

From Alkynes to Spiroindole δ -Lactams via a Copper-Nitrene Intermediate with Unusual 1,1- Addition and High Z Selectivity

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Supporting Information

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1. General information

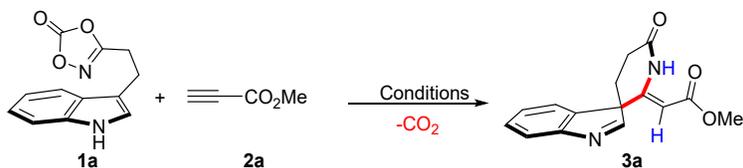
Solvents and reagents: All commercially reactants don't need further purification. The ultra dry solvents were used as commercially supplied, such as THF, CH₂Cl₂, ClCH₂CH₂Cl and MeOH et al. **Chromatography:** Flash chromatography was performed on silica gel (200-300 mesh). **¹H NMR spectra:** These were recorded at 400 MHz on a JNM-ECZ400S (JEOL, Japan) spectrometer. Chemical shifts (δ H) are quoted in parts per million (ppm) referenced to the appropriate residual solvent peak, with the abbreviations s, d, t, and m denoting singlet, doublet, triplet and multiplet respectively. **¹³C NMR spectra:** These were recorded at 100 MHz on a JNM-ECZ400S (JEOL, Japan) spectrometer. Chemical shifts (δ C) are quoted in parts per million (ppm) referenced to the appropriate residual solvent peak, with the abbreviations s, d, t, and q denoting C, CH, CH₂ and CH₃ respectively. **¹⁹F NMR spectra:** These were recorded at 376 MHz on a JNM-ECZ400S (JEOL, Japan) spectrometer and quoted in ppm to 1 decimal place and with coupling constants (J) to the nearest 0.1 Hz.

Mass spectra: Low resolution and high resolution spectra were recorded on a DIONEX UltiMate 300& Bruker ESI-TOF Compact spectrometer, using electrospray ionisation (ESI-TOF), HRMS values are valid to 5 ppm.

X-ray: X-ray spectra were recorded on a D8VENTURE Bruker Compact spectrometer.

2. Experimental Procedures

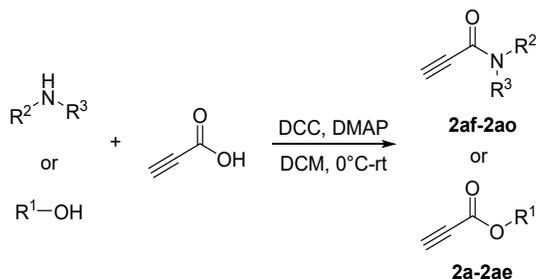
2.1 Screening of catalyst^a



Entry	Catalyst	Additive	Solvent	Temp./°C	Time/h	Yield/%	Z/E ^c
1	IPrCuCl (10 mol%)	AgOAc (20 mol%)	DCE	80	0.25	77	>20:1
2	Cu(OAc) ₂ (10 mol%)	AgOAc (20 mol%)	DCE	80	0.25	38	>20:1
3	CuBr (10 mol%)	AgOAc (20 mol%)	DCE	80	0.25	31	>20:1
4	[(CH ₃ CN) ₄ Cu]PF ₆ (10 mol%)	AgOAc (20 mol%)	DCE	80	0.25	n.r. ^b	
5	[(MeCN) ₄ Cu]BF ₄ (10 mol%)	AgOAc (20 mol%)	DCE	80	0.25	n.r. ^b	
6	CuCl (10 mol%)	AgOAc (20 mol%)	DCE	80	0.25	28	>20:1
7	IMesCuCl (10 mol%)	AgOAc (20 mol%)	DCE	80	0.25	20	>20:1
8	IPrCuCl (10 mol%)	AgNO ₃ (20 mol%)	DCE	80	0.25	18	>20:1
9	IPrCuCl (10 mol%)	AgOTf (20 mol%)	DCE	80	0.25	15	>20:1
10	IPrCuCl (10 mol%)	Ag ₂ CO ₃ (20 mol%)	DCE	80	0.25	trace	
11	IPrCuCl (10 mol%)	AgSbF ₆ (20 mol%)	DCE	80	0.25	26	>20:1
12	IPrCuCl (10 mol%)	AgNTf ₂ (20 mol%)	DCE	80	0.25	13	>20:1
13	IPrCuCl (10 mol%)	Ag ₃ PO ₄ (20 mol%)	DCE	80	0.25	10	>20:1
14	IPrCuCl (5 mol%)	AgOAc (10 mol%)	DCE	80	0.25	58	>20:1
15	IPrCuCl (15 mol%)	AgOAc (30 mol%)	DCE	80	0.25	88	>20:1
16	IPrCuCl (20 mol%)	AgOAc (40 mol%)	DCE	80	0.25	49	>20:1
17	IPrCuCl (15 mol%)	AgOAc (30 mol%)	DCM	80	0.25	69	>20:1
18	IPrCuCl (15 mol%)	AgOAc (30 mol%)	CHCl ₃	80	0.25	67	>20:1
19	IPrCuCl (15 mol%)	AgOAc (30 mol%)	Tol	80	0.25	29	>20:1
20	IPrCuCl (15 mol%)	AgOAc (30 mol%)	THF	80	0.25	trace	
21	IPrCuCl (15 mol%)	AgOAc (30 mol%)	CH ₃ CN	80	0.25	54	>20:1
22	IPrCuCl (15 mol%)	AgOAc (30 mol%)	DCE	40	2	64	>20:1
23	IPrCuCl (15 mol%)	AgOAc (30 mol%)	DCE	60	1	68	>20:1

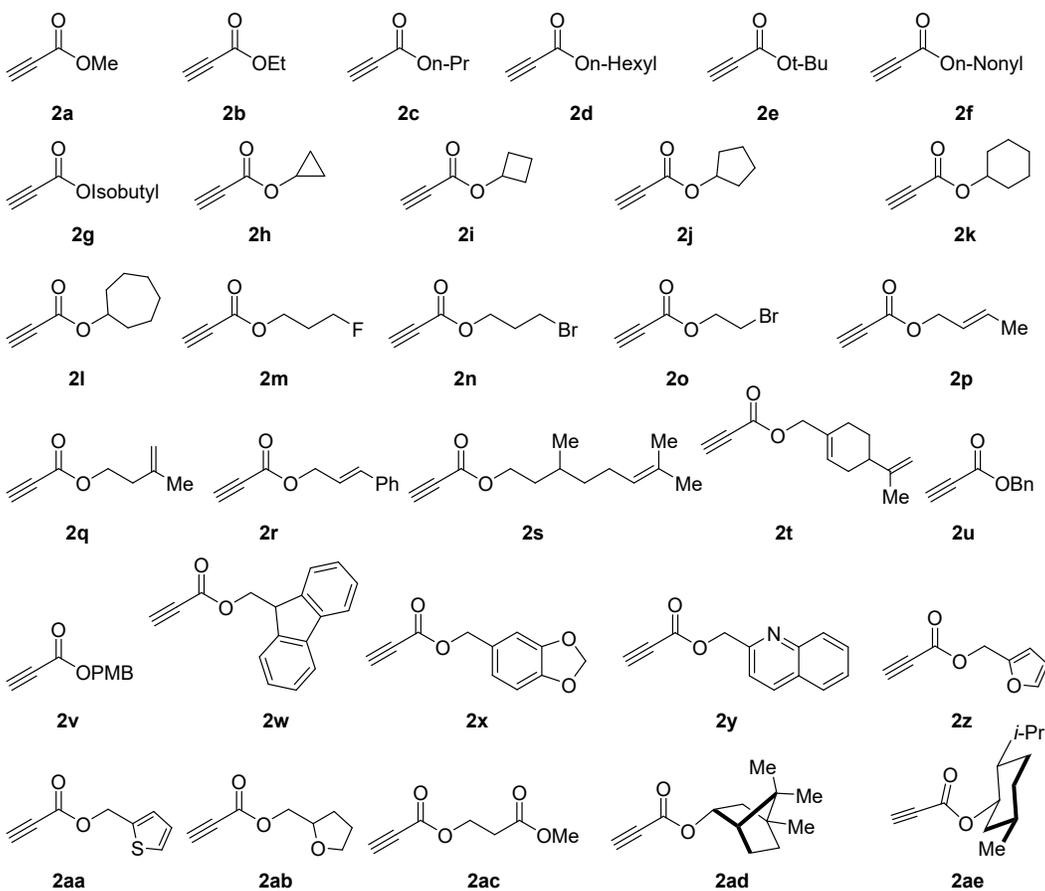
^aReaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), catalyst (x mmol), additive (y mmol), solvent (3 mL), at 80 °C for 15 mins. Isolated yield. ^bNo reaction. DCE = 1,2-dichloroethane, DCM = Dichloromethane, Tol = Toluene, THF = Tetrahydrofuran. ^cZ/E determined by NMR and XRD.

2.2 General Procedure for the Synthesis of Esters and Amides

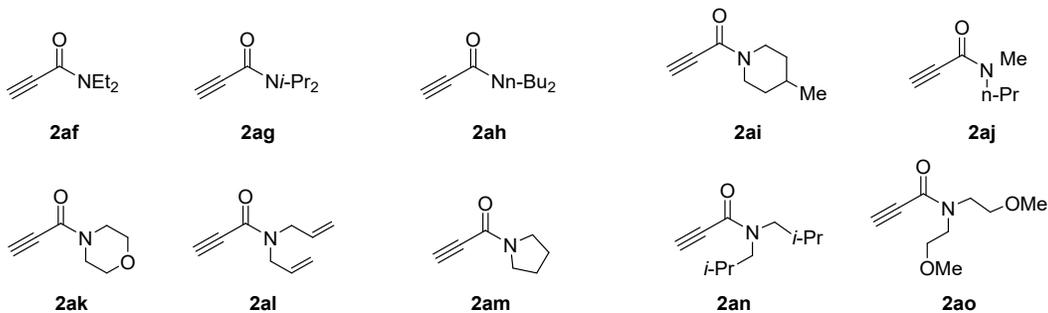


The DMAP (85.5 mg, 0.7 mmol, 0.07 eq) was dissolved in dry CH_2Cl_2 (25 mL) and cooled to 0°C with an ice bath. The reaction vessel was filled with alcohols and amines (10 mmol), followed by DCC (2.1 g, 10.2 mmol, 1.02 eq). Finally, propionic acid (714.5 mg, 10.2 mmol, 1.02 eq) was added dropwise and the reaction mixture was allowed to room temperature overnight with stirring. The crude reaction mixture was filtered to remove urea and purified by column chromatography (silica gel), affording the esters and amides^[1].

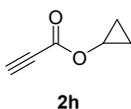
Esters



Amides



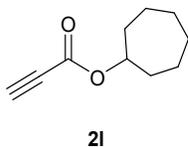
Most synthesized esters and amides were known compounds (**2a-2g**, **2i-2k**, **2o-2p**, **2r-2u**, **2z-2ab**, **2ad-2ah**, **2ak**, **2am-2an**).



Compound **2h** was an unknown compound, and was obtained in 68% yield via a known procedure;

¹H NMR (400 MHz, CDCl₃) δ 4.22-4.17 (m, 1H), 2.92 (s, 1H), 0.77-0.75 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃) δ 153.5, 75.3, 74.5, 50.7, 5.3.

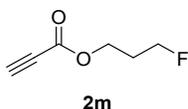
HRMS (ESI) Calcd. For C₆H₇O₂: [M+H]⁺ : 111.0368, Found: m/z 110.0370.



Compound **2l** was an unknown compound, and was obtained in 53% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 5.05-4.99 (m, 1H), 2.85 (s, 1H), 1.95-1.90 (m, 2H), 1.72-1.66 (m, 4H), 1.56-1.52 (m, 4H), 1.47-1.39 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 152.4, 78.0, 75.4, 74.1, 33.9, 33.7, 28.4, 23.1, 22.8.

HRMS (ESI) Calcd. For C₁₀H₁₅O₂: [M+H]⁺ : 167.1068, Found: m/z 167.1067.

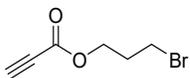


Compound **2m** was an unknown compound, and was obtained in 62% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 4.59 (t, *J* = 5.7 Hz, 1H), 4.47 (t, *J* = 5.7 Hz, 1H), 4.31 (t, *J* = 6.3 Hz, 2H), 2.91 (s, 1H), 2.12-1.99 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 152.6, 80.3

(d, $J = 64$ Hz), 75.1, 74.5, 62.2 (d, $J = 5$ Hz), 29.5 (d, $J = 20$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -222.7--222.4 (m, 1F).

HRMS (ESI) Calcd. For $\text{C}_6\text{H}_8\text{FO}_2$: $[\text{M}+\text{Na}]^+$: 153.0320, Found: m/z 153.0321.

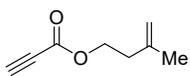


2n

Compound **2n** was an unknown compound, and was obtained in 67% yield isolated yield via a known procedure;

^1H NMR (400 MHz, CDCl_3), δ 4.34 (d, $J = 6.0$ Hz, 2H), 3.48 (d, $J = 6.5$ Hz, 2H), 2.91 (s, 1H), 2.23 (q, $J = 6.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 75.2, 74.5, 64.0, 31.4, 29.1.

HRMS (ESI) Calcd. For $\text{C}_6\text{H}_8\text{BrO}_2$: $[\text{M}+\text{H}]^+$: 190.9629, Found: m/z 190.9626.

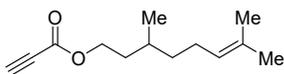


2q

Compound **2q** was an unknown compound, and was obtained in 71% isolated yield via a known procedure;

^1H NMR (400 MHz, CDCl_3), δ 4.83 (s, 1H), 4.75 (s, 1H), 4.32-4.29 (m, 2H), 2.88 (s, 1H), 2.38 (t, $J = 6.8$ Hz, 2H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.8, 141.0, 112.9, 74.8, 64.5, 36.4, 22.6.

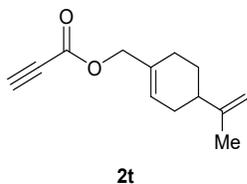
HRMS (ESI) Calcd. For $\text{C}_8\text{H}_{11}\text{O}_2$: $[\text{M}+\text{H}]^+$: 139.0753, Found: m/z 139.0754.



2s

Compound **2s** was an unknown compound, and was obtained in 73% isolated yield via a known procedure;

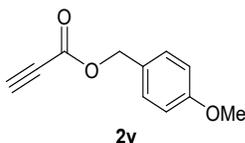
^1H NMR (400 MHz, CDCl_3), δ 5.09-5.05 (m, 1H), 4.27-4.17 (m, 2H), 2.87 (s, 1H), 2.03-1.93 (m, 1H), 1.75-1.69 (m, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.55-1.44 (m, 2H), 1.36-1.29 (m, 1H), 1.22-1.17 (m, 1H), 0.91 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 131.6, 124.5, 74.9, 74.6, 65.0, 37.0, 35.2, 29.4, 25.8, 25.4, 19.4, 17.8. **HRMS (ESI)** Calcd. For $\text{C}_{13}\text{H}_{21}\text{O}_2$: $[\text{M}+\text{H}]^+$: 209.1536, Found: m/z 209.1538.



Compound **2t** was an unknown compound, and was obtained in 78% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 5.81 (s, 1H), 4.73-4.70 (m, 2H), 4.57 (s, 2H), 2.89 (s, 1H), 2.19-2.09 (m, 4H), 2.01-1.96 (m, 1H), 1.88-1.83 (m, 1H), 1.73 (s, 3H), 1.54-1.44 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 149.5, 131.6, 127.6, 109.0, 74.8, 70.4, 40.7, 30.6, 27.3, 26.4, 20.9.

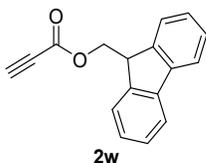
HRMS (ESI) Calcd. For C₁₃H₁₇O₂: [M+H]⁺ : 205.1225, Found: m/z 205.1223.



Compound **2v** was an unknown compound, and was obtained in 65% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.16 (s, 2H), 3.81 (s, 3H), 2.88 (s, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 160.1, 152.7, 130.7, 126.7, 114.1, 75.0, 74.7, 67.9, 55.4.

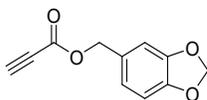
HRMS (ESI) Calcd. For C₁₀H₁₁O₃: [M+H]⁺ : 191.0700, Found: m/z 191.0703.



Compound **2w** was an unknown compound, and was obtained via in 65% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 4.51 (d, *J* = 7.5 Hz, 2H), 4.30 (t, *J* = 7.4 Hz, 1H), 3.00 (s, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 152.6, 143.1, 141.2, 128.0, 127.2, 125.1, 120.1, 76.8, 75.5, 68.0, 46.2.

HRMS (ESI) Calcd. For C₁₇H₁₃O₂: [M+H]⁺ : 249.0832, Found: m/z 249.0837.

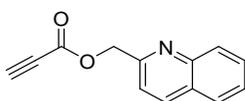


2x

Compound **2x** was an unknown compound, and was obtained in 70% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 6.86-6.84 (m, 2H), 6.78 (d, *J* = 8.5 Hz, 1H), 5.96 (s, 2H), 5.10 (s, 2H), 3.91 (s, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 152.6, 148.1, 147.9, 128.2, 122.9, 109.4, 108.4, 101.3, 75.2, 74.6, 68.0.

HRMS (ESI) Calcd. For C₁₁H₈O₄Na : [M+Na]⁺ : 227.0317, Found: m/z 227.0315.

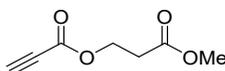


2y

Compound **2y** was an unknown compound, and was obtained in 69% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 8.18 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.74-7.70 (m, 1H), 7.56-7.47 (m, 2H), 5.49 (s, 2H), 2.98 (s, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 154.8, 152.4, 147.7, 137.3, 130.1, 129.3, 127.7, 127.0, 119.4, 75.8, 74.4, 68.9.

HRMS (ESI) Calcd. For C₁₃H₁₀NO₂: [M+H]⁺ : 212.0709, Found: m/z 212.0706.

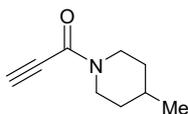


2ac

Compound **2ac** was an unknown compound, and was obtained in 69% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 4.46 (t, *J* = 6.4 Hz, 2H), 3.72 (s, 3H), 2.90 (s, 1H), 2.71 (t, *J* = 6.3 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 170.7, 152.5, 75.4, 74.5, 61.5, 52.2 33.3.

HRMS (ESI) Calcd. For C₇H₉O₄: [M+H]⁺ : 157.0423, Found: m/z 157.0426.

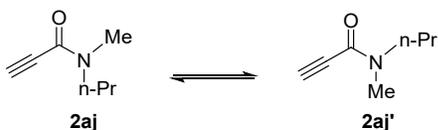


2ai

Compound **2ai** was an unknown compound, and was obtained in 52% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 4.50-4.45 (m, 1H), 4.35-4.30 (m, 1H), 3.09 (s, 1H), 3.06-3.03 (m, 1H), 2.66-2.59 (m, 1H), 1.72-1.56 (m, 3H), 1.19-1.04 (m, 2H), 0.93 (d, *J* = 6.5 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 151.7, 79.0, 75.8, 47.5, 41.7, 34.5, 33.5, 31.1, 21.7.

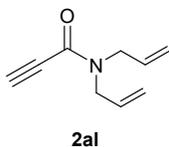
HRMS (ESI) Calcd. For C₉H₁₄NO: [M+H]⁺ : 152.0997, Found: m/z 152.0994.



Compound **2aj** was an unknown compound, and was obtained in 57% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 3.52-3.48 and 3.33-3.29 (m, 2H), 3.14 (s, 1H), 2.98, 3.06, 3.09 (s, 3H), 1.63-1.47 (m, 2H), 1.83-1.90 (m, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 153.5, 78.9, 78.5, 76.1, 76.0, 52.6, 48.2, 36.3, 32.1, 21.4, 20.1, 11.2, 10.9.

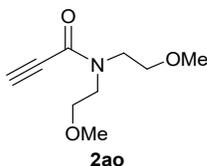
HRMS (ESI) Calcd. For C₇H₁₂NO: [M+H]⁺ : 126.0841, Found: m/z 126.0843.



Compound **2ai** was an unknown compound, and was obtained in 66% isolated yield via a known procedure;

¹H NMR (400 MHz, CDCl₃), δ 5.80-5.65 (m, 2H), 5.23-5.11 (m, 4H), 4.13 (d, *J* = 5.4 Hz, 1H), 3.97 (d, *J* = 5.7 Hz, 1H), 3.09 (m, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 153.3, 132.5, 131.8, 118.3, 118.3, 78.7, 75.8, 50.6, 46.3.

HRMS (ESI) Calcd. For C₉H₁₂NO: [M+H]⁺ : 150.0841, Found: m/z 150.0845.

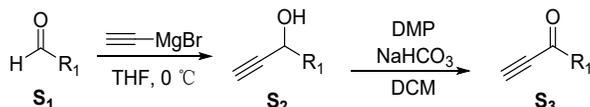


Compound **2ao** was an unknown compound, and was obtained in 54% isolated yield via a known procedure;

$^1\text{H NMR}$ (400 MHz, CDCl_3), δ 3.81 (t, $J = 5.8$ Hz, 2H), 3.61 (t, $J = 5.3$ Hz, 2H), 3.54-3.48 (m, 4H), 3.32 (s, 3H), 3.30 (s, 3H), 3.10 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 153.8, 78.8, 76.1, 71.1, 70.6, 59.1, 58.9, 49.8, 45.7.

HRMS (ESI) Calcd. For $\text{C}_9\text{H}_{16}\text{NO}_3$: $[\text{M}+\text{H}]^+$: 186.1052, Found: m/z 186.1056.

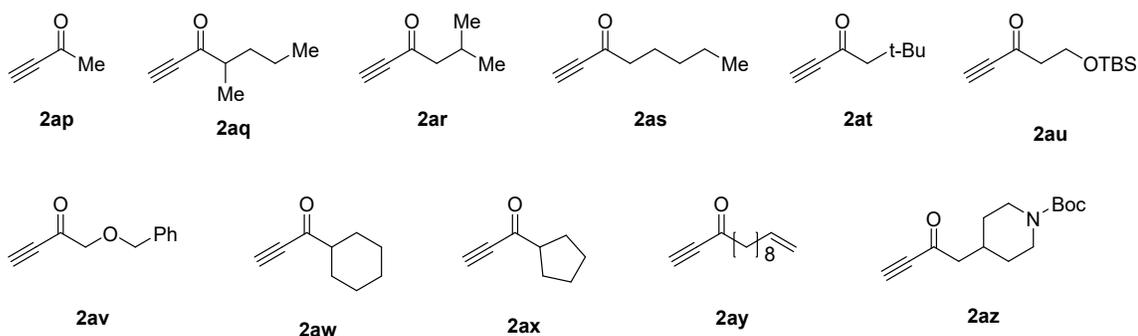
2.3 General Procedure for the Synthesis of Ketone.



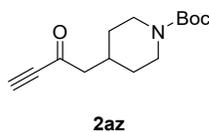
A solution of ethynylmagnesium bromide (0.5 M in THF, 30.0 mL, 15.0 mmol, 1.5 equiv.) was added to a solution of aldehyde (10.0 mmol, 1.0 equiv.) in THF (15.0 mL) at 0 °C, and allowed the solution to react for 30 minutes^[2]. The reaction mixture was then quenched with saturated aqueous NH_4Cl (30.0 mL), and extracted with EtOAc (3×30.0 mL). The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated to obtain crude **S2** for the next step without further purification.

Dissolve **S2** (10.0 mmol, 1.0 eq) in CH_2Cl_2 (35.0 mL). Then added NaHCO_3 (15.0 mmol, 1.5 eq) and Dess-Martin periodinane (DMP) (12.0 mmol, 1.2 eq) sequentially. After stirring the mixture for about 0.5 hours, added an excess of saturated $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution and NaHCO_3 . Extracted with DCM (3×20.0 mL) and dry over anhydrous Na_2SO_4 and concentrated^[3]. And purified by column chromatography (silica gel, Petroleum ether : EtOAc = 20:1) affording **S3**.

Ketone



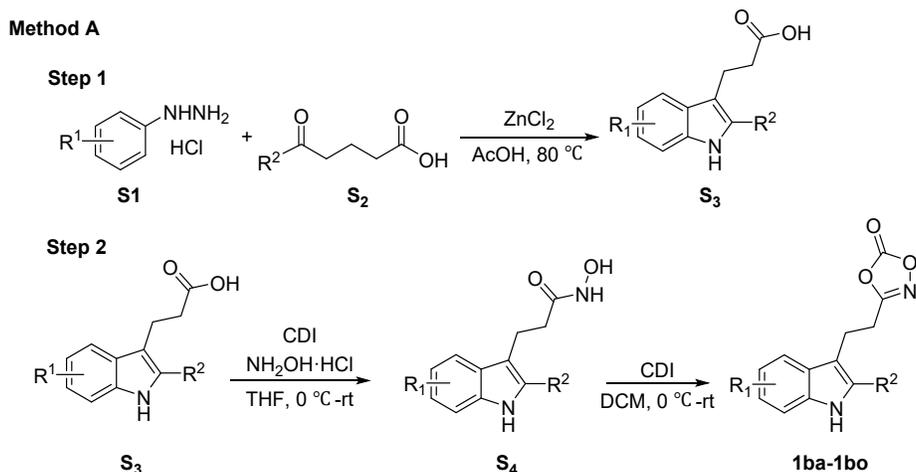
Most synthesized ketone were known compounds (**2ap-2ay**).



Compound **2az** was an unknown compound, and was obtained in 73% isolated yield via a known procedure;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.07 (bs, 2H), 3.24 (s, 1H), 2.75-2.70 (m, 2H), 2.53 (d, $J = 6.8$ Hz, 2H), 2.13-2.03 (m, 1H), 1.68 (d, $J = 12.8$ Hz, 2H), 1.44 (s, 9H), 1.19-1.11 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 186.3, 154.9, 81.7, 79.6, 78.8, 52.0, 43.9, 32.2, 31.8, 28.5. **HRMS (ESI)** Calcd. For $\text{C}_{14}\text{H}_{22}\text{NO}_3$: $[\text{M}+\text{H}]^+$: 252.1523, Found: m/z 252.1521.

2.4 General Procedure for the Synthesis of Dioxazolones



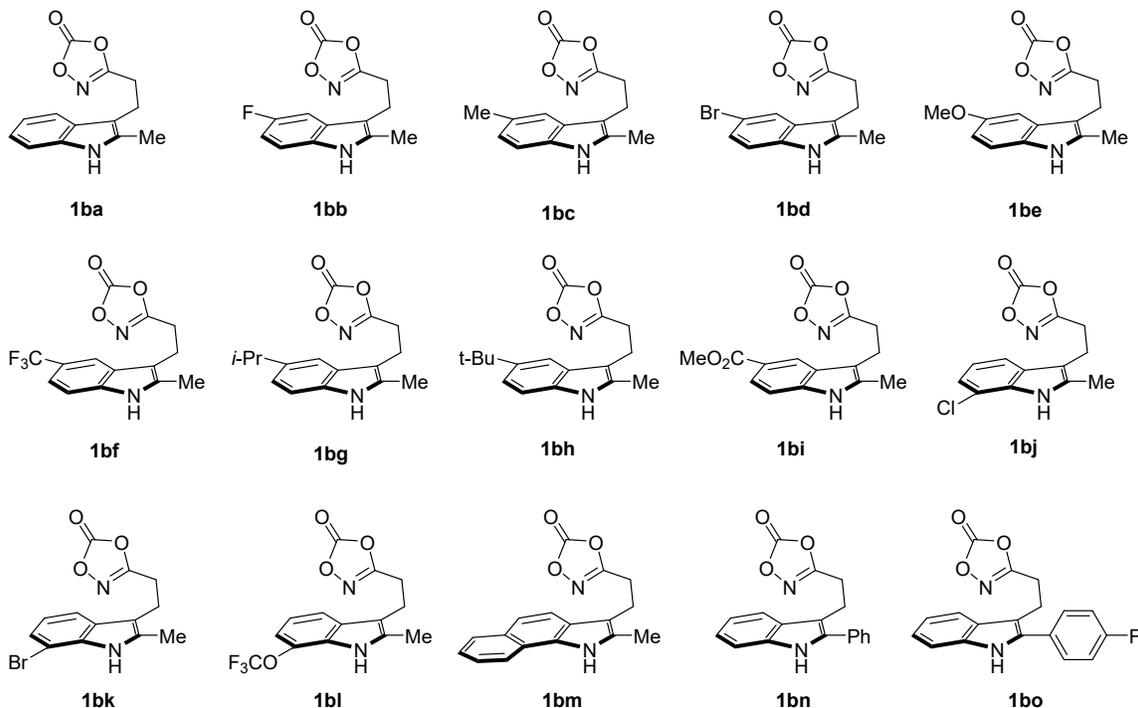
Step 1: To a stirring solution of 5-oxohexanoic acid (10.0 mmol, 1.0 equiv.) and Phenylhydrazine hydrochloride (1.3 g, 10.0 mmol, 1.0 equiv.) in AcOH (20.0 mL) was added zinc chloride (1.4 g, 10.0 mmol, 1.0 equiv.) and the mixture was heated to 70 °C. After 16 h, the mixture was cooled to rt, washed with water, extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 , concentrated. And purified by column chromatography (silica gel, (Petroleum ether : EtOAc = 5:1) affording **S3** as known compound^[4].

Step 2: The Carboxylic acids (5.0 mmol) was dissolved in THF (30.0 mL) and cooled to 0 °C before addition of CDI (1.22 g, 7.5 mmol, 1.5 equiv). The mixture was stirred for 1-2 hours, and the $\text{NH}_2\text{OH}\cdot\text{HCl}$ (694.90 mg, 10.0 mmol, 2.0 equiv) was added. The resulting mixture was stirred for overnight, quenched with 5% KHSO_4 , and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 , concentrated.

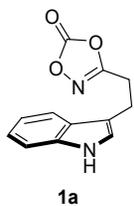
The crude product was dissolved in CH_2Cl_2 (35.0 mL) and cooled to 0 °C. The CDI (1.22 g, 7.5 mmol, 1.5 equiv) was slowly added. The resulting mixture was stirred for 15 mins,

quenched with 2 M HCl, and extracted with CH₂Cl₂. The organic phase was concentrated and purified by column chromatography (silica gel, CH₂Cl₂), affording the dioxazolones.^[5]

Dioxazolones

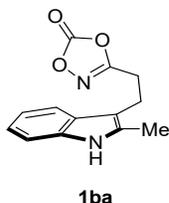


All the above compounds are unknown products, with yields ranging from 70% to 80%.



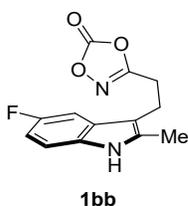
¹H NMR (400 MHz, CDCl₃), δ 8.06 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 3.21 (t, *J* = 7.3 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.4, 154.3, 136.4, 126.8, 122.6, 122.0, 119.9, 118.3, 112.7, 111.6, 26.0, 20.7.

HRMS (ESI) Calcd. For C₁₂H₁₁N₂O₃: [M+H]⁺ : 231.0672, Found: *m/z* 231.0671.



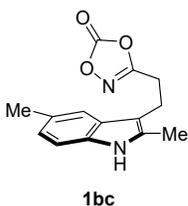
¹H NMR (400 MHz, CDCl₃), δ 7.86 (s, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 8.1 Hz, 1H), 7.14 (q, *J* = 7.3 Hz, 1H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.4, 154.3, 135.4, 131.9, 127.8, 121.6, 119.8, 117.3, 110.7, 108.1, 26.0, 19.8, 11.6.

HRMS (ESI) Calcd. For C₁₃H₁₃N₂O₃: [M+H]⁺ : 245.0846, Found: *m/z* 245.0847.



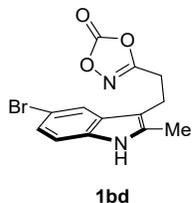
¹H NMR (400 MHz, CDCl₃), δ 7.85 (s, 1H), 7.20 (dd, *J* = 8.7 Hz, *J* = 4.3 Hz, 1H), 7.08 (dd, *J* = 1.8 Hz, *J* = 9.4 Hz, 1H), 6.89 (dt, *J* = 2.1 Hz, *J* = 9.1 Hz, 1H), 3.09 (t, *J* = 7.3 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.2, 158.1 (d, *J* = 234 Hz), 154.2, 133.9, 131.8, 128.2, 111.3 (d, *J* = 8 Hz), 109.7 (d, *J* = 26 Hz), 108.4, 102.6 (d, *J* = 23 Hz), 25.9, 19.8, 11.8. **¹⁹F NMR** (376 MHz, CDCl₃) δ -114.8--124.1 (m, 1F).

HRMS (ESI) Calcd. For C₁₃H₁₂N₂O₃F: [M+H]⁺ : 263.0762, Found: *m/z* 263.0763.



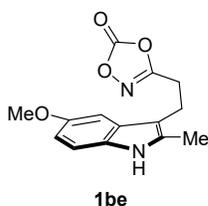
¹H NMR (400 MHz, CDCl₃), δ 7.76 (s, 1H), 7.22 (s, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.10 (t, *J* = 7.3 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.4, 154.3, 133.6, 132.0, 128.9, 128.0, 122.9, 117.1, 110.3, 107.5, 25.9, 21.6, 19.7, 11.5.

HRMS (ESI) Calcd. For C₁₄H₁₅N₂O₃: [M+H]⁺ : 259.1004, Found: *m/z* 259.1002.



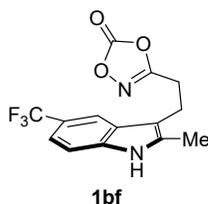
¹H NMR (400 MHz, CDCl₃), δ 8.09 (s, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.40 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.2, 154.2, 134.0, 132.9, 128.9, 123.8, 120.9, 116.5, 109.3, 104.3, 25.9, 19.8, 11.6.

HRMS (ESI) Calcd. For C₁₃H₁₂N₂O₃Br: [M+H]⁺ : 322.9931, Found: m/z 322.9937.



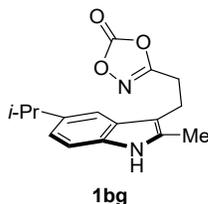
¹H NMR (400 MHz, CDCl₃), δ 8.04 (s, 1H), 7.13 (d, *J* = 8.7 Hz, 1H), 6.91 (s, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 3.87 (s, 3H), 3.08 (t, *J* = 7.3 Hz, 3H), 2.88 (t, *J* = 7.4 Hz, 4H), 2.32 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.4, 154.3, 154.0, 132.9, 130.4, 128.2, 111.3, 110.8, 107.7, 99.7, 56.0, 25.8, 19.6, 11.5.

HRMS (ESI) Calcd. For C₁₄H₁₅N₂O₄: [M+H]⁺ : 275.0967, Found: m/z 275.0969.



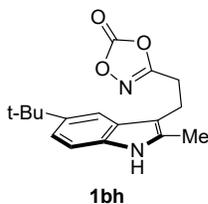
¹H NMR (400 MHz, CDCl₃), δ 8.07 (s, 1H), 7.71 (s, 1H), 7.40-7.34 (m, 2H), 3.16 (t, *J* = 7.3 Hz, 2H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.2, 154.3, 136.8, 134.1, 127.3, 126.7 (d, *J* = 455 Hz), 122.0, 118.4, 114.9, 110.9, 109.0, 26.0, 19.4, 11.6; **¹⁹F NMR** (376 MHz, CDCl₃) δ -60.0 (s, 3F).

HRMS (ESI) Calcd. For C₁₄H₁₂N₂O₃F₃: [M+H]⁺ : 313.0791, Found: m/z 313.0794.



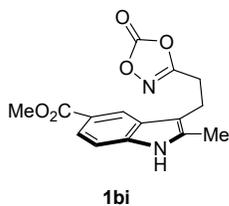
¹H NMR (400 MHz, CDCl₃), δ 7.90 (s, 1H), 7.32 (s, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 3.16 (t, *J* = 7.4 Hz, 2H), 3.08 (septet, *J* = 6.9 Hz, 1H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 1.38 (d, *J* = 7.0 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.6, 154.3, 147.9, 140.4, 133.8, 132.1, 127.9, 120.4, 114.2, 110.4, 107.7, 34.4, 26.0, 24.8, 19.7, 11.5.

HRMS (ESI) Calcd. For C₁₆H₁₉N₂O₃: [M+H]⁺ : 287.1319, Found: m/z 287.1314.



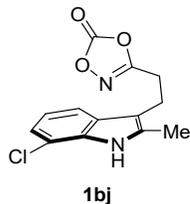
¹H NMR (400 MHz, CDCl₃), δ 7.76 (s, 1H), 7.42 (s, 1H), 7.24-7.26 (m, 2H), 3.15 (t, *J* = 7.4 Hz, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 1.41 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.5, 154.3, 142.8, 133.4, 132.0, 127.6, 119.8, 113.0, 110.2, 108.1, 34.7, 32.1, 26.1, 19.7, 11.7.

HRMS (ESI) Calcd. For C₁₇H₂₀N₂O₃Na: [M+Na]⁺ : 323.1364, Found: m/z 323.1367.



¹H NMR (400 MHz, CDCl₃), δ 8.19 (s, 2H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H), 3.15 (t, *J* = 7.5 Hz, 2H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.38 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 168.3, 166.2, 154.2, 138.1, 133.6, 127.5, 123.2, 121.8, 120.2, 110.3, 109.4, 52.1, 26.1, 19.5, 11.7.

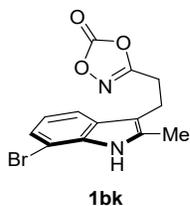
HRMS (ESI) Calcd. For C₁₅H₁₅N₂O₅: [M+H]⁺ : 303.0913, Found: m/z 303.0917.



¹H NMR (400 MHz, CDCl₃), δ 8.09 (s, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 6.8 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 3.12 (t, *J* = 7.4 Hz, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.41 (s,

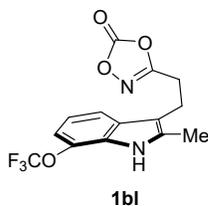
3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 154.2, 132.9, 132.6, 129.3, 121.0, 120.6, 116.2, 116.0, 109.2, 26.0, 19.8, 11.7.

HRMS (ESI) Calcd. For $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3\text{Cl}$: $[\text{M}+\text{H}]^+$: 279.0458, Found: m/z 279.0459.



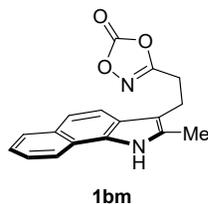
^1H NMR (400 MHz, CDCl_3), δ 8.09 (s, 1H), 7.38 (d, $J = 7.9$ Hz, 1H), 7.29 (d, $J = 7.2$ Hz, 1H), 6.99 (t, $J = 7.8$ Hz, 1H), 3.10 (t, $J = 7.2$ Hz, 2H), 2.91 (t, $J = 7.6$ Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 154.2, 134.0, 132.9, 128.9, 123.8, 120.9, 116.5, 109.3, 104.3, 25.9, 19.8, 11.6.

HRMS (ESI) Calcd. For $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3\text{Br}$: $[\text{M}+\text{H}]^+$: 322.9968, Found: m/z 322.9967.



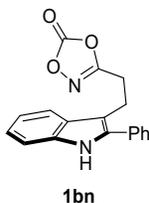
^1H NMR (400 MHz, CDCl_3), δ 8.12 (s, 1H), 7.36 (d, $J = 7.2$ Hz, 1H), 7.10-7.04 (m, 2H), 3.13 (t, $J = 7.3$ Hz, 2H), 2.94 (t, $J = 7.1$ Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 154.2, 134.3, 133.2, 131.0, 127.6, 121.1 (d, $J = 257$ Hz), 120.0, 116.1, 113.2, 109.0, 25.9, 19.7, 11.7. ^{19}F NMR (376 MHz, CDCl_3) δ -57.5 (s, 3F)

HRMS (ESI) Calcd. For $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{F}_3$: $[\text{M}+\text{H}]^+$: 329.0745, Found: m/z 329.0749.



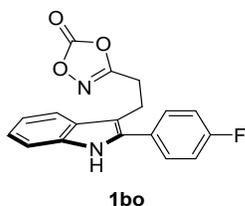
^1H NMR (400 MHz, CDCl_3), δ 8.71 (s, 1H), 7.92 (t, $J = 9.7$ Hz, 1H), 7.56-7.48 (m, 3H), 7.43-7.38 (m, 1H), 3.17 (t, $J = 7.3$ Hz, 2H), 2.94 (t, $J = 7.3$ Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 154.3, 130.1, 129.9, 129.6, 129.1, 125.7, 123.8, 123.5, 121.4, 120.7, 119.3, 117.7, 109.9, 26.4, 19.9, 11.7.

HRMS (ESI) Calcd. For $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 295.1077, Found: m/z 295.1074.



¹H NMR (400 MHz, CDCl₃), δ 8.14 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.51-7.50 (m, 4H), 7.45-7.41 (m, 2H), 7.28-7.18 (m, 2H), 3.35 (t, *J* = 7.6 Hz, 2H), 2.92 (t, *J* = 7.7 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.1, 154.1, 135.9, 135.6, 132.5, 129.3, 128.5, 128.2, 128.1, 122.9, 120.3, 118.3, 111.3, 109.2, 26.0, 20.2.

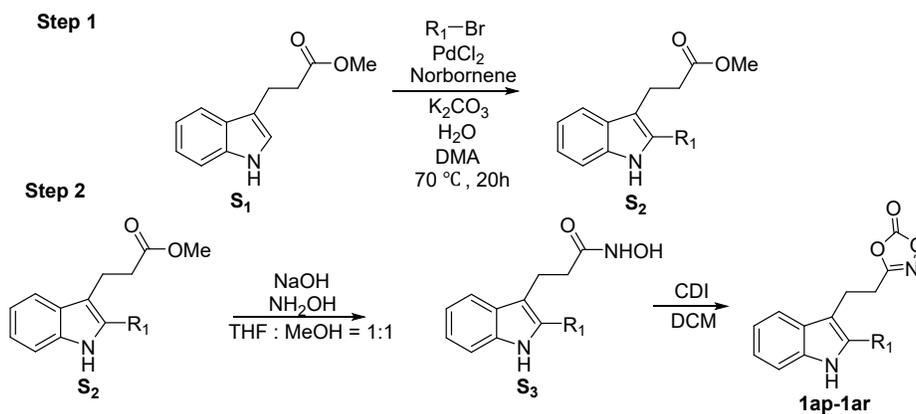
HRMS (ESI) Calcd. For C₁₈H₁₅N₂O₃: [M+H]⁺ : 307.1078, Found: m/z 307.1074.



¹H NMR (400 MHz, CDCl₃), δ 8.10 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.28-7.18 (m, 4H), 3.30 (t, *J* = 7.8 Hz, 2H), 2.91 (t, *J* = 7.8 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.1, 162.8 (d, *J* = 254 Hz), 154.1, 135.9, 134.7, 130.0 (d, *J* = 8 Hz), 123.0, 128.6, 128.1, 123.0, 120.4, 118.3, 116.5 (d, *J* = 22 Hz), 111.3, 109.3, 26.0, 20.1. **¹⁹F NMR** (376 MHz, CDCl₃) δ -112.4 (s, 1F).

HRMS (ESI) Calcd. For C₁₈H₁₄N₂O₃F: [M+H]⁺ : 325.0986, Found: m/z 325.0985.

Method B

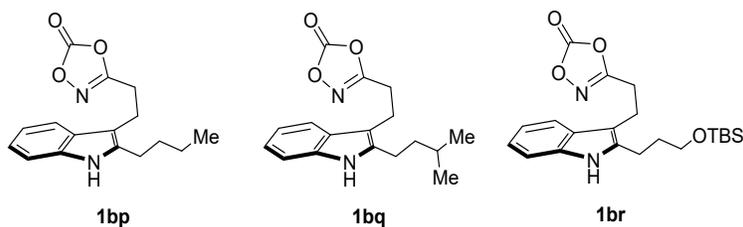


Step 1: Adapted from literature. To a stirring mixture of methyl 3-(1H-indol-3-yl)propanoate (0.304 g, 1.50 mmol), norbornene (0.282 g, 3.00 mmol, 2.0 eq), K₂CO₃ (0.415g, 3.00 mmol, 2.0 eq), PdCl₂ (0.026 g, 0.15 mmol, 0.10 eq) and H₂O (0.110 mL, 0.60 mmol,

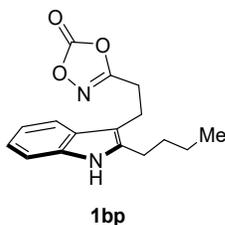
0.40 eq) in *N,N*-dimethylacetamide (7.50 mL) was added alkyl bromide (6.00 mmol, 4.0 eq) at 25 °C under a nitrogen atmosphere. After stirring at 70 °C for 20 h, the resulting mixture was cooled to 25 °C and filtered through a short pad of celite with EtOAc (50 mL)^[6]. The filtrate was washed with water (twice) and brine. The organic layers were dried over anhydrous Na₂SO₄ and solvents were removed in vacuo. The residue was purified by flash column chromatography on silica gel (Petroleum ether : EtOAc = 10:1) affording **S2**.

Step 2: To a solution of **S2** (2.0 mmol, 1.0 eq) and NaOH (0.4 g, 10.0 mmol, 5.0 eq) in (1:1) MeOH/THF (0.25 M) at room temperature was added 50% aqueous hydroxylamine (2.0 mL, 64.0 mmol, 32.0 eq). The mixture was stirred for 4.5 h at room temperature and then concentrated under reduced pressure^[7]. The combined organic extracts were washed with brine, dried over Na₂SO₄, concentrated.

The crude product was dissolved in CH₂Cl₂ (35.0 mL) and cooled to 0 °C. The CDI (0.326 g, 3.0 mmol, 1.5 equiv) was slowly added. The resulting mixture was stirred for 15 mins, quenched with 2 M HCl, and extracted with CH₂Cl₂. The organic phase was concentrated and purified by column chromatography (silica gel, CH₂Cl₂), affording the dioxazolones^[5].



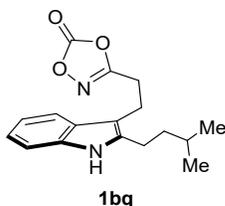
These compounds are unknown products, with yields ranging from 70% to 80%.



¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.46, (d, *J* = 7.6 Hz, 1H) 7.31 (d, *J* = 7.6 Hz, 1H), 7.18-7.09 (m, 2H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 1.64 (t, *J* = 7.6 Hz, 2H), 1.44-1.35 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ¹³C NMR

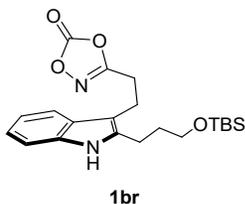
(100 MHz, CDCl₃) δ 166.3, 154.3, 136.5, 135.4, 127.7, 121.6, 119.7, 117.5, 110.7, 107.8, 32.1, 26.2, 25.8, 22.6, 19.9, 12.0.

HRMS (ESI) Calcd. For C₁₆H₁₉N₂O₃F: [M+H]⁺ : 287.1315, Found: m/z 287.1317.



¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.18-7.09 (m, 2H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.94 (t, *J* = 8 Hz, 2H), 2.72 (t, *J* = 8 Hz, 2H), 1.64 (q, *J* = 6.8 Hz, 1H), 1.57-1.51 (m, 2H), 0.97 (d, *J* = 6.4 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.3, 154.3, 136.6, 135.4, 127.7, 121.6, 119.7, 117.5, 110.7, 107.6, 39.0, 28.0, 26.21, 24.0, 22.5, 19.9.

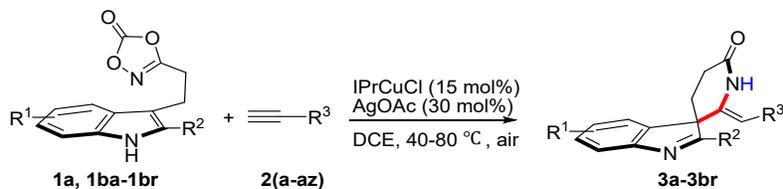
HRMS (ESI) Calcd. For C₁₇H₂₁N₂O₃F: [M+H]⁺ : 301.1472, Found: m/z 301.1474.



¹H NMR (400 MHz, CDCl₃) δ 8.65 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.17-7.09 (m, 2H), 3.73 (t, *J* = 6.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 2H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 1.89- 1.83 (m, 2H), 0.97 (s, 9H), 0.13 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.4, 154.3, 136.2, 135.4, 127.7, 121.5, 119.5, 117.6, 110.8, 107.6, 62.6, 31.9, 26.3, 26.1, 22.6, 19.8, 18.5, -5.2.

HRMS (ESI) Calcd. For C₂₁H₃₁N₂O₄Si: [M+H]⁺ : 403.1976, Found: m/z 403.1975.

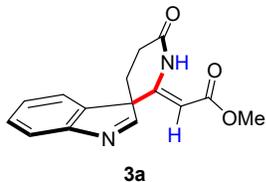
2.5 General procedure for the reaction of Dioxazolones and Alkynes



The **1a**, **1(ba-br)** (0.20 mmol), IPrCuCl (14.6 mg, 0.03 mmol, 0.15 equiv), and AgOAc (10.0 mg, 0.06 mmol, 0.3 equiv) was dissolved in DCE (3 mL), and the **2(a-az)** (0.6 mmol,

3.0 equiv) was added. The mixture was heated 40-80 °C in an oil bath for 15-60 mins. The organic layer was concentrated and purified by column chromatography.

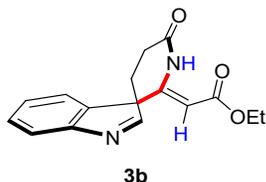
1) Compound of 3a



Yellow solid, yield 88% (47.6 mg), $R_f = 0.50$ (DCM : EtOAc = 8:1), M. p. = 109-110 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.02 (bs, 1H), 8.16 (s, 1H), 7.70 (d, $J = 7.8$ Hz, 1H), 7.47-7.43 (m, 1H), 7.33 (t, $J = 6.7$ Hz, 2H), 4.46 (s, 1H), 3.61 (s, 1H), 2.96-2.78 (m, 2H), 2.07-2.06 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.4, 168.7, 168.4, 155.0, 150.2, 139.6, 129.7, 127.6, 122.8, 122.6, 91.3, 59.4, 51.5, 30.0, 27.0.

HRMS (ESI) Calcd. For $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 271.1078, Found: m/z 271.1077.

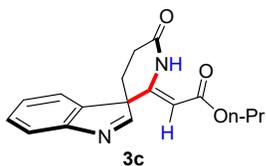
2) Compound of 3b



Yellow oil, yield 85% (48.3 mg), $R_f = 0.50$ (DCM : EtOAc = 8:1); $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.07 (bs, 1H), 8.16 (s, 1H), 7.69 (d, $J = 7.8$ Hz, 1H), 7.46-7.42 (m, 1H), 7.34 (t, $J = 5.9$ Hz, 2H), 4.44 (s, 1H), 4.10-4.02 (m, 2H), 2.94-2.76 (m, 2H), 2.14-2.06 (m, 2H), 1.16 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.4, 168.7, 168.0, 154.9, 150.0, 139.6, 129.6, 127.5, 122.8, 122.4, 91.6, 60.4, 59.4, 29.9, 26.9, 14.2.

HRMS (ESI) Calcd. For $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 285.1161, Found: m/z 285.1160.

3) Compound of 3c

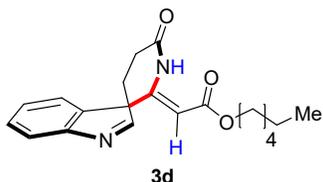


Yellow oil, yield 83% (49.5 mg), $R_f = 0.53$ (DCM : EtOAc = 8:1); $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.09 (bs, 1H), 8.17 (s, 1H), 7.71 (d, $J = 7.7$ Hz, 1H), 7.48-7.44 (m, 1H), 7.35-7.31 (m, 2H), 4.47 (s, 1H), 4.01-3.95 (m, 2H), 2.96-2.78 (m, 2H), 2.19-

2.04 (m, 2H), 1.59-1.54 (m, 2H), 0.87 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 168.7, 168.1, 155.0, 150.0, 139.7, 129.7, 127.6, 122.9, 122.6, 91.7, 66.1, 59.4, 30.0, 27.0, 22.0, 10.4.

HRMS (ESI) Calcd. For $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 299.1317, Found: m/z 299.1316.

4) Compound of 3d

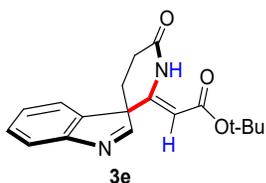


Yellow oil, yield 89% (60.6 mg), $R_f = 0.55$ (DCM : EtOAc = 8:1);

^1H NMR (400 MHz, CDCl_3), δ 11.08 (bs, 1H), 8.16 (s, 1H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.47-7.42 (m, 1H), 7.34 (t, $J = 5.9$ Hz, 2H), 4.45 (s, 1H), 4.05-3.94 (m, 2H), 2.94-2.76 (m, 2H), 2.17-2.05 (m, 2H), 1.53-1.48 (m, 2H), 1.27-1.19 (m, 6H), 0.83 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 168.6, 168.1, 154.9, 149.9, 139.6, 129.6, 127.5, 122.8, 122.5, 91.6, 64.6, 59.3, 31.4, 29.9, 28.5, 26.9, 25.5, 22.5, 14.1.

HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 341.1860, Found: m/z 341.1861.

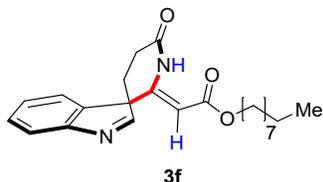
5) Compound of 3e



Yellow solid, yield 87% (54.3 mg), $R_f = 0.53$ (DCM : EtOAc = 8:1), M. p. = 163-164 °C;

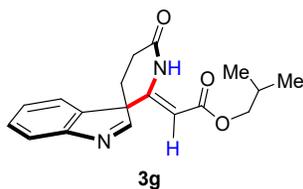
^1H NMR (400 MHz, CDCl_3), δ 11.17 (bs, 1H), 8.16 (s, 1H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.47-7.43 (m, 1H), 7.38-7.30 (m, 2H), 4.38 (s, 1H), 4.05-3.94 (m, 2H), 2.93-2.76 (m, 2H), 2.18-2.01 (m, 2H), 0.38 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.8, 168.7, 167.7, 154.9, 149.0, 139.8, 129.6, 127.5, 122.9, 122.4, 93.6, 81.3, 59.3, 29.9, 28.2, 27.0. **HRMS (ESI)** Calcd. For $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 313.1548, Found: m/z 313.1540.

6) Compound of 3f



Yellow solid, yield 85% (62.6 mg), $R_f = 0.55$ (DCM : EtOAc = 8:1), M. p. = 69-70 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.09 (bs, 1H), 8.17 (s, 1H), 7.71 (d, $J = 7.7$ Hz, 1H), 7.48-7.44 (m, 1H), 7.37-7.31 (m, 2H), 4.46 (s, 1H), 4.06-3.95 (m, 2H), 2.96-2.77 (m, 2H), 2.18-2.04 (m, 2H), 1.54-1.49 (m, 2H), 1.27-1.20 (m, 12H), 0.84 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.5, 168.6, 168.1, 155.0, 149.9, 139.7, 129.7, 127.5, 122.8, 122.5, 91.6, 64.6, 59.4, 31.8, 29.9, 29.2, 29.2, 28.6, 27.0, 25.9, 22.7, 14.2. **HRMS (ESI)** Calcd. For $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 269.2129, Found: m/z 269.2126.

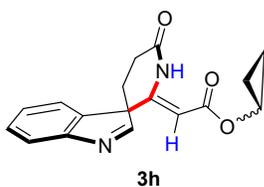
7) Compound of 3g



Yellow solid, yield 84% (52.4 mg), $R_f = 0.53$ (DCM : EtOAc = 8:1), M. p. = 50-51 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.08 (bs, 1H), 8.16 (s, 1H), 7.69 (d, $J = 7.7$ Hz, 1H), 7.46-7.42 (m, 1H), 7.36-7.29 (m, 2H), 4.46 (s, 1H), 3.83-3.73 (m, 2H), 2.92-2.77 (m, 2H), 2.17-2.02 (m, 2H), 1.86-1.76 (m, 1H), 0.83 (d, $J = 6.8$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.6, 168.6, 168.0, 154.8, 149.9, 139.6, 129.6, 127.5, 122.8, 122.4, 91.5, 70.4, 59.3, 29.8, 27.6, 26.8, 19.1.

HRMS (ESI) Calcd. For $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 313.1550, Found: m/z 313.1545.

8) Compound of 3h



Yellow solid, yield 91% (53.9 mg), $R_f = 0.50$ (DCM : EtOAc = 8:1), M. p. = 100-101 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.05 (bs, 1H), 8.16 (s, 1H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.48-7.44 (m, 1H), 7.36-7.31 (m, 2H), 4.39 (s, 1H), 3.09-3.04 (m, 1H), 2.98-2.78 (m, 2H), 2.18-2.06 (m, 2H), 1.68-1.58 (m, 4H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.3, 168.9, 168.6, 155.0, 150.4, 139.6, 129.7, 127.6, 122.8, 122.5, 91.1, 59.4, 48.9, 30.0, 26.9, 5.2, 5.1.

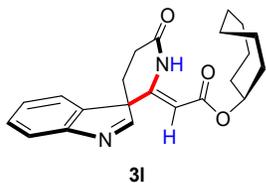
HRMS (ESI) Calcd. For $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 297.1234, Found: m/z 297.1233.

9) Compound of 3i

MHz, CDCl₃) δ 171.6, 168.7, 167.5, 154.9, 149.6, 139.7, 129.7, 127.5, 122.9, 122.5, 92.2, 73.0, 59.4, 31.7, 29.9, 27.0, 25.4, 23.8.

HRMS (ESI) Calcd. For C₂₀H₂₃N₂O₃ : [M+H]⁺ : 339.1603, Found: m/z 339.1610.

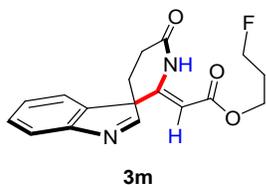
12) Compound of 3l



Yellow solid, yield 89% (65.2 mg), R_f = 0.55 (DCM : EtOAc = 8:1), M. p. = 75-76 °C; ¹H NMR (400 MHz, CDCl₃), δ 11.13 (bs, 1H), 8.17 (bs, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.47-7.43 (m, 1H), 7.37-7.32 (m, 2H), 4.90-4.85 (m, 1H), 4.43 (s, 1H), 2.94-2.76 (m, 2H), 2.19-2.02 (m, 2H), 1.81-1.79 (m, 2H), 1.56-1.49 (m, 8H), 1.37 (bs, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 171.6, 168.6, 167.4, 154.9, 149.6, 139.7, 129.6, 127.5, 122.9, 122.5, 92.2, 75.4, 59.3, 33.8, 29.9, 28.3, 26.9, 22.8.

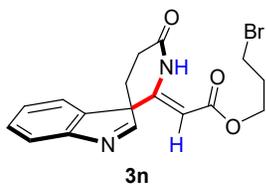
HRMS (ESI) Calcd. For C₂₂H₂₇N₂O₃ : [M+H]⁺ : 367.1960, Found: m/z 367.1965.

13) Compound of 3m



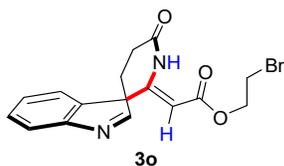
Yellow solid, yield 85% (53.7 mg), R_f = 0.52 (DCM : EtOAc = 8:1), M. p. = 82-83 °C; ¹H NMR (400 MHz, CDCl₃), δ 11.03 (bs, 1H), 8.17 (bs, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.47-7.43 (m, 1H), 7.36-7.32 (m, 2H), 4.85 (t, J = 5.8 Hz, 1H), 4.44 (s, 1H), 4.37 (t, J = 5.8 Hz, 1H), 4.19-4.09 (m, 2H), 2.94-2.76 (m, 2H), 2.17-2.04 (m, 2H), 1.99-1.87 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 168.7, 167.8, 154.9, 150.5, 139.6, 129.7, 127.6, 122.8, 122.5, 91.1, 81.3-79.7 (d, J = 164 Hz), 60.3-60.2 (d, J = 5 Hz), 59.4, 29.9, 29.7-29.5 (d, J = 20 Hz), 26.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -221.9--222.4 (m, 1F). **HRMS (ESI)** Calcd. For C₁₇H₁₈FN₂O₃ : [M+H]⁺ : 317.1296, Found: m/z 317.1304.

14) Compound of 3n



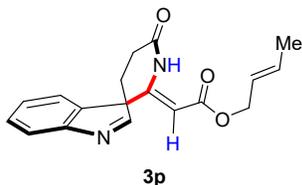
Yellow solid, yield 88% (66.2 mg), R_f = 0.52 (DCM : EtOAc = 8:1), M. p. = 48-49 °C;
 $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.04 (s, 1H), 8.20 (bs, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.49-7.45 (m, 1H), 7.38-7.32 (m, 2H), 4.45 (s, 1H), 4.22-4.12 (m, 2H), 3.37 (t, J = 6.5 Hz, 1H), 2.97-2.79 (m, 2H), 2.16-2.06 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.4, 168.7, 167.8, 155.0, 150.6, 139.6, 129.8, 127.6, 122.9, 122.6, 91.1, 62.0, 59.4, 31.6, 30.0, 29.5, 26.9.
HRMS (ESI) Calcd. For $\text{C}_{17}\text{H}_{18}\text{BrN}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 377.0495, Found: m/z 377.0488.

15) Compound of 3o



Yellow solid, yield 84% (60.8 mg), R_f = 0.52 (DCM : EtOAc = 8:1), M. p. = 66-67 °C;
 $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 10.98 (s, 1H), 8.18 (s, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.49-7.45 (m, 1H), 7.37-7.32 (m, 2H), 4.50 (s, 1H), 4.40-4.29 (m, 2H), 3.43 (t, J = 6.1 Hz, 1H), 2.98-2.79 (m, 2H), 2.20-2.06 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.2, 168.9, 167.4, 155.0, 151.2, 139.5, 129.8, 127.7, 122.8, 122.6, 90.7, 63.8, 59.5, 30.0, 28.6, 26.9.
HRMS (ESI) Calcd. For $\text{C}_{16}\text{H}_{16}\text{BrN}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 363.0330, Found: m/z 363.0334.

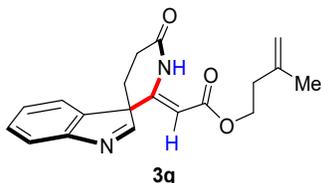
16) Compound of 3p



Yellow solid, yield 76% (47.1 mg), R_f = 0.54 (DCM : EtOAc = 8:1), M. p. = 67-68 °C;
 $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.06 (s, 1H), 8.16 (s, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.46-7.41 (m, 1H), 7.35-7.29 (m, 2H), 5.77-5.68 (m, 1H), 5.52-5.44 (m, 1H), 4.45 (s, 1H), 4.46-4.43 (m, 2H), 2.94-2.77 (m, 2H), 1.65 (d, J = 6.5 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.2, 168.9, 167.4, 155.0, 151.2, 139.5, 129.8, 127.7, 122.8, 122.6, 90.7, 63.8, 59.5, 30.0, 28.6, 26.9.

HRMS (ESI) Calcd. For $C_{18}H_{19}N_2O_3$: $[M+H]^+$: 311.1390, Found: m/z 311.1387.

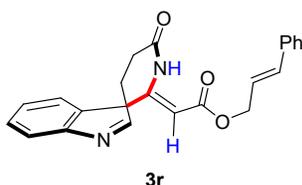
17) Compound of 3q



White solid, yield 90% (58.3 mg), R_f = 0.54 (DCM : EtOAc = 8:1), M. p. = 125-126 °C; 1H NMR (400 MHz, $CDCl_3$), δ 11.05 (s, 1H), 8.16 (s, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.47-7.43 (m, 1H), 7.35-7.30 (m, 2H), 4.75 (s, 1H), 4.66 (s, 1H), 4.45 (s, 1H), 4.19-4.07 (m, 2H), 2.95-2.77 (m, 2H), 2.25 (t, J = 6.9 Hz, 2H), 2.18-2.03 (m, 2H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 168.7, 167.9, 154.9, 150.1, 141.4, 139.6, 129.7, 127.6, 122.8, 122.6, 112.5, 91.5, 62.6, 59.4, 36.6, 29.9, 27.0, 22.6.

HRMS (ESI) Calcd. For $C_{19}H_{21}N_2O_3$: $[M+H]^+$: 325.1540, Found: m/z 325.1543.

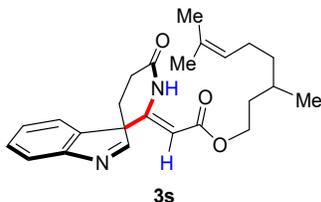
18) Compound of 3r



Yellow solid, yield 94% (70.0 mg), R_f = 0.56 (DCM : EtOAc = 8:1), M. p. = 89-90 °C; 1H NMR (400 MHz, $CDCl_3$), δ 11.08 (s, 1H), 8.17 (s, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.48-7.44 (m, 1H), 7.37-7.22 (m, 7H), 6.59 (d, J = 15.9 Hz, 1H), 6.19 (dt, J = 15.9 Hz, J = 6.5 Hz, 1H), 4.68 (d, J = 6.6 Hz, 2H), 4.51 (s, 1H), 2.97-2.79 (m, 2H), 2.16-2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 168.6, 167.7, 155.0, 150.5, 139.6, 136.0, 134.8, 129.7, 128.7, 128.2, 127.6, 126.7, 122.8, 122.7, 122.5, 91.3, 65.0, 59.4, 30.0, 26.9.

HRMS (ESI) Calcd. For $C_{23}H_{21}N_2O_3$: $[M+H]^+$: 372.1447, Found: m/z 372.1443.

19) Compound of 3s

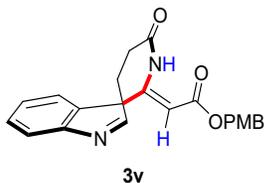


Yellow oil, yield 83% (65.4 mg), R_f = 0.56 (DCM : EtOAc = 8:1);

155.0, 150.6, 139.6, 135.6, 129.7, 128.7, 128.6, 127.6, 122.9, 122.6, 91.4, 66.3, 59.5, 30.0, 27.0.

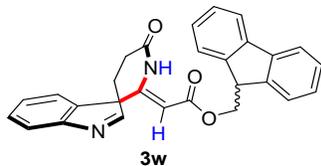
HRMS (ESI) Calcd. For $C_{21}H_{19}N_2O_3$: $[M+H]^+$: 347.1390, Found: m/z 347.1399.

22) Compound of 3v



Yellow solid, yield 62% (46.6 mg), R_f = 0.55 (DCM : EtOAc = 8:1), M. p. = 131-132 °C; 1H NMR (400 MHz, $CDCl_3$), δ 11.09 (s, 1H), 8.15 (s, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.46-7.42 (m, 1H), 7.34-7.29 (m, 7H), 7.22 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 1H), 5.03-4.96 (m, 2H), 4.48 (s, 1H), 3.78 (s, 3H), 2.96-2.78 (m, 2H), 2.11 (t, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 168.7, 167.8, 159.8, 155.0, 150.4, 139.5, 130.4, 129.7, 127.6, 127.6, 122.8, 122.5, 114.0, 91.5, 66.1, 59.4, 55.4, 30.0, 26.9. **HRMS (ESI)** Calcd. For $C_{22}H_{21}N_2O_4$: $[M+H]^+$: 377.1496, Found: m/z 377.1494.

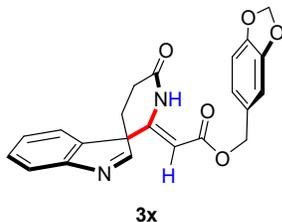
23) Compound of 3w



Yellow solid, yield 77% (64.7 mg), R_f = 0.57 (DCM : EtOAc = 8:1), M. p. = 65-66 °C; 1H NMR (400 MHz, $CDCl_3$), δ 11.11 (s, 1H), 8.21 (s, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.74 (d, J = 7.5 Hz, 2H), 7.53-7.47 (m, 1H), 7.38 (d, J = 7.4 Hz, 4H), 7.30-7.27 (m, 2H), 4.60 (s, 1H), 4.39-4.27 (m, 2H), 4.13 (d, J = 7.2 Hz, 1H), 2.99-2.80 (m, 2H), 2.25-2.18 (m, 1H), 2.09-2.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 168.7, 168.0, 154.9, 150.8, 143.7, 143.6, 141.3, 139.7, 129.8, 127.9, 127.6, 127.2, 125.1, 122.8, 122.7, 120.2, 91.0, 66.4, 59.4, 46.7, 29.8, 26.9.

HRMS (ESI) Calcd. For $C_{27}H_{21}N_2O_3$: $[M+H]^+$: 420.1473, Found: m/z 420.1471.

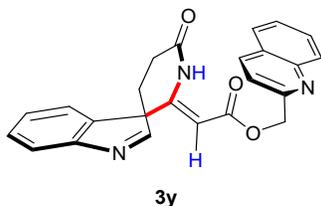
24) Compound of 3x



Yellow solid, yield 66% (51.5 mg), $R_f = 0.57$ (DCM : EtOAc = 8:1), M. p. = 45-46 °C;
 $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.07 (s, 1H), 8.15 (s, 1H), 7.77 (d, $J = 7.7$ Hz, 1H), 7.56-7.42 (m, 1H), 7.35-7.31 (m, 2H), 6.77-6.75 (m 2H), 6.74 (s, 1H), 5.92 (s, 2H), 4.91-4.98 (m, 2H), 4.48 (s, 1H), 2.94-2.79 (m, 2H), 2.09-2.13 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.3, 168.6, 167.7, 155.0, 150.6, 147.8, 139.5, 129.7, 129.2, 127.6, 122.8, 122.6, 122.5, 109.2, 108.3, 101.3, 91.3, 66.2, 59.4, 30.0, 26.9.

HRMS (ESI) Calcd. For $\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}_5$: $[\text{M}+\text{H}]^+$: 391.1288, Found: m/z 391.1290.

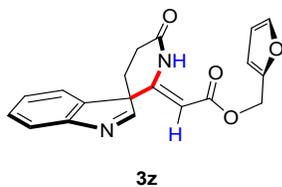
25) Compound of 3y



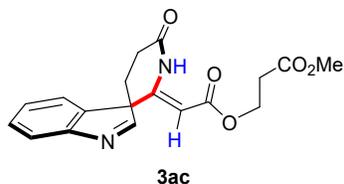
Brown solid, yield 74% (58.8 mg), $R_f = 0.48$ (DCM : EtOAc = 8:1), M. p. = 72-73 °C;
 $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.03 (s, 1H), 8.15 (s, 1H), 8.09 (d, $J = 8.5$ Hz, 1H), 8.02 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 7.5$ Hz, 1H), 7.70-7.64 (m, 2H), 7.51-7.41 (m, 2H), 7.35-7.30 (m, 3H), 5.38-5.28 (m, 2H), 4.60 (s, 1H), 2.98-2.76 (m, 2H), 2.07 (t, $J = 8.2$ Hz, 2H)); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.2, 168.6, 167.5, 155.7, 154.9, 151.0, 147.6, 139.4, 137.0, 129.9, 129.6, 129.1, 127.6, 127.5, 126.7, 122.8, 122.4, 119.5, 90.8, 67.1, 59.4, 29.8, 26.8.

HRMS (ESI) Calcd. For $\text{C}_{24}\text{H}_{20}\text{N}_3\text{O}_3$: $[\text{M}+\text{H}]^+$: 398.1459, Found: m/z 398.1458.

26) Compound of 3z



Yellow solid, yield 74% (49.7 mg), $R_f = 0.49$ (DCM : EtOAc = 8:1), M. p. = 77-78 °C;

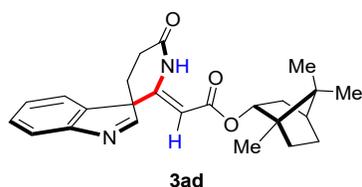


Yellow oil, yield 89% (57.7 mg), $R_f = 0.45$ (DCM : EtOAc = 8:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.00 (s, 1H), 8.15 (s, 1H), 7.70 (d, $J = 7.5$ Hz, 1H), 7.47-7.43 (m, 1H), 7.35-7.30 (m, 2H), 4.44 (s, 1H), 4.34-4.25 (m, 2H), 3.65 (s, 3H), 2.95-2.77 (m, 2H), 2.57 (t, $J = 6.2$ Hz, 1H), 2.17-2.02 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.3, 171.1, 168.6, 167.6, 154.9, 150.6, 139.5, 129.7, 127.6, 122.8, 122.5, 91.0, 59.7, 59.4, 52.0, 33.5, 29.9, 26.9.

HRMS (ESI) Calcd. For $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_5$: $[\text{M}+\text{H}]^+$: 343.1254, Found: m/z 343.1257.

30) Compound of 3ad

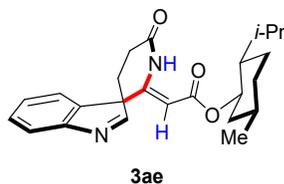


Yellow solid, yield 73% (57.3 mg), $R_f = 0.55$ (DCM : EtOAc = 8:1), M. p. = 85-86 °C;

$^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.13 (s, 1H), 8.17 (d, $J = 2.2$ Hz, 1H), 7.48-7.44 (m, 1H), 7.38-7.31 (m, 2H), 4.85-4.78 (m, 1H), 4.49 (s, 1H), 2.95-2.76 (m, 2H), 2.31-2.14 (m, 2H), 2.06-1.98 (m, 1H), 1.76-1.60 (m, 3H), 1.29-1.08 (m, 3H), 0.85 (s, 1H), 0.81 (s, 1H), 0.73 (d, $J = 8.8$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.9, 171.8, 168.6, 168.5, 154.9, 149.6, 139.7, 129.7, 127.5, 122.9, 122.5, 92.0, 91.9, 80.2, 80.2, 59.3, 48.8, 48.8, 47.9, 44.8, 36.8, 36.6, 29.8, 29.8, 28.0, 27.0, 26.9, 26.9, 19.8, 18.9, 13.6.

HRMS (ESI) Calcd. For $\text{C}_{24}\text{H}_{29}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 393.2154, Found: m/z 393.2151.

31) Compound of 3ae



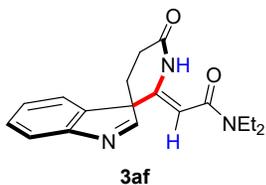
White solid, yield 75% (59.1 mg), $R_f = 0.55$ (DCM : EtOAc = 8:1), M. p. = 185-186 °C;

$^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.15 (s, 1H), 8.17 (d, $J = 6.4$ Hz, 1H), 7.71 (d, $J = 7.7$ Hz, 1H), 7.48-7.44 (m, 2H), 7.37-7.32 (m, 2H), 4.65 (dt, $J = 4.4$ Hz, $J = 10.9$ Hz, 1H), 4.43 (d,

$J = 6.2$ Hz, 1H), 2.94-2.77 (m, 2H), 2.16-2.03 (m, 2H), 1.90-1.87 (m, 1H), 1.74-1.58 (m, 4H), 1.45-1.40 (m, 1H), 1.27-1.20 (m, 2H), 1.05-0.94 (m, 1H), 0.85-0.80 (m, 6H), 0.68 (t, $J = 6.8$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.6, 168.6, 167.7, 155.0, 149.8, 139.7, 129.6, 127.5, 122.9, 122.5, 92.0, 74.2, 59.4, 47.0, 46.9, 41.0, 34.2, 31.4, 30.0, 27.0, 26.0, 23.3, 22.1, 20.8, 16.2.

HRMS (ESI) Calcd. For $\text{C}_{24}\text{H}_{31}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 395.2332, Found: m/z 395.2331.

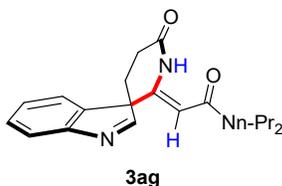
32) Compound of 3af



Yellow solid, yield 61% (38.0 mg), $R_f = 0.45$ (DCM : EtOAc = 8:1), M. p. = 142-143 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 12.26 (s, 1H), 8.19 (s, 1H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.46-7.42 (m, 1H), 7.37-7.29 (m, 2H), 4.57 (s, 1H), 3.29 (q, $J = 7.0$ Hz, 2H), 2.99 (q, $J = 7.2$ Hz, 2H), 2.90-2.74 (m, 2H), 2.17-2.03 (m, 2H), 1.05 (t, $J = 7.1$ Hz, 3H), 0.90 (t, $J = 7.1$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.3, 168.6, 166.7, 154.9, 147.3, 140.3, 129.5, 127.3, 122.8, 122.4, 90.1, 59.8, 42.5, 40.8, 30.0, 27.0, 14.5, 13.2.

HRMS (ESI) Calcd. For $\text{C}_{18}\text{H}_{22}\text{N}_3\text{O}_2$: $[\text{M}+\text{H}]^+$: 312.1607, Found: m/z 312.1606.

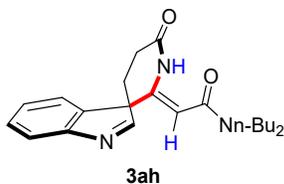
33) Compound of 3ag



Green solid, yield 55% (37.3 mg), $R_f = 0.43$ (DCM : EtOAc = 8:1), M. p. = 63-64 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 12.20 (s, 1H), 8.19 (s, 1H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.46-7.43 (m, 1H), 7.36-7.30 (m, 2H), 4.53 (s, 1H), 3.25-3.11 (m, 2H), 2.88-2.77 (m, 4H), 2.21-2.01 (m, 2H), 1.46 (q, $J = 7.4$ Hz, 2H), 1.31-1.24 (m, 2H), 0.83 (t, $J = 7.4$ Hz, 3H), 0.60 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.1, 168.5, 167.2, 155.0, 147.1, 140.2, 129.5, 127.3, 122.9, 122.3, 90.5, 59.9, 50.1, 48.3, 30.2, 27.1, 22.6, 21.2, 11.5, 11.1.

HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{26}\text{N}_3\text{O}_2$: $[\text{M}+\text{H}]^+$: 340.1907, Found: m/z 340.1906.

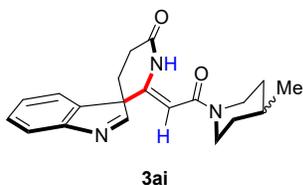
34) Compound of 3ah



Yellow solid, yield 52% (38.2 mg), $R_f = 0.48$ (DCM : EtOAc = 8:1), M. p. = 51-52 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 12.21 (s, 1H), 8.19 (s, 1H), 7.69 (d, $J = 7.7$ Hz, 1H), 7.45-7.41 (m, 1H), 7.36-7.31 (m, 2H), 4.53 (s, 1H), 3.27-3.15 (m, 2H), 2.88-2.77 (m, 4H), 2.21-2.01 (m, 2H), 1.45-1.37 (m, 2H), 1.27-1.21 (m, 4H), 0.98 (q, $J = 7.4$ Hz, 2H), 0.87 (t, $J = 7.5$ Hz, 3H), 0.70 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.0, 168.5, 167.0, 155.1, 147.1, 140.2, 129.4, 127.3, 122.8, 122.3, 90.5, 59.9, 48.2, 46.4, 31.4, 30.2, 30.2, 27.1, 20.3, 19.8, 14.0, 13.6.

HRMS (ESI) Calcd. For $\text{C}_{22}\text{H}_{30}\text{N}_3\text{O}_2$: $[\text{M}+\text{H}]^+$: 367.2267, Found: m/z 367.2262.

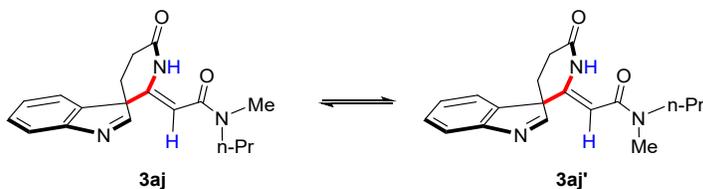
35) Compound of 3ai



Green solid, yield 67% (50.5 mg), $R_f = 0.48$ (DCM : EtOAc = 8:1), M. p. = 161-162 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 12.21 (s, 1H), 8.18 (s, 1H), 7.69 (d, $J = 7.7$ Hz, 1H), 7.46-7.42 (m, 1H), 7.36-7.30 (m, 2H), 4.68 (s, 1H), 4.48 (bs, 1H), 3.43 (d, $J = 13.1$ Hz, 1H), 2.90-2.72 (m, 3H), 2.45 (q, $J = 13.8$ Hz, 1H), 2.19-2.12 (m, 1H), 2.02-1.96 (m, 1H), 1.62-1.47 (m, 3H), 0.98-0.91 (m, 2H), 0.86 (d, $J = 5.6$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.0, 168.5, 167.0, 155.1, 147.1, 140.2, 129.4, 127.3, 122.8, 122.3, 90.5, 59.9, 48.2, 46.4, 31.4, 30.2, 30.2, 27.1, 20.3, 19.8, 14.0, 13.6.

HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{24}\text{N}_3\text{O}_2$: $[\text{M}+\text{H}]^+$: 338.1763, Found: m/z 338.1764.

36) Compound of 3aj



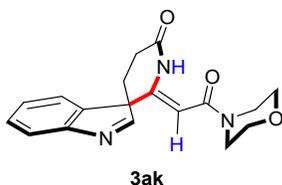
Yellow solid, yield 59% (39.8 mg), $R_f = 0.45$ (DCM : EtOAc = 8:1), M. p. = 62-63 °C;

For 3aj or 3aj' $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 12.26 (s, 1H), 8.19 (s, 1H), 7.69 (d, $J = 7.7$ Hz, 1H), 7.46-7.42 (m, 1H), 7.36-7.29 (m, 2H), 4.62 (s, 1H), 3.32-3.17 (m, 1H), 2.85 (s, 3H), 2.91-2.73 (m, 3H), 1.48-1.42 (m, 1H), 1.32-1.26 (m, 1H), 0.82 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.4, 168.6, 167.4, 155.0, 147.5, 140.2, 129.4, 127.3, 122.8, 122.3, 90.0, 59.8, 51.8, 35.5, 30.1, 27.0, 21.8, 11.3.

For 3aj or 3aj' $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 12.15 (s, 1H), 8.19 (s, 1H), 7.69 (d, $J = 7.7$ Hz, 1H), 7.46-7.42 (m, 1H), 7.36-7.29 (m, 2H), 4.57 (s, 1H), 3.32-3.17 (m, 1H), 2.91-2.73 (m, 3H), 2.69 (s, 3H), 1.48-1.42 (m, 1H), 1.32-1.26 (m, 1H), 0.62 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.1, 168.5, 167.3, 154.8, 147.2, 140.2, 129.4, 127.3, 122.8, 122.3, 89.9, 51.9, 49.3, 33.9, 29.9, 20.6, 11.0.

HRMS (ESI) Calcd. For $\text{C}_{18}\text{H}_{22}\text{N}_3\text{O}_2$: $[\text{M}+\text{H}]^+$: 312.1633, Found: m/z 312.1634.

37) Compound of 3ak

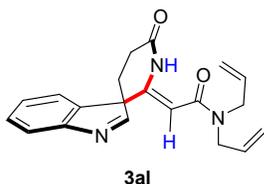


Yellow oil, yield 69% (44.9 mg), $R_f = 0.47$ (DCM : EtOAc = 8:1);

$^1\text{H NMR}$ (400 MHz, acetone- d_6), δ 12.21 (s, 1H), 8.43 (s, 1H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.51-7.49 (m, 1H), 7.46-7.41 (m, 1H), 7.34-7.30 (m, 1H), 4.65 (s, 1H), 3.50-3.42 (m, 2H), 3.19 (bs, 1H), 2.88-2.72 (m, 2H), 2.15-2.11 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, acetone- d_6) δ 173.0, 168.3, 166.6, 155.6, 149.6, 140.8, 129.2, 127.1, 123.1, 121.8, 87.7, 66.3, 60.0, 45.6, 41.4, 27.1.

HRMS (ESI) Calcd. For $\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_3$: $[\text{M}+\text{H}]^+$: 326.1497, Found: m/z 326.1494.

38) Compound of 3al



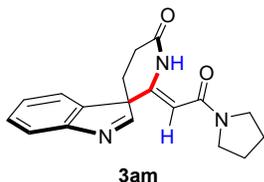
Green solid, yield 51% (34.2 mg), $R_f = 0.48$ (DCM : EtOAc = 8:1), M. p. = 53-54 $^\circ\text{C}$;

$^1\text{H NMR}$ (400 MHz, CDCl_3), δ 12.09 (s, 1H), 8.17 (s, 1H), 7.68 (d, $J = 7.7$ Hz, 1H), 7.55-7.41 (m, 1H), 7.34-7.28 (m, 2H), 7.73-5.63 (m, 1H), 5.53-5.43 (m, 1H), 5.12-5.04 (m, 1H), 4.95 (dd, $J = 0.68$ Hz, $J = 10.3$ Hz, 1H), 4.72 (dd, $J = 0.64$ Hz, $J = 17.2$ Hz, 1H), 4.56 (s,

1H), 3.90 (d, $J = 5.9$ Hz, 2H), 3.53 (d, $J = 5.2$ Hz, 2H), 2.91-2.73 (m, 2H), 2.12-2.05 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.0, 168.5, 167.6, 155.0, 147.9, 140.1, 133.0, 132.5, 129.4, 127.3, 122.9, 122.3, 117.5, 117.0, 90.2, 59.8, 49.8, 48.5, 30.0, 27.0.

HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{22}\text{N}_3\text{O}_2$: $[\text{M}+\text{H}]^+$: 336.1705, Found: m/z 336.1701.

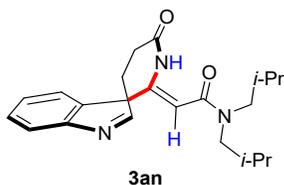
39) Compound of 3am



Yellow solid, yield 72% (44.5 mg), $R_f = 0.48$ (DCM : EtOAc = 8:1), M. p. = 96-97 °C; ^1H NMR (400 MHz, CDCl_3), δ 12.26 (s, 1H), 8.16 (s, 1H), 7.68 (d, $J = 7.7$ Hz, 1H), 7.45-7.41 (m, 1H), 7.35-7.29 (m, 2H), 7.73-5.63 (m, 1H), 4.48 (s, 1H), 3.37 (t, $J = 5.8$ Hz, 2H), 3.12-3.02 (m, 2H), 2.89-2.71 (m, 2H), 2.16-2.09 (m, 1H), 2.04-1.97 (m, 1H), 1.82-1.71 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.4, 168.6, 165.9, 154.8, 147.0, 140.2, 129.4, 127.3, 122.8, 122.3, 91.5, 59.5, 46.4, 45.5, 29.8, 27.0, 25.9, 24.3.

HRMS (ESI) Calcd. For $\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_2$: $[\text{M}+\text{H}]^+$: 310.1423, Found: m/z 310.18424.

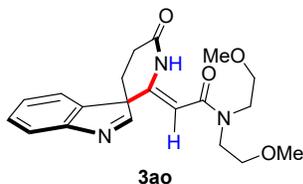
40) Compound of 3an



White solid, yield 44% (32.3 mg), $R_f = 0.50$ (DCM : EtOAc = 8:1), M. p. = 144-145 °C; ^1H NMR (400 MHz, CDCl_3), δ 12.17 (s, 1H), 8.18 (s, 1H), 7.69 (d, $J = 7.7$ Hz, 1H), 7.45-7.41 (m, 1H), 7.34-7.29 (m, 2H), 7.73-5.63 (m, 1H), 4.52 (s, 1H), 3.24-3.19 (m, 1H), 2.97-2.92 (m, 2H), 2.24-2.16 (m, 1H), 2.03-1.97 (m, 1H), 1.92-1.86 (m, 1H), 1.56-1.49 (m, 1H), 1.25-1.18 (m, 1H), 0.79 (d, $J = 2.5$ Hz, 3H), 0.77 (d, $J = 2.5$ Hz, 3H), 0.65 (d, $J = 6.6$ Hz, 3H), 0.58 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.4, 168.6, 165.9, 154.8, 147.0, 140.2, 129.4, 127.3, 122.8, 122.3, 91.5, 59.5, 46.4, 45.5, 29.8, 27.0, 25.9, 24.3.

HRMS (ESI) Calcd. For $\text{C}_{22}\text{H}_{30}\text{N}_3\text{O}_2$: $[\text{M}+\text{H}]^+$: 368.2263, Found: m/z 368.2264.

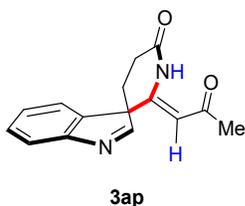
41) Compound of 3ao



White solid, yield 59% (43.8 mg), $R_f = 0.48$ (DCM : EtOAc = 8:1), M. p. = 118-119 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 12.13 (s, 1H), 8.19 (s, 1H), 7.71 (d, $J = 7.7$ Hz, 1H), 7.47-7.43 (m, 1H), 7.39-7.32 (m, 2H), 7.73-5.63 (m, 1H), 4.77 (s, 1H), 3.50-3.46 (m, 4H), 3.28 (s, 3H), 3.26-3.22 (m, 4H), 3.10 (s, 3H), 2.93-2.75 (m, 2H), 2.17-2.05 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.3, 168.7, 168.0, 155.0, 147.3, 140.3, 129.5, 127.3, 122.9, 122.4, 90.6, 71.3, 70.8, 59.9, 58.9, 49.1, 47.0, 30.0, 27.1.

HRMS (ESI) Calcd. For $\text{C}_{21}\text{H}_{28}\text{N}_3\text{O}_4$: $[\text{M}+\text{H}]^+$: 386.2018, Found: m/z 386.2021.

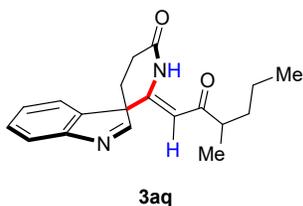
42) Compound of 3ap



Yellow solid, yield 89% (45.2 mg), $R_f = 0.30$ (DCM : EtOAc = 10:1), M. p. = 100-101 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.05 (s, 1H), 8.16 (s, 1H), 7.72 (d, $J = 8$ Hz, 1H), 7.49-7.45 (m, 1H), 7.34 (d, $J = 6$ Hz, 2H), 4.79 (s, 1H), 2.97-2.77 (m, 2H), 2.21-2.03 (m, 2H), 1.98 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 199.9, 171.6, 169.4, 154.9, 149.7, 139.6, 129.7, 127.6, 122.8, 122.5, 99.0, 59.1, 30.9, 29.9, 26.8.

HRMS (ESI) Calcd. For $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_4$: $[\text{M}+\text{H}]^+$: 255.1137, Found: m/z 255.1135.

43) Compound of 3aq

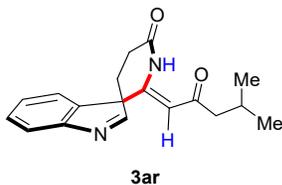


Yellow solid, yield 82% (50.9 mg), $R_f = 0.35$ (DCM : EtOAc = 10:1), M. p. = 73-74 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.15 (s, 1H), 8.19 (s, 1H), 7.74 (d, $J = 7.6$ Hz, 1H), 7.50-7.46 (m, 1H), 7.35 (d, $J = 5.2$ Hz, 2H), 4.80 (s, 1H), 2.97- 2.78 (m, 2H), 2.28-2.22 (m, 1H), 2.20- 2.05 (m, 2H), 1.24-1.15 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H), 0.82-0.76 (m, 3H); ^{13}C

NMR (100 MHz, CDCl₃) δ 206.3, 171.7, 169.3, 154.9, 150.0, 129.7, 127.6, 122.8, 122.5, 98.1, 98.1, 59.3, 46.6, 35.6, 35.5, 30.0, 29.9, 27.0, 26.9, 20.5, 20.4, 16.7, 16.6, 14.2.

HRMS (ESI) Calcd. For C₁₉H₂₃N₂O₂: [M+H]⁺ : 311.1680, Found: m/z 311.1683.

44) Compound of 3ar

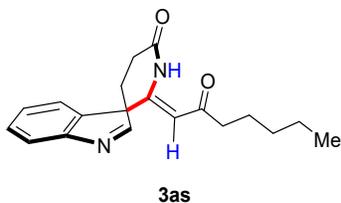


Brown oil, yield 87% (51.7 mg), R_f = 0.35 (DCM : EtOAc = 10:1);

¹H NMR (400 MHz, CDCl₃) δ 12.14 (s, 1H), 8.17 (s, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.50-7.46 (m, 1H), 7.35 (s, 2H), 4.77 (s, 1H), 2.97-2.78 (m, 2H), 2.22-2.12 (m, 2H), 2.09 (d, J = 7.6 Hz, 2H), 2.00-1.90 (m, 1H), 0.82 (dd, J = 6.4 Hz, J = 3.2 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 202.3, 171.6, 169.3, 155.0, 149.4, 139.9, 129.7, 127.6, 122.8, 122.5, 99.1, 59.2, 52.7, 29.9, 26.9, 25.4, 22.6, 22.5.

HRMS (ESI) Calcd. For C₁₈H₂₁N₂O₂: [M+H]⁺ : 297.1527, Found: m/z 297.1525.

45) Compound of 3as

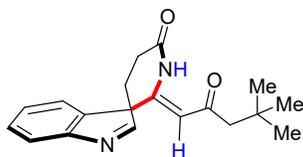


White solid, yield 94% (58.3 mg), R_f = 0.45 (DCM : EtOAc = 10:1), M. p. = 106-107 °C;

¹H NMR (400 MHz, CDCl₃) δ 12.09 (s, 1H), 8.17 (s, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.47 (s, 1H), 7.35 (s, 1H), 4.78 (s, 1H), 2.94-2.79 (m, 2H), 2.20 (t, J = 6.8 Hz, 2H), 1.44 (t, J = 7.2 Hz, 2H), 1.29-1.15 (m, 6H), 0.82 (t, J = 6.8 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 202.7, 171.7, 169.3, 154.9, 149.4, 139.8, 129.7, 127.6, 122.8, 122.5, 98.8, 43.7, 31.4, 29.9, 26.9, 24.1, 22.5, 14.0.

HRMS (ESI) Calcd. For C₁₉H₂₃N₂O₂: [M+H]⁺ : 311.1760, Found: m/z 311.1764.

46) Compound of 3at



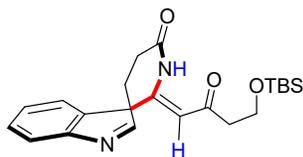
3at

Yellow solid, yield 83% (51.7mg), R_f = 0.48 (DCM : EtOAc = 8:1), M. p. = 54-55 °C;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.17(s, 1H), 8.18 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 6.4 Hz, 1H), 7.34 (d, J = 6.4 Hz, 2H), 4.72 (s, 1H), 2.95-2.77 (m, 2H), 2.18-2.09 (m, 2H), 2.06 (s, 2H), 0.86 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 202.3, 171.5, 169.4, 154.9, 149.0, 139.9, 129.7, 127.6, 122.7, 122.5, 100.7, 59.4, 56.5, 31.8, 30.0, 29.8, 26.9.

HRMS (ESI) Calcd. For $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_2$: $[\text{M}+\text{H}]^+$: 311.1763, Found: m/z 311.1762.

47) Compound of 3au



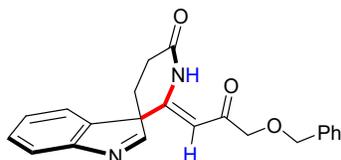
3au

Brown oil, yield 65% (51.8 mg), R_f = 0.60 (DCM : EtOAc = 8:1);

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.10 (s, 1H), 8.15 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.33 (t, J = 6.8 Hz, 2H), 4.85 (s, 1H), 3.76 (t, J = 6.0 Hz, 2H), 2.96-2.77 (m, 2H), 2.41 (t, J = 6.4 Hz, 2H), 2.22-2.02 (m, 2H), 0.78 (s, 9H), -0.06 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 201.0, 171.5, 169.3, 155.0, 149.6, 139.7, 129.7, 127.6, 122.8, 122.6, 99.3, 59.3, 46.6, 29.9, 26.9, 25.9, 18.3, -5.4.

HRMS (ESI) Calcd. For $\text{C}_{22}\text{H}_{31}\text{N}_2\text{O}_3\text{Si}$: $[\text{M}+\text{H}]^+$: 399.2025, Found: m/z 399.2027.

48) Compound of 3av



3av

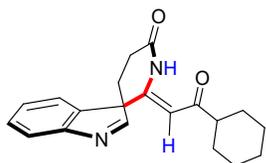
Yellow solid, yield 78% (56.2 mg), R_f = 0.60 (DCM : EtOAc = 8:1), M. p. = 60-61 °C;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.02 (s, 1H), 8.19 (s, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 6.0 Hz, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.32-1.28 (m, 3H), 7.13 (dd, J = 7.6 Hz, J =

2.8 Hz, 2H), 5.14 (s, 1H), 4.41 (s, 2H), 3.88 (s, 2H), 2.98-2.80 (m, 2H), 2.22-2.09 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.6, 171.2, 169.3, 155.1, 151.56, 139.7, 137.0, 129.8, 128.6, 128.1, 127.9, 127.7, 122.8, 122.6, 94.9, 74.6, 73.4, 59.2, 30.0, 26.9.

HRMS (ESI) Calcd. For $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 361.1472, Found: m/z 361.1478.

49) Compound of 3aw

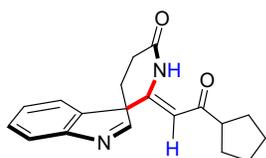


3aw

Yellow solid, yield 86% (55.4 mg), R_f = 0.35 (DCM : EtOAc = 10:1), M. p. = 141-142 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.14 (s, 1H), 8.17 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 6 Hz, 2H), 4.81 (s, 1H), 2.95-2.76 (m, 2H), 2.21-2.15 (m, 1H), 2.10-2.03 (m, 2H), 1.67-1.57 (m, 5H), 1.20-1.12 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 205.5, 171.7, 169.3, 154.9, 150.0, 139.9, 129.7, 127.6, 122.8, 122.5, 97.9, 59.3, 51.2, 29.9, 28.8, 28.6, 27.0, 25.7, 25.6, 25.6.

HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}_2$: $[\text{M}+\text{H}]^+$: 323.1762, Found: m/z 323.1765.

50) Compound of 3ax

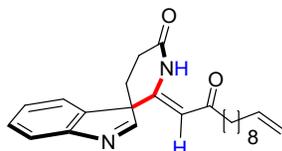


3ax

Yellow solid, yield 91% (56.1 mg), R_f = 0.50 (DCM : EtOAc = 10:1), M. p. = 121-122 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.11 (s, 1H), 8.18 (s, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 6.0 Hz, 1H), 7.35 (t, J = 6.4 Hz, 2H), 4.80 (s, 1H), 2.95-2.77 (m, 2H), 2.60 (quint, J = 7.6 Hz, 1H), 2.21-2.04 (m, 2H), 1.66-1.45 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 205.0, 171.7, 169.2, 155.0, 149.6, 139.9, 129.6, 127.5, 122.8, 122.5, 98.6, 52.0, 29.9, 29.5, 29.2, 27.0, 26.0.

HRMS (ESI) Calcd. For $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2$: $[\text{M}+\text{H}]^+$: 309.1523, Found: m/z 309.1524.

51) Compound of 3ay

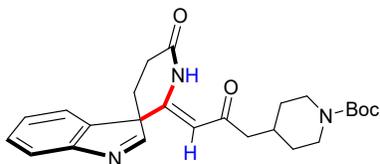


3ay

Yellow solid, yield 84% (47.1 mg), R_f = 0.48 (DCM : EtOAc = 10:1), M. p. = 118-119 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.10 (s, 1H), 8.17 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 6.0 Hz, 1H), 7.35 (t, J = 6.4 Hz, 2H), 5.83-5.73 (m, 1H), 4.92 (t, J = 10.0 Hz, 2H), 4.78 (s, 1H), 2.95-2.77 (m, 2H), 2.21-2.05 (m, 4H), 2.00 (q, J = 7.2 Hz, 2H), 1.47-1.40 (m, 2H), 1.34-1.28 (m, 4H), 1.24-1.19 (m, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 202.7, 171.7, 169.3, 154.9, 149.4, 139.9, 139.3, 129.7, 127.6, 122.8, 122.5, 114.2, 98.8, 59.2, 43.7, 33.9, 29.9, 29.3, 29.2, 29.1, 28.9, 26.9, 24.4.

HRMS (ESI) Calcd. For $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_2$: $[\text{M}+\text{H}]^+$: 281.1216, Found: m/z 281.1215.

52) Compound of 3az

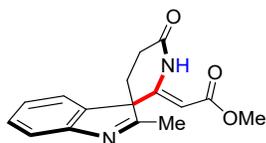


3az

Yellow solid, yield 91% (79.6 mg), R_f = 0.30 (DCM : EtOAc = 4:1), M. p. = 55-56 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.09 (s, 1H), 8.17 (s, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.49 (quint, J = 4.0 Hz, 1H), 7.36 (d, J = 4.4 Hz, 2H), 4.75 (s, 1H), 4.01 (bs, 1H), 2.97-2.79 (m, 2H), 2.65 (t, J = 12.0 Hz, 2H), 2.23-2.17 (m, 1H), 2.15 (d, J = 7.2 Hz, 2H), 2.11-2.02 (m, 1H), 1.88-1.81 (m, 1H), 1.54 (d, J = 12.8 Hz, 2H), 1.42 (s, 9H), 1.01 (q, J = 12.0 Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 201.2, 171.5, 169.3, 155.0, 154.9, 149.9, 129.8, 127.6, 122.7, 122.6, 99.0, 79.4, 59.2, 50.1, 32.5, 31.7, 29.9, 28.5, 26.9, 22.8, 14.2.

