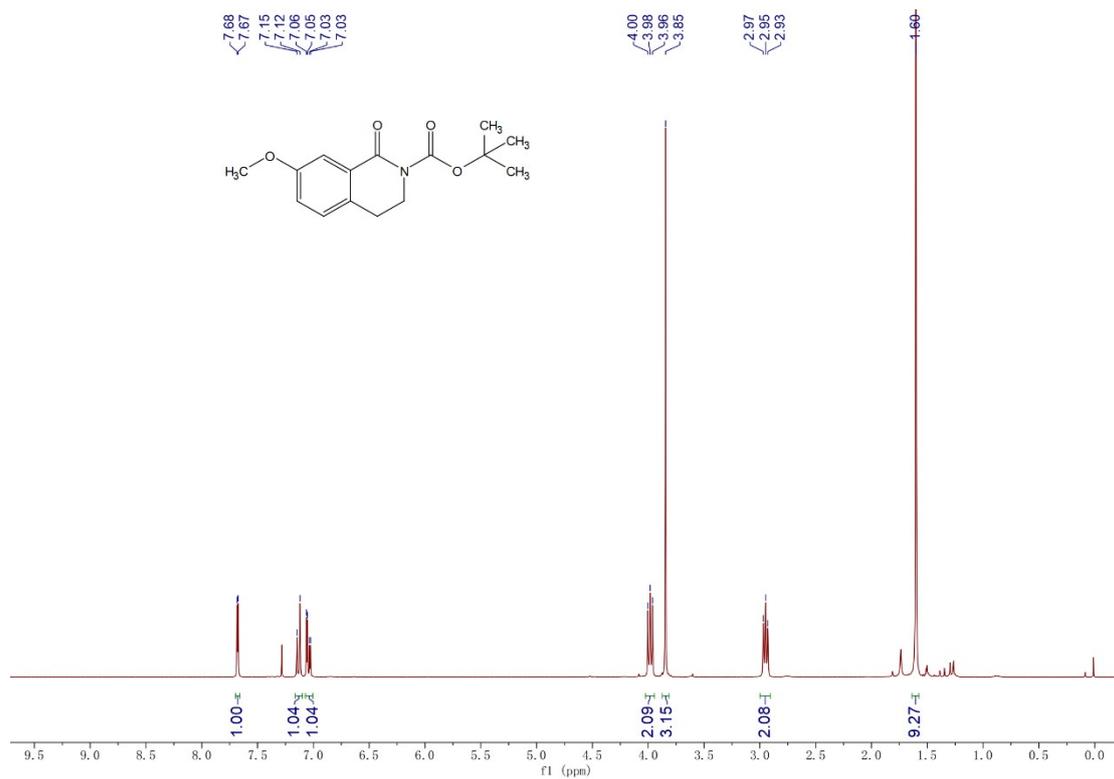
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **23b**



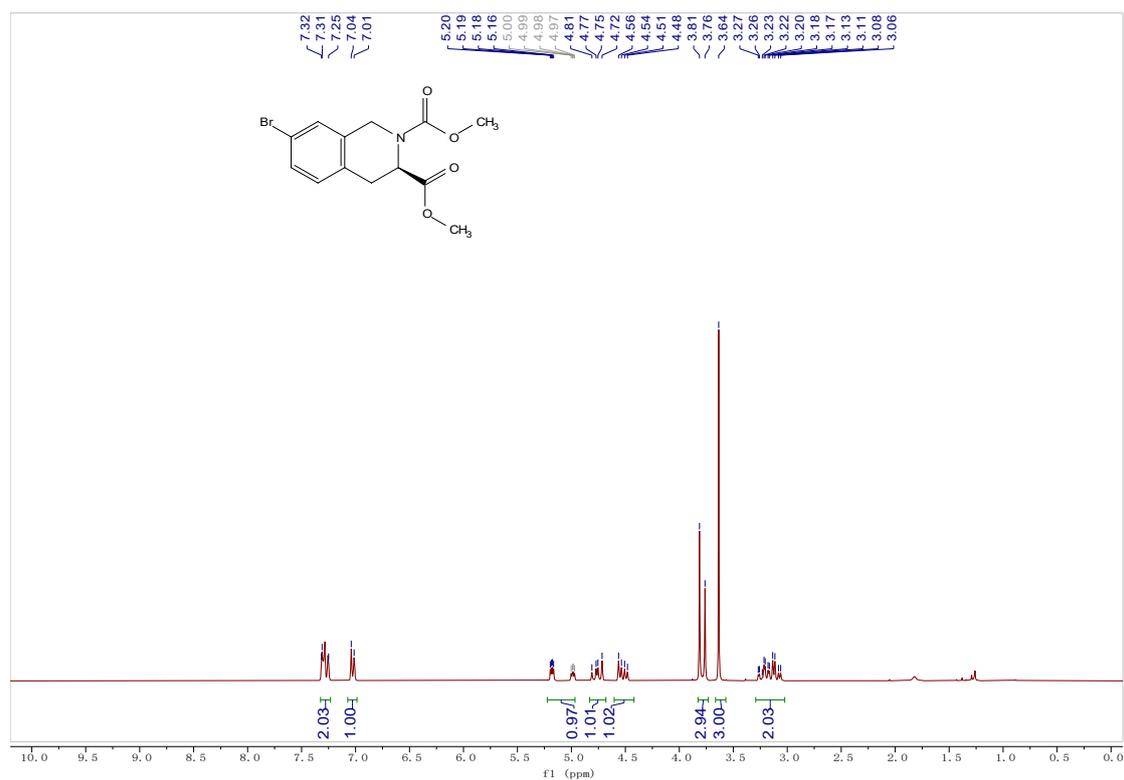
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **24b**