HRMS (ESI) Calcd. For $\text{C}_{25}\text{H}_{31}\text{N}_3\text{O}_4\text{Na}$: $[\text{M}+\text{Na}]^+$: 460.2211, Found: m/z 460.2214.

53) Compound of 3ba



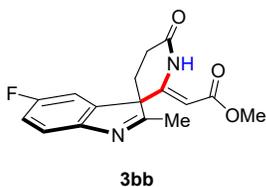
3ba

Yellow solid, yield 96% (54.6 mg), R_f = 0.53 (DCM : EtOAc = 8:1), M. p. = 99-100 °C;

¹H NMR (400 MHz, CDCl₃), δ 11.04 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 4.33 (s, 1H), 3.02-2.93 (m, 1H), 2.82 (d, *J* = 17.9 Hz, 1H), 2.42 (dd, *J* = 5.0 Hz, *J* = 13.1 Hz, 1H), 2.37 (s, 3H), 1.66 (d, *J* = 12.8 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 181.4, 168.8, 168.7, 154.3, 151.5, 141.8, 129.4, 126.2, 122.4, 121.4, 91.0, 59.5, 51.5, 28.5, 26.9, 16.9.

HRMS (ESI) Calcd. For C₁₆H₁₇N₂O₃: [M+H]⁺ : 285.1143, Found: m/z 285.1144.

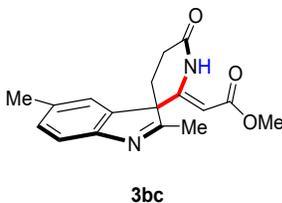
54) Compound of 3bb



Yellow solid, yield 95% (57.4 mg), *R_f* = 0.53 (DCM : EtOAc = 8:1), M. p. = 124-125 °C; **¹H NMR** (400 MHz, CDCl₃), δ 11.03 (s, 1H), 7.54 (dd, *J* = 7.7 Hz, *J* = 8.4 Hz, 1H), 7.11-7.04 (m, 2H), 4.34 (s, 1H), 3.63 (s, 3H), 2.97-2.80 (m, 2H), 2.37-2.43 (m, 1H), 2.34 (s, 3H), 1.74-1.68 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 181.2, 168.3 (d, *J* = 4 Hz), 161.2 (d, *J* = 246 Hz), 150.8 122.1 (d, *J* = 8 Hz), 116.0 (d, *J* = 23 Hz), 110.6 (d, *J* = 26 Hz), 91.4, 59.9, 51.6, 28.3, 26.9, 17.0. **¹⁹F NMR** (376 MHz, CDCl₃) δ -114.8 (s, 1F).

HRMS (ESI) Calcd. For C₁₆H₁₆N₂O₃F: [M+H]⁺ : 303.1053, Found: m/z 303.1057.

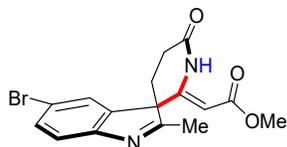
55) Compound of 3bc



Brown solid, yield 92% (54.9 mg), *R_f* = 0.56 (DCM : EtOAc = 8:1), M. p. = 110-111 °C; **¹H NMR** (400 MHz, CDCl₃), δ 11.05 (s, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 7.9, 1H), 7.12 (s, 1H), 4.34 (s, 1H), 3.62 (s, 3H), 3.04-2.95 (m, 1H), 2.85-2.78 (m, 1H), 2.44-2.37 (m, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 1.67-1.61 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 180.3, 168.9, 168.5, 152.0, 151.8, 141.9, 136.2, 129.9, 123.2, 120.9, 91.0, 59.4, 51.5, 28.5, 26.9, 21.6, 16.8.

HRMS (ESI) Calcd. For C₁₇H₁₉N₂O₃: [M+H]⁺ : 299.1390, Found: m/z 299.1394.

56) Compound of 3bd

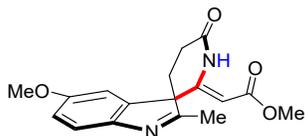


3bd

Yellow solid, yield 90% (65.2 mg), $R_f = 0.56$ (DCM : EtOAc = 8:1), M. p. = 145-146 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.04 (s, 1H), 7.54-7.45 (m, 3H), 4.33 (s, 1H), 3.64 (s, 3H), 2.98-2.81 (m, 2H), 2.44-2.36 (m, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 1.70-1.67 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 181.9, 168.4, 153.3, 150.6, 143.8, 132.5, 125.7, 122.7, 119.9, 91.5, 59.9, 51.6, 28.4, 26.9, 17.0.

HRMS (ESI) Calcd. For $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3\text{Br}$: $[\text{M}+\text{H}]^+$: 363.0270, Found: m/z 363.0273.

57) Compound of 3be

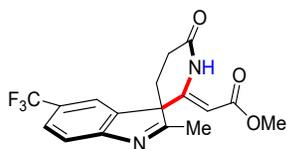


3be

Yellow solid, yield 44% (27.6 mg), $R_f = 0.55$ (DCM : EtOAc = 8:1), M. p. = 131-132 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.03 (s, 1H), 7.49 (d, $J = 8.4$ Hz, 1H), 6.89 (d, $J = 9.7$ Hz, 1H), 6.86 (s, 1H), 4.35 (s, 1H), 3.79 (s, 3H), 3.62 (s, 3H), 3.00-2.92 (m, 1H), 2.82-2.78 (m, 1H), 2.41-2.35 (m, 1H), 2.32 (s, 3H), 2.34 (s, 3H), 1.71-1.67 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 178.9, 168.7, 168.5, 158.3, 151.6, 147.8, 143.3, 121.6, 113.5, 109.6, 91.2, 59.6, 55.9, 51.5, 28.2, 27.0, 16.8.

HRMS (ESI) Calcd. For $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_4$: $[\text{M}+\text{H}]^+$: 315.1257, Found: m/z 315.1254.

58) Compound of 3bf



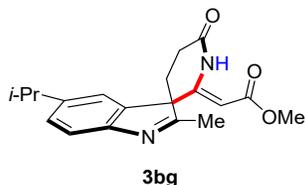
3bf

Yellow solid, yield 64% (45.1 mg), $R_f = 0.55$ (DCM : EtOAc = 8:1), M. p. = 140-141 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.07 (s, 1H), 7.69 (s, 2H), 7.54 (s, 1H), 4.31 (s, 1H), 3.63 (s, 3H), 2.98-2.84 (m, 2H), 2.47-2.43 (m, 1H), 2.42 (s, 3H), 1.73-1.70 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 184.7, 168.2, 157.2, 150.3, 142.4, 128.6 (q, $J = 32$ Hz), 127.2 ($J = 3$

Hz), 125.4, 122.7, 121.6, 119.3 ($J = 3$ Hz), 91.6, 59.8, 51.6, 28.4, 26.9, 17.3. ^{19}F NMR (376 MHz, CDCl_3) δ -61.3 (s, 1F).

HRMS (ESI) Calcd. For $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3\text{F}_3$: $[\text{M}+\text{H}]^+$: 353.1083, Found: m/z 353.1087.

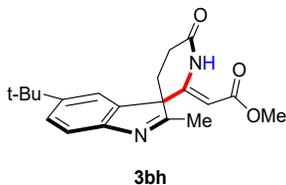
59) Compound of 3bg



Yellow solid, yield 82% (53.5 mg), $R_f = 0.57$ (DCM : EtOAc = 8:1), M. p. = 139-140 °C; ^1H NMR (400 MHz, CDCl_3), δ 11.06 (s, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.25 (d, $J = 5.8$ Hz, 1H), 7.13 (s, 1H), 4.35 (s, 1H), 3.62 (s, 3H), 3.02-2.79 (m, 3H), 2.44-2.37 (m, 1H), 1.67-1.61 (m, 1H), 1.23 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 180.4, 168.9, 168.6, 152.3, 151.8, 147.4, 141.9, 127.2, 121.0, 120.7, 91.1, 59.4, 51.5, 34.3, 28.5, 27.0, 24.4, 24.2, 16.8.

HRMS (ESI) Calcd. For $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 392.1913, Found: m/z 392.1915.

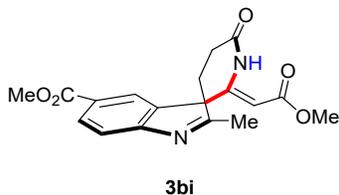
60) Compound of 3bh



Yellow solid, yield 70% (47.6 mg), $R_f = 0.57$ (DCM : EtOAc = 8:1), M. p. = 162-163 °C; ^1H NMR (400 MHz, CDCl_3), δ 11.06 (s, 1H), 7.50 (d, $J = 8.2$ Hz, 1H), 7.42 (d, $J = 8.2$ Hz, 1H), 7.29 (s, 1H), 4.35 (s, 1H), 3.62 (s, 3H), 3.01-2.92 (m, 1H), 3.01-2.92 (m, 1H), 2.43-2.36 (m, 1H), 2.34 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 180.6, 168.9, 168.6, 151.9, 151.8, 149.7, 141.7, 126.3, 120.6, 119.2, 91.2, 59.5, 51.4, 35.0, 31.8, 28.4, 27.1, 16.9.

HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 341.1769, Found: m/z 341.1767.

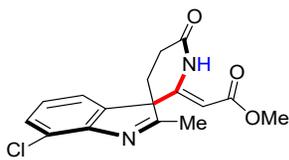
61) Compound of 3bi



Yellow solid, yield 62% (42.4 mg), $R_f = 0.50$ (DCM : EtOAc = 8:1), M. p. = 155-156 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.07 (s, 1H), 8.13 (d, $J = 8.0$ Hz, 1H), 7.96 (s, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 4.29 (s, 1H), 3.90 (s, 3H), 3.61 (s, 3H), 3.04-2.95 (m, 1H), 2.86-2.82 (m, 1H), 2.46-2.44 (m, 1H), 2.40 (s, 3H), 1.70-1.66 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 184.9, 168.4, 168.3, 166.5, 158.2, 150.7, 142.1, 131.8, 128.1, 123.4, 121.2, 91.3, 59.6, 52.5, 51.5, 28.5, 27.0, 17.2.

HRMS (ESI) Calcd. For $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_5$: $[\text{M}+\text{H}]^+$: 343.1288, Found: m/z 343.1287.

62) Compound of 3bj

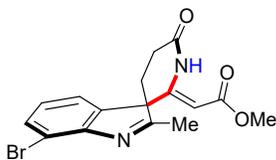


3bj

Yellow solid, yield 91% (57.9 mg), $R_f = 0.56$ (DCM : EtOAc = 8:1), M. p. = 55-56 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.03 (s, 1H), 7.40-7.38 (m, 1H), 7.96 (s, 1H), 7.23-7.21 (m, 1H), 7.18-7.14 (m, 1H), 4.35 (s, 1H), 3.90 (s, 3H), 3.62 (s, 3H), 2.96-2.80 (m, 2H), 2.45-2.28 (m, 1H), 2.41 (s, 3H), 1.71-1.65 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 182.9, 168.4, 168.3, 150.6, 143.5, 129.9, 127.3, 126.3, 120.7, 91.4, 60.8, 51.6, 28.3, 26.9, 17.2.

HRMS (ESI) Calcd. For $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3\text{Cl}$: $[\text{M}+\text{H}]^+$: 319.0846, Found: m/z 319.0843.

63) Compound of 3bk

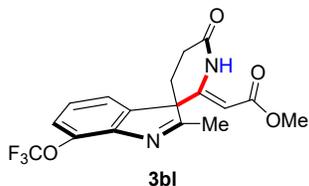


3bk

Yellow solid, yield 91% (65.9 mg), $R_f = 0.56$ (DCM : EtOAc = 8:1), M. p. = 59-60 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.02 (s, 1H), 7.55 (dd, $J = 0.80$ Hz, $J = 8.0$ Hz, 1H), 7.25 (dd, $J = 0.84$ Hz, $J = 7.5$ Hz, 1H), 7.09 (t, $J = 7.8$ Hz, 1H), 4.36 (s, 1H), 3.62 (s, 3H), 2.97-2.79 (m, 2H), 2.45-2.38 (m, 1H), 2.41 (s, 3H), 1.71-1.65 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 183.0, 168.4, 168.3, 152.7, 150.6, 143.2, 132.9, 127.6, 121.3, 115.1, 91.4, 61.1, 51.6, 28.3, 27.0, 17.2.

HRMS (ESI) Calcd. For $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3\text{Br}$: $[\text{M}+\text{H}]^+$: 363.0223, Found: m/z 338.0224.

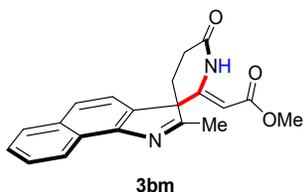
64) Compound of 3bl



Yellow solid, yield 66% (48.6 mg), $R_f = 0.55$ (DCM : EtOAc = 8:1), M. p. = 167-168 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.04 (s, 1H), 7.28-7.24 (m, 2H), 4.33 (s, 1H), 3.62 (s, 3H), 2.97-2.79 (m, 2H), 2.45-2.38 (m, 1H), 2.41 (s, 3H), 1.72-1.68 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 183.1, 168.4, 168.3, 150.5, 146.1, 144.4, 140.8, 127.4, 121.7, 120.7, 120.6 (d, $J = 258$ Hz), 91.4, 60.3, 51.5, 28.3, 26.9, 17.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.5 (s, 1F).

HRMS (ESI) Calcd. For $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_4\text{F}_3$: $[\text{M}+\text{H}]^+$: 369.0933, Found: m/z 369.0936.

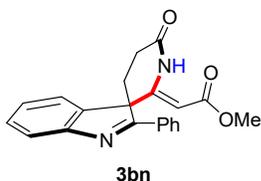
65) Compound of 3bm



Yellow solid, yield 78% (52.1 mg), $R_f = 0.55$ (DCM : EtOAc = 8:1), M. p. = 170-171 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.11 (s, 1H), 8.55 (d, $J = 8.3$ Hz, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.75 (d, $J = 8.3$ Hz, 1H), 7.62 (t, $J = 7.2$ Hz, 3H), 7.54 (d, $J = 7.3$ Hz, 1H), 7.45 (d, $J = 8.4$ Hz, 1H), 4.37 (s, 1H), 3.60 (s, 3H), 3.08-2.85 (m, 2H), 2.49 (s, 3H), 2.45-2.40 (m, 1H), 1.80-1.75 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 182.0, 168.8, 168.6, 151.4, 150.3, 138.3, 134.2, 128.1, 127.1, 126.7, 126.6, 123.5, 119.7, 91.0, 60.7, 51.5, 28.8, 27.2, 17.2. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.5 (s, 1F).

HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 335.1389, Found: m/z 335.1387.

66) Compound of 3bn

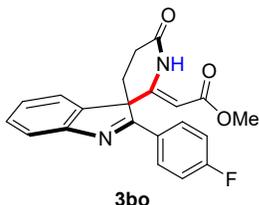


Yellow solid, yield 67% (43.4 mg), $R_f = 0.50$ (DCM : EtOAc = 10:1), M. p. = 185-186 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3), δ 11.23 (s, 1H), 8.02 (d, $J = 5.6$ Hz, 1H), 7.76 (d, $J = 7.4$ Hz, 1H), 7.49-7.39 (m, 5H), 7.29-7.26 (m, 1H), 4.44 (s, 1H), 3.54 (s, 3H), 3.08-2.99 (m, 1H),

2.80-2.68 (m, 2H), 1.59-1.54 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.7, 169.0, 168.5, 153.8, 152.5, 143.5, 131.6, 130.5, 129.5, 129.1, 128.9, 126.5, 122.4, 121.9, 91.8, 58.1, 51.3, 28.5, 28.4. ^{19}F NMR (376 MHz, CDCl_3) δ -57.5 (s, 1F).

HRMS (ESI) Calcd. For $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 347.1317, Found: m/z 347.1319.

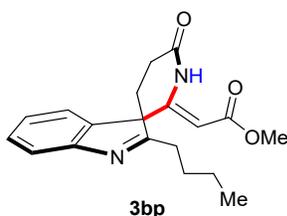
67) Compound of 3bo



Yellow solid, yield 65% (47.3 mg), R_f = 0.50 (DCM : EtOAc = 10:1), M. p. = 194-195 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.23 (s, 1H), 8.05 (t, J = 5.9 Hz, 2H), 7.76 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 7.3 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.18 (d, J = 8.2 Hz, 2H), 4.42 (s, 1H), 3.57 (s, 3H), 3.10-3.00 (m, 1H), 2.82-2.65 (m, 2H), 1.60-1.55 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.5, 168.9, 168.5, 164.7 (d, J = 252 Hz), 163.5, 153.7, 152.4, 143.4, 131.4 (d, J = 9 Hz), 129.6, 126.9, 126.6, 122.4, 122.0, 116.2 (d, J = 22 Hz), 91.9, 60.5, 58.1, 51.4, 28.5, 28.5. ^{19}F NMR (376 MHz, CDCl_3) δ -107.0 (s, 1F).

HRMS (ESI) Calcd. For $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3\text{F}$: $[\text{M}+\text{H}]^+$: 365.1294, Found: m/z 365.1298.

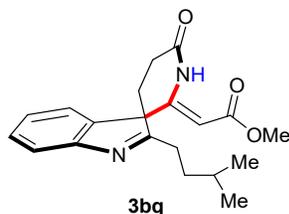
68) Compound of 3bp



Yellow solid, yield 86% (56.1 mg), R_f = 0.60 (DCM : EtOAc = 4:1), M. p. = 75-76 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.04 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.41 (d, J = 6.8 Hz, 2H), 4.15 (s, 1H), 3.59 (s, 3H), 3.11 (t, J = 7.2 Hz, 2H), 2.89-2.87 (m, 1H), 2.84 (d, J = 3.2 Hz, 2H), 2.81-2.79 (m, 1H), 1.75 (q, J = 7.2 Hz, 2H), 1.25 (s, 1H), 1.00 (t, J = 8.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.9, 168.9, 168.5, 154.4, 151.8, 141.6, 129.3, 126.1, 122.3, 121.4, 90.9, 59.8, 51.5, 30.1, 28.7, 28.5, 26.9, 22.8, 14.0.

HRMS (ESI) Calcd. For $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 327.1632, Found: m/z 327.1635.

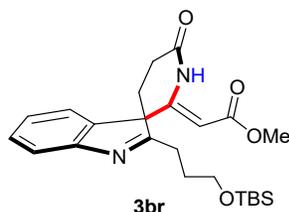
69) Compound of 3bq



Yellow solid, yield 81% (55.1 mg), $R_f = 0.60$ (DCM : EtOAc = 5:1), M. p. = 100-101 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 11.06 (s, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 7.2$ Hz, 1H), 7.21 (t, $J = 7.6$ Hz, 1H), 4.32 (s, 1H), 3.63 (s, 3H), 3.03-2.94 (m, 1H), 2.86-2.79 (m, 1H), 2.67-2.50 (m, 2H), 1.82-1.76 (m, 2H), 1.31-1.27 (m, 2H), 1.22 (dd, $J = 2.0$ Hz, $J = 6.8$ Hz, 1H), 0.97 (dd, $J = 3.2$ Hz, $J = 6.0$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 185.2, 168.9, 168.5, 154.4, 151.78, 141.6, 129.4, 126.1, 122.3, 121.4, 90.9, 51.5, 35.5, 28.5, 28.3, 28.2, 26.9, 22.6, 22.4.

HRMS (ESI) Calcd. For $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$: 341.1785, Found: m/z 341.1783.

70) Compound of 3br

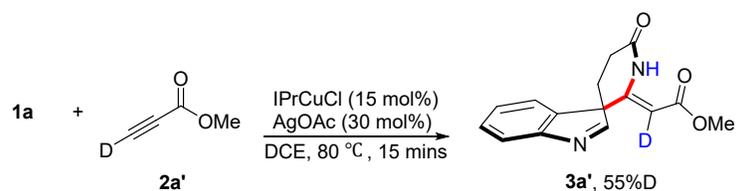


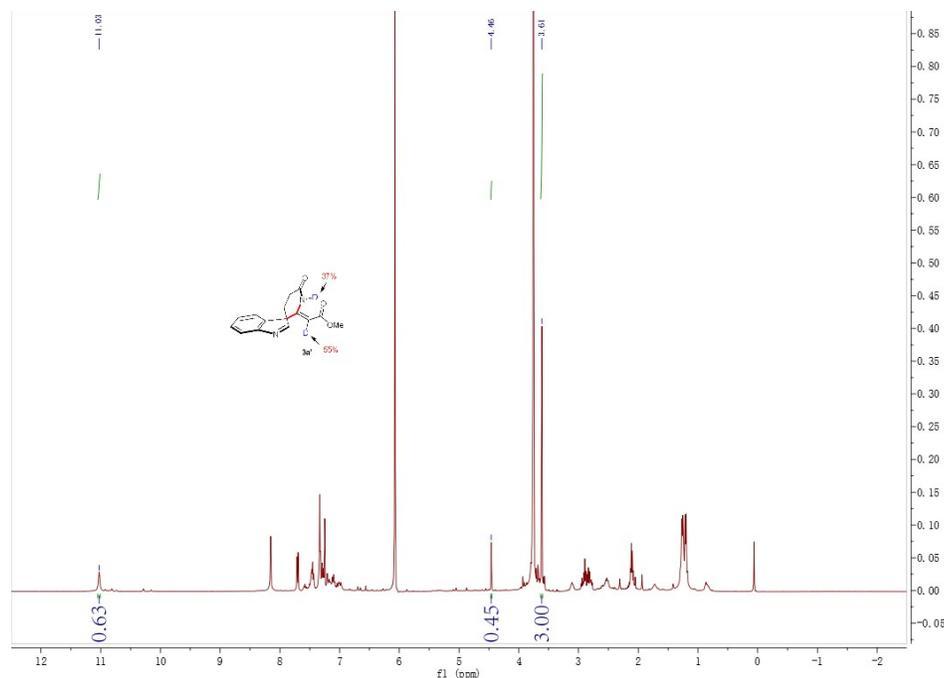
Yellow solid, yield 88% (78.0 mg), $R_f = 0.30$ (DCM : EtOAc = 4:1), M. p. = 74-75 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 11.06 (s, 1H), 7.65 (d, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.21 (t, $J = 7.6$ Hz, 1H), 4.32 (s, 1H), 3.75 (t, $J = 6.0$ Hz, 2H), 3.61 (s, 3H), 3.02-2.93 (m, 1H), 2.85-2.79 (m, 1H), 2.77-2.60 (m, 2H), 2.47-2.39 (m, 1H), 2.19-2.01 (m, 2H), 1.68-1.62 (m, 1H), 0.87 (s, 9H), 0.04 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 184.7, 168.8, 168.5, 154.4, 151.8, 141.7, 129.3, 126.1, 122.3, 121.4, 91.0, 62.1, 59.8, 51.4, 29.4, 28.5, 27.0, 26.4, 26.0, 18.4, -5.2.

HRMS (ESI) Calcd. For $\text{C}_{24}\text{H}_{35}\text{N}_2\text{O}_4\text{Si}$: $[\text{M}+\text{H}]^+$: 443.2370, Found: m/z 443.2374.

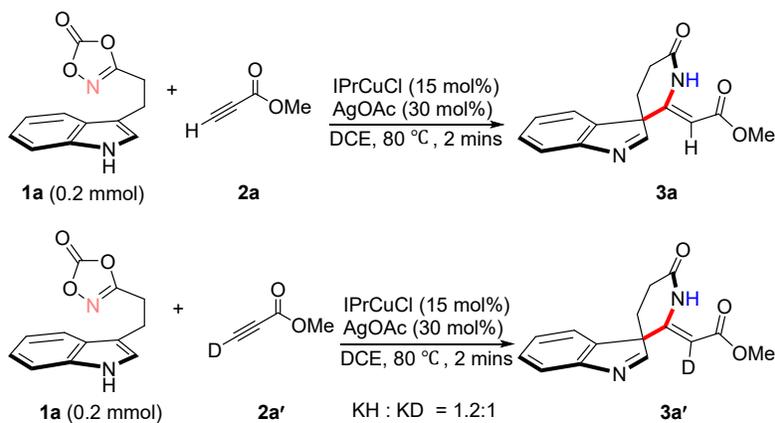
2.6 Kinetic Isotope Effect Studies in the Indole Derivatives

1) Deuterium Exchange Experiment





2) Kinetic Isotope Effect from an Intermolecular Competition between Methyl propiolate and 1-d1-Methyl propiolate



Dioxazolones (**1a**) (46.0 mg, 0.20 mmol), IPrCuCl (14.6 mg, 0.03 mmol, 0.15 equiv), and AgOAc (10.0 mg, 0.06 mmol, 0.30 equiv) was dissolved in DCE (3.0 mL), and the Methyl propiolate (**2a**) and 1-d1-Methyl propiolate (**2a'**) (1:1) (total 50.4 mg, 0.6 mmol, 3.0 equiv) was added. The mixture was heated 80 °C in an oil bath for 2 mins. The resulting mixture was concentrated and afford crude isolated mixture. The $k_H/k_D = 1.2:1$ was calculated by the NMR yields.

2.7 Kinetic studies

General method for kinetic studies: according to the standard condition, using **1a**, **2a**, IPrCuCl, and AgOAc in several different equivalents, and 1,3,5-Trimethoxybenzene was used as an internal standard. After placing the round-bottomed flask in the oil bath, the stopwatch starts. A small amount of the reaction mixture was taken out by syringe after initiation period at about every 1 minutes. After filtering the obtained sample with a filter membrane, concentrate it for ^1H NMR analysis.

1) The rate on the concentration of IPrCuCl^[9]

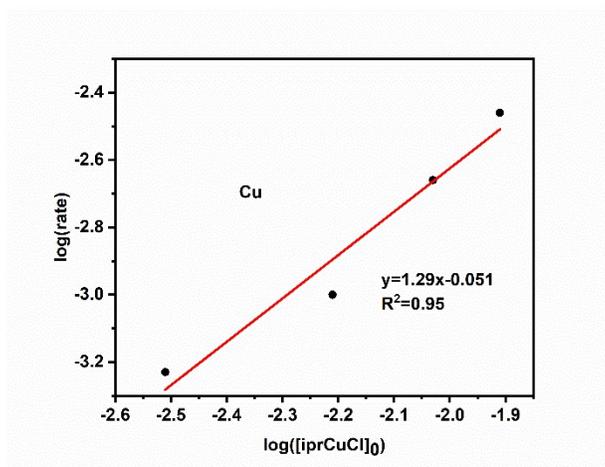
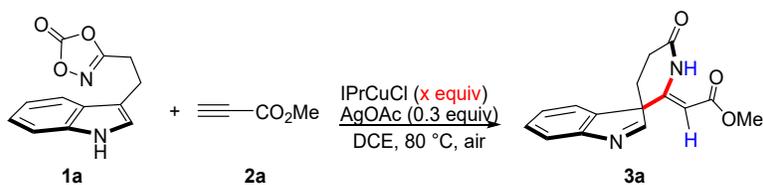


Figure S1. Rate on the concentration of IPrCuCl from the reaction of **1a** (0.06 M), **2a** (0.19 M), AgOAc (0.019 M), with 0.003 M, 0.006 M, 0.009 M, 0.012 M of IPrCuCl.

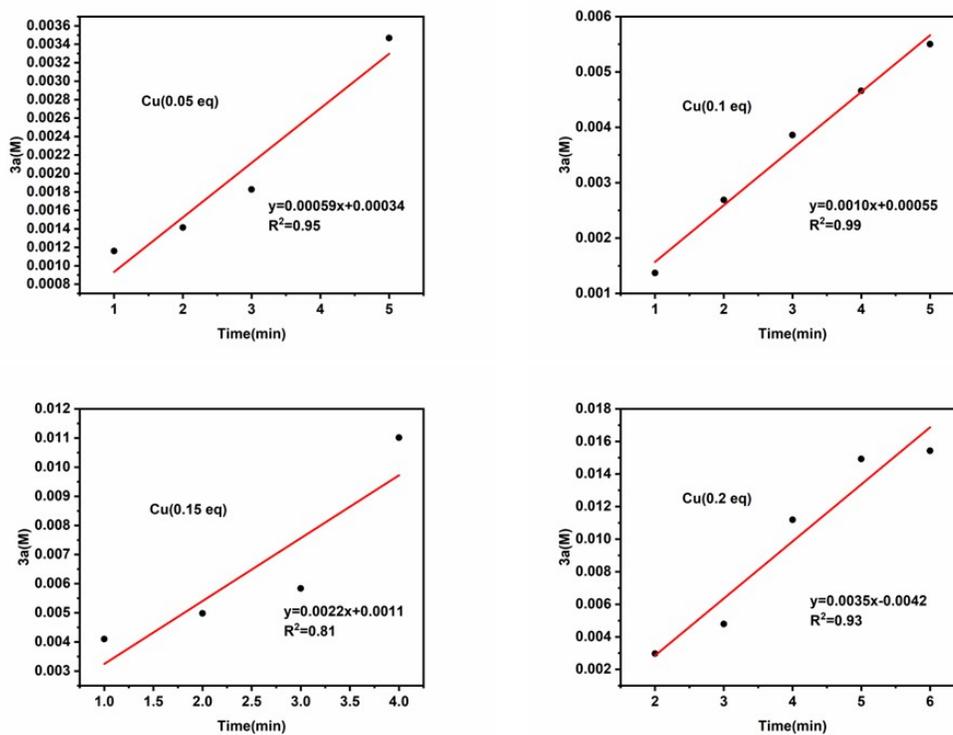


Figure S2. Rate on the concentration of IPrCuCl from the reaction of **1a** (0.06 M), **2a** (0.19 M), AgOAc (0.019 M), with 0.003 M, 0.006 M, 0.009 M, 0.012 M of IPrCuCl.

2) The rate on the concentration of AgOAc

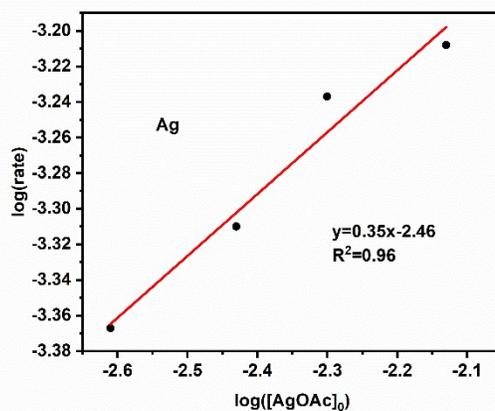
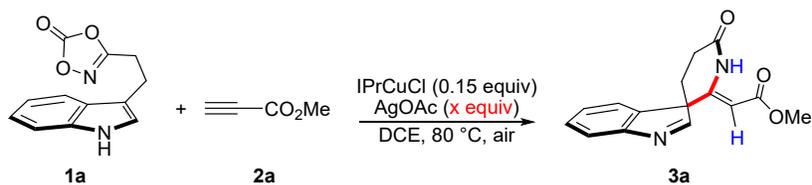


Figure S3. Rate on the concentration of AgOAc from the reaction of **1a** (0.06 M), **2a** (0.19 M), IPrCuCl (0.009 M), with 0.0024 M, 0.0037 M, 0.005 M, 0.0074 M of AgOAc.

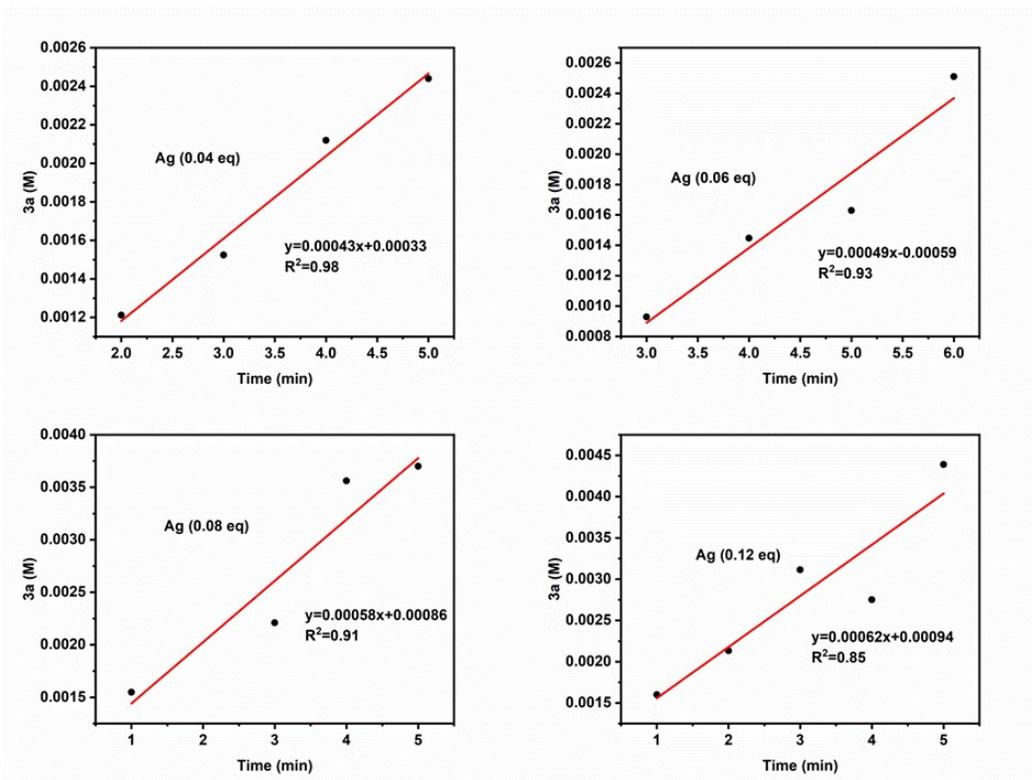
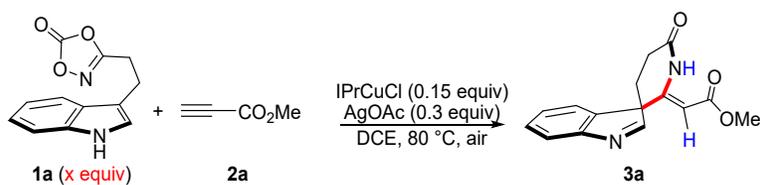


Figure S4. Rate on the concentration of AgOAc from the reaction of **1a** (0.06 M), **2a** (0.19 M), IPrCuCl (0.009 M), with 0.0024 M, 0.0037 M, 0.005 M, 0.0074 M of AgOAc.

3) The rate on the concentration of **1a**



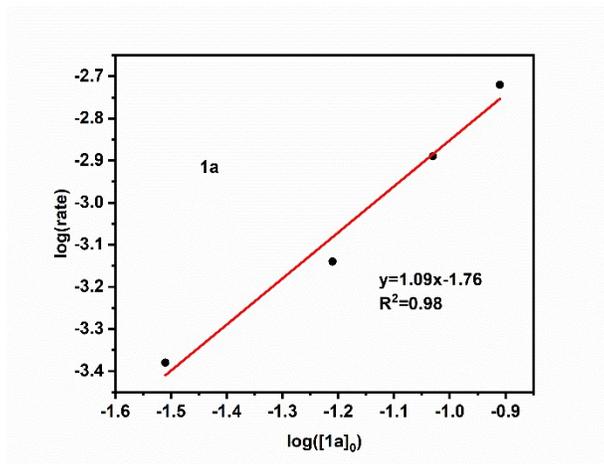


Figure S5. Rate on the concentration of **1a** from the reaction of **2a** (0.19 M), IPrCuCl (0.009 M), AgOAc (0.019 M), with 0.03 M, 0.06 M, 0.09 M, 0.12 M of **1a**.

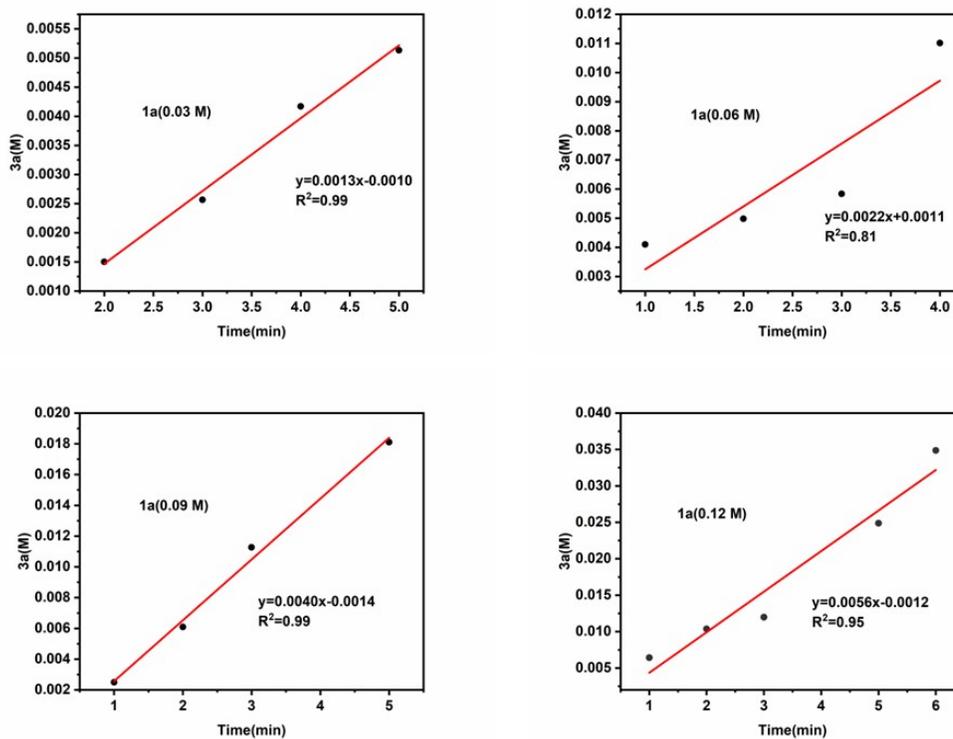


Figure S6. Rate on the concentration of **1a** from the reaction of **2a** (0.19 M), IPrCuCl (0.009 M), AgOAc (0.019 M), with 0.03 M, 0.06 M, 0.09 M, 0.12 M of **1a**.

4) The rate on the concentration of **2a**

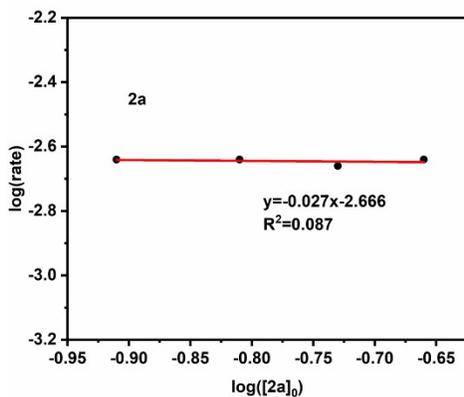
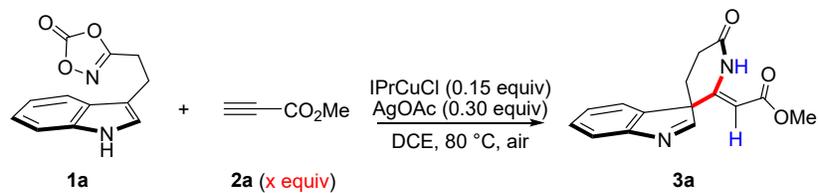


Figure S7. Rate on the concentration of **2a** from the reaction of **1a** (0.06 M), IPrCuCl (0.009 M), AgOAc (0.019 M), with 0.12 M, 0.15 M, 0.19 M, 0.22 M of **2a**.

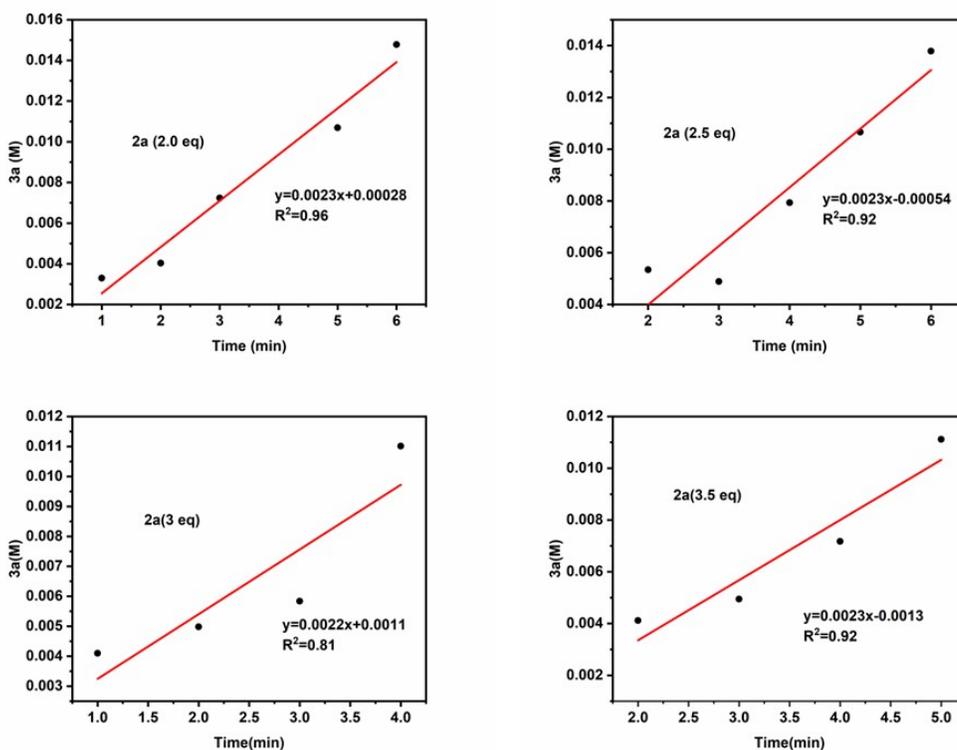
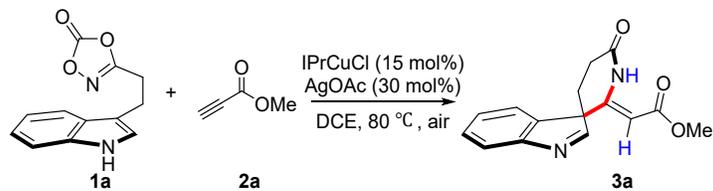


Figure S8. Rate on the concentration of **2a** from the reaction of **1a** (0.06 M), IPrCuCl (0.009 M), AgOAc (0.019 M), with 0.12 M, 0.15 M, 0.19 M, 0.22 M of **2a**.

2.8 Control experiments



Entry	Conditions	Result
1	IPrCuCl (15 mol%), DCE, 80 °C	<10%
2	Standard Conditions, no 2a	Decomposed
3	AgOAc (30 mol%), DCE, 80 °C	No reaction
4	DCE, 80 °C	No reaction

Four Schlenk tubes were named 1, 2, 3 and 4. **1a** (46.0 mg, 0.20 mmol), **2a** (50.4 mg, 0.60 mmol, 3 equiv), IPrCuCl (14.6 mg, 0.03 mmol, 0.15 equiv) and DCE (3 mL) were added to **tube 1**.

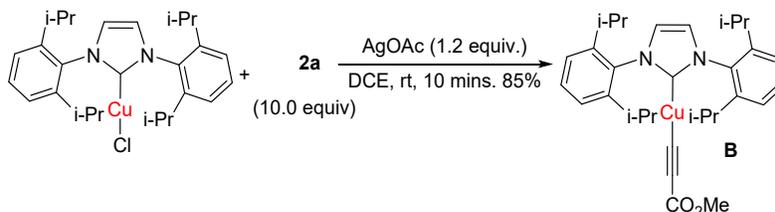
1a (46.0 mg, 0.20 mmol), IPrCuCl (14.6 mg, 0.03 mmol, 0.15 equiv), AgOAc (10.0 mg, 0.06 mmol, 0.30 equiv), and DCE (3 mL) were added to **tube 2**.

1a (46.0 mg, 0.20 mmol), **2a** (50.4 mg, 0.60 mmol, 3 equiv), AgOAc (10.0 mg, 0.06 mmol, 0.30 equiv) and DCE (3 mL) were added to **tube 3**.

1a (46.0 mg, 0.20 mmol), **2a** (50.4 mg, 0.60 mmol, 3 equiv), and DCE (3 mL) were added to **tube 4**. All reactions were stirred in an 80 °C oil bath for 30 minutes.

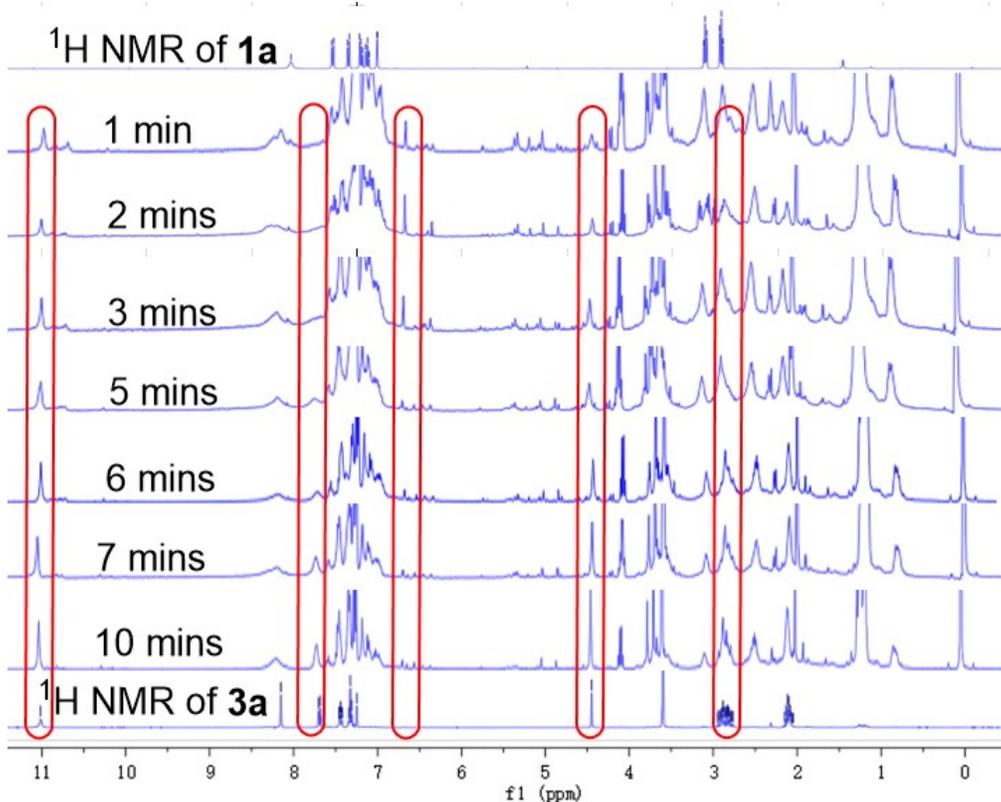
The resulting samples were filtered through a filter membrane, concentrated, and analyzed by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard.

2.9 Synthesis route of intermediate B



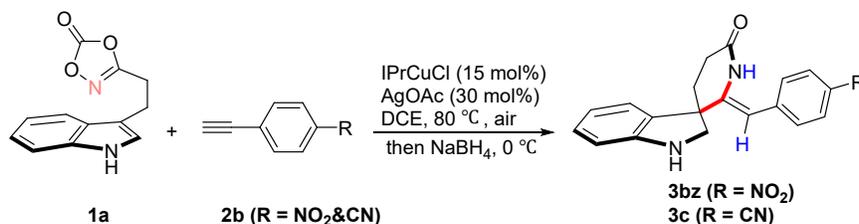
The catalyst IPrCuCl (10.0 mg, 0.021 mmol) and AgOAc (4.2 mg, 0.025 mmol, 1.2 equiv) was dissolved in DCE (0.5 mL), and the **2a** (17.7 mg, 0.21 mmol, 10.0 equiv) was added. The mixture was stirred at room temperature for 10 mins. After filtering the obtained sample with a filter membrane, concentrate it for X-ray analysis.

2.10 Insitu ¹H NMR analysis over time^[9]



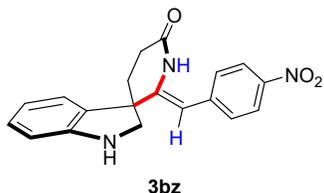
In a Schlenk tube (10 mL) equipped with a magnetic stir bar, **1a** (42.0 mg, 0.18 mmol), **2a** (46.0 mg, 0.55 mmol, 3 equiv), IPrCuCl (13.3 mg, 0.03 mmol, 0.15 equiv) and AgOAc (9.1 mg, 0.05 mmol, 0.30 equiv) were added and dissolved in DCE (3.0 mL). The reaction was carried out at 80 °C. A 1.0 mL syringe was used to draw 0.6 mL of the reaction solution each time, and data were collected at 1 minute, 2 minutes, 3 minutes, 5 minutes, 6 minutes, 7 minutes, and 10 minutes.

2.11 With another alkynes



The **1a** (46.0 mg, 0.2 mmol), IPrCuCl (14.6 mg, 0.03 mmol, 0.15 equiv), and AgOAc (10.0 mg, 0.06 mmol, 0.30 equiv) was dissolved in DCE (3.0 mL), and the **2b** (0.6 mmol, 3.0 equiv) was added. The mixture was heated 80 °C in an oil bath for 10 mins. The resulting mixture was concentrated and the crude product was used for next step without further purification. The crude product was dissolved in MeOH (5 mL), and NaBH₄ (9.1

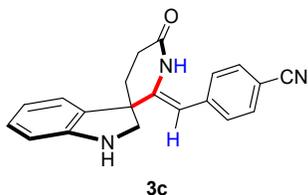
mg, 0.24 mmol, 2.0 equiv) was added at 0 °C. The mixture was stirred at an ice-water bath for 25 mins. The reaction residue was quenched with NH₄Cl and extracted with CH₂Cl₂. The organic layers were dried over Na₂SO₄, concentrated, purified by column chromatography (EtOAc) to afford the unknown product **3bz** and **3c**.



Yellow solid, yield 45% (30.2 mg), R_f = 0.5 (EtOAc), M. p. = 168-169 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.19 (t, J = 8 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 6.86-6.77 (m, 2H), 5.17 (s, 1H), 3.73 (d, J = 8.8 Hz, 1H) 3.65 (d, J = 8.8 Hz, 1H), 2.74-2.61 (m, 2H), 2.45-2.36 (m, 1H), 2.15-2.10 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.7, 151.3, 146.2, 142.6, 142.1, 131.1, 129.4, 129.0, 124.4, 119.6, 113.9, 110.7, 105.4, 58.5, 48.9, 30.5, 28.8.

HRMS (ESI) Calcd. For C₁₉H₁₇N₃O₃: [M+H]⁺ : 336.1352, Found: m/z 336.1353.



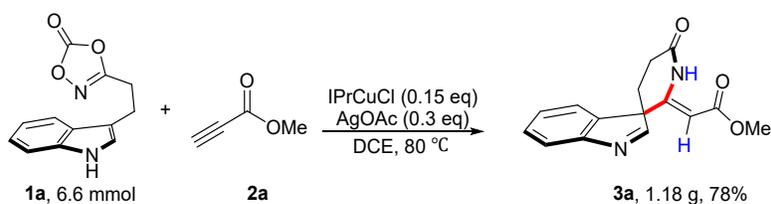
White solid, yield 35% (22.1 mg), R_f = 0.5 (EtOAc), M. p. = 114-115 °C;

¹H NMR (400 MHz, CDCl₃), δ 7.71 (bs, 1H), 7.59 (d, J = 8 Hz, 2H), 7.26 (d, J = 6.8 Hz, 2H), 7.17 (t, J = 8 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 6.84-6.76 (m, 2H), 5.13 (s, 1H), 3.91 (bs, 1H), 3.70 (d, J = 8.8 Hz, 1H), 3.63 (d, J = 8.8 Hz, 1H), 2.72-2.59 (m, 2H), 2.42-2.33 (m, 1H), 2.13-2.08 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 169.7, 151.3, 142.0, 140.0, 132.8, 131.1, 129.3, 129.0, 124.4, 119.6, 118.8, 110.6, 110.2, 105.7, 77.5, 77.1, 76.8, 58.5, 48.8, 30.5, 28.8.

HRMS (ESI) Calcd. For C₂₀H₁₇N₃O: [M+H]⁺ : 316.1447, Found: m/z 316.1445.

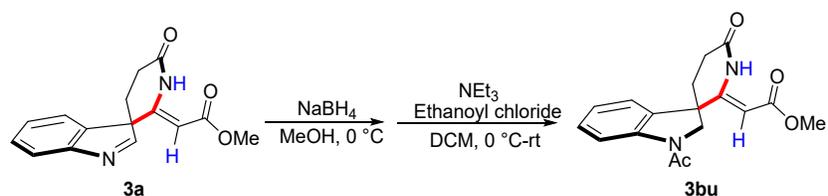
2.12 Broaden scale Synthesis and Synthetic Transformation of **3a**

1) Broaden scale Synthesis of **3a**



The Dioxazolone **1a** (1.52 g, 6.60 mmol), IPrCuCl (482.72 mg, 0.99 mmol, 0.15 equiv), and AgOAc (330.48 mg, 1.98 mmol, 0.3 equiv) was dissolved in DCE (15 mL), and the **2a** (1.66 g, 19.80 mmol, 3.0 equiv) was added. The mixture was heated 80 °C in an oil bath for 30 mins. The organic layer was concentrated and purified by column chromatography to afford the product **3a** (1.18 g, yield 78%).

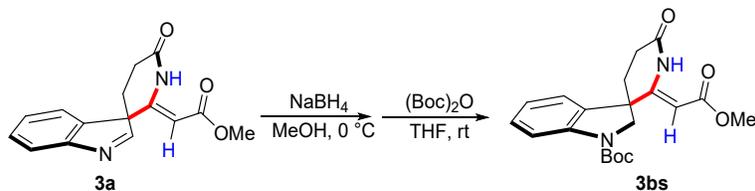
2) Synthetic Transformation of **3a**



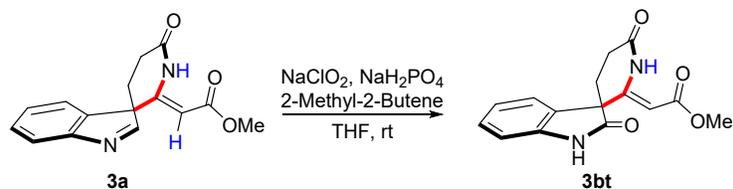
The compound **3a** (54.0 mg, 0.20 mmol) was dissolved in MeOH (10 mL), and NaBH₄ (9.1 mg, 0.24 mmol, 1.2 equiv) was added at 0 °C. The mixture was stirred at an ice-water bath for 25 mins. The reaction residue was quenched with NH₄Cl and extracted with CH₂Cl₂. The organic layers were dried over Na₂SO₄, concentrated, the crude product was used for next step without further purification. The crude product was dissolved in dry DCM (10 mL). Triethylamine (60.7 mg, 0.60 mmol, 3.0 equiv) and Ethanoyl chloride (23.6 mg, 0.30 mmol, 1.5 equiv) were added to the reaction at 0 °C. The mixture was stirred at an ice-water bath for 20 mins. The reaction residue was quenched with NaHCO₃ and extracted with EtOAc. The organic layers were dried over Na₂SO₄, filtered, and concentrated in vacuo, purified by column chromatography (Petroleum ether : EtOAc = 1:1) to afford the unknown product **3bu** (53.4 mg, yield 85%) as a slightly white solid, R_f = 0.3, (Petroleum ether : EtOAc = 1:1), M. p. = 171-172 °C.^[10]

¹H NMR (400 MHz, CDCl₃), δ 10.90 (s, 1H), 8.24 (d, *J* = 8.1, 1H), 7.34-7.31 (m, 1H), 7.22-7.17 (m, 3H), 4.38 (s, 1H), 4.10 (q, *J* = 10.4 Hz, 2H), 3.62 (s, 3H), 2.79-2.63 (m, 2H), 2.43-2.38 (m, 1H), 2.23 (s, 3H), 2.08-2.01 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 157.6, 143.1, 132.7, 129.9, 124.6, 123.9, 117.5, 94.1, 60.7, 51.5, 46.8, 31.0, 28.6, 24.4.

HRMS (ESI) Calcd. For C₁₇H₁₉N₂O₄: [M+H]⁺ : 315.1339, Found: *m/z* 315.1332.



The compound **3a** (54.0 mg, 0.20 mmol) was dissolved in MeOH (10 mL), and NaBH₄ (9.1 mg, 0.24 mmol, 1.2 equiv) was added at 0 °C. The mixture was stirred at an ice-water bath for 25 mins. The reaction residue was quenched with NH₄Cl and extracted with CH₂Cl₂. The organic layers were dried over Na₂SO₄, concentrated, the crude product was used for next step without further purification^[11]. The crude product was dissolved in THF (10 mL). Di-tert-butyl dicarbonate ((Boc)₂O, 104.8 mg, 0.48 mmol, 2.4 equiv) were added to the reaction. The mixture was stirred at room temperature for 48 hours^[12]. The reaction residue was concentrated in vacuo, purified by column chromatography (Petroleum ether : EtOAc = 3:1) to afford the unknown product **3bs** (34.2mg, yield 46%) as a slightly white solid, R_f = 0.45, (Petroleum ether : EtOAc = 3:1), M. p. = 158-159 °C. ¹H NMR (400 MHz, CDCl₃) δ = 10.88 (s, 1H), 7.92 (s, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.08-6.99 (m, 2H), 4.42 (s, 1H), 4.01 (s, 2H), 3.63 (s, 3H), 2.69 (dd, *J* = 12.0 Hz, *J* = 5.2 Hz, 2H), 2.43–1.96 (m, 2H), 1.55 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 168.9, 168.7, 158.3, 152.0, 143.1, 132.3, 129.7, 124.1, 123.1, 115.3, 93.8, 81.7, 77.5, 77.2, 76.8, 59.6, 51.4, 46.1, 31.1, 28.5. **HRMS (ESI)** Calcd. For C₂₀H₂₅N₂O₅ : [M+H]⁺ : 373.1758, Found: m/z 373.1763.

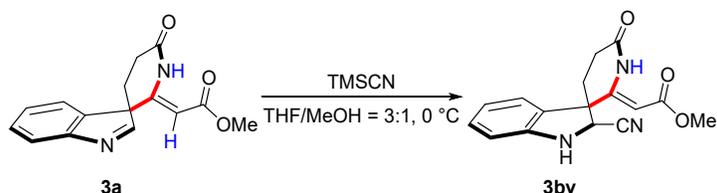


The compound **3a** (54.0 mg, 0.20 mmol) was dissolved in THF (5 mL). 2-methyl-2-butene (154.3 mg, 2.20 mmol, 11 equiv) and NaClO₂ (103.1 mg, 1.14 mmol, 5.7 equiv) were added to the reaction at room temperature. The resulting reaction solution was stirred vigorously, and NaH₂PO₄ (0.31 mL, 1 M in H₂O, 0.34 mmol, 1.7 equiv) was added dropwise. After completion of addition, the reaction mixture was stirred at ambient temperature for 20 mins before being quenched by the addition of saturated aq. Na₂S₂O₃ at 0 °C. The layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure^[12]. The residue

was purified by silica gel column chromatography (Petroleum ether : EtOAc = 2:1) to afford **3bt** (38.9 mg, 68% yield) as a slightly yellow solid, $R_f = 0.35$, (Petroleum ether : EtOAc = 2:1), M. p. = 188-189 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3), δ 10.97 (s, 1H), 9.29 (s, 1H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.17 (d, $J = 7.4$ Hz, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 7.02 (d, $J = 7.4$ Hz, 1H), 4.53 (s, 1H), 3.62 (s, 3H), 3.32-3.23 (m, 1H), 2.74-2.67 (m, 1H), 2.39-2.31 (m, 1H), 2.23-2.21 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 177.4, 169.6, 168.4, 152.3, 140.8, 130.4, 129.7, 124.2, 123.6, 111.0, 93.1, 51.5, 50.6, 29.0, 27.3.

HRMS (ESI) Calcd. For $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_4$: $[\text{M}+\text{H}]^+$: 287.1026, Found: m/z 287.1024.

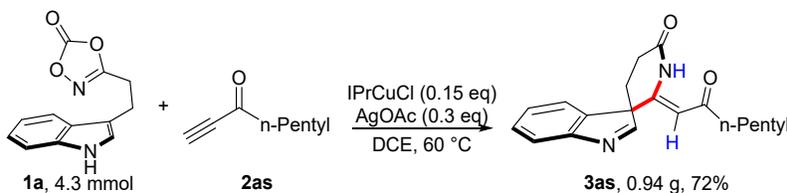


TMSCN (59.5 mg, 0.60 mmol, 3.0 equiv) was added to the mixture of compound **3a** (54.0 mg, 0.20 mmol) in THF/MeOH (6 mL/3 mL). The reaction was stirred at 0 °C for 36 hours^[13]. After the solvents were evaporated, the crude product was purified by column chromatography (Petroleum ether : EtOAc = 2:1) to give the compound **3bv** as a white solid (26.2 mg, yield 44%), $R_f = 0.3$, (Petroleum ether : EtOAc = 2:1), M. p. = 121-122 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.83 (s, 1H), 7.27 (d, $J = 14.8$ Hz, 1H) 7.06 (d, $J = 7.6$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 1H), 4.62 (s, 1H), 4.34 (s, 1H), 3.63 (s, 3H), 2.83-2.80 (m, 2H), 2.66-2.48 (m, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.4, 168.3, 153.8, 148.4, 130.5, 127.6, 124.0, 121.8, 117.6, 111.6, 94.9, 58.0, 51.6, 51.1, 28.7, 27.3.

HRMS (ESI) Calcd. For $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}_3$: $[\text{M}+\text{H}]^+$: 298.1115, Found: m/z 298.1113.

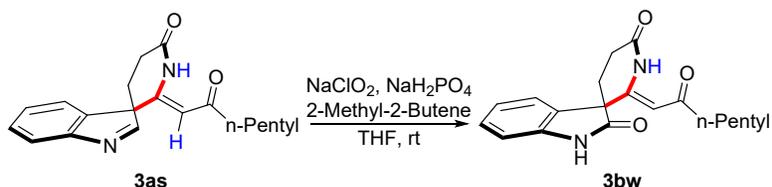
3) Broaden scale Synthesis of **3as**



The Dioxazolone **1a** (1.0 g, 4.3 mmol), IPrCuCl (314.5 mg, 0.65 mmol, 0.15 equiv), and AgOAc (215.3 mg, 1.29 mmol, 0.3 equiv) was dissolved in DCE (10 mL), and the **2as**

(1.60 g, 12.90 mmol, 3.0 equiv) was added. The mixture was heated 60 °C in an oil bath for 4 hours. The organic layer was concentrated and purified by column chromatography to afford the product **3as** (0.94 g, yield 72%).

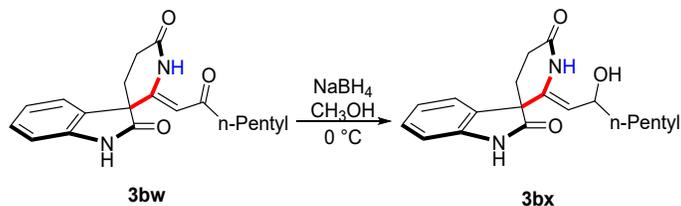
4) Synthetic Transformation of **3as**



The compound **3as** (200.0 mg, 064 mmol) was dissolved in THF (10.0 mL). 2-methyl-2-butene (497.1 mg, 3.50 mmol, 11.0 equiv) and NaClO₂ (332.2 mg, 1.84 mmol, 5.7 equiv) were added to the reaction at room temperature. The resulting reaction solution was stirred vigorously, and NaH₂PO₄ (1.0 mL, 1 M in H₂O, 1.10 mmol, 1.7 equiv) was added dropwise. After completion of addition, the reaction mixture was stirred at ambient temperature for 20 mins before being quenched by the addition of saturated aq. Na₂S₂O₃ at 0 °C. The layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure^[8]. The residue was purified by silica gel column chromatography (Petroleum ether : EtOAc = 1:1) to afford **3bw** (96.7 mg, 62% yield) as a slightly yellow solid, R_f = 0.35, (Petroleum ether : EtOAc = 1:1), M. p. = 145-146 °C.

¹H NMR (400 MHz, CDCl₃) δ 12.06 (s, 1H), 8.84 (s, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 4.86 (s, 1H), 3.29-3.20 (m, 1H), 2.70 (dt, *J* = 4.8 Hz, *J* = 18.0 Hz, 1H), 2.38-2.30 (m, 1H), 2.22-2.18 (m, 1H), 1.47 (quint, *J* = 7.6 Hz, 2H), 1.28-1.15 (m, 6H), 0.83 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 201.2, 171.5, 169.3, 154.9, 149.9, 129.8, 127.6, 122.7, 122.6, 99.0, 79.4, 59.2, 50.1, 32.5, 31.7, 29.9, 28.5, 26.9, 14.2.

HRMS (ESI) Calcd. For C₁₄H₁₂N₂O₃: [M+H]⁺ : 256.0773, Found: m/z 256.0778.



The compound **3a** (96.7 mg, 0.26 mmol) was dissolved in MeOH (10 mL), and NaBH₄ (14.6 mg, 0.39 mmol, 1.5 equiv) was added at 0 °C. The mixture was stirred at an ice-water bath for 25 mins^[12]. The reaction residue was quenched with NH₄Cl and extracted with CH₂Cl₂. The organic layers were dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc) to afford **3bx** (75.9 mg, 90% yield) as a slightly yellow solid, R_f = 0.35, (EtOAc), M. p. = 112-113 °C.

¹H NMR (400 MHz, CDCl₃) δ 9.23 (s, 1H), 8.76 (bs, 1H), 7.27 (d, *J* = 10.4 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 4.36-4.33 (m, 1H), 4.13 (d, *J* = 5.2 Hz, 1H), 3.17-3.01 (m, 2H), 2.62-2.57 (m, 1H), 2.28-2.06 (m, 2H), 1.79-1.16 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 179.3, 170.5, 170.1, 141.0, 135.0, 131.7, 128.9, 124.1, 123.0, 110.8, 67.6, 50.1, 37.7, 31.7, 29.2, 27.3, 24.9, 22.6, 14.1.

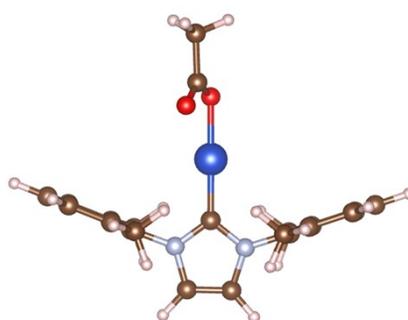
HRMS (ESI) Calcd. For C₁₄H₁₄N₂O₃: [M+H]⁺ : 258.0925, Found: m/z 258.0929.

2.13 Computational details

Computational Methods: The DFT calculations of the possible intermediates in the reactions were performed by using the software ORCA 5.0^[13]. The stationary points were carried out using the B3LYP-D3(BJ) functional^[14], which was the robust method for similar systems. The SDD basis set was used for Cu and the def2-TZVP^[3] basis set was used for the other atoms. The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum (zero imaginary frequency) and to evaluate its zero-point vibration energy (ZPE) and thermal corrections at 298.15 K. The solvent effects in dichloroethane were computed using the PCM solvation model^[15]. To reduce computational cost, we replaced the isopropyl group with a methyl group. Although the steric hindrance effect is weakened, this approximation leaves the relative energetics of the reaction profile essentially unchanged. The optimized structures are illustrated using VESTA^[16].

	E	ZPE	H	G
1a	-798.38449768	0.20517533	-798.16491929	-798.21942710
2a	-304.68572217	0.05882008	-304.61970697	-304.65685767

3a	-915.13598754	0.26825681	-914.85009818	-914.91058874
A'	-1269.92021643	0.39346544	-1269.49827589	-1269.58257756
B'	-1574.63959057	0.45383294	-1574.14951525	-1574.24995618
TS1	-2373.04421536	0.66024898	-2372.33259750	-2372.46179752
C'	-1955.80555236	0.59605885	-1955.16693182	-1955.27769258
TS2	-1955.81194100	0.59618265	-1955.17339410	-1955.28484172
D'	-1955.92266581	0.59714201	-1955.28287323	-1955.39602199
H'	-1955.92122166	0.59664243	-1955.28160247	-1955.39600517
TS3	-1955.89291185	0.59556668	-1955.25610033	-1955.36407199
E'	-915.09042276	0.26370298	-914.80706756	-914.87338753
G	-1955.96470069	0.59937071	-1955.32452420	-1955.43165620
HAc	-229.08742136	0.06117971	-229.02072193	-229.05309324

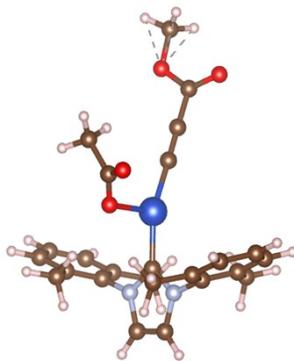


A'

Number	Label	Charge	SybylType	X	Y	Z
1	C	0	C.2	-0.5661	-1.9052	-0.0344
2	C	0	C.2	0.7864	-1.8732	-0.0366
3	C	0	C.3	0.0597	0.2702	-0.0212
4	N	0	N.3	-0.9882	-0.5841	-0.025
5	H	0	H	-1.2579	-2.7282	-0.0375
6	H	0	H	1.5165	-2.6624	-0.0417
7	N	0	N.3	1.1464	-0.5333	-0.0287
8	C	0	C.2	2.4893	-0.0294	-0.0153

9	C	0	C.2	3.131	0.1917	-1.2356
10	C	0	C.2	3.0813	0.2501	1.2184
11	C	0	C.2	4.4292	0.6987	-1.1995
12	C	0	C.2	4.3804	0.7561	1.2103
13	C	0	C.2	5.0491	0.9763	0.0127
14	H	0	H	4.9507	0.8805	-2.131
15	H	0	H	4.8643	0.9814	2.1526
16	H	0	H	6.0579	1.3698	0.0237
17	C	0	C.2	-2.3512	-0.1365	-0.0113
18	C	0	C.2	-2.9565	0.1134	1.2222
19	C	0	C.2	-2.9963	0.0708	-1.2323
20	C	0	C.2	-4.2719	0.5753	1.213
21	C	0	C.2	-4.3113	0.5324	-1.1971
22	C	0	C.2	-4.9438	0.781	0.0147
23	H	0	H	-4.7655	0.7788	2.1551
24	H	0	H	-4.8358	0.7026	-2.1292
25	H	0	H	-5.9651	1.1407	0.0251
26	C	0	C.3	-2.2057	-0.0838	2.5089
27	H	0	H	-1.805	-1.0962	2.5885
28	C	0	C.3	-2.2855	-0.1703	-2.5344
29	H	0	H	-1.9173	-1.1956	-2.6078
30	C	0	C.3	2.333	0.0353	2.5038
31	H	0	H	1.9634	-0.9886	2.5867
32	C	0	C.3	2.434	-0.0852	-2.5382
33	H	0	H	1.5326	0.5248	-2.6321
34	Cu	0	Cu	-0.0198	2.1627	0.0374
35	O	0	O.co2	-0.1116	4.0937	0.0491
36	C	0	C.2	-0.5317	4.5642	1.1712
37	O	0	O.co2	-0.8318	3.8718	2.1558
38	C	0	C.3	-0.6486	6.0767	1.2293

39	H	0	H	-0.9829	6.4068	2.2105
40	H	0	H	0.3174	6.5298	0.9989
41	H	0	H	-1.3555	6.4173	0.47
42	H	0	H	-2.9524	0.0168	-3.3746
43	H	0	H	-1.418	0.4873	-2.6285
44	H	0	H	-1.3575	0.6021	2.5698
45	H	0	H	-2.8563	0.0986	3.3627
46	H	0	H	3.0904	0.1377	-3.3779
47	H	0	H	2.1217	-1.1288	-2.6126
48	H	0	H	2.9748	0.2412	3.359
49	H	0	H	1.4627	0.6938	2.559

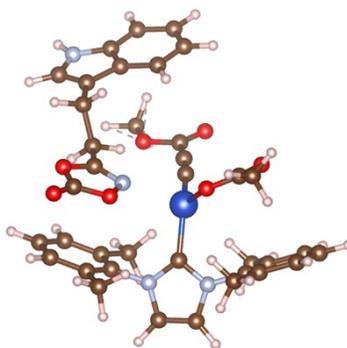


B'

Number	Label	Charge	SybylType	X	Y	Z
1	C	0	C.2	-2.9685	-0.3759	-1.1073
2	C	0	C.2	-2.4855	-1.6385	-1.097
3	C	0	C.3	-0.9256	-0.31	-0.1188
4	N	0	N.3	-1.9989	0.4169	-0.506
5	H	0	H	-3.8932	0.029	-1.4775
6	H	0	H	-2.9027	-2.5621	-1.4561
7	N	0	N.3	-1.2384	-1.5738	-0.4898
8	C	0	C.2	-0.3644	-2.6883	-0.2674
9	C	0	C.2	0.6267	-2.9528	-1.2155
10	C	0	C.2	-0.5214	-3.4414	0.8982

11	C	0	C.2	1.4806	-4.0287	-0.9772
12	C	0	C.2	0.3533	-4.5092	1.0987
13	C	0	C.2	1.3444	-4.8007	0.1701
14	H	0	H	2.2601	-4.2531	-1.6949
15	H	0	H	0.2569	-5.1064	1.997
16	H	0	H	2.0174	-5.6314	0.3437
17	C	0	C.2	-2.0964	1.8321	-0.3037
18	C	0	C.2	-2.6529	2.2994	0.8889
19	C	0	C.2	-1.6038	2.6815	-1.2969
20	C	0	C.2	-2.7299	3.6808	1.0666
21	C	0	C.2	-1.6995	4.0555	-1.0804
22	C	0	C.2	-2.2598	4.5507	0.0907
23	H	0	H	-3.1574	4.0709	1.9821
24	H	0	H	-1.3245	4.7364	-1.8345
25	H	0	H	-2.3261	5.6205	0.2454
26	Cu	0	Cu	0.6944	0.2712	0.8331
27	C	0	C.1	2.4876	0.8922	1.0287
28	C	0	C.1	3.6327	1.3027	1.1759
29	C	0	C.2	4.974	1.7433	1.3652
30	O	0	O.2	5.9763	1.0936	1.1183
31	O	0	O.3	5.0297	2.9993	1.8655
32	C	0	C.3	6.3463	3.5324	2.0943
33	H	0	H	6.1892	4.5374	2.4761
34	H	0	H	6.8806	2.9273	2.8263
35	H	0	H	6.9134	3.5629	1.1645
36	C	0	C.3	-3.1182	1.3447	1.9519
37	H	0	H	-3.8285	0.6168	1.5546
38	H	0	H	-2.2701	0.7866	2.3568
39	H	0	H	-3.599	1.8868	2.7655
40	C	0	C.3	-1.57	-3.088	1.9141

41	H	0	H	-1.3635	-2.1014	2.3363
42	H	0	H	-2.5665	-3.0564	1.4686
43	H	0	H	-1.5761	-3.8164	2.7239
44	C	0	C.3	-0.9682	2.1272	-2.5408
45	H	0	H	-0.0855	1.5343	-2.2902
46	H	0	H	-1.6509	1.4678	-3.0808
47	H	0	H	-0.6657	2.9324	-3.2087
48	C	0	C.3	0.7785	-2.0891	-2.436
49	H	0	H	-0.1468	-2.047	-3.0145
50	H	0	H	1.0226	-1.0631	-2.1515
51	H	0	H	1.5718	-2.4688	-3.0783
52	C	0	C.2	0.6674	-0.1813	3.9353
53	O	0	O.co2	-0.1284	-0.0245	2.9565
54	O	0	O.co2	0.9783	-1.2819	4.4424
55	C	0	C.3	1.2948	1.0912	4.5051
56	H	0	H	1.7873	0.9051	5.4591
57	H	0	H	2.0334	1.4596	3.789
58	H	0	H	0.5392	1.8698	4.6228



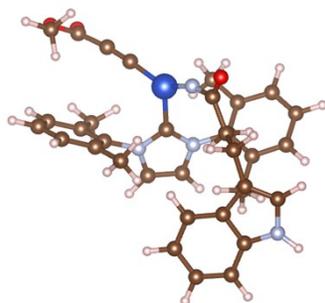
TS1

Number	Label	Charge	SybylType	X	Y	Z
1	C	0	C.2	-0.2795	-1.499	1.0287
2	C	0	C.2	1.0586	-1.5759	0.8639

3	C	0	C.3	0.4828	0.6209	0.6836
4	N	0	N.3	-0.6097	-0.1535	0.9134
5	H	0	H	-1.0184	-2.2579	1.2139
6	H	0	H	1.7293	-2.4164	0.8724
7	N	0	N.3	1.5005	-0.2751	0.6564
8	C	0	C.2	2.8669	0.0869	0.4199
9	C	0	C.2	3.3116	0.1864	-0.9003
10	C	0	C.2	3.6934	0.3341	1.5176
11	C	0	C.2	4.6493	0.5206	-1.1095
12	C	0	C.2	5.0256	0.658	1.2661
13	C	0	C.2	5.5011	0.7459	-0.0357
14	H	0	H	5.0191	0.6059	-2.1239
15	H	0	H	5.6869	0.8547	2.1008
16	H	0	H	6.5373	1.0043	-0.2151
17	C	0	C.2	-1.9395	0.3647	1.023
18	C	0	C.2	-2.484	0.542	2.2973
19	C	0	C.2	-2.6359	0.6803	-0.1466
20	C	0	C.2	-3.7758	1.0601	2.3865
21	C	0	C.2	-3.9211	1.2057	-0.0133
22	C	0	C.2	-4.4869	1.3939	1.2407
23	H	0	H	-4.215	1.2158	3.3639
24	H	0	H	-4.4763	1.4699	-0.9048
25	H	0	H	-5.4833	1.8089	1.3269
26	Cu	0	Cu	0.6371	2.5793	0.2076
27	C	0	C.1	0.258	3.3664	-1.5252
28	C	0	C.1	-0.1072	3.7107	-2.6463
29	C	0	C.2	-0.6102	4.0482	-3.9306
30	O	0	O.2	0.0542	4.273	-4.9301
31	O	0	O.3	-1.9664	4.0815	-3.9455
32	C	0	C.3	-2.5795	4.4145	-5.2011

33	H	0	H	-3.6477	4.4437	-5.003
34	H	0	H	-2.2348	5.3863	-5.5488
35	H	0	H	-2.3533	3.6551	-5.9497
36	N	0	N.2	-1.1788	3.6383	1.579
37	C	0	C.2	-2.2887	4.1923	1.2678
38	O	0	O.3	-1.2653	3.4178	2.9902
39	C	0	C.3	-2.6995	4.6752	-0.0635
40	O	0	O.3	-3.1193	4.3686	2.3384
41	C	0	C.2	-2.4591	3.8591	3.4236
42	C	0	C.3	-2.9727	6.1974	-0.0598
43	H	0	H	-1.9019	4.4201	-0.7599
44	H	0	H	-3.6005	4.1381	-0.3661
45	O	0	O.2	-2.8758	3.8218	4.5396
46	C	0	C.2	-3.2066	6.7318	-1.435
47	H	0	H	-2.114	6.7044	0.3876
48	H	0	H	-3.834	6.4036	0.5776
49	C	0	C.2	-2.1962	7.1511	-2.3696
50	C	0	C.2	-4.4121	6.8986	-2.0662
51	C	0	C.2	-2.8658	7.5722	-3.549
52	C	0	C.2	-0.7972	7.2062	-2.3252
53	N	0	N.3	-4.2126	7.3989	-3.3359
54	H	0	H	-5.4092	6.7033	-1.7052
55	C	0	C.2	-2.1763	8.0515	-4.6621
56	C	0	C.2	-0.11	7.6769	-3.4311
57	H	0	H	-0.2606	6.8696	-1.4473
58	H	0	H	-4.9422	7.6252	-3.9903
59	C	0	C.2	-0.7929	8.0971	-4.5871
60	H	0	H	-2.7024	8.367	-5.5546
61	H	0	H	0.972	7.7123	-3.4139
62	H	0	H	-0.2263	8.4558	-5.4372

63	C	0	C.3	3.1535	0.2923	2.9185
64	H	0	H	3.9545	0.4458	3.6404
65	H	0	H	2.4113	1.0817	3.0552
66	H	0	H	2.6654	-0.659	3.1386
67	C	0	C.3	2.3714	-0.0344	-2.0521
68	H	0	H	1.8858	-1.0107	-1.9914
69	H	0	H	1.5814	0.72	-2.0484
70	H	0	H	2.9053	0.0283	-2.9993
71	C	0	C.3	-2.018	0.4745	-1.4998
72	H	0	H	-2.7433	0.6827	-2.2854
73	H	0	H	-1.1627	1.1382	-1.6352
74	H	0	H	-1.6582	-0.5497	-1.6187
75	C	0	C.3	-1.6955	0.2079	3.5325
76	H	0	H	-2.2033	0.5818	4.4204
77	H	0	H	-1.5666	-0.8715	3.6425
78	H	0	H	-0.6989	0.6492	3.491
79	C	0	C.2	3.1357	3.8688	1.4865
80	O	0	O.co2	1.9579	3.4506	1.7002
81	O	0	O.co2	3.6569	4.0678	0.3679
82	C	0	C.3	3.9939	4.1177	2.7292
83	H	0	H	4.5669	3.21	2.9364
84	H	0	H	4.7027	4.9281	2.5578
85	H	0	H	3.3799	4.3359	3.6028

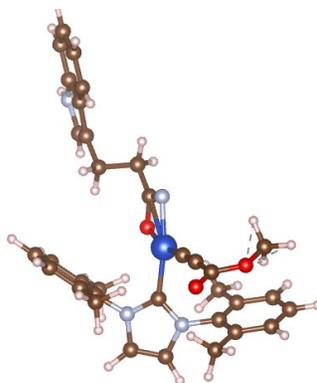


c'

Number	Label	Charge	SybylType	X	Y	Z
1	C	0	C.2	-2.6453	-0.6769	-1.0793
2	C	0	C.2	-2.5964	-1.179	0.1725
3	C	0	C.3	-0.4774	-0.9407	-0.5417
4	N	0	N.3	-1.3312	-0.5405	-1.5044
5	H	0	H	-3.475	-0.4048	-1.7059
6	H	0	H	-3.3759	-1.4408	0.8641
7	N	0	N.3	-1.2522	-1.3309	0.4916
8	C	0	C.2	-0.7823	-1.8144	1.7596
9	C	0	C.2	-0.0975	-3.0334	1.807
10	C	0	C.2	-1.0543	-1.0524	2.9022
11	C	0	C.2	0.3619	-3.4666	3.0504
12	C	0	C.2	-0.5772	-1.5285	4.1223
13	C	0	C.2	0.1318	-2.7192	4.1968
14	H	0	H	0.8958	-4.4066	3.113
15	H	0	H	-0.7603	-0.9473	5.0174
16	H	0	H	0.4987	-3.0703	5.1531
17	C	0	C.2	-0.9448	-0.061	-2.8024
18	C	0	C.2	-0.353	1.1998	-2.9023
19	C	0	C.2	-1.172	-0.8881	-3.9062
20	C	0	C.2	0.0378	1.627	-4.1715
21	C	0	C.2	-0.771	-0.4184	-5.1542
22	C	0	C.2	-0.1668	0.8256	-5.2859

23	H	0	H	0.4992	2.6007	-4.2788
24	H	0	H	-0.9192	-1.0458	-6.0241
25	H	0	H	0.1469	1.1708	-6.263
26	Cu	0	Cu	1.4634	-1.0713	-0.7723
27	C	0	C.1	1.5992	-2.0891	-2.3873
28	C	0	C.1	1.6375	-2.683	-3.4484
29	C	0	C.2	1.5924	-3.2867	-4.7434
30	O	0	O.2	1.0164	-4.3293	-4.9903
31	O	0	O.3	2.2152	-2.6409	-5.7481
32	C	0	C.3	2.9251	-1.4126	-5.4859
33	H	0	H	3.3156	-1.0989	-6.45
34	H	0	H	2.2482	-0.6586	-5.0895
35	H	0	H	3.7426	-1.5875	-4.7879
36	N	0	N.3	2.3672	-0.2191	0.4787
37	C	0	C.2	2.6355	0.5886	1.4642
38	C	0	C.3	1.4494	1.1761	2.208
39	O	0	O.2	3.8265	0.8311	1.7747
40	C	0	C.3	1.7378	2.5586	2.816
41	H	0	H	0.5942	1.2285	1.5364
42	H	0	H	1.1884	0.471	2.9998
43	C	0	C.2	0.5059	3.0954	3.4685
44	H	0	H	2.0755	3.2351	2.0263
45	H	0	H	2.55	2.478	3.5378
46	C	0	C.2	-0.6569	3.5923	2.7843
47	C	0	C.2	0.1977	3.1008	4.805
48	C	0	C.2	-1.6379	3.8789	3.77
49	C	0	C.2	-0.9651	3.801	1.4349
50	N	0	N.3	-1.0863	3.571	4.991
51	H	0	H	0.7957	2.7945	5.6483
52	C	0	C.2	-2.9027	4.3608	3.4353

53	C	0	C.2	-2.223	4.2725	1.0977
54	H	0	H	-0.2308	3.5925	0.6683
55	H	0	H	-1.5337	3.6969	5.8833
56	C	0	C.2	-3.1821	4.5492	2.0896
57	H	0	H	-3.6416	4.5752	4.1974
58	H	0	H	-2.4757	4.4318	0.0569
59	H	0	H	-4.1572	4.9177	1.7968
60	C	0	C.3	-1.8348	0.2323	2.8551
61	H	0	H	-1.5965	0.847	3.7208
62	H	0	H	-1.6242	0.8135	1.9593
63	H	0	H	-2.9099	0.0361	2.8706
64	C	0	C.3	0.1366	-3.8761	0.5838
65	H	0	H	-0.6897	-3.8092	-0.1237
66	H	0	H	1.0404	-3.5692	0.0528
67	H	0	H	0.2655	-4.9193	0.8704
68	C	0	C.3	-1.7983	-2.246	-3.7592
69	H	0	H	-1.6625	-2.8234	-4.6718
70	H	0	H	-1.3487	-2.7985	-2.9338
71	H	0	H	-2.8701	-2.1715	-3.5613
72	C	0	C.3	-0.1428	2.0756	-1.6991
73	H	0	H	-0.0311	3.1154	-2.004
74	H	0	H	-0.9769	2.0075	-1.0013
75	H	0	H	0.7585	1.7901	-1.1511

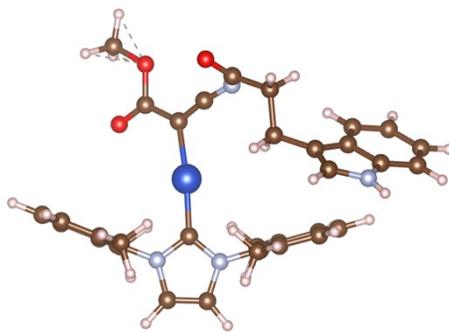


TS2

Number	Label	Charge	SybylType	X	Y	Z
1	C	0	C.2	-0.09	-0.3693	0.0314
2	C	0	C.2	1.1304	-0.3371	0.6136
3	C	0	C.3	0.3871	1.7834	0.4755
4	N	0	N.3	-0.5262	0.9478	-0.0501
5	H	0	H	-0.687	-1.1898	-0.3232
6	H	0	H	1.8191	-1.1224	0.8683
7	N	0	N.3	1.4037	0.9986	0.8756
8	C	0	C.2	2.5967	1.5266	1.4795
9	C	0	C.2	3.6178	1.9783	0.6405
10	C	0	C.2	2.6521	1.6178	2.8717
11	C	0	C.2	4.7381	2.5489	1.2439
12	C	0	C.2	3.7909	2.1928	3.4324
13	C	0	C.2	4.822	2.658	2.626
14	H	0	H	5.5452	2.9112	0.6195
15	H	0	H	3.859	2.2848	4.5091
16	H	0	H	5.6964	3.1096	3.0778
17	C	0	C.2	-1.7745	1.3761	-0.6123
18	C	0	C.2	-2.7596	1.8687	0.2473
19	C	0	C.2	-1.9394	1.3025	-1.9985
20	C	0	C.2	-3.9548	2.3037	-0.3264
21	C	0	C.2	-3.1511	1.7427	-2.5267

22	C	0	C.2	-4.1495	2.2408	-1.6992
23	H	0	H	-4.737	2.6877	0.3165
24	H	0	H	-3.3	1.7085	-3.5987
25	H	0	H	-5.0825	2.5849	-2.1276
26	Cu	0	Cu	0.4216	3.7707	0.6553
27	C	0	C.1	0.3845	4.0032	-1.1922
28	C	0	C.1	0.3245	4.0937	-2.4003
29	C	0	C.2	0.2112	4.0992	-3.8262
30	O	0	O.2	1.0717	3.6783	-4.5748
31	O	0	O.3	-0.9268	4.5859	-4.351
32	C	0	C.3	-1.9435	5.1318	-3.4821
33	H	0	H	-2.7463	5.4423	-4.1447
34	H	0	H	-2.2999	4.3724	-2.7896
35	H	0	H	-1.5531	5.9885	-2.9348
36	N	0	N.3	0.6459	5.6581	1.1036
37	C	0	C.2	0.6312	5.3078	2.3431
38	C	0	C.3	0.8503	6.2327	3.4945
39	O	0	O.3	0.4279	4.0183	2.574
40	C	0	C.3	2.0703	5.8056	4.3387
41	H	0	H	0.9782	7.2478	3.1156
42	H	0	H	-0.047	6.2174	4.1211
43	C	0	C.2	2.3038	6.7119	5.5027
44	H	0	H	2.9514	5.7882	3.6899
45	H	0	H	1.9174	4.7848	4.6906
46	C	0	C.2	2.8034	8.0611	5.456
47	C	0	C.2	2.0523	6.4405	6.8228
48	C	0	C.2	2.8295	8.5457	6.792
49	C	0	C.2	3.2396	8.9008	4.4217
50	N	0	N.3	2.3638	7.5369	7.5997
51	H	0	H	1.6707	5.5394	7.2756

52	C	0	C.2	3.2737	9.8294	7.1072
53	C	0	C.2	3.6818	10.1765	4.7324
54	H	0	H	3.2323	8.5575	3.3943
55	H	0	H	2.2807	7.5803	8.6013
56	C	0	C.2	3.6971	10.6365	6.0622
57	H	0	H	3.2876	10.1818	8.1312
58	H	0	H	4.0214	10.834	3.9418
59	H	0	H	4.0472	11.6392	6.2732
60	C	0	C.3	1.5164	1.1385	3.7294
61	H	0	H	1.7533	1.2748	4.7835
62	H	0	H	0.608	1.6998	3.5057
63	H	0	H	1.3036	0.0812	3.5586
64	C	0	C.3	3.5107	1.8611	-0.8541
65	H	0	H	3.3346	0.8275	-1.1597
66	H	0	H	2.6797	2.4553	-1.2389
67	H	0	H	4.4273	2.2079	-1.3286
68	C	0	C.3	-0.8506	0.7872	-2.8978
69	H	0	H	-1.0594	1.0539	-3.9327
70	H	0	H	0.1199	1.2017	-2.6243
71	H	0	H	-0.7691	-0.301	-2.8407
72	C	0	C.3	-2.5556	1.9368	1.736
73	H	0	H	-3.5168	2.0078	2.2436
74	H	0	H	-2.0272	1.0592	2.1101
75	H	0	H	-1.9637	2.8108	2.018

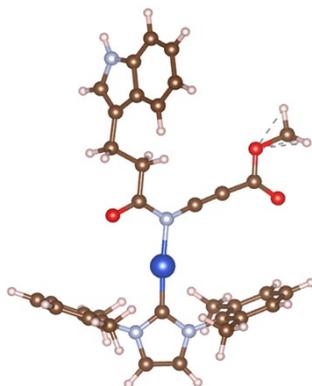


D'

Number	Label	Charge	SybylType	X	Y	Z
1	C	0	C.2	-0.6353	-3.196	2.8122
2	C	0	C.2	-0.2295	-2.0251	3.3535
3	C	0	C.3	-0.0648	-1.8191	1.1054
4	N	0	N.3	-0.5286	-3.0461	1.4381
5	H	0	H	-0.9858	-4.1057	3.2656
6	H	0	H	-0.1526	-1.703	4.3764
7	N	0	N.3	0.1131	-1.1983	2.2924
8	C	0	C.2	0.5691	0.1545	2.437
9	C	0	C.2	1.9428	0.404	2.4242
10	C	0	C.2	-0.3851	1.1627	2.5953
11	C	0	C.2	2.3598	1.7242	2.5947
12	C	0	C.2	0.0751	2.4643	2.7815
13	C	0	C.2	1.4348	2.7437	2.7791
14	H	0	H	3.4195	1.9478	2.5806
15	H	0	H	-0.6424	3.2632	2.9042
16	H	0	H	1.771	3.7653	2.8985
17	C	0	C.2	-0.8789	-4.0373	0.4615
18	C	0	C.2	0.1197	-4.889	-0.0149
19	C	0	C.2	-2.1982	-4.0812	0.0051
20	C	0	C.2	-0.2415	-5.8347	-0.9734
21	C	0	C.2	-2.518	-5.0418	-0.9531
22	C	0	C.2	-1.5487	-5.9123	-1.4361

23	H	0	H	0.5142	-6.5051	-1.3631
24	H	0	H	-3.5334	-5.0982	-1.3253
25	H	0	H	-1.8124	-6.6507	-2.1829
26	Cu	0	Cu	0.2822	-1.2579	-0.7093
27	C	0	C.1	0.3215	0.3582	-2.9063
28	C	0	C.3	0.6079	-0.8634	-2.6107
29	C	0	C.2	0.991	-1.8828	-3.5695
30	O	0	O.2	1.1574	-3.0638	-3.3139
31	O	0	O.3	1.1738	-1.4004	-4.8271
32	C	0	C.3	1.5718	-2.3557	-5.8227
33	H	0	H	1.6731	-1.79	-6.7452
34	H	0	H	2.5228	-2.8162	-5.5551
35	H	0	H	0.8147	-3.1316	-5.9358
36	N	0	N.2	0.0844	1.5633	-3.0163
37	C	0	C.2	-1.1865	2.1267	-3.2403
38	C	0	C.3	-1.4605	3.2927	-2.3307
39	O	0	O.2	-1.9525	1.7183	-4.0879
40	C	0	C.3	-1.5389	2.8448	-0.852
41	H	0	H	-0.638	4.0014	-2.446
42	H	0	H	-2.3863	3.7785	-2.6351
43	C	0	C.2	-1.3996	3.9794	0.1058
44	H	0	H	-0.7413	2.121	-0.6622
45	H	0	H	-2.4835	2.3237	-0.6858
46	C	0	C.2	-0.1954	4.7269	0.3517
47	C	0	C.2	-2.3483	4.4803	0.957
48	C	0	C.2	-0.486	5.6635	1.3789
49	C	0	C.2	1.1061	4.6626	-0.1617
50	N	0	N.3	-1.8057	5.4917	1.7242
51	H	0	H	-3.3753	4.1816	1.0919
52	C	0	C.2	0.483	6.5249	1.8916

53	C	0	C.2	2.0704	5.5183	0.3446
54	H	0	H	1.36	3.9449	-0.9322
55	H	0	H	-2.3003	6.0171	2.4251
56	C	0	C.2	1.7613	6.4408	1.3607
57	H	0	H	0.2474	7.2282	2.6807
58	H	0	H	3.0817	5.4746	-0.0402
59	H	0	H	2.5374	7.0942	1.739
60	C	0	C.3	-1.8558	0.8588	2.5341
61	H	0	H	-2.4373	1.7711	2.6546
62	H	0	H	-2.1162	0.4099	1.5725
63	H	0	H	-2.1568	0.1514	3.3093
64	C	0	C.3	2.9315	-0.7112	2.228
65	H	0	H	2.8481	-1.4601	3.0192
66	H	0	H	2.7567	-1.2282	1.282
67	H	0	H	3.9493	-0.3239	2.228
68	C	0	C.3	-3.2268	-3.1094	0.5123
69	H	0	H	-4.1961	-3.307	0.0572
70	H	0	H	-3.336	-3.1694	1.597
71	H	0	H	-2.9383	-2.0819	0.2777
72	C	0	C.3	1.5375	-4.7648	0.467
73	H	0	H	2.1663	-5.5246	0.0056
74	H	0	H	1.9427	-3.7816	0.217
75	H	0	H	1.6039	-4.8713	1.5518

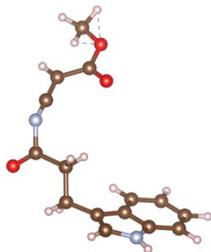


H'

Number	Label	Charge	SybylType	X	Y	Z
1	C	0	C.2	-0.8509	-3.9039	1.5819
2	C	0	C.2	0.3678	-4.3817	1.2408
3	C	0	C.3	0.0894	-2.4106	0.1555
4	N	0	N.3	-0.9996	-2.7006	0.9079
5	H	0	H	-1.6138	-4.2999	2.2278
6	H	0	H	0.8874	-5.2769	1.532
7	N	0	N.3	0.9225	-3.4538	0.3693
8	C	0	C.2	2.2346	-3.5338	-0.2024
9	C	0	C.2	2.3924	-4.1774	-1.4308
10	C	0	C.2	3.292	-2.9315	0.4828
11	C	0	C.2	3.6765	-4.2292	-1.9724
12	C	0	C.2	4.5592	-3.0025	-0.0938
13	C	0	C.2	4.7504	-3.6485	-1.3089
14	H	0	H	3.8281	-4.7232	-2.9242
15	H	0	H	5.3968	-2.5416	0.4148
16	H	0	H	5.7409	-3.6952	-1.7441
17	C	0	C.2	-2.1381	-1.8303	0.9766
18	C	0	C.2	-3.2338	-2.1036	0.1548
19	C	0	C.2	-2.0814	-0.7159	1.8179
20	C	0	C.2	-4.3159	-1.2264	0.2033
21	C	0	C.2	-3.1854	0.1354	1.8373

22	C	0	C.2	-4.2929	-0.117	1.0384
23	H	0	H	-5.1749	-1.4132	-0.429
24	H	0	H	-3.1676	1.0059	2.4808
25	H	0	H	-5.1384	0.5591	1.0608
26	Cu	0	Cu	0.2821	-0.757	-0.8068
27	C	0	C.2	-0.0797	2.1711	-0.7484
28	C	0	C.2	1.1883	2.3512	-0.2525
29	C	0	C.2	2.2899	1.4363	-0.351
30	O	0	O.3	2.2979	0.2882	-0.796
31	O	0	O.3	3.4314	1.988	0.1352
32	C	0	C.3	4.6037	1.1598	0.1021
33	H	0	H	5.3995	1.765	0.528
34	H	0	H	4.4546	0.2583	0.6947
35	H	0	H	4.8487	0.8796	-0.9222
36	N	0	N.2	-0.4821	1.0273	-1.3497
37	C	0	C.2	-1.6507	0.9122	-2.0398
38	C	0	C.3	-2.6029	2.0829	-2.1003
39	O	0	O.2	-1.9326	-0.1448	-2.6144
40	C	0	C.3	-2.4977	2.9348	-0.848
41	H	0	H	-2.3724	2.6702	-2.9943
42	H	0	H	-3.6098	1.6872	-2.2285
43	C	0	C.3	-1.0394	3.3702	-0.6177
44	H	0	H	-2.8206	2.3544	0.0182
45	H	0	H	-3.1357	3.817	-0.9105
46	C	0	C.2	-0.9006	4.1357	0.6759
47	C	0	C.2	-0.6324	4.472	-1.5928
48	C	0	C.2	-0.5182	5.4421	0.3546
49	C	0	C.2	-1.1032	3.7637	1.9906
50	N	0	N.2	-0.3599	5.6024	-1.0511
51	H	0	H	-0.5774	4.3224	-2.665

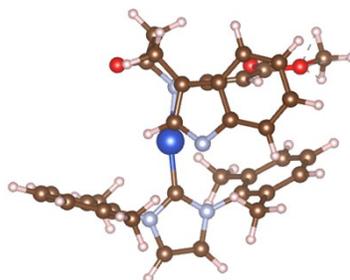
52	C	0	C.2	-0.3301	6.4047	1.3339
53	C	0	C.2	-0.9123	4.7246	2.9871
54	H	0	H	-1.391	2.7525	2.2474
55	C	0	C.2	-0.5312	6.0266	2.6621
56	H	0	H	-0.0338	7.4128	1.074
57	H	0	H	-1.0593	4.455	4.0253
58	H	0	H	-0.3886	6.7535	3.4516
59	C	0	C.3	3.0603	-2.2104	1.7802
60	H	0	H	4.0004	-1.8394	2.1855
61	H	0	H	2.3889	-1.3623	1.6308
62	H	0	H	2.596	-2.8611	2.5239
63	C	0	C.3	1.2134	-4.7708	-2.1497
64	H	0	H	0.7109	-5.5249	-1.5405
65	H	0	H	0.4726	-4.0012	-2.3788
66	H	0	H	1.528	-5.236	-3.0827
67	C	0	C.3	-0.8617	-0.4174	2.6439
68	H	0	H	-1.0817	0.3503	3.3845
69	H	0	H	-0.4931	-1.3056	3.159
70	H	0	H	-0.0483	-0.0548	2.0097
71	C	0	C.3	-3.224	-3.2778	-0.7818
72	H	0	H	-4.1477	-3.3157	-1.3571
73	H	0	H	-2.3859	-3.2061	-1.479
74	H	0	H	-3.1138	-4.222	-0.2447
75	H	0	H	1.414	3.2882	0.2324



E'

Number	Label	Charge	SybylType	X	Y	Z
1	C	0	C.1	0.6152	-2.5571	-0.7692
2	C	0	C.2	-0.0393	-2.9531	-1.8469
3	C	0	C.2	-1.0099	-2.0312	-2.4418
4	O	0	O.2	-1.2312	-0.9149	-2.0107
5	O	0	O.3	-1.691	-2.4399	-3.5269
6	C	0	C.3	-1.5047	-3.753	-4.0874
7	H	0	H	-2.1914	-3.807	-4.9272
8	H	0	H	-0.4818	-3.8801	-4.4418
9	H	0	H	-1.7555	-4.5235	-3.3584
10	N	0	N.2	1.1565	-2.2129	0.2425
11	C	0	C.2	2.3429	-1.4426	0.4745
12	C	0	C.3	2.1101	0.0324	0.3376
13	O	0	O.2	3.3618	-1.9919	0.7909
14	C	0	C.3	3.3455	0.8837	0.6393
15	H	0	H	1.7469	0.2042	-0.6805
16	H	0	H	1.2755	0.299	0.9928
17	C	0	C.2	3.0894	2.3347	0.3847
18	H	0	H	4.1744	0.5321	0.0195
19	H	0	H	3.6434	0.7336	1.6782
20	C	0	C.2	2.9051	2.9575	-0.8997
21	C	0	C.2	2.944	3.3266	1.3193
22	C	0	C.2	2.6519	4.3361	-0.6643
23	C	0	C.2	2.9345	2.4886	-2.2205

24	N	0	N.3	2.6818	4.528	0.6957
25	H	0	H	3.0083	3.2699	2.3941
26	C	0	C.2	2.4304	5.2374	-1.7052
27	C	0	C.2	2.7133	3.3818	-3.256
28	H	0	H	3.1283	1.4436	-2.4303
29	H	0	H	0.1814	-3.9312	-2.2471
30	C	0	C.2	2.4624	4.7425	-3.0001
31	H	0	H	2.2396	6.2851	-1.5085
32	H	0	H	2.7319	3.0312	-4.2803
33	H	0	H	2.2917	5.4159	-3.8305
34	H	0	H	2.5446	5.407	1.1657



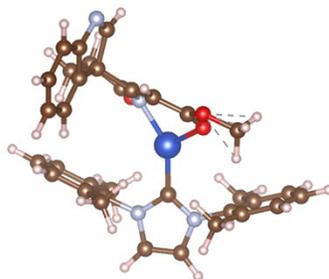
TS3

Number	Label	Charge	SybylType	X	Y	Z
1	Cu	0	Cu	0.4866	0.389	-0.6404
2	C	0	C.3	1.9394	-1.4786	-1.6841
3	C	0	C.2	2.816	-2.241	-1.0798
4	C	0	C.2	2.3655	-3.5131	-0.4852
5	O	0	O.2	1.2287	-3.9351	-0.4882
6	O	0	O.3	3.4035	-4.1563	0.0667
7	C	0	C.3	3.1073	-5.4169	0.6984
8	H	0	H	4.0538	-5.7678	1.0982
9	H	0	H	2.3821	-5.276	1.4981
10	H	0	H	2.7152	-6.1212	-0.0339

11	N	0	N.2	0.861	-0.9735	-2.0499
12	C	0	C.2	0.4957	-0.8632	-3.4334
13	C	0	C.3	1.6247	-1.0742	-4.3822
14	O	0	O.2	-0.6259	-0.5136	-3.7166
15	C	0	C.3	2.6418	0.122	-4.3242
16	H	0	H	2.1544	-1.995	-4.1308
17	H	0	H	1.2229	-1.1519	-5.3903
18	C	0	C.2	3.3001	0.4104	-3.0158
19	H	0	H	2.106	1.0088	-4.6706
20	H	0	H	3.3965	-0.1077	-5.0792
21	C	0	C.2	4.5414	-0.0829	-2.5053
22	C	0	C.2	2.9294	1.4277	-2.1057
23	C	0	C.2	4.7796	0.6553	-1.2948
24	C	0	C.2	5.4292	-1.0958	-2.8881
25	N	0	N.2	3.7835	1.586	-1.08
26	H	0	H	2.0506	2.058	-2.1975
27	C	0	C.2	5.8867	0.3597	-0.4938
28	C	0	C.2	6.5217	-1.3754	-2.077
29	H	0	H	5.2599	-1.671	-3.7919
30	H	0	H	3.8581	-1.9657	-1.0259
31	C	0	C.2	6.7489	-0.6543	-0.8896
32	H	0	H	6.0584	0.9069	0.4257
33	H	0	H	7.2119	-2.1613	-2.3598
34	H	0	H	7.6074	-0.8989	-0.2759
35	C	0	C.3	0.3231	1.4684	0.9259
36	N	0	N.3	-0.233	2.6887	1.0696
37	N	0	N.3	0.7436	1.1351	2.1655
38	C	0	C.2	-0.1701	3.1191	2.3871
39	C	0	C.2	-0.7596	3.4324	-0.0388
40	C	0	C.2	0.4473	2.1346	3.0809

41	C	0	C.2	1.4557	-0.0812	2.4427
42	H	0	H	-0.5634	4.0699	2.6987
43	C	0	C.2	-2.0789	3.2007	-0.4324
44	C	0	C.2	0.0909	4.3207	-0.7017
45	H	0	H	0.7026	2.0528	4.122
46	C	0	C.2	0.7357	-1.2744	2.5374
47	C	0	C.2	2.8478	-0.0203	2.5609
48	C	0	C.2	-2.5586	3.9138	-1.5305
49	C	0	C.3	-2.9388	2.2018	0.2899
50	C	0	C.2	-0.4285	5.0123	-1.7956
51	C	0	C.3	1.5157	4.5096	-0.2616
52	C	0	C.2	1.4567	-2.4457	2.7688
53	C	0	C.3	-0.7578	-1.3091	2.3717
54	C	0	C.2	3.5275	-1.2154	2.7897
55	C	0	C.3	3.5908	1.2764	2.411
56	C	0	C.2	-1.7411	4.8123	-2.2048
57	H	0	H	-3.5787	3.7556	-1.8579
58	H	0	H	-3.9454	2.1926	-0.125
59	H	0	H	-2.52	1.1965	0.2034
60	H	0	H	-3.0055	2.4285	1.356
61	H	0	H	0.2078	5.7069	-2.3297
62	H	0	H	2.0229	5.2207	-0.912
63	H	0	H	1.5691	4.884	0.763
64	H	0	H	2.0676	3.5678	-0.2879
65	C	0	C.2	2.8385	-2.4168	2.894
66	H	0	H	0.9239	-3.3851	2.8441
67	H	0	H	-1.2419	-0.4867	2.9
68	H	0	H	-1.0336	-1.2186	1.3176
69	H	0	H	-1.1596	-2.2502	2.7447
70	H	0	H	4.6064	-1.1977	2.8789

71	H	0	H	4.6535	1.1245	2.5939
72	H	0	H	3.4759	1.6678	1.3969
73	H	0	H	3.2283	2.0346	3.1071
74	H	0	H	-2.128	5.3569	-3.057
75	H	0	H	3.3827	-3.3359	3.0691

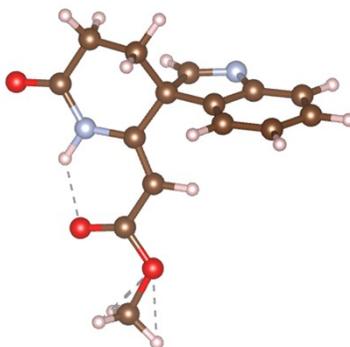


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8	C	0	C.2	2.7077	0.0929	0.2377
9	C	0	C.2	3.0338	0.5153	-1.0531
10	C	0	C.2	3.6375	0.0381	1.278
11	C	0	C.2	4.3576	0.8767	-1.2984
12	C	0	C.2	4.9517	0.4031	0.9891
13	C	0	C.2	5.3084	0.8185	-0.2875
14	H	0	H	4.6373	1.2151	-2.2881
15	H	0	H	5.6933	0.3711	1.7776
16	H	0	H	6.3311	1.1077	-0.4939

17	C	0	C.2	-1.9611	0.5981	1.4014
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19	C	0	C.2	-2.8328	0.9859	0.382
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28	C	0	C.1	3.333	5.2204	-0.0177
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35	H	0	H	6.1115	6.9709	-2.2639
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44	H	0	H	-0.6224	7.2886	3.2615
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53	C	0	C.2	2.8447	10.0562	4.486
54	H	0	H	1.9481	8.1339	4.1544
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58	H	0	H	3.5901	9.672	5.1712
59	H	0	H	3.5607	12.0831	4.6498
60	C	0	C.3	3.2266	-0.3757	2.6632
61	H	0	H	4.0704	-0.3077	3.348
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64	C	0	C.3	1.9869	0.606	-2.1275
65	H	0	H	1.471	-0.3464	-2.2655
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68	C	0	C.3	-2.4814	0.7667	-1.0627
69	H	0	H	-3.2659	1.1553	-1.7101
70	H	0	H	-1.5439	1.2675	-1.3146
71	H	0	H	-2.3457	-0.294	-1.2849
72	C	0	C.3	-1.2317	0.428	3.8117
73	H	0	H	-1.6193	0.6547	4.8036
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3a

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5	O	0	O.3	2.6693	-2.519	-0.2931
6	C	0	C.3	3.2421	-3.8383	-0.3546
7	H	0	H	4.3094	-3.6841	-0.4842
8	H	0	H	3.0447	-4.3812	0.5689
9	H	0	H	2.8314	-4.3911	-1.1985
10	N	0	N.am	-1.4156	-1.6577	0.1779
11	C	0	C.2	-2.7627	-1.4564	0.3708
12	C	0	C.3	-3.2313	-0.0292	0.4685
13	O	0	O.2	-3.5166	-2.4131	0.4461
14	C	0	C.3	-2.1247	0.9378	0.8678
15	H	0	H	-3.6496	0.2371	-0.5065
16	H	0	H	-4.0558	-0.0042	1.1803
17	C	0	C.3	-0.8596	0.7368	0.0052
18	H	0	H	-1.8467	0.7809	1.9119
19	H	0	H	-2.4633	1.9686	0.7694
20	C	0	C.2	0.2172	1.7352	0.3542

21	C	0	C.2	-1.1041	1.1433	-1.4551
22	C	0	C.2	0.4271	2.5369	-0.7723
23	C	0	C.2	0.9233	1.9587	1.5196
24	N	0	N.2	-0.4	2.1333	-1.8576
25	H	0	H	-1.8114	0.6363	-2.1011
26	C	0	C.2	1.3438	3.5751	-0.7647
27	C	0	C.2	1.8531	3.0021	1.5384
28	H	0	H	0.7732	1.3398	2.3954
29	C	0	C.2	2.0598	3.7975	0.4119
30	H	0	H	1.4972	4.1881	-1.6433
31	H	0	H	2.4218	3.1942	2.4392
32	H	0	H	2.7862	4.5991	0.4512
33	H	0	H	1.624	-0.3015	-0.1889
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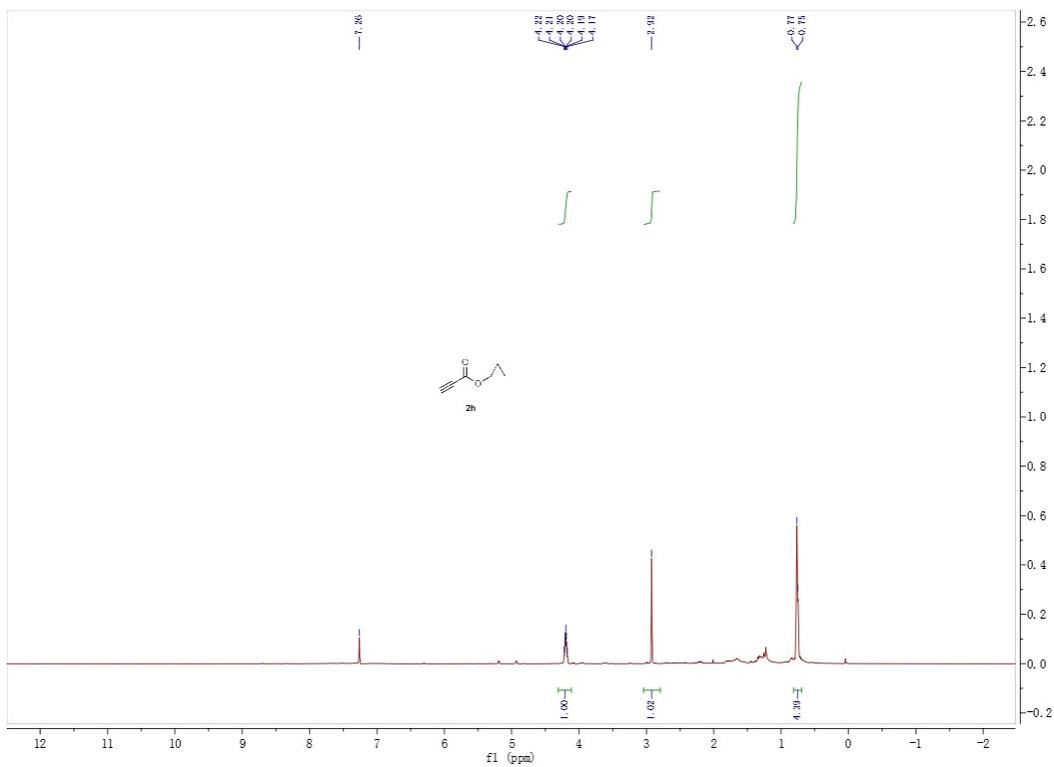
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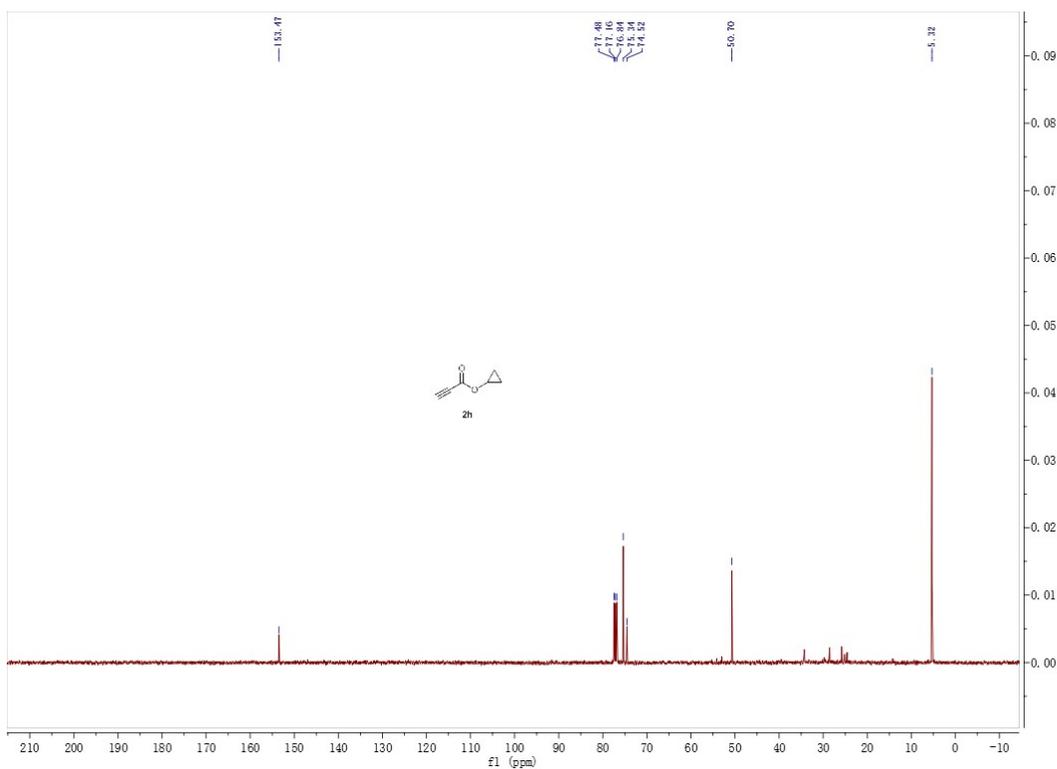
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3. NMR spectra

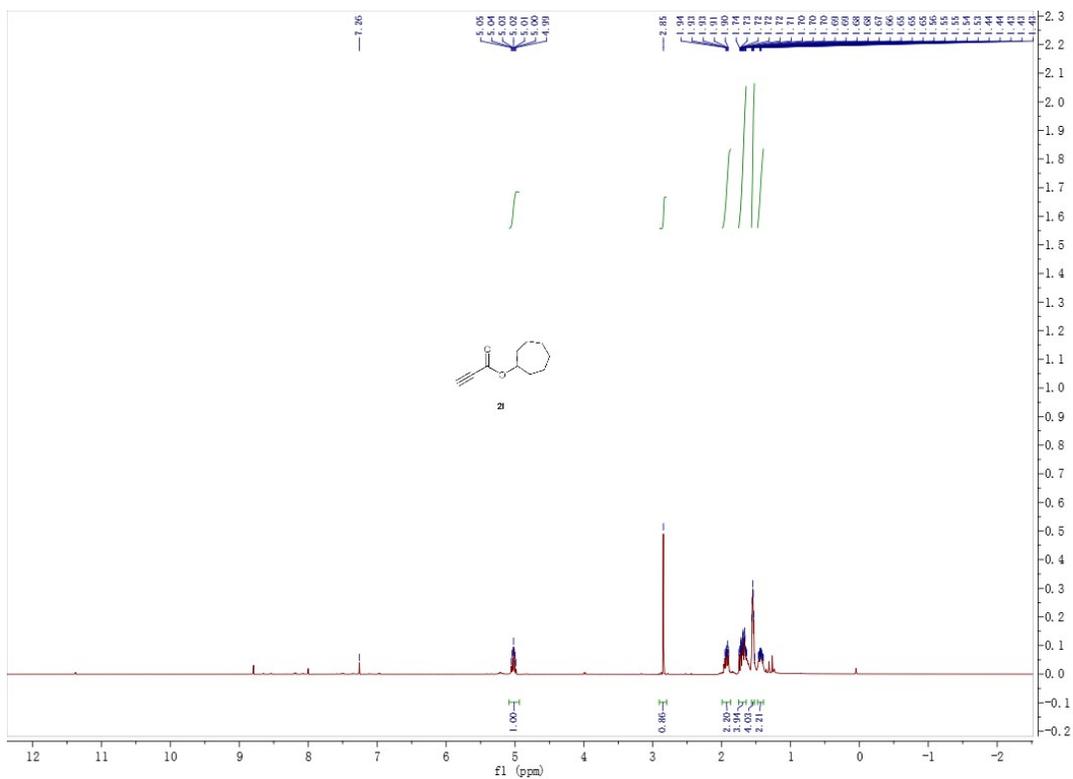
^1H NMR spectrum of compound **2h** (400 MHz, CDCl_3)



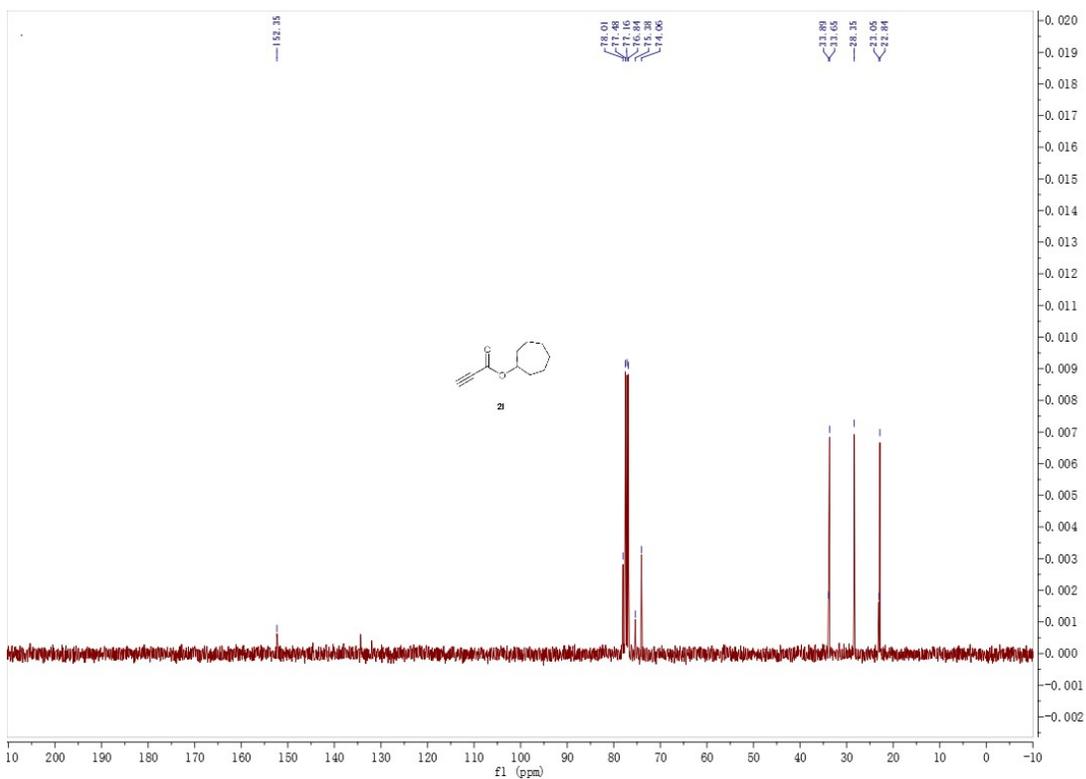
^{13}C NMR spectrum of compound **2h** (100 MHz, CDCl_3)



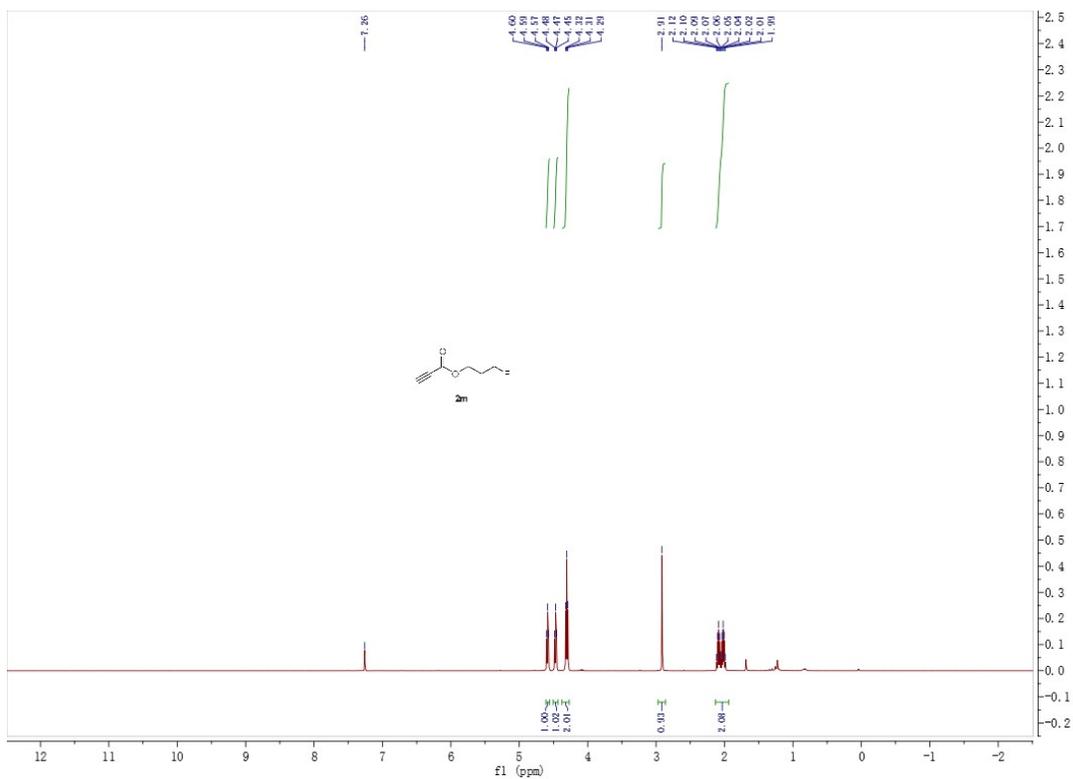
¹H NMR spectrum of compound 2I (400 MHz, CDCl₃)



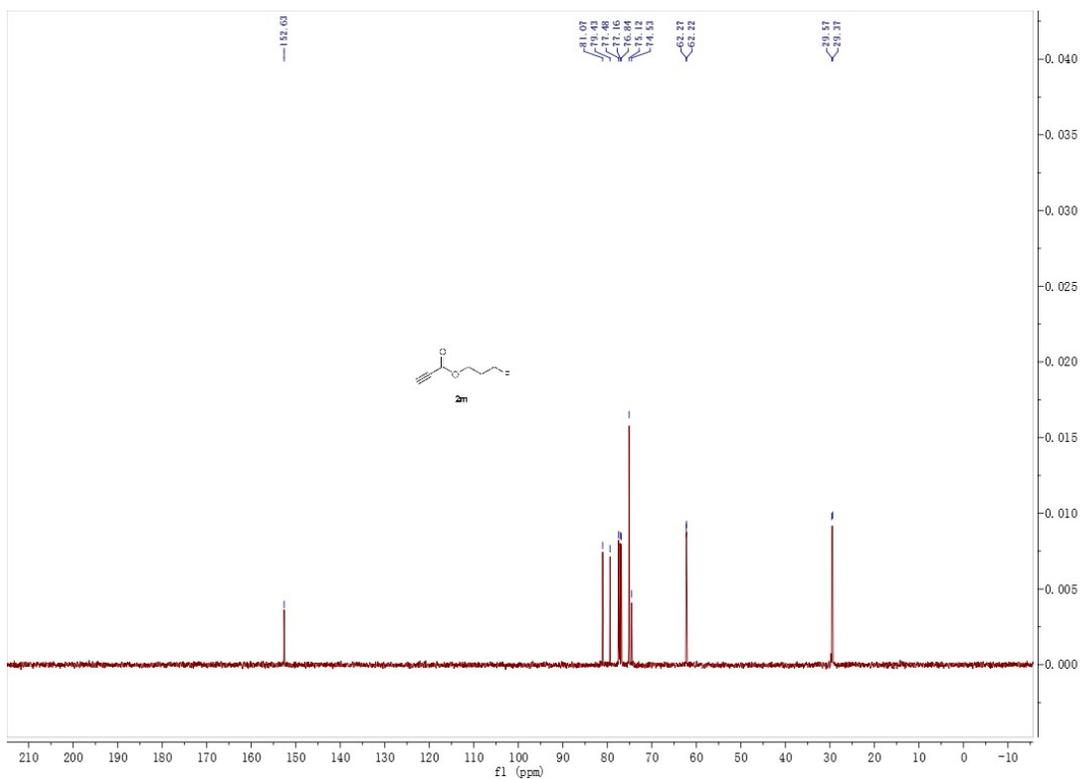
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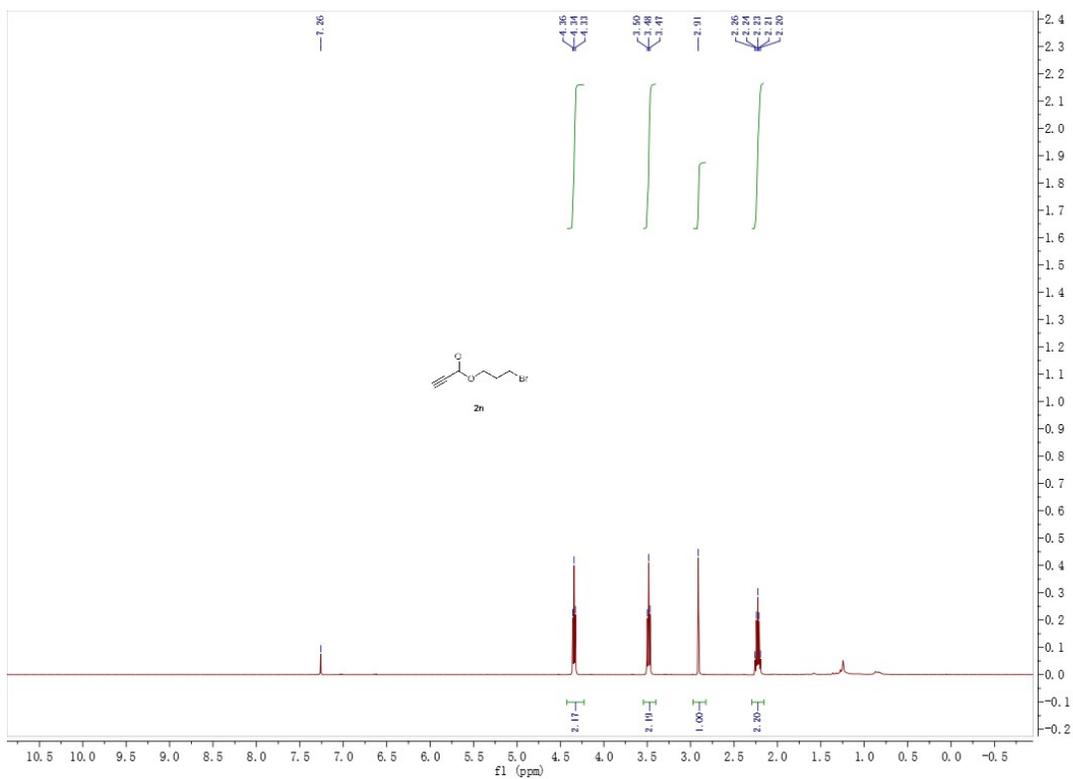
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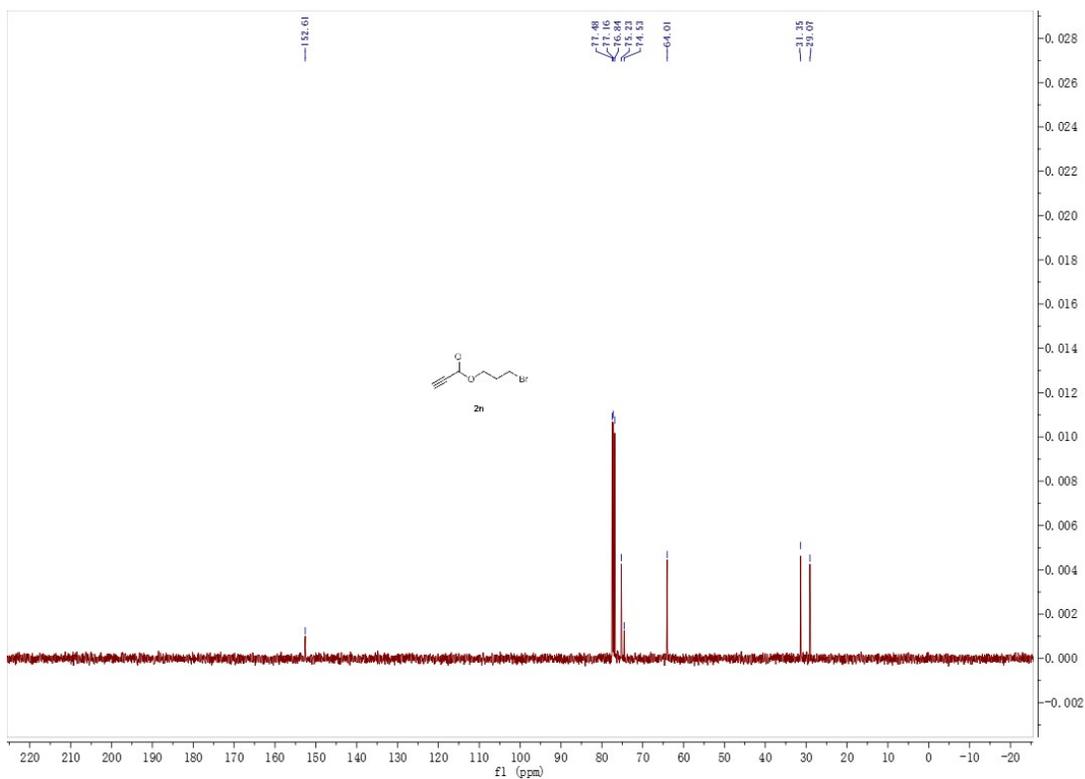
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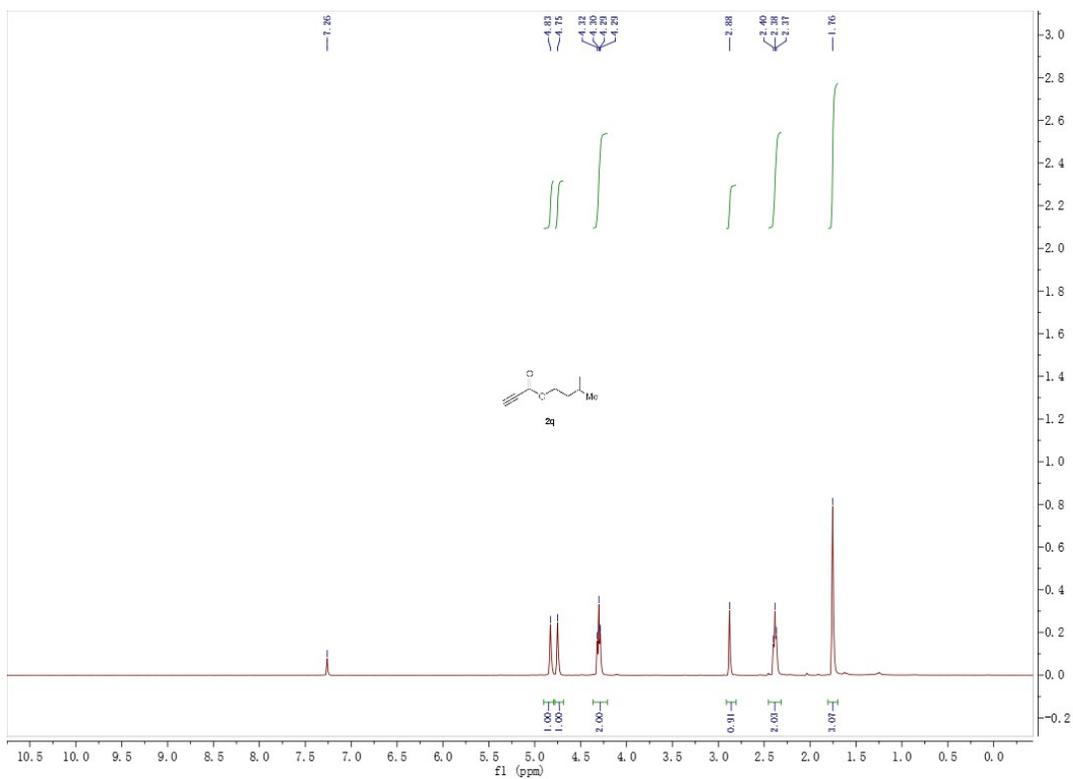
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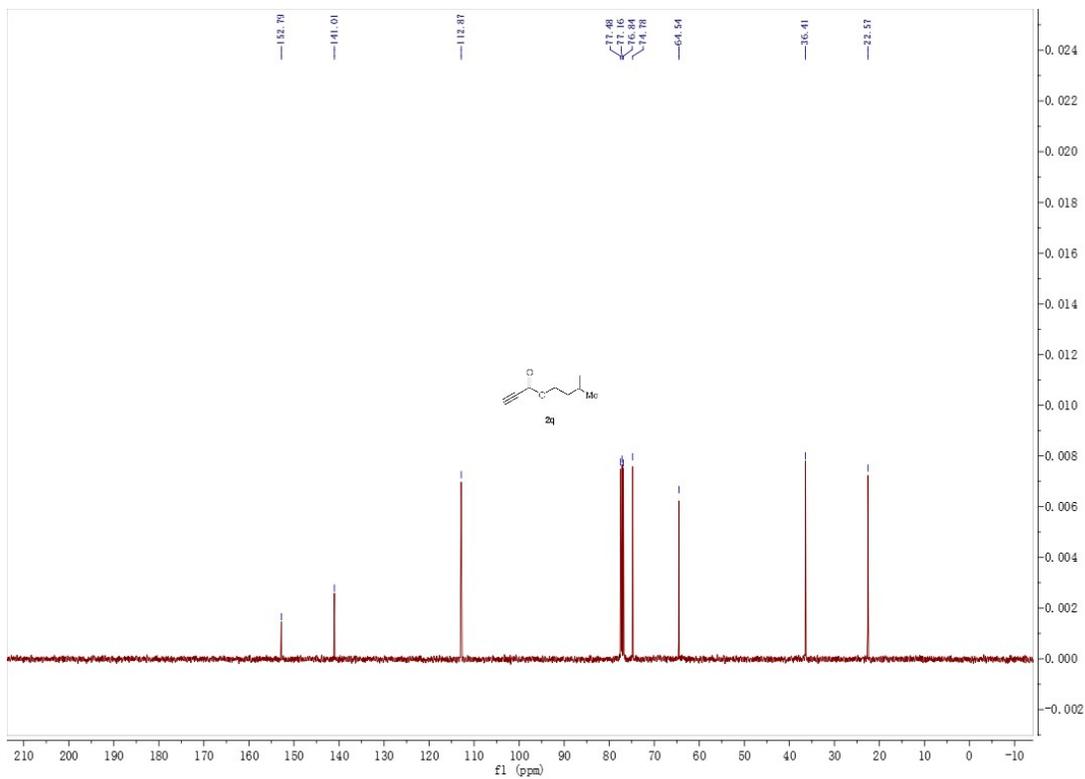
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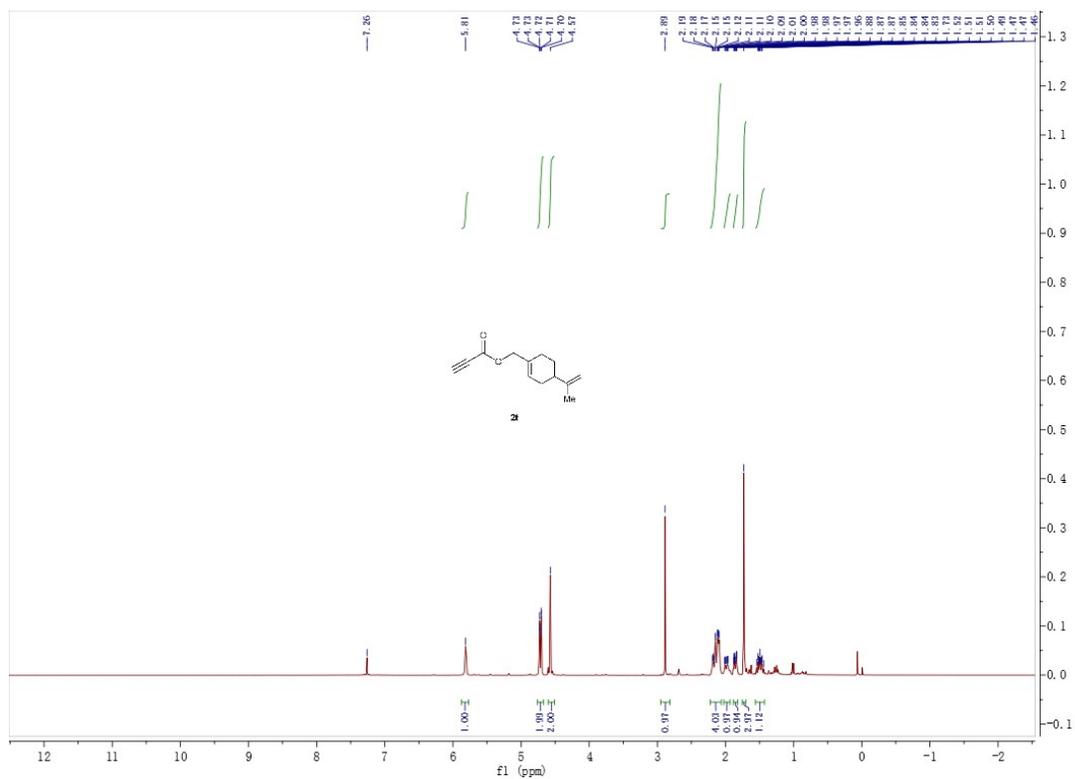
¹H NMR spectrum of compound 2q (400 MHz, CDCl₃)



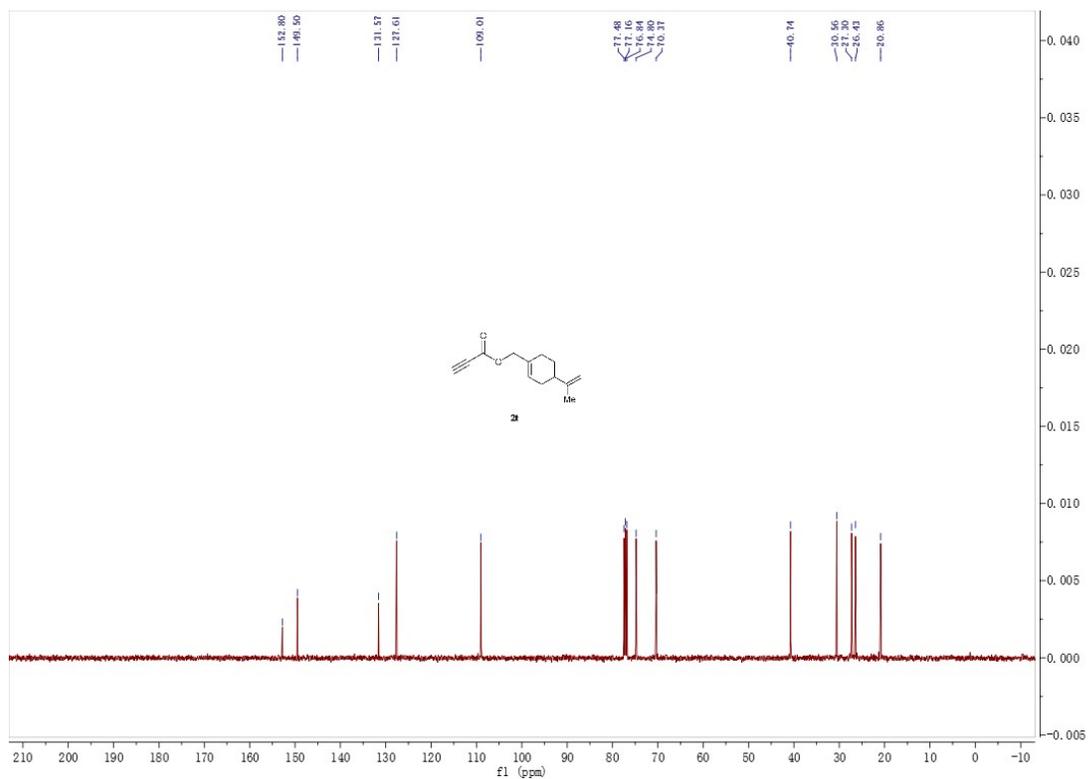
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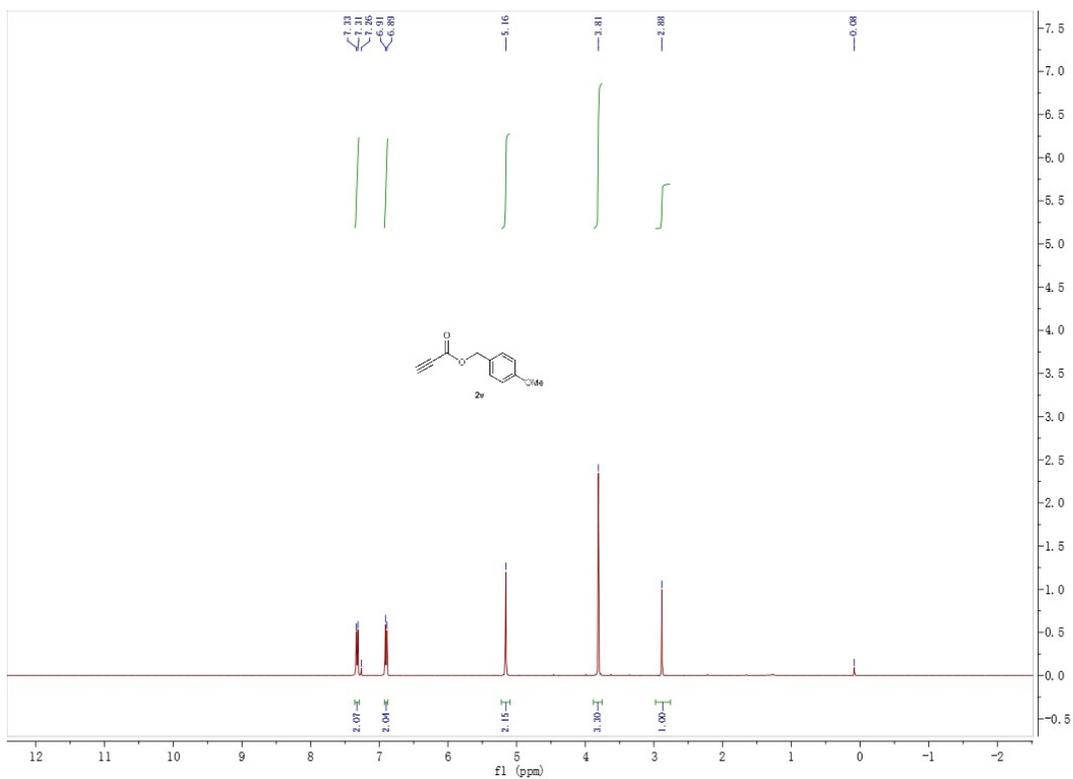
¹H NMR spectrum of compound **2t** (400 MHz, CDCl₃)



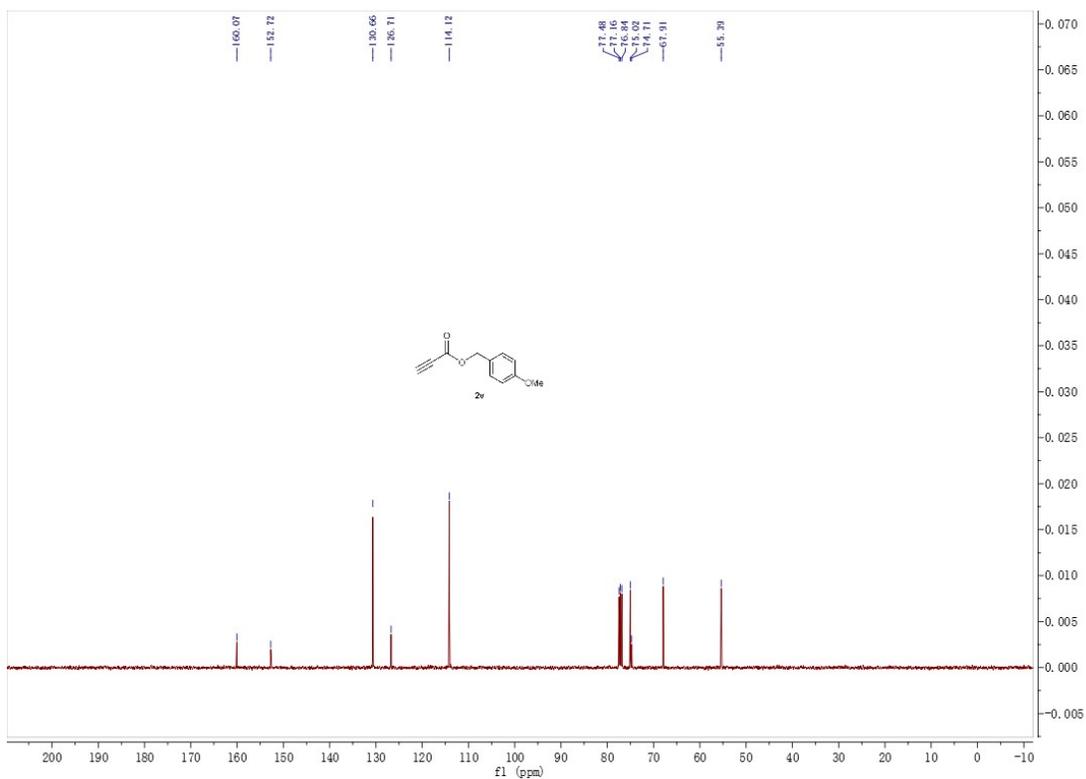
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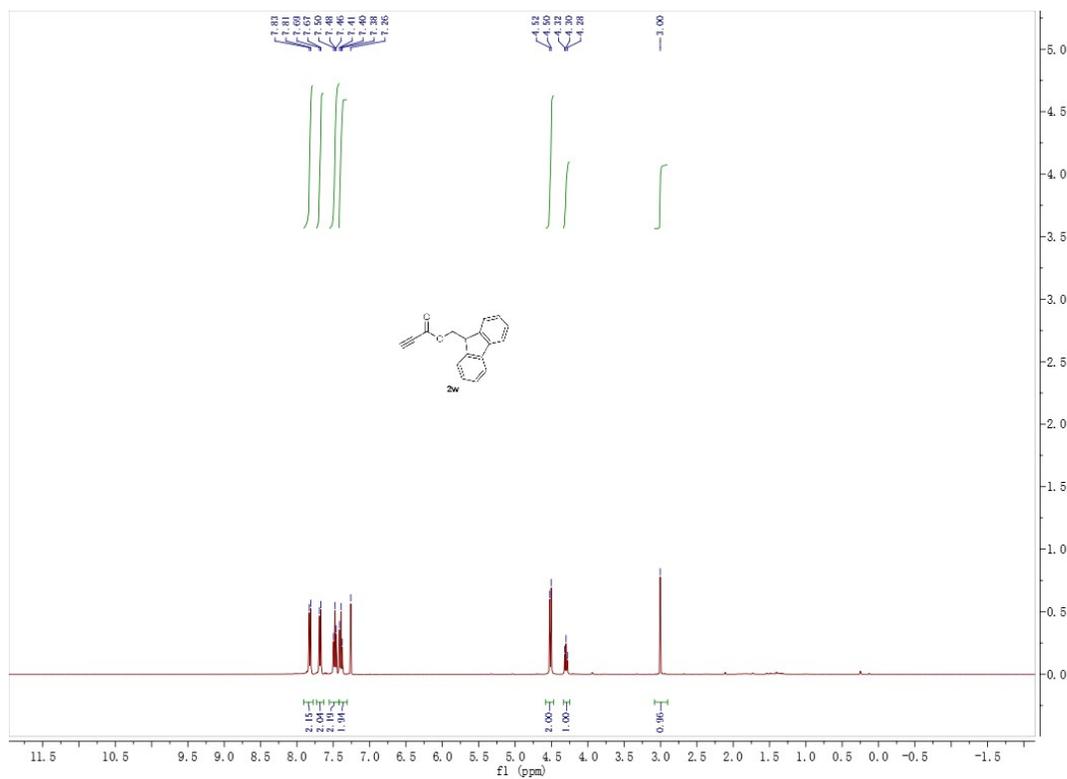
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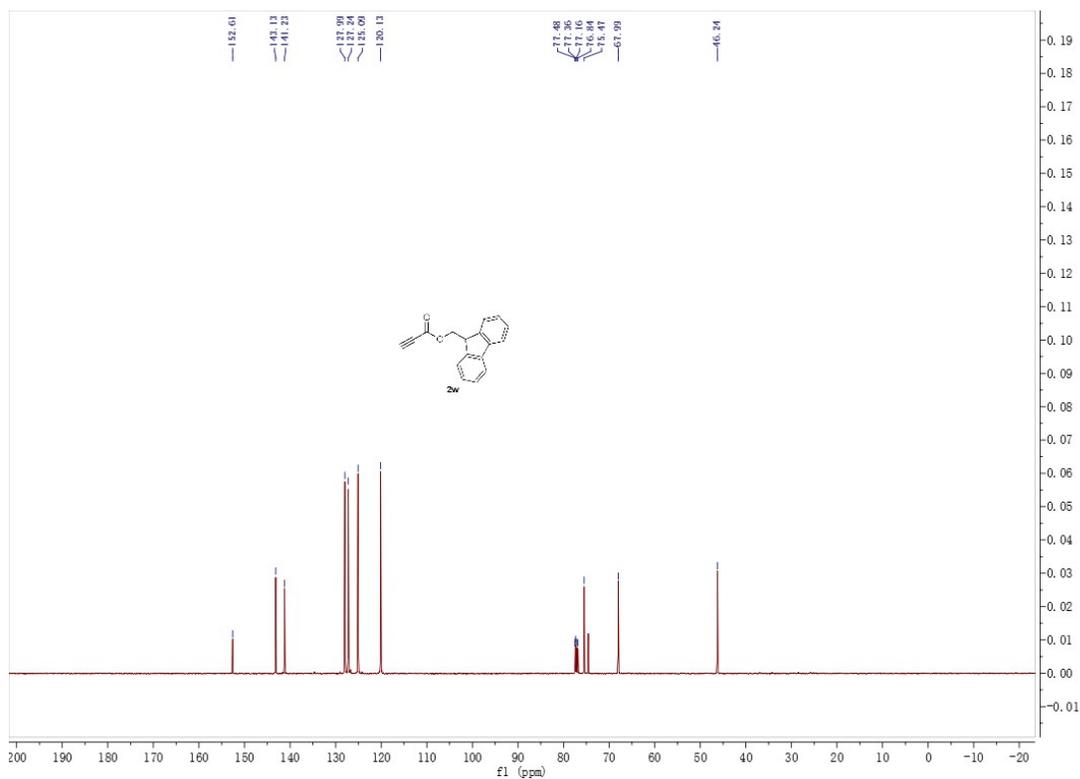
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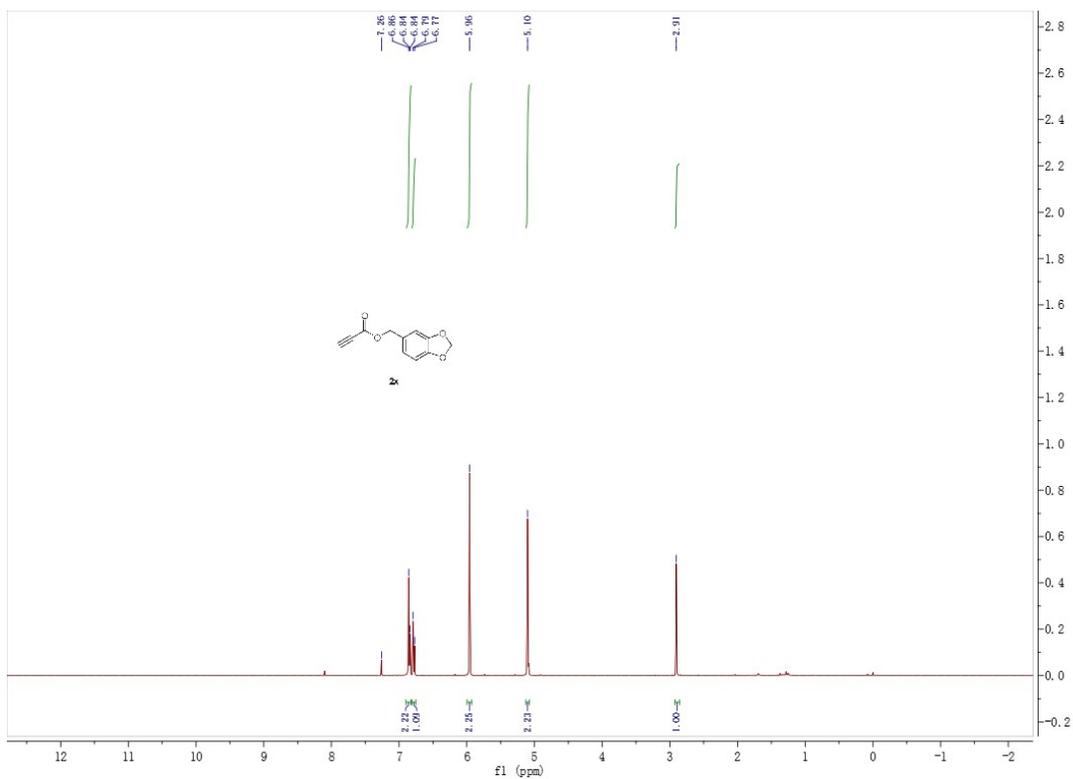
^1H NMR spectrum of compound **2w** (400 MHz, CDCl_3)



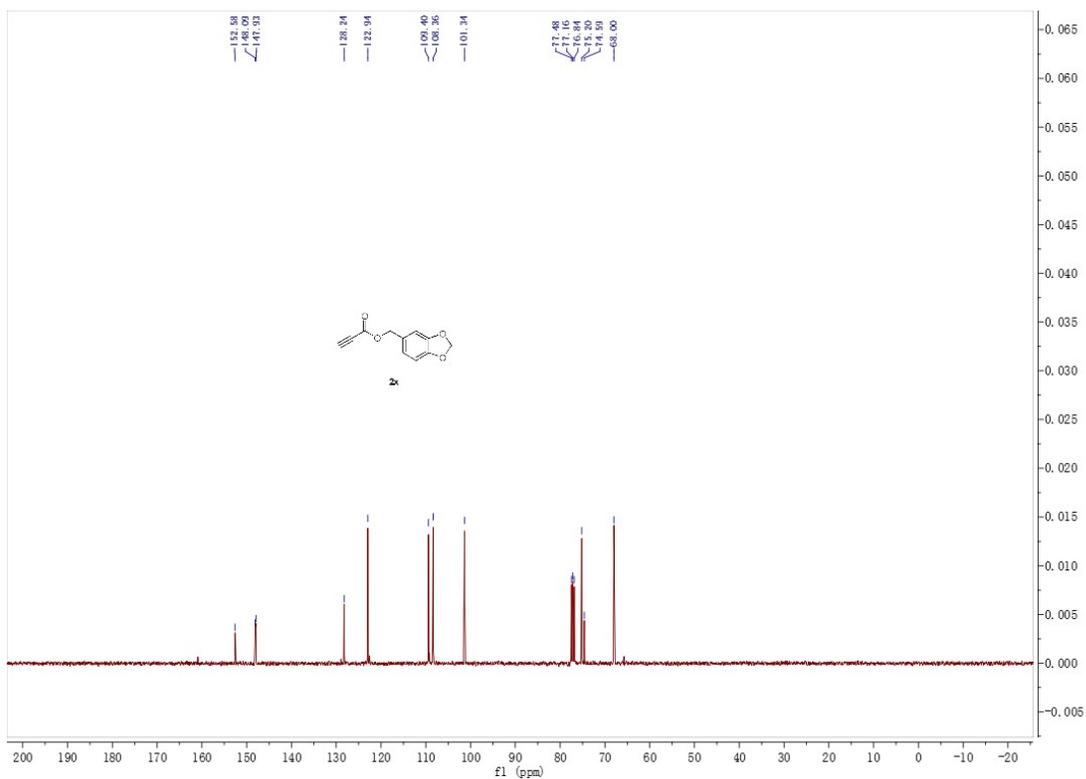
^{13}C NMR spectrum of compound **2w** (100 MHz, CDCl_3)



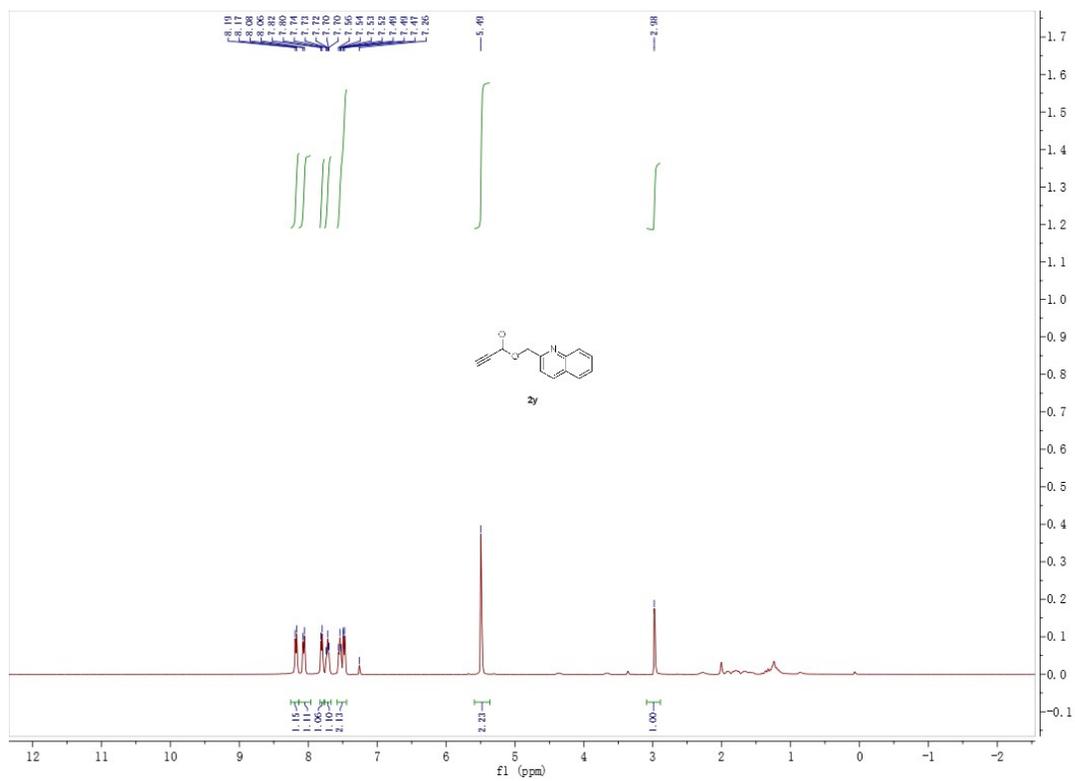
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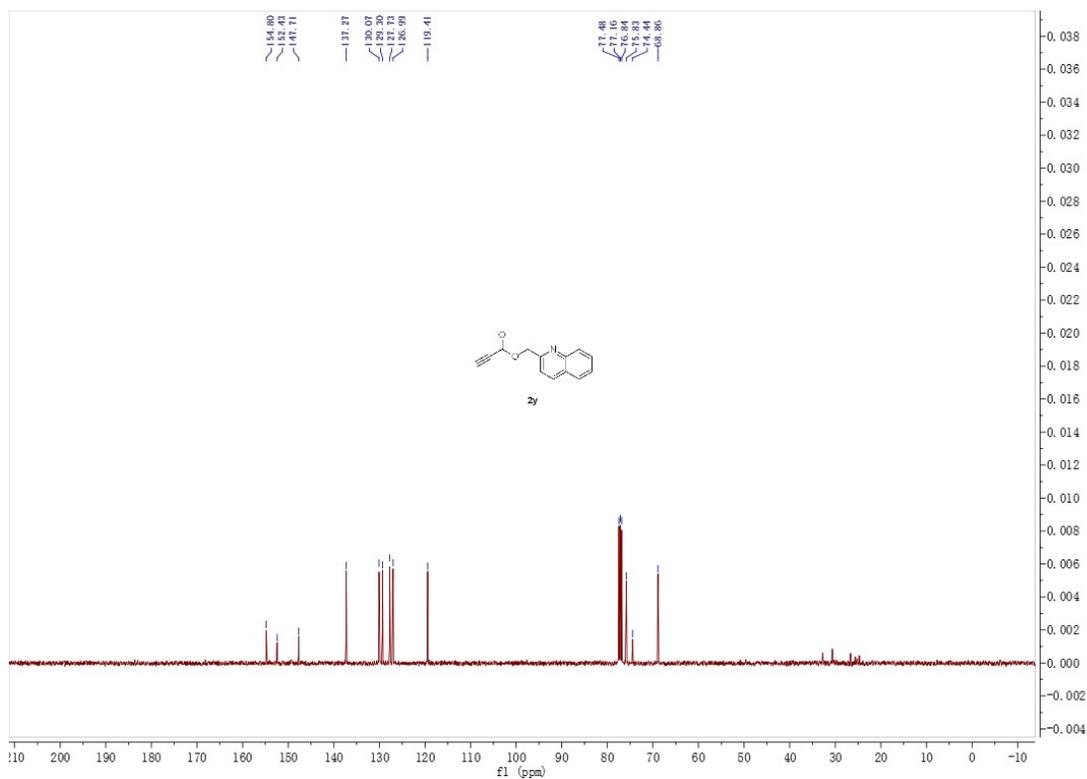
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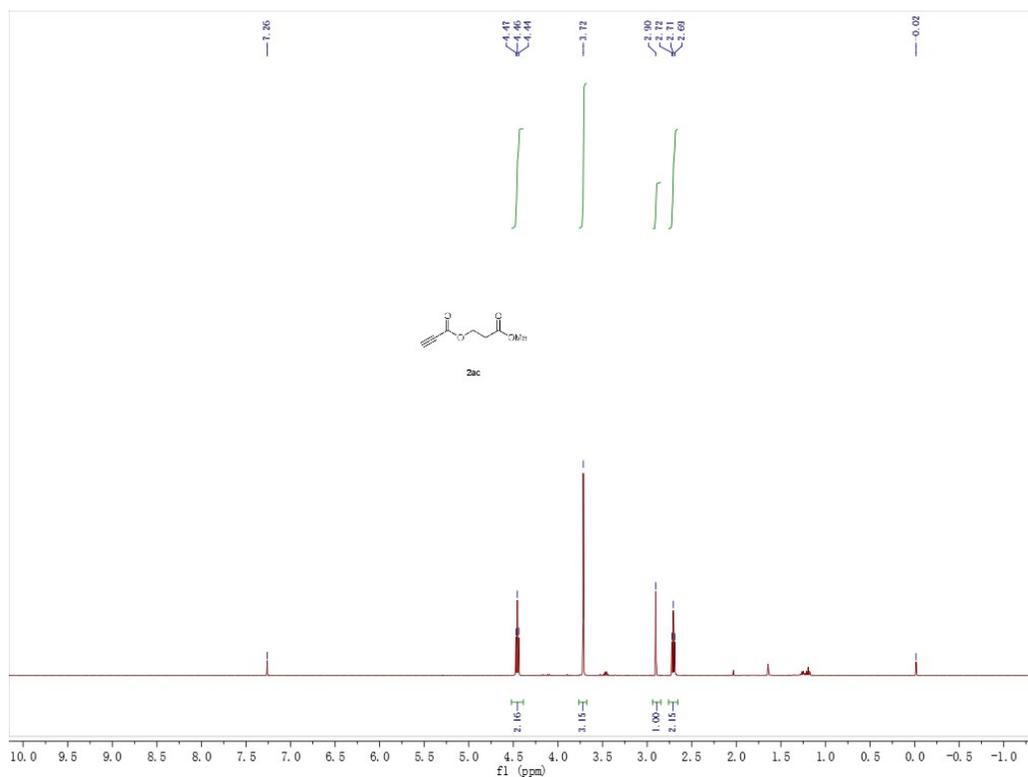
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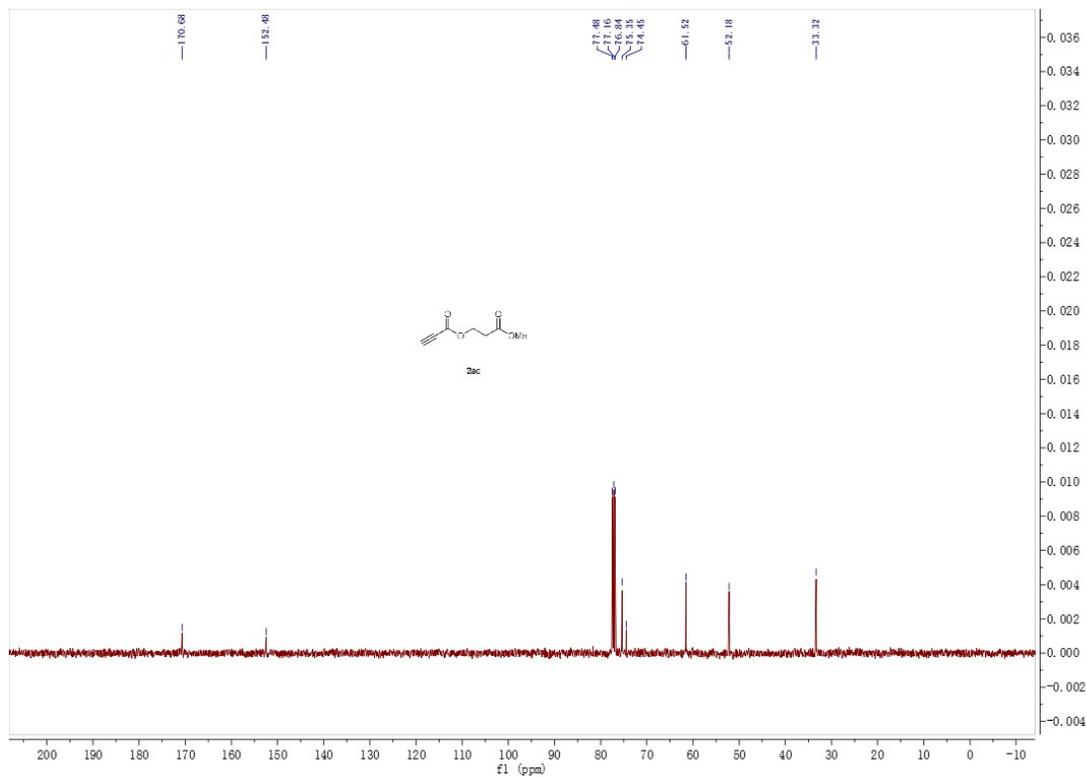
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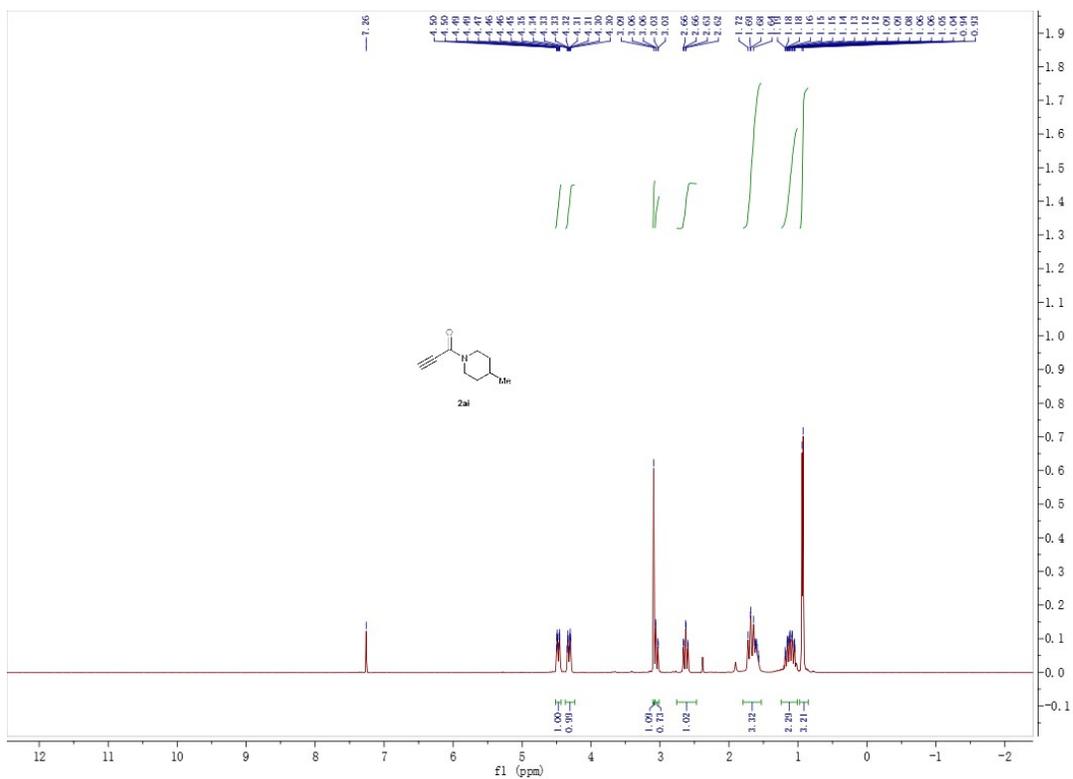
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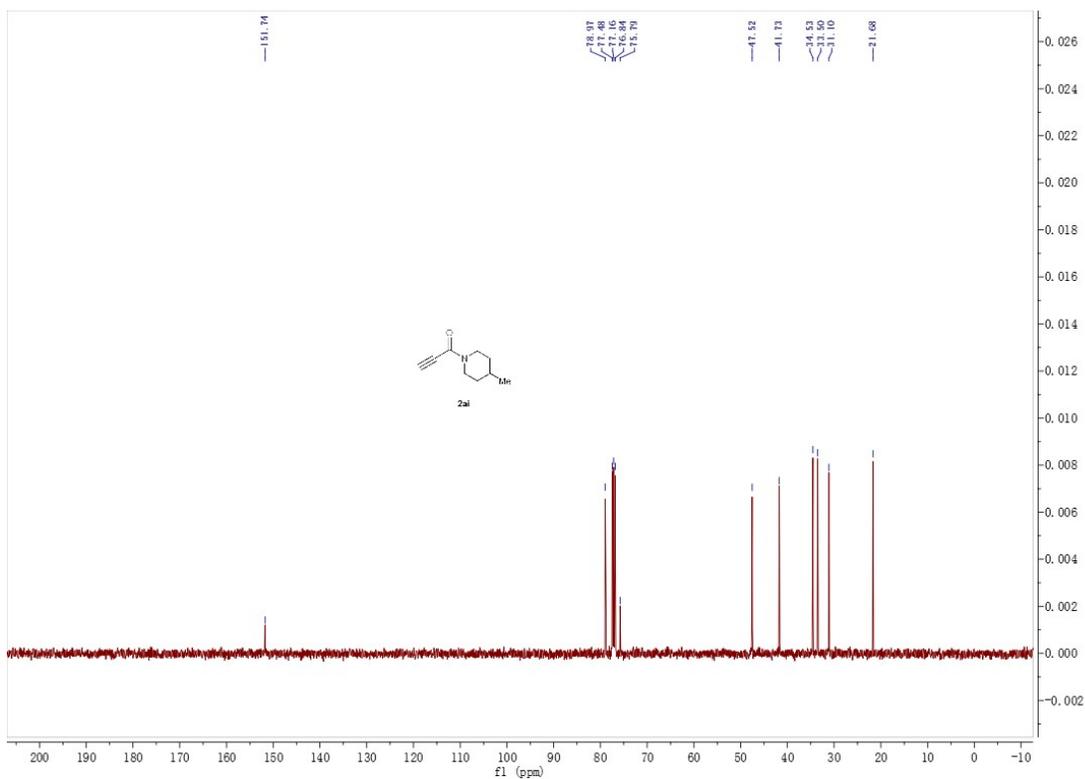
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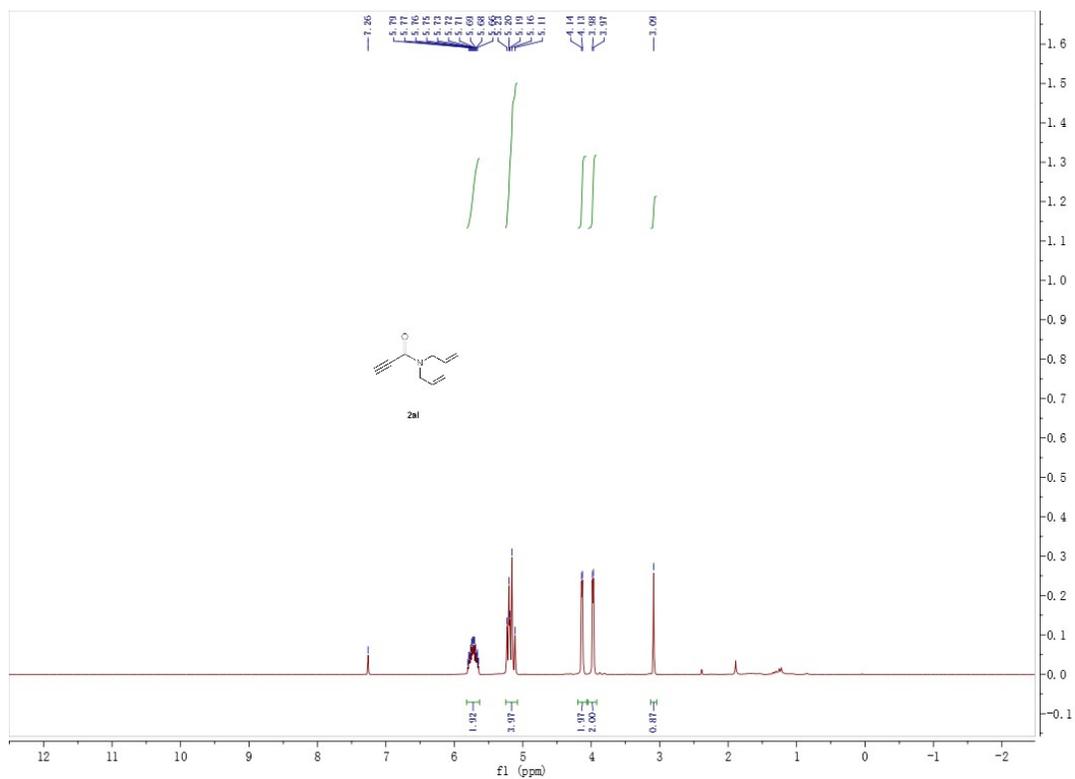
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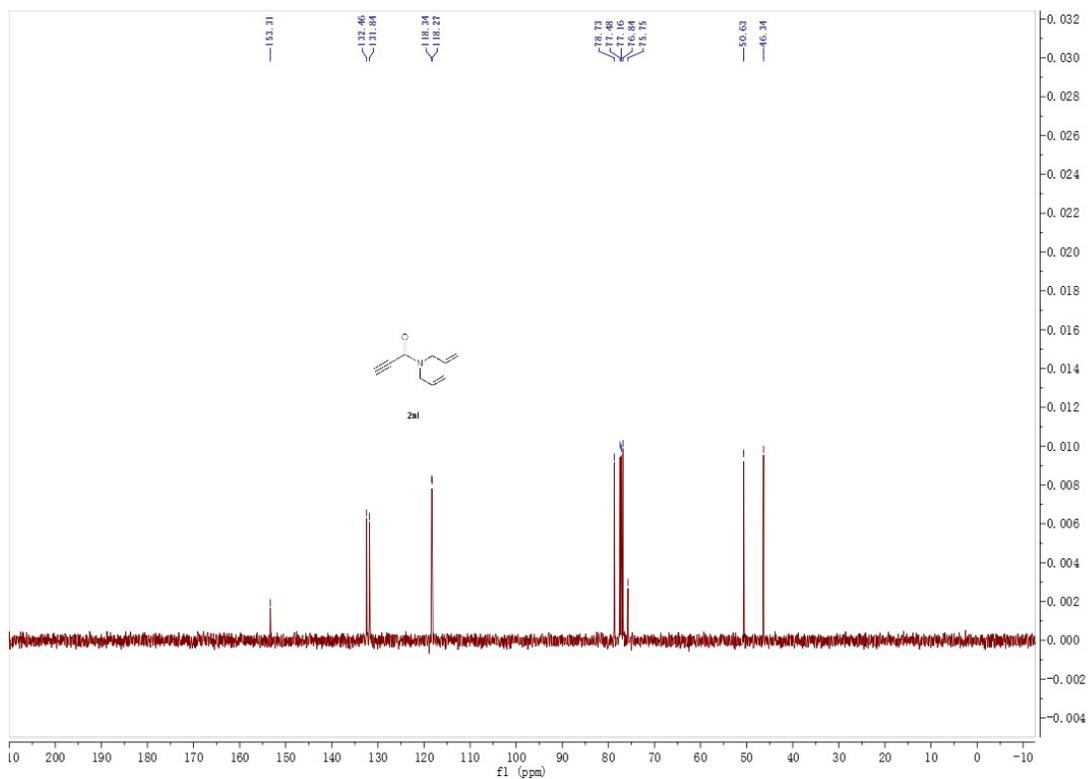
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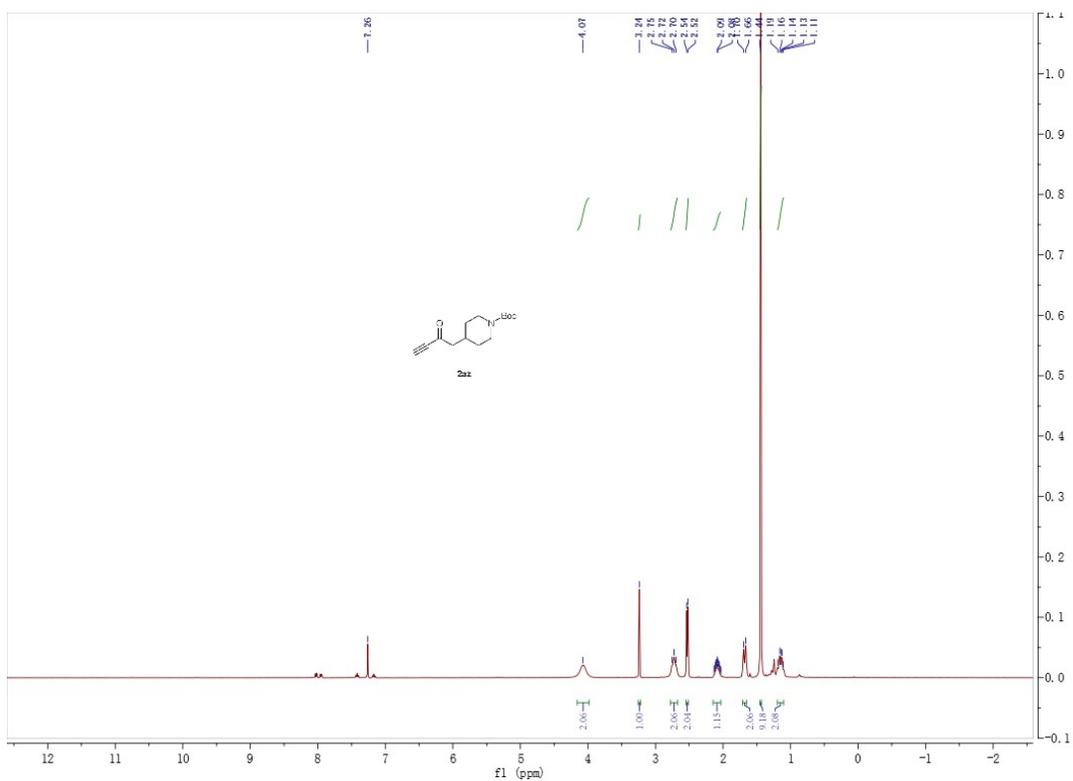
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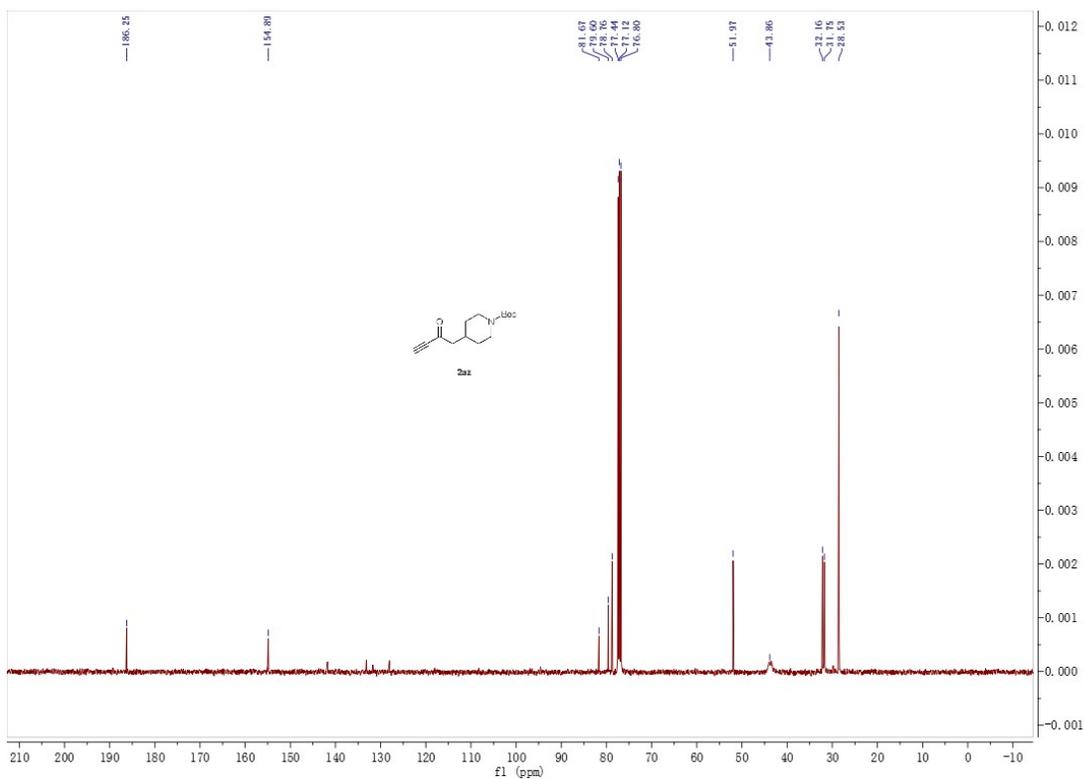
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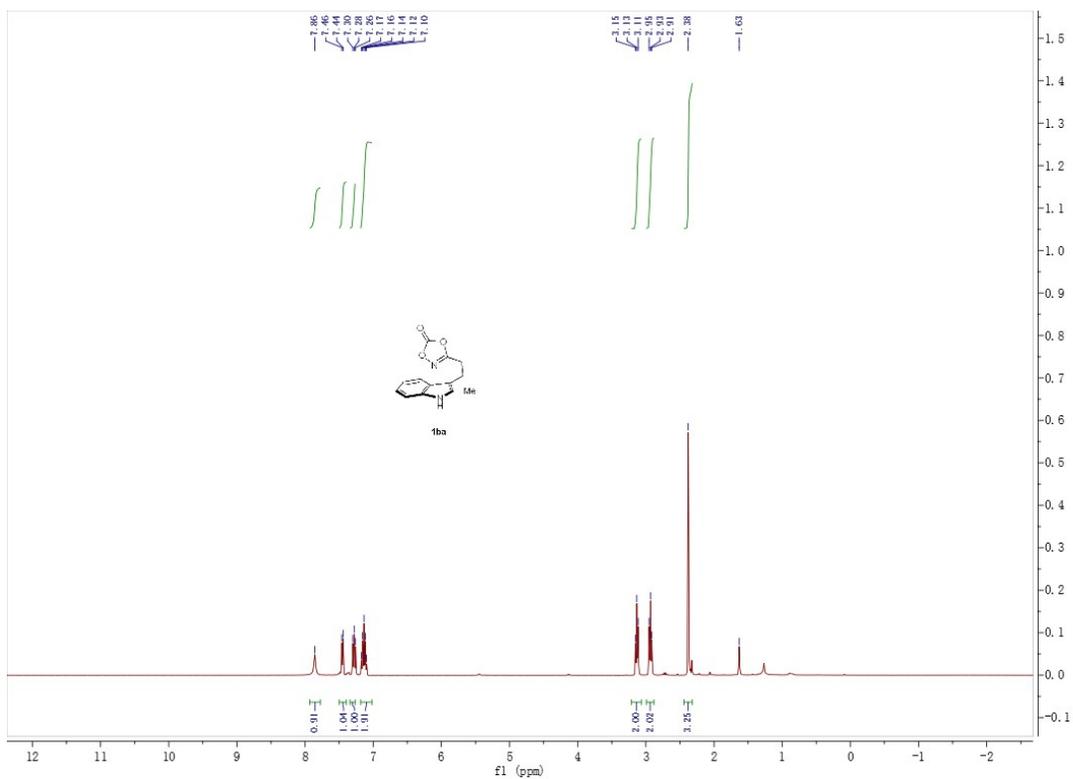
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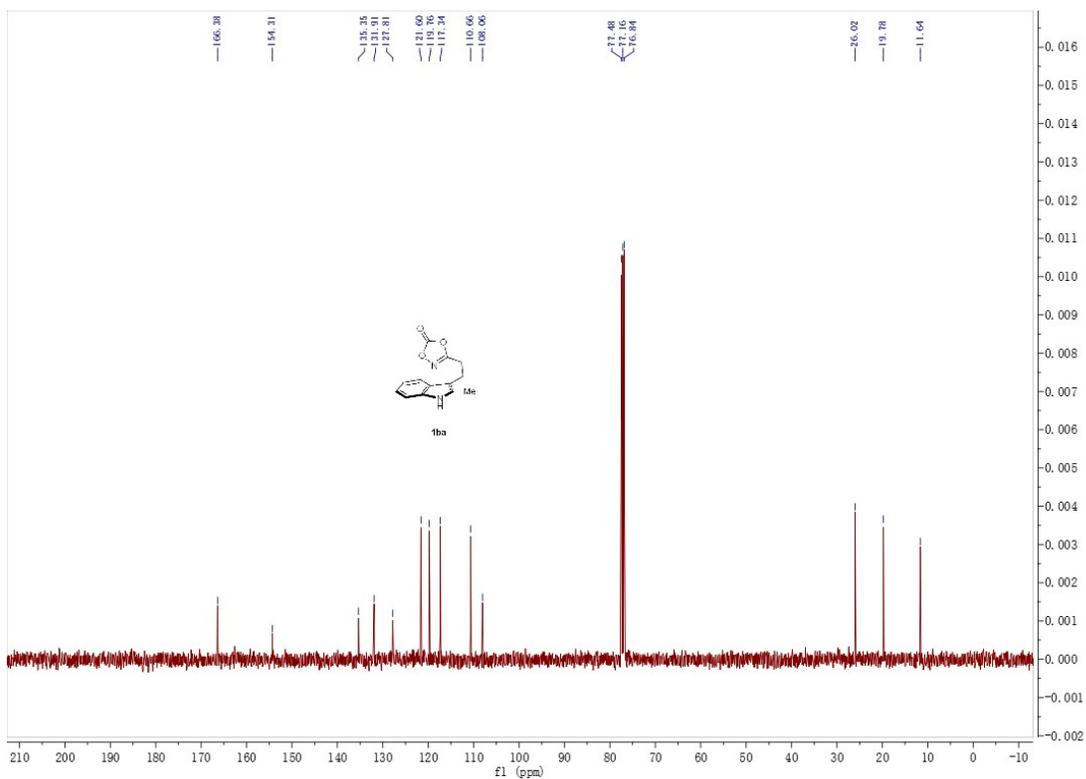
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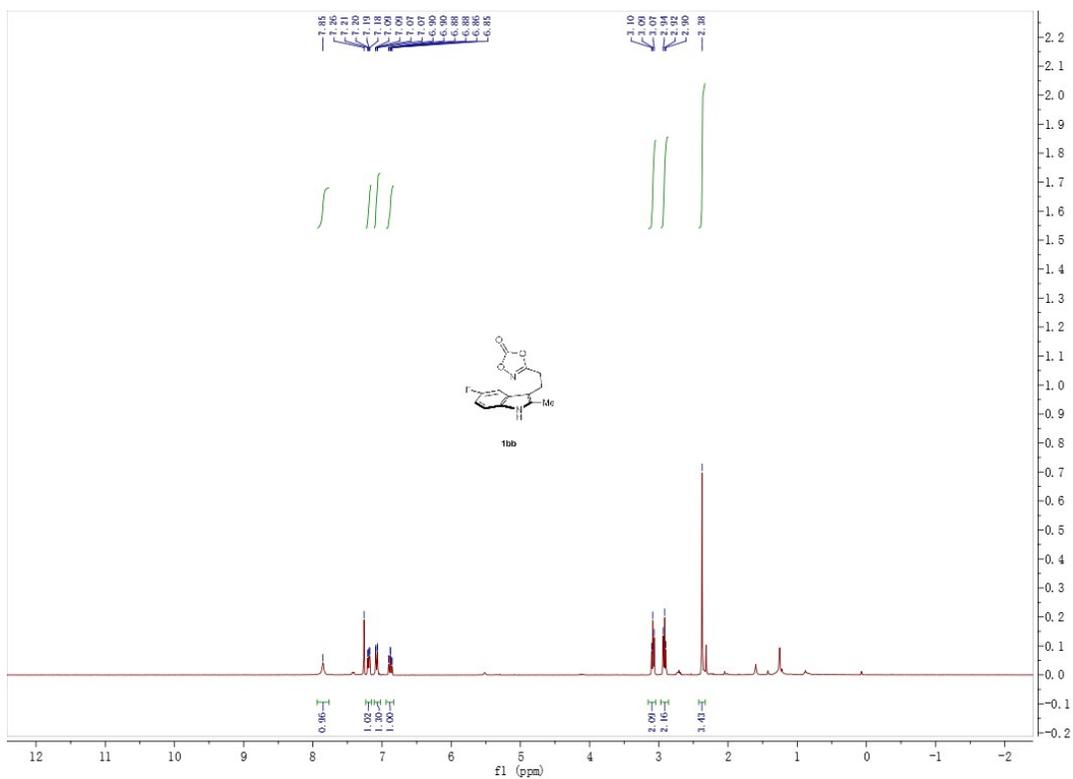
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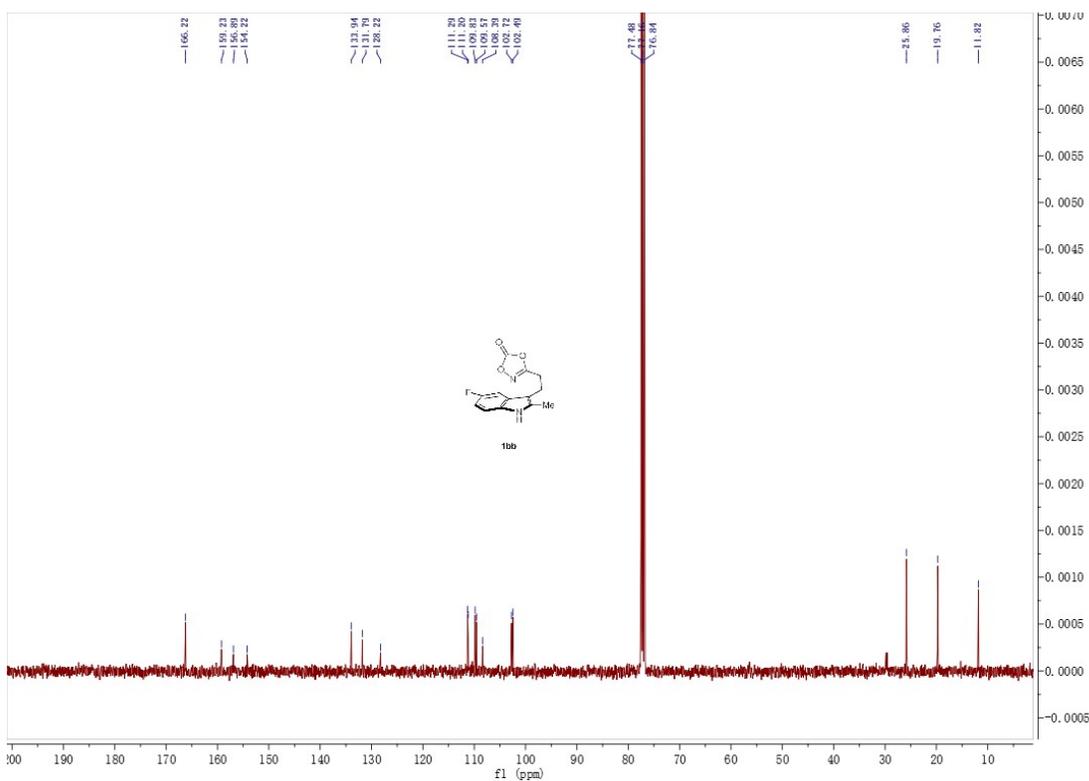
¹³C NMR spectrum of compound **1ba** (100 MHz, CDCl₃)



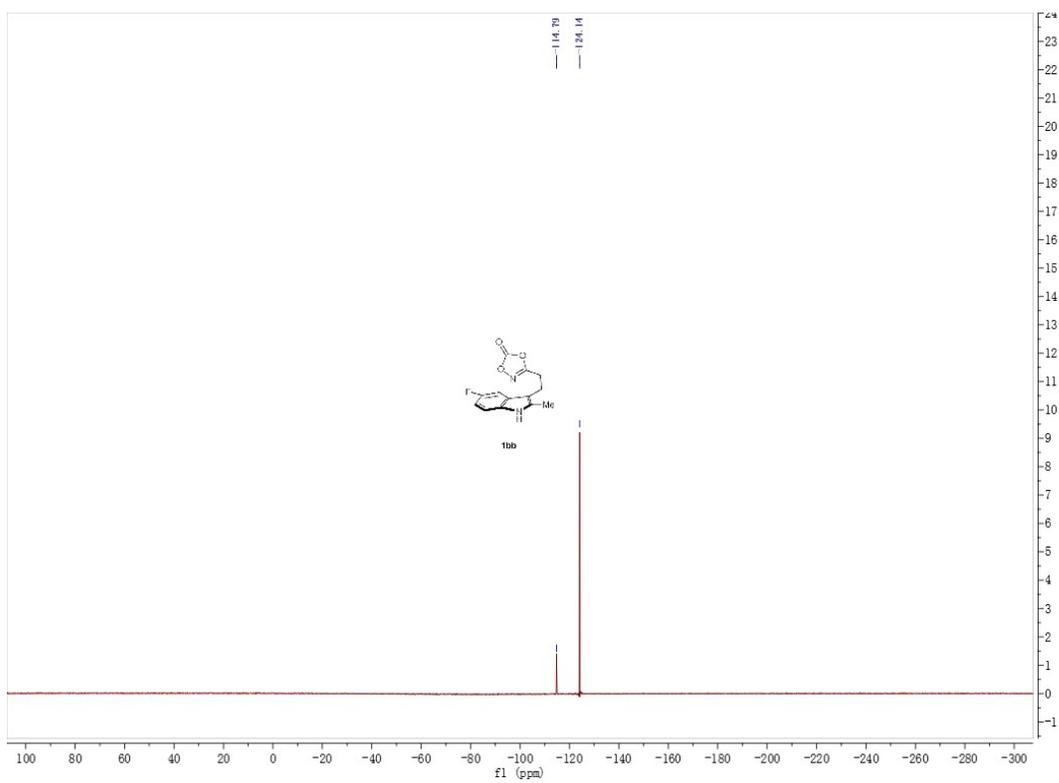
¹H NMR spectrum of compound **1bb** (400 MHz, CDCl₃)



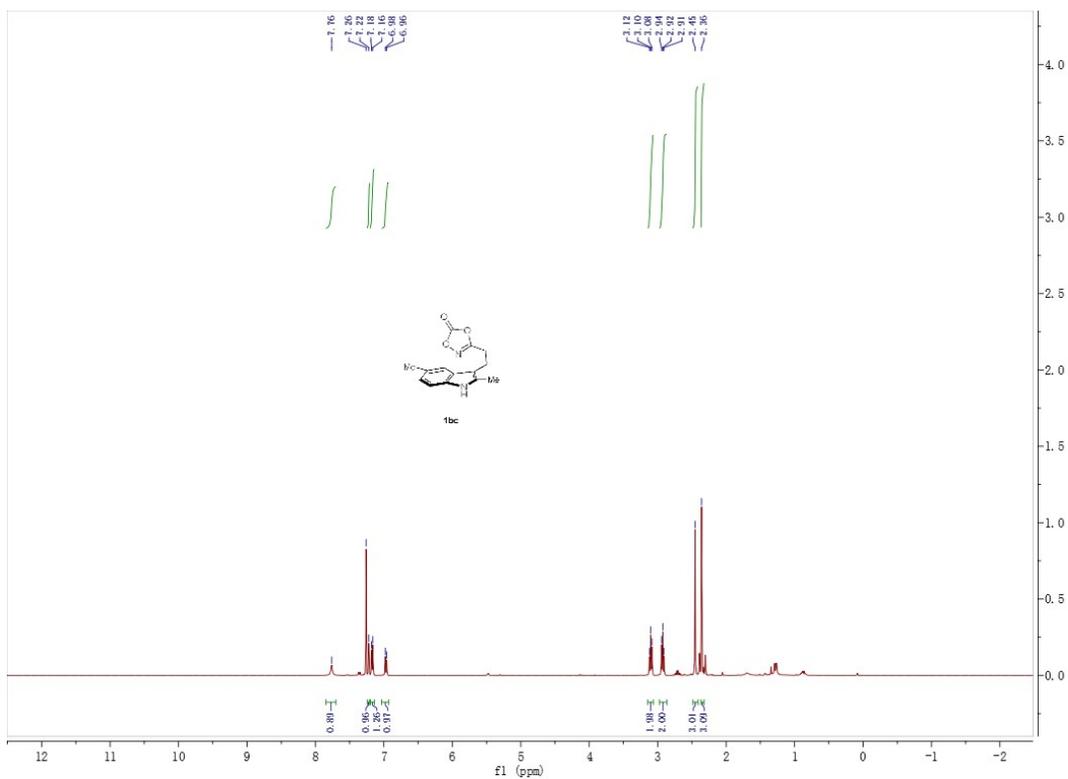
¹³C NMR spectrum of compound **1bb** (100 MHz, CDCl₃)