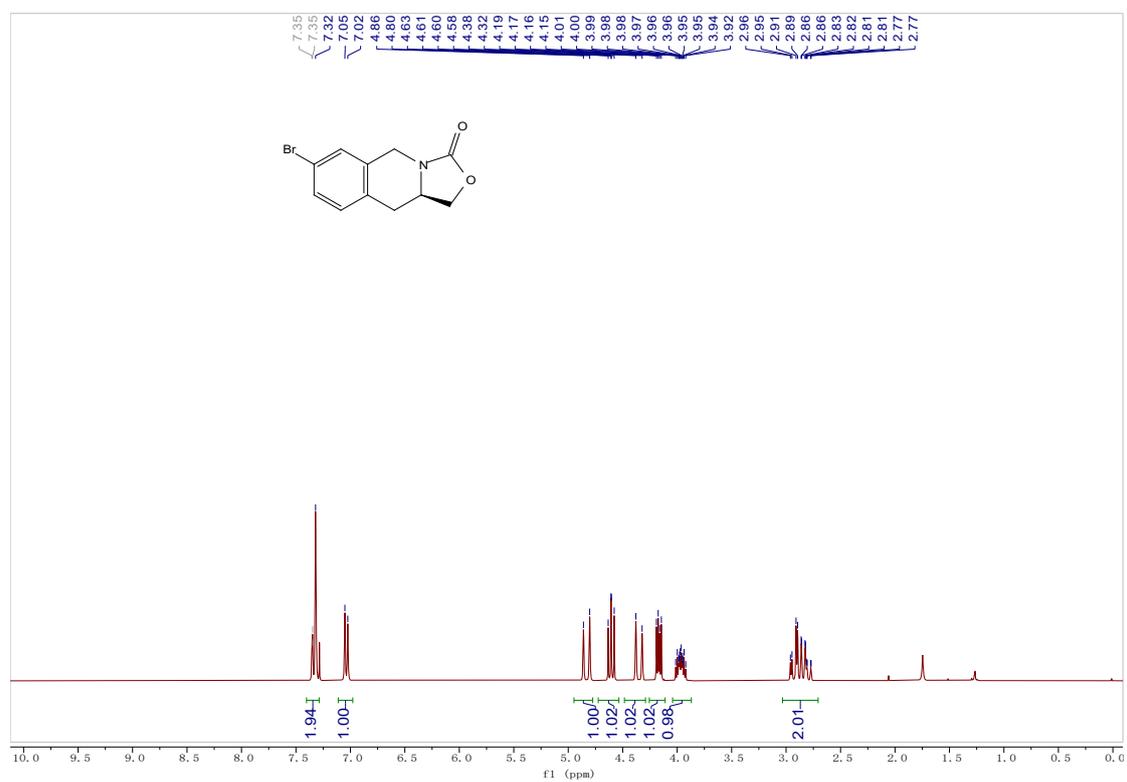
^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **25b**