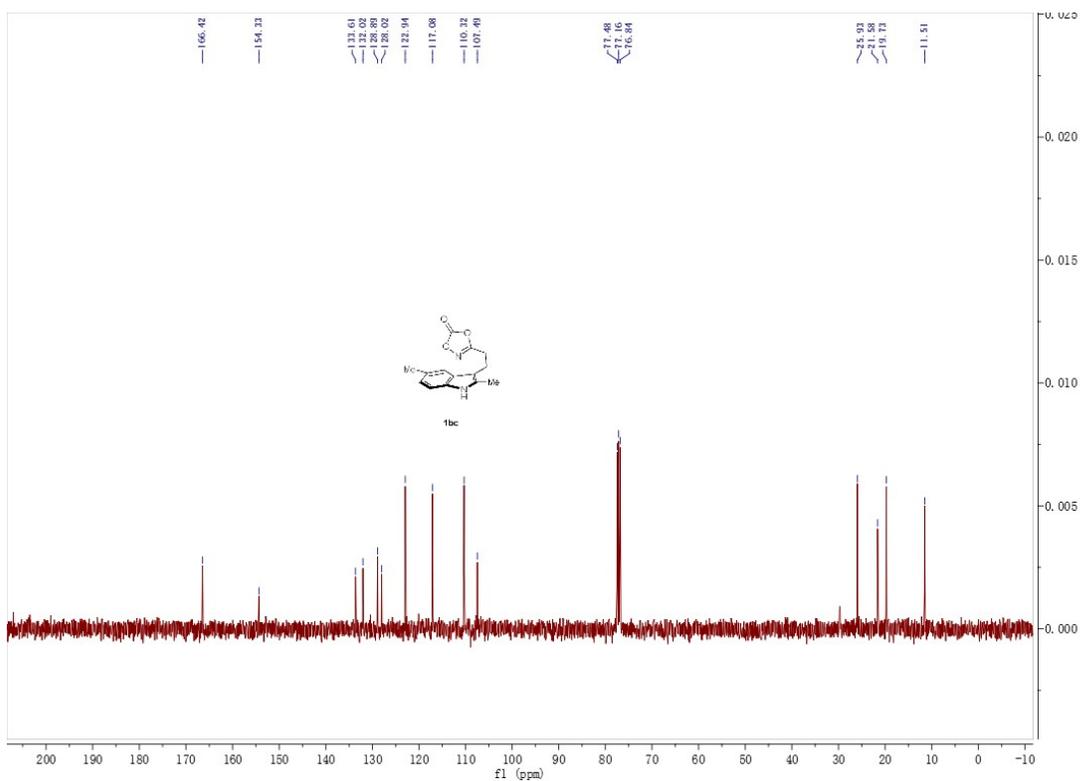
¹⁹F NMR spectrum of compound **1bb (376 MHz, CDCl₃)**



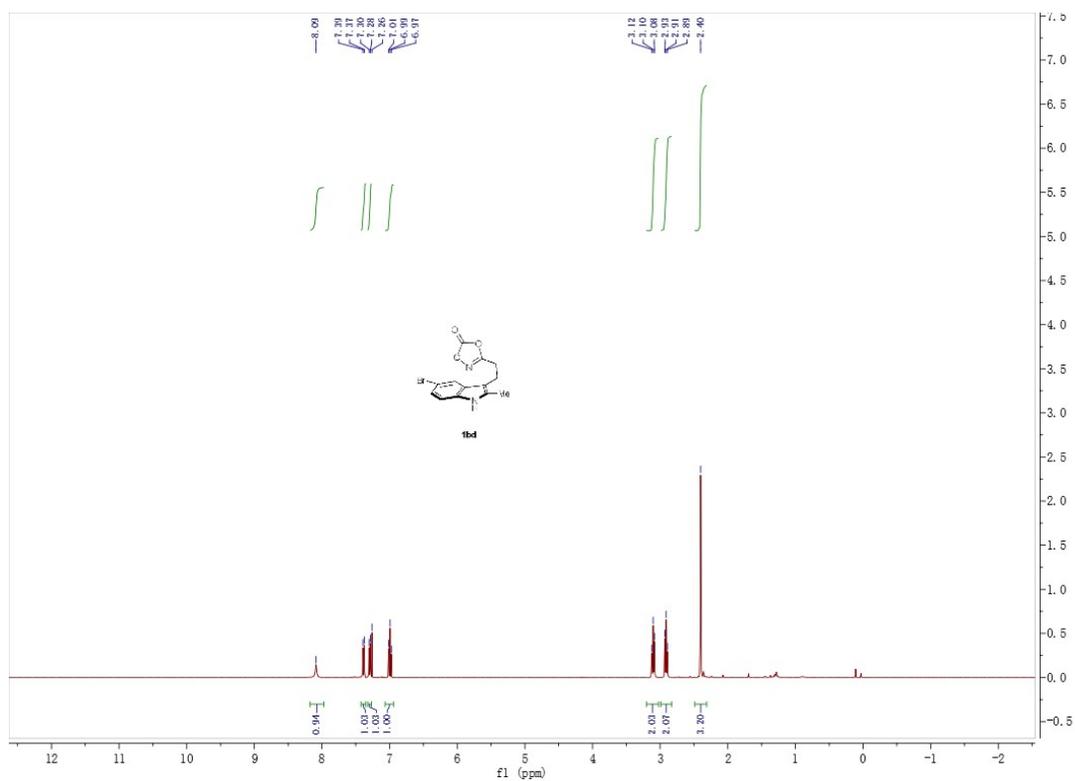
^1H NMR spectrum of compound **1bc** (400 MHz, CDCl_3)



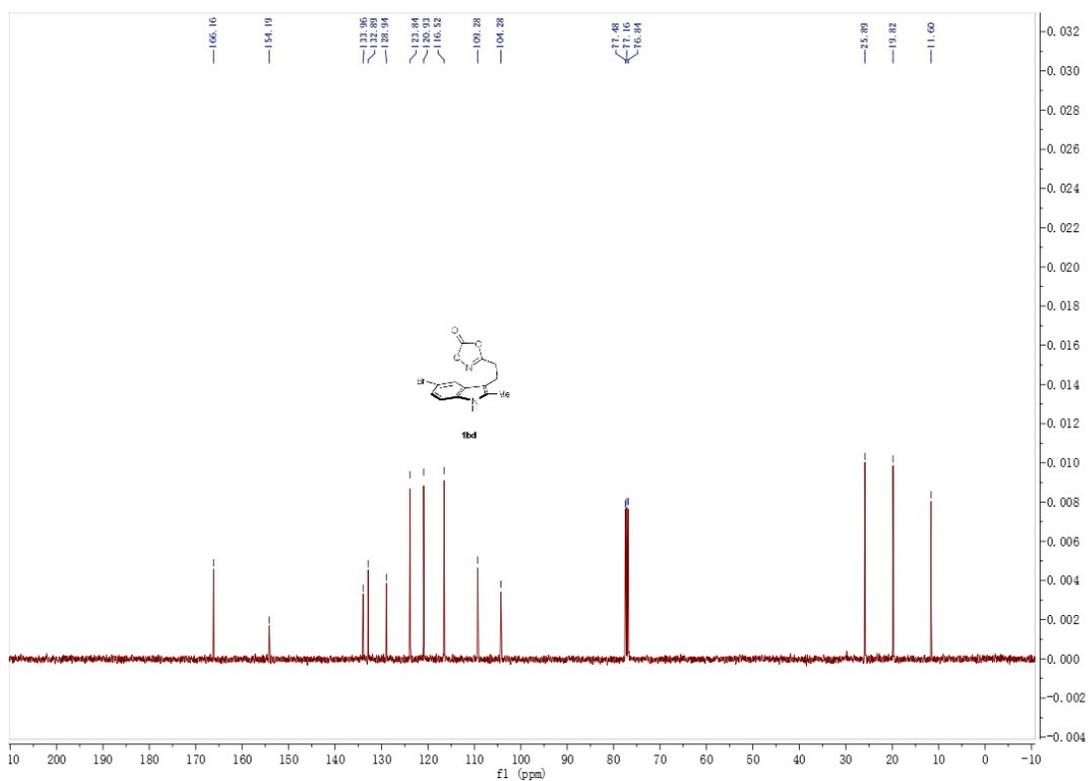
^{13}C NMR spectrum of compound **1bc** (100 MHz, CDCl_3)



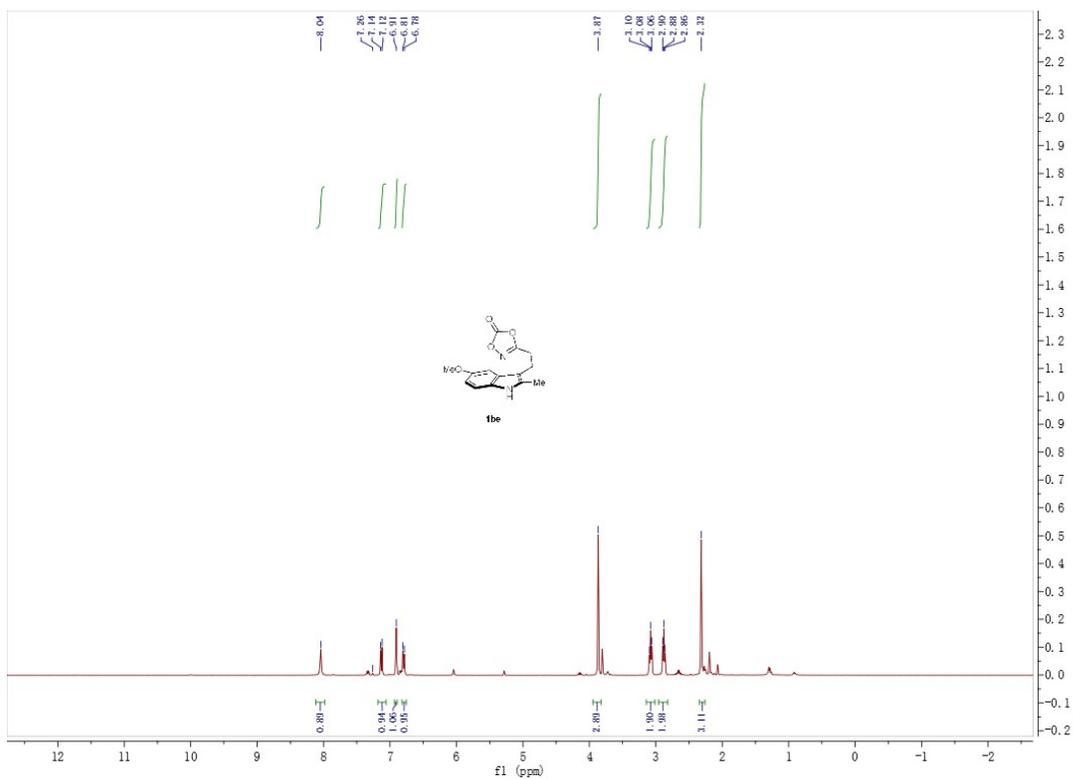
¹H NMR spectrum of compound **1bd** (400 MHz, CDCl₃)



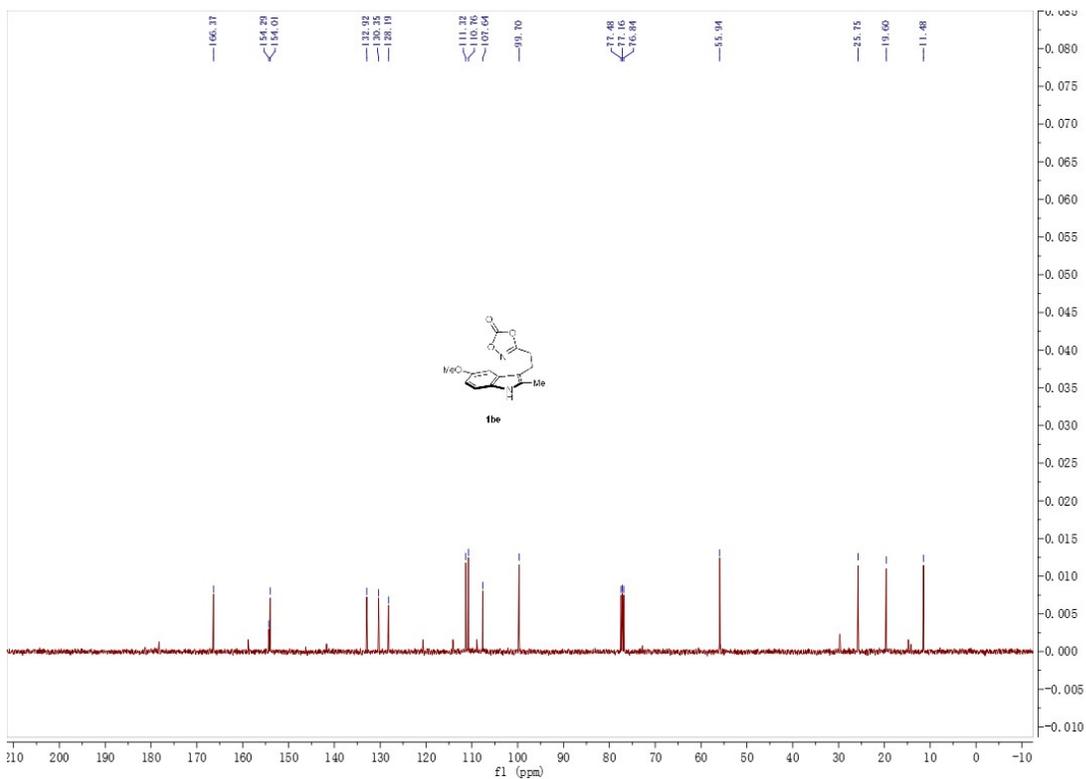
¹³C NMR spectrum of compound **1bd** (100 MHz, CDCl₃)



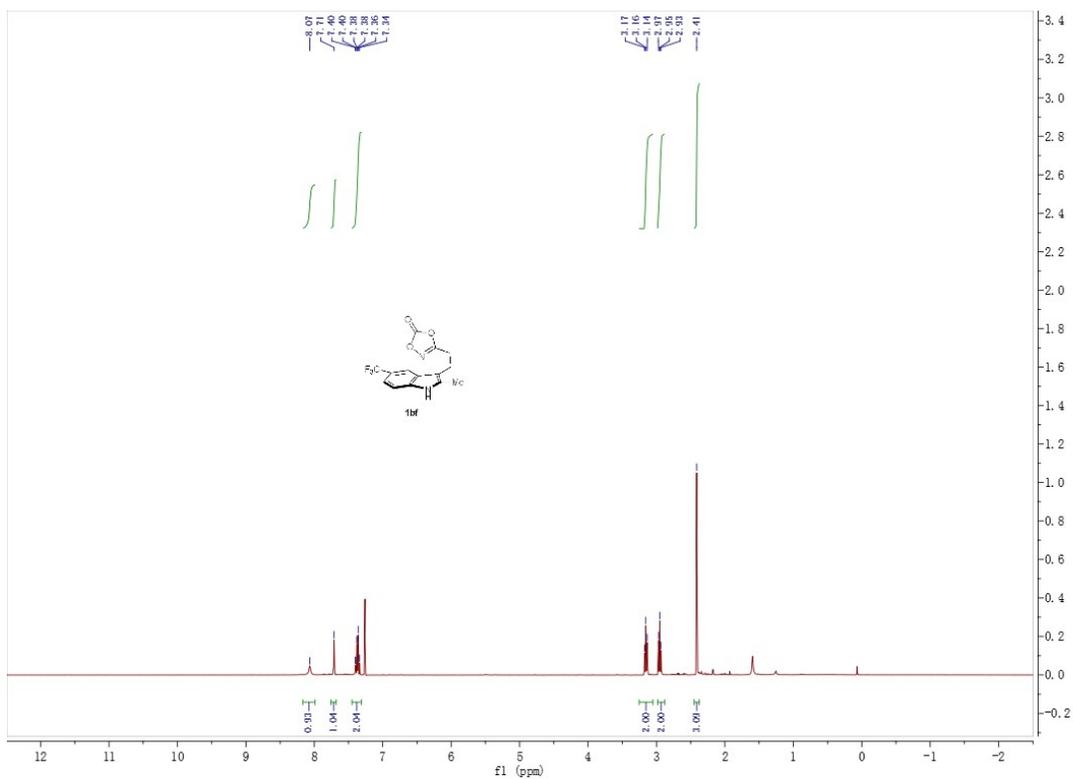
¹H NMR spectrum of compound **1be** (400 MHz, CDCl₃)



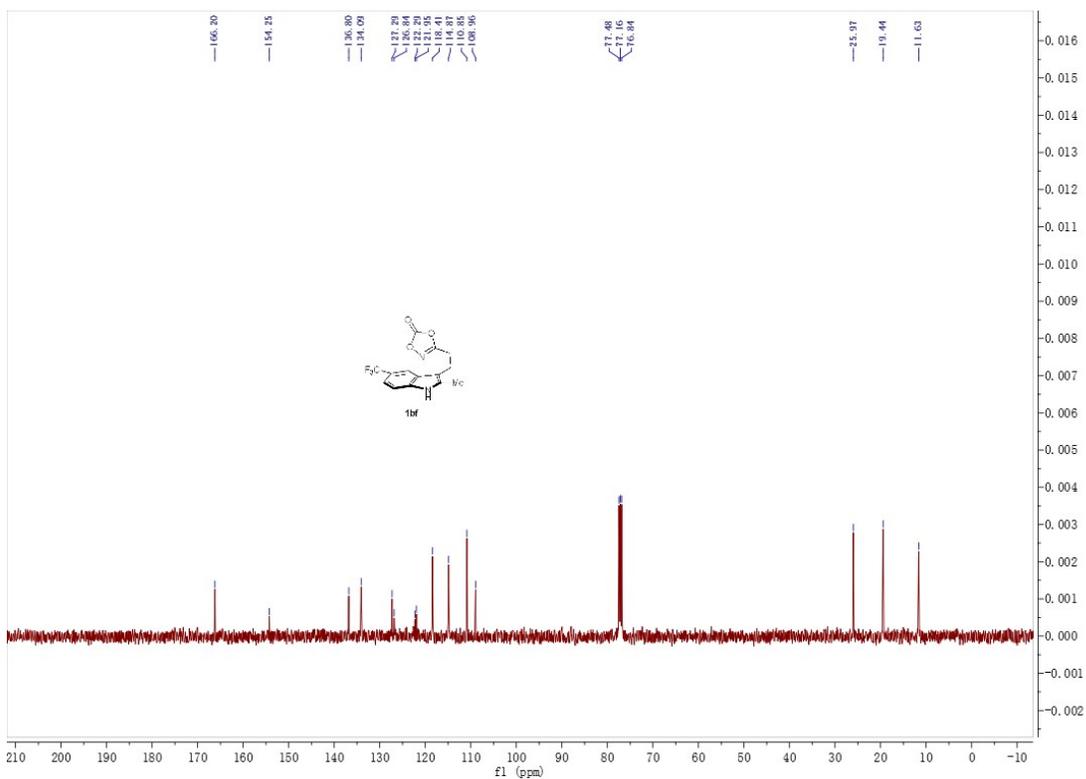
¹³C NMR spectrum of compound **1be** (100 MHz, CDCl₃)



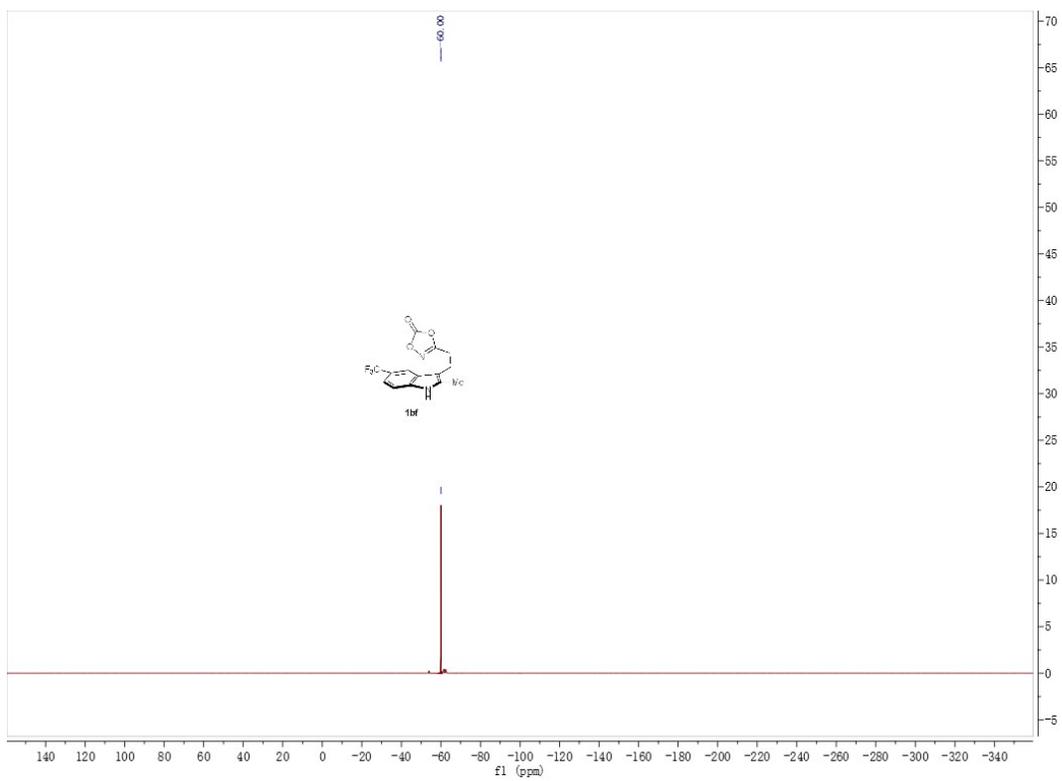
¹H NMR spectrum of compound **1bf** (400 MHz, CDCl₃)



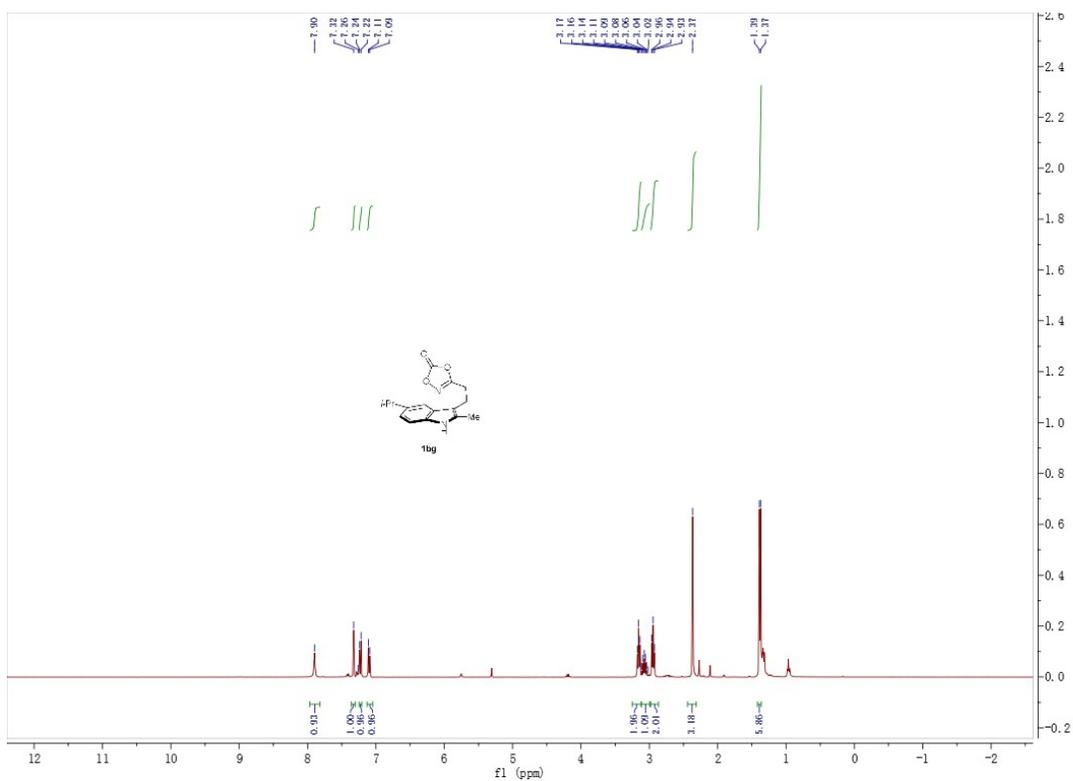
¹³C NMR spectrum of compound **1bf** (100 MHz, CDCl₃)



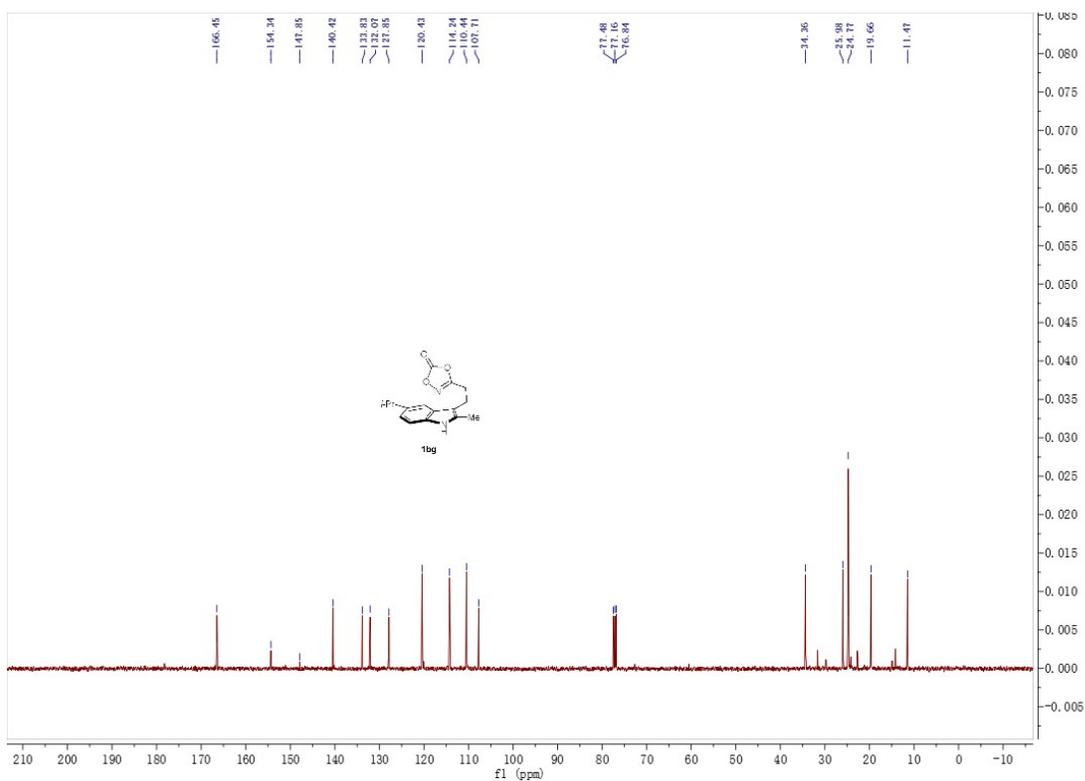
¹⁹F NMR spectrum of compound **1bf (376 MHz, CDCl₃)**



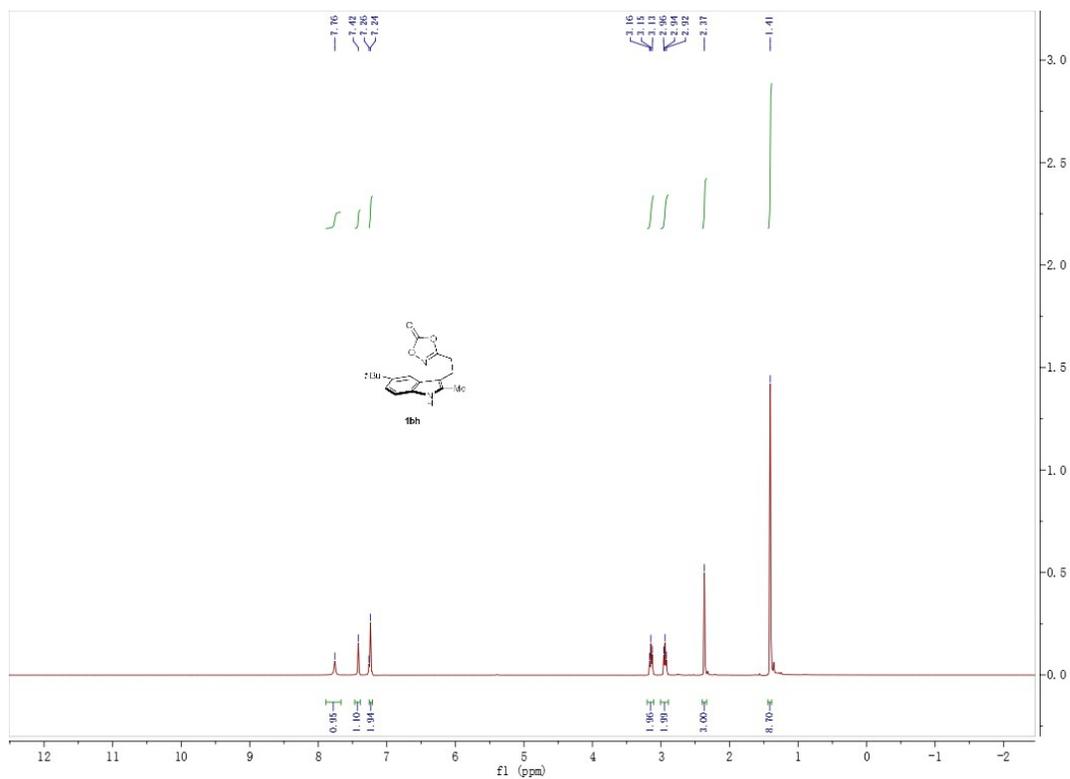
¹H NMR spectrum of compound **1bg** (400 MHz, CDCl₃)



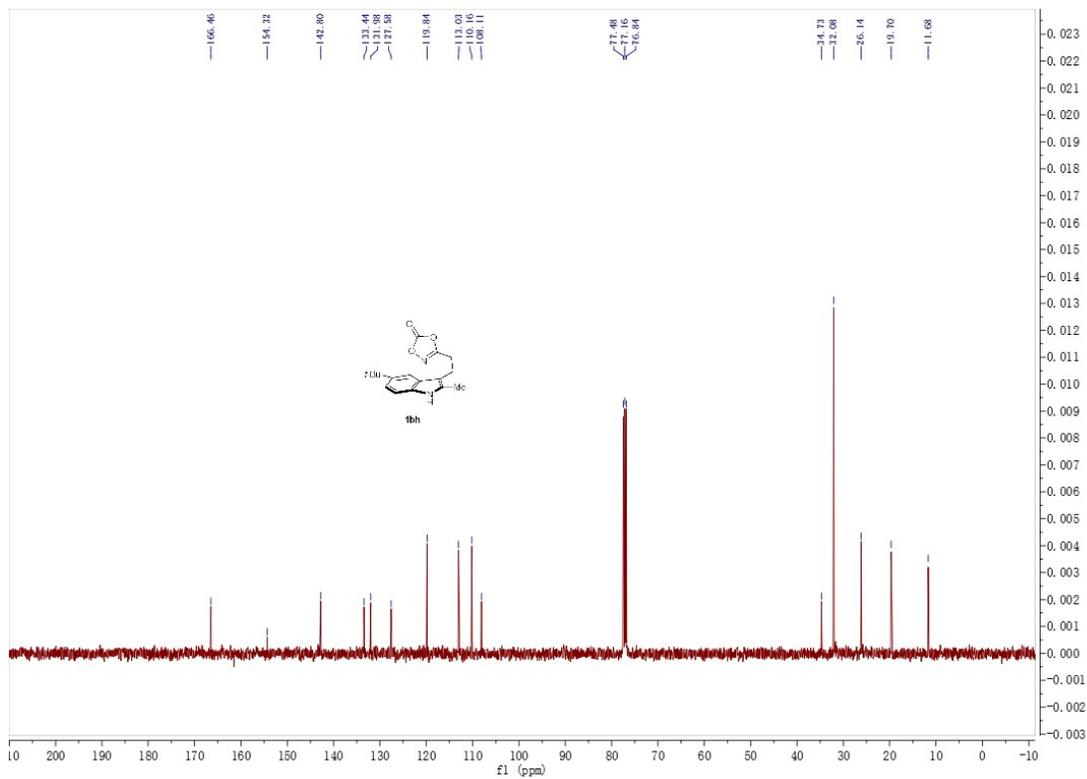
¹³C NMR spectrum of compound **1bg** (100 MHz, CDCl₃)



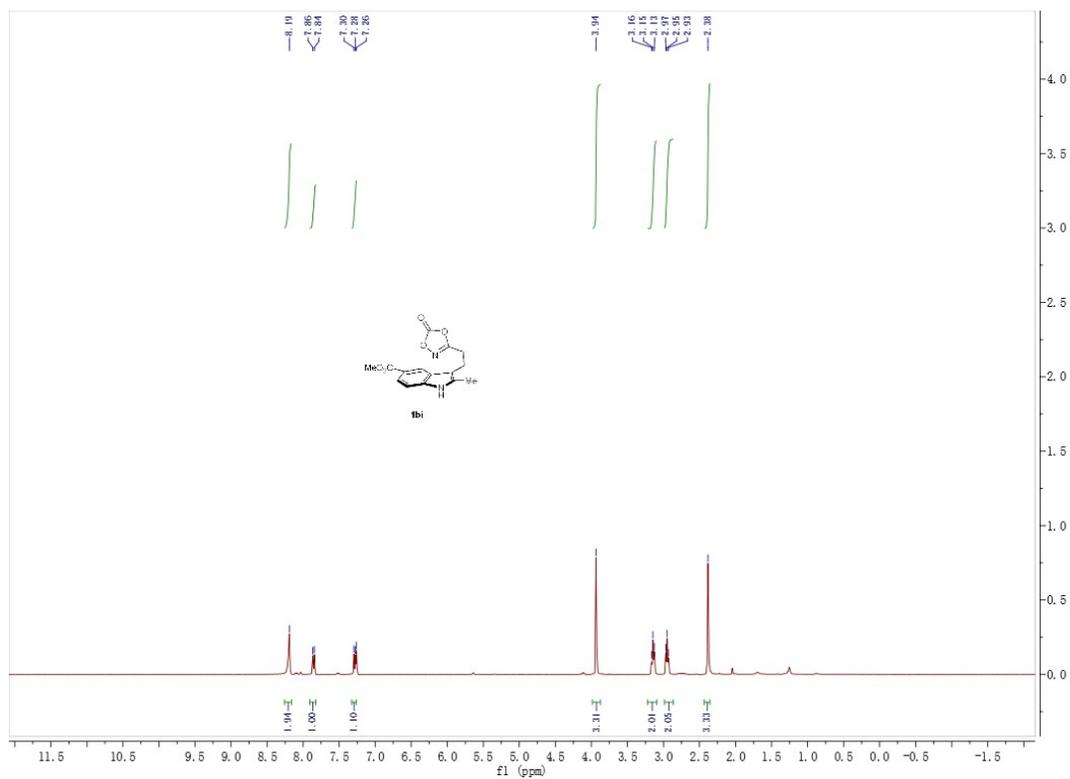
^1H NMR spectrum of compound **1bh** (400 MHz, CDCl_3)



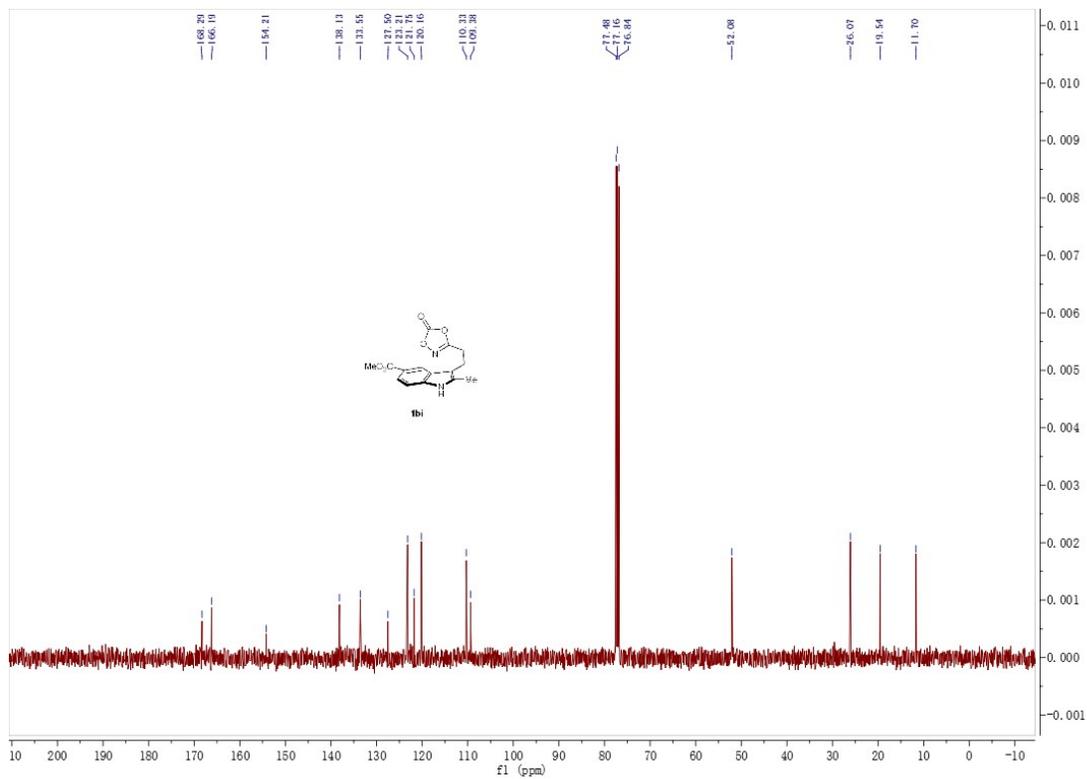
^{13}C NMR spectrum of compound **1bh** (100 MHz, CDCl_3)



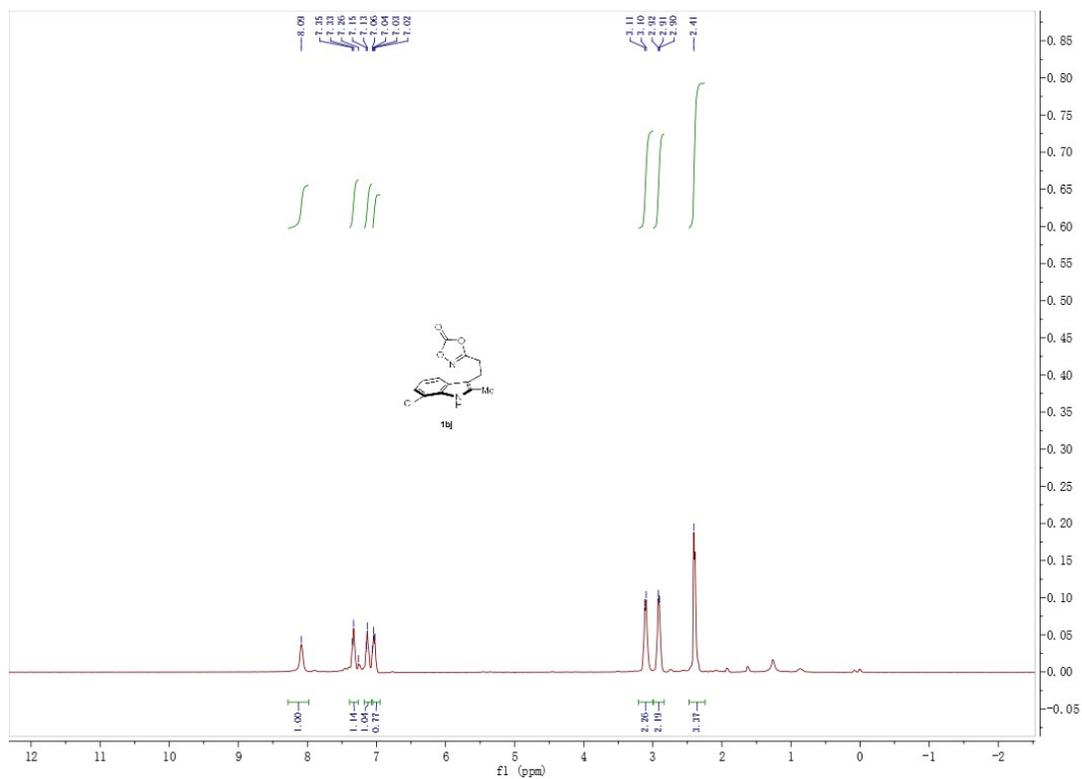
¹H NMR spectrum of compound **1bi** (400 MHz, CDCl₃)



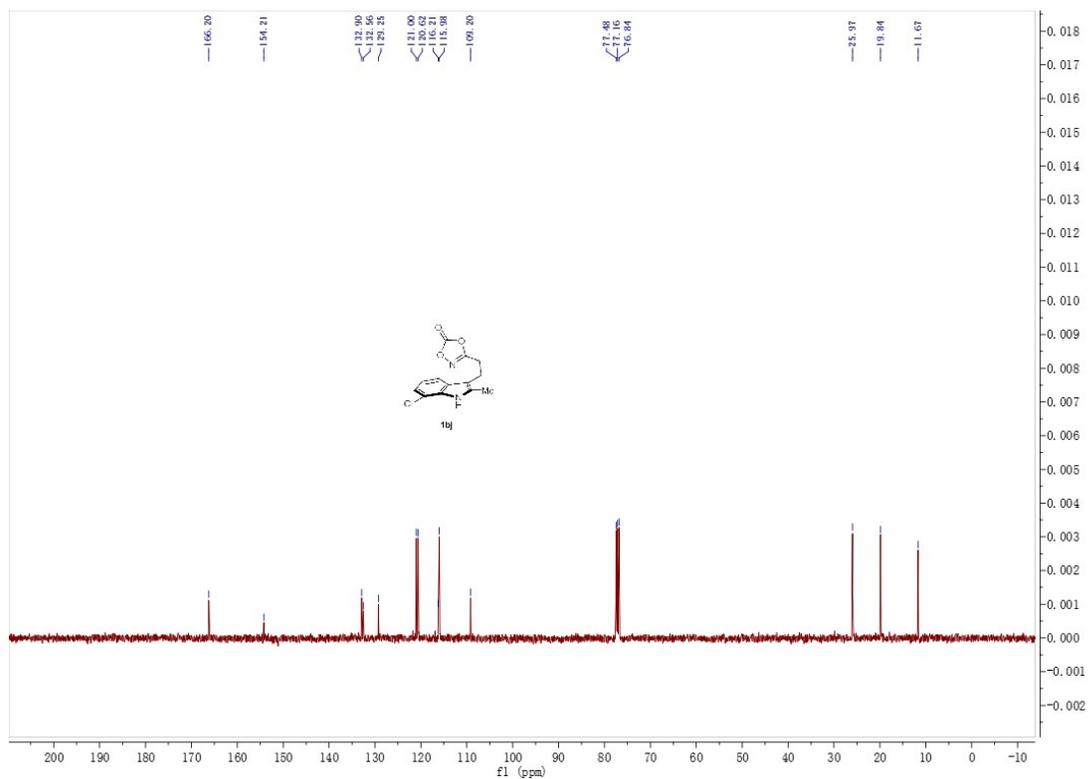
¹³C NMR spectrum of compound **1bi** (100 MHz, CDCl₃)



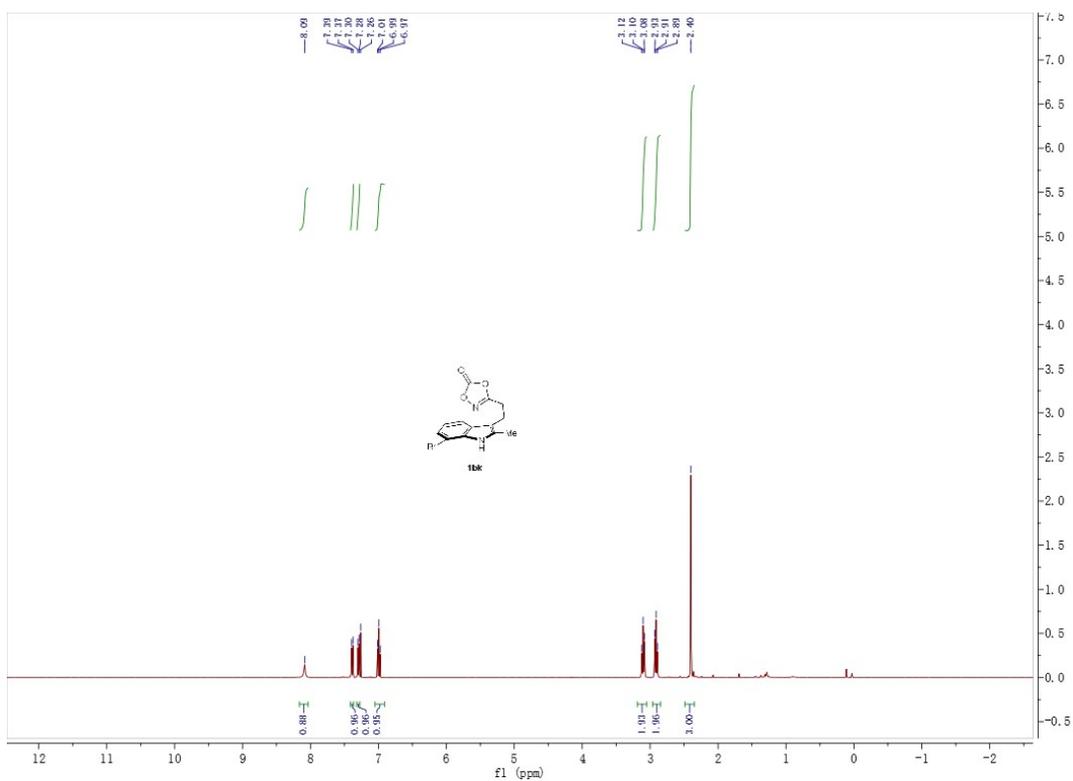
¹H NMR spectrum of compound 1bj (400 MHz, CDCl₃)



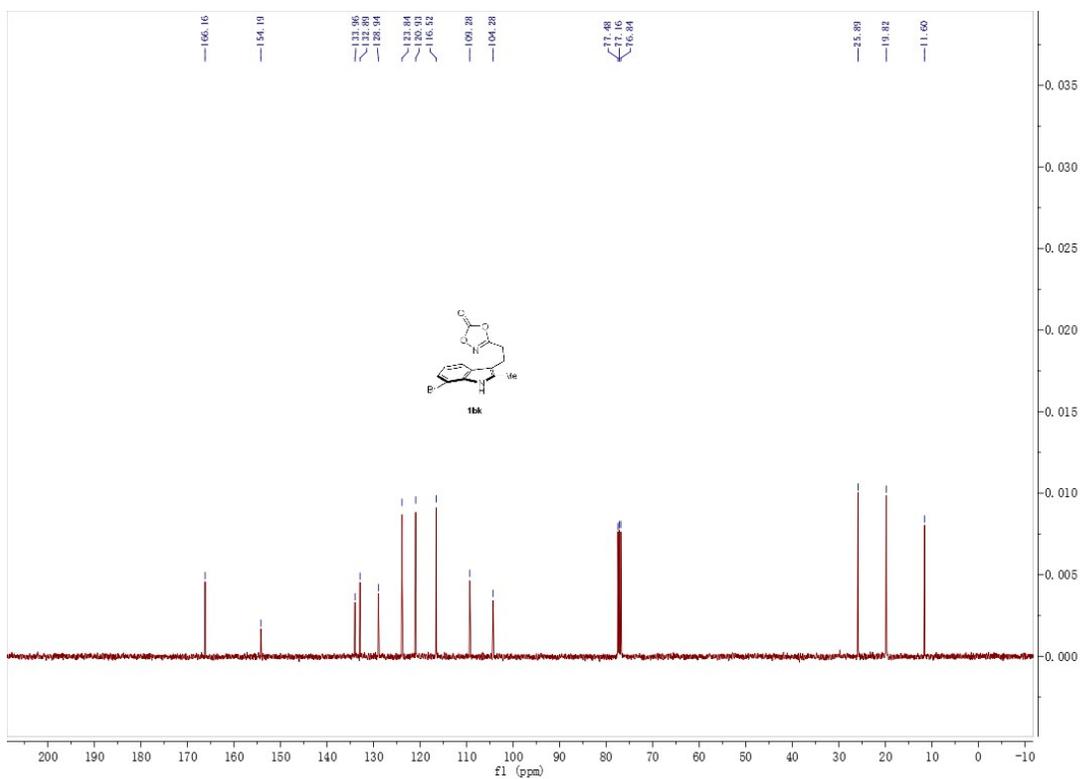
¹³C NMR spectrum of compound 1bj (100 MHz, CDCl₃)



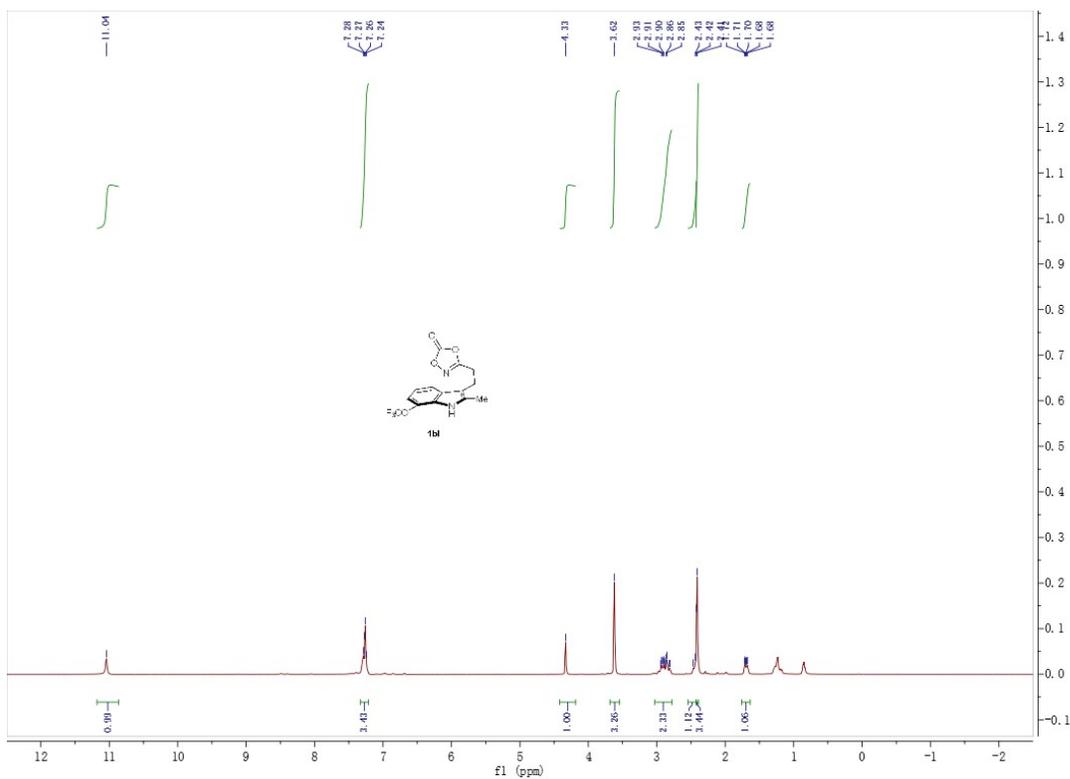
¹H NMR spectrum of compound **1bk (400 MHz, CDCl₃)**



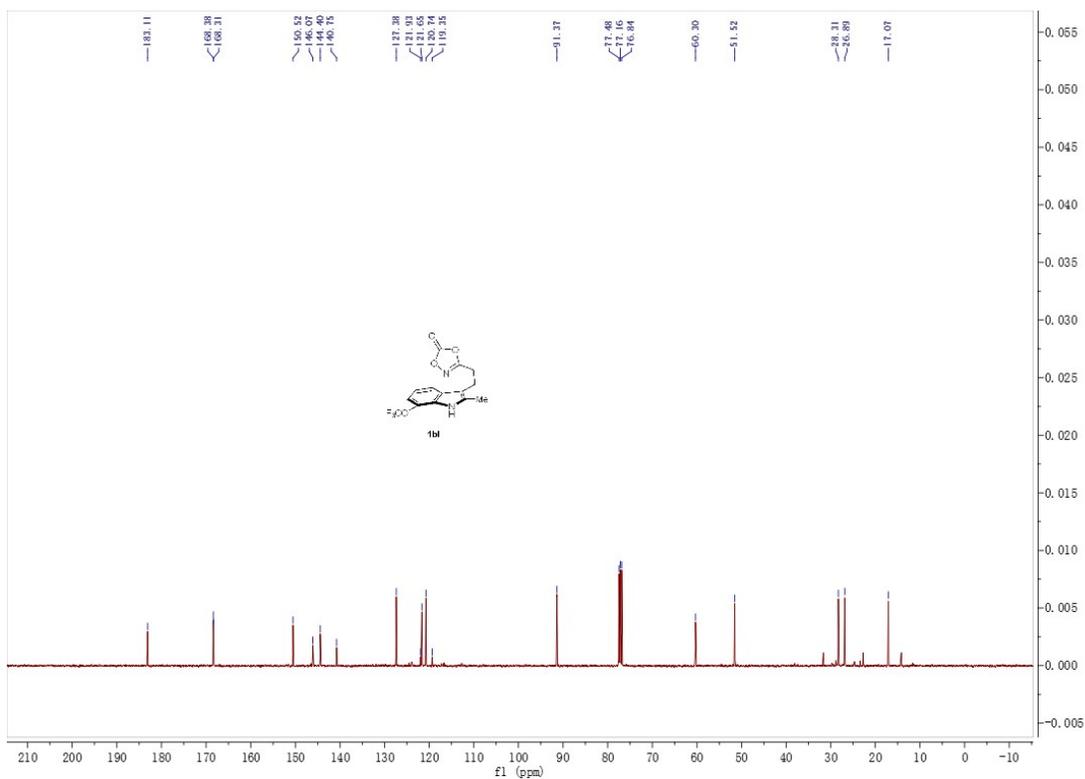
¹³C NMR spectrum of compound **1bk (100 MHz, CDCl₃)**



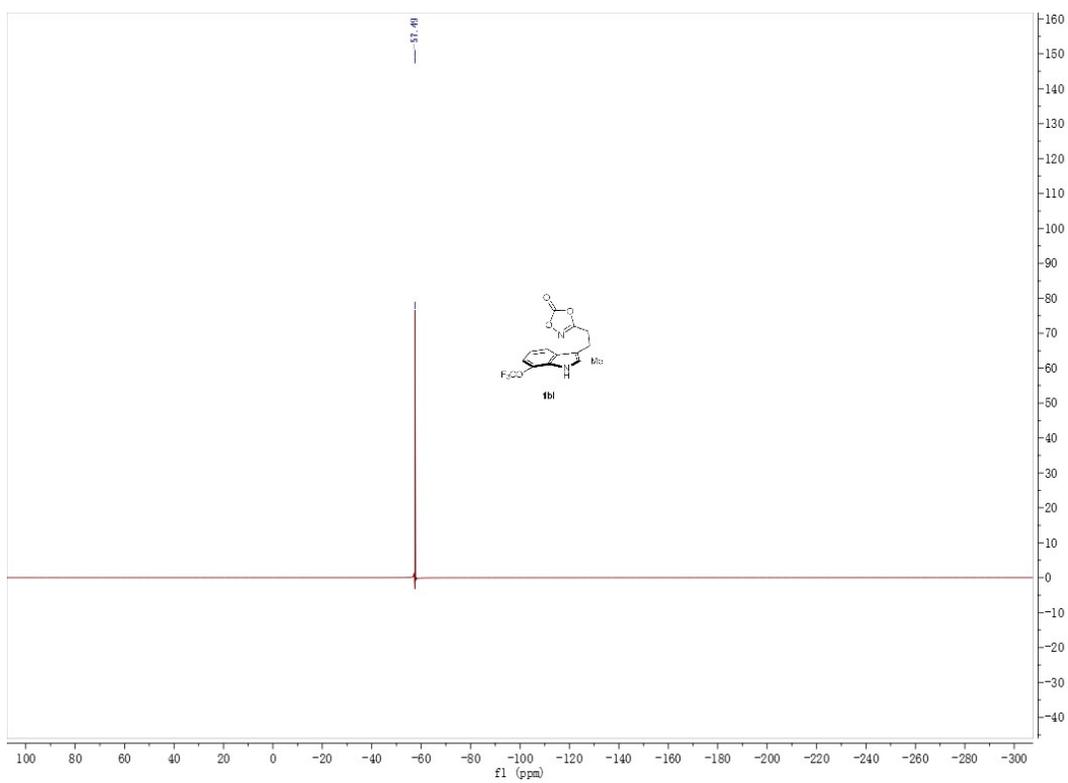
¹H NMR spectrum of compound **1bl** (400 MHz, CDCl₃)



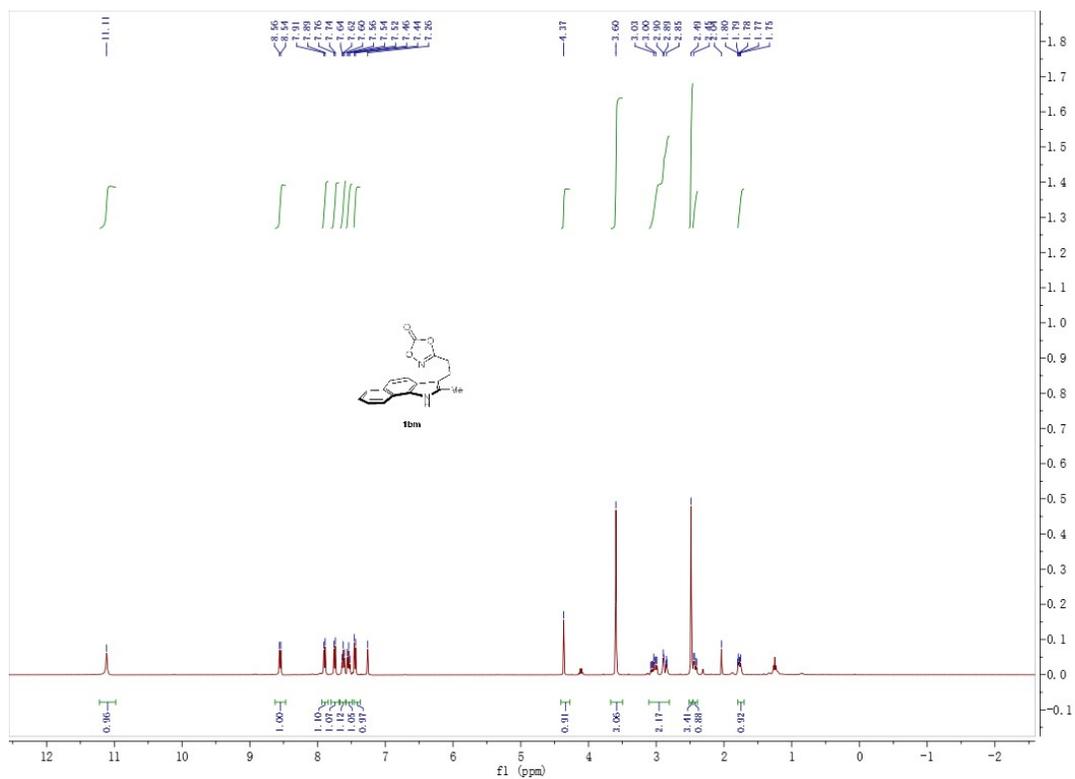
¹³C NMR spectrum of compound **1bl** (100 MHz, CDCl₃)



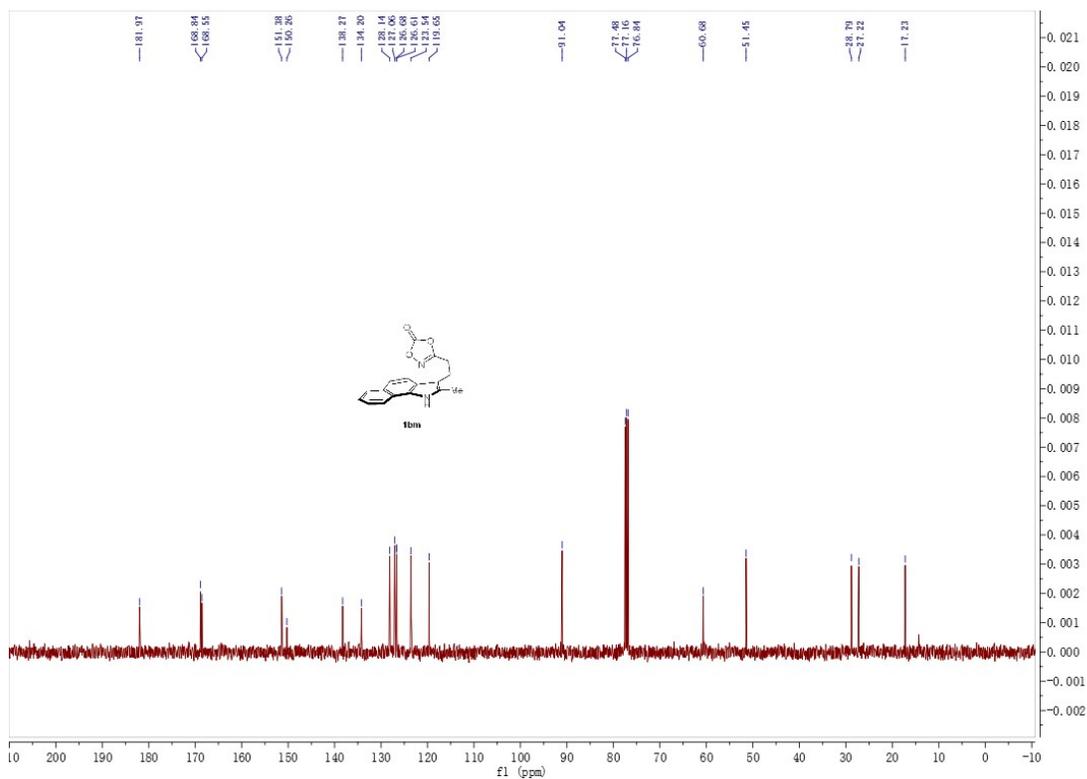
¹⁹F NMR spectrum of compound **1bl (376 MHz, CDCl₃)**



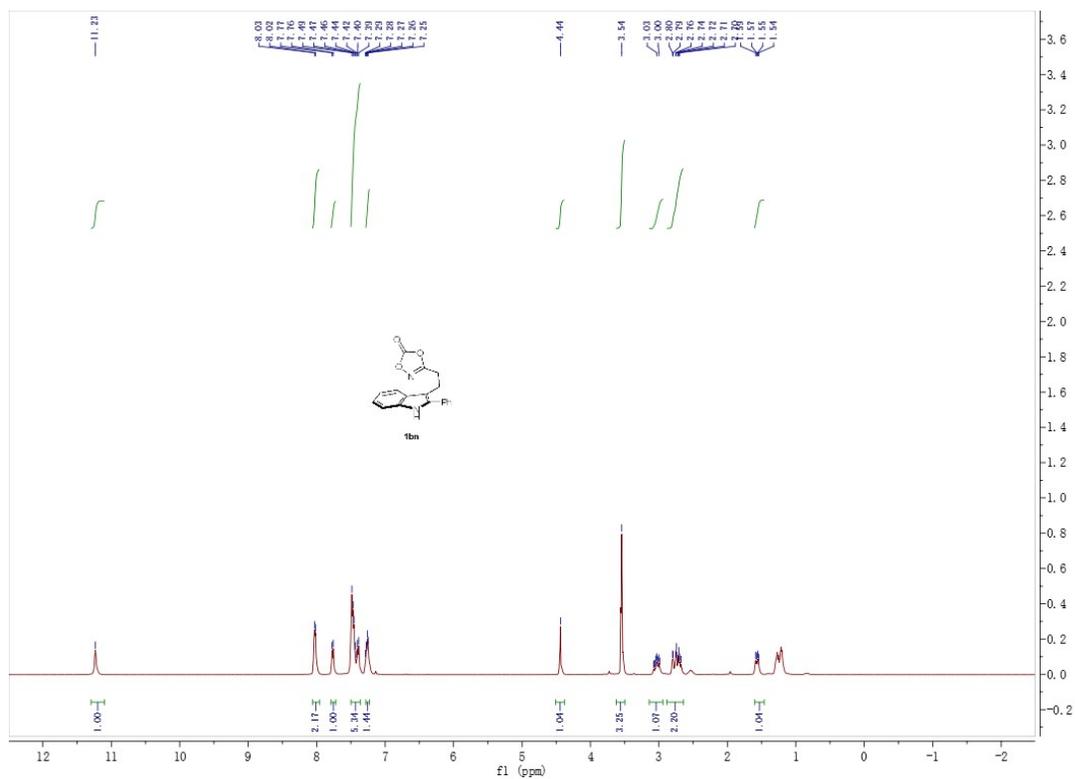
¹H NMR spectrum of compound **1bm** (400 MHz, CDCl₃)



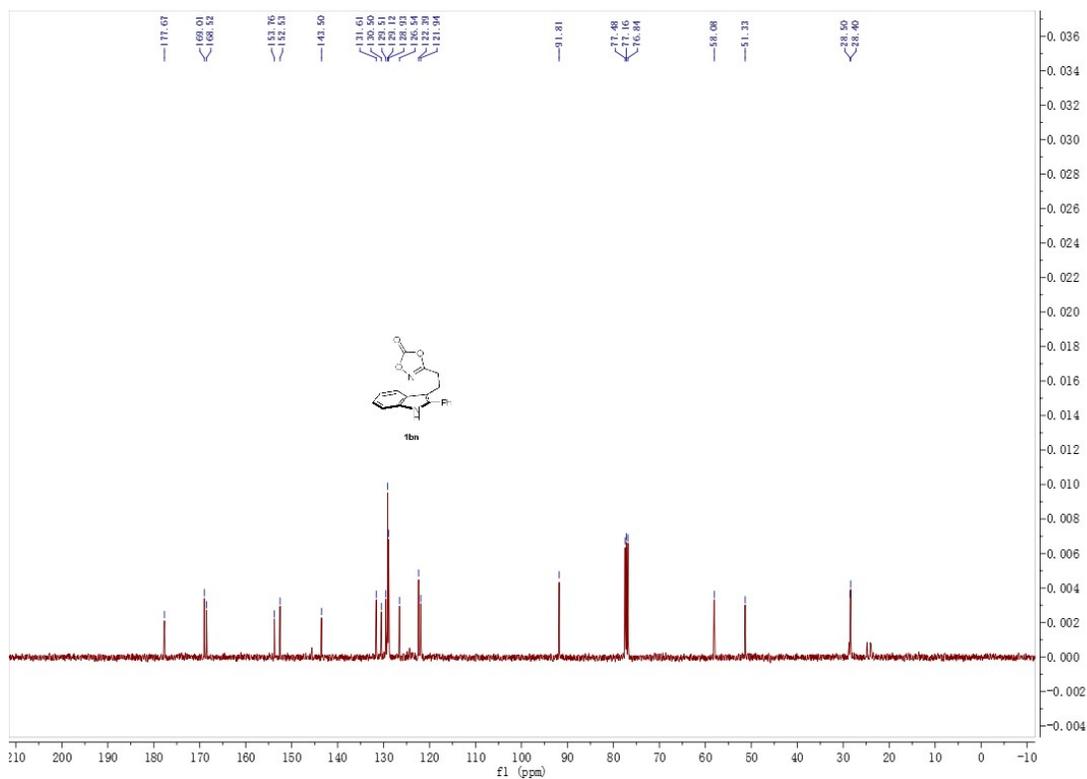
¹³C NMR spectrum of compound **1bm** (100 MHz, CDCl₃)



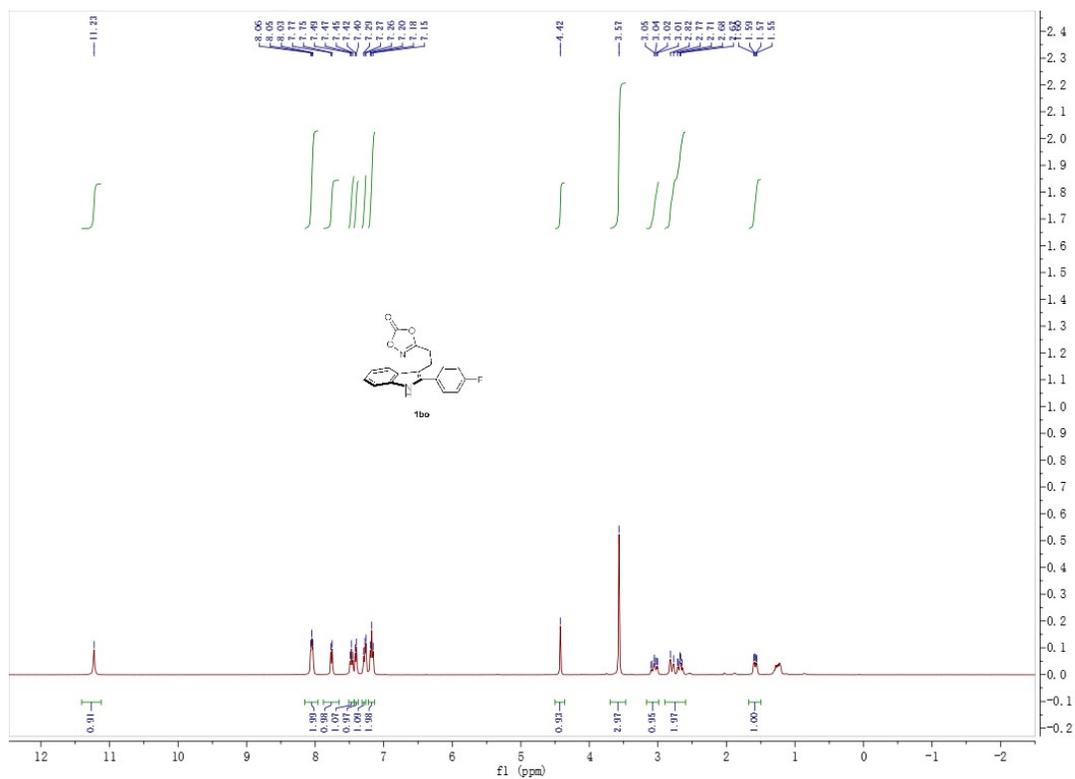
¹H NMR spectrum of compound **1bn** (400 MHz, CDCl₃)



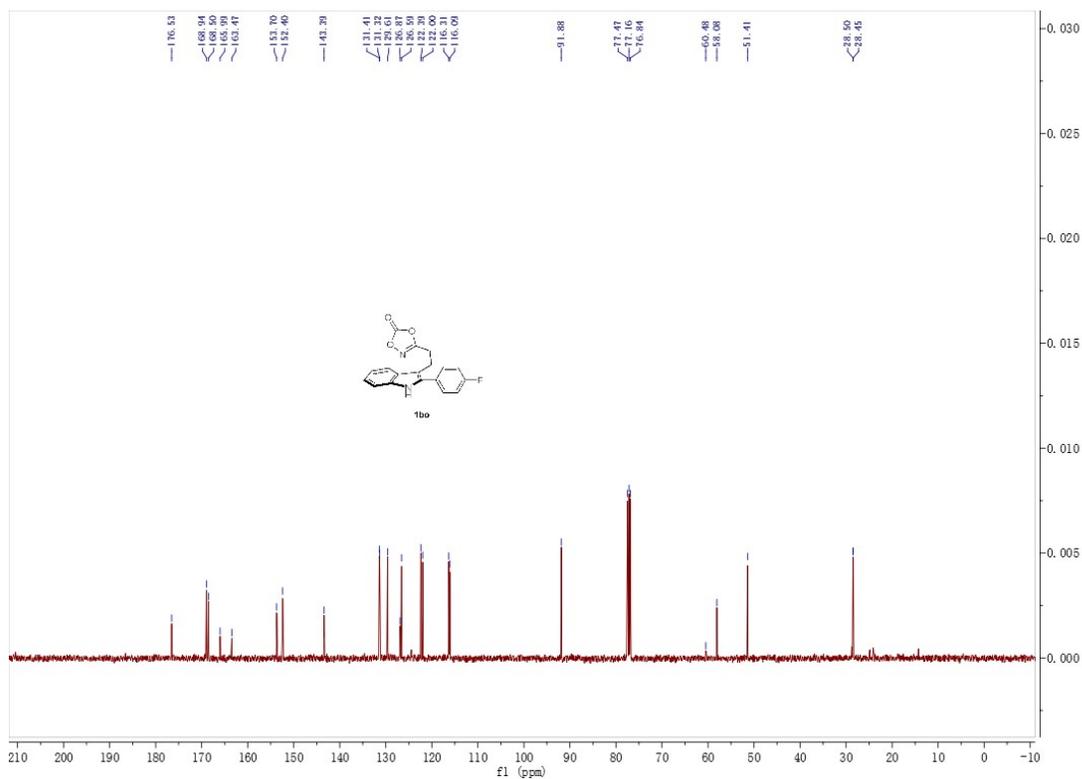
¹³C NMR spectrum of compound **1bn** (100 MHz, CDCl₃)



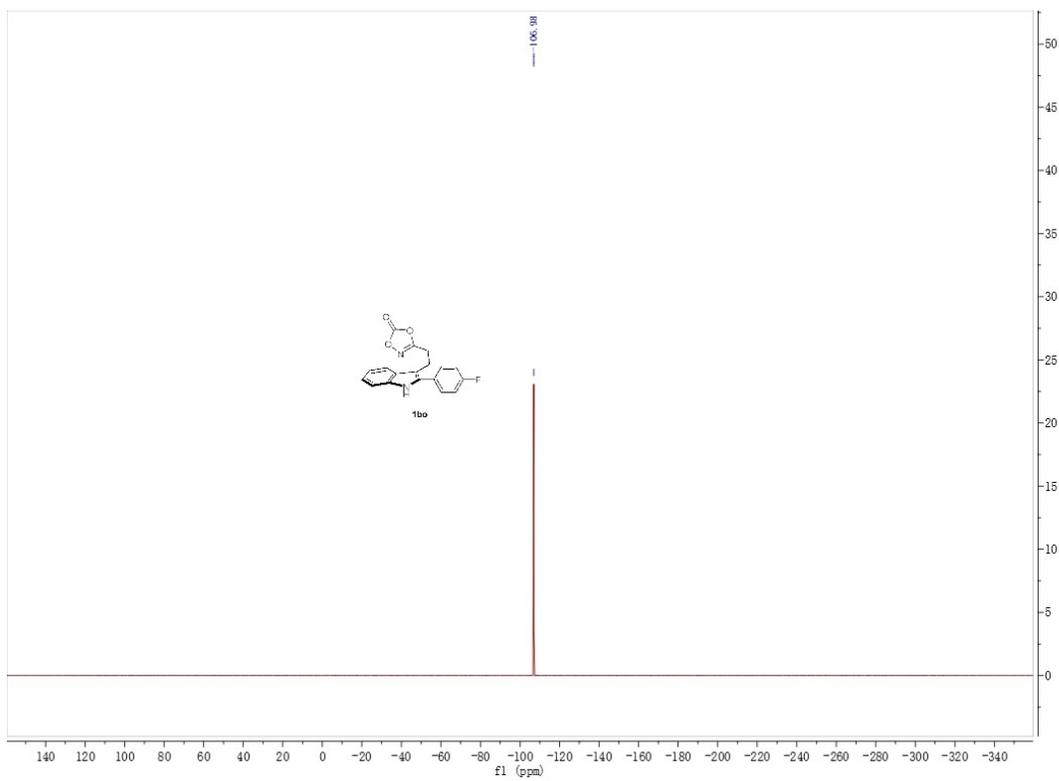
¹H NMR spectrum of compound **1bo** (400 MHz, CDCl₃)



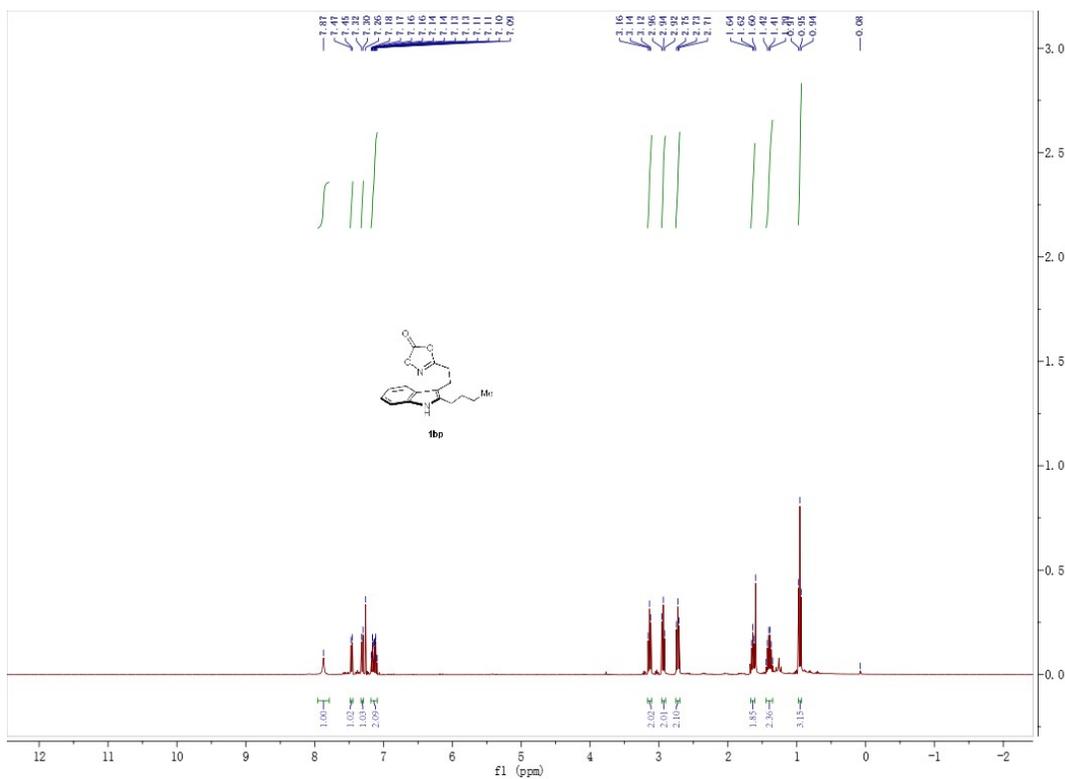
¹³C NMR spectrum of compound **1bo** (100 MHz, CDCl₃)



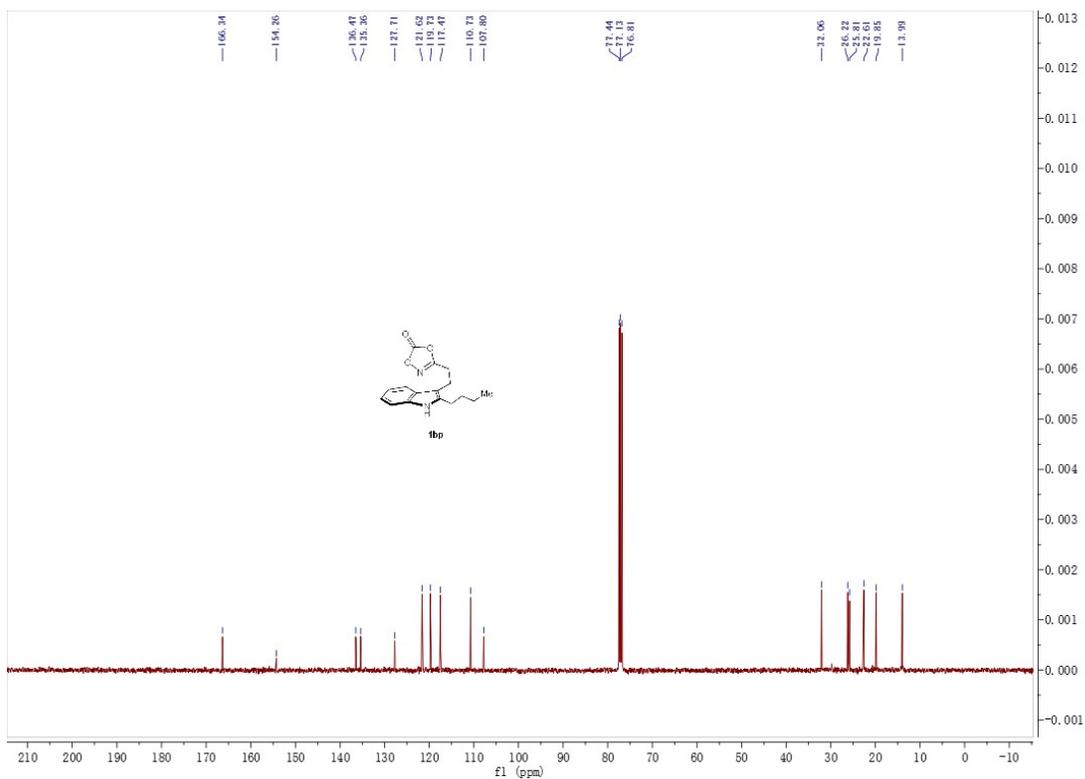
¹⁹F NMR spectrum of compound **1bo (376 MHz, CDCl₃)**



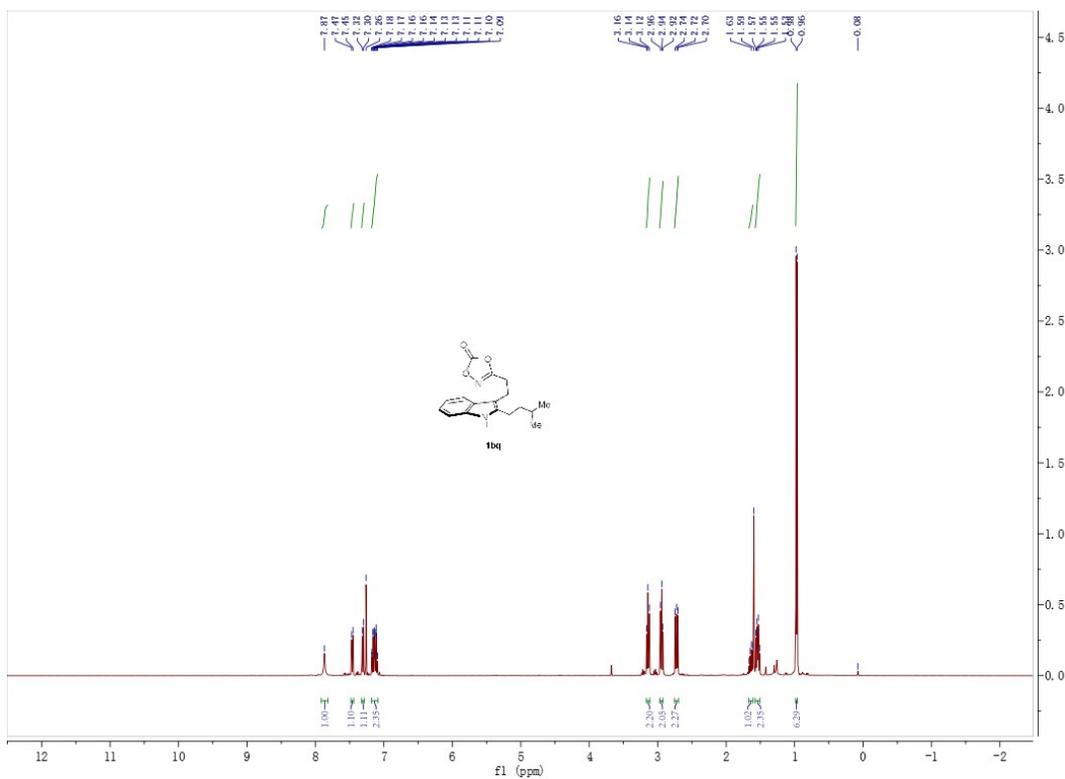
^1H NMR spectrum of compound **1bp** (400 MHz, CDCl_3)



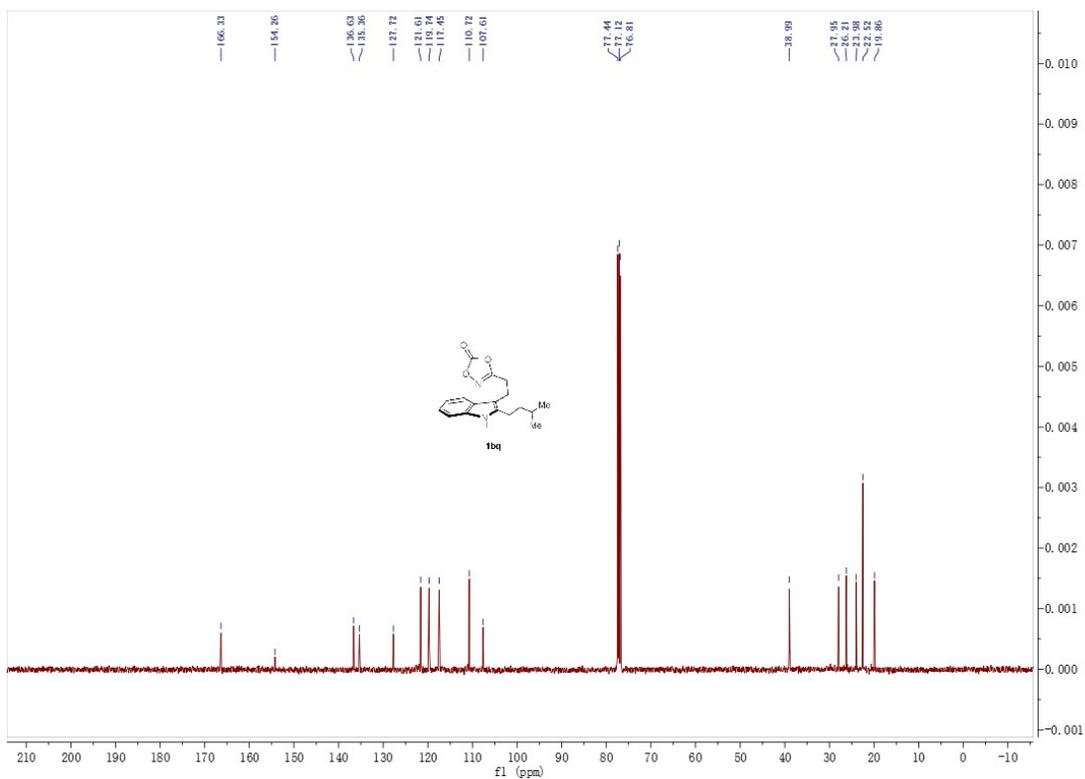
^{13}C NMR spectrum of compound **1bp** (100 MHz, CDCl_3)



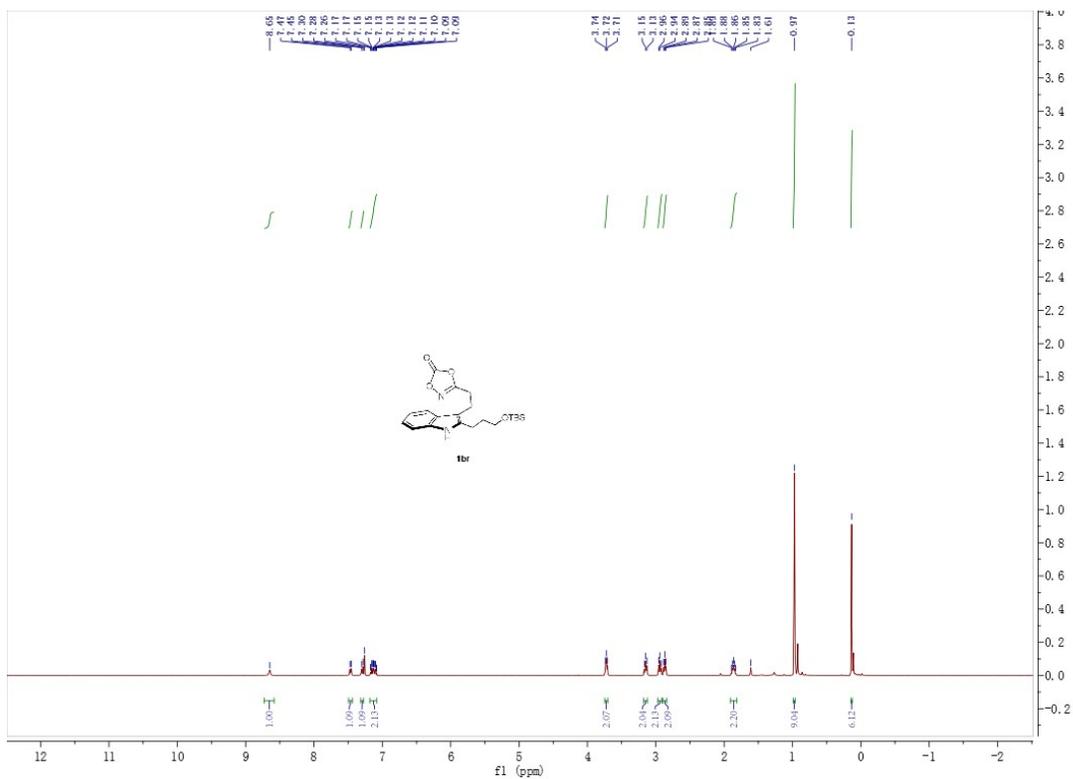
^1H NMR spectrum of compound **1bq** (400 MHz, CDCl_3)



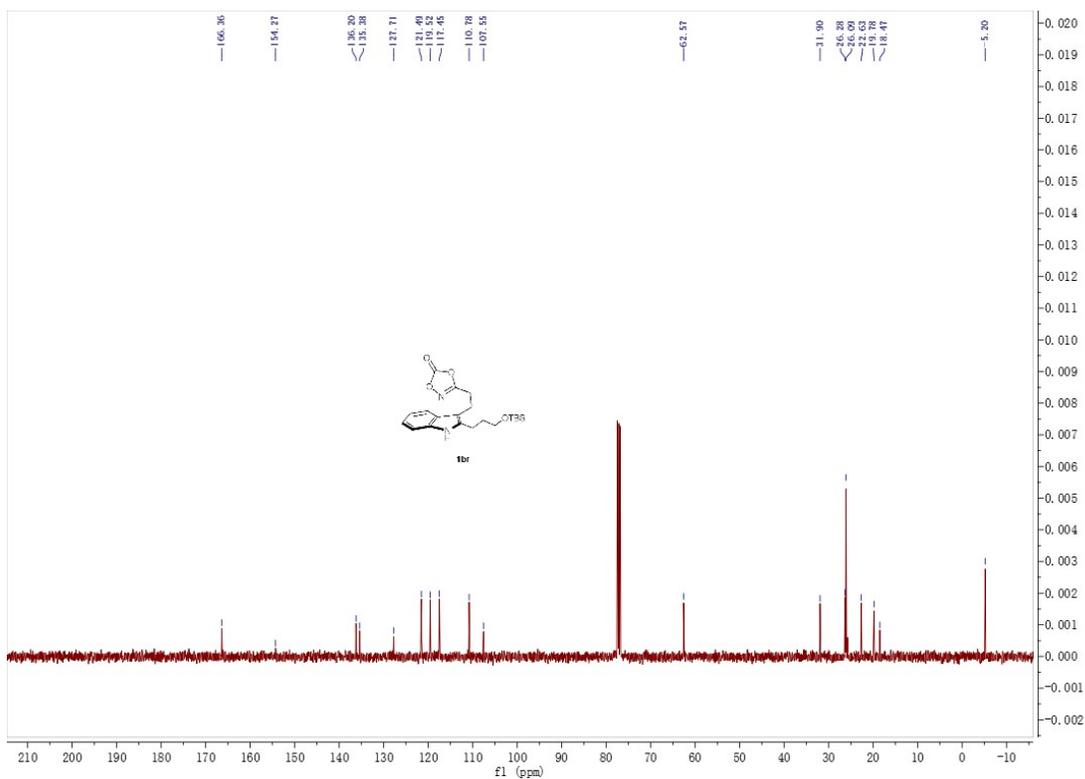
^{13}C NMR spectrum of compound **1bq** (100 MHz, CDCl_3)



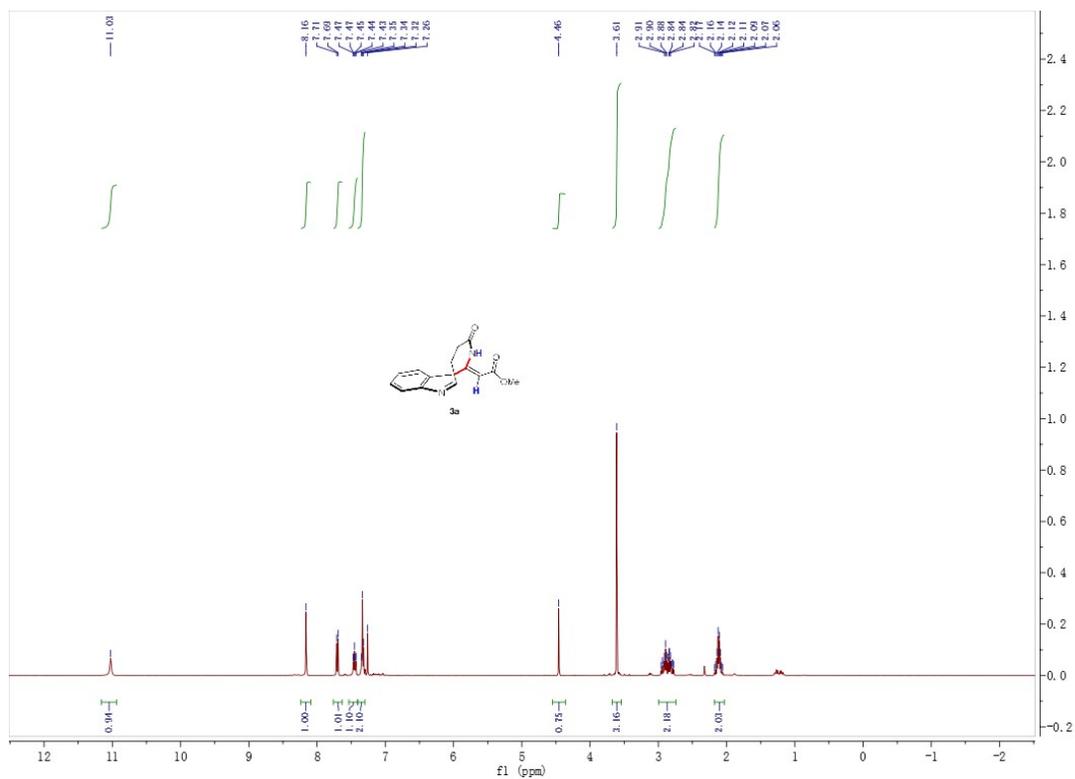
¹H NMR spectrum of compound **1br** (400 MHz, CDCl₃)



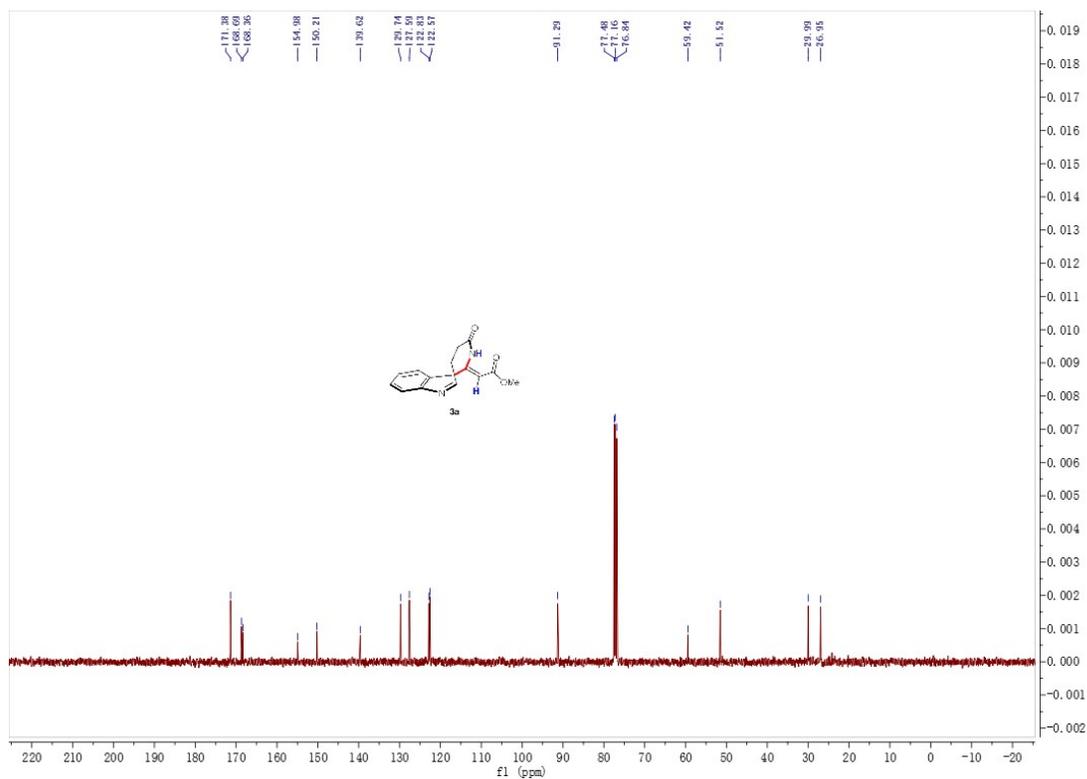
¹³C NMR spectrum of compound **1br** (100 MHz, CDCl₃)



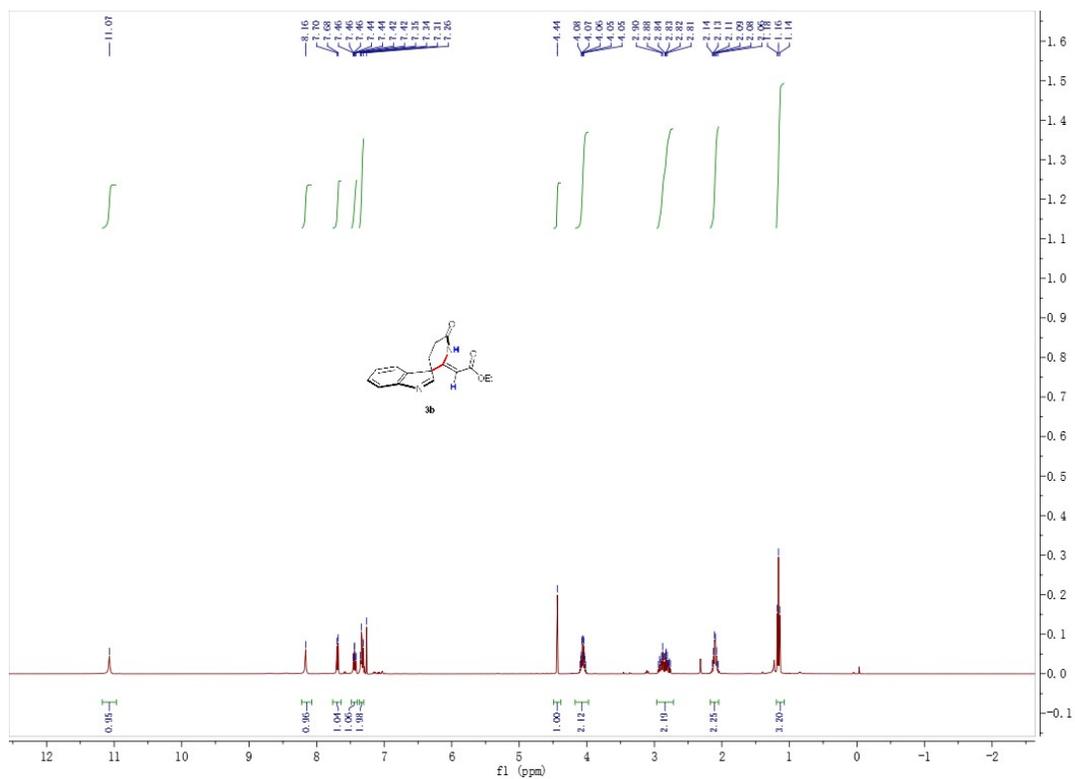
^1H NMR spectrum of compound **3a** (400 MHz, CDCl_3)



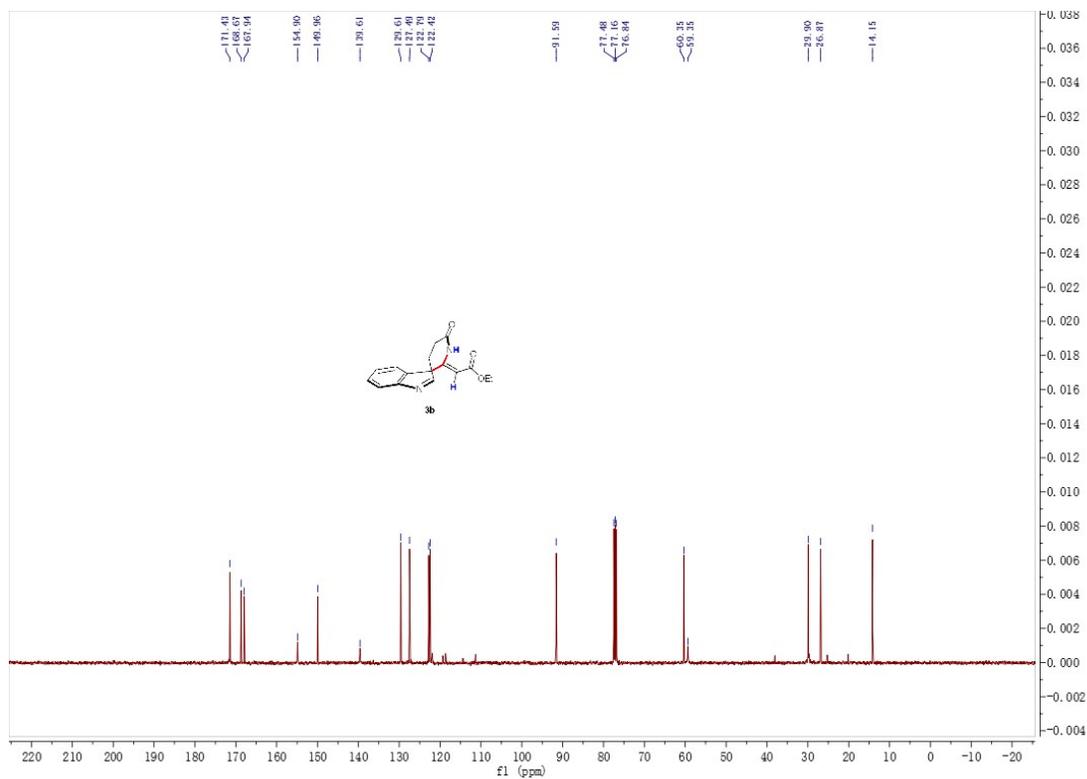
^{13}C NMR spectrum of compound **3a** (100 MHz, CDCl_3)



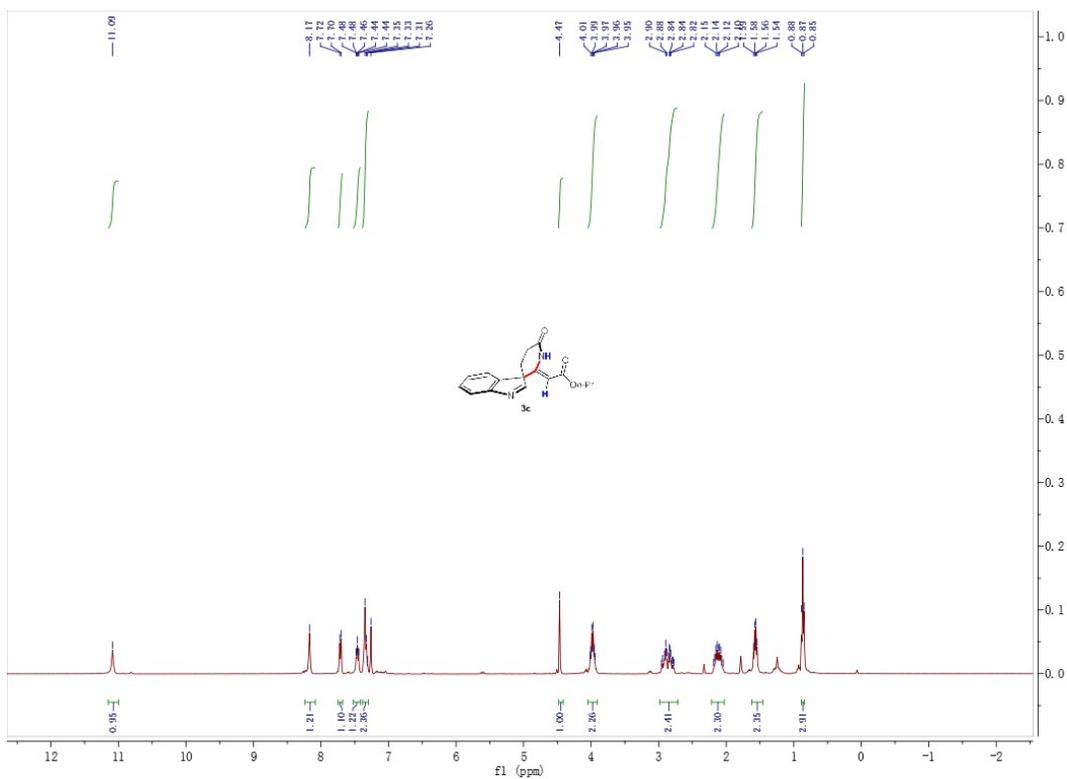
¹H NMR spectrum of compound **3b (400 MHz, CDCl₃)**



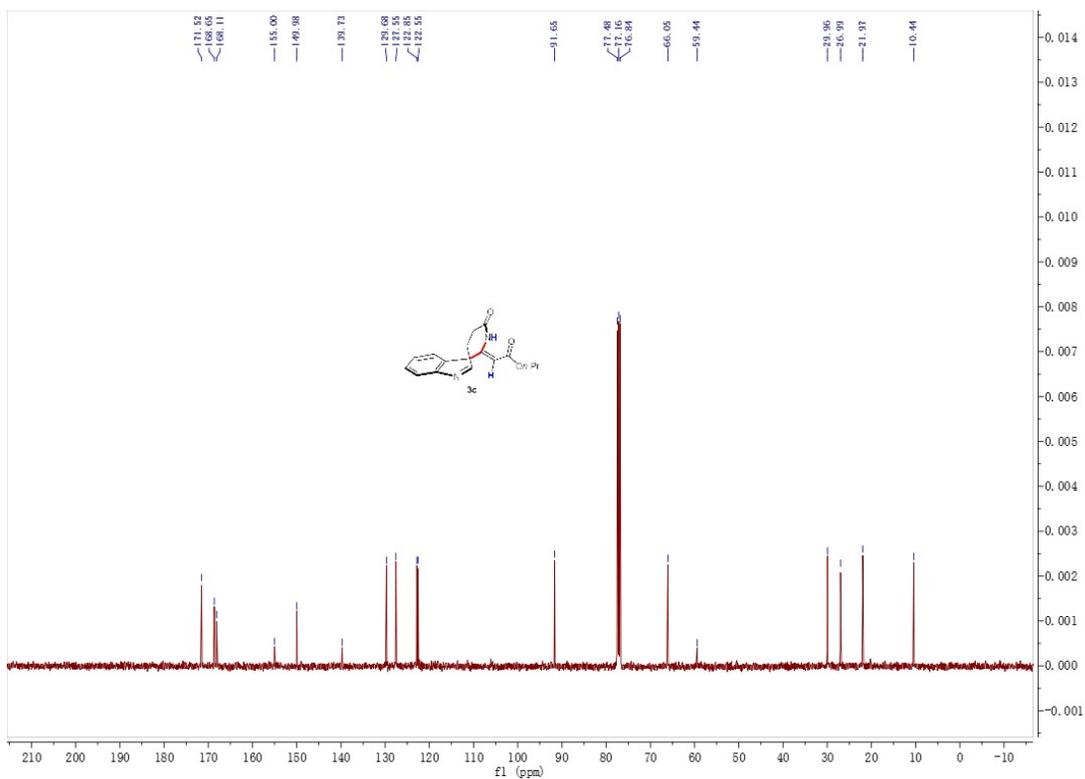
¹³C NMR spectrum of compound **3b (100 MHz, CDCl₃)**



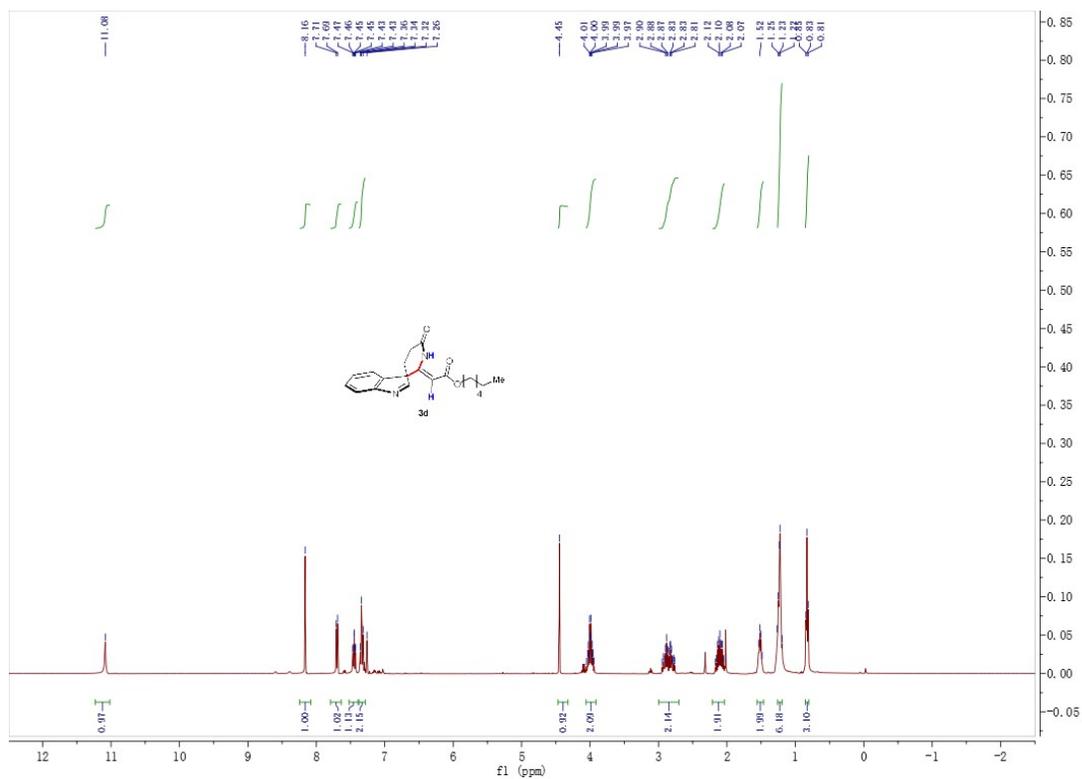
^1H NMR spectrum of compound **3c** (400 MHz, CDCl_3)



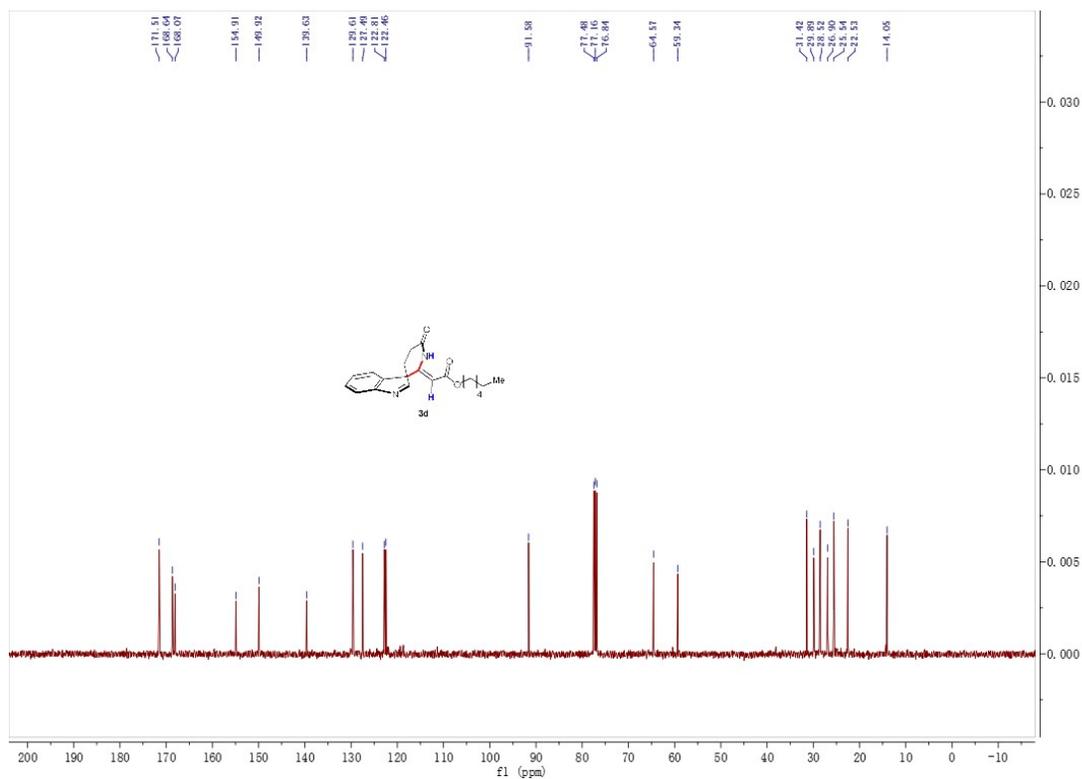
^{13}C NMR spectrum of compound **3c** (100 MHz, CDCl_3)



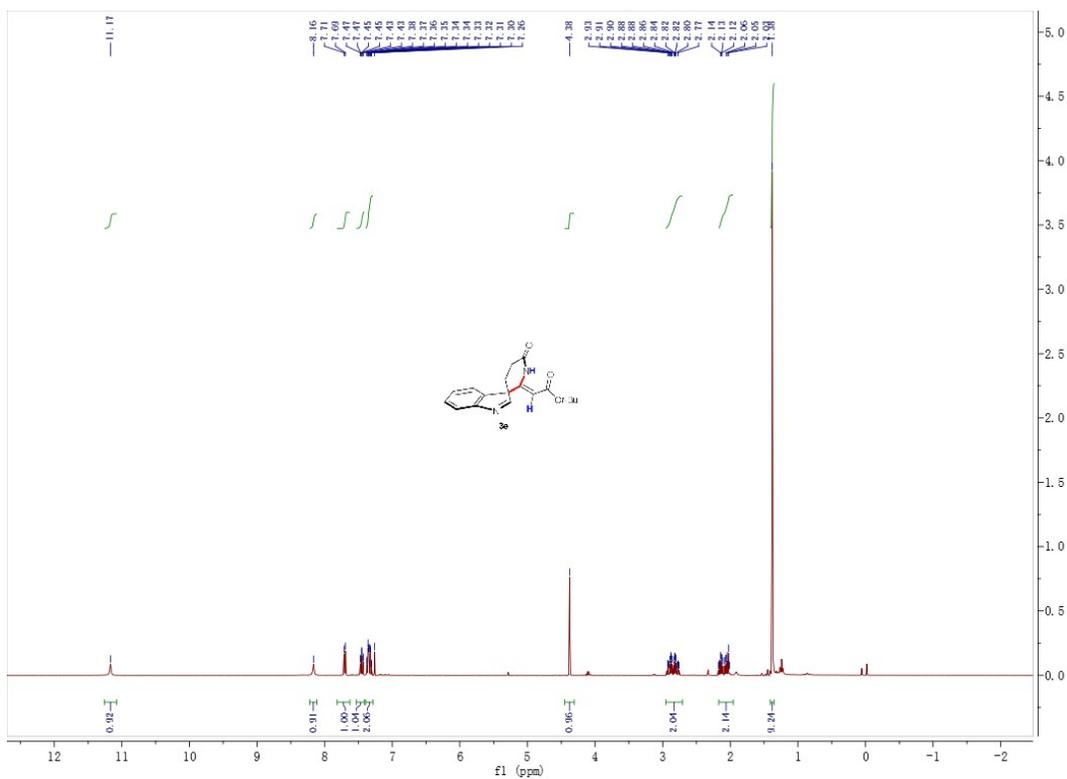
¹H NMR spectrum of compound **3d** (400 MHz, CDCl₃)



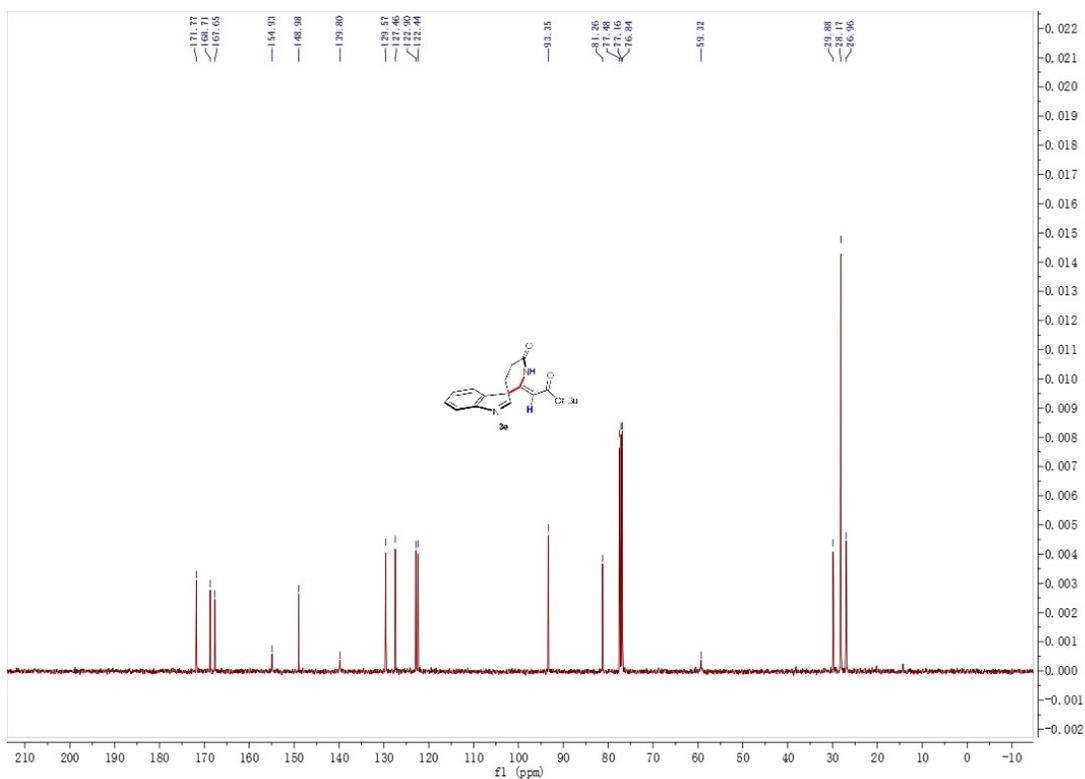
¹³C NMR spectrum of compound **3d** (100 MHz, CDCl₃)



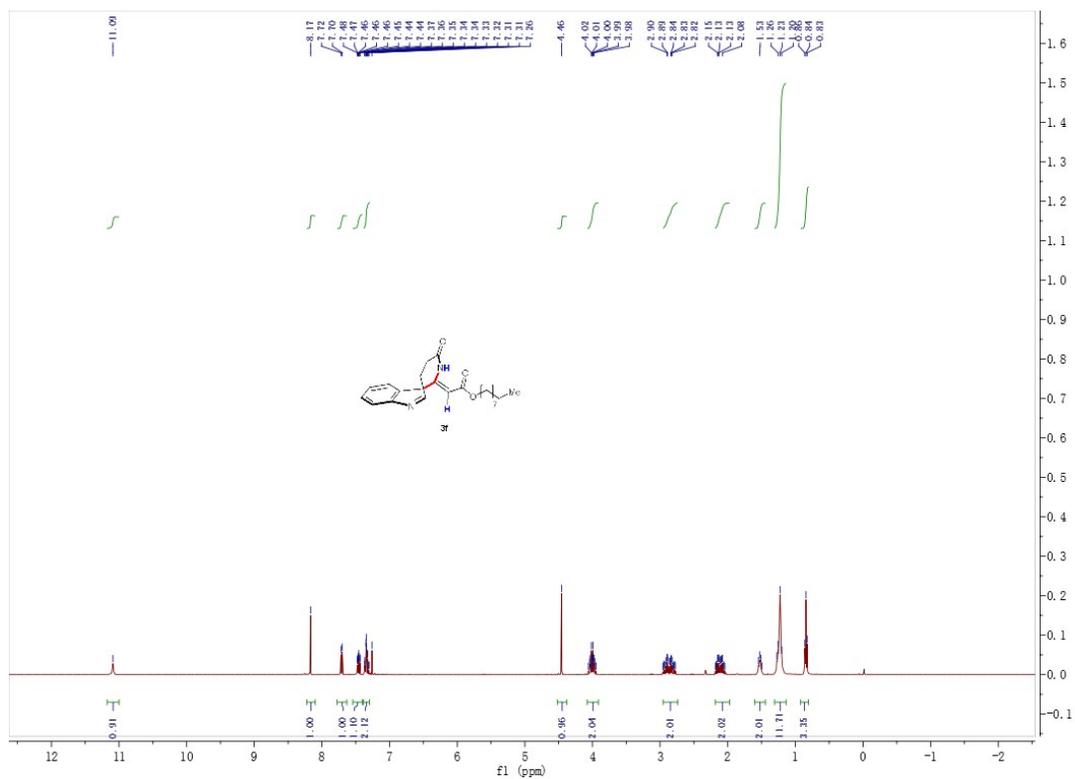
^1H NMR spectrum of compound **3e** (400 MHz, CDCl_3)



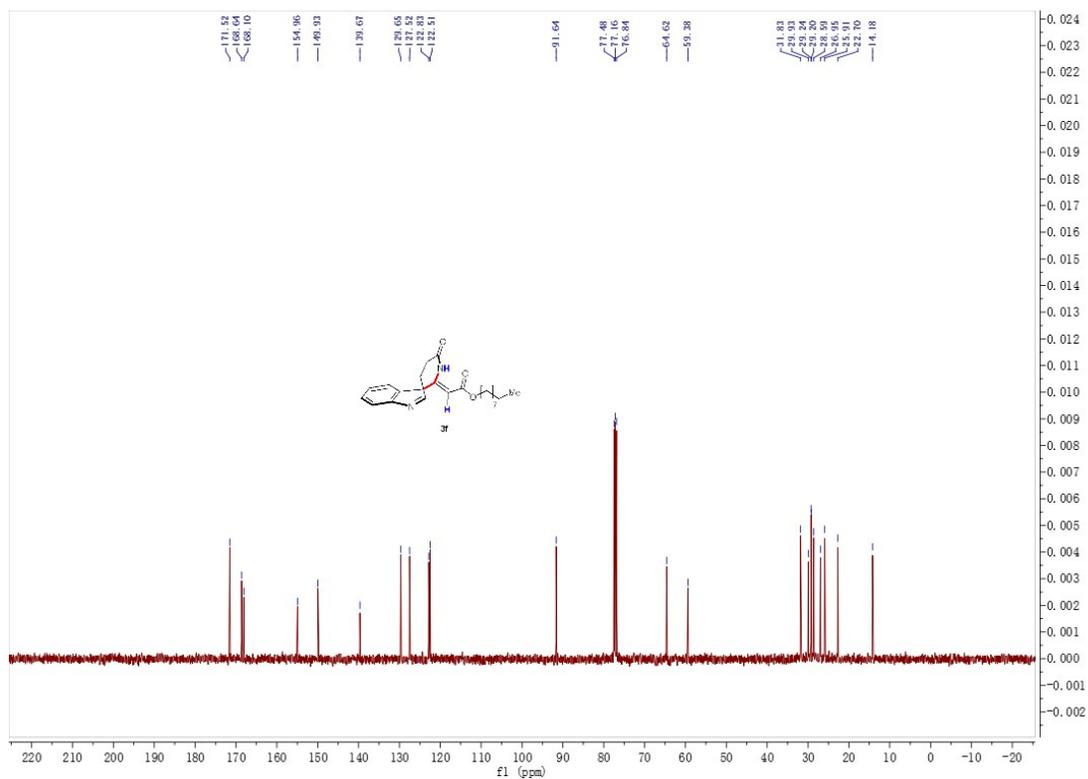
^{13}C NMR spectrum of compound **3e** (100 MHz, CDCl_3)



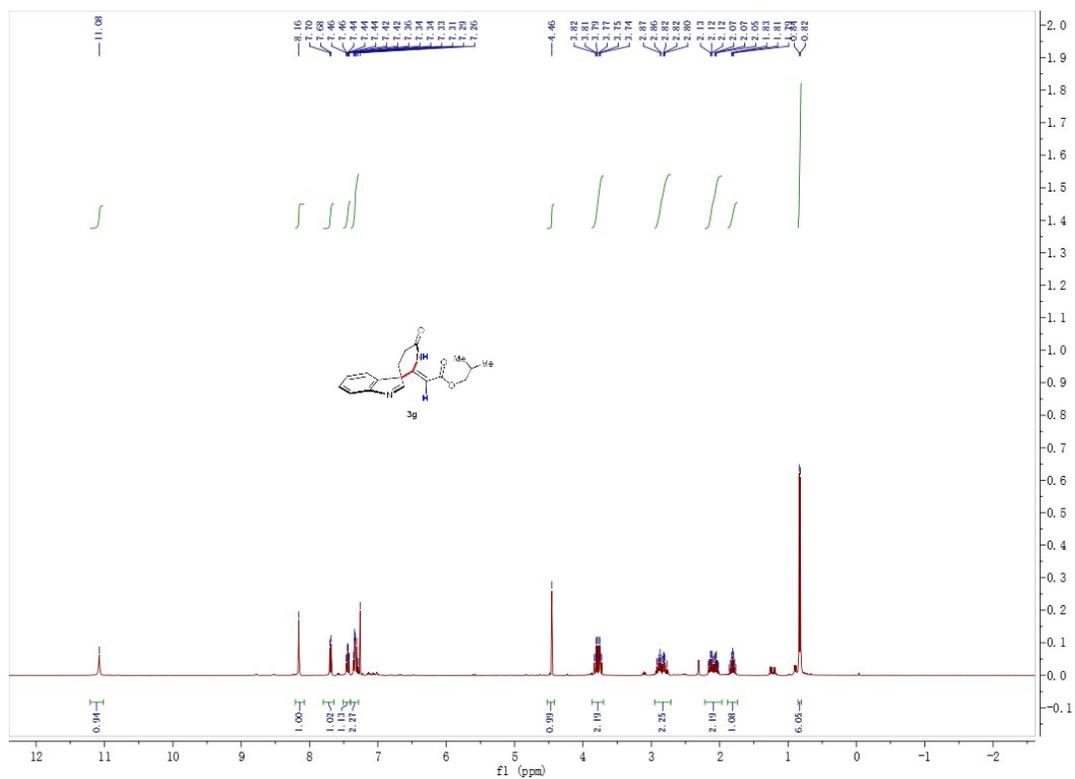
¹H NMR spectrum of compound **3f** (400 MHz, CDCl₃)



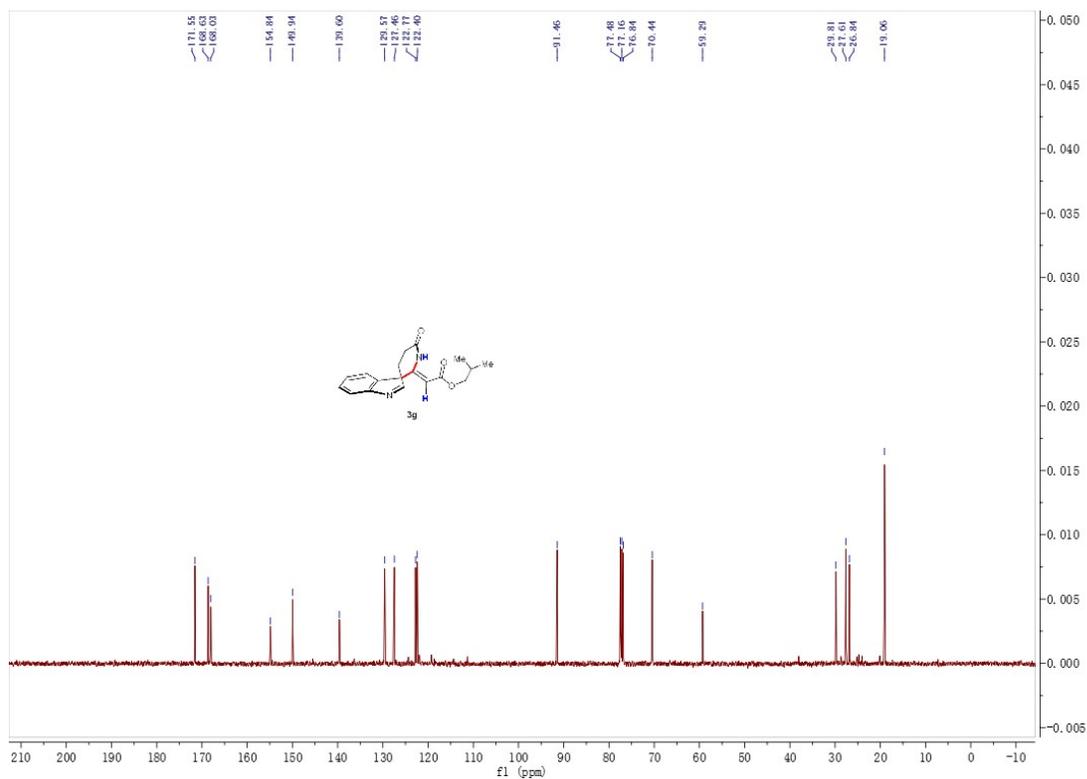
¹³C NMR spectrum of compound **3f** (100 MHz, CDCl₃)



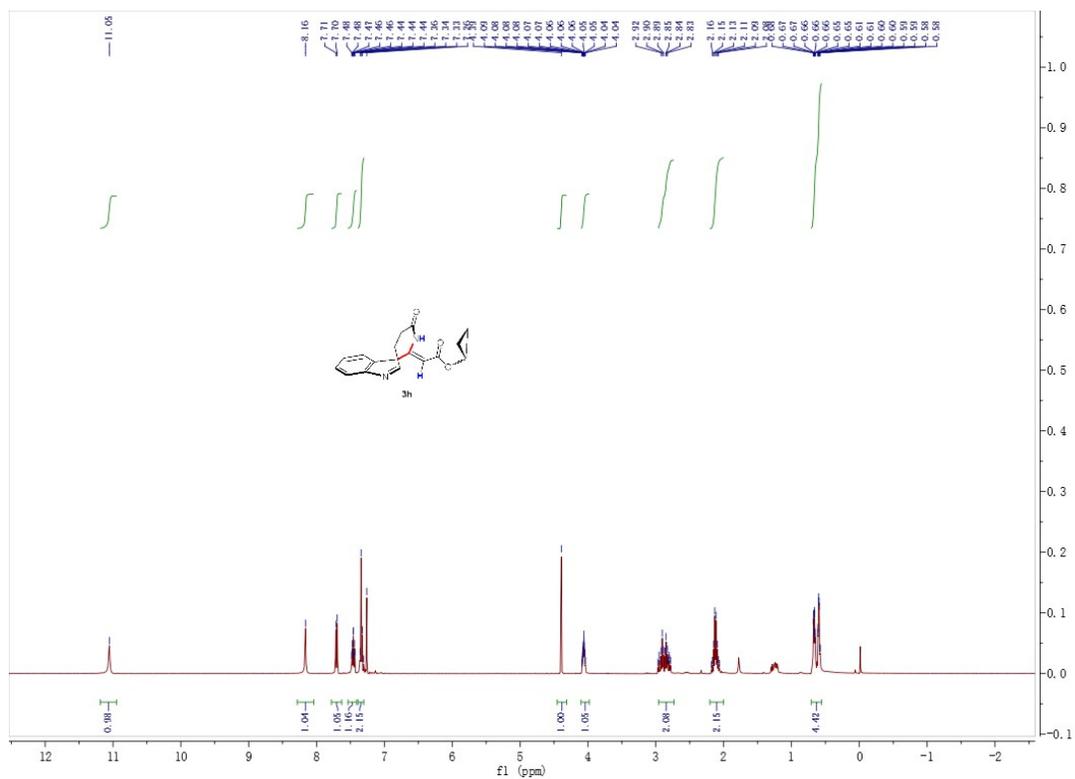
¹H NMR spectrum of compound **3g** (400 MHz, CDCl₃)



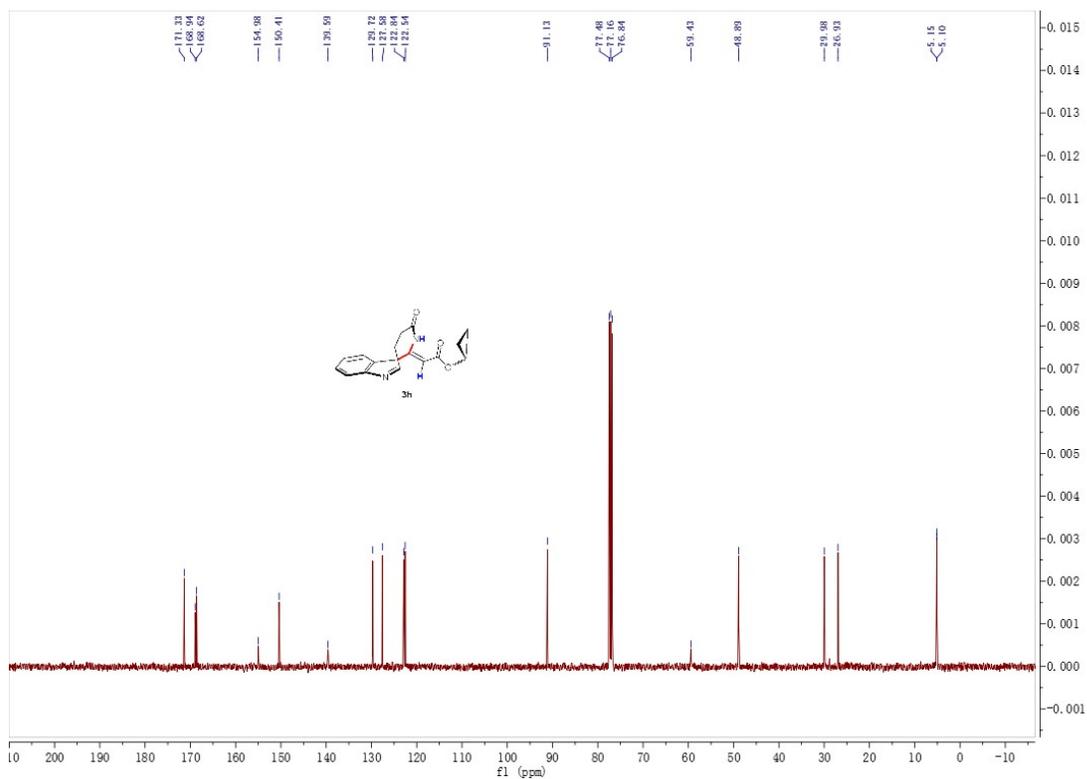
¹³C NMR spectrum of compound **3g** (100 MHz, CDCl₃)



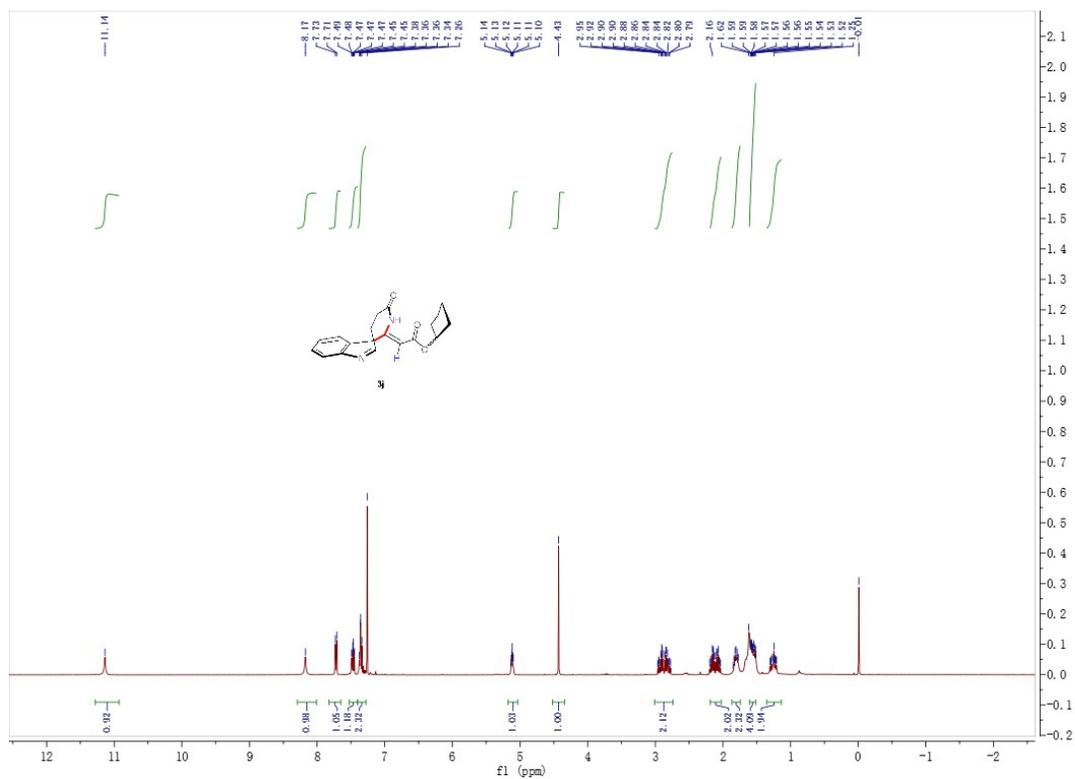
¹H NMR spectrum of compound **3h** (400 MHz, CDCl₃)



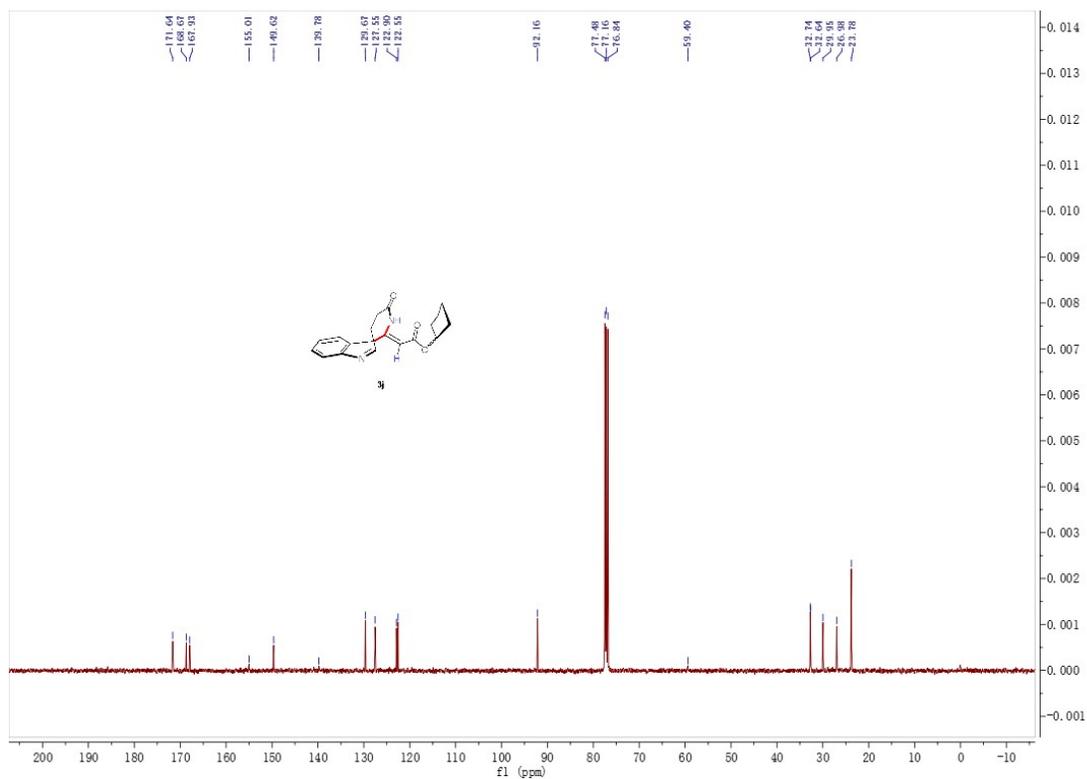
¹³C NMR spectrum of compound **3h** (100 MHz, CDCl₃)



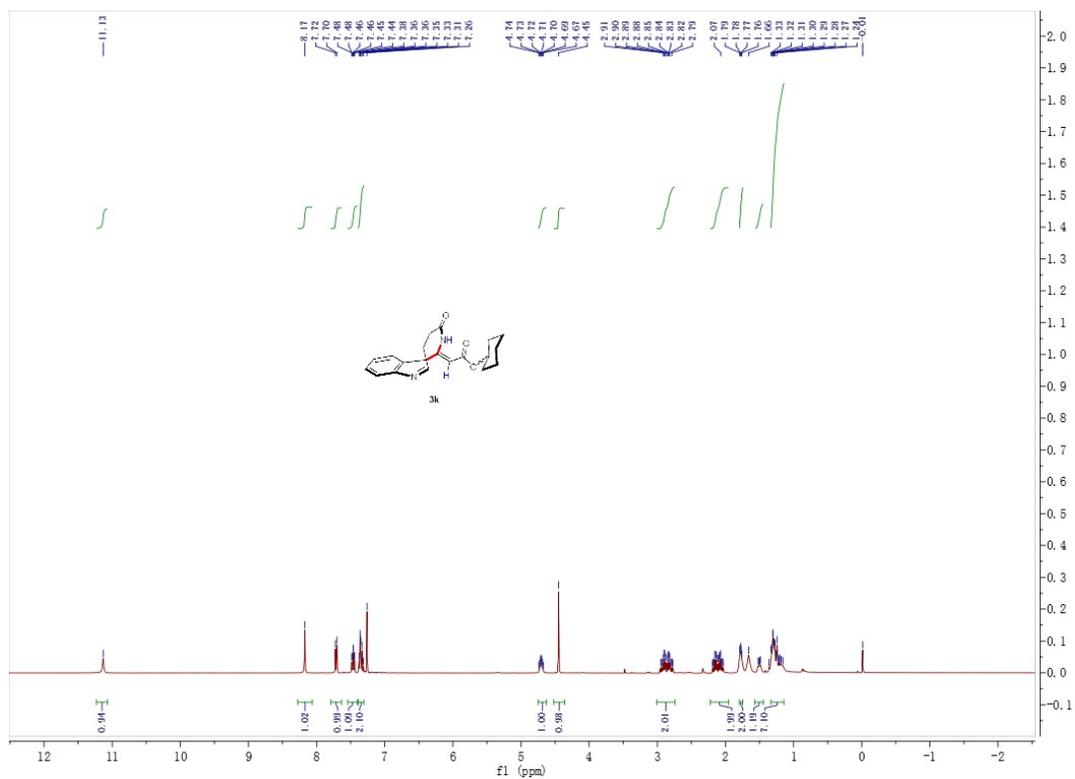
¹H NMR spectrum of compound **3j** (400 MHz, CDCl₃)



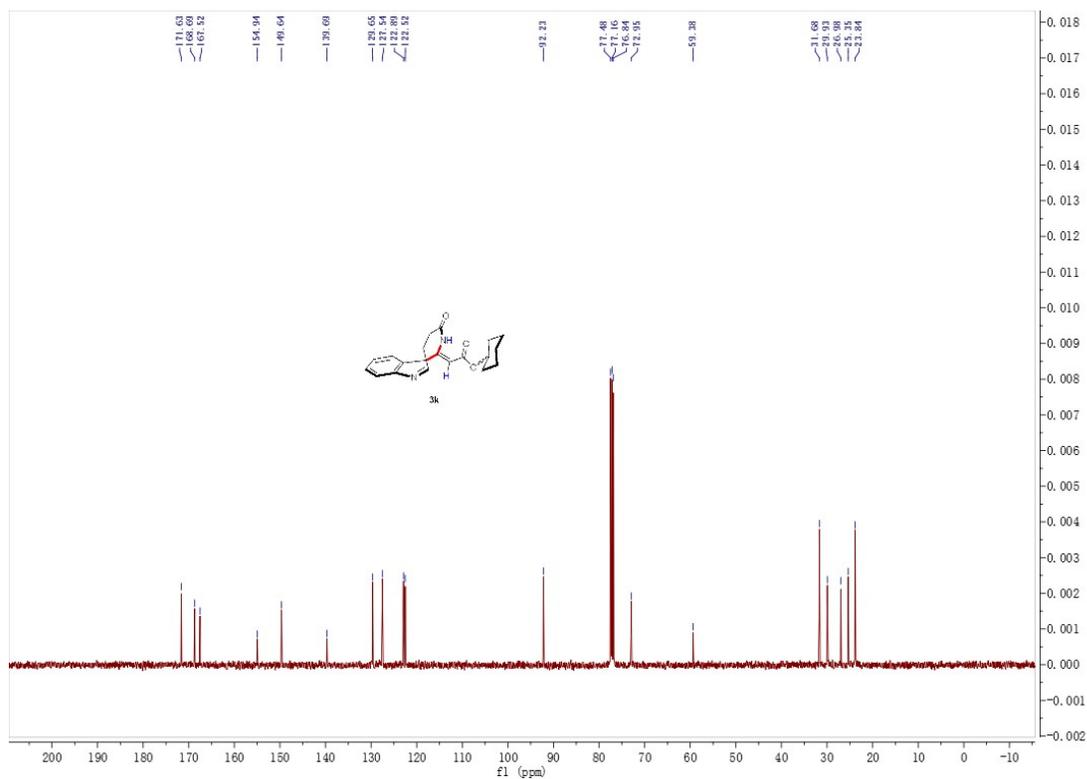
¹³C NMR spectrum of compound **3j** (100 MHz, CDCl₃)



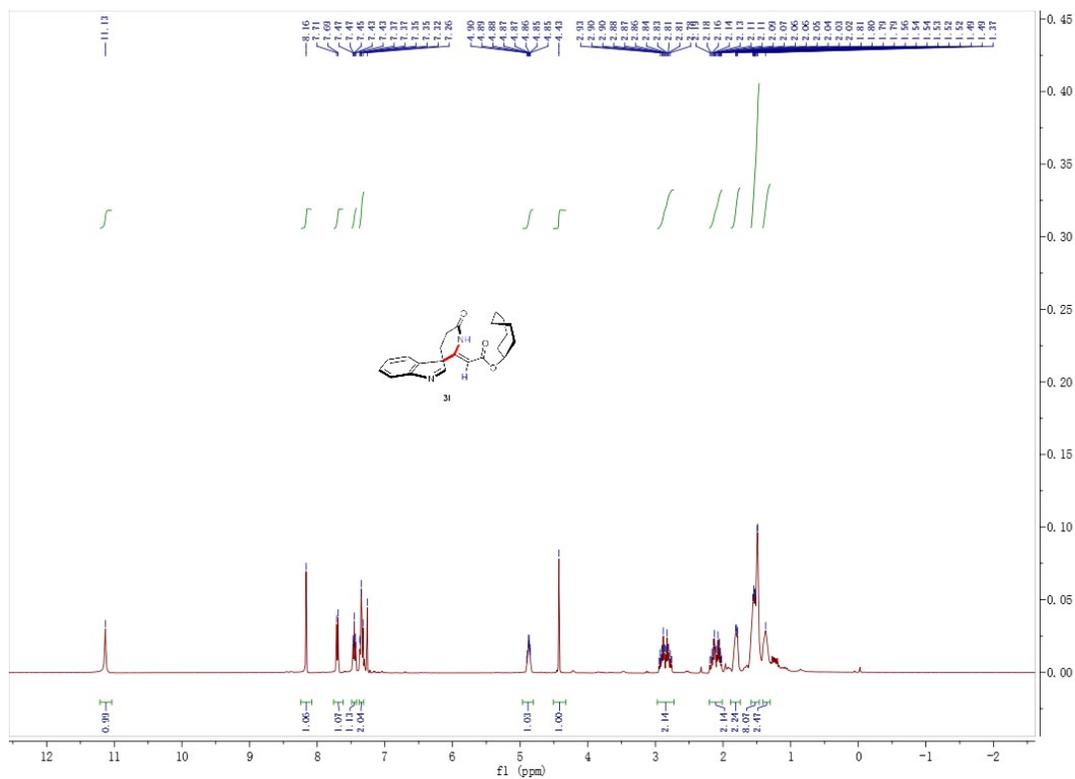
¹H NMR spectrum of compound **3k** (400 MHz, CDCl₃)



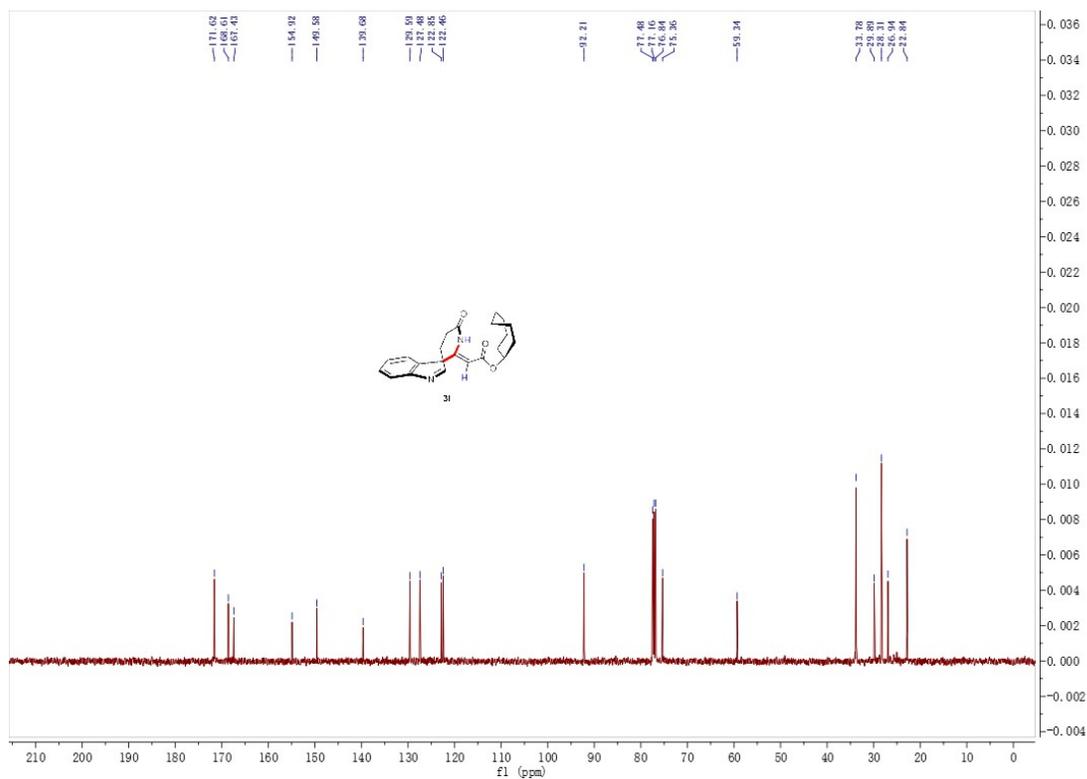
¹³C NMR spectrum of compound **3k** (100 MHz, CDCl₃)



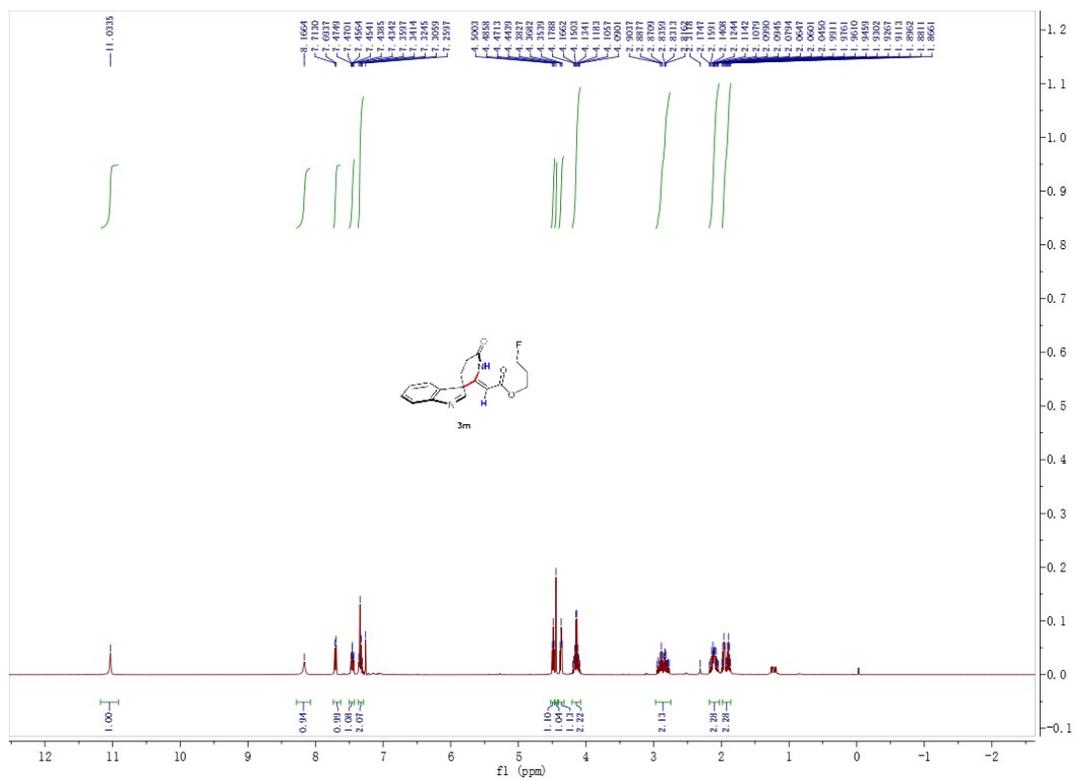
¹H NMR spectrum of compound 31 (400 MHz, CDCl₃)



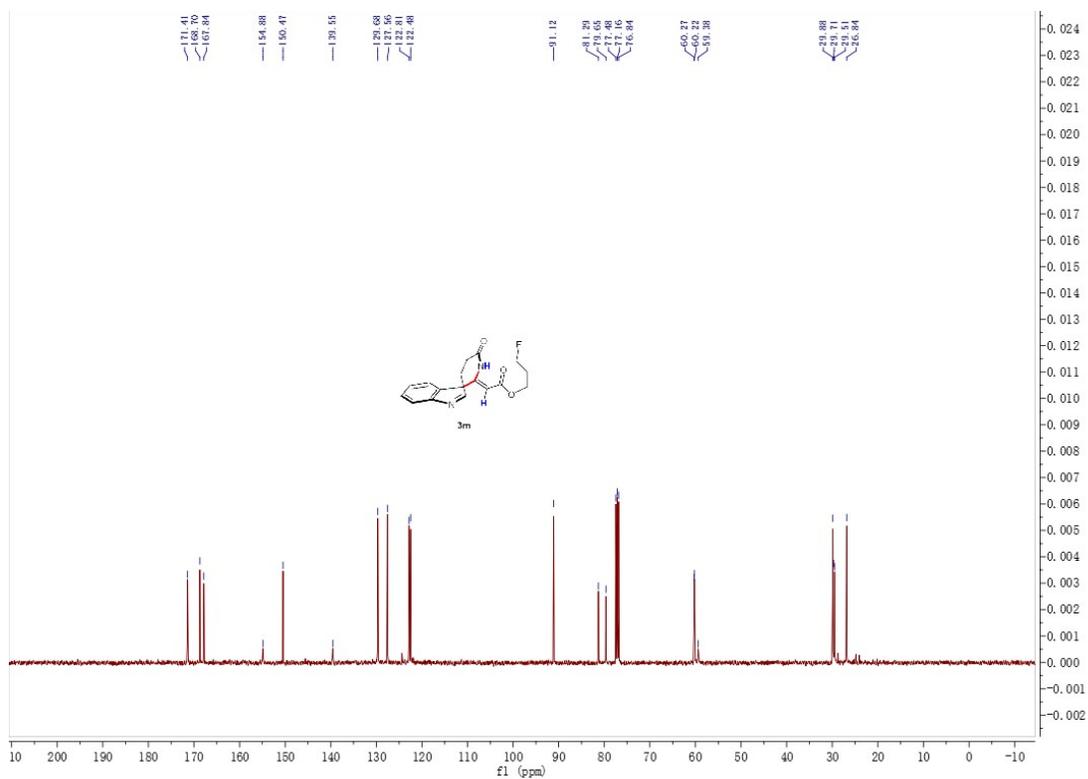
¹³C NMR spectrum of compound 31 (100 MHz, CDCl₃)



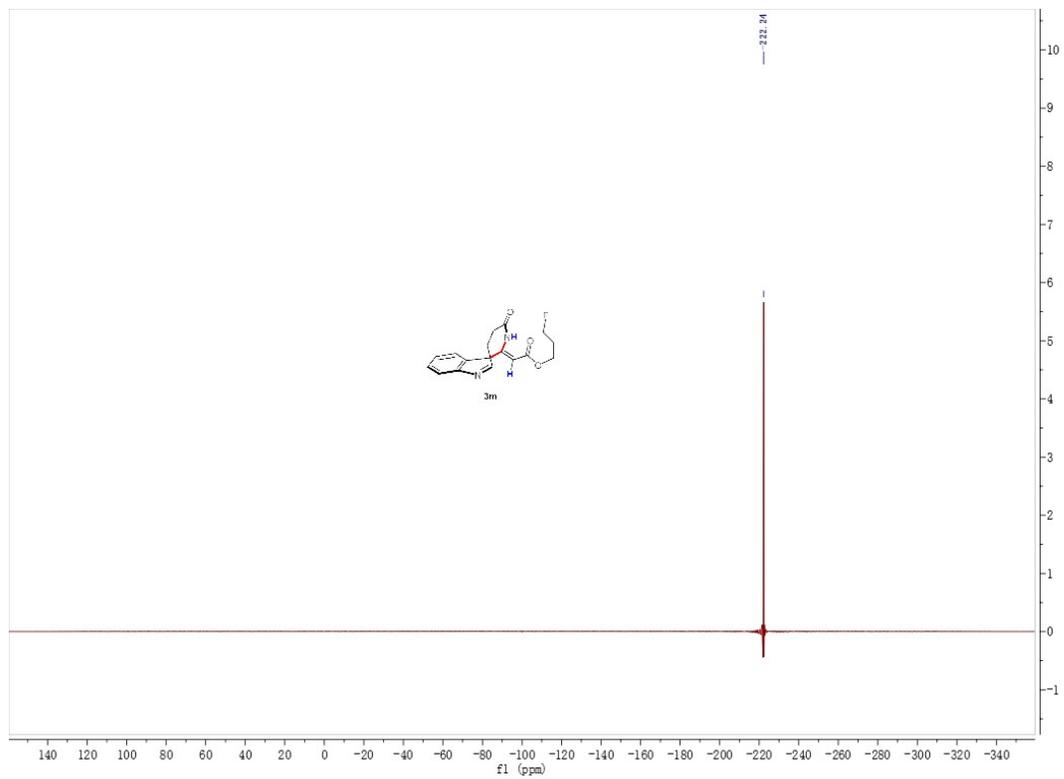
^1H NMR spectrum of compound **3m** (400 MHz, CDCl_3)



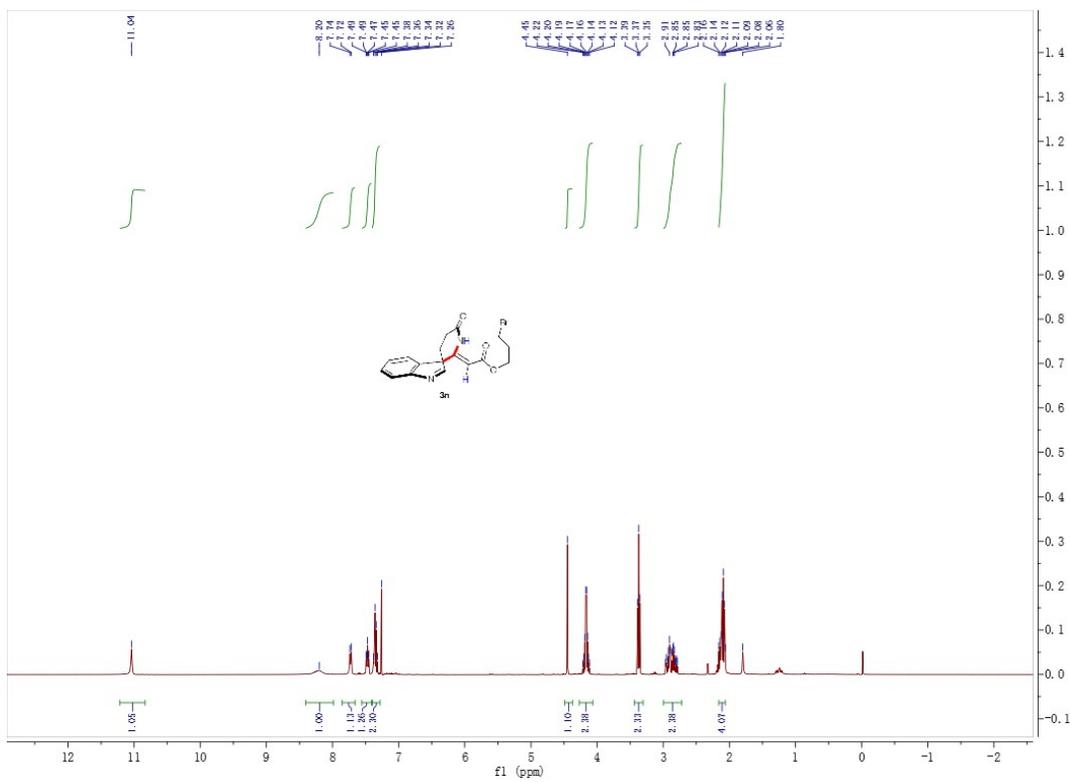
^{13}C NMR spectrum of compound **3m** (100 MHz, CDCl_3)



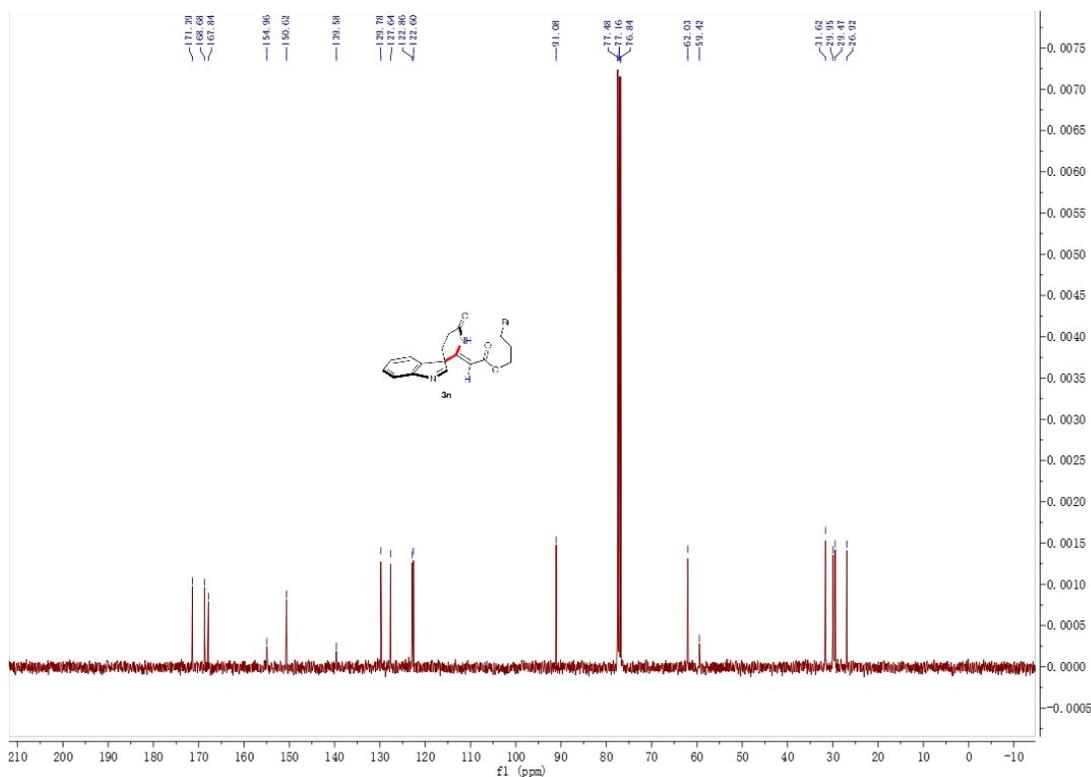
¹⁹F NMR spectrum of compound **3m (379 MHz, CDCl₃)**



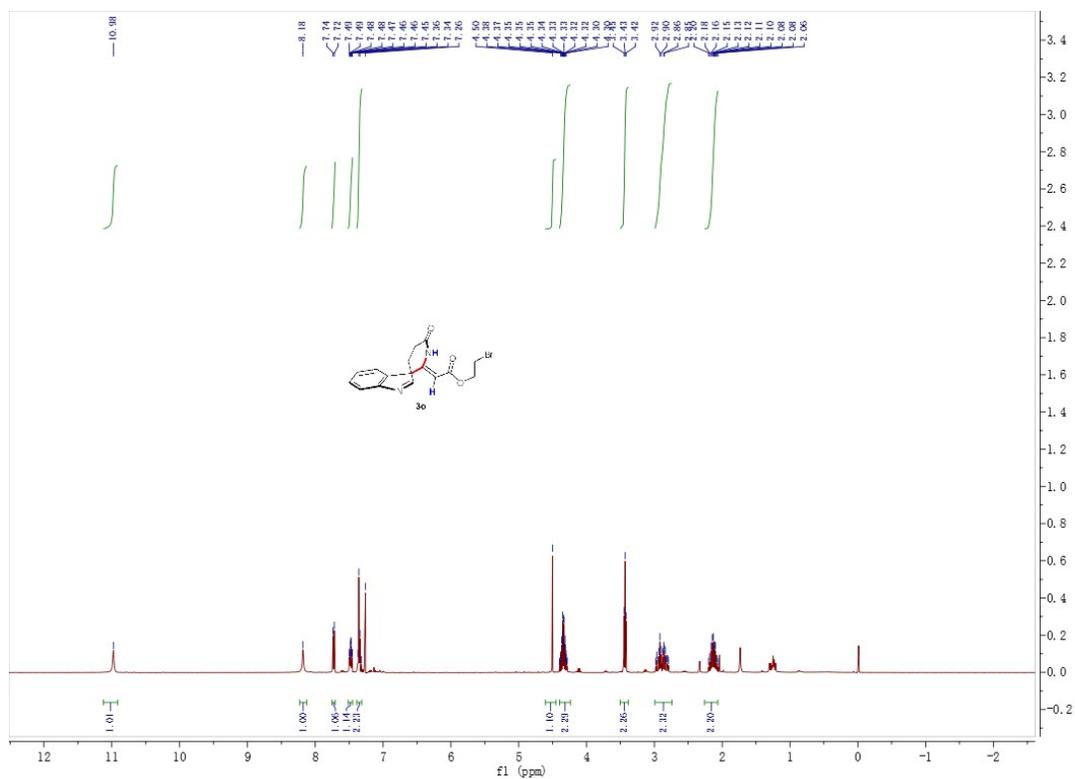
^1H NMR spectrum of compound **3n** (400 MHz, CDCl_3)



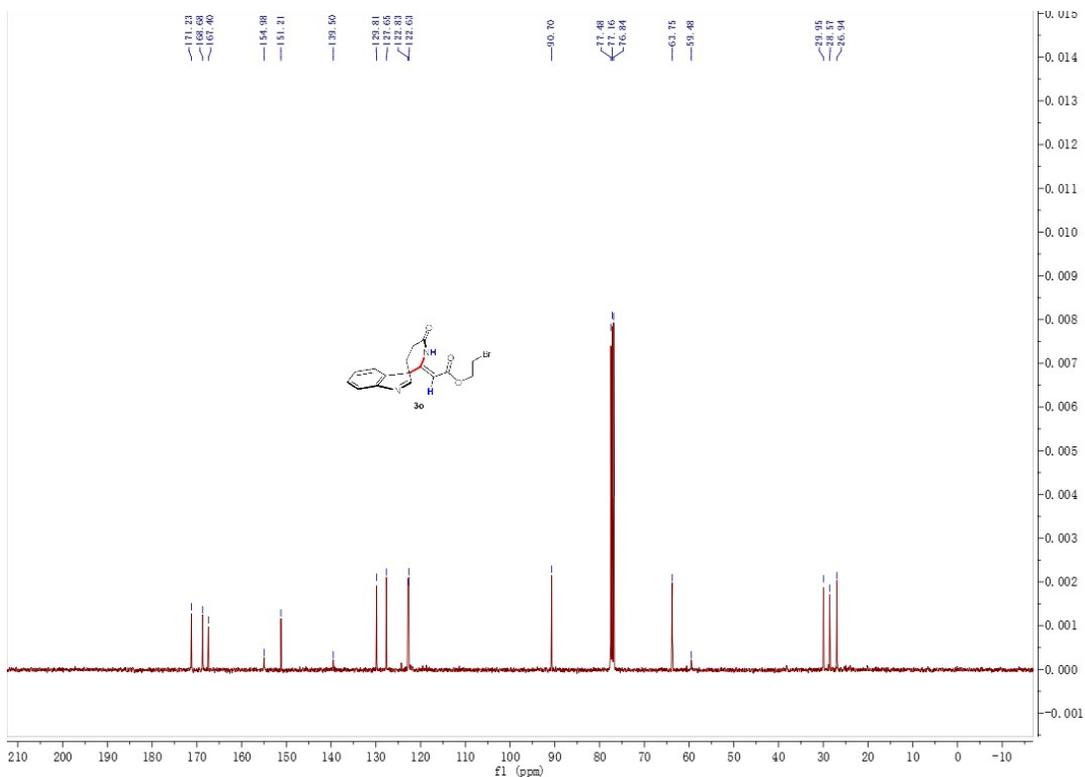
^{13}C NMR spectrum of compound **3n** (100 MHz, CDCl_3)



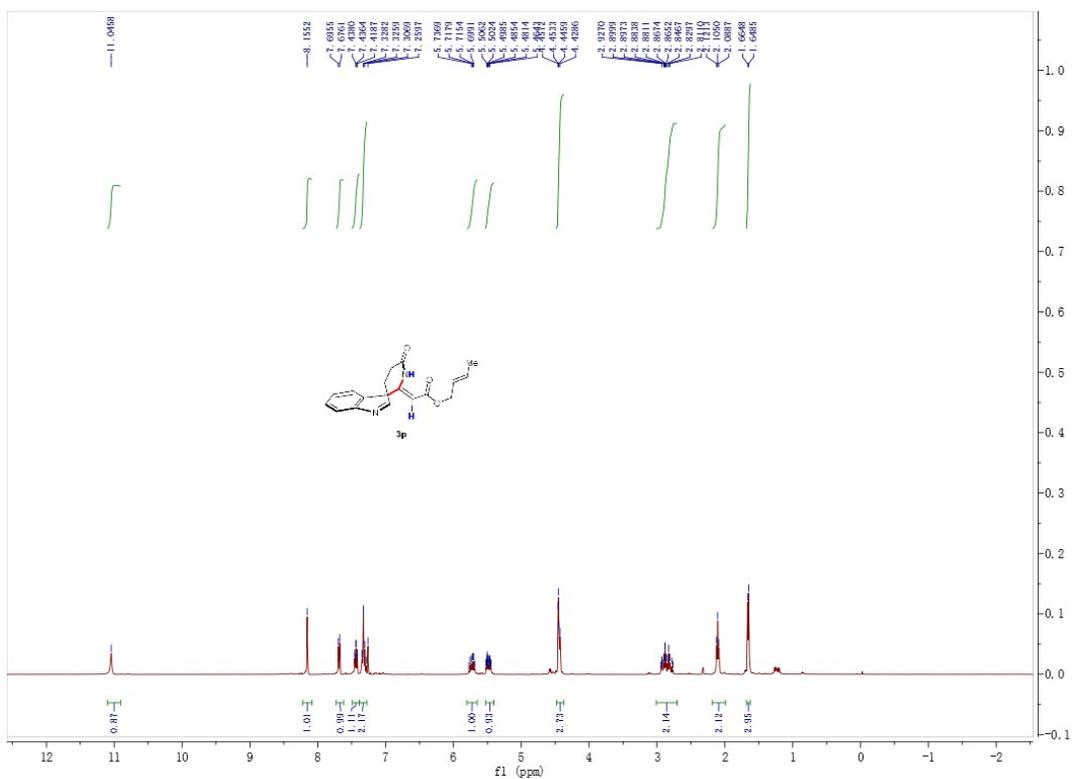
¹H NMR spectrum of compound 3o (400 MHz, CDCl₃)



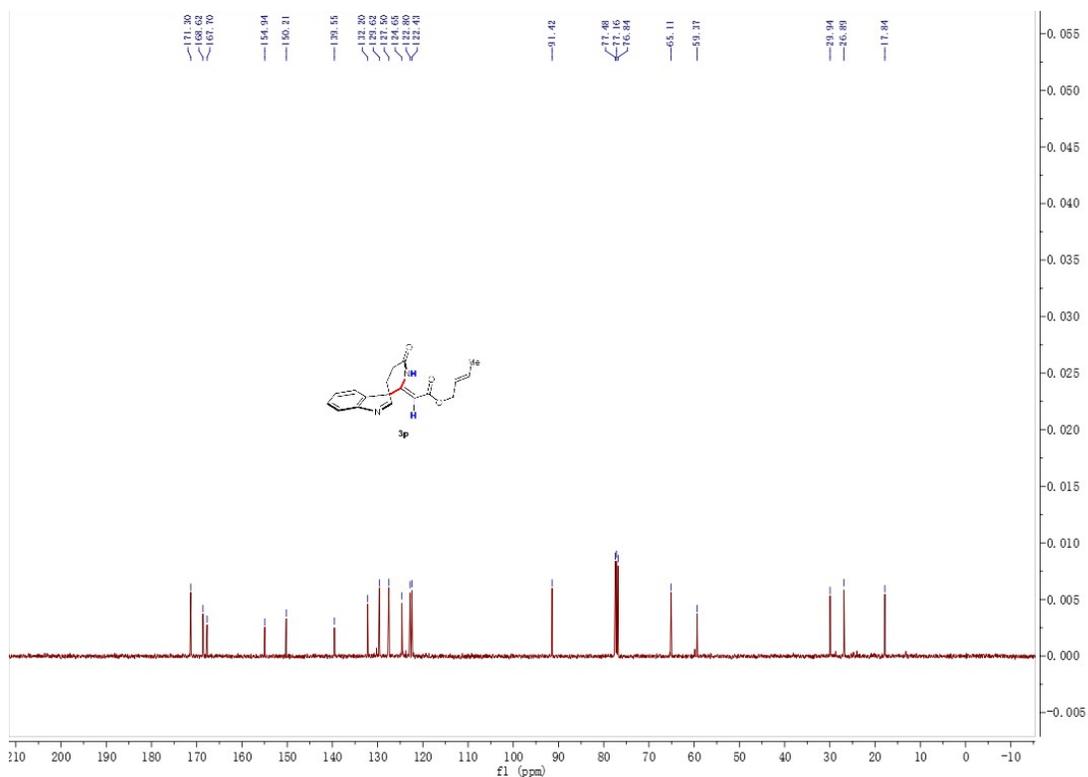
¹³C NMR spectrum of compound 3o (100 MHz, CDCl₃)



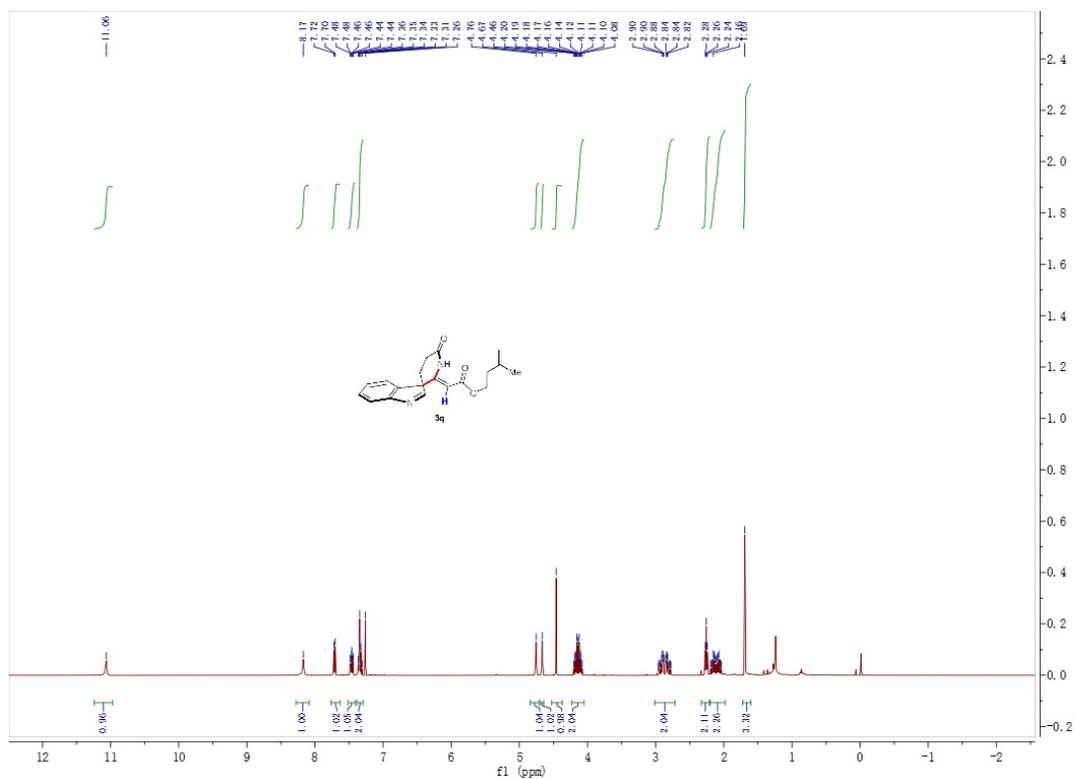
^1H NMR spectrum of compound **3p** (400 MHz, CDCl_3)



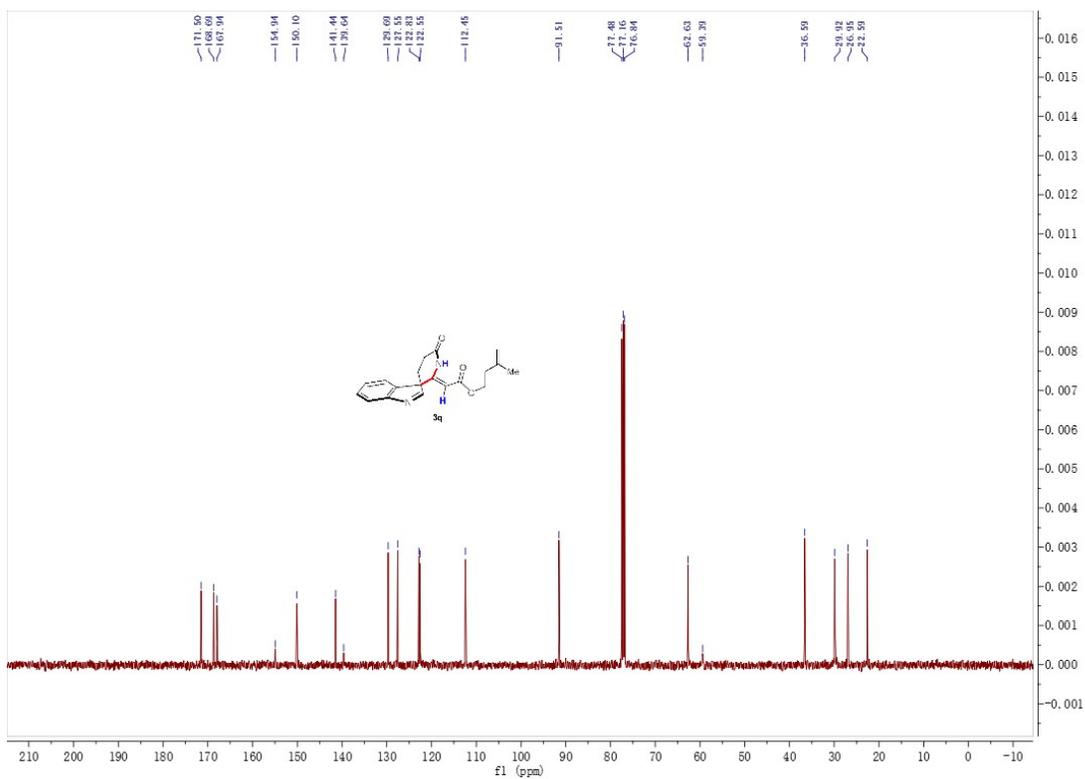
^{13}C NMR spectrum of compound **3p** (100 MHz, CDCl_3)



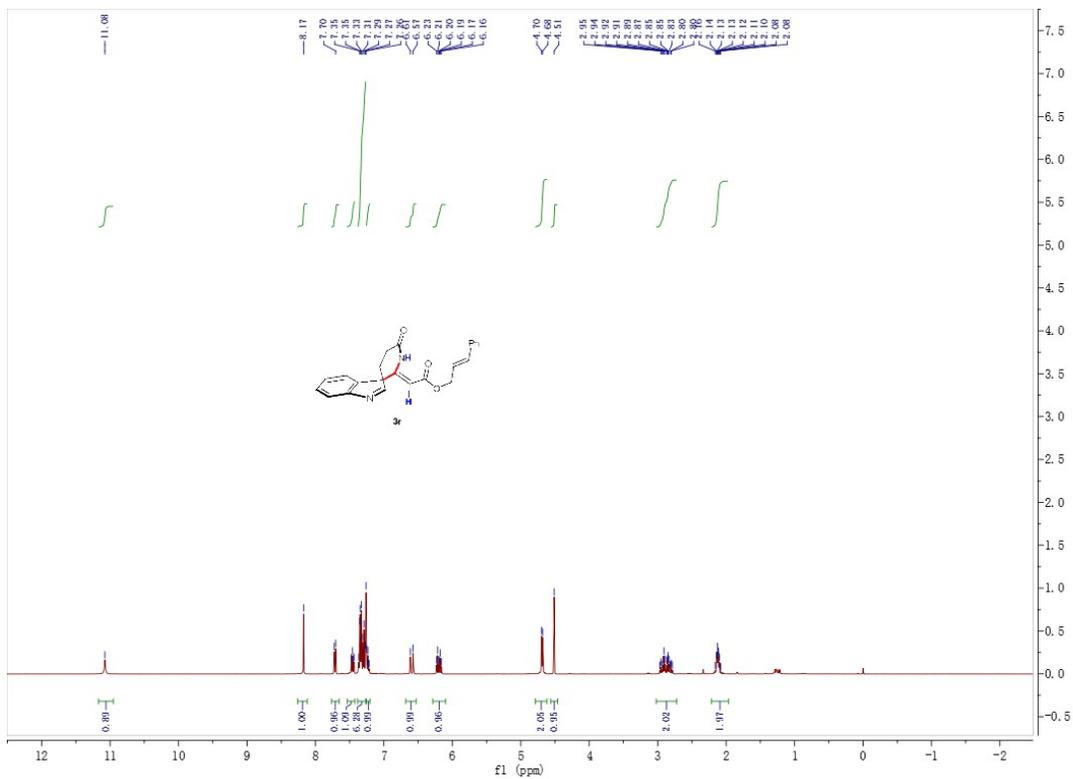
¹H NMR spectrum of compound 3q (400 MHz, CDCl₃)



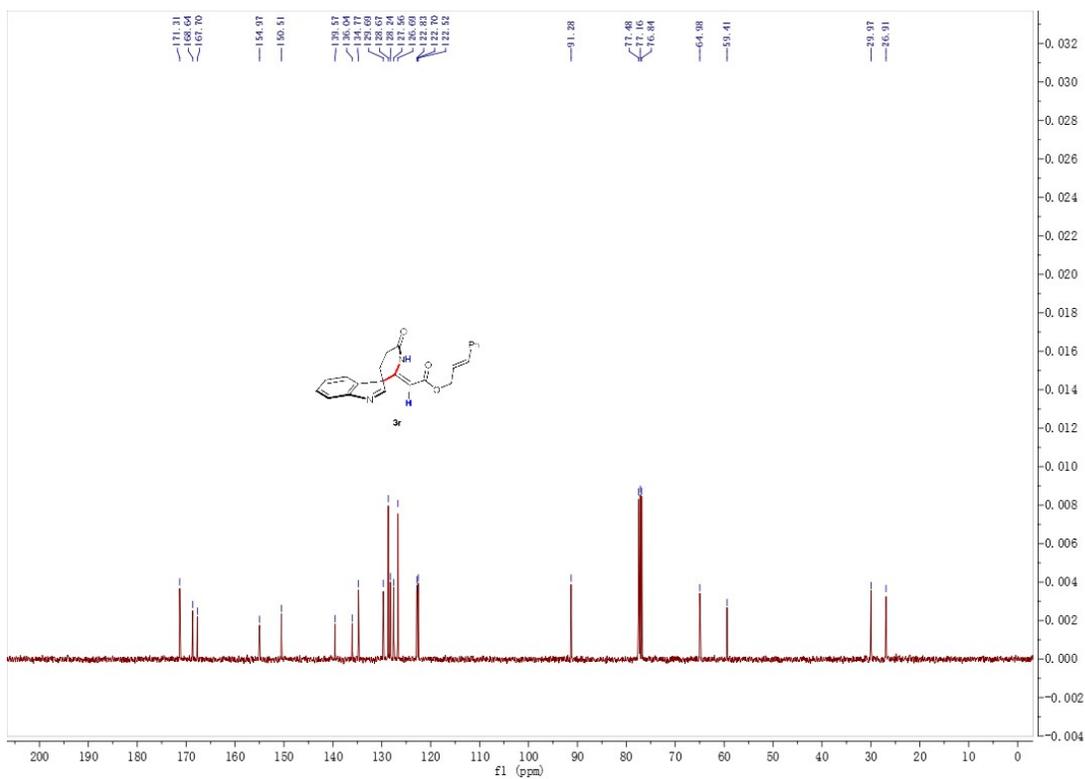
^{13}C NMR spectrum of compound **3q** (100 MHz, CDCl_3)



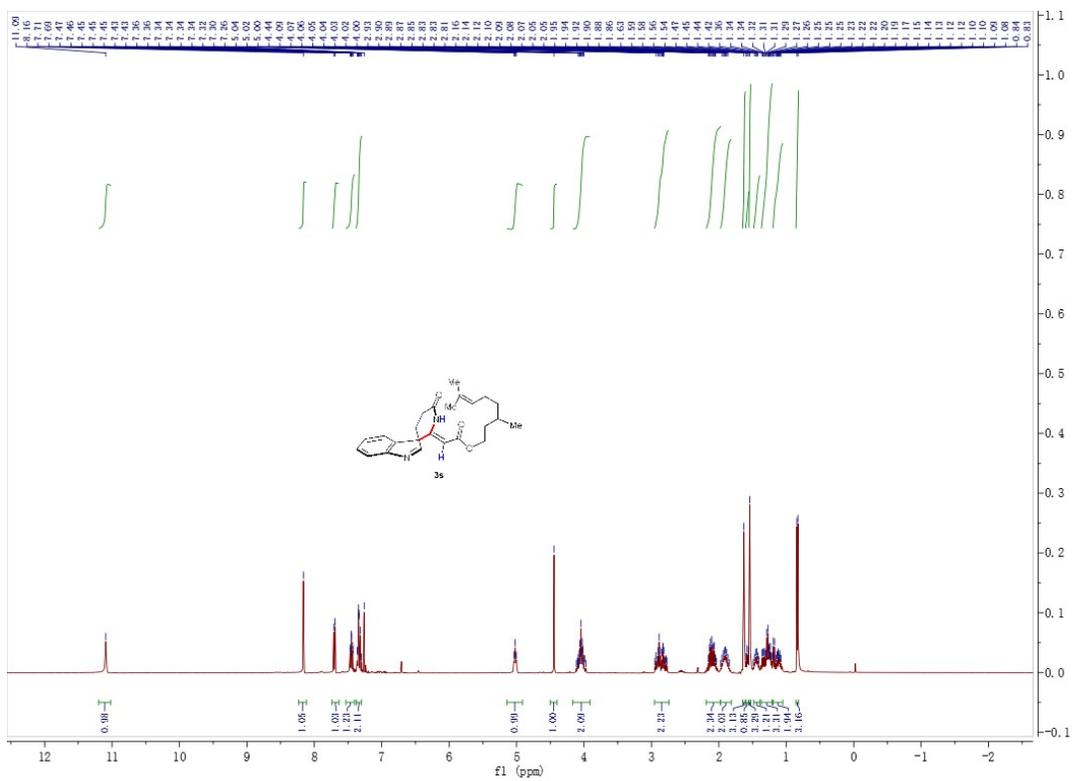
^1H NMR spectrum of compound **3r** (400 MHz, CDCl_3)



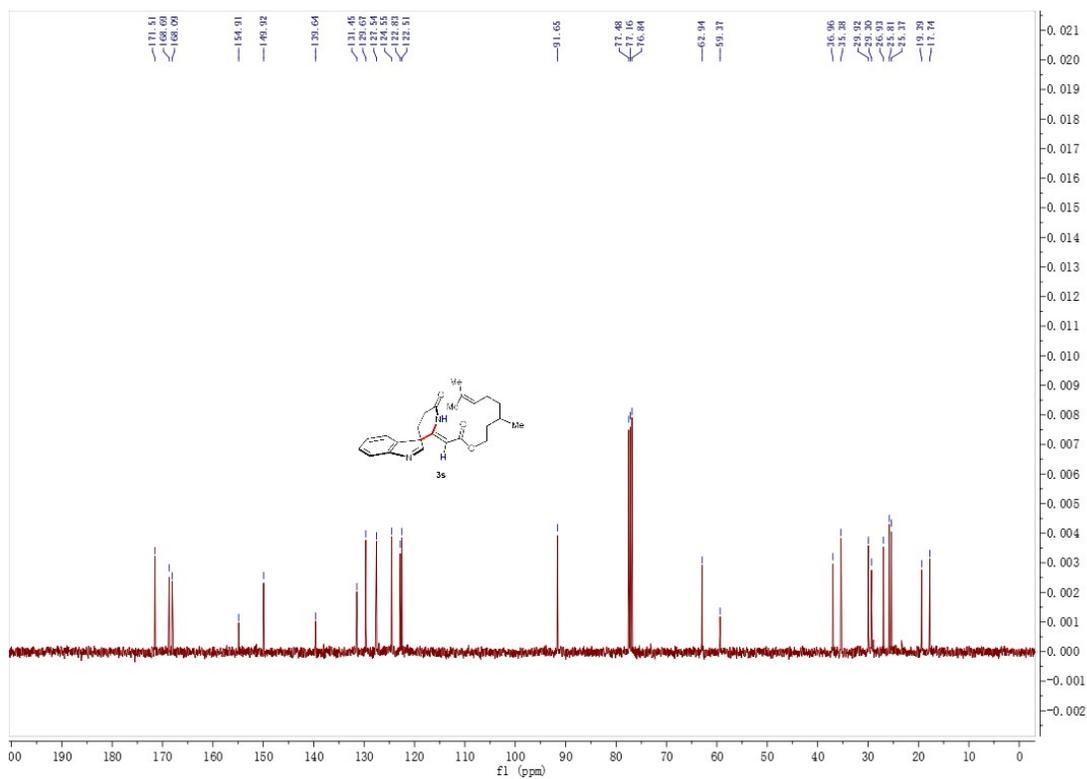
^{13}C NMR spectrum of compound **3r** (100 MHz, CDCl_3)



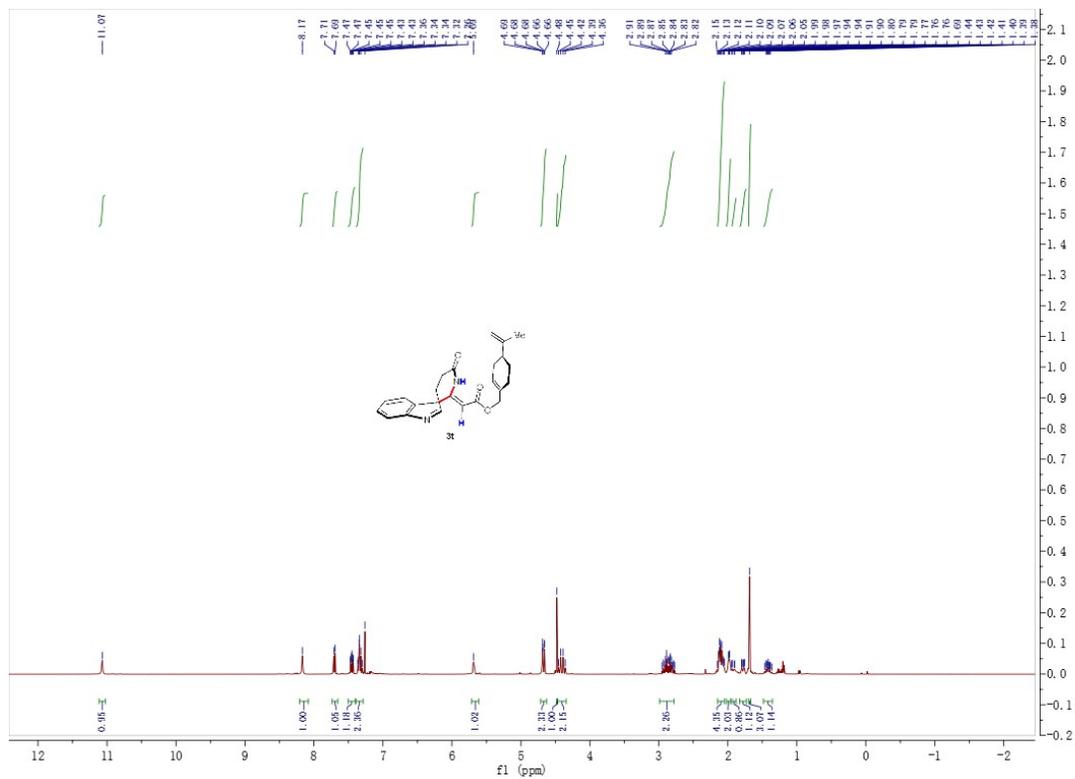
^1H NMR spectrum of compound **3s** (400 MHz, CDCl_3)



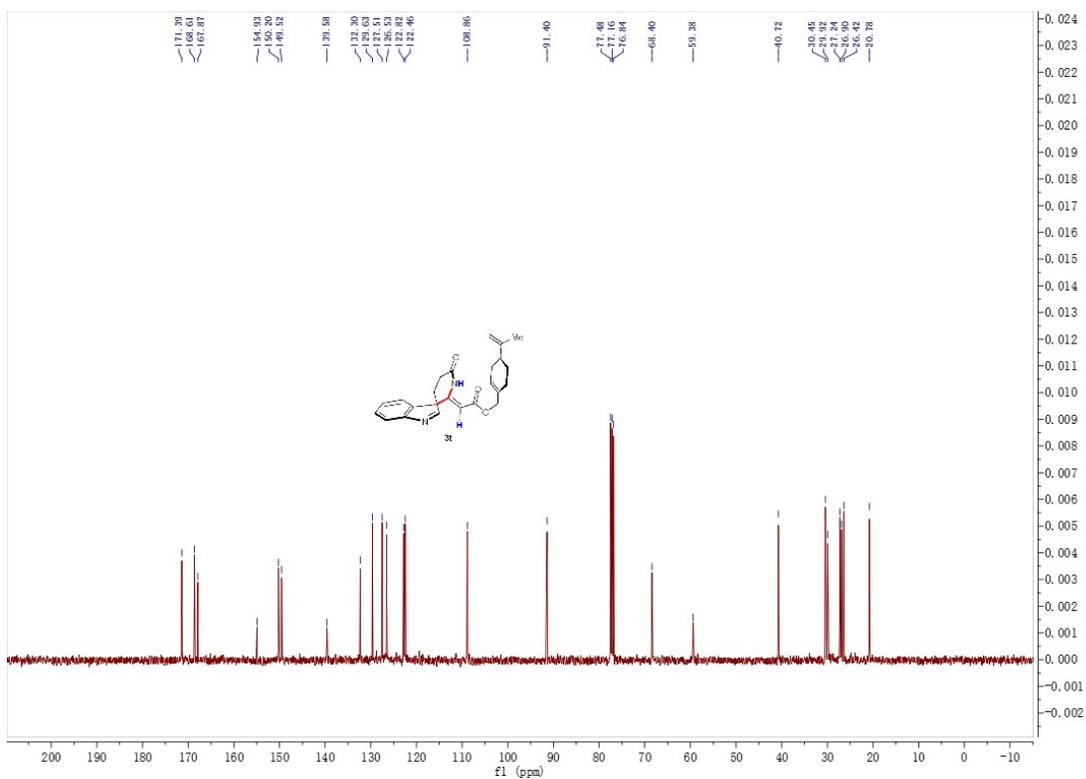
^{13}C NMR spectrum of compound **3s** (100 MHz, CDCl_3)



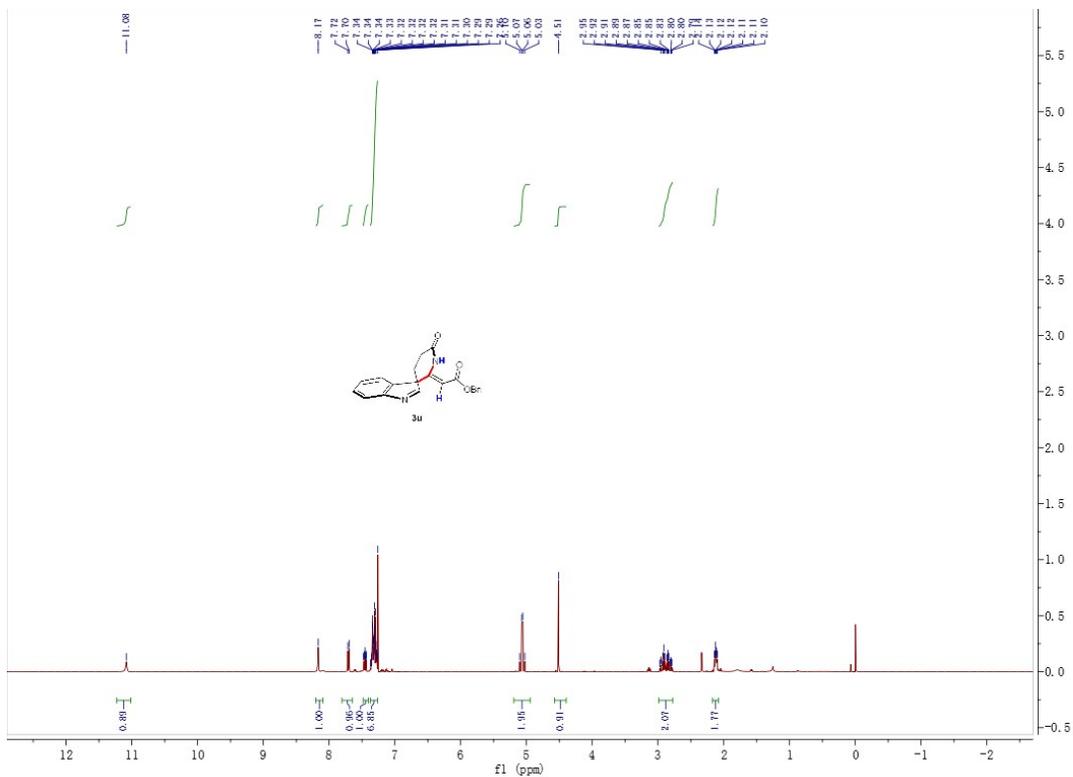
^1H NMR spectrum of compound **3t** (400 MHz, CDCl_3)



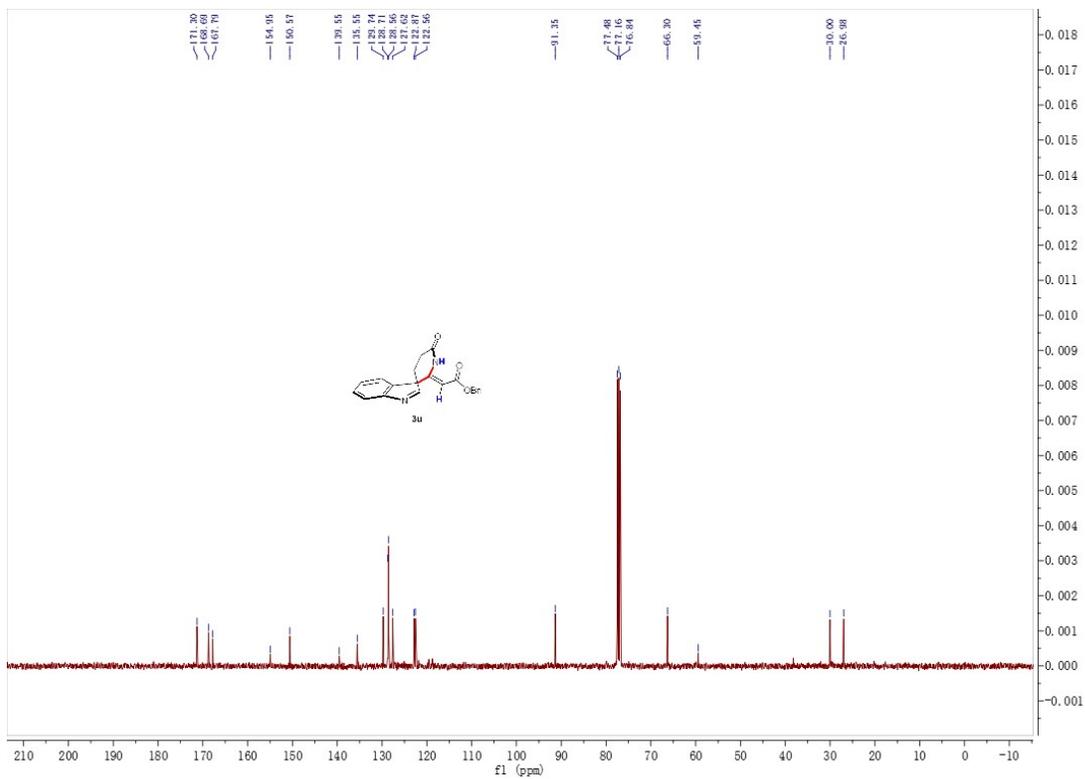
^{13}C NMR spectrum of compound **3t (100 MHz, CDCl_3)**