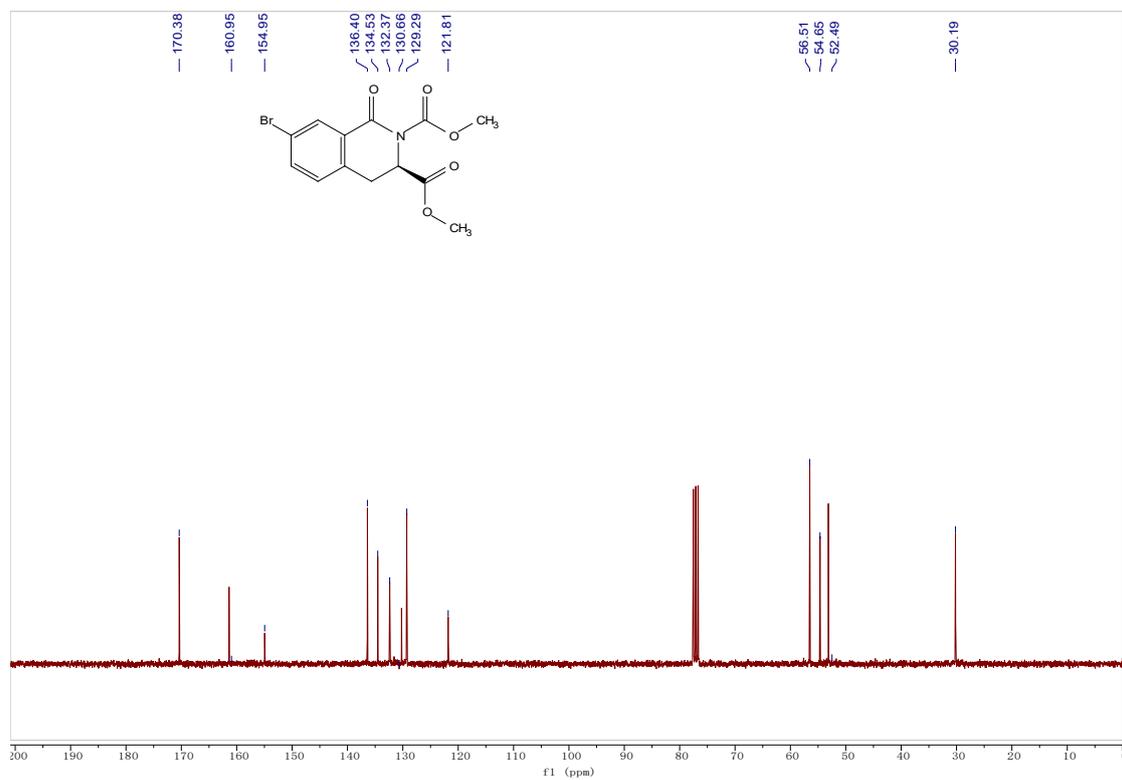
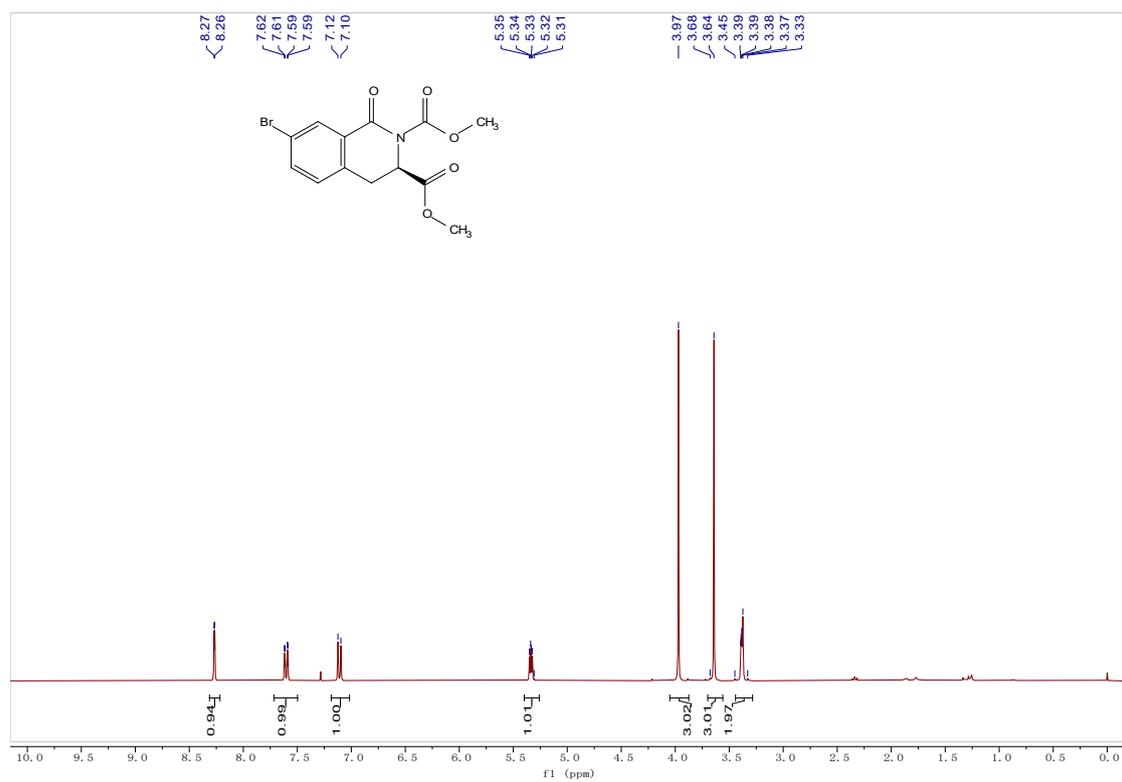
^1H NMR (300 MHz, CDCl_3), **33**



^1H NMR (300 MHz, CDCl_3), **34**



^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, CDCl_3), **31**



^1H NMR (300 MHz, CDCl_3) and ^{13}C NMR (300 MHz, $\text{DMSO}-d_6$), **32**