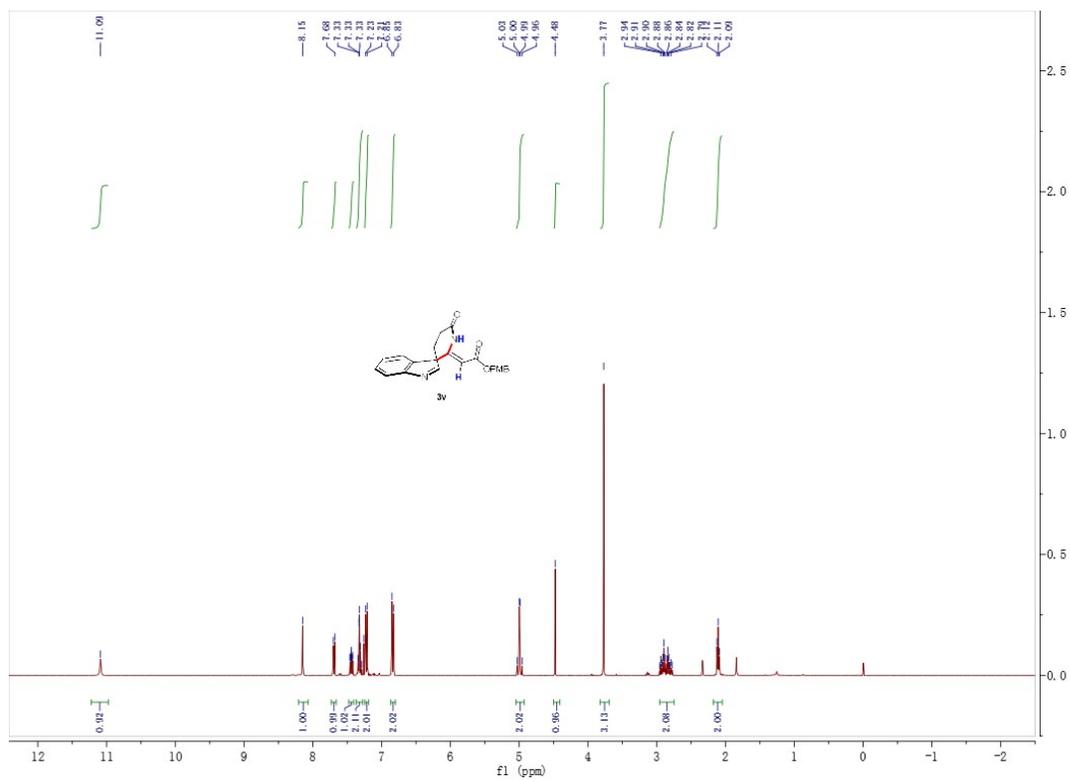
^1H NMR spectrum of compound **3u (400 MHz, CDCl_3)**



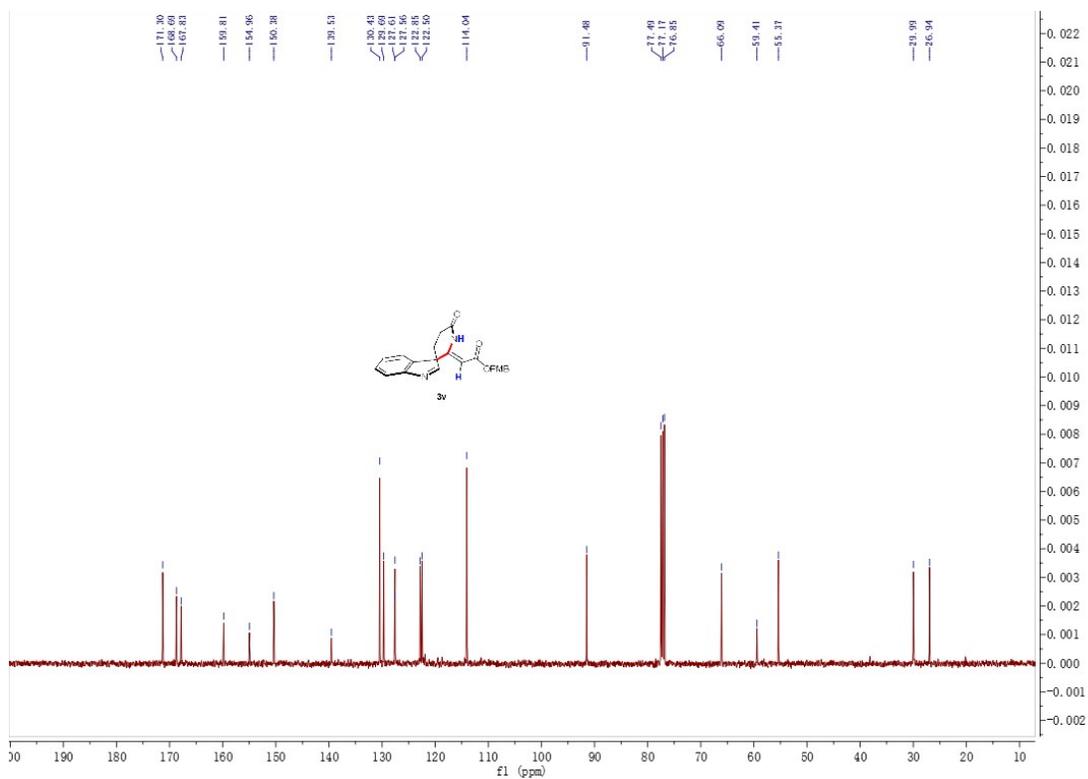
¹³C NMR spectrum of compound 3u (100 MHz, CDCl₃)



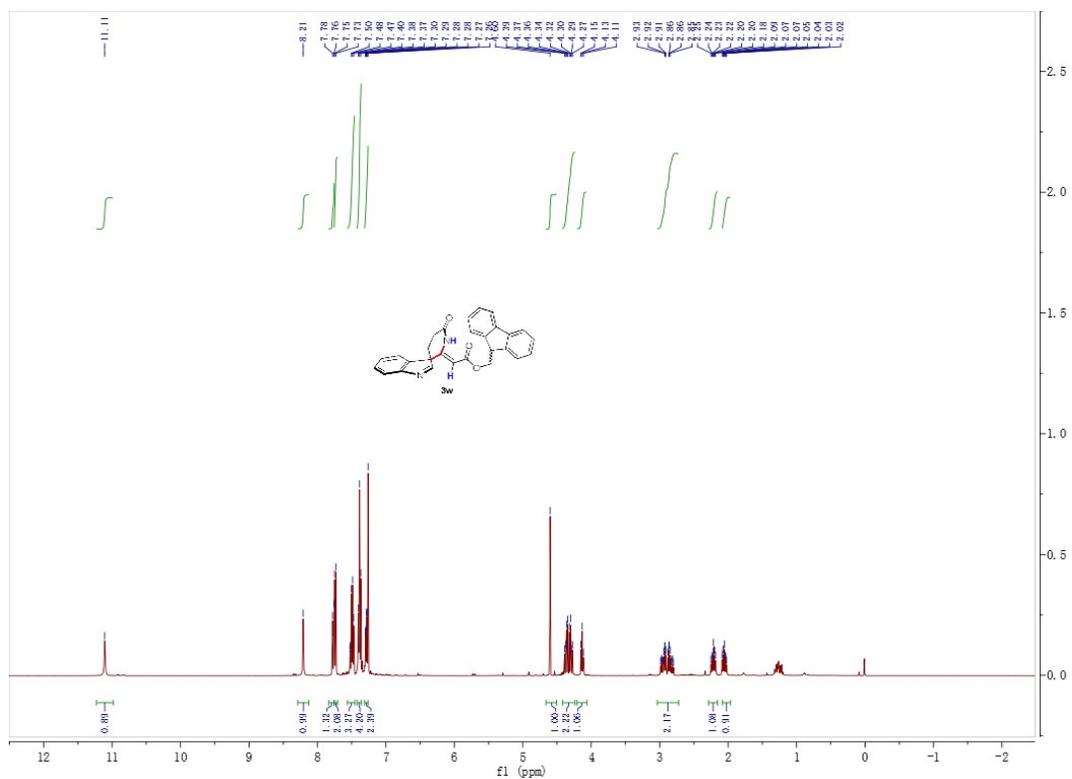
¹H NMR spectrum of compound 3v (400 MHz, CDCl₃)



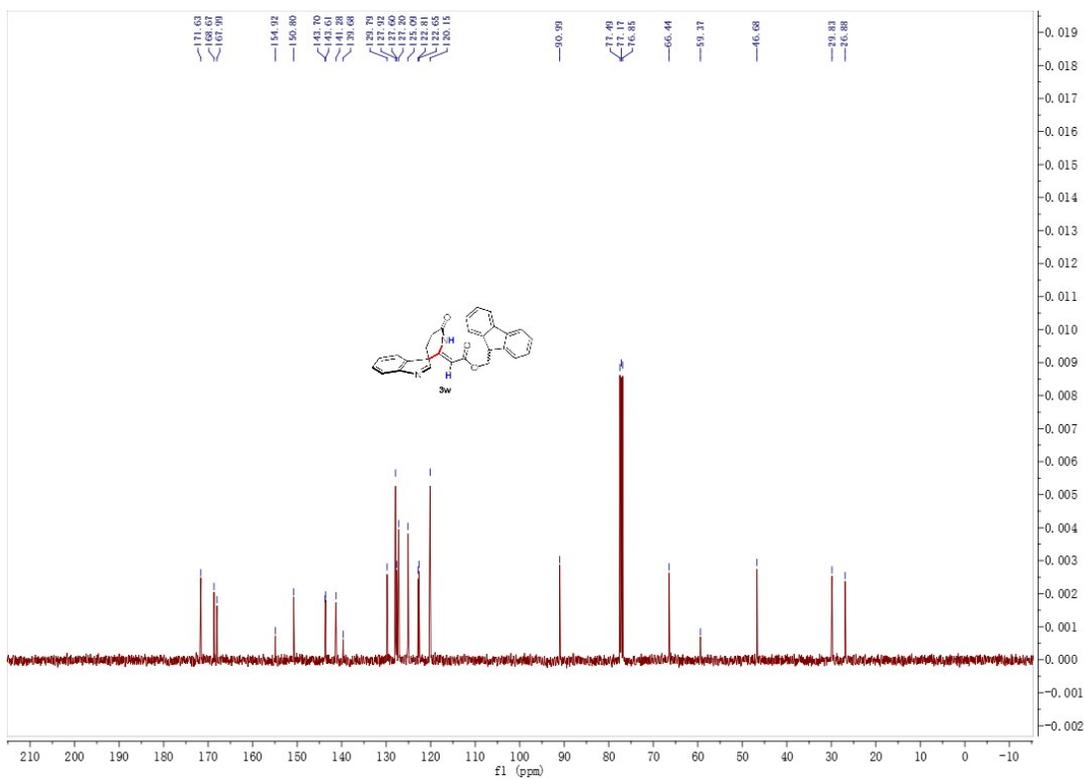
¹³C NMR spectrum of compound 3v (100 MHz, CDCl₃)



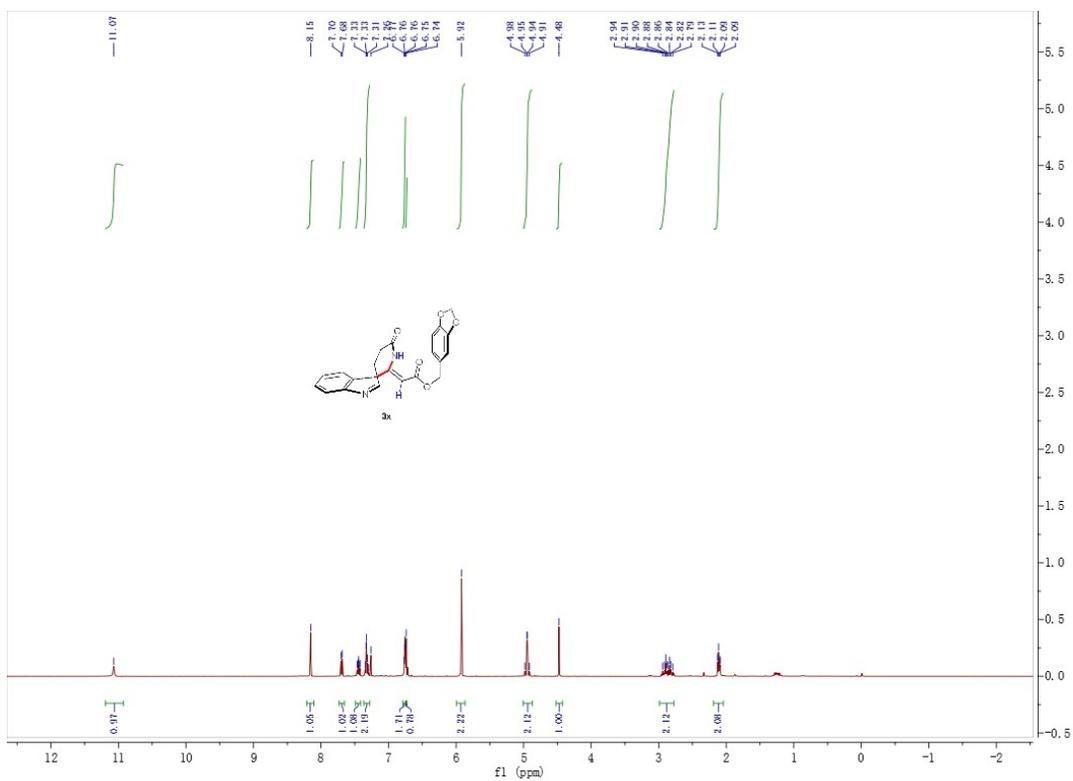
¹H NMR spectrum of compound 3w (400 MHz, CDCl₃)



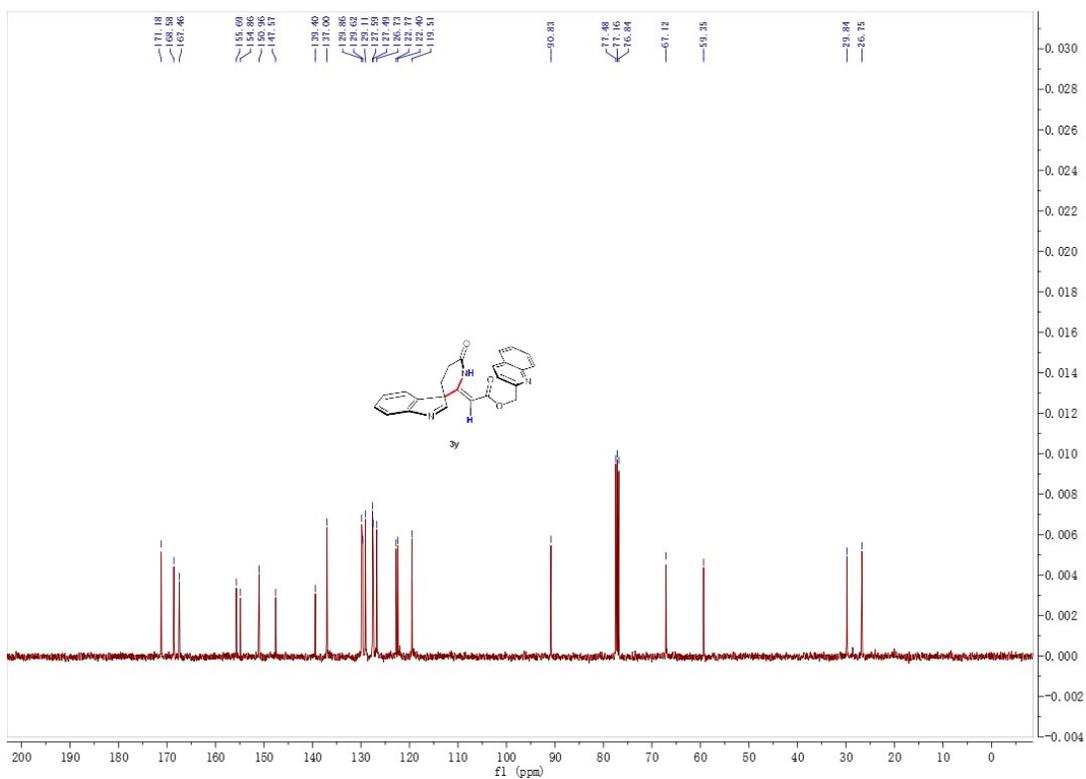
^{13}C NMR spectrum of compound **3w** (100 MHz, CDCl_3)



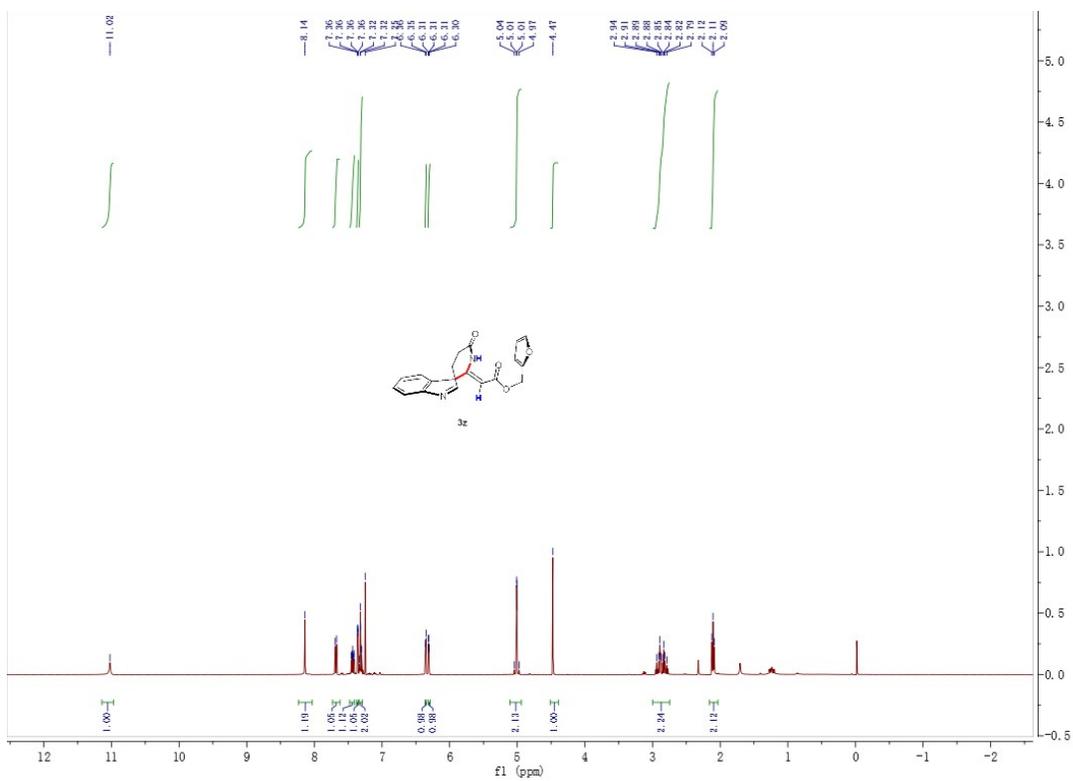
^1H NMR spectrum of compound **3x** (400 MHz, CDCl_3)



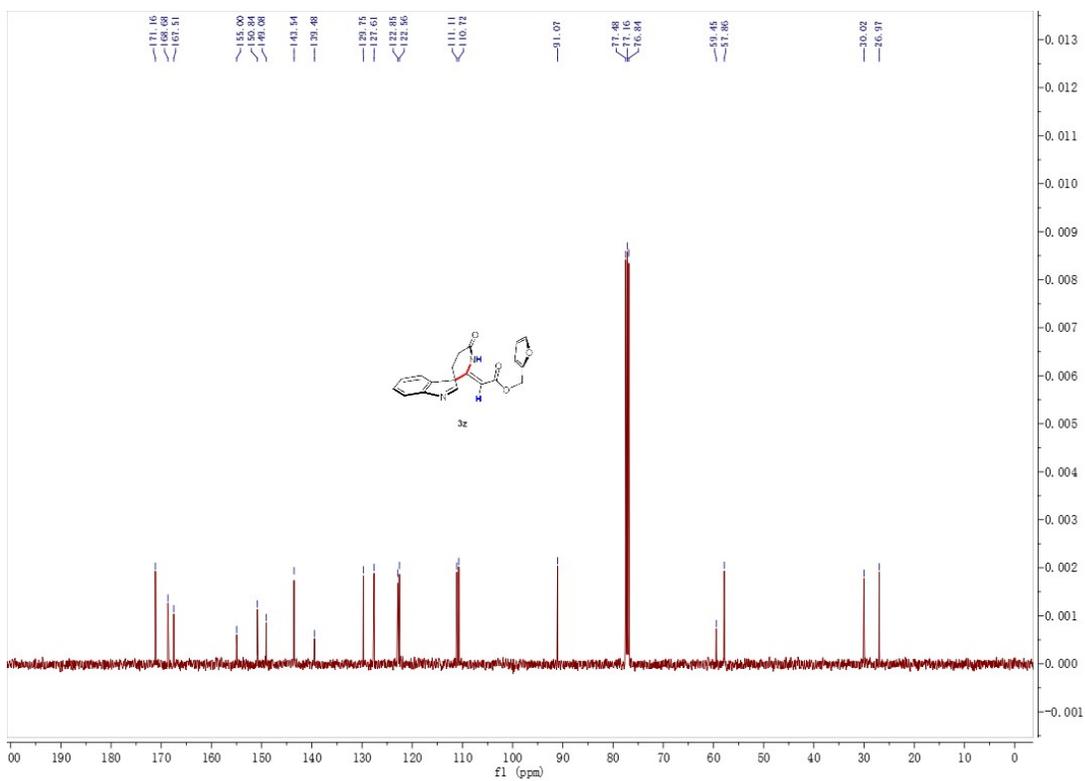
¹³C NMR spectrum of compound 3y (100 MHz, CDCl₃)



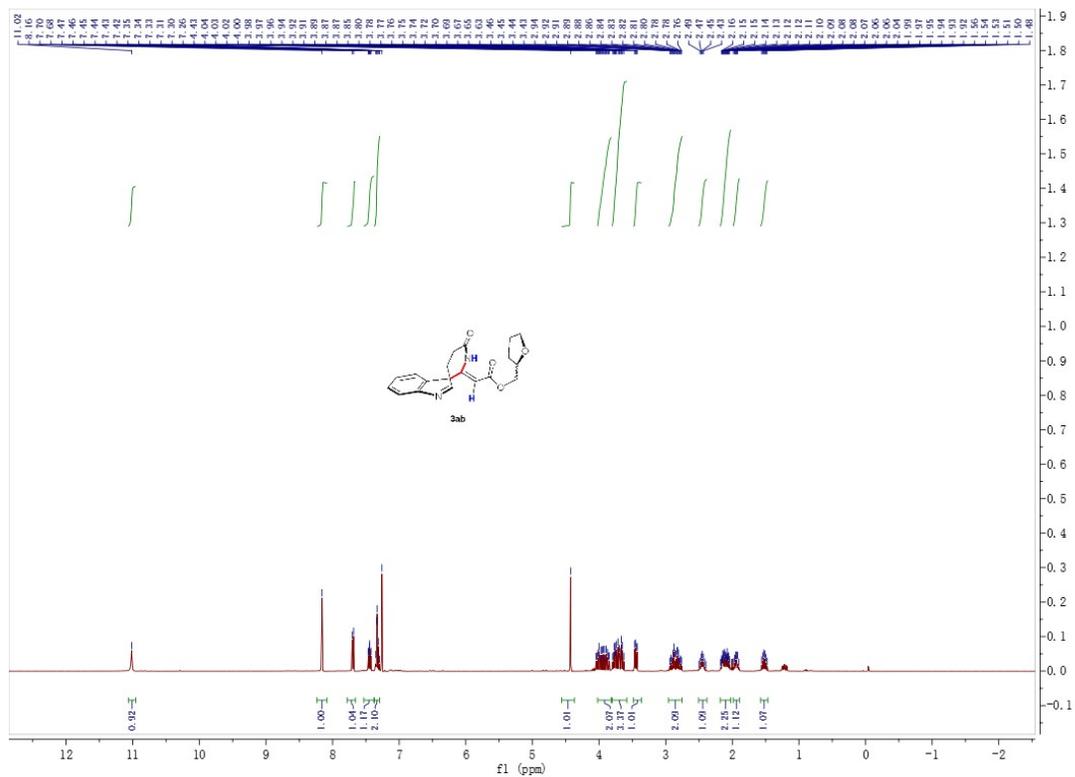
¹H NMR spectrum of compound 3z (400 MHz, CDCl₃)



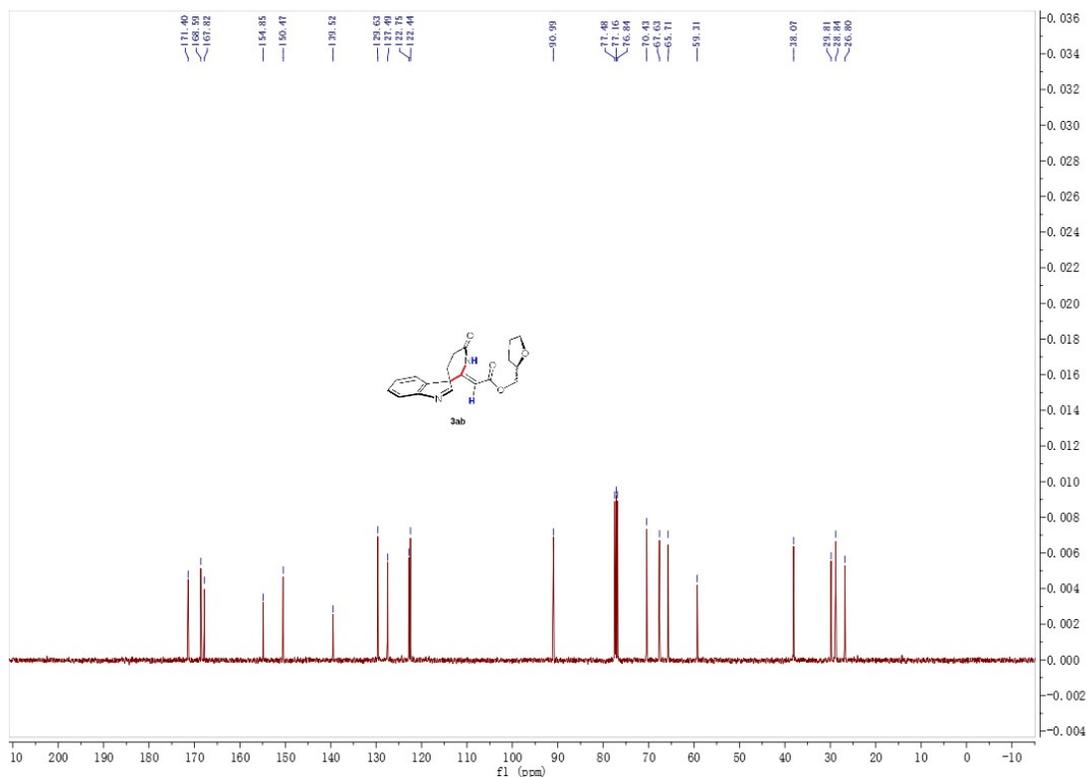
¹³C NMR spectrum of compound 3z (100 MHz, CDCl₃)



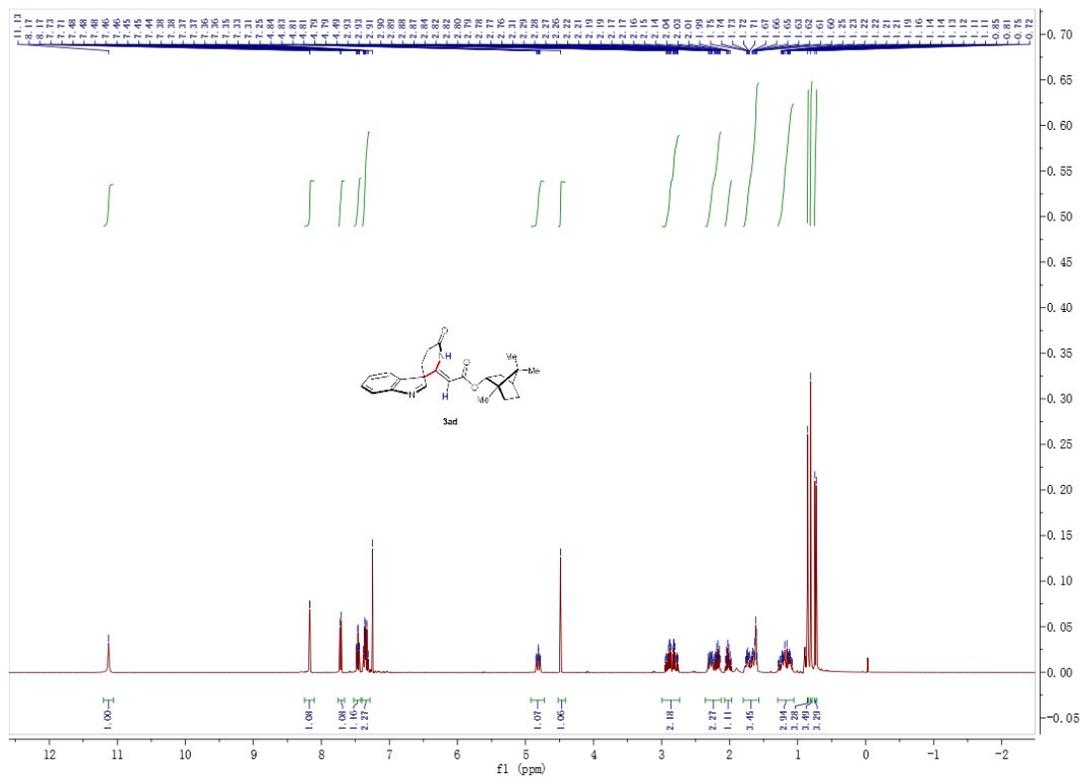
¹H NMR spectrum of compound 3ab (400 MHz, CDCl₃)



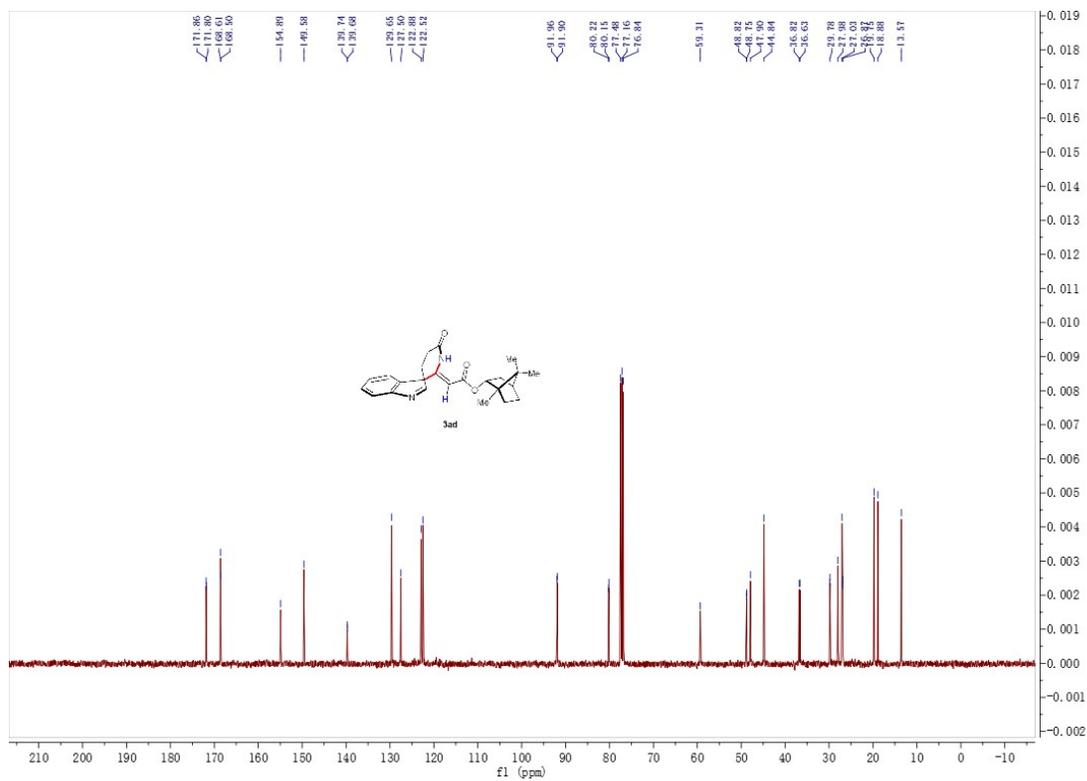
¹³C NMR spectrum of compound 3ab (100 MHz, CDCl₃)



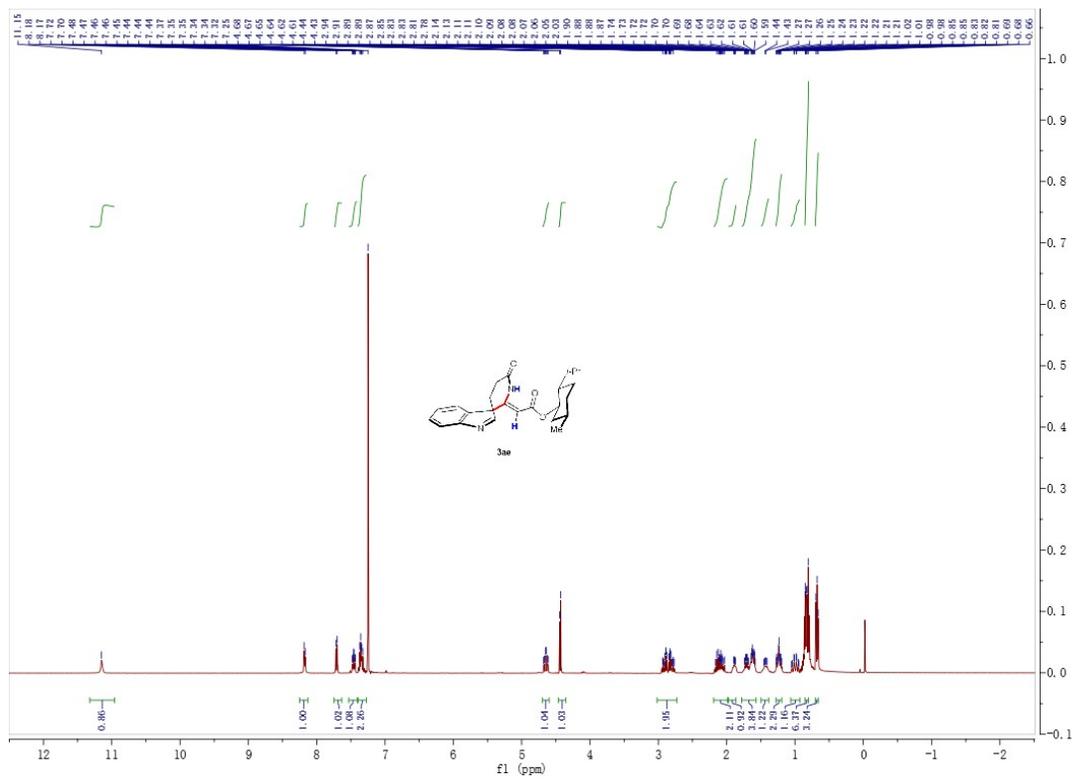
¹H NMR spectrum of compound **3ad** (400 MHz, CDCl₃)



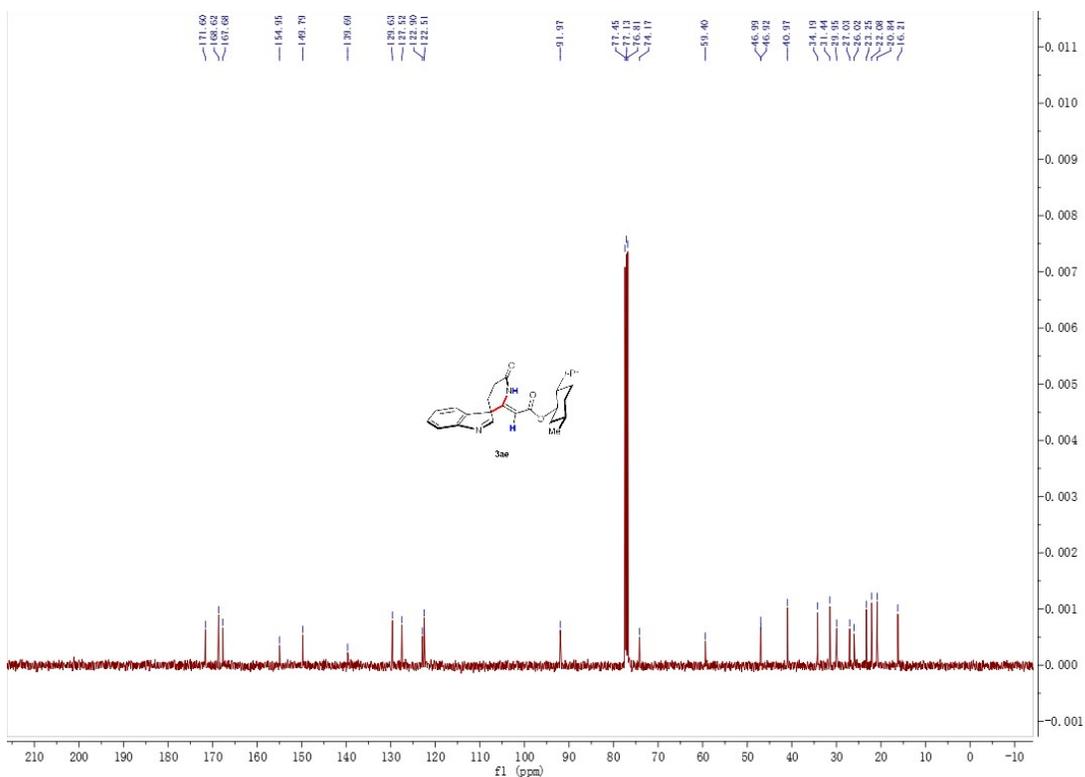
¹³C NMR spectrum of compound **3ad** (100 MHz, CDCl₃)



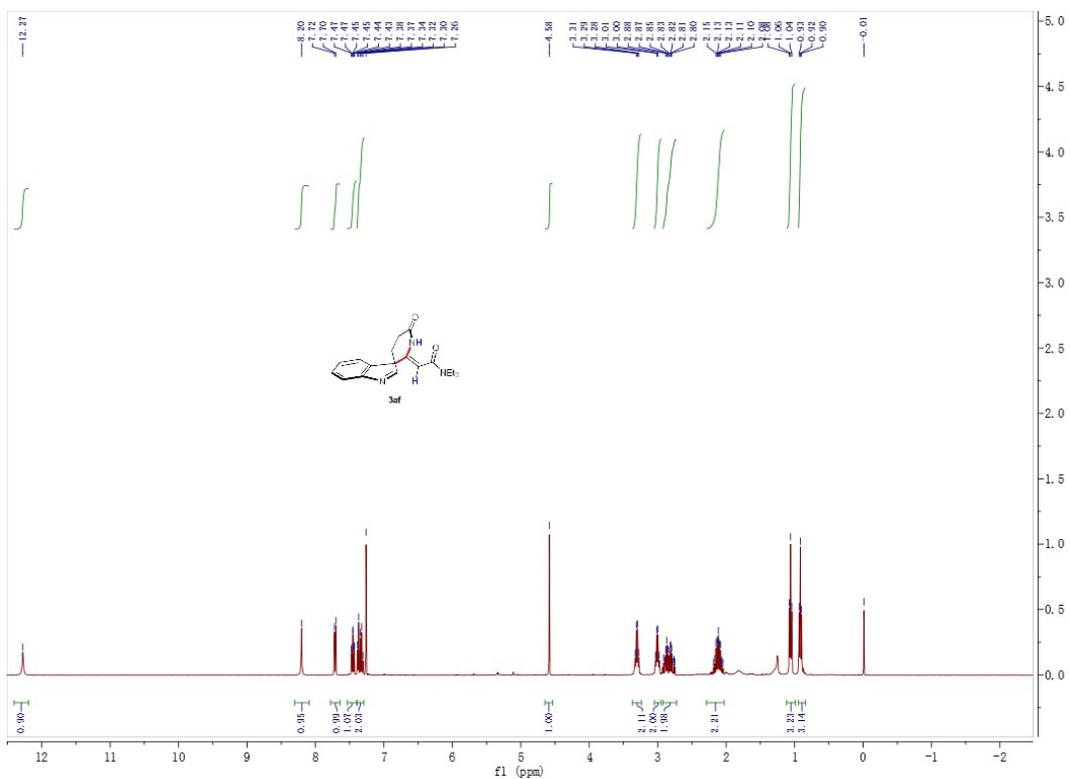
¹H NMR spectrum of compound 3ae (400 MHz, CDCl₃)



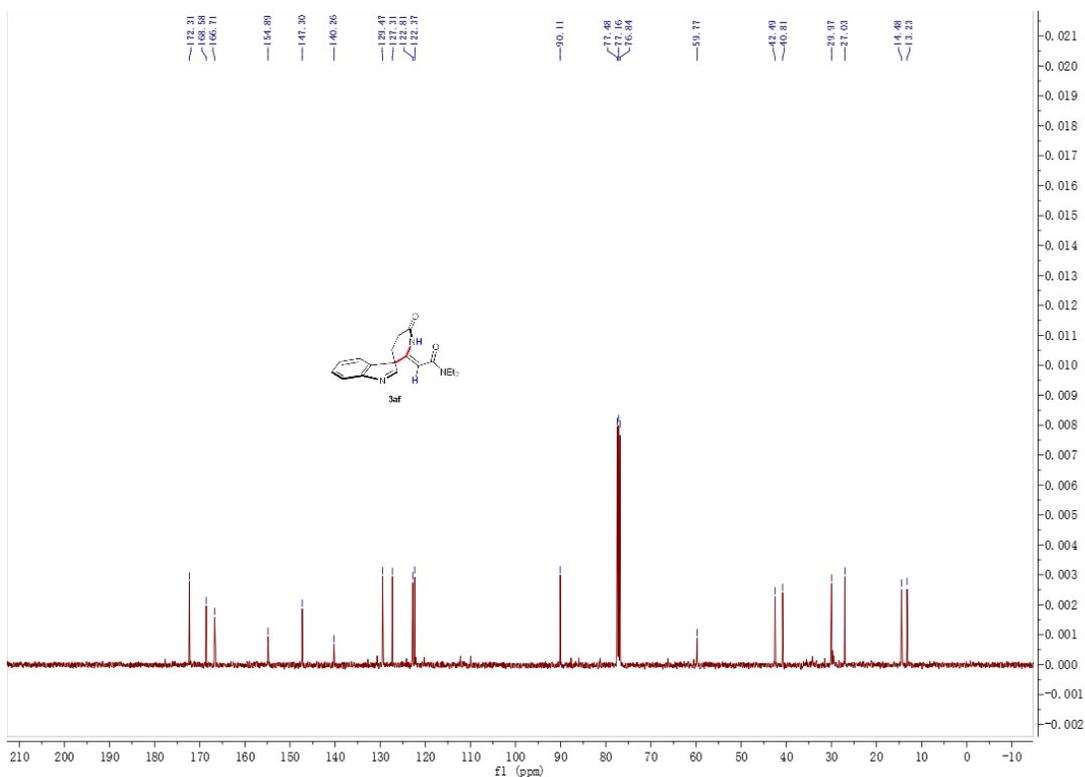
¹³C NMR spectrum of compound 3ae (100 MHz, CDCl₃)



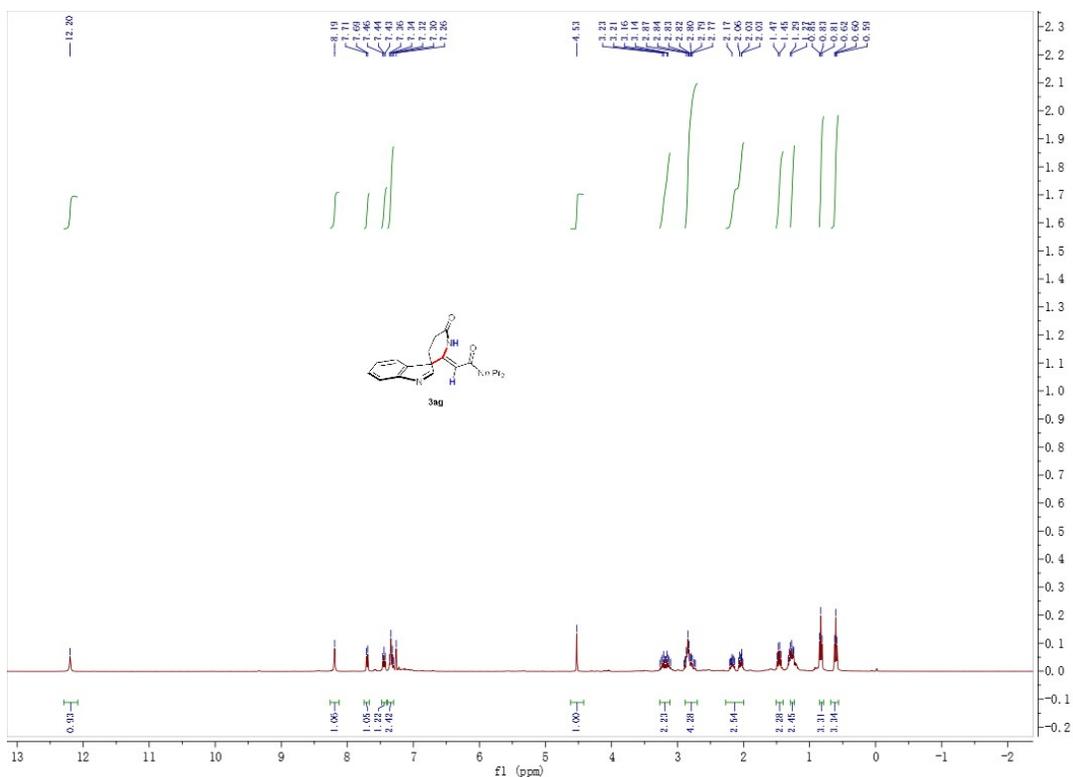
¹H NMR spectrum of compound 3af (400 MHz, CDCl₃)



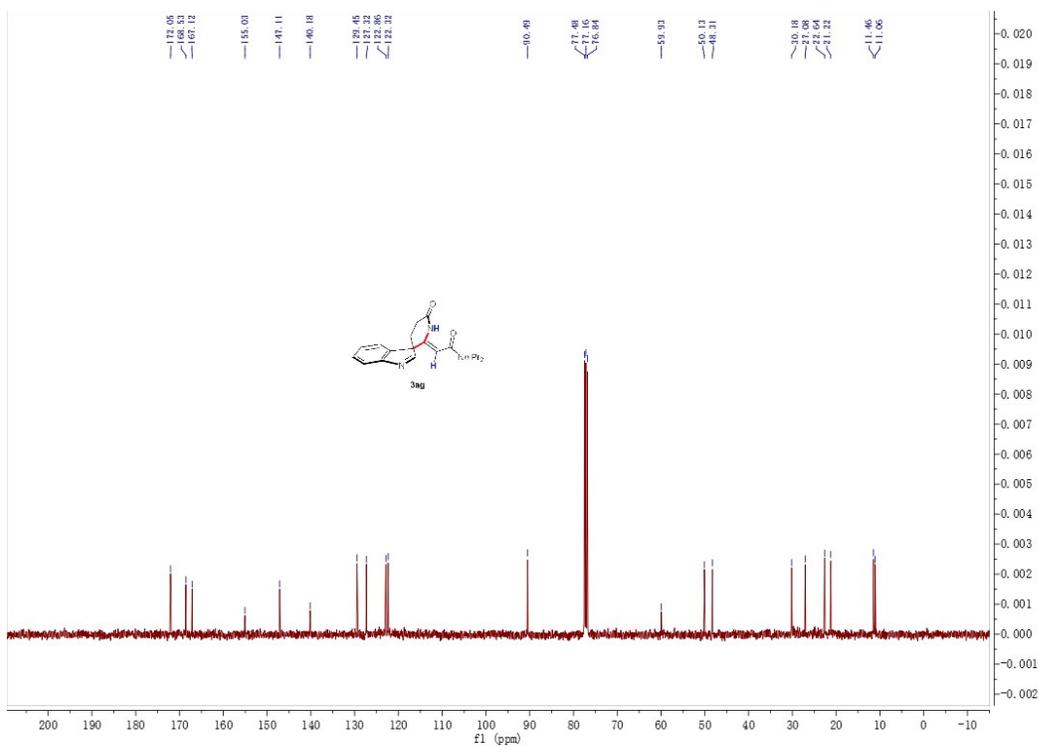
¹³C NMR spectrum of compound 3af (100 MHz, CDCl₃)



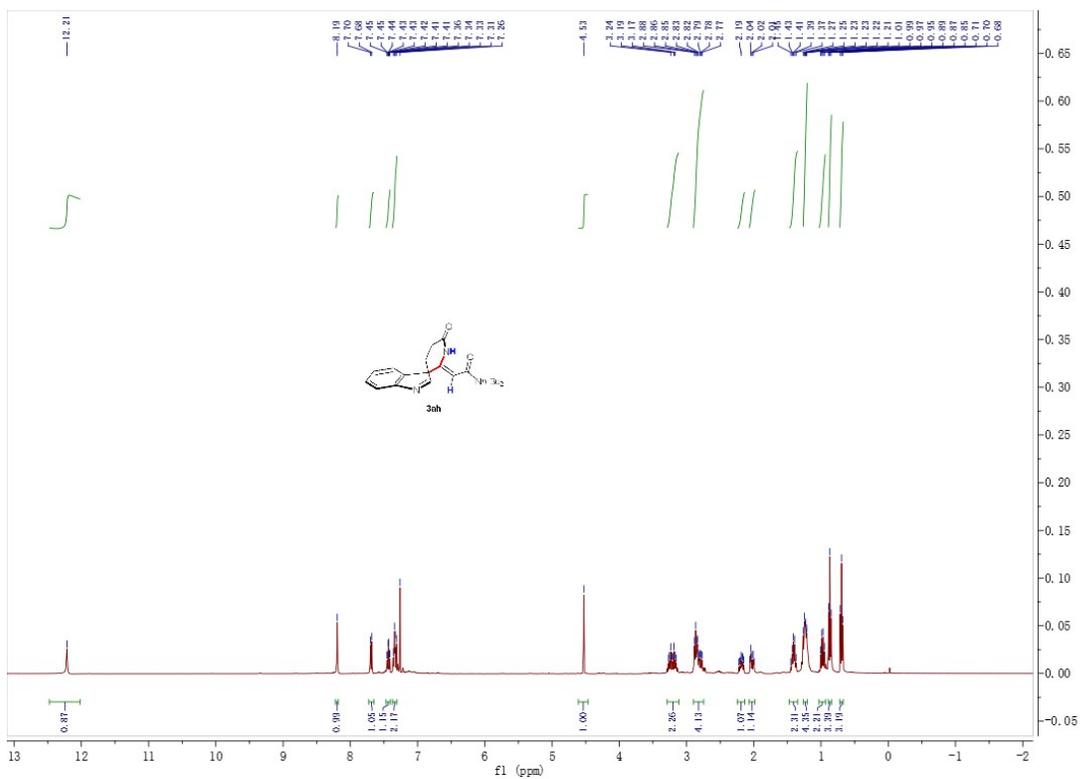
¹H NMR spectrum of compound 3ag (400 MHz, CDCl₃)



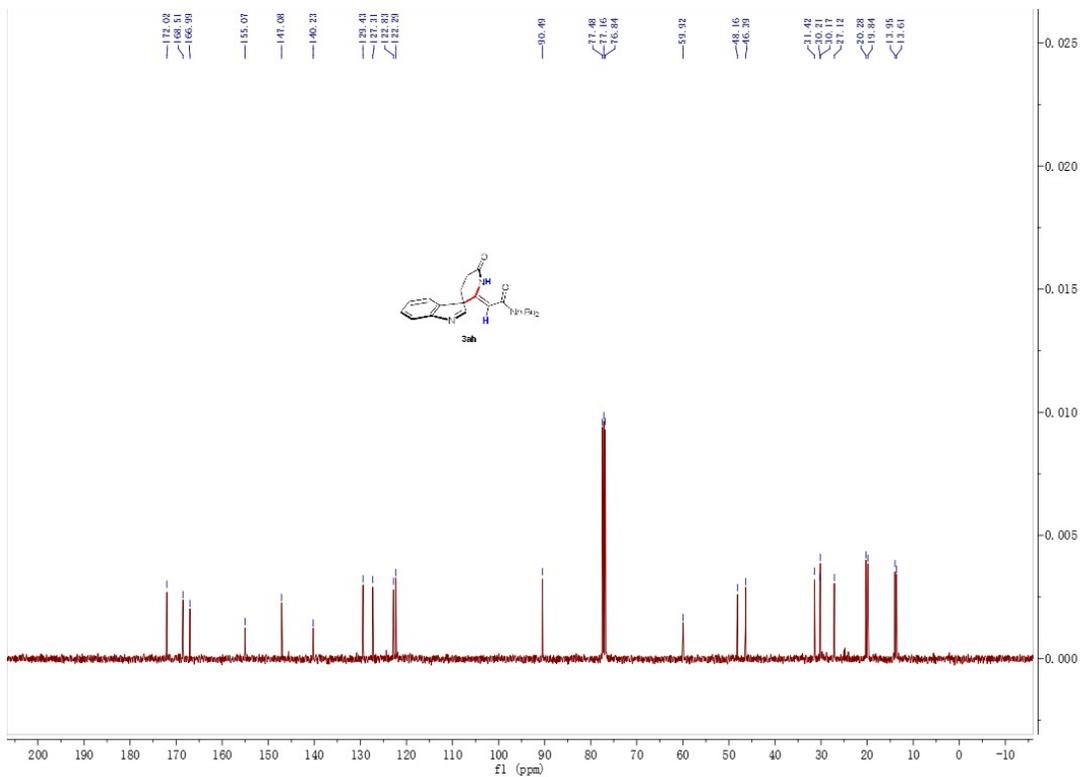
¹³C NMR spectrum of compound 3ag (100 MHz, CDCl₃)



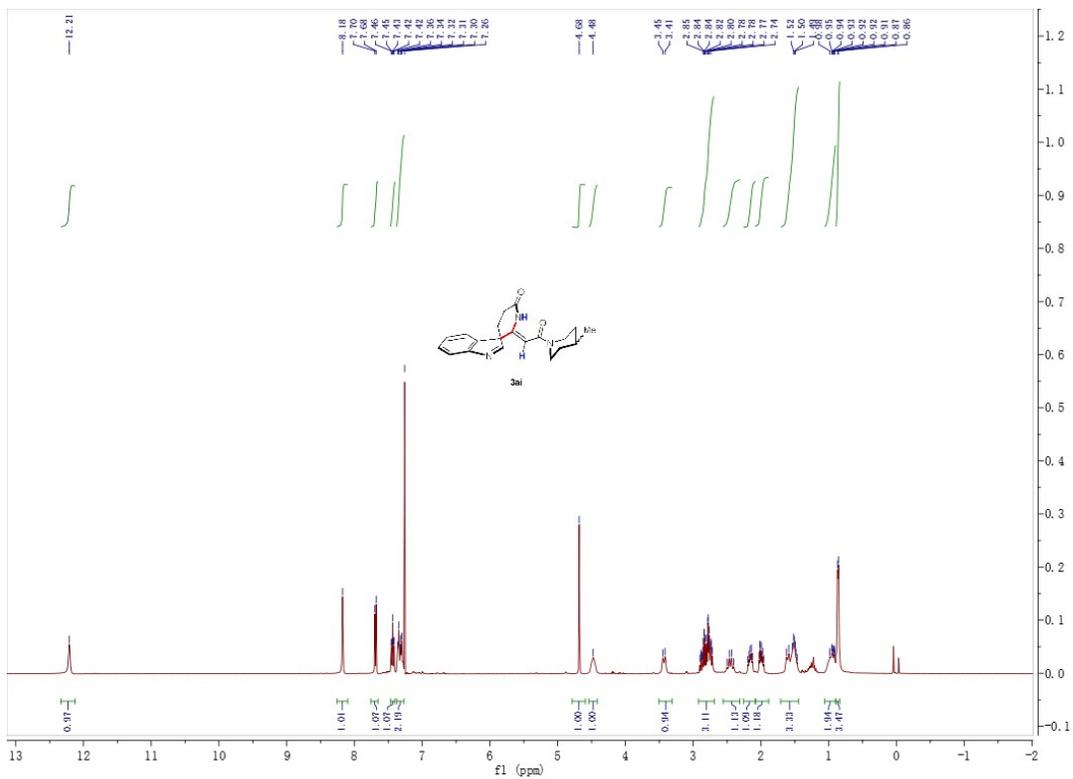
¹H NMR spectrum of compound **3ah** (400 MHz, CDCl₃)



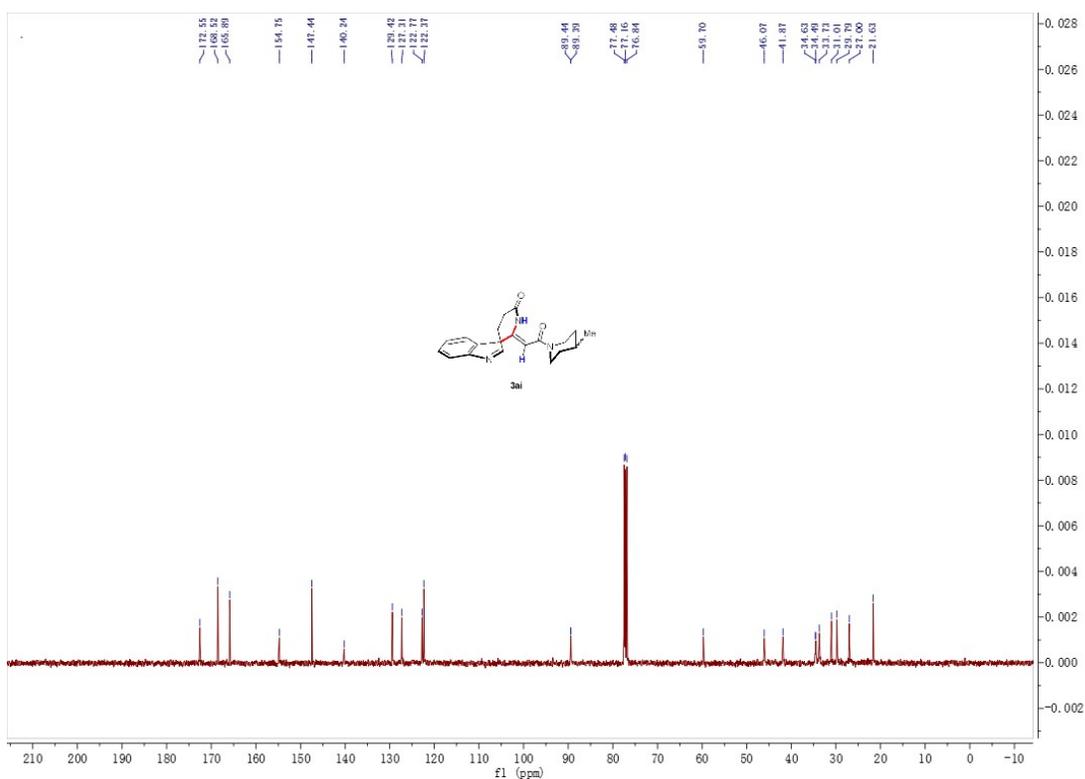
¹³C NMR spectrum of compound **3ah** (100 MHz, CDCl₃)



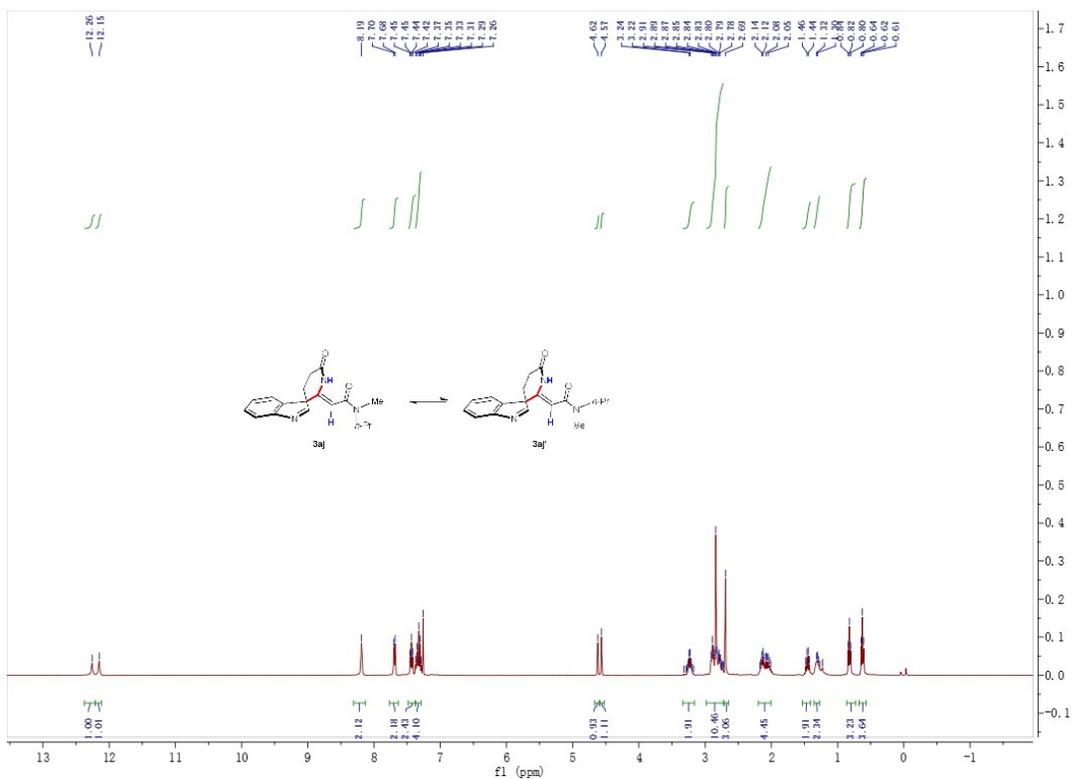
¹H NMR spectrum of compound 3ai (400 MHz, CDCl₃)



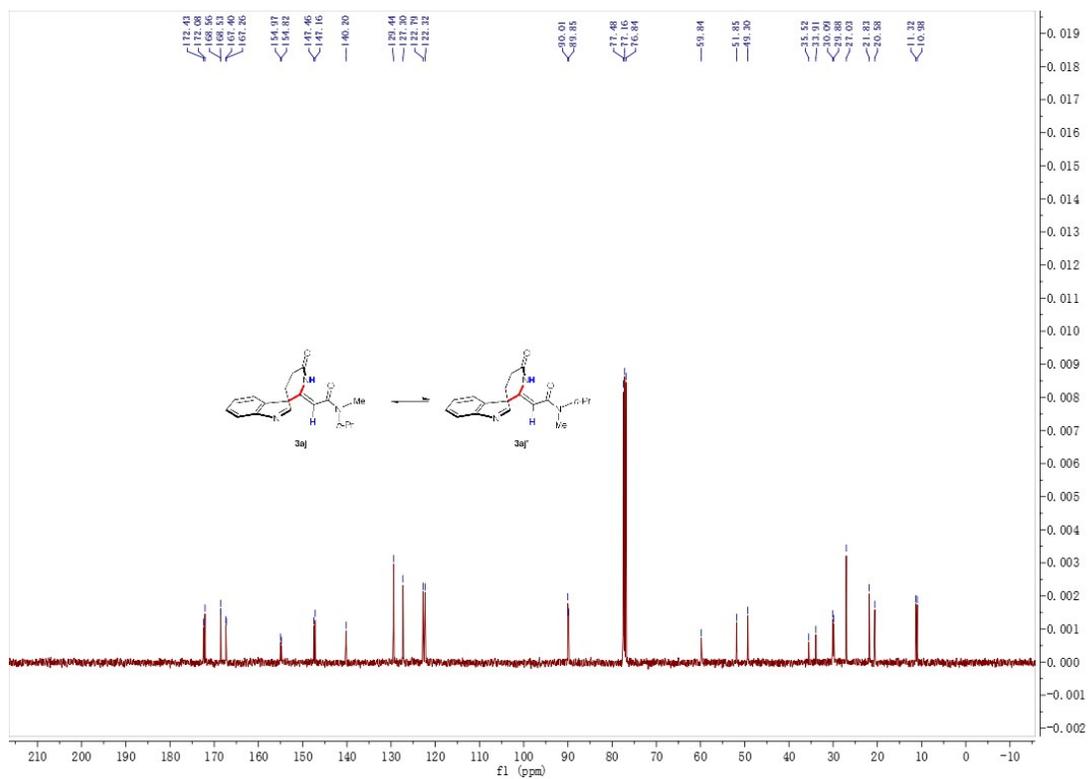
¹³C NMR spectrum of compound **3ai** (100 MHz, CDCl₃)



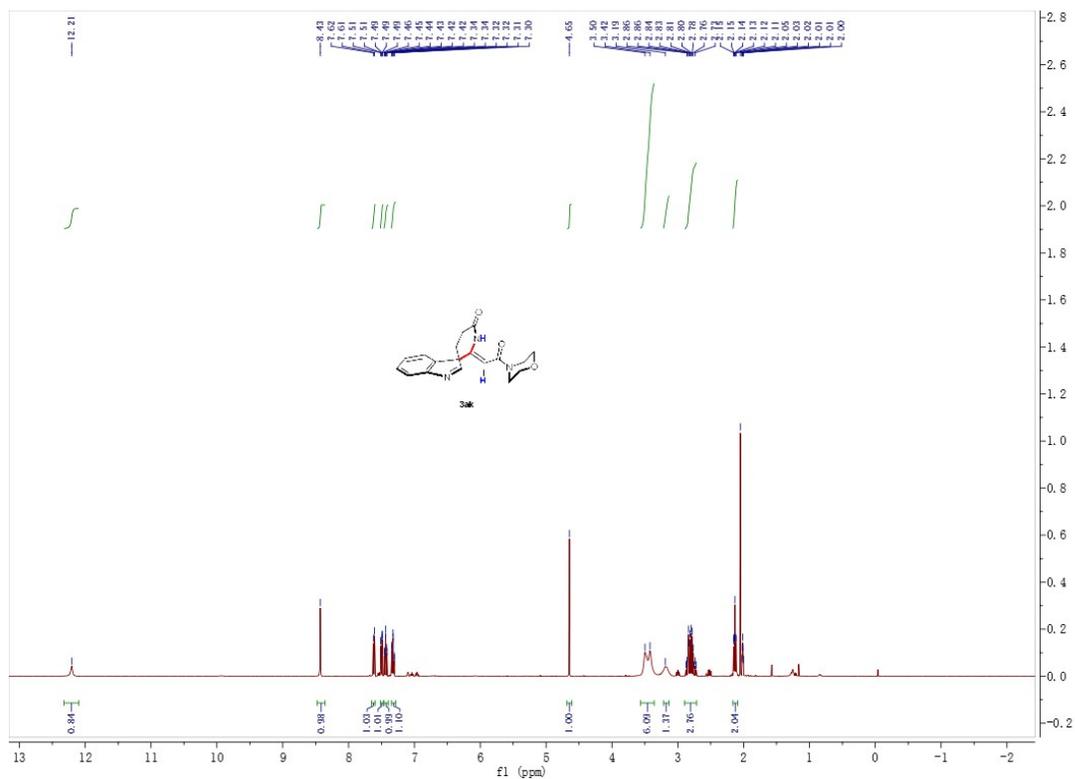
¹H NMR spectrum of compound **3aj** (400 MHz, CDCl₃)



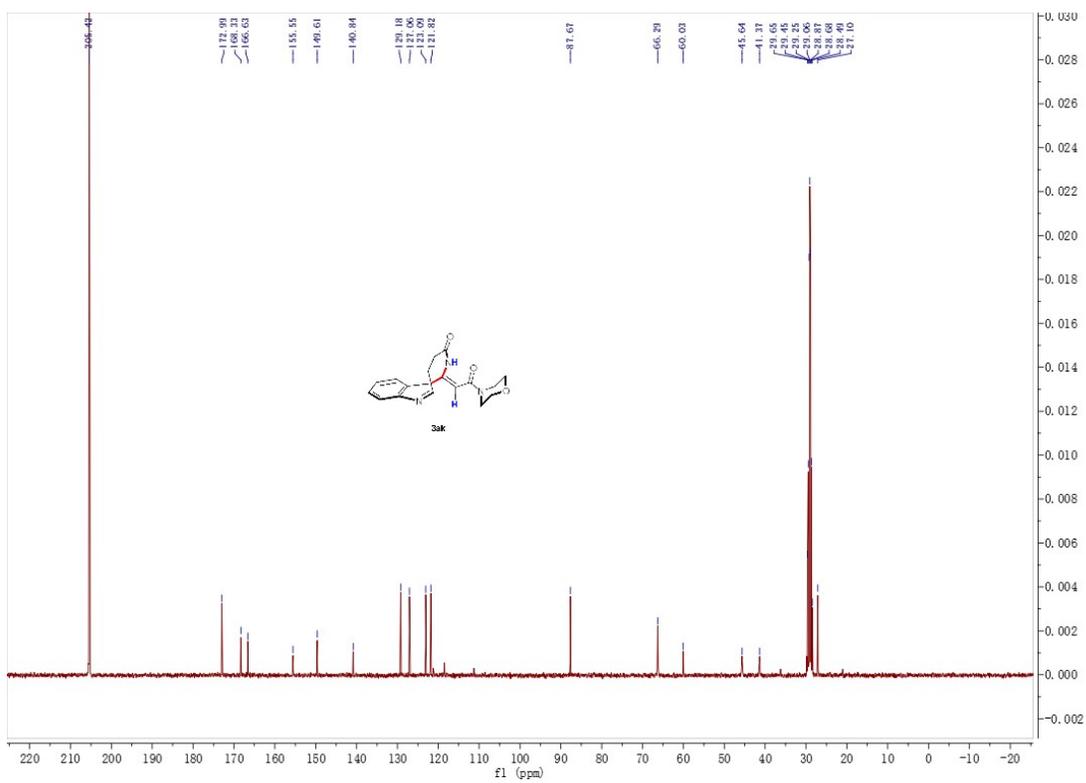
¹³C NMR spectrum of compound **3aj** (100 MHz, CDCl₃)



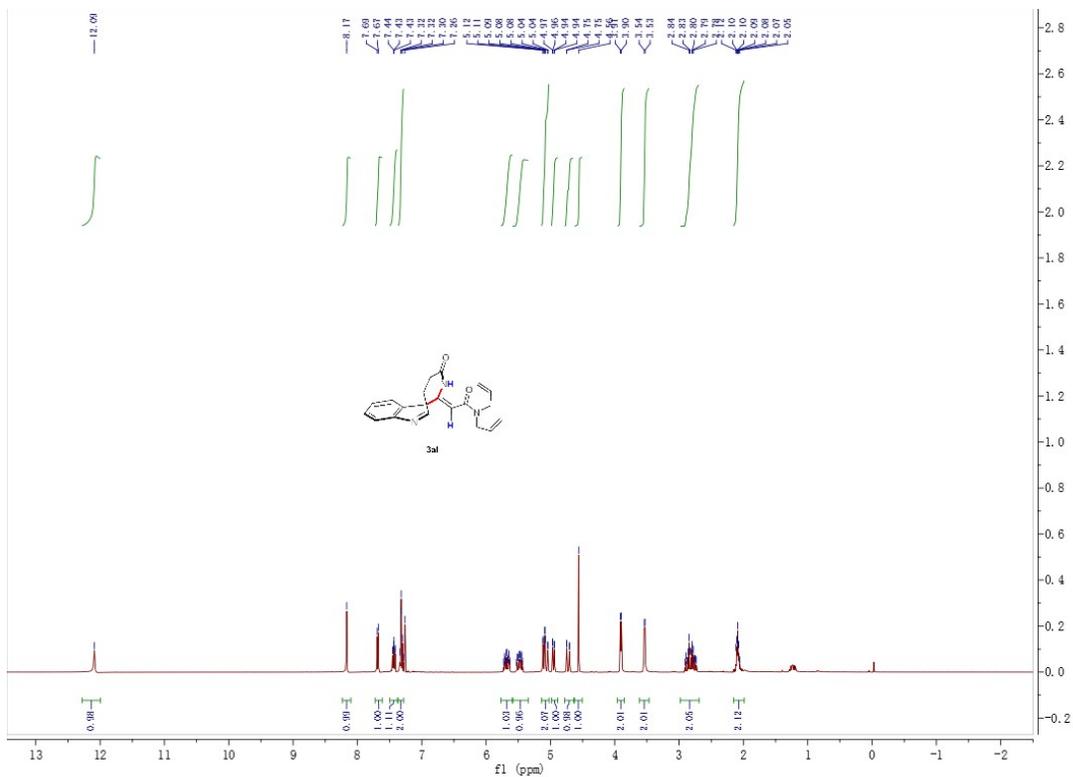
¹H NMR spectrum of compound **3ak** (400 MHz, Acetone-d₆)



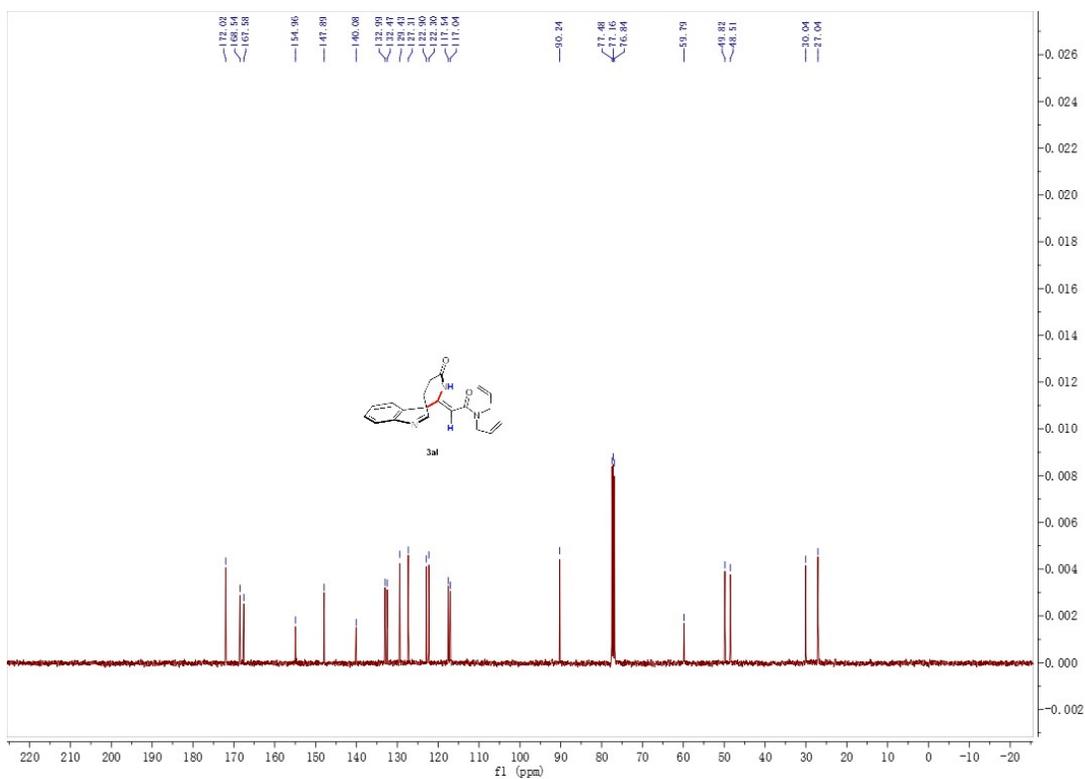
^{13}C NMR spectrum of compound **3ak** (100 MHz, Acetone- d_6)



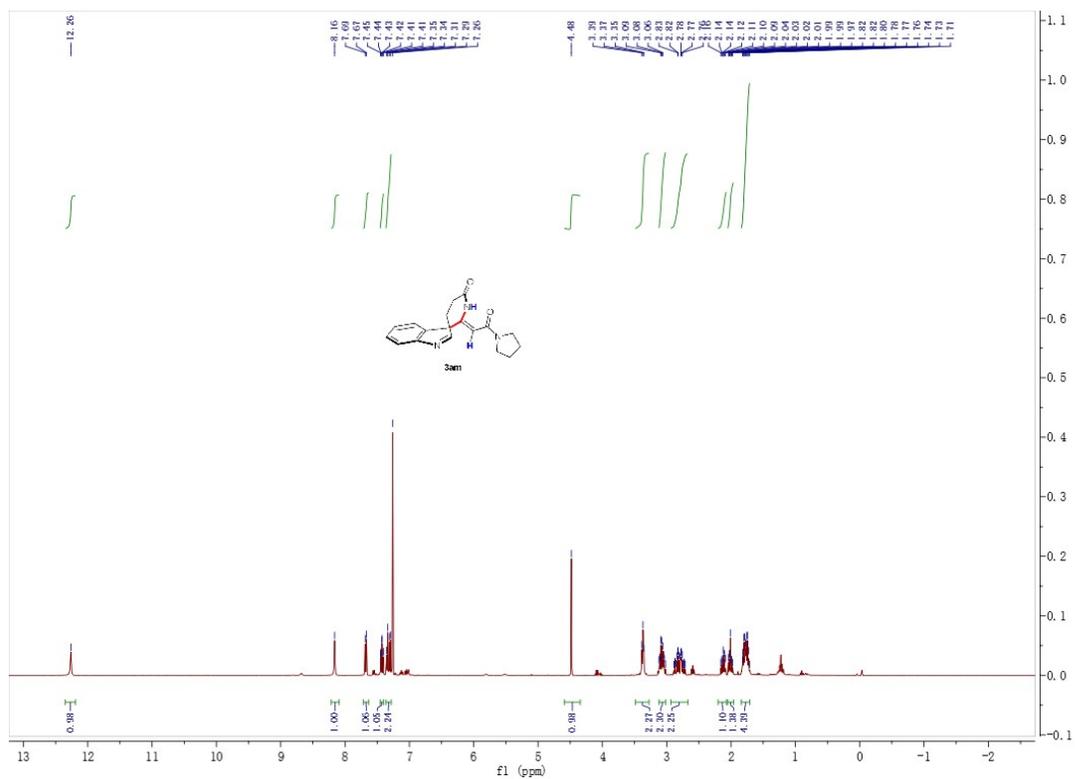
^1H NMR spectrum of compound **3al** (400 MHz, CDCl_3)



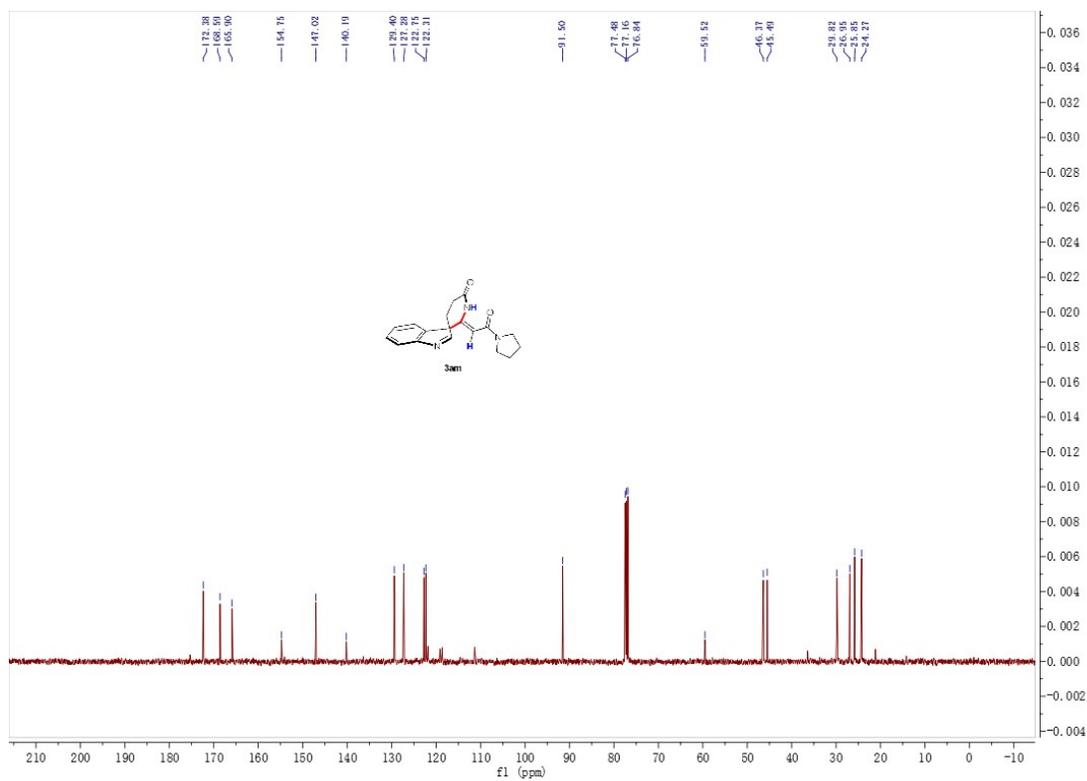
¹³C NMR spectrum of compound 3al (100 MHz, CDCl₃)



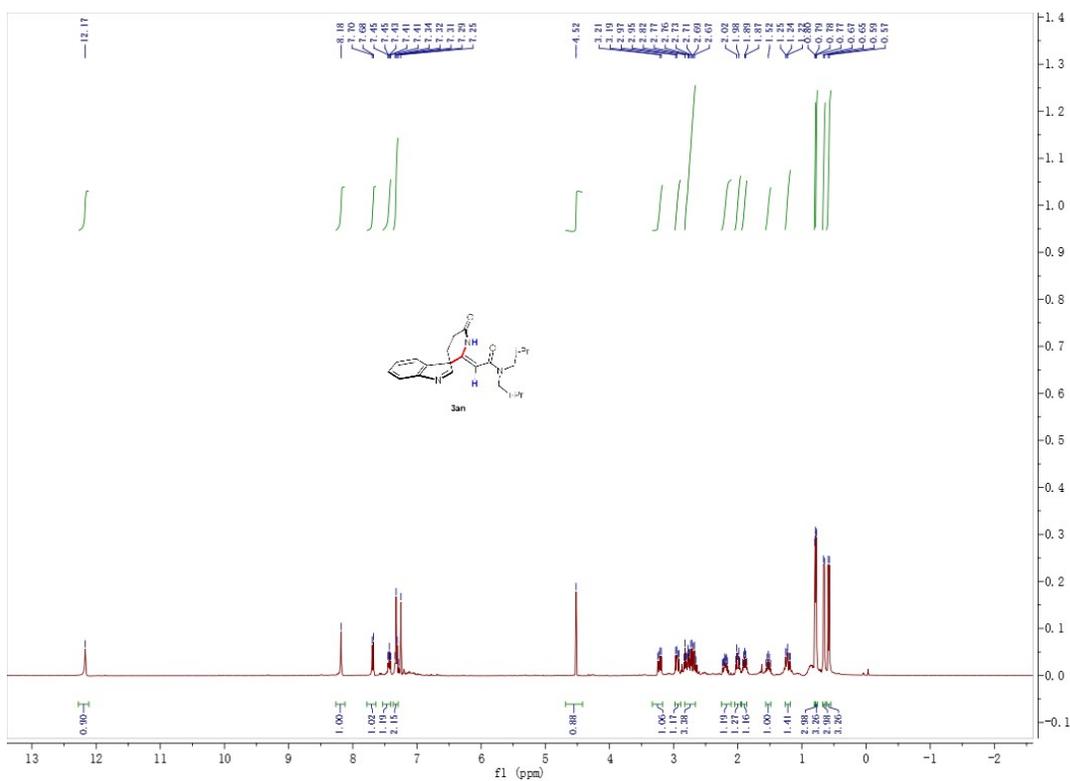
¹H NMR spectrum of compound **3am** (400 MHz, CDCl₃)



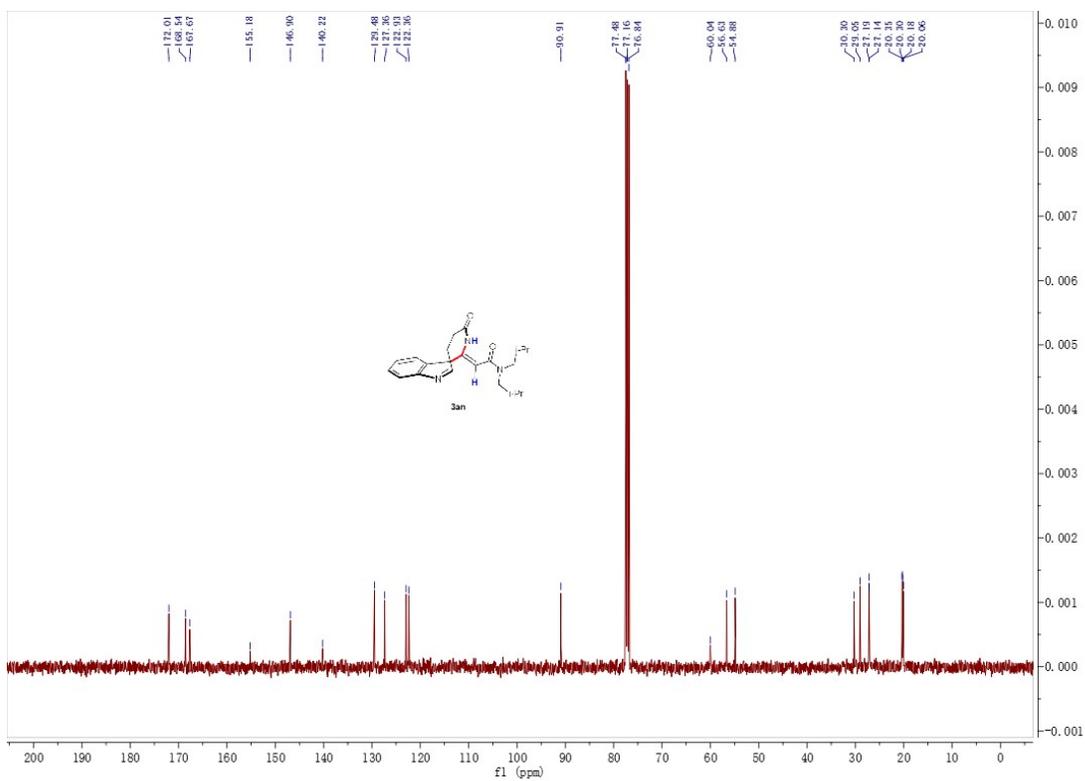
¹³C NMR spectrum of compound **3am** (100 MHz, CDCl₃)



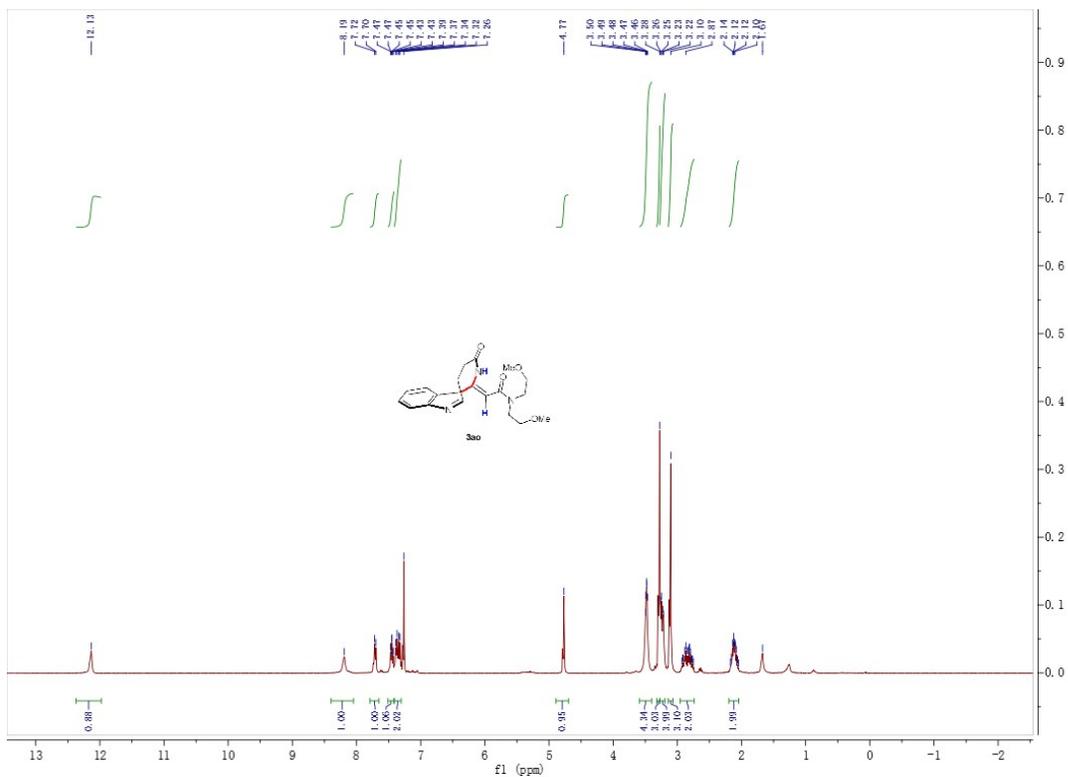
¹H NMR spectrum of compound 3an (400 MHz, CDCl₃)



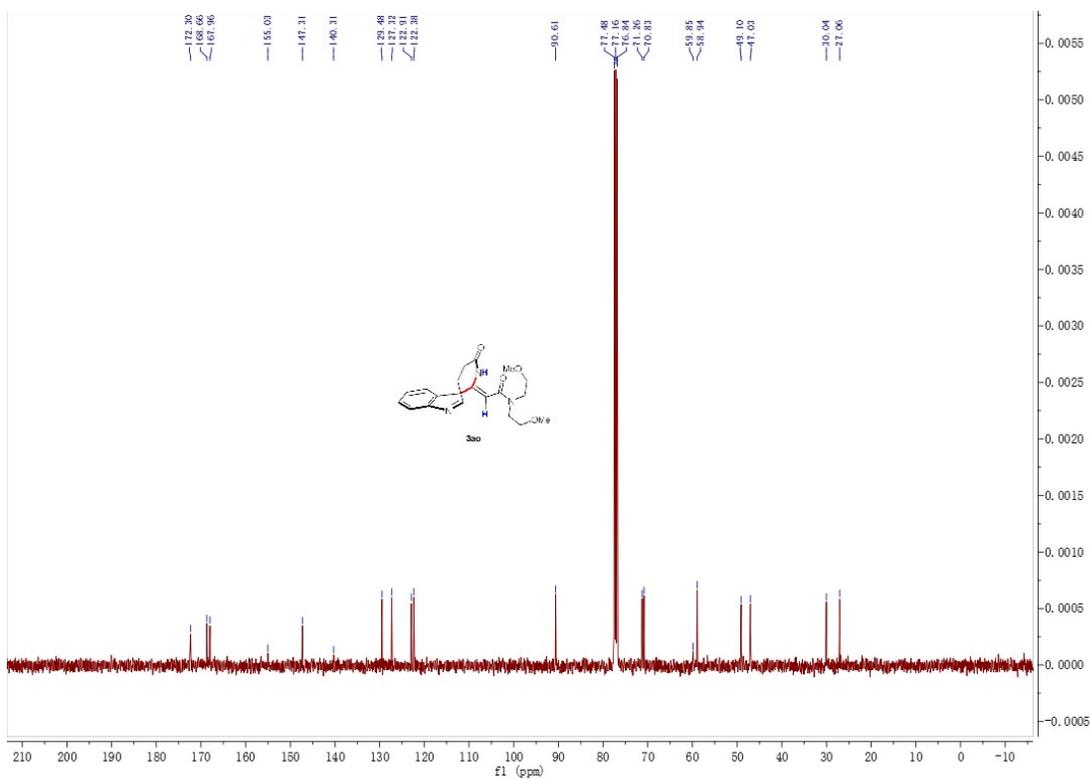
¹³C NMR spectrum of compound 3an (100 MHz, CDCl₃)



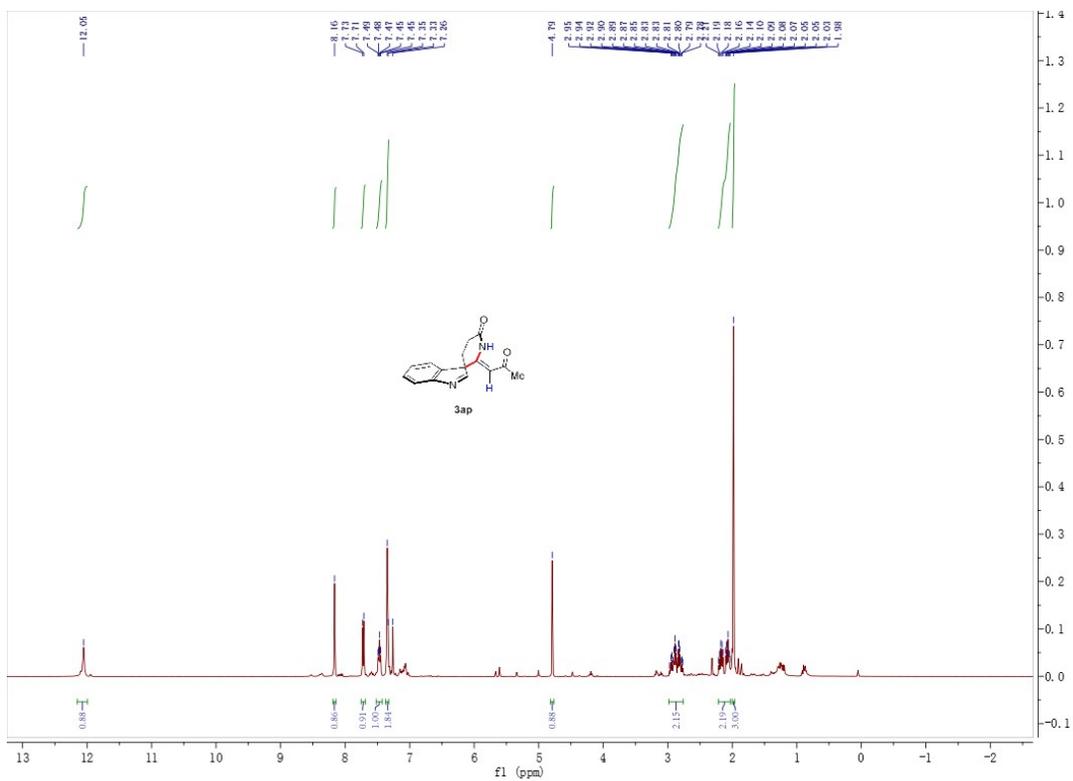
¹H NMR spectrum of compound 3ao (400 MHz, CDCl₃)



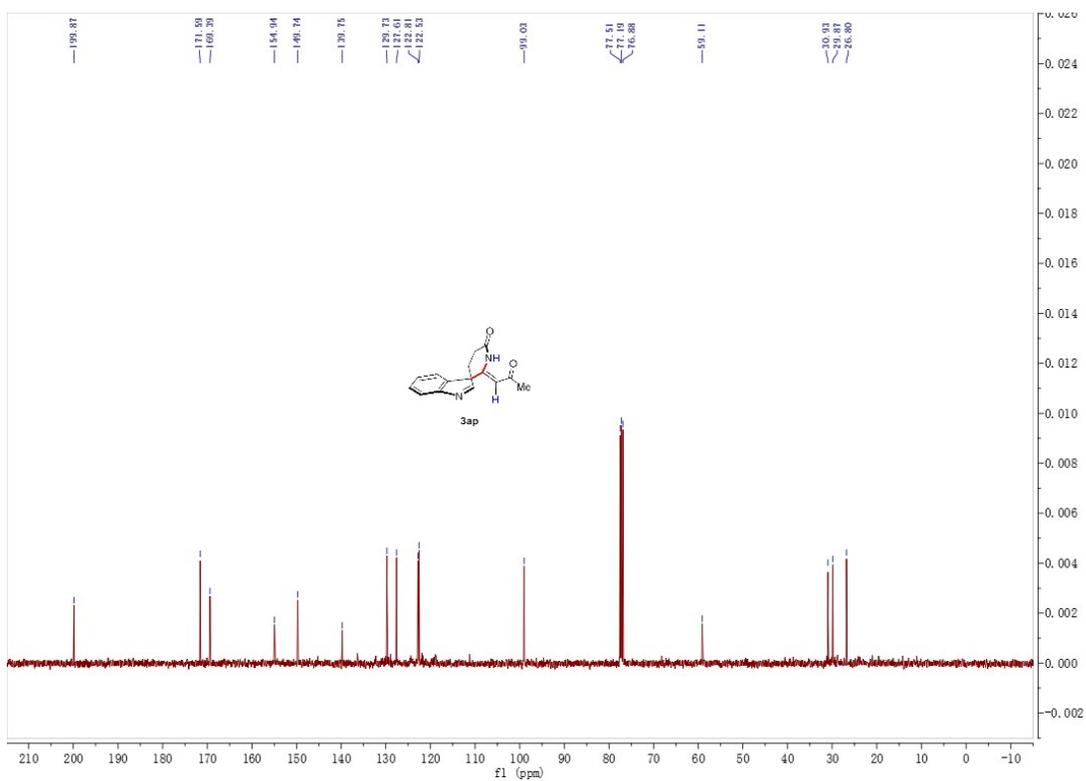
¹³C NMR spectrum of compound 3ao (100 MHz, CDCl₃)



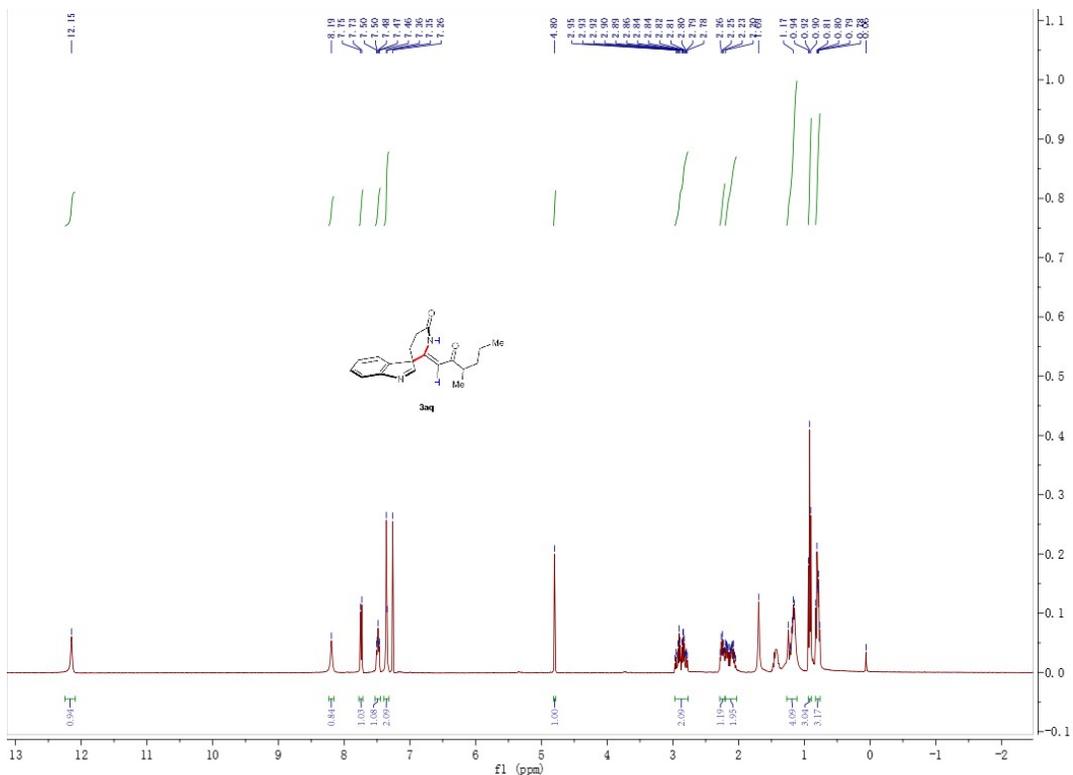
^1H NMR spectrum of compound **3ap** (400 MHz, CDCl_3)



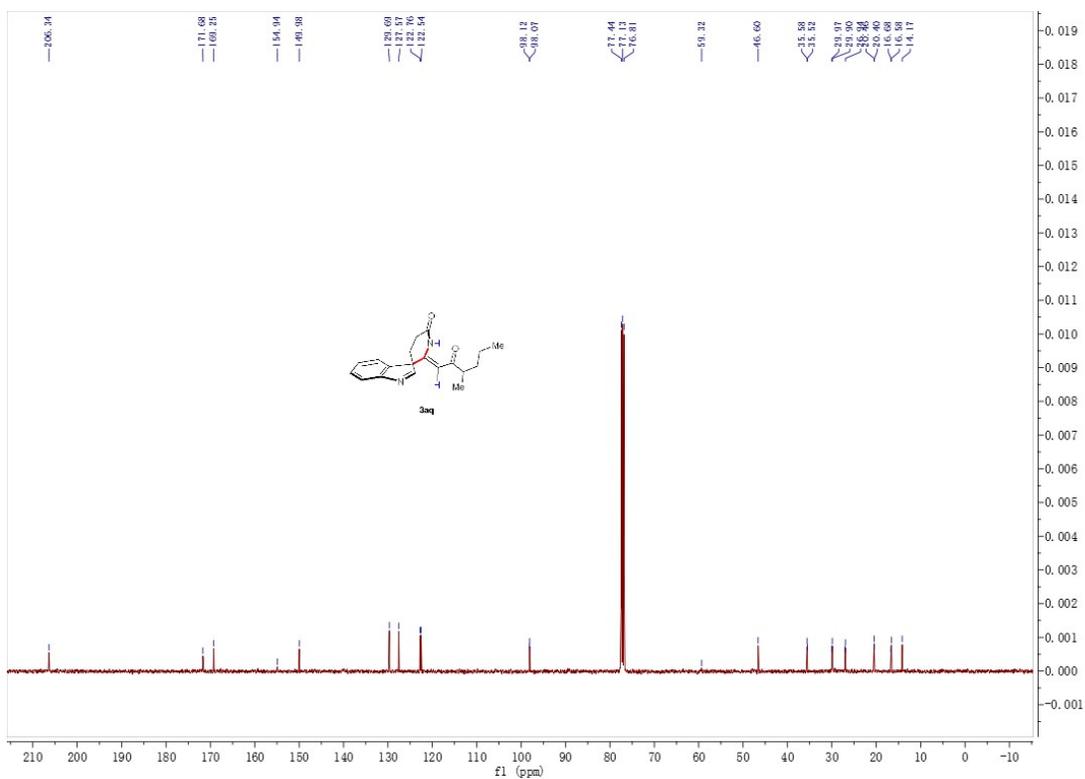
^{13}C NMR spectrum of compound **3ap** (100 MHz, CDCl_3)



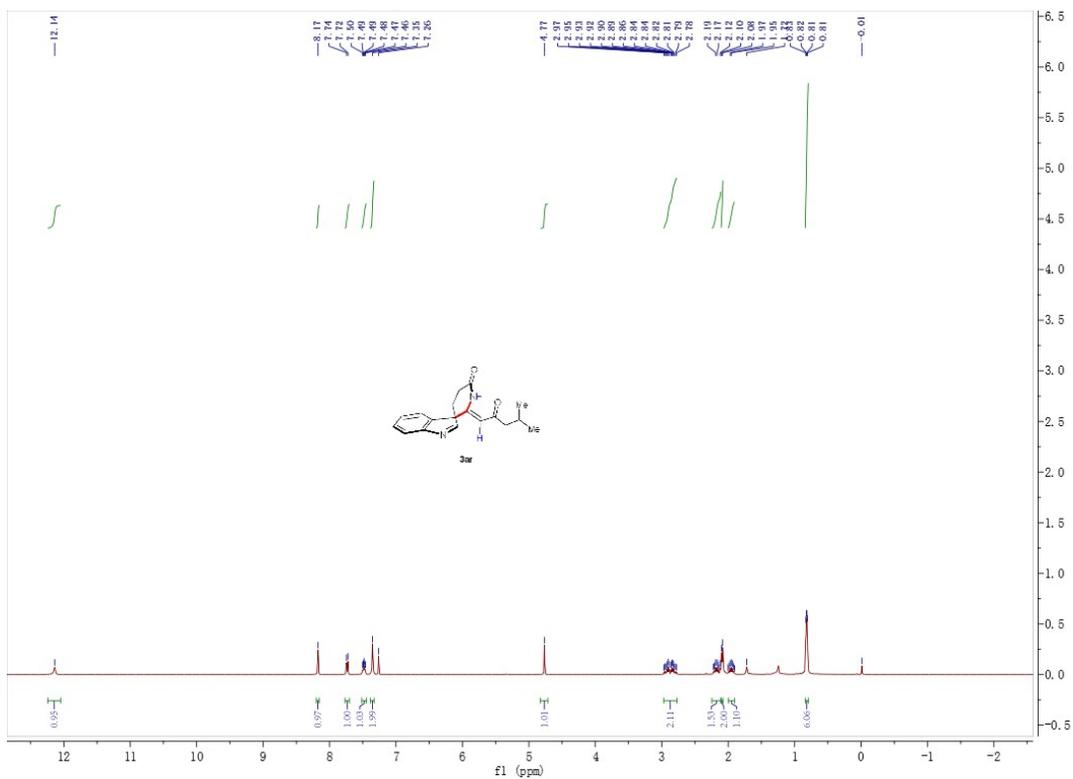
^1H NMR spectrum of compound **3aq** (400 MHz, CDCl_3)



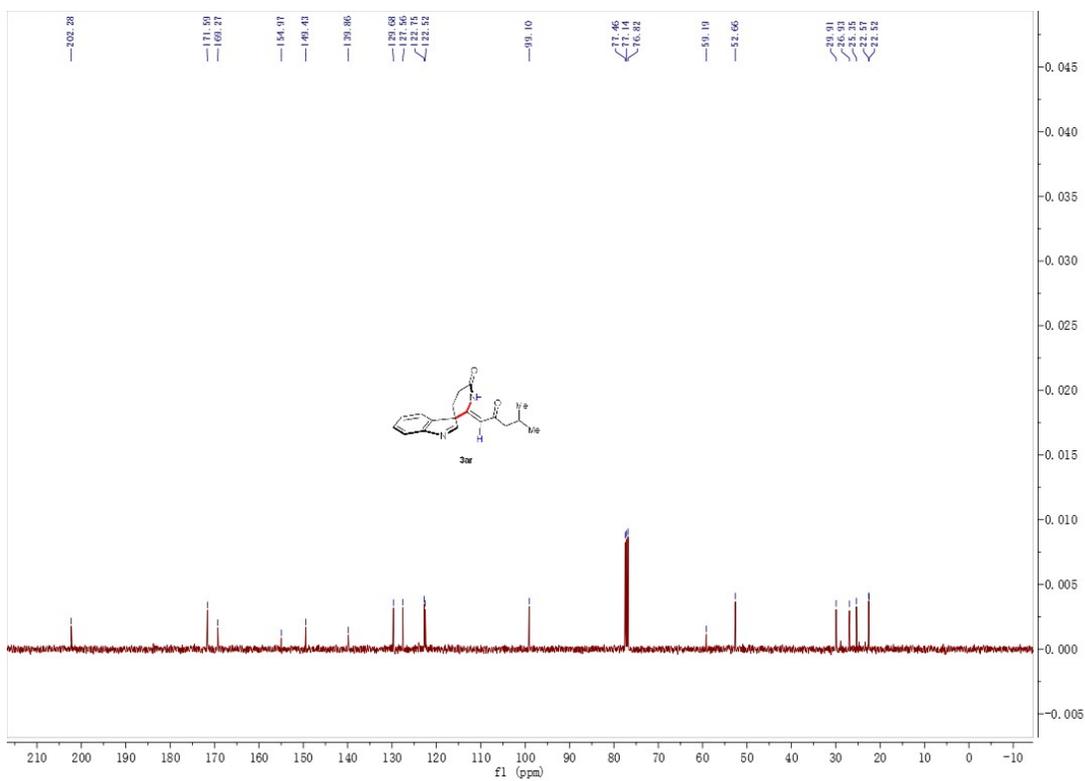
¹³C NMR spectrum of compound 3aq (100 MHz, CDCl₃)



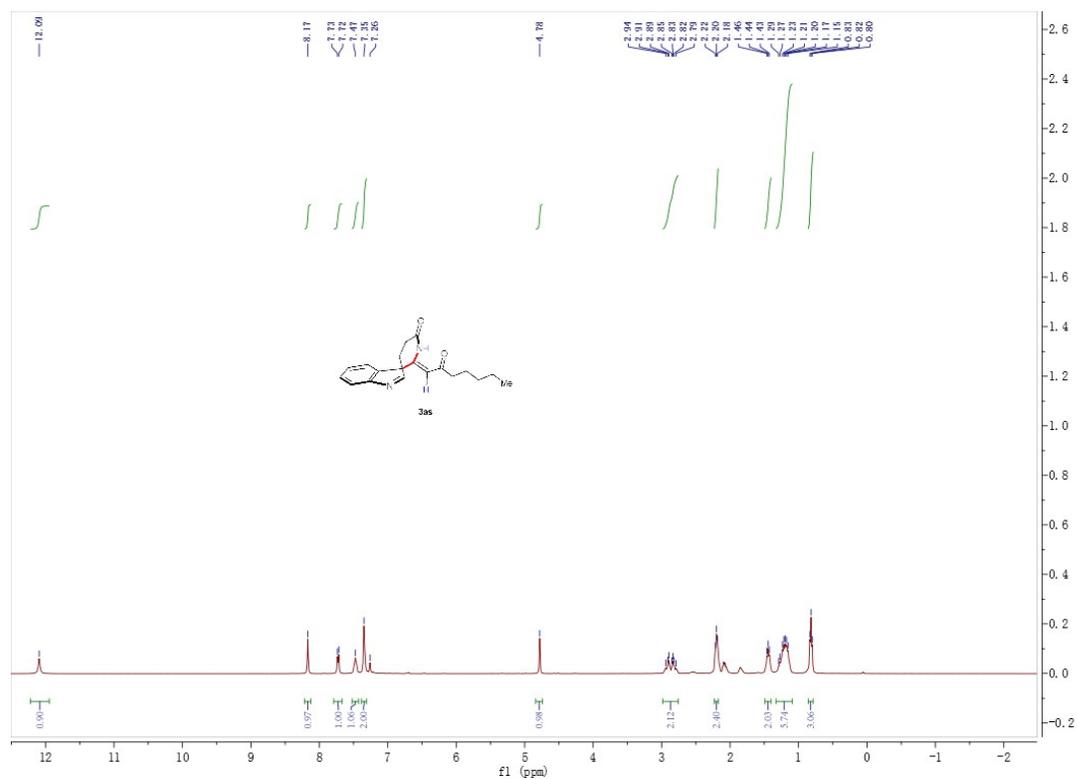
¹H NMR spectrum of compound 3ar (400 MHz, CDCl₃)



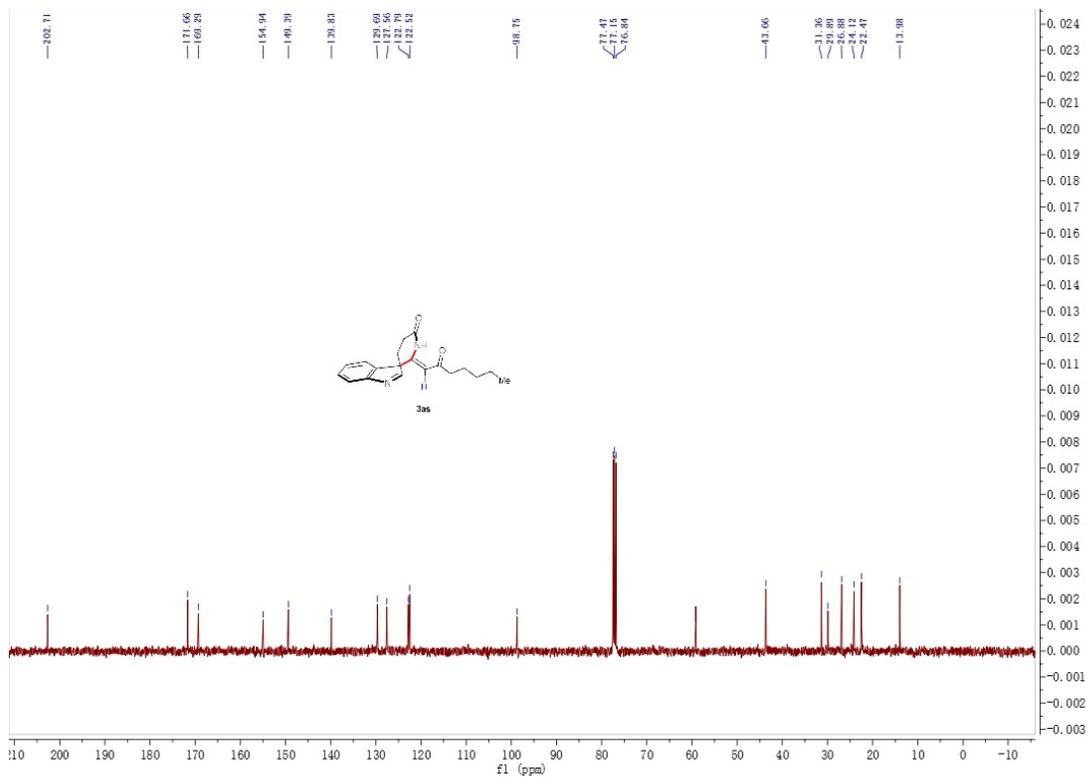
¹³C NMR spectrum of compound 3ar (100 MHz, CDCl₃)



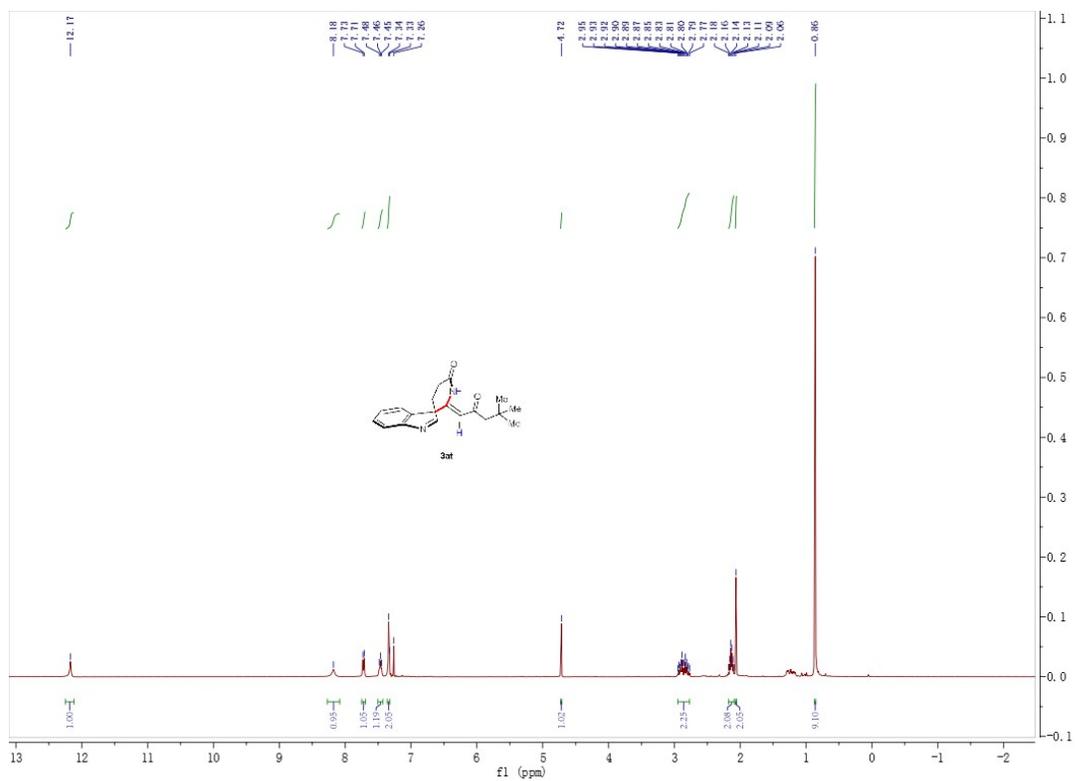
^1H NMR spectrum of compound **3as** (400 MHz, CDCl_3)



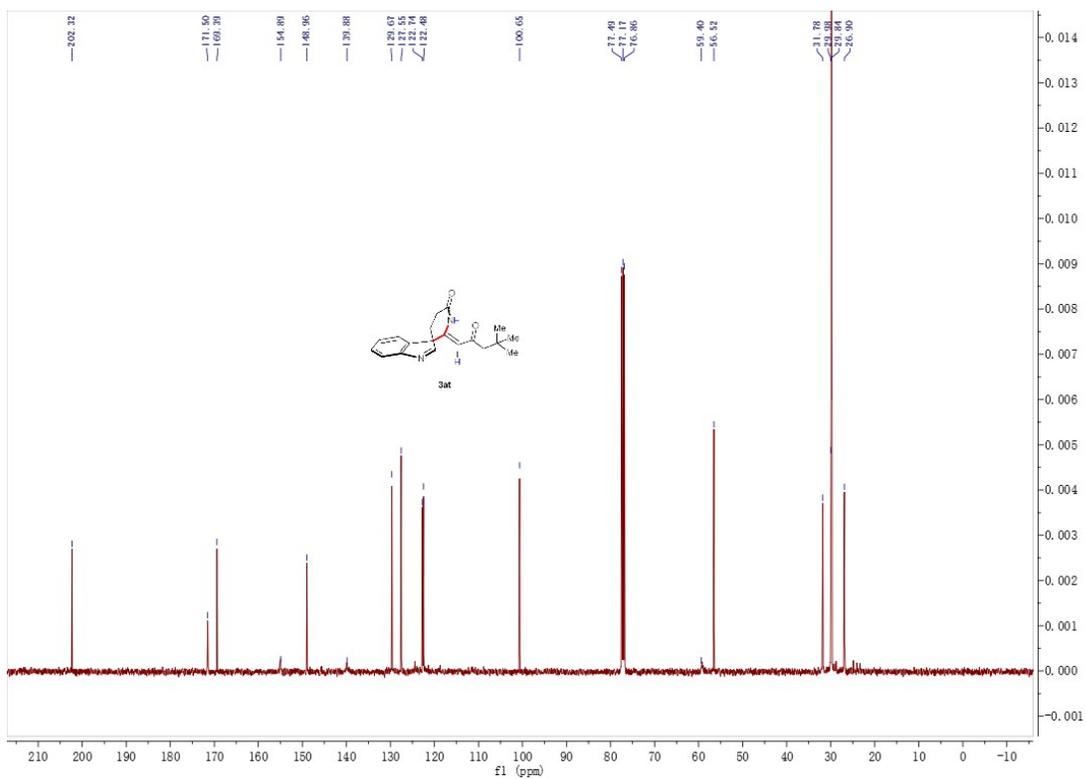
^{13}C NMR spectrum of compound **3as** (100 MHz, CDCl_3)



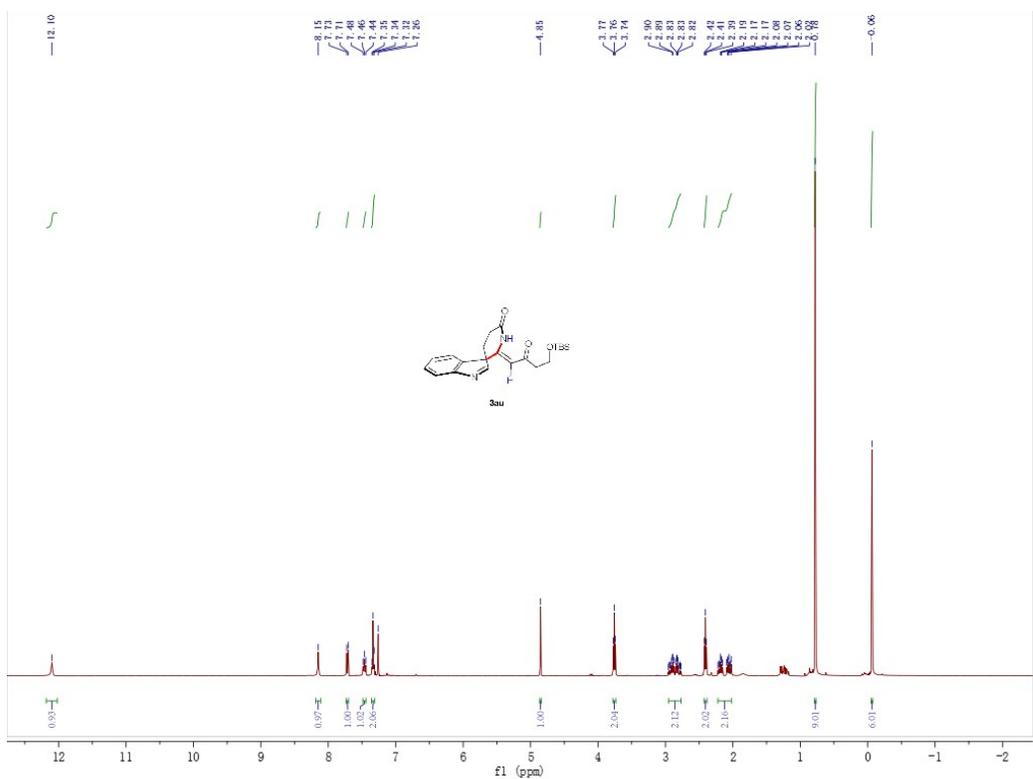
¹H NMR spectrum of compound 3at (400 MHz, CDCl₃)



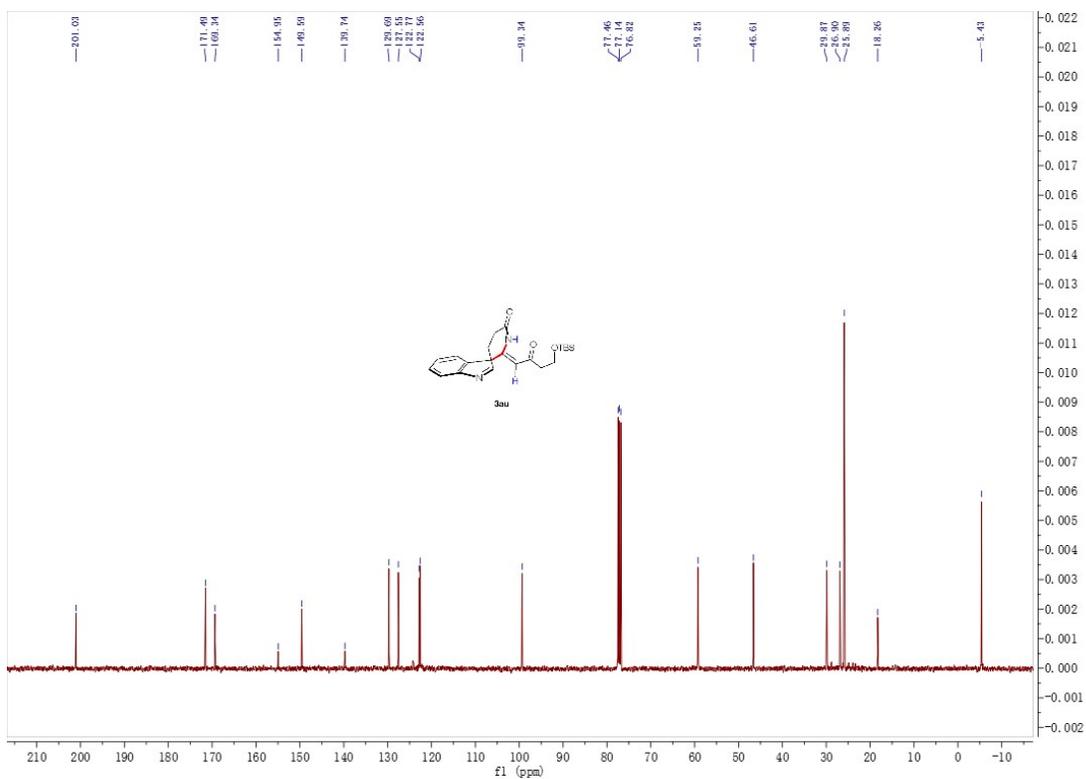
^{13}C NMR spectrum of compound **3at** (100 MHz, CDCl_3)



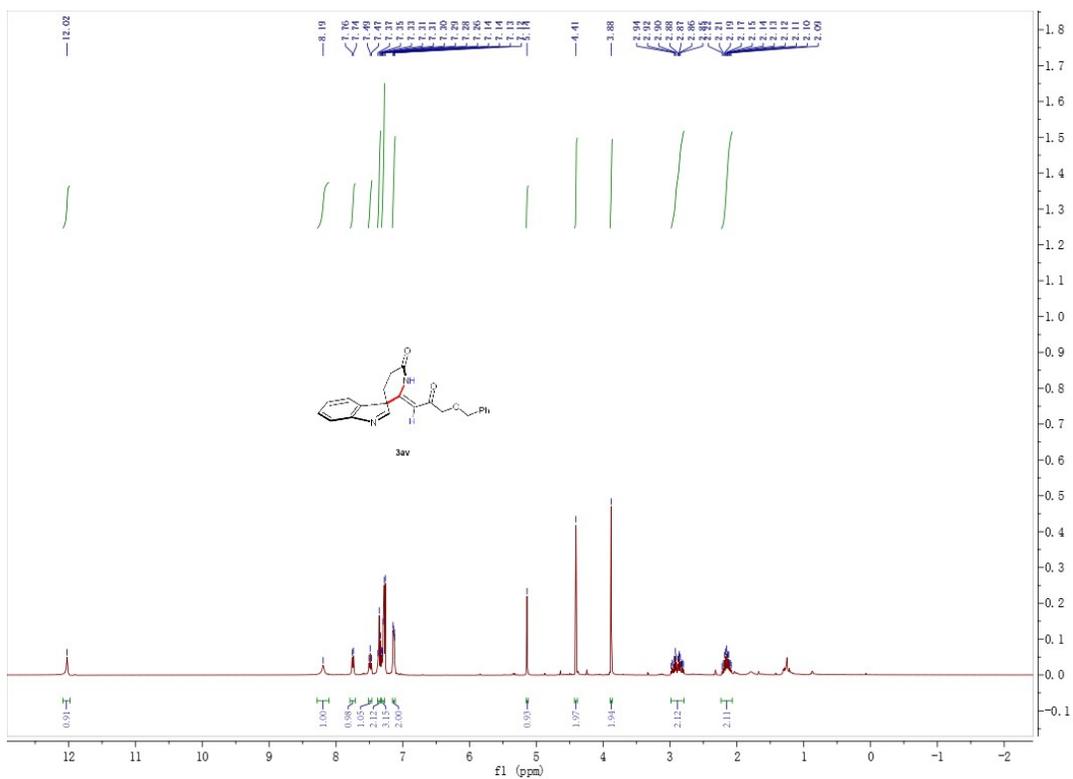
^1H NMR spectrum of compound **3au** (400 MHz, CDCl_3)



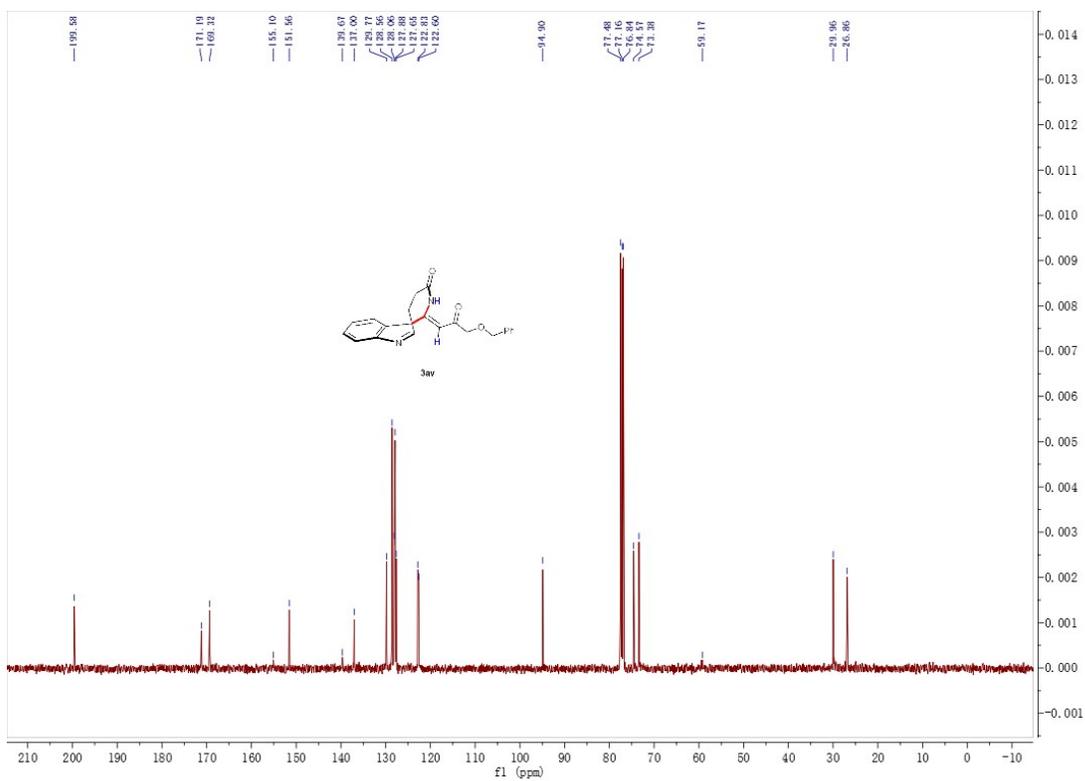
¹³C NMR spectrum of compound 3au (100 MHz, CDCl₃)



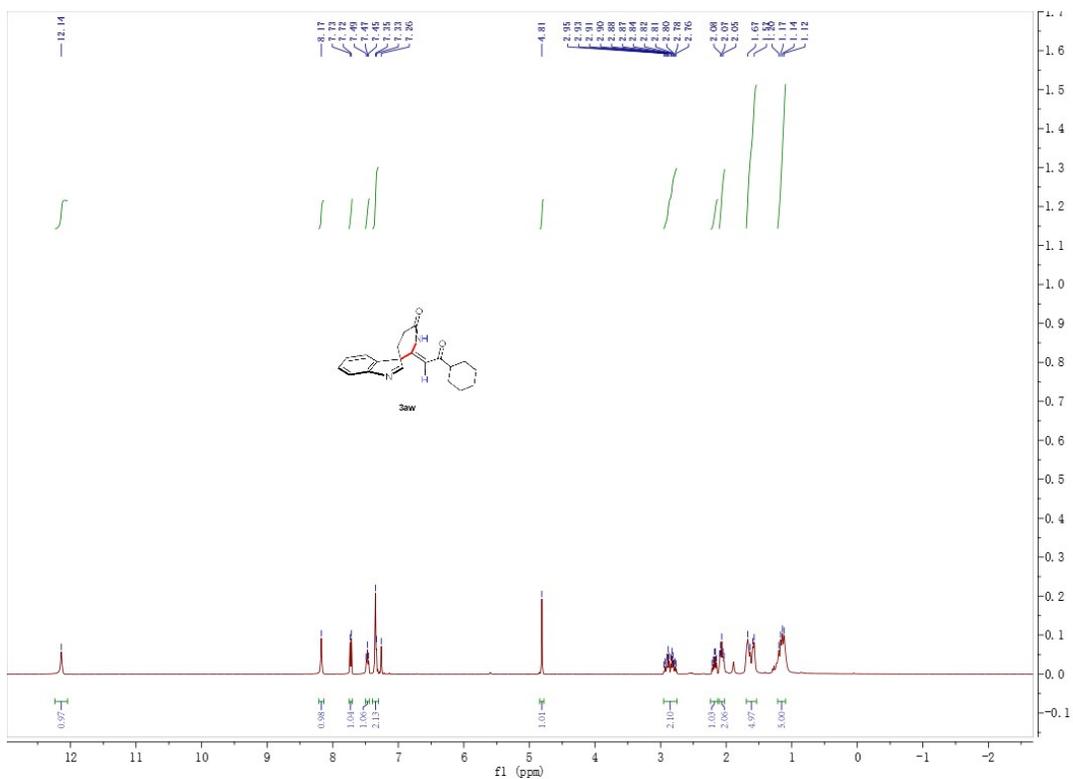
¹H NMR spectrum of compound **3av** (400 MHz, CDCl₃)



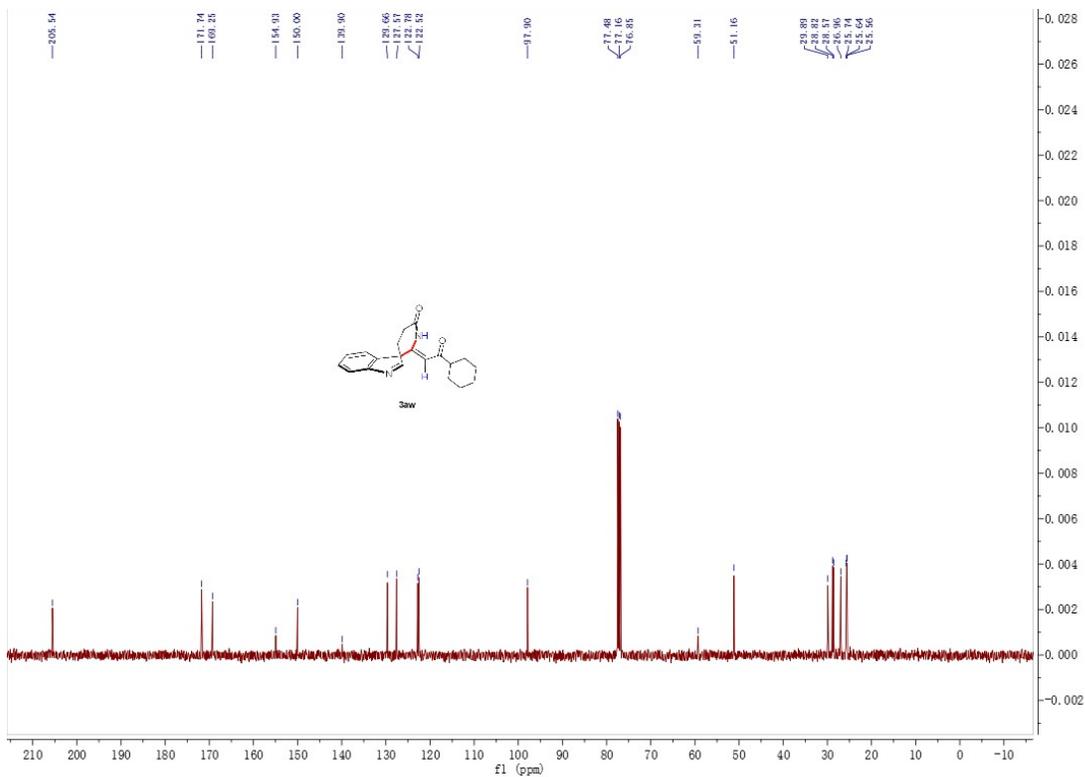
¹³C NMR spectrum of compound **3av** (100 MHz, CDCl₃)



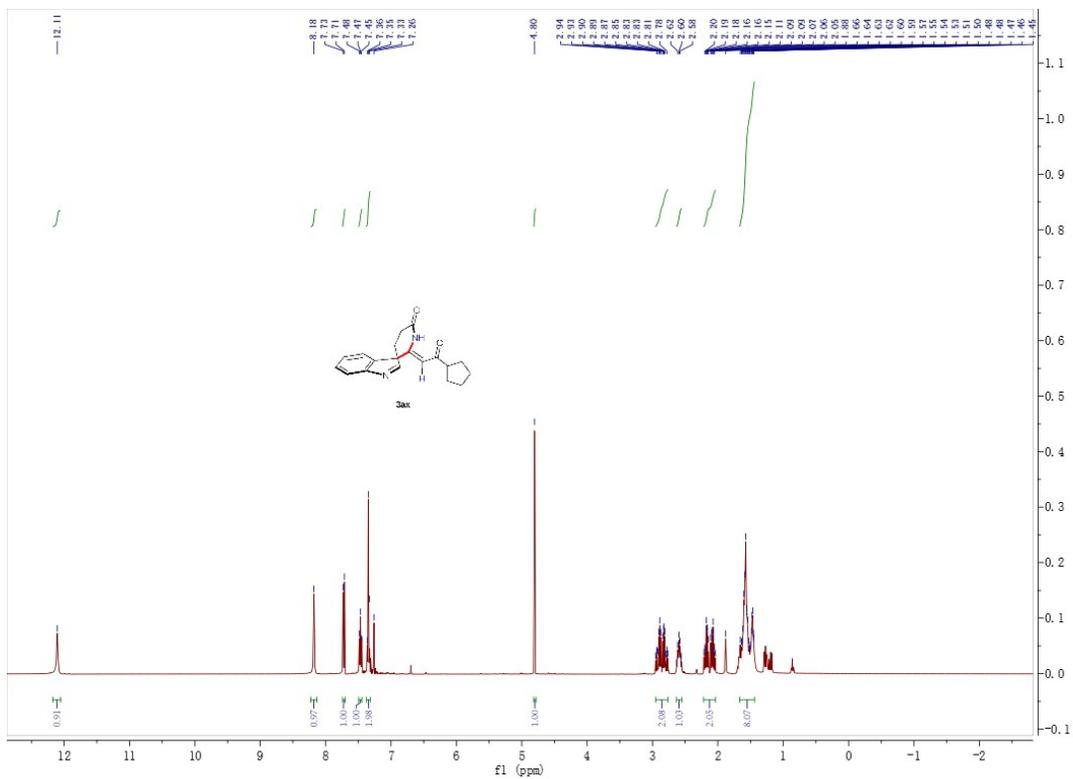
¹H NMR spectrum of compound **3aw (400 MHz, CDCl₃)**



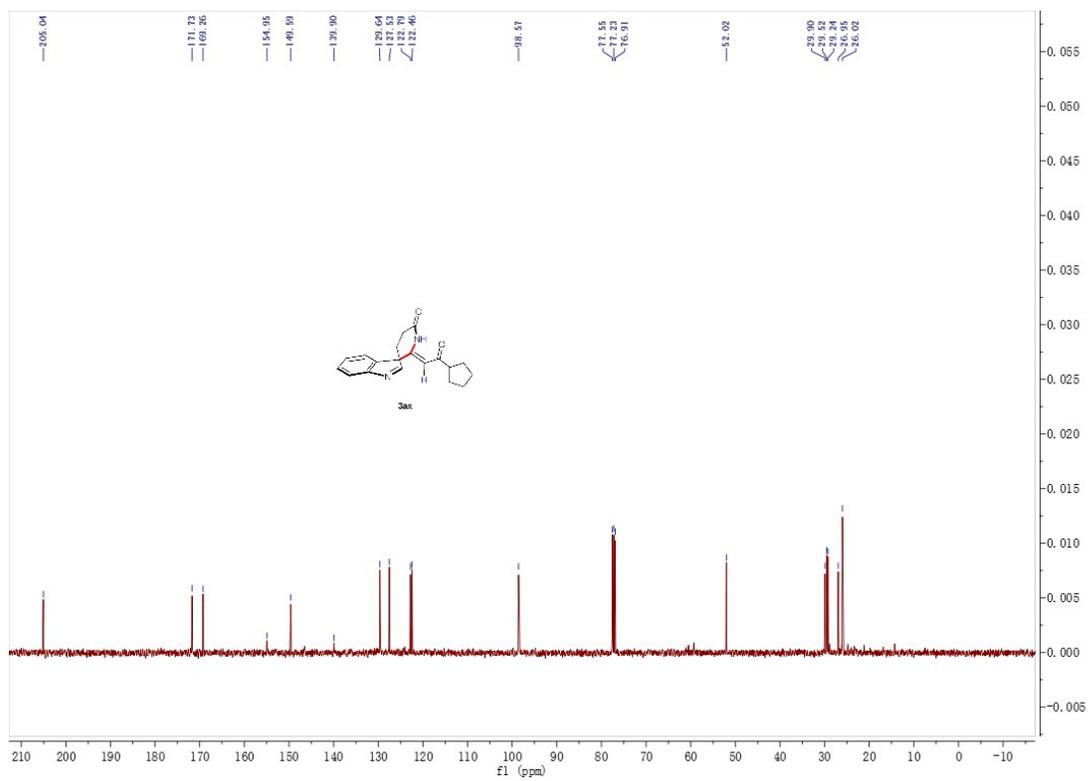
¹³C NMR spectrum of compound **3av (100 MHz, CDCl₃)**



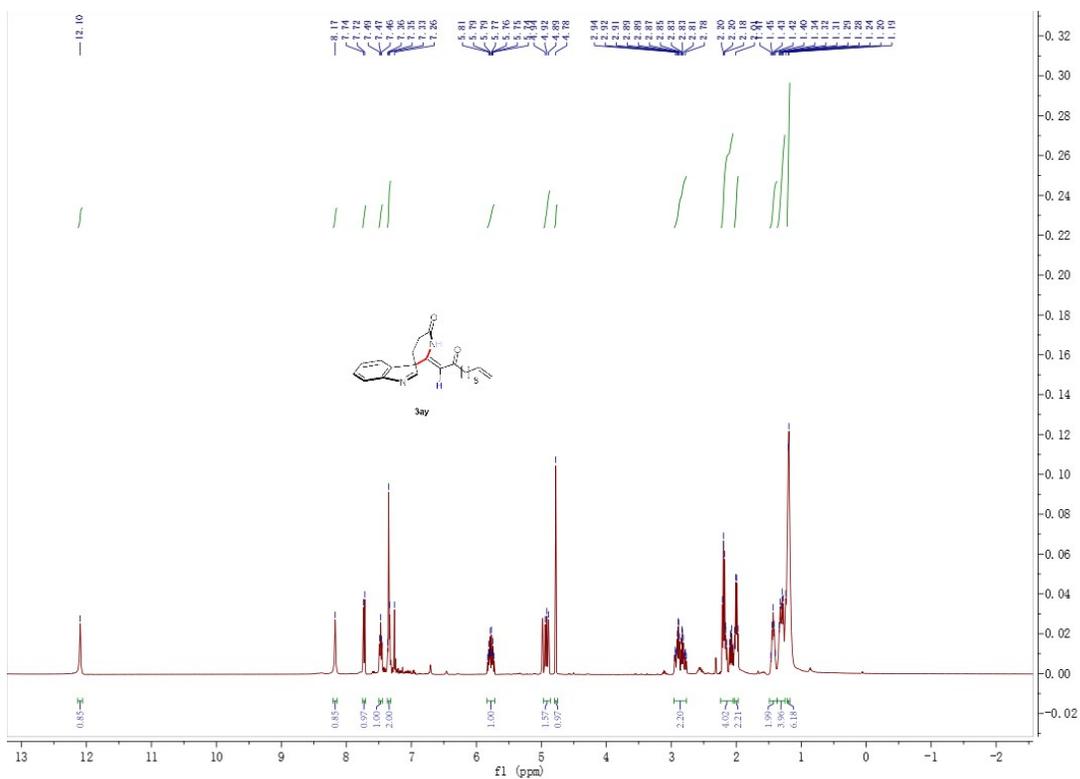
^1H NMR spectrum of compound **3ax** (400 MHz, CDCl_3)



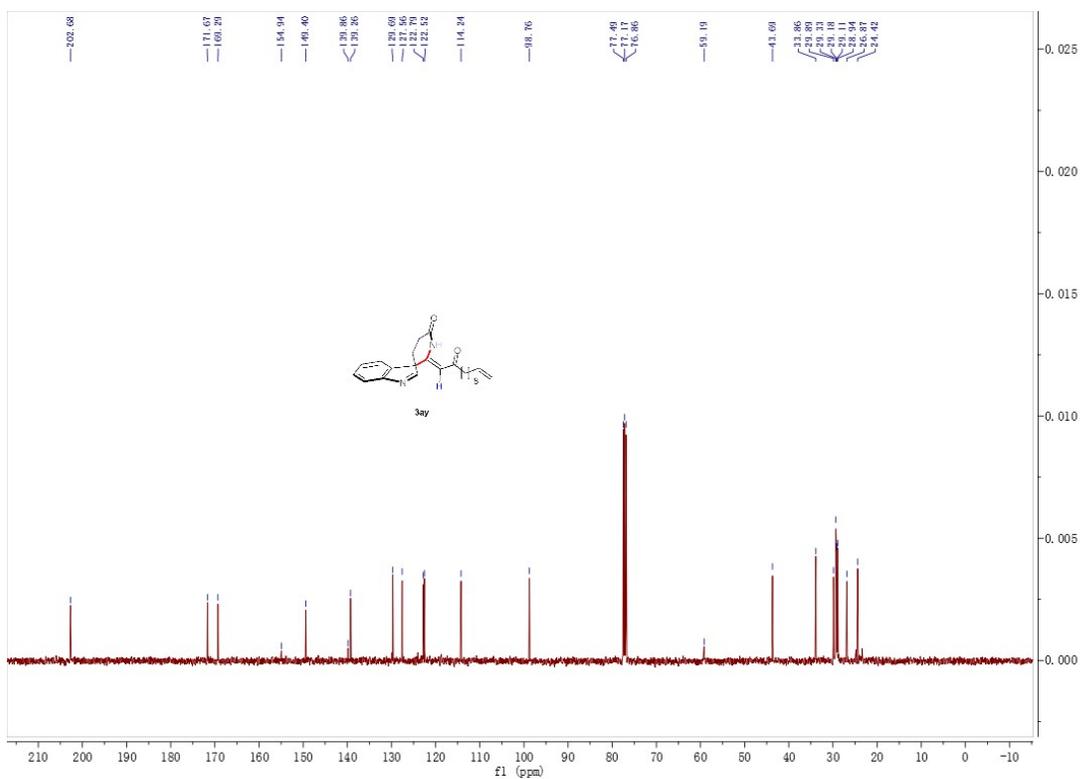
¹³C NMR spectrum of compound 3ax (100 MHz, CDCl₃)



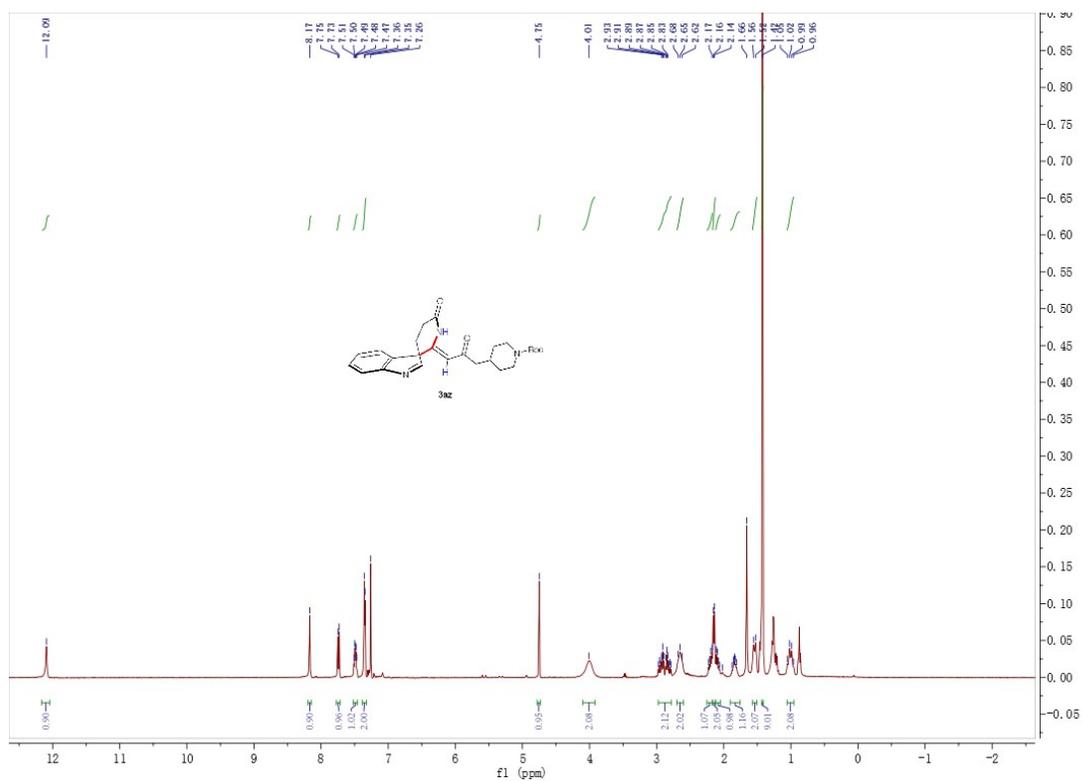
¹H NMR spectrum of compound 3ay (400 MHz, CDCl₃)



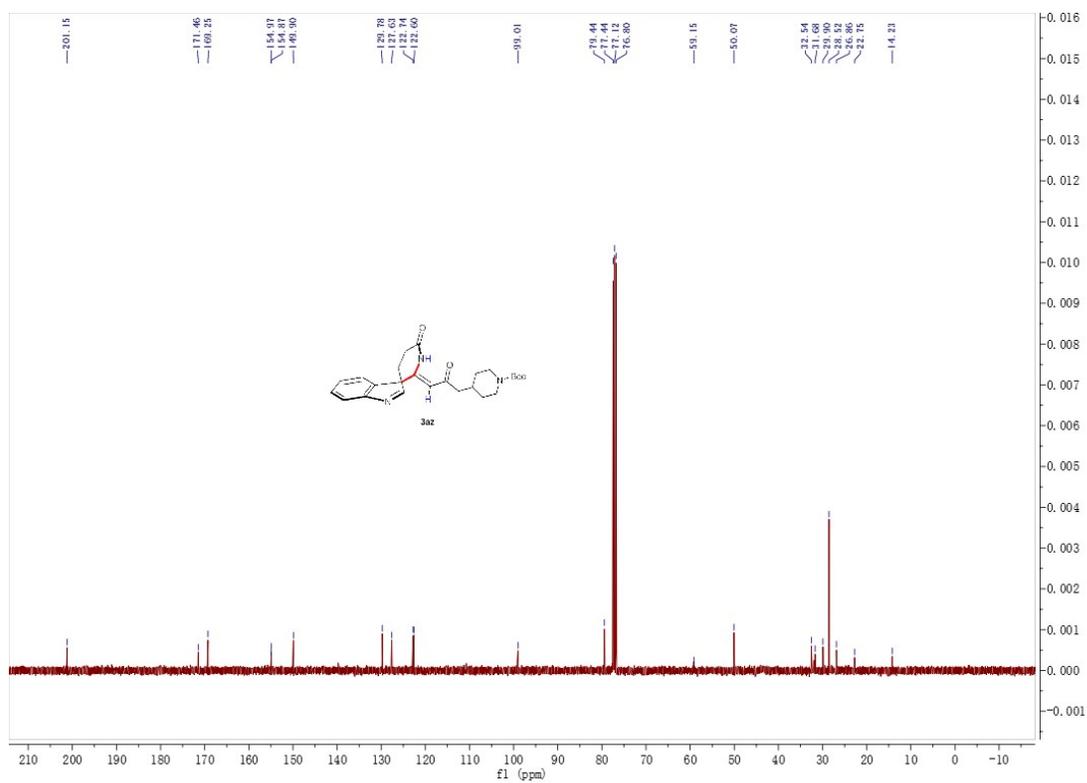
¹³C NMR spectrum of compound 3ay (100 MHz, CDCl₃)



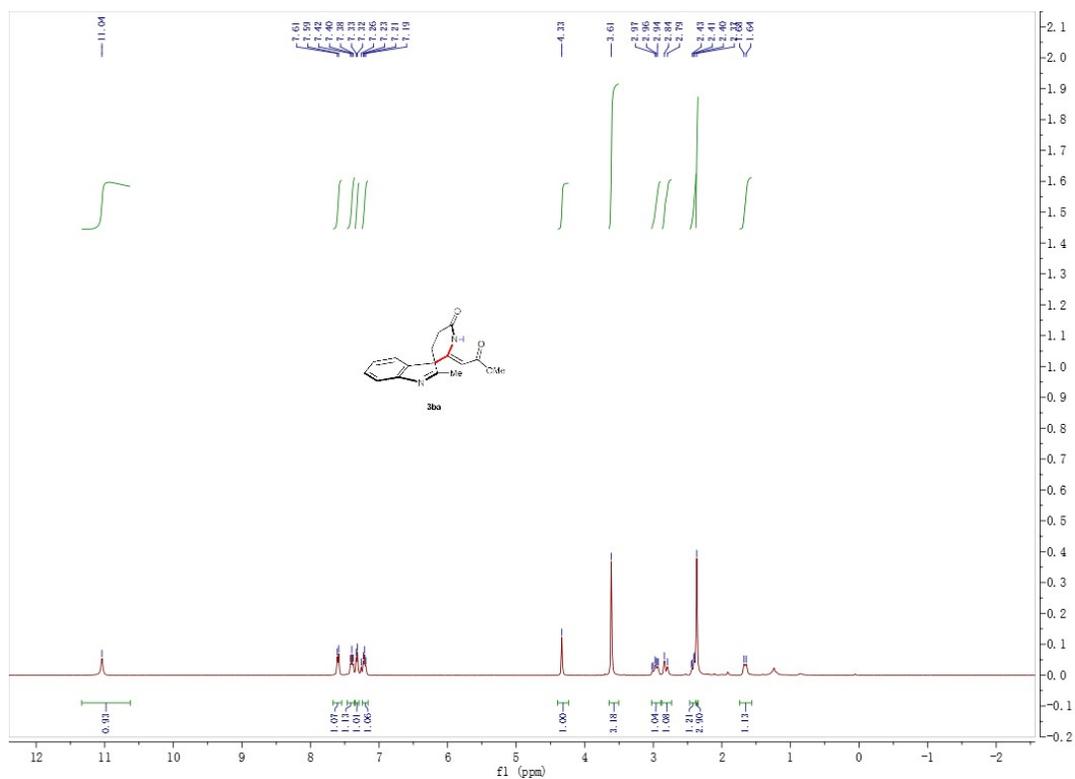
¹H NMR spectrum of compound **3az** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **3az** (100 MHz, CDCl₃)

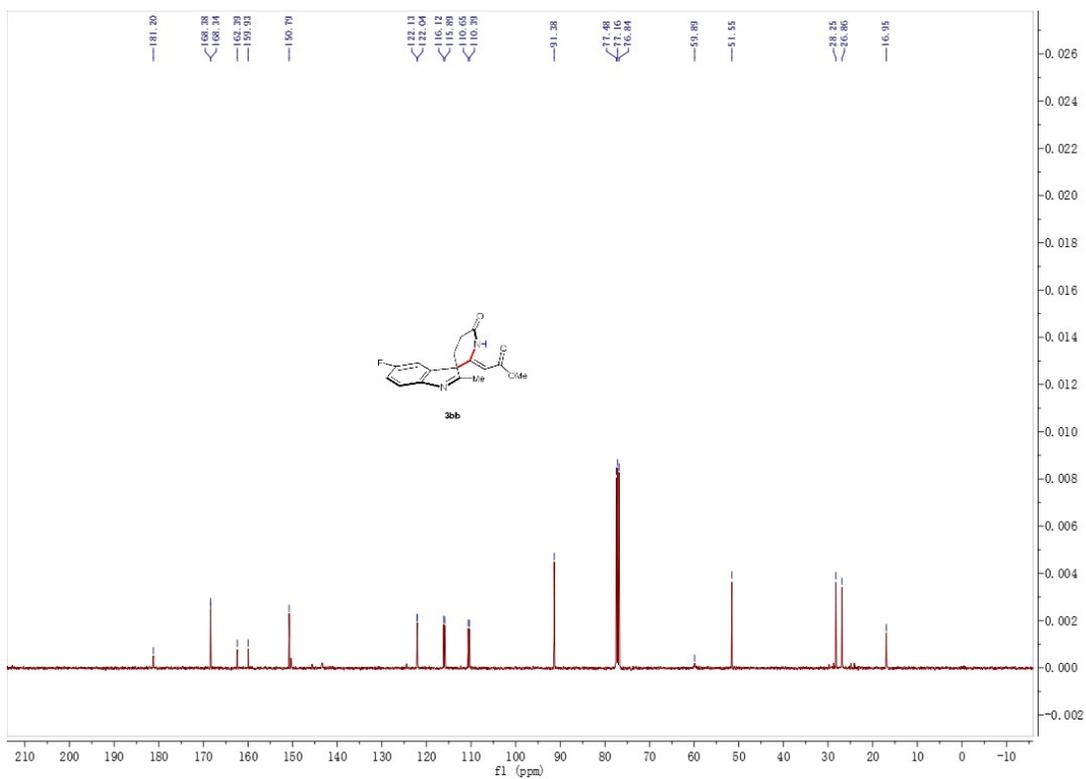


¹H NMR spectrum of compound 3ba (400 MHz, CDCl₃)

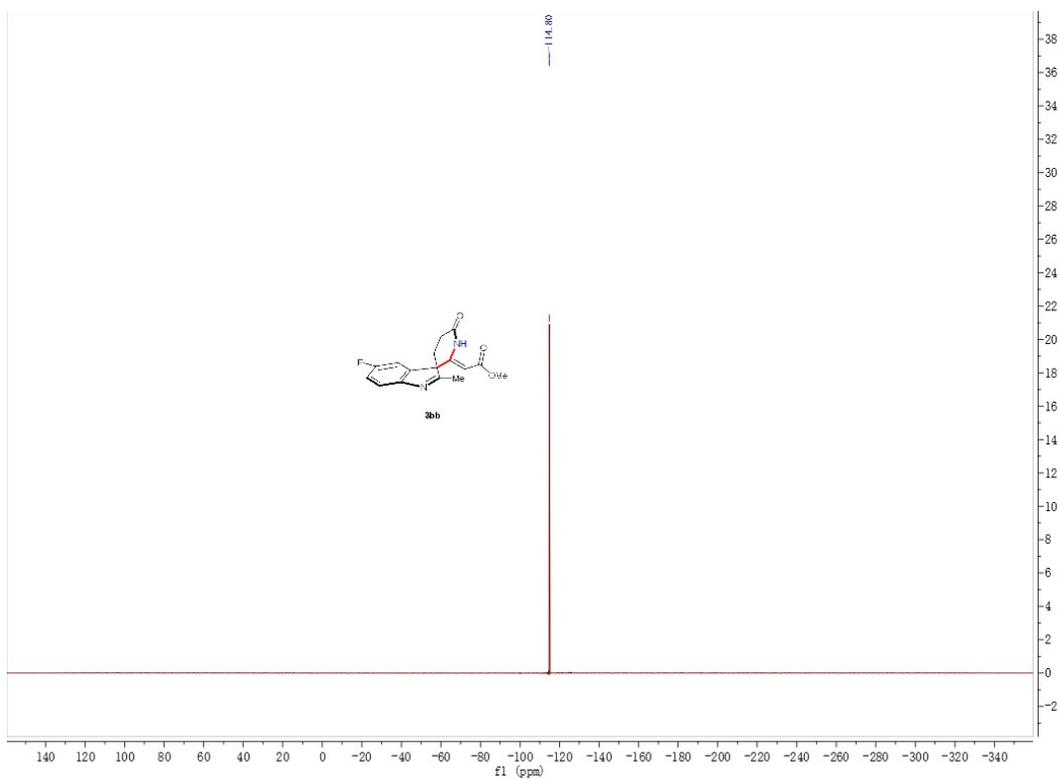


¹³C NMR spectrum of compound 3ba (100 MHz, CDCl₃)

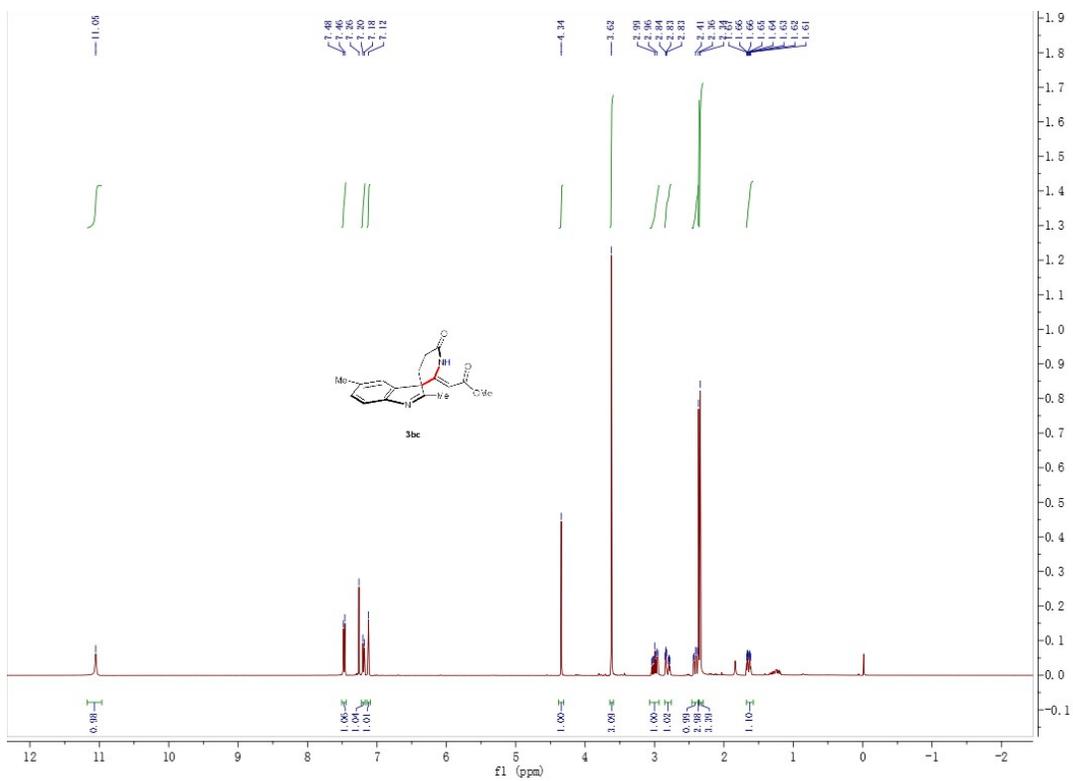
¹³C NMR spectrum of compound **3bb (100 MHz, CDCl₃)**



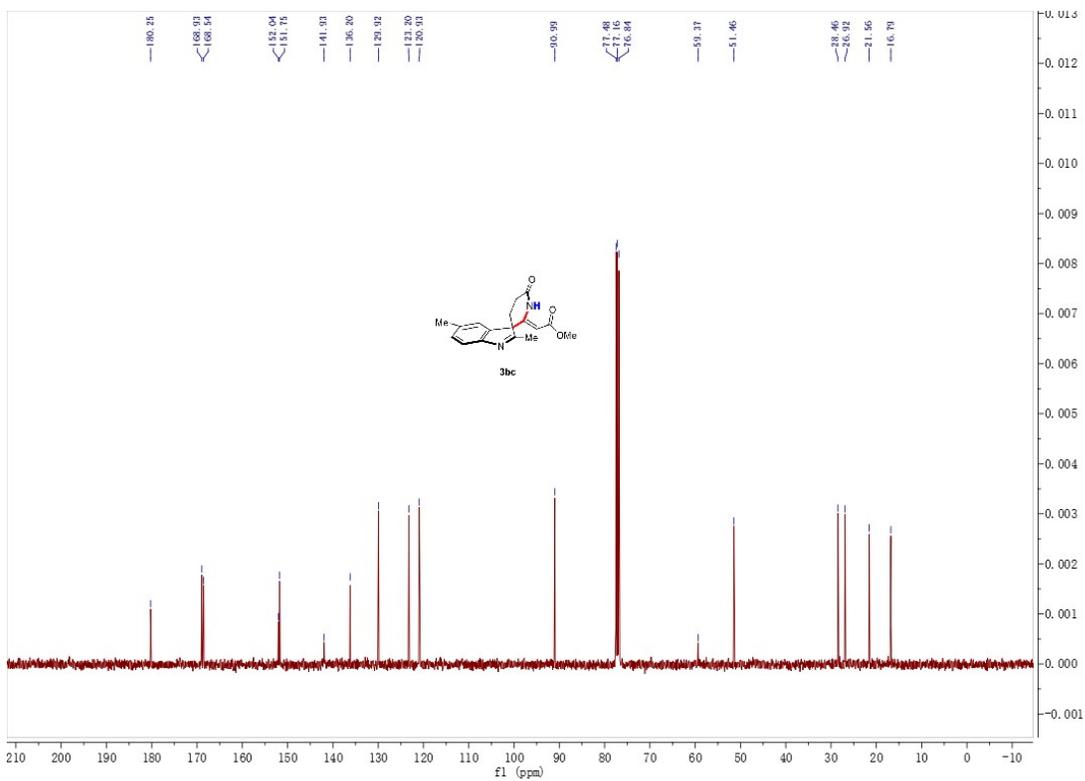
¹⁹F NMR spectrum of compound **3bb (376 MHz, CDCl₃)**



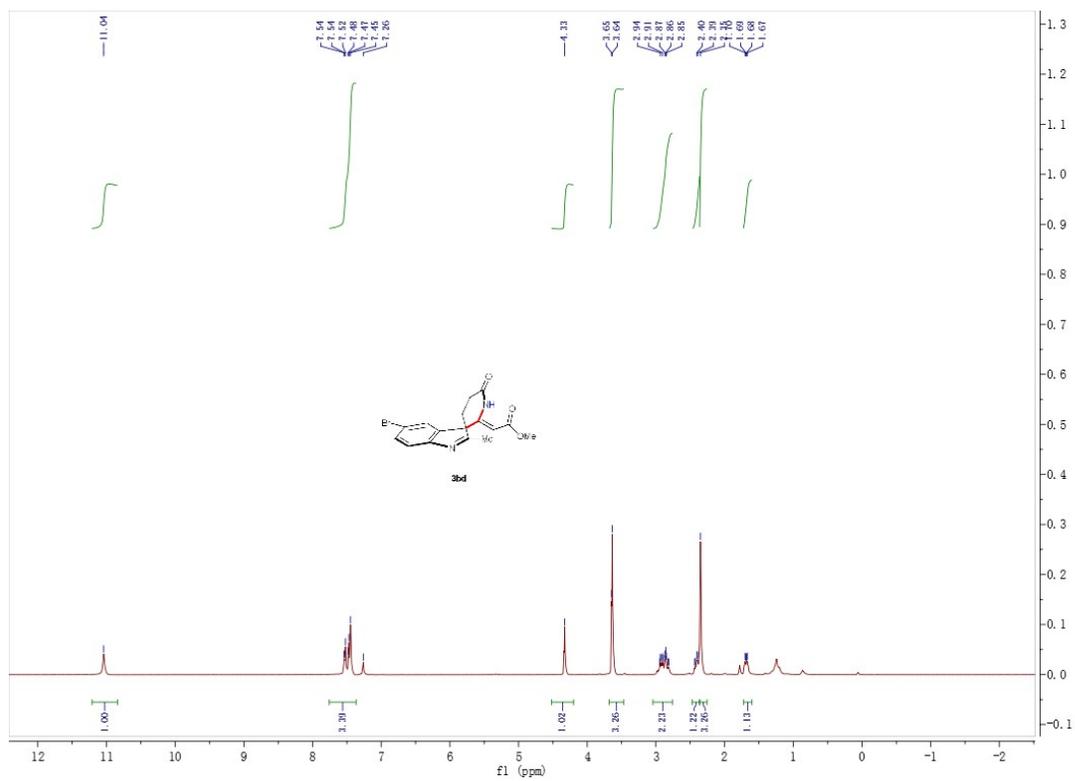
^1H NMR spectrum of compound **3bc** (400 MHz, CDCl_3)



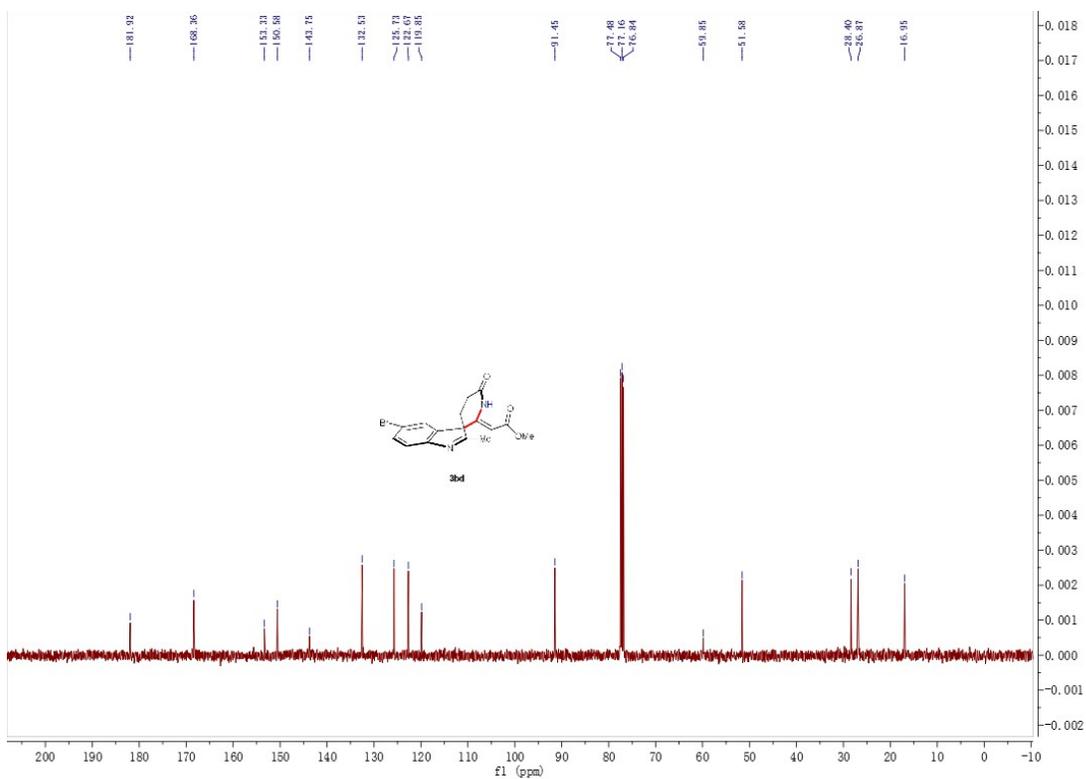
¹³C NMR spectrum of compound 3bc (100 MHz, CDCl₃)



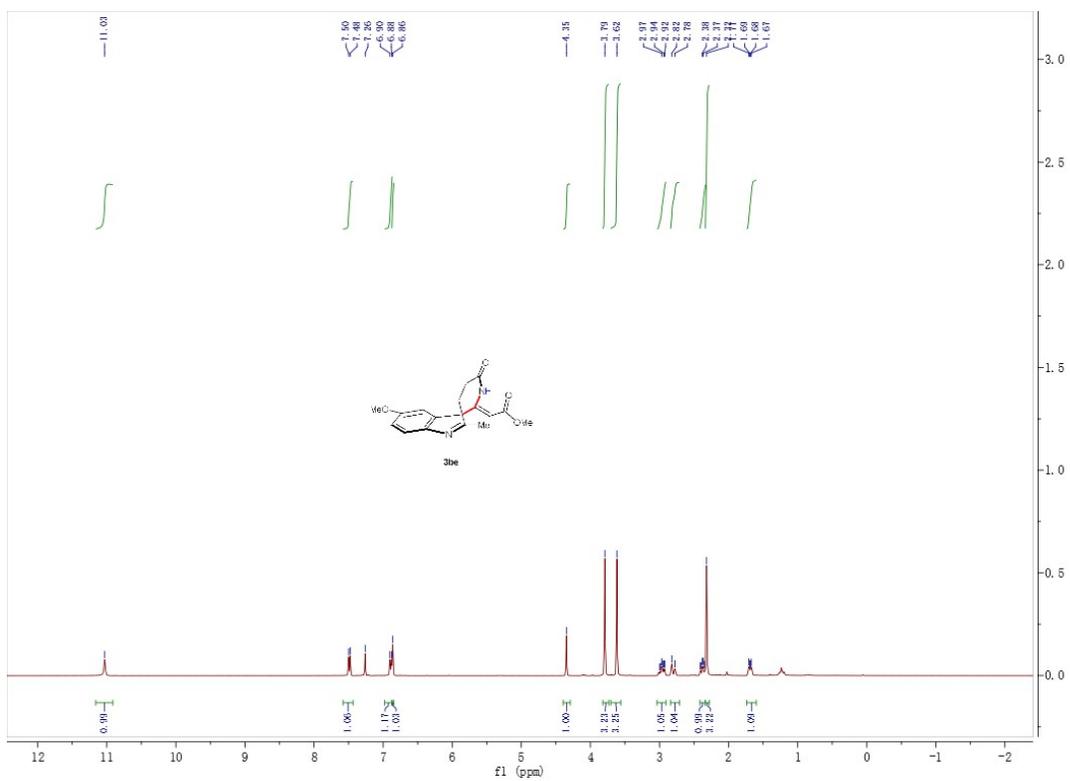
^1H NMR spectrum of compound **3bd** (400 MHz, CDCl_3)



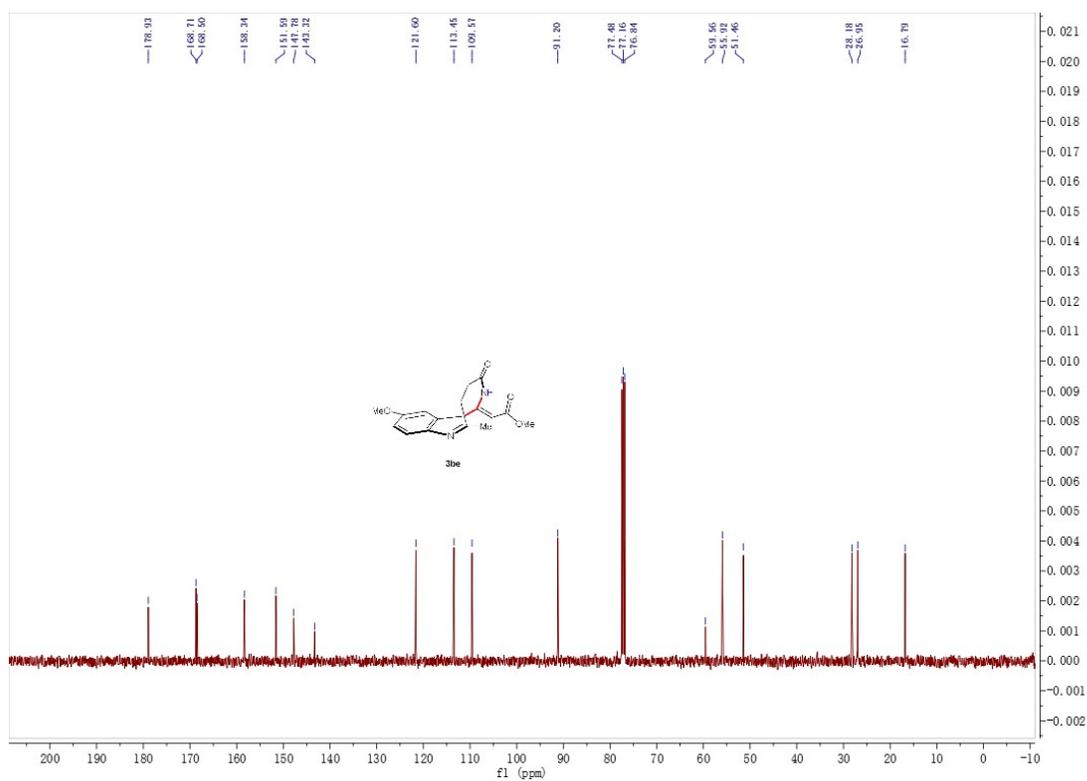
^{13}C NMR spectrum of compound **3bd** (100 MHz, CDCl_3)



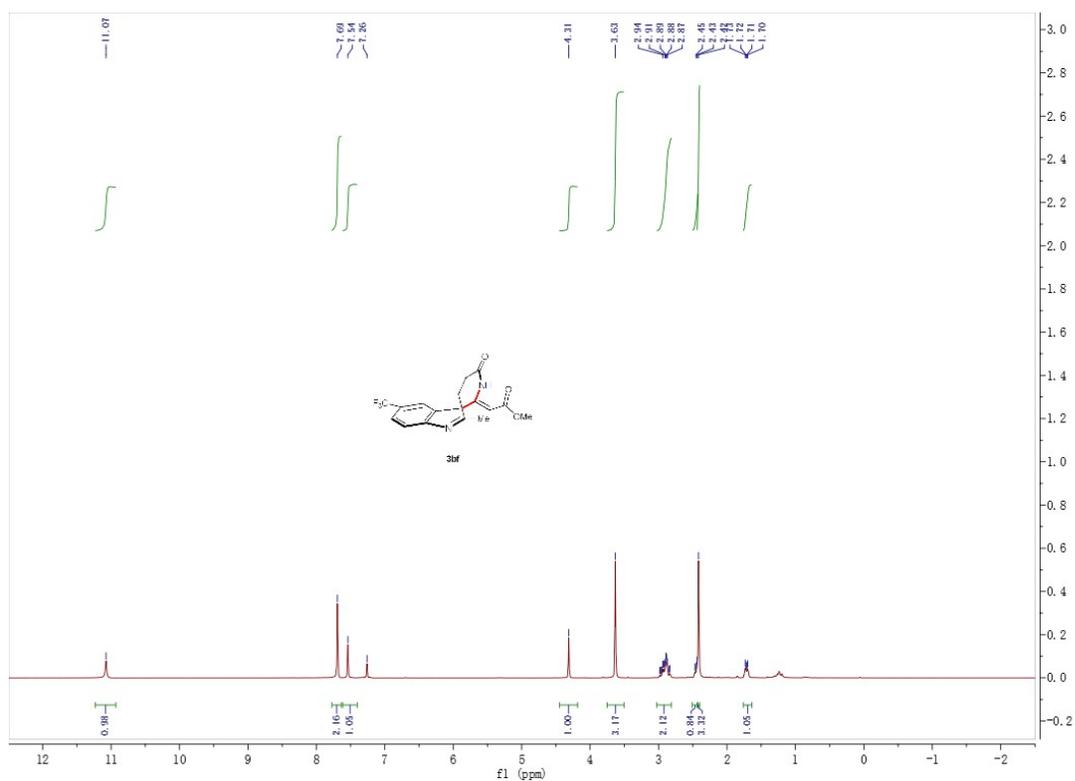
¹H NMR spectrum of compound 3be (400 MHz, CDCl₃)



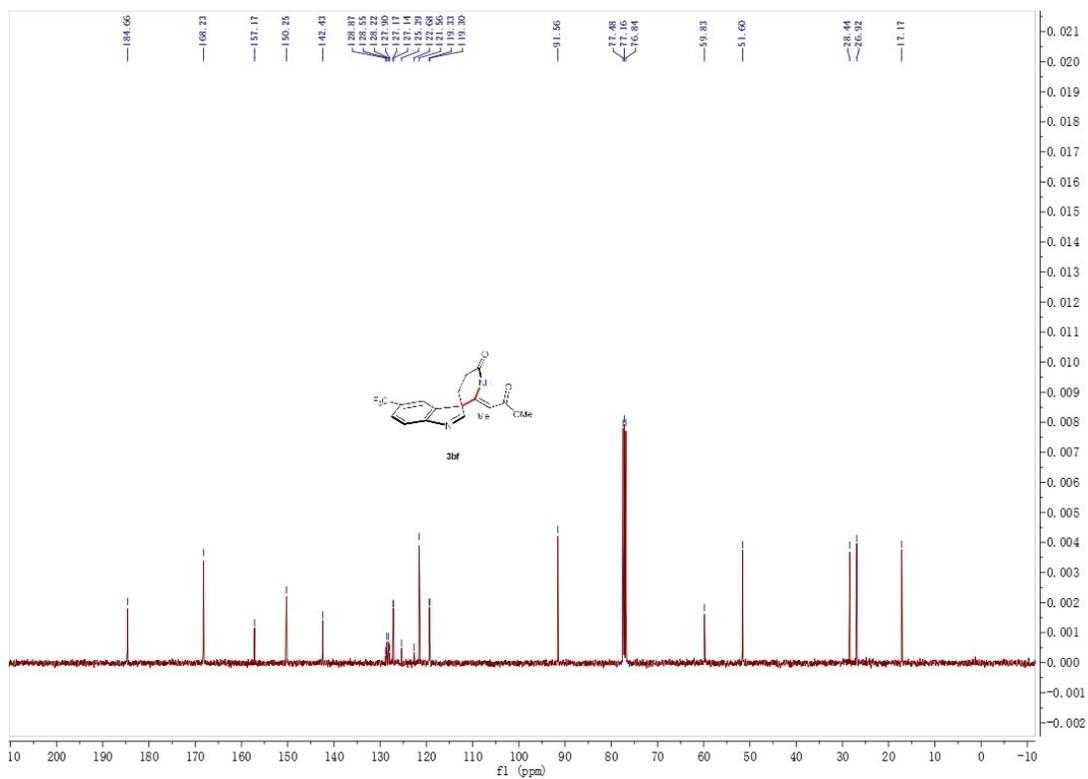
¹³C NMR spectrum of compound 3be (100 MHz, CDCl₃)



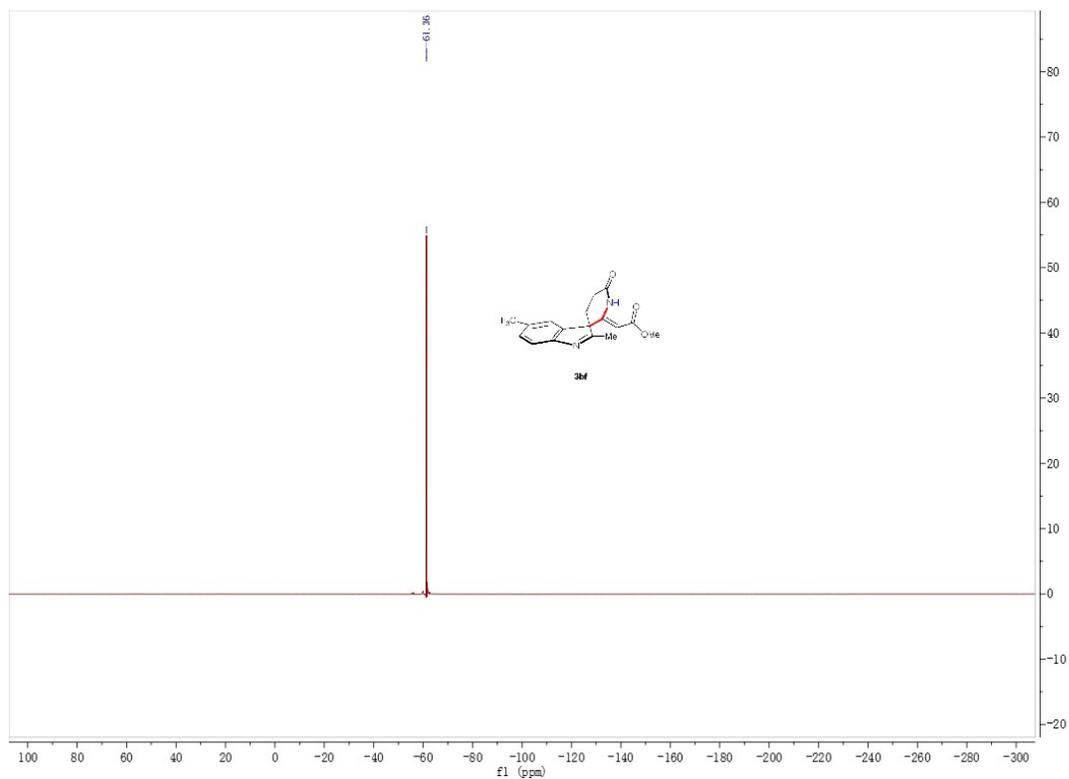
¹H NMR spectrum of compound 3bf (400 MHz, CDCl₃)



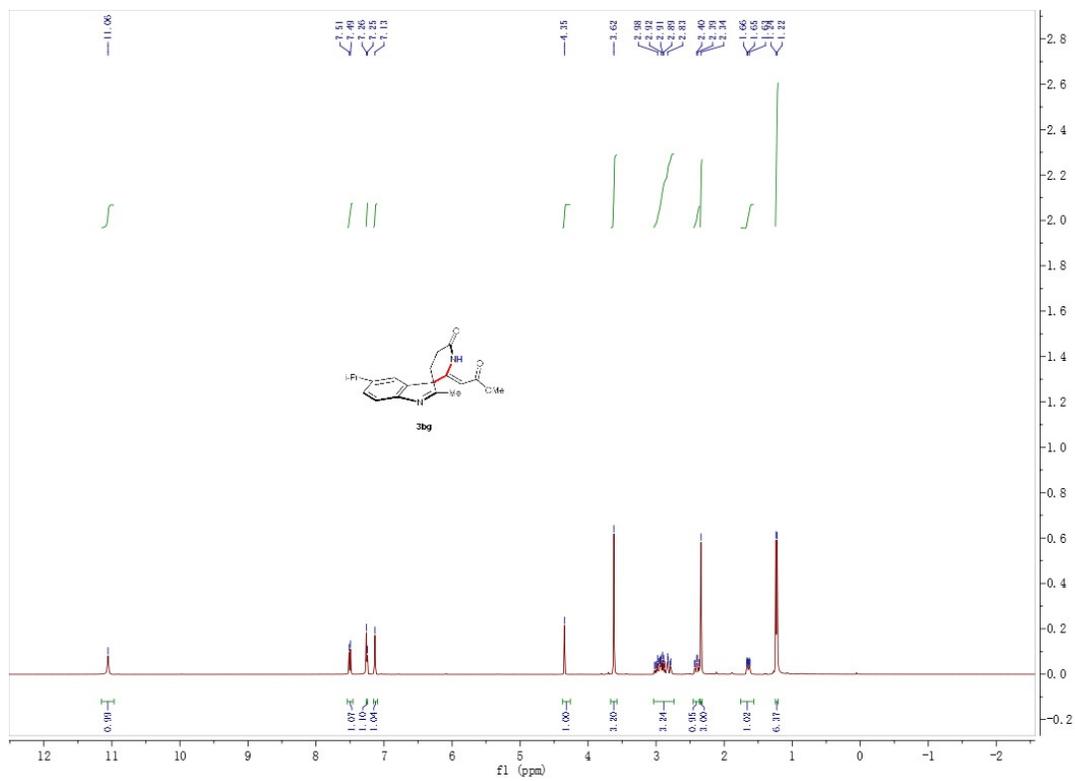
¹³C NMR spectrum of compound 3bf (100 MHz, CDCl₃)



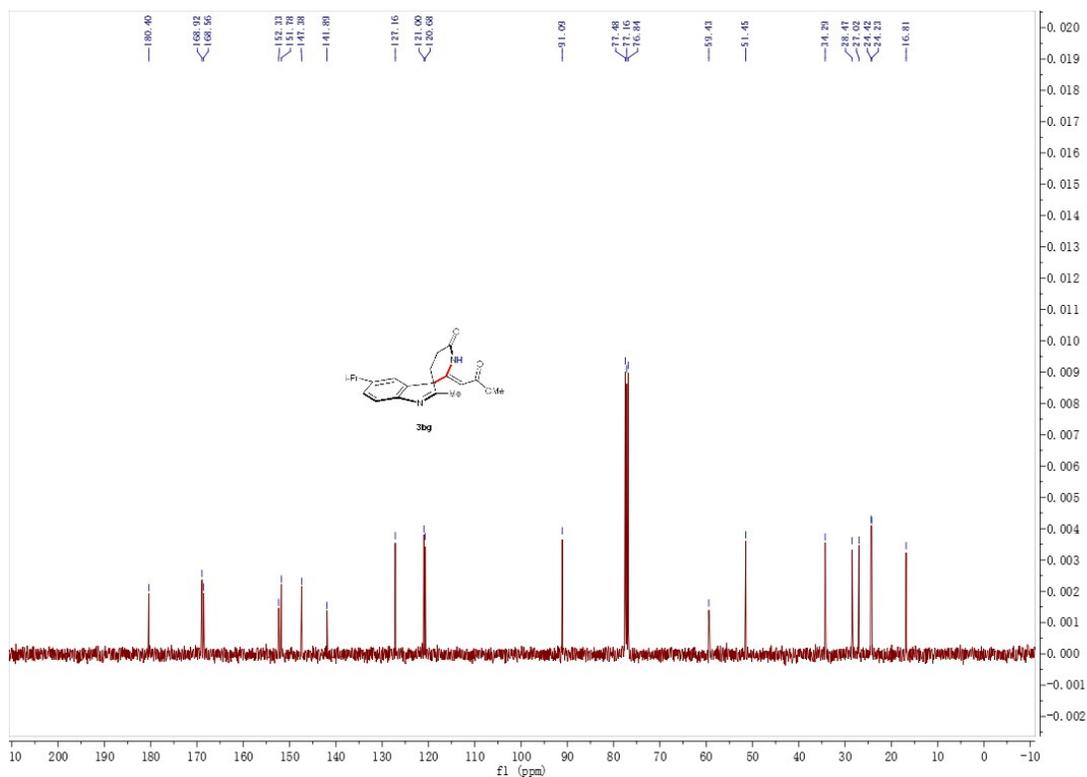
¹⁹F NMR spectrum of compound 3bf (376 MHz, CDCl₃)



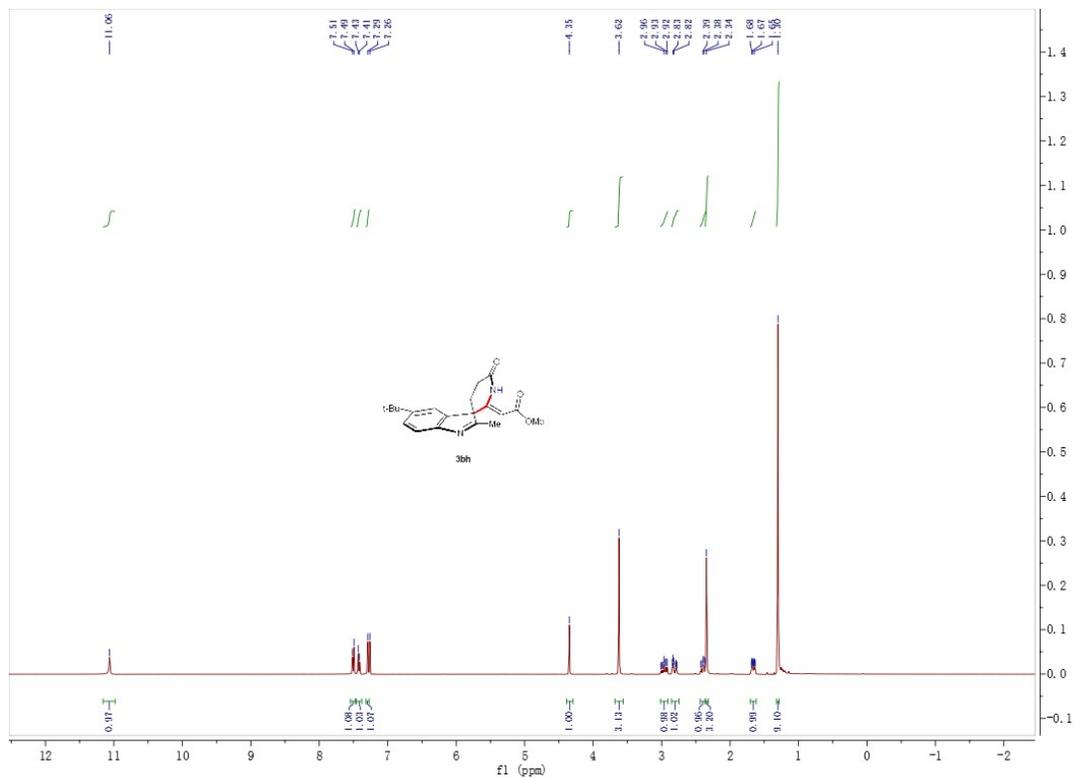
^1H NMR spectrum of compound **3bg** (400 MHz, CDCl_3)



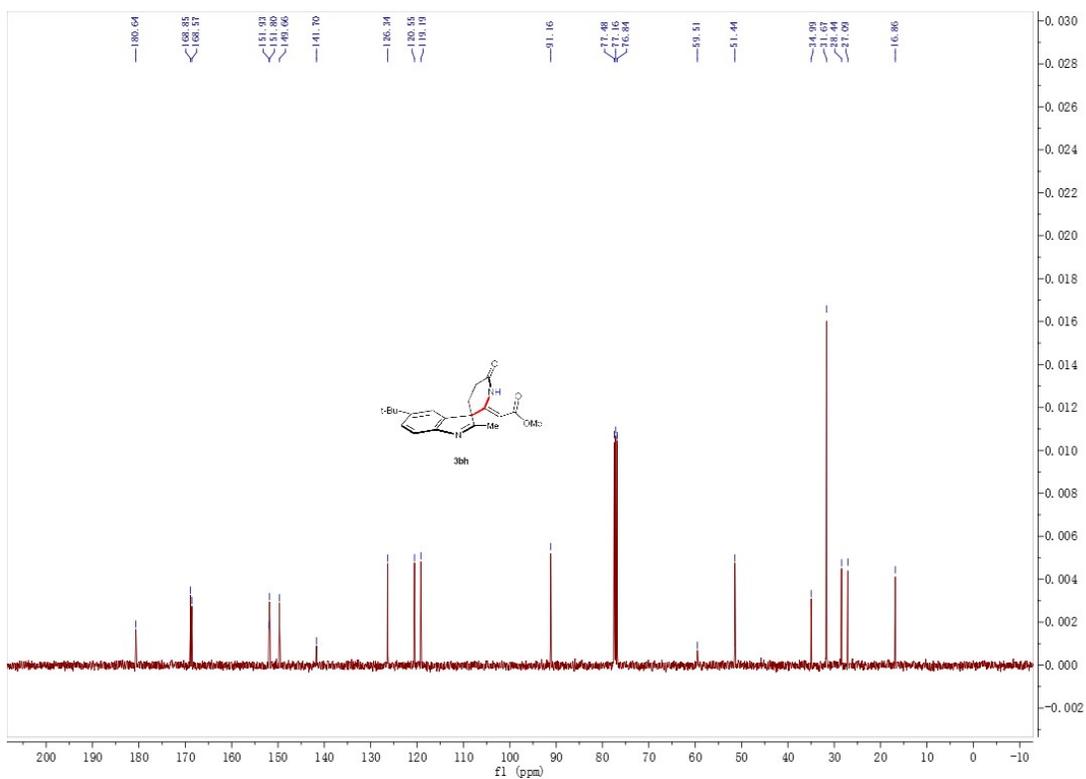
¹³C NMR spectrum of compound 3bg (100 MHz, CDCl₃)



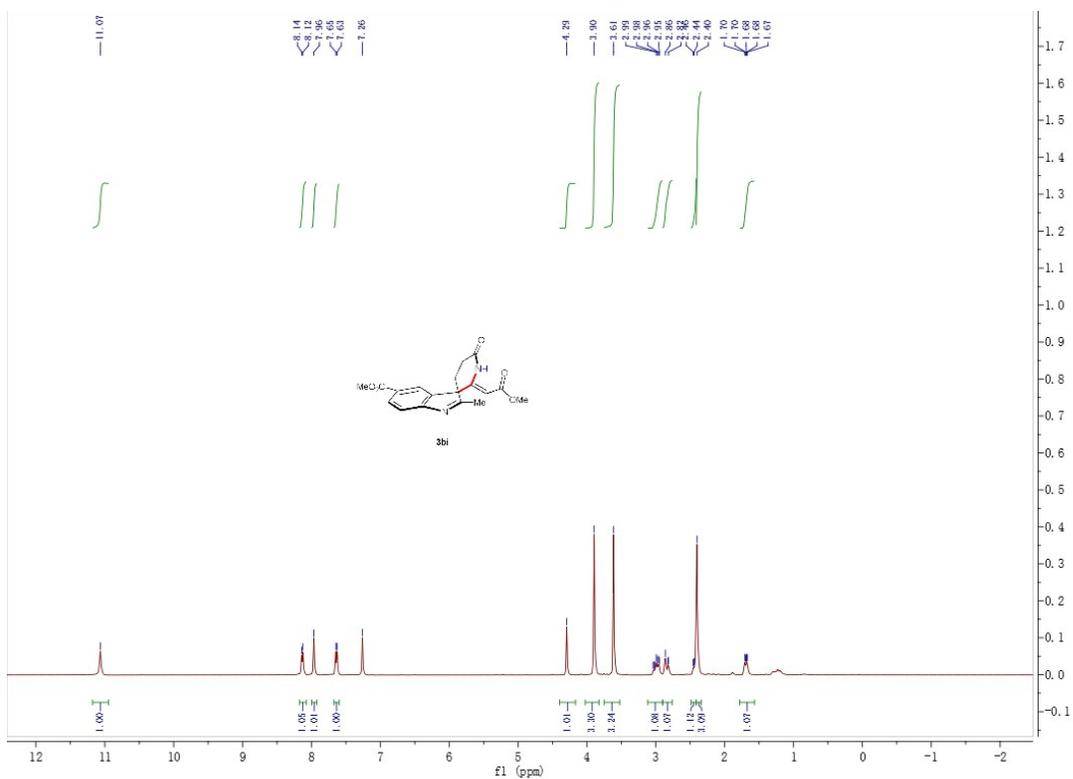
¹H NMR spectrum of compound 3bh (400 MHz, CDCl₃)



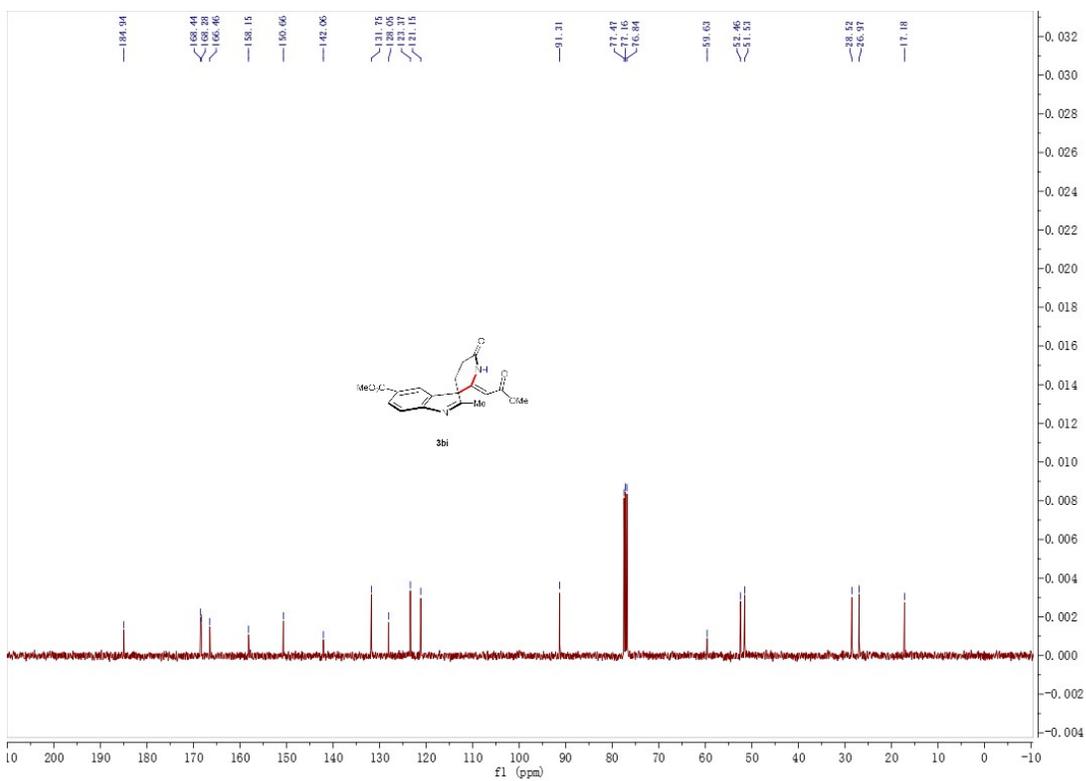
¹³C NMR spectrum of compound 3bh (100 MHz, CDCl₃)



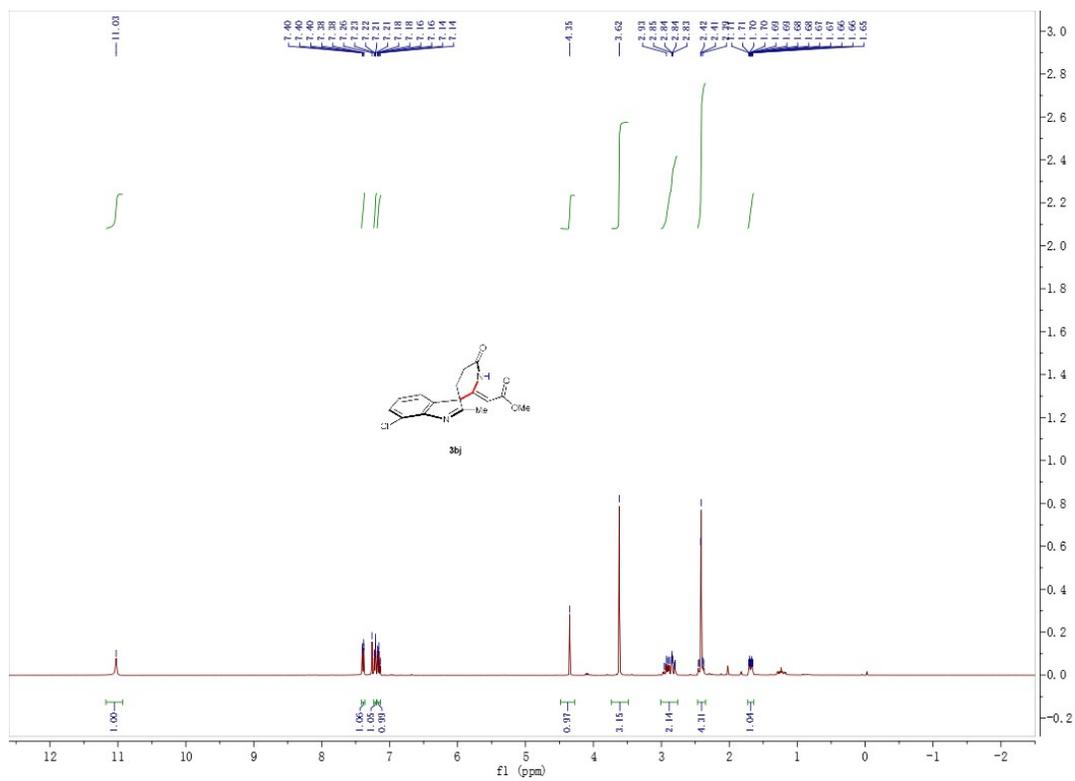
¹H NMR spectrum of compound 3bi (400 MHz, CDCl₃)



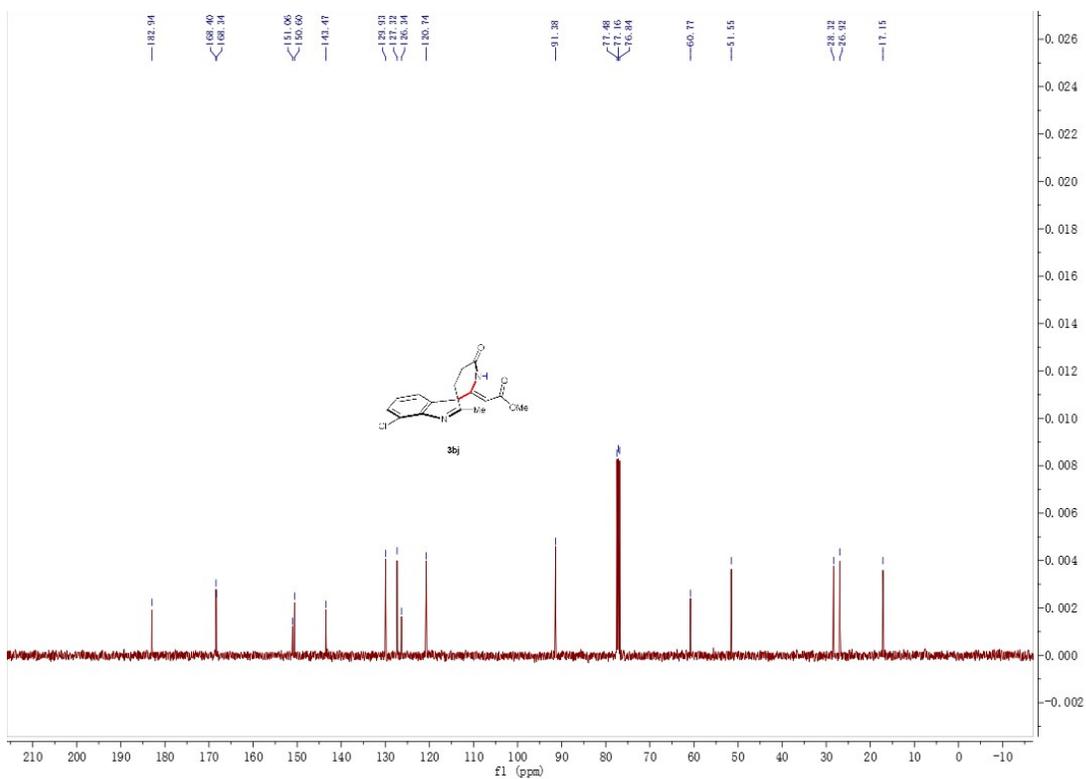
¹³C NMR spectrum of compound 3bi (100 MHz, CDCl₃)



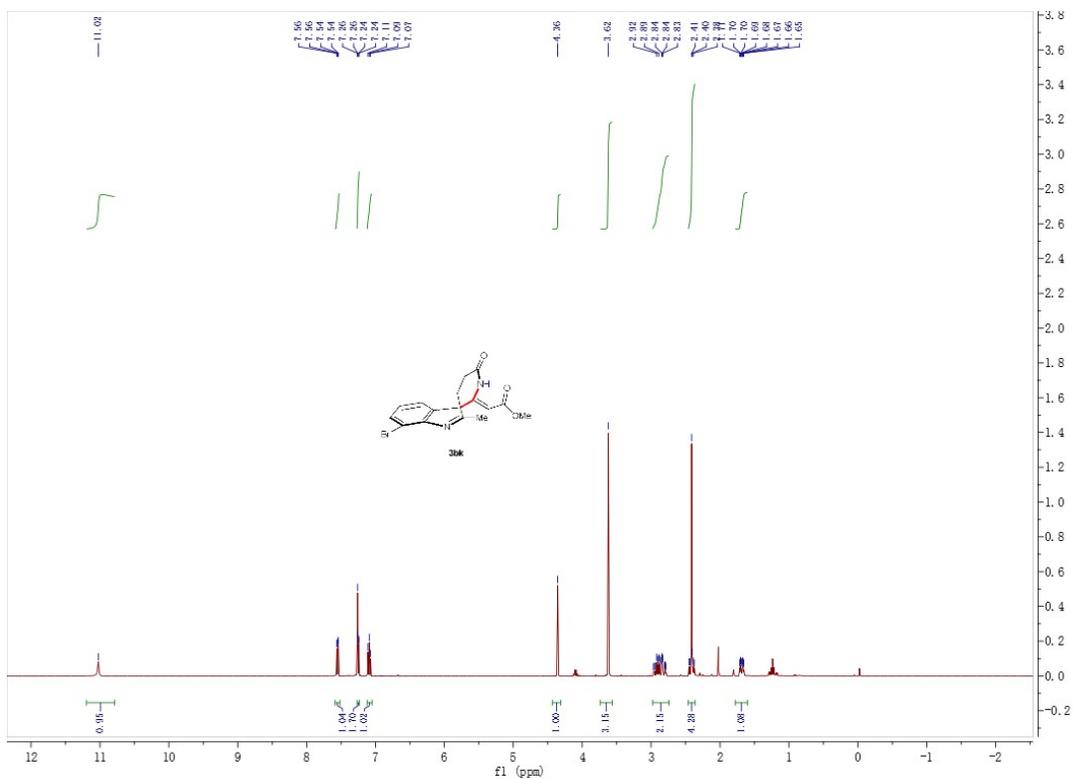
^1H NMR spectrum of compound **3bj** (400 MHz, CDCl_3)



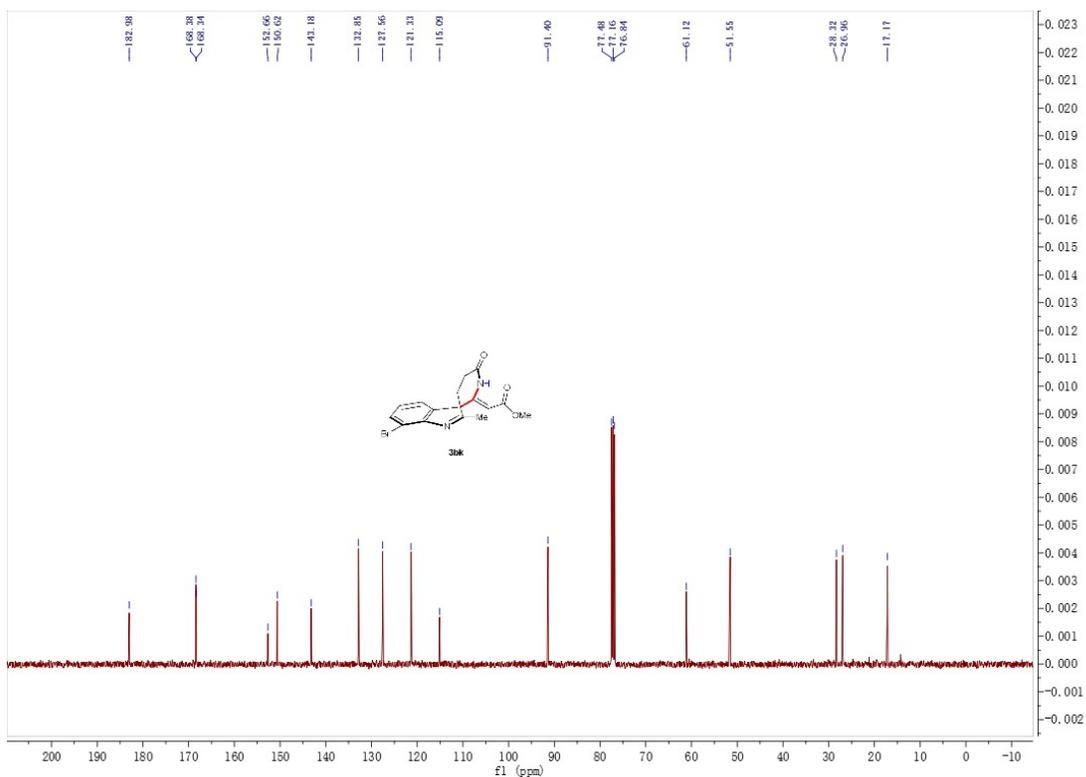
^{13}C NMR spectrum of compound **3bj** (100 MHz, CDCl_3)



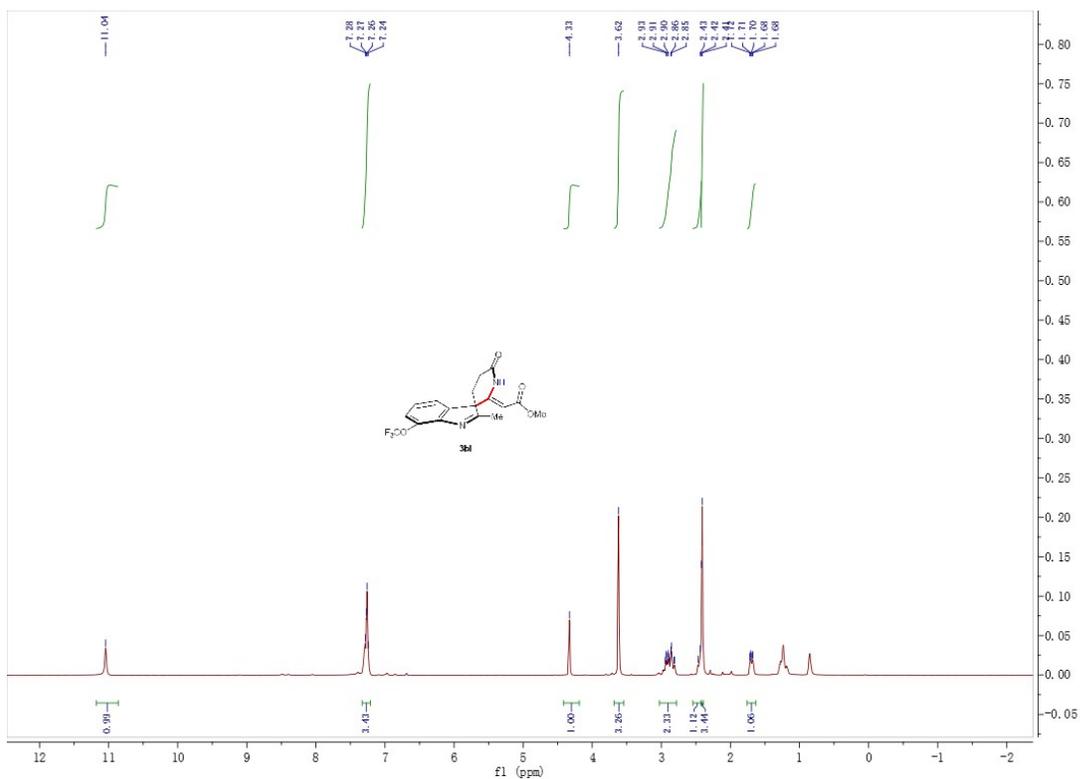
¹H NMR spectrum of compound 3bk (400 MHz, CDCl₃)



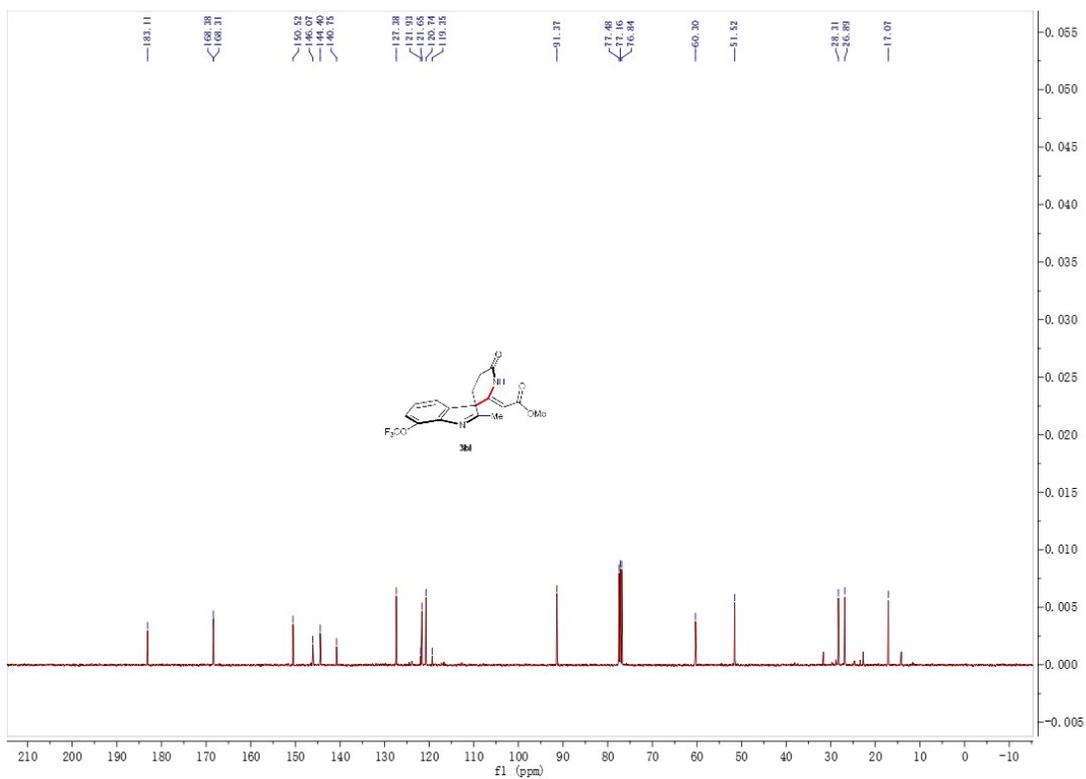
¹³C NMR spectrum of compound **3bk** (100 MHz, CDCl₃)



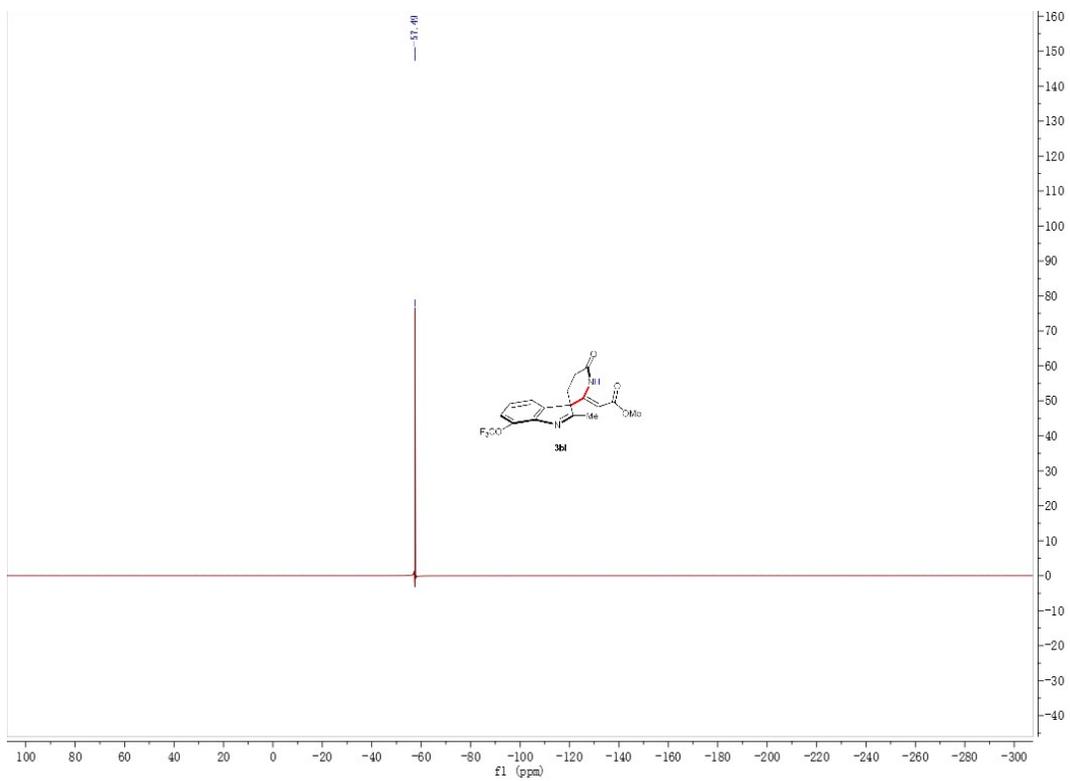
¹H NMR spectrum of compound **3bl** (400 MHz, CDCl₃)



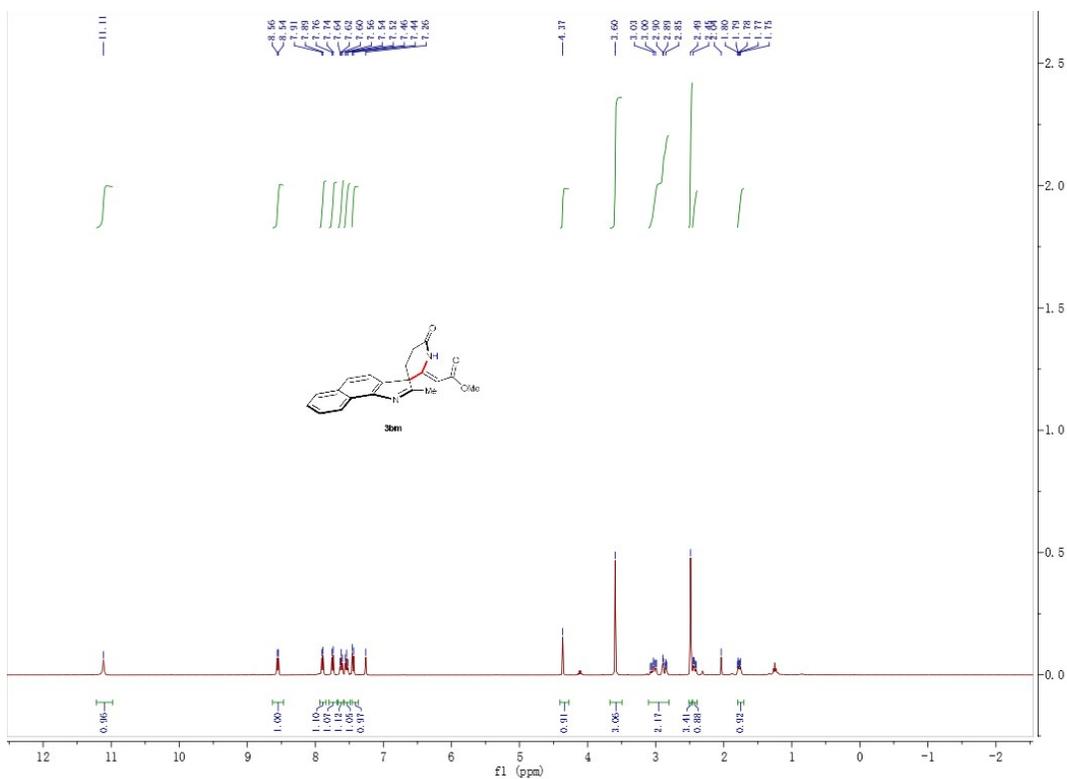
¹³C NMR spectrum of compound 3bl (100 MHz, CDCl₃)



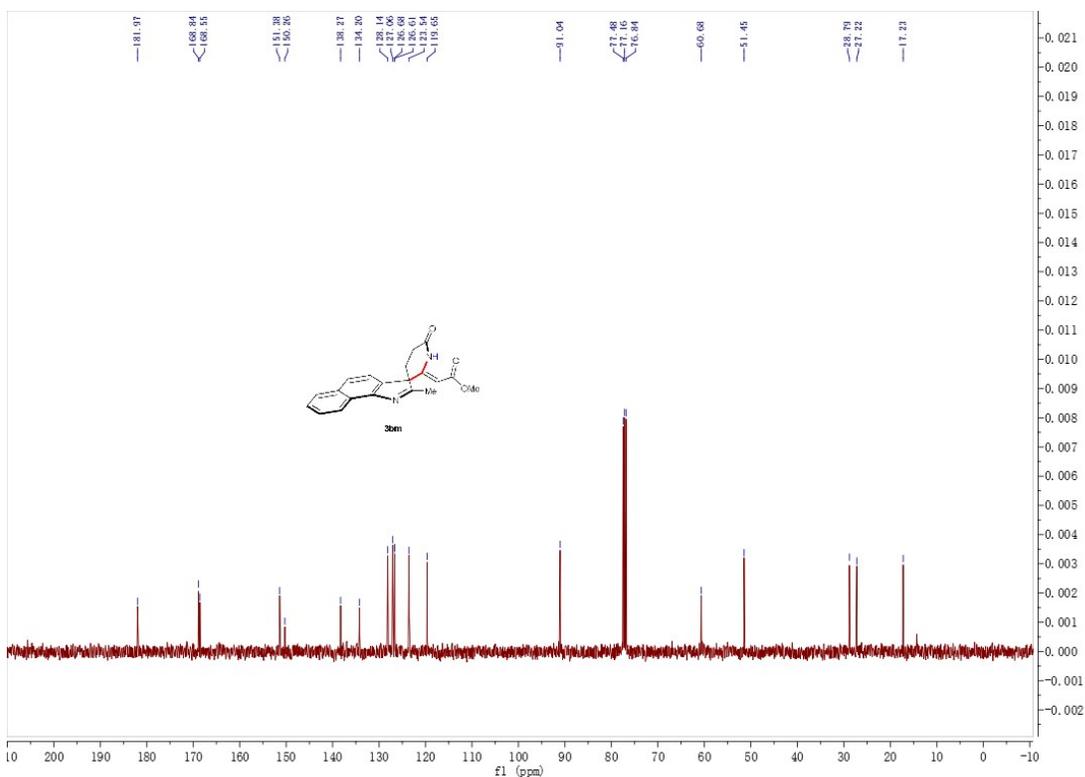
¹⁹F NMR spectrum of compound 3bl (376 MHz, CDCl₃)



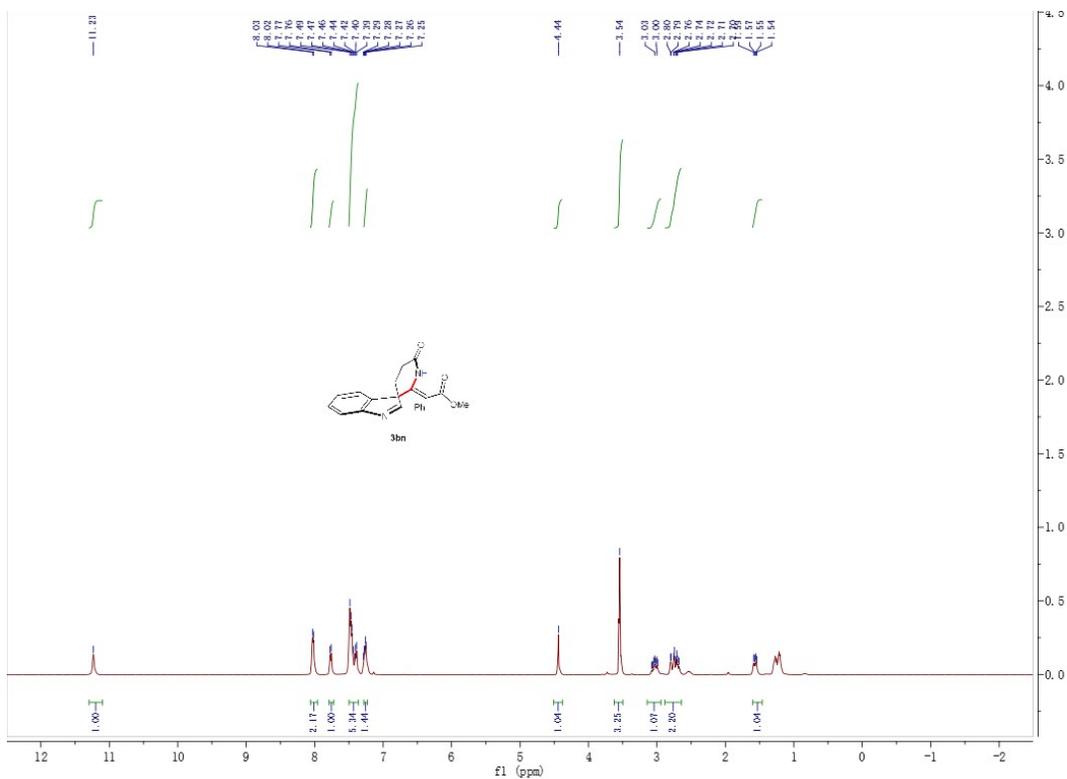
^1H NMR spectrum of compound **3bm** (400 MHz, CDCl_3)



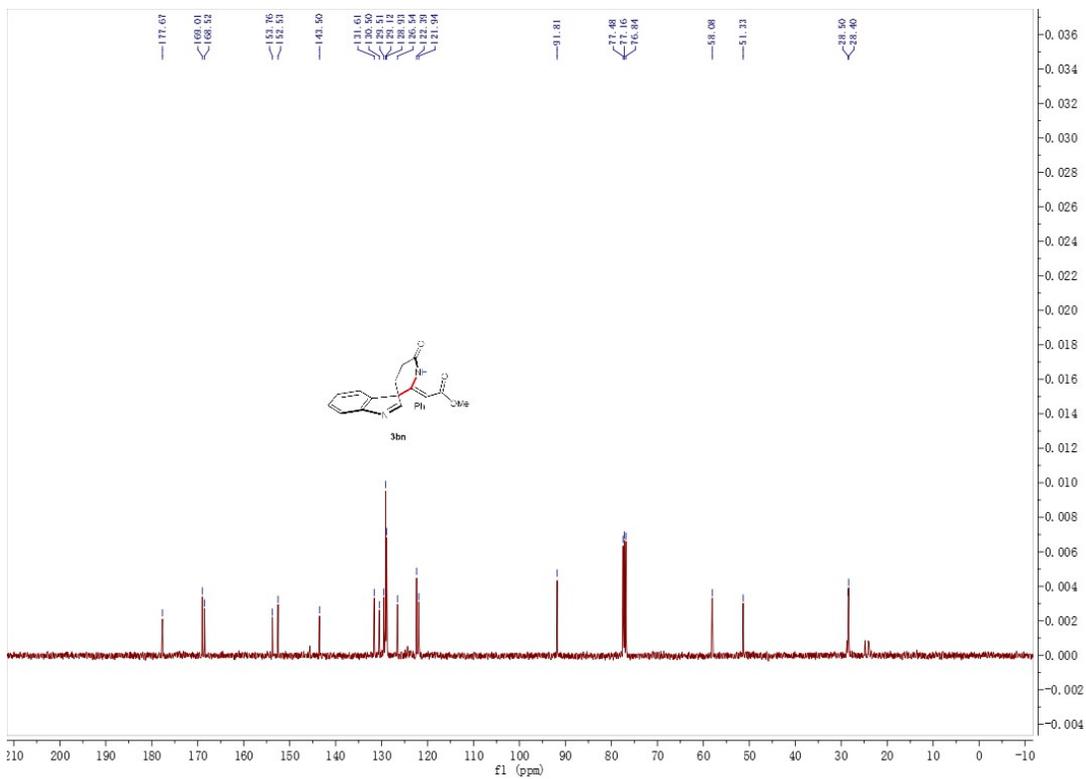
¹³C NMR spectrum of compound **3bm (100 MHz, CDCl₃)**



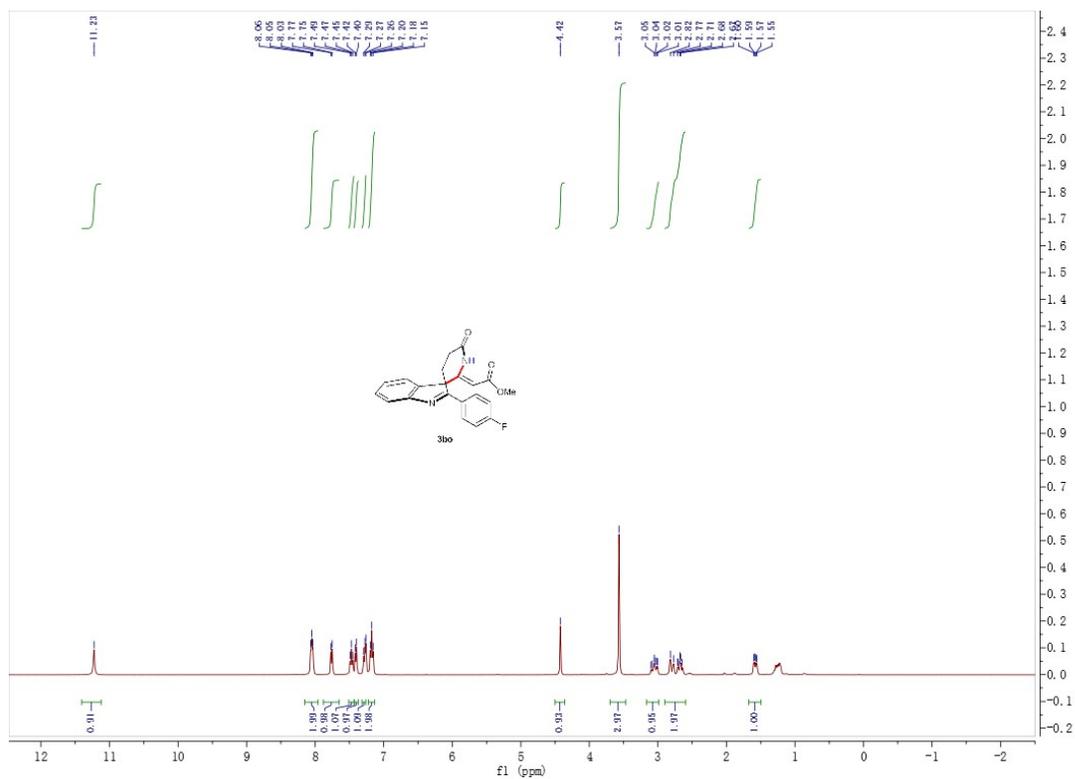
¹H NMR spectrum of compound **3bm (400 MHz, CDCl₃)**



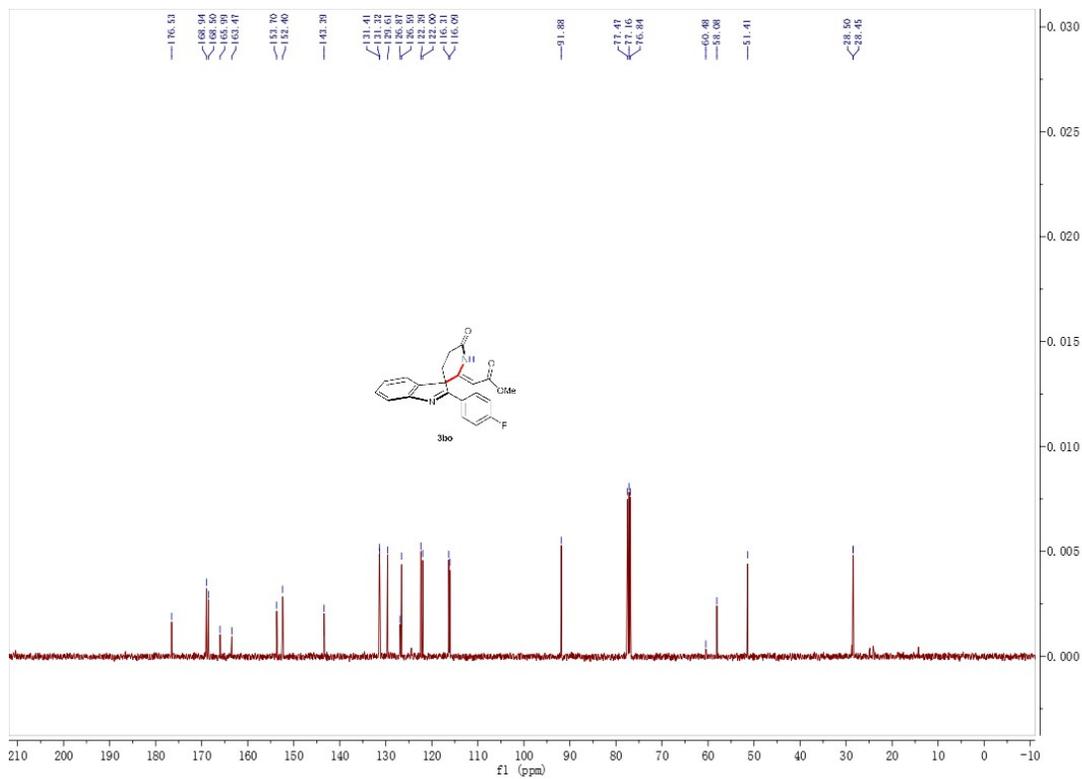
¹³C NMR spectrum of compound 3bn (100 MHz, CDCl₃)



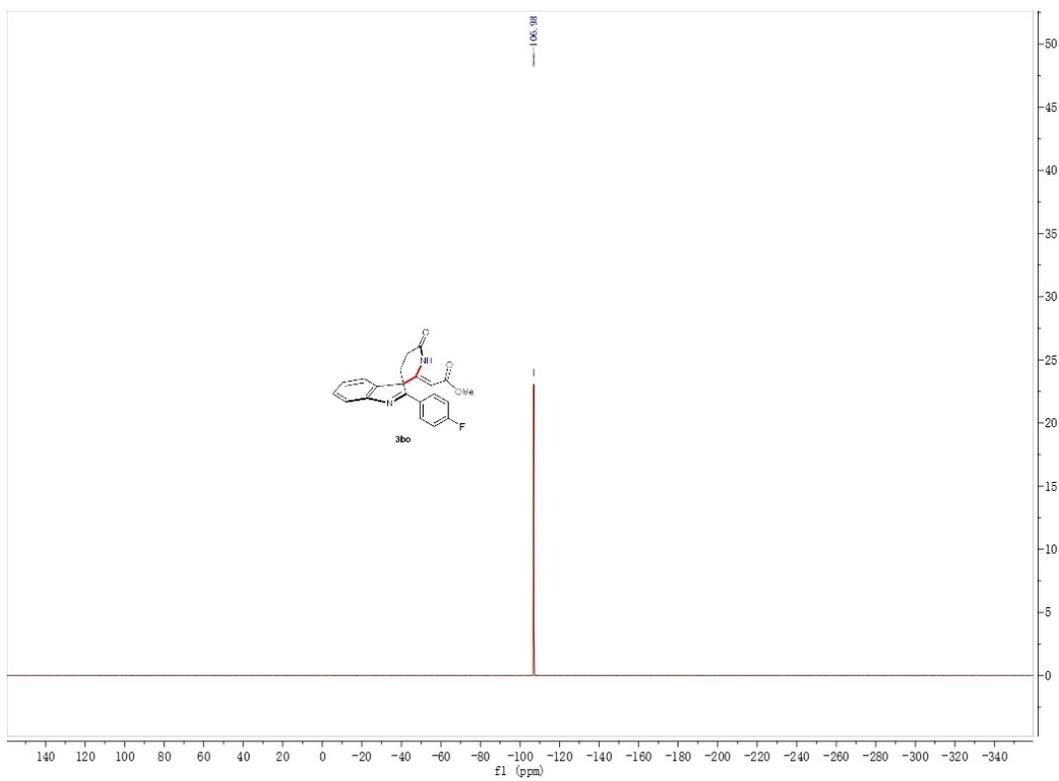
¹H NMR spectrum of compound 3bo (400 MHz, CDCl₃)



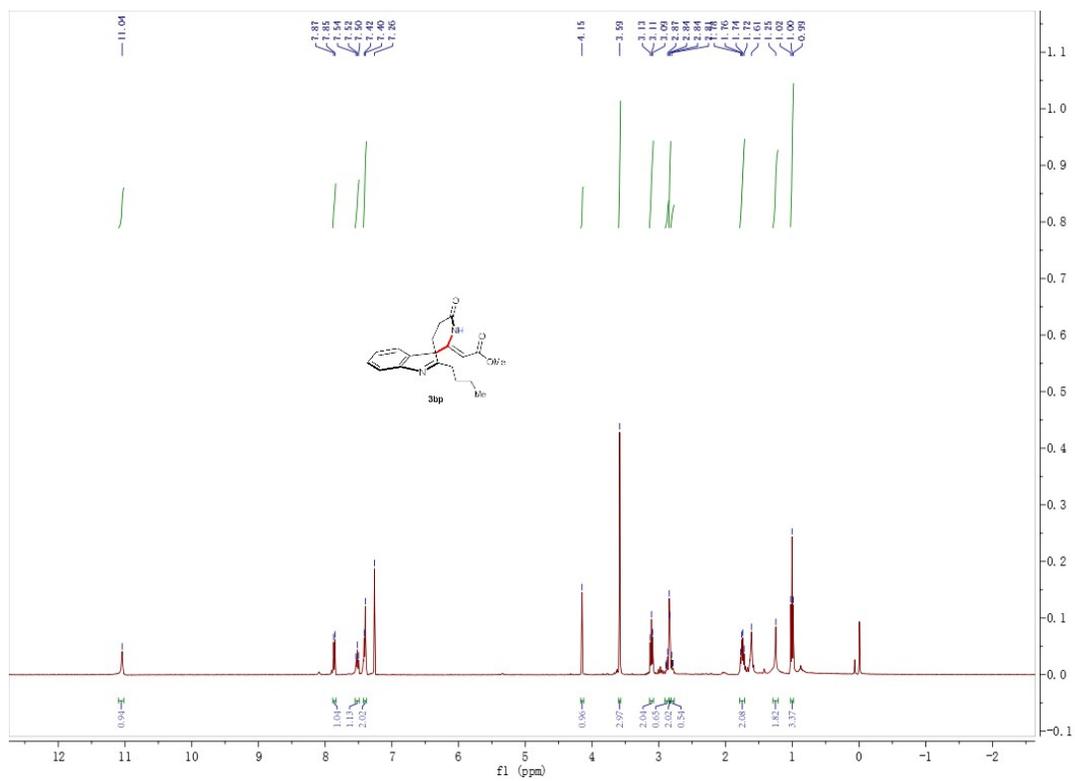
¹³C NMR spectrum of compound 3bo (100 MHz, CDCl₃)



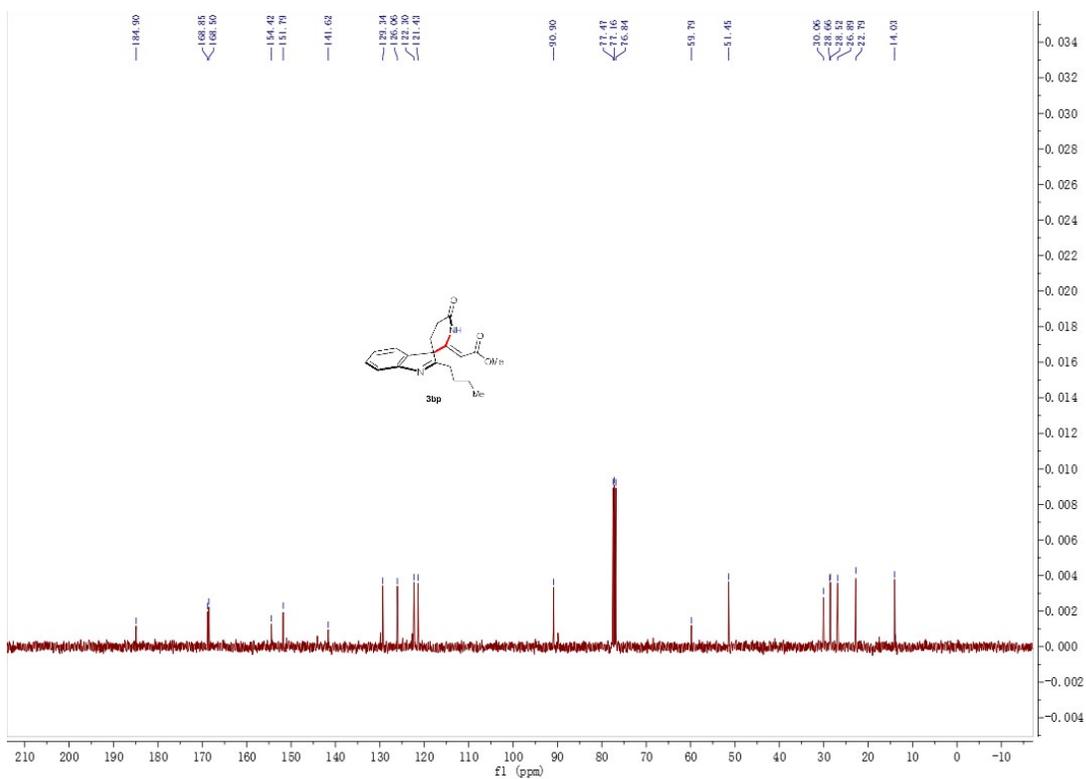
¹⁹F NMR spectrum of compound **3bo (376 MHz, CDCl₃)**



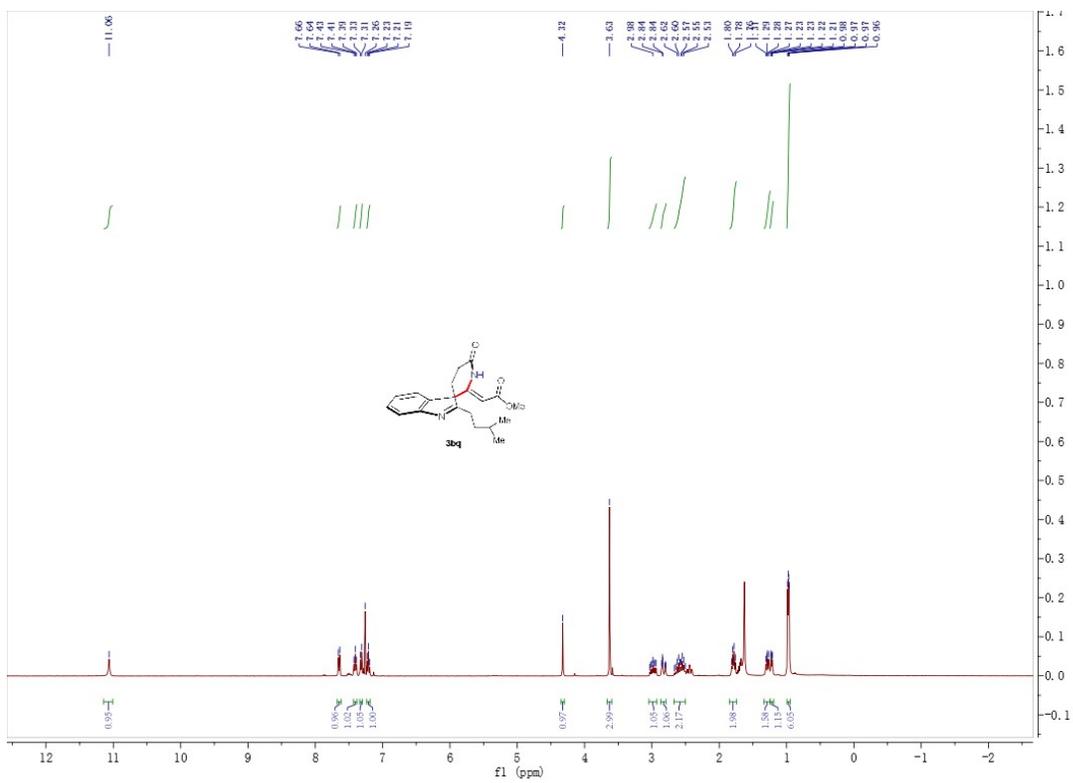
¹H NMR spectrum of compound 3bp (400 MHz, CDCl₃)



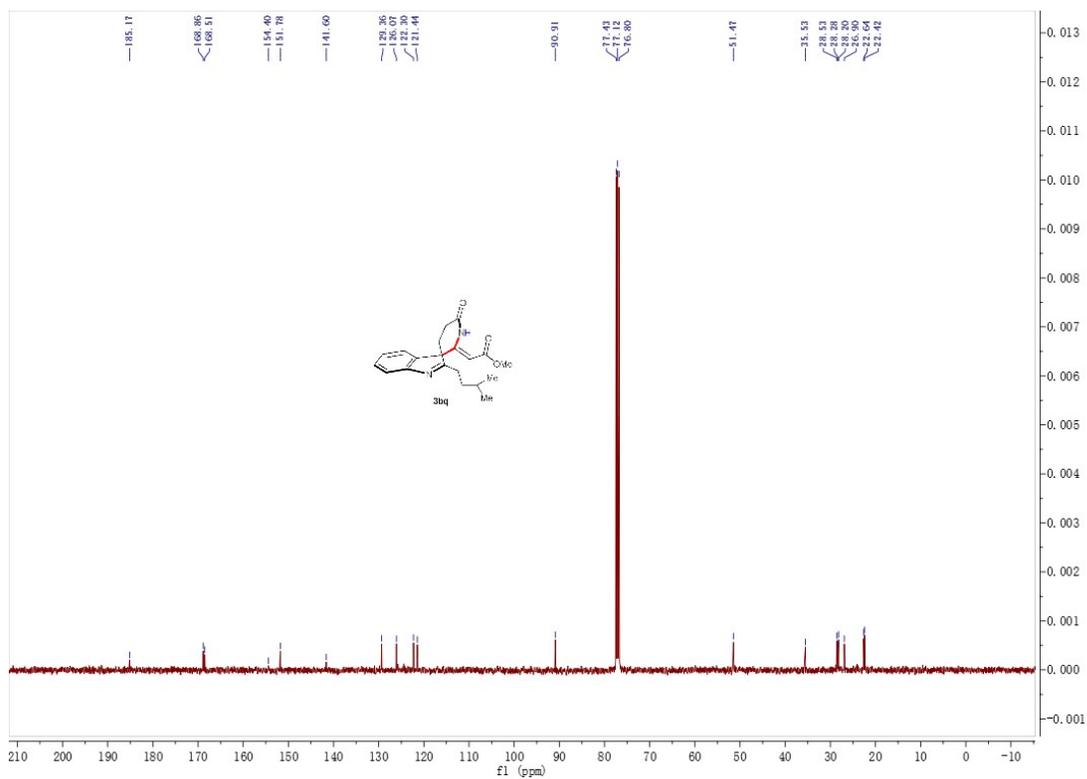
¹³C NMR spectrum of compound 3bp (100 MHz, CDCl₃)



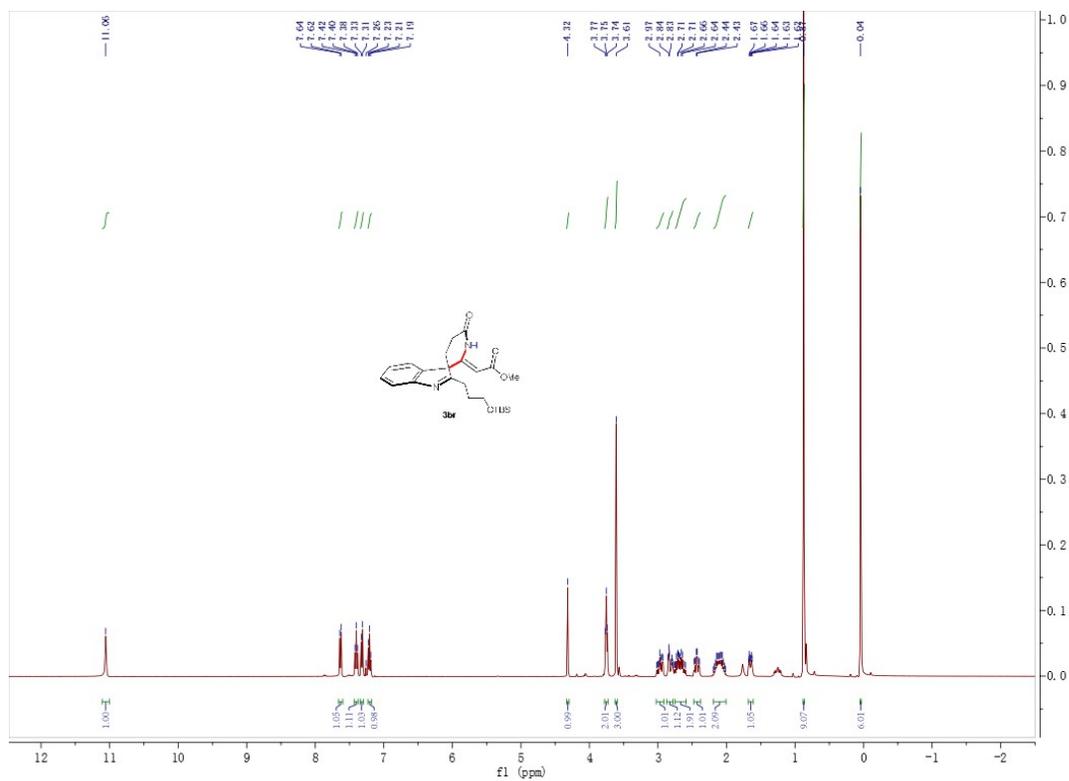
^{13}C NMR spectrum of compound **3bp** (400 MHz, CDCl_3)



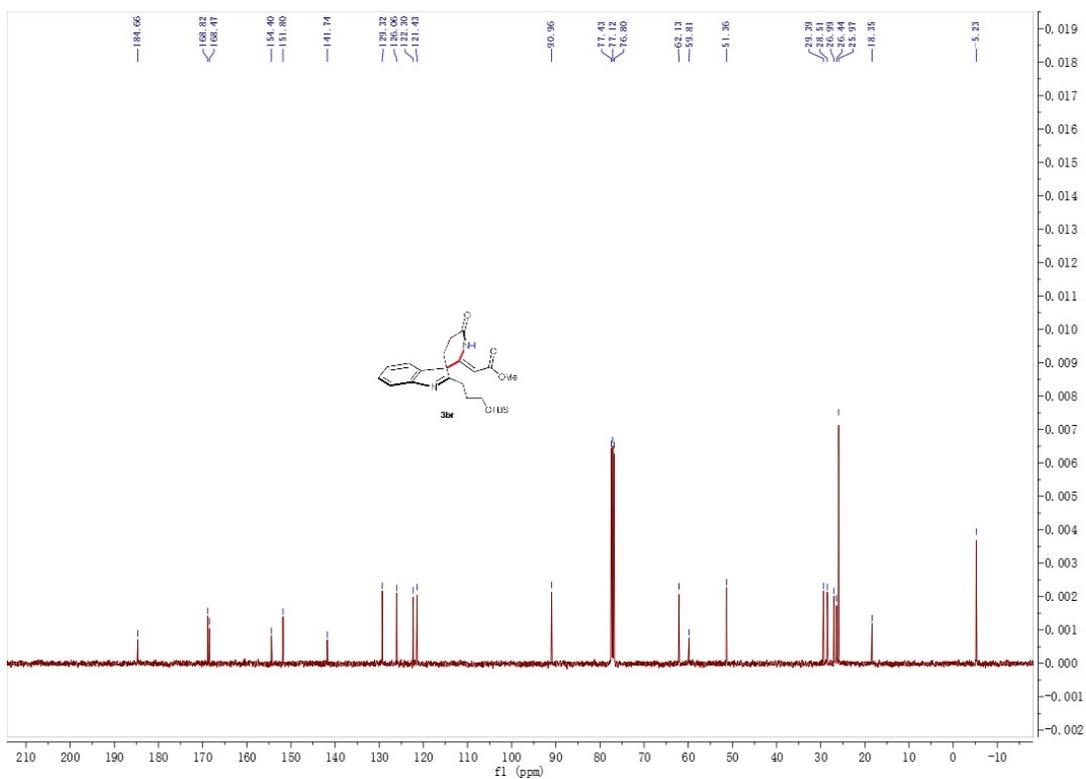
^{13}C NMR spectrum of compound **3bq** (100 MHz, CDCl_3)



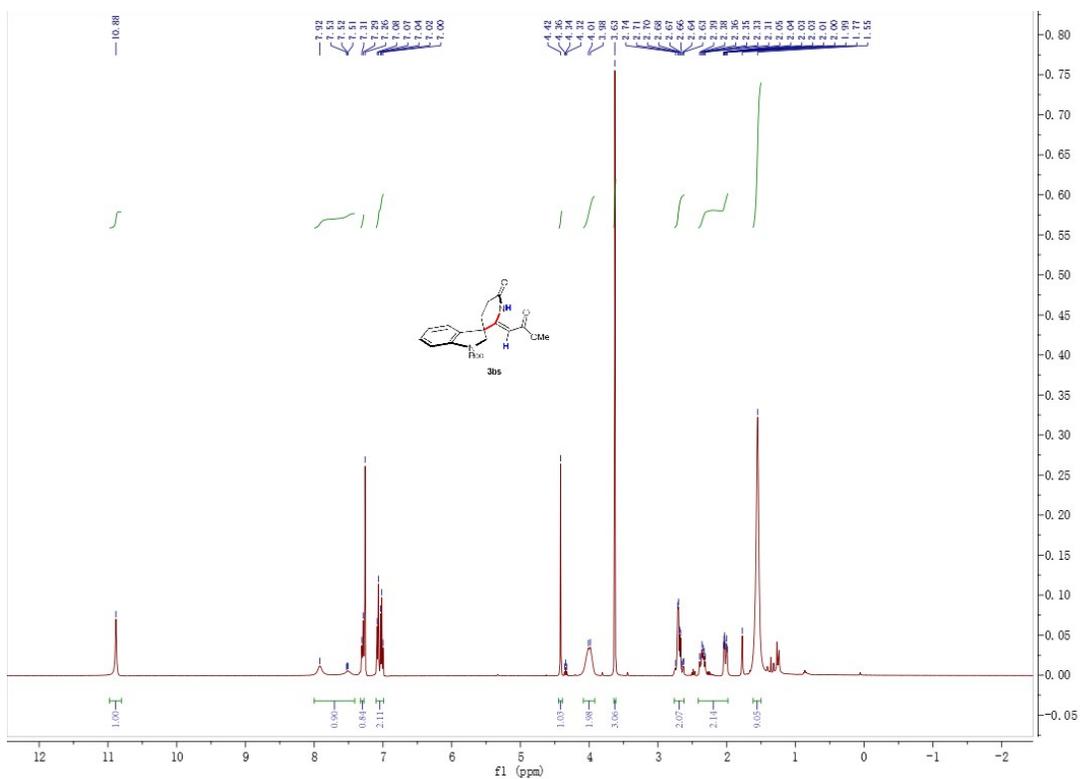
^1H NMR spectrum of compound **3br** (400 MHz, CDCl_3)



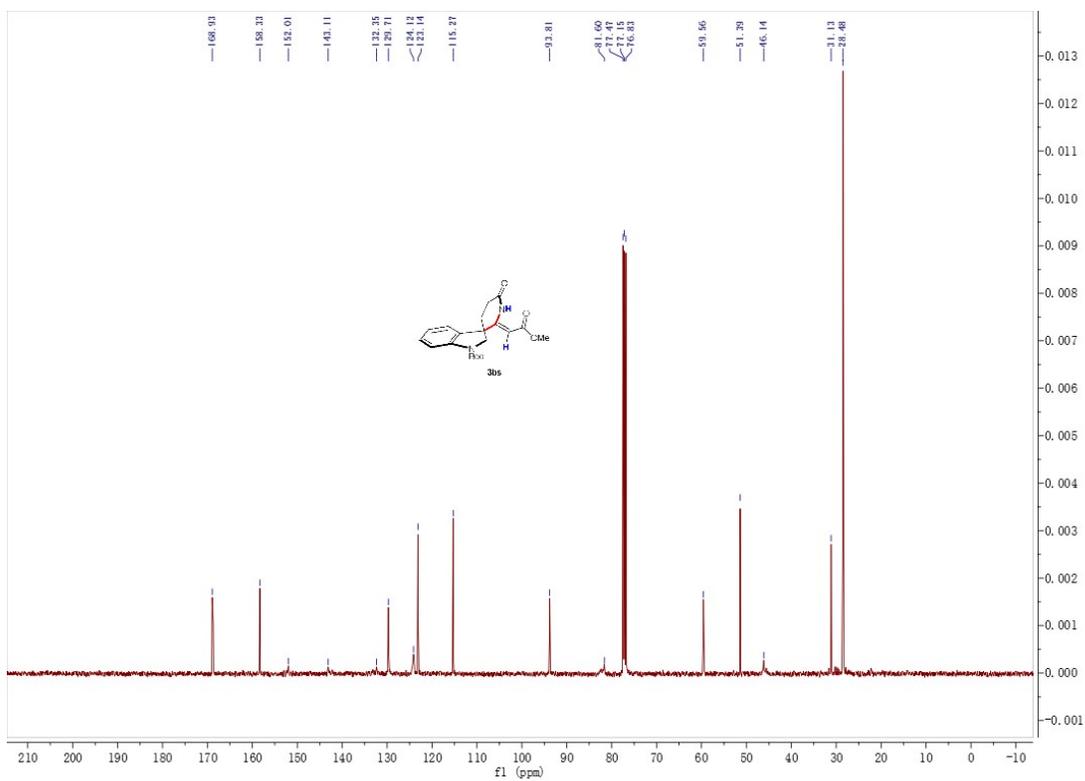
¹³C NMR spectrum of compound 3br (100 MHz, CDCl₃)



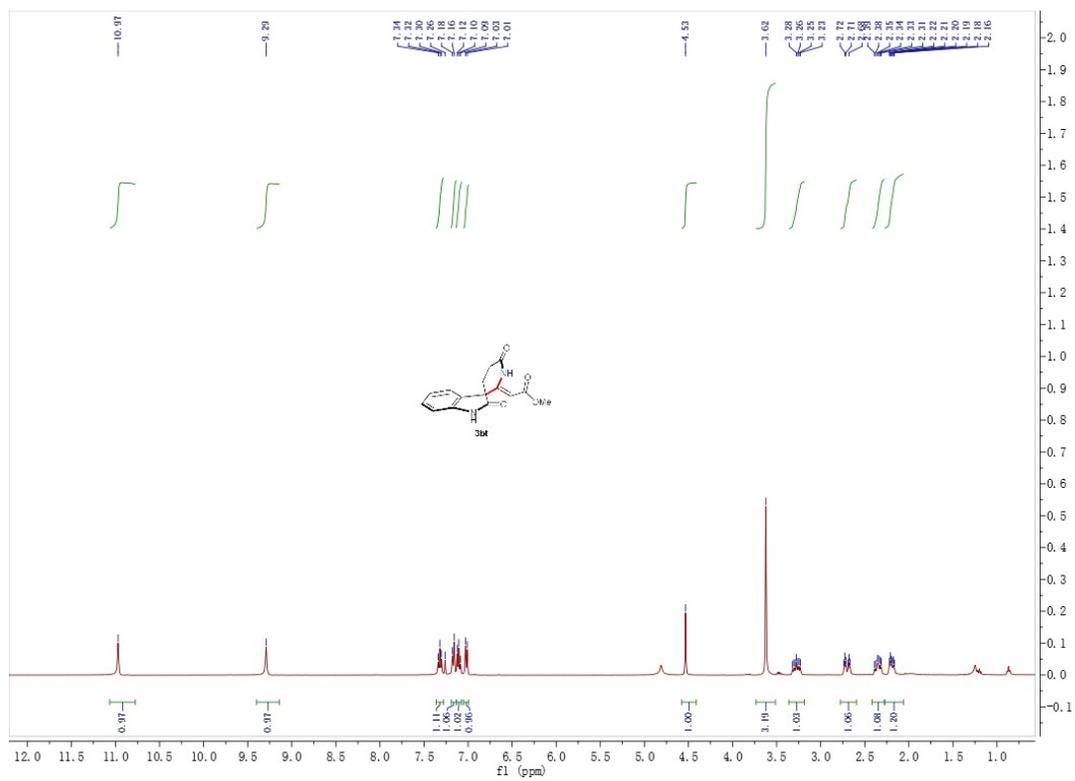
¹H NMR spectrum of compound 3bs (400 MHz, CDCl₃)



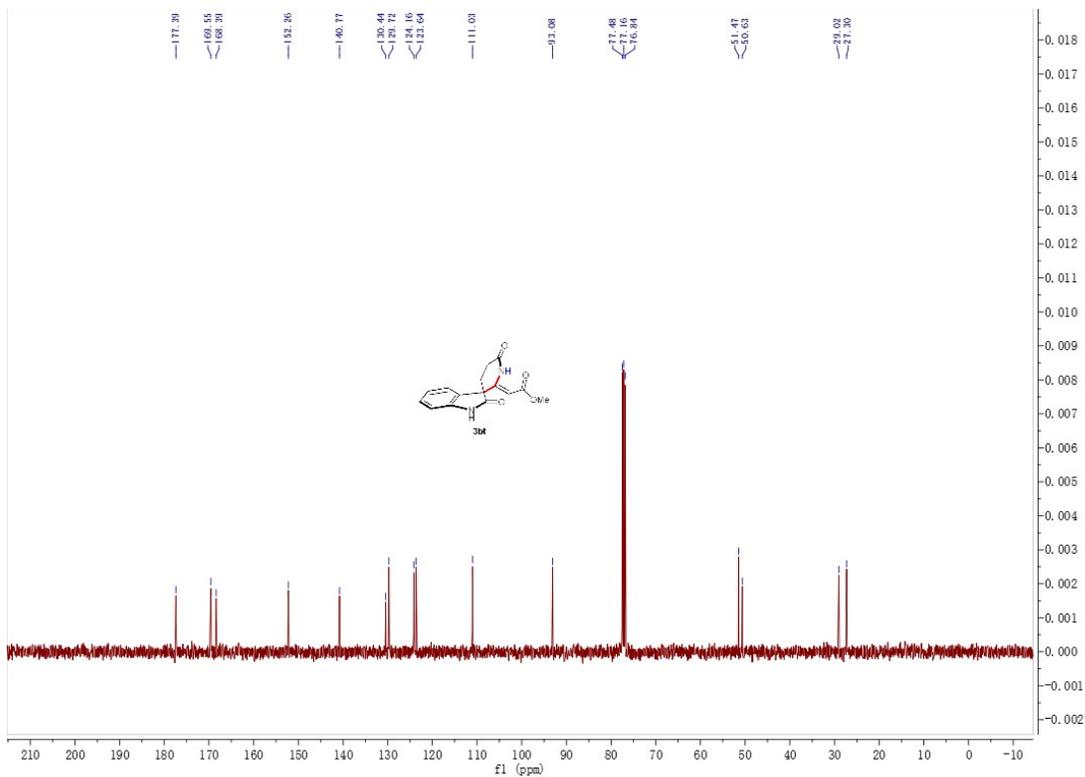
¹³C NMR spectrum of compound 3bs (100 MHz, CDCl₃)



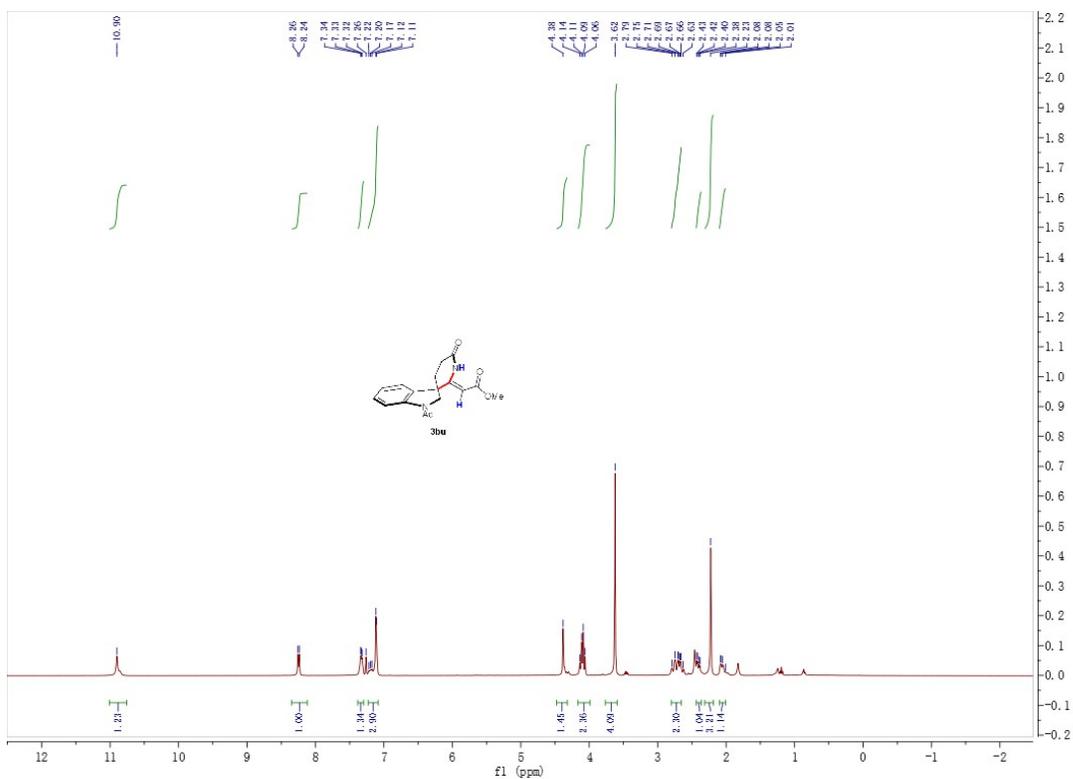
¹H NMR spectrum of compound 3bt (400 MHz, CDCl₃)



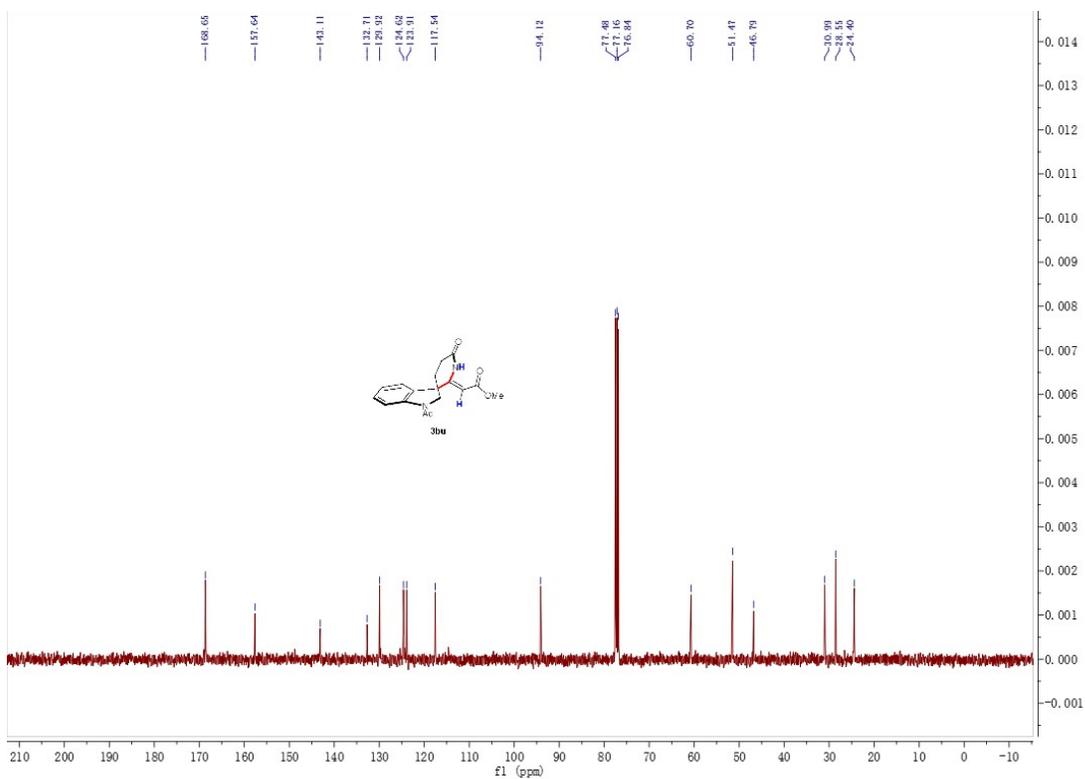
¹³C NMR spectrum of compound 3bt (100 MHz, CDCl₃)



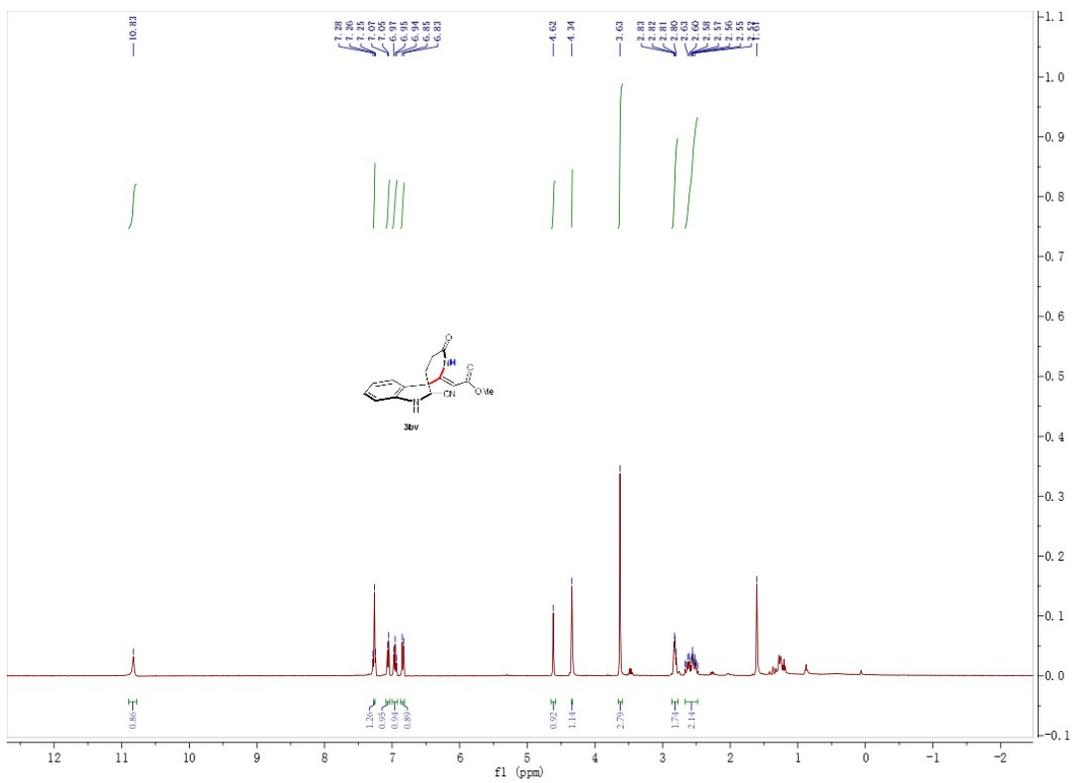
¹H NMR spectrum of compound **3bu (400 MHz, CDCl₃)**



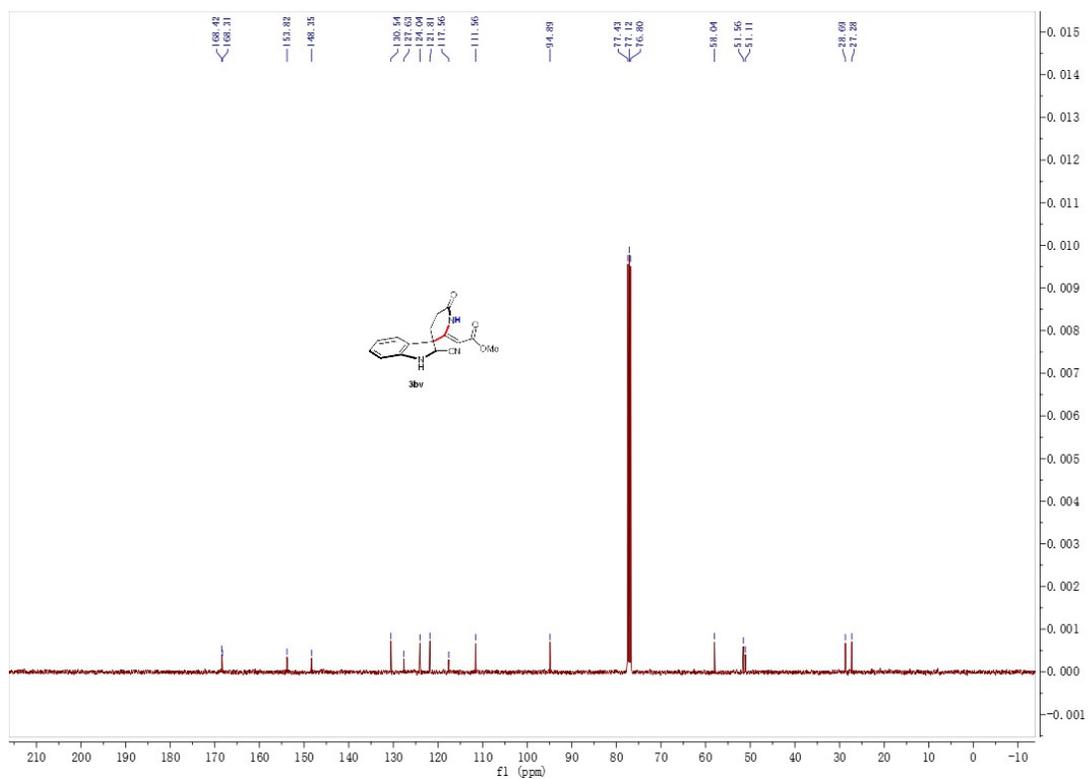
¹³C NMR spectrum of compound **3bu (100 MHz, CDCl₃)**



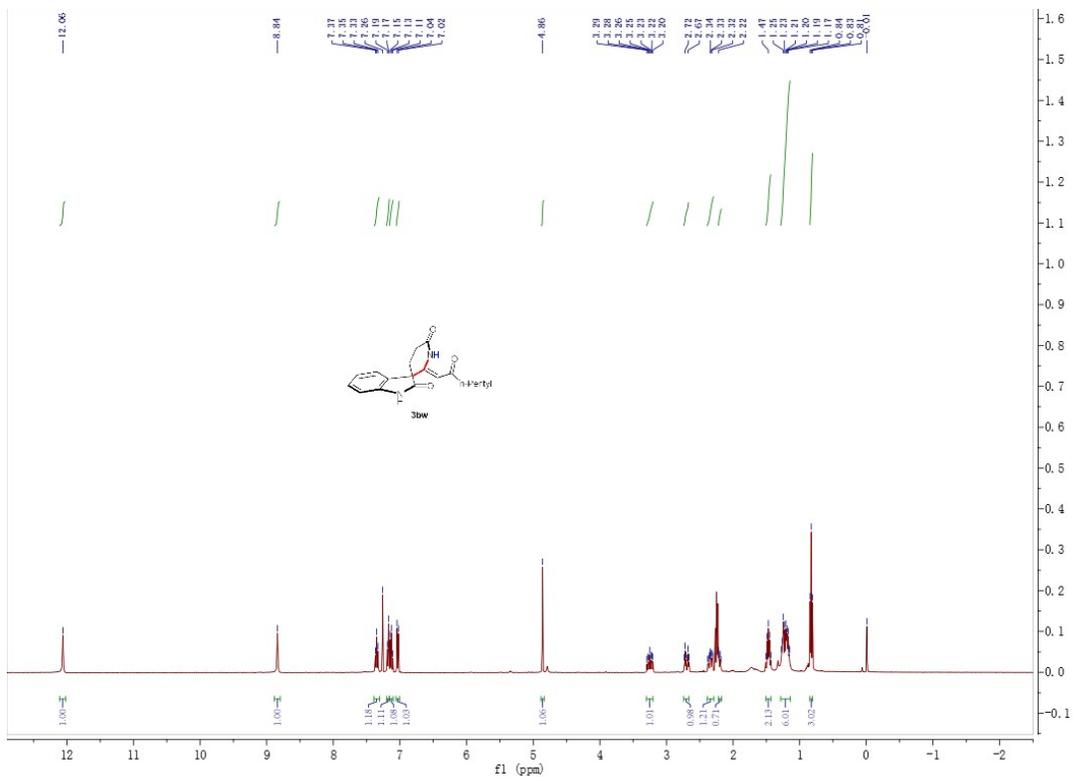
¹H NMR spectrum of compound 3bv (400 MHz, CDCl₃)



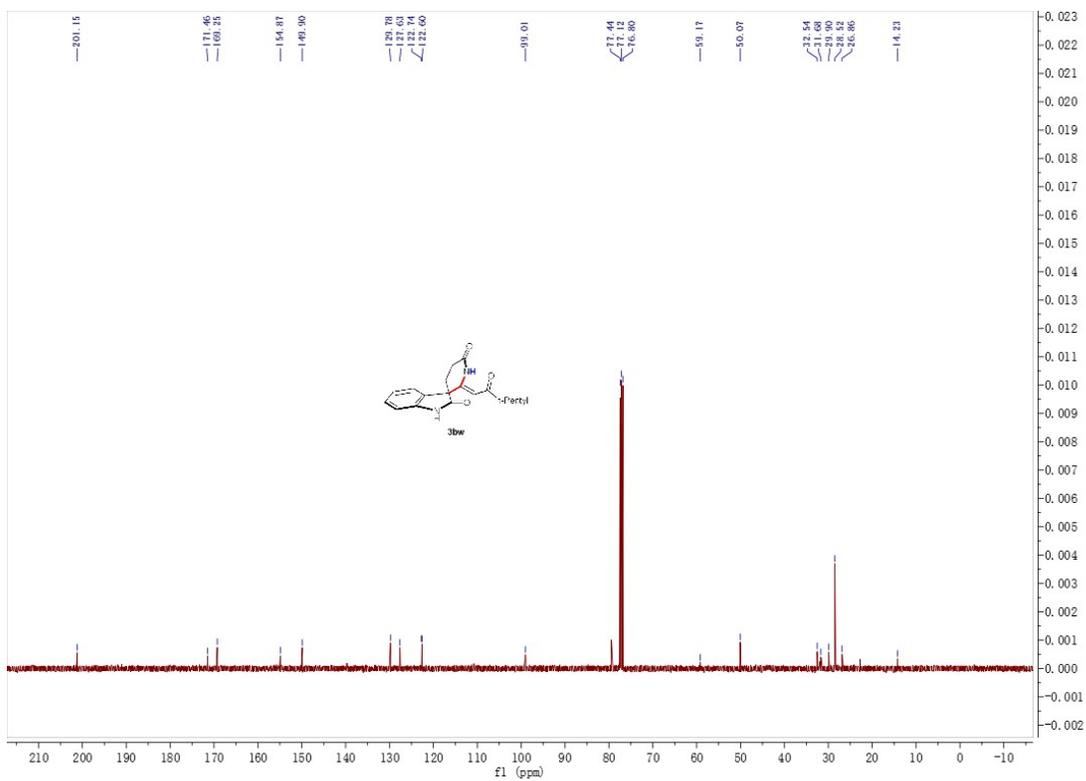
¹³C NMR spectrum of compound **3bv (100 MHz, CDCl₃)**



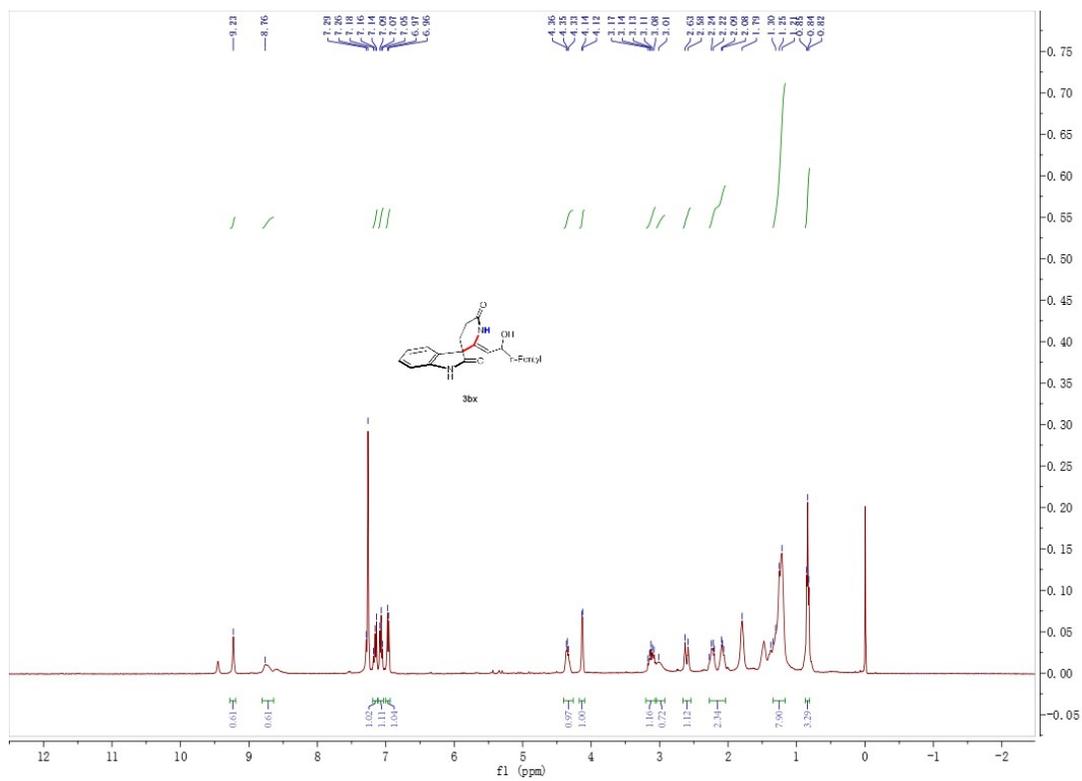
¹H NMR spectrum of compound **3bw (400 MHz, CDCl₃)**



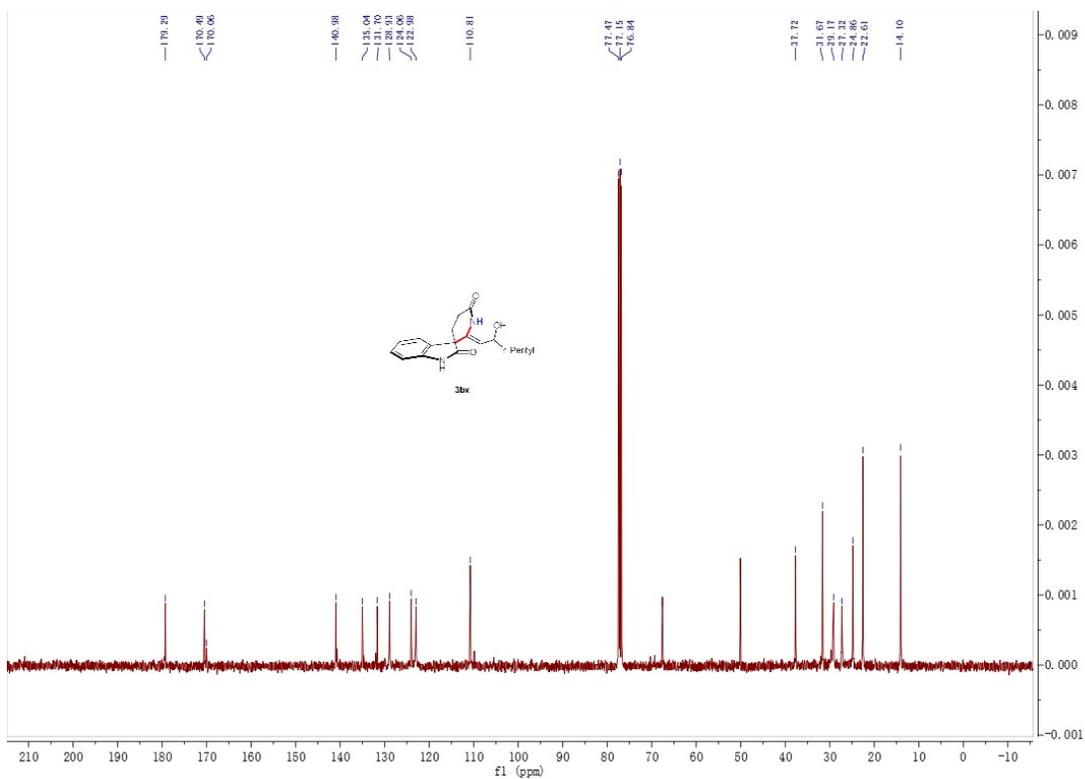
¹³C NMR spectrum of compound 3bw (100 MHz, CDCl₃)



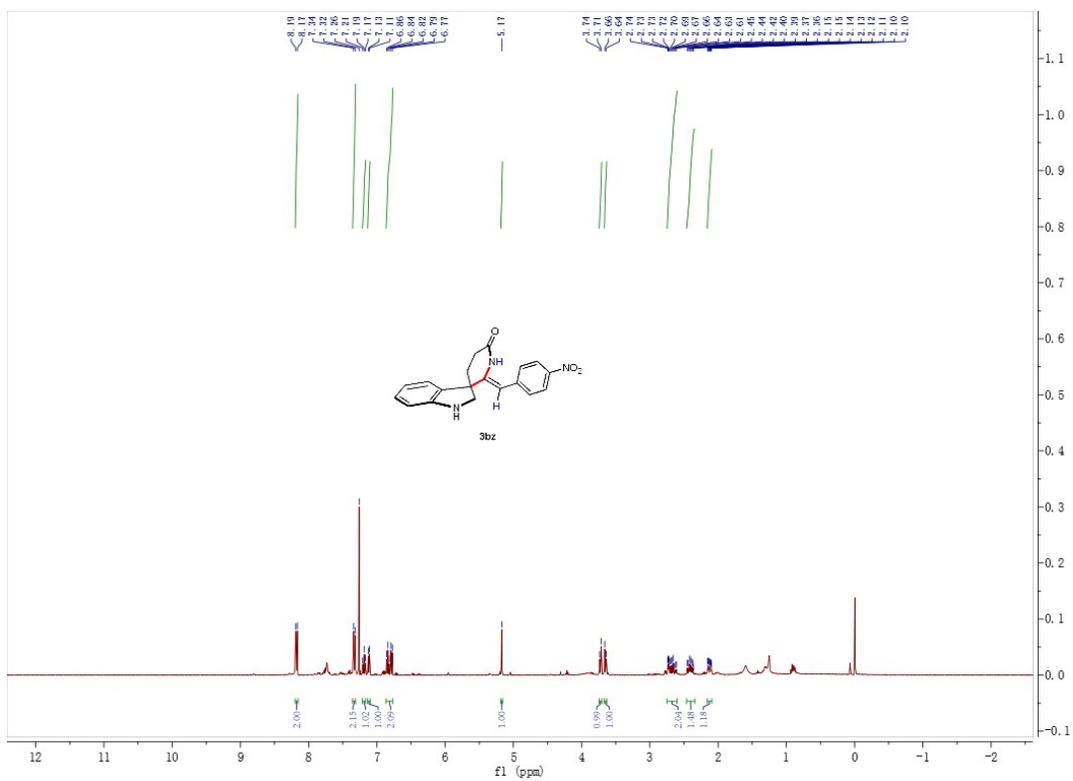
¹H NMR spectrum of compound **3bx** (400 MHz, CDCl₃)



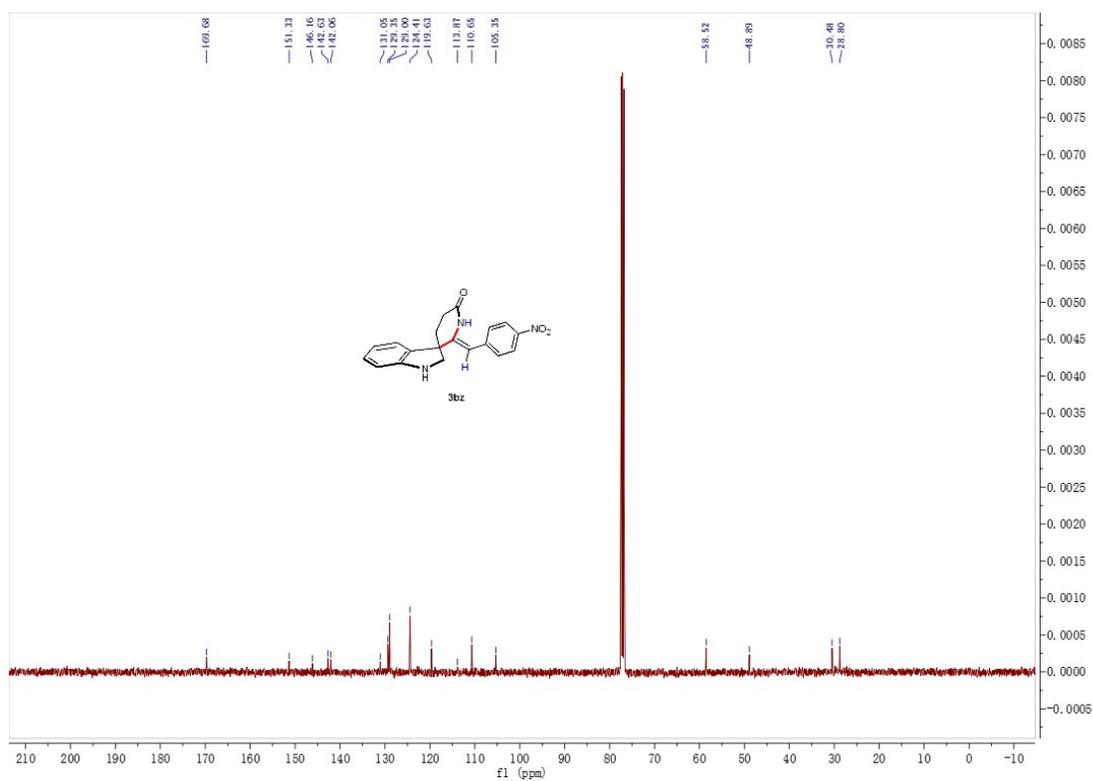
¹³C NMR spectrum of compound **3bx** (100 MHz, CDCl₃)



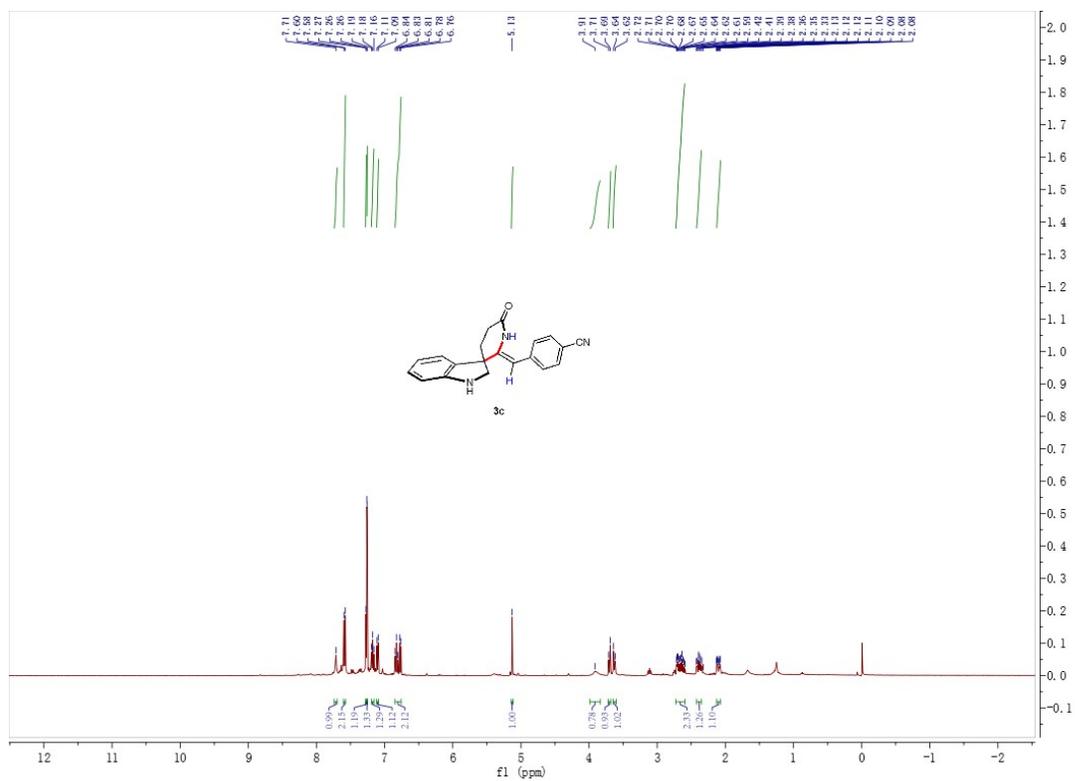
^1H NMR spectrum of compound **3bz** (400 MHz, CDCl_3)



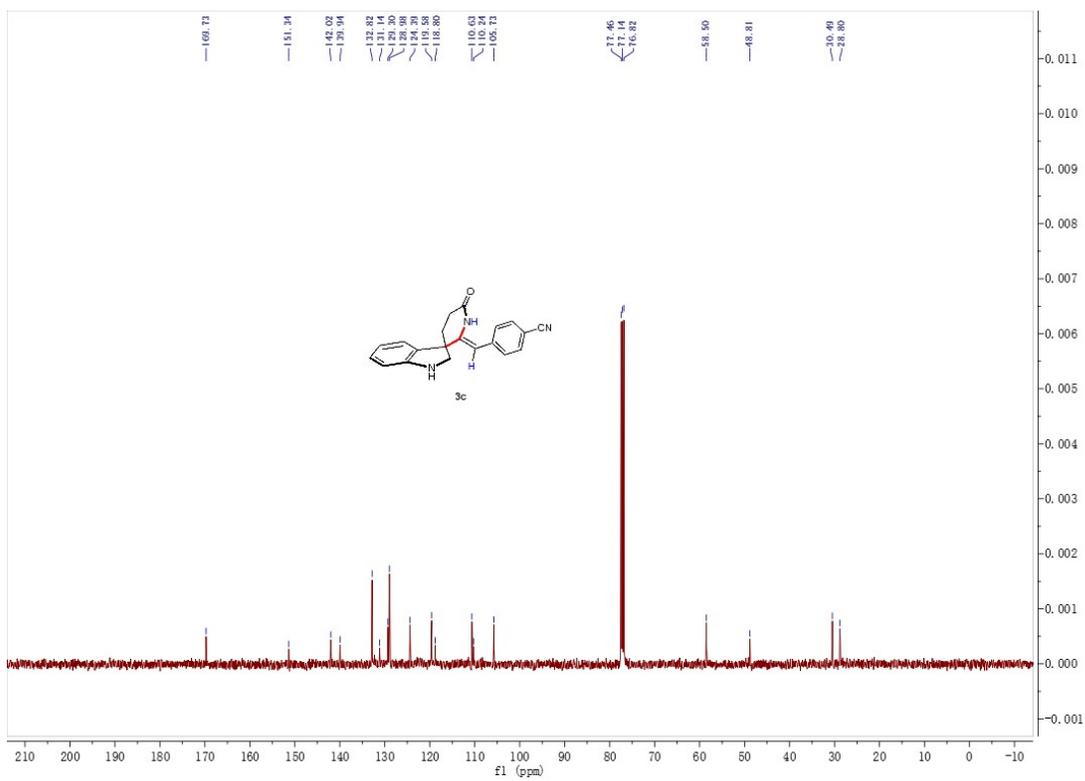
¹³C NMR spectrum of compound **3bz** (100 MHz, CDCl₃)



¹H NMR spectrum of compound **3c** (400 MHz, CDCl₃)



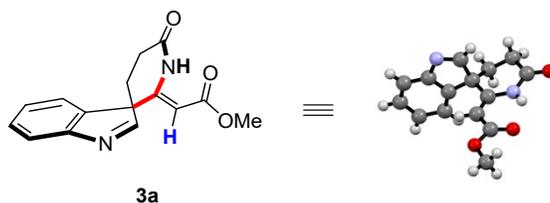
¹³C NMR spectrum of compound **3c** (100 MHz, CDCl₃)



4. X-ray structure of 3a, 3an, 3bc and B

According to diffusion in CH₂Cl₂ and *n*-hexane solvent system, the X-ray structure of 3a, 3ab and 3ar were preparation.

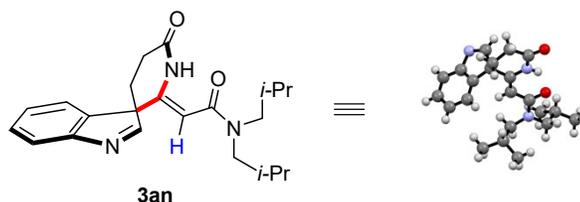
1) X-ray structure of 3a



Datablock: b_a

Bond precision:	C-C = 0.0061	A	Wavelength=1.54178
Cell:	a=10.5758(9)	b=19.7461(17)	c=6.5522(7)
	alpha=90	beta=107.700(4)	gamma=90
Temperature:	173 K		
	Calculated	Reported	
Volume	1303.5(2)	1303.5(2)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C15 H14 N2 O3	C15 H14 N2 O3	
Sum formula	C15 H14 N2 O3	C15 H14 N2 O3	
Mr	270.28	270.28	
Dx,g cm-3	1.377	1.377	
Z	4	4	
Mu (mm-1)	0.803	0.803	
F000	568.0	568.0	
F000'	569.82		
h,k,lmax	12,23,7	12,22,7	
Nref	2163	2093	
Tmin,Tmax	0.865,0.887	0.590,0.752	
Tmin'	0.852		
Correction method= # Reported T Limits: Tmin=0.590 Tmax=0.752			
AbsCorr = MULTI-SCAN			
Data completeness = 0.968	Theta(max)= 63.915		
wR2(reflections) = 0.2185 (2093)			
R(reflections)= 0.0829 (1753)			
S = 1.048	Npar= 186		

2) X-ray structure of 3an



Datablock: a_a

Bond precision: C-C = 0.0020 A Wavelength=1.54178

Cell: a=7.6565(2) b=10.3732(3) c=14.0443(4)
alpha=100.852(1) beta=94.300(1) gamma=107.078(1)

Temperature: 213 K

	Calculated	Reported
Volume	1037.05(5)	1037.05(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C22 H29 N3 O2	C22 H29 N3 O2
Sum formula	C22 H29 N3 O2	C22 H29 N3 O2
Mr	367.48	367.48
Dx,g cm-3	1.177	1.177
Z	2	2
Mu (mm-1)	0.602	0.602
F000	396.0	396.0
F000'	397.11	
h,k,lmax	9,12,16	9,12,16
Nref	3664	3518
Tmin,Tmax	0.930,0.942	0.674,0.753
Tmin'	0.930	

Correction method= # Reported T Limits: Tmin=0.674 Tmax=0.753

AbsCorr = NONE

Data completeness= 0.960 Theta(max)= 66.702

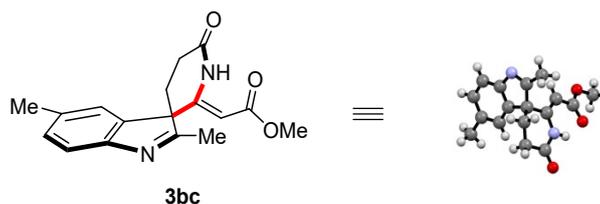
wR2(reflections)= 0.1048(3518)

R(reflections)= 0.0410(3344)

S = 1.029

Npar= 256

3) X-ray structure of 3ar



Datablock: a

Bond precision:	C-C = 0.0019	A	Wavelength=1.54178
Cell:	a=10.1923(8) alpha=90	b=12.3323(10) beta=109.121(3)	c=13.0563(11) gamma=90
Temperature:	243 K		
	Calculated		Reported
Volume	1550.6(2)		1550.6(2)
Space group	P 21/n		P 1 21/n 1
Hall group	-P 2yn		-P 2yn
Moiety formula	C17 H18 N2 O3		C17 H18 N2 O3
Sum formula	C17 H18 N2 O3		C17 H18 N2 O3
Mr	298.33		298.33
Dx,g cm-3	1.278		1.278
Z	4		4
Mu (mm-1)	0.722		0.722
F000	632.0		632.0
F000'	633.96		
h,k,lmax	12,14,15		12,14,15
Nref	2735		2642
Tmin,Tmax	0.917,0.937		0.687,0.753
Tmin'	0.917		

Correction method= # Reported T Limits: Tmin=0.687 Tmax=0.753

AbsCorr = NONE

Data completeness= 0.966

Theta(max)= 66.591

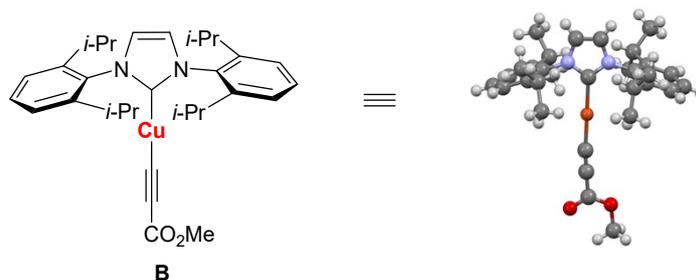
wR2(reflections)= 0.1067(2642)

R(reflections)= 0.0387(2539)

S = 1.056

Npar= 210

3) X-ray structure of B



Datablock: a

Bond precision:	C-C = 0.0126 Å	Wavelength=1.54178
Cell:	a=12.4903(7)	b=12.6689(7) c=22.1306(11)
	alpha=90	beta=90.773(2) gamma=90
Temperature:	223 K	
	Calculated	Reported
Volume	3501.6(3)	3501.6(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C31 H39 Cu N2O2	C31 H39 Cu N2 O2
	[+ solvent]	
Sum formula	C31 H39 Cu	C31 H39 Cu N2 O2
	N2O2[+solvent]	
Mr	535.19	535.18
Dx,g cm-3	1.015	1.015
Z	4	4
Mu (mm-1)	1.055	1.055
F000	1136.0	1136.0
F000'	1130.82	
h,k,lmax	14,15,26	14,15,26
Nref	6183	6111
Tmin,Tmax	0.859,0.881	0.561,0.753
Tmin'	0.854	

Correction method= # Reported T Limits: Tmin=0.561 Tmax=0.753

AbsCorr = NONE

Data completeness= 0.988

Theta(max)= 66.590

wR2(reflections)=

0.3873(6111)

R(reflections)= 0.1019(5546)

S = 1.126

Npar= 325